Supporting Information

for

Enantioselective Cyanation of Propargylic C-H Bonds via Cooperative Photoredox and Copper Catalysis

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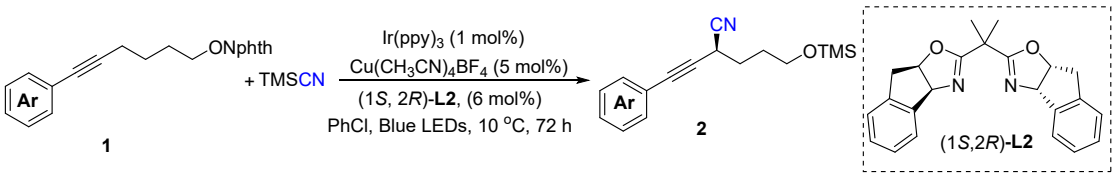
1. General Considerations

All commercially available compounds were purchased from Aldrich, Alfa Aesar, TCI or Adamas and used without further purification, unless otherwise stated. NMR spectra were recorded on Varian Inova 400, Agilent 400 or Bruker 400 (400 MHz for ^{1}H, 376 MHz for ^{19}F, 100 MHz for ^{13}C) spectrometer. The chemical shifts (δ) are given in parts per million relative to $CDCl_3$ (7.26 ppm for ^{1}H) or TMS (0 ppm for ^{1}H) and $CDCl_3$ (77.0 ppm for ^{13}C), and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as outside standard and low field is positive. ^{1}H and ^{19}F multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), doublet of doublets (dd), quartet (q), multiple (m), and broad resonance (br). High performance liquid chromatography was performed on Waters 2487-600E, Waters ACQUITY UPC2, and Ultimate 3000 Series HPLC, using AD-H, OD-H, IG, IH, OJ-H, AY-3, AS-RH and AD-RH chiral column eluted with a mixture of hexane and isopropyl alcohol or water and acetonitrile. Optical rotation was measured on a Rudolph-Autopol I using 10 cm glass cells with a sodium 589 nm filter. High Resolution Mass spectral data were obtained on an Aglient Technologies 7250 GCQTOF spectrometer in EI mode or an Agilent Technologies 6224 TOF LC MS spectrometer in ESI mode or a Thermo Fisher Scientific LTQ FTICR-MS in DART mode or a JEOL AccuTOF GCv4G GCT MS in FI mode. Flash column chromatography was performed on silica gel (particle size 200-300 mesh, purchased from Canada) and eluted with petroleum ether/ethyl acetate. Solvent was purified according to the procedure from the book named "Purification of Laboratory Chemicals". PhCl were deoxygenated with anhydrous Ar bubble for at least 30 min before use.

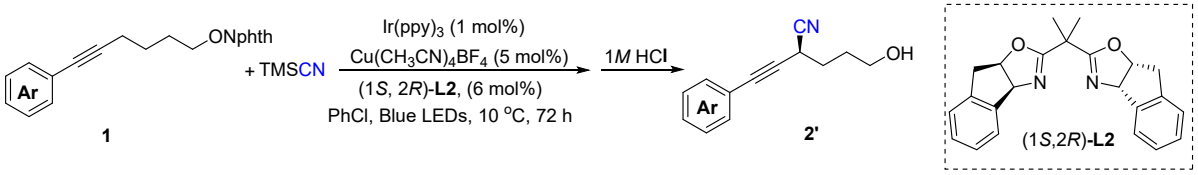
2. General Procedure for Enantioselective Cyanation of Remote Propargylic C-H Bonds

a) Condition A:



In a dried sealed tube, substrate **1** (0.2 mmol, 1.0 equiv), $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol%), **L2** (0.015 mmol, 6 mol%) and $Ir(ppy)_3$ (0.001 mmol, 0.5 mol%) were dissolved in PhCl (2.0 mL) under Ar atmosphere, and stirred for 30 minutes. Then TMSCN (106 μL, 4.0 equiv.) were added slowly under Ar atmosphere. After that, the tube was sealed with a Teflon-lined cap, and the mixture was stirred under the irradiation of 2×3 W blue LEDs in a freezer for 72 hours, and the temperature detected of the reaction mixture was 10 ℃. After the reaction was completed, as monitored by TLC analysis. The product was purified by flash column chromatography on silica gel (petrol ether/ EtOAc = 20/1) to afford the desired product **2**.

b) Condition B:



In a dried sealed tube, substrate **1** (0.2 mmol, 1.0 equiv), $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol%), **L2** (0.015 mmol, 6 mol%) and $Ir(ppy)_3$ (0.001 mmol, 0.5 mol%) were dissolved in PhCl (2.0 mL) under Ar atmosphere, and stirred for 30 minutes. Then TMSCN (106 μL, 4.0 equiv.) were added slowly under Ar atmosphere. After that, the tube was sealed with a Teflon-lined cap, and the mixture was stirred under the irradiation of 2×3 W blue LEDs in a freezer for 72 hours, and the temperature detected of the reaction mixture was 10 ℃. Alternatively, after the reaction was completed, the mixture was quenched by a short pad of silica gel with a gradient eluent of petroleum ether and ethyl acetate. A solution of 1*M* HCl (20 mL) was added to facilitate the deprotection. The mixture was stirred for 3 hours monitored by TLC analysis and then washed with water (3×10 mL) and dried over anhydrous Na_2SO_4. After filtration and concentration, the residue was purified by flash column chromatography on silica gel to give the desired product **2'**. These results were summarized in Table **2**.

In some cases, the TMS-protected products were easily deprotected by fluoride to give free alcohols, thus we deprotected TMS with 1N HCl to separate free alcohols. However, some of the alcohols with a propargylic nitriles were converted to allenyl nitriles. For these products, we carried out with condition A to obtain the TMS-protected products.

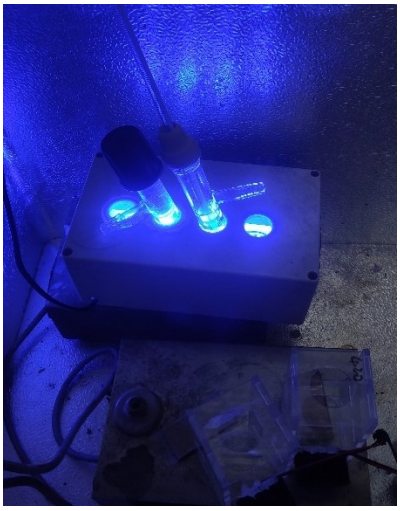
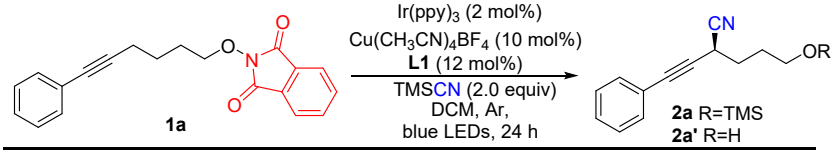


Figure S1. Photoreactor used in this study in a refrigerator to keep the temperature at 10 °C

3. Optimization of Reaction Conditions

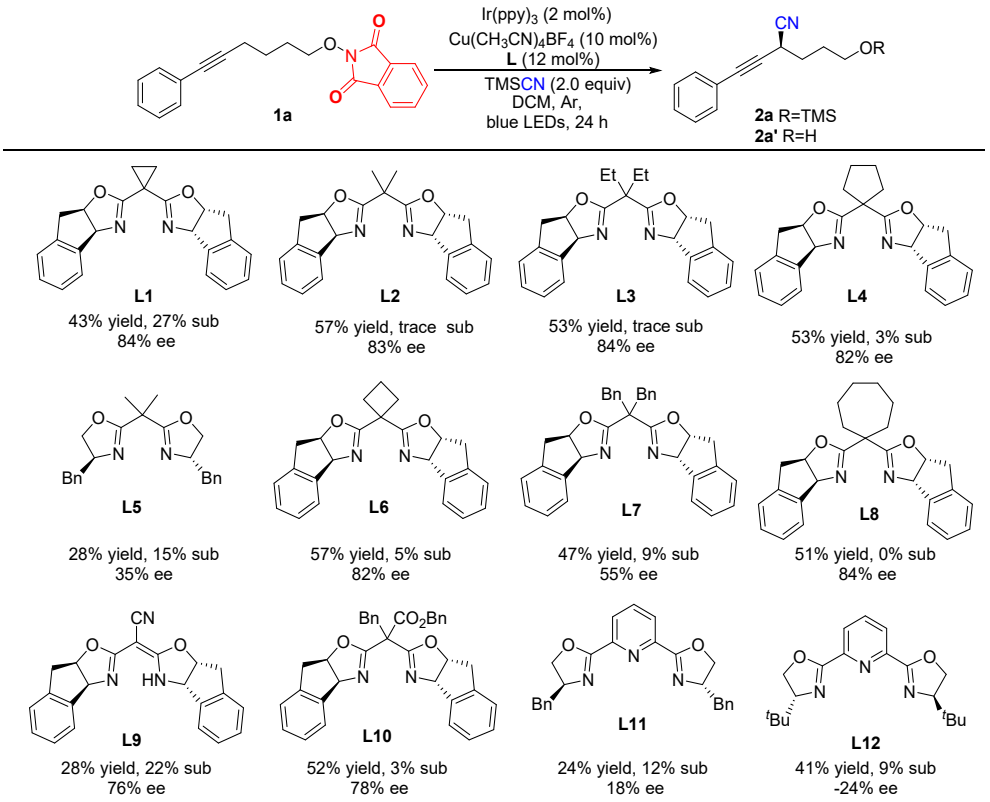
Table S1. Optimization of Copper catalyst [a, b, c]



Entry	[Cu]	conversion	Yield of **2a**+**2a'**	ee of **2a'**
1	$Cu(CH_3CN)_4BF_4$	80%	42%	84%
2	$Cu(CH_3CN)_4PF_6$	85%	41%	76%
3	CuTc	55%	16%	77%
4	CuOTf·PhH	65%	28%	78%
5	CuBr	63%	16%	76%
6	$Cu(OTf)_2$	9%	0%	n.d.
7	CuOAc	45%	27%	83%
8	without Cu	30%	trace	--

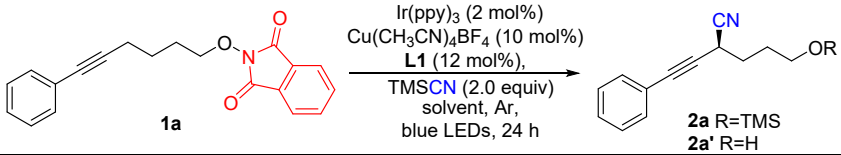
[a]All reactions were run on 0.1 mmol scale in DCM (1.0 mL) at room temperature under the irradiation of 2 x 3 W blue LEDs. [b]Yields (**2a**+**2a'**) were determined by crude ^1H NMR with CH_2Br_2 as internal standard. [c]Enantiomeric excess (ee) value of **2a'** was determined by HPLC on a chiral stationary phase.

Table S2. Optimization of ligands [a, b, c]



[a]All reactions were run on 0.1 mmol scale in DCM (1.0 mL) at room temperature under the irradiation of 2 x 3 W blue LEDs. [b]Yields(**2a**+**2a'**) were determined by crude ^{1}H NMR with CH_2Br_2 as internal standard. [c]Enantiomeric excess (ee) value of **2a'** was determined by HPLC on a chiral stationary phase.

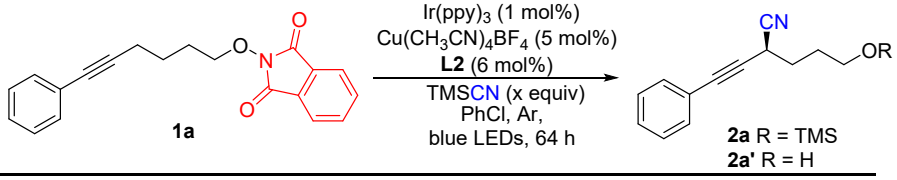
Table S3. Optimization of solvents [a, b, c]



Entry	Solvent	Conversion	Yield of **2a**+**2a'**	*ee* of **2a'**
1	DCM	80%	42%	84%
2	THF	44%	15%	64%
3	CH_3CN	56%	36%	71%
4	$PhCH_3$	31%	15%	76%
5	Et_2O	24%	5%	71%
6	Acetone	39%	12%	78%
7	EA	6%	trace	n.d.
8	$PhCF_3$	57%	31%	80%
9	DMA	11%	trace	n.d.
10	DMF	80%	41%	84%
11	PhCl	37%	36%	84%
12	MeOH	45%	0%	n.d.
13	PhCl[d]	59%	55%	84%
14	PhCl[e]	71%	51%	83%

[a]All reactions were run on 0.1 mmol scale in solvent (1.0 mL) at room temperature under the irradiation of 2 x 3 W blue LEDs. [b]Yields(**2a**+**2a'**) were determined by crude ^{1}H NMR with CH_2Br_2 as internal standard. [c]Enantiomeric excess (ee) value of **2a'** was determined by HPLC on a chiral stationary phase. [d]**L2**. [e]**L3.**

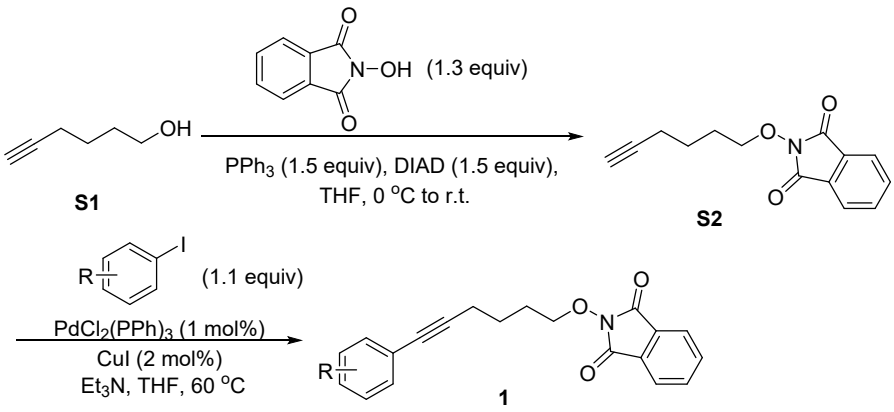
Table S4. Optimization of TMSCN equivalents [a, b, c]



Entry	x	Conversion	Yield of **2a**+**2a'**	ee of **2a'**
1	1.0	45%	29%	84%
2	2.0	70%	54%	84%
3	3.0	81%	64%	84%
4	4.0	0%	80%	84%
5	5.0	0%	81%	84%
6	4.0[d]	0%	78%	88%

[a]All reactions were run on 0.1 mmol scale in PhCl (1.0 mL) at room temperatureunder the irradiation of 2 x 3 W blue LEDs. [b]Yields(**2a**+**2a'**) were determined by crude ^{1}H NMR with CH_2Br_2 as internal standard. [c]Enantiomeric excess (ee) value of **2a'** was determined by HPLC on a chiral stationary phase. [d]10 °C and 72 h

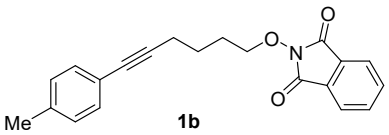
4. General Procedure for the Preparation of the Substrates



A 250 mL, three-necked, round-bottomed flask was equipped with a stirring bar, and pressure equalizing dropping funnel. The flask was charged with 5-hexyn-1-ol (5 mL, 45 mmol), N-Hydroxyphthalimide (9.62 g, 58.5 mmol), triphenylphosphine (18.00 g, 68 mmol), and anhydrous THF (150 mL). Diisopropyl azodicarboxylate (DIAD, 13.75 g, 68 mmol) in anhydrous THF (50 mL) was added to dropping funnel. The flask was immersed in an ice bath, and DIAD was added dropwise at a rate such that the temperature of the reaction mixture is maintained below 5 °C. Upon completion of the addition, the flask was removed from the ice bath and the solution was allowed to

stir at room temperature overnight. The solvent was removed and the residue purified by flash column chromatography on silica gel (using EtOAc/Hexane as eluent) to give **S2** (9.9 g, 91% yield) as a white solid [1].

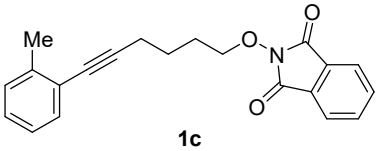
To a 10 mL Schlenk tube, under N_2, was added $PdCl_2(PPh_3)_2$ (15.0 mg, 0.02 mmol), CuI (8 mg, 0.04 mmol), iodobenzene (2.5 mmol) and anhydrous TEA (1 mL). The mixture was stirred at room temperature for 1 min and then **S1** (0.5 g, 2.1 mmol) was added. The tube was placed in a pre-heated oil bath (60 °C). The reaction was stirred for 3 hours and then cooled to room temperature and checked by TLC. The reaction was filtered over celite, washed with dichloromethane. The solvent was removed and the residue purified by flash column chromatography on silica gel (using 20% petroleum ether/ethyl acetate as eluent) to afford substrate **1** (yield: 50% to 90%).



1b

1b (339 mg, 51% yield), white solid, m.p. 68.9-69.8 ℃.

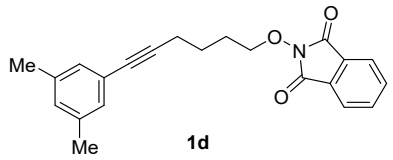
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.75 – 7.72 (m, 2H), 7.27 (d, J = 7.6 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 4.27 (t, J = 6.4 Hz, 2H), 2.52 (t, J = 6.8 Hz, 2H), 2.32 (s, 3H), 1.99 – 1.96 (m, 2H), 1.88 – 1.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 137.5, 134.4, 131.4, 128.9, 128.8, 123.5, 120.7, 88.6, 81.2, 77.9, 27.3, 24.8, 21.4, 19.0. IR (neat): 2956, 1785, 1717, 1609, 1508, 1464, 1404, 1184, 1128, 1029, 874, 699, 517 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{21}H_{19}NO_3Na^+$ $[M+Na]^+$: 356.1257, found: 356.1255.



1c

1c (1.62 g, 81% yield), yellow oil.

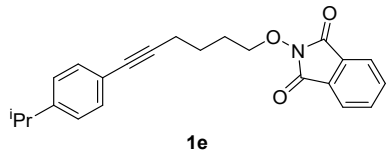
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.80 (m, 2H), 7.75 – 7.73 (m, 2H), 7.17 (t, J = 7.6 Hz, 1H), 6.97 (d, J = 7.2 Hz, 1H), 6.92 (s, 1H), 6.81 (d, J = 8.4 Hz, 1H), 4.28 (t, J = 6.4 Hz, 2H), 2.57 (t, J = 6.8 Hz, 2H), 2.39 (s, 3H), 2.01 – 1.94 (m, 2H), 1.89 – 1.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 139.9, 134.4, 131.8, 129.2, 128.9, 127.5, 125.3, 123.5, 123.4, 93.4, 80.0, 77.9, 27.2, 24.8, 20.7, 19.1. IR (neat): 1789, 1720, 1371, 1243, 1188, 1131, 1082, 1039, 987, 875, 794, 758, 700 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{21}H_{19}NO_3Na^+$ $[M+Na]^+$: 356.1257, found: 356.1251.



1d

1d (1.72 g, 86% yield), yellow oil.

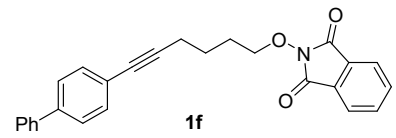
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.81 (m, 2H), 7.74 – 7.72 (m, 2H), 7.01 (m, 2H), 6.89 (s, 1H), 4.27 (t, *J* = 6.4 Hz, 2H), 2.51 (t, *J* = 6.8 Hz, 2H), 2.25 (s, 6H), 2.00 – 1.94 (m, 2H), 1.88 – 1.81 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 137.6, 134.4, 129.4, 129.2, 128.9, 123.41, 123.37, 88.6, 81.4, 77.9, 27.2, 24.7, 21.0, 18.9. IR (neat): 1788, 1730, 1372, 1188, 1128, 979, 878, 835, 700 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{22}H_{21}NO_3Na^+$ $[M+Na]^+$: 370.1414, found: 370.1404.



1e

1e (1.24 g, 81% yield), yellow solid, m.p. 71.8-69.8 ℃.

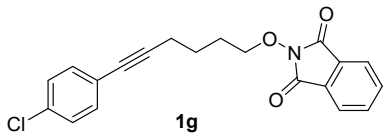
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 2H), 7.75 – 7.73 (m, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.27 (t, *J* = 6.4 Hz, 2H), 2.90 – 2.84 (m, 1H), 2.52 (t, *J* = 6.8 Hz, 2H), 2.02 – 1.90 (m, 2H), 1.86 – 1.81 (m, 2H), 1.21 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 Hz, $CDCl_3$) δ 163.6, 148.4, 134.4, 131.5, 128.9, 126.3, 123.5, 121.1, 88.5, 81.2, 77.9, 33.9, 27.2, 24.8, 23.8, 19.0. IR (neat): 3248, 1738, 1689, 1526, 1471, 1375, 1255, 1185, 1134, 1110, 1051, 976, 926, 880, 780, 701, 678, 655 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{21}H_{19}NO_4Na^+$ $[M+Na]^+$: 384.1570, found: 384.1563.



1f

1f (705 mg, 44% yield), white solid, m.p. 90.7-91.3 ℃.

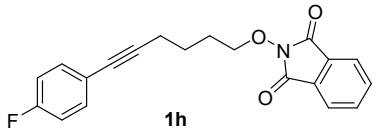
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.82 (m, 2H), 7.75 – 7.73 (m, 2H), 7.59 – 7.57 (m, 2H), 7.52 – 7.50 (m, 2H), 7.46 – 7.42 (m, 4H), 7.36 – 7.32 (m, 1H), 4.29 (t, *J* = 6.4 Hz, 2H), 2.56 (t, *J* = 6.8 Hz, 2H), 2.02 – 1.97 (m, 2H), 1.92 – 1.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 140.5, 140.3, 134.4, 132.0, 128.9, 128.8, 127.4, 127.0, 126.8, 123.5, 122.8, 90.2, 81.0, 77.9, 27.3, 24.8, 19.0. IR (neat): 2937, 1786, 1729, 1484, 1464, 1265, 1185, 1081, 1014, 989, 877, 791, 697, 519 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{26}H_{21}NO_3Na^+$ $[M+Na]^+$: 418.1414, found: 418.1414.



1g

1g (478 mg, 68% yield), white solid, m.p. 75.5-76.8 ℃.

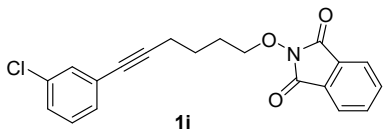
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 2H), 7.75 – 7.73 (m, 2H), 7.31 – 7.29 (m, 2H), 7.25 – 7.22 (m, 2H), 4.27 (t, *J* = 6.4 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 1.98 – 1.93 (m, 2H), 1.89 – 1.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 134.5, 133.5, 132.8, 128.9, 128.5, 123.5, 122.4, 90.6, 80.1, 77.8, 27.3, 24.7, 19.0. IR (neat): 2927, 1785, 1716, 1487, 1374, 1184, 1128, 1087, 1013, 966, 874, 831, 699, 516 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{20}H_{16}NO_3NaCl^+$ $[M+Na]^+$: 376.0711, found: 376.0708.



1h

1h (410 mg, 61% yield), white solid, m.p. 89.7-90.5 ℃.

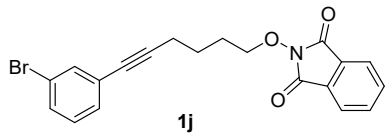
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 2H), 7.76 – 7.73 (m, 2H), 7.37 – 7.34 (m, 2H), 6.98 – 6.93 (m, 2H), 4.27 (t, *J* = 6.4 Hz, 2H), 2.52 (t, *J* = 6.8 Hz, 2H), 1.99 – 1.95 (m, 2H), 1.87 – 1.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 162.0 (d, *J* = 246.6 Hz), 134.4, 133.3 (d, *J* = 8.2 Hz), 128.9, 123.5, 119.9 (d, *J* = 3.7 Hz), 115.3 (d, *J* = 21.8 Hz), 89.1 (d, *J* = 1.8 Hz), 80.1, 77.9, 27.3, 24.7, 18.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.3 – -112.4 (m). IR (neat): 2963, 1785, 1737, 1503, 1466, 1218, 1127, 1025, 996, 879, 658, 519 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{20}H_{16}NO_3NaF^+$ $[M+Na]^+$: 360.1006, found: 360.1004.



1i

1i (2.29 g, 68% yield), white solid, m.p. 80.3-81.1 ℃.

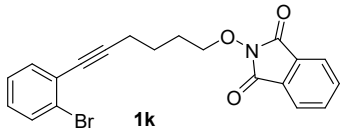
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 2H), 7.75 – 7.73 (m, 2H), 7.36 (s, 1H), 7.24 – 7.16 (m, 3H), 4.27 (t, *J* = 6.0 Hz, 2H), 2.52 (t, *J* = 6.8 Hz, 2H), 1.98 – 1.93 (m, 2H), 1.87 – 1.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 134.4, 133.9, 131.4, 129.7, 129.3, 128.9, 127.8, 125.6, 123.5, 90.9, 79.9, 77.8, 27.3, 24.6, 18.9. IR (neat): 2894, 1785, 1735, 1591, 1468, 1401, 1358, 1185, 1131, 974, 879, 779, 700, 517 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{20}H_{16}NO_3ClNa^+$ $[M+Na]^+$: 376.0711, found: 376.0712.



1j

1j (1.54 g, 86% yield), yellow oil solid, m.p. 90.3-93.1 ℃.

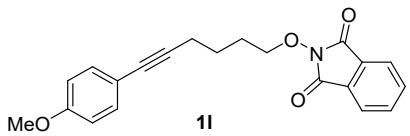
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.69 (m, 2H), 7.64 – 7.62 (m, 2H), 7.40 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 5.6 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 4.17 (t, *J* = 6.4 Hz, 2H), 2.43 (t, *J* = 6.4 Hz, 2H), 1.89 – 1.83 (m, 2H), 1.79 – 1.72 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 134.3, 134.1, 130.5, 130.0, 129.5, 128.7, 125.7, 123.3, 121.8, 91.0, 79.6, 77.6, 27.1, 24.5, 18.8. IR (neat): 3248, 1738, 1689, 1526, 1471, 1375, 1255, 1185, 1134, 1110, 1051, 976, 926, 880, 780, 701, 678, 655 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{20}H_{16}NO_3BrNa^+$ $[M+Na]^+$: 420.0206, found: 420.0201.



1k

1k (1.55 g, 39% yield), white solid, m.p. 82.7-84.1 ℃.

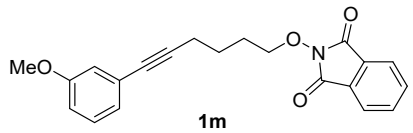
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 2H), 7.75 – 7.73 (m, 2H), 7.53 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.41 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.21 (td, *J* = 11.4, 0.8 Hz, 1H), 7.10 (td, *J* = 8.0, 1.6 Hz, 1H), 4.29 (t, *J* = 6.4 Hz, 2H), 2.59 (t, *J* = 6.8 Hz, 2H), 2.07 – 2.00 (m, 2H), 1.93 – 1.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 134.4, 133.3, 132.2, 128.9, 128.7, 126.9, 125.8, 125.4, 123.5, 94.6, 80.0, 77.8, 27.2, 24.5, 19.1. IR (neat): 2969, 2934, 1784, 1713, 1467, 1400, 1185, 1128, 980, 873, 754, 698, 516 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{20}H_{16}NO_3NaBr^+$ $[M+Na]^+$: 420.0206, found: 420.0205.



1l

1l (1.27 g, 48% yield), white solid, m.p. 86.5-87.3 ℃.

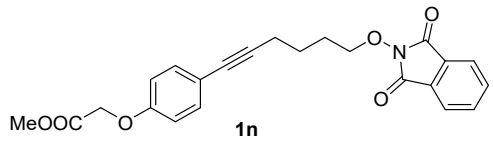
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.76 – 7.73 (m, 2H), 7.32 – 7.30 (m, 2H), 6.81 – 6.78 (m, 2H), 4.27 (t, *J* = 6.4 Hz, 2H), 3.79 (s, 3H), 2.51 (t, *J* = 6.8 Hz, 2H), 1.99 – 1.94 (m, 2H), 1.88 – 1.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 159.0, 134.4, 132.9, 128.9, 123.5, 116.0, 113.8, 87.8, 80.8, 77.9, 55.2, 27.2, 24.8, 19.0. IR (neat): 2940, 1785, 1728, 1606, 1506, 1463, 1287, 1185, 1080, 1015, 946, 699, 518 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{21}H_{19}NO_4Na^+$ $[M+Na]^+$: 372.1206, found: 372.1201.



1m

1m (1.46 g, 84% yield), yellow oil.

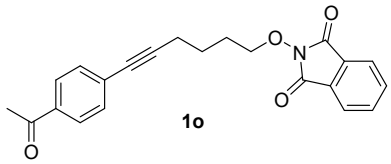
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.75 – 7.73 (m, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.92 (s, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 4.26 (t, *J* = 6.4 Hz, 2H), 3.78 (s, 3H), 2.52 (t, *J* = 6.8 Hz, 2H), 2.01 – 1.94 (m, 2H), 1.89 – 1.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 159.2, 134.4, 129.2, 128.9, 124.8, 124.1, 123.5, 116.3, 114.2, 89.3, 81.1, 77.9, 55.2, 27.3, 24.7, 19.0. IR (neat): 3673, 2970, 1788, 1721, 1374, 1245, 1188, 1131, 1042, 987, 875, 794, 758, 700 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{21}H_{19}NO_4Na^+$ $[M+Na]^+$: 372.1206, found: 372.1203.



1n

1n (1.56 g, 83% yield), yellow solid, m.p. 98.9-91.8 ℃.

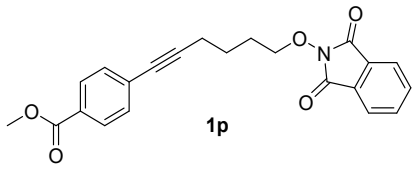
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 2H), 7.75 – 7.73 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 4.62 (s, 2H), 4.26 (t, *J* = 6.4 Hz, 2H), 3.80 (s, 3H), 2.50 (t, *J* = 6.8 Hz, 2H), 1.98 – 1.93 (m, 2H), 1.87 – 1.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 163.6, 157.1, 134.4, 133.0, 128.9, 123.5, 117.3, 114.5, 88.3, 80.6, 77.9, 65.2, 52.3, 27.3, 24.8, 19.0. IR (neat): 3672, 2970, 1788, 1720, 1403, 1245, 1189, 1131, 1068, 987, 875, 794, 758, 700 cm-1. HRMS: m/z (ESI) calculated for $C_{23}H_{21}NO_6Na^+$ $[M+Na]^+$: 430.1261, found: 430.1253.



1o

1o (784 mg, 72% yield), white solid, m.p. 96.4-97.8 ℃.

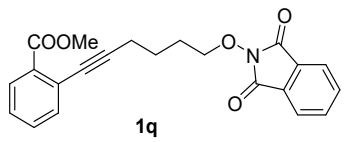
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.85 (m, 2H), 7.84 – 7.82 (m, 2H), 7.78 – 7.74 (m, 2H), 7.47 – 7.45 (m, 2H), 4.28 (t, *J* = 6.4 Hz, 2H), 2.58 (s, 3H), 2.56 (t, *J* = 6.4 Hz, 2H), 2.00 – 1.96 (m, 2H), 1.90 – 1.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 163.6, 135.7, 134.5, 131.6, 128.9, 128.1, 123.4, 93.4, 80.6, 77.8, 27.3, 26.6, 24.6, 19.1. IR (neat): 2961, 1785, 1735, 1672, 1599, 1433, 1400, 1285, 1285, 1183, 1034, 876, 698, 551, 515 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{22}H_{19}NO_4Na^+$ $[M+Na]^+$: 384.1206, found: 384.1200.



1p

1p (1.37 g, 65% yield), white solid, m.p. 103.2-104.5 ℃.

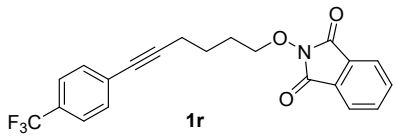
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.84 – 7.81 (m, 2H), 7.77 – 7.73 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 4.27 (t, *J* = 6.0 Hz, 2H), 3.91 (s, 3H), 2.56 (t, *J* = 6.8 Hz, 2H), 2.00 – 1.95 (m, 2H), 1.91 – 1.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 163.6, 134.5, 131.5, 129.3, 128.9, 128.9, 128.7, 123.5, 93.0, 80.7, 77.8, 52.1, 27.3, 24.6, 19.1. IR (neat): 2955, 1786, 1710, 1605, 1272, 1186, 1104, 875, 823, 698, 517 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{22}H_{19}NO_5Na^+$ $[M+Na]^+$: 400.1155, found: 400.1144.



1q

1q (1.72 g, 86% yield), yellow oil.

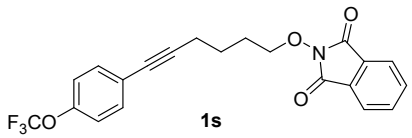
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 1H), 7.80 – 7.77 (m, 2H), 7.73 – 7.70 (m, 2H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.30 – 7.26 (m, 1H), 4.26 (t, *J* = 6.4 Hz, 2H), 3.88 (s, 3H), 2.57 (t, *J* = 6.8 Hz, 2H), 2.03 – 1.96 (m, 2H), 1.90 – 1.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 163.5, 134.3, 134.1, 131.7, 131.4, 130.0, 128.8, 127.1, 124.1, 123.3, 94.9, 79.7, 77.8, 52.0, 27.1, 24.6, 19.2. IR (neat): 2970, 1788, 1720, 1374, 1247, 1189, 1131, 1079, 987, 875, 794, 758, 700 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{22}H_{19}NO_5Na^+$ $[M+Na]^+$: 400.1155, found: 400.1158.



1r

1r (458 mg, 59% yield), white solid, m.p. 56.3-57.7 ℃.

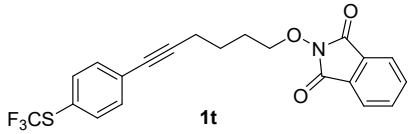
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.76 – 7.73 (m, 2H), 7.53 – 7.51 (m, 2H), 7.48 – 7.46 (m, 2H), 4.28 (t, *J* = 6.4 Hz, 2H), 2.55 (t, *J* = 6.8 Hz, 2H), 1.99 – 1.94 (m, 2H), 1.91 – 127.7, 125.1 (q, *J* = 3.1 Hz), 124.0 (q, *J* = 270.5 Hz), 123.5, 92.3, 80.1, 77.8, 27.3, 24.6, 19.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.76 (s). IR (neat): 2939, 1786, 1729, 1615, 1400, 1321, 1172, 1127. 1105, 1015, 877, 699, 480 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{21}H_{16}NO_3F_3Na^+$ $[M+Na]^+$: 410.0975, found: 410.0968.



1s

1s (717 mg, 89% yield), white solid, m.p. 46.9-48.0 °C.

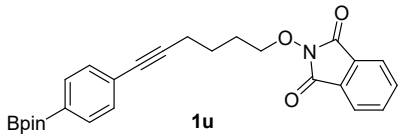
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.79 (m, 2H), 7.73 – 7.71 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 4.26 (t, *J* = 6.4 Hz, 2H), 2.51 (t, *J* = 6.8 Hz, 2H), 1.97 – 1.92 (m, 2H), 1.88 – 1.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 148.3 (d, *J* = 1.8 Hz), 134.4, 132.9, 128.9, 123.4, 122.7, 120.7, 120.3 (q, *J* = 255.9 Hz), 90.5, 79.8, 77.8, 27.2, 24.6, 18.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.89 (s). IR (neat): 2893, 1786, 1730, 1504, 1402, 1252, 1160, 1080, 1018, 923, 877, 696, 521 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{21}H_{16}NO_4F_3Na^+$ $[M+Na]^+$: 426.0924, found: 426.0917.



1t

1t (674 mg, 80% yield), white solid, m.p. 81.4-82.5 °C.

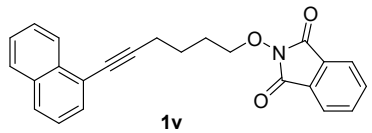
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 2H), 7.76 – 7.73 (m, 2H), 7.56 – 7.54 (m, 2H), 7.43 – 7.40 (m, 2H), 4.27 (t, *J* = 6.0 Hz, 2H), 2.55 (t, *J* = 6.8 Hz, 2H), 1.99 – 1.95 (m, 2H), 1.89 – 1.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 136.0, 134.5, 132.4, 129.4 (q, *J* = 301.0 Hz), 128.9, 126.8, 123.5, 123.3 (q, *J* = 2.1 Hz), 92.7, 80.1, 77.8, 27.3, 24.6, 19.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.69 (s). IR (neat): 2950, 1786, 1716, 1377, 1131, 1108, 1082, 874, 699, 517 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{21}H_{16}NO_3F_3NaS^+$ $[M+Na]^+$: 442.0695, found: 442.0688.



1u

1u (550 mg, 80% yield), white solid, m.p. 102.3-103.1 °C.

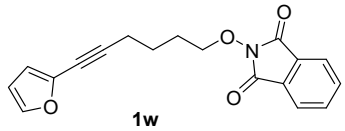
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.80 (m, 2H), 7.73 – 7.71 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.26 (t, *J* = 6.4 Hz, 2H), 2.53 (t, *J* = 6.8 Hz, 2H), 1.98 – 1.93 (m, 2H), 1.87 – 1.83 (m, 2H), 1.32 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 134.41, 134.39, 130.7, 128.9, 126.6, 123.4, 90.9, 83.8, 81.3, 77.8, 27.2, 24.8, 24.6, 19.0. IR (neat): 2980, 1785, 1732, 1606, 1394, 1356, 1324, 1168, 1087, 981, 841, 697, 651, 516 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{26}H_{28}BNO_5Na^+$ $[M+Na]^+$: 468.1953, found: 468.1943.



1v

1v (1.68 g, 85% yield), yellow solid, m.p. 106.3-107.4 ℃

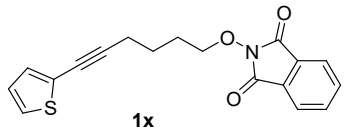
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.0 Hz, 1H), 7.83 – 7.70 (m, 6H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 4.32 (t, *J* = 6.4 Hz, 2H), 2.70 (t, *J* = 6.8 Hz, 2H), 2.10 – 2.02 (m, 2H), 2.00 – 1.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 134.3, 133.3, 133.1, 130.0, 128.8, 128.1, 127.9, 126.5, 126.3, 126.2, 125.1, 123.4, 121.5, 94.5, 79.1, 77.8, 27.3, 24.9, 19.3. IR (neat): 1718, 1369, 1188, 1130, 1031, 987, 875, 799, 774, 699 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{24}H_{19}NO_3Na^+$ $[M+Na]^+$: 392.1257, found: 392.1249.



1w

1w (391 mg, 63% yield), white solid, m.p. 49.1-50.2 ℃.

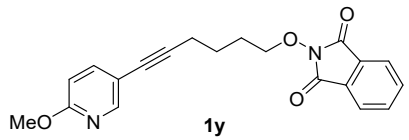
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.76 – 7.73 (m, 2H), 7.31 (d, *J* = 1.2 Hz, 1H), 6.46 (d, *J* = 3.2Hz, 1H), 6.34 – 6.33 (m, 1H), 4.25 (t, *J* = 6.4 Hz, 2H), 2.59 (t, *J* = 7.2 Hz, 2H), 1.97 – 1.92 (m, 2H), 1.90 – 1.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 142.7, 137.4, 134.4, 128.9, 123.5, 113.8, 110.6, 93.9, 77.8, 71.5, 27.2, 24.4, 19.0. IR (neat): 2964, 1786, 1714, 1211, 1127, 1018, 873, 757, 697, 516 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{18}H_{15}NO_4Na^+$ $[M+Na]^+$: 332.0893, found: 332.0890.



1x

1x (193 mg, 30% yield), white solid, m.p. 73.0-74.2 ℃.

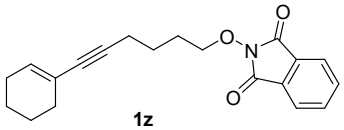
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 2H), 7.76 – 7.73 (m, 2H), 7.16 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.11 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.92 (dd, *J* = 5.2, 3.6 Hz, 1H), 4.27 (t, *J* = 6.0 Hz, 2H), 2.55 (t, *J* = 6.8 Hz, 2H), 1.98 – 1.95 (m, 2H), 1.88 – 1.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 134.4, 131.1, 129.0, 126.7, 126.0, 124.0, 123.5, 93.5, 77.8, 74.3, 27.3, 24.6, 19.3. IR (neat): 2929, 1784, 1727, 1466, 1392, 1186, 1130, 984, 878, 693, 518 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{18}H_{15}NO_3SNa^+$ $[M+Na]^+$: 348.0665, found: 348.0660.



1y

1y (1.2 g, 69% yield), white solid, m.p. 81.5-78.3 ℃.

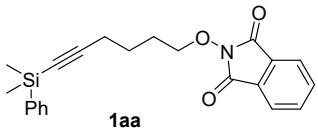
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.84 – 7.81 (m, 2H), 7.76 – 7.73 (m, 2H), 7.56 – 7.53 (m, 1H), 6.65 (d, *J* = 8.8 Hz, 1H), 4.27 (t, *J* = 6.4 Hz, 2H), 3.92 (s, 3H), 2.52 (t, *J* = 6.8 Hz, 2H), 2.00 – 1.93 (m, 2H), 1.89 – 1.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 162.8, 149.7, 141.2, 134.4, 128.8, 123.4, 113.6, 110.3, 90.7, 77.8, 53.5, 27.2, 24.7, 19.0. HRMS: *m/z* (ESI) calculated for $C_{20}H_{19}N_2O_4^+$ $[M+H]^+$: 351.1339, found: 351.1337.



1z

1z (1.0 g, 91% yield), white solid, m.p. 45.6-46.0 ℃.

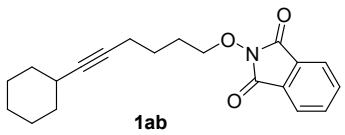
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 2H), 7.76 – 7.73 (m, 2H), 5.99 (s, 1H), 4.23 (t, *J* = 6.4 Hz, 2H), 2.40 (t, *J* = 6.8 Hz, 2H), 2.07 – 2.04 (m, 4H), 1.93 – 1.88 (m, 2H), 1.79 – 1.73 (m, 2H), 1.60 – 1.53 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 134.4, 133.4, 129.0, 123.5, 120.9, 86.4, 83.0, 78.0, 29.5, 27.2, 25.5, 24.9, 22.4, 21.6, 18.9. IR (neat): 2922, 1786, 1717, 1367, 1240, 1186, 1034, 917, 873, 796, 516 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{20}H_{21}NO_3Na^+$ $[M+Na]^+$: 346.1414, found: 346.1411.



1aa

1aa (1.54 g, 54% yield), white solid, m.p. 59.5-60.7 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.76 – 7.73 (m, 2H), 7.63 – 7.61 (m, 2H), 7.36 – 7.35 (m, 3H), 4.24 (t, *J* = 6.0 Hz, 2H), 2.40 (t, *J* = 7.2 Hz, 2H), 1.95 – 1.89 (m, 2H), 1.82 – 1.79 (m, 2H), 0.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 137.5, 134.4, 133.6, 129.2, 128.9, 127.8, 123.5, 108.5, 83.0, 77.9, 27.2, 24.6, 19.5, -0.7. IR (neat): 2956, 2895, 2192, 1788, 1728, 1428, 1248, 1017, 876, 814, 779, 697 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{22}H_{23}NO_3SiNa^+$ $[M+Na]^+$: 400.1339, found: 400.1331.



1ab

1ab (2.00 g, 76% yield), white solid, m.p. 50.8-51.6 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.82 (m, 2H), 7.77 – 7.73 (m, 2H), 4.24 (t, *J* = 6.4 Hz, 2H), 2.31 – 2.25 (m, 1H), 2.27 (t, *J* = 6.8 Hz, 2H), 1.94 – 1.87 (m, 2H), 1.76 – 1.67 (m, 6H). 1.50 – 1.49 (m, 1H), 1.41 – 1.33 (m, 2H), 1.27 – 1.23 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 134.4, 128.9, 123.5, 85.3, 79.1, 78.0, 33.1, 29.1, 27.2, 25.9, 25.0, 24.9, 18.3. IR (neat): 2928, 2853, 1787, 1729, 1451, 1186, 1129, 1082, 1014, 936, 791, 699, 519 cm^{-1}. HRMS: m/z (ESI) calculated for $C_{20}H_{23}NO_3Na^+$ $[M+Na]^+$: 348.1570, found: 348.1579.

5. Preliminary Mechanistic Study

5.1 Cyclic Voltammetry Experiments

Cyclic Voltammetry was performed on a CH Instruments Electrochemical Workstation model CHI600E. A solution of **1a** in MeCN (0.005 M) was tested with 0.1 M Bu_4NPF_6 as the supporting electrolyte. The working electrode is a glassy carbon, the counter electrode is a Pt wire, and the reference electrode is $Ag/AgNO_3$. The scan rate was set to 0.05 V/s. Solutions were degassed with argon prior to measurement and experiments were performed under an atmosphere of argon. Reduction potential was normalized to the ferrocene/ferrocenium redox couple (Fc/Fc^+) [2].

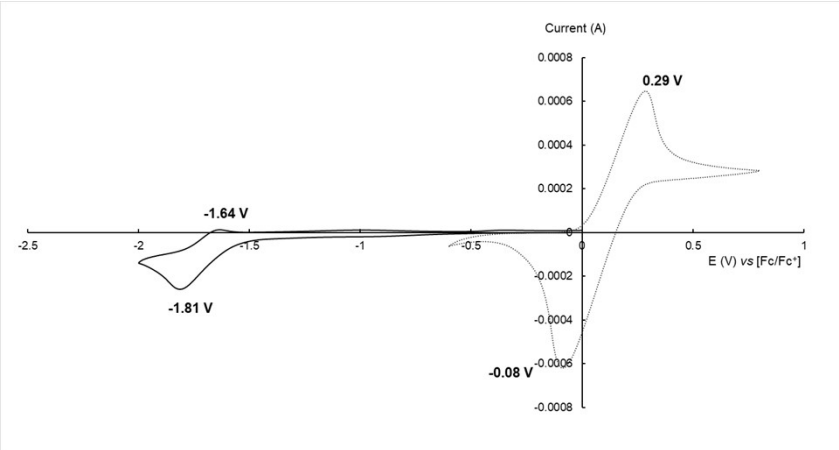


Figure **S1**. Cyclic voltammogram of **1a** and ferrocene as standard

5.2 Stern-Volmer Fluorescence Quenching Experiments

Emission intensities were recorded using Microplate Accessory F-2700 FL spectrometer for all experiments. All *fac*-Ir(ppy)$_3$ solutions were excited at 380 nm and the emission intensity was collected at 528 nm. The solution of *fac*-Ir(ppy)$_3$ in a mixture solvent of PhCl (125 μM) was added the appropriate amount of **1a** in a screw-top 1.0 cm quartz cuvette. After degassing with nitrogen for 10 min, the emission spectra of the samples were collected.

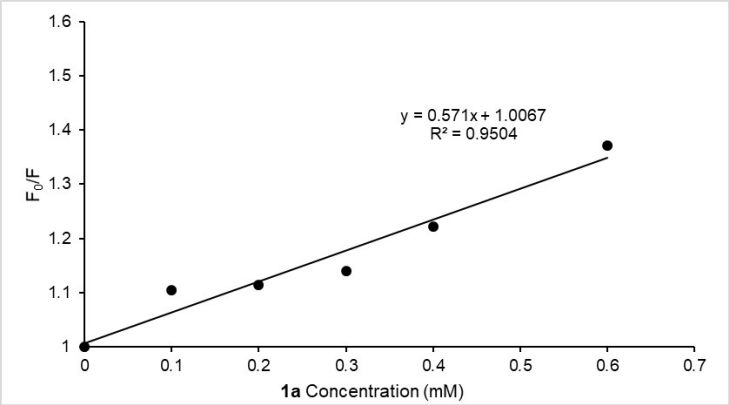


Figure **S2**. *fac*-Ir(ppy)$_3$ emission quenching by **1a**

5.3 Light On-Off Experiments

Light On-Off experiments were carried out independently and stopped at different times. In a dried sealed 25 mL Schlenk tube, Cu(CH$_3$CN)$_4$BF$_4$ (37.7 mg, 10 mol%), **L2** (51.6 mg, 12 mol%) and *fac*-Ir(ppy)$_3$ (14.4 mg, 2 mol%) were dissolved in PhCl (10 mL) under an Ar atmosphere, and the mixture was stirred for 30 min to get a light yellow solution. To a sealed tube containing **1a** (0.1 mmol), 1 mL of the above solution and TMSCN (53 μL, 0.4 mmol) were sequentially added under an Ar atmosphere. The tube was sealed with Teflon-septum, the reaction mixture was stirred at room temperature under the irradiation of 2 x 3 W blue LEDs for the indicated time. All the reactions were quenched by a short pad of silica gel with a gradient eluent of petroleum ether and ethyl acetate. The yield of **2a**+**2a'** was determined by ^{1}H NMR using CH$_2$Br$_2$ as an internal standard.

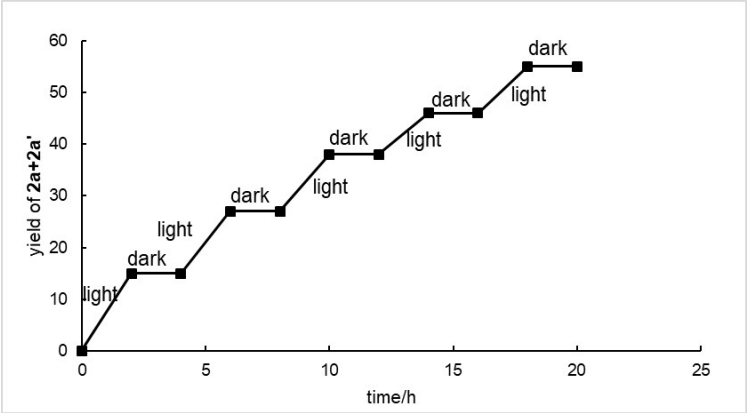
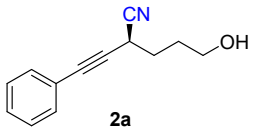


Figure **S3**. Light on-off experiments

6. Product Characterizations

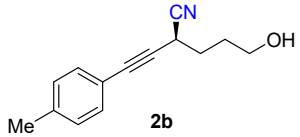
Note: Some products will isomerized to allenyl nitriles during the deprotection process, so we choose to quickly separate products with OTMS protection.



2a

The reaction was conducted according to the general procedure **B** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to afford the product **2a** (31.3 mg, 78% yield, 88% ee) as colorless oil.

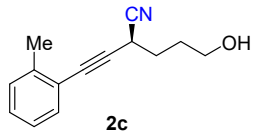
$[\alpha]_D^{28.4}$ +4.89 (*c* 0.55, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 2H), 7.36 – 7.30 (m, 3H), 3.87 (t, *J* = 6.8 Hz, 1H), 3.77 (t, *J* = 6.0 Hz, 2H), 2.12 – 2.06 (m, 2H), 1.93 – 1.86 (m, 2H), 1.46 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8, 128.9, 128.4, 121.6, 117.6, 84.2, 80.9, 61.7, 30.1, 29.4, 23.7. IR (neat): 3383, 2936, 1490, 1444, 1323, 1059, 917, 756, 690, 528 cm^{-1}. HRMS: *m/z* (FI) calculated for $C_{13}H_{13}NO^+$ $[M]^+$: 199.0992, found: 199.0996. HPLC (AY-3, 0.46*15 cm, 3 μm, hexane/isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 5.54 min (major) and 6.21 min (minor).



2b

The reaction was conducted according to the general procedure **B** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to afford the product **2b** (34.7 mg, 81% yield, 90% ee) as colorless oil.

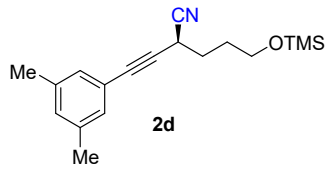
$[\alpha]_D^{27.6}$ +1.82 (*c* 2.56, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.85 (t, *J* = 6.8 Hz, 1H), 3.76 (t, *J* = 6.0 Hz, 2H), 2.35 (s, 3H), 2.10 – 2.04 (m, 2H), 1.90 – 1.87 (m, 2H), 1.60 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 131.7, 129.1, 118.5, 117.7, 84.3, 80.2, 61.7, 30.1, 29.4, 23.6, 21.5; IR (neat): 3379, 2923, 2245, 1608, 1510, 1451, 1323, 1059, 816, 527 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{14}H_{16}NO^+$ $[M+H]^+$: 214.1226, found: 214.1219. HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow 0.7 mL/min, detection at 214 nm) retention time = 14.28 min (major) and 15.67 min (minor).



2c

The reaction was conducted according to the general procedure **B** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum dichloromethane/ethyl acetate (4:1) to afford the product **2c** (22.2 mg, 52% yield, 89% ee) as colorless oil.

$[\alpha]_D^{21.8}$ -2.57 (*c* 0.41, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.6 Hz, 1H), 7.27 – 7.18 (m, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 3.91 (t, *J* = 6.8 Hz, 1H), 3.75 (t, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 2.13 – 2.07 (m, 2H), 1.94 – 1.87 (m, 2H), 1.63 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5. 132.1, 129.5, 128.9, 125.6, 121.4, 117.7, 84.7, 83.2, 61.6, 30.2, 29.4, 23.8, 20.6. IR (neat): 3672, 2970, 2246, 1720, 1485, 1453, 1405, 1452, 1064, 876, 759, 714, 633 cm^{-1}. HRMS: *m/z* (EI) calculated for $C_{14}H_{15}NO^+$ $[M]^+$: 213.1148, found: 213.1144. HPLC (IG, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow 0.7 mL/min, detection at 214 nm) retention time = 14.02 min (major) and 14.61 min (minor).

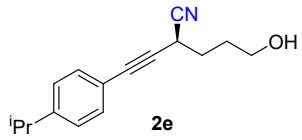


2d

The reaction was conducted according to the general procedure **A** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum dichloromethane/ethyl acetate (20:1) to afford the product **2d** (37.3 mg, 62% yield, 89% ee) as colorless oil.

$[\alpha]_D^{22.0}$ -7.66 (*c* 0.33, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.06 (s, 2H), 6.98 (s, 1H), 3.82 (t, *J* = 7.2 Hz, 1H), 3.68 (t, *J* = 6.0 Hz, 2H), 2.32 (s, 6H), 2.05 – 2.00 (m, 2H), 1.86 – 1.82 (m, 2H), 0.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 130.8, 129.4, 121.3, 117.7, 84.4, 80.3, 61.4, 30.4, 29.5,

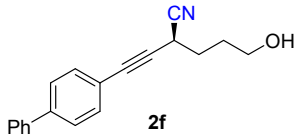
23.6, 21.0, -0.6. IR (neat): 3672, 2970, 2246, 1787, 1720, 1403, 1247, 1189, 1131, 1067, 987, 875, 794, 758, 700 cm^{-1}. HRMS: *m/z* (EI) calculated for $C_{18}H_{25}NO^+$ $[M]^+$: 299.1700, found: 299.1704. HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 9.48 min (minor) and 13.84 min (major).



2e

The reaction was conducted according to the general procedure **B** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to afford the product **2e** (35.7 mg, 74% yield, 89% ee) as colorless oil.

$[\alpha]_D^{22.2}$ +2.25 (*c* 0.18, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 3.85 (t, *J* = 7.2 Hz, 1H), 3.75 (t, *J* = 6.0 Hz, 2H), 2.91 – 2.87 (m, 1H), 2.10 – 2.04 (m, 2H), 1.90 – 1.86 (m, 2H), 1.70 (br, 1H), 1.23 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 131.8, 126.5, 118.9, 117.7, 84.3, 80.1, 61.6, 34.0, 30.1, 29.4, 23.7, 23.6. IR (neat): 3673, 2970, 2247, 1788, 1720, 1404, 1246, 1189, 1131, 1068, 987, 875, 794, 758, 700 cm^{-1}. HRMS: *m/z* (EI) calculated for $C_{16}H_{19}NO^+$ $[M]^+$: 241.1461, found: 241.1460. HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow 0.7 mL/min, detection at 214 nm) retention time = 12.61 min (minor) and 13.58 min (major).

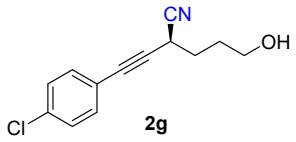


2f

The reaction was conducted according to the general procedure **B** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to afford the product **2f** (33.6 mg, 61% yield, 89% ee) as a white soild, m.p. 89.4-90.5 ℃.

$[\alpha]_D^{27.1}$ +0.94 (*c* 1.25, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 4H), 7.52 – 7.50 (m, 2H), 7.47 – 7.43 (m, 2H), 7.39 – 7.35 (m, 1H), 3.90 (t, *J* = 6.8 Hz, 1H), 3.76 (t, *J* = 6.0 Hz, 2H), 2.14 – 2.08 (m, 2H), 1.95 – 1.90 (m, 2H), 1.52 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 140.1, 132.2, 128.9, 127.8, 127.1, 127.0, 120.5, 117.6, 84.1, 81.5, 61.7, 30.2, 29.5, 23.7; IR (neat): 3372, 2924, 1484, 1448, 1328, 1260, 1063, 976, 909, 839, 760, 687, 506 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{19}H_{18}NO^+$ $[M+H]^+$: 276.1383, found: 276.1376. HPLC (OD-H, 0.46*25 cm, 5 μm,

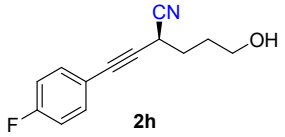
hexane/isopropanol = 80/20, flow 0.7 mL/min, detection at 214 nm) retention time = 16.74 min (minor) and 19.14 min (major).



2g

The reaction was conducted according to the general procedure **B** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to afford the product **2g** (32.6 mg, 70% yield, 89% ee) as colorless oil.

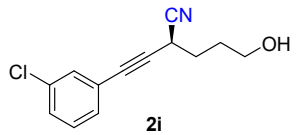
$[\alpha]_D^{26.5}$ +0.56 (*c* 1.82, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 2H), 3.86 (t, *J* = 7.2 Hz, 1H), 3.76 (t, *J* = 6.0 Hz, 2H), 2.11 – 2.05 (m, 2H), 1.92 – 1.86 (m, 2H), 1.57 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 133.0, 128.7, 120.1, 117.4, 83.1, 81.9, 61.6, 30.1, 29.4, 23.6; IR (neat): 3387, 2933, 2247, 1592, 1488, 1398, 1322, 1089, 1060, 1014, 827, 525 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{13}H_{12}NONaCl^+$ $[M+Na]^+$: 256.0500, found: 256.0508. HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 80/20, flow 0.7 mL/min, detection at 214 nm) retention time = 10.04 min (minor) and 11.50 min (major).



2h

The reaction was conducted according to the general procedure **B** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to afford the product **2h** (28.1 mg, 65% yield, 94% *ee*) as colorless oil.

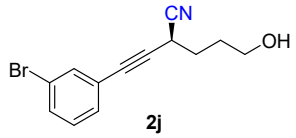
$[\alpha]_D^{28.3}$ +2.91 (*c* 1.54, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 2H), 7.04 – 6.99 (m, 2H), 3.85 (t, *J* = 6.8 Hz, 1H), 3.76 (t, *J* = 6.0 Hz, 2H), 2.10 – 2.05 (m, 2H), 1.91 – 1.84 (m, 2H), 1.62 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, *J* = 249.1 Hz), 133.8 (d, *J* = 8.1 Hz), 117.7 (d, *J* = 3.6 Hz), 117.5, 115.7 (d, *J* = 21.9 Hz), 83.2, 80.7 (d, *J* = 1.7 Hz), 61.6, 30.1, 29.4, 23.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.69 – -109.77 (m); IR (neat): 3376, 2936, 1601, 1505, 1452, 1222, 1156, 1060, 836, 529 cm^{-1}. HRMS: *m/z* (DART) calculated for $C_{13}H_{13}NFO^+$ $[M+H]^+$: 218.0976, found: 218.0975. HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 80/20, flow 0.7 mL/min, detection at 254 nm) retention time = 10.93 min (major) and 15.62 min (minor).



2i

The reaction was conducted according to the general procedure **B** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to afford the product **2i** (28.9 mg, 62% yield, 84% *ee*) as colorless oil.

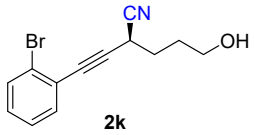
$[\alpha]_D^{27.9}$ -6.40 (*c* 1.69 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.40 (m, 1H), 7.33 – 7.29 (m, 2H), 7.24 – 7.22 (m, 1H), 3.86 (t, *J* = 6.8 Hz, 1H), 3.76 (t, *J* = 6.0 Hz, 2H), 2.10 – 2.05 (m, 2H), 1.91 – 1.85 (m, 2H), 1.58 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.2, 131.7, 129.9, 129.6, 129.3, 123.3, 117.3, 82.8, 82.2, 61.4, 30.1, 29.4, 23.6. IR (neat): 3383, 2927, 1593, 1563, 1475, 1408, 1265, 1058, 881, 784, 681, 440 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{13}H_{12}NClONa^+$ $[M+Na]^+$: 256.0500, found: 256.0507. HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 80/20, flow 0.7 mL/min, detection at 214 nm) retention time = 7.59 min (major) and 8.27 min (minor).



2j

The reaction was conducted according to the general procedure **B** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum dichloromethane/ethyl acetate (4:1) to afford the product **2j** (42.1 mg, 76% yield, 86% ee) as colorless oil.

$[\alpha]_D^{22.4}$ -8.42 (*c* 0.34, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.17 (m, 1H), 3.87 (t, *J* = 6.8 Hz, 1H), 3.75 (t, *J* = 6.0 Hz, 2H), 2.10 – 2.05 (m, 2H), 1.91 – 1.84 (m, 2H), 1.73 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.5, 132.1. 130.3, 129.8, 123.5, 122.1, 117.3, 82.6, 82.3, 61.5, 30.0, 29.3, 23.6. IR (neat): 2968, 2245, 1591, 1556, 1473, 1451, 1406, 1244, 1068, 882, 784, 736, 680 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{13}H_{12}NONaBr^+$ $[M+Na]^+$: 299.9994, found: 299.9993. HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 80/20, flow 0.7 mL/min, detection at 214 nm) retention time = 9.47 min (major) and 10.89 min (minor).

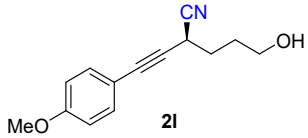


2k

The reaction was conducted according to the general procedure **B** on a 0.2 mmol scale. The

residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to afford the product **2k** (28.8 mg, 65% yield, 88% *ee*) as colorless oil.

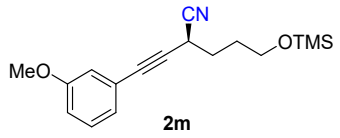
$[\alpha]_D^{28.4}$ +0.29 (*c* 1.33 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.23 – 7.19 (m, 1H), 3.93 (t, *J* = 7.2 Hz, 1H), 3.78 (t, *J* = 6.0 Hz, 2H), 2.16 – 2.11 (m, 2H), 1.98 – 1.92 (m, 2H), 1.40 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.6, 132.5, 130.1, 127.1, 125.7, 123.9, 117.2, 85.5, 82.8, 61.7, 30.0, 29.4, 23.8. IR (neat): 3361, 2924, 1563, 1471, 1437, 1050, 1023, 827, 751, 669, 444 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{13}H_{12}NBrO^+$ $[M]^+$: 277.0097, found: 277.0092. HPLC (OJ-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow 0.7 mL/min, detection at 214 nm) retention time = 13.85 min (major) and 14.78 min (minor).



2l

The reaction was conducted according to the general procedure **B** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to afford the product **2l** (34.5 mg, 75% yield, 91% *ee*) as colorless oil.

$[\alpha]_D^{28.2}$ +0.59 (*c* 1.19, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 6.86 – 6.82 (m, 2H), 3.84 (t, *J* = 6.8 Hz, 1H), 3.81 (s, 3H), 3.76 (t, *J* = 6.0 Hz, 2H), 2.10 – 2.04 (m, 2H), 1.92 – 1.85 (m, 2H), 1.44 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 133.3, 117.8, 114.0, 113.7, 84.2, 79.5, 61.7, 55.3, 30.2, 29.4, 23.7; IR (neat): 3414, 2932, 2240, 1605, 1508, 1456, 1293, 1250, 1174, 1028, 832, 669, 557 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{14}H_{16}NO_2^+$ $[M+H]^+$: 230.1176, found: 230.1181. HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 80/20, flow 0.7 mL/min, detection at 214 nm) retention time = 14.39 min (major) and 15.83 min (minor).

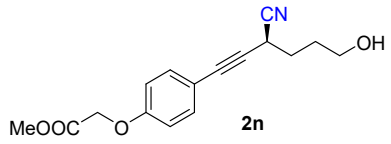


2m

The reaction was conducted according to the general procedure A on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum dichloromethane/ethyl acetate (20:1) to afford the product **2m** (39.4 mg, 65% yield, 89% ee) as colorless oil.

$[\alpha]_D^{22.6}$ +1.35 (*c* 0.58, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 1H), 7.05 (d, *J* =

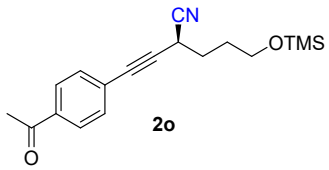
8.0 Hz, 1H), 6.98 (s, 1H), 6.92 (d, J = 7.6 Hz, 1H), 3.88 – 3.83 (m, 4H), 3.70 (t, J = 6.0 Hz, 2H), 2.10 – 2.04 (m, 2H), 1.89 – 1.83 (m, 2H), 0.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 129.4, 124.3, 122.7, 117.6, 116.6, 115.5, 83.9, 80.9, 61.4, 55.3, 30.4, 29.5, 23.6, -0.6. IR (neat): 2961, 2247, 1601, 1486, 1287, 1252, 1206, 1087, 1047, 841, 784, 750, 687, 635 cm^{-1}. HRMS: *m/z* (EI) calculated for $C_{17}H_{23}NO_2Si^+$ $[M]^+$: 301.1493, found: 301.1494. HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 18.56 min (minor) and 25.34 min (major).



2n

The reaction was conducted according to the general procedure **B** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum dichloromethane/ethyl acetate (1:1) to afford the product **2n** (46.1 mg, 80% yield, 89% ee) as colorless oil.

$[\alpha]_D^{21.2}$ -1.18 (*c* 0.46, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 7.2 Hz, 2H), 4.63 (s, 2H), 3.85 – 3.80 (m, 4H), 3.74 (t, J = 6.4 Hz, 2H), 2.08 – 2.02 (m, 2H), 1.90 – 1.83 (m, 2H), 1.66 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 158.1, 133.3, 117.7, 114.9, 114.6, 83.8, 80.0, 65.1, 61.6, 52.3, 30.1, 29.4, 23.6. IR (neat): 2969, 2249, 1755, 1605, 1509, 1438, 1212, 1176, 1076, 834, 646 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{16}H_{18}NO_4^+$ $[M]^+$: 288.1230, found: 288.1232. HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 70/30, flow 0.7 mL/min, detection at 214 nm) retention time = 15.05 min (minor) and 21.55 min (major).

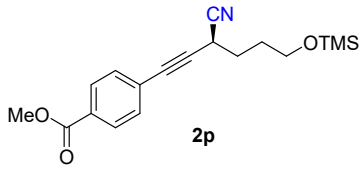


2o

The reaction was conducted according to the general procedure **A** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) to afford the product **2o** (25.0 mg, 43% yield, 84% *ee*) as colorless oil.

$[\alpha]_D^{28.7}$ -5.63 (*c* 0.60, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 3.88 (t, J = 7.2 Hz, 1H), 3.68 (t, J = 5.6 Hz, 2H), 2.60 (s, 3H), 2.09 – 2.03 (m, 2H), 1.87 – 1.81 (m, 2H), 0.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 136.8, 132.0, 128.2, 126.5, 117.3, 84.4, 83.2, 61.3, 30.3, 29.5, 26.6, 23.7, -0.6; IR (neat): 3404, 2922, 1678, 1602, 1404, 1359,

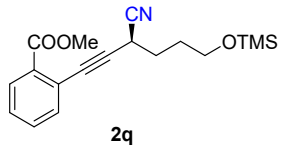
1263, 1180, 1058, 959, 836, 592 cm^{-1}. HRMS: *m/z* (EI) calculated for $C_{18}H_{23}NO_2Si^+$ $[M]^+$: 313.1493, found: 313.1491. HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow 0.7 mL/min, detection at 214 nm) retention time = 21.48 min (major) and 25.57 min (minor).



2p

The reaction was conducted according to the general procedure **A** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) to afford the product **2p** (51.2 mg, 78% yield, 82% *ee*) as colorless oil.

$[\alpha]_D^{27.3}$ -0.75 (*c* 0.60, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 3.92 (s, 3H), 3.87 (t, *J* = 7.2 Hz, 1H), 3.68 (t, *J* = 6.0 Hz, 2H), 2.07 – 2.03 (m, 2H), 1.85 – 1.82 (m, 2H), 0.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 131.7, 130.2, 129.5, 126.3, 117.3, 84.1, 83.3, 61.3, 52.3, 30.3, 29.4, 23.7, -0.6; IR (neat): 3416, 2950, 1716, 1606, 1435, 1405, 1274, 1177, 1108, 1060, 1018, 859, 768, 695, 528 cm^{-1}. HRMS: *m/z* (EI) calculated for $C_{18}H_{23}NSiO_3^+$ $[M]^+$: 329.1442, found: 329.1441. HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 95/5, flow 0.7 mL/min, detection at 214 nm) retention time = 10.01 min (minor) and 11.95 min (major).

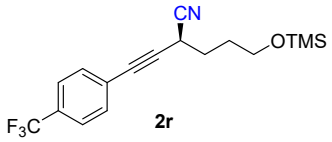


2q

The reaction was conducted according to the general procedure **A** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum dichloromethane/ethyl acetate (20:1) to afford the product **2q** (47.4 mg, 72% yield, 88% ee) as colorless oil.

$[\alpha]_D^{21.6}$ -6.49 (*c* 0.38, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 3.93 – 3.88 (m, 4H), 3.68 (t, *J* = 6.0 Hz, 2H), 2.10 – 2.05 (m, 2H), 1.90 – 1.83 (m, 2H), 0.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 134.2, 132.2, 131.7, 130.5, 128.5, 122.1, 117.6, 86.0, 82.6, 61.3, 52.3, 30.3, 29.4, 23.9, -0.6. IR (neat): 2956, 2243, 1729, 1449, 1294, 1253, 1086, 963, 841, 758, 700, 633 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{18}H_{23}NO_3NaSi^+$ $[M+Na]^+$: 352.1339, found: 352.1332. HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 35.14 min

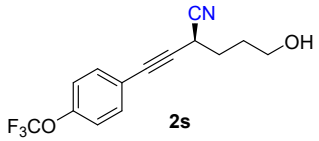
(major) and 40.97 min (minor).



2r

The reaction was conducted according to the general procedure **A** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) to afford the product **2r** (42.7 mg, 63% yield, 81% *ee*) as colorless oil.

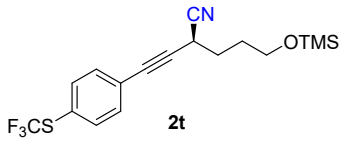
$[\alpha]_D^{28.4}$ +2.10 (*c* 2.10, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 3.88 (t, *J* = 7.2 Hz, 1H), 3.69 (t, *J* = 5.6 Hz, 2H), 2.10 – 2.04 (m, 2H), 1.87 – 1.80 (m, 2H), 0.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1, 130.7 (q, *J* = 31.6 Hz), 125.5, 125.3 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 275.6 Hz), 117.3, 83.7, 82.7, 61.3, 30.3, 29.4, 23.6, -0.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.94 (s). IR (neat): 3383, 2925, 1593, 1563, 1474, 1408, 1059, 881, 785, 681, 440 cm^{-1}. HRMS: *m/z* (EI) calculated for $C_{17}H_{20}NF_3OSi^+$ $[M]^+$: 339.1261, found: 339.1268. HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow 0.7 mL/min, detection at 214 nm) retention time = 7.64 min (major) and 8.35 min (minor).



2s

The reaction was conducted according to the general procedure **B** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to afford the product **2s** (34.0 mg, 60% yield, 84% *ee*) as colorless oil.

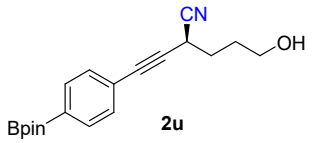
$[\alpha]_D^{28.1}$ +0.12 (*c* 3.30 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 3.87 (t, *J* = 6.8 Hz, 1H), 3.76 (t, *J* = 6.4 Hz, 2H), 2.12 – 2.06 (m, 2H), 1.92 – 1.87 (m, 2H), 1.59 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4 (d, *J* = 1.4 Hz), 133.4, 120.8, 120.4, 120.3 (q, *J* = 256.4 Hz), 117.3, 82.8, 81.9, 61.6, 30.1, 29.4, 23.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.86 (s). IR (neat): 3378, 2930, 1507, 1251, 1203, 1159, 1060, 922, 851, 669, 539 cm^{-1}. HRMS: *m/z* (EI) calculated for $C_{14}H_{12}NF_3O_2^+$ $[M]^+$: 283.0815, found: 283.0814. HPLC (AD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 80/20, flow 0.7 mL/min, detection at 214 nm) retention time = 32.75 min (major) and 36.33 min (minor).



2t

The reaction was conducted according to the general procedure **A** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) to afford the product **2t** (49.8 mg, 67% yield, 86% *ee*) as yellow oil.

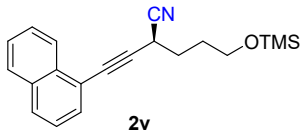
$[\alpha]_D^{28.4}$ -4.56 (*c* 1.61 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 3.87 (t, *J* = 6.8 Hz, 1H), 3.68 (t, *J* = 6.8 Hz, 2H), 2.09 – 2.03 (m, 2H), 1.87 – 1.81 (m, 2H), 0.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 132.7, 129.3 (q, *J* = 309.0 Hz), 125.2 (q, *J* = 1.6 Hz), 124.6, 117.3, 84.0, 82.8, 61.3, 30.4, 29.5, 23.7, -0.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -42.42 (s). IR (neat): 3360, 2927, 1593, 1493, 1110, 1082, 1015, 854, 755, 566, 520 cm^{-1}. HRMS: *m/z* (EI) calculated for $C_{17}H_{20}NSF_3OSi^+$ $[M]^+$:2371.0981, found: 371.0975. HPLC (OJ-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow 0.7 mL/min, detection at 214 nm) retention time = 17.08 min (major) and 22.83 min (minor).



2u

The reaction was conducted according to the general procedure **B** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to afford the product **2u** (30.7 mg, 47% yield, 87% *ee*) as colorless oil.

$[\alpha]_D^{26.9}$ +4.43 (*c* 0.35 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 3.87 (t, *J* = 6.8 Hz, 1H), 3.77 (t, *J* = 6.4 Hz, 2H), 2.12 – 2.06 (m, 2H), 1.93 – 1.88 (m, 2H), 1.34 (s, 12H), 1.25 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.6, 130.9, 124.2, 117.5, 84.3, 84.0, 82.1, 61.7, 30.1, 29.4, 24.9, 23.7. IR (neat): 3378, 2923, 1608, 1397, 1358, 1322, 1260, 1142, 1088, 1020, 962, 856, 800, 739, 653 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{19}H_{25}BNO_3^+$ $[M+H]^+$: 326.1922, found: 326.1914. HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 80/20, flow 0.7 mL/min, detection at 214 nm) retention time = 9.76 min (major) and 11.95 min (minor).

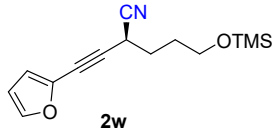


2v

The reaction was conducted according to the general procedure **A** on a 0.2 mmol scale. The

residue was purified by column chromatography on silica gel with petroleum dichloromethane/ethyl acetate (20:1) to afford the product **2v** (34.6 mg, 54% yield, 90% ee) as colorless oil.

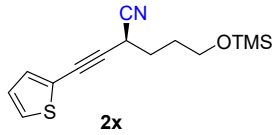
$[\alpha]_D^{22.8}$ -9.88 (*c* 0.25, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.45 – 7.41 (m, 1H), 4.02 (t, *J* = 7.2 Hz, 1H), 3.73 (t, *J* = 6.0 Hz, 2H), 2.19 – 2.14 (m, 2H), 1.96 – 1.89 (m, 2H), 0.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.2, 133.0, 130.9, 129.4, 128.3, 127.0, 126.5, 125.7, 125.1, 119.3, 117.7, 85.9, 82.3, 61.4, 30.6, 29.6, 23.9, -0.6. IR (neat): 2959, 2246, 1396, 1251, 1098, 841, 800, 774, 634 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{20}H_{24}NOSi^+$ $[M+H]^+$: 322.1622, found: 322.1613. HPLC (OJ-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 29.48 min (minor) and 33.55 min (major).



2w

The reaction was conducted according to the general procedure **B** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) to afford the product **2w** (18.3 mg, 34% yield, 85% *ee*) as light yellow oil.

$[\alpha]_D^{28.7}$ +4.03 (*c* 2.50 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 0.4 Hz, 1H), 6.62 (d, *J* = 3.2 Hz, 1H), 6.40 – 6.38 (m, 1H), 3.88 (t, *J* = 7.2 Hz, 1H), 3.67 (t, *J* = 5.6 Hz, 2H), 2.08 – 2.02 (m, 2H), 1.85 – 1.80 (m, 2H), 0.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 135.8, 117.0, 116.2, 110.9, 85.6, 74.6, 61.3, 30.2, 29.4, 23.7, -0.6. IR (neat): 3371, 2926, 1633, 1573, 1483, 1452, 1321, 1214, 1060, 1020, 930, 886, 819, 746, 592 cm^{-1}. HRMS: *m/z* (EI) calculated for $C_{14}H_{19}NSiO_2^+$ $[M]^+$: 261.1180, found: 261.1175. HPLC (OJ-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 14.68 min (major) and 16.25 min (minor).

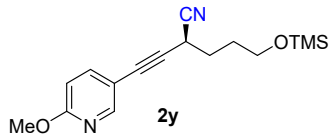


2x

The reaction was conducted according to the general procedure **A** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) to afford the product **2x** (22.6 mg, 41% yield, 91% *ee*) as yellow oil.

$[\alpha]_D^{28.0}$ -1.14 (*c* 0.16 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 1H), 7.24 – 7.23

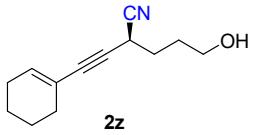
(m, 1H), 6.99 – 6.97 (m, 1H), 3.87 (t, *J* = 6.8 Hz, 1H), 3.68 (t, *J* = 5.6 Hz, 2H), 2.07 – 2.02 (m, 2H), 1.86 – 1.80 (m, 2H), 0.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.8, 127.7, 127.0, 121.5, 117.3, 85.0, 77.5, 61.3, 30.3, 29.4, 23.9, -0.6. IR (neat): 3370, 2922, 2853, 1606, 1452, 1376, 1258, 1053, 795, 755, 700, 492 cm^{-1}. HRMS: *m/z* (EI) calculated for $C_{14}H_{19}NSOSi^+$ $[M]^+$: 277.0951, found: 277.0950; HPLC (OJ-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 14.57 min (major) and 15.53 min (minor).



2y

The reaction was conducted according to the general procedure A on a 0.2 mmolscale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) to afford the product **2y** (33.8 mg, 56% yield, 84% *ee*) as light yellow oil.

$[\alpha]_D^{24.4}$ +4.46 (*c* 1.95 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 1.2 Hz, 1H), 7.59 – 7.56 (m, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 3.93 (s, 3H), 3.84 (t, *J* = 7.2 Hz, 1H), 3.67 (t, *J* = 6.0 Hz, 2H), 2.06 – 2.00 (m, 2H), 1.85 – 1.78 (m, 2H), 0.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 150.4, 141.2, 117.5, 110.7, 82.6, 81.0, 61.3, 53.7, 30.3, 29.4, 23.6, -0.6. IR (neat): 2243, 1601, 1492, 1372, 1286, 1252, 1094, 1026, 838, 752 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{16}H_{23}N_2SiO_2^+$ $[M]^+$: 303.1523, found: 303.1517. HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 16.64 min (minor) and 28.06 min (major).

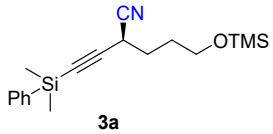


2z

The reaction was conducted according to the general procedure **B** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to afford the product **2z** (21.7 mg, 53% yield, 83% *ee*) as colorless oil.

$[\alpha]_D^{27.5}$ +2.21 (*c* 0.16 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (t, *J* = 1.6 Hz, 1H), 3.73 (t, *J* = 6.4 Hz, 3H), 2.09 – 2.07 (m, 4H), 2.02 – 1.96 (m, 2H), 1.86 – 1.83 (m, 2H), 1.63 – 1.54 (m, 4H), 1.51 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 119.5, 117.9, 86.0, 78.1, 61.7, 30.2, 29.4, 28.8, 25.6, 23.5, 22.1, 21.3. IR (neat): 3374, 2928, 2860, 1704, 1435, 1320, 1268, 1059, 919, 844, 800, 736, 523 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{13}H_{18}NO^+$ $[M+H]^+$: 204.1383, found: 204.1382;

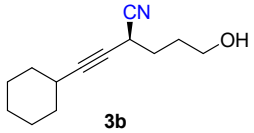
HPLC (OJ-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 90/10, flow 0.7 mL/min, detection at 214 nm) retention time = 45.50 min (major) and 48.07 min (minor).



3a

The reaction was conducted according to the general procedure **A** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) to afford the product **3a** (44.8 mg, 68% yield, 81% *ee*) as colorless oil.

$[\alpha]_D^{26.1}$ -1.23 (*c* 1.06 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 2H), 7.40 – 7.37 (m, 3H), 3.69 (t, *J* = 6.8 Hz, 1H), 3.66 (t, *J* = 6.0 Hz, 2H), 2.01 – 1.96 (m, 2H), 1.82 – 1.77 (m, 2H), 0.44 (s, 6H), 0.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0, 133.6, 129.6, 127.9, 117.3, 98.6, 87.6, 61.3, 30.3, 29.4, 23.9, -0.6, -1.2. IR (neat): 3374, 2923, 1931, 1428, 1251, 1114, 1055, 816, 782, 732, 700, 470, 438 cm^{-1}. HRMS: *m/z* (EI) calculated for $C_{18}H_{27}NOSi_2^+$ $[M]^+$: 329.1626, found: 329.1622; HPLC (OD-H, 0.46*25 cm, 5 μm, hexane/isopropanol = 99/1, flow 0.7 mL/min, detection at 214 nm) retention time = 23.87 min (major) and 28.35 min (minor).



3b

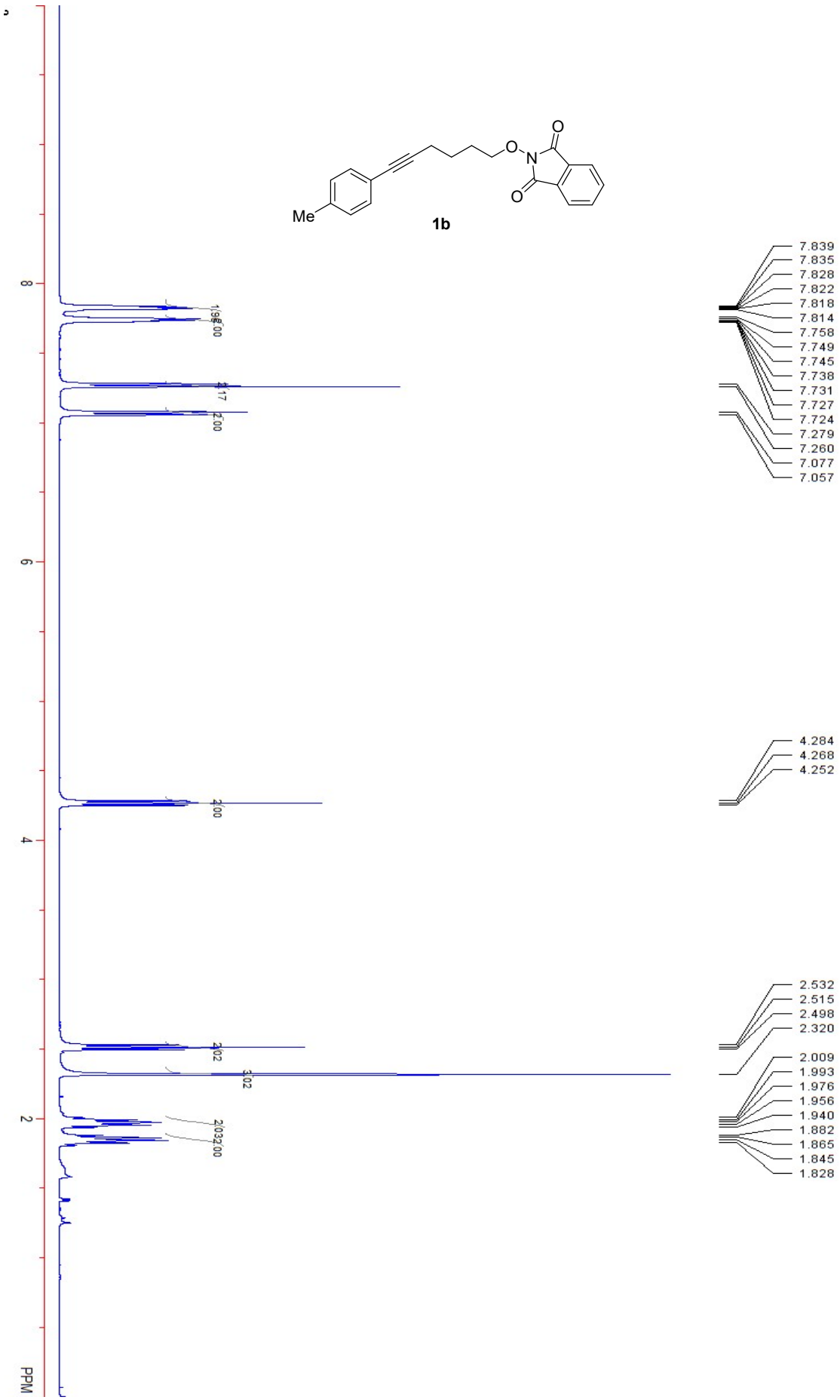
The reaction was conducted according to the general procedure **B** on a 0.2 mmol scale. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) to afford the product **3b** (32.0 mg, 78% yield, 66% *ee*) as colorless oil.

$[\alpha]_D^{26.7}$ +0.88 (*c* 1.00 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 3.71 (t, *J* = 6.0 Hz, 2H), 3.59 (dt, *J* = 6.8, 2.0 Hz, 1H), 2.38 – 2.34 (m, 1H), 1.97 – 1.91 (m, 2H), 1.84 – 1.74 (m, 4H), 1.53 – 1.49 (m, 2H), 1.66 (br, 1H), 1.44 – 1.37 (m, 2H), 1.31 – 1.27 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.3, 89.0, 71.9, 61.7, 32.3, 30.2, 29.4, 28.8, 25.7, 24.7, 23.0. IR (neat): 3381, 2928, 2854, 2246, 1718, 1448, 1320, 1058, 935, 889, 798 cm^{-1}. HRMS: *m/z* (ESI) calculated for $C_{13}H_{20}NO^+$ $[M+H]^+$: 206.1539, found: 206.1538; Chiral GC (CP, Chiral-DEX CB Varian, 25 m*0.25 mm, 0.25 μm film thickness, nitrogen (10.0 pis) was used as the carrier gas. Colum oven: T = 50 ℃, kept for 2 min, then heated (3 ℃/min) to 150 ℃, kept for 10 mins, detected by FID) retention time = 35.83 min (miajor) and 36.12 min (minor).

7. References

[1] Xu, X.; Liu, Y.; Park, C.-M. *Angew. Chem. Int. Ed.* **2012**, *51*, 9372.
[2] Pavlishchuk, V. V.; Addison, A. W. *Inorganica Chimica Acta*, **2000**, *298*, 97.

8. NMR Spectra of the New Compound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7.077
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6
4
2
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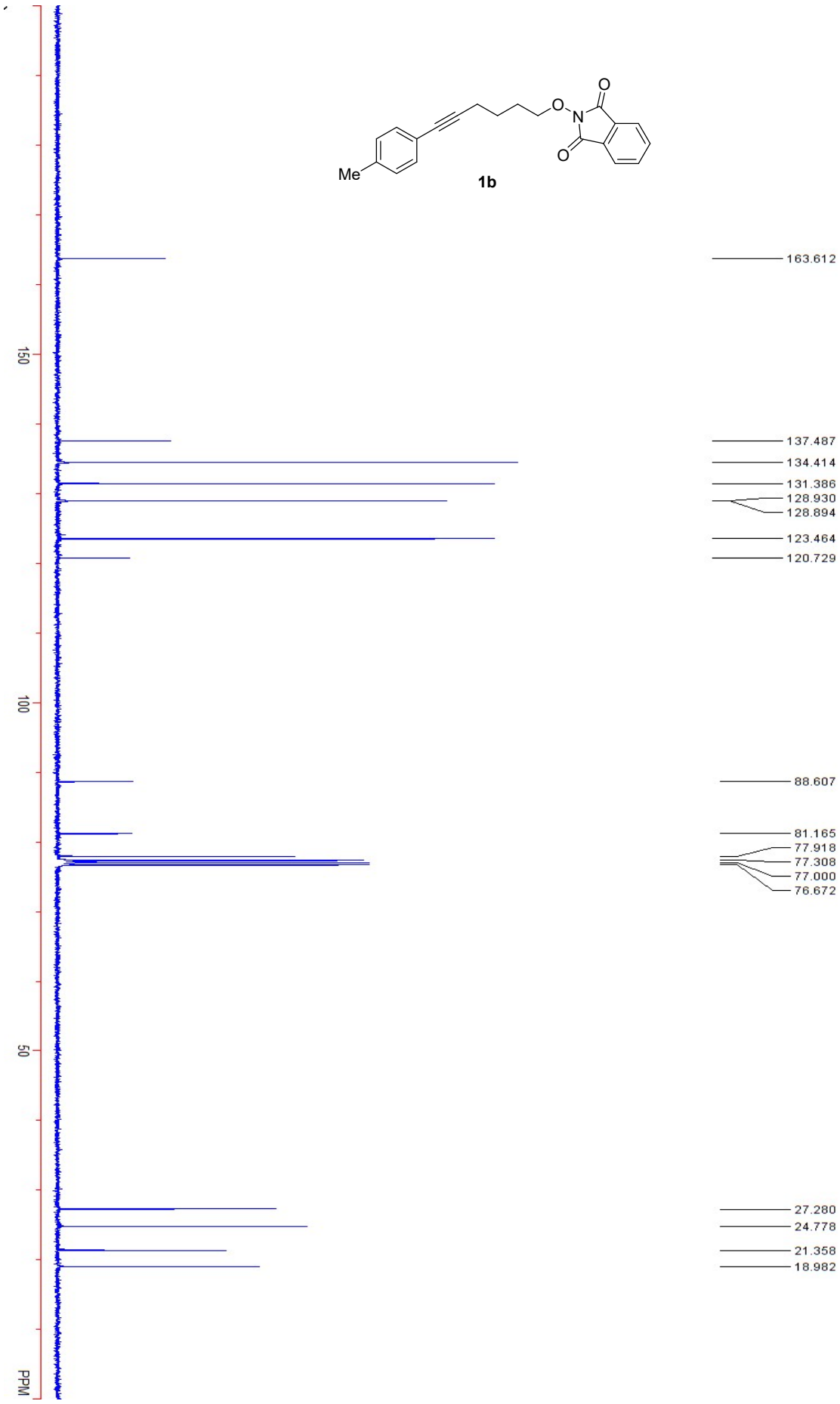
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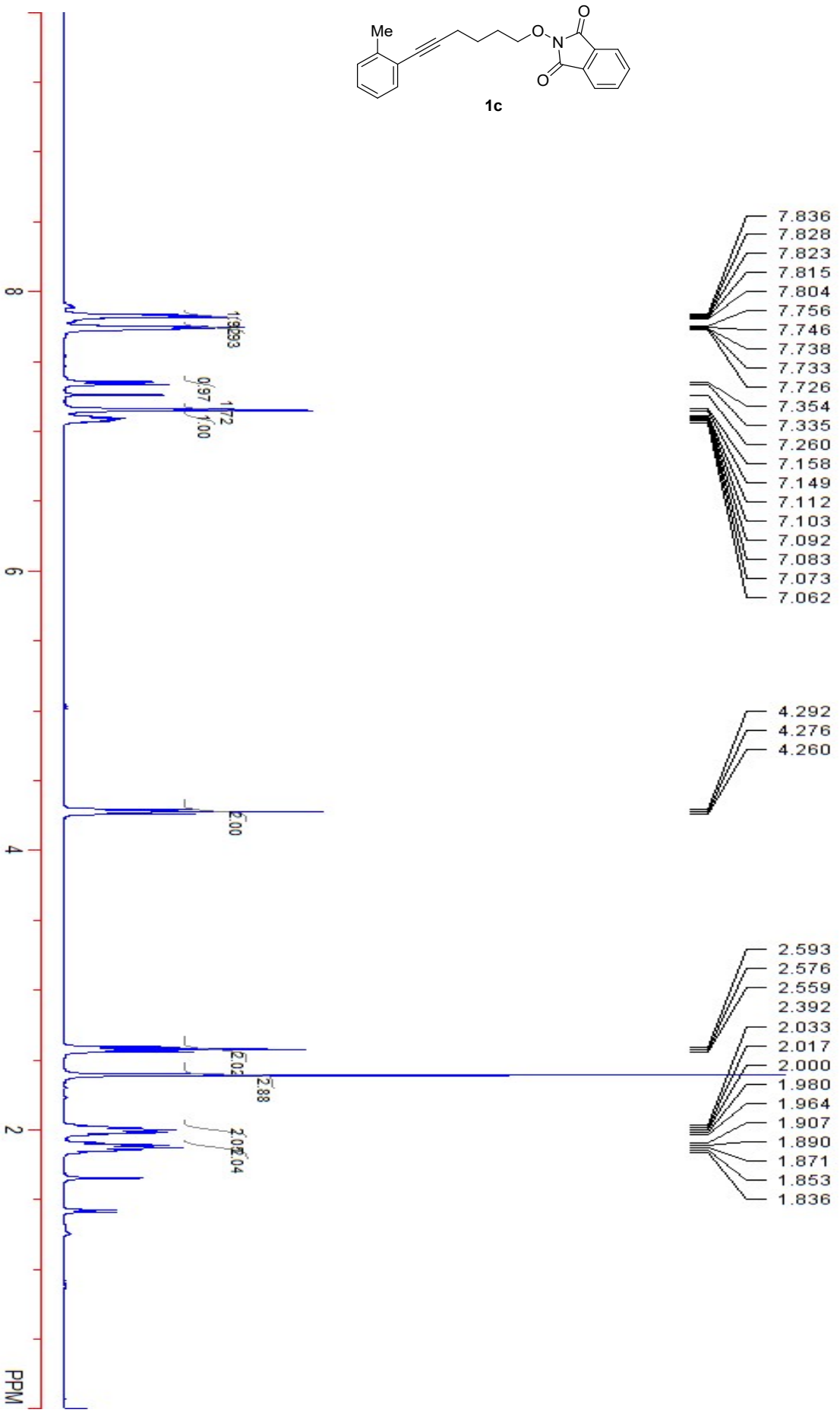
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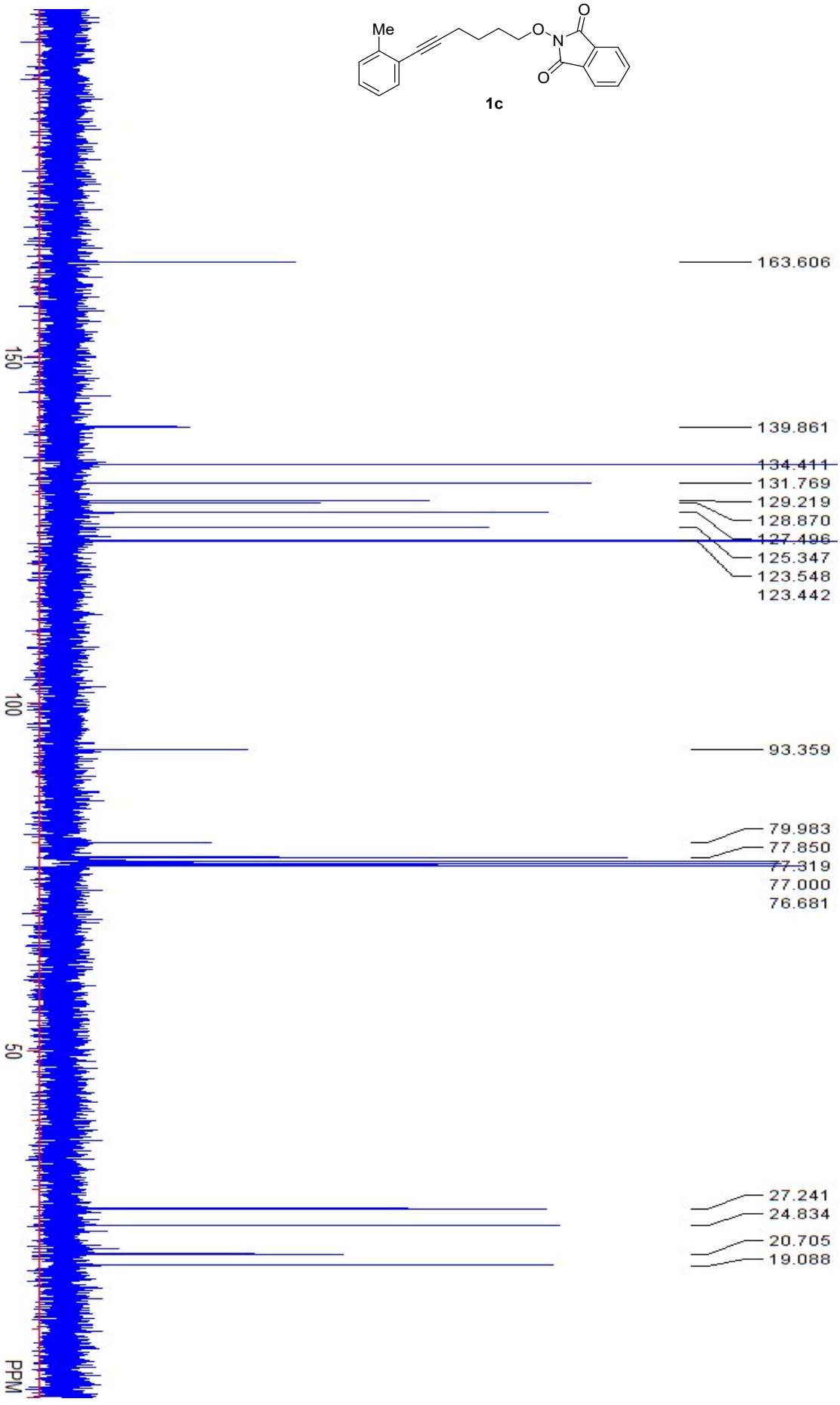
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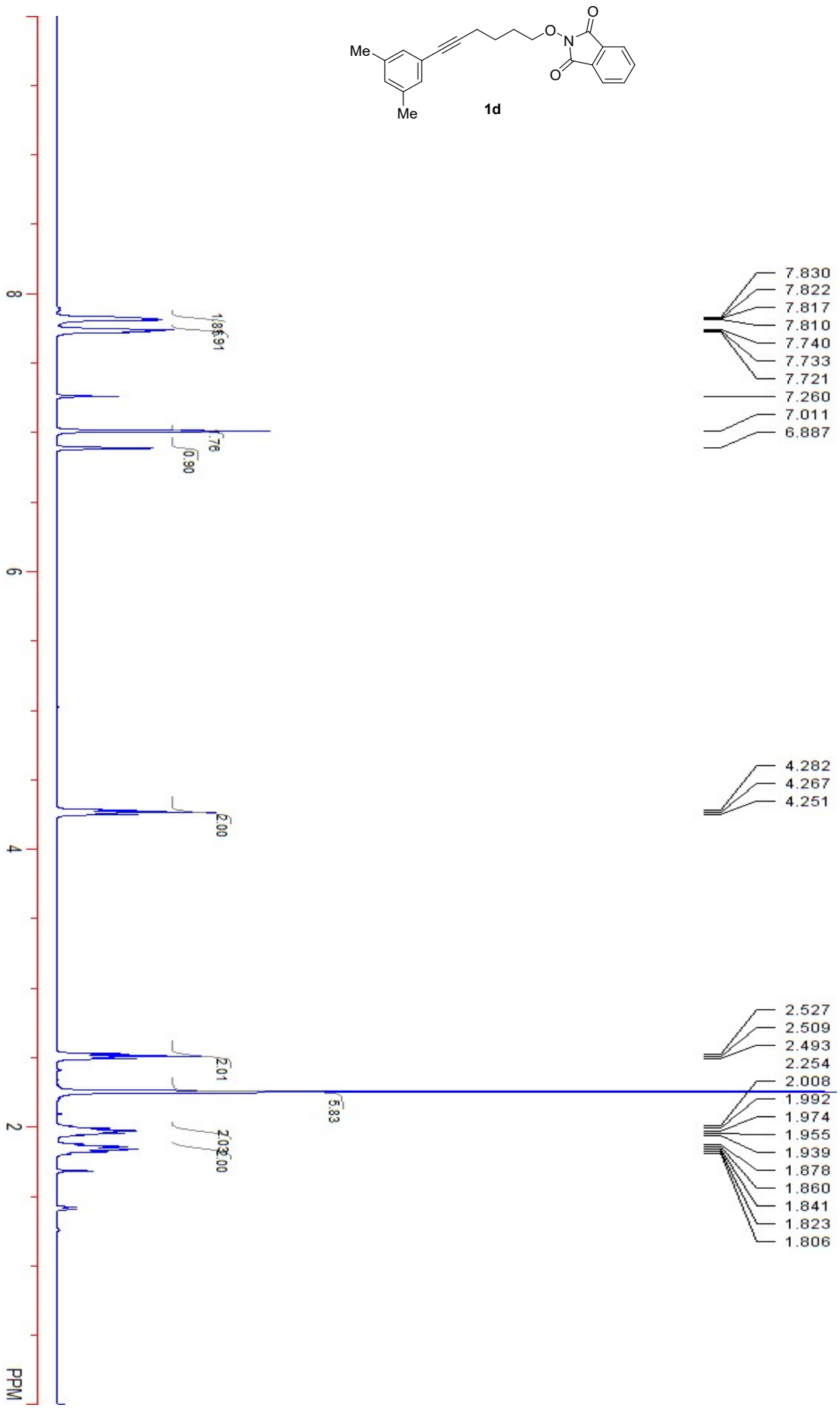
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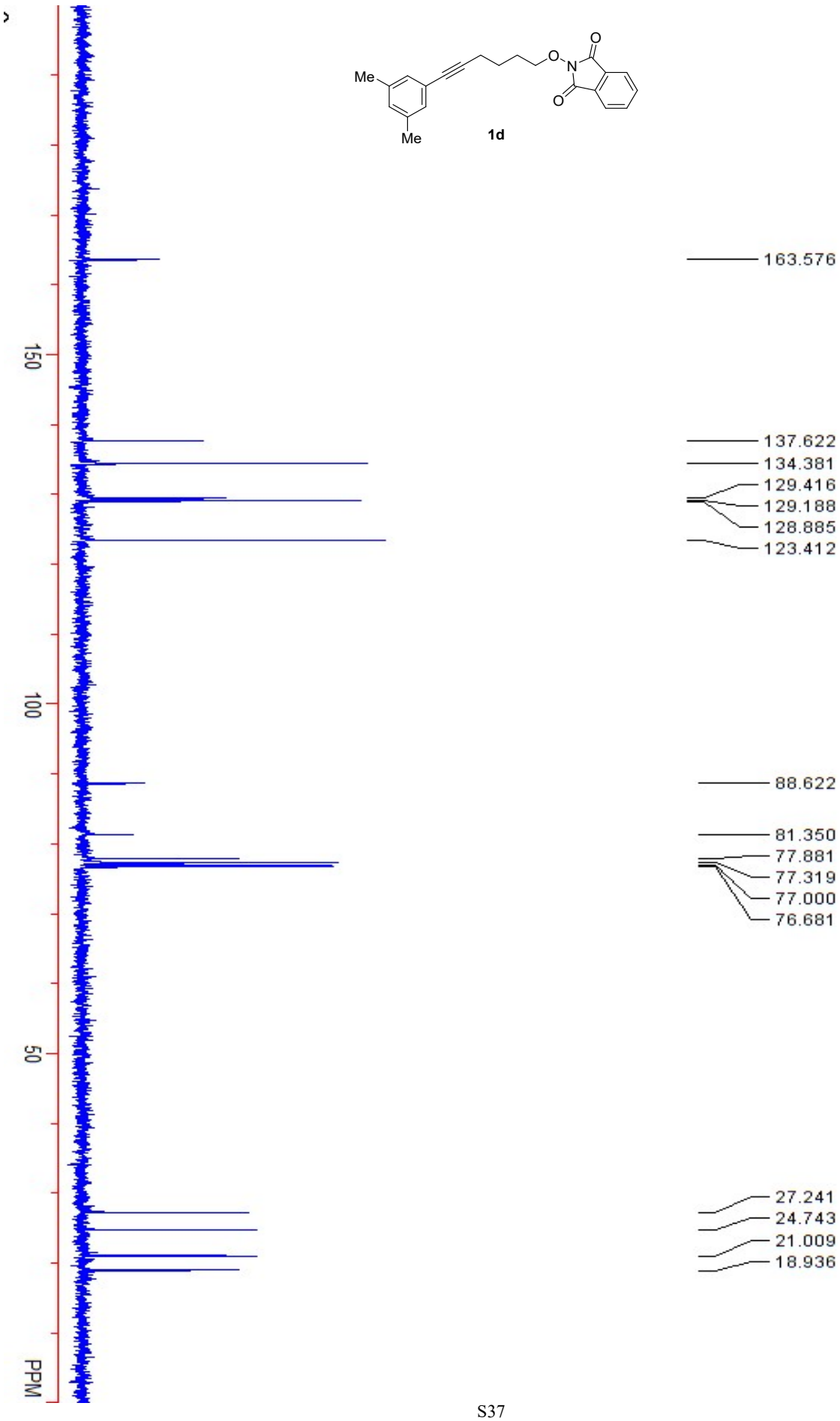
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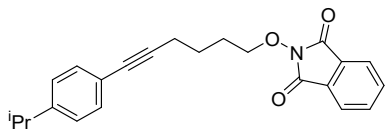
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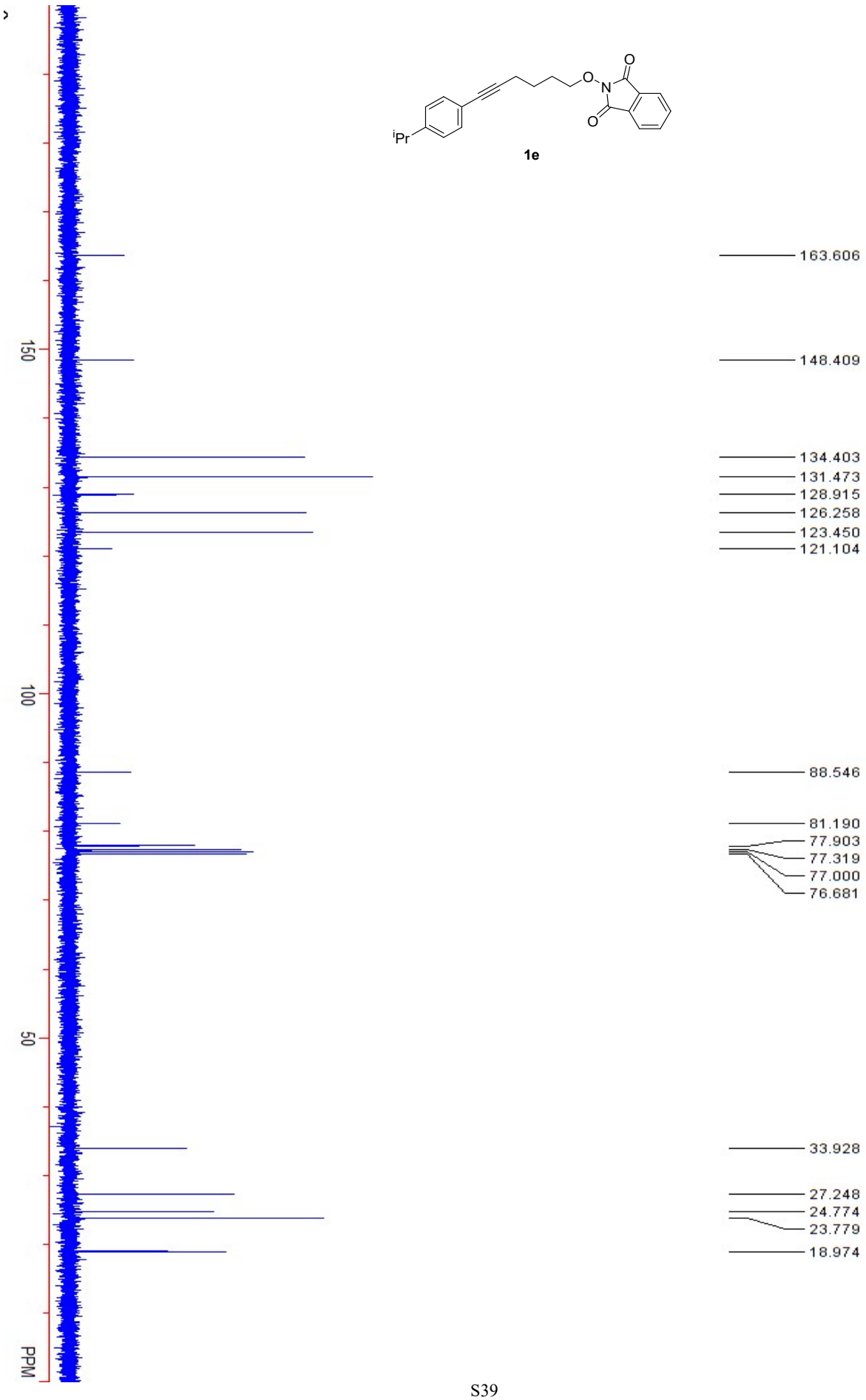
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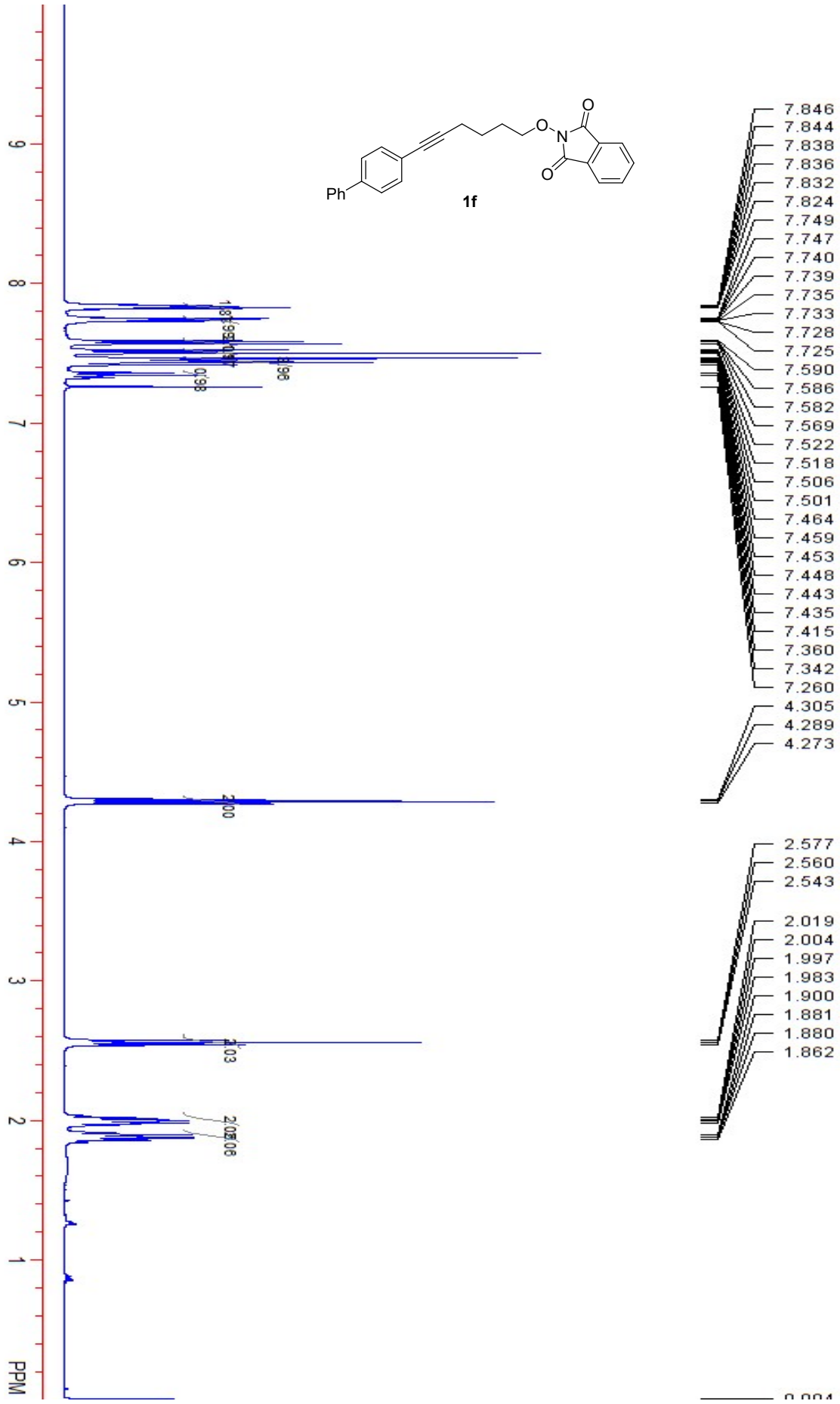
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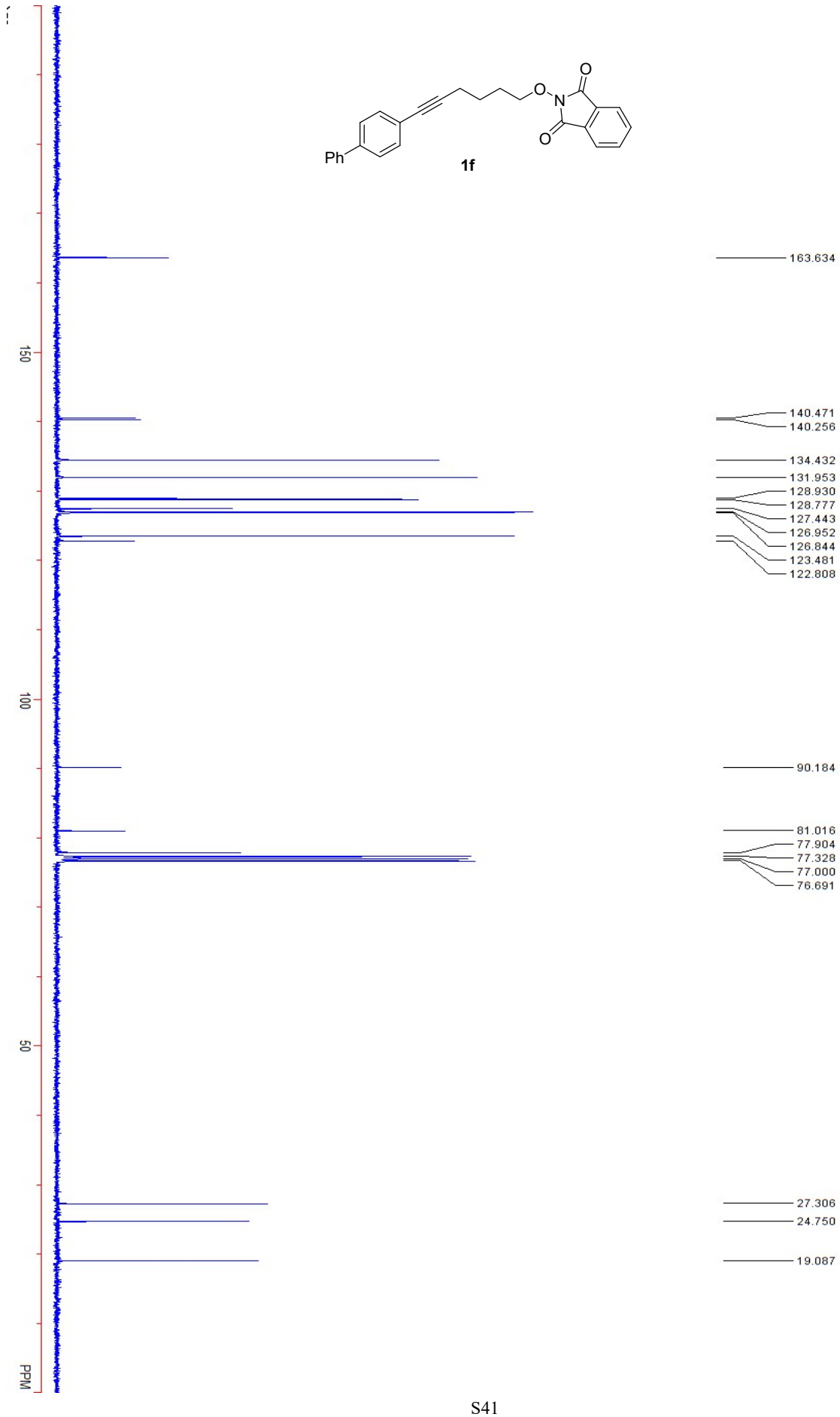
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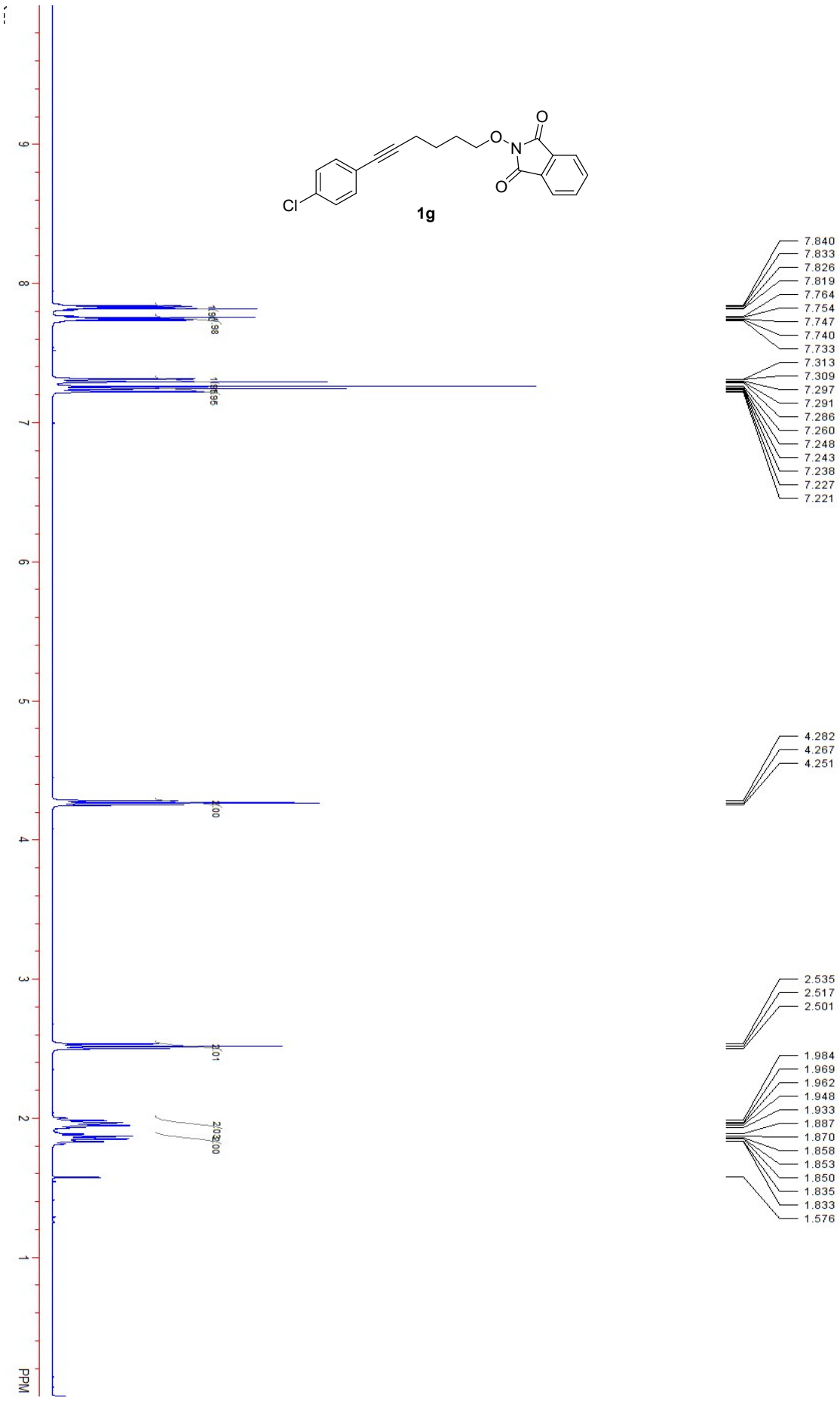
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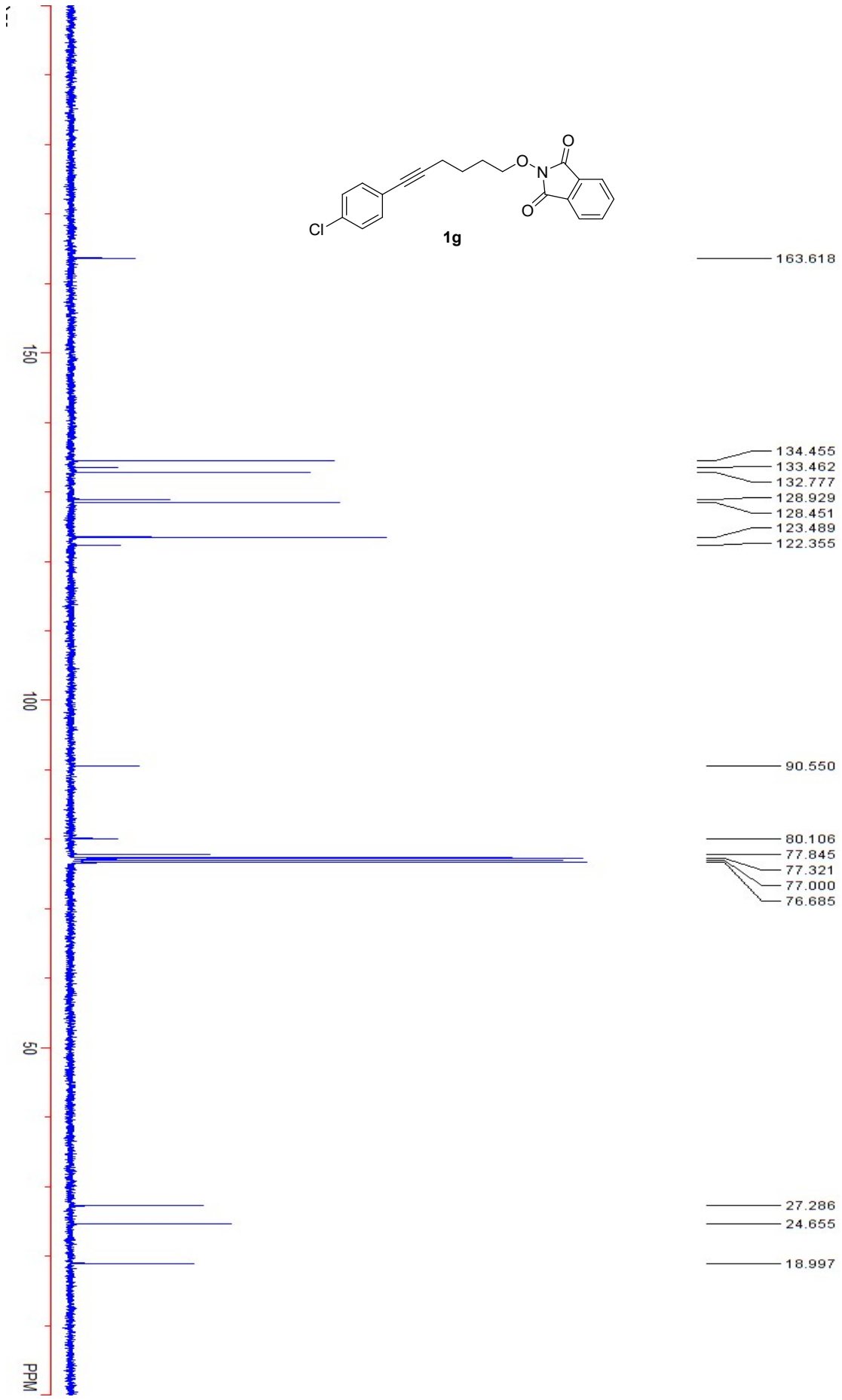
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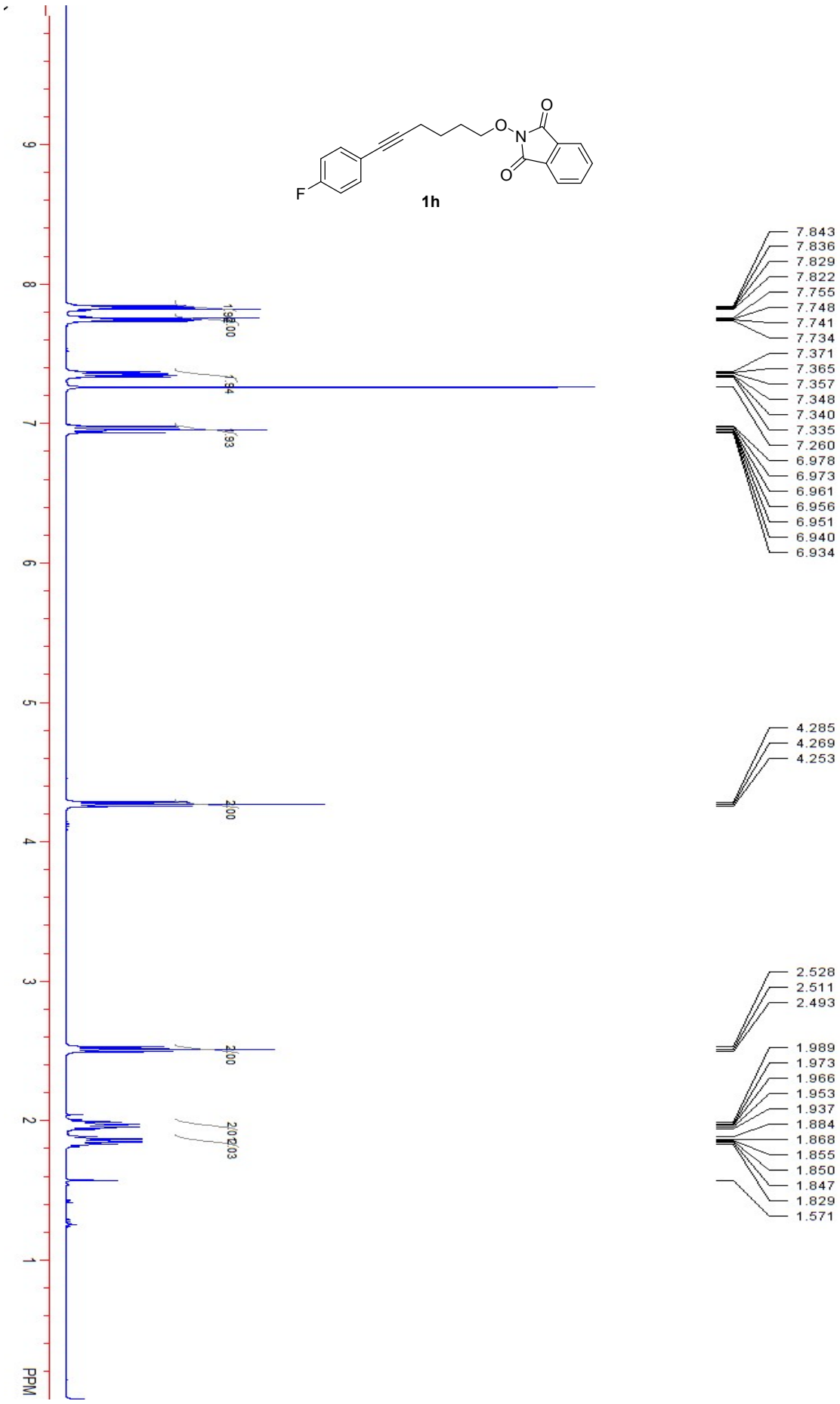
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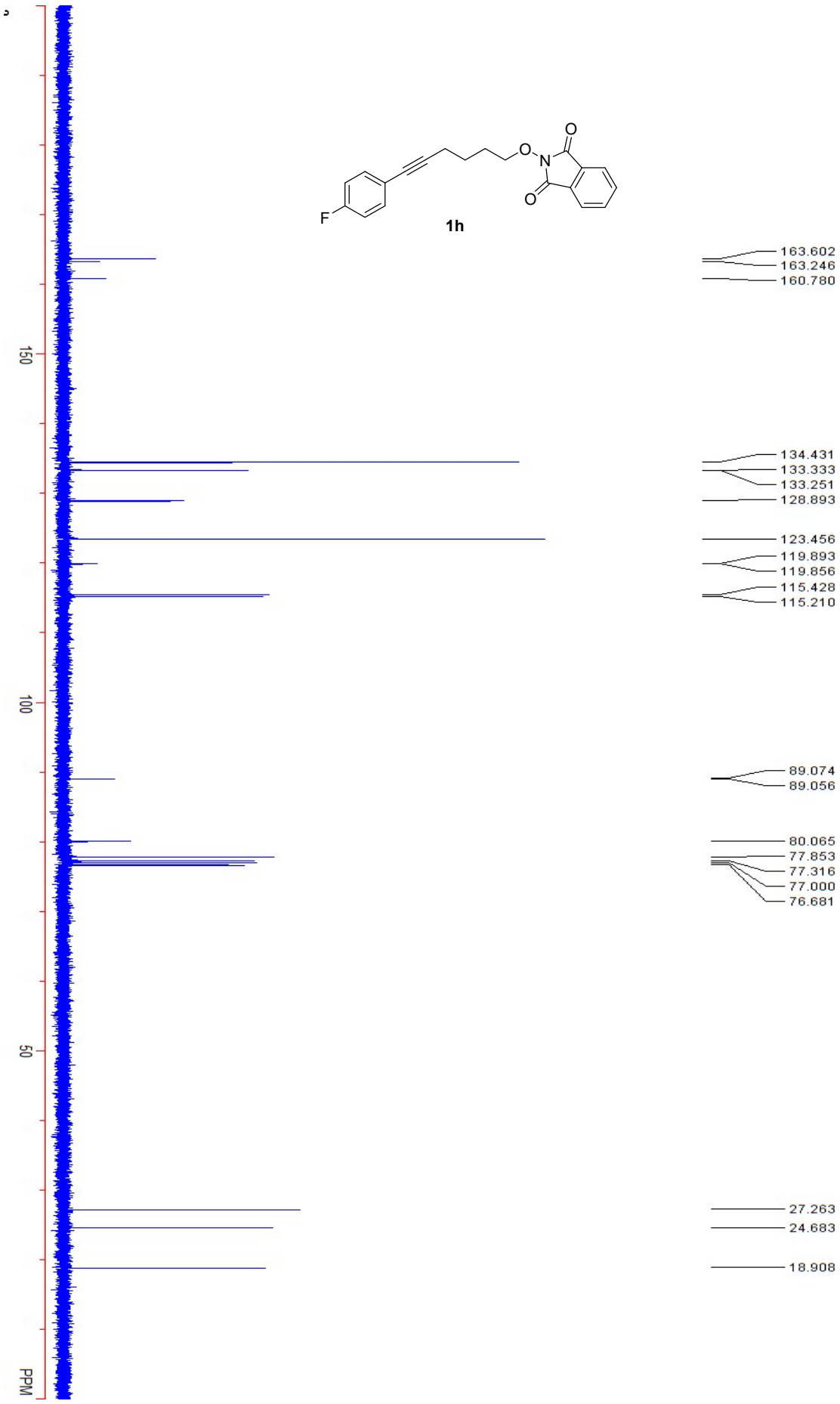
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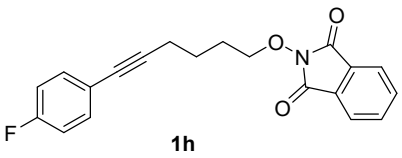
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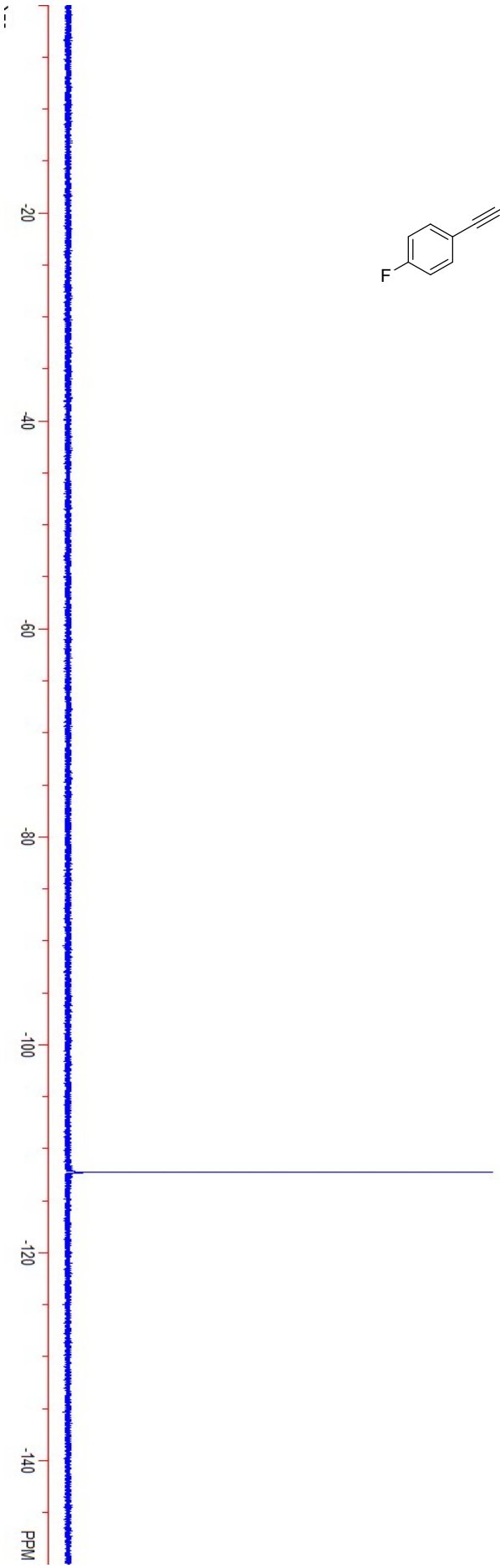
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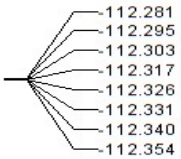
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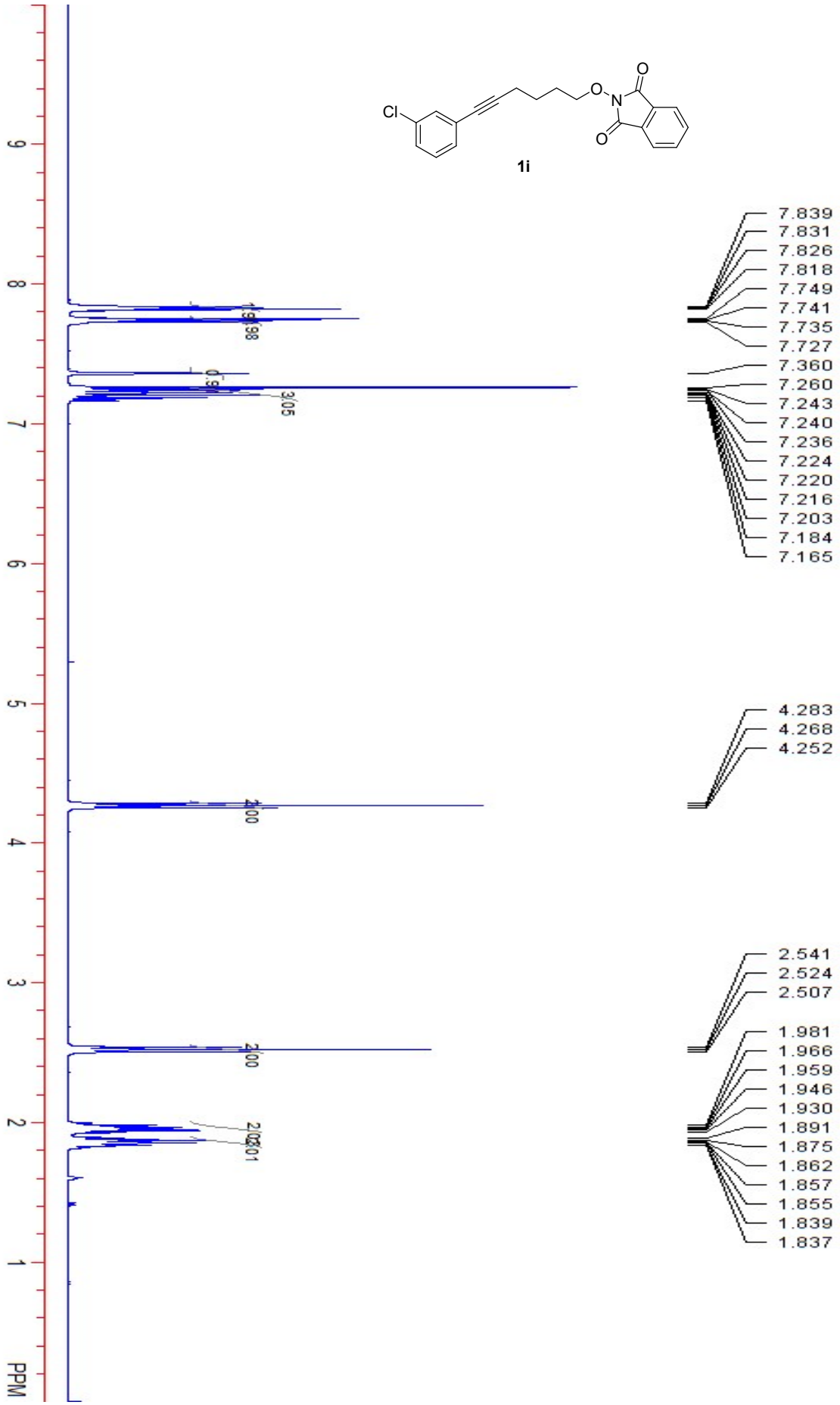
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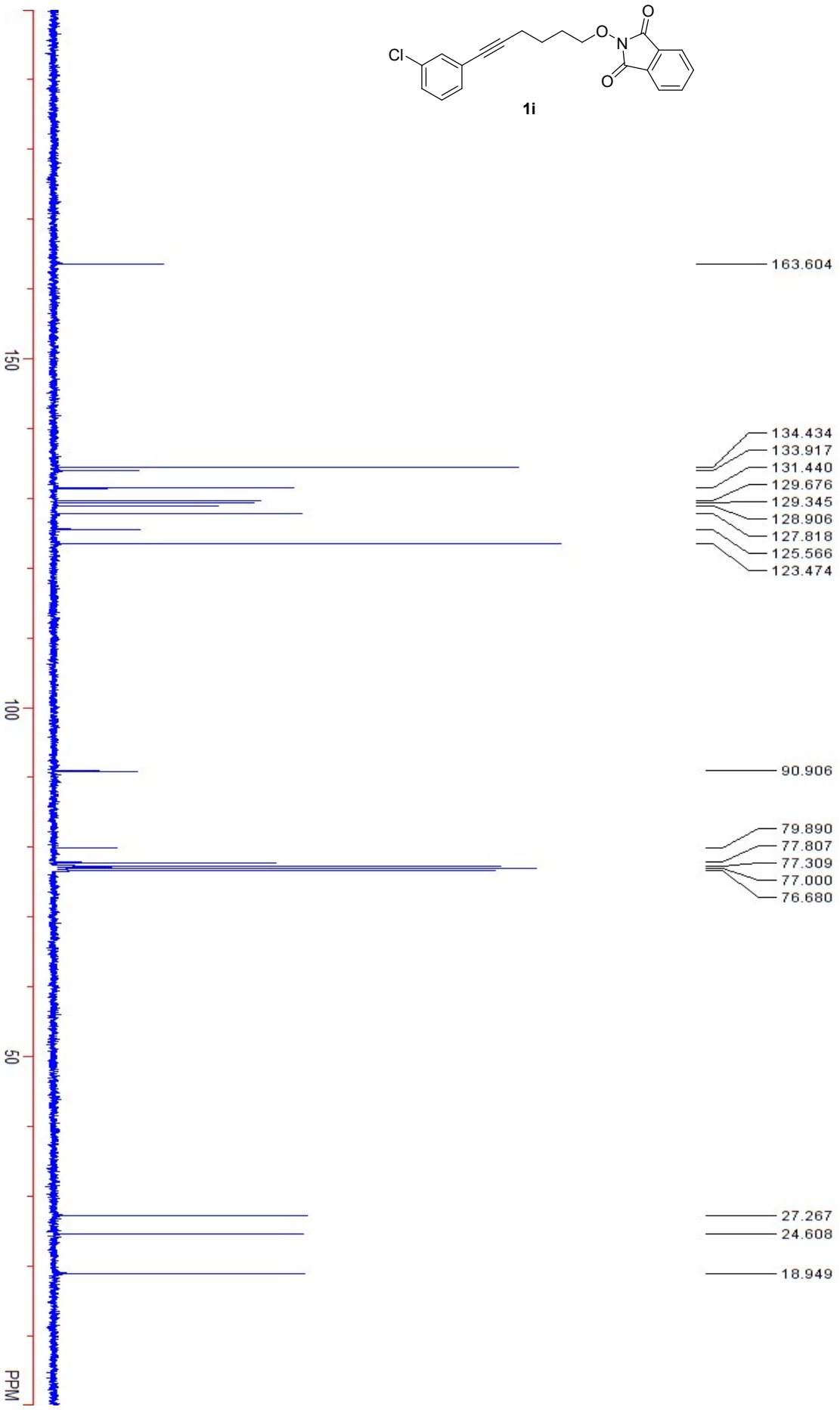
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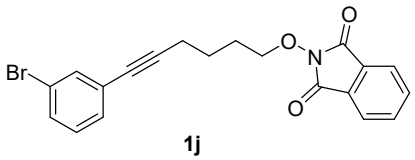
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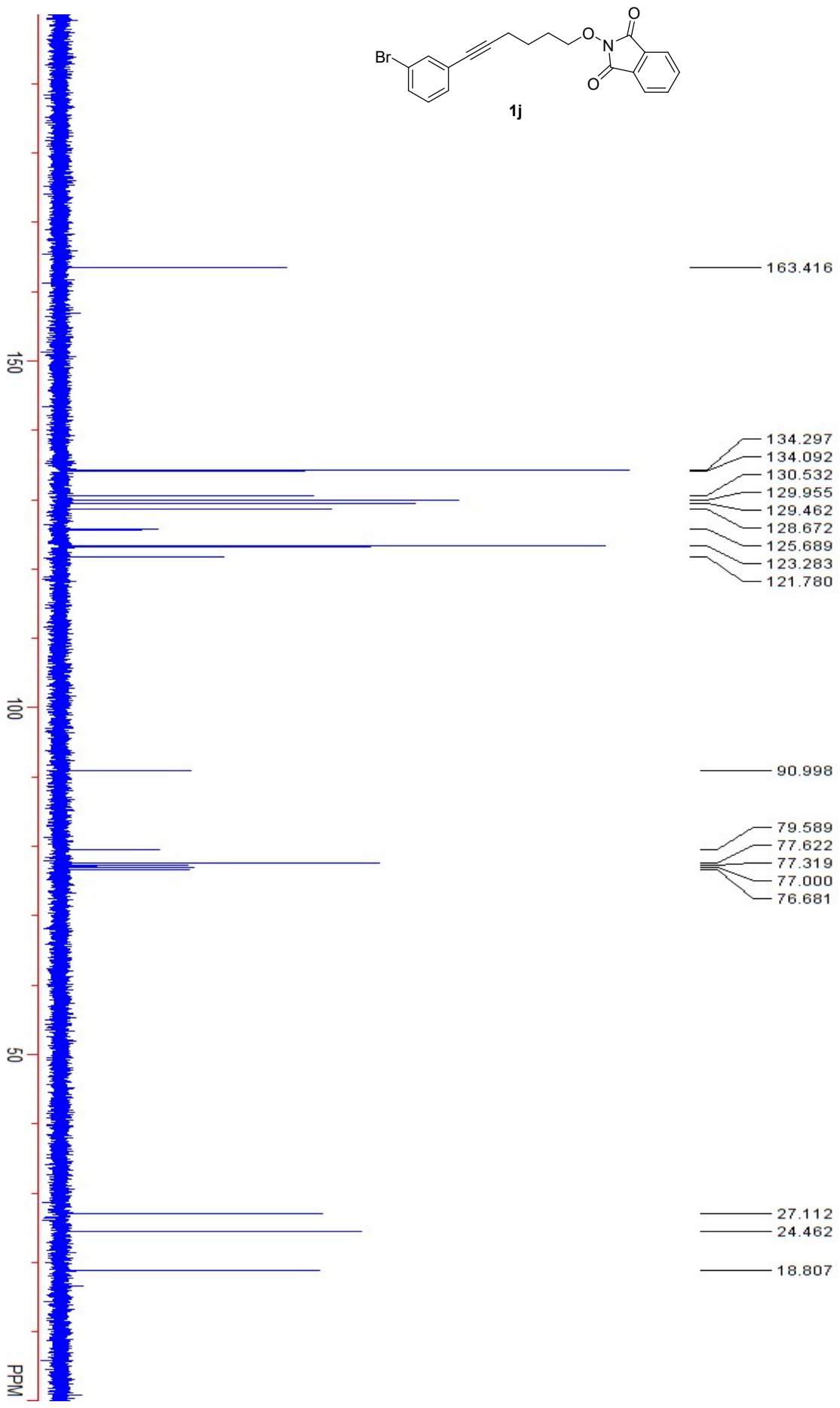
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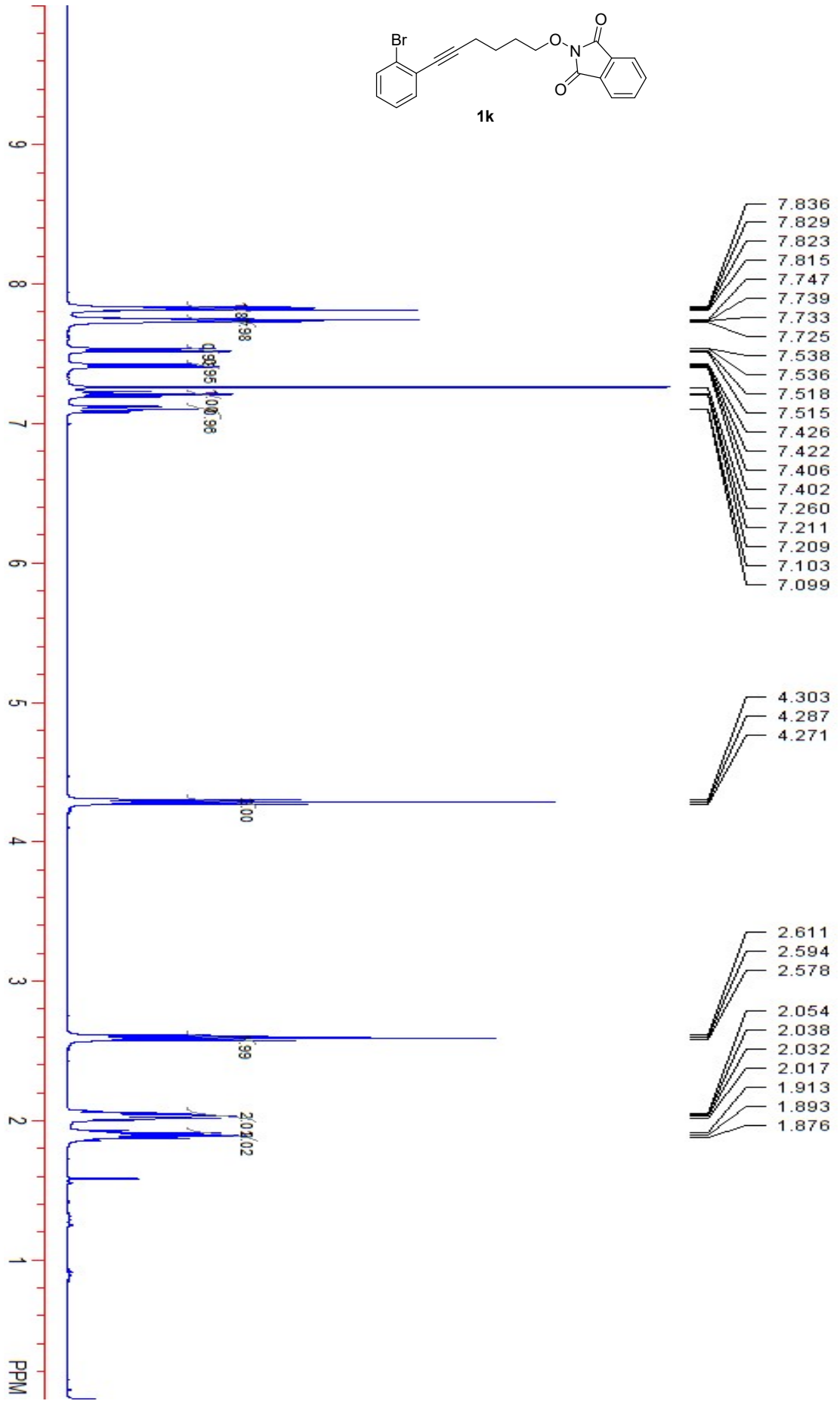
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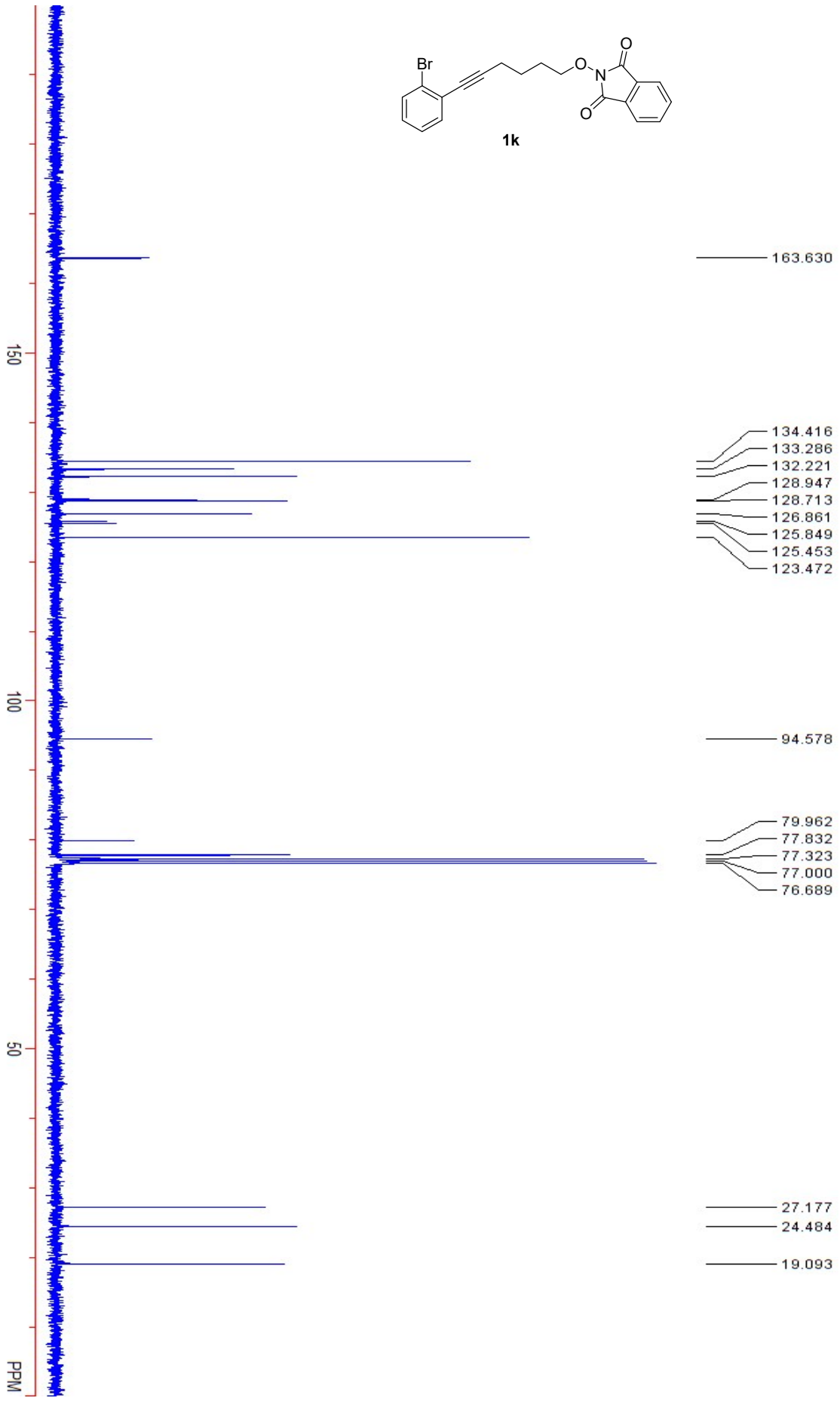
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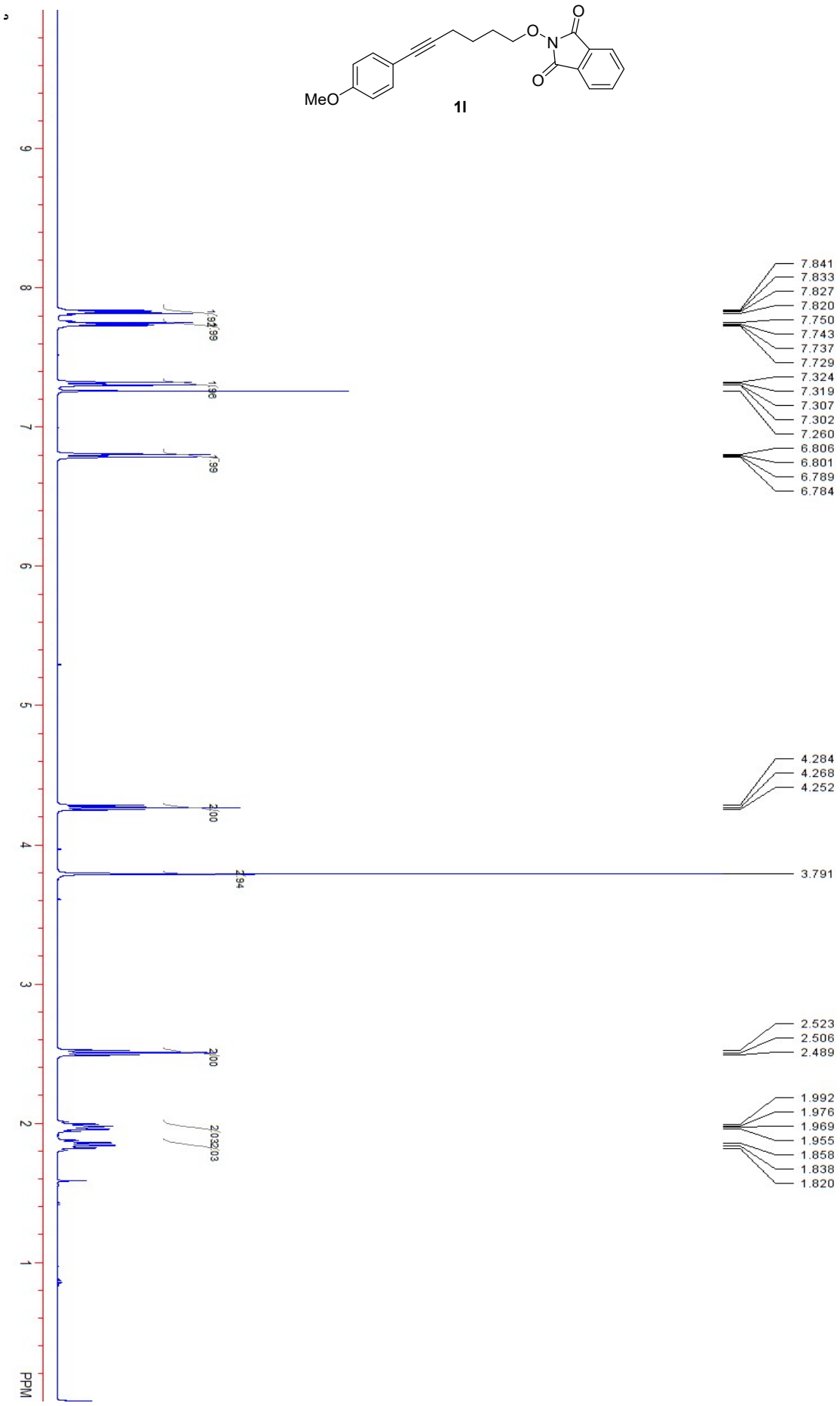
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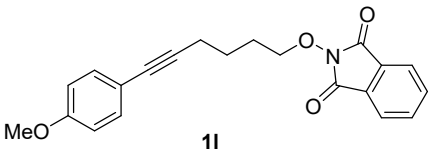
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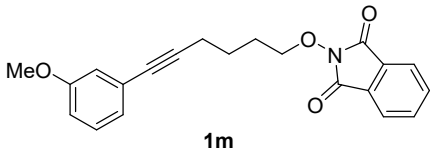
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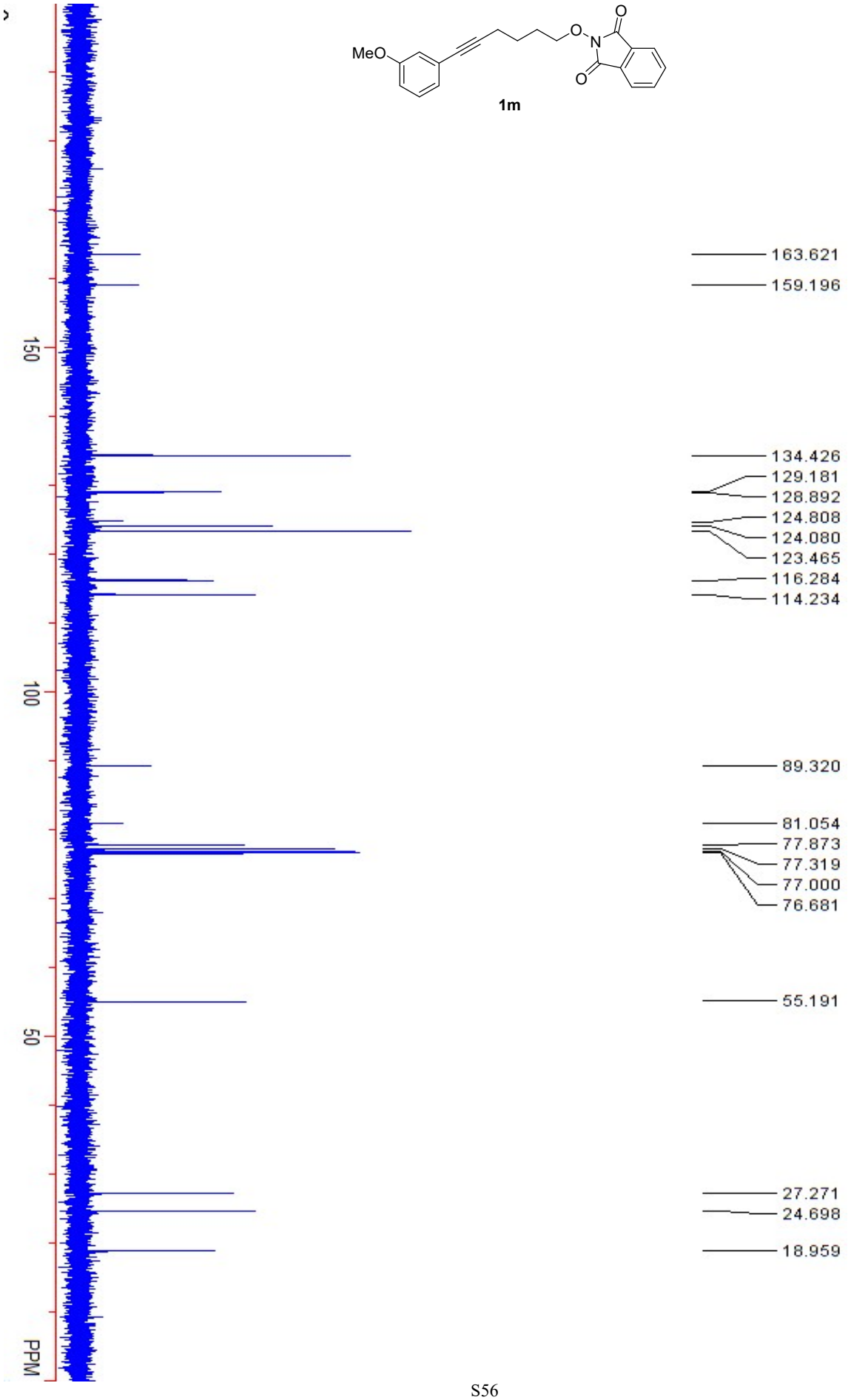
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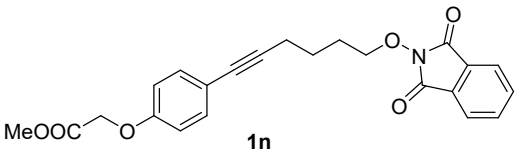
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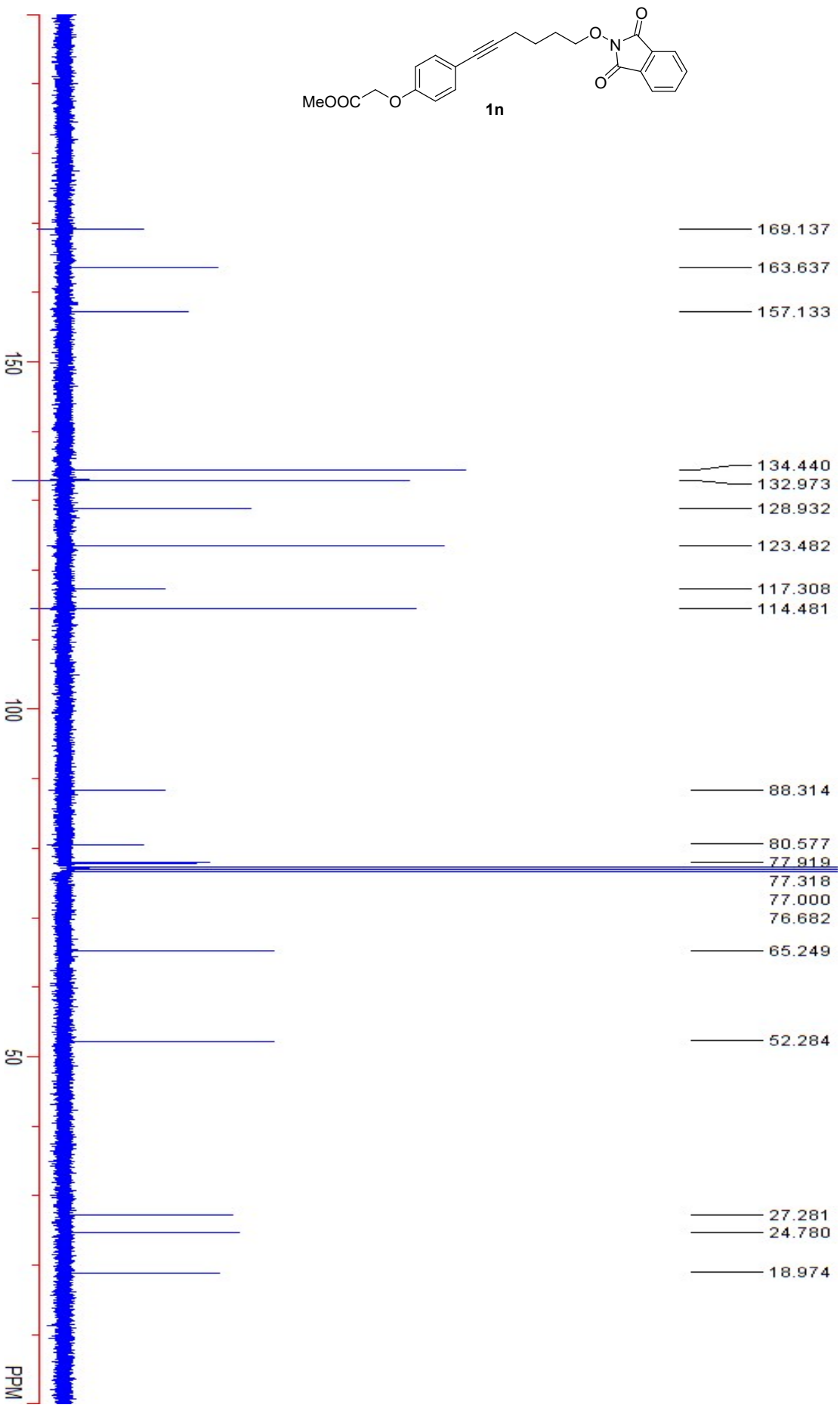
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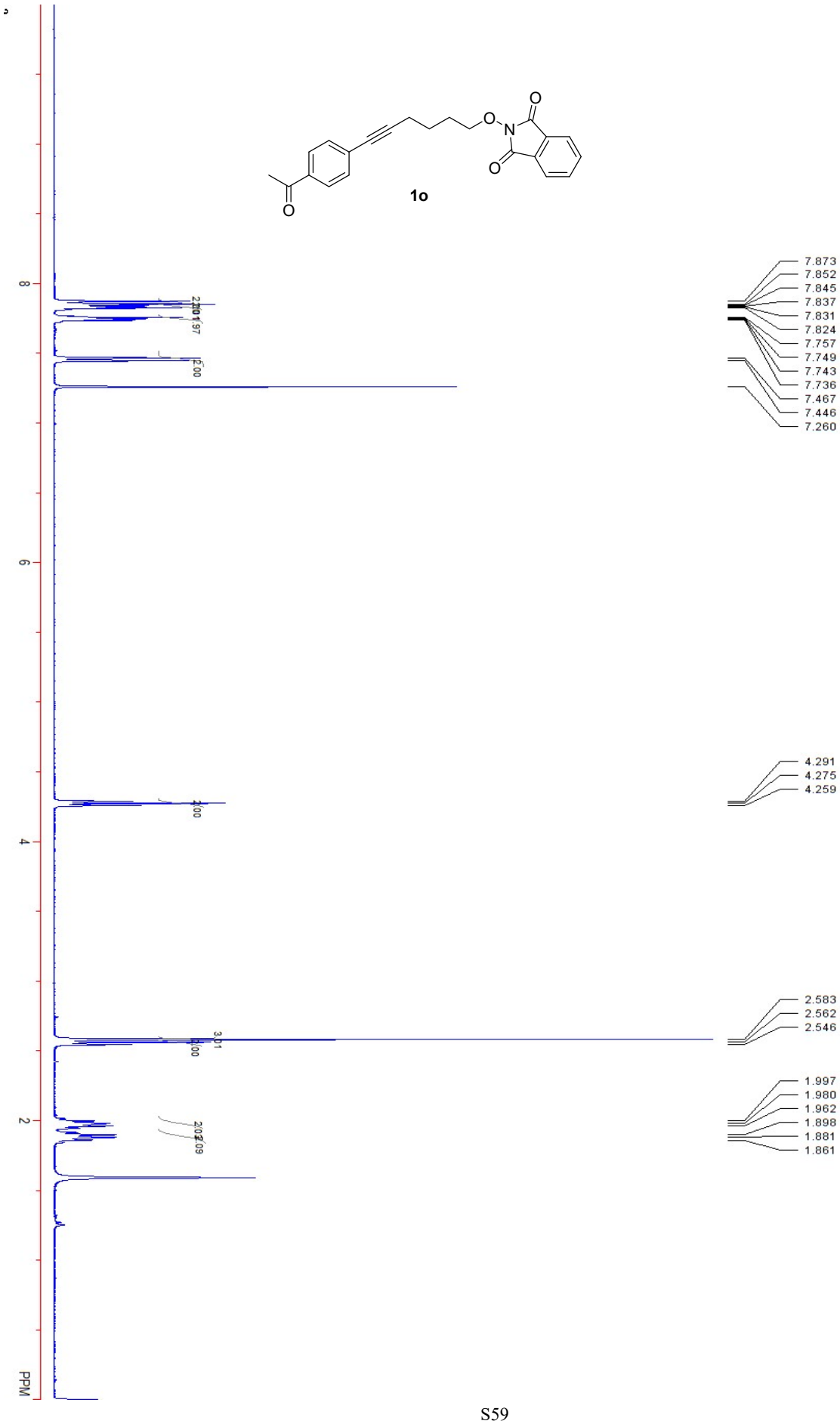
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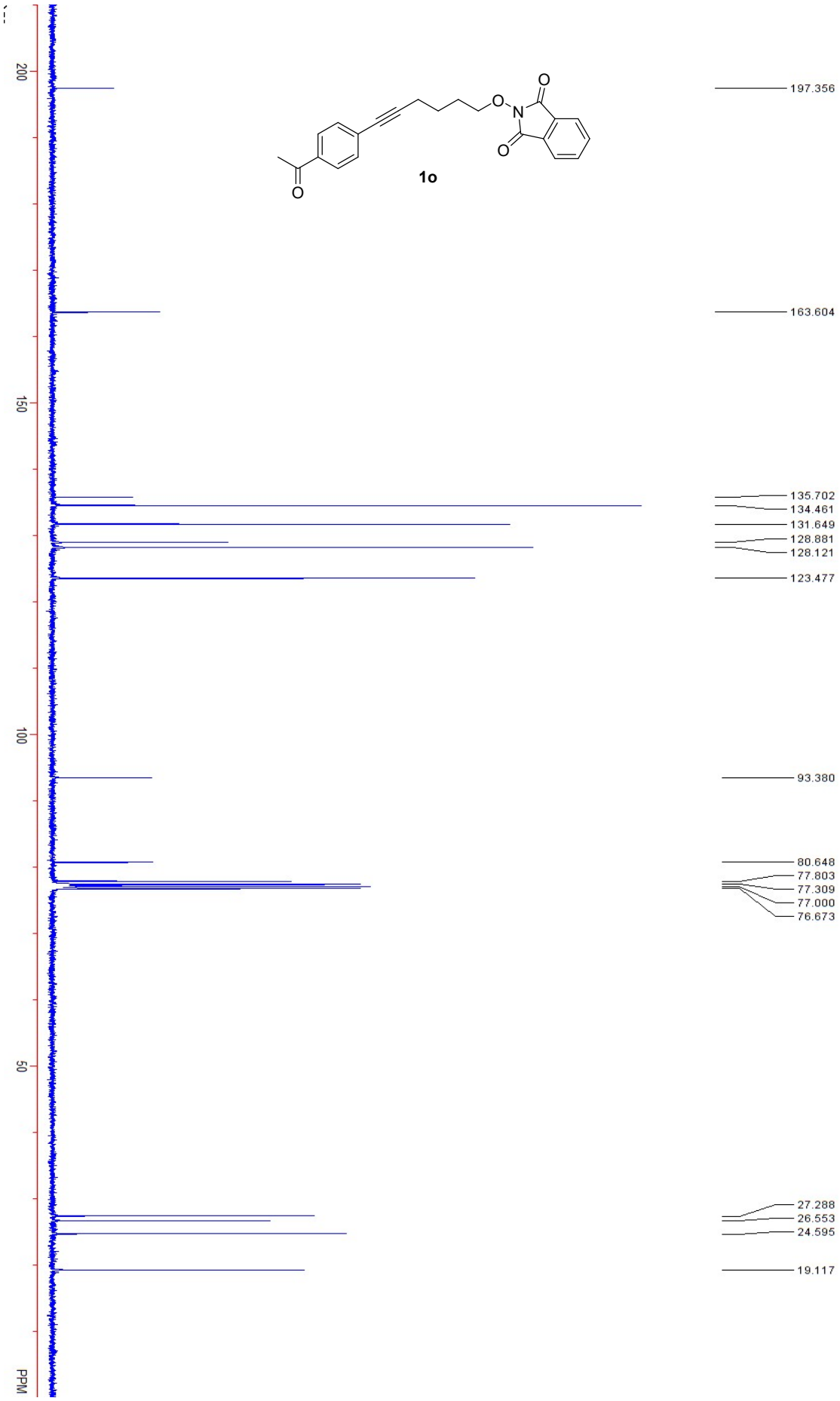
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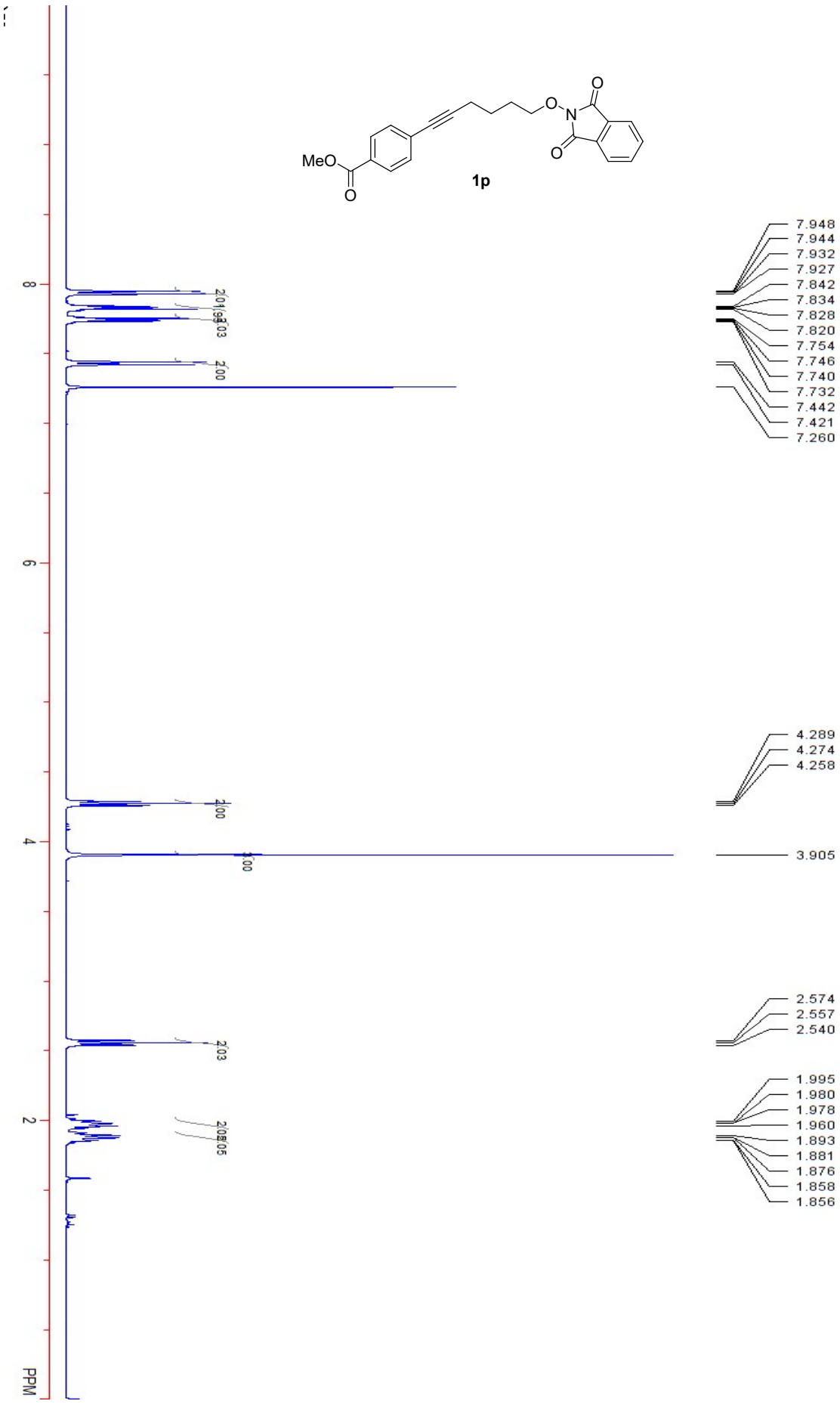
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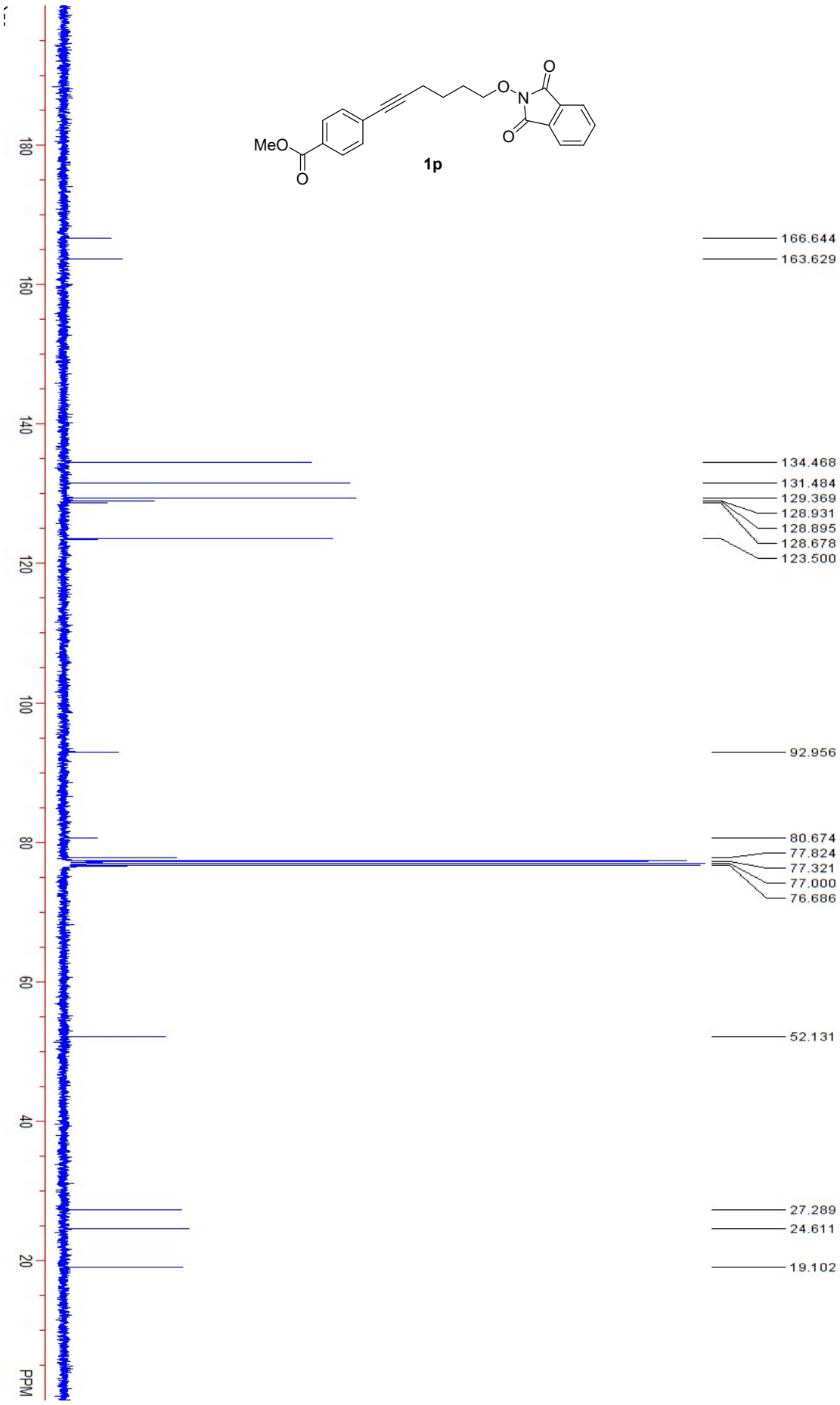
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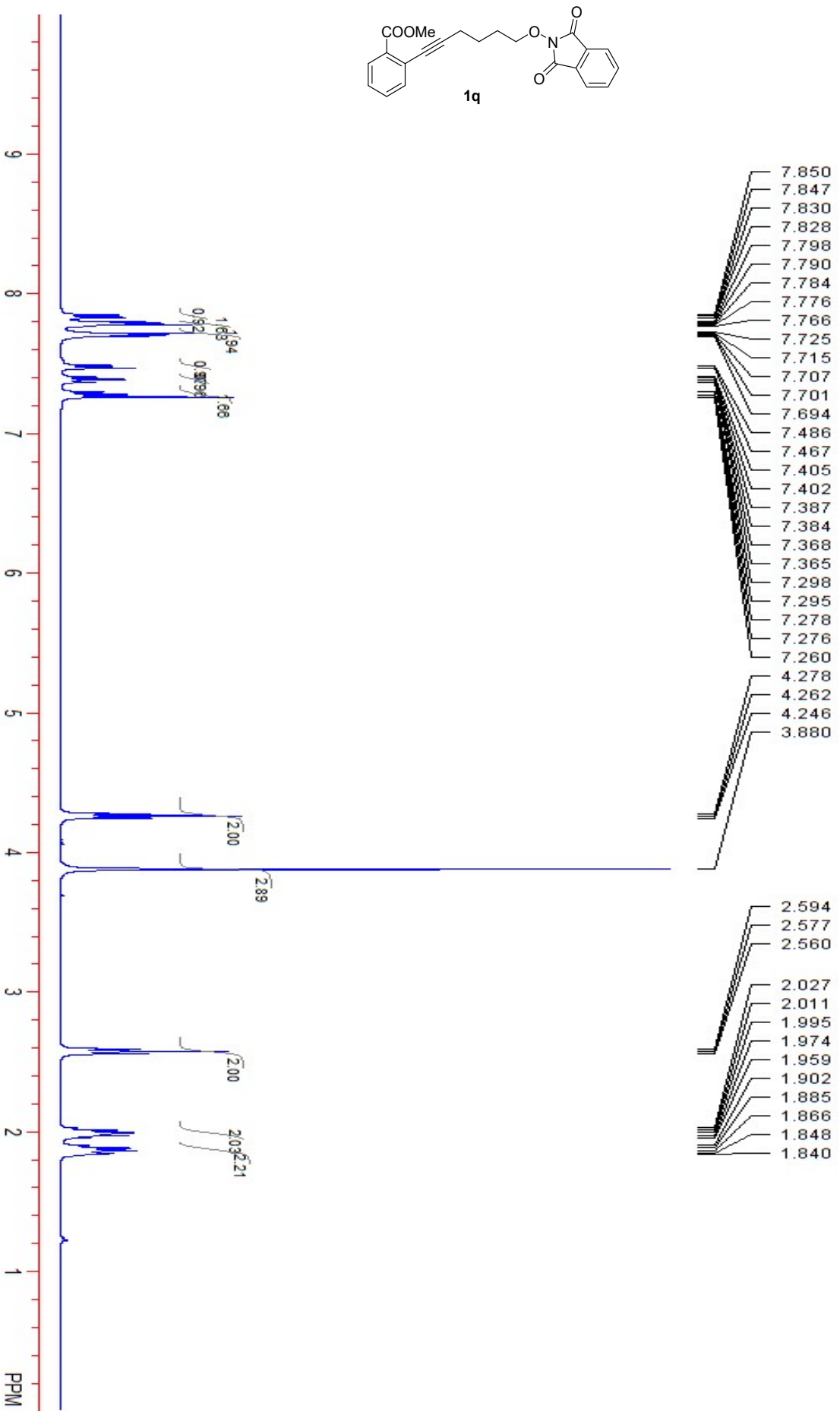
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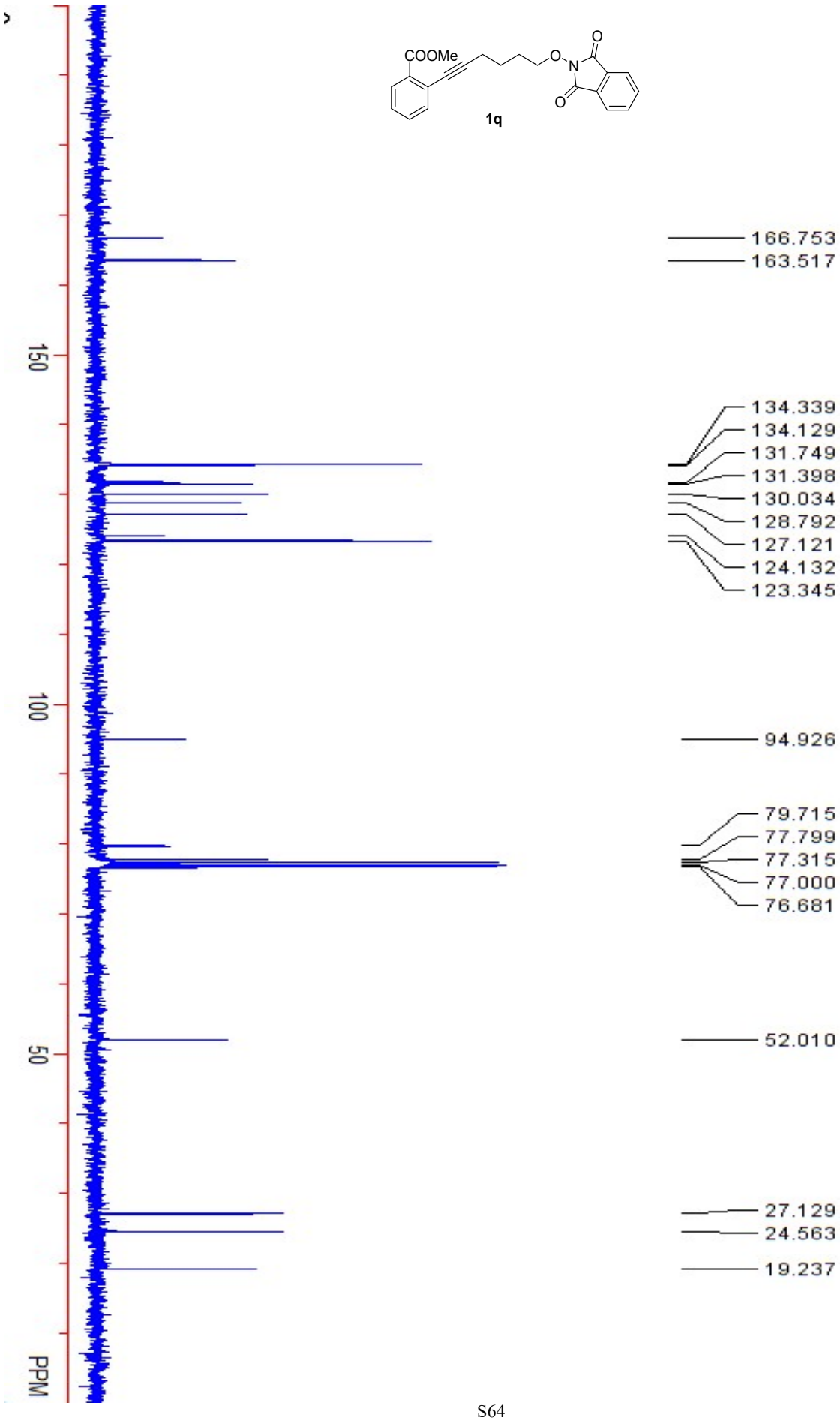
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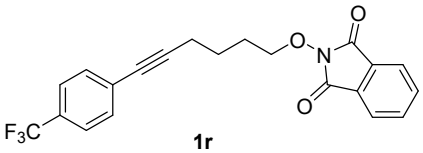
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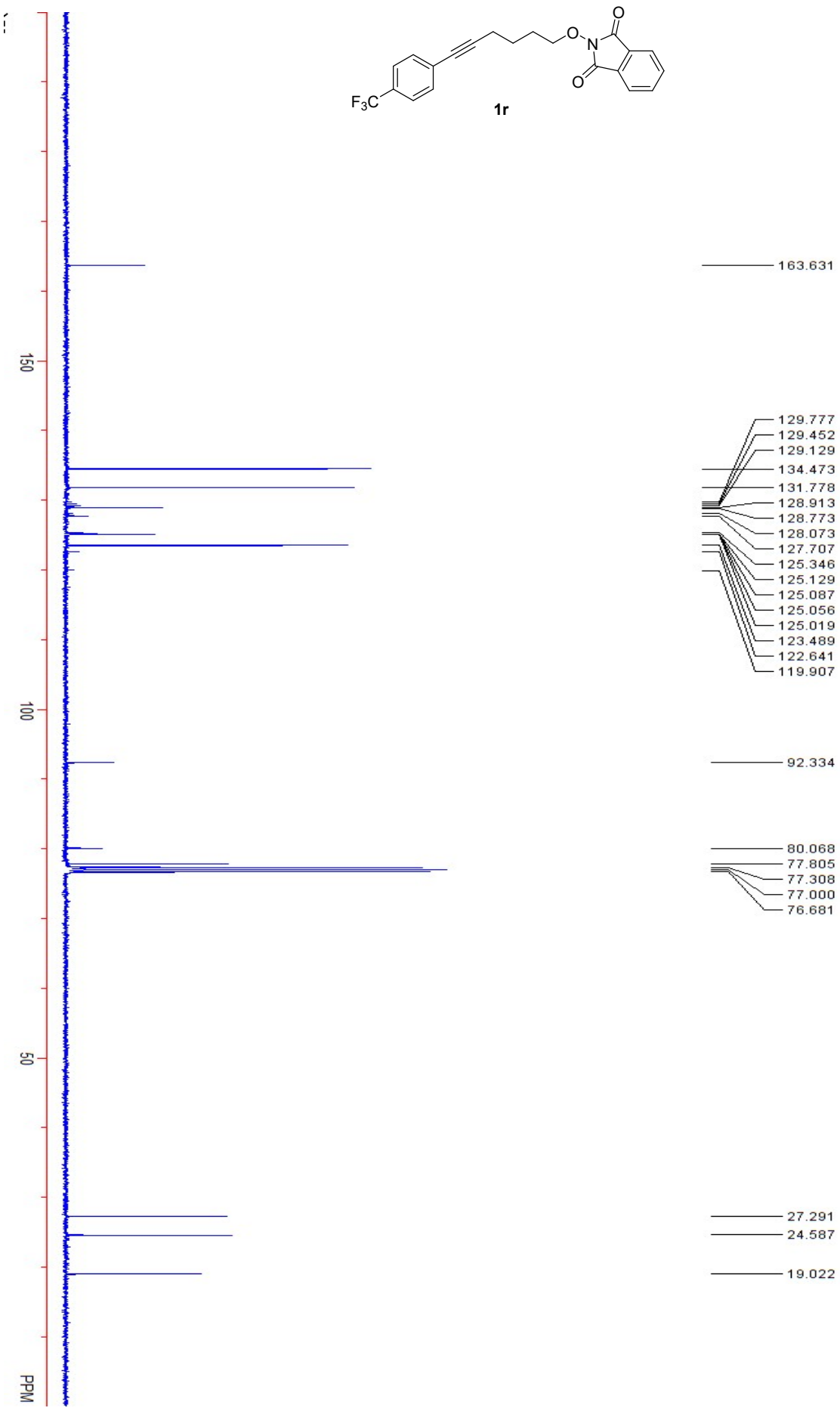
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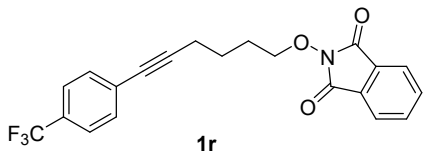

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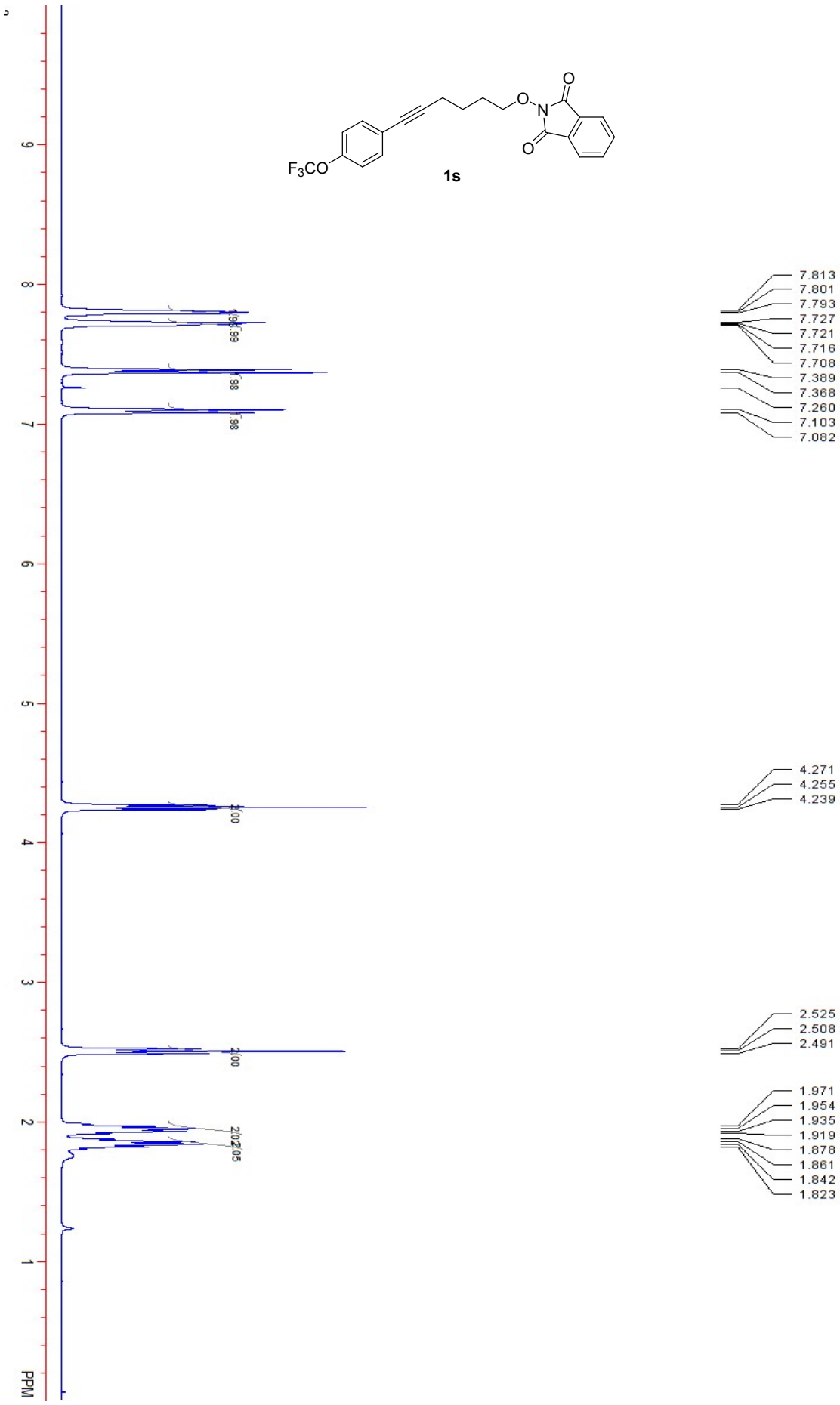
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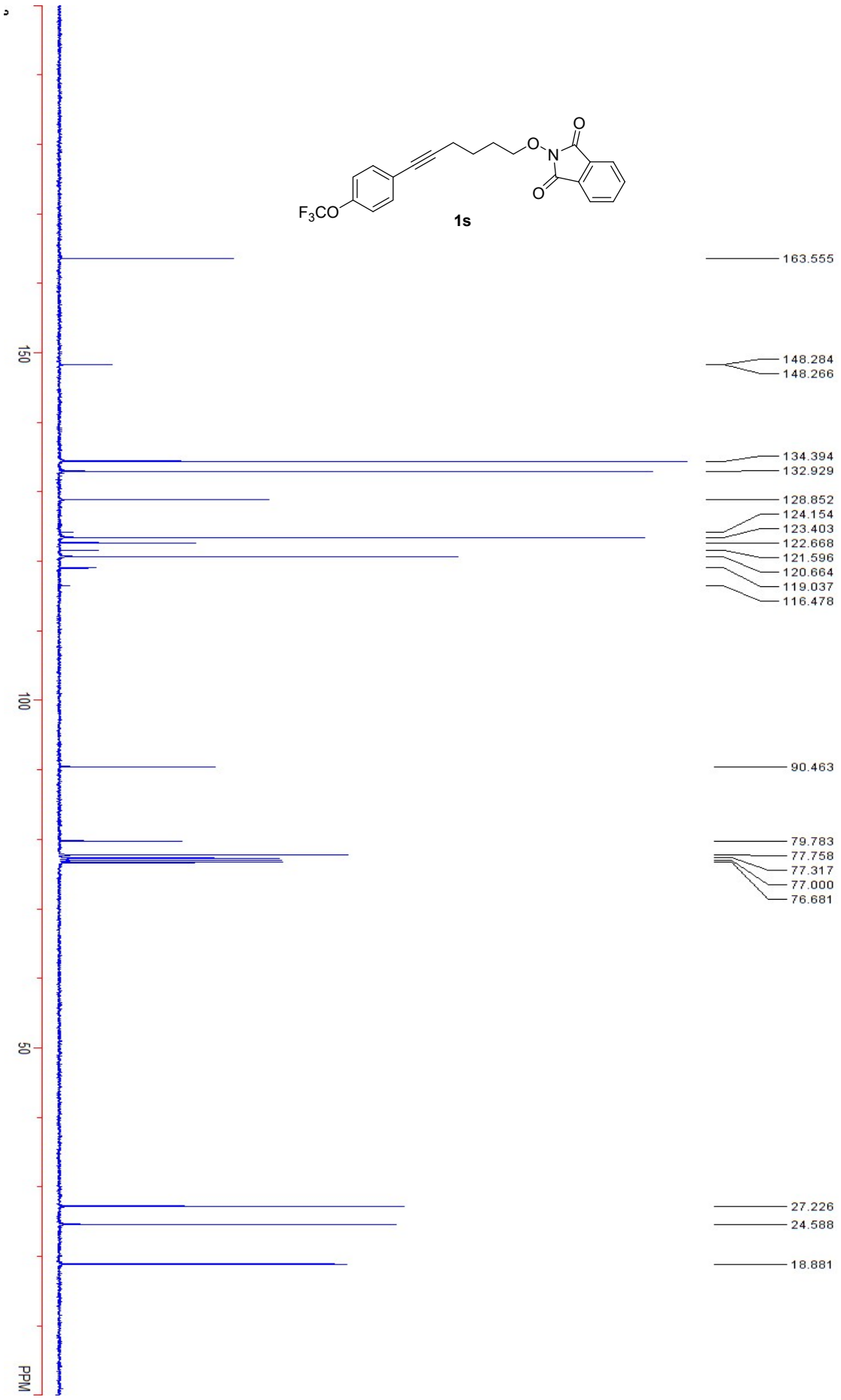
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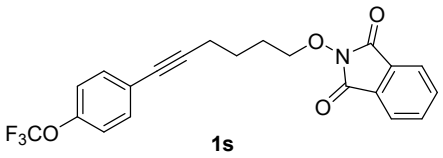

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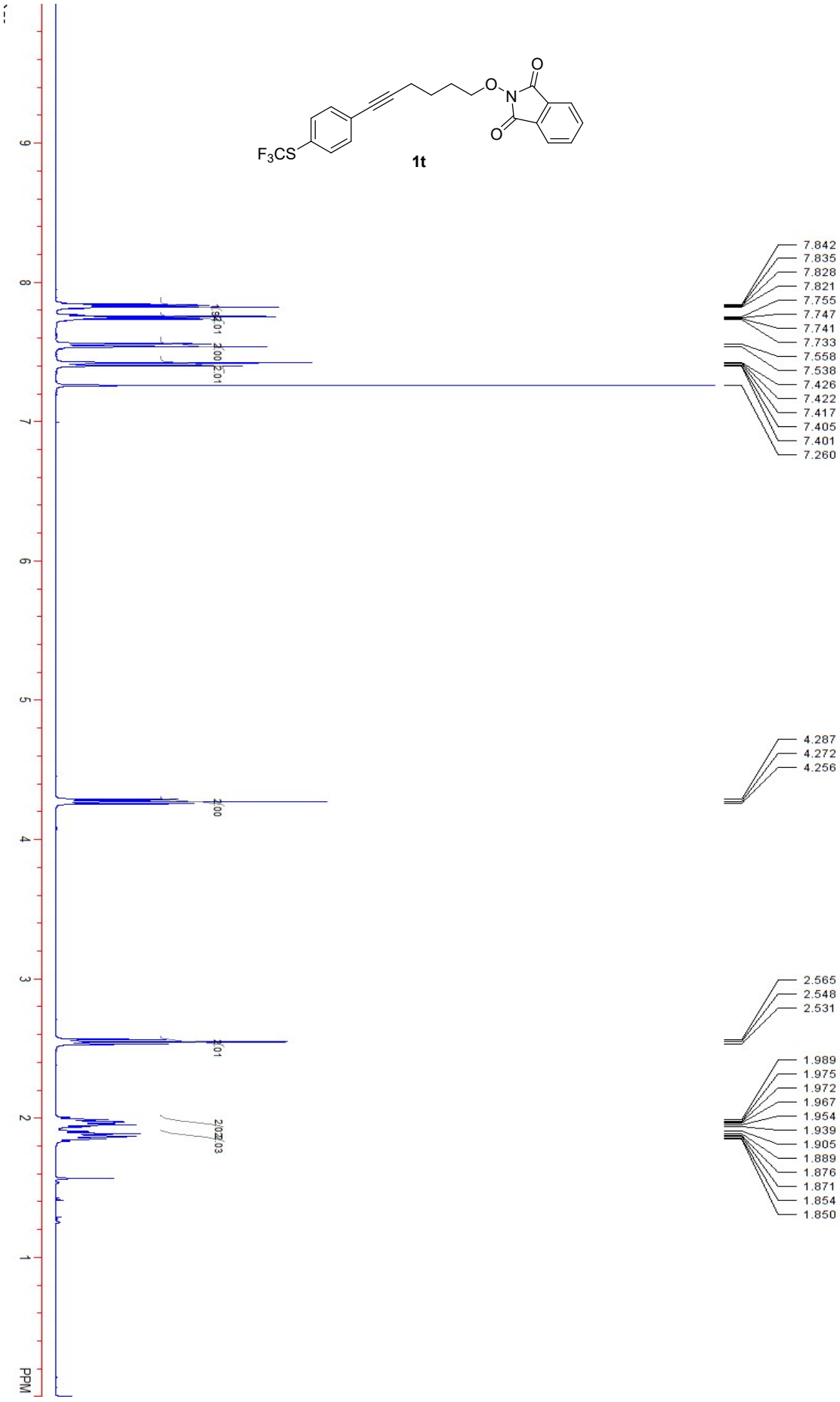
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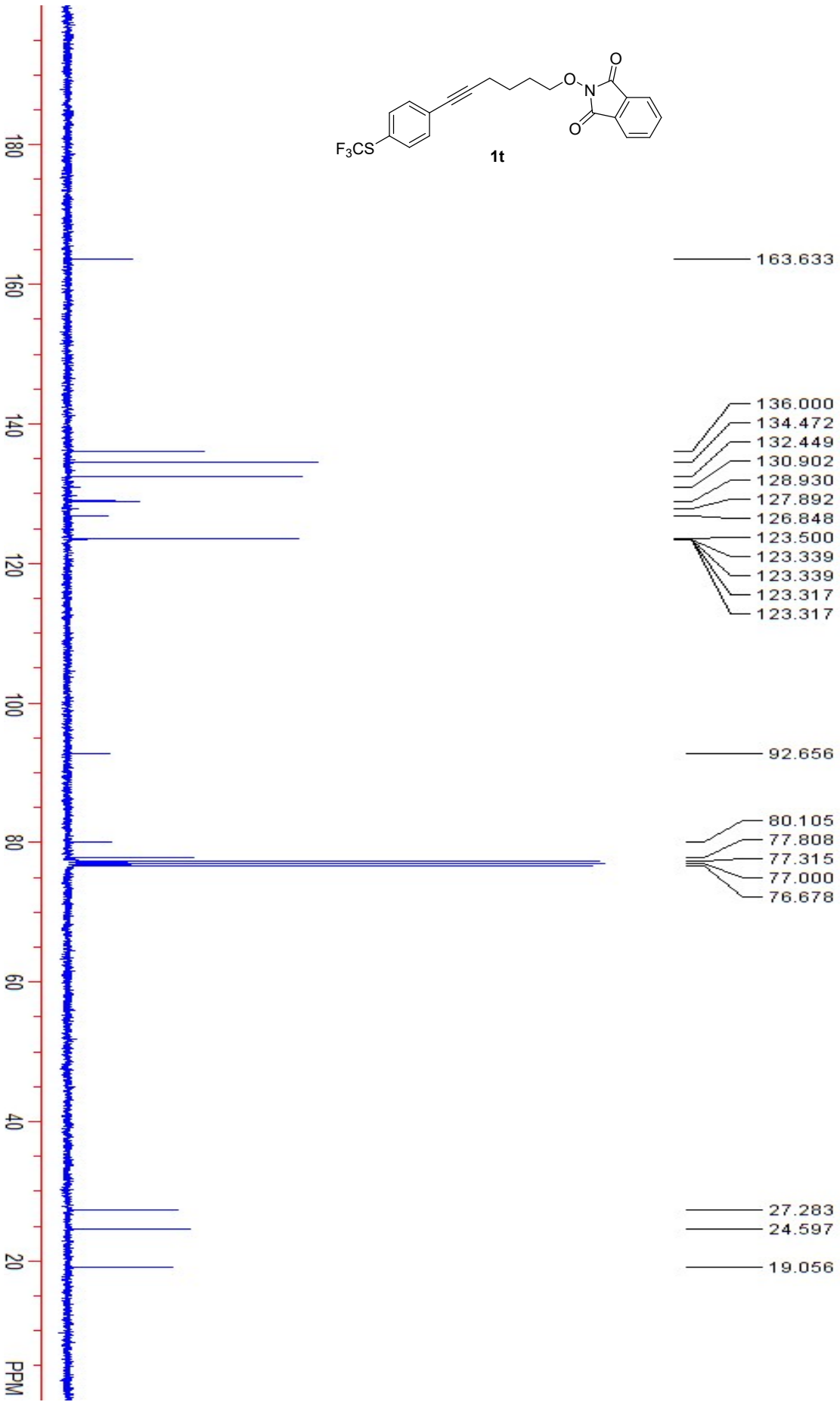
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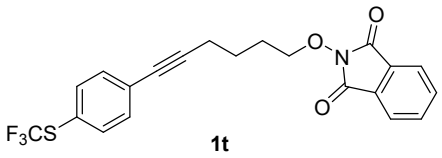

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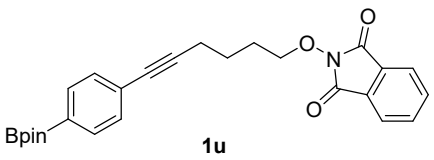
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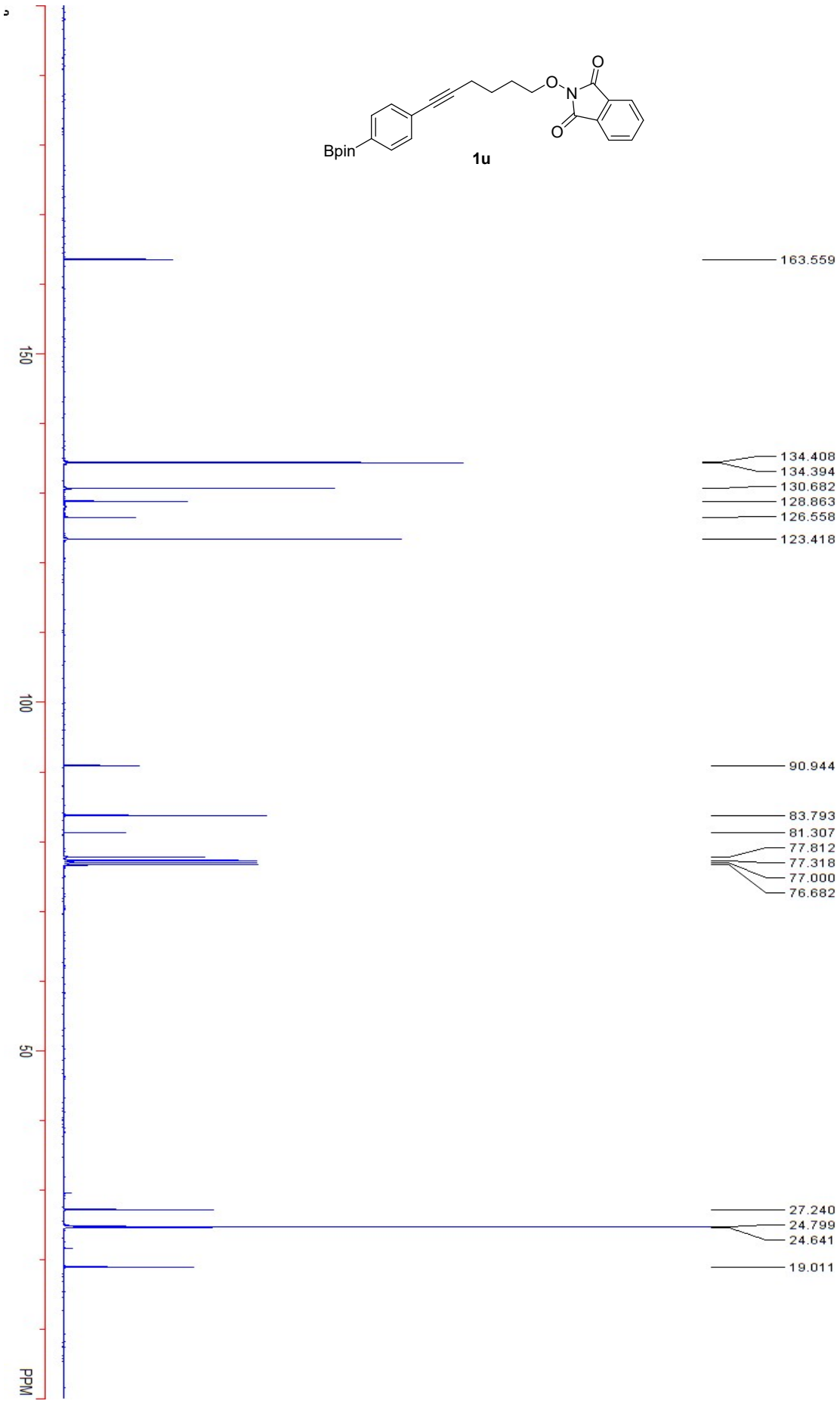
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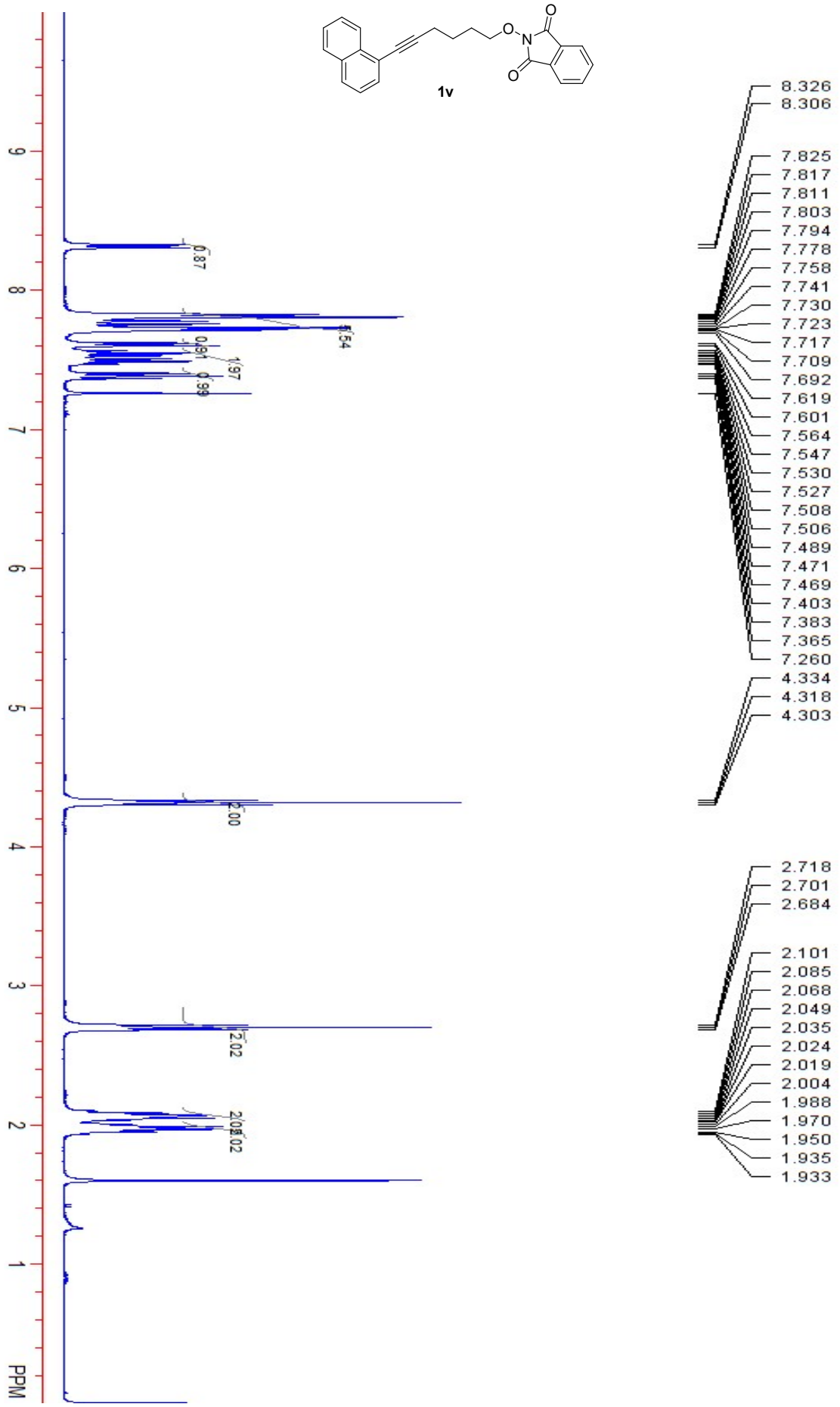
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7.717
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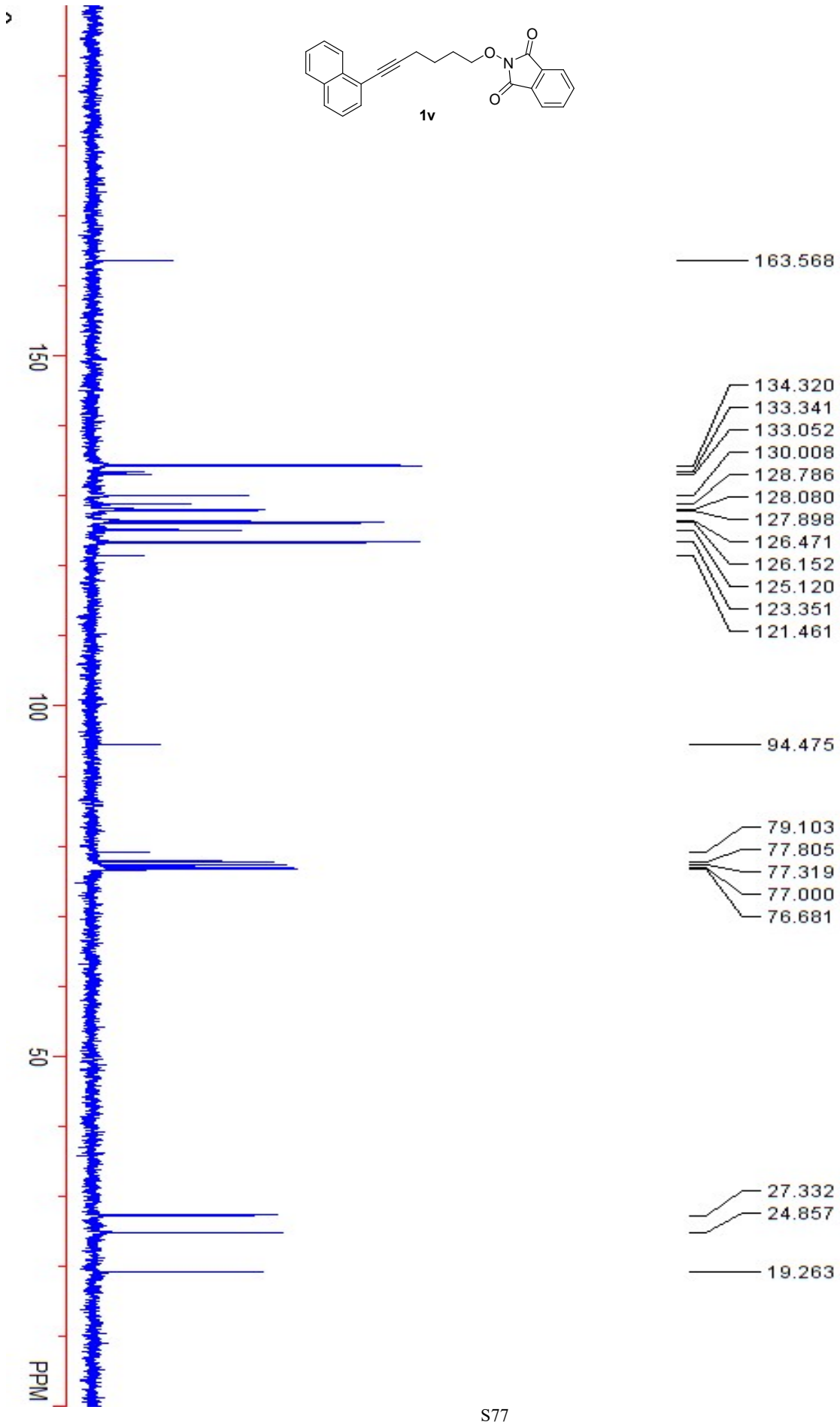
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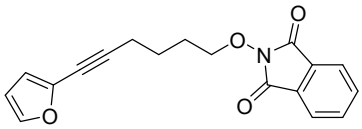

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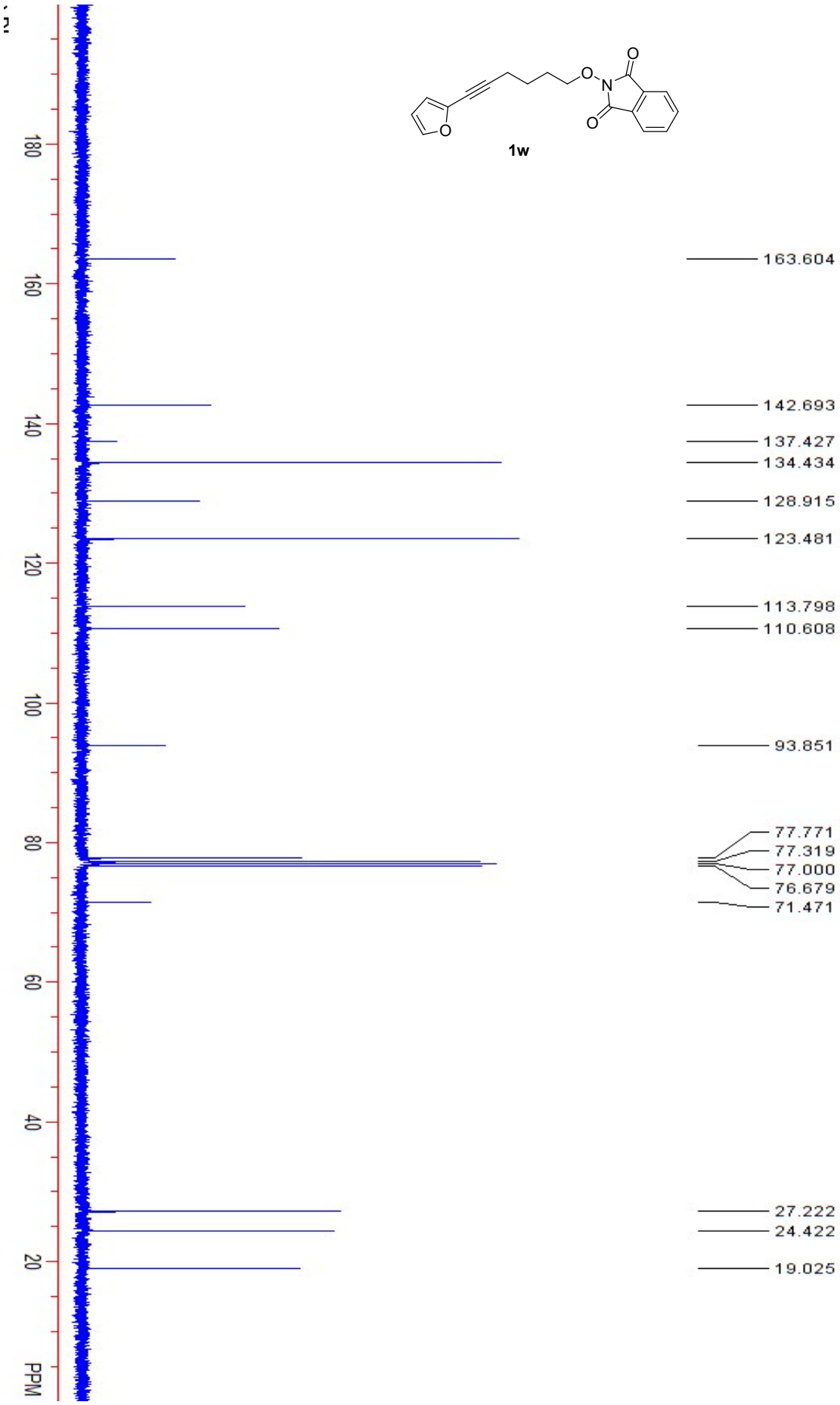
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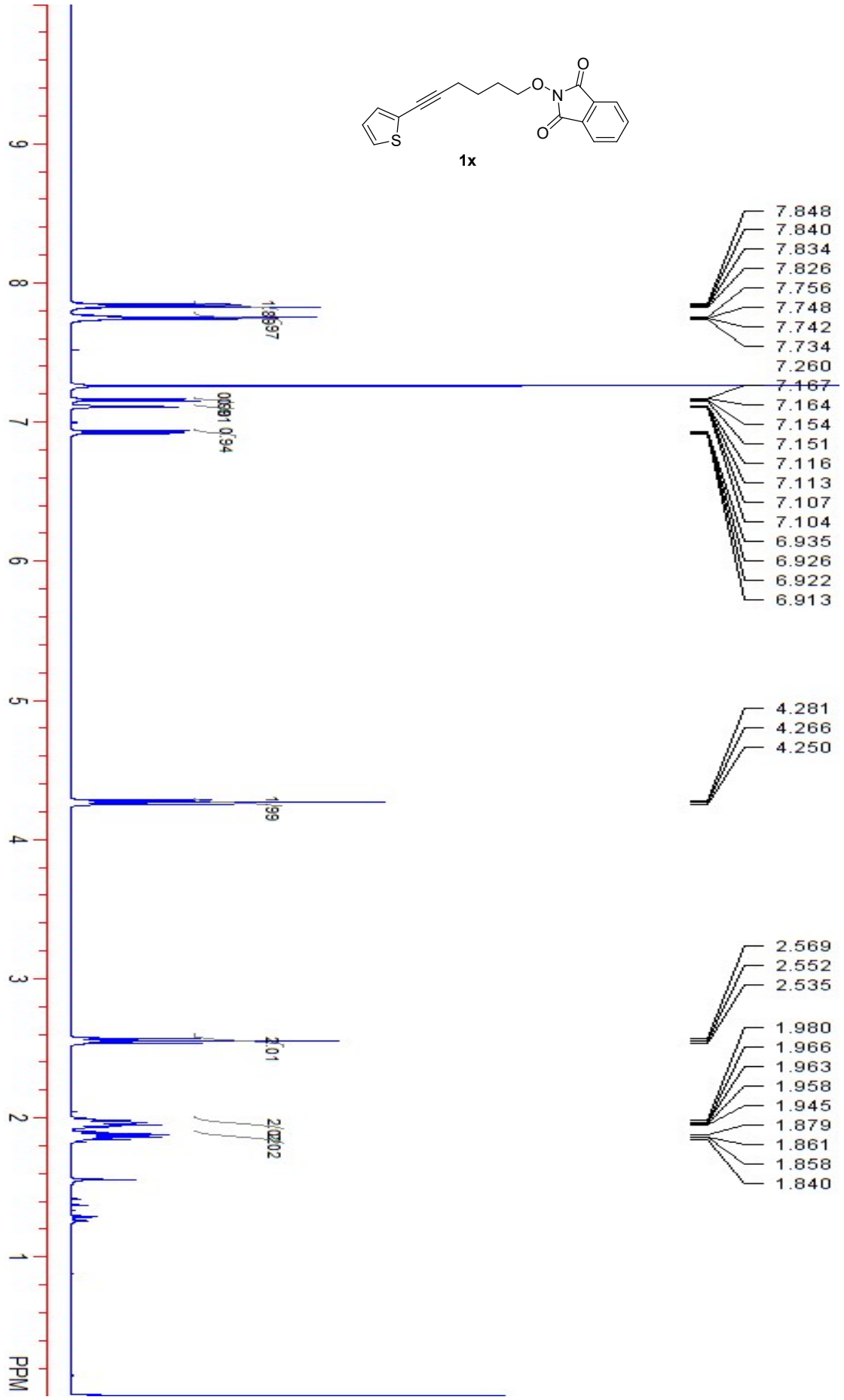
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7.151
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7.113
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7.104
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6.926
6.922
6.913
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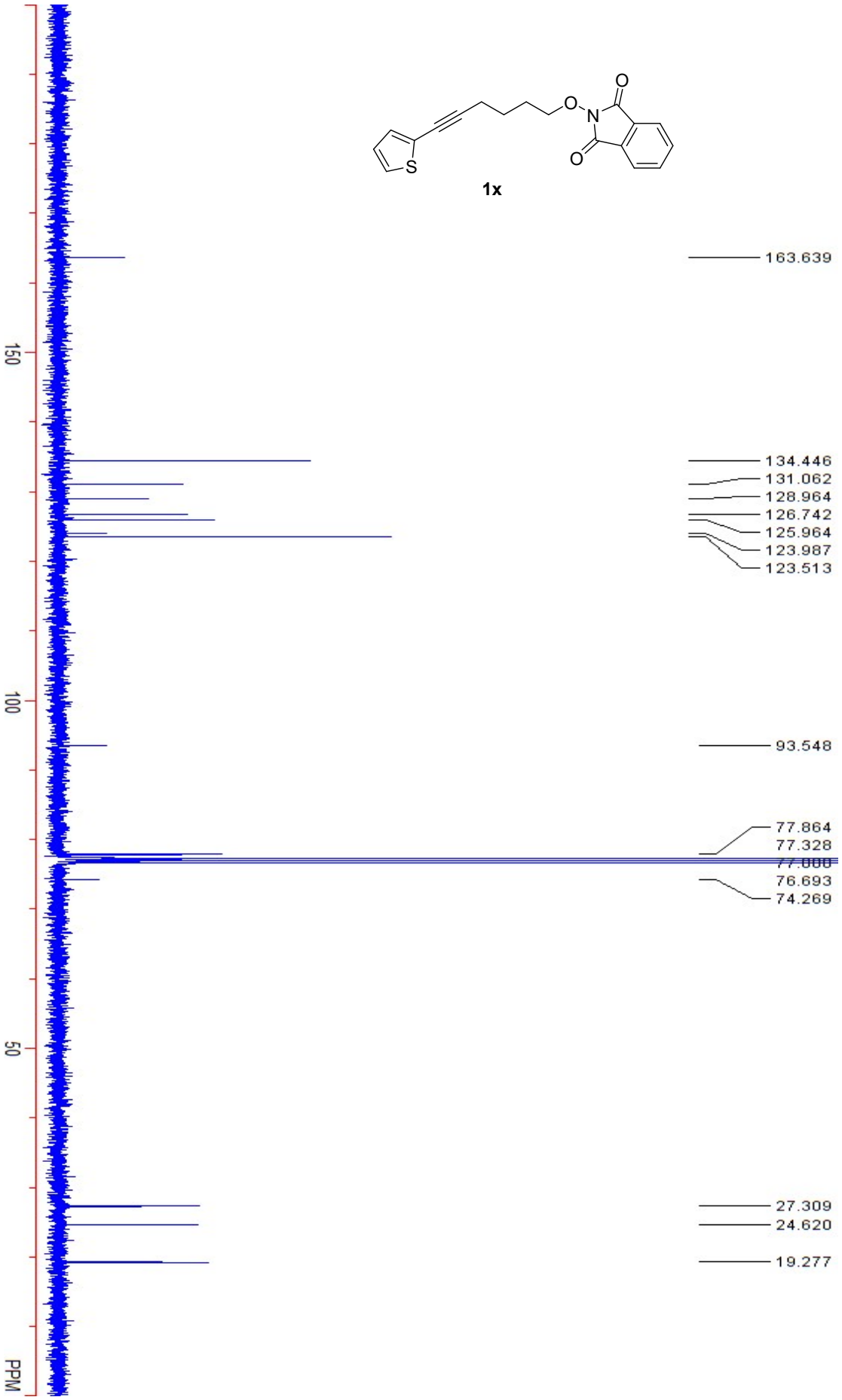
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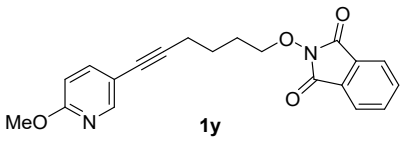
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1y

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7.753
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7.740
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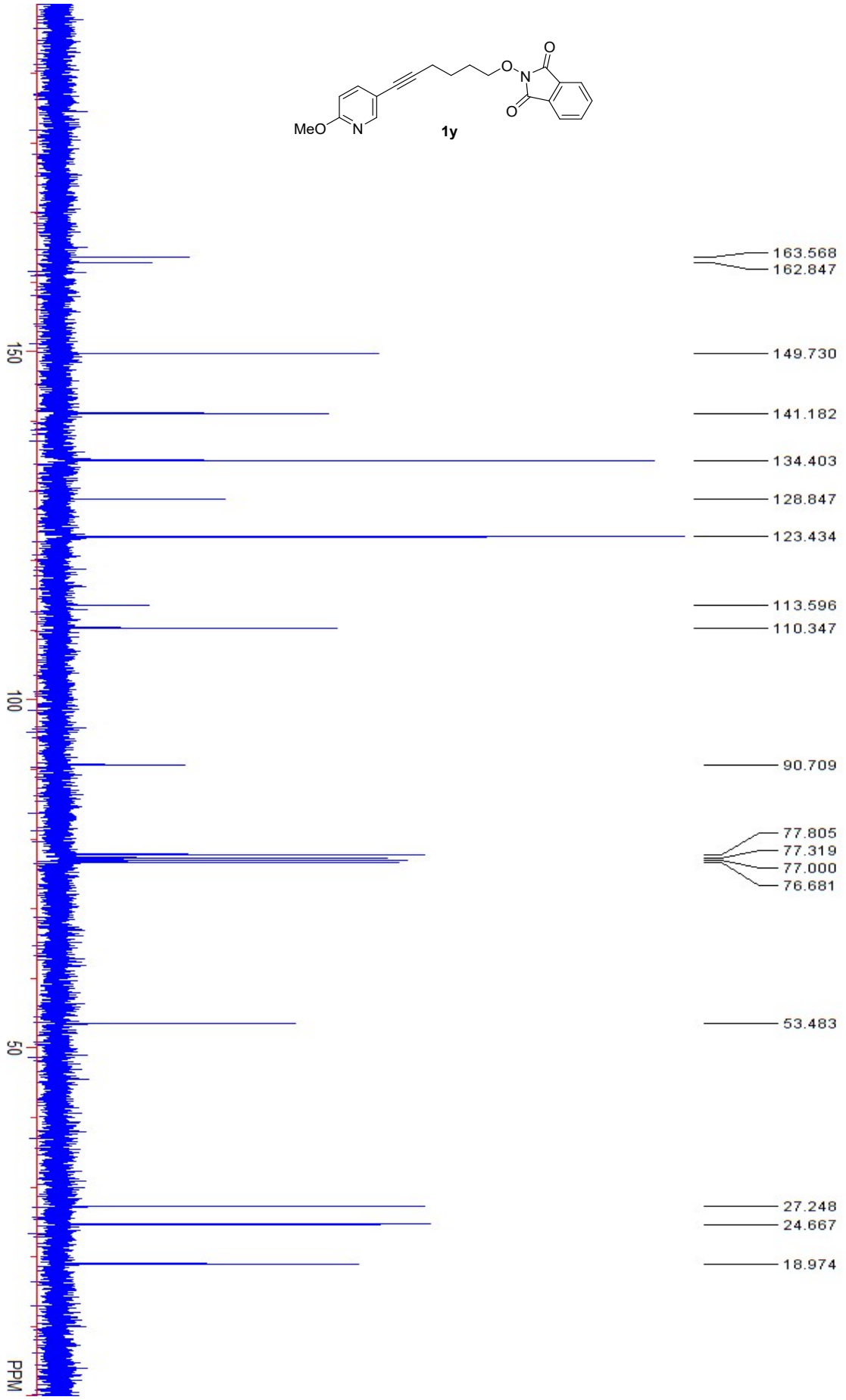
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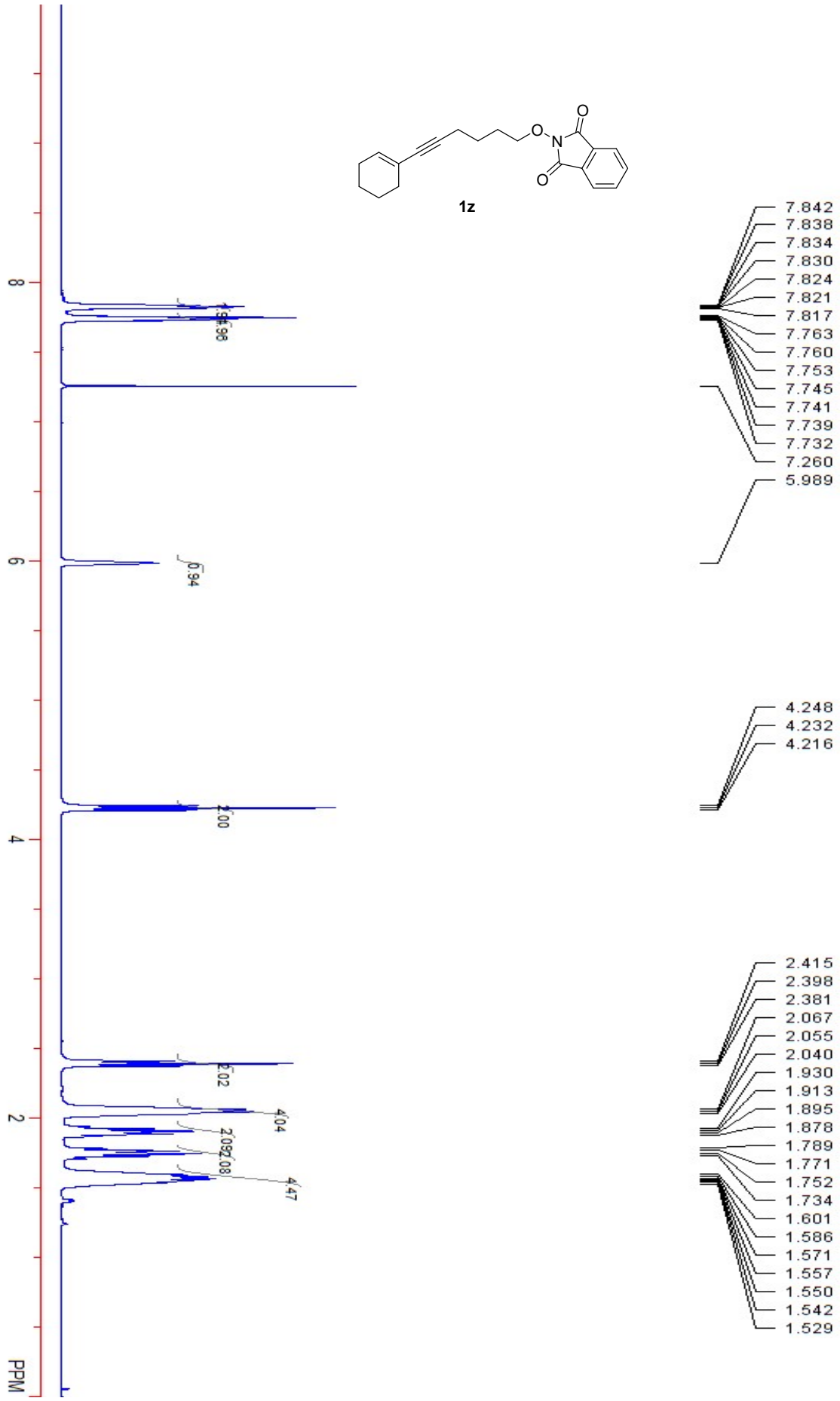
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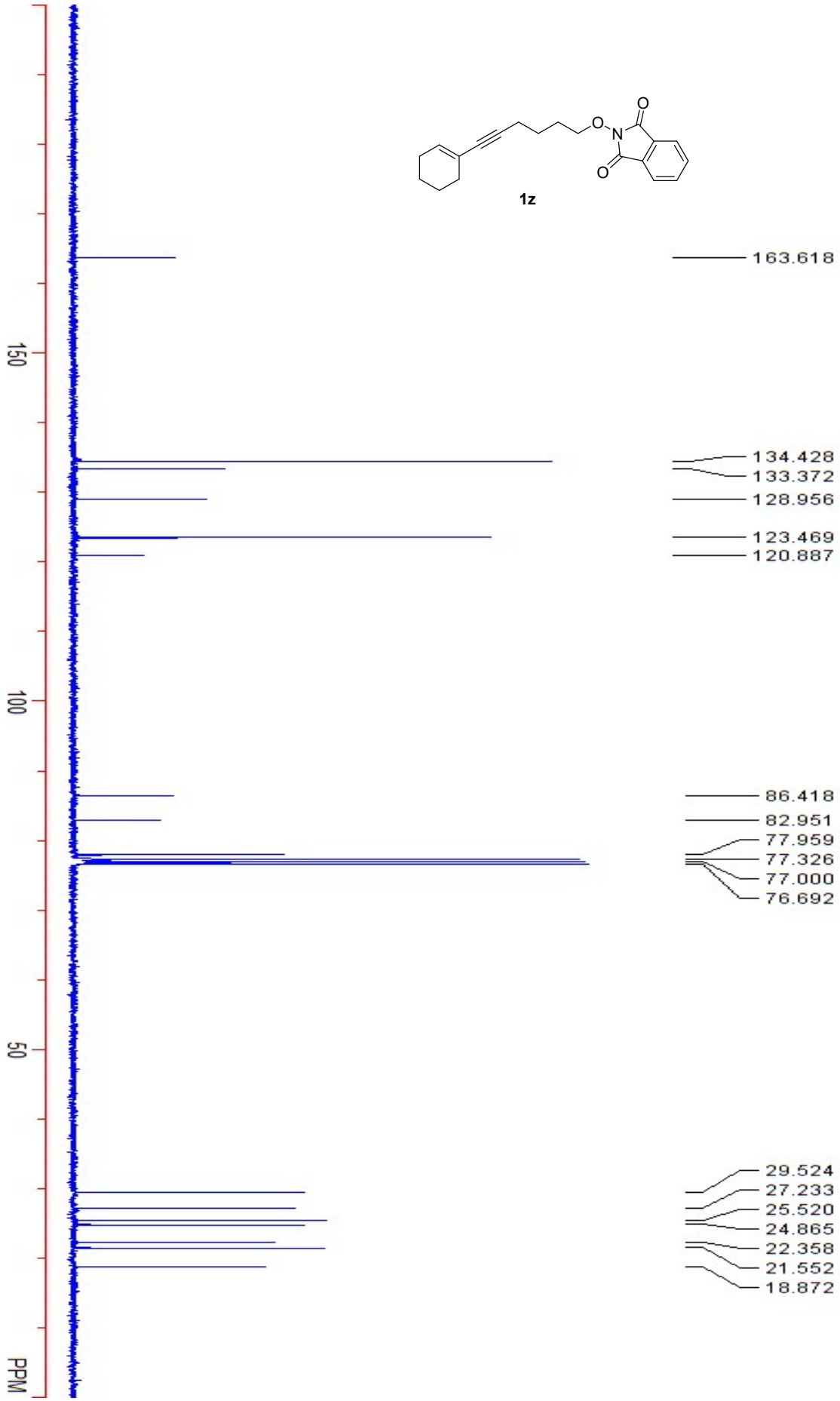
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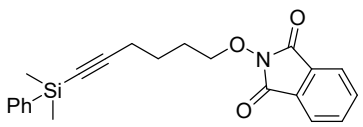
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1aa

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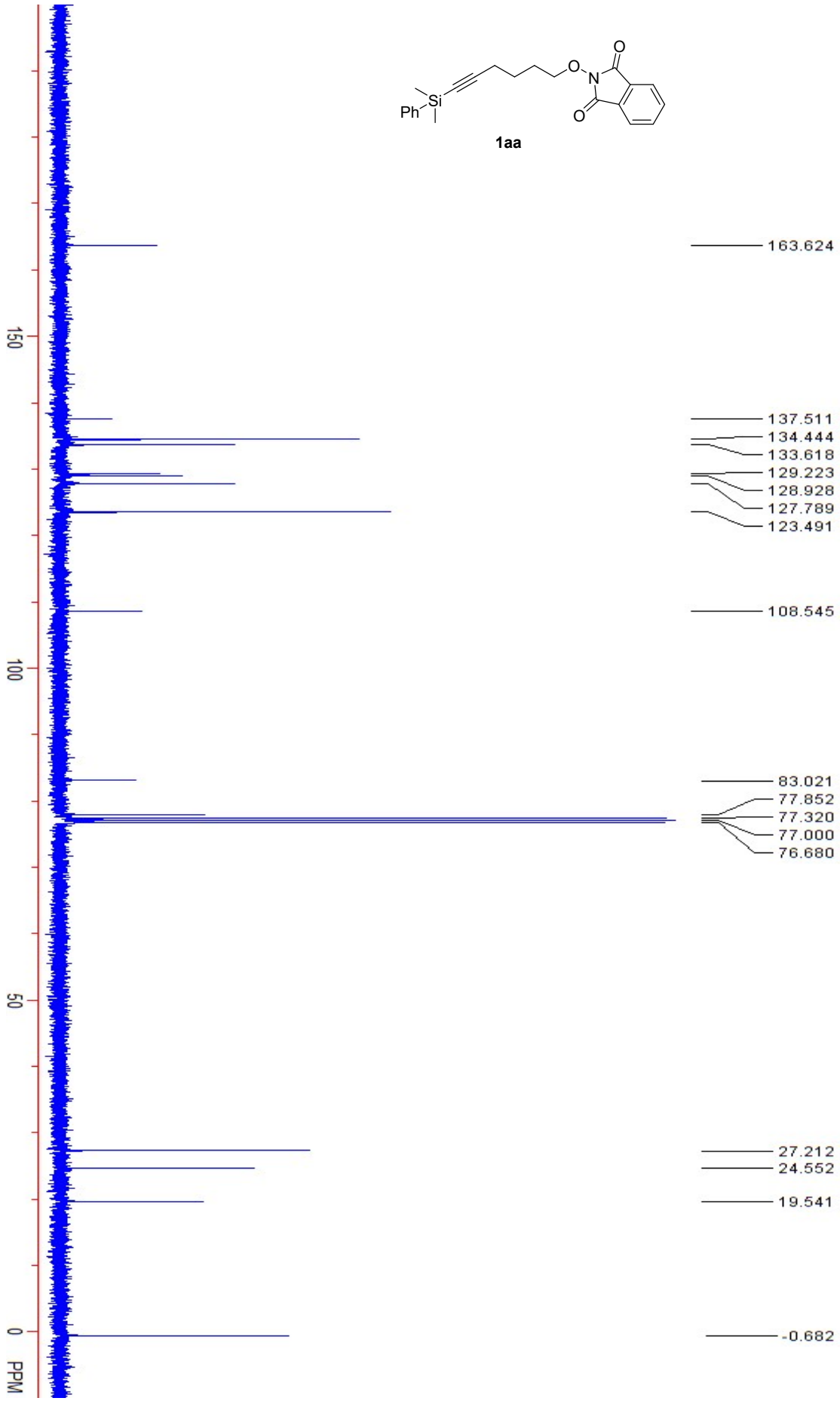
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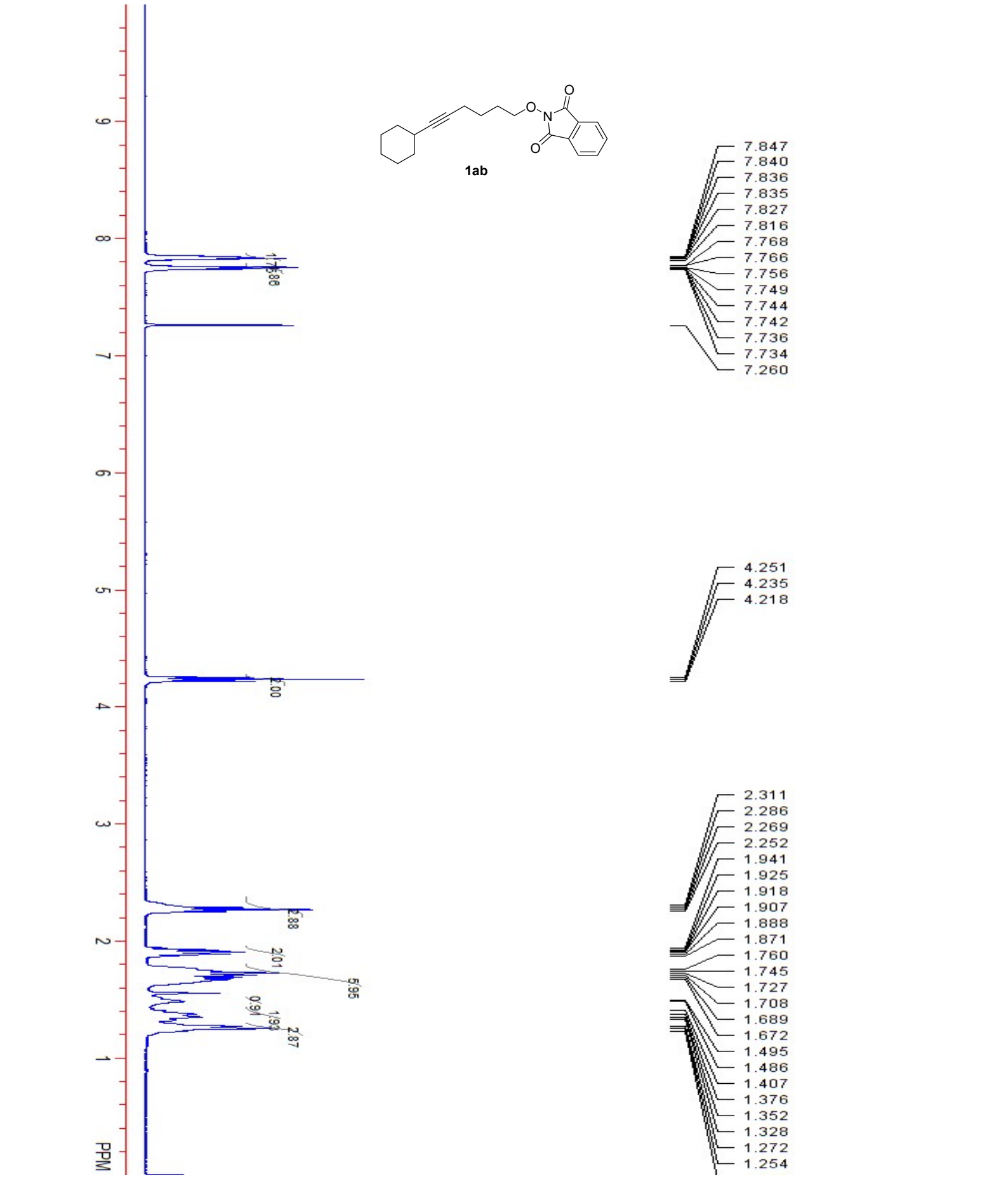
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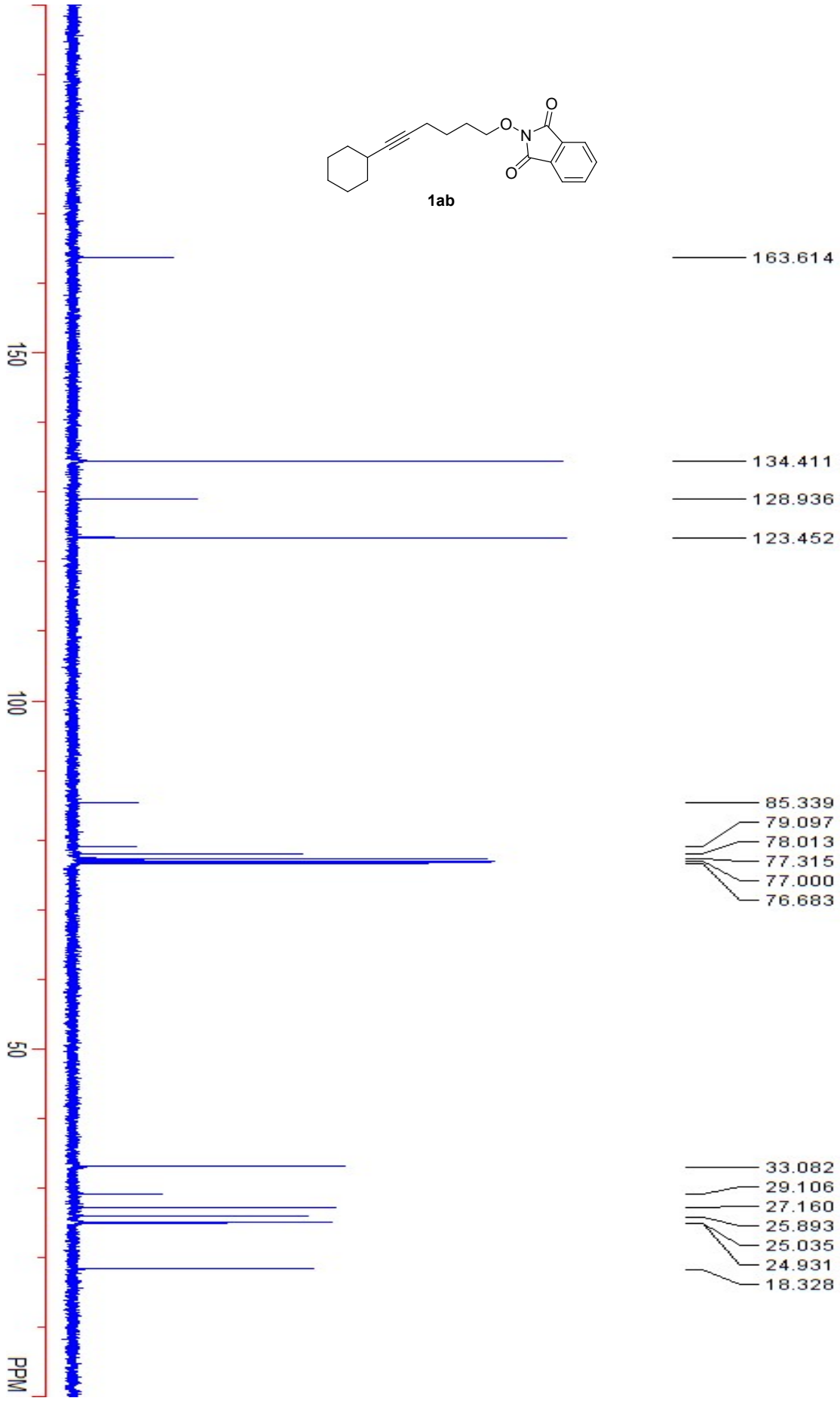
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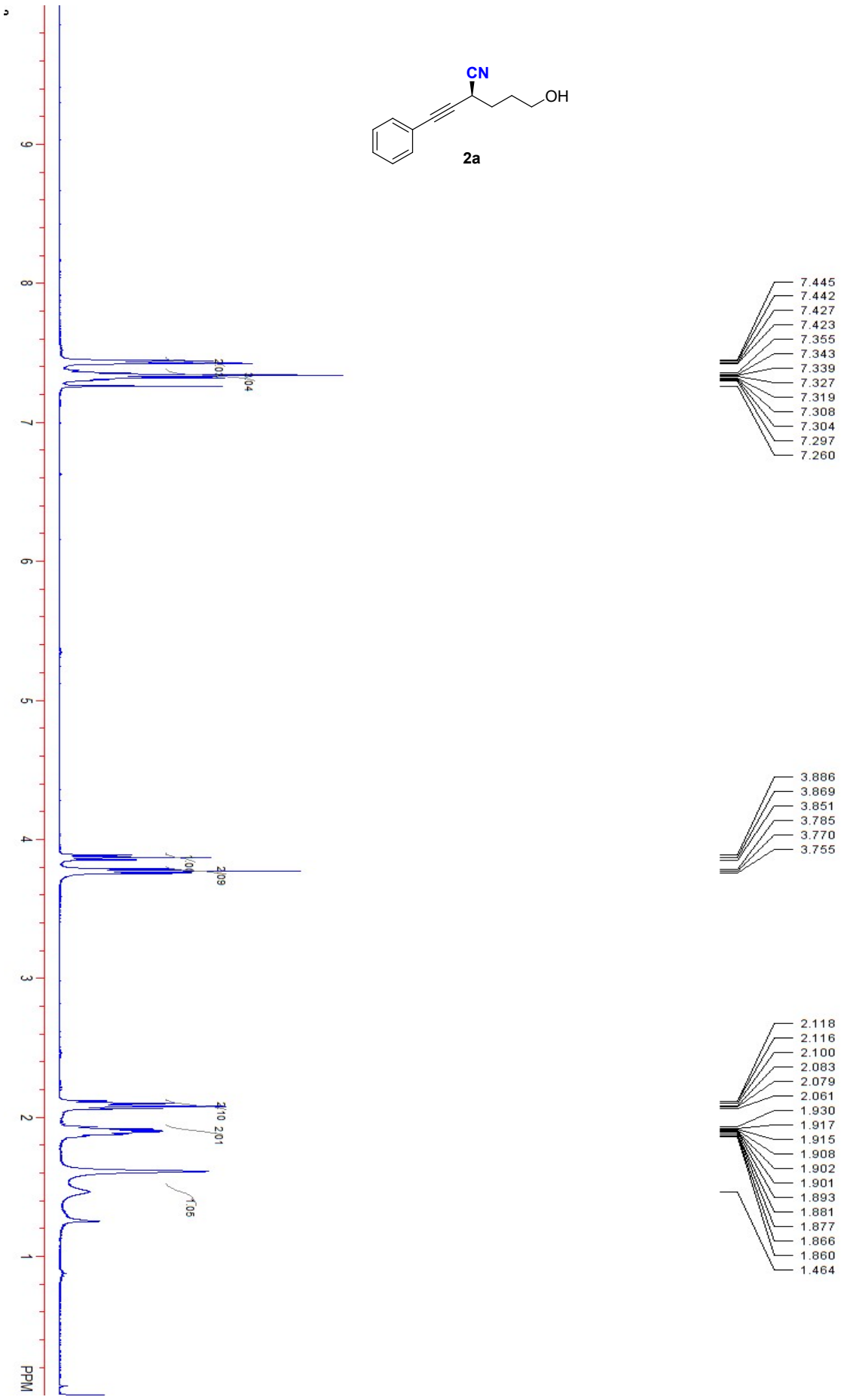
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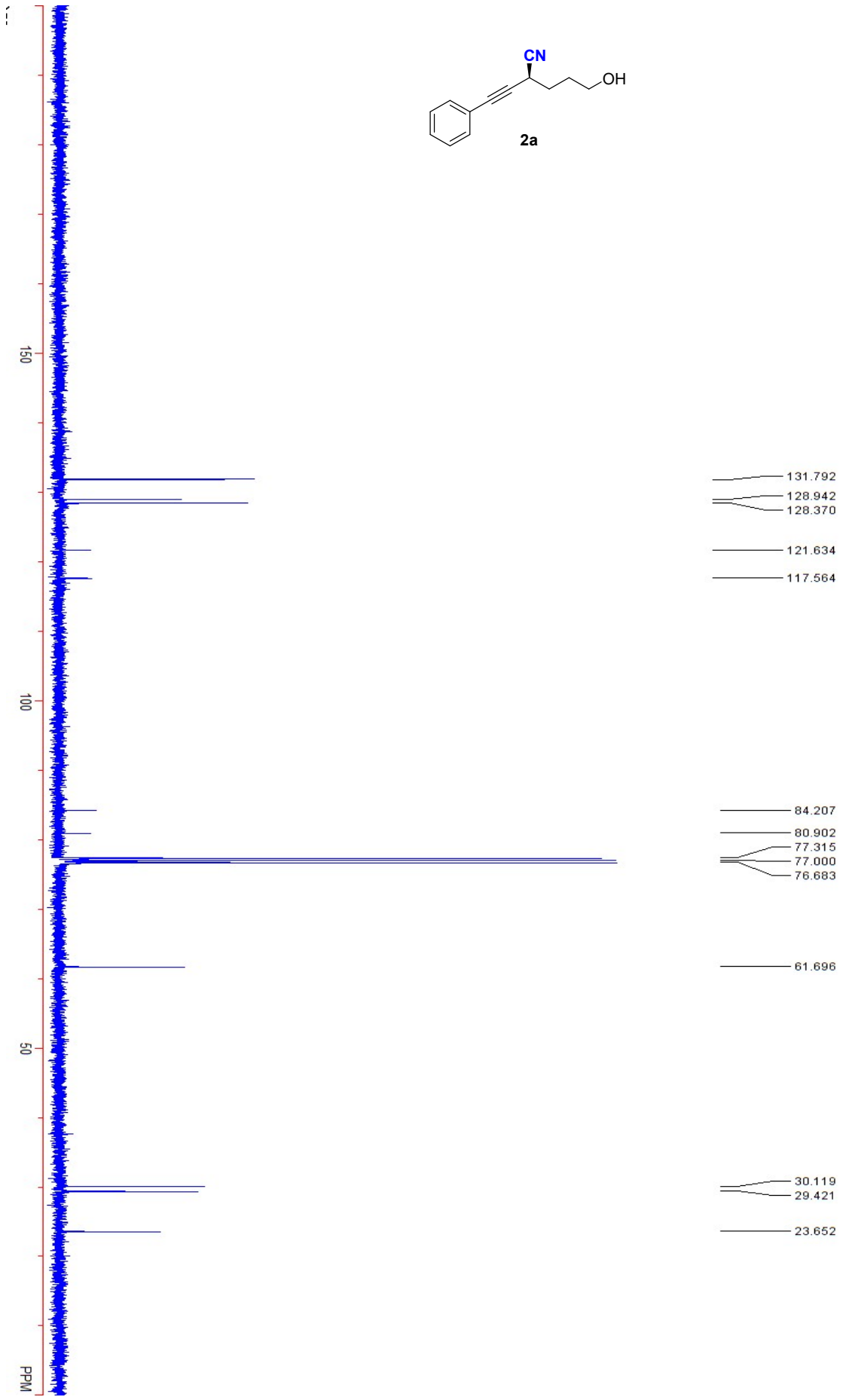
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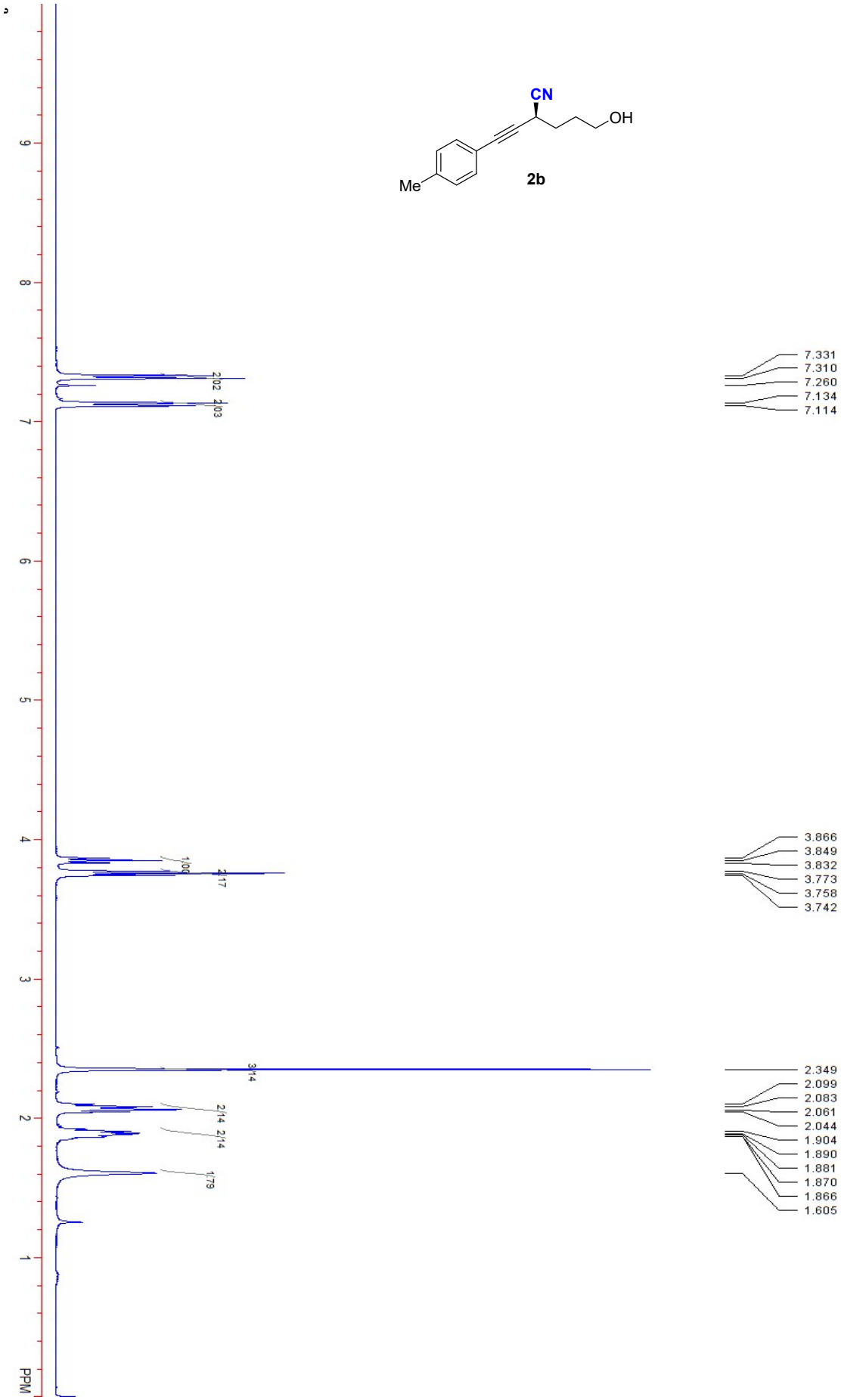
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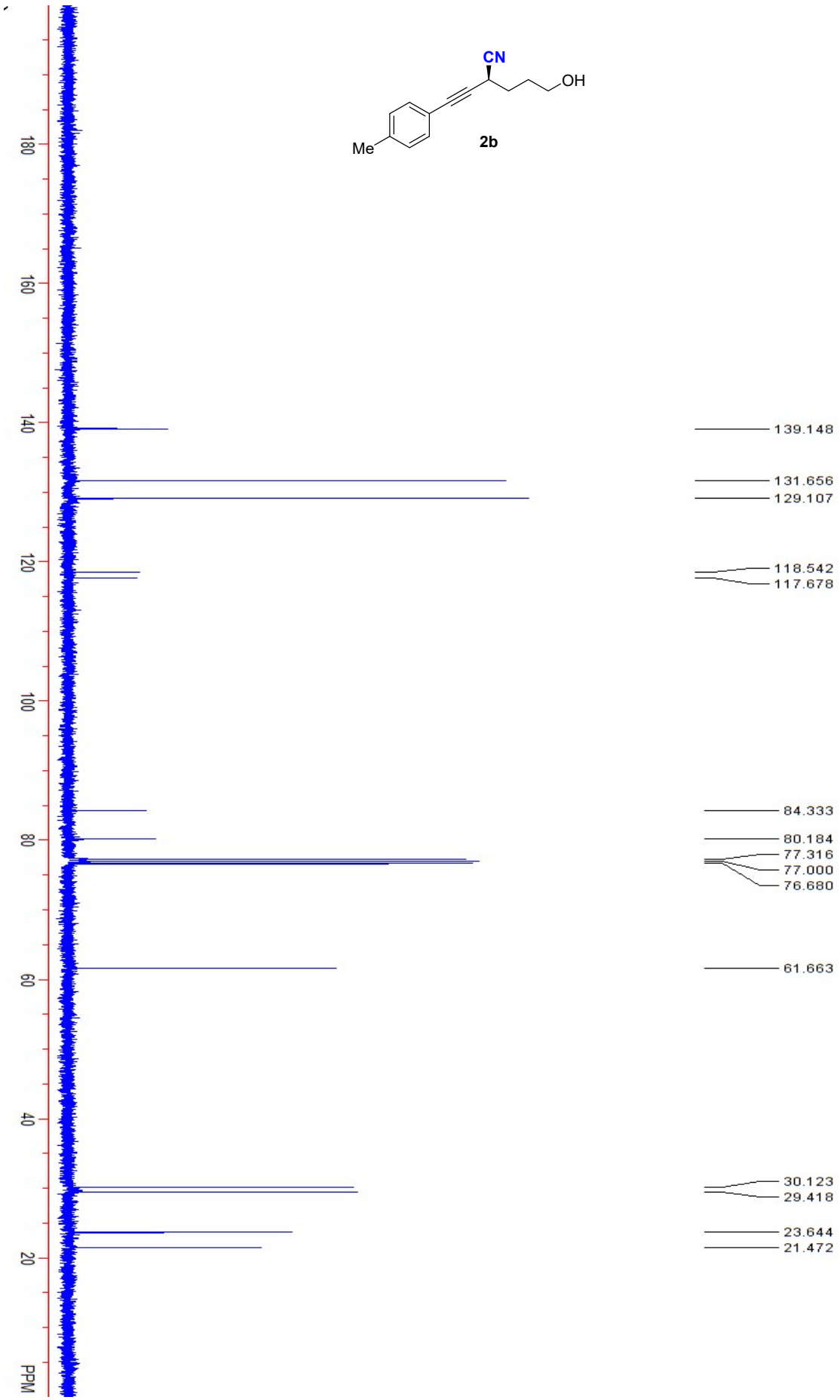
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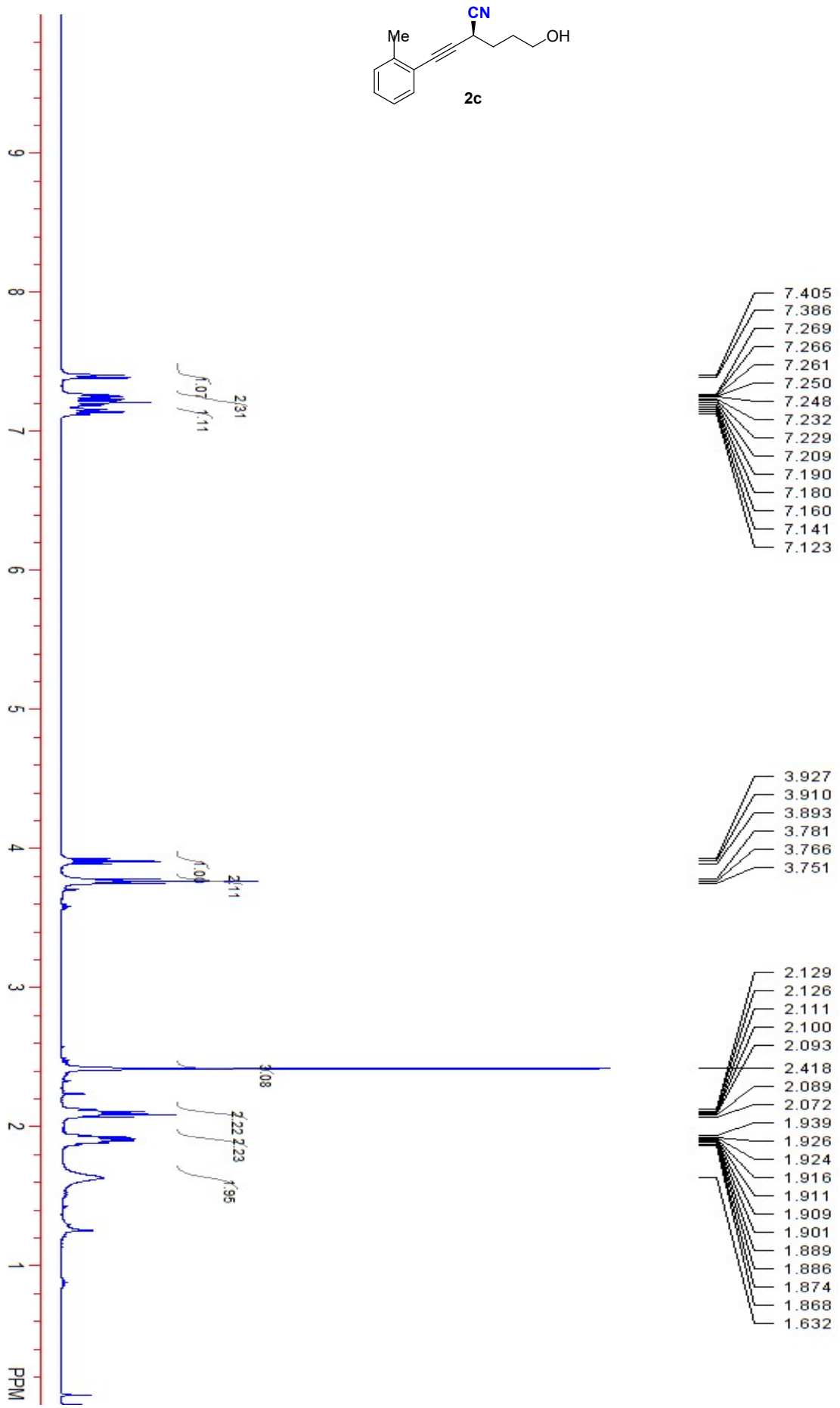
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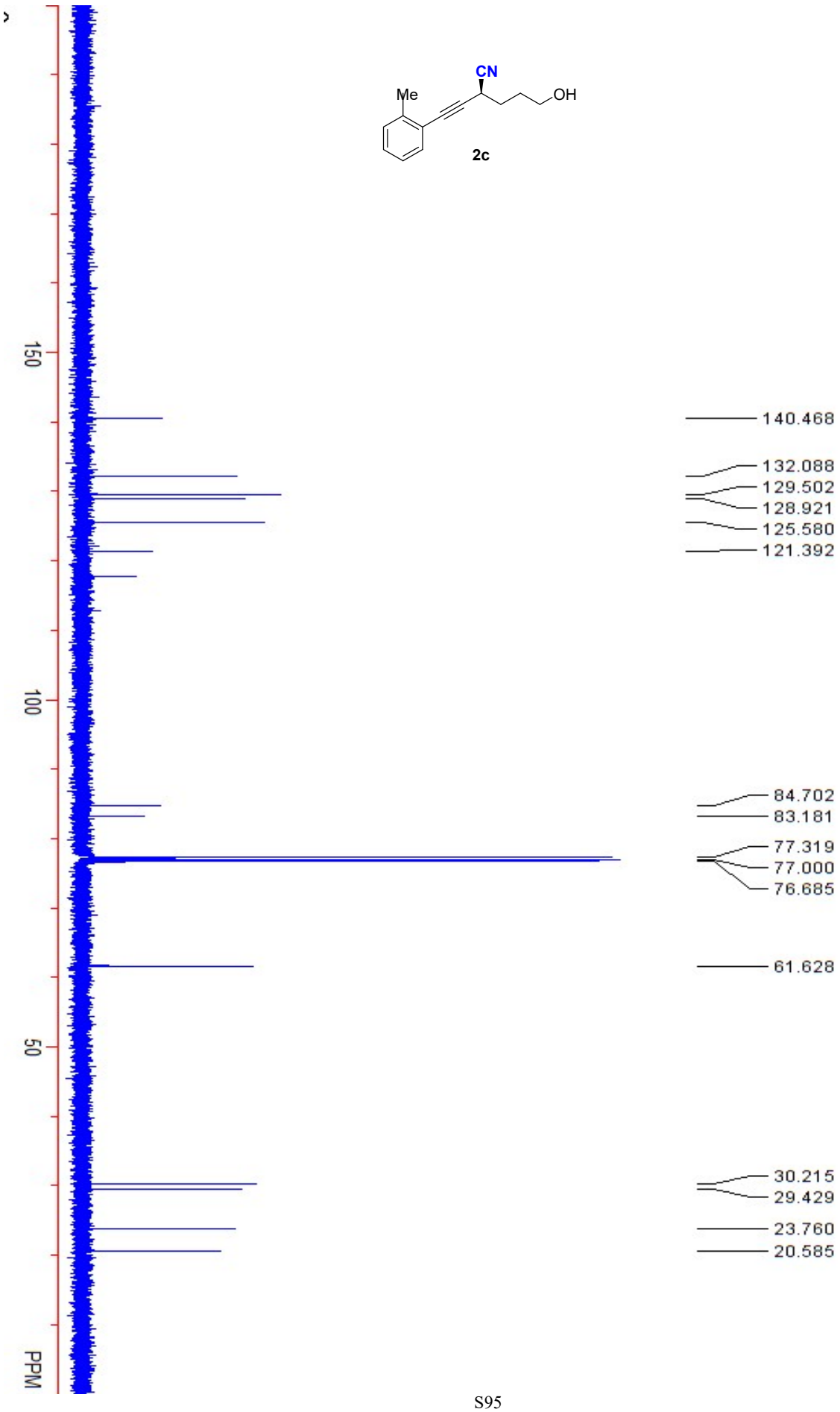
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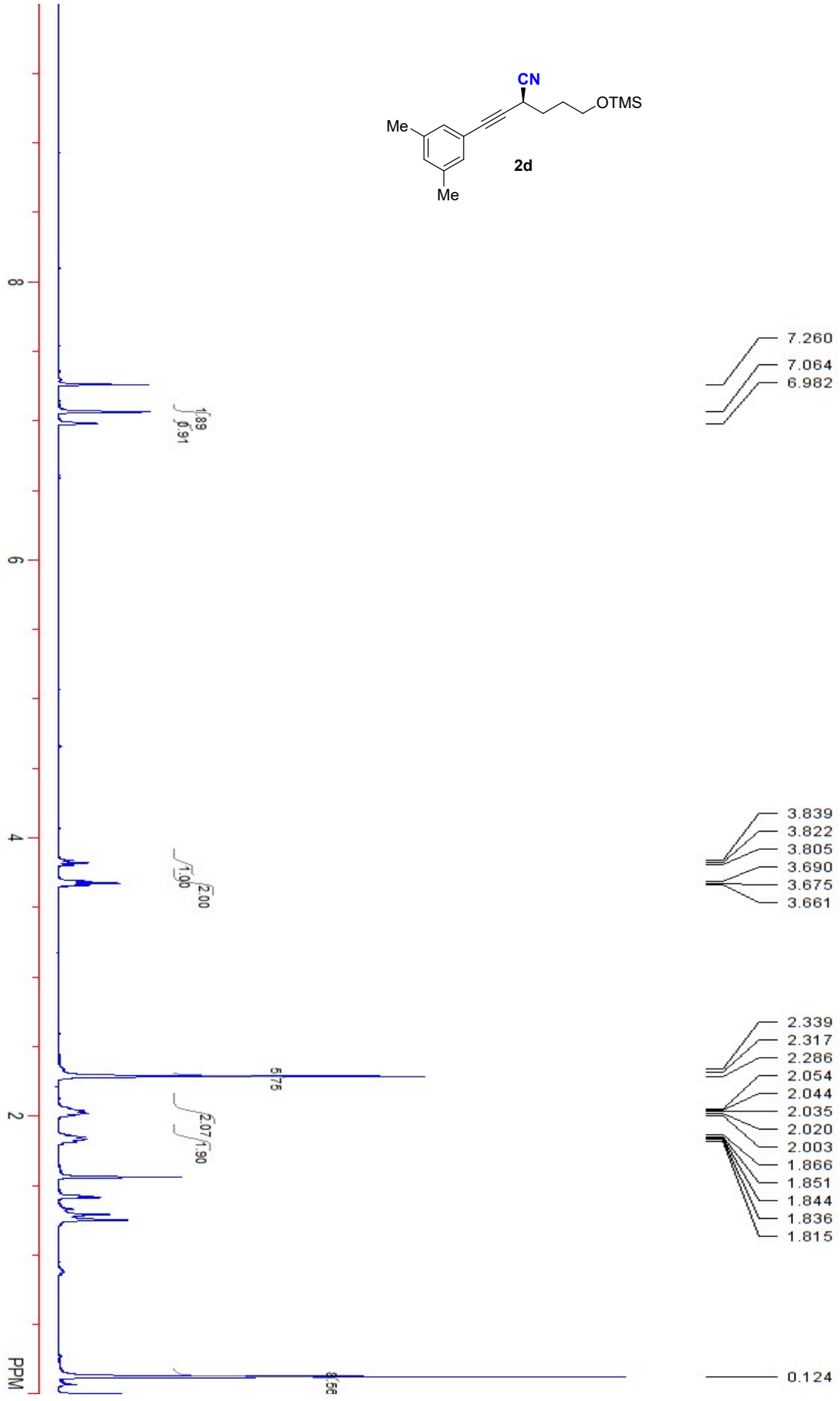
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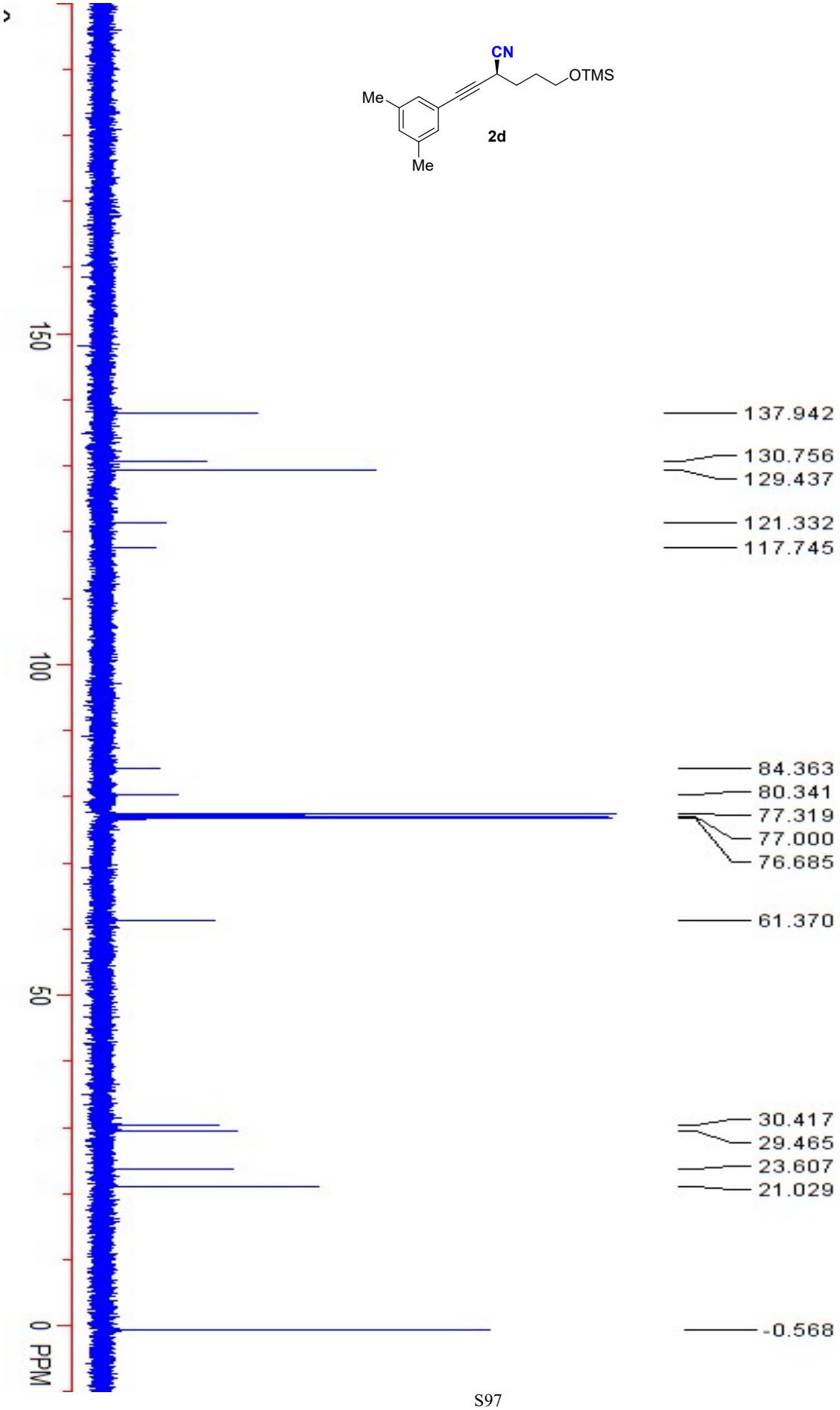
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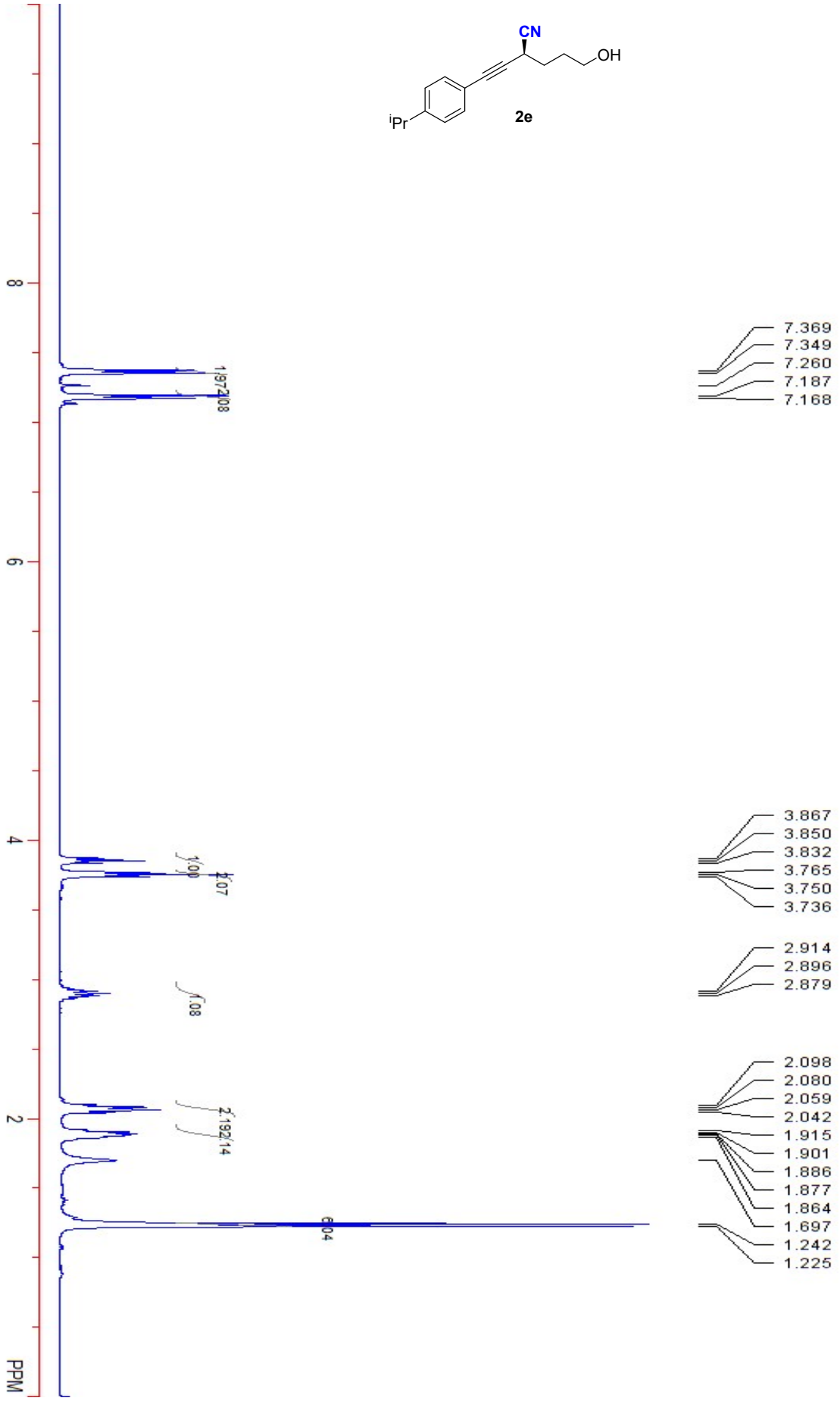
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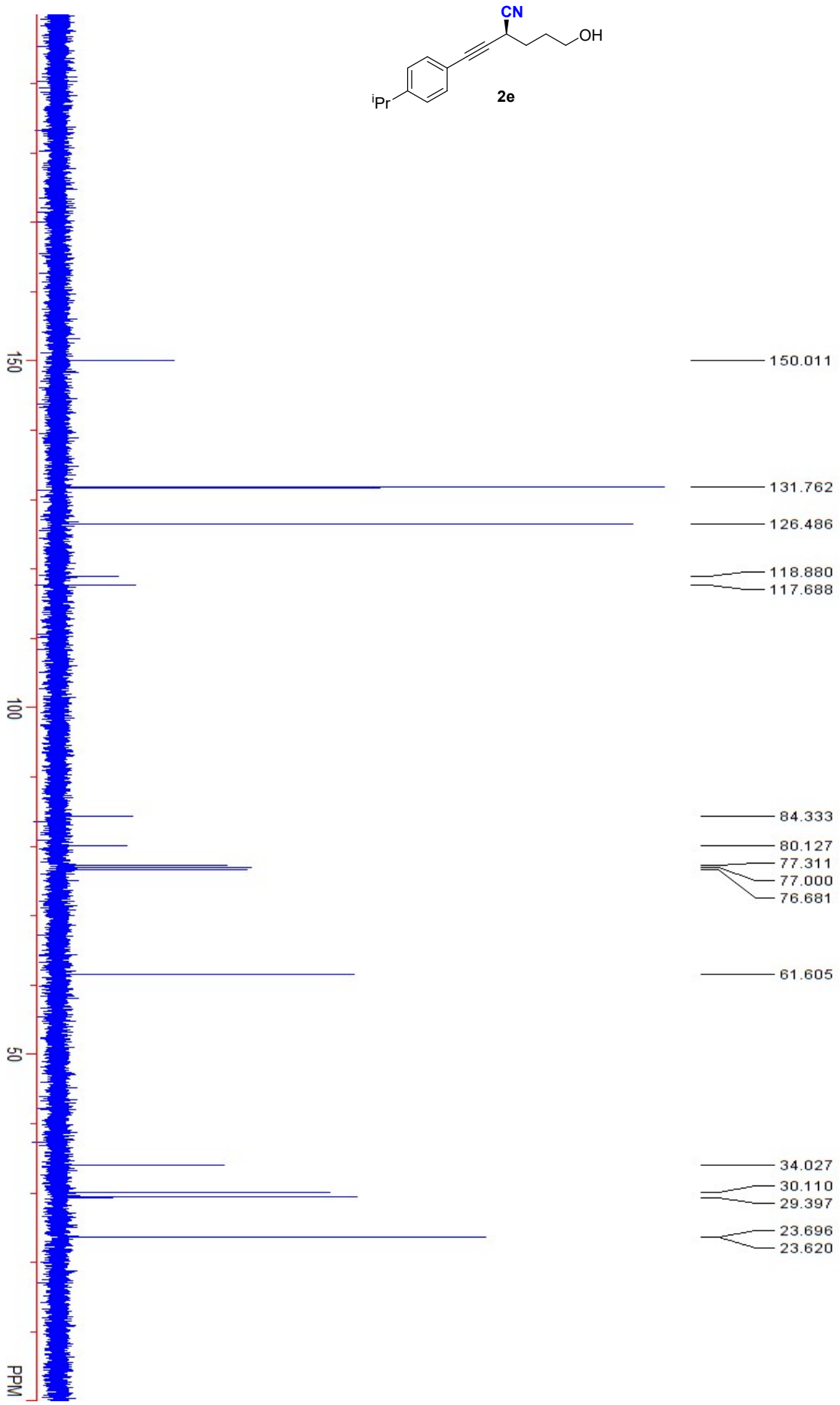
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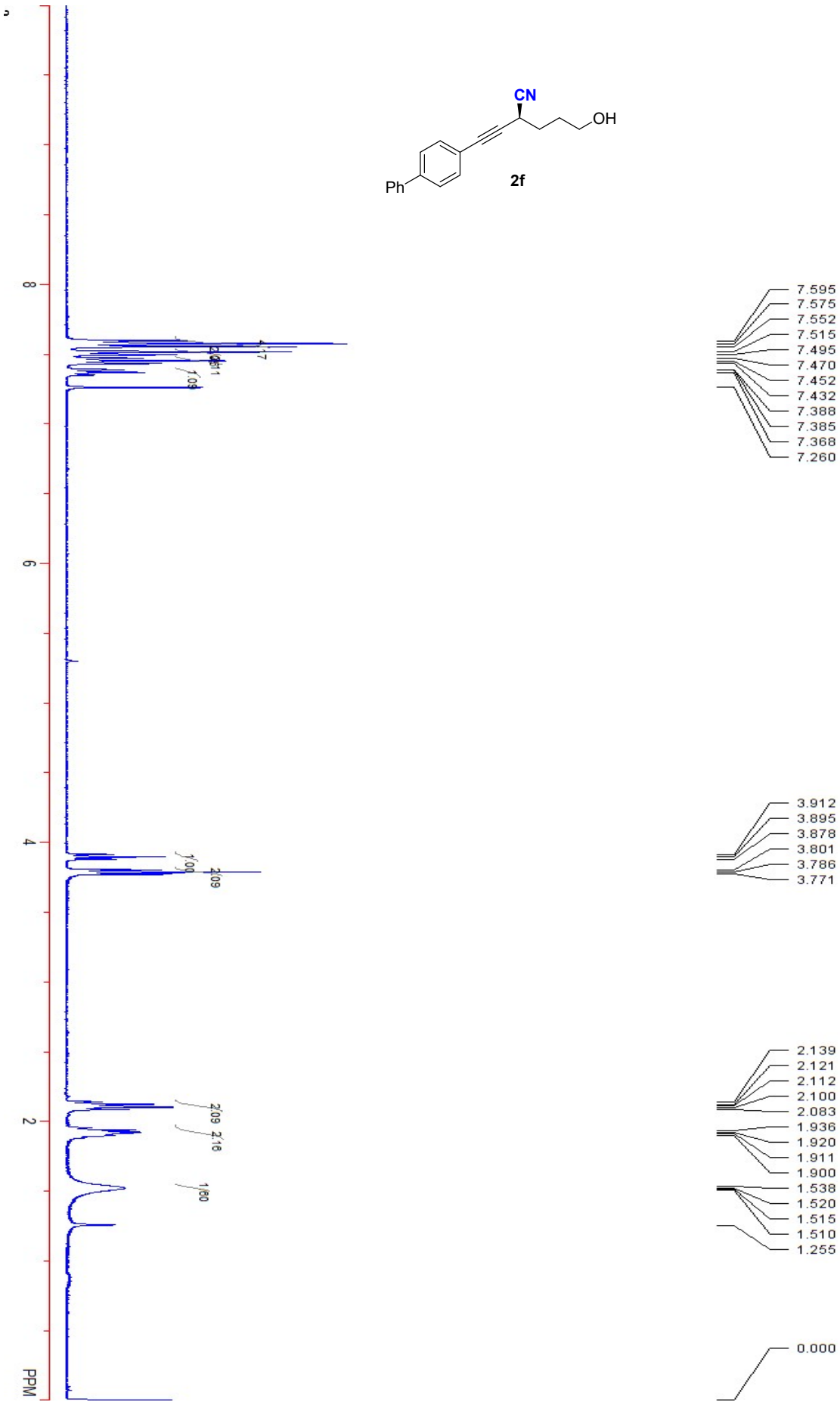
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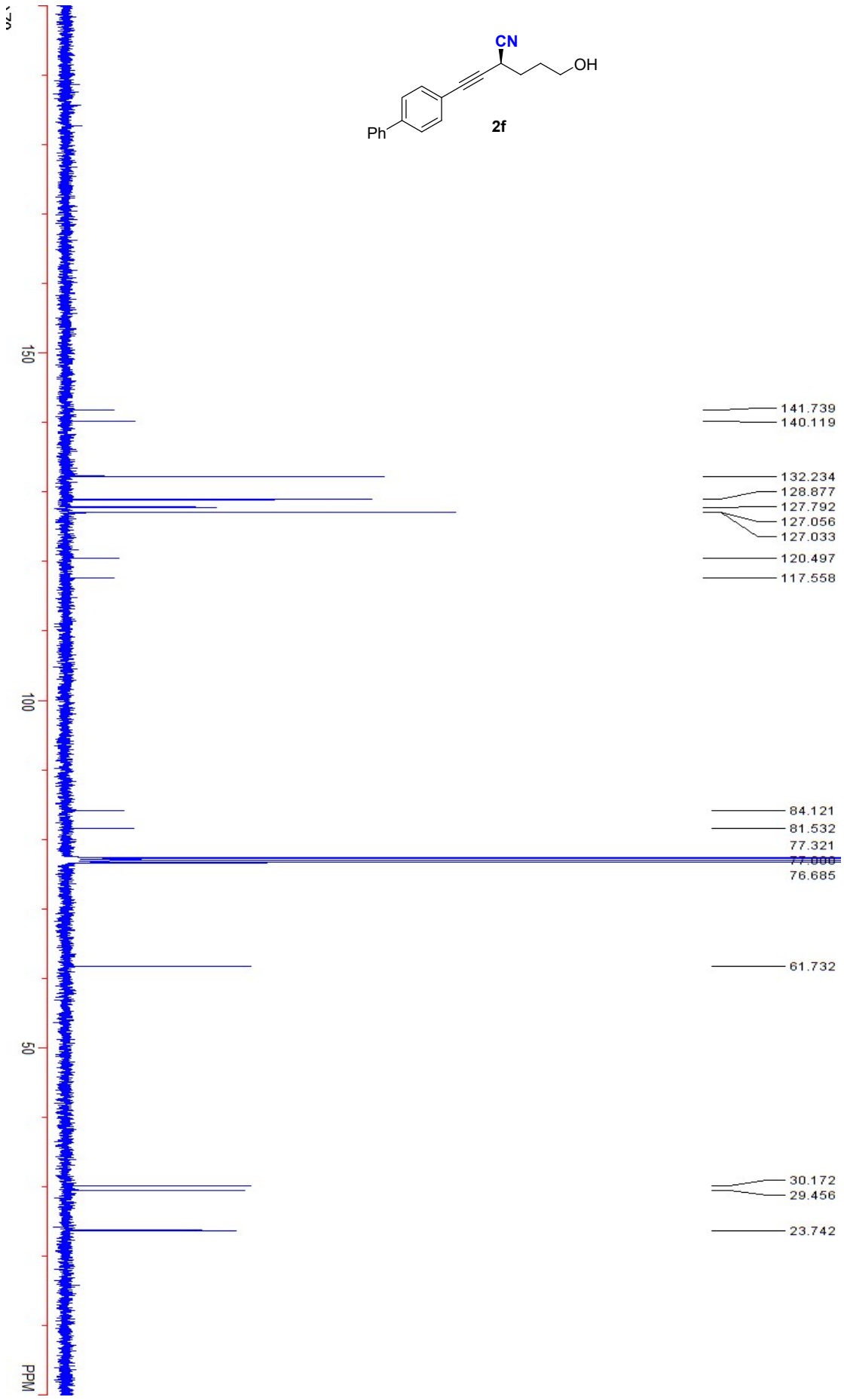
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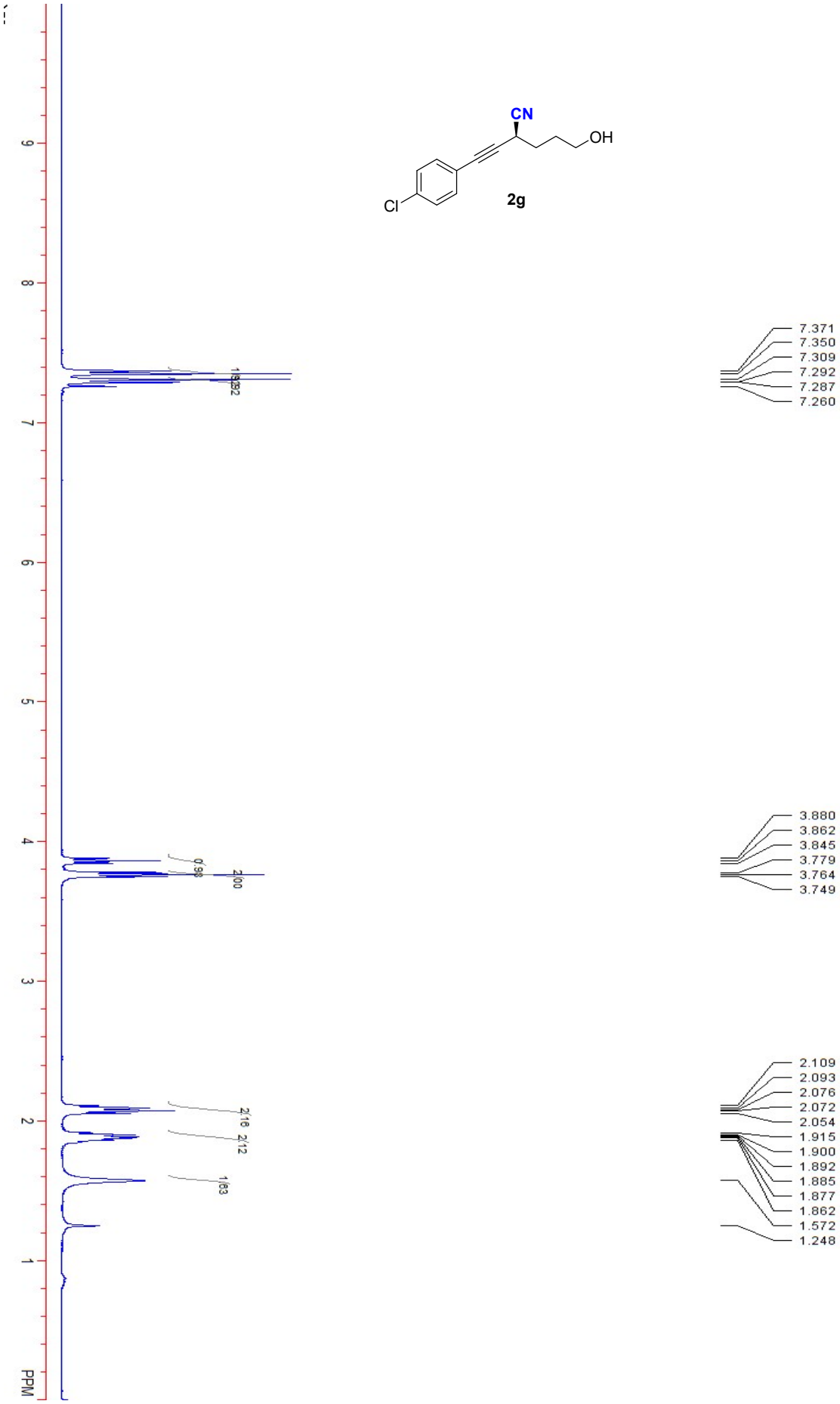
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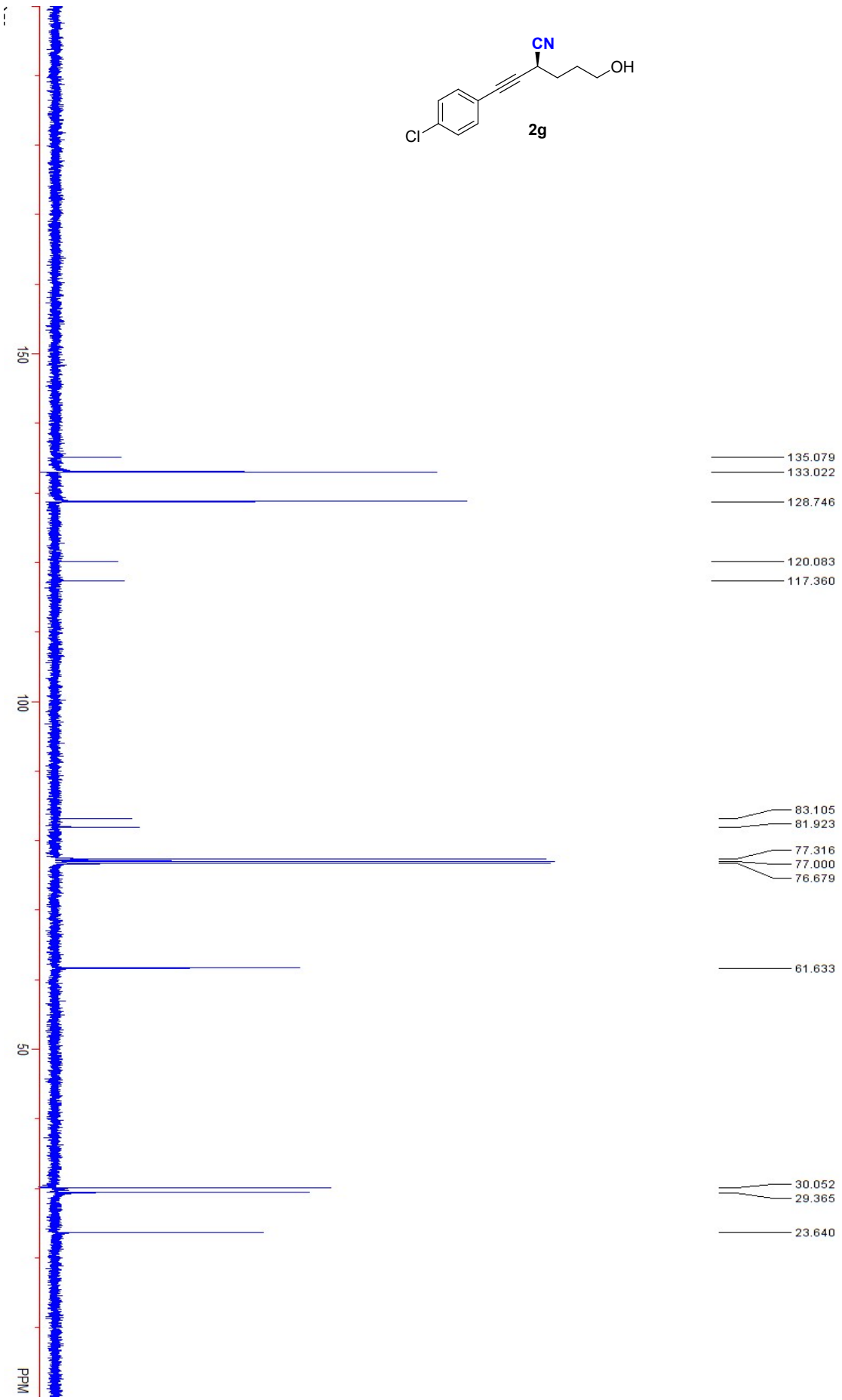
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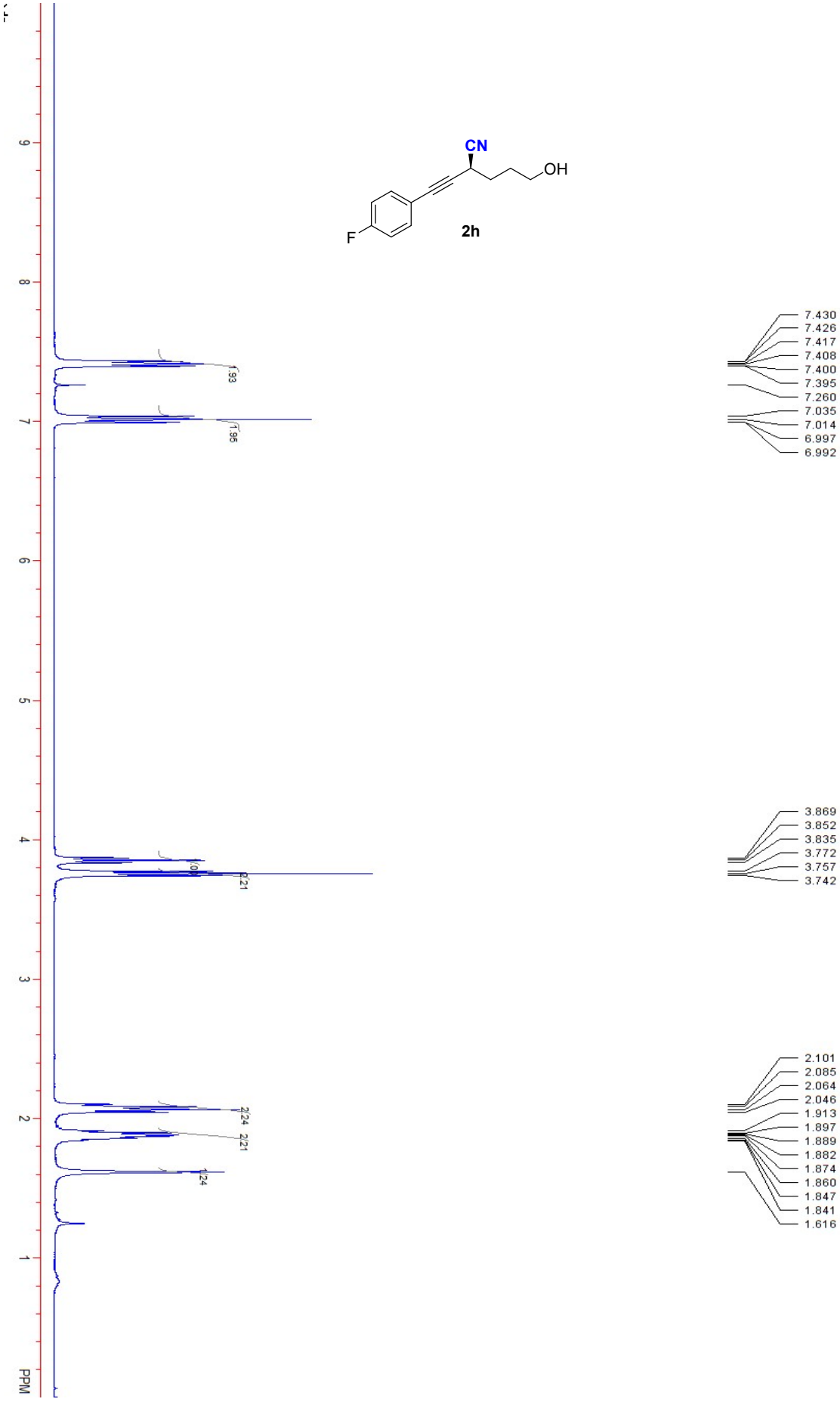
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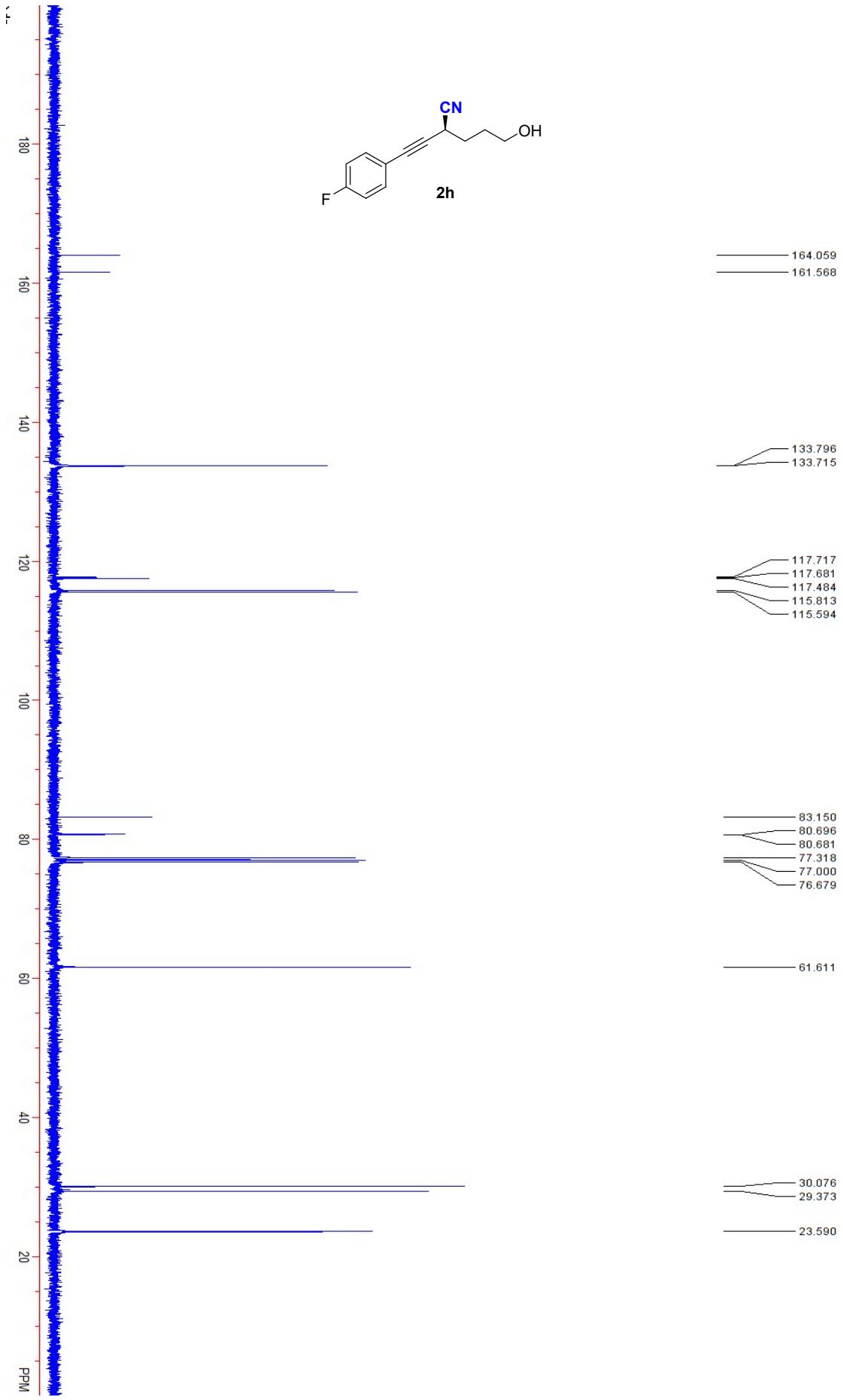
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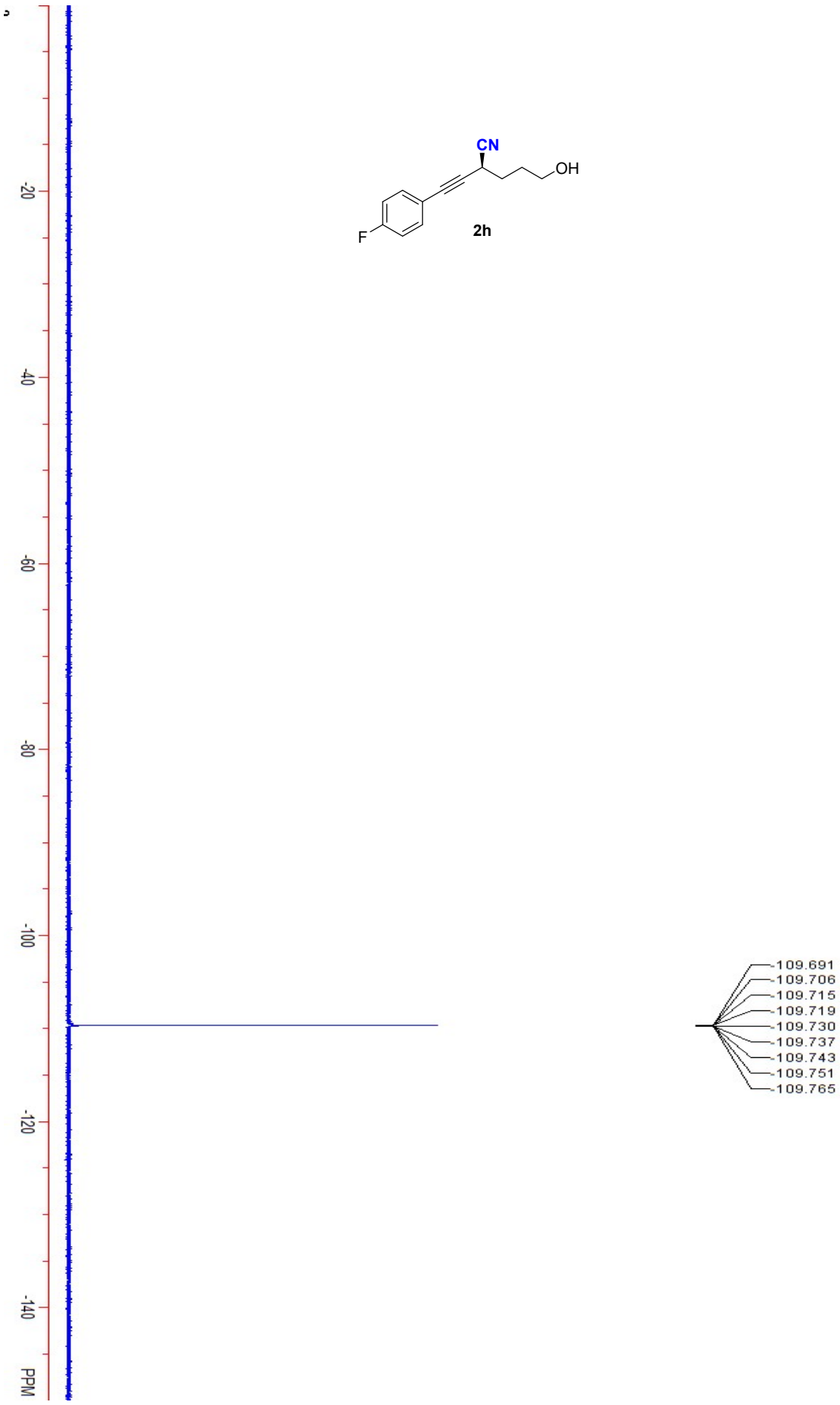
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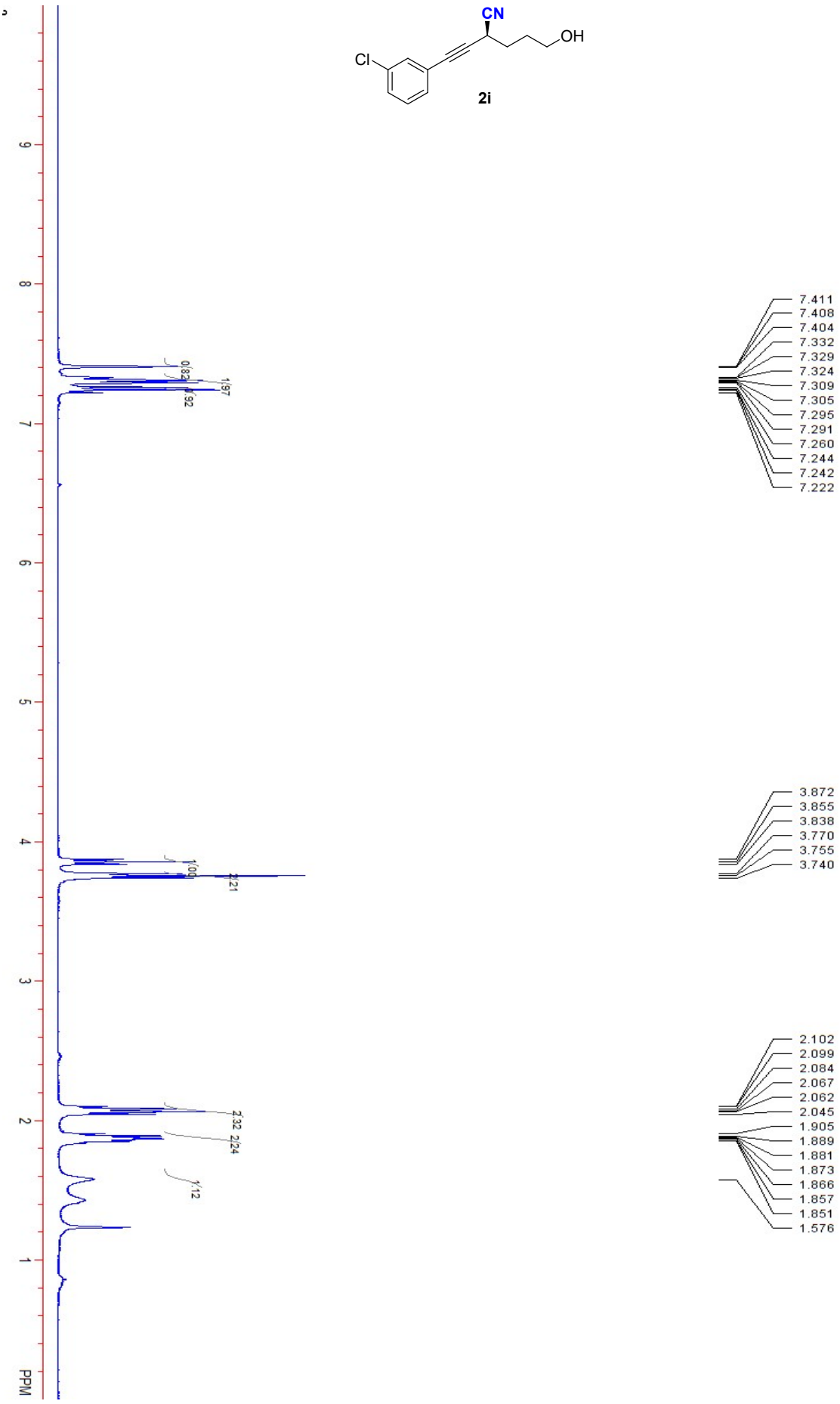
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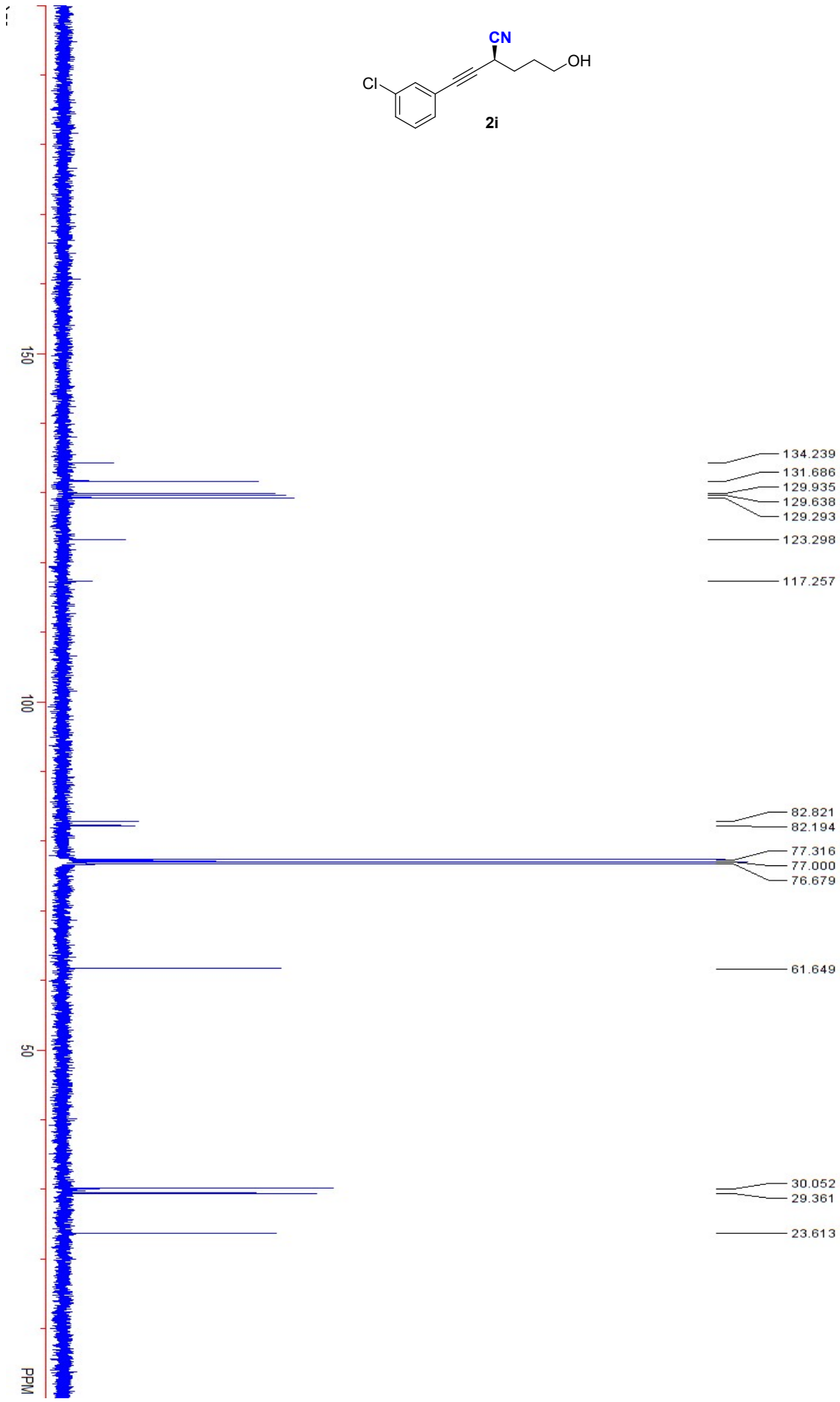
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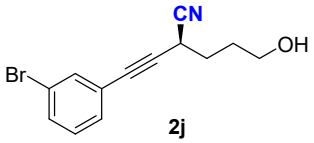
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OH
Br

2j

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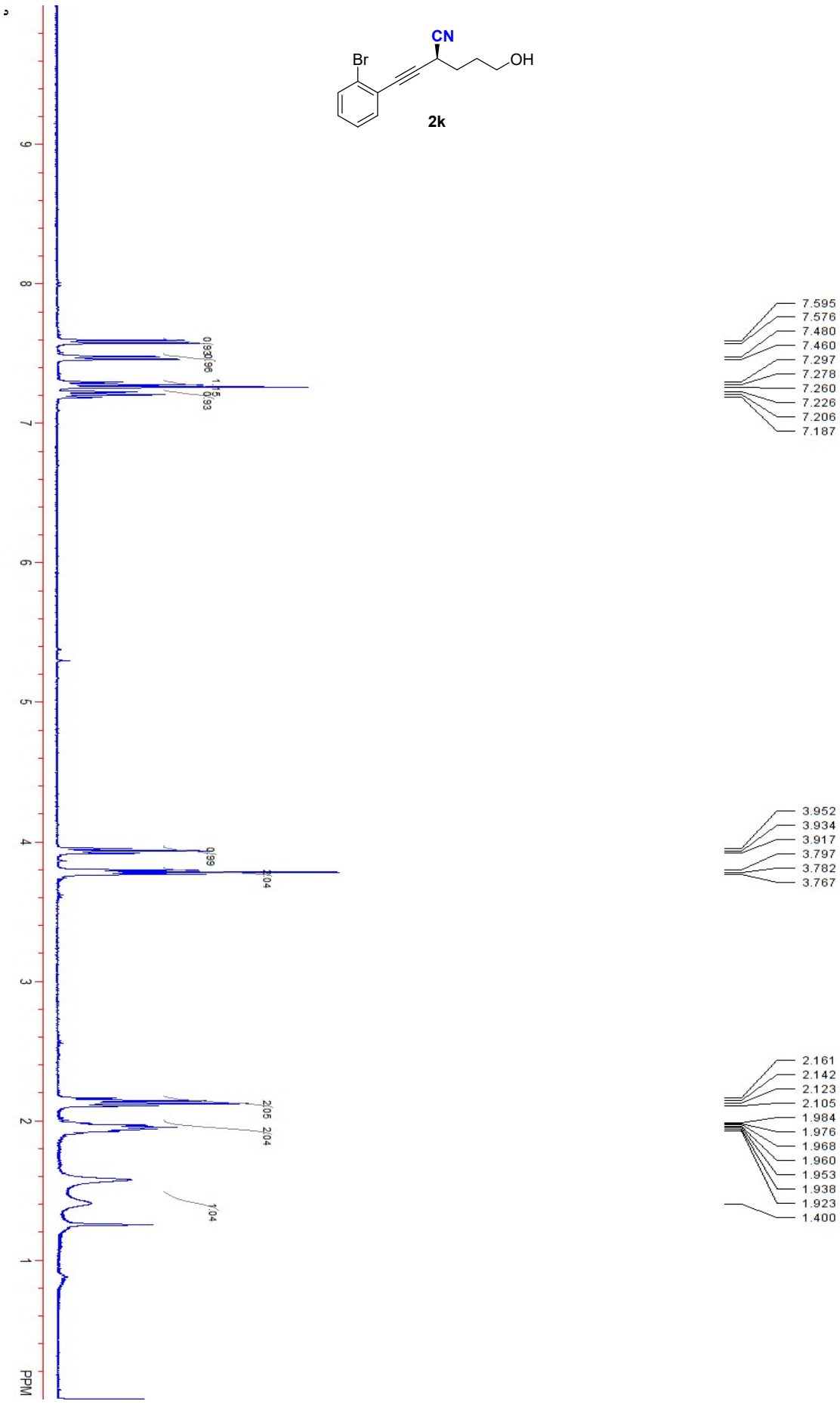
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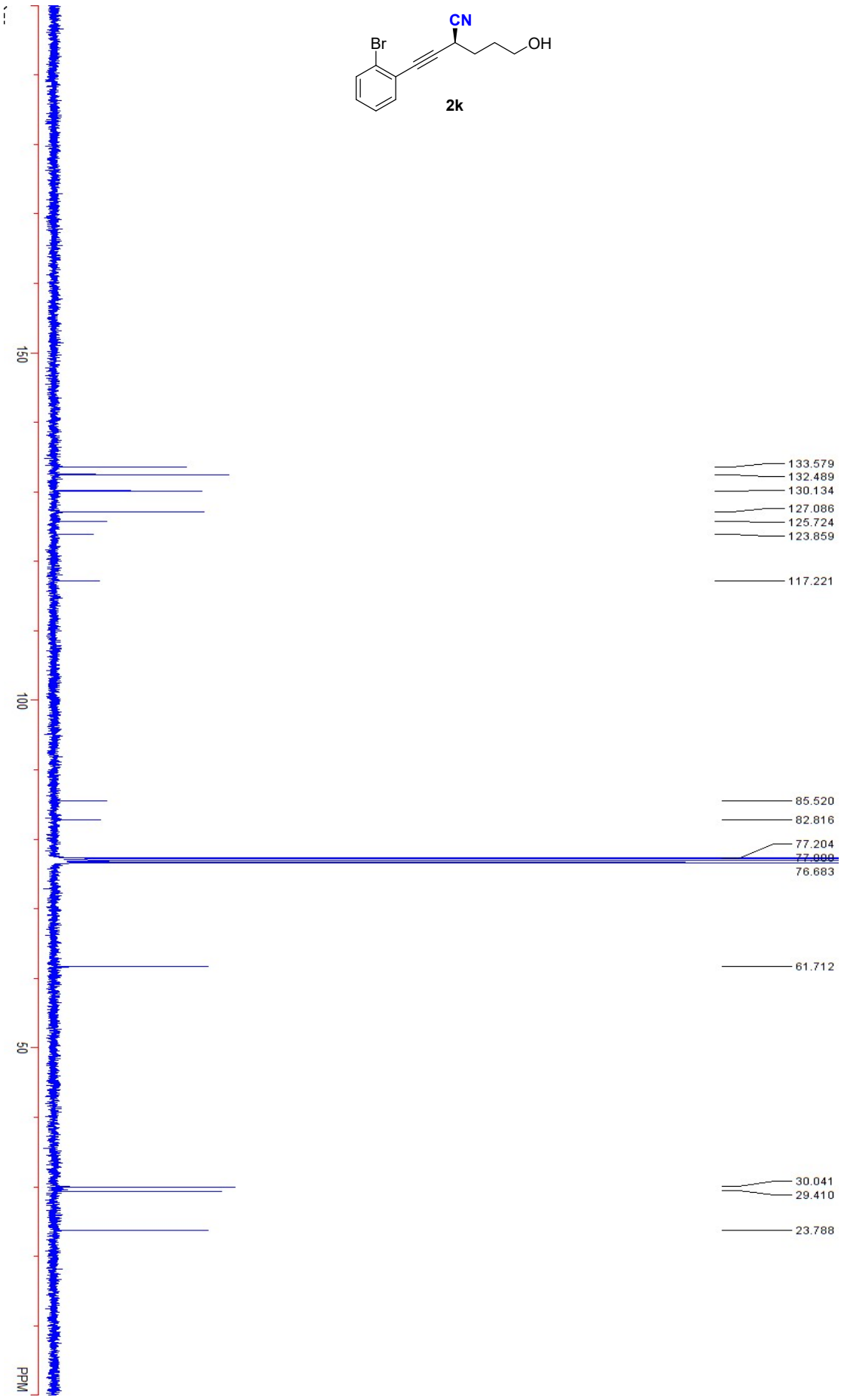
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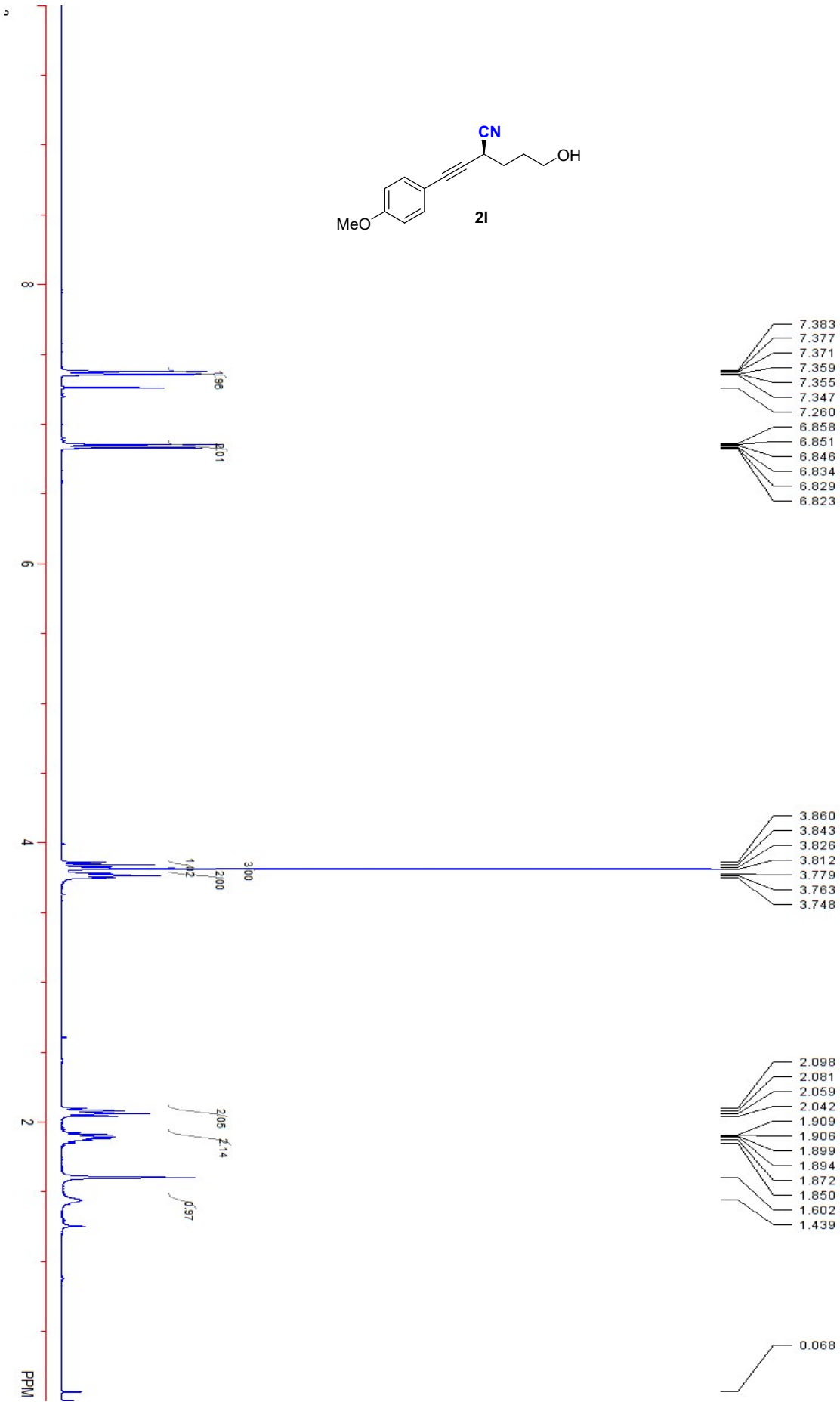
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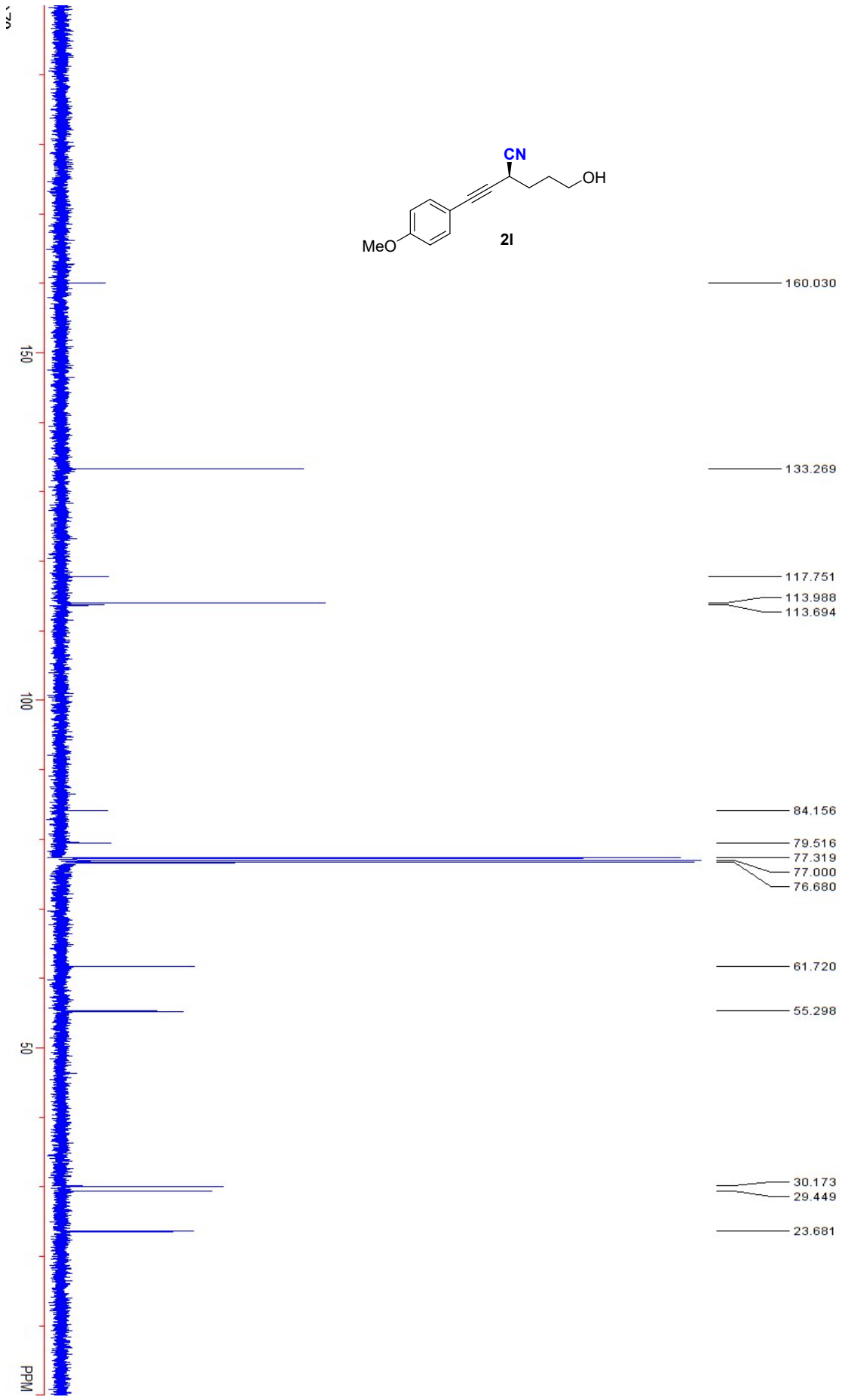
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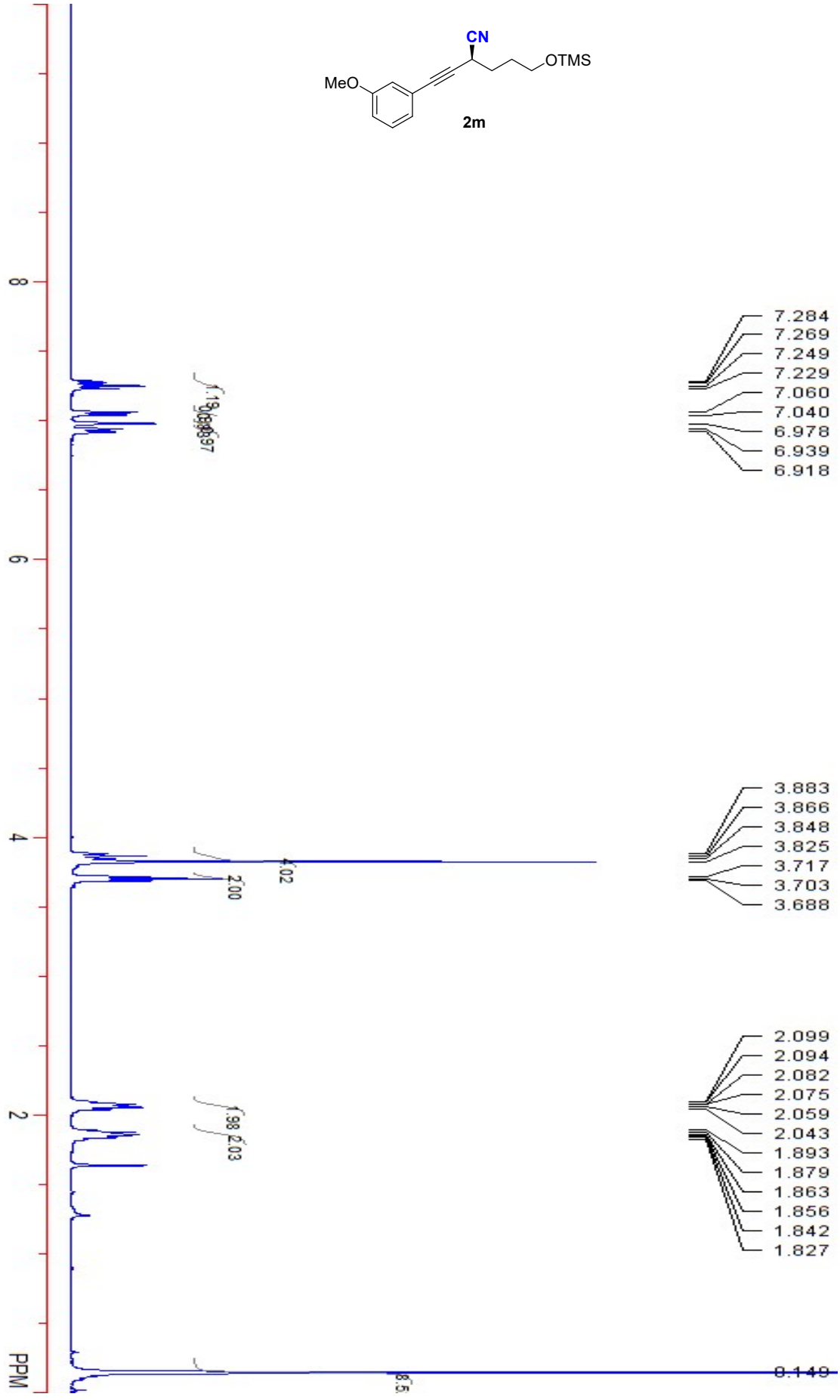
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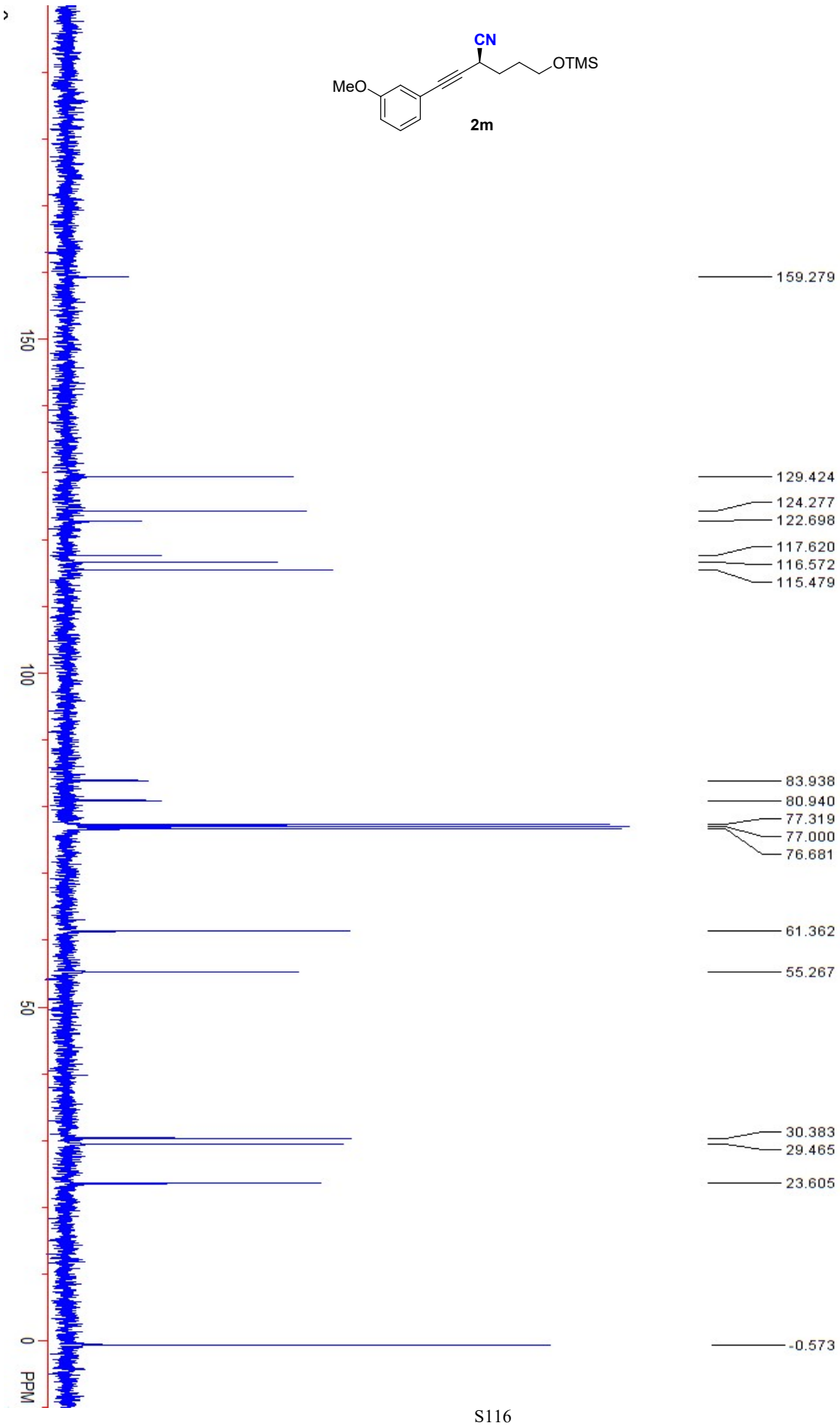
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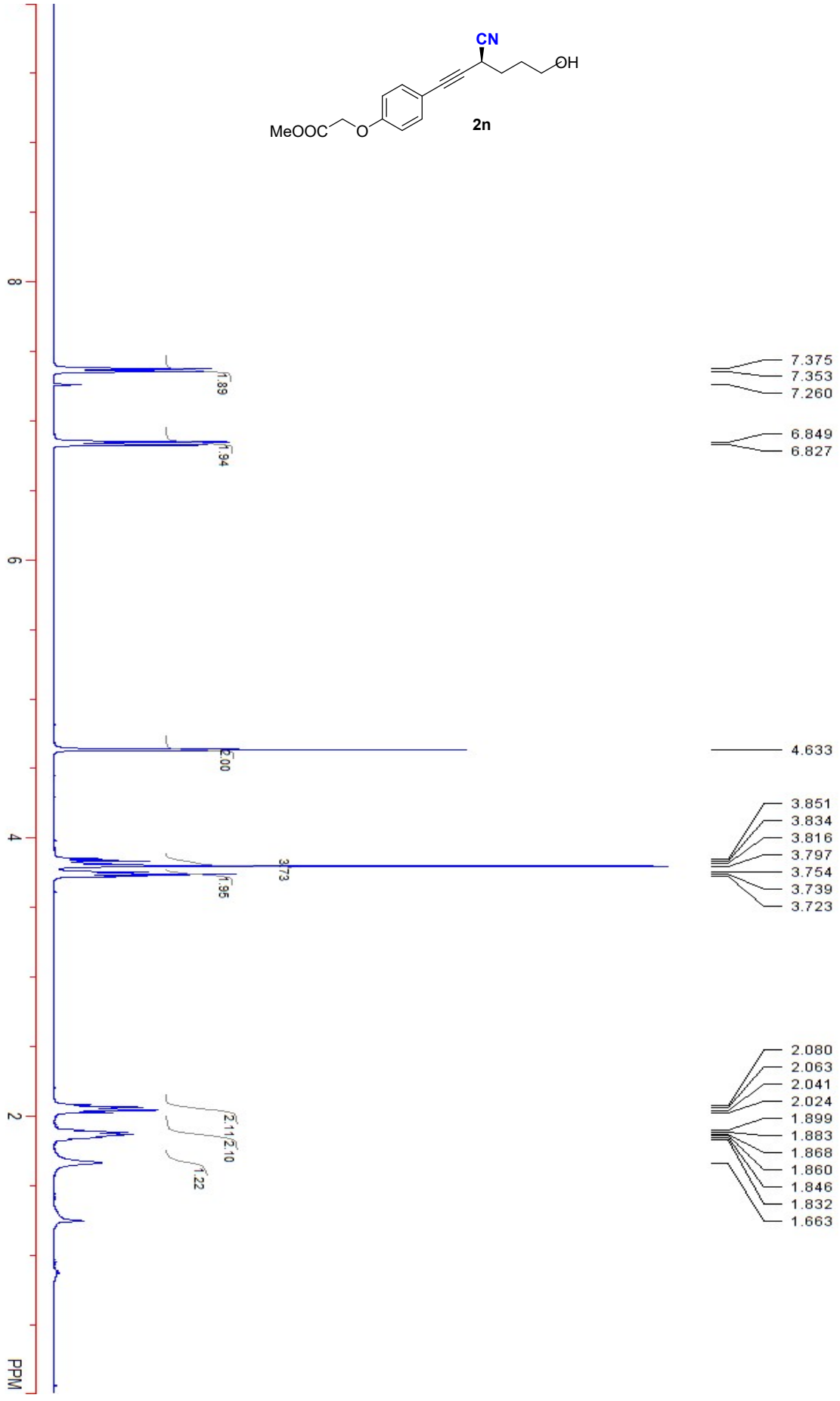
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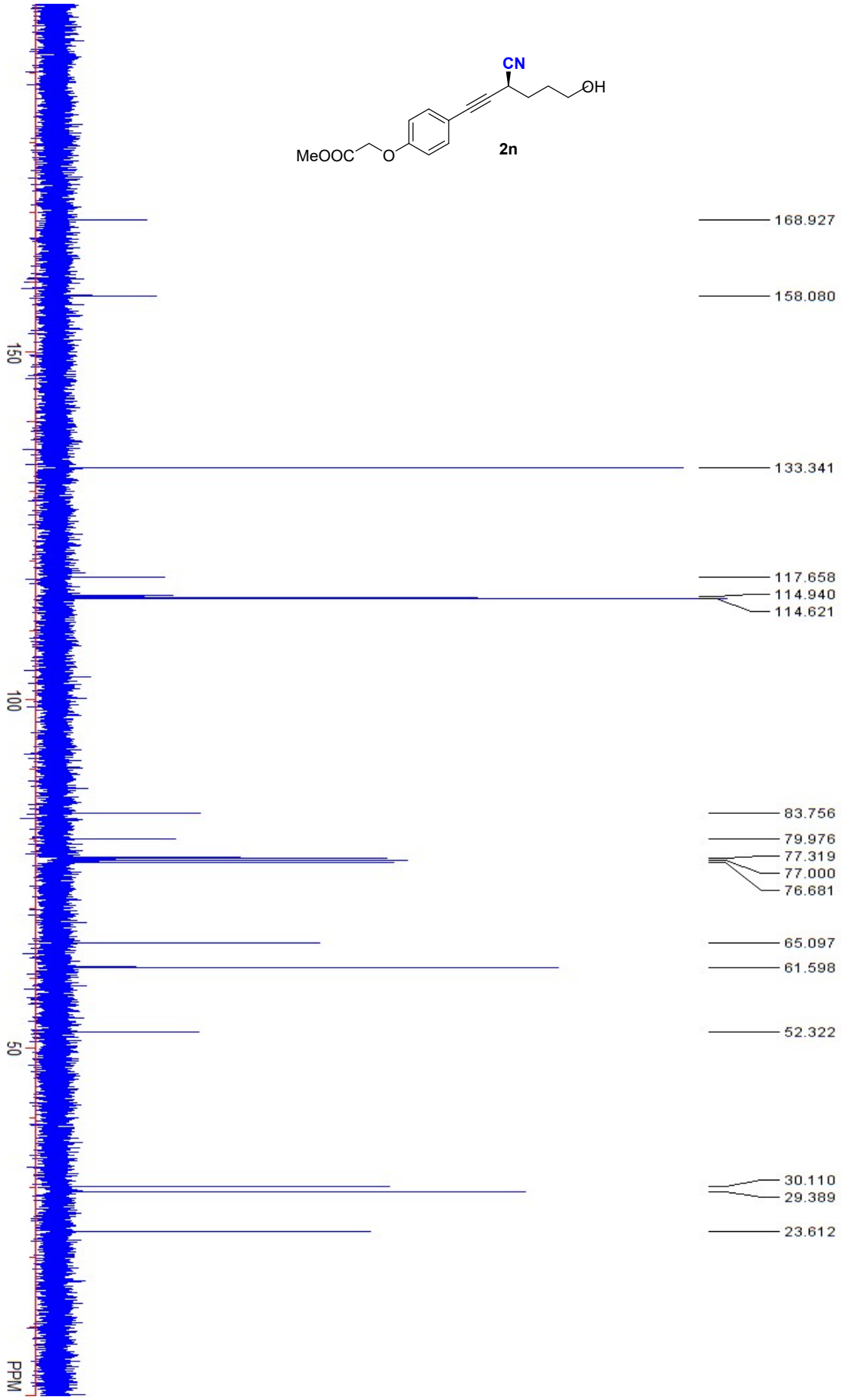
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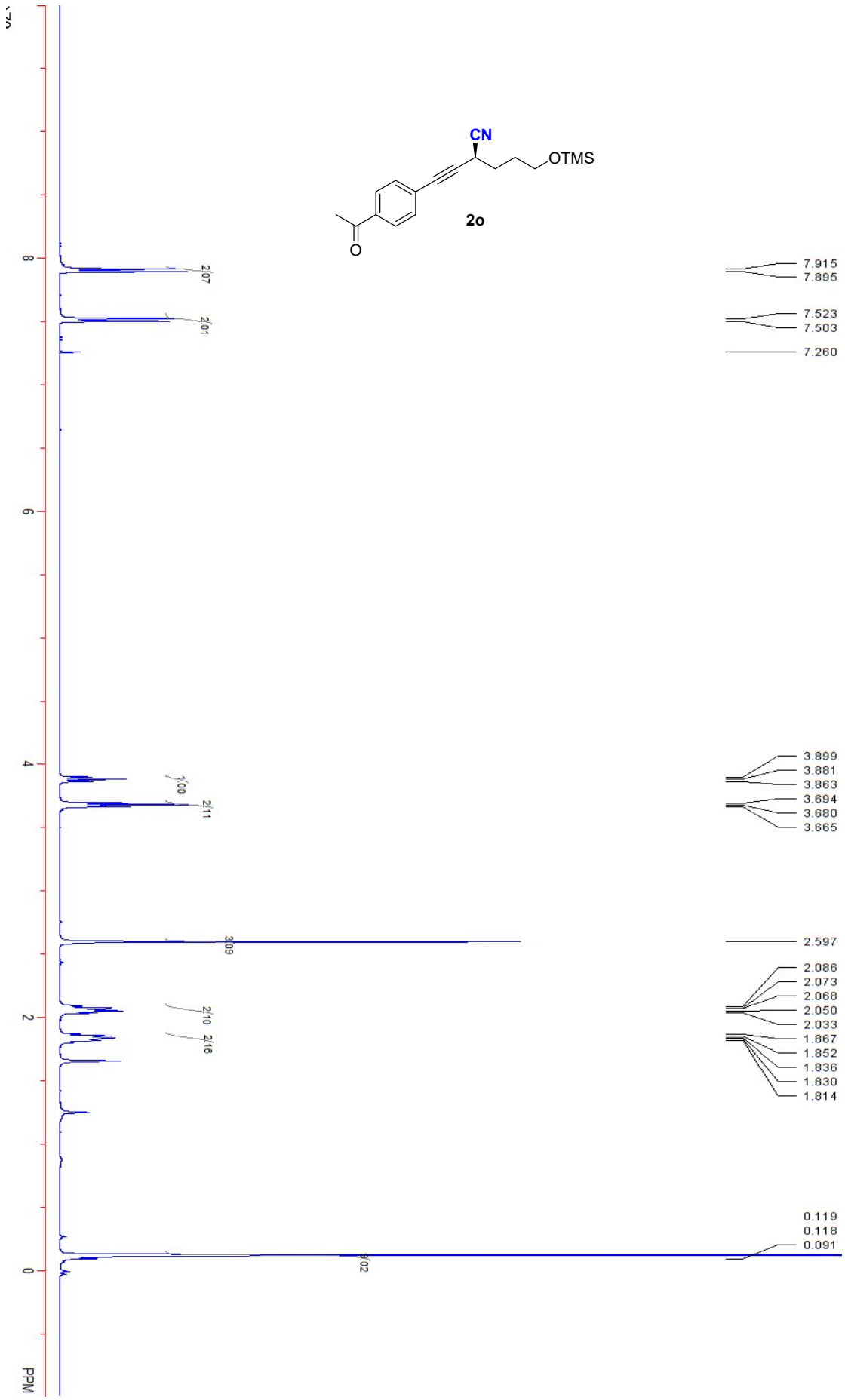
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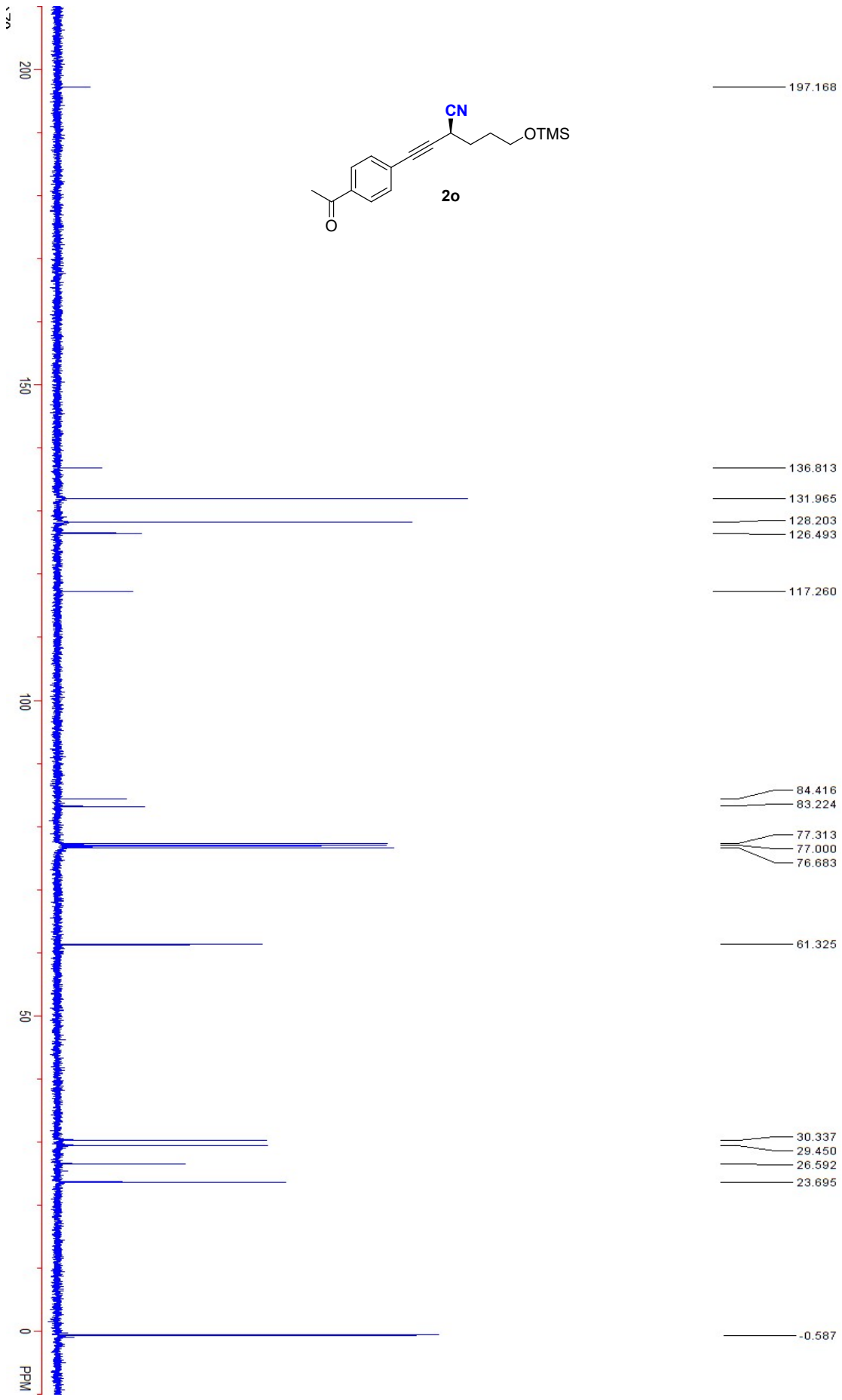
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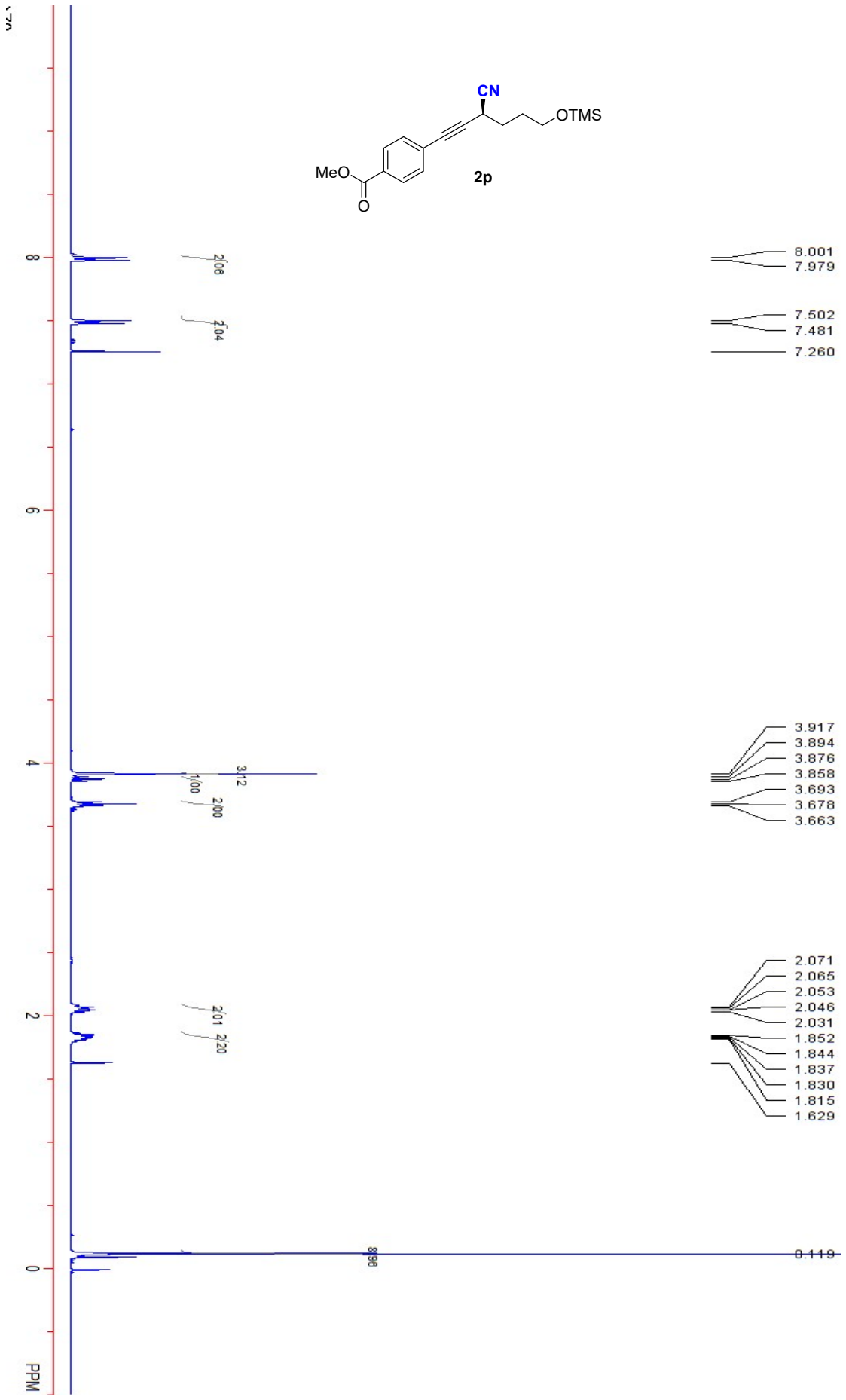
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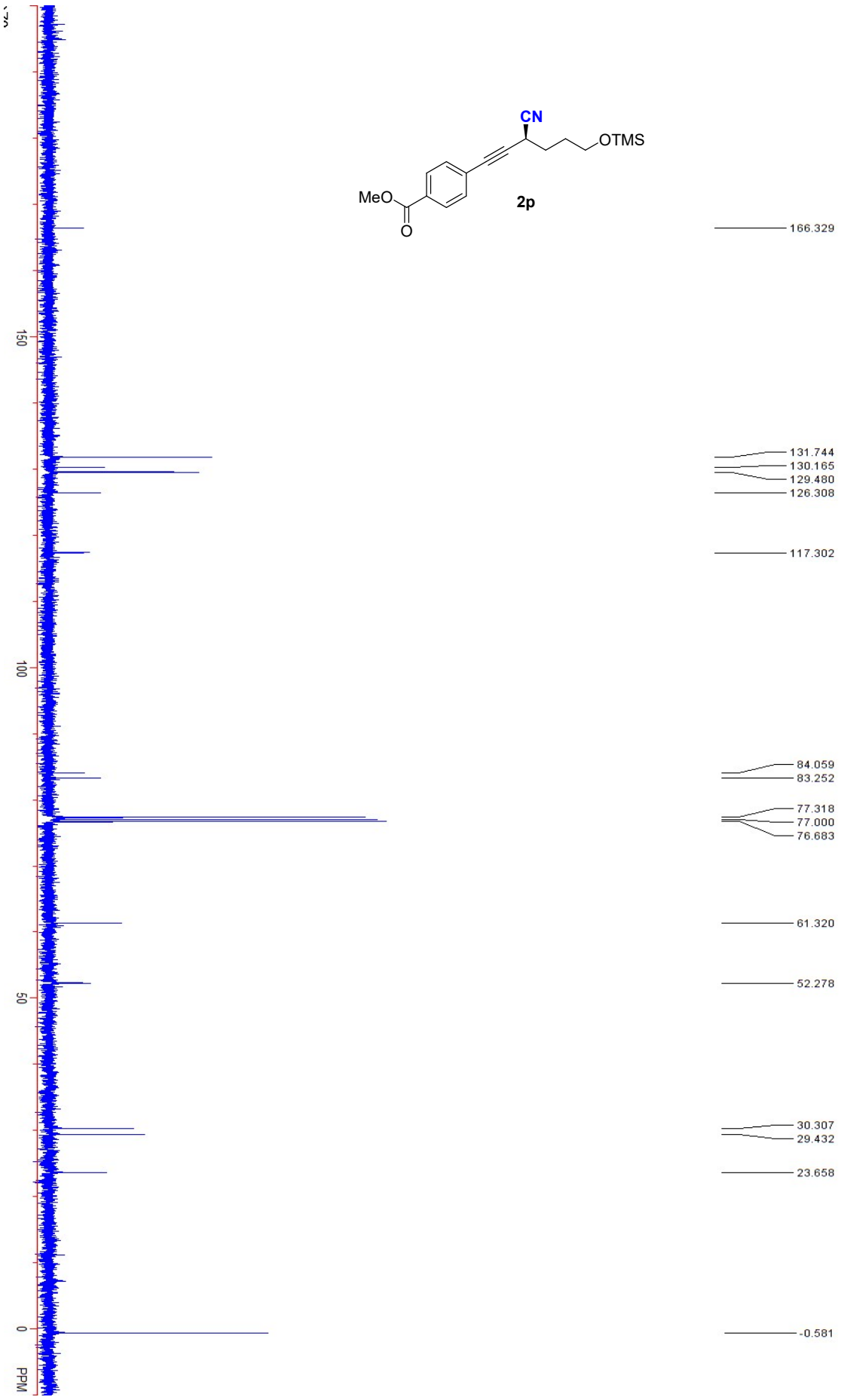
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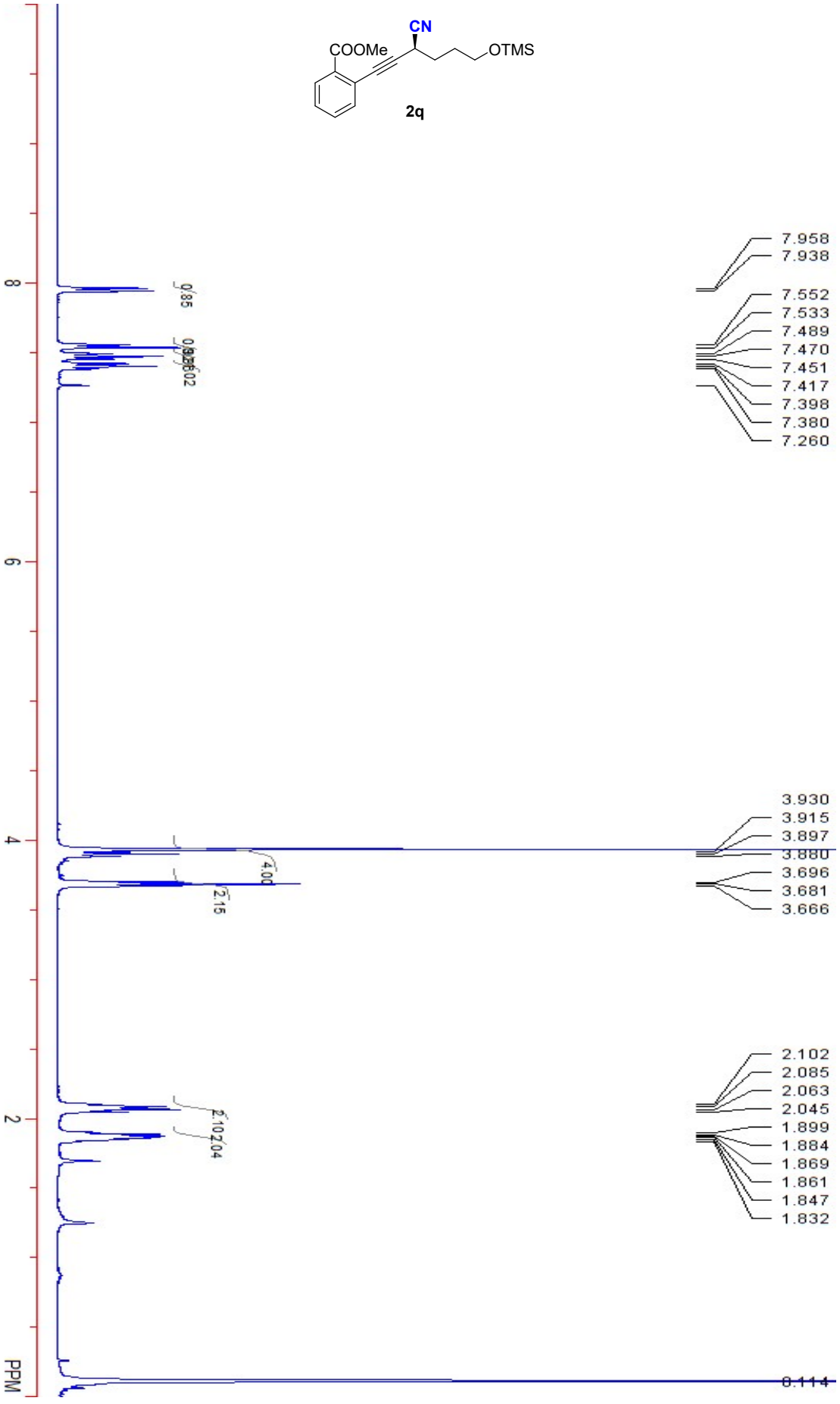
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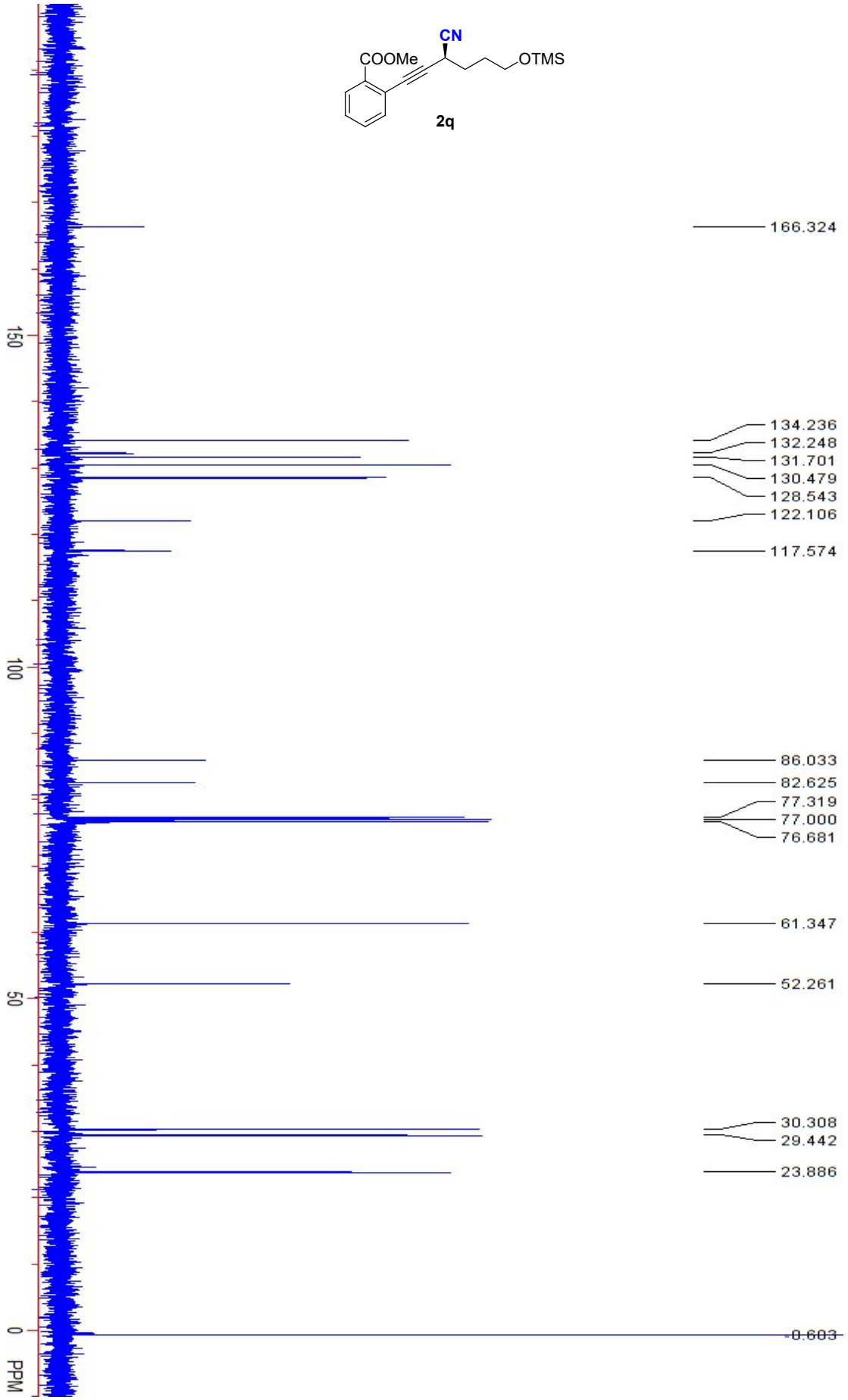
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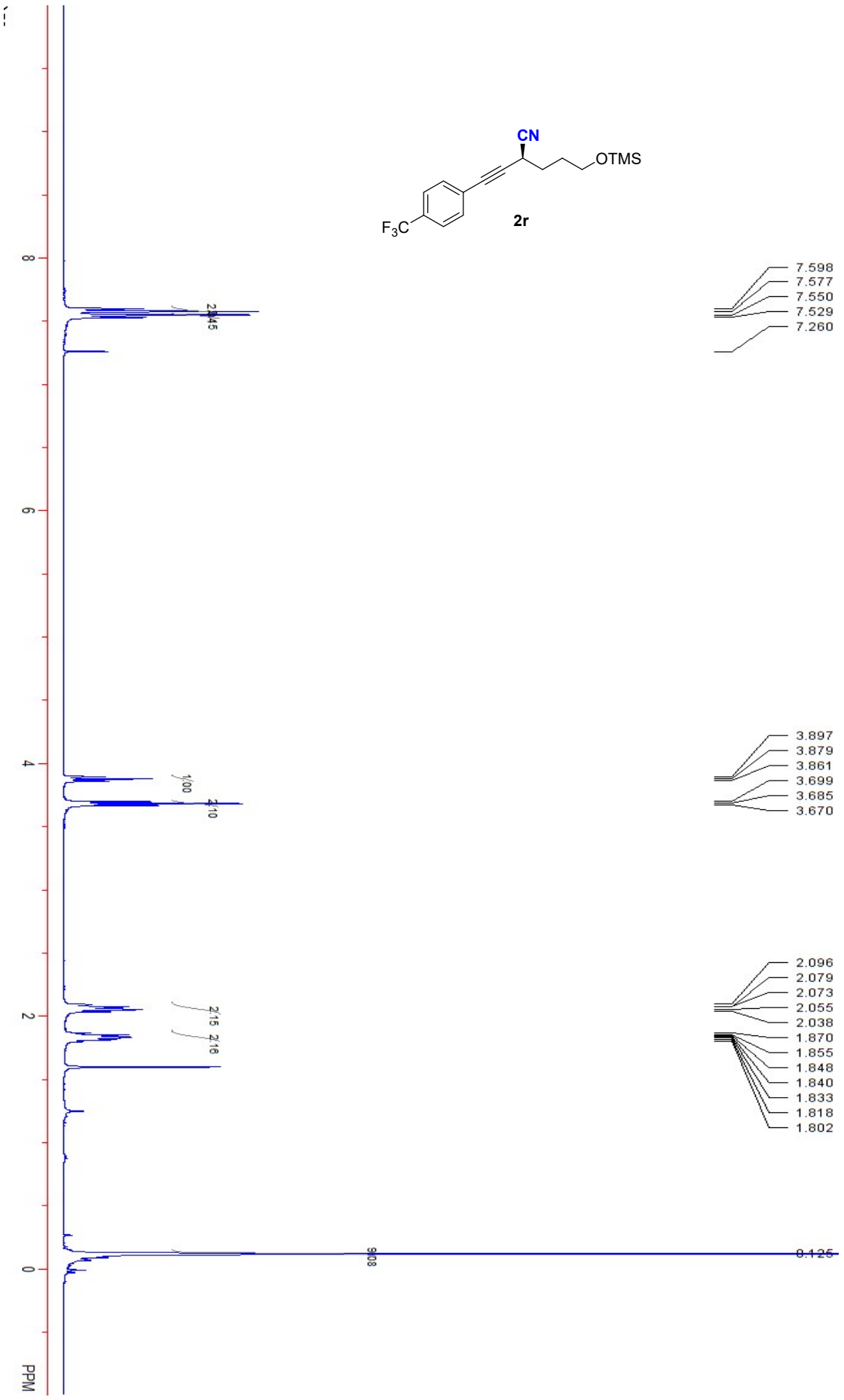
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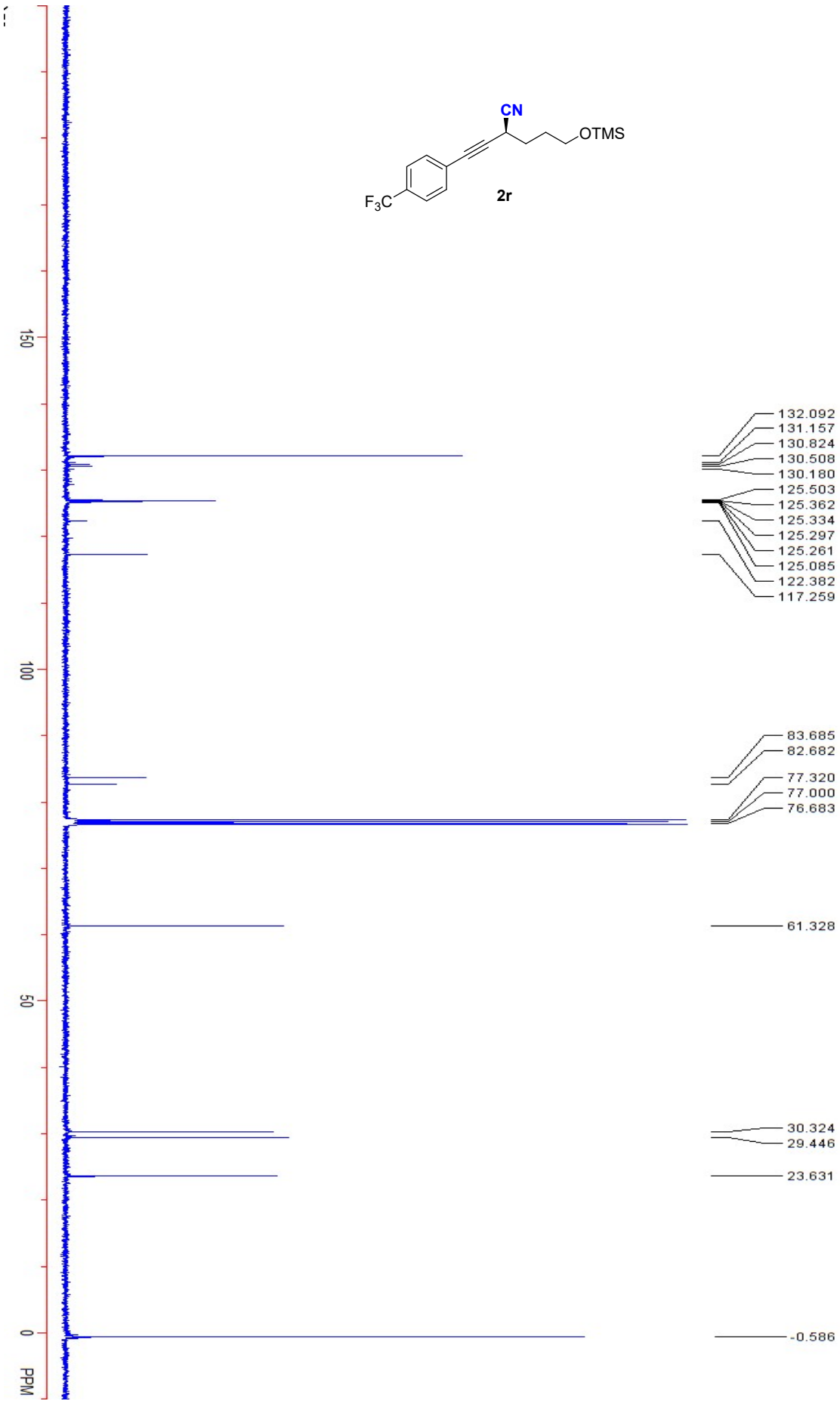
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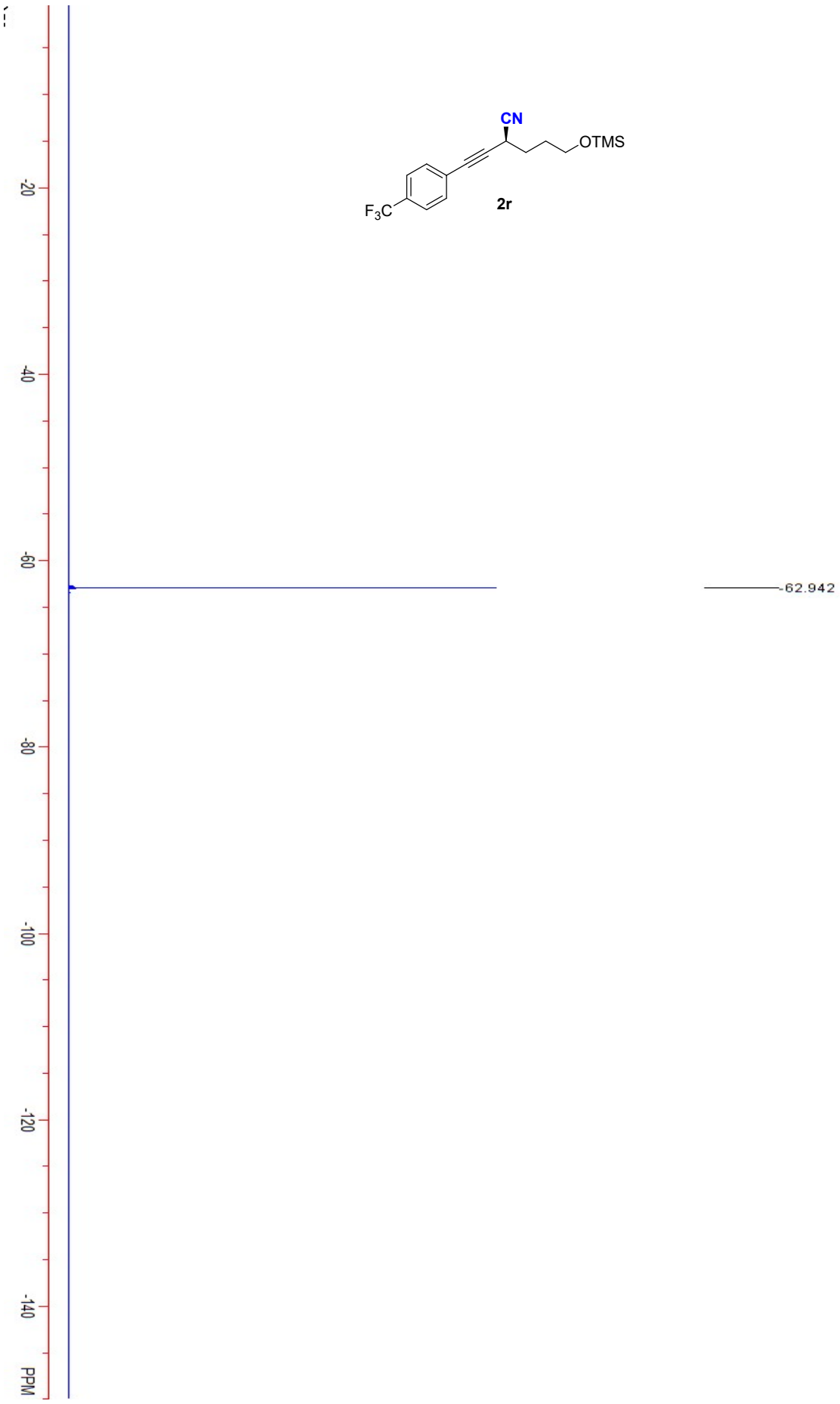
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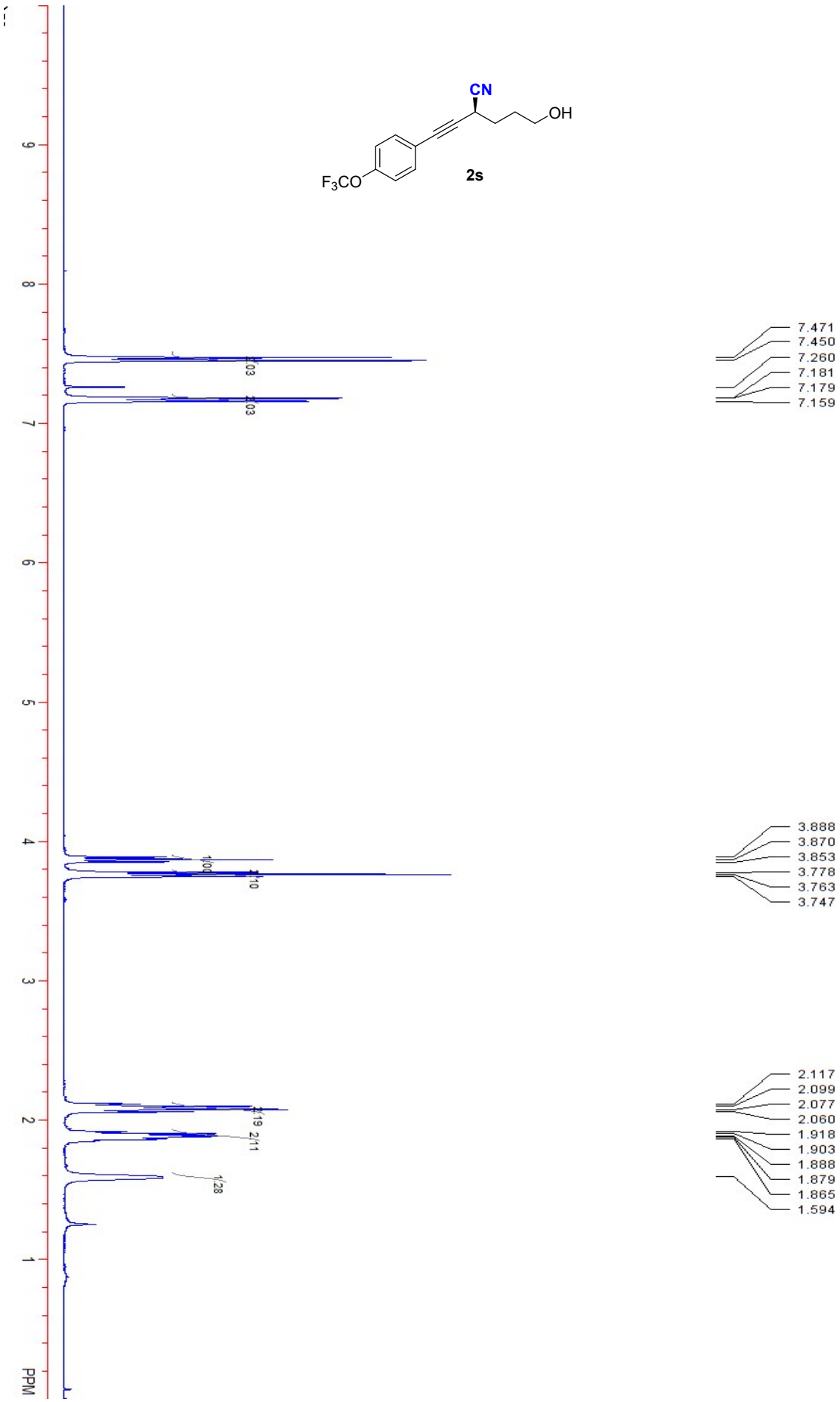
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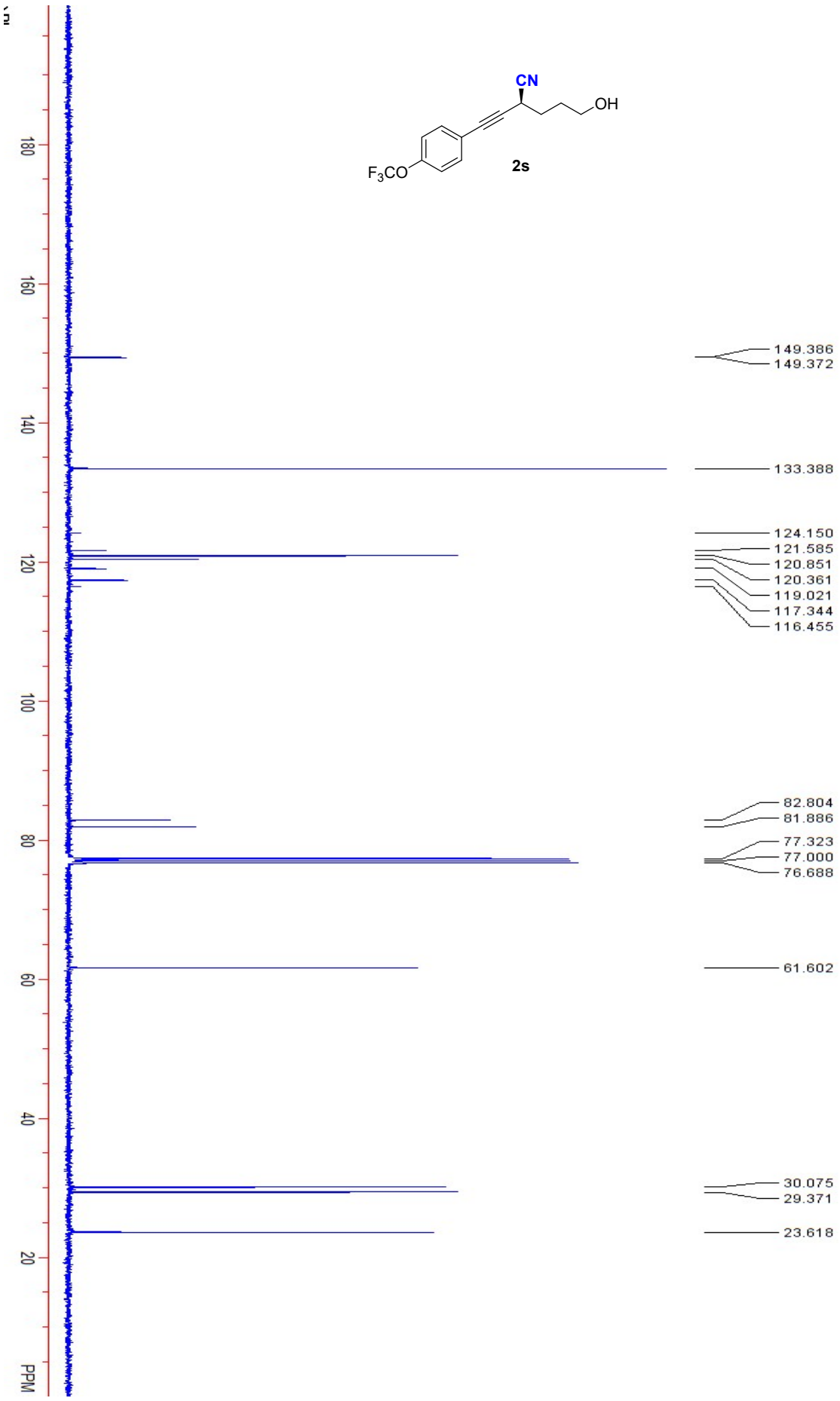
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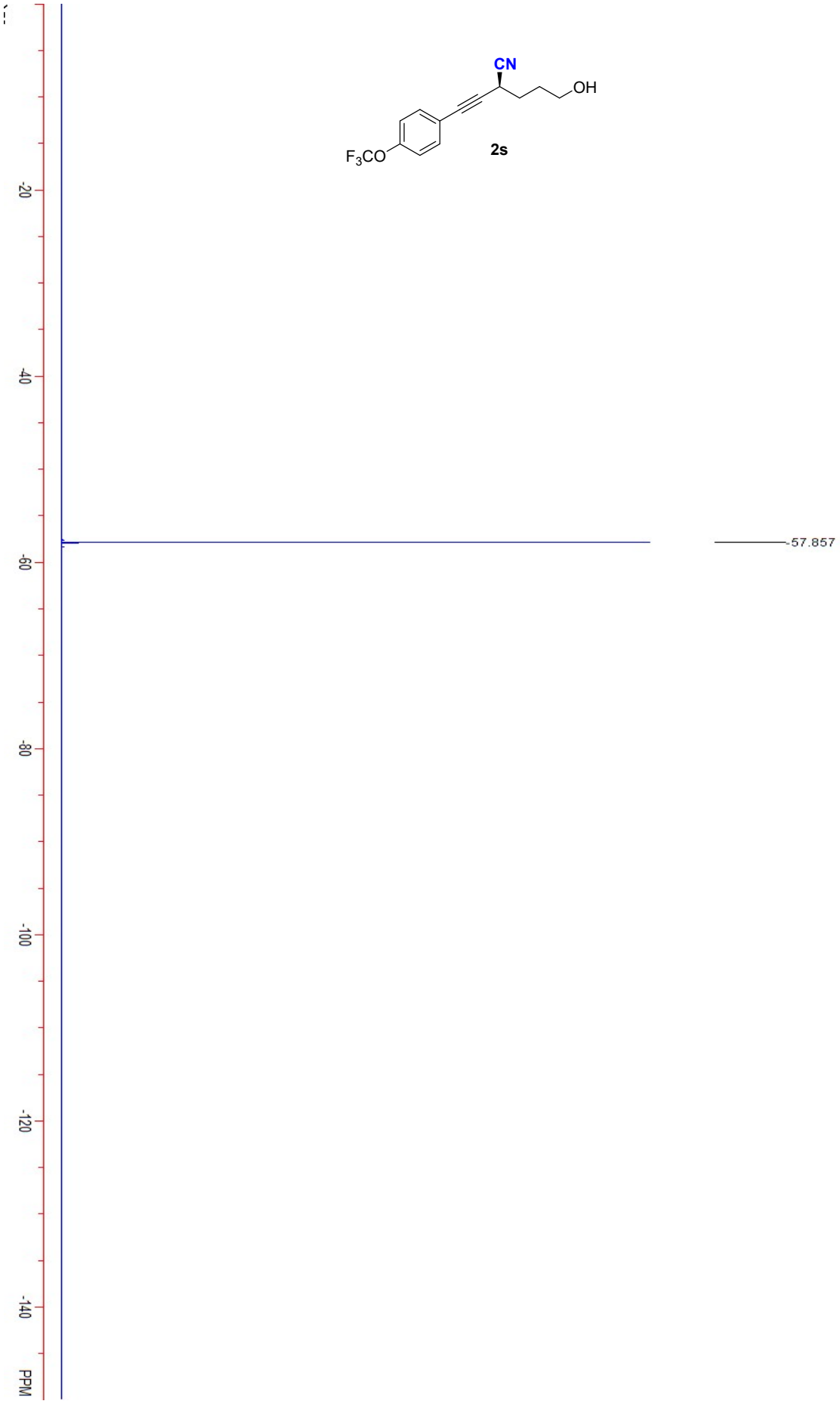
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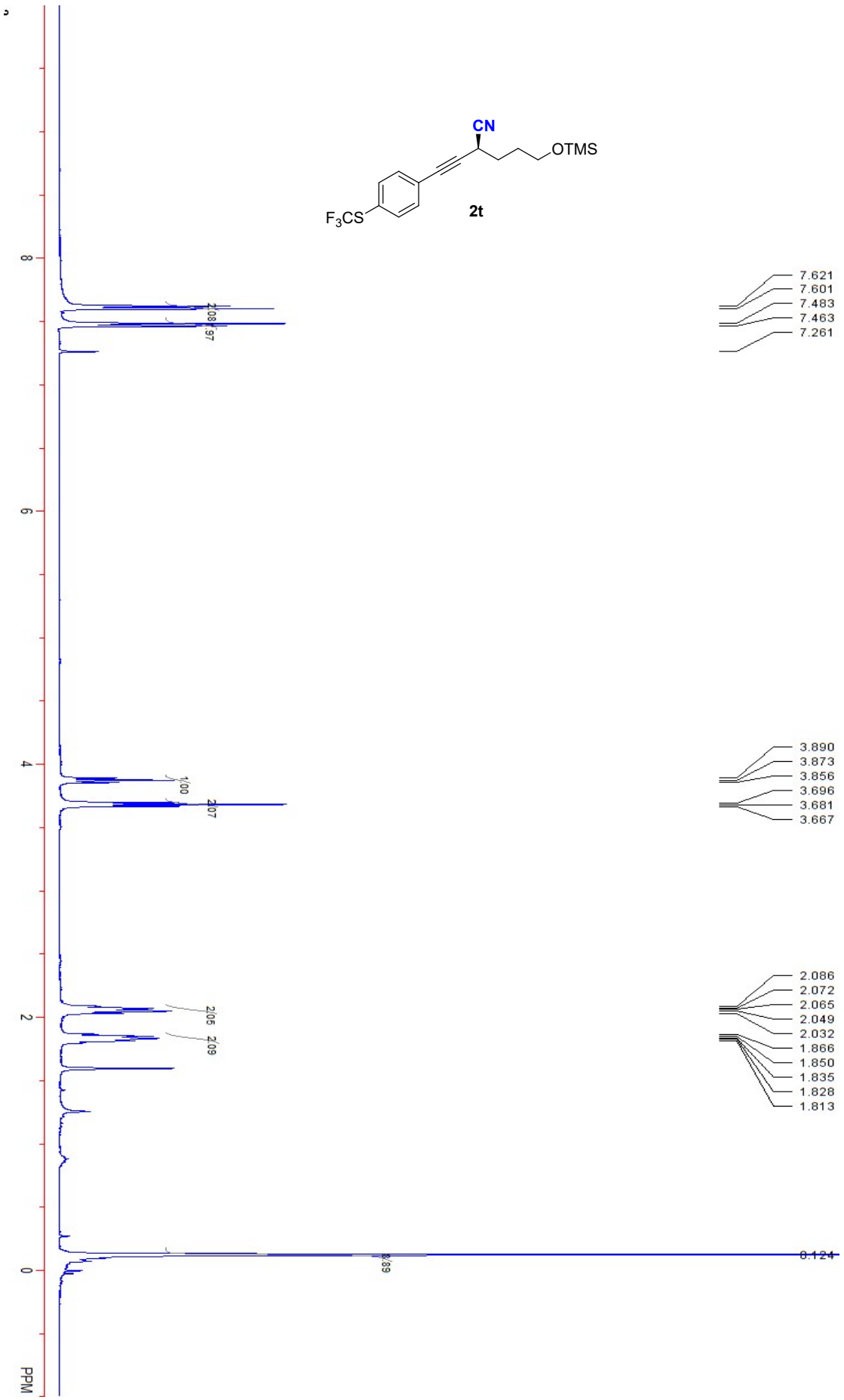
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3.696
3.681
3.667
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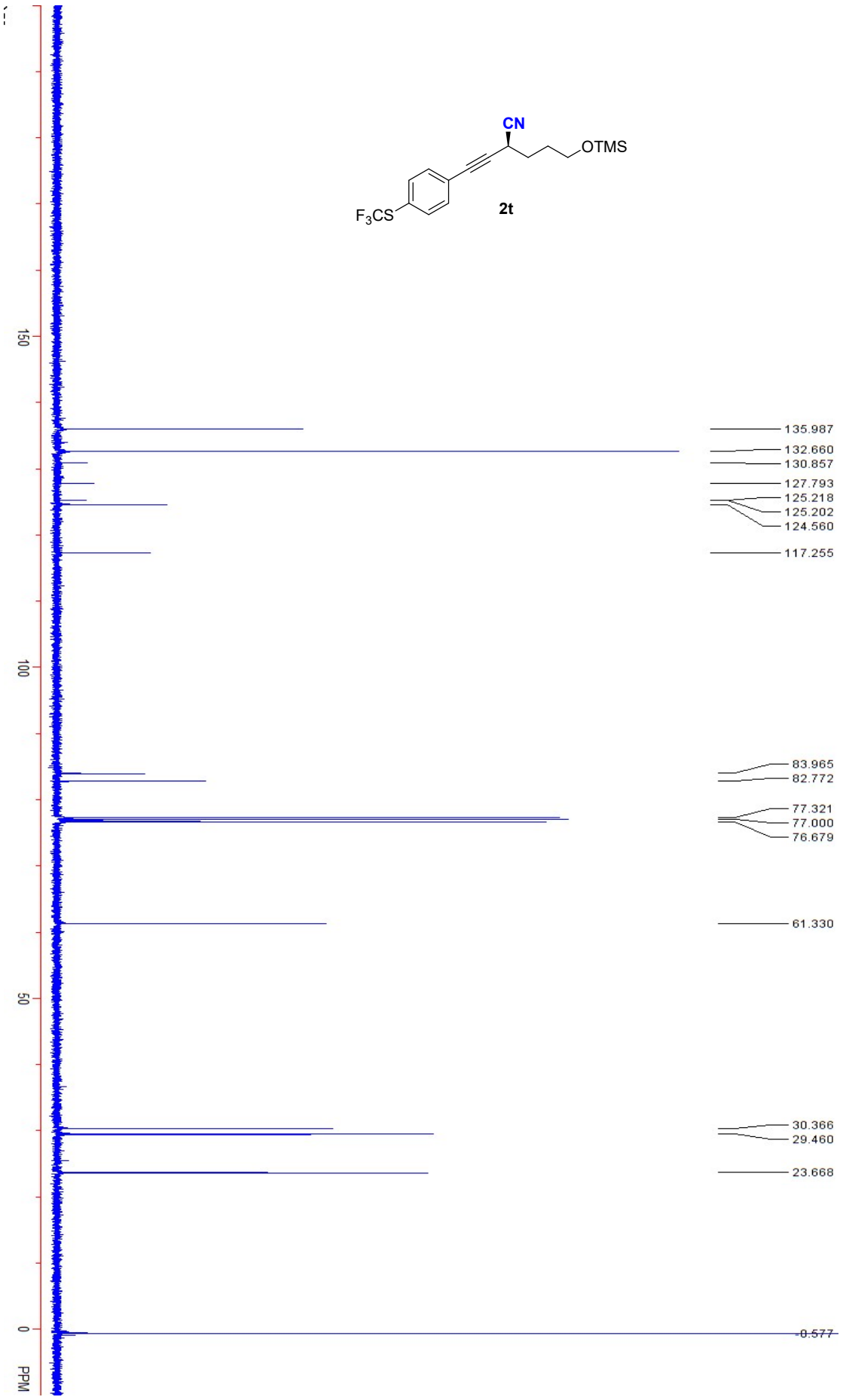
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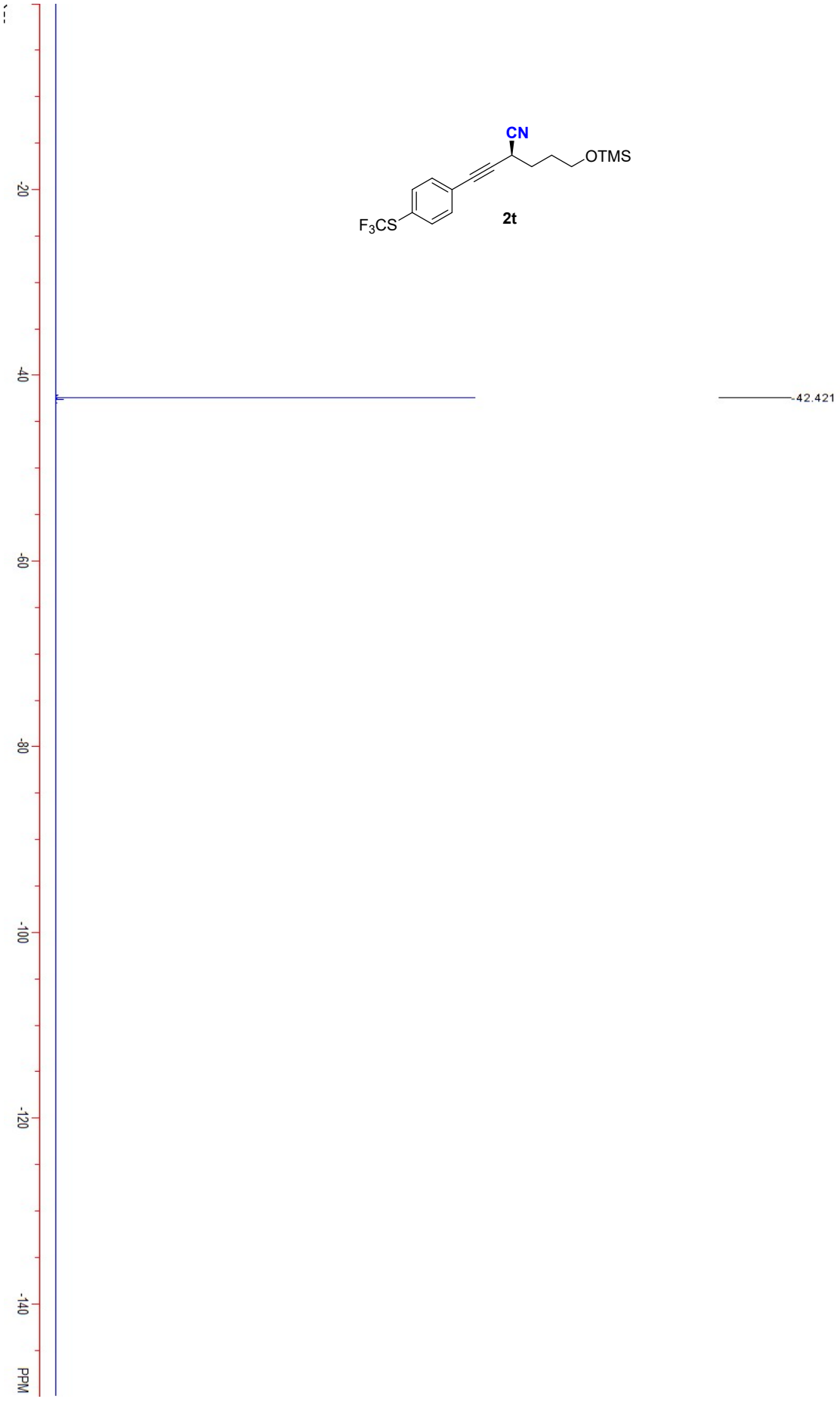
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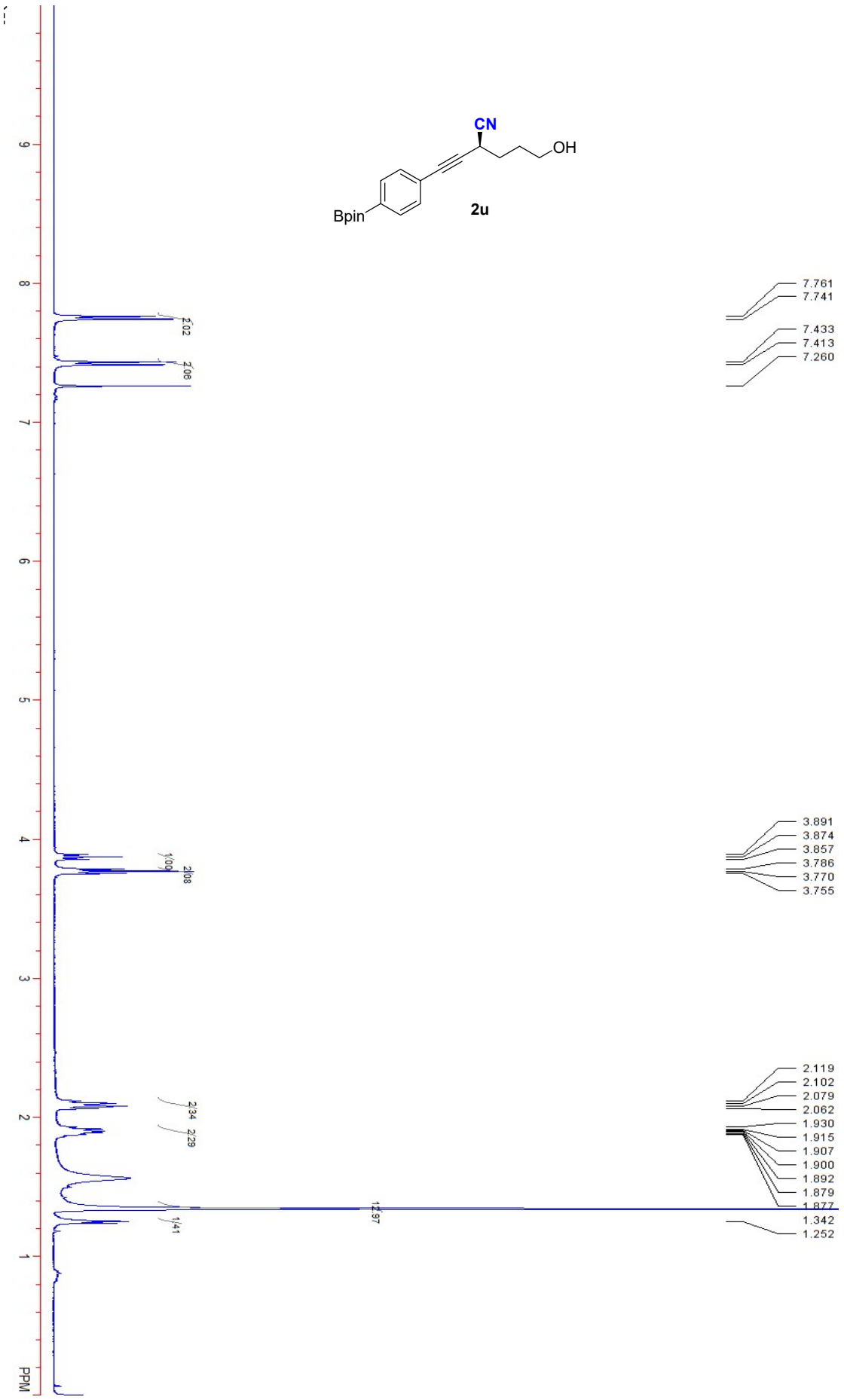
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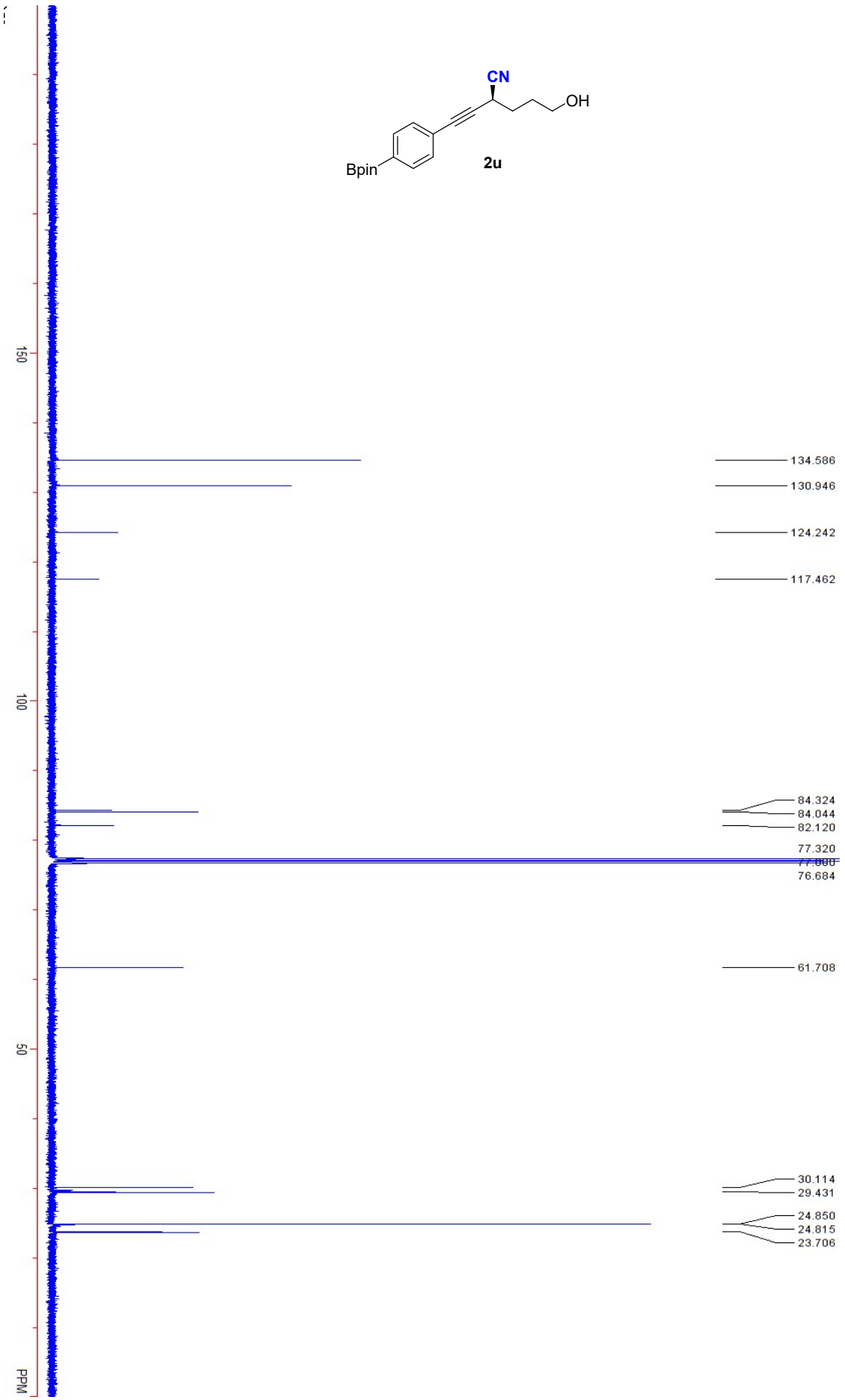
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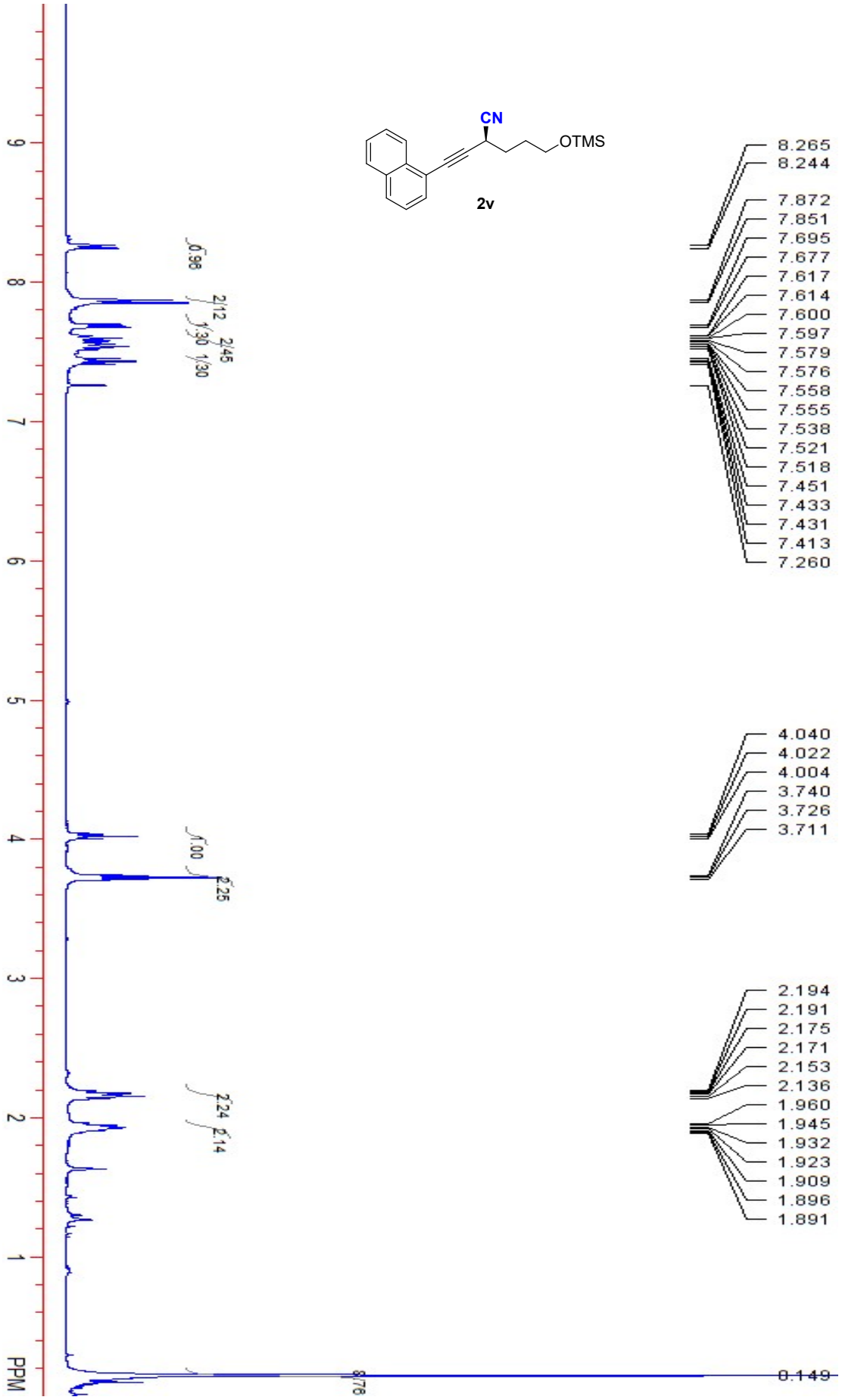
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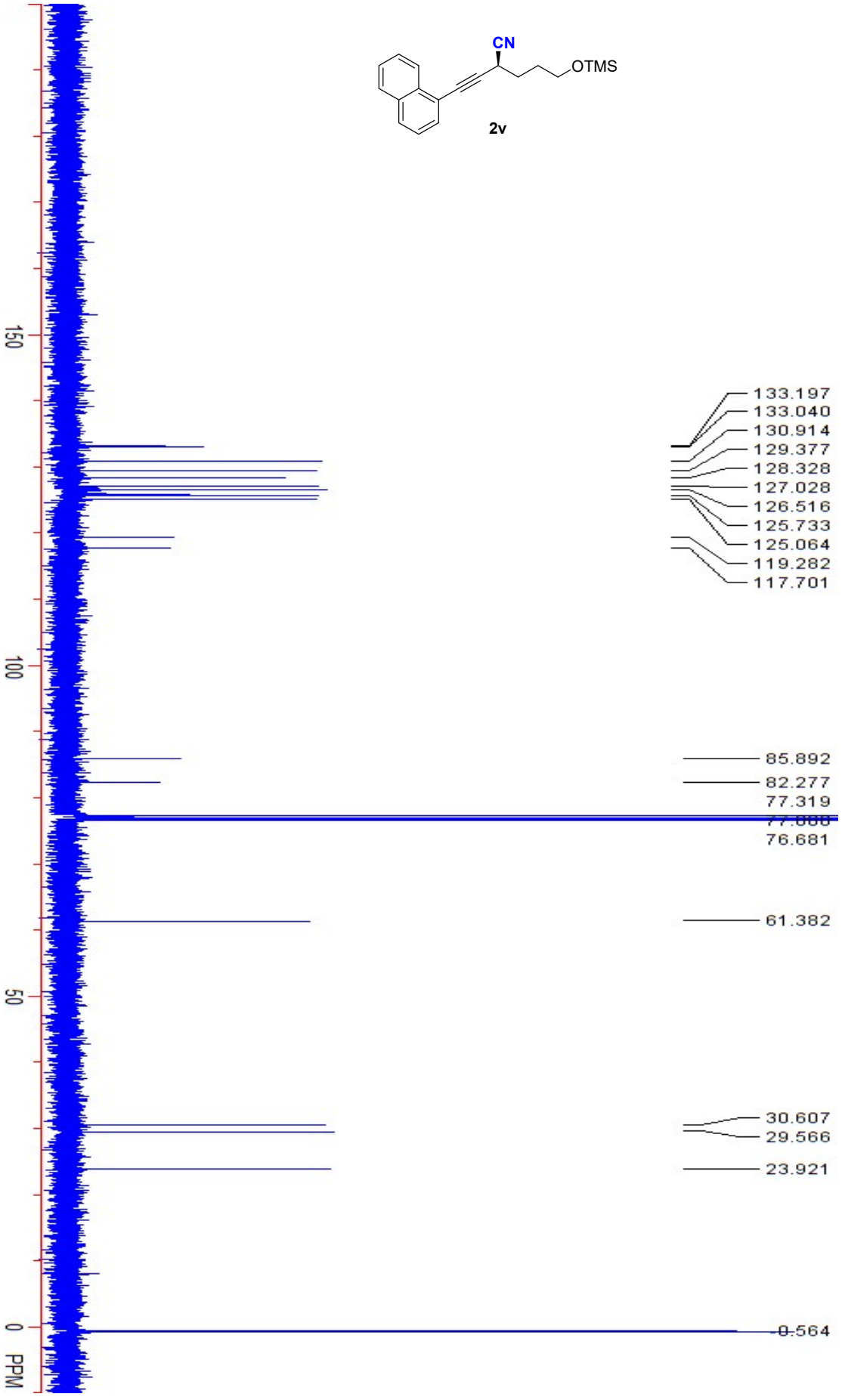
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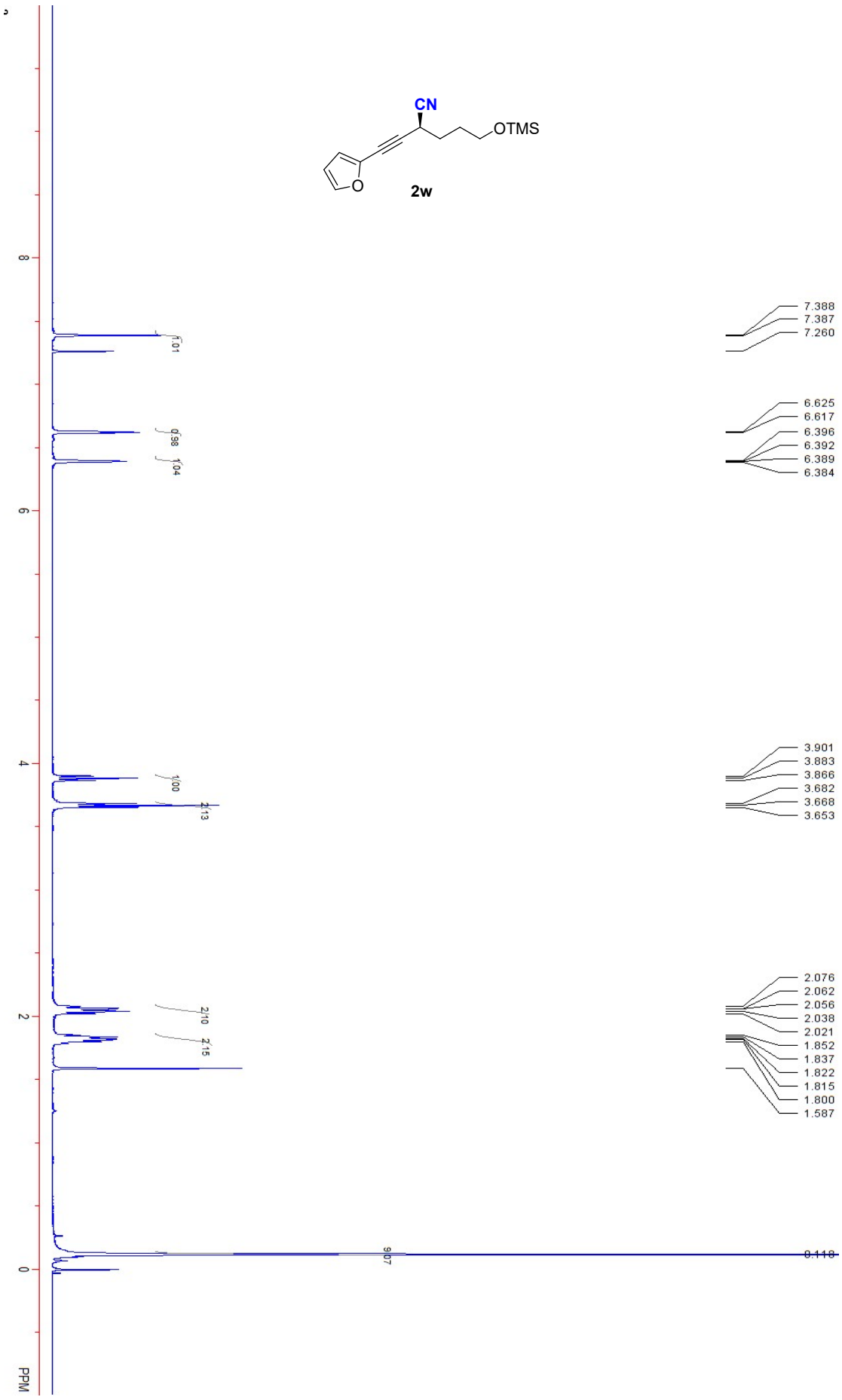
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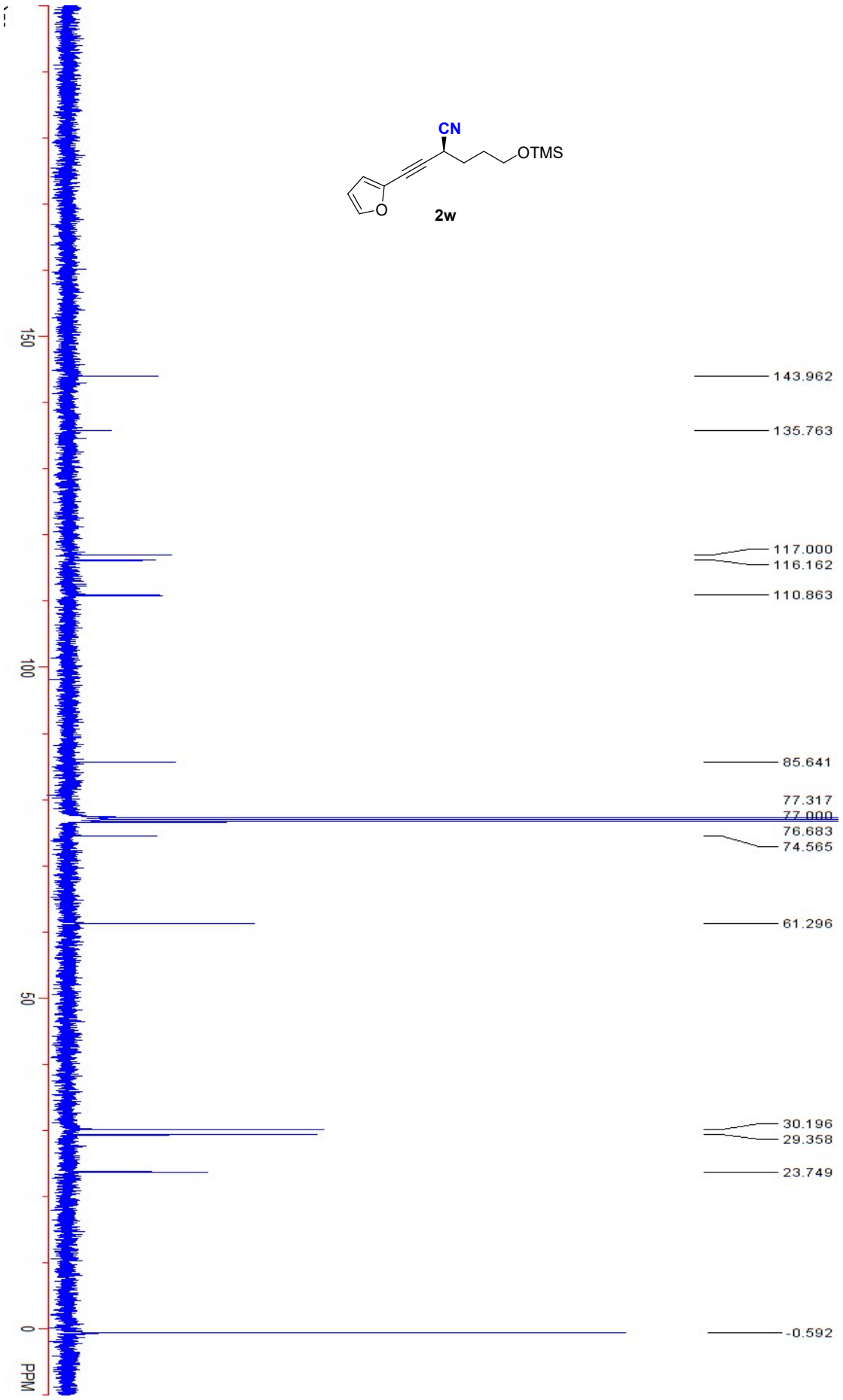
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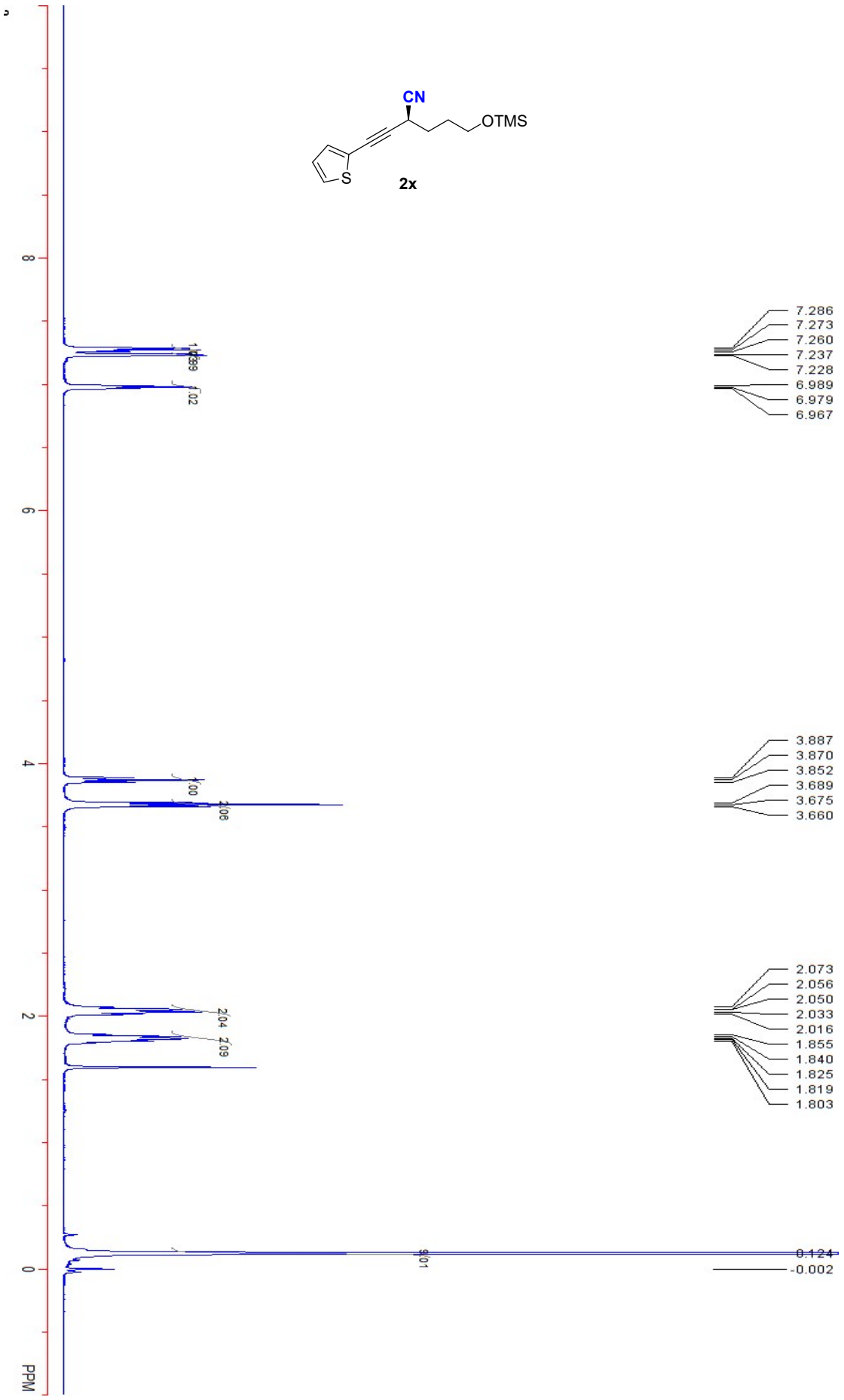
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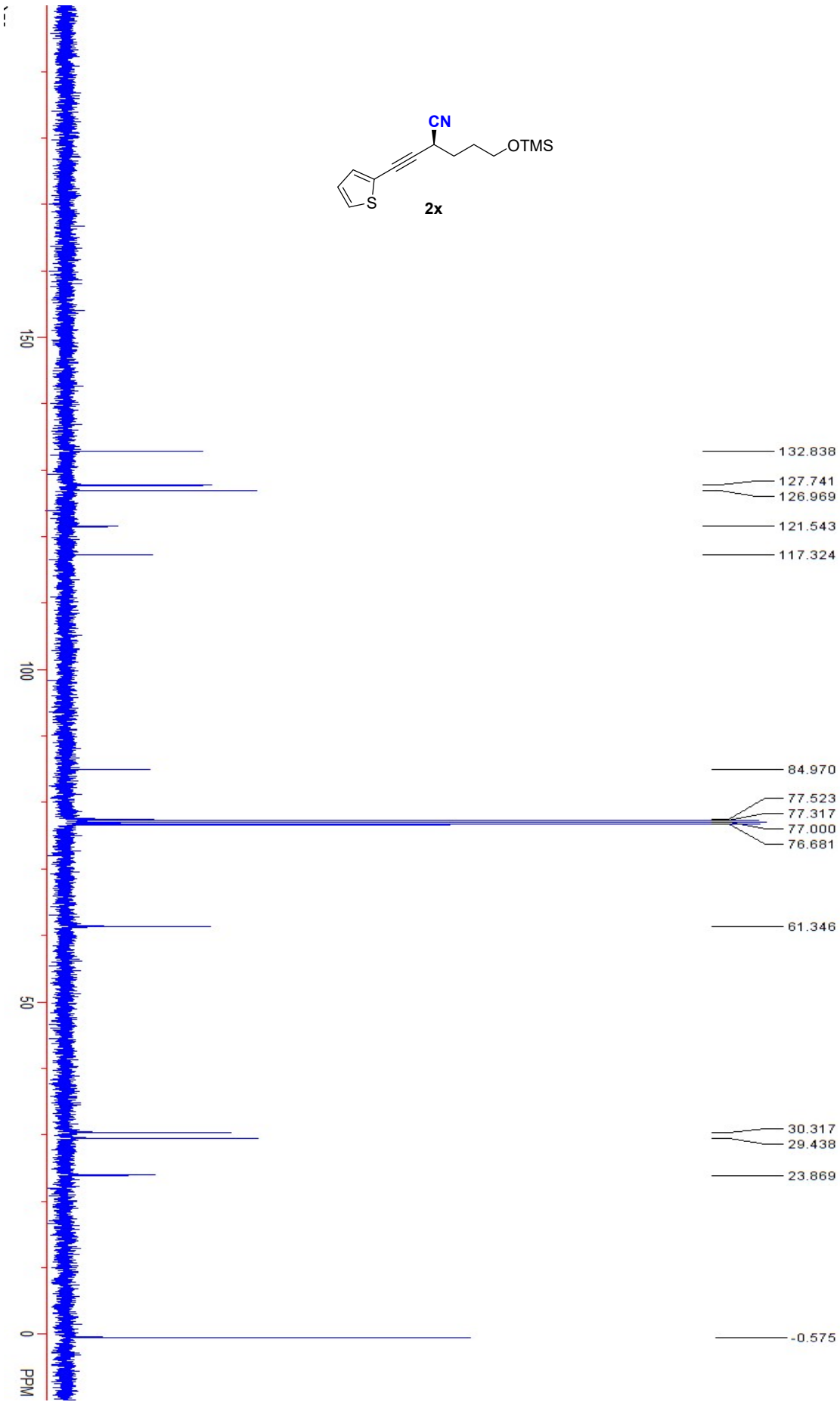
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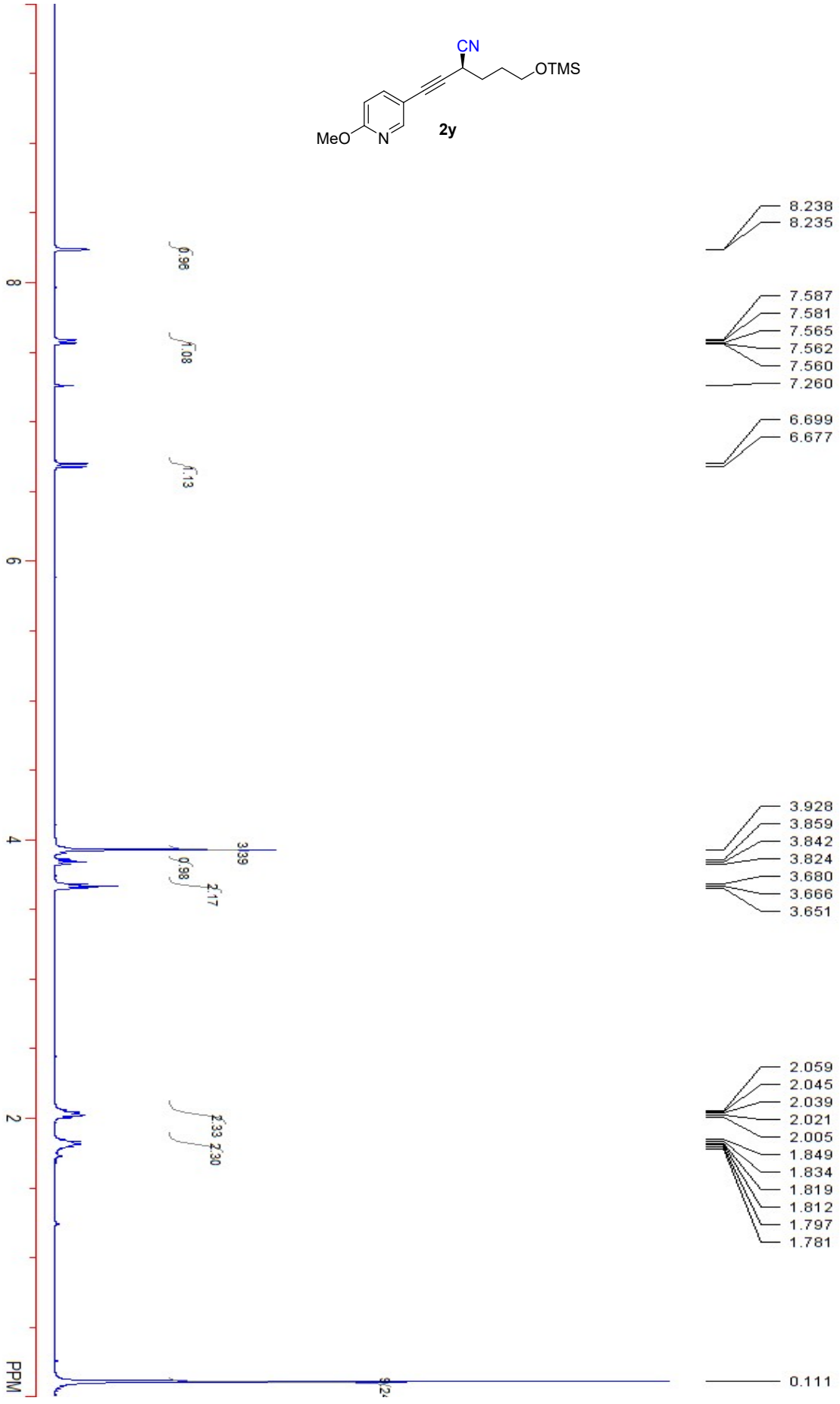
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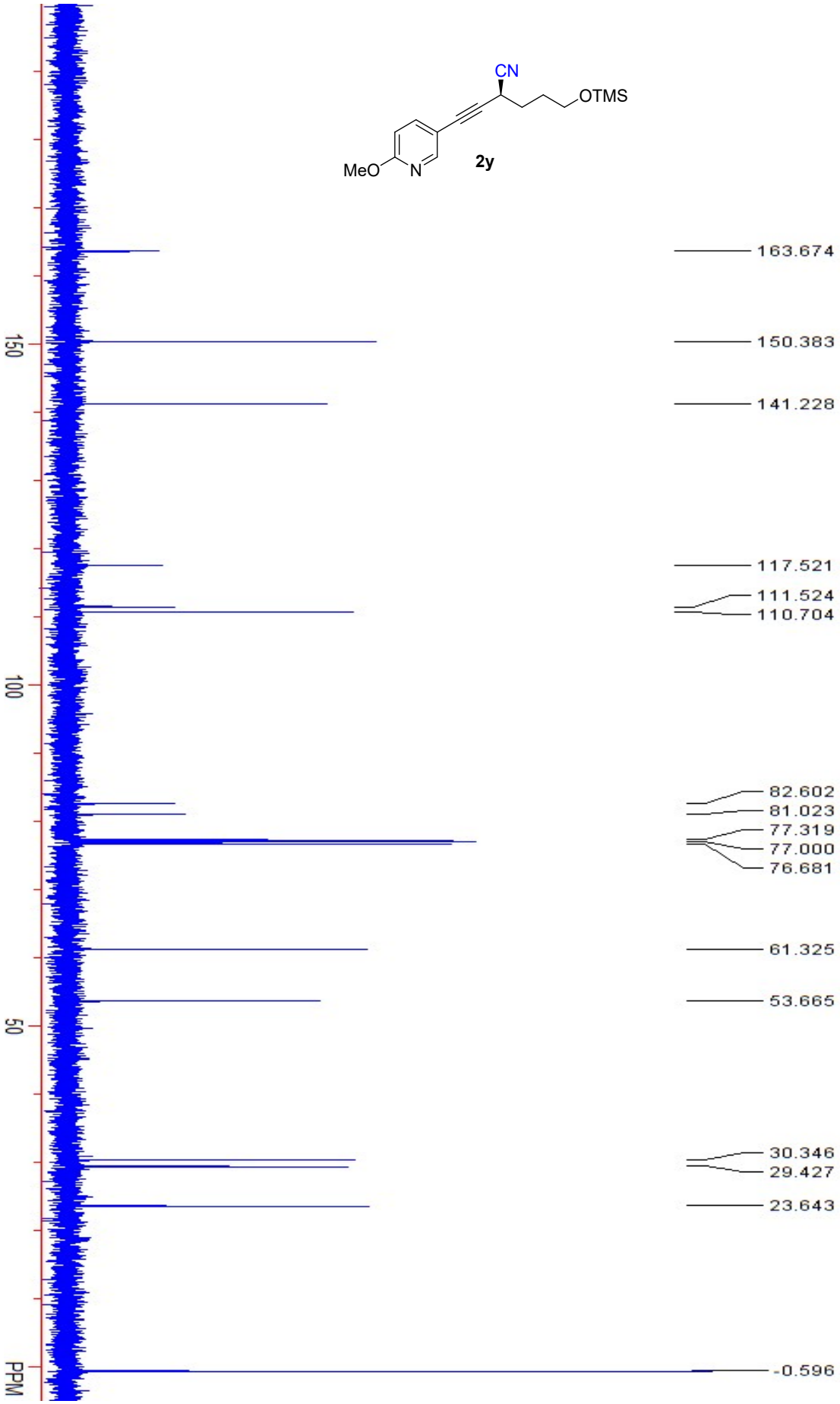
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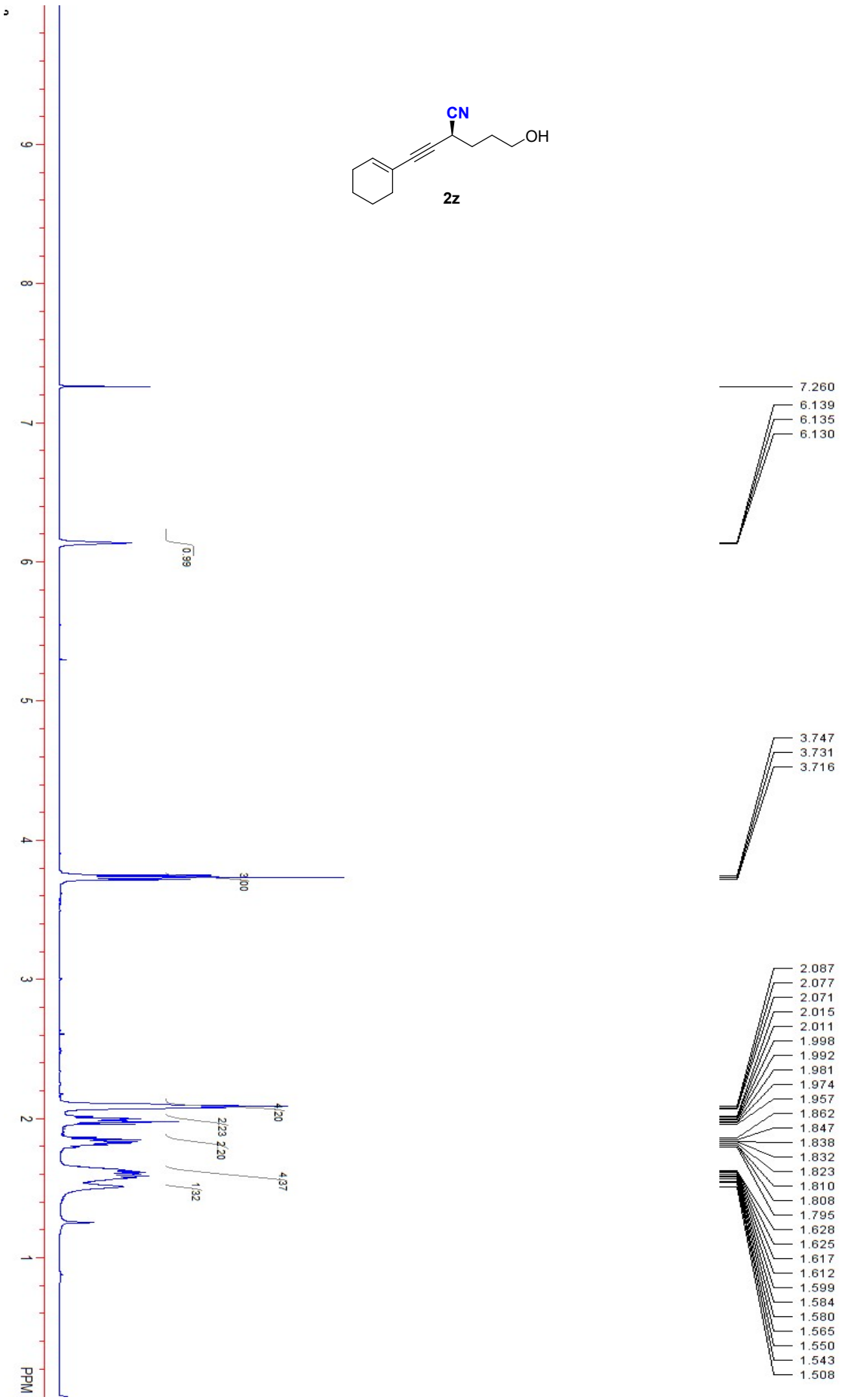
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1.832
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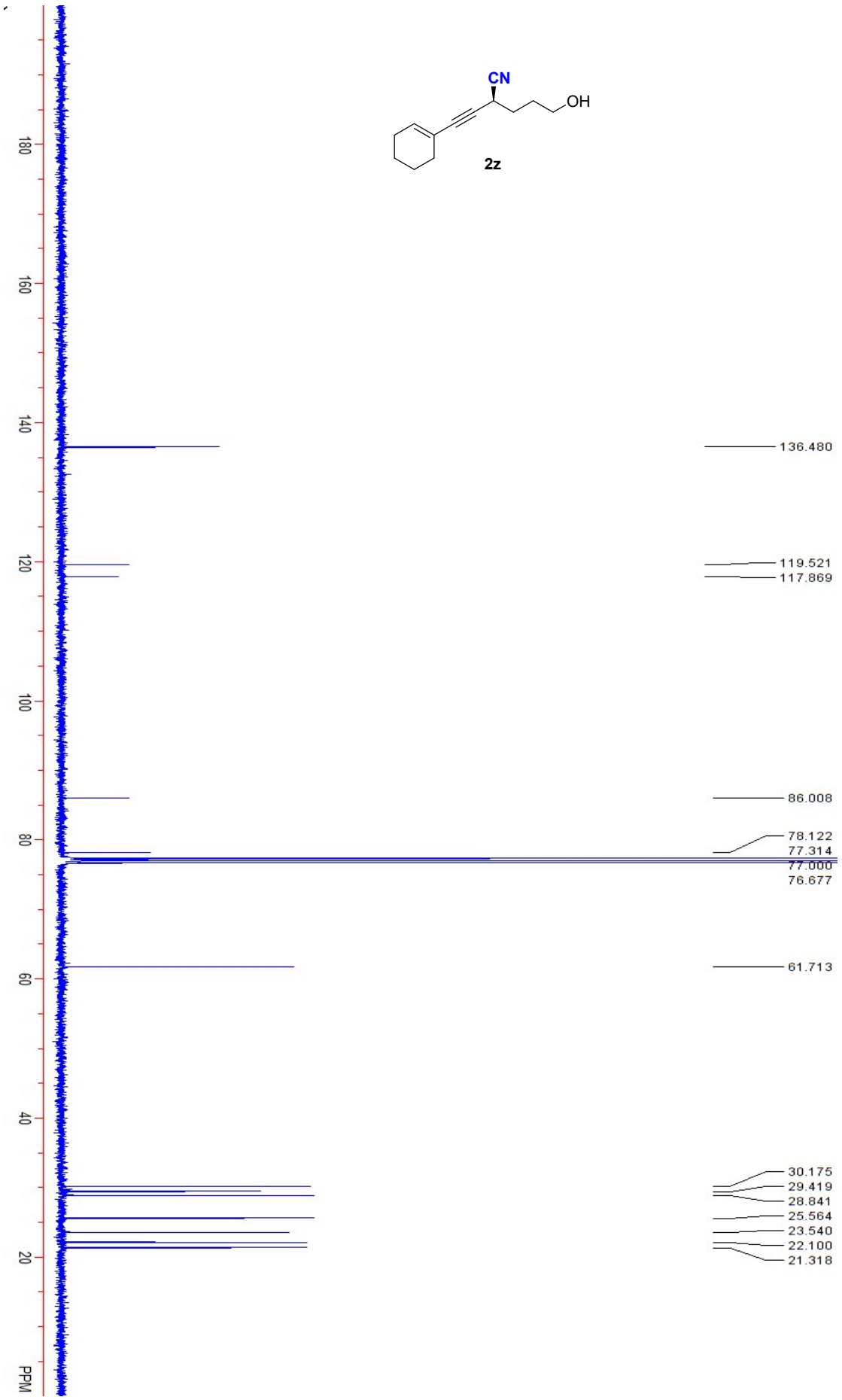
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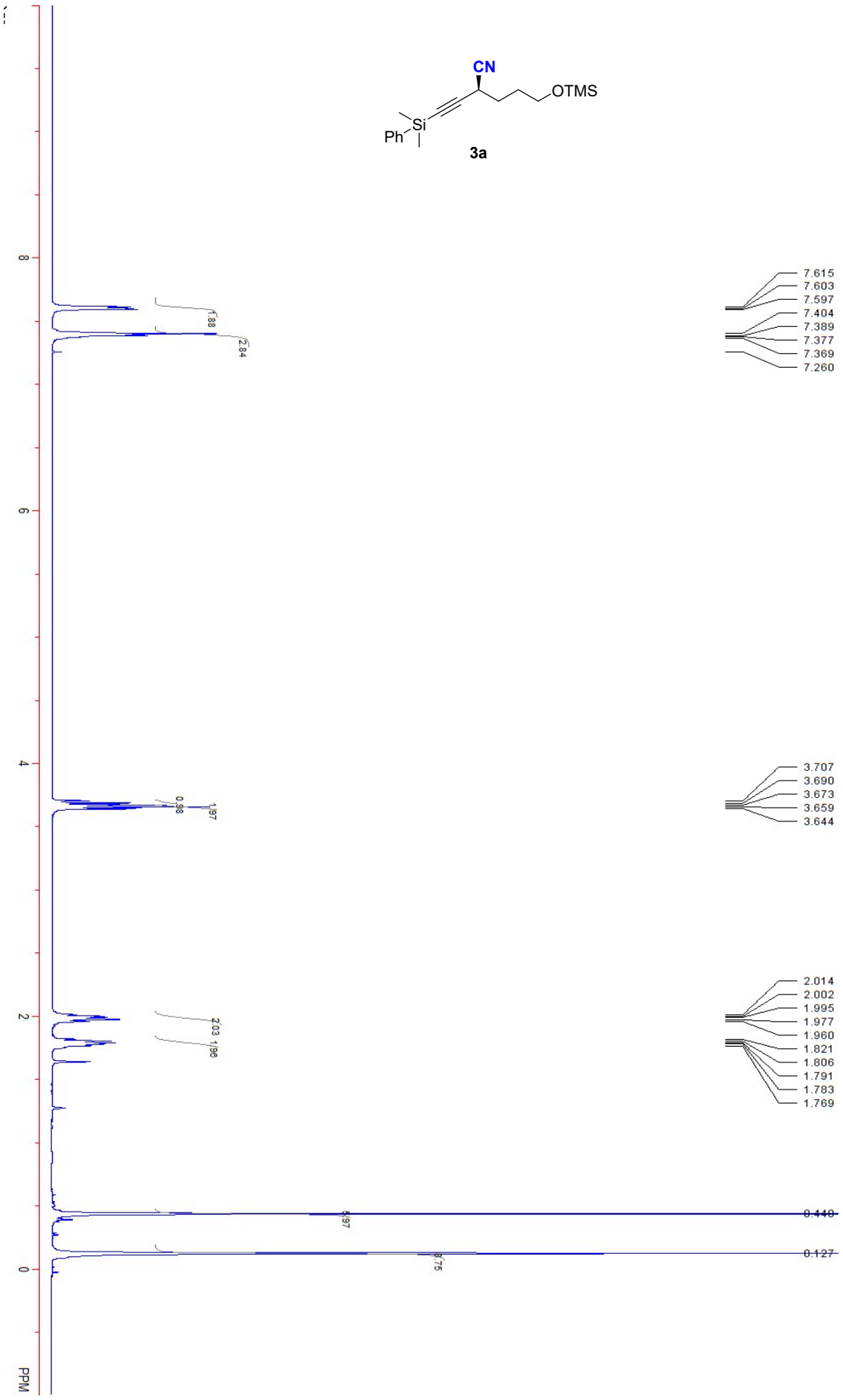
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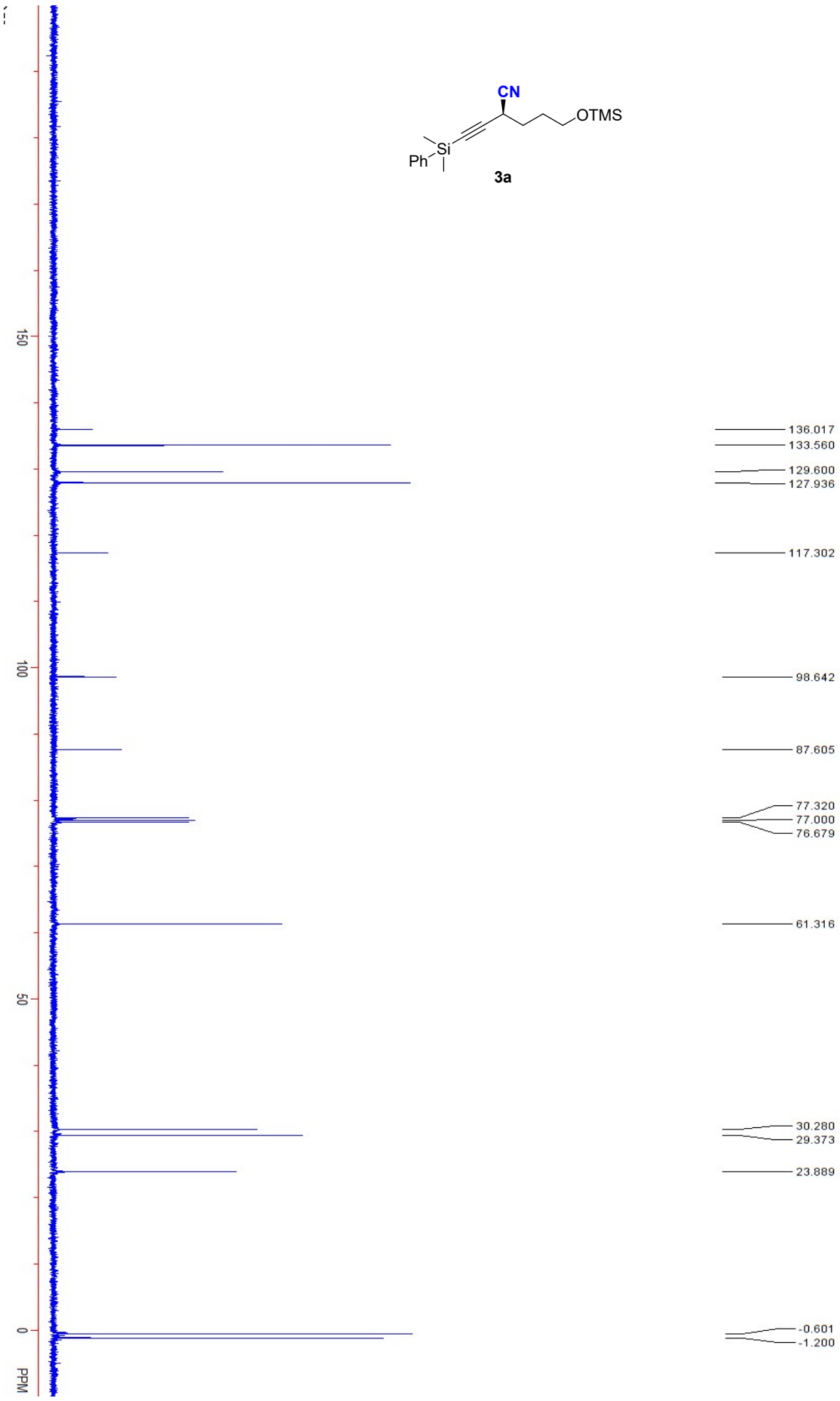
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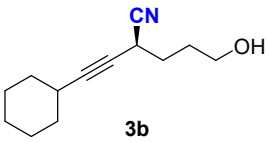
CN
OH

3b

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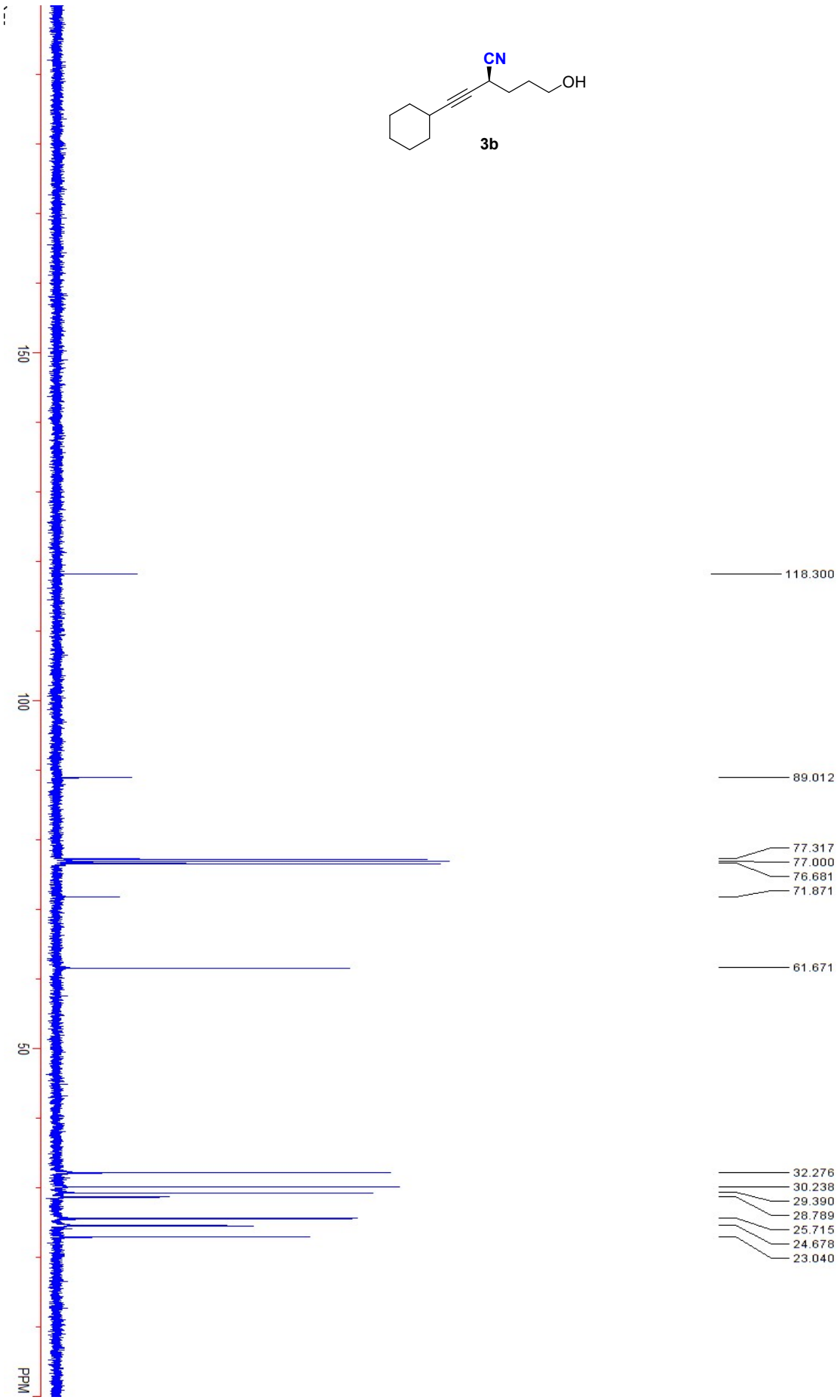
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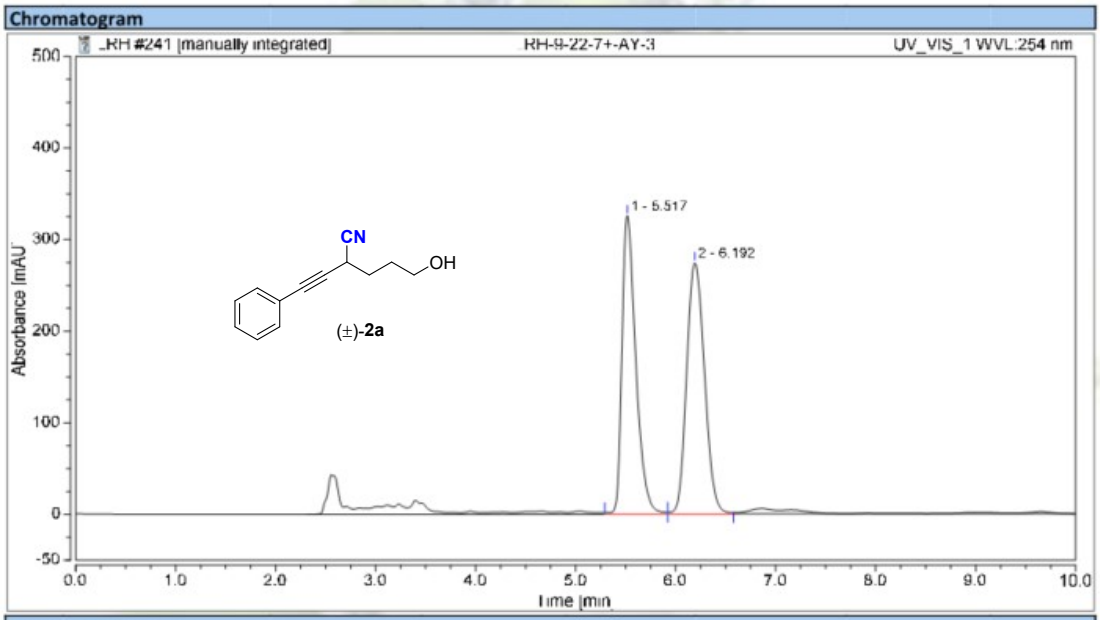
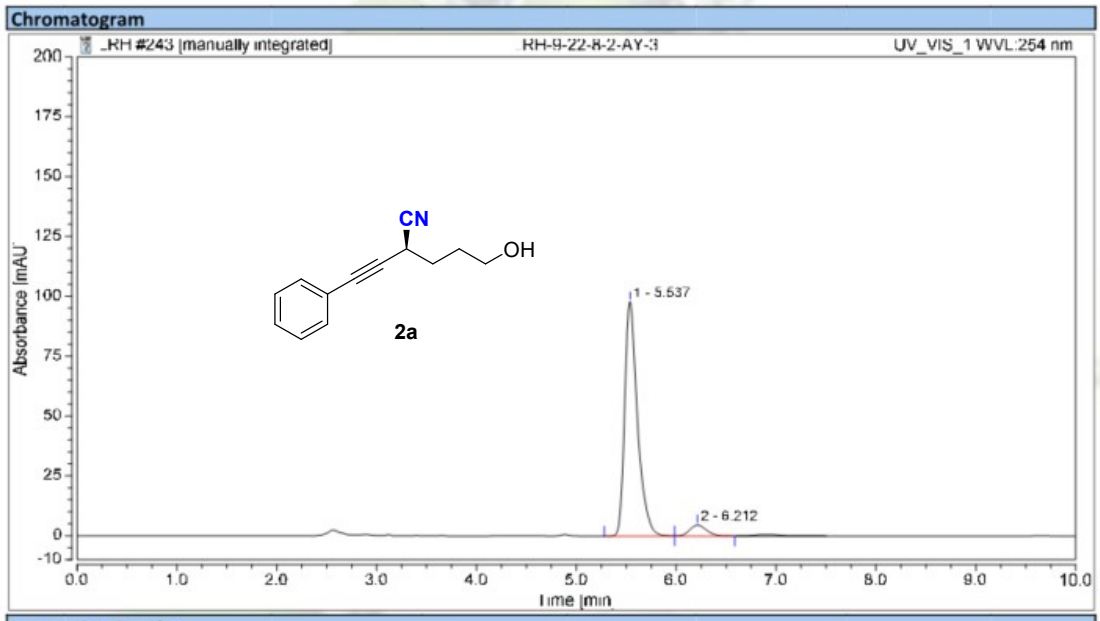
9. HPLC Analysis of Products



Integration Results

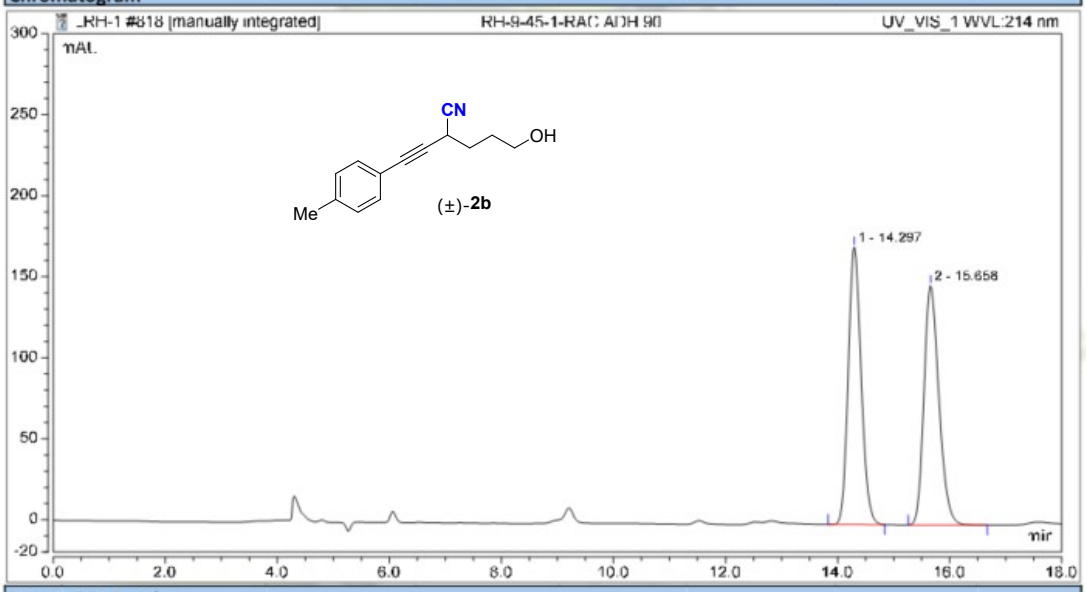
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.517	52.352	326.145	47.91	54.27	n.a.
2		6.192	56.911	274.828	52.09	45.73	n.a.
Total:			**109.263**	**600.973**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.537	14.598	97.892	94.05	95.48	n.a.
2		6.212	0.923	4.635	5.95	4.52	n.a.
Total:			**15.521**	**102.527**	**100.00**	**100.00**	

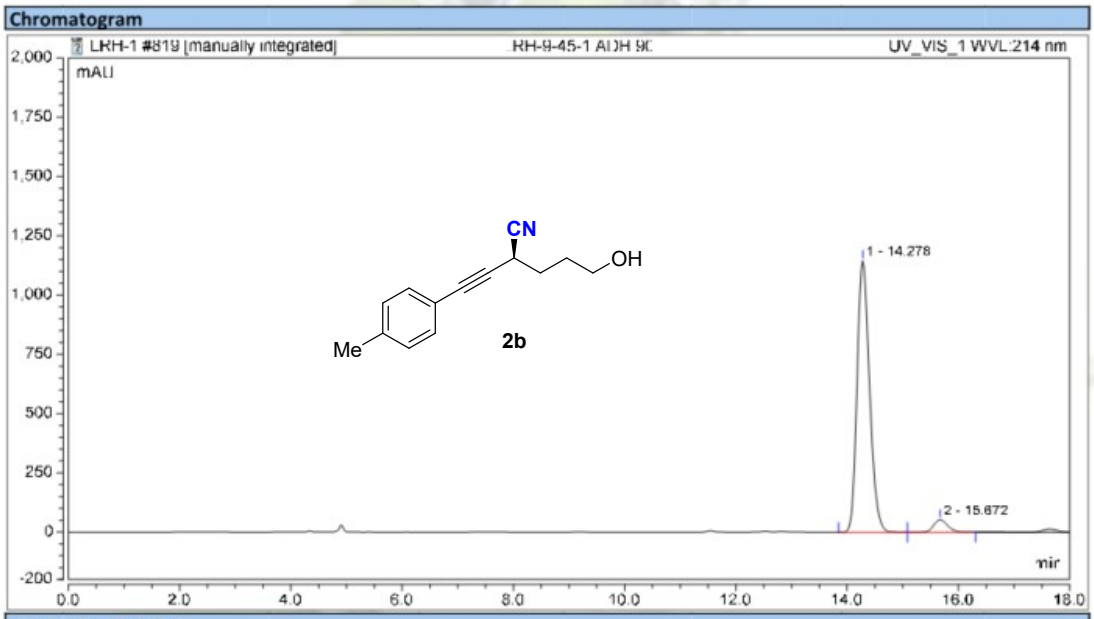
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.297	45.597	171.326	49.91	53.67	n.a.
2		15.658	45.761	147.924	50.09	46.33	n.a.
Total:			**91.358**	**319.250**	**100.00**	**100.00**	

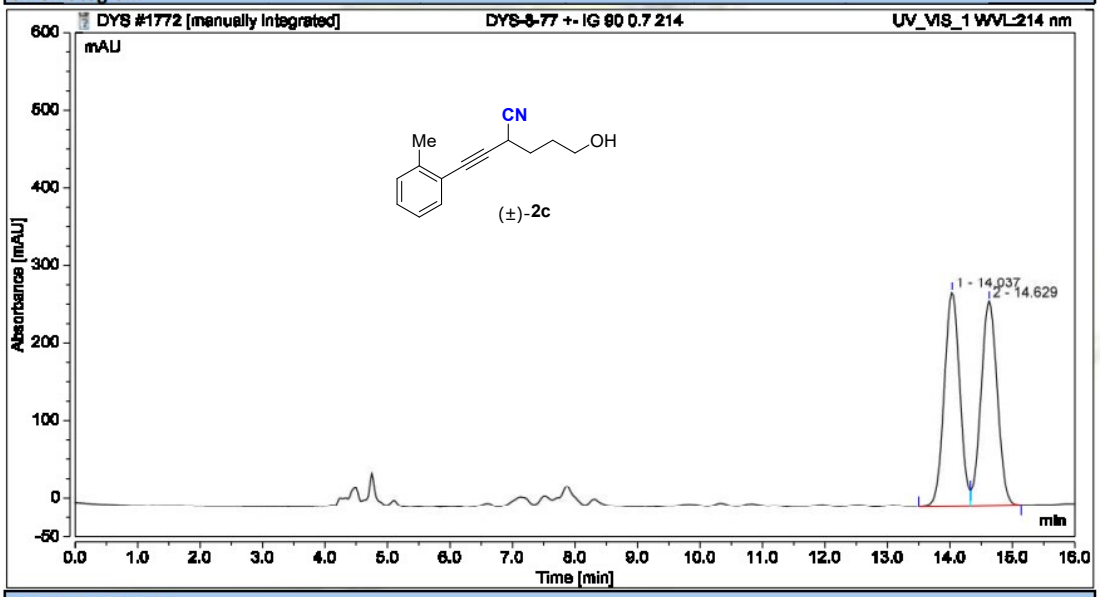
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.278	297.791	1147.058	94.86	95.52	n.a.
2		15.672	16.151	53.736	5.14	4.48	n.a.
Total:			**313.942**	**1200.794**	**100.00**	**100.00**	

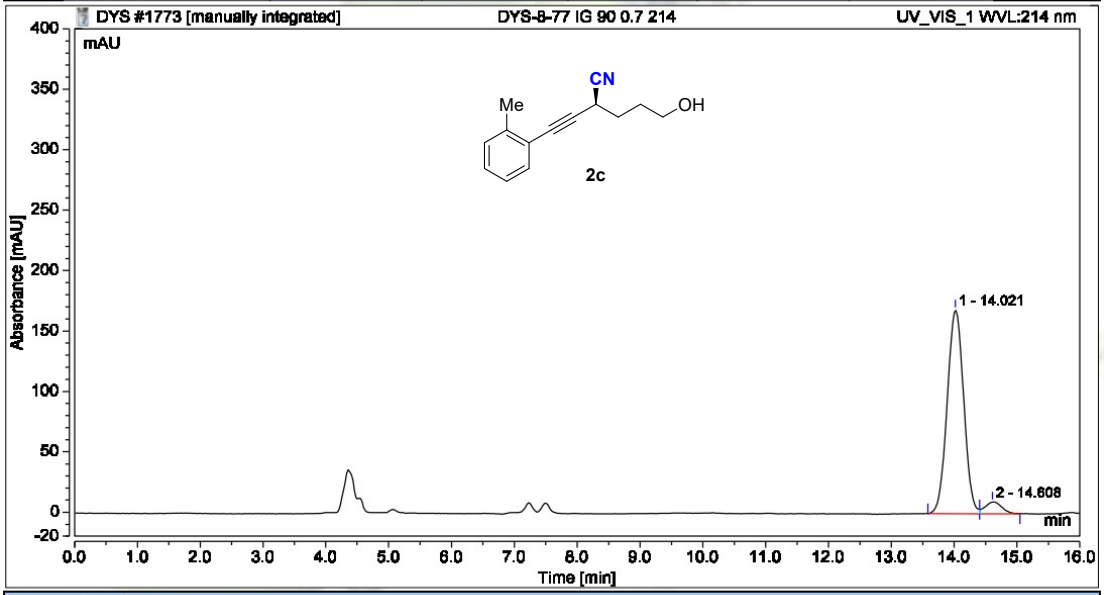
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.037	78.852	275.634	49.84	51.14	n.a.
2		14.629	79.354	263.315	50.16	48.86	n.a.
Total:			**158.206**	**538.949**	**100.00**	**100.00**	

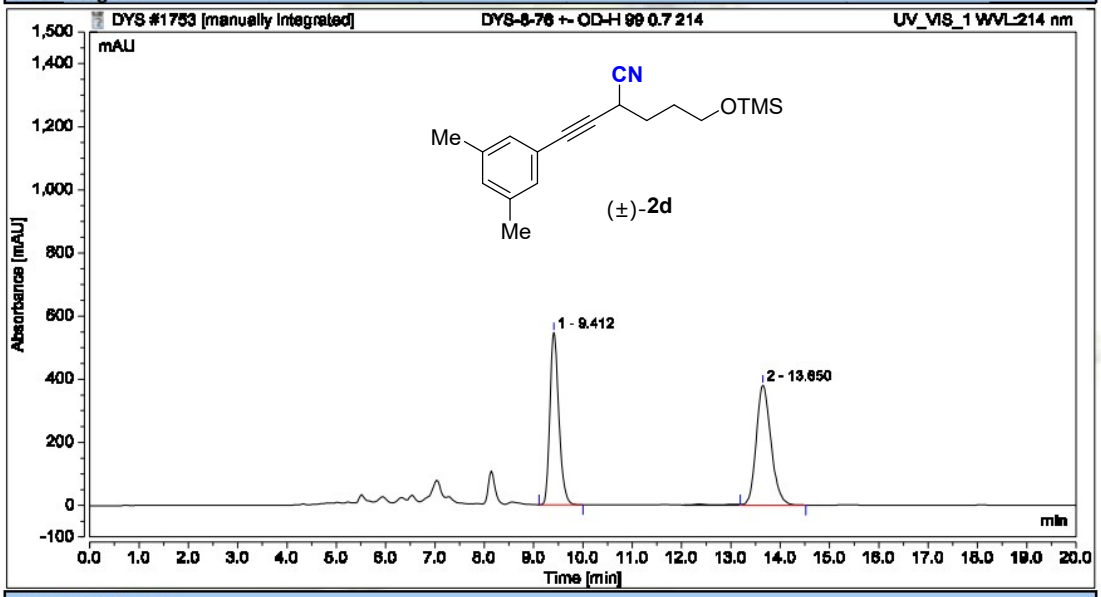
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.021	51.075	168.665	94.37	94.48	n.a.
2		14.608	3.046	9.850	5.63	5.52	n.a.

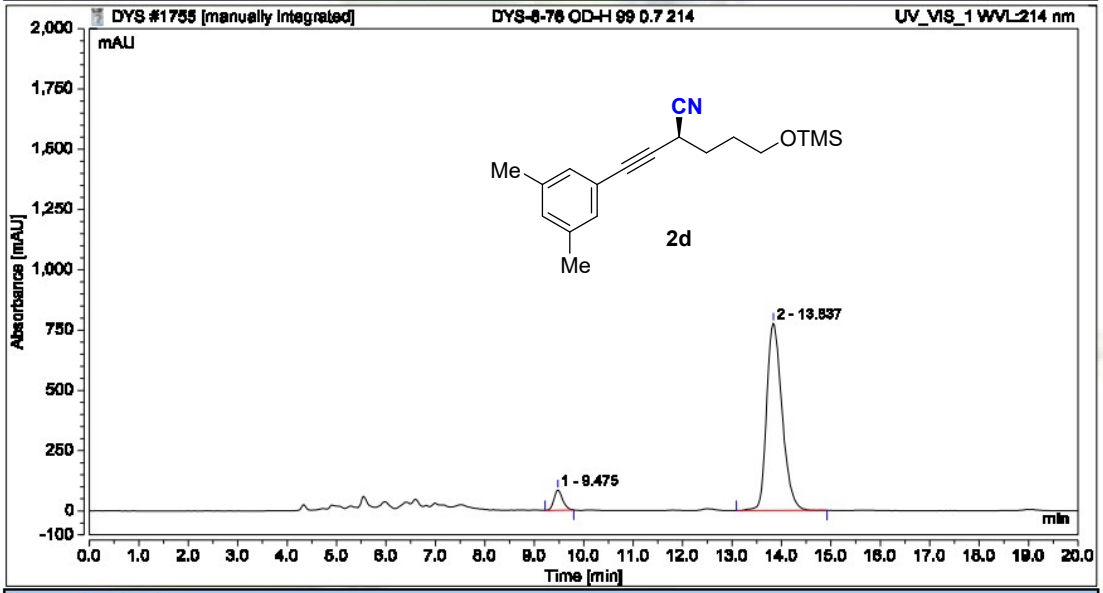
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.412	114.773	545.868	46.47	58.91	n.a.
2		13.650	132.229	380.723	53.53	41.09	n.a.
Total:			**247.003**	**926.591**	**100.00**	**100.00**	

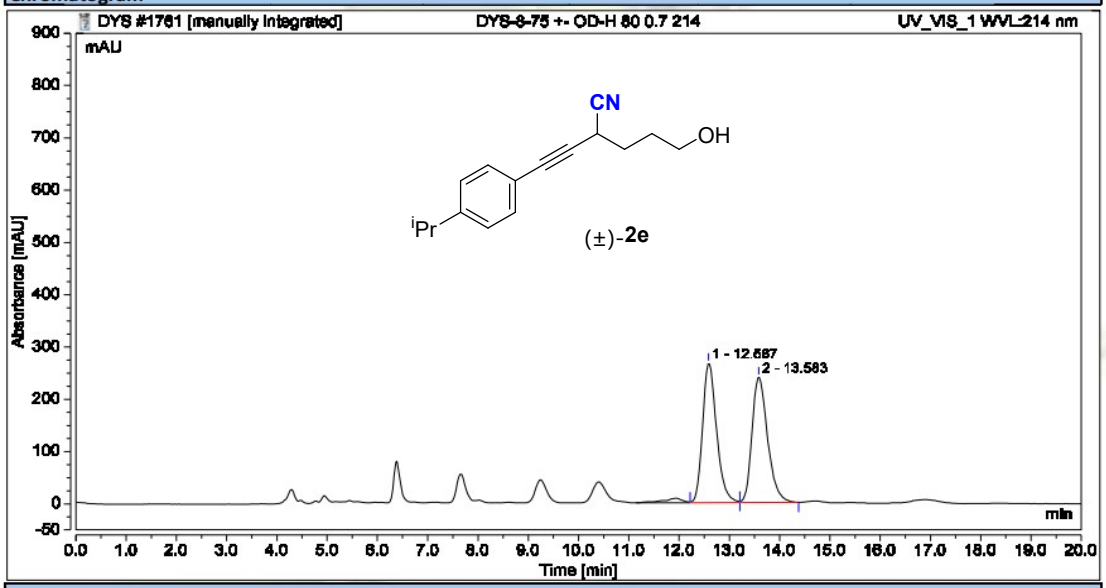
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.475	17.102	84.296	5.74	9.78	n.a.
2		13.837	281.013	777.515	94.26	90.22	n.a.
Total:			**298.115**	**861.811**	**100.00**	**100.00**	

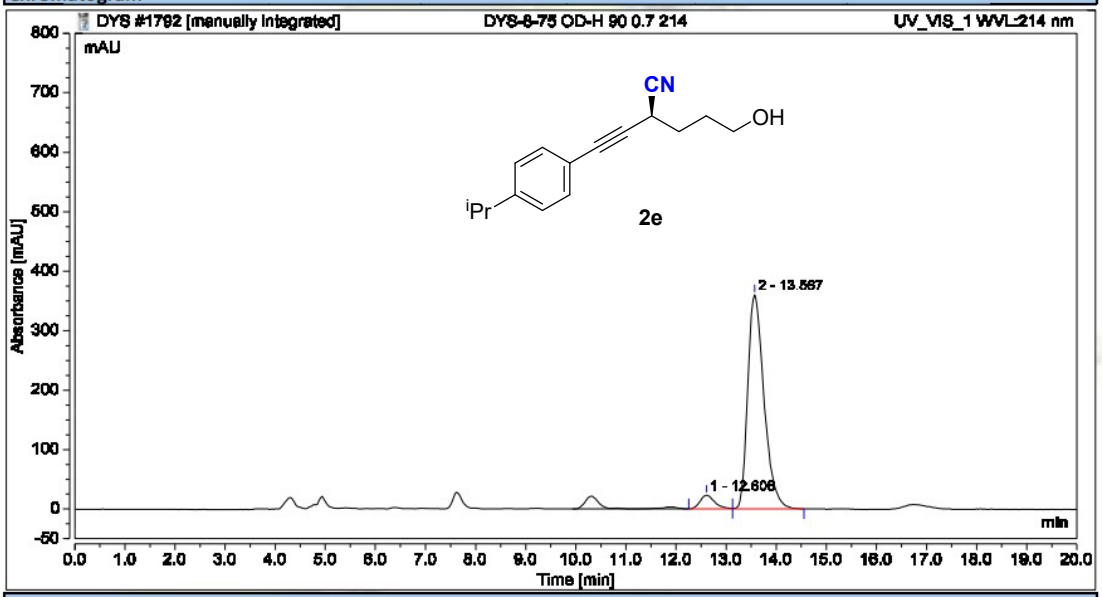
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.587	86.445	267.092	50.19	52.67	n.a.
2		13.583	85.801	239.992	49.81	47.33	n.a.
Total:			**172.246**	**507.084**	**100.00**	**100.00**	

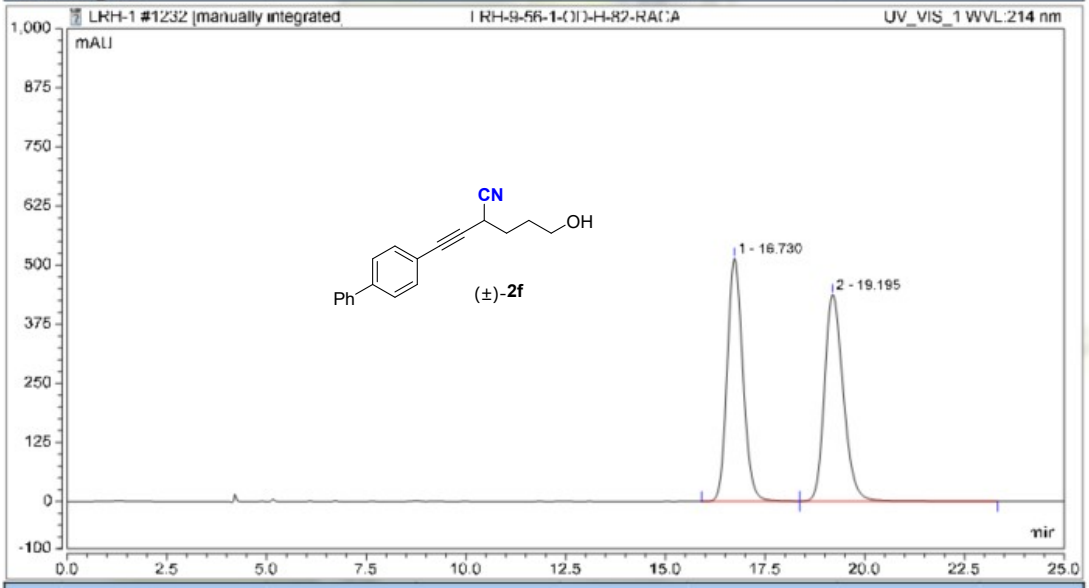
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.608	7.918	23.355	5.54	6.09	n.a.
2		13.567	135.038	360.372	94.46	93.91	n.a.
Total:			**142.956**	**383.727**	**100.00**	**100.00**	

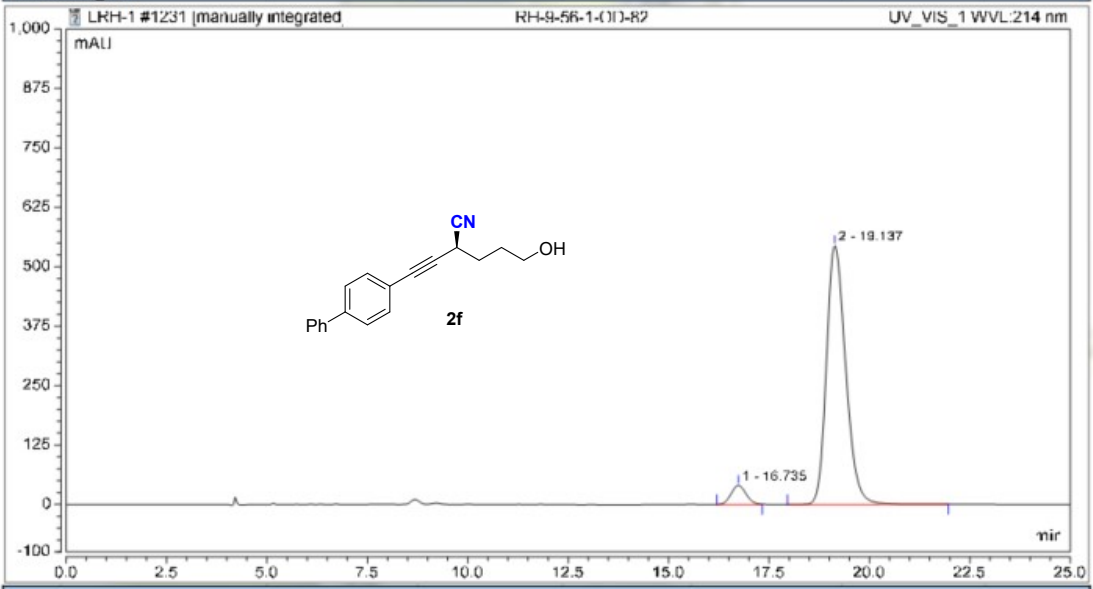
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.730	235.483	515.024	49.42	54.03	n.a.
2		19.195	241.038	438.160	50.58	45.97	n.a.
Total:			**476.522**	**953.184**	**100.00**	**100.00**	

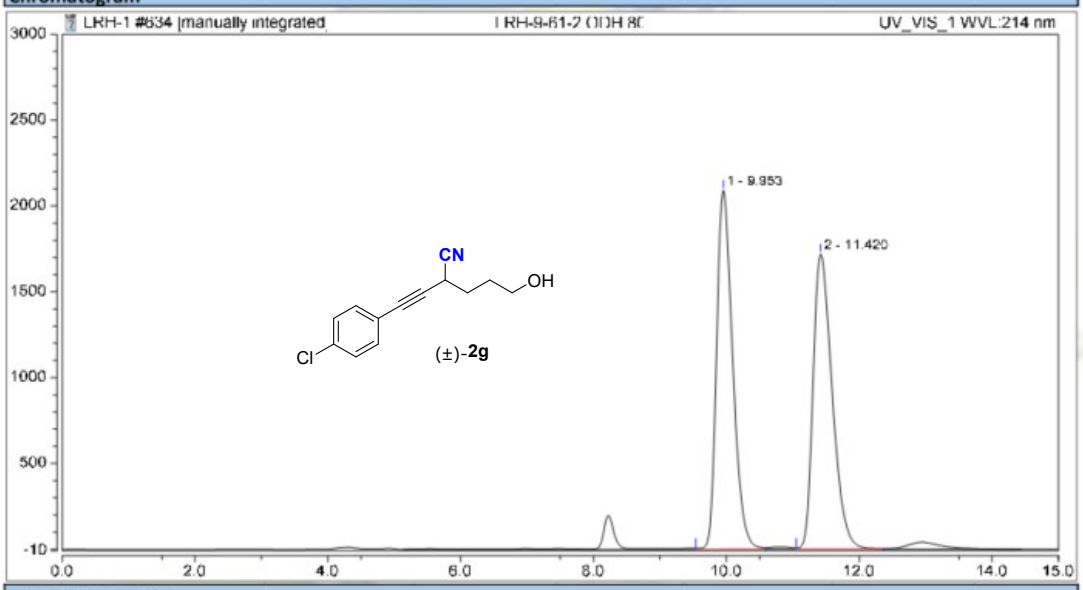
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.735	17.501	40.377	5.49	6.90	n.a.
2		19.137	301.306	544.736	94.51	93.10	n.a.
Total:			**318.807**	**585.114**	**100.00**	**100.00**	

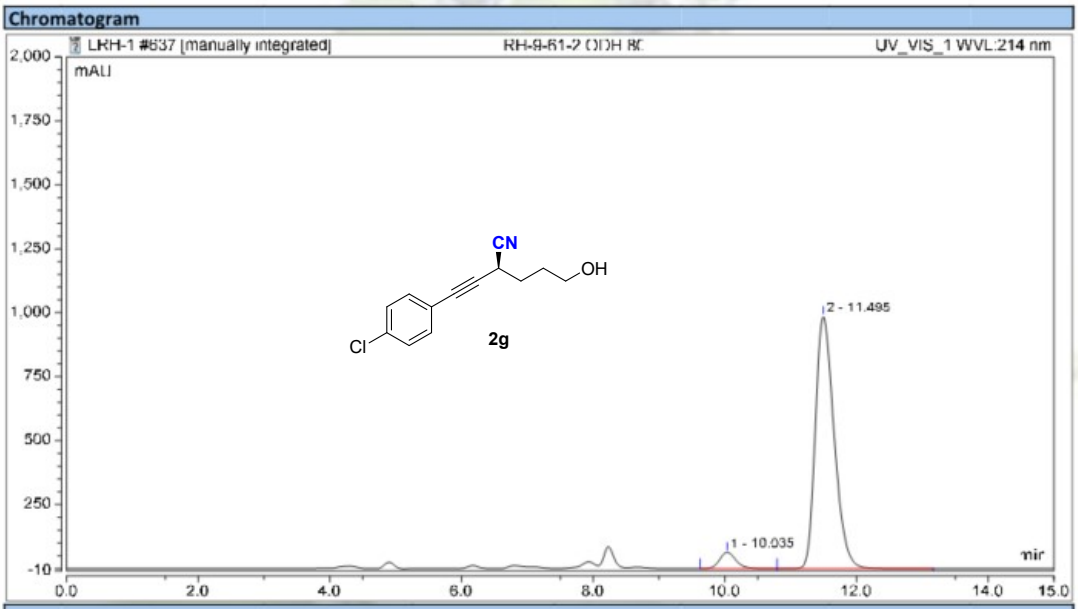
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.953	585.571	2092.913	50.56	54.88	n.a.
2		11.420	572.653	1720.895	49.44	45.12	n.a.
Total:			**1158.225**	**3813.809**	**100.00**	**100.00**	

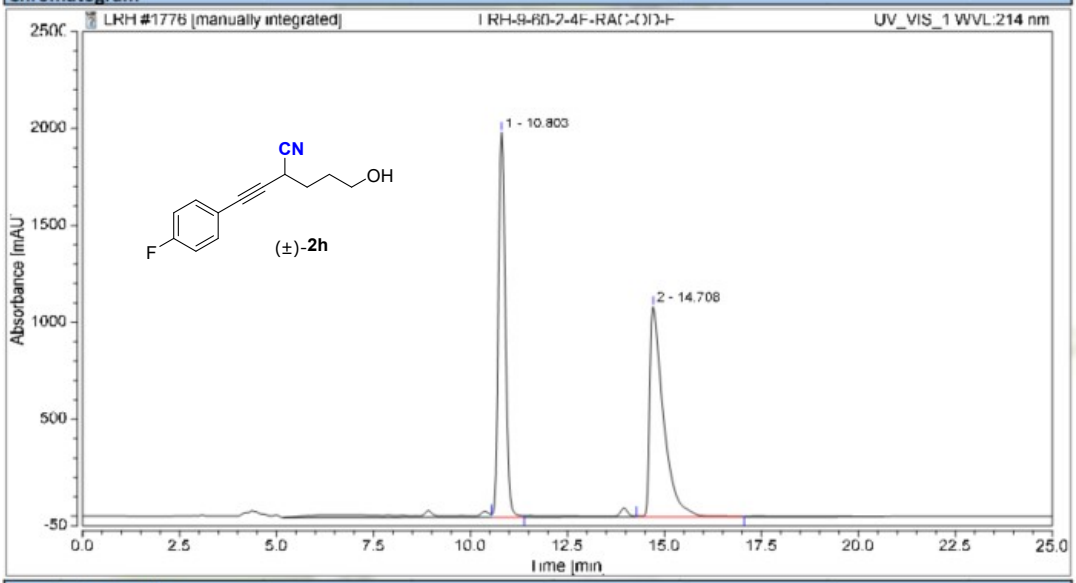
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.035	18.024	63.448	5.26	6.05	n.a.
2		11.495	324.655	985.154	94.74	93.95	n.a.
Total:			**342.678**	**1048.602**	**100.00**	**100.00**	

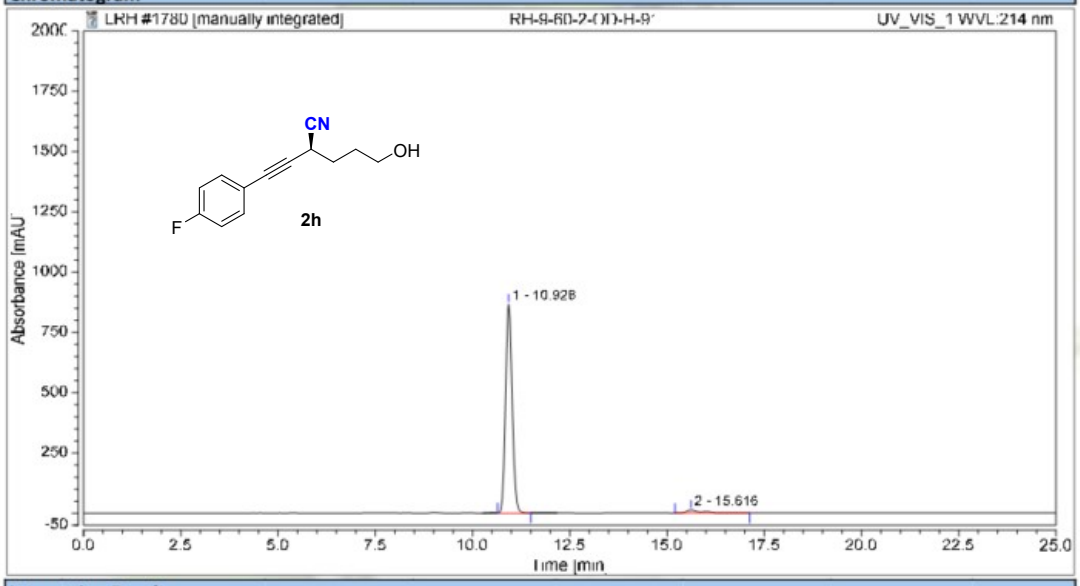
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.803	412.584	1985.558	47.93	64.64	n.a.
2		14.708	448.159	1086.135	52.07	35.36	n.a.
Total:			**860.744**	**3071.693**	**100.00**	**100.00**	

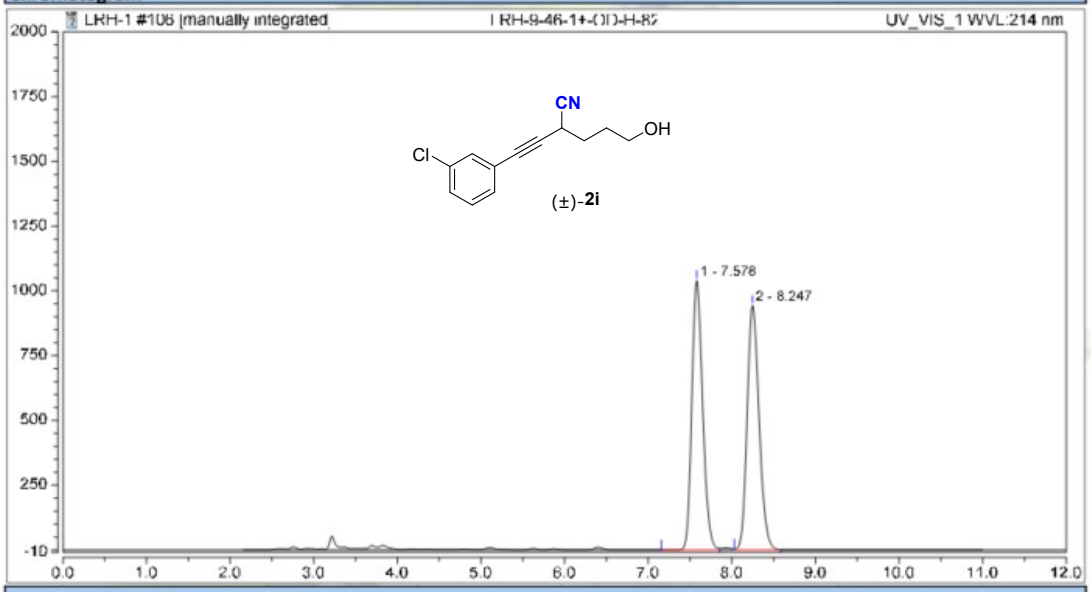
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.928	168.433	866.592	96.78	98.54	n.a.
2		15.616	5.596	12.805	3.22	1.46	n.a.
Total:			**174.029**	**879.396**	**100.00**	**100.00**	

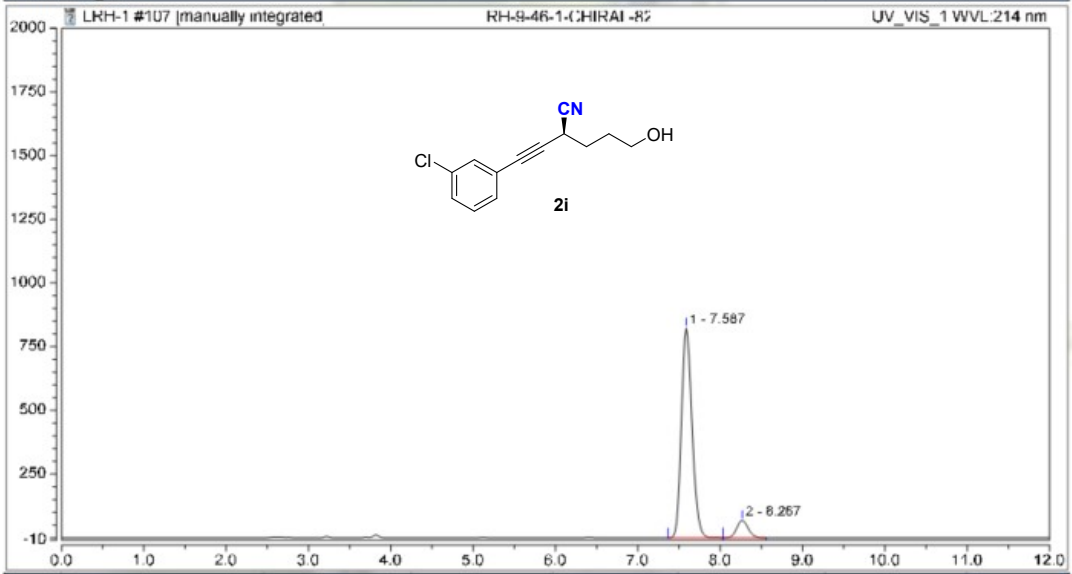
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.578	156.047	1040.684	49.97	52.43	n.a.
2		8.247	156.260	944.377	50.03	47.57	n.a.
Total:			**312.306**	**1985.062**	**100.00**	**100.00**	

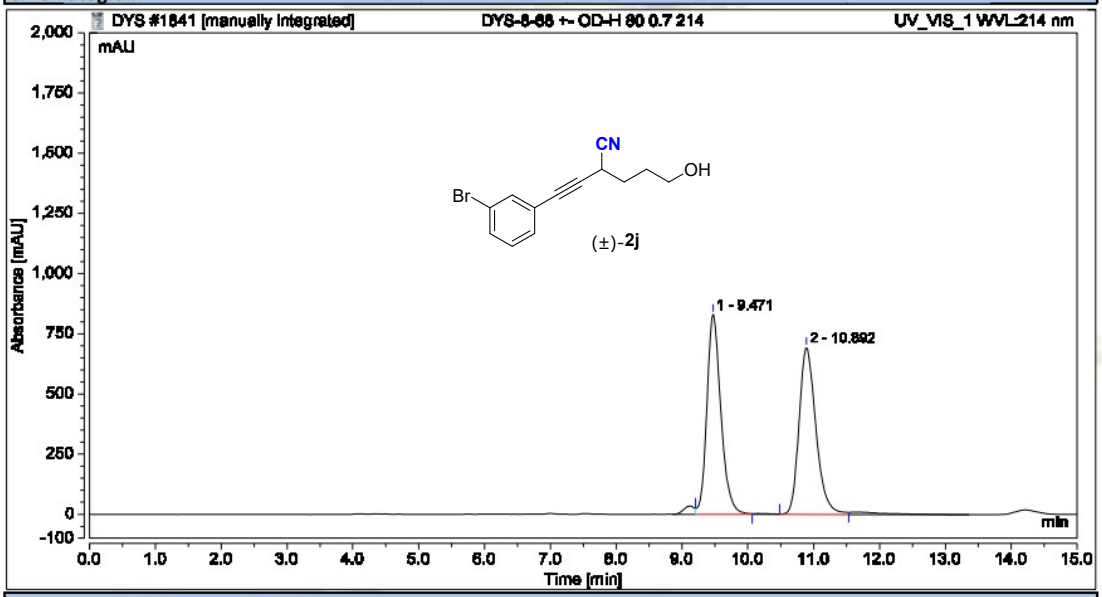
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.587	122.962	823.664	91.83	92.35	n.a.
2		8.267	10.943	68.257	8.17	7.65	n.a.
Total:			**133.905**	**891.921**	**100.00**	**100.00**	

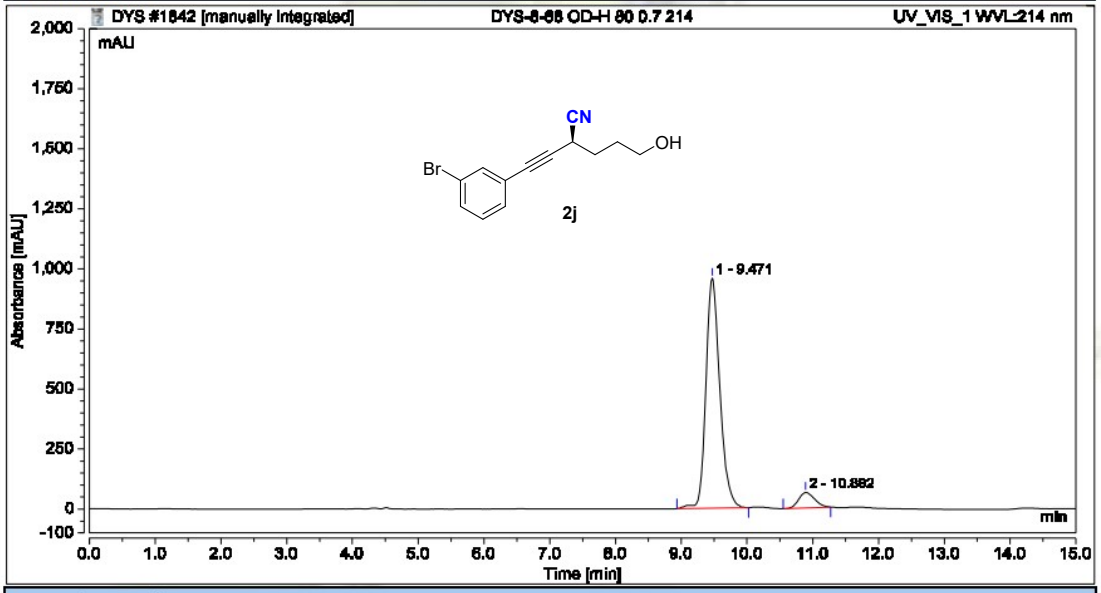
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.471	205.263	831.239	49.82	54.46	n.a.
2		10.892	206.770	695.102	50.18	45.54	n.a.
Total:			**412.032**	**1526.341**	**100.00**	**100.00**	

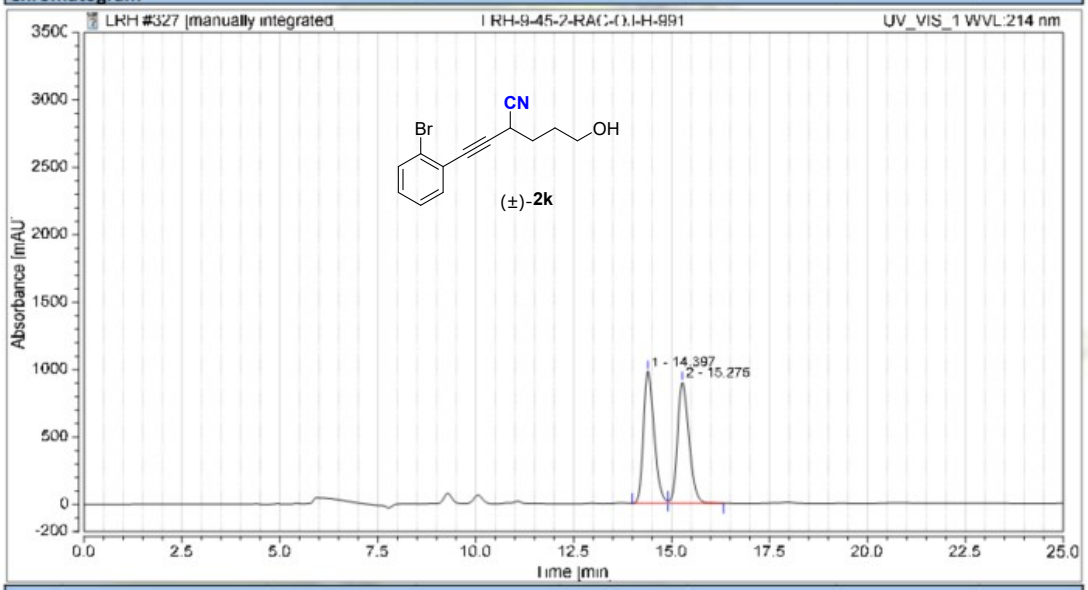
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.471	235.572	957.452	92.84	93.67	n.a.
2		10.892	18.178	64.751	7.16	6.33	n.a.
Total:			**253.750**	**1022.204**	**100.00**	**100.00**	

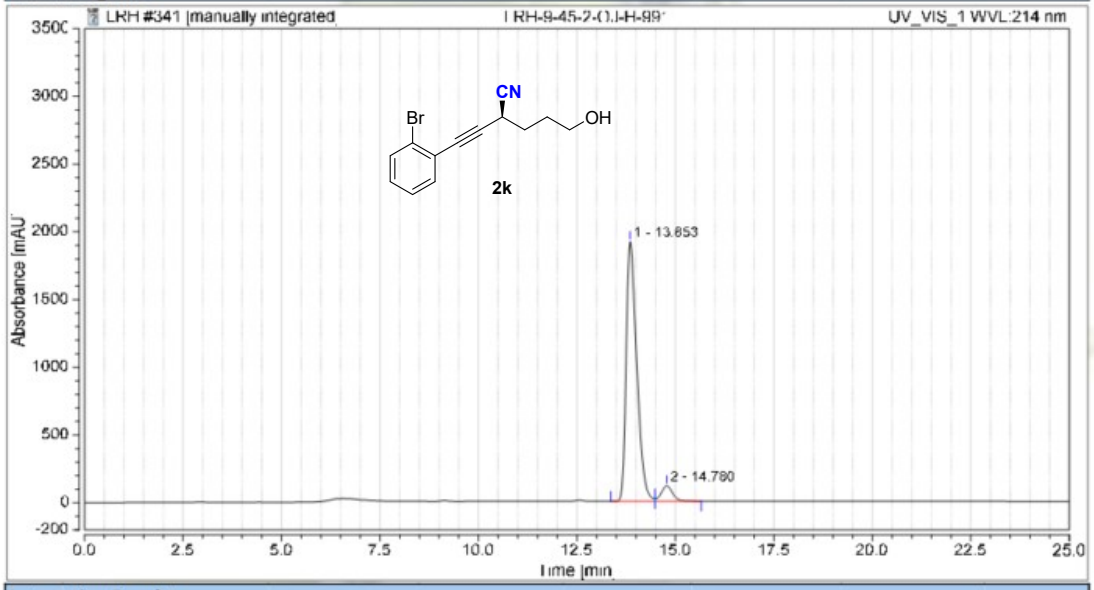
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.397	311.548	982.128	50.37	52.15	n.a.
2		15.275	306.929	901.044	49.63	47.85	n.a.
Total:			**618.477**	**1883.172**	**100.00**	**100.00**	

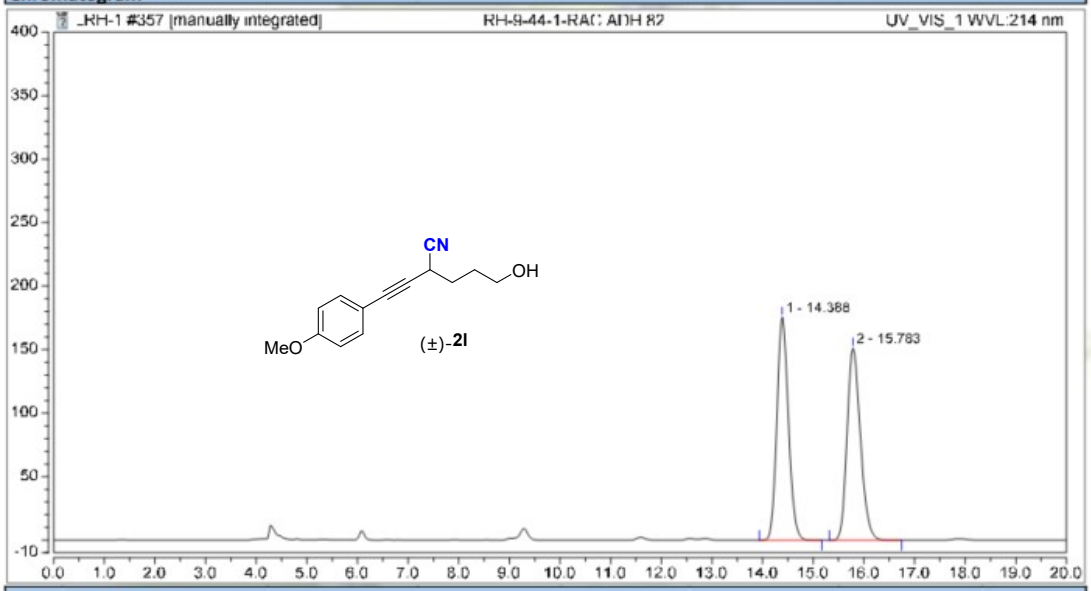
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.853	593.746	1917.586	93.96	94.37	n.a.
2		14.780	38.166	114.502	6.04	5.63	n.a.
Total:			**631.912**	**2032.089**	**100.00**	**100.00**	

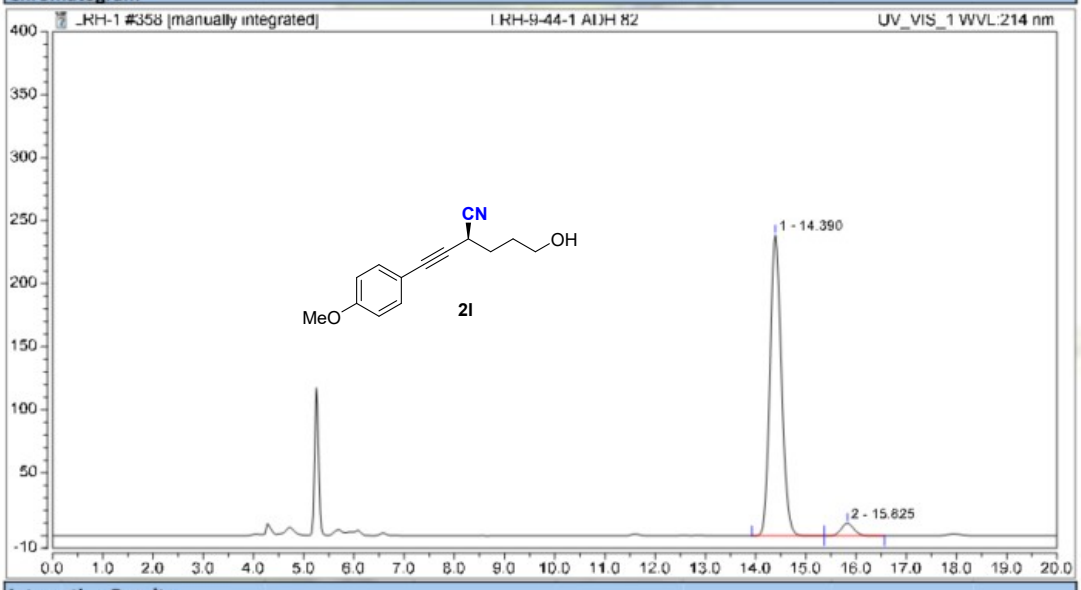
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.388	46.341	175.790	50.00	53.70	n.a.
2		15.783	46.349	151.540	50.00	46.30	n.a.
Total:			**92.690**	**327.330**	**100.00**	**100.00**	

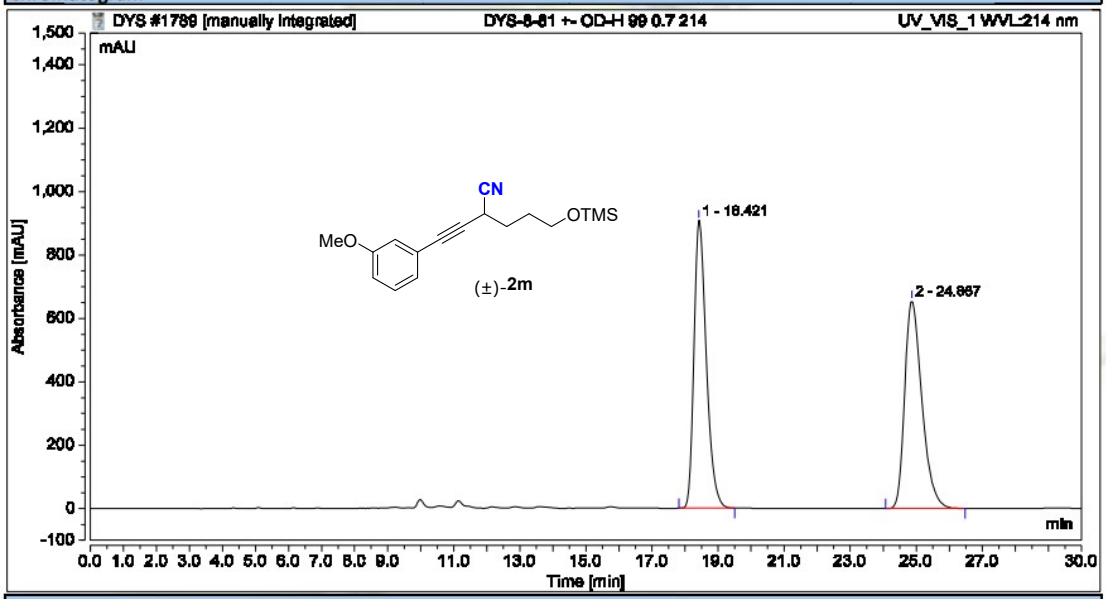
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.390	63.214	238.732	95.48	95.99	n.a.
2		15.825	2.990	9.965	4.52	4.01	n.a.
Total:			**66.204**	**248.698**	**100.00**	**100.00**	

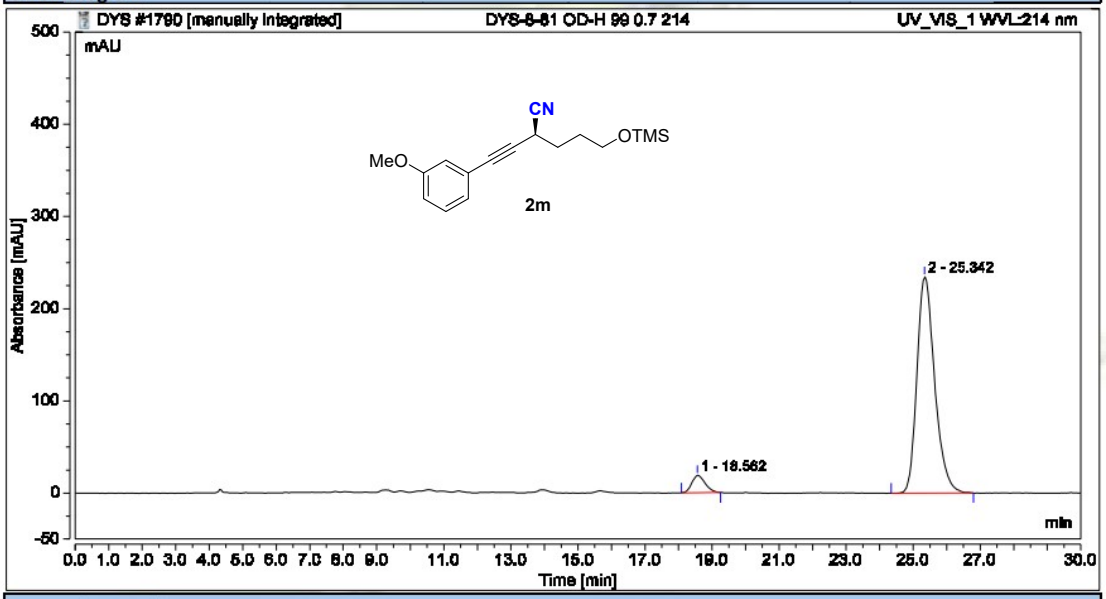
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.421	392.477	908.602	49.78	58.06	n.a.
2		24.867	395.994	656.343	50.22	41.94	n.a.
Total:			**788.471**	**1564.945**	**100.00**	**100.00**	

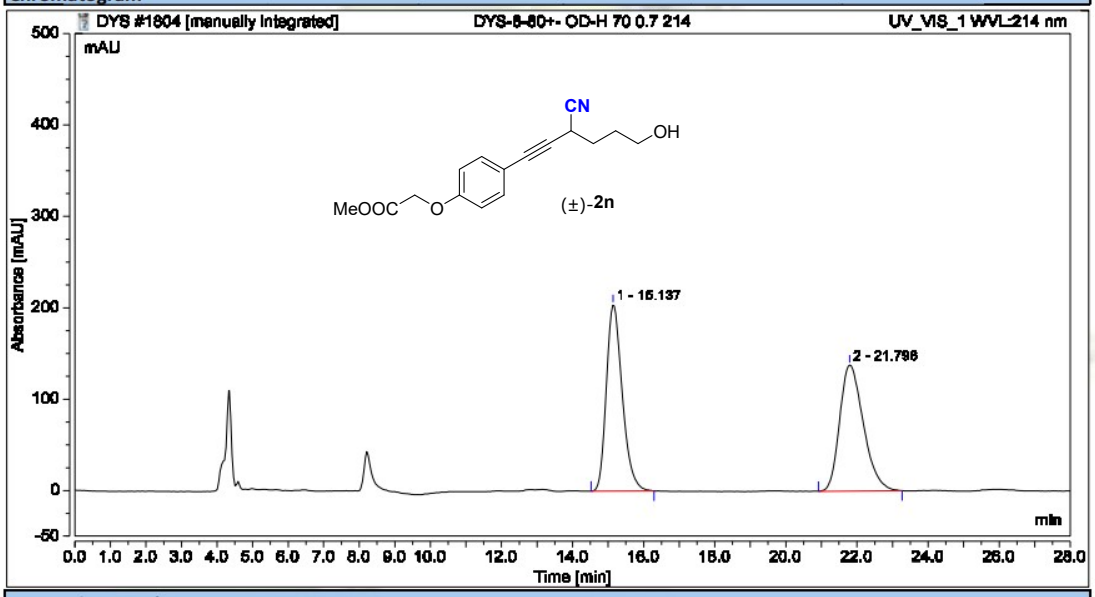
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.562	8.761	18.921	5.74	7.46	n.a.
2		25.342	143.862	234.652	94.26	92.54	n.a.
Total:			**152.624**	**253.573**	**100.00**	**100.00**	

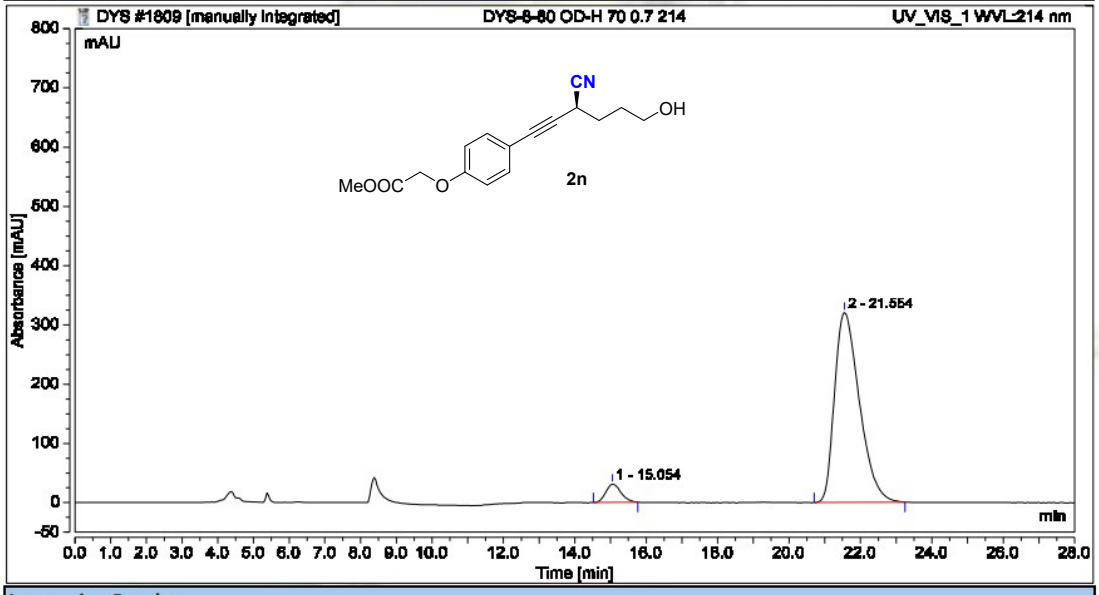
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.137	105.829	204.028	49.84	59.65	n.a.
2		21.796	106.519	138.004	50.16	40.35	n.a.
Total:			**212.349**	**342.032**	**100.00**	**100.00**	

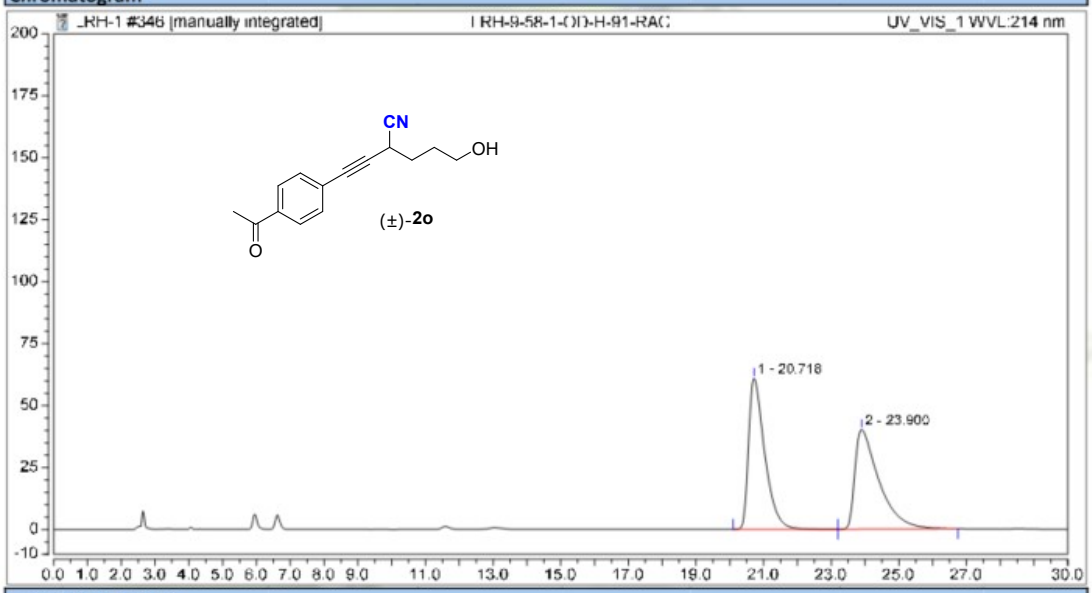
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.054	15.295	31.067	5.58	8.83	n.a.
2		21.554	258.764	320.818	94.42	91.17	n.a.
Total:			**274.059**	**351.886**	**100.00**	**100.00**	

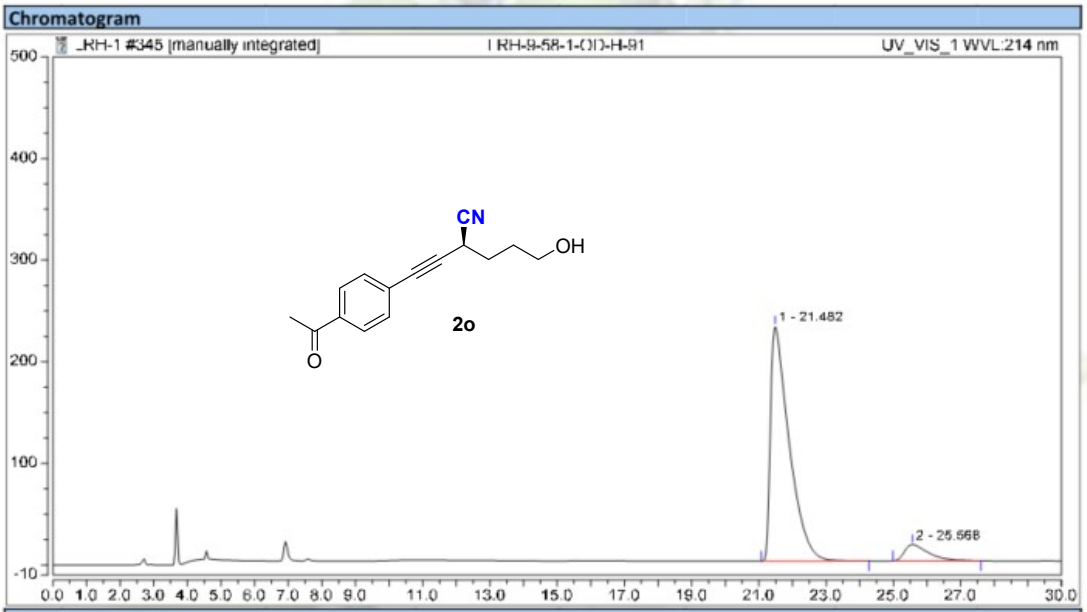
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.718	33.636	60.945	50.36	60.29	n.a.
2		23.900	33.157	40.140	49.64	39.71	n.a.
Total:			**66.792**	**101.085**	**100.00**	**100.00**	

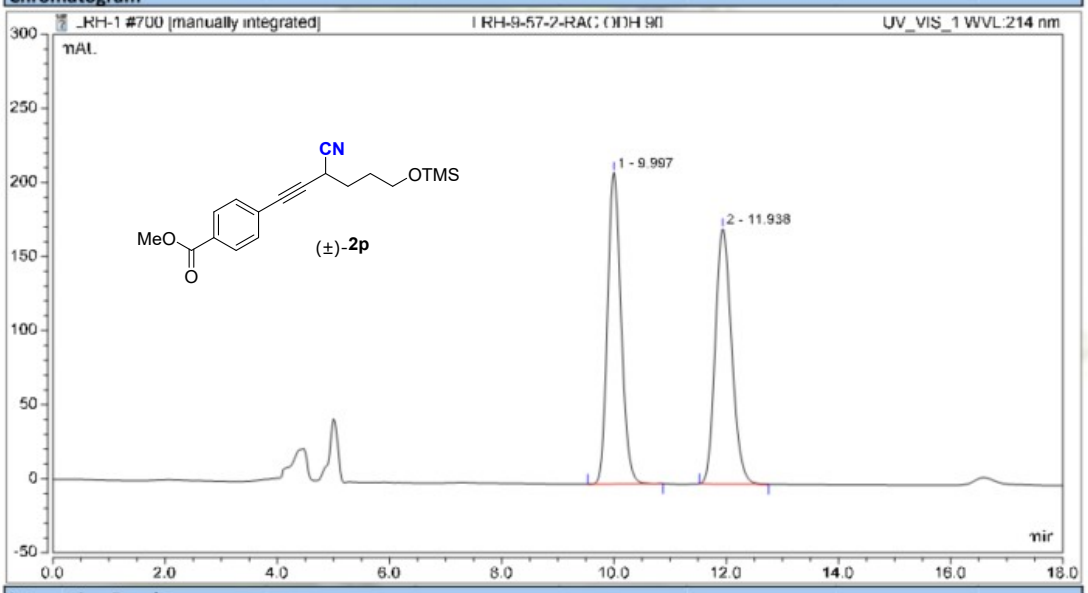
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.482	148.009	231.181	91.81	93.55	n.a.
2		25.568	13.212	15.936	8.19	6.45	n.a.
Total:			**161.221**	**247.117**	**100.00**	**100.00**	

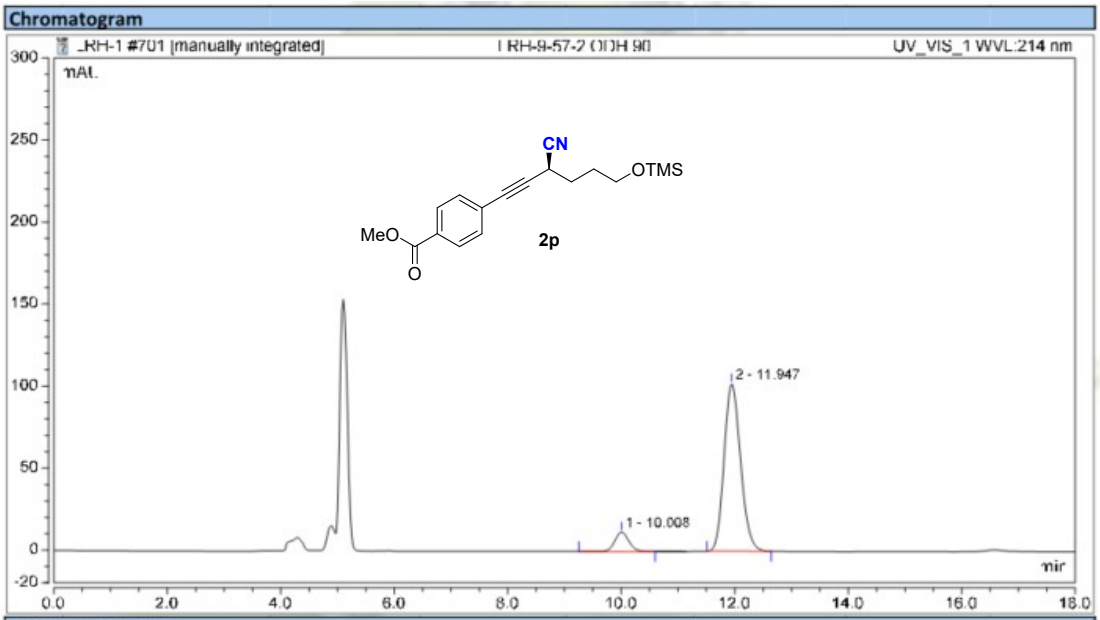
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.997	58.447	210.401	50.08	54.96	n.a.
2		11.938	58.252	172.390	49.92	45.04	n.a.
Total:			**116.699**	**382.791**	**100.00**	**100.00**	

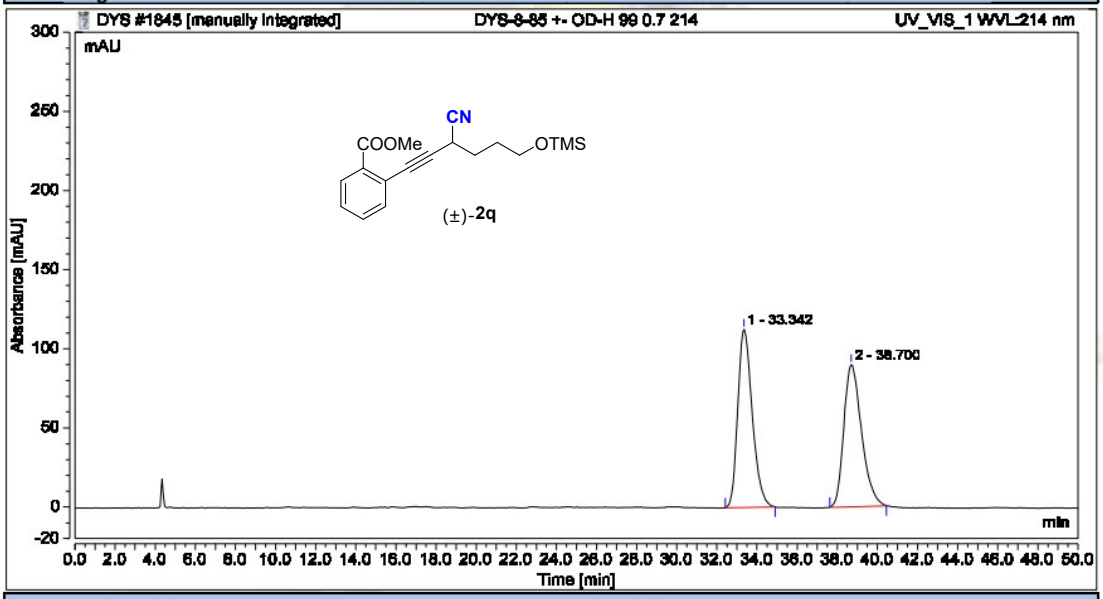
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.008	3.465	11.884	9.17	10.43	n.a.
2		11.947	34.333	102.010	90.83	89.57	n.a.
Total:			**37.798**	**113.894**	**100.00**	**100.00**	

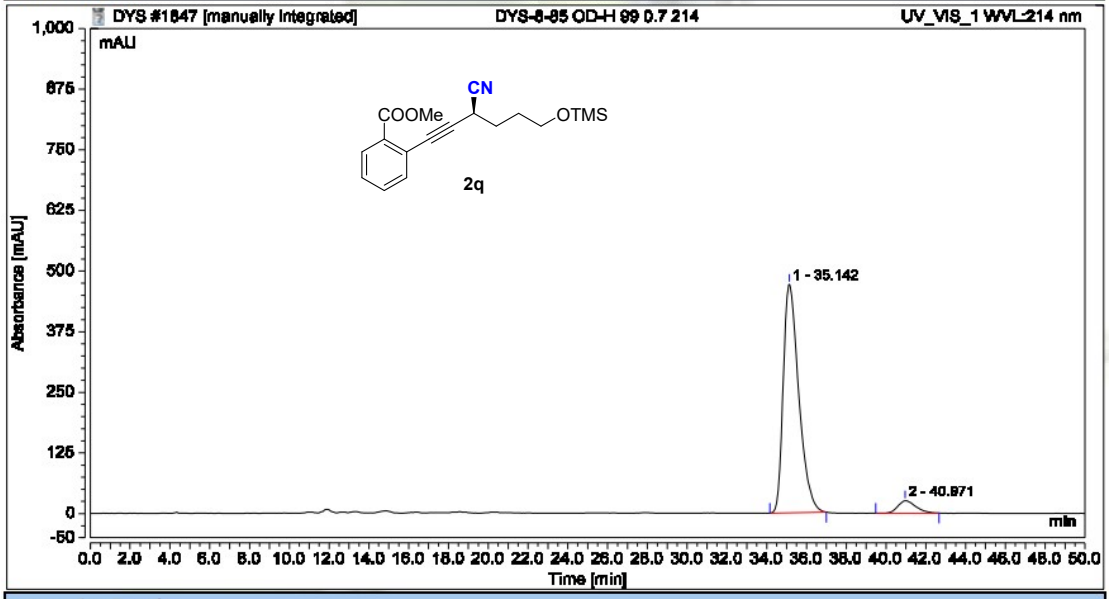
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		33.342	93.735	112.684	50.51	55.60	n.a.
2		38.700	91.829	89.972	49.49	44.40	n.a.
Total:			**185.565**	**202.656**	**100.00**	**100.00**	

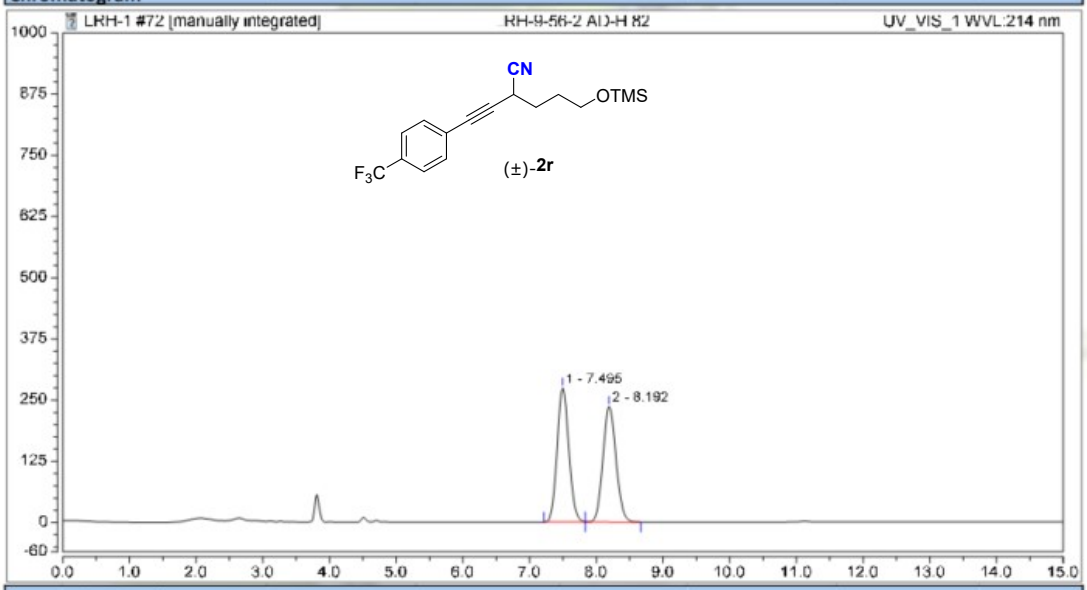
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		35.142	426.663	471.356	94.08	94.84	n.a.
2		40.971	26.872	25.624	5.92	5.16	n.a.
Total:			**453.535**	**496.980**	**100.00**	**100.00**	

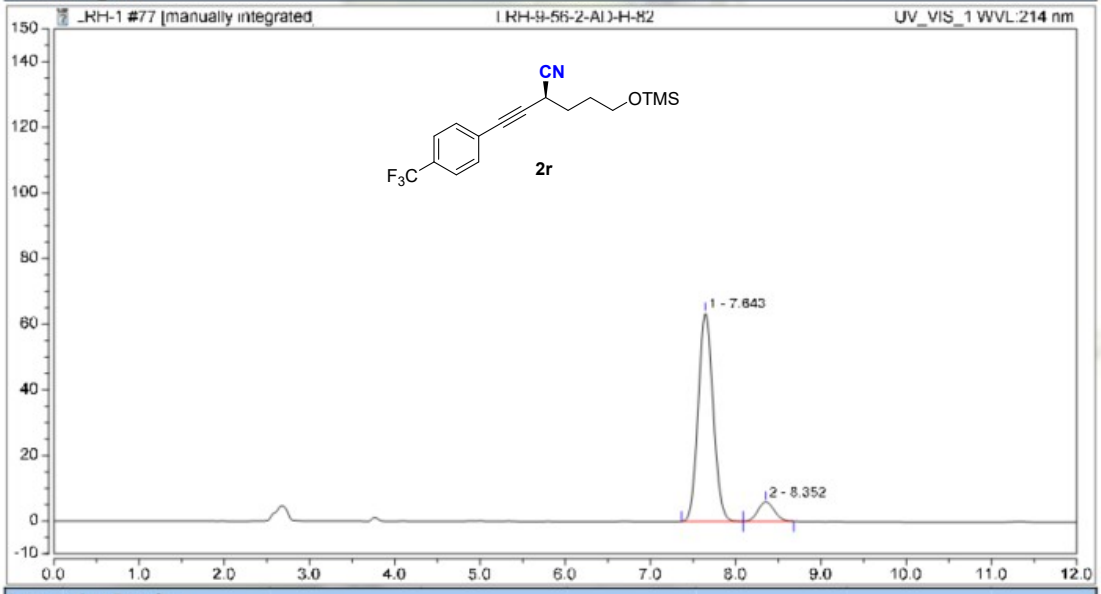
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.495	55.726	273.784	50.90	53.67	n.a.
2		8.192	53.760	236.361	49.10	46.33	n.a.
Total:			**109.487**	**510.144**	**100.00**	**100.00**	

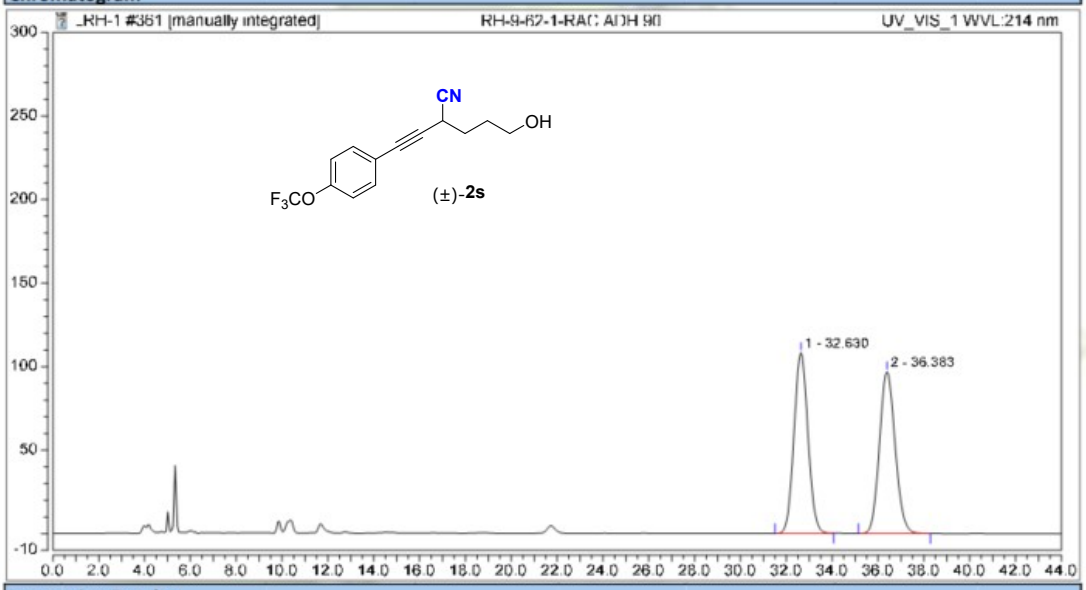
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.643	12.913	63.599	90.65	91.41	n.a.
2		8.352	1.333	5.975	9.35	8.59	n.a.
Total:			**14.246**	**69.574**	**100.00**	**100.00**	

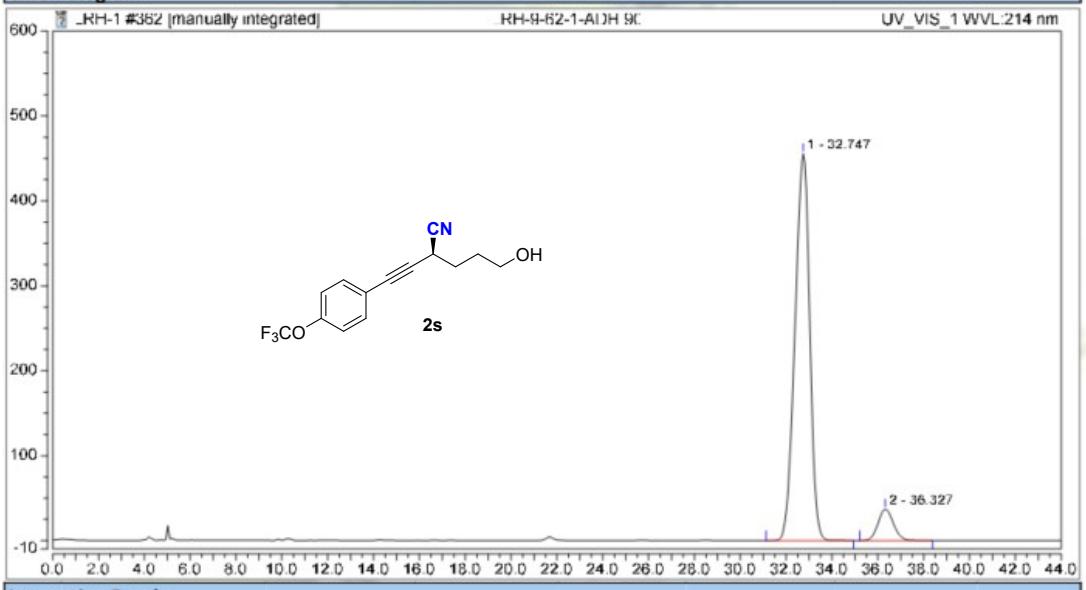
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		32.630	76.464	108.341	49.84	52.77	n.a.
2		36.383	76.965	96.970	50.16	47.23	n.a.
Total:			**153.430**	**205.311**	**100.00**	**100.00**	

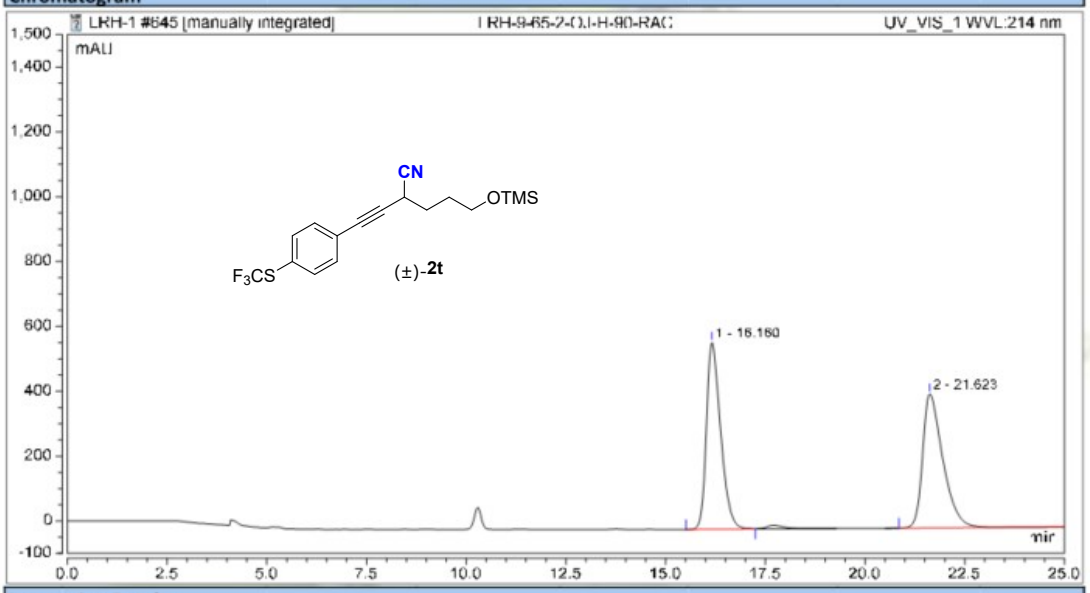
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		32.747	338.577	455.633	92.13	92.49	n.a.
2		36.327	28.928	37.011	7.87	7.51	n.a.
Total:			**367.505**	**492.644**	**100.00**	**100.00**	

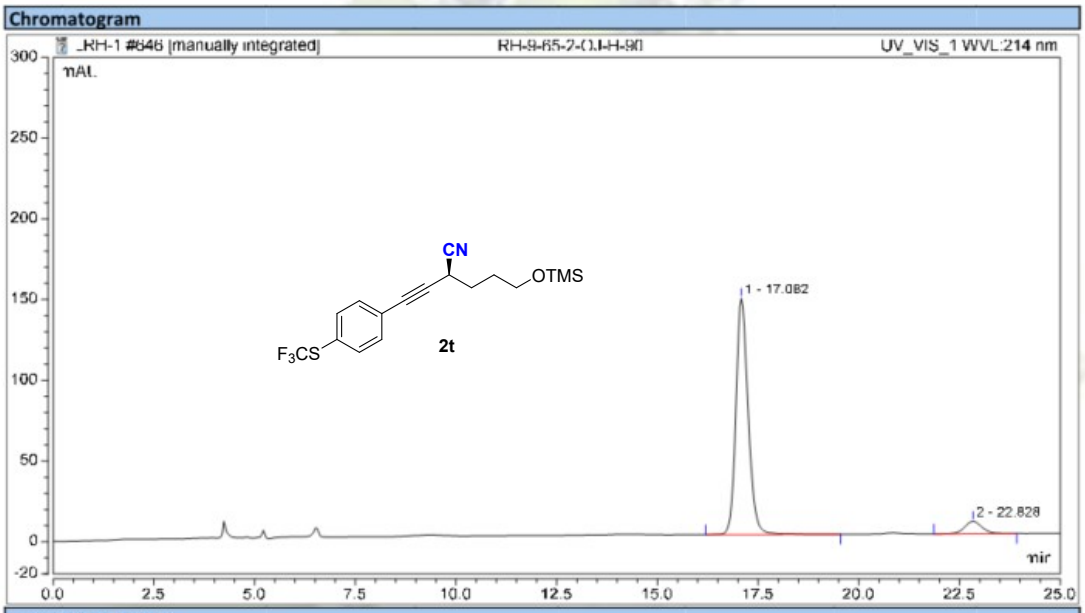
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.160	238.430	577.386	49.47	58.26	n.a.
2		21.623	243.562	413.693	50.53	41.74	n.a.
Total:			**481.993**	**991.079**	**100.00**	**100.00**	

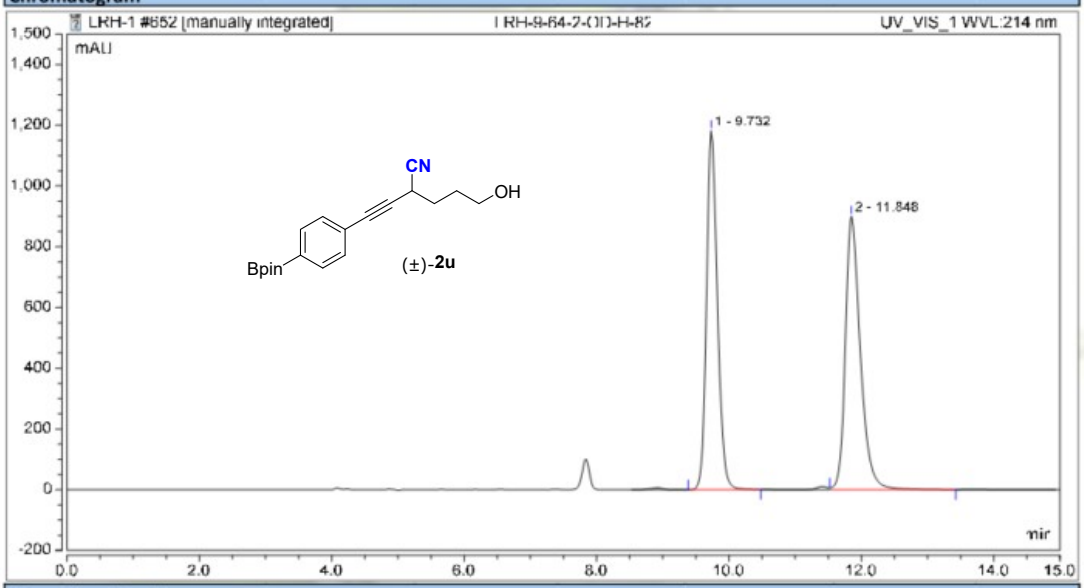
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.082	51.545	146.301	92.90	94.98	n.a.
2		22.828	3.942	7.730	7.10	5.02	n.a.
Total:			**55.487**	**154.030**	**100.00**	**100.00**	

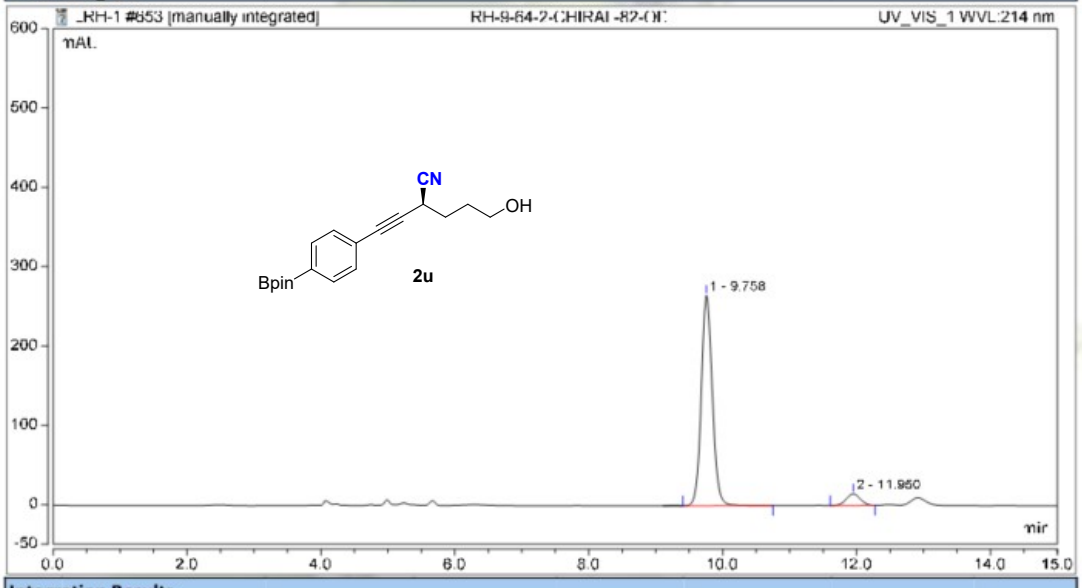
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.732	225.486	1183.390	48.81	56.77	n.a.
2		11.848	236.457	900.963	51.19	43.23	n.a.
Total:			**461.943**	**2084.353**	**100.00**	**100.00**	

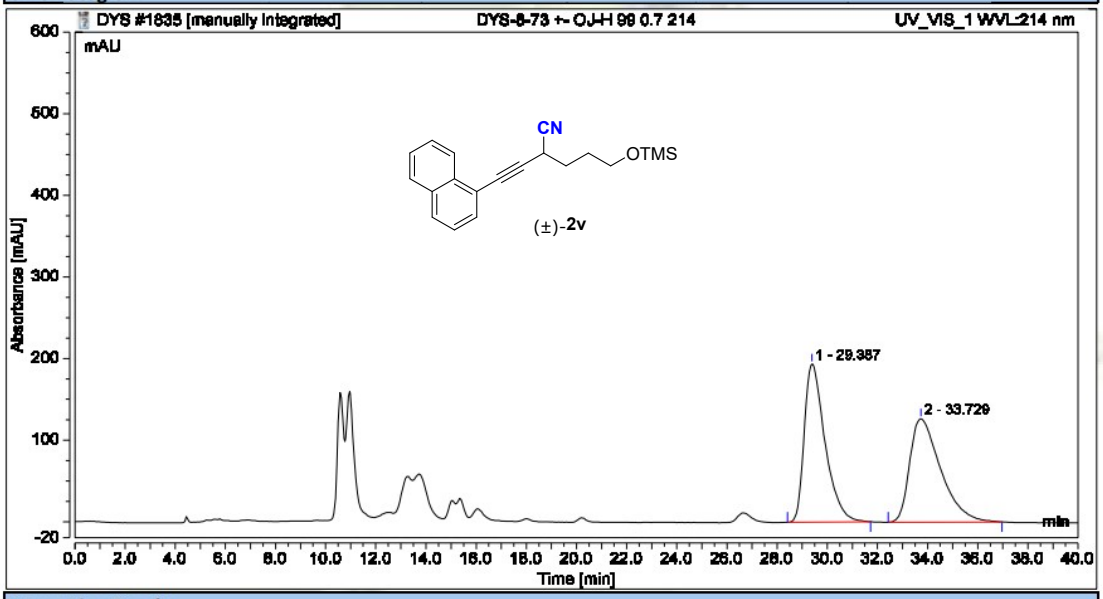
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.758	50.577	265.172	93.46	94.80	n.a.
2		11.950	3.542	14.539	6.54	5.20	n.a.
Total:			**54.119**	**279.711**	**100.00**	**100.00**	

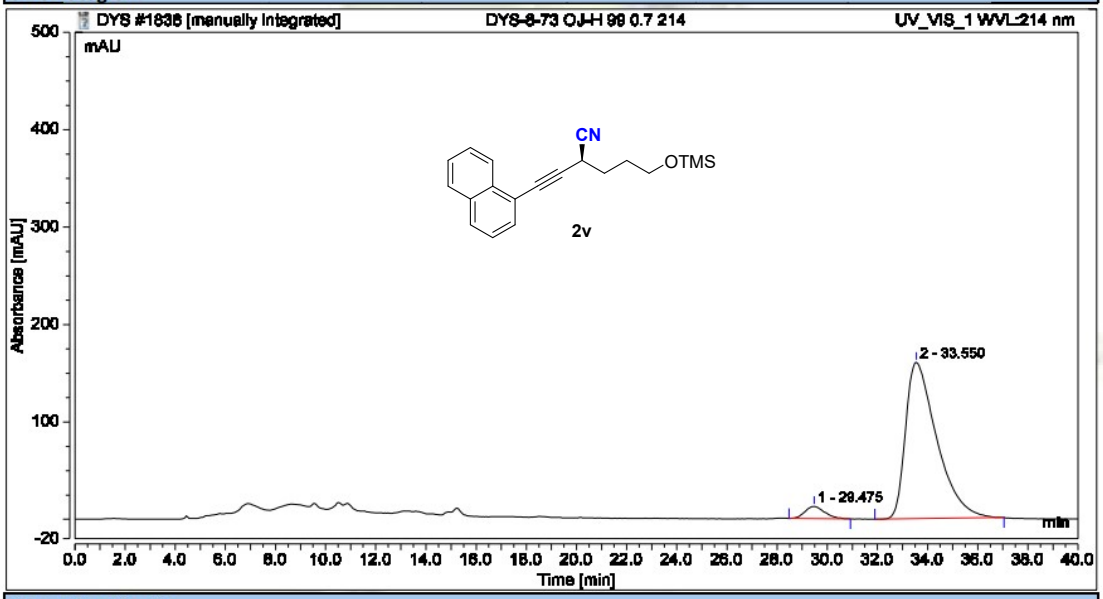
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		29.387	186.193	194.016	50.73	60.47	n.a.
2		33.729	180.818	126.817	49.27	39.53	n.a.
Total:			**367.011**	**320.833**	**100.00**	**100.00**	

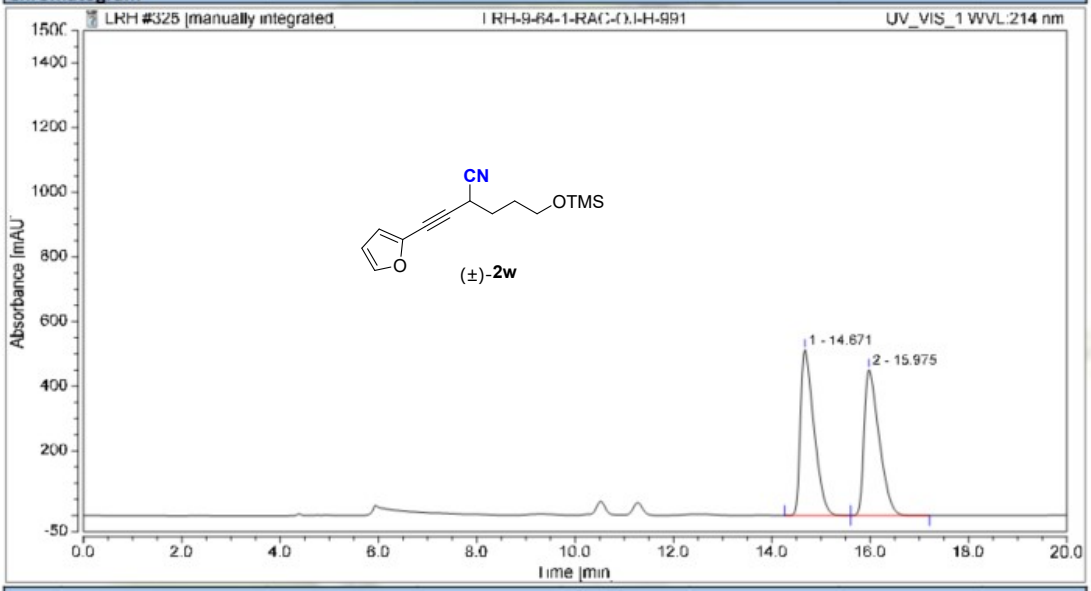
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		29.475	11.298	12.404	4.65	7.17	n.a.
2		33.550	231.418	160.502	95.35	92.83	n.a.
Total:			**242.716**	**172.906**	**100.00**	**100.00**	

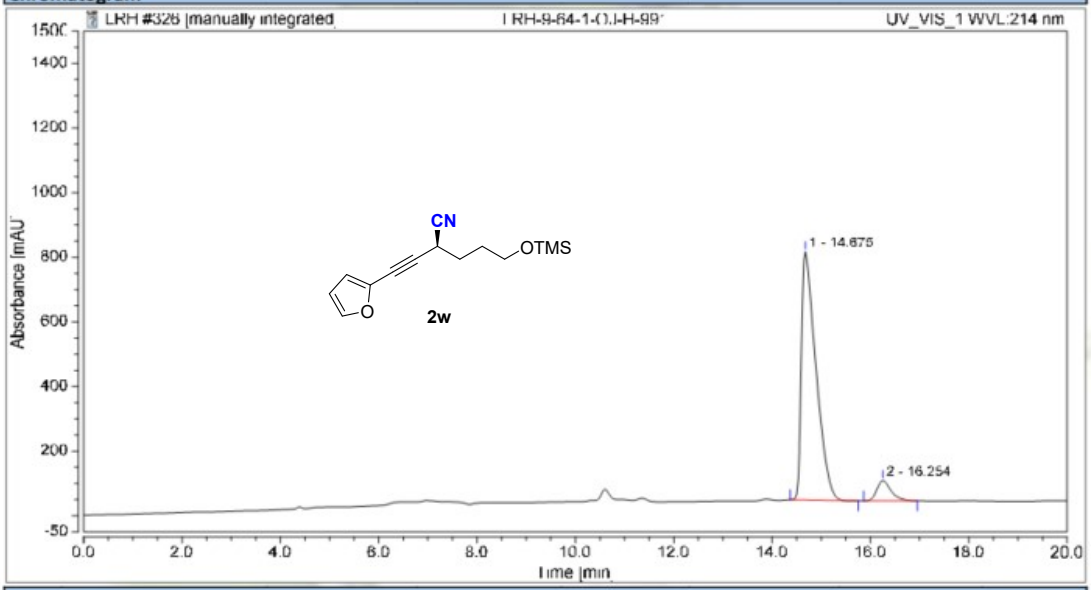
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.671	162.703	513.472	50.52	53.15	n.a.
2		15.975	159.322	452.551	49.48	46.85	n.a.
Total:			**322.025**	**966.023**	**100.00**	**100.00**	

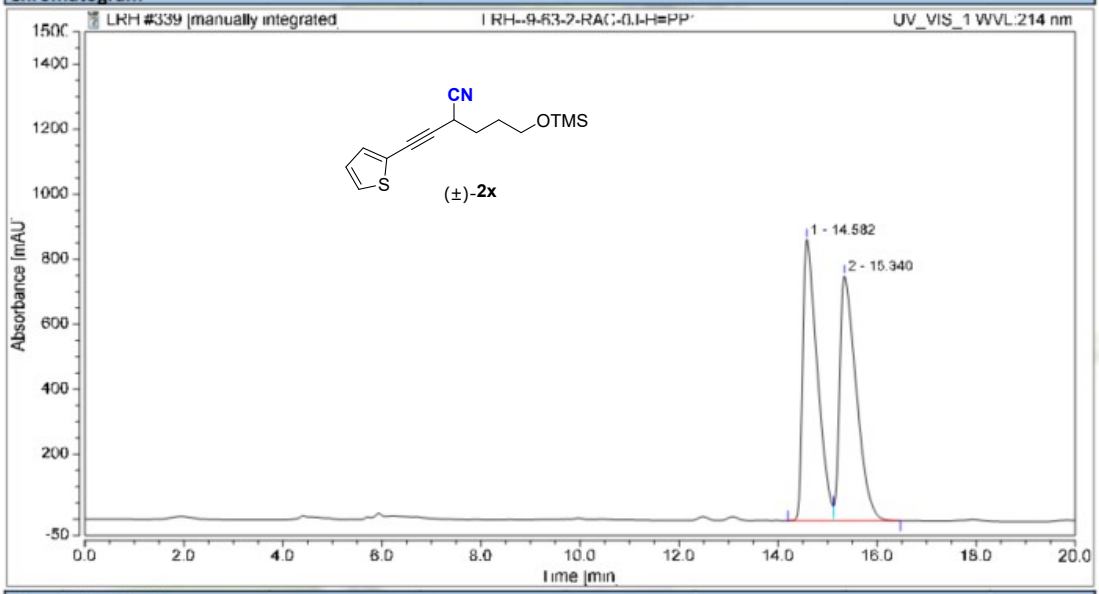
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.675	263.293	768.359	92.51	92.41	n.a.
2		16.254	21.321	63.101	7.49	7.59	n.a.
Total:			**284.614**	**831.460**	**100.00**	**100.00**	

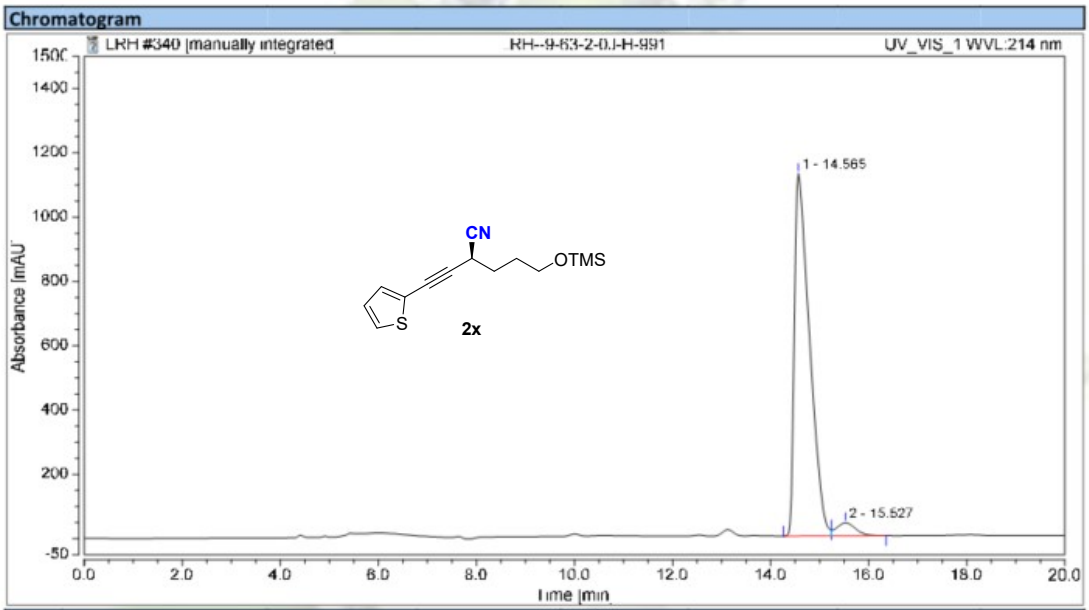
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.582	294.881	866.498	50.12	53.41	n.a.
2		15.340	293.424	755.707	49.88	46.59	n.a.
Total:			**588.306**	**1622.205**	**100.00**	**100.00**	

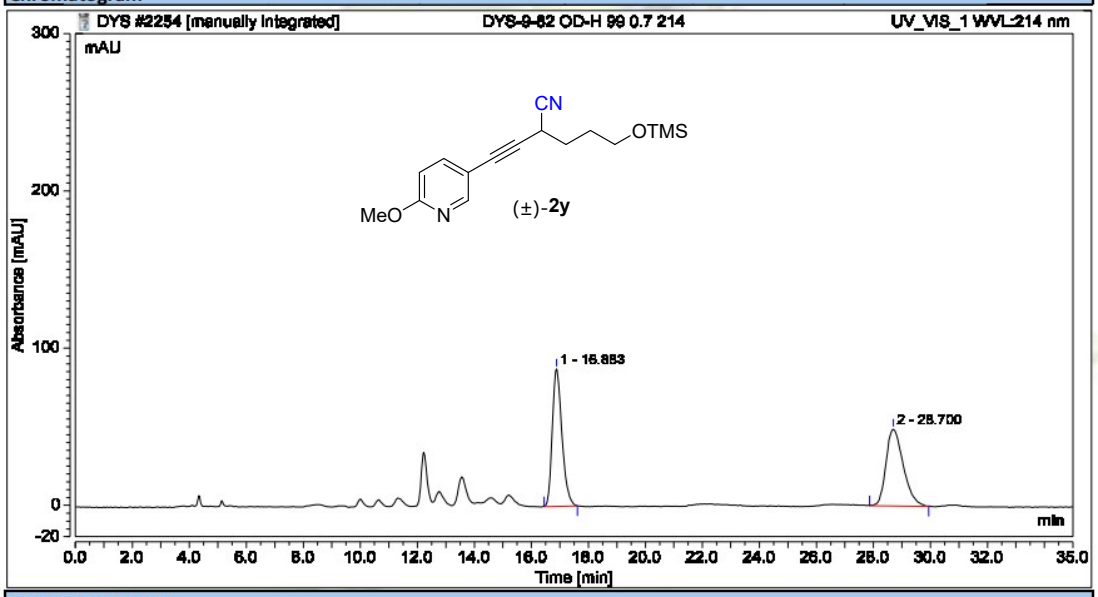
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.565	403.873	1127.726	95.65	96.50	n.a.
2		15.527	18.365	40.854	4.35	3.50	n.a.
Total:			**422.239**	**1168.580**	**100.00**	**100.00**	

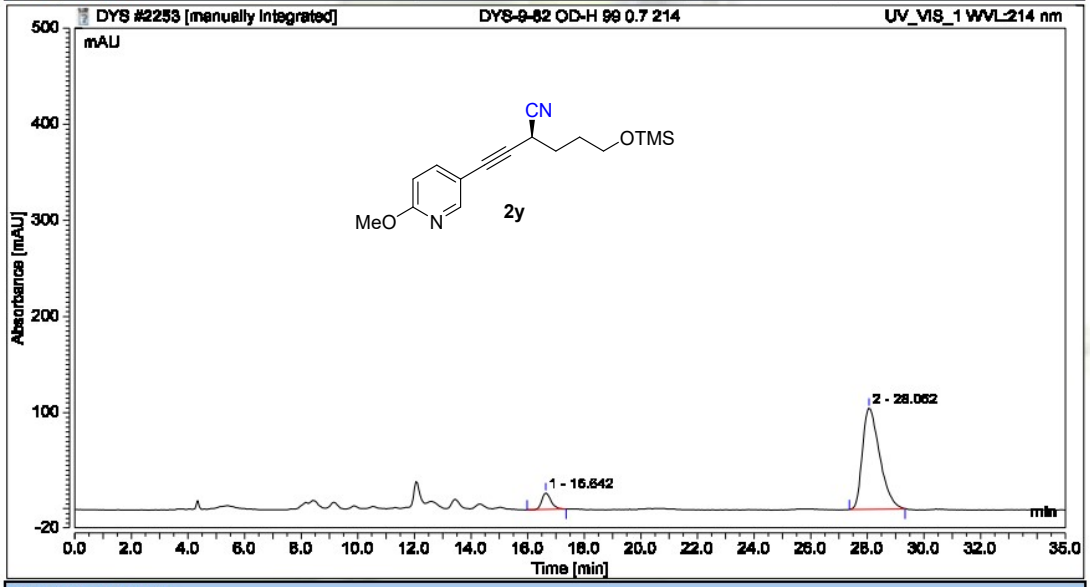
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.883	34.172	87.395	50.04	64.10	n.a.
2		28.700	34.118	48.955	49.96	35.90	n.a.
Total:			**68.291**	**136.350**	**100.00**	**100.00**	

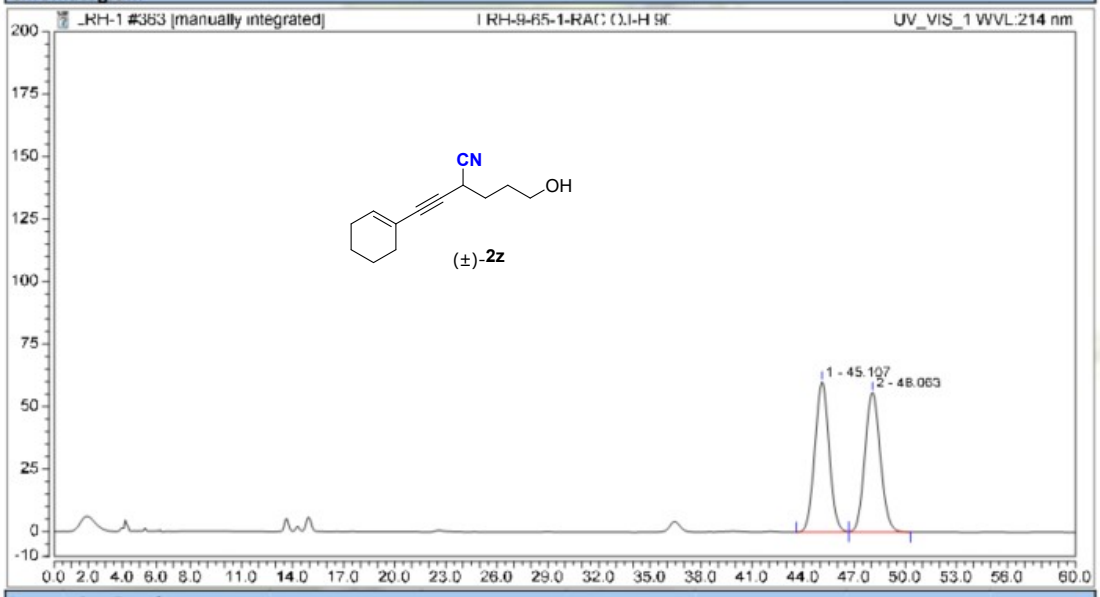
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.642	6.482	17.363	7.98	14.16	n.a.
2		28.062	74.720	105.253	92.02	85.84	n.a.
Total:			**81.202**	**122.616**	**100.00**	**100.00**	

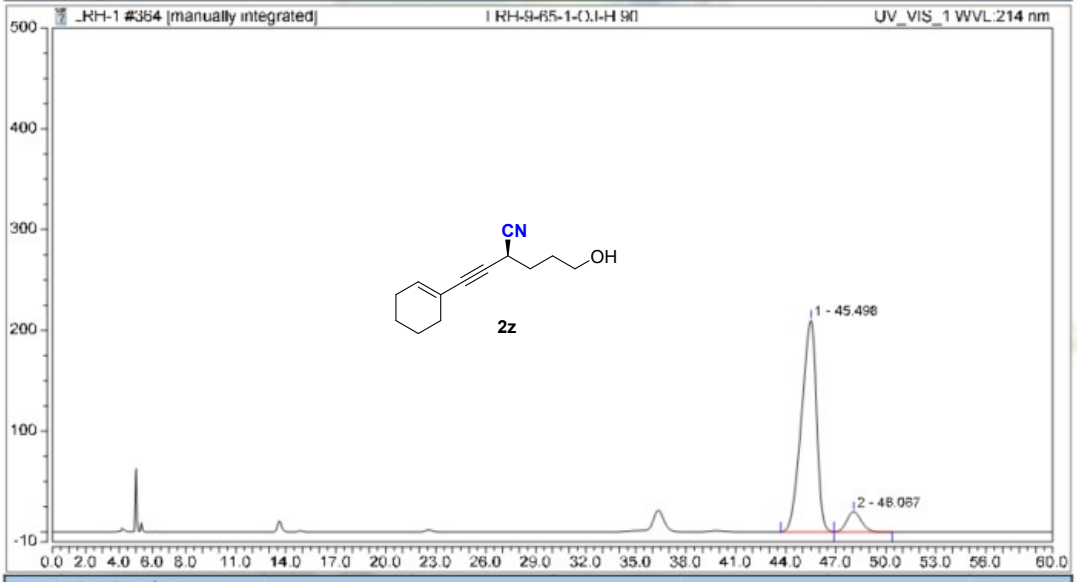
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		45.107	58.984	60.239	50.03	51.81	n.a.
2		48.063	58.912	56.024	49.97	48.19	n.a.
Total:			**117.896**	**116.262**	**100.00**	**100.00**	

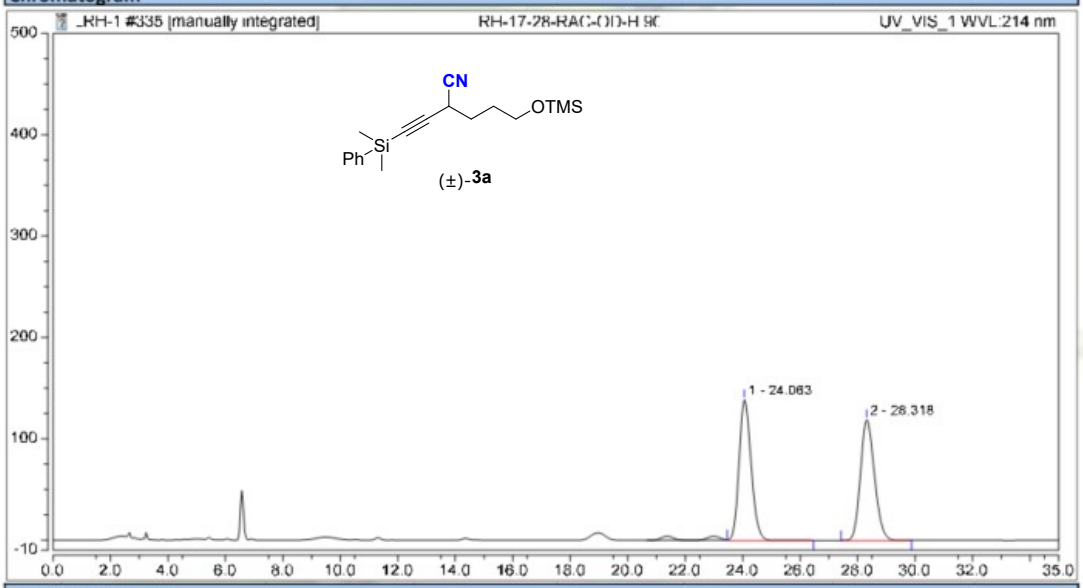
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		45.498	219.852	210.266	91.45	91.27	n.a.
2		48.067	20.548	20.100	8.55	8.73	n.a.
Total:			**240.400**	**230.366**	**100.00**	**100.00**	

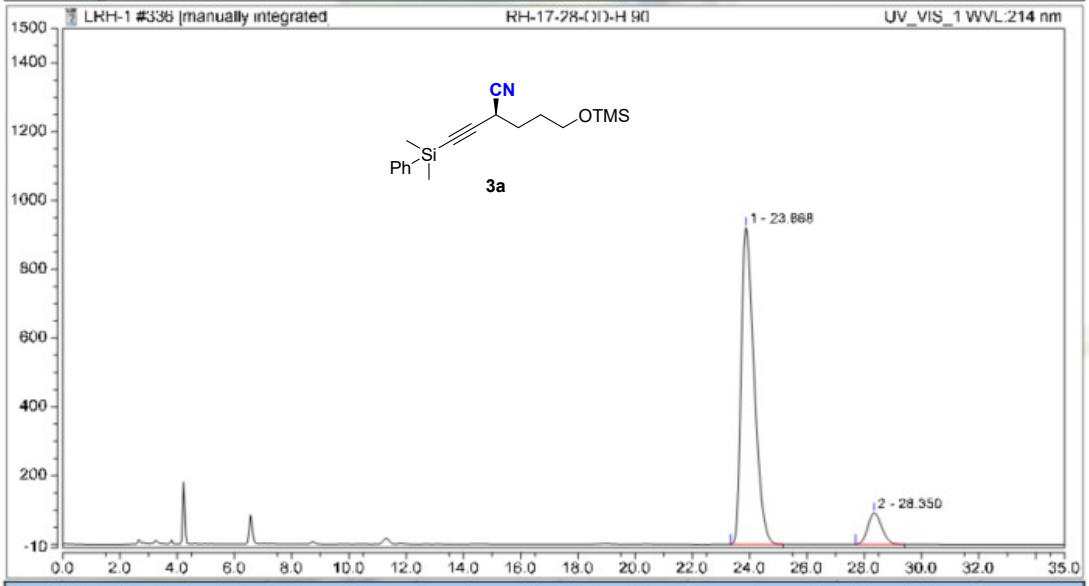
Chromatogram



Integration Results

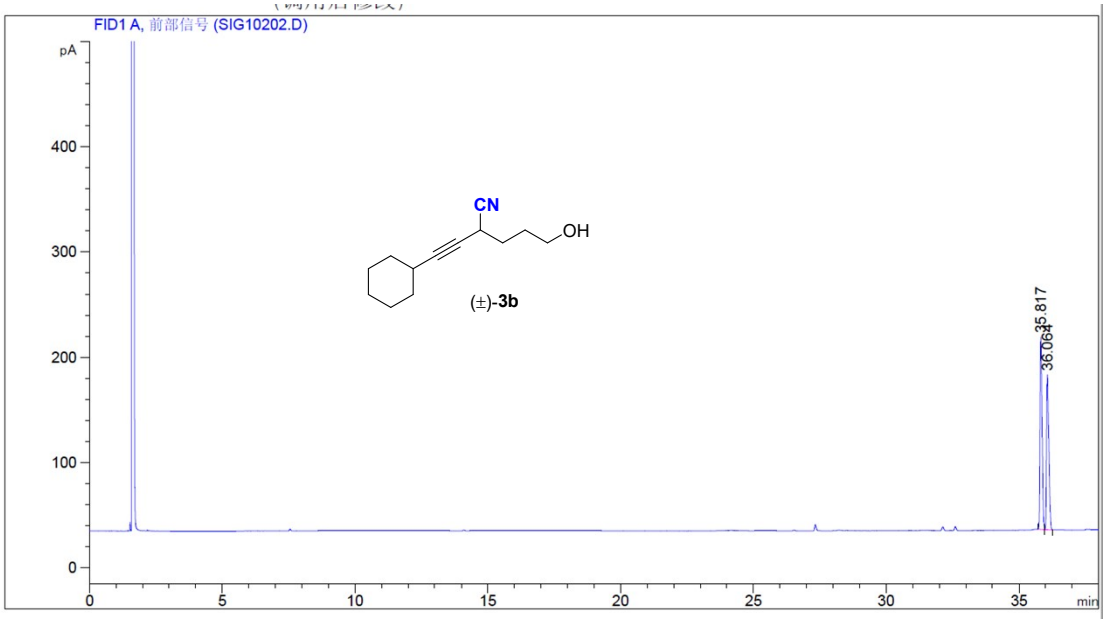
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		24.063	67.808	139.032	50.03	53.83	n.a.
2		28.318	67.714	119.224	49.97	46.17	n.a.
Total:			**135.522**	**258.255**	**100.00**	**100.00**	

Chromatogram



Integration Results

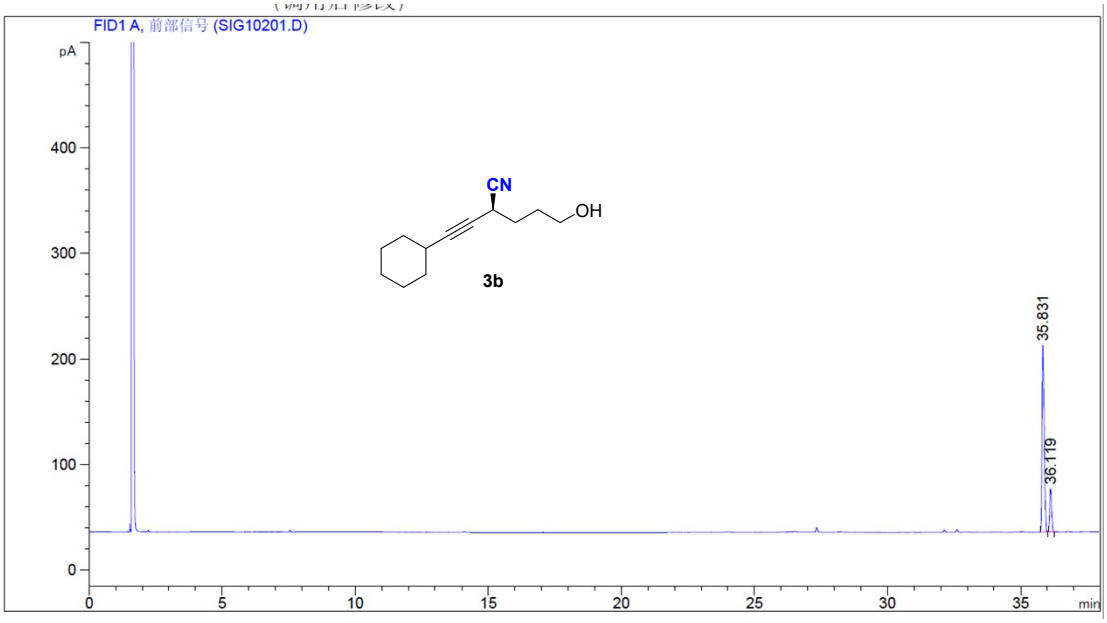
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.868	480.635	921.161	90.27	90.97	n.a.
2		28.350	51.832	91.454	9.73	9.03	n.a.
Total:			**532.468**	**1012.615**	**100.00**	**100.00**	



信号 1: FID1 A, 前部信号

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	35.817	BV	0.0858	990.27557	182.32732	53.15409
2	36.064	VB	0.0868	872.75238	147.04311	46.84591

总量 : 1863.02795 329.37042



信号 1: FID1 A, 前部信号

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [pA*s]	峰高 [pA]	峰面积 %
1	35.831	BB	0.0846	1002.27759	176.63605	83.09714
2	36.119	BB	0.0724	203.87419	41.00781	16.90286

总量 : 1206.15178 217.64386