Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Rhodium-catalysed decarbonylative C(sp^2)–H alkylation of indolines with alkyl carboxylic acids and carboxylic anhydrides under redox-neutral conditions

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1. General Information

All reactions were performed in an oven-dried glassware using Schlenk techniques under argon atmosphere, unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECA 500II (500 MHz for ^{1}H and 125 MHz for ^{13}C) spectrometer in $CDCl_3$. Tetramethylsilane (TMS) served as an internal standard (for ^{1}H, $\delta = 0$), and $CDCl_3$ served as an internal standard (for ^{13}C, $\delta = 77.0$). IR spectra were recorded on an FT/IR-4600 (JASCO Co., Ltd.). ESI-MS were measured on a Bruker ESI-TOF-MS. Preparative thin-layer chromatography (PTLC) was performed on Wakogel® B-5F. Flash column chromatography was performed on Wakogel® C-200 (75–150 μm). Tetrahydrofuran (THF) was purchased from Kanto Chemical as "Dehydrated Solvent System". Other solvents were purchased from FUJIFILM Wako Pure Chemicals and Nacalai Tesque and used without further purification. $[RhCl(CO)_2]_2$ was purchased from Kanto Chemical. $RhCl(PPh_3)_3$ was purchased from Sigma-Aldrich. $[RhCl(cod)]_2$,[1] $[RhOAc(cod)]_2$,[2] $[Rh(cod)_2]BF_4$,[3] and $[Rh(cod)_2]OTf$[4] were synthesised according to the literature. 1-(Pyrimidin-2-yl)indolines **1** was synthesised according to the literature.[5] Pivalic anhydride (Piv_2O) was purchased from Kanto Chemical and distilled before use. Acetic acid and propionic acid were purchased from Nacalai Tesque. *n*-Octanoic acid, 3-phenylpropionic acid, isovaleric acid, 4-phenoxybutyric acid, 4-methoxyphenylacetic acid, and 4-*tert*-butylbenzoic acid were purchased from Tokyo Chemical Industry. 4-(1,3-Dioxoisoindolin-2-yl)butanoic acid[6] and 4-methoxy-4-oxobutanoic acid[7] were synthesised according to the literature. Acetic anhydride and propionic anhydride were purchased from FUJIFILM Wako Pure Chemicals and distilled before use. Other carboxylic anhydrides were synthesised according to the literature.[8] All carboxylic acids and their anhydrides were distilled or recrystallised before use.

2. Experimental Procedure:

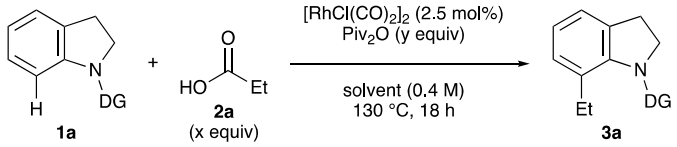
2.1 General procedure for the rhodium-catalysed alkylation of indolines 1 with carboxylic acid 2:

To an oven-dried test tube equipped with a stirring bar charged with indoline **1** (0.3 mmol) and $[RhCl(CO)_2]_2$ (2.9 mg, 7.5×10^{-3} mmol) were added 1,2-dichloroethane (0.75 mL). Subsequently, carboxylic acid **2** (0.6 mmol) and Piv_2O (139.7 mg, 0.75 mmol) were injected to the solution via syringe, and the tube was sealed with a PTFE cap. The reaction mixture was stirred at 130 °C for 18 h. After cooling to room temperature, the resulting mixture was poured into water and extracted with EtOAc. The combined organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine and dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuo, and the residue was purified by preparative thin-layer chromatography to give the product **3**.

2.2 General procedure for the rhodium-catalysed alkylation of indolines 1a with carboxylic anhydride 4:

To an oven-dried test tube equipped with a stirring bar charged with indoline **1a** (59.2 mg, 0.300 mmol) and $[RhCl(CO)_2]_2$ (2.9 mg, 7.5×10^{-3} mmol) were added 1,2-dichloroethane (0.75 mL). Subsequently, carboxylic anhydride **4** (0.3 mmol) was injected to the solution via syringe, and the tube was sealed with a PTFE cap. The reaction mixture was stirred at 150 °C for 18 h. After cooling to room temperature, the resulting mixture was concentrated in vacuo. The crude mixture was purified by preparative thin-layer chromatography to give the product **3**.

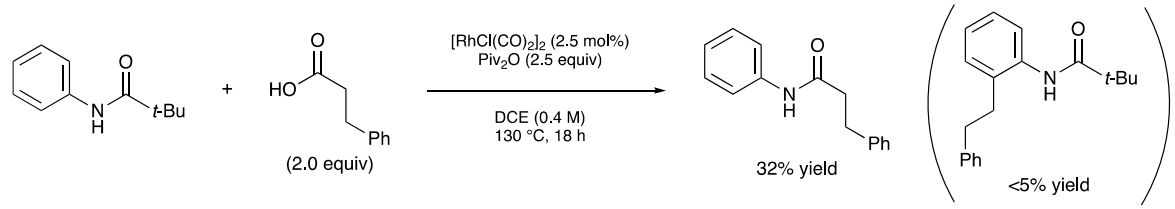
3. Optimisation of Reaction Conditions[a]



entry	DG	x (equiv)	y (equiv)	yield (%)[b]
1	2-pyrimidyl	1.2	1.3	74
2	2-pyrimidyl	1.2	1.5	79
3	2-pyrimidyl	1.5	1.6	78
4	2-pyrimidyl	1.5	2.0	81
5	2-pyrimidyl	2.0	2.1	78
6	2-pyrimidyl	2.0	2.5	91 (92)
7	2-pyridyl	2.0	2.5	<10

[a] Reaction conditions: **1a** (0.3 mmol), **2a**, Piv_2O and $[RhCl(CO)_2]_2$ (2.5 mol%) were heated in DCE (0.75 mL) at 130 ºC for 18 h unless otherwise noted. [b] Yield was determined by ^1H NMR analysis using 1,2,4,5-tetramethylbenzene as an internal standard. Value in parentheses indicates isolated yield.

4. Decarbonylative Alkylation of *N*-Phenylpivalamide

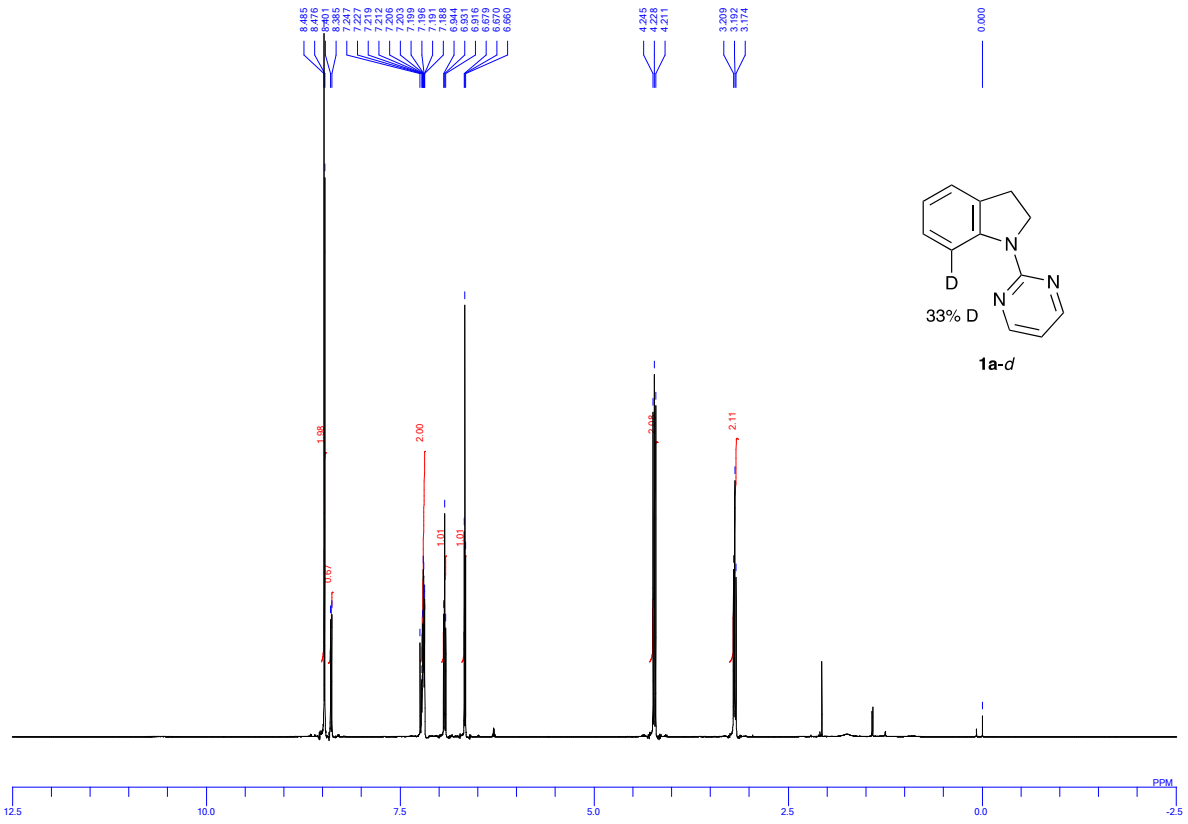


Reaction conditions: *N*-phenylpivalamide (0.3 mmol), 3-phenylpropionic acid (0.6 mmol), $[RhCl(CO)_2]_2$ (2.5 mol%) and Piv_2O (0.75 mmol) were reacted in DCE (0.75 mL) at 130 °C for 18 h.

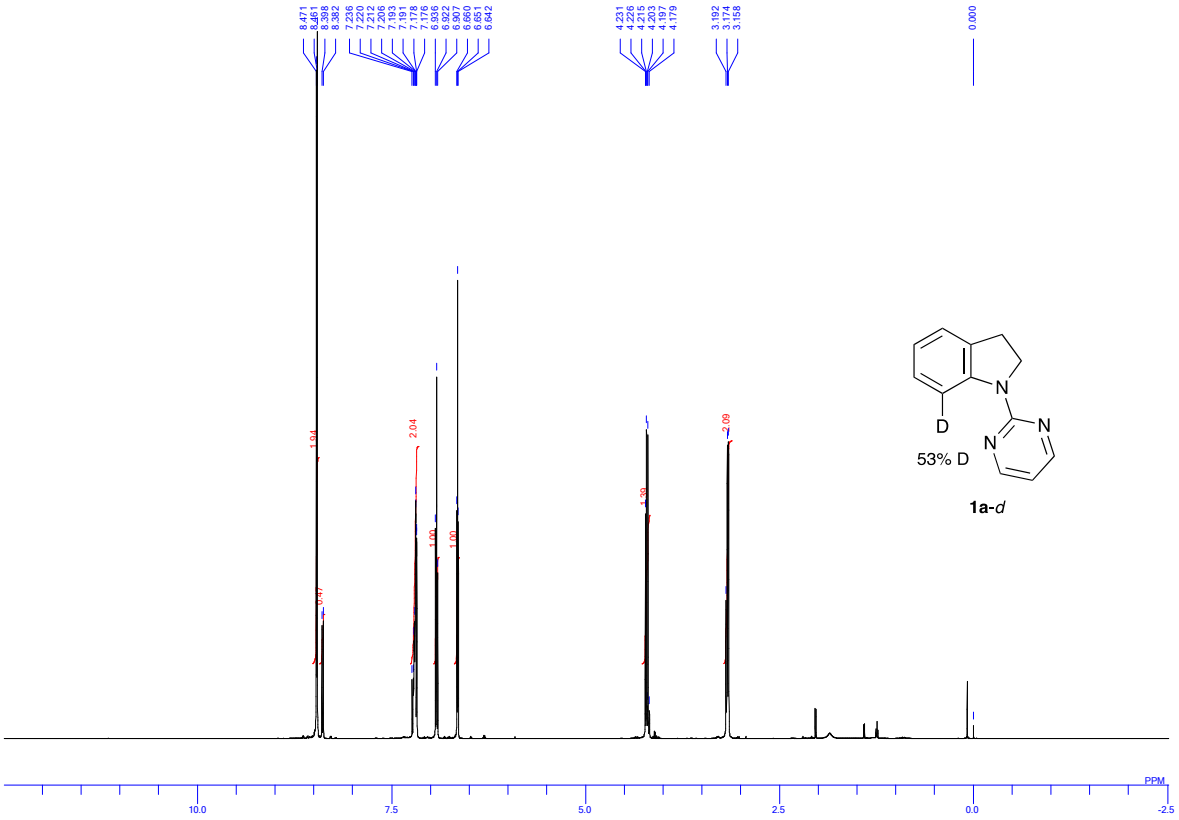
5. Preliminary Mechanistic Studies

5.1. H/D exchange experiment

To an oven-dried test tube equipped with a stirring bar charged with $[RhCl(CO)_2]_2$ (3.0 mg, 7.7×10^{-3} mmol) and 1-(pyrimidin-2-yl)indoline **1a** (59.1 mg, 0.300 mmol) in 1,2-dichloroethane (DCE, 0.75 mL) was added propionic acid **2a** (44.4 mg, 0.599 mmol), Piv_2O (142.3 mg, 0.7640 mmol) and D_2O (30.6 mg, 1.53 mmol) at room temperature, and stirred under argon atmosphere at 130 °C for 1 h. The reaction mixture was cooled to room temperature and concentrate in *vacuo*. The residue was purified by preparative thin-layer chromatography to give the product **1a**-*d* (30.2 mg, 51%) as a white solid.



To an oven-dried test tube equipped with a stirring bar charged with $[RhCl(CO)_2]_2$ (2.9 mg, 7.5×10^{-3} mmol) and 1-(pyrimidin-2-yl)indoline **1a** (59.3 mg, 0.301 mmol) in 1,2-dichloroethane (DCE, 0.75 mL) was added D_2O (30.2 mg, 1.51 mmol) at room temperature and stirred under argon atmosphere at 130 °C for 18 h. The reaction mixture was cooled to room temperature and concentrate in *vacuo*. The residue was purified by preparative thin-layer chromatography to give the product **1a**-*d* (56.5 mg, 95%) as a white solid.



5.2. Short time experiment

To an oven-dried test tube equipped with a stirring bar charged with $[RhCl(CO)_2]_2$ (3.0 mg, 7.7×10^{-3} mmol) and 1-(pyrimidin-2-yl)indoline **1a** (59.4 mg, 0.301 mmol) in 1,2-dichloroethane (DCE, 0.75 mL) was added propionic acid **2a** (44.0 mg, 0.594 mmol) and Piv_2O (140.9 mg, 0.7565 mmol) at room temperature. The reaction mixture was allowed to stir at 130 °C for 1 h. The resulting solutions were concentrated in *vacuo* and analysed by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (82.1 mg, 0.489 mmol) as an internal standard.

5.3. Decarbonylation of C7-acylated indoline 5

To an oven-dried test tube equipped with a stirring bar charged with indoline **5** (50.5 mg, 0.200 mmol) and $[RhCl(CO)_2]_2$ (1.8 mg, 4.6×10^{-3} mmol) were added 1,2-dichloroethane (0.5 mL). Subsequently, the tube was sealed with a PTFE cap and the reaction mixture was stirred at 130°C for 18 h. After cooling to room temperature, the resulting solutions were concentrated in *vacuo* and analysed by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (81.3 mg, 0.484 mmol) as an internal standard.

5.4. Radical trapping experiment

To an oven-dried test tube equipped with a stirring bar charged with $[RhCl(CO)_2]_2$ (3.0 mg, 7.7×10^{-3} mmol), 1-(pyrimidin-2-yl)indoline **1a** (59.4 mg, 0.301 mmol) and BHT (33.1 mg, 0.150 mmol) in 1,2-dichloroethane (DCE, 0.75 mL) was added propionic acid **2a** (44.4 mg, 0.599 mmol) and Piv_2O (139.7 mg, 0.7501 mmol) at room temperature. The reaction mixture was allowed to stir at 130 °C for 18 h. The resulting solutions were concentrated in *vacuo* and analysed by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (81.9 mg, 0.488 mmol) as an internal standard.

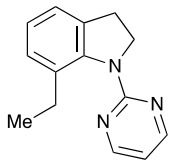
To an oven-dried test tube equipped with a stirring bar charged with $[RhCl(CO)_2]_2$ (2.8 mg, 7.2×10^{-3} mmol), 1-(pyrimidin-2-yl)indoline **1a** (59.4 mg, 0.301 mmol) and BHT (33.0 mg, 0.150 mmol) in 1,2-dichloroethane (DCE, 0.75 mL) was added propionic anhydride **4a** (79.0 mg, 0.607 mmol) at room temperature. The reaction mixture was allowed to stir at 150 °C for 18 h. The resulting solutions were concentrated in *vacuo* and analysed by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane (81.4 mg, 0.485 mmol) as an internal standard.

5.5. KIE experiment

Kinetic isotope effect (KIE) was measured by two sets of parallel experiments using 1-(pyrimidin-2-yl)indoline **1a** and **1a**-*d*. To an oven-dried test tube equipped with a stirring bar charged with indoline **1a** (59.1 mg, 0.300 mmol) and $[RhCl(CO)_2]_2$ (3.0 mg, 7.7×10^{-3} mmol) was added DCE (0.75 mL) followed by the addition of propionic acid **2a** (44.6 mg, 0.602 mmol) and Piv_2O (138.9 mg, 0.7458 mmol) at room temperature. To another oven-dried test tube equipped with a stirring bar charged with indoline **1a**-*d* (59.5 mg, 0.300 mmol) and $[RhCl(CO)_2]_2$ (2.8 mg, 7.2×10^{-3} mmol) was added DCE (0.75 mL) propionic acid **2a** (44.4 mg, 0.599 mmol) and Piv_2O (140.0 mg, 0.7517 mmol) at room temperature. Both reactions were allowed to stir at 130 °C in an oil bath for 30 min. The resulting solutions were concentrated in *vacuo*. The ^{1}H NMR yields of **3a** and **5** for each reaction were given using 1,1,2,2-tetrachloroethane (80.6 mg, 0.481 mmol for **1a** and 81.5 mg, 0.486 mmol for

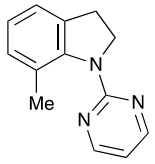
1a-*d*) as an internal standard. The yields of **3a** were 12.0% for **1a** and 2.4% for **1a**-*d*, and the yields of **5** were 21.6% for **1a** and 12.4% for **1a**-*d* respectively. A KIE value of 2.3 was determined on the basis of the sum of **3a** and **5** to assess the rate of the C–H activation step.

6. Characterisation of the Products



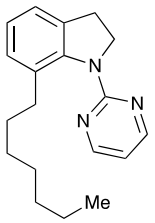
7-Ethyl-1-(pyrimidin-2-yl)indoline (3a):

The title compound was obtained as a white solid (from carboxylic acid: 68.7 mg, 92%; from anhydride: 56.8 mg, 84%); mp: 93.1–93.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.41 (d, J = 4.6 Hz, 2H), 7.14 (d, J = 7.4 Hz, 1H), 7.09 (d, J = 6.9 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H), 6.67 (t, J = 4.9 Hz, 1H), 4.41 (t, J = 7.4 Hz, 2H), 3.04 (t, J = 7.7 Hz, 2H), 2.59 (q, J = 7.4 Hz, 2H), 1.16 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.4, 157.5, 142.1, 134.5, 134.0, 127.1, 124.3, 121.8, 112.1, 53.3, 29.9, 26.4, 13.2; IR (neat): $\tilde{\nu}$ = 2965, 2893, 1579, 1551, 1459, 1423, 1281, 798 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{14}H_{16}N_3$ $[M + H]^+$ 226.1339, found 226.1348.



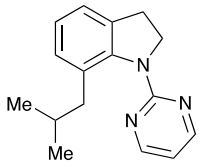
7-Methyl-1-(pyrimidin-2-yl)indoline (3b):

The title compound was obtained as a white solid (from carboxylic acid: 52.1 mg, 82%; from anhydride: 35.2 mg, 56%); mp: 112.2–112.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.43 (d, J = 4.6 Hz, 2H), 7.09 (d, J = 7.4 Hz, 1H), 7.05 (d, J = 7.4 Hz, 1H), 6.98 (t, J = 7.4 Hz, 1H), 6.67 (t, J = 4.6 Hz, 1H), 4.41 (t, J = 7.7 Hz, 2H), 3.06 (t, J = 7.7 Hz, 2H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.1, 157.5, 142.8, 134.4, 129.5, 128.0, 123.9, 121.8, 112.0, 53.2, 29.9, 20.7; IR (neat): $\tilde{\nu}$ = 2956, 2893, 1575, 1555, 1464, 1419, 1281, 774 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{13}H_{14}N_3$ $[M + H]^+$: 212.1182, found 212.1174. The spectral data matched those reported in the literature.[9]



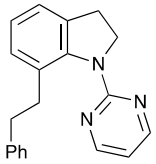
7-Heptyl-1-(pyrimidin-2-yl)indoline (3c):

The title compound was obtained as a colourless oil (from carboxylic acid: 73.3 mg, 82%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.41 (d, J = 4.6 Hz, 2H), 7.11–7.08 (m, 2H), 7.01 (t, J = 7.4 Hz, 1H), 6.67 (t, J = 4.6 Hz, 1H), 4.40 (t, J = 7.7 Hz, 2H), 3.03 (t, J = 7.7 Hz, 2H), 2.57 (t, J = 7.7 Hz, 2H), 1.58–1.52 (m, 2H), 1.25–1.15 (m, 8H), 0.84 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.3, 157.5, 142.3, 134.7, 133.0, 128.0, 124.2, 121.9, 112.0, 53.3, 33.8, 31.7, 29.9, 29.6, 29.1, 28.9, 22.6, 14.0; IR (neat): $\tilde{\nu}$ = 2954, 2926, 2853, 1579, 1551, 1457, 1187, 798 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{19}H_{26}N_3$ $[M + H]^+$ 296.2121, found 296.2116.



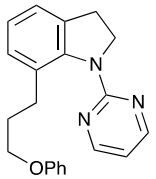
7-Isobutyl-1-(pyrimidin-2-yl)indoline (3d):

The title compound was obtained as a colourless oil (from carboxylic acid: 55.8 mg, 73%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.42 (d, *J* = 4.6 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 6.9 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.66 (t, *J* = 4.6 Hz, 1H), 4.39 (t, *J* = 7.7Hz, 2H), 3.02 (t, *J* = 7.7 Hz, 2H), 2.56 (d, *J* = 7.4 Hz, 2H), 1.81 (sept, *J* = 6.8 Hz, 1H), 0.71 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.1, 157.5, 142.6, 134.7, 131.9, 129.0, 124.1, 122.0, 112.0, 53.4, 43.6, 29.9, 27.7, 22.5; IR (neat): $\tilde{\nu}$ = 2954, 2866, 1551, 1258, 1177, 1055, 799, 759 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{63}H_{20}N_3$ $[M + H]^+$ 254.1652, found 254.1661.



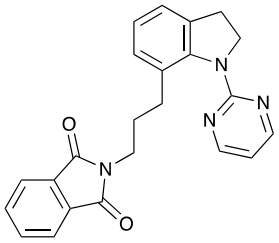
7-Phenethyl-1-(pyrimidin-2-yl)indoline (3e):

The title compound was obtained as a brown solid (from carboxylic acid: 77.1 mg, 85%; 236.1 mg, 78% (1.0 mmol scale)); mp: 79.0–80.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.41 (d, *J* = 4.6 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 2H), 7.15–7.10 (m, 3H), 7.04–7.00 (m, 3H), 6.66 (t, *J* = 4.6 Hz, 1H), 4.40 (t, *J* = 7.4 Hz, 2H), 3.02 (t, *J* = 7.4 Hz, 2H), 2.95–2.86 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.2, 157.6, 142.3, 142.3, 134.9, 131.9, 128.2, 128.2, 128.1, 125.5, 124.3, 122.2, 112.1, 53.3, 35.9, 35.2, 29.8; IR (neat): $\tilde{\nu}$ = 3025, 2953, 2921, 1582, 1551, 1455, 1432, 1284, 699 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{20}H_{20}N_3$ $[M + H]^+$ 302.1652, found 302.1653.



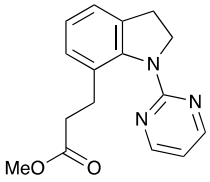
7-(3-Phenoxypropyl)-1-(pyrimidin-2-yl)indoline (3f):

The title compound was obtained as a white solid (from carboxylic acid: 83.1 mg, 83%); mp: 114.8–115.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.40 (d, *J* = 4.6 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 2H), 7.14–7.09 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.66 (t, *J* = 4.9 Hz, 1H), 4.40 (t, *J* = 7.7 Hz, 2H), 3.84 (t, *J* = 6.3 Hz, 2H), 3.02 (t, *J* = 7.7 Hz, 2H), 2.79 (t, *J* = 7.7 Hz, 2H), 2.06 (tt, *J* = 6.3, 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.2, 158.9, 157.5, 142.4, 134.9, 131.7, 129.2, 128.1, 124.3, 122.2, 120.3, 114.3, 112.1, 67.4, 53.2, 30.3, 29.8, 28.5; IR (neat): $\tilde{\nu}$ = 2953, 2885, 1579, 1547, 1455, 1432, 1253, 763 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{21}H_{22}N_3O$ $[M + H]^+$ 332.1757, found 332.1762.



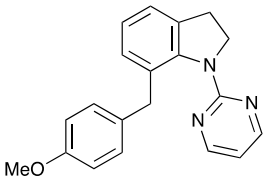
2-{3-[1-(Pyrimidin-2-yl)indolin-7-yl]propyl}isoindoline-1,3-dione (3g):

The title compound was obtained as a pale yellow solid (from carboxylic acid: 77.8 mg, 67%); mp: 135.0–136.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.38 (d, *J* = 5.2 Hz, 2H), 7.78 (dd, *J* = 5.2, 2.9 Hz, 2H), 7.67 (dd, *J* = 5.7, 2.9 Hz, 2H), 7.09 (d, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 6.9 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.59 (t, *J* = 4.6 Hz, 1H), 4.40 (t, *J* = 8.0 Hz, 2H), 3.60 (t, *J* = 7.4 Hz, 2H), 3.00 (t, *J* = 7.7 Hz, 2H), 2.66 (t, *J* = 7.7 Hz, 2H), 2.05–1.99 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 168.1, 161.1, 157.4, 142.2, 134.8, 133.6, 132.0, 131.0, 127.9, 124.2, 122.9, 122.1, 112.0, 53.0, 38.0, 31.2, 29.7, 27.4; IR (neat): $\tilde{\nu}$ = 2953, 2876, 2361, 1709, 1574, 1422, 1022, 717 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{23}H_{21}N_4O_2$ $[M + H]^+$ 385.1659, found 385.1676.



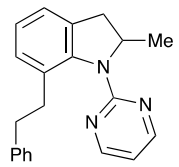
Methyl 3-(1-(pyrimidin-2-yl)indolin-7-yl)propanoate (3h):

The title compound was obtained as a white solid (from carboxylic acid: 43.4 mg, 51%); mp: 77.9–78.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.41 (d, *J* = 5.1 Hz, 2H), 7.11 (d, *J* = 6.9 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.69 (t, *J* = 4.9 Hz, 1H), 4.42 (t, *J* = 7.4 Hz, 2H), 3.60 (s, 3H), 3.03 (t, *J* = 7.7 Hz, 2H), 2.93 (t, *J* = 8.0 Hz, 2H), 2.65 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 173.8, 161.2, 157.6, 142.3, 135.1, 130.6, 127.9, 124.3, 122.5, 112.3, 53.1, 51.4, 33.5, 29.8, 29.0; IR (neat): $\tilde{\nu}$ = 2949, 2917, 1734, 1575, 1551, 1440, 1296, 1193, 1157, 754 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{16}H_{18}N_3O_2$ $[M + H]^+$ 284.1394, found 284.1382.



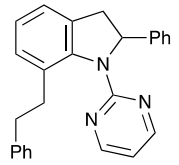
7-(4-Methoxybenzyl)-1-(pyrimidin-2-yl)indoline (3i):

The title compound was obtained as a yellow oil (from carboxylic acid: 54.5 mg, 57%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.39 (d, *J* = 4.6 Hz, 2H), 7.10 (d, *J* = 6.9 Hz, 1H), 6.97–6.89 (m, 4H), 6.75 (d, *J* = 8.6 Hz, 2H), 6.66 (t, *J* = 4.6 Hz, 1H), 4.38 (t, *J* = 7.4 Hz, 2H), 3.90 (s, 2H), 3.74 (s, 3H), 3.05 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.2, 157.6, 157.5, 142.4, 134.7, 132.8, 131.8, 130.0, 128.9, 124.1, 122.2, 113.5, 112.1, 55.1, 53.3, 38.9, 29.9; IR (neat): $\tilde{\nu}$ = 2960, 2899, 2833, 1576, 1508, 1419, 1241, 1174, 1033, 755 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{20}H_{20}N_3O$ $[M + H]^+$ 318.1601, found 318.1587.



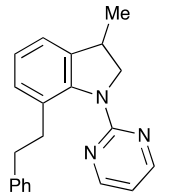
2-Methyl-7-phenethyl-1-(pyrimidin-2-yl)indoline (3j):

The title compound was obtained as a brown solid (from carboxylic acid: 88.1 mg, 94%); mp: 93.1–93.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.41 (d, *J* = 4.6 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.13-7.09 (m, 3H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 2H), 6.65 (t, *J* = 4.9 Hz, 1H), 5.03–4.98 (m, 1H), 3.43 (dd, *J* = 15.5, 8.6 Hz, 1H), 3.10–3.02 (m, 1H), 2.92–2.77 (m, 3H), 2.46 (d, *J* = 15.5 Hz, 1H), 1.34 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 160.8, 157.6, 142.3, 140.6, 133.6, 132.1, 128.4, 128.2, 128.1, 125.5, 124.2, 122.8, 112.2, 60.4, 36.7, 36.0, 35.0, 20.9; IR (neat): $\tilde{\nu}$ = 3020, 2925, 1575, 1547, 1455, 1427, 1061, 703 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{21}H_{22}N_3$ $[M + H]^+$ 316.1808, found 316.1812.



7-Phenethyl-2-phenyl-1-(pyrimidin-2-yl)indoline (3k):

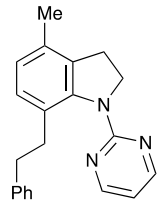
The title compound was obtained as a yellow solid (from carboxylic acid: 108.8 mg, 96%); mp: 90.4–91.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.40 (d, *J* = 4.6 Hz, 2H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.26–7.11 (m, 7H), 7.06-7.02 (m, 4H), 6.66 (t, *J* = 4.6 Hz, 1H), 6.00 (d, *J* = 8.6 Hz, 1H), 3.80 (dd, *J* = 15.5, 9.2 Hz, 1H) 3.08–2.90 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.4, 157.7, 143.4, 142.3, 141.8, 133.0, 131.8, 128.4, 128.2, 128.2, 128.2, 126.9, 125.6, 125.5, 124.6, 122.5, 112.7, 66.9, 38.2, 35.7, 35.1; IR (neat): $\tilde{\nu}$ = 3029, 2953, 1579, 1547, 1455, 1427, 1057, 699 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{26}H_{24}N_3$ $[M + H]^+$ 378.1965, found 378.1965.



3-Methyl-7-phenethyl-1-(pyrimidin-2-yl)indoline (3l):

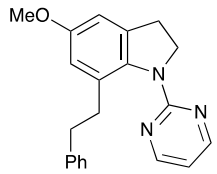
The title compound was obtained as a brown solid (from carboxylic acid: 76.8 mg, 81%); mp: 89.0–89.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.42 (d, *J* = 4.6 Hz, 2H), 7.21–7.10 (m, 4H), 7.07–7.06 (m, 2H), 7.01 (d, *J* = 6.9 Hz, 2H), 6.66 (t, *J* = 4.6 Hz, 1H), 4.61 (dd, *J* = 10.9, 8.0 Hz, 1H), 3.87 (dd, *J* = 11.5, 7.4 Hz, 1H), 3.36 (dq, *J* = 13.7, 6.9 Hz, 1H), 2.96–2.83 (m, 4H), 1.26 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.4, 157.6, 142.4, 142.0, 140.1, 131.9, 128.3, 128.2, 128.1, 125.6, 124.5, 121.0, 112.1, 61.0, 36.3, 35.8, 35.2, 18.3; IR (neat): $\tilde{\nu}$ = 3025, 2965,

1582, 1555, 1451, 1427, 1057, 703 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{21}H_{22}N_3$ $[M + H]^+$ 316.1808, found 316.1821.



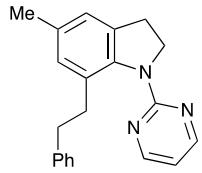
4-Methyl-7-phenethyl-1-(pyrimidin-2-yl)indoline (3m):

The title compound was obtained as a brown oil (from carboxylic acid: 80.0 mg, 84%); ^1H NMR (500 MHz, $CDCl_3$) δ: 8.40 (d, *J* = 5.2 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 6.9 Hz, 2H), 6.87 (d, *J* = 7.4 Hz, 1H), 6.65 (t, *J* = 4.9 Hz, 1H), 4.41 (t, *J* = 7.7 Hz, 2H), 2.95–2.84 (m, 6H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.4, 157.5, 142.5, 141.8, 133.4, 131.4, 129.1, 128.2, 128.1, 128.1, 125.5, 125.4, 112.1, 53.0, 35.6, 35.3, 28.5, 18.4; IR (neat): $\tilde{\nu}$ = 3020, 2917, 1579, 1551, 1459, 1284, 806, 699 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{21}H_{22}N_3$ $[M + H]^+$ 316.1808, found 316.1815.



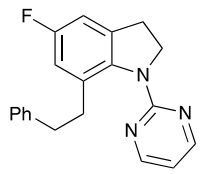
5-Methoxy-7-phenethyl-1-(pyrimidin-2-yl)indoline (3n):

The title compound was obtained as a yellow oil (from carboxylic acid: 87.4 mg, 88%); ^1H NMR (500 MHz, $CDCl_3$) δ: 8.40 (d, *J* = 4.6 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 6.9 Hz, 2H), 6.71–6.64 (m, 3H), 4.41 (t, *J* = 7.7 Hz, 2H), 3.78 (s, 3H), 3.00 (t, *J* = 7.4 Hz, 2H), 2.94–2.88 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.5, 157.5, 156.9, 142.2, 136.4, 135.9, 133.0, 128.2, 128.1, 125.5, 113.0, 111.8, 108.3, 55.5, 53.4, 35.8, 35.2, 30.2; IR (neat): $\tilde{\nu}$ = 3025, 2941, 1579, 1547, 1455, 1419, 1137, 699 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{21}H_{22}N_3O$ $[M + H]^+$ 332.1757, found 332.1759.



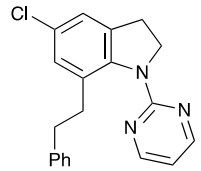
5-Methyl-7-phenethyl-1-(pyrimidin-2-yl)indoline (3o):

The title compound was obtained as a brown oil (from carboxylic acid: 80.9 mg, 85%); ^1H NMR (500 MHz, $CDCl_3$) δ: 8.40 (d, *J* = 4.6 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 2H), 6.97 (s, 1H), 6.94 (s, 1H), 6.65 (t, *J* = 4.6 Hz, 1H), 4.39 (t, *J* = 7.7 Hz, 2H), 2.99 (t, *J* = 7.4 Hz, 2H), 2.91–2.87 (m, 4H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.4, 157.5, 142.4, 140.0, 135.1, 133.9, 131.6, 128.7, 128.2, 128.1, 125.5, 123.0, 111.9, 53.3, 35.8, 35.3, 29.8, 21.0; IR (neat): $\tilde{\nu}$ = 3025, 2917, 1579, 1547, 1455, 1221, 703 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{21}H_{22}N_3$ $[M + H]^+$ 316.1808, found 316.1814.



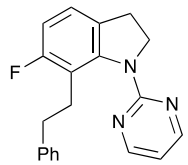
5-Fluoro-7-phenethyl-1-(pyrimidin-2-yl)indoline (3p):

The title compound was obtained as a white solid (from carboxylic acid: 85.7 mg, 89%); mp: 103.0–103.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.42 (d, J = 5.2 Hz, 2H), 7.20 (t, J = 7.4 Hz, 2H), 7.13 (t, J = 7.2 Hz, 1H), 7.02 (d, J = 6.9 Hz, 2H), 6.85–6.82 (m, 2H), 6.69 (t, J = 4.6 Hz, 1H), 4.42 (t, J = 7.4 Hz, 2H), 3.01 (t, J = 7.4 Hz, 2H), 2.92–2.85 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.4, 160.1 ($^{1}J_{C–F}$ = 242.3 Hz), 157.7, 141.9, 138.6 ($^{4}J_{C–F}$ = 2.4 Hz), 136.9 ($^{3}J_{C–F}$ = 8.4 Hz), 133.6 ($^{3}J_{C–F}$ = 7.2 Hz), 128.2, 128.2, 125.7, 114.2 ($^{2}J_{C–F}$ = 22.8 Hz), 112.3, 109.5 ($^{3}J_{C–F}$ = 24.0 Hz), 53.6, 35.6, 35.0, 30.1 ($^{4}J_{C–F}$ = 2.4 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ: 119.6; IR (neat): $\tilde{\nu}$ = 3032, 2959, 2924, 1580, 1551, 1450, 1120, 797 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{20}H_{19}FN_3$ $[M + H]^+$ 320.1558, found 320.1565.



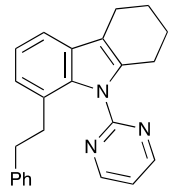
5-Chloro-7-phenethyl-1-(pyrimidin-2-yl)indoline (3q):

The title compound was obtained as a white solid (from carboxylic acid: 87.4 mg, 86%); mp: 95.2–95.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.41 (d, J = 4.6 Hz, 2H), 7.19 (t, J = 7.4 Hz, 2H), 7.14–7.11 (m, 2H), 7.07 (s, 1H), 6.99 (d, J = 6.9 Hz, 2H), 6.69 (t, J = 4.9 Hz, 1H), 4.39 (t, J = 7.7 Hz, 2H), 2.99 (t, J = 7.7 Hz, 2H), 2.91–2.83 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.1, 157.6, 141.8, 141.2, 136.8, 133.3, 129.1, 128.2, 128.2, 128.0, 125.7, 122.4, 112.5, 53.3, 35.6, 35.0, 29.7; IR (neat): $\tilde{\nu}$ = 3029, 2969, 1579, 1555, 1447, 1423, 699 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{20}H_{19}ClN_3$ $[M + H]^+$ 336.1262, found 336.1265.



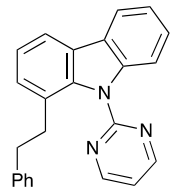
6-Fluoro-7-phenethyl-1-(pyrimidin-2-yl)indoline (3r):

The title compound was obtained as a white solid (from carboxylic acid: 83.9 mg, 88%); mp: 96.0–97.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.44 (d, J = 4.6 Hz, 2H), 7.18 (t, J = 7.2 Hz, 2H), 7.12 (t, J = 7.4 Hz, 1H), 7.03–6.98 (m, 3H), 6.78–6.72 (m, 2H), 4.38 (t, J = 7.4 Hz, 2H), 2.98–2.87 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.4 ($^{1}J_{C–F}$ = 241.1 Hz), 161.1, 157.7, 144.0 ($^{3}J_{C–F}$ = 8.4 Hz), 142.2, 130.3 ($^{4}J_{C–F}$ = 2.4 Hz), 128.2, 128.1, 125.6, 122.4 ($^{3}J_{C–F}$ = 10.8 Hz), 120.2 ($^{2}J_{C–F}$ = 20.4 Hz), 112.6, 110.6 ($^{2}J_{C–F}$ = 24.0 Hz), 54.1, 34.1 ($^{4}J_{C–F}$ = 2.4 Hz), 29.5 ($^{3}J_{C–F}$ = 3.6 Hz), 29.2; ^{19}F NMR (470 MHz, $CDCl_3$) δ: 119.8; IR (neat): $\tilde{\nu}$ = 3030, 2953, 29117, 1581, 1436, 1154, 1020, 798 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{20}H_{19}FN_3$ $[M + H]^+$ 320.1558, found 320.1565



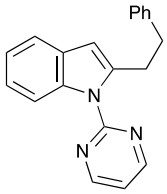
8-Phenethyl-9-(pyrimidin-2-yl)-2,3,4,9-tetrahydro-1*H*-carbazole (3t):

The title compound was obtained as a brown solid (from carboxylic acid: 77.9 mg, 73%); mp: 68.5–69.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.65 (d, *J* = 4.6 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 1H) , 7.09–6.99 (m, 5H), 6.95 (d, *J* = 6.9 Hz, 1H), 6.73 (d, *J* = 6.9 Hz, 2H), 2.73–2.52 (m, 8H), 1.79–1.75 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.7, 158.2, 141.9, 136.9, 134.8, 130.5, 128.1, 128.0, 126.3, 125.6, 124.3, 121.2, 118.2, 116.1, 113.8, 36.0, 35.6, 23.7, 23.3, 22.6, 21.0; IR (neat): $\tilde{\nu}$ = 3057, 2937, 1559, 1416, 1217, 703 cm^{-1}; HRMS(ESI): *m/z* Calcd for $C_{24}H_{24}N_3$ $[M+H]^+$ 354.1965, found: 354.1964.



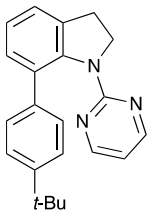
1-Phenethyl-9-(pyrimidin-2-yl)carbazole (3u):

The title compound was obtained as a colourless oil (from carboxylic acid: 54.3 mg, 52%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.80 (d, *J* = 4.6 Hz, 2H), 8.06–8.03 (m, 2H), 7.96 (dd, *J* = 6.9, 1.7 Hz, 1H), 7.41–7.38 (m, 1H), 7.33–7.28 (m, 3H), 7.18–7.07 (m, 4H), 6.83 (d, *J* = 8.0 Hz, 2H), 2.96–2.93 (m, 2H), 2.74–2.71 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.0, 158.4, 141.7, 141.4, 138.2, 128.5, 128.2, 128.0, 128.0, 126.8, 126.5, 125.7, 125.5, 122.4, 122.0, 119.8, 118.1, 117.9, 112.3, 36.2, 35.4. The spectral data matched those reported in the literature.[10]



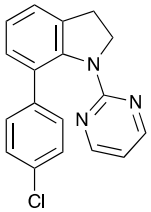
2-Phenethyl-1-(pyrimidin-2-yl)indole (3v):

The title compound was obtained as a pale yellow solid (from carboxylic acid: 66.1 mg, 73%); mp: 97.5–100.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.71 (d, *J* = 4.6 Hz, 2H), 8.28 (d, *J* = 8.6 Hz, 1H) , 7.52 (d, *J* = 7.4 Hz, 1H), 7.30–7.13 (m, 7H), 7.03 (t, *J* = 4.6 Hz, 1H), 6.49 (s, 1H), 3.46 (t, *J* = 8.0 Hz, 2H), 2.97 (t, *J* = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.2, 158.0, 141.8, 141.3, 136.8, 129.2, 128.3, 128.3, 125.9, 122.6, 121.8, 119.7, 117.0, 113.9, 105.9, 35.7, 31.5. The spectral data matched those reported in the literature.[10]



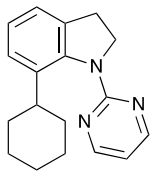
7-(4-(*tert*-Butyl)phenyl)-1-(pyrimidin-2-yl)indoline (3w):

The title compound was obtained as a yellow solid (from carboxylic acid: 68.3 mg, 69%; from anhydride: 62.9 mg, 62%); mp: 111.2–112.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.89 (d, J = 4.6 Hz, 2H), 7.28 (d, J = 7.4 Hz, 1H), 7.23–7.20 (m, 3H), 7.16–7.14 (m, 2H), 7.08 (t, J = 7.7 Hz, 1H), 6.31 (t, J = 4.9 Hz, 1H), 4.43 (t, J = 8.0 Hz, 2H), 3.17 (t, J = 8.0 Hz, 2H), 1.24 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.9, 156.2, 149.1, 141.1, 139.2, 134.7, 129.8, 128.7, 126.3, 124.5, 123.5, 123.3, 111.3, 52.0, 34.3, 31.4, 29.5; IR (neat): $\tilde{\nu}$ = 3033, 2955, 1575, 1550, 1455, 1431, 831, 810, 776 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{22}H_{24}N_3$ $[M + H]^+$ 330.1965, found 330.1973. The spectral data matched those reported in the literature.[11]



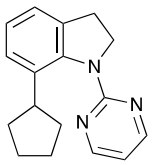
7-(4-Chlorophenyl)-1-(pyrimidin-2-yl)indoline (3x):

The title compound was obtained as a white solid (from carboxylic acid: 64.3 mg, 70%); mp: 146.1–147.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.99 (d, J = 4.6 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H), 7.24–7.21 (m, 2H), 7.13–7.08 (m, 3H), 6.42 (t, J = 4.9 Hz, 1H), 4.45 (t, J = 8.0 Hz, 2H), 3.16 (t, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.1, 156.5, 140.9, 140.7, 135.0, 131.7, 129.1, 128.6, 127.9, 127.9, 123.9, 123.8, 112.0, 52.1, 29.4. The spectral data matched those reported in the literature.[11]



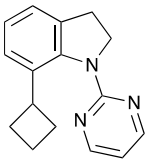
7-Cyclohexyl-1-(pyrimidin-2-yl)indoline (3y):

The title compound was obtained as a yellow oil (from anhydride: 71.6 mg, 85%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.42 (d, J = 5.2 Hz, 2H), 7.17–7.14 (m, 1H), 7.08–7.05 (m, 2H), 6.70 (t, J = 4.9 Hz, 1H), 4.41 (t, J = 7.7 Hz, 2H), 3.03 (t, J = 7.7 Hz, 2H), 2.40 (tt, J = 12.0, 3.1 Hz, 1H), 1.97 (d, J = 12.0 Hz, 2H), 1.76 (d, J = 13.2 Hz, 2H), 1.65 (d, J = 12.6 Hz, 1H), 1.44–1.36 (m, 2H), 1.26–1.20 (m, 1H), 1.17–1.08 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.4, 157.3, 141.1, 38.6, 134.6, 125.6, 124.9, 121.8, 112.2, 53.5, 40.9, 33.7, 30.1, 26.9, 26.3; IR (neat): $\tilde{\nu}$ = 2924, 2848, 1578, 1449, 1427, 1184, 797, 777 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{18}H_{22}N_3$ $[M + H]^+$ 280.1808, found 280.1819.



7-Cyclopentyl-1-(pyrimidin-2-yl)indoline (3z):

The title compound was obtained as a yellow oil (from anhydride: 59.0 mg, 72%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.40 (d, *J* = 4.6 Hz, 2H), 7.19–7.16 (m, 1H), 7.08=7.04 (m, 2H), 6.67 (t, *J* = 4.9 Hz, 1H), 4.42 (t, *J* = 7.4 Hz, 2H), 3.03–2.91 (m, 3H), 2.12–2.04 (m, 2H), 1.77–1.72 (m, 2H), 1.59-1.44 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.9, 157.4, 142.2, 137.8, 134.6, 125.6, 124.7, 121.7, 112.2, 53.3, 42.4, 34.5, 30.0, 25.8; IR (neat): $\tilde{\nu}$ = 2953, 2866, 1579, 1551, 1455, 1427, 799, 757 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{17}H_{20}N_3$ $[M + H]^+$ 266.1652, found 266.1649.



7-Cyclobutyl-1-(pyrimidin-2-yl)indoline (3A)

The title compound was obtained as a yellow solid (from anhydride: 53.5 mg, 71%); mp: 93.5–95.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.42 (d, *J* = 4.6 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.09–7.03 (m, 2H), 6.68 (t, *J* = 4.6 Hz, 1H), 4.38 (t, *J* = 7.7 Hz, 2H), 3.69 (quint, *J* = 8.9 Hz, 1H), 3.04 (t, *J* = 7.7 Hz, 2H), 2.07–2.01 (m, 4H), 1.86–1.68 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.2, 157.5, 141.1, 136.3, 134.1, 125.8, 124.0, 121.7, 112.0, 53.0, 38.4, 29.7, 29.1, 18.2; IR (neat): $\tilde{\nu}$ = 2980, 2941, 2889, 2862, 1576, 1428, 1282, 787 cm^{-1}; HRMS (ESI): *m/z* Calcd for $C_{16}H_{18}N_3$ $[M + H]^+$ 252.1495, found 252.1507.

7. References

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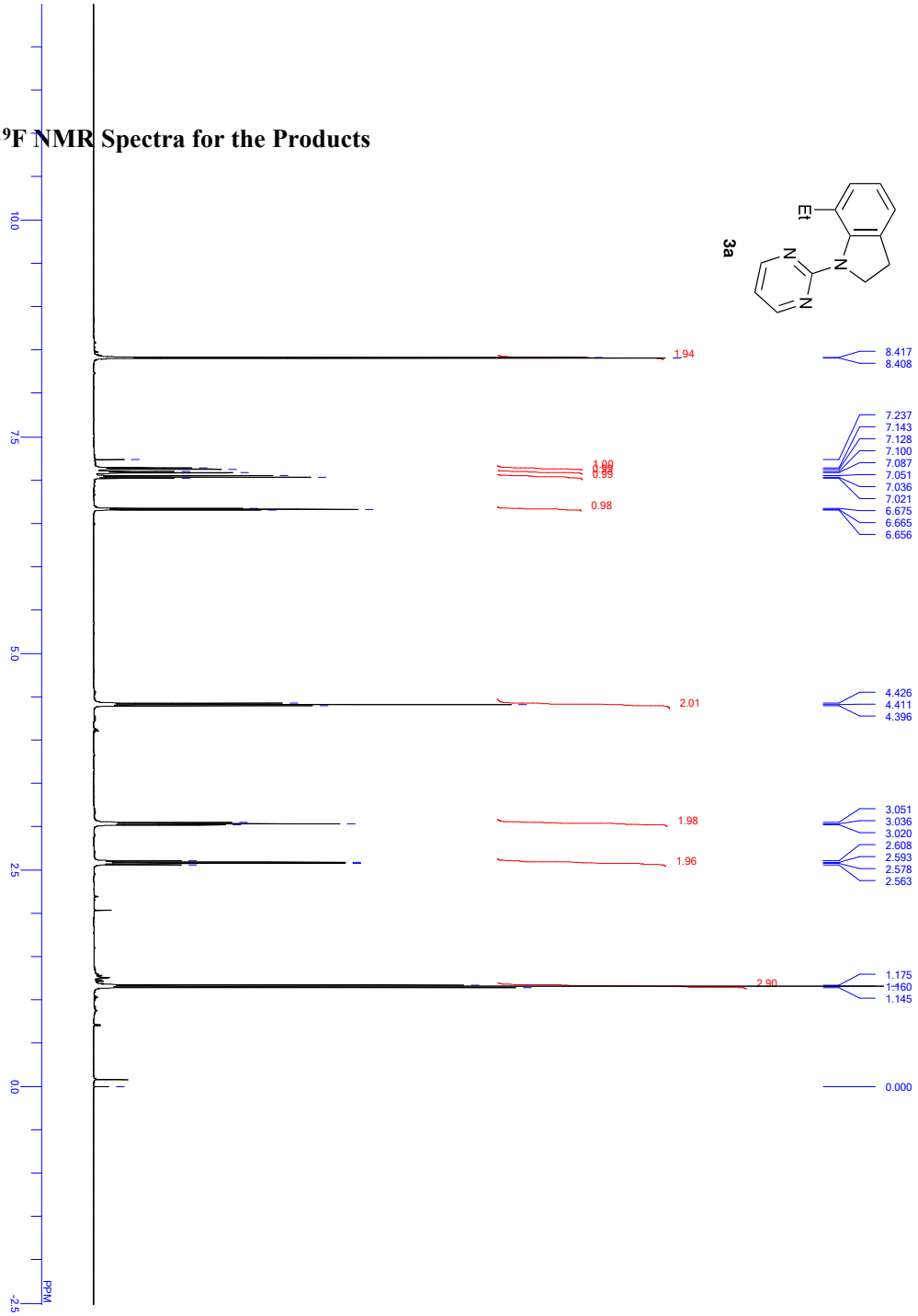
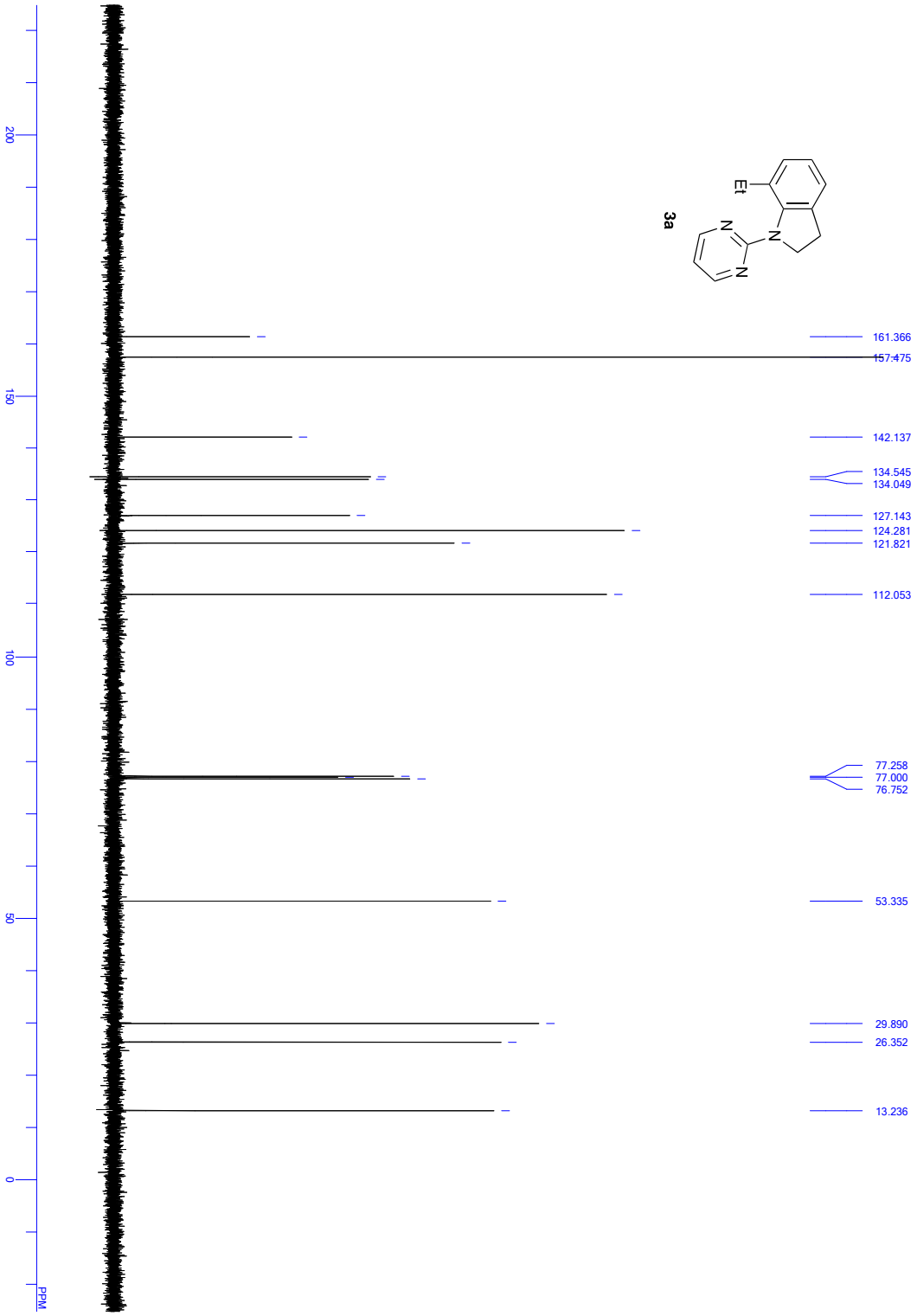
12. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra for the Products

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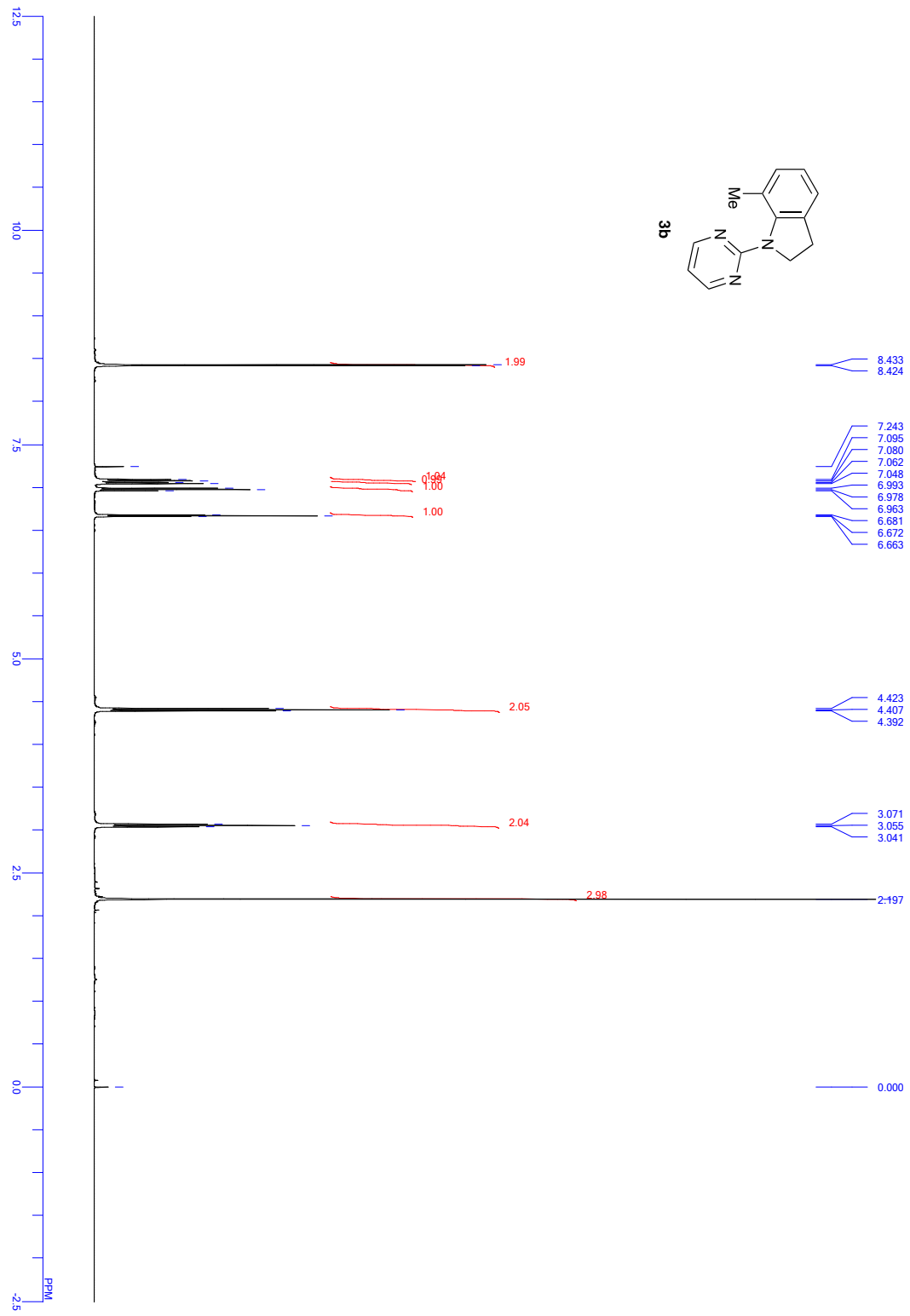
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1.00
2.05
2.04
2.98
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0.000
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7.243
7.095
7.080
7.062
7.048
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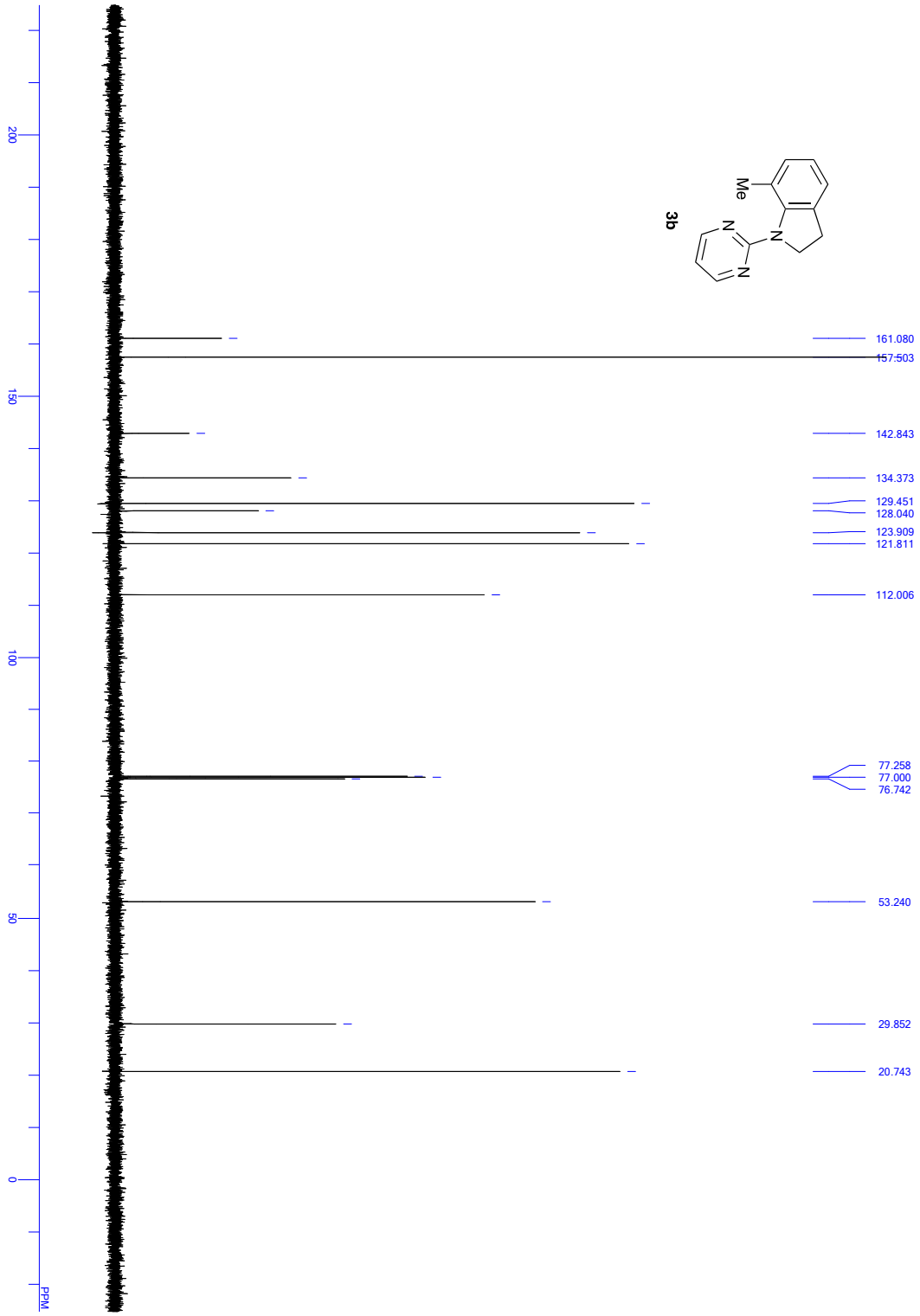
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100
50
0
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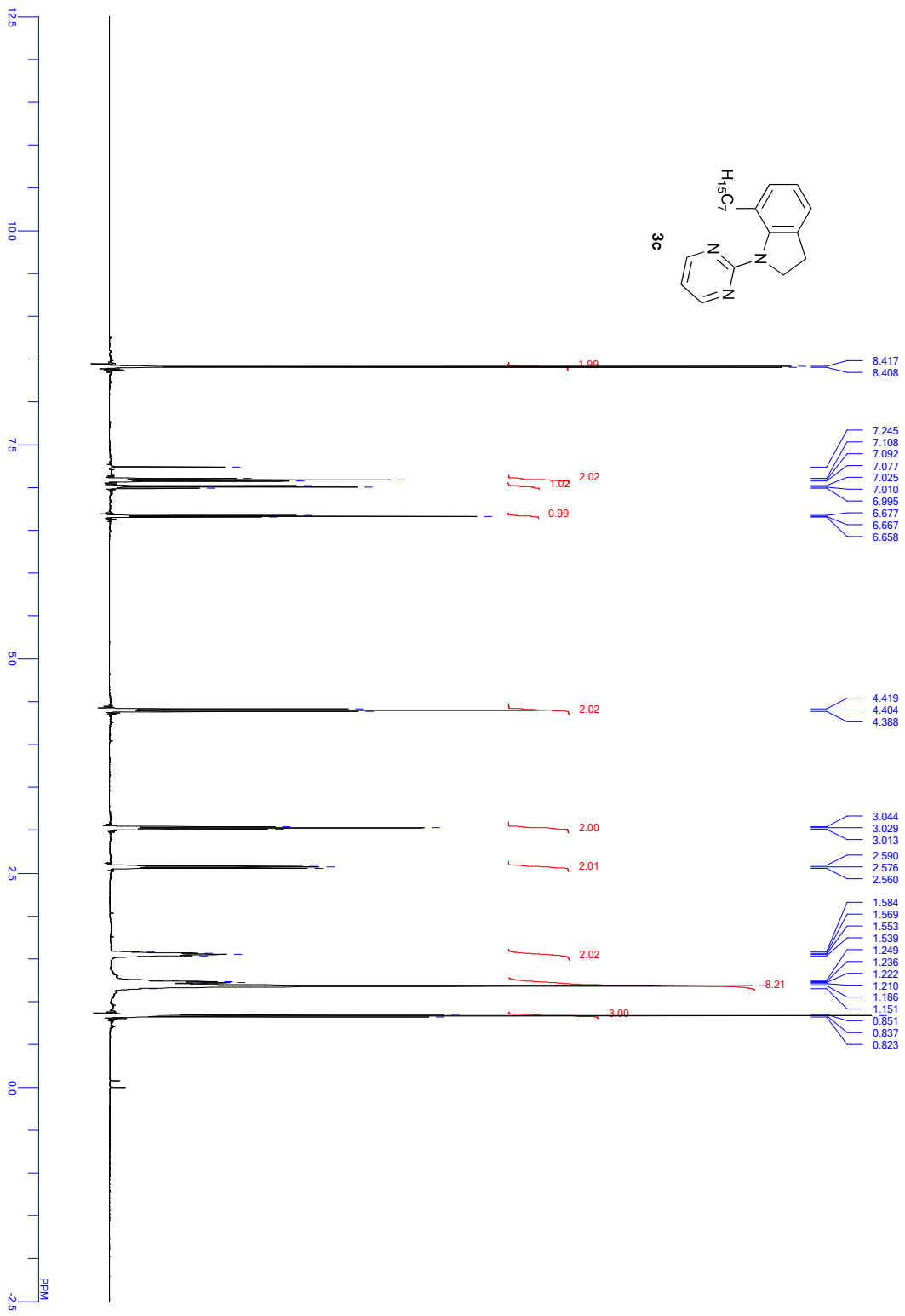
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7.077
7.025
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6.677
6.667
6.658
4.419
4.404
4.388
3.044
3.029
3.013
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2.576
2.560
1.584
1.569
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1.222
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2.00
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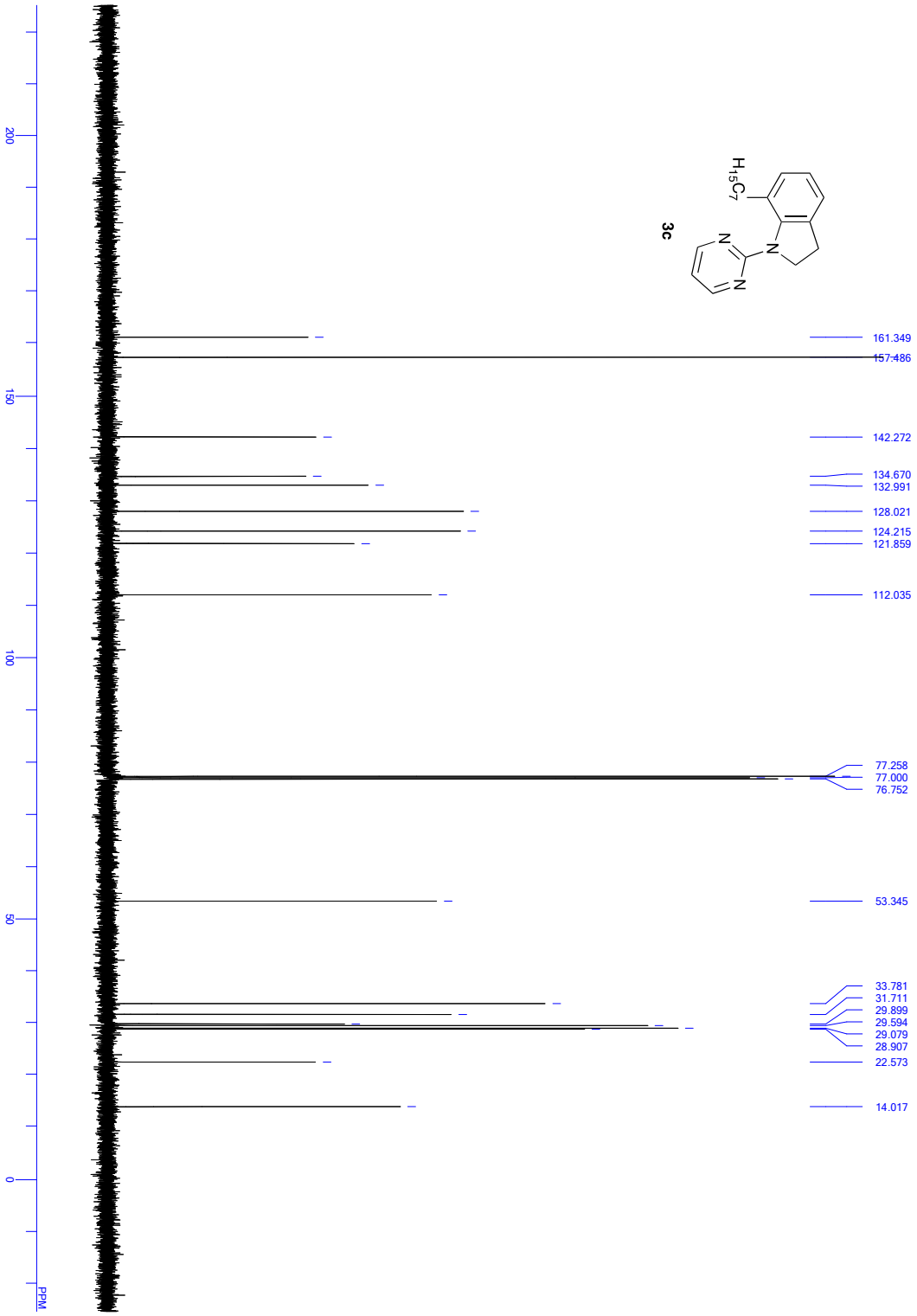
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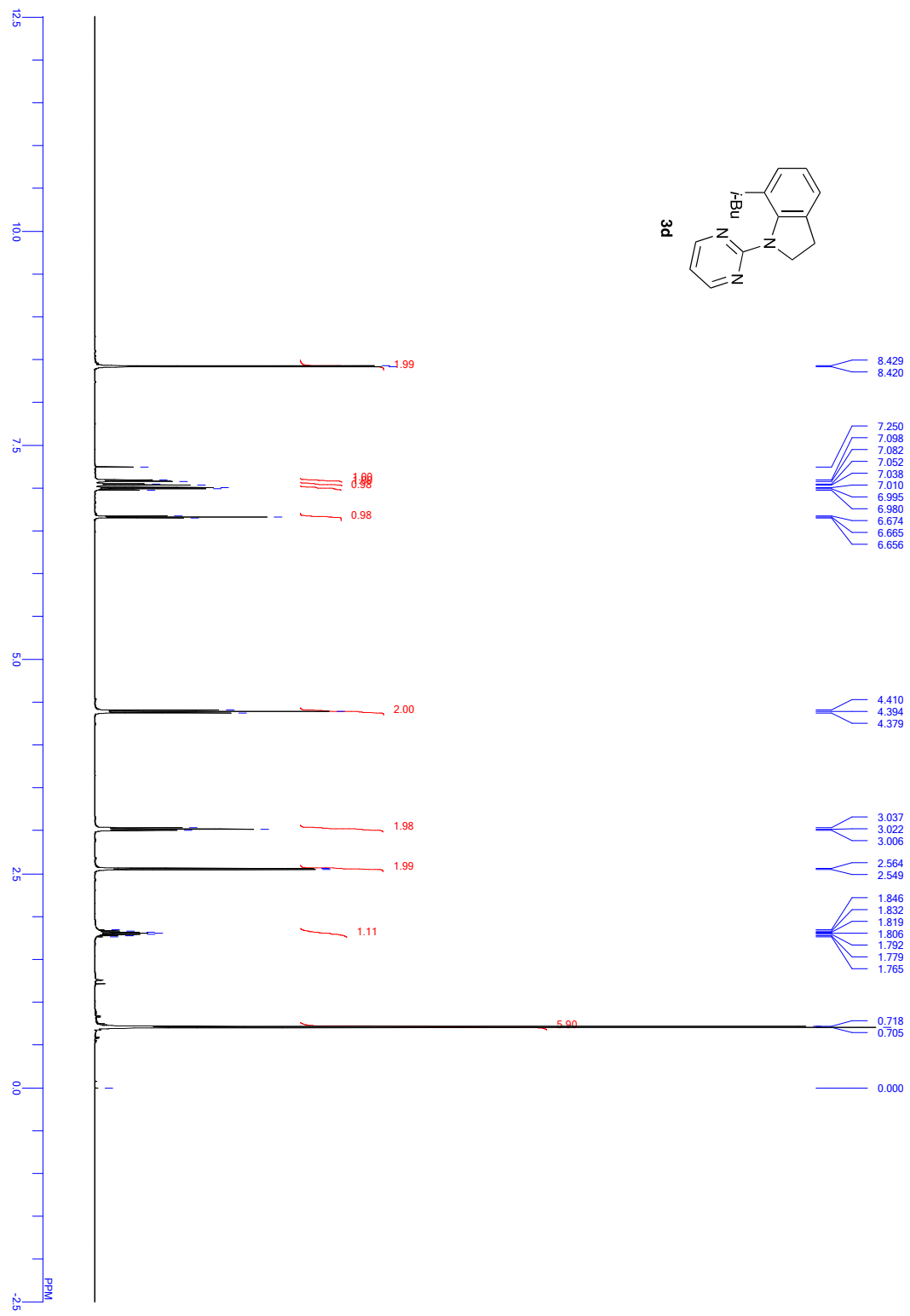
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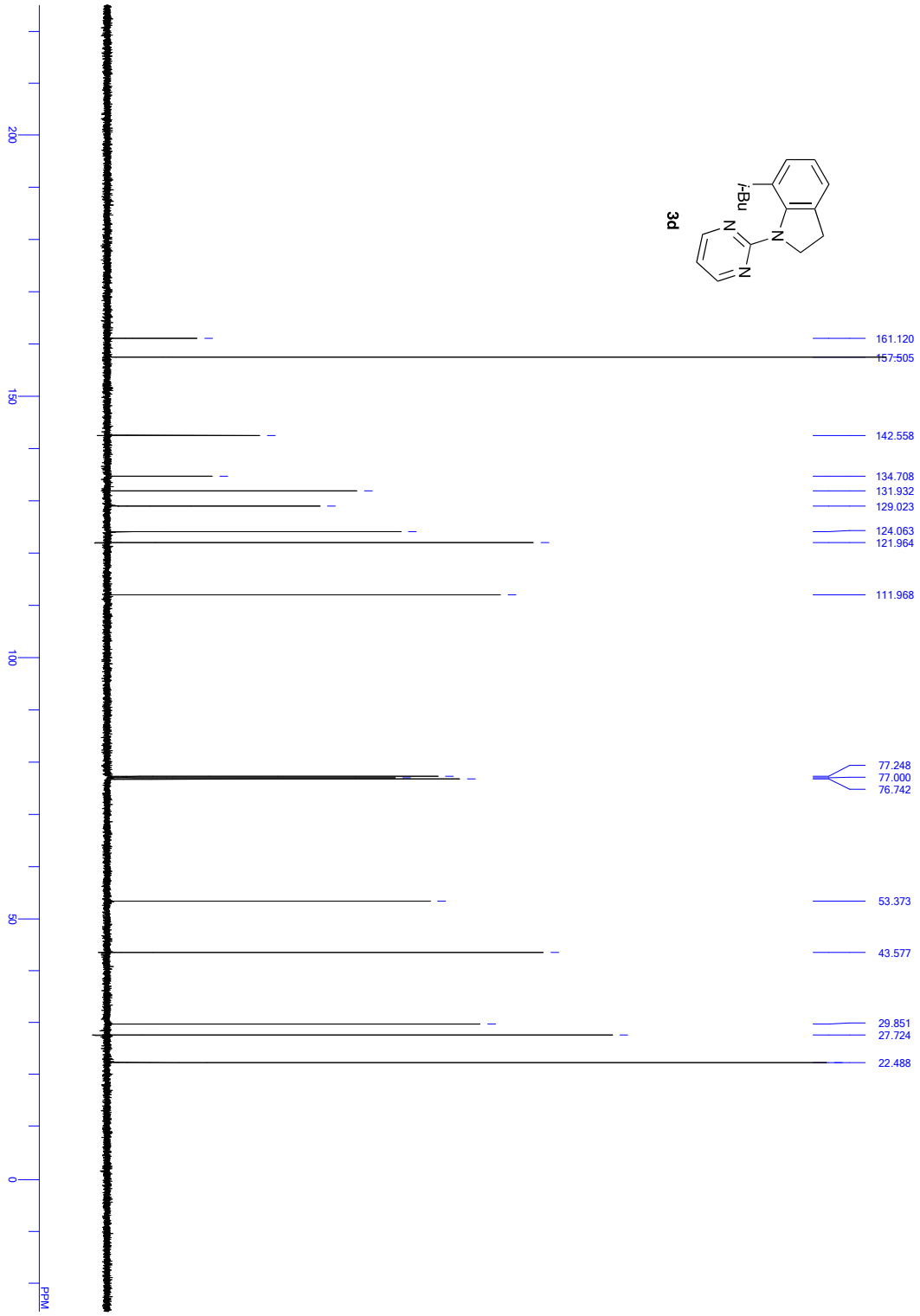
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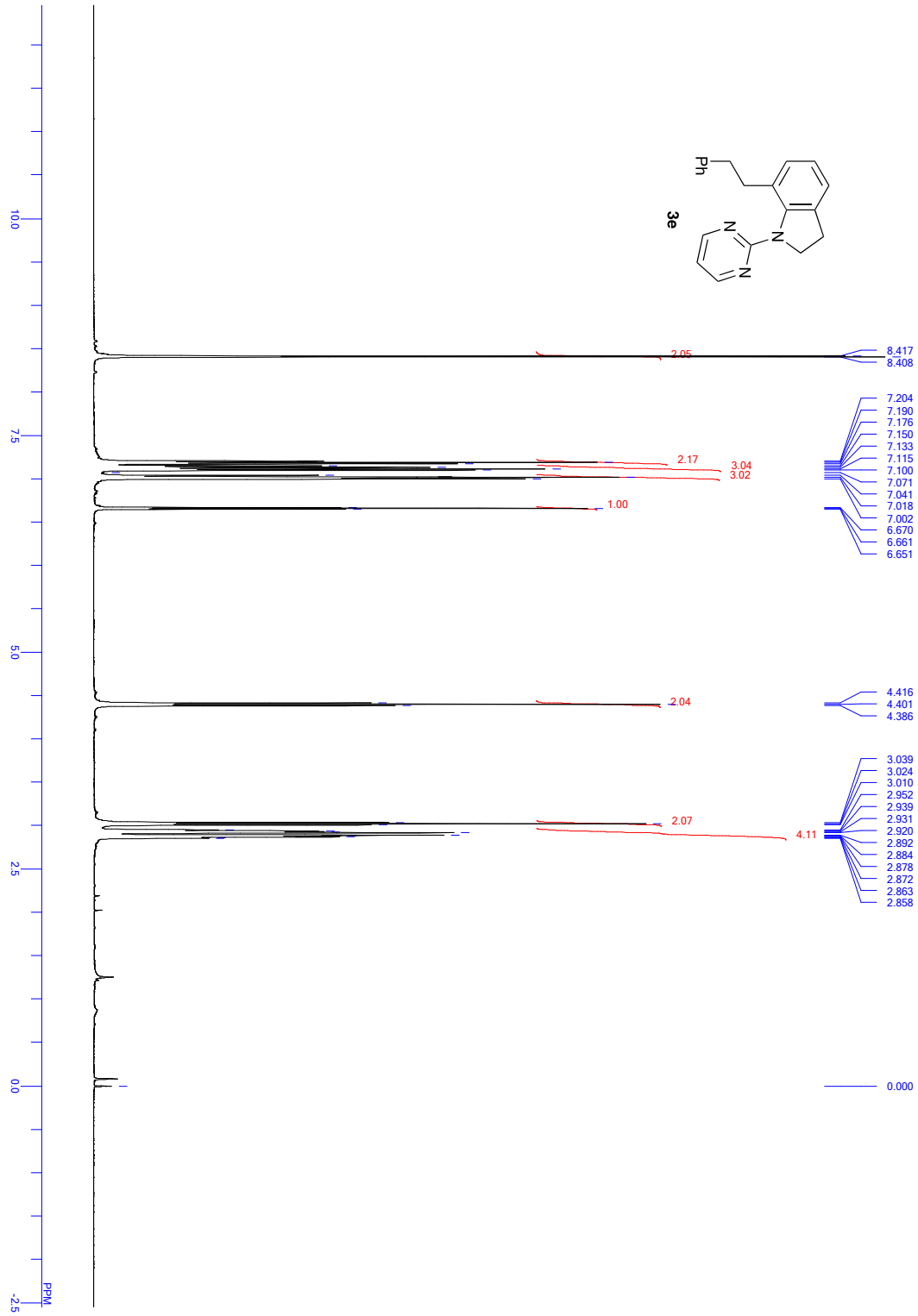
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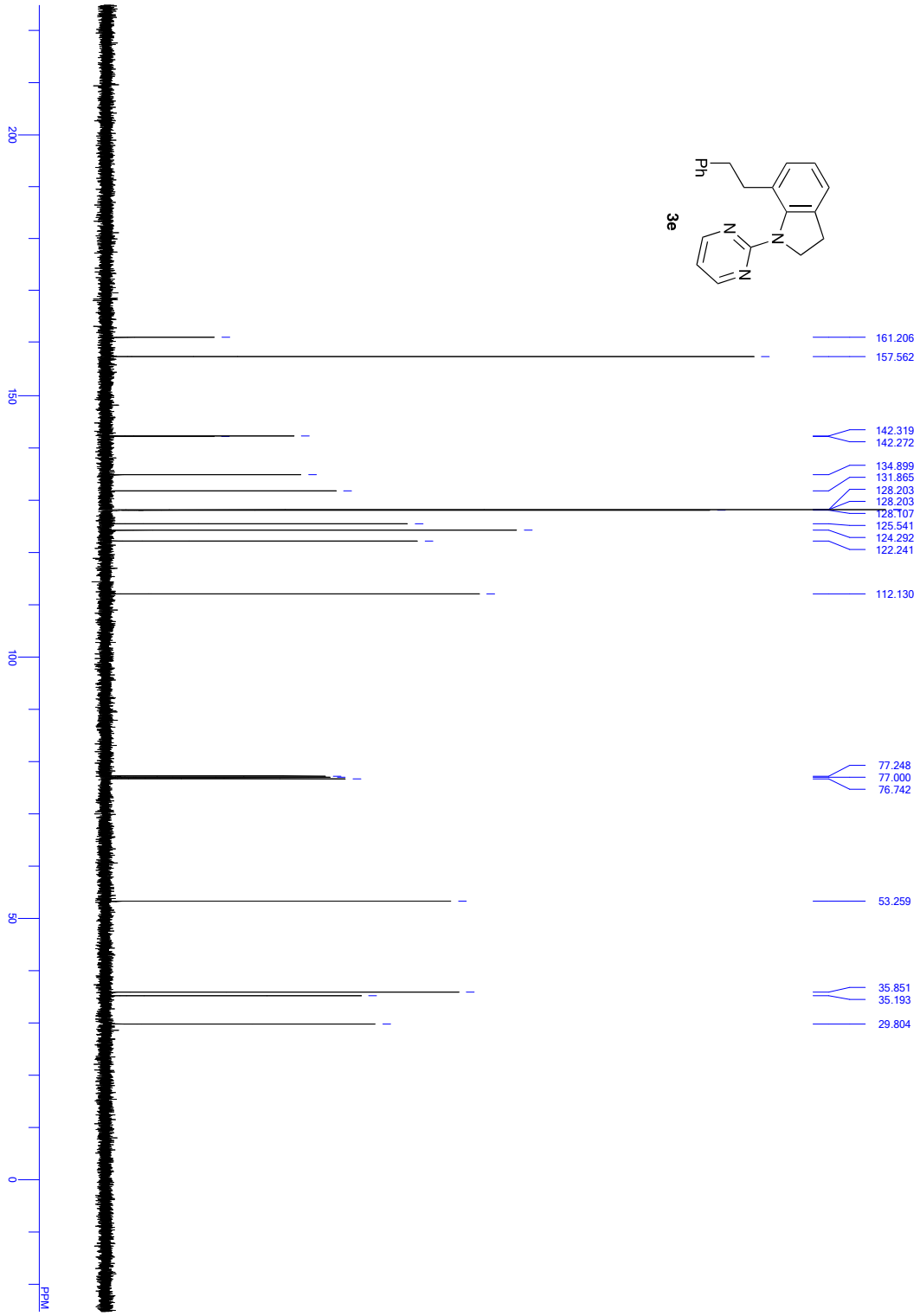
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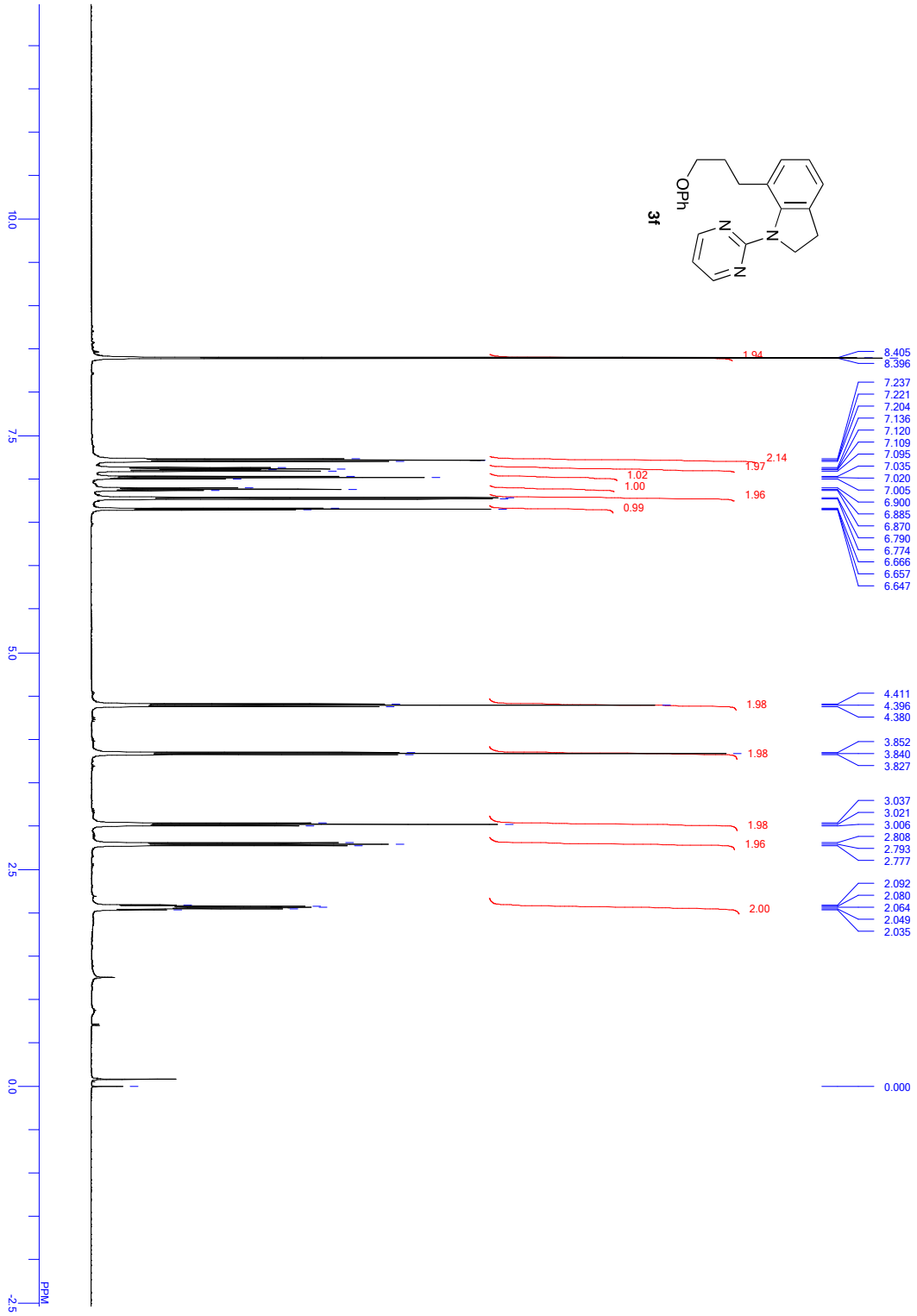
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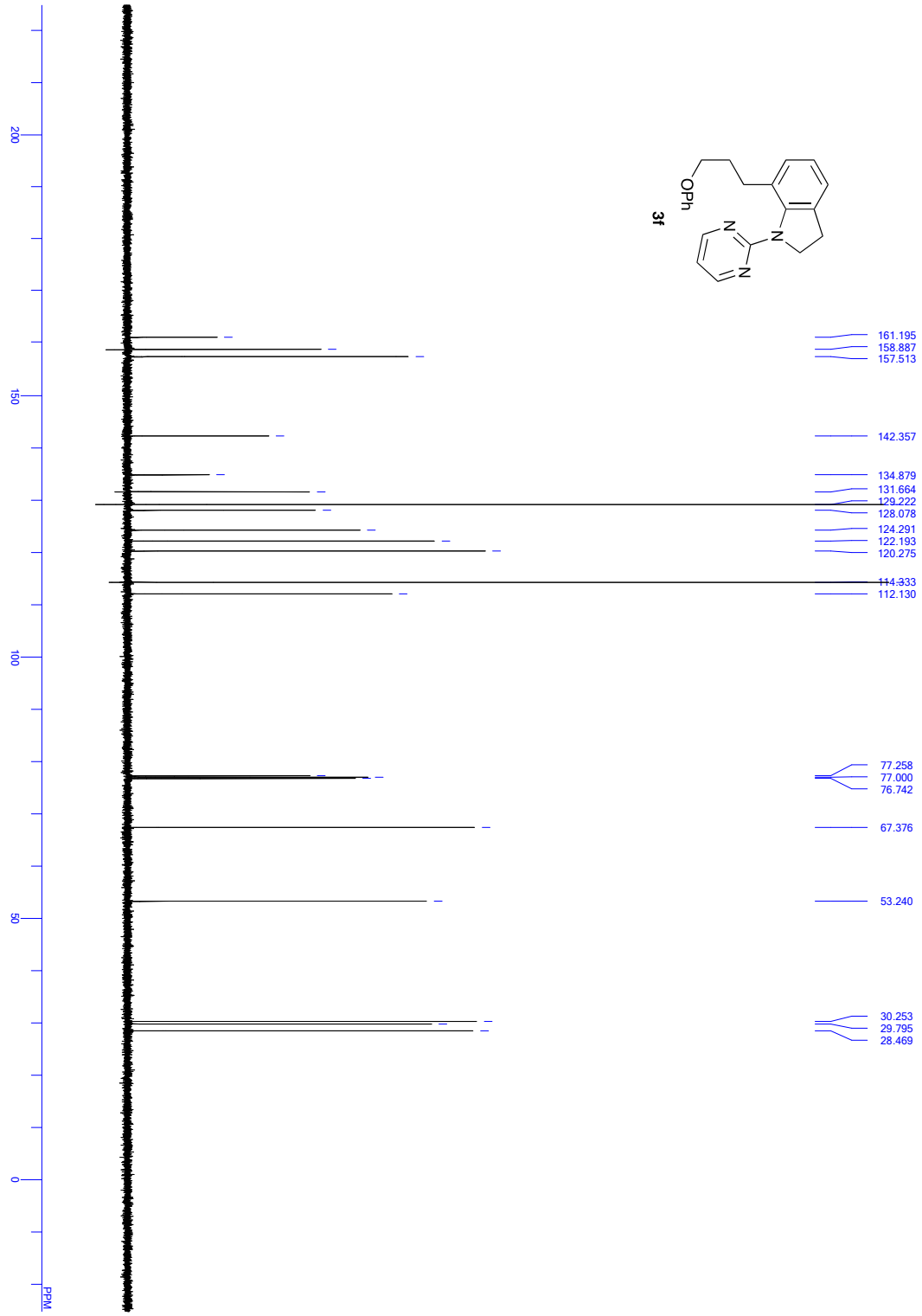
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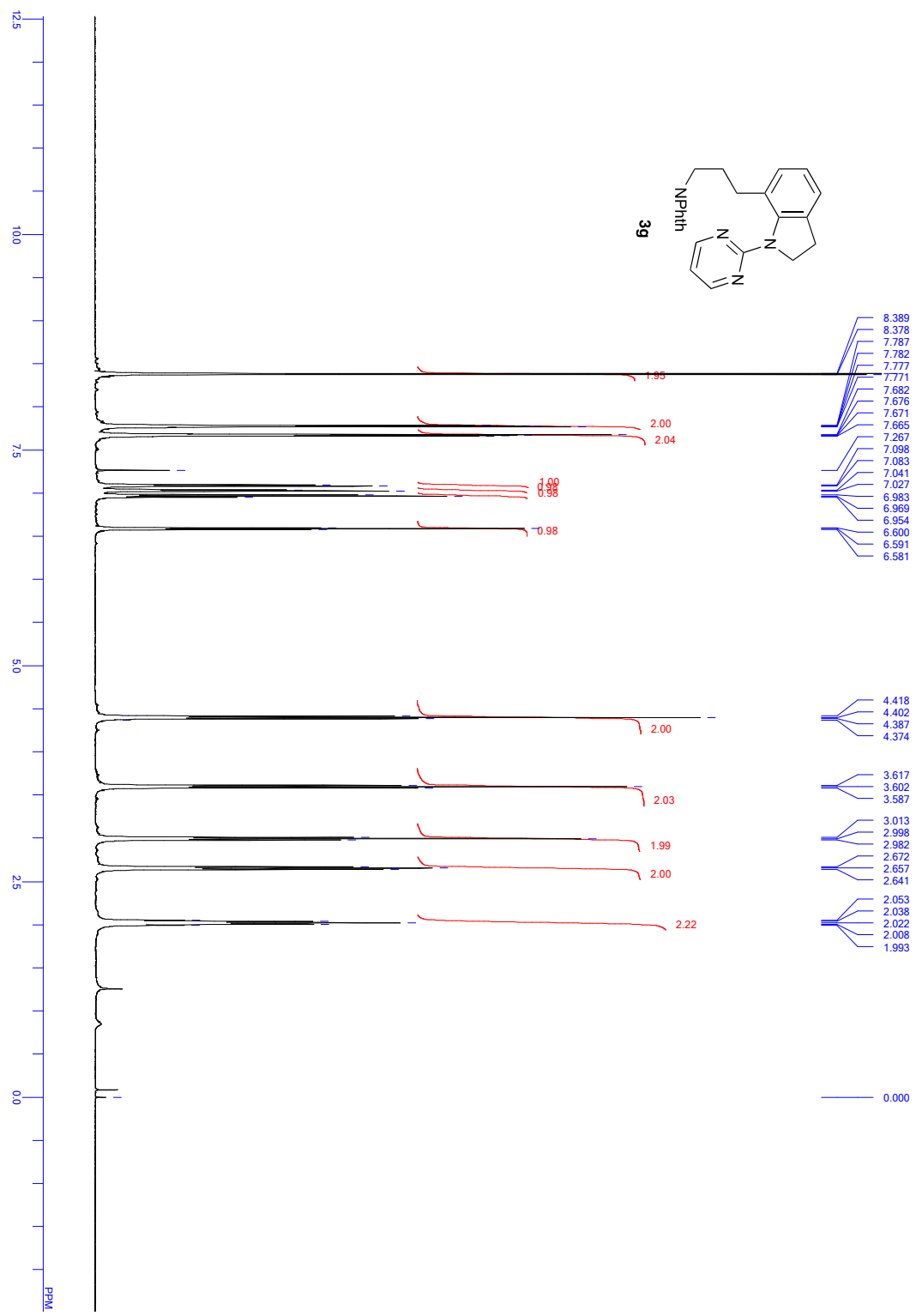
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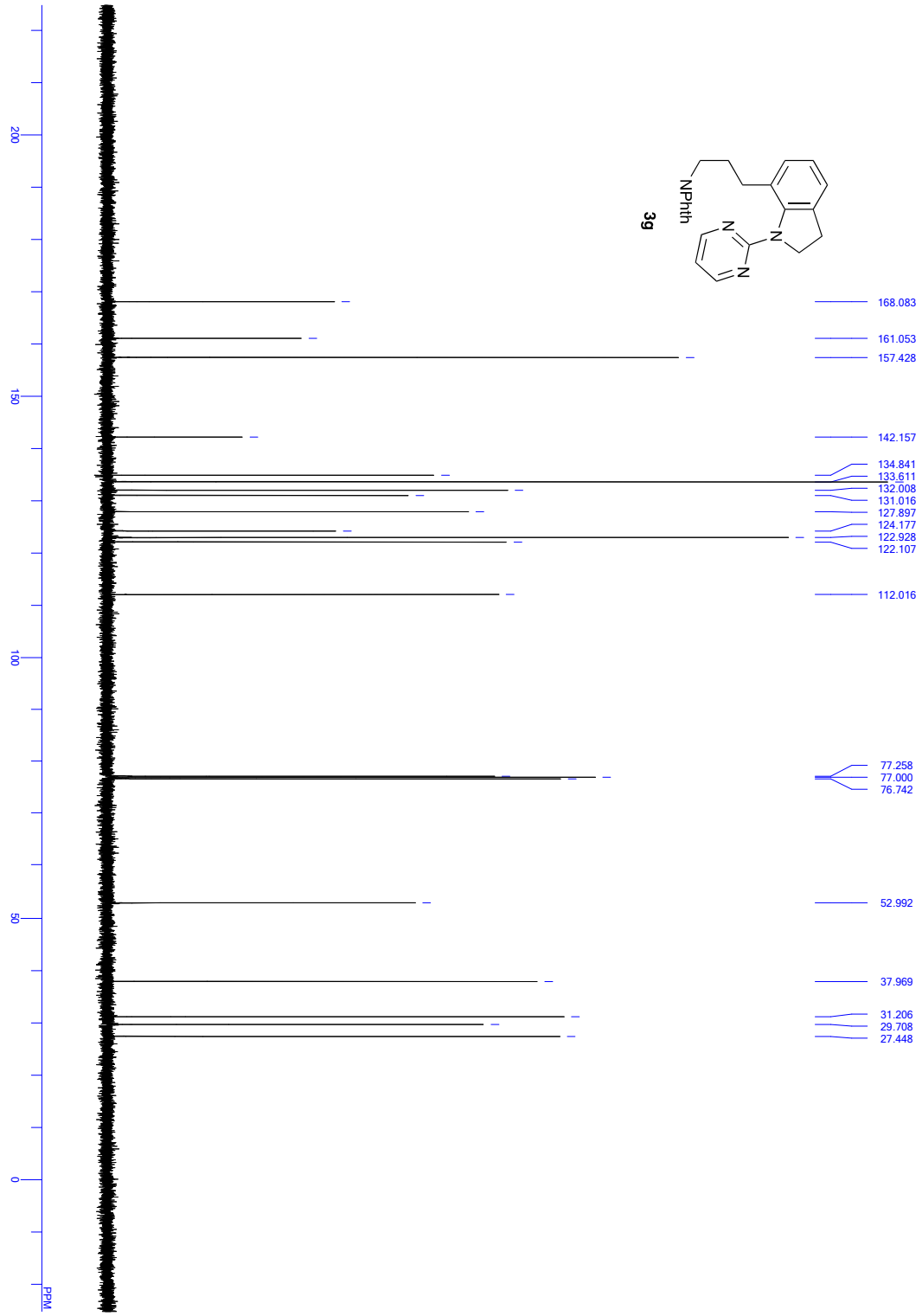
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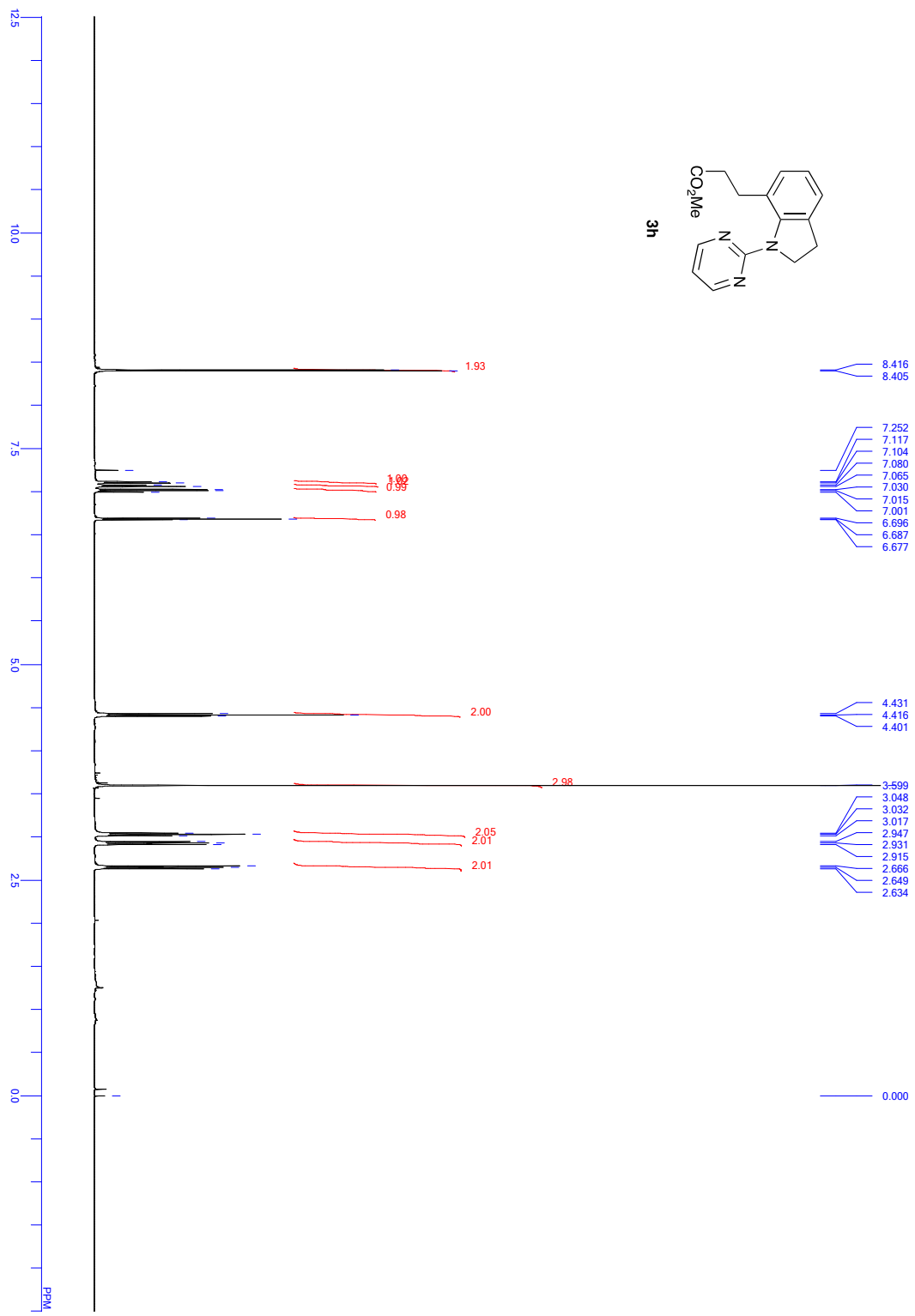
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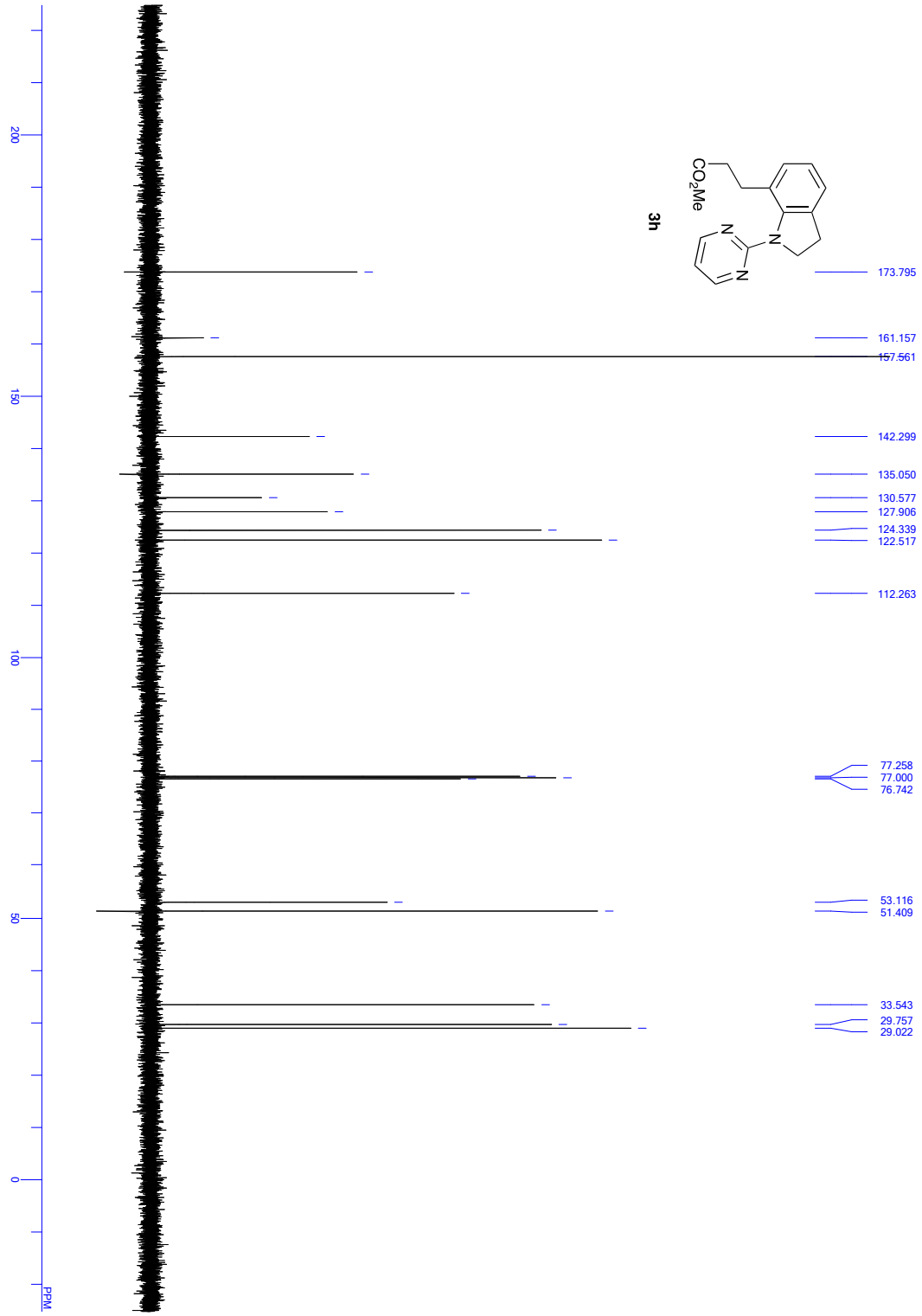
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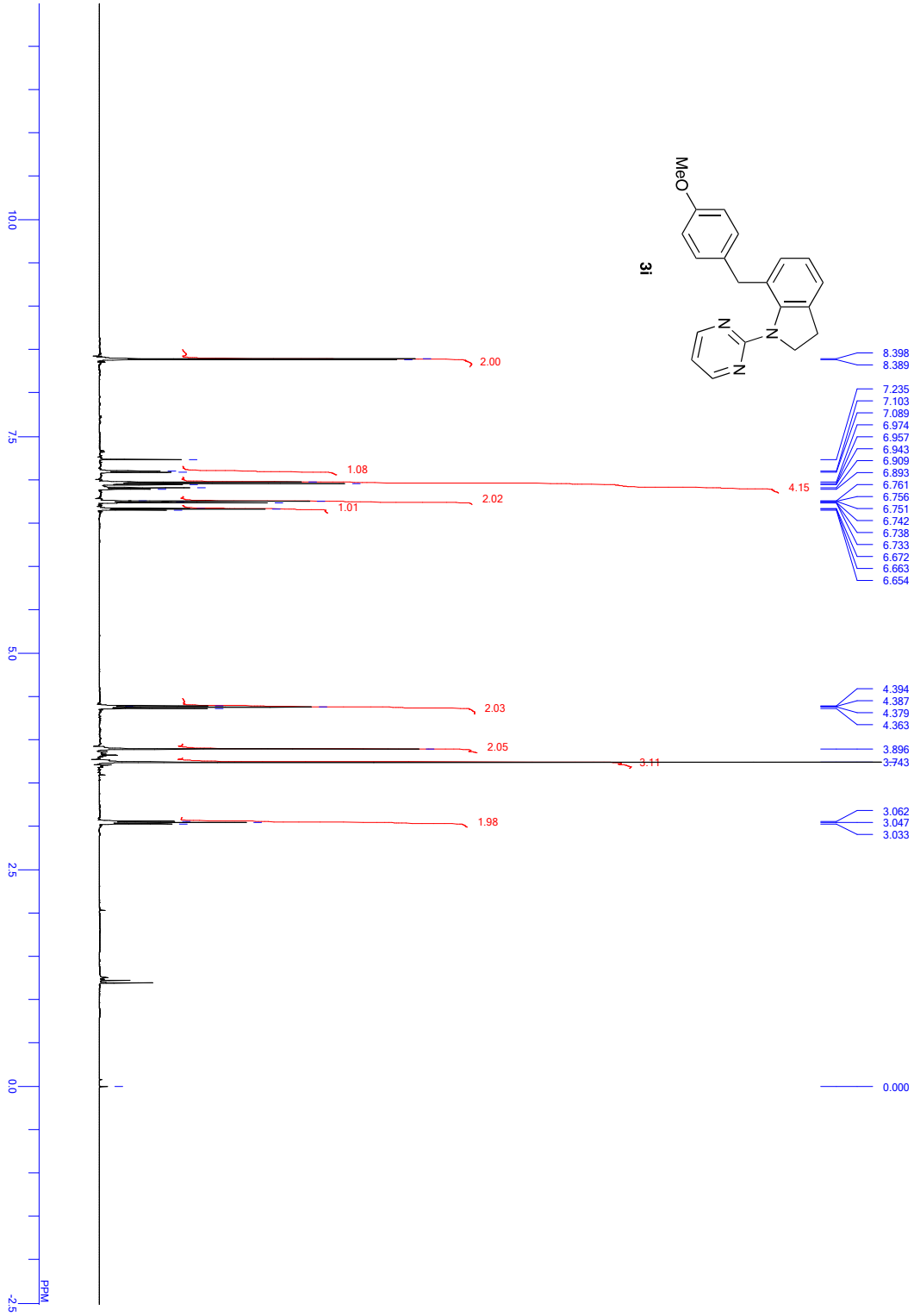
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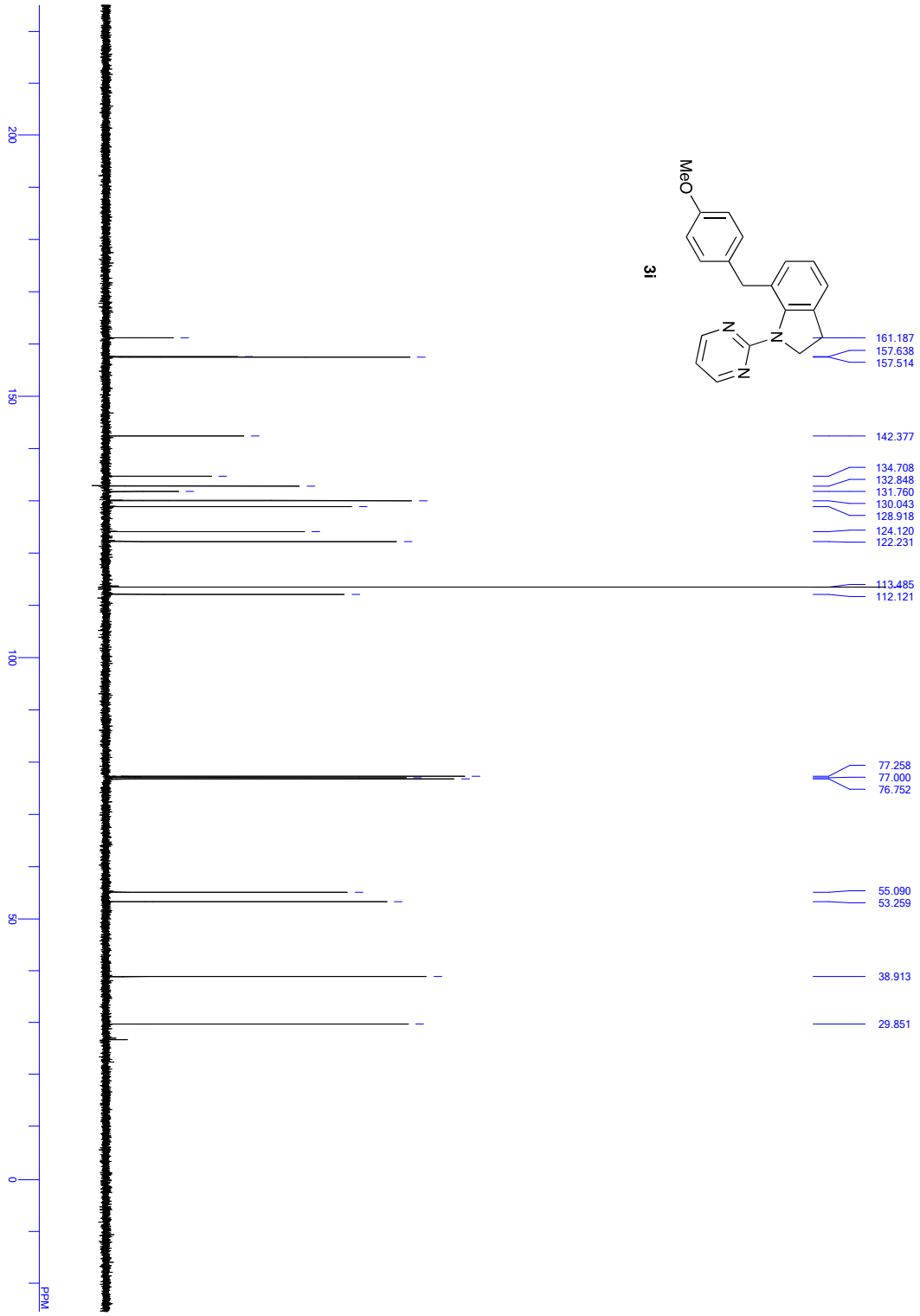
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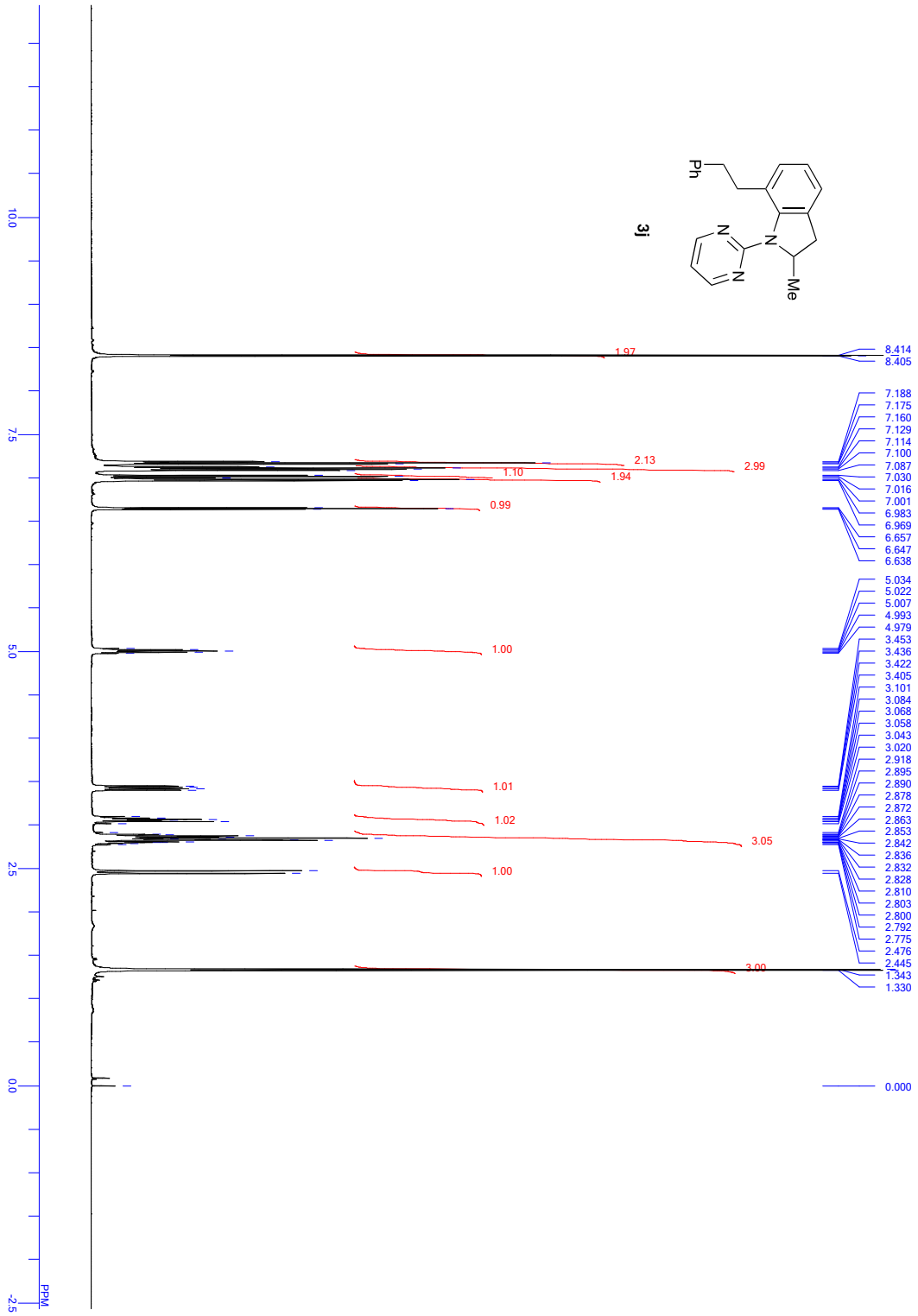
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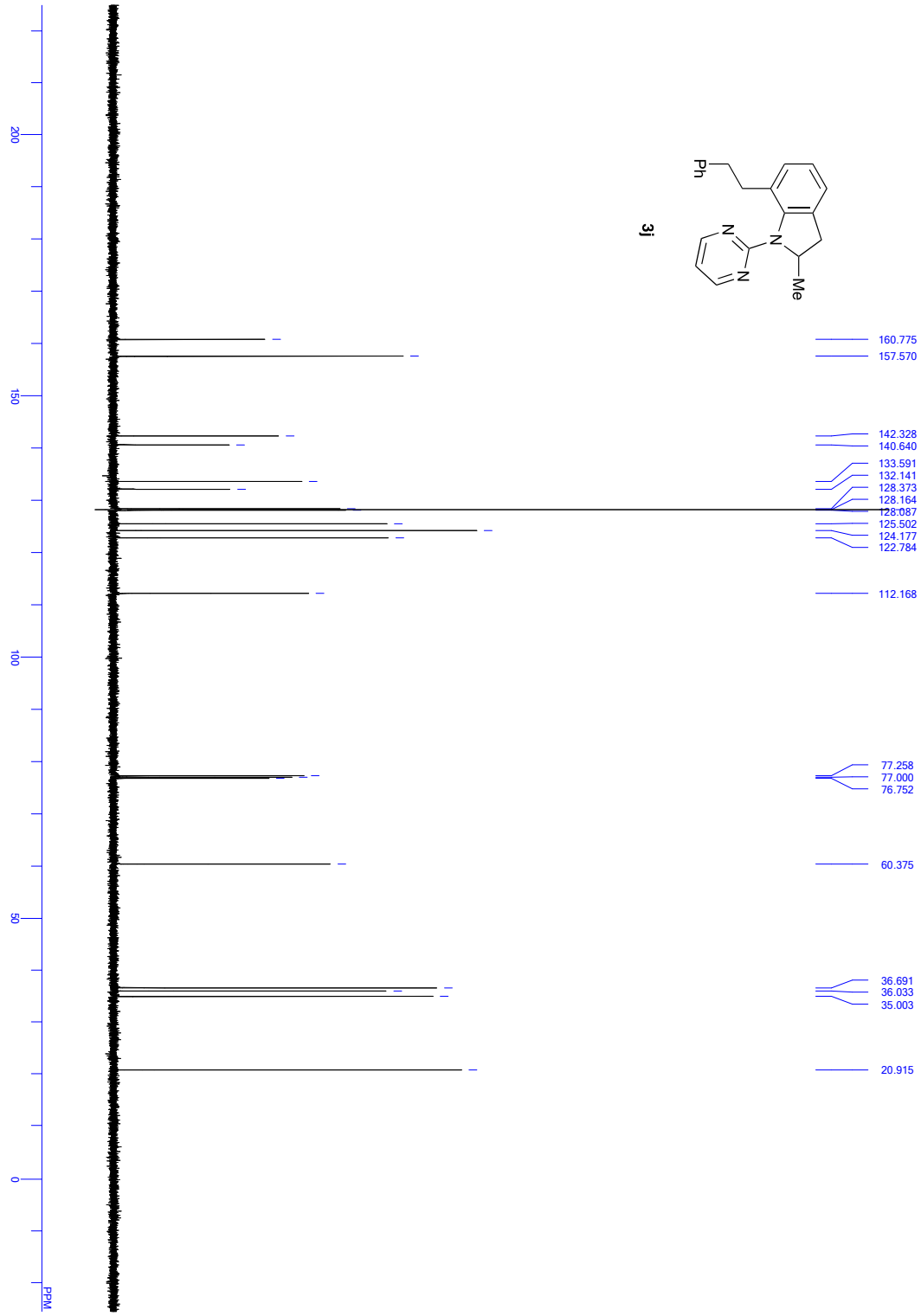
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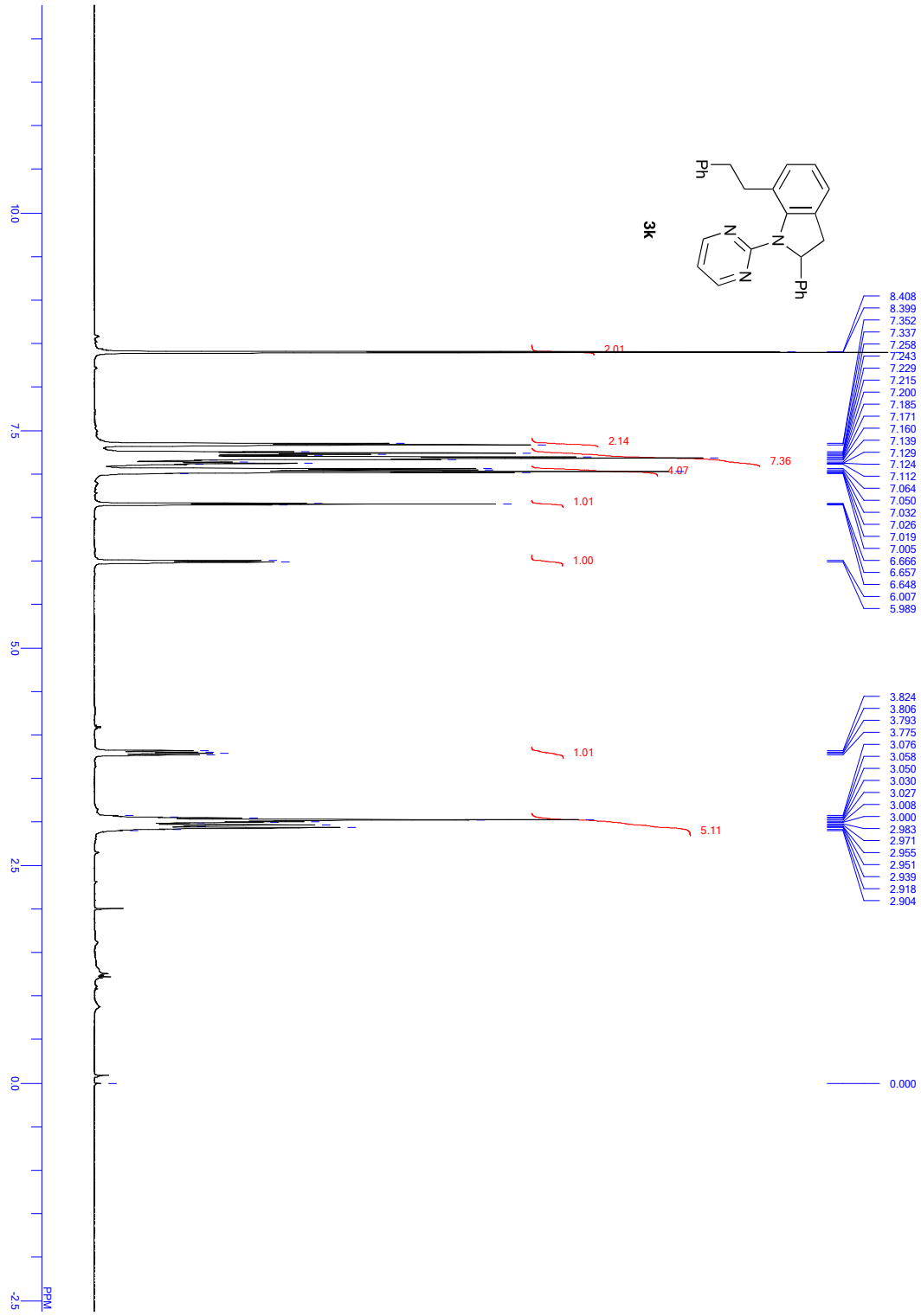
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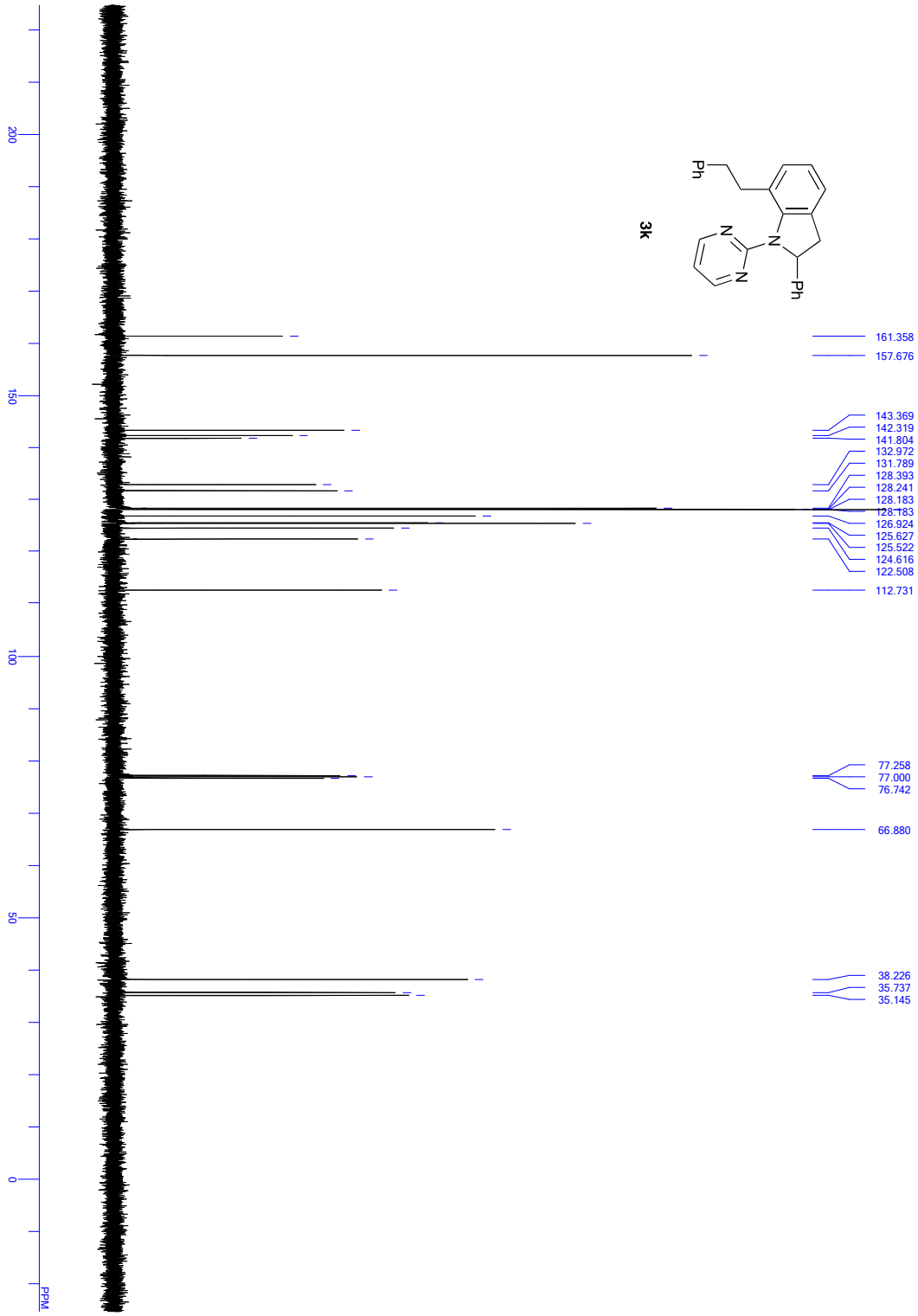
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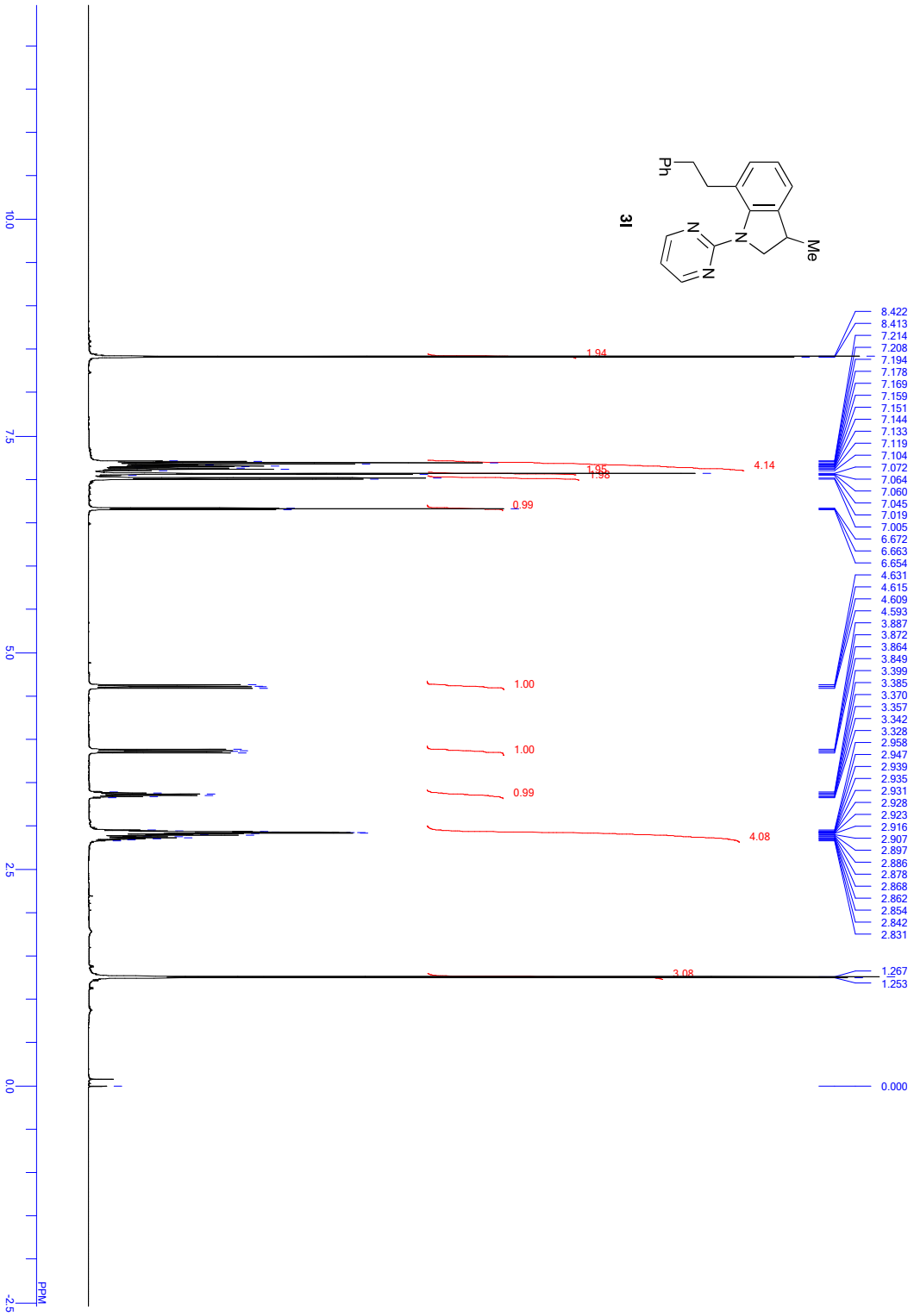
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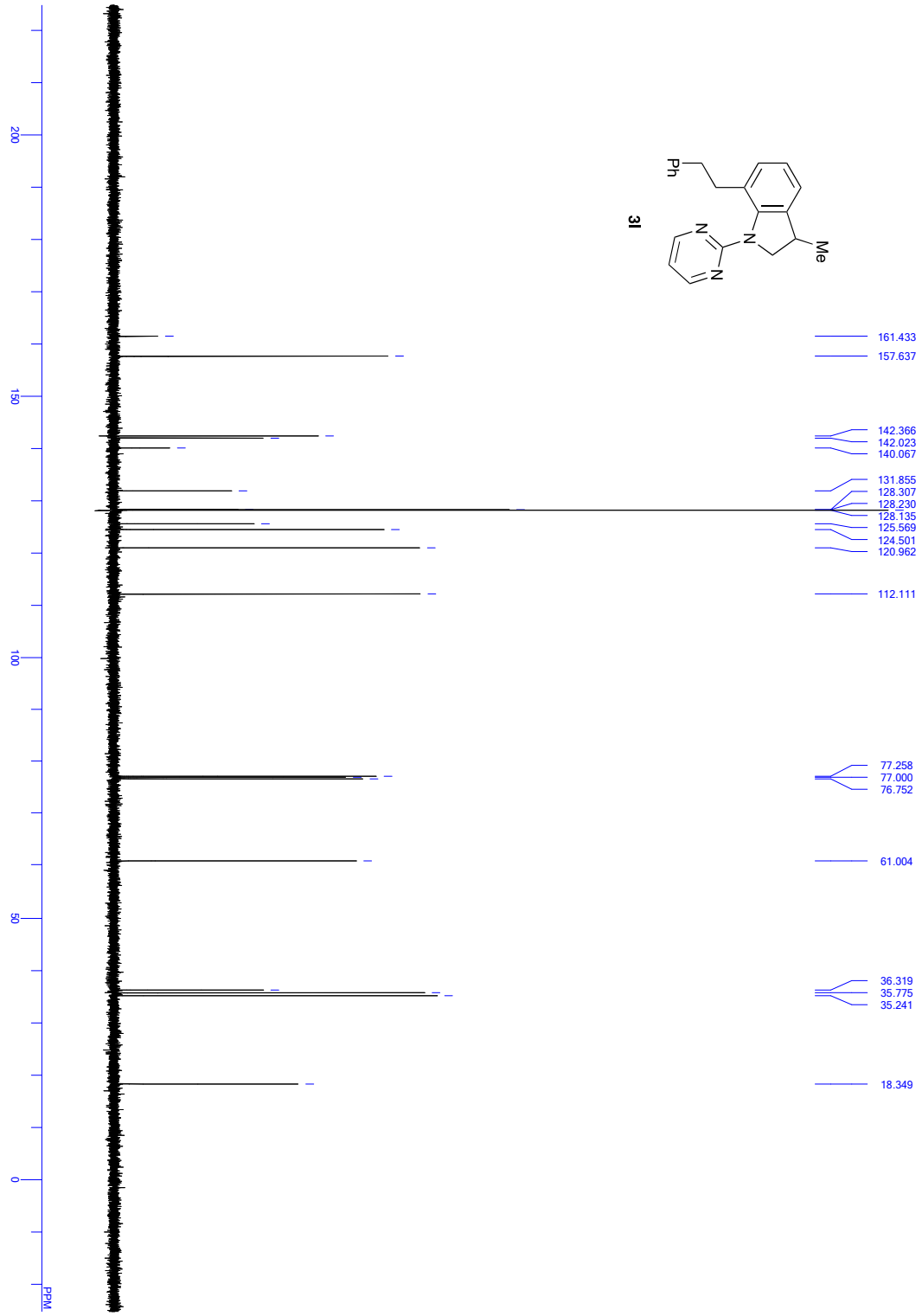
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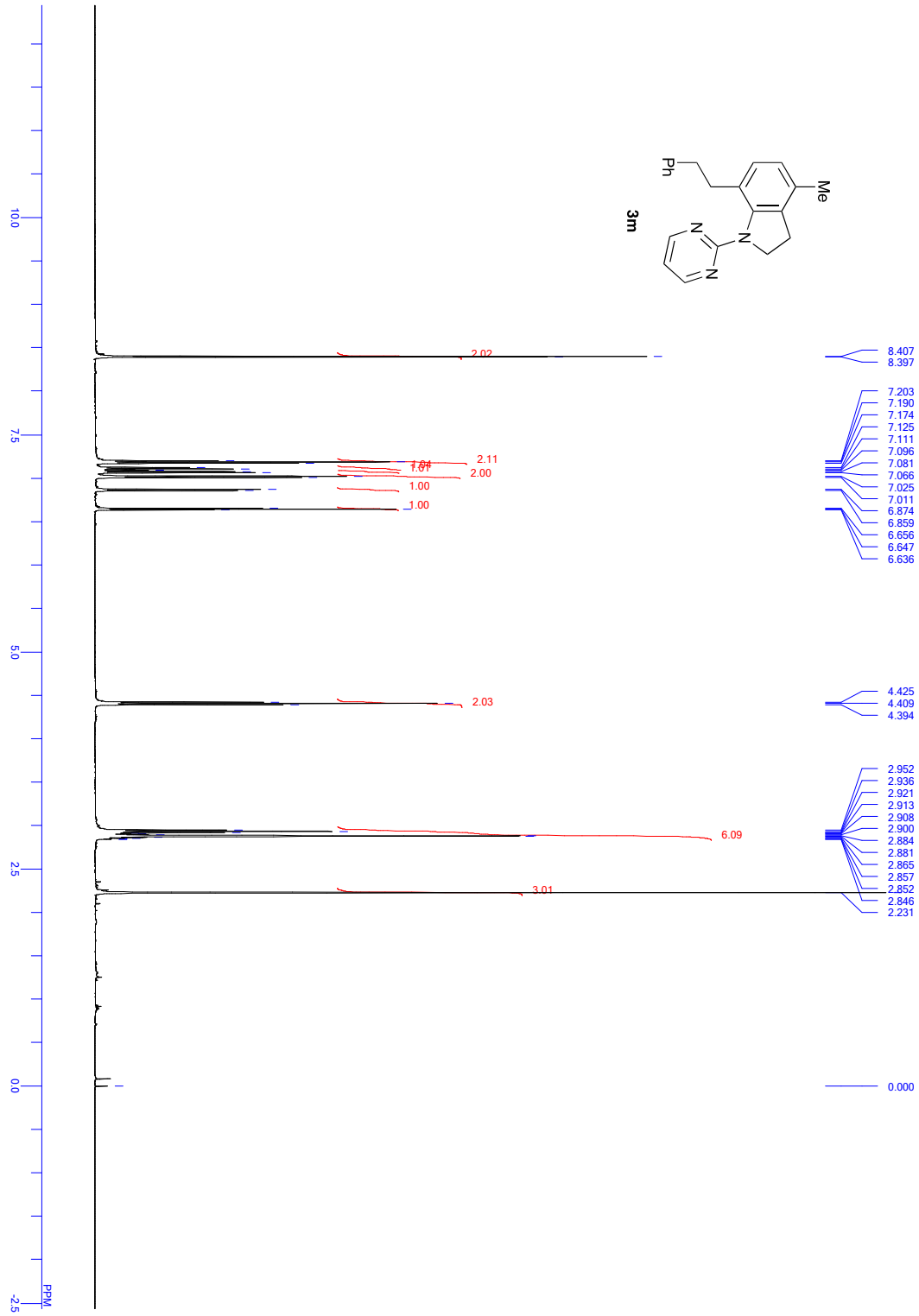
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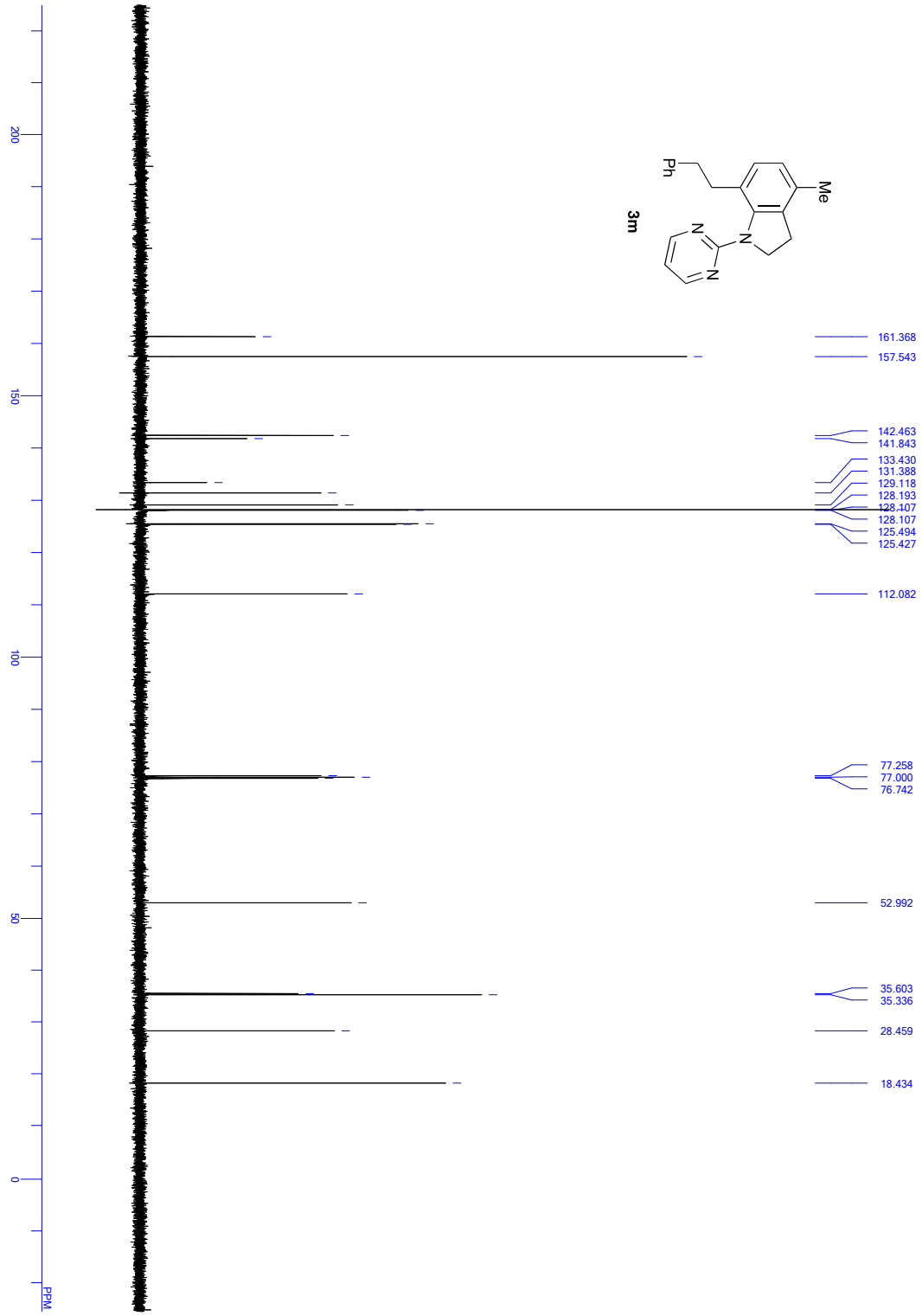
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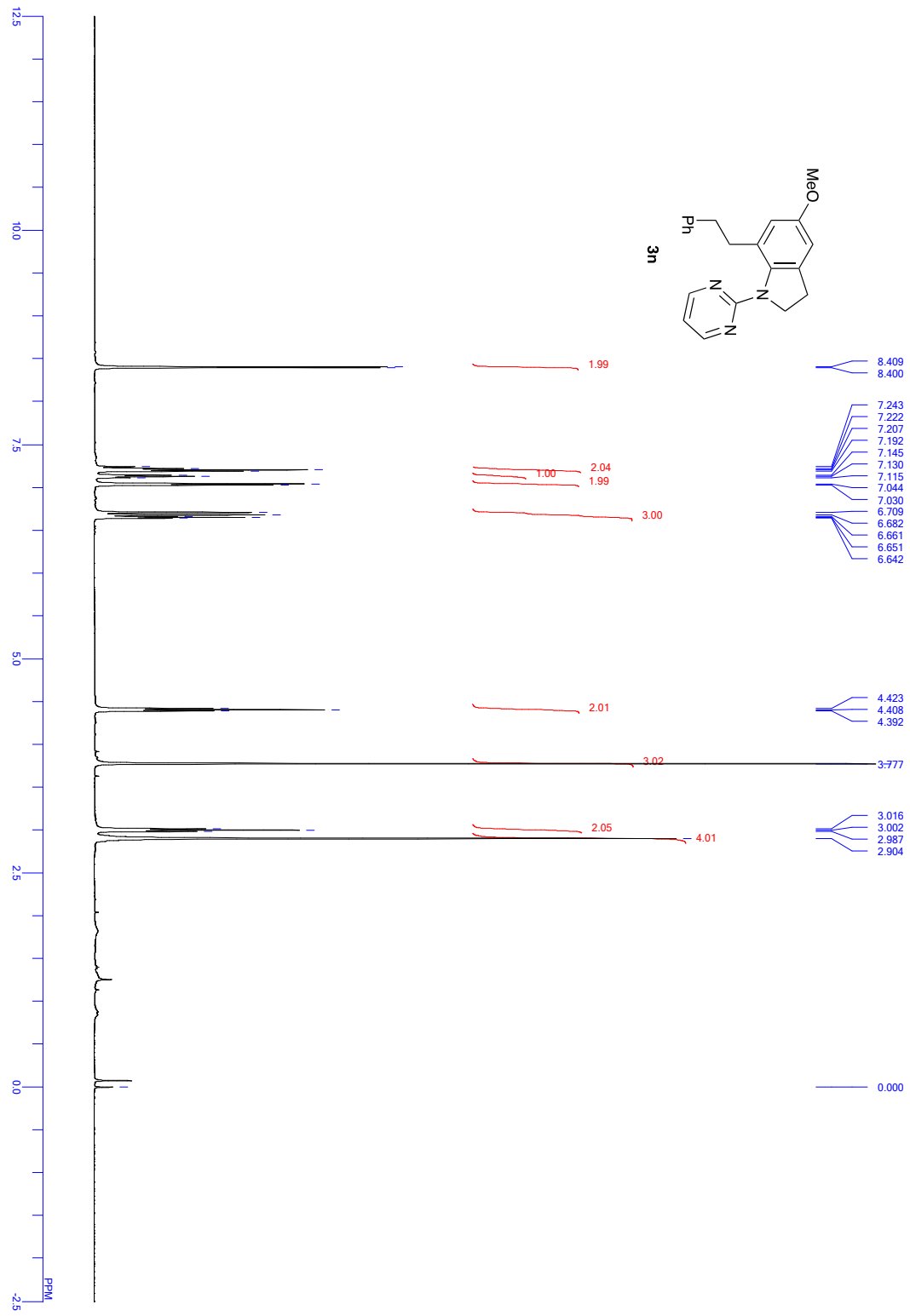
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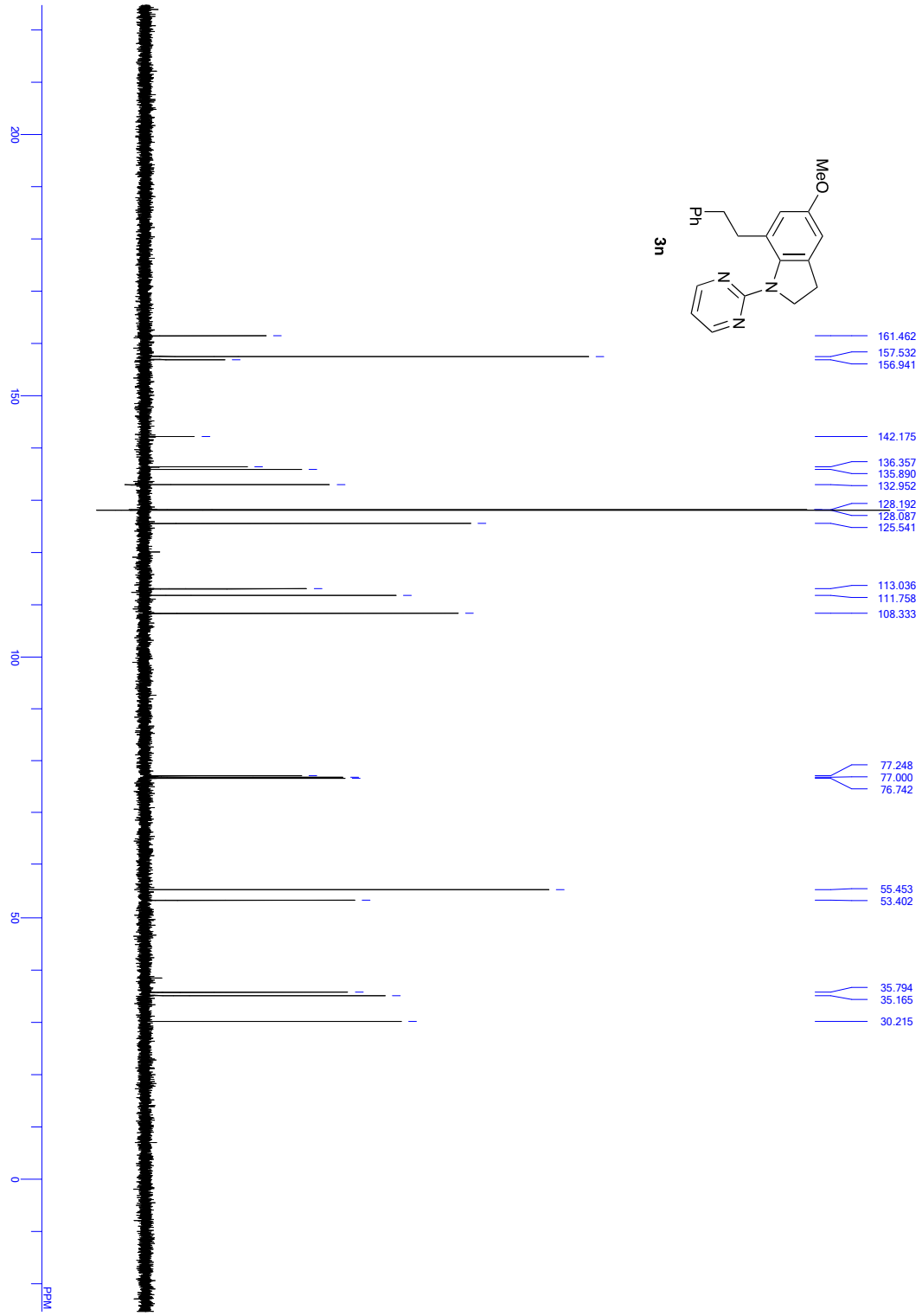
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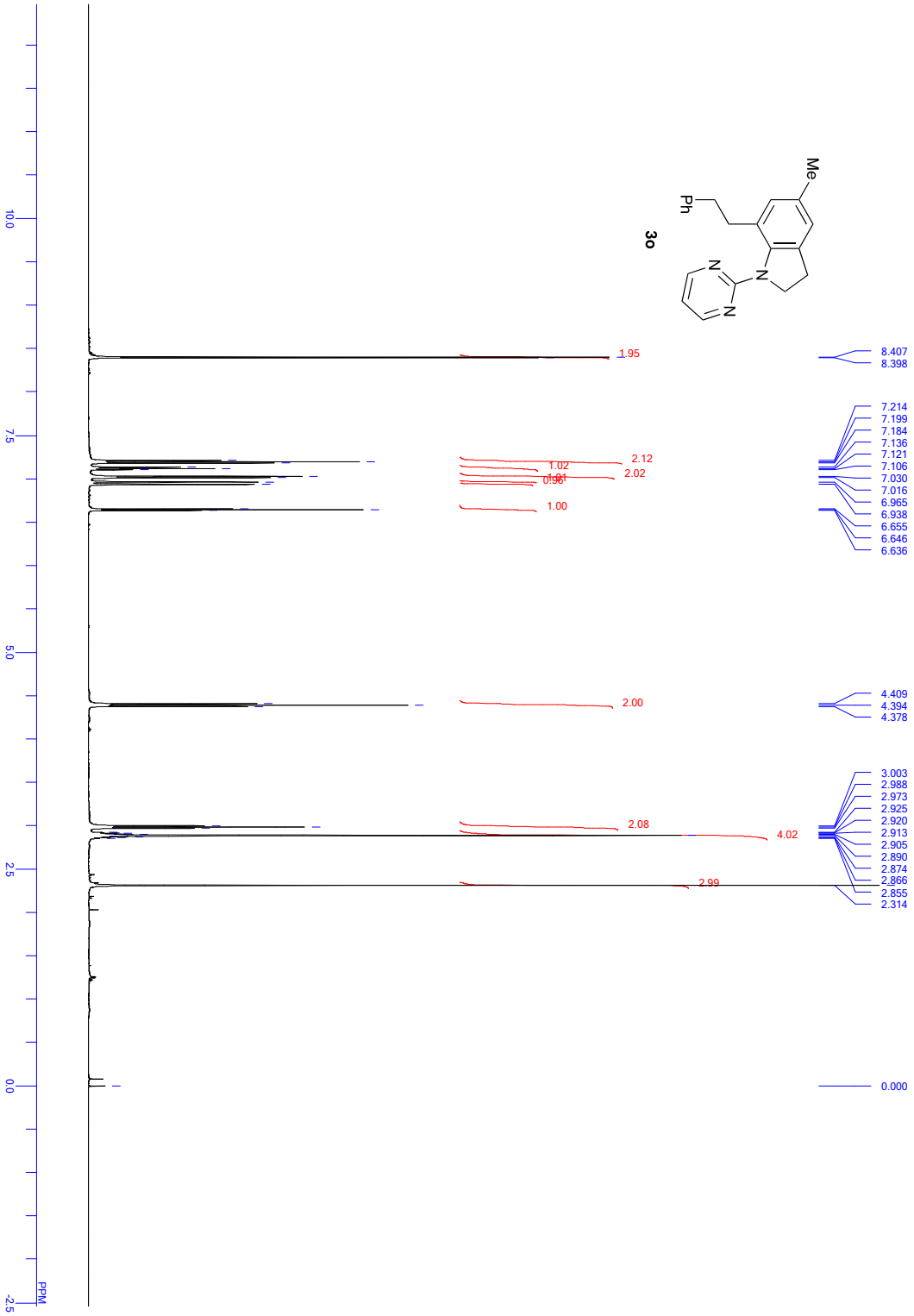
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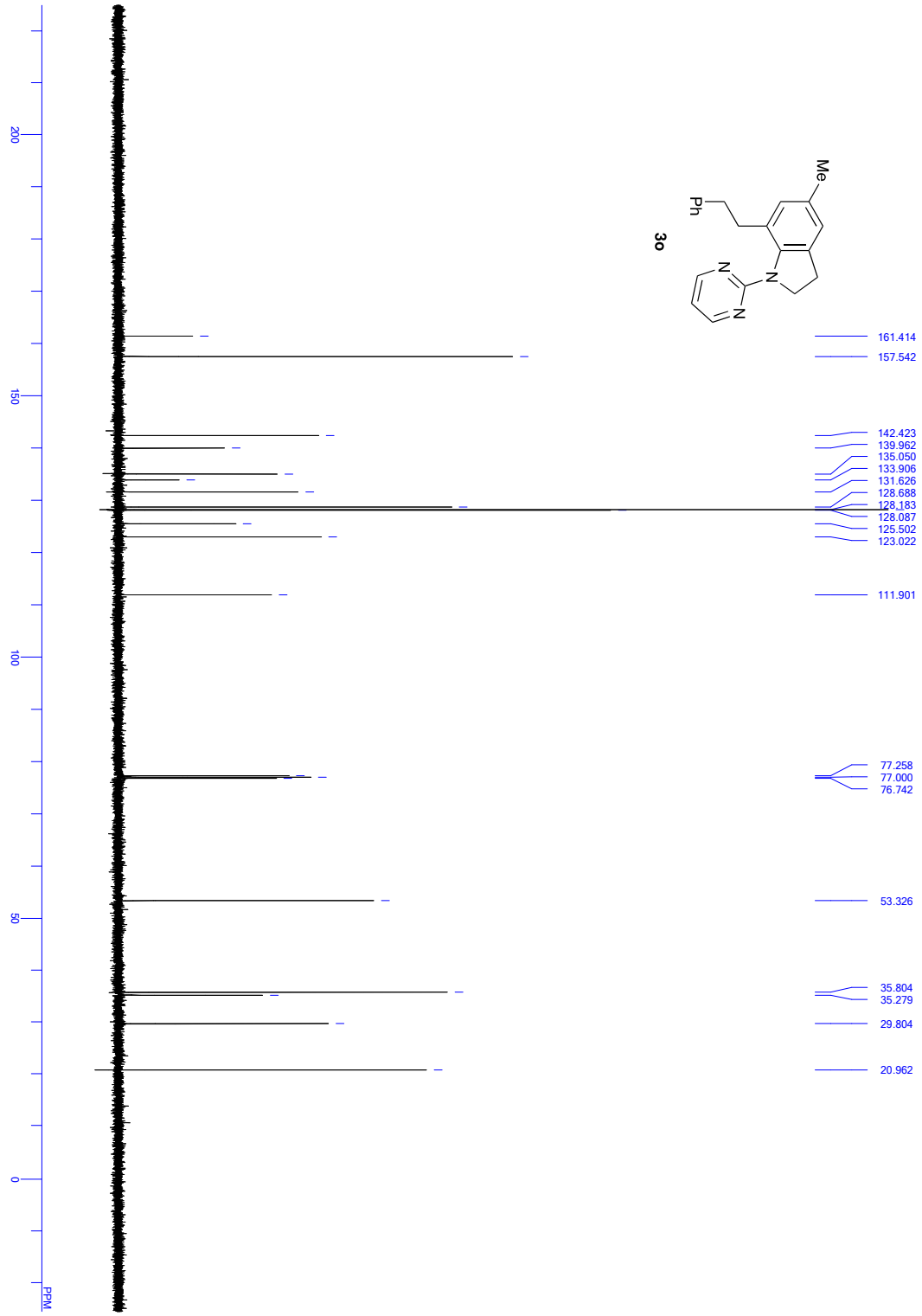
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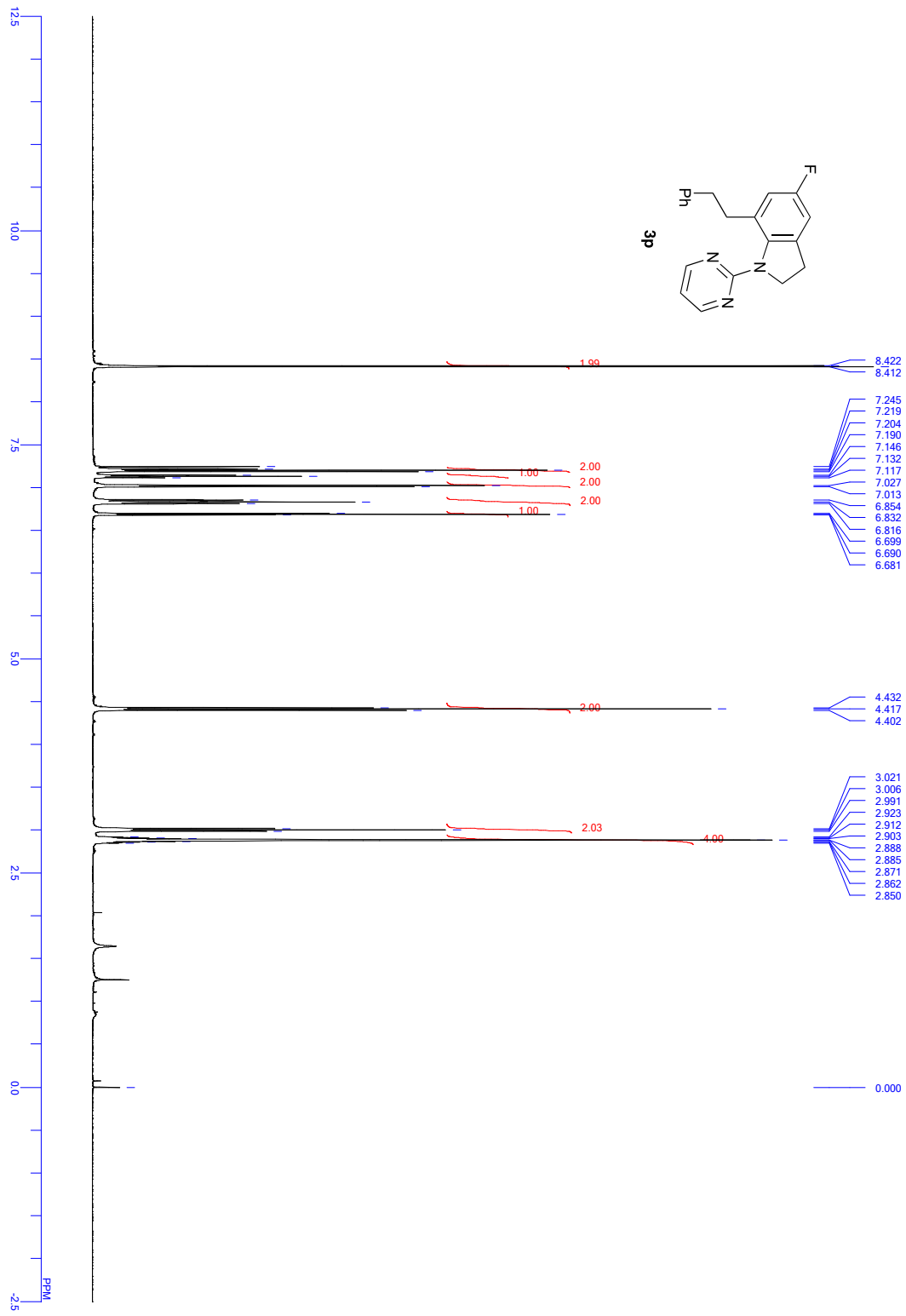
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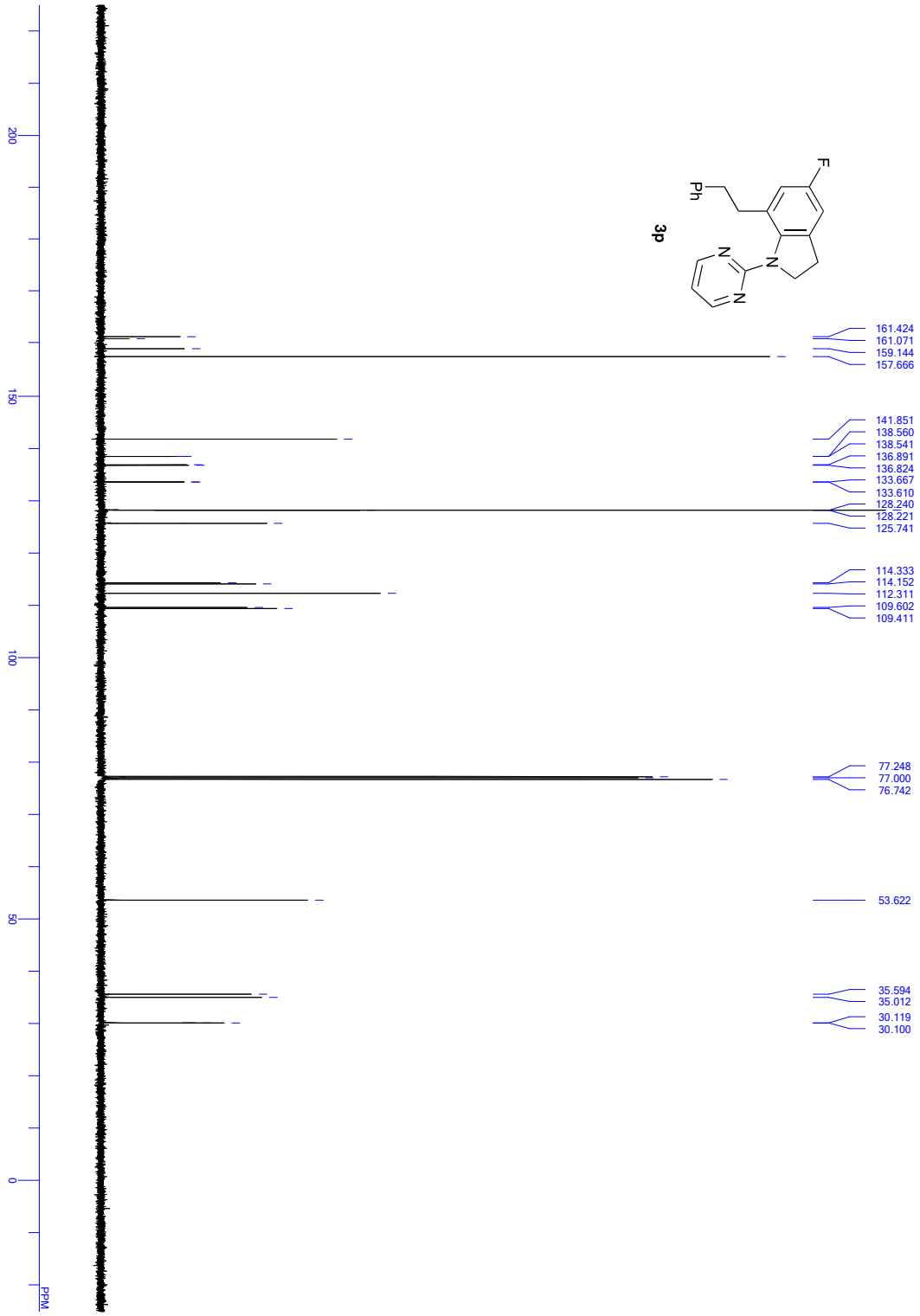
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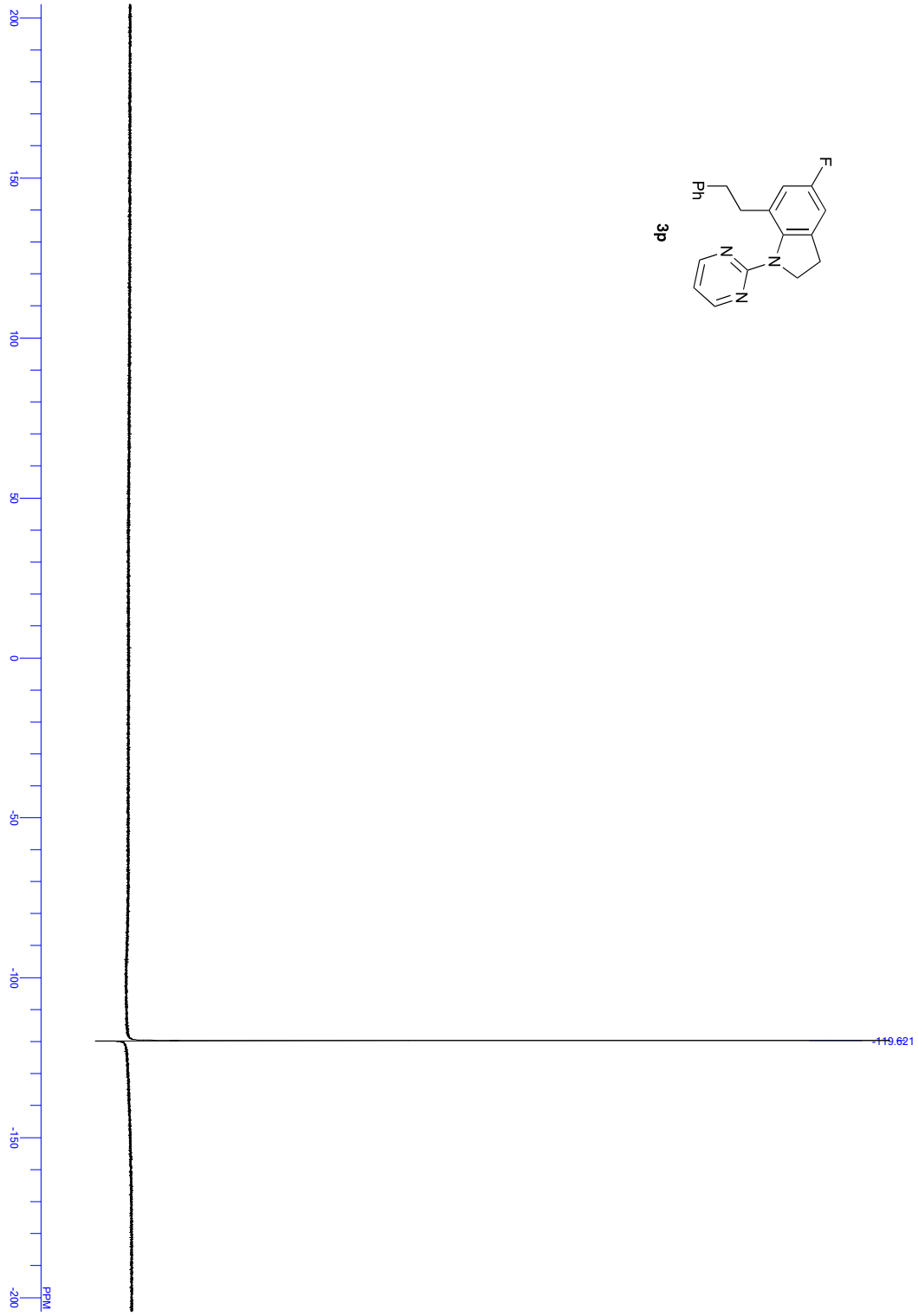

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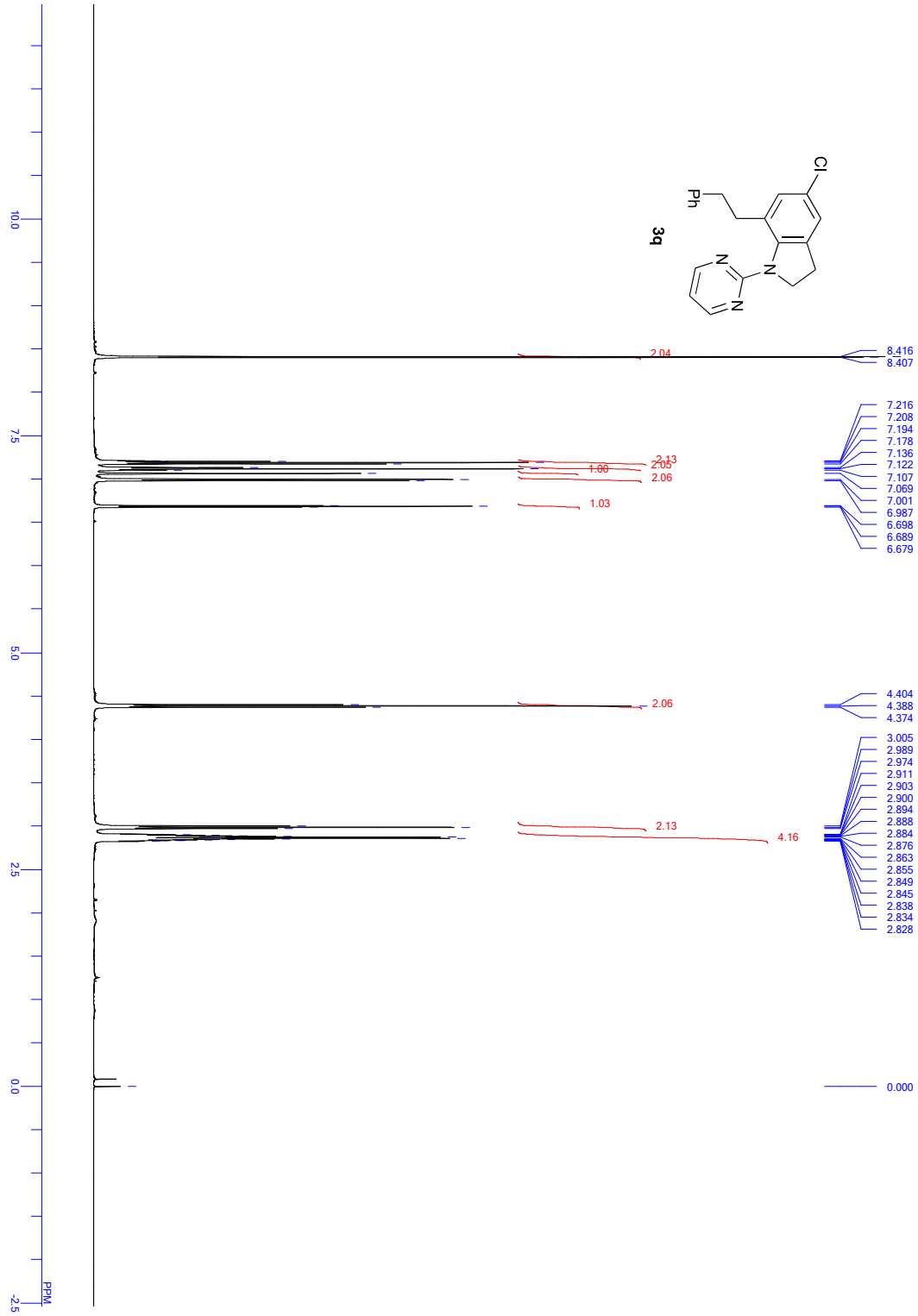
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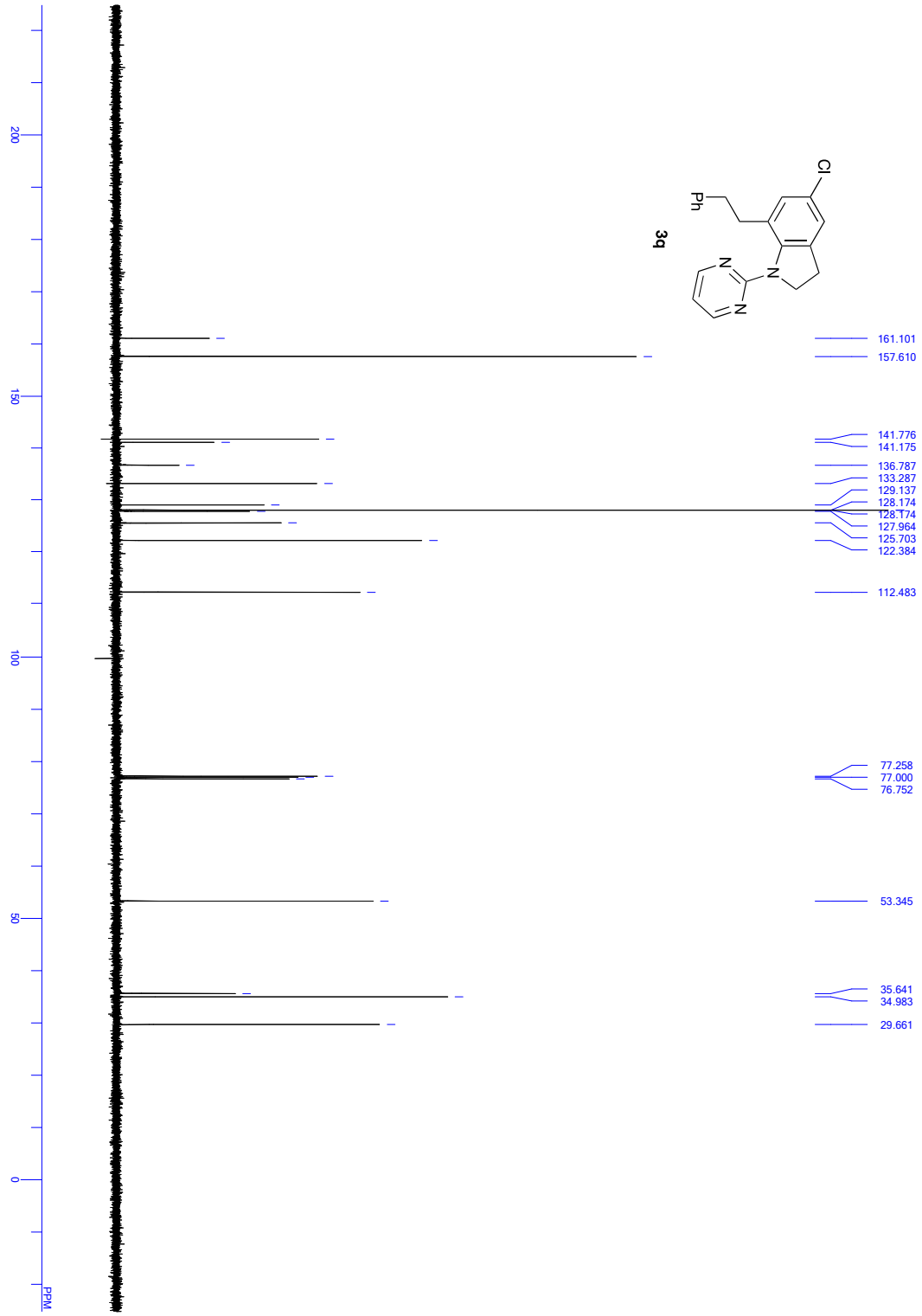
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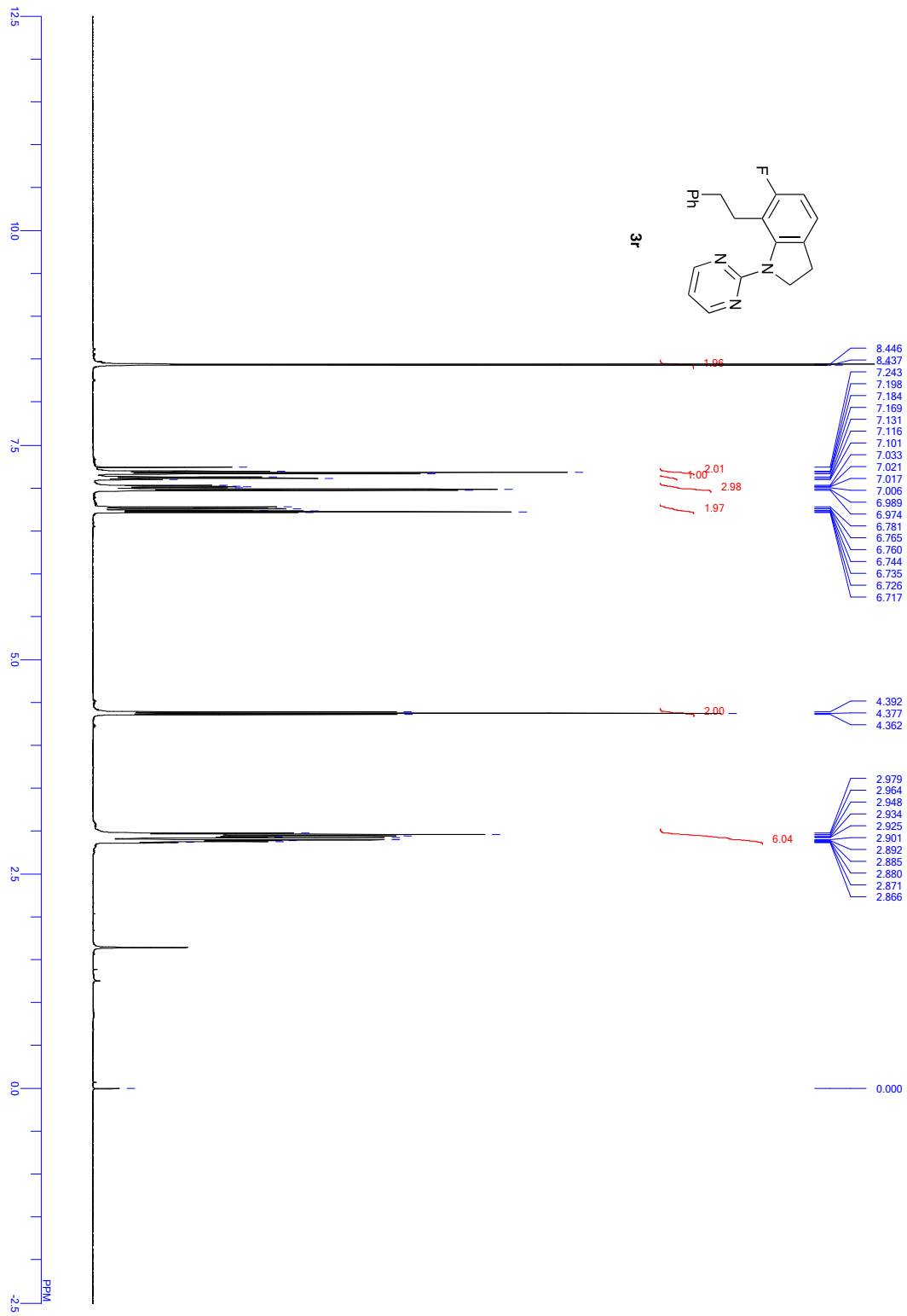
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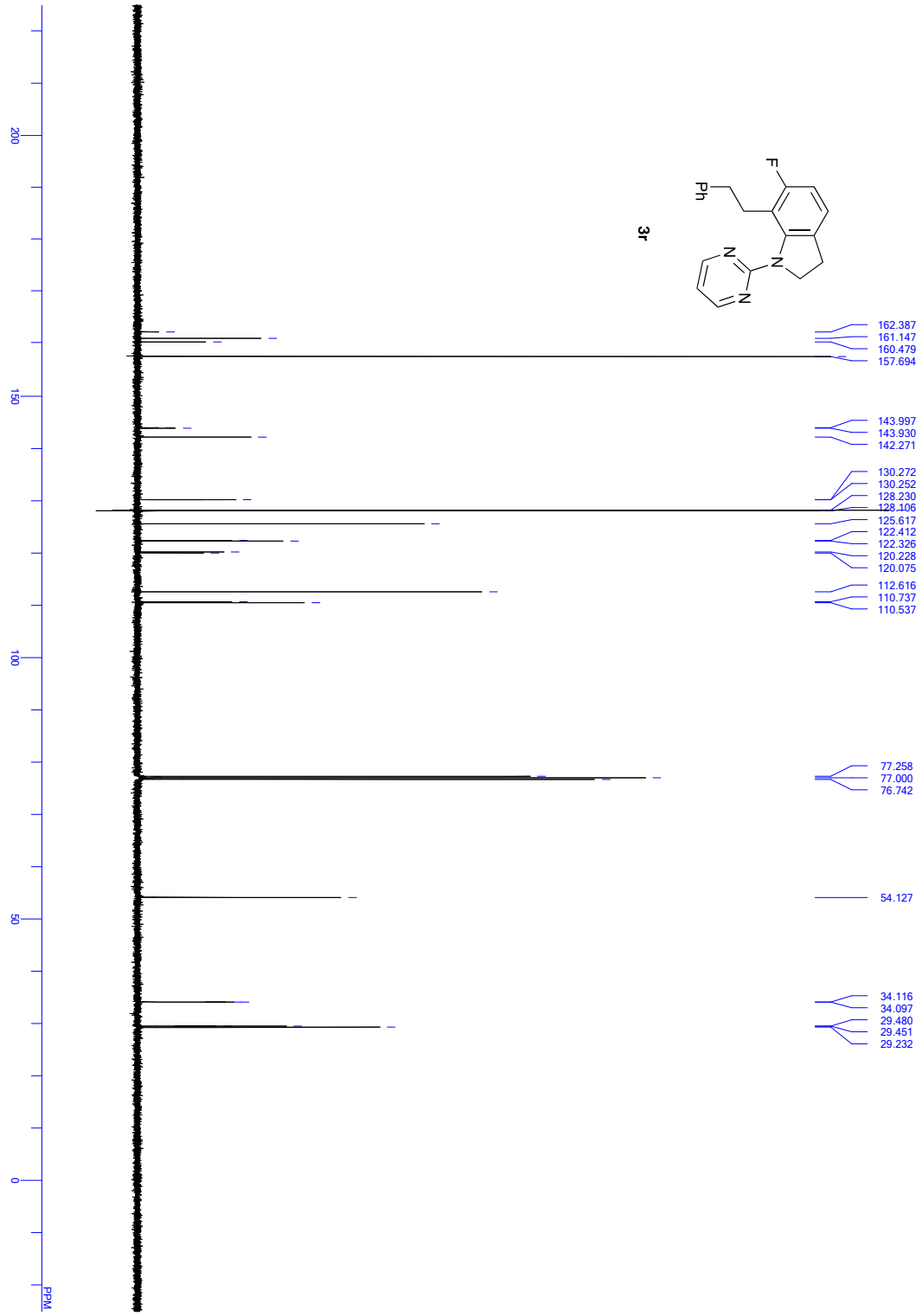
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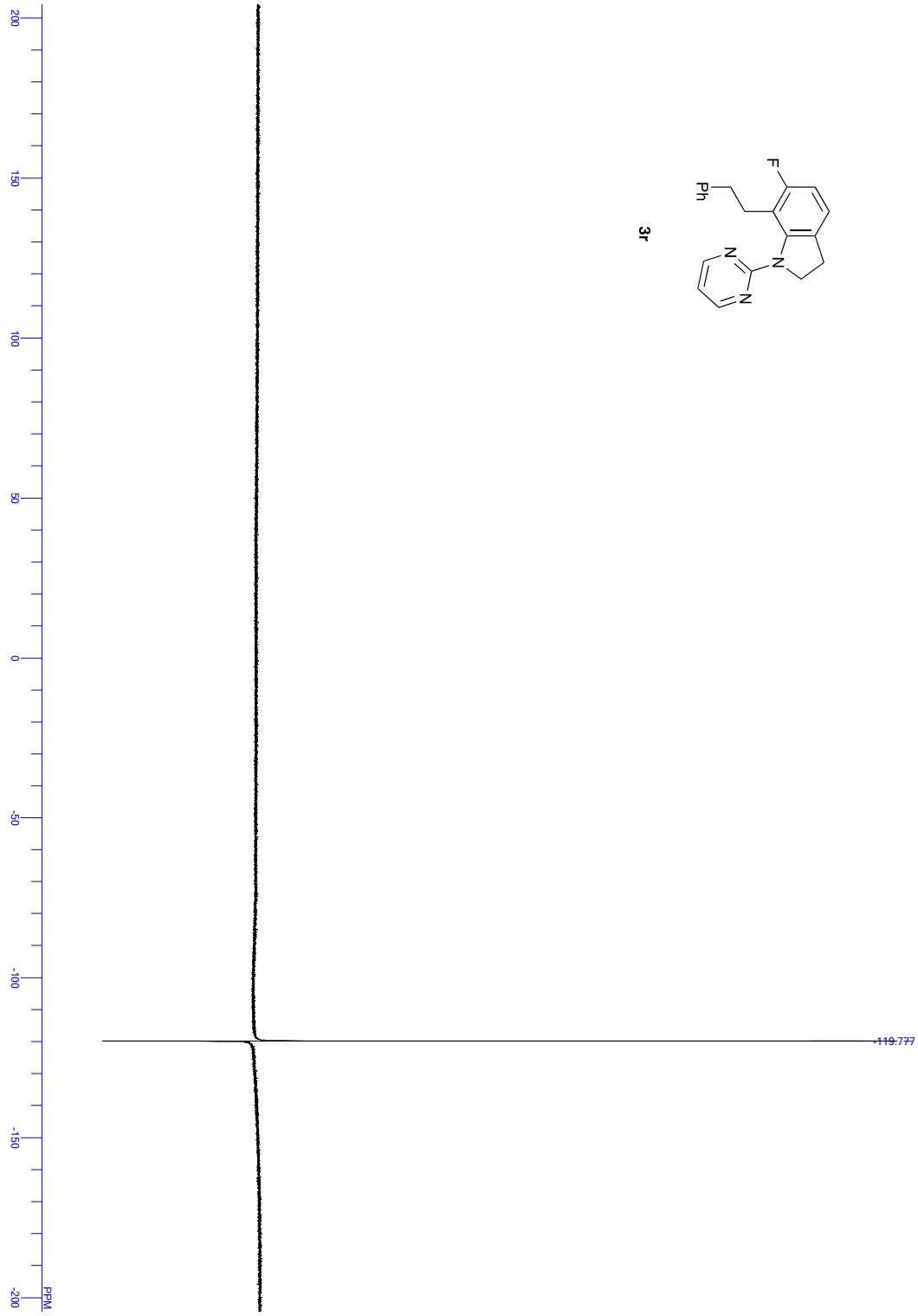
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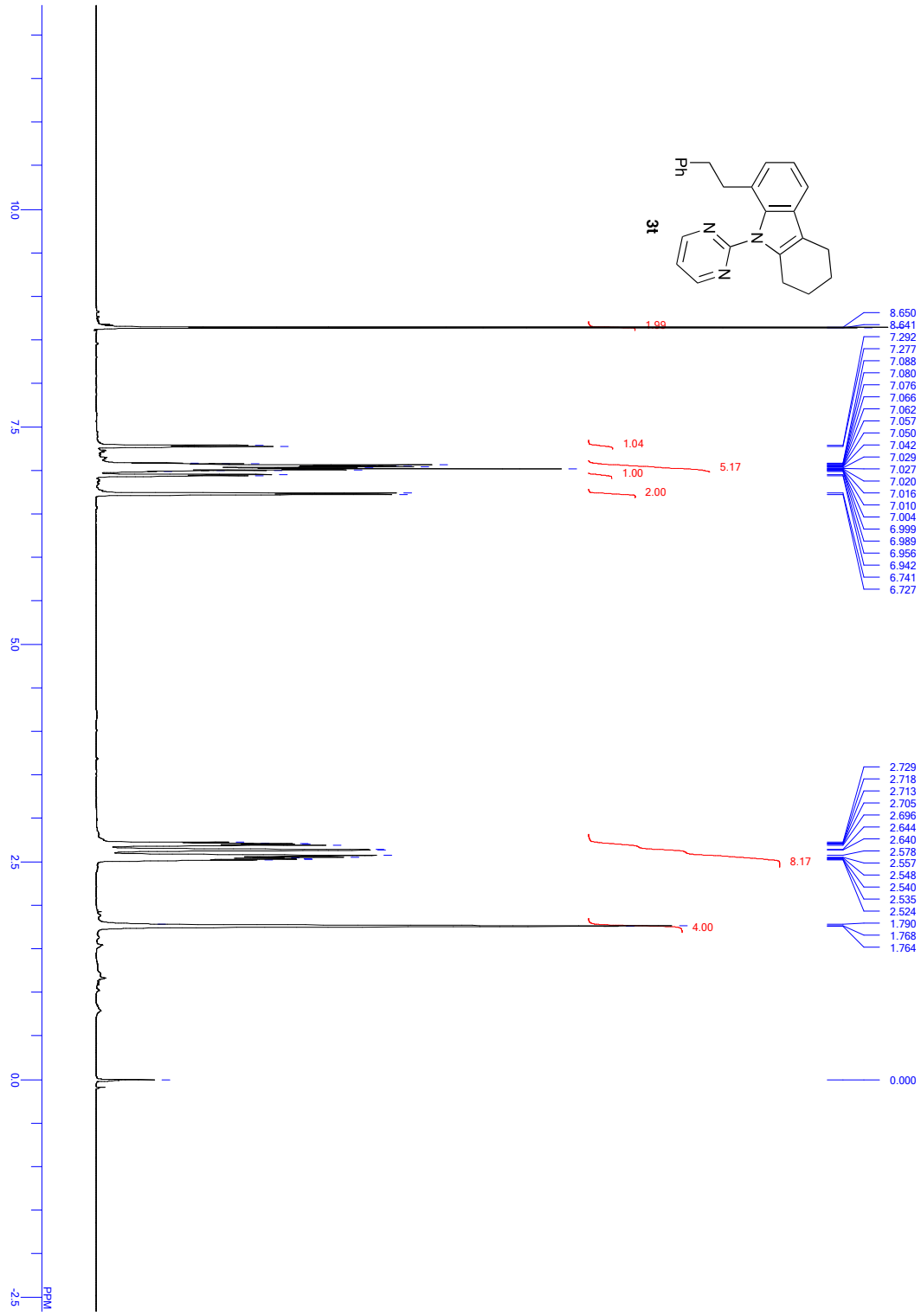
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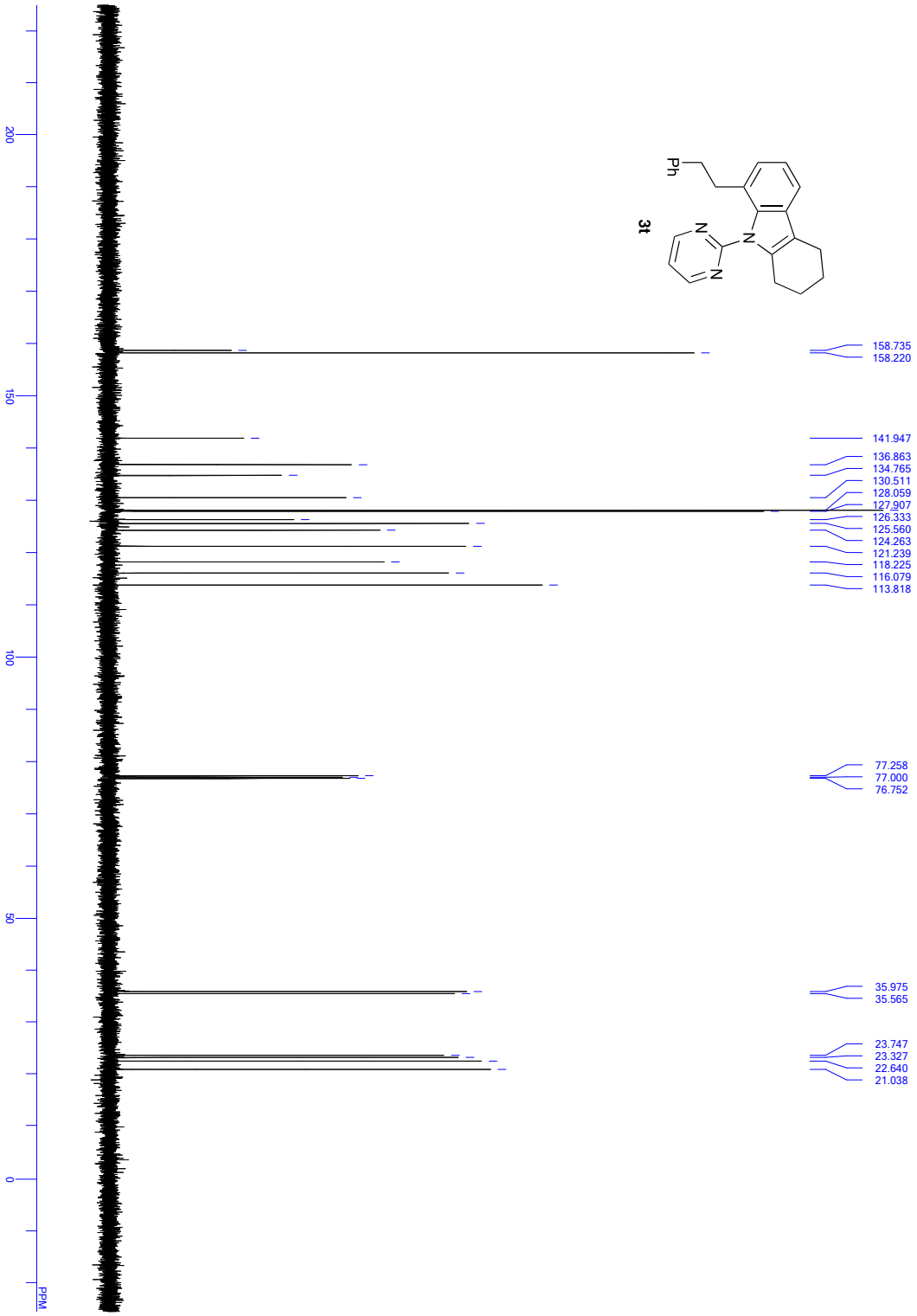
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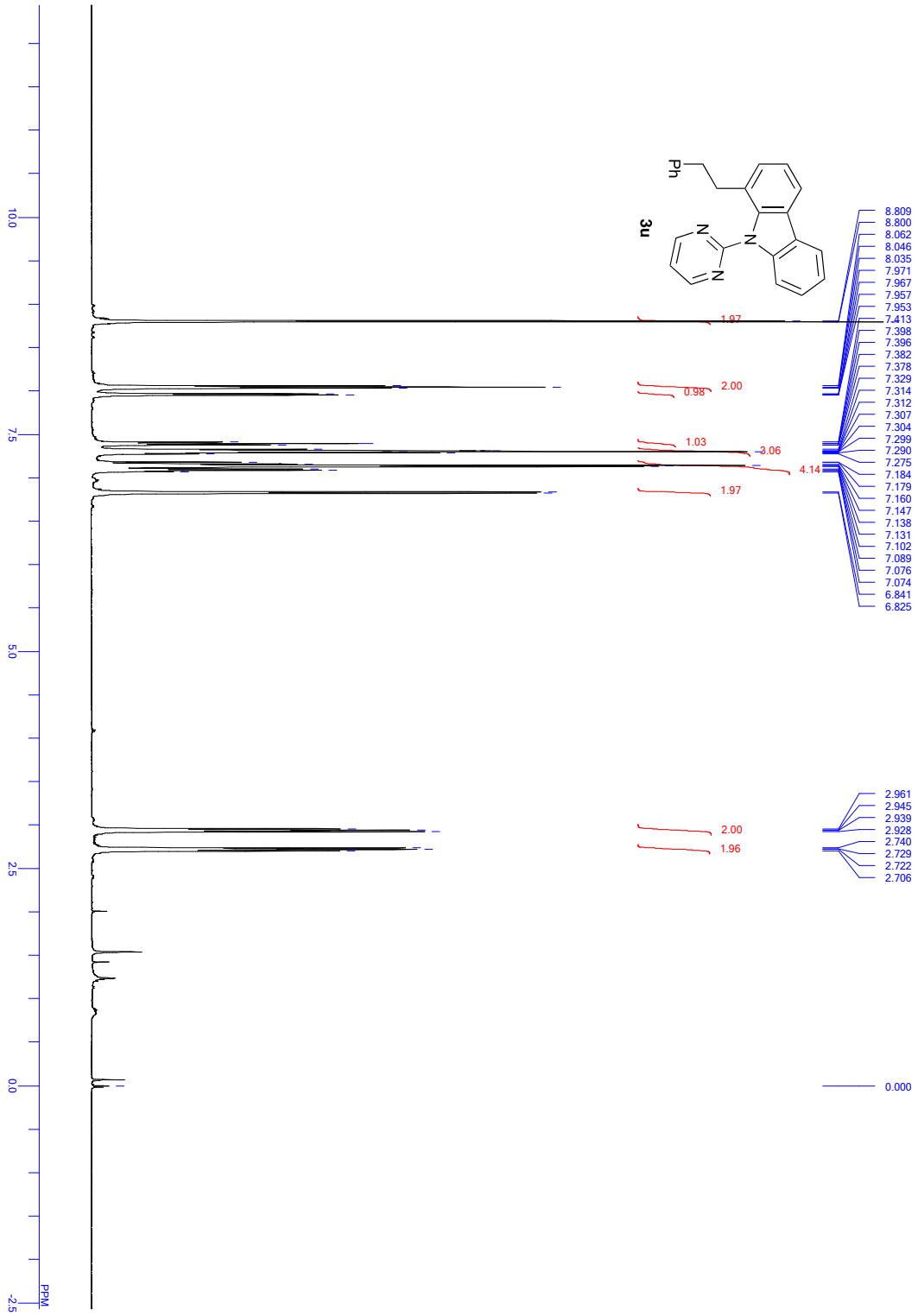
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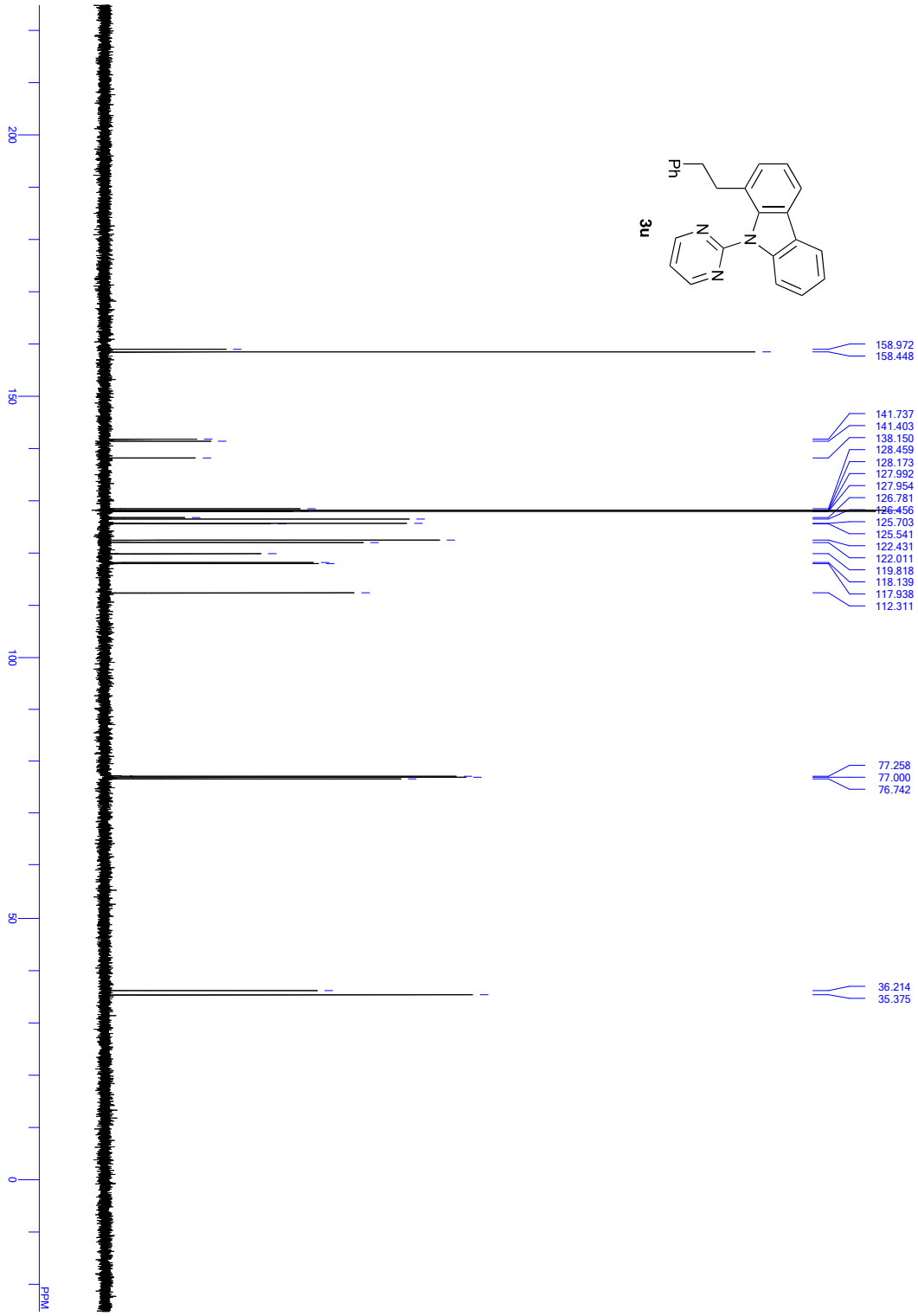
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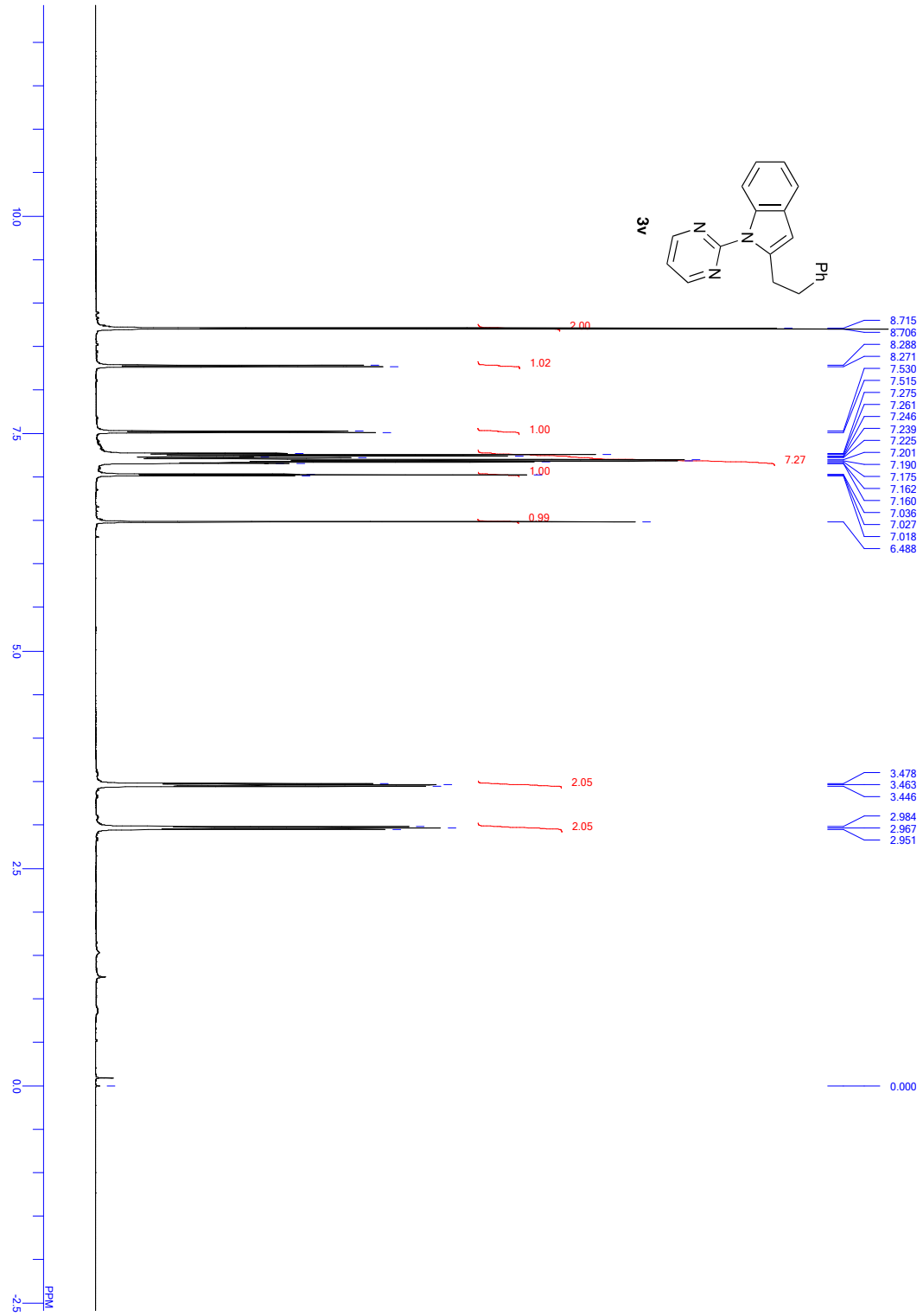
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2.05
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7.515
7.275
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7.190
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7.162
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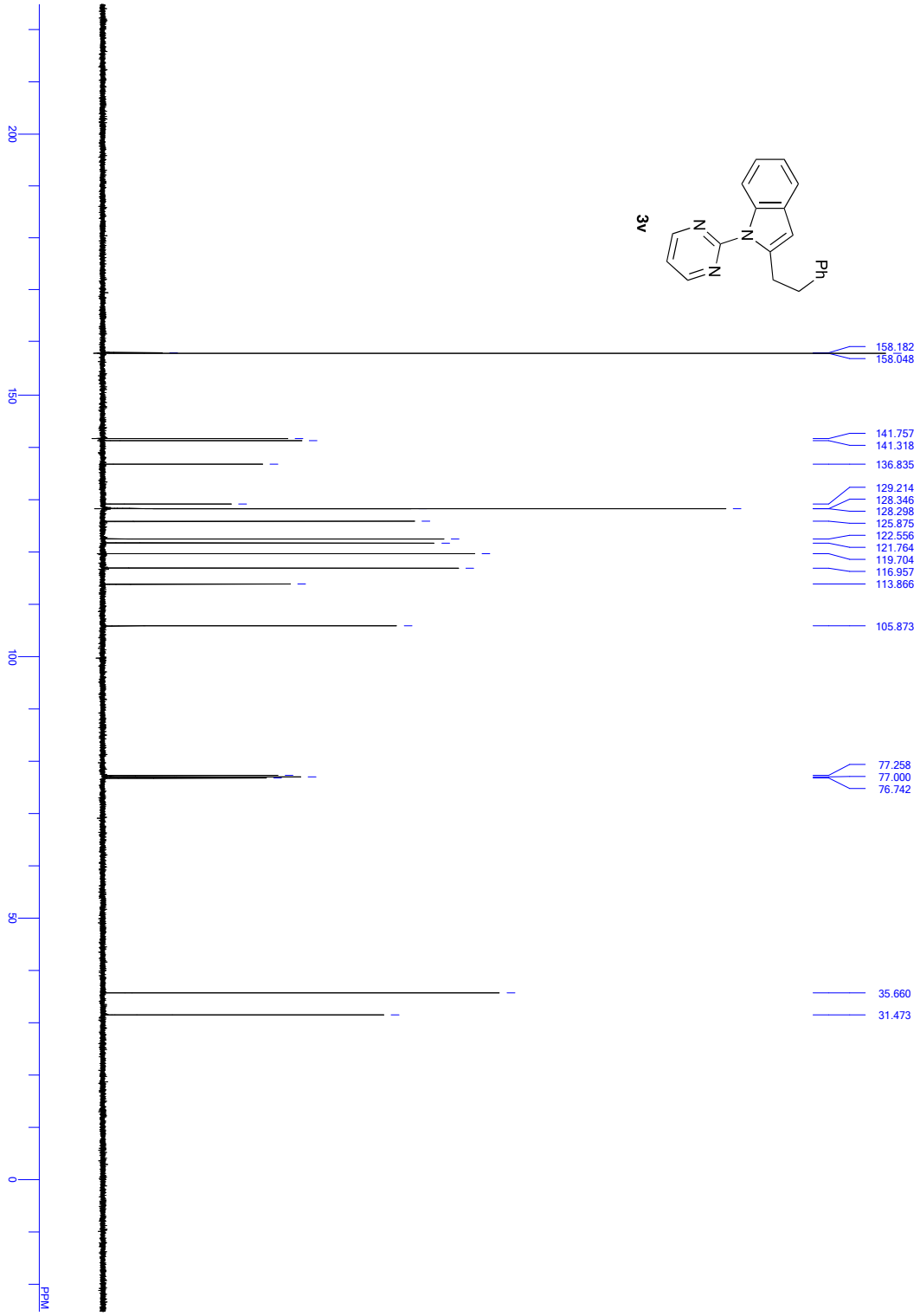
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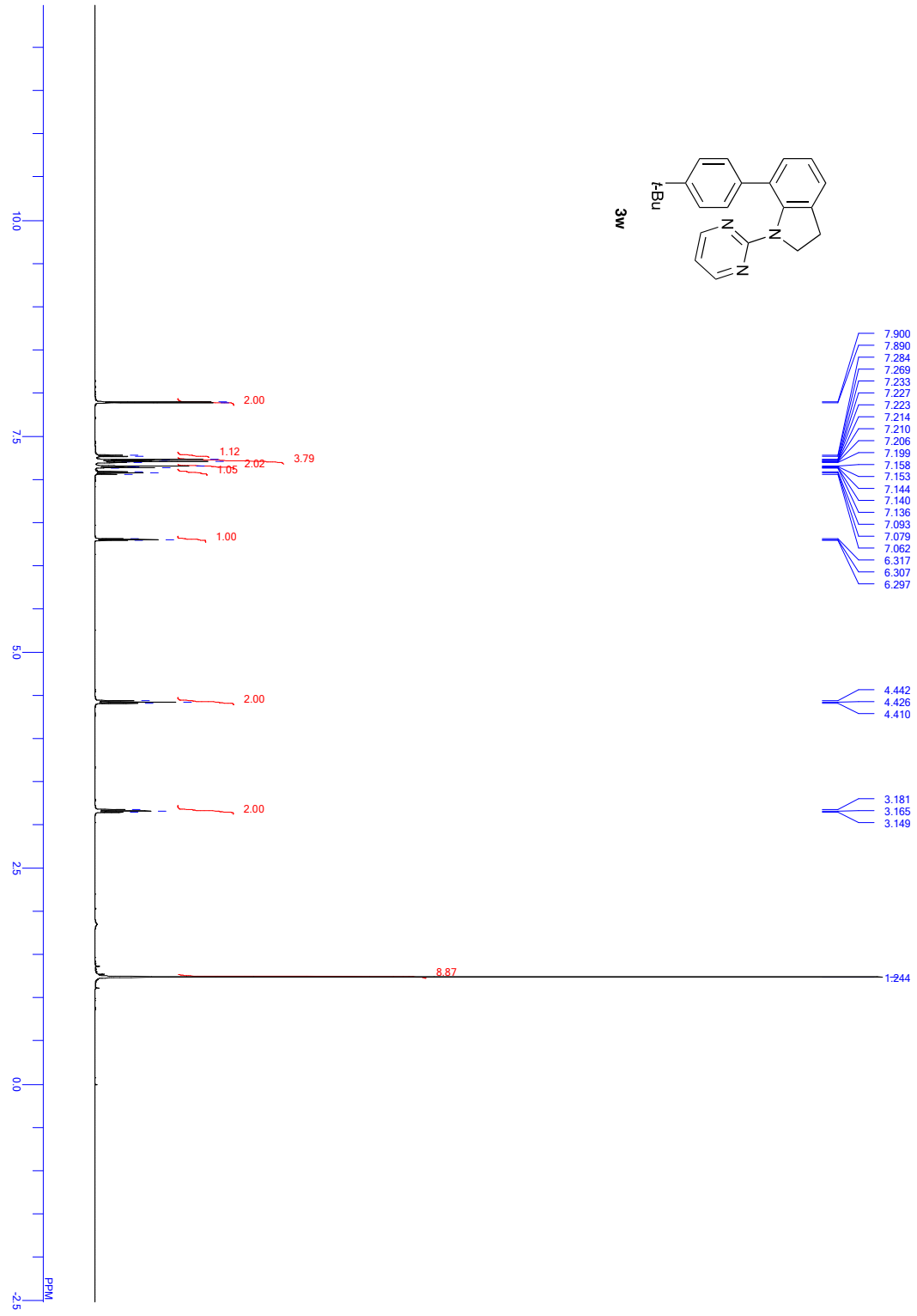
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1.00
2.00
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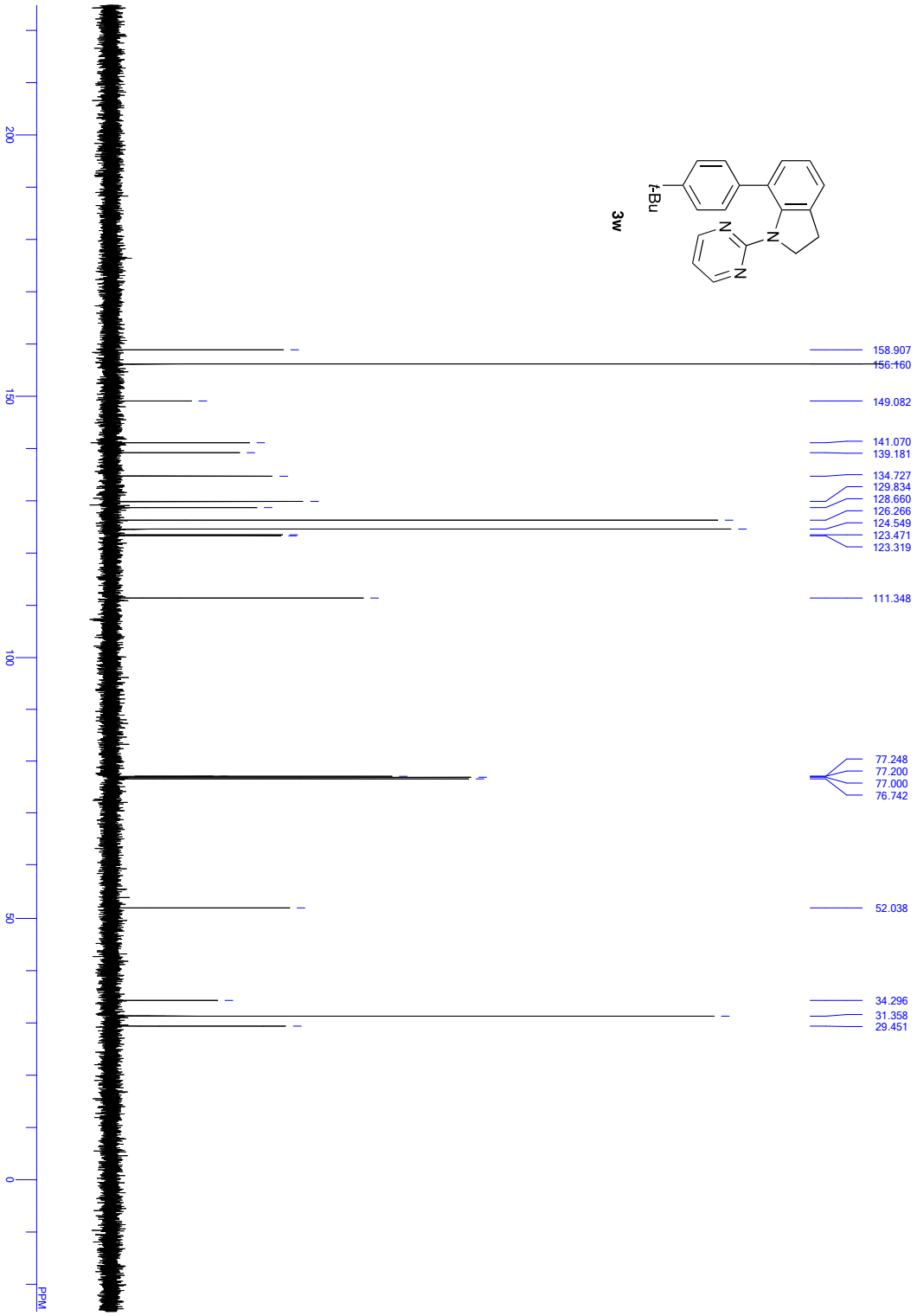
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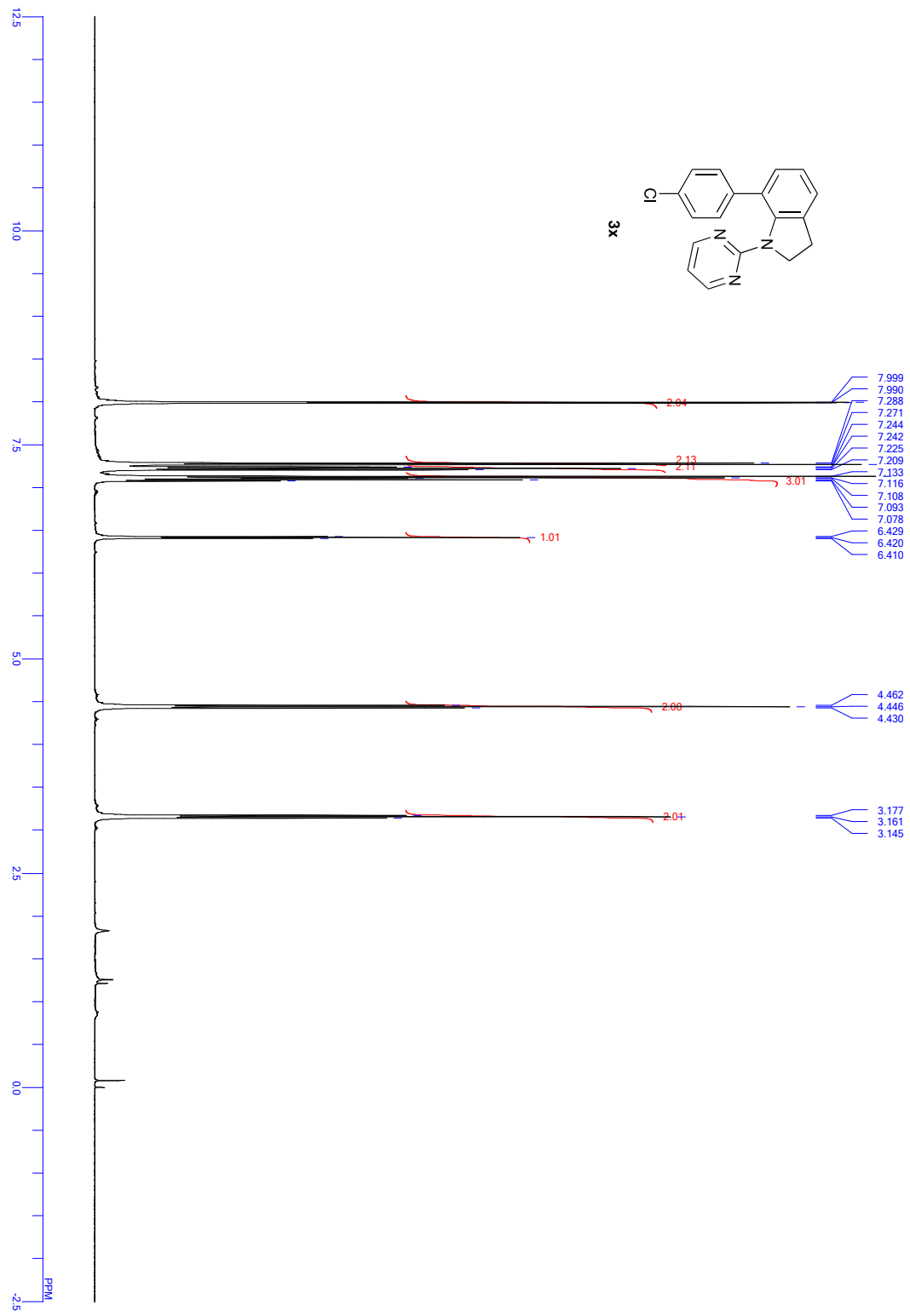
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7.225
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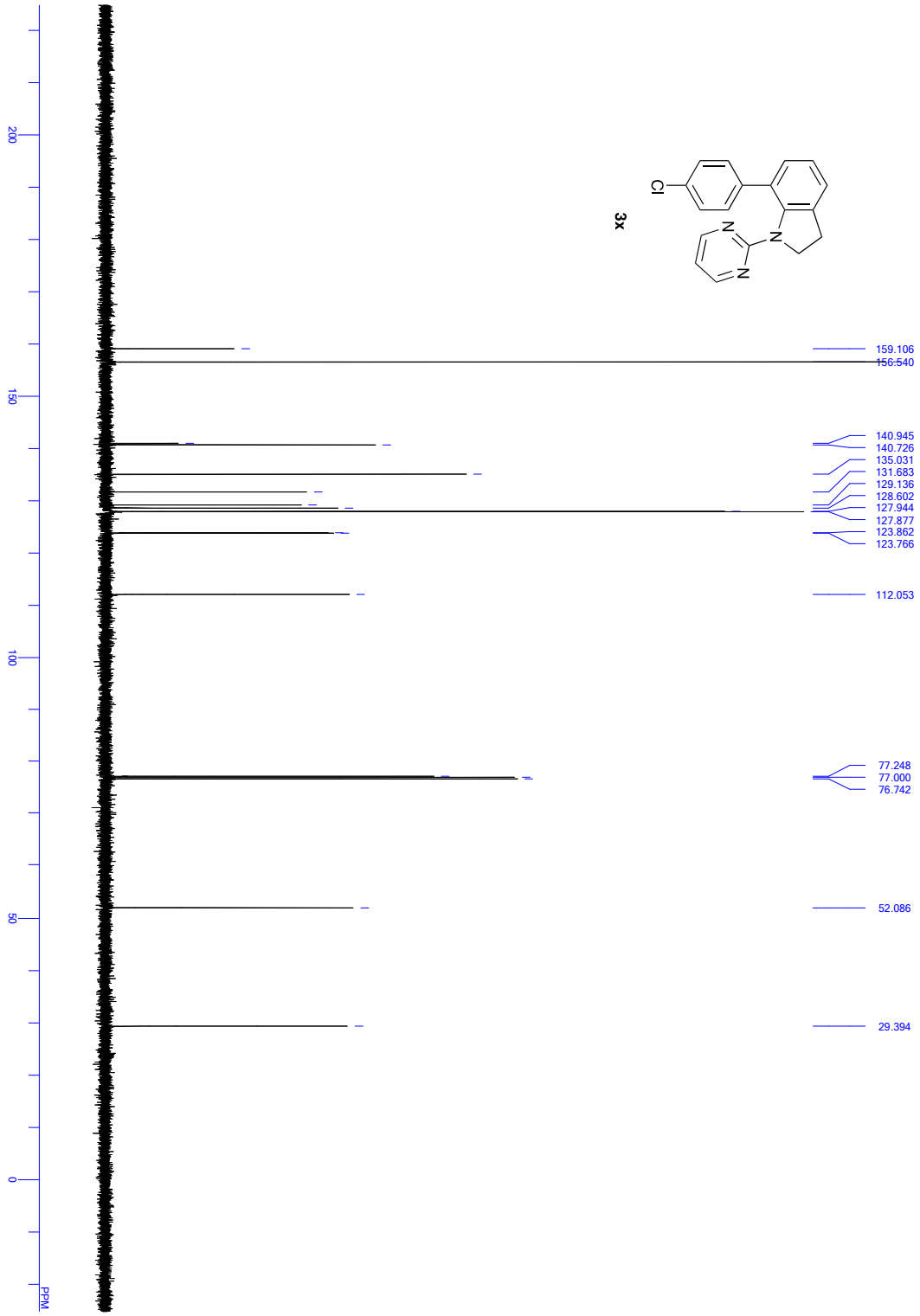
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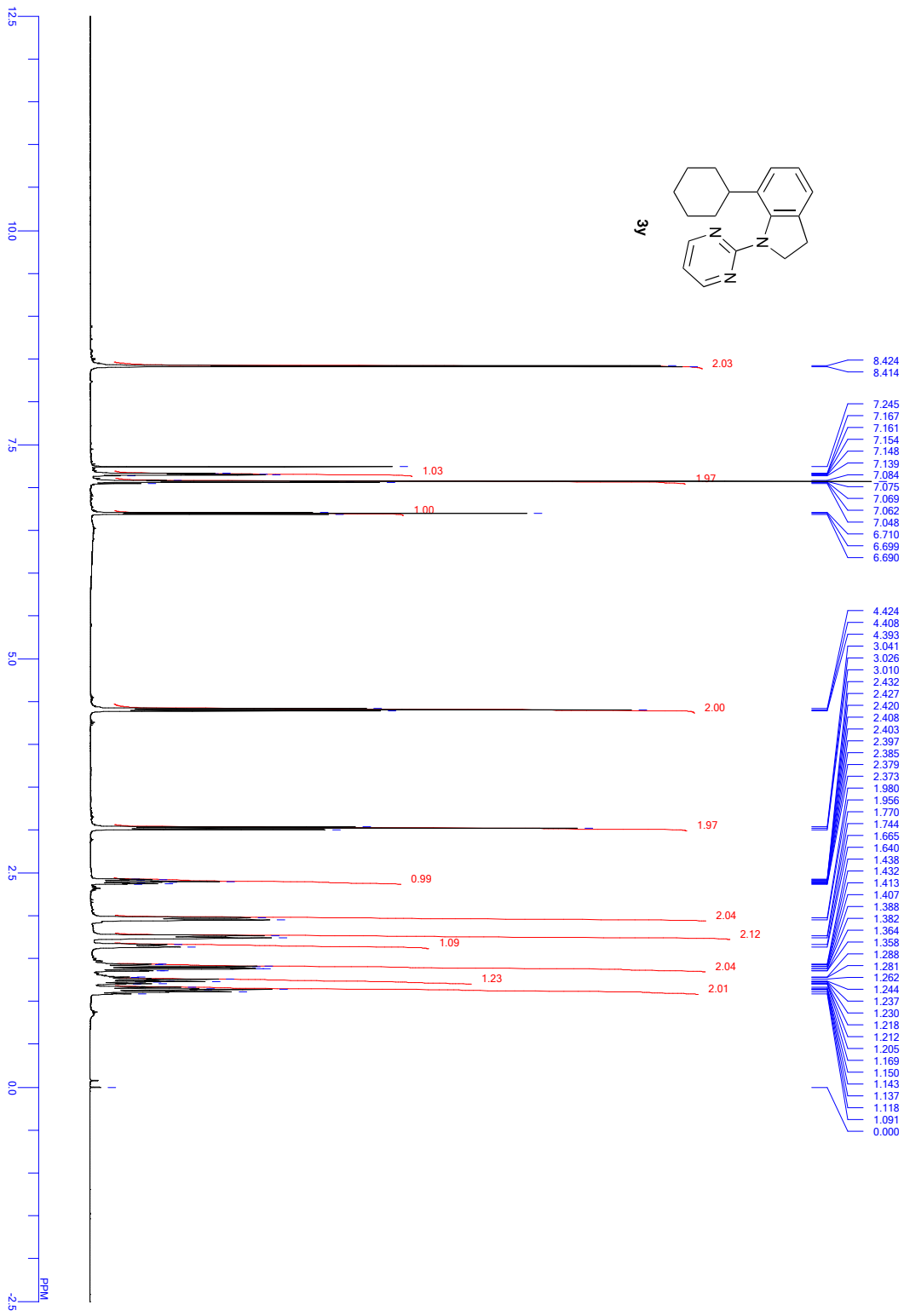
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2.00
1.97
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2.12
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2.04
1.23
2.01
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8.414
7.245
7.167
7.161
7.154
7.148
7.139
7.084
7.075
7.069
7.062
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6.699
6.690
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3.026
3.010
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2.403
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1.244
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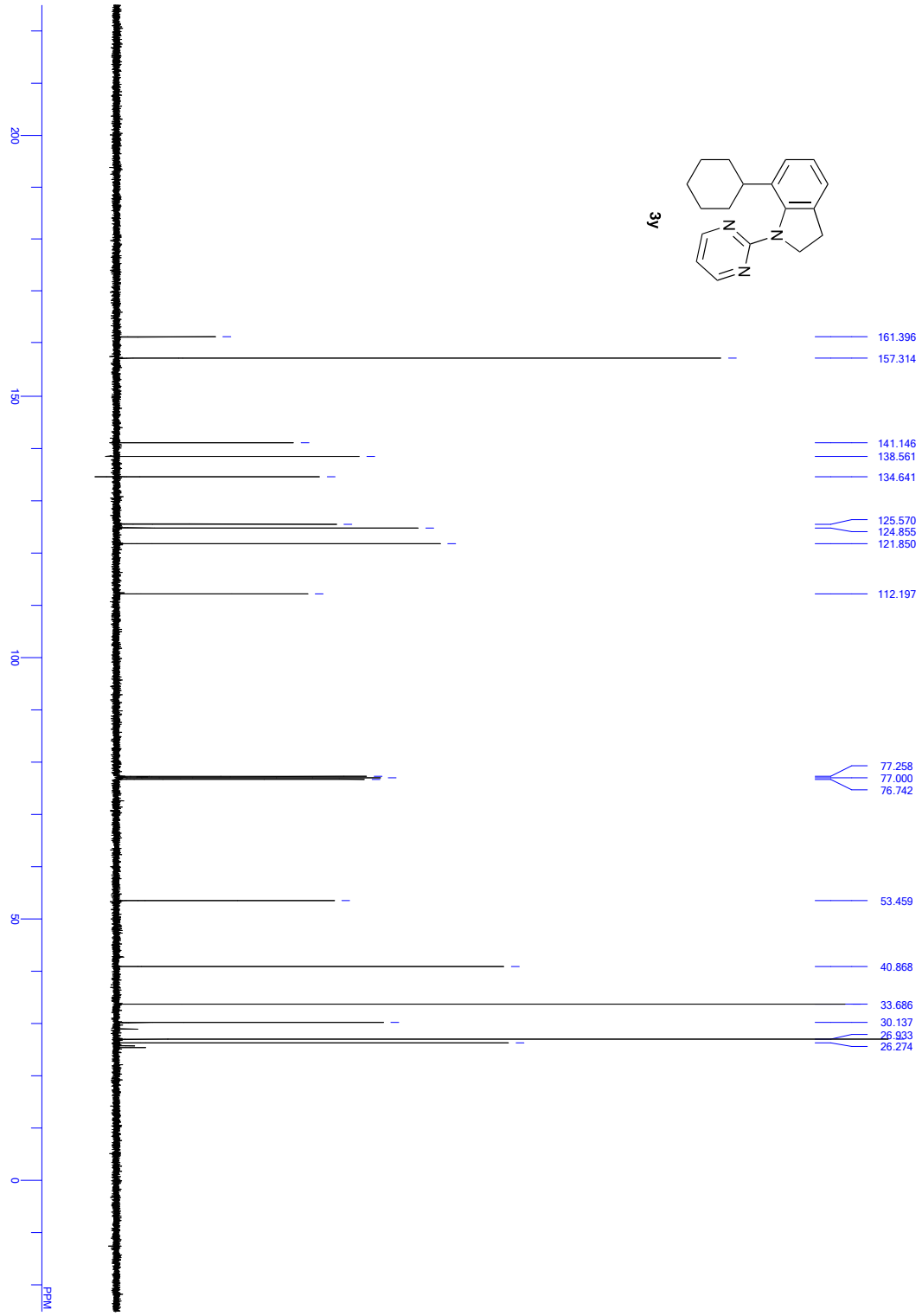
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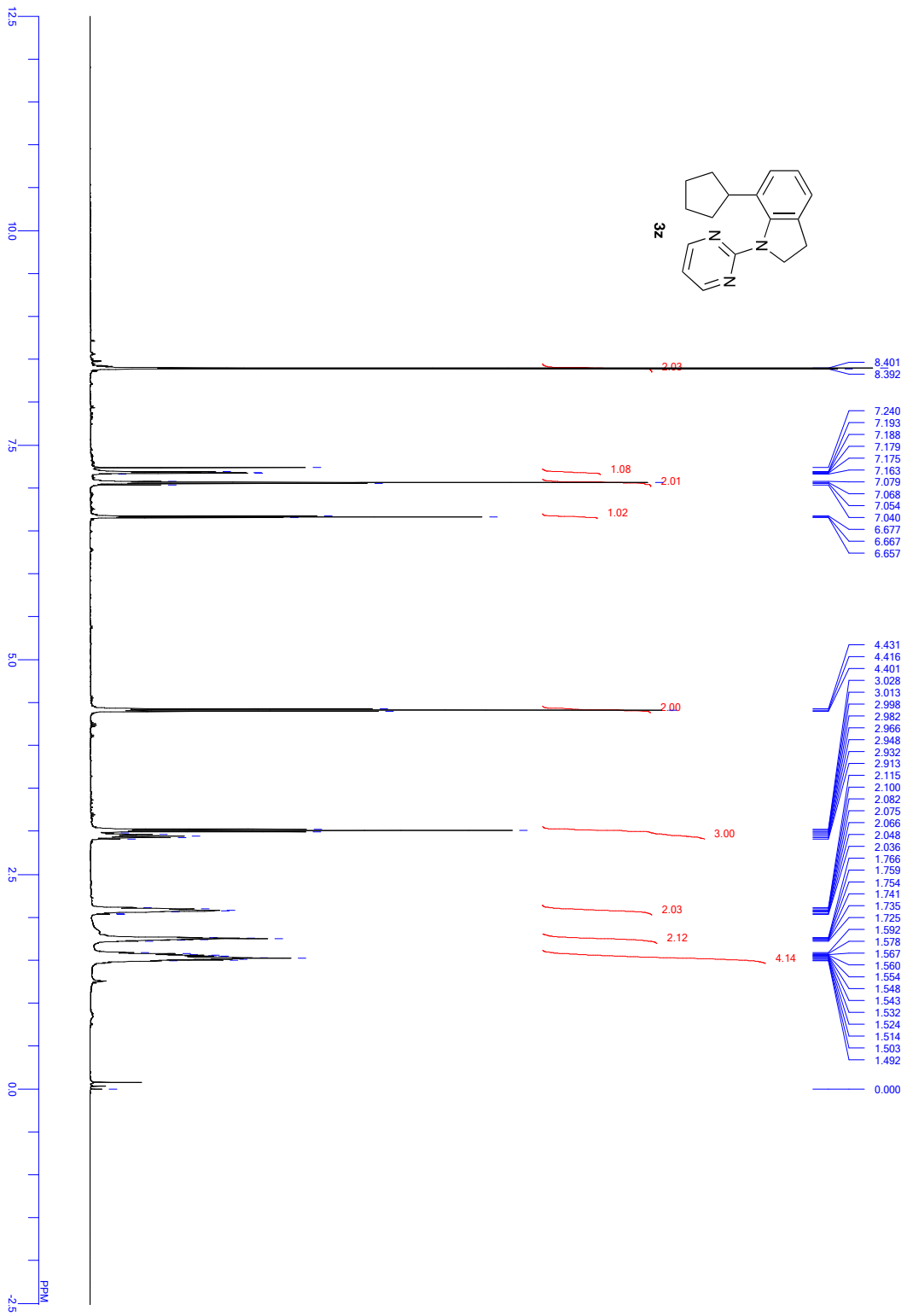
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2.00
3.00
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125.579
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200
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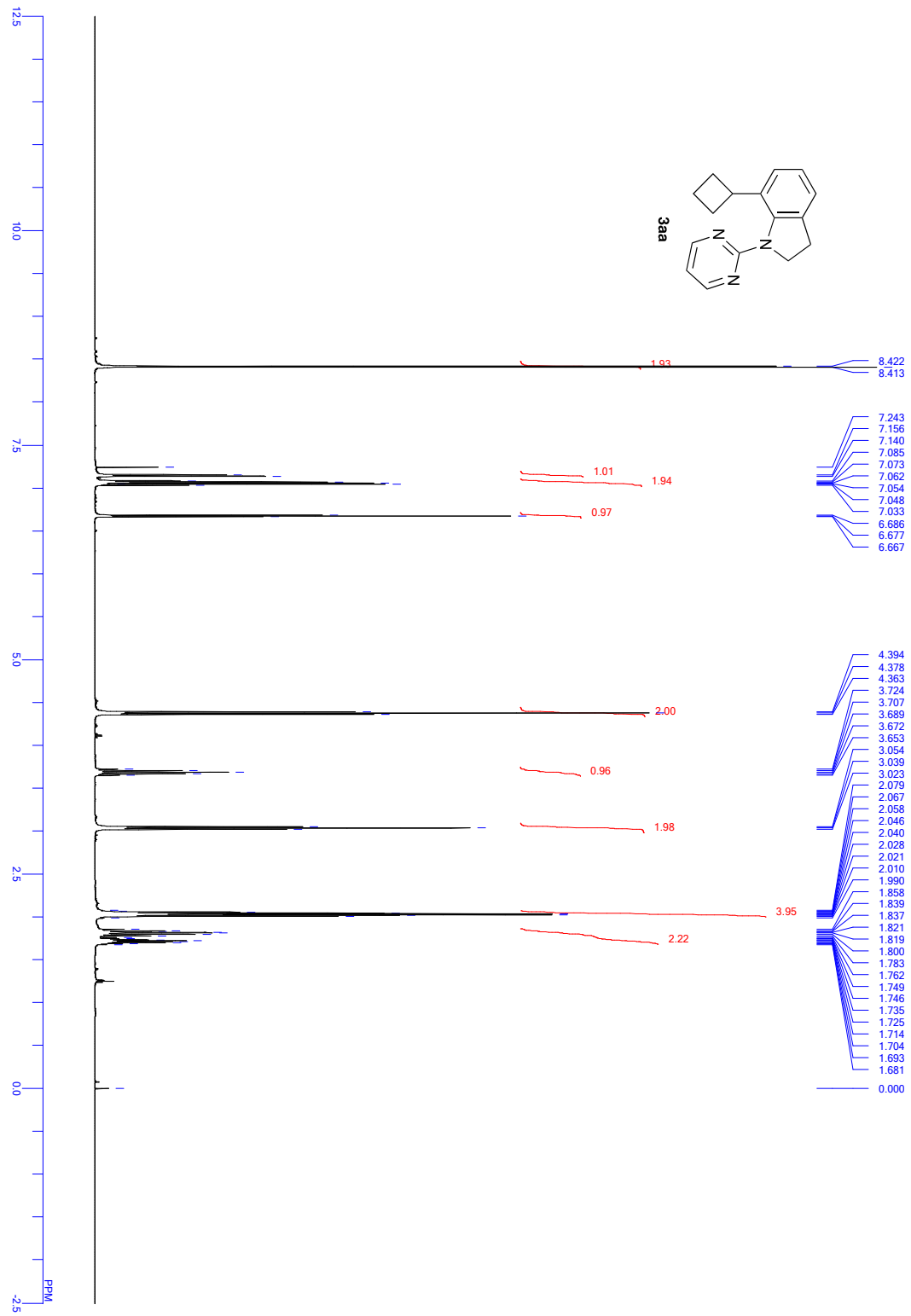
100
50
0
PPM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0.96
1.98
3.95
2.22
8.422
8.413
7.243
7.156
7.140
7.085
7.073
7.062
7.054
7.048
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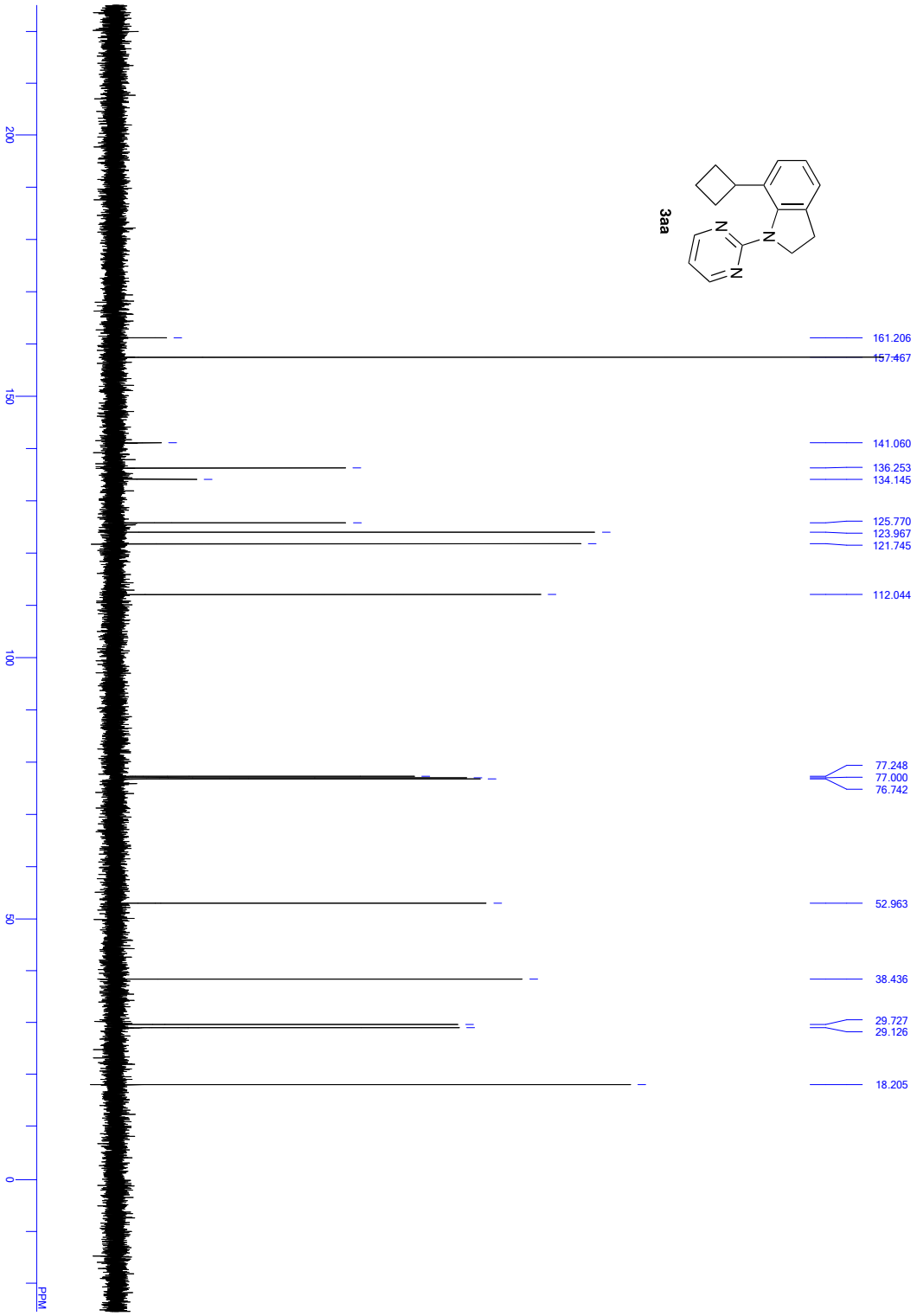
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PPM