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Pd-Catalyzed Cascade Allylic Alkylation and Dearomatization Reactions of Indoles with Vinyloxirane

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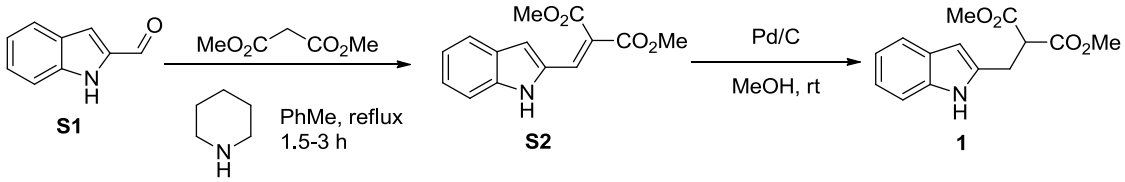
Table of Contents

General Methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

^{1}H spectra were recorded on a Varian (300MHz or 400 MHz) or Agilent instrument (400 MHz) and internally referenced to tetramethylsilane signal or residual solvent signals. ^{13}C NMR spectra were recorded on a Varian (100 MHz or 75 MHz) or Agilent instrument (100 MHz) and internally referenced to residual solvent signals. ^{19}F NMR spectra were recorded on a Varian or Agilent instrument (376 MHz) and referenced relative to $CFCl_3$. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling constant (s) in Hz, integration). Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ, ppm).

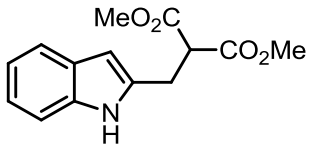
General Procedure for the Synthesis of the Substrates

The synthesis of substituted indoles **4** was accomplished following the reported procedures.

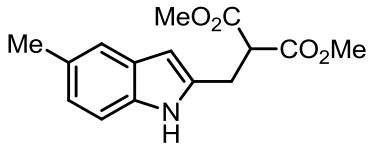


To a solution of Indole-2-carboxaldehyde **S3** (10.0 mmol, 1.0 equiv.) in PhMe (25 mL) was added dimethyl malonate (1.3 mL, 12.0 mmol, 1.2 equiv.) and piperidine (0.2 mL, 2.0 mmol, 0.2 equiv.). The reaction mixture was refluxed until completion (monitored by TLC). The solvent was removed under reduced pressure to give the crude product **S2**.

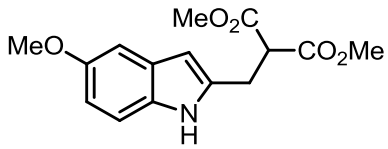
The crude **S2** obtained above was dissolved in MeOH (20 mL) in argon, and Pd/C (100 mg) was added to the solution. The reaction mixture was hydrogenated at room temperature after exchange hydrogen for three times. After the reaction was complete (monitored by TLC or LC-MS), the solution was then filtered and washed with EtOAc. The organic phase was filtered and concentrated in vacuo. The crude mixture was then purified by column chromatography on silica gel to afford product **1** (Hexane/EtOAc: 8/1-5/1).



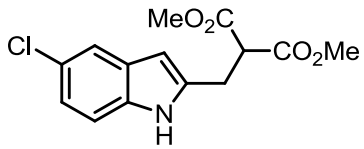
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (brs, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.14-7.10 (m, 1H), 7.07-7.03 (m, 1H), 6.26 (s, 1H), 3.76 (t, *J* = 7.2 Hz, 1H), 3.72 (s, 6H), 3.34 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 136.0, 135.0, 128.2, 121.5, 120.0, 119.6, 110.7, 101.0, 52.8, 52.1, 27.3; IR (film): ν_{max} (cm^{-1}) = 3370, 3035, 2946, 1728, 1587, 1548, 1442, 1336, 1292, 1244, 1184, 1021, 922, 835, 783, 745; HRMS (ESI): Exact mass calcd. for $C_{14}H_{16}NO_4$ ($[M+H]^+$): 262.1074. Found: 262.1076.



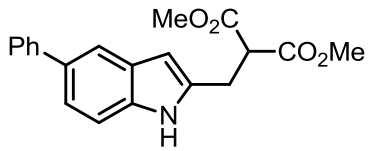
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (brs, 1H), 7.31 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.19 (s, 1H), 3.744-3.739 (m, 1H), 3.74 (s, 6H), 3.33 (d, *J* = 7.2 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 135.1, 134.3, 128.8, 128.5, 123.1, 119.7, 110.3, 100.6, 52.8, 52.2, 27.4, 21.4; IR (film): v_{max} (cm^{-1}) = 3671, 3377, 2985, 2910, 1725, 1430, 1334, 1290, 1214, 1170, 991, 862, 787; HRMS (ESI): Exact mass calcd. for $C_{15}H_{18}NO_4$ ($[M+H]^+$): 276.1230. Found: 276.1233.



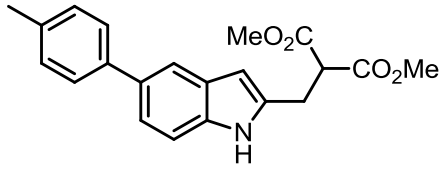
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (brs, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 2.0 Hz, 1H), 6.79 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.20 (s, 1H), 3.83 (s, 3H), 3.76-3.73 (m, 1H), 3.75 (s, 6H), 3.33 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 154.0, 135.7, 131.2, 128.7, 111.6, 111.3, 101.9, 101.0, 55.8, 52.9, 52.2, 27.4; IR (film): v_{max} (cm^{-1}) = 3662, 3364, 2985, 2911, 1726, 1439, 1333, 1237, 1175, 1075, 1032, 995, 836, 787, 715; HRMS (ESI): Exact mass calcd. for $C_{15}H_{18}NO_5$ ($[M+H]^+$): 292.1179. Found: 292.1181.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (brs, 1H), 7.47 (s, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.08-7.06 (m, 1H), 6.21 (s, 1H), 3.78-3.74 (m, 1H), 3.74 (s, 6H), 3.33 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 136.5, 134.4, 129.3, 125.2, 121.8, 119.4, 111.7, 100.9, 52.9, 51.9, 27.2; IR (film): v_{max} (cm^{-1}) = 3661, 3359, 2994, 2945, 1726, 1578, 1442, 1291, 1240, 1185, 1069, 1039, 916, 853, 778, 727; HRMS (ESI): Exact mass calcd. for $C_{14}H_{15}ClNO_4$ ($[M+H]^+$): 296.0684. Found: 296.0687.

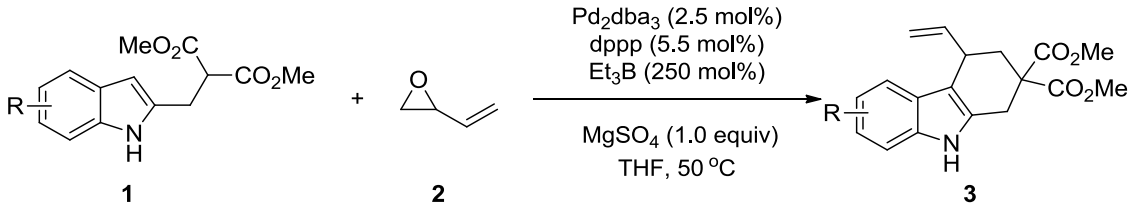


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.73 (s, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.41-7.35 (m, 3H), 7.30-7.27 (m, 2H), 6.29 (s, 1H), 3.77 (t, *J* = 7.2 Hz, 1H), 3.70 (s, 6H), 3.32 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 142.4, 135.7, 135.5, 133.0, 128.7, 128.5, 127.2, 126.1, 121.3, 118.4, 110.9, 101.3, 52.8, 51.9, 27.3; IR (film): v_{max} (cm^{-1}) = 3296, 3029, 2952, 1720, 1432, 1298, 1236, 1200, 1161, 1080, 1023, 916, 844, 760, 692; HRMS (ESI): Exact mass calcd. for $C_{20}H_{20}NO_4$ ($[M+H]^+$): 338.1387. Found: 338.1390.

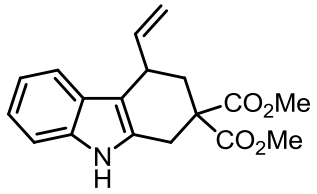


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.71 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.36 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.30 (s, 1H), 3.76 (t, *J* = 7.2 Hz, 1H), 3.72 (s, 6H), 3.34 (d, *J* = 6.8 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 139.6, 135.7, 135.6, 135.4, 133.0, 129.2, 128.7, 127.0, 121.2, 118.2, 110.8, 101.2, 52.8, 52.0, 27.3, 20.9; IR (film): v_{max} (cm^{-1}) = 3667, 3331, 2976, 2919, 1722, 1440, 1297, 1236, 1172, 1073, 1034, 993, 912, 839, 789, 673; HRMS (ESI): Exact mass calcd. for $C_{21}H_{22}NO_4$ ($[M+H]^+$): 352.1543. Found: 352.1546.

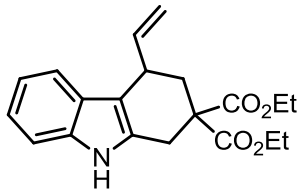
General Procedures for Pd-Catalyzed cascade Reaction of Indoles with Vinyloxirane



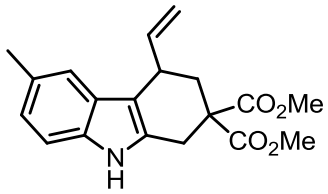
A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added Pd_2dba_3 (4.6 mg, 0.005 mmol, 2.5 mol%), 1,3-bis(diphenylphosphino)propane (4.5 mg, 0.011 mmol, 5.5 mol%), and THF (1.0 mL). The reaction mixture was stirred at room temperature for 30 min. After that, substrate **1** (0.2 mmol), vinyloxirane **2** (15.4 mg, 0.22 mmol, 110 mol%), $MgSO_4$ (24.0 mg, 0.2 mmol, 100 mol%), Et_3B (0.5 mL, 250 mol%, 1.0 M in THF) and THF (1.0 mL) were added. The reaction mixture was stirred at 50 ^oC. After the reaction was complete (monitored by TLC or LC-MS), the reaction was filtered through celite and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the desired product (Hexane/EtOAc: 6/1-5/1).



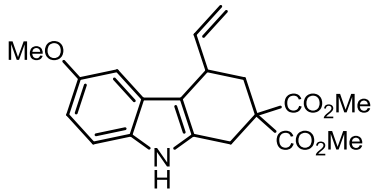
3a: colorless oil, 50.9 mg, 82% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (brs, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 5.80-5.72 (m, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 5.09 (d, *J* = 10.4 Hz, 1H), 3.67 (s, 3H), 3.67-3.63 (m, 1H), 3.60 (s, 3H), 3.30 (AB, J_{AB} = 16.0 Hz, 1H), 3.12 (BA, J_{BA} = 14.8 Hz, 1H), 2.60 (dd, *J* = 13.2, 5.6 Hz, 1H), 2.00 (dd, *J* = 13.6, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 170.9, 141.2, 136.2, 131.0, 127.0, 121.2, 119.4, 119.1, 115.5, 110.6, 109.5, 54.2, 52.89, 52.87, 36.2, 36.0, 29.1; IR (film): v_{max} (cm^{-1}) = 3341, 2955, 2922, 2852, 1714, 1620, 1449, 1333, 1287, 1071, 1045, 968, 880, 746; HRMS (ESI): Exact mass calcd. for $C_{18}H_{20}NO_4$ ($[M+H]^+$): 314.1387. Found: 314.1390.



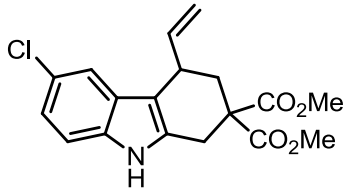
3b: colorless oil, 56.0 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (brs, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 5.82-5.73 (m, 1H), 5.22 (d, *J* = 16.8 Hz, 1H), 5.09 (d, *J* = 10.0 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 4.06 (q, *J* = 7.2 Hz, 2H), 3.65 (dd, *J* = 15.6, 8.8 Hz, 1H), 3.31 (AB, J_{AB} = 16.0 Hz, 1H), 3.10 (dd, *J* = 16.0, 1.6 Hz, 1H), 2.60 (dd, *J* = 13.2, 5.6 Hz, 1H), 1.97 (dd, *J* = 13.6, 10.0 Hz, 1H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 170.3, 141.4, 136.2, 131.2, 127.0, 121.2, 119.4, 119.0, 115.4, 110.6, 109.6, 61.7, 61.6, 54.2, 36.3, 36.0, 29.0, 13.95, 13.93; IR (film): v_{max} (cm^{-1}) = 3386, 2925, 2853, 1725, 1619, 1488, 1464, 1367, 1245, 1185, 1095, 918, 746; HRMS (ESI): Exact mass calcd. for $C_{20}H_{24}NO_4$ ($[M+H]^+$): 342.1700. Found: 342.1698.



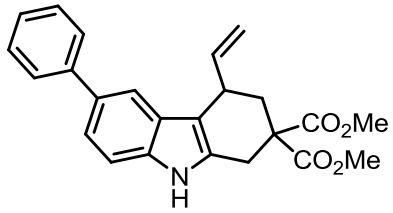
3c: yellow oil, 44.0 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (brs, 1H), 7.22 (s, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 5.81-5.72 (m, 1H), 5.21 (d, *J* = 16.8 Hz, 1H), 5.09 (d, *J* = 10.0 Hz, 1H), 3.67 (s, 3H), 3.60 (s, 4H), 3.67-3.60 (m, 1H), 3.29 (AB, J_{AB} = 16.0 Hz, 1H), 3.12 (BA, J_{BA} = 16.0 Hz, 1H), 2.59 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.32 (s, 3H), 1.98 (dd, *J* = 12.8, 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 170.8, 141.3, 134.5, 131.1, 128.3, 127.3, 122.7, 119.2, 115.5, 110.3, 109.2, 54.2, 52.9, 52.8, 36.2, 36.1, 29.1, 21.5; IR (film): v_{max} (cm^{-1}) = 3398, 2953, 1729, 1635, 1433, 1249, 1047, 915, 796; HRMS (ESI): Exact mass calcd. for $C_{19}H_{22}NO_4$ ($[M+H]^+$): 328.1543. Found: 328.1546.



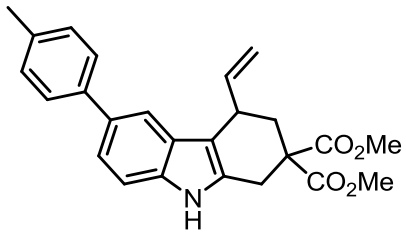
3d: yellow oil, 50.7 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (brs, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 2.0 Hz, 1H), 6.75 (dd, *J* = 8.8, 2.0 Hz, 1H), 5.87-5.79 (m, 1H), 5.29 (d, *J* = 16.8 Hz, 1H), 5.17 (d, *J* = 10.0 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.75-3.69 (m, 1H), 3.69 (s, 3H), 3.37 (AB, J_{AB} = 16.0 Hz, 1H), 3.19 (BA, J_{BA} = 17.2 Hz, 1H), 2.67 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.07 (dd, *J* = 13.2, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 170.8, 153.5, 141.1, 131.9, 131.3, 127.4, 115.5, 111.2, 110.7, 109.3, 102.0, 55.8, 54.1, 52.88, 52.86, 36.2, 36.0, 29.2; IR (film): ν_{max} (cm^{-1}) = 3663, 3388, 2985, 2939, 1736, 1444, 1297, 1211, 1055, 975, 914, 846, 760; HRMS (ESI): Exact mass calcd. for $C_{19}H_{22}NO_5$ ($[M+H]^+$): 344.1492. Found: 344.1495.



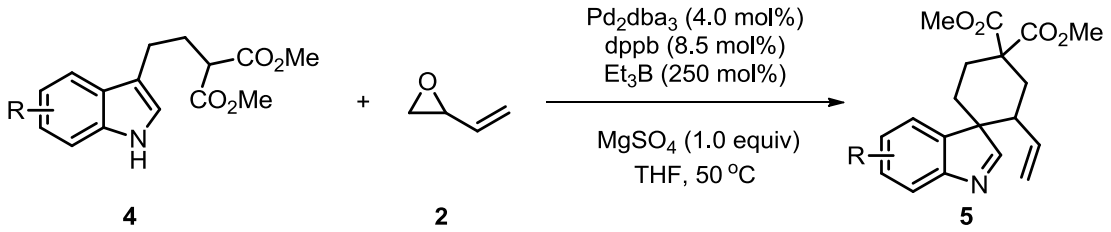
3e: yellow solid, 56.0 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (brs, 1H), 7.46 (d, *J* = 1.6 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.01 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.81-5.78 (m, 1H), 5.27 (d, *J* = 17.2 Hz, 1H), 5.19 (dd, *J* = 10.0, 0.8 Hz, 1H), 3.76 (s, 3H), 3.70 (s, 3H), 3.65 (dd, *J* = 15.6, 8.4 Hz, 1H), 3.36 (AB, J_{AB} = 16.4 Hz, 1H), 3.17 (dd, *J* = 16.4, 2.0 Hz, 1H), 2.67 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.07 (dd, *J* = 13.6, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 170.9, 140.6, 134.5, 132.6, 128.0, 124.7, 121.4, 118.8, 116.0, 111.5, 109.3, 54.0, 53.0, 52.9, 36.0, 35.9, 29.1; IR (film): ν_{max} (cm^{-1}) = 3375, 2989, 2942, 2862, 1727, 1438, 1337, 1239, 1051, 922, 869, 790; HRMS (ESI): Exact mass calcd. for $C_{18}H_{19}ClNO_4$ ($[M+H]^+$): 348.0997. Found: 348.0999.



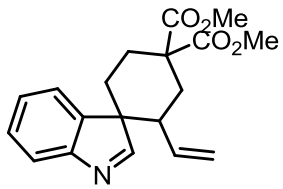
3f: yellow solid, 69.1 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (brs, 1H), 7.74 (s, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.34-7.20 (m, 3H), 5.91-5.83 (m, 1H), 5.31 (d, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 10.0 Hz, 1H), 3.78-3.75 (m, 1H), 3,75 (s, 3H), 3.69 (s, 3H), 3.38 (AB, J_{AB} = 16.4 Hz, 1H), 3.20 (BA, J_{BA} = 16.0 Hz, 1H), 2.70 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.10 (dd, *J* = 13.2, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 170.9, 142.6, 141.1, 135.7, 132.7, 131.8, 128.5, 127.5, 127.3, 126.1, 121.0, 118.0, 115.7, 110.8, 109.9, 54.2, 52.9, 36.2, 36.0, 29.1; IR (film): v_{max} (cm^{-1}) = 3401, 1731, 1464, 1251, 1058, 916, 814, 757, 700; HRMS (ESI): Exact mass calcd. for $C_{24}H_{24}NO_4$ ($[M+H]^+$): 390.1700. Found: 390.1702.



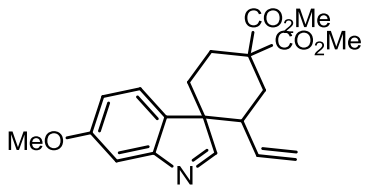
3g: yellow solid, 61.0 mg, 76% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (brs, 1H), 7.71 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.32 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.23 (m, 3H), 5.89-5.84 (m, 1H), 5.31 (d, *J* = 16.8 Hz, 1H), 5.17 (dd, *J* = 10.0, 1.2 Hz, 1H), 3.75 (s, 3H), 3.75-3.69 (m, 1H), 3.69 (s, 3H), 3.39 (AB, J_{AB} = 16.0 Hz, 1H), 3.21 (dd, *J* = 16.0, 2.0 Hz, 1H), 2.69 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.38 (s, 3H), 2.09 (dd, *J* = 13.6, 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 170.9, 141.1, 139.8, 135.8, 135.6, 132.7, 131.7, 129.3, 127.5, 127.2, 121.0, 117.8, 115.7, 110.8, 109.9, 54.2, 52.9, 36.2, 36.1, 29.1, 21.0; IR (film): v_{max} (cm^{-1}) = 3661, 3391, 2986, 2920, 1732, 1439, 1289, 1239, 1056, 974, 917, 769; HRMS (ESI): Exact mass calcd. for $C_{25}H_{26}NO_4$ ($[M+H]^+$): 404.1856. Found: 404.1858.



A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added Pd_2dba_3 (7.4 mg, 0.008 mmol, 4.0 mol%), 1,4-bis(diphenylphosphino)butane (7.3 mg, 0.017 mmol, 8.5 mol%), and THF (1.0 mL). The reaction mixture was stirred at room temperature for 30 min. After that, substrate **1** (0.2 mmol), vinyloxirane **2** (15.4 mg, 0.22 mmol, 110 mol%), $MgSO_4$ (24.0 mg, 0.2 mmol, 100 mol%), Et_3B (0.5 mL, 250 mol%, 1.0 M in THF) and THF (1.0 mL) were added. The reaction mixture was stirred at 50 ^oC. After the reaction was complete (monitored by TLC or LC-MS), the reaction was filtered through celite and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the desired product (Hexane/EtOAc: 6/1-4/1).

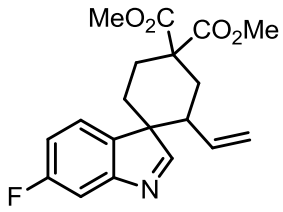


5a: colorless oil, 57.6 mg, 80/20 dr, 88% yield. ^1H NMR (400 MHz, $CDCl_3$) (chemical shifts marked with asterisk are of minor diastereomer) δ 8.32 (s, 1H), 7.79 (s, 1H*), 7.54 (d, *J* = 7.6 Hz, 1H), 7.27-7.24 (m, 1H), 7.19-7.13 (m, 2H), 5.00-4.90 (m, 1H), 4.71 (d, *J* = 17.2 Hz, 1H), 4.61 (d, *J* = 10.4 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H*), 3.71 (s, 3H), 2.72-2.67 (m, 1H), 2.60-2.50 (m, 2H), 2.10-2.01 (m, 3H), 1.40-1.35 (m, 1H).

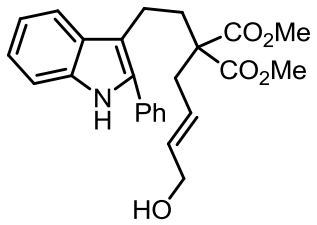


5b: colorless oil, 60.1 mg, 78/22 dr, 84% yield. ^1H NMR (400 MHz, $CDCl_3$)

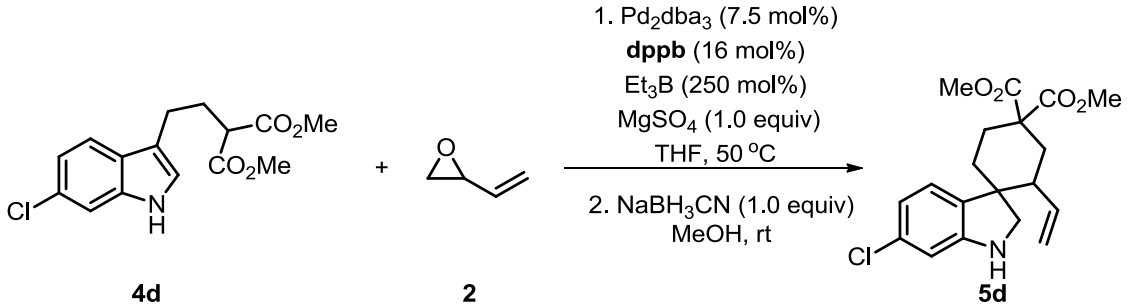
(chemical shifts marked with asterisk are of minor diastereomer) δ 8.33 (s, 1H), 7.80 (s, 1H*), 7.11 (d, *J* = 2.0 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.73 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.02-4.93 (m, 1H), 4.72 (d, *J* = 17.2 Hz, 1H), 4.63 (d, *J* = 10.4 Hz, 1H), 3.78 (s, 3H), 3.770 (s, 3H*), 3.765 (s, 3H*), 3.72 (s, 3H*), 3.71 (s, 3H), 2.69-2.63 (m, 1H), 2.59-2.48 (m, 2H), 2.07-1.94 (m, 4H), 1.39-1.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 172.1, 170.9, 159.9, 155.8, 135.4, 121.4, 116.6, 112.4, 106.6, 55.43, 55.40, 54.7, 52.9, 52.8, 42.8, 34.5, 30.1, 29.7; IR (film): ν_{max} (cm^{-1}) = 3643, 3467, 3075, 2999, 2950, 2850, 1730, 1614, 1474, 1444, 1233, 1140, 1095, 1023, 920, 854, 736; HRMS (ESI): Exact mass calcd. for $C_{20}H_{24}NO_5$ ($[M+H]^+$): 358.1649. Found: 358.1653.



5c: colorless oil, 52.7 mg, 74/26 dr, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (chemical shifts marked with asterisk are of minor diastereomer) δ 8.46 (s, 1H), 7.93 (s, 1H*), 7.32 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.15 (dd, *J* = 8.4, 5.2 Hz, 1H), 6.99-6.94 (m, 1H), 5.07-4.98 (m, 1H), 4.79 (d, *J* = 17.2 Hz, 1H), 4.72 (d, *J* = 10.4 Hz, 1H), 3.862 (s, 3H), 3.857 (s, 3H*), 3.81 (s, 1H*), 3.79 (s, 3H), 2.78-2.72 (m, 1H), 2.67-2.58 (m, 2H), 2.16-2.04 (m, 4H), 1.47-1.43 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 172.0, 170.9, 162.8 (d, *J* = 242.9 Hz), 155.9 (d, *J* = 10.7 Hz), 134.9, 121.7 (d, *J* = 9.6 Hz), 117.0, 113.0 (d, *J* = 23.1 Hz), 108.9 (d, *J* = 23.8 Hz), 60.2, 54.6, 53.0, 52.8, 43.0, 34.5, 29.9, 29.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.14 (m); IR (film): ν_{max} (cm^{-1}) = 3628, 3459, 3078, 2954, 1731, 1607, 1555, 1468, 1229, 1152, 1085, 992, 811, 702; HRMS (ESI): Exact mass calcd. for $C_{19}H_{21}FNO_4$ ($[M+H]^+$): 346.1449. Found: 346.1454.

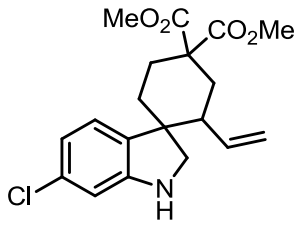


5e: yellow solid, 44.4 mg, 53% yield. ^{1}H NMR (400 MHz, CD_3OD) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.52-7.46 (m, 3H), 7.37-7.35 (m, 2H), 7.13-7.09 (m, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 5.71 (dt, *J* = 15.6, 5.2 Hz, 1H), 5.57-5.49 (m, 1H), 4.00 (d, *J* = 5.2 Hz, 2H), 3.70 (s, 6H), 2.80-2.76 (m, 2H), 2.72 (d, *J* = 7.6 Hz, 2H), 2.25-2.20 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 173. 1, 137.8, 135.8, 135.4, 134.8, 130.1, 129.7, 129.2, 128.4, 125.8, 122.7, 119.9, 119.4, 112.0, 111.9, 63.2, 59.1, 52.9, 36.7, 34.5, 20.5; IR (film): ν_{max} (cm^{-1}) =3470, 3265, 2924, 2858, 1725, 1447, 1311, 1244, 1040, 972, 740, 694; HRMS (ESI): Exact mass calcd. for $C_{25}H_{28}NO_5$ ($[M+H]^+$): 422.1962. Found: 422.1964.

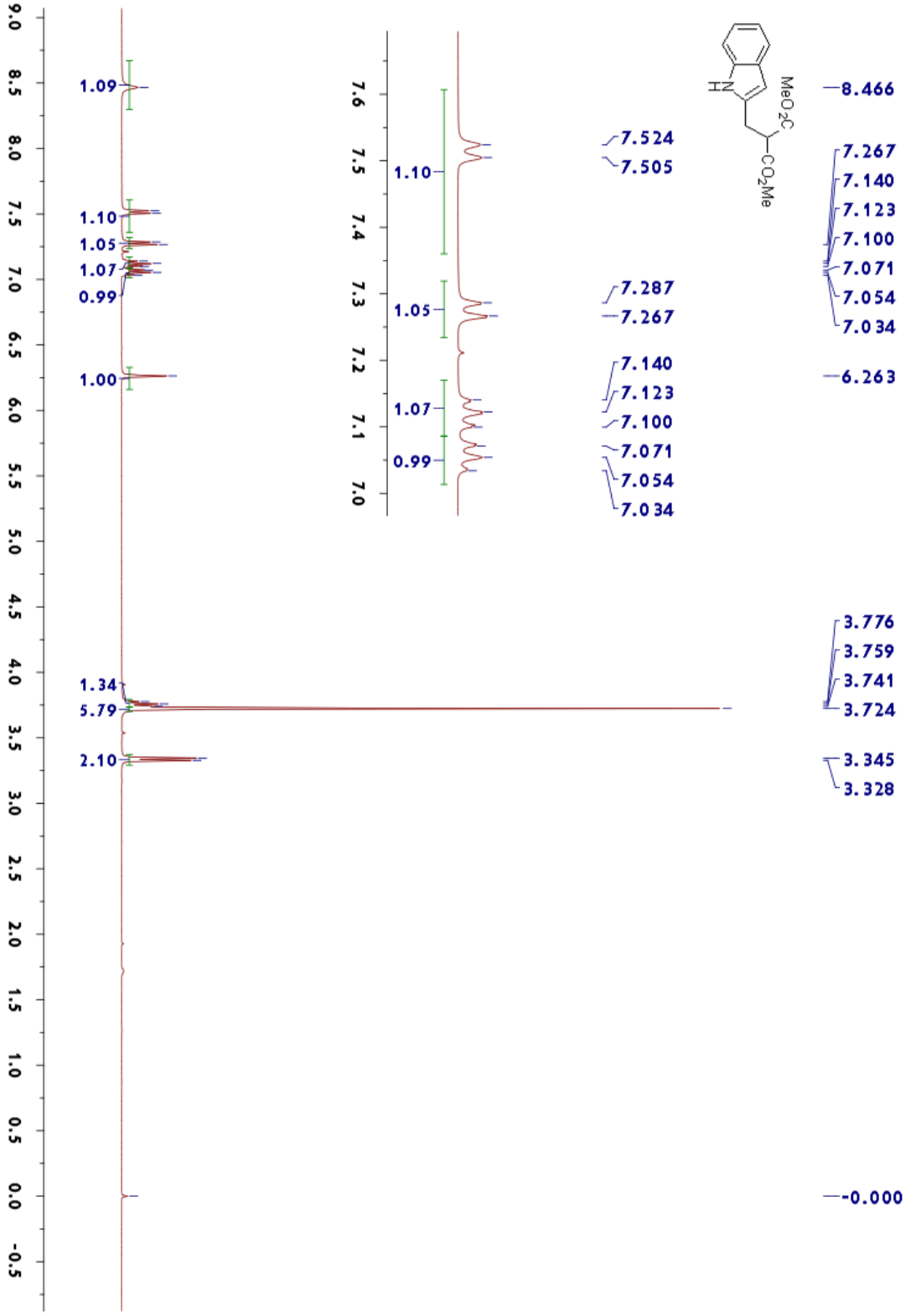


A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added Pd_2dba_3 (13.8 mg, 0.015 mmol, 7.5 mol%), 1,4-bis(diphenylphosphino)butane (13.7 mg, 0.032 mmol, 16 mol%), and THF (1.0 mL). The reaction mixture was stirred at room temperature for 30 min. After that, substrate **1** (61.9 mg, 0.2 mmol), vinyloxirane **2** (15.4 mg, 0.22 mmol, 110 mol%), $MgSO_4$ (24.0 mg, 0.2 mmol, 100 mol%), Et_3B (0.5 mL, 250 mol%, 1.0 M in THF) and THF (1.0 mL) were added. The reaction mixture was stirred at 50 °C. After the reaction was complete (monitored by TLC), the reaction was filtered through celite and concentrated in vacuo. MeOH (4.0 mL) was added and the mixture was cooled to 0 °C, after that $NaBH_3CN$ (12.8 mg, 0.2 mmol) was added. The reaction mixture was

stirred at room temperature until completion (monitored by TLC). Then saturated $NaHCO_3$ (2.0 mL) was added and concentrated in vacuo. The mixture was extracted with ethyl acetate and dried with Na_2SO_4. After filtration and concentration under reduced pressure, the obtained residue was purified by silica gel column chromatography to afford the desired product.



5d: colorless oil, 38.8mg, 61/39 dr, 54% yield.^{1}H NMR (400 MHz, $CDCl_3$) (chemical shifts marked with asterisk are of minor diastereomer) δ 7.23 (d, *J* = 8.0 Hz, 1H*), 6.84 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 2.0 Hz, 1H), 6.63 (d, *J* = 2.0 Hz, 1H*), 6.55 (d, *J* = 2.0 Hz, 1H*), 6.51 (d, *J* = 1.6 Hz, 1H), 5.58 (m, 1H), 5.42 (m, 1H*), 5.01-4.88 (m, 2H), 3.82 (s, 3H), 3.80 (s, 3H*), 3.76 (s, 3H*), 3.74 (s, 3H), 3.54 (AB, J_{AB} = 9.2 Hz, 1H*), 3.53 (AB, J_{AB} = 9.6 Hz, 1H), 3.32 (BA, J_{BA} = 9.6 Hz, 1H), 3.16 (BA, J_{BA} = 9.2 Hz, 1H*), 2.48-2.17 (m, 4H), 2.01-1.80 (m, 1H), 1.75-1.52 (m, *2*H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 171.2, 152.0, 137.9, 133.5, 133.2, 123.1, 118.1, 115.6, 109.2, 54.4, 52.8, 52.7, 51.8, 48.4, 44.1, 34.8, 32.0, 27.5; IR (film): ν_{max} (cm^{-1}) = 3670, 2979, 2902, 1731, 1398, 1247, 1064, 895; HRMS (ESI): Exact mass calcd. for $C_{19}H_{23}ClNO_4$ ($[M+H]^+$): 364.1310. Found: 364.1311.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1.07
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1.00
1.34
5.79
2.10
7.6 7.5 7.4 7.3 7.2 7.1 7.0
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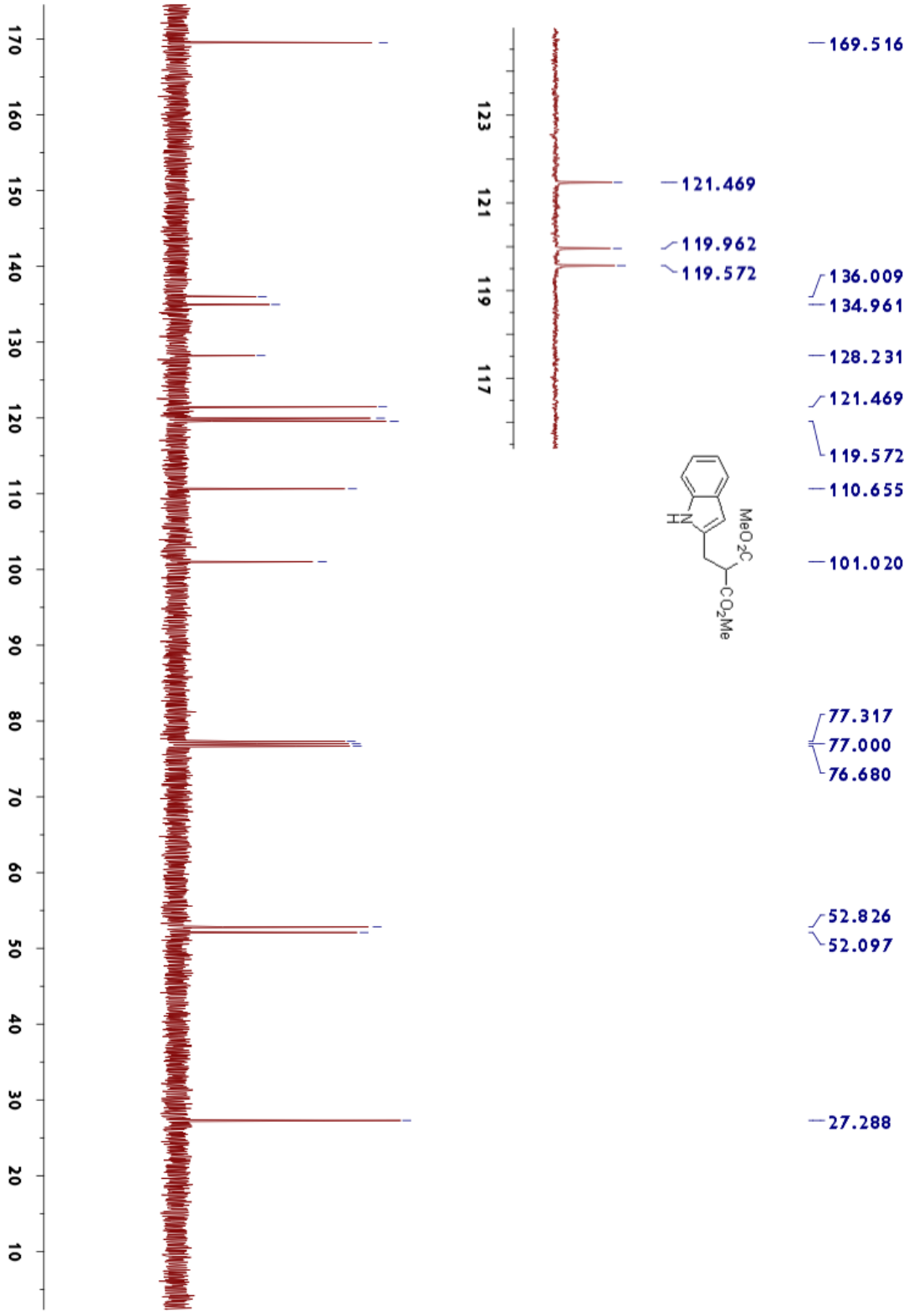
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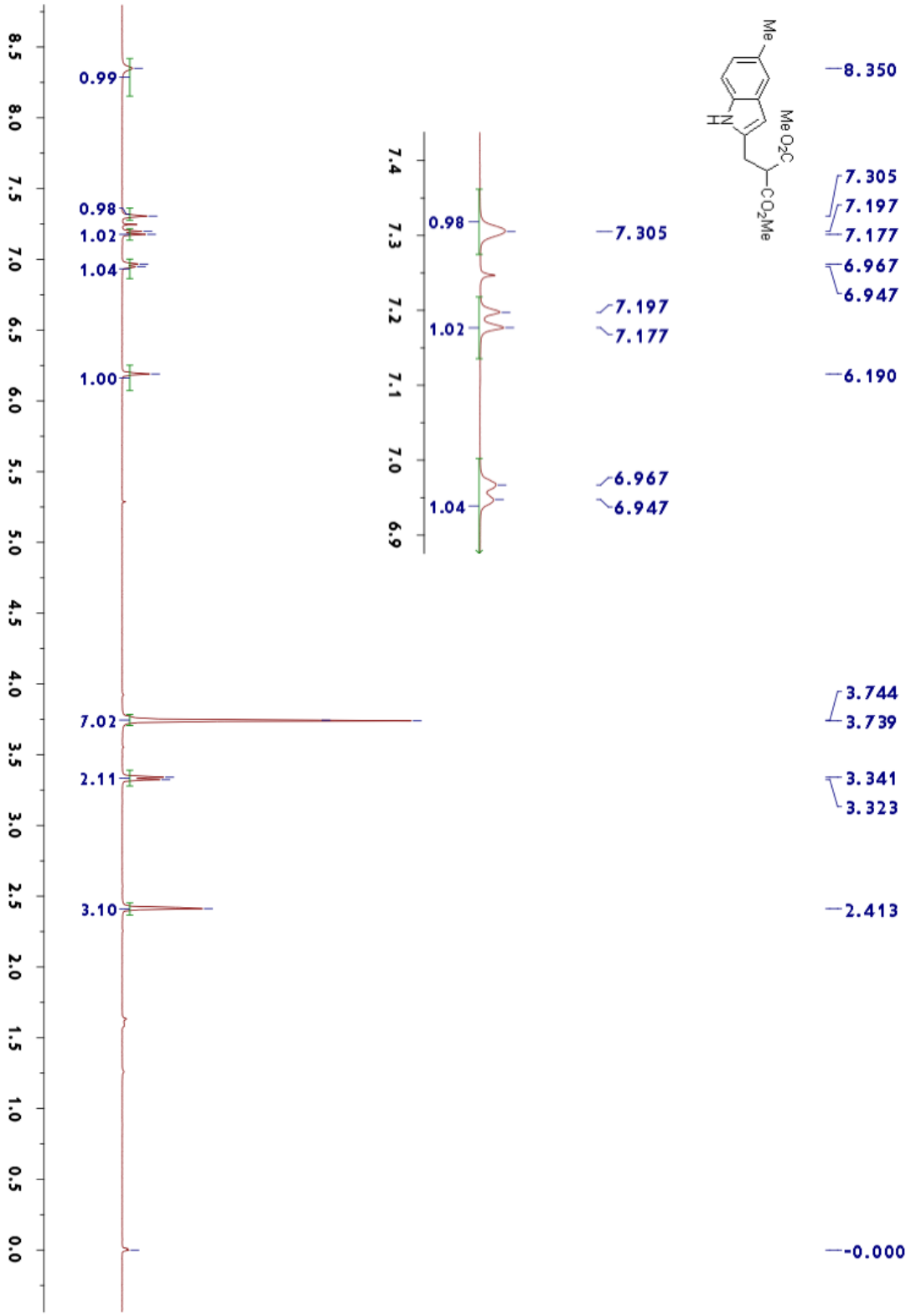
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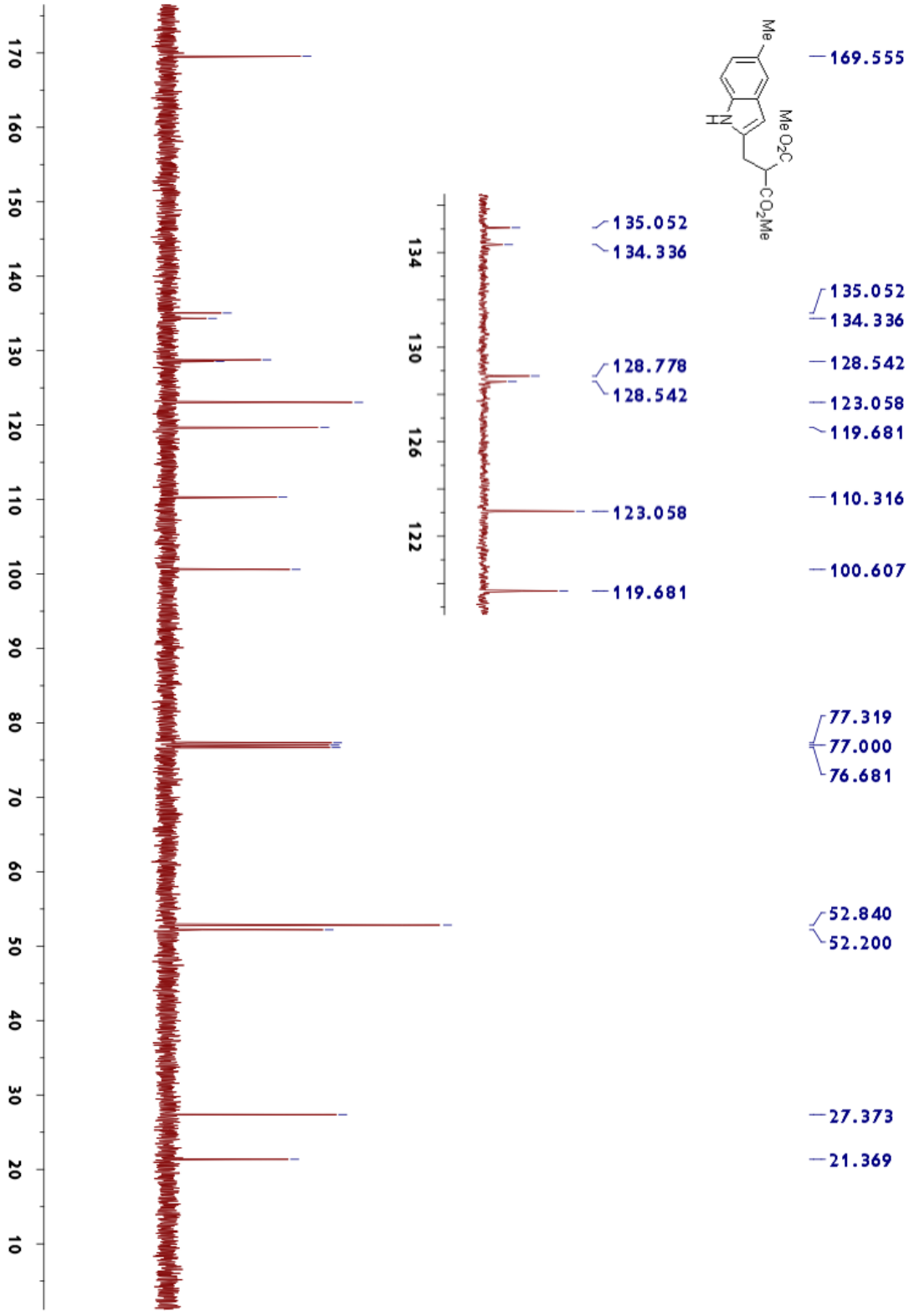
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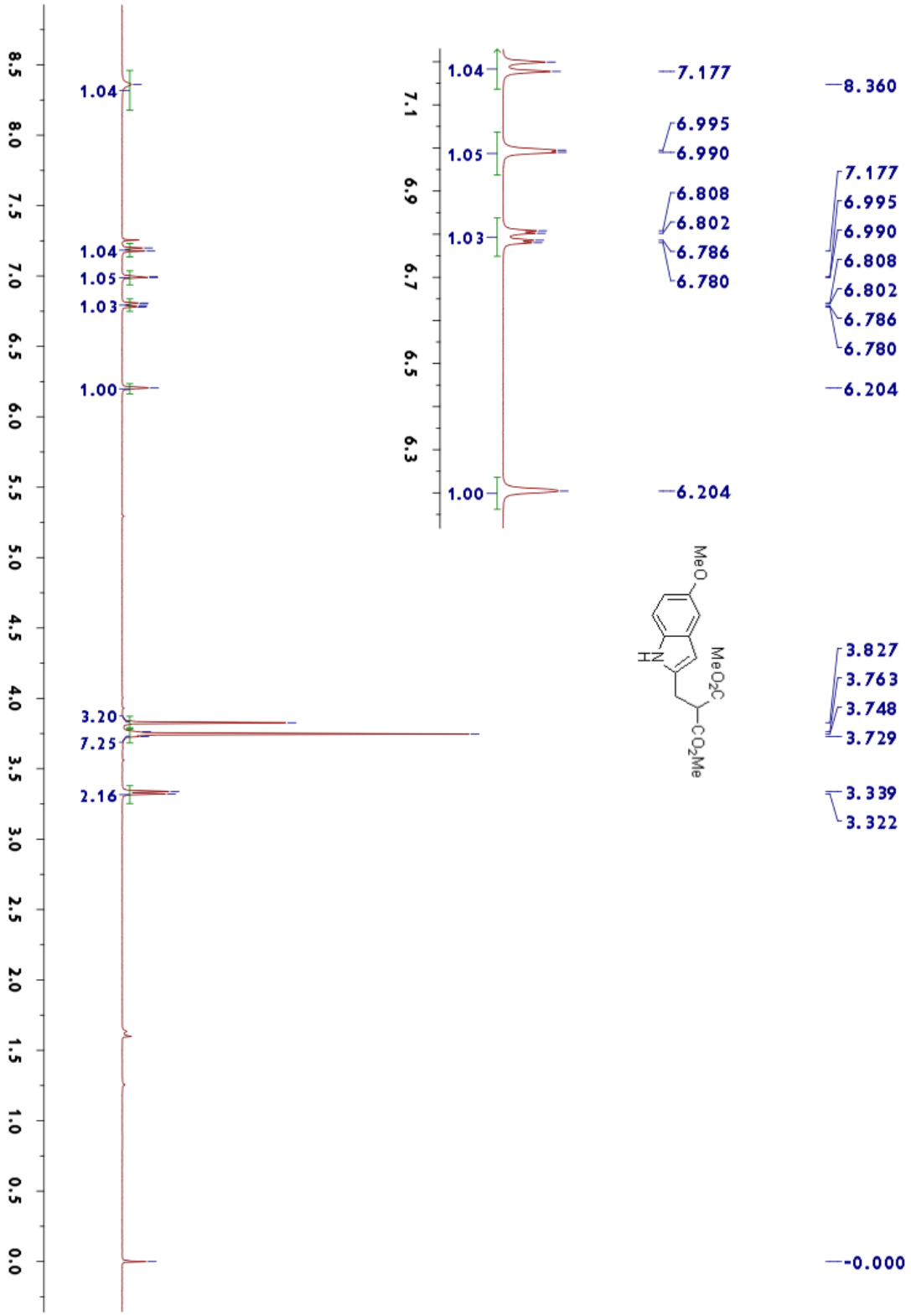
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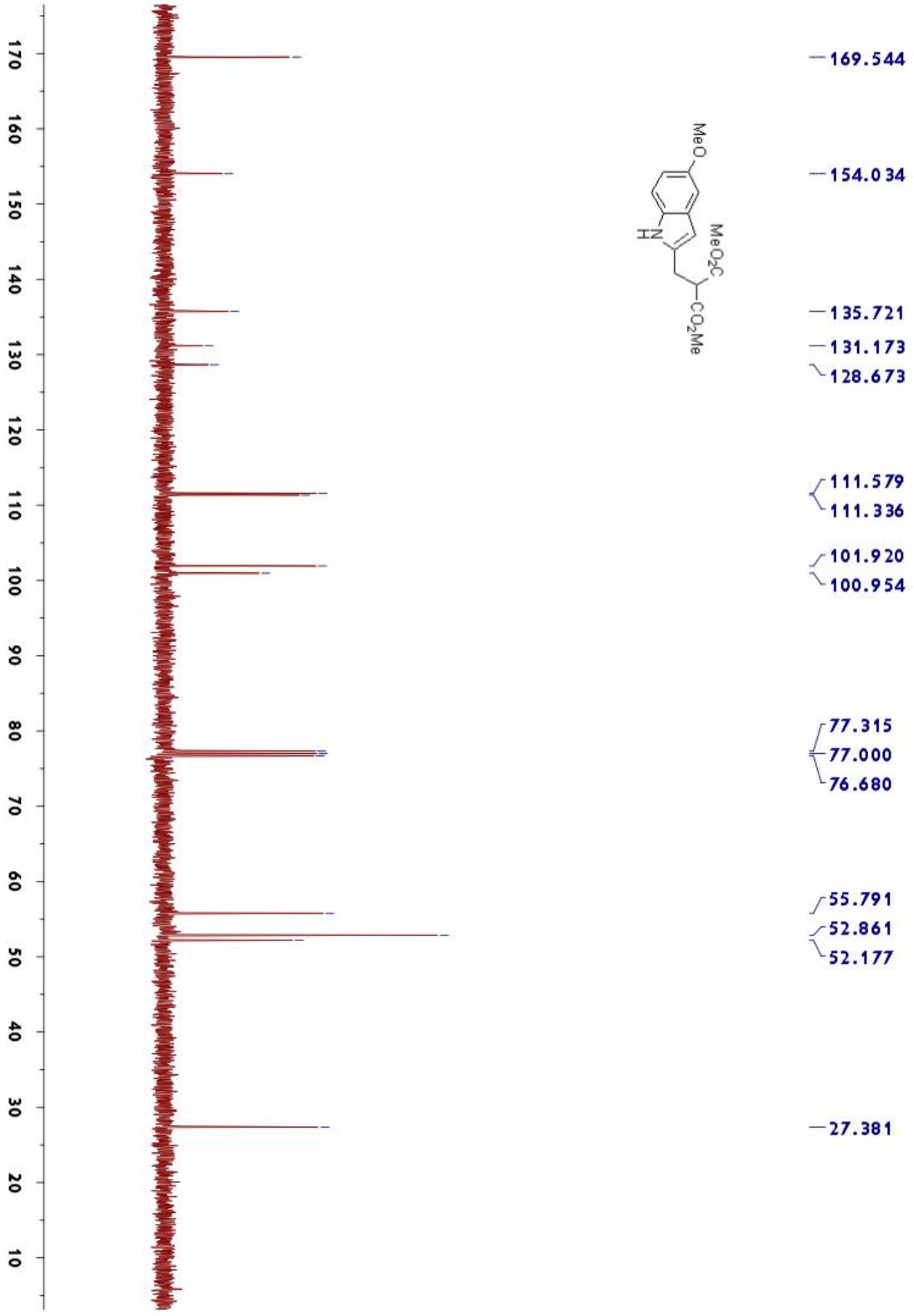
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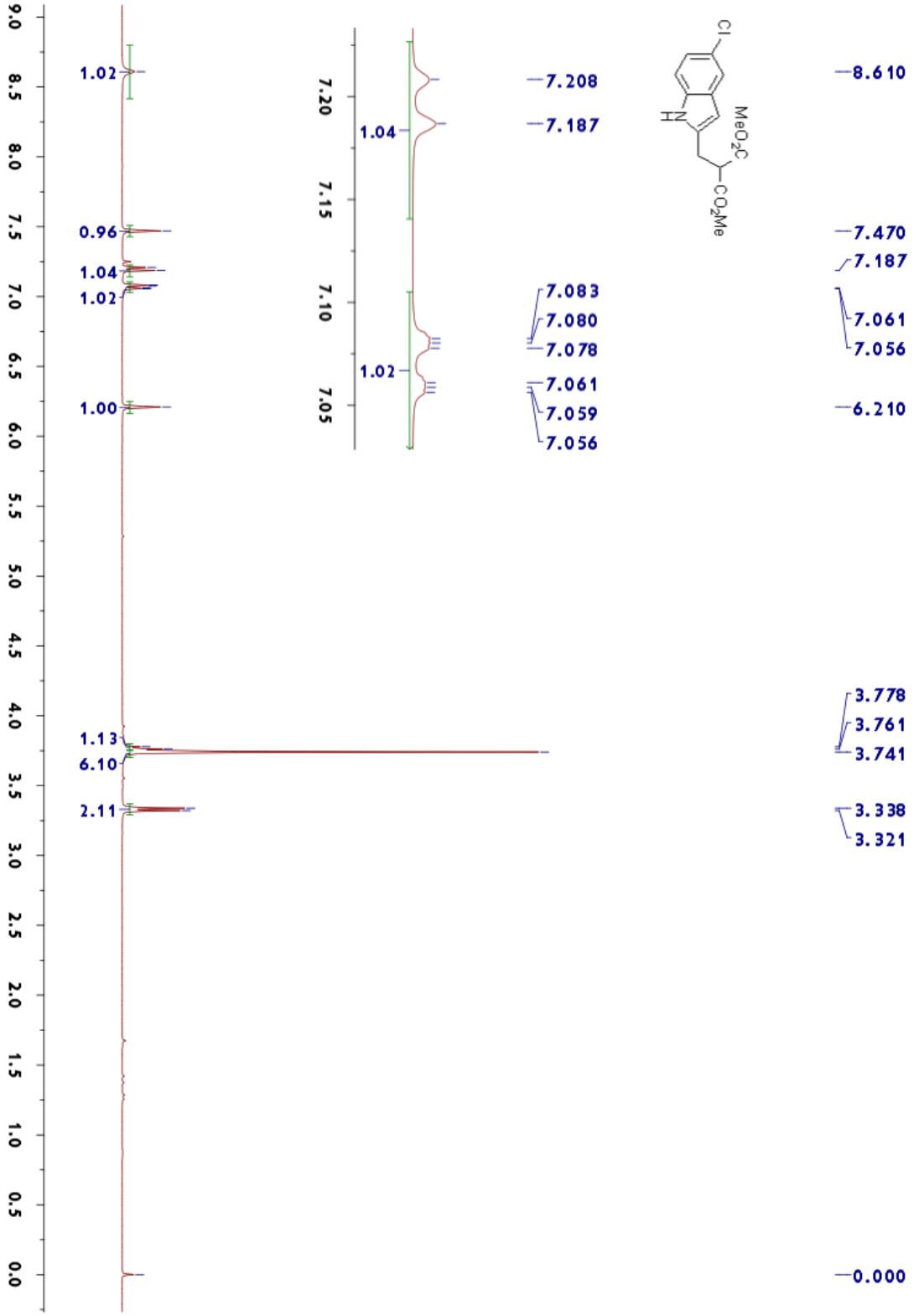
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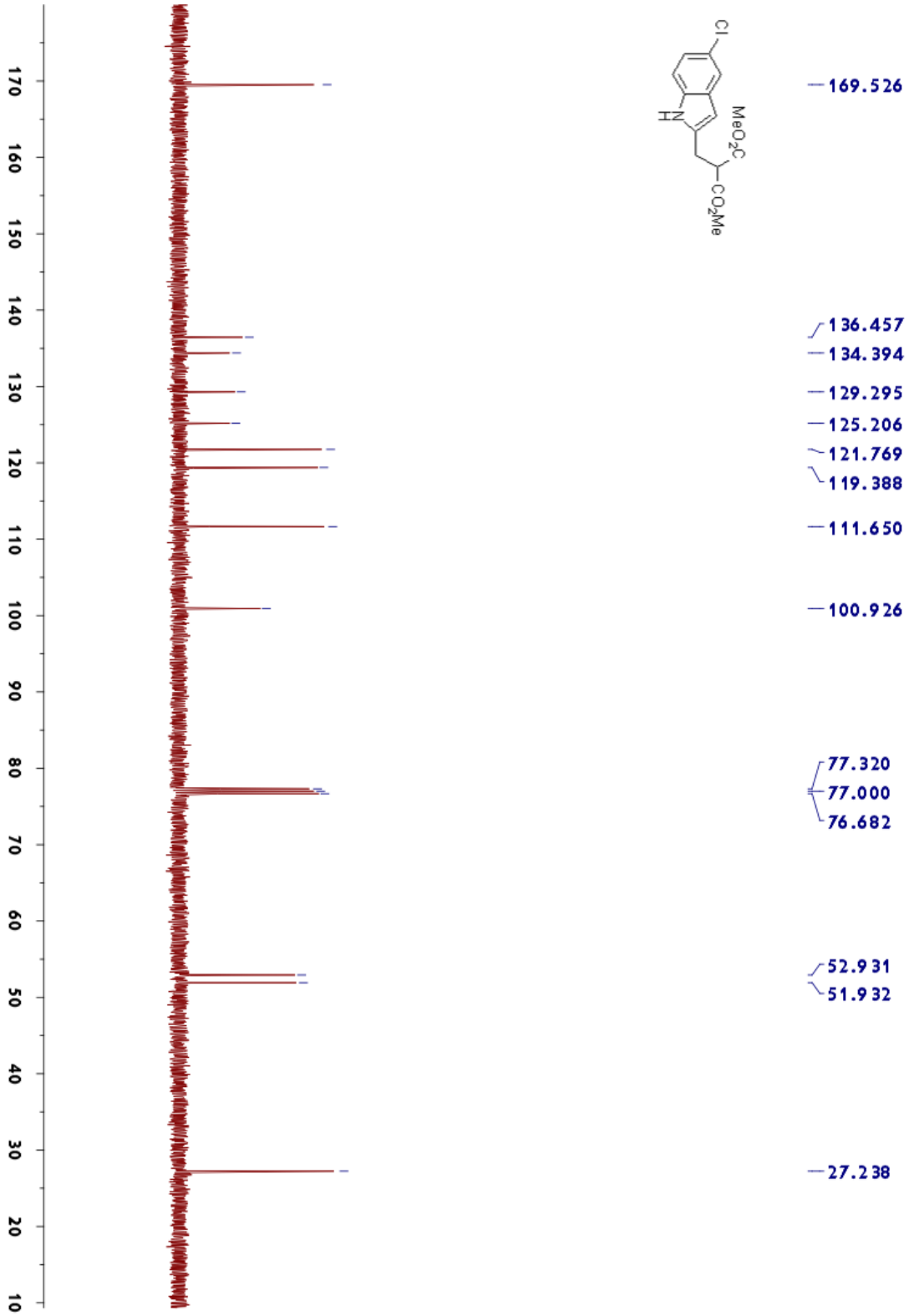
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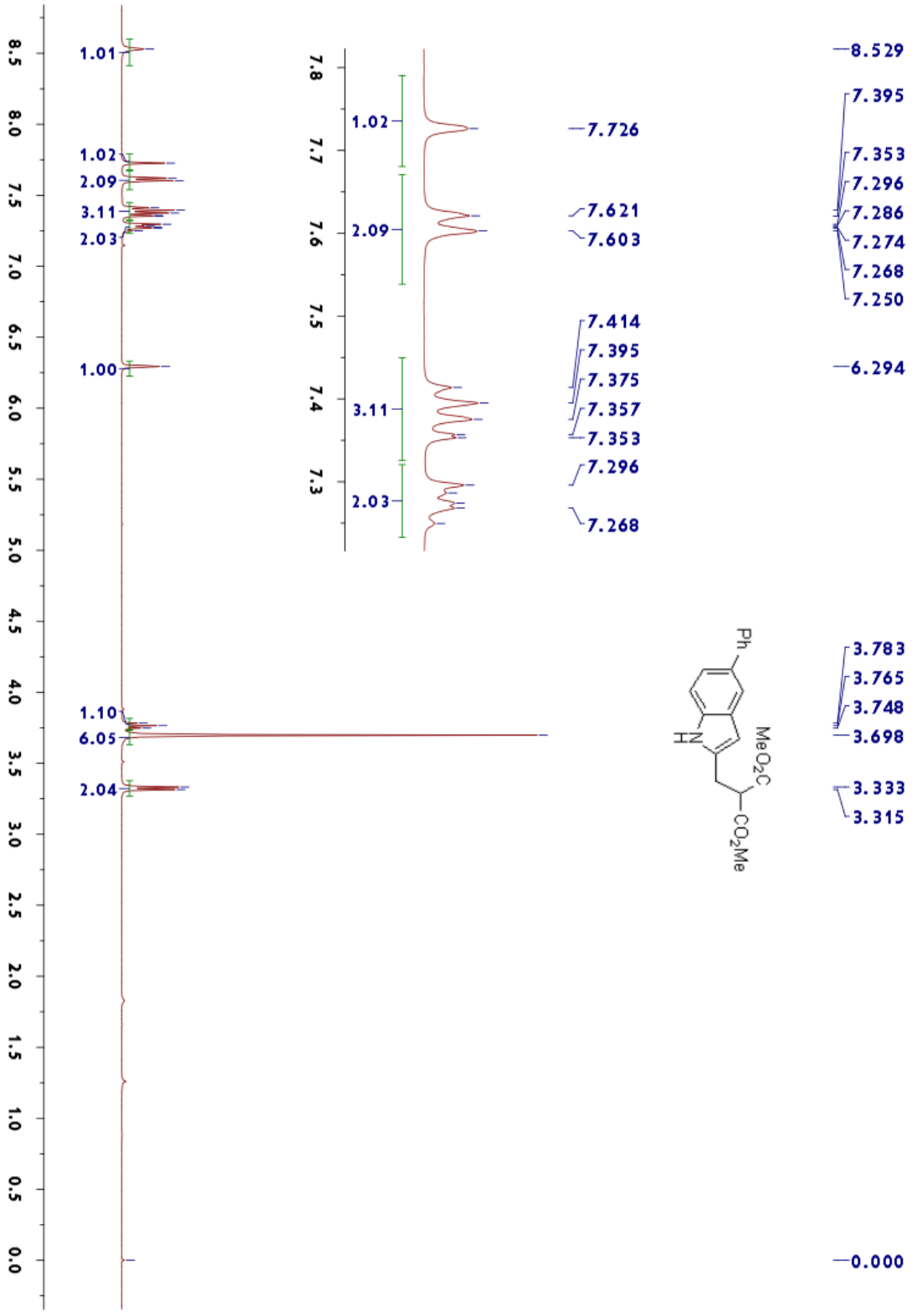
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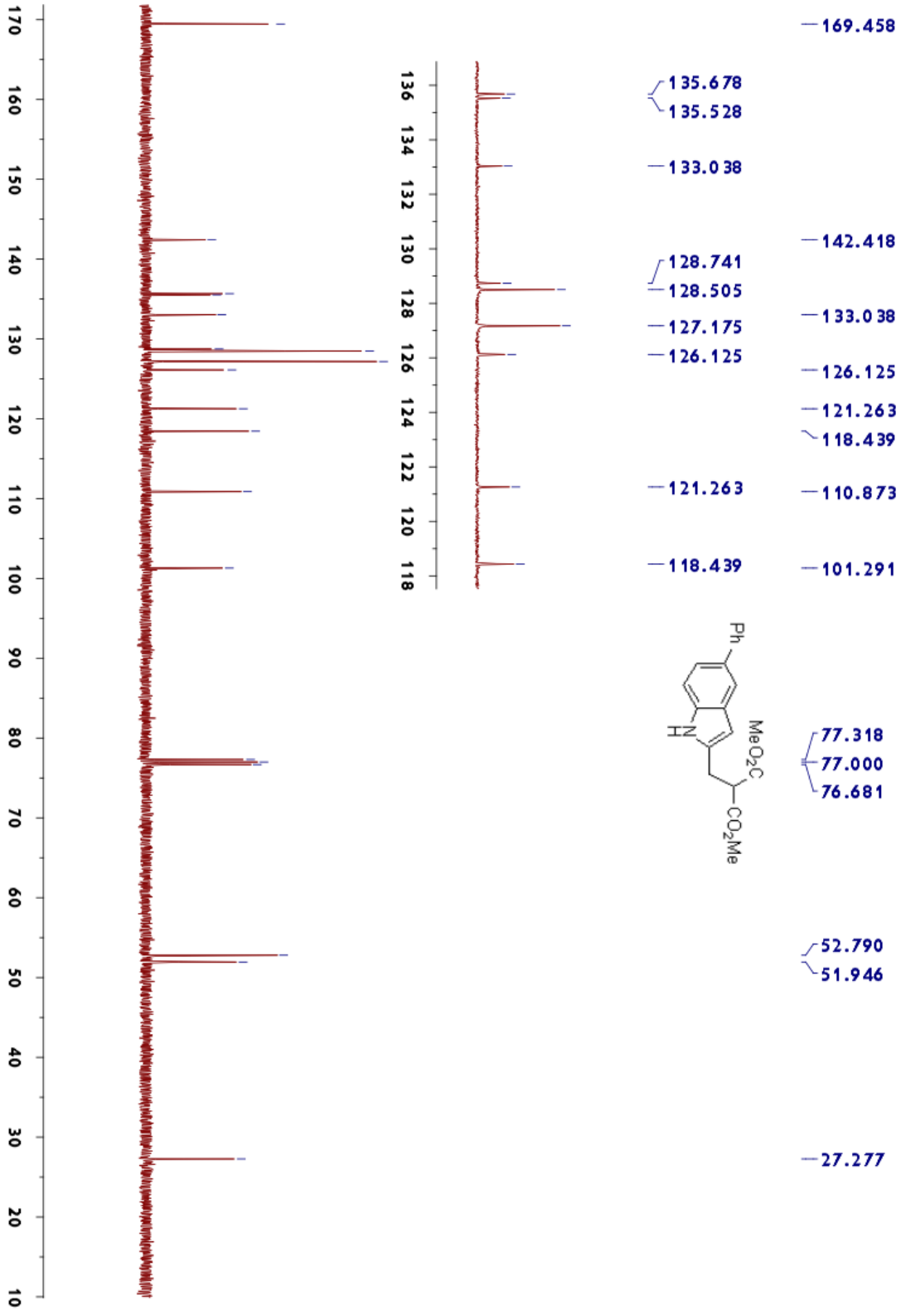
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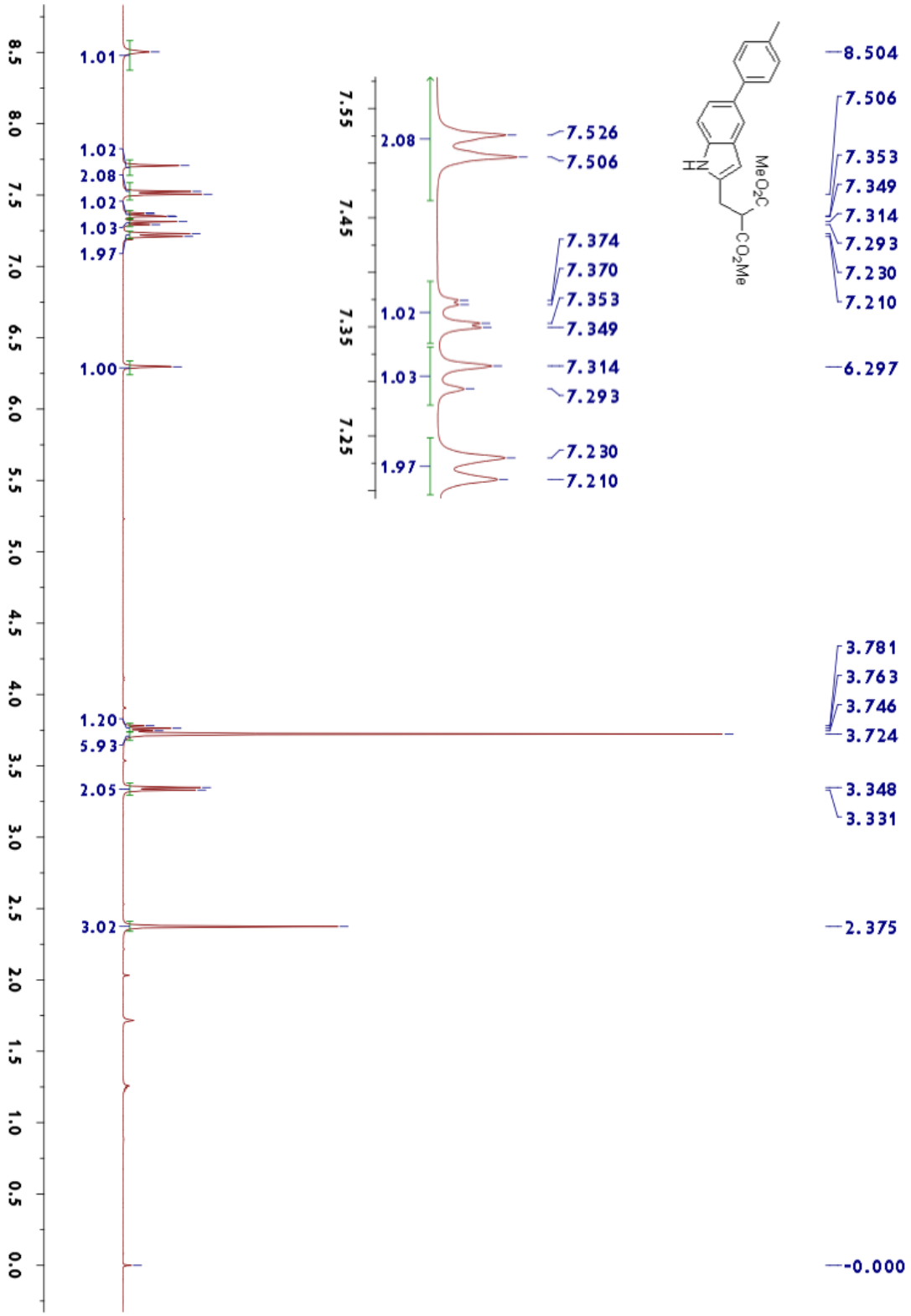
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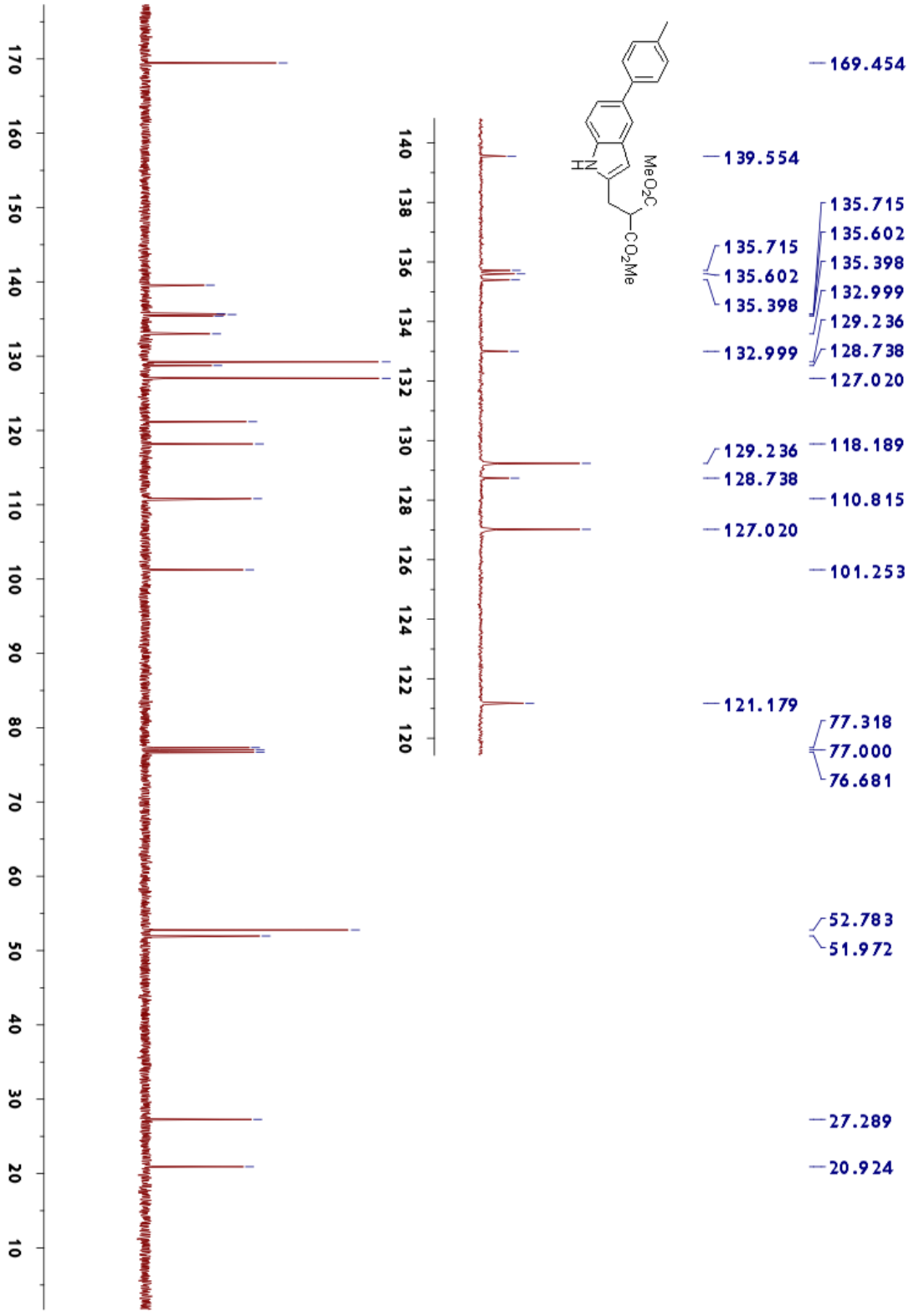
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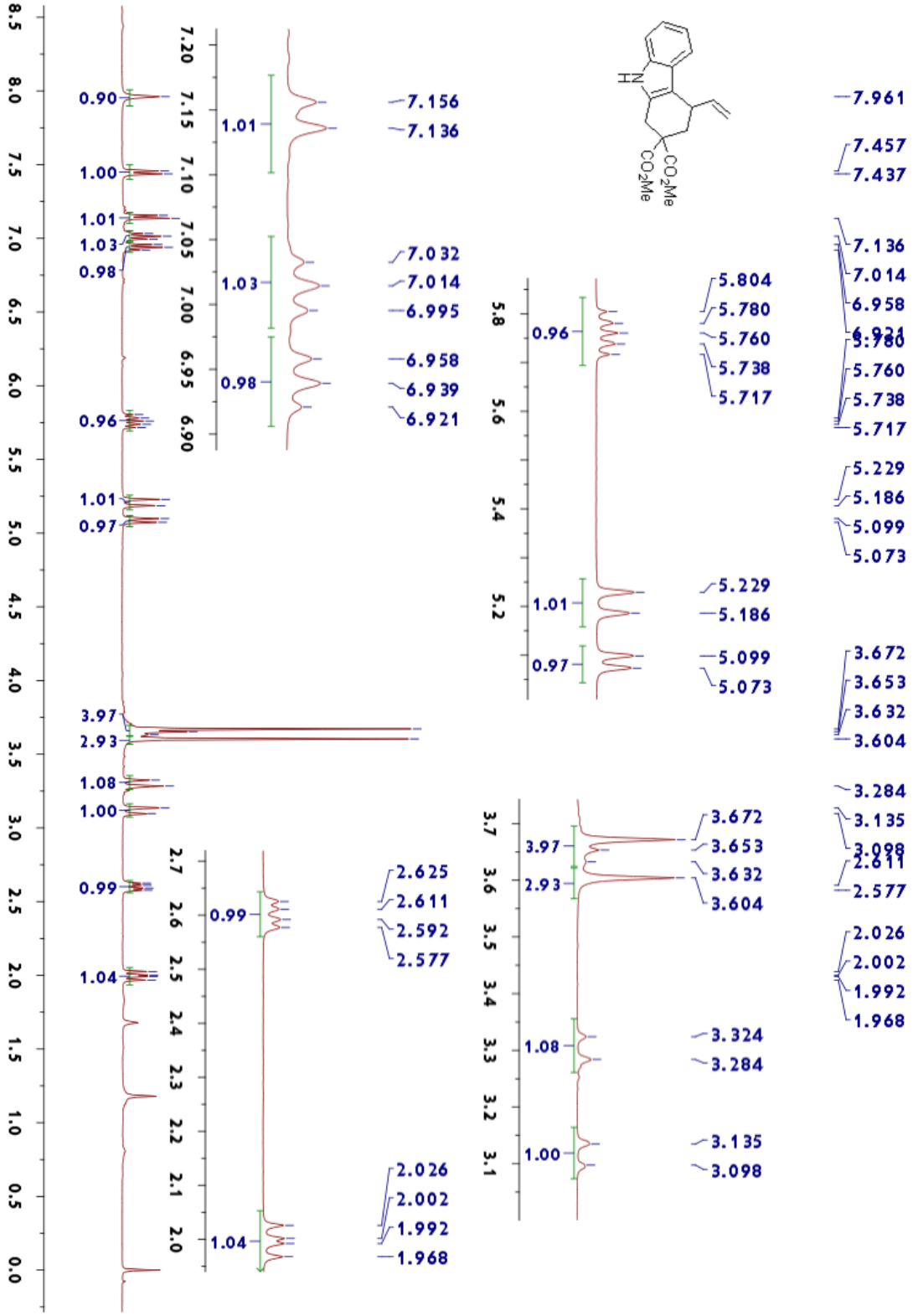
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CO2Me
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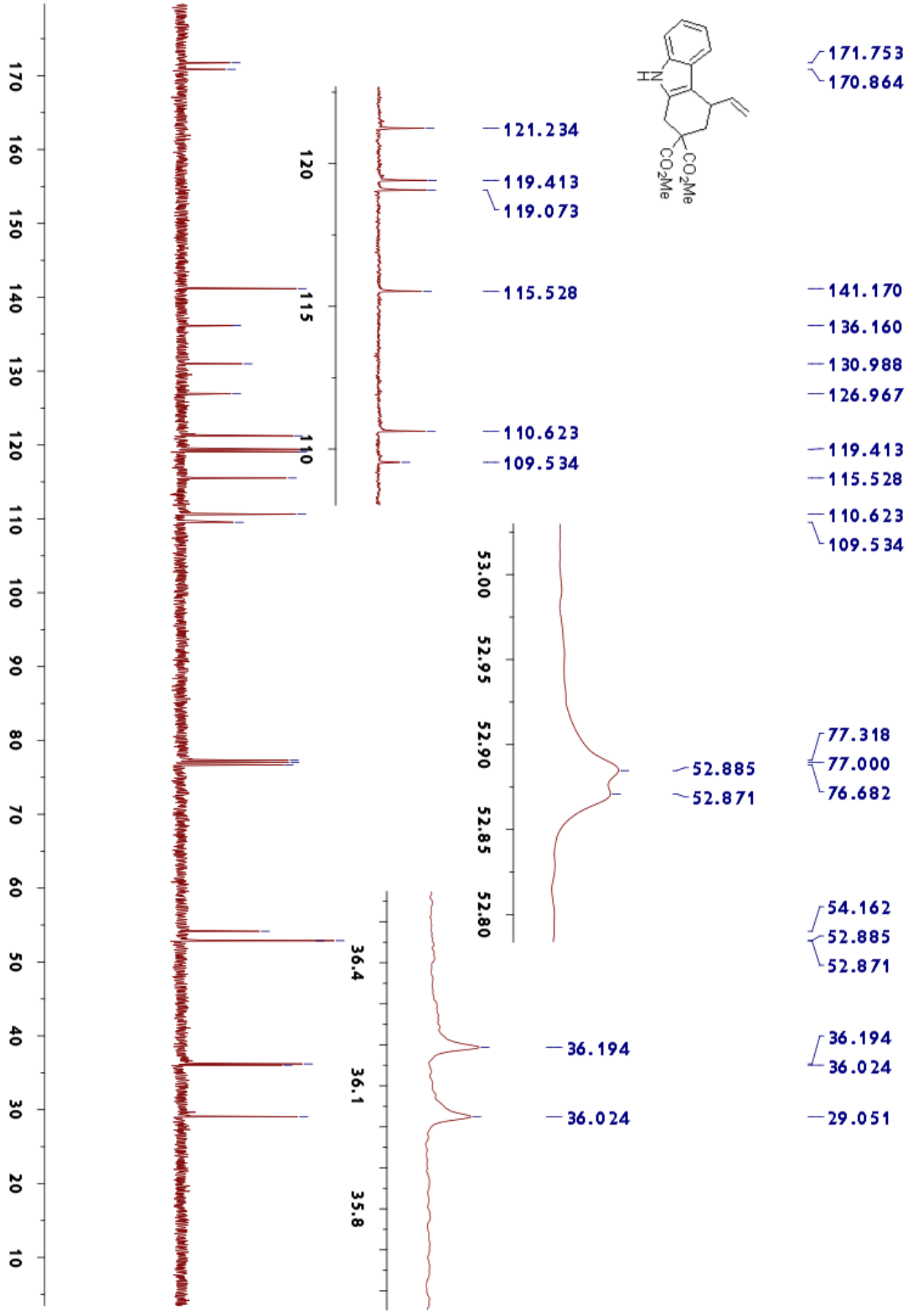
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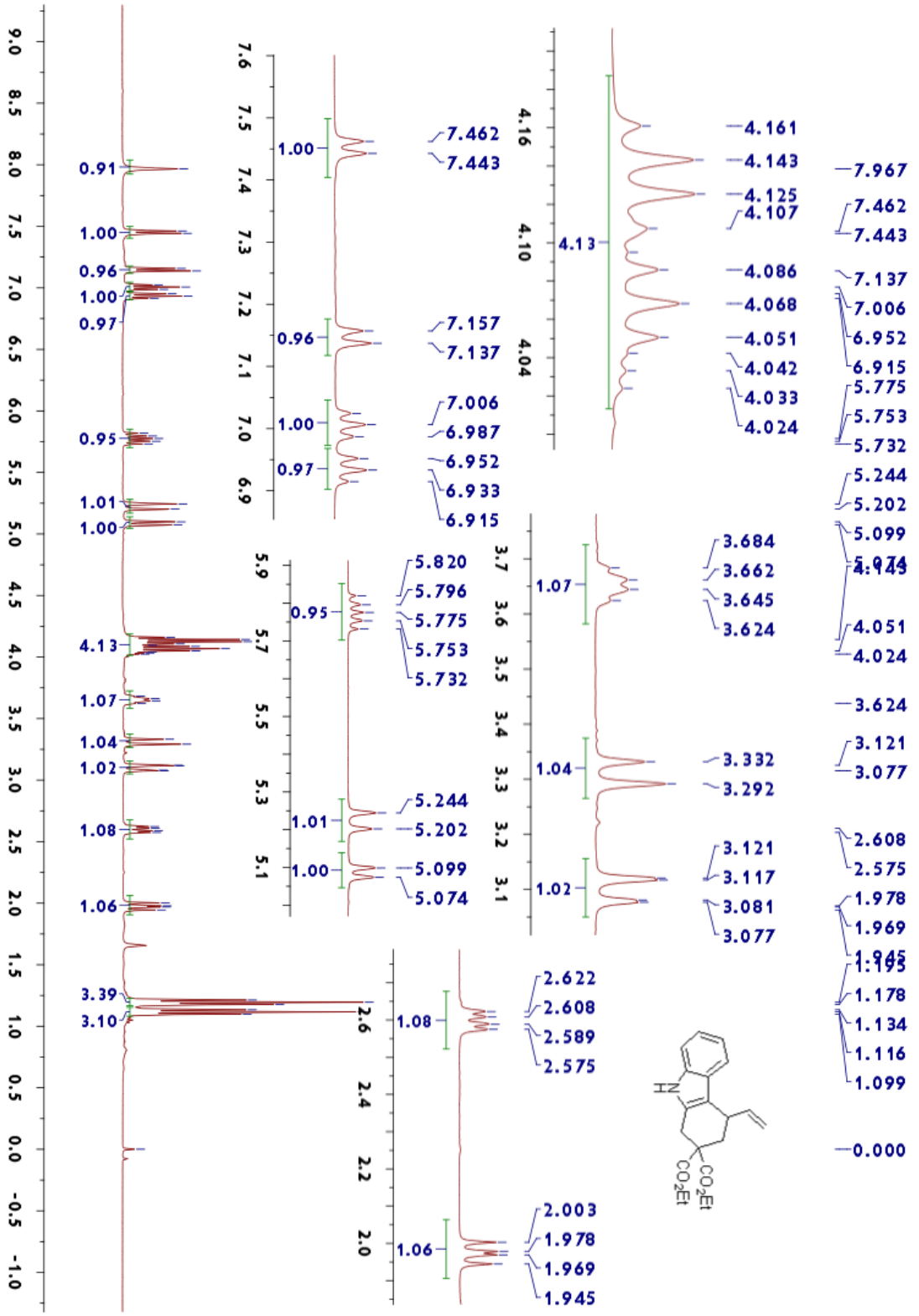
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0.96
1.00
0.97
0.95
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1.00
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1.02
1.08
1.06
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3.10
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1.00
0.97
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7.006
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6.952
6.933
6.915
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1.00
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5.202
5.099
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4.068
4.051
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4.033
4.024
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1.02
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3.624
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3.292
3.121
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3.081
3.077
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1.06
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2.608
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2.575
2.003
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1.969
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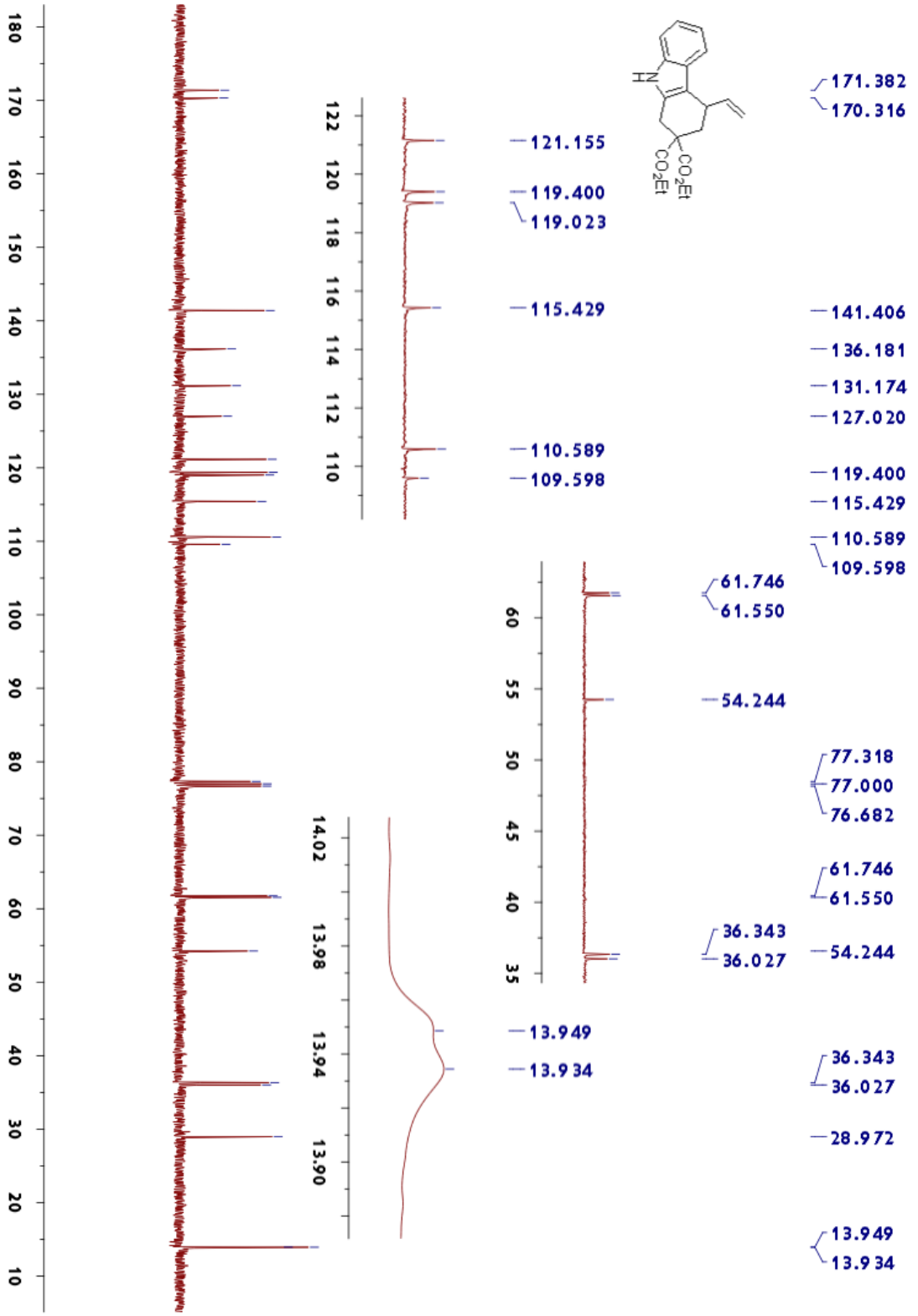
CO2Et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CO2Et
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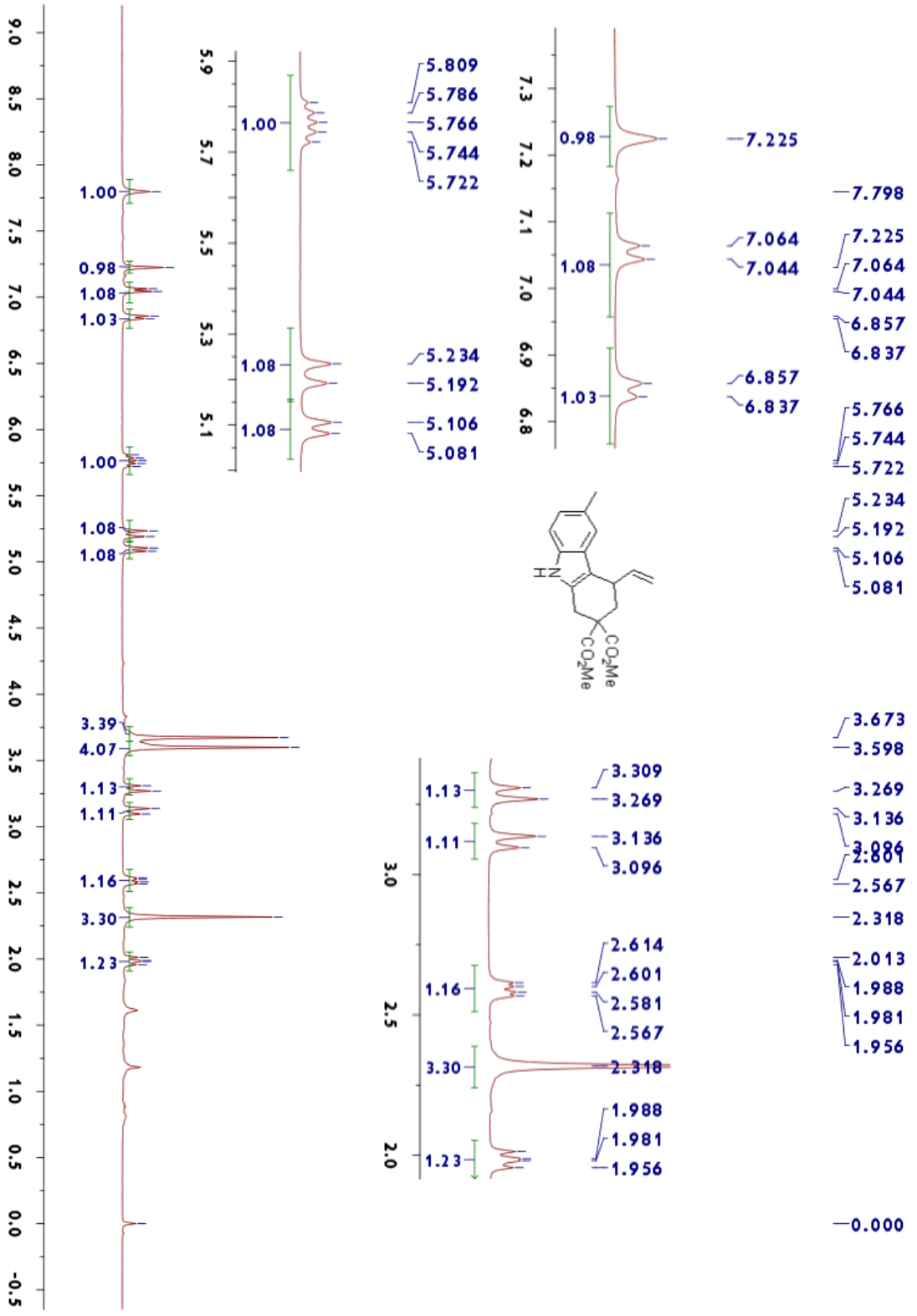
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0.98
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1.03
1.00
1.08
1.08
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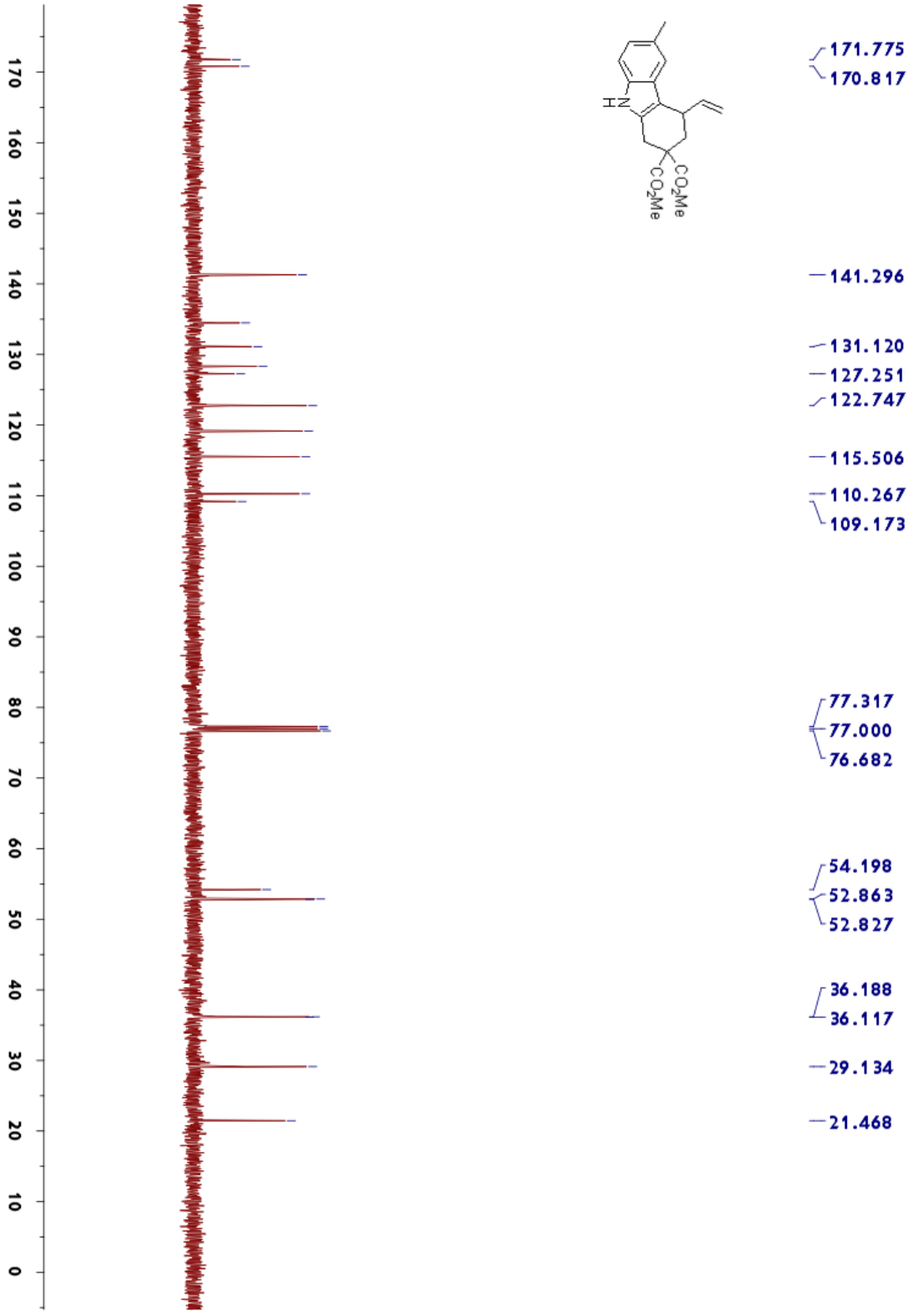
CO2Me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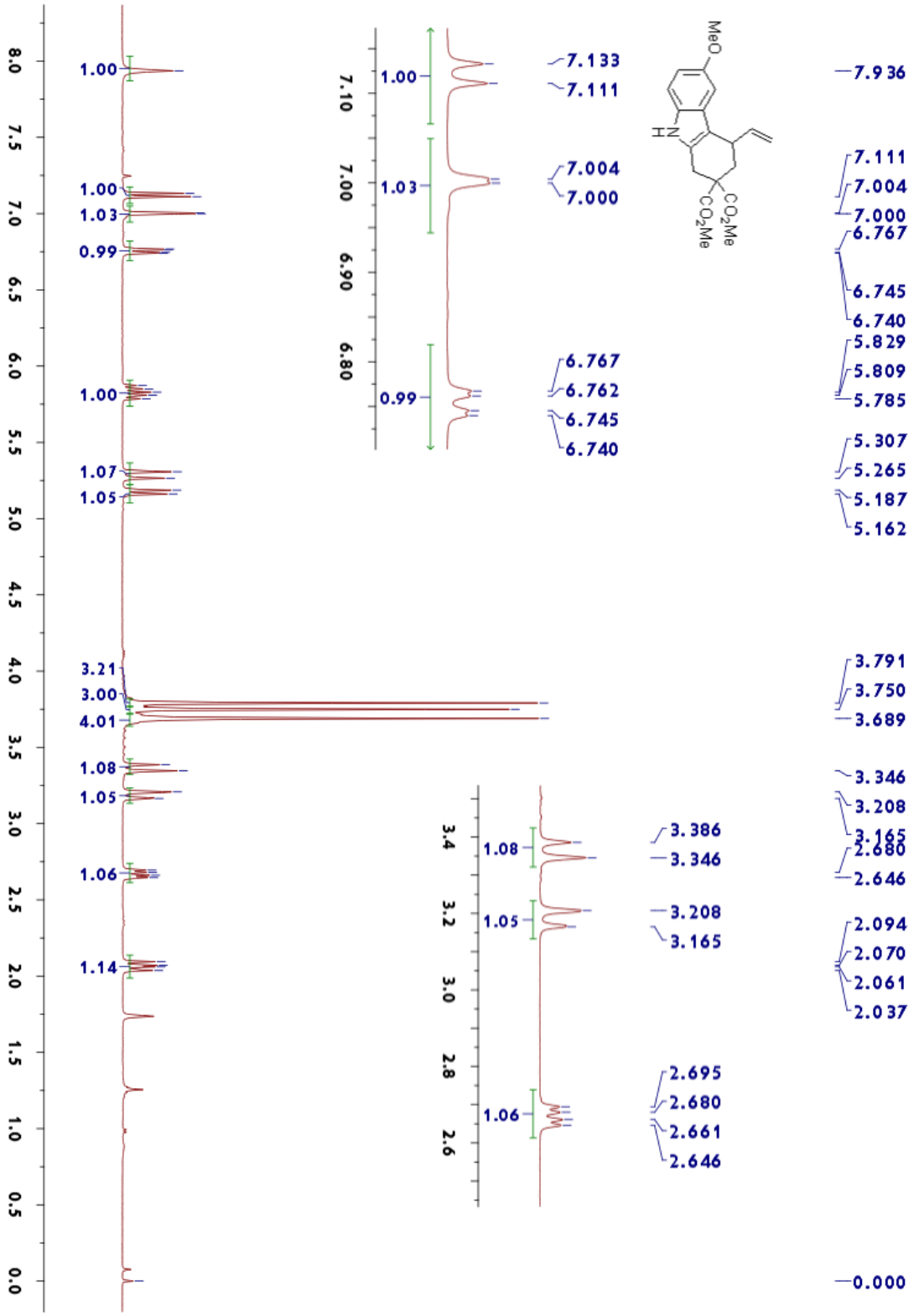
N
H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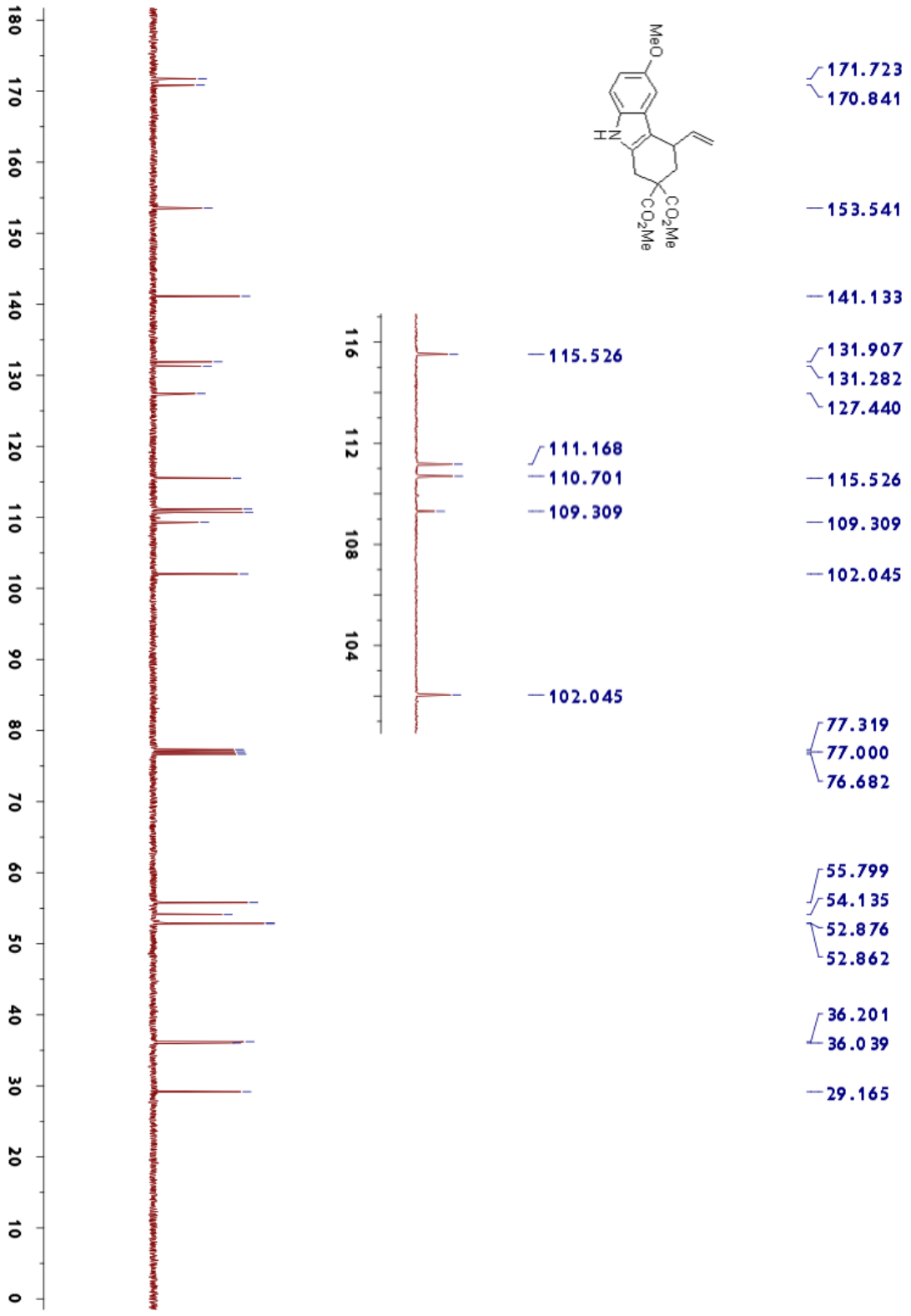
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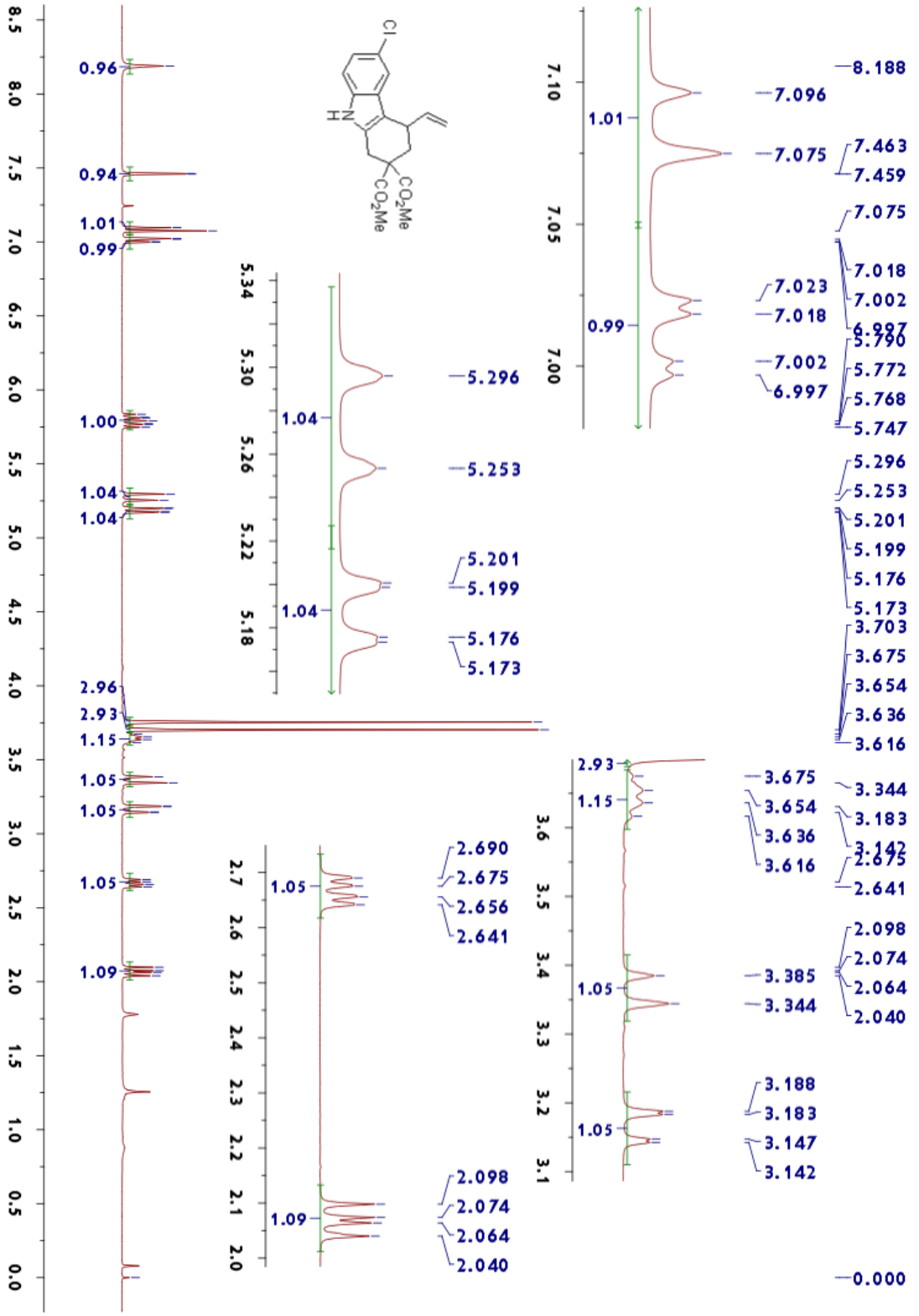
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5.173
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3.654
3.636
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3.142
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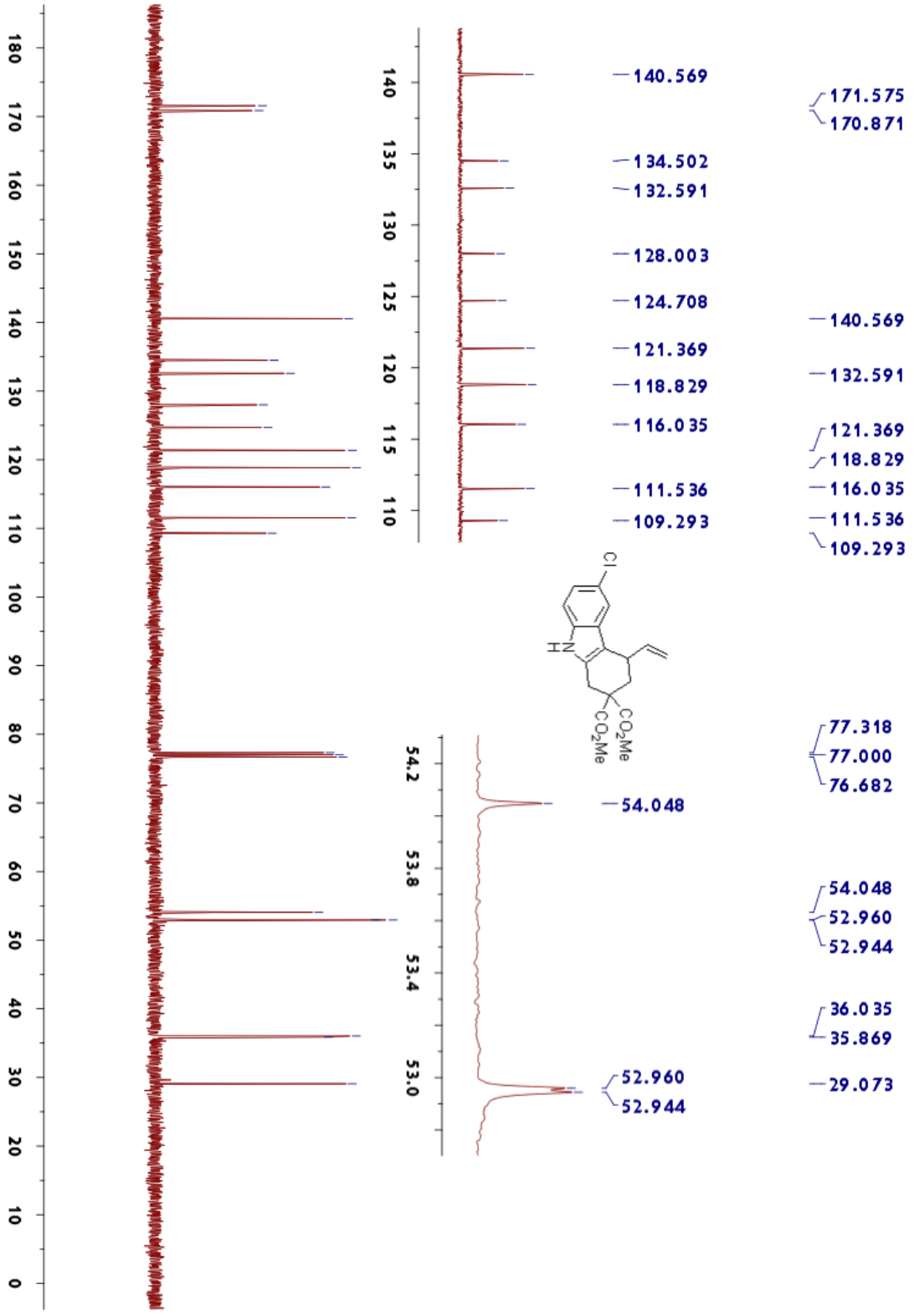
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N
H
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CO2Me
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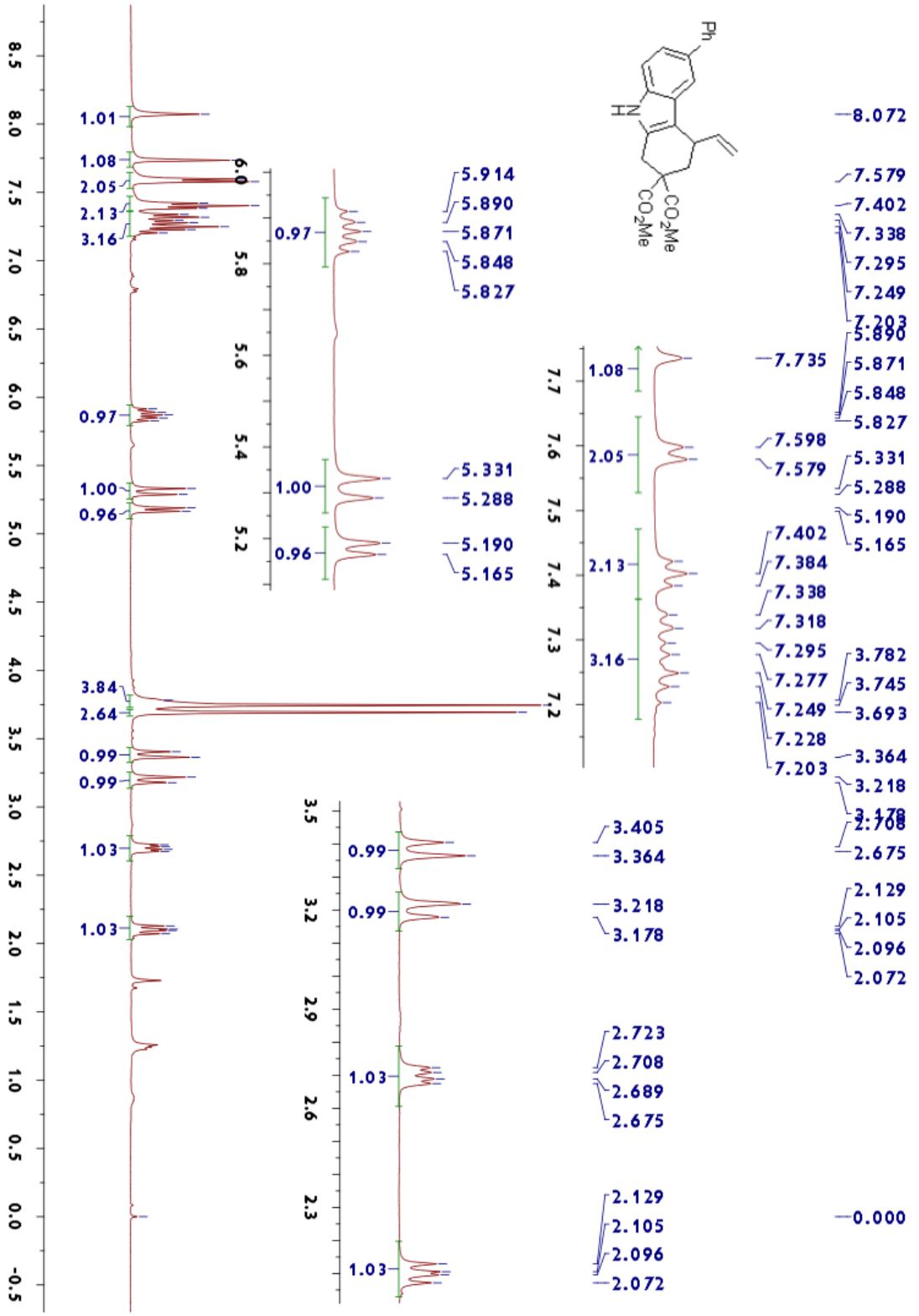
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5.190
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7.203
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3.178
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2.096
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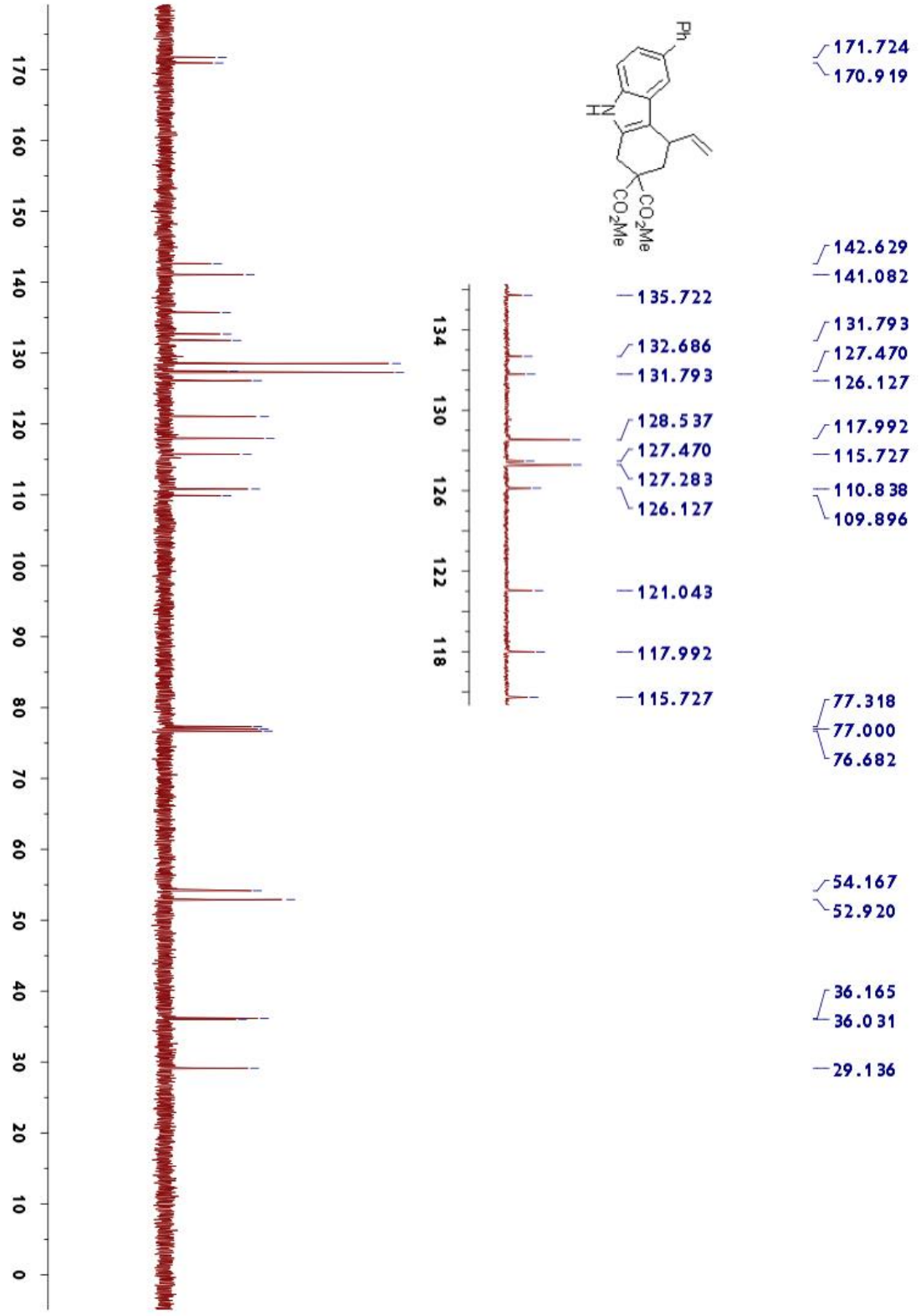
1.03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CO2Me
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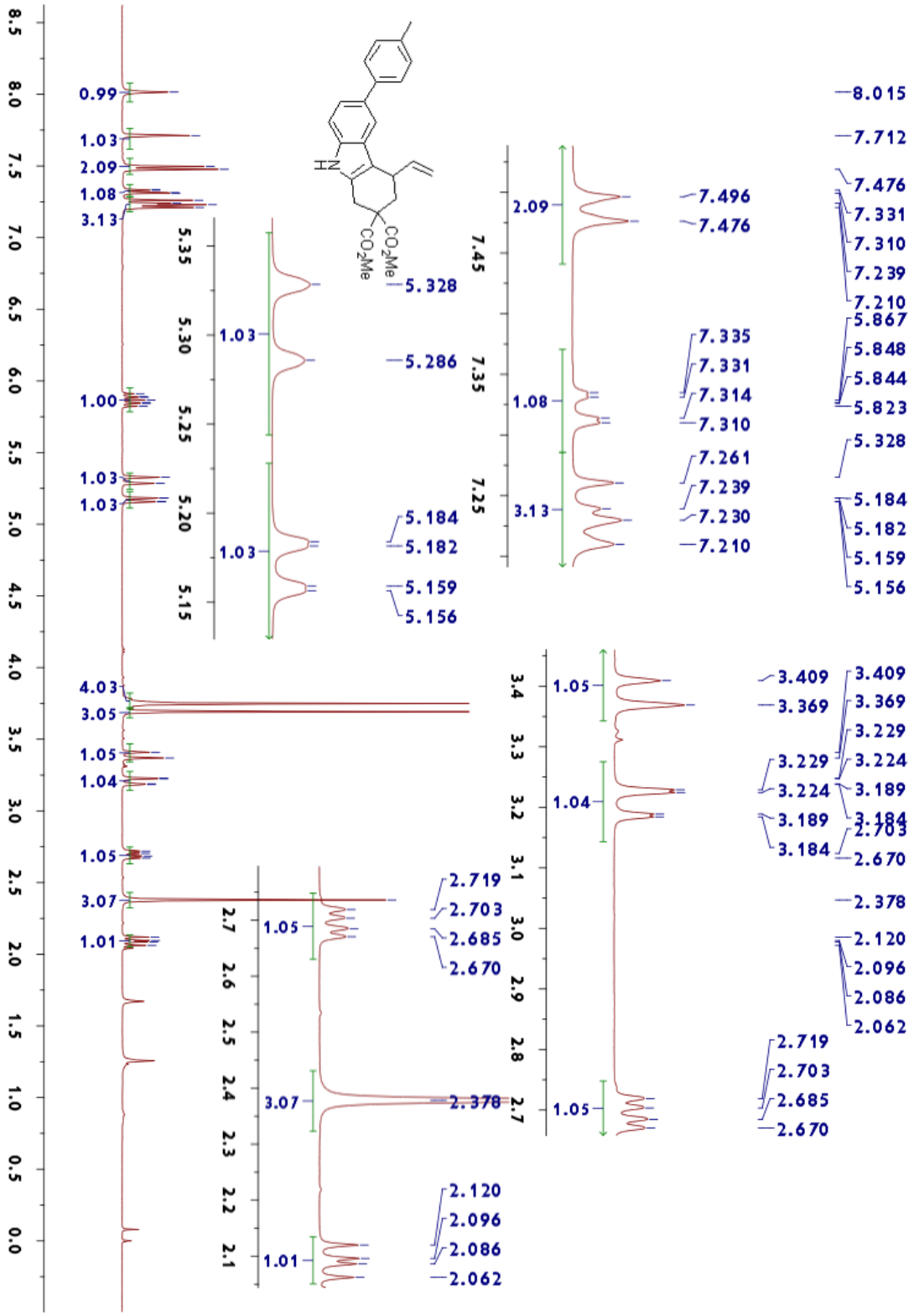
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3.07
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1.03
1.03
2.09
1.08
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1.05
3.07
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5.844
5.823
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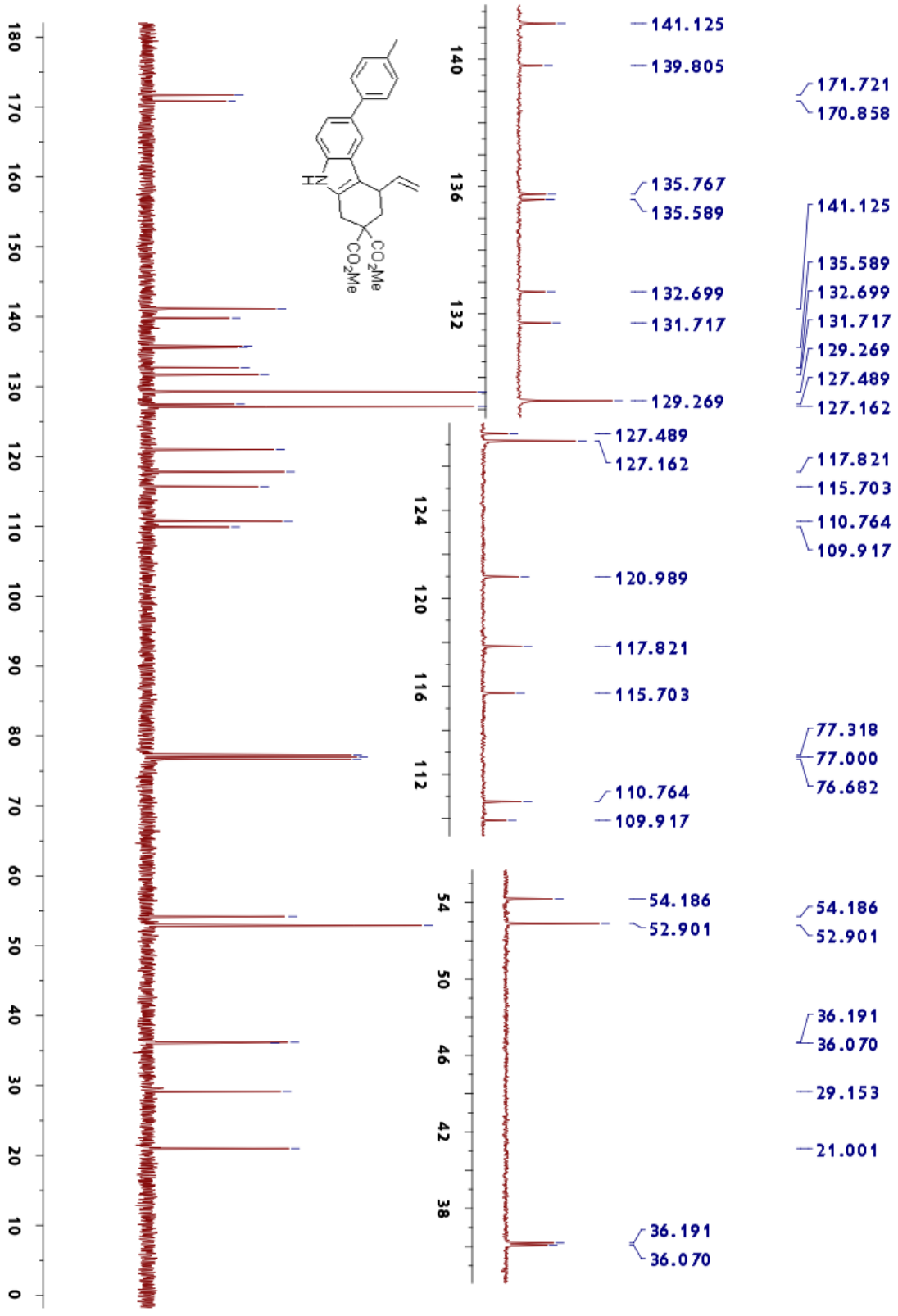
CO2Me
H
N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CO2Me
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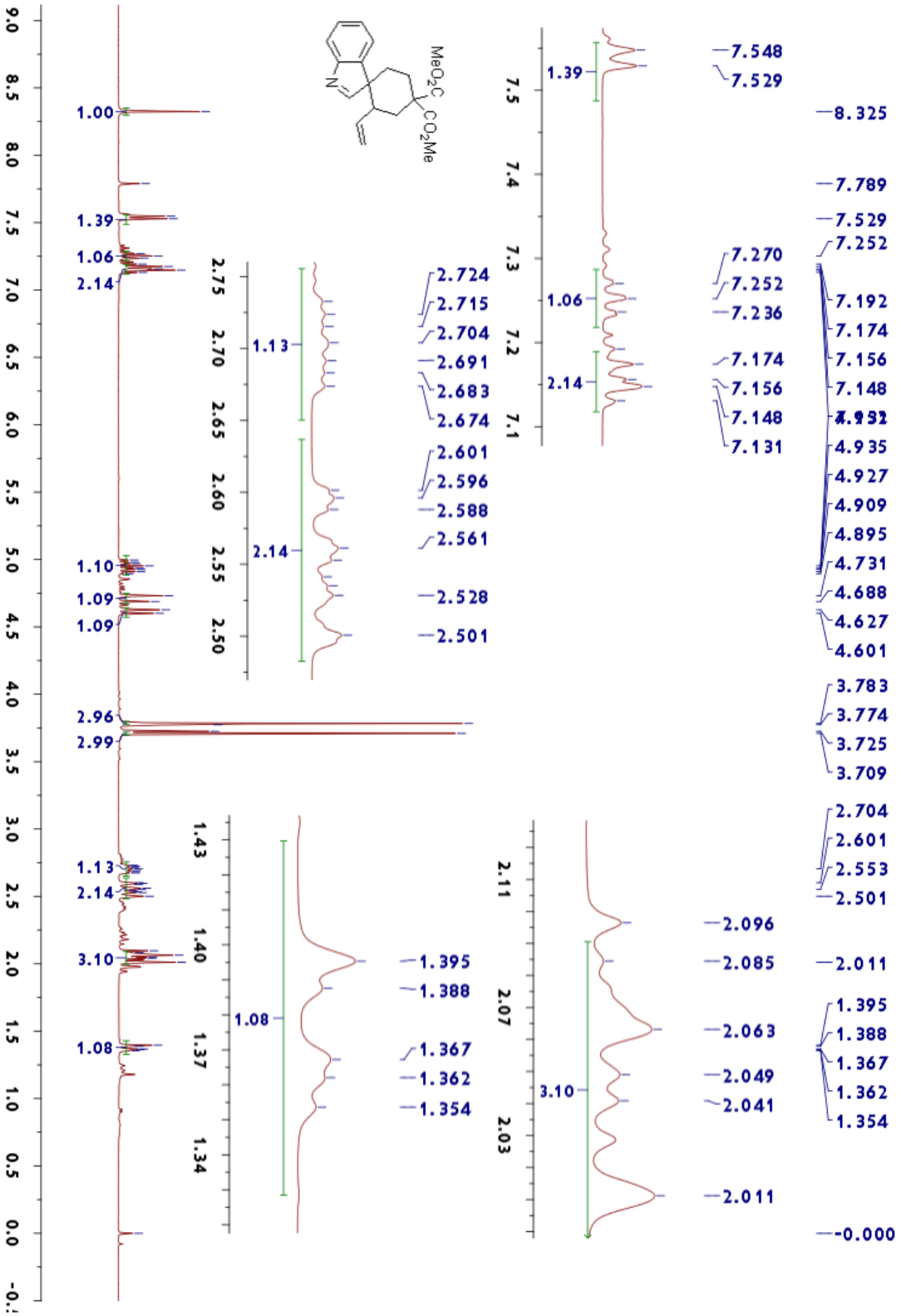
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2.14
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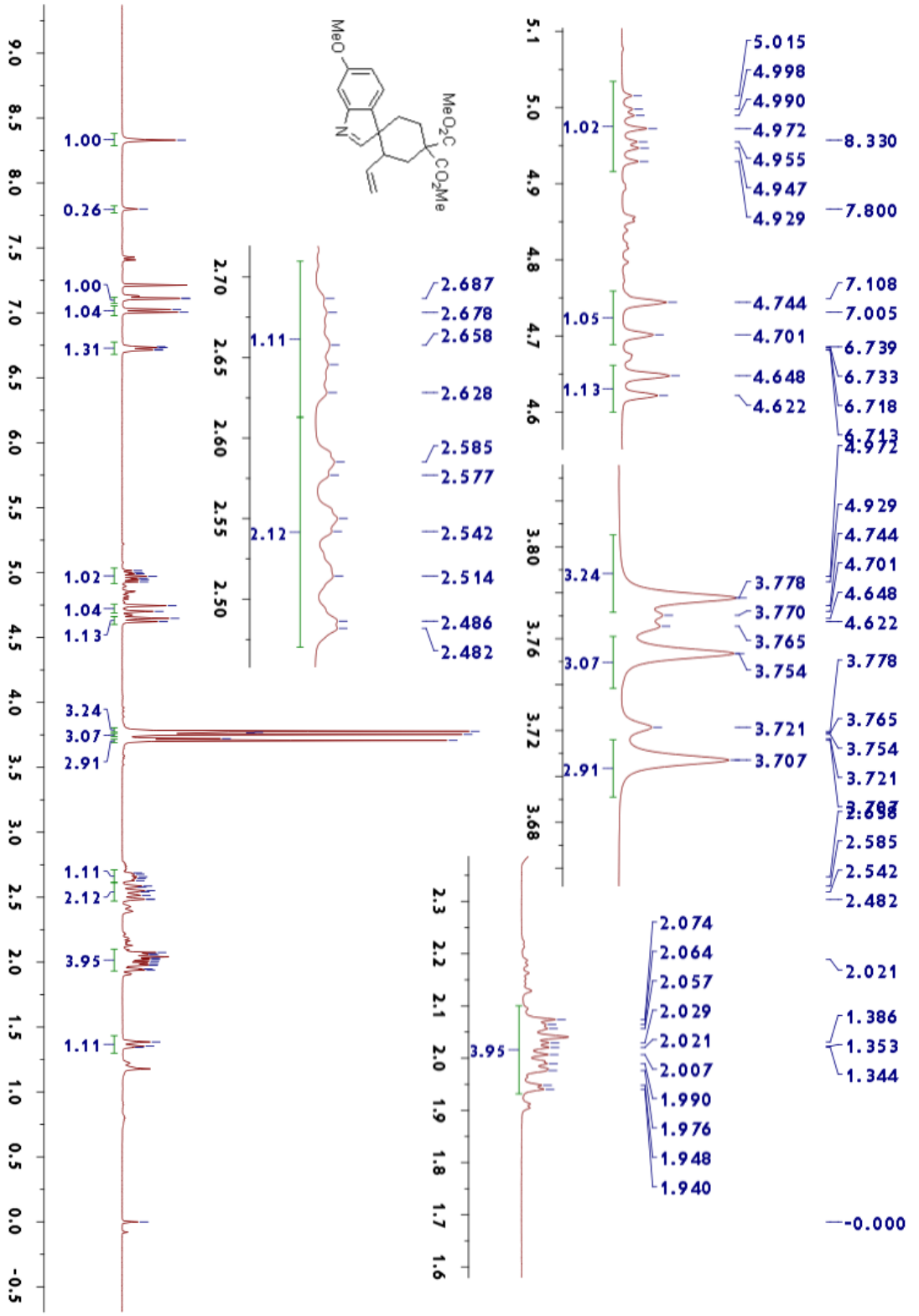
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CO2Me
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1.00
0.26
1.00
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1.04
1.13
3.24
3.07
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1.05
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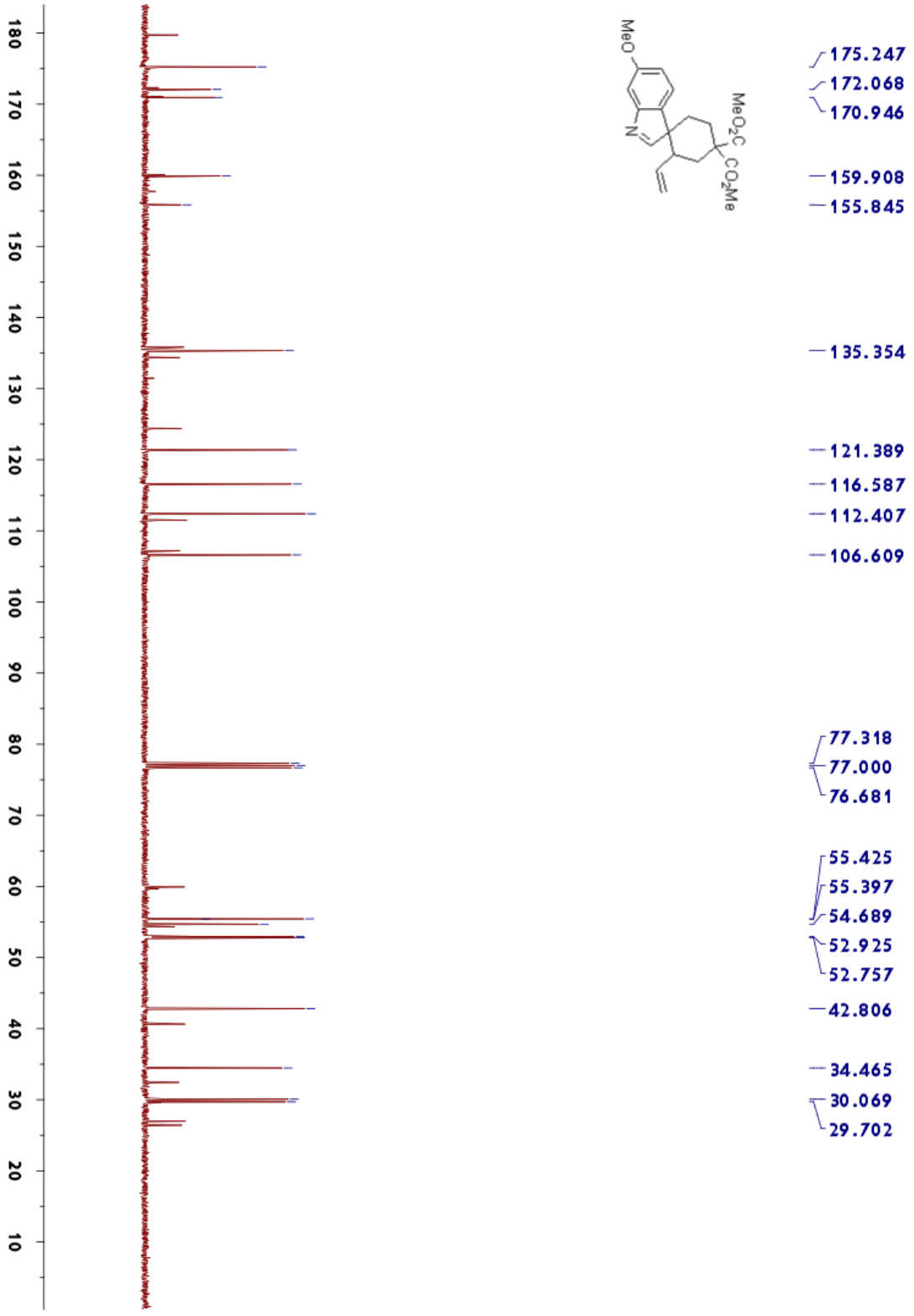
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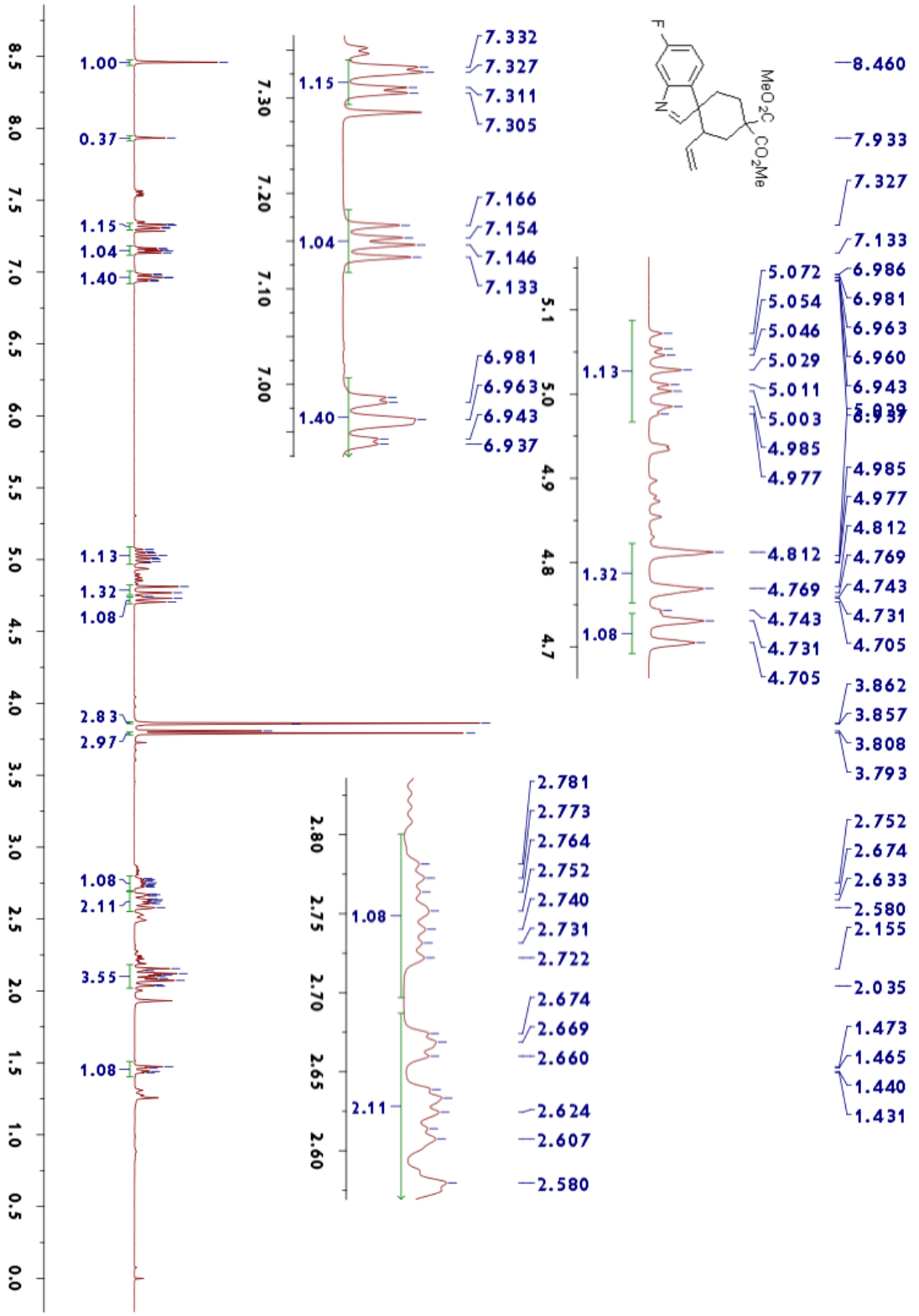
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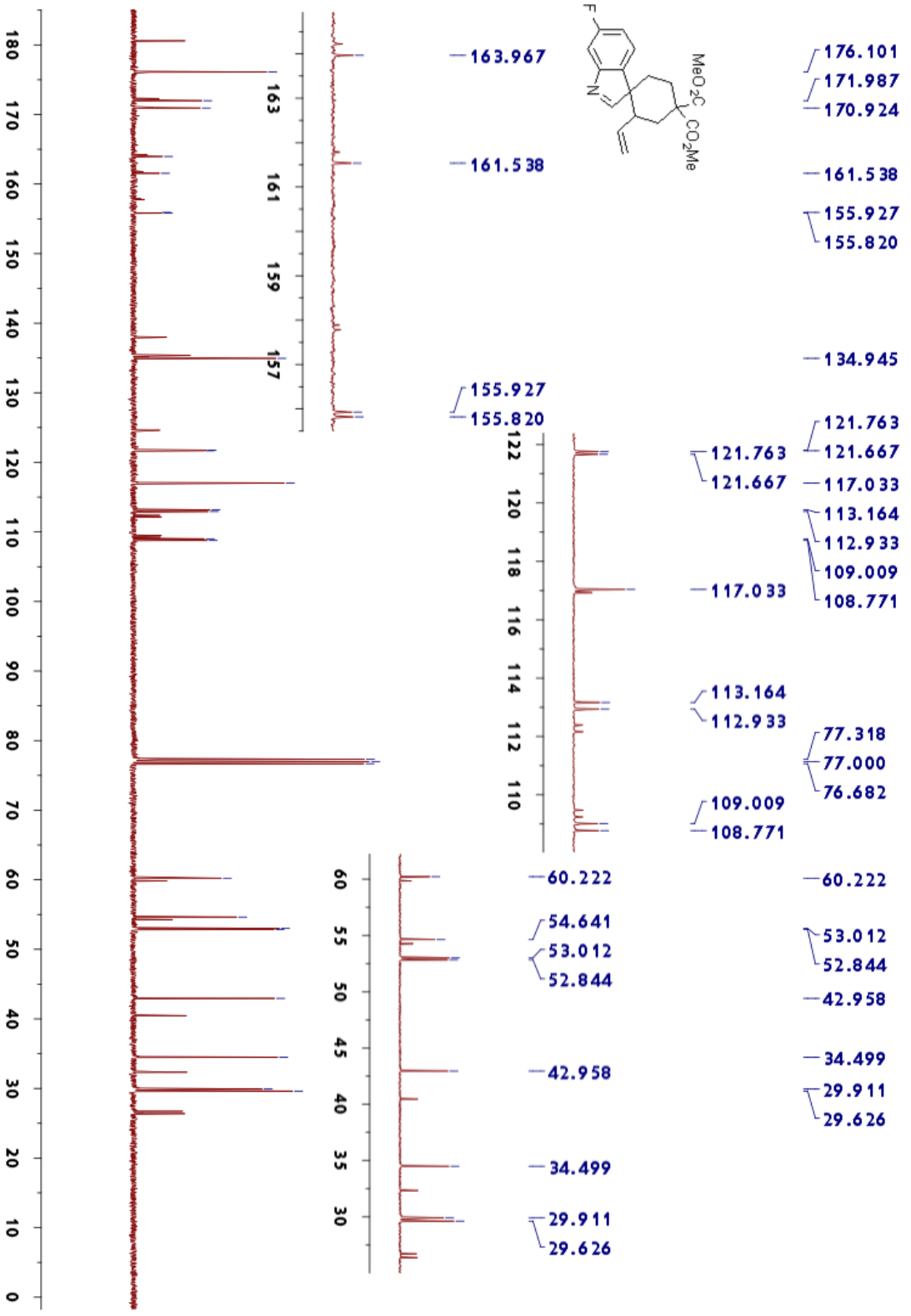
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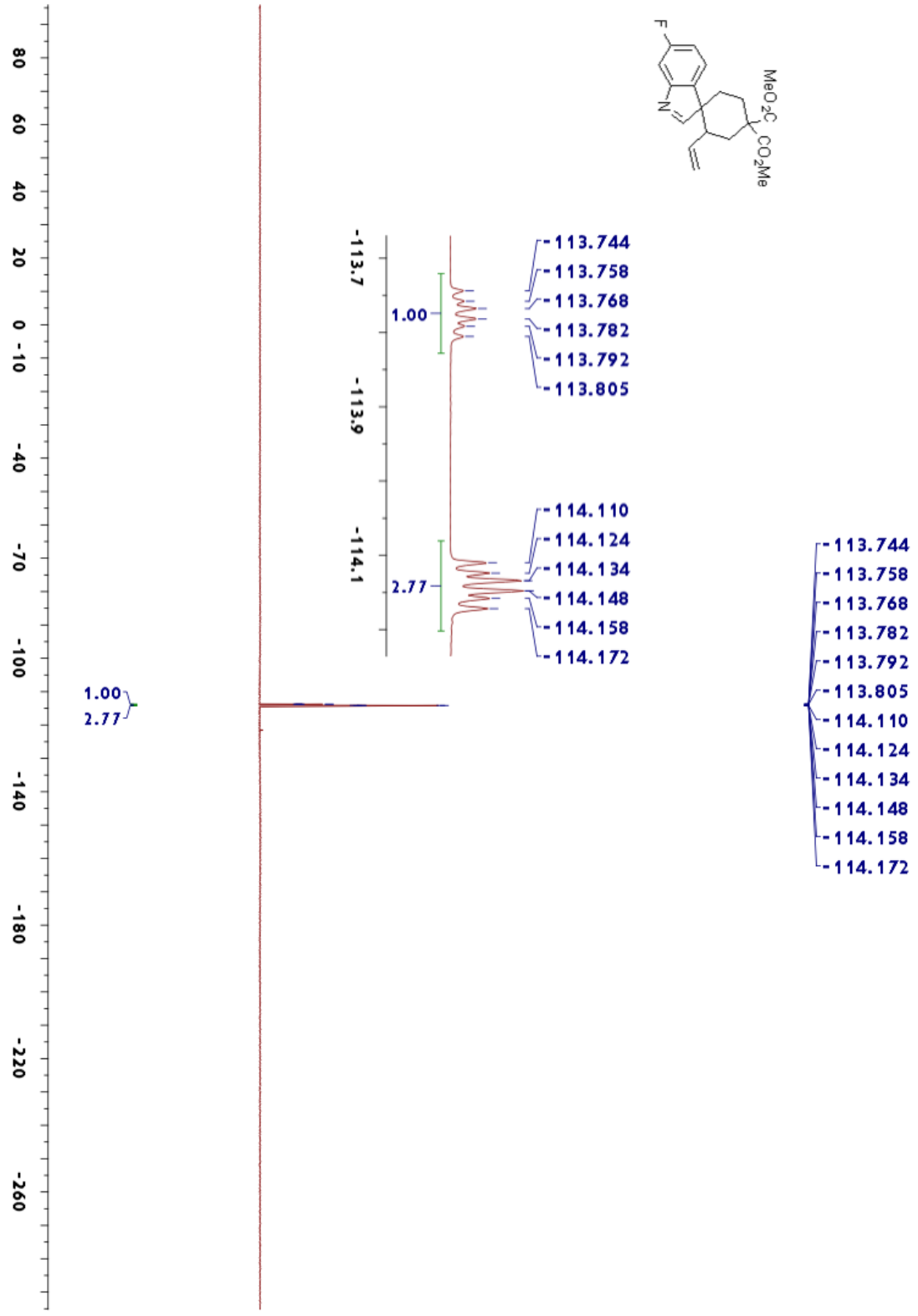
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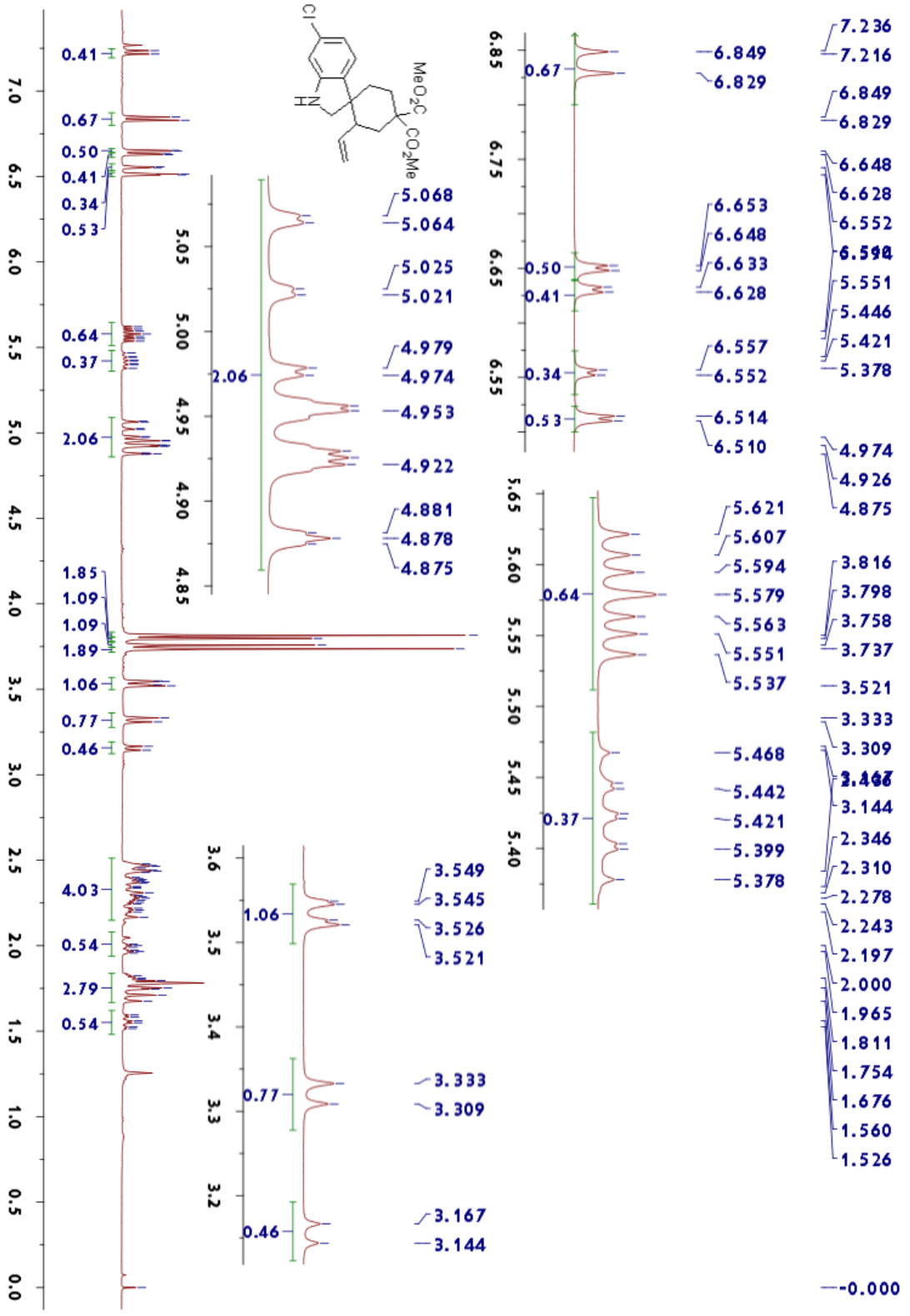
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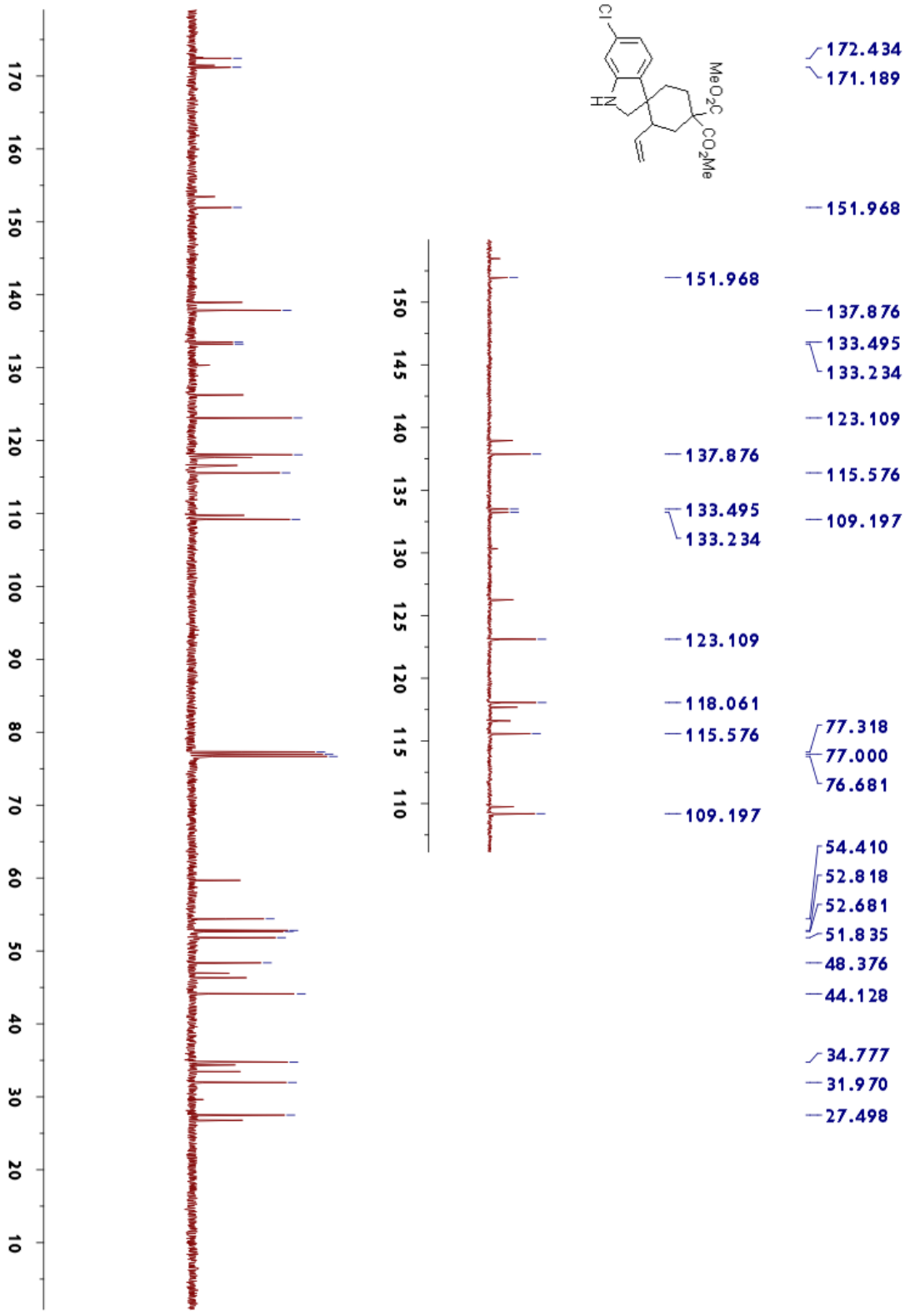
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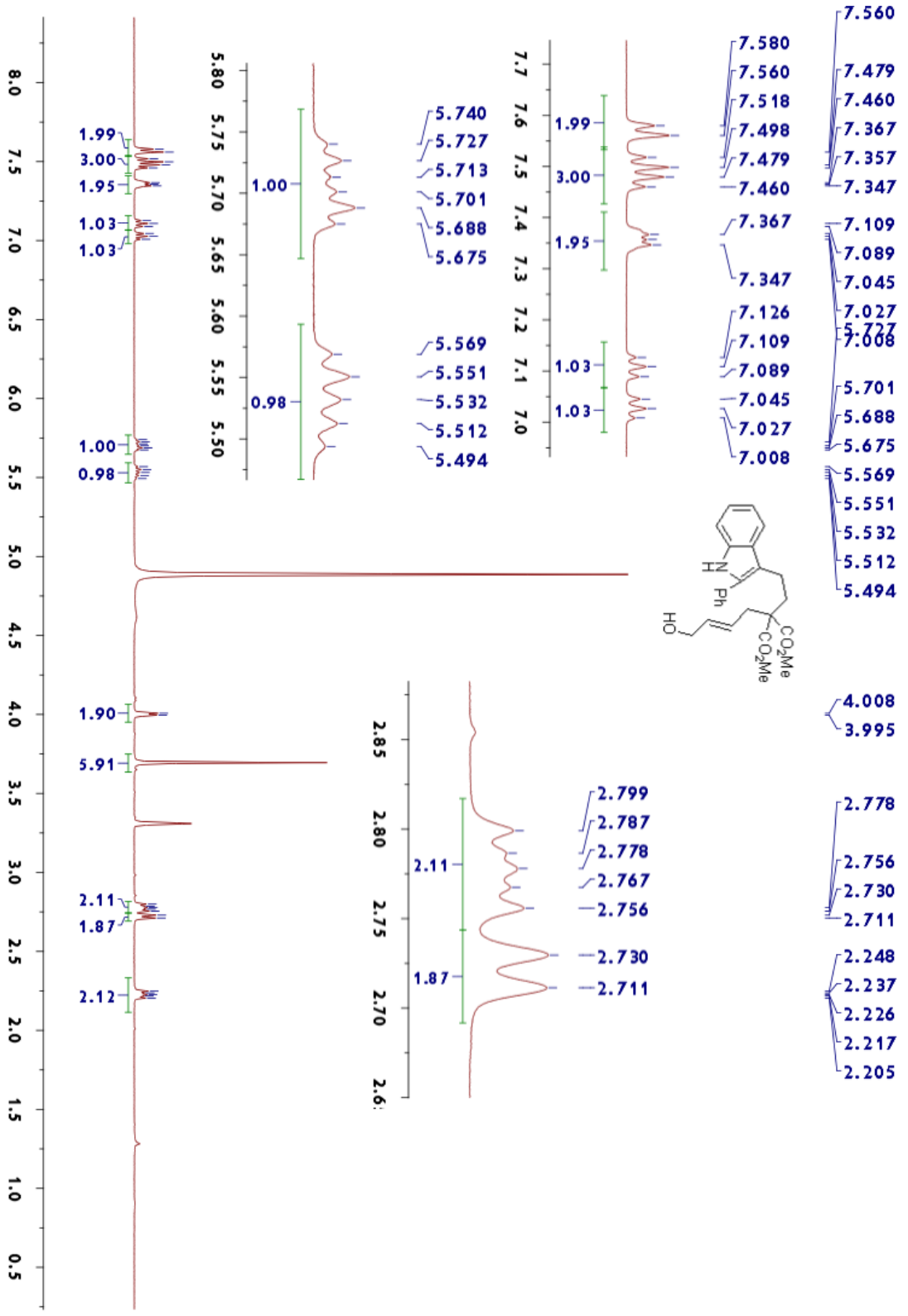
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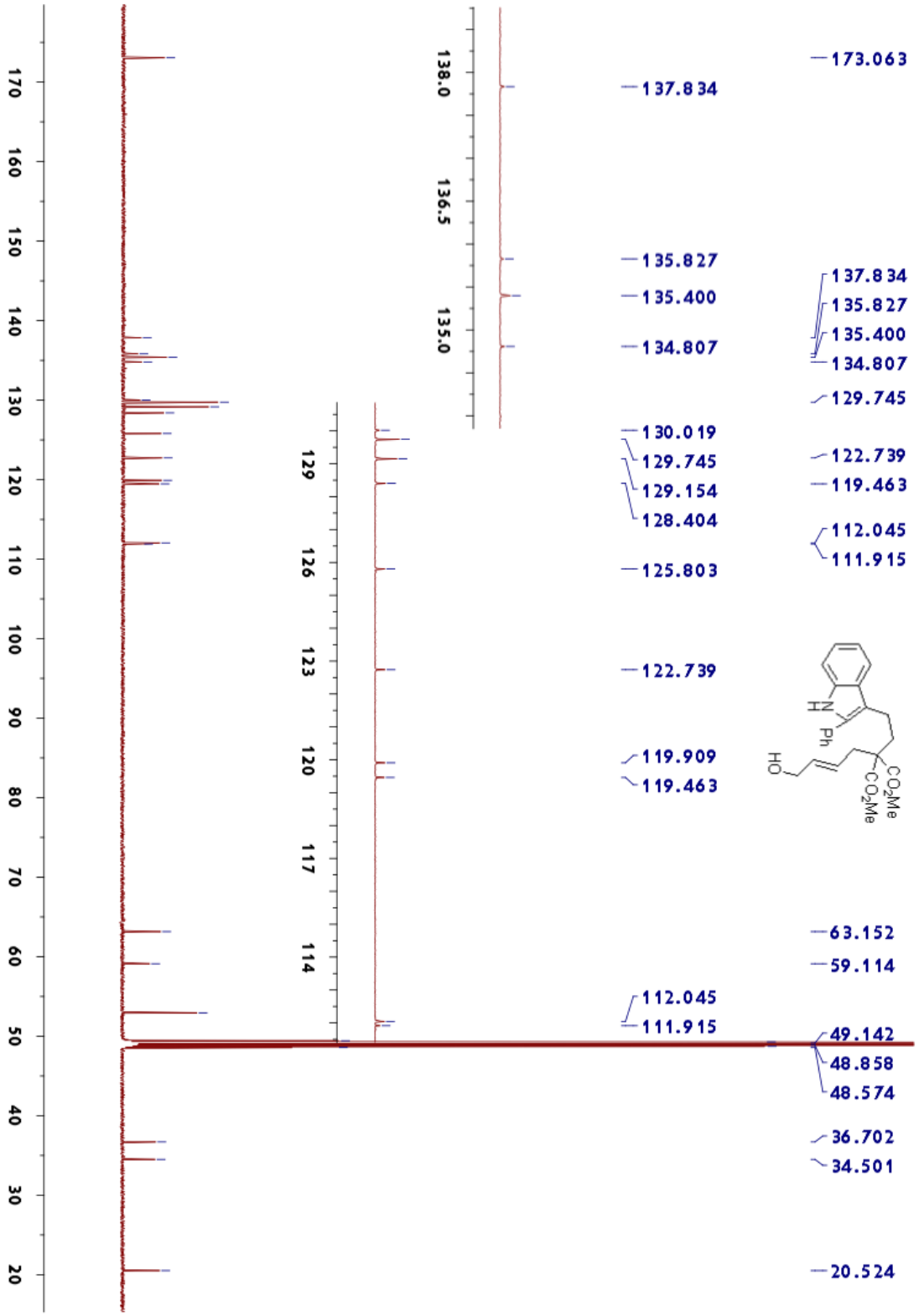
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CO2Me