Supporting Information

For

Ring-Closing Metathesis/Isomerization/Pictet-Spengler Cascade *via* Ruthenium/ Chiral Phosphoric Acid Sequential Catalysis

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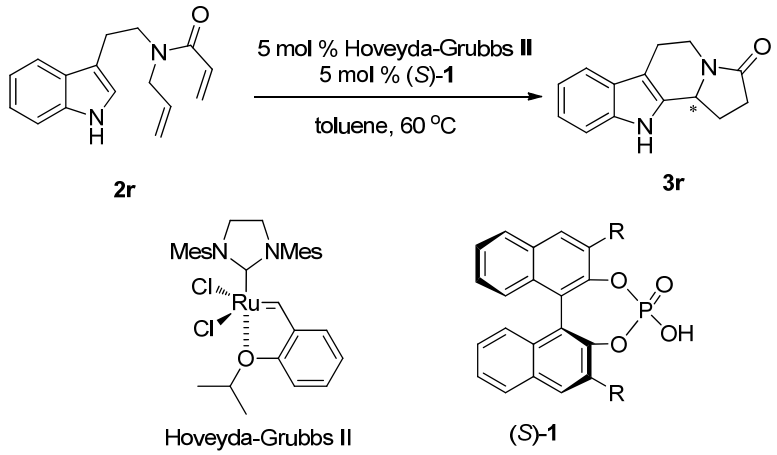
1. **General methods**. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Varian instrument (300 MHz and 75 MHz, 400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

2. Experimental sections

2.1 Initial investigation

For the initial investigation, we studied the tandem RCM/isomerization/PS reaction of **2r** with various chiral phosphoric acids (Table S-1). To our delight, in the presence of catalytic amount of chiral phosphoric acid, the cascade reaction went on smoothly to afford product **3r**, but with only moderate enantioselectivity (entry 10).

Table S-1 Screening chiral phosphoric acids for the tandem reaction of **2r**.[a]

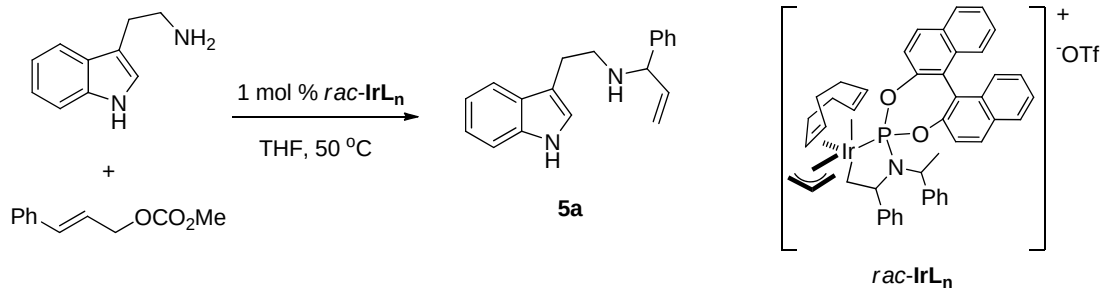


entry[a]	**1**	R	yield (%)[b]	*ee* (%)[c]
1	**1a**	1-naphthyl	62	8
2	**1c**	4-NO_2-C_6H_4	80	0
3	**1d**	4-biphenyl	87	11
4	**1e**	9-anthryl	87	-1
6	**1f**	9-phenanthryl	80	6

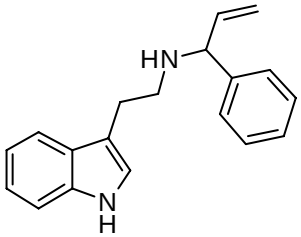
7	**1h**	2,4,6-(^{i}Pr)$_3$-C$_6$H$_2$	68	22
8	**1i**	4-^{t}Bu-2,6-(^{i}Pr)$_2$-C$_6$H$_2$	82	18
9	**1j**	$SiPh_3$	87	22
10	**1k**	4-anthryl-2,6-(^{i}Pr)$_2$-C$_6$H$_2$	84	56

[a] Reaction conditions: 5 mol % (S)-**1**, 5 mol % Hoveyda-Grubbs II, 0.1 mol/L of **2r** in toluene at 60 ℃. [b] Isolated yield of **3r**. [c] Determined by HPLC analysis.

2.2 General method for the preparation of 5a-5q



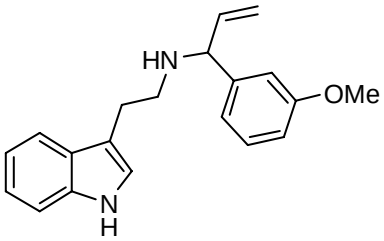
rac-**IrL$_n$**[1] (30.9 mg, 0.03 mmol, 1 mol %) and tryptamine (528 mg, 3.3 mmol) were dissolved in THF (5 mL) in a dry Schelenk tube filled with argon. Then cinnamyl methyl carbonate (576 mg, 3.0 mmol) was added slowly. The reaction mixture was heated at 50 ℃ for 30 min. After the reaction was complete (monitored by TLC), water (5 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phase was washed with brine, separated, dried over Na_2SO_4, filtrated, and evaporated under reduced pressure. The ratio of regioisomers (branch to linear b/l) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by flash chromatography to afford product **5a**.



***N*-(2-(1H-Indol-3-yl)ethyl)-1-phenylprop-2-en-1-amine (5a)**

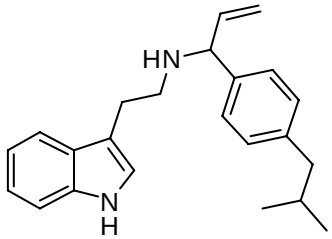
Viscous oil (89% yield, b/l > 95/5) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM/Et_3N = 250/100/100/2.5, v/v). Analytical data for **5a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72 (br, 1H), 2.83-3.00 (m, 4H), 4.20 (d, J = 7.2 Hz, 1H), 5.06 (ddd, J = 0.8, 1.2, 10.4 Hz, 1H), 5.17 (ddd, J = 1.2, 2.4, 17.2 Hz, 1H), 5.90 (ddd, J = 6.8, 10.0, 17.2 Hz, 1H), 6.94 (d, J = 2.0 Hz, 1H), 7.07-7.11 (m, 1H), 7.15-7.19 (m, 1H), 7.20-7.24 (m, 1H), 7.27-7.31 (m, 5H), 7.57 (dd, J = 7.6, 0.4 Hz, 1H), 8.12 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 47.5, 66.0, 111.1, 113.8, 115.0, 118.9, 119.1, 121.9, 127.1, 127.2, 127.4, 128.5, 136.3, 141.0, 142.8; IR (film) 3416, 2929,

1454, 1340, 1228, 1093, 991, 922, 739, 700 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{19}H_{20}N_2$ requires m/z 276.1626. Found m/z 276.1629.



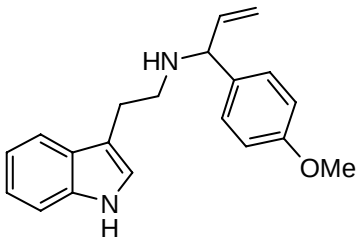
***N*-(2-(1H-Indol-3-yl)ethyl)-1-(3-methoxyphenyl)prop-2-en-1-amine (5b)**

Viscous oil (84% yield, b/l > 95/5) following silica gel column chromatography (petroleum ether /ethyl acetate/DCM/Et_3N = 250/100/100/2.5, v/v). Analytical data for **5b**: ^1H NMR (300 MHz, $CDCl_3$) δ 1.64 (br, 1H), 2.82-3.00 (m, 4H), 3.72 (s, 3H), 4.17 (d, J = 6.9 Hz, 1H), 5.06 (d, J = 10.5 Hz, 1H), 5.17 (d, J = 17.1 Hz, 1H), 5.89 (ddd, J = 7.2, 10.5, 17.1 Hz, 1H), 6.76 (dd, J = 1.2, 7.5 Hz, 1H), 6.86-6.88 (m, 2H), 6.93 (d, J = 1.8 Hz, 1H), 7.06-7.22 (m, 3H), 7.28 (d, J = 8.1 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 8.22 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.6, 47.4, 55.1, 66.0, 111.1, 112.4, 112.6, 113.7, 115.0, 118.8, 119.1, 119.5, 121.8, 121.9, 127.3, 129.4, 136.2, 140.8, 144.5, 159.7; IR (film) 3416, 2834, 1731, 1597, 1454, 1251, 1042, 738 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{20}H_{22}N_2O$ requires m/z 306.1732. Found m/z 306.1730.



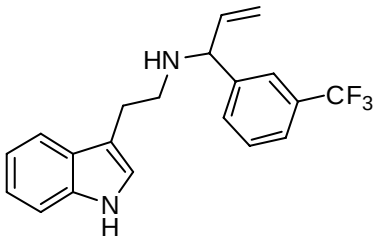
***N*-(2-(1H-Indol-3-yl)ethyl)-1-(4-isobutylphenyl)prop-2-en-1-amine (5c)**

White solid (91% yield, b/l > 95/5) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM/Et_3N = 400/100/100/4, v/v). Analytical data for **5c**: Mp = 90-92 ℃; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (d, J = 6.6 Hz, 6H), 1.78 (br, 1H), 1.80-1.87 (m, 1H), 2.43 (d, J = 7.2 Hz, 2H), 2.84-3.00 (m, 4H), 4.17 (d, J = 7.2 Hz, 1H), 5.05 (d, J = 9.9 Hz, 1H), 5.16 (d, J = 17.1 Hz, 1H), 5.91 (ddd, J = 7.2, 9.9, 17.1 Hz, 1H), 6.93 (d, J = 1.8 Hz, 1H), 7.05-7.10 (m, 3H), 7.14-7.19 (m, 3H), 7.29 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 8.18 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.4, 25.7, 30.1, 45.0, 47.5, 65.7, 111.1 , 113.8, 114.8, 118.9, 119.1, 121.9, 121.9, 126.9, 127.4, 129.2, 136.3, 140.0, 140.5, 141.1; IR (film) 3293, 2918, 1727, 1643, 1453, 1352, 1260, 1042, 1103, 739 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{23}H_{28}N_2$ requires m/z 332.2252. Found m/z 332.2247.



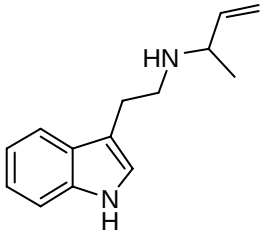
***N*-(2-(1H-Indol-3-yl)ethyl)-1-(4-methoxyphenyl)prop-2-en-1-amine (5d)**

Viscous oil (78% yield, b/l > 95/5) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM/Et_3N = 400/100/100/4, v/v). Analytical data for **5d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.58 (br, 1H), 2.81-3.00 (m, 4H), 3.75 (s, 3H), 4.15 (d, J = 7.2 Hz, 1H), 5.04 (d, J = 10.2 Hz, 1H), 5.14 (d, J = 17.1 Hz, 1H), 5.89 (ddd, J = 7.2, 10.2, 17.1 Hz, 1H), 6.82 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 1.8 Hz, 1H), 7.06-7.21 (m, 4H), 7.28 (d, J = 8.1 Hz, 1H), 7.57 (d, J = 8.1 Hz, 1H), 8.27 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.6, 47.4, 55.2, 65.3, 111.1, 113.7, 113.8, 114.6, 118.8, 119.1, 121.8, 121.9, 127.3, 128.2, 134.9, 136.3, 141.1, 158.6; IR (film) 3416, 2834, 1731, 1597, 1454, 1251, 1042, 738 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{20}H_{22}N_2O$ requires m/z 306.1732. Found m/z 306.1727.



***N*-(2-(1H-Indol-3-yl)ethyl)-1-(3-(trifluoromethyl)phenyl)prop-2-en-1-amine (5e)**

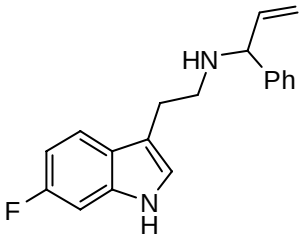
Viscous oil (86% yield, b/l > 95/5) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM/Et_3N = 300/100/100/3, v/v). Analytical data for **5e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.71 (br, 1H), 2.78-2.83 (m, 1H), 2.90-3.00 (m, 3H), 4.24 (d, J = 7.2 Hz, 1H), 5.09 (d, J = 9.9 Hz, 1H), 5.17 (d, J = 17.1 Hz, 1H), 5.84 (ddd, J = 7.5, 10.2, 17.1 Hz, 1H), 6.96 (d, J = 1.8 Hz, 1H), 7.07-7.20 (m, 2H), 7.29-7.39 (m, 2H), 7.45-7.49 (m, 2H), 7.57-7.59 (m, 2H), 8.07 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.6, 47.5, 65.6, 111.1, 113.7, 115.7, 118.8, 119.2, 121.9, 122.0, 123.9, 127.3, 128.9, 130.6, 136.3, 140.2, 143.9; IR (film) 3414, 1455, 1326, 1260, 1162, 1120, 1071, 924, 802, 740, 703 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{20}H_{19}N_2F_3$ requires m/z 344.1500. Found m/z 344.1502.



***N*-(2-(1H-Indol-3-yl)ethyl)but-3-en-2-amine (5f)**

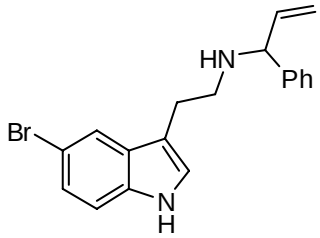
White solid (82% yield, b/l > 95/5) following silica gel column chromatography (DCM/MeOH//Et_3N = 100/1/1, v/v). Analytical data for **5f**: Mp = 70-72 ℃, ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (d, J = 6.3 Hz, 3H), 1.45 (br, 1H), 2.87-2.98 (m, 4H), 3.16-3.24 (m, 1H), 5.02 (d, J = 10.2 Hz, 1H), 5.07 (d, J = 17.1 Hz, 1H), 5.66 (ddd, J = 7.8, 10.2, 17.1 Hz, 1H), 6.96 (d, J = 1.5 Hz, 1H), 7.07-7.20 (m, 2H),

7.31 (d, J = 7.8 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 8.72 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 25.7, 47.3, 56.6, 111.1, 113.5, 114.6, 118.8, 119.0, 121.7, 122.0, 127.3, 136.3, 142.3; IR (film) 3271, 2973, 2857, 1620, 1452, 1228, 1102, 913, 870, 742 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{14}H_{18}N_2$ requires m/z 214.1470. Found m/z 214.1466.



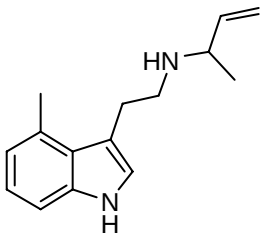
***N*-(2-(6-Fluoro-1H-indol-3-yl)ethyl)-1-phenylprop-2-en-1-amine (5g)**

Viscous oil (53% yield, b/l > 95/5, 50 ℃) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM/Et_3N = 400/100/100/4, v/v). Analytical data for **5g**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.64 (br, 1H), 2.81-2.96 (m, 4H), 4.20 (d, J = 7.2 Hz, 1H), 5.07 (d, J = 10.2 Hz, 1H), 5.17 (d, J = 17.1 Hz, 1H), 5.90 (ddd, J = 7.2, 10.2, 17.1Hz, 1H), 6.82-6.99 (m, 3H), 7.20-7.32 (m, 5H), 7.44 (dd, J = 5.4, 8.7 Hz, 1H), 8.27 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.6, 47.3, 66.0, 97.3 (d, J = 25.5 Hz), 107.8 (d, J = 24.8 Hz), 113.8, 115.1, 119.5 (d, J = 10.1 Hz), 122.1 (d, J = 3.8 Hz), 127.1, 128.5, 136.1 (d, J = 12.5 Hz), 140.8, 142.6, 159.9 (d, J = 235.5 Hz); IR (film) 3428, 2914, 2839, 1727, 1627, 1454, 1250, 1139, 922, 800, 700 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{19}H_{19}N_2F$ requires m/z 294.1532. Found m/z 294.1528.



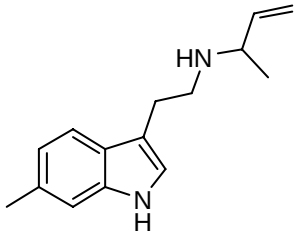
***N*-(2-(5-Bromo-1H-indol-3-yl)ethyl)-1-phenylprop-2-en-1-amine (5h)**

White solid (65% yield, b/l > 95/5) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM/Et_3N = 400/100/100/4, v/v).Analytical data for **5h**: Mp = 96-98 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48 (br, 1H), 2.77-2.94 (m, 4H), 4.20 (d, J = 7.2 Hz, 1H), 5.07 (d, J = 9.9 Hz, 1H), 5.18 (d, J = 17.1 Hz, 1H), 5.90 (ddd, J = 6.9, 9.9, 17.1 Hz, 1H), 6.91 (d, J = 1.8 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 7.21-7.33 (m, 6H), 7.68 (s, 1H), 8.39 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.5, 47.3, 66.0, 112.4, 112.5, 113.4, 115.1, 121.4, 123.2, 124.6, 127.1, 127.2, 128.5, 129.1, 134.8, 140.8, 142.6; IR (film) 3289, 3120, 3022, 2852, 1639, 1455, 1230, 1102, 919, 791, 703, 657 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{19}H_{19}N_2Br$ requires m/z 354.0732. Found m/z 354.0735.



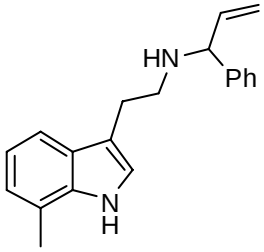
***N*-(2-(4-Methyl-1H-indol-3-yl)ethyl)but-3-en-2-amine (5i)**

Viscous oil (79% yield, b/l > 95/5) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM/Et_3N = 250/100/100/2.5, v/v). Analytical data for **5i**: Mp = 69-70 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 1.16 (d, J = 6.6 Hz, 3H), 1.62 (br, 1H), 2.69 (s, 3H), 2.81-3.00 (m, 2H), 3.09-3.23 (m, 3H), 5.02 (dd, J = 1.2, 10.2 Hz, 1H), 5.09 (d, J = 17.1 Hz, 1H), 5.69 (ddd, J = 7.8, 10.2, 17.7 Hz, 1H), 6.83 (d, J = 6.9 Hz, 1H), 6.93 (d, J = 1.8 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 7.16 (d, J = 7.8 Hz, 1H), 8.52 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.3, 21.6, 27.5, 48.6, 56.8, 109.0, 114.4, 114.7, 120.8, 121.8, 122.1, 125.7, 130.8, 136.7, 142.3; IR (film) 3270, 2855, 1744, 1616, 1517, 1462, 1342, 1245, 918, 745, 719; HRMS (EI): Exact mass calcd for $C_{15}H_{20}N_2$ requires m/z 228.1626. Found m/z 228.1625.



***N*-(2-(6-Methyl-1H-indol-3-yl)ethyl)but-3-en-2-amine (5j)**

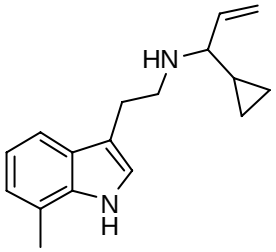
Viscous oil (77% yield, b/l > 95/5) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM/Et_3N = 400/100/100/4, v/v). Analytical data for **5j**: Mp = 89-90 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 1.13 (d, J = 6.6 Hz, 3H), 1.76 (br, 1H), 2.45 (s, 3H), 2.85-2.98 (m, 4H), 3.17-3.22 (m, 1H), 5.02 (d, J = 10.2 Hz, 1H), 5.07 (d, J = 17.7 Hz, 1H), 5.67 (ddd, J = 7.8, 10.2, 17.4 Hz, 1H), 6.92-6.96 (m, 2H), 7.11 (s, 1H), 7.50 (d, J = 7.8 Hz, 1H), 8.28 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 21.6, 25.7, 47.3, 56.6, 111.1, 113.5, 114.6, 118.5, 120.9, 121.3, 125.2, 131.6, 136.8, 142.3; IR (film) 3267, 2916, 1629, 1452, 1337, 1227, 1106, 911, 793 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{15}H_{20}N_2$ requires m/z 228.1626. Found m/z 228.1631.



***N*-(2-(7-Methyl-1H-indol-3-yl)ethyl)-1-phenylprop-2-en-1-amine (5k)**

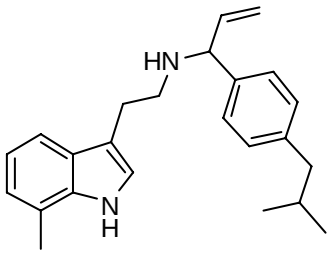
Viscous oil (94% yield, b/l > 95/5) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM/Et_3N = 400/100/100/4, v/v). Analytical data for **5k**: ^1H NMR (300 MHz, $CDCl_3$) δ 1.82 (br, 1H), 2.41 (s, 3H), 2.80-2.99 (m, 4H), 4.18 (d, J = 7.2 Hz, 1H), 5.05 (d, J = 10.2 Hz, 1H), 5.16 (d, J = 17.1 Hz, 1H), 5.90 (ddd, J = 6.9, 10.8, 17.1 Hz, 1H), 6.92-7.05 (m, 3H), 7.18-7.29 (m, 5H), 7.43 (d, J = 7.2 Hz, 1H), 7.95 (br, 1H); ^{13}C NMR (75 MHz,

$CDCl_3$) δ 16.5, 25.7, 47.5, 66.0, 114.2, 115.0, 116.6, 119.4, 120.2, 121.6, 122.4, 126.9, 127.1, 127.2, 128.4, 135.8, 140.9, 142.7; IR (film) 3420, 2916, 1727, 1492, 1244, 1092, 1044, 920, 781, 744, 700 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{20}H_{22}N_2$ requires m/z 290.1783. Found m/z 290.1781.



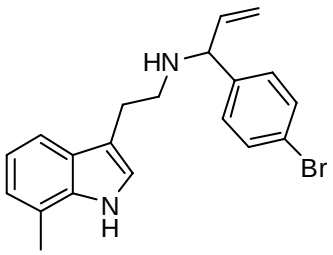
1-Cyclopropyl-*N*-(2-(7-methyl-1H-indol-3-yl)ethyl)prop-2-en-1-amine (5l)

Viscous oil (63% yield, b/l > 95/5) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM/Et_3N = 250/100/100/2.5, v/v). Analytical data for **5l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12-0.17 (m, 2H), 0.43-0.50 (m, 2H), 0.84-0.96 (m, 1H), 1.86 (br, 1H), 2.31 (t, J = 6.3 Hz, 1H), 2.47 (s, 3H), 2.90-2.99 (m, 4H), 5.04-5.10 (m, 2H), 5.72-5.81 (m, 1H), 6.98-7.06 (m, 3H), 7.47 (d, J = 7.6 Hz, 1H), 8.08 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.0, 4.2, 16.3, 16.6, 25.9, 47.5, 66.8, 114.4, 115.3, 116.6, 119.4, 120.3, 121.6, 122.4, 126.9, 135.9, 140.3; IR (film) 3418, 2918, 2848, 1720, 1617, 1451, 1342, 1287, 1096, 919, 781, 743 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{17}H_{22}N_2$ requires m/z 254.1783. Found m/z 254.1779.



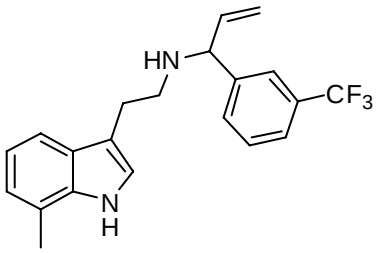
1-(4-Isobutylphenyl)-*N*-(2-(7-methyl-1H-indol-3-yl)ethyl)prop-2-en-1-amine (5m)

Viscous oil (78% yield, b/l > 95/5) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM/Et_3N = 400/100/100/4, v/v). Analytical data for **5m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (d, J = 6.4 Hz, 6H), 1.69 (br, 1H), 1.79-1.86 (m, 1H), 2.42-2.43 (m, 5H), 2.82-2.99 (m, 4H), 4.17 (d, J = 7.6, Hz, 1H), 5.05 (dd, J = 10.0, 0.8 Hz, 1H), 5.16 (dt, J = 16.9, 1.6 Hz, 1H), 5.90 (ddd, J = 7.2, 10.0, 17.2 Hz, 1H), 6.96-7.07 (m, 4H), 7.17-7.21 (m, 2H), 7.42 (d, J = 7.2 Hz, 1H), 7.91 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.6, 22.4, 25.8, 30.2, 45.0, 47.5, 65.8, 114.5, 114.7, 116.6, 119.4, 120.2, 121.6, 122.4, 126.9, 126.9, 129.2, 135.9, 140.1, 140.5, 141.2; IR (film) 3422, 2953, 2921, 1616, 1453, 1382, 1341, 1092, 920, 782, 745 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{24}H_{30}N_2$ requires m/z 346.2409. Found m/z 346.2411.



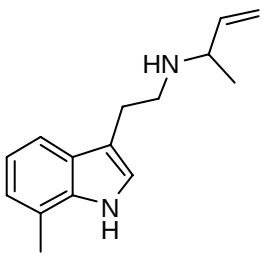
1-(4-Bromophenyl)-*N*-(2-(7-methyl-1H-indol-3-yl)ethyl)prop-2-en-1-amine (5n)

Viscous oil (87% yield, b/l > 95/5) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM/Et_3N = 400/100/100/4, v/v). Analytical data for **5n**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.68 (br, 1H), 2.46 (s, 3H), 2.78-2.98 (m, 4H), 4.15 (d, J = 6.9 Hz, 1H), 5.06 (d, J = 10.2 Hz, 1H), 5.14 (d, J = 17.1 Hz, 1H), 5.83 (ddd, J = 7.5, 10.5, 17.1 Hz, 1H), 6.98-7.06 (m, 3H), 7.16 (d, J = 8.4 Hz, 2H), 7.42 (t, J = 8.1 Hz, 3H), 7.93 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.6, 25.8, 47.4, 65.4, 114.3, 115.3, 115.3, 116.6, 119.5, 120.3, 120.8, 121.6, 122.5, 126.8, 129.0, 131.5, 135.9, 140.6 141.9; IR (film) 3419, 2916, 1589, 1485, 1453, 1070, 1010, 922, 817, 782, 745; HRMS (EI): Exact mass calcd for $C_{20}H_{21}N_2Br$ requires m/z 368.0888. Found m/z 368.0887.



***N*-(2-(7-Methyl-1H-indol-3-yl)ethyl)-1-(3-(trifluoromethyl)phenyl)prop-2-en-1-amine (5o)**

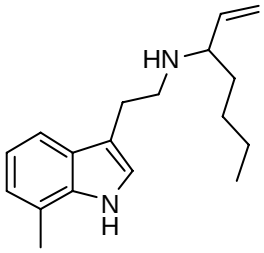
Viscous oil (86% yield, b/l > 95/5) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM/Et_3N = 300/100/100/3, v/v). Analytical data for **5o**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.61 (br, 1H), 2.44 (s, 3H), 2.78-2.83 (m, 1H), 2.90-2.99 (m, 3H), 4.23 (d, J = 7.2 Hz, 1H), 5.09 (ddd, J = 0.8, 1.2, 10.0 Hz, 1H), 5.17 (ddd, J = 1.2, 1.2, 16.9 Hz, 1H), 5.84 (ddd, J = 7.2, 10.0, 16.8 Hz, 1H), 6.97-7.05 (m, 3H), 7.37 (t, J = 7.2 Hz, 1H), 7.43-7.58 (m, 3H), 7.58 (s, 1H), 7.89 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.5, 25.8, 47.5, 65.7, 114.3, 115.7, 116.6, 119.5, 120.3, 121.6, 122.5, 124.2 (q, J = 271 Hz), 124.0 (q, J = 2.7 Hz), 126.9, 130.6, 130.7 (q, J = 32.0 Hz), 135.9, 140.3, 144.0; IR (film) 3420, 2918, 2849, 1444, 1327, 1162, 1121, 1070, 924, 803, 745, 704 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{21}H_{21}N_2F_3$ requires m/z 358.1657. Found m/z 358.1661.



***N*-(2-(7-Methyl-1H-indol-3-yl)ethyl)but-3-en-2-amine (5p)**

Viscous oil (78% yield, b/l > 95/5) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM/Et_3N =

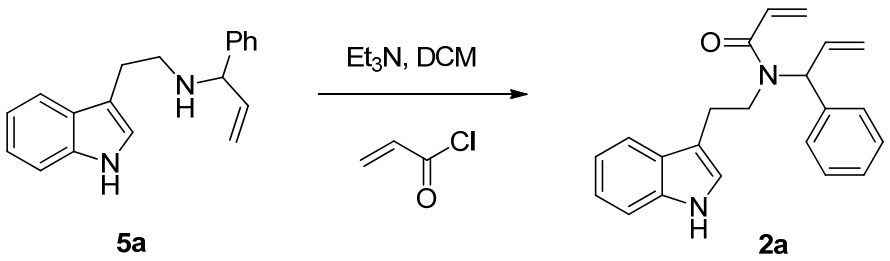
200/100/100/2, v/v). Analytical data for **5p**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (d, J = 6.6 Hz, 3H), 1.38 (br, 1H), 2.45 (s, 3H), 2.85-2.99 (m, 4H), 3.16-3.20 (m, 1H), 5.01 (d, J = 10.2 Hz, 1H), 5.07 (d, J = 17.4 Hz, 1H), 5.66 (ddd, J = 8.1, 10.2, 17.7Hz, 1H), 7.00-7.07 (m, 3H), 7.47 (d, J = 7.5 Hz, 1H), 8.12 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.6, 21.6, 25.9, 47.3, 56.6, 114.1, 114.5, 116.5, 119.3, 120.3, 121.7, 122.3, 126.8, 135.9, 142.5; IR (film) 3282, 2918, 1617, 1499, 1349, 1233, 1106, 922, 783, 747 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{15}H_{20}N_2$ requires m/z 228.1626. Found m/z 228.1623.



***N*-(2-(7-Methyl-1H-indol-3-yl)ethyl)hept-1-en-3-amine (5q)**

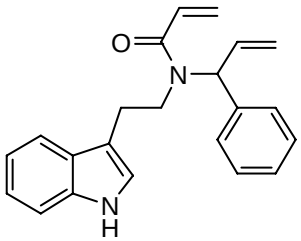
Purification following silica gel column chromatography (petroleum ether/ethyl acetate/DCM/Et_3N = 250/100/100/2.5, v/v). Clean NMR data are difficult to be obtained, and the sample can be utilized directly in the next step without any problem. Analytical data for **5q**: IR (film) 3419, 2927, 2856, 1617, 1453, 1342, 1231, 1104, 995, 919, 781, 743 cm^{-1}; HRMS (EI): Exact mass calcd for $C_{14}H_{18}N_2$ requires m/z 214.1470. Found m/z 214.1466.

2.3 General procedure for the preparation of 2a-2q



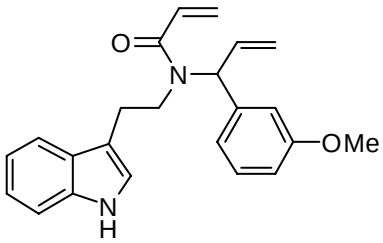
5a **2a**

A three-necked flask was charged with **5a** (654 mg, 2.37 mmol), triethyl amine (479 mg, 2.84 mmol) and DCM (20 mL). Then acryloyl chloride (256 mg, 2.84 mmol) was added dropwise. The mixture was stirred at room temperature. After the reaction was complete (monitored by TLC), water (10 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phase was washed with brine, separated, dried over Na_2SO_4, filtrated, and evaporated under reduced pressure. The residue was purified by flash chromatography to afford product **2a**.



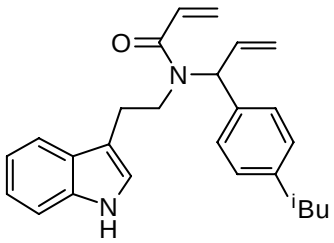
***N*-(2-(1H-Indol-3-yl)ethyl)-*N*-(1-phenylallyl)acrylamide (2a)**

White solid (82% yield) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 3/1/1, v/v). Analytical data for **2a**: Mp = 87-88 ℃; ^{1}H NMR (400 MHz, $CDCl_3$, 60 ℃) δ 2.54 (br, 1H), 2.90 (br, 1H), 3.47-3.63 (m, 2H), 5.23 (d, J = 16.8 Hz, 1H), 5.36 (d, J = 10.0 Hz, 1H), 5.67 (d, J = 10.0 Hz, 1H), 6.13-6.22 (m, 1H), 6.40 (d, J = 16.8 Hz, 1H), 6.67 (dd, J = 10.4, 16.4 Hz, 1H), 5.21-6.64 (NCH, br, 1H), 6.78 (s, 1H), 7.04 (t, J = 7.2 Hz, 1H), 7.12 (t, J = 7.2 Hz, 1H), 7.21-7.34 (m, 7H), 8.14 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 60 ℃) δ 24.7-26.7, 46.2, 60.1-63.5, 111.2, 112.8, 118.2, 118.6, 119.2, 121.9, 127.3, 127.8, 128.3, 128.6, 135.1, 136.4, 139.1, 167.0; IR (film) 3236, 3057, 2924, 2869, 1633, 1581, 1441, 1422, 1237, 1001, 921, 753, 702 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{22}H_{22}N_2O$ requires m/z 330.1732. Found m/z 330.1735.



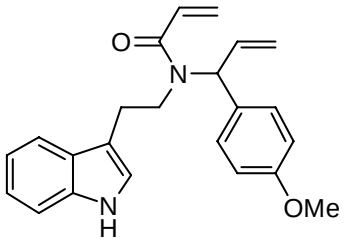
***N*-(2-(1H-Indol-3-yl)ethyl)-*N*-(1-(3-methoxyphenyl)allyl)acrylamide (2b)**

Viscous oil (72% yield) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 3/1/1, v/v). Analytical data for **2b**: ^{1}H NMR (400 MHz, $CDCl_3$, 60 ℃) δ 2.57 (br, 1H), 2.91 (br, 1H), 3.50-3.62 (m, 2H), 3.76 (s, 3H), 5.24 (d, J = 16.8 Hz, 1H), 5.35 (d, J = 10.0 Hz, 1H), 5.67 (d, J = 10.0 Hz, 1H), 6.11-6.20 (m, 1H), 6.40 (d, J = 16.4 Hz, 1H), 6.63 (dd, J = 10.0, 16.8 Hz, 1H), 5.22-6.67 (NCH, br, 1H), 6.79 (s, 1H), 6.84 (dd, J = 2.0, 8.0 Hz, 1H), 6.89-6.94 (m, 2H), 7.04 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 7.24-7.28 (m, 2H), 7.37 (s, 1H), 8.23 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 60 ℃) δ 26.8, 46.3, 55.3, 60.2, 111.2, 112.9, 113.3, 114.4, 118.3, 118.6, 119.3, 120.7, 121.9, 121.9, 127.3, 127.8, 128.6, 129.7, 135.1, 136.4, 140.8, 160.1, 167.0; IR (film) 3287, 2936, 1644, 1602, 1489, 1430, 1269, 1165, 1049, 977, 744, 701 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{23}H_{24}N_2O_2$ requires m/z 360.1838. Found m/z 360.1844.



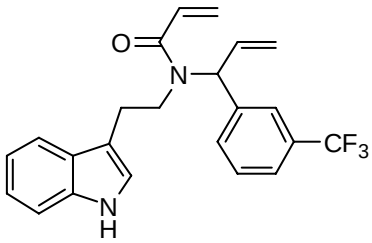
***N*-(2-(1H-Indol-3-yl)ethyl)-*N*-(1-(4-isobutylphenyl)allyl)acrylamide (2c).**

Viscous oil (80% yield) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 3/1/1, v/v). Analytical data for **2c**: ^{1}H NMR (400 MHz, $CDCl_3$, 60 ℃) δ 0.87 (d, J = 2.0, 3H), 0.88 (d, J = 2.0, 3H), 1.80-1.90 (m, 1H), 2.45-2.47 (br, 3H), 2.88 (br, 1H), 3.44-3.51 (m, 1H), 3.57-3.62 (m, 1H), 5.20 (d, J = 16.8 Hz, 1H), 5.32 (d, J = 10.4 Hz, 1H), 5.62 (d, J = 10.4 Hz, 1H), 6.10-6.19 (m, 1H), 6.39 (d, J = 16.4 Hz, 1H), 6.64 (dd, J = 10.4, 16.8 Hz, 1H), 5.18-6.67 (NCH, br, 1H), 6.73 (s, 1H), 6.99-7.03 (m, 1H), 7.07-7.13 (m, 3H), 7.22-7.24 (m, 3H), 7.35 (br, 1H), 8.59 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 60 ℃) δ 22.2, 24.6-26.7, 29.9, 44.9, 46.1, 59.7, 63.2, 111.2, 112.5, 117.8, 118.4, 118.6, 121.6, 121.9, 127.2, 128.1, 129.3, 135.2, 136.1, 136.4, 141.4, 166.8; IR (film) 3288, 2955, 2925, 2867, 1645, 1604, 1457, 1425, 1271, 1183, 977, 928, 742 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{26}H_{30}N_2O$ requires m/z 386.2358. Found m/z 386.2361.



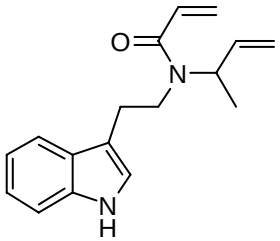
***N*-(2-(1H-Indol-3-yl)ethyl)-*N*-(1-(4-methoxyphenyl)allyl)acrylamide (2d)**

White solid (30% yield) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 3/1/1, v/v). Analytical data for **2d**: Mp = 111-112 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, 60 ℃) δ 2.51 (br, 1H), 2.89 (br, 1H), 3.42-3.50 (m, 1H), 3.55-3.63 (m, 1H), 3.77 (s, 3H), 5.21 (d, J = 17.2 Hz, 1H), 5.33 (d, J = 7.8 Hz, 1H), 5.67 (d, J = 7.8 Hz, 1H), 6.10-6.18 (m, 1H), 6.40 (d, J = 16.8 Hz, 1H), 6.63 (dd, J = 7.8, 16.4 Hz 1H), 5.18-6.67 (NCH, br, 1H), 6.78 (s, 1H), 6.88 (d, J = 8.4 Hz, 2H), 7.03 (t, J = 7.6 Hz, 1H), 7.11 (t, J = 7.2 Hz, 1H), 7.21-7.37 (m, 4H), 8.29 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 60 ℃) δ 24.9-26.5, 46.0, 55.3, 59.7, 63.0, 111.2, 112.9, 114.2, 117.7, 118.6, 119.2, 121.8, 127.3, 127.6, 128.7, 129.6, 131.1, 135.5, 136.4, 159.5, 166.9; IR (film) 3239, 2955, 1636, 1583, 1510, 1456, 1423, 1249, 1178, 1035, 923, 816, 753, 598 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{23}H_{24}N_2O_2$ requires m/z 360.1838. Found m/z 360.1844.



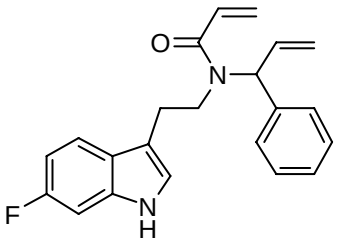
_N_-(2-(1H-Indol-3-yl)ethyl)-_N_-(1-(3-(trifluoromethyl)phenyl) allyl)acrylamide (2e)

Viscous oil (84% yield) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 3/1/1, v/v). Analytical data for **2e**: ^{1}H NMR (400 MHz, $CDCl_3$, 60 ℃) δ 2.58-2.65 (m, 1H), 2.94 (br, 1H), 3.51-3.62 (m, 2H), 5.28 (d, J = 16.8 Hz, 1H), 5.42 (d, J = 10.0 Hz, 1H), 5.69 (d, J = 10.4 Hz, 1H), 6.14-6.22 (m, 1H), 6.41 (d, J = 16.8 Hz, 1H), 6.62 (d, J = 10.4, 16.4 Hz, 1H), 5.26-6.65 (NCH, br, 1H), 6.79 (s, 1H), 7.05 (t, J = 7.2 Hz, 1H), 7.13 (t, J = 7.2 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1H), 7.35-7.50 (m, 2H), 7.54-7.56 (m, 2H), 7.59 (s, 1H), 8.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 60 ℃) δ 46.4, 111.3, 112.5, 118.4, 119.5, 119.5, 121.9, 122.1, 124.1 (q, J = 271 Hz), 124.6, 124.7 (q, J = 4.2 Hz), 127.2, 128.3, 129.2, 131.3 (q, J = 31 Hz), 131.6, 134.4, 136.5, 140.6, 166.9; IR (film) 3295, 3059, 2967, 2869, 1644, 1608, 1427, 1331, 1167, 1128, 1075, 977, 797, 745, 704 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{23}H_{21}F_3N_2O$ requires m/z 398.1606. Found m/z 398.1609.



_N_-(2-(1H-Indol-3-yl)ethyl)-_N_-(but-3-en-2-yl)acrylamide (2f)

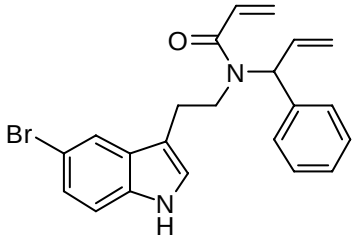
Viscous oil (84% yield) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 3/1/1, v/v). Analytical data for **2f**: ^{1}H NMR (400 MHz, $CDCl_3$, 60 ℃) δ 1.33 (d, J = 6.8 Hz, 3H), 3.00-3.04 (m, 2H), 3.43-3.56 (m, 2H), 4.57, 5.14-5.24 (m, 3H), 5.62 (dd, J = 2.0, 10.4 Hz, 1H), 5.89 (br, 1H), 6.34 (d, J = 16.8 Hz, 1H), 6.58 (dd, J = 10.8, 16.8 Hz, 1H), 6.92 (d, J = 2.0 Hz, 1H), 7.07-7.20 (m, 2H), 7.30 (d, J = 8.0 Hz, 1H), 7.59 (br, 1H), 8.62 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 60 ℃) δ 17.0-17.9, 25.2-27.5, 44.6, 51.8, 54.6, 111.3, 112.3, 115.9, 118.5, 119.2, 121.8, 122.0, 127.4, 128.8, 136.5, 138.5, 166.5; IR (film) 3412, 3274, 2978, 1641, 1603, 1457, 1429, 1169, 978, 927, 742 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{17}H_{20}N_2O$ requires m/z 268.1576. Found m/z 268.1581.



_N_-(2-(6-Fluoro-1H-indol-3-yl)ethyl)-_N_-(1-phenylallyl)acrylamide (2g)

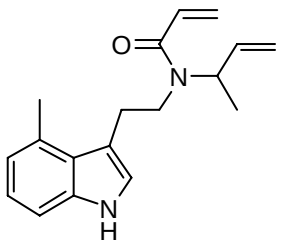
White solid (86% yield) following silica gel column

chromatography (petroleum ether/ethyl acetate/DCM = 3/1/1, v/v). Analytical data for **2g**: Mp = 117-118 ℃; ^{1}H NMR (400 MHz, $CDCl_3$, 60 ℃) δ 2.49-2.51 (m, 1H), 2.87 (br, 1H), 3.44-3.62 (m, 2H), 5.23 (d, J = 17.2 Hz, 1H), 5.36 (d, J = 10.4 Hz, 1H), 5.66 (d, J = 10.8 Hz, 1H), 6.11-6.19 (m, 1H), 6.38 (d, J = 16.8 Hz, 1H), 6.62 (dd, J = 10.4, 16.8 Hz, 1H), 5.25-6.65 (NCH, br, 1H), 6.73 (s, 1H), 6.78 (t, J = 8.8 Hz, 1H), 6.92 (d, J = 9.2 Hz, 1H), 7.19-7.34 (m, 6H), 8.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 60 ℃) δ 24.6-26.1, 46.1, 60.2-63.2, 97.4 (d, J = 25.7 Hz), 107.8 (d, J = 24.6 Hz), 112.8, 118.3, 119.2, 122.2 (d, J = 3.3 Hz), 123.9, 127.9, 128.3, 128.7, 135.0, 136.3 (J = 12.7 Hz), 138.9, 160.0 (d, J = 236 Hz), 167.1; IR (film) 3277, 2926, 1640, 1605, 1496, 1454, 1425, 1344, 1140, 951, 802, 754, 702 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{22}H_{21}FN_2NaO^+$($M+Na^+$) requires m/z 348.1638. Found m/z 348.1647.



***N*-(2-(5-Bromo-1H-indol-3-yl)ethyl)-*N*-(1-phenylallyl)acrylamide (2h)**

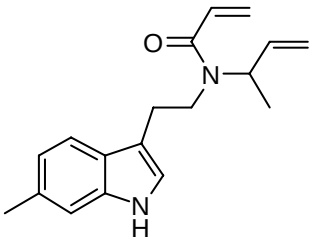
Pale yellow solid (86% yield) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 3/1/1, v/v). Analytical data for **2h**: Mp = 93-94 ℃; ^{1}H NMR (400 MHz, $CDCl_3$, 60 ℃) δ 2.41 (br, 1H), 2.85 (br, 1H), 3.43-3.55 (m, 2H), 5.22 (d, J = 16.8 Hz, 1H), 5.36 (d, J = 9.6 Hz, 1H), 5.68 (d, J = 10.0 Hz, 1H), 6.12-6.19 (m, 1H), 6.38 (d, J = 16.0 Hz, 1H), 6.59-6.66 (m, 1H), 5.20-6.66 (NCH, br, 1H), 6.78 (s, 1H), 7.10-7.38 (m, 8H), 8.60 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 60 ℃) δ 24.3-26.2, 46.1, 60.0-63.3, 112.5, 112.7, 118.2, 121.1, 123.2, 123.3, 124.7, 128.1, 128.4, 128.8, 129.0, 135.0, 138.8, 167.1; IR (film) 3246, 2930, 1638, 1603, 1452, 1419, 1274, 795, 701, 611 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{22}H_{21}BrN_2O$ requires m/z 408.0837. Found m/z 408.0842.



***N*-(But-3-en-2-yl)-*N*-(2-(4-methyl-1H-indol-3-yl)ethyl)acrylamide (2i)**

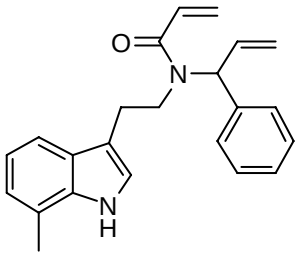
Viscous oil (99% yield) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 3/1/1, v/v). Analytical data for **2i**: ^{1}H NMR (400 MHz, $CDCl_3$, 60 ℃) δ 1.32 (d, J = 6.8 Hz, 3H), 2.70 (s, 3H), 3.16-3.26 (m, 2H), 3.49-3.57 (m, 2H), 4.59, 5.14-5.17 (m, 3H), 5.15 (d, J = 12.0 Hz, 1H), 5.86-5.89 (m, 1H), 6.31 (d,

J = 16.4 Hz, 1H), 6.50-6.53 (m, 1H), 6.81 (d, *J* = 6.8 Hz, 1H), 6.91 (s, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 8.41 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 60 ℃) δ 17.4, 20.2, 26.8-29.1, 45.8, 51.7-54.4, 109.2, 113.7, 115.9, 121.1, 122.0, 122.2, 125.8, 127.0, 128.8, 130.3, 136.9, 138.6, 166.7; IR (film) 3277, 2975, 2942, 1641, 1603, 1431, 1343, 1153, 978, 749 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{18}H_{22}N_2O$ requires m/z 282.1732. Found m/z 282.1739.



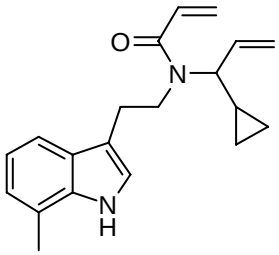
_N_-(But-3-en-2-yl)-_N_-(2-(6-methyl-1H-indol-3-yl)ethyl)acrylamide (2j)

Viscous oil (78% yield) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 3/1/1, v/v). Analytical data for **2j**: ^{1}H NMR (400 MHz, $CDCl_3$, 60 ℃) 1.32 (d, *J* = 6.8 Hz, 3H), 2.42 (s, 3H), 2.99-3.01 (m, 2H), 3.45-3.54 (m, 2H), 4.59, 5.14-5.18 (m, 3H), 5.62 (dd, *J* = 1.6, 10.4 Hz, 1H), 5.90 (br, 1H), 6.34 (d, *J* = 16.4 Hz, 1H), 6.58 (dd, *J* = 16.8, 10.4 Hz 1H), 6.85 (s, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 7.09 (s, 1H), 7.47 (br, 1H), 8.46 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 60 ℃) δ 17.1-17.8, 21.5, 25.2-27.6, 44.7, 51.7-54.3, 111.3, 112.3, 115.8, 118.2, 121.1, 121.3, 125.2, 127.3, 128.8, 131.6, 137.0, 138.5, 166.5; IR (film) 3407, 3281, 2918, 1640, 1602, 1428, 1370, 1156, 978, 927, 797, 590 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{18}H_{22}N_2O$ requires m/z 282.1732. Found m/z 282.1737.



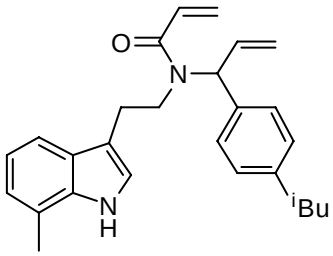
_N_-(2-(7-Methyl-1H-indol-3-yl)ethyl)-_N_-(1-phenylallyl)acrylamide (2k)

Viscous oil (82% yield) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 3/1/1, v/v). Analytical data for **2k**: ^{1}H NMR (400 MHz, $CDCl_3$, 60 ℃) δ 2.40 (s, 3H), 2.53 (br, 1H), 2.90 (br, 1H), 3.46-3.63 (m, 2H), 5.23 (dd, *J* = 14.7, 1.2 Hz, 1H), 5.35 (d, *J* = 10.4 Hz, 1H), 5.66 (d, *J* = 10.4 Hz, 1H), 6.13-6.21 (m, 1H), 6.40 (d, *J* = 16.4 Hz, 1H), 6.64 (dd, J_1 = 16.8, 10.8 Hz, 1H), 5.21-6.67 (NCH, br, 1H), 6.77 (s, 1H), 6.91-6.98 (m, 2H), 7.20-7.34 (m, 6H), 8.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 60 ℃) δ 16.4, 26.8, 46.3, 59.8-63.2, 113.4, 116.3, 118.2, 119.5, 120.3, 121.6, 122.5, 126.9, 127.8, 128.3, 128.6, 135.2, 136.0, 139.2, 167.0; IR (film) 3407, 3296, 1640, 1605, 1453, 1425, 1193, 977, 931, 799, 753, 701, 589 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{23}H_{24}N_2O$ requires m/z 344.1889. Found m/z 344.1894.



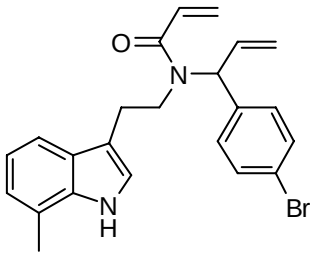
***N*-(1-Cyclopropylallyl)-*N*-(2-(7-methyl-1H-indol-3-yl)ethyl)acrylamide (2l)**

Viscous oil (72% yield) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 3/1/1, v/v). Analytical data for **2l**: ^{1}H NMR (400 MHz, $CDCl_3$, 60 ℃) δ 0.36-0.54 (m, 3H), 0.73 (br, 1H), 1.15 (br, 1H), 2.43 (s, 3H), 3.13 (br, 2H), 3.53-3.71, 4.46 (m, 3H), 5.18 (d, J = 10.4 Hz, 1H), 5.28 (d, J = 16.8 Hz, 1H), 5.61 (d, J = 10.0 Hz, 1H), 5.86-5.89 (m, 1H), 6.33 (d, J = 15.2 Hz, 1H), 6.56 (br, 1H), 6.95-7.02 (m, 3H), 7.43 (br, 1H), 8.56 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 60 ℃) δ 3.7, 5.6, 13.0, 16.4, 25.1, 27.5, 45.3, 61.3, 65.0, 112.9, 116.3, 119.5, 120.5, 121.7, 122.4, 126.9, 127.4, 128.5, 136.1, 136.8, 166.5; IR (film) 3417, 3280, 2921, 1639, 1600, 1427, 1155, 976, 925, 782, 744 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{20}H_{24}N_2O$ requires m/z 308.1889. Found m/z 308.1893.



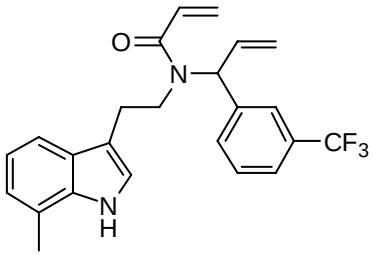
***N*-(1-(4-Isobutylphenyl)allyl)-*N*-(2-(7-methyl-1H-indol-3-yl)ethyl)acrylamide (2m)**

Viscous oil (72% yield) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 3/1/1, v/v). Analytical data for **2m**: ^{1}H NMR (400 MHz, $CDCl_3$, 60 ℃) δ 0.88 (dd, J = 2.8, 6.8 Hz, 6H), 1.80-1.91 (m, 1H), 2.39 (s, 3H), 2.45-2.54 (m, 3H), 2.87 (br, 1H), 3.44-3.52 (m, 1H), 3.55-3.63 (m, 1H), 5.21 (dt, J = 1.2 Hz, 17.2 Hz, 1H), 5.33 (d, J = 10.4 Hz, 1H), 5.65 (dd, J = 1.2 Hz, 10.4 Hz, 1H), 6.16 (m, 1H), 6.40 (d, J = 16.4 Hz, 1H), 6.65 (dd, J = 10.4, 16.8 Hz, 1H), 5.19-6.68 (NCH, br, 1H), 6.77 (s, 1H), 6.90-6.97 (m, 2H), 7.12-7.16 (m, 2H), 7.20-7.25 (m, 3H), 8.31 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 60 ℃) δ 16.3, 22.3, 24.6, 26.7, 30.0, 45.0, 46.2, 59.6-63.2, 113.3, 116.3, 117.8, 119.4, 120.3, 121.6, 122.4, 126.9, 127.7, 128.1, 128.6, 129.4, 135.3, 136.0, 136.2, 141.4, 166.8; IR (film) 3294, 2953, 1639, 1603, 1423, 1269, 1160, 1066, 976, 926, 780, 744 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{27}H_{32}N_2O$ requires m/z 400.2515. Found m/z 400.2519.



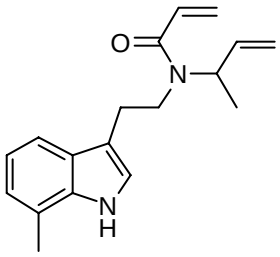
***N*-(1-(4-Bromophenyl)allyl)-*N*-(2-(7-methyl-1H-indol-3-yl)ethyl) acrylamide (2n)**

Viscous oil (61% yield) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 3/1/1, v/v). Analytical data for **2n**: ^{1}H NMR (400 MHz, $CDCl_3$, 60 ℃) δ 2.41 (s, 3H), 2.62 (br, 1H), 2.93 (br, 1H), 3.46-3.61 (m, 2H), 5.24 (d, J = 16.4 Hz, 1H), 5.37 (d, J = 10.0 Hz, 1H), 5.68 (d, J = 10.0 Hz, 1H), 6.10-6.17 (m, 1H), 6.40 (d, J = 16.4 Hz, 1H), 6.61 (dd, J = 10.8, 16.8 Hz, 1H), 5.22-6.65 (NCH, br, 1H), 6.80 (s, 1H), 6.94-7.02 (m, 2H), 7.16-7.22 (m, 3H), 7.45 (d, J = 10.0 Hz, 2H), 8.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 60 ℃) δ 16.4, 26.2, 46.3, 60.2, 113.2, 116.2, 118.8, 119.7, 120.4, 121.6, 121.8, 122.6, 126.8, 128.1, 128.4, 129.9, 131.8, 134.7, 136.0, 138.3, 166.8; IR (film) 3417, 3294, 1640, 1603, 1423, 1266, 1071, 1010, 781, 729 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{23}H_{23}BrN_2O$ requires m/z 422.0994. Found m/z 422.0985.



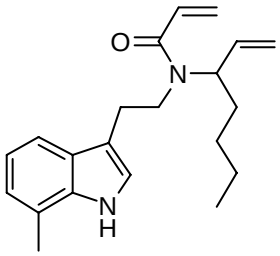
***N*-(2-(7-Methyl-1H-indol-3-yl)ethyl)-*N*-(1-(3-(trifluoromethyl)phenyl)allyl)acrylamide (2o)**

Viscous oil (80% yield) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 3/1/1, v/v). Analytical data for **2o**: ^{1}H NMR (400 MHz, $CDCl_3$, 60 ℃) δ 2.40 (s, 3H), 2.60-2.65 (m, 1H), 2.94 (br, 1H), 3.54-3.60 (m, 2H), 5.28 (dd, J_1 = 1.2, 16.0 Hz, 1H), 5.42 (d, J = 10.0 Hz, 1H), 5.69 (dd, J = 2.0, 10.4 Hz, 1H), 6.14-6.22 (m, 1H), 6.41 (d, J = 16.0 Hz, 1H), 6.62 (dd, J = 16.8, 10.4 Hz, 1H), 5.21-6.66 (NCH, br, 1H), 6.80 (d, J = 2.4 Hz, 1H), 6.92-7.00 (m, 2H), 7.20 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.49-7.54 (m, 2H), 7.59 (s, 1H), 8.19 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 60 ℃) δ 16.3, 26.8, 46.5, 60.4, 113.0, 116.1, 119.4, 119.7, 120.5, 121.6, 122.6, 122.7, 124.6, 124.7 (q, J = 3.7 Hz), 125.4, 128.3, 129.1, 131.3 (q, J = 32 Hz), 131.5, 134.4, 136.0, 140.6, 166.9; IR (film) 3419, 2927, 2856, 1617, 1454, 1342, 1105, 919, 781, 743 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{24}H_{23}F_3N_2O$ requires m/z 412.1762. Found m/z 412.1761.



***N*-(But-3-en-2-yl)-*N*-(2-(7-methyl-1H-indol-3-yl)ethyl)acrylamide (2p)**

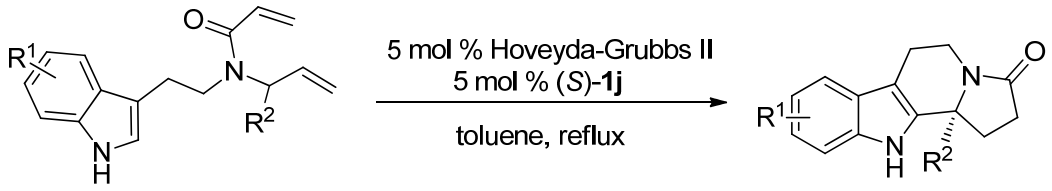
Viscous oil (77% yield) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 3/1/1, v/v). Analytical data for **2p**: ^{1}H NMR (400 MHz, $CDCl_3$, 60 ℃) 1.33 (d *J* = 7.2 Hz, 3H), 2.44 (s, 3H), 2.99-3.03 (m, 2H), 3.43-3.55 (m, 2H), 4.59, 5.14-5.18 (m, 3H), 5.62 (dd, *J* = 2.0, 10.8 Hz 1H), 5.90 (br, 1H), 6.33 (d, *J* = 16.8 Hz, 1H), 6.56 (dd, *J* = 16.8, 10.4 Hz, 1H), 6.93-7.04 (m, 3H), 7.44 (br, 1H), 8.54 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 60 ℃) δ 16.3, 17.0, 25.3-27.8, 44.6, 51.7, 113.0, 115.8, 116.2, 119.5, 120.5, 121.8, 122.4, 126.9, 128.8, 136.1, 138.5, 166.5; IR (film) 3416, 3282, 2976, 2936, 1640, 1602, 1431, 1371, 1271, 1232, 1163, 1065, 978, 928, 782, 746 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{18}H_{22}N_2O$ requires m/z 282.1732. Found m/z 282.1733.



***N*-(Hept-1-en-3-yl)-*N*-(2-(7-methyl-1H-indol-3-yl)ethyl)acrylamide (2q)**

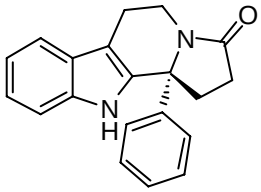
Viscous oil (68% yield) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 3/1/1, v/v). Analytical data for **2q**: ^{1}H NMR (400 MHz, $CDCl_3$, 60 ℃) 0.88 (t, *J* = 6.8 Hz, 3H), 1.31 (br, 4H), 1.70 (br, 2H), 2.44 (s, 3H), 3.05 (br, 2H), 3.53 (t, *J* = 7.6 Hz, 2H), 4.35, 5.02 (1H), 5.17-5.20 (m, 2H), 5.63 (dd, *J* = 2.0, 10.4 Hz, 1H), 5.90 (br, 1H), 6.33 (d, *J* = 14.4 Hz, 1H), 6.60 (dd, *J* = 16.8 Hz, 10.4 Hz, 1H), 6.95-7.04 (m, 3H), 7.44 (br, 1H), 8.52-8.63 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 60 ℃) δ 13.7, 16.4, 22.4, 24.9-27.5, 28.5, 31.4-32.1, 44.7-45.4, 57.2-60.1, 112.8, 116.0, 116.7, 119.5, 120.5, 121.8, 122.4, 126.5, 126.9, 127.3, 128.7, 129.1, 136.1, 137.5, 166.5; IR (film) 3292, 2930, 2859, 1640, 1602, 1427, 1343, 1267, 1128, 1104, 925, 783, 744 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{21}H_{28}N_2O$ requires m/z 324.2202. Found m/z 324.2202.

2.4 General procedure for the RCM/Pictet-Spengler cascade reaction



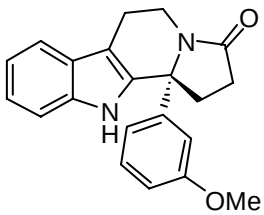
2 **3**

In a dry Schlenk tube, substrate **2** (0.2 mmol) was dissolved in toluene (4 mL) under argon. The solution was heated to reflux, and then chiral phosphoric acid (8.7 mg, 0.01 mmol) and Hoveyda-Grubbs II (6.3 mg, 0.01 mmol) were added in one portion. After the reaction was complete (monitored by TLC or ^{1}H NMR), the solvent was removed to leave about 2 mL under reduced pressure and the residue was purified by flash chromatography to afford product **3**.



(*R*)-11b-Phenyl-5,6,11,11b-tetrahydro-1H-indolizino[8,7-b]indol-3(2H)-one (3a)

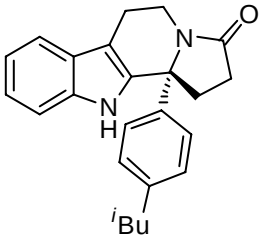
White solid (95% yield, 84% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 2/1/1, v/v). Analytical data for **3a**: $[\alpha]_D^{20}$ = -58.2 (*c* = 0.9, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49-2.64 (m, 2H), 2.66-2.82 (m, 3H), 2.90-4.01 (m, 2H), 4.36-4.41 (m, 1H), 7.13-7.17 (m, 1H), 7.20-7.33 (m, 6H), 7.38-7.40 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 8.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 31.1, 33.6, 35.3, 65.4, 109.2, 111.1, 118.6, 119.9, 122.4, 126.1, 126.6, 128.0, 128.7, 135.1, 136.2, 143.4, 173.6; IR (film) 3250, 2924, 1661, 1492, 1446, 1448, 1295, 1235, 930, 876, 743, 699 cm^{-1}; HRMS (MALDI/DHB): Exact mass calcd for $C_{20}H_{18}N_2O$ requires m/z 302.1419. Found m/z 302.1434. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t_R (major) = 21.24 min, t_R (minor) = 10.68 min.



(*R*)-11b-(3-Methoxyphenyl)-5,6,11,11b-tetrahydro-1H-indolizino[8,7-b]indol-3(2H)-one (3b)

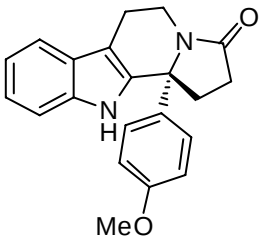
White solid (93% yield, 80% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 2/1/1, v/v). Analytical data for **3b**: $[\alpha]_D^{20}$ = +11.1 (*c* = 0.58, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42-2.73

(m, 5H), 2.85-2.99 (m, 2H), 3.68 (s, 3H), 4.29-4.39 (m, 1H), 6.74 (d, J = 8.4 Hz, 1H), 6.79-6.85 (m, 2H), 7.09-7.28 (m, 3H), 7.34-7.40 (m, 1H), 7.43-7.50 (m, 1H), 9.17-9.20 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.7, 31.0, 33.6, 35.4, 55.1, 65.4, 108.6, 111.2, 112.0, 113.0, 118.2, 118.5, 119.6, 122.2, 126.4, 129.7, 135.1, 136.3, 145.1, 159.7, 173.9; IR (film) 3230, 1662, 1594, 1398, 1258, 1184, 1035, 743 cm^{-1}; HRMS (MALDI/DHB): Exact mass calcd for $C_{21}H_{21}N_2O_2^{+1}$ (M+H) requires m/z 333.1598. Found m/z 333.1594. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t_R (major) = 32.11 min, t_R (minor) = 11.85 min.



(*R*)-11b-(4-Isobutylphenyl)-5,6,11,11b-tetrahydro-1H-indolizino[8,7-b]indol-3(2H)-one (3c)

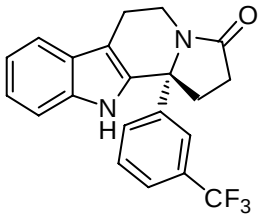
White solid (92% yield, 91% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 2/1/1, v/v). Analytical data for **3c**: $[\alpha]_D^{20}$ = +7.7 (c = 1.08, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (d, J = 4.8 Hz, 6H), 1.75-1.82 (m, 1H), 2.39 (d, J = 5.4 Hz, 2H), 2.47-2.67 (m, 2H), 2.72-2.77 (m, 3H), 2.90-2.96 (m, 2H), 4.34-4.38 (m, 1H), 7.04 (d, J = 8.4 Hz, 2H), 7.11-7.23 (m, 4H), 7.37 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 8.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 22.3, 30.1, 31.2, 33.6, 35.3, 44.7, 65.3, 108.7, 111.2, 118.5, 119.7, 122.2, 125.9, 126.5, 129.3, 135.5, 136.3, 140.6, 141.6, 173.6; IR (film) 2952, 1654, 1421, 1290, 1232, 932, 731, 670 cm^{-1}; HRMS (MALDI/DHB): Exact mass calcd for $C_{24}H_{27}N_2O^{+1}$ (M+H) requires m/z 359.2118. Found m/z 359.2118. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t_R (major) = 12.10 min, t_R (minor) = 7.13 min.



(*R*)-11b-(4-Methoxyphenyl)-5,6,11,11b-tetrahydro-1H-indolizino[8,7-b]indol-3(2H)-one (3d)

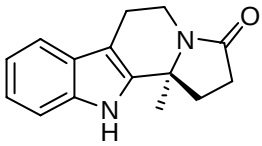
White solid (93% yield, 86% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 2/1/1, v/v). Analytical data for **3d**: $[\alpha]_D^{20}$ = -50.0 (c = 0.50, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.44-2.78 (m, 5H), 2.82-2.99 (m, 2H), 3.72 (s, 3H), 4.27-4.33 (m, 1H), 6.78 (d, J = 8.4 Hz, 2H), 7.11-7.25 (m, 4H), 7.37 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 7.2 Hz, 1H), 8.88 (s, 1H); ^{13}C NMR (75 MHz,

$CDCl_3$) δ 20.8, 31.2, 33.5, 35.1, 55.2, 65.0, 108.7, 111.2, 113.8, 118.5, 119.7, 122.3, 126.5, 127.5, 135.4, 136.2, 159.1, 173.5; IR (film) 2925, 1651, 1509, 1446, 1419, 1253, 1178, 1022, 825, 746, 664 cm^{-1}; HRMS (MALDI/DHB): Exact mass calcd for $C_{21}H_{21}N_2O_2^{+1}$ (M+H) requires m/z 333.1598. Found m/z 333.1603. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t_R (major) = 38.34 min, t_R (minor) = 11.81 min.



(*R*)-11b-(3-(Trifluoromethyl)phenyl)-5,6,11,11b-tetrahydro-1H-indolizino[8,7-b]indol-3(2H)-one (3e)

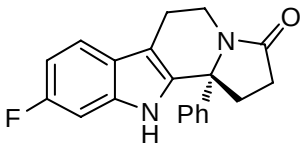
White solid (95% yield, 82% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 2/1/1, v/v). Analytical data for **3e**: $[\alpha]_D^{20}$ = -5.5 (*c* = 0.50, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.44-2.57 (m, 1H), 2.60-2.86 (m, 4H), 2.87-3.04 (m, 2H), 4.36-4.49 (m, 1H), 7.15-7.25 (m, 2H), 7.25-7.63 (m, 6H), 9.23 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6, 30.9, 33.3, 35.3, 65.2, 108.8, 111.2, 118.5, 119.8, 122.0, 122.4, 126.4, 127.9, 131.7, 134.4, 136.3, 142.6, 173.8; IR (film) 3286, 1668, 1414, 1329, 1237, 1116, 1074, 801, 744, 701 cm^{-1}; HRMS (MALDI/DHB): Exact mass calcd for $C_{21}H_{18}N_2OF_3^{+1}$ (M+H) requires m/z 371.1366. Found m/z 371.1361. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t_R (major) = 9.98 min, t_R (minor) = 6.09 min.



(*S*)-11b-Methyl-5,6,11,11b-tetrahydro-1H-indolizino[8,7-b]indol-3(2H)-one (3f)

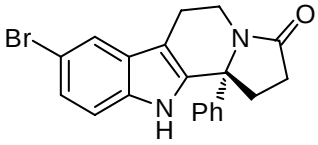
White solid (82% yield, 74% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 1/1/1, v/v). Analytical data for **3f**: $[\alpha]_D^{20}$ = -78.6 (*c* = 0.50, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61 (s, 3H), 2.17-2.34 (m, 2H), 2.41-2.51 (m, 1H), 2.63-2.85 (m, 3H), 3.06-3.16 (m, 1H), 4.45-4.50 (m, 1H), 7.09-7.21 (m, 2H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 8.47 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 25.4, 30.7, 32.8, 35.0, 59.5, 106.7, 111.0, 118.5, 119.7, 122.1, 126.6, 136.1, 137.7, 172.8; IR (film) 3264, 1659, 1435, 1416, 1291, 1172, 748, 704 cm^{-1}; HRMS (MALDI/DHB): Exact mass calcd for $C_{15}H_{17}N_2O^{+1}$ (M+H) requires m/z 241.1335. Found m/z 241.1341. The enantiomeric excess was

determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t_R (major) = 21.34 min, t_R (minor) = 8.10 min.



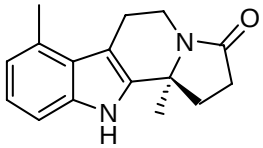
(*R*)-9-Fluoro-11b-phenyl-5,6,11,11b-tetrahydro-1H-indolizino[8,7-b]indol-3(2H)-one (3g)

White solid (95% yield, 82% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 2/1/1, v/v). Analytical data for **3h**: $[\alpha]_D^{20}$ = -44.0 (*c* = 0.50, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42-2.55 (m, 1H), 2.60-2.79 (m, 4H), 2.82-2.95 (m, 2H), 4.30-4.34 (m, 1H), 6.89 (dt, *J* = 2.1, 9.6 Hz, 1H), 7.09 (dd, *J* = 2.1, 9.6 Hz, 1H), 7.21-7.30 (m, 5H), 7.30-7.42 (m, 1H), 9.29 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.7, 31.1, 33.5, 35.3, 65.4, 97.7 (d, *J* = 26.0 Hz), 108.1, 108.4, 108.5 (d, *J* = 15.8 Hz), 119.2 (d, *J* = 10.2 Hz), 123.1, 126.0, 128.0, 128.7, 135.4 (d, *J* = 3.5 Hz), 136.3 (d, *J* = 12.5 Hz), 143.2, 160.0 (d, *J* = 236.0 Hz), 173.8; IR (film) 3269, 1675, 1395, 1250, 1132, 1107, 843, 803, 702 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{20}H_{17}FN_2O$ requires m/z 320.1325. Found m/z 320.1321. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t_R (major) = 20.71 min, t_R (minor) = 12.09 min.



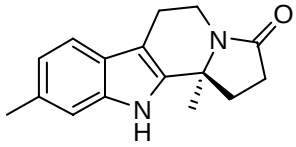
(*R*)-8-Bromo-11b-phenyl-5,6,11,11b-tetrahydro-1H-indolizino[8,7-b]indol-3(2H)-one (3h)

White solid (95% yield, 83% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 2/1/1, v/v). Analytical data for **3i**: $[\alpha]_D^{20}$ = -56.0 (*c* = 0.50, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43-2.76 (m, 5H), 2.79-2.92 (m, 2H), 4.30-4.33 (m, 1H), 7.18-7.30 (m, 7H), 7.61 (s, 1H), 9.37 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6, 31.0, 33.4, 35.2, 65.4, 108.3, 112.7, 112.8, 121.1, 125.0, 125.9, 128.0, 128.2, 128.7, 134.9, 136.5, 143.0, 173.7; IR (film) 3311, 2923, 1679, 1445, 1396, 1312, 1144, 802, 697 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{20}H_{17}BrN_2O$ requires m/z 380.0524. Found m/z 380.0527. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t_R (major) = 23.11 min, t_R (minor) = 26.27 min.



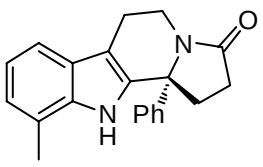
(*S*)-7,11b-Dimethyl-5,6,11,11b-tetrahydro-1H-indolizino[8,7-b]indol-3(2H)-one (3i)

White solid (94% yield, 69% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 1/1/1, v/v). Analytical data for **3i**: $[\alpha]_D^{20}$ = -119 (*c* = 0.50, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61 (s, 3H), 2.15-2.22 (m, 1H), 2.27-2.35 (m, 1H), 2.42-2.51 (m, 1H), 2.63-2.74 (m, 4H), 3.05-3.13 (m, 3H), 4.41-4.45 (m, 1H), 6.83 (d, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 8.55 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.8, 23.6, 25.4, 30.7, 32.8, 35.1, 59.3, 106.9, 108.8, 120.9, 122.0, 125.6, 130.7, 136.1, 137.3, 172.8; IR (film) 3216, 2924, 1657, 1454, 1417, 1295, 773, 745 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{16}H_{18}N_2O$ requires m/z 254.1419. Found m/z 254.1418. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t_R (major) = 14.63 min, t_R (minor) = 8.69 min.



(*S*)-9,11b-Dimethyl-5,6,11,11b-tetrahydro-1H-indolizino[8,7-b]indol-3(2H)-one (3j)

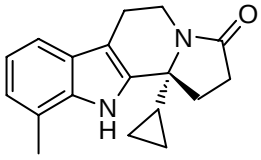
White solid (98% yield, 68% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 1/1/1, v/v). Analytical data for **3j**: $[\alpha]_D^{20}$ = -137 (*c* = 0.50, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.58 (s, 3H), 1.78-2.33 (m, 2H), 2.40-2.48 (m, 4H), 2.60-2.88 (m, 3H), 3.04-3.14 (m, 1H), 4.42-4.48 (m, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 7.12 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 8.52 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 21.7, 25.3, 30.7, 32.7, 35.0, 59.6, 106.3, 111.0, 118.0, 121.3, 124.4, 131.8, 136.5, 137.0, 172.9; IR (film) 3256, 2921, 1660, 1417, 1303, 1181, 801, 751, 661 cm^{-1}; HRMS (MALDI/DHB): Exact mass calcd for $C_{16}H_{19}N_2O^{+1}$ (M+H) requires m/z 255.1492. Found m/z 255.1497. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t_R (major) = 23.65 min, t_R (minor) = 7.81 min.



(*R*)-10-Methyl-11b-phenyl-5,6,11,11b-tetrahydro-1H-indolizino[8,7-b]indol-3(2H)-one (3k)

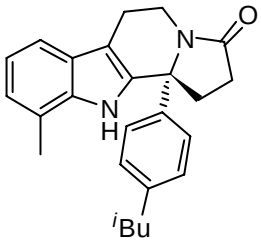
White solid (94% yield, 99% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 2/1/1, v/v). Analytical data for **3k**: $[\alpha]_D^{20}$ =

-38.0 (*c* = 0.50, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40-2.53 (m, 4H), 2.56-2.83 (m, 4H), 2.87-2.97 (m, 2H), 4.25-4.31 (m, 1H), 7.01-7.10 (m, 2H), 7.19-7.29 (m, 5H), 7.36 (d, *J* = 7.5 Hz, 1H), 8.86 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.8, 20.8, 31.1, 33.3, 35.2, 65.4, 109.4, 116.1, 120.0, 120.5, 123.0, 126.1, 126.2, 127.9, 128.6, 134.9, 135.8, 143.6, 173.5; IR (film) 3175, 1661, 1450, 1412, 1298, 1071, 859, 776, 761, 701, 675 cm^{-1}; HRMS (MALDI/DHB): Exact mass calcd for $C_{21}H_{21}N_2O^+$ (M+H) requires m/z 317.1648. Found m/z 317.1652. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t_R (major) = 8.37 min, t_R (minor) = 6.75 min.



(*R*)-11b-Cyclopropyl-10-methyl-5,6,11,11b-tetrahydro-1H-indolizino [8,7-b]indol-3(2H)-one (3l)

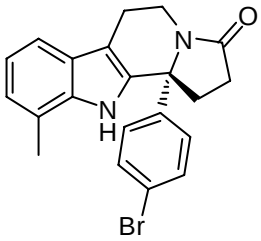
White solid (96% yield, 95% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 1/1/1, v/v). Analytical data for **3l**: $[\alpha]_D^{20}$ = -217 (*c* = 0.50, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.38-0.53 (m, 3H), 0.57-0.63 (m, 1H), 1.32-1.39 (m, 1H), 2.17-2.25 (m, 1H), 2.31-2.45 (m, 2H), 2.49 (s, 3H), 2.63-2.70 (m, 1H), 2.73-2.91 (m, 2H), 3.33-3.41 (m, 1H), 4.45-4.50 (m, 1H), 6.97-7.06 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 1H), 8.38 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.60, 2.24, 16.8, 19.5, 20.9, 30.3, 30.9, 35.4, 63.1, 108.6, 116.0, 119.8, 120.3, 122.8, 126.0, 134.6, 135.6, 173.1; IR (film) 3257, 2960, 1726, 1659, 1432, 1282, 1165, 1073, 952, 781, 748, 666 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{18}H_{20}N_2O$ requires m/z 280.1576. Found m/z 280.1565. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t_R (major) = 12.60 min, t_R (minor) = 7.99 min.



(*R*)-11b-(4-Isobutylphenyl)-10-methyl-5,6,11,11b-tetrahydro-1H-indo lizino[8,7-b]indol-3(2H)-one (3m)

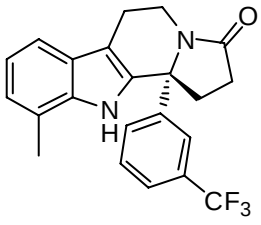
White solid (91% yield, 94% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 2/1/1, v/v). Analytical data for **3m**: $[\alpha]_D^{20}$ = -37.0 (*c* = 0.50, acetone); ^{1}H MR (300 MHz, $CDCl_3$) δ 0.87 (d, *J* = 6.6 Hz, 6H), 1.75-1.83 (m, 1H), 2.41 (d, *J* = 6.9 Hz, 2H), 2.48-2.62 (m, 5H), 2.71-2.01 (m, 5H), 4.32-4.36 (m, 1H), 7.02-7.15 (m, 6H), 7.37 (d, *J* = 7.2 Hz, 1H), 8.30 (s, 1H); ^{13}C NMR (75 MHz,

$CDCl_3$) δ 16.8, 20.9, 22.3, 30.1, 31.3, 33.4, 35.2, 44.8, 65.2, 109.6, 116.3, 120.1, 120.4, 123.1, 126.1, 126.2, 129.3, 135.2, 135.7, 140.8, 141.7, 173.4; IR (film) 3304, 2957, 1726, 1658, 1414, 1283, 1123, 1073, 743 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{25}H_{28}N_2O$ requires m/z 372.2202. Found m/z 372.2193. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t_R (major) = 7.32 min, t_R (minor) = 6.27 min.



(*R*)-11b-(4-Bromophenyl)-10-methyl-5,6,11,11b-tetrahydro-1H-indolizino[8,7-b]indol-3(2H)-one (3n)

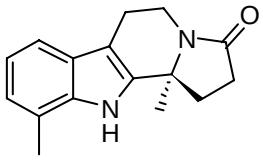
White solid (95% yield, 99% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 2/1/1, v/v). Analytical data for **3o**: $[\alpha]_D^{20}$ = -22.0 (*c* = 0.50, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47-2.55 (m, 4H), 2.62-2.86 (m, 5H), 2.91-2.99 (m, 1H), 4.30-4.35 (m, 1H), 7.04-7.12 (m, 4H), 7.36-7.43 (m, 3H), 8.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.8, 20.8, 31.0, 33.2, 35.2, 65.0, 110.1, 116.4, 120.3, 120.5, 122.2, 123.4, 126.1, 128.1, 131.8, 134.1, 135.8, 142.8, 173.5; IR (film) 3257, 1663, 1411, 1292, 1170, 1073, 1007, 881, 821, 779, 745 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{21}H_{19}N_2OBr$ requires m/z 394.0681. Found m/z 394.0680. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t_R (major) = 12.68 min, t_R (minor) = 9.84 min.



(*R*)-10-Methyl-11b-(3-(trifluoromethyl)phenyl)-5,6,11,11b-tetrahydro-1H-indolizino[8,7-b]indol-3(2H)-one (3o)

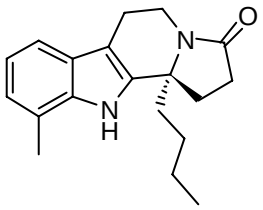
White solid (96% yield, 97% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 2/1/1, v/v). Analytical data for **3o**: $[\alpha]_D^{20}$ = -17.3 (*c* = 0.50, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.93-2.97 (m, 10H), 4.29-4.34 (m, 1H), 7.04-7.11 (m, 2H), 7.35-7.41 (m, 3H), 7.47-7.52 (m, 1H), 7.61 (s, 1H), 9.02 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.8, 20.6, 30.8, 33.5, 35.5, 65.4, 109.9, 116.3, 120.2, 120.6, 122.7-122.8, 123.3, 123.8 (q, *J* = 272 Hz), 126.1, 129.2, 129.8, 131.1 (q, *J* = 32 Hz), 133.8, 136.0, 144.9, 174.0; IR (film) 3276, 2929, 1666, 1439, 1411, 1328, 1165, 1121, 1073, 803, 780, 754, 702 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{21}H_{19}N_2OF_3$ requires m/z 384.1449. Found m/z 384.1443. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25

cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t_R (major) = 7.84 min, t_R (minor) = 6.21 min.



(*S*)-10,11b-Dimethyl-5,6,11,11b-tetrahydro-1H-indolizino[8,7-b]indol-3(2H)-one (3p)

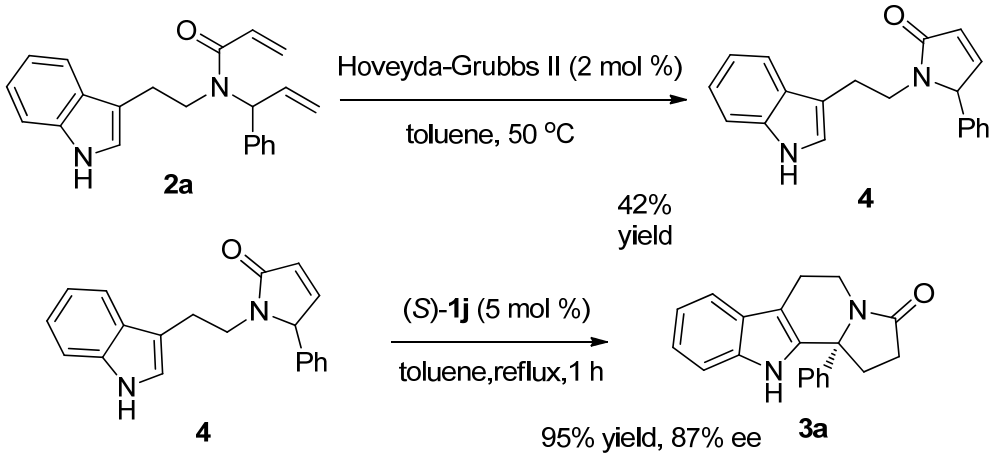
White solid (96% yield, 93% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 1/1/1, v/v). Analytical data for **3p**: $[\alpha]_D^{20}$ = -208 (*c* = 0.50, acetone); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.64 (s, 3H), 2.16-2.27 (m, 1H), 2.33-2.39 (m, 1H), 2.43-2.50 (m, 4H), 2.63-2.84 (m, 3H), 3.06-3.16 (m, 1H), 4.44-4.50 (m, 1H), 6.97-7.07 (m, 2H), 7.33 (d, *J* = 7.5 Hz, 1H), 8.65 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.8, 21.3, 25.3, 30.7, 32.9, 35.0, 59.6, 107.2, 116.1, 119.9, 120.3, 122.8, 126.2, 135.6, 137.5, 172.8; IR (film) 3244, 1666, 1450, 1296, 1178, 1063, 778, 737, 710, 666 cm^{-1}; HRMS (MALDI/DHB): Exact mass calcd for $C_{16}H_{19}N_2O^+$ (M+H) requires m/z 255.1492. Found m/z 255.1498. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t_R (major) = 7.39 min, t_R (minor) = 5.61 min.



(*S*)-11b-Butyl-10-methyl-5,6,11,11b-tetrahydro-1H-indolizino[8,7-b]indol-3(2H)-one (3q)

White solid (93% yield, 95% *ee*) following silica gel column chromatography (petroleum ether/ethyl acetate/DCM = 1/1/1, v/v). Analytical data for **3r**: $[\alpha]_D^{20}$ = -142.7 (*c* = 0.50, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.19-1.43 (m, 5H), 1.93-2.05 (m, 2H), 2.18-2.26 (m, 1H), 2.37-2.50 (m, 4H), 2.61-2.90 (m, 3H), 3.11-3.17 (m, 1H), 4.47-4.52 (m, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 8.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 16.8, 21.1, 22.9, 26.3, 30.5, 31.2, 35.6, 39.7, 62.6, 107.2, 116.0, 119.9, 120.2, 122.7, 126.2, 135.5, 137.5, 173.6; IR (film) 3259, 2926, 1661, 1413, 1347, 1268, 1162, 1065, 778, 747, 704, 648 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{19}H_{24}N_2O$ requires m/z 296.1889. Found m/z 296.1881. The enantiomeric excess was determined by Daicel Chiralpak AD-H (25 cm), Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 254 nm, t_R (major) = 5.70 min, t_R (minor) = 4.59 min.

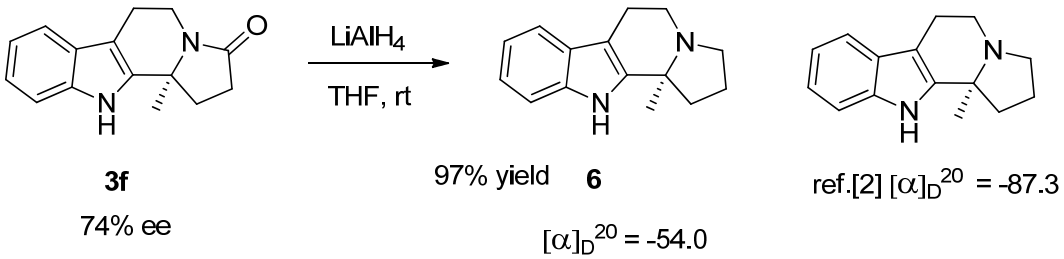
2.5 Investigation of the reaction mechanism



In a dry Schlenk tube, the readily available tryptamine derivative **2a** (250.0 mg, 0.76 mmol) was added to toluene (7 mL) under argon. The solution was heated to 50 ℃, then Hoveyda-Grubbs II (9.5 mg, 0.015 mmol) were added in one portion. After the reaction mixture was stirred for 7 hours, the solvent was removed to leave about 2 mL under reduced pressure and the residue was purified by flash chromatography (ethyl acetate/DCM/petroleum ether= 1/1/1) to afford product **4**. Analytical data for **4**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.83-2.93 (m, 1H), 2.97-3.11 (m, 2H), 4.01-4.10 (m, 1H), 4.77 (s, 1H), 6.21 (dd, J = 1.2, 7.6 Hz, 1H), 6.89-6.95 (m, 4H), 7.05 (t, J = 7.5 Hz, 1H), 7.17 (d, J = 7.5 Hz, 1H), 7.29-7.38 (m, 5H), 8.51 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.4, 40.2, 67.3, 111.2, 112.5, 118.5, 119.1, 121.9, 122.0, 126.3, 127.2, 127.4, 128.7, 128.9, 134.2, 136.2, 148.0, 171.5; IR (film) 3223, 2963, 1674, 1417, 1261, 1093, 1020, 799 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{20}H_{18}N_2O$ requires m/z 302.1419. Found m/z 302.1416.

In a dry Schlenk tube, compound **5** (30.2 mg, 0.1 mmol) was dissolved in toluene (2 mL) under argon. After the solution was heated to reflux, chiral phosphoric acid (*S*)-**1j** (8.7 mg, 0.01 mmol) was added. After the reaction was complete (monitored by TLC), the solvent was removed and the residue was purified by flash chromatography to afford product **3a (**95% yield, 87% ee**)**.

2.6 The determination of the absolute configuration

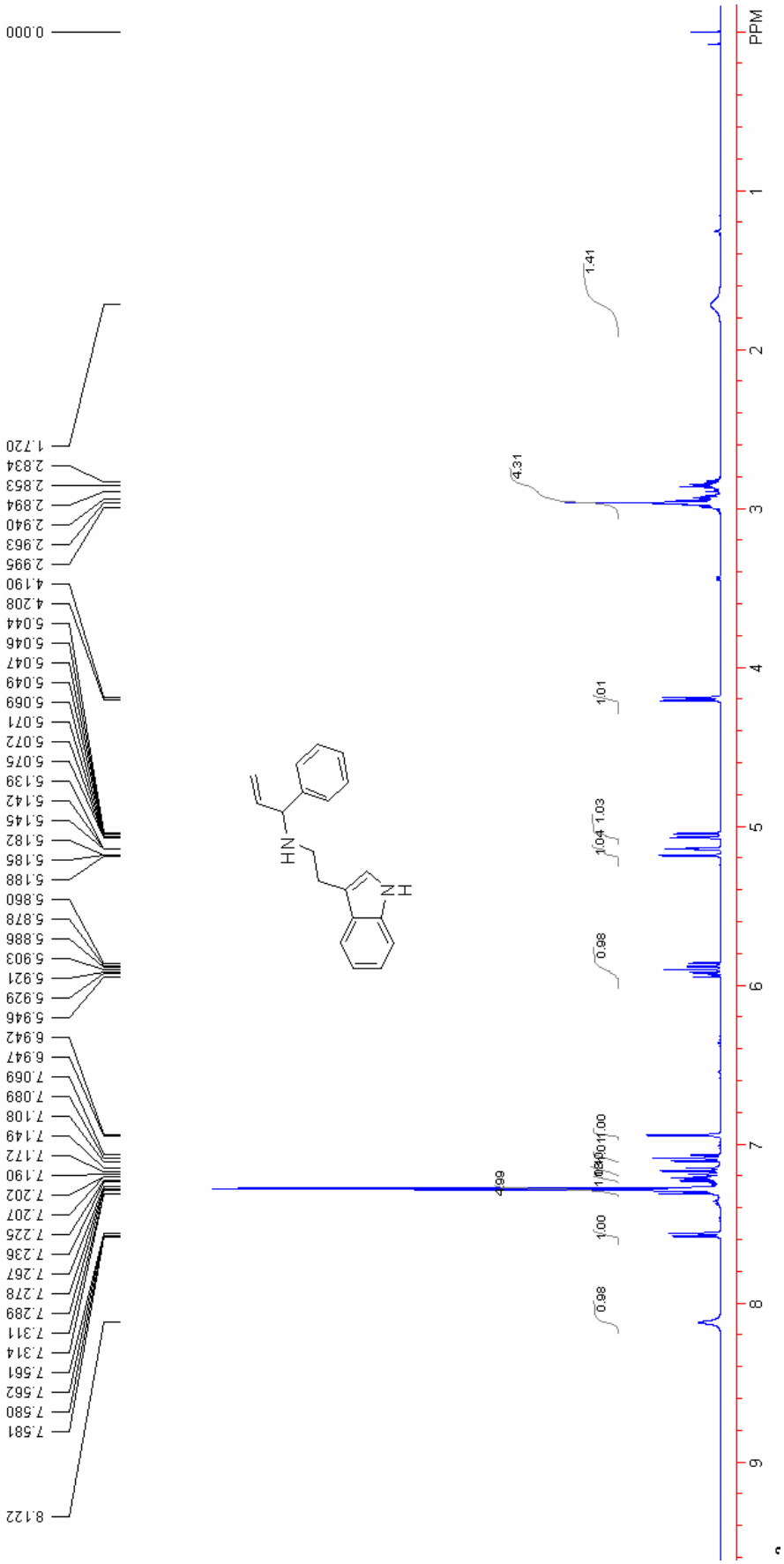


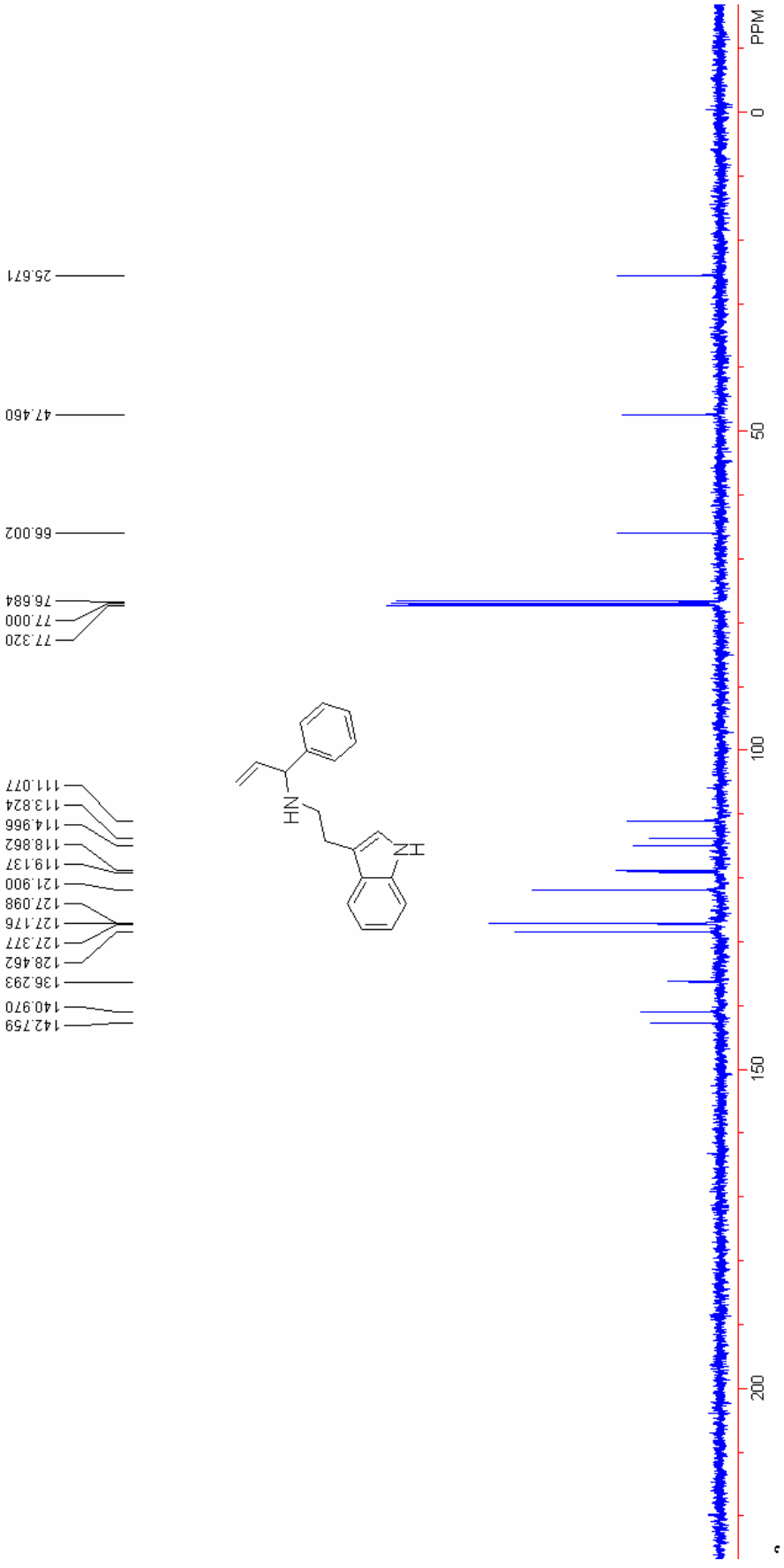
A flame-dried 25 mL round-bottom flask was charged with **3f** (43.2 mg, 0.18 mmol, 74% ee) and anhydrous THF (4 mL). Then $LiAlH_4$ (40 mg, 1.08 mmol) was added portionwise. After stirring at room temperature for 16 h. the reaction mixture was cooled to 0 ℃, and then slowly quenched by dropwise addition of H_2O (40 μ L), NaOH (80 mg) and H_2O (120 μL). The reaction was stirred at 0 ℃ for 30 min, and then filtered through a pad of Celite, the solid was washed with DCM. The combined organic filtrates were washed with DCM. The combined organic phase was washed with brine, separated, dried over Na_2SO_4, filtrated, and evaporated under reduced pressure. The residue was purified by flash chromatography (MeOH/Et_3N/DCM = 5/1/100) to afford product **6** (39.5 mg, 97% yield). The sample showed identical characterization to that of the previously reported synthesis[2] with a same observed optical rotation, allowing us to assign the absolute stereochemistry as (*S*). Analytical data for **6**: $[\alpha]_D^{20}$ = -54.0 (*c* = 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.52 (s, 3H), 1.59-1.66 (m, 1H), 1.84-2.16 (m, 3H), 2.49-2.55 (m, 1H), 2.87-3.06 (m, 3H), 3.24-3.28 (m, 2H), 7.07-7.17 (m, 2H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.73 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.1, 22.2, 27.9, 38.0, 42.2, 49.1, 59.7, 106.7, 110.6, 118.1, 119.3, 121.4, 127.1, 135.7, 138.9; IR (film) 3405, 3220, 2926, 1452, 1347, 1319, 1294, 1259, 1235, 1010, 797, 744 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{15}H_{18}N_2$ requires m/z 226.1470. Found m/z 226.1463.

3. References

1. The catalyst **(*rac*)-IrL_n** was prepared according to the literature: Spiess, S.; Raskatov, J. A.; Gnamm, C.; Brodner, K.; Helmchen, G. *Chem. Eur. J.* **2009**, *15*, 11087.
2. Allin, S. M.; Thomas, C. I.; Allard, J. E.; Duncton, M.; Elsegood, M. R. J.; Edgar, M. *Tetrahedron Lett.* **2003**, *44*, 2335.

4. Copies of ^{1}H NMR and ^{13}C NMR spectra of the compounds

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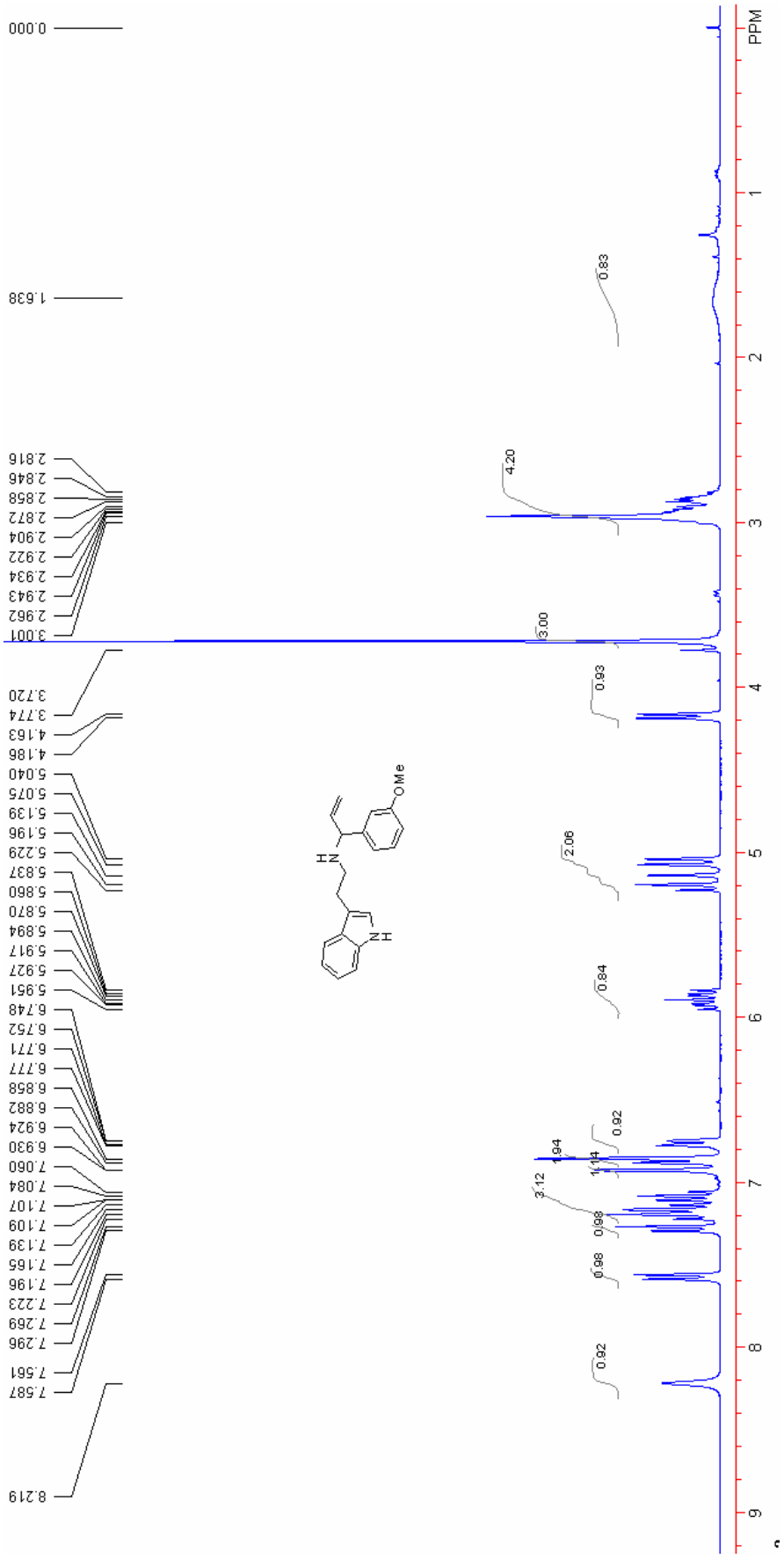
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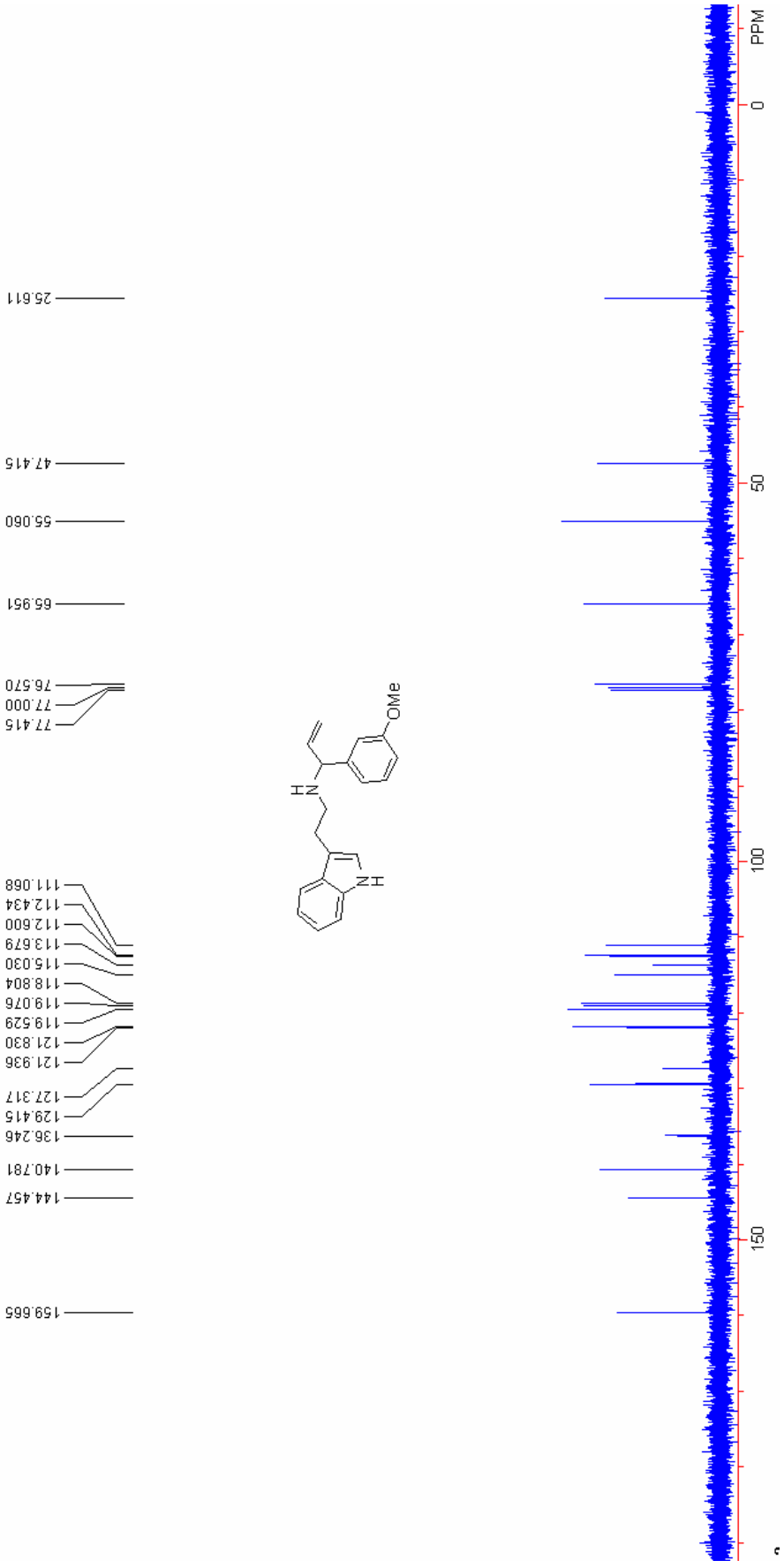
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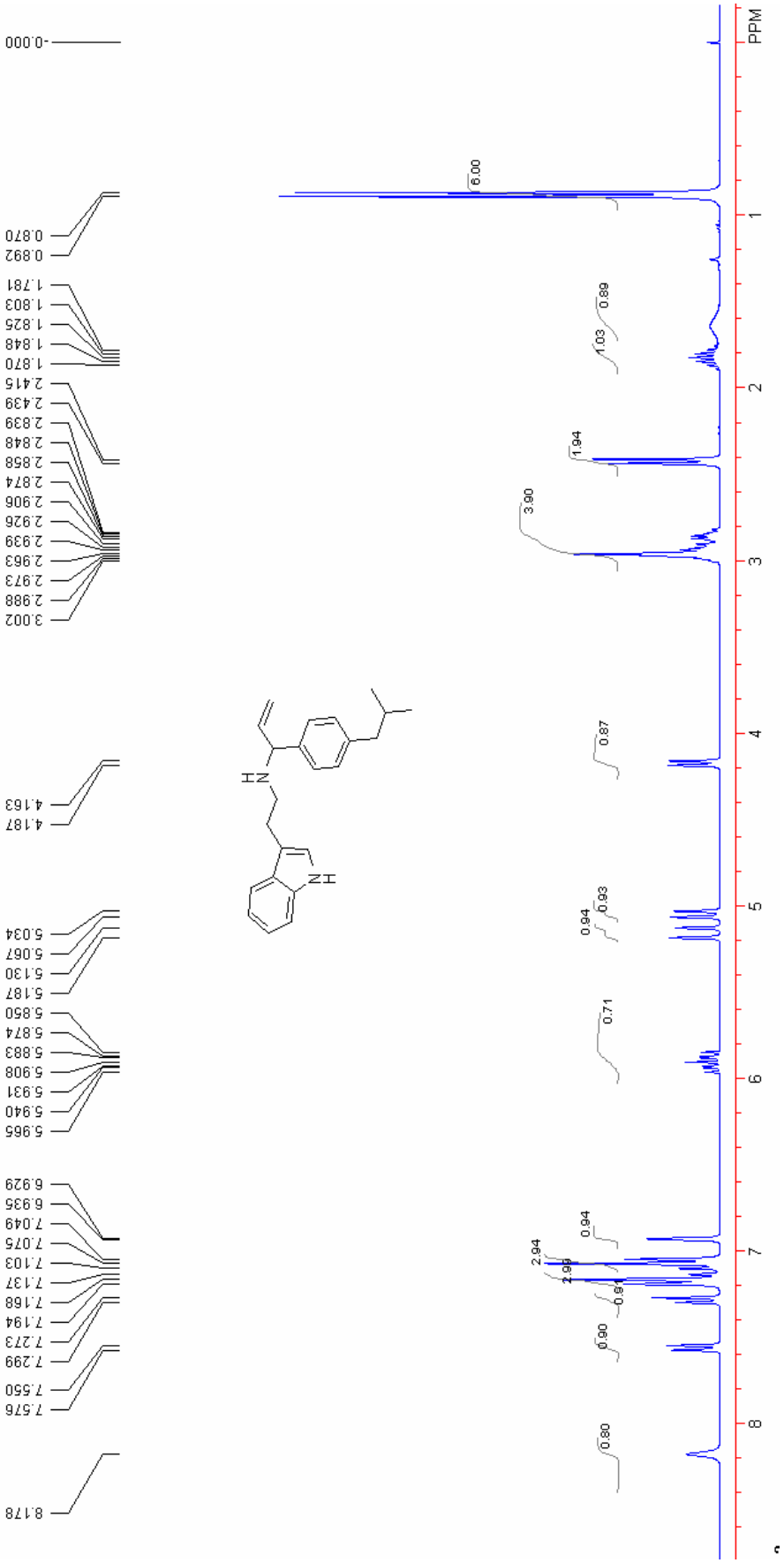
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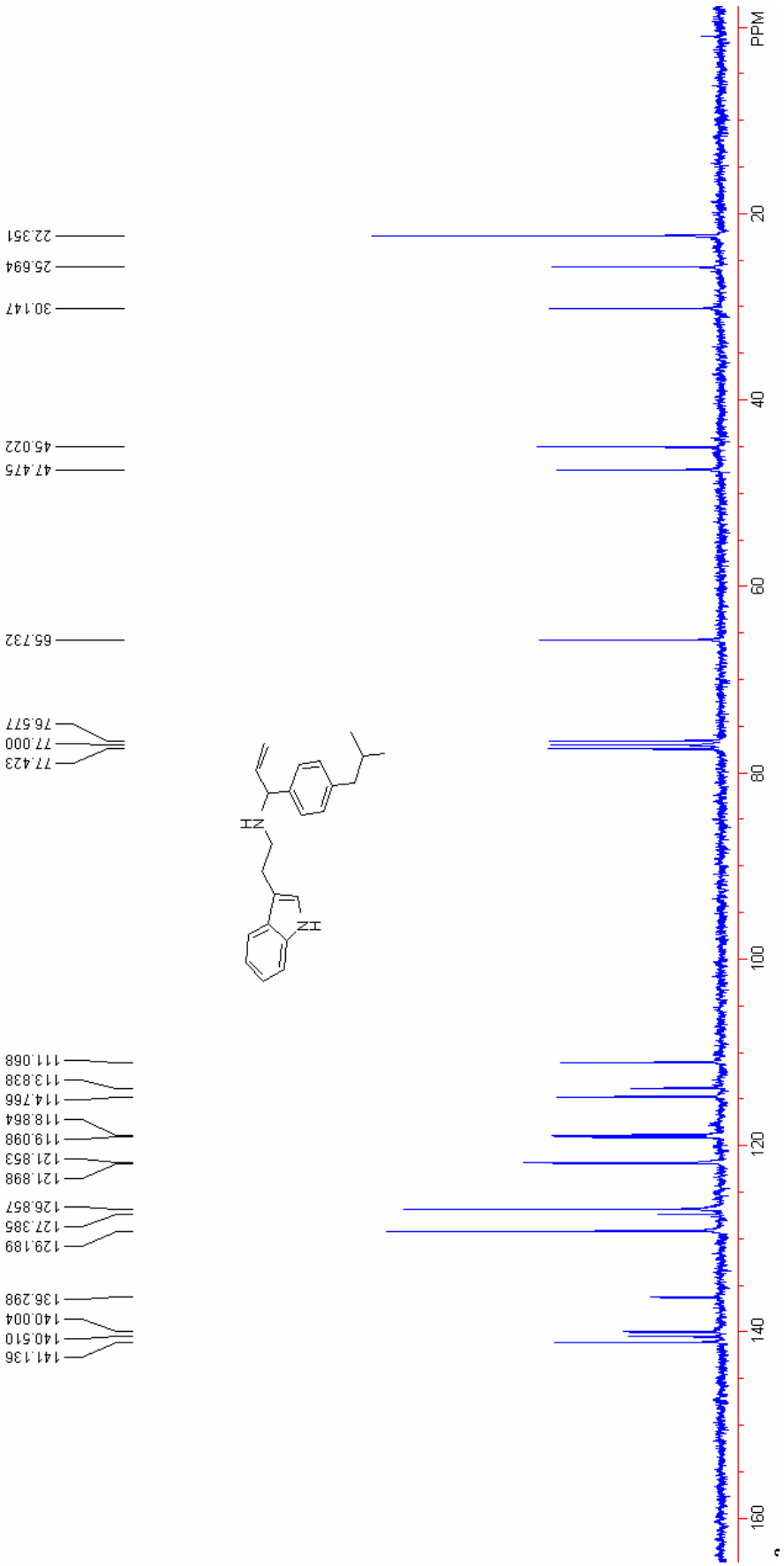
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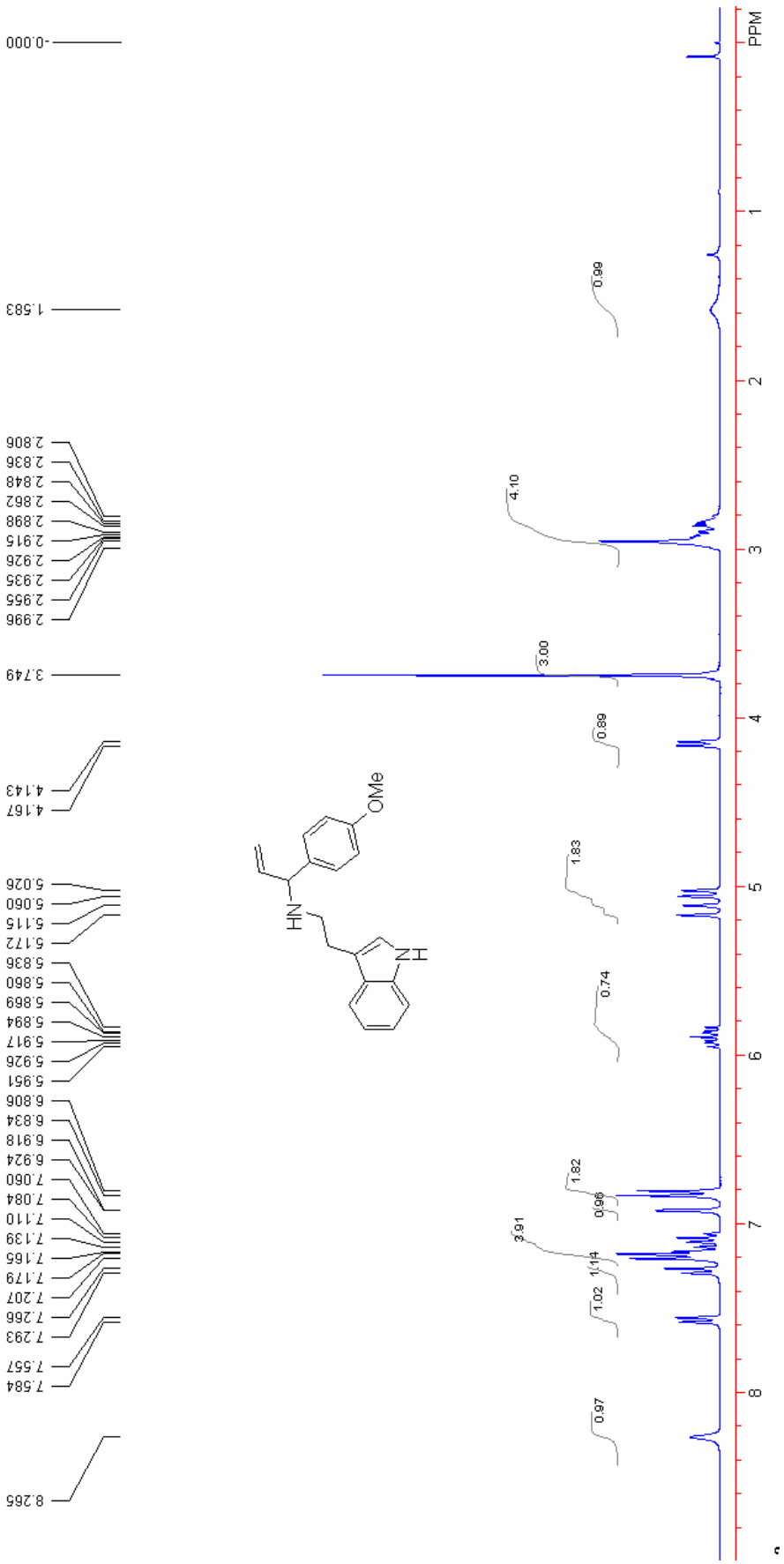
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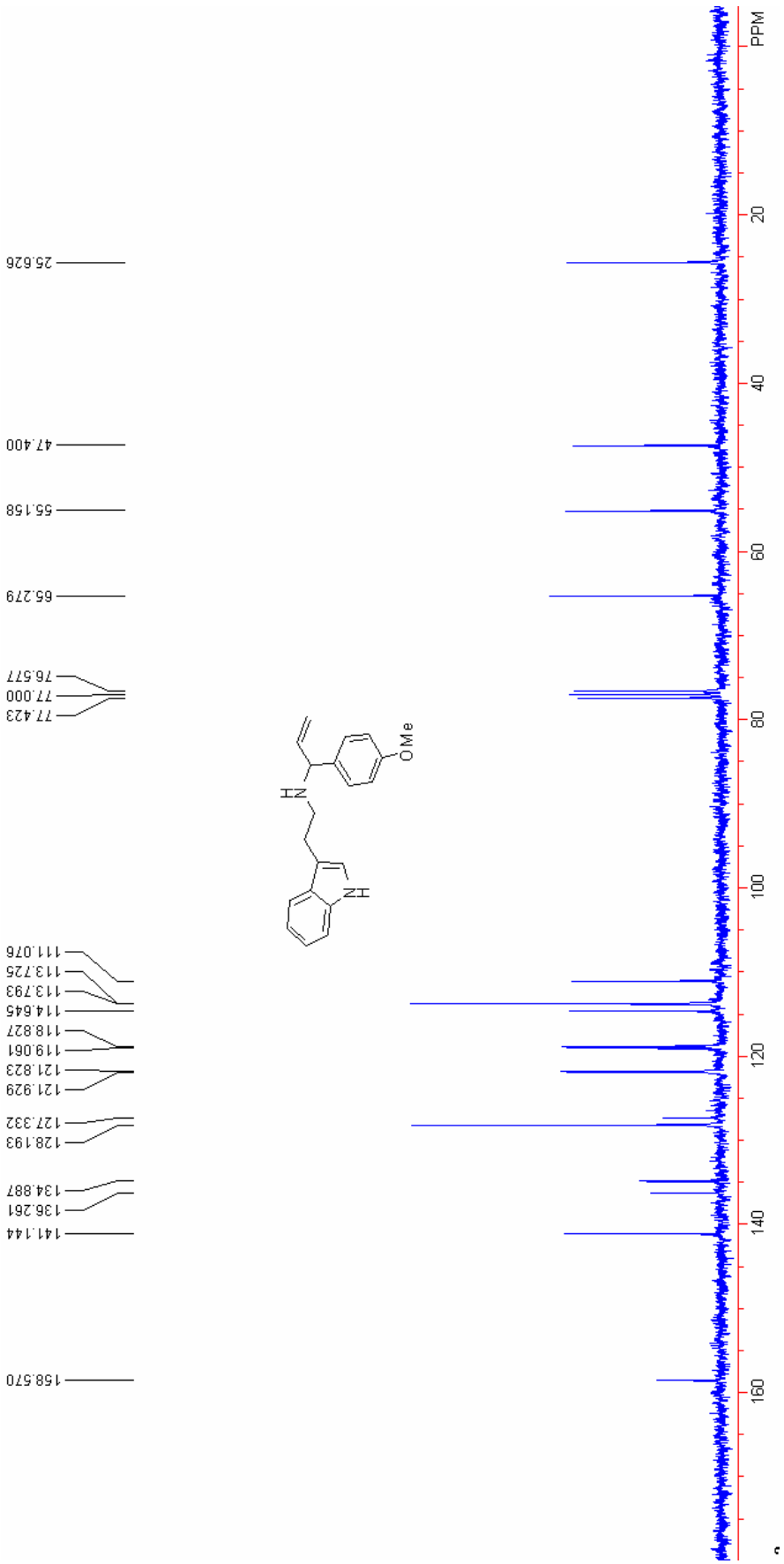
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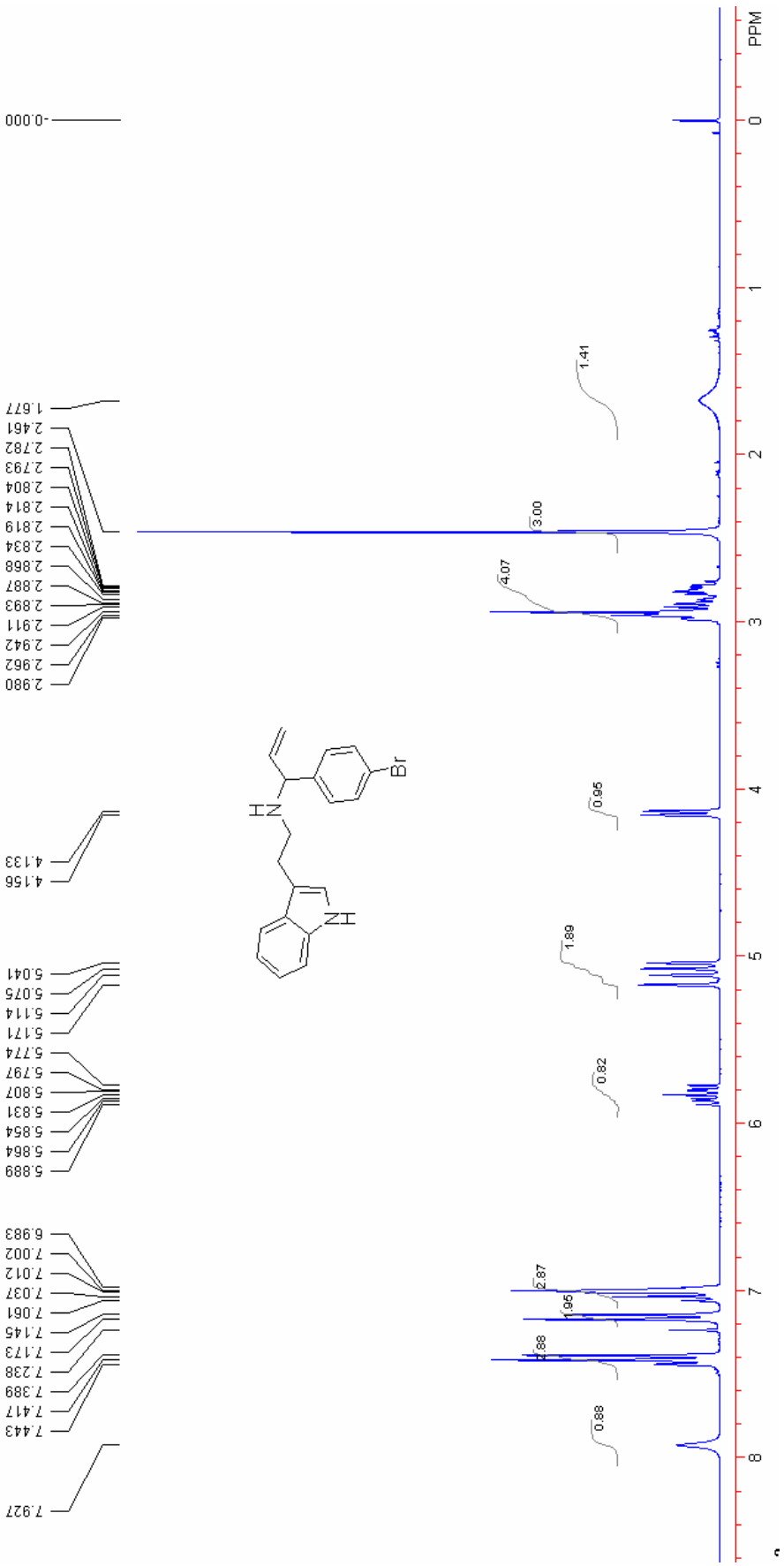
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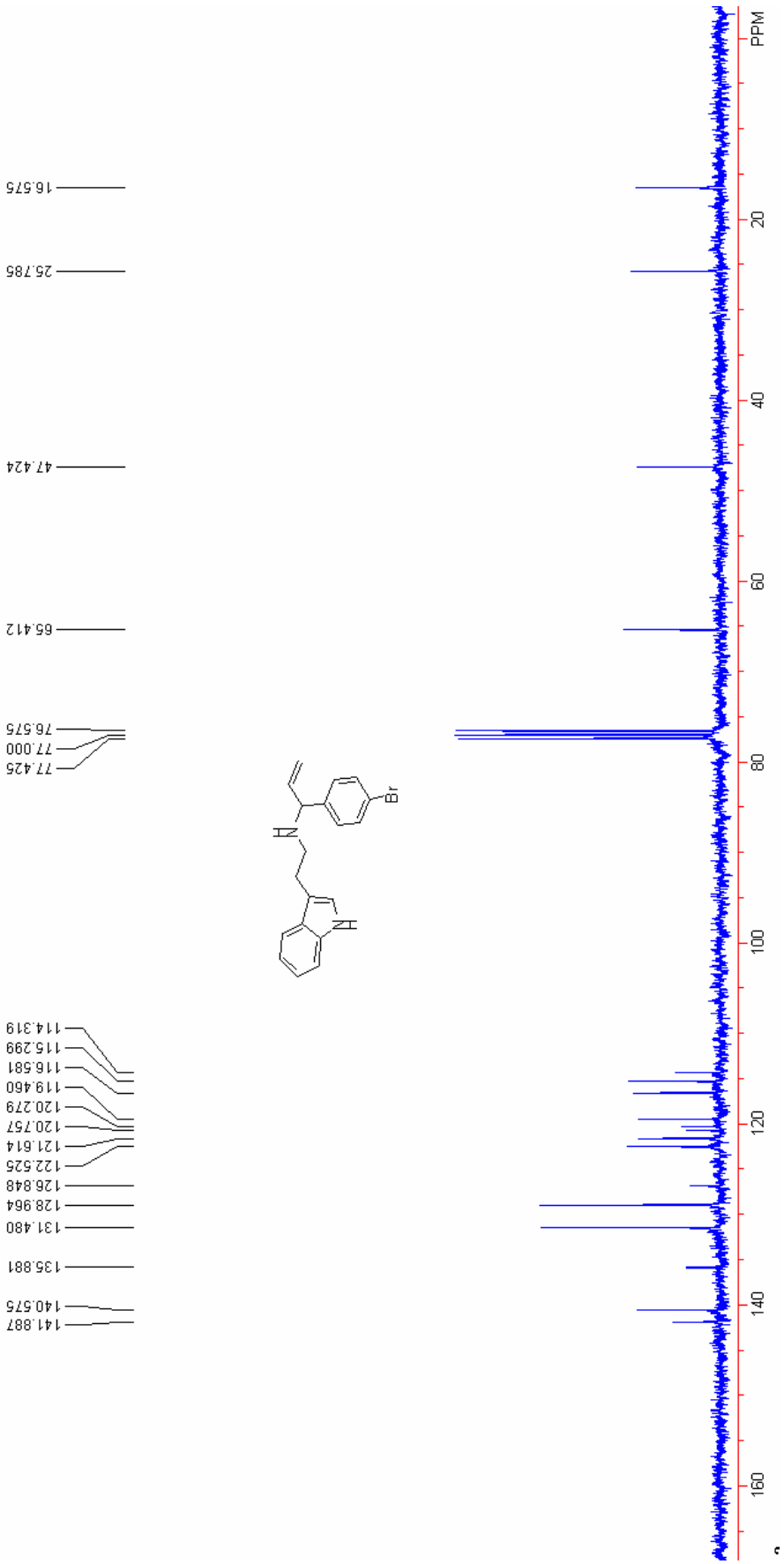
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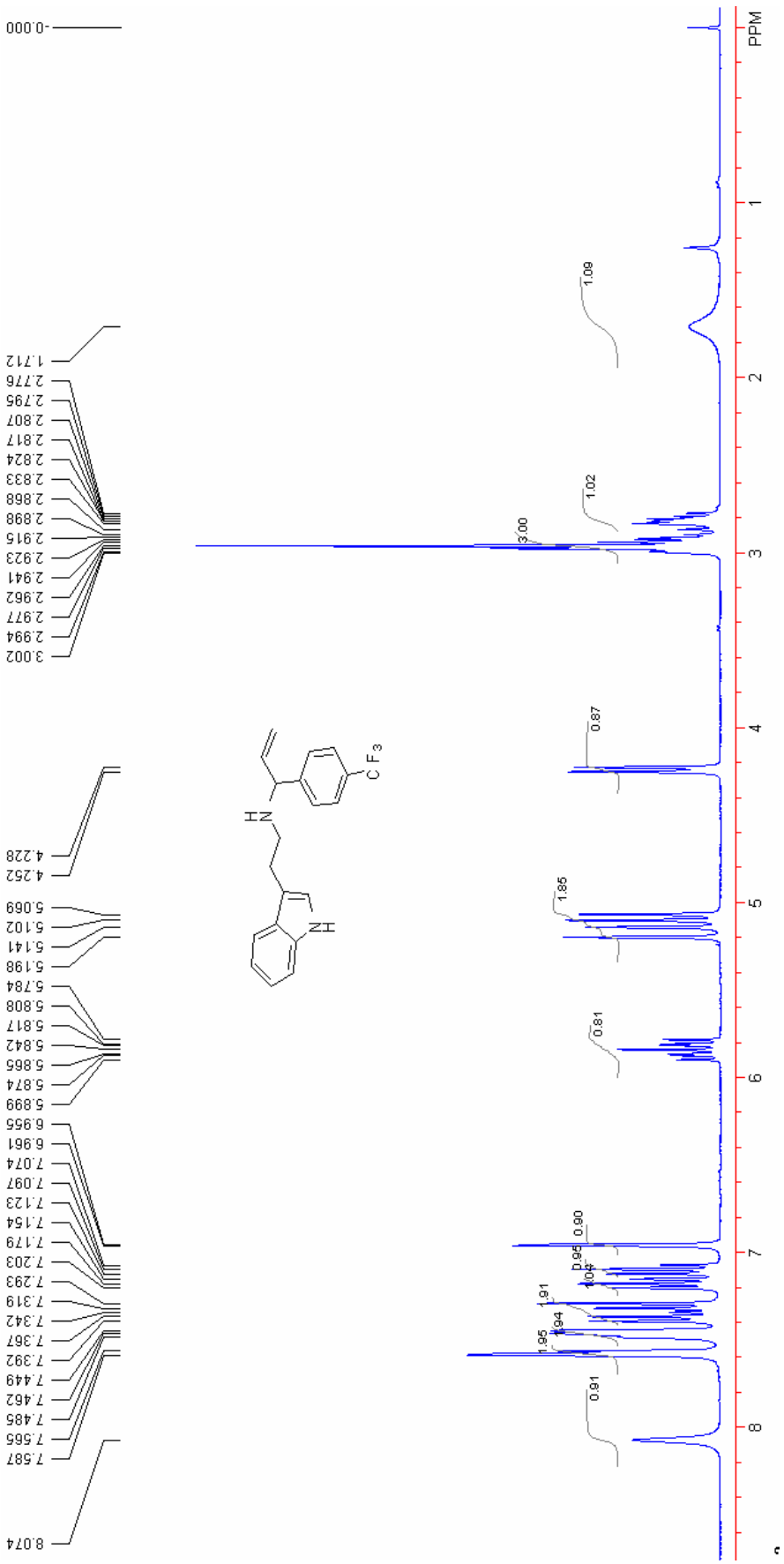
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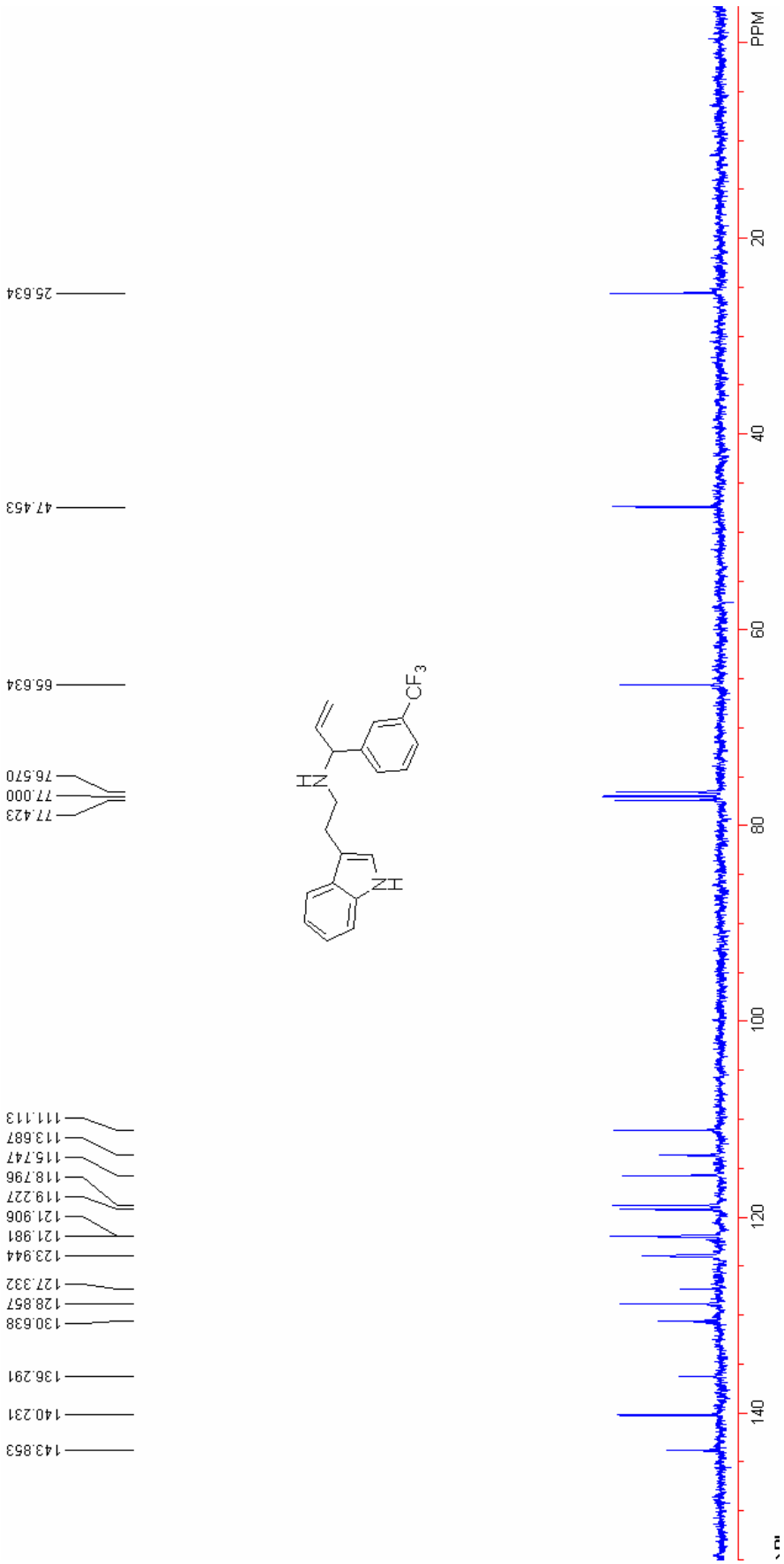
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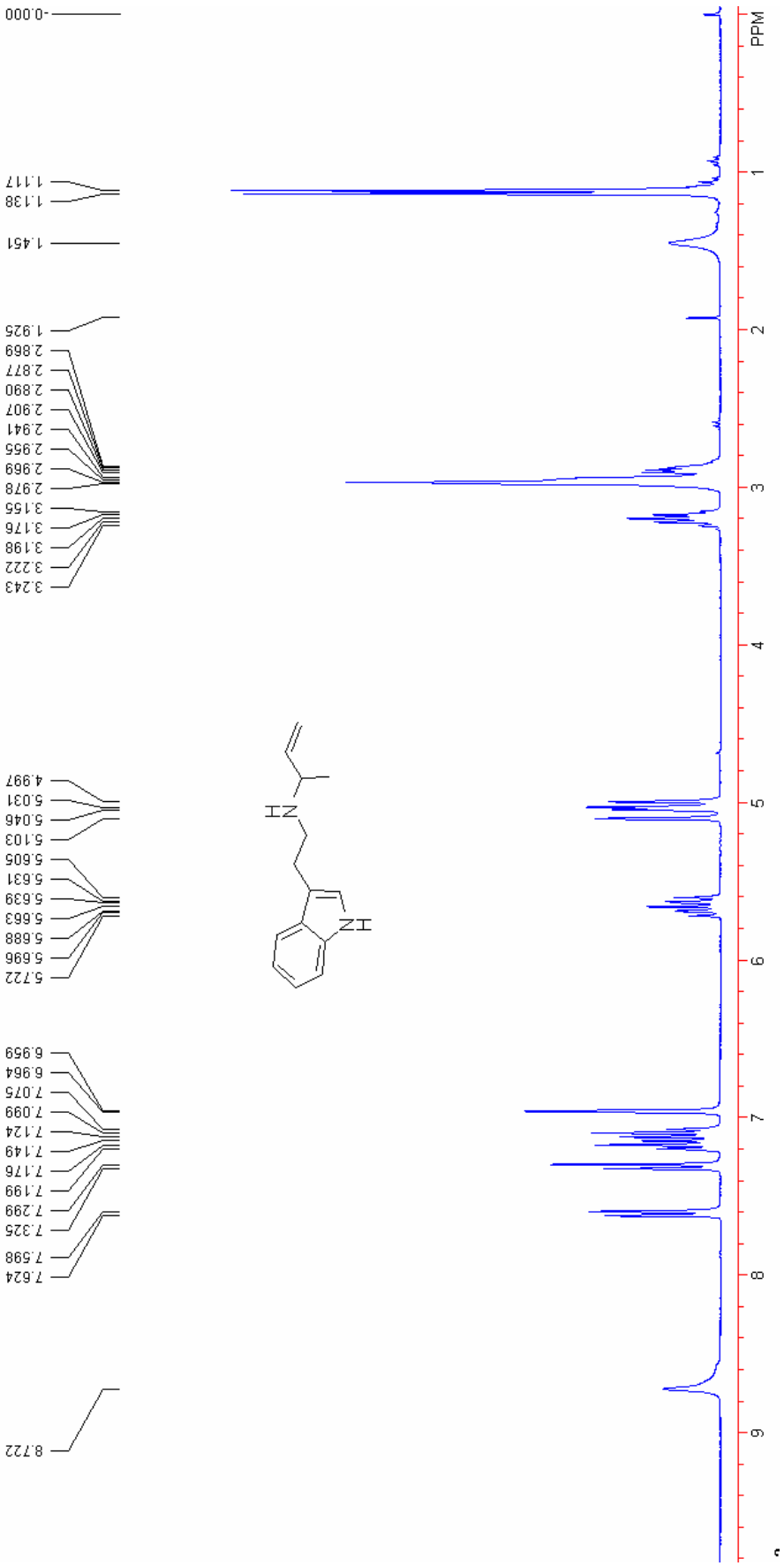
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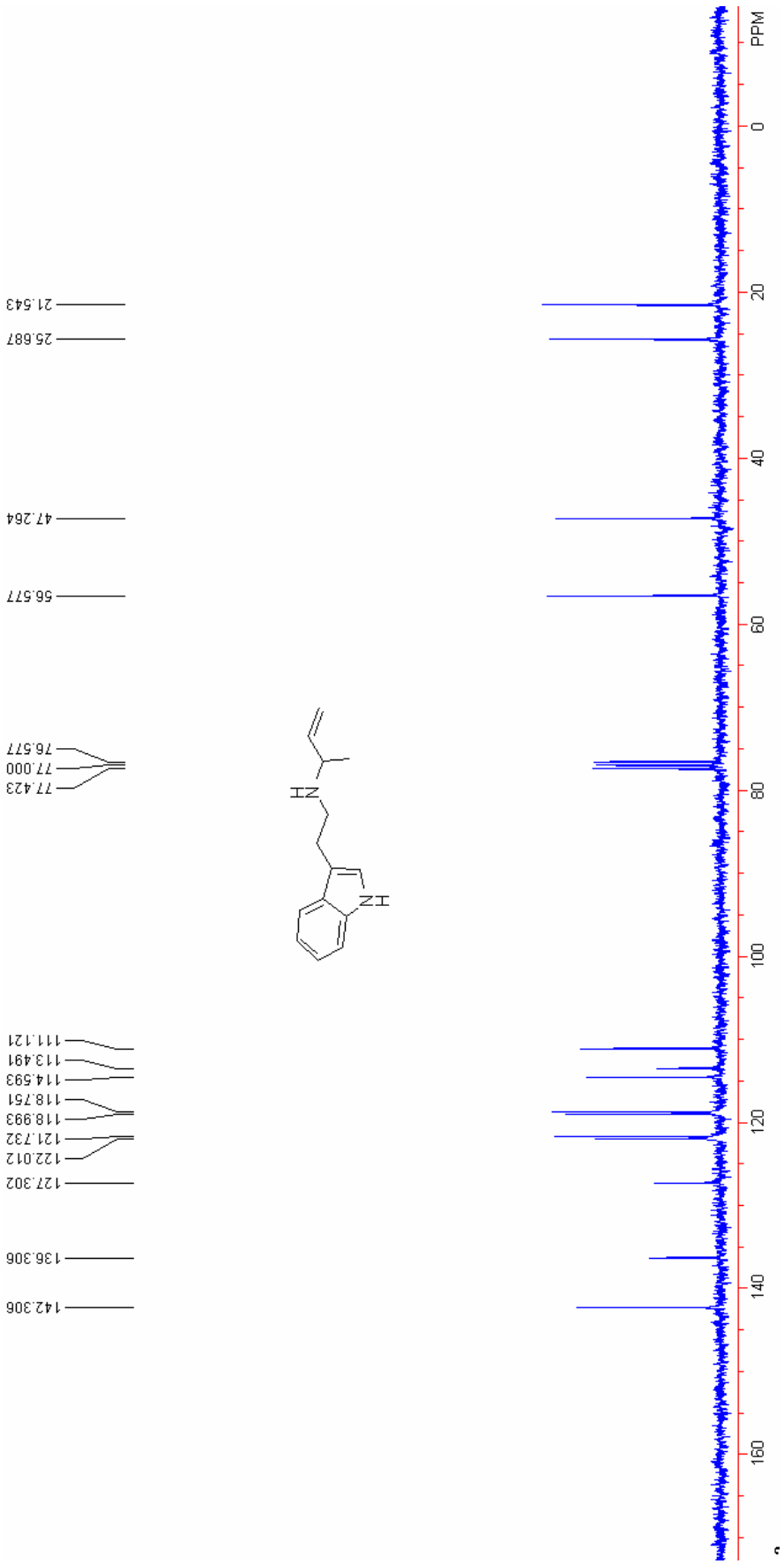
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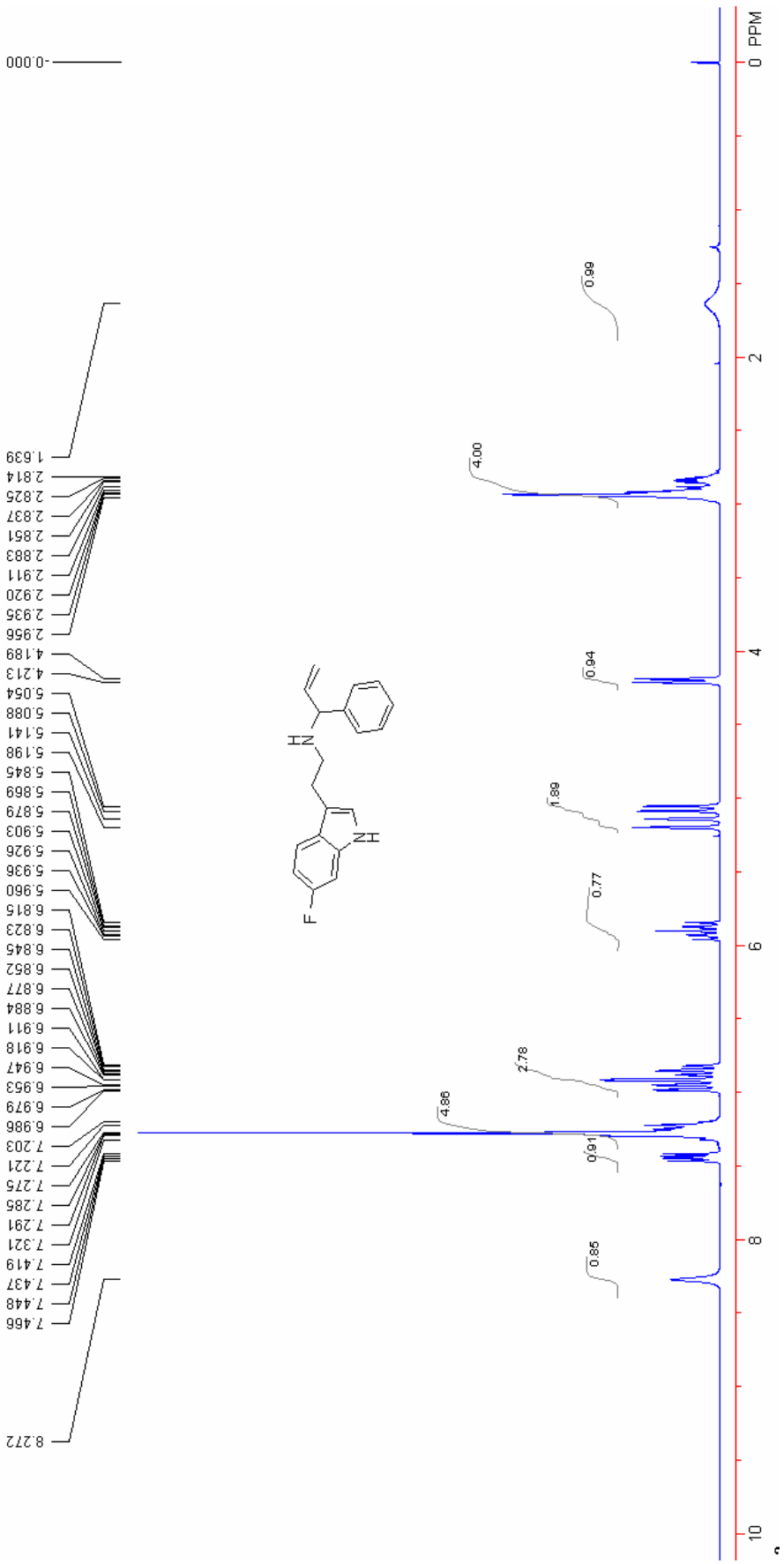
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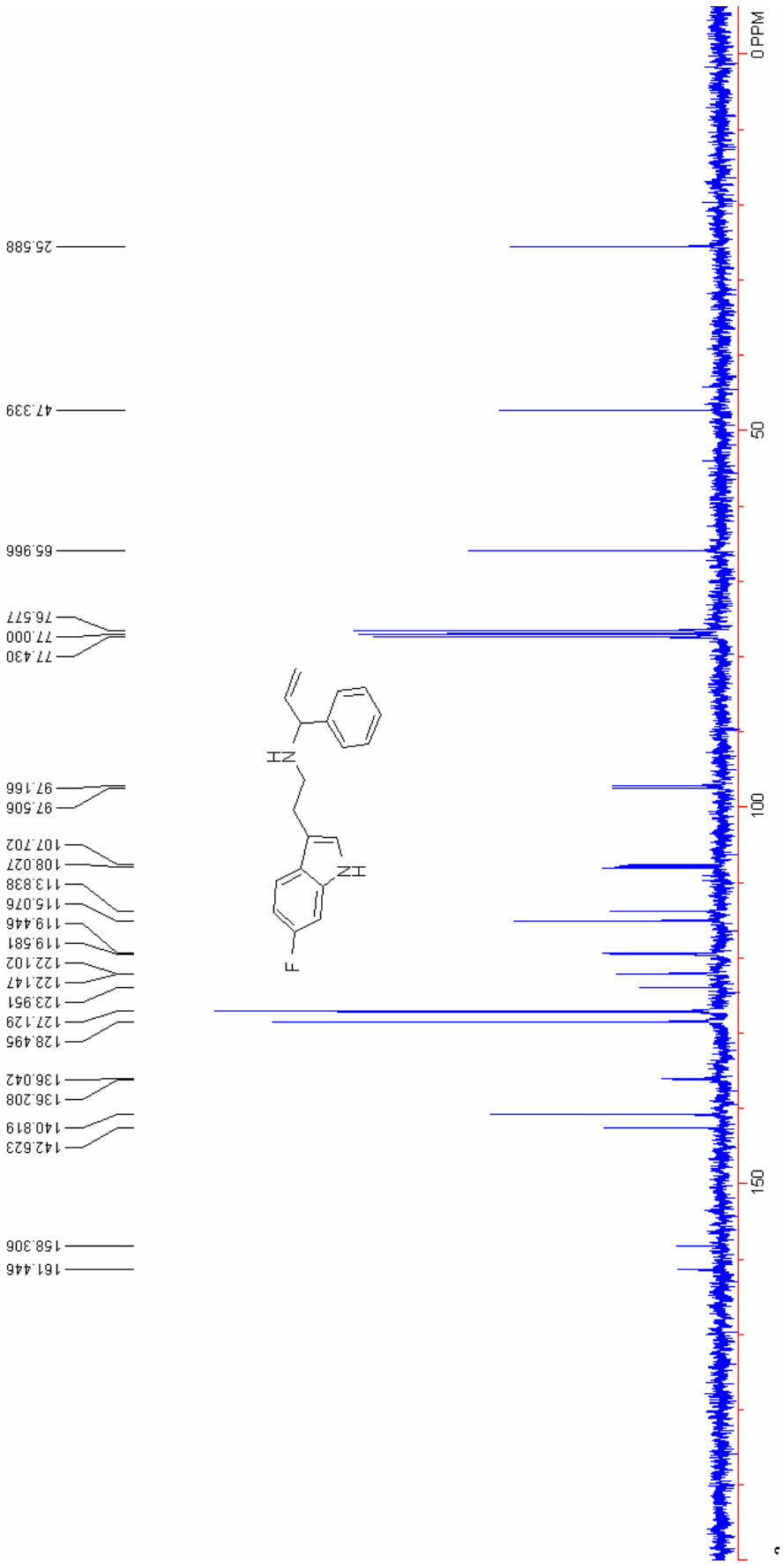
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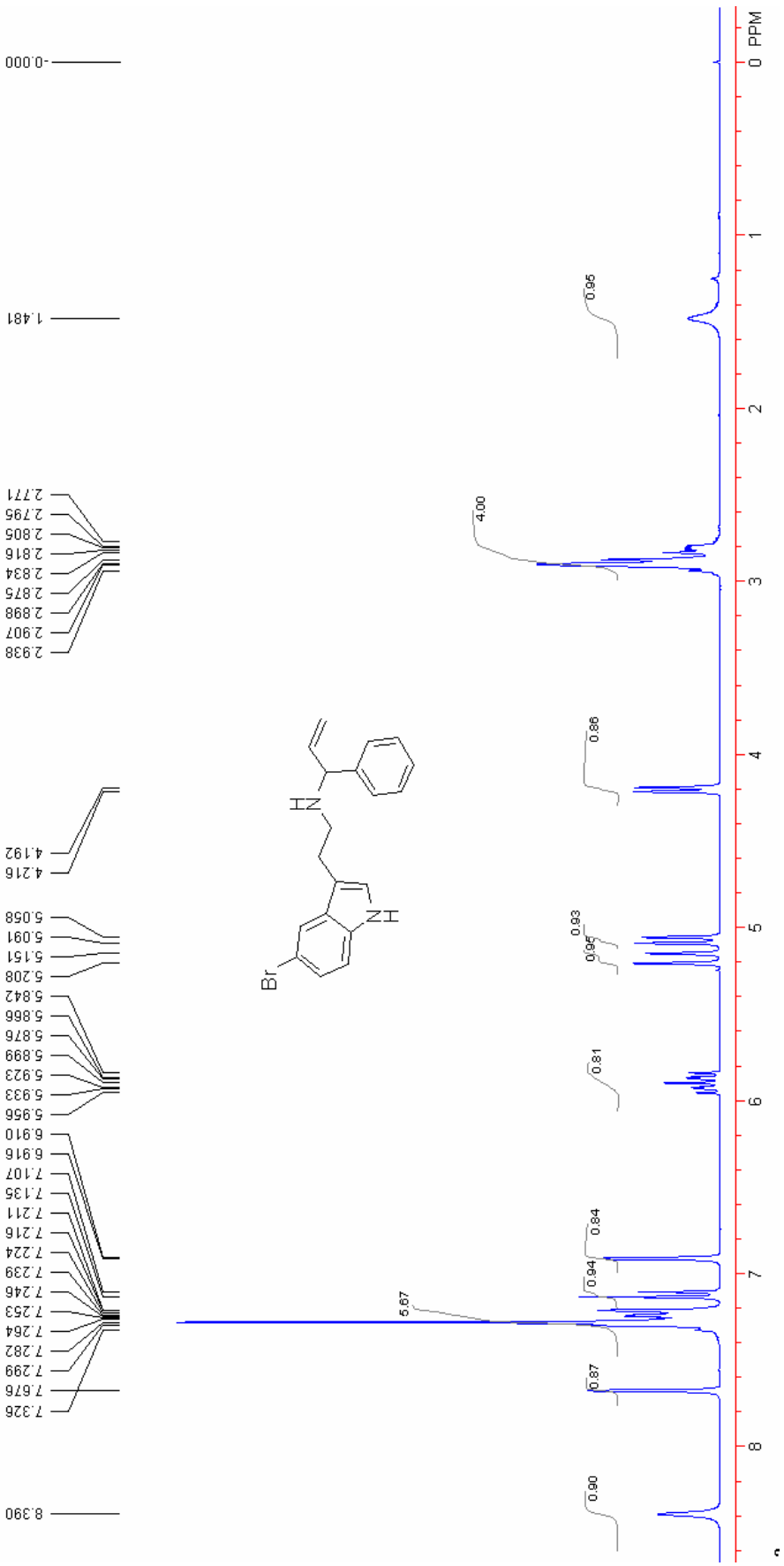
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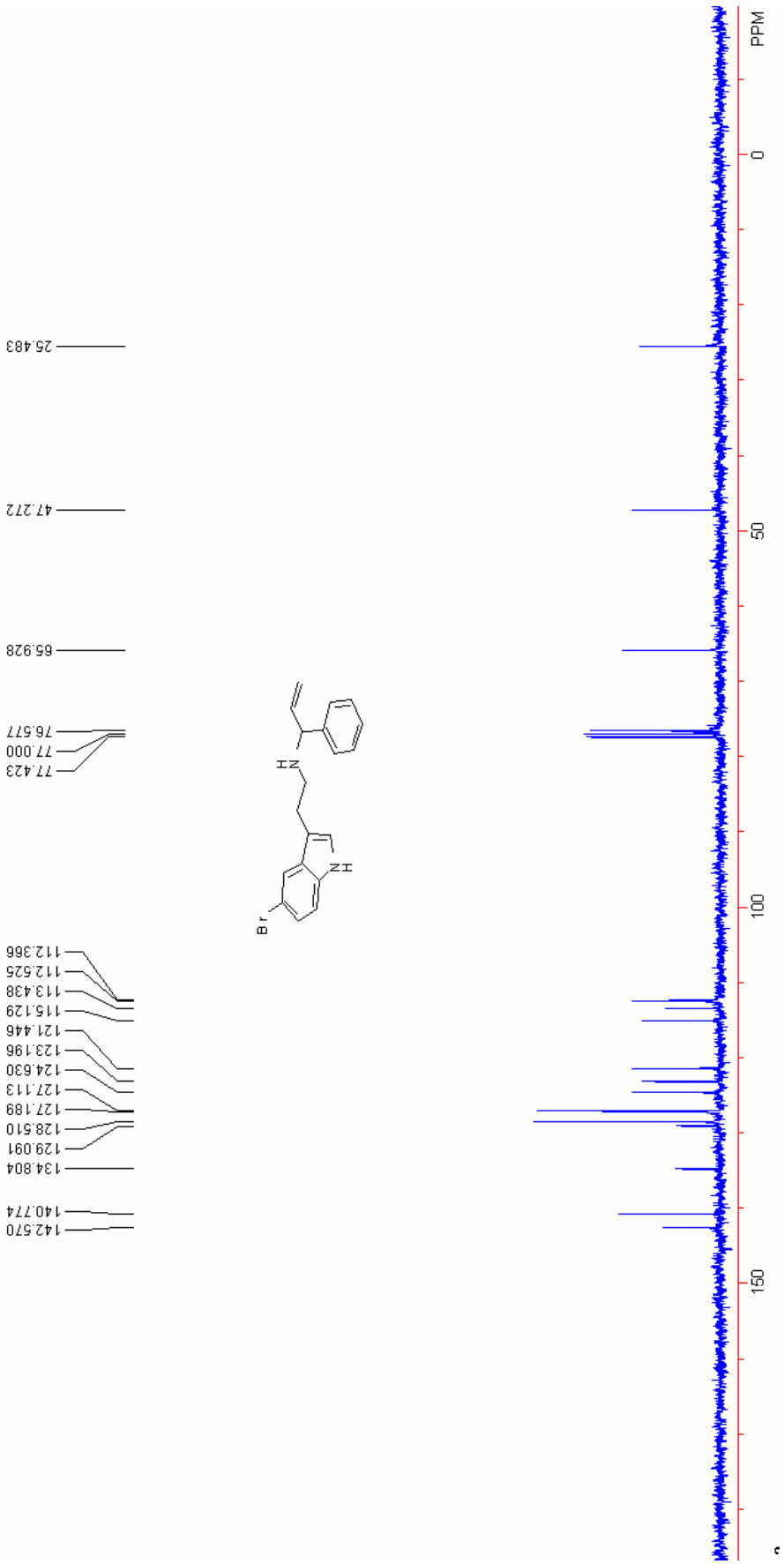
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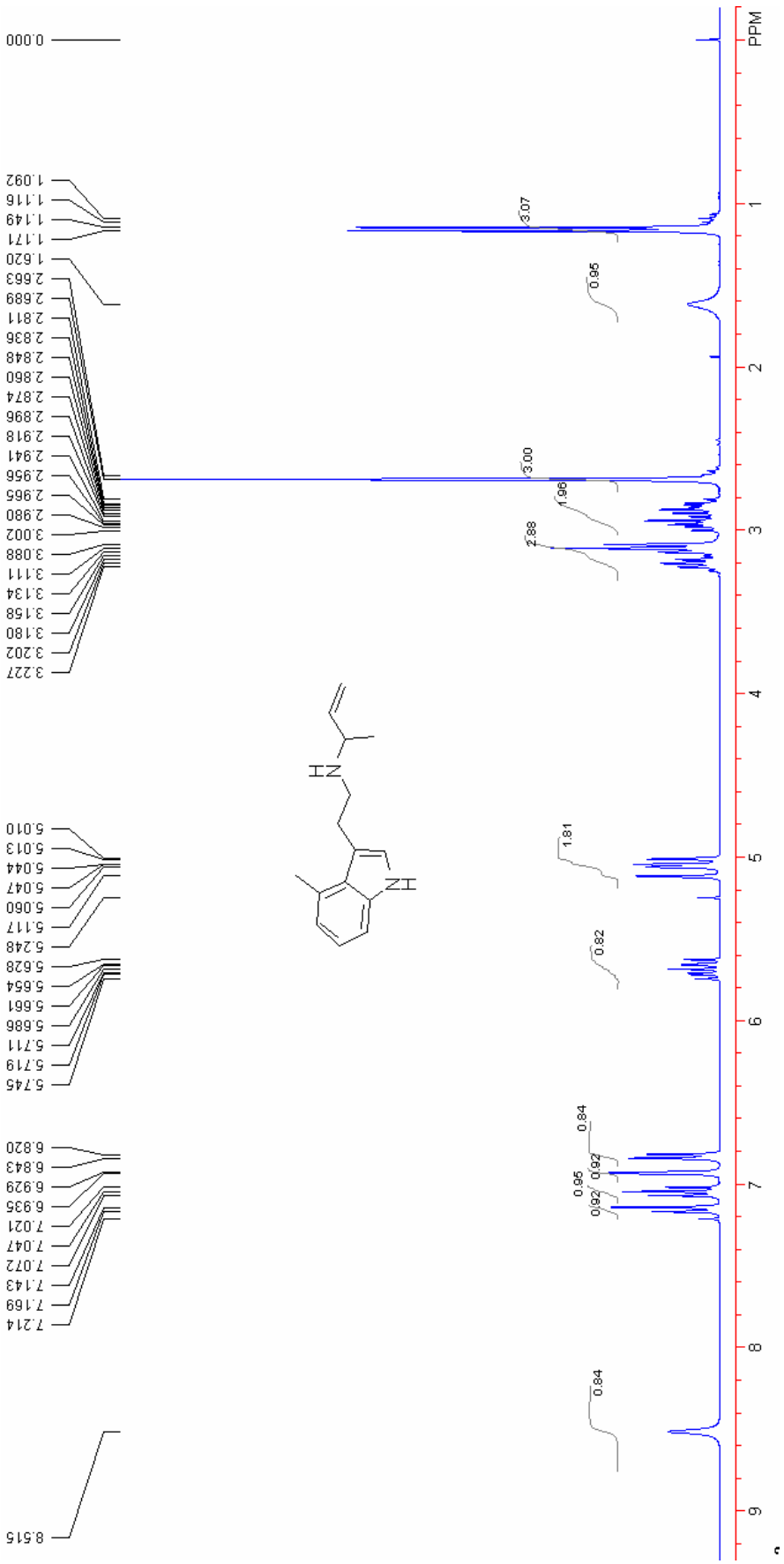
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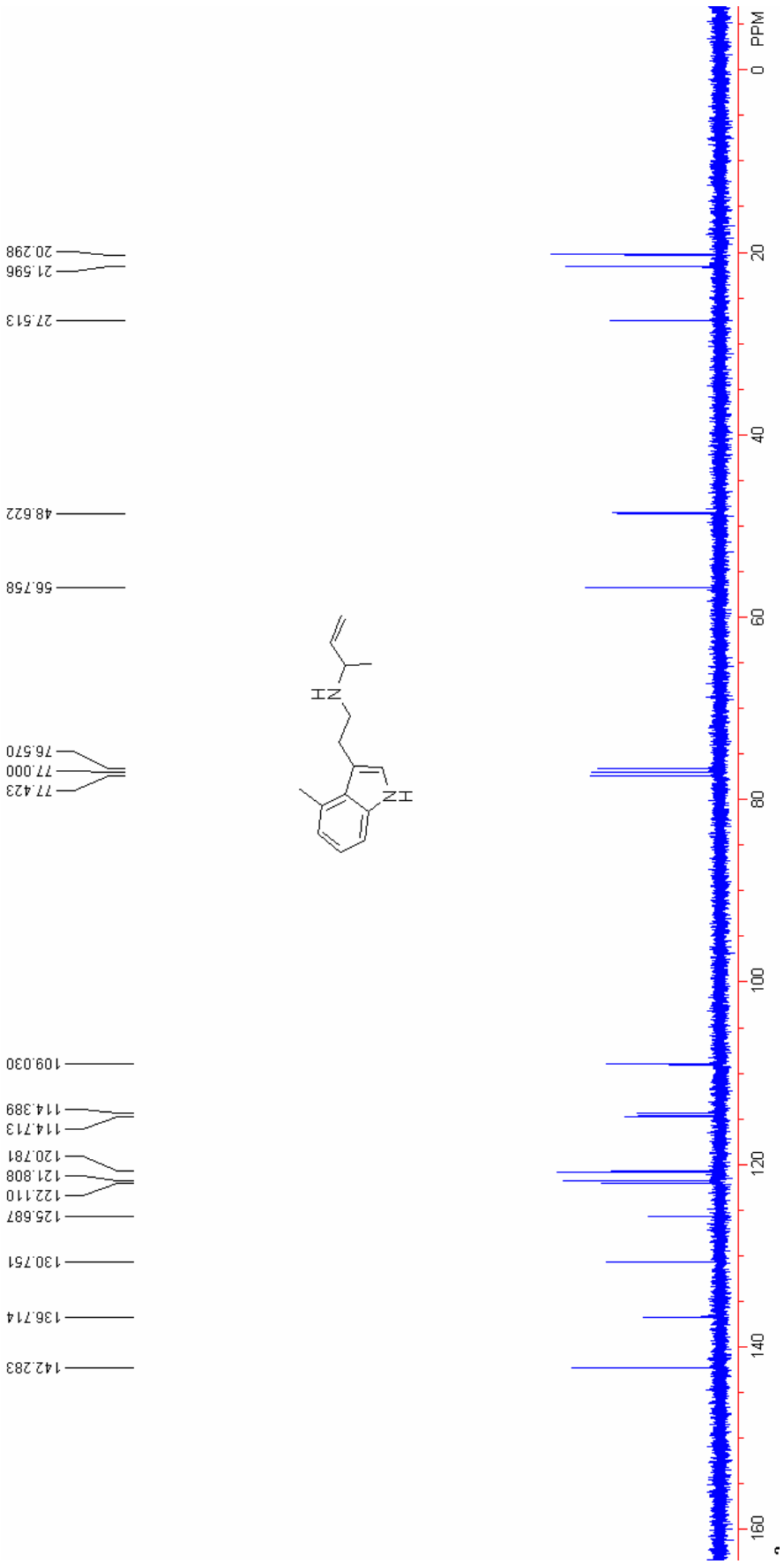
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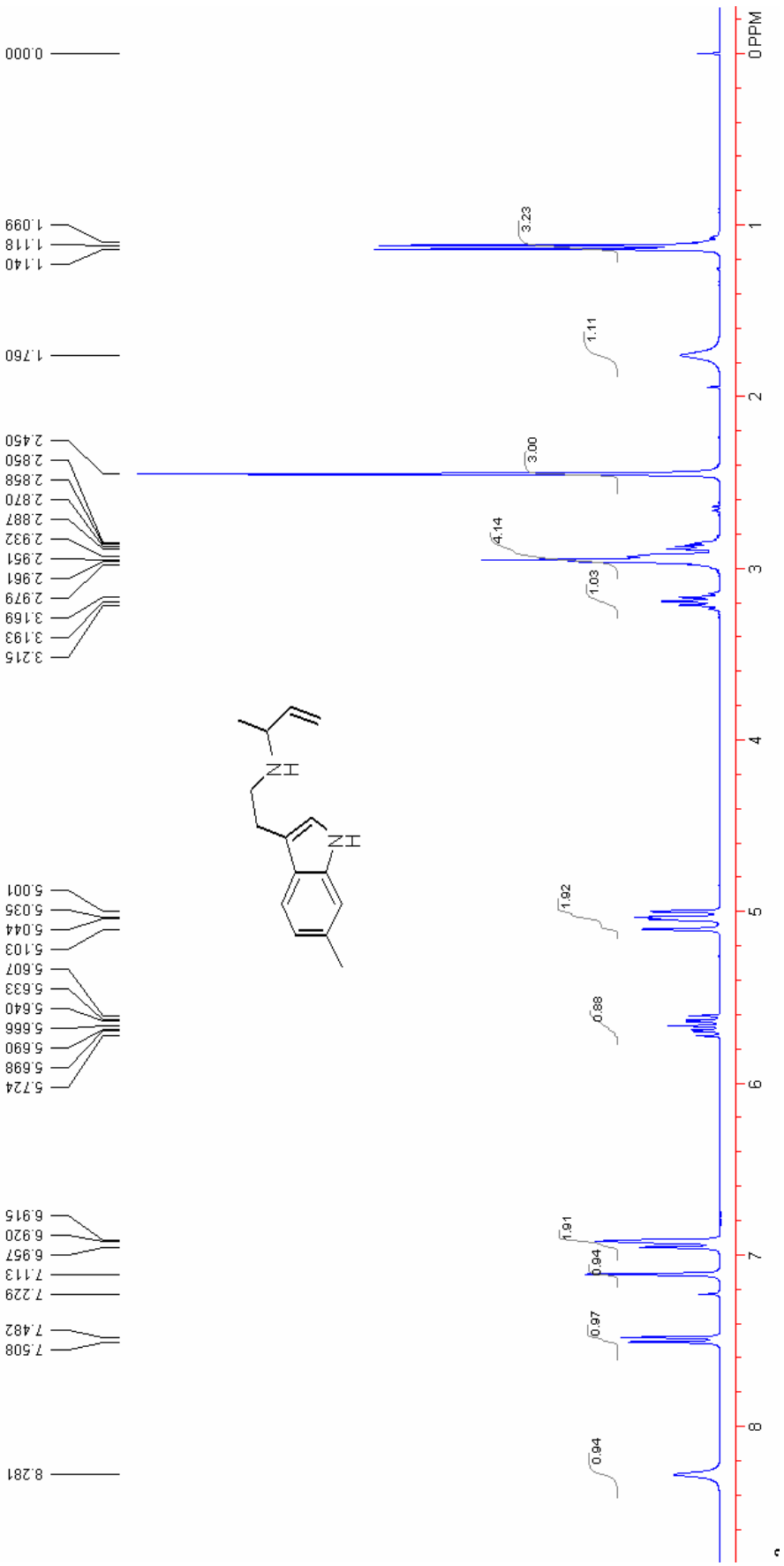
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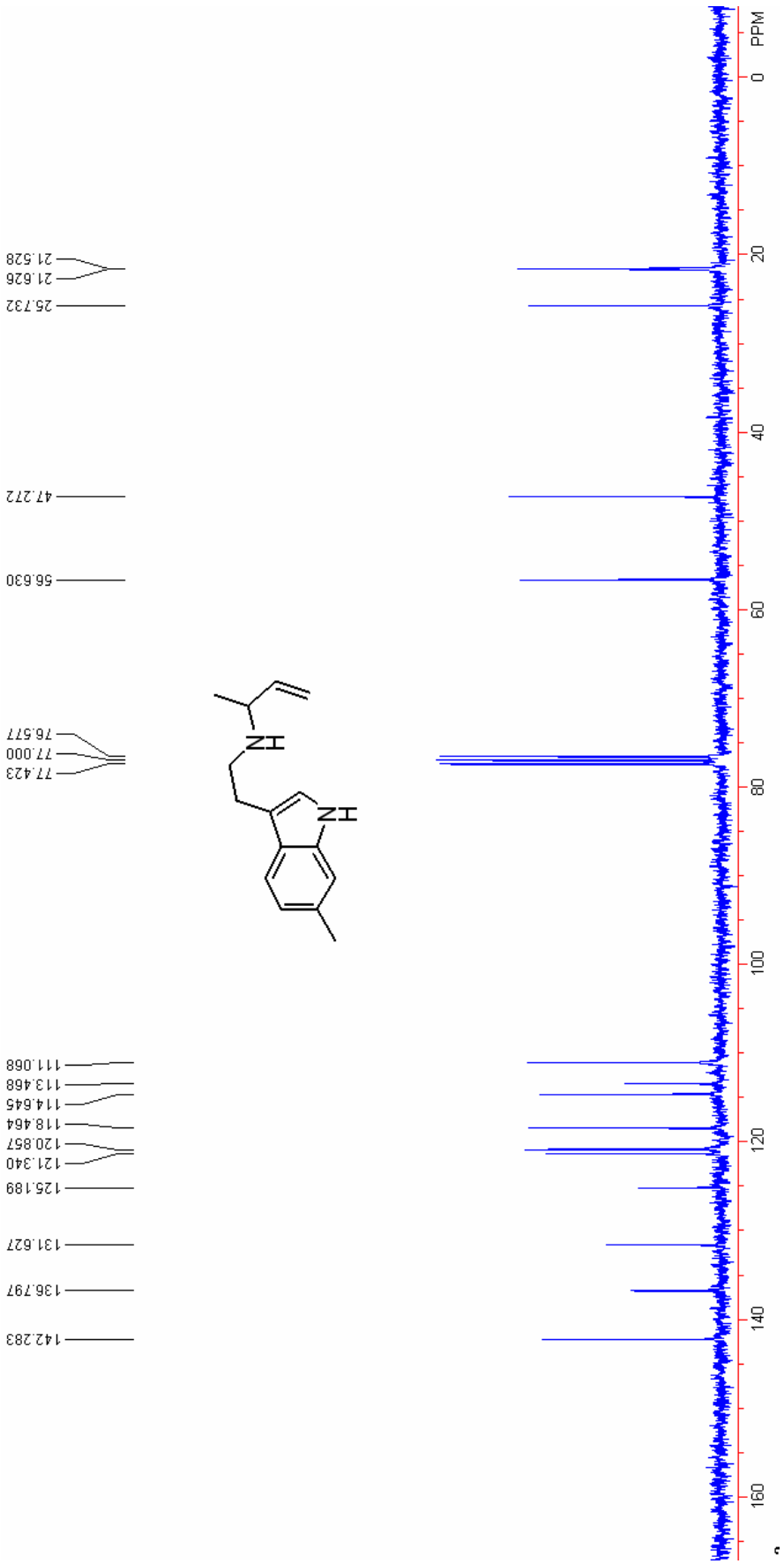
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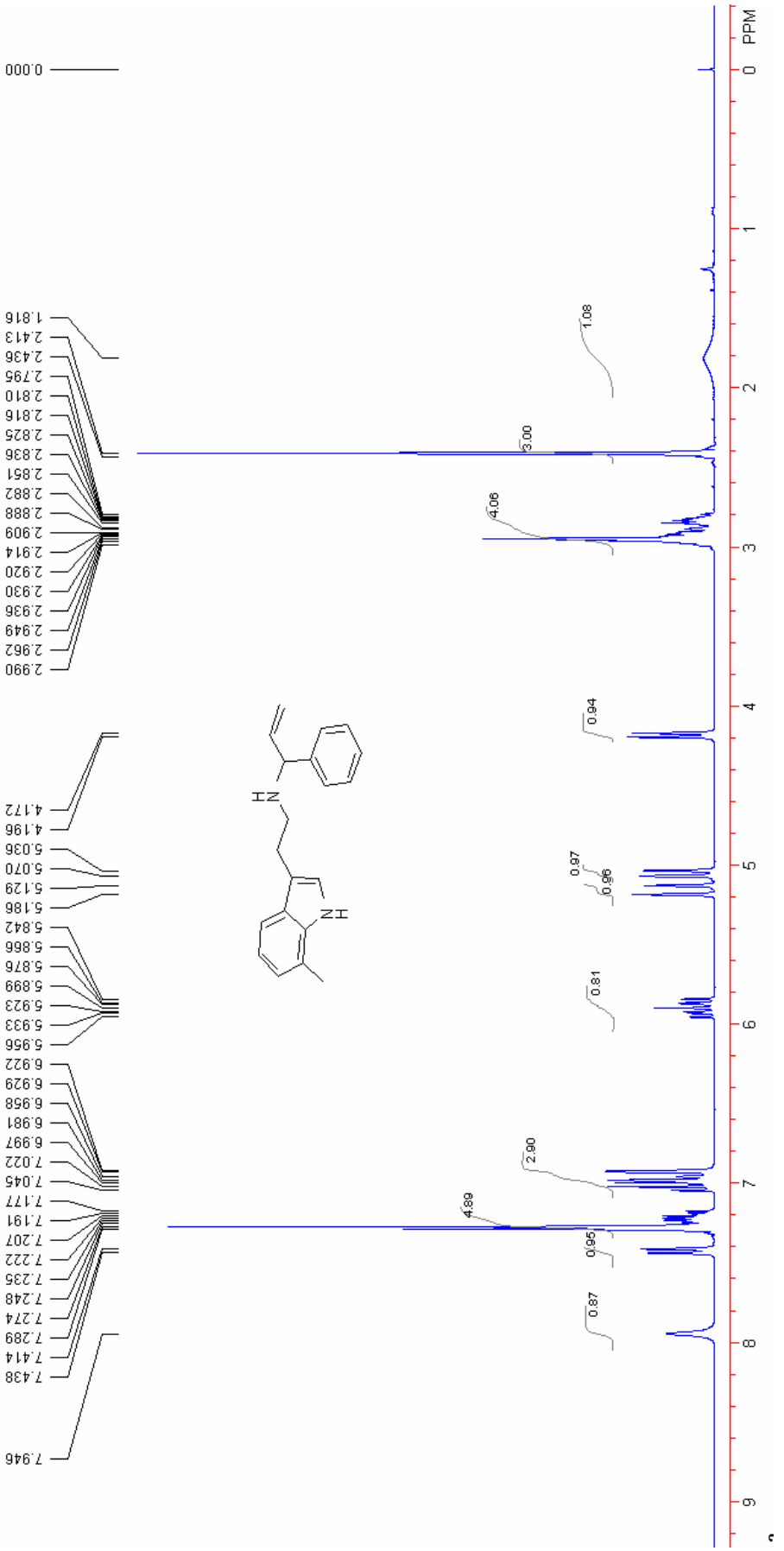
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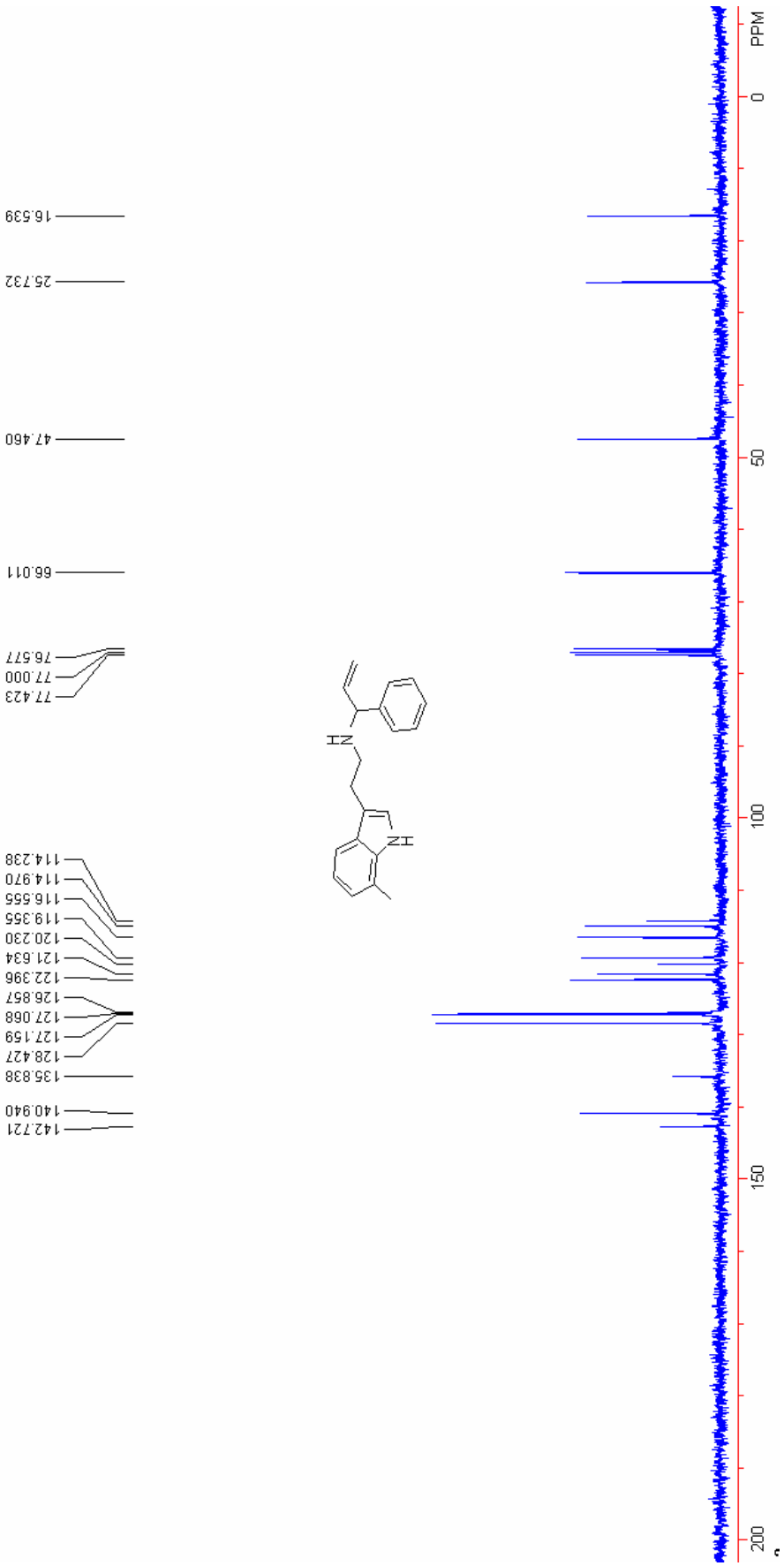
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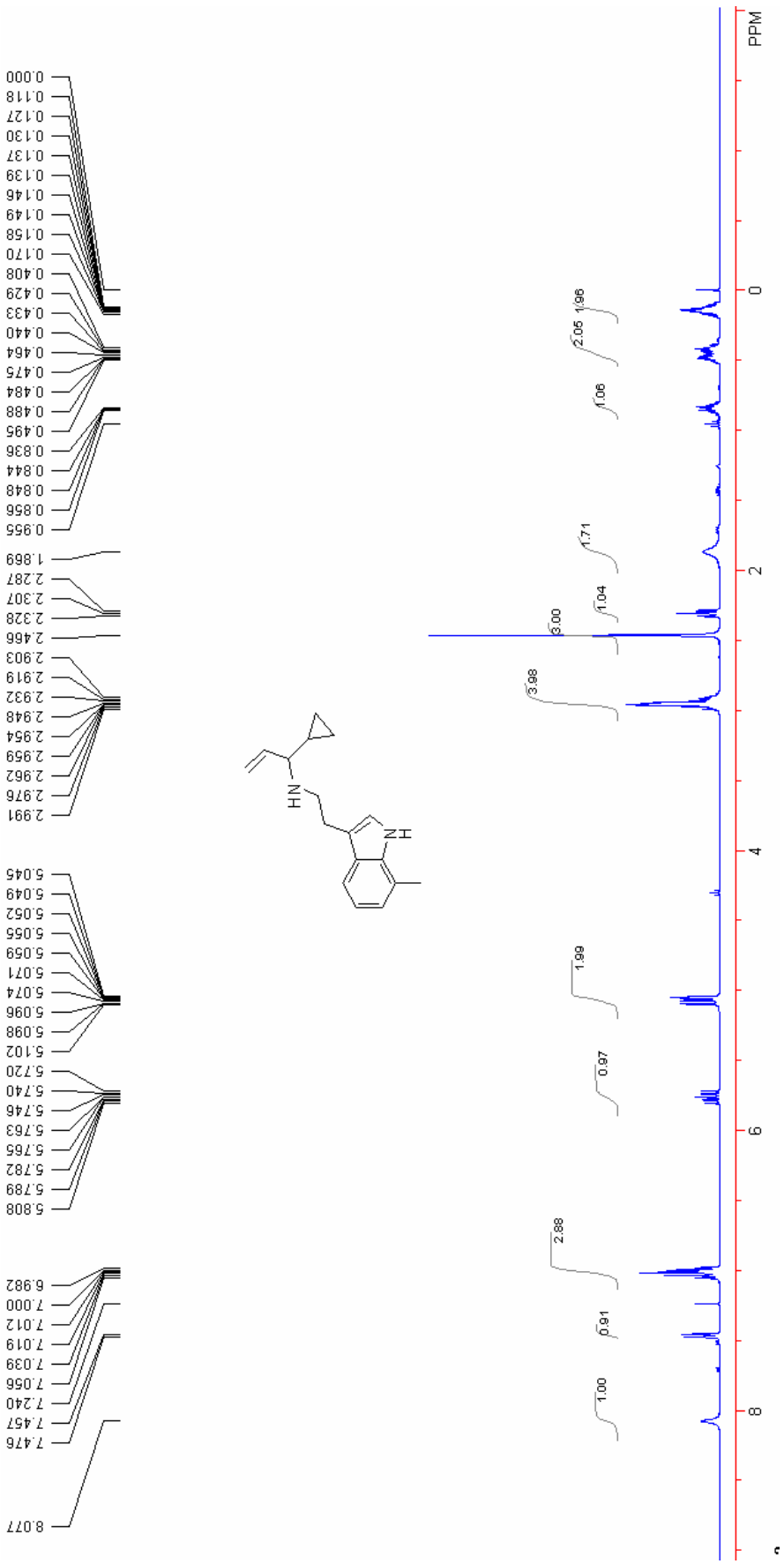
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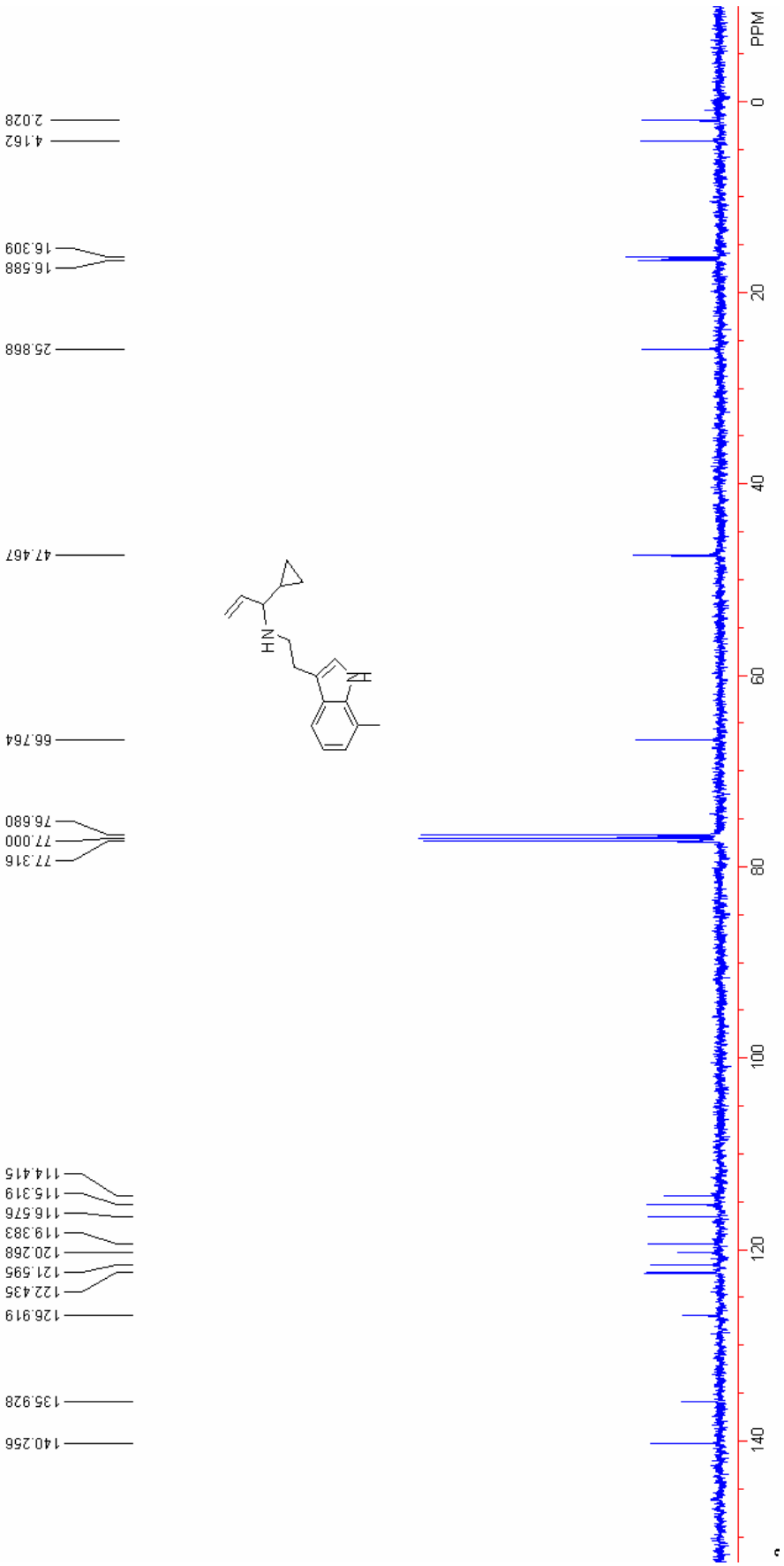
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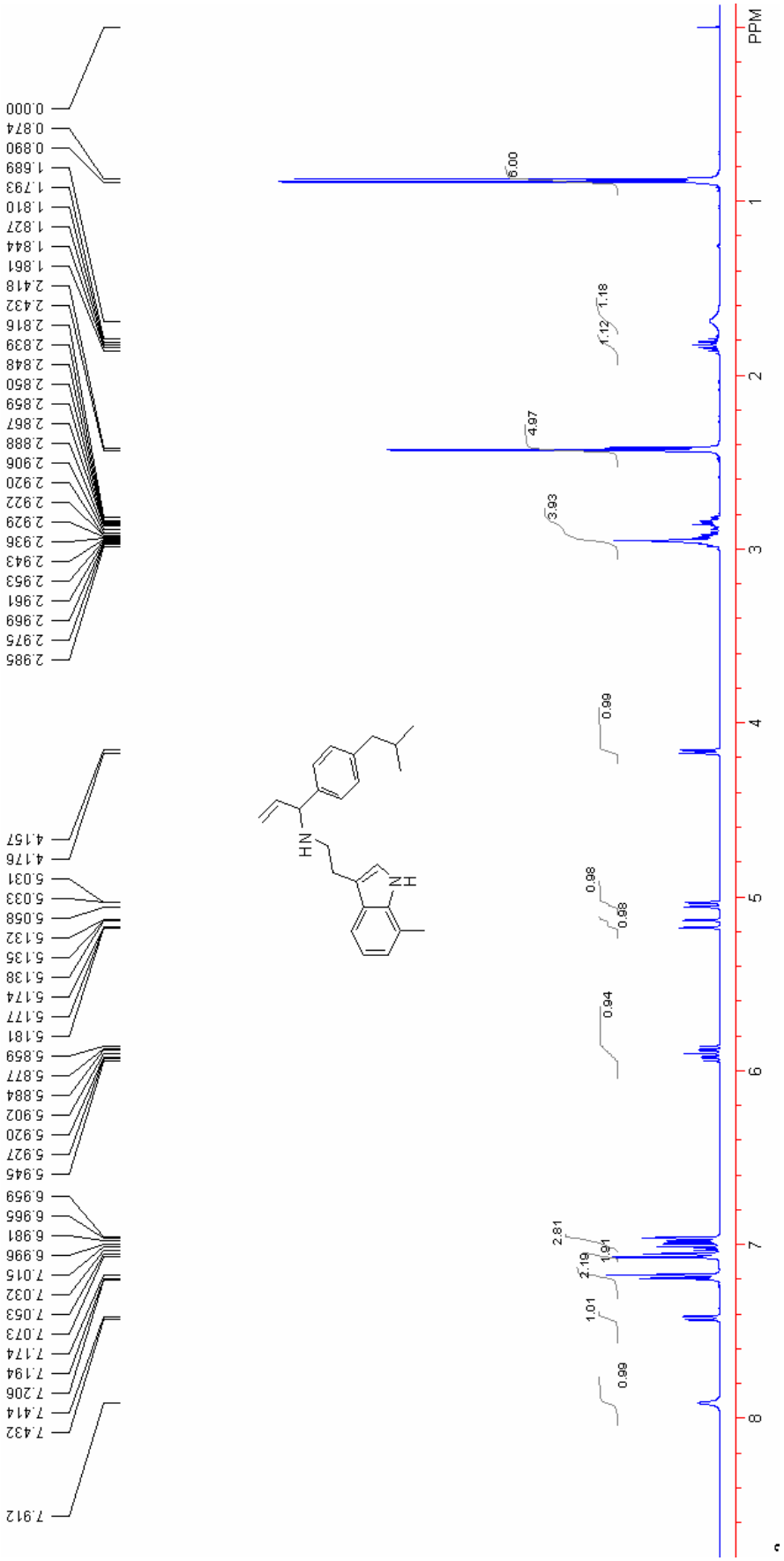
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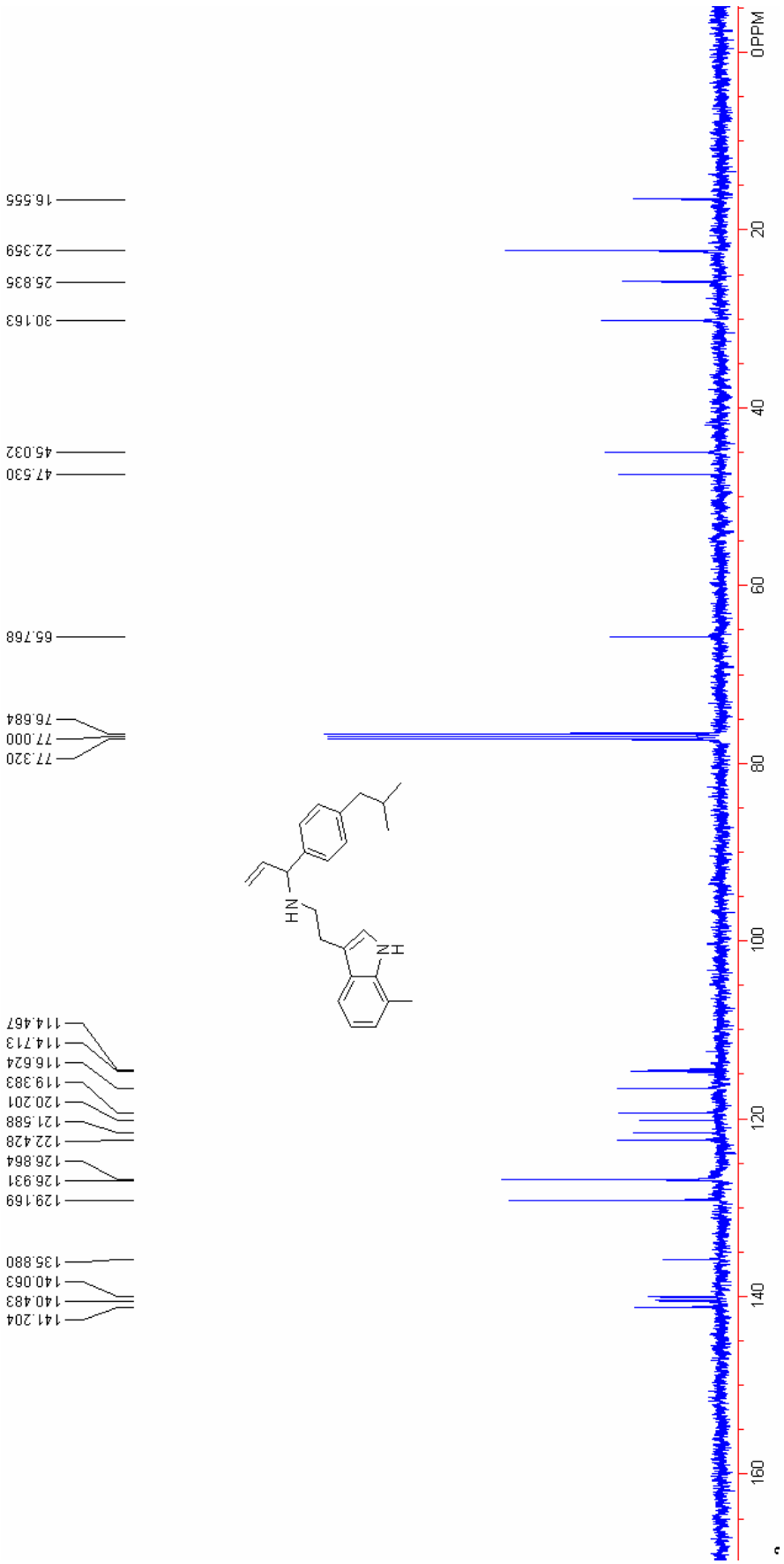
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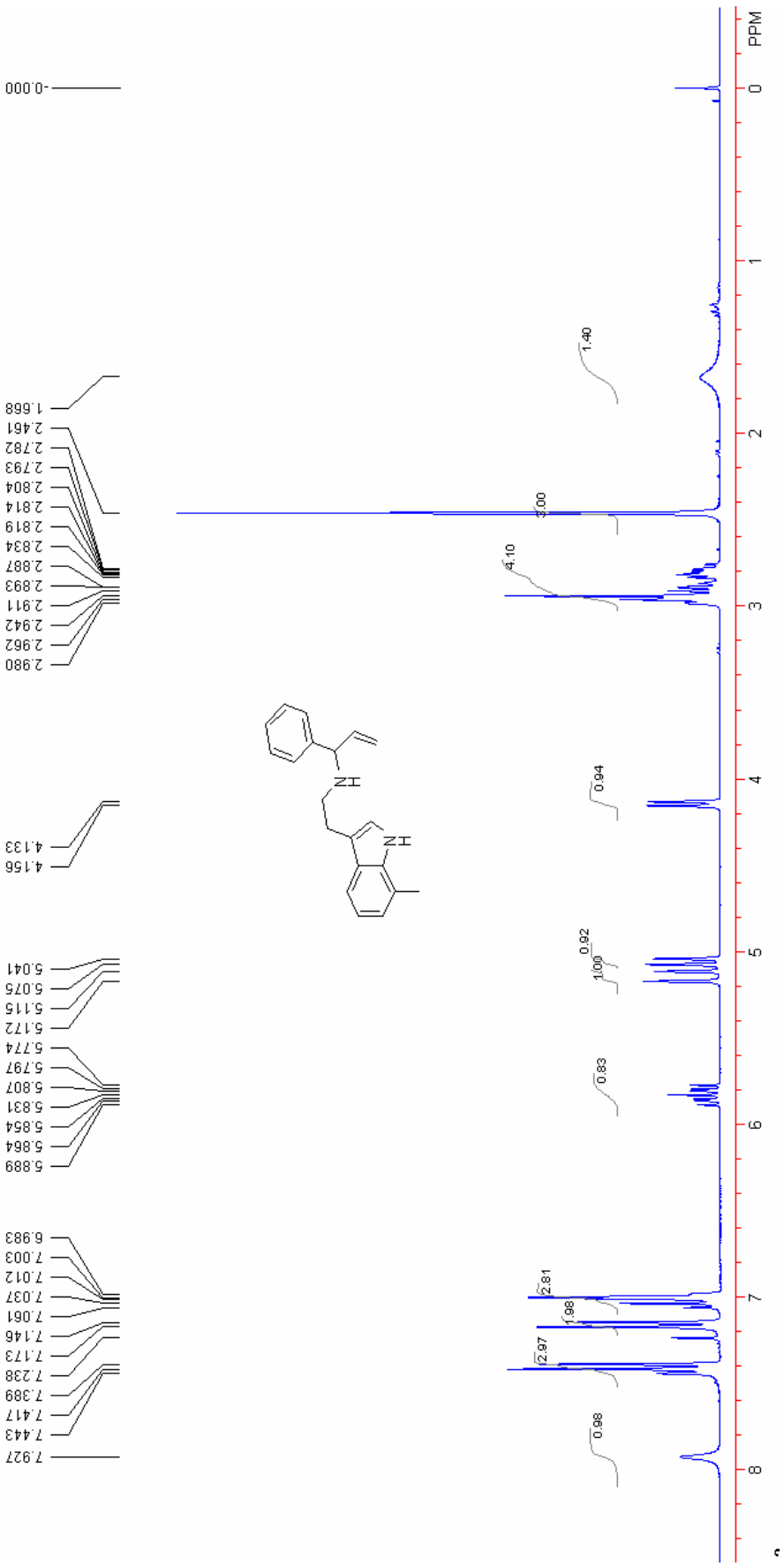
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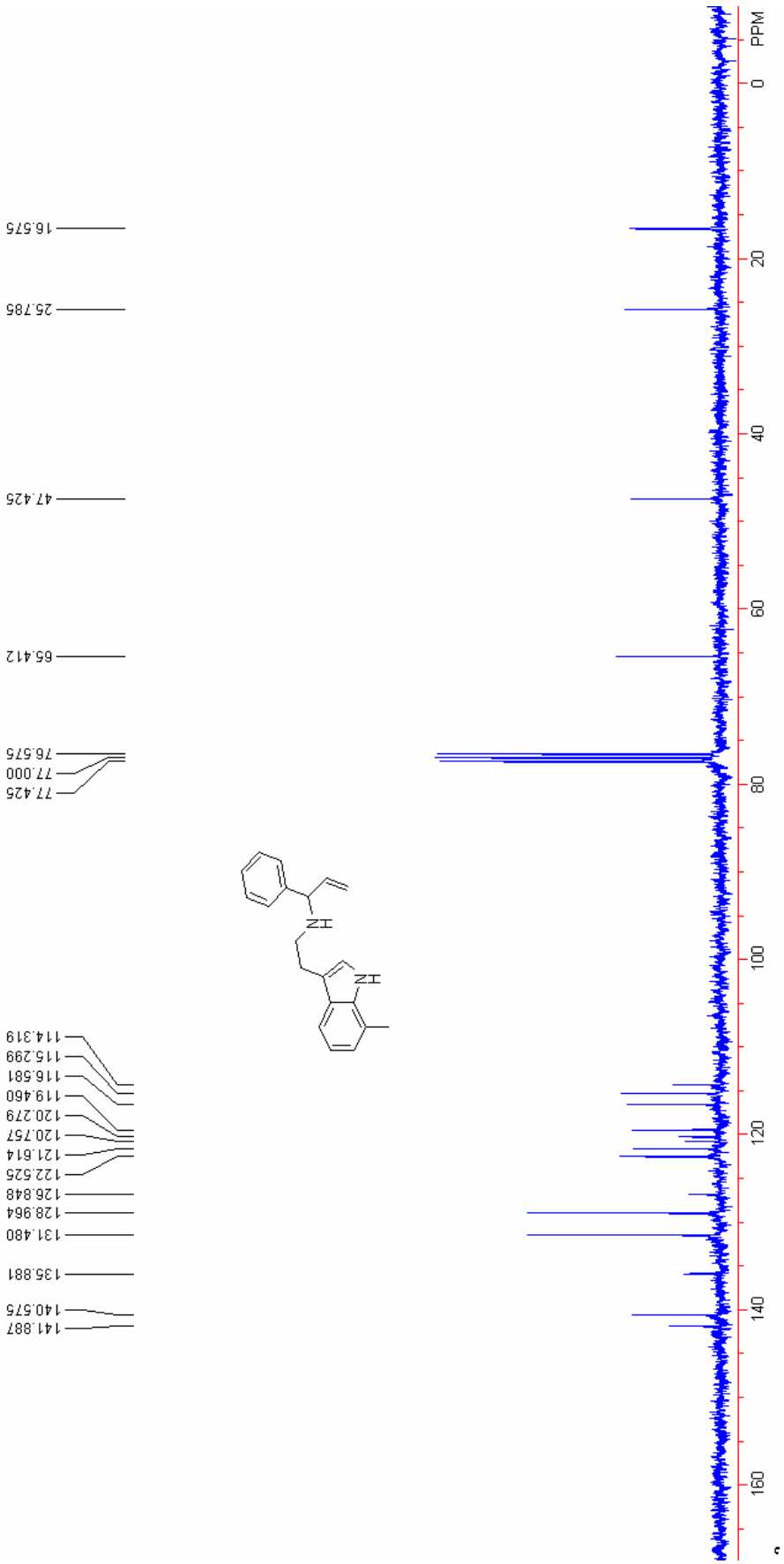
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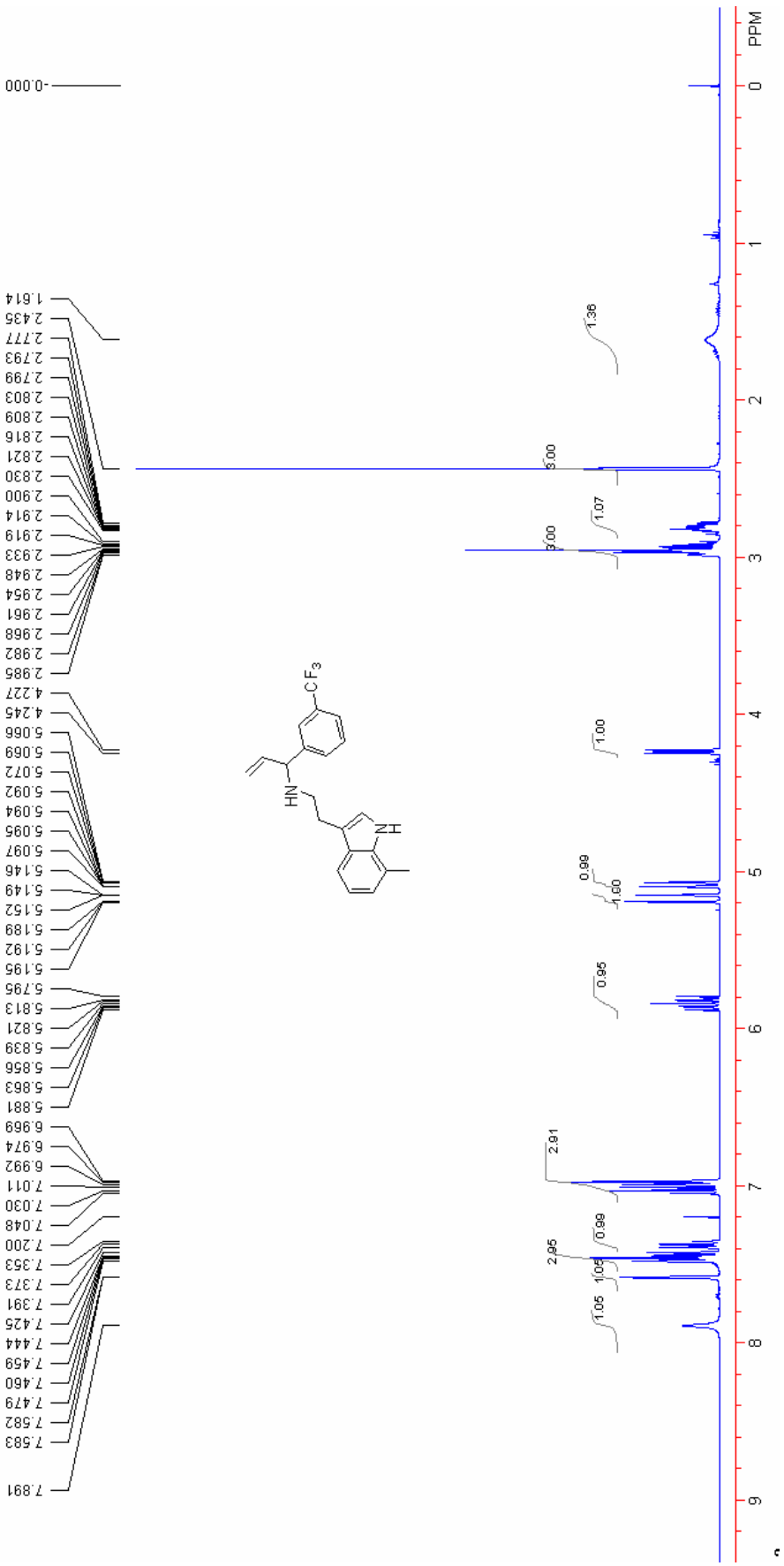
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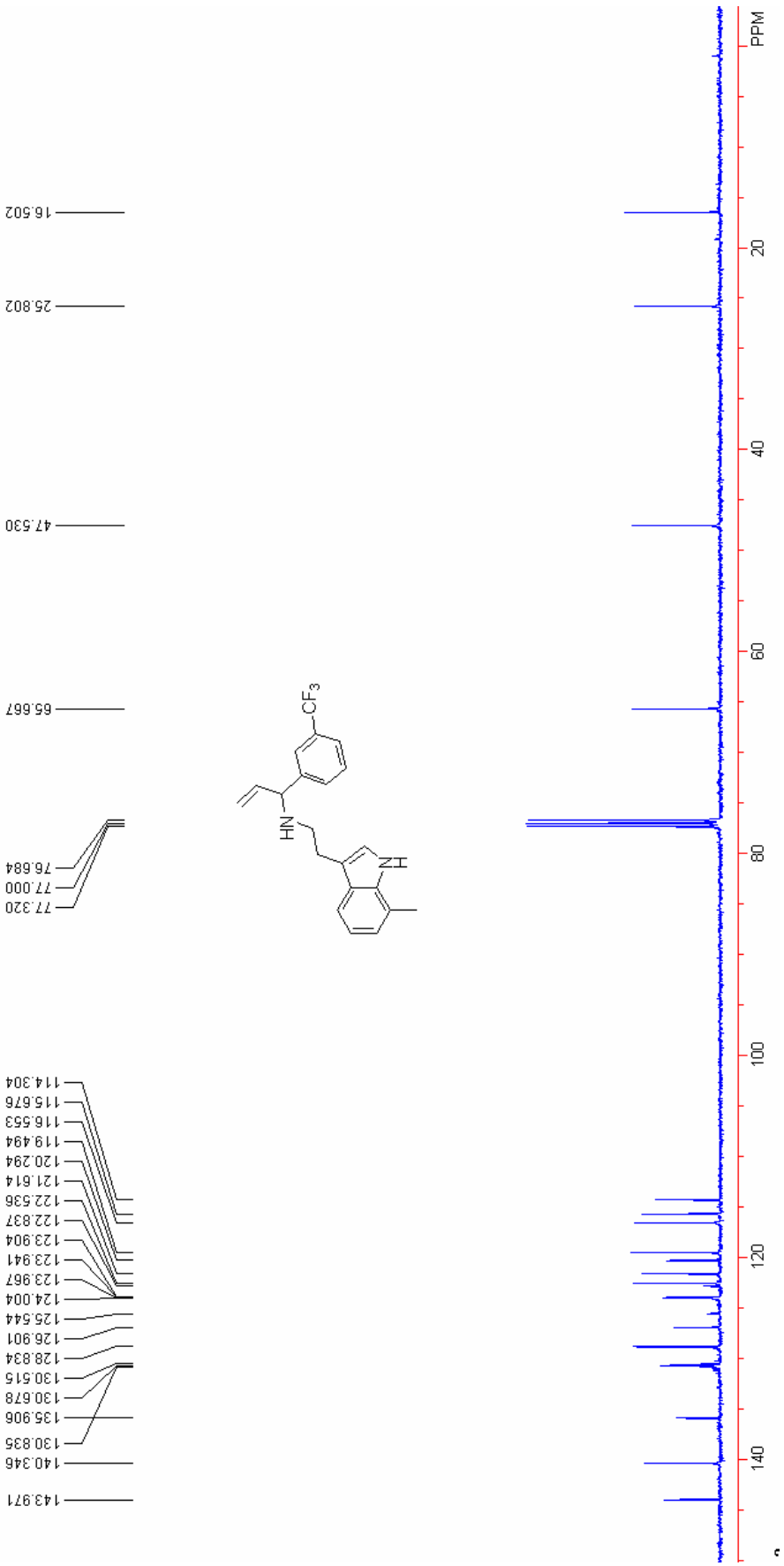
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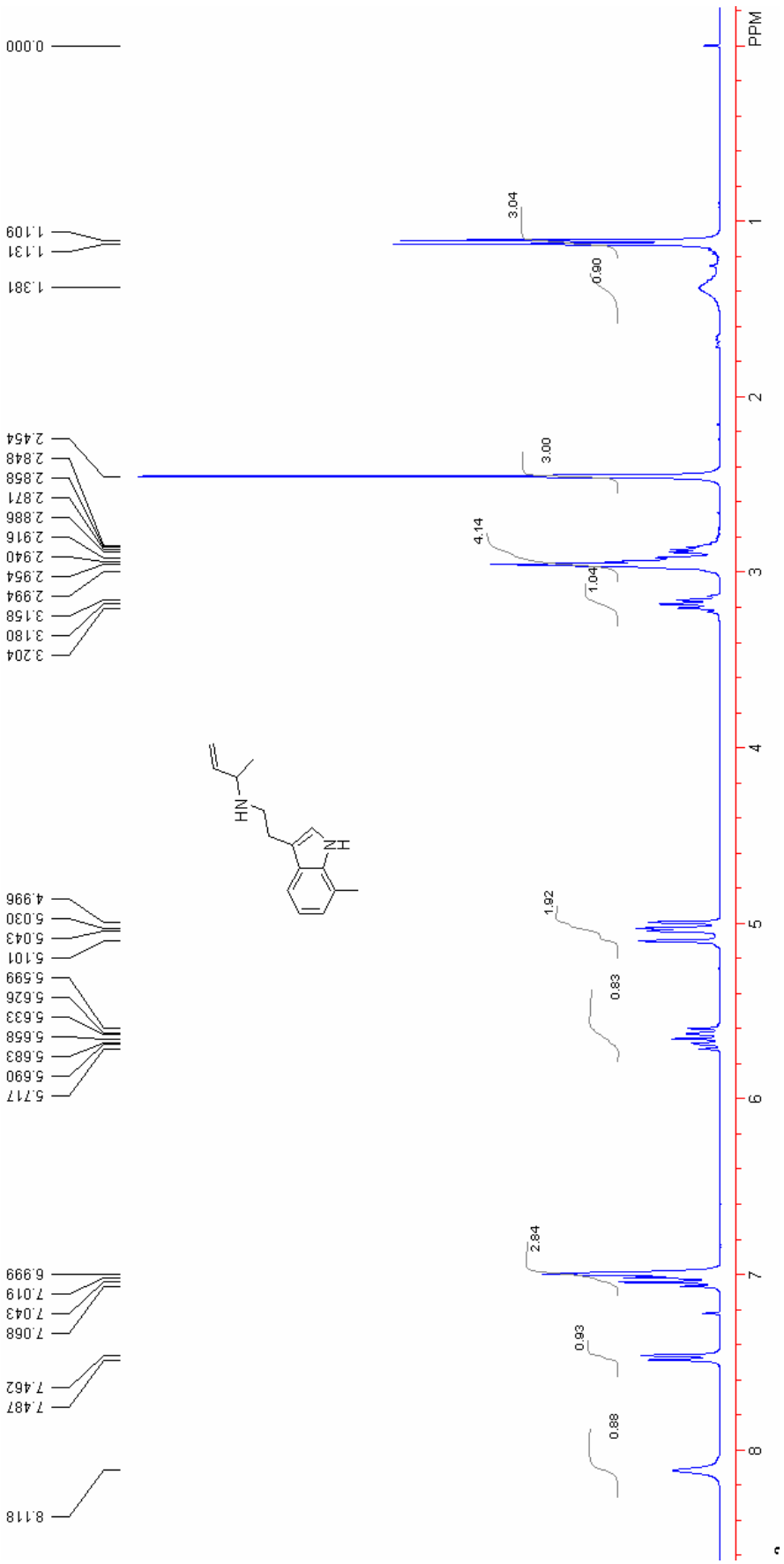
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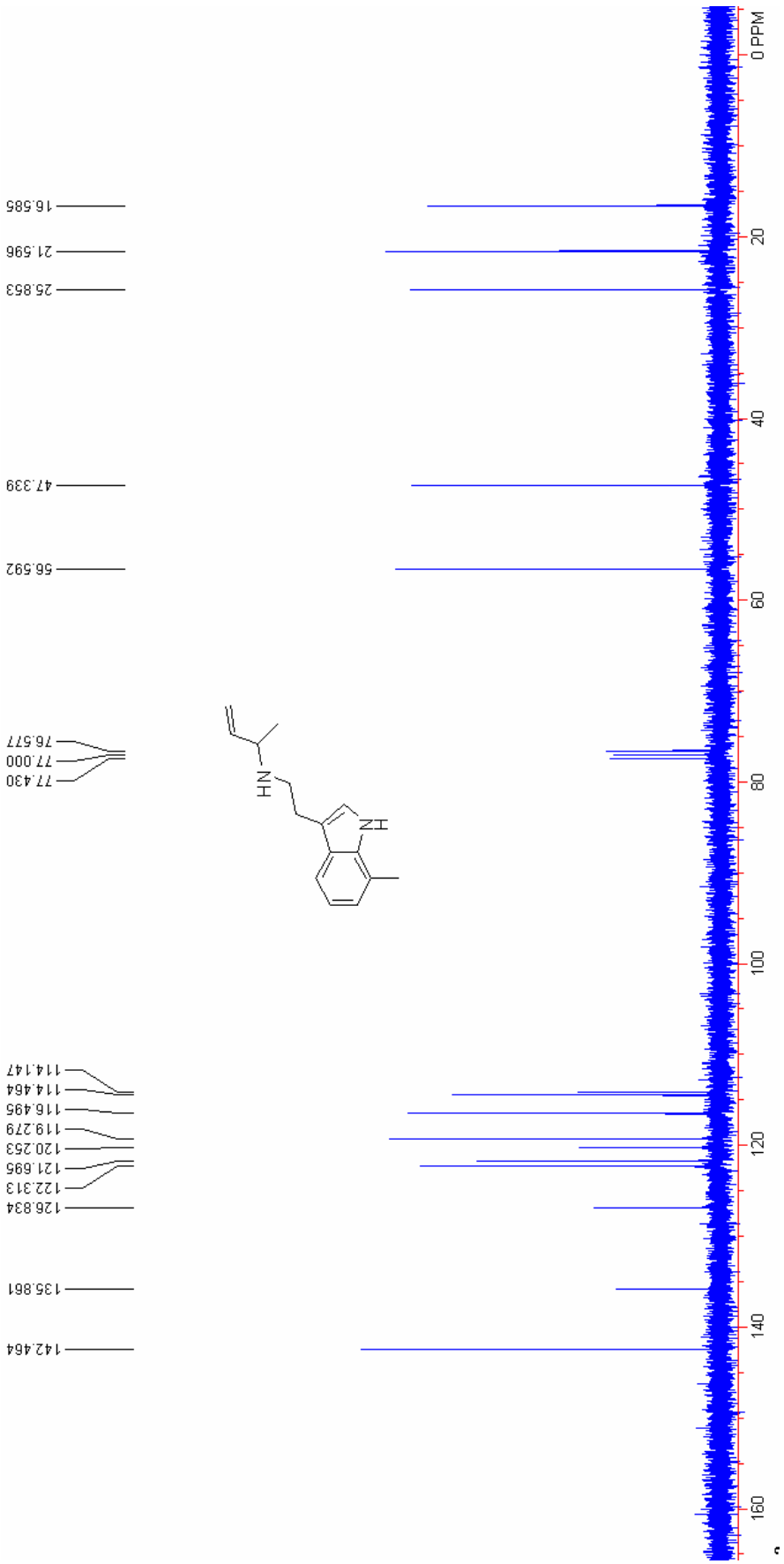
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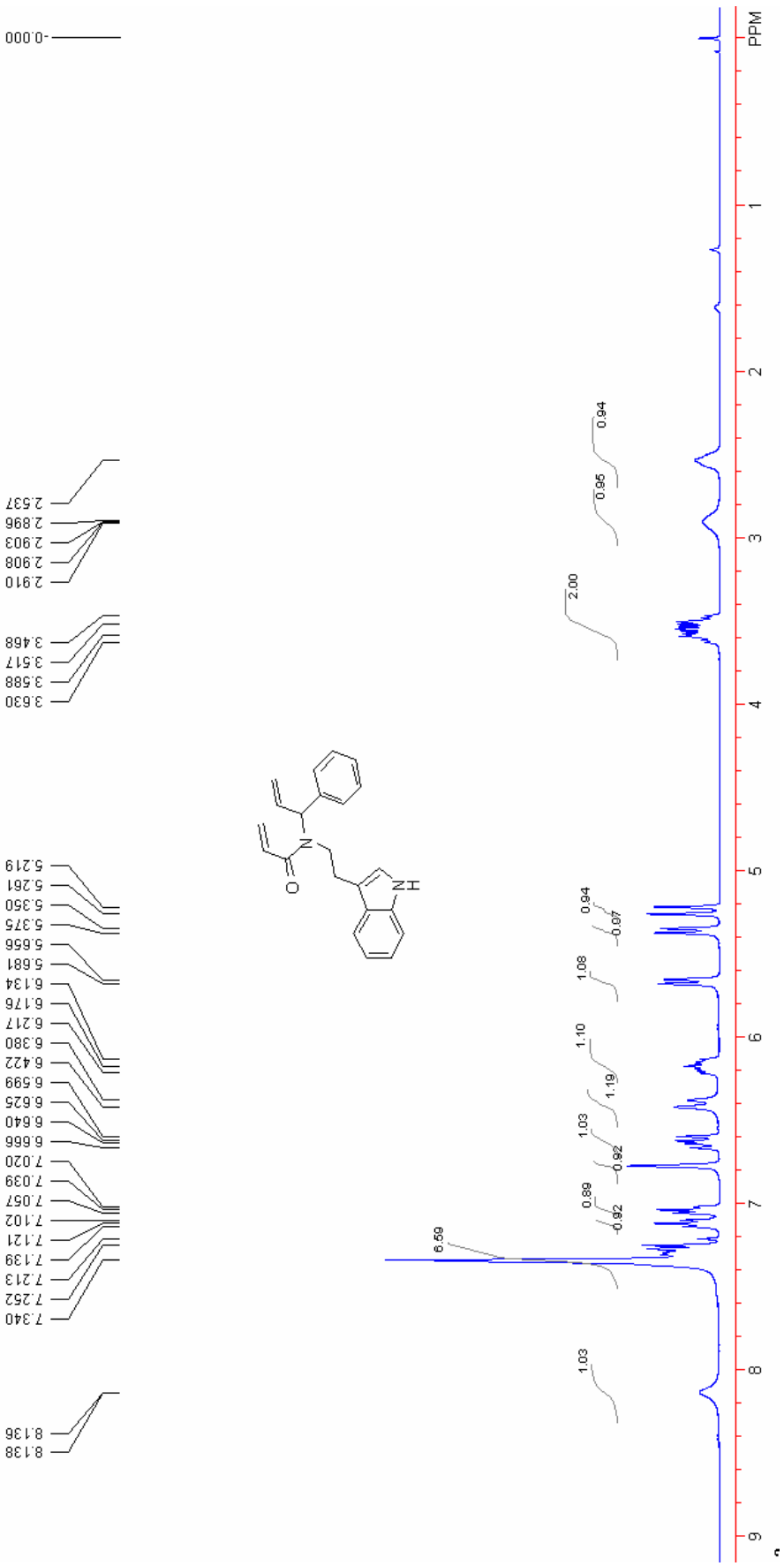
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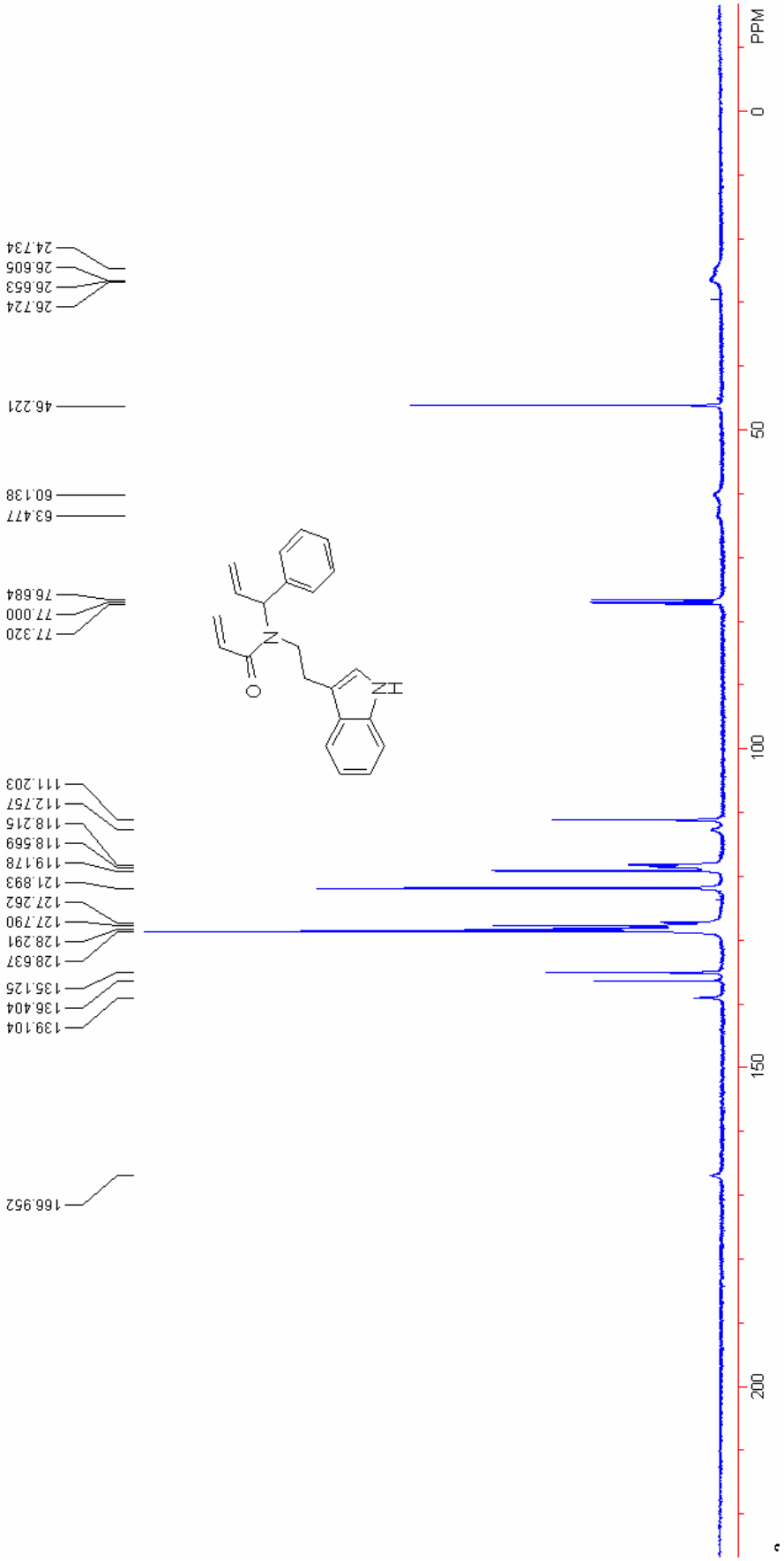
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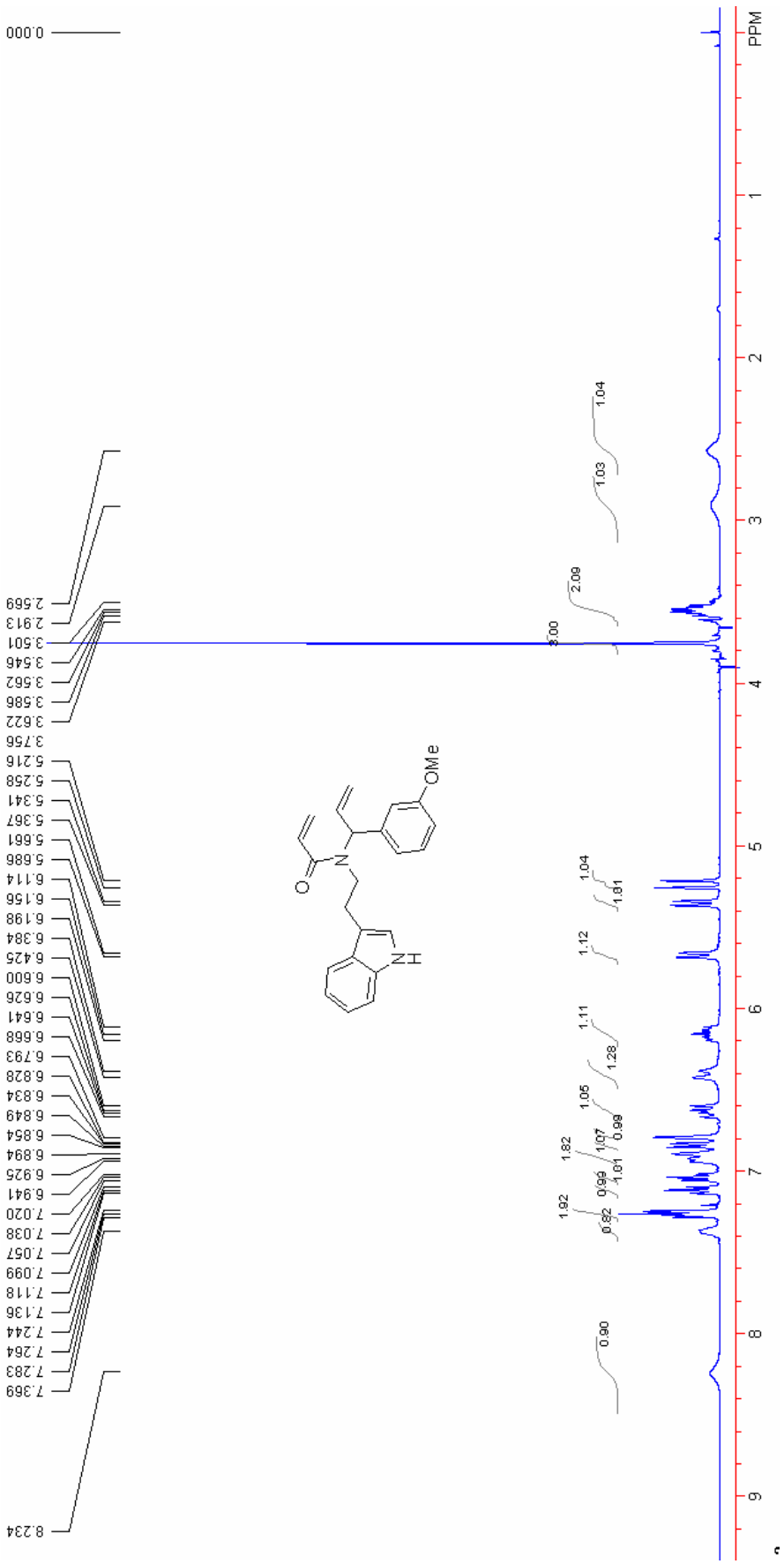
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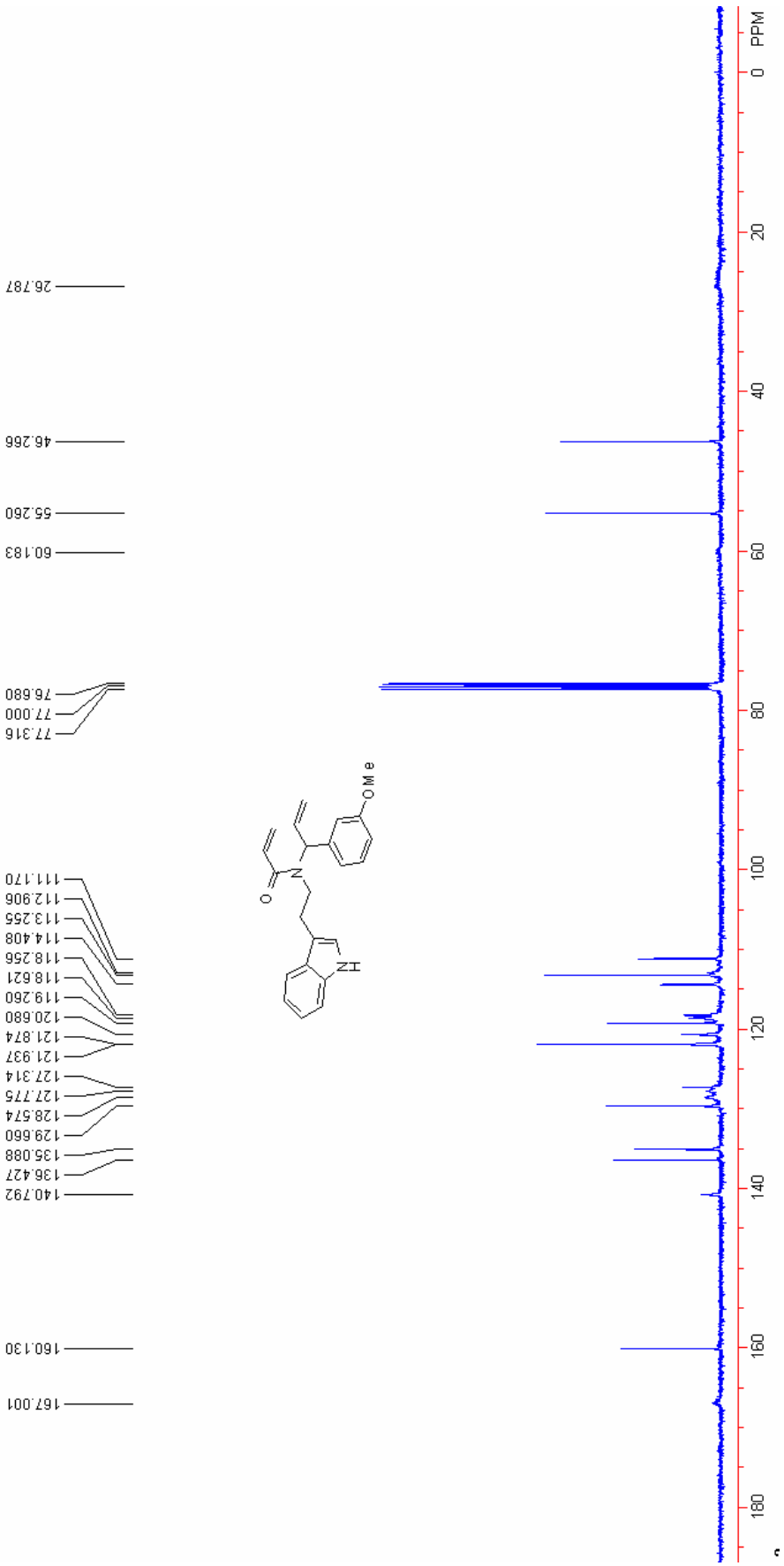
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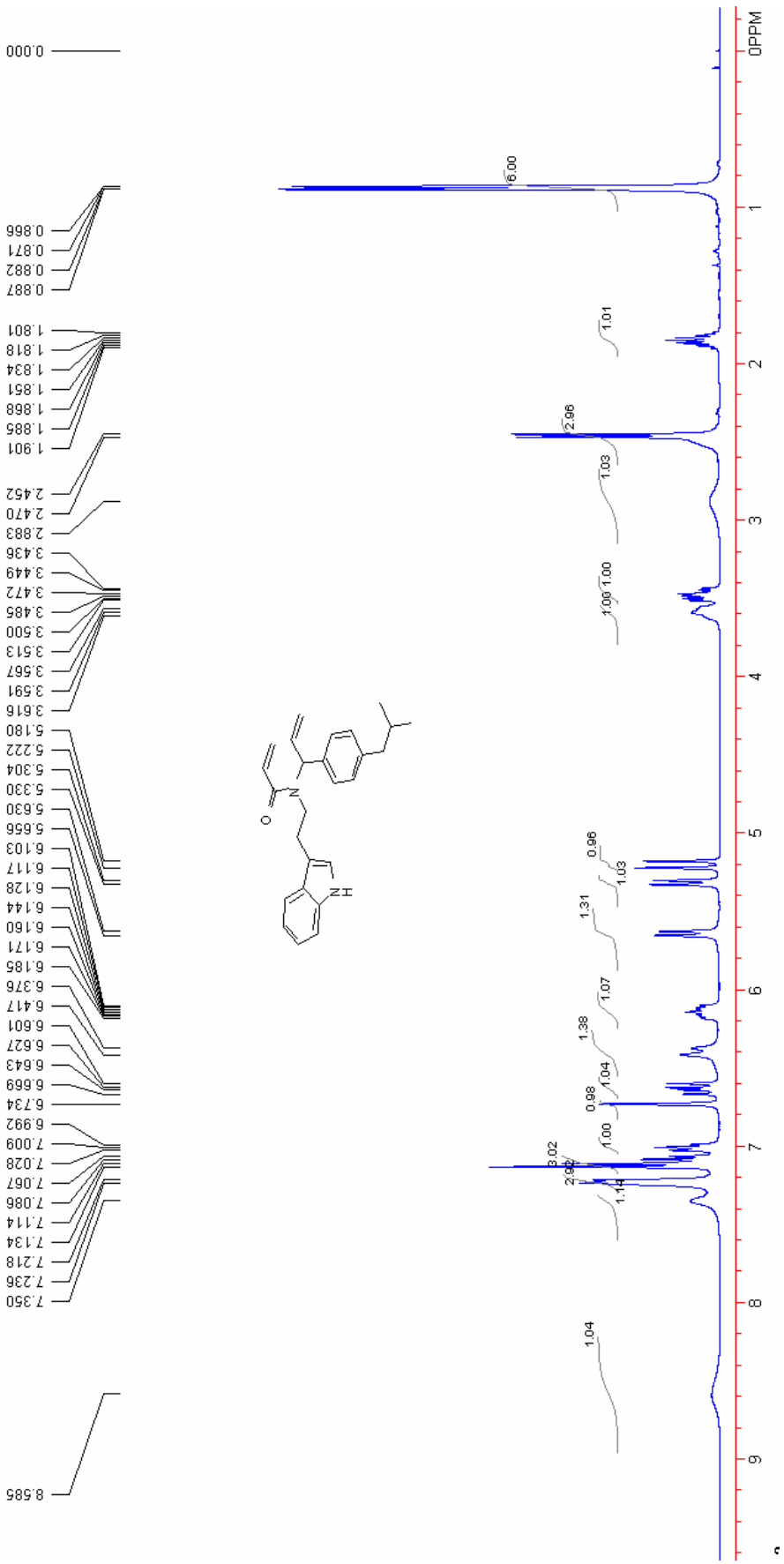
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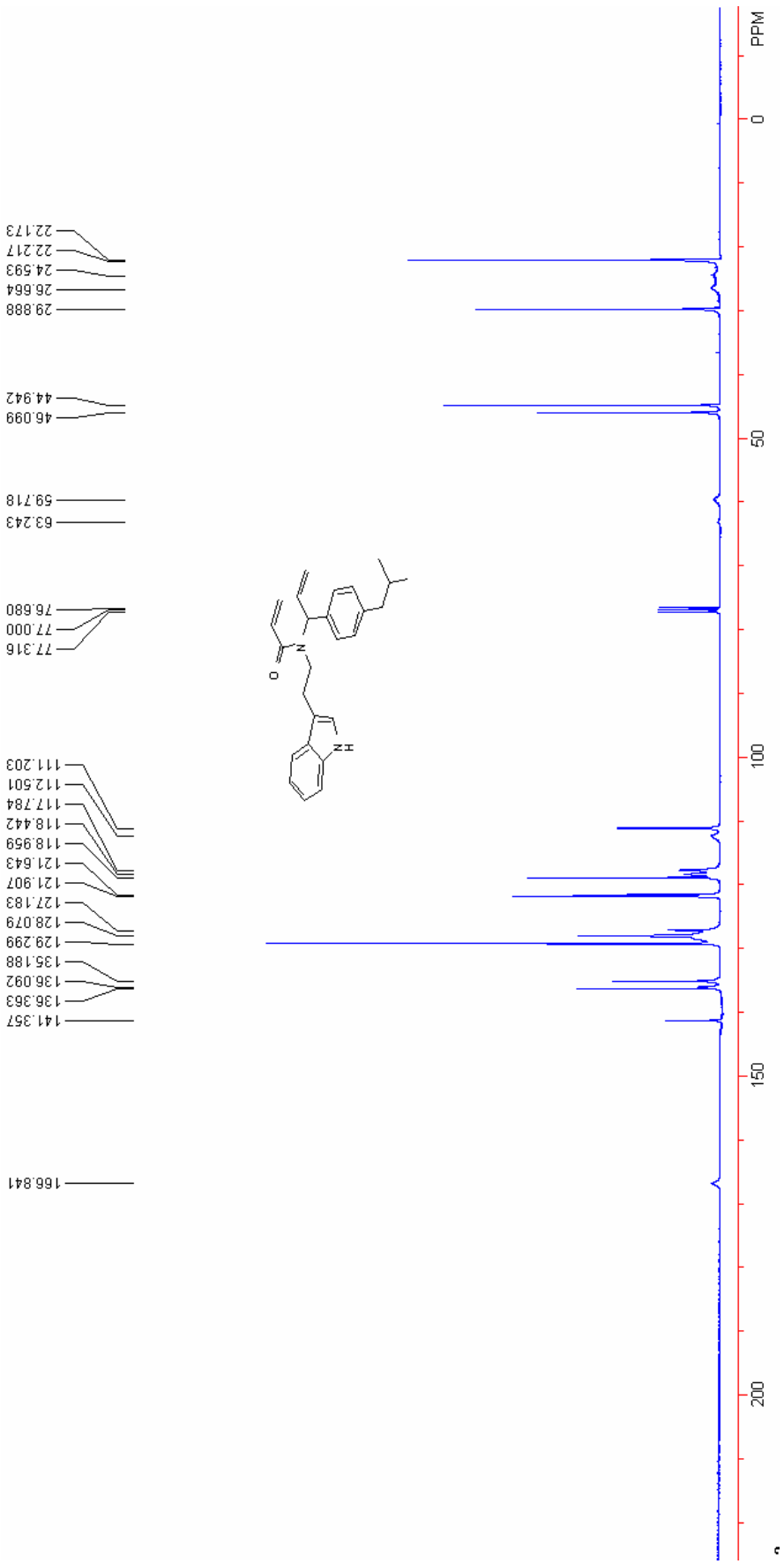
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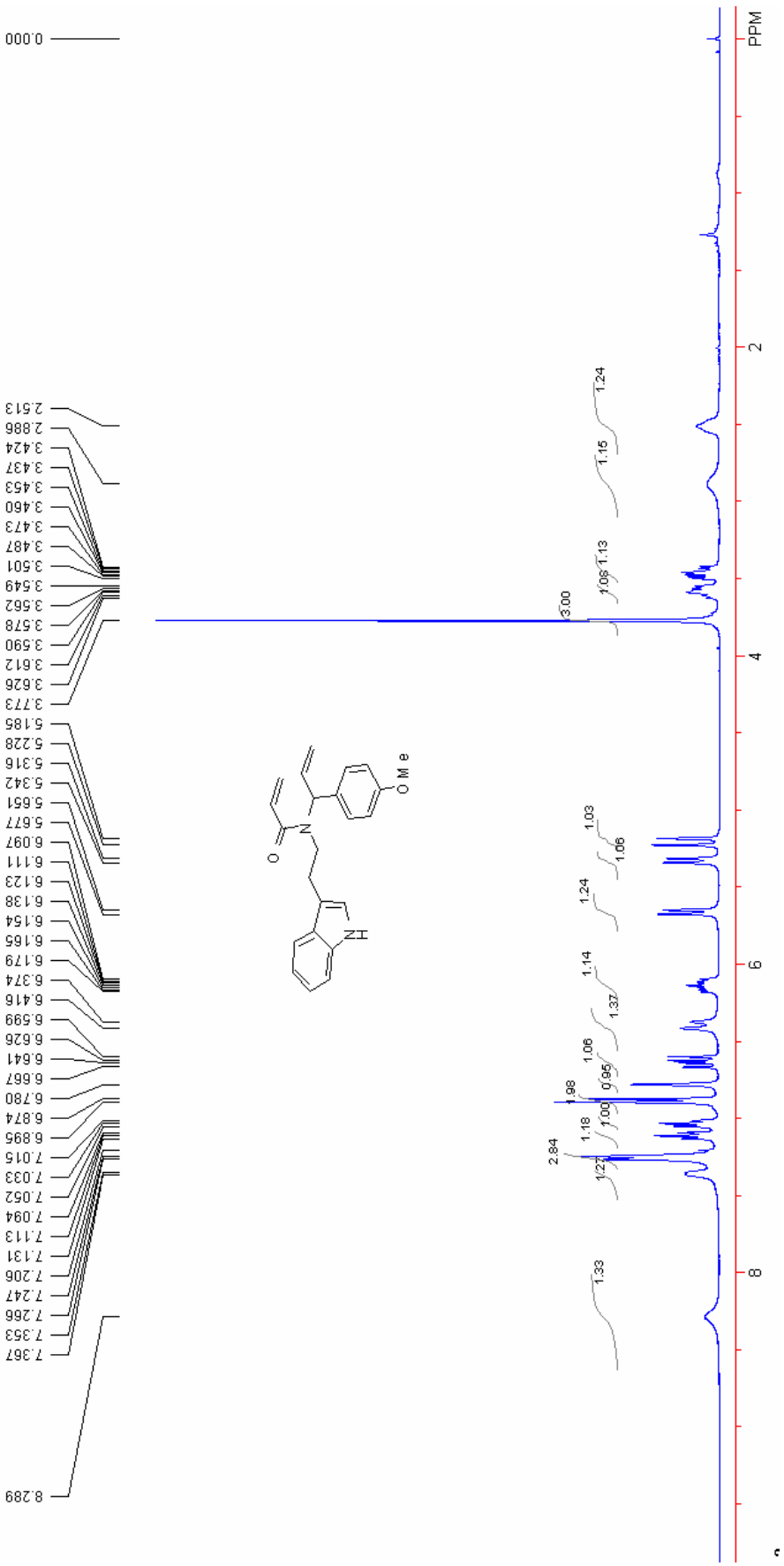
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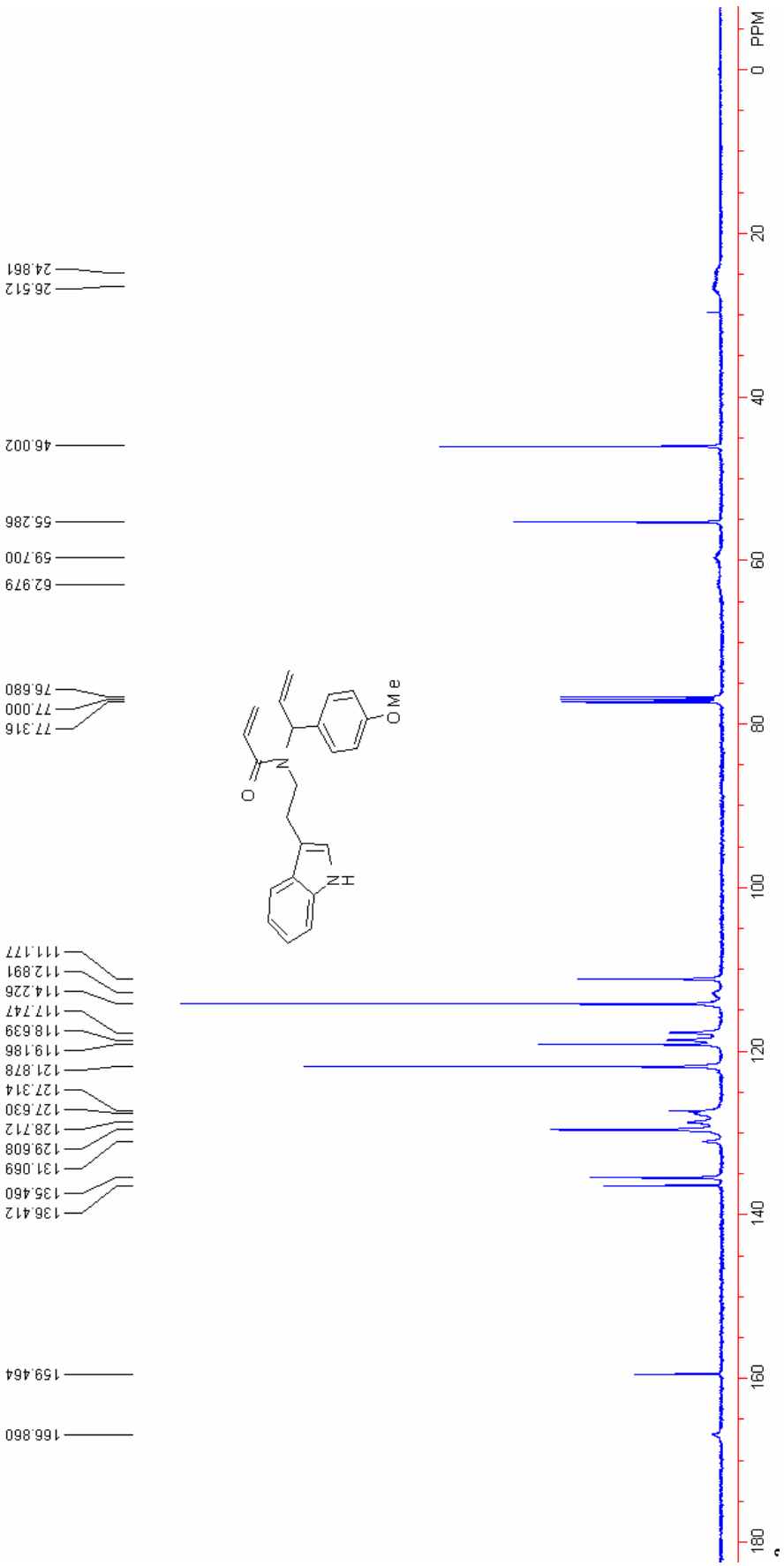
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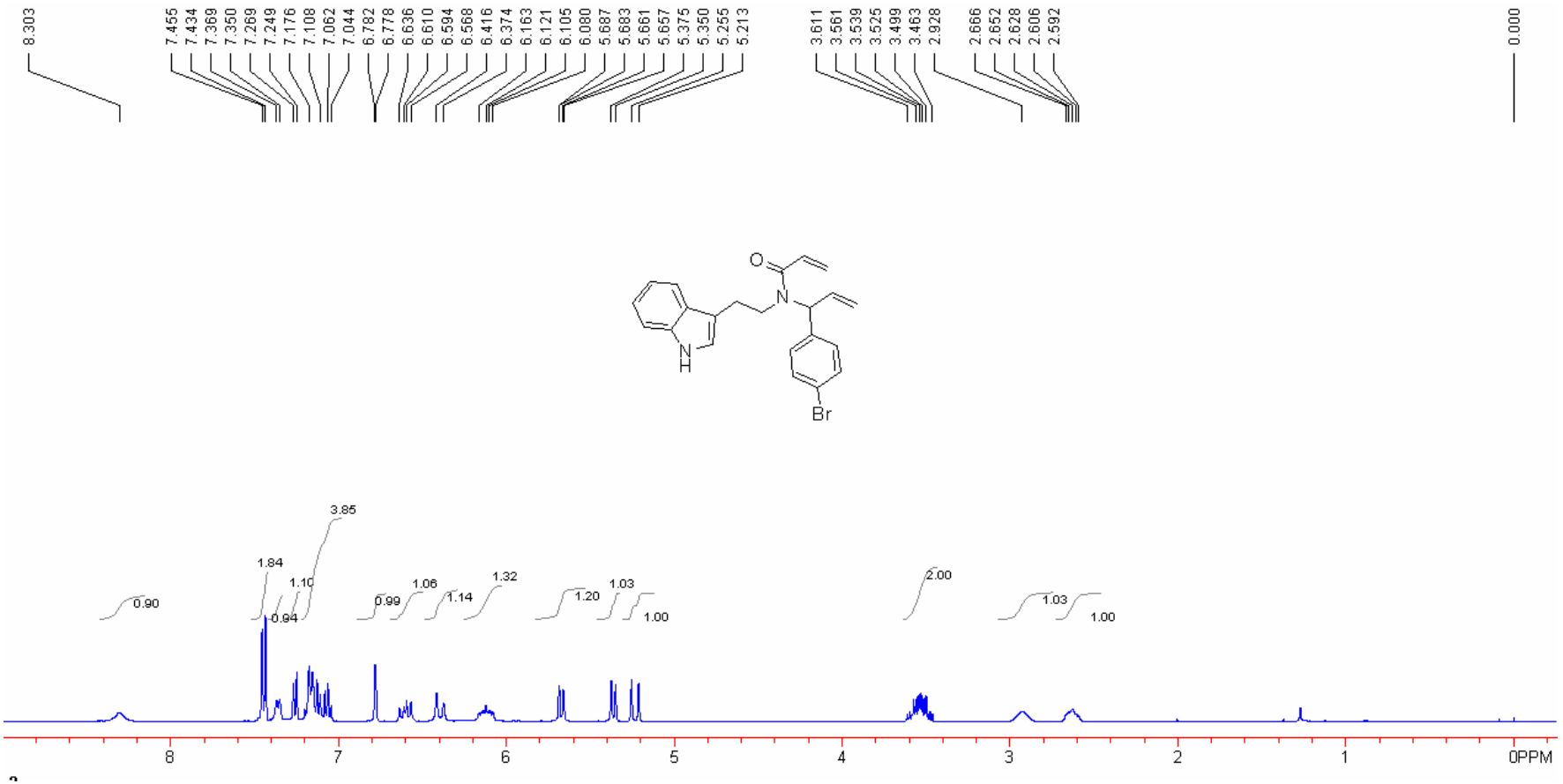
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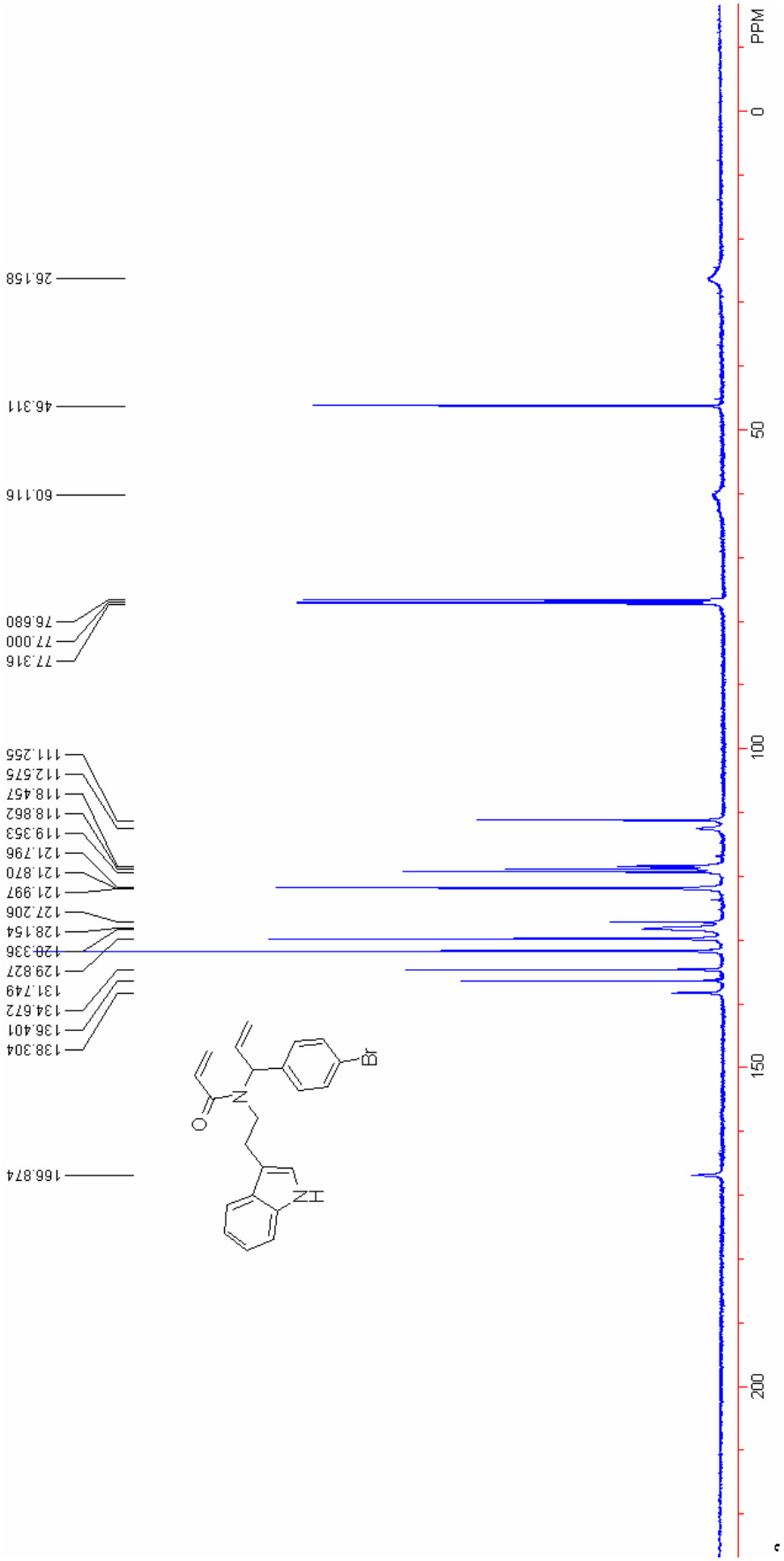
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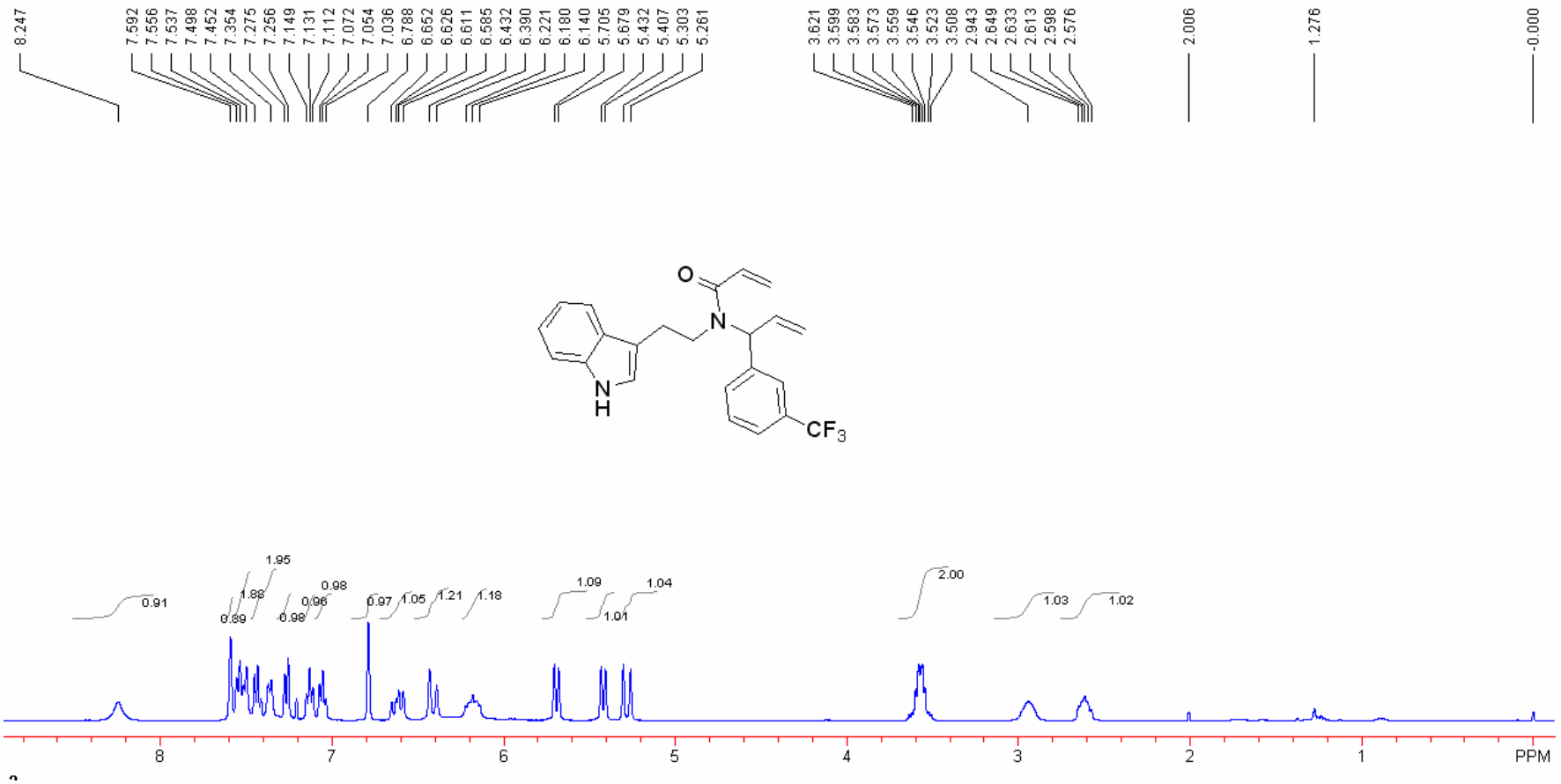
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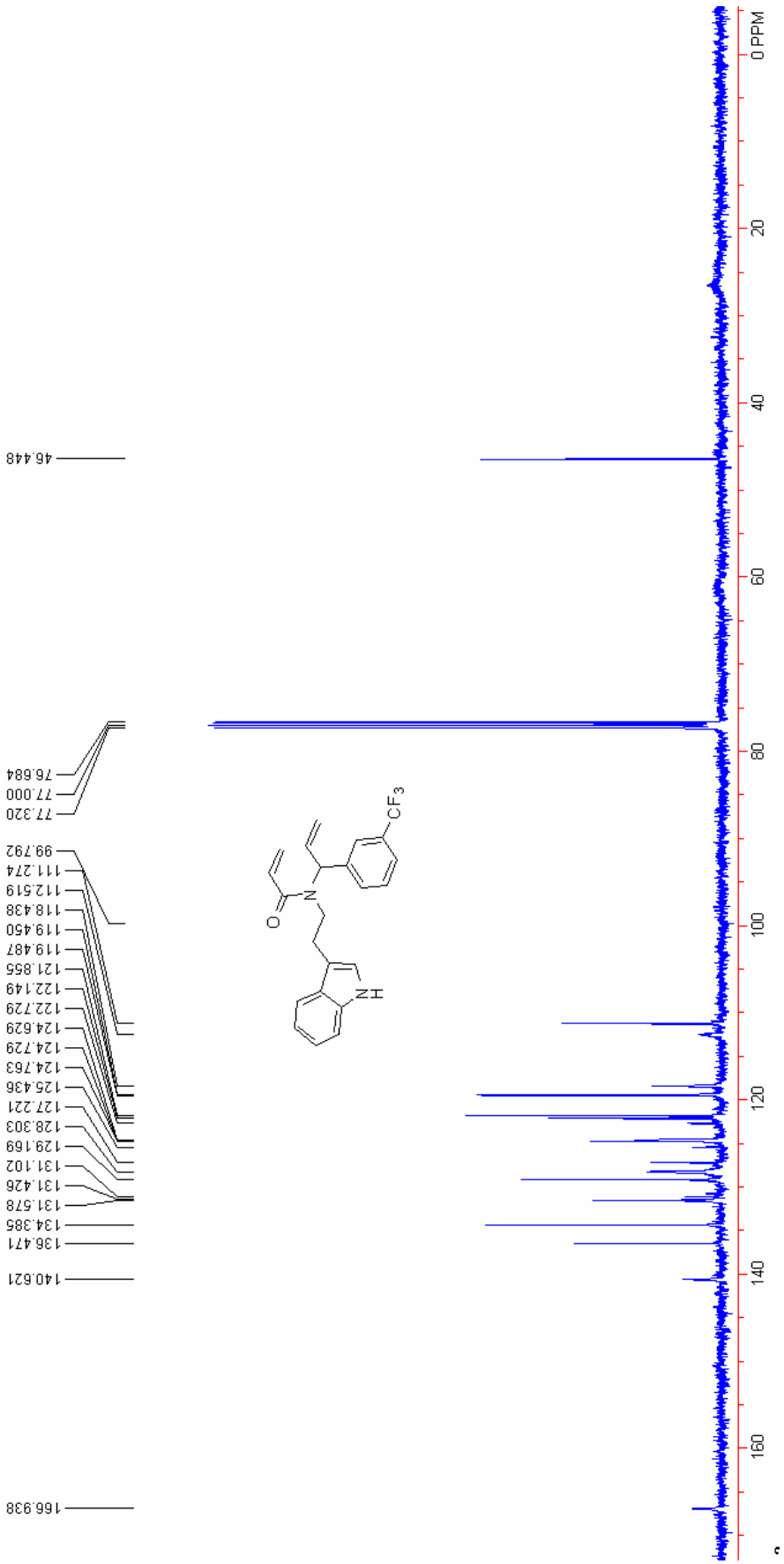
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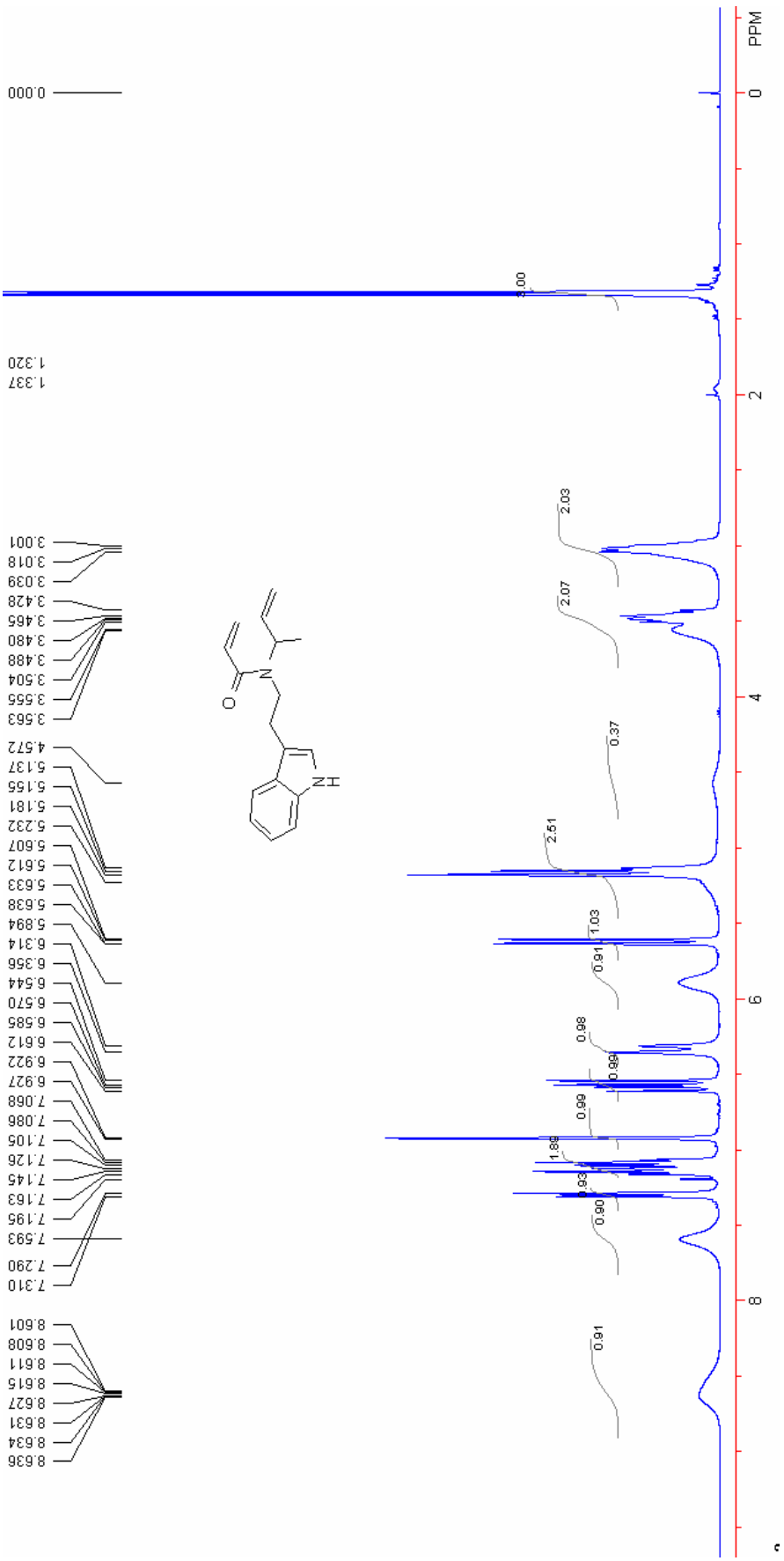
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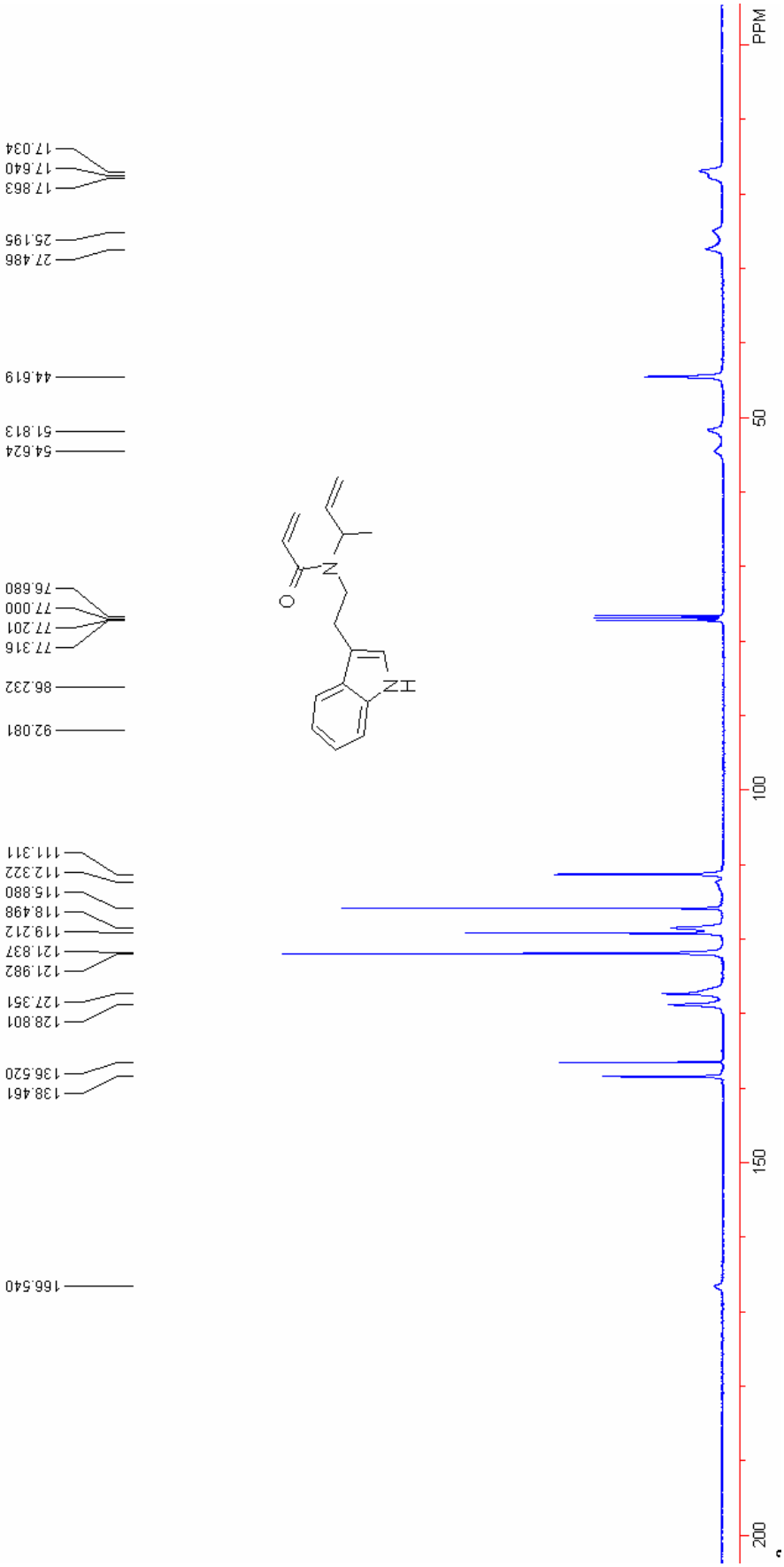
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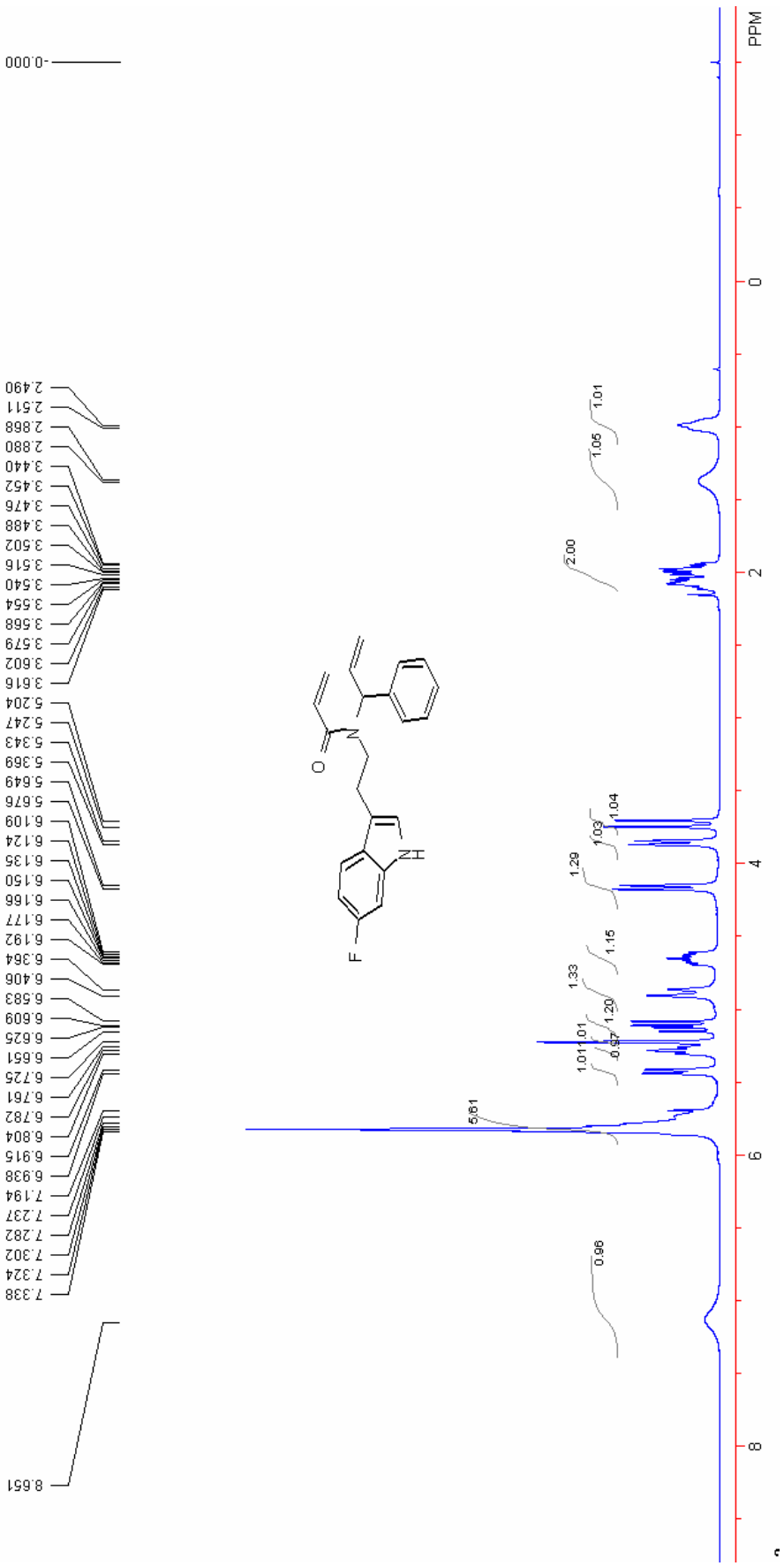
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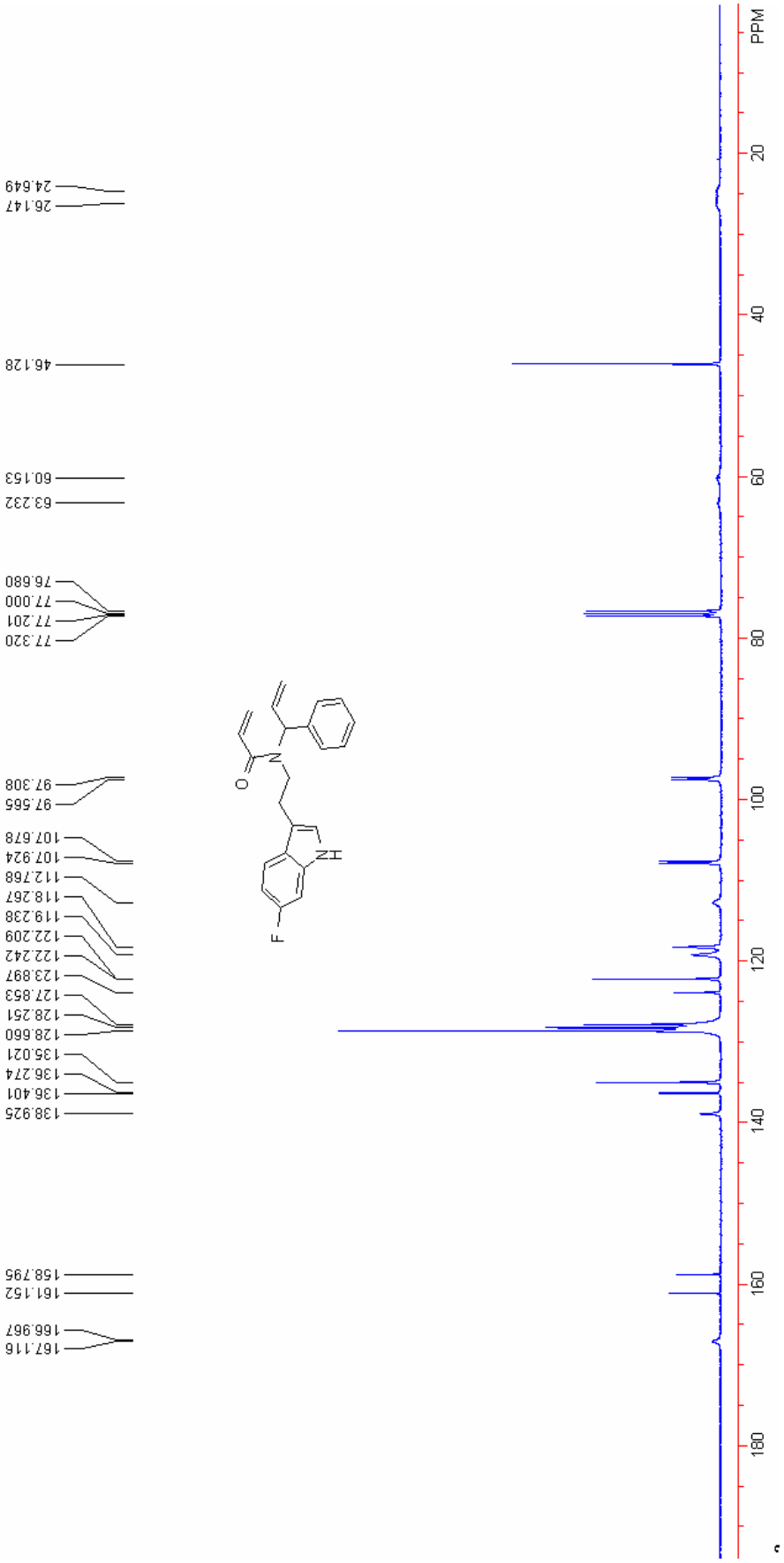
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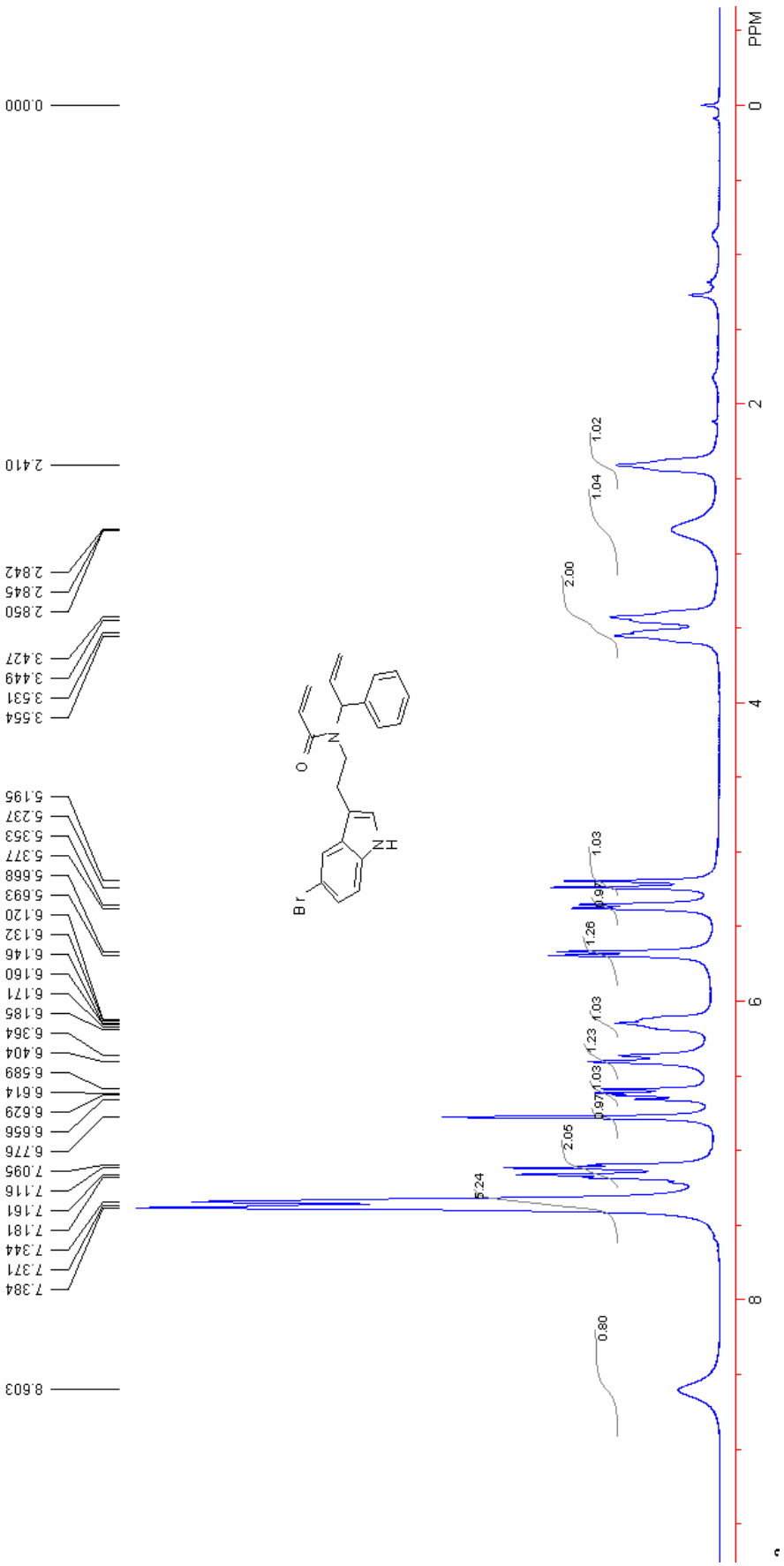
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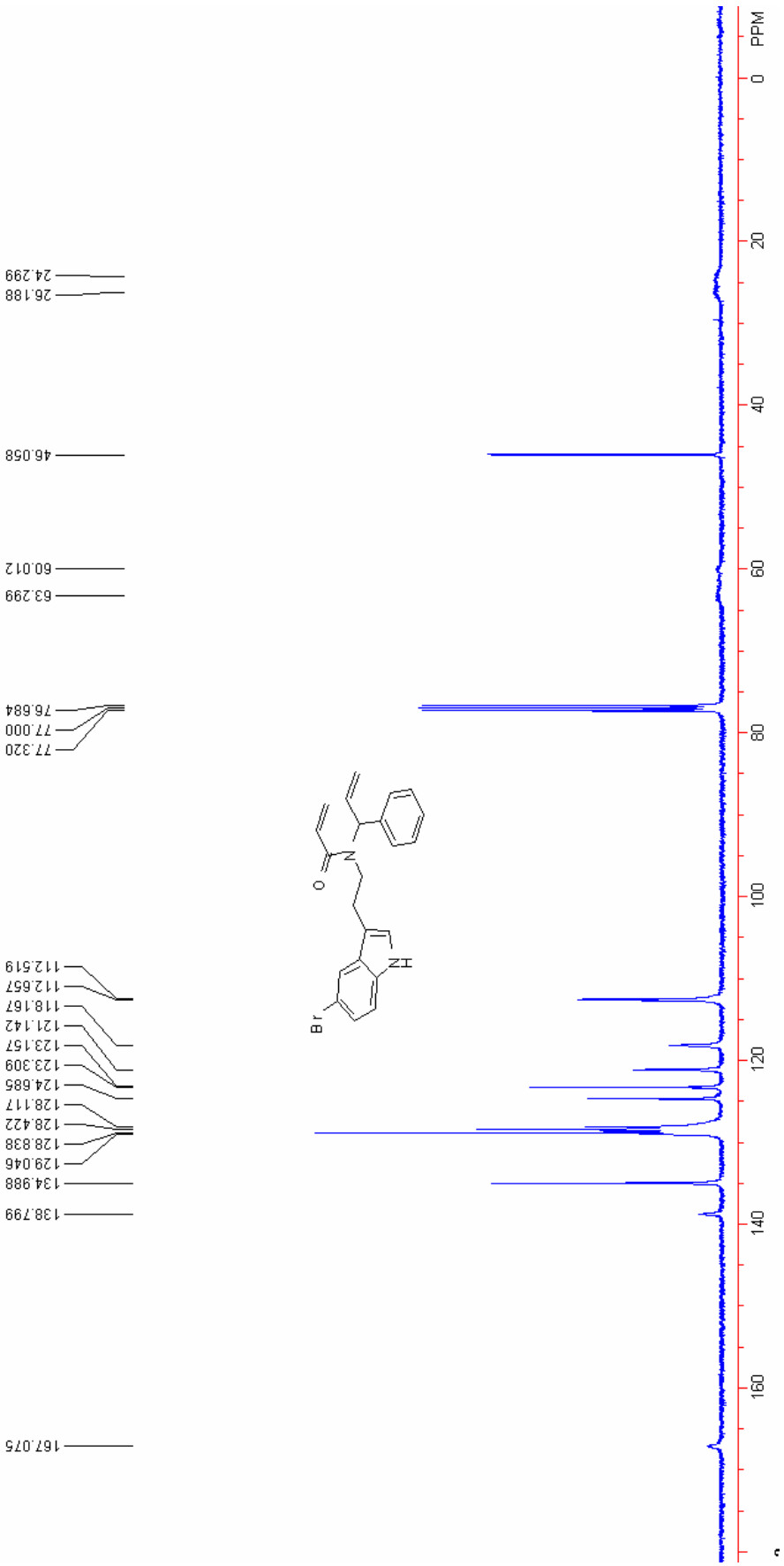
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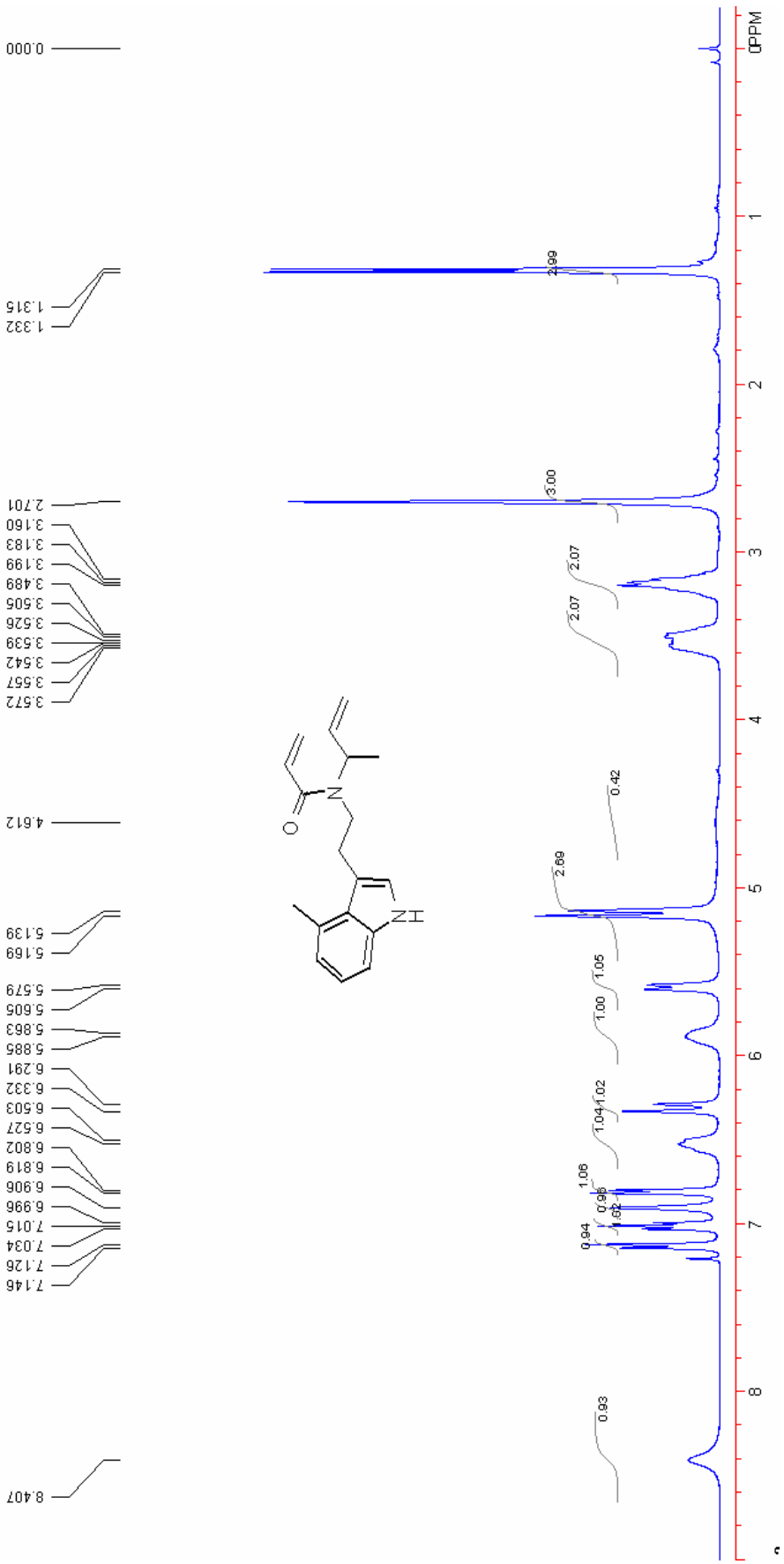
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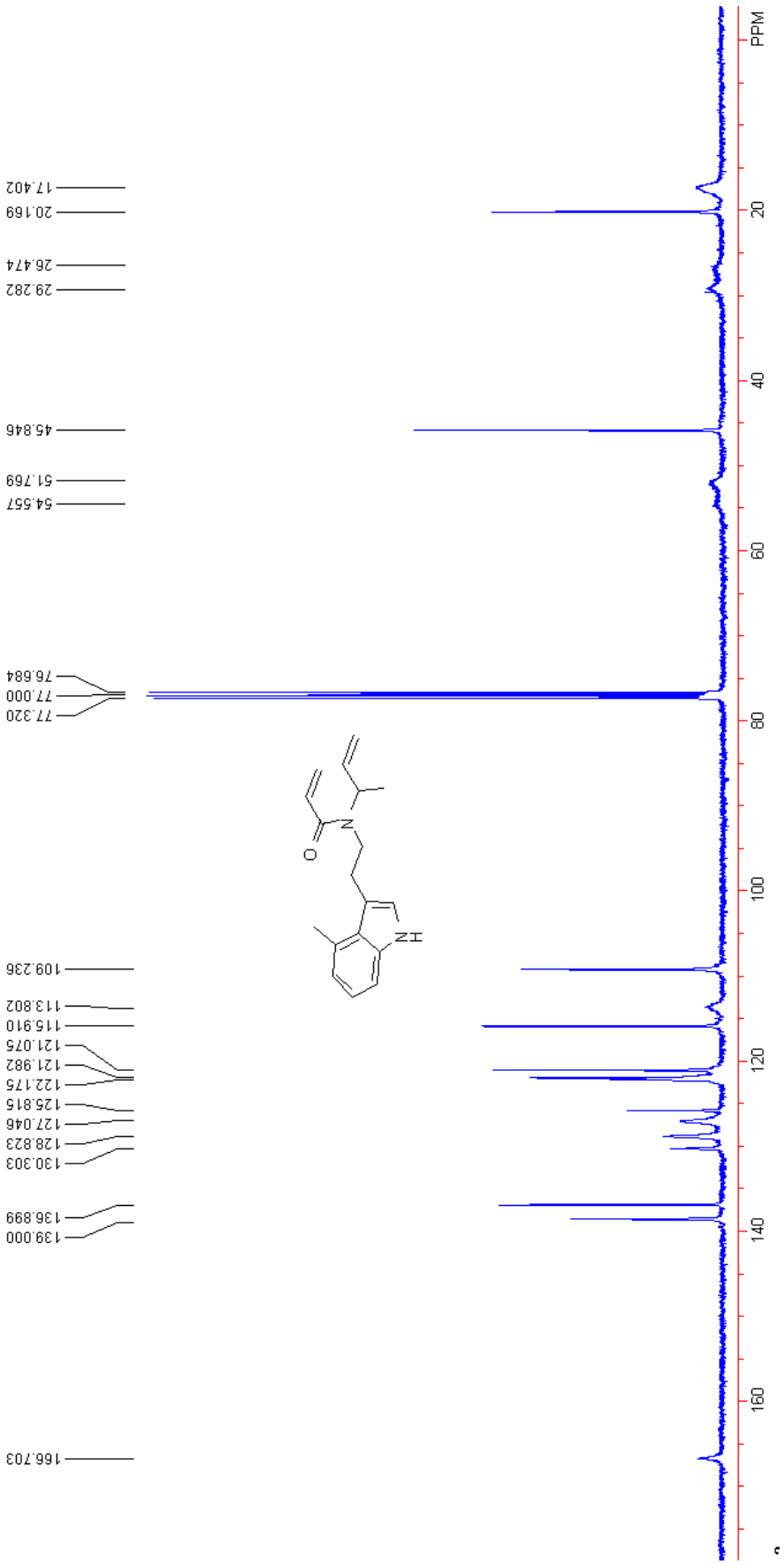
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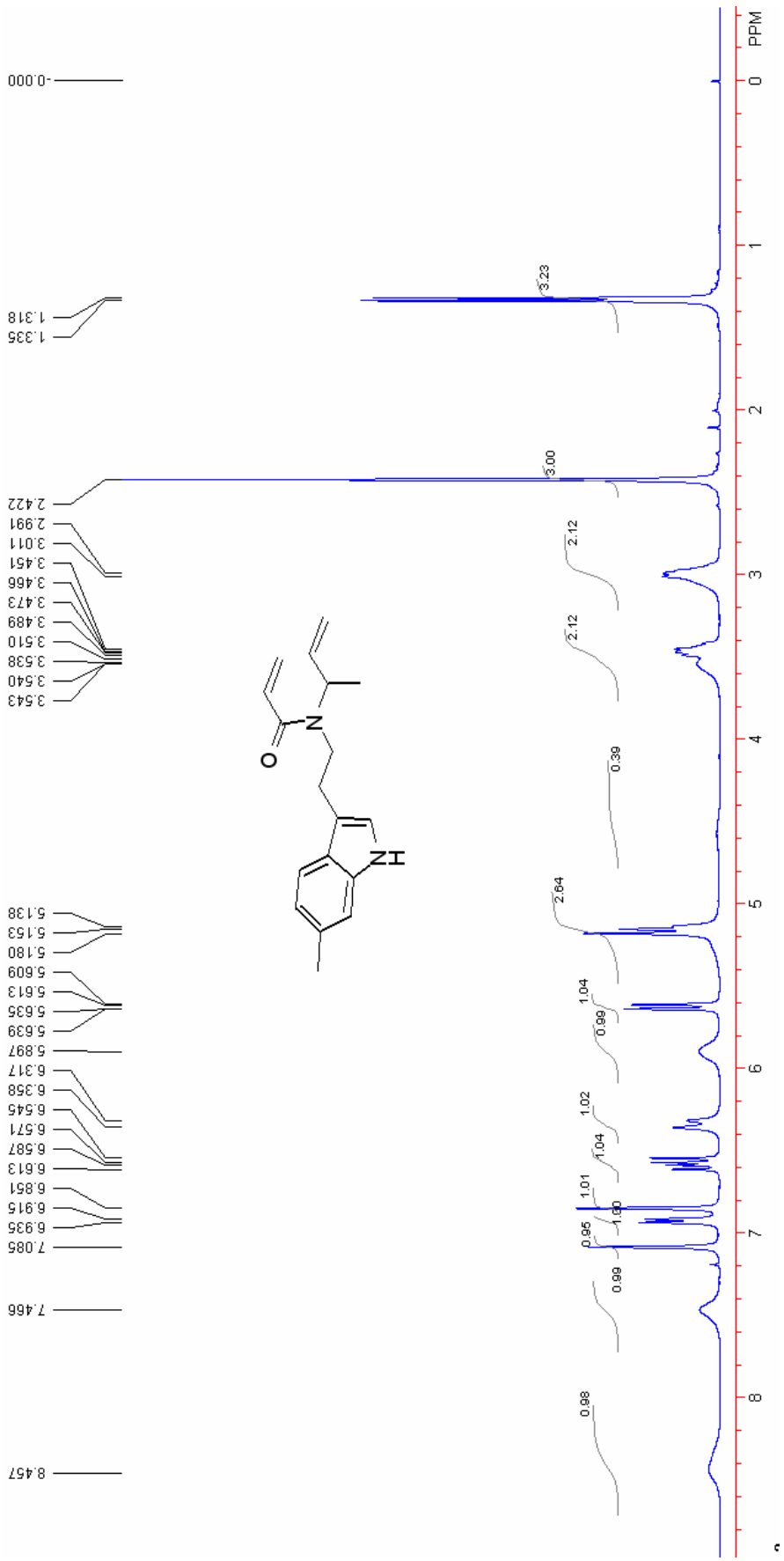
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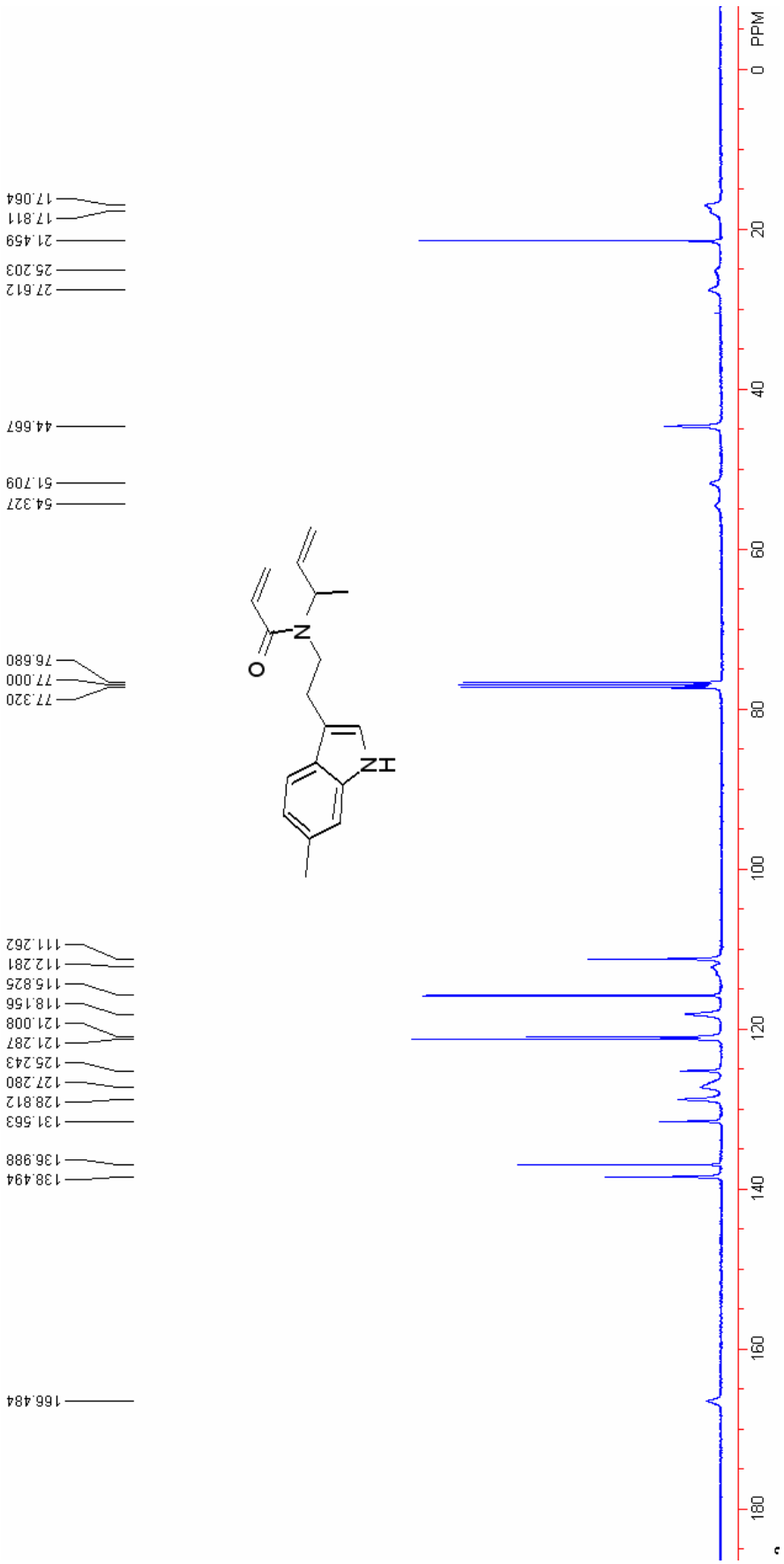
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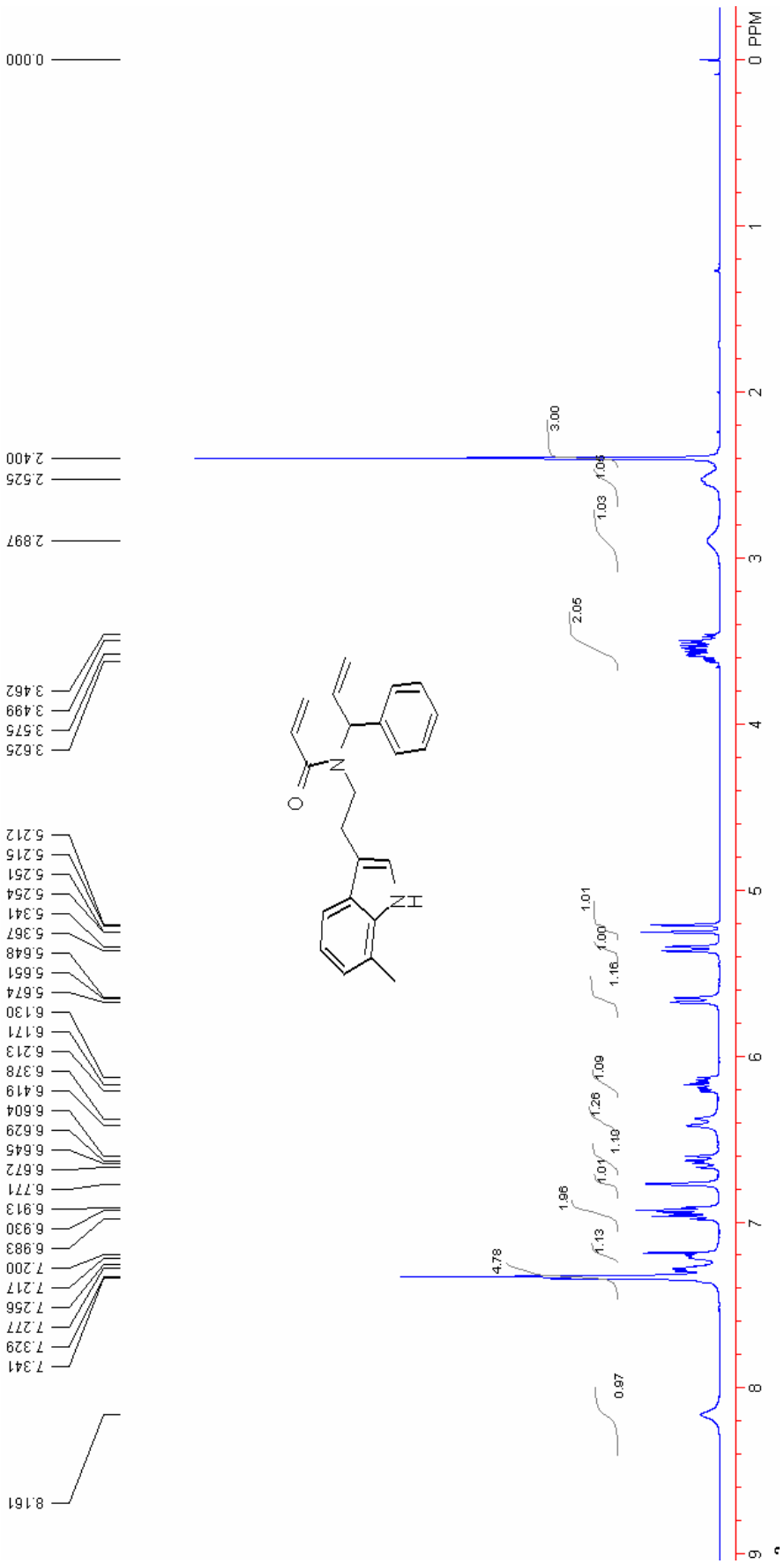
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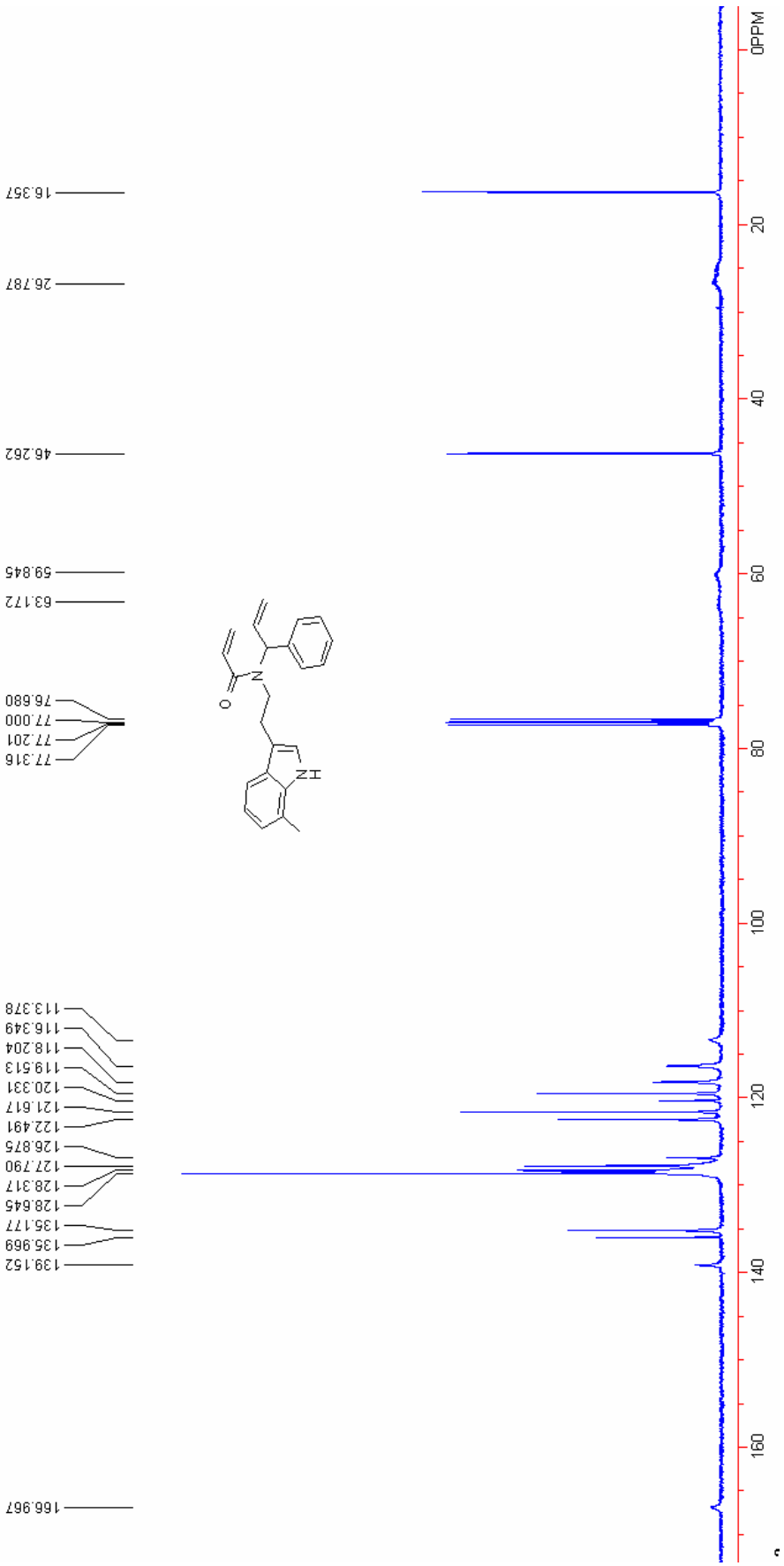
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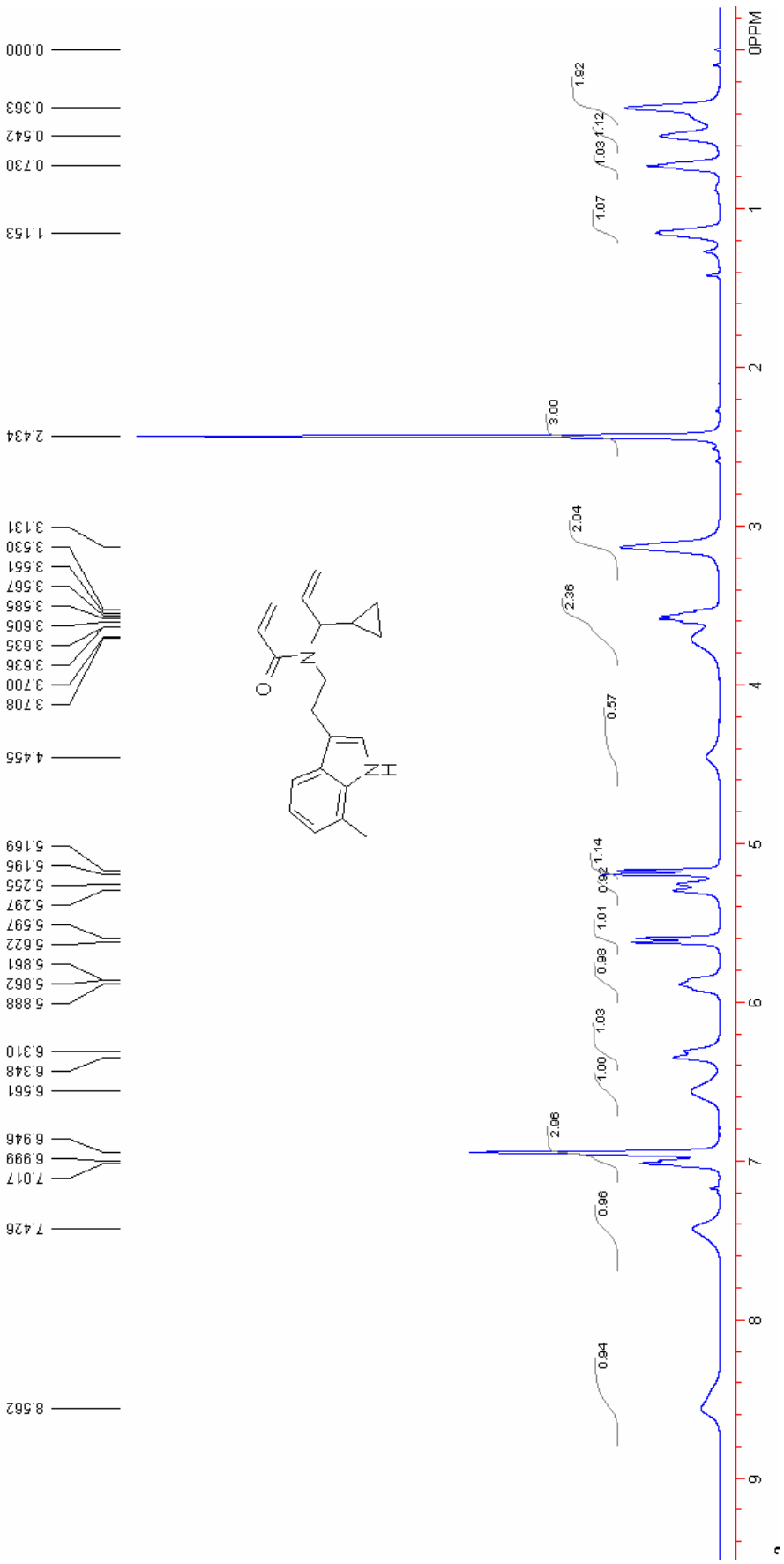
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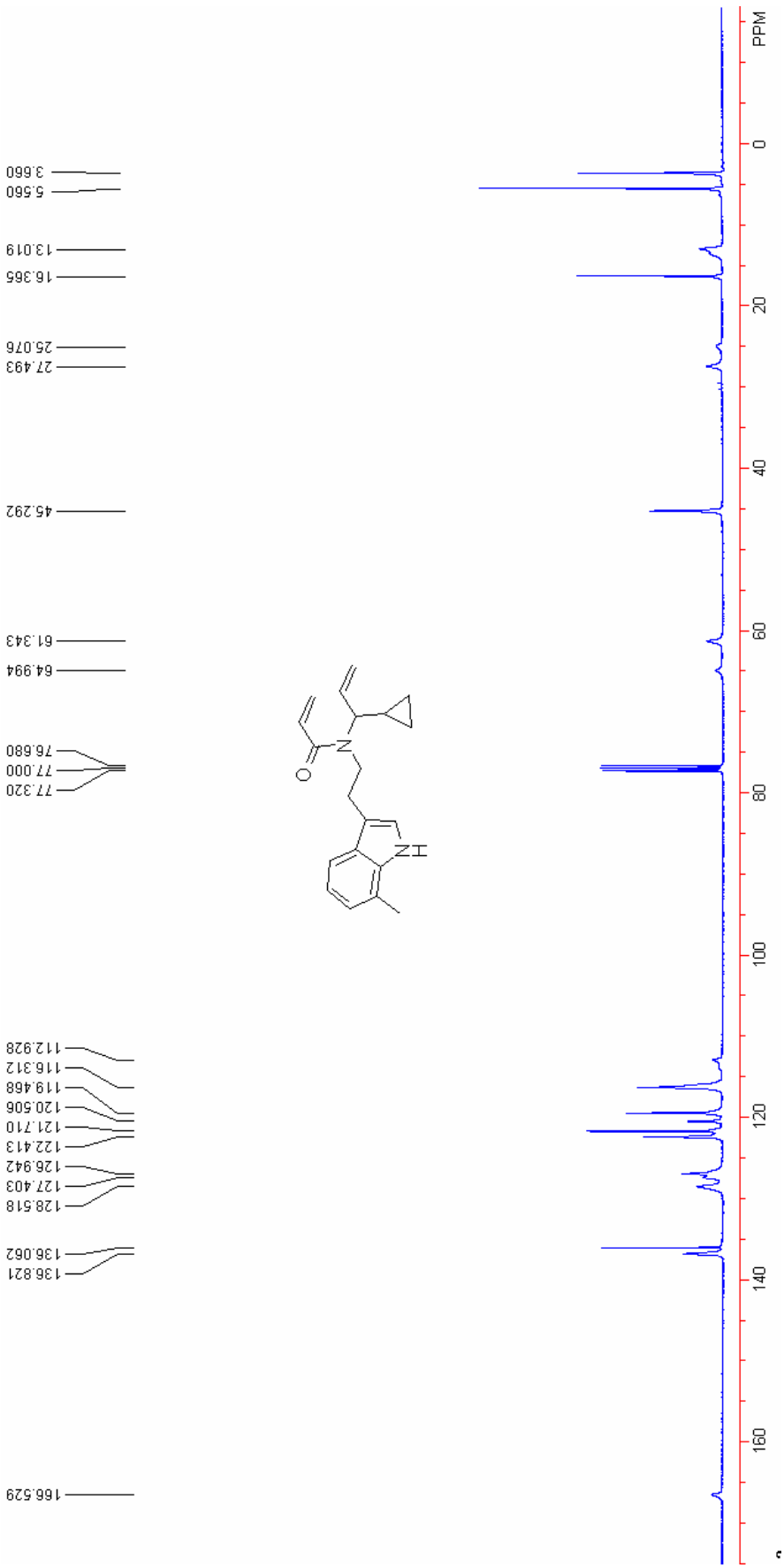
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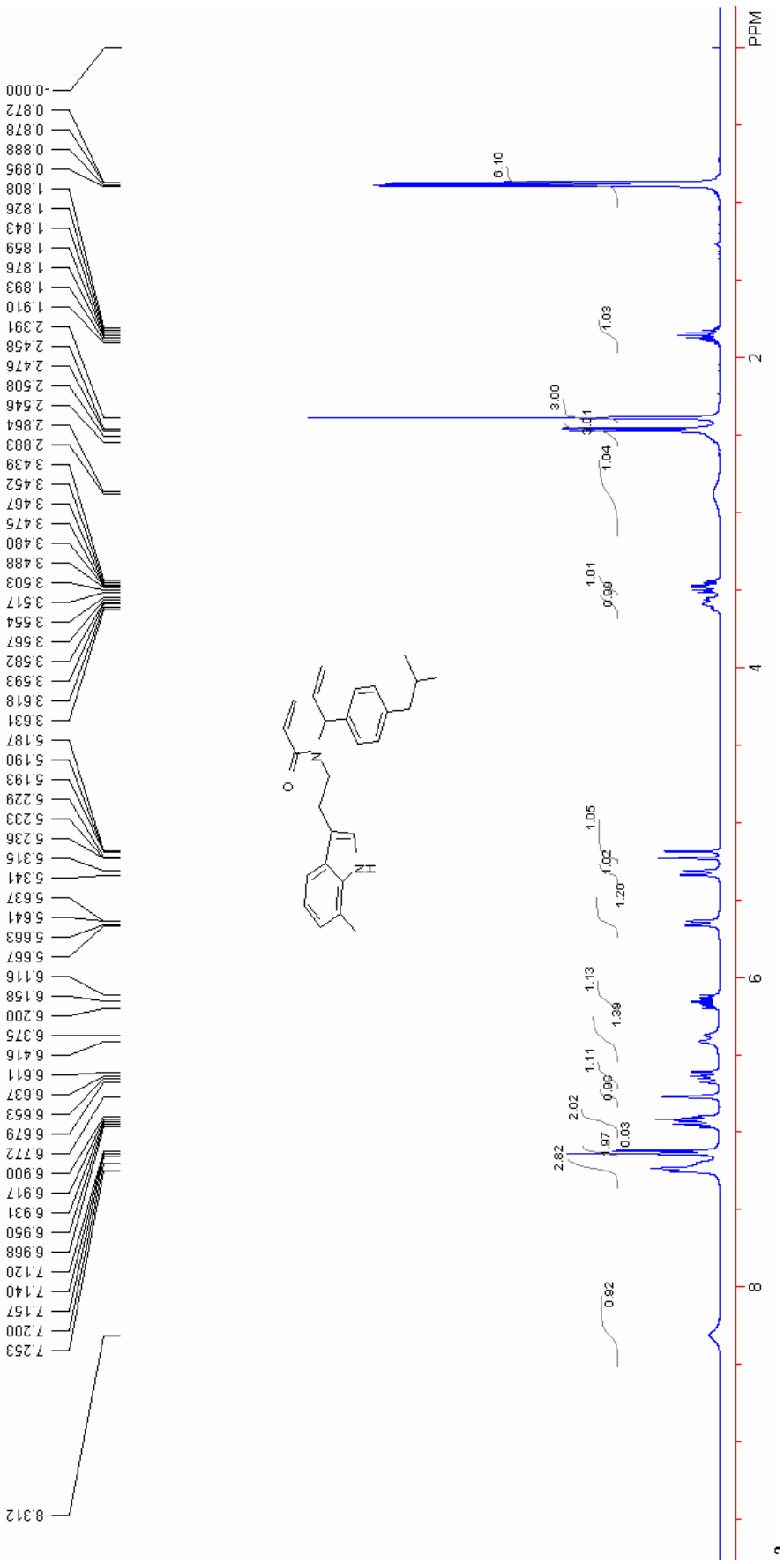
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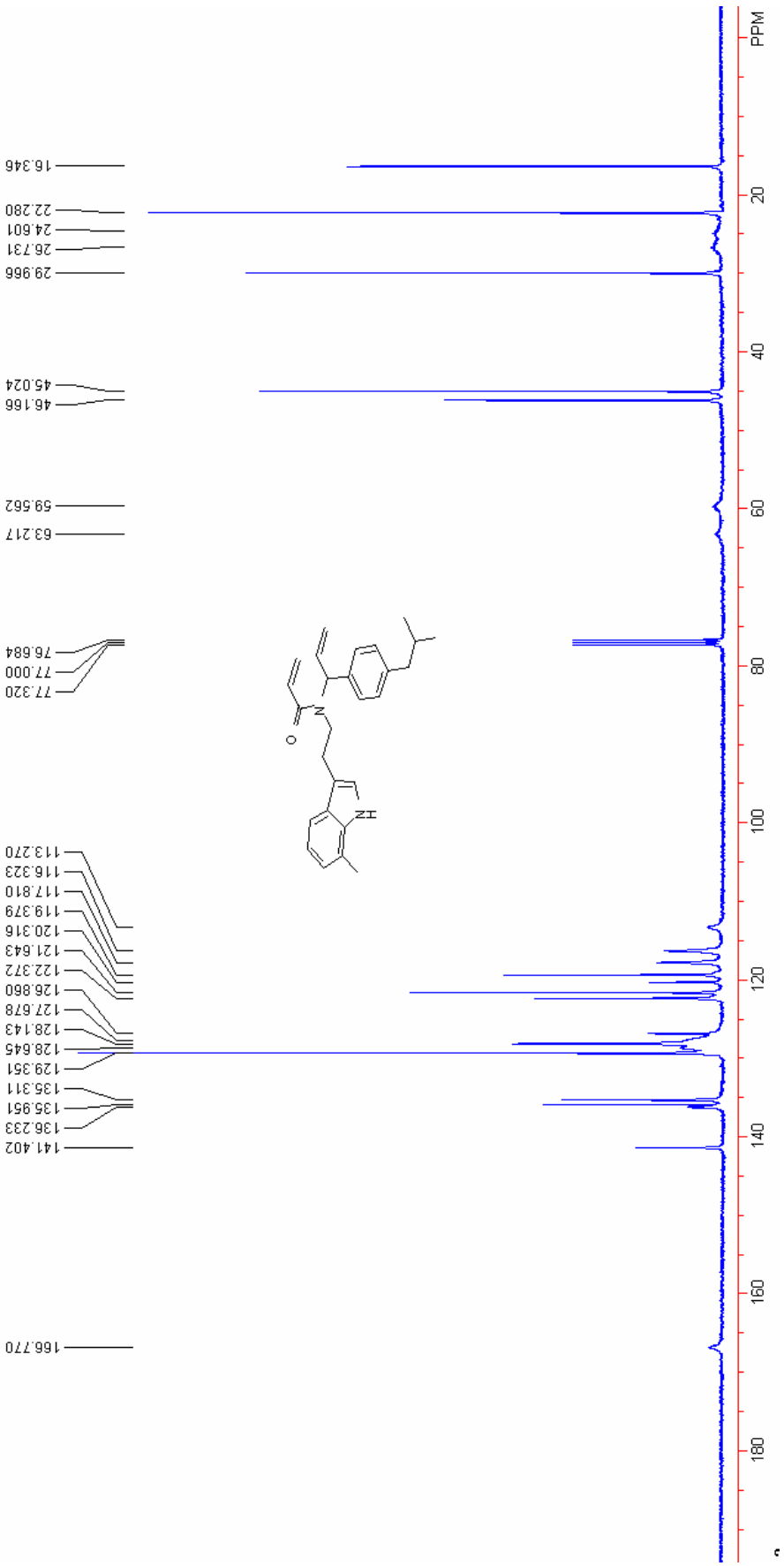
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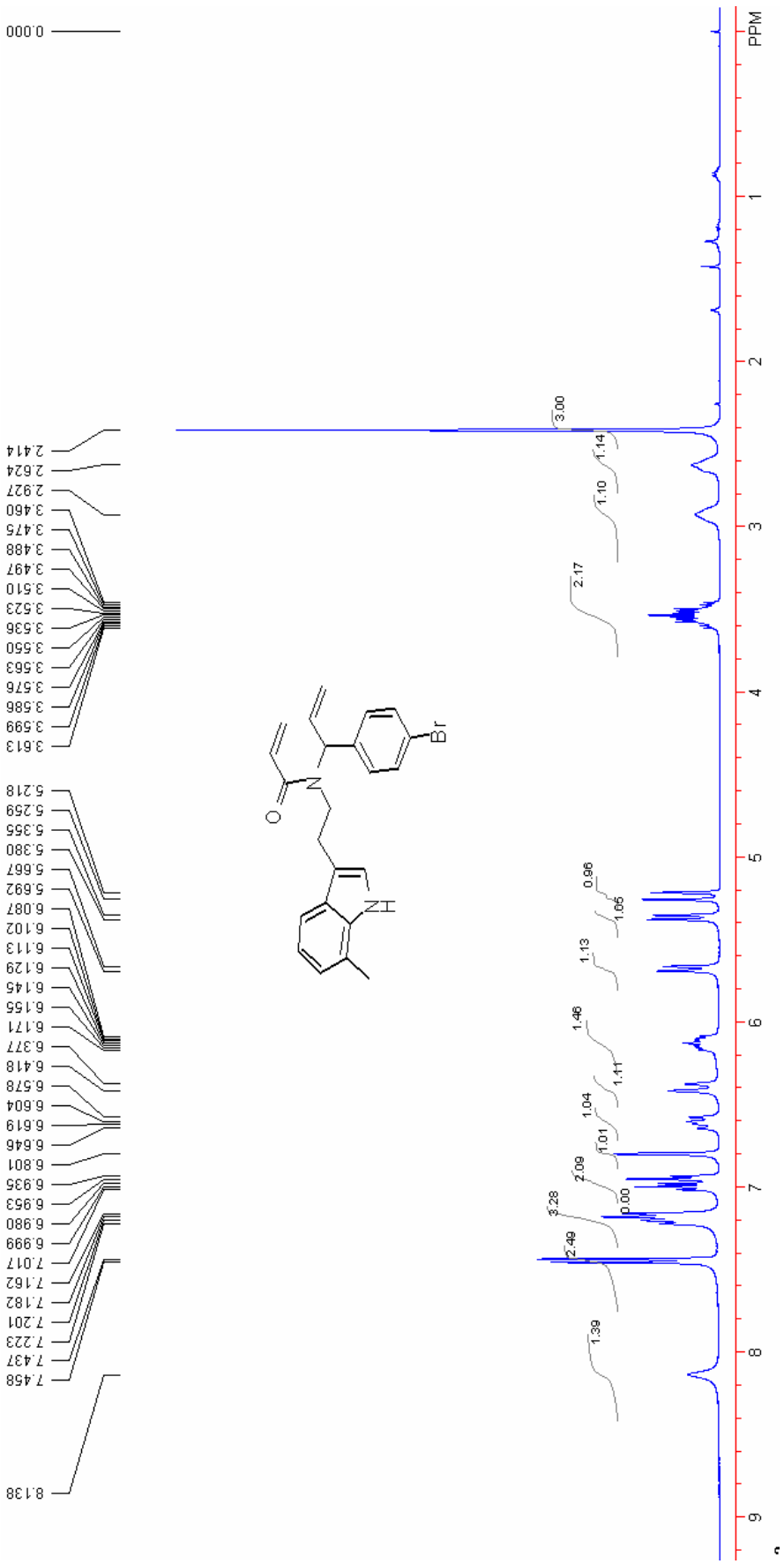
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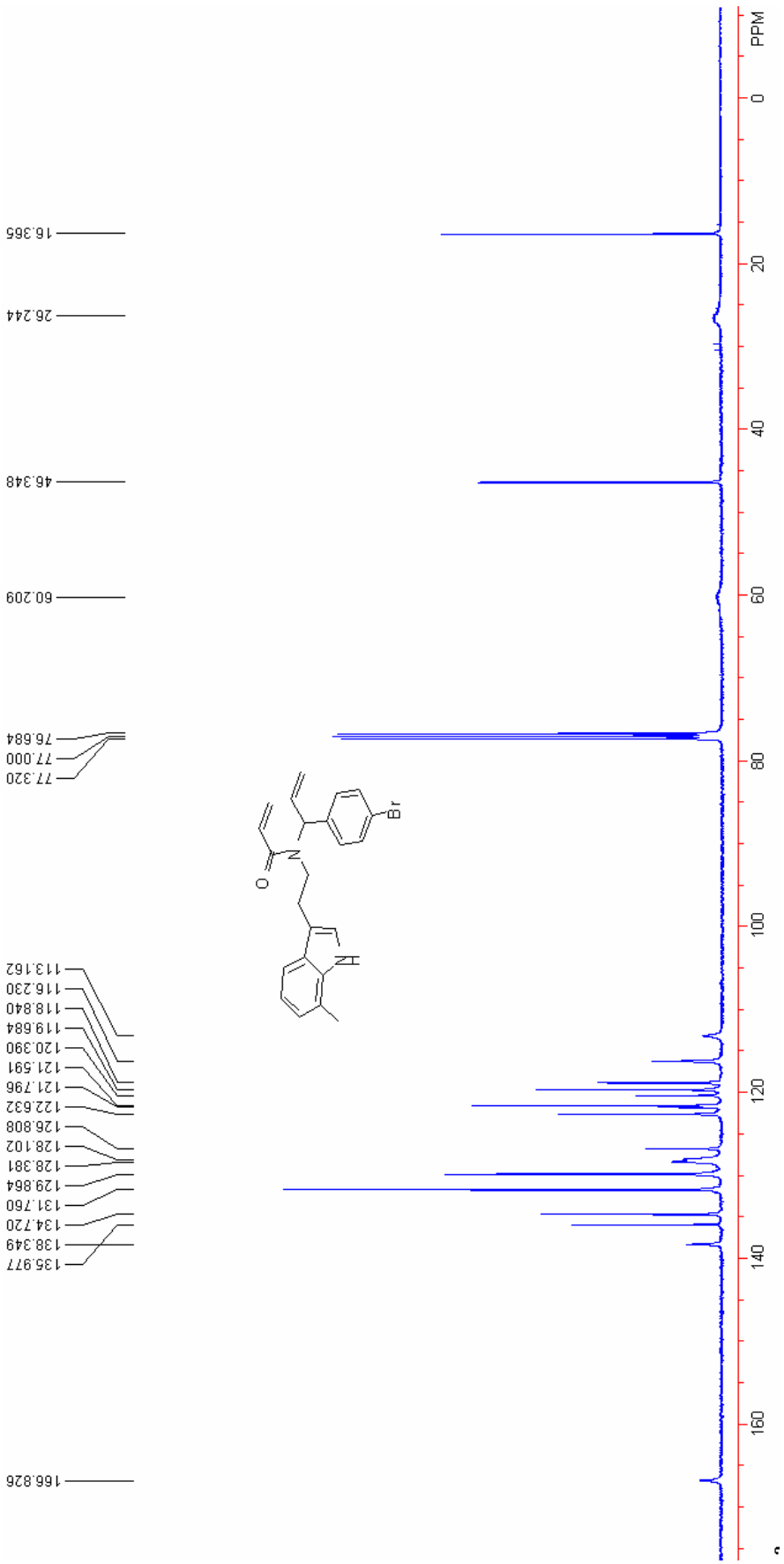
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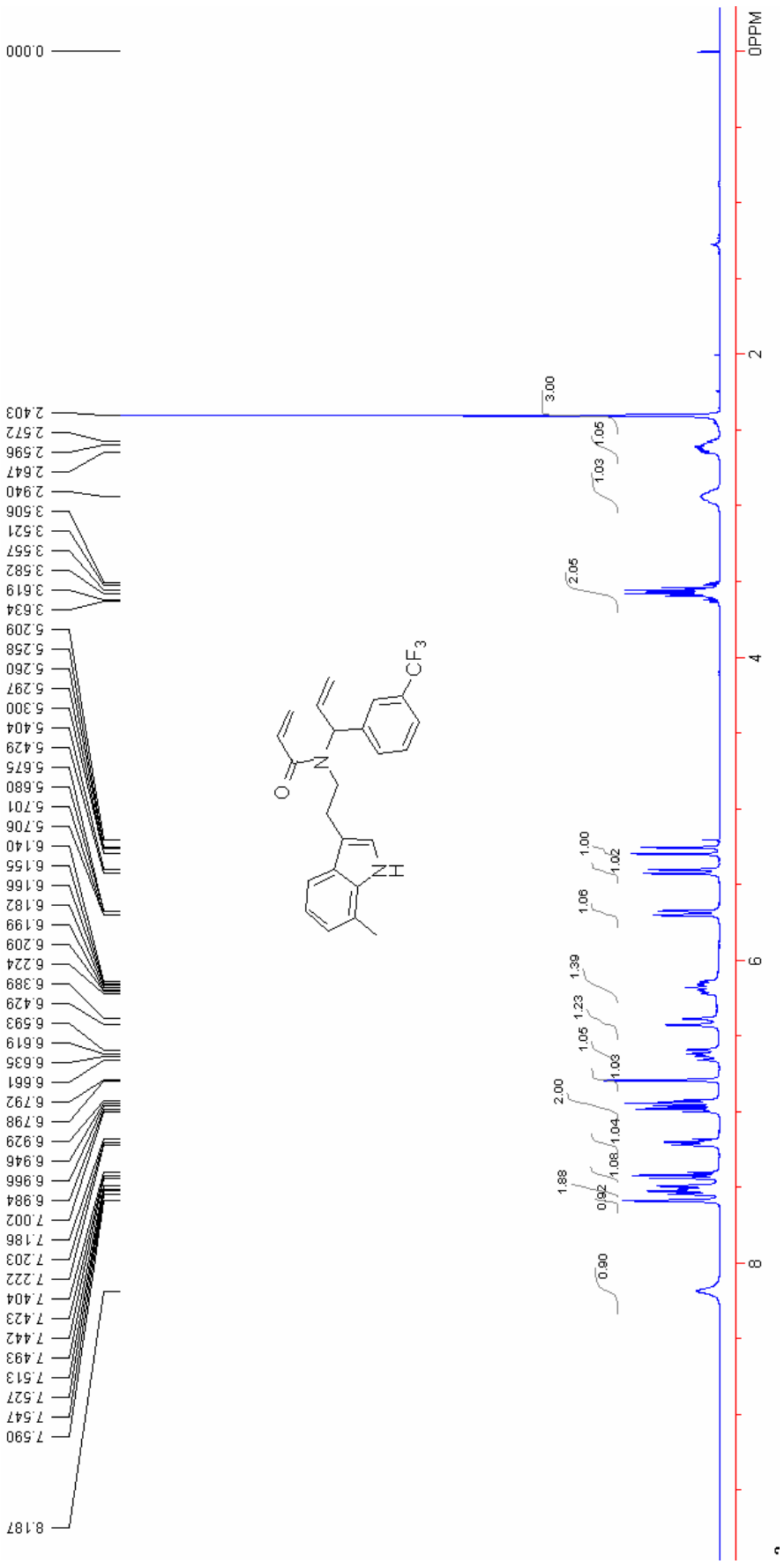
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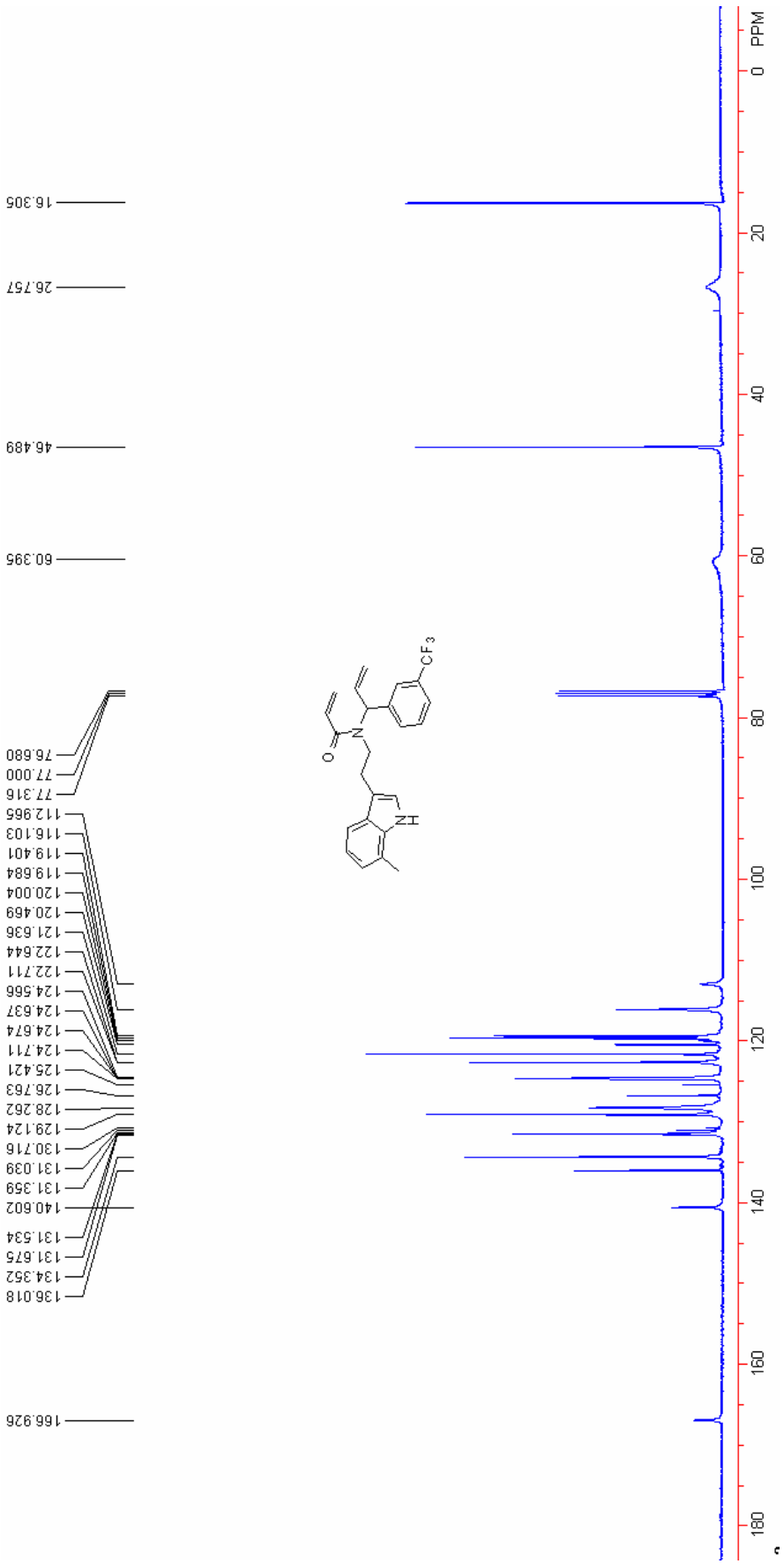
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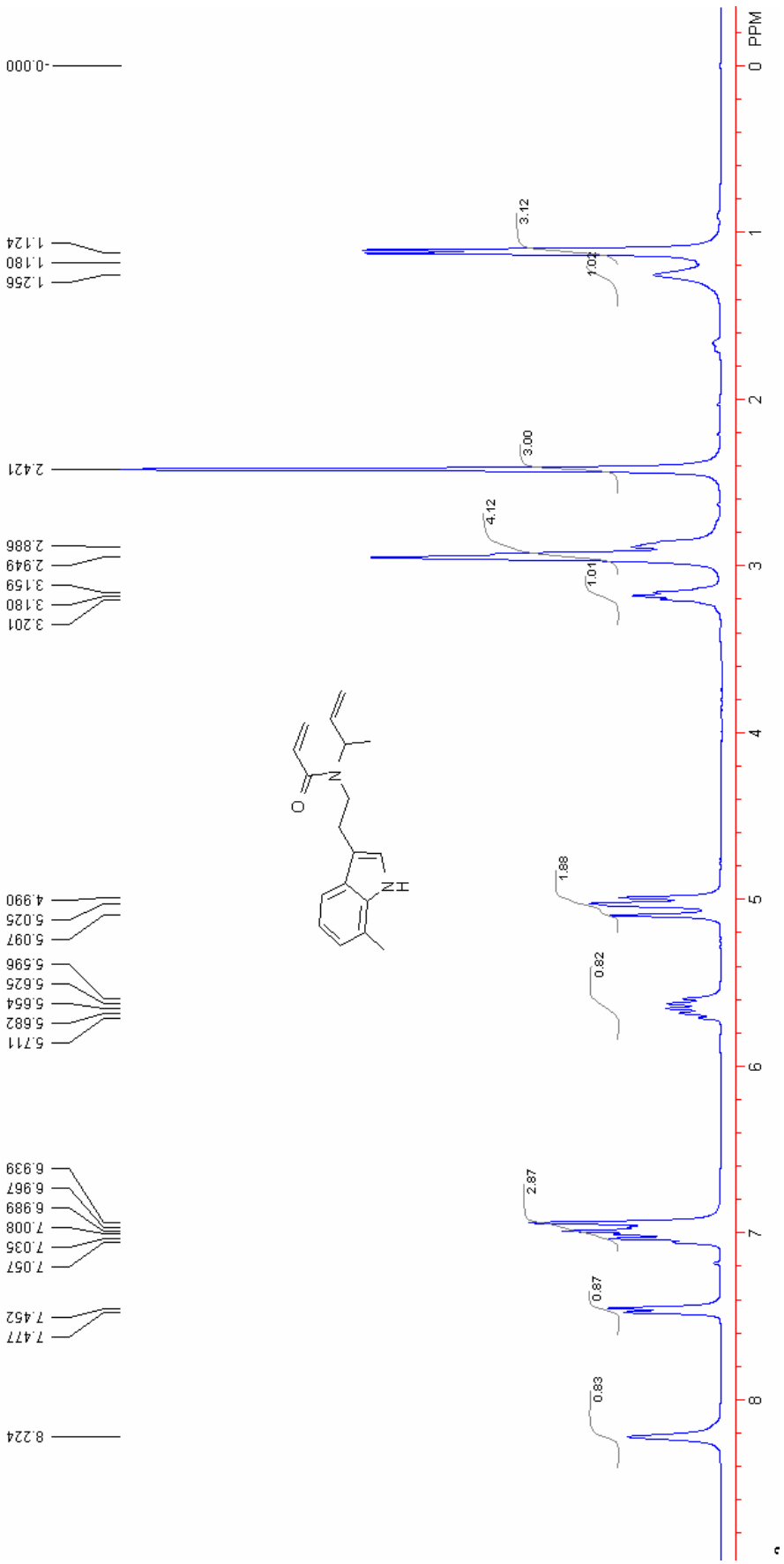
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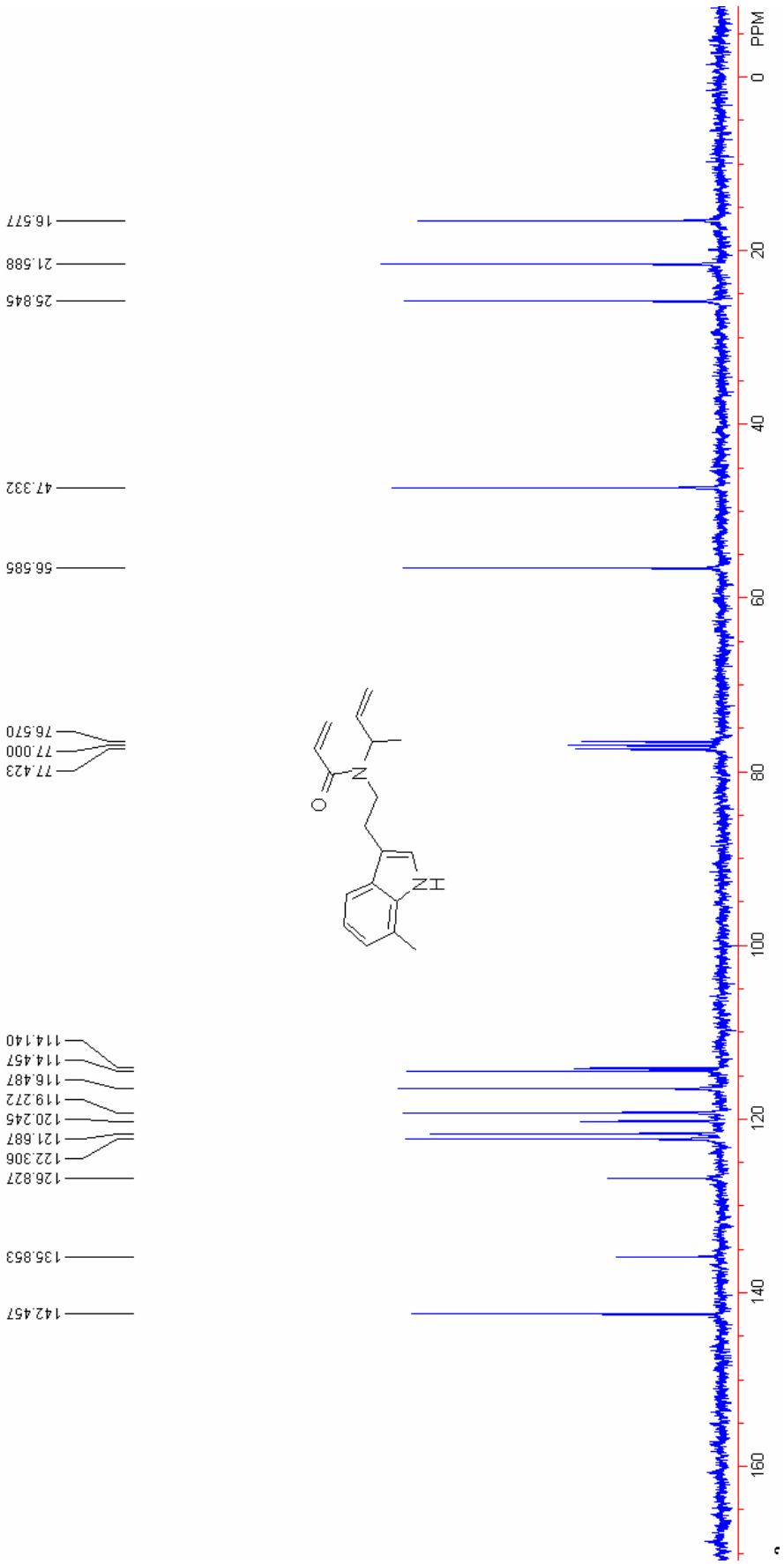
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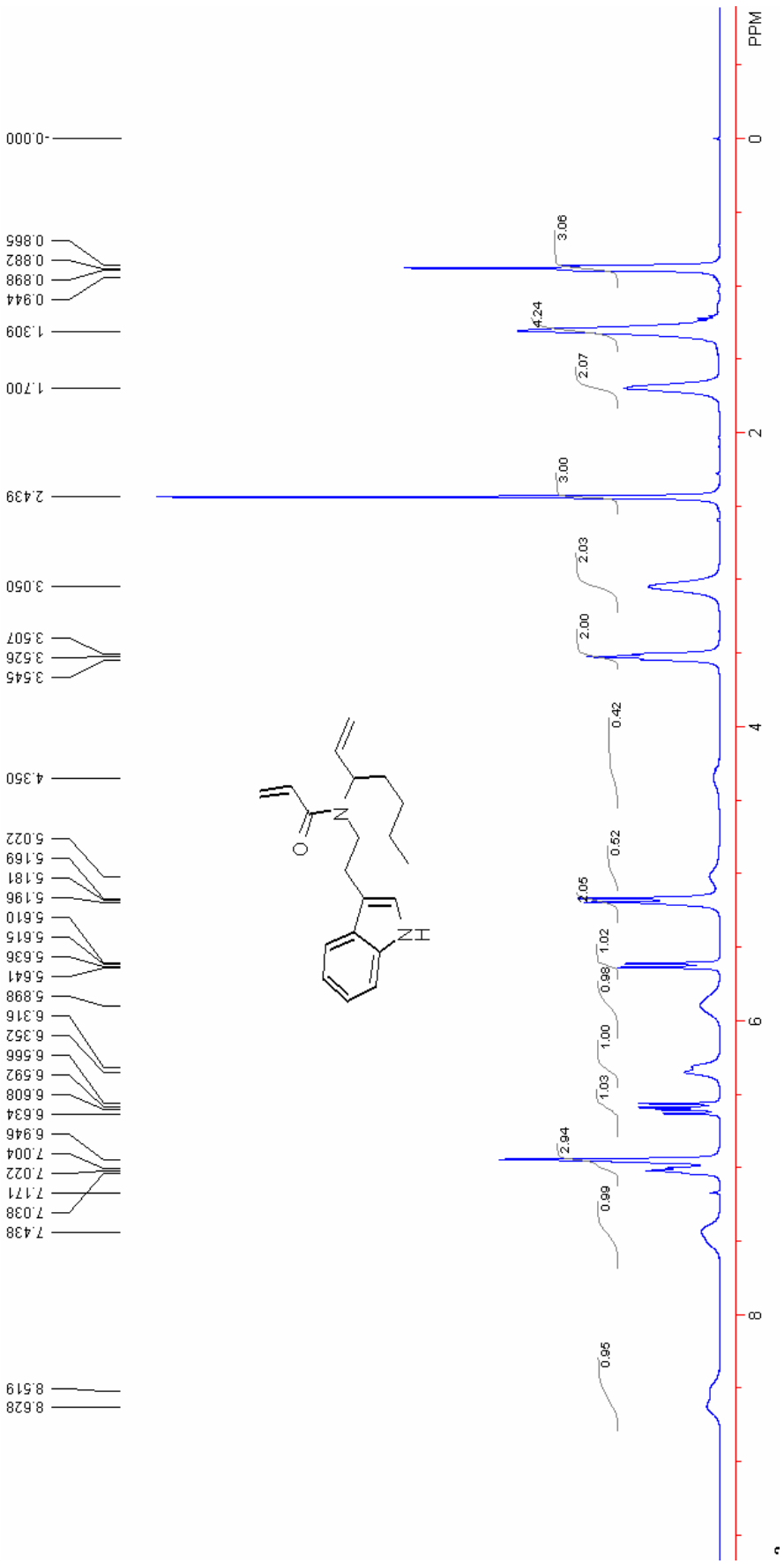
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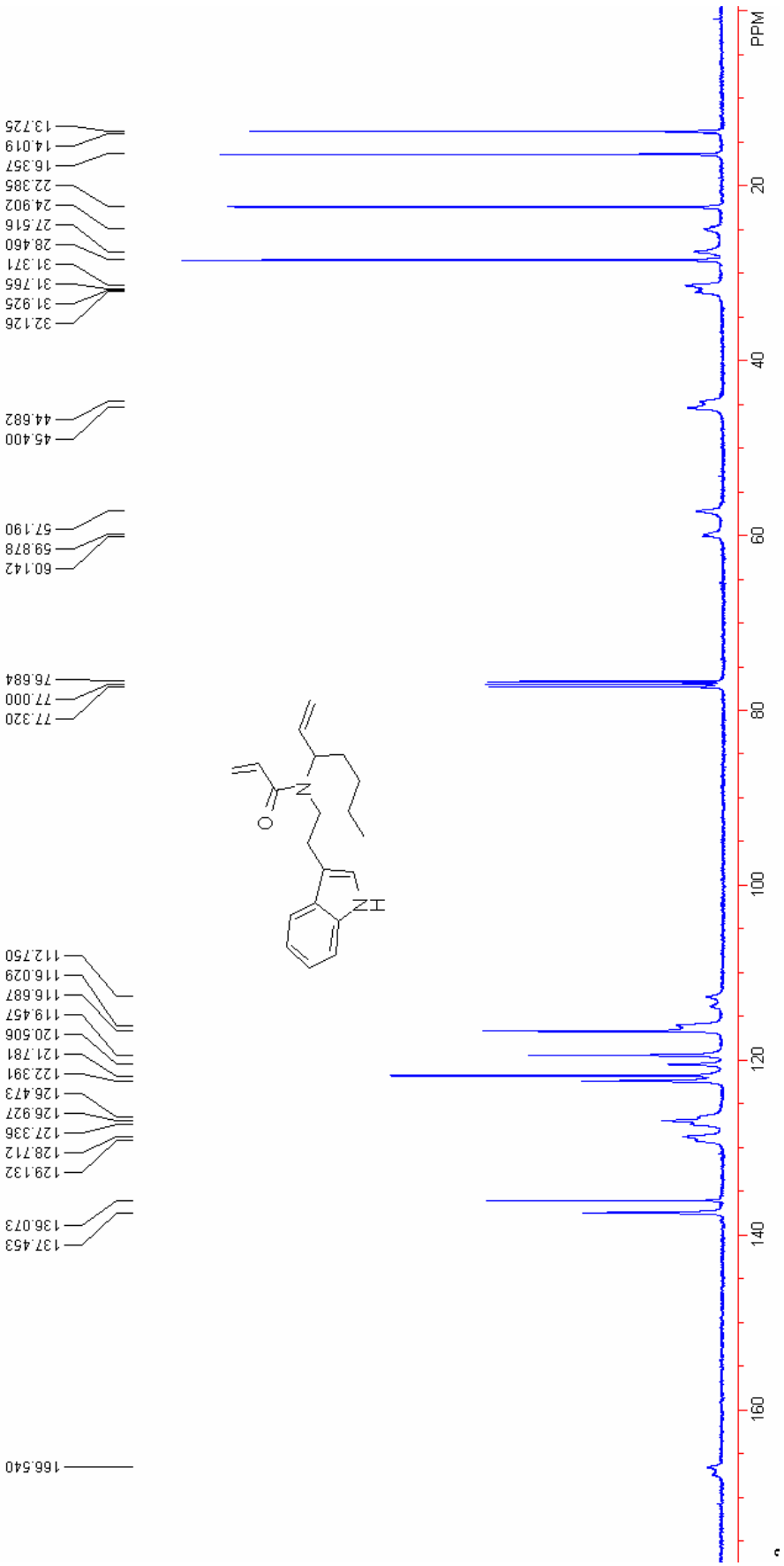
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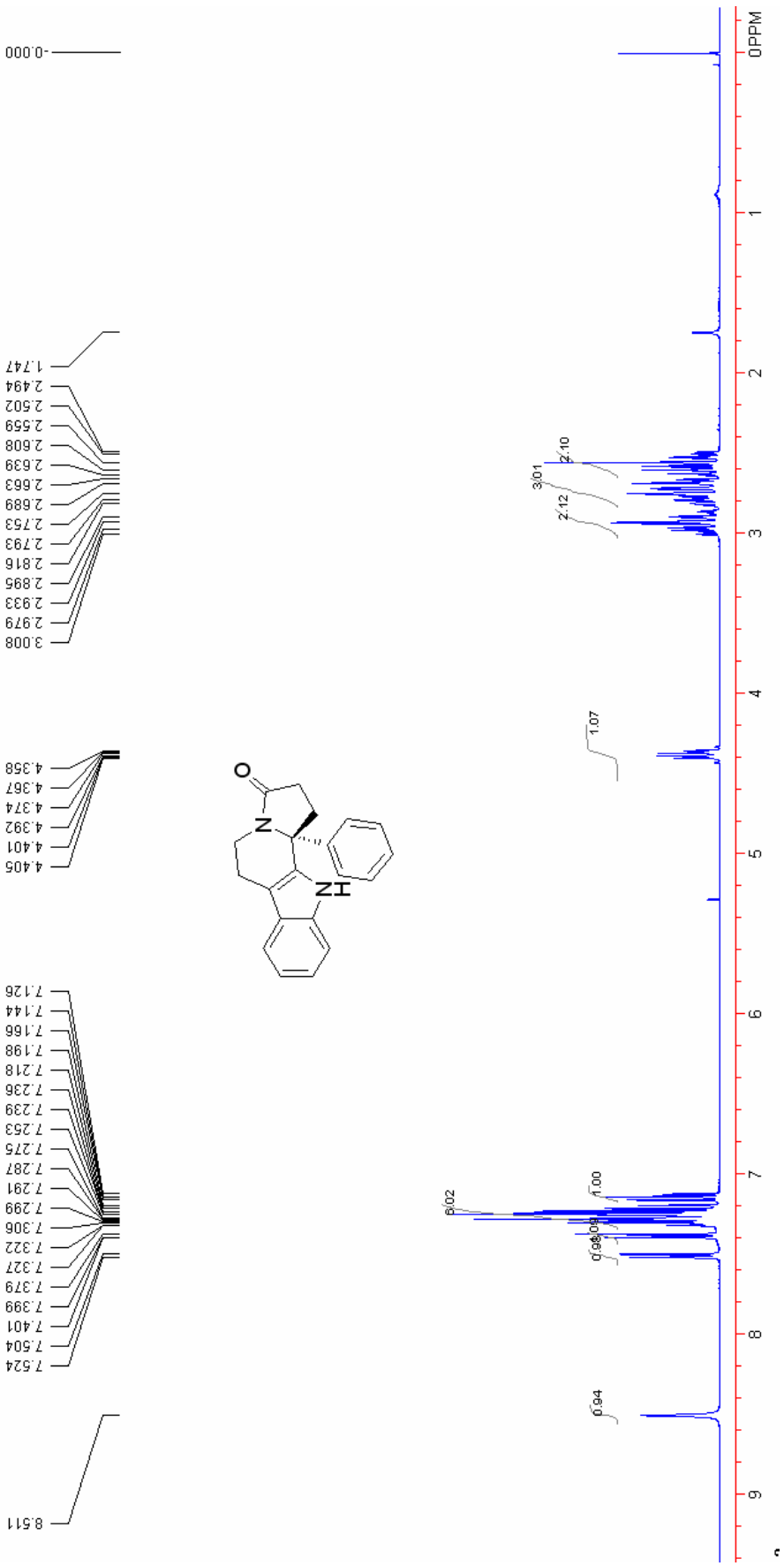
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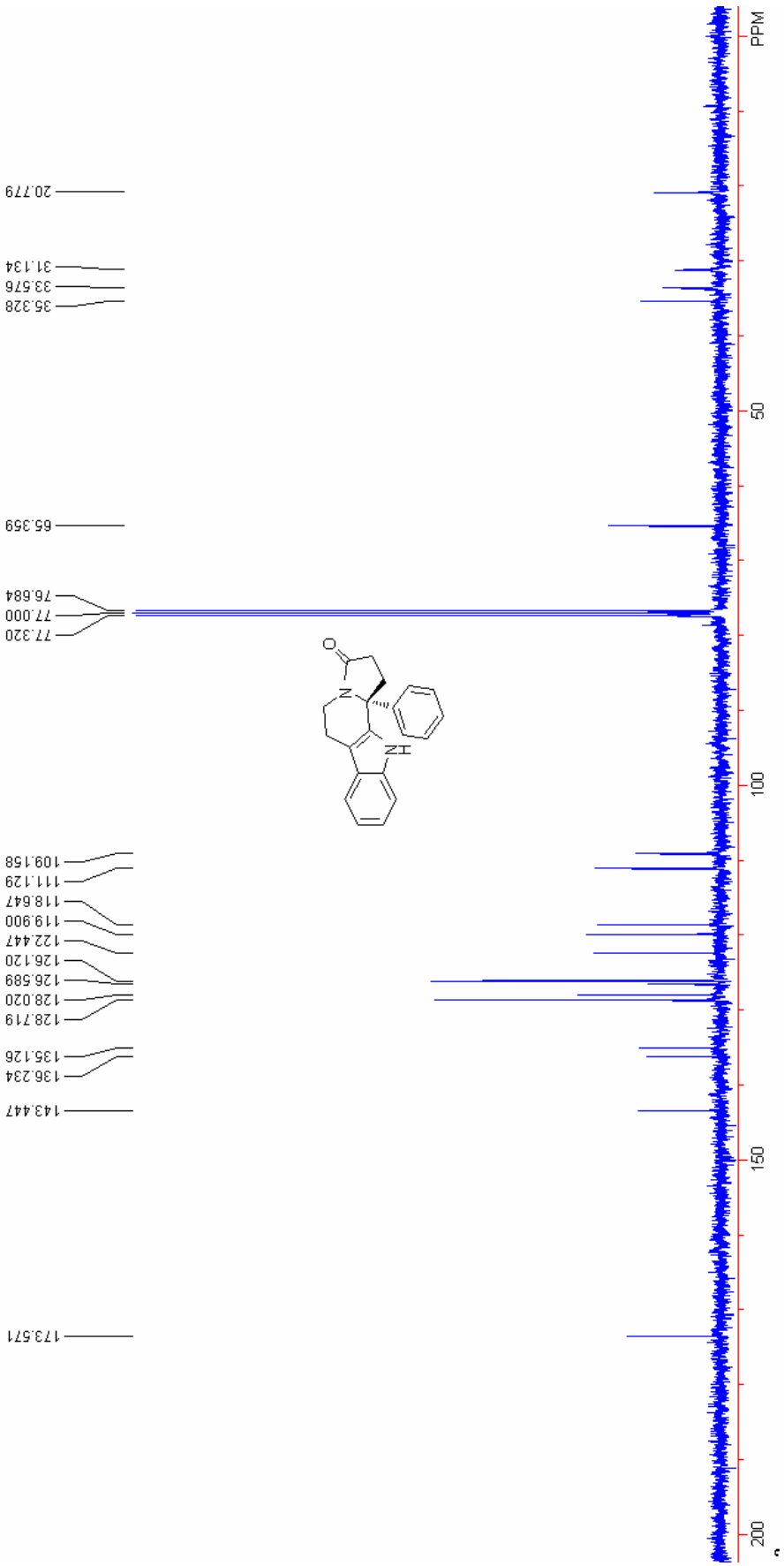
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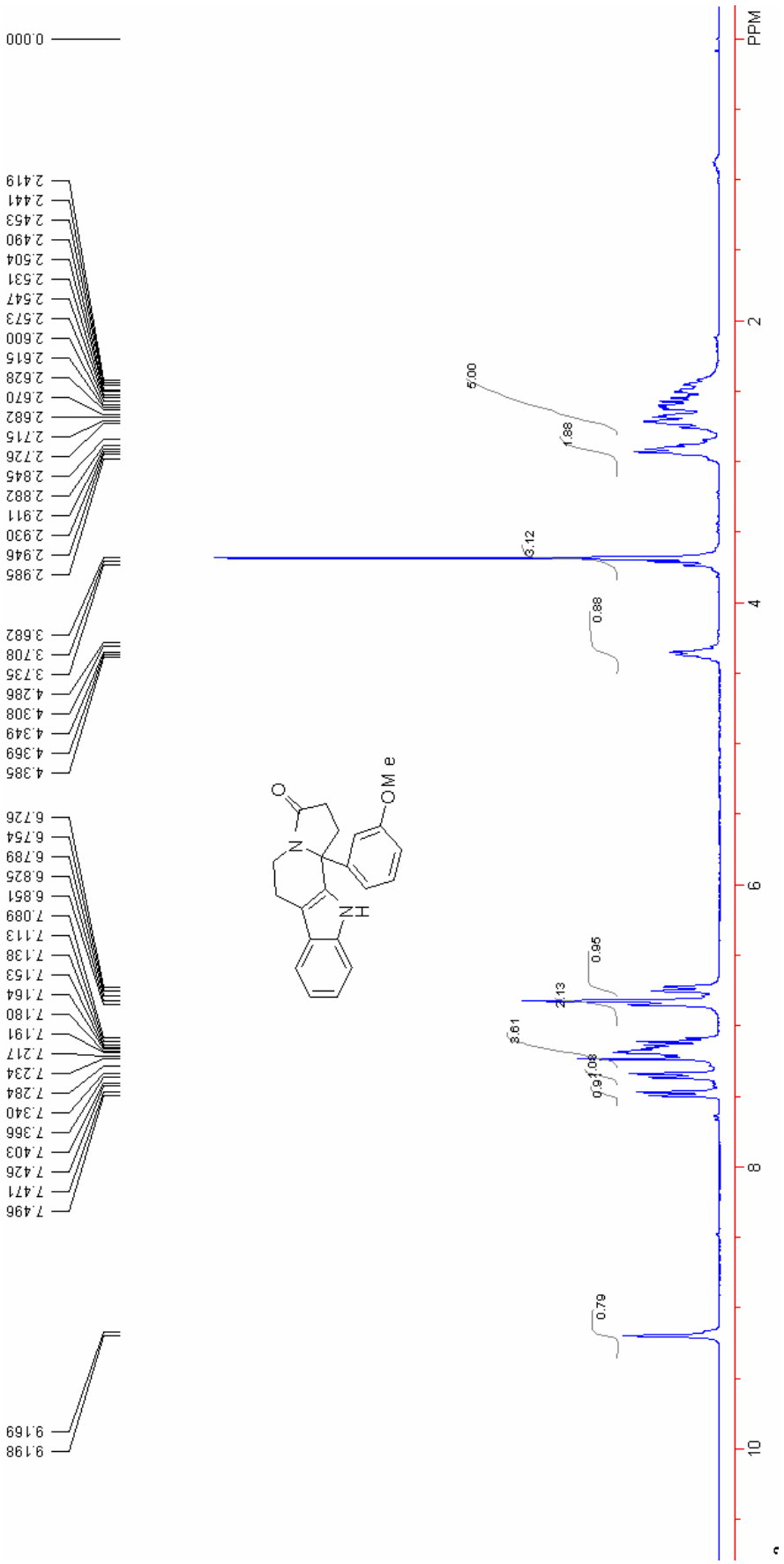
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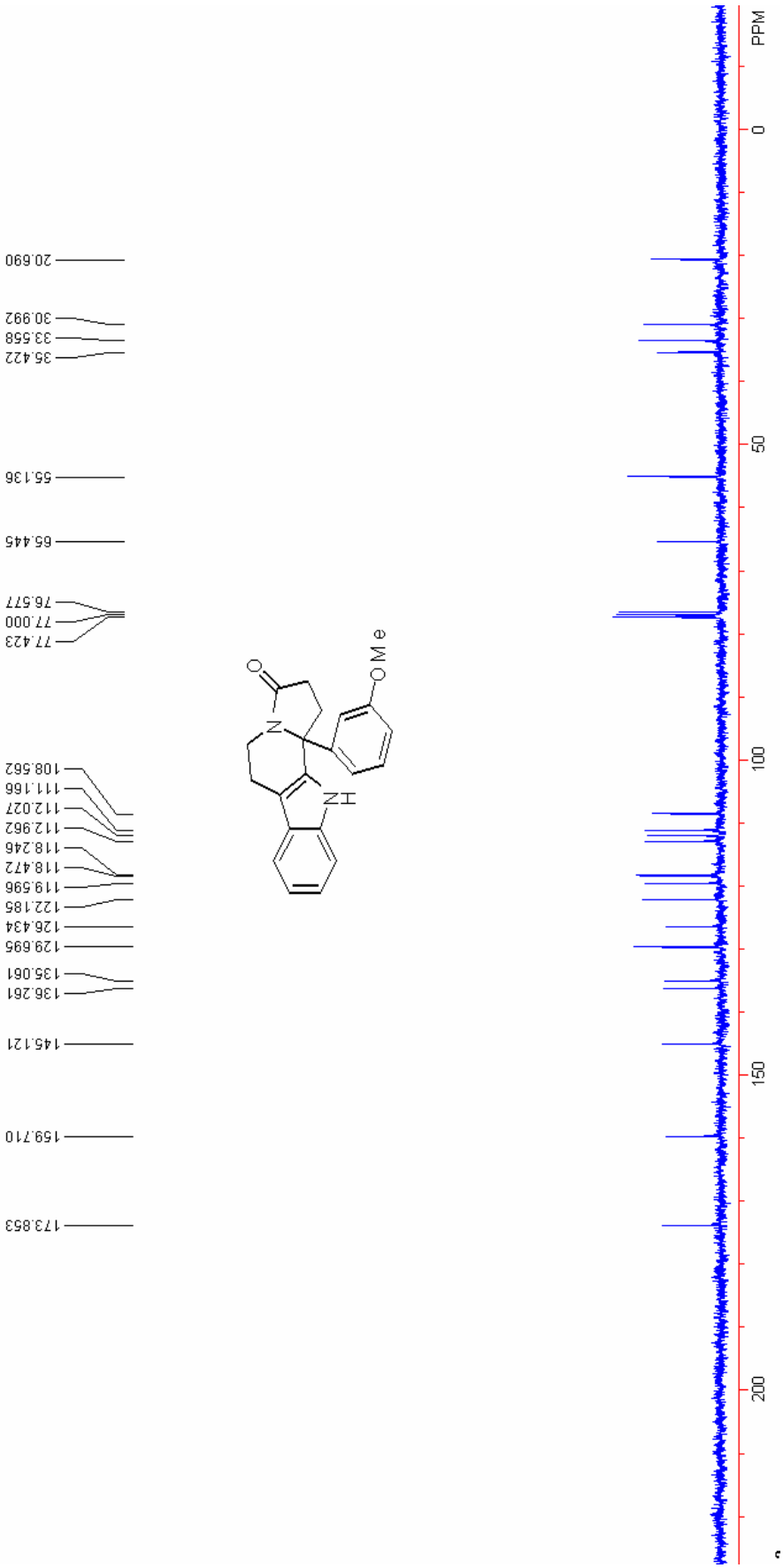
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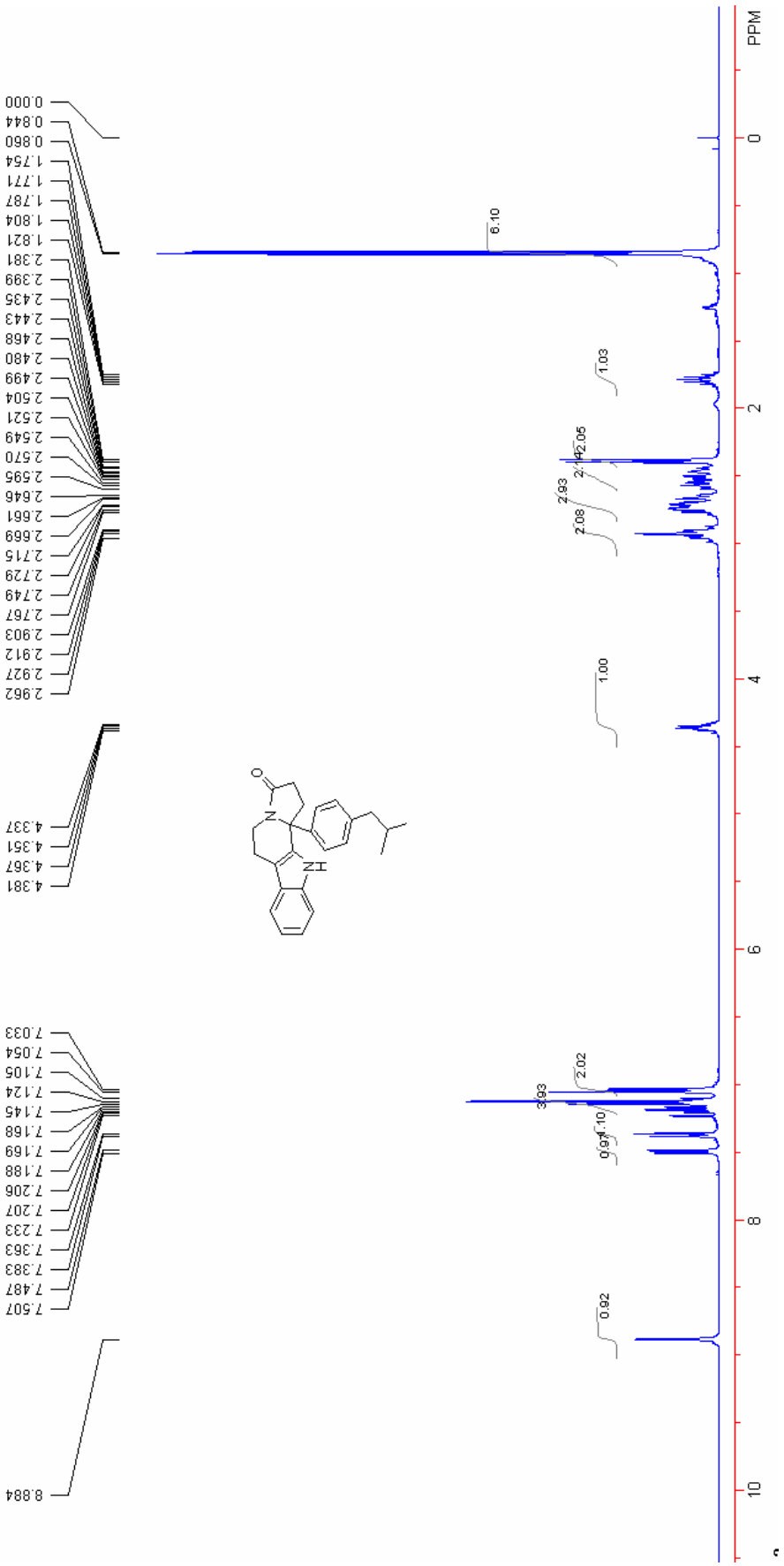
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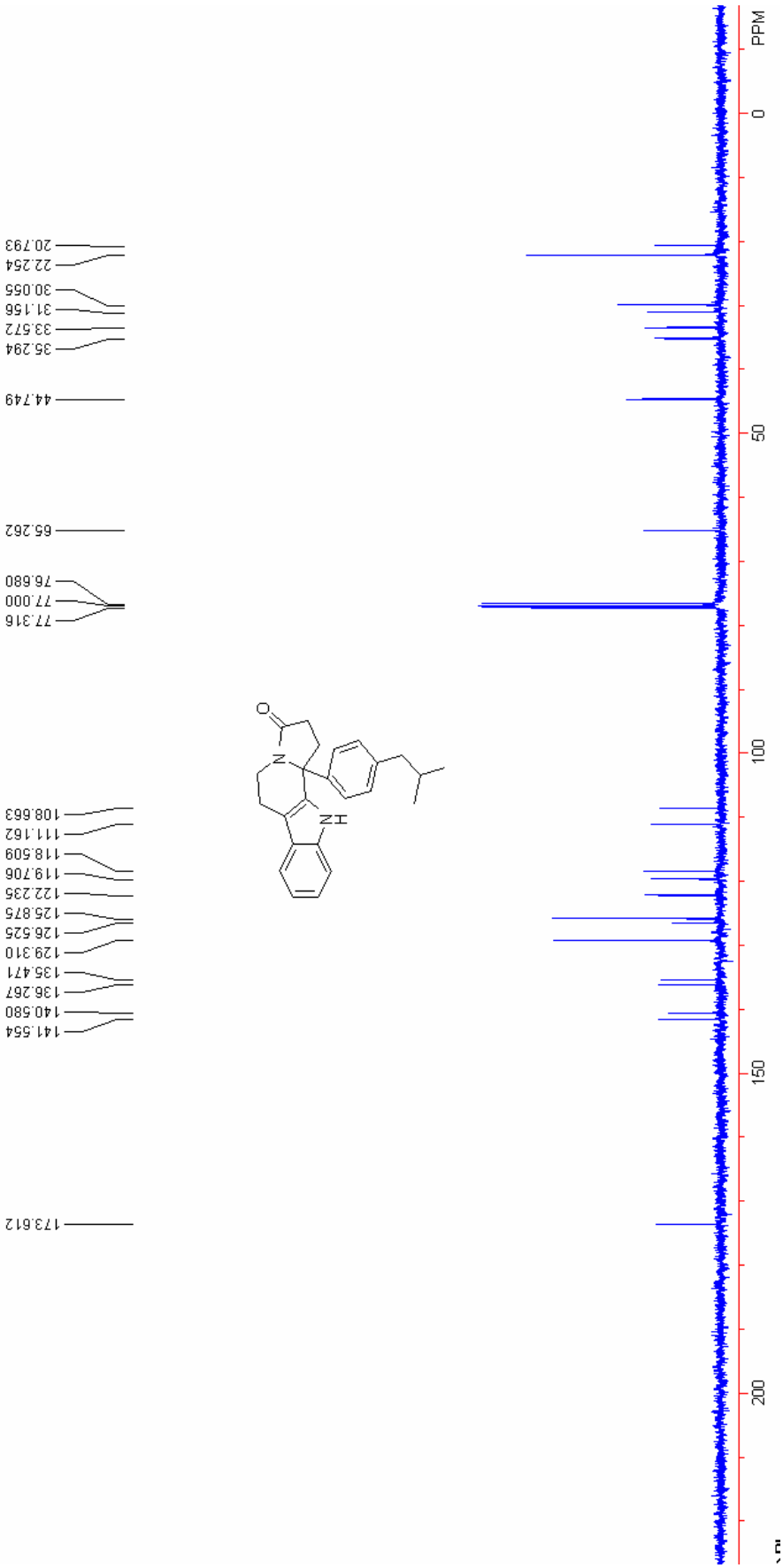
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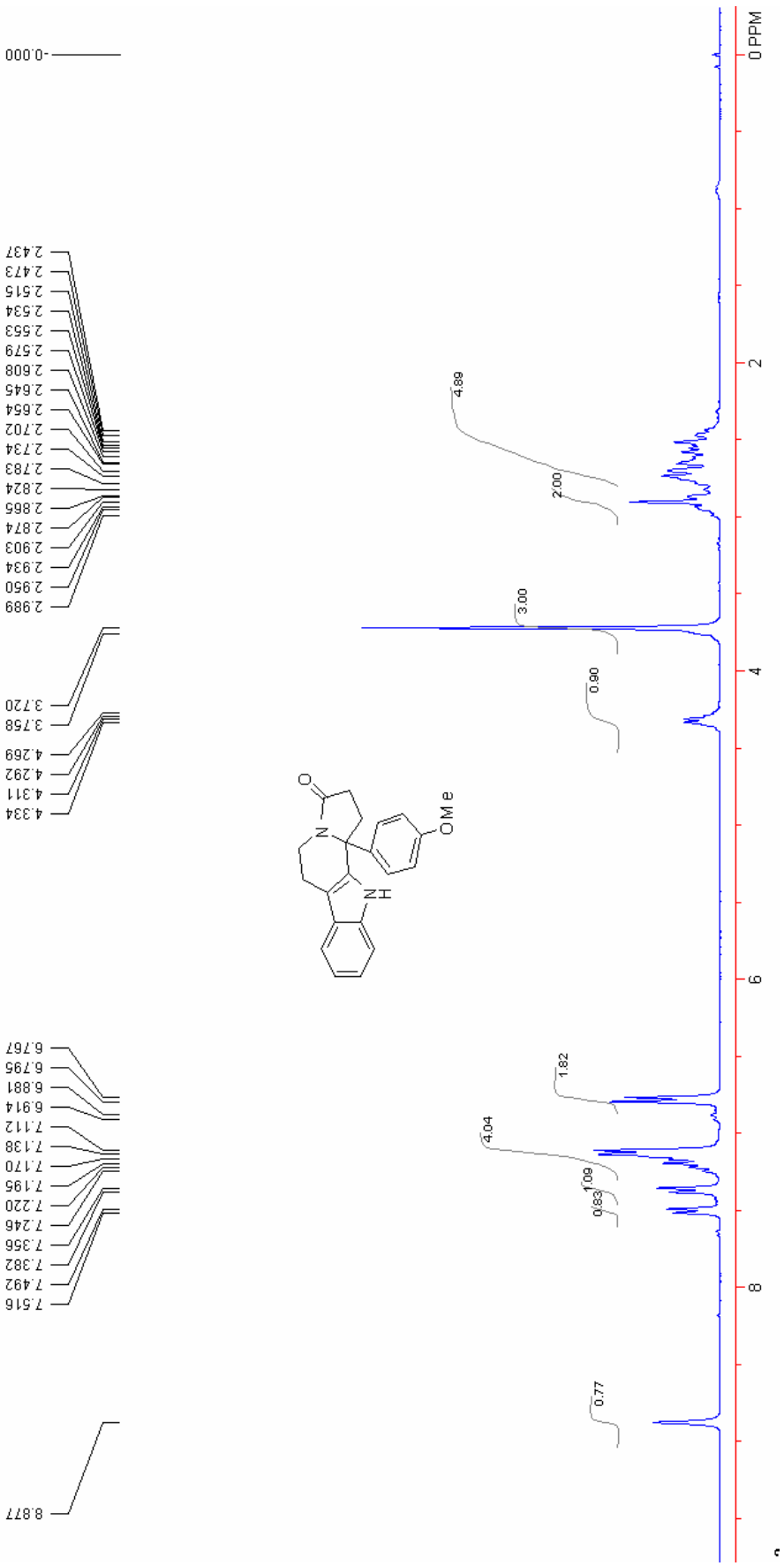
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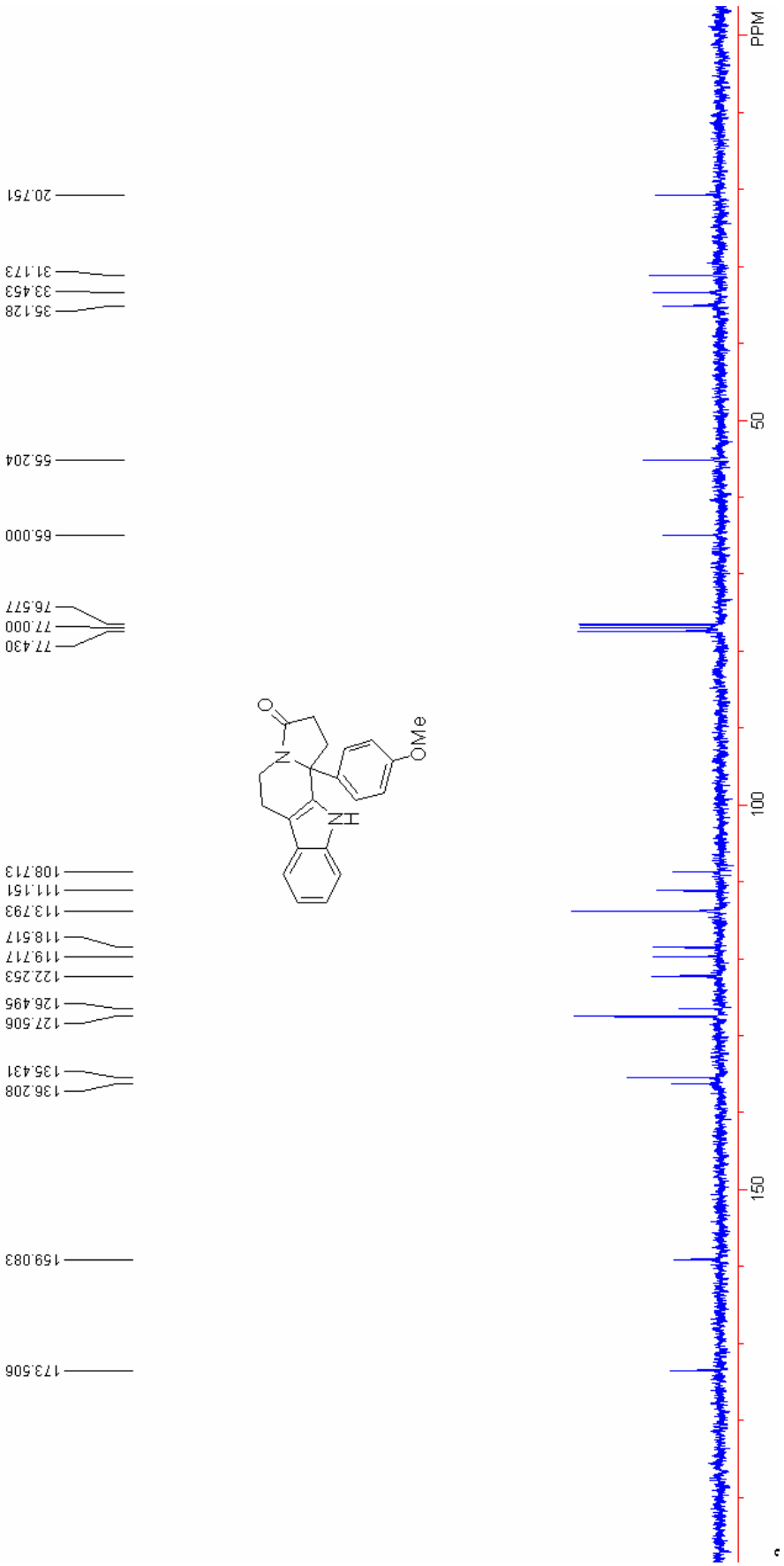
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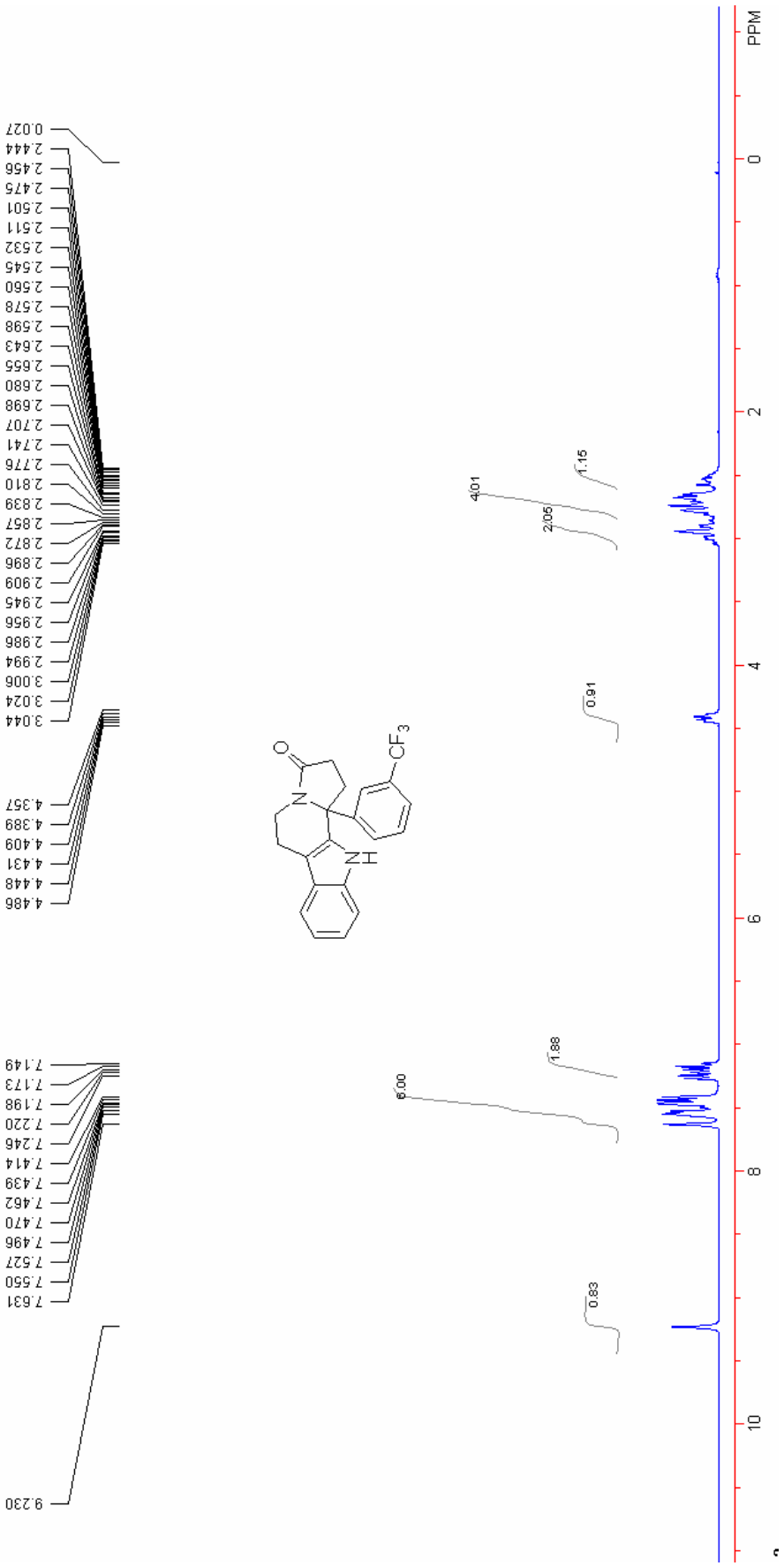
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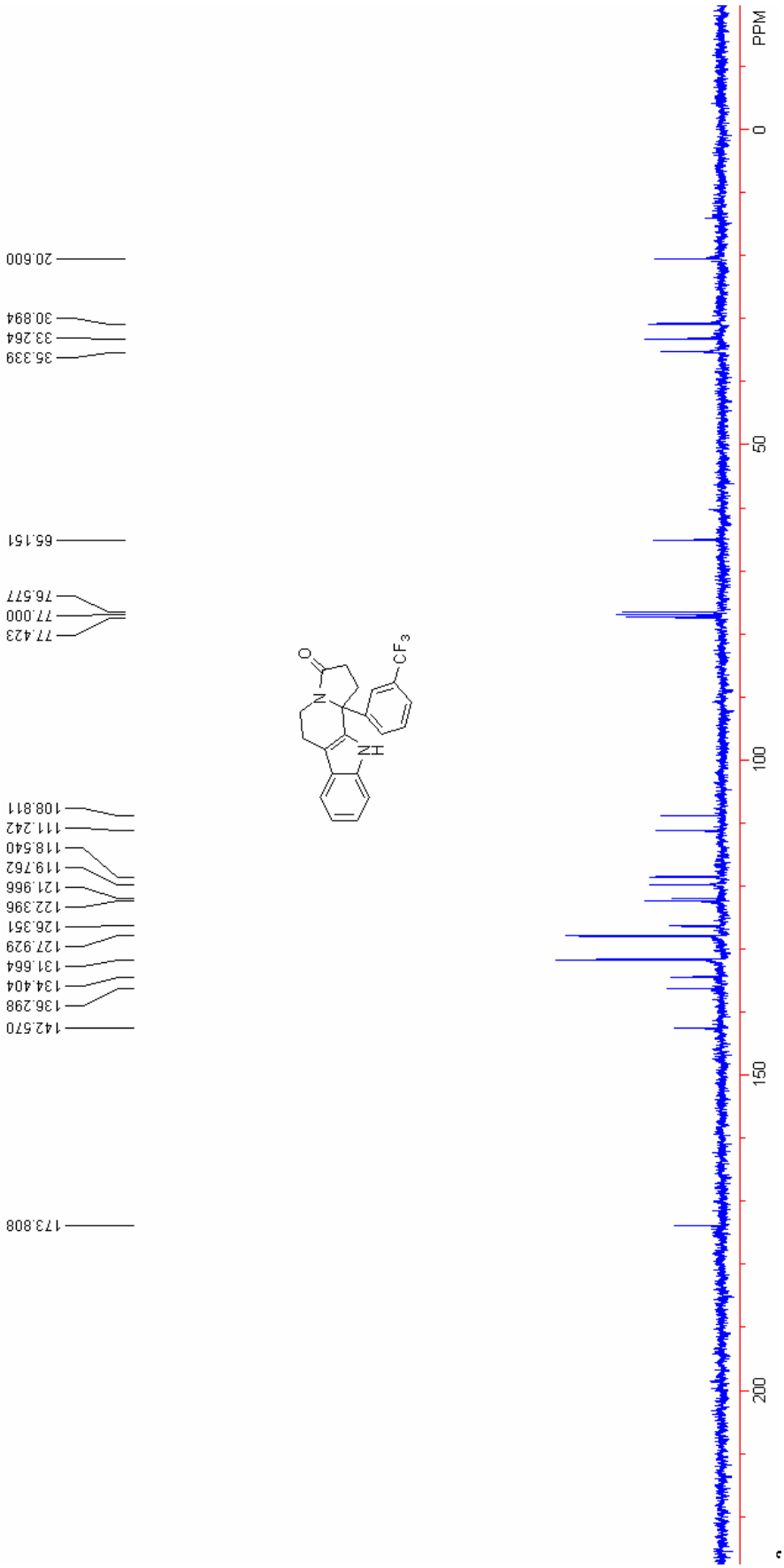
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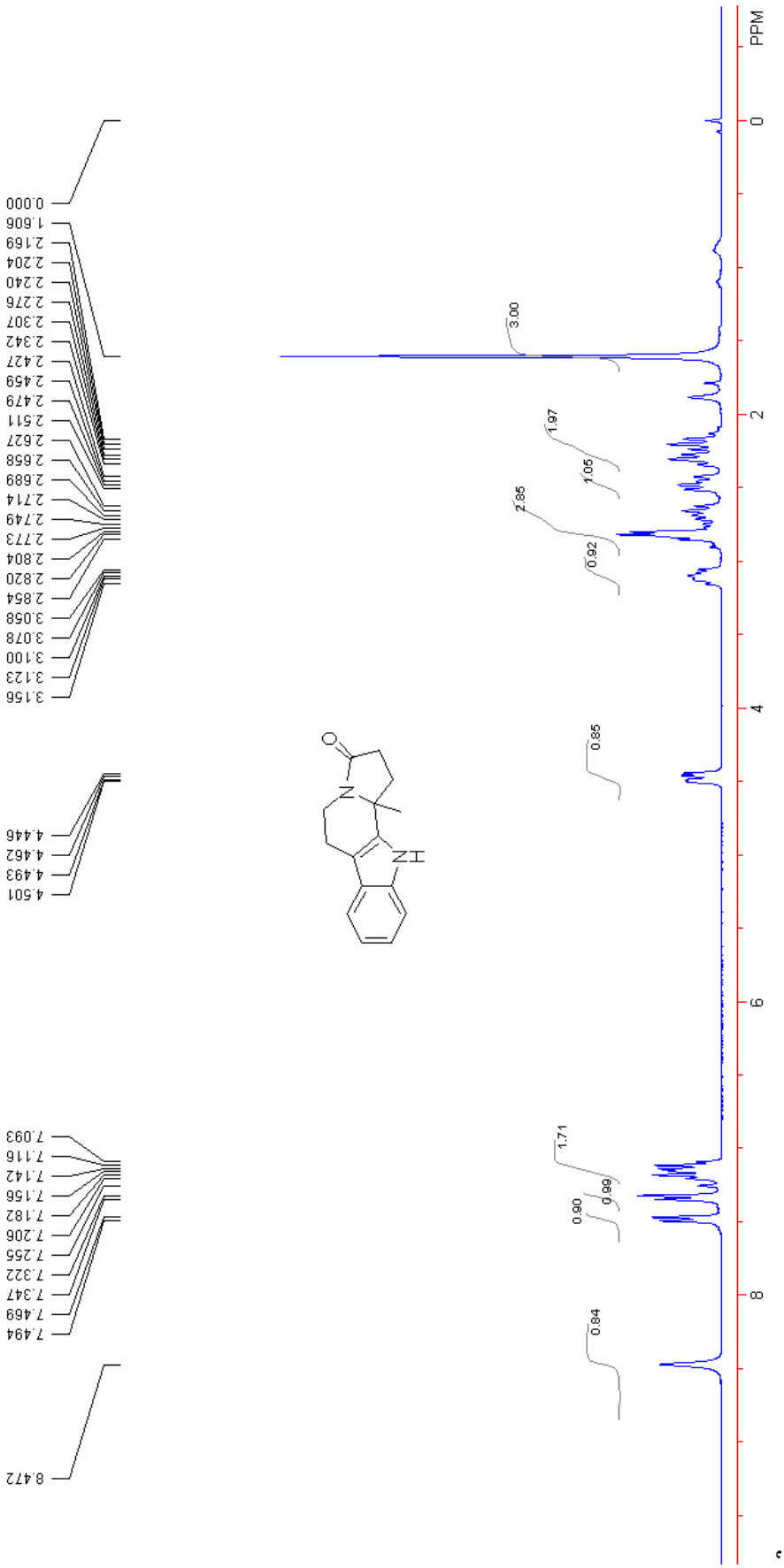
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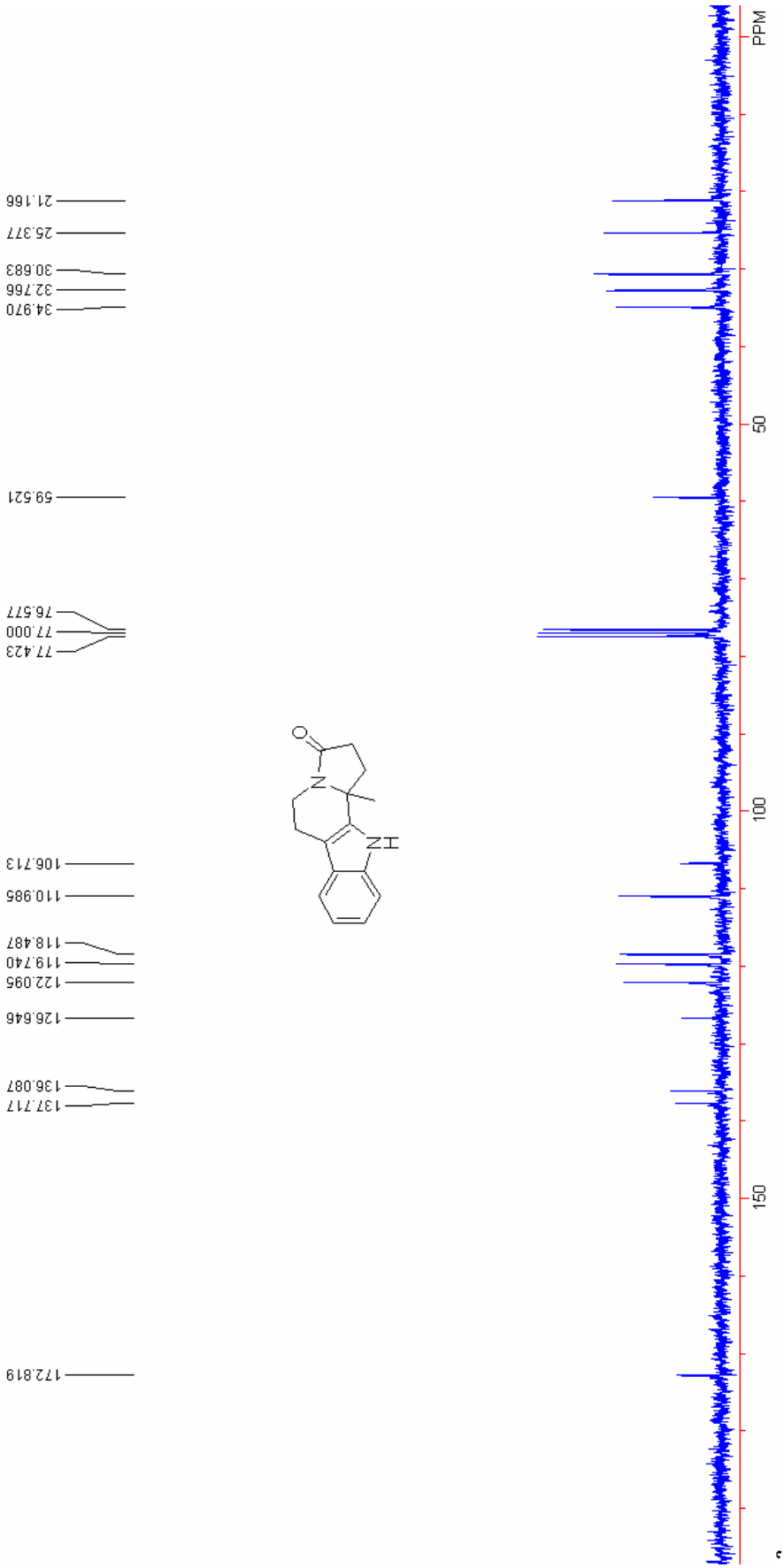
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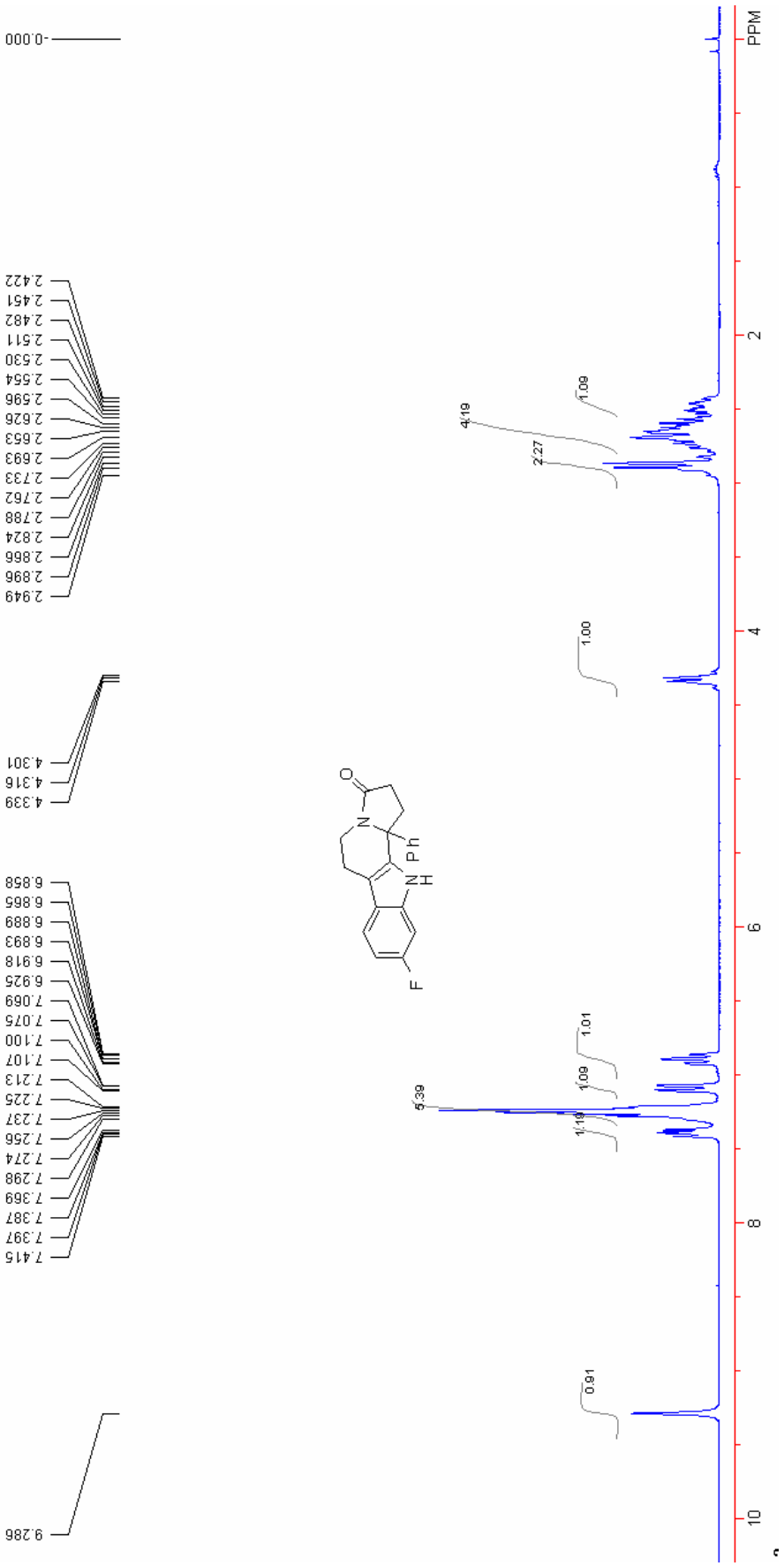
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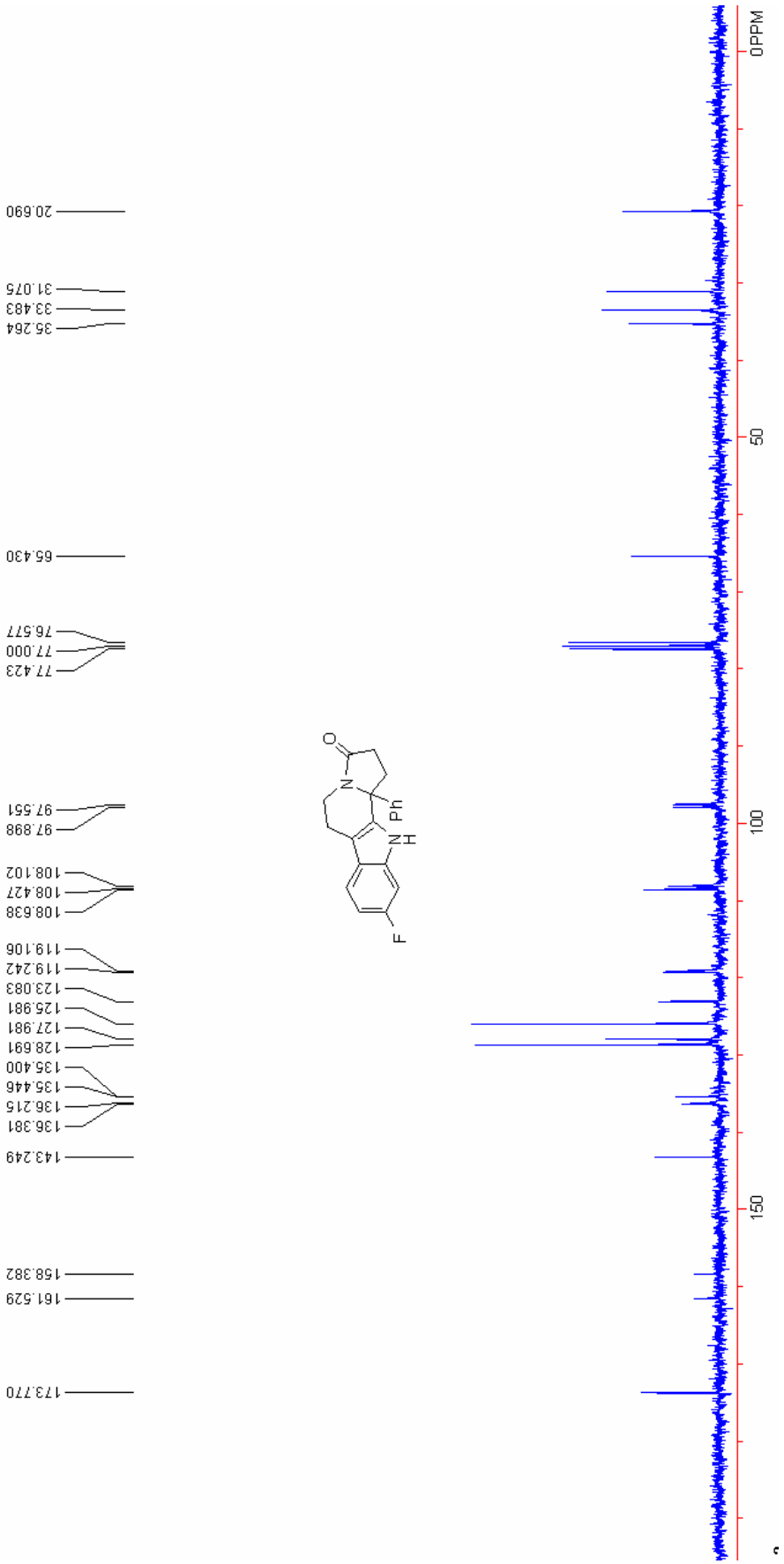
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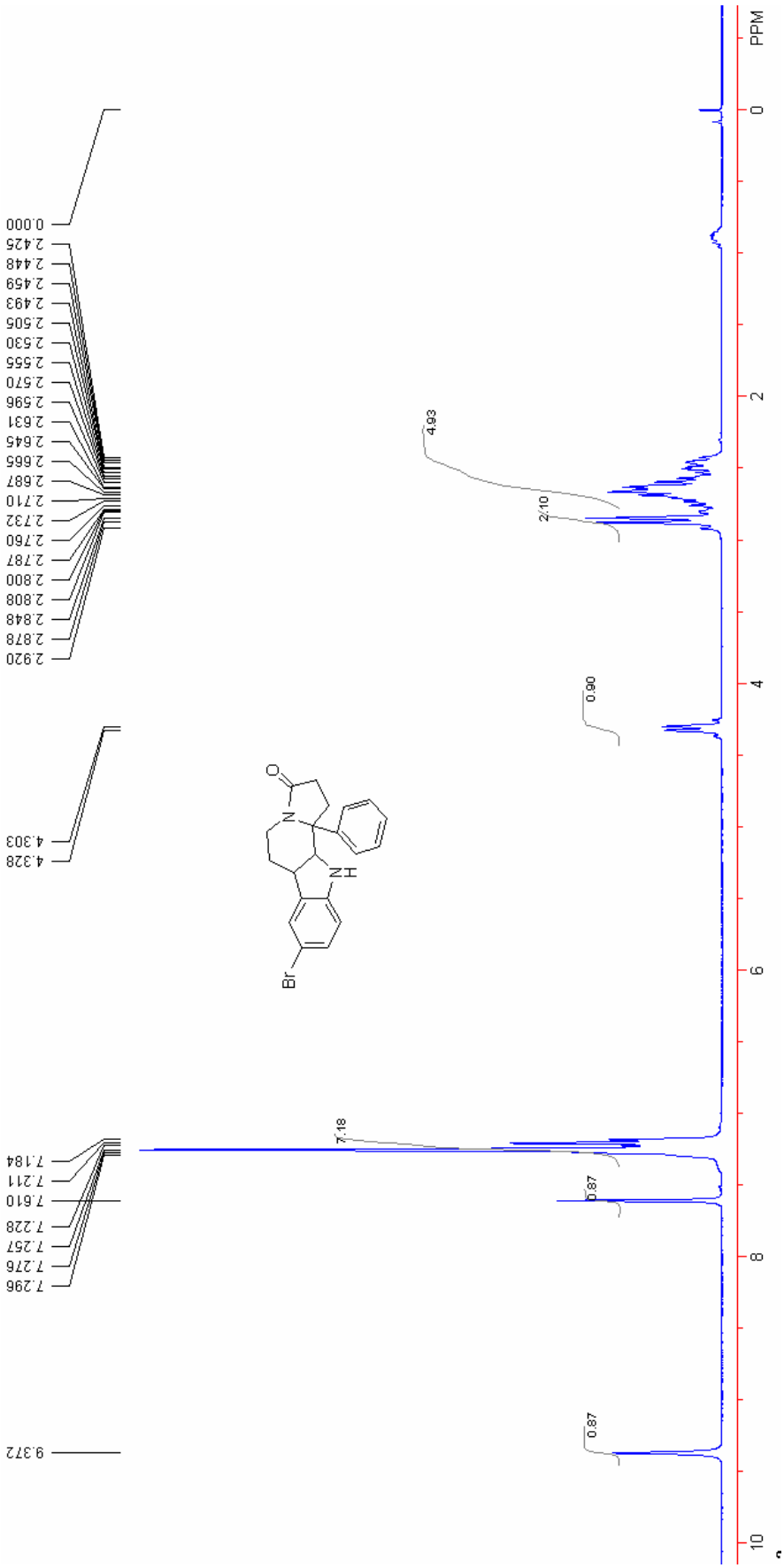
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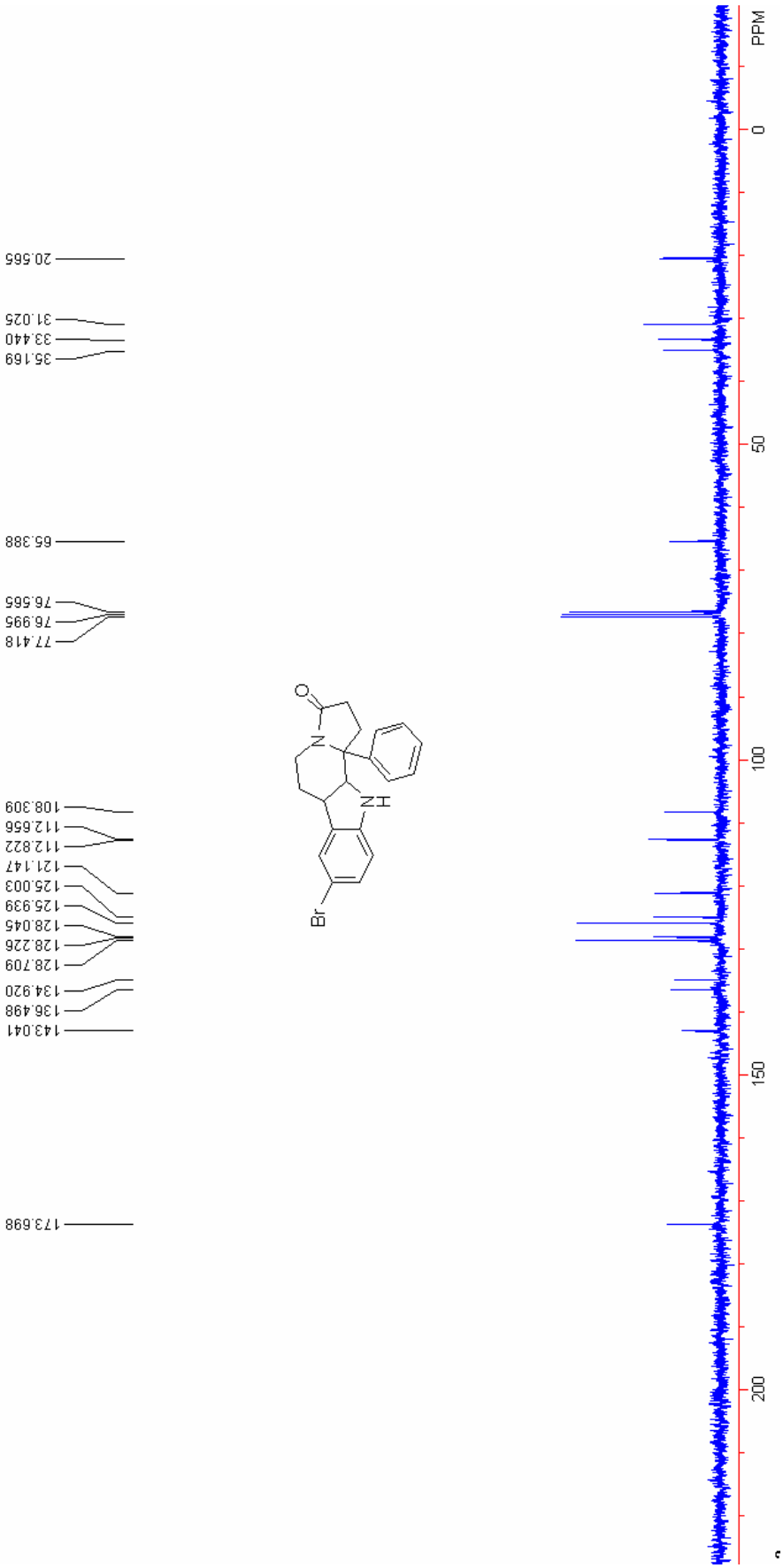
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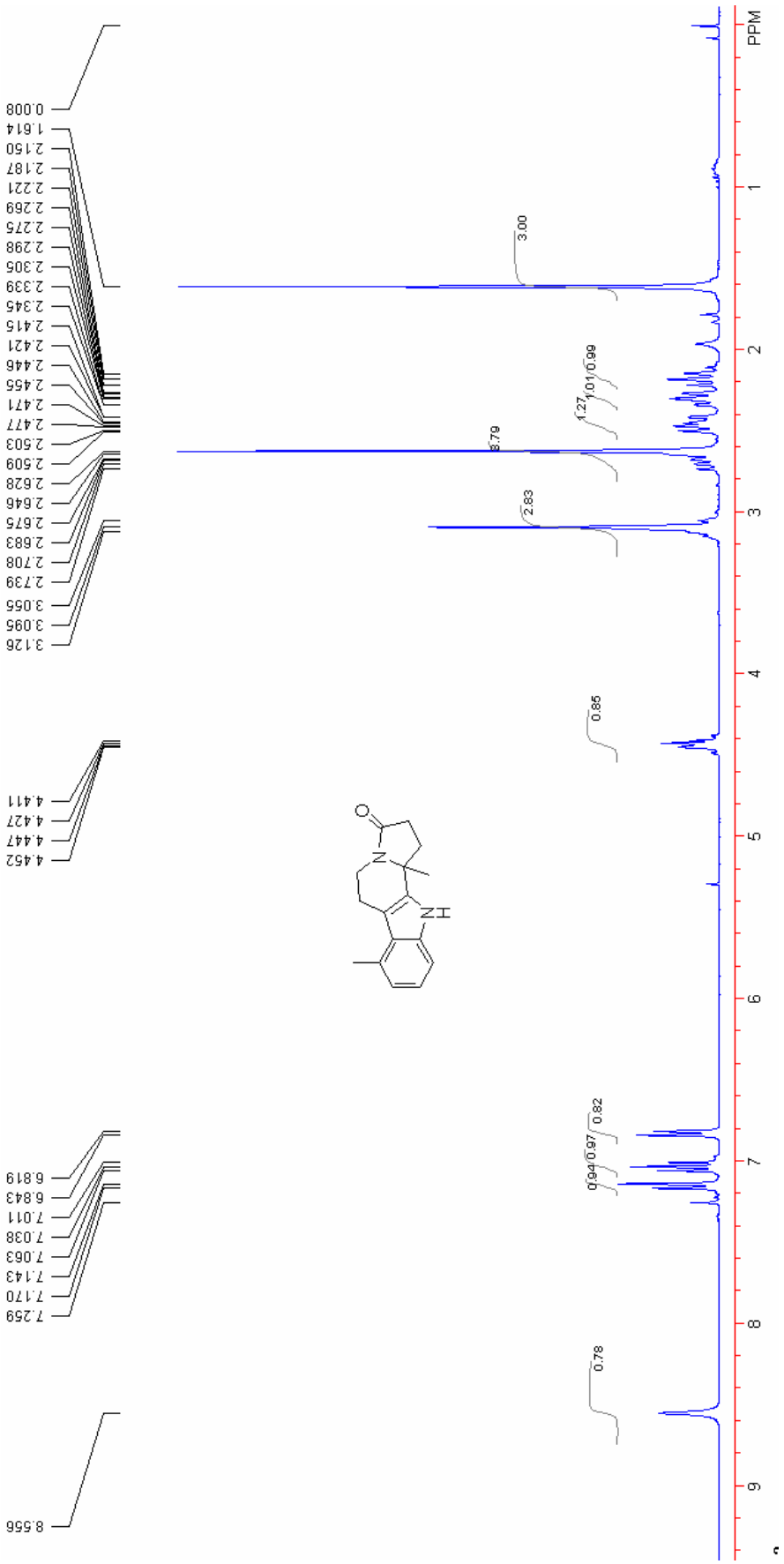
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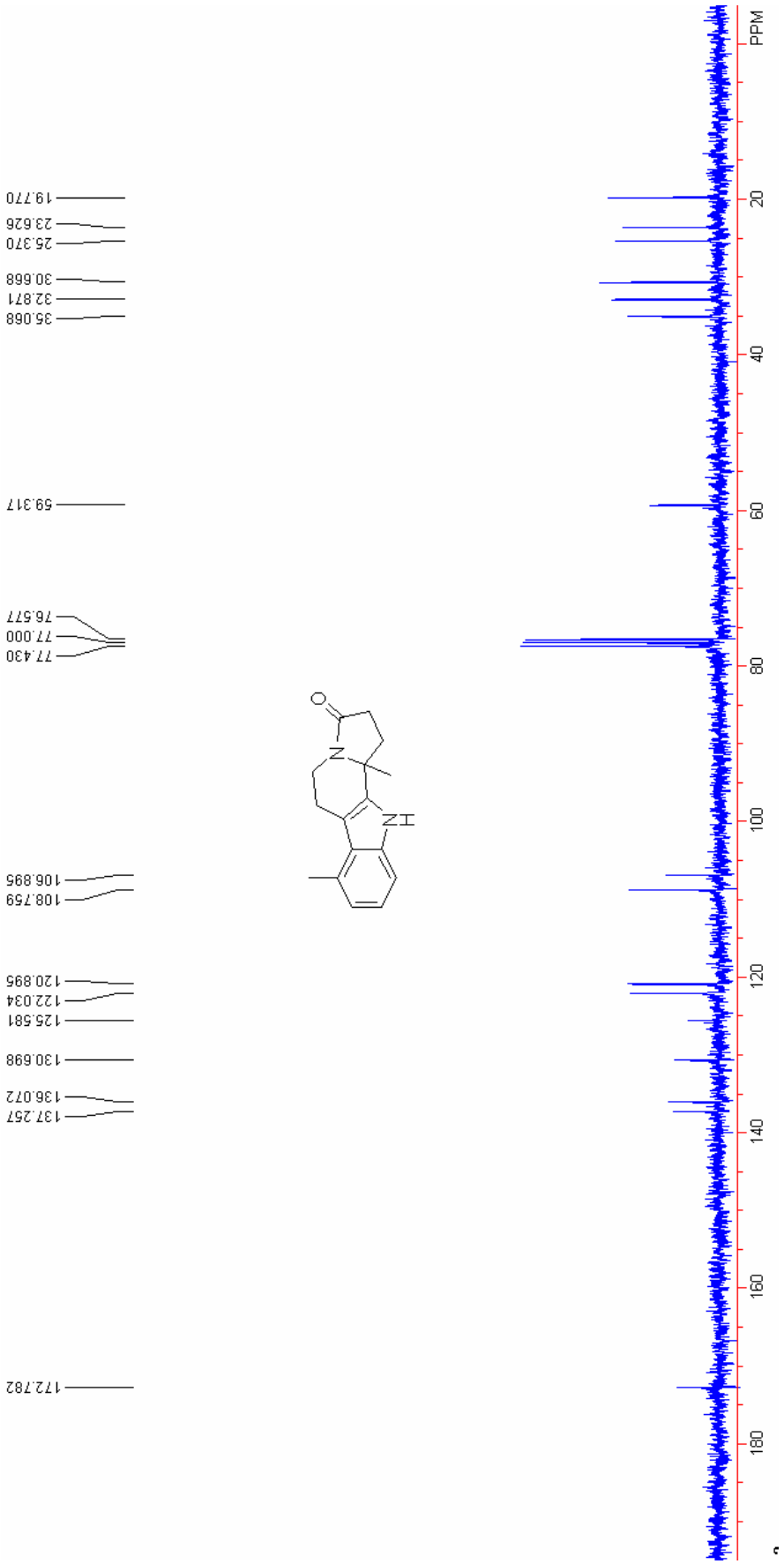
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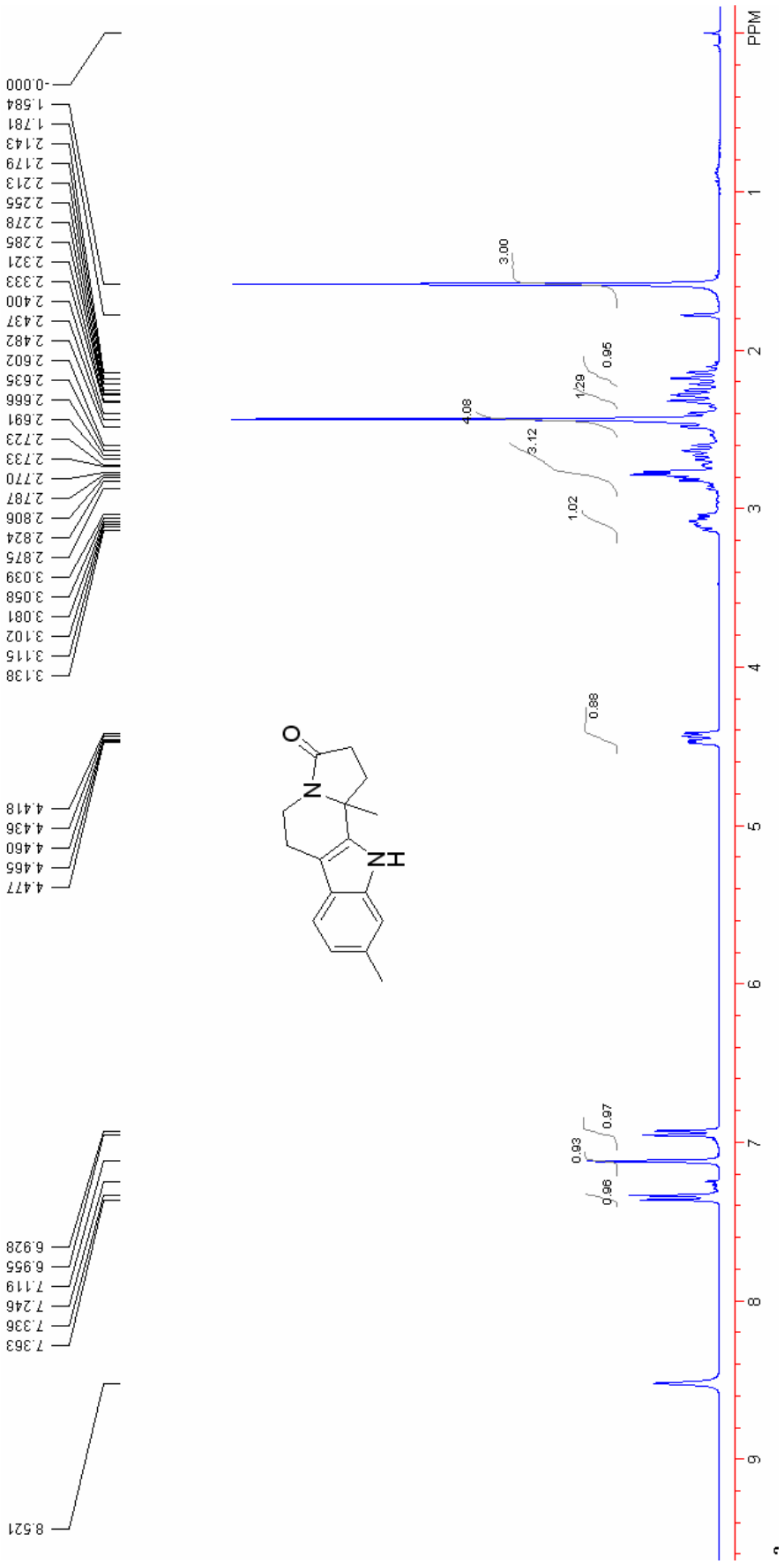
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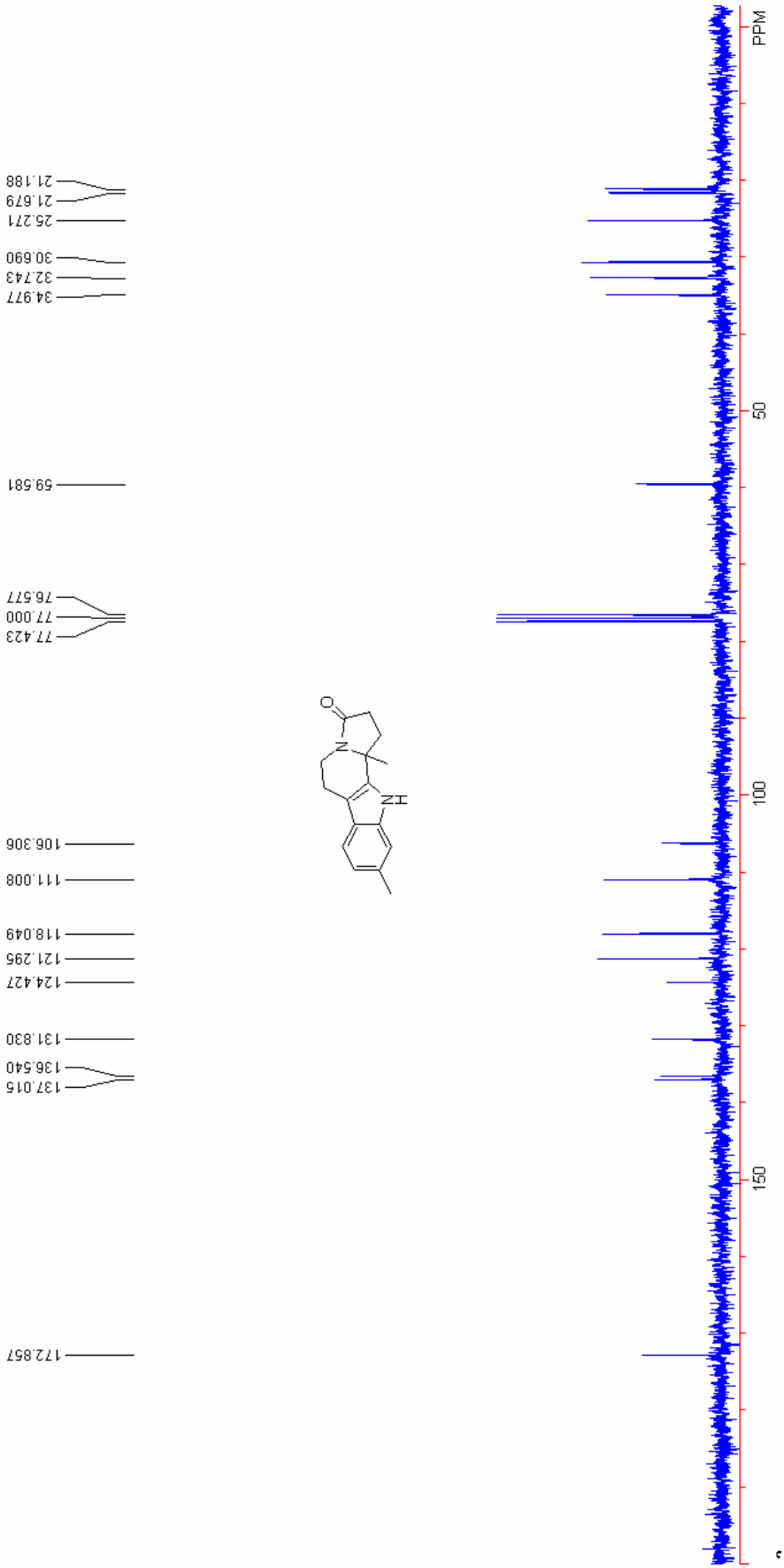
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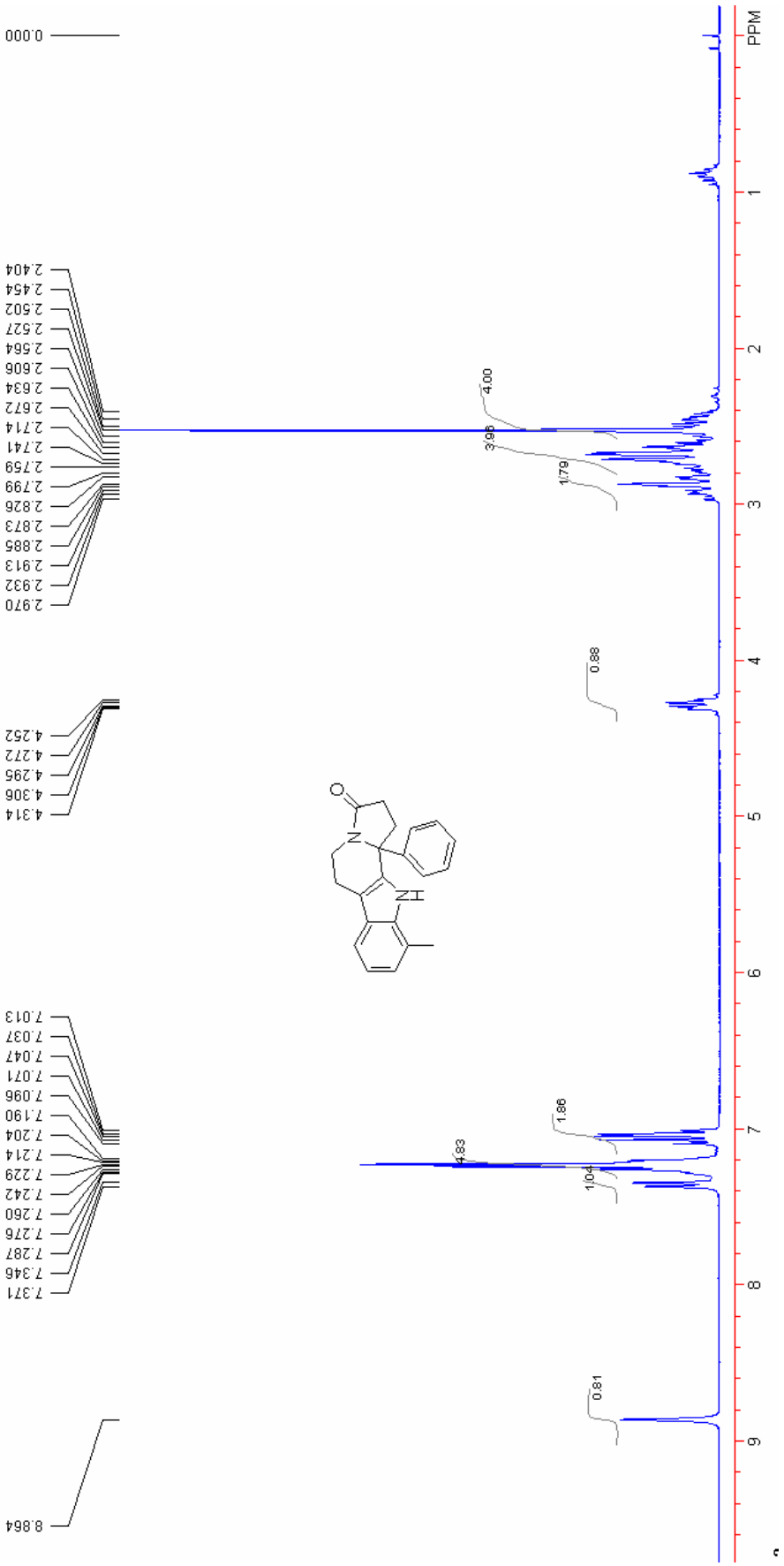
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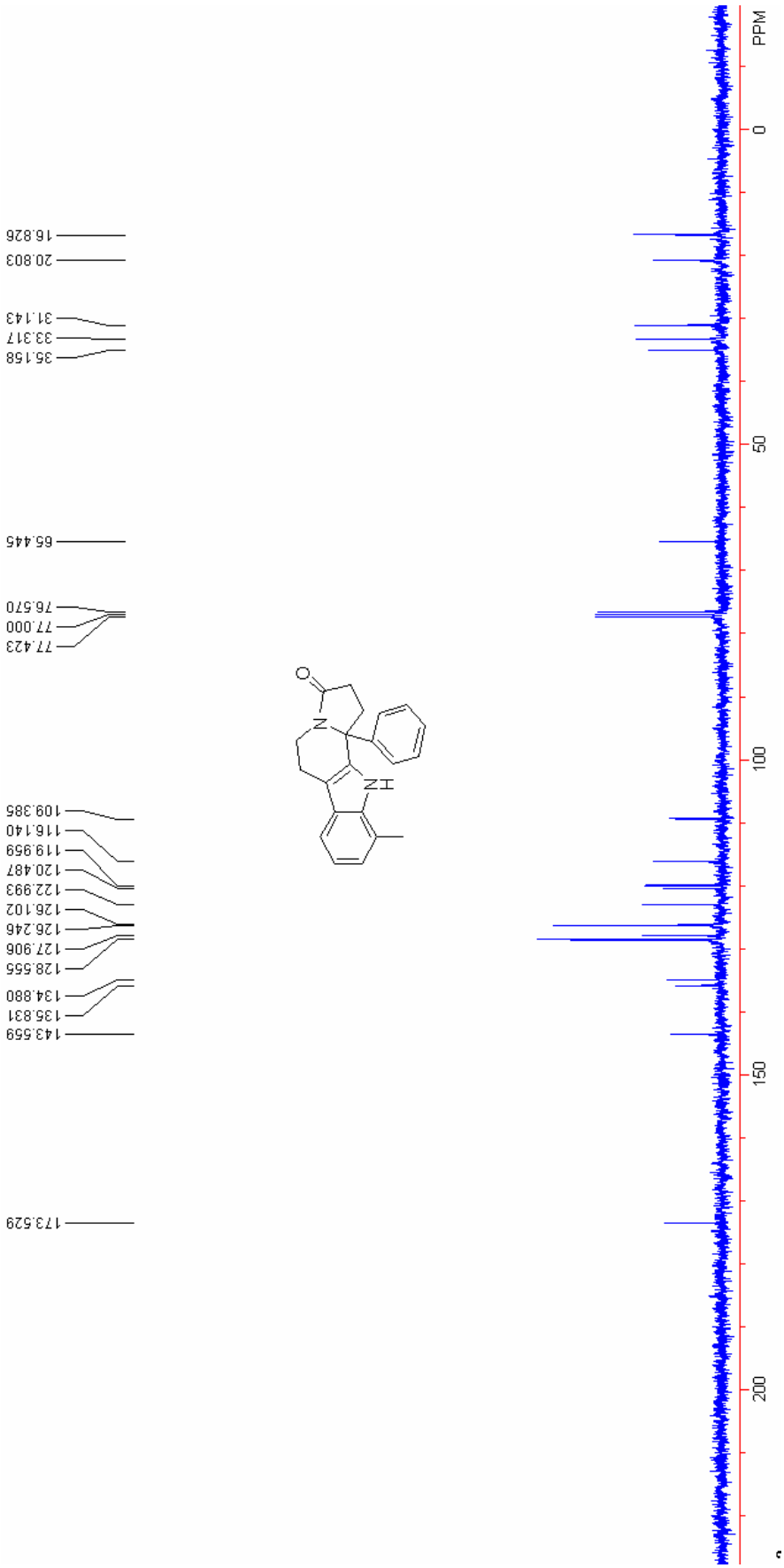
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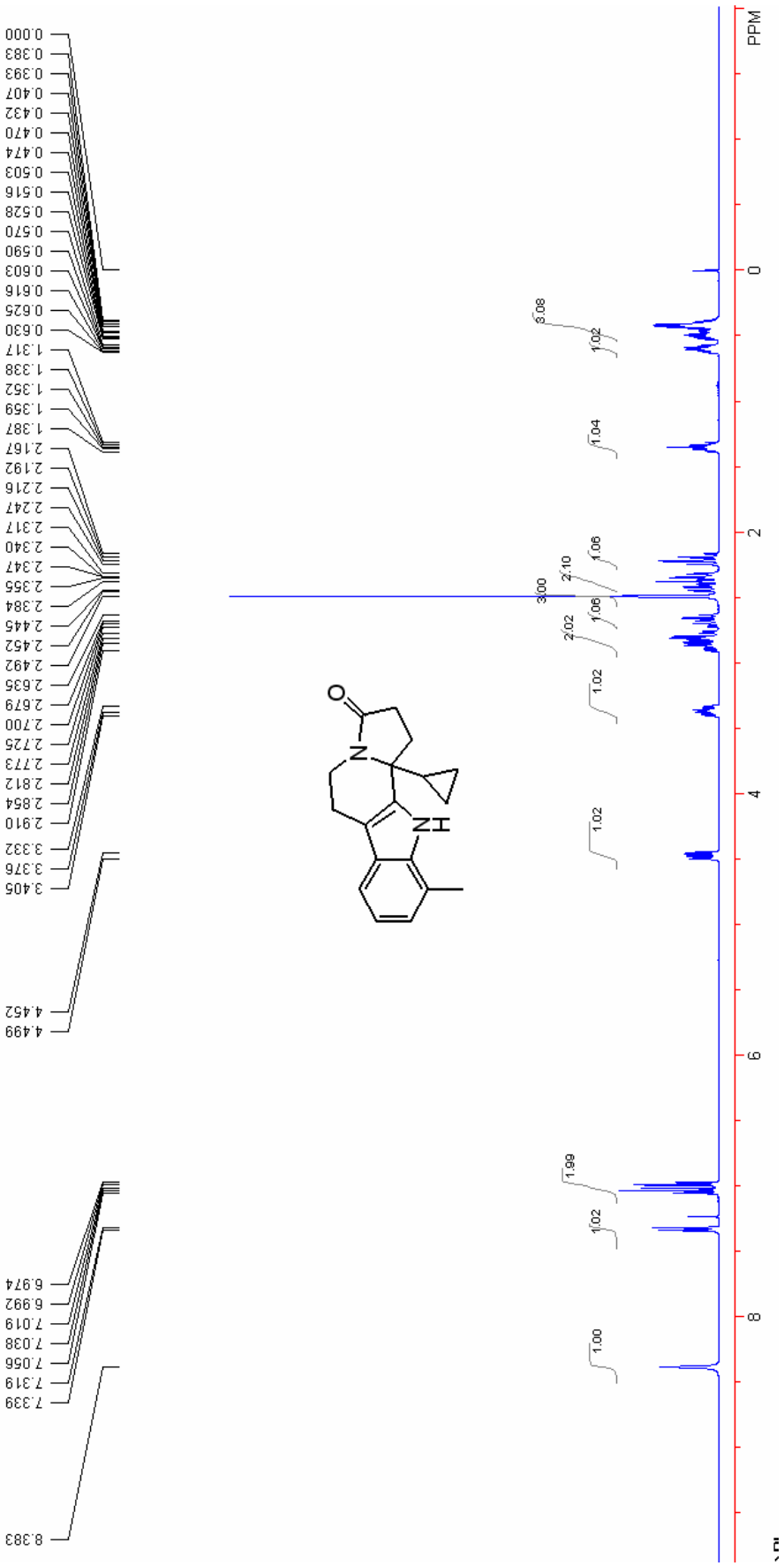
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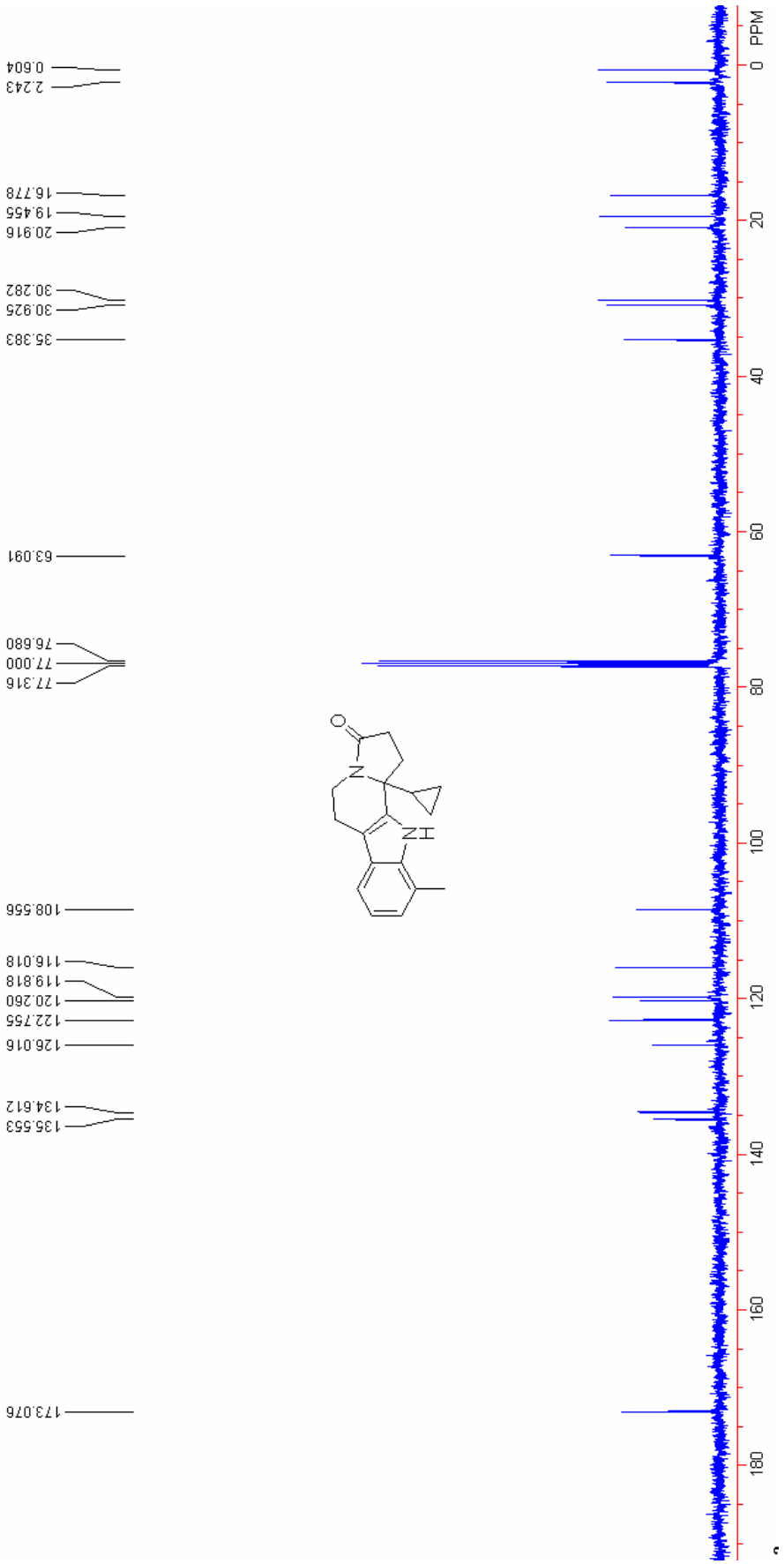
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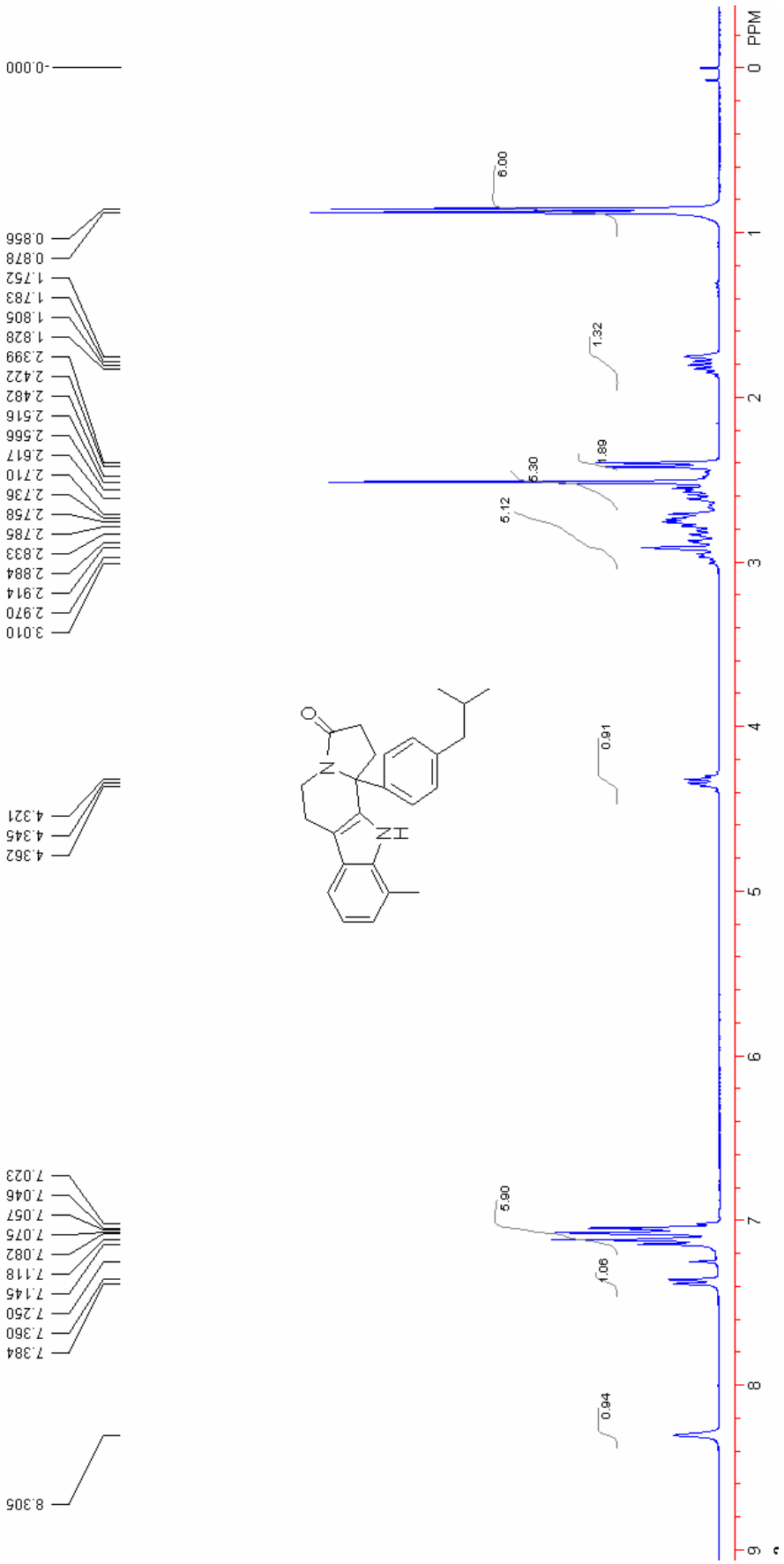
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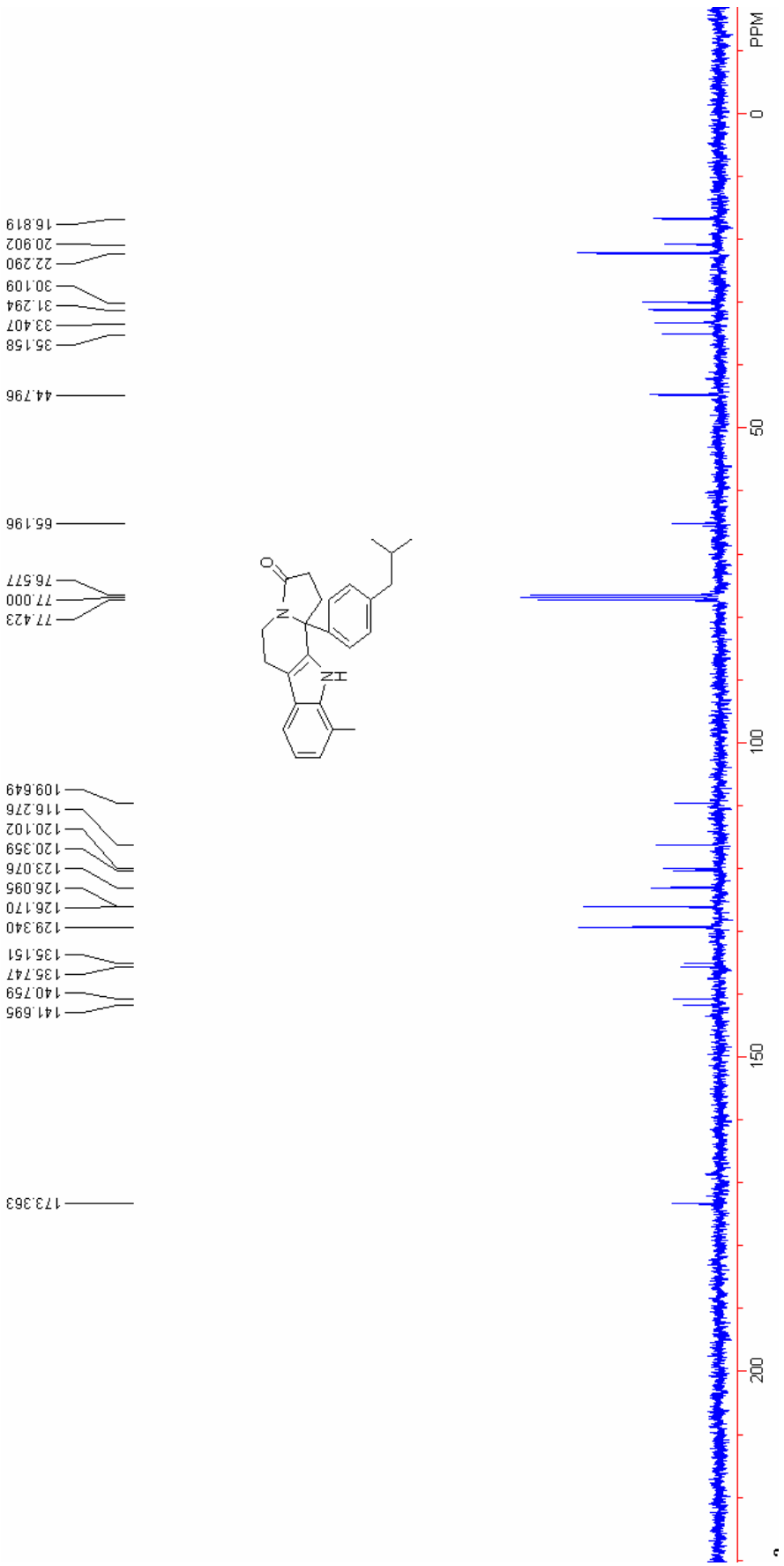
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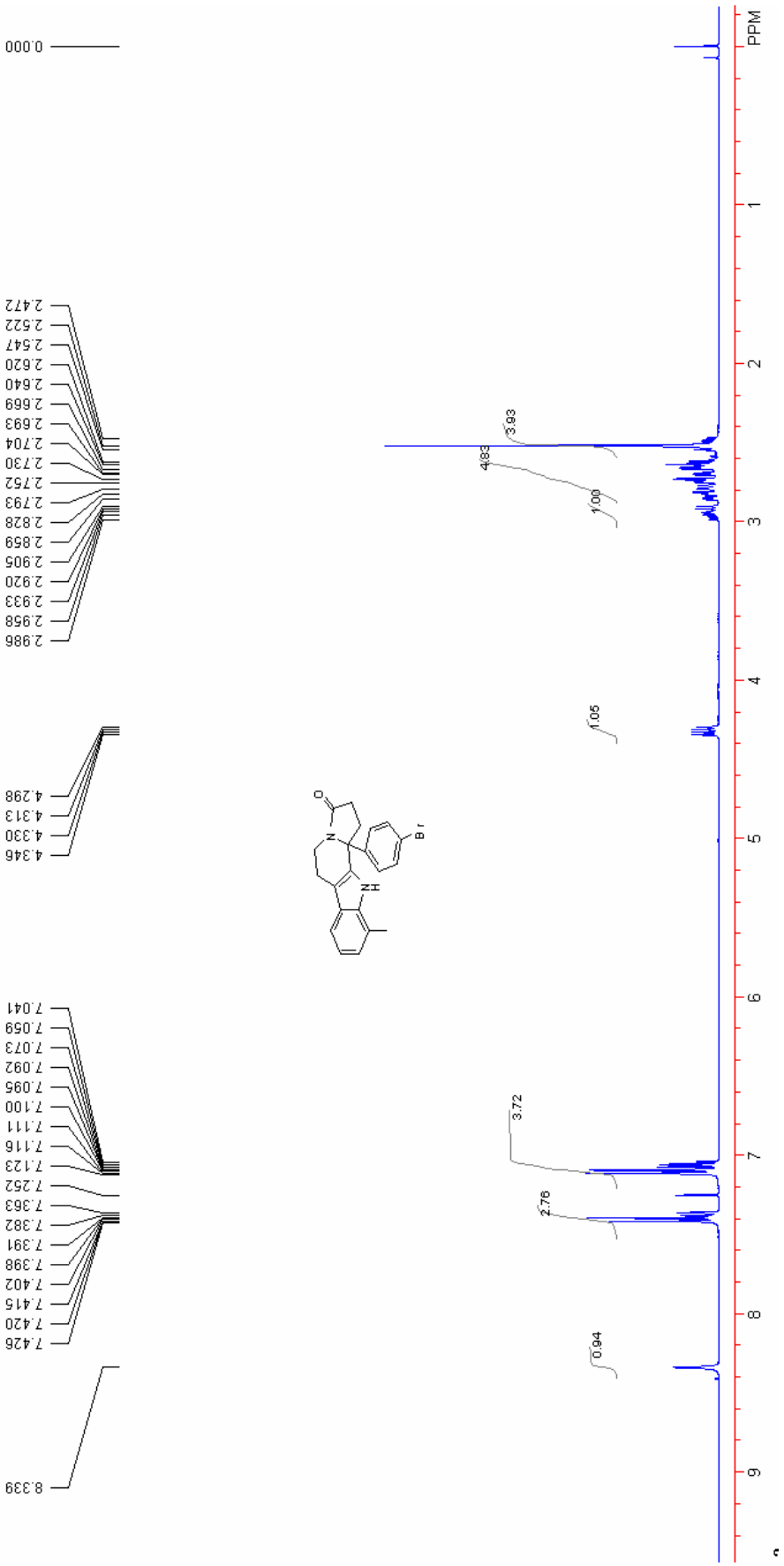
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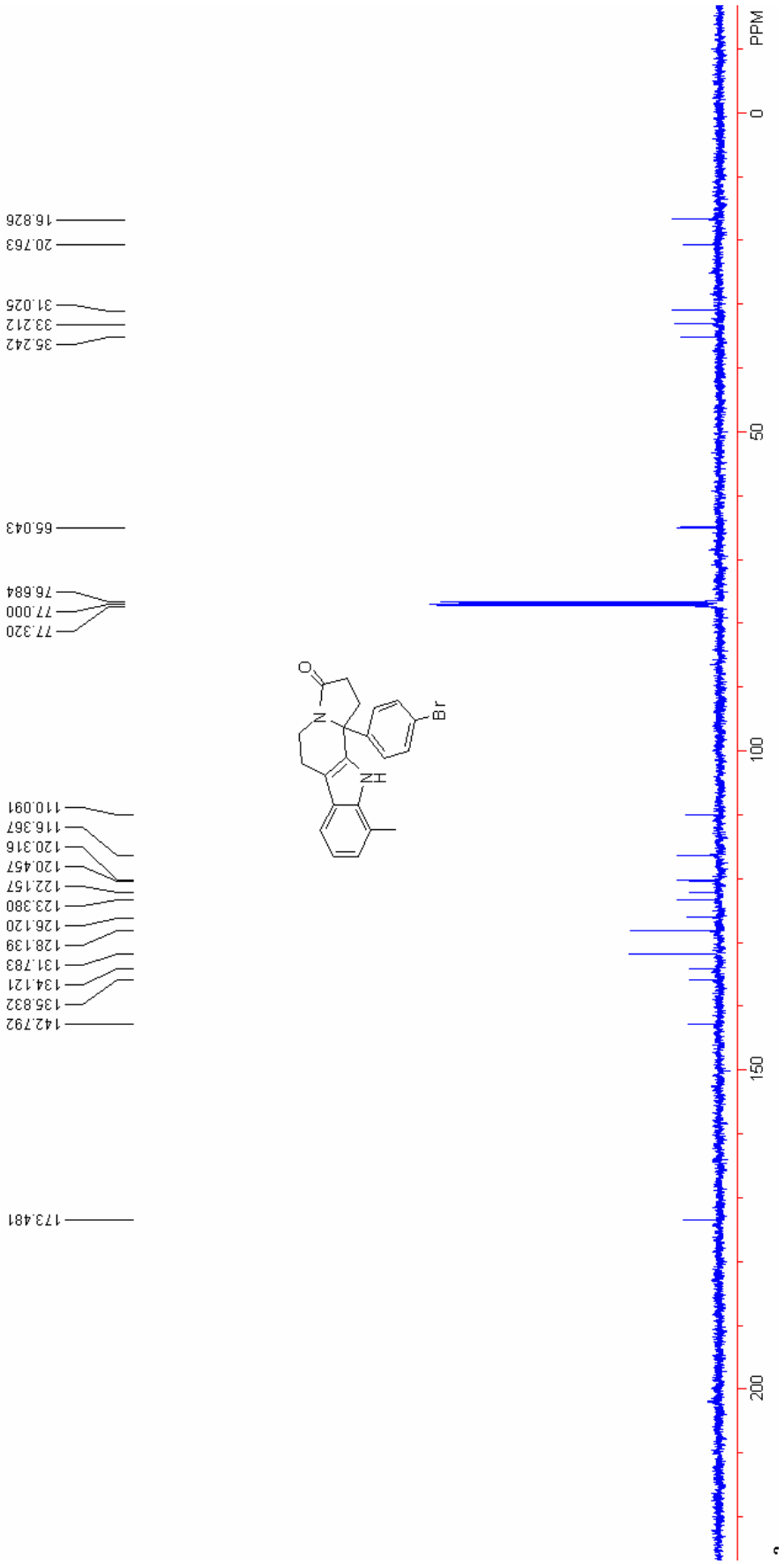
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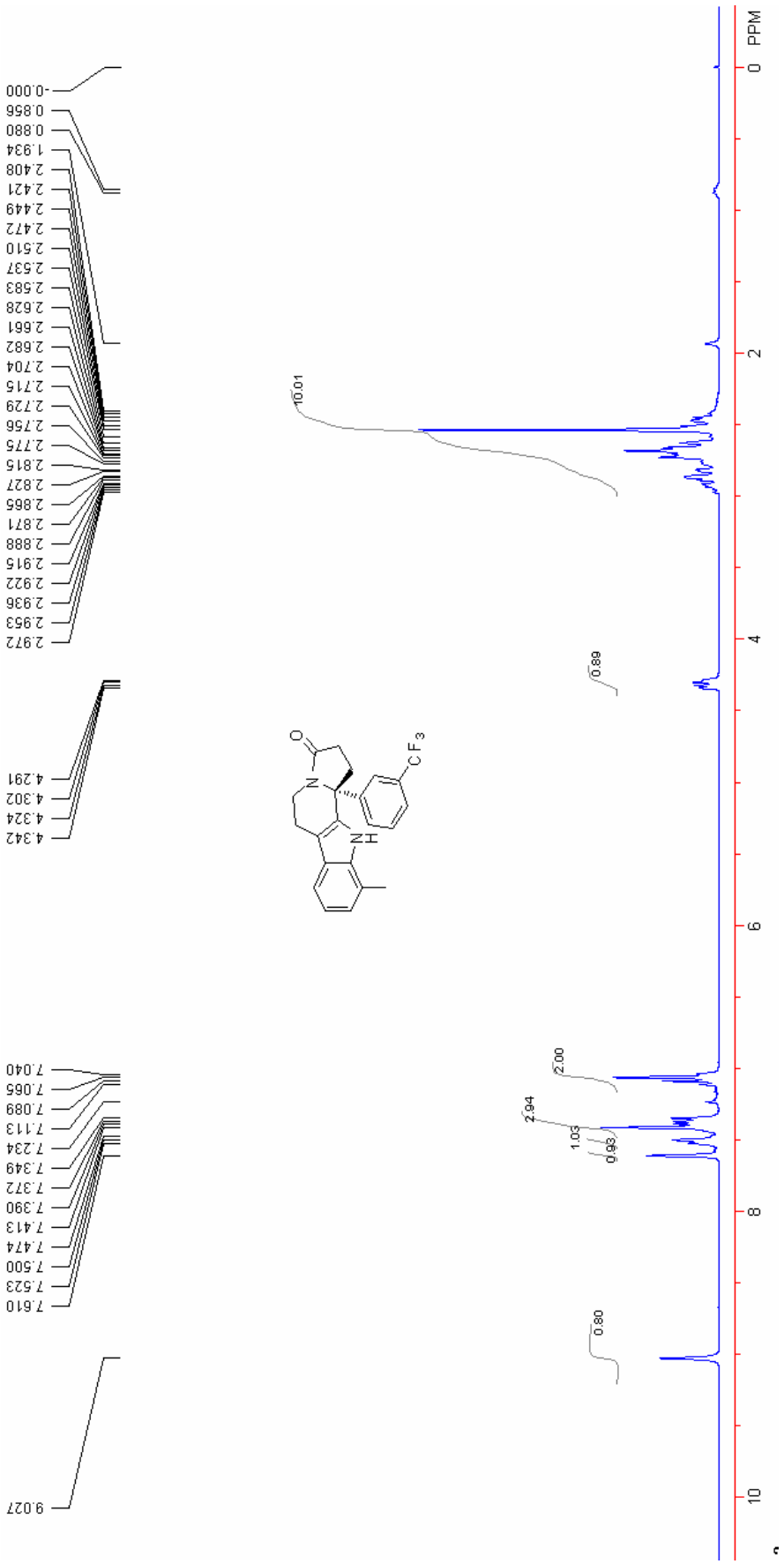
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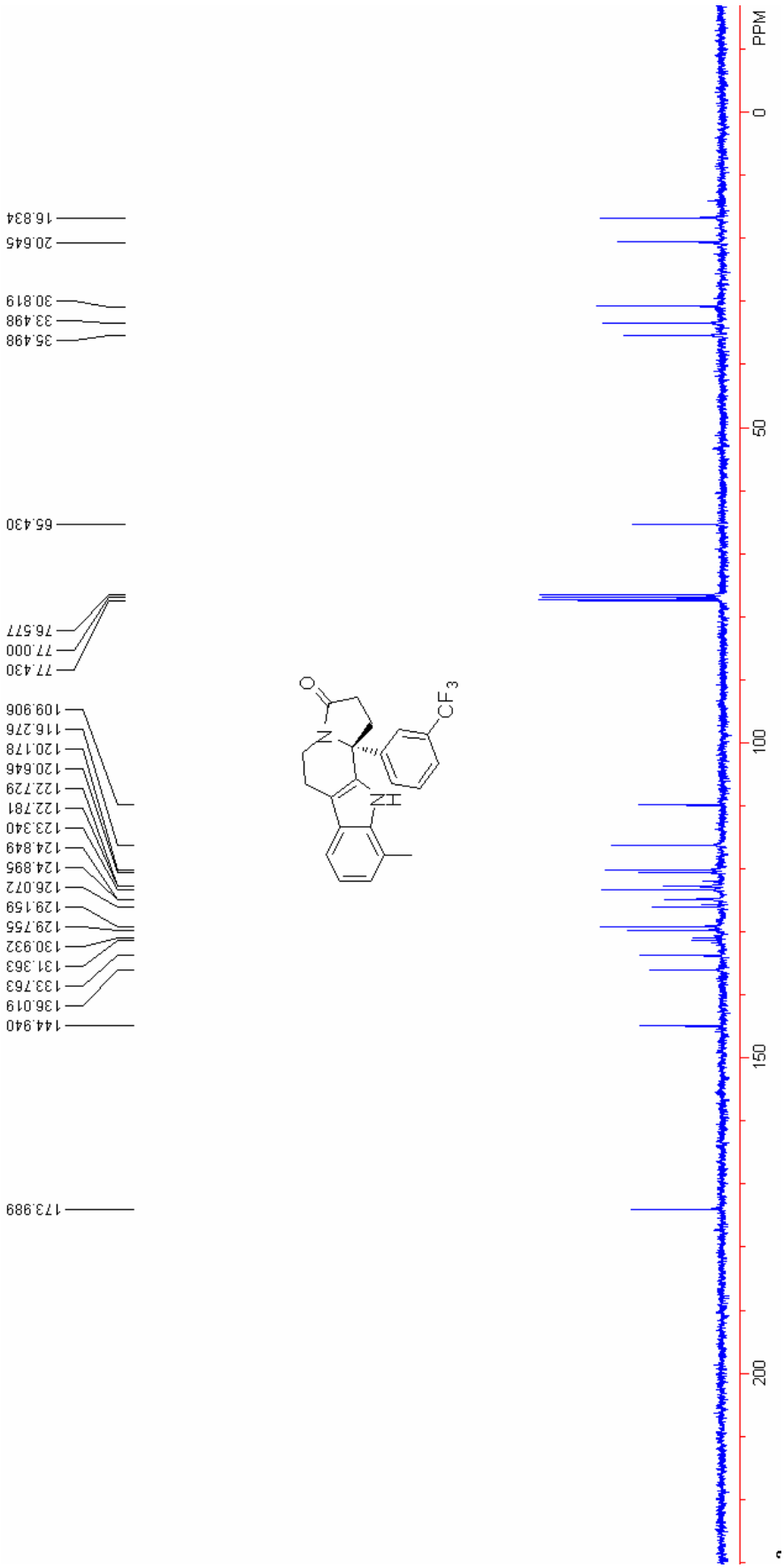
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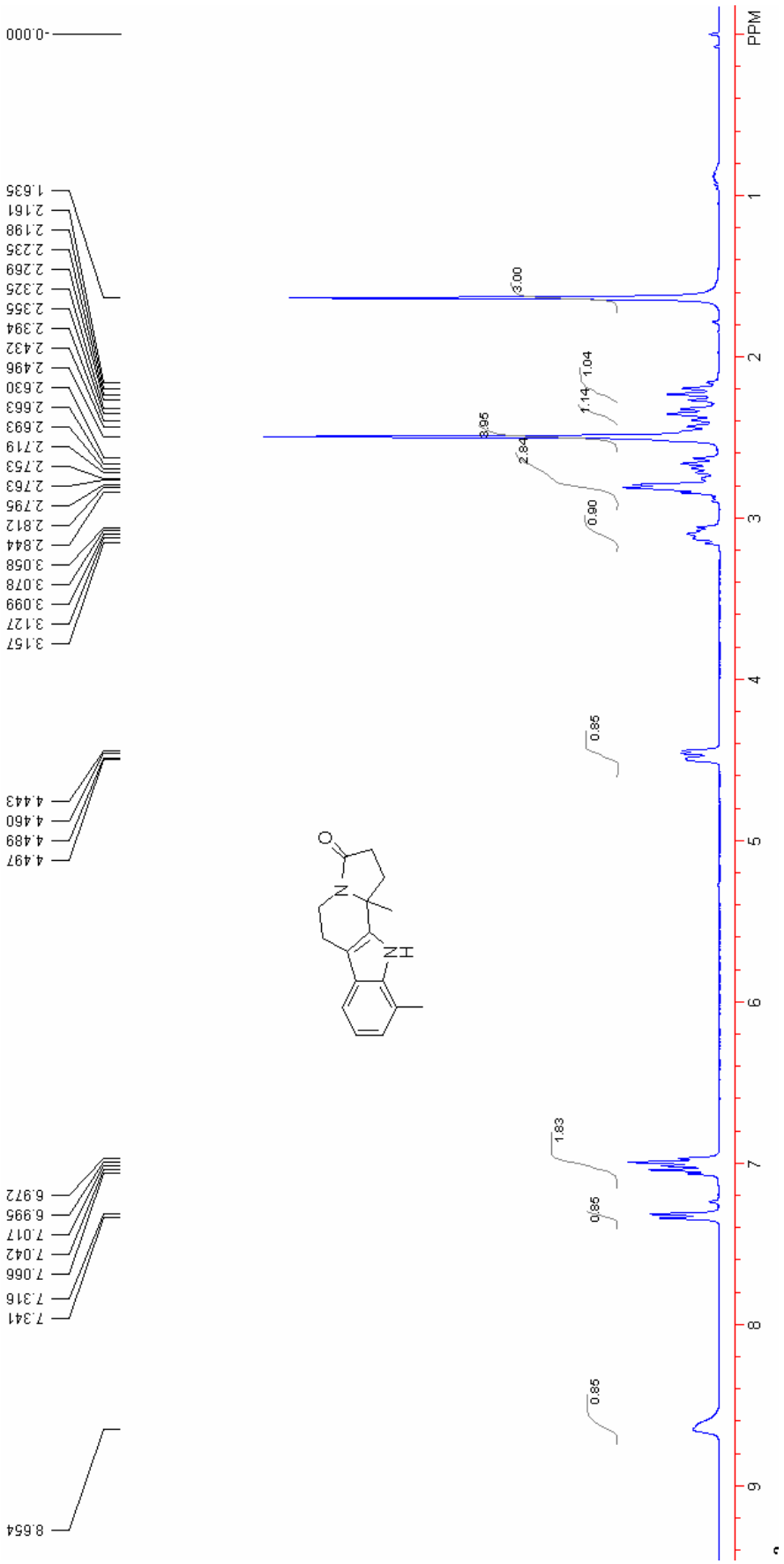
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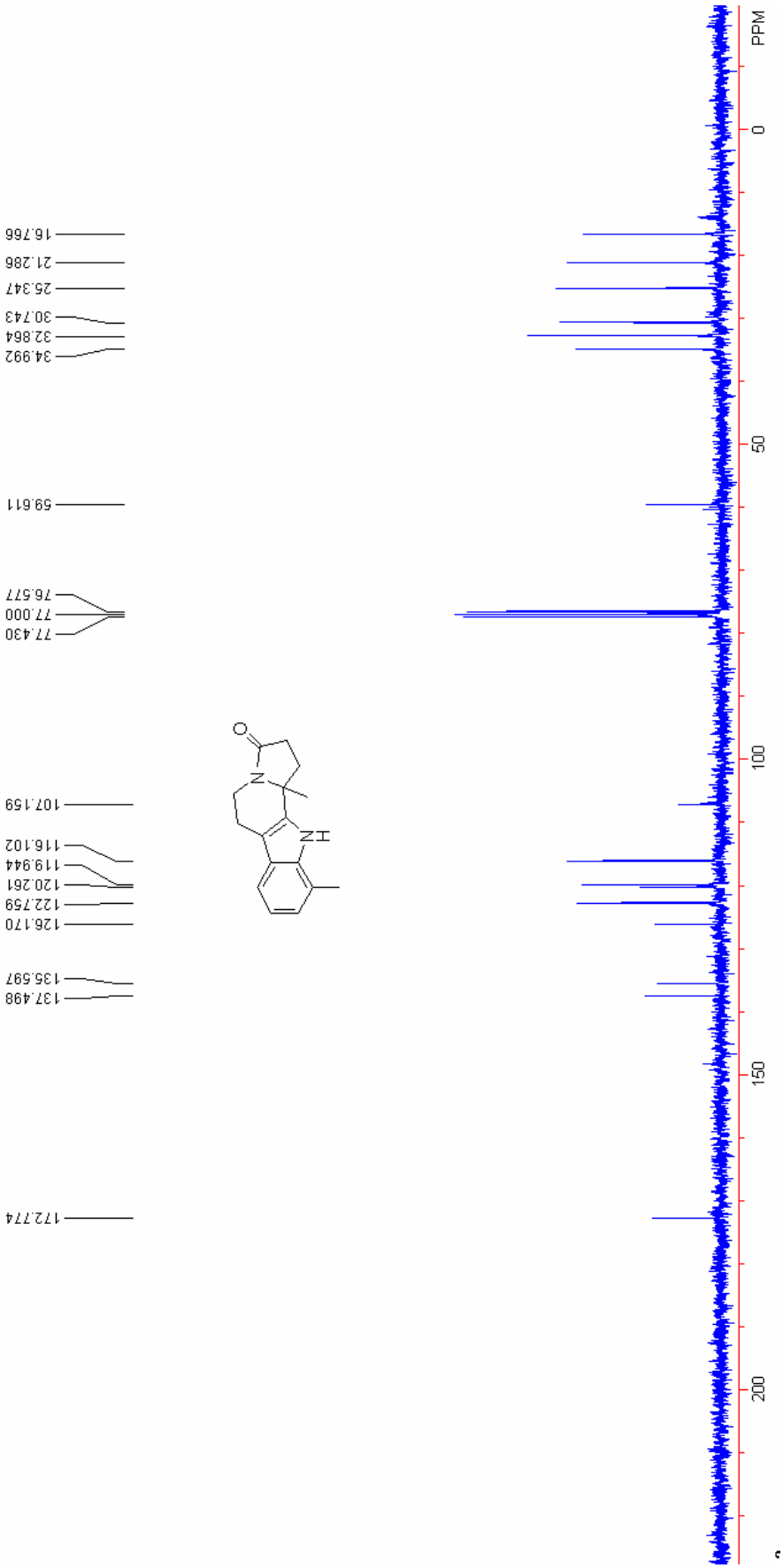
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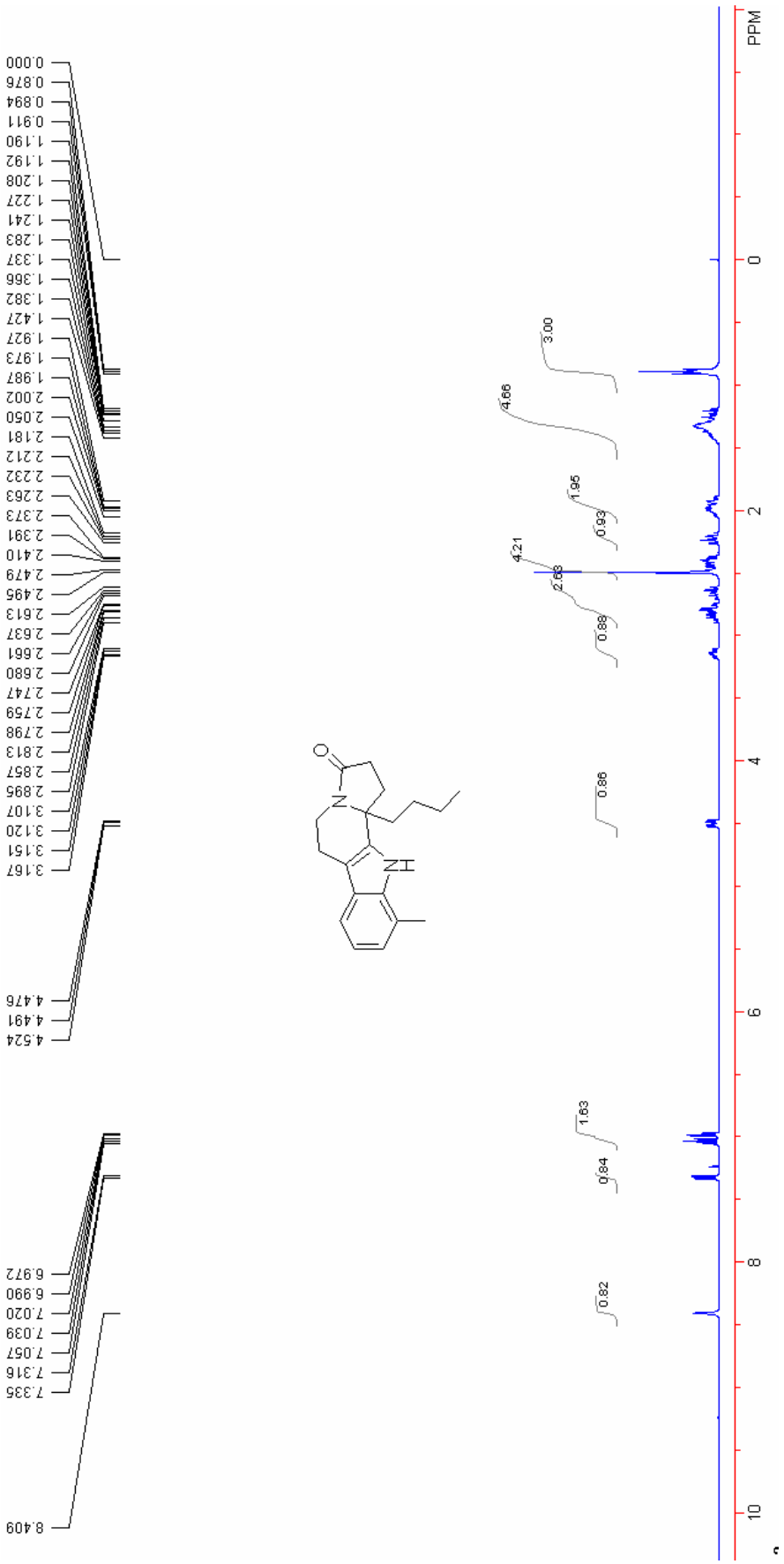
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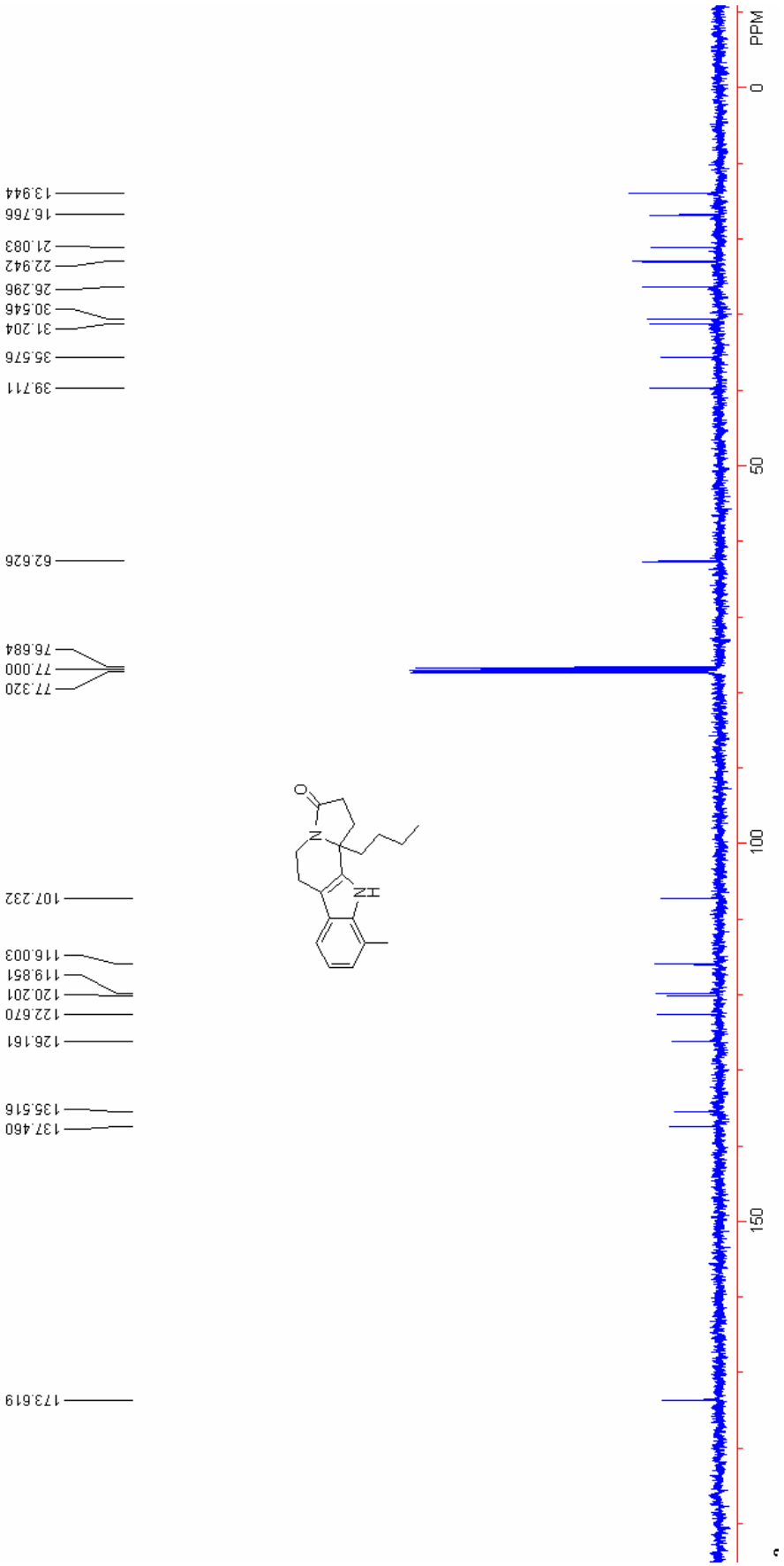
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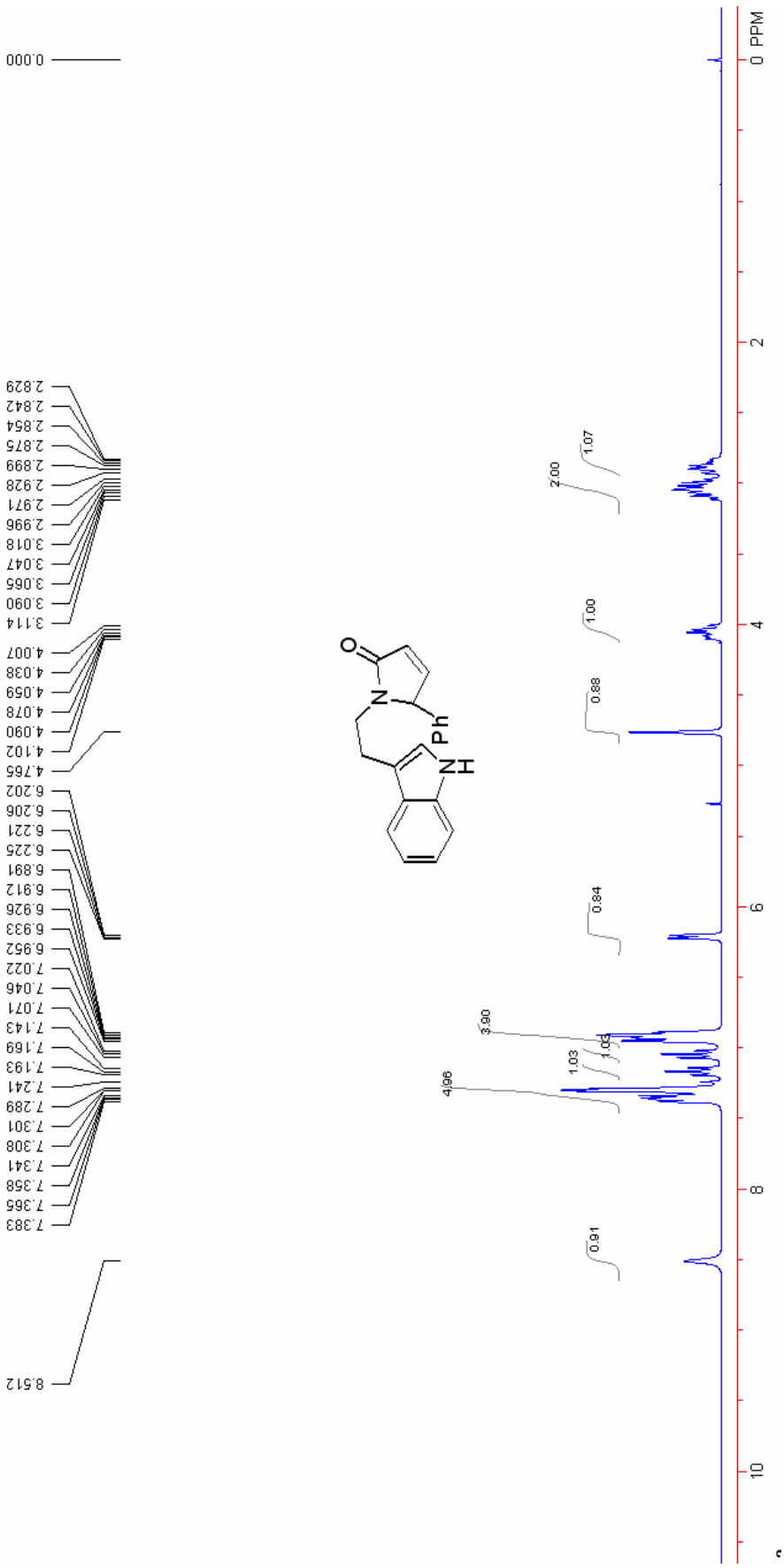
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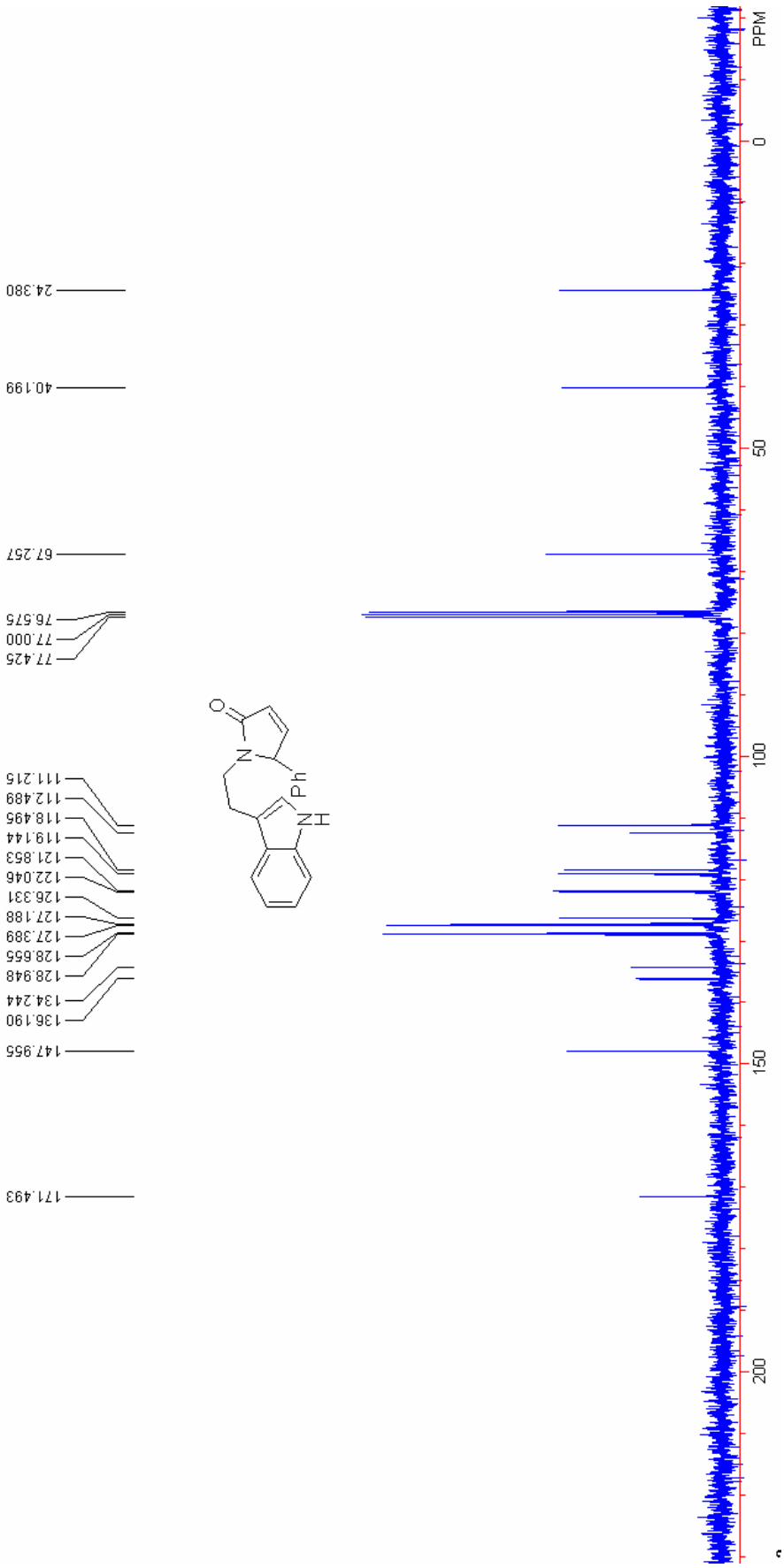
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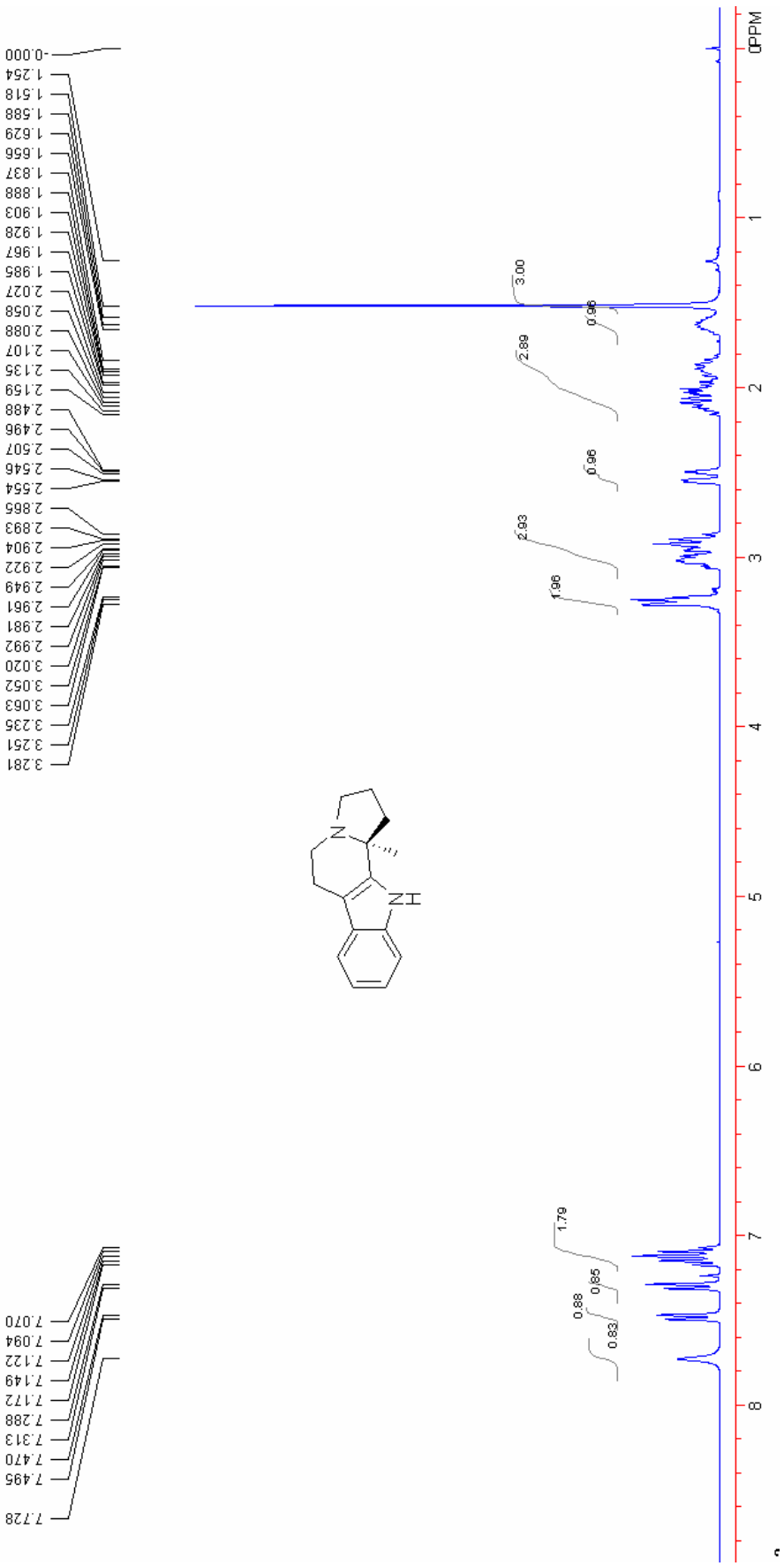
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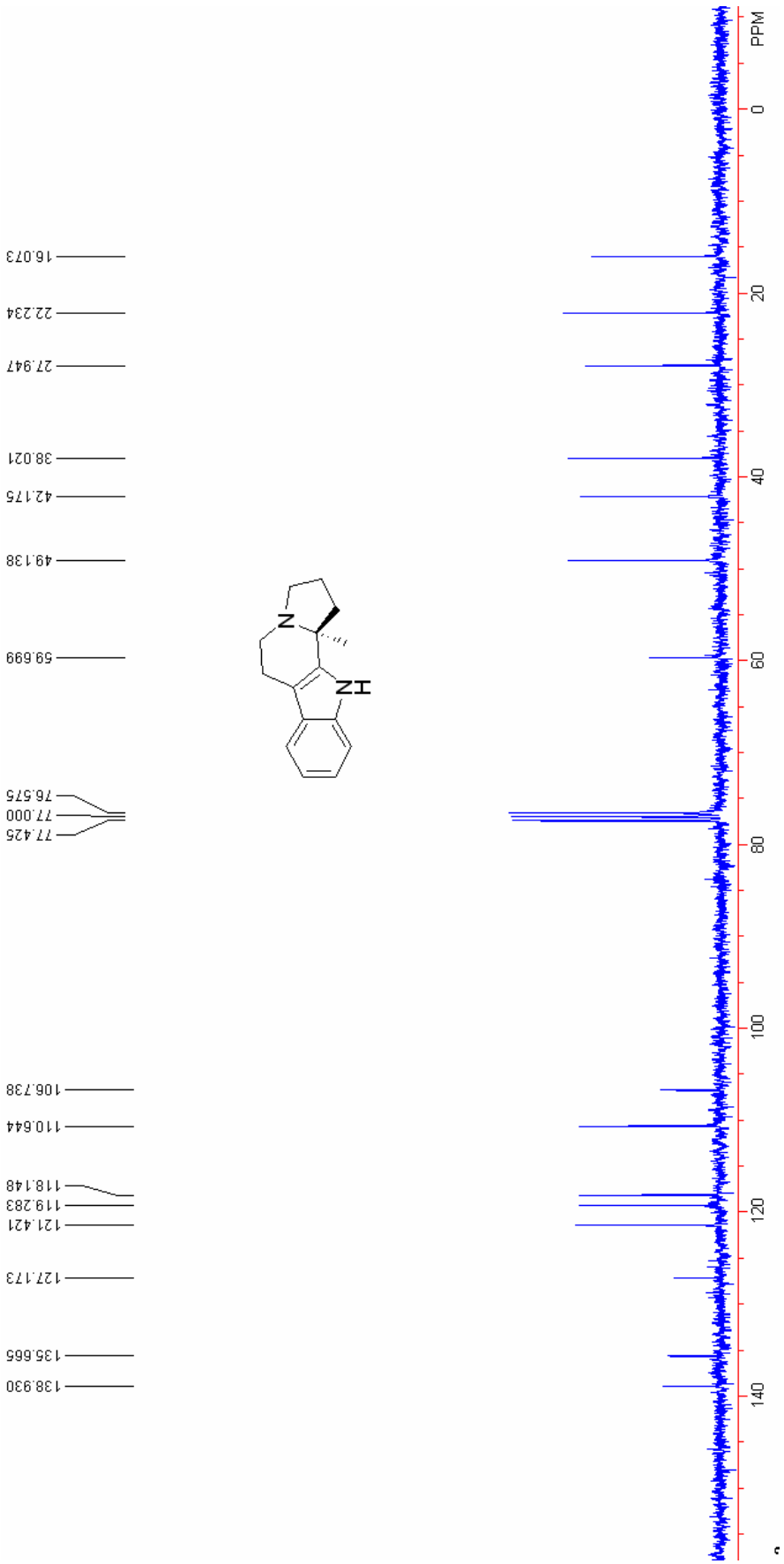
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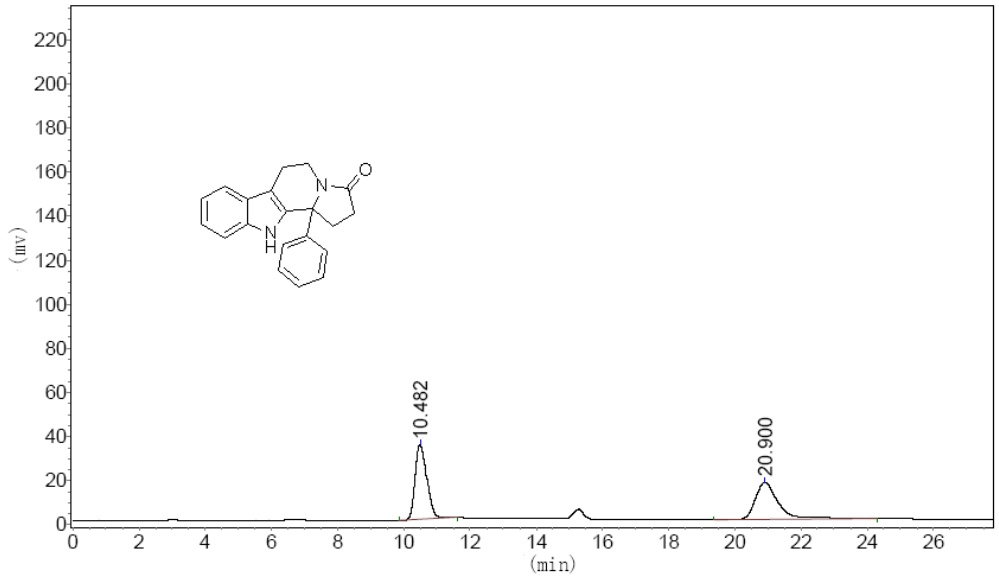
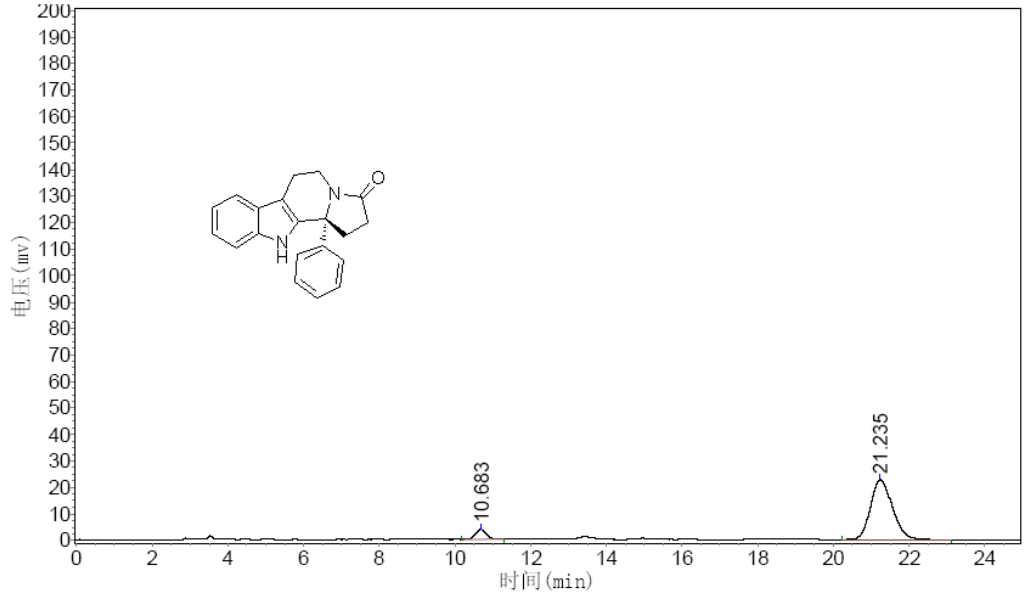
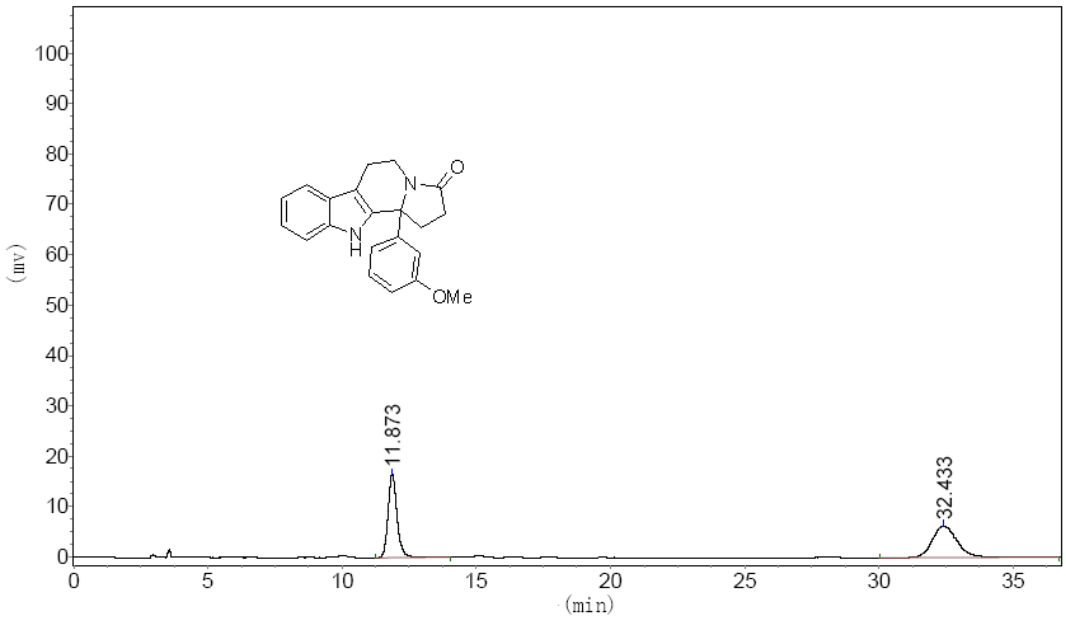
5. Copies of HPLC spectra of the compounds



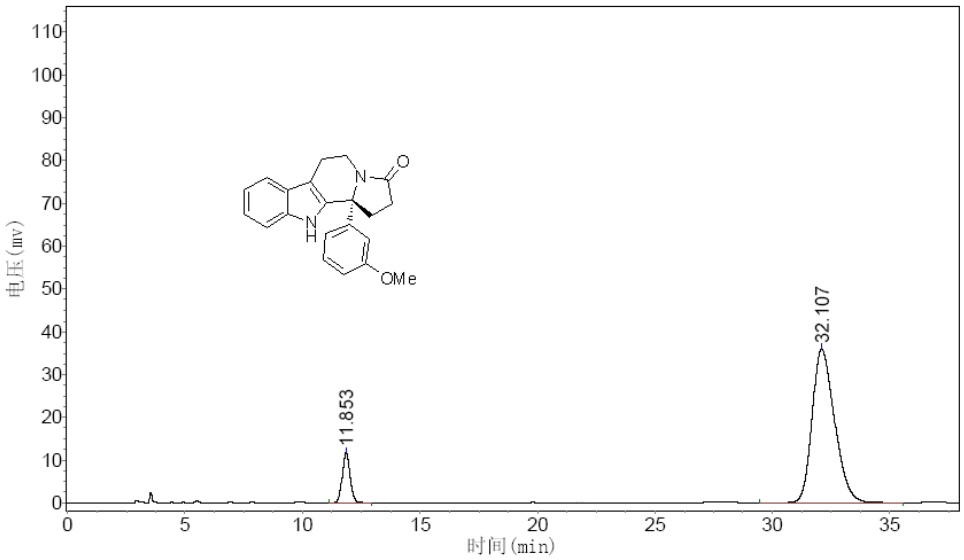
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	10.482	33762.113	833540.063	50.9784
2	20.900	16635.732	801544.938	49.0216
Total		50397.846	1635085.000	100.0000



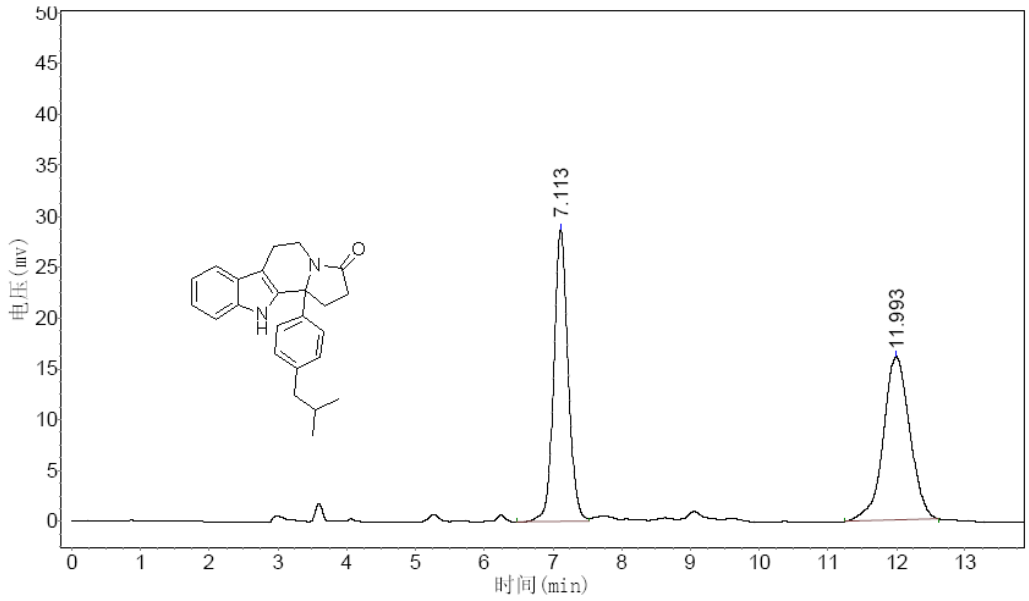
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	10.683	3862.580	76820.148	7.7589
2	21.235	22595.980	913264.250	92.2411
Total		26458.560	990084.398	100.0000



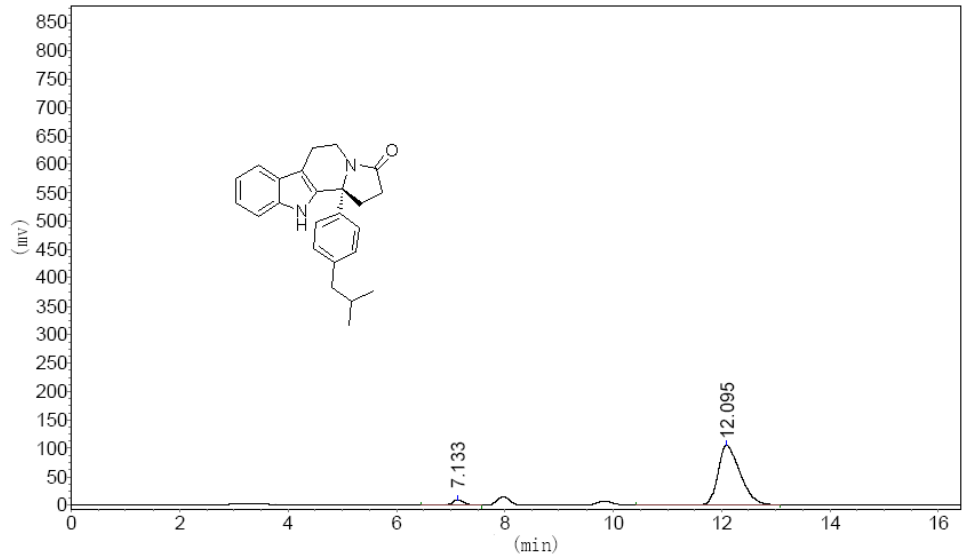
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11.873	16612.994	395673.313	48.8642
2	32.433	6279.149	414067.156	51.1358
Total		22892.143	809740.469	100.0000



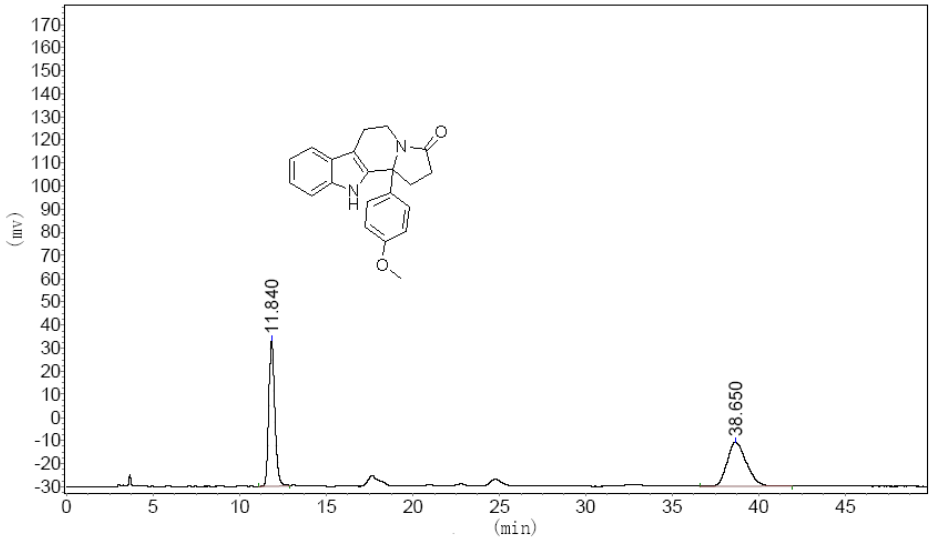
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11.853	11783.927	273552.250	10.2124
2	32.107	36012.563	2405081.500	89.7876
Total		47796.489	2678633.750	100.0000



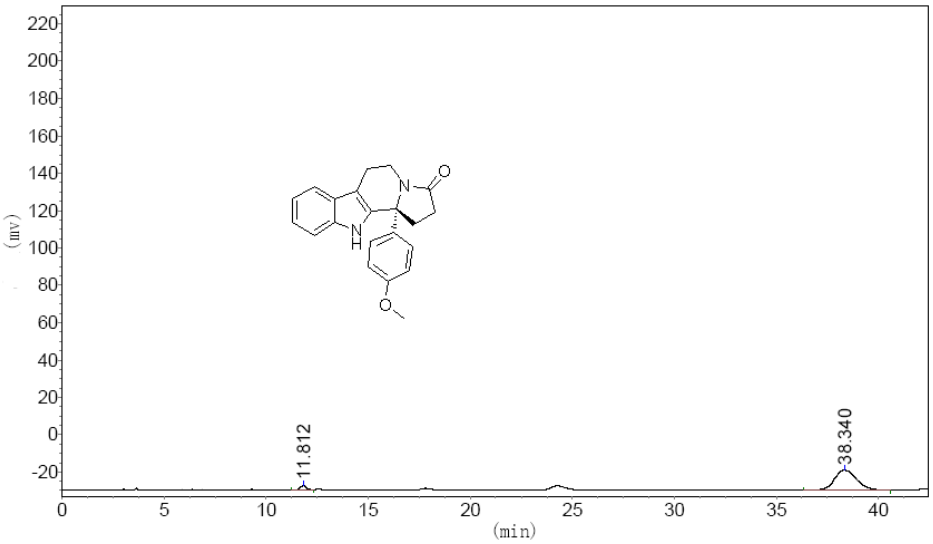
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	7.113	28692.682	417838.156	49.3166
2	11.993	16079.663	429418.938	50.6834
Total		44772.345	847257.094	100.0000



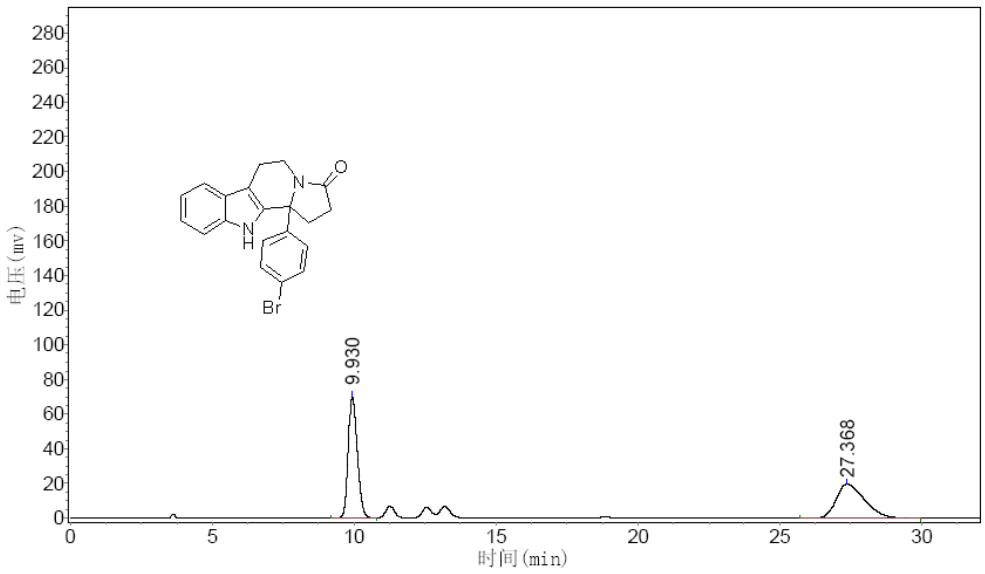
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	7.133	9925.117	147540.719	4.7170
2	12.095	105010.305	2980329.000	95.2830
Total		114935.422	3127869.719	100.0000



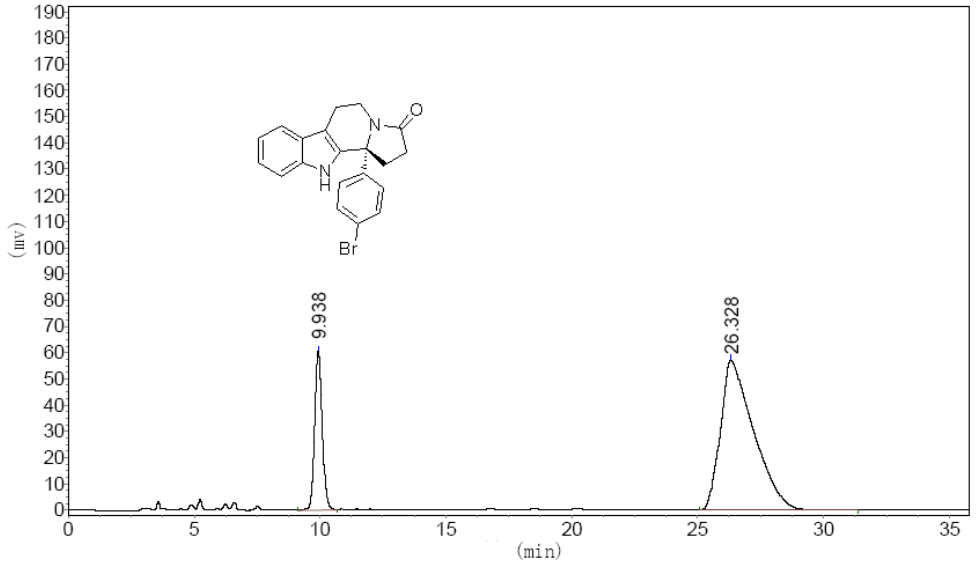
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11.840	62937.516	1491082.250	50.1358
2	38.650	19128.859	1483002.500	49.8642
Total		82066.375	2974084.750	100.0000



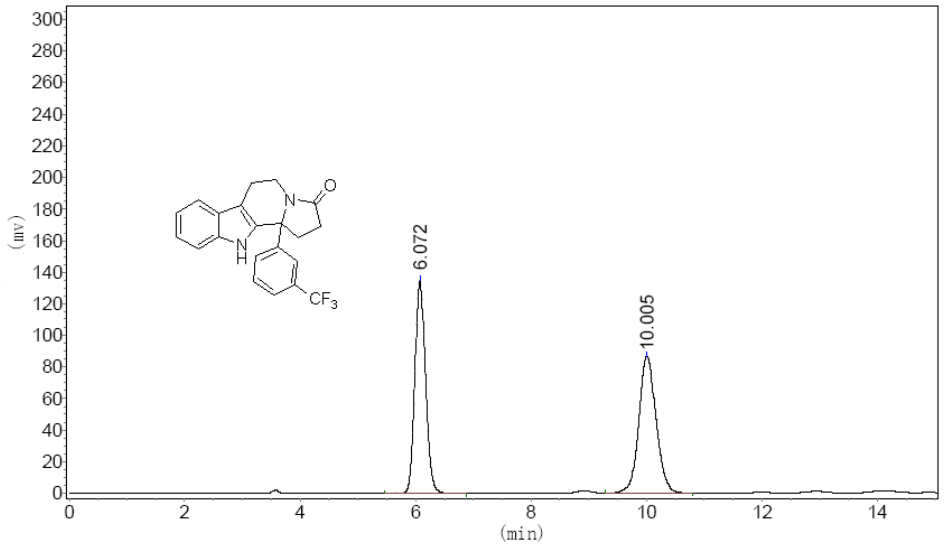
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11.812	2436.556	58754.473	6.8402
2	38.340	10671.179	800209.000	93.1598
Total		13107.735	858963.473	100.0000



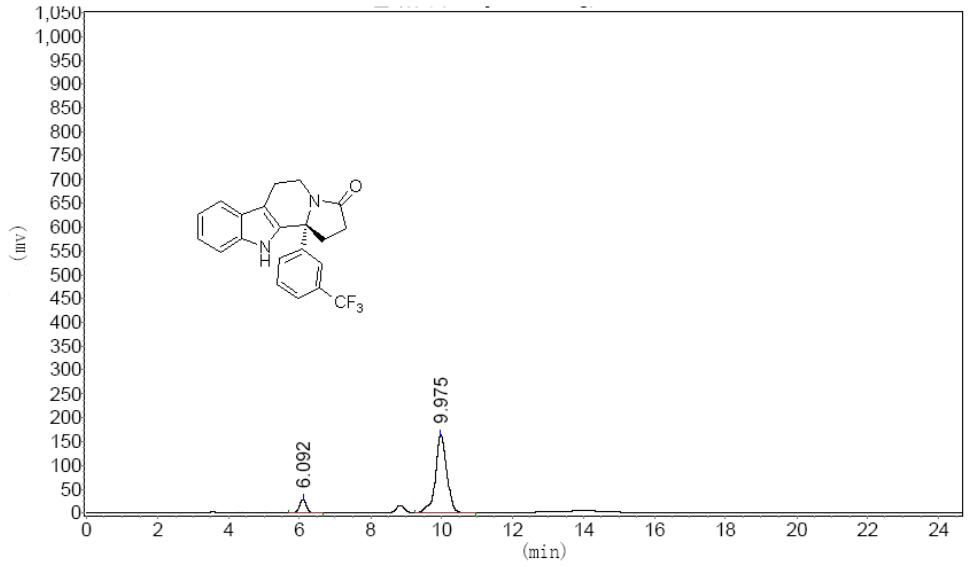
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	9.930	70025.063	1548815.875	53.0129
2	27.368	19860.705	1372764.875	46.9871
Total		89885.768	2921580.750	100.0000



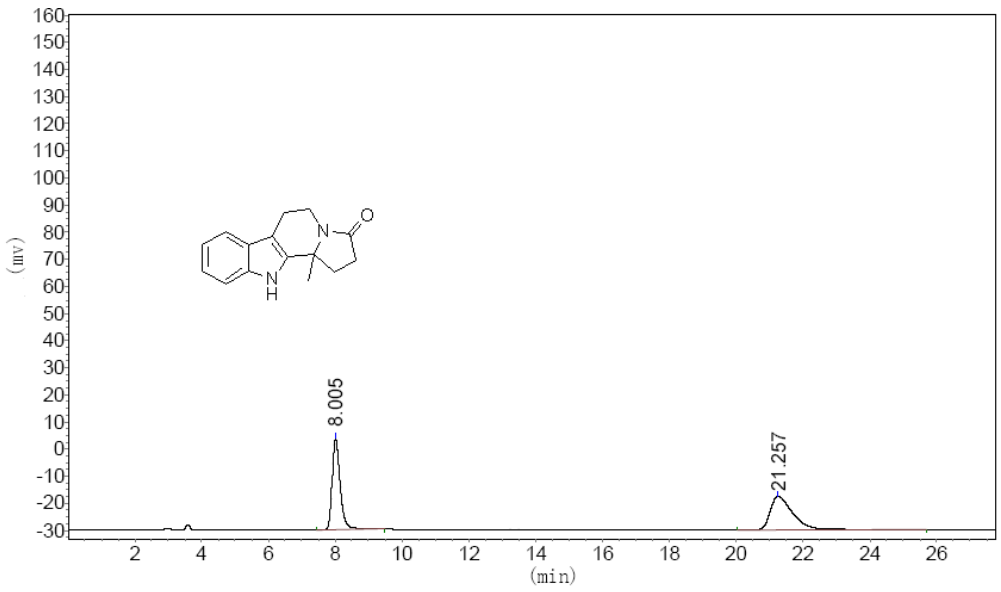
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	9.938	60732.770	1287192.250	19.8063
2	26.328	57247.863	5211695.500	80.1937
Total		117980.633	6498887.750	100.0000



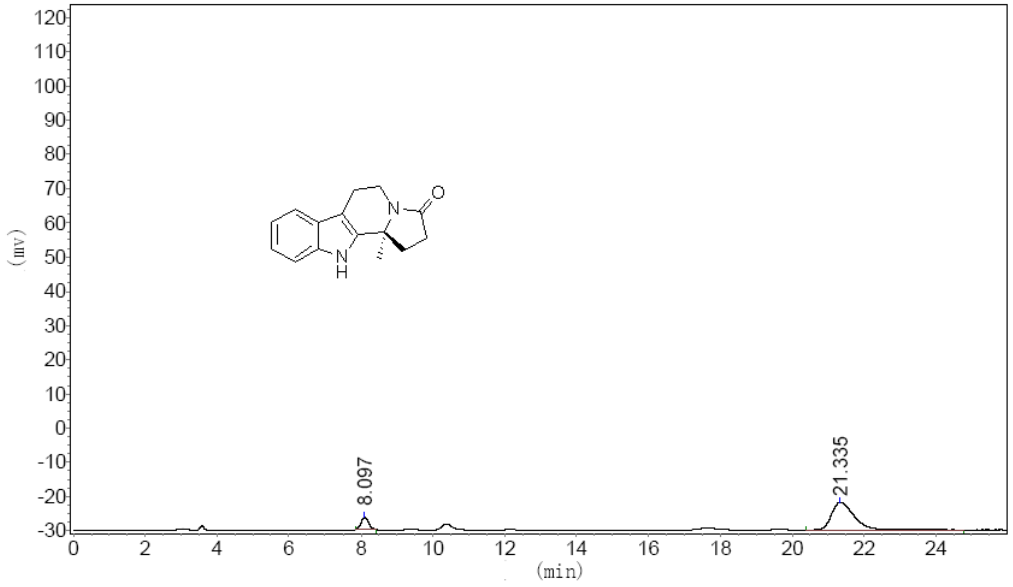
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	6.072	134545.484	1741191.750	49.0669
2	10.005	86343.648	1807416.375	50.9331
Total		220889.133	3548608.125	100.0000



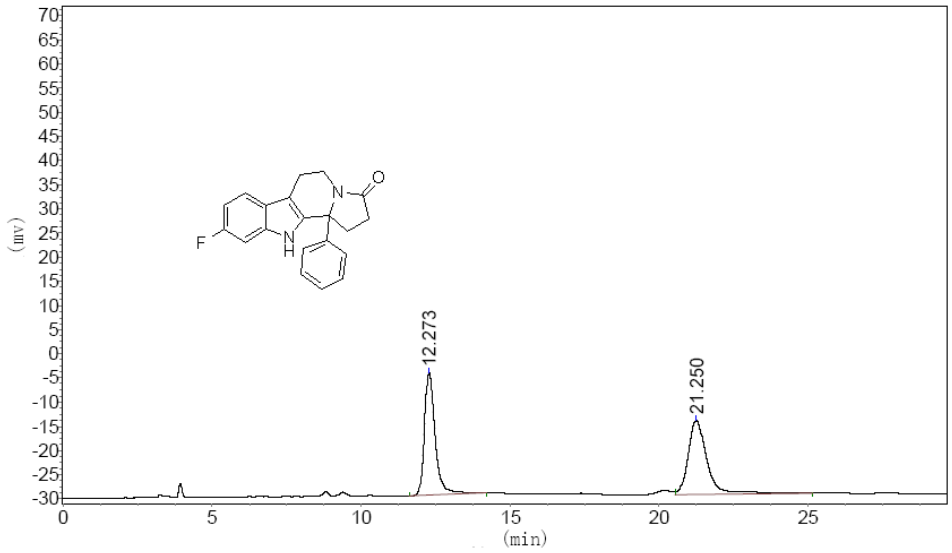
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	6.092	28562.365	364253.594	9.0880
2	9.975	164282.828	3643801.250	90.9120
Total		192845.193	4008054.844	100.0000



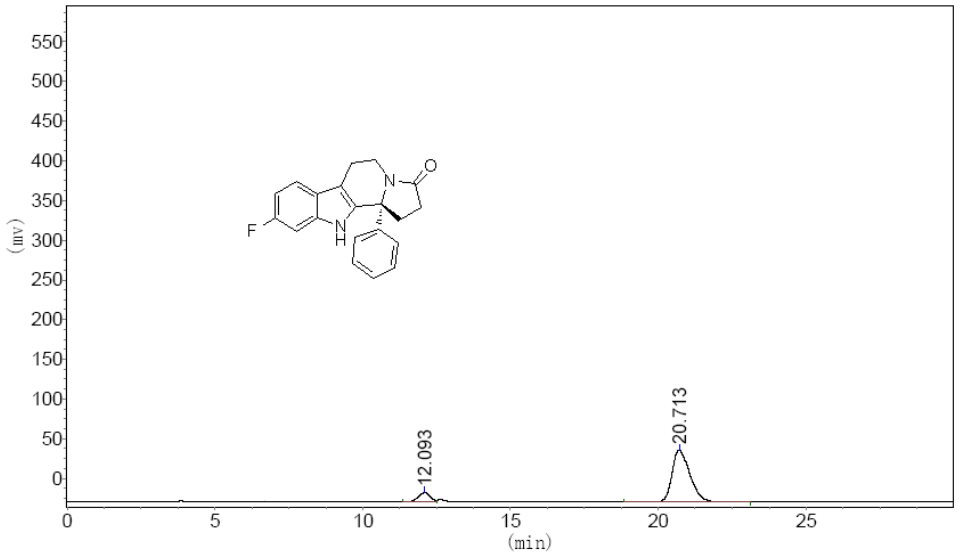
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	8.005	33621.453	558849.688	48.5673
2	21.257	12222.426	591821.188	51.4327
Total		45843.879	1150670.875	100.0000



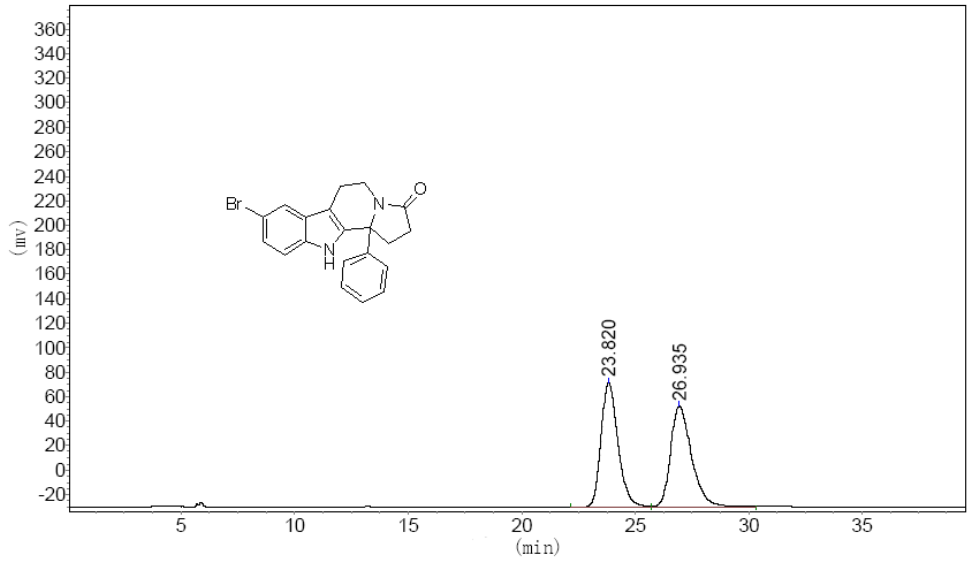
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	8.097	3696.792	54686.770	13.2201
2	21.335	8126.362	358977.563	86.7799
Total		11823.154	413664.332	100.0000



Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12.273	25367.740	642793.375	48.0604
2	21.250	15315.154	694676.563	51.9396
Total		40682.895	1337469.938	100.0000



Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12.093	12292.794	347638.844	11.2492
2	20.713	65922.289	2742716.250	88.7508
Total		78215.083	3090355.094	100.0000



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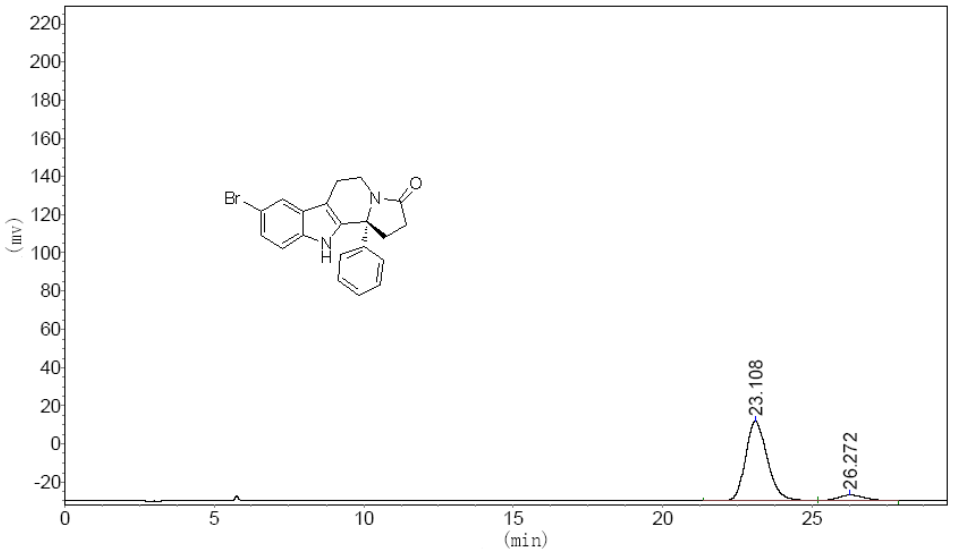
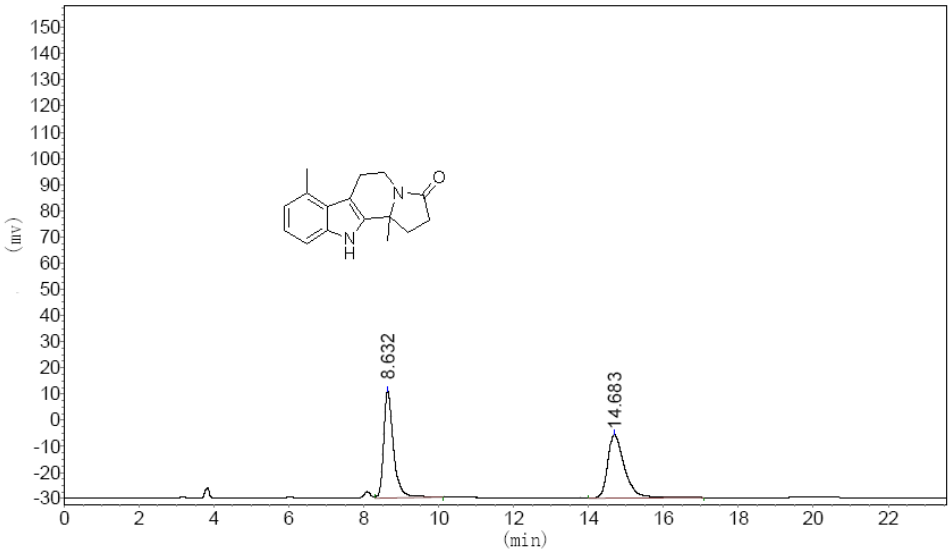
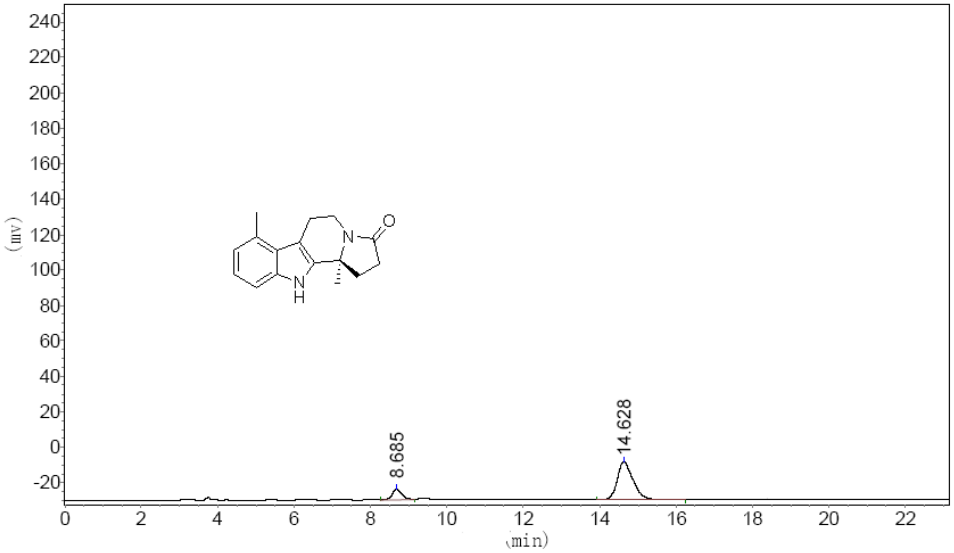
1	23.820	101440.375	5263268.000	49.6811
2	26.935	82266.906	5330847.500	50.3189
Total		183707.281	10594115.500	100.0000



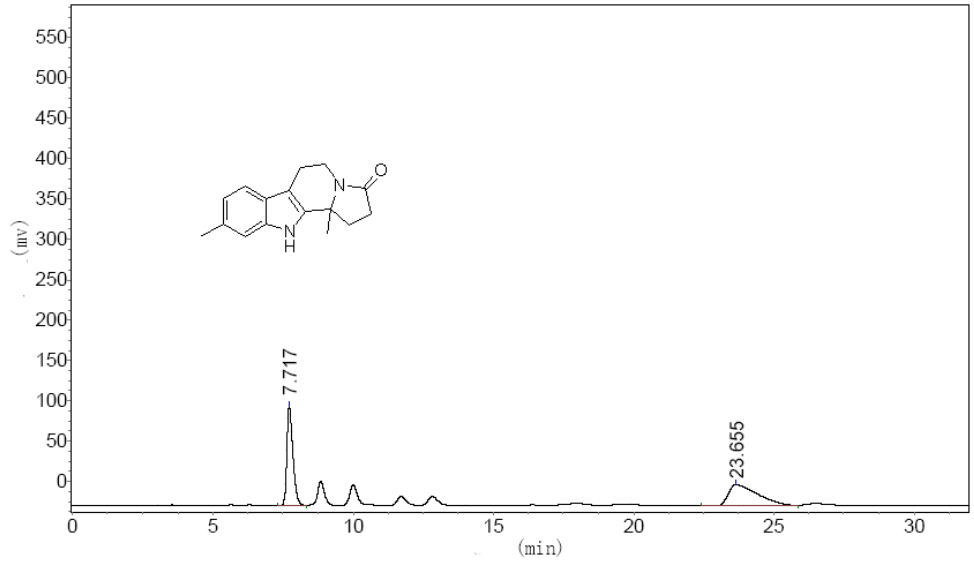
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	23.108	41662.922	2126172.750	91.6039
2	26.272	3072.864	194878.406	8.3961
Total		44735.785	2321051.156	100.0000



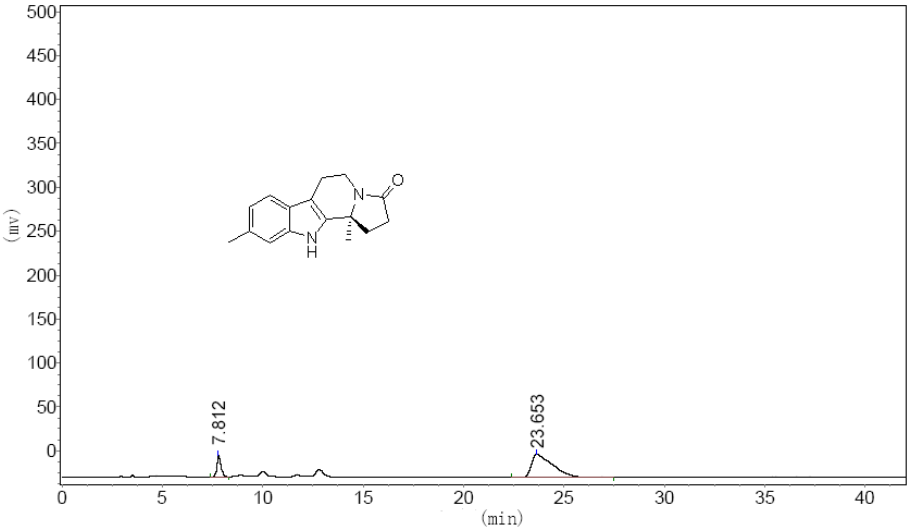
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	8.632	40860.879	753057.875	50.0321
2	14.683	24144.760	752091.313	49.9679
Total		65005.639	1505149.188	100.0000



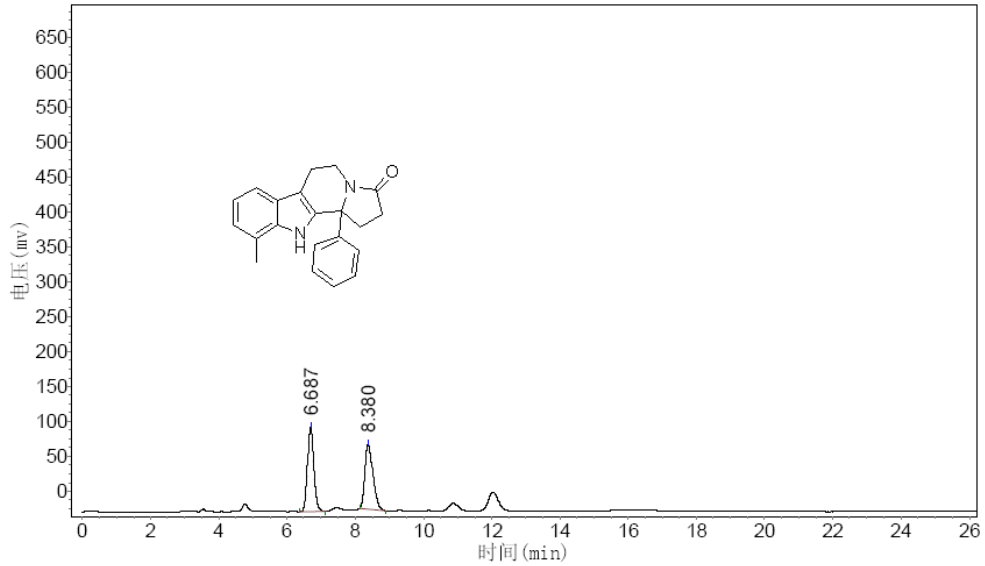
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	8.685	6150.597	115264.156	15.4656
2	14.628	21442.963	630029.563	84.5344
Total		27593.560	745293.719	100.0000



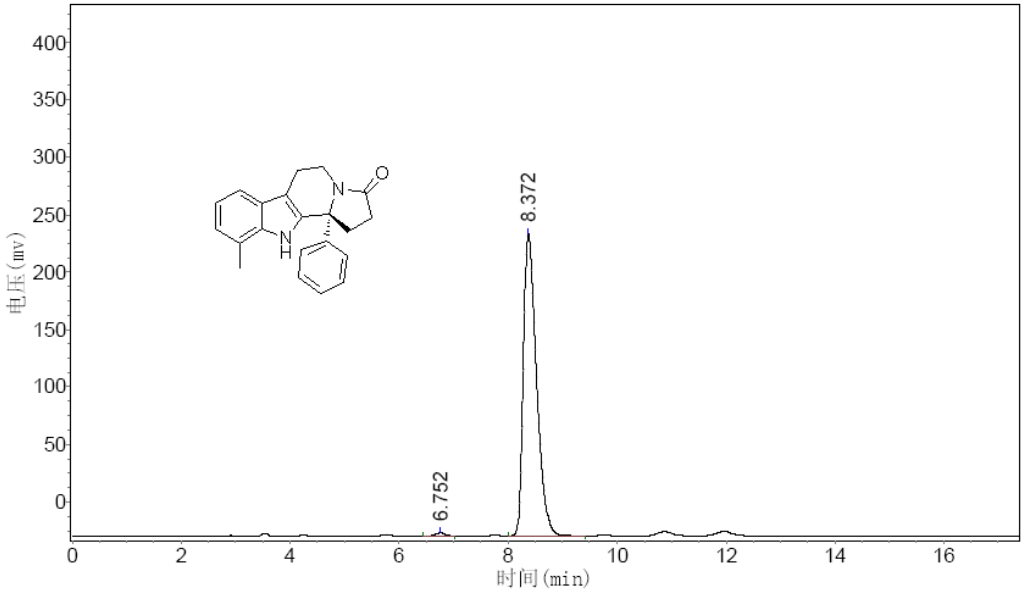
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	7.717	123013.977	1885617.875	49.8658
2	23.655	26238.838	1895765.875	50.1342
Total		149252.814	3781383.750	100.0000



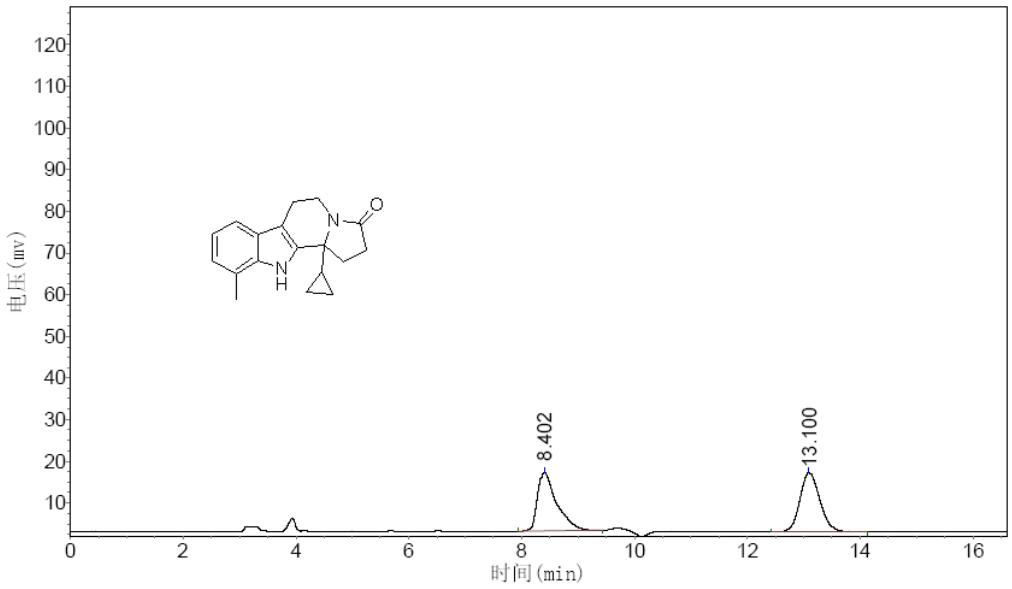
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	7.812	24607.537	375254.875	16.6616
2	23.653	26137.172	1876953.750	83.3384
Total		50744.709	2252208.625	100.0000



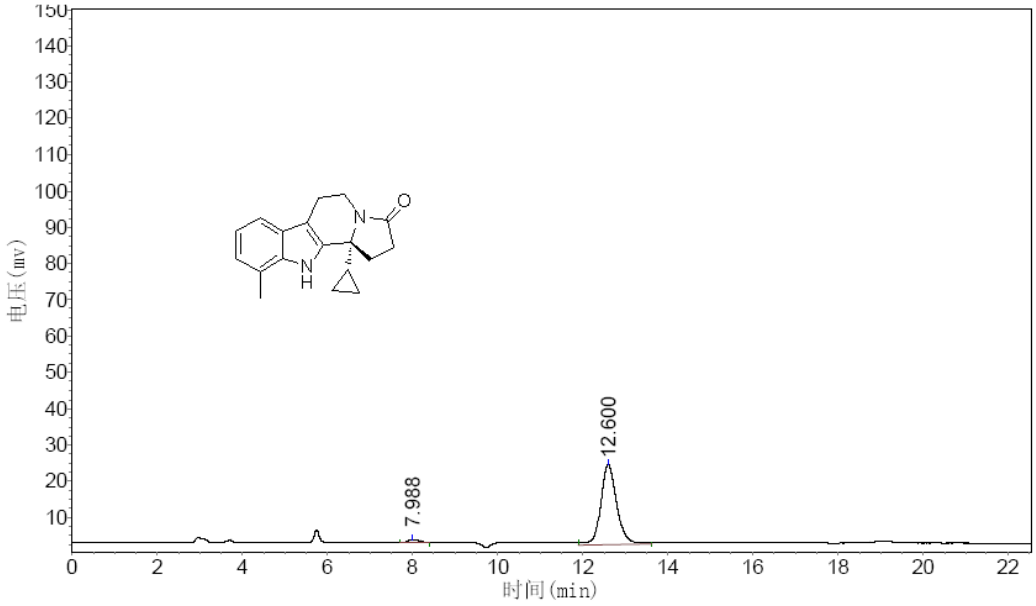
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	6.687	121525.305	1559553.750	50.7612
2	8.380	93227.047	1512780.375	49.2388
Total		214752.352	3072334.125	100.0000



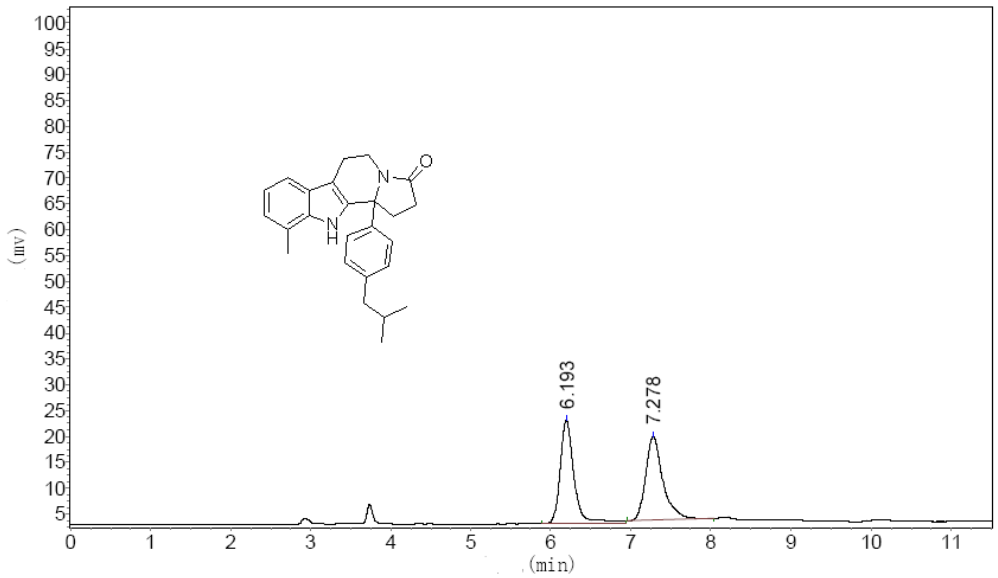
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	6.752	2826.124	36225.488	0.8161
2	8.372	263317.406	4402703.500	99.1839
Total		266143.530	4438928.988	100.0000



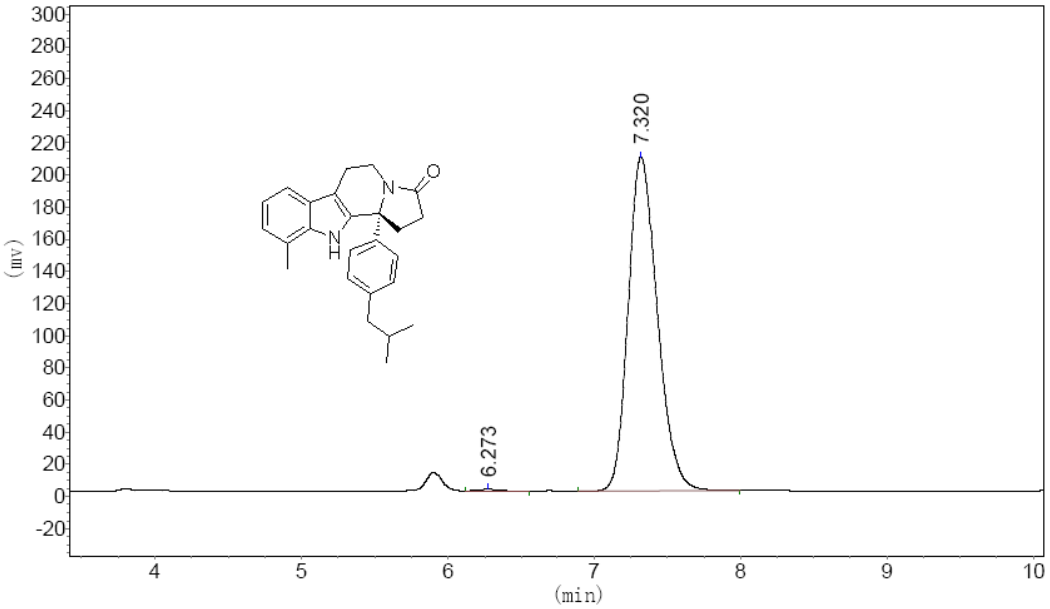
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	8.402	14054.094	335749.656	49.0077
2	13.100	14141.723	349346.594	50.9923
Total		28195.816	685096.250	100.0000



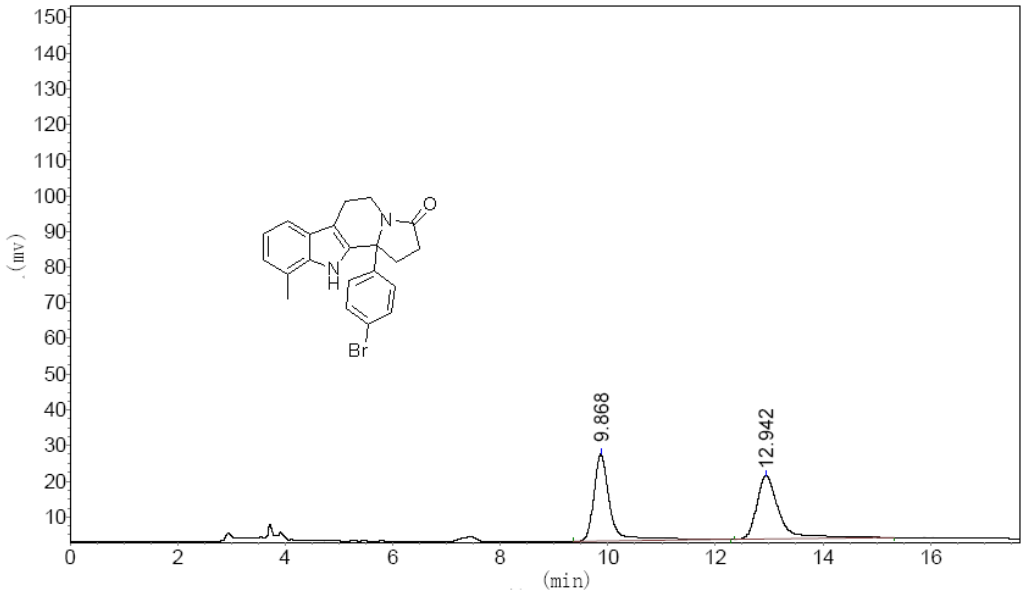
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	7.988	904.455	16582.555	2.7296
2	12.600	22073.418	590921.250	97.2704
Total		22977.873	607503.805	100.0000



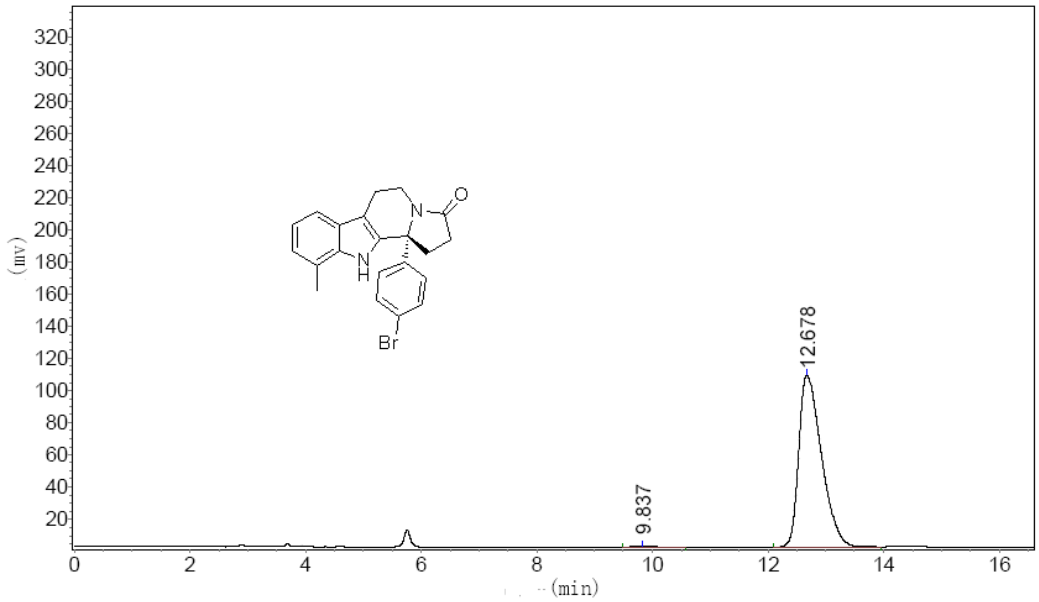
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	6.193	20040.391	247657.734	50.4556
2	7.278	16115.119	243184.703	49.5444
Total		36155.510	490842.438	100.0000



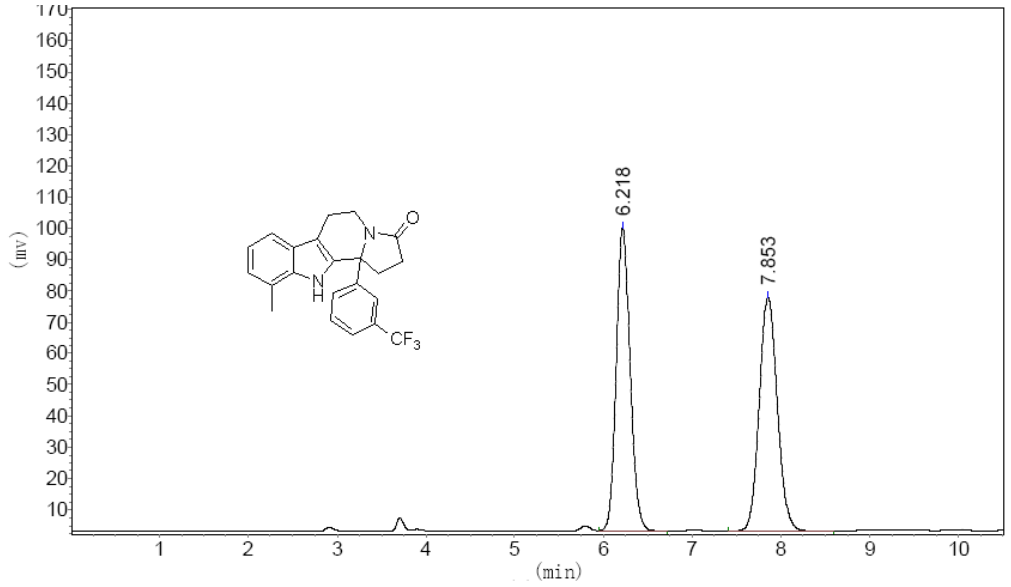
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	6.273	1210.606	13523.702	0.4673
2	7.320	208014.297	2880415.500	99.5327
Total		209224.902	2893939.202	100.0000



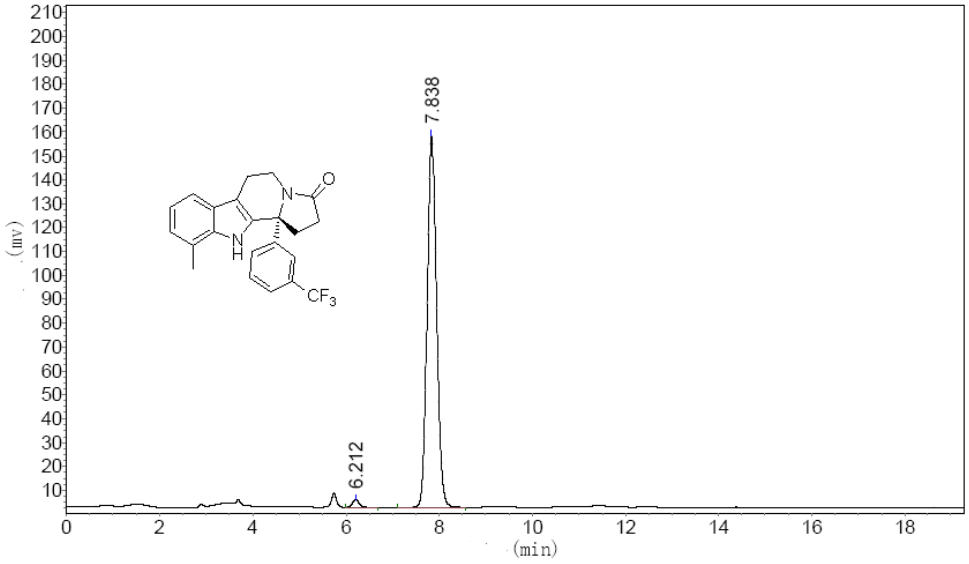
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	9.868	24314.236	527695.188	50.0832
2	12.942	17784.354	525941.250	49.9168
Total		42098.590	1053636.438	100.0000



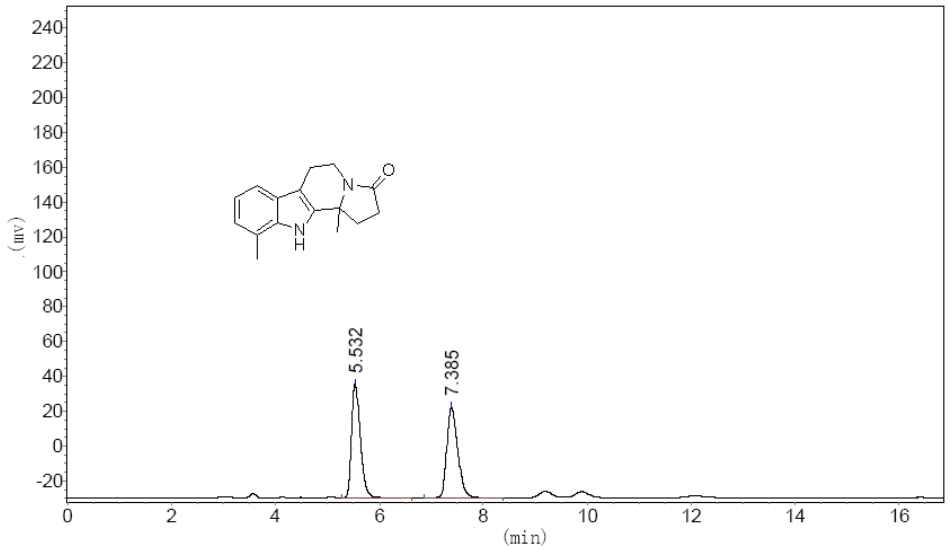
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	9.837	945.879	17963.109	0.6108
2	12.678	107345.844	2922955.500	99.3892
Total		108291.723	2940918.609	100.0000



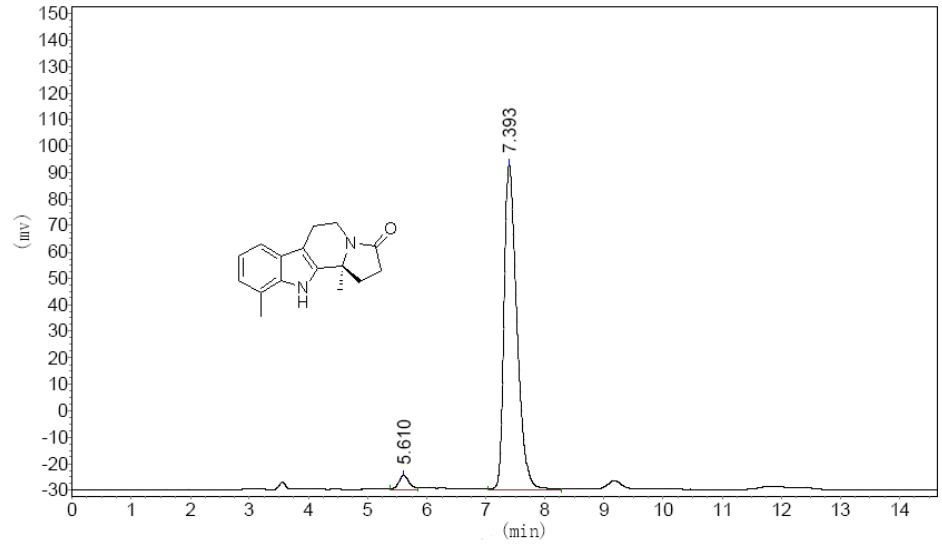
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	6.218	97120.891	1054446.750	49.9780
2	7.853	74824.727	1055374.750	50.0220
Total		171945.617	2109821.500	100.0000



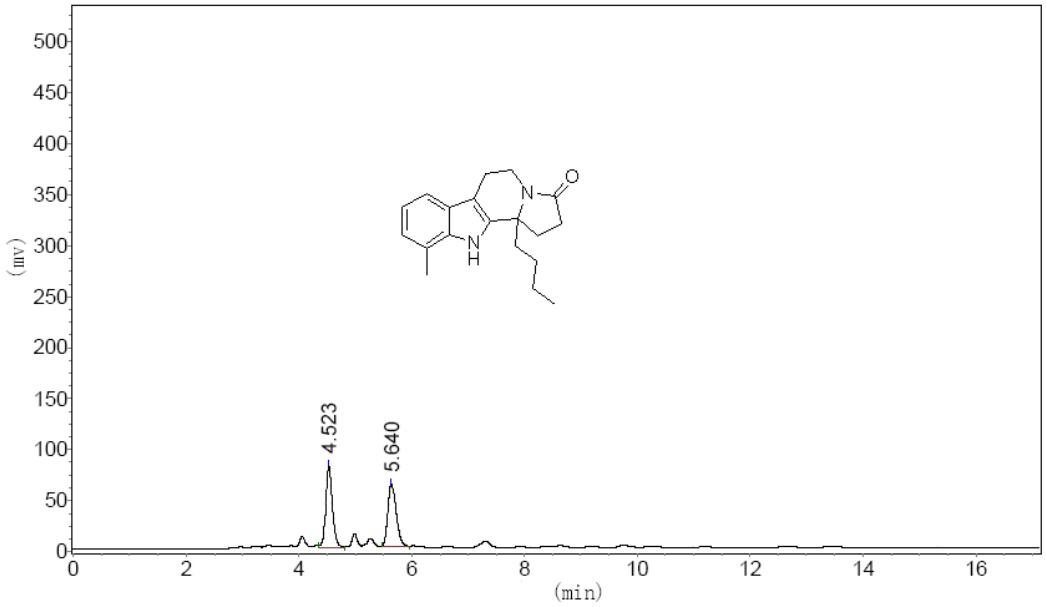
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	6.212	3186.751	34044.746	1.5216
2	7.838	155758.313	2203331.750	98.4784
Total		158945.063	2237376.496	100.0000



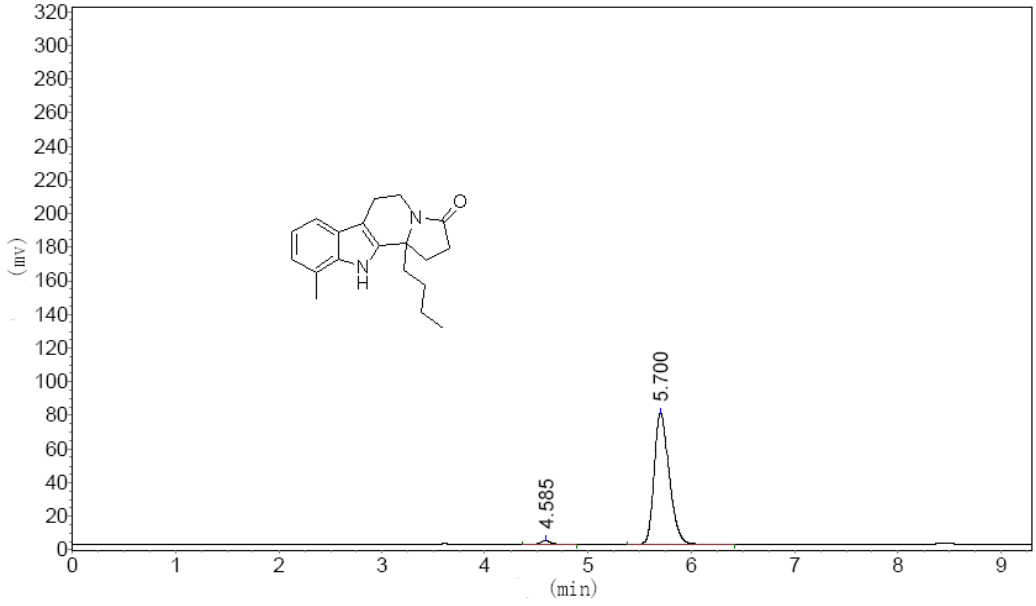
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	5.532	65363.188	761123.188	49.9798
2	7.385	52058.758	761738.750	50.0202
Total		117421.945	1522861.938	100.0000



Peak No.	R. Time	Peak Height	Peak Area	Percent
1	5.610	5209.897	64550.434	3.4153
2	7.393	122909.711	1825509.250	96.5847
Total		128119.608	1890059.684	100.0000



Peak No.	R. Time	Peak Height	Peak Area	Percent
1	4.523	79217.445	643562.125	51.2478
2	5.640	60534.098	612223.438	48.7522
Total		139751.543	1255785.563	100.0000



Peak No.	R. Time	Peak Height	Peak Area	Percent
1	4.585	2458.703	19728.615	2.4019
2	5.700	78256.086	801645.250	97.5981
Total		80714.789	821373.865	100.0000