Supporting Information

Construction of 2,3-Quaternary Fused Indolines from Alkynyl tethered Oximes and Diaryliodonium Salts through A Cascade Strategy of N-Arylation/Cycloaddition/[3,3]-Rearrangement

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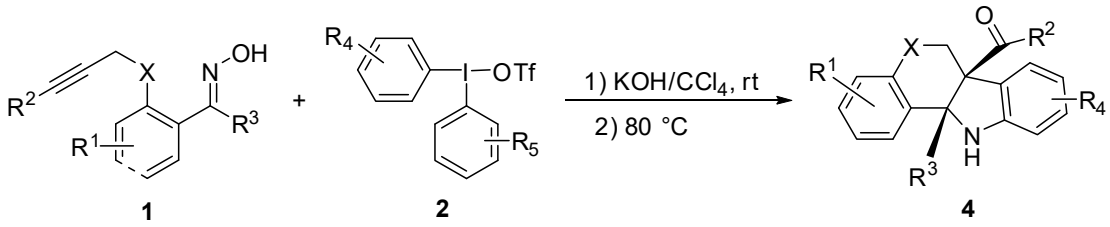
Contents

1. General Experimental Information:

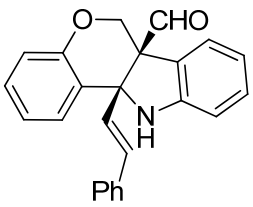
^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 400, 500 or 600 MHz spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. High resolution mass spectra were acquired on an LTQ FT spectrometer, and were obtained by peak matching. Melting points are reported uncorrected. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Chromatography was performed using with 300-400 mesh silica gel (SiO_2). Unless otherwise noted, all reactions were performed under air atmosphere. All reagents and solvents were obtained from commercial sources and, where appropriate, purified prior to use.

2. Synthesis of fused indoline 4 and 5oa



1 2 4

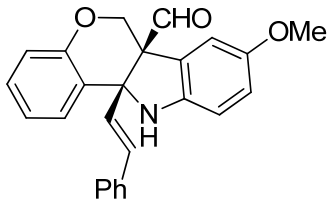
General procedure A: In a Teflon-sealed reaction flask was charged with alkynyl tethered oximes **1** (0.2 mmol), diaryliodonium salts **2** (0.4 mmol, 2.0 equiv) and KOH (0.24 mmol, 1.2 equiv) under an air atmosphere, CCl_4 (2.0 mL) was added. The reaction vessel was sealed with a Teflon cap and stirred vigorously at 25 °C for 3–12 h until the substrate **1** disappeared (monitored by TLC). And then, the reaction mixture was stirred vigorously at 80 °C for 3–6 h until the substrate **3** disappeared (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (the crude residue was dry loaded with silica gel, 1/50 to 1/10, ethyl acetate/petroleum ether) to provide product **4**.



4aa

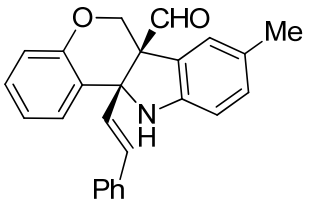
4aa was prepared by general procedure A. **1a** (0.055 g, 0.20 mmol), **2a** (0.172 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 3 h at 25 °C, and then stirring for 3

h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4aa** as a light yellow solid (0.051 g, 72%). Mp: 161–162 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 1H), 7.29 (d, J = 7.2 Hz, 2H), 7.24 (t, J = 7.2 Hz, 2H), 7.19–7.15 (m, 1H), 7.11 (d, J = 7.6 Hz, 1H), 7.07–7.03 (m, J = 6.8 Hz, 3H), 6.90–6.86 (m, 2H), 6.76–6.73 (m, 2H), 6.63 (d, J = 8.0 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 4.66 (d, J = 12.8 Hz, 1H), 4.30 (brs, 1H), 4.27 (d, J = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 154.2, 149.9, 135.7, 132.7, 130.1, 129.1, 129.0, 128.6, 128.2, 127.4, 126.9, 126.8, 124.6, 122.7, 122.1, 120.3, 117.6, 110.8, 69.9, 63.0, 61.6; IR (thin film) 3367, 2925, 2848, 1709, 1602, 1482, 1214, 1059, 755 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{20}NO_2$ $[M + H]^+$: 354.1494, found: 354.1495.



4ab

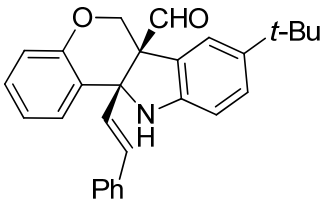
4ab was prepared by general procedure A. **1a** (0.055 g, 0.20 mmol), **2b** (0.196 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 0.5 h at 25 °C, and then stirring for 2 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ab** as a light yellow solid (0.052 g, 67%). Mp: 51–52 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.51 (s, 1H), 7.29 (d, J = 7.2 Hz, 2H), 7.24–7.21 (m, 2H), 7.19–7.15 (m, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.08–7.04 (m, 1H), 6.90–6.86 (m, 2H), 6.77 (d, J = 8.4 Hz, 1H), 6.64 (d, J = 6.4 Hz, 3H), 6.40 (d, J = 16.0 Hz, 1H), 4.65 (d, J = 16.4 Hz, 1H), 4.28 (d, J = 12.4 Hz, 1H), 4.10 (brs, 1H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.2, 154.6, 144.3, 139.6, 136.2, 131.5, 129.8, 128.6, 128.5, 128.4, 127.9, 127.7, 127.5, 126.6, 122.1, 117.5, 115.4, 111.9, 110.4, 71.0, 66.5, 64.9, 55.3; IR (thin film) 3433, 3025, 2924, 1709, 1638, 1459, 1272, 752 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{22}NO_3$ $[M + H]^+$: 384.1600, found: 384.1594.



4ac

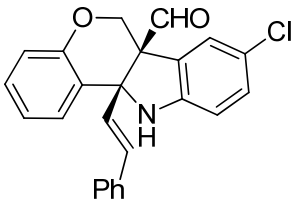
4ac was prepared by general procedure A. **1a** (0.055 g, 0.20 mmol), **2c** (0.183 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 4 h at 25 °C, and then stirring for 3

h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ac** as a light yellow solid (0.046 g, 63%). Mp: 186–188 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.49 (s, 1H), 7.30 (d, J = 7.6 Hz, 2H), 7.25–7.21 (m, 2H), 7.19–7.15 (m, 1H), 7.11 (d, J = 7.2 Hz, 1H), 7.08–7.04 (m, 1H), 7.90–6.86 (m, 4H), 6.77 (d, J = 8.4 Hz, 1H), 6.55 (d, J = 8.4 Hz, 1H), 6.40 (d, J = 15.6 Hz, 1H), 4.66 (d, J = 12.4 Hz, 1H), 4.29 (d, J = 12.8 Hz, 1H), 4.20 (brs, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 154.2, 147.6, 135.8, 132.6, 130.7, 129.9, 129.3, 128.9, 128.6, 128.1, 127.5, 127.1, 126.8, 125.1, 122.8, 122.1, 117.6, 110.7, 70.0, 63.0, 61.7, 20.8; IR (thin film) 3360, 3028, 2923, 1709, 1614, 1493, 1263, 821, 748 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{22}NO_2$ $[M + H]^+$: 368.1651, found: 368.1664.



4ad

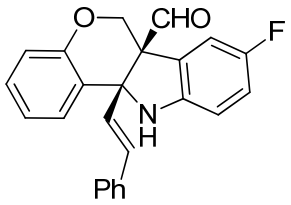
4ad was prepared by general procedure A. **1a** (0.055 g, 0.20 mmol), **2d** (0.217 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 3 h at 25 °C, and then stirring for 3 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ad** as a light yellow solid (0.049 g, 60%). Mp: 163–164 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 1H), 7.30 (d, J = 7.2 Hz, 2H), 7.25–7.21 (m, 2H), 7.19–7.16 (m, 1H), 7.11–7.03 (m, 4H), 6.89–6.85 (m, 2H), 6.77 (d, J = 8.0 Hz, 1H), 6.59 (d, J = 8.4 Hz, 1H), 6.41 (d, J = 16.0 Hz, 1H), 4.67 (d, J = 12.4 Hz, 1H), 4.31 (d, J = 12.4 Hz, 1H), 4.19 (brs, 1H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 154.3, 147.5, 143.6, 135.8, 132.5, 129.5, 128.9, 128.6, 128.1, 127.5, 127.2, 127.1, 126.8, 122.4, 122.0, 121.3, 117.7, 110.4, 70.0, 63.1, 61.9, 34.3, 31.5; IR (thin film) 3376, 3033, 2960, 1716, 1613, 1490, 1270, 824, 749 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{28}NO_2$ $[M + H]^+$: 410.2120, found: 410.2115.



4ae

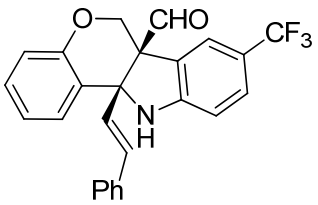
4ae was prepared by general procedure A. **1a** (0.055 g, 0.20 mmol), **2e** (0.199 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 5 h at 25 °C, and then stirring for 4

h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ae** as a light yellow solid (0.041 g, 53%). Mp: 167–168 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 1H), 7.29–7.17 (m, 5H), 7.10 (t, J = 7.2 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 6.90–6.84 (m, 2H), 6.79 (d, J = 8.0 Hz, 1H), 6.55 (d, J = 8.0 Hz, 1H), 6.38 (d, J = 15.6 Hz, 1H), 4.62 (d, J = 12.4 Hz, 1H), 4.32 (brs, 1H), 4.28 (d, J = 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 154.2, 148.4, 135.5, 133.0, 130.1, 129.2, 128.7, 128.6, 128.3, 127.4, 126.8, 126.5, 125.0, 124.9, 124.6, 122.3, 117.7, 111.7, 70.4, 62.8, 61.6; IR (thin film) 3360, 2923, 2854, 1713, 1602, 1482, 756, 690 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{19}ClNO_2$ [M + H]$^+$: 388.1104, found: 388.1087.



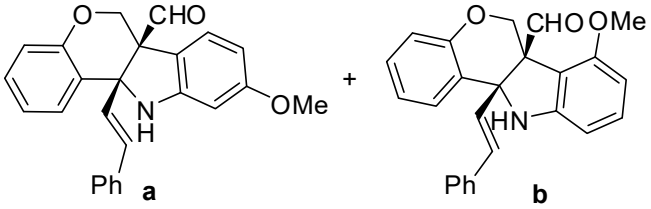
4af

4af was prepared by general procedure A. **1a** (0.055 g, 0.20 mmol), **2f** (0.186 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 3 h at 25 °C, and then stirring for 5 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ag** as a light yellow solid (0.045 g, 60%). Mp: 169–170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.52 (s, 1H), 7.30 (d, J = 7.2 Hz, 2H), 7.26–7.18 (m, 3H), 7.12–7.06 (m, 2H), 6.91–6.86 (m, 2H), 6.80–6.75 (m, 3H), 6.57 (dd, J = 8.4 Hz, 4.0 Hz, 1H), 6.39 (d, J = 16.0 Hz, 1H), 4.63 (d, J = 12.4 Hz, 1H), 4.28 (d, J = 12.4 Hz, 1H), 4.20 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 158.8 (d, J = 237.0 Hz), 154.2, 145.9, 135.6, 132.9, 129.1, 128.8, 128.6, 128.3, 127.4, 126.8, 126.7, 124.4 (d, J = 8.0 Hz), 122.3, 117.7, 116.8 (d, J = 23.3 Hz), 112.1 (d, J = 24.1 Hz), 111.4 (d, J = 8.1 Hz), 70.6, 62.8, 61.8; IR (thin film) 3359, 2925, 2853, 1708, 1608, 1487, 1221, 757 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{19}FNO_2$ [M + H]$^+$: 372.1400, found: 372.1385.



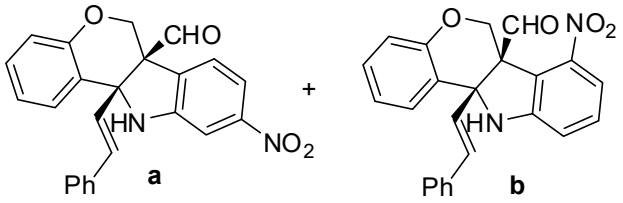
4ag

4ag was prepared by general procedure A. **1a** (0.055 g, 0.20 mmol), **2g** (0.226 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 2 h at 25 °C, and then stirring for for 6 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ag** as a light yellow solid (0.034 g, 40%). Mp 122–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.60 (s, 1H), 7.40–7.24 (m, 7H), 7.19–7.15 (m, 2H), 6.99–6.96 (m, 1H), 6.94 (d, J = 15.6 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 6.74 (d, J = 8.4 Hz, 1H), 6.47 (d, J = 16.0 Hz, 1H), 4.71 (d, J = 12.8 Hz, 1H), 4.66 (brs, 1H), 4.40 (d, J = 12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 154.2, 152.5, 135.4, 133.1, 129.3, 128.7, 128.5, 128.4, 128.1, 128.0, 127.4, 126.8, 126.1, 123.3, 122.4, 122.2, 122.1, 117.9, 110.0, 70.3, 63.1, 61.3; IR (thin film) 3339, 2923, 2853, 1710, 1623, 1274, 1104, 758 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{25}H_{19}F_3NO_2$ $[M + H]^+$: 422.1368, found: 422.1368.



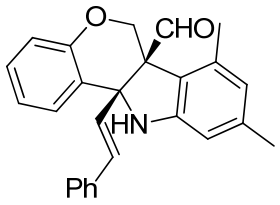
4ah (a/b = 1:1)

4ah was prepared by general procedure A. **1a** (0.055 g, 0.20 mmol), **2h** (0.196 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 3 h at 25 °C, and then stirring for 3 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ah** as a light yellow solid (0.048 g, 63%). Mp: 43–44 °C; ***4ah-a***: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.48 (s, 1H), 7.30 (d, J = 7.2 Hz, 2H), 7.24 (t, J = 7.2 Hz, 2H), 7.19–7.16 (m, 1H), 7.11–7.03 (m, 2H), 6.95–6.83 (m, 3H), 6.77 (d, J = 8.0 Hz, 1H), 6.58 (d, J = 7.6 Hz, 1H), 6.47–6.36 (m, 2H), 4.97 (d, J = 12.4 Hz, 1H), 4.28–4.19 (m, 2H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 155.0, 150.2, 140.4, 135.8, 132.6, 129.2, 128.9, 128.6, 128.2, 127.4, 127.2, 126.9, 126.7, 122.8, 122.0, 119.8, 117.7, 111.6, 70.4, 63.0, 62.6, 21.3; ***4ah-b***: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.46 (s, 1H), 7.30 (d, J = 7.2 Hz, 2H), 7.24 (t, J = 7.2 Hz, 2H), 7.19–7.16 (m, 1H), 7.11–7.03 (m, 2H), 6.95–6.83 (m, 3H), 6.77 (d, J = 8.0 Hz, 1H), 6.51 (d, J = 7.6 Hz, 1H), 6.47–6.36 (m, 2H), 4.65 (d, J = 12.0 Hz, 1H), 4.28–4.19 (m, 2H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3, 154.2, 150.0, 137.0, 133.0, 130.1, 129.0, 128.8, 128.5, 128.1, 127.3, 127.0, 126.8, 124.3, 122.1, 121.2, 119.5, 117.5, 108.6, 70.0, 62.9, 61.4, 18.5; IR (thin film) 3368, 3025, 2924, 1708, 1614, 1459, 1272, 752 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{25}H_{22}NO_3$ $[M + H]^+$: 384.1600, found: 384.1583.



4ai (a/b = 1:1)

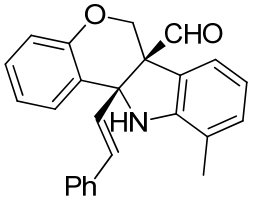
4ai was prepared by general procedure A. **1a** (0.055 g, 0.20 mmol), **2i** (0.208 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 10 h at 25 °C, and then stirring for 6 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ai** as a light yellow solid (0.038 g, 48%). Mp: 187–188 °C; ***4ai-a***: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.67 (s, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.49–7.48 (m, 1H), 7.36–7.25 (m, 5H), 7.20–7.17 (m, 2H), 6.99–6.84 (m, 3H), 6.79 (d, J = 15.6 Hz, 1H), 6.47 (d, J = 15.6 Hz, 1H), 4.75–4.67 (m, 2H), 4.64–4.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 154.6, 152.8, 150.6, 135.5, 133.5, 130.9, 129.5, 128.9, 128.7, 128.4, 127.9, 127.4, 126.8, 125.9, 122.6, 117.8, 115.4, 105.1, 71.0, 63.9, 62.9; ***4ai-b***: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.61 (s, 1H), 7.49–7.48 (m, 1H), 7.36–7.25 (m, 6H), 7.20–7.17 (m, 2H), 6.99–6.84 (m, 4H), 6.35 (d, J = 15.6 Hz, 1H), 4.75–4.67 (m, 1H), 4.64–4.58 (m, 1H), 4.39 (d, J = 12.4 Hz, 1H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 154.1, 150.0, 147.7, 135.3, 132.8, 130.0, 129.3, 138.9, 128.7, 128.6, 128.4, 127.6, 126.8, 125.0, 122.3, 118.3, 115.7, 105.1, 70.8, 63.2, 61.5; IR (thin film) 3349, 2923, 2852, 1716, 1529, 1351, 802, 759 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{19}N_2O_4$ $[M + H]^+$: 399.1345, found: 399.1339.



4aj

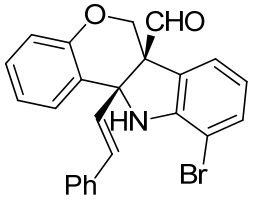
4aj was prepared by general procedure A. **1a** (0.055 g, 0.20 mmol), **2j** (0.194 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 5 h at 25 °C, and then stirring for 4 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4aj** as a light yellow solid (0.046 g, 60%). Mp: 78–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.42 (s, 1H), 7.26 (d, J = 7.2 Hz, 2H), 7.21–7.13 (m, 3H), 7.05–6.98 (m, 2H), 6.84 (s, 1H), 6.82 (d, J = 8.4 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 6.29 (d, J = 18.8 Hz, 2H), 4.93 (d, J = 12.8 Hz, 1H), 4.24 (brs, 1H), 4.19 (d, J = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 154.9, 150.4, 140.3, 136.5, 135.7, 132.9, 129.1, 128.7, 128.6, 128.1, 127.4, 127.3,

126.7, 123.7, 122.0, 117.4, 116.5, 109.4, 70.4, 62.9, 62.3, 21.3, 18.2; IR (thin film) 3358, 3023, 2919, 2862, 1707, 1592, 1451, 1059, 754 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{26}H_{24}NO_2$ $[M + H]^+$: 382.1807, found: 382.1784.



4ak

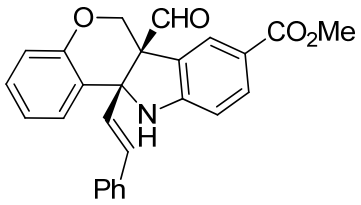
4ak was prepared by general procedure A. **1a** (0.055 g, 0.20 mmol), **2k** (0.183 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 5 h at 25 °C, and then stirring for 3 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ak** as a light yellow solid (0.050 g, 68%). Mp: 220–221 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 1H), 7.30 (d, J = 7.6 Hz, 2H), 7.25–7.21 (m, 2H), 7.19–7.13 (m, 2H), 7.08–7.04 (m, 1H), 6.89–6.86 (m, 4H), 6.77 (d, J = 8.0 Hz, 1H), 6.72 (t, J = 7.6 Hz, 1H), 6.43 (d, J = 16.0 Hz, 1H), 4.64 (d, J = 12.4 Hz, 1H), 4.31 (d, J = 12.4 Hz, 1H), 4.09 (brs, 1H), 2.07 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 197.1, 154.3, 148.5, 135.8, 132.6, 131.1, 129.4, 128.9, 128.6, 128.5, 128.2, 127.4, 127.2, 126.8, 122.2, 122.0, 120.5, 120.2, 117.7, 69.7, 63.2, 62.0, 16.7; IR (thin film) 3352, 3023, 2926, 1705, 1582, 1485, 1058, 762, 688 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{25}H_{22}NO_2$ $[M + H]^+$: 368.1651, found: 368.1640.



4al

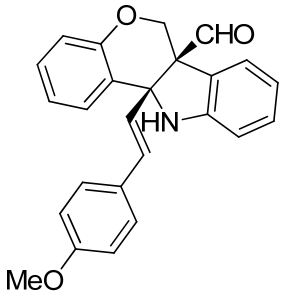
4al was prepared by general procedure A. **1a** (0.055 g, 0.20 mmol), **2l** (0.215 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 3 h at 25 °C, and then stirring for 4 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4al** as a light yellow solid (0.050 g, 58%). Mp: 214–215 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.62 (s, 1H), 7.38 (d, J = 7.2 Hz, 2H), 7.33–7.26 (m, 4H), 7.24–7.21 (m, 1H), 7.18–7.14 (m, 1H), 7.07 (d, J = 7.6 Hz, 1H), 7.00–6.93 (m, 2H), 6.86 (d, J = 8.0 Hz, 1H), 6.73–6.69 (m, 1H), 6.47 (d, J = 16.0 Hz, 1H), 4.69 (d, J = 12.4 Hz, 1H), 4.59 (brs, 1H), 4.37 (d, J = 12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 154.1, 148.4, 135.5, 133.1, 132.6, 129.2, 128.6, 128.5, 128.3, 127.5,

126.8, 126.3, 124.0, 123.6, 122.4, 121.4, 117.7, 104.5, 69.6, 63.1, 62.7; IR (thin film) 3453, 3041, 2966, 2864, 1707, 1604, 1451, 1058, 751 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{19}BrNO_2$ $[M + H]^+$: 432.0599, found: 432.0596.



4am

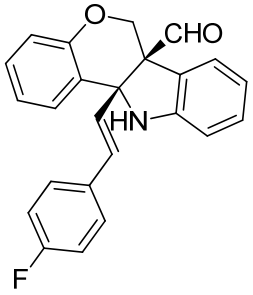
4am was prepared by general procedure A. **1a** (0.055 g, 0.20 mmol), **2m** (0.195 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 6 h at 25 °C, and then stirring for 6 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4am** as a light yellow solid (0.040 g, 49%). Mp: 73–74 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.51 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.75 (s, 1H), 7.30–7.18 (m, 5H), 7.11–7.07 (m, 2H), 6.91–6.83 (m, 2H), 6.79 (d, J = 8.4 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H), 6.39 (d, J = 16.0 Hz, 1H), 4.71 (brs, 1H), 4.67 (d, J = 12.4 Hz, 1H), 4.33 (d, J = 12.8 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 166.5, 154.2, 153.7, 135.4, 133.0, 132.9, 129.3, 128.7, 128.4, 128.0, 127.4, 126.8, 126.6, 126.2, 122.8, 122.3, 122.0, 117.9, 109.6, 70.4, 63.1, 61.2, 51.7; IR (thin film) 3345, 3025, 2924, 1708, 1518, 1285, 753 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{26}H_{22}NO_4$ $[M + H]^+$: 412.1549, found: 412.1552.



4ba

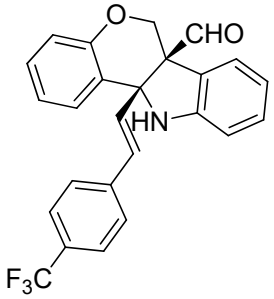
4ba was prepared by general procedure A. **1b** (0.061 g, 0.20 mmol), **2a** (0.172 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 2 h at 25 °C, and then stirring for 3 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ba** as a light yellow solid (0.058 g, 75%). Mp: 59–60 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (s, 1H), 7.30 (d, J = 8.8 Hz, 2H), 7.19 (d, J = 8.0 Hz, 1H), 7.14–7.10 (m, 3H), 6.96–6.92 (m, 1H), 6.85–6.80 (m, 4H), 6.70 (d, J = 8.0 Hz, 1H), 6.34 (d, J = 16.0 Hz, 1H), 4.73 (d, J = 12.4 Hz, 1H), 4.37 (brs, 1H), 4.34 (d,

J = 12.4 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 159.6, 154.2, 149.9, 132.2, 130.1, 128.9, 128.5, 128.0, 127.5, 127.1, 126.8, 124.6, 122.7, 122.1, 120.2, 117.6, 114.0, 110.7, 70.0, 62.9, 61.6, 55.2; IR (thin film) 3360, 3032, 2924, 1709, 1606, 1257, 809, 753 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{22}NO_3$ $[M + H]^+$: 384.1600, found: 384.1586.



4ca

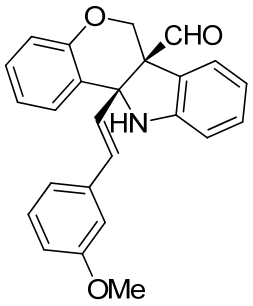
4ca was prepared by general procedure A. **1c** (0.059 g, 0.20 mmol), **2a** (0.172 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 3 h at 25 °C, and then stirring for 4 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ca** as a light yellow solid (0.035 g, 47%). Mp: 168–169 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.57 (s, 1H), 7.34 (dd, J = 8.0 Hz, 5.6 Hz, 2H), 7.18–7.11 (m, 4H), 7.01–6.95 (m, 3H), 6.93 (d, J = 16.0 Hz, 1H), 6.85–6.82 (m, 2H), 6.72 (d, J = 8.4 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 4.74 (d, J = 12.0 Hz, 1H), 4.37 (brs, 1H), 4.34 (d, J = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 163.8 (d, J = 246.5 Hz), 154.2, 149.8, 131.9 (d, J = 3.7 Hz), 131.5, 130.1, 129.0 (d, J = 3.6 Hz), 128.4, 128.3, 127.3, 126.8, 124.6, 122.6, 122.1, 120.4, 117.7, 115.7 (d, J = 21.9 Hz), 110.8, 69.9, 62.9, 61.6; IR (thin film) 3356, 3054, 2956, 2840, 1711, 1600, 1483, 1223, 822, 756 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{19}NO_2$ $[M + H]^+$: 372.1400, found: 372.1387.



4da

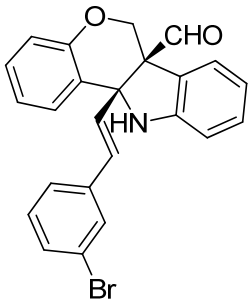
4da was prepared by general procedure A. **1d** (0.069 g, 0.20 mmol), **2a** (0.172 g, 0.40

mmol) and KOH (0.013 g, 0.24 mmol) stirring for 5 h at 25 °C, and then stirring for 5 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4da** as a light yellow solid (0.048 g, 57%). Mp: 60–61 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.56 (s, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.17–7.13 (m, 4H), 7.03–6.96 (m, 2H), 6.87–6.83 (m, 2H), 6.73 (d, J = 7.6 Hz, 1H), 6.58 (d, J = 16.0 Hz, 1H), 4.75 (d, J = 12.4 Hz, 1H), 4.38 (brs, 1H), 4.35 (d, J = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 154.3, 149.7, 139.2, 131.9, 131.2, 130.2, 129.2, 127.3, 126.9, 126.4, 125.7, 125.6, 124.7, 122.6, 122.2, 120.6, 117.8, 111.0, 69.9, 63.0, 61.7; IR (thin film) 3352, 3050, 2925, 2867, 1712, 1607, 1325, 1065, 754 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{19}F_3NO_2$ $[M + H]^+$: 422.1368, found: 422.1347.



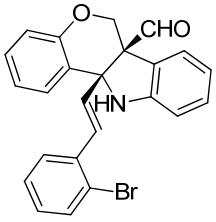
4ea

4ea was prepared by general procedure A. **1e** (0.061 g, 0.20 mmol), **2a** (0.172 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 2 h at 25 °C, and then stirring for 4 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ea** as a light yellow oil (0.048 g, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.57 (s, 1H), 7.25 (d, J = 9.2 Hz, 1H), 7.19–7.16 (m, 2H), 7.14 (d, J = 7.2 Hz, 2H), 6.97–6.89 (m, 4H), 6.86–6.81 (m, 3H), 6.72 (d, J = 8.0 Hz, 1H), 6.47 (d, J = 16.0 Hz, 1H), 4.75 (d, J = 12.4 Hz, 1H), 4.38 (brs, 1H), 4.35 (d, J = 12.4 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 159.8, 154.2, 149.8, 137.1, 132.6, 130.1, 129.6, 129.3, 129.0, 127.4, 126.9, 124.6, 122.6, 122.1, 120.4, 119.4, 117.7, 113.9, 112.0, 110.8, 69.9, 63.0, 61.6, 55.2; IR (thin film) 3362, 3029, 2924, 2851, 1711, 1604, 1159, 752 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{22}NO_3$ $[M + H]^+$: 384.1600, found: 384.1605.



4fa

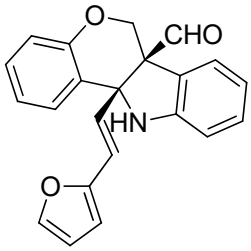
4fa was prepared by general procedure A. **1f** (0.071 g, 0.20 mmol), **2a** (0.172 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 3 h at 25 °C, and then stirring for 3 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4fa** as a light yellow solid (0.056 g, 65%). Mp: 56–57 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.49 (s, 1H), 7.44 (s, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.21–7.18 (m, 2H), 7.12–7.05 (m, 4H), 6.91 (t, J = 7.2 Hz, 1H), 6.85 (d, J = 16.0 Hz, 1H), 6.79–6.75 (m, 2H), 6.65 (d, J = 7.6 Hz, 1H), 6.41 (d, J = 15.6 Hz, 1H), 4.67 (d, J = 12.4 Hz, 1H), 4.35 (brs, 1H), 4.30 (d, J = 12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 154.2, 149.7, 137.9, 131.2, 131.0, 130.8, 130.2, 130.1, 129.6, 129.1, 127.3, 126.5, 125.4, 124.7 122.8, 122.6, 122.2, 120.5, 117.8, 110.9, 69.8, 63.0, 61.7; IR (thin film) 3368, 2925, 2854, 1709, 1606, 1483, 1261, 1022, 752 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{19}BrNO_2$ $[M + H]^+$: 432.0599, found: 432.0583.



4ha

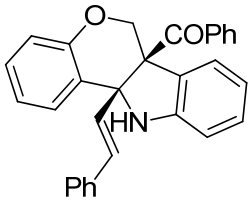
4ga was prepared by general procedure A. **1g** (0.071 g, 0.20 mmol), **2a** (0.172 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 3 h at 25 °C, and then stirring for 4 h at 80 °C . Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ga** as a light yellow solid (0.052 g, 60%). Mp: 54–55 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.46 (s, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.28 (d, J = 15.6 Hz, 1H), 7.18–7.13 (m, 2H), 7.09–7.02 (m, 4H), 6.92–6.89 (m, 1H), 6.79 (t, J = 7.6 Hz, 2H), 6.67 (d, J = 8.0 Hz, 1H), 6.29 (d, J = 16.0 Hz, 1H), 4.69 (d, J = 12.4 Hz, 1H), 4.35 (brs, 1H), 4.31 (d, J = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 154.2, 149.9, 136.2, 132.8, 132.2, 131.8, 130.2, 129.4, 129.1, 127.5, 127.4, 127.3, 126.6, 124.6, 123.9, 122.6, 122.2, 120.4, 117.7,

110.9, 69.9, 63.0, 61.5; IR (thin film) 3360, 2923, 2852, 1703, 1609, 1465, 1259, 741 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{19}BrNO_2$ $[M + H]^+$: 432.0599, found: 432.0583.



4ha

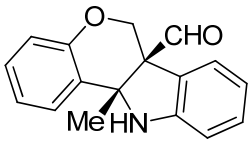
4ha was prepared by general procedure A. **1h** (0.053 g, 0.20 mmol), **2a** (0.172 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 2 h at 25 °C, and then stirring for 4 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ha** as a light yellow solid (0.038 g, 55%). Mp: 59–60 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 1H), 7.27–7.24 (m, 1H), 7.11–7.04 (m, 4H), 6.90–6.86 (m, 1H), 6.78–6.74 (m, 2H), 6.69–6.61 (m, 2H), 6.37 (d, J = 15.6 Hz, 1H), 6.31–6.28 (m, 1H), 6.21 (m, 1H), 4.65 (d, J = 12.4 Hz, 1H), 4.28 (brs, 1H), 4.25 (d, J = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 154.3, 151.5, 149.8, 142.5, 130.1, 129.0, 127.6, 127.4, 126.7, 124.7, 122.7, 122.1, 121.0, 120.4, 117.6, 111.4, 110.8, 109.5, 69.8, 63.0, 61.7; IR (thin film) 3364, 2924, 2853, 1714, 1604, 1261, 1016, 752 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{18}NO_3$ $[M + H]^+$: 344.1287, found: 344.1275.



4ia

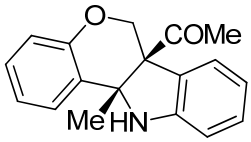
4ia was prepared by general procedure A. **1i** (0.071 g, 0.20 mmol), **2a** (0.172 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 3 h at 25 °C, and then stirring for 3 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ia** as a light yellow solid (0.057 g, 66%). Mp: 208–209 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.08 (m, 9H), 7.06 (dd, J = 17.6 Hz, 8.0 Hz, 5H), 6.87–6.83 (m, 1H), 6.77–6.72 (m, 2H), 6.60–6.56 (m, 2H), 6.31 (d, J = 16.0 Hz, 1H), 4.72 (d, J = 12.0 Hz, 1H), 4.60 (d, J = 12.0 Hz, 1H), 4.07 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.9, 154.7, 150.5, 139.7, 136.1, 131.5, 131.4, 129.7, 129.0, 128.6, 128.5, 128.4, 127.9, 127.8, 127.5, 127.4, 126.8, 126.6, 124.6, 122.1, 120.4, 117.7,

111.1, 70.9, 67.1, 64.6; IR (thin film) 3329, 2924, 2852, 1651, 1484, 1238, 744 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{30}H_{24}NO_2$ $[M + H]^+$: 430.1807, found: 430.1803.



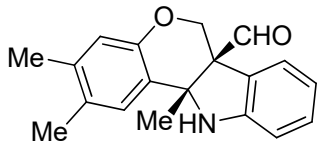
4ja

4ja was prepared by general procedure A. **1j** (0.038 g, 0.20 mmol), **2a** (0.172 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 2 h at 25 °C, and then stirring for 4 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ja** as a light yellow solid (0.024 g, 46%). Mp: 123–124 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 9.72 (s, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.15–7.09 (m, 3H), 7.00–6.96 (m, 1H), 6.83 (dd, J = 13.2 Hz, 7.6 Hz, 2H), 6.65 (d, J = 7.6 Hz, 1H), 4.55 (d, J = 12.4 Hz, 1H), 4.36 (brs, 1H), 4.34 (d, J = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7, 153.5, 149.8, 129.9, 129.4, 128.7, 125.6, 124.8, 123.4, 121.9, 120.0, 117.5, 110.7, 65.5, 62.7, 60.9, 24.5; IR (thin film) 3365, 3072, 2952, 1707, 1606, 1251, 1094, 804 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{16}NO_2$ $[M + H]^+$: 266.1181, found: 266.1208.



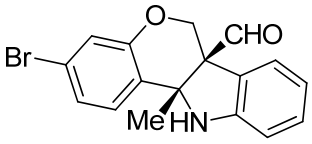
4ka

4ka was prepared by general procedure A. **1k** (0.041 g, 0.20 mmol), **2a** (0.172 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 2 h at 25 °C, and then stirring for for 3 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ka** as a light yellow solid (0.025 g, 44%). Mp: 138–139 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, J = 7.6 Hz, 1H), 7.05–6.98 (m, 3H), 6.89 (t, J = 7.2 Hz, 1H), 6.76–6.72 (m, 1H), 6.65 (d, J = 8.0 Hz, 1H), 6.53 (d, J = 7.6 Hz, 1H), 4.53 (d, J = 12.4 Hz, 1H), 4.26 (d, J = 12.8 Hz, 1H), 4.23 (brs, 1H), 2.00 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.1, 153.7, 150.1, 130.0, 129.3, 128.3, 127.2, 125.7, 123.9, 121.7, 120.1, 117.3, 110.9, 66.1, 64.1, 62.7, 28.7, 24.3; IR (thin film) 3434, 3013, 2925, 1697, 1607, 1464, 1093, 755, 630 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{18}NO_2$ $[M + H]^+$: 280.1338, found: 280.1325.



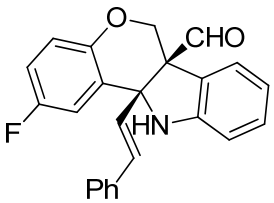
4la

4la was prepared by general procedure A. **1l** (0.043 g, 0.20 mmol), **2a** (0.172 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 1 h at 25 °C, and then stirring for 3 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4la** as a light yellow solid (0.028 g, 48%). Mp: 187–188 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71 (s, 1H), 7.15–7.08 (m, 2H), 7.03 (s, 1H), 6.82–6.78 (m, 1H), 6.65 (d, J = 7.6 Hz, 1H), 6.57 (s, 1H), 4.46 (d, J = 12.4 Hz, 1H), 4.26 (brs, 1H), 4.21 (d, J = 12.0, 1H), 2.12 (s, 3H), 2.07 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.9, 151.4, 149.9, 137.5, 130.1, 129.8, 126.1, 125.7, 124.8, 123.7, 120.0, 118.1, 110.7, 65.4, 62.8, 61.1, 24.6, 19.4, 19.1; IR (thin film) 3368, 3021, 2924, 1717, 1604, 1463, 1261, 1094, 803 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{20}NO_2$ $[M + H]^+$: 294.1494, found: 294.1475.



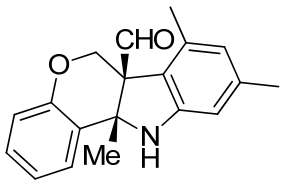
4ma

4ma was prepared by general procedure A. **1m** (0.053 g, 0.20 mmol), **2a** (0.172 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 4 h at 25 °C, and then stirring for 3 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4ma** as a light yellow solid (0.026 g, 38%). Mp: 187–188 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.69 (s, 1H), 7.19 (d, J = 8.8 Hz, 1H), 7.14–7.08 (m, 3H), 6.96 (s, 1H), 6.84–6.80 (m, 1H), 6.65 (d, J = 7.6 Hz, 1H), 4.57 (d, J = 12.0 Hz, 1H), 4.32 (brs, 1H), 4.29 (d, J = 12.0, 1H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 154.4, 149.6, 130.1, 127.9, 127.0, 125.0, 124.8, 123.1, 121.6, 120.5, 120.2, 110.7, 65.4, 62.8, 60.7, 24.3; IR (thin film) 3350, 2925, 1709, 1597, 1261, 1034, 832 cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{15}BrNO_2$ $[M + H]^+$: 344.0286, found: 344.0274.



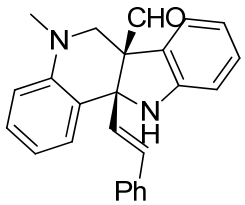
4na

4na was prepared by general procedure A. **1n** (0.059 g, 0.20 mmol), **2a** (0.172 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 4 h at 25 °C, and then stirring for 3 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4na** as a light yellow solid (0.039 g, 52%). Mp: 204–205 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 1H), 7.31–7.18 (m, 5H), 7.10 (dd, *J* = 18.4 Hz, 7.6 Hz, 2H), 6.91 (d, *J* = 16.0 Hz, 1H), 6.81–6.71 (m, 4H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 15.6 Hz, 1H), 4.66 (d, *J* = 12.4 Hz, 1H), 4.28 (brs, 1H), 4.25 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 158.9 (d, *J* = 239.1 Hz), 150.4, 149.6, 135.5, 133.1, 130.2, 128.8, 128.7, 128.4, 128.1 (d, *J* = 5.8 Hz), 126.8, 124.6, 122.4, 120.5, 119.1 (d, *J* = 8 Hz), 116.4 (d, *J* = 23.3 Hz), 113.2 (d, *J* = 23.3 Hz), 110.8, 70.0, 63.3, 61.4; IR (thin film) 3351, 3034, 2961, 2832, 1721, 1598, 1491, 1260, 749 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{19}FNO_2$ $[M + H]^+$: 372.1400, found: 372.1395.



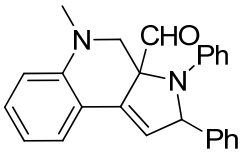
4jj

4jj was prepared by general procedure A. **1j** (0.038 g, 0.20 mmol), **2j** (0.194 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 4 h at 25 °C, and then stirring for 3 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4jj** as a light yellow solid (0.022 g, 37%). Mp: 125–126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 9.65 (s, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.25 (s, 1H), 7.13–7.10 (m, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.44 (s, 1H), 4.87 (d, *J* = 12.4 Hz, 1H), 4.57 (brs, 1H), 4.22 (d, *J* = 12.8, 1H), 2.21 (s, 3H), 2.20 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 197.7, 154.1, 147.4, 137.2, 134.5, 129.1, 128.6, 125.5, 124.4, 122.1, 119.0, 117.3, 114.2, 66.3, 62.9, 62.5, 24.4, 19.3, 18.0; IR (thin film) 3350, 3012, 2967, 2874, 1702, 1609, 1448, 1067, 758 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{20}NO_2$ $[M + H]^+$: 294.1494, found: 294.1481.



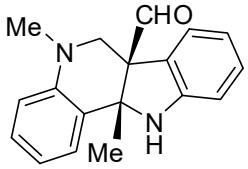
4oa

4oa was prepared by general procedure A. **1o** (0.058 g, 0.20 mmol), **2a** (0.172 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 4 h at 25 °C, and then stirring for 3 h at 80 °C . Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4oa** as a yellow solid (0.032 g, 44%). Mp: 121–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (s, 1H), 7.36 (d, J = 7.2 Hz, 2H), 7.31–7.27 (m, 2H), 7.24–7.21 (m, 1H), 7.12–7.08 (m, 3H), 7.01 (d, J = 7.2 Hz, 1H), 6.96 (d, J = 16.0 Hz, 1H), 6.80–6.76 (m, 1H), 6.74–6.69 (m, 2H), 6.63 (d, J = 8.4 Hz, 1H), 6.47 (d, J = 15.6 Hz, 1H), 4.38 (brs, 1H), 3.65 (dd, J = 22.8 Hz, 12.8 Hz, 2H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 150.1, 146.5, 136.0, 131.3, 130.5, 129.7, 128.5, 128.4, 127.9, 127.8, 127.5, 126.7, 124.6, 124.1, 119.9, 118.0, 112.4, 110.7, 71.1, 62.4, 49.3, 39.7; IR (thin film) 3365, 3025, 2927, 2830, 1710, 1603, 1502, 980, 744 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{23}N_2O$ $[M + H]^+$: 367.1810, found: 367.1819.



5oa

5oa was prepared by general procedure A. **1o** (0.058 g, 0.20 mmol), **2a** (0.172 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 4 h at 25 °C, and then stirring for 3 h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **5oa** as a yellow solid (0.040 g, 55%). Mp: 197–198 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.45 (s, 1H), 7.38–7.24 (m, 6H), 7.18–7.09 (m, 3H), 6.73 (t, J = 7.2 Hz, 1H), 6.67–6.59 (m, 4H), 6.11 (s, 1H), 5.83 (s, 1H), 4.59 (d, J = 12.0 Hz, 1H), 3.88 (d, J = 11.6 Hz, 1H), 3.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 144.5, 144.3, 142.0, 131.7, 130.4, 129.2, 129.0, 127.7, 125.9, 125.4, 125.0, 118.4, 116.4, 114.5, 113.8, 111.4, 74.5, 72.2, 57.0, 39.4; IR (thin film) 3022, 2924, 2851, 1725, 1599, 1498, 748, 695 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{23}N_2O$ $[M + H]^+$: 367.1810, found: 367.1788.

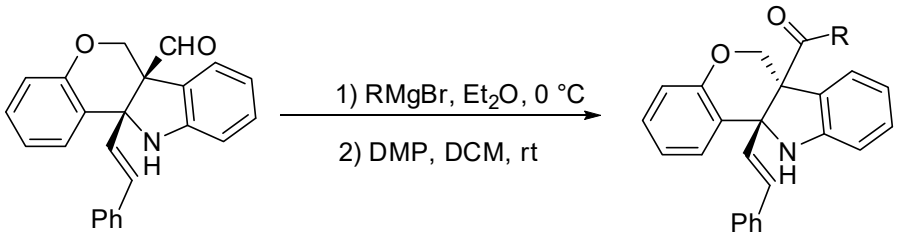


4pa

4pa was prepared by general procedure A. **1p** (0.040 g, 0.20 mmol), **2a** (0.172 g, 0.40 mmol) and KOH (0.013 g, 0.24 mmol) stirring for 3 h at 25 °C, and then stirring for 4

h at 80 °C. Purification using medium pressure chromatography (1:50; ethyl acetate: petroleum ether) afforded **4pa** as a yellow oil (0.033 g, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.73 (brs, 1H), 7.26 (d, J = 7.6 Hz, 1H), 7.12–7.02 (m, 3H), 6.80–6.74 (m, 2H), 6.63 (d, J = 7.6 Hz, 1H), 6.58 (d, J = 8.0 Hz, 1H), 4.43 (brs, 1H), 3.46 (s, 2H), 2.89 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.5, 149.9, 145.8, 129.6, 129.4, 128.2, 125.6, 125.5, 124.3, 119.7, 117.6, 112.1, 110.6, 66.7, 61.7, 49.3, 39.5, 25.6; IR (thin film) 3369, 3050, 2968, 1712, 1606, 1464, 909, 748 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{19}N_2O$ $[M + H]^+$: 279.1497, found: 279.1498.

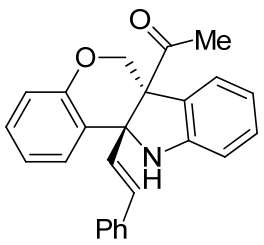
3. One-pot synthesis of compound 6 from 4aa



4aa **6ab-ad**

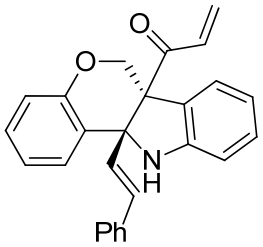
General procedure B: To a solution of **4aa** (0.3 mmol) in Et_2O (3 mL) at 0 °C was added slowly a solution of Grignard reagent magnesium bromide (2.5 equiv, 0.75 mmol). The resulting mixture was allowed to warm to room temperature and stirred for 1-5 h. Upon completion, the reaction was quenched with a saturated solution of NH_4Cl, extracted with diethylether (10 mL), The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude product was used directly in the next step.

In a round-bottle flask was charged with the above crude mixture and CH_2Cl_2 (3 mL). Deiss Martin reagent (2.5 equiv.) was added at room temperature. The resulting mixture was stirred for 3-6 h at room temperature until the substrate disappeared (monitored by TLC). Then the solid was filtered, and solvents were removed under the reduced pressure. The crude product was purified by flash chromatography (the crude residue was dry loaded with silica gel, 1/30 to 1/10, ethyl acetate/petroleum ether) to provide product **6ab-ad**.



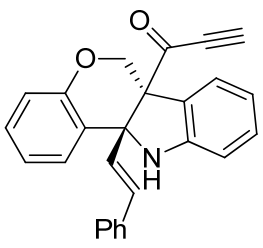
6ab

6ab was prepared by general procedure B. **4aa** (0.106 g, 0.30 mmol), methylmagnesium bromide (0.25 mL, 0.75 mmol, 3.0 M solution in Et_2O) and Deiss Martin reagent (0.318 g, 0.75 mmol). Purification using medium pressure chromatography (1:20; ethyl acetate: petroleum ether) afforded **6ab** as a light yellow solid (0.087 g, 79%). Mp: 68–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 7.2 Hz, 2H), 7.32–7.28 (m, 2H), 7.26–7.22 (m, 1H), 7.19 (d, J = 7.2 Hz, 1H), 7.11–7.03 (m, 4H), 6.92–6.88 (m, 1H), 6.85 (t, J = 7.2 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.68 (d, J = 8.0 Hz, 1H), 6.39 (d, J = 15.6 Hz, 1H), 4.71 (d, J = 12.8 Hz, 1H), 4.46 (d, J = 12.4 Hz, 1H), 4.24 (s, 1H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.4, 154.3, 150.0, 136.1, 130.7, 129.5, 129.1, 128.7, 128.6, 128.0, 127.6, 126.7, 126.5, 126.4, 123.8, 122.0, 120.3, 117.6, 111.2, 70.3, 64.8, 64.0, 28.2; IR (thin film) 3453, 3040, 2924, 1686, 1483, 1373, 730 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{22}NO_2$ $[M + H]^+$: 368.1650, found: 368.1645.



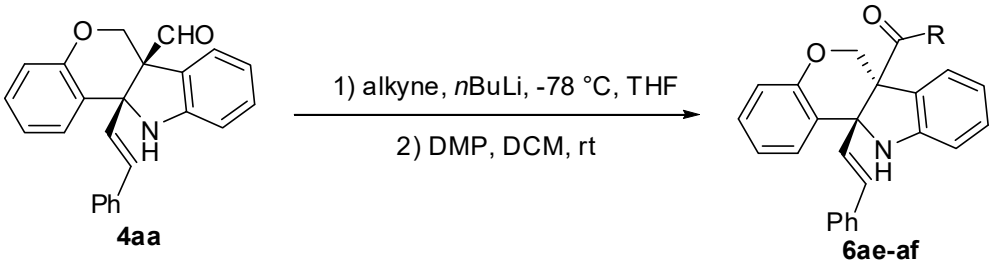
6ac

6ac was prepared by general procedure B. **4aa** (0.106 g, 0.30 mmol), vinylmagnesium bromide (0.75 mL, 0.75 mmol, 1.0 M solution in THF) and Deiss Martin reagent (0.318 g, 0.75 mmol). Purification using medium pressure chromatography (1:20; ethyl acetate: petroleum ether) afforded **6ac** as a light yellow solid (0.078 g, 69%). Mp: 94–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.18 (m, 6H), 7.13 (dd, J = 14.2 Hz, 7.2 Hz, 3H), 6.93–6.89 (m, 2H), 6.84–6.79 (m, 2H), 6.69 (d, J = 7.6 Hz, 1H), 6.55–6.48 (m, 1H), 6.40 (d, J = 15.6 Hz, 1H), 6.14 (d, J = 16.8 Hz, 1H), 5.41 (d, J = 10.0 Hz, 1H), 4.80 (d, J = 12.4 Hz, 1H), 4.48 (d, J = 12.0 Hz, 1H), 4.30 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 154.5, 150.2, 136.2, 133.4, 131.9, 129.7, 129.6, 128.7, 128.5, 128.1, 128.0, 127.9, 127.6, 126.7, 125.5, 124.2, 122.0, 120.4, 117.6, 111.0, 70.7, 64.8, 62.7; IR (thin film) 3344, 3024, 2921, 1676, 1607, 1485, 759, 693 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{22}NO_2$ $[M + H]^+$: 380.1650, found: 380.1642.



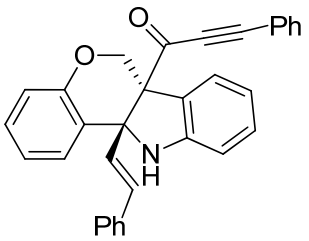
6ad

6ad was prepared by general procedure B. **4aa** (0.106 g, 0.30 mmol), ethynylmagnesium bromide (1.5 mL, 0.75 mmol, 0.5 M solution in THF) and Deiss Martin reagent (0.318 g, 0.75 mmol). Purification using medium pressure chromatography (1:20; ethyl acetate: petroleum ether) afforded **6ad** as a light yellow solid (0.077 g, 68%). Mp: 132–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 7.6 Hz, 2H), 7.32–7.29 (m, 2H), 7.26–7.10 (m, 5H), 6.96–6.91 (m, 2H), 6.87–6.80 (m, 2H), 6.71 (d, J = 8.0 Hz, 1H), 6.55 (d, J = 15.6 Hz, 1H), 4.67 (d, J = 12.4 Hz, 1H), 4.48 (d, J = 12.4 Hz, 1H), 4.28 (brs, 1H), 3.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.1, 154.2, 150.4, 136.1, 133.1, 130.0, 129.2, 128.8, 128.6, 128.0, 127.8, 127.7, 126.8, 124.8, 124.5, 122.2, 120.1, 117.5, 111.0, 80.6, 80.2, 70.8, 64.6, 64.0; IR (thin film) 3431, 3296, 3021, 2923, 2847, 2187, 1657, 1483, 745 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{26}H_{20}NO_2$ $[M + H]^+$: 378.1494, found: 378.1488.



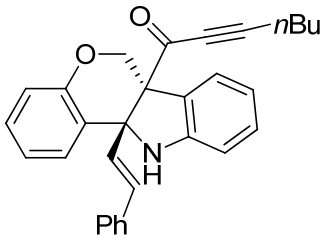
General procedure C: To a stirred solution of alkyne (0.75 mmol) in dry THF (3 mL) under argon was added *n*-BuLi (0.3 mL, 0.75 mmol, 2.5 M solution in hexane) via a syringe at -78 °C. The mixture was allowed to stir for 30 min at -78 °C. Then **4aa** (0.3 mmol) was added. The mixture was allowed to stir for an additional 30 min at -78 °C, and then for 0.5 h at room temperature. The reaction was quenched with a saturated solution of NH_4Cl, extracted with diethylether (10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude product was used directly in the next step.

In a round-bottle flask was charged with the above crude mixture and CH_2Cl_2 (3 mL). Deiss Martin reagent (2.5 equiv.) was added at room temperature. The resulting mixture was stirred for 3-6 h at room temperature until the substrate disappeared (monitored by TLC). Then the solid was filtered, and the solvents were removed under reduced pressure. the crude product was purified by flash chromatography (the crude residue was dry loaded with silica gel, 1/30 to 1/10, ethyl acetate/petroleum ether) to provide product **6ae-af.**



6ae

6ae was prepared by general procedure C. **4aa** (0.106 g, 0.30 mmol), phenylacetylene (0.08 mL, 0.75 mmol) and Deiss Martin reagent (0.318 g, 0.75 mmol). Purification using medium pressure chromatography (1:20; ethyl acetate: petroleum ether) afforded **6ae** as a light yellow solid (0.105 g, 77%). Mp: 82–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.36 (m, 1H), 7.31–7.10 (m, 12H), 6.96–6.82 (m, 5H), 6.75 (d, J = 7.6 Hz, 1H), 6.58 (d, J = 15.6 Hz, 1H), 4.72 (d, J = 12.4 Hz, 1H), 4.56 (d, J = 12.4 Hz, 1H), 4.34 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1, 154.3, 150.6, 136.3, 133.4, 132.5, 130.7, 129.8, 129.6, 128.7, 128.5, 128.4, 128.1, 127.8, 127.7, 126.8, 125.9, 124.6, 122.0, 120.1, 119.8, 117.5, 110.7, 93.2, 87.7, 71.0, 64.9, 64.3; IR (thin film) 3367, 3010, 2927, 2195, 1650, 1485, 1271, 750 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{32}H_{24}NO_2$ $[M + H]^+$: 454.1807, found: 454.1802.

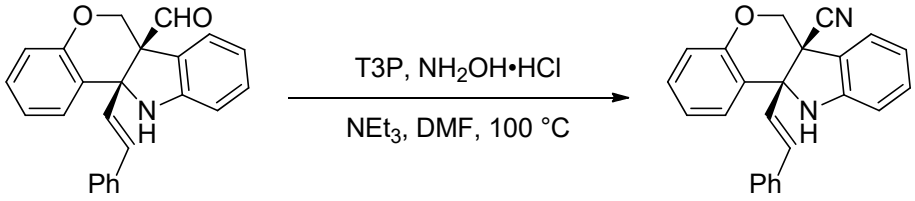


6af

6af was prepared by general procedure C. **4aa** (0.106 g, 0.30 mmol), 1-hexyne (0.09 mL, 0.75 mmol) and Deiss Martin reagent (0.318 g, 0.75 mmol). Purification using medium pressure chromatography (1:20; ethyl acetate: petroleum ether) afforded **6af** as a light yellow oil (0.083 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 7.2 Hz, 2H), 7.31–7.27 (m, 2H), 7.24–7.19 (m, 3H), 7.16 (d, J = 7.6 Hz, 1H), 7.12 (t, J = 7.6 Hz, 2H), 6.94–6.91 (m, 1H), 6.87–6.79 (m, 2H), 6.66 (d, J = 7.6 Hz, 1H), 6.55 (d, J = 15.6 Hz, 1H), 4.64 (d, J = 12.0 Hz, 1H), 4.49 (d, J = 12.4 Hz, 1H), 4.24 (brs, 3H), 2.14–2.11 (m, 2H), 1.27–1.20 (m, 4H), 0.83–0.79 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.9, 154.3, 150.3, 136.3, 132.4, 129.8, 129.5, 128.6, 128.5, 128.0, 127.9, 127.8, 126.7, 125.9, 124.4, 122.0, 119.8, 117.5, 110.7, 97.2, 80.4, 70.6, 64.6, 64.4, 29.3, 21.6, 18.6, 13.4; IR (thin film) 364, 3030, 2930, 2827, 2209, 1652, 1464, 1221,

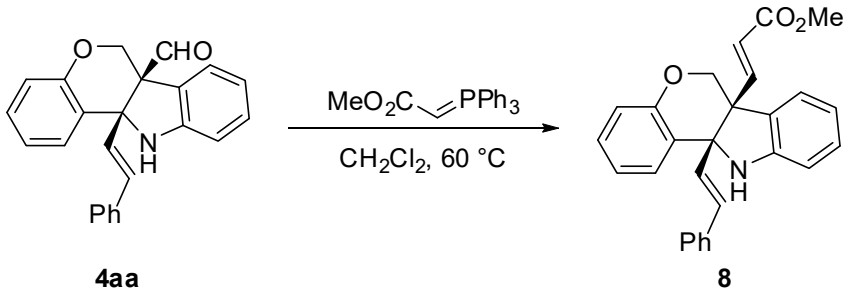
746 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{30}H_{28}NO_2$ $[M + H]^+$: 434.2120, found: 434.2114.

4. Synthesis of compounds 7-13 from 4aa



4aa **7**

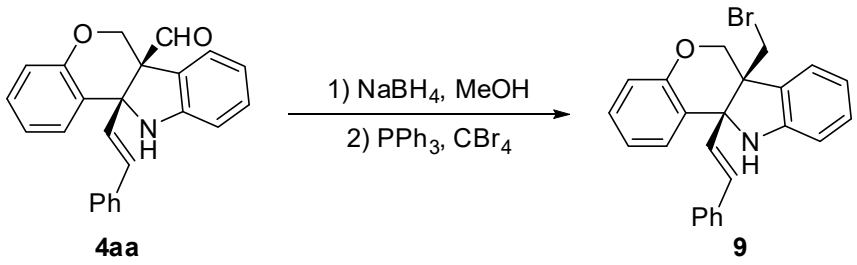
To a mixture of **4aa** (0.2 mmol), hydroxylamine hydrochloride (0.22 mmol), and Et_3N (0.22 mmol) in DMF (2 mL) was added T3P (1.2 mmol, 50% in DMF), and the mixture was stirred at 100 °C for 12 h. The completion of reaction was monitored by TLC. The mixture was cooled and extracted with Et_2O (10 mL). The combined organic phase was washed with brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtrated and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum-EtOAc: 10/1) to afford compound **7** (0.057 g, 81%) as a light yellow solid. Mp: 66–67 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (t, J = 7.2 Hz, 3H), 7.28–7.17 (m, 6H), 7.02–6.98 (m, 2H), 6.88 (d, J = 7.6 Hz, 1H), 6.76–6.69 (m, 2H), 6.51 (d, J = 16.0 Hz, 1H), 4.53 (brs, 1H), 4.40 (d, J = 11.2 Hz, 1H), 4.13 (d, J = 11.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 148.2, 135.6, 132.5, 130.5, 129.9, 129.5, 129.1, 128.5, 128.2, 126.9, 124.4, 123.5, 122.9, 122.5, 120.4, 117.9, 117.8, 110.4, 67.9, 67.3, 49.6; IR (thin film) 3363, 3030, 2926, 2868, 2245, 1609, 972, 746 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{19}N_2O$ $[M + H]^+$: 351.1497, found: 351.1500.



4aa **8**

In a Teflon-sealed flask charged with **4aa** (0.2 mmol), methyl 2-(triphenylphosphoranylidene)acetate (0.22 mmol) and CH_2Cl_2 (4 mL). Then, the reaction mixture was stirred vigorously at 60 °C for 3 days until the substrate **4aa** disappeared (monitored by TLC). The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum-EtOAc: 20/1) to afford compound **8** (0.075 g, 91%) as a white solid. Mp: 92–93 °C; ^{1}H NMR (400

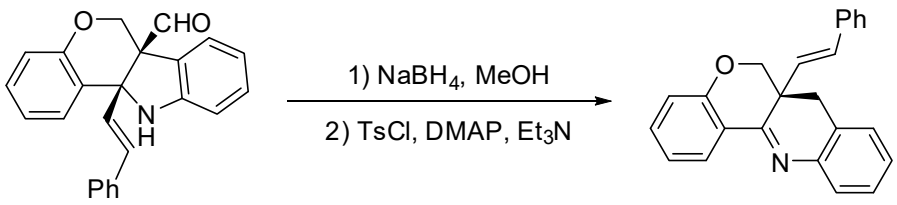
MHz, $CDCl_3$): δ 7.31–7.25 (m, 4H), 7.22–7.13 (m, 3H), 7.10–7.04 (m, 3H), 6.94 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 6.81 (t, J = 7.6 Hz, 1H), 6.69–6.61 (m, 2H), 6.31 (d, J = 16.4 Hz, 1H), 5.94 (d, J = 16.0 Hz, 1H), 4.43 (brs, 1H), 4.31–4.21 (m, 2H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 153.9, 149.0, 146.1, 136.2, 131.6, 131.5, 129.1, 128.9, 128.5, 127.8, 127.7, 126.6, 125.8, 124.5, 122.5, 121.8, 119.7, 117.4, 110.1, 70.0, 66.7, 54.0, 51.5; IR (thin film) 3364, 3029, 2951, 2863, 1713, 1606, 1486, 1220, 744 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{24}NO_3$ $[M + H]^+$: 410.1756, found: 410.1749.



4aa **9**

In a round-bottle flask charged with **4aa** (0.2 mmol) and MeOH (2 mL), $NaBH_4$ (0.4 mmol, 2.0 equiv) was added. Then, the reaction mixture was stirred vigorously at 25 °C for 0.5 h until the substrate **4aa** disappeared (monitored by TLC). At this time, the reaction was diluted with H_2O (10 mL) and exacted with Et_2O H_2O (20 mL). The combined organic layers were washed with brine H_2O (10 mL), dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure to give crude alcohol as a yellow oil which was used directly without purification for the next step.

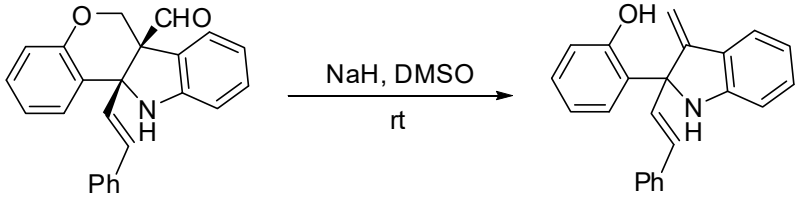
To the mixture of crude alcohol in CH_2Cl_2 (2 mL) was added PPh_3 (0.5 mmol), CBr_4 (0.5 mmol) and the mixture was stirred at 60 °C for 12 h. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum-EtOAc: 20/1) to afford compound **9** (0.078 g, 94%) as a white solid. Mp: 191–192 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (t, J = 8.0 Hz, 3H), 7.34–7.31 (m, 2H), 7.28–7.25 (m, 1H), 7.17–7.07 (m, 3H), 6.94–6.90 (m, 1H), 6.86–6.81 (m, 3H), 6.65 (d, J = 7.6 Hz, 1H), 6.47 (d, J = 15.6 Hz, 1H), 4.70 (d, J = 11.6 Hz, 1H), 4.23 (brs, 1H), 4.20 (d, J = 11.6 Hz, 1H), 3.63 (d, J = 10.4 Hz, 1H), 3.56 (d, J = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 148.4, 136.1, 131.8, 129.5, 129.0, 128.8, 128.7, 128.2, 128.0, 127.9, 127.1, 126.7, 125.5, 121.8, 119.3, 117.4, 110.3, 70.3, 66.8, 50.7, 36.2; IR (thin film) 3353, 3068, 2966, 2854, 1605, 1463, 1222, 747 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{21}BrNO$ $[M + H]^+$: 418.0806, found: 418.0801.



4aa **10**

In a round-bottle flask charged with **4aa** (0.2 mmol) and MeOH (2 mL), $NaBH_4$ (0.4 mmol, 2.0 equiv) was added. Then, the reaction mixture was stirred vigorously at 25 °C for 0.5 h until the substrate **4aa** disappeared (monitored by TLC). At this time, the reaction was diluted with H_2O (10 mL) and exacted with Et_2O (20 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure to give crude alcohol as a yellow oil which was used directly without purification for the next step.

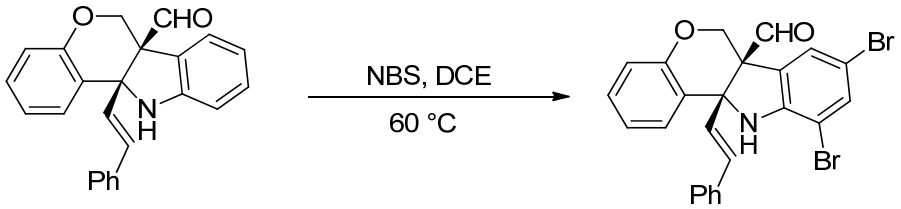
The crude alcohol, Et_3N (0.4 mmol), and TsCl (3.5 mmol) were dissolved in DCM (4 mL), followed by addition of catalytic amount of DMAP (3.5 mmol). The reaction was stirred for 48 hours at 70 °C, then the solution was washed with water (10 mL) and brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4, filtrated and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum-EtOAc: 30/1) to afford compound **10** (0.053 g, 79%) as a white solid. Mp: 156–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.26–7.22 (m, 1H), 7.15–7.03 (m, 8H), 6.90 (d, J = 8.0 Hz, 1H), 6.35 (d, J = 16.4 Hz, 1H), 6.14 (d, J = 16.0 Hz, 1H), 4.46 (d, J = 10.8 Hz, 1H), 4.30 (d, J = 10.8 Hz, 1H), 2.94 (d, J = 15.6 Hz, 1H), 2.73 (d, J = 16.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 158.5, 144.2, 136.4, 132.7, 131.7, 128.2, 127.9, 127.9, 127.5, 127.0, 126.8, 126.5, 126.4, 126.3, 124.7, 121.7, 120.3, 117.5, 74.7, 41.7, 32.5; IR (thin film) 3453, 3016, 2926, 2876, 1609, 1477, 1207, 757 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{20}NO$ $[M + H]^+$: 338.1544, found: 338.1541.



4aa **11**

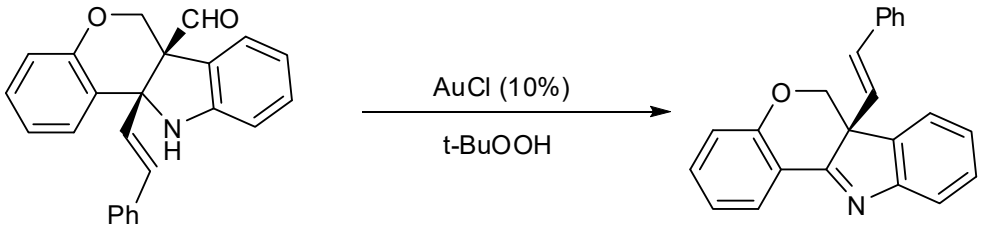
To a mixture of **4aa** (0.2 mmol) in DMSO (2 mL) was added NaH (0.4 mmol), and the mixture was stirred at 25 °C for 2 h. The mixture was extracted with Et_2O. The combined organic phase was washed with brine, The organic layer was dried over anhydrous Na_2SO_4, filtrated and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum-EtOAc: 10/1) to yield **11** (0.058 g, 89%)

as a light yellow solid. Mp: 165–166 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (brs, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.36 (d, J = 7.2 Hz, 2H), 7.30–7.16 (m, 6H), 6.96–6.93 (m, 1H), 6.90–6.84 (m, 3H), 6.60 (d, J = 15.6 Hz, 1H), 6.46 (d, J = 15.6 Hz, 1H), 5.70 (s, 1H), 4.70 (s, 1H), 4.43 (brs, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 156.7, 148.1, 147.0, 135.9, 131.2, 130.3, 130.1, 129.4, 129.0, 128.7, 128.6, 128.0, 126.7, 126.4, 121.9, 121.3, 119.1, 117.9, 113.6, 106.6, 74.5; IR (thin film) 3432, 3323, 3031, 2930, 2856, 1602, 1250, 876, 751 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{20}NO$ $[M + H]^+$: 326.1544, found: 326.1528.



4aa **12**

To a mixture of **4aa** (0.2 mmol) in DCE (2 mL) was added NBS (0.4 mmol), and the mixture was stirred at 60 °C for 2 h. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (petroleum-EtOAc: 10/1) to afford **12** (0.080 g, 78%) as a light yellow solid. Mp: 224–225 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.61 (brs, 1H), 7.41 (s, 1H), 7.36–7.23 (m, 5H), 7.21–7.16 (m, 3H), 7.00–6.96 (m, 1H), 6.93–6.95 (m, 2H), 6.44 (d, J = 16.0 Hz, 1H), 4.63–4.59 (m, 2H), 4.34 (d, J = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9, 154.0, 147.6, 135.3, 134.7, 133.4, 129.4, 128.7, 128.5, 127.9, 127.4, 126.9, 126.8, 125.8, 125.7, 122.6, 117.8, 111.7, 104.8, 69.9, 63.1, 62.6; IR (thin film) 3336, 3079, 2923, 1708, 1460, 1056, 758, 688 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{18}BrNO_2$ $[M + H]^+$: 509.9704, found: 509.9704.



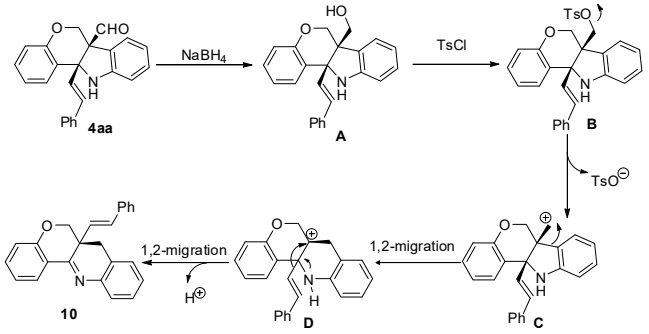
4aa **13**

To a mixture of **4aa** (0.2 mmol) in H_2O:CH_2Cl_2 (2:1) (2 mL) was added AuCl (10% mol), Neocuproine Hydrochloride Monohydrate (10% mol), *t*BuOOH (1 mmol), and the mixture was stirred at 90 °C for 10 h. The mixture was extracted with CH_2Cl_2. The combined organic phase was washed with brine. The organic layer was dried over anhydrous Na_2SO_4, filtrated and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum-CH_2Cl_2: 1/1) to afford **13** (0.042 g, 64%)

as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.46–7.37 (m, 4H), 7.28–7.21 (m, 5H), 7.08 (t, J = 7.2 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 6.43–6.33 (m, 2H), 4.94 (d, J = 10.8 Hz, 1H), 4.10 (d, J = 10.8 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 175.5, 156.9, 156.8, 137.5, 136.3, 133.3, 131.3, 129.3, 128.4, 127.8, 126.4, 125.8, 125.7, 124.3, 123.7, 121.8, 121.1, 118.2, 117.1, 72.8, 56.7; IR (thin film) 3060, 2959, 2869, 2248, 1608, 1212, 755, 694 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{23}H_{18}NO$ $[M + H]^+$: 324.1388, found: 324.1386.

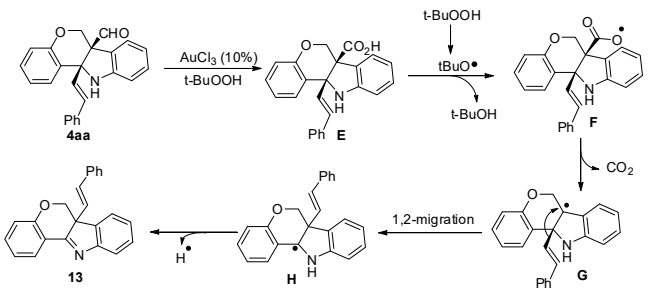
5. Proposed mechanisms for formation of 10 and 13

5.1 Possible mechanism for formation of compound **10**



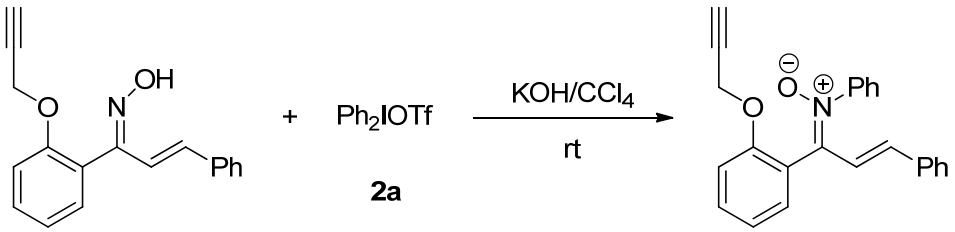
We proposed a possible reaction pathway: Reduction of **4aa** with $NaBH_4$ provided A, which was converted to **B** by reaction with TsCl. The **B** could be isolated in high yield and converted to **C** by C-O bond cleavage. The C took place with aryl migration to provide more stable carbon cation **D**. Then **D** continued to proceed 1,2-styrenyl migration to afford more stable compound **10**. The driving force for the migration was the stability of the carbon cation. We performed two controlled experiments. When **B** was isolated and then heated at 70 °C directly, the compound **10** was observed. Treatment of **B** wtih TEMPO at 70 °C, the compound **10** was also observed. These results suggested that the fomration of compound **10** did not involve a radical process.

5.2 Possible mechanism for formation of compound **13**



We proposed a possible reaction pathway: Compound **4aa** was oxidized by t-BuOOH under gold-catalyst to provide compound **E**, which formed **F** by t-BuO• and went through decarboxyaltion to give **G**. The **G** udnerwent 1,2-migration to afford **H,** which then converted to stable compound **13.** We also performed a controlled reaction. When the **E** was added with radical trapping reagents TEMPO, compound **13** could not be obtained, which suggested that formation of **13** involved a radical process.

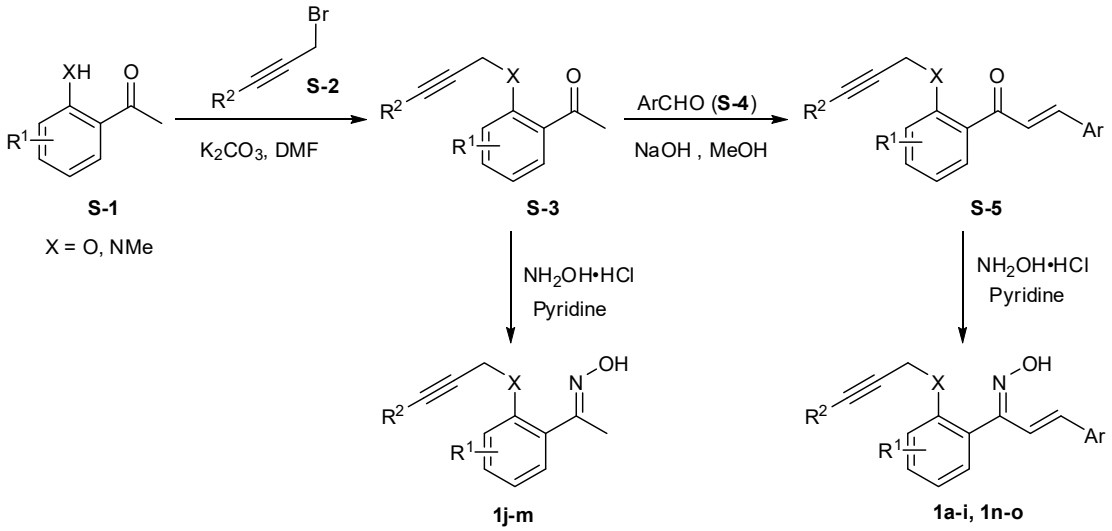
6. Synthesis of nitrone 3aa



1a **3aa**

General procedure D: In a round-bottle flask was charged with **1a** (0.2 mmol), **2a** (0.4 mmol), KOH (0.24 mmol) and CCl_4 (2 mL). And then, the reaction mixture was stirred vigorously at 25 °C for 3 h until the substrate **1a** disappeared (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (the crude residue was dry loaded with silica gel, 1/10 to 1/2, ethyl acetate/petroleum ether) to provide **3aa** as a yellow oil (0.028 g, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 16.4 Hz, 1H), 7.46−7.36 (m, 2H), 7.23−7.22 (m, 2H), 7.15−7.7.12 (m, 4H), 7.02−6.98 (m, 4H), 6.81−6.76 (m, 2H), 6.49 (d, J = 16.4 Hz, 1H), 4.46−4.36 (m, 2H), 2.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4, 146.9, 146.1, 139.2, 136.1, 131.7, 130.6, 128.8, 128.4, 127.9, 127.2, 126.6, 124.3, 123.7, 121.7, 121.0, 112.1, 77.6, 75.7, 55.2; IR (thin film) 3429, 3060, 2925, 2869, 2221, 1601, 1451, 753. 693 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{20}NO_2$ $(M+H)^+$ 354.1494, found 354.1495.

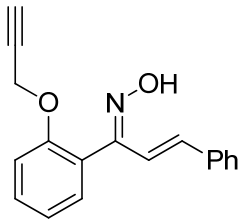
7. Synthesis of Alkynyl tethered Oximes 1:



General Procedure E: To a well stirred solution of anhydrous DMF (25 mL) was added **S-1** (10 mmol), K_2CO_3 (1.67 g, 12 mmol) and **S-2** (12 mmol). The reaction mixture was stirred at 60 °C for 12 h (monitored by TLC) before it was slowly poured into water. Extracted with Et_2O (30 mL), then the combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure to give product **S-3** as a brown oil, which was used directly without purification for the next step.

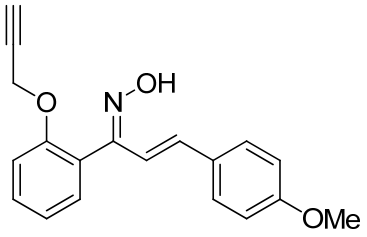
To the stirred solution of **S-3** in methanol was added dropwise aqueous solution of sodium hydroxide (2.6 mL, 40%). Then, the resulting mixture was further treated with **S-4** (10 mmol) and stirred at room temperature until the conversion was complete (disappearance of acetophenone, monitored by TLC). The solvent was removed by evaporation, and the residue was treated with water (20 mL) and extracted with ethyl acetate (20 mL). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated to give a yellow oil **S-5** which was used directly without purification for the next step.

To a solution of **S-3** or **S-5** in MeOH (20 mL) was added hydroxylamine hydrochloride (1.03 g, 15 mmol) and pyridine (2.4 mL, 2.5 equiv). The reaction mixture was then stirred at 25 °C until the **S-3** was consumed. The solvent was evaporated and the residue was diluted with water (20 mL) and ethyl acetate (20 mL). The aqueous layer was extracted with ethyl acetate (20 mL). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, and concentrated. Purification of the crude product by flash column chromatography (petroleum/EtOAc: 6/1) afforded the corresponding oxime **1**.



1a (*E*/*Z* = 3/1)

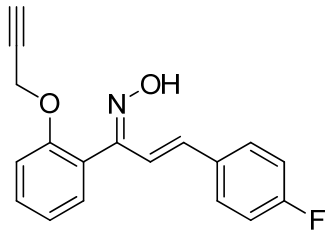
1a was prepared by general procedure E. 2-Hydroxyacetophenone (1.2 mL, 10 mmol), 3-bromo-1-propyne (0.93 mL, 12 mmol) and benzaldehyde (1.0 mL, 10 mmol). Purification using medium pressure chromatography (1:6; ethyl acetate: petroleum ether) afforded **1a** as a white solid (1.17 g, 42%). Mp: 85–86 °C; *major isomer*: ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.62 (brs, 1H), 7.71 (d, J = 16.5 Hz, 1H), 7.43–7.39 (m, 3H), 7.33 (d, J = 7.5 Hz, 1H), 7.30–7.24 (m, 3H), 7.13 (d, J = 17.5 Hz, 1H), 7.08–7.05 (m, 1H), 6.55 (d, J = 16.0 Hz, 1H), 4.66 (s, 2H), 2.41 (s, 1H); ^{13}C NMR (125MHz, $CDCl_3$): δ 155.6, 155.5, 138.6, 136.4, 131.5, 130.1, 128.8, 128.5, 127.5, 126.9, 124.4, 121.6, 113.1, 78.5, 75.5, 56.0; *minor isomer*: ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.62 (brs, 1H), 7.43–7.39 (m, 1H), 7.37–7.35 (m, 3H), 7.33 (d, J = 7.5 Hz, 1H), 7.18–7.15 (m, 3H), 7.13 (d, J = 17.5 Hz, 1H), 7.08–7.05 (m, 1H), 6.42 (d, J = 16.0 Hz, 1H), 4.66 (s, 2H), 3.01 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 154.3, 136.3, 136.0, 130.0, 129.7, 128.3, 128.2, 126.6, 125.2, 121.6, 116.7, 113.5, 78.6, 75.5, 56.3; IR (thin film) 3280, 3021, 2917, 1599, 1492, 1450, 1220, 951, 748 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{16}NO_2$ $[M + H]^+$: 278.1181, found: 278.1173.



1b (*E*/*Z* = 1.2/1)

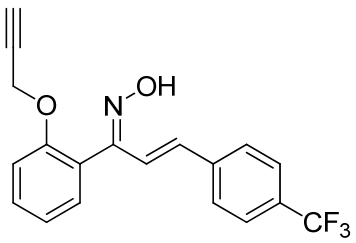
1b was prepared by general procedure E. 2-Hydroxyacetophenone (1.2 mL, 10 mmol), 3-bromo-1-propyne (0.93 mL, 12 mmol) and 4-methoxybenzaldehyde (1.2 mL, 10 mmol). Purification using medium pressure chromatography (1:6; ethyl acetate: petroleum ether) afforded **1b** as a white solid (1.36 g, 45%). Mp: 51–52 °C; *major isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 12.4 Hz, 1H), 7.36–7.30 (m, 2H), 7.24–7.17 (m, 1H), 7.12–6.96 (m, 2H), 6.77–6.76 (m, 1H), 6.75–6.73 (m, 2H), 6.42 (d, J = 12.4 Hz, 1H), 4.62 (s, 2H), 3.71 (s, 3H), 2.35 (s, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 157.2, 155.6, 138.4,

131.5, 130.0, 129.7, 128.9, 128.2, 123.0, 121.5, 114.0, 113.2, 78.6, 75.5, 56.0, 55.2; *minor isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.30 (m, 2H), 7.24–7.17 (m, 2H), 7.12–6.96 (m, 2H), 6.90 (d, J = 16.0 Hz, 1H), 6.75–6.73 (m, 2H), 6.30 (d, J = 16.0 Hz, 1H), 4.59 (s, 2H), 3.71 (s, 3H), 2.34 (s, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (100MHz, $CDCl_3$): δ 159.8, 155.9, 154.3, 135.7, 130.1, 129.1, 128.9, 128.2, 124.6, 122.0, 121.7, 114.5, 113.5, 78.7, 75.5, 56.4, 55.2; IR (thin film) 3285, 3051, 2930, 2840, 1601, 1453, 1253, 972 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{18}NO_3$ $[M + H]^+$: 308.1286, found: 308.1278.



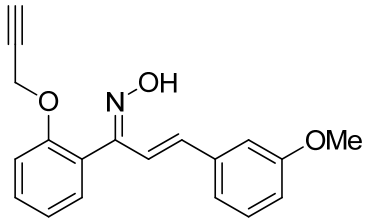
1c (*E*/*Z* = 2/1)

1c was prepared by general procedure E. 2-Hydroxyacetophenone (1.2 mL, 10 mmol), 3-bromo-1-propyne (0.93 mL, 12 mmol) and 4-fluorobenzaldehyde (1.1 mL, 10 mmol). Purification using medium pressure chromatography (1:6; ethyl acetate: petroleum ether) afforded **1c** as a light yellow oil (1.1 g, 36%). *Major isomer*: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (d, J = 16.2 Hz, 1H), 7.36–7.33 (m, 2H), 7.27–7.22 (m, 2H), 7.11–7.07 (m, 1H), 7.05–7.02 (m, 1H), 7.00–6.97 (m, 1H), 6.93–6.88 (m, 1H), 6.43 (d, J = 16.8 Hz, 1H), 4.60 (s, 2H), 2.35 (s, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (150 MHz, $CDCl_3$): δ 163.9 (d, J = 248.2 Hz), 156.8, 155.5, 137.4, 132.6, 131.5, 130.2, 129.7, 129.2 (d, J = 7.3 Hz), 121.6, 116.4, 115.7 (d, J = 22.0 Hz), 113.1; *minor isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.33 (m, 2H), 7.27–7.22 (m, 2H), 7.15–7.14 (m, 1H), 7.05–7.02 (m, 1H), 6.93–6.88 (m, 3H), 6.30 (d, J = 16.2 Hz, 1H), 4.59 (s, 2H), 2.34 (s, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5 (d, J = 247.2 Hz), 155.5, 154.3, 134.8, 132.5, 130.1, 129.7, 128.5 (d, J = 8.8 Hz), 124.3, 121.7, 116.4, 115.6 (d, J = 21.9 Hz, 1H), 113.4; IR (thin film) 3293, 3070, 2932, 2871, 1599, 1445, 1225, 1020, 755 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{15}FNO_2$ $[M + H]^+$: 296.1086, found: 296.1075.



1d (*E*/*Z* = 3.3/1)

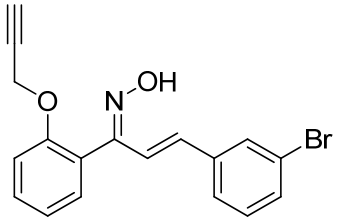
1d was prepared by general procedure E. 2-Hydroxyacetophenone (1.2 mL, 10 mmol), 3-bromo-1-propyne (0.93 mL, 12 mmol) and 4-(trifluoromethyl)benzaldehyde (1.3 mL, 10 mmol). Purification using medium pressure chromatography (1:6; ethyl acetate: petroleum ether) afforded **1d** as a light yellow oil (1.03 g, 30%). *major isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 16.0 Hz, 1H), 7.55–7.54 (m, 3H), 7.47–7.43 (m, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.21–7.07 (m, 2H), 6.57 (d, *J* = 16.4 Hz, 1H), 4.69 (s, 2H), 2.42 (s, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 156.7, 155.5, 154.4, 139.8, 134.4, 131.4, 130.4, 127.6, 125.9, 125.5, 122.7, 121.6, 118.8, 113.0; *minor isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.55–7.54 (m, 3H), 7.47–7.43 (m, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.21–7.05 (m, 3H), 6.45 (d, *J* = 16.4 Hz, 1H), 4.70 (s, 2H), 2.42 (s, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 156.7, 155.3, 154.2, 142.1, 136.9, 131.8, 130.3, 127.0, 125.6, 124.0, 121.7, 121.3, 113.4, 112.9; IR (thin film) 3297, 3070, 2927, 2870, 1600, 1488, 1121, 754 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{15}F_3NO_2$ $[M + H]^+$: 346.1054, found: 346.1047.



1e (*E*/*Z* = 2.5/1)

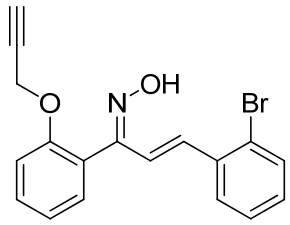
1e was prepared by general procedure E. 2-Hydroxyacetophenone (1.2 mL, 10 mmol), 3-bromo-1-propyne (0.93 mL, 1.2 mmol) and 3-methoxybenzaldehyde (1.2 mL, 10 mmol). Purification using medium pressure chromatography (1:6; ethyl acetate: petroleum ether) afforded **1e** as a light yellow oil (0.97 g, 32%). *Major isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.61 (d, *J* = 16.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.11–7.06 (m, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.94–6.91 (m, 1H), 6.87–6.81 (m, 1H), 6.73–6.68 (m, 1H), 6.43 (d, *J* = 16.4 Hz, 1H), 4.55 (s, 2H), 3.65 (s, 3H), 2.32 (s, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 159.7, 156.8, 155.6, 138.6, 137.7, 131.5, 130.1, 129.7, 125.4, 121.5, 120.2, 116.8, 114.9, 113.4, 112.2, 78.6, 75.5, 55.9, 55.1; *minor isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.32 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.11–7.06 (m, 1H), 7.02 (d, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.94–6.91 (m, 1H), 6.87–6.81 (m, 1H), 6.73–6.68 (m, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 4.55 (s, 2H), 3.65 (s, 3H), 2.32 (s, 1H) (the N−OH resonance was too broad to be

observed); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 155.4, 154.3, 137.7, 135.9, 130.0, 129.4, 124.4, 121.8, 121.6, 119.6, 116.8, 114.4, 131.1, 111.6, 78.5, 75.5, 56.3, 53.3; IR (thin film) 3288, 3006, 2937, 2870, 1598, 1490, 1222, 1022, 756 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{18}NO_3$ $[M + H]^+$: 308.1286, found: 308.1273.



1f (*E*/*Z* = 1/1)

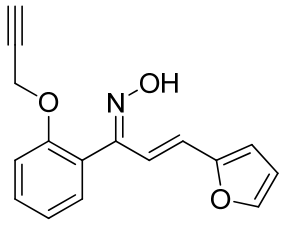
1f was prepared by general procedure E. 2-Hydroxyacetophenone (1.2 mL, 10 mmol), 3-bromo-1-propyne (0.93 mL, 12 mmol) and 3-bromobenzaldehyde (1.2 mL, 10 mmol). Purification using medium pressure chromatography (1:6; ethyl acetate: petroleum ether) afforded **1f** as a light yellow oil (1.0 g, 28%). *Major isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 16.4 Hz, 1H), 7.52 (s, 1H), 7.39–7.29 (m, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.13–6.96 (m, 4H), 6.40 (d, *J* = 16.4 Hz, 1H), 4.63 (s, 2H), 2.36 (s, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 154.3, 138.5, 137.0, 131.6, 131.1, 130.4, 130.0, 129.7, 126.6, 125.2, 122.7, 121.6, 117.8, 113.4, 78.5, 75.5, 56.3; *minor isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 1H), 7.39–7.29 (m, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.18–7.17 (m, 1H), 7.13–6.96 (m, 4H), 6.27 (d, *J* = 16.4 Hz, 1H), 4.61 (s, 2H), 2.36 (s, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 138.5, 134.4, 131.4, 131.0, 130.3, 129.9, 129.6, 125.9, 121.7, 124.1, 117.8, 121.7, 121.4, 113.1, 78.4, 75.5, 55.9; IR (thin film) 3257, 3021, 2966, 2871, 1598, 1449, 1233, 1023, 753 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{15}BrNO_2$ $[M + H]^+$: 356.0286, found: 356.0291.



1g (*E*/*Z* = 2.5/1)

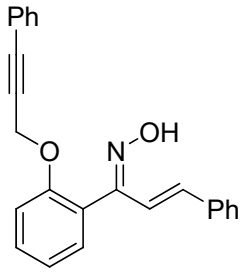
1g was prepared by general procedure F. 2-hydroxyacetophenone (1.2 mL, 10 mmol), 3-bromo-1-propyne (0.93 mL, 12 mmol) and 2-bromobenzaldehyde (1.2 mL, 10 mmol). Purification using medium pressure chromatography (1:6; ethyl acetate:

petroleum ether) afforded **1g** as a light yellow oil (0.92 g, 26%). Mp: 120–121 °C; *major isome*r: ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.31 (brs, 1H), 7.70 (d, J = 7.5 Hz, 1H), 7.63–7.60 (m, 1H), 7.50–7.48 (m, 1H), 7.43–7.40 (m, 1H), 7.35 (d, J = 7.0 Hz, 1H), 7.29–7.24 (m, 1H), 7.15–7.06 (m, 3H), 6.93 (d, J = 16.0 Hz, 1H), 4.68 (s, 2H), 2.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 155.4, 137.2, 134.8, 132.9, 130.4, 129.8, 127.6, 127.5, 127.0, 124.7, 124.3, 121.6, 119.2, 113.4, 78.5, 75.7, 56.3; *minor isomer*: ^{1}H NMR (125 MHz, $CDCl_3$): δ 7.63–7.60 (m, 1H), 7.50–7.48 (m, 1H), 7.43–7.40 (m, 1H), 7.29–7.24 (m, 1H), 7.20 (d, J = 7.5 Hz, 1H), 7.15–7.06 (m, 3H), 7.02 (d, J = 16.5 Hz, 1H), 6.80 (d, J = 16.5 Hz, 1H), 4.68 (s, 2H), 2.43 (s, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 154.4, 136.3, 136.2, 131.4, 130.3, 129.8, 129.7, 129.4, 127.8, 127.0, 124.1, 121.6, 121.5, 113.4, 78.6, 75.6, 56.5; IR (thin film) 3289, 3041, 2983, 2891, 1601, 1459, 1216, 757 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{15}BrNO_2$ $[M + H]^+$: 356.0286, found: 356.0279.



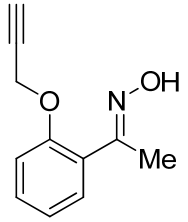
1h (E/Z = 2.5/1)

1h was prepared by general procedure E. 2-Hydroxyacetophenone (1.2 mL, 10 mmol), 3-bromo-1-propyne (0.93 mL, 12 mmol) and 2-furanylaldehyde (0.85 mL, 10 mmol). Purification using medium pressure chromatography (1:6; ethyl acetate: petroleum ether) afforded **1h** as a light yellow solid (0.80 g, 30%). Mp: 114–115 °C; *major isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.62 (brs, 1H), 7.57 (d, J = 16.4 Hz, 1H), 7.39–7.36 (m, 2H), 7.29 (d, J = 7.2 Hz, 1H), 7.17–6.97 (m, 2H), 6.35–6.32 (m, 2H), 6.28 (d, J = 16.8 Hz, 1H), 4.65 (s, 2H), 2.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 155.0, 152.4, 143.5, 131.5, 130.1, 125.5, 123.4, 121.6, 124.8, 113.2, 111.9, 111.8, 78.6, 75.5, 56.3; *minor isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (brs, 1H), 7.39–7.36 (m, 2H), 7.17–6.97 (m, 4H), 6.35–6.32 (m, 2H), 6.23 (d, J = 14.4 Hz, 1H), 4.65 (s, 2H), 2.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 154.3, 152.4, 142.8, 130.0, 129.7, 124.1, 123.3, 121.7, 121.6, 113.5, 111.7, 110.3, 78.6, 75.5, 56.3; IR (thin film) 3294, 3031, 2927, 1602, 1452, 1221, 935, 742 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{14}NO_3$ $[M + H]^+$: 268.0973, found: 268.0964.



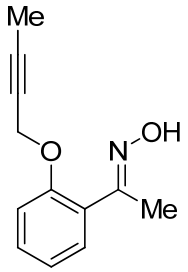
1i (*E*/*Z* = 3.3/1)

1i was prepared by general procedure E. 2-Hydroxyacetophenone (1.2 mL, 10 mmol), (3-bromoprop-1-yn-1-yl)benzene (2.33 g, 12 mmol) and Benzaldehyde (1.0 mL, 10 mmol). Purification using medium pressure chromatography (1:6; ethyl acetate: petroleum ether) afforded **1i** as a light yellow oil (1.2 g, 35%). *Major isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 16.4 Hz, 1H), 7.38–7.31 (m, 4H), 7.24–7.10 (m, 8H), 7.06–6.98 (m, 2H), 6.50 (d, J = 16.4 Hz, 1H), 4.83 (s, 2H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (100MHz, $CDCl_3$): δ 155.9, 155.8, 138.9, 136.3, 131.8, 130.2, 128.8, 128.7, 128.5, 128.3, 127.6, 126.9, 124.3, 122.2, 121.4, 116.5, 113.3, 83.9, 56.8; *minor isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 16.4 Hz, 1H), 7.38–7.31 (m, 4H), 7.24–7.10 (m, 8H), 7.06–6.98 (m, 2H), 6.37 (d, J = 16.4 Hz, 1H), 4.85 (s, 2H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 154.5, 136.3, 136.2, 131.4, 130.1, 129.7, 129.8, 128.7, 128.4, 126.9, 125.1, 124.3, 122.2, 121.5, 116.5, 113.8, 87.1, 57.2; IR (thin film) 3212, 3059, 2925, 1599, 1450, 1221, 999, 753 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{20}NO_2$ $[M + H]^+$: 354.1494, found: 354.1489.



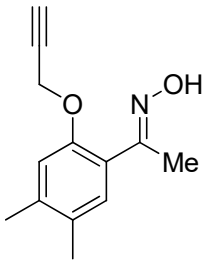
1j

1j was prepared by general procedure E. 2-Hydroxyacetophenone (1.2 mL, 10 mmol), 3-bromo-1-propyne (0.93 mL, 12 mmol). Purification using medium pressure chromatography (1:6; ethyl acetate: petroleum ether) afforded **1j** as a white solid (1.1 g, 59%). Mp: 82–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.0 (brs, 1H), 7.33–7.29 (m, 2H), 7.02–6.96 (m, 2H), 4.68 (brs, 2H), 2.48 (s, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 155.1, 129.9, 129.5, 127.3, 121.5, 112.7, 78.2, 75.6, 55.9, 15.3; IR (thin film) 3266, 3011, 2915, 2871, 1652, 1493, 1235, 1024, 754 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{11}H_{12}NO_2$ $[M + H]^+$: 190.0868, found: 190.0859.



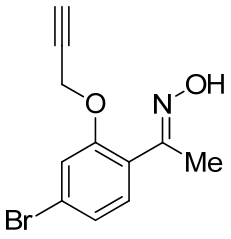
1k

1k was prepared by general procedure E. 2-hydroxyacetophenone (1.2 mL, 10 mmol), 1-bromobut-2-yne (1.1 mL, 12 mmol). Purification using medium pressure chromatography (1:6; ethyl acetate: petroleum ether) afforded **1k** as a white solid (1.1 g, 52%). Mp: 100–101 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.92 (brs, 1H), 7.34 (t, J = 7.2 Hz, 2H), 7.04 (d, J = 8.4 Hz, 1H), 6.98 (t, J = 7.2 Hz, 1H), 4.66 (s, 2H), 2.25 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 155.6, 129.9, 129.4, 127.3, 121.1, 112.8, 83.7, 73.9, 56.6, 15.3, 3.5; IR (thin film) 3306, 3084, 2918, 2864, 1648, 1447, 1227, 738 cm^{-1}; HRMS (ESI) m/z calcd for $C_{12}H_{14}NO_2$ $[M + H]^+$: 204.1024, found: 204.1017.



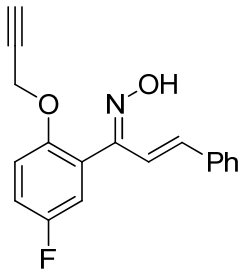
1l

1l was prepared by general procedure E. 1-(2-Hydroxy-4,5-dimethylphenyl)ethanone (1.64 g, 10 mmol), 3-bromo-1-propyne (0.93 mL, 12 mmol). Purification using medium pressure chromatography (1:6; ethyl acetate: petroleum ether) afforded **1l** as a white solid (0.889 g, 41%). Mp: 126–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (s, 1H), 6.82 (s, 1H), 4.68 (s, 2H), 2.48 (s, 1H), 2.27 (s, 3H), 2.23 (s, 3H), 2.19 (s, 3H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 153.3, 138.5, 130.5, 129.6, 124.8, 114.6, 78.6, 75.4, 56.3, 20.0, 18.6, 15.3; IR (thin film) 3270, 3062, 2973, 2857, 1608, 1454, 1245, 912, 729 cm^{-1}; HRMS (ESI) m/z calcd for $C_{13}H_{16}NO_2$ $[M + H]^+$: 218.1181, found: 218.1174.



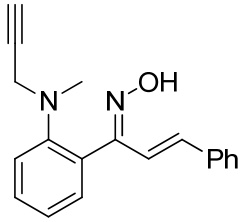
1m

1m was prepared by general procedure E. 1-(4-Bromo-2-hydroxyphenyl)ethanone (2.14 g, 10 mmol), 3-bromo-1-propyne (0.93 mL, 12 mmol). Purification using medium pressure chromatography (1:6; ethyl acetate: petroleum ether) afforded **1m** as a white solid (0.889 g, 41%). Mp: 125–126 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.98 (brs, 1H), 7.25–7.05 (m, 3H), 4.71 (s, 2H), 2.55 (s, 1H), 2.21 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.0, 155.8, 130.6, 126.5, 124.7, 123.3, 116.3, 77.5, 76.3, 56.3, 21.1, 15.2; IR (thin film) 3270, 3081, 2931, 2864, 1590, 1489, 1241, 1025, 817 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{11}H_{11}BrNO_2$ $[M + H]^+$: 267.9973, found: 267.9967.



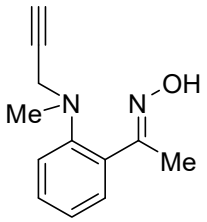
1n (*E*/*Z* = 3.3/1)

1n was prepared by general procedure E. 1-(5-Fluoro-2-hydroxyphenyl)ethanone (1.5 g, 10 mmol), 3-bromo-1-propyne (0.93 mL, 12 mmol) and benzaldehyde (1.0 mL, 10 mmol). Purification using medium pressure chromatography (1:6; ethyl acetate: petroleum ether) afforded **1n** as a yellow oil (0.92 g, 31%). *Major isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 16.4 Hz, 1H), 7.56–7.52 (m, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.24–7.07 (m, 3H), 6.57 (d, *J* = 16.4 Hz, 1H), 4.69 (s, 2H), 2.42 (s, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 155.5, 155.2, 139.8, 136.9, 131.5, 130.4, 130.3, 129.7, 127.5, 125.5, 124.0, 118.8, 113.0, 78.4, 75.6, 56.2; *minor isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.78 (d, *J* = 16.4 Hz, 1H), 7.56–7.52 (m, 5H), 7.24–7.07 (m, 3H), 6.45 (d, *J* = 16.4 Hz, 1H), 4.69 (s, 2H), 2.42 (s, 1H) (the N−OH resonance was too broad to be observed); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 156.6, 154.2, 139.7, 134.3, 130.5, 130.2, 127.5, 127.0, 125.5, 121.7, 121.3, 118.8, 113.4, 78.5, 75.6, 56.2. IR (thin film) 3292, 3030, 2929, 2869, 1598, 1492, 1190, 1023, 695 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{15}FNO_2$ $[M + H]^+$: 296.1086, found: 296.1078.



1o (*E*/*Z* = 1/1)

1o was prepared by general procedure E. 1-(2-(Methylamino)phenyl)ethanone (1.49 g, 10 mmol), 3-bromo-1-propyne (0.93 mL, 12 mmol) and benzaldehyde (1.0 mL, 10 mmol). Purification using medium pressure chromatography (1:6; ethyl acetate: petroleum ether) afforded **1o** as a yellow oil (0.98 g, 34%). *One isomer*: ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.82 (brs, 1H), 7.73 (d, J = 16.5 Hz, 1H), 7.44 (d, J = 7.0 Hz, 1H), 7.40–7.35 (m, 1H), 7.31–7.22 (m, 5H), 7.15–7.04 (m, 2H), 6.59 (d, J = 16.5 Hz, 1H), 3.80 (s, 2H), 2.78 (s, 3H), 2.18 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 150.1, 138.4, 136.3, 131.8, 129.5, 128.8, 128.5, 128.1, 126.4, 125.2, 122.7, 120.0, 79.4, 72.9, 45.2, 40.1; *another isomer*: ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.82 (brs, 1H), 7.44 (d, J = 7.0 Hz, 1H), 7.40–7.35 (m, 2H), 7.31–7.22 (m, 5H), 7.15–7.04 (m, 2H), 6.42 (d, J = 16.0 Hz, 1H), 3.78 (s, 2H), 2.77 (s, 3H), 2.15 (s, 1H); ^{13}C NMR (125MHz, $CDCl_3$): δ 157.3, 149.4, 136.4, 135.7, 130.1, 129.5, 128.2, 127.4, 126.8, 123.8, 122.3, 120.4, 116.3, 79.3, 72.7, 45.0, 40.1; IR (thin film) 3291, 3061, 2864, 1595, 1491, 1330, 969, 756 cm^{-1}; HRMS (ESI) m/z calcd for $C_{19}H_{19}N_2O$ [M + H]$^{+}$: 291.1497, found: 291.1490.



1p (E/Z = 20/1)

1p was prepared by general procedure E. 1-(2-(Methylamino)phenyl)ethanone (1.49 g, 10 mmol), and 3-bromo-1-propyne (0.93 mL, 12 mmol). Purification using medium pressure chromatography (1:6; ethyl acetate: petroleum ether) afforded **1p** as a yellow oil (1.32 g, 66%). *E- isomer*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.54 (brs, 1H), 7.33–7.24 (m, 2H), 7.17 (d, J = 7.6 Hz, 1H), 7.04–7.00 (m, 1H), 3.79 (s, 2H), 2.81 (s, 3H), 2.25 (s, 3H), 2.22 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 149.3, 131.7, 129.9, 129.4, 122.7, 119.8, 79.1, 73.0, 45.3, 39.8, 14.3; IR (thin film) 3293, 3066, 2924, 2109, 1595, 1492, 1012, 755, 646 cm^{-1}; HRMS (ESI) m/z calcd for $C_{12}H_{15}N_2O$ [M + H]$^{+}$: 203.1184, found: 203.1178.

8. Synthesis of Diaryliodonium Salts 2:

Aryl boronic acid (10 mmol, 1.0 equiv) and CH_2Cl_2 (40 mL) were combined in a dried round-bottom flask. The mixture was cooled to 0 °C for 5 min, BF_3•OEt_2 (1.12 mL, 1.10 equiv) was added, and the mixture was stirred for 10 min. A solution of 2-(diacetoxyiodo)arene (1.05 equiv) in CH_2Cl_2 (20 mL) was added slowly for 10-15 min and stirred for additional 10 min. The mixture was warmed to room temperature and stirred for 1 h. The reaction was cooled to 0 °C again and TfOH (1.67 mL, 1.1

equiv) was dropped into the mixture. Then, the mixture was stirred for 10 min at 0 °C and warmed to room temperature for additional 10 min. At this time, the solvent was removed under reduced pressure and the residual ran through a short silica gel column (about 5 cm) with 5% of MeOH in CH_2Cl_2 quickly. The mixture was concentrated under vacuum and Et_2O (100 mL) was added to the residual to form a white solid. Filtrated and obtained the diaryliodonium salts **2** as white solid.

The diaryliodonium salts **2a**-**f**[1], **2i**-**m**[1] and **2g**[2], **2h**[3] were prepared according to literature methods and their spectral data matched literature values.

9. Reference

[1] X.-P. Ma, W.-M. Shi, X.-L. Mo, X.-H. Li, L.-G. Li, C.-X. Pan, B. Chen, G.-F. Su, D.-L. Mo, *J. Org. Chem.* **2015**, *80*, 10098.

[2] Y. Gu, D. Cheng, X. Leng, Y. Gu, Q. Shen, *Organometallics.* **2015**, *34*, 3065.

[3] D. Wang, B. Ge, L. Li, J. Shan, Y. Ding, *J. Org. Chem*. **2014**, *79*, 8607.

10. X-ray structures for compound 4aa, 5oa and 12

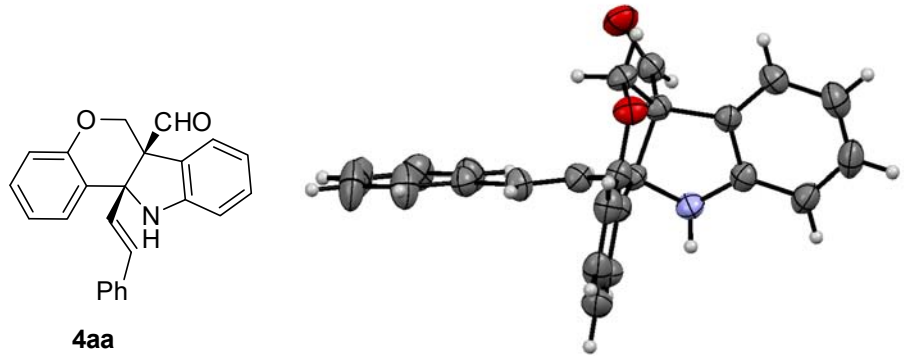


Figure S1: ORTEP diagram of **4aa** at 50% ellipsoid probability.

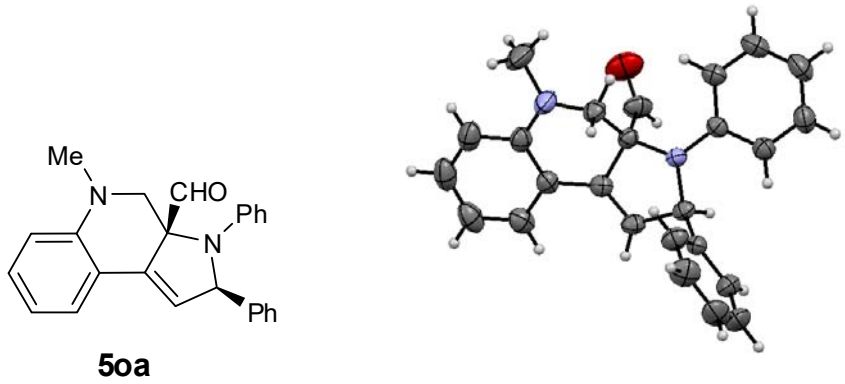


Figure S2: ORTEP diagram of **5oa** at 50% ellipsoid probability.

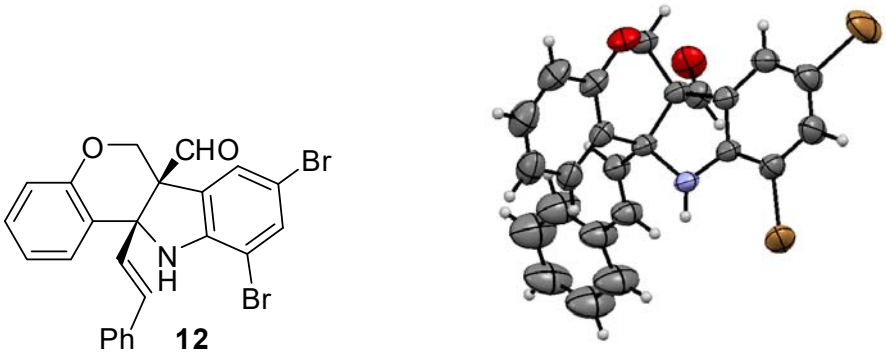
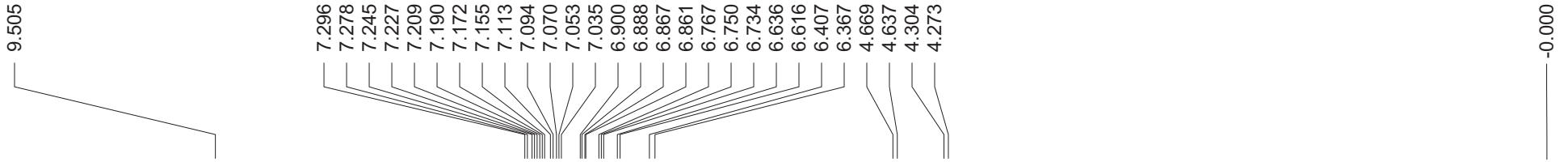


Figure S3: ORTEP diagram of **12** at 50% ellipsoid probability.

11. NMR spectra for compounds 4, 5oa, 6-13, 3aa, and 1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6.900
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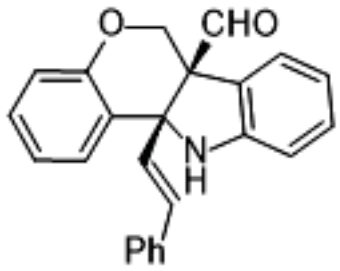
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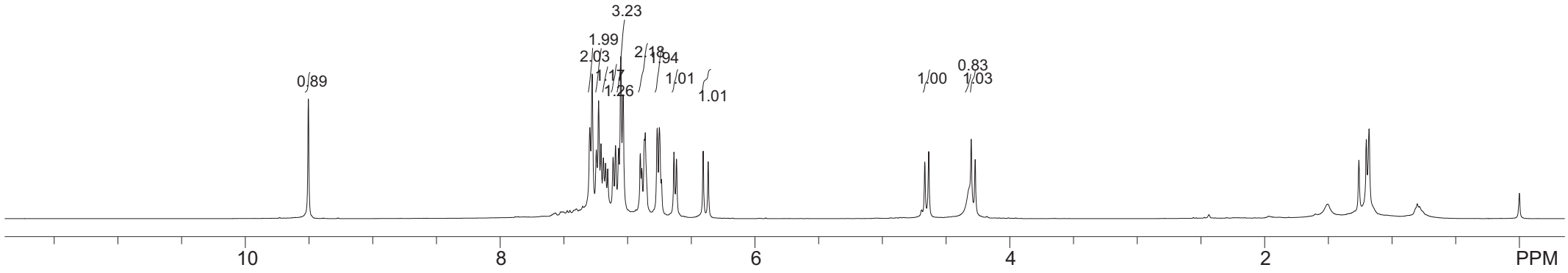
Ph

4aa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10
8
6
4
2
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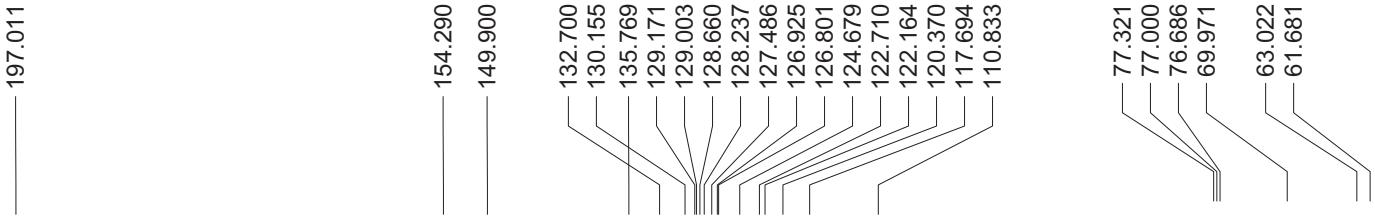
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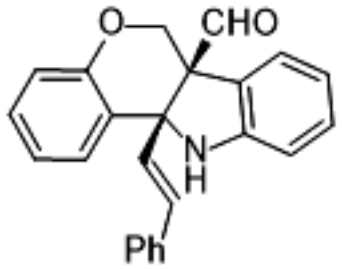
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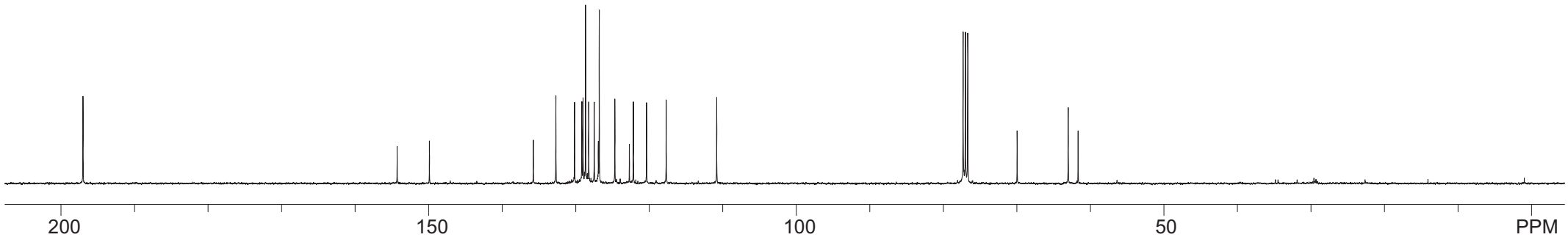
N
H
Ph

4aa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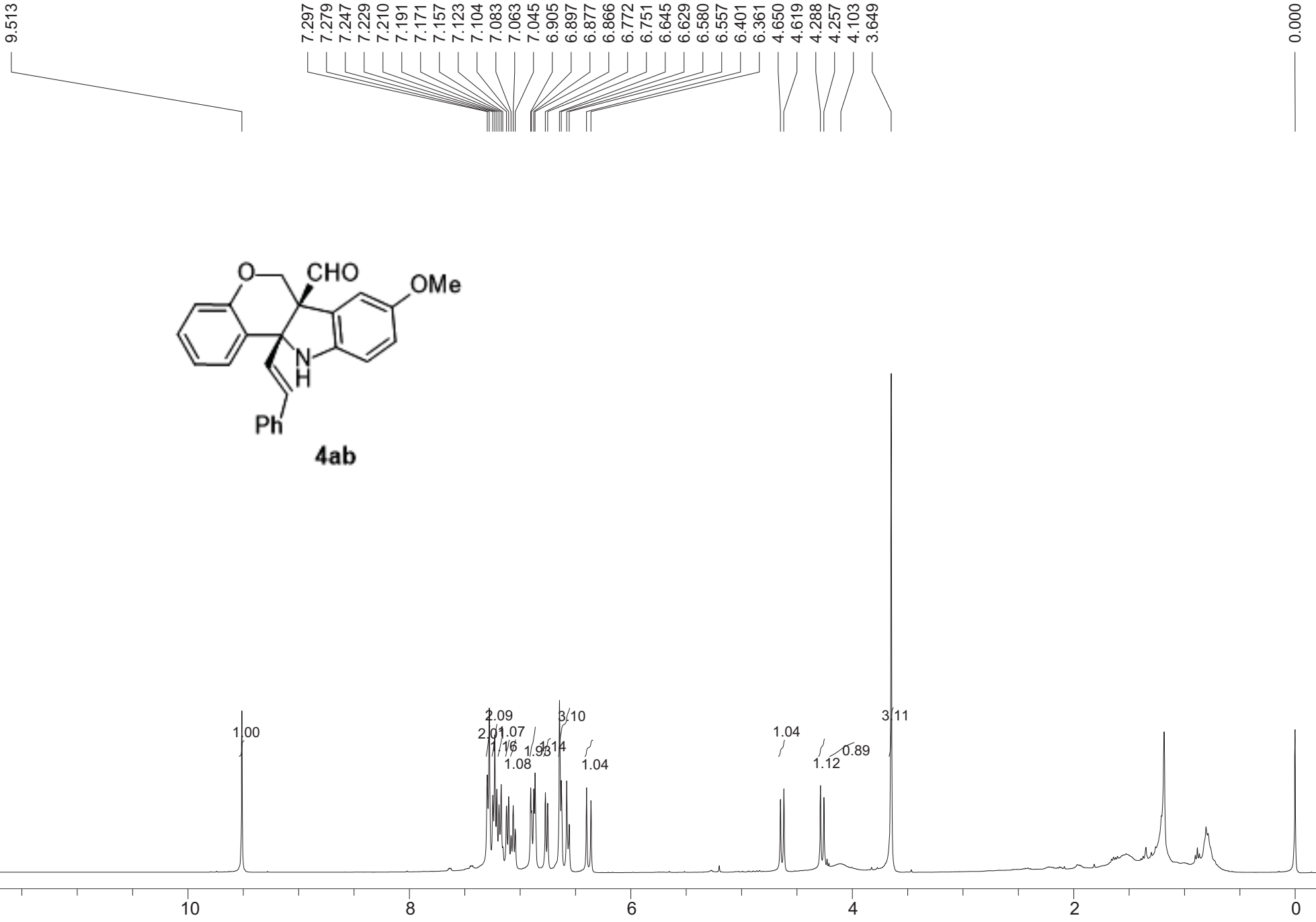
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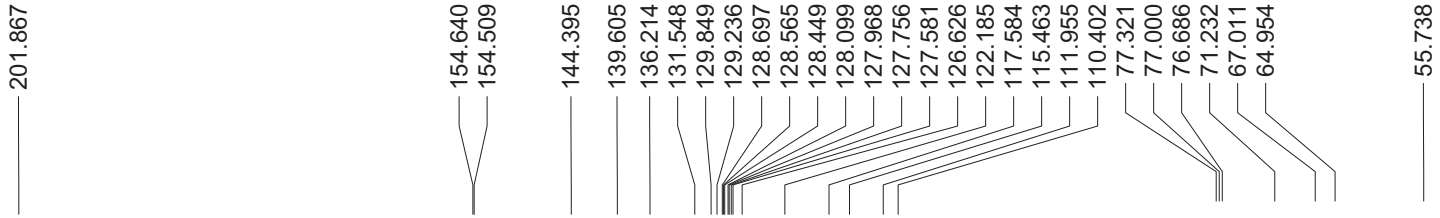
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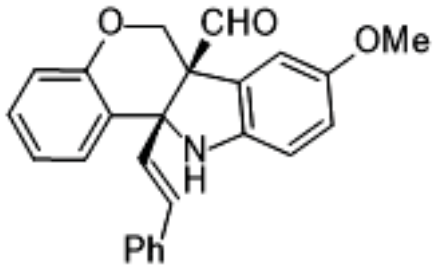
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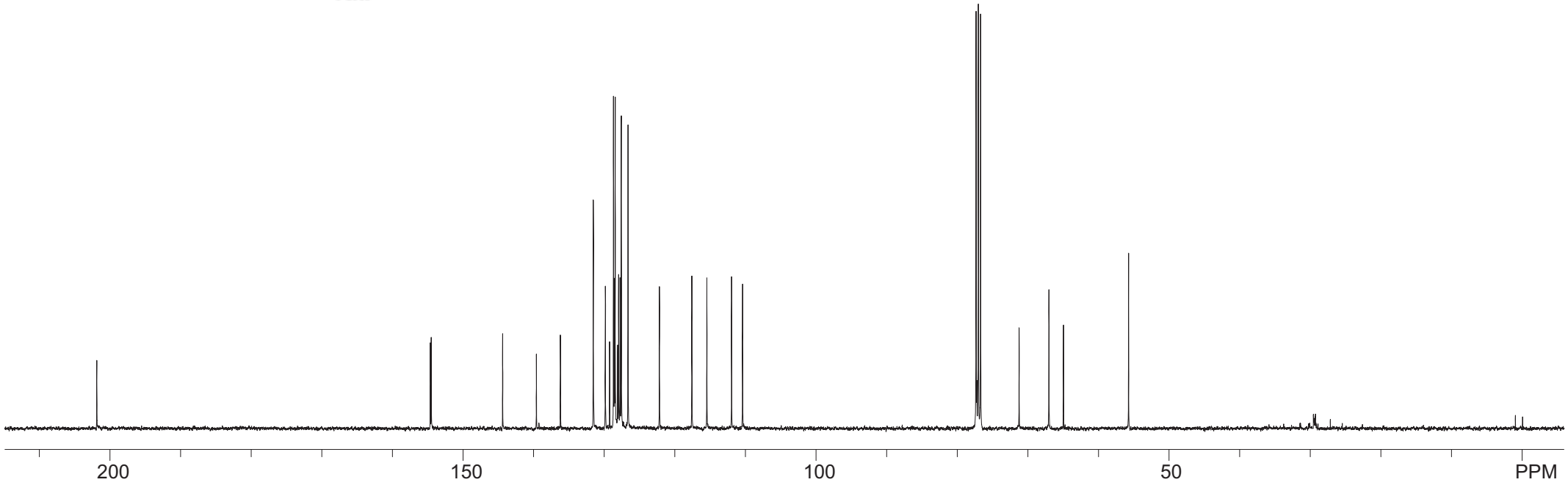
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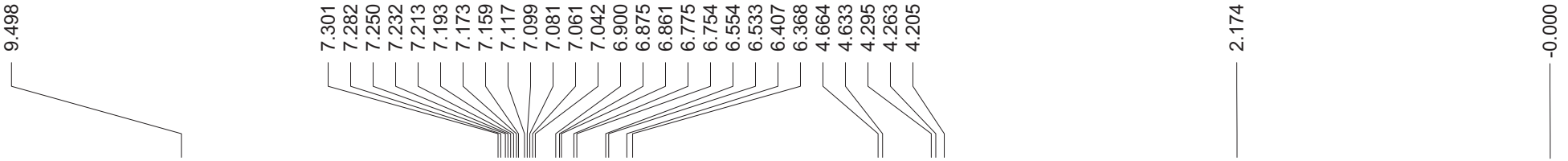
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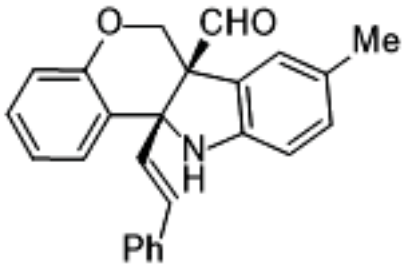
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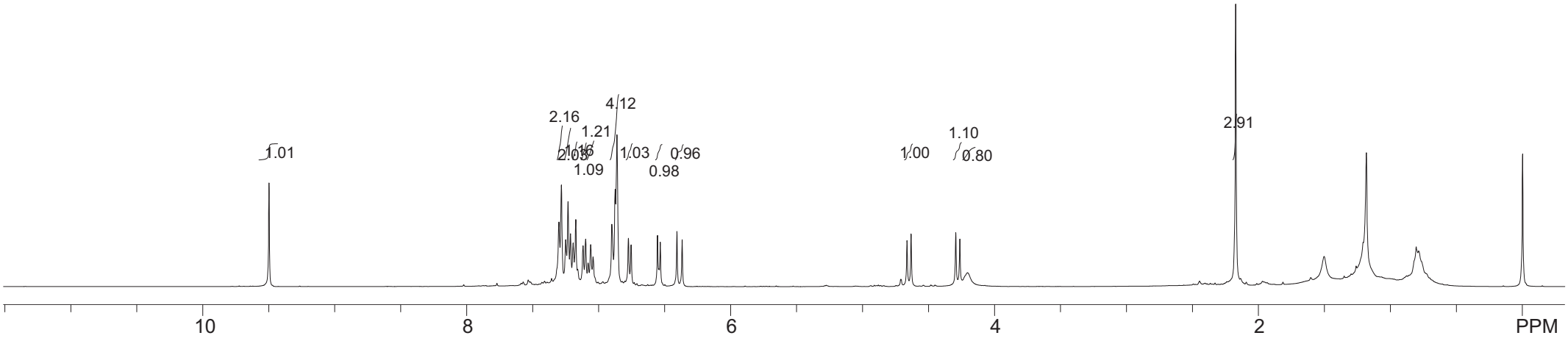
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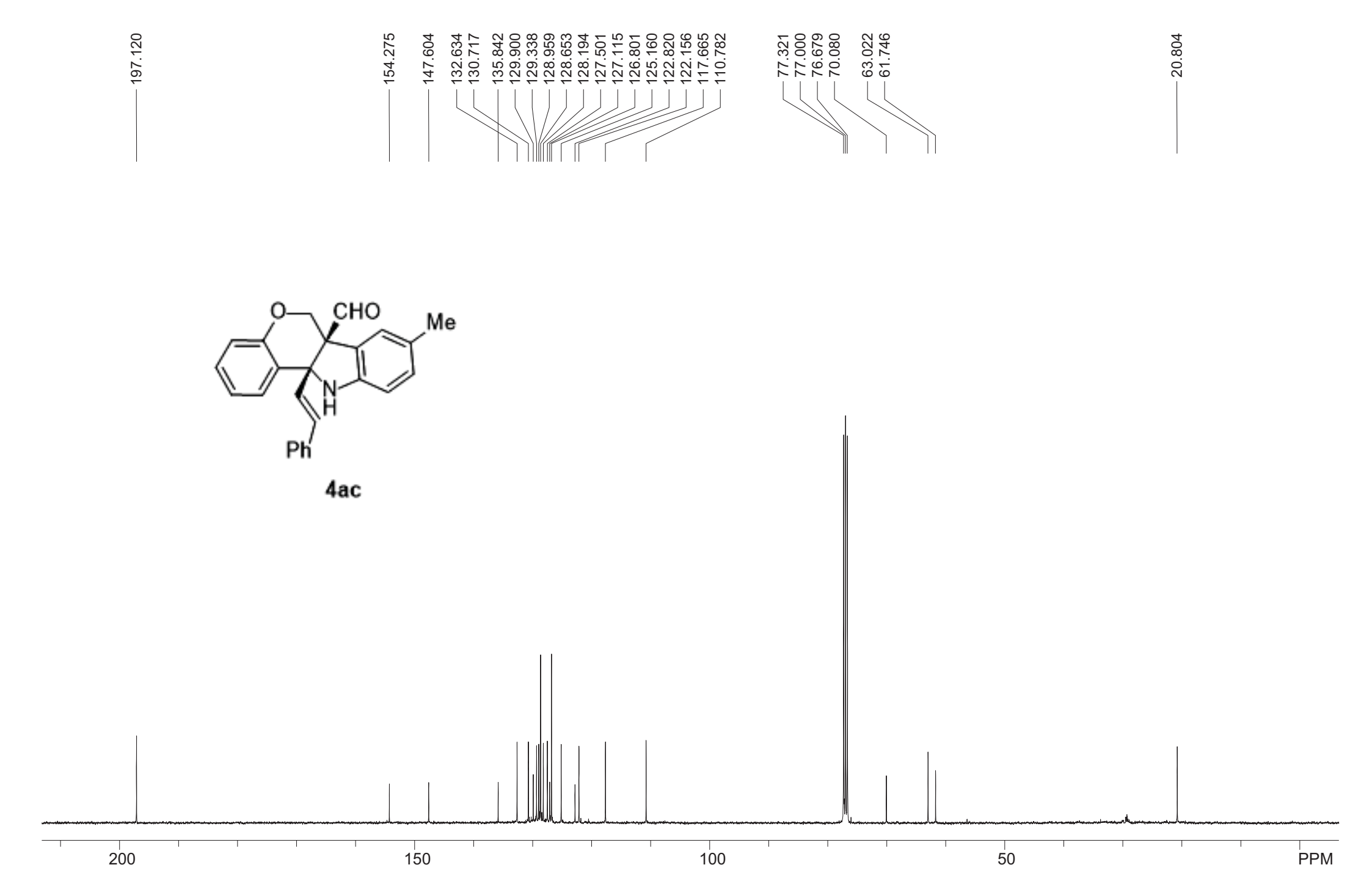
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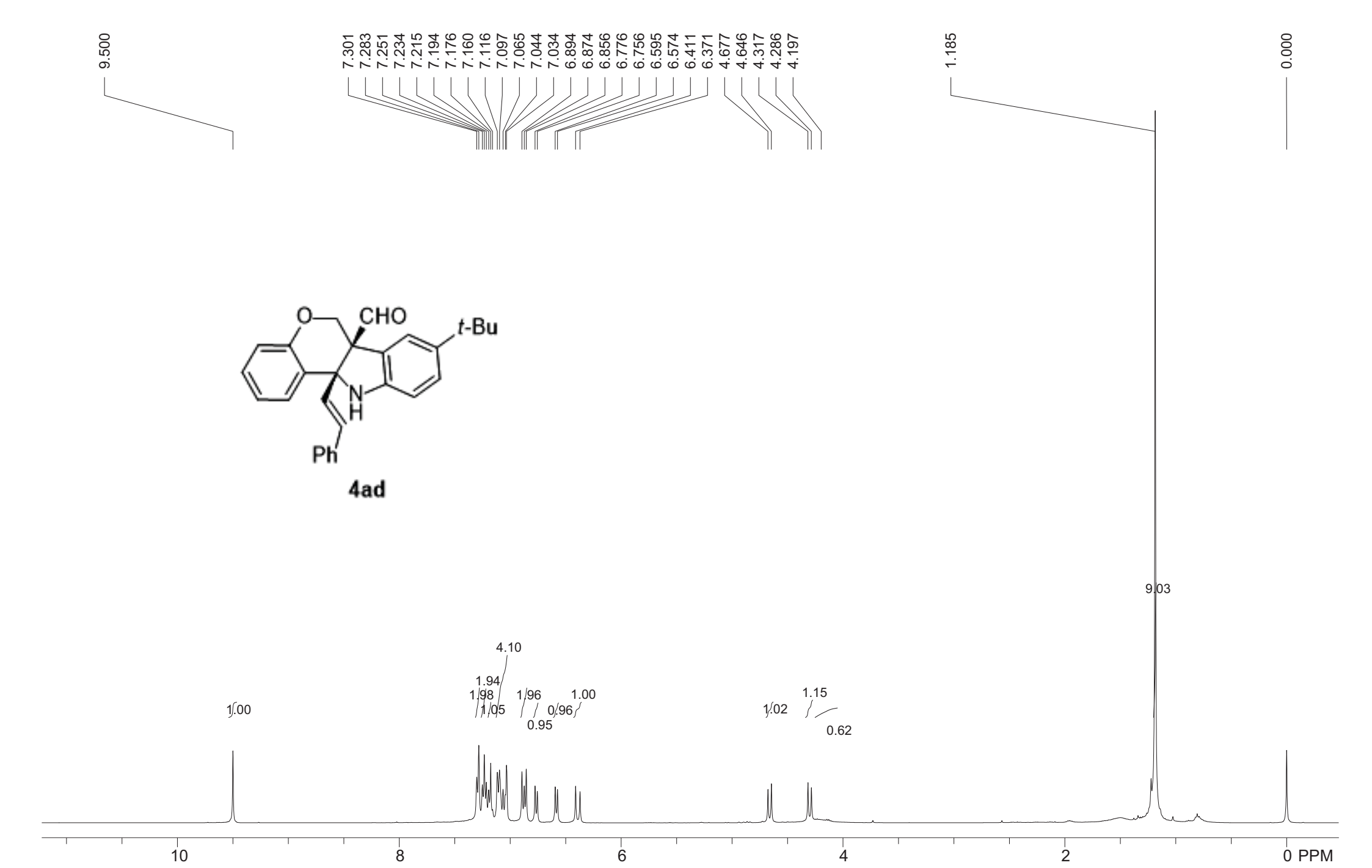
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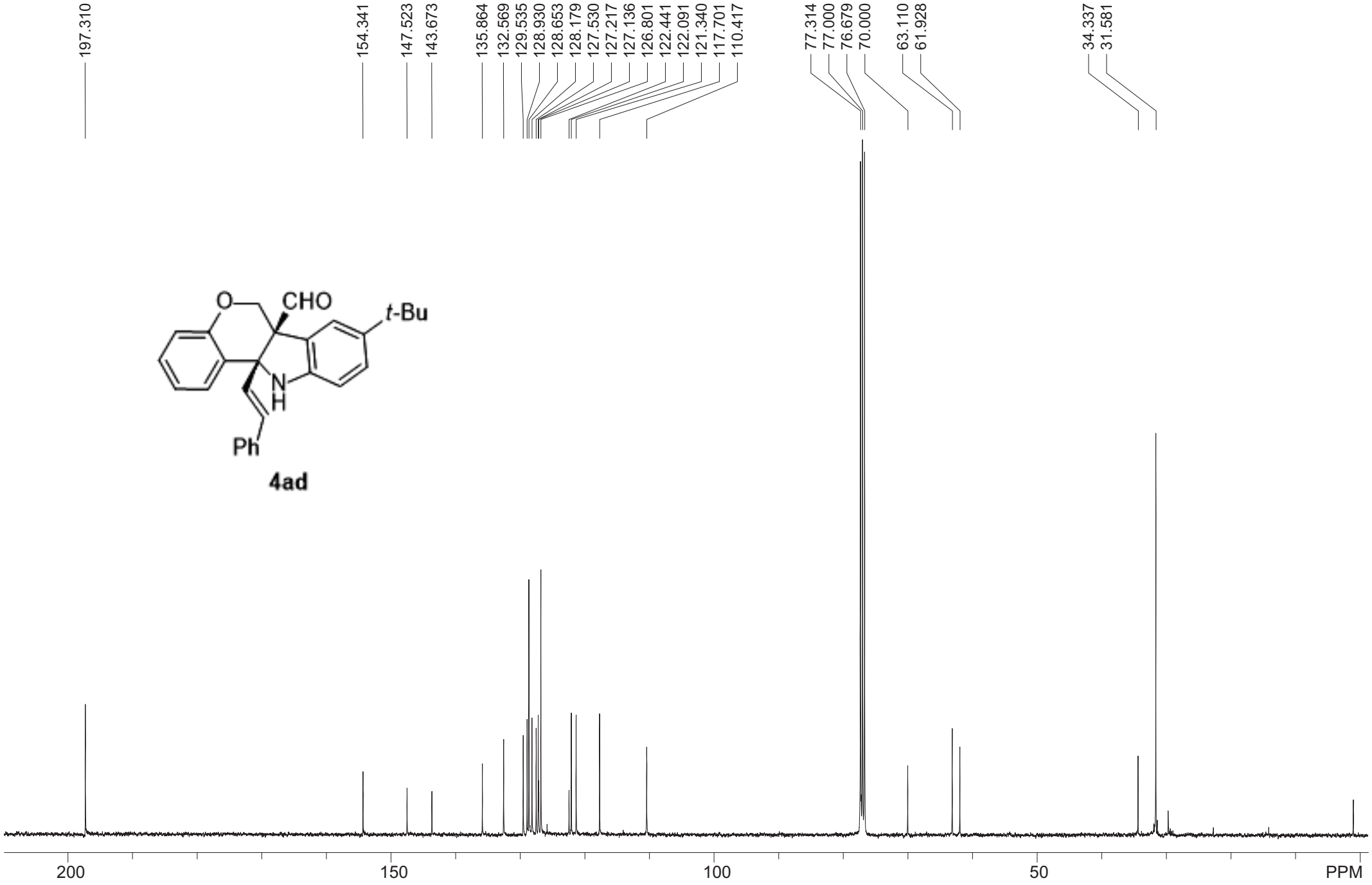
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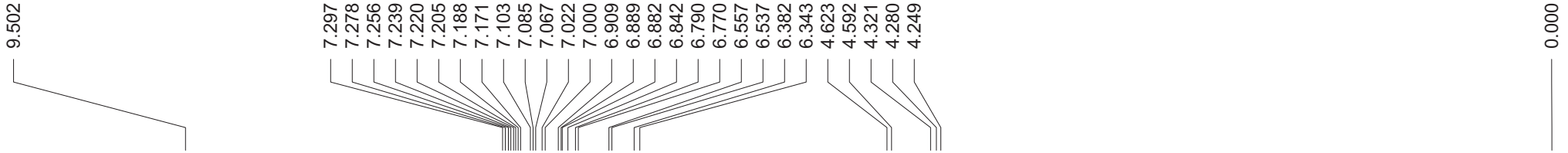
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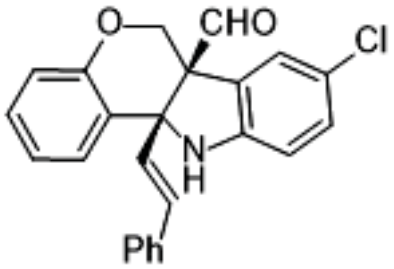
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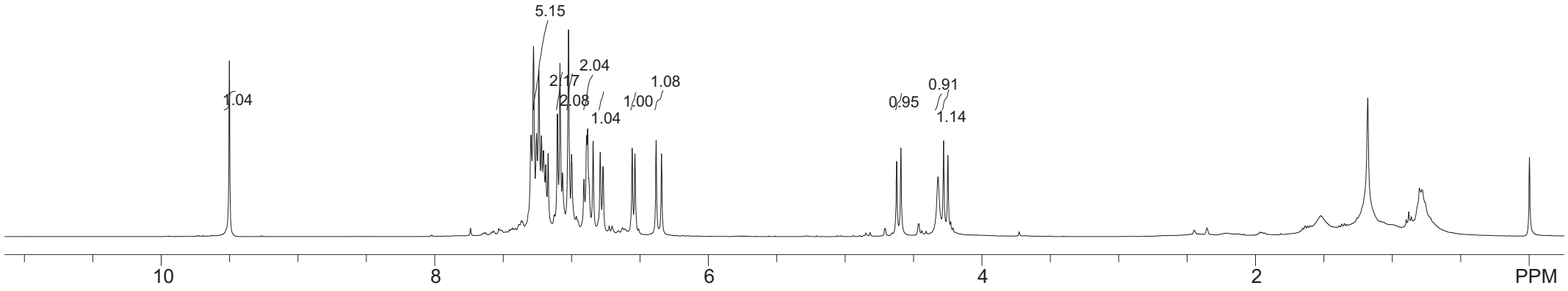
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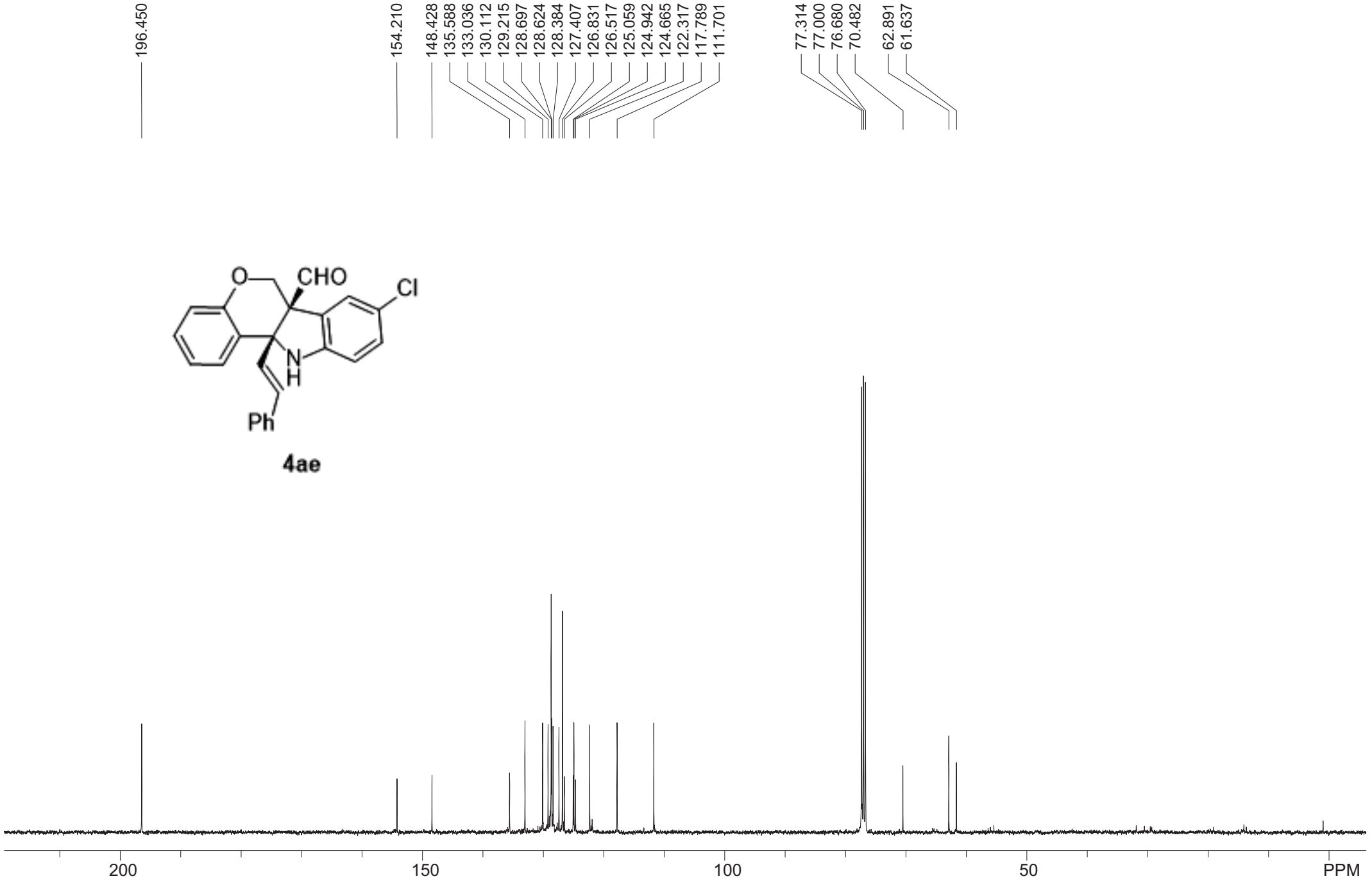
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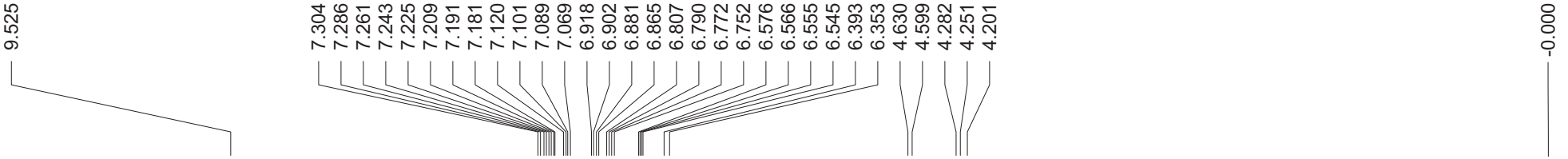
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7.191
7.181
7.120
7.101
7.089
7.069
6.918
6.902
6.881
6.865
6.807
6.790
6.772
6.752
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6.545
6.393
6.353
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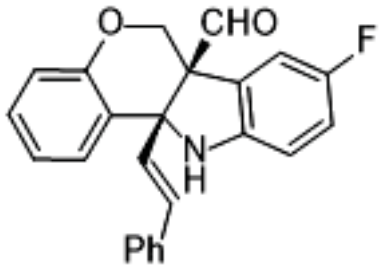
-0.000


O
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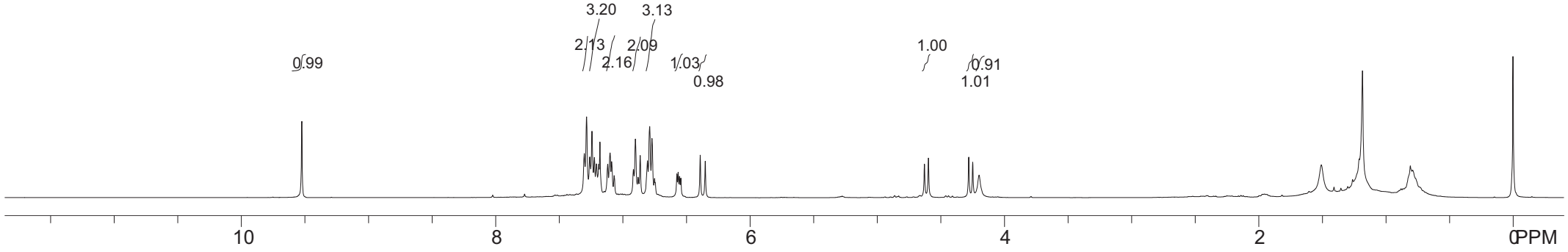
F
N
H
Ph

4af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3.13
2.13
2.09
2.16
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0.98
1.00
0.99
0.91
1.01
10
8
6
4
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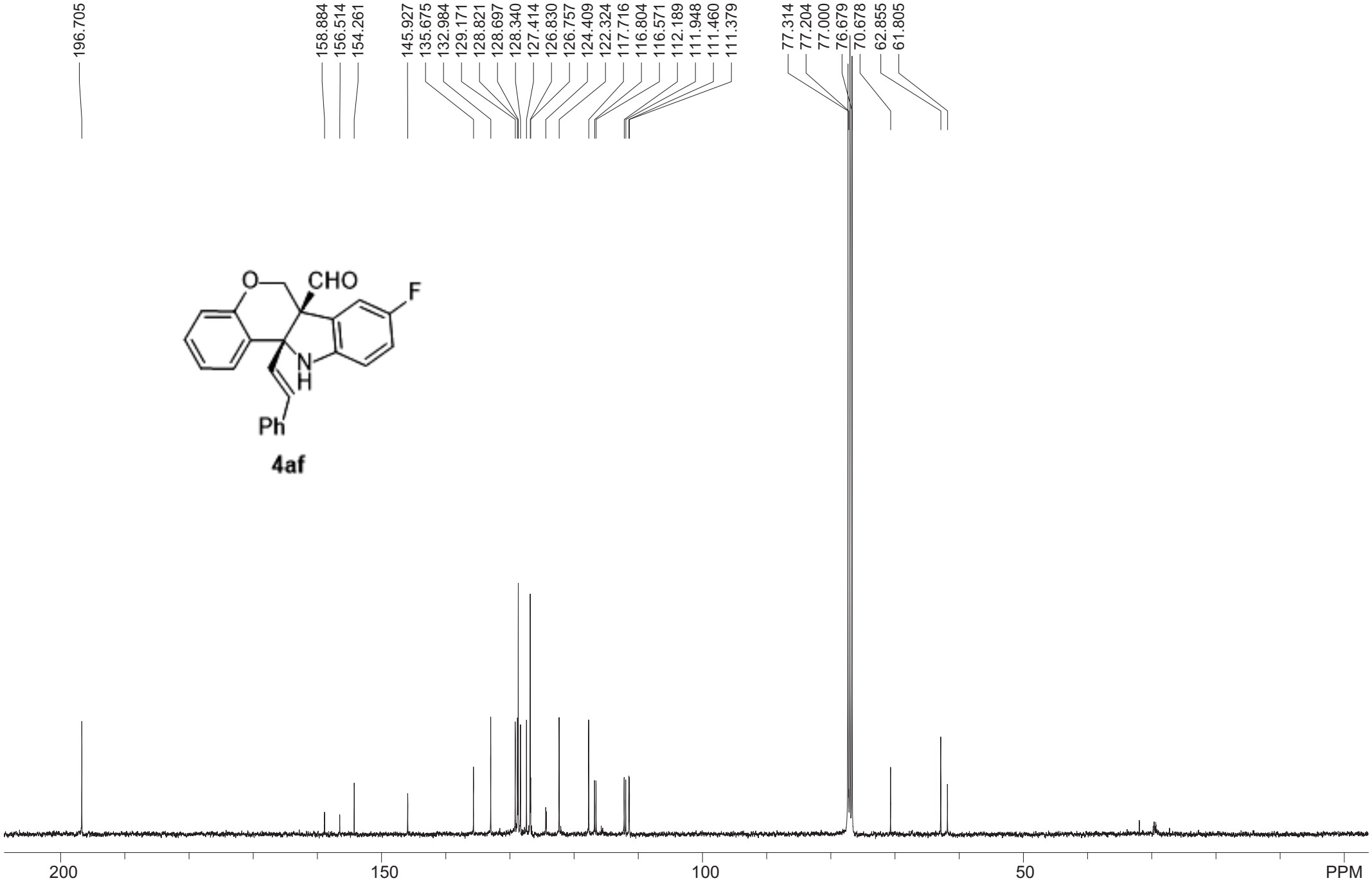
PPM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145.927
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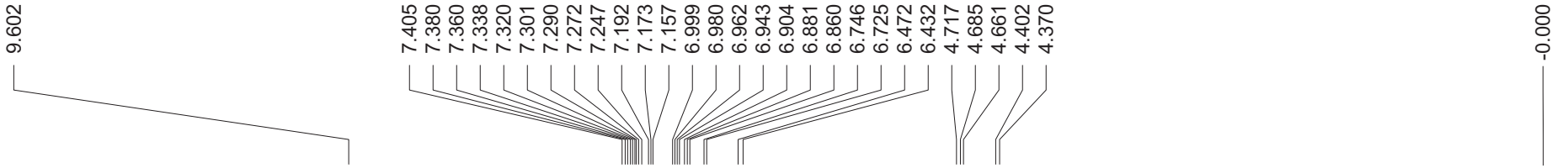
132.984
129.171
128.821
128.697
128.340
127.414
126.830
126.757
124.409
122.324
117.716
116.804
116.571
112.189
111.948
111.460
111.379
77.314
77.204
77.000
76.679
70.678
62.855
61.805
O
CHO
F
N
H
Ph
4af
200
150
100
50
PPM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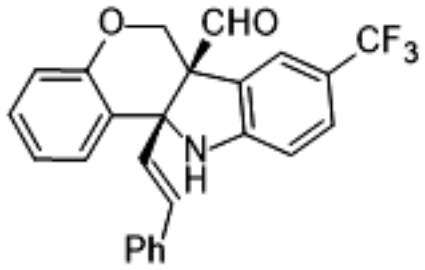
7.380
7.360
7.338
7.320
7.301
7.290
7.272
7.247
7.192
7.173
7.157
6.999
6.980
6.962
6.943
6.904
6.881
6.860
6.746
6.725
6.472
6.432
4.717
4.685
4.661
4.402
4.370
-0.000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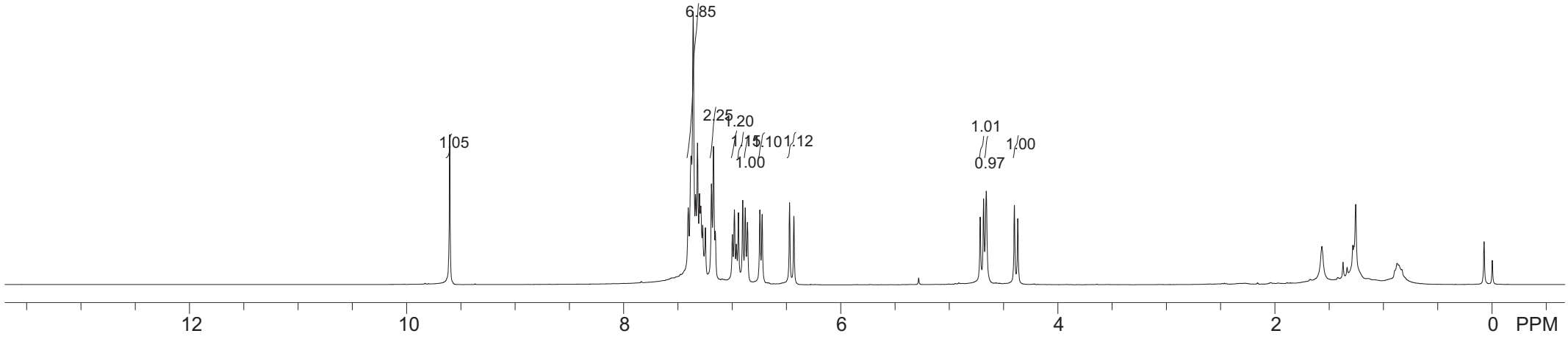
CHO
CF3
N
H
Ph

4ag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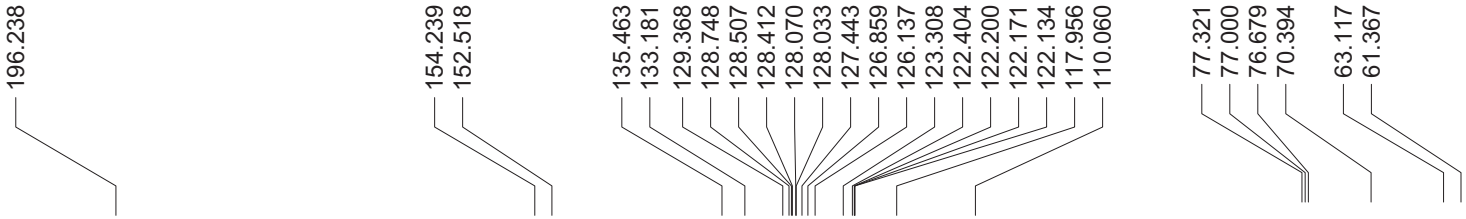
2.25
1.20
1.15
1.01
1.12
1.00
1.05
1.01
0.97
1.00
12
10
8
6
4
2
0
PPM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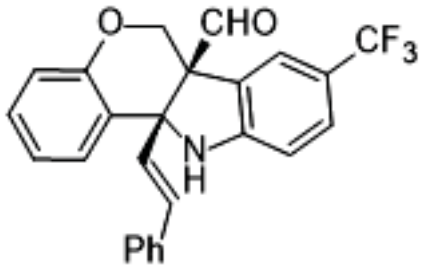
152.518
135.463
133.181
129.368
128.748
128.507
128.412
128.070
128.033
127.443
126.859
126.137
123.308
122.404
122.200
122.171
122.134
117.956
110.060
77.321
77.000
76.679
70.394
63.117
61.367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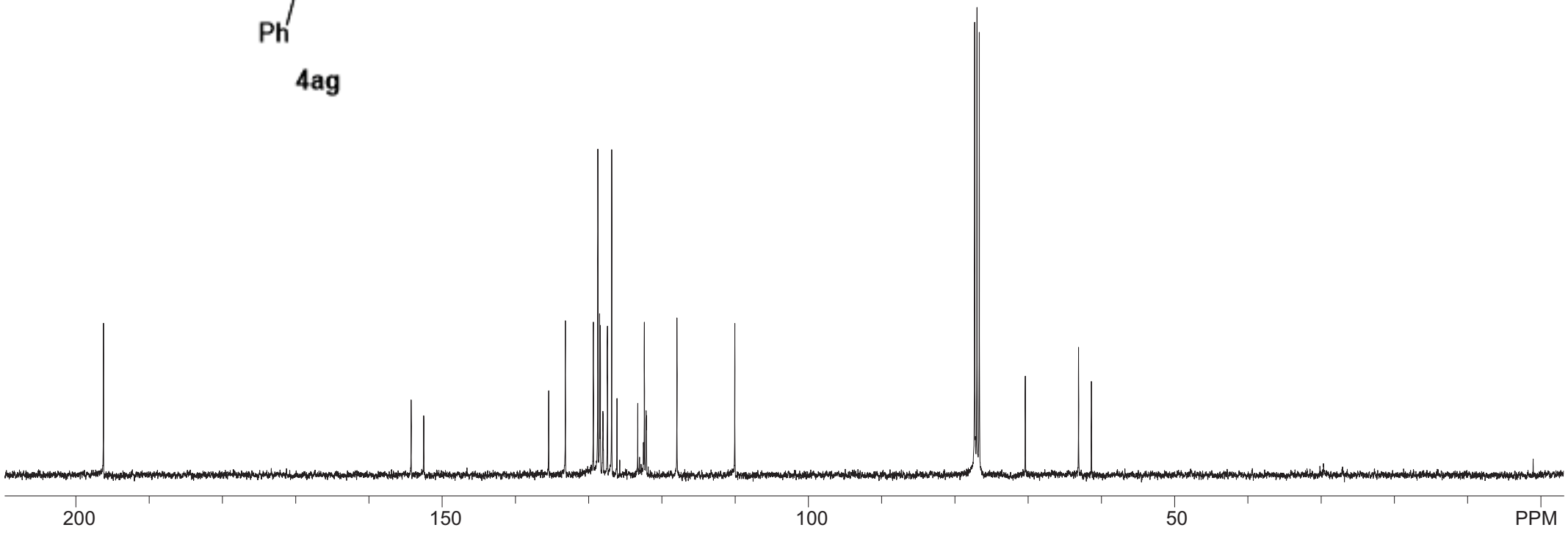
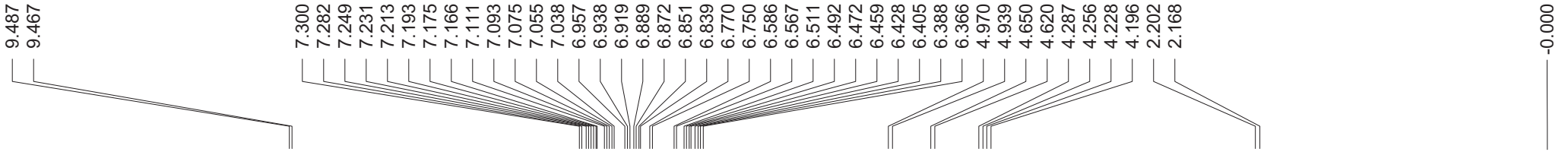
CHO
CF3
N
H
Ph

4ag


200
150
100
50
PPM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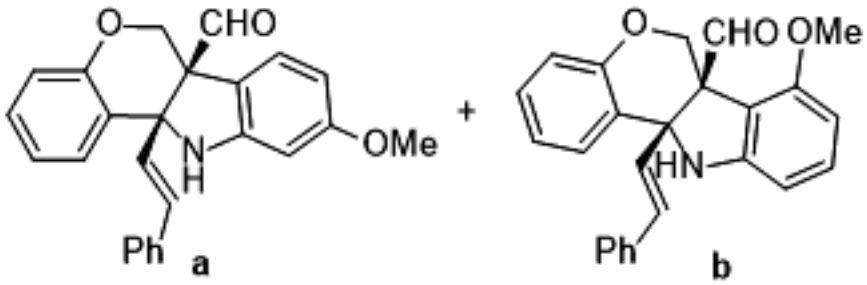
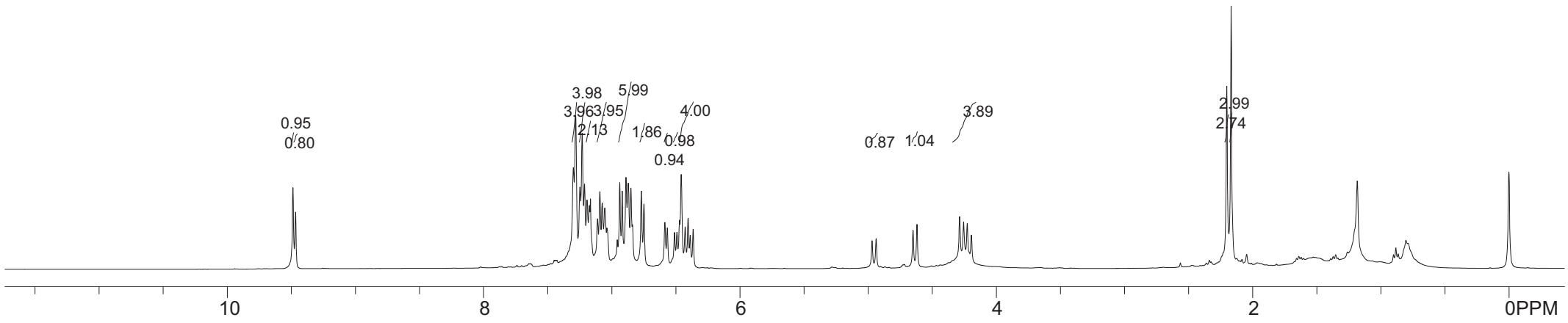
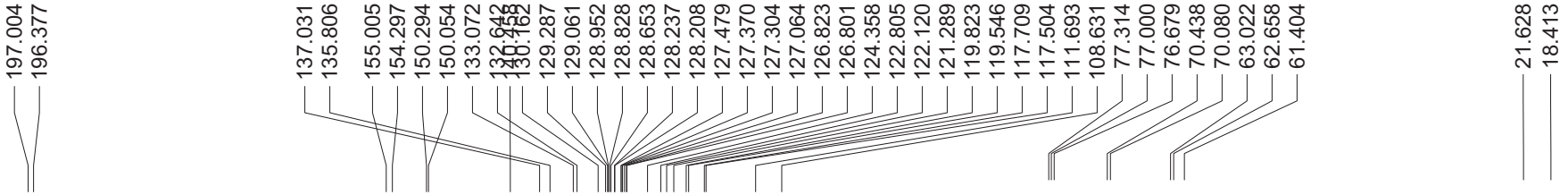
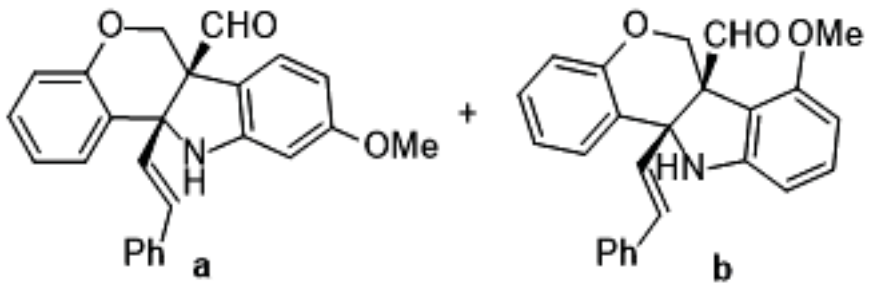
7.231
7.213
7.193
7.175
7.166
7.111
7.093
7.075
7.055
7.038
6.957
6.938
6.919
6.889
6.872
6.851
6.839
6.770
6.750
6.586
6.567
6.511
6.492
6.472
6.459
6.428
6.405
6.388
6.366
4.970
4.939
4.650
4.620
4.287
4.256
4.228
4.196
2.202
2.168
-0.000


O
CHO
OMe
N
H
Ph
a
+
O
CHO OMe
HN
Ph
b

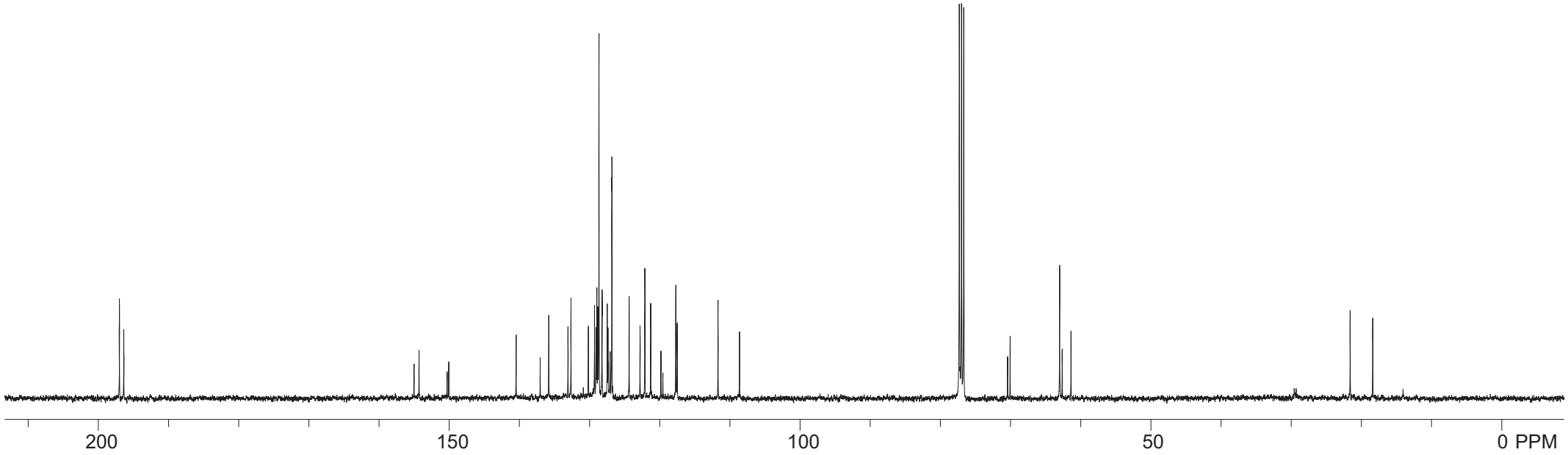
4ah (a:b = 1:1)

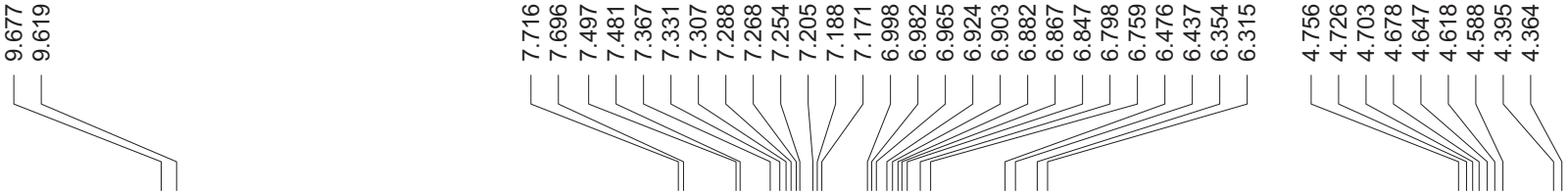

0.95
0.80
3.98
3.96
3.95
2.13
5.99
1.86
4.00
0.98
0.94
0.87
1.04
3.89
2.99
2.74
10
8
6
4
2
0PPM


197.004
196.377
137.031
135.806
155.005
154.297
150.294
150.054
133.072
129.287
129.061
128.952
128.828
128.653
128.237
128.208
127.479
127.370
127.304
127.064
126.823
126.801
124.358
122.805
122.120
121.289
119.823
119.546
117.709
117.504
111.693
108.631
77.314
77.000
76.679
70.438
70.080
63.022
62.658
61.404
21.628
18.413


O
CHO
OMe
N
H
Ph
a
+
O
CHO OMe
HN
Ph
b

4ah (a:b = 1:1)


200
150
100
50
0 PPM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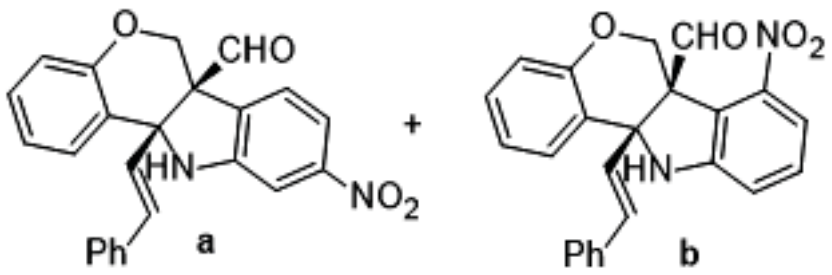
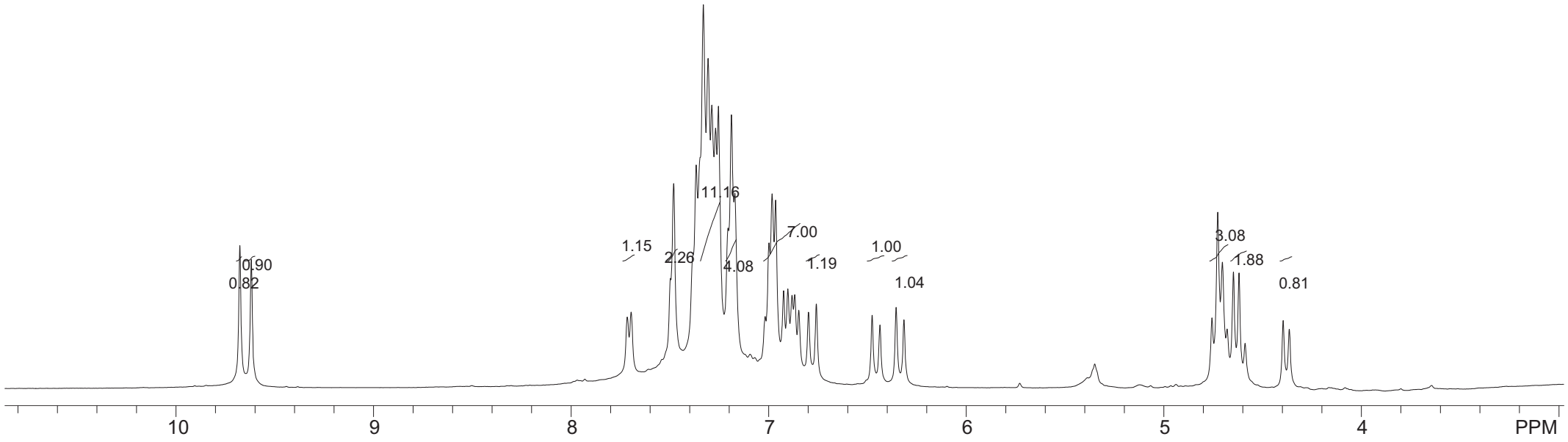
7.696
7.497
7.481
7.367
7.331
7.307
7.288
7.268
7.254
7.205
7.188
7.171
6.998
6.982
6.965
6.924
6.903
6.882
6.867
6.847
6.798
6.759
6.476
6.437
6.354
6.315
4.756
4.726
4.703
4.678
4.647
4.618
4.588
4.395
4.364


O
CHO
HN
NO2
Ph
a
+
O
CHO NO2
HN
Ph
b

4ai (a:b = 1:1)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2.26
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4.08
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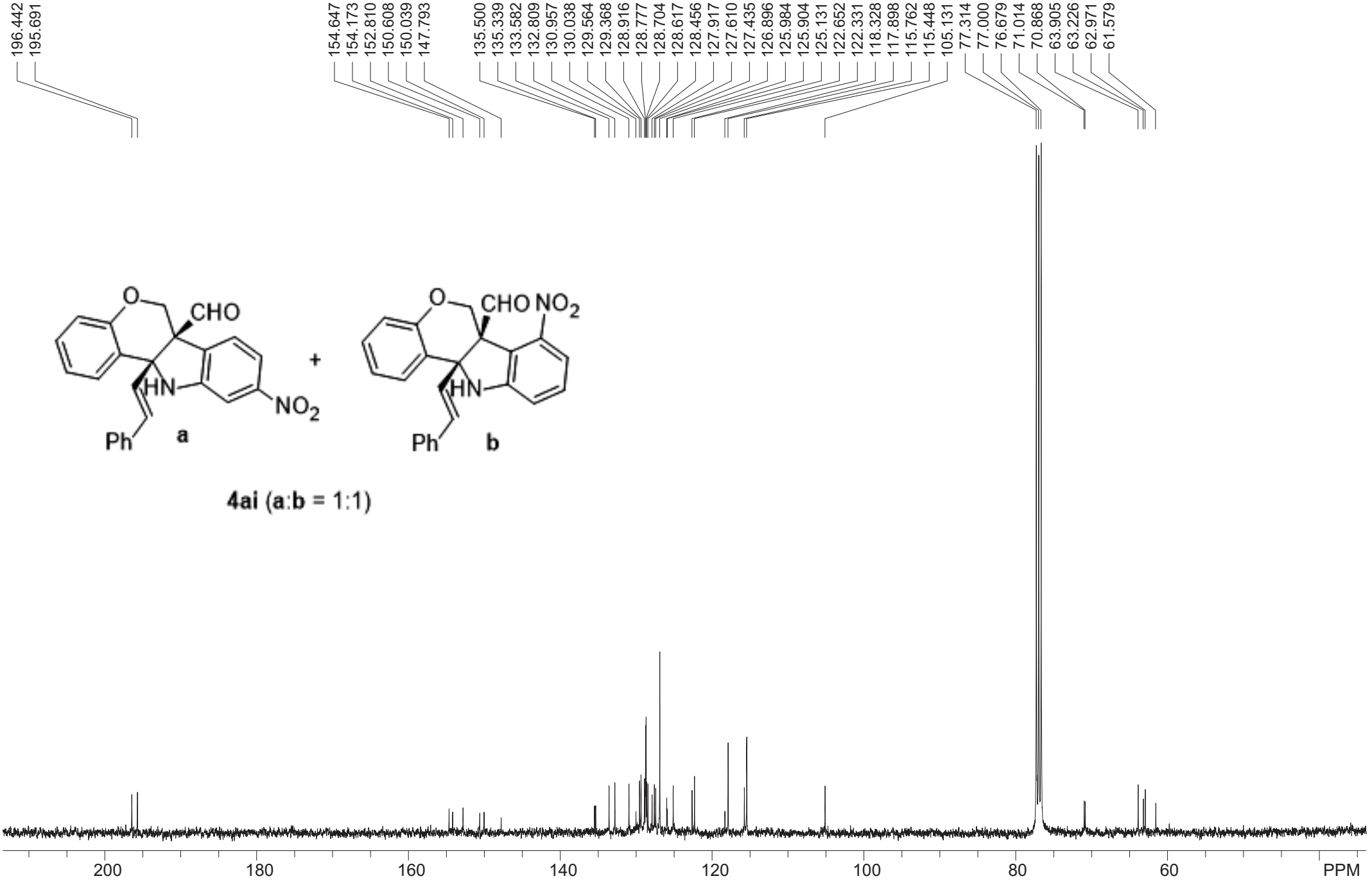
1.19
1.00
1.04
3.08
1.88
0.81
10
9
8
7
6
5
4
PPM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152.810
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150.039
147.793
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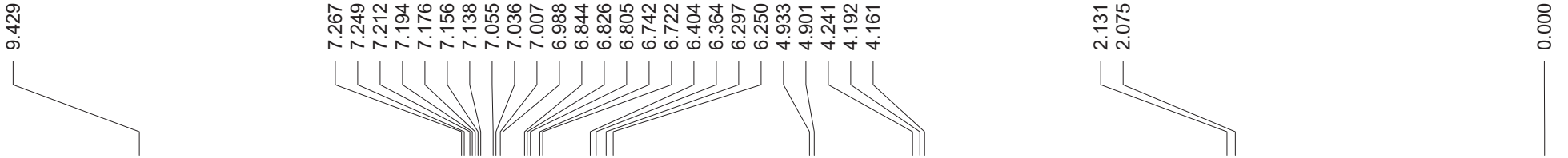
135.339
133.582
132.809
130.957
130.038
129.564
129.368
128.916
128.777
128.704
128.617
128.456
127.917
127.610
127.435
126.896
125.984
125.904
125.131
122.652
122.331
118.328
117.898
115.762
115.448
105.131
77.314
77.000
76.679
71.014
70.868
63.905
63.226
62.971
61.579
O
CHO
HN
NO2
Ph
a
+
O
CHO NO2
HN
Ph
b
4ai (a:b = 1:1)
200
180
160
140
120
100
80
60
PPM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7.249
7.212
7.194
7.176
7.156
7.138
7.055
7.036
7.007
6.988
6.844
6.826
6.805
6.742
6.722
6.404
6.364
6.297
6.250
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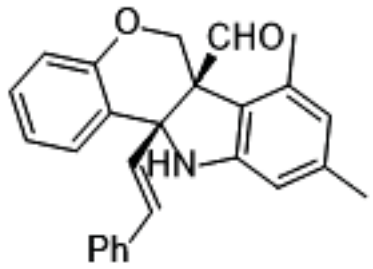
4.901
4.241
4.192
4.161
2.131
2.075
0.000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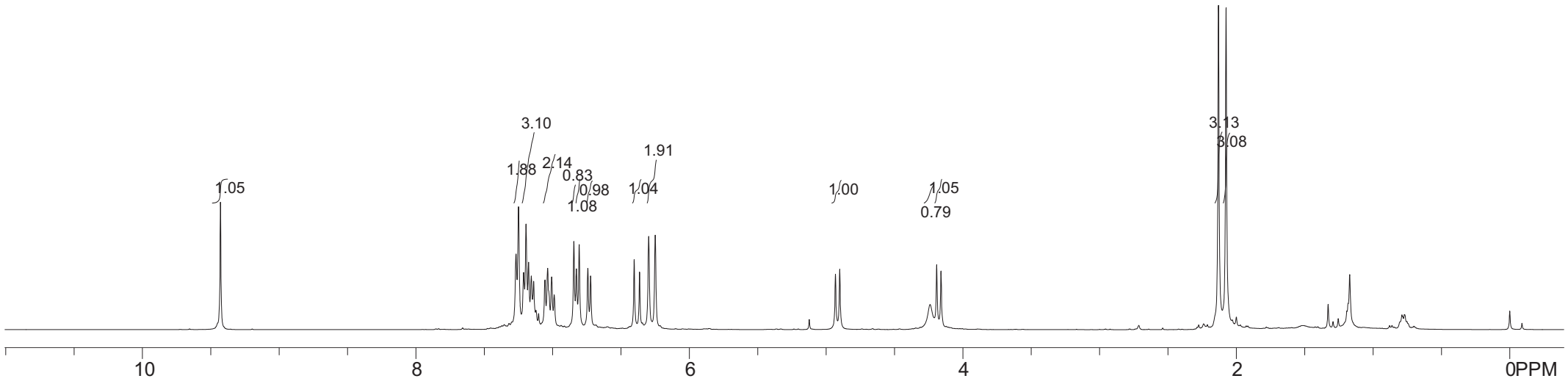
CHO
HN
Ph

4aj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2.14
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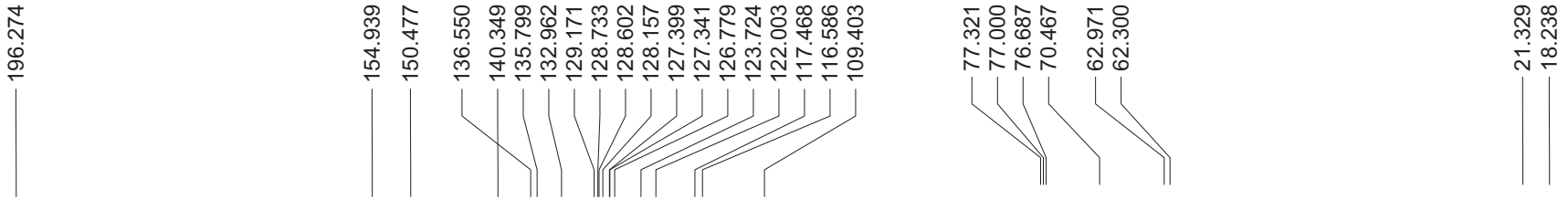
0.98
1.08
1.04
1.91
1.00
1.05
0.79
3.13
3.08
10
8
6
4
2
0PPM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140.349
135.799
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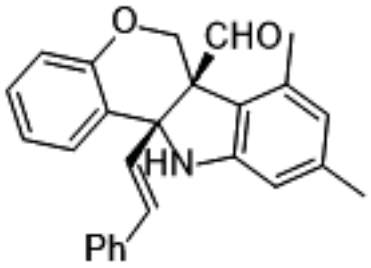
129.171
128.733
128.602
128.157
127.399
127.341
126.779
123.724
122.003
117.468
116.586
109.403
77.321
77.000
76.687
70.467
62.971
62.300
21.329
18.238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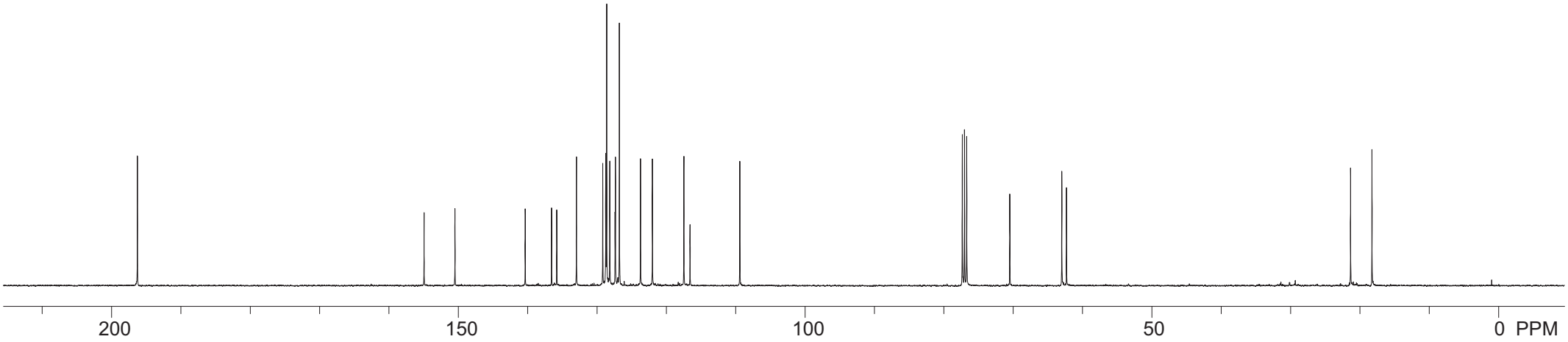
CHO
HN
Ph

4aj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100
50
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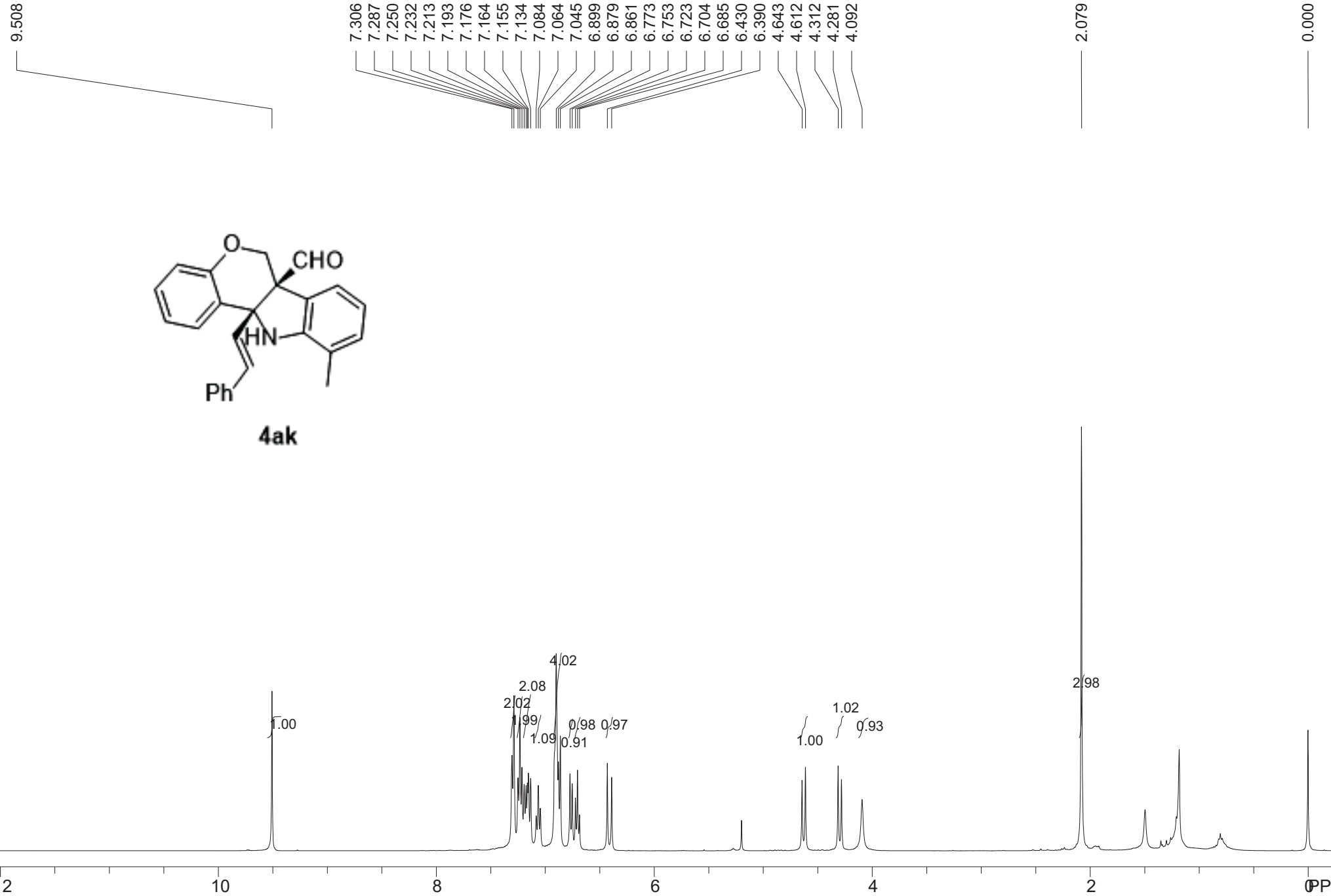
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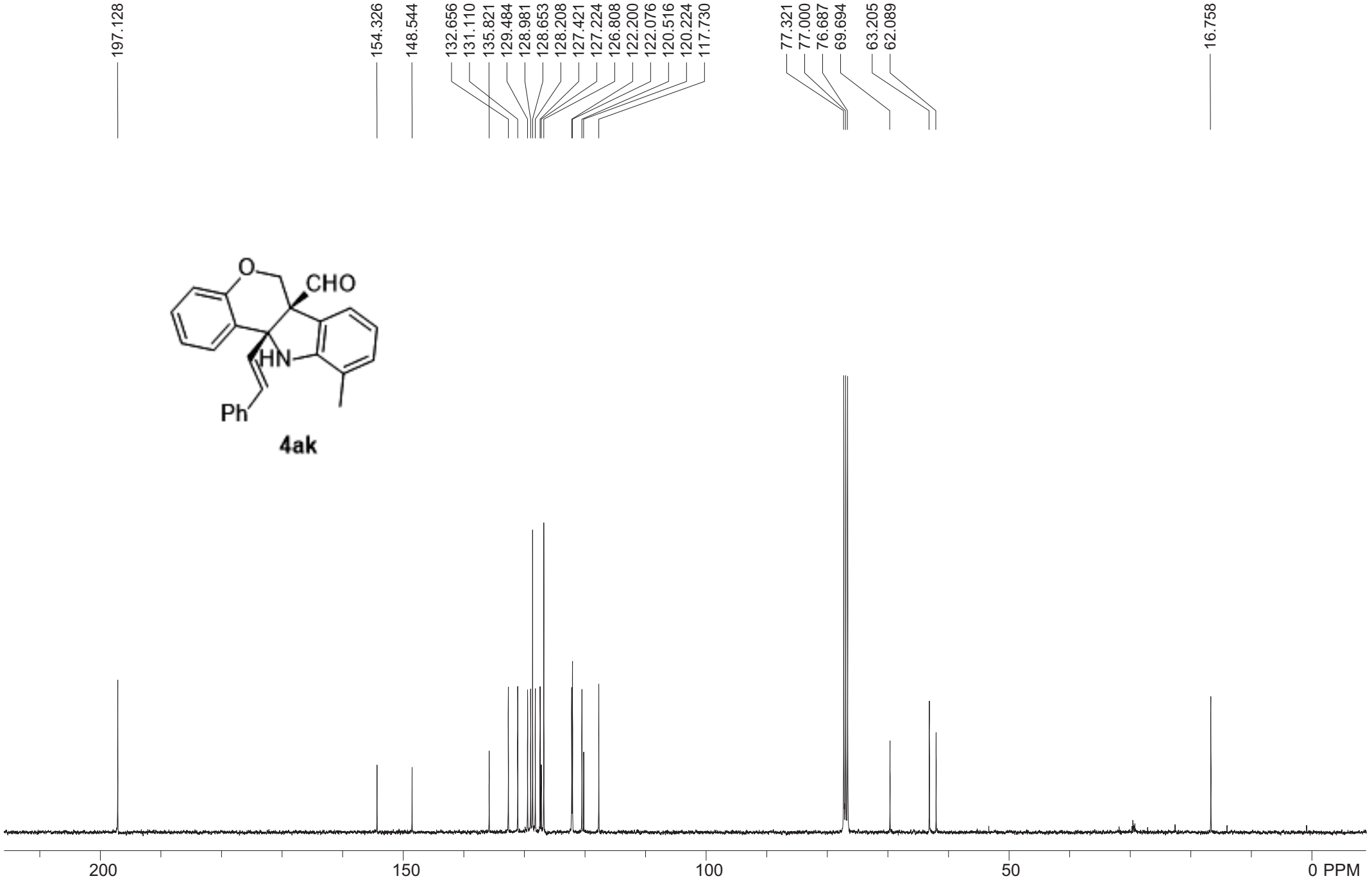
7.250
7.232
7.213
7.193
7.176
7.164
7.155
7.134
7.084
7.064
7.045
6.899
6.879
6.861
6.773
6.753
6.723
6.704
6.685
6.430
6.390
4.643
4.612
4.312
4.281
4.092
2.079
0.000
O
CHO
HN
Ph
4ak
1.00
2.08
2.02
1.99
1.09
4.02
0.98
0.97
0.91
1.00
1.02
0.93
2.98
12
10
8
6
4
2
0
PPM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148.544
132.656
131.110
135.821
129.484
128.981
128.653
128.208
127.421
127.224
126.808
122.200
122.076
120.516
120.224
117.730
77.321
77.000
76.687
69.694
63.205
62.089
16.758
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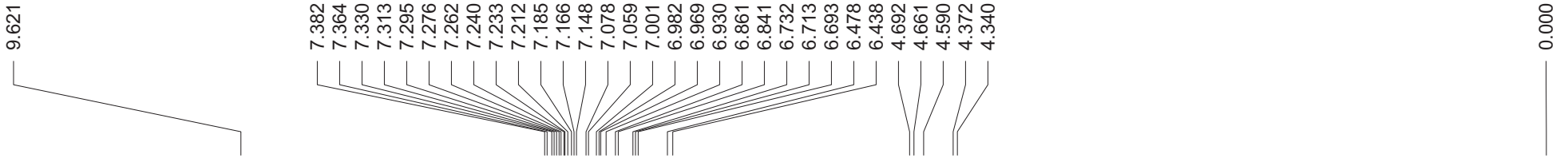
CHO
HN
Ph
4ak
200
150
100
50
0 PPM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7.276
7.262
7.240
7.233
7.212
7.185
7.166
7.148
7.078
7.059
7.001
6.982
6.969
6.930
6.861
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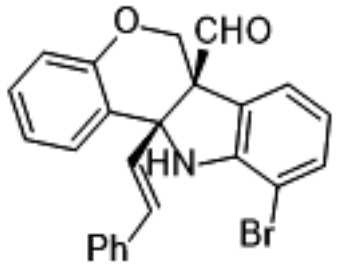
4.692
4.661
4.590
4.372
4.340
0.000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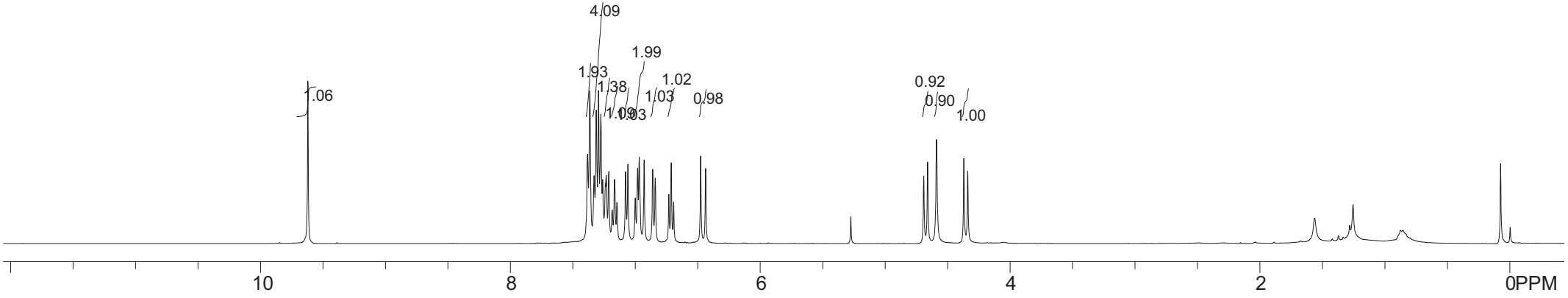
CHO
HN
Ph
Br

4al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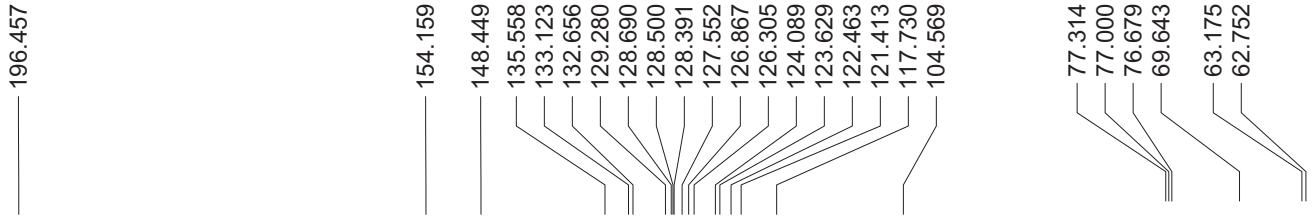
1.99
1.93
1.38
1.02
1.03
0.98
1.06
0.92
0.90
1.00
10
8
6
4
2
0PPM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135.558
133.123
132.656
129.280
128.690
128.500
128.391
127.552
126.867
126.305
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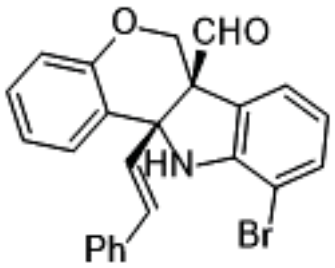
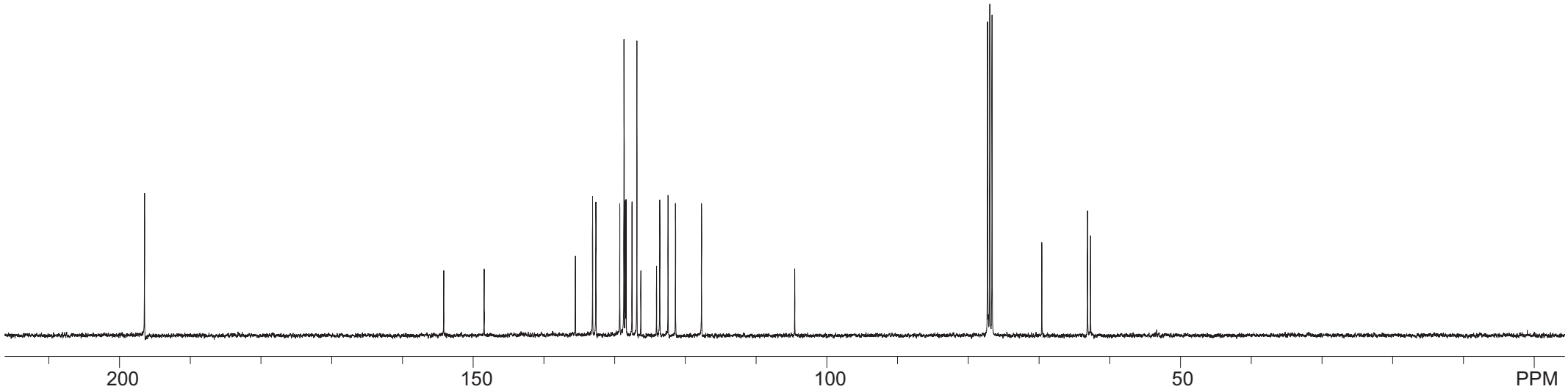
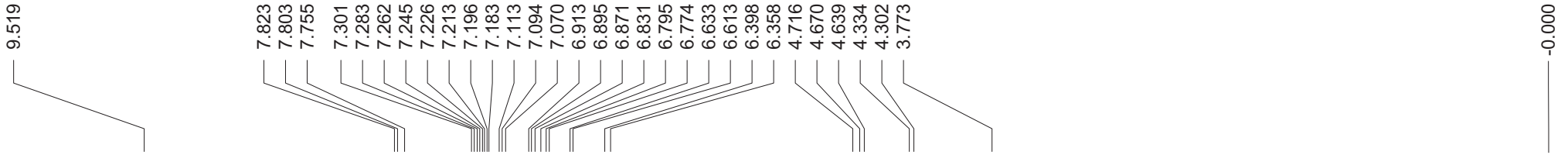
77.000
76.679
69.643
63.175
62.752


O
CHO
HN
Ph
Br

4al


200
150
100
50
PPM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7.823
7.803
7.755
7.301
7.283
7.262
7.245
7.226
7.213
7.196
7.183
7.113
7.094
7.070
6.913
6.895
6.871
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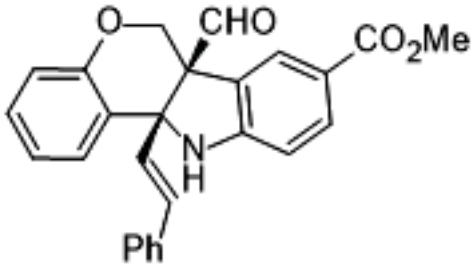
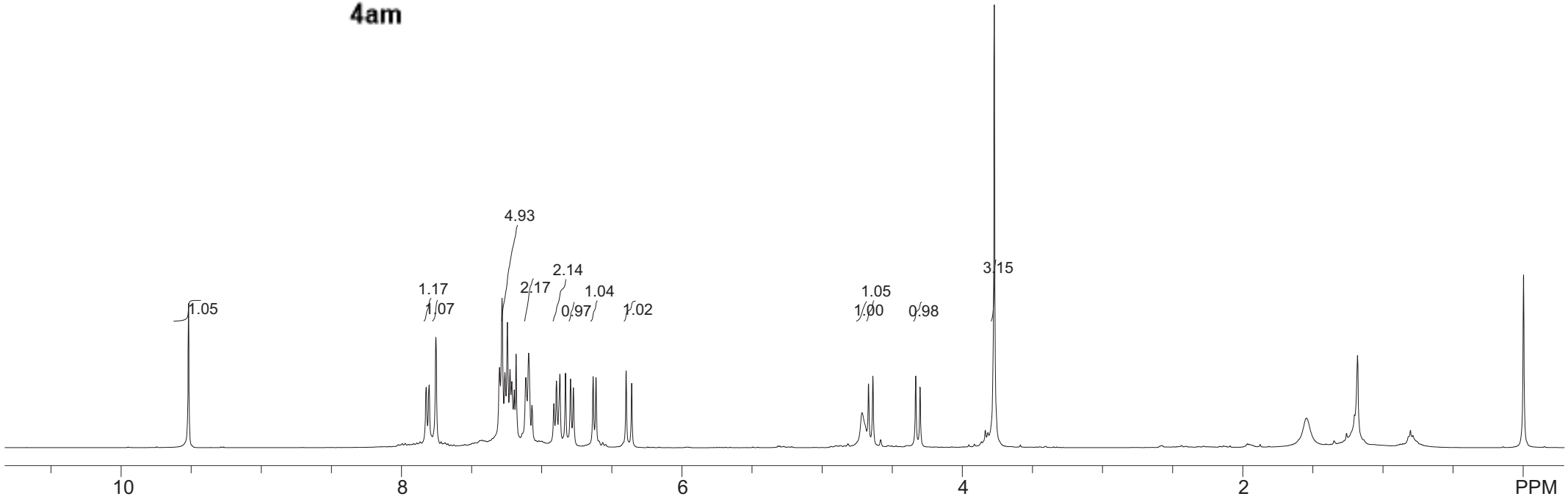
6.795
6.774
6.633
6.613
6.398
6.358
4.716
4.670
4.639
4.334
4.302
3.773
-0.000


O
CHO
CO2Me
N
H
Ph

4am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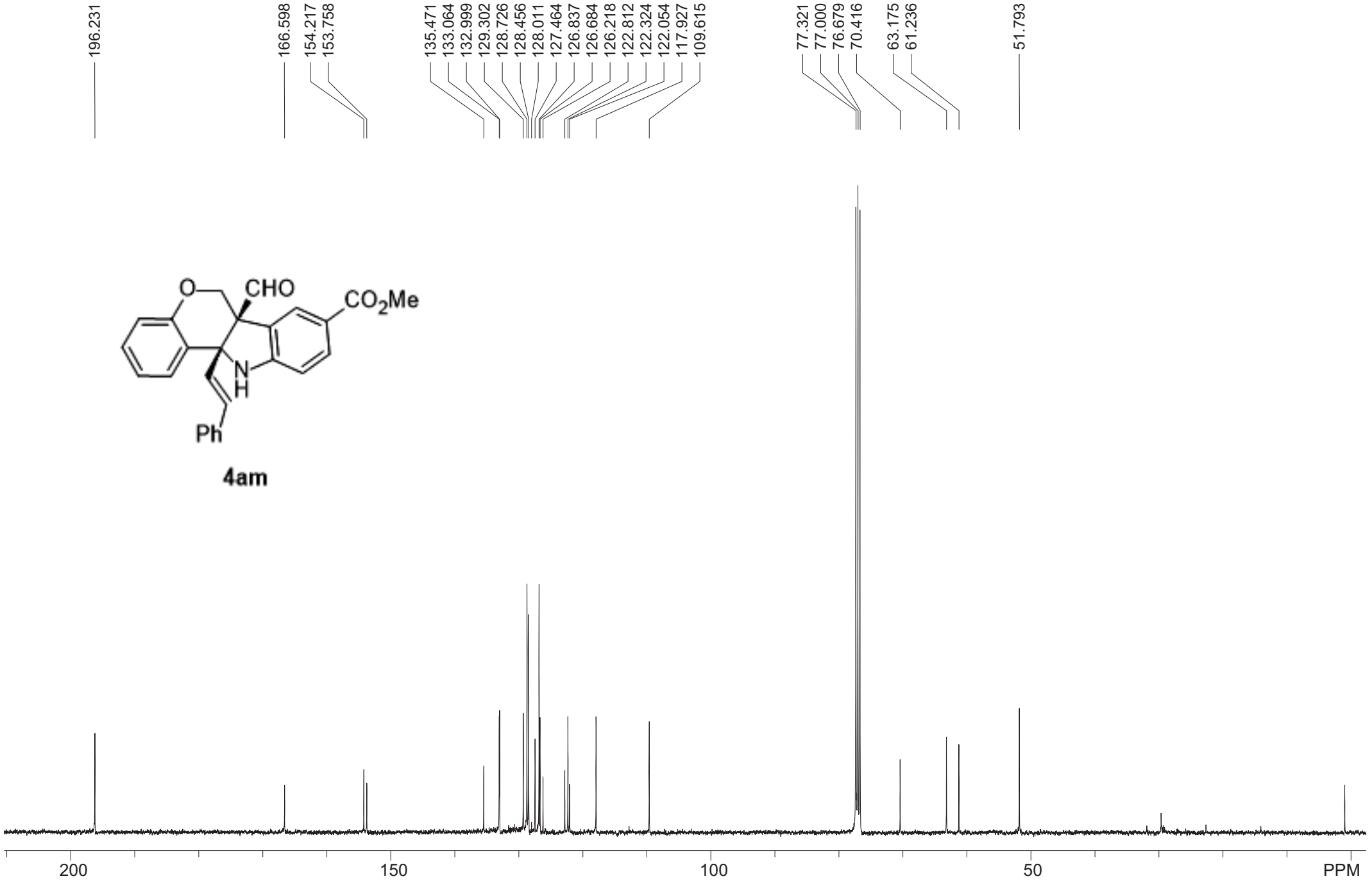
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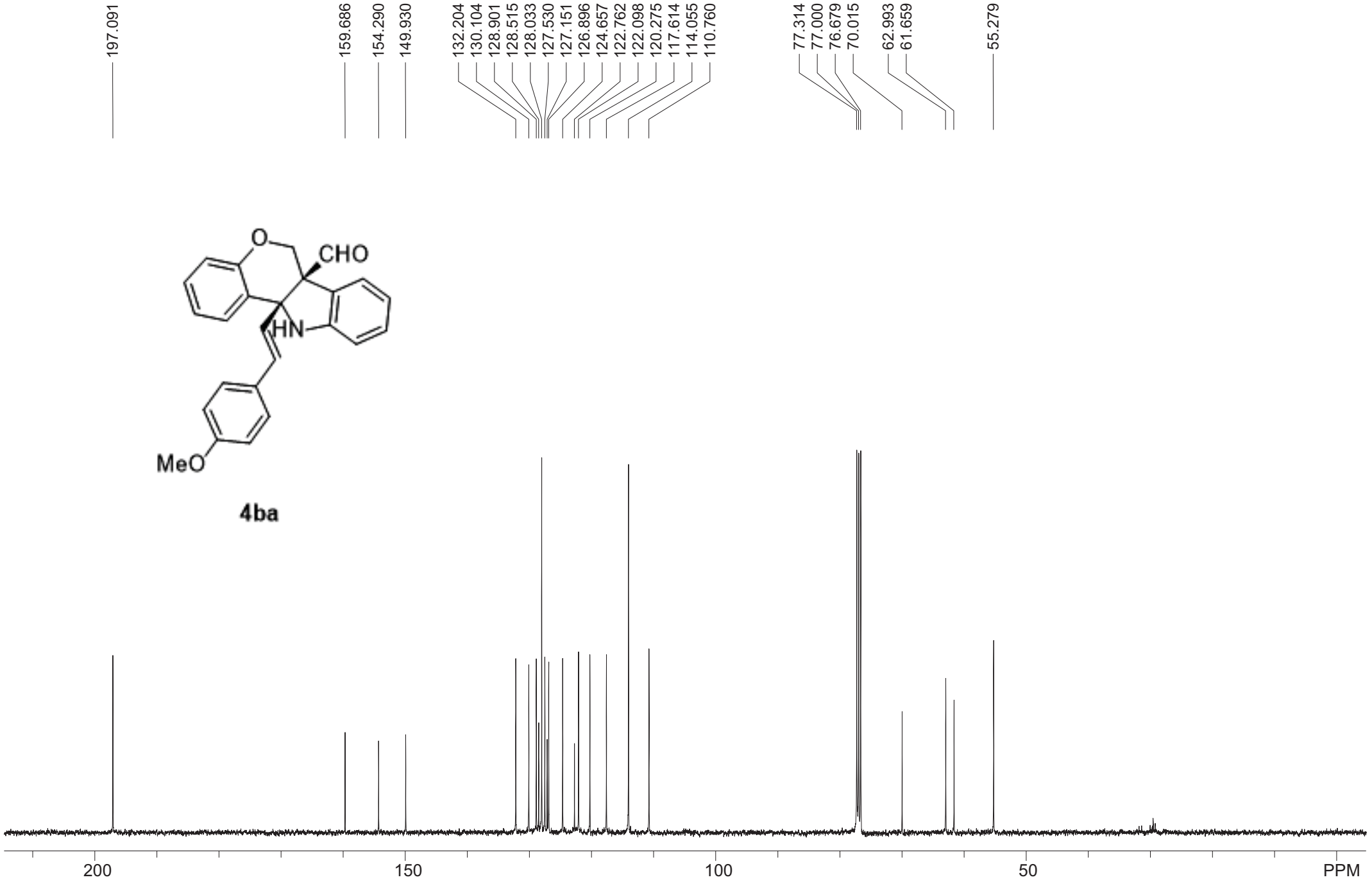
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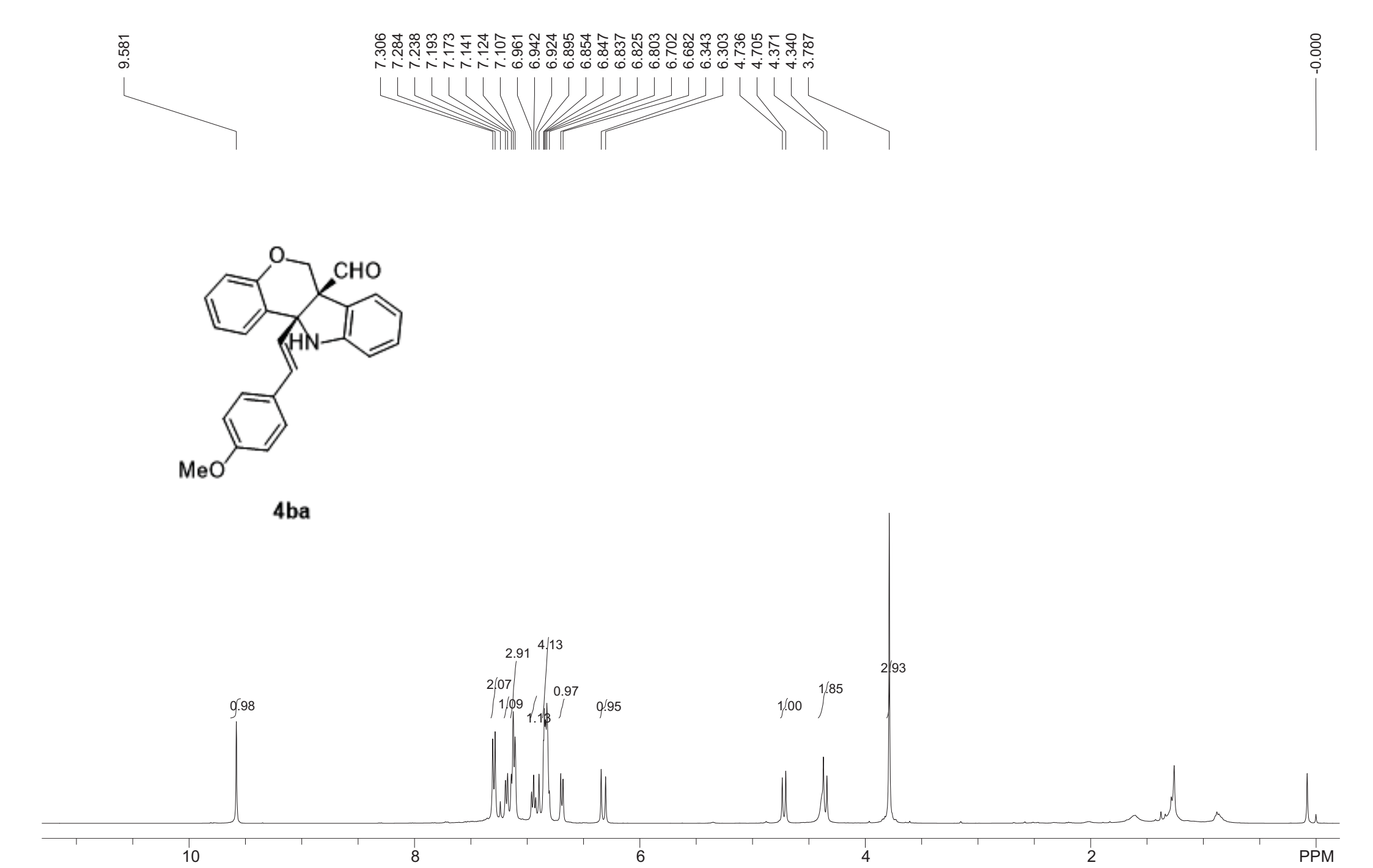
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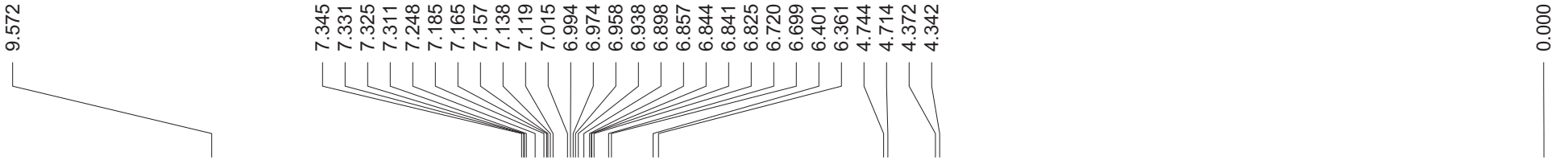
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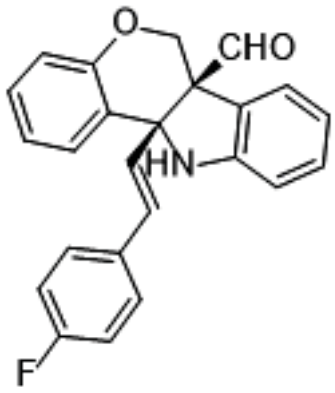
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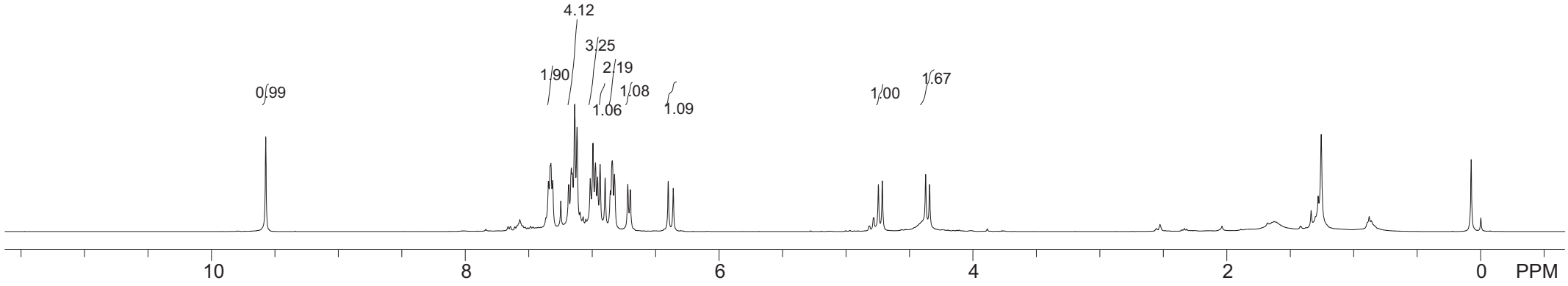
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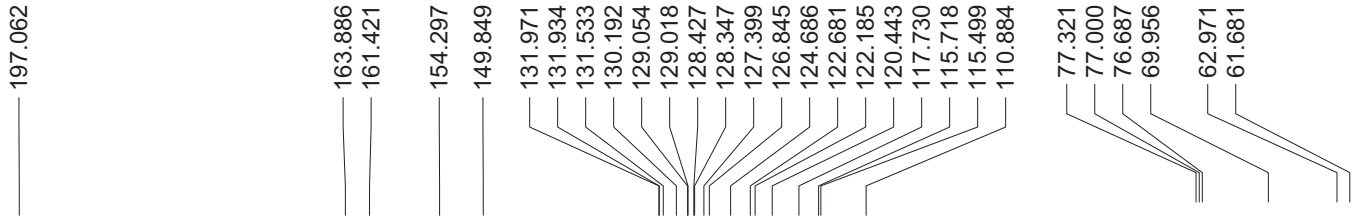
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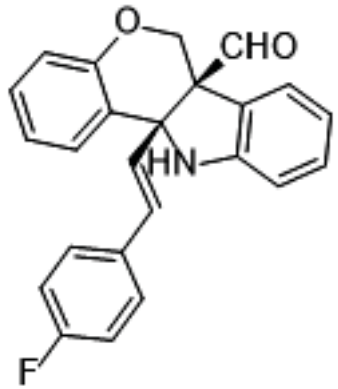
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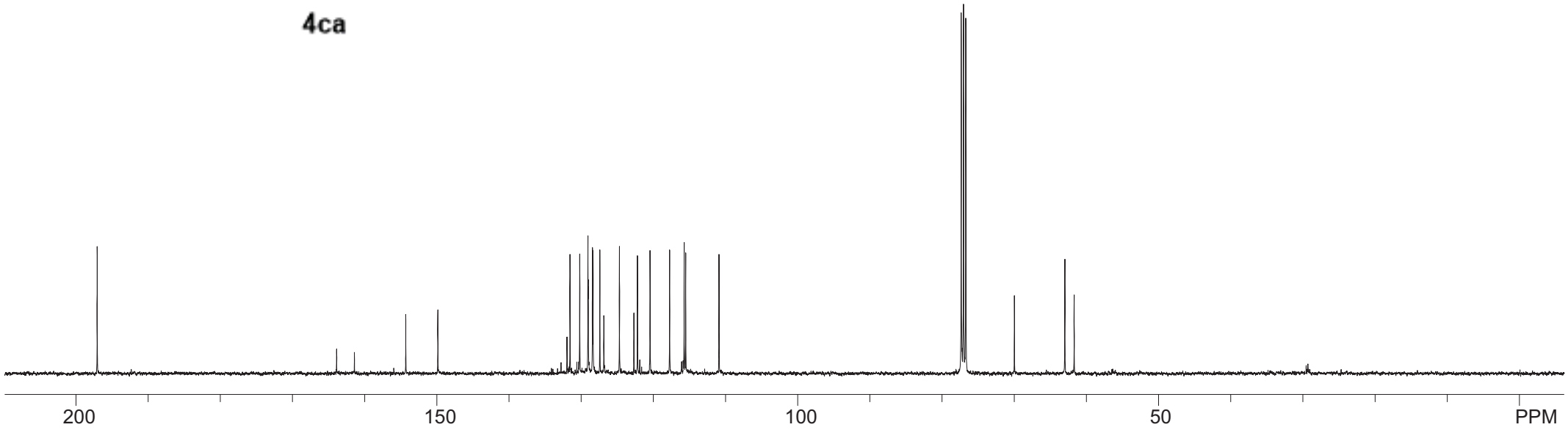
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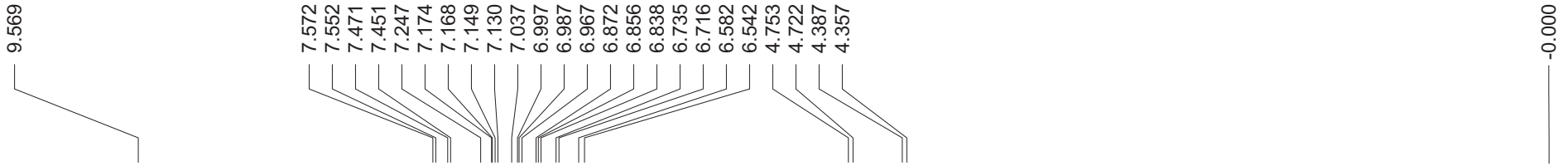
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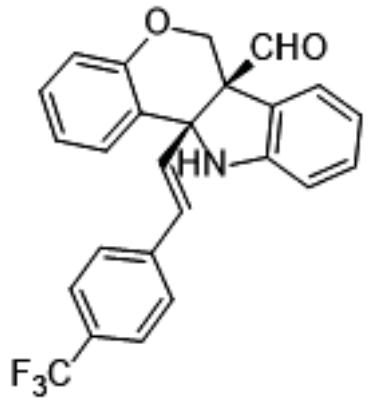
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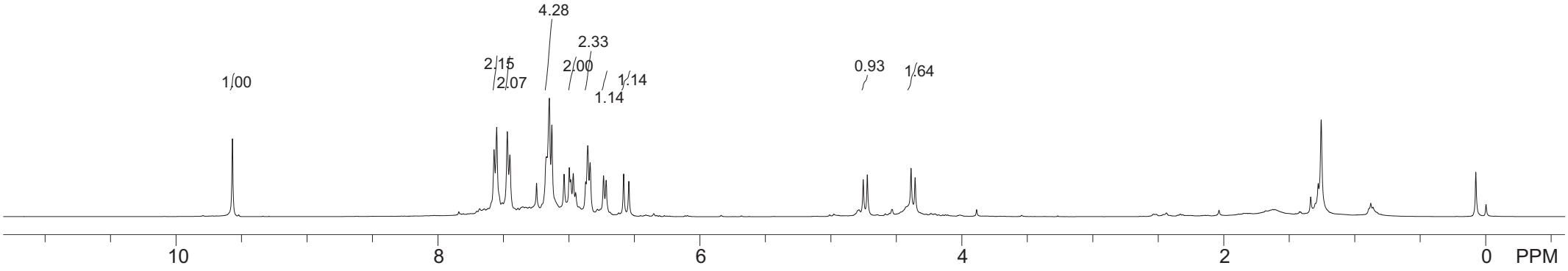
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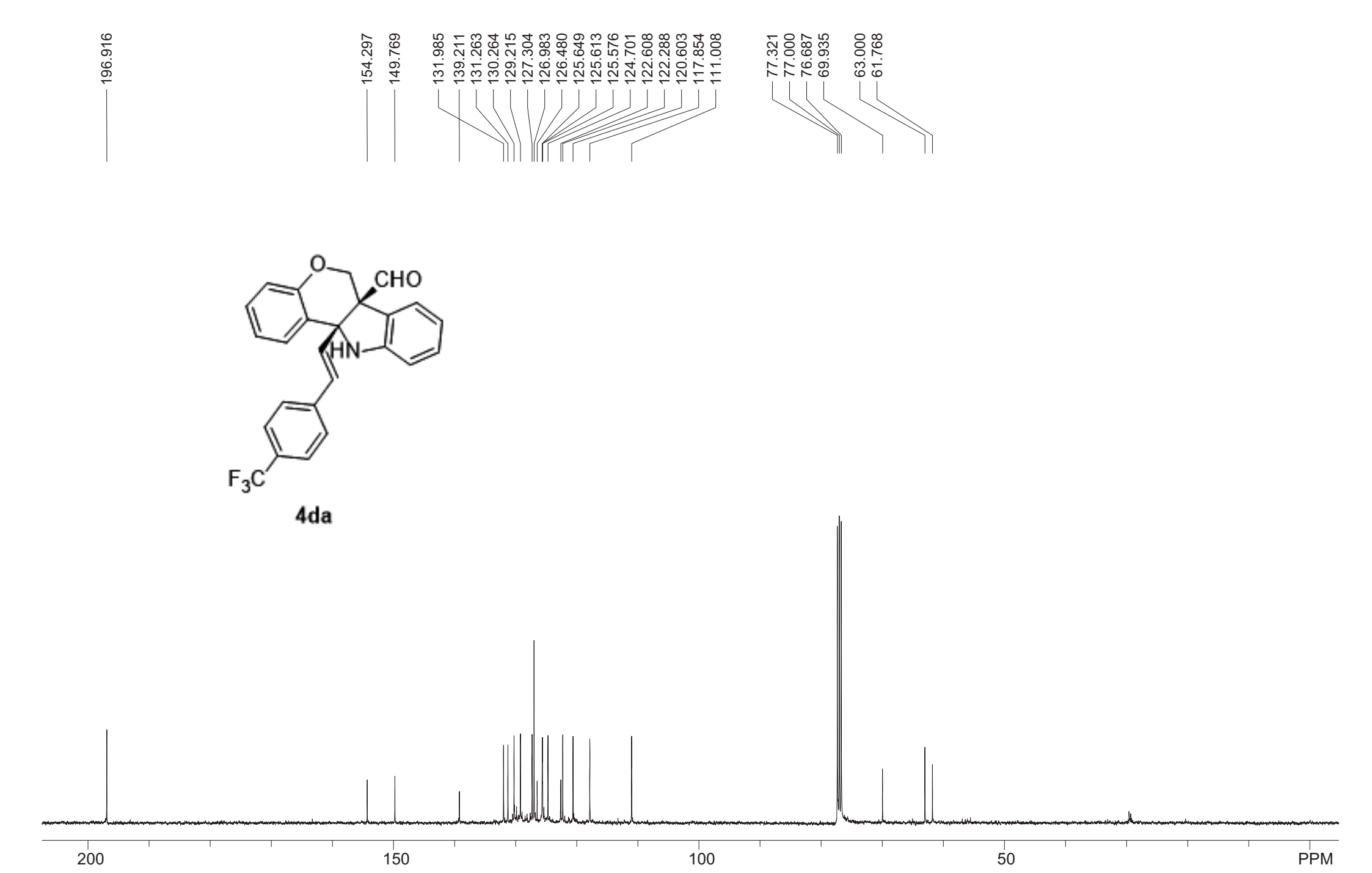
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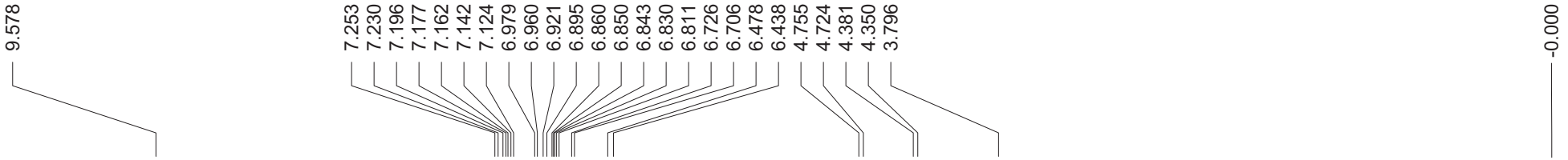
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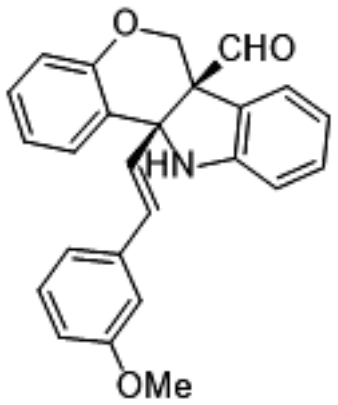
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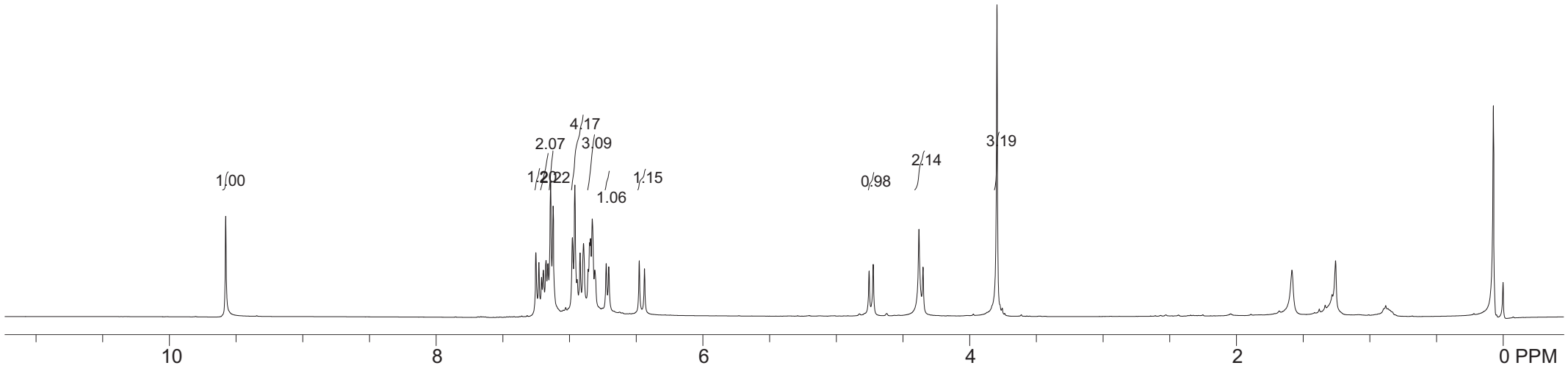
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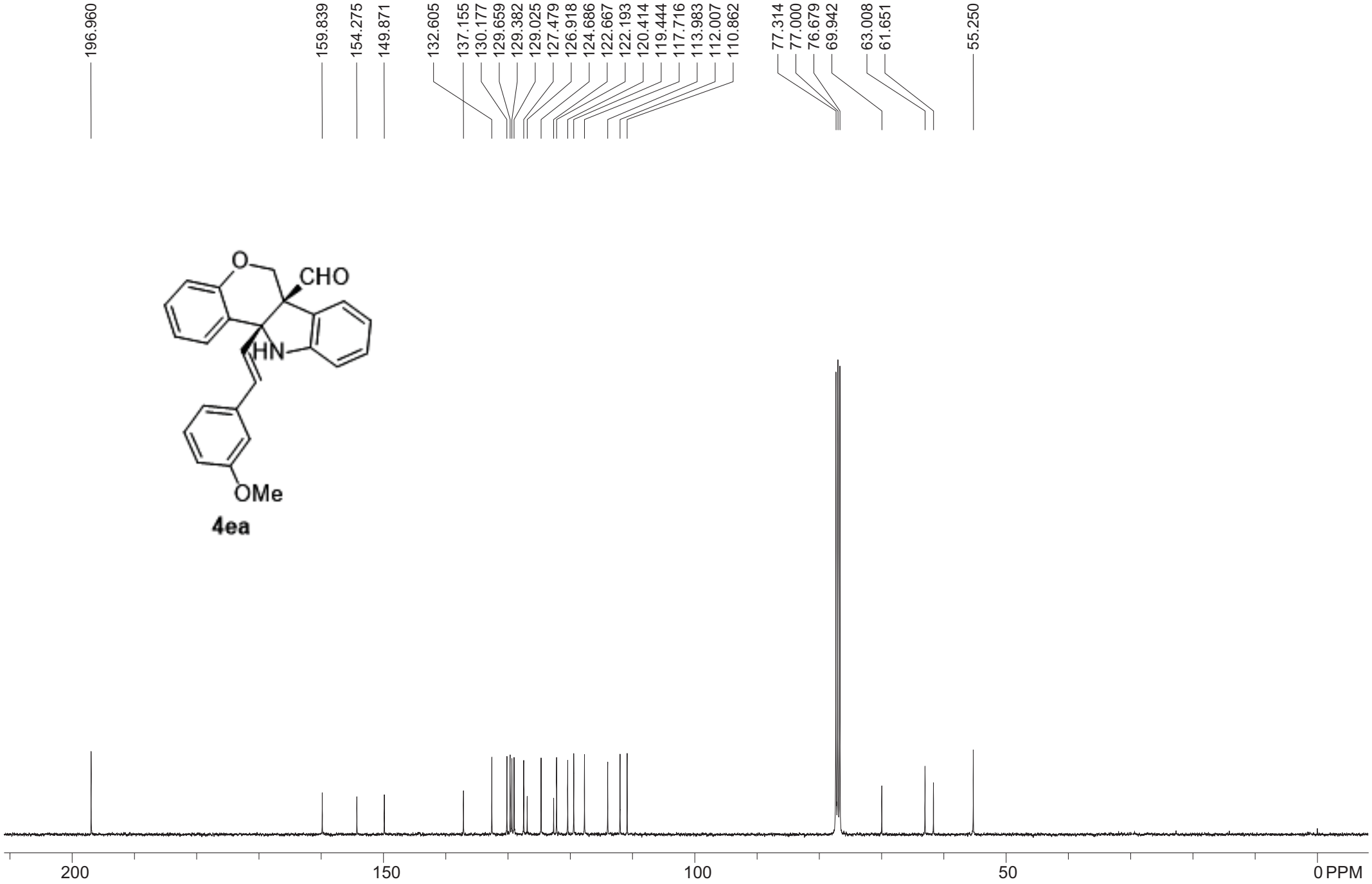
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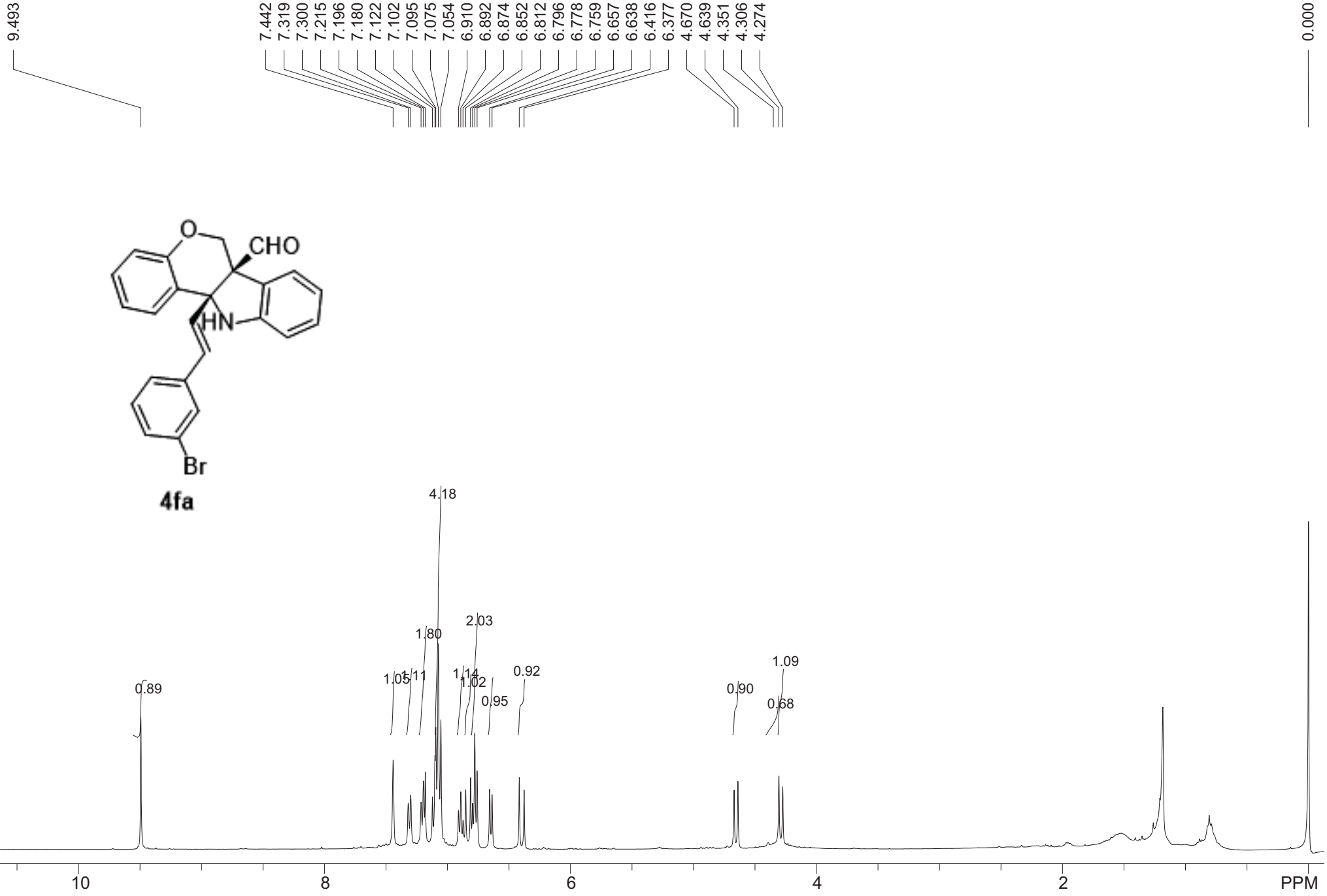
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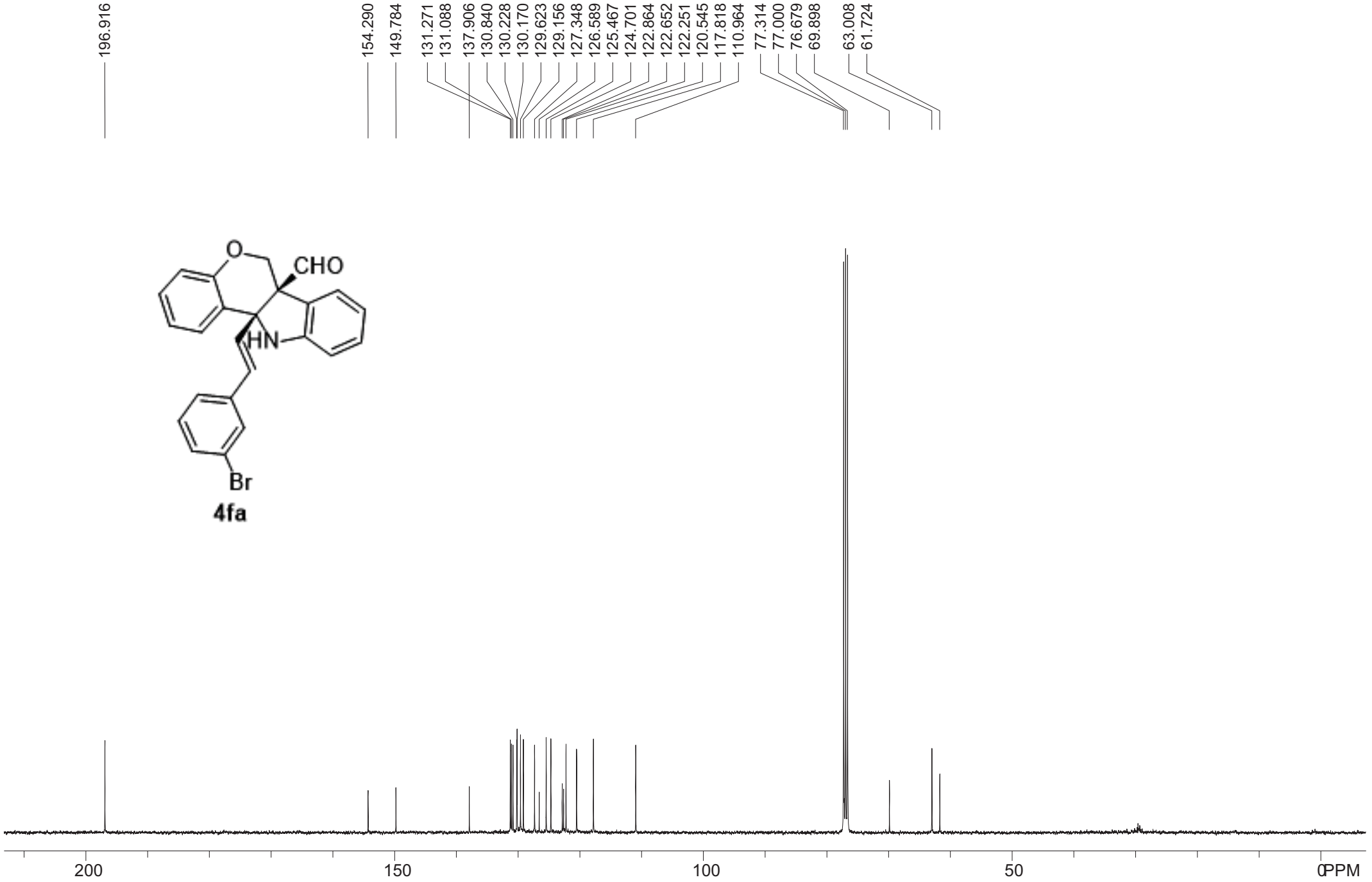
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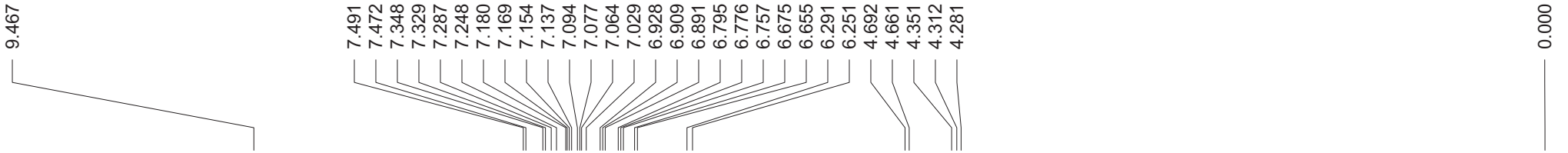
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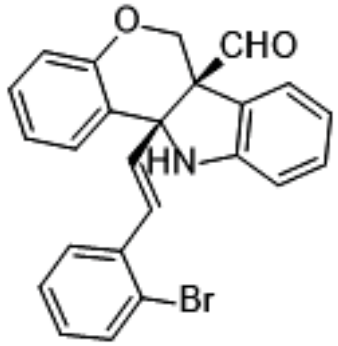
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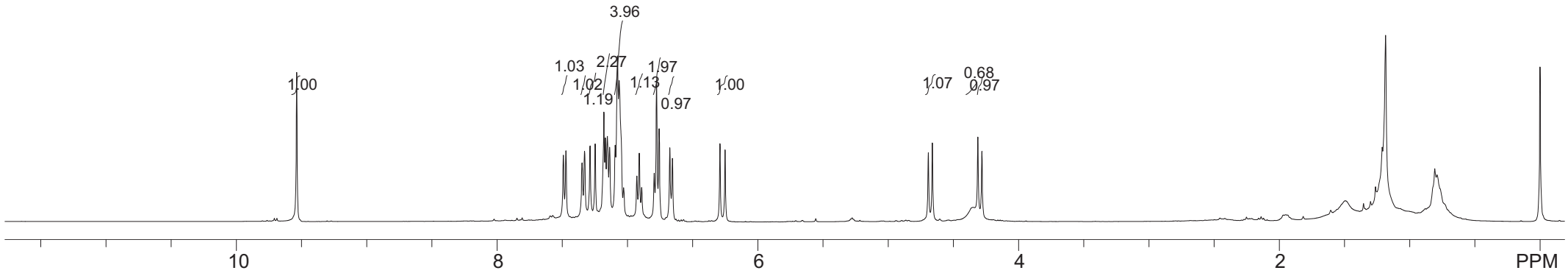
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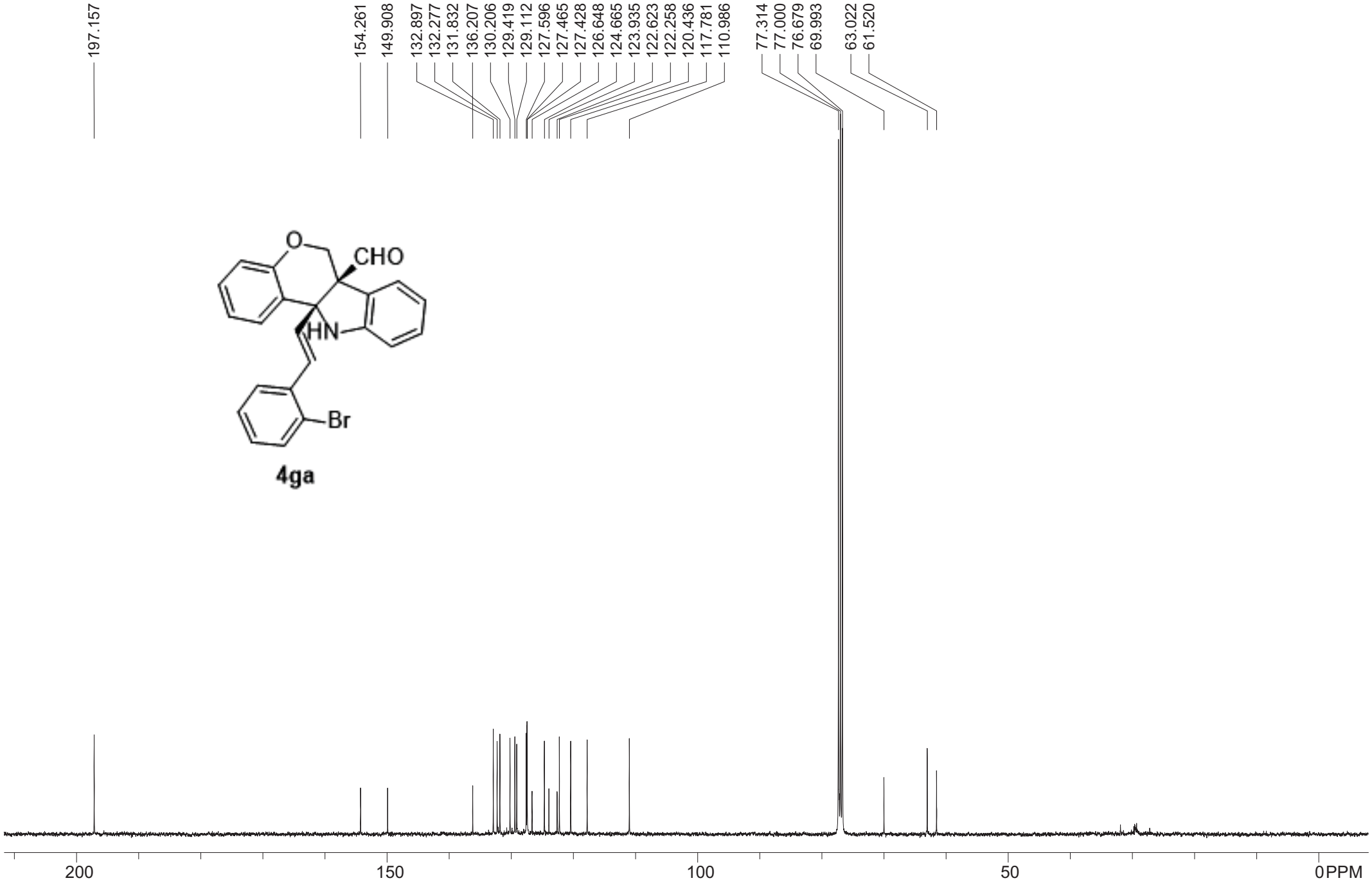
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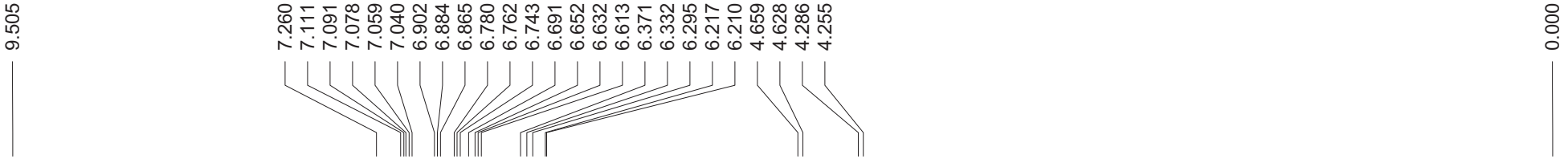
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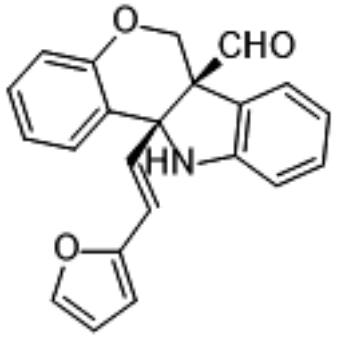
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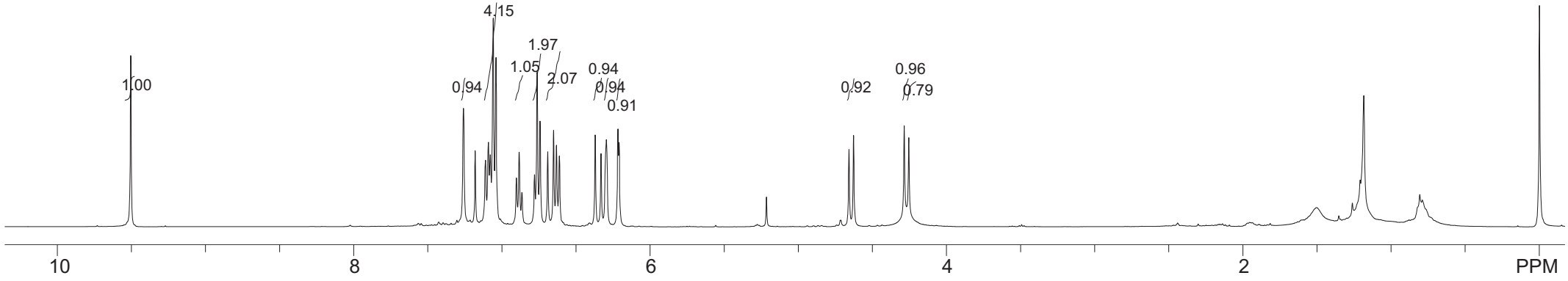
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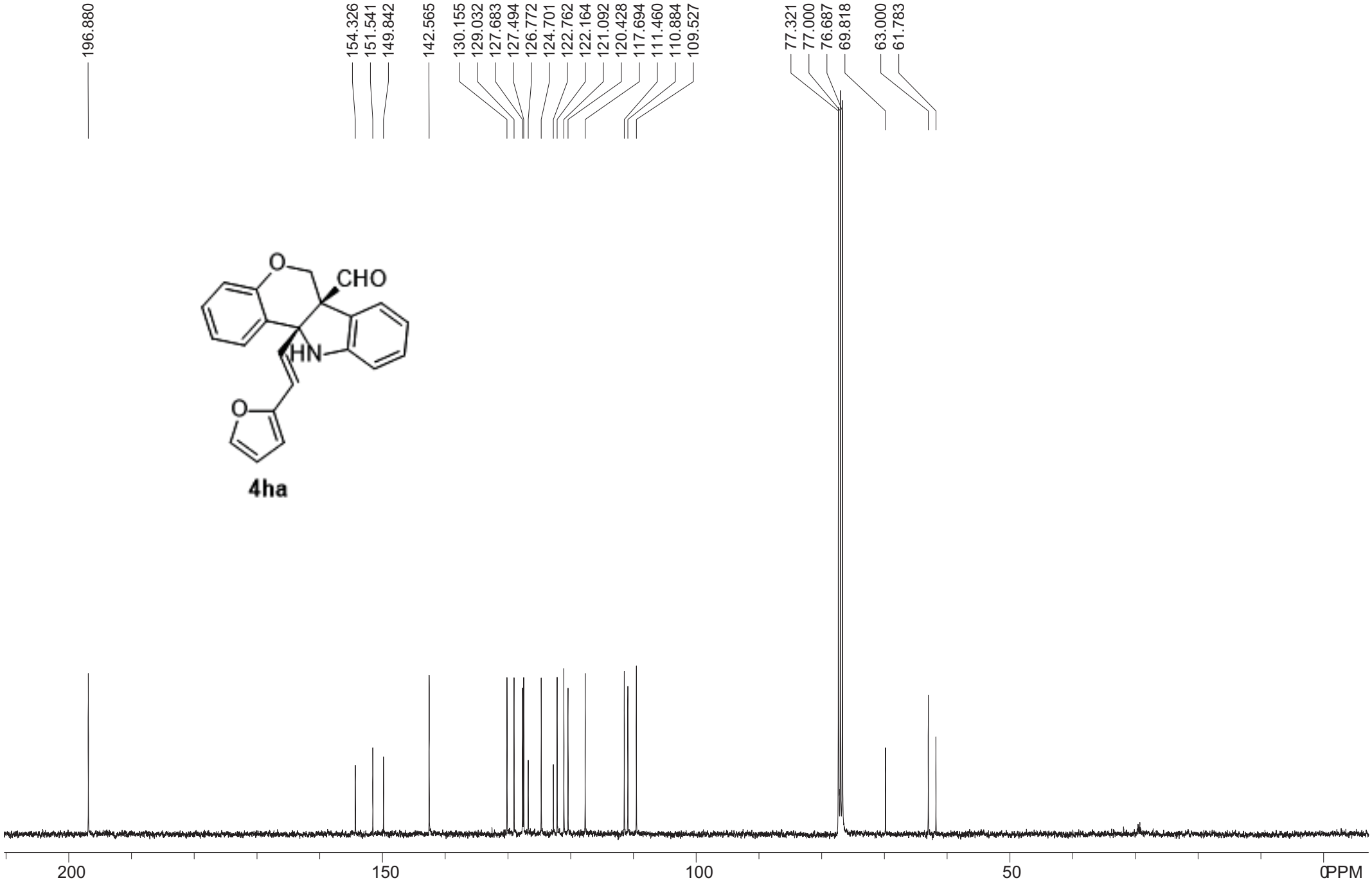
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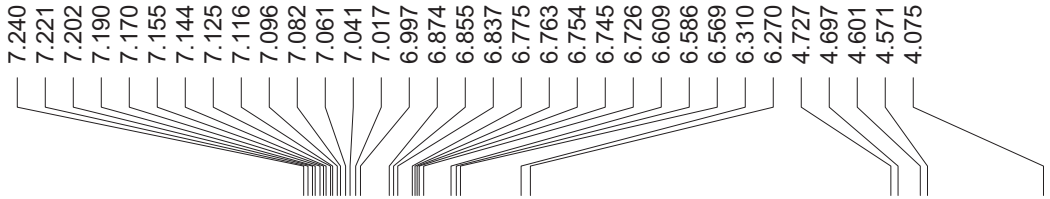
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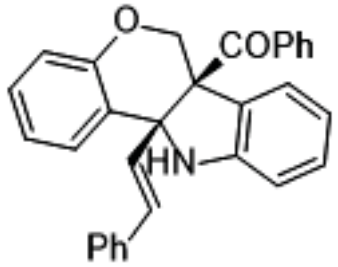
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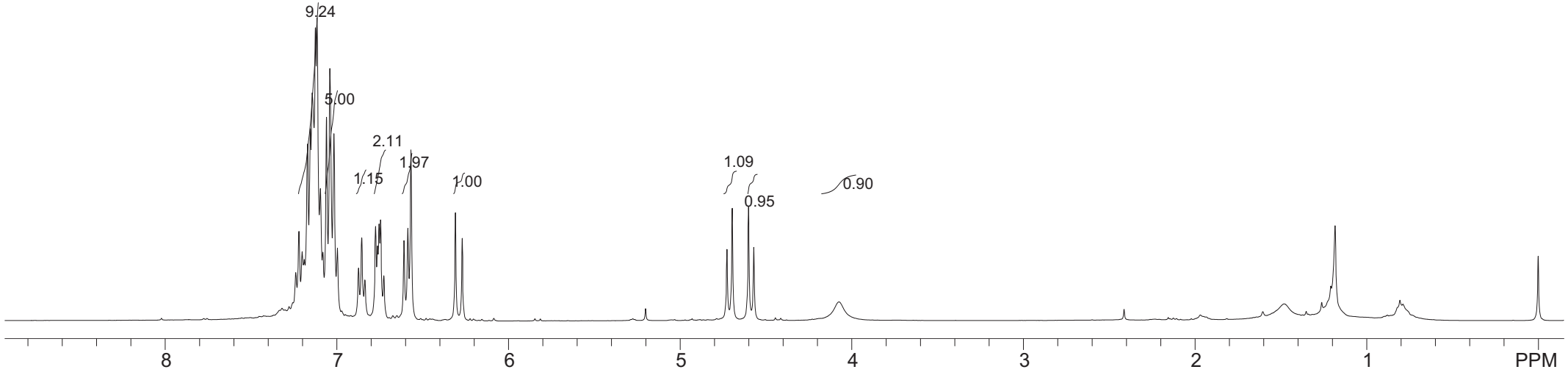
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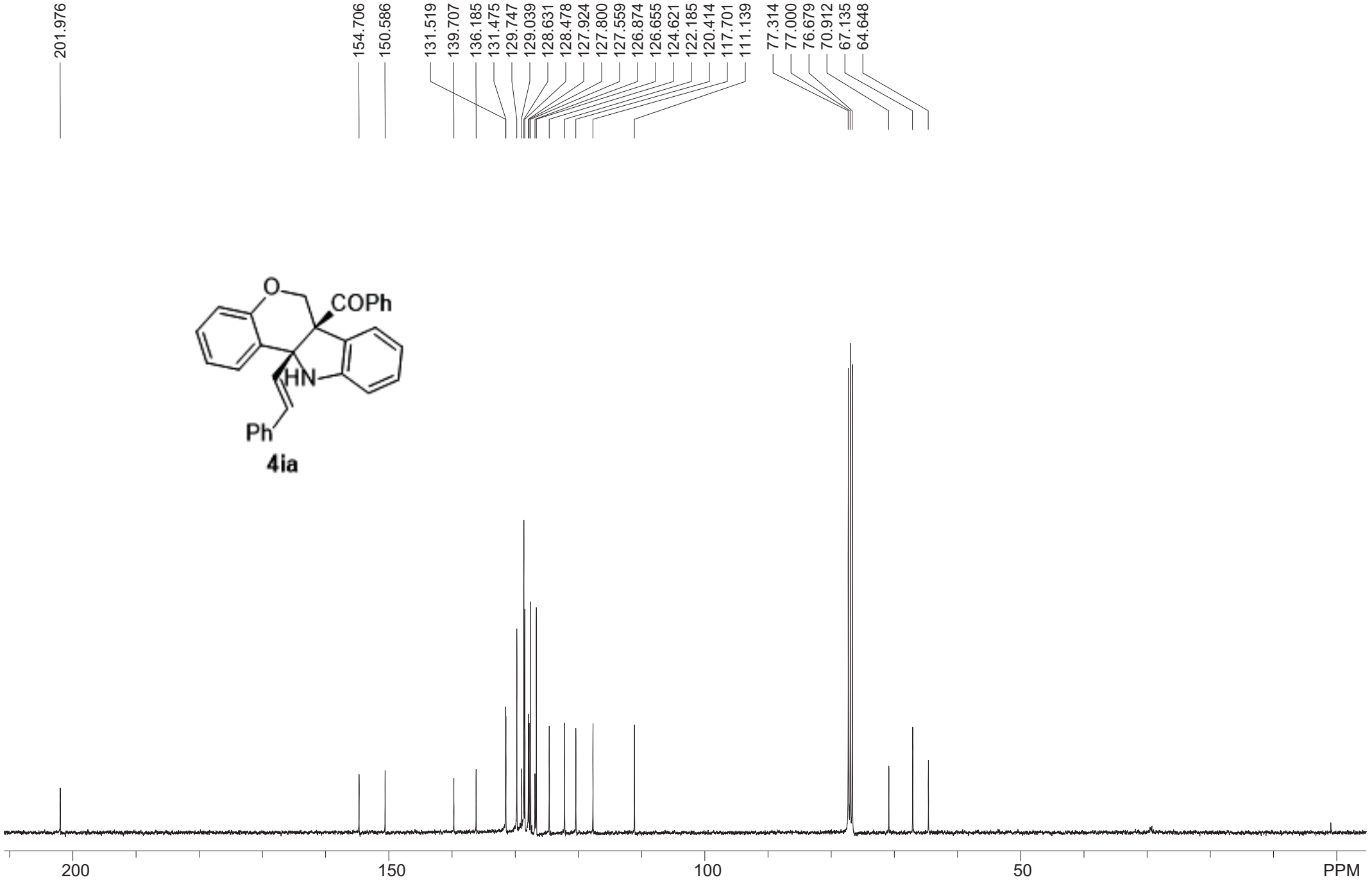
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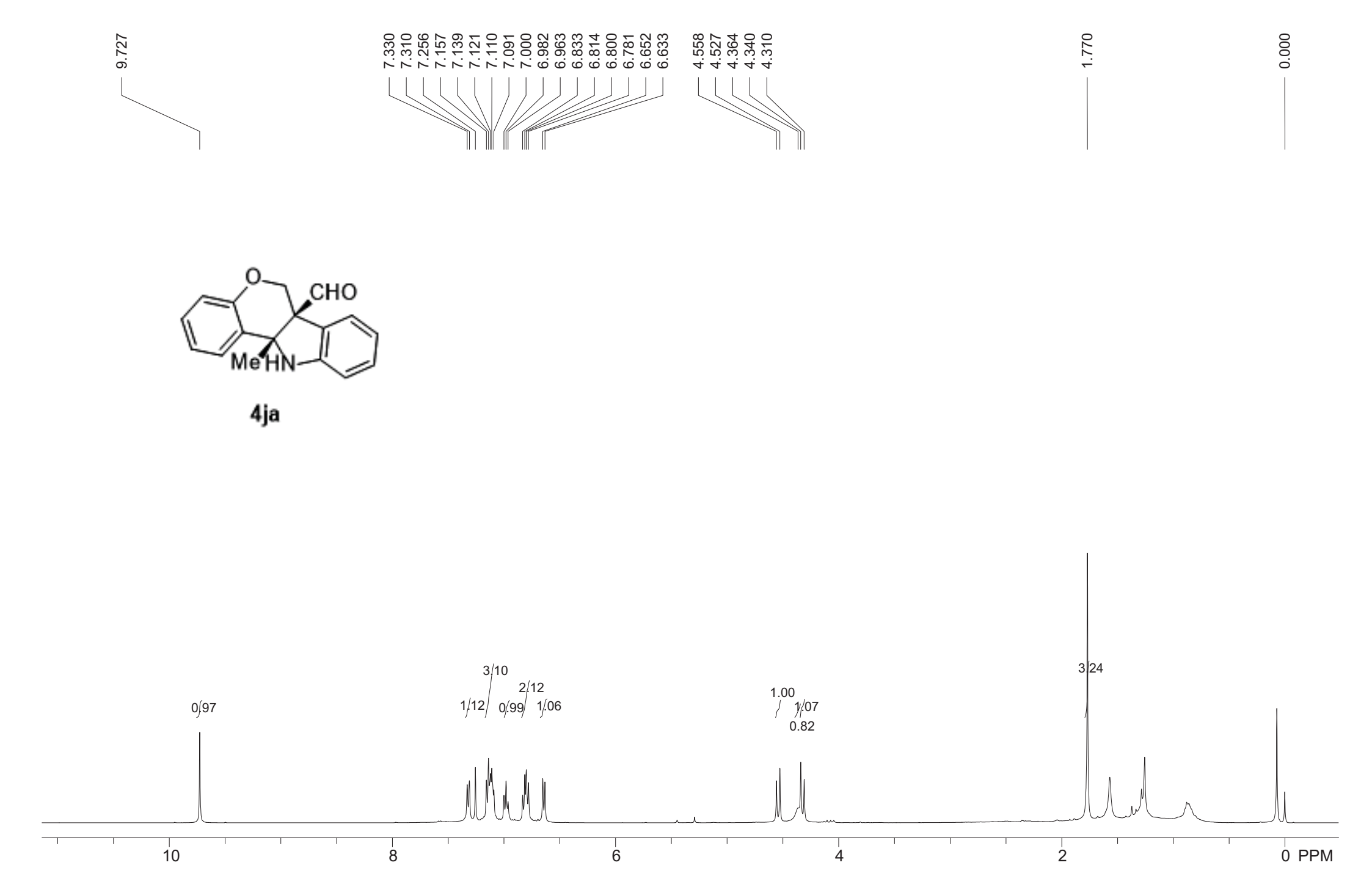
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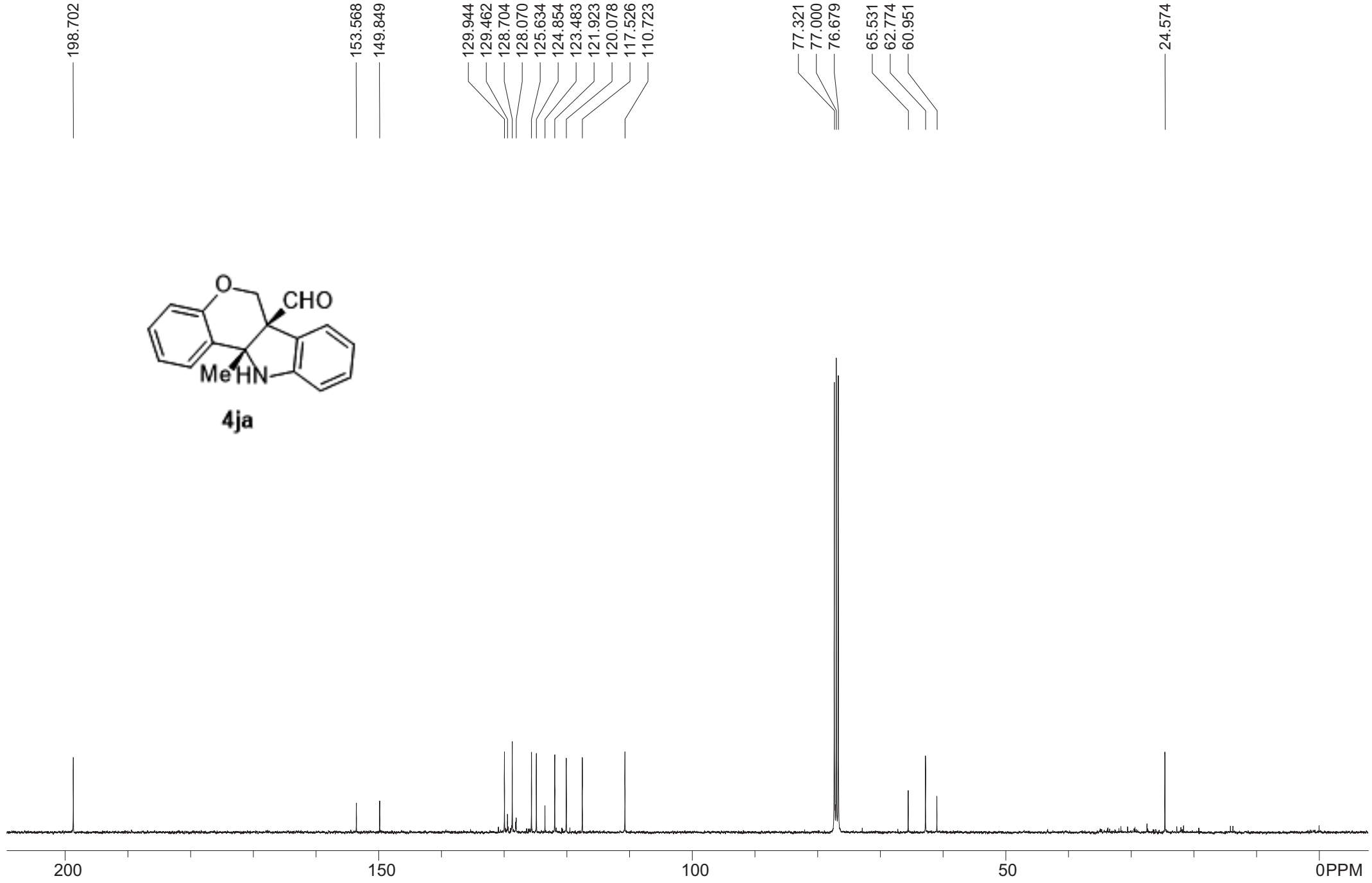
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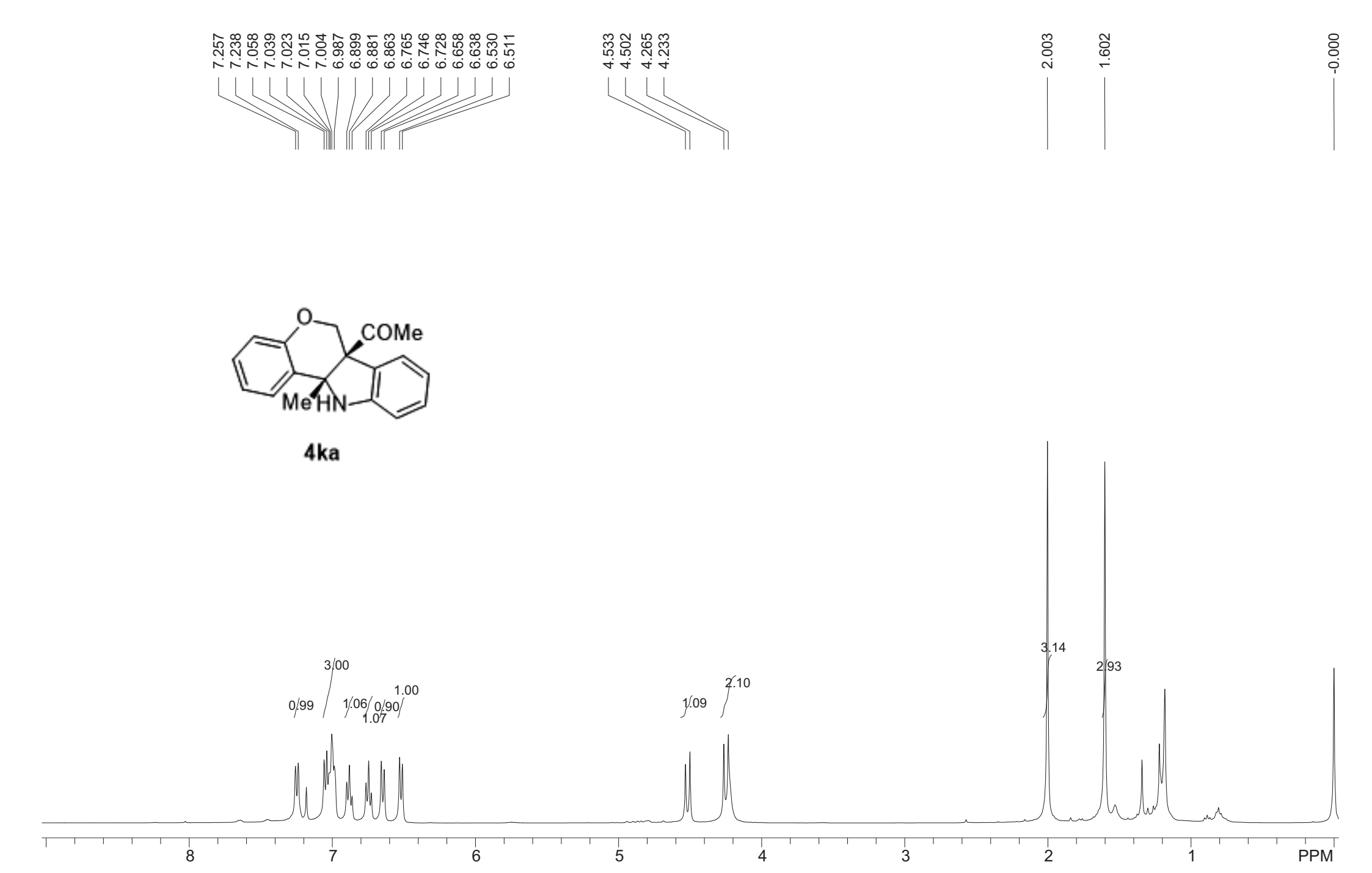
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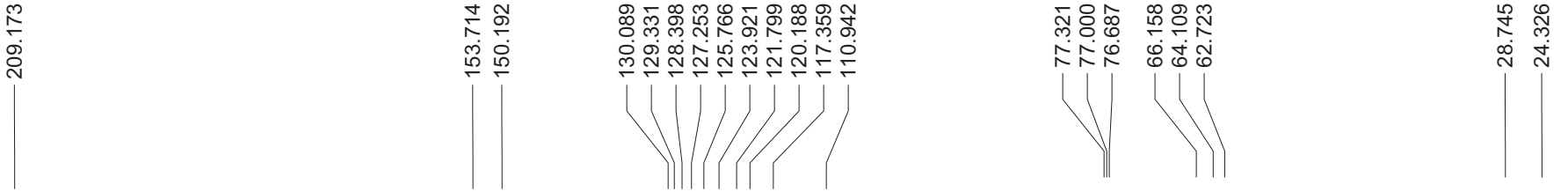
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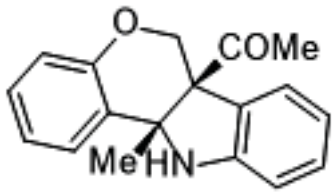
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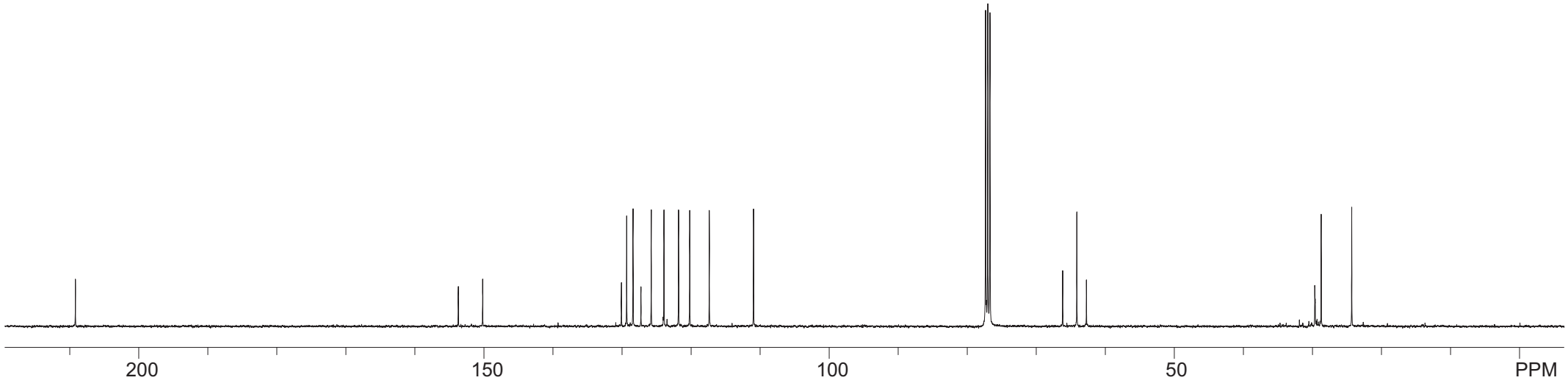
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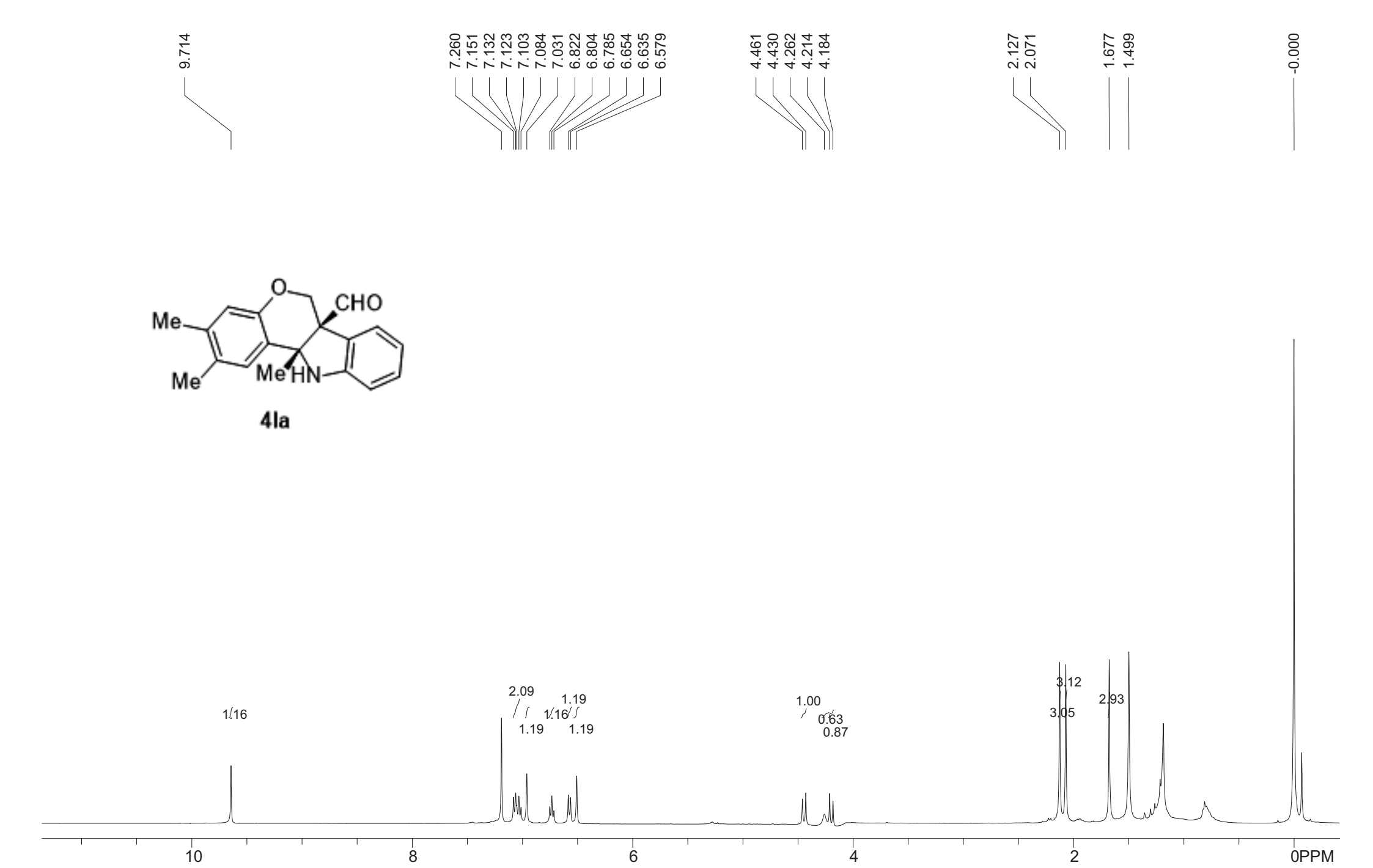
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Me
Me
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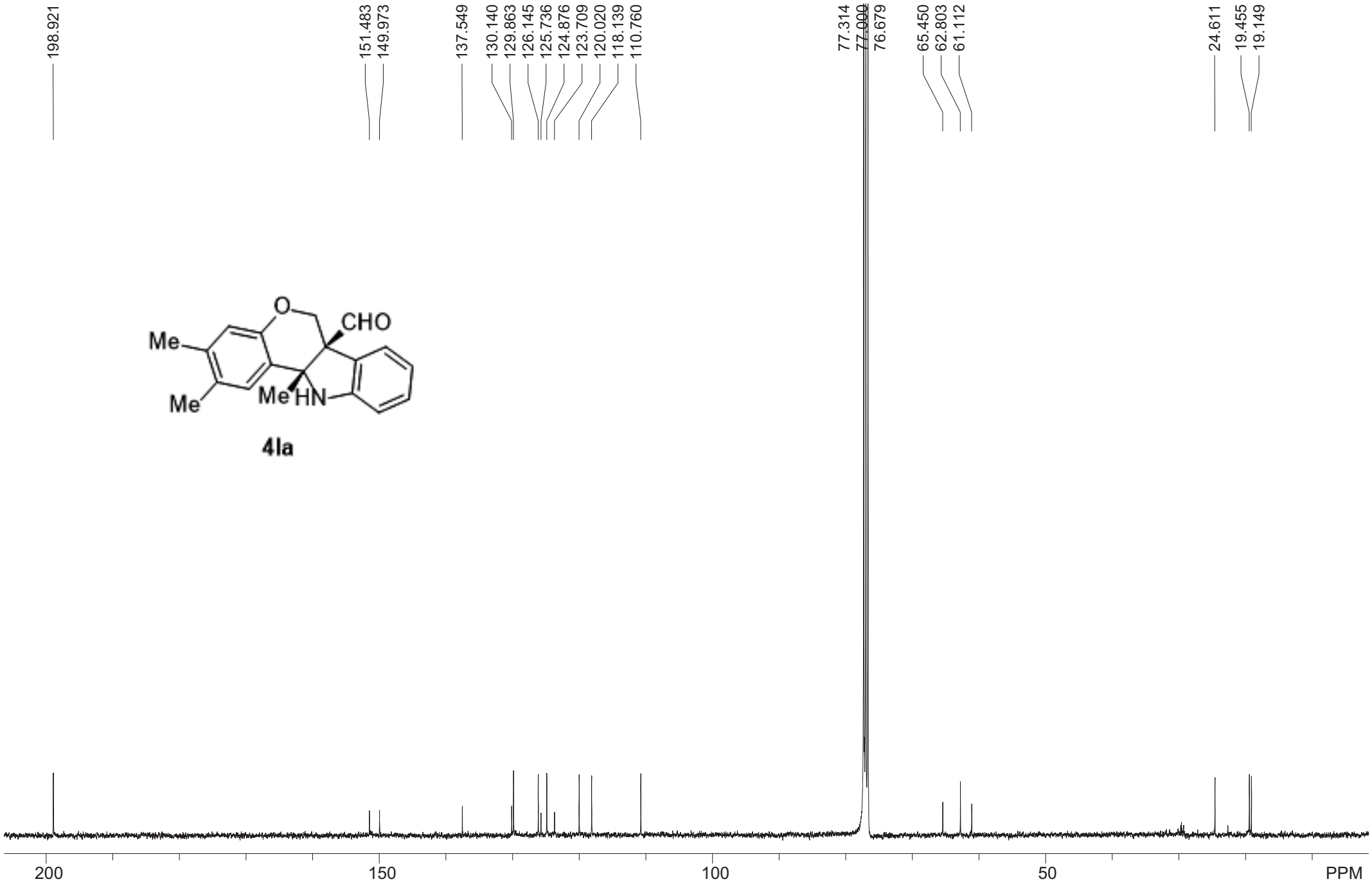
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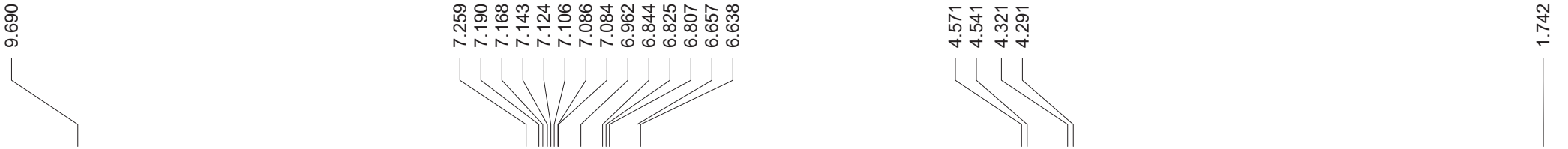
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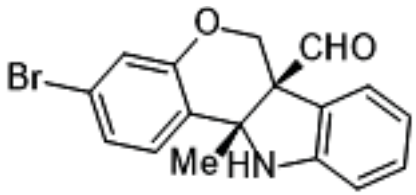
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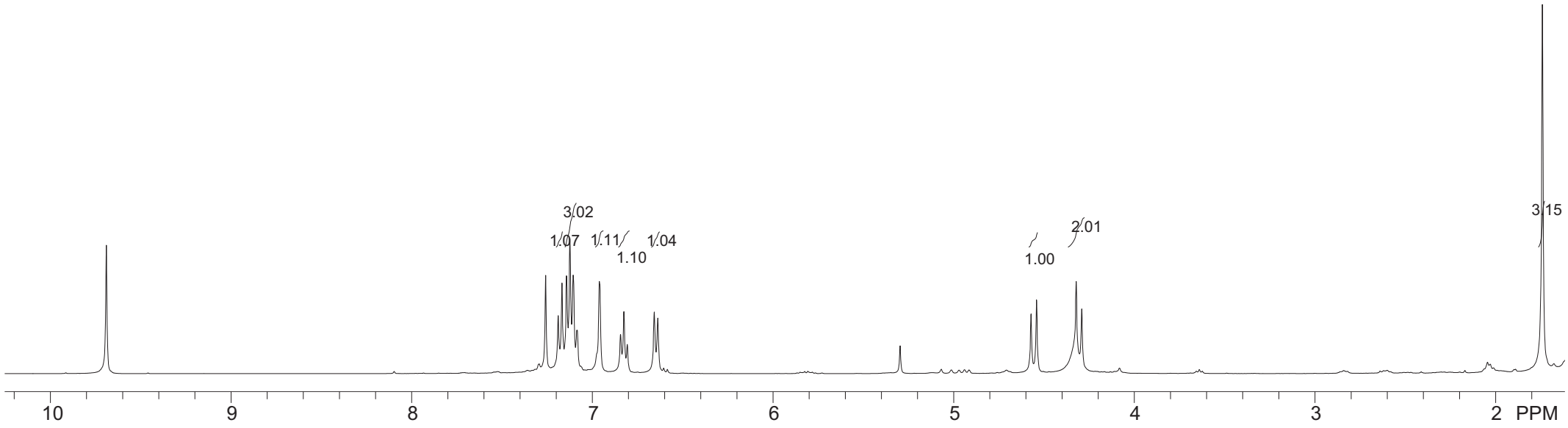
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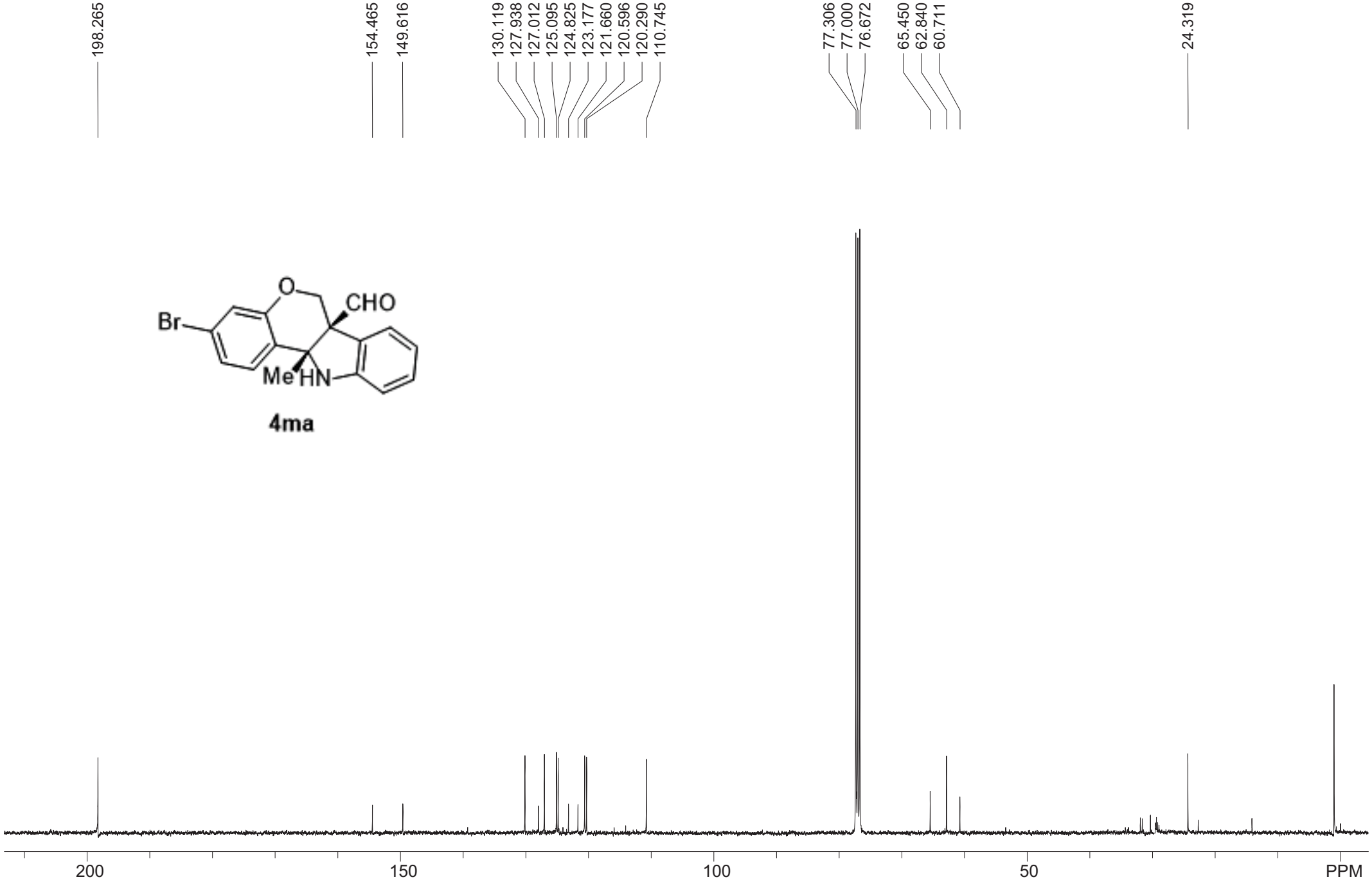
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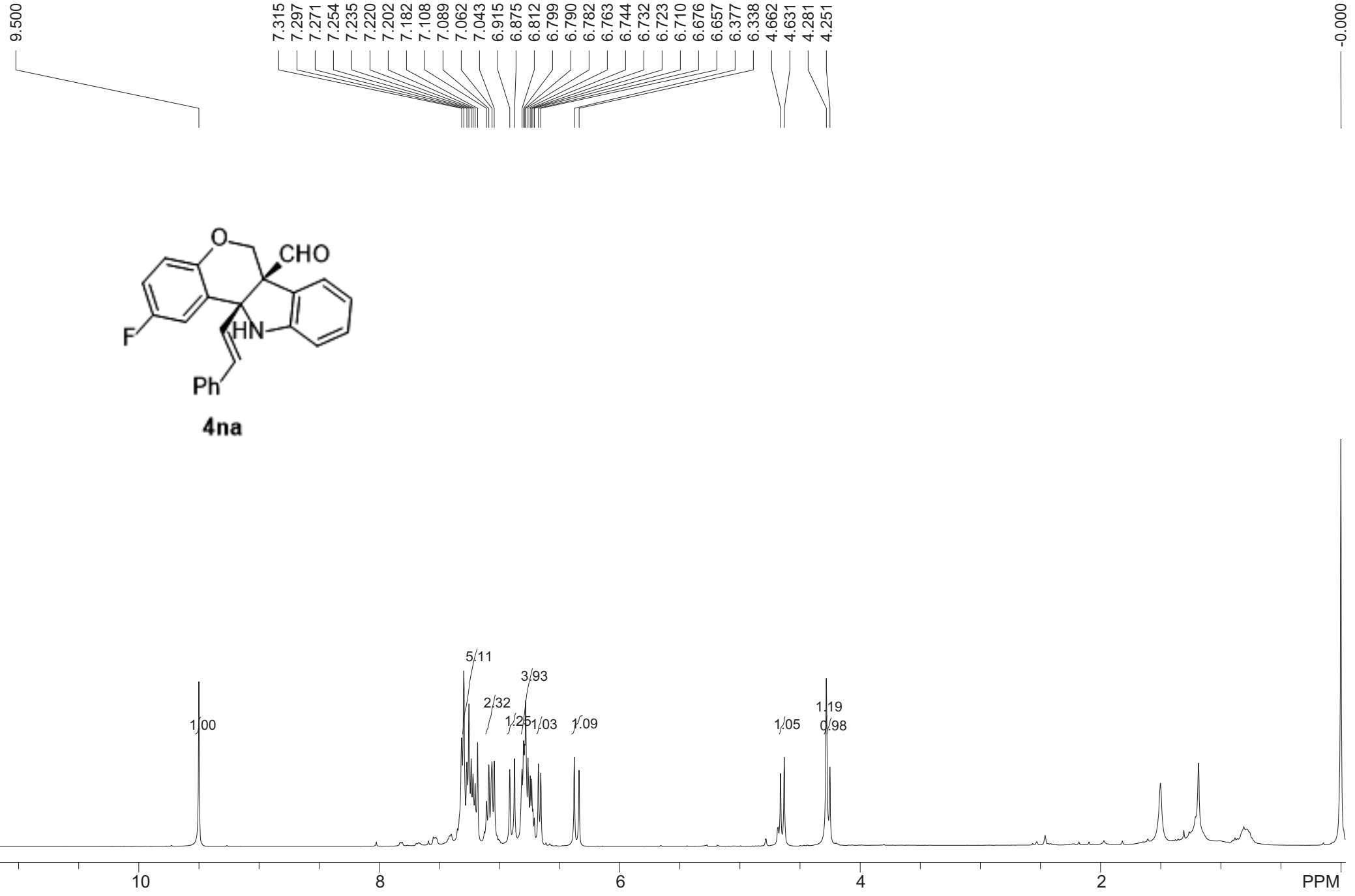
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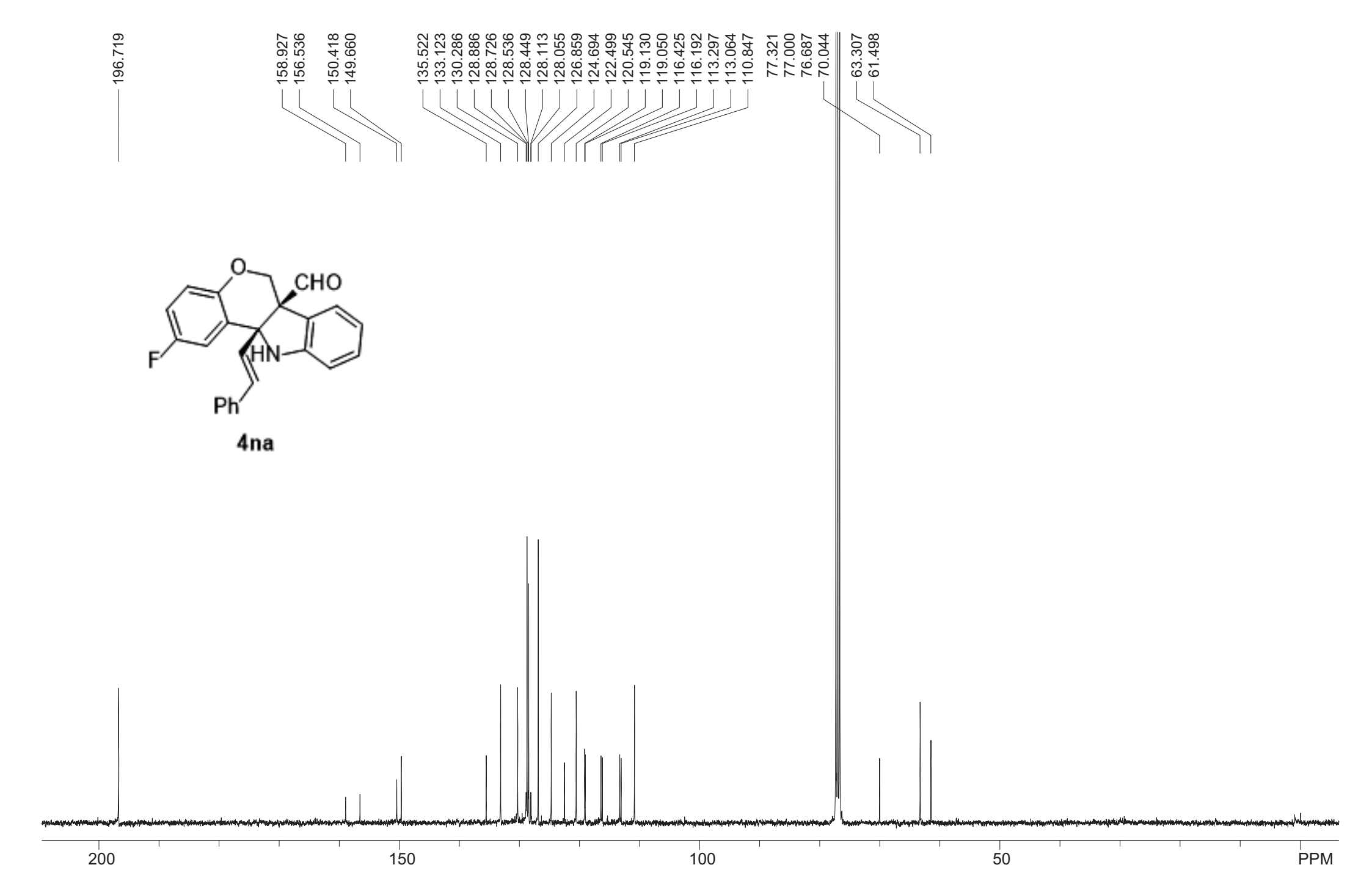
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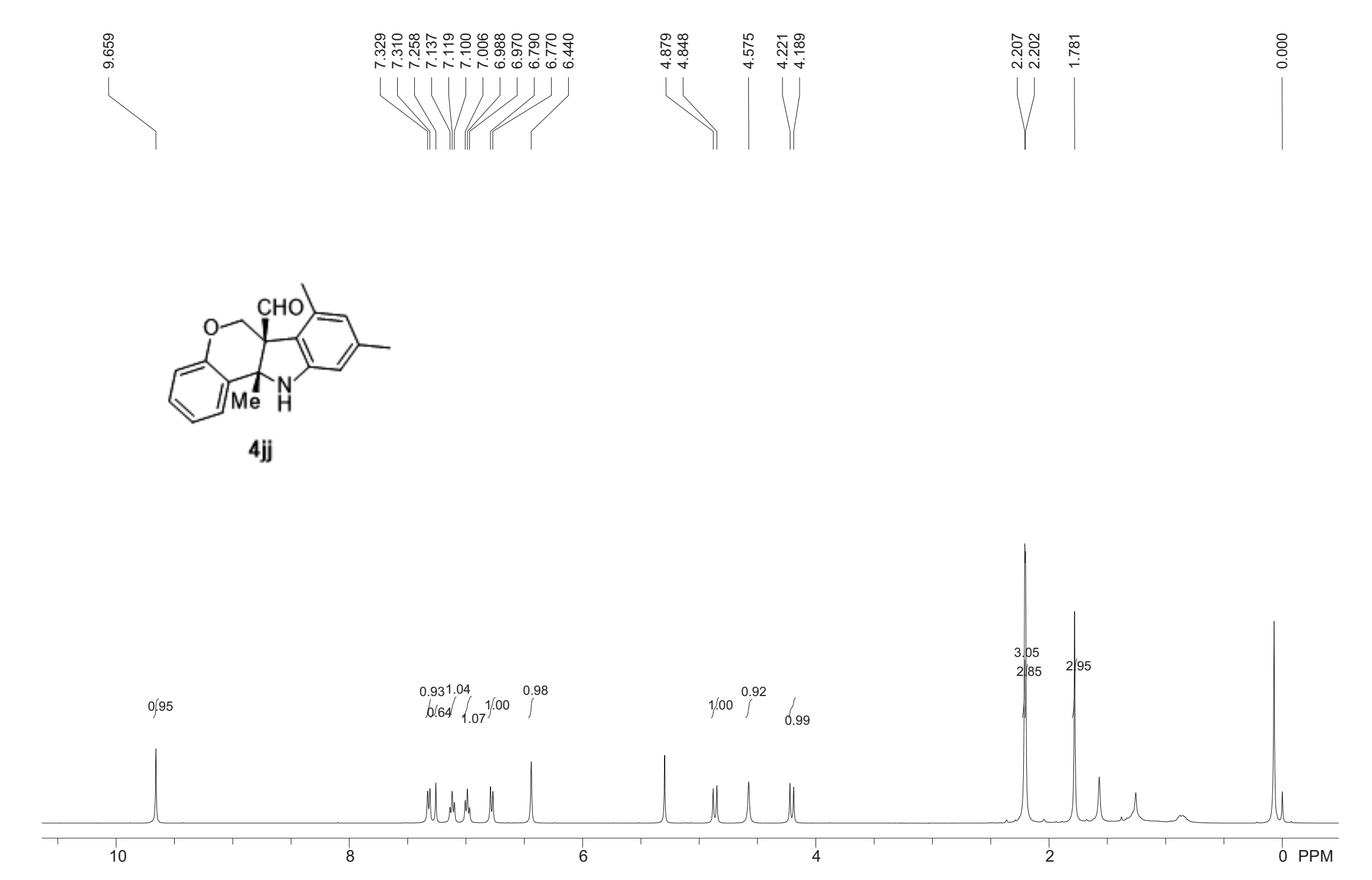
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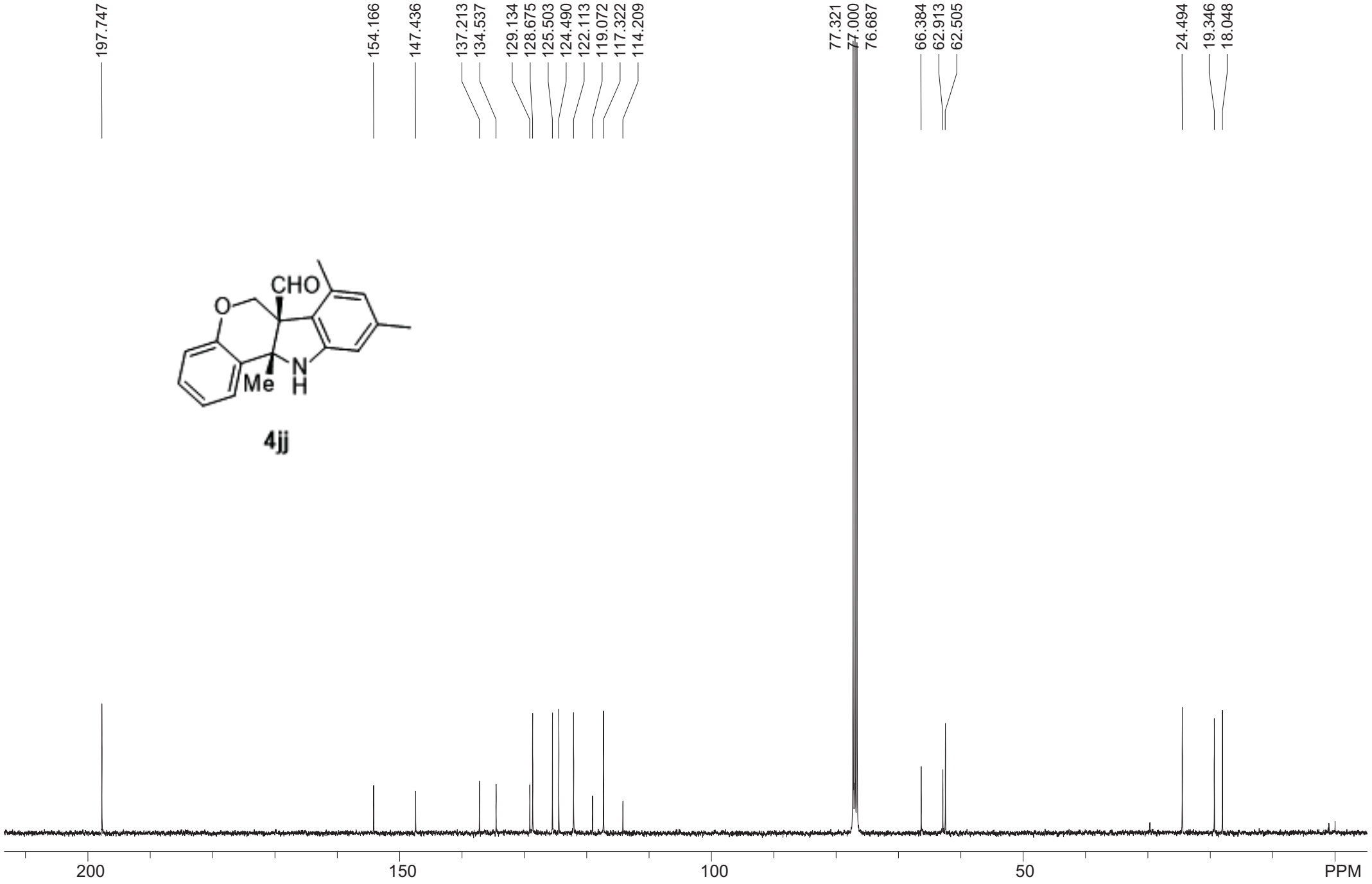
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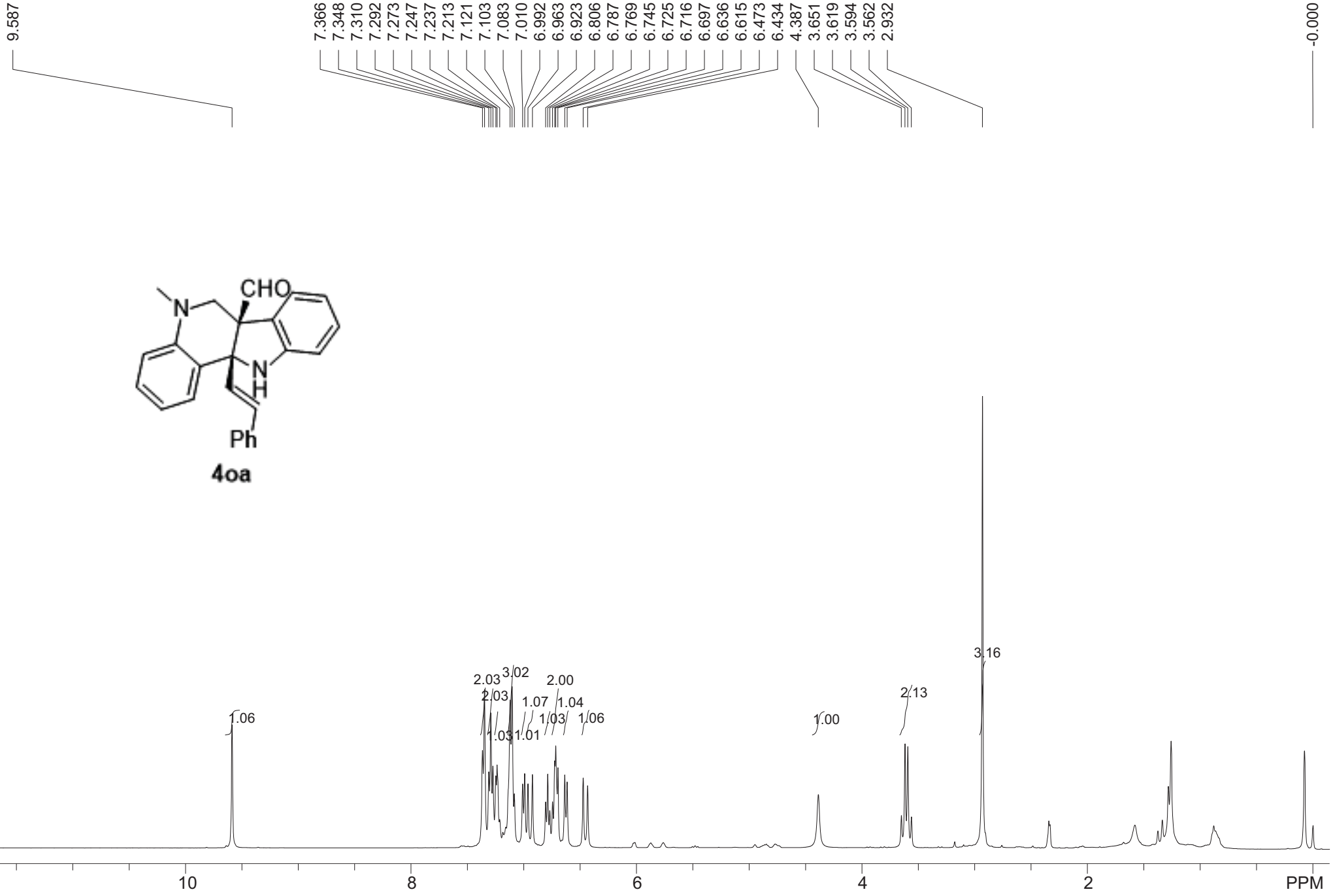
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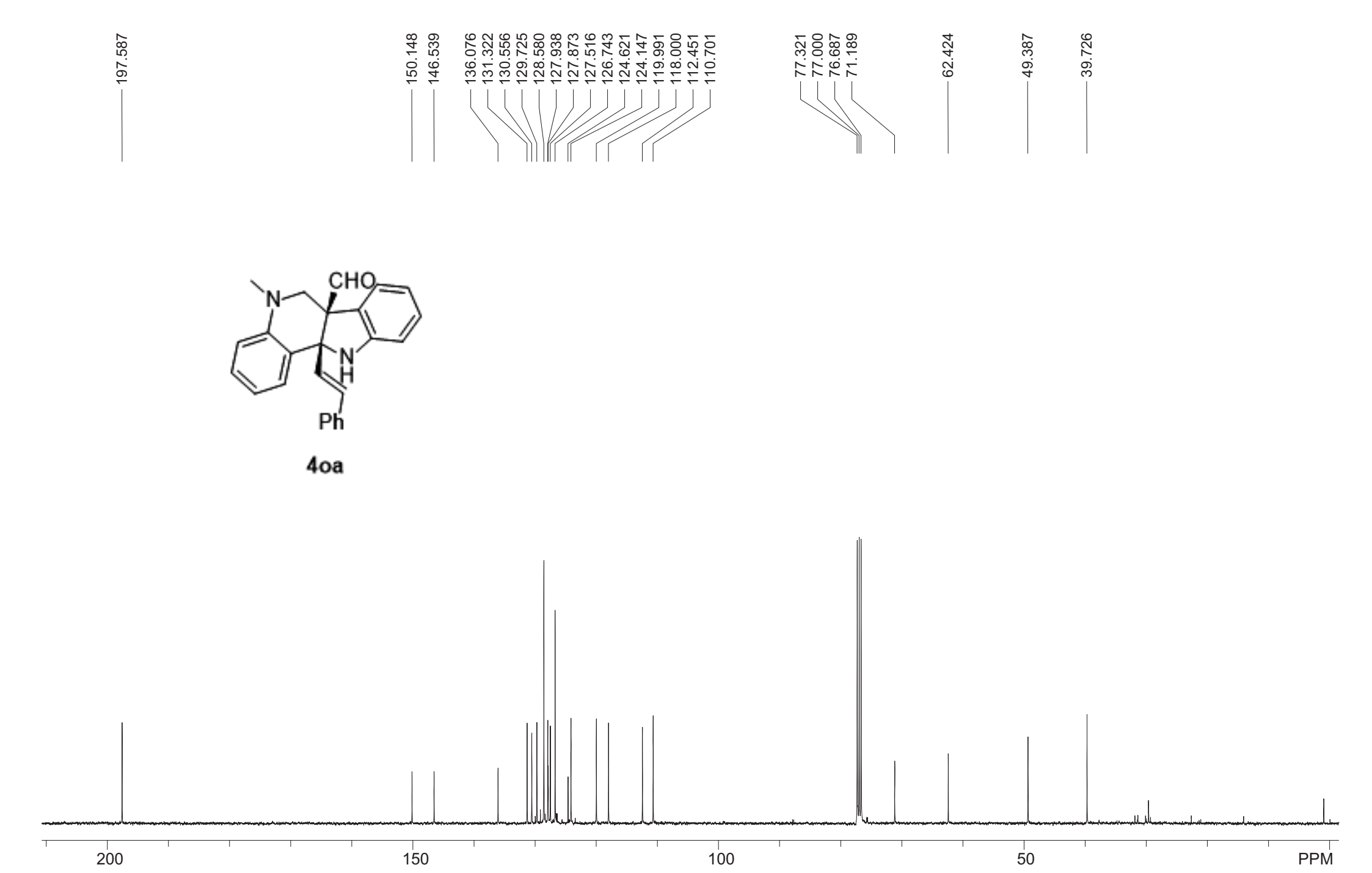
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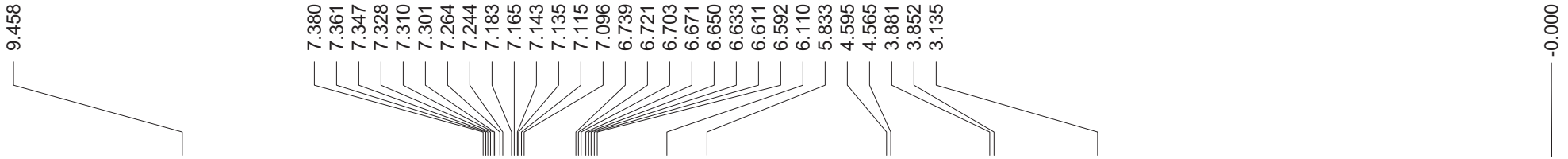
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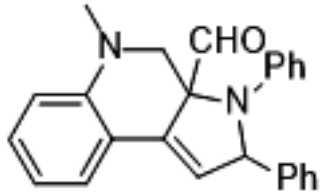
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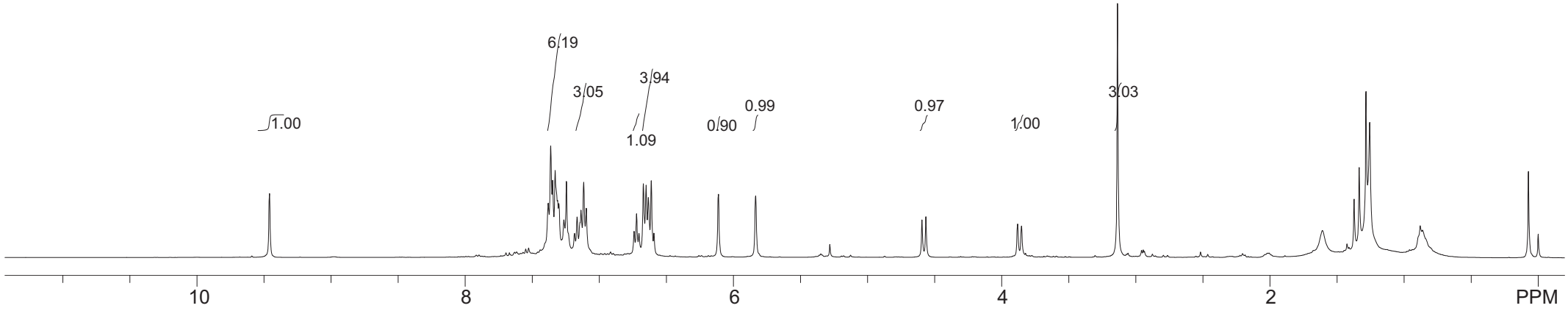
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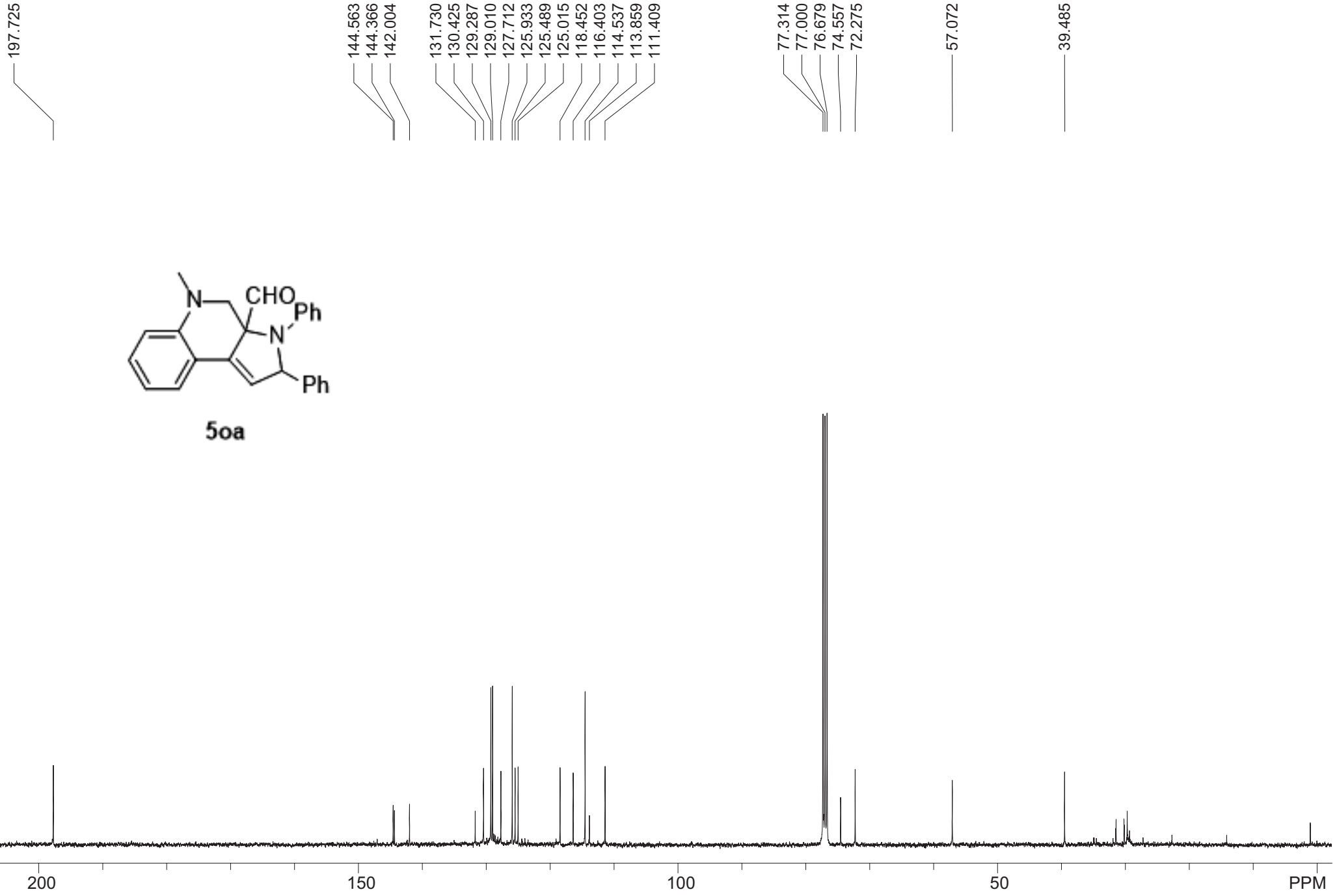
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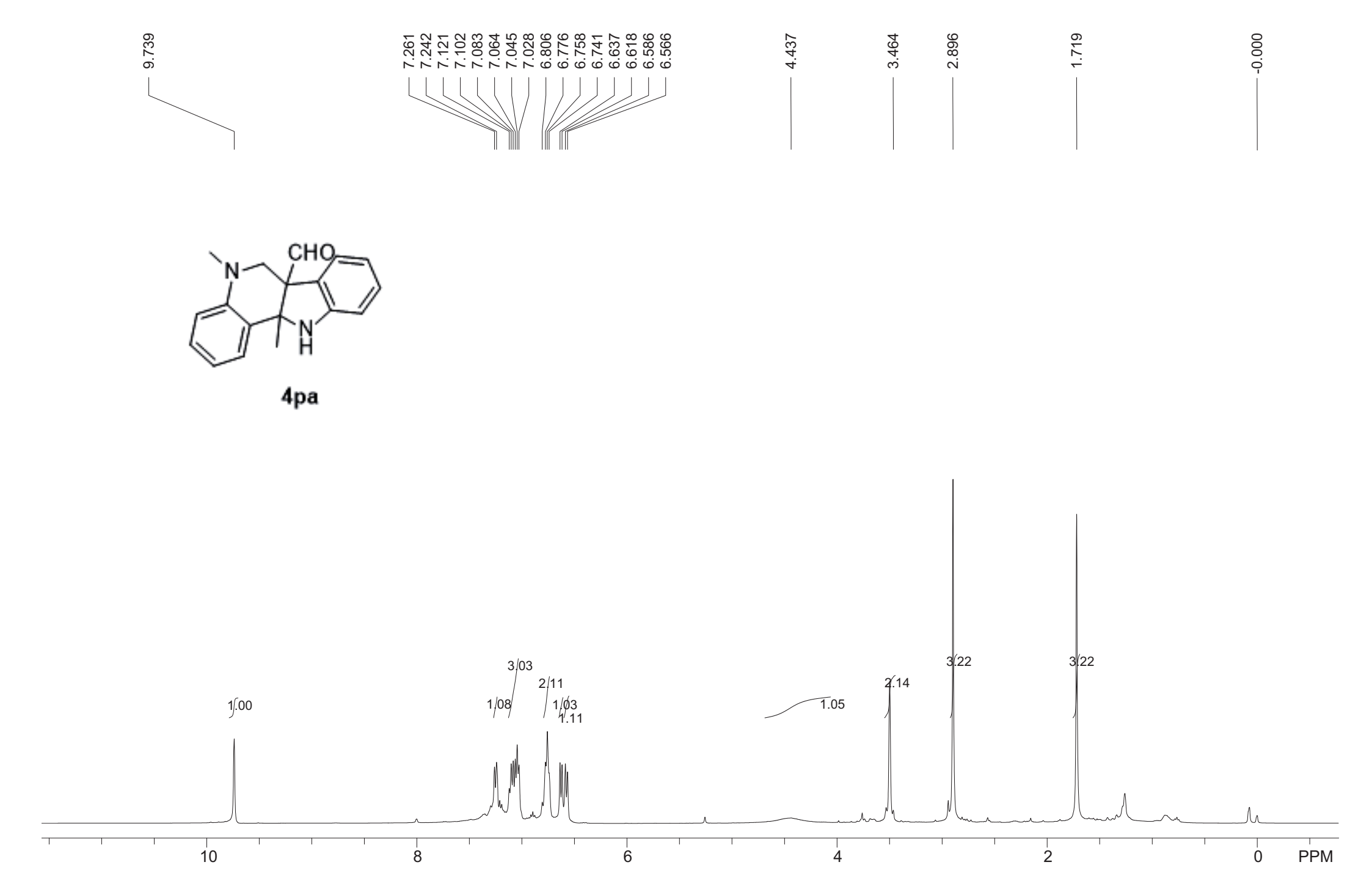
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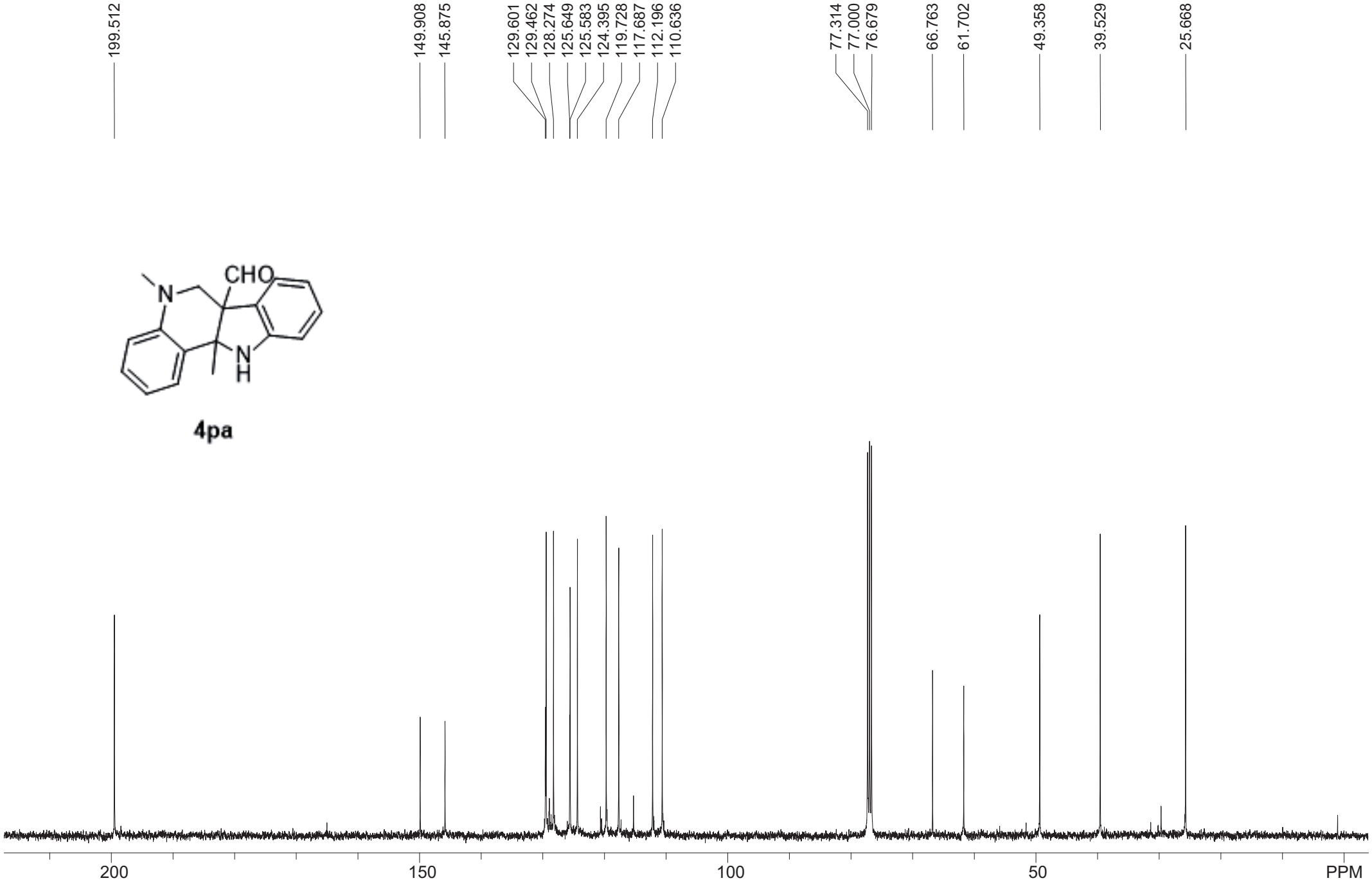
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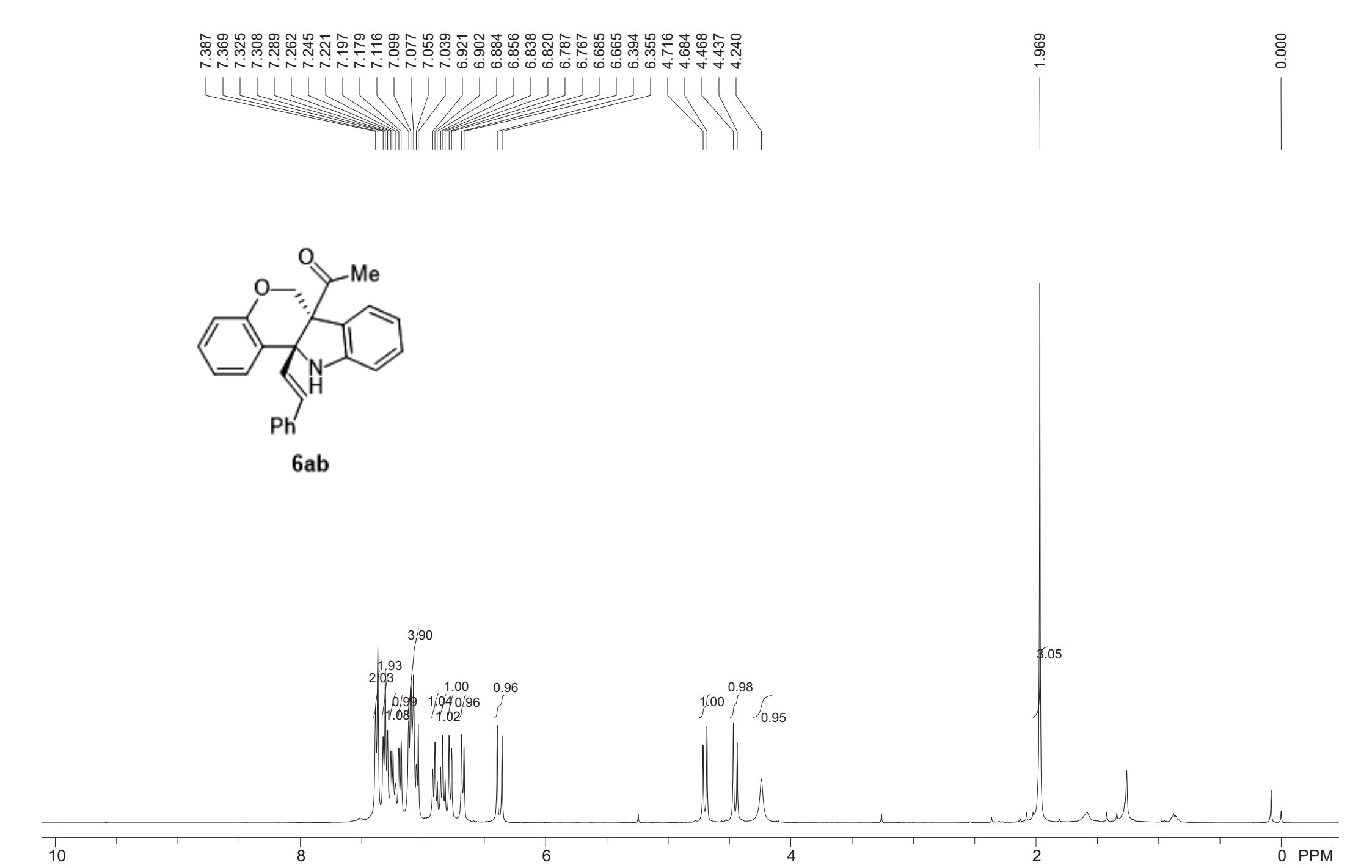
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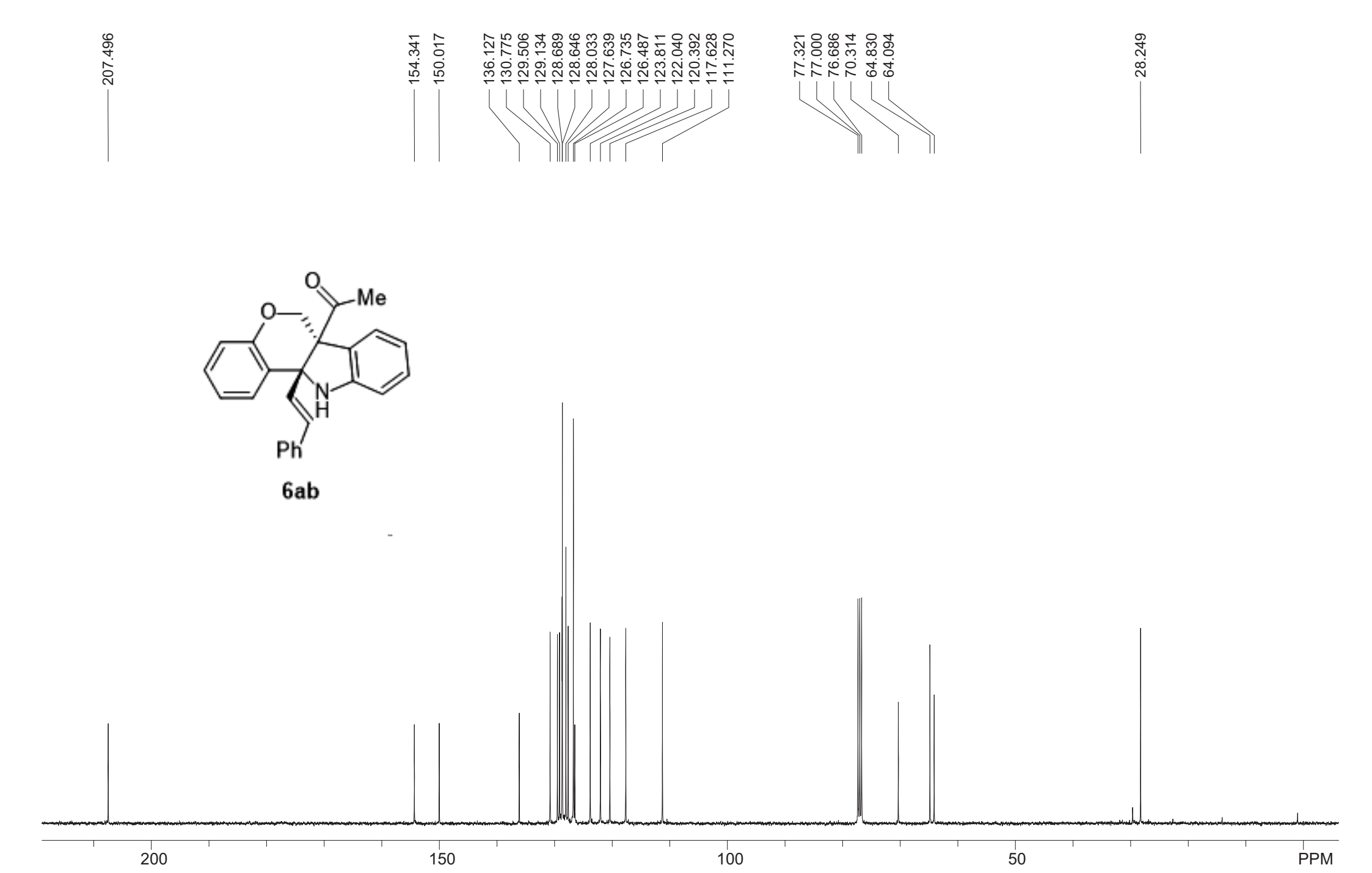
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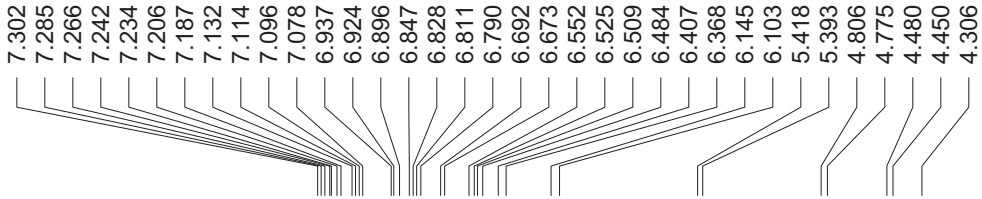
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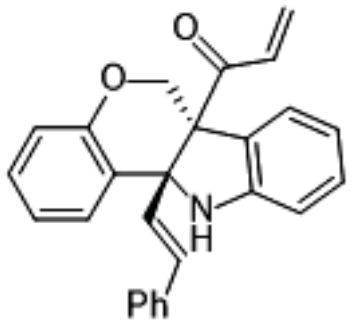
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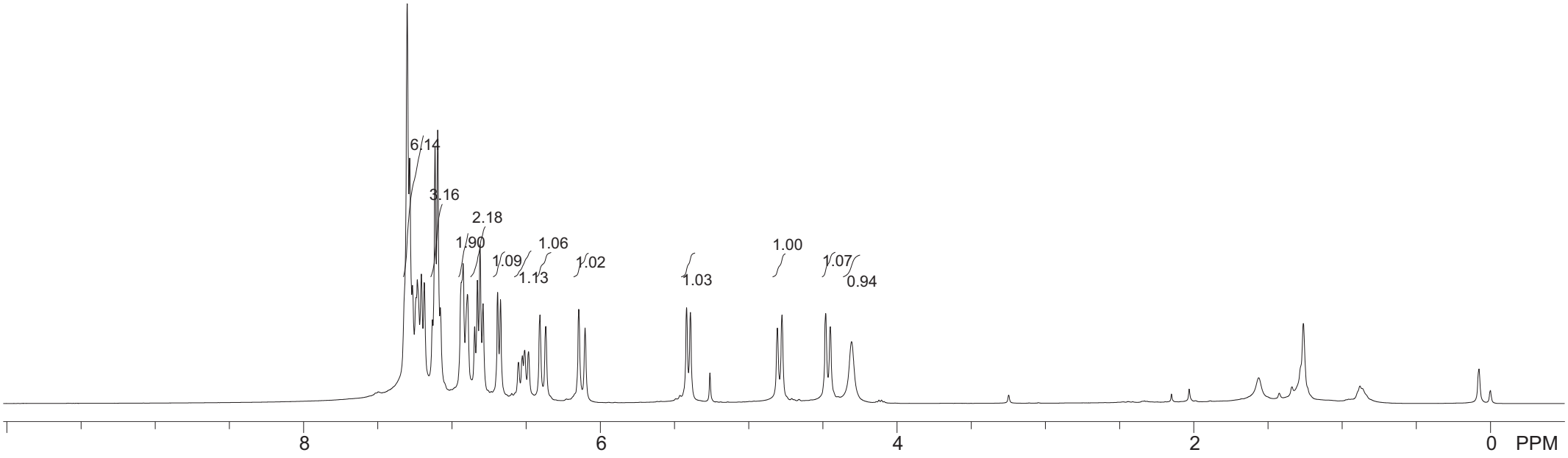
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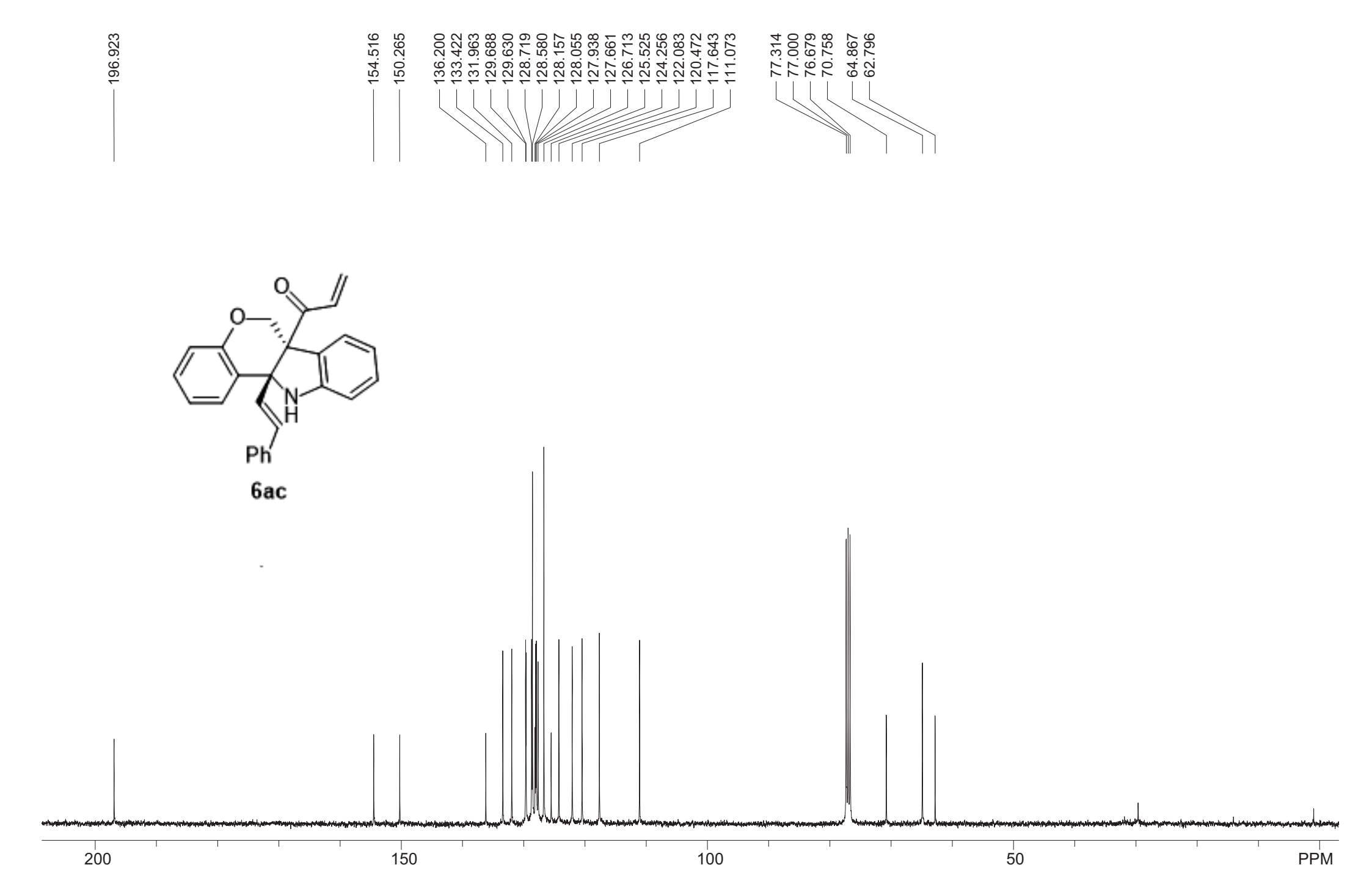
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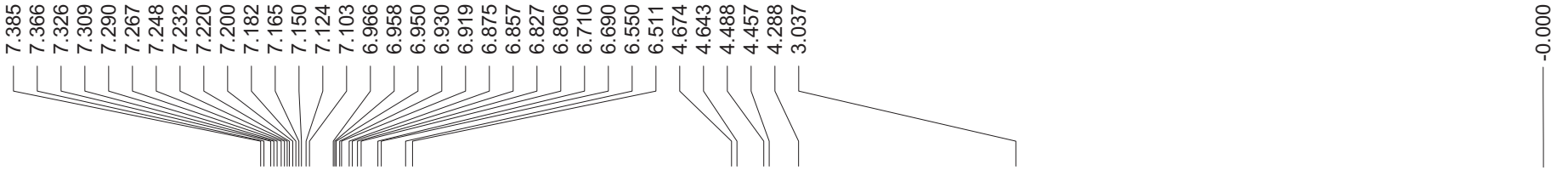
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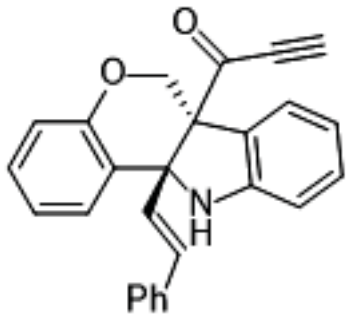
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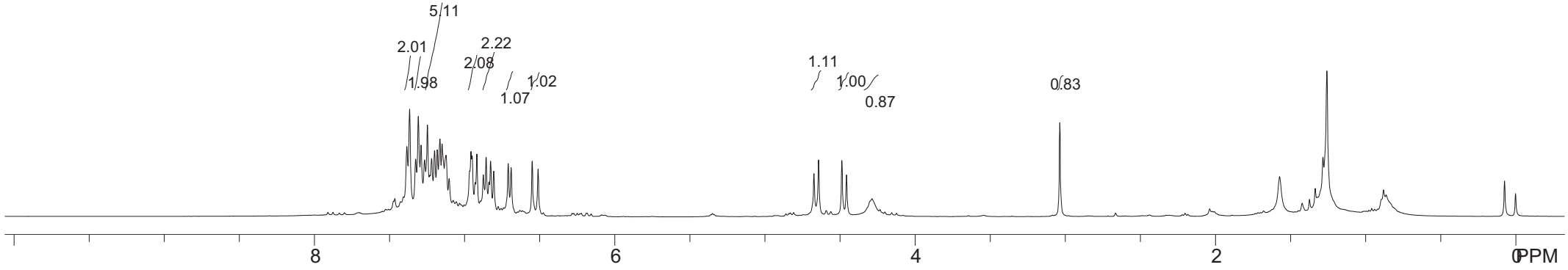
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1.02
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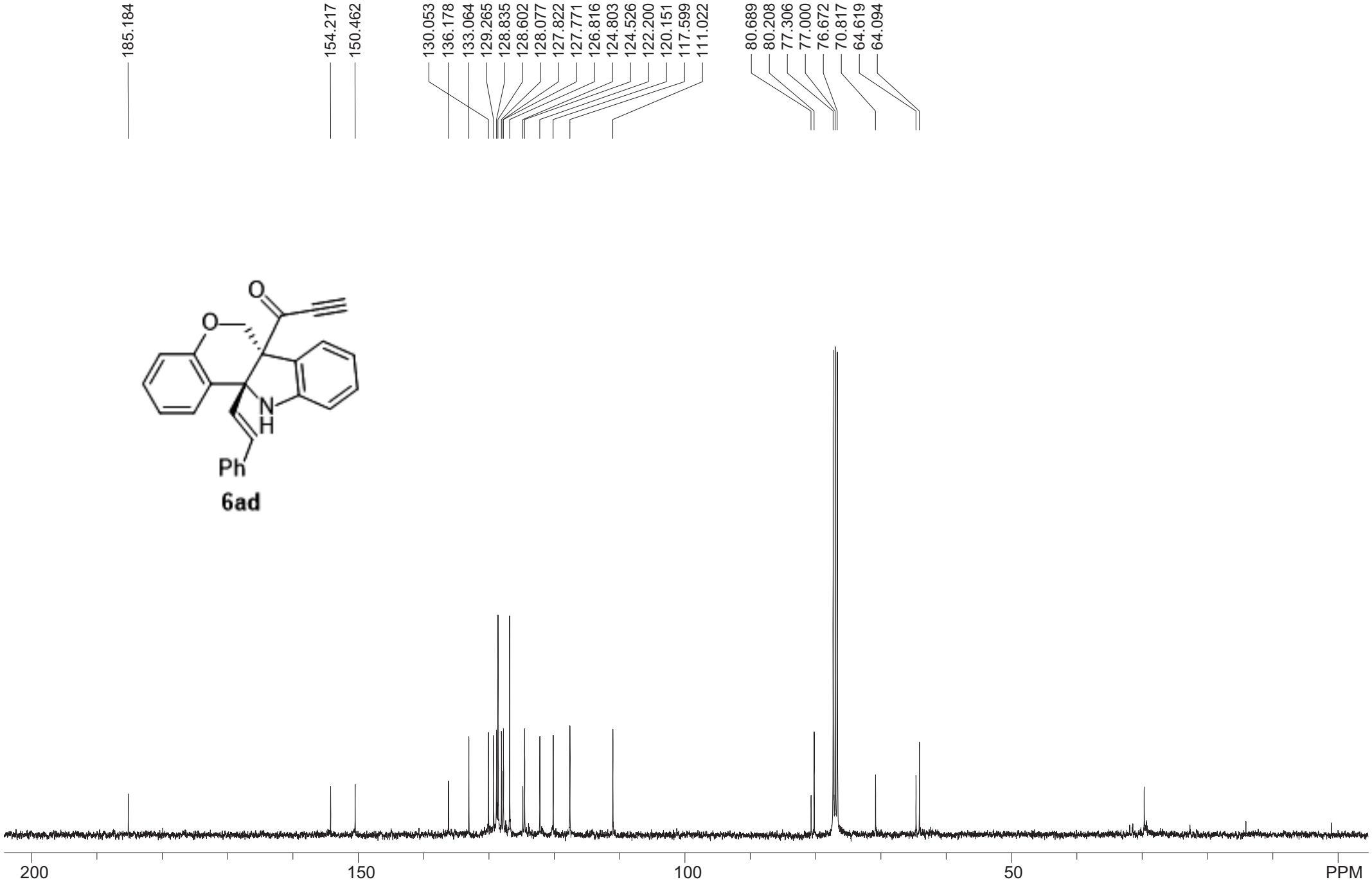
PPM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128.077
127.822
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126.816
124.803
124.526
122.200
120.151
117.599
111.022
80.689
80.208
77.306
77.000
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64.094
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O
N
H
Ph
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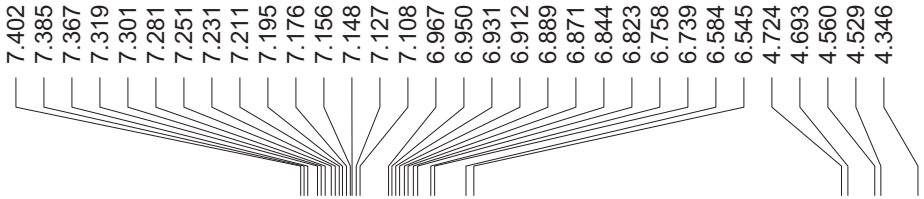
150
100
50
PPM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7.367
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7.251
7.231
7.211
7.195
7.176
7.156
7.148
7.127
7.108
6.967
6.950
6.931
6.912
6.889
6.871
6.844
6.823
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6.739
6.584
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4.693
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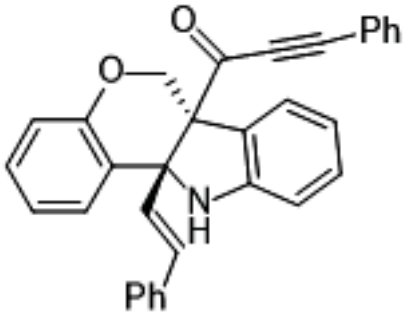
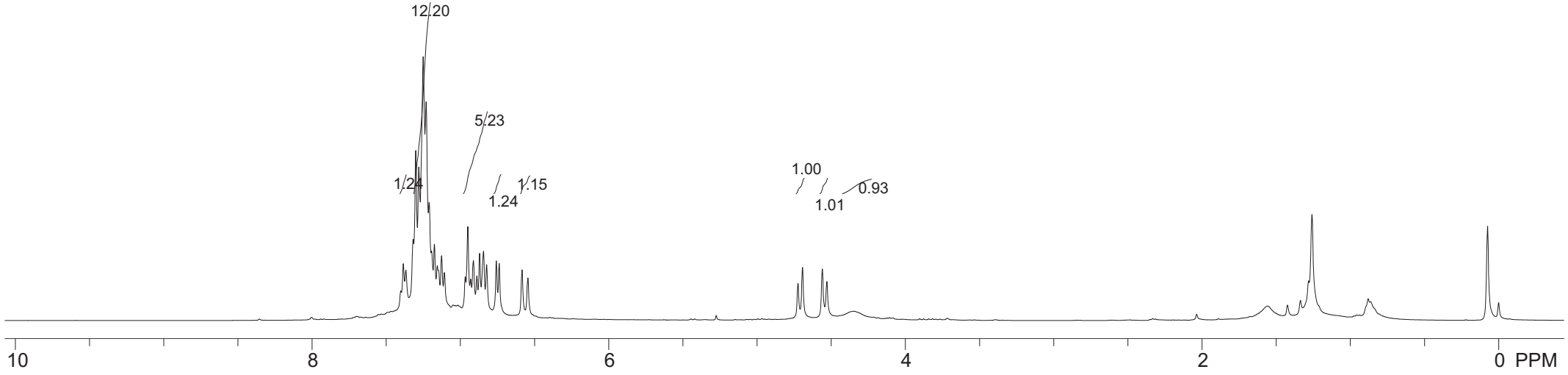

O
Ph
O
N
H
Ph

6ae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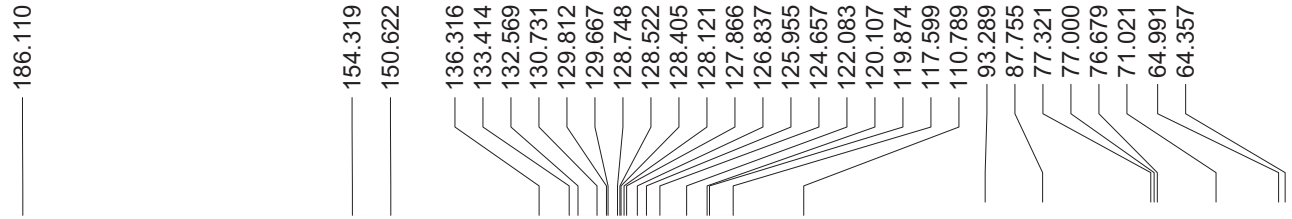
1.24
1.24
1.15
1.00
1.01
0.93
10
8
6
4
2
0 PPM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136.316
133.414
132.569
130.731
129.812
129.667
128.748
128.522
128.405
128.121
127.866
126.837
125.955
124.657
122.083
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87.755
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77.000
76.679
71.021
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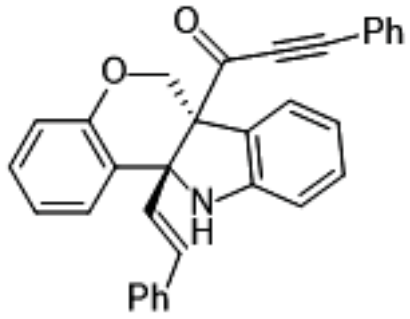
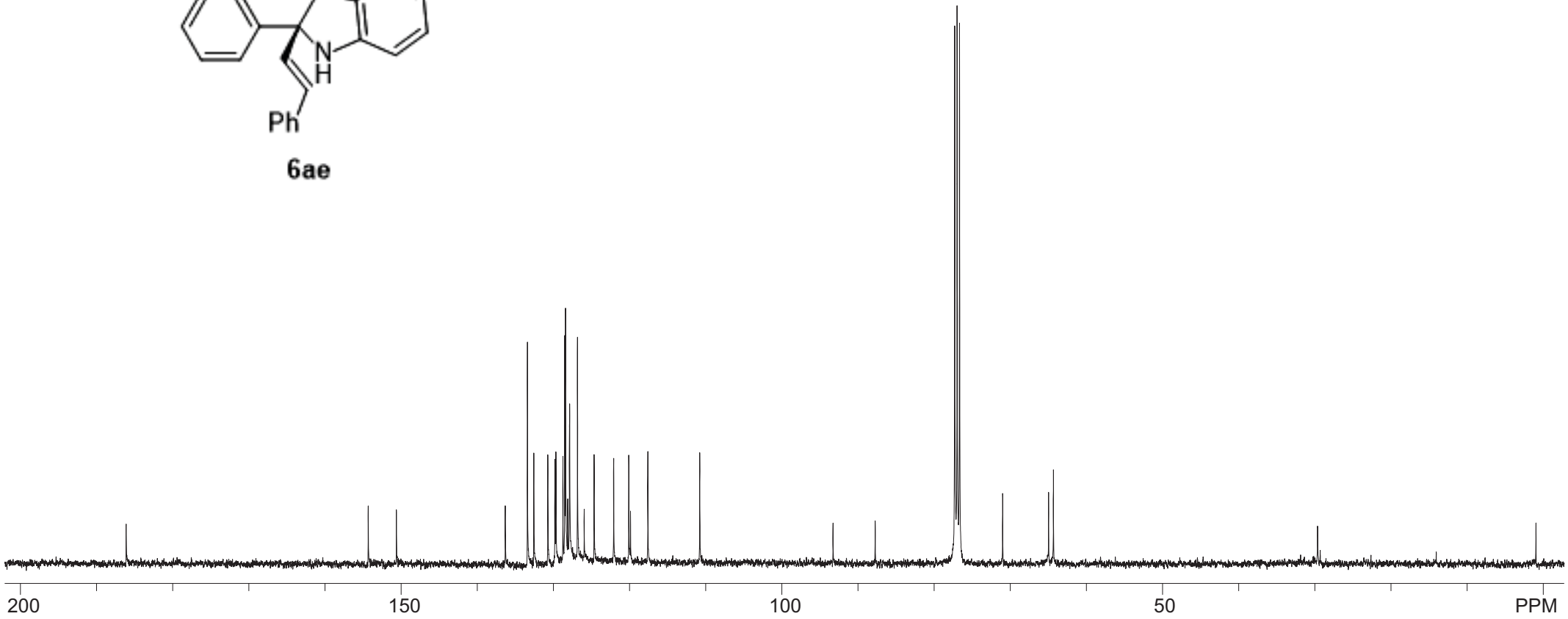
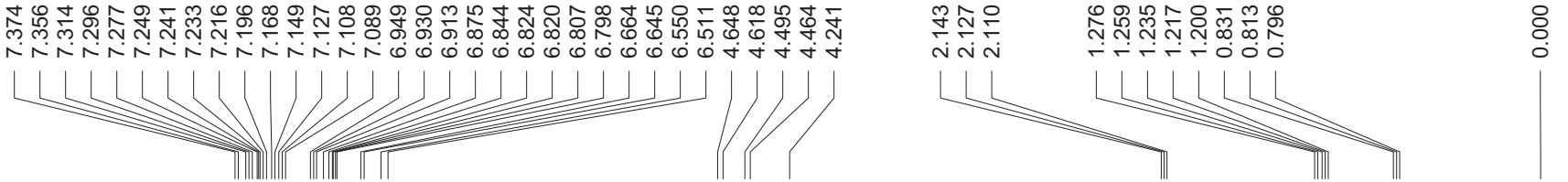
64.357


O
Ph
O
N
H
Ph

6ae


200
150
100
50
PPM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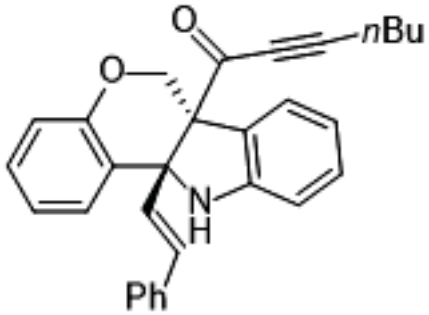
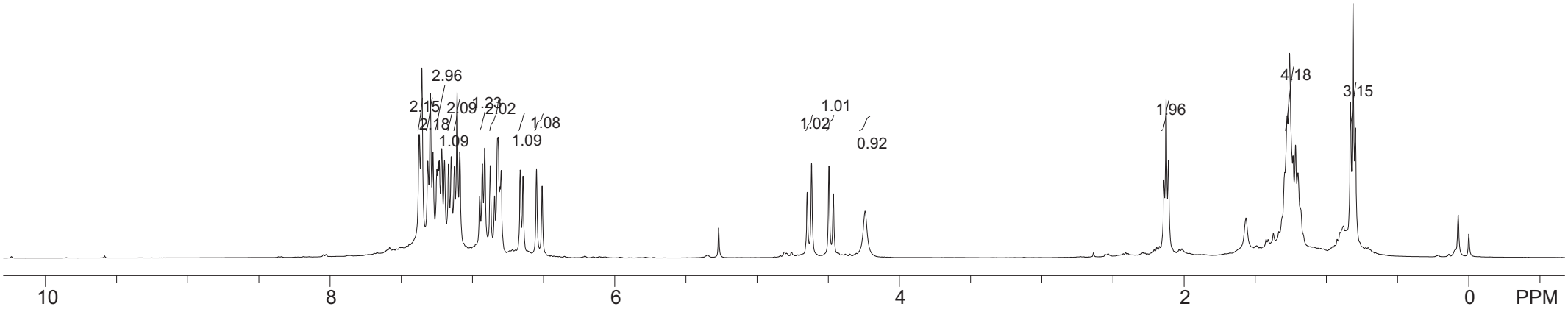
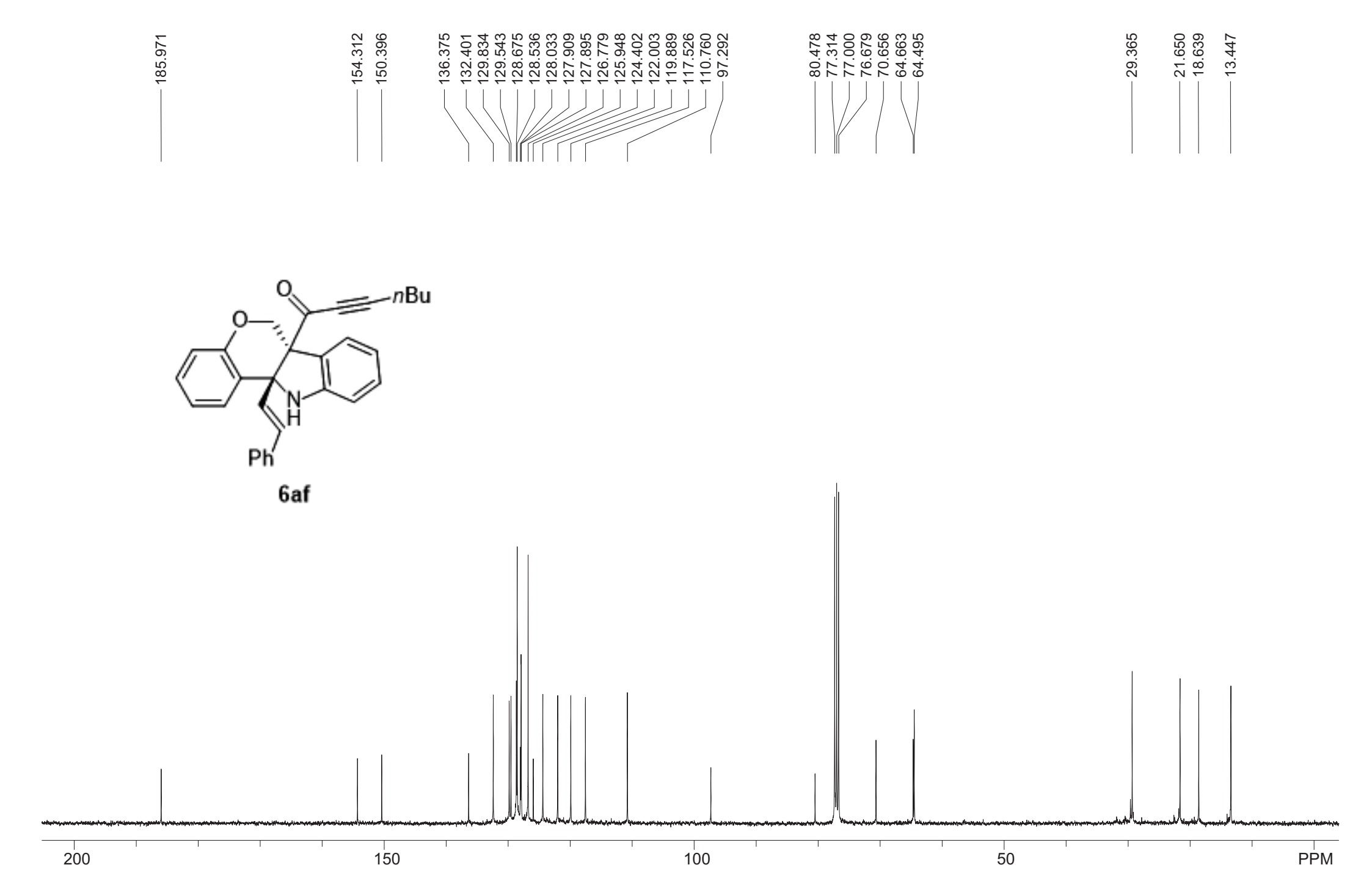
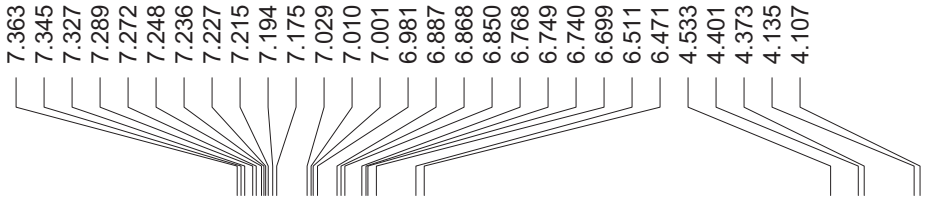
7.314
7.296
7.277
7.249
7.241
7.233
7.216
7.196
7.168
7.149
7.127
7.108
7.089
6.949
6.930
6.913
6.875
6.844
6.824
6.820
6.807
6.798
6.664
6.645
6.550
6.511
4.648
4.618
4.495
4.464
4.241
2.143
2.127
2.110
1.276
1.259
1.235
1.217
1.200
0.831
0.813
0.796
0.000


O
nBu
O
N
H
Ph

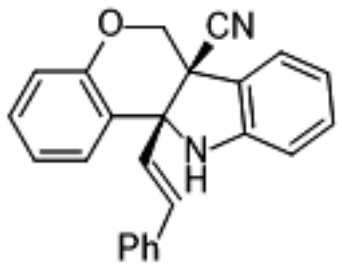
6af


2.96
2.15
2.09
1.23
2.18
2.02
1.08
1.09
1.09
1.01
1.02
0.92
1.96
4.18
3.15
10
8
6
4
2
0
PPM

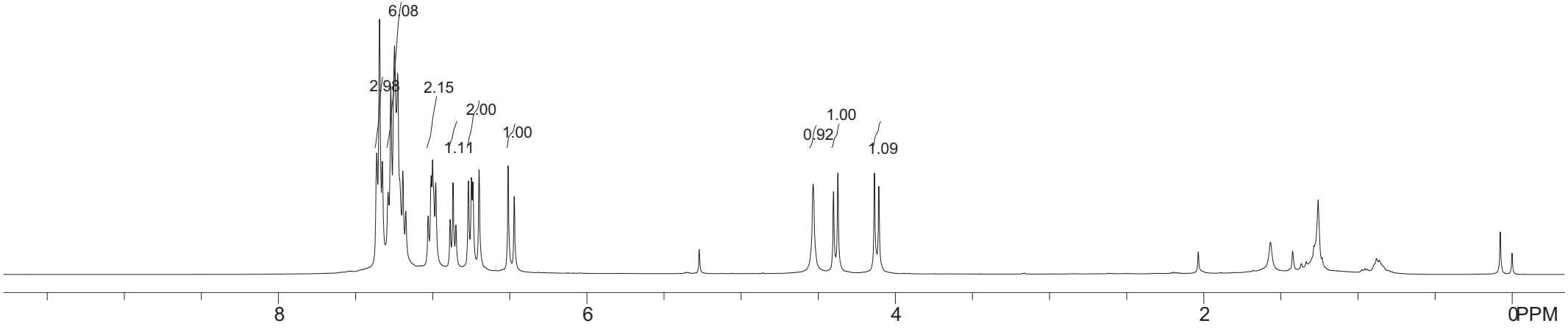

185.971
154.312
150.396
136.375
132.401
129.834
129.543
128.675
128.536
128.033
127.909
127.895
126.779
125.948
124.402
122.003
119.889
117.526
110.760
97.292
80.478
77.314
77.000
76.679
70.656
64.663
64.495
29.365
21.650
18.639
13.447
O
nBu
O
N
H
Ph
6af
200
150
100
50
PPM

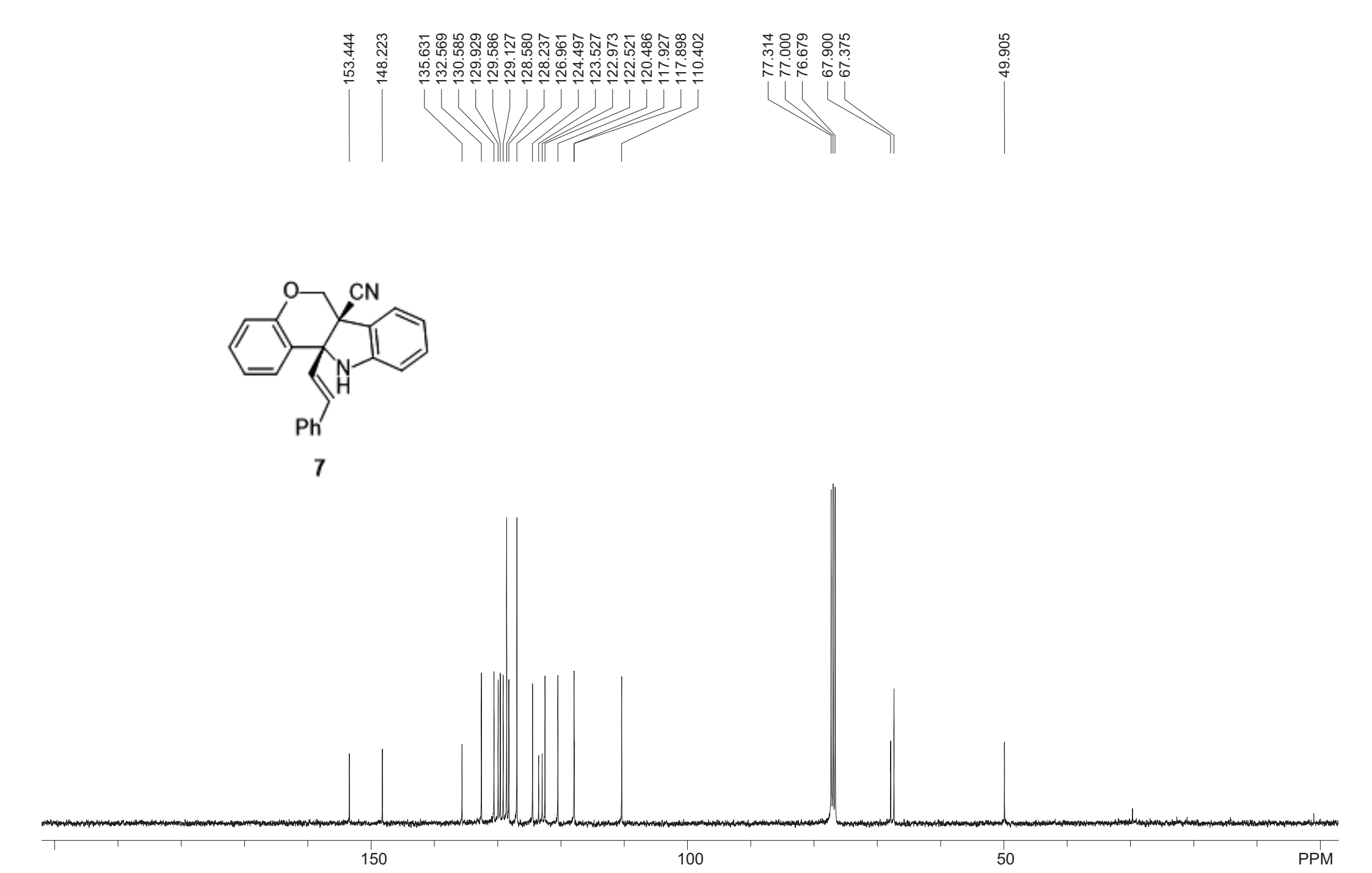

7.363
7.345
7.327
7.289
7.272
7.248
7.236
7.227
7.215
7.194
7.175
7.029
7.010
7.001
6.981
6.887
6.868
6.850
6.768
6.749
6.740
6.699
6.511
6.471
4.533
4.401
4.373
4.135
4.107


-0.000


O
CN
N
H
Ph

7


6.08
2.98
2.15
2.00
1.11
1.00
1.00
0.92
1.09
8
6
4
2
0
PPM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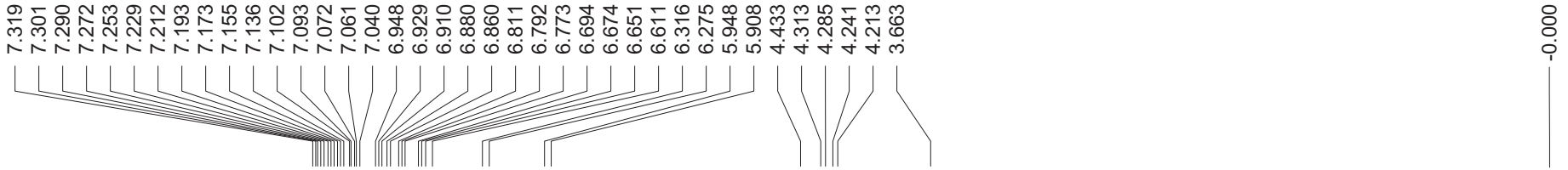
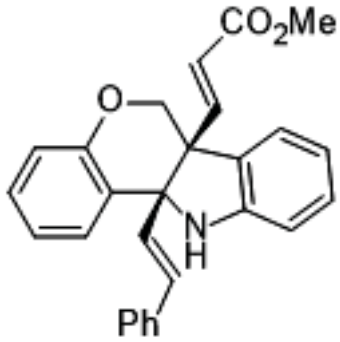
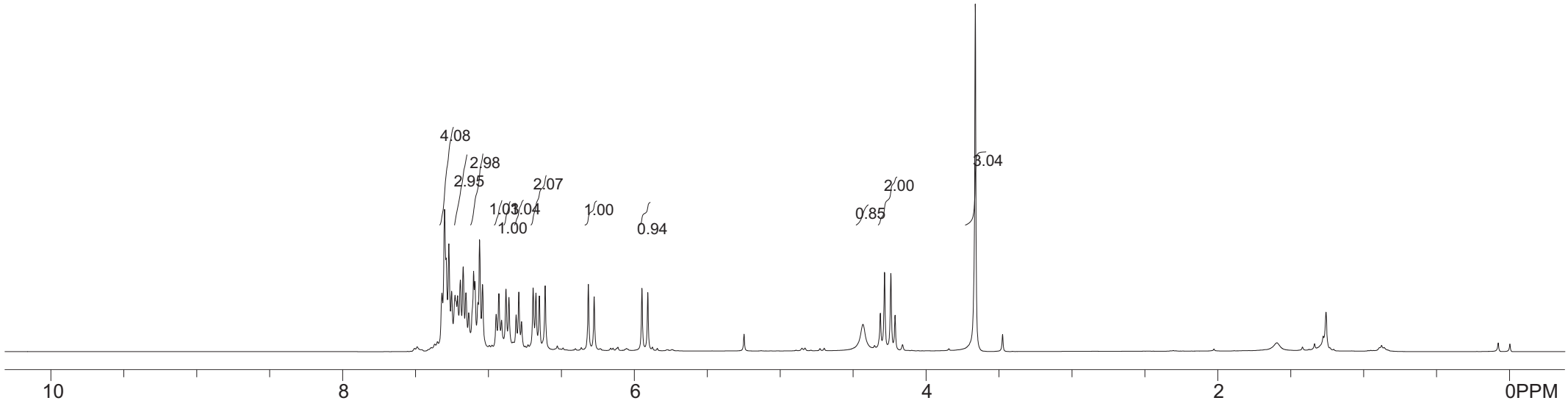
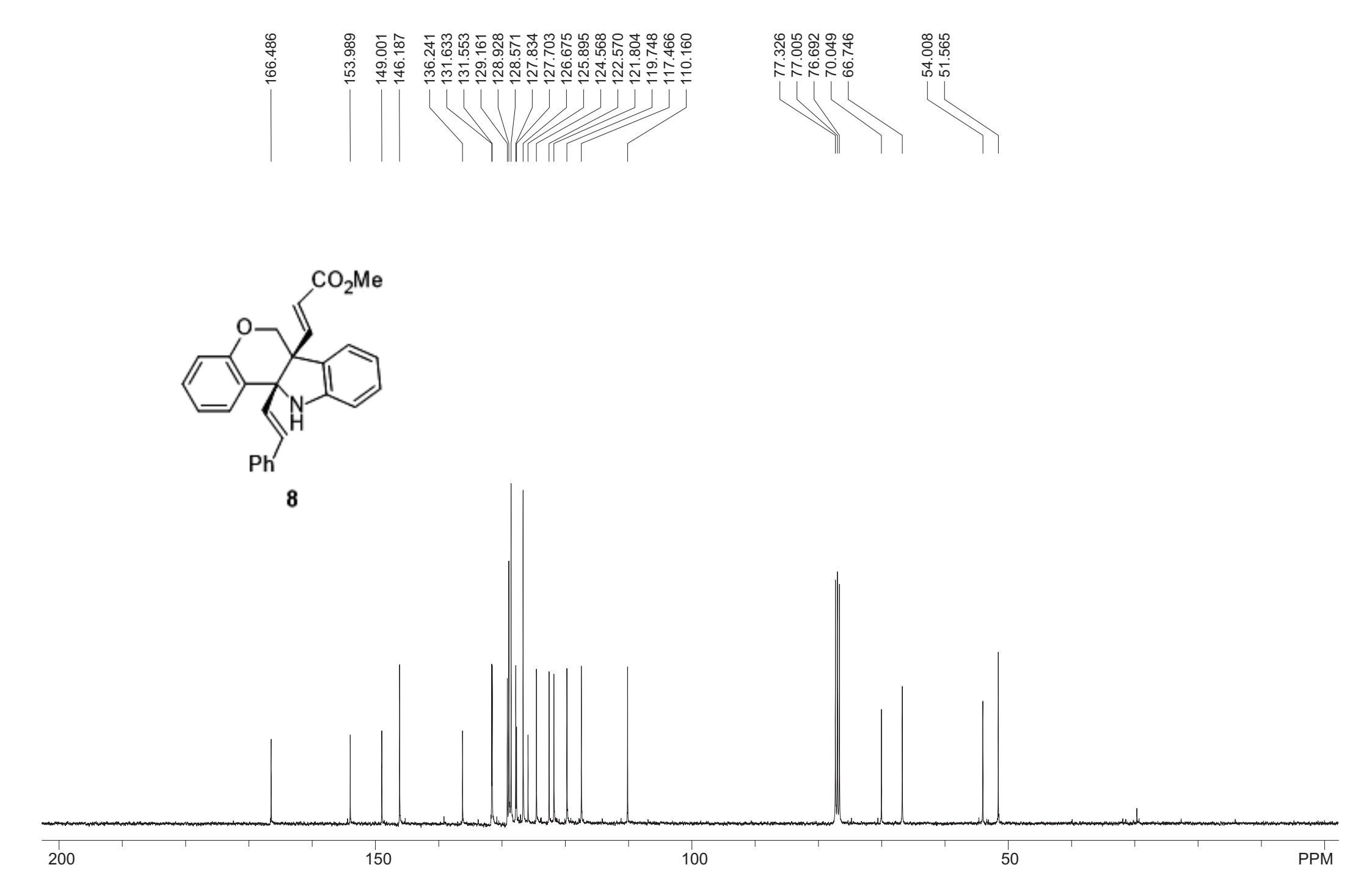
148.223
135.631
132.569
130.585
129.929
129.586
129.127
128.580
128.237
126.961
124.497
123.527
122.973
122.521
120.486
117.927
117.898
110.402
77.314
77.000
76.679
67.900
67.375
49.905
O
CN
N
H
Ph
7
150
100
50
PPM


7.319
7.301
7.290
7.272
7.253
7.229
7.212
7.193
7.173
7.155
7.136
7.102
7.093
7.072
7.061
7.040
6.948
6.929
6.910
6.880
6.860
6.811
6.792
6.773
6.694
6.674
6.651
6.611
6.316
6.275
5.948
5.908
4.433
4.313
4.285
4.241
4.213
3.663
-0.000


CO2Me
O
N
H
Ph

8


4.08
2.98
2.95
2.07
1.03
1.04
1.00
1.00
0.94
0.85
2.00
3.04
10
8
6
4
2
0PPM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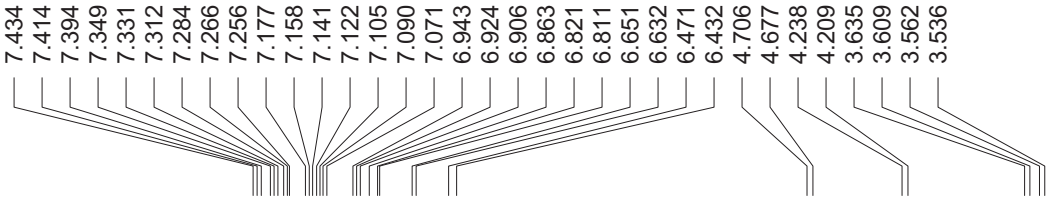
153.989
149.001
146.187
136.241
131.633
131.553
129.161
128.928
128.571
127.834
127.703
126.675
125.895
124.568
122.570
121.804
119.748
117.466
110.160
77.326
77.005
76.692
70.049
66.746
54.008
51.565
CO2Me
O
N
H
Ph
8
200
150
100
50
PPM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7.394
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7.331
7.312
7.284
7.266
7.256
7.177
7.158
7.141
7.122
7.105
7.090
7.071
6.943
6.924
6.906
6.863
6.821
6.811
6.651
6.632
6.471
6.432
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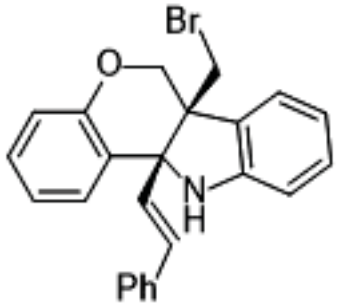
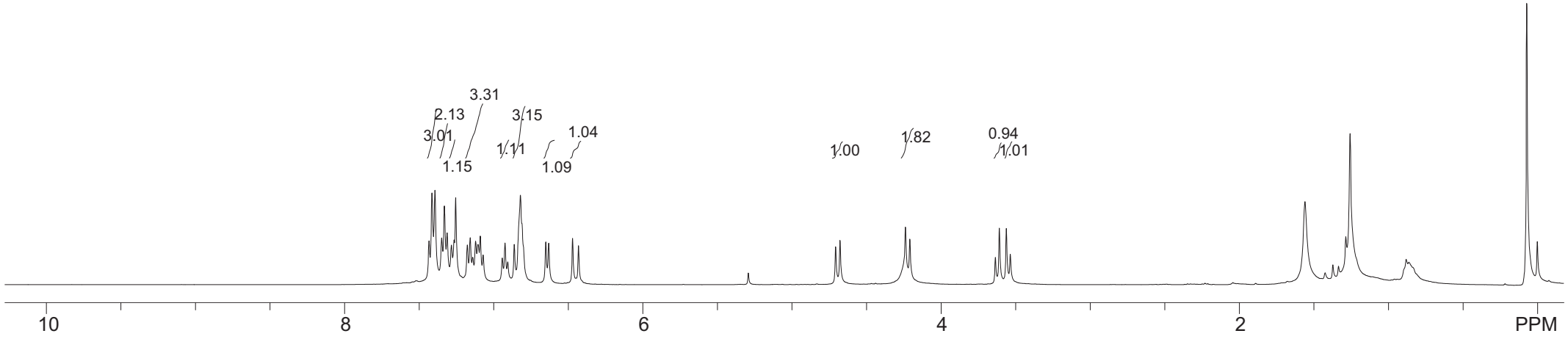
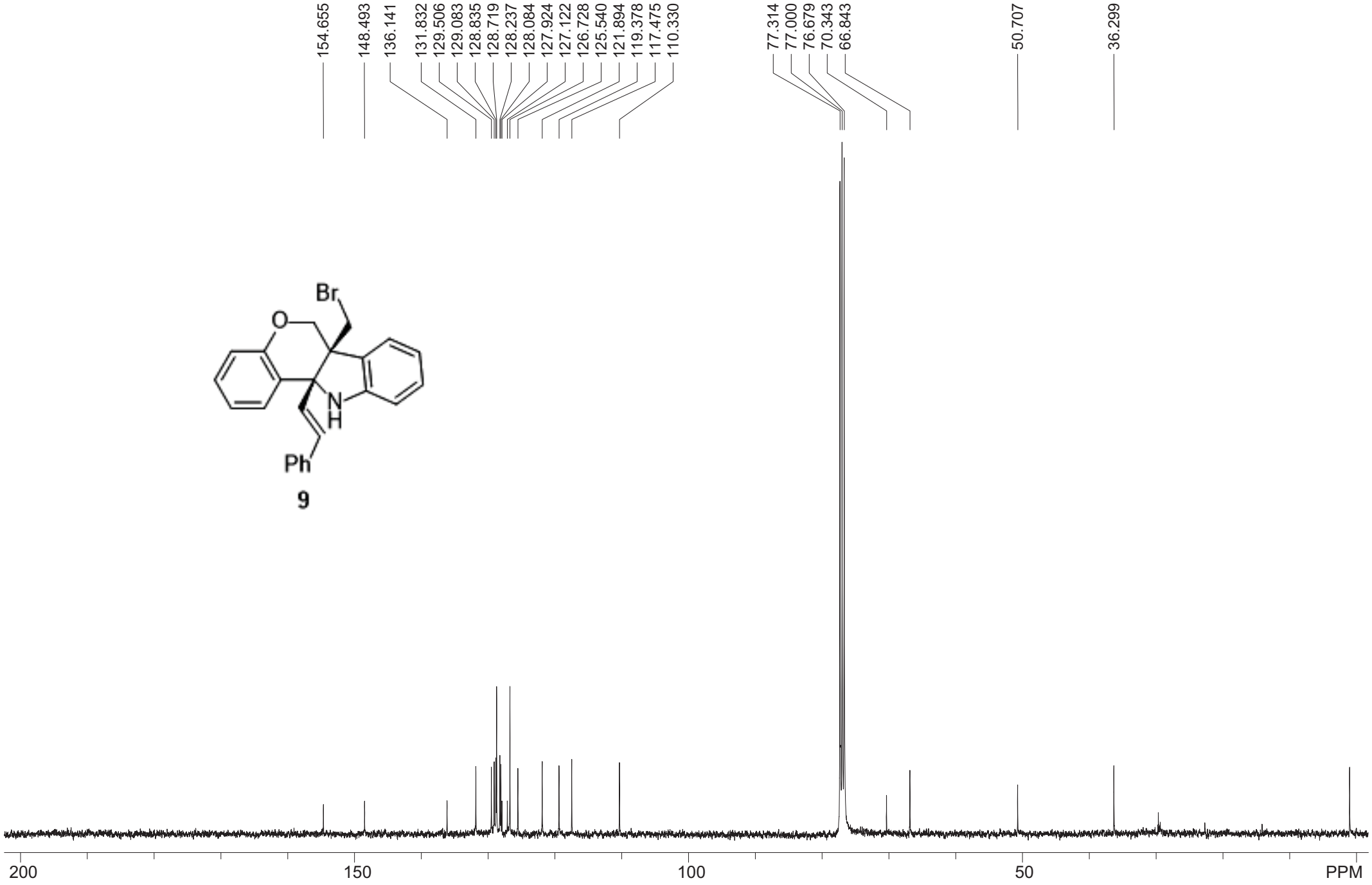
4.209
3.635
3.609
3.562
3.536
-0.000


Br
O
N
H
Ph

9


3.31
2.13
3.15
3.01
1.04
1.15
1.11
1.09
1.00
1.82
0.94
1.01
10
8
6
4
2
PPM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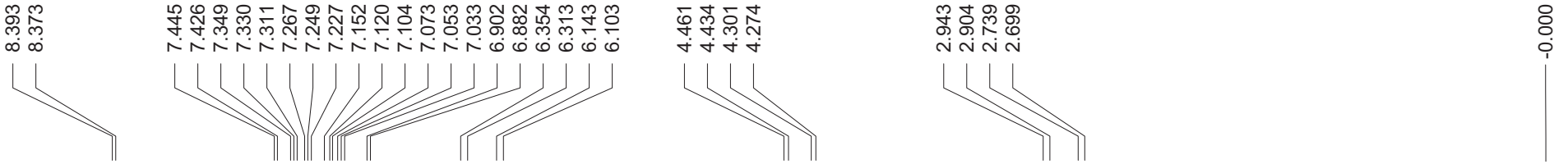
128.719
128.237
128.084
127.924
127.122
126.728
125.540
121.894
119.378
117.475
110.330
77.314
77.000
76.679
70.343
66.843
50.707
36.299
Br
O
N
H
Ph
9
200
150
100
50
PPM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8.373
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7.426
7.349
7.330
7.311
7.267
7.249
7.227
7.152
7.120
7.104
7.073
7.053
7.033
6.902
6.882
6.354
6.313
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6.103
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4.434
4.301
4.274
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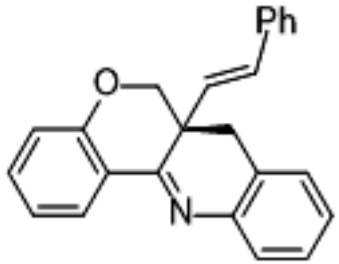
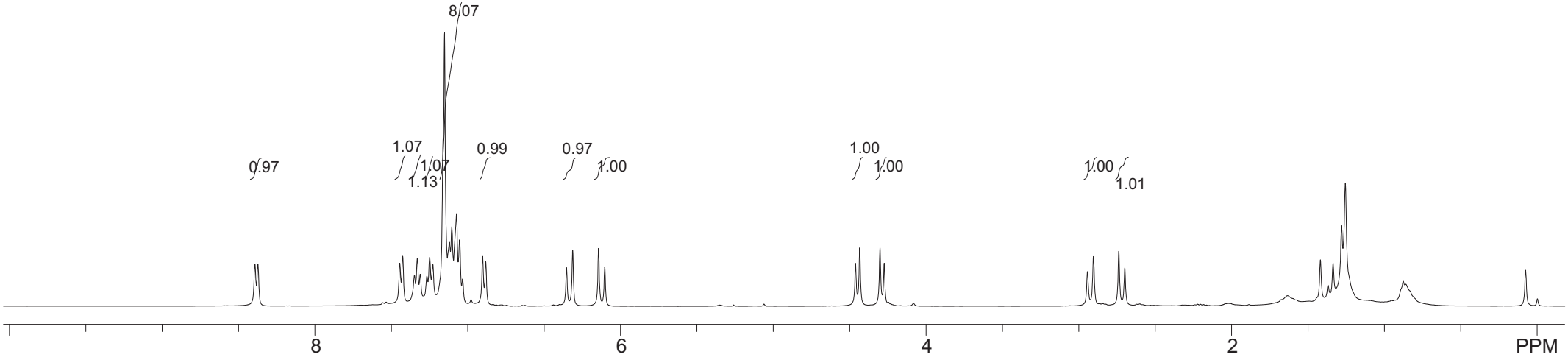
2.904
2.739
2.699
-0.000


Ph
O
N

10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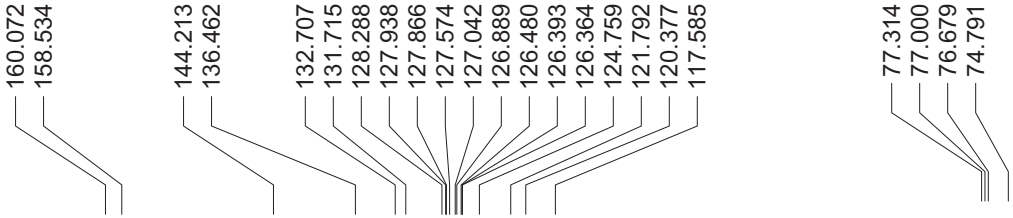
0.97
1.07
1.13
1.07
0.99
0.97
1.00
1.00
1.00
1.00
1.01
8
6
4
2
PPM


160.072
158.534
144.213
136.462
132.707
131.715
128.288
127.938
127.866
127.574
127.042
126.889
126.480
126.393
126.364
124.759
121.792
120.377
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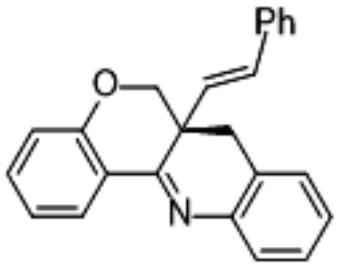
77.314
77.000
76.679
74.791
41.738
32.573


Ph
O
N

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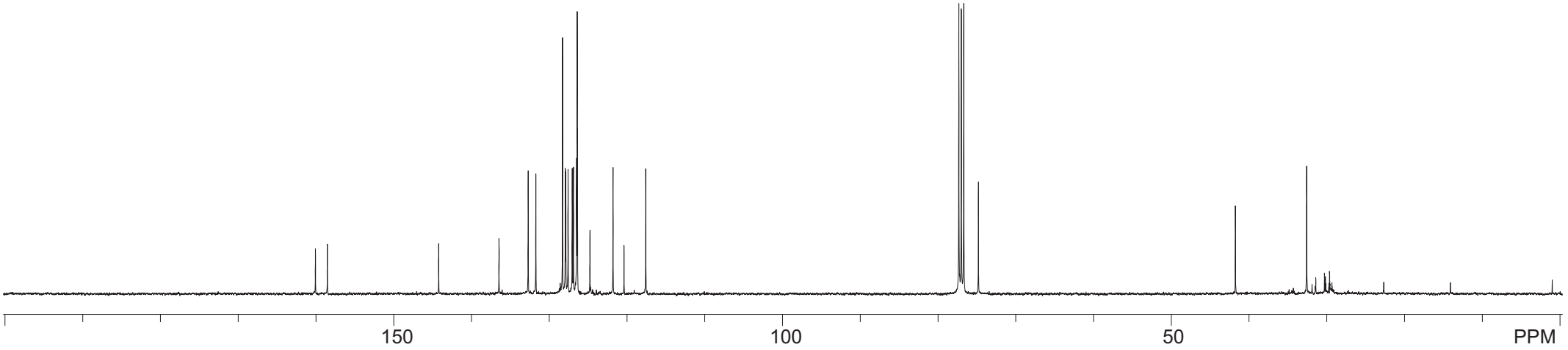
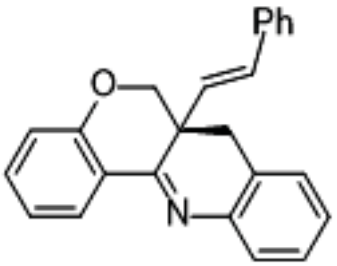
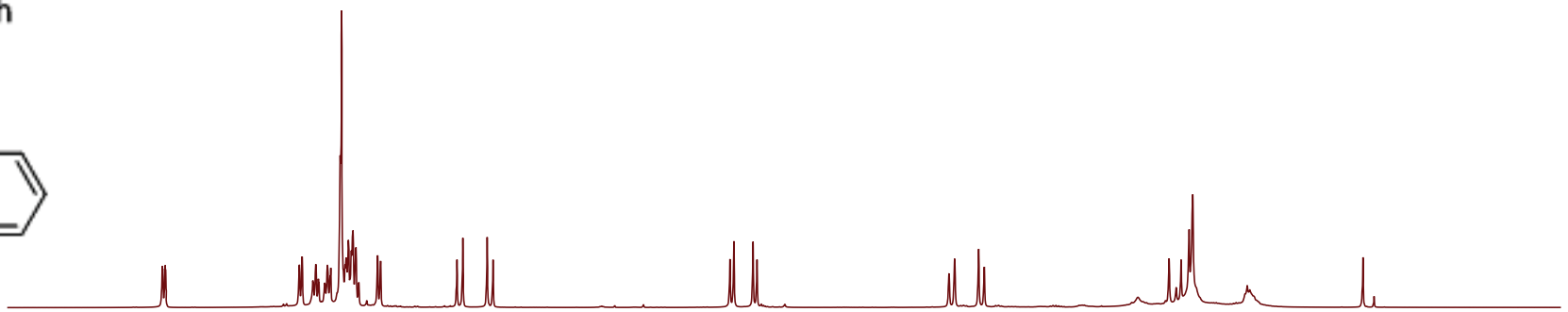
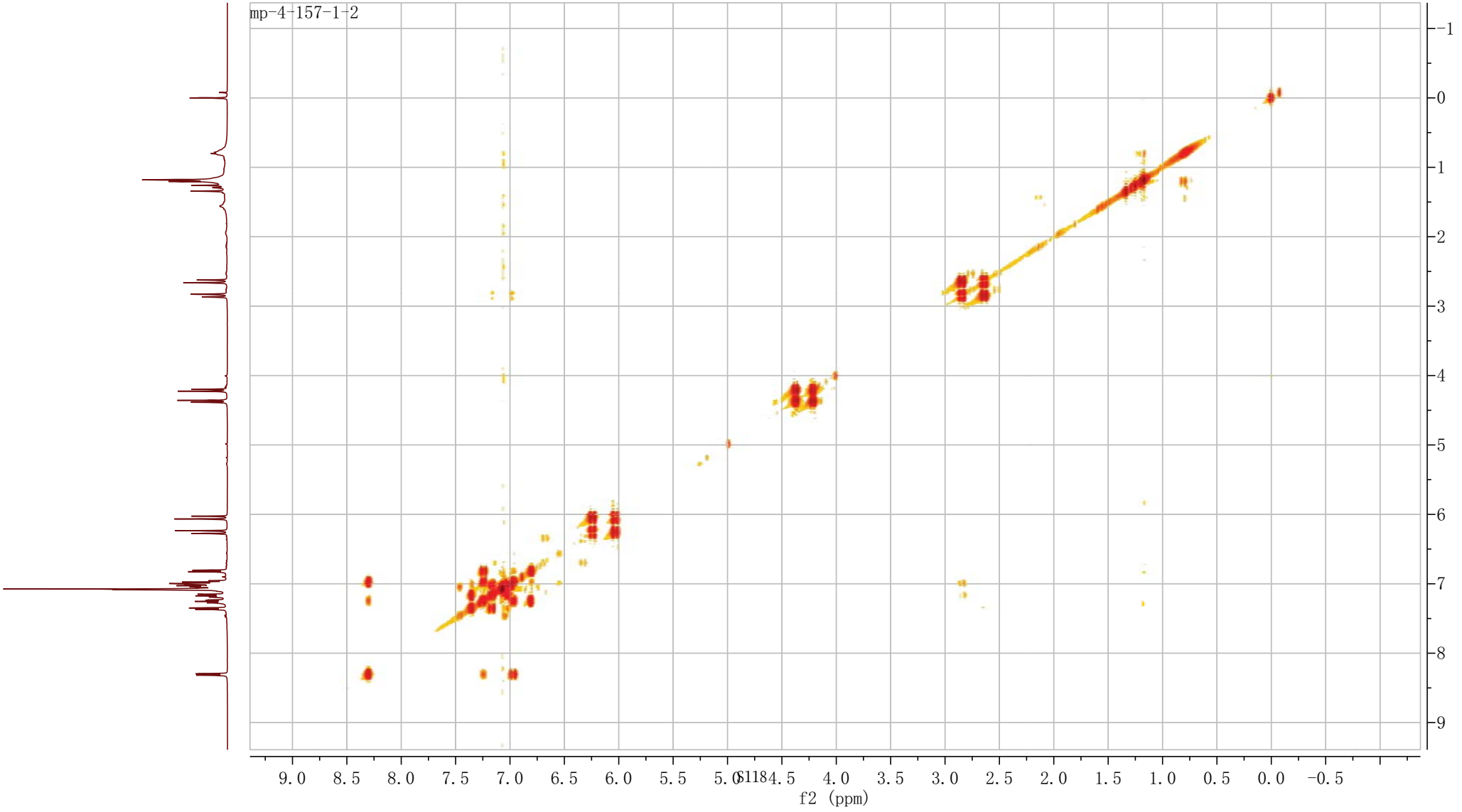

150
100
50
PPM


Ph
O
N

10 COSY




mp-4-157-1-2
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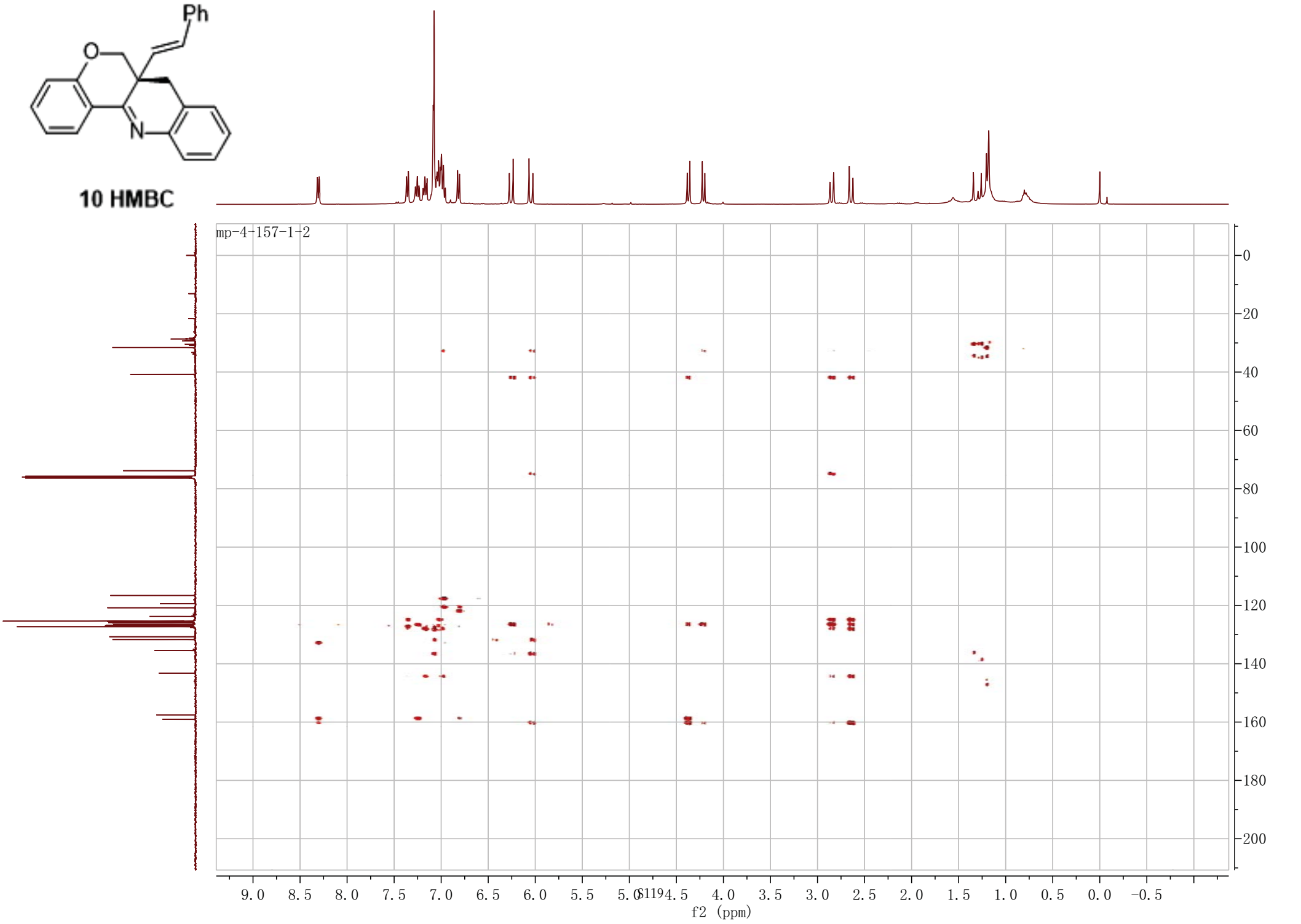
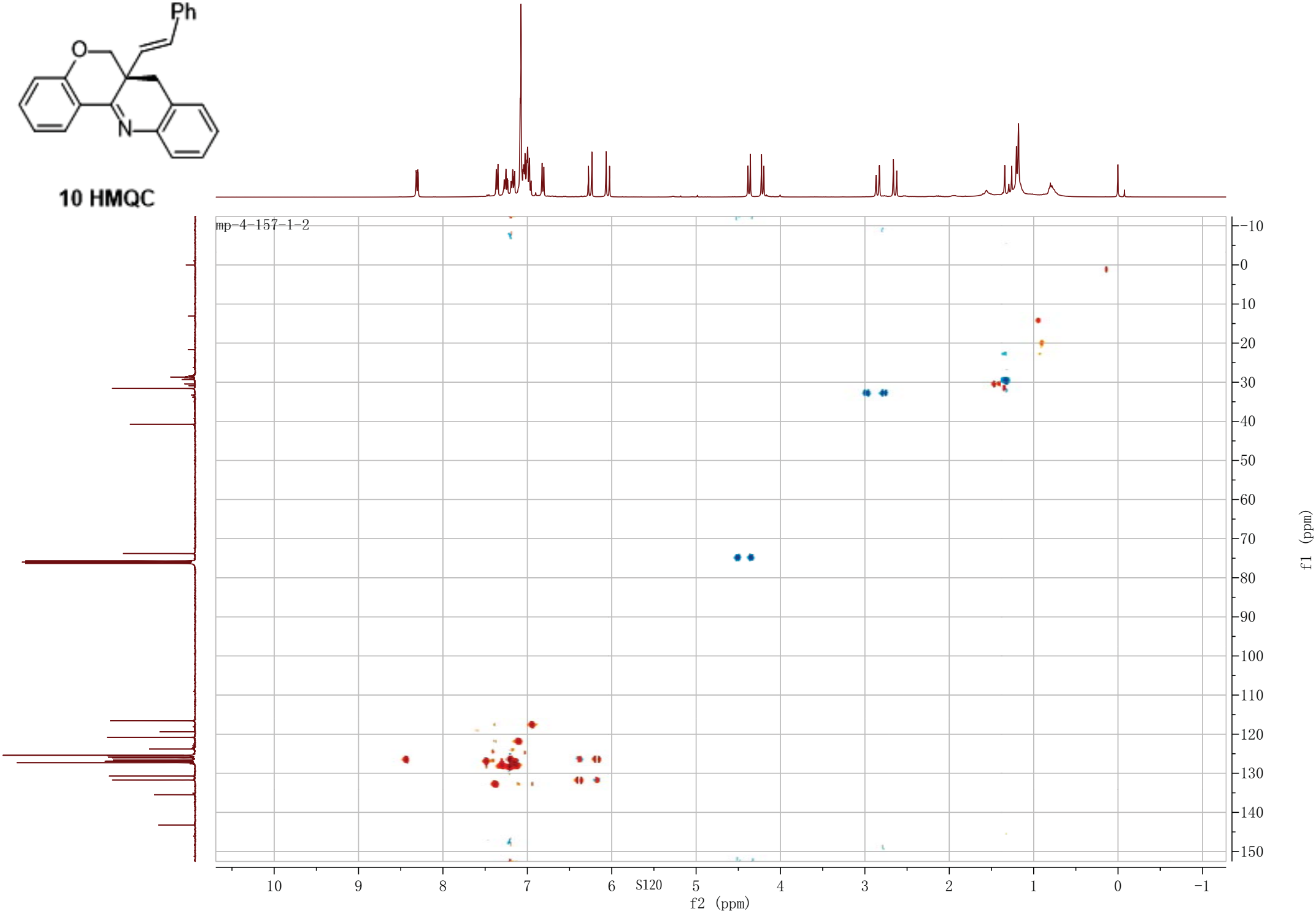
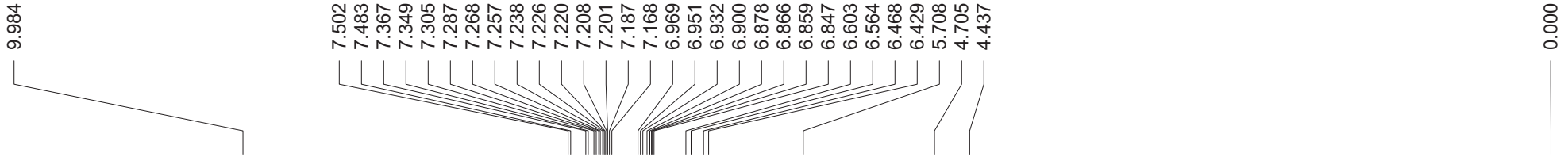
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
-1
0
1
2
3
4
5
6
7
8
9
f1 (ppm)


Ph
O
N
10 HMBC
mp-4-157-1-2
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)

Ph
O
N

10 HMQC


mp-4-157-1-2
10
9
8
7
6
S120
5
4
3
2
1
0
-1
f2 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)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7.305
7.287
7.268
7.257
7.238
7.226
7.220
7.208
7.201
7.187
7.168
6.969
6.951
6.932
6.900
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6.847
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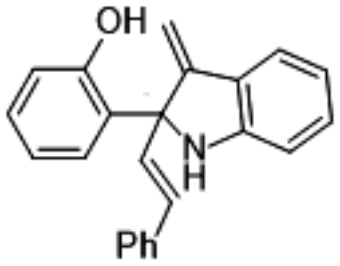
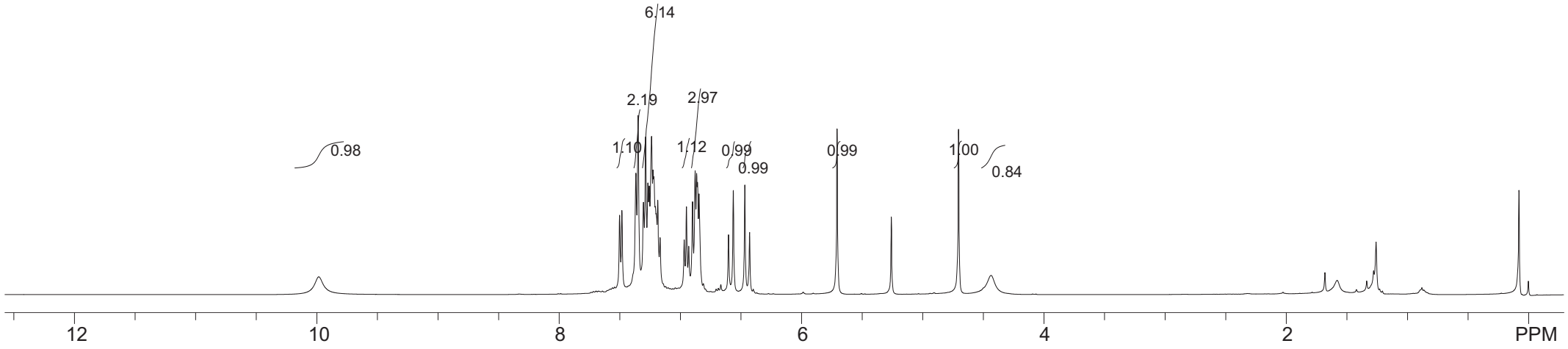
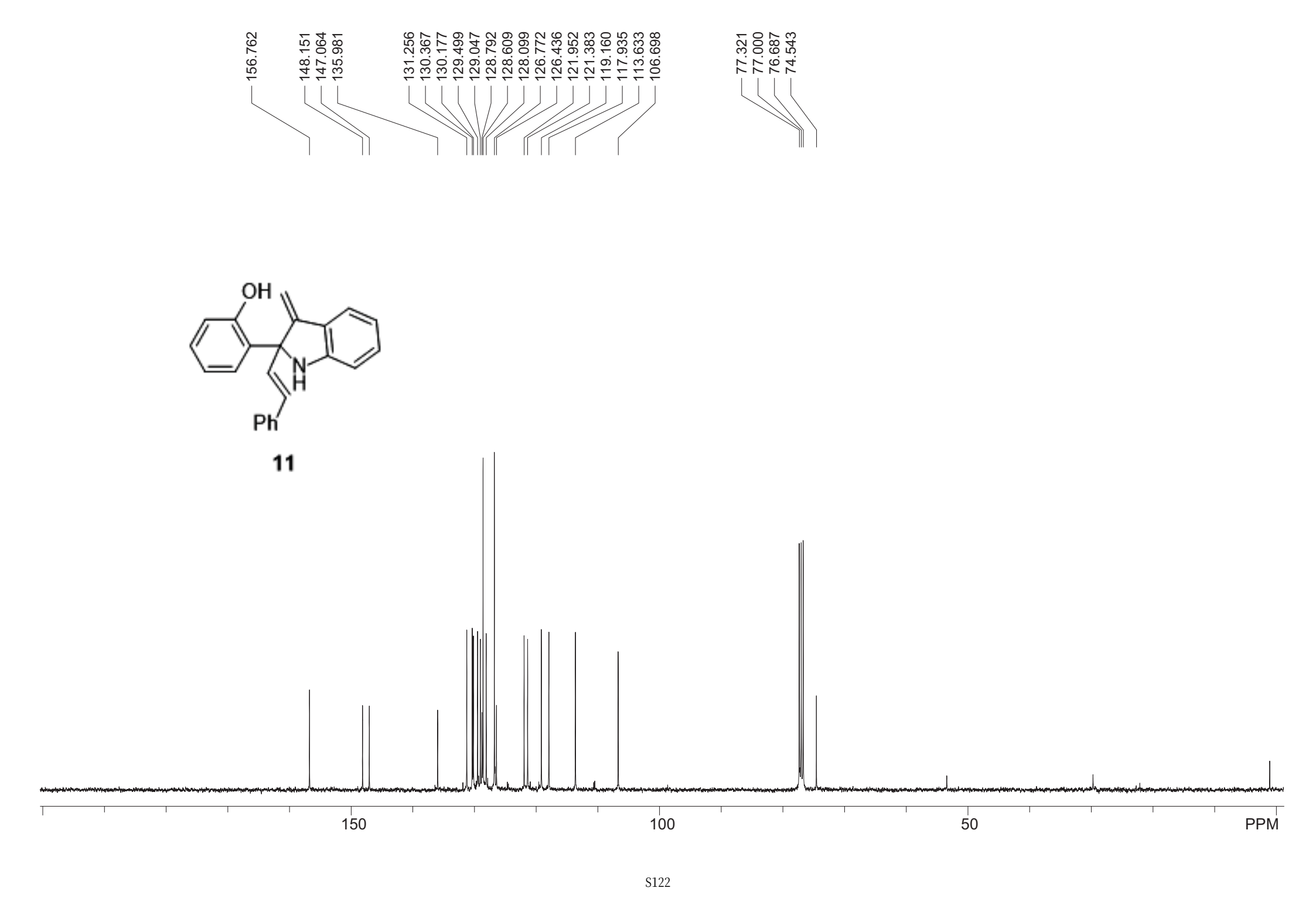
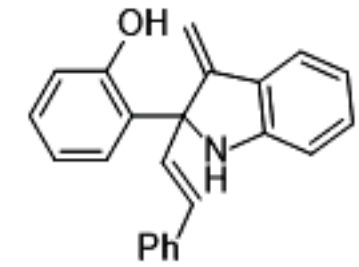
6.564
6.468
6.429
5.708
4.705
4.437
0.000


OH
N
H
Ph

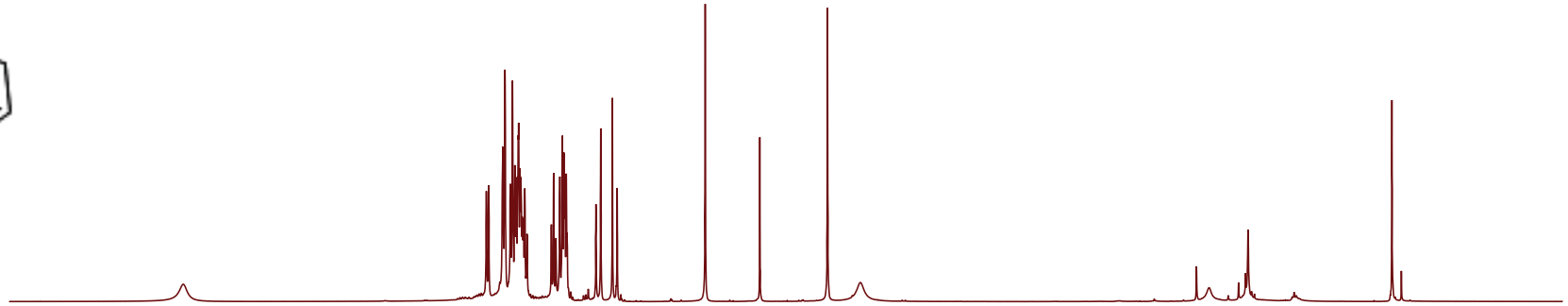
11

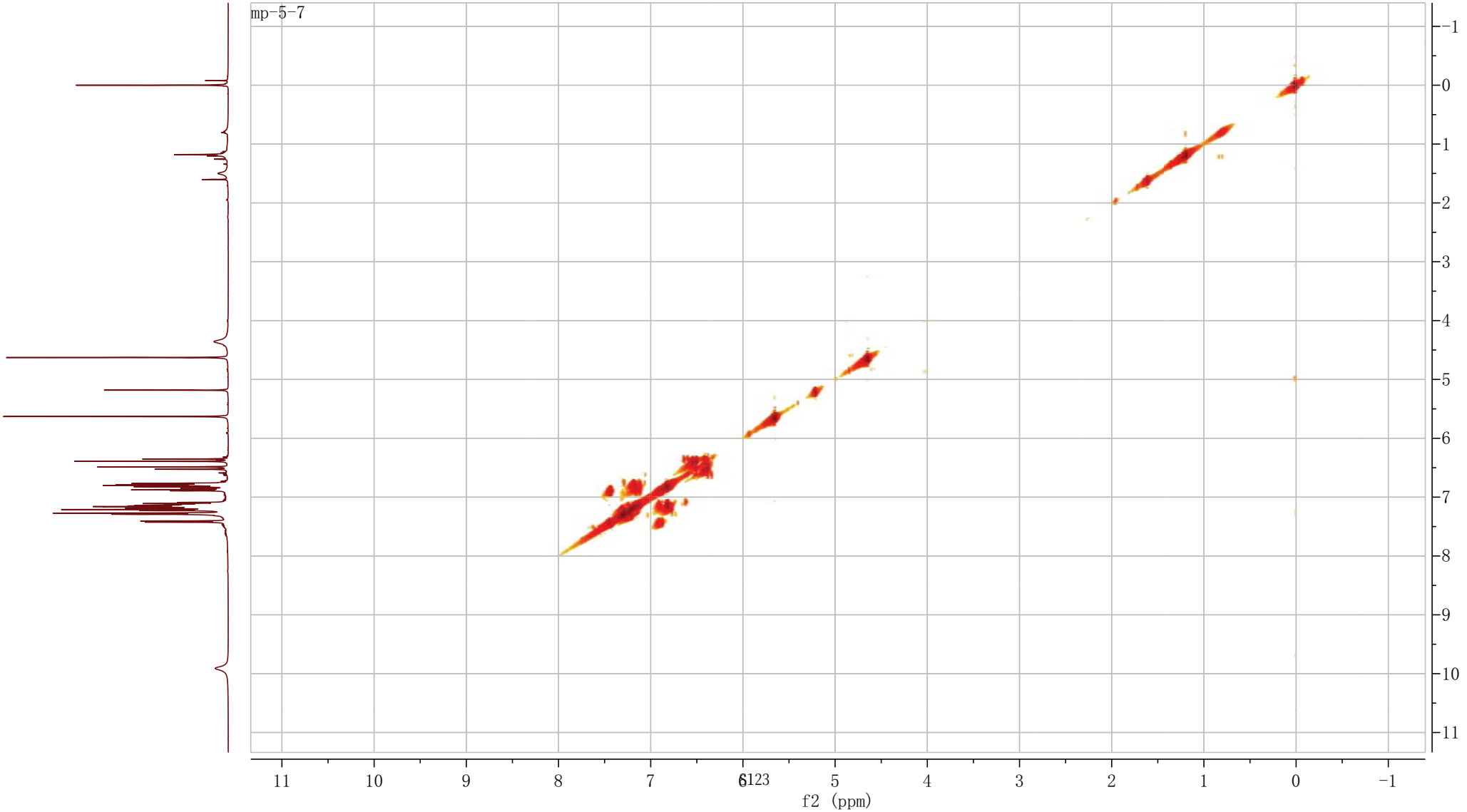

6.14
2.19
2.97
0.98
1.10
1.12
0.99
0.99
0.99
1.00
0.84
12
10
8
6
4
2
PPM

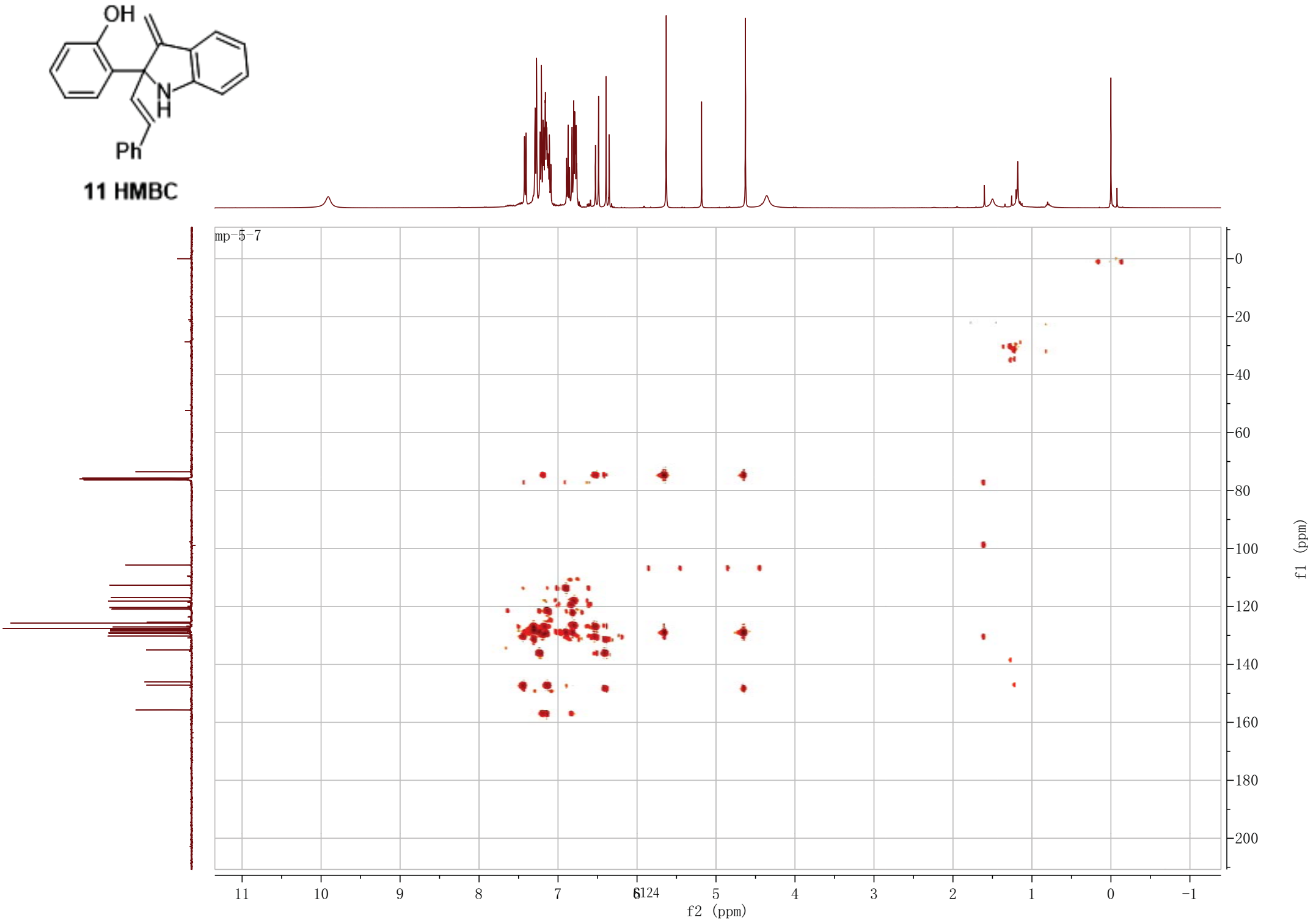

156.762
148.151
147.064
135.981
131.256
130.367
130.177
129.499
129.047
128.792
128.609
128.099
126.772
126.436
121.952
121.383
119.160
117.935
113.633
106.698
77.321
77.000
76.687
74.543
OH
N
H
Ph
11
150
100
50
PPM

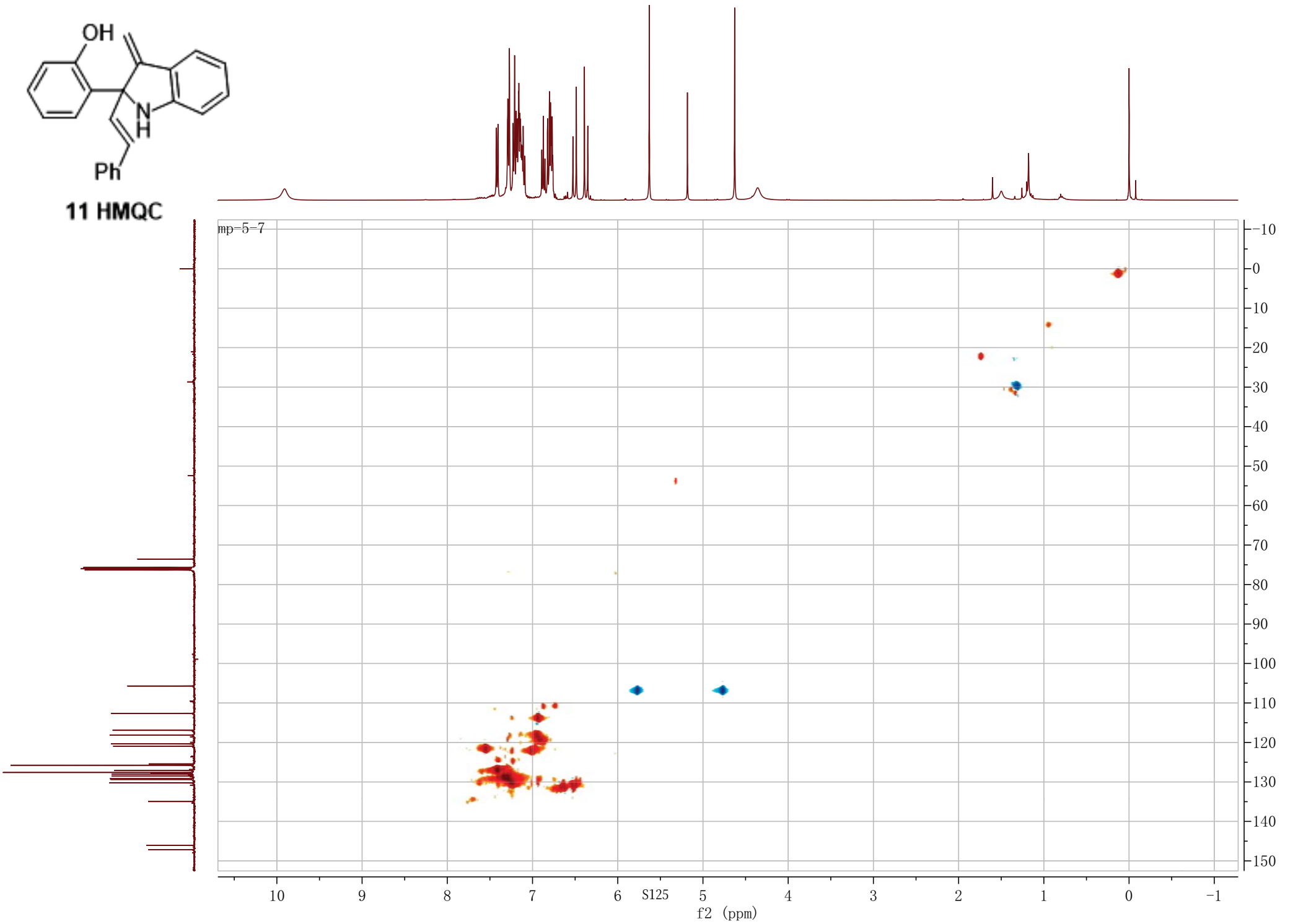


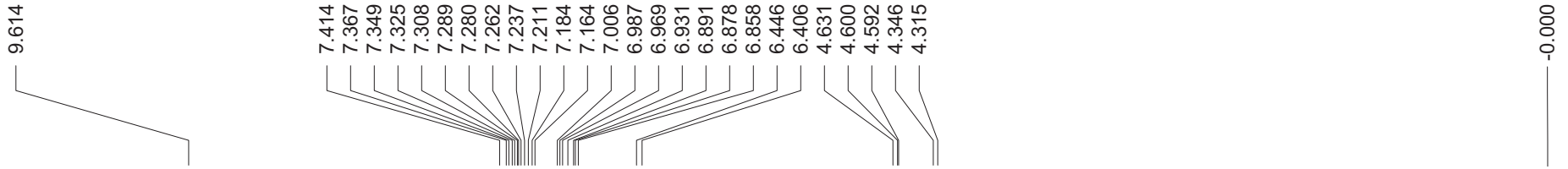
11 COSY

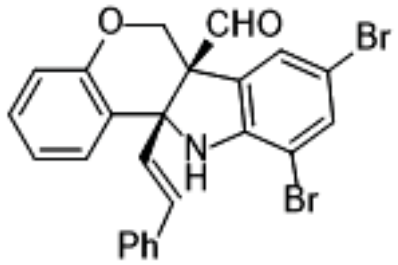




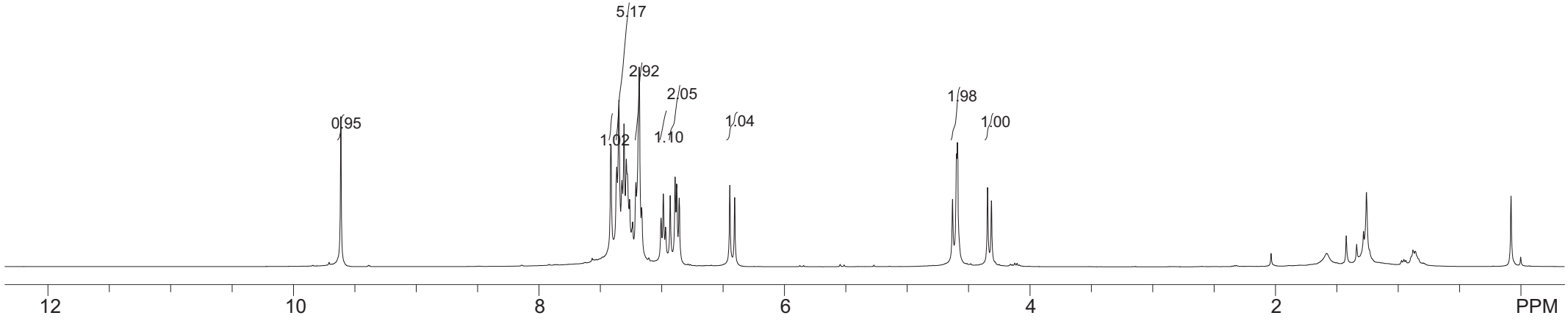

OH
N
H
Ph
11 HMBC
mp-5-7
f2 (ppm)
f1 (ppm)

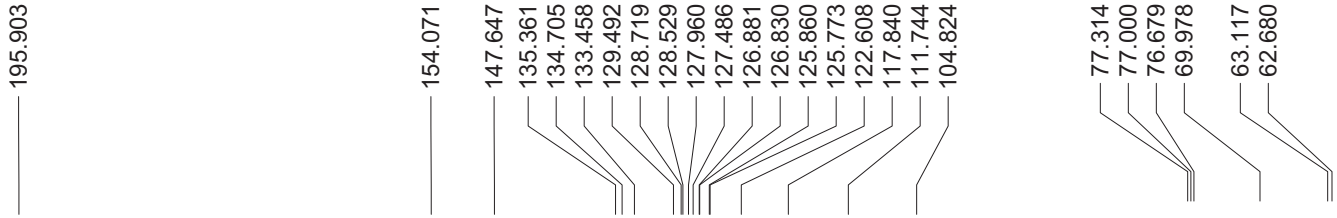

OH
N
H
Ph
11 HMQC
mp-5-7
10
9
8
7
6
S125
5
4
3
2
1
0
-1
f2 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

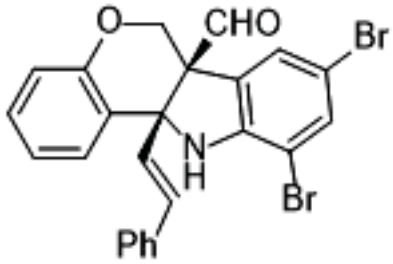

9.614
7.414
7.367
7.349
7.325
7.308
7.289
7.280
7.262
7.237
7.211
7.184
7.164
7.006
6.987
6.969
6.931
6.891
6.878
6.858
6.446
6.406
4.631
4.600
4.592
4.346
4.315
-0.000


O
CHO
Br
N
H
Br
Ph

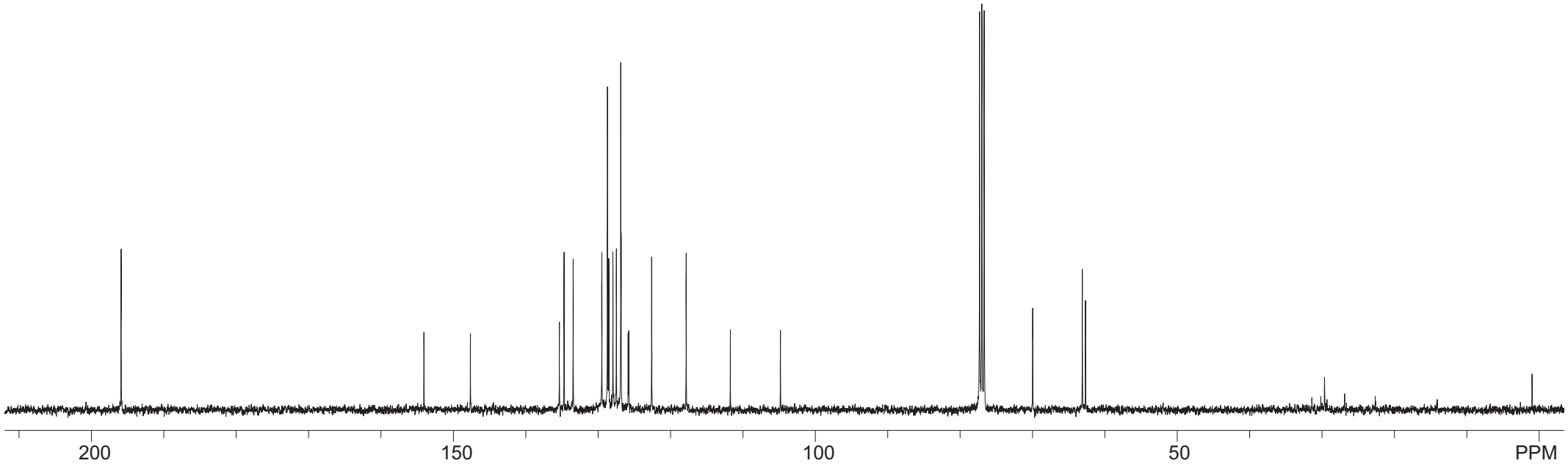
12

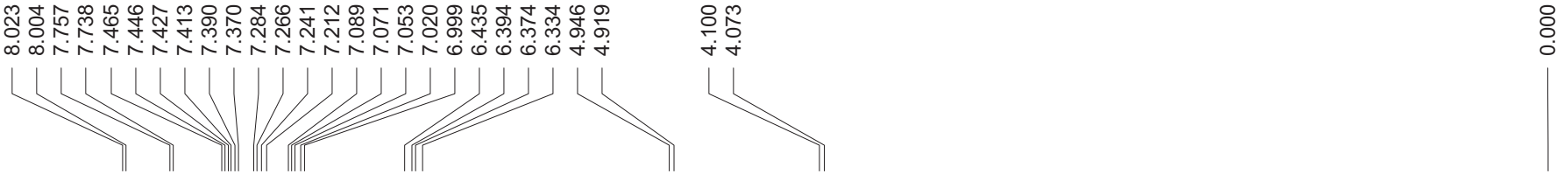

5.17
2.92
2.05
1.98
0.95
1.02
1.10
1.04
1.00
12
10
8
6
4
2
PPM

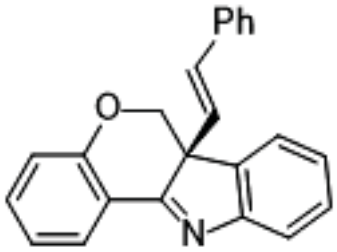

195.903
154.071
147.647
135.361
134.705
133.458
129.492
128.719
128.529
127.960
127.486
126.881
126.830
125.860
125.773
122.608
117.840
111.744
104.824
77.314
77.000
76.679
69.978
63.117
62.680


O
CHO
Br
N
H
Br
Ph

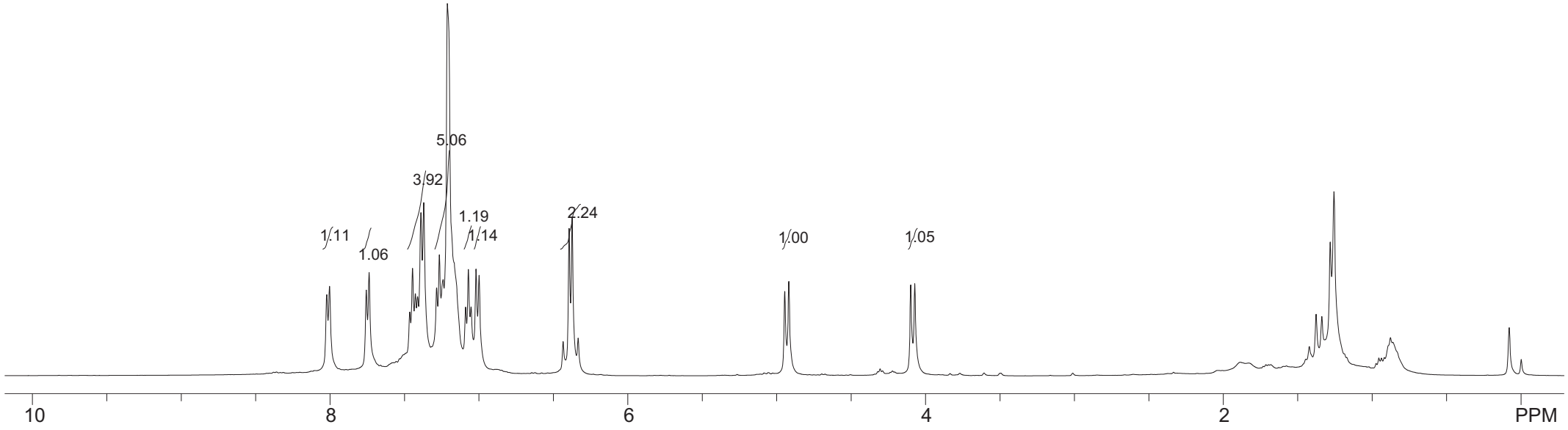
12

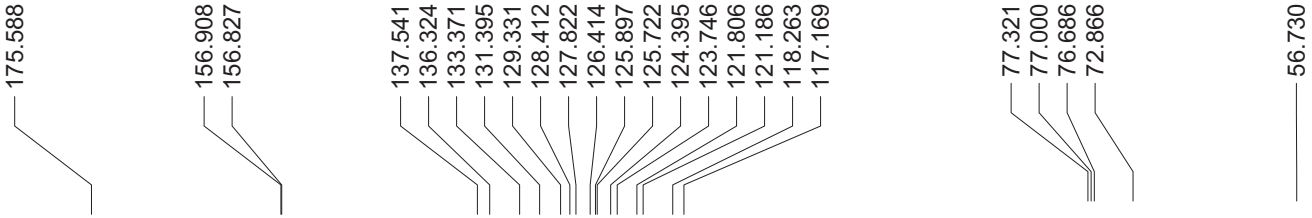

200
150
100
50
PPM

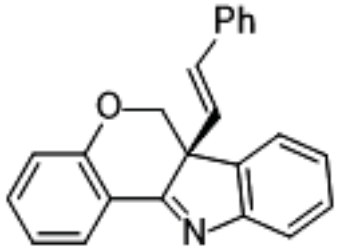

8.023
8.004
7.757
7.738
7.465
7.446
7.427
7.413
7.390
7.370
7.284
7.266
7.241
7.212
7.089
7.071
7.053
7.020
6.999
6.435
6.394
6.374
6.334
4.946
4.919
4.100
4.073
0.000


Ph
O
N

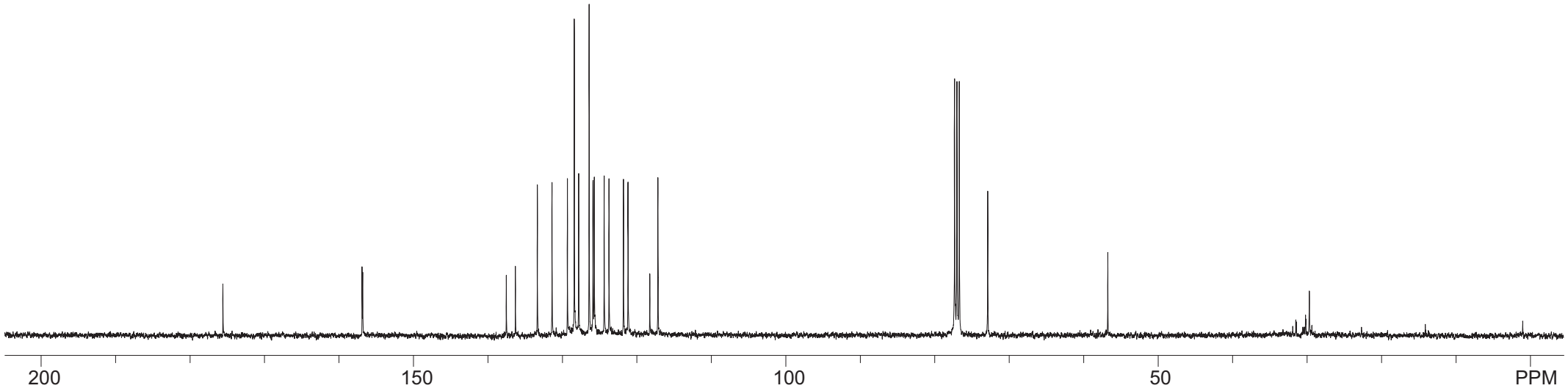
13

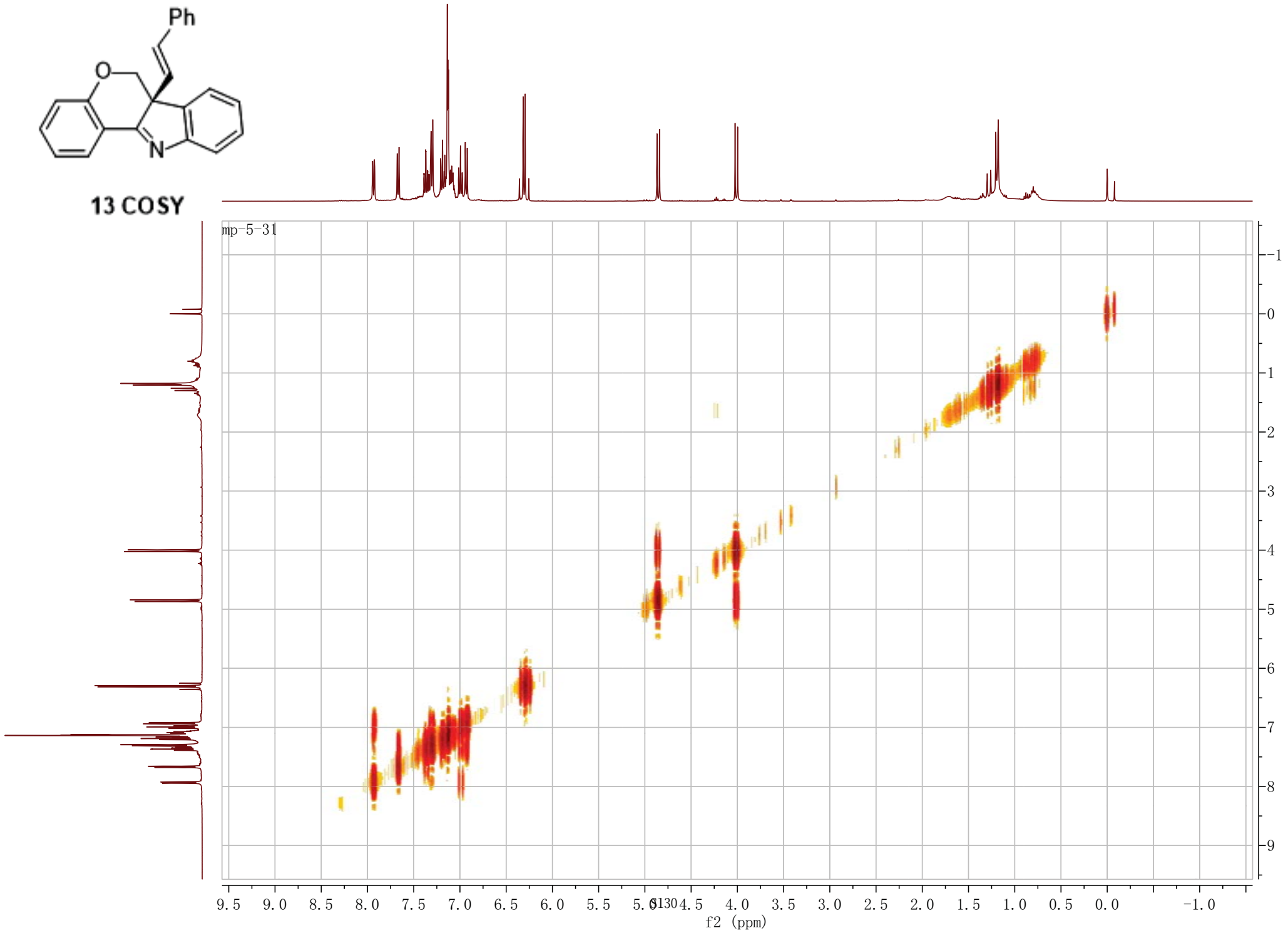

1.11
1.06
3.92
5.06
1.19
1.14
2.24
1.00
1.05
10
8
6
4
2
PPM

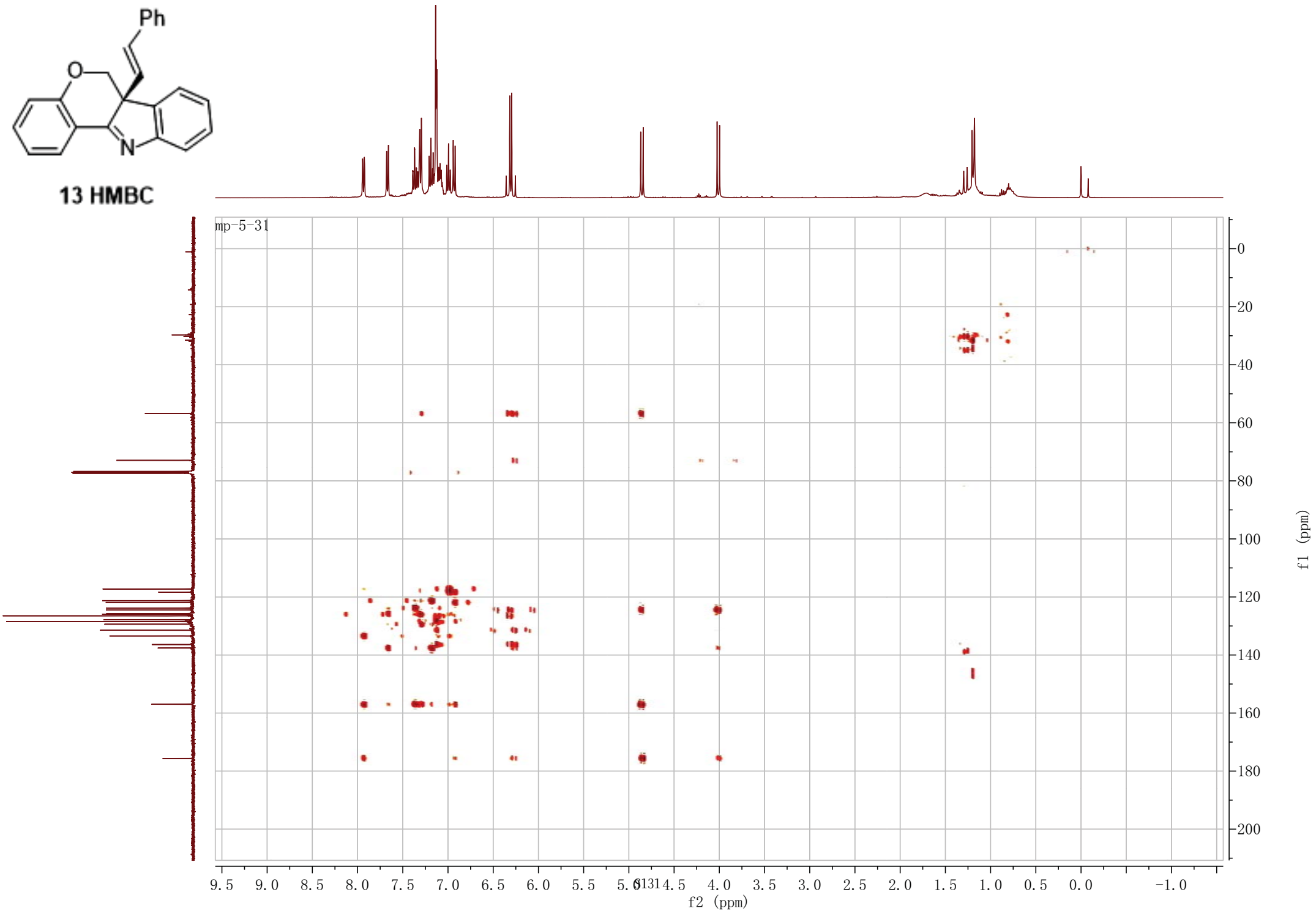

175.588
156.908
156.827
137.541
136.324
133.371
131.395
129.331
128.412
127.822
126.414
125.897
125.722
124.395
123.746
121.806
121.186
118.263
117.169
77.321
77.000
76.686
72.866
56.730

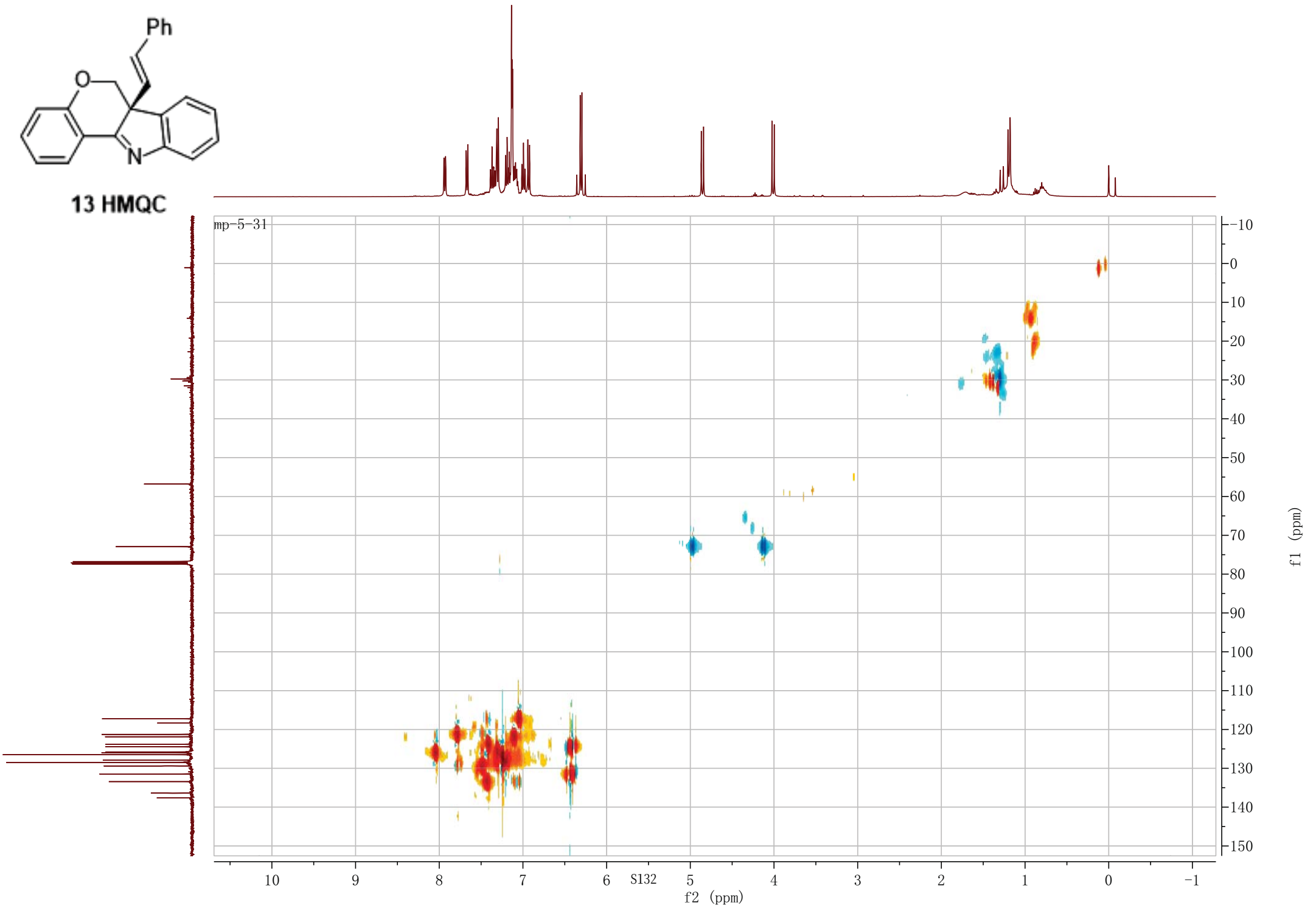

Ph
O
N

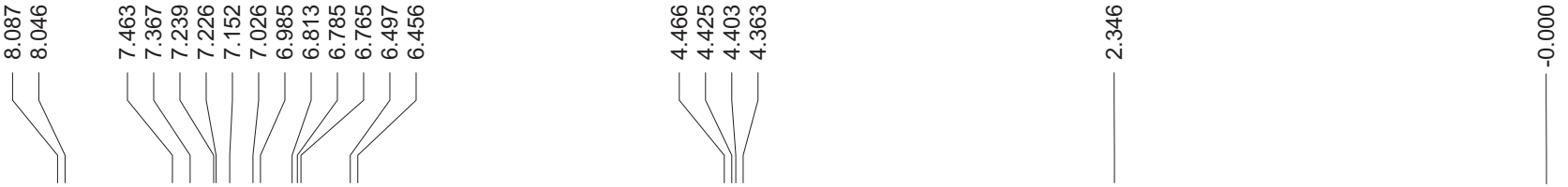
13

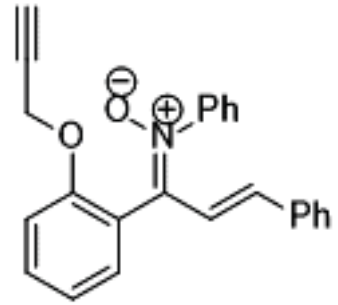

200
150
100
50
PPM


Ph
O
N
13 COSY
mp-5-31
f2 (ppm)
f1 (ppm)

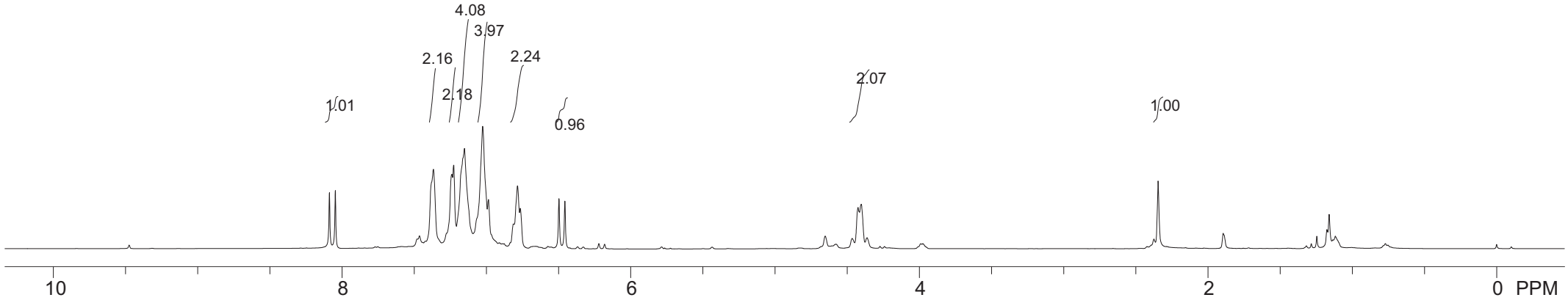

Ph
O
N
13 HMBC
mp-5-31
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f2 (ppm)

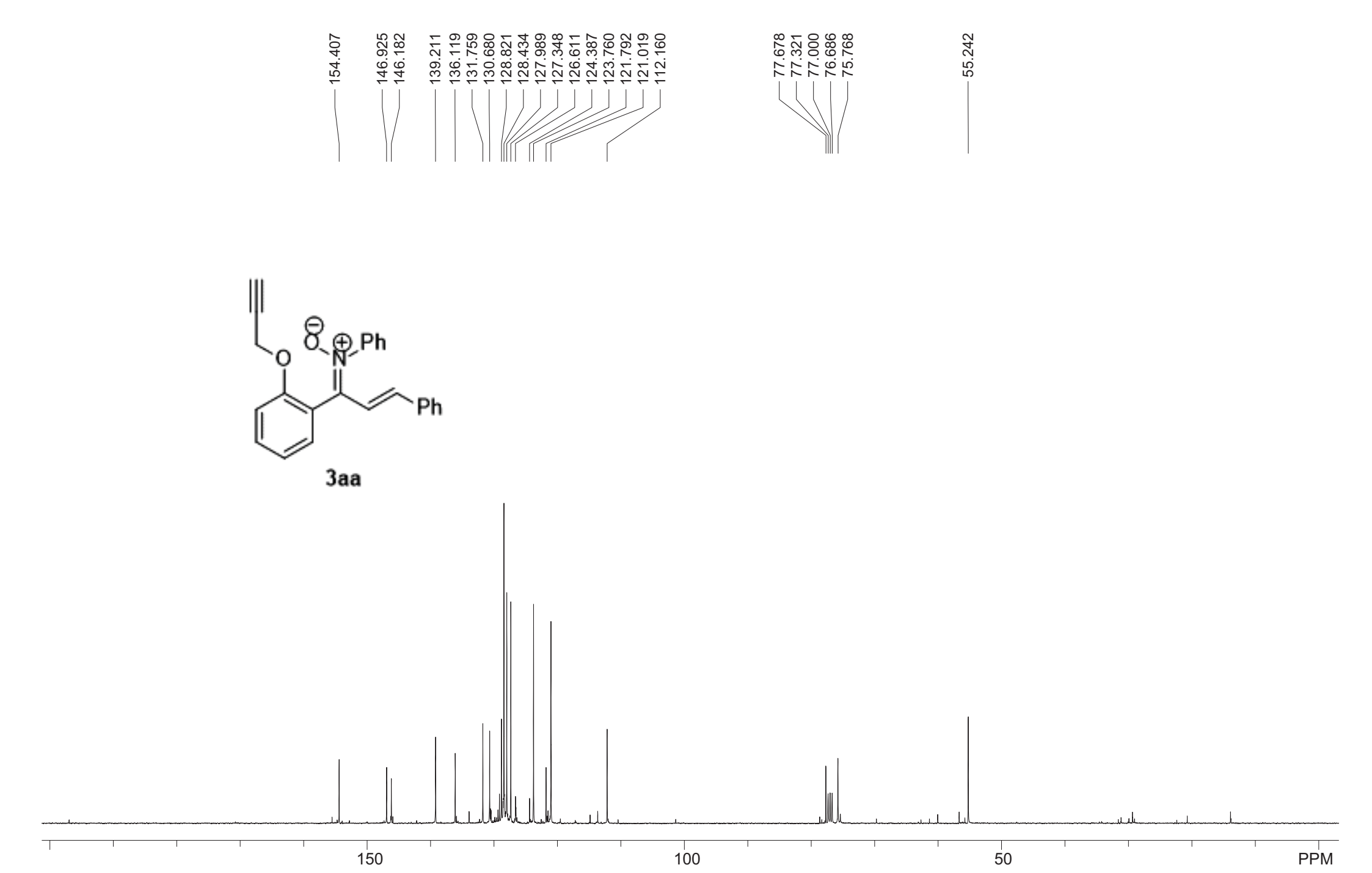

Ph
O
N
13 HMQC
mp-5-31
S132
f2 (ppm)
f1 (ppm)


8.087
8.046
7.463
7.367
7.239
7.226
7.152
7.026
6.985
6.813
6.785
6.765
6.497
6.456
4.466
4.425
4.403
4.363
2.346
-0.000

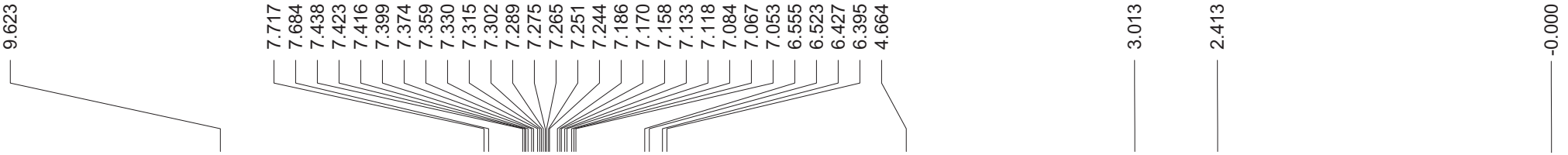

Ph
Ph

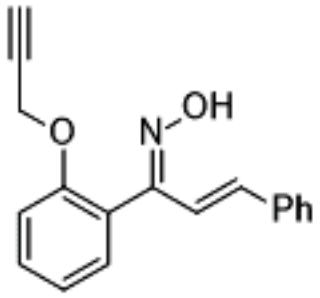
3aa


4.08
3.97
2.16
2.24
2.18
2.07
1.01
0.96
1.00
10
8
6
4
2
0
PPM

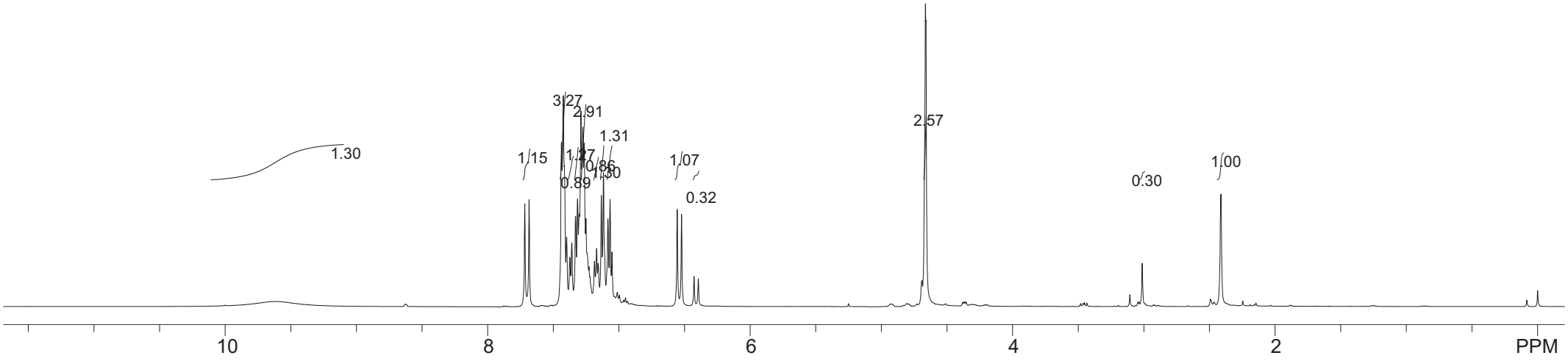

154.407
146.925
146.182
139.211
136.119
131.759
130.680
128.821
128.434
127.989
127.348
126.611
124.387
123.760
121.792
121.019
112.160
77.678
77.321
77.000
76.686
75.768
55.242
O
N
Ph
Ph
150
100
50
PPM

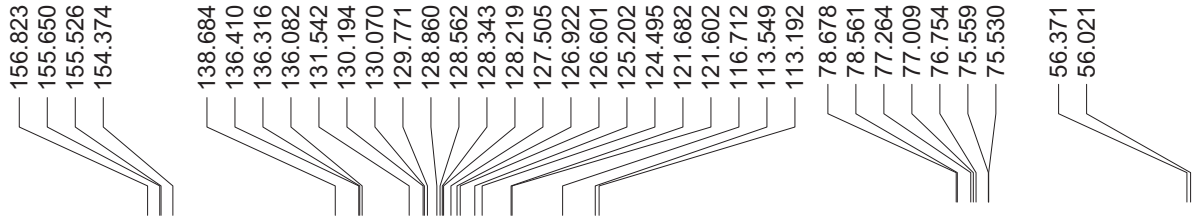
3aa

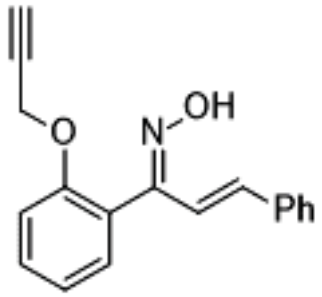

9.623
7.717
7.684
7.438
7.423
7.416
7.399
7.374
7.359
7.330
7.315
7.302
7.289
7.275
7.265
7.251
7.244
7.186
7.170
7.158
7.133
7.118
7.084
7.067
7.053
6.555
6.523
6.427
6.395
4.664
3.013
2.413
-0.000


O
N
OH
Ph

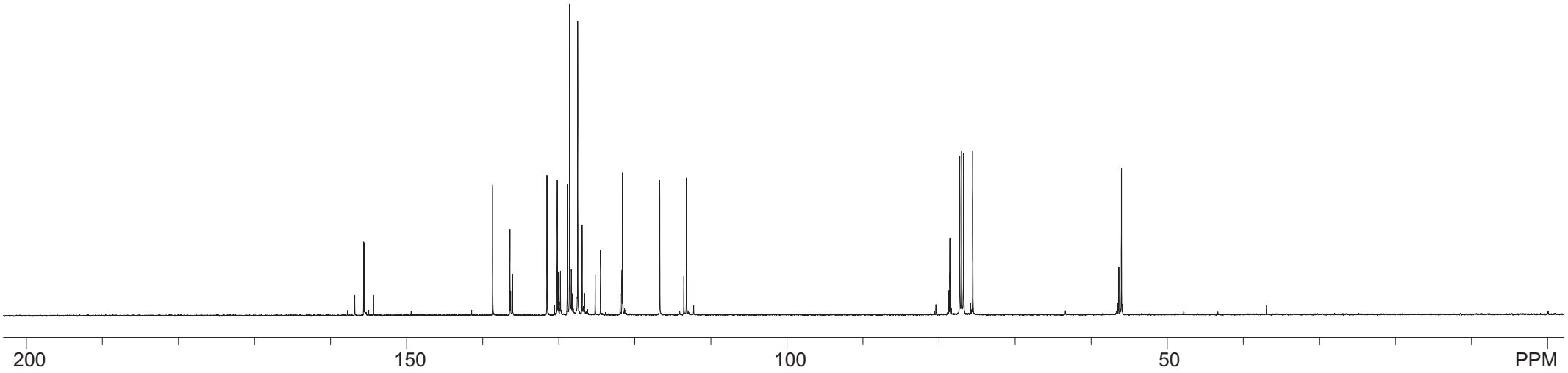
1a (*E*/*Z* = 3/1)

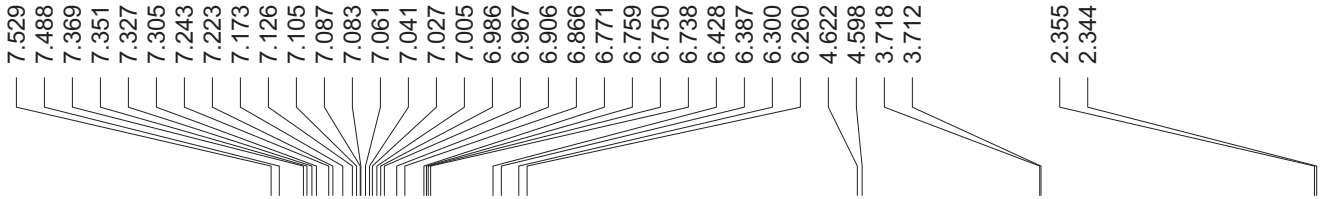

1.30
1.15
3.27
2.91
1.31
1.27
0.89
1.07
0.32
2.57
0.30
1.00
10
8
6
4
2
PPM

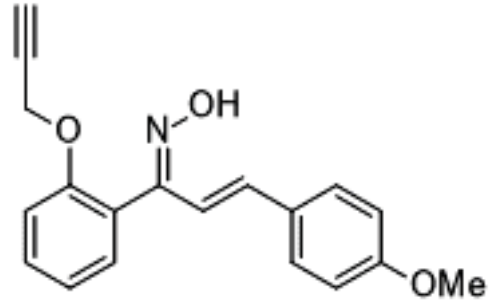

156.823
155.650
155.526
154.374
138.684
136.410
136.316
136.082
131.542
130.194
130.070
129.771
128.860
128.562
128.343
128.219
127.505
126.922
126.601
125.202
124.495
121.682
121.602
116.712
113.549
113.192
78.678
78.561
77.264
77.009
76.754
75.559
75.530
56.371
56.021


O
N
OH
Ph

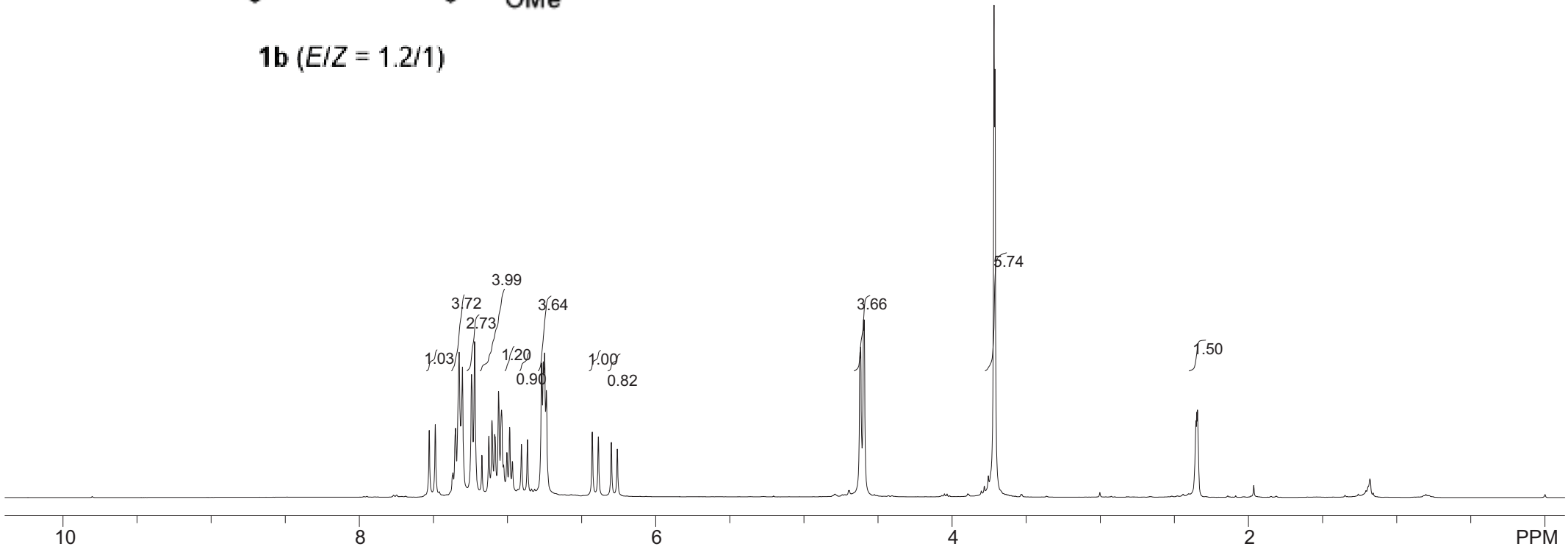
1a (*E*/*Z* = 3/1)

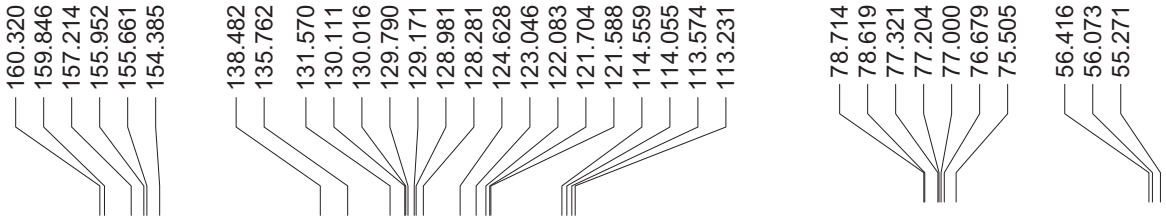

200
150
100
50
PPM

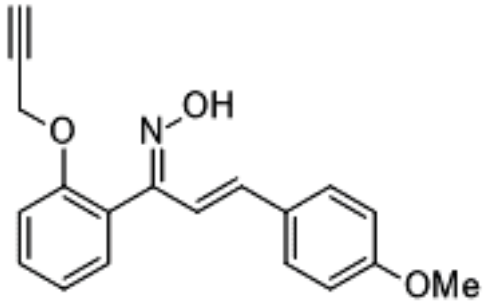

7.529
7.488
7.369
7.351
7.327
7.305
7.243
7.223
7.173
7.126
7.105
7.087
7.083
7.061
7.041
7.027
7.005
6.986
6.967
6.906
6.866
6.771
6.759
6.750
6.738
6.428
6.387
6.300
6.260
4.622
4.598
3.718
3.712
2.355
2.344


O
N
OH
OMe

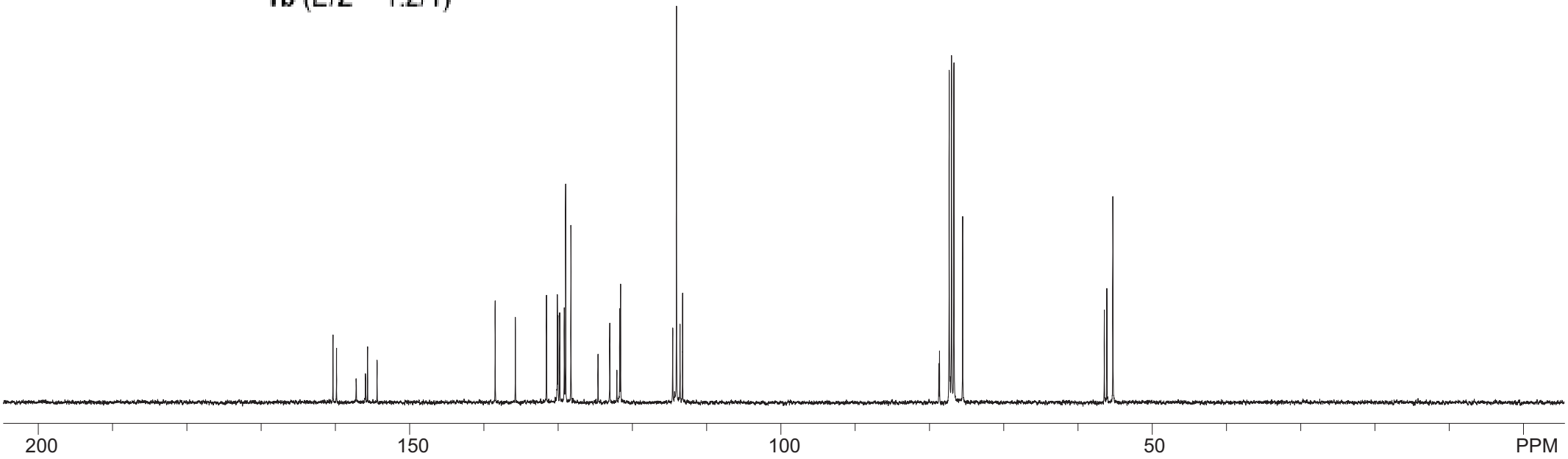
1b (*E*/*Z* = 1.2/1)

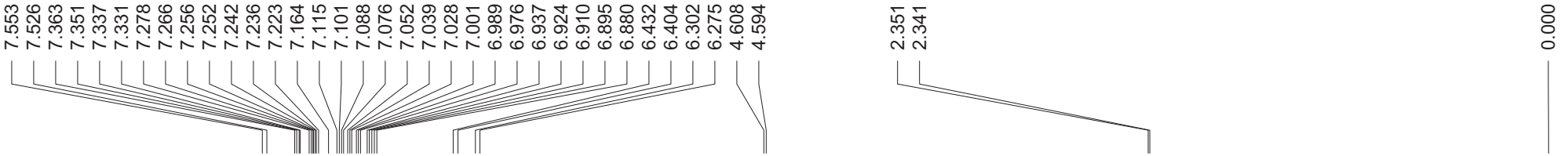

3.99
3.72
2.73
3.64
3.66
5.74
1.50
1.03
1.20
0.90
1.00
0.82
10
8
6
4
2
PPM

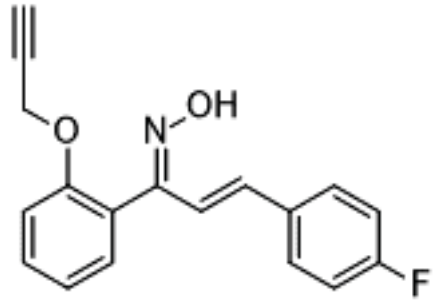

160.320
159.846
157.214
155.952
155.661
154.385
138.482
135.762
131.570
130.111
130.016
129.790
129.171
128.981
128.281
124.628
123.046
122.083
121.704
121.588
114.559
114.055
113.574
113.231
78.714
78.619
77.321
77.204
77.000
76.679
75.505
56.416
56.073
55.271


O
N
OH
OMe

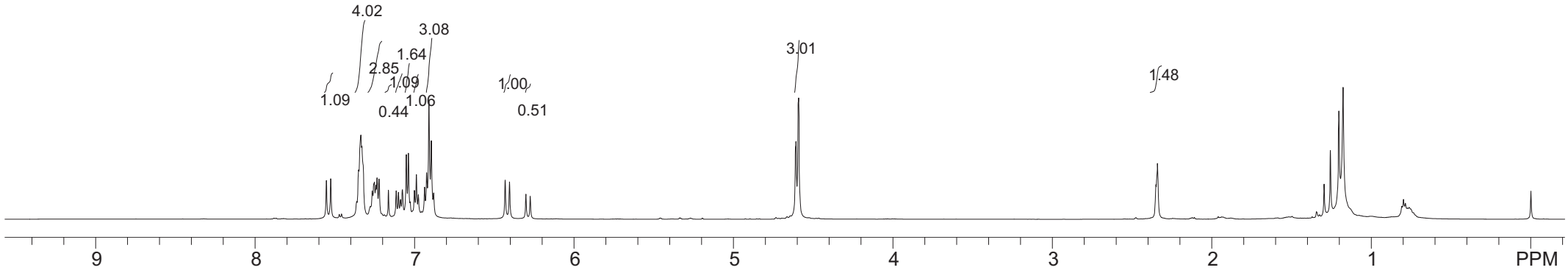
1b (*E*/*Z* = 1.2/1)

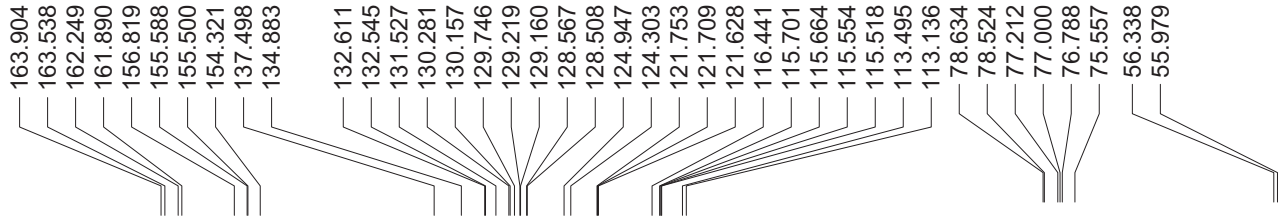

200
150
100
50
PPM

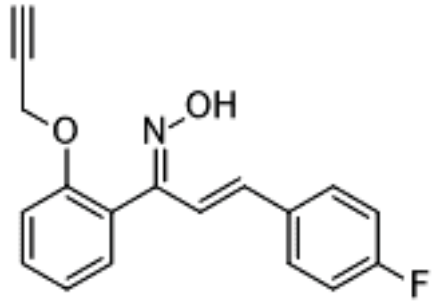

7.553
7.526
7.363
7.351
7.337
7.331
7.278
7.266
7.256
7.252
7.242
7.236
7.223
7.164
7.115
7.101
7.088
7.076
7.052
7.039
7.028
7.001
6.989
6.976
6.937
6.924
6.910
6.895
6.880
6.432
6.404
6.302
6.275
4.608
4.594
2.351
2.341
0.000


O
N
OH
F

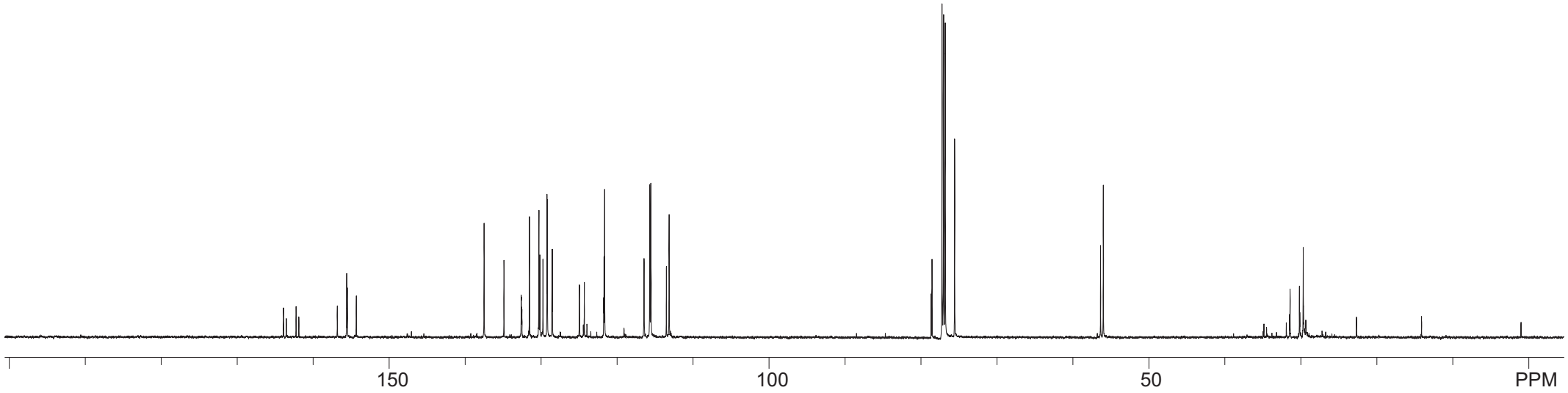
1c (*E*/*Z* = 2/1)

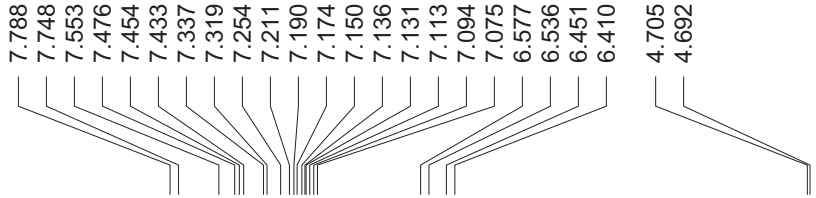

4.02
3.08
1.64
2.85
1.09
1.09
1.06
0.44
1.00
0.51
3.01
1.48
9
8
7
6
5
4
3
2
1
PPM


163.904
163.538
162.249
161.890
156.819
155.588
155.500
154.321
137.498
134.883
132.611
132.545
131.527
130.281
130.157
129.746
129.219
129.160
128.567
128.508
124.947
124.303
121.753
121.709
121.628
116.441
115.701
115.664
115.554
115.518
113.495
113.136
78.634
78.524
77.212
77.000
76.788
75.557
56.338
55.979

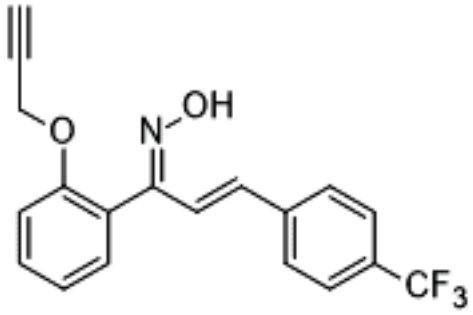

O
N
OH
F

1c (*E*/*Z* = 2/1)

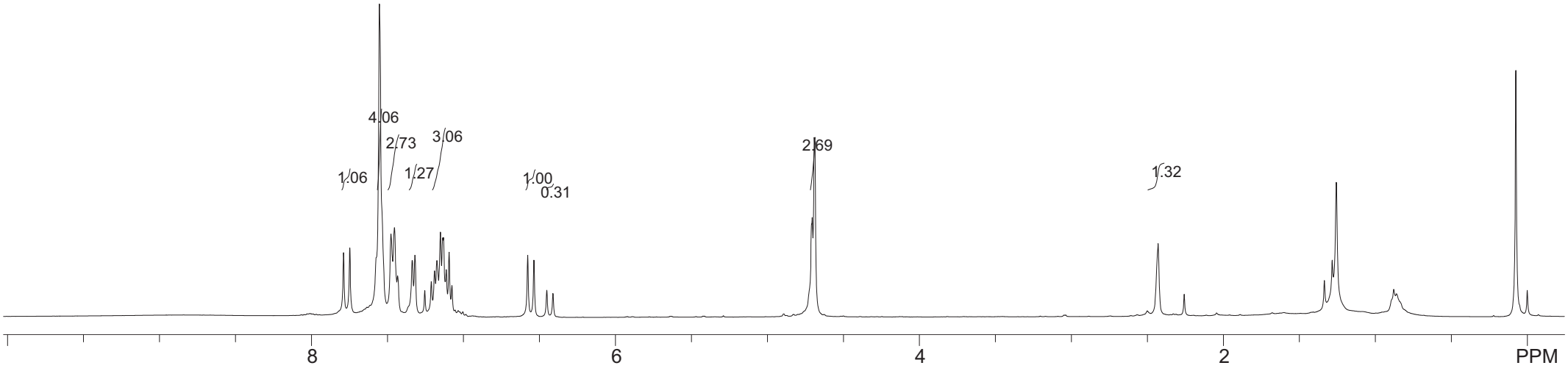

150
100
50
PPM


7.788
7.748
7.553
7.476
7.454
7.433
7.337
7.319
7.254
7.211
7.190
7.174
7.150
7.136
7.131
7.113
7.094
7.075
6.577
6.536
6.451
6.410
4.705
4.692

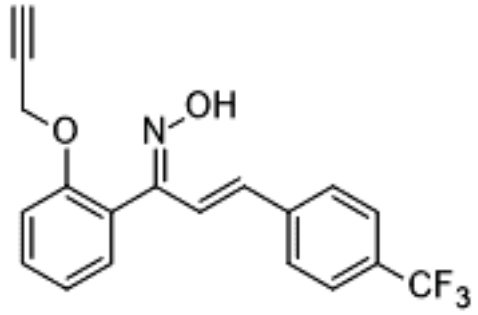

2.429
0.000


O
N
OH
CF3

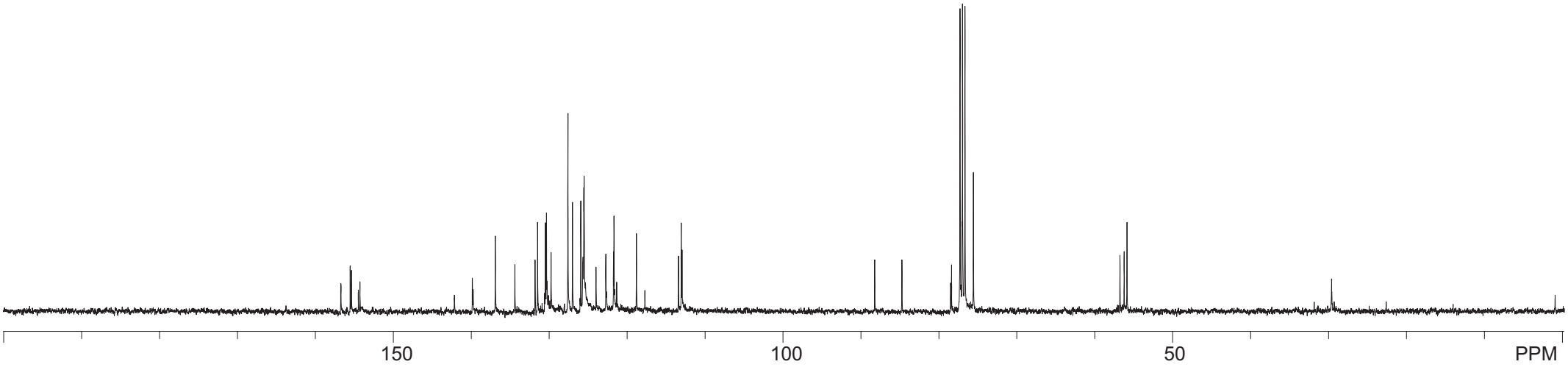
1d (*E*/*Z* = 3.3/1)

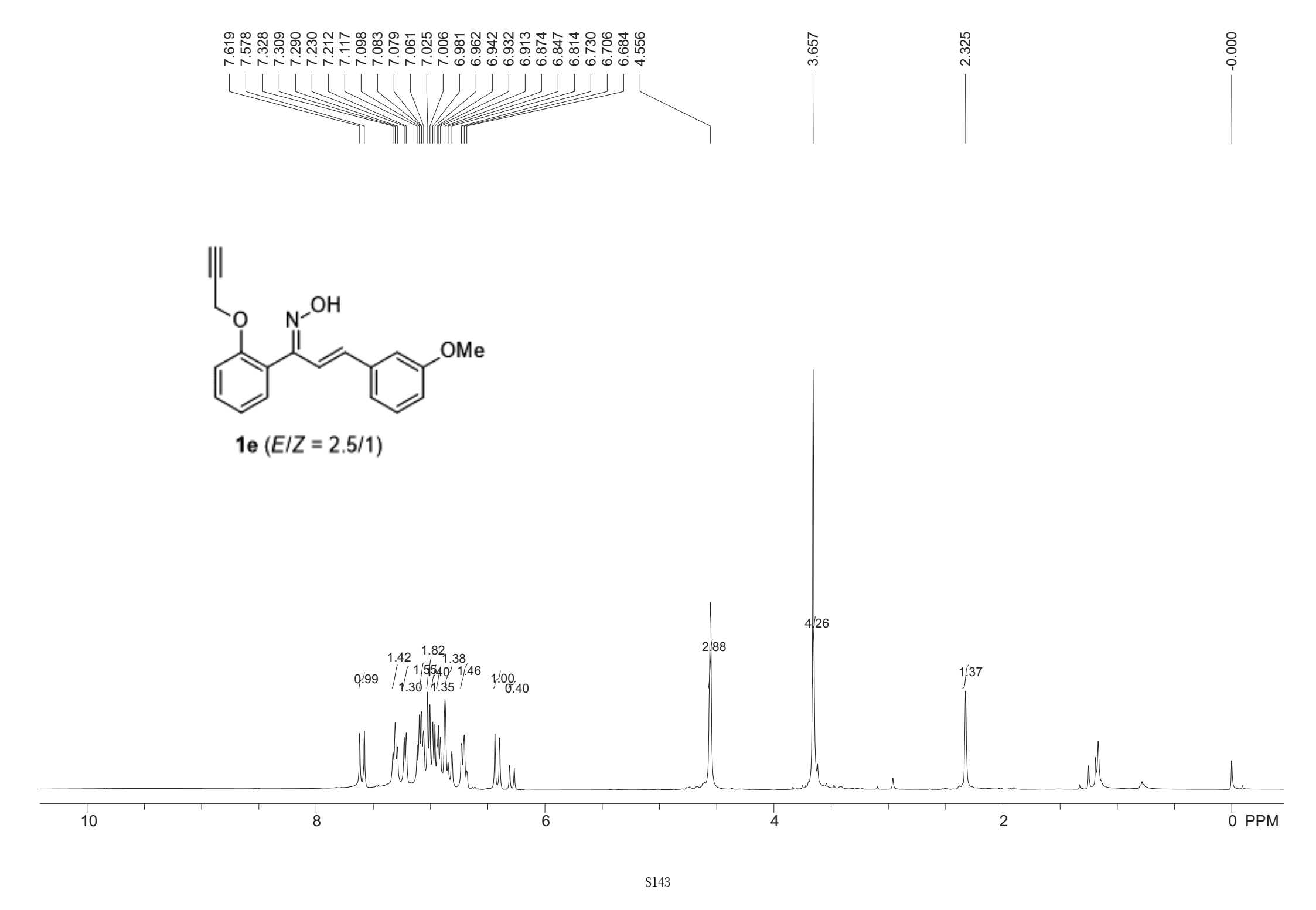

1.06
4.06
2.73
1.27
3.06
1.00
0.31
2.69
1.32
8
6
4
2
PPM

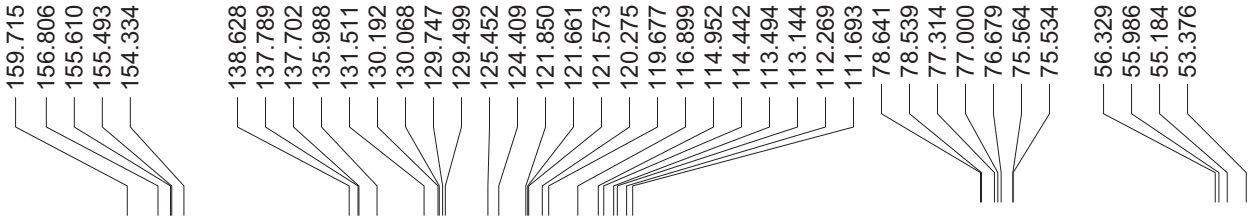
156.754
156.725
155.544
155.369
154.479
154.283
142.164
139.860
139.765
136.922
134.406
131.825
131.497
130.498
130.352
129.761
127.603
127.027
125.955
125.707
125.671
125.561
125.525
124.001
122.740
121.763
121.697
121.354
118.817
113.436
113.071
112.969
88.258
84.773
78.407
77.321
77.000
76.686
75.607
56.803
55.906

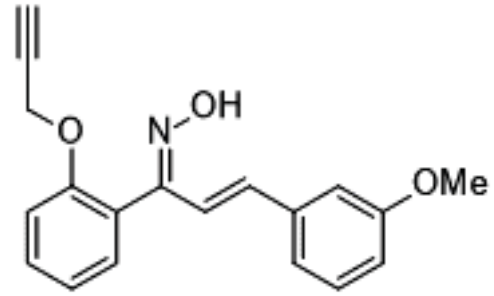


1d (*E*/*Z* = 3.3/1)

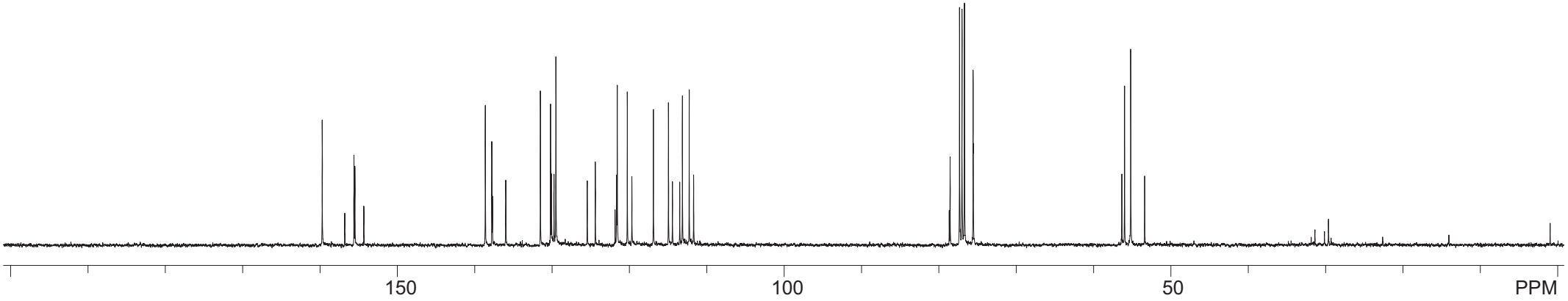


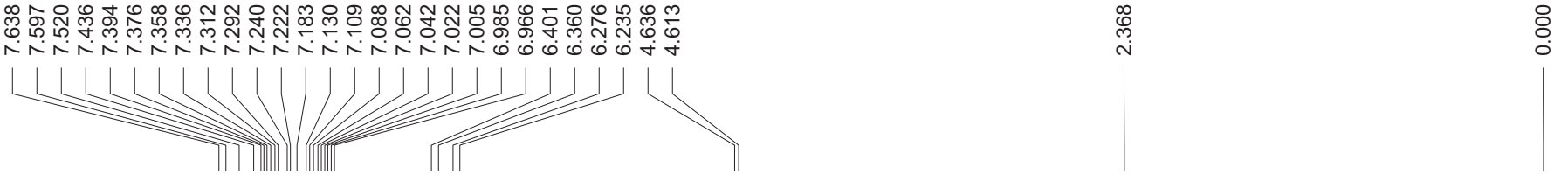

7.619
7.578
7.328
7.309
7.290
7.230
7.212
7.117
7.098
7.083
7.079
7.061
7.025
7.006
6.981
6.962
6.942
6.932
6.913
6.874
6.847
6.814
6.730
6.706
6.684
4.556
3.657
2.325
-0.000
O
N
OH
OMe
1e (E/Z = 2.5/1)
0.99
1.42
1.30
1.82
1.55
1.40
1.35
1.38
1.46
1.00
0.40
2.88
4.26
1.37
10
8
6
4
2
0 PPM

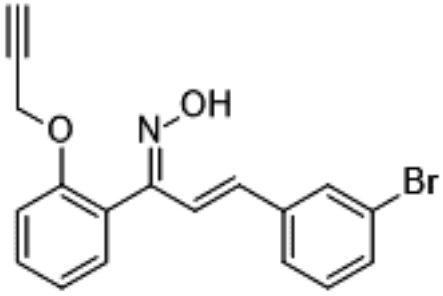

159.715
156.806
155.610
155.493
154.334
138.628
137.789
137.702
135.988
131.511
130.192
130.068
129.747
129.499
125.452
124.409
121.850
121.661
121.573
120.275
119.677
116.899
114.952
114.442
113.494
113.144
112.269
111.693
78.641
78.539
77.314
77.000
76.679
75.564
75.534
56.329
55.986
55.184
53.376


O
N
OH
OMe

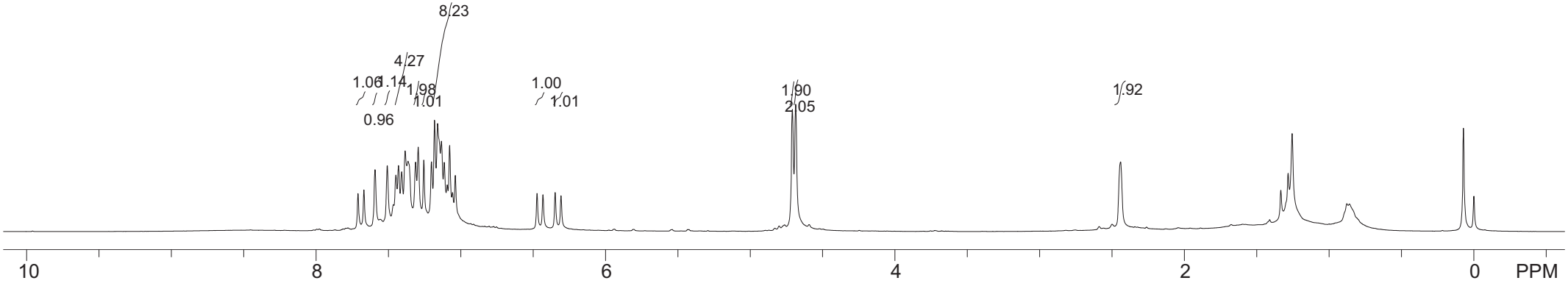
1e (*E*/*Z* = 2.5/1)

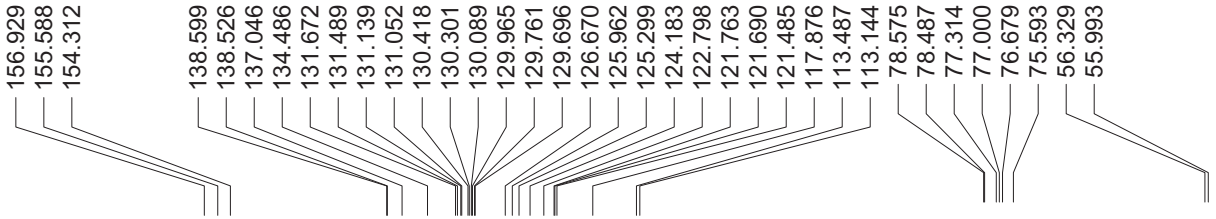

150
100
50
PPM


7.638
7.597
7.520
7.436
7.394
7.376
7.358
7.336
7.312
7.292
7.240
7.222
7.183
7.130
7.109
7.088
7.062
7.042
7.022
7.005
6.985
6.966
6.401
6.360
6.276
6.235
4.636
4.613
2.368
0.000


O
N
OH
Br

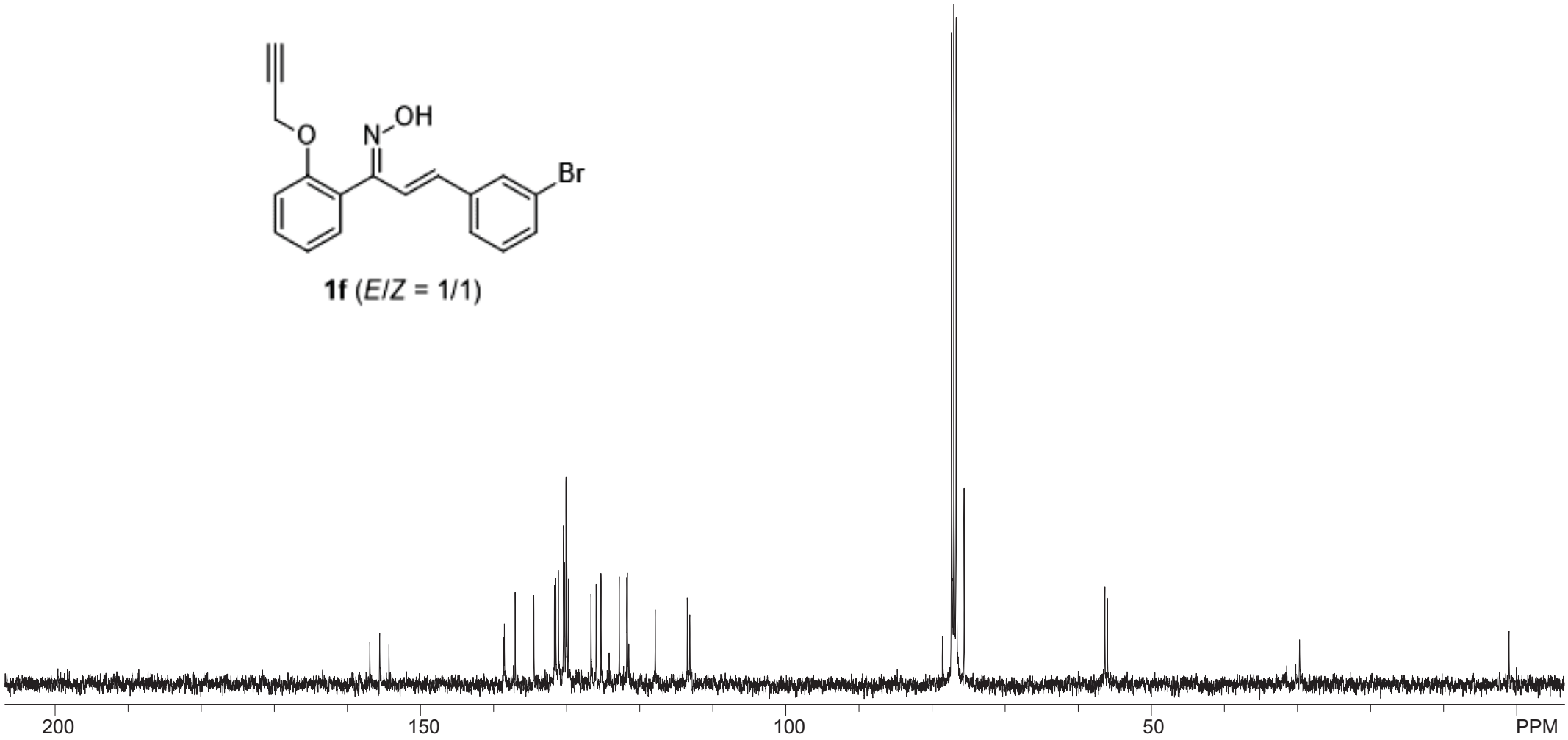
1f (*E*/*Z* = 1/1)

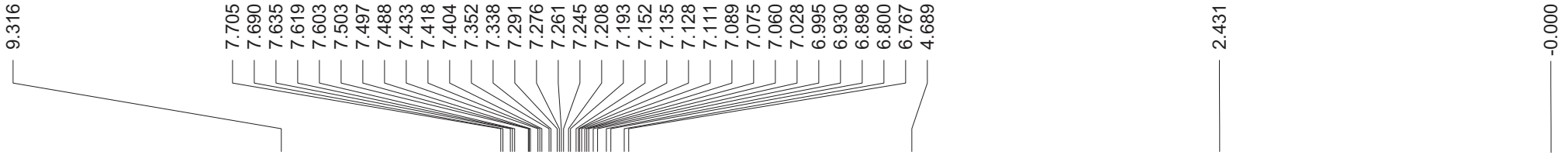

8.23
4.27
1.06
1.14
1.98
1.01
0.96
1.00
1.01
1.90
2.05
1.92
10
8
6
4
2
0
PPM

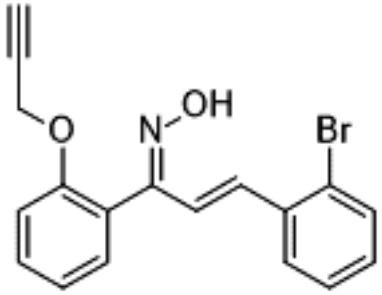

156.929
155.588
154.312
138.599
138.526
137.046
134.486
131.672
131.489
131.139
131.052
130.418
130.301
130.089
129.965
129.761
129.696
126.670
125.962
125.299
124.183
122.798
121.763
121.690
121.485
117.876
113.487
113.144
78.575
78.487
77.314
77.000
76.679
75.593
56.329
55.993

O
N
OH
Br

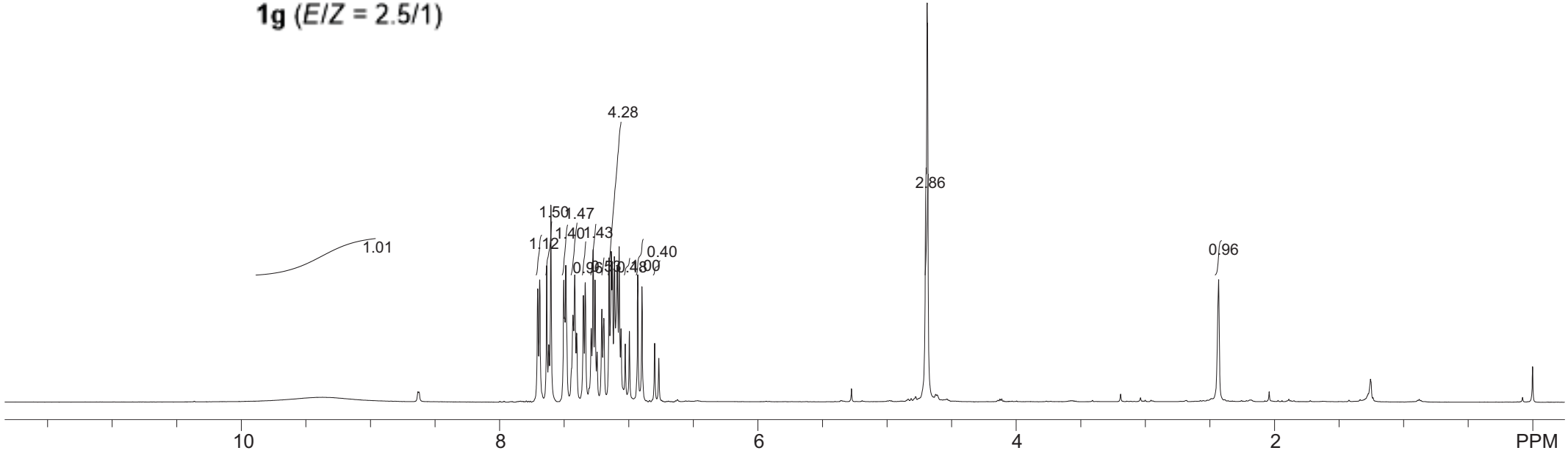
1f (*E*/*Z* = 1/1)

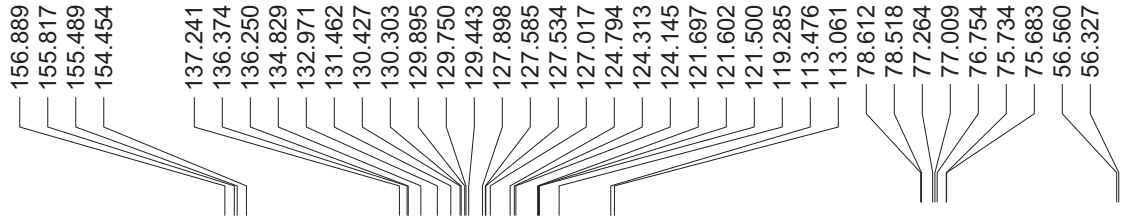

200
150
100
50
PPM

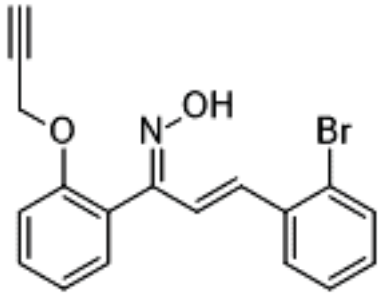

9.316
7.705
7.690
7.635
7.619
7.603
7.503
7.497
7.488
7.433
7.418
7.404
7.352
7.338
7.291
7.276
7.261
7.245
7.208
7.193
7.152
7.135
7.128
7.111
7.089
7.075
7.060
7.028
6.995
6.930
6.898
6.800
6.767
4.689
2.431
-0.000


O
N
OH
Br

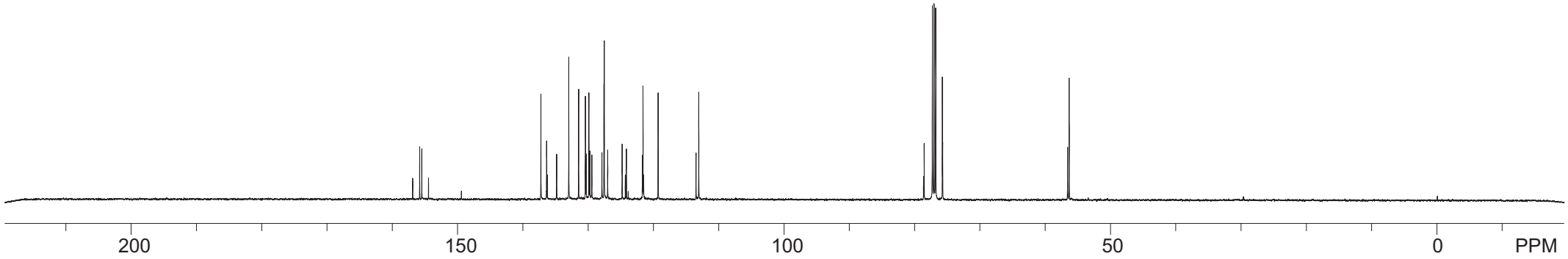
1g (*E*/*Z* = 2.5/1)

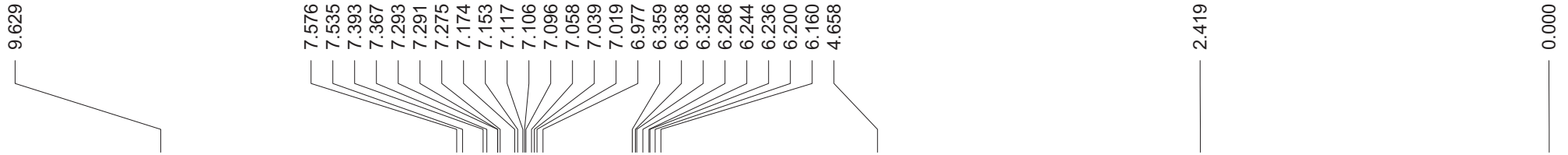

4.28
2.86
1.50
1.47
1.40
1.43
1.12
1.01
0.40
0.96
10
8
6
4
2
PPM

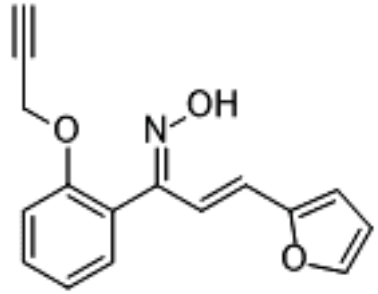

156.889
155.817
155.489
154.454
137.241
136.374
136.250
134.829
132.971
131.462
130.427
130.303
129.895
129.750
129.443
127.898
127.585
127.534
127.017
124.794
124.313
124.145
121.697
121.602
121.500
119.285
113.476
113.061
78.612
78.518
77.264
77.009
76.754
75.734
75.683
56.560
56.327


O
N
OH
Br

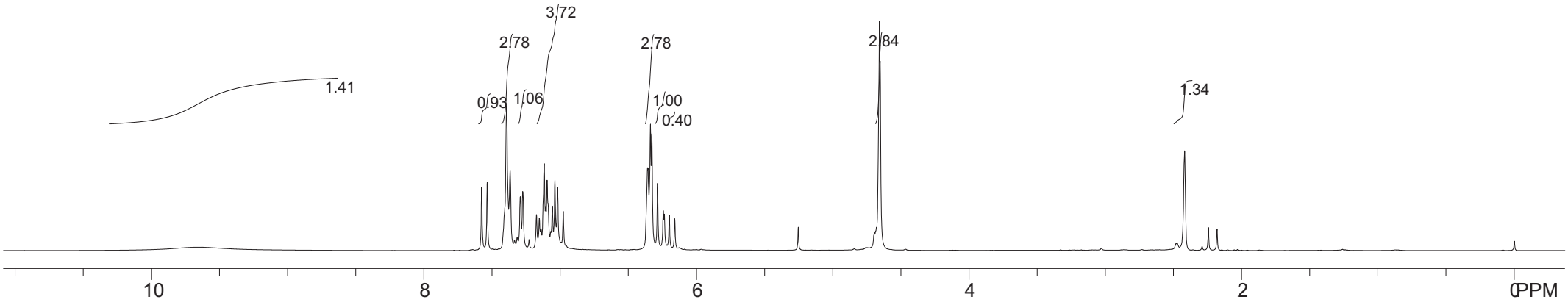
1g (*E*/*Z* = 2.5/1)

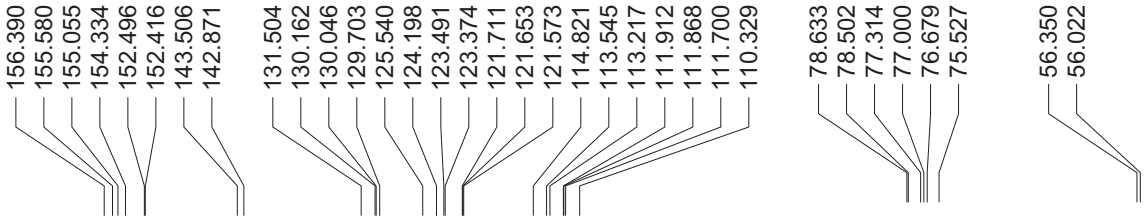

200
150
100
50
0
PPM

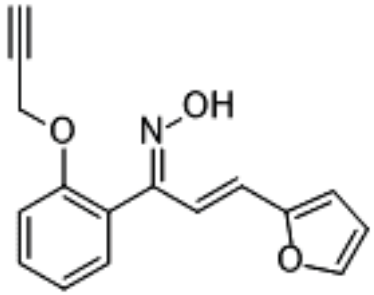

9.629
7.576
7.535
7.393
7.367
7.293
7.291
7.275
7.174
7.153
7.117
7.106
7.096
7.058
7.039
7.019
6.977
6.359
6.338
6.328
6.286
6.244
6.236
6.200
6.160
4.658
2.419
0.000


O
N
OH
O

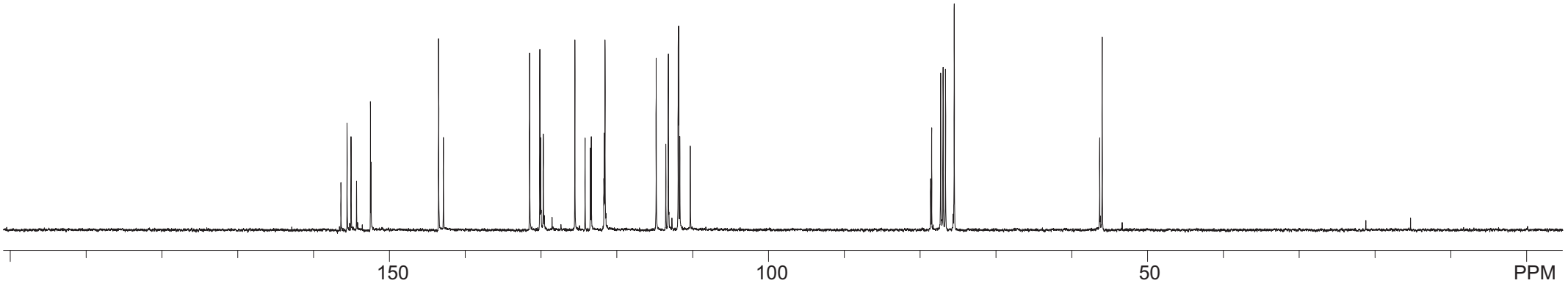
1h (*E*/*Z* = 2.5/1)

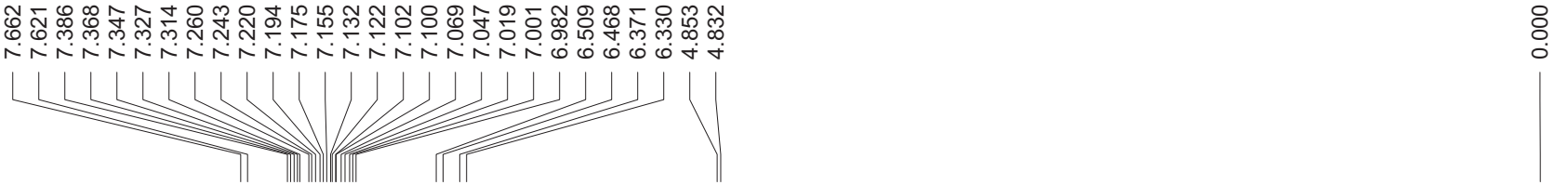

1.41
0.93
2.78
1.06
3.72
2.78
1.00
0.40
2.84
1.34
10
8
6
4
2
0
PPM

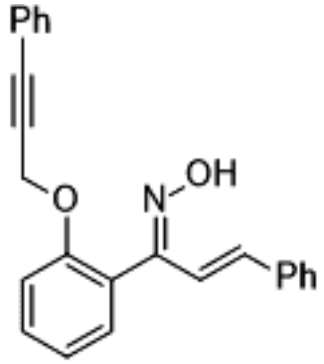

156.390
155.580
155.055
154.334
152.496
152.416
143.506
142.871
131.504
130.162
130.046
129.703
125.540
124.198
123.491
123.374
121.711
121.653
121.573
114.821
113.545
113.217
111.912
111.868
111.700
110.329
78.633
78.502
77.314
77.000
76.679
75.527
56.350
56.022


O
N
OH
O

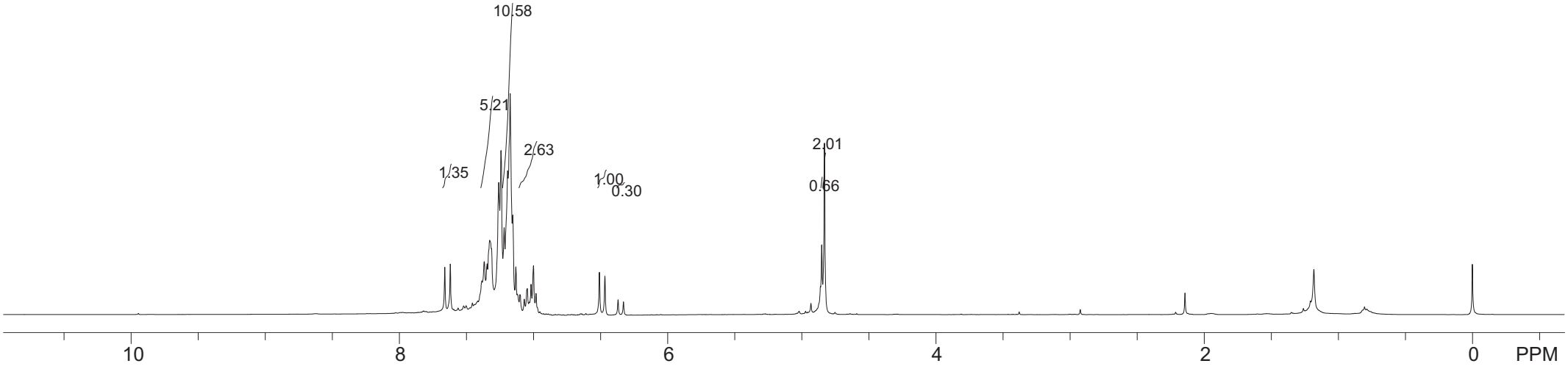
1h (*E*/*Z* = 2.5/1)

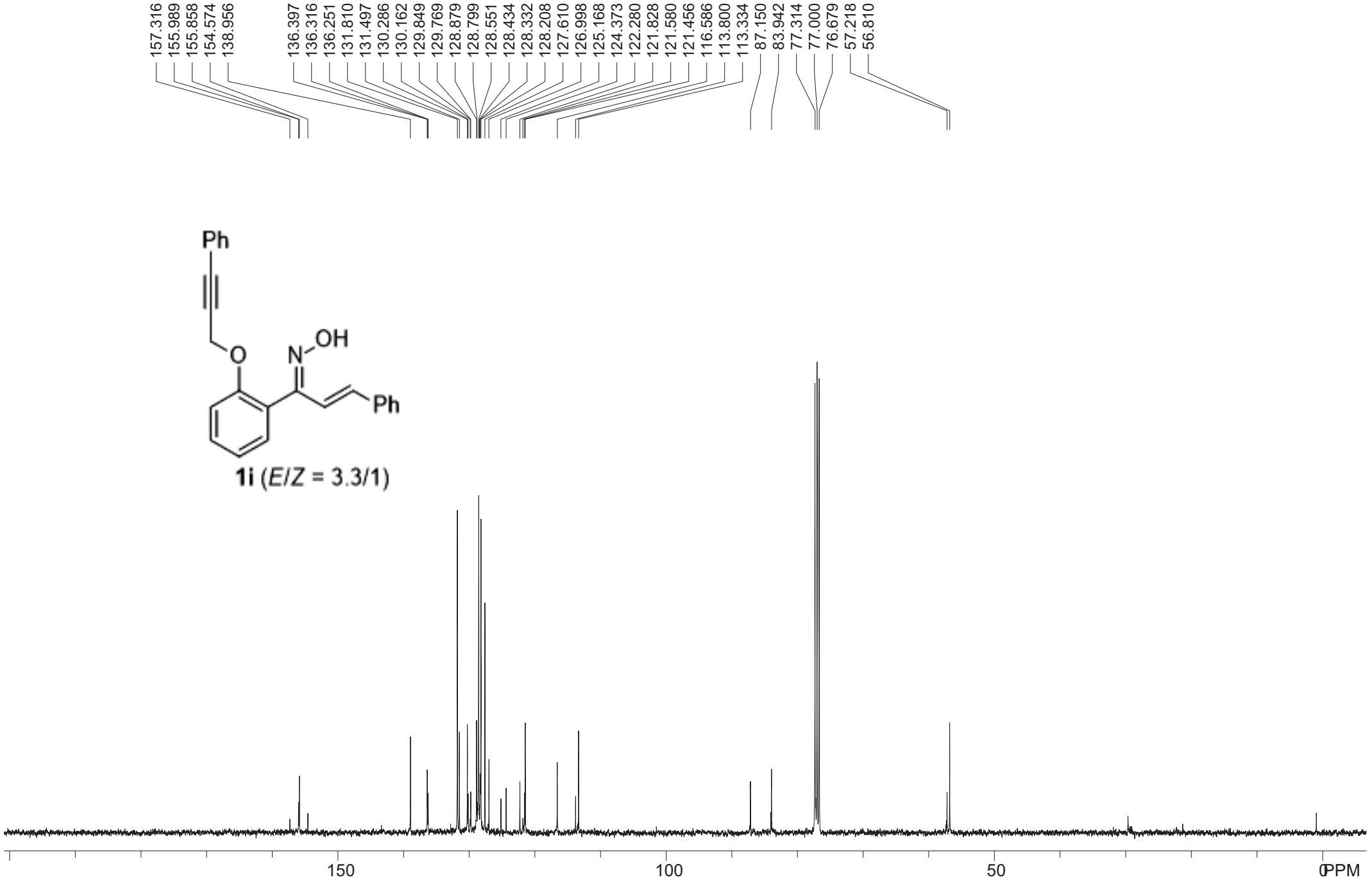

150
100
50
PPM


7.662
7.621
7.386
7.368
7.347
7.327
7.314
7.260
7.243
7.220
7.194
7.175
7.155
7.132
7.122
7.102
7.100
7.069
7.047
7.019
7.001
6.982
6.509
6.468
6.371
6.330
4.853
4.832
0.000

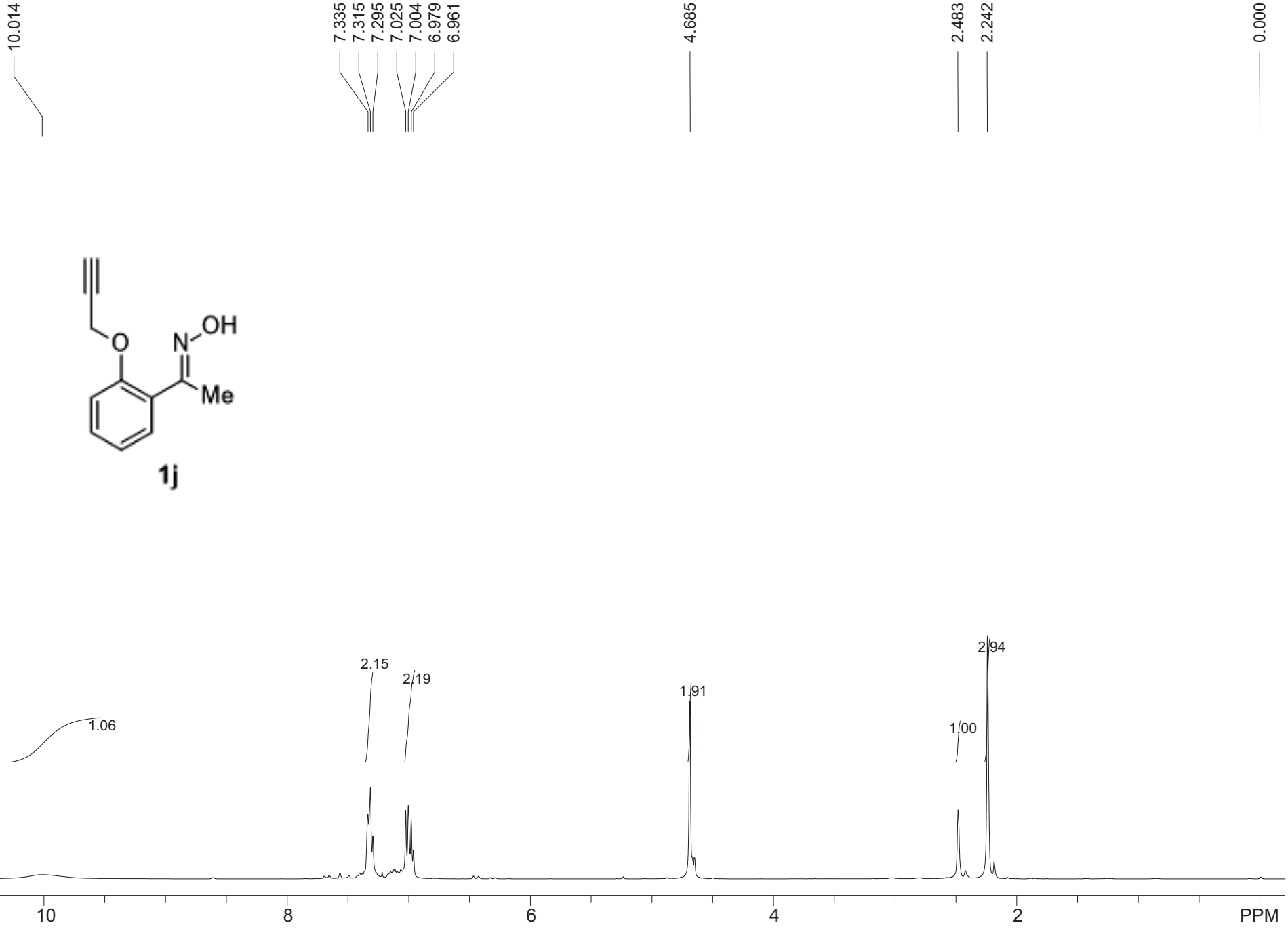

Ph
O
N
OH
Ph

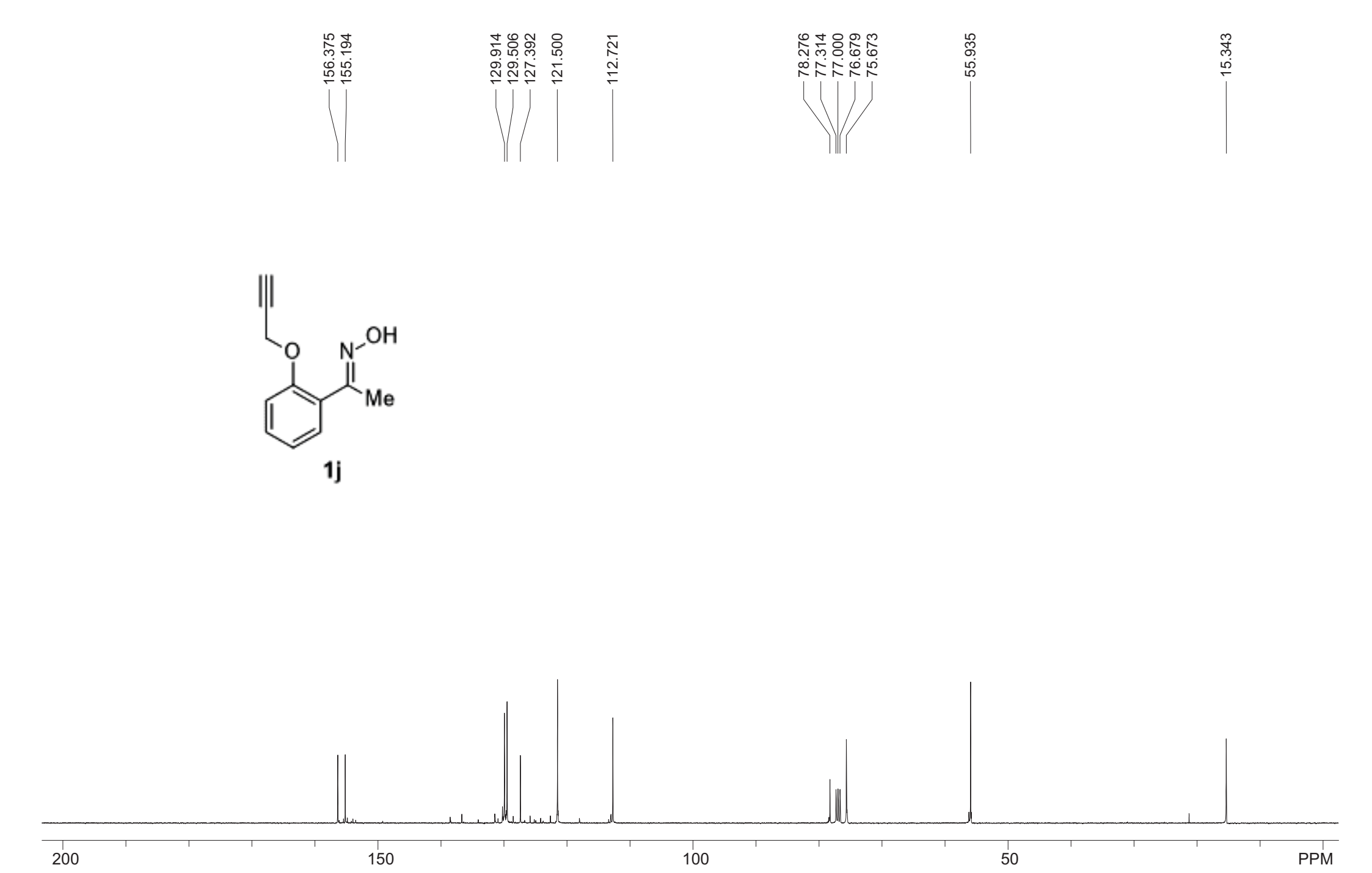
1i (*E*/*Z* = 3.3/1)

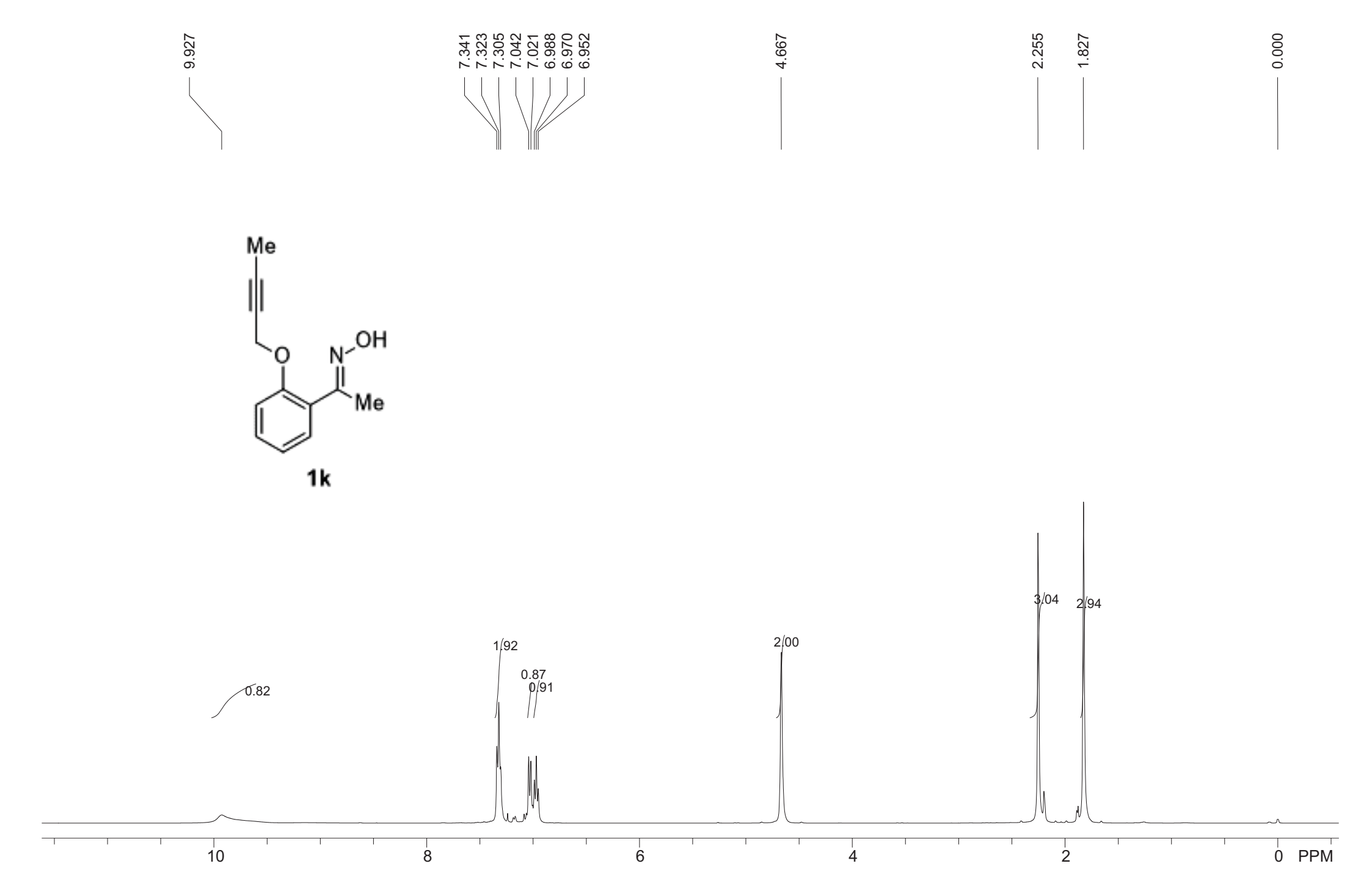

10.58
5.21
2.63
1.35
1.00
0.30
2.01
0.66
10
8
6
4
2
0
PPM

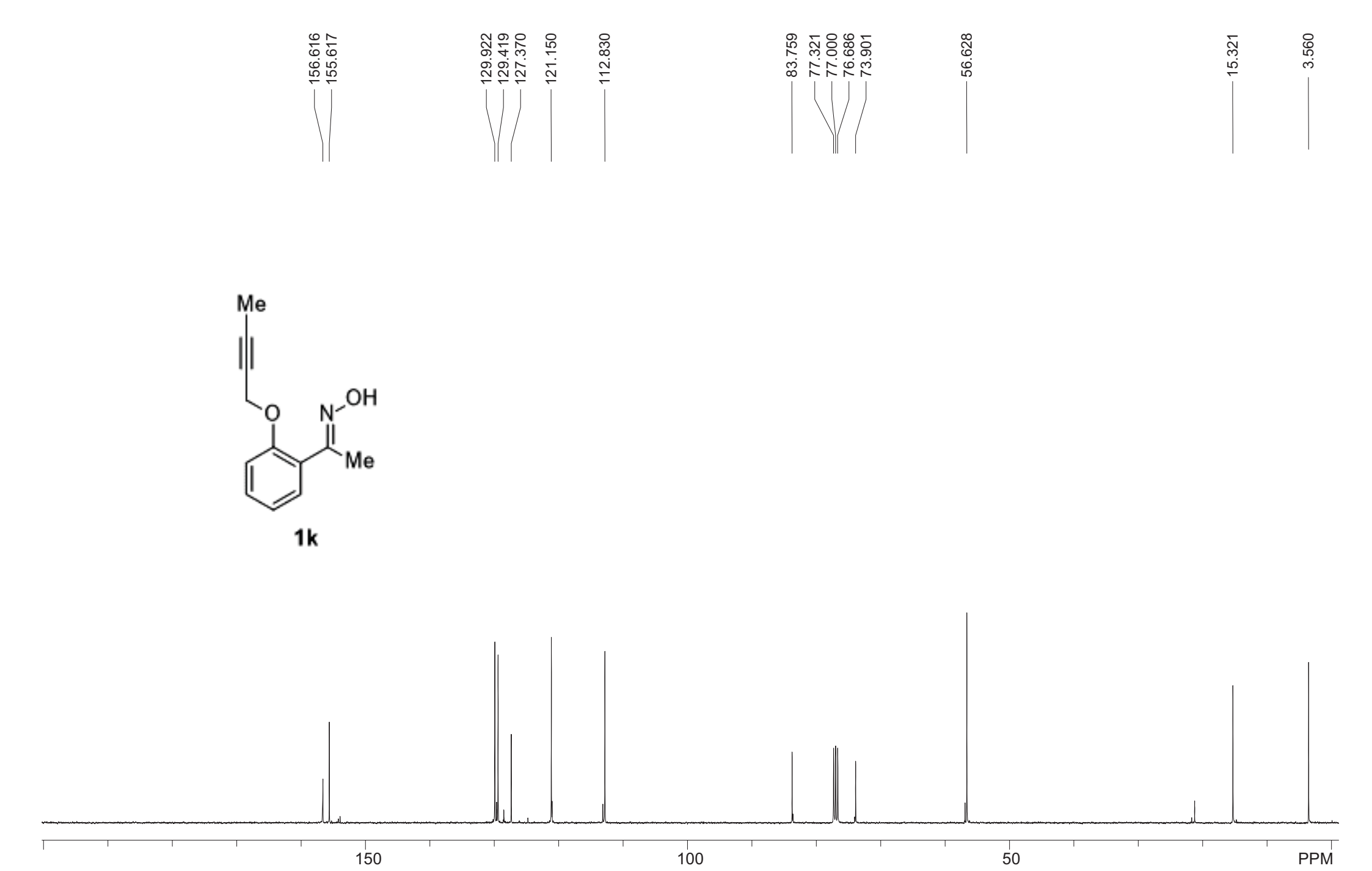

157.316
155.989
155.858
154.574
138.956
136.397
136.316
136.251
131.810
131.497
130.286
130.162
129.849
129.769
128.879
128.799
128.551
128.434
128.332
128.208
127.610
126.998
125.168
124.373
122.280
121.828
121.580
121.456
116.586
113.800
113.334
87.150
83.942
77.314
77.000
76.679
57.218
56.810
Ph
O
N
OH
Ph
150
100
50
0
PPM

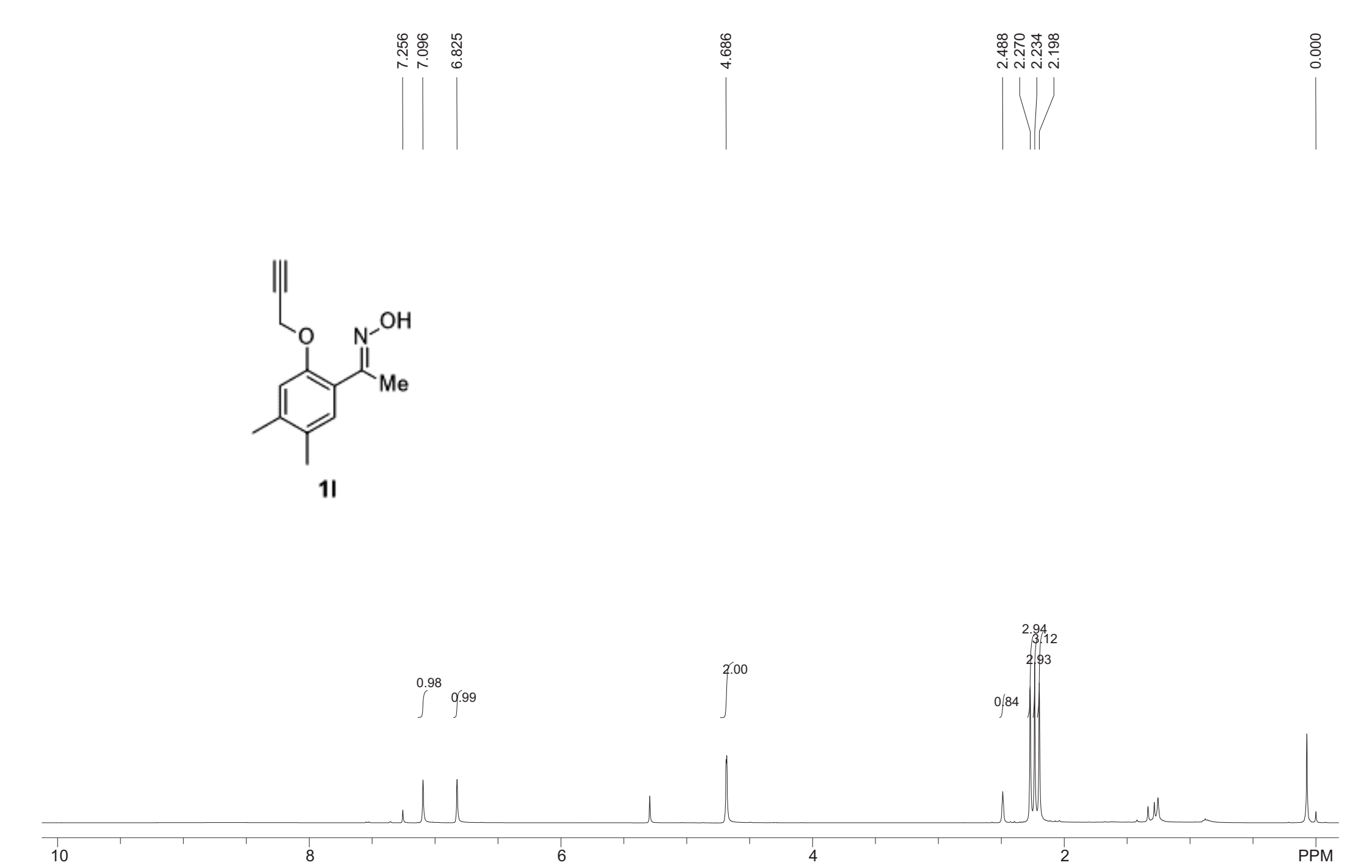
1i (*E*/*Z* = 3.3/1)

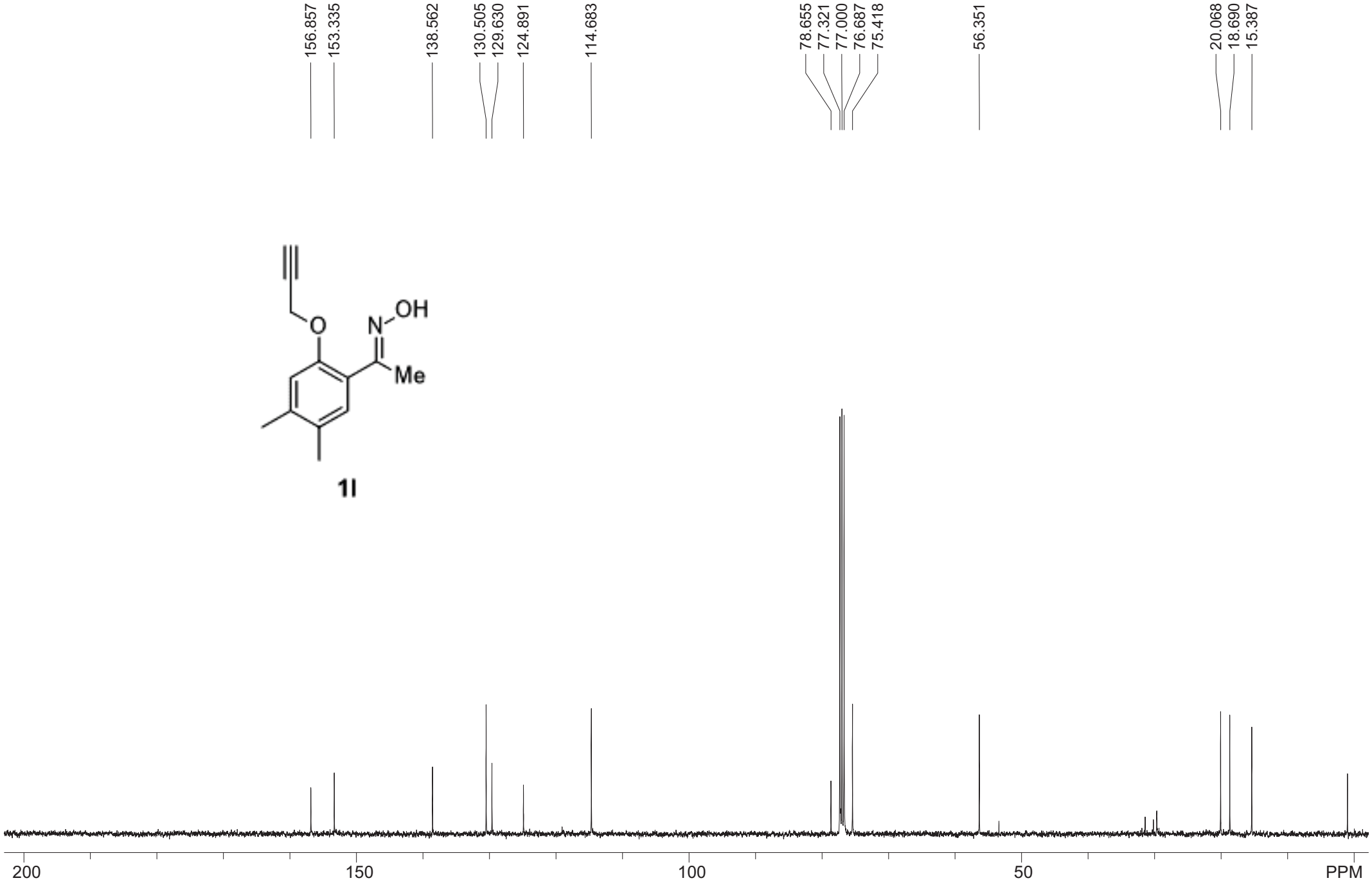

10.014
7.335
7.315
7.295
7.025
7.004
6.979
6.961
4.685
2.483
2.242
0.000
OH
N
O
Me
1j
1.06
2.15
2.19
1.91
1.00
2.94
10
8
6
4
2
PPM


156.375
155.194
129.914
129.506
127.392
121.500
112.721
78.276
77.314
77.000
76.679
75.673
55.935
15.343
O
N
OH
Me
1j
200
150
100
50
PPM

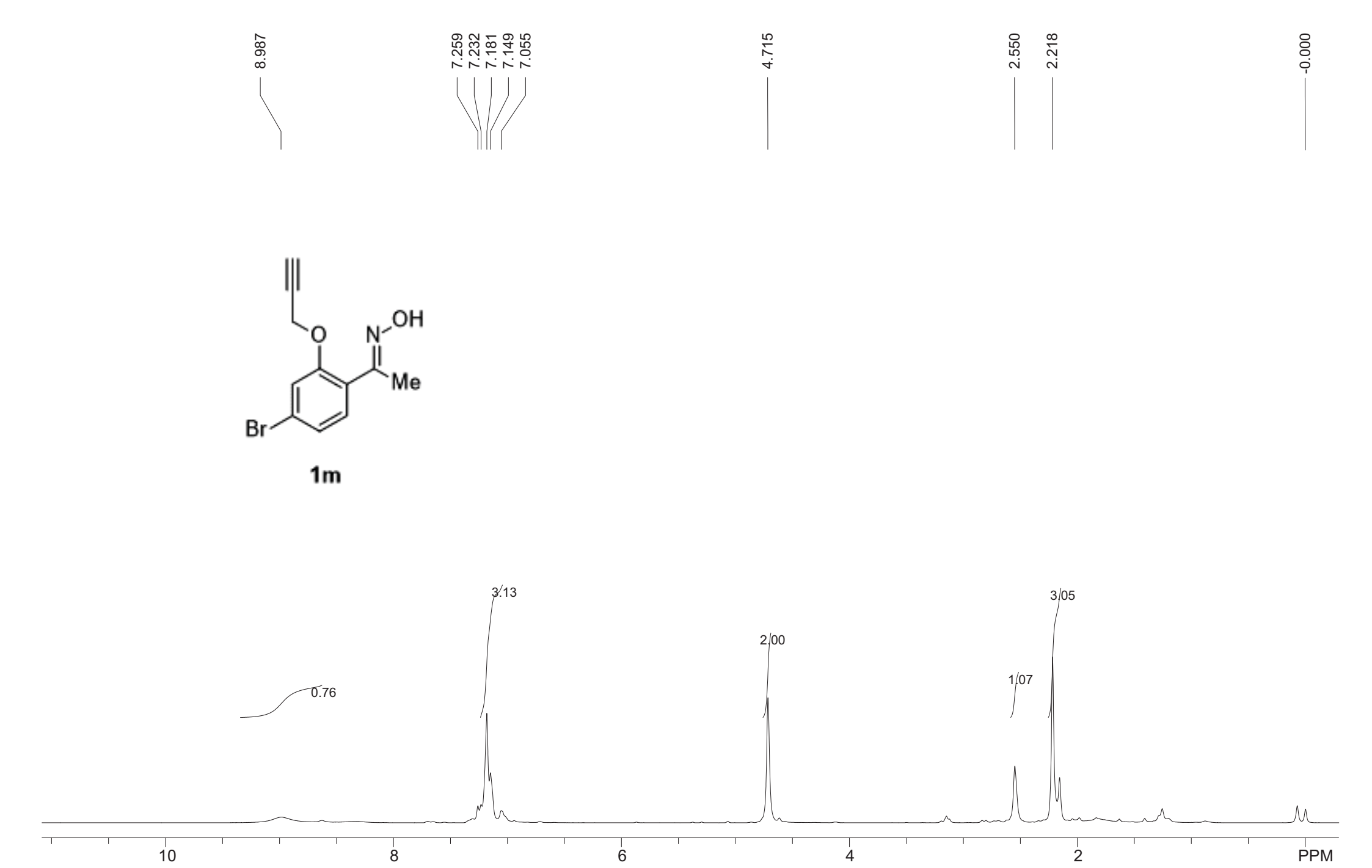

9.927
7.341
7.323
7.305
7.042
7.021
6.988
6.970
6.952
4.667
2.255
1.827
0.000
Me
O
N
OH
Me
1k
0.82
1.92
0.87
0.91
2.00
3.04
2.94
10
8
6
4
2
0
PPM

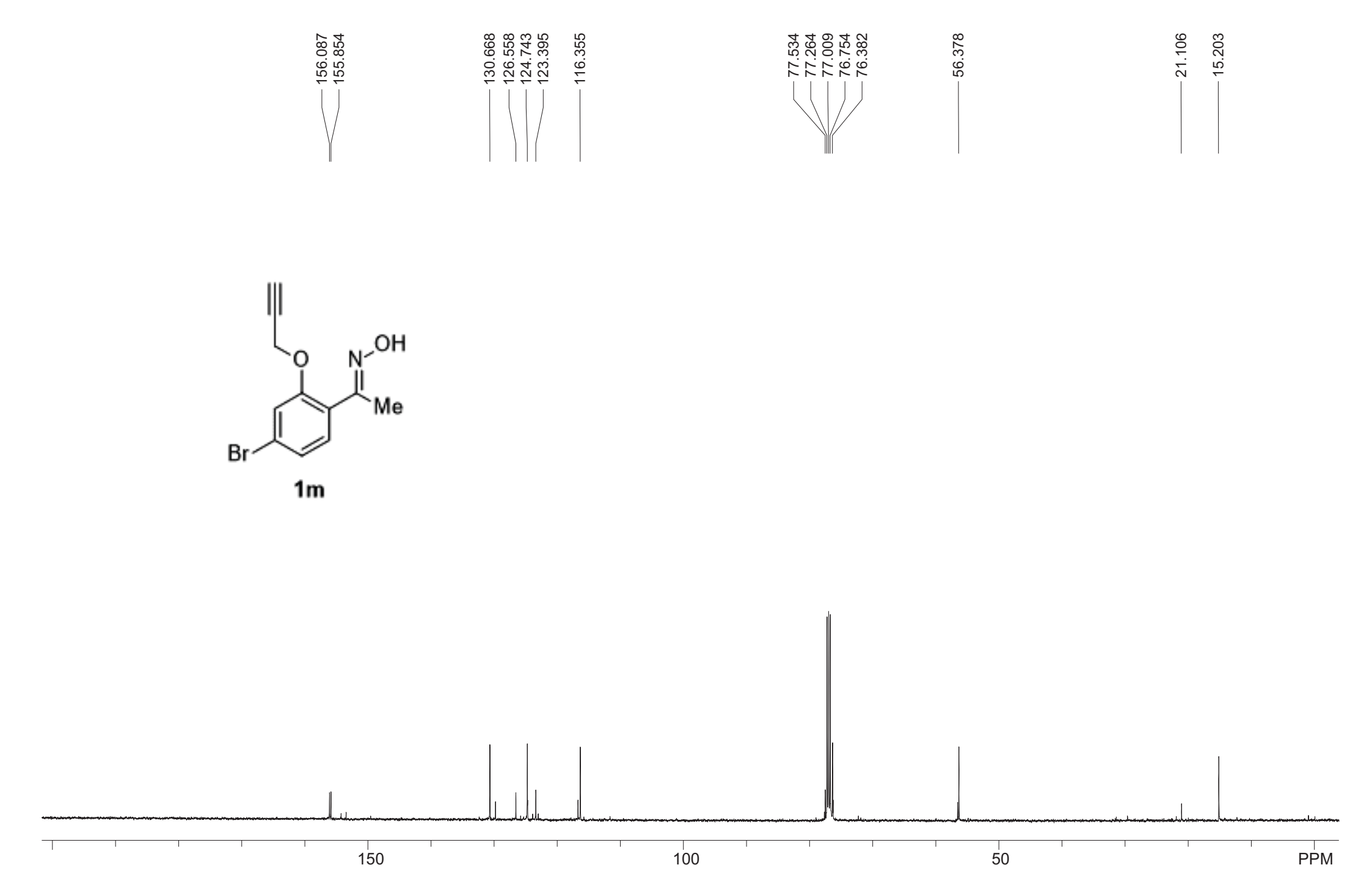

156.616
155.617
129.922
129.419
127.370
121.150
112.830
83.759
77.321
77.000
76.686
73.901
56.628
15.321
3.560
Me
O
N
OH
Me
1k
150
100
50
PPM

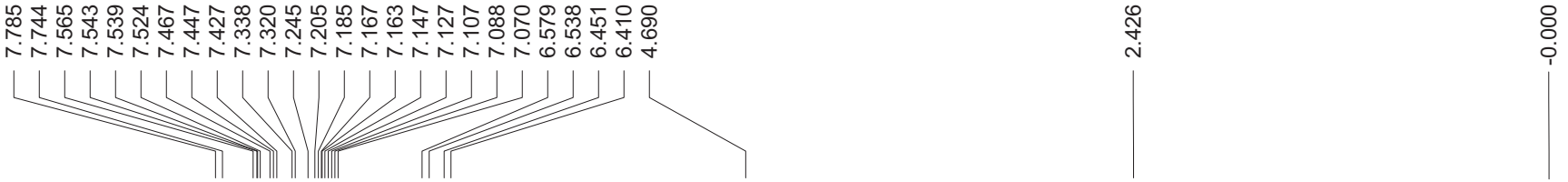

7.256
7.096
6.825
4.686
2.488
2.270
2.234
2.198
0.000
O
N
OH
Me
1l
0.98
0.99
2.00
0.84
2.94
3.12
2.93
10
8
6
4
2
PPM

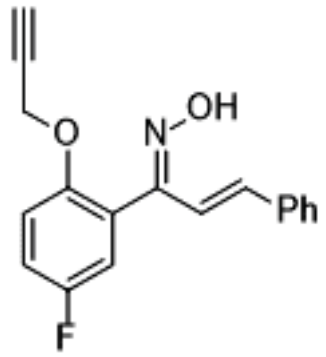

156.857
153.335
138.562
130.505
129.630
124.891
114.683
78.655
77.321
77.000
76.687
75.418
56.351
20.068
18.690
15.387
O
N
OH
Me
200
150
100
50
PPM

1l

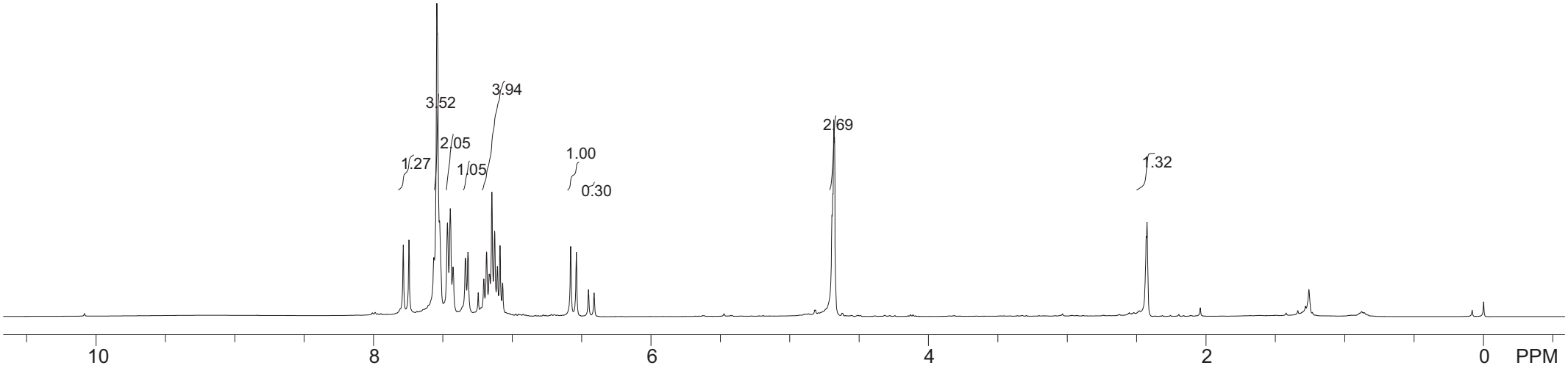

8.987
7.259
7.232
7.181
7.149
7.055
4.715
2.550
2.218
-0.000
O
N
OH
Me
Br
1m
0.76
3.13
2.00
1.07
3.05
10
8
6
4
2
PPM

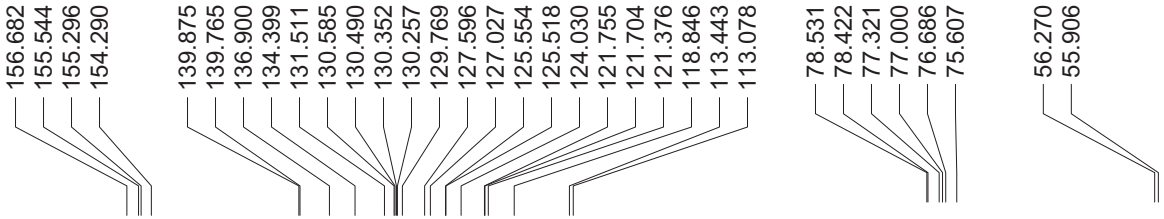

156.087
155.854
130.668
126.558
124.743
123.395
116.355
77.534
77.264
77.009
76.754
76.382
56.378
21.106
15.203
O
N
OH
Me
Br
1m
150
100
50
PPM

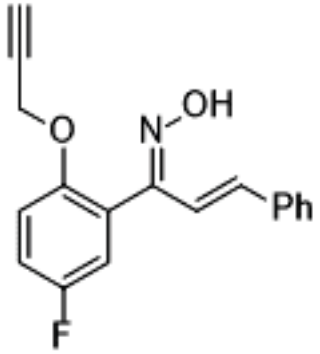

7.785
7.744
7.565
7.543
7.539
7.524
7.467
7.447
7.427
7.338
7.320
7.245
7.205
7.185
7.167
7.163
7.147
7.127
7.107
7.088
7.070
6.579
6.538
6.451
6.410
4.690
2.426
-0.000


O
N
OH
Ph
F

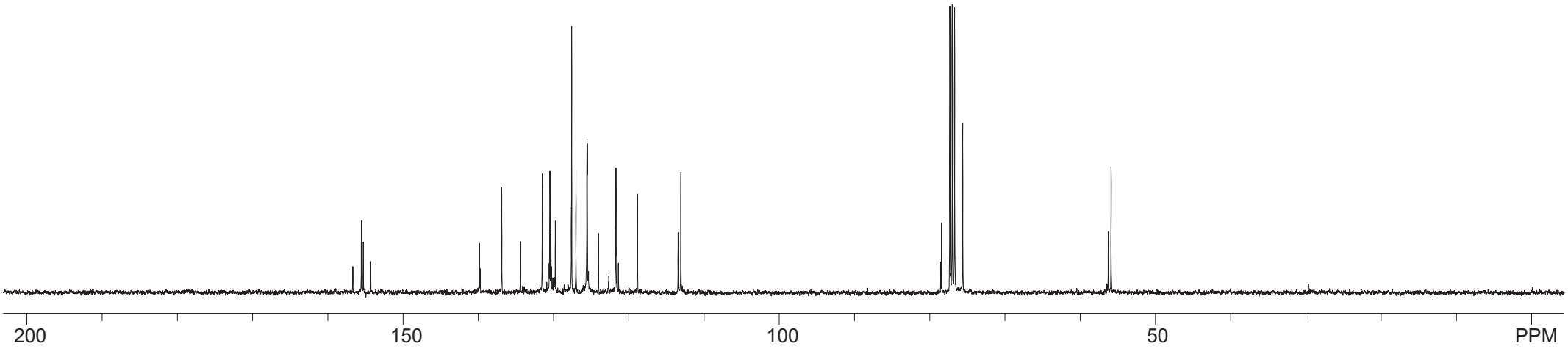
1n (*E*/*Z* = 3.3/1)

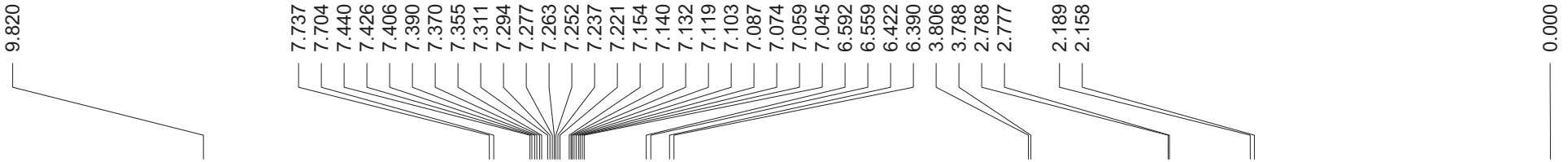

1.27
3.52
2.05
1.05
3.94
1.00
0.30
2.69
1.32
10
8
6
4
2
0
PPM

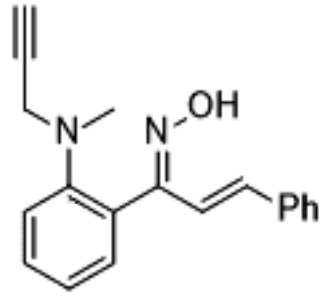

156.682
155.544
155.296
154.290
139.875
139.765
136.900
134.399
131.511
130.585
130.490
130.352
130.257
129.769
127.596
127.027
125.554
125.518
124.030
121.755
121.704
121.376
118.846
113.443
113.078
78.531
78.422
77.321
77.000
76.686
75.607
56.270
55.906


O
N
OH
Ph
F

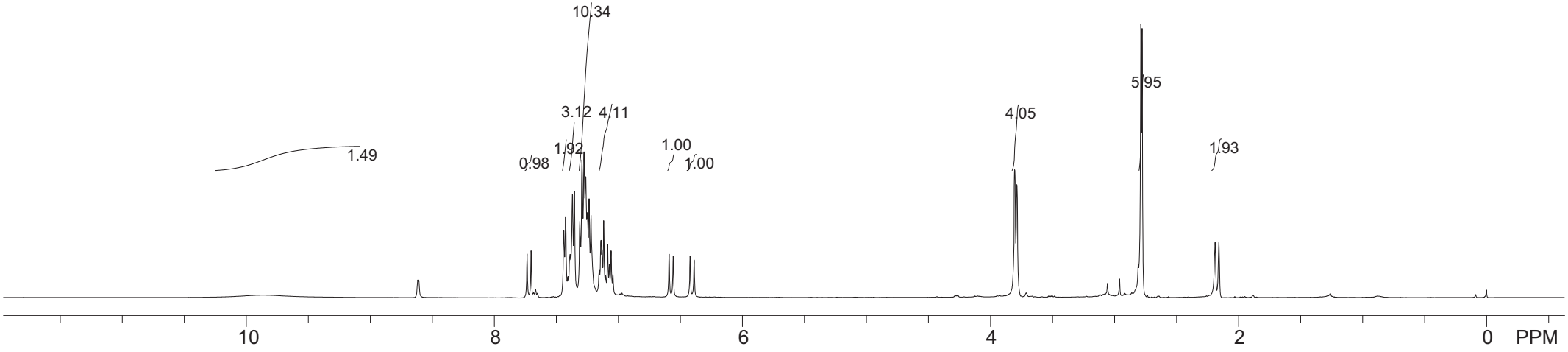
1n (*E*/*Z* = 3.3/1)

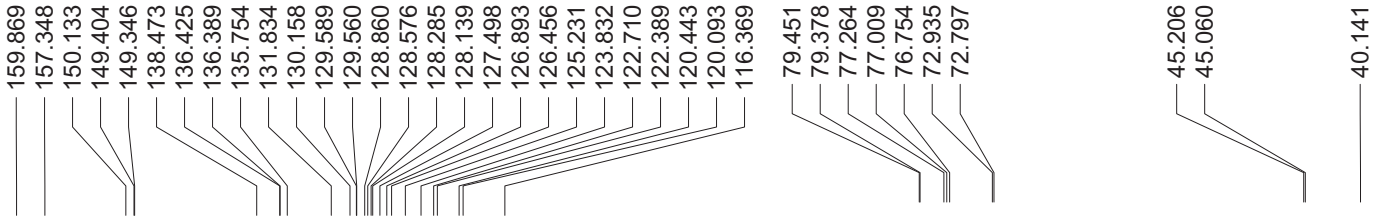

200
150
100
50
PPM

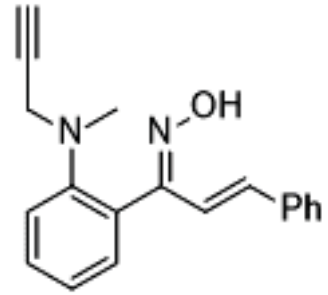

9.820
7.737
7.704
7.440
7.426
7.406
7.390
7.370
7.355
7.311
7.294
7.277
7.263
7.252
7.237
7.221
7.154
7.140
7.132
7.119
7.103
7.087
7.074
7.059
7.045
6.592
6.559
6.422
6.390
3.806
3.788
2.788
2.777
2.189
2.158
0.000


N
OH
N
Ph

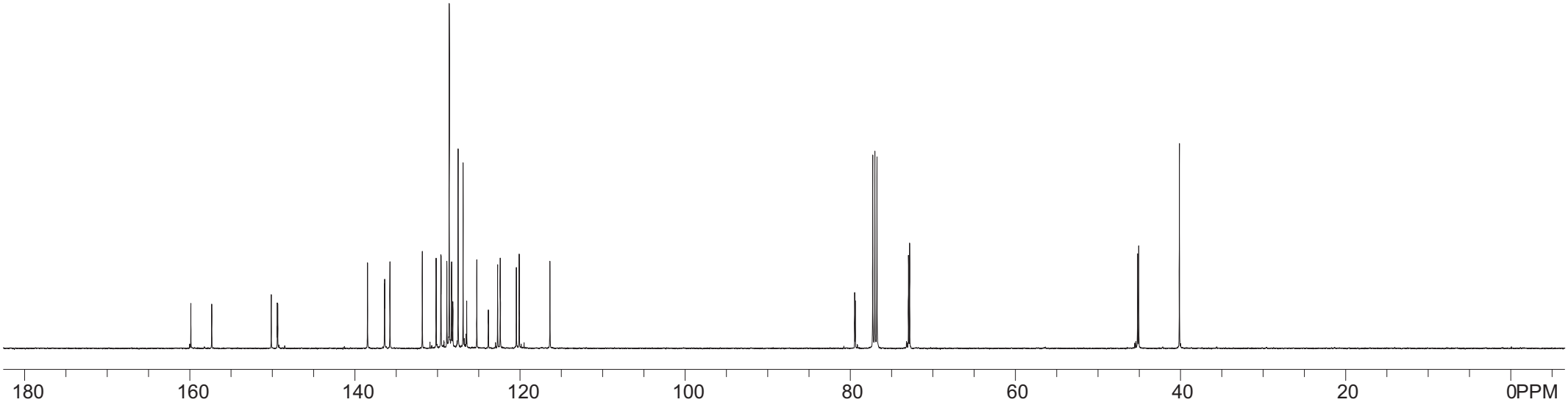
1o (*E*/*Z* = 1/1)

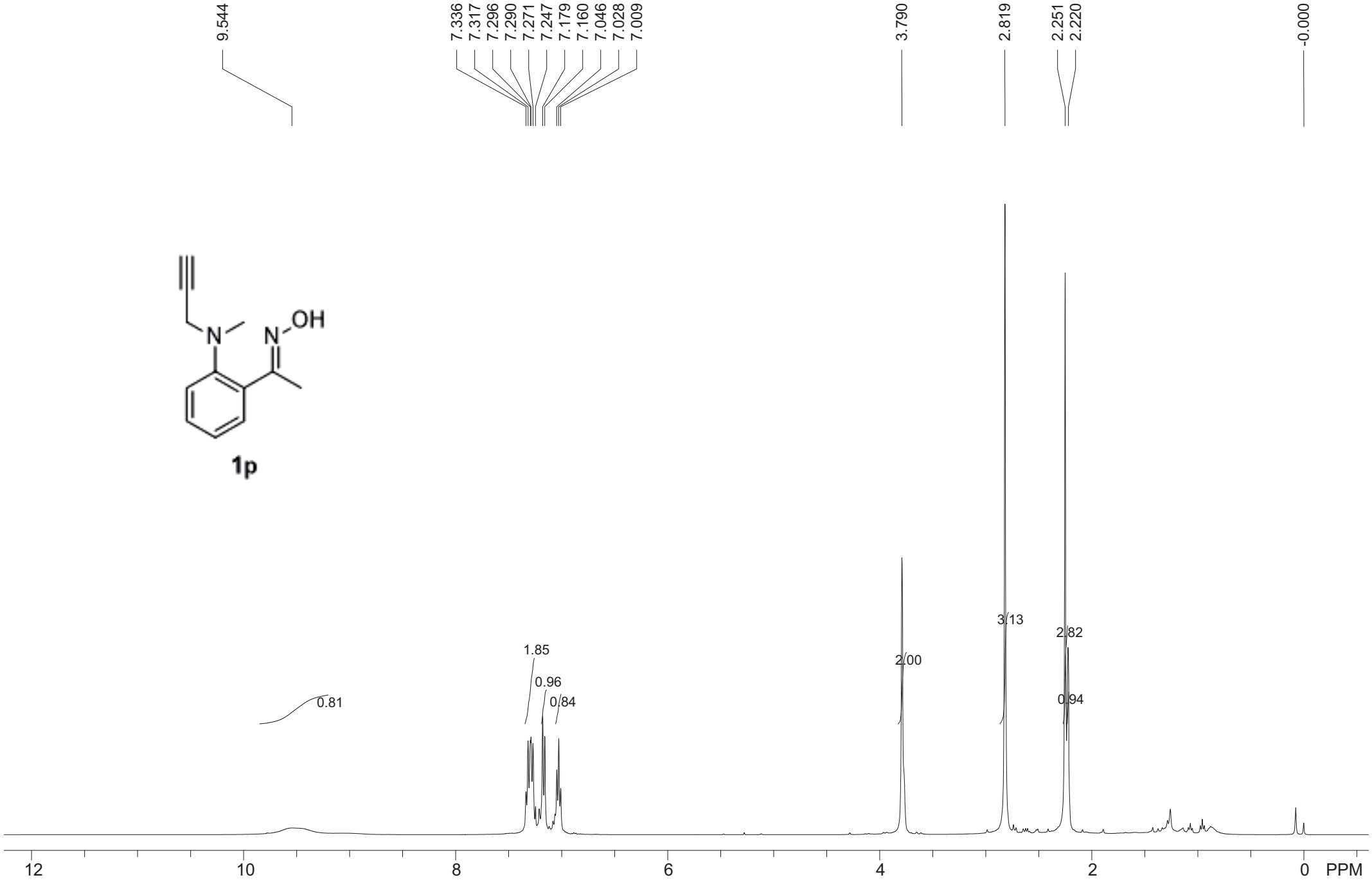

10.34
5.95
4.05
3.12
4.11
1.92
1.00
1.00
1.93
1.49
0.98
10
8
6
4
2
0
PPM

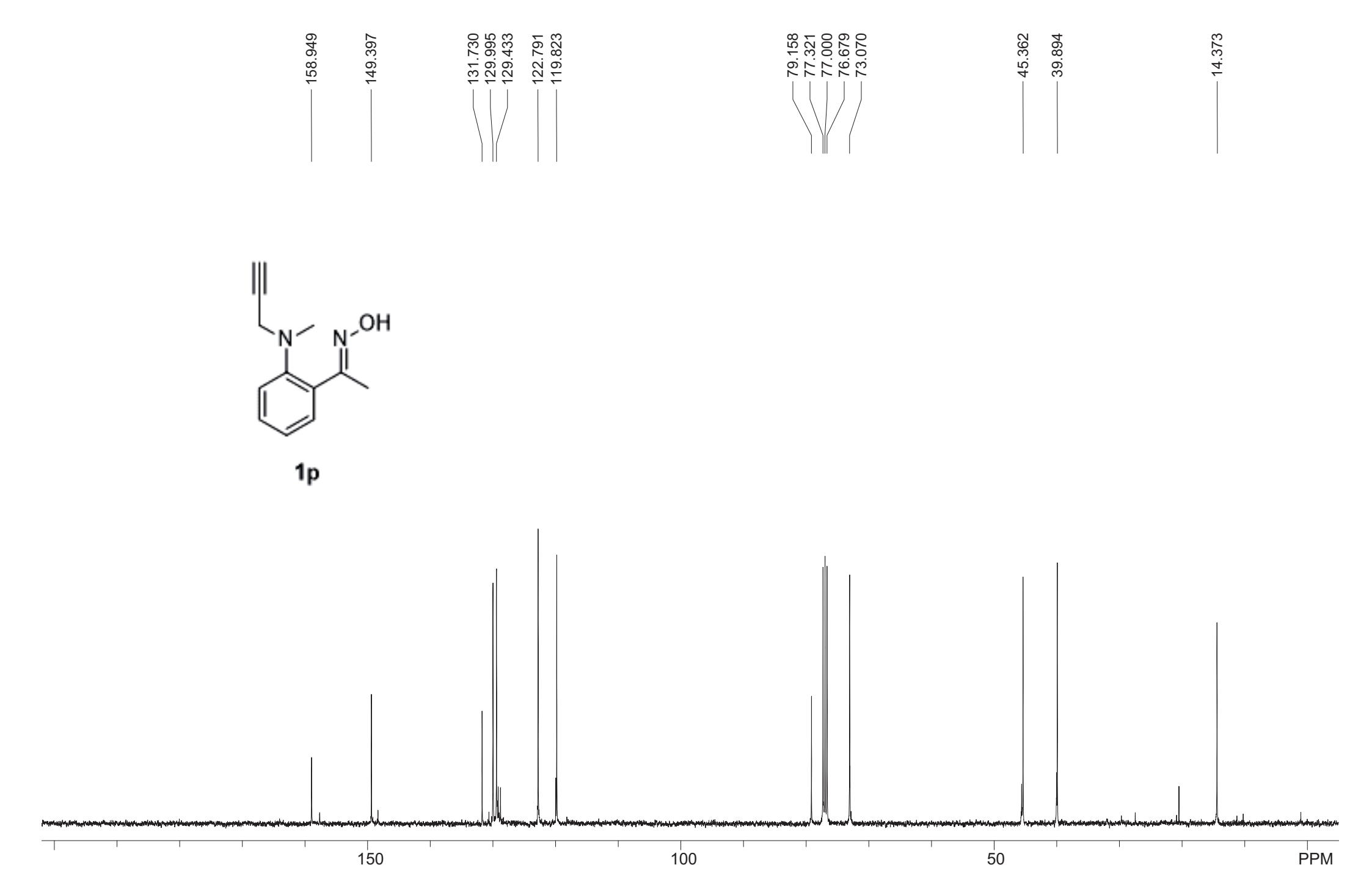

159.869
157.348
150.133
149.404
149.346
138.473
136.425
136.389
135.754
131.834
130.158
129.589
129.560
128.860
128.576
128.285
128.139
127.498
126.893
126.456
125.231
123.832
122.710
122.389
120.443
120.093
116.369
79.451
79.378
77.264
77.009
76.754
72.935
72.797
45.206
45.060
40.141


N
N
OH
Ph

1o (*E*/*Z* = 1/1)


180
160
140
120
100
80
60
40
20
0PPM


9.544
7.336
7.317
7.296
7.290
7.271
7.247
7.179
7.160
7.046
7.028
7.009
3.790
2.819
2.251
2.220
-0.000
N
N
OH
1p
0.81
1.85
0.96
0.84
2.00
3.13
2.82
0.94
12
10
8
6
4
2
0
PPM


158.949
149.397
131.730
129.995
129.433
122.791
119.823
79.158
77.321
77.000
76.679
73.070
45.362
39.894
14.373
N
N
OH
150
100
50
PPM

1p