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

Transition-Metal-Free Oxychlorination of Alkenyl Oximes: In Situ Generated Radical with *tert*-butyl Nitrite

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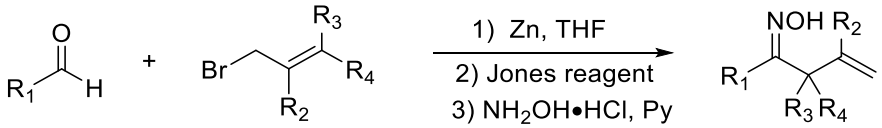
Tables of Contents

1. General Information

Solvents were pre-dried over activated 4Å molecular sieves and heated to reflux over sodium (toluene, THF) or calcium hydride (CH_2Cl_2) under a nitrogen atmosphere and collected by distillation. ^1H, ^{13}C NMR spectra were recorded on a 400 MHz spectrometer; Chemical shifts are reported in δ units relative to [TMS, ^1H δ = 0; $CDCl_3$, ^1H δ = 7.26, ^{13}C δ = 77.36]. HRMS were recorded by the mass spectrometry service at University of Science and Technology of China (Cl-35, Br-79). $AlCl_3$, CBr_4 and *t*-BuONO were commercially available and used directly as received.

2. Experimental Procedures

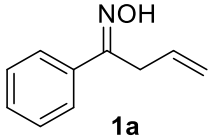
2.1. General procedure for the synthesis of oximes



1) To a solution of the allylbromide (2.0 equiv) in anhydrous THF was slowly added zinc dust (2.0 equiv) at 0 °C. Aldehyde (1.0 equiv) was dissolved in anhydrous THF and added to the solution. The resulting suspension was stirred overnight at this temperature. The reaction was quenched with saturated aqueous NH_4Cl carefully at 0 °C, filtered and extracted with ethyl acetate for 3 times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude homoallylic alcohol product was directly used in the next step without further purification.

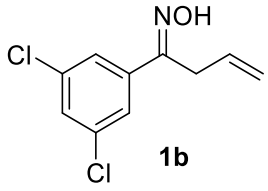
2) A solution of the homoallylic alcohol in diethyl ether was stirred at 0 °C while Jones reagent (2.0-4.0 equiv) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for 1 hour. The diethyl ether layer was separated and the aqueous layer was extracted with ethyl acetate for 3 times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The crude β,γ-unsaturated ketone product was directly used in the next step without further purification.

3) To a solution of β,γ-unsaturated ketone (1.0 equiv) in pyridine was added hydroxylamine hydrochloride (2.0 equiv). The mixture was stirred at room temperature (110 °C for **1k**) for 4 h and concentrated in *vacuo*. Then, the mixture was diluted with water and extracted with ethyl acetate, the combined organic layers were dried with $MgSO_4$, filtered, and concentrated in *vacuo*. The crude material was purified by flash chromatography on silica gel to afford the β,γ-unsaturated oxime.



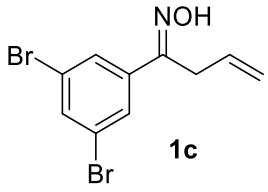
1a **1-phenylbut-3-en-1-one oxime**

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 40:1), colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.95 (br s, 1 H), 7.69-7.65 (m, 2 H), 7.44-7.39 (m, 3 H), 6.04-5.93 (m, 1 H), 5.24-5.13 (m, 2 H), 3.64 (dt, *J* = 6.0, 1.6 Hz, 2 H).[1]



1b **1-(3,5-dichlorophenyl)but-3-en-1-one oxime**

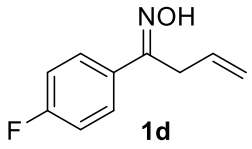
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 70:1), white solid, mp: 87.0-88.1 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (br s, 1 H), 7.51 (d, *J* = 2.0 Hz, 2 H), 7.36 (t, *J* = 2.0 Hz, 1 H), 5.94-5.84 (m, 1 H), 5.18-5.12 (m, 2 H), 3.53 (dt, *J* = 6.0, 1.6 Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.3, 138.8, 135.5, 131.6, 129.5, 125.2, 118.0, 30.9. **HRMS (ESI):** calcd for $C_{10}H_{10}NOCl_2$ $[M+H]^+$ 230.0139, found 230.0135.



1c

1-(3,5-dibromophenyl)but-3-en-1-one oxime

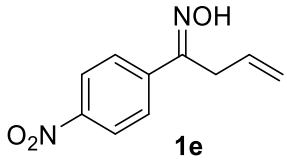
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 70:1), brown solid, mp: 105.5-105.9 ˚C . **^{1}H NMR** (400 MHz, $CDCl_3$) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.53 (br s, 1 H), 7.70-7.69 (m, 2 H), 7.67-7.66 (m, 1 H), 5.94-5.83 (m, 1 H), 5.19-5.13 (m, 2 H), 3.54 (dt, *J* = 6.0, 1.6 Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.3, 139.2, 135.0, 131.5, 128.5, 123.4, 118.1, 31.1. **HRMS(ESI)** calcd for $C_{10}H_{10}NOBr_2$ $[M+H]^+$ 317.9129, found 317.9128.



1d

1-(4-fluorophenyl)but-3-en-1-one oxime

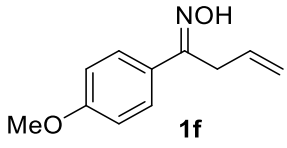
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 20:1), colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.11 (br s, 1 H), 7.65-7.59 (m, 2 H), 7.10-7.04 (m, 2 H), 5.98-5.87 (m, 1 H), 5.20-5.10 (m, 2 H), 3.59-3.58 (m, 1 H), 3.58-3.56 (m, 1 H).[1]



1e

1-(4-nitrophenyl)but-3-en-1-one oxime

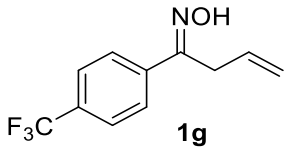
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 10:1), white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.49 (br s, 1 H), 8.24-8.20 (m, 2 H), 7.81-7.77 (m, 2 H), 5.96-5.85 (m, 1 H), 5.19-5.12 (m, 2 H), 3.62 (dt, *J* = 6.4, 1.6 Hz, 2 H).[1]



1f

1-(4-methoxyphenyl)but-3-en-1-one oxime

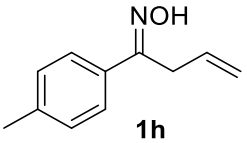
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 20:1), light yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.81 (br s, 1 H), 7.62-7.59 (m, 2 H), 6.94-6.90 (m, 2 H), 6.02-5.91 (m, 1 H), 5.22-5.10 (m, 2 H), 3.83 (s, 3 H), 3.62-3.59 (m, 2 H).[1]



1g

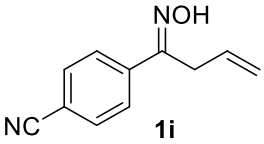
1-(4-(trifluoromethyl)phenyl)but-3-en-1-one oxime

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 40:1), white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.85 (br s, 1 H), 7.77-7.74 (m, 2 H), 7.66-7.62 (m, 2 H), 5.97-5.87 (m, 1 H), 5.20-5.12 (m, 2 H), 3.62-3.61 (m, 1 H), 3.61 (dt, *J* = 6.0, 1.6 Hz, 1 H).[2]



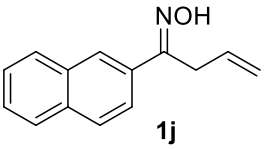
1h **1-(*p*-tolyl)but-3-en-1-one oxime**

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 40:1), white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.83 (br s, 1 H), 7.55-7.52 (m, 2 H), 7.20-7.17 (m, 2 H), 6.00-5.89 (m, 1 H), 5.20-5.09 (m, 2 H), 3.59 (dt, *J* = 6.0, 1.6 Hz, 2 H), 2.37 (s, 3 H).[2]



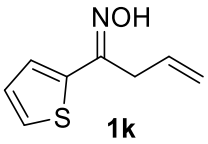
1i **4-(1-(hydroxyimino)but-3-en-1-yl)benzonitrile**

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 40:1), white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.45 (br s, 1 H), 7.74 (d, *J* = 8.0 Hz, 2 H), 7.66 (d, *J* = 8.0 Hz, 2 H), 5.94-5.84 (m, 1 H), 5.17-5.11 (m, 2 H), 3.59-3.57 (m, 2 H).[3]



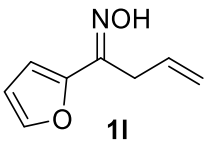
1j **1-(naphthalen-2-yl)but-3-en-1-one oxime**

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 40:1), white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (br s, 1 H), 8.04 (s, 1 H), 7.88-7.82 (m, 4 H), 7.52-7.48 (m, 2 H), 6.06-5.96 (m, 1 H), 5.25-5.12 (m, 2 H), 3.72 (dt, *J* = 6.0, 1.6 Hz, 2 H).[1]



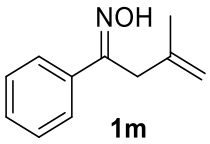
1k **1-(thiophen-2-yl)but-3-en-1-one oxime**

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 20:1), white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.30 (br s, 1 H), 7.59- 7.56 (m, 2 H), 7.13-7.10 (m, 1 H), 6.09-5.98 (m, 1 H), 5.30-5.25 (m, 1 H), 5.21-5.17 (m, 1 H), 3.55 – 3.53 (m, 2 H).[1]



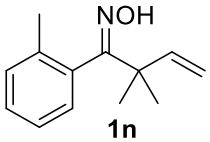
1l **1-(furan-2-yl)but-3-en-1-one oxime**

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 20:1), white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.54 (br s, 1 H), 7.48- 7.45 (m, 2 H), 6.55-6.54 (m, 1 H), 6.05-5.95 (m, 1 H), 5.23-5.11 (m, 2 H), 3.45 (dt, *J* = 6.4, 1.6 Hz, 2 H).[1]



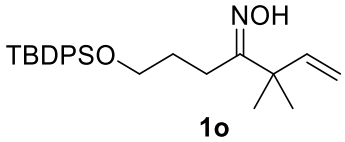
1m **3-methyl-1-phenylbut-3-en-1-one oxime**

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 20:1), colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.80 (br s, 1 H), 7.67-7.61 (m, 2 H), 7.39-7.35 (m, 3 H), 4.85-4.83 (m, 1 H), 4.76-4.74 (m, 1 H), 3.55 (s, 2 H), 1.82 (s, 3 H).[1]



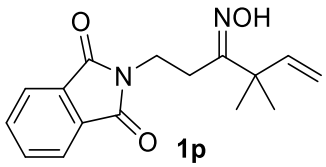
1n **2,2-dimethyl-1-(*o*-tolyl)but-3-en-1-one oxime**

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 20:1), white solid, mp: 132.5-133.9 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (br s, 1 H), 7.29-7.16 (m, 3 H), 7.03-7.01 (m, 1 H), 5.95 (dd, *J* = 17.6, 10.8 Hz, 1 H), 5.05-4.99 (m, 2 H), 2.23 (s, 3 H), 1.28 (s, 3 H), 1.21 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 144.8, 136.2, 133.6, 130.2, 128.6, 127.4, 125.4, 112.9, 43.9, 26.4, 24.9, 20.5. **HRMS (ESI)** calcd for $C_{13}H_{18}NO$ $[M+H]^+$ 204.1388, found 204.1389.



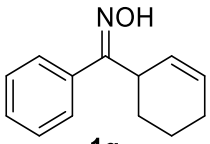
1o **7-((*tert*-butyldiphenylsilyl)oxy)-3,3-dimethylhept-1-en-4-one oxime**

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 10:1), white solid, mp: 91.9-93.4 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.02 (br s, 1 H), 7.70-7.67 (m, 4 H), 7.45-7.36 (m, 6 H), 5.84 (dd, *J* = 17.6, 10.4 Hz, 1 H), 5.10-5.05 (m, 2 H), 3.71 (t, *J* = 6.0 Hz, 2 H), 2.38-2.33 (m, 2 H), 1.87-1.79 (m, 2 H), 1.23 (s, 6 H), 1.07 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.6, 144.7, 135.9, 134.4, 129.9, 127.9, 113.2, 64.4, 44.1, 29.6, 27.2, 25.0, 23.5, 19.6. **HRMS (ESI)** calcd for $C_{25}H_{36}NO_2Si$ $[M+H]^+$ 410.2515, found 410.2512.



1p **2-(3-(hydroxyimino)-4,4-dimethylhex-5-en-1-yl)isoindoline-1,3-dione**

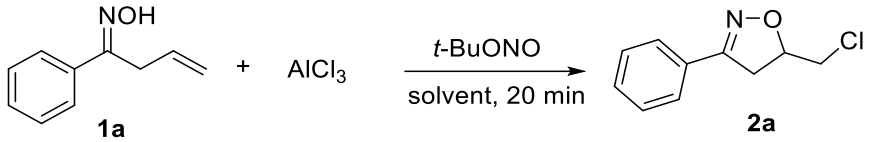
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 20:1), white solid, mp: 121.6-122.3 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (br s, 1 H), 7.87-7.81 (m, 2 H), 7.72-7.67 (m, 2 H), 5.81 (dd, *J* = 17.6, 10.8 Hz, 1 H), 5.09-5.02 (m, 2 H), 3.93 (t, *J* = 7.4 Hz, 2 H), 2.63 (t, *J* = 7.4 Hz, 2 H), 1.22 (s, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 162.2, 144.2, 134.2, 132.6, 123.5, 113.7, 44.0, 35.0, 25.8, 24.8. **HRMS (ESI)** calcd for $C_{16}H_{18}N_2O_3Na$ $[M+Na]^+$ 309.1215, found 309.1216.



1q **cyclohex-2-en-1-yl(phenyl)methanone oxime**

Prepared according to the reported procedure,[1] purified by flash column chromatography (PE/EA = 10:1), white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.83 (br s, 1 H), 7.55-7.53 (m, 2 H), 7.37-7.33 (m, 3 H), 5.85-5.80 (m, 1 H), 5.63-5.60 (m, 1 H), 4.33-4.30 (m, 1 H), 2.10-2.07 (m, 2 H), 2.05-2.01 (m, 1 H), 1.86-1.82 (m, 1 H), 1.73-1.64 (m, 2 H).[1]

Table S1. Optimization Reaction Conditions for Oxychlorination[a]



1a **2a**

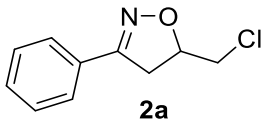
entry	solvent	H_2O (equiv)	$AlCl_3$ (equiv)	*t*-BuONO (equiv)	yield (%)[b]
1	CH_3CN	0	1.2	1.5	48
2	CH_3CN	2	1.2	1.5	80
3	CH_3CN	10	1.2	1.5	54
4	CH_3CN	5	1.2	1.5	59
5	CH_3CN	3	1.2	1.5	79
6	CH_3CN	1	1.2	1.5	70
7	CH_3CN	4	1.2	1.5	60
8[c]	CH_3CN	2	1.2	1.5	79
9	CH_3CN	2	1.2	2	60
10	CH_3CN	2	1.2	0.5	54
11	CH_3CN	2	1.2	1	71

12	CH_3CN	2	1.2	0	0
13	CH_3CN	2	0.5	1.5	84
14	CH_3CN	1	0.5	1.5	60
15	CH_3CN	3	0.5	1.5	61
16[d]	CH_3CN	2	TBAC (1.5 equiv)	1.5	trace
17[d]	CH_3CN	2	LiCl (1.5 equiv)	1.5	trace
18[d]	CH_3CN	2	NH_4Cl (1.5 equiv)	1.5	trace
19	$CHCl_3$	2	0.5	1.5	63
20	toluene	2	0.5	1.5	38
21	**THF**	**2**	**0.5**	**1.5**	**88**
22	dioxane	2	0.5	1.5	71
23	DCM	2	0.5	1.5	80
24	Et_2O	2	0.5	1.5	61
25	CH_3CO_2H	2	0.5	1.5	83

[a] Reaction conditions: **1a** (0.25 mmol), solvent (2 mL), argon atmosphere, room temperature. [b] Isolated yield. [c] Under open air. [d] Other chlorine source were used instead of $AlCl_3$

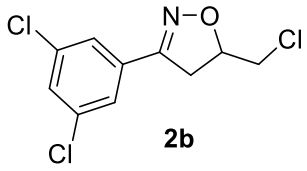
2.2. General Procedure for Oxychlorination

$AlCl_3$ (0.5 equiv) was weighed directly into a Schlenk tube and dried under high vacuum for 5 min, then the solution of oxime 1 (0.25 mmol) in THF (2 ml), *t*-BuONO (1.5 equiv) and water (2 equiv) were added sequentially under argon atmosphere. The reaction mixture was stirred at room temperature for 20 min, then the mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography to give the product.



2a **5-(chloromethyl)-3-phenyl-4,5-dihydroisoxazole**

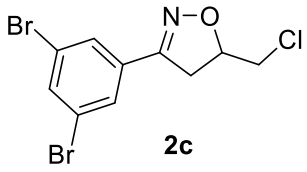
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 50:1), white solid (43.3 mg, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69-7.66 (m, 2 H), 7.45-7.38 (m, 3 H), 5.02-4.94 (m, 1 H), 3.71 (dd, *J* = 11.2, 4.4 Hz, 1 H), 3.58 (dd, *J* = 11.2, 7.2 Hz, 1 H), 3.49 (dd, *J* = 16.8, 10.4 Hz, 1 H), 3.33 (dd, *J* = 16.8, 6.4 Hz, 1 H).[4]



2b

5-(chloromethyl)-3-(3,5-dichlorophenyl)-4,5-dihydroisoxazole

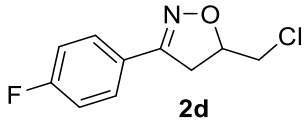
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 50:1), white solid, mp: 106.4-107.7 ˚C, (48.8 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 1.6 Hz, 2 H), 7.41 (t, *J* = 1.6 Hz, 1 H), 5.09-5.01 (m, 1 H), 3.72 (dd, *J* = 11.6, 4.4 Hz, 1 H), 3.60 (dd, *J* = 11.6, 7.2 Hz, 1 H), 3.45 (dd, *J* = 16.8, 10.4 Hz, 1 H), 3.30 (dd, *J* = 17.2, 6.8 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.6, 135.9, 132.3, 130.4, 125.4, 80.7, 45.0, 38.3. **HRMS (ESI)** calcd for $C_{10}H_9NOCl_3$ $[M+H]^+$ 263.9750, found 263.9752.



2c

5-(chloromethyl)-3-(3,5-dibromophenyl)-4,5-dihydroisoxazole

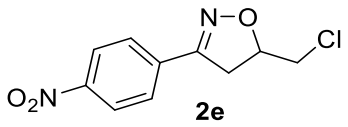
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 50:1), brown solid, mp: 121.8-122.6 ˚C (70.4 mg, 80% yield). **^{1}H NMR (**400 MHz, CDCl3) δ 7.75-7.74 (m, 2 H), 7.72-7.71 (m, 1 H), 5.08-5.00 (m, 1 H), 3.72 (dd, *J* = 11.6, 4.0 Hz, 1 H), 3.60 (dd, *J* = 11.6, 7.2 Hz, 1 H), 3.44 (dd, *J* = 16.8, 10.4 Hz, 1 H), 3.29 (dd, *J* = 17.2, 6.8 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.4, 135.9, 132.8, 128.7, 123.7, 80.7, 45.0, 38.3. **HRMS (ESI)** calcd for $C_{10}H_9NOClBr_2$ $[M+H]^+$ 351.8739, found 351.8736.



2d

5-(chloromethyl)-3-(4-fluorophenyl)-4,5-dihydroisoxazole

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 25:1), colorless crystal (45.7 mg, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70-7.64 (m, 2 H), 7.14-7.07 (m, 2 H), 5.04-4.96 (m, 1 H), 3.72 (dd, *J* = 11.2, 4.4 Hz, 1 H), 3.58 (dd, *J* = 11.6, 7.6 Hz, 1 H), 3.49 (dd, *J* = 17.2, 10.8 Hz, 1 H), 3.33 (dd, *J* = 17.2, 6.4 Hz, 1 H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.4.[4]

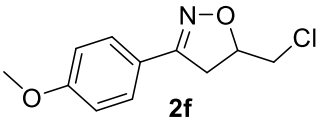


2e

5-(chloromethyl)-3-(4-nitrophenyl)-4,5-dihydroisoxazole

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 10:1), white solid, mp: 152.9-154.2 ˚C (55.5 mg, 92% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30-8.26 (m, 2 H), 7.87-7.83 (m, 2 H), 5.14-5.07 (m, 1 H),), 3.75 (dd, *J* = 11.2, 4.0 Hz, 1 H), 3.65 (dd, *J* = 11.2, 7.2 Hz, 1 H), 3.54 (dd, *J* = 16.8, 10.8 Hz, 1 H), 3.39 (dd, *J* = 17.2, 6.8 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ

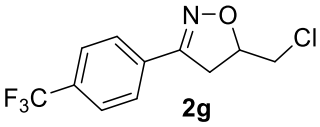
155.0, 149.0, 135.4, 127.9, 124.4, 81.0, 45.0, 38.2. **HRMS (ESI)** calcd for $C_{10}H_{10}N_2O_3Cl$ $[M+H]^+$ 241.0380, found 241.0378.



2f

5-(chloromethyl)-3-(4-methoxyphenyl)-4,5-dihydroisoxazole

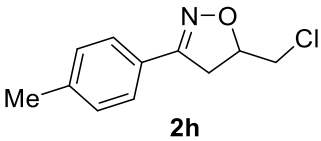
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 20:1), colorless crystal (35.3 mg, 63% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64-7.59 (m, 2 H), 6.95-6.90 (m, 2 H), 4.99-4.91 (m, 1 H), 3.71 (dd, *J* = 11.2, 4.4 Hz, 1 H), 3.56 (dd, *J* = 11.2, 7.6 Hz, 1 H), 3.48 (dd, *J* = 16.8, 10.4 Hz, 1 H), 3.32 (dd, *J* = 16.8, 6.4 Hz, 1 H).[4]



2g

5-(chloromethyl)-3-(4-(trifluoromethyl)phenyl)-4,5-dihydroisoxazole

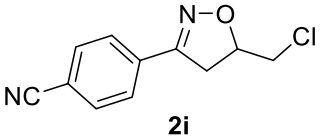
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 20:1), white solid, mp: 65.3-65.9 ˚C, (56.2 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2 H), 7.68 (d, *J* = 8.4 Hz, 2 H), 5.10-5.02 (m, 1 H), 3.74 (dd, *J* = 11.2, 4.0 Hz, 1 H), 3.62 (dd, *J* = 11.2, 7.2 Hz, 1 H), 3.52 (dd, *J* = 17.2, 10.8 Hz, 1 H), 3.37 (dd, *J* = 16.8, 6.4 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.5, 132.8, 132.6, 132.2, 127.4, 126.1 (q, *J* = 3.8 Hz), 125.4, 122.6, 80.7, 45.1, 38.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.9. **HRMS (ESI)** calcd for $C_{11}H_{10}NOClF_3$ $[M+H]^+$ 246.0403, found 246.0404.



2h

5-(chloromethyl)-3-(*p*-tolyl)-4,5-dihydroisoxazole

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 10:1), white solid (45.7 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 5.00-4.93 (m, 1 H), 3.71 (dd, *J* = 11.2, 4.4 Hz, 1 H), 3.56 (dd, *J* = 11.2, 7.6 Hz, 1 H), 3.49 (dd, *J* = 16.8, 10.4 Hz, 1 H), 3.33 (dd, *J* = 16.8, 6.4 Hz, 1 H), 2.38 (S, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.4, 141.0, 129.8, 127.1, 126.5, 79.9, 45.1, 39.0, 21.8. **HRMS (ESI)** calcd for $C_{11}H_{13}NOCl$ $[M+H]^+$ 210.0686, found 210.0683.

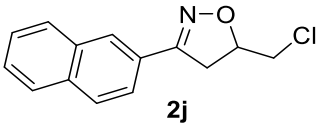


2i

4-(5-(chloromethyl)-4,5-dihydroisoxazol-3-yl)benzonitrile

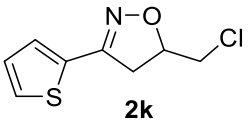
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 5:1), white solid, mp: 146.3-147.1 ˚C (46.2 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz,

2 H), 7.70 (d, *J* = 8.4 Hz, 2 H), 5.11-5.03 (m, 1 H), 3.73 (dd, *J* = 11.6, 4.4 Hz, 1 H), 3.63 (dd, *J* = 11.6, 6.8 Hz, 1 H), 3.50 (dd, *J* = 16.8, 10.8 Hz, 1 H), 3.35 (dd, *J* = 17.2, 6.8 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.3, 133.6, 132.9, 127.5, 118.6, 114.0, 80.9, 45.1, 38.1. **HRMS (ESI)** calcd for $C_{11}H_{10}NOCl$ $[M+H]^+$ 221.0482, found 221.0486.



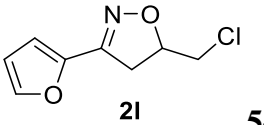
2j **5-(chloromethyl)-3-(naphthalen-2-yl)-4,5-dihydroisoxazole**

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 50:1), white solid, mp: 84.4-86.3 ˚C, (43.5 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99-7.91 (m, 2 H), 7.87-7.84 (m, 3 H), 7.56-7.50 (m, 2 H), 5.09-5.01 (m, 1 H), 3.76 (dd, *J* = 11.2, 4.4 Hz, 1 H), 3.66-3.58 (m, 2 H), 3.47 (dd, *J* = 16.8, 6.4 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.6, 134.4, 133.3, 128.9, 128.7, 128.2, 127.6, 127.5, 127.1, 126.9, 123.8, 80.3, 45.2, 38.9. **HRMS (ESI)** calcd for $C_{14}H_{13}NOCl$ $[M+H]^+$ 246.0686, found 246.0686.



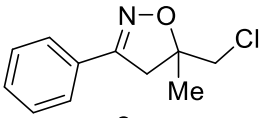
2k **5-(chloromethyl)-3-(thiophen-2-yl)-4,5-dihydroisoxazole**

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 20:1), colorless oil (41.8 mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.41 (m, 1 H), 7.25-7.23 (m, 1 H), 7.09-7.06 (m, 1 H), 5.03-4.95 (m, 1 H), 3.72 (dd, *J* = 11.2, 4.0 Hz, 1 H), 3.58 (dd, *J* = 11.2, 7.6 Hz, 1 H), 3.52 (dd, *J* = 12.8, 6.4 Hz, 1 H), 3.37 (dd, *J* = 16.8, 6.0 Hz, 1 H).[4]



2l **5-(chloromethyl)-3-(furan-2-yl)-4,5-dihydroisoxazole**

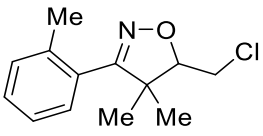
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 30:1), white solid, mp: 68.4-69.1 (30.2 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 1.6 Hz, 1 H), 6.75 (d, *J* = 3.6 Hz, 1 H), 6.50 (q, *J* = 1.6 Hz, 1 H), 4.99-4.91 (m, 1 H), 3.70 (dd, *J* = 11.6, 4.4 Hz, 1 H), 3.55 (dd, *J* = 11.2, 7.2 Hz, 1 H), 3.46 (dd, *J* = 16.8, 10.4 Hz, 1 H), 3.31 (dd, *J* = 16.8, 6.4 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.7, 144.9, 144.7, 112.6, 112.1, 79.8, 44.8, 38.8. **HRMS (ESI)** calcd for $C_8H_9NO_2Cl$ $[M+H]^+$ 186.0322, found 186.0322.



2m

5-(chloromethyl)-5-methyl-3-phenyl-4,5-dihydroisoxazole

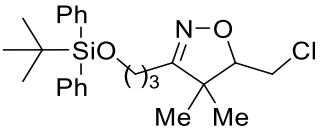
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 20:1), colorless crystal (43.3 mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68-7.65 (m, 2 H), 7.42-7.40 (m, 3 H), 3.65-3.51 (m, 3 H), 3.13-3.08 (m, 1 H), 1.62 (s, 3 H).[4]



2n

5-(chloromethyl)-4,4-dimethyl-3-(o-tolyl)-4,5-dihydroisoxazole

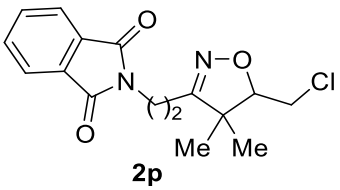
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 50:1), white solid, mp: 61.2-62.0 ˚C (37.0 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, 2 H), 7.25-7.15 (m, 2 H), 4.45 (t, *J* = 6.4 Hz, 1 H), 3.83 (dd, *J* = 11.6, 6.4 Hz, 1 H), 3.73 (dd, *J* = 11.6, 7.2 Hz, 1 H), 2.36 (s, 3 H), 1.34 (s, 3 H), 1.21 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 138.1, 131.2, 129.7, 129.3, 128.2, 125.8, 88.5, 54.2, 41.3, 25.7, 20.6, 18.8. **HRMS (ESI)** calcd for $C_{13}H_{17}NOCl$ $[M+H]^+$ 238.0999, found 238.0995.



2o

3-(3-((*tert*-butyldiphenylsilyl)oxy)propyl)-5-(chloromethyl)-4,4-dimethyl-4,5-dihydroisoxazole

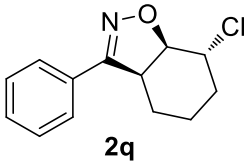
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 30:1), white solid, mp: 75.3-76.8 ˚C, (64.2 mg, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 4 H), 7.45-7.36 (m, 6 H), 4.20 (dd, *J* = 7.6, 6.0 Hz, 1 H), 3.75 (t, *J* = 6.0 Hz, 2 H), 3.70 (dd, *J* = 11.6, 6.0 Hz, 1 H), 3.60 (dd, *J* = 11.6, 7.6 Hz, 1 H), 2.32-2.28 (m, 2 H), 1.94-1.87 (m, 2 H), 1.26 (s, 3 H), 1.12 (s, 3 H), 1.06 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 135.9, 134.1, 130.0, 128.0, 87.8, 63.3, 52.2, 41.3, 29.2, 27.2, 25.2, 21.3, 19.6, 18.4. **HRMS (ESI)** calcd for $C_{25}H_{34}NO_2NaSiCl$ $[M+Na]^+$ 466.1945, found 466.1945.



2p

2-(2-(5-(chloromethyl)-4,4-dimethyl-4,5-dihydroisoxazol-3-yl)ethyl)isoindoline-1,3-dione

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 10:1), white solid, mp: 157.0-158.5 ˚C, (55.1 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85-7.82 (m, 2 H), 7.73-7.70 (m, 2 H), 4.23 (t, *J* = 7.0 Hz, 1 H), 4.00 (t, *J* = 7.4 Hz, 2 H), 3.70 (dd, *J* = 11.6, 6.4 Hz, 1 H), 3.60 (dd, *J* = 11.6, 7.4 Hz, 1 H), 2.58 (t, *J* = 7.4 Hz, 2 H), 1.31 (s, 3 H), 1.16 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 163.7, 134.4, 132.3, 123.7, 87.8, 52.1, 41.1, 35.1, 25.1, 23.8, 18.4. **HRMS (ESI)** calcd for $C_{16}H_{17}N_2O_3NaCl$ $[M+Na]^+$ 343.0825, found 345.0828.

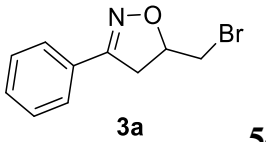


2q **7-chloro-3-phenyl-3a,4,5,6,7,7a-hexahydrobenzo[*d*]isoxazole**

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 50:1), white solid, mp: 92.1-93.5 ˚C, (32.3 mg, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70-7.67 (m, 2 H), 7.44-7.40 (m, 3 H), 4.59-4.53 (m, 2 H), 3.62-3.56 (m, 1 H), 2.10-1.96 (m, 3 H), 1.85-1.73 (m, 1 H), 1.56-1.49 (m, 1 H), 1.41-1.30 (m, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.1, 130.7, 129.2, 128.8, 127.4, 84.1, 55.1, 43.0, 29.5, 25.9, 17.3. **HRMS (ESI)** calcd for $C_{13}H_{15}NOCl$ $[M+H]^+$ 236.0842, found 236.0841.[4] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70-7.67 (m, 2 H), 7.44-7.40 (m, 3 H), 4.58 (dd, *J* = 7.2, 3.0 Hz, 1 H, H7a), 4.55 (q, *J* = 3.6 Hz, 1 H, H7), 3.59 (ddd, *J* = 10.2, 7.2, 7.2, Hz, 1 H, H3a), 2.08-1.98 (m, 3 H), 1.82-1.76 (m, 1 H), 1.54-1.50 (m, 1 H), 1.39-1.33 (m, 1 H).

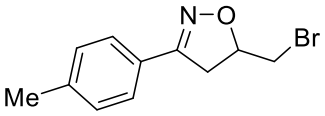
2.3. Procedure for Oxybromination

CBr_4 (1.5 equiv) was weighed directly into a Schlenk tube and dried under high vacuum for 5 min, then the solution of oxime **1** (0.25 mmol) in THF (2 ml), *t*-BuONO (1.5 equiv) were added sequentially under argon atmosphere. The reaction mixture was stirred at room temperature for 20 min, then the mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography to give the compound **3**.



3a **5-(bromomethyl)-3-phenyl-4,5-dihydroisoxazole**

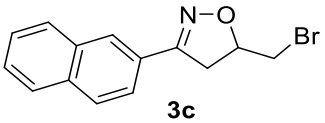
Purified by flash column chromatography (PE/EA = 30:1), light yellow solid (54.8 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68-7.66 (m, 2 H), 7.42-7.39 (m, 3 H), 5.03-4.95 (m, 1 H), 3.57 (dd, *J* = 10.4, 4.4 Hz, 1 H), 3.51 (dd, *J* = 17.2, 10.8 Hz, 1 H), 3.41 (dd, *J* = 10.8, 8.4 Hz, 1 H), 3.32 (dd, *J* = 17.2, 6.4 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.3, 130.6, 129.3, 129.0, 127.0, 79.9, 39.8, 33.5.[4]



3b

5-(bromomethyl)-3-(*p*-tolyl)-4,5-dihydroisoxazole

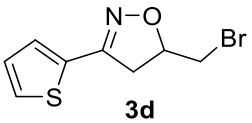
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 30:1), white solid (60.3 mg, 95% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 5.01-4.93 (m, 1 H), 3.57 (dd, *J* = 10.4, 4.4 Hz, 1 H), 3.49 (dd, *J* = 17.2, 10.4 Hz, 1 H), 3.40 (dd, *J* = 10.4, 8.4 Hz, 1 H), 3.30 (dd, *J* = 17.2, 6.4 Hz, 1 H), 2.38 (S, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.4, 141.0, 129.8, 127.0, 126.4, 79.8, 40.0, 33.5, 21.7.[4]



3c

5-(bromomethyl)-3-(naphthalen-2-yl)-4,5-dihydroisoxazole

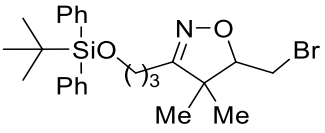
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 30:1), white solid, mp: 93.6-94.2 ˚C, (65.8 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.8, 1.6 Hz, 1 H), 7.91-7.90 (m, 1 H), 7.87-7.83 (m, 3 H), 7.56-7.50 (m, 2 H), 5.09-5.01 (m, 1 H), 3.66-3.58 (m, 2 H), 3.48-3.41 (m, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.5, 134.4, 133.2, 128.9, 128.7, 128.2, 127.6, 127.5, 127.1, 126.9, 123.8, 80.2, 39.8, 33.6. **HRMS (ESI)** calcd for $C_{14}H_{13}NOBr$ $[M+H]^+$ 290.0175, found 290.0180.



3d

5-(bromomethyl)-3-(thiophen-2-yl)-4,5-dihydroisoxazole

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 30:1), light yellow oil (54.6 mg, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.39 (m, 1 H), 7.23-7.21 (m, 1 H), 7.09-7.05 (m, 1 H), 5.04-4.95 (m, 1 H), 3.59-3.48 (m, 2 H), 3.40 (dd, *J* = 10.4, 8.4 Hz, 1 H), 3.37-3.29 (m, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.2, 131.7, 129.2, 129.0, 127.7, 80.2, 40.7, 33.4.[4]



3e

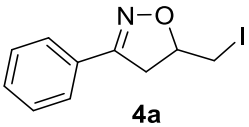
3-(3-((*tert*-butyldiphenylsilyl)oxy)propyl)-5-(bromomethyl)-4,4-dimethyl-4,5-dihydroisoxazole

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 50:1), colorless oil (99.7 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 4 H), 7.45-7.36 (m, 6 H), 4.27 (dd, *J* = 7.6, 6.0 Hz, 1 H), 3.75 (t, *J* = 6.0 Hz, 2 H), 3.53 (dd, *J* = 10.4, 6.0 Hz, 1 H), 3.42 (dd, *J* = 10.8, 7.6 Hz, 1 H), 2.30 (dd, *J* = 9.2, 7.2 Hz, 2 H), 1.94-1.87 (m, 2 H), 1.27 (s, 3 H), 1.11 (s, 3 H), 1.06

(s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 135.9, 134.1, 130.0, 128.0, 87.7, 63.3, 52.3, 29.2, 28.3, 27.2, 25.3, 21.4, 19.6, 18.4. **HRMS (ESI)** calcd for $C_{25}H_{35}NO_2SiBr$ $[M+H]^+$ 488.1615, found 488.1620.

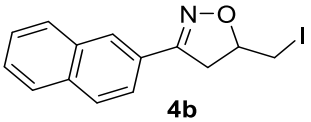
2.4. Procedure for Oxyiodination

CHI_3 (2.0 equiv) was weighed directly into a Schlenk tube and dried under high vacuum for 5 min, then the solution of oxime **1** (0.25 mmol) in THF (2 ml), *t*-BuONO (1.5 equiv) were added sequentially under argon atmosphere. The reaction mixture was stirred at room temperature for 20 min, then the mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography to give the compound **4**.



4a **5-(iodomethyl)-3-phenyl-4,5-dihydroisoxazole**

Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 30:1), white solid (63.2 mg, 88% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66-7.63 (m, 2 H), 7.42-7.36 (m, 3 H), 4.91-4.83 (m, 1 H), 3.47 (dd, *J* = 16.8, 11.2 Hz, 1 H), 3.38 (dd, *J* = 10.0, 4.0 Hz, 1 H), 3.22 (dd, *J* = 10.0, 8.8 Hz, 1 H), 3.18 (dd, *J* = 16.8, 6.4 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.1, 130.6, 129.3, 129.0, 127.0, 80.6, 41.2, 8.0.[5]



4b **5-(iodomethyl)-3-(naphthalen-2-yl)-4,5-dihydroisoxazole**

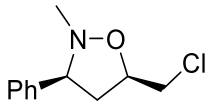
Prepared according to the general procedure, purified by flash column chromatography (PE/EA = 50:1), light yellow solid, mp: 101.2-103.3 ˚C, (55.6 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96-7.83 (m, 5 H), 7.56-7.50 (m, 2 H), 5.09- 5.01 (m, 1 H), 3.66-3.58 (m, 2 H), 3.48-3.41 (m, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.3, 134.4, 133.2, 128.9, 128.7, 128.2, 127.6, 127.4, 127.1, 126.9, 123.7, 80.9, 41.2, 8.0. **HRMS (ESI)** calcd for $C_{14}H_{13}NOI$ $[M+H]^+$ 338.0036, found 338.0038.

2.5. Procedure for formation of compound 6

1) To a solution of **2a** (0.4 mmol) in nitromethane (3 mL) was added trimethyloxonium tetrafluoroborate (2 equiv). The mixture was stirred at room temperature for 5 h and concentrated in *vacuo*. The crude tetrafluoroborate product was dissolved in ethanol (4 mL) and stirred at -30 ˚C, while sodium borohydride (10 equiv) was added portionwise. The mixture was stirred at this temperature for 3 h before saturated ammonium chloride solution was added to quench the reaction. Then, the mixture was extracted with ethyl acetate and the combined organic layers were washed with water and brine, dried with $MgSO_4$,

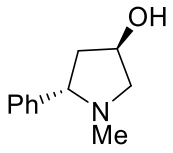
filtered, and concentrated in *vacuo*. The crude material was purified by flash column chromatography (PE/EA = 30:1) and gave compound **5**, 66.1 mg, 78% yield with 6.3:1 *cis*-selectivity.

2) The *cis*-product **5** (0.2 mmol) and activated zinc powder (10 equiv) were weighed directly into a flask before acetic acid (2 mL) and water (2 mL) were added. The reaction was stirred at 50 ˚C for 4 h, then neutralized by NaOH solution, filtrated, and the mixture was extracted with DCM and the combined organic layers were washed with water and brine, dried with $MgSO_4$, filtered, and concentrated in *vacuo*. The crude material was purified by flash column chromatography (DCM/MeOH = 50:1), and gave 38.2 mg of **6** with a yield of 86%.



5 ***cis*-5-(chloromethyl)-2-methyl-3-phenylisoxazolidine**

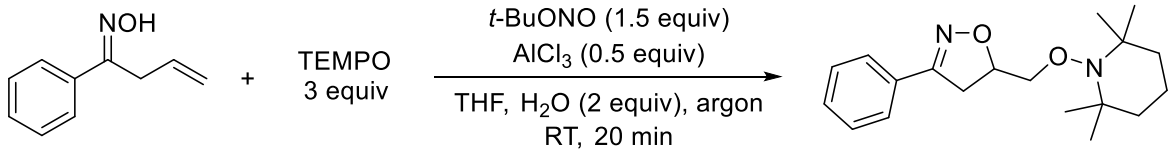
White solid, mp: 58.5-59.9 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 5 H), 4.42-4.34 (m, 1 H), 3.82 (dd, *J* = 10.8, 6.8 Hz, 1 H), 3.57 (dd, *J* = 10.8, 6.8 Hz, 2 H), 2.91-2.83 (m, 1 H), 2.58 (s, 3 H), 2.19-2.12 (m, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.8, 129.1, 128.4, 127.9, 76.7, 73.8, 47.1, 44.5, 43.4. **HRMS (ESI)** calcd for $C_{11}H_{15}NOCl$ $[M+H]^+$ 212.0842, found 212.0840.



6 ***trans*-1-methyl-5-phenylpyrrolidin-3-ol**

Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.30 (m, 4 H), 7.29-7.23 (m, 1 H), 4.56-4.51 (m, 1 H), 3.65 (dd, *J* = 10.0, 6.4 Hz, 1 H), 3.44 (dd, *J* = 9.6, 7.2 Hz, 1 H), 2.42 (br s, 1 H), 2.32 (dd, *J* = 10.0, 5.2 Hz, 1 H), 2.19 (s, 3 H), 2.13-2.04 (m, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.1, 128.8, 127.9, 127.7, 69.9, 69.8, 66.0, 46.2, 40.5. **HRMS (ESI)** calcd for $C_{11}H_{16}NO$ $[M+H]^+$ 178.1232, found 178.1234.

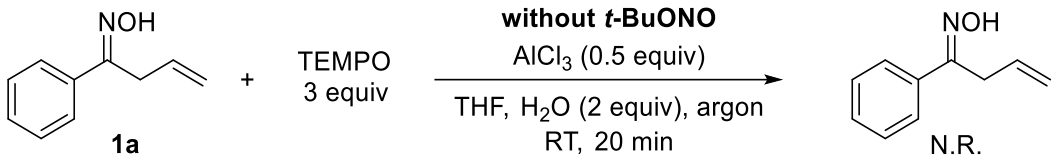
2.6. Control experiments



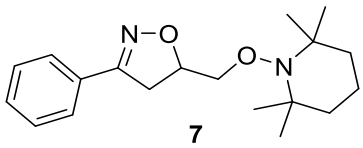
7, 72%, **2a**, 0%

$AlCl_3$ (0.5 equiv) and TEMPO (3 equiv) were weighed directly into a Schlenk tube and dried under high

vacuum for 5 min, then the solution of oxime **1a** (0.25 mmol) in THF (2 ml), *t*-BuONO (1.5 equiv) and water (2 equiv) were added sequentially under argon atmosphere. The reaction was stirred at room temperature for 20 min, then the mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (PE/EA = 15:1) to afford the product **7** (57.0 mg, 72%), while **2a** could not be detected.

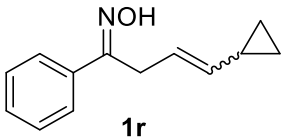


$AlCl_3$ (0.5 equiv) and TEMPO (3 equiv) were weighed directly into a Schlenk tube and dried under high vacuum for 5 min, then the solution of oxime **1a** (0.25 mmol) in THF (2 ml) and water (2 equiv) were added sequentially under argon atmosphere. The reaction was stirred at room temperature for 20 min, **2a** and **7** couldn't be found while the starting material was totally recovered.



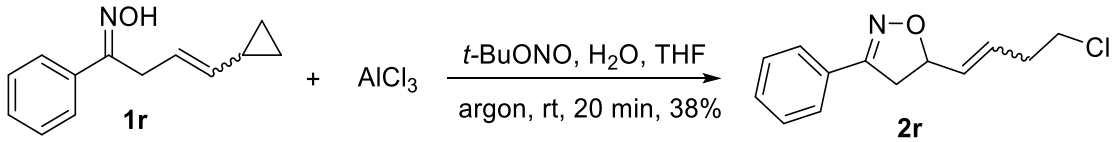
3-phenyl-5-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-4,5-dihydroisoxazole

Colorless crystal. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70-7.67 (m, 2 H), 7.42-7.38 (m, 3 H), 4.91-4.83 (m, 1 H), 4.01-3.94 (m, 2 H), 3.38 (dd, *J*= 16.4, 10.8 Hz, 1 H), 3.25 (dd, *J*= 16.4, 7.6 Hz, 1 H), 1.48-1.42 (m, 5 H), 1.33-1.25 (m, 1 H), 1.19 (s, 6 H), 1.07 (s, 6 H).[6]

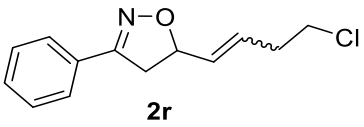


3-cyclopropyl-1-phenylbut-3-en-1-one oxime

Prepared according to the reported procedure[3], purified by flash column chromatography (PE/EA = 50:1), colorless crystal. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.00 (br, 1 H), 7.69-7.60 (m, 2 H), 7.41-7.36 (m, 3 H), 5.65-5.58 (m, 0.6 H), 5.39-5.33 (m, 0.4 H), 5.14 (dd, *J* = 15.2, 8.8 Hz, 0.6 H), 4.88 (t, *J* = 10.4 Hz, 0.4 H), 3.74 (dd, *J* = 7.2, 1.6 Hz, 0.8 H), 3.52 (dd, *J* = 6.4, 1.2 Hz, 1.2 H), 1.76-1.67 (m, 0.4 H), 1.39-1.30 (m, 0.6 H), 0.82-0.77 (m, 0.8 H), 0.67-0.62 (m, 1.2 H), 0.39-0.35 (m, 0.8 H), 0.33-0.29 (m, 1.2 H).[3]



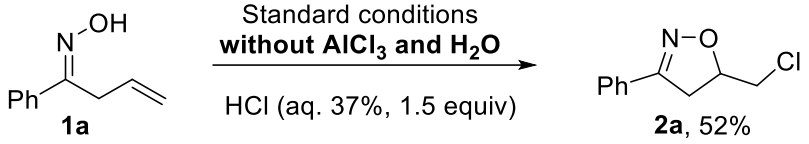
$AlCl_3$ (0.5 equiv) was weighed directly into a Schlenk tube and dried under high vacuum for 5 min, then the solution of oxime **1r** (0.25 mmol) in THF (2 ml), *t*-BuONO (1.5 equiv) and water (2 equiv) were added sequentially under argon atmosphere. The reaction mixture was stirred at room temperature for 20 min, then the mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (PE/EA = 50:1),to give the product **2r**.



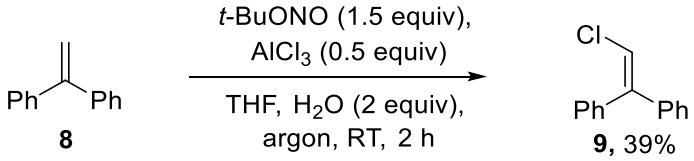
2r

5-(4-chlorobut-1-en-1-yl)-3-phenyl-4,5-dihydroisoxazole

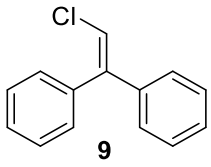
21.2 mg, (Z/E = 1/4), colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68-7.65 (m, 2 H), 7.42-7.40 (m, 3 H), 5.87-5.77 (m, 1 H), 5.75-5.67 (m, 1 H), 5.46 (q, *J* = 9.6 Hz, 0.2 H), 5.18-5.11 (m, 0.8 H), 3.67-3.54 (m, 2 H), 3.49 (dd, *J* = 16.8, 10.4 Hz, 1 H), 3.15-3.07 (m, 1 H), 2.70-2.63 (m, 0.4 H), 2.61-2.48 (m, 1.6 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0, 156.9, 131.4, 130.8, 130.5, 130.4, 129.9, 129.8, 129.1, 127.0, 127.0, 82.0, 77.3, 44.1, 43.8, 41.5, 41.0, 35.5, 31.2. **HRMS (ESI)** calcd for $C_{13}H_{15}NOCl$ $[M+H]^+$ 236.0842, found 236.0846.



1a (0.25 mmol) was weighed directly into a Schlenk tube and dried under high vacuum for 5 min, then THF (2 ml), the solution of HCl (aq. 37%, 0.375 mmol), *t*-BuONO (0.375 mmol) were added sequentially under argon atmosphere. The reaction mixture was stirred at room temperature for 20 min, then the mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (PE/EA = 50:1), to give the product **2a** (25.4 mg, 52%).



$AlCl_3$ (0.5 mmol) was weighed directly into a Schlenk tube and dried under high vacuum for 5 min, then the solution of **8** (1 mmol) in THF (8 ml), *t*-BuONO (1.5 mmol) and water (2 mmol) were added sequentially under argon atmosphere. The reaction was stirred at room temperature for 2 h, then the mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (pure PE) to afford the product **9** (83.2 mg, 39%).



9 **(2-chloroethene-1,1-diyl)dibenzene**

Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.28 (m, 8 H), 7.22-7.19 (m, 2 H), 6.59 (s, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.2, 140.5, 137.9, 130.2, 128.8, 128.6, 128.4, 128.3, 128.1, 116.2. **HRMS (ESI)** calcd for $C_{14}H_{12}Cl$ $[M+H]^+$ 215.0628, found 215.0626.

3. Reference

1 L. Zhu, H. Yu, Z. Xu, X. Jiang, L. Lin and R. Wang, *Org. Lett.*, 2014, **16**, 1562.

2 X.-Q. Hu, G. Feng, J.-R. Chen, D.-M. Yan, Q.-Q. Zhao, Q. Wei and W.-J. Xiao, *Org. Biomol. Chem.*, 2015, **13**, 3457.

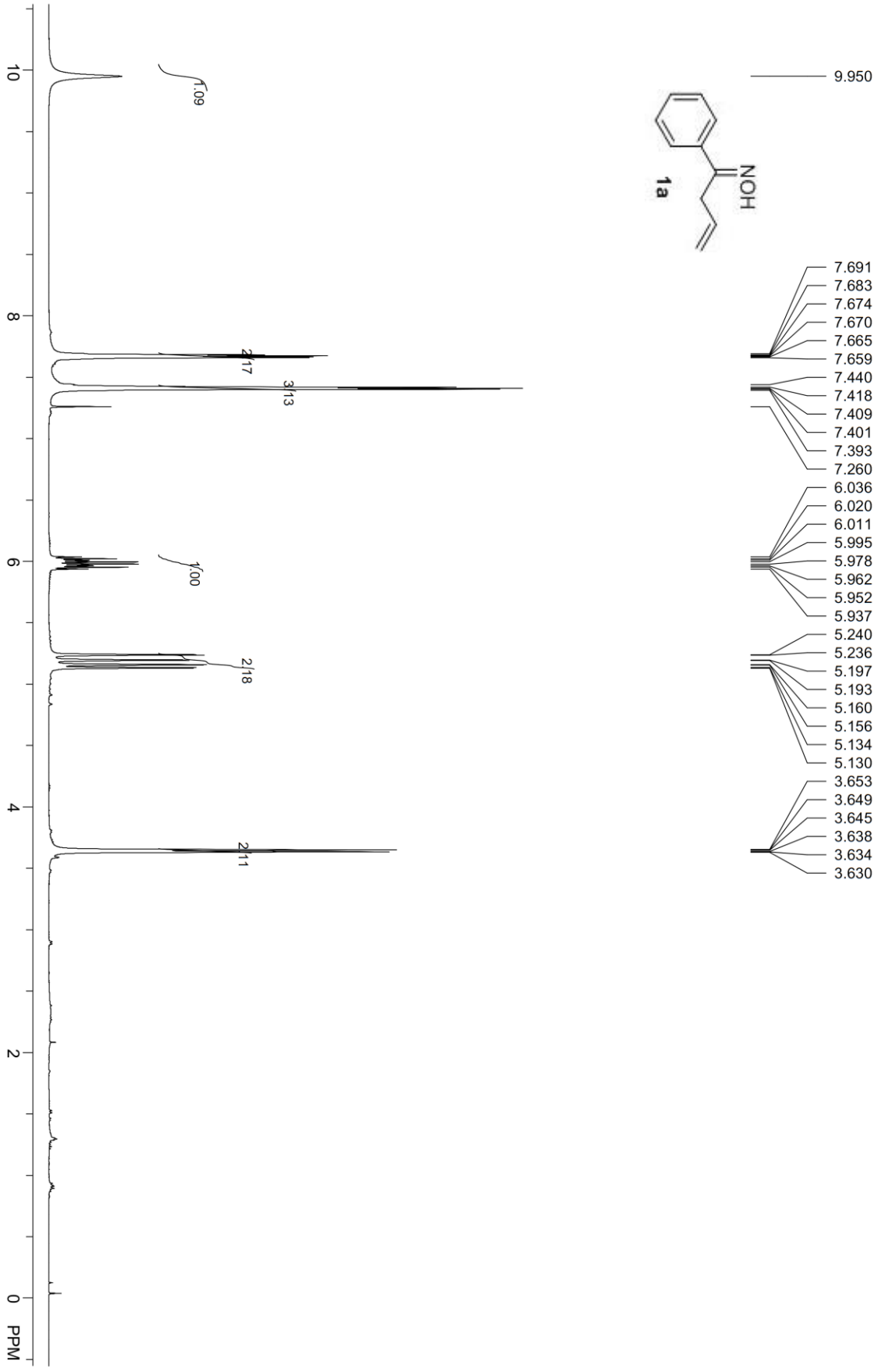
3 W. Li, P. Jia, B. Han, D. Li and W. Yu, *Tetrahedron,* 2013, **69**, 3274.

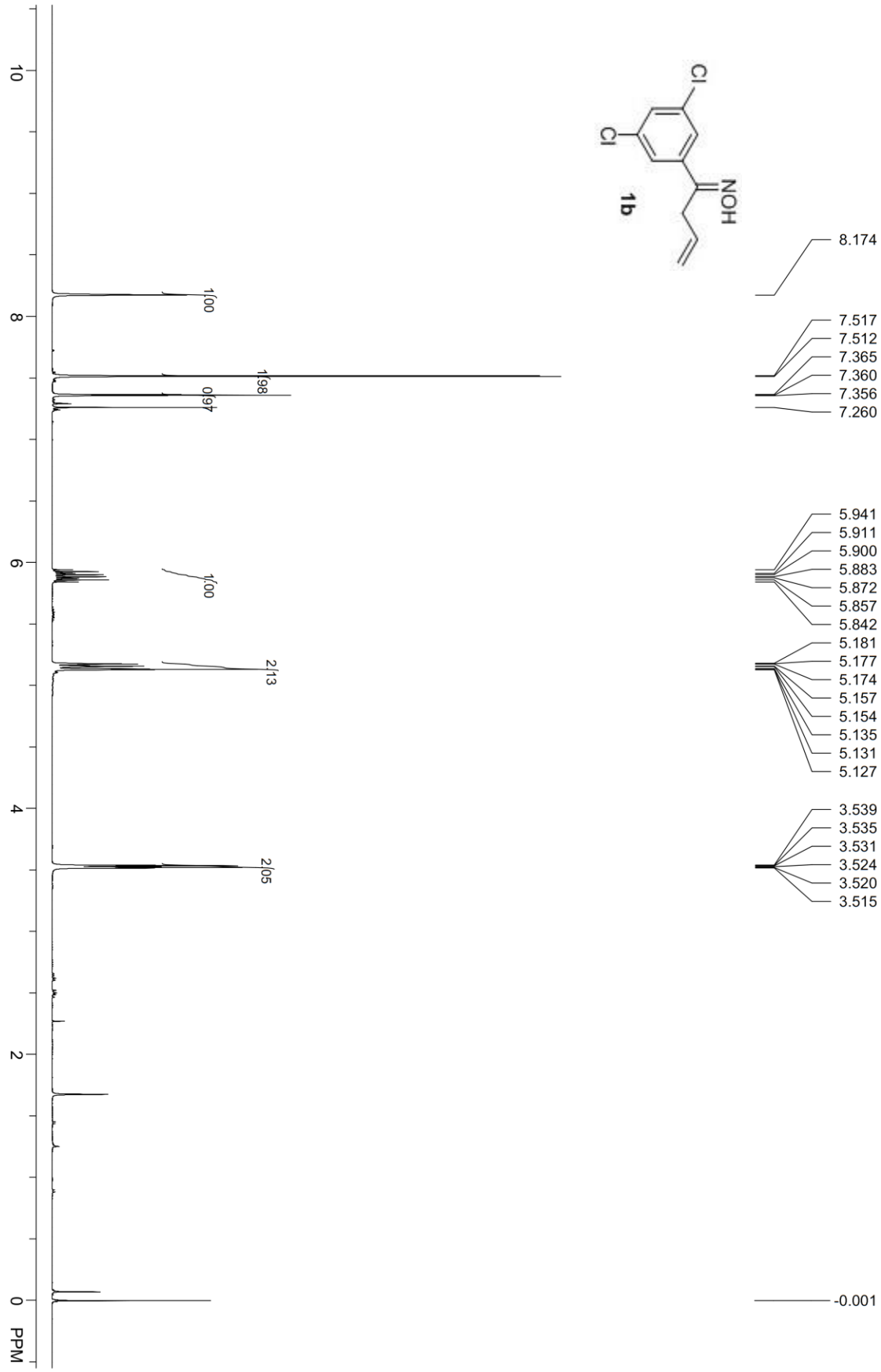
4 K.-Y. Dong, H.-T. Qin, F. Liu and C. Zhu, Eur. *J. Org. Chem*., 2015, 1419.

5 W.-M. Xu, Y.-G. Wang, M.-Z. Miao and X. Huang, *Synthesis*. 2005, **13**, 2143.

6 B. Han, X.-L. Yang, R. Fang, W. Yu, C. Wang, X.-Y. Duan and S. Liu, *Angew. Chem. Int. Ed.*, 2012, **51**, 8816.

4. NMR Spectra

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5.135
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5.127
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3.535
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3.520
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10
8
6
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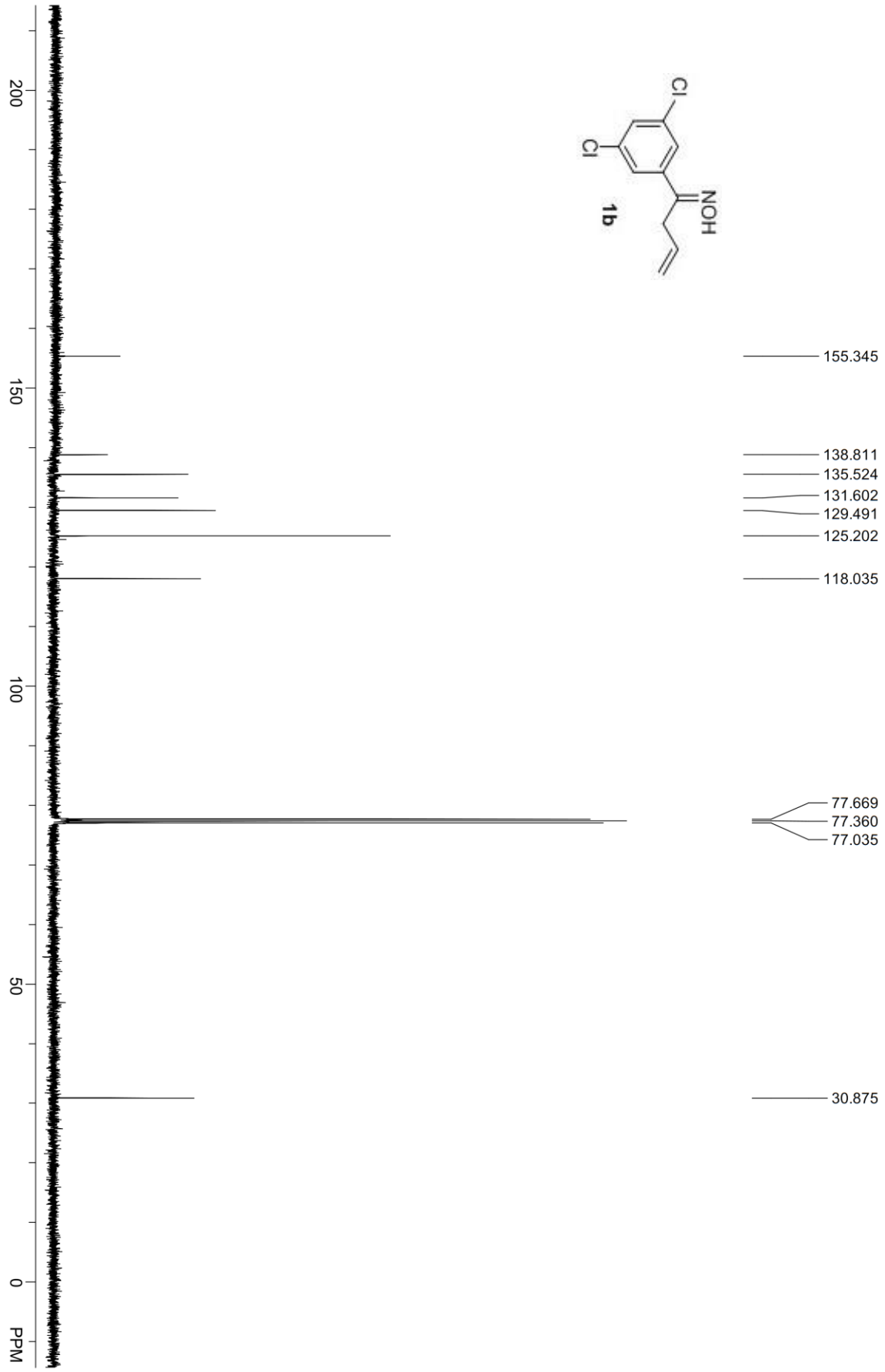
PPM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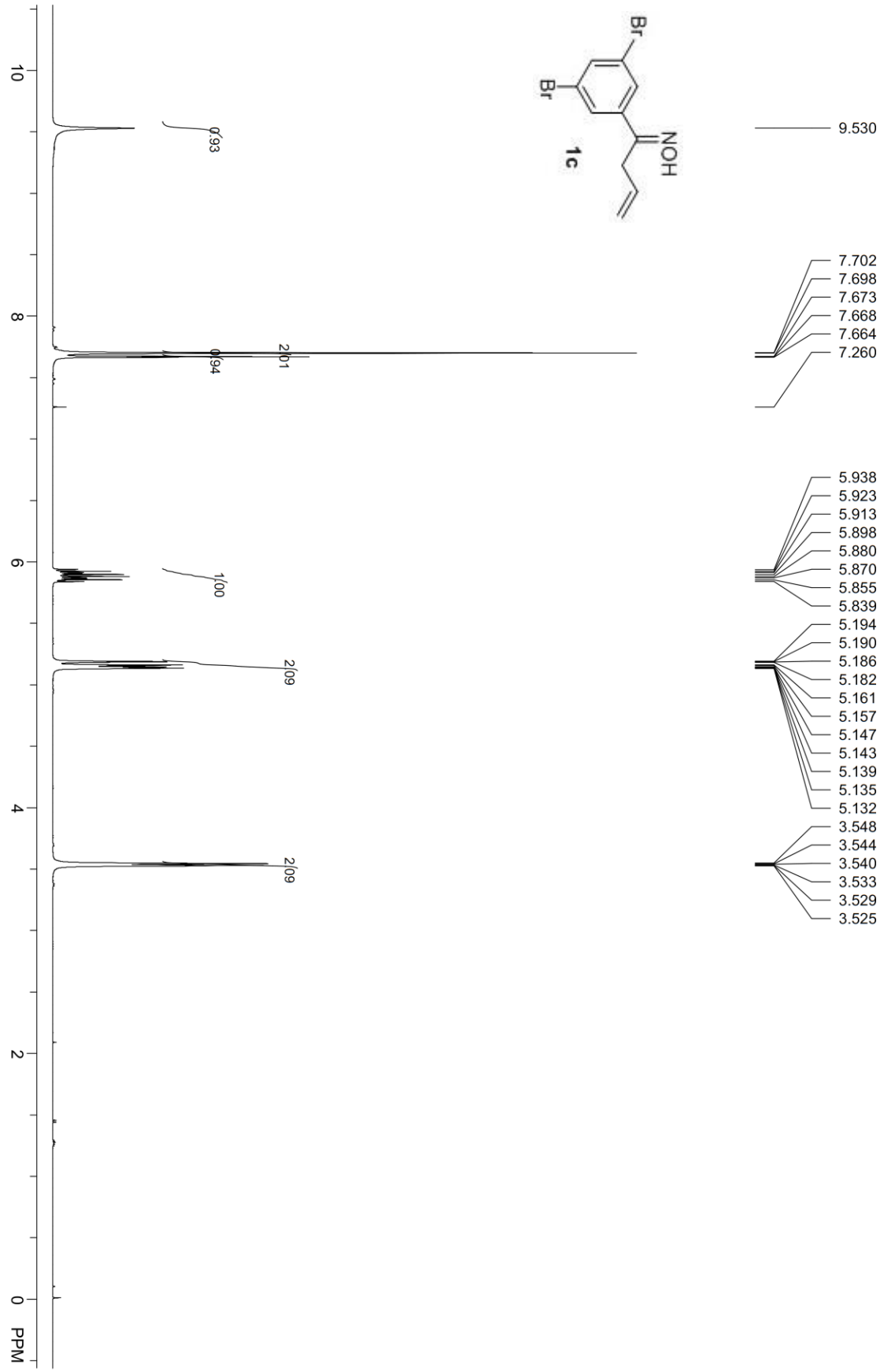
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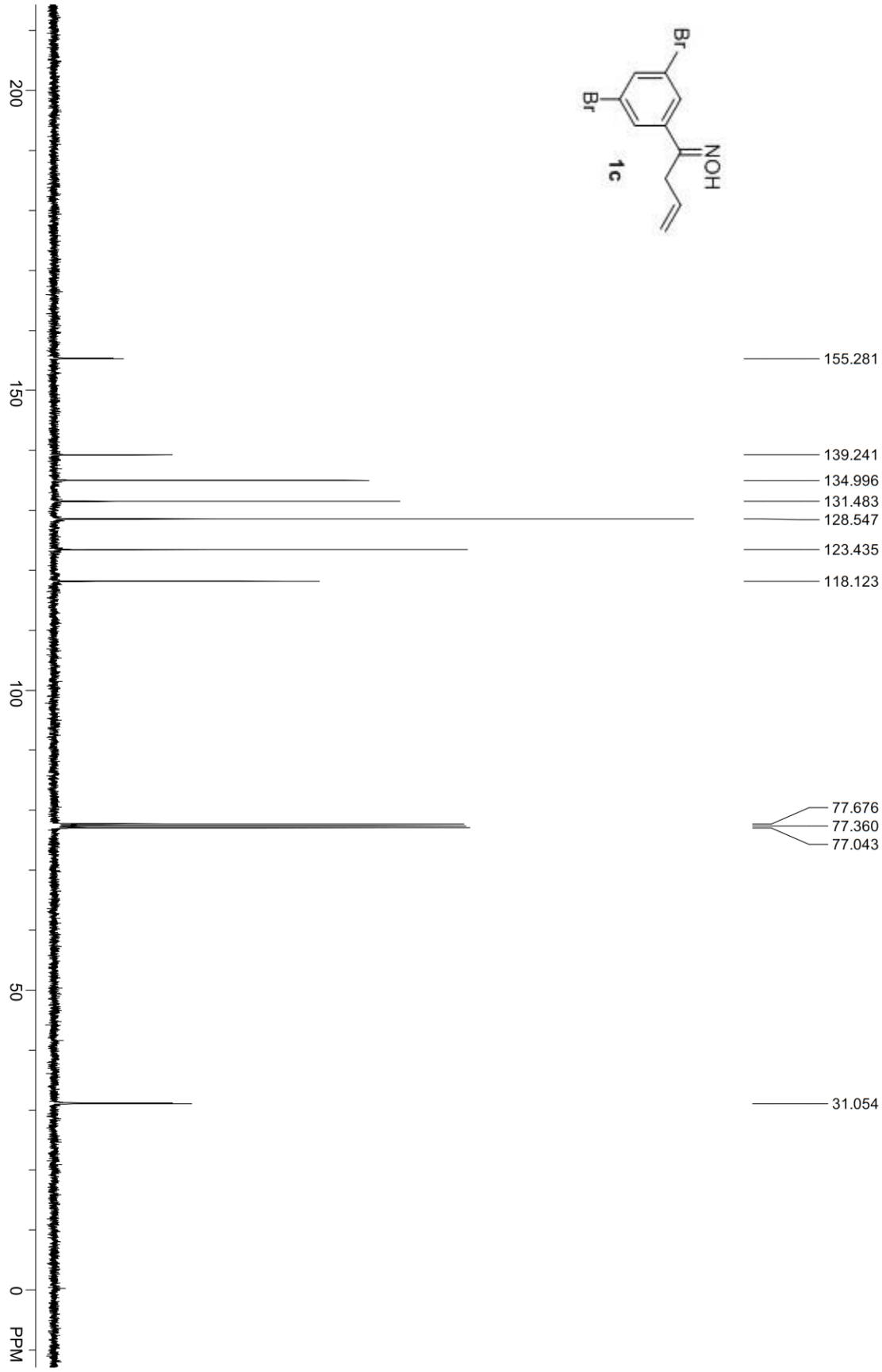
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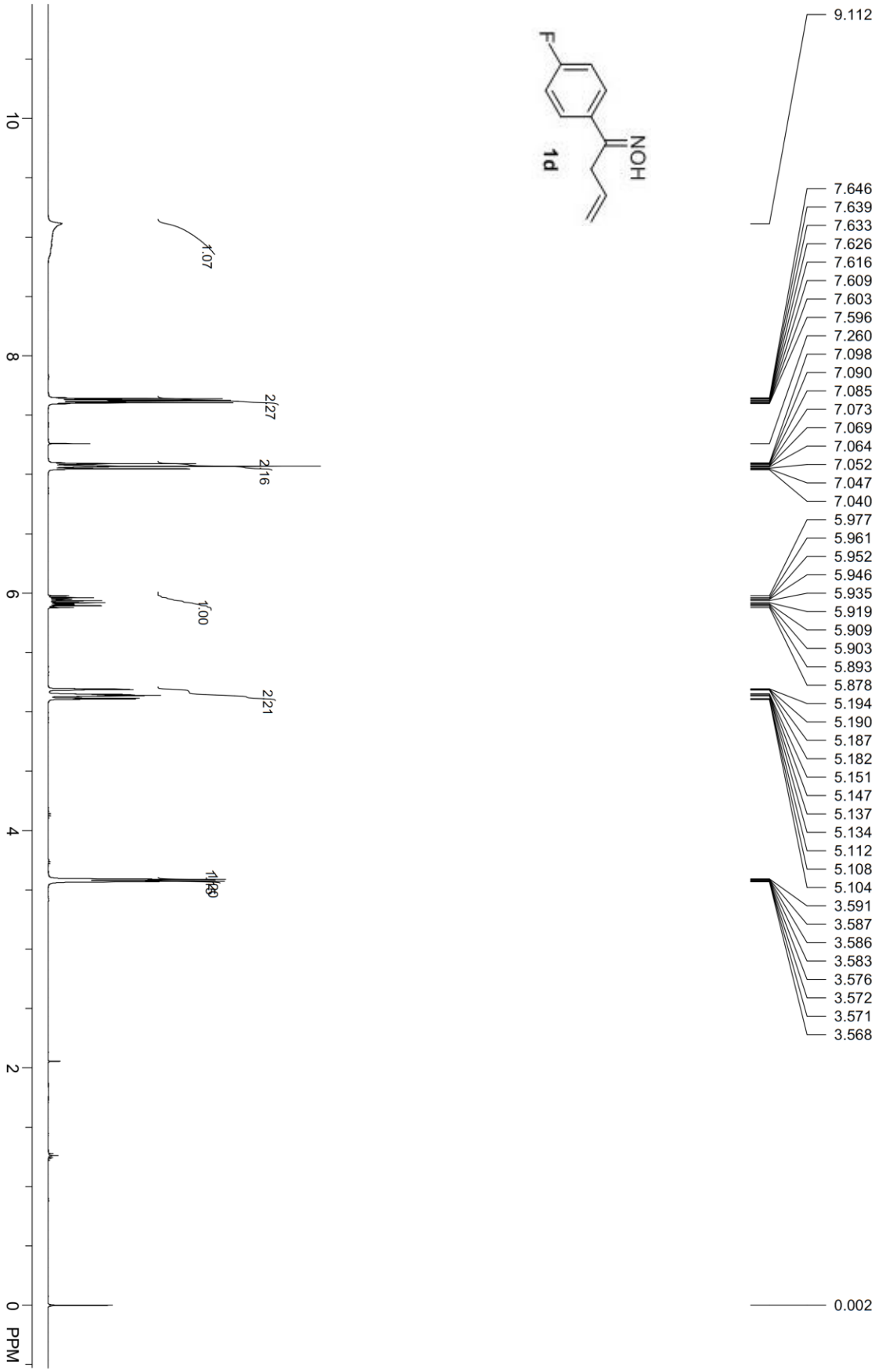
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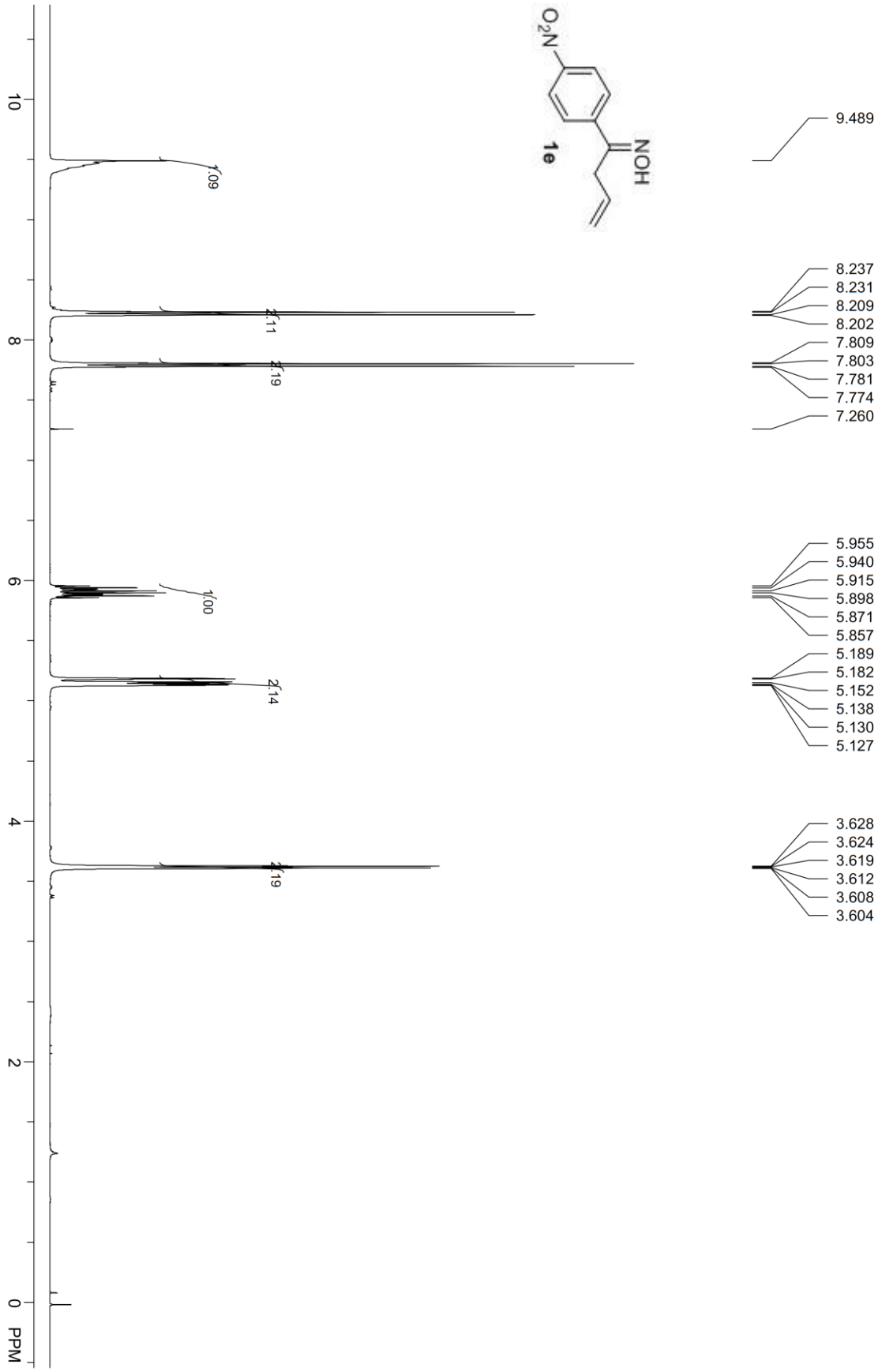
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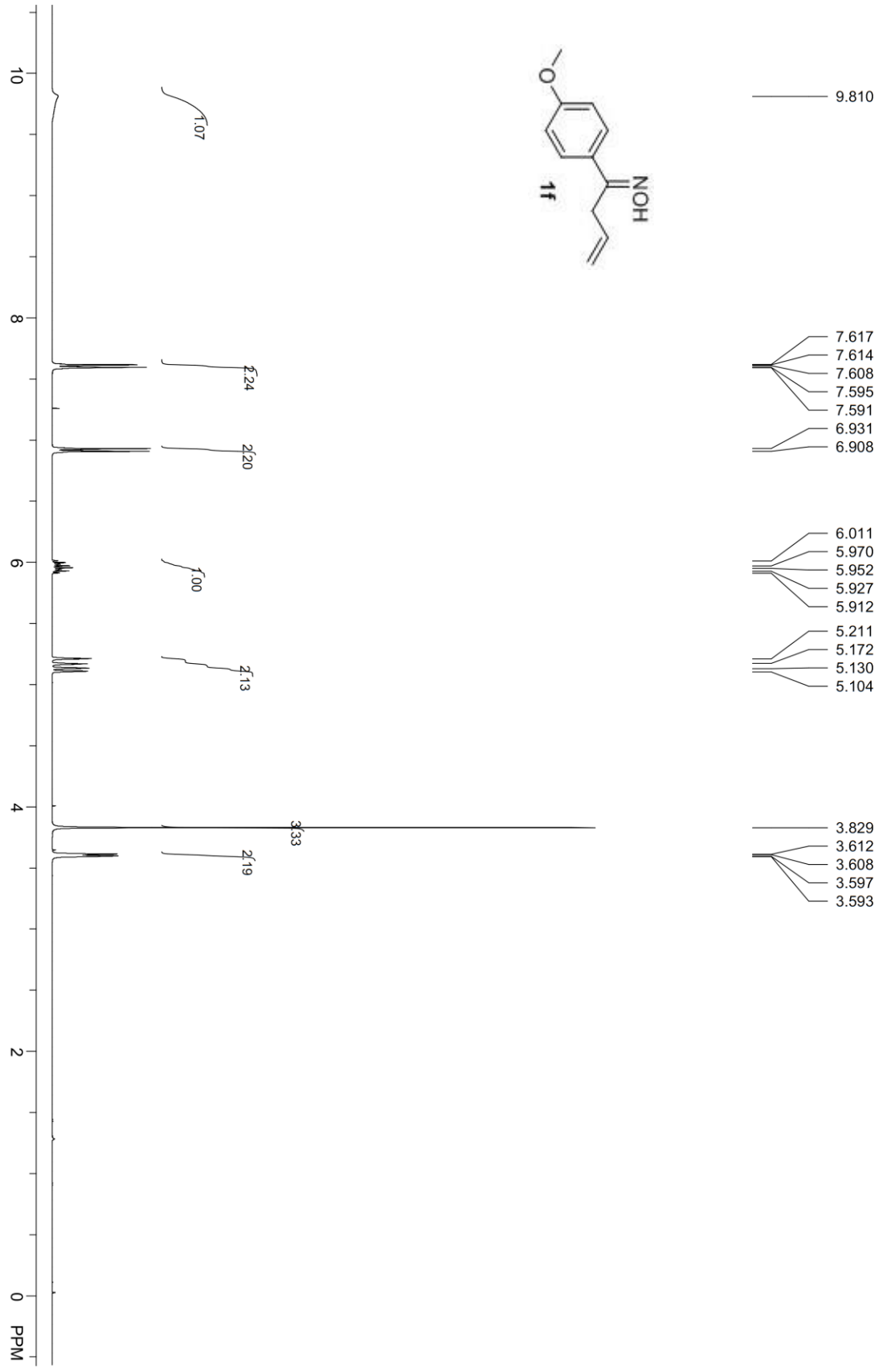
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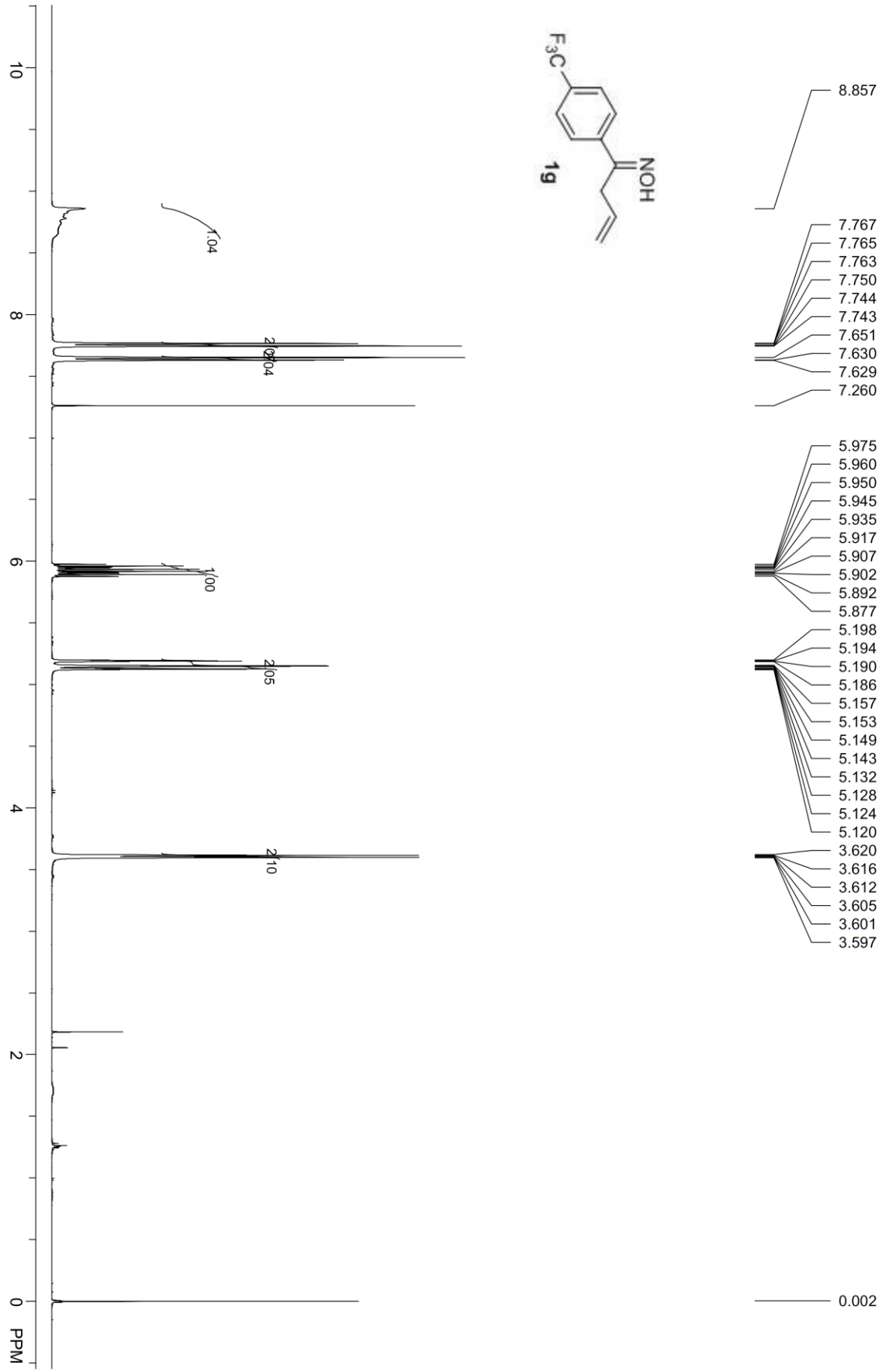
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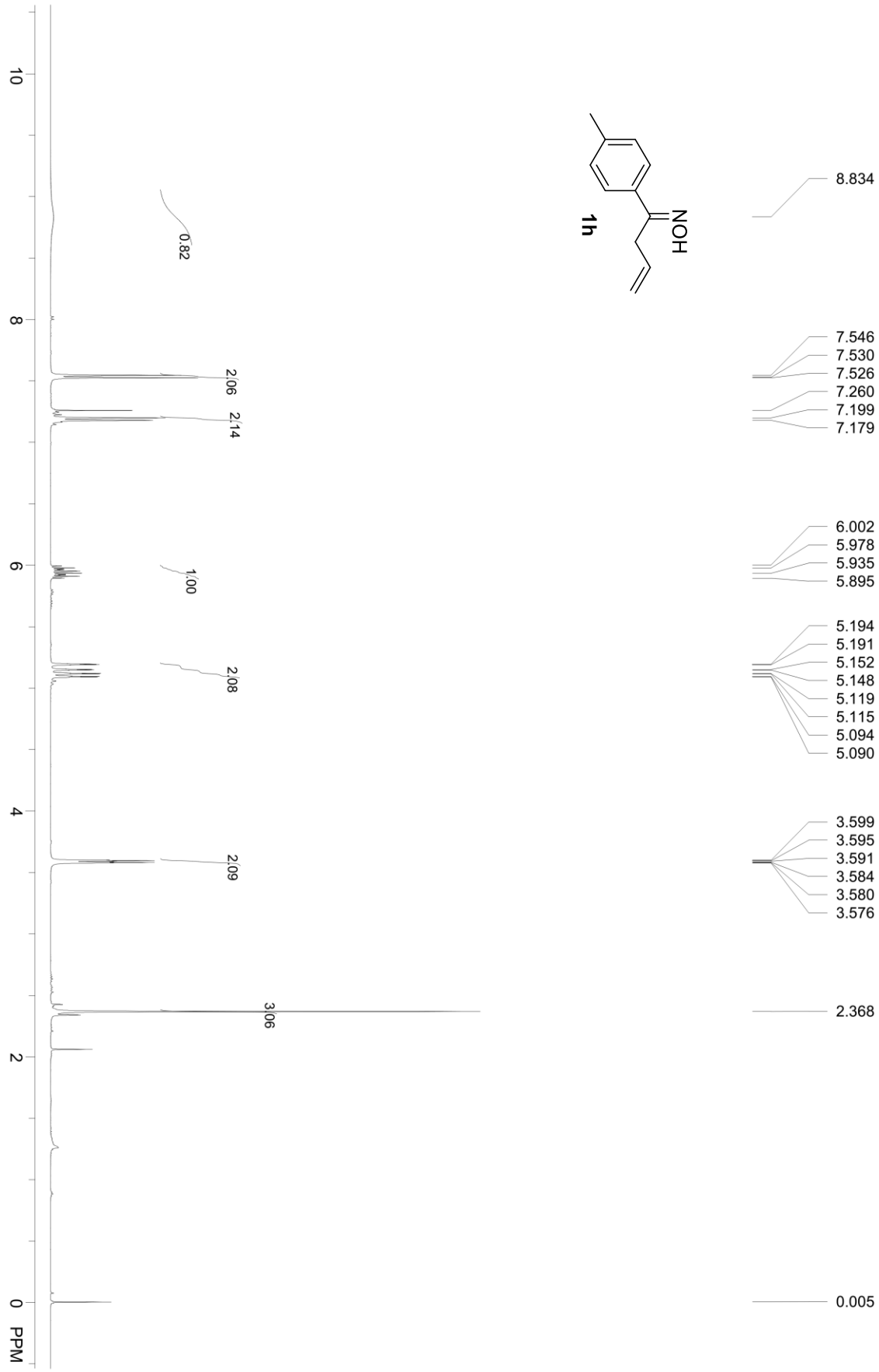
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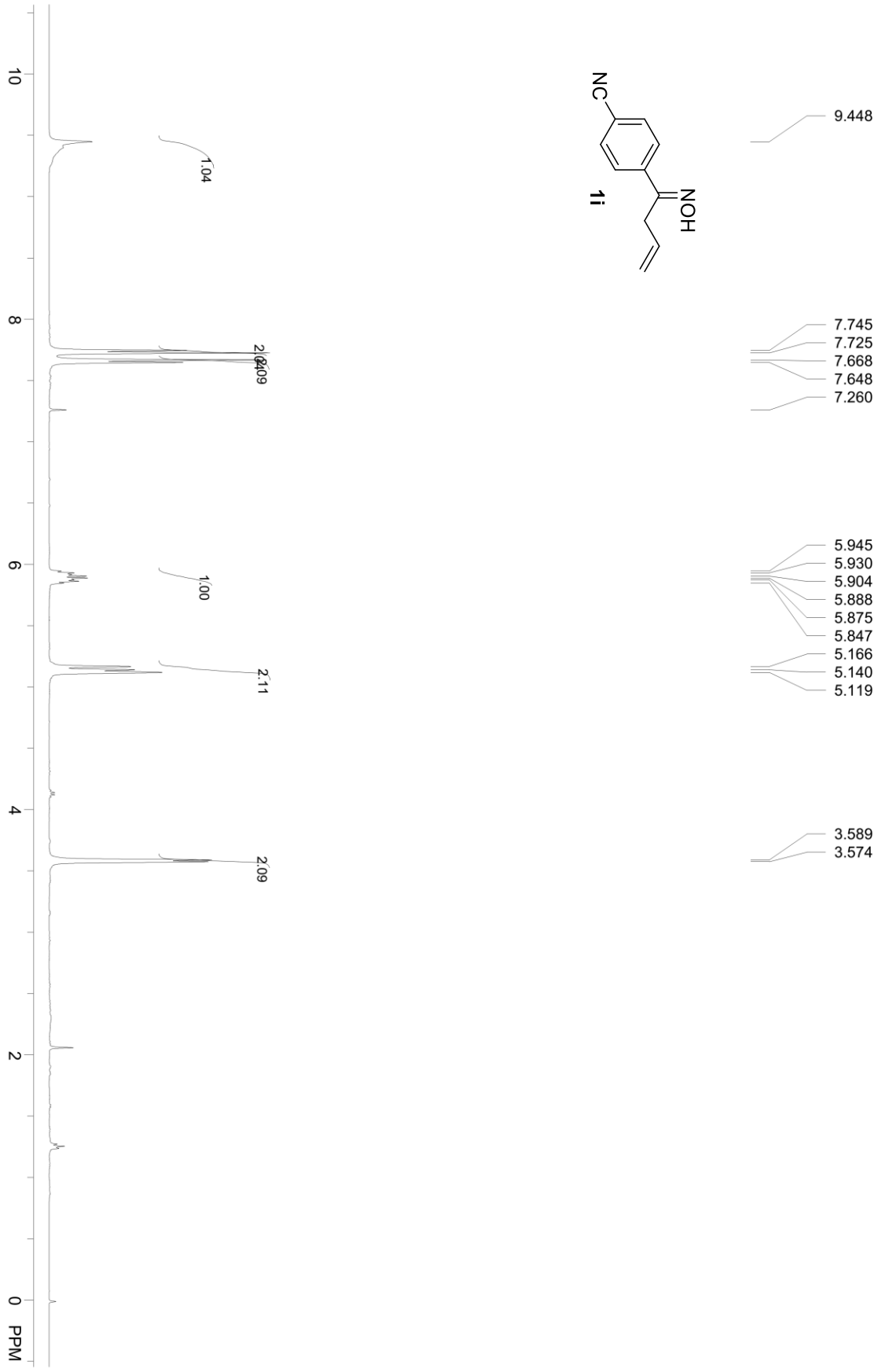
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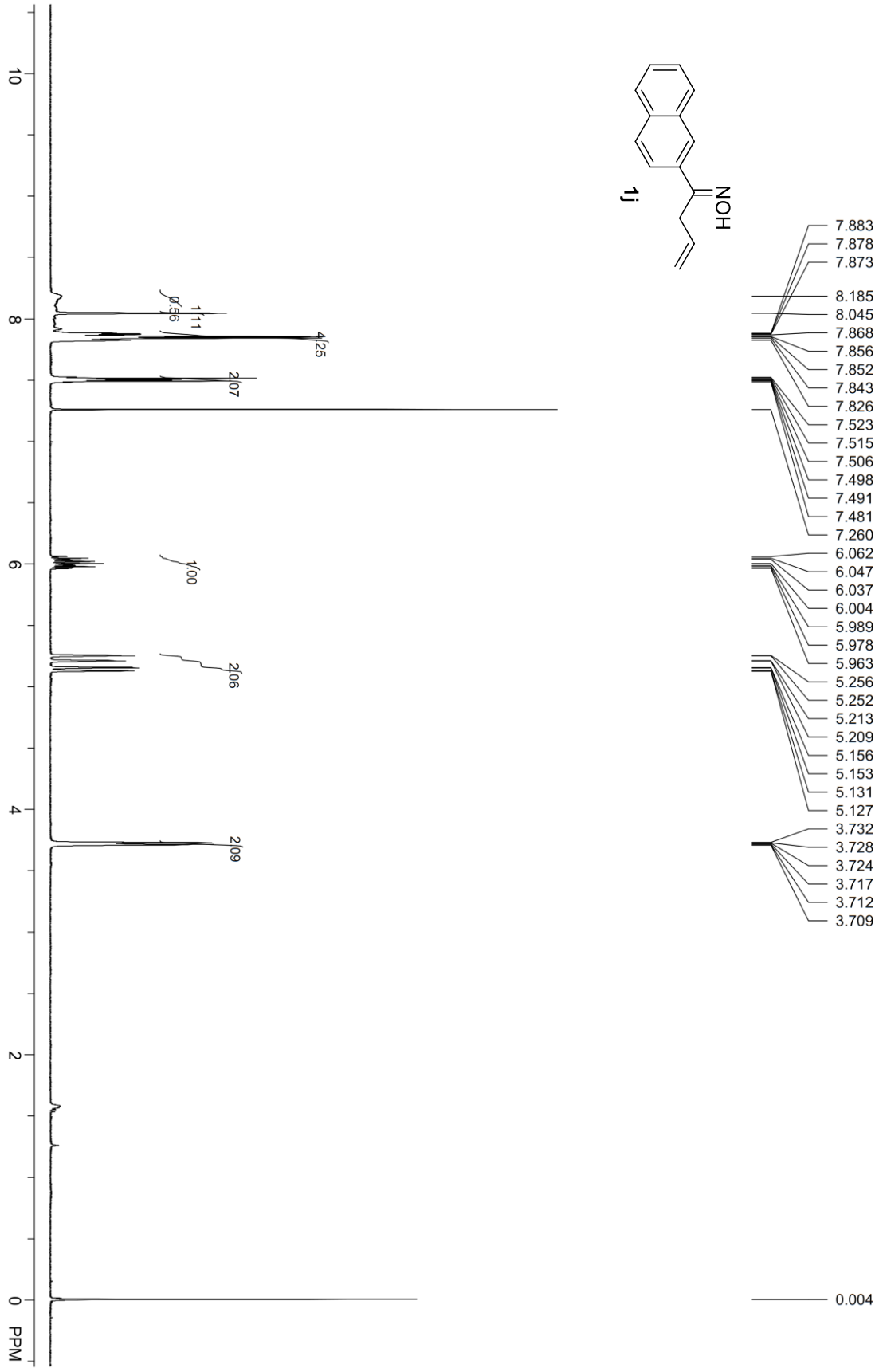
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7.506
7.498
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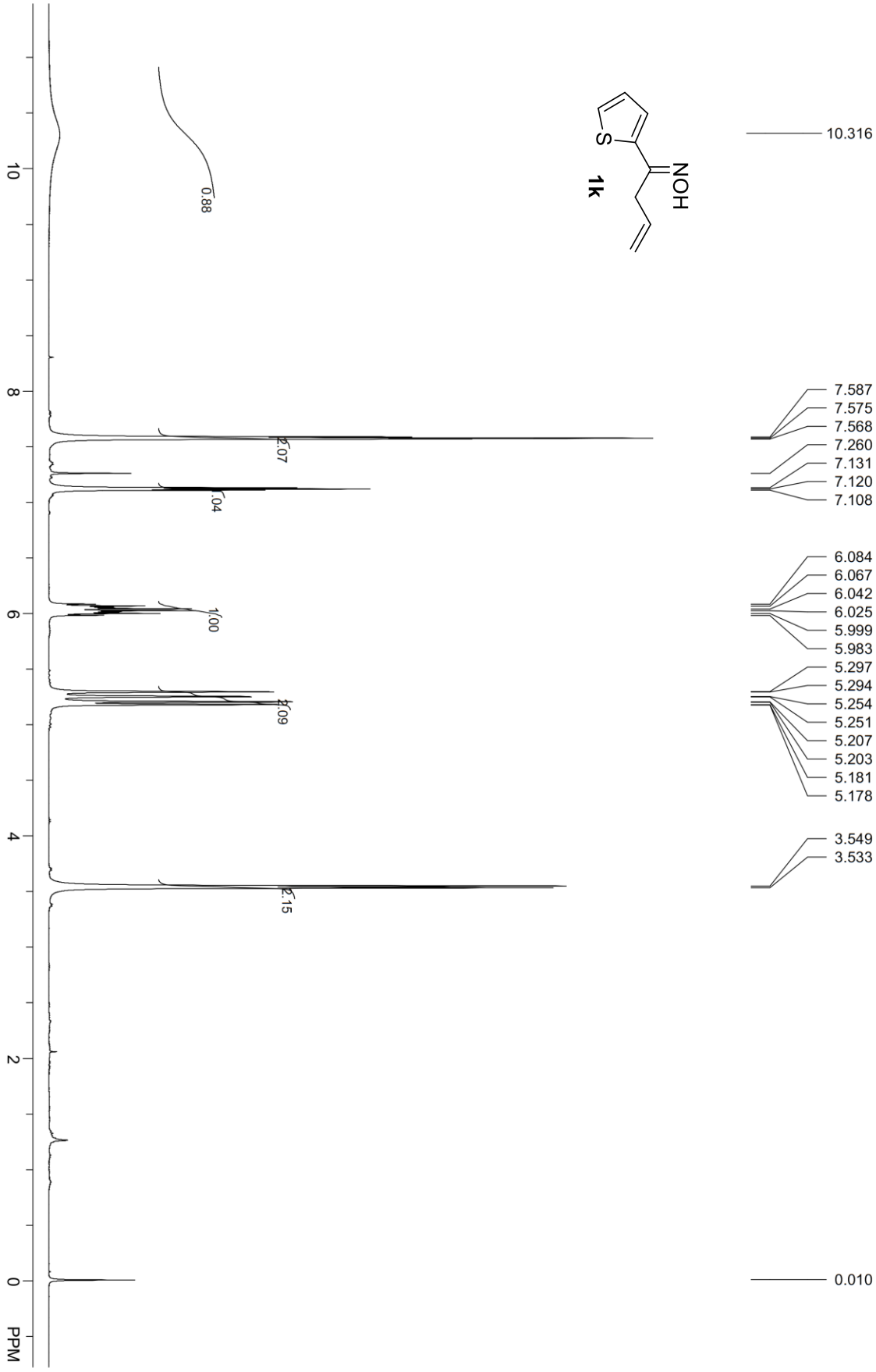
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5.294
5.254
5.251
5.207
5.203
5.181
5.178
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S
1k
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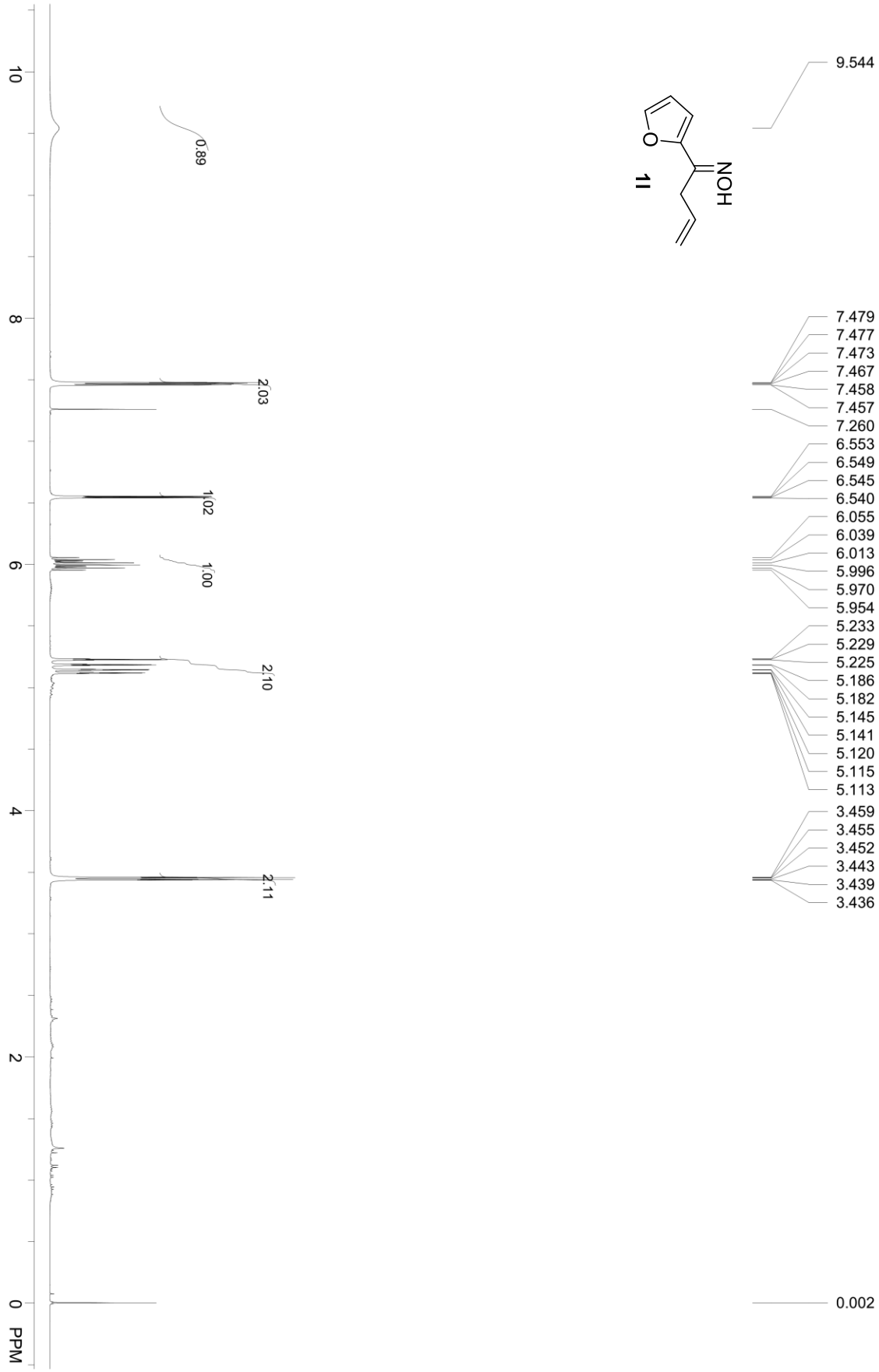
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6.039
6.013
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5.182
5.145
5.141
5.120
5.115
5.113
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3.455
3.452
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3.439
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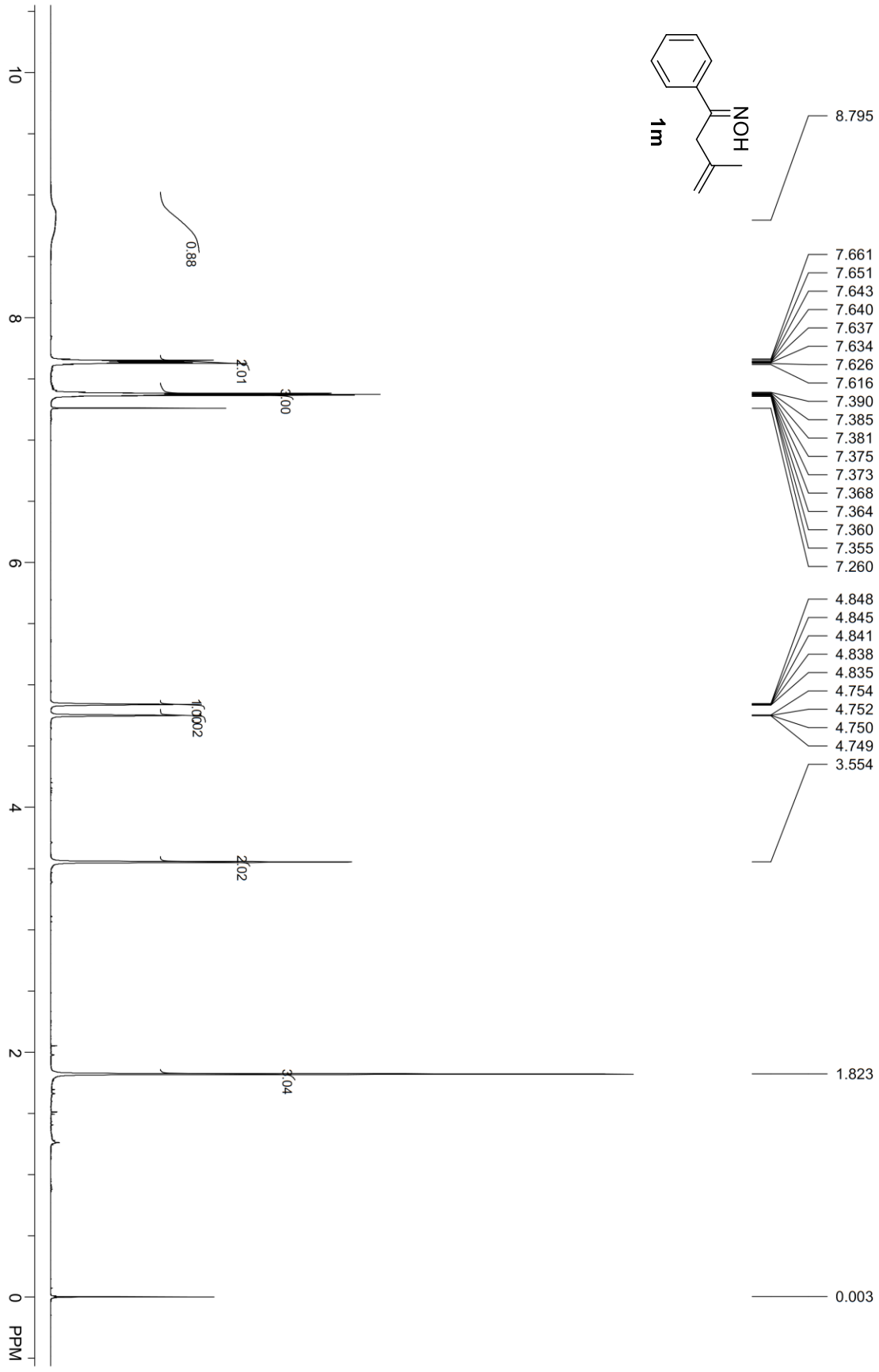
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7.385
7.381
7.375
7.373
7.368
7.364
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7.355
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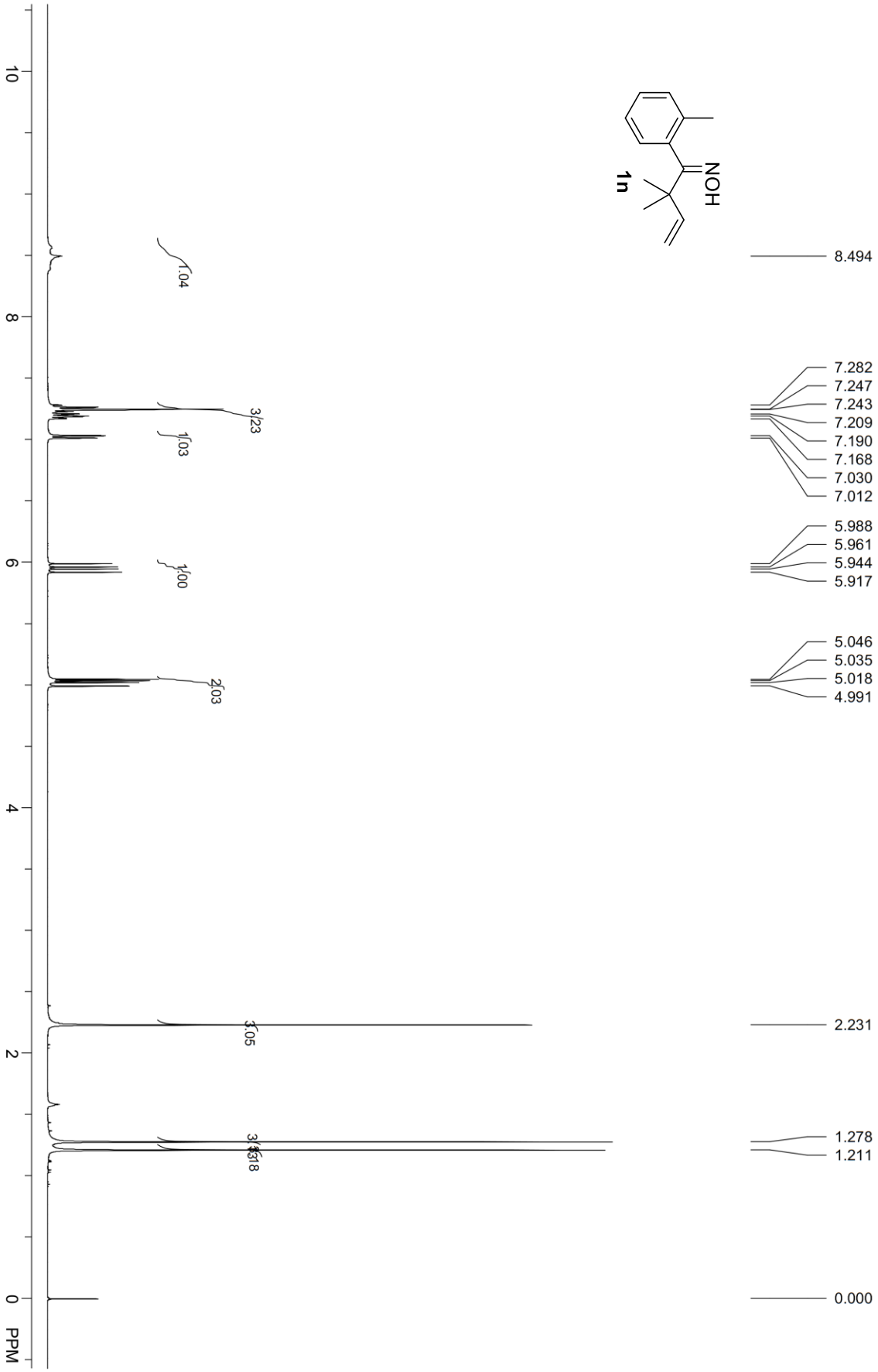
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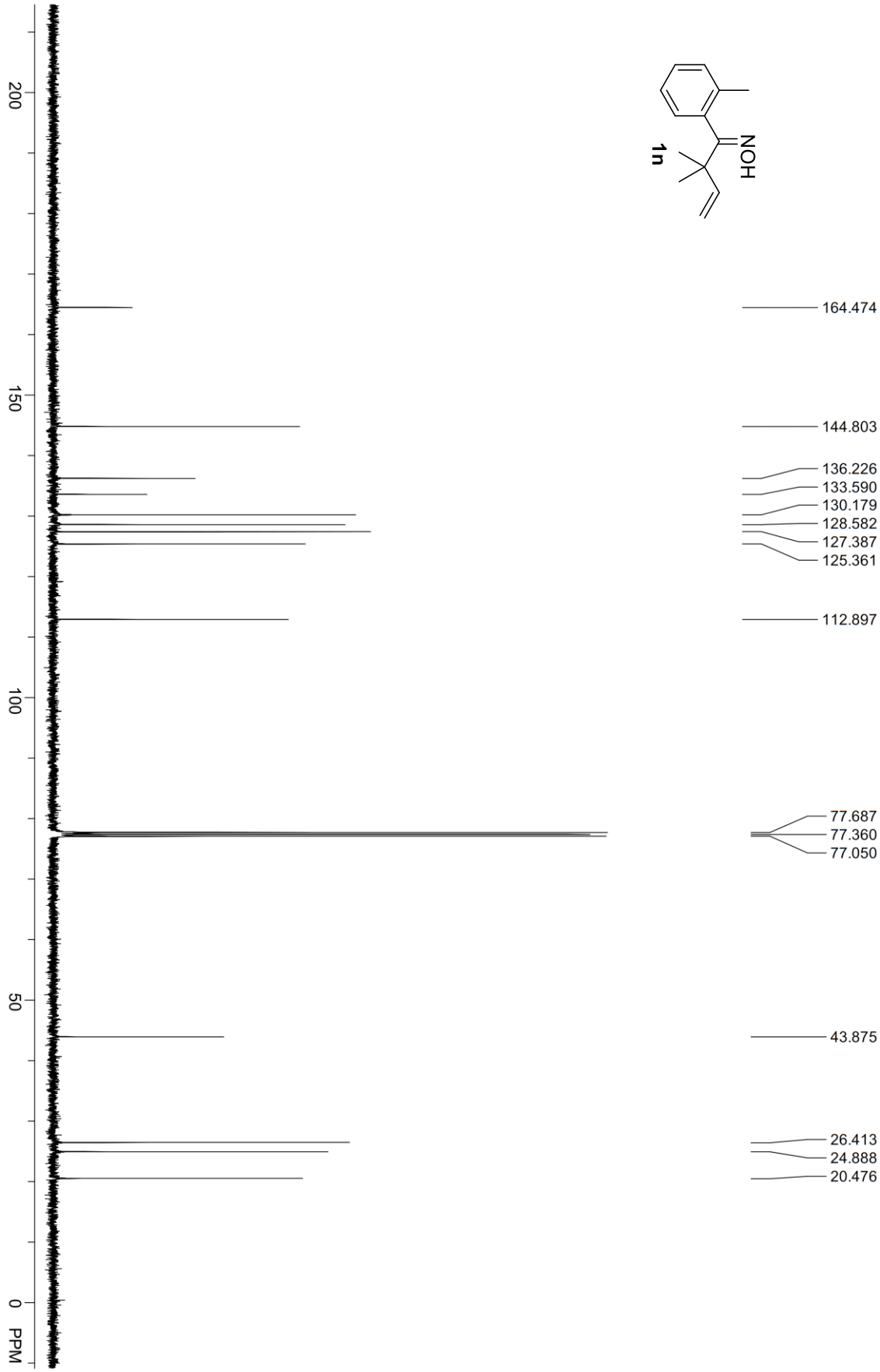
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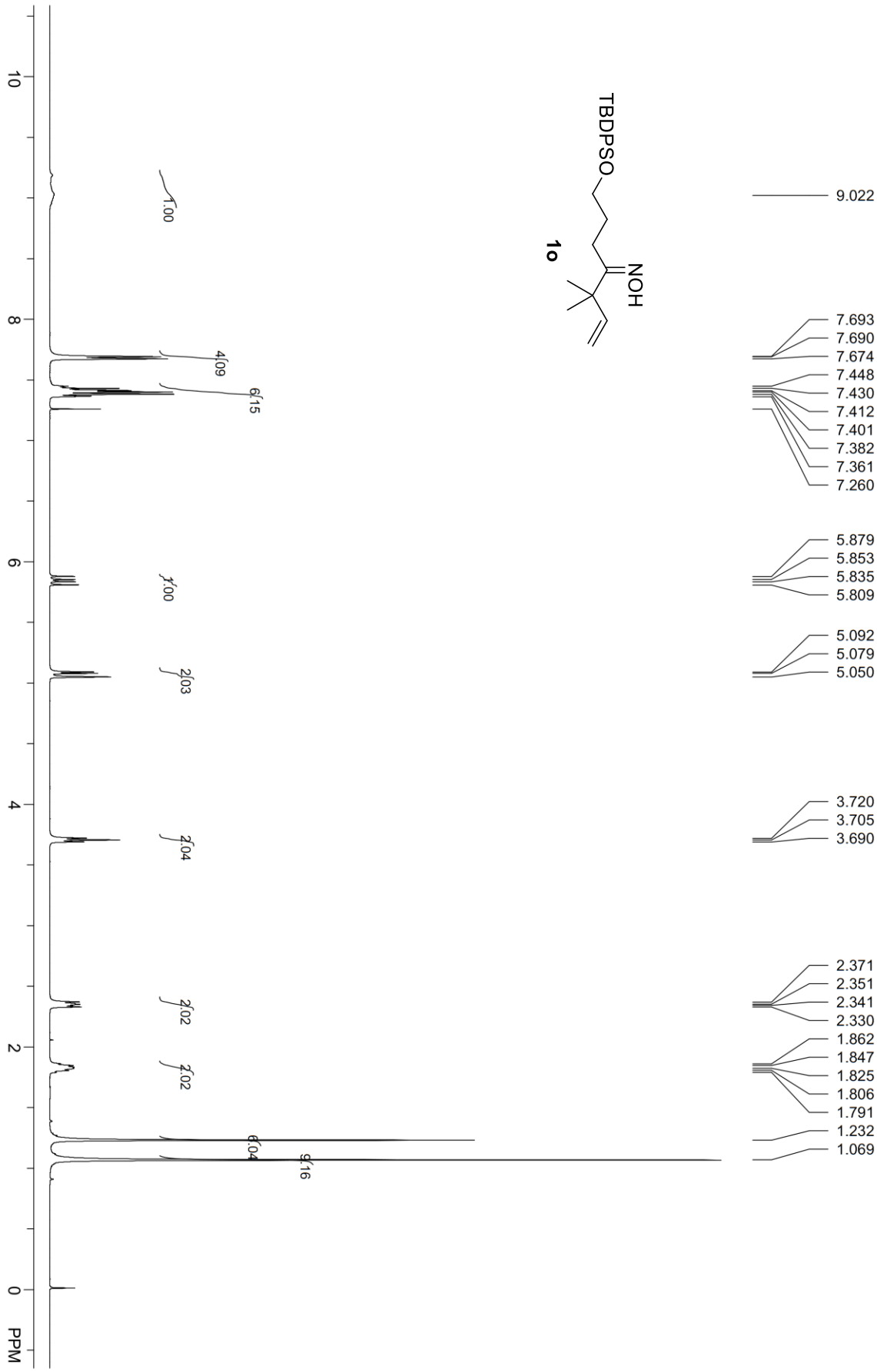
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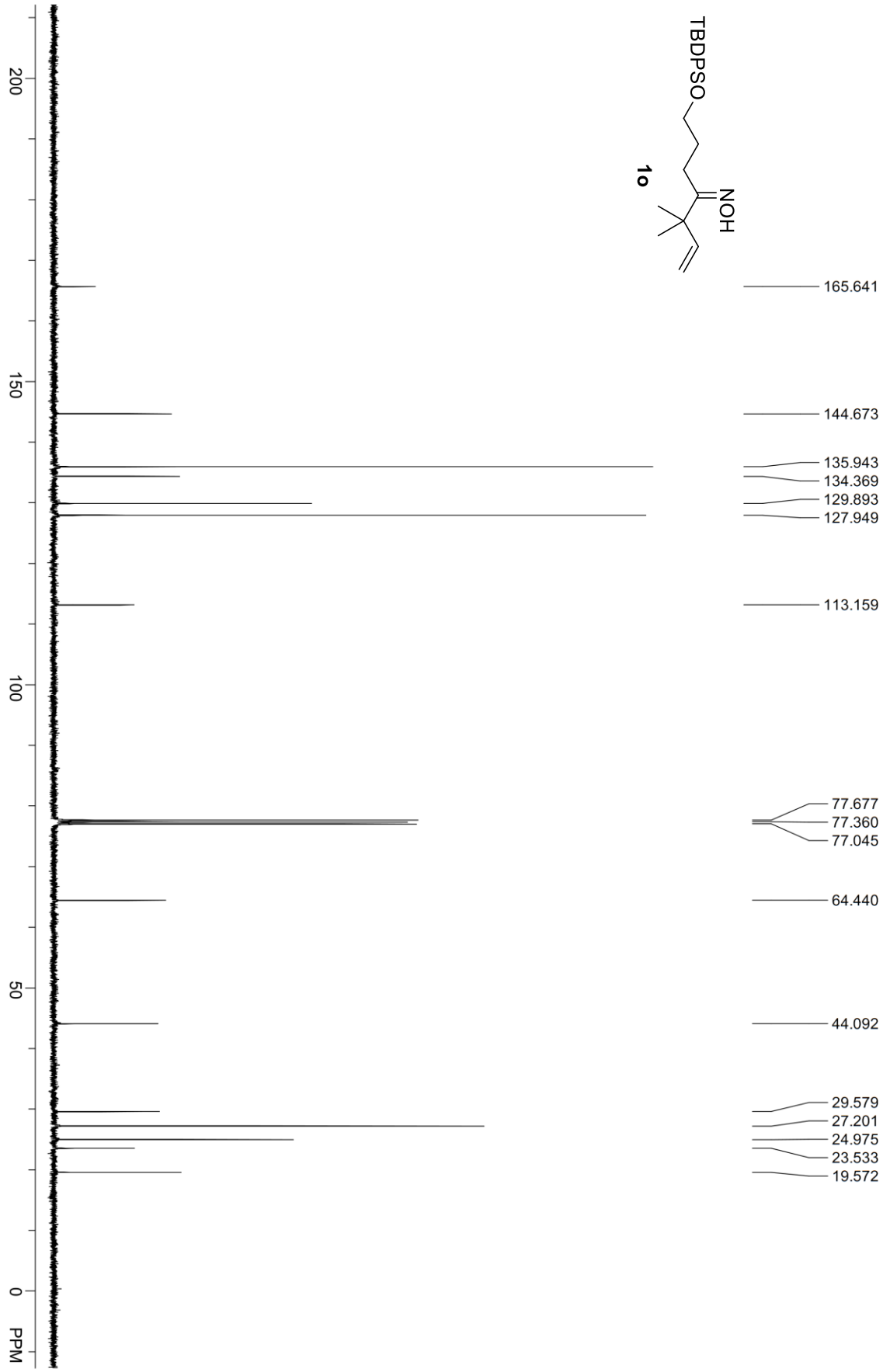
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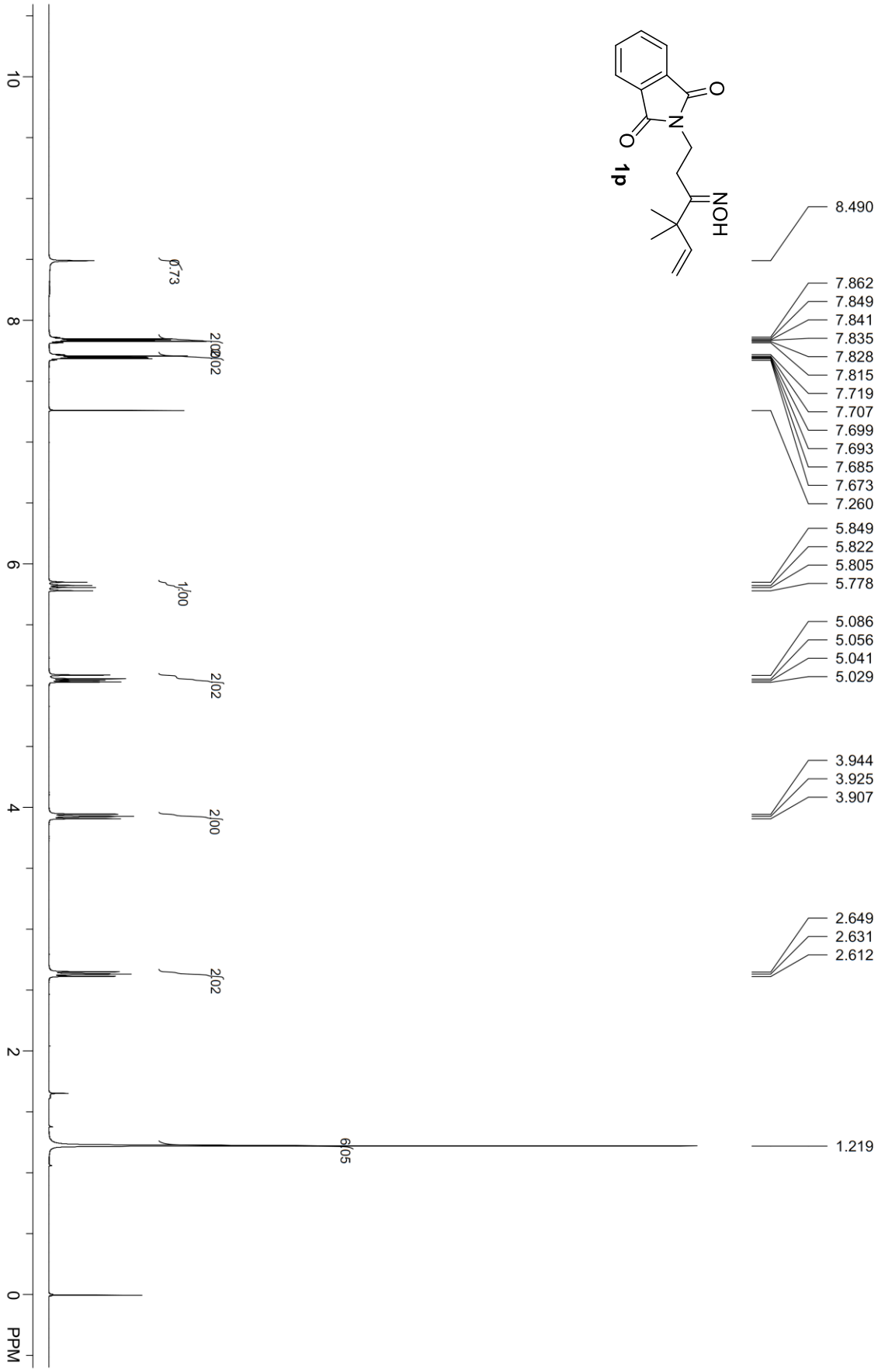
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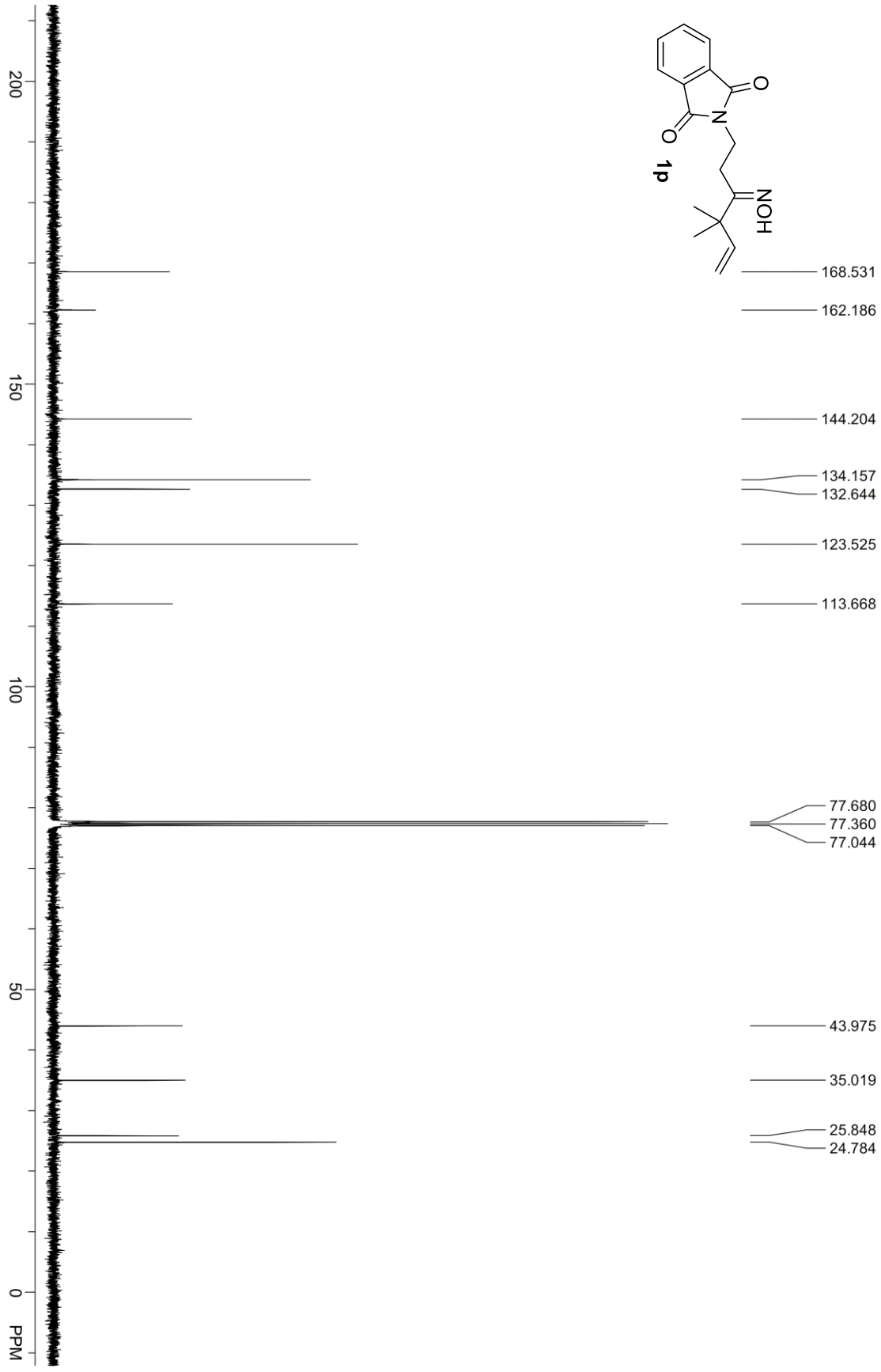
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N
O
HON
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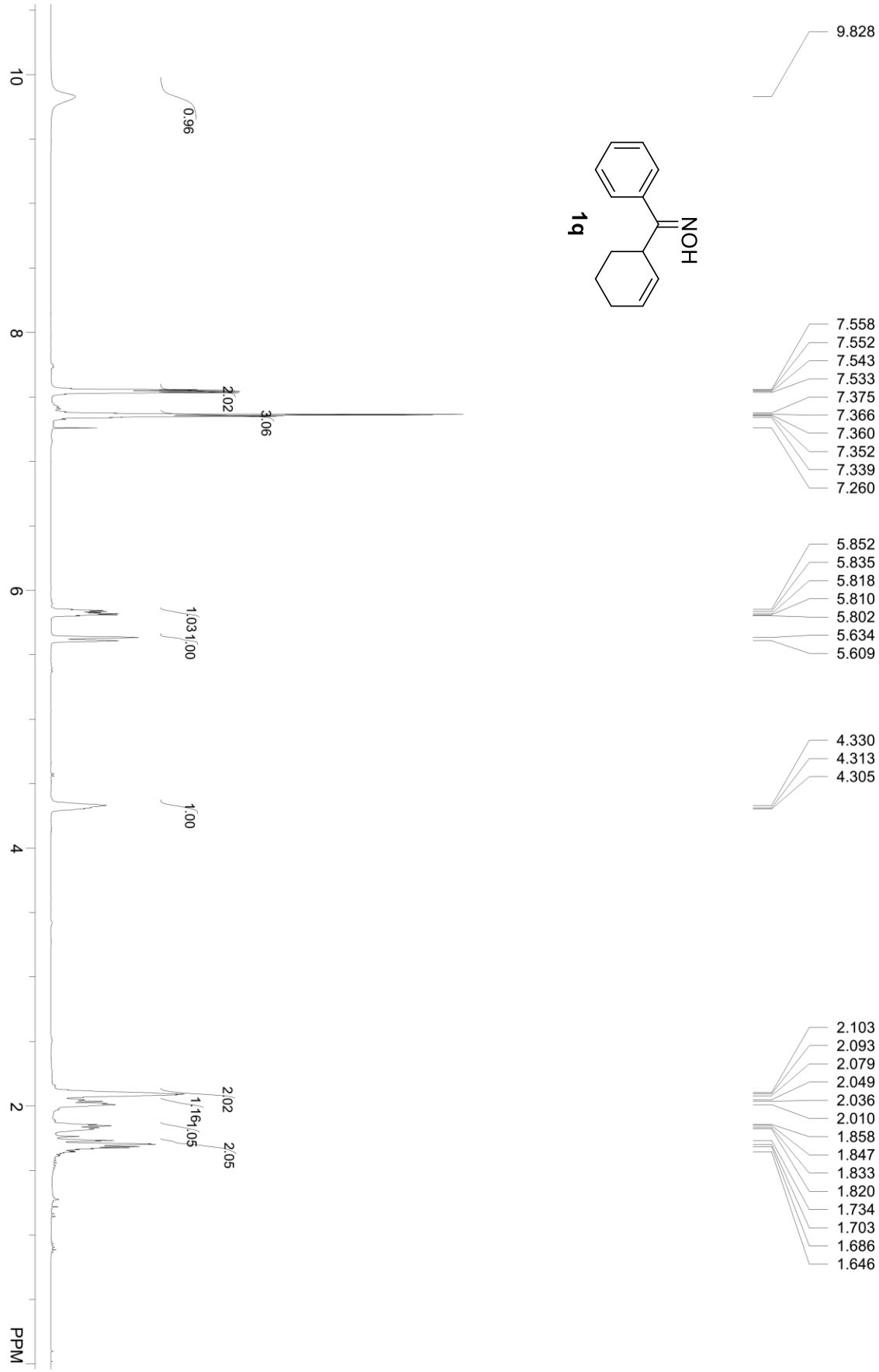
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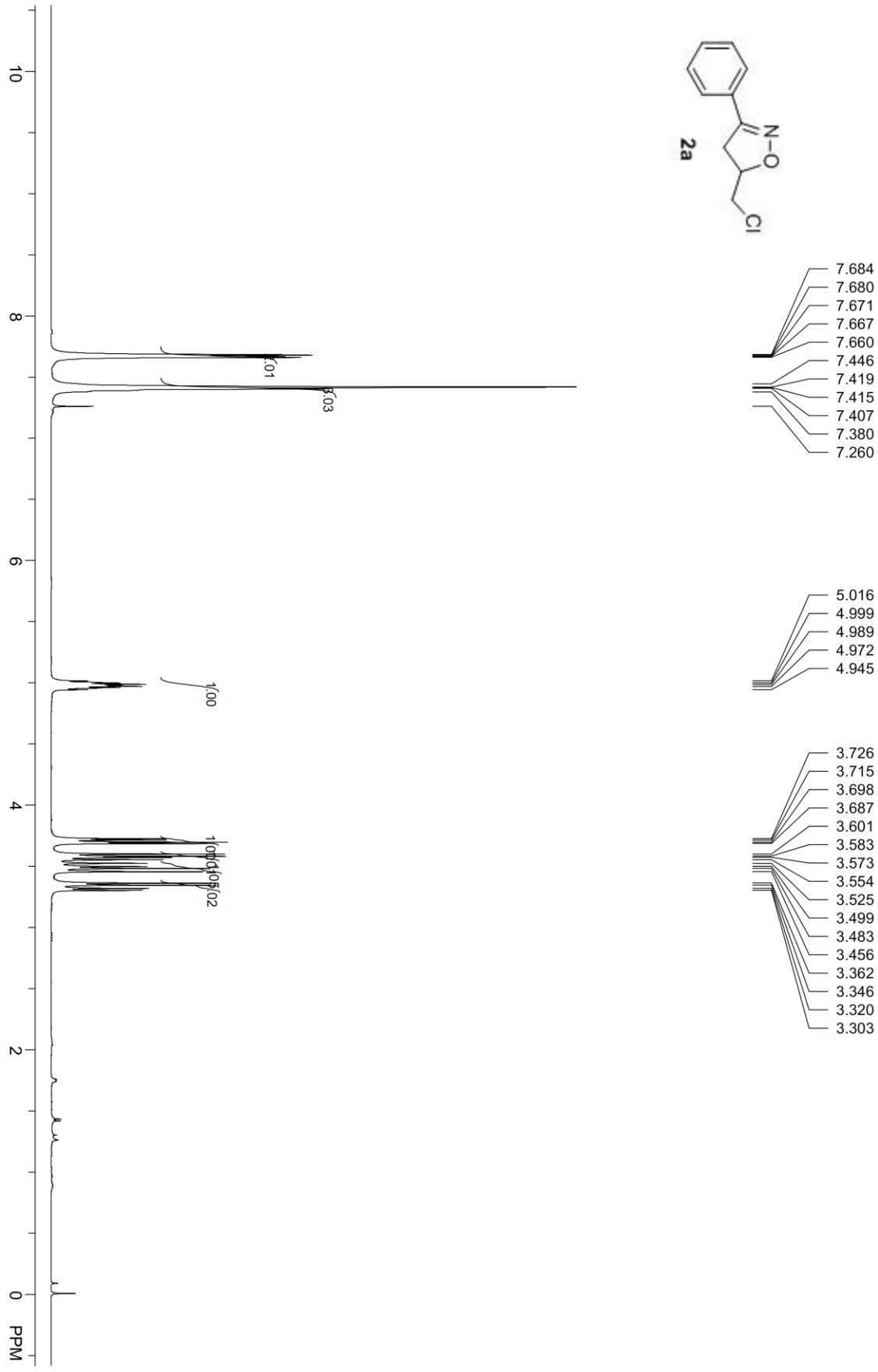
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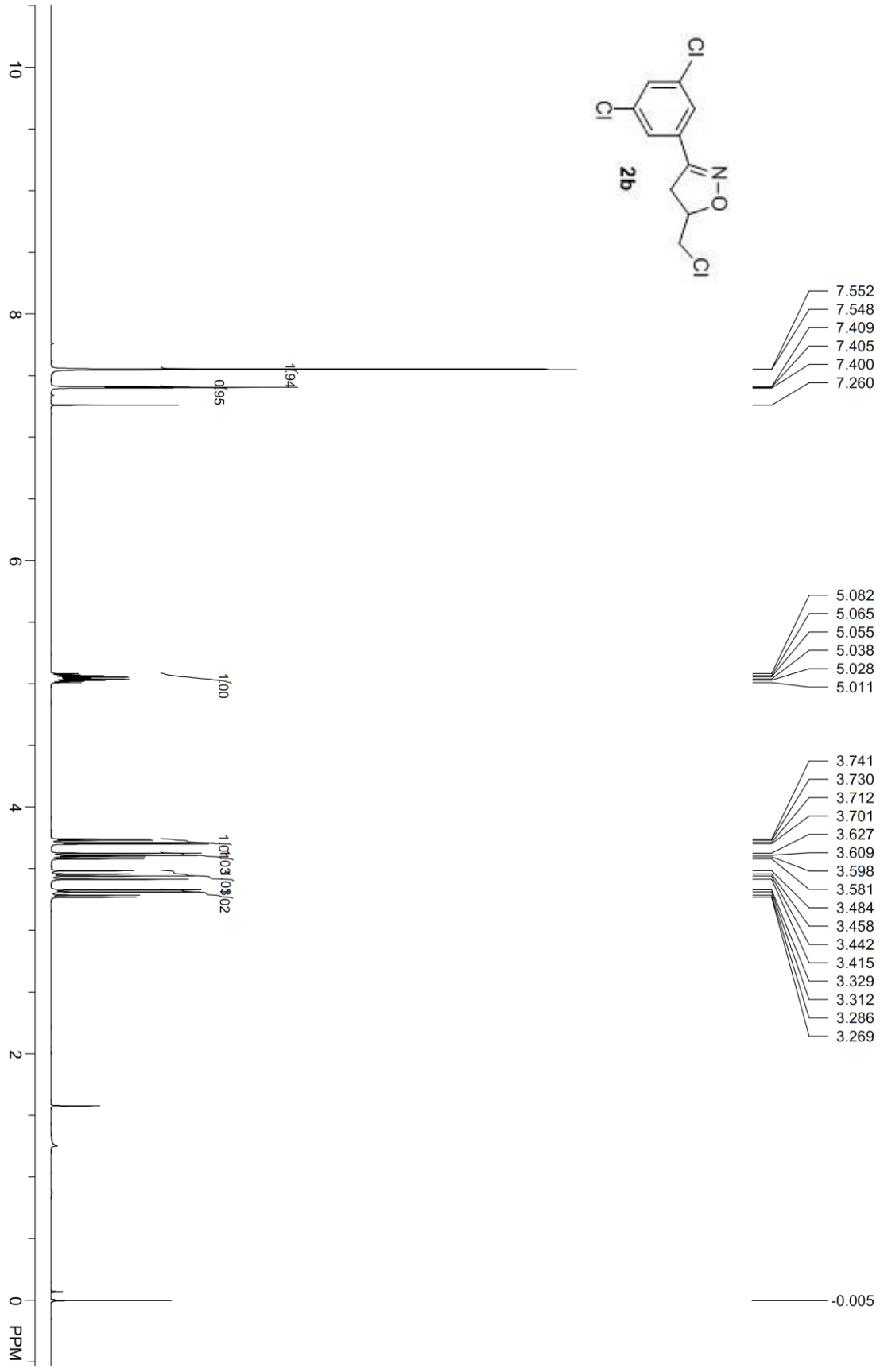
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Cl
N–O
Cl
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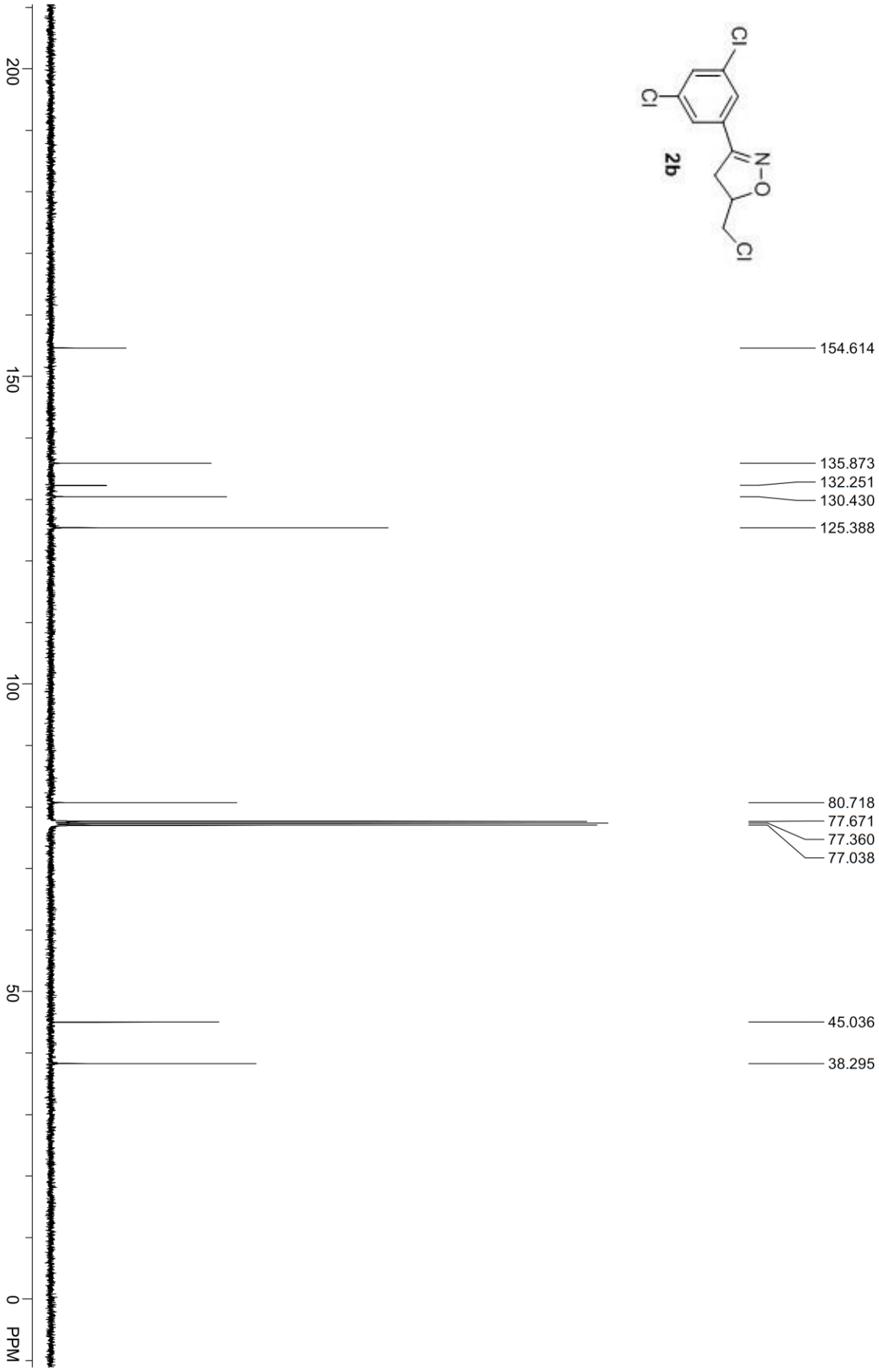
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Cl
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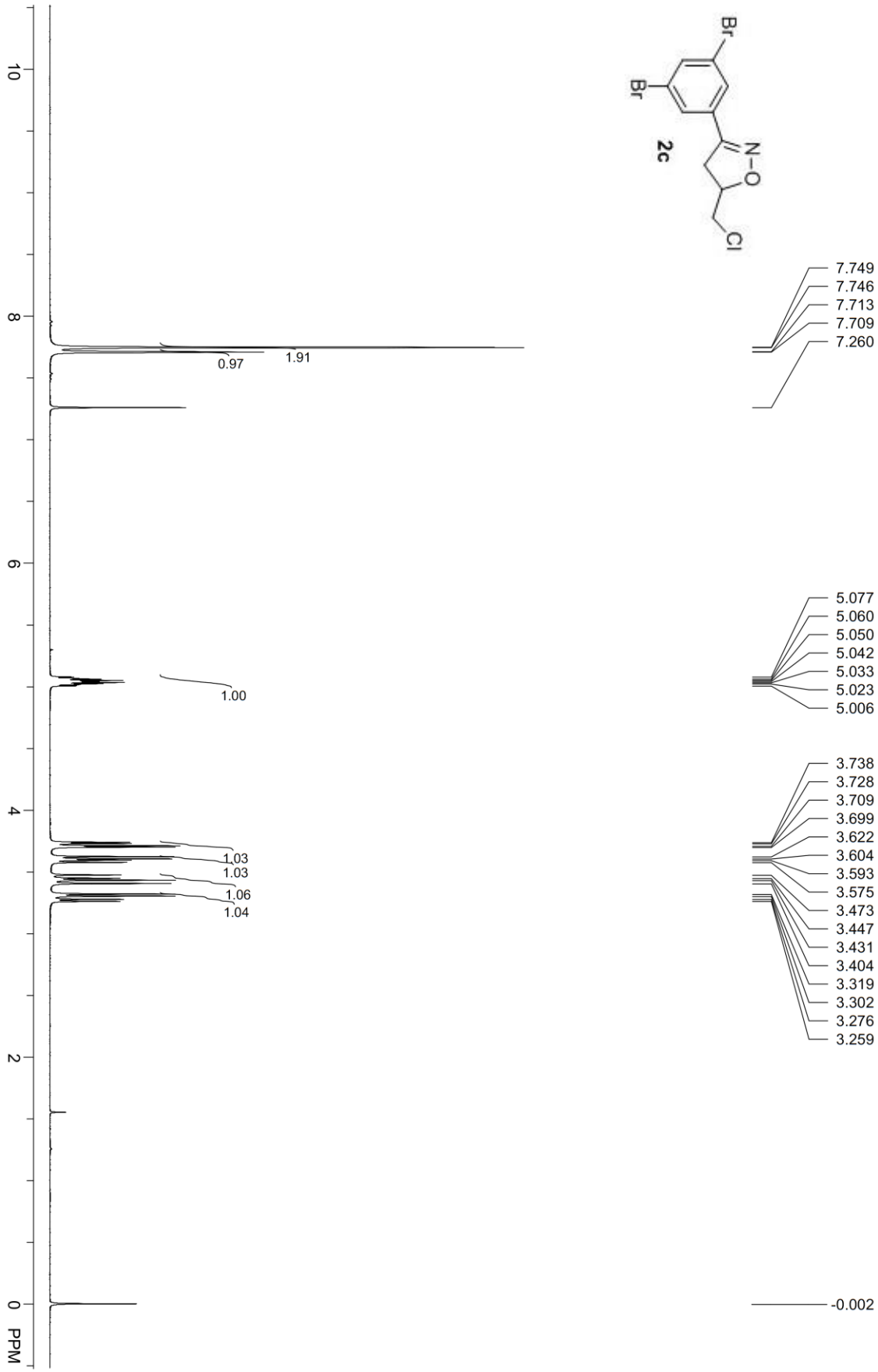
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Br
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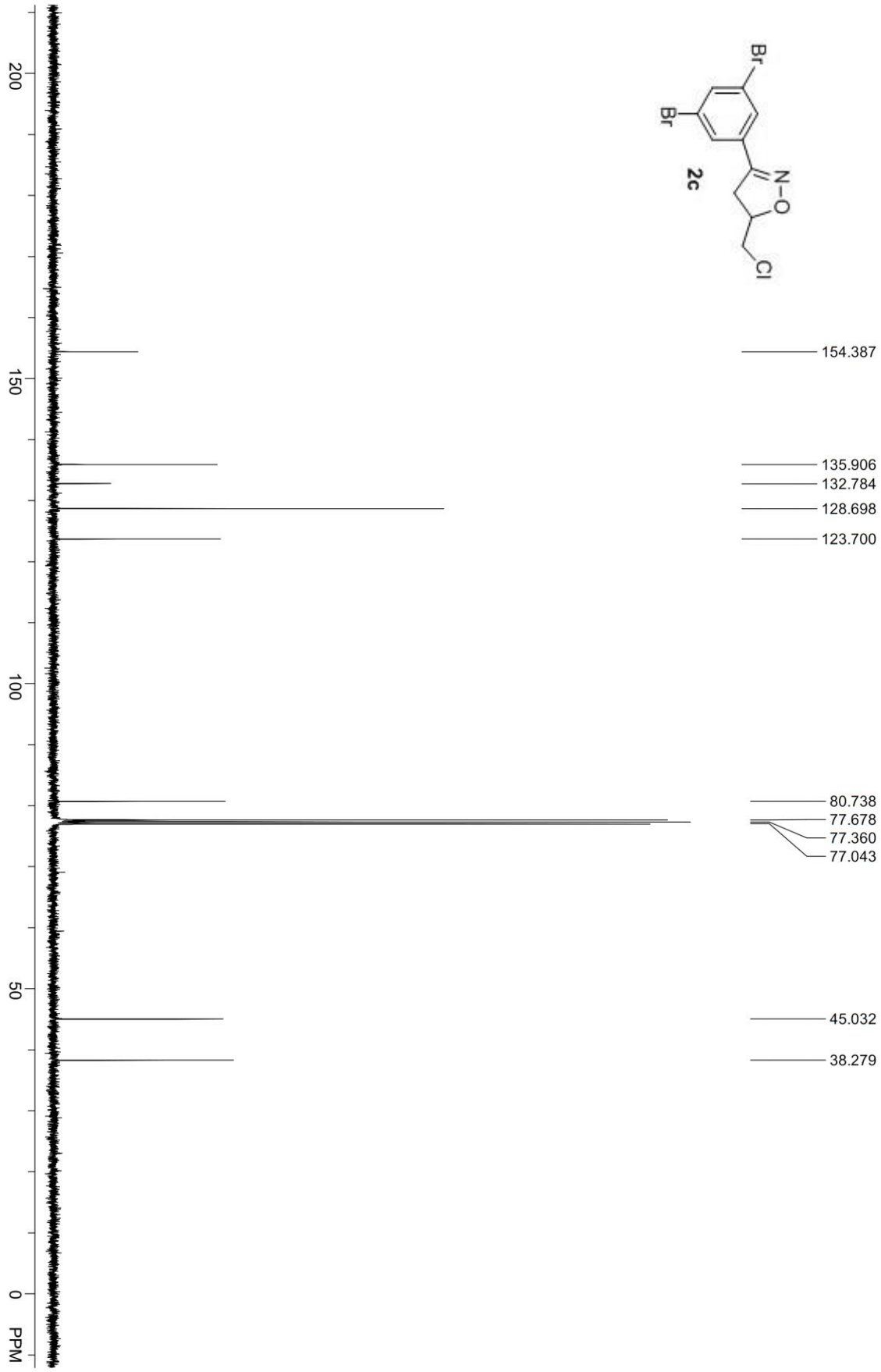
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Br
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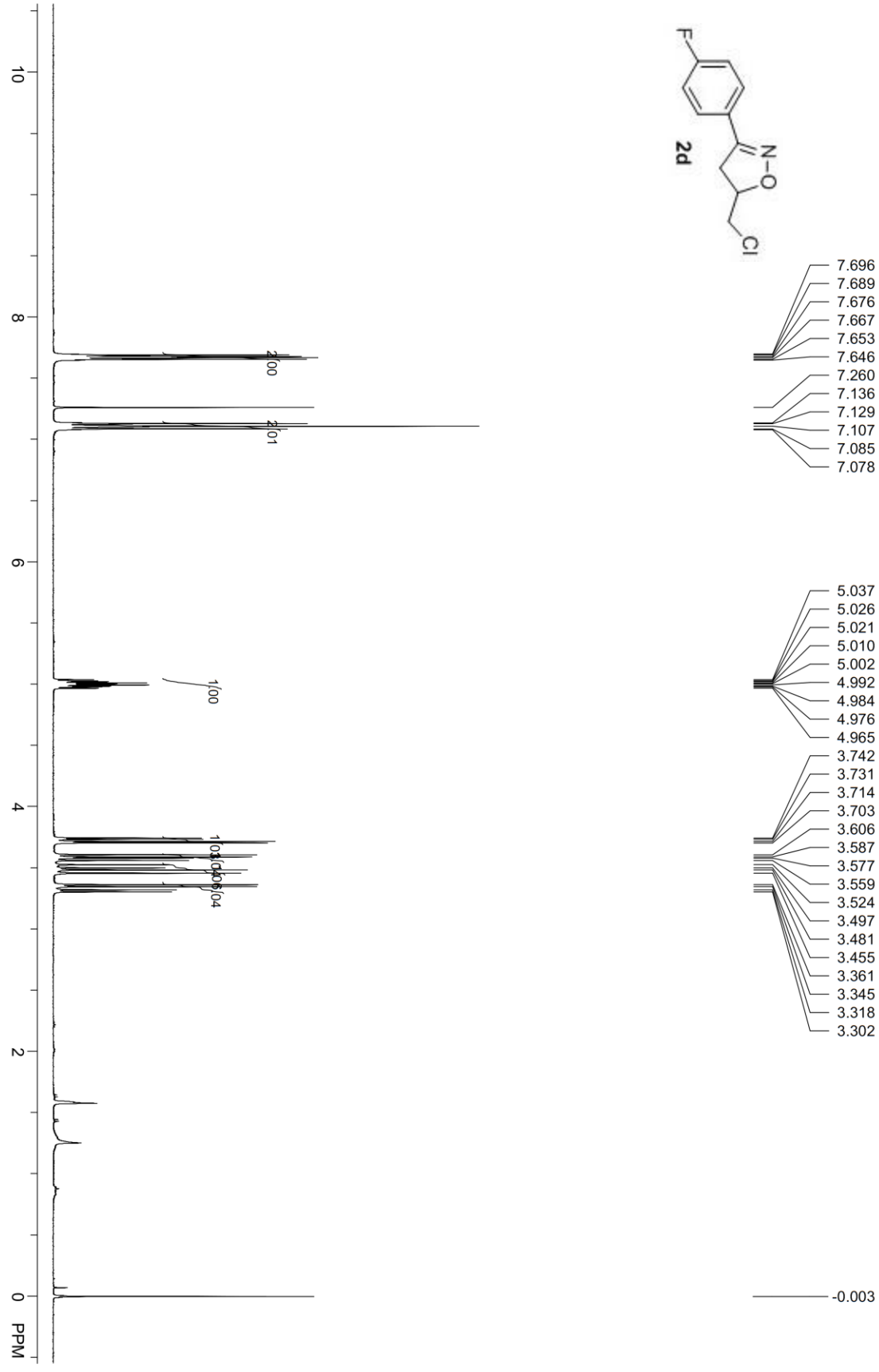
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1.04
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PPM

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F
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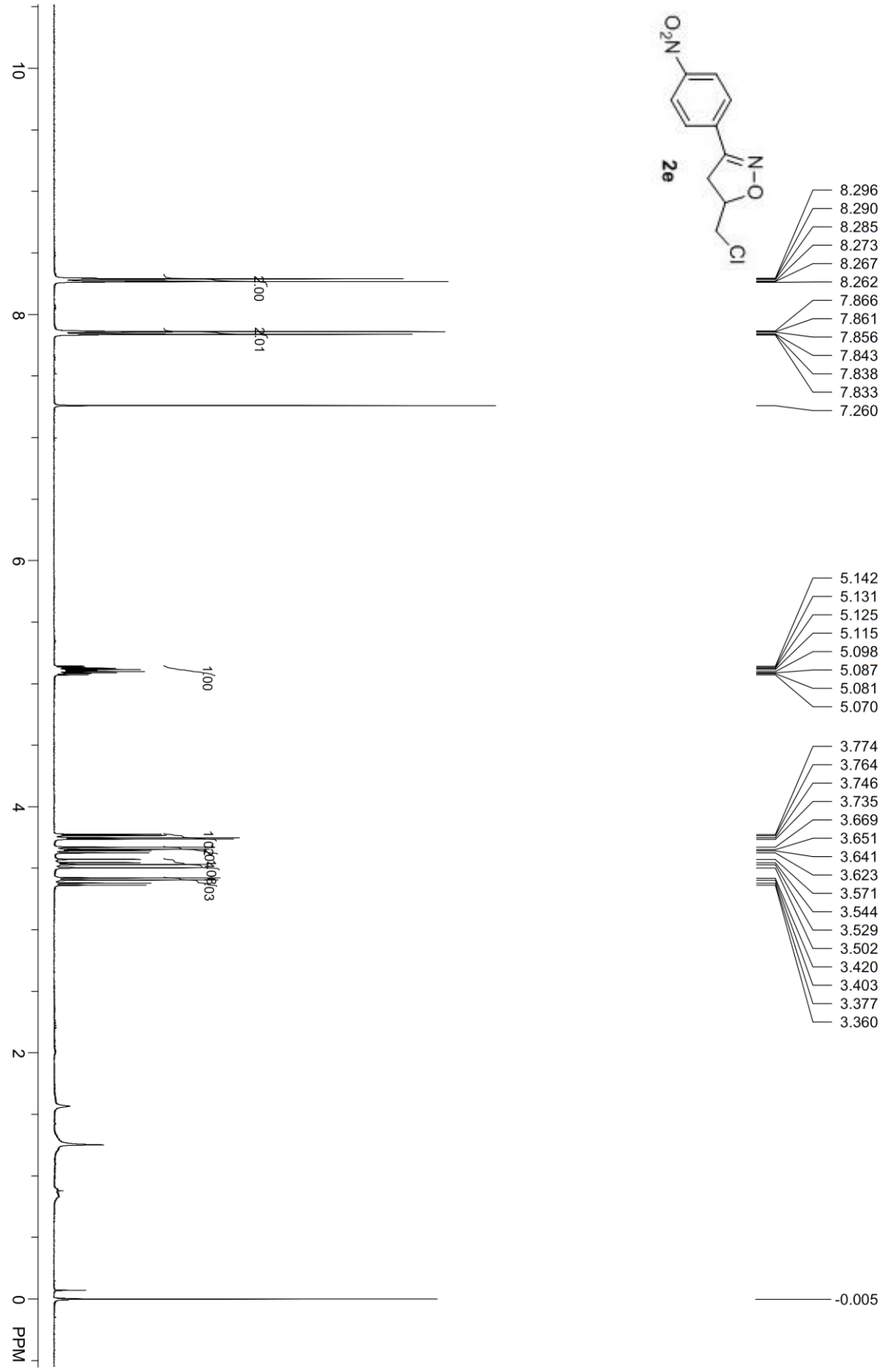
O
Cl
2d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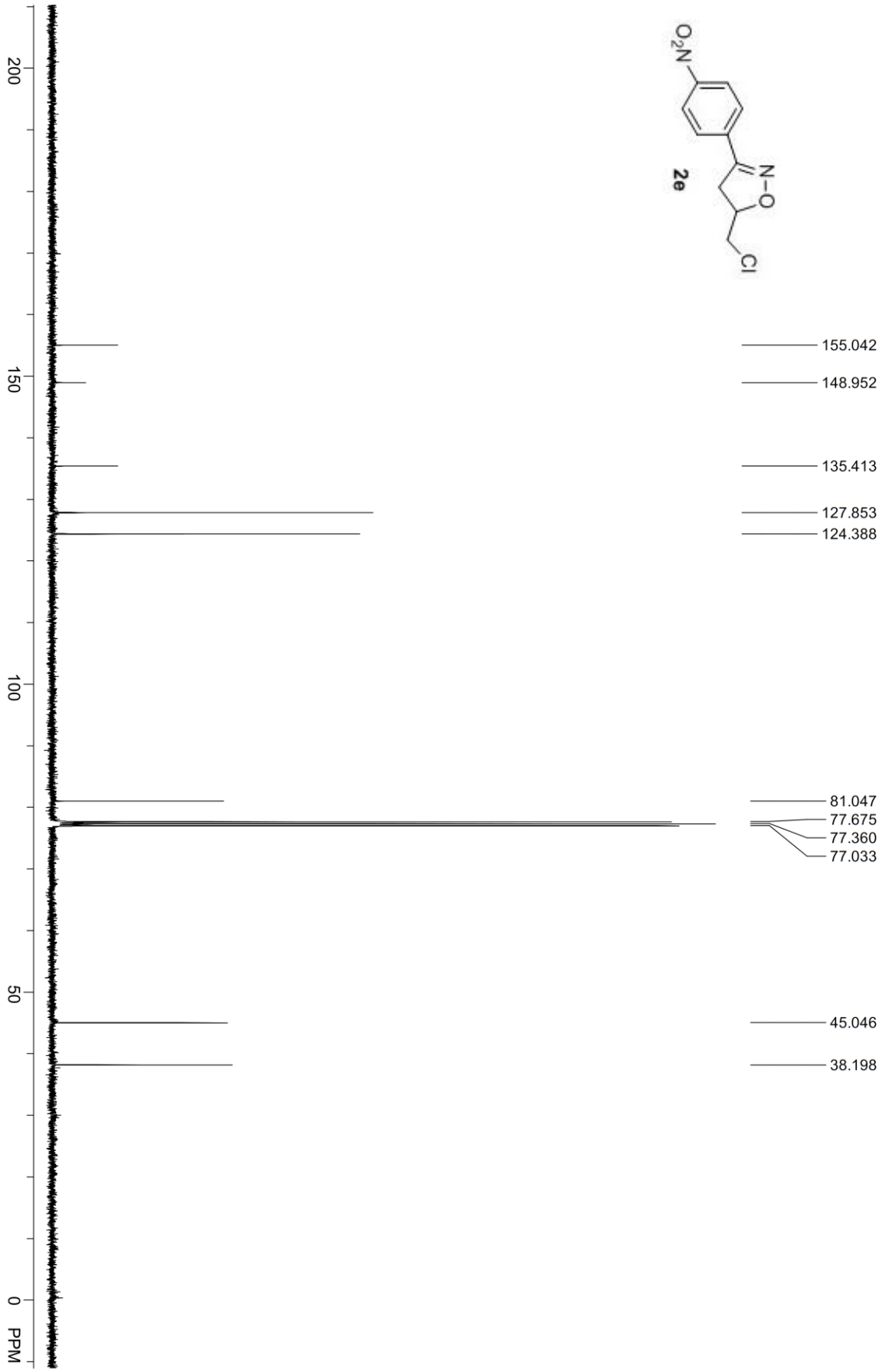
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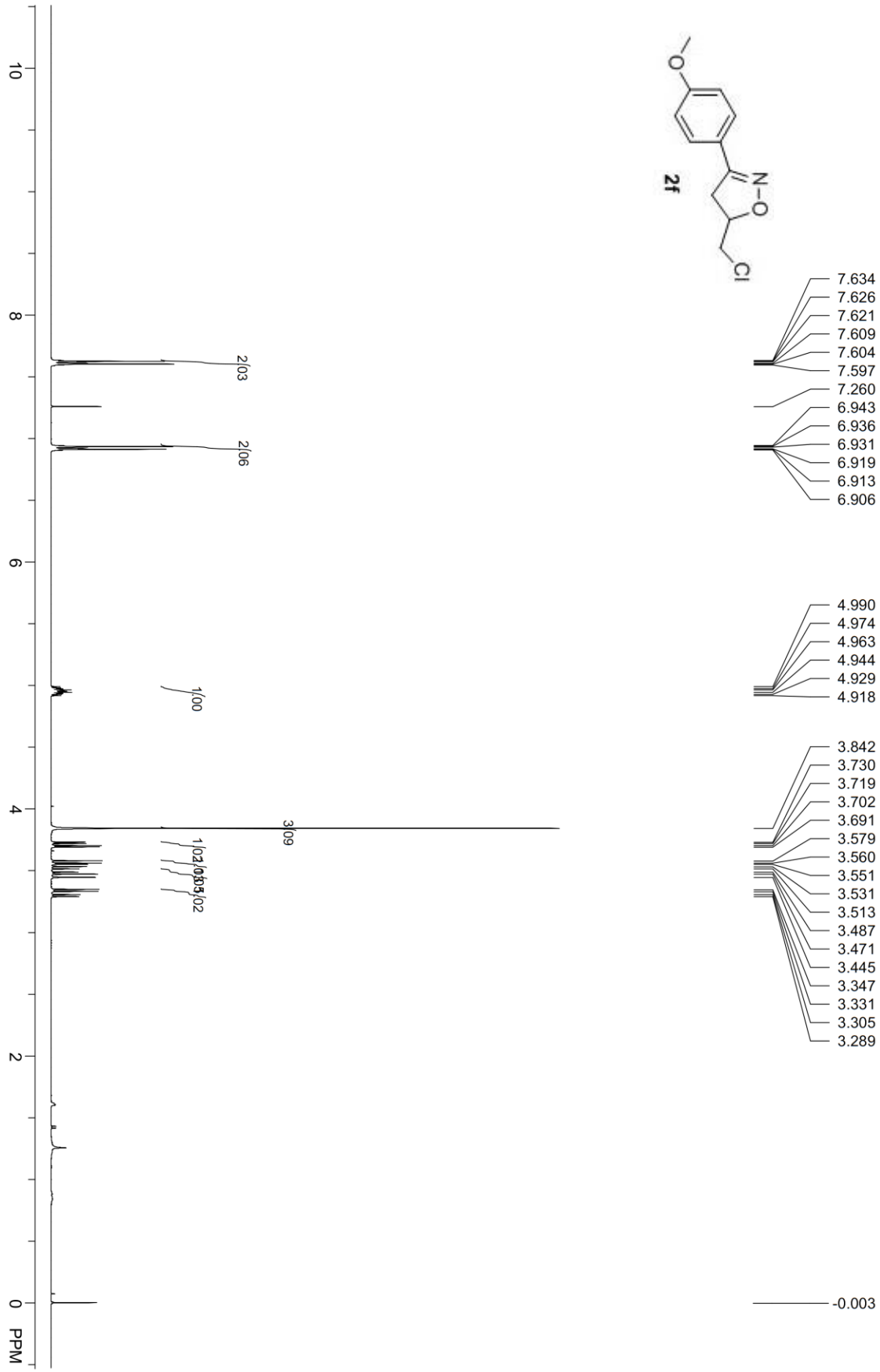
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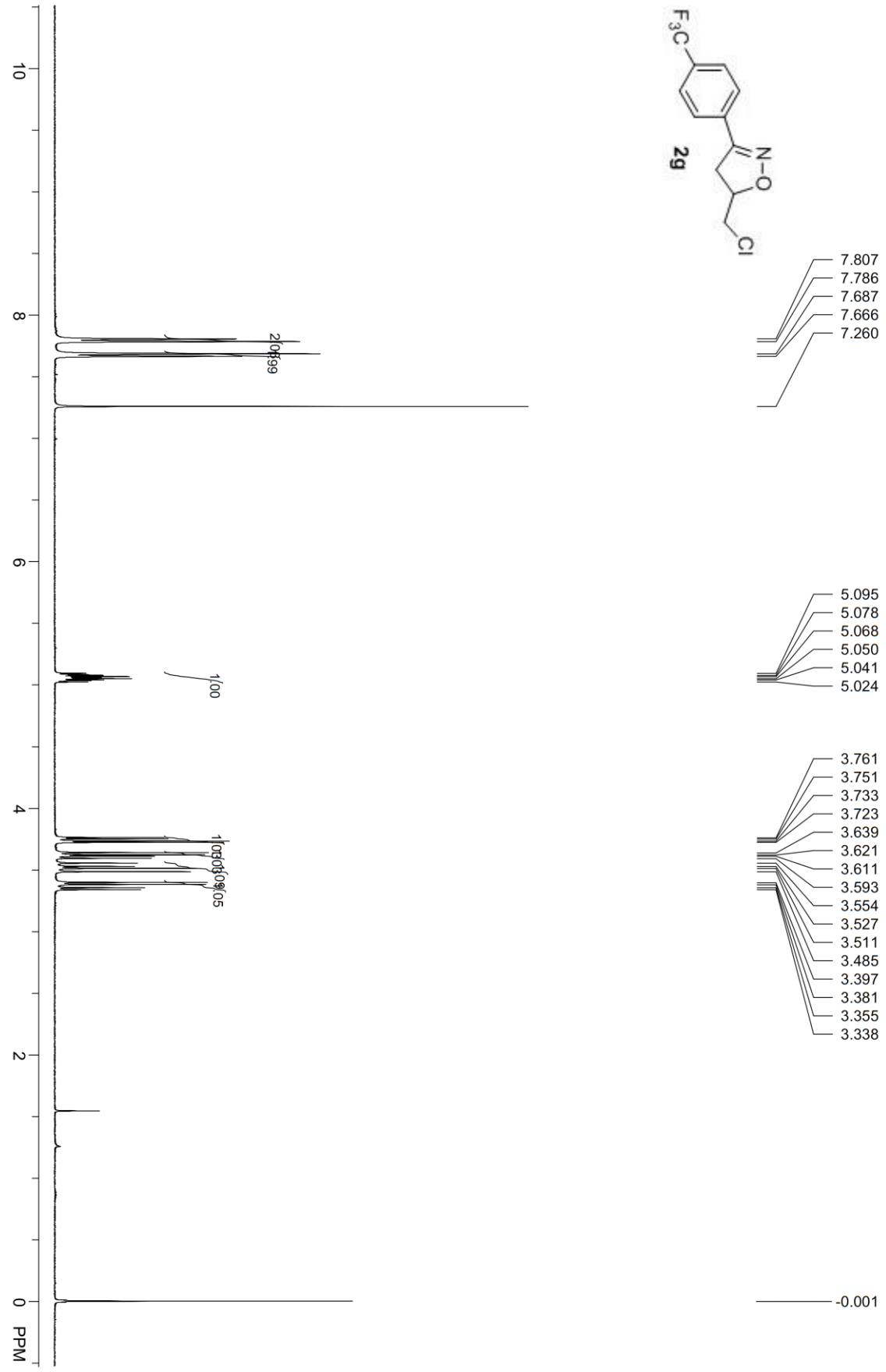
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N–O
Cl
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5.050
5.041
5.024
3.761
3.751
3.733
3.723
3.639
3.621
3.611
3.593
3.554
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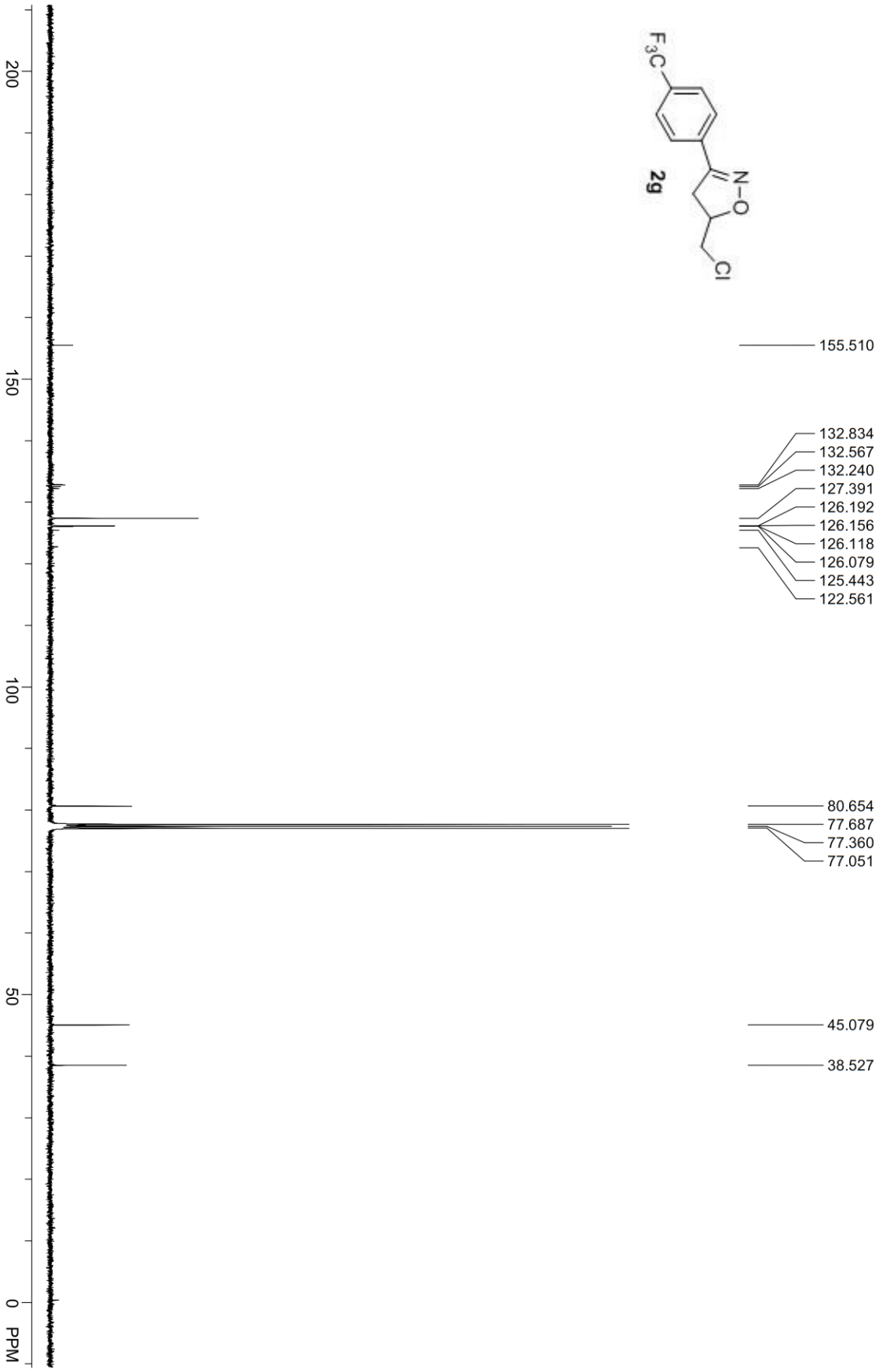
PPM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O
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126.079
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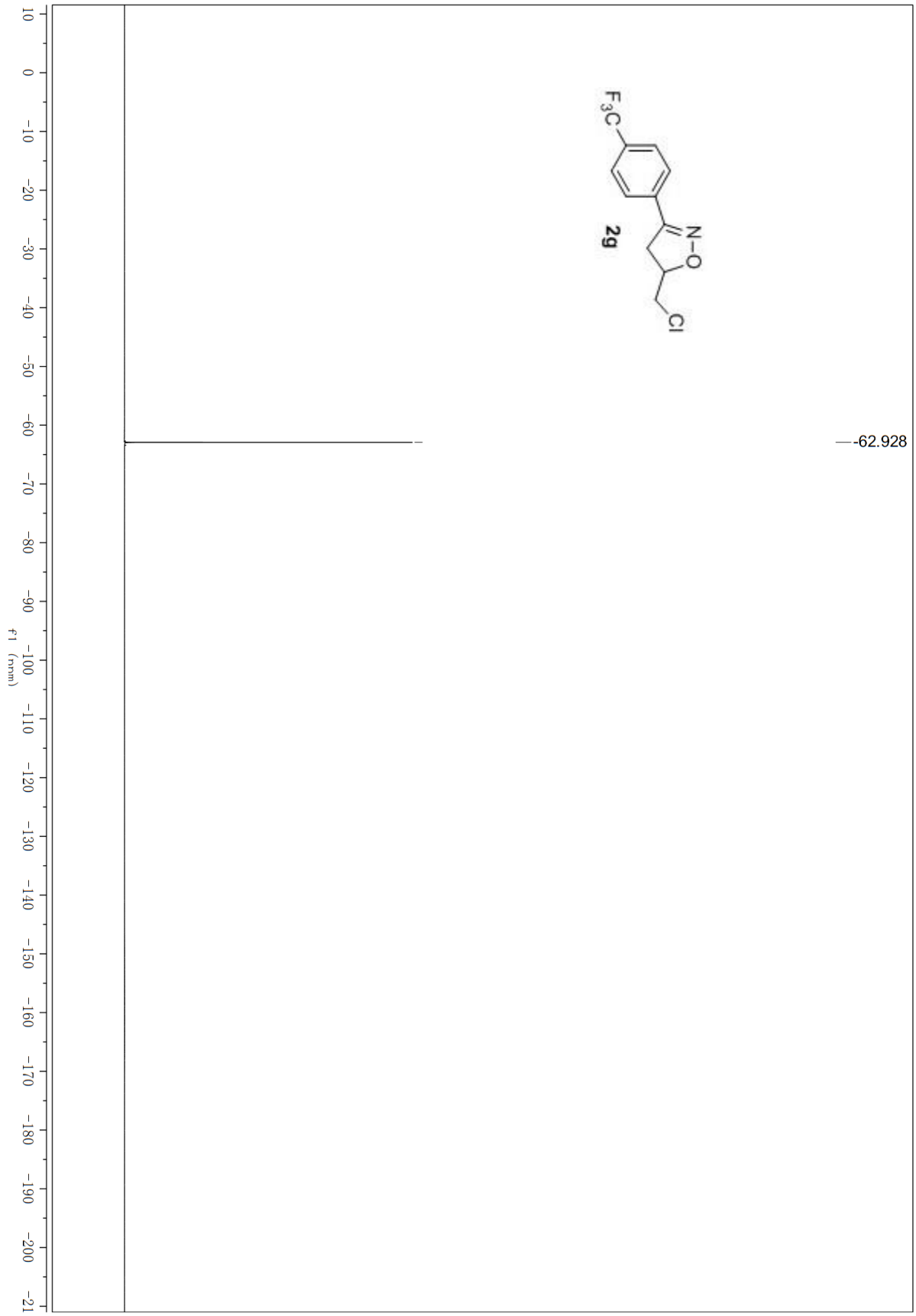
PPM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O
Cl
2g
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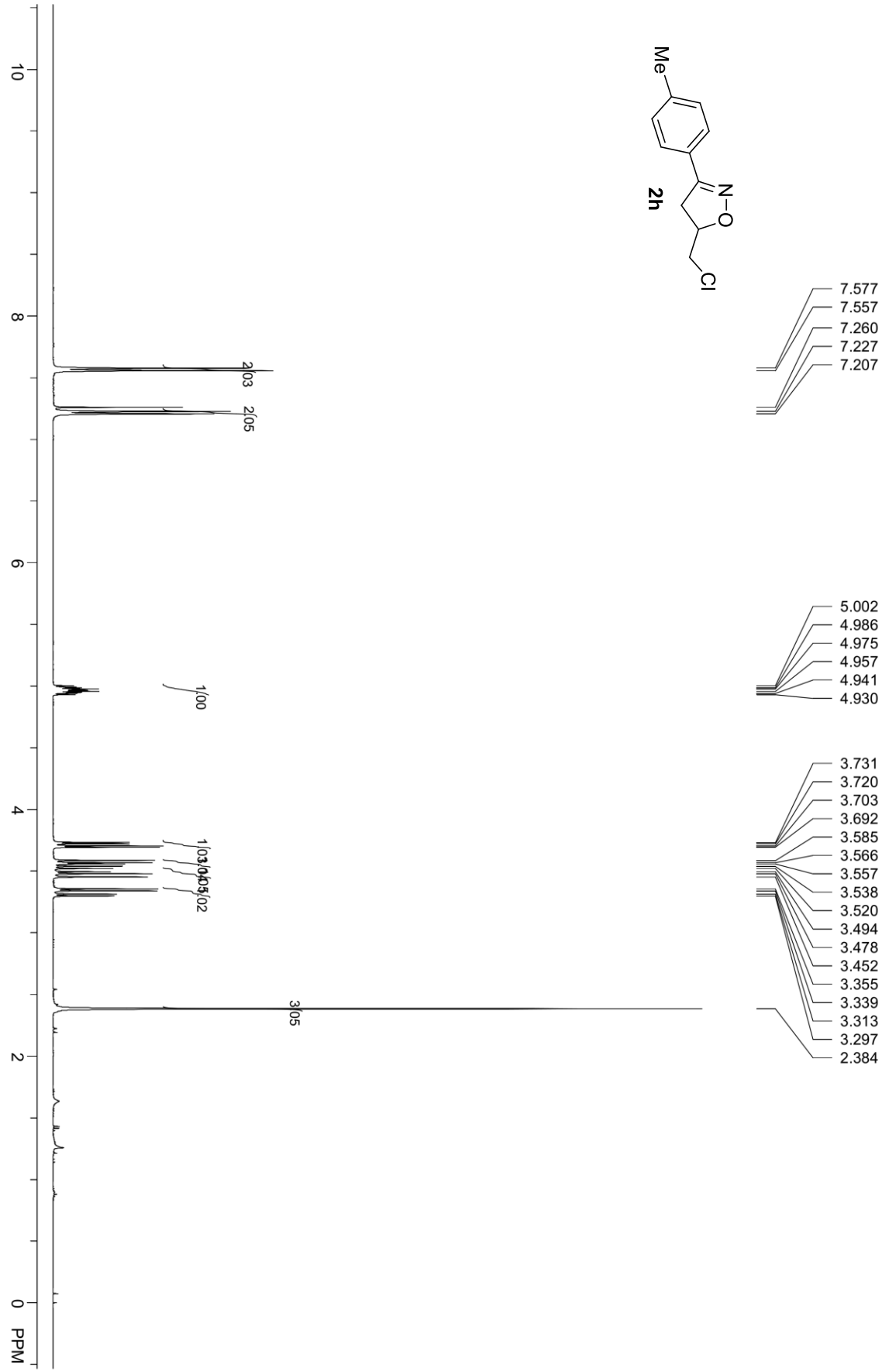
f1 (ppm)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Cl
2h
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7.207
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4.957
4.941
4.930
3.731
3.720
3.703
3.692
3.585
3.566
3.557
3.538
3.520
3.494
3.478
3.452
3.355
3.339
3.313
3.297
2.384
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1.03
1.04
1.05
1.02
3.05
10
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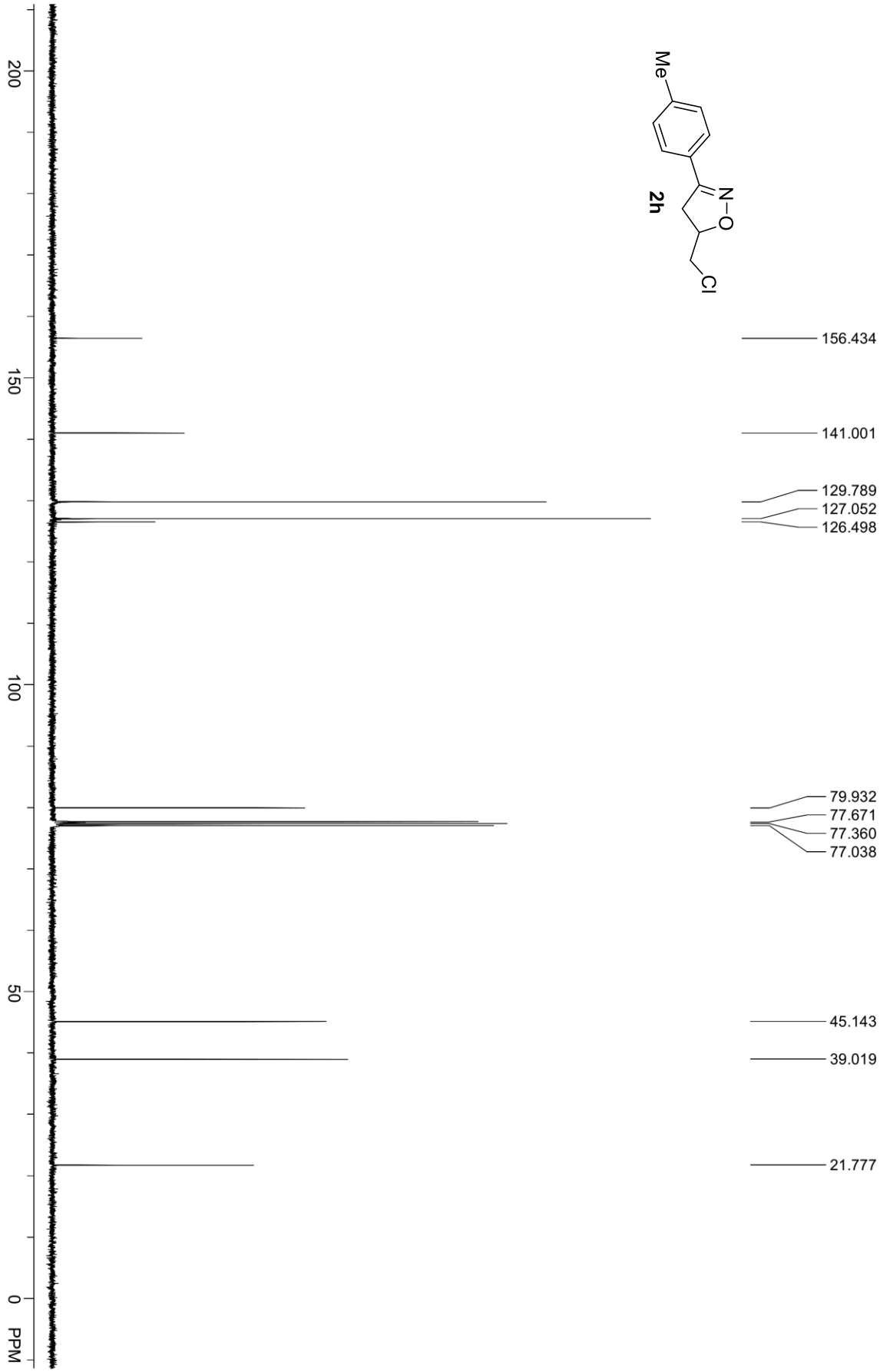
6
4
2
0
PPM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O
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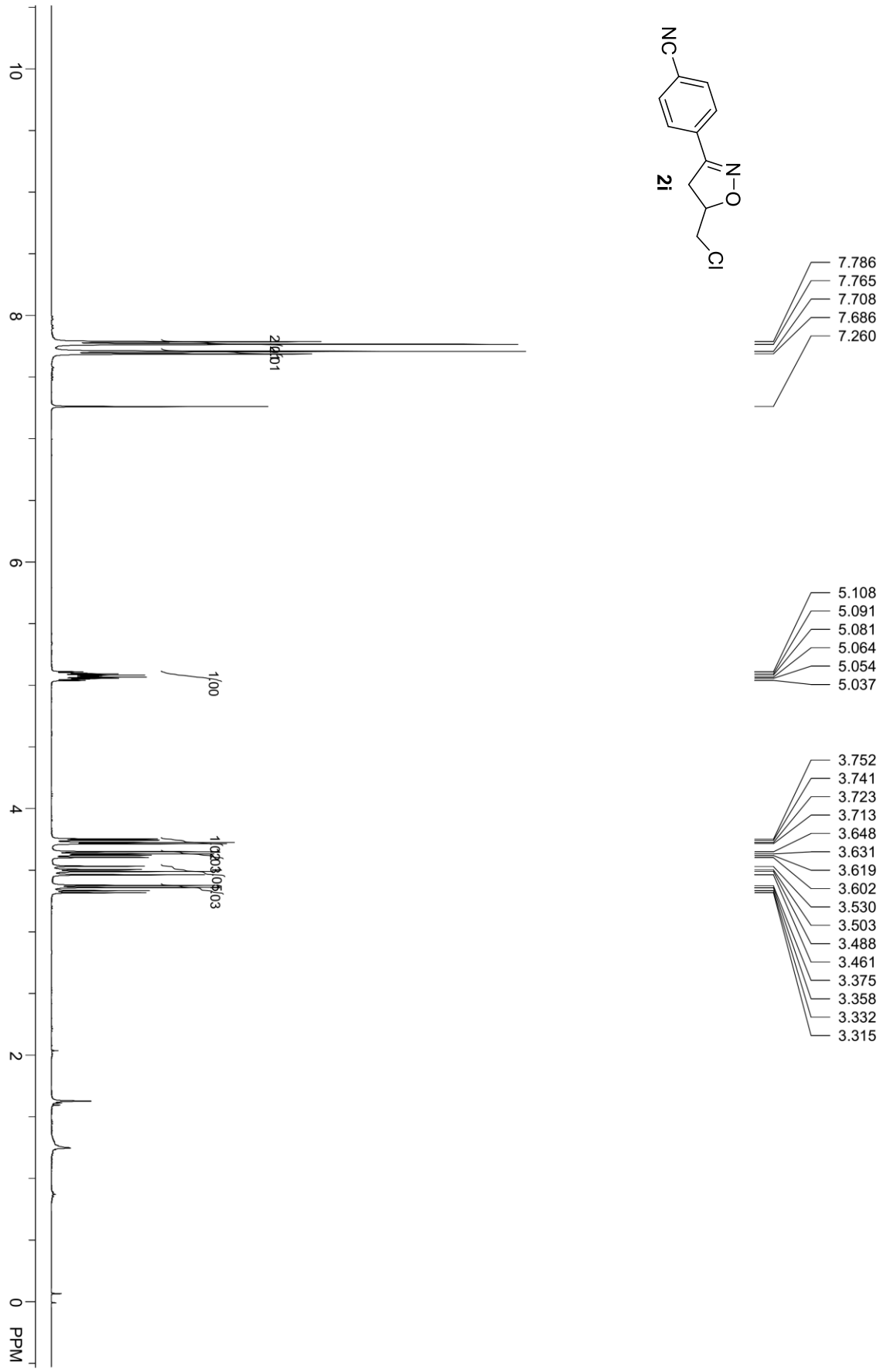
NC
N–O
Cl
2i
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7.708
7.686
7.260
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5.091
5.081
5.064
5.054
5.037
3.752
3.741
3.723
3.713
3.648
3.631
3.619
3.602
3.530
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3.461
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3.358
3.332
3.315
10
8
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2
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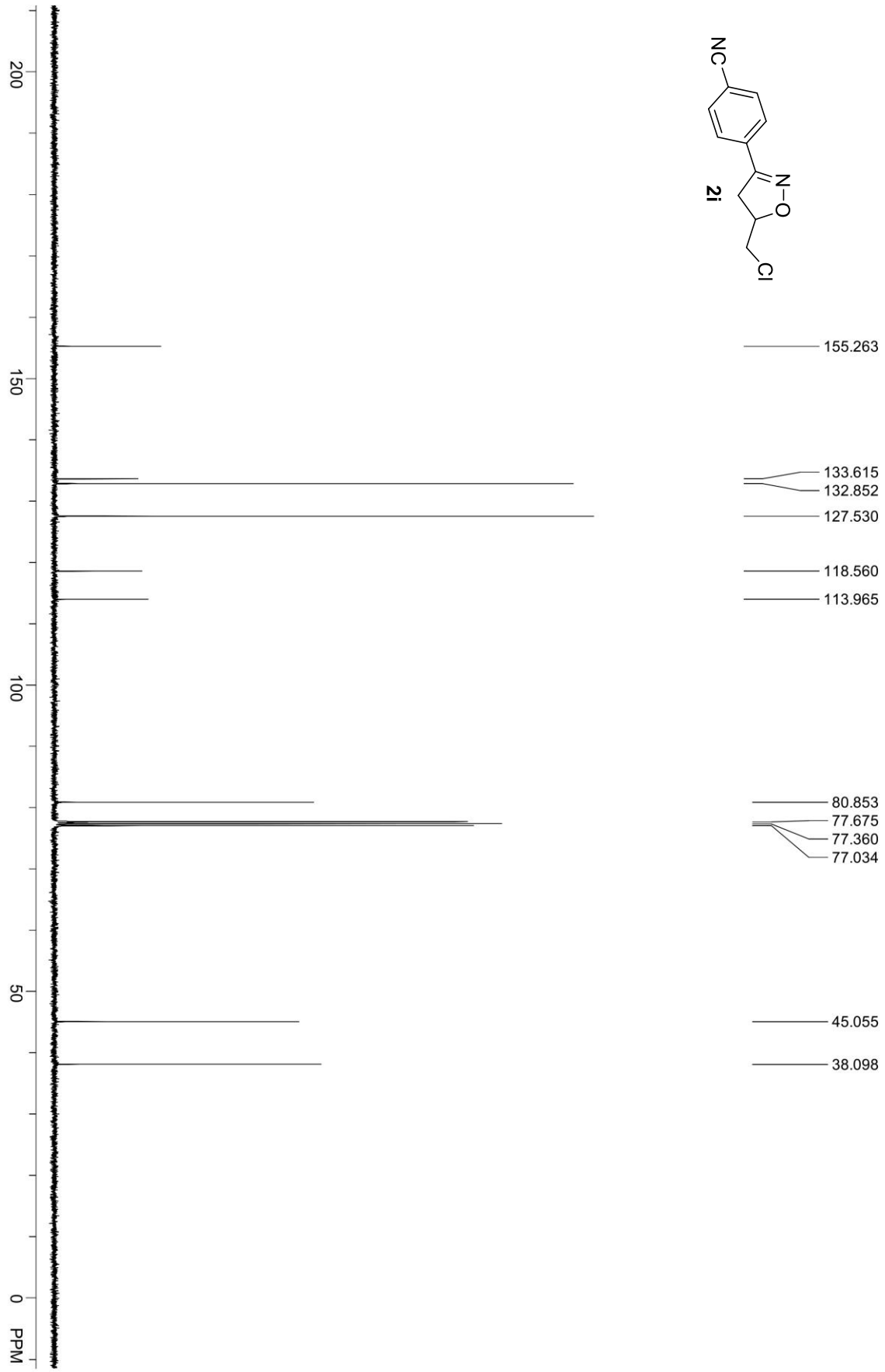
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N
O
Cl
2i
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80.853
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38.098
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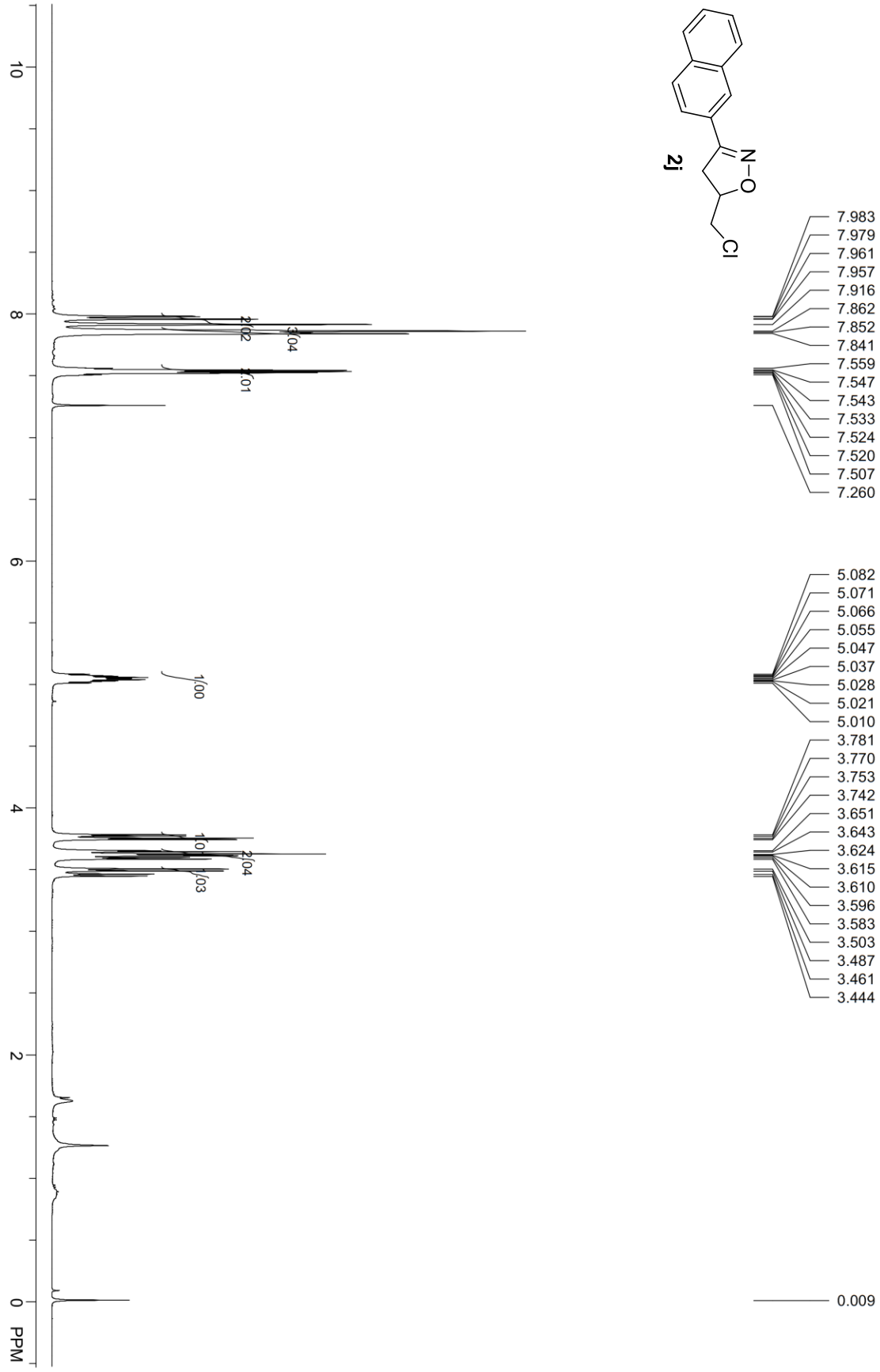
100
50
0
PPM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N
O
Cl
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7.957
7.916
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7.852
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7.559
7.547
7.543
7.533
7.524
7.520
7.507
7.260
5.082
5.071
5.066
5.055
5.047
5.037
5.028
5.021
5.010
3.781
3.770
3.753
3.742
3.651
3.643
3.624
3.615
3.610
3.596
3.583
3.503
3.487
3.461
3.444
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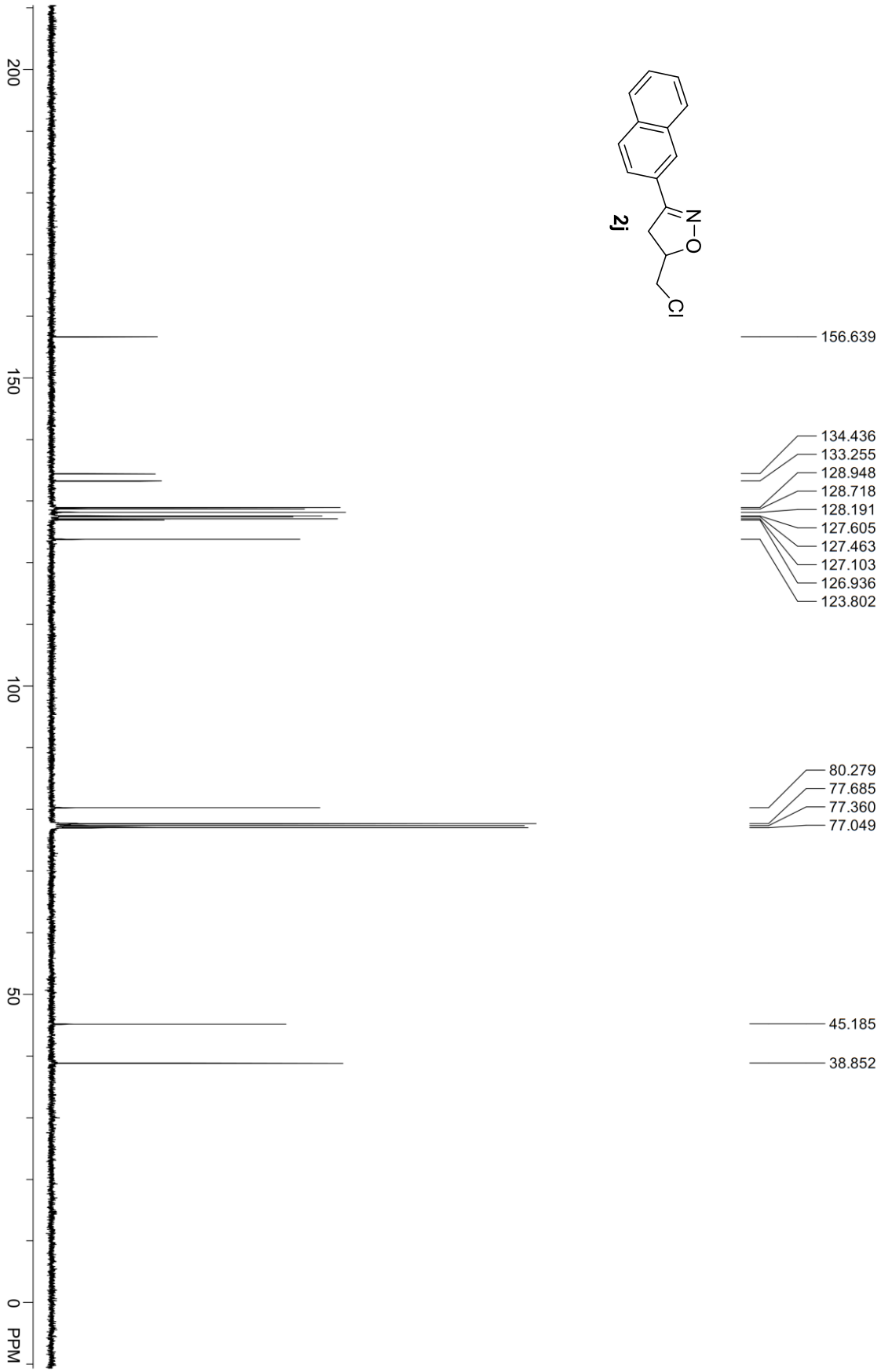
3.04
2.01
1.00
1.01
2.04
1.03
10
8
6
4
2
0
PPM


200
150
100
50
0
PPM
2j
N
O
Cl
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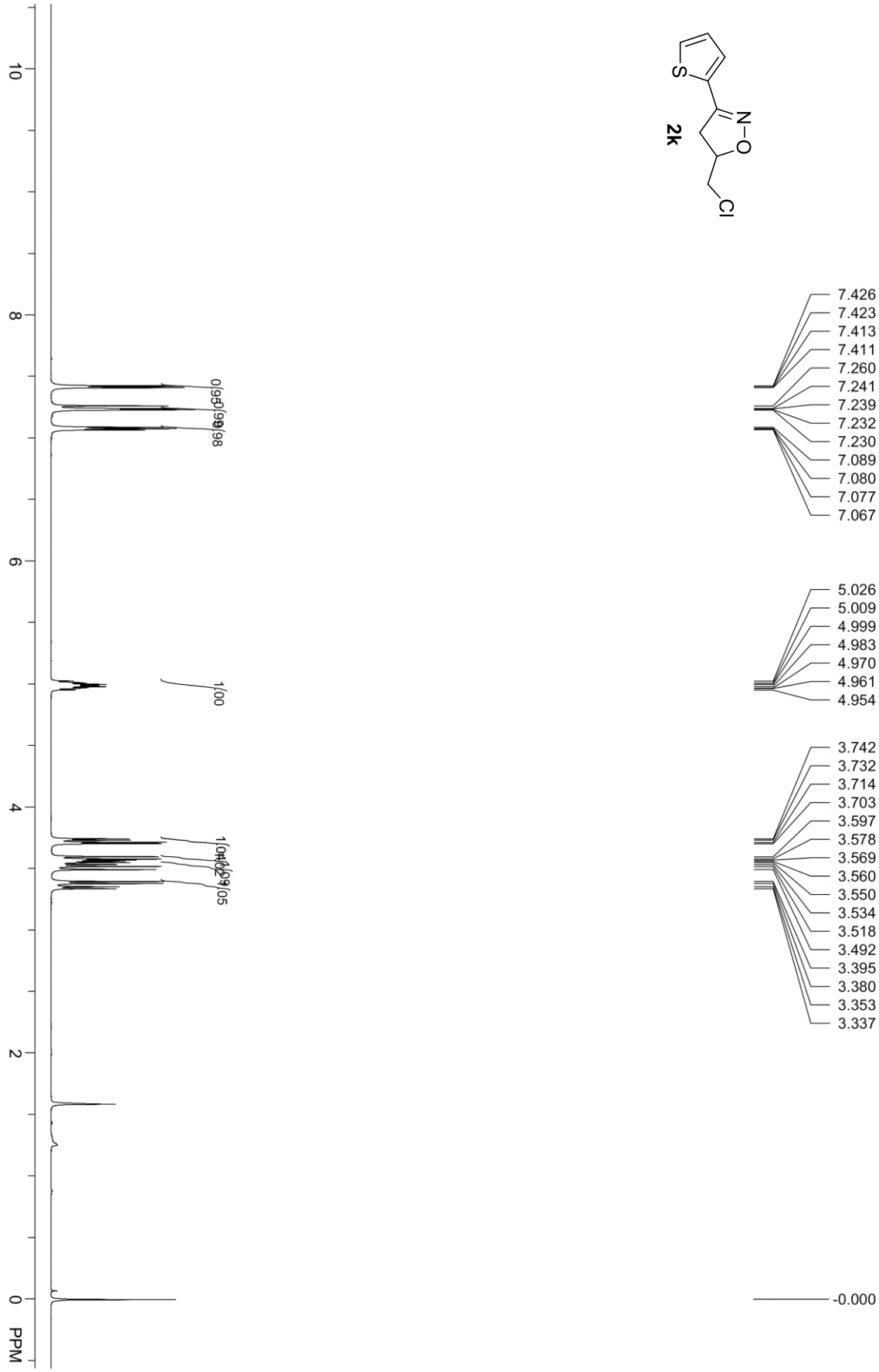
134.436
133.255
128.948
128.718
128.191
127.605
127.463
127.103
126.936
123.802
80.279
77.685
77.360
77.049
45.185
38.852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S
N
O
Cl
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7.423
7.413
7.411
7.260
7.241
7.239
7.232
7.230
7.089
7.080
7.077
7.067
5.026
5.009
4.999
4.983
4.970
4.961
4.954
3.742
3.732
3.714
3.703
3.597
3.578
3.569
3.560
3.550
3.534
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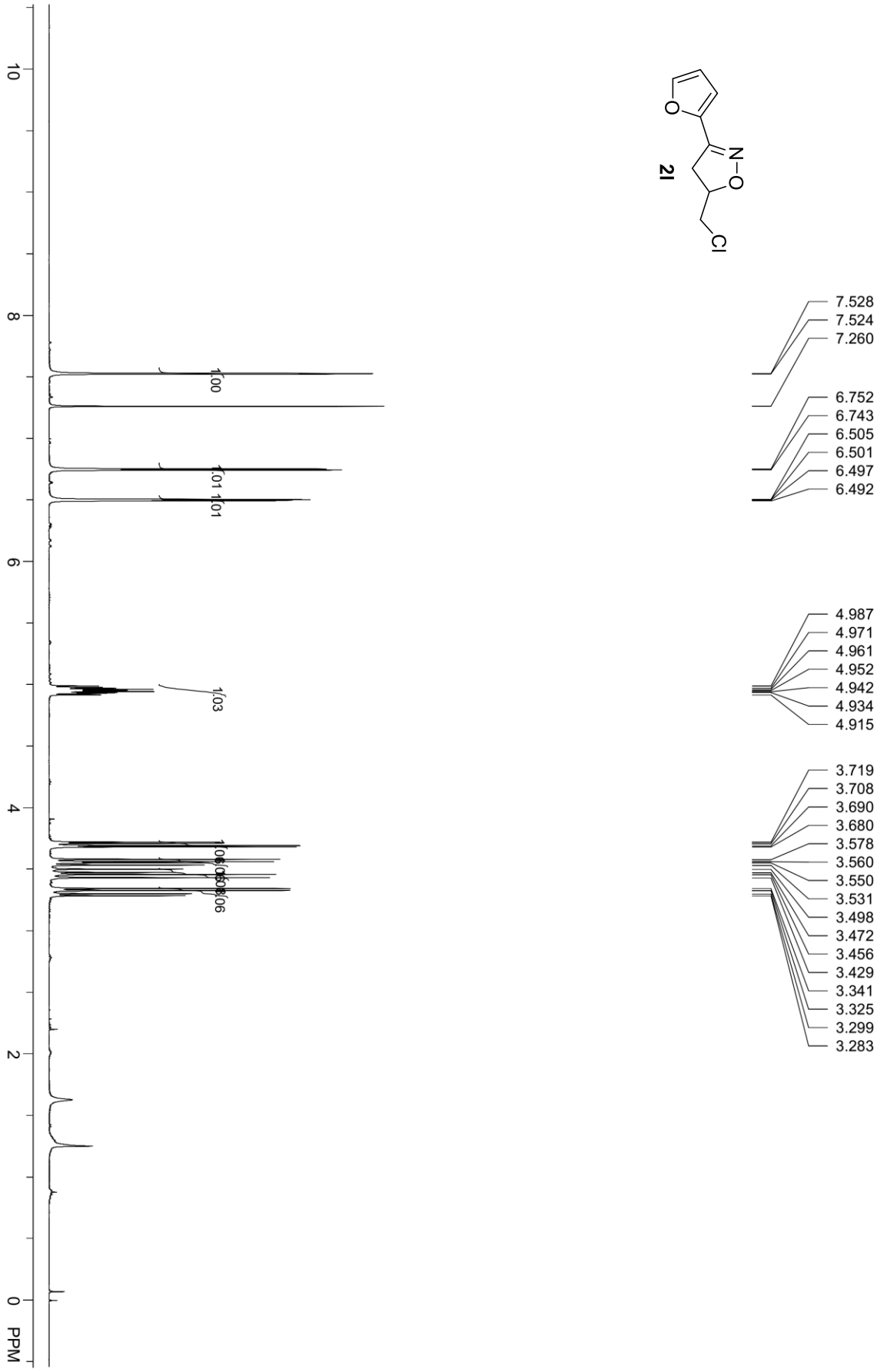
3.395
3.380
3.353
3.337
-0.000
10
8
6
4
2
0
PPM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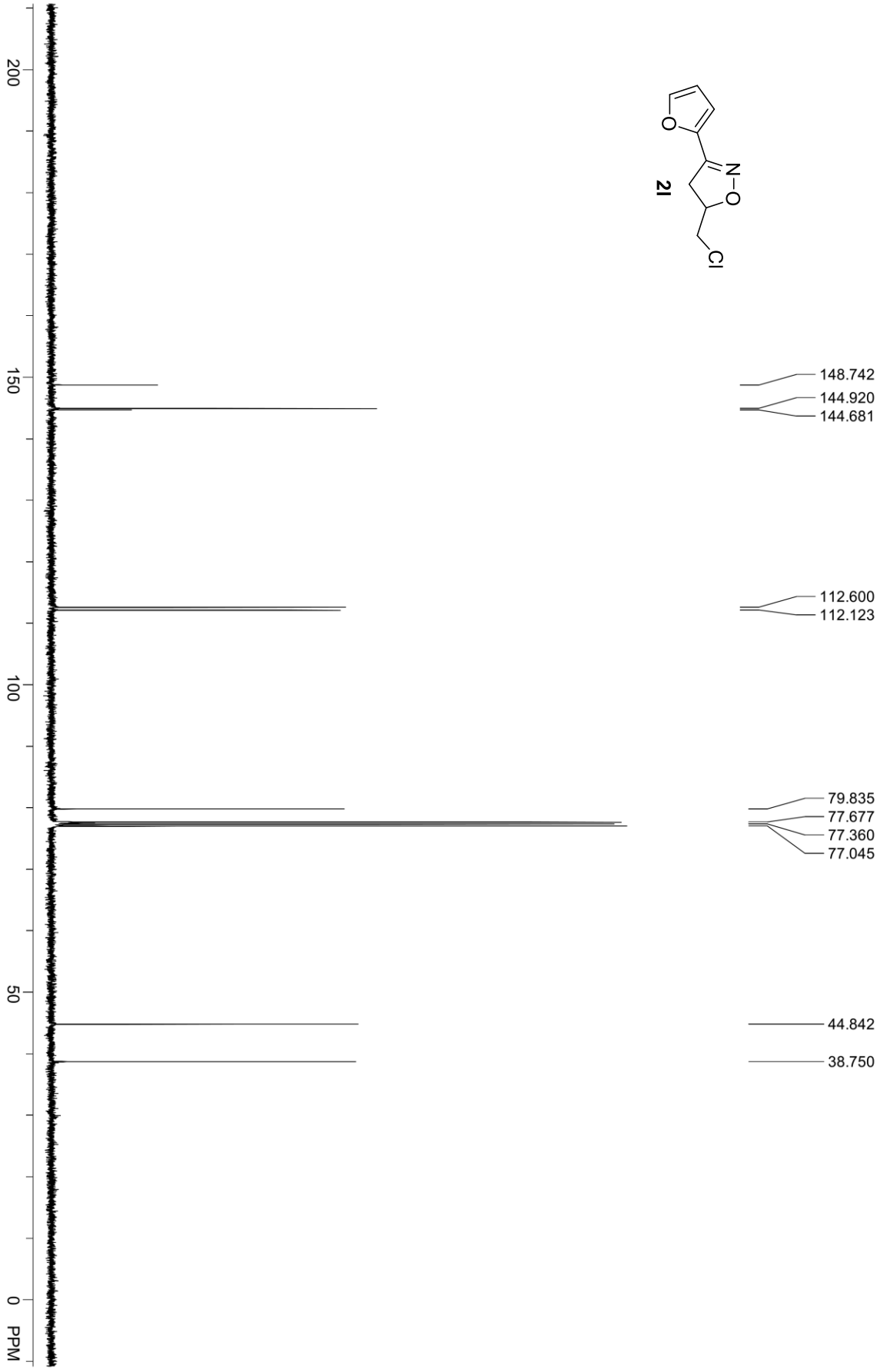
7.260
6.752
6.743
6.505
6.501
6.497
6.492
4.987
4.971
4.961
4.952
4.942
4.934
4.915
3.719
3.708
3.690
3.680
3.578
3.560
3.550
3.531
3.498
3.472
3.456
3.429
3.341
3.325
3.299
3.283
1.00
1.01
1.01
1.03
1.06
1.06
1.03
1.06
10
8
6
4
2
0
PPM


200
150
100
50
0
PPM
O
N–O
Cl
21
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112.123
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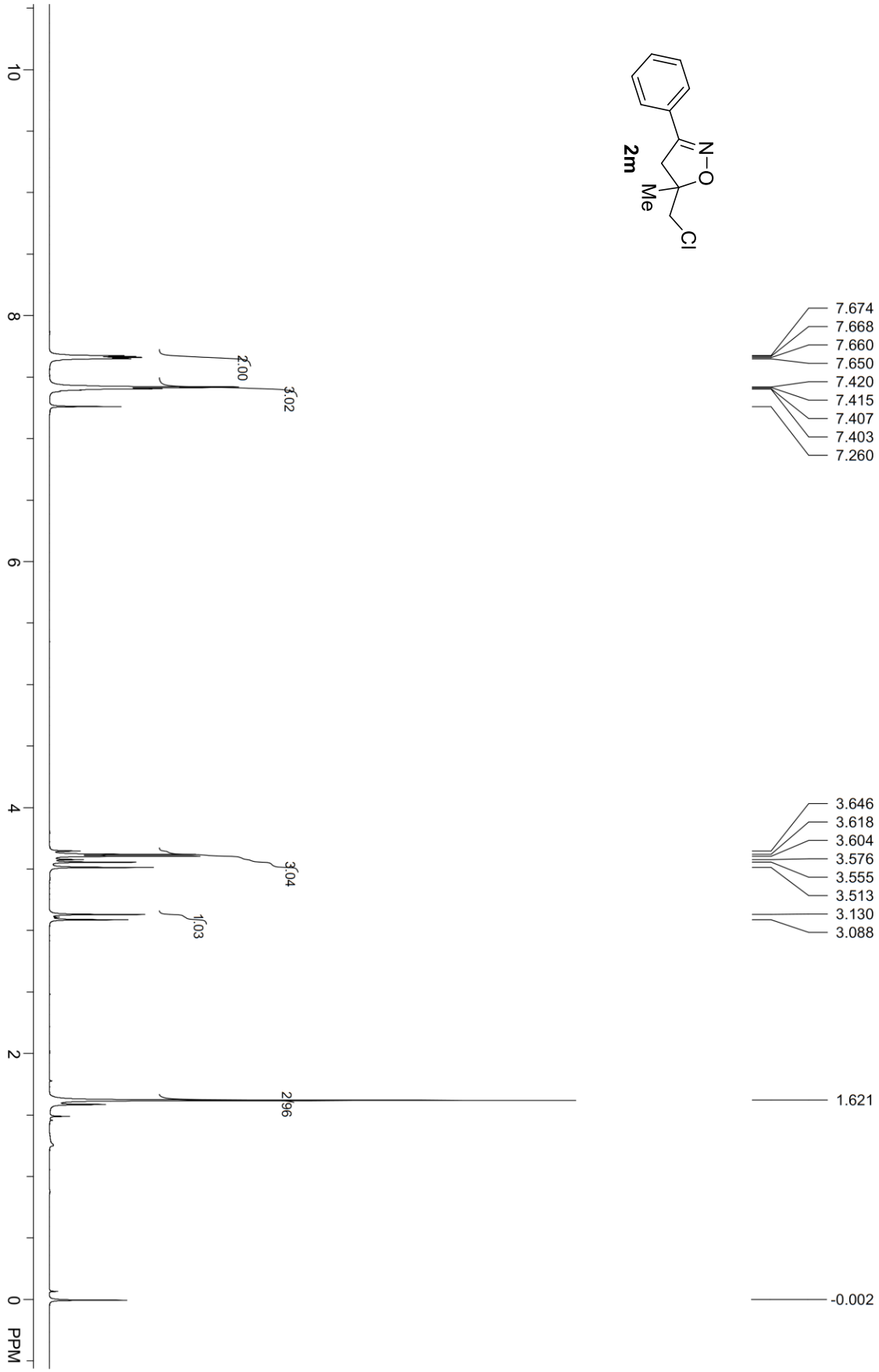
77.677
77.360
77.045
44.842
38.750


10
8
6
4
2
0
PPM
2.00
3.02
3.04
1.03
2.96
N–O
Me
Cl
2m
7.674
7.668
7.660
7.650
7.420
7.415
7.407
7.403
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3.618
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3.555
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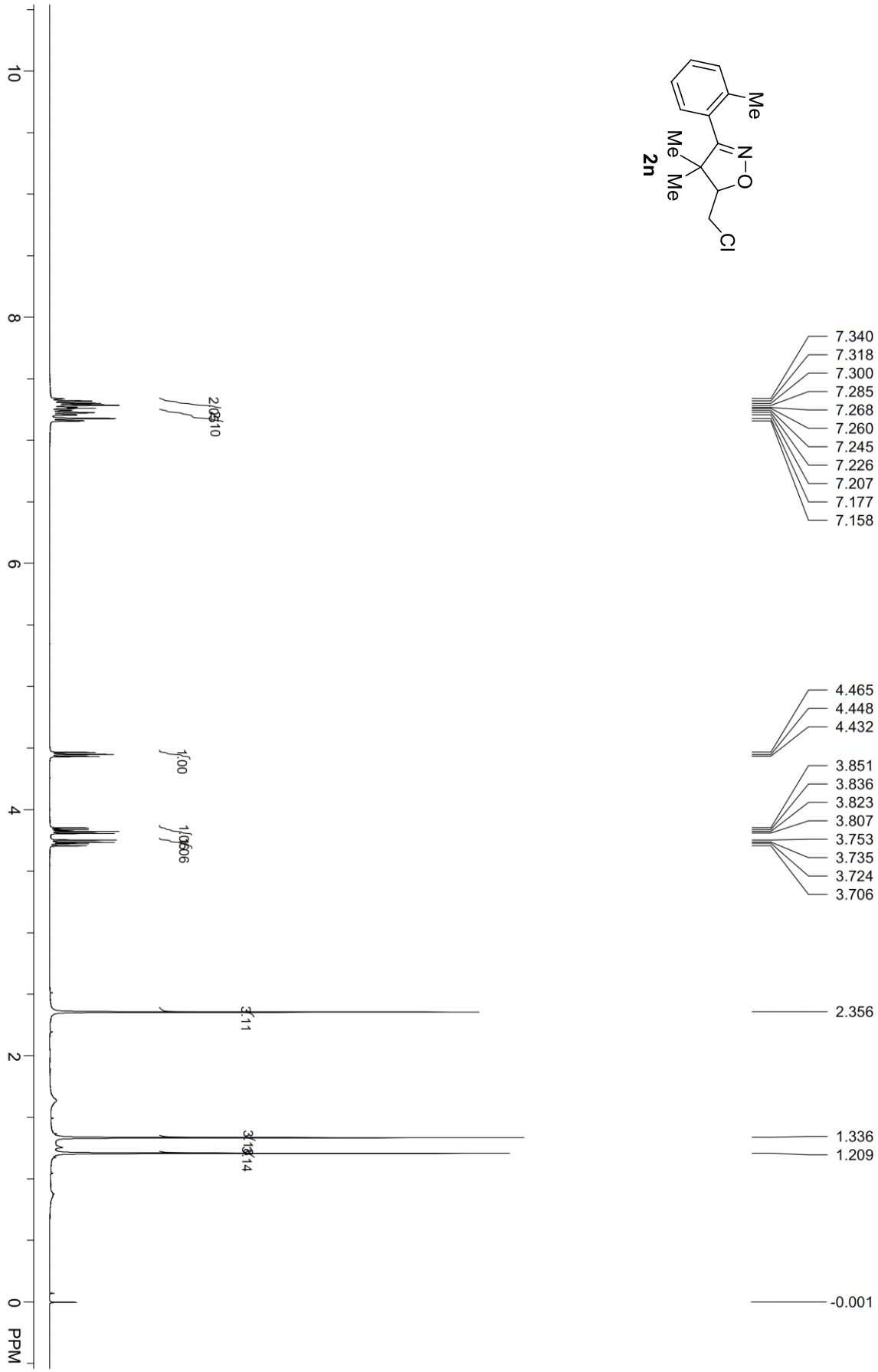
3.130
3.088
1.621
-0.002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Me
Me
N–O
Cl
2n
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7.300
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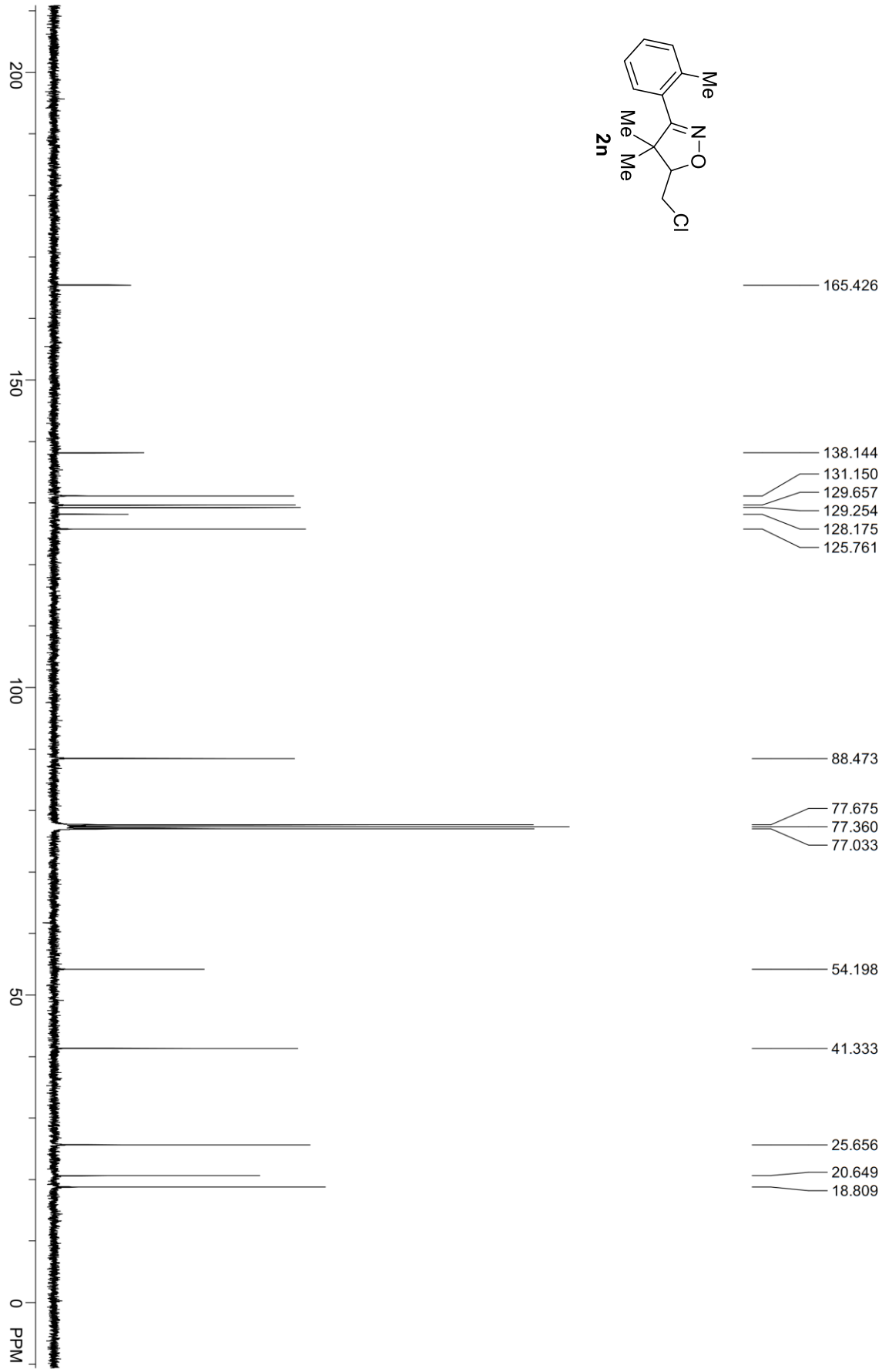
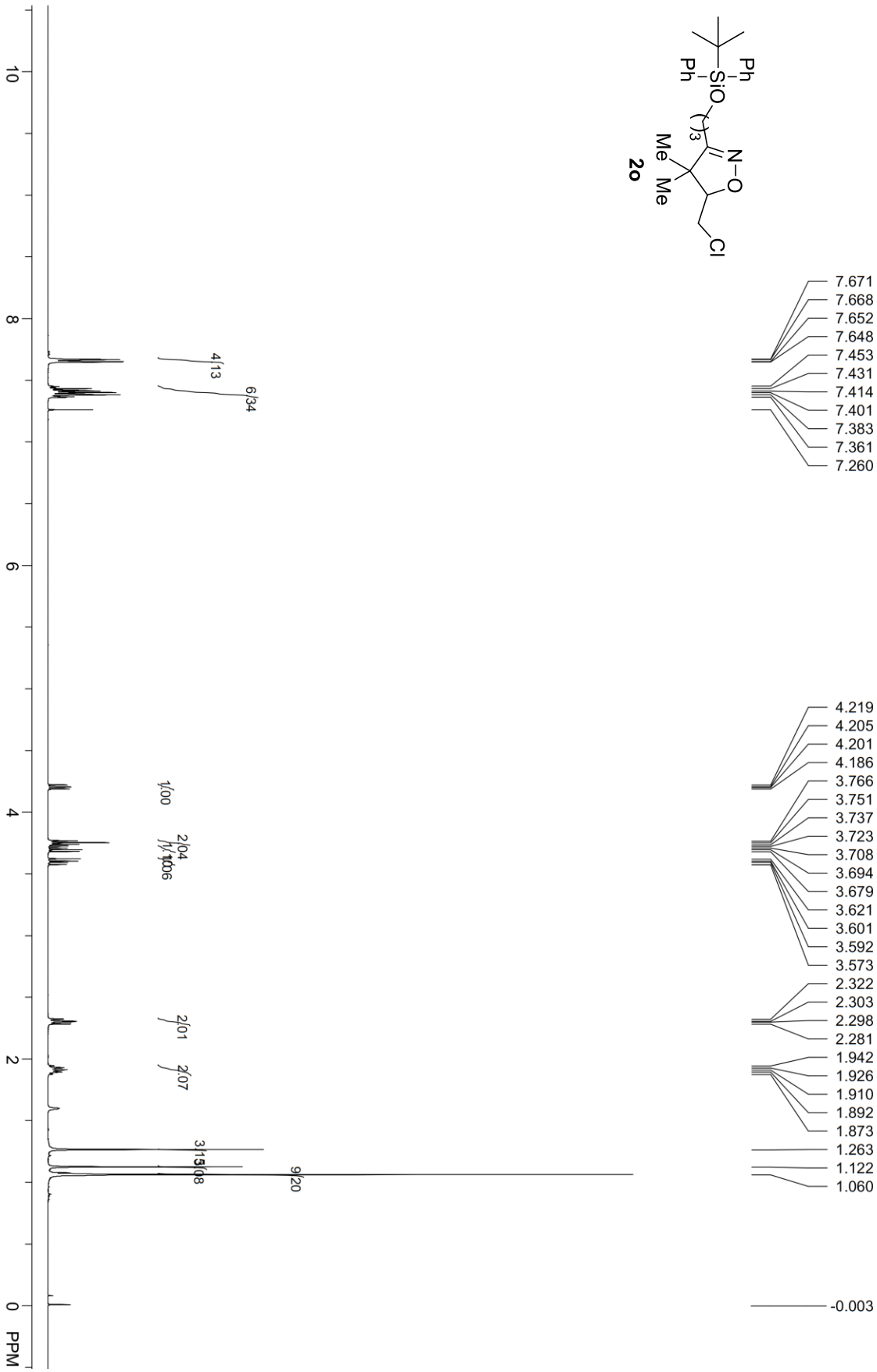
7.268
7.260
7.245
7.226
7.207
7.177
7.158
4.465
4.448
4.432
3.851
3.836
3.823
3.807
3.753
3.735
3.724
3.706
2.356
1.336
1.209
-0.001
10
8
6
4
2
0
PPM


Me
Me
Me
N–O
Cl
2n
165.426
138.144
131.150
129.657
129.254
128.175
125.761
88.473
77.675
77.360
77.033
54.198
41.333
25.656
20.649
18.809
200
150
100
50
0
PPM


Ph
Ph
SiO
3
N–O
Me Me
Cl
2o
7.671
7.668
7.652
7.648
7.453
7.431
7.414
7.401
7.383
7.361
7.260
4.219
4.205
4.201
4.186
3.766
3.751
3.737
3.723
3.708
3.694
3.679
3.621
3.601
3.592
3.573
2.322
2.303
2.298
2.281
1.942
1.926
1.910
1.892
1.873
1.263
1.122
1.060
-0.003
4.13
6.34
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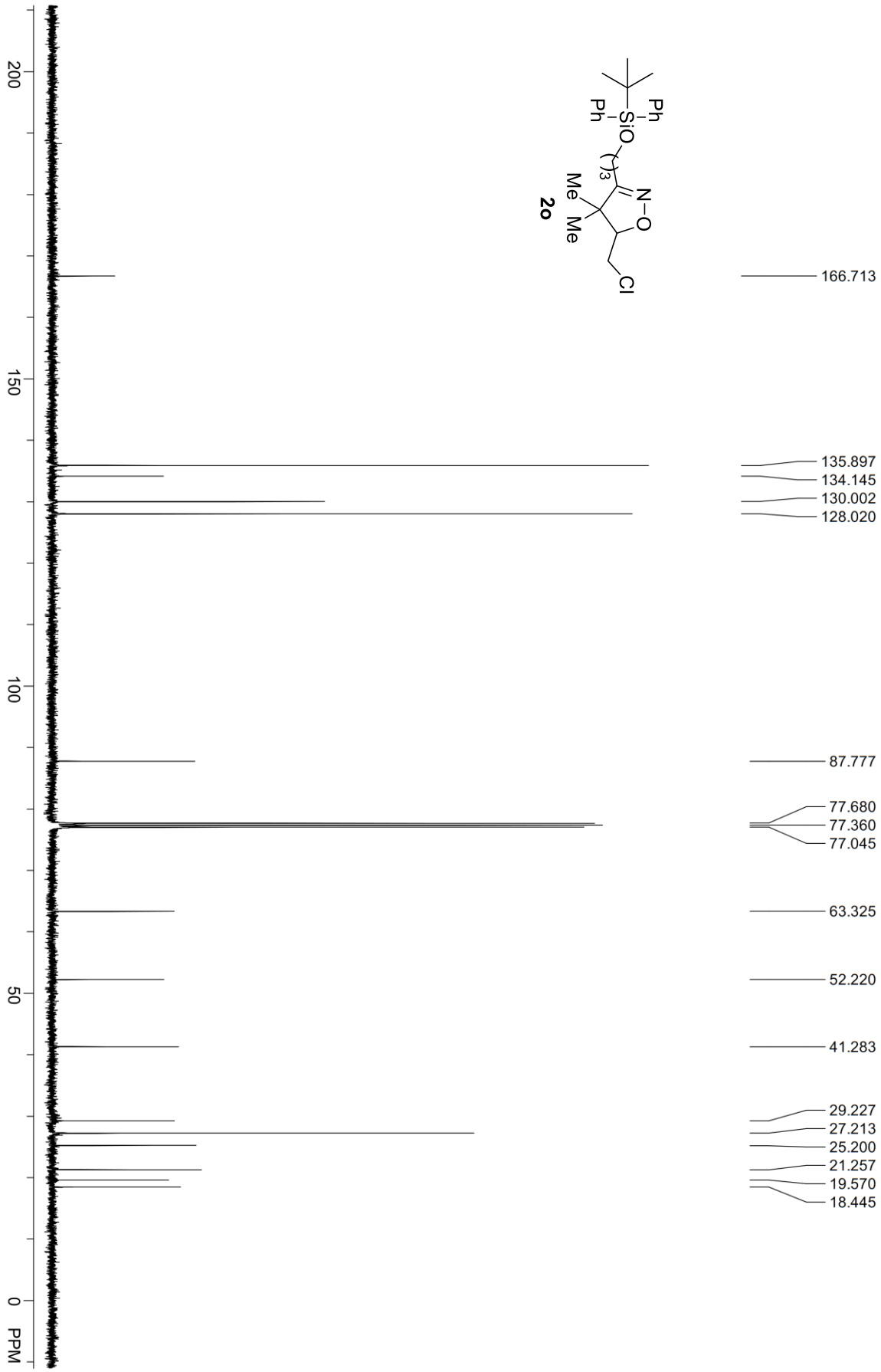
2.01
2.07
3.15
3.08
9.20
10
8
6
4
2
0
PPM


200
150
100
50
0
PPM
Ph
Ph
SiO
3
N
O
Me
Me
Cl
2o
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135.897
134.145
130.002
128.020
87.777
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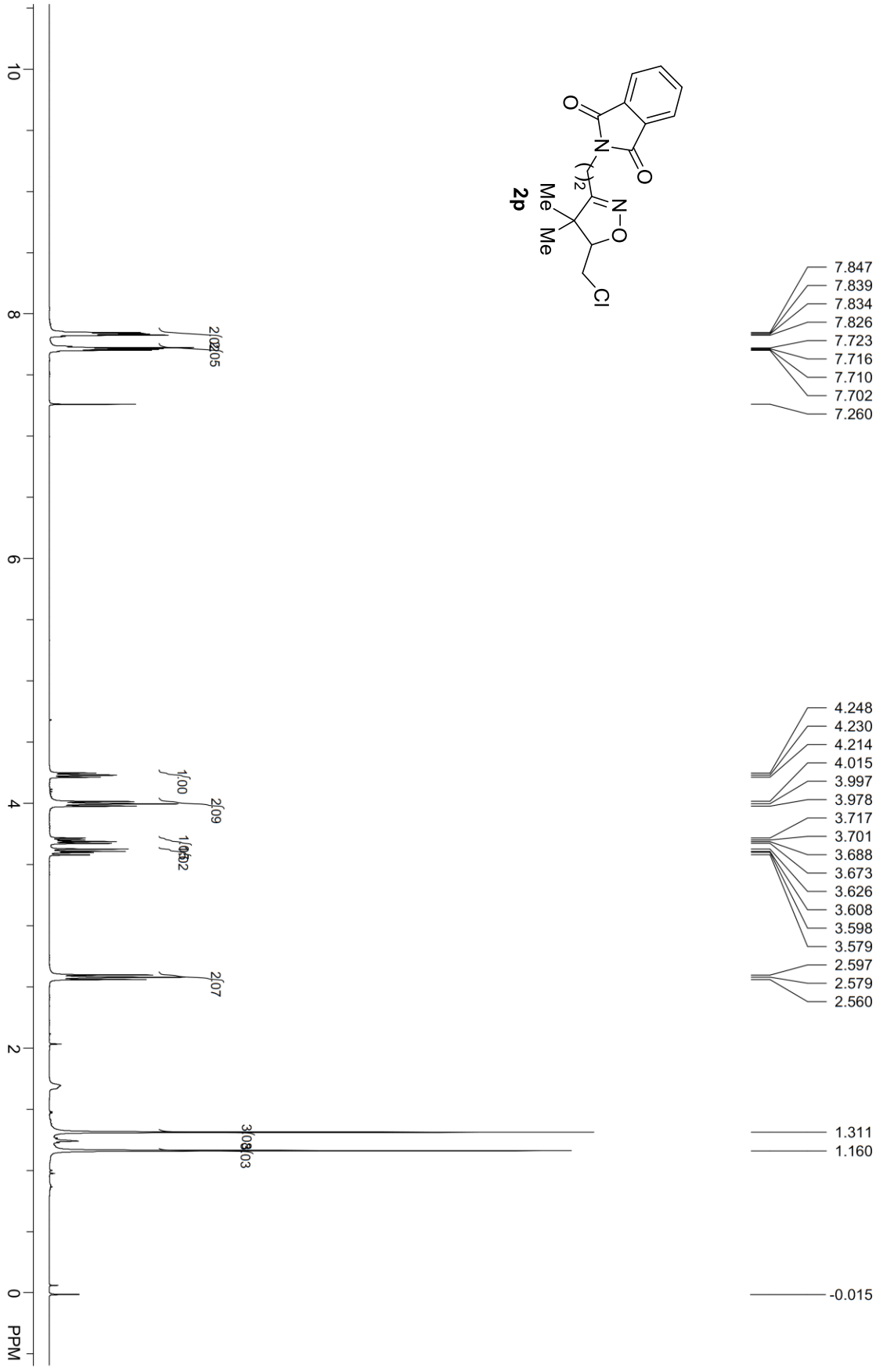
77.045
63.325
52.220
41.283
29.227
27.213
25.200
21.257
19.570
18.445


2p
Me Me
Cl
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7.834
7.826
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7.716
7.710
7.702
7.260
4.248
4.230
4.214
4.015
3.997
3.978
3.717
3.701
3.688
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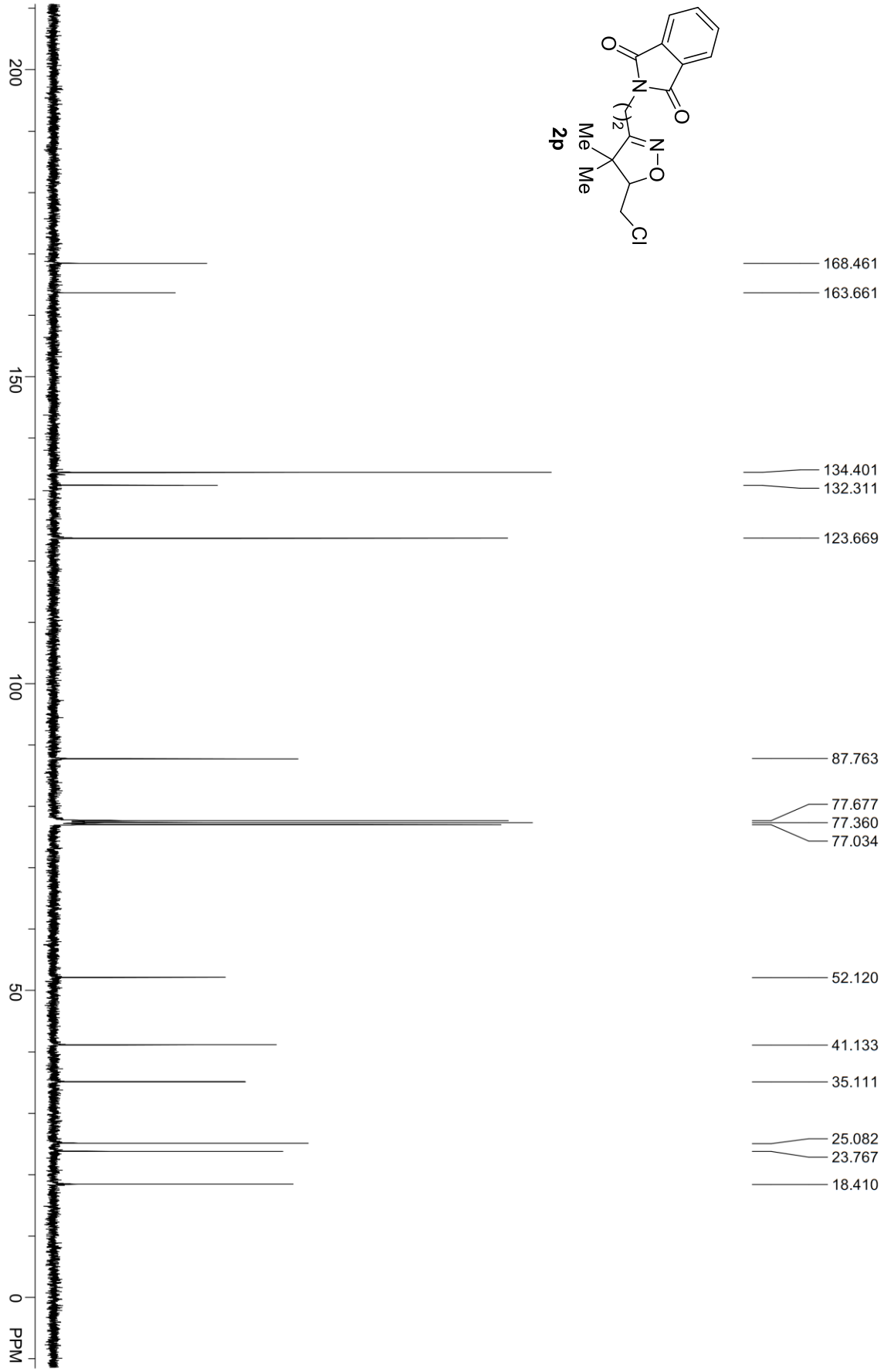
3.598
3.579
2.597
2.579
2.560
1.311
1.160
-0.015
PPM


2p
Me
Me
Cl
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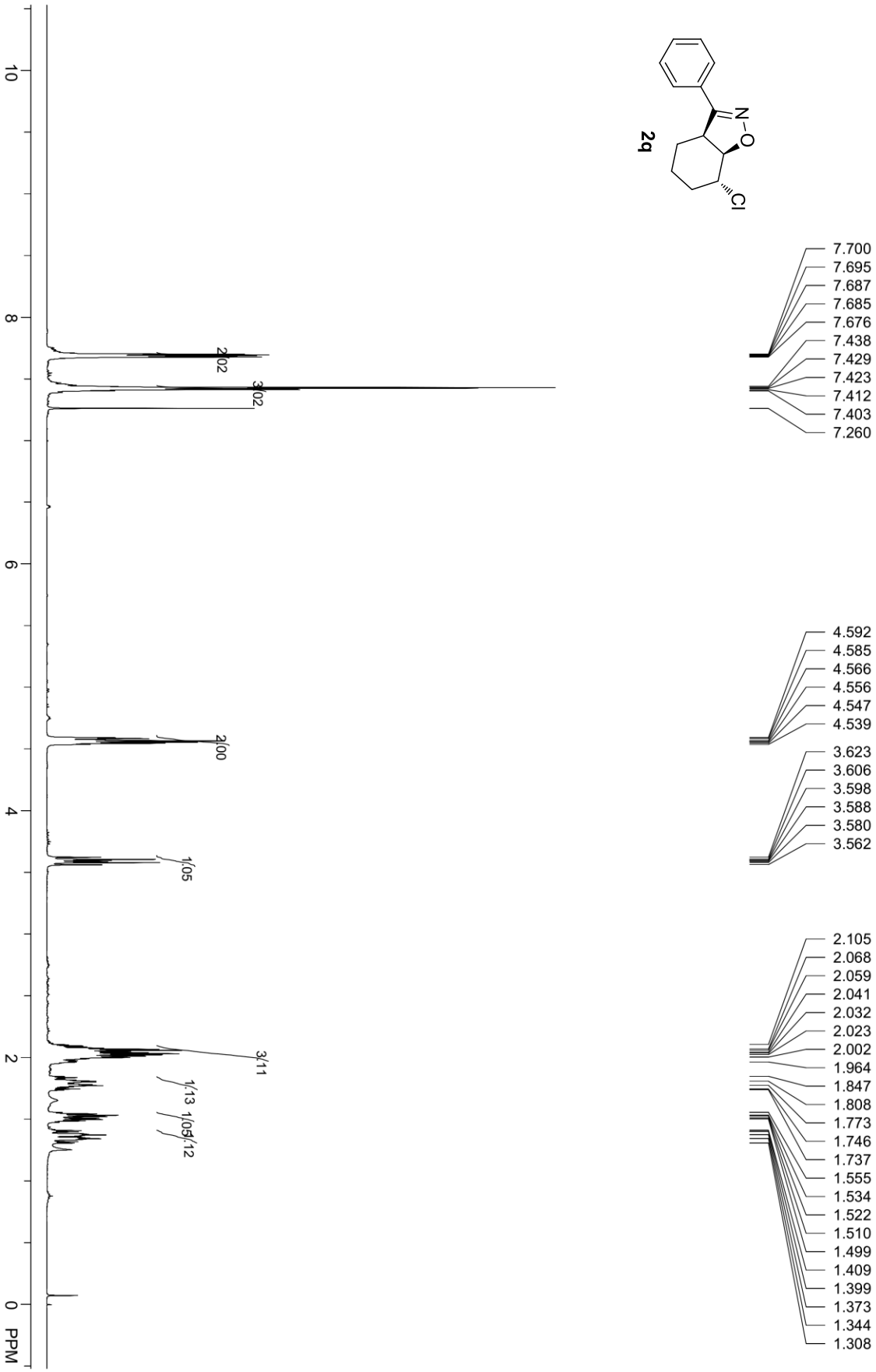
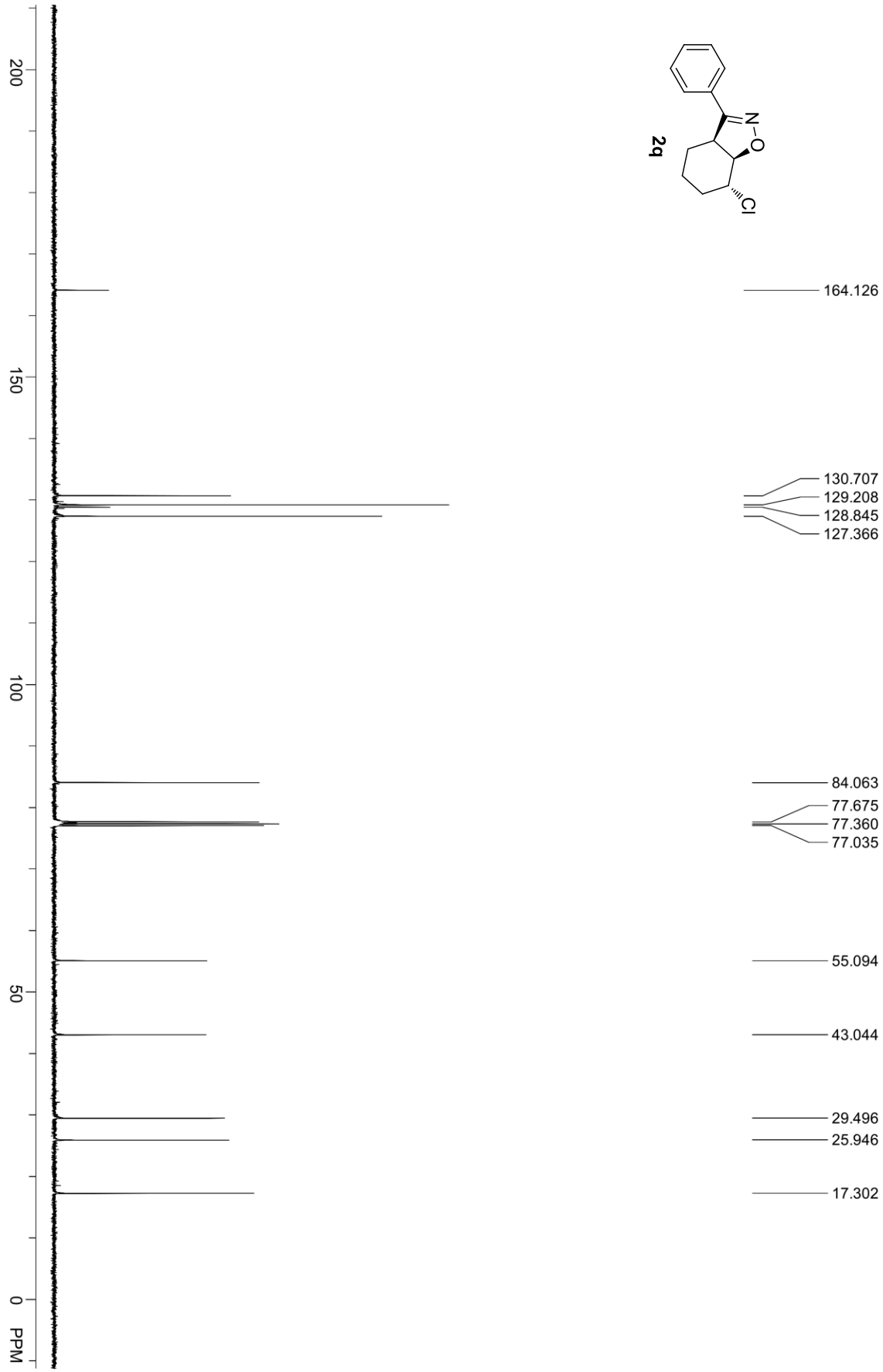
163.661
134.401
132.311
123.669
87.763
77.677
77.360
77.034
52.120
41.133
35.111
25.082
23.767
18.410
200
150
100
50
0
PPM

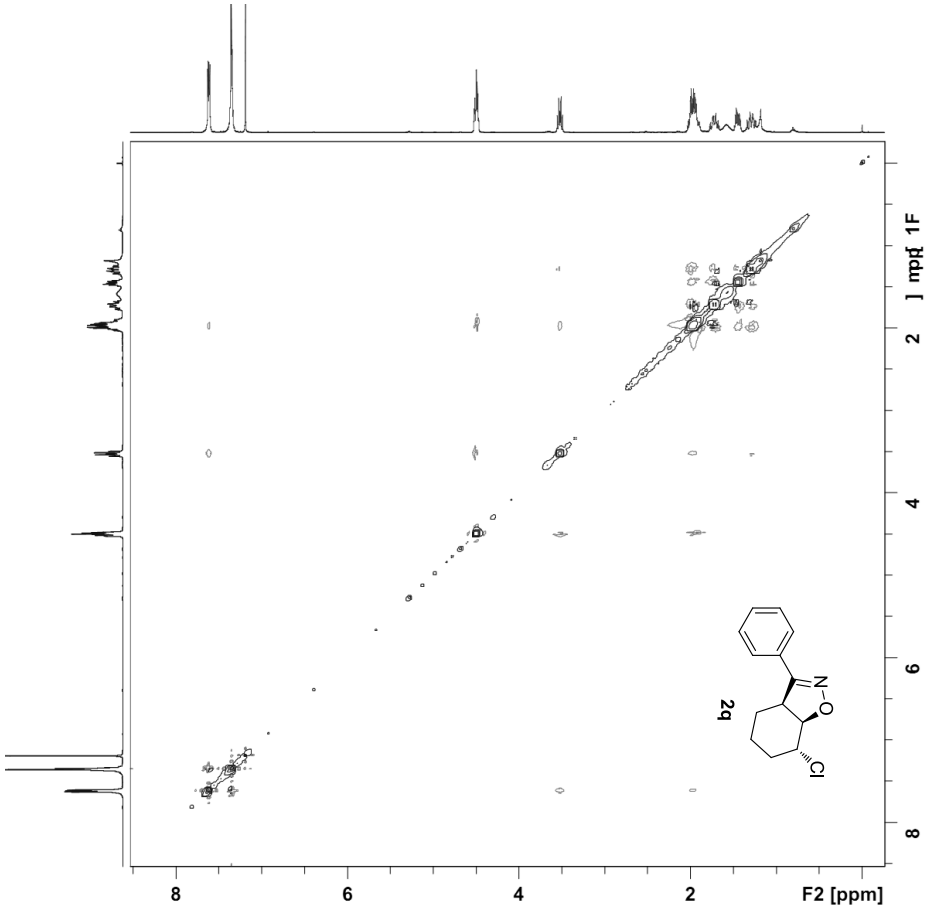
400M ^{1}H NMR of **2q**



400M ^{13}C NMR of **2q**



400M NOESY:



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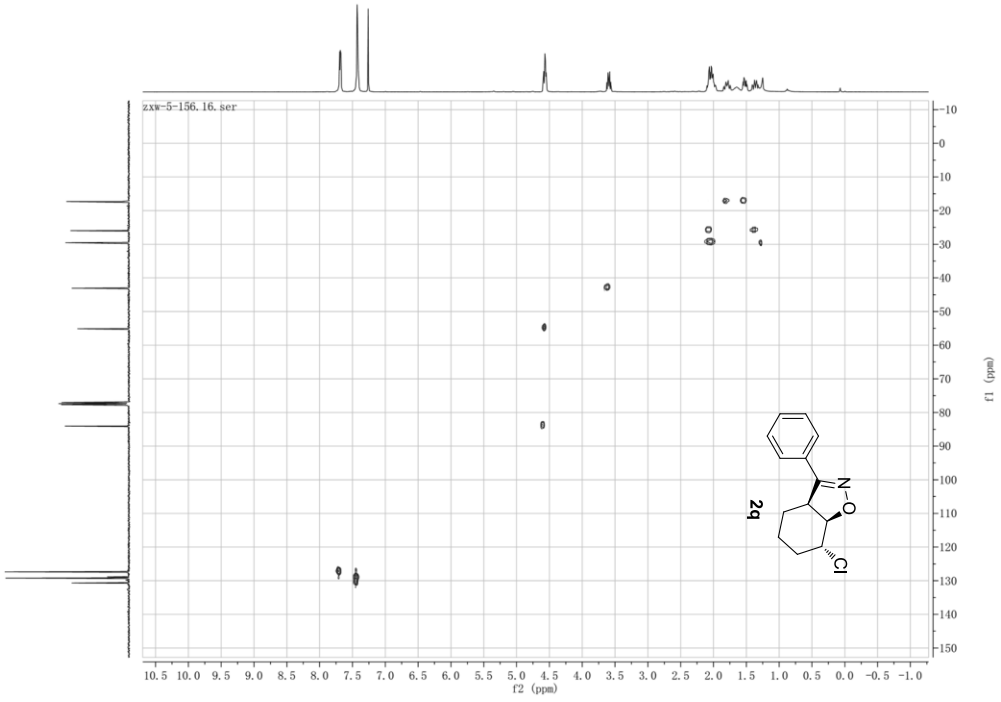
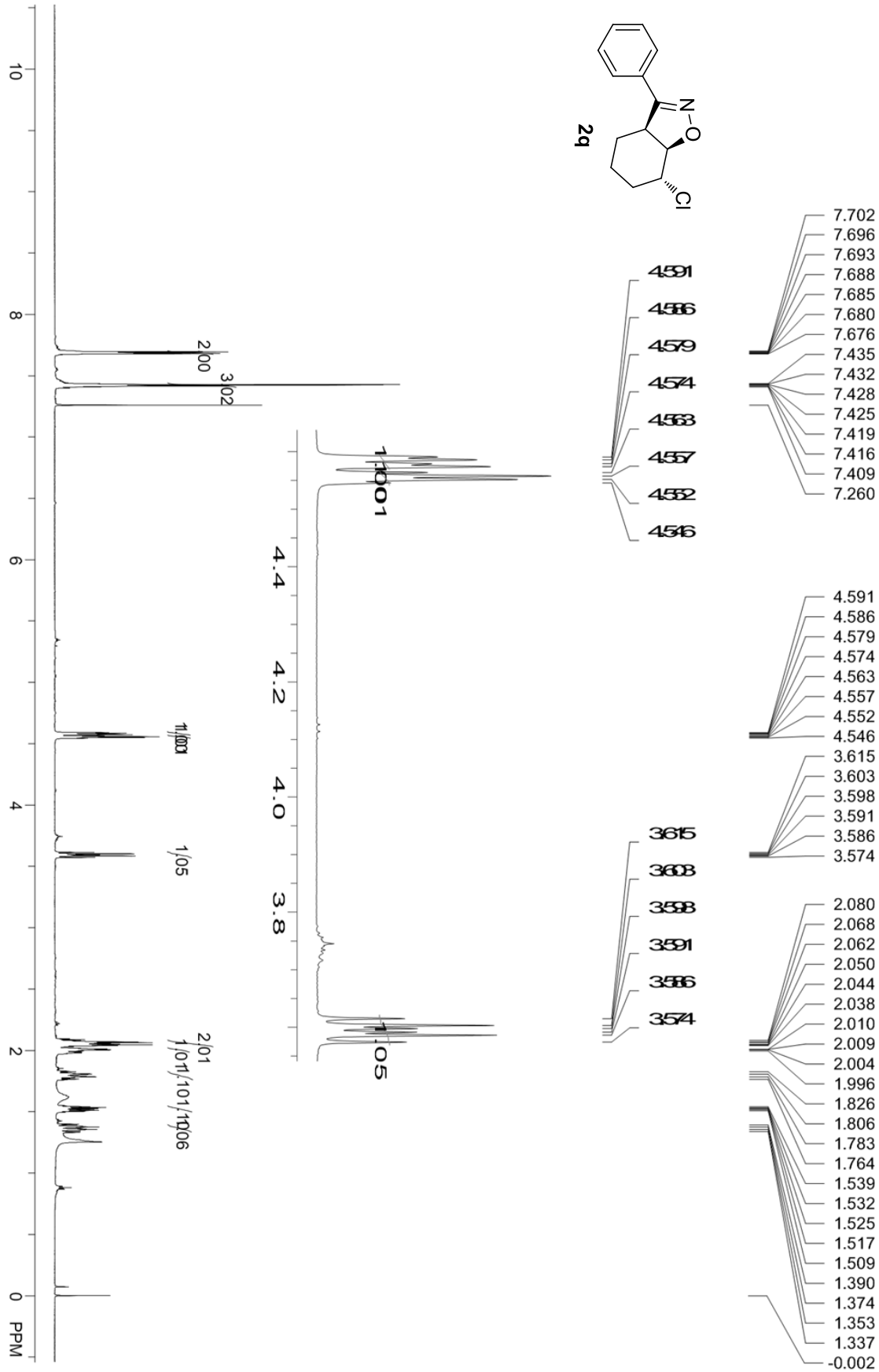
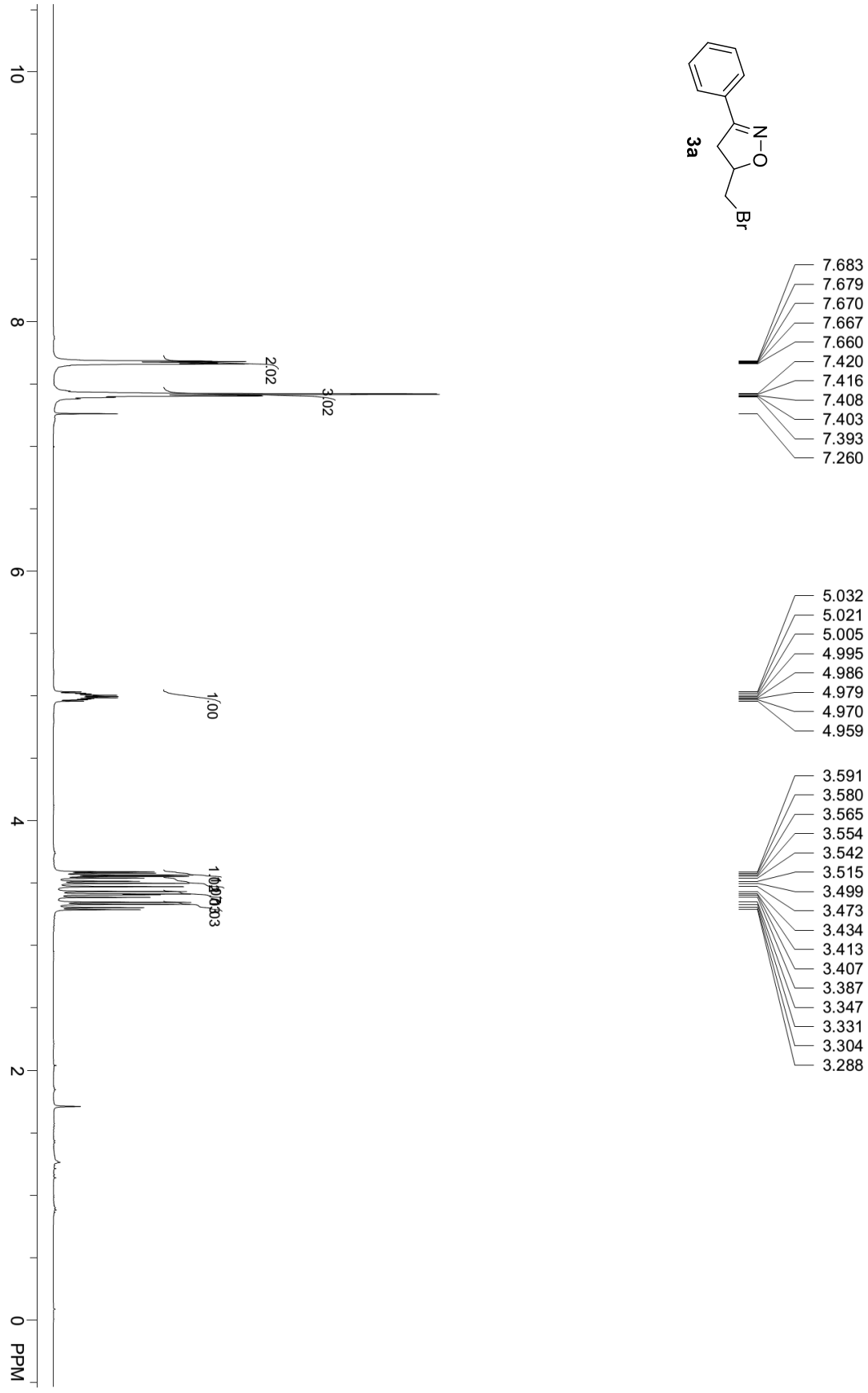


600M ^{1}H NMR of **2q**




3a
N–O
Br
7.683
7.679
7.670
7.667
7.660
7.420
7.416
7.408
7.403
7.393
7.260
5.032
5.021
5.005
4.995
4.986
4.979
4.970
4.959
3.591
3.580
3.565
3.554
3.542
3.515
3.499
3.473
3.434
3.413
3.407
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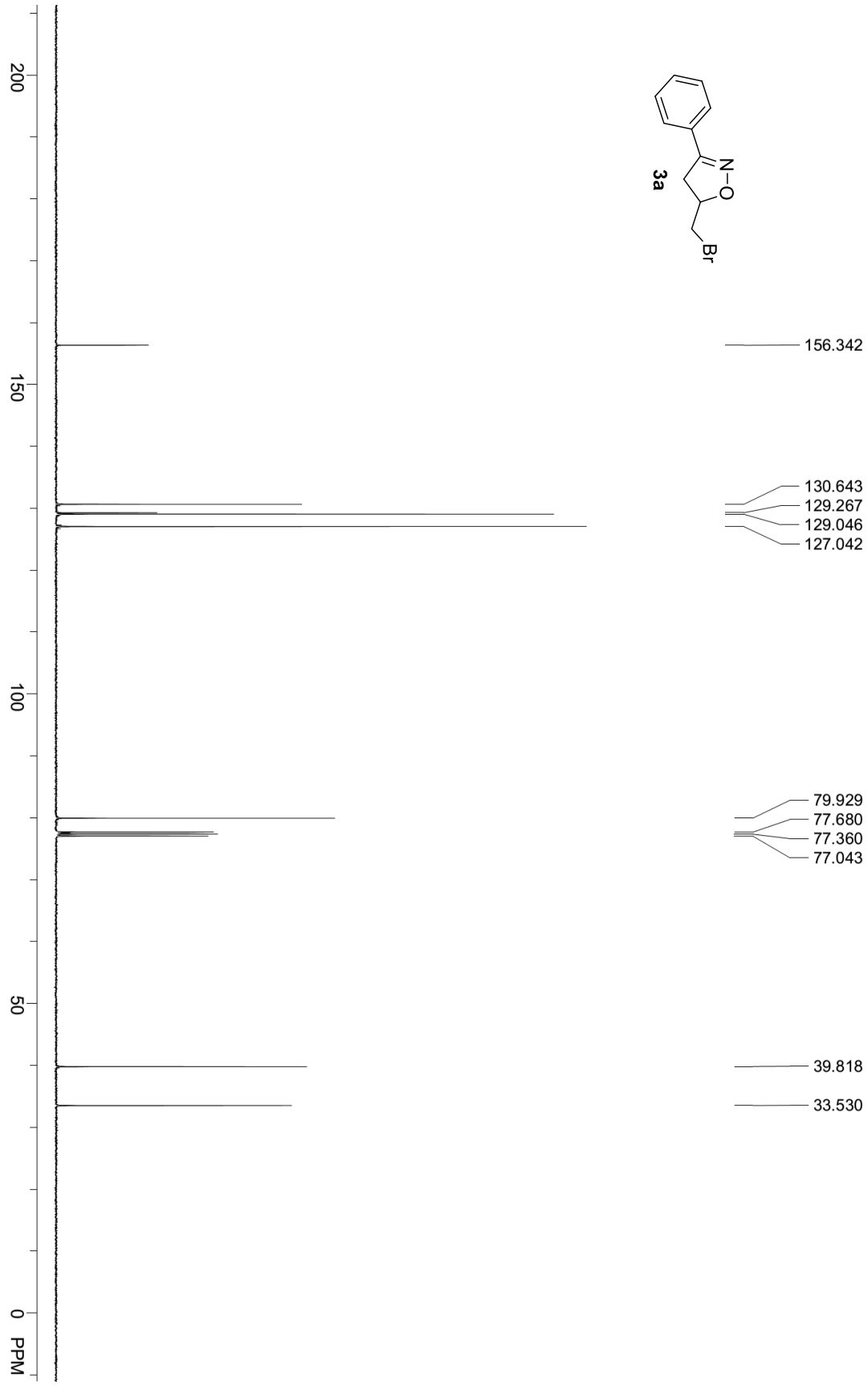
3.304
3.288
2.02
3.02
1.00
10
8
6
4
2
0
PPM


200
150
100
50
0
PPM
3a
N
O
Br
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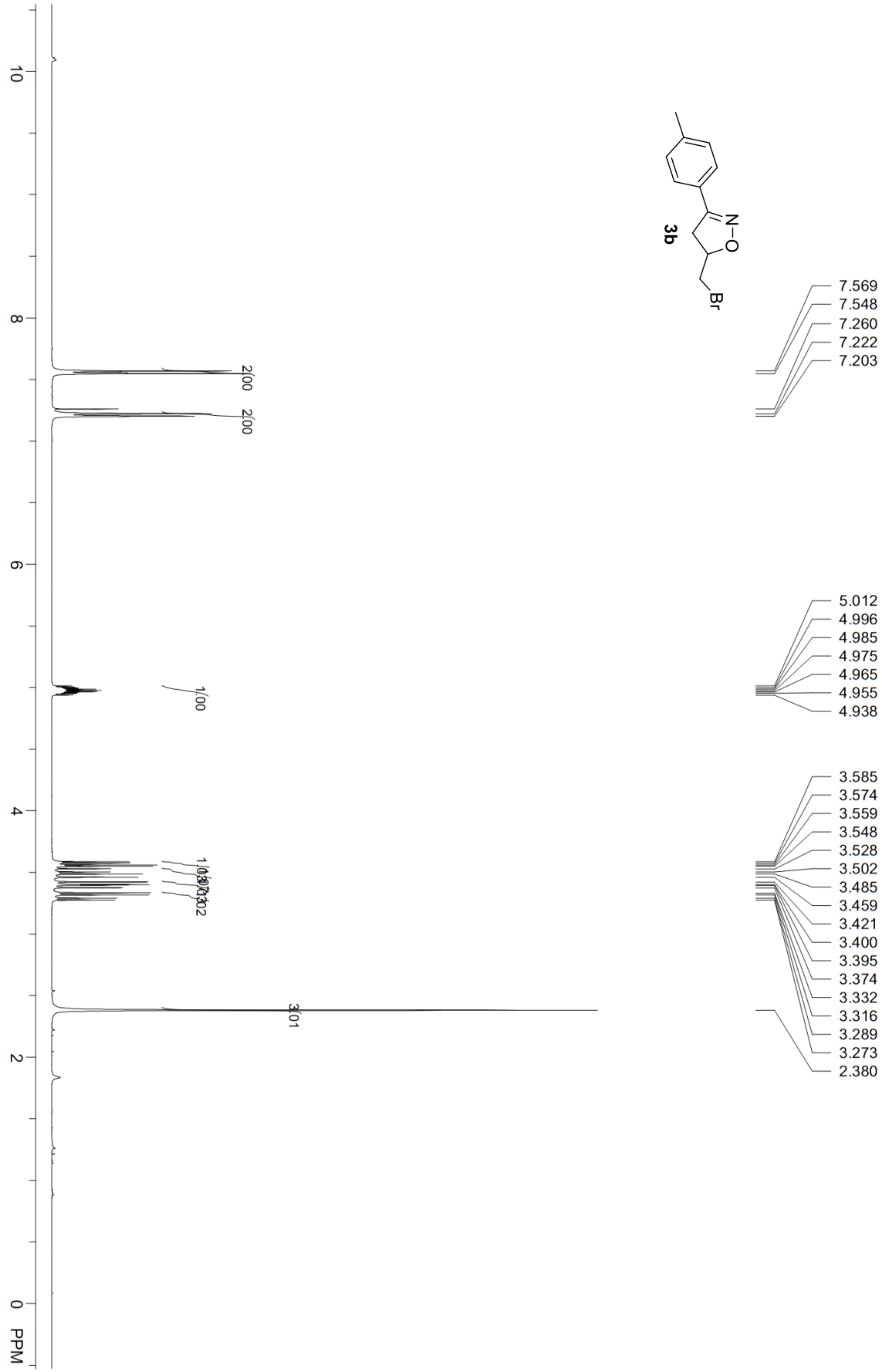
130.643
129.267
129.046
127.042
79.929
77.680
77.360
77.043
39.818
33.530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N–O
Br
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7.260
7.222
7.203
5.012
4.996
4.985
4.975
4.965
4.955
4.938
3.585
3.574
3.559
3.548
3.528
3.502
3.485
3.459
3.421
3.400
3.395
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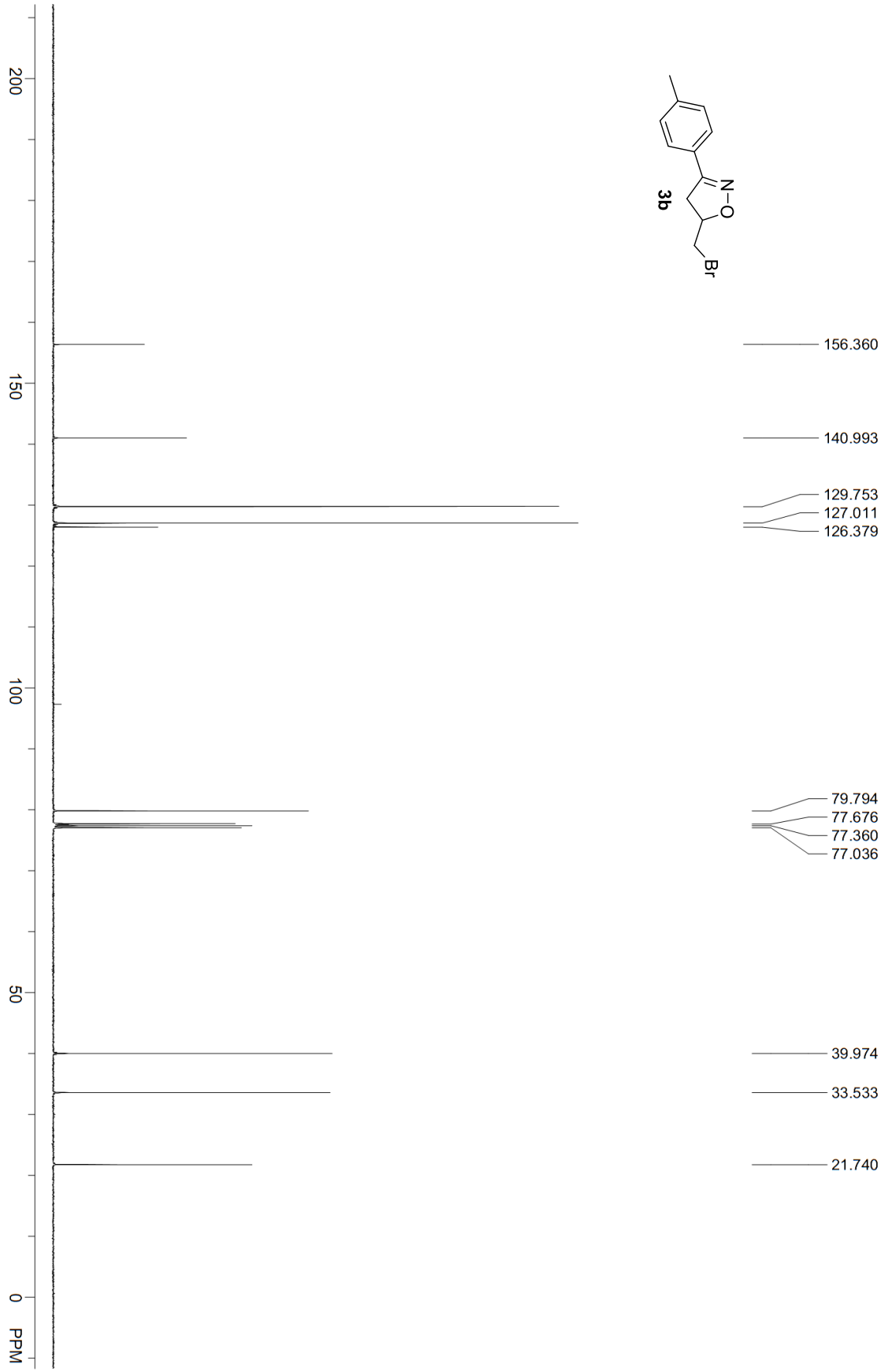
3.332
3.316
3.289
3.273
2.380
2.00
2.00
1.00
3.01
PPM


3b
N
O
Br
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77.360
77.036
39.974
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21.740
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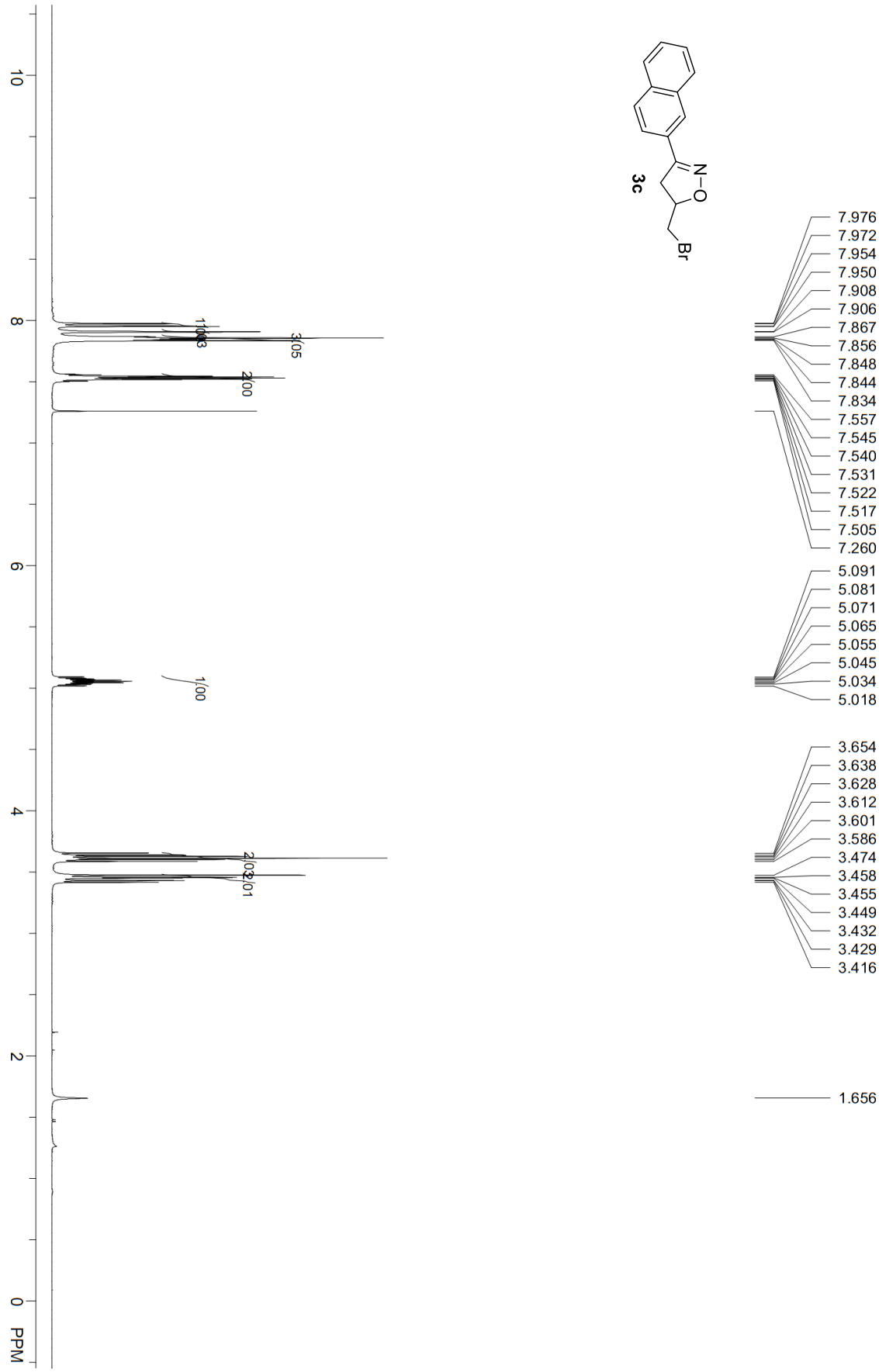
150
100
50
0
PPM


3c
N
O
Br
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7.844
7.834
7.557
7.545
7.540
7.531
7.522
7.517
7.505
7.260
5.091
5.081
5.071
5.065
5.055
5.045
5.034
5.018
3.654
3.638
3.628
3.612
3.601
3.586
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3.416
1.656
10
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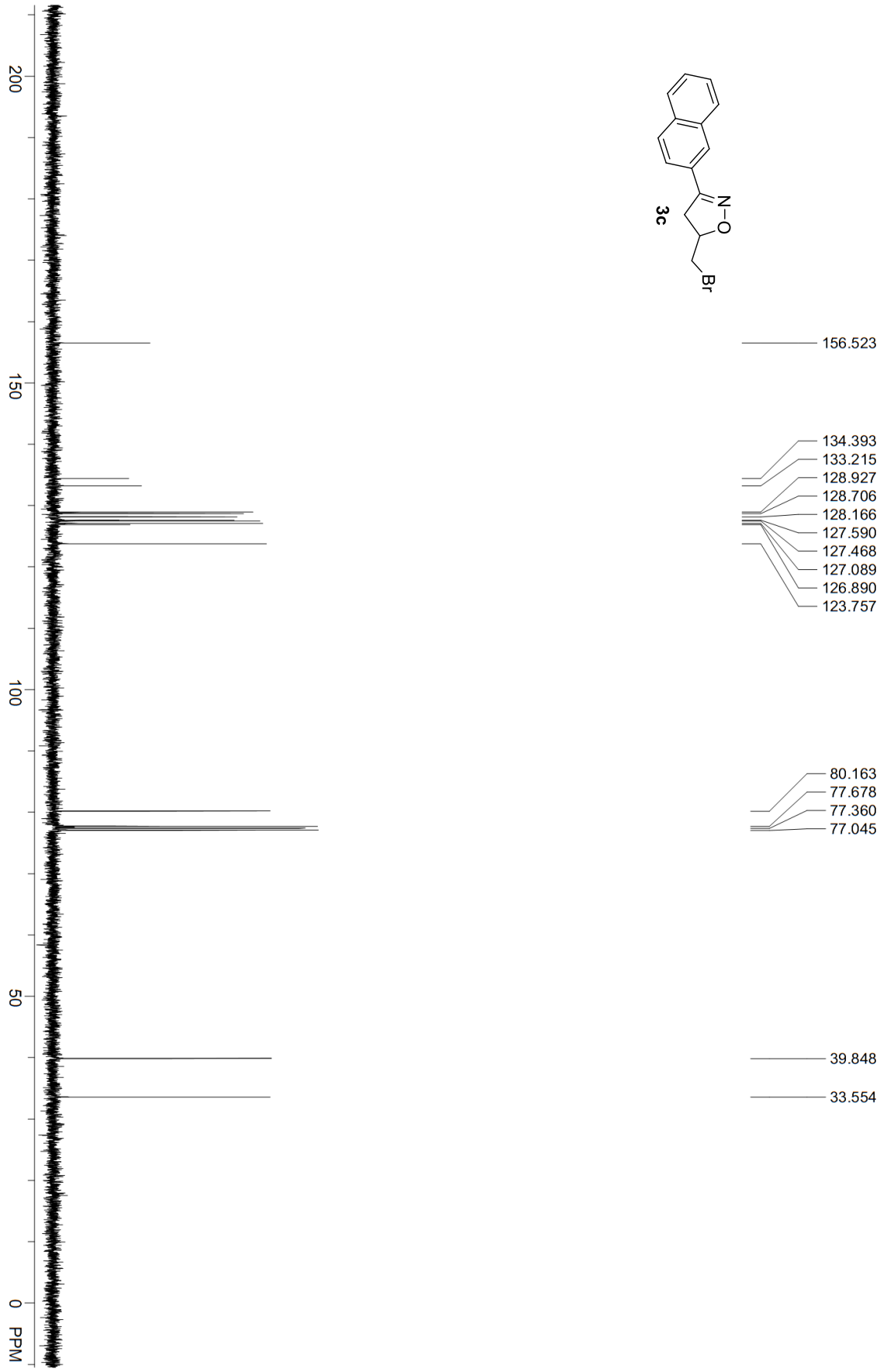
PPM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150
100
50
0
PPM
3c
N–O
Br
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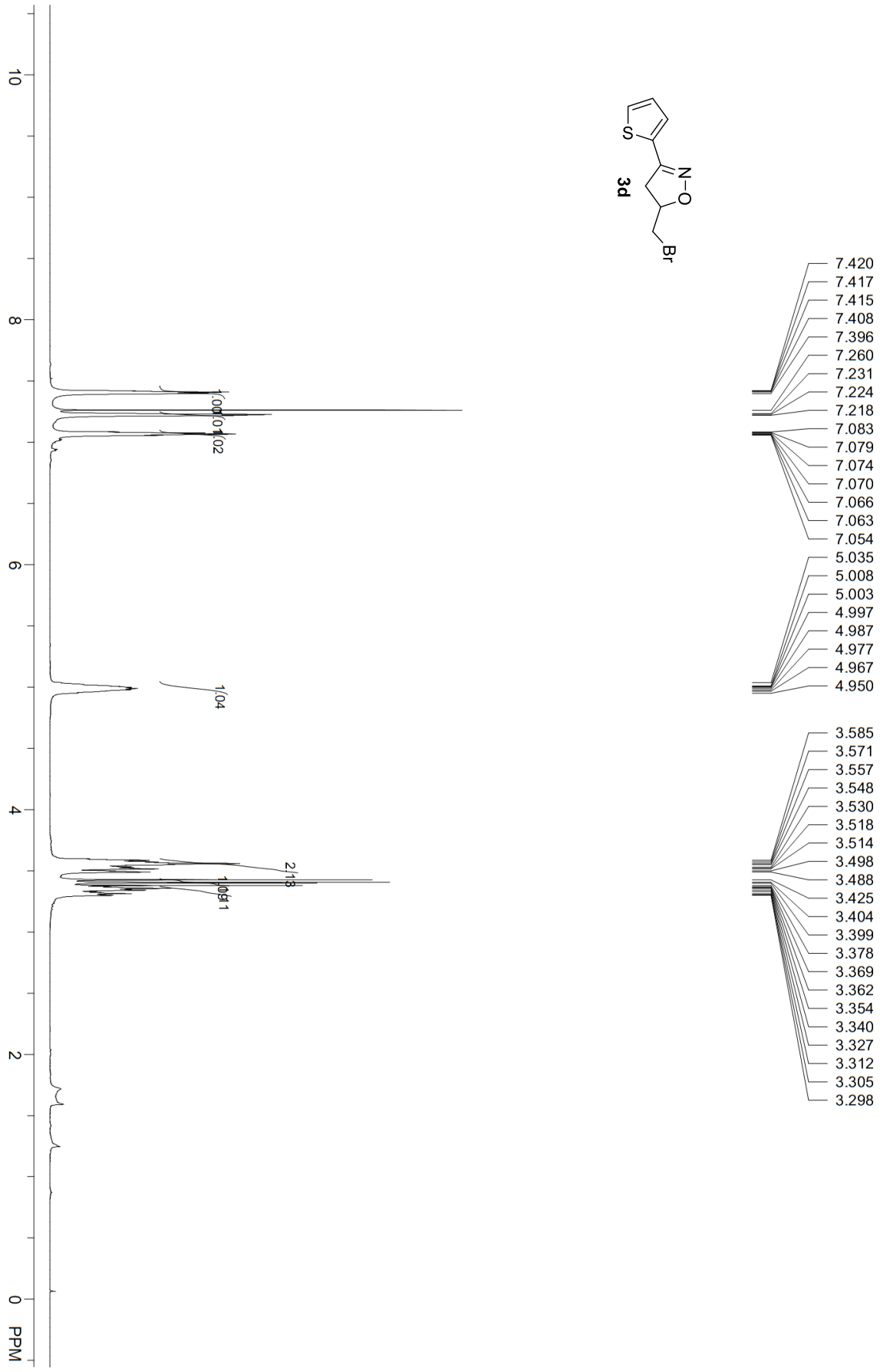
134.393
133.215
128.927
128.706
128.166
127.590
127.468
127.089
126.890
123.757
80.163
77.678
77.360
77.045
39.848
33.554


3d
S
N
O
Br
7.420
7.417
7.415
7.408
7.396
7.260
7.231
7.224
7.218
7.083
7.079
7.074
7.070
7.066
7.063
7.054
5.035
5.008
5.003
4.997
4.987
4.977
4.967
4.950
3.585
3.571
3.557
3.548
3.530
3.518
3.514
3.498
3.488
3.425
3.404
3.399
3.378
3.369
3.362
3.354
3.340
3.327
3.312
3.305
3.298
1.00
1.01
1.02
1.04
2.13
1.09
1.11
10
8
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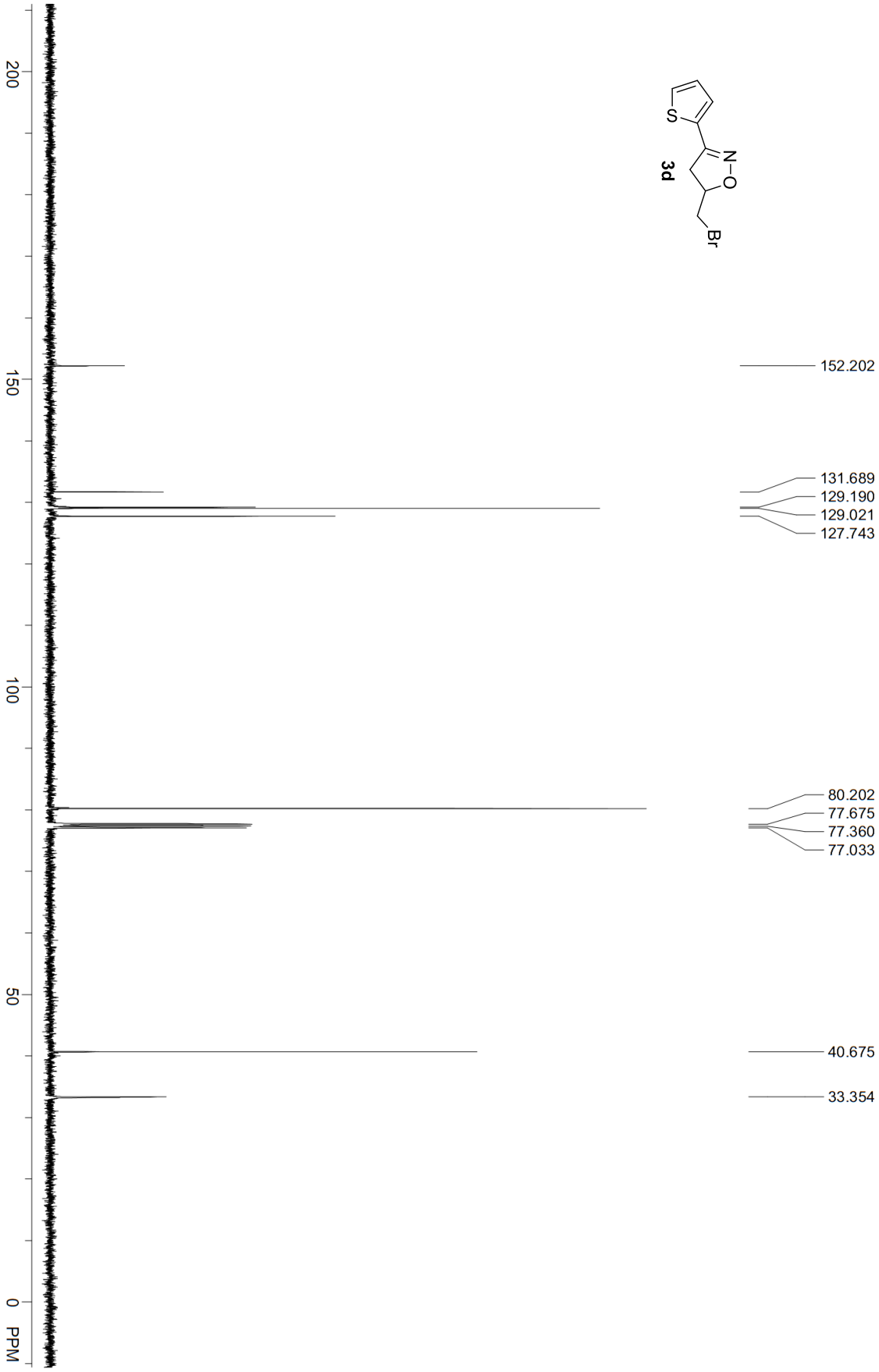
PPM


200
150
100
50
0
PPM
S
N
O
Br
3d
152.202
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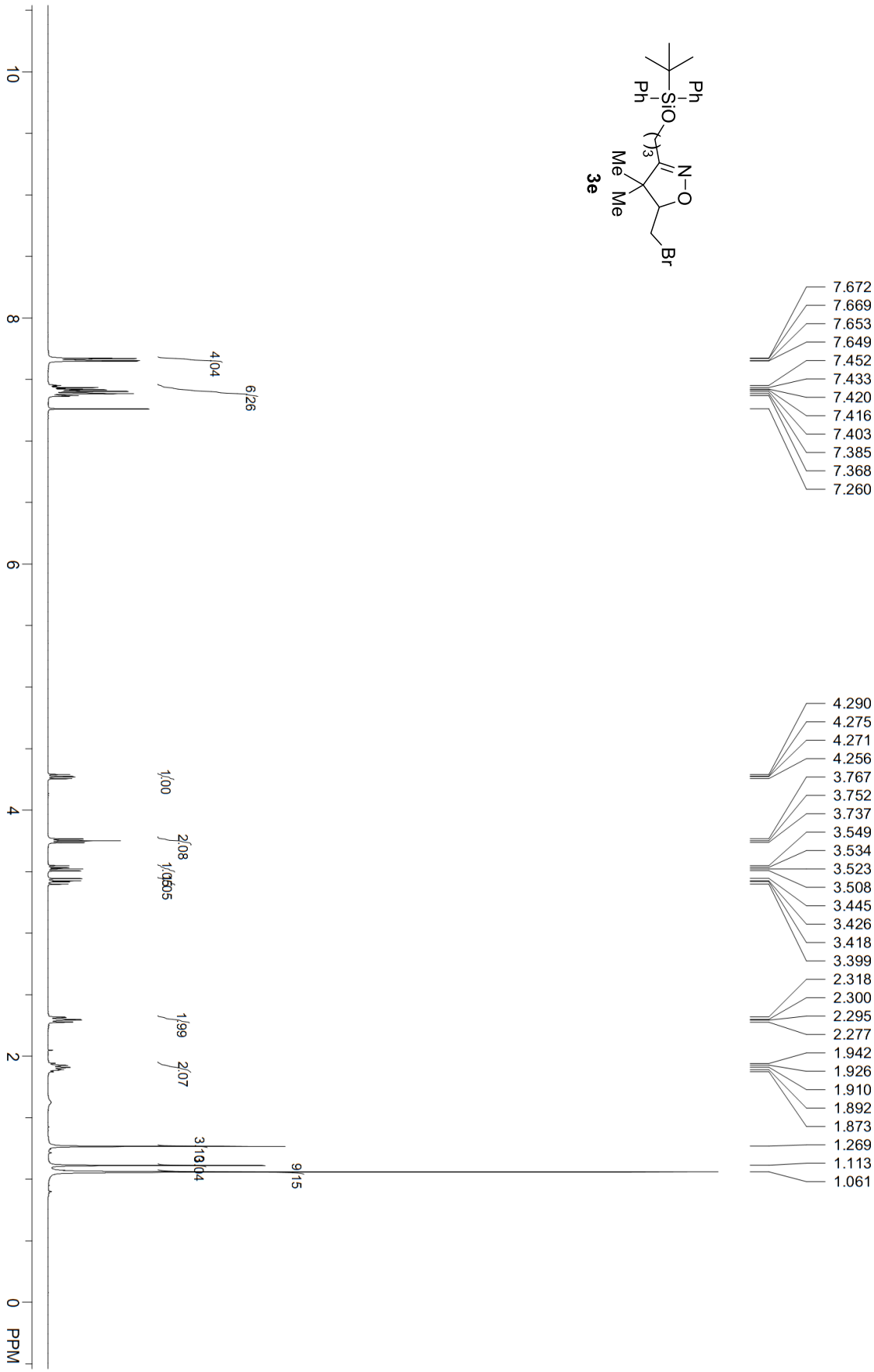
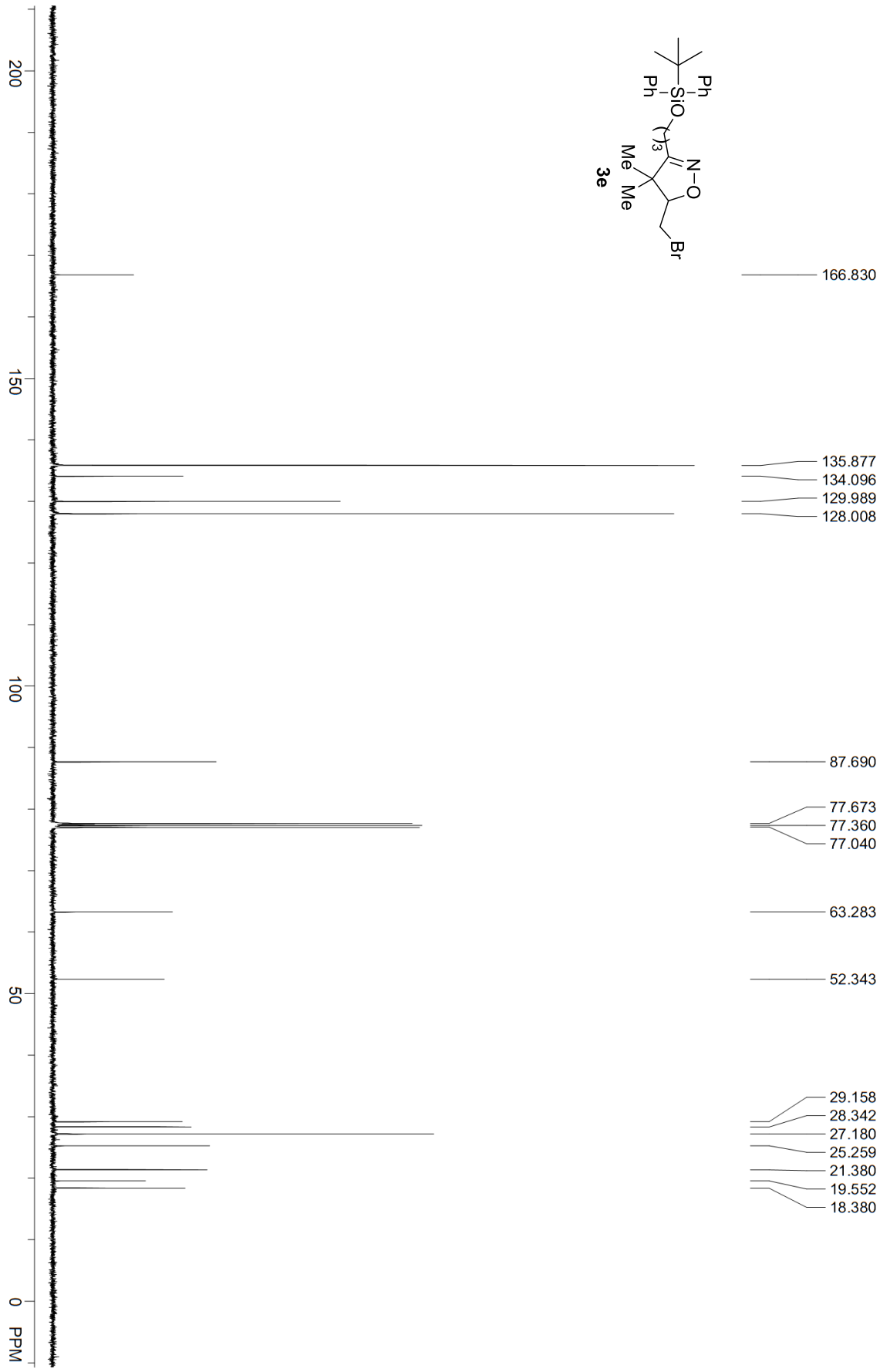
129.190
129.021
127.743
80.202
77.675
77.360
77.033
40.675
33.354


Ph
Ph
SiO
( )3
N–O
Me Me
Br
3e
7.672
7.669
7.653
7.649
7.452
7.433
7.420
7.416
7.403
7.385
7.368
7.260
4.290
4.275
4.271
4.256
3.767
3.752
3.737
3.549
3.534
3.523
3.508
3.445
3.426
3.418
3.399
2.318
2.300
2.295
2.277
1.942
1.926
1.910
1.892
1.873
1.269
1.113
1.061
4.04
6.26
1.00
2.08
1.95
1.99
2.07
3.18
9.15
10
8
6
4
2
0
PPM


Ph
Ph
SiO
( )3
N–O
Me
Me
Br
3e
166.830
135.877
134.096
129.989
128.008
87.690
77.673
77.360
77.040
63.283
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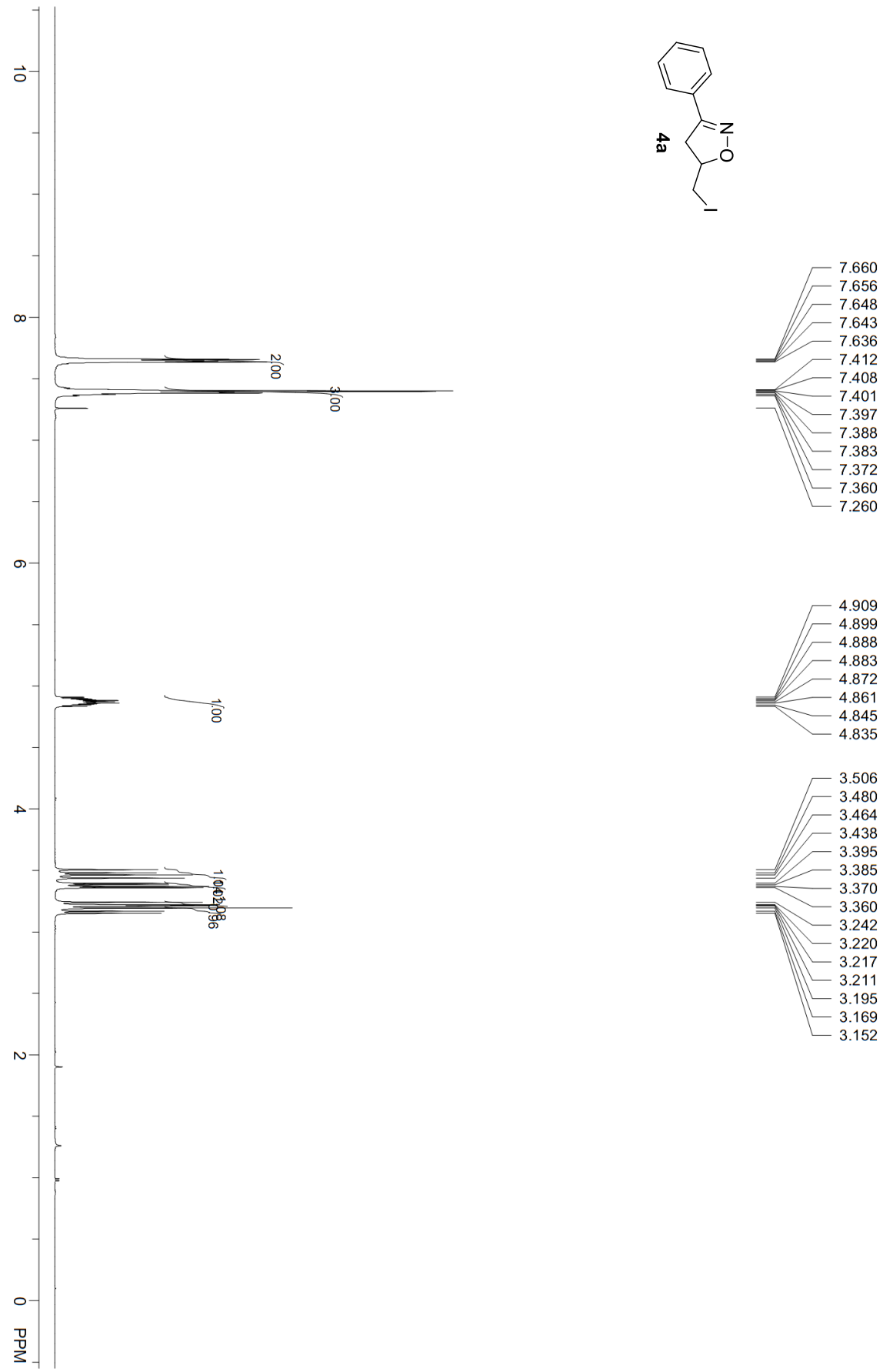
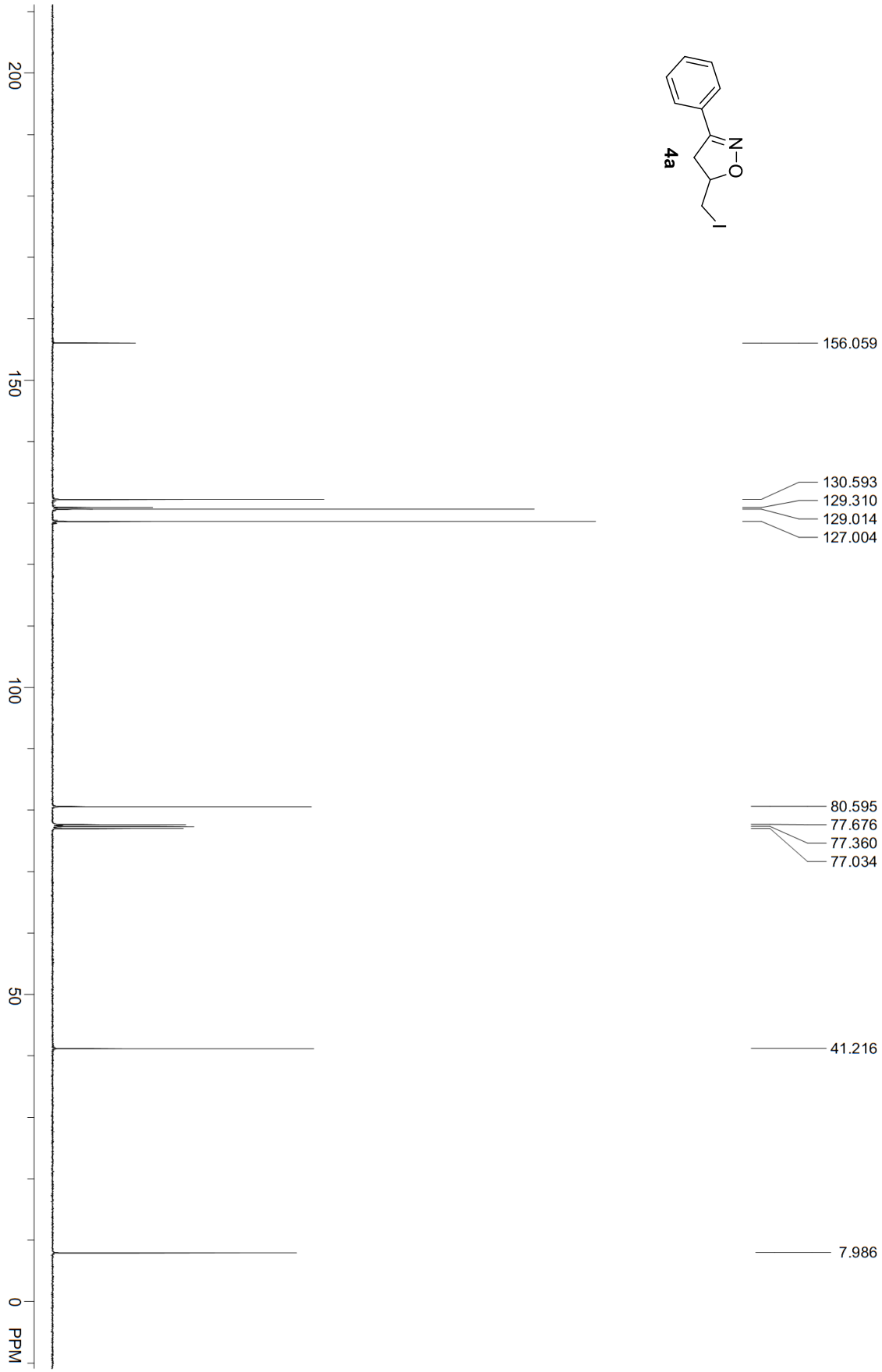
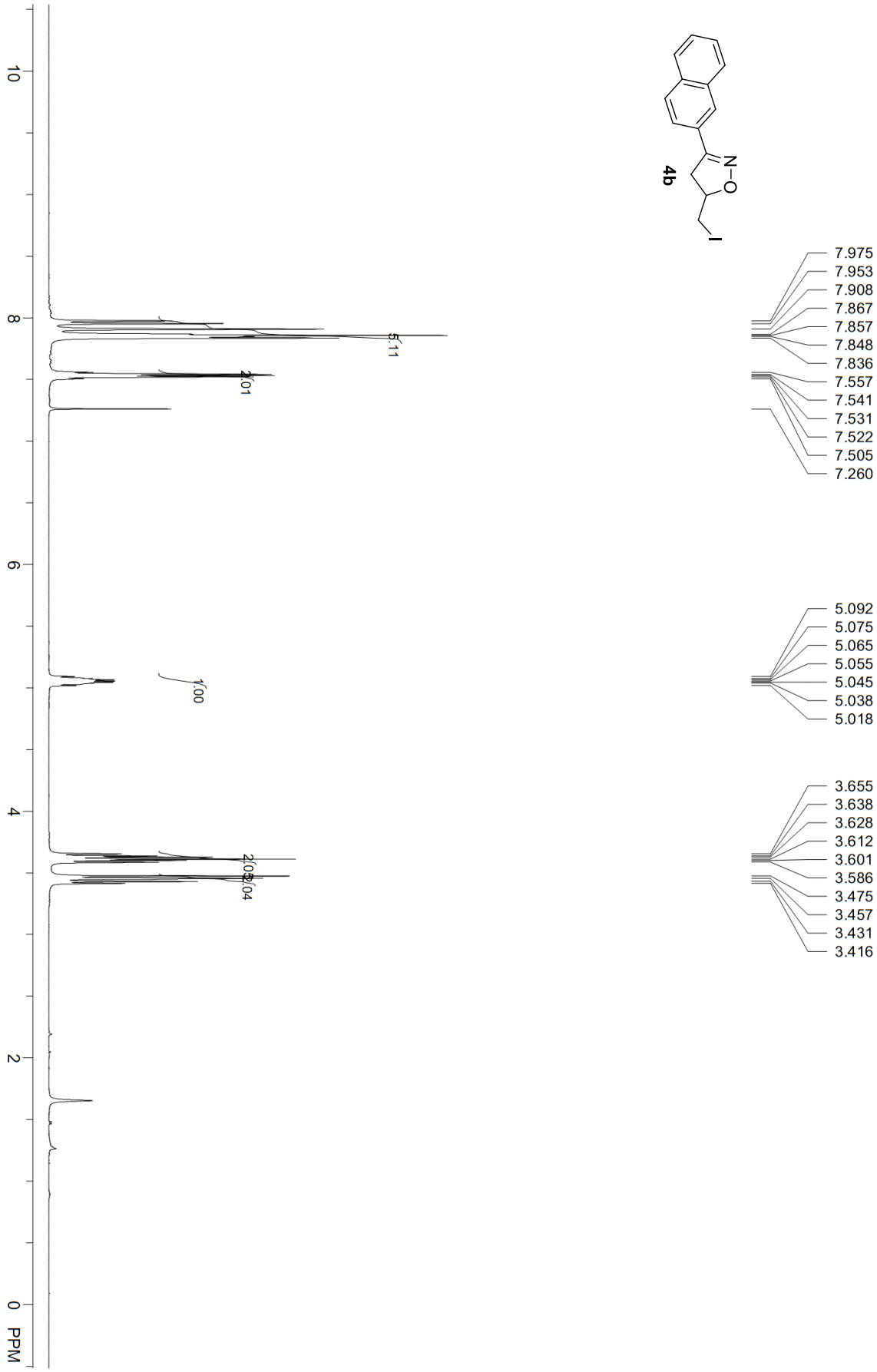
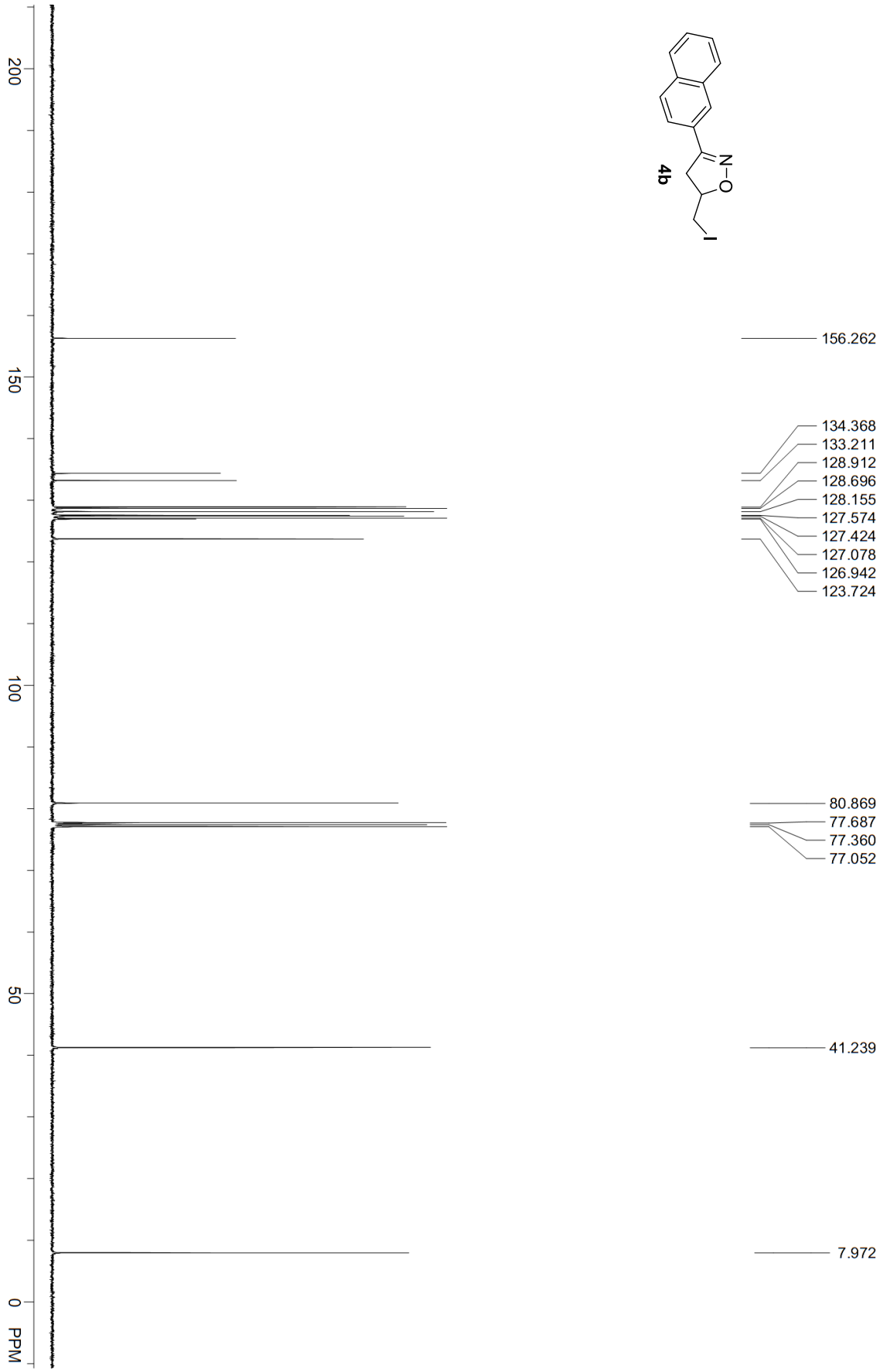
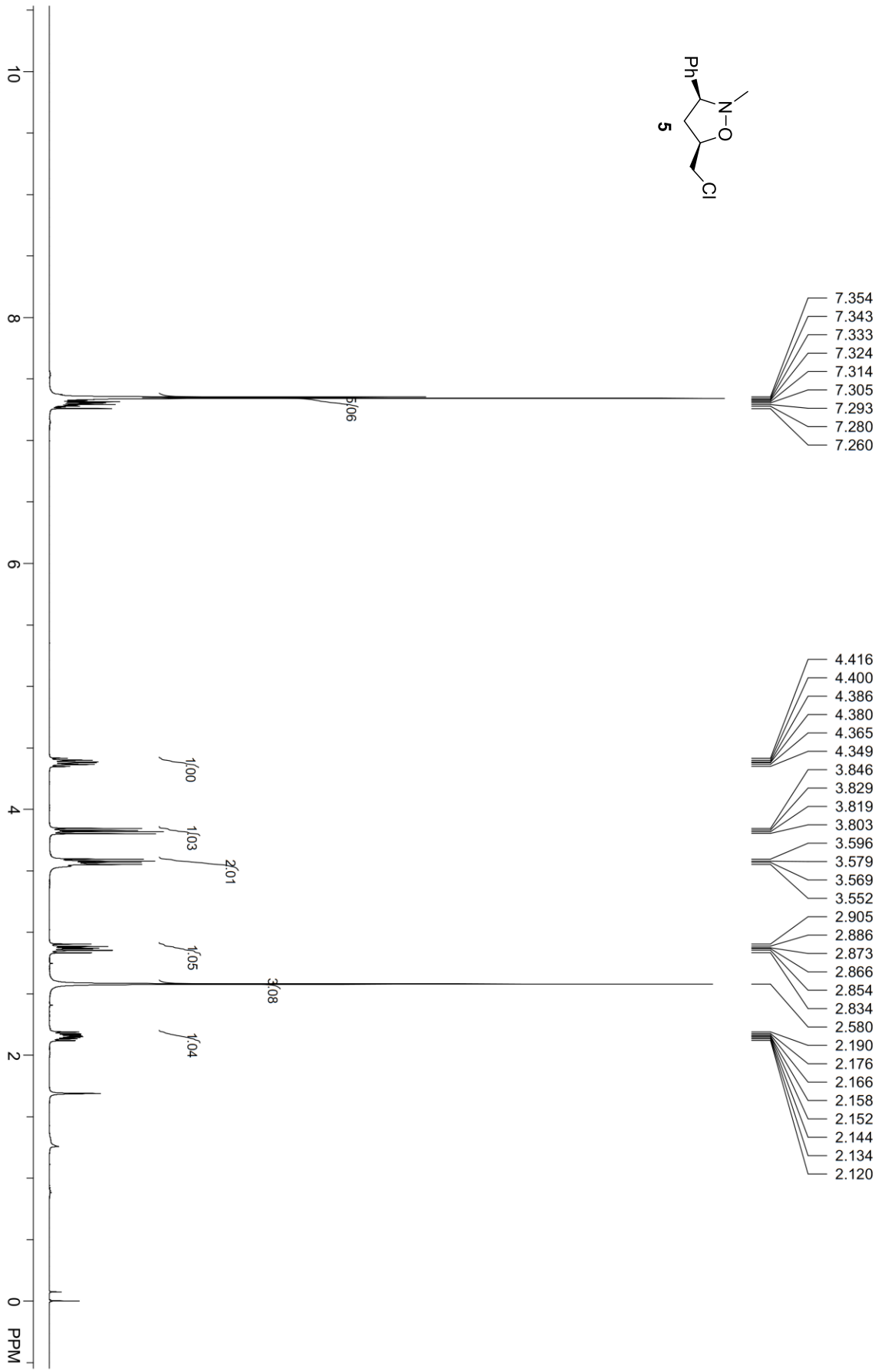
29.158
28.342
27.180
25.259
21.380
19.552
18.380
200
150
100
50
0
PPM


4a
7.660
7.656
7.648
7.643
7.636
7.412
7.408
7.401
7.397
7.388
7.383
7.372
7.360
7.260
4.909
4.899
4.888
4.883
4.872
4.861
4.845
4.835
3.506
3.480
3.464
3.438
3.395
3.385
3.370
3.360
3.242
3.220
3.217
3.211
3.195
3.169
3.152
2.00
3.00
1.00
1.04
2.08
0.96
10
8
6
4
2
0
PPM


4a
N
O
I
156.059
130.593
129.310
129.014
127.004
80.595
77.676
77.360
77.034
41.216
7.986
200
150
100
50
0
PPM


4b
7.975
7.953
7.908
7.867
7.857
7.848
7.836
7.557
7.541
7.531
7.522
7.505
7.260
5.092
5.075
5.065
5.055
5.045
5.038
5.018
3.655
3.638
3.628
3.612
3.601
3.586
3.475
3.457
3.431
3.416
5.11
2.01
1.00
2.03
2.04
10
8
6
4
2
0
PPM


4b
156.262
134.368
133.211
128.912
128.696
128.155
127.574
127.424
127.078
126.942
123.724
80.869
77.687
77.360
77.052
41.239
7.972
200
150
100
50
0
PPM


Ph
N
O
Cl
5
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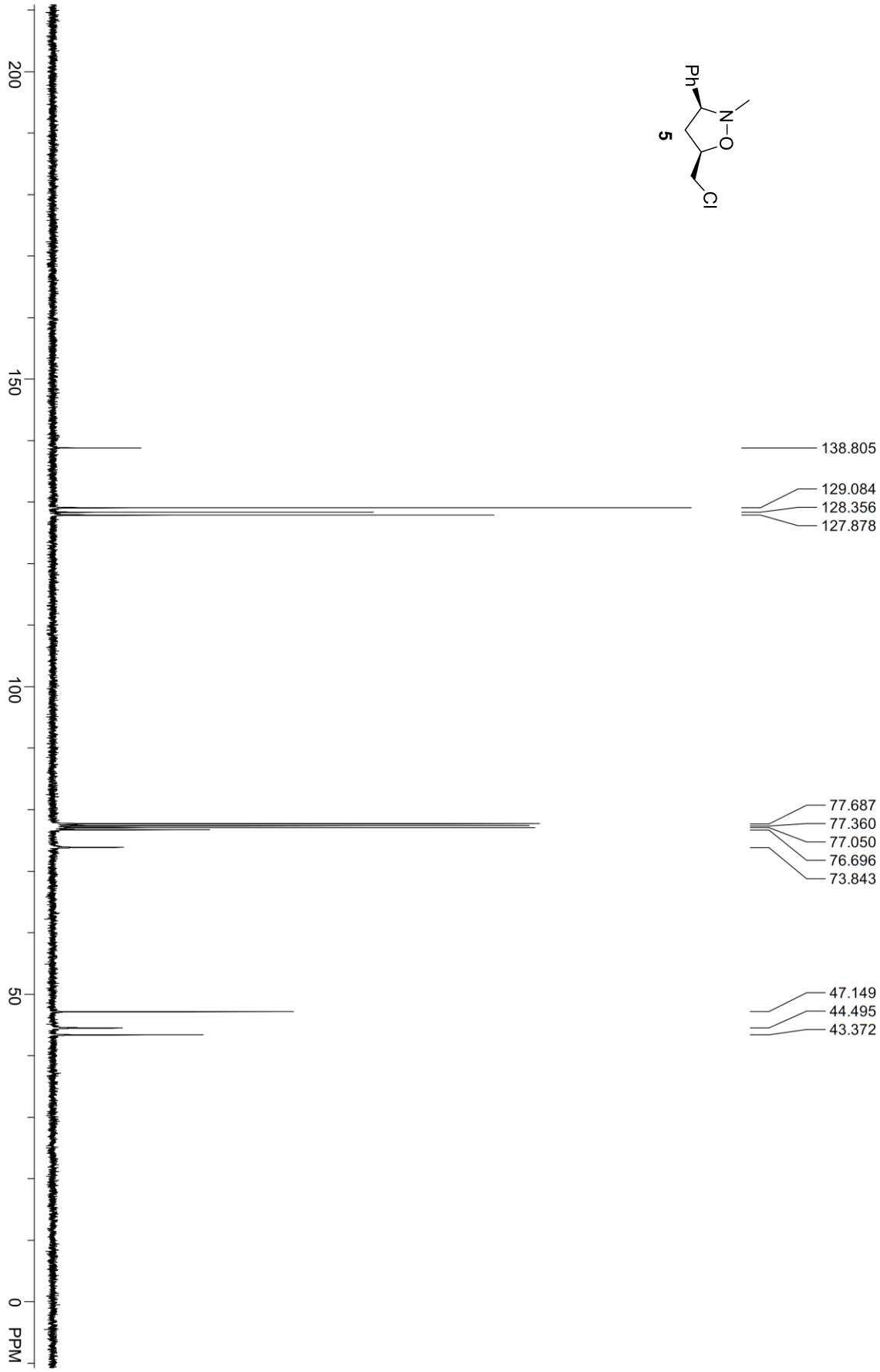
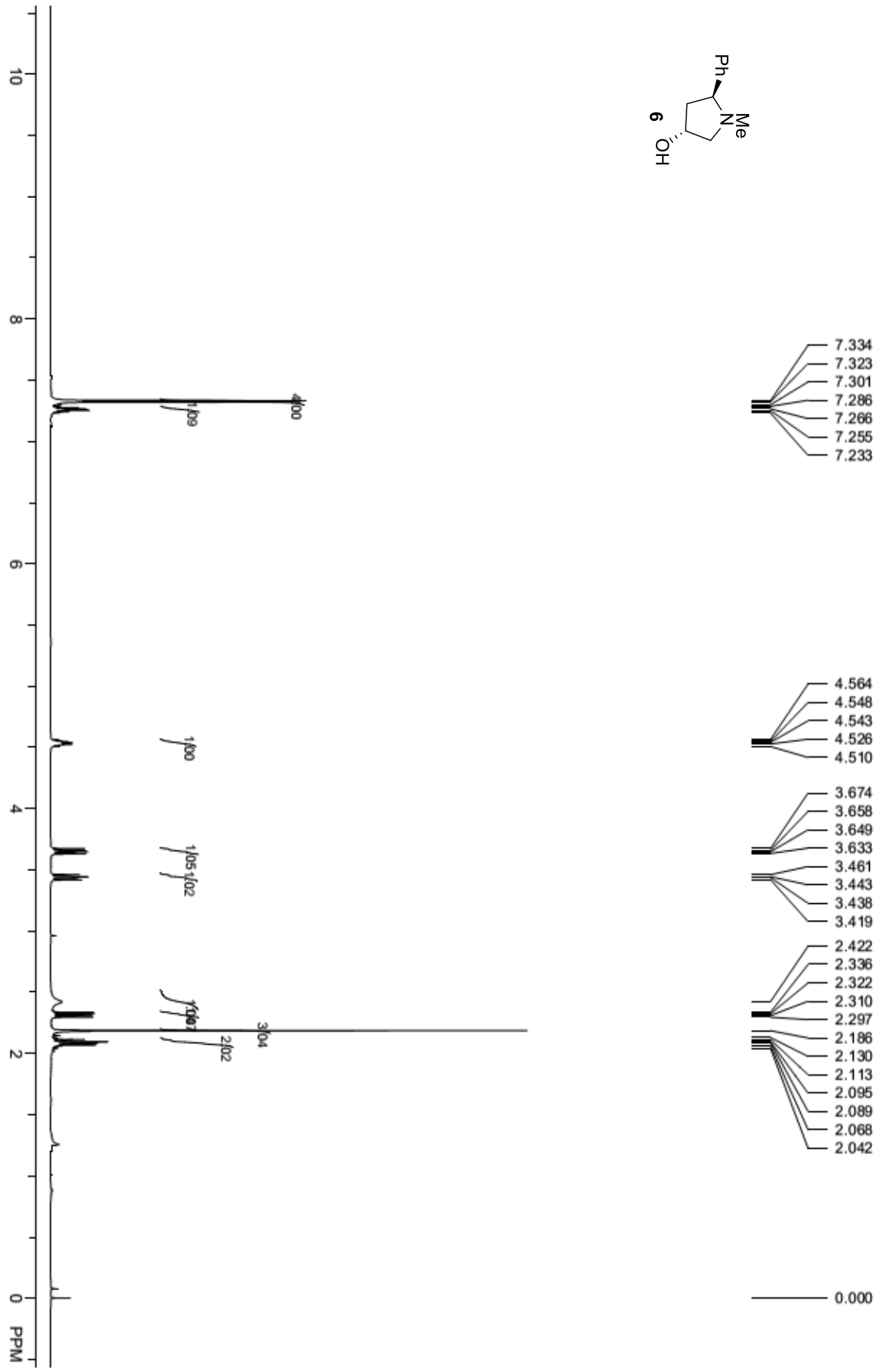
7.343
7.333
7.324
7.314
7.305
7.293
7.280
7.260
4.416
4.400
4.386
4.380
4.365
4.349
3.846
3.829
3.819
3.803
3.596
3.579
3.569
3.552
2.905
2.886
2.873
2.866
2.854
2.834
2.580
2.190
2.176
2.166
2.158
2.152
2.144
2.134
2.120
5.06
1.00
1.03
2.01
1.05
3.08
1.04
10
8
6
4
2
0
PPM


Ph
N
O
Cl
5
200
150
100
50
0
PPM
138.805
129.084
128.356
127.878
77.687
77.360
77.050
76.696
73.843
47.149
44.495
43.372


Ph
Me
N
OH
6
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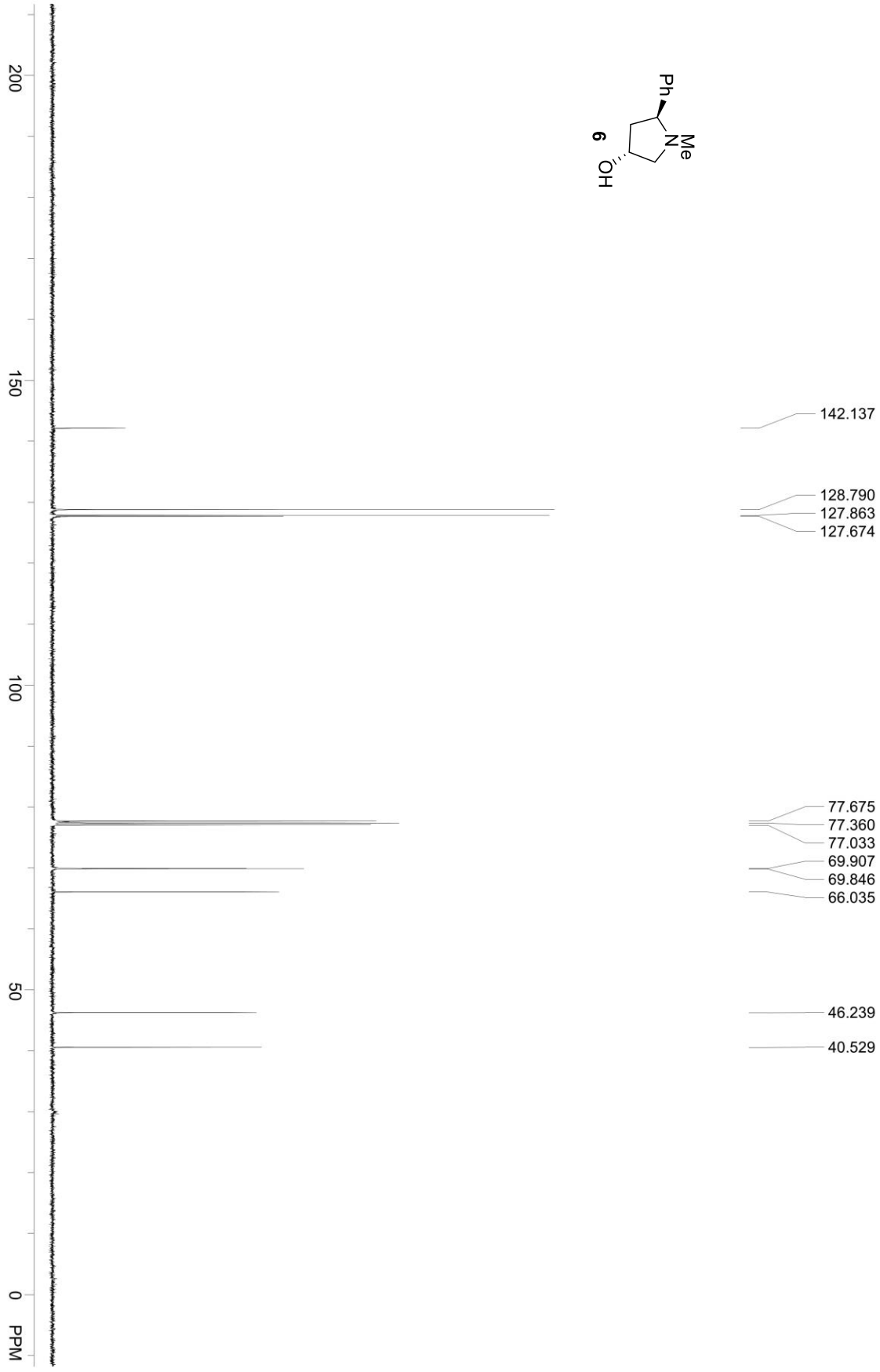
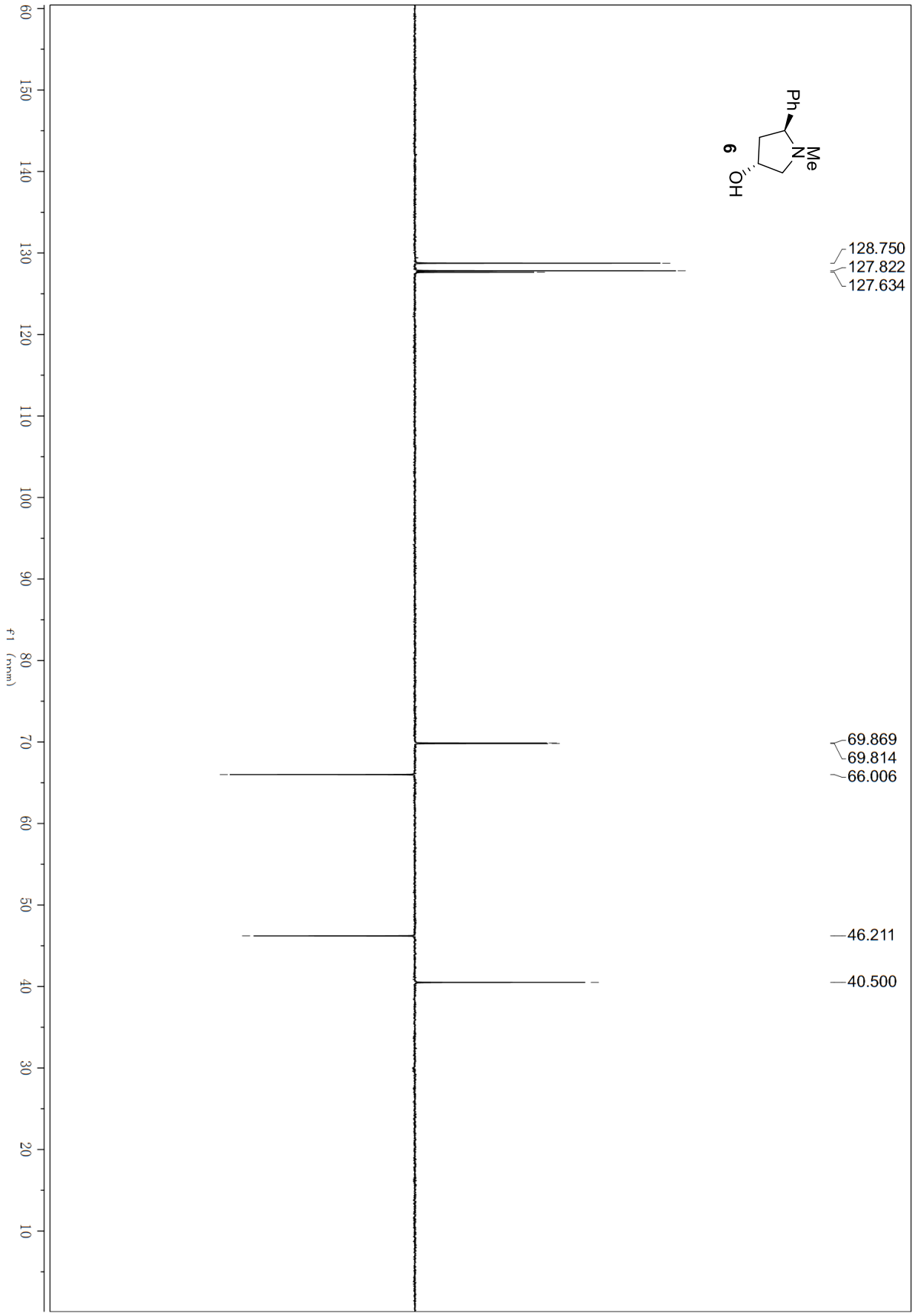
7.323
7.301
7.286
7.266
7.255
7.233
4.564
4.548
4.543
4.526
4.510
3.674
3.658
3.649
3.633
3.461
3.443
3.438
3.419
2.422
2.336
2.322
2.310
2.297
2.186
2.130
2.113
2.095
2.089
2.068
2.042
0.000
4.00
1.09
1.00
1.05
1.02
3.04
2.02
10
8
6
4
2
0
PPM


Ph
N
Me
6
OH
142.137
128.790
127.863
127.674
77.675
77.360
77.033
69.907
69.846
66.035
46.239
40.529
200
150
100
50
0
PPM

dept-135


Ph
Me
N
OH
6
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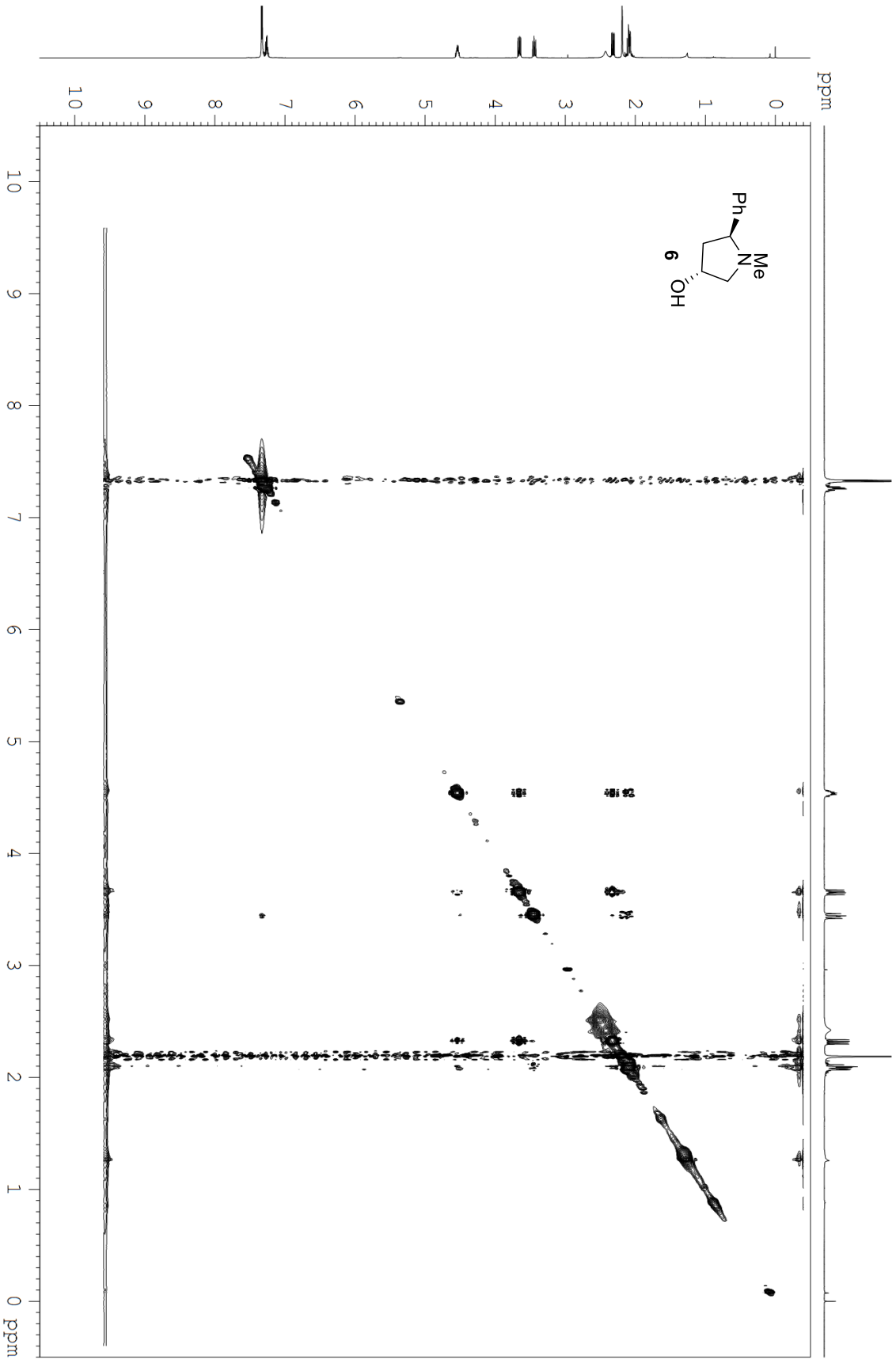
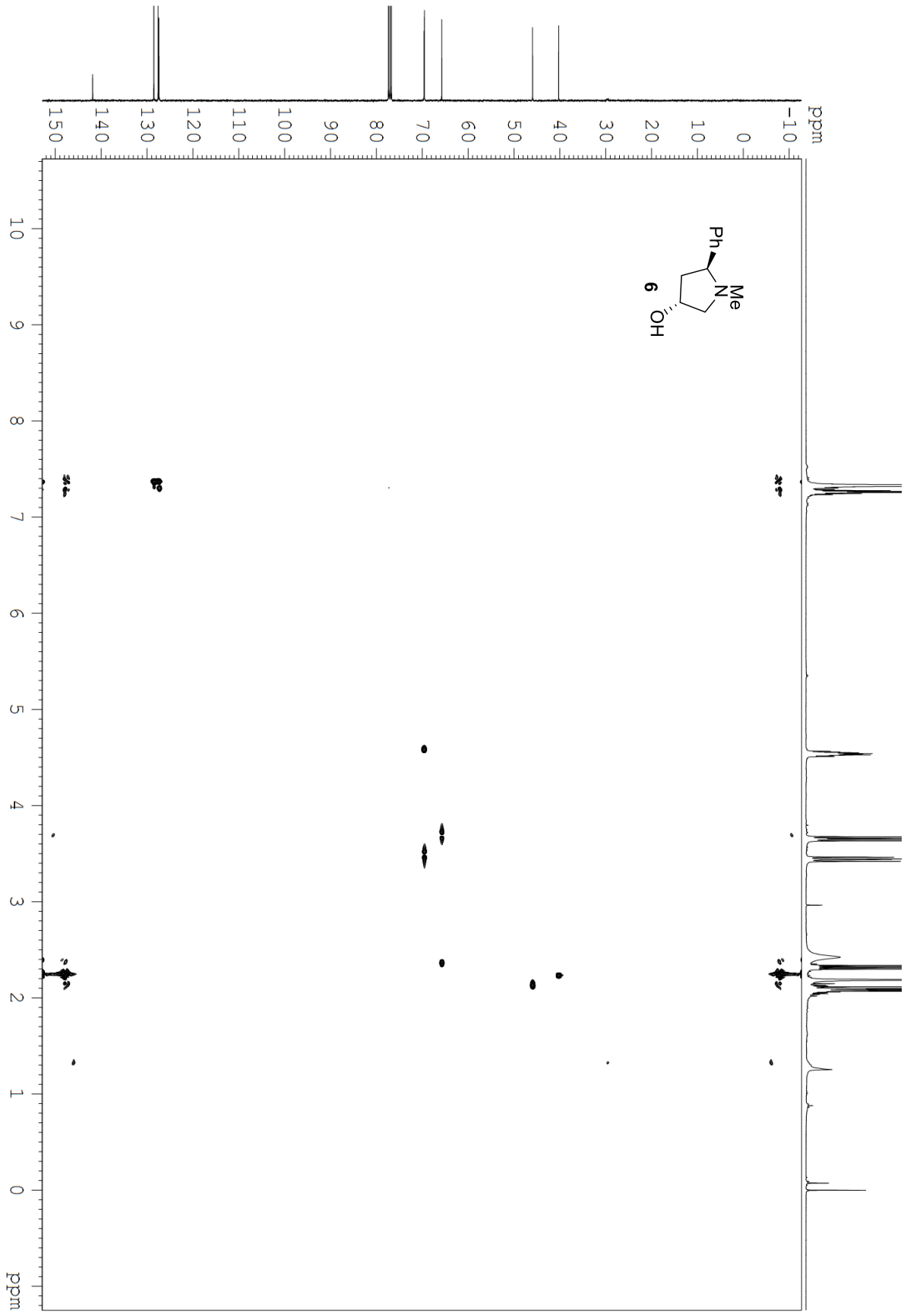
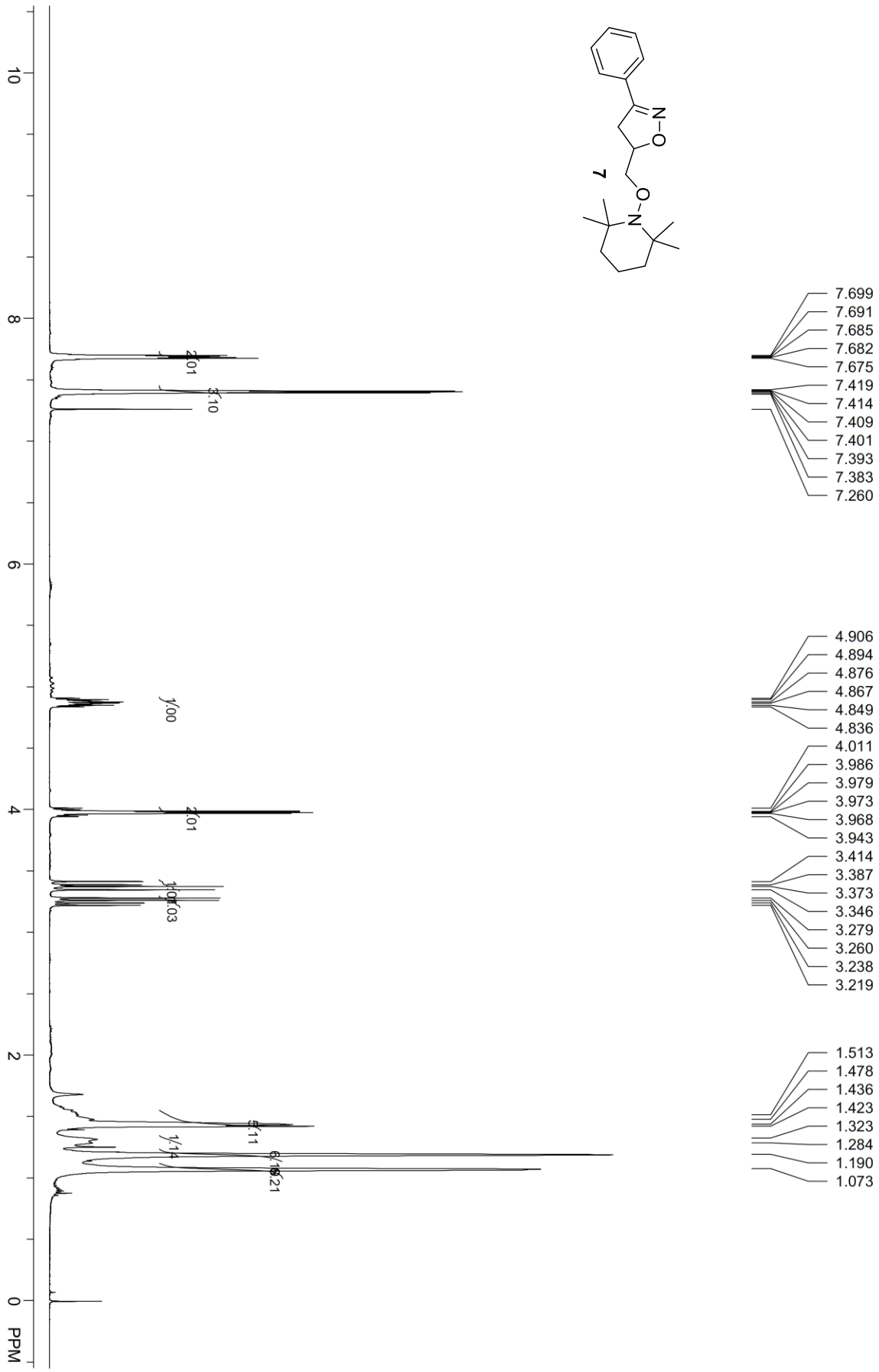
127.822
127.634
69.869
69.814
66.006
46.211
40.500
f1 (ppm)

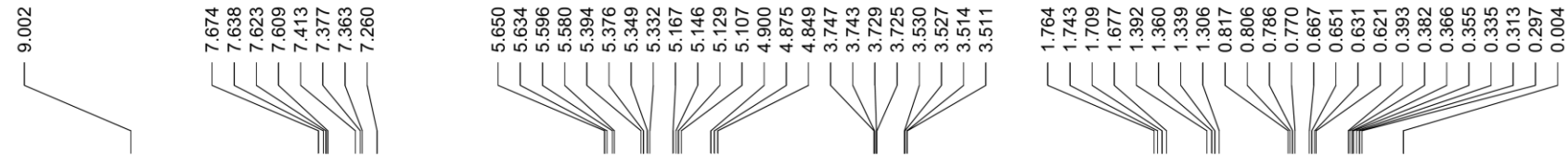
NOESY:

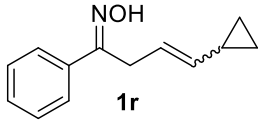


HSQC:

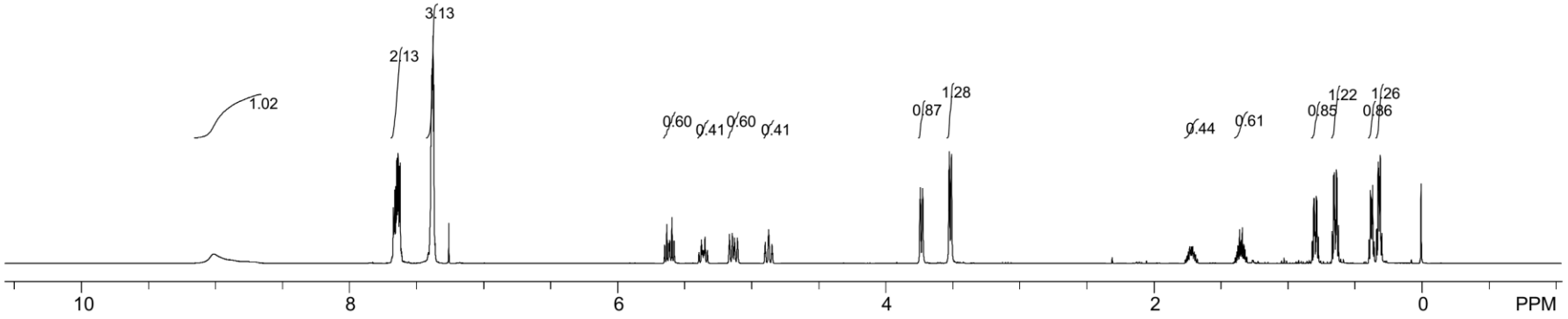


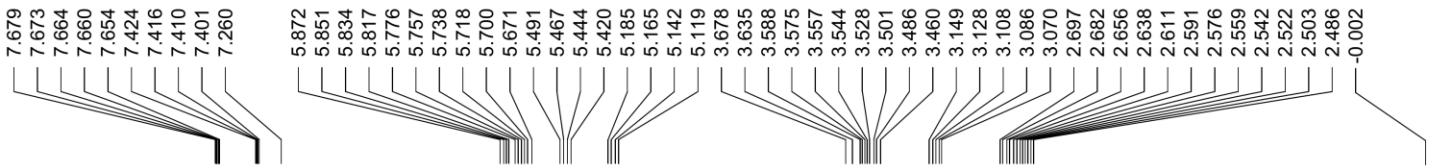

7
7.699
7.691
7.685
7.682
7.675
7.419
7.414
7.409
7.401
7.393
7.383
7.260
4.906
4.894
4.876
4.867
4.849
4.836
4.011
3.986
3.979
3.973
3.968
3.943
3.414
3.387
3.373
3.346
3.279
3.260
3.238
3.219
1.513
1.478
1.436
1.423
1.323
1.284
1.190
1.073
PPM


9.002
7.674
7.638
7.623
7.609
7.413
7.377
7.363
7.260
5.650
5.634
5.596
5.580
5.394
5.376
5.349
5.332
5.167
5.146
5.129
5.107
4.900
4.875
4.849
3.747
3.743
3.729
3.725
3.530
3.527
3.514
3.511
1.764
1.743
1.709
1.677
1.392
1.360
1.339
1.306
0.817
0.806
0.786
0.770
0.667
0.651
0.631
0.621
0.393
0.382
0.366
0.355
0.335
0.313
0.297
0.004


NOH

1r


1.02
2.13
3.13
0.60
0.41
0.60
0.41
0.87
1.28
0.44
0.61
0.85
1.22
0.86
1.26
10
8
6
4
2
0
PPM


7.679
7.673
7.664
7.660
7.654
7.424
7.416
7.410
7.401
7.260
5.872
5.851
5.834
5.817
5.776
5.757
5.738
5.718
5.700
5.671
5.491
5.467
5.444
5.420
5.185
5.165
5.142
5.119
3.678
3.635
3.588
3.575
3.557
3.544
3.528
3.501
3.486
3.460
3.149
3.128
3.108
3.086
3.070
2.697
2.682
2.656
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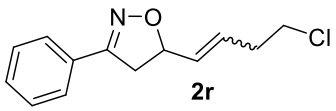
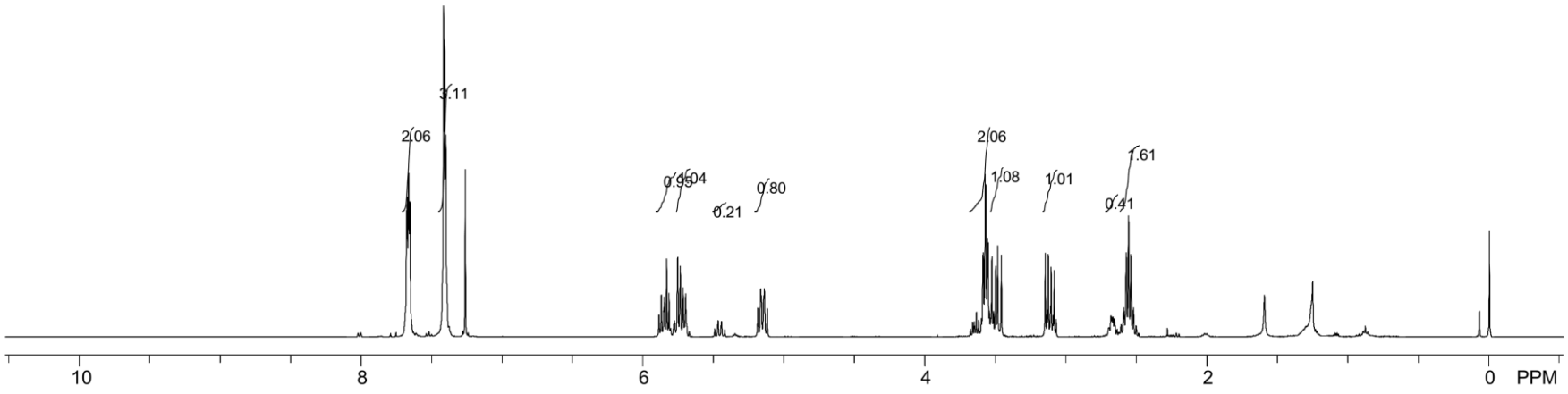
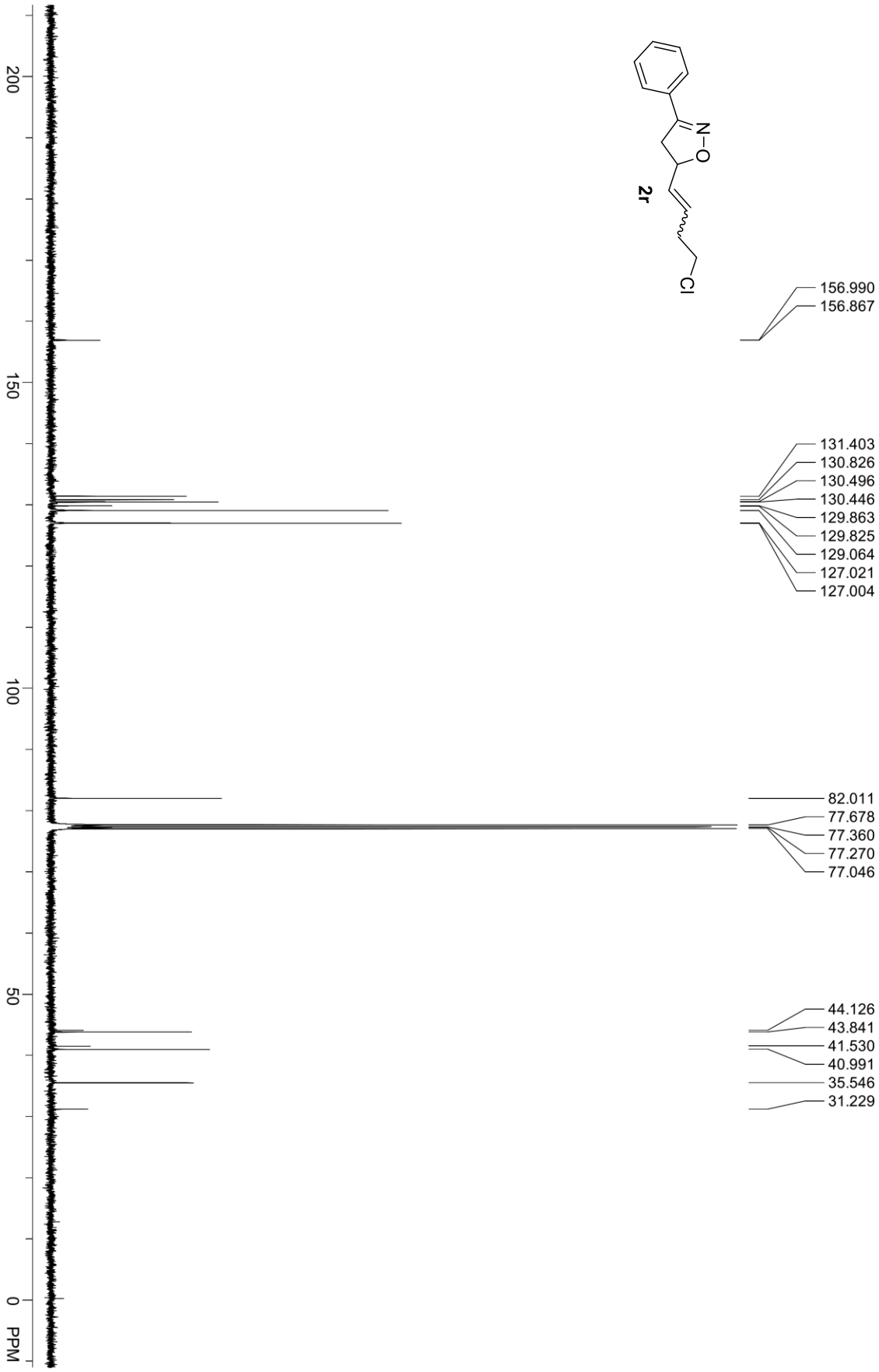
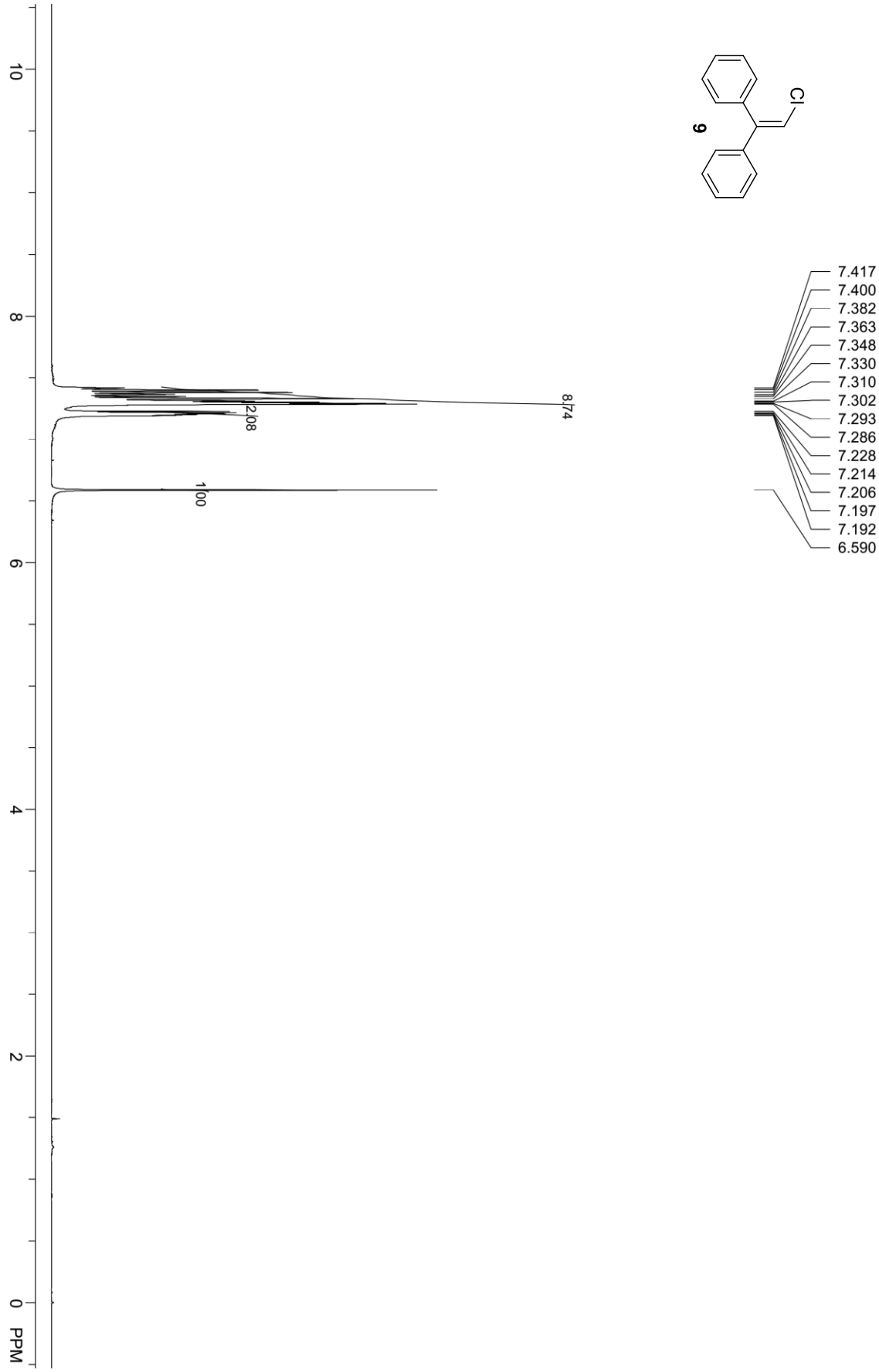
2.576
2.559
2.542
2.522
2.503
2.486
-0.002

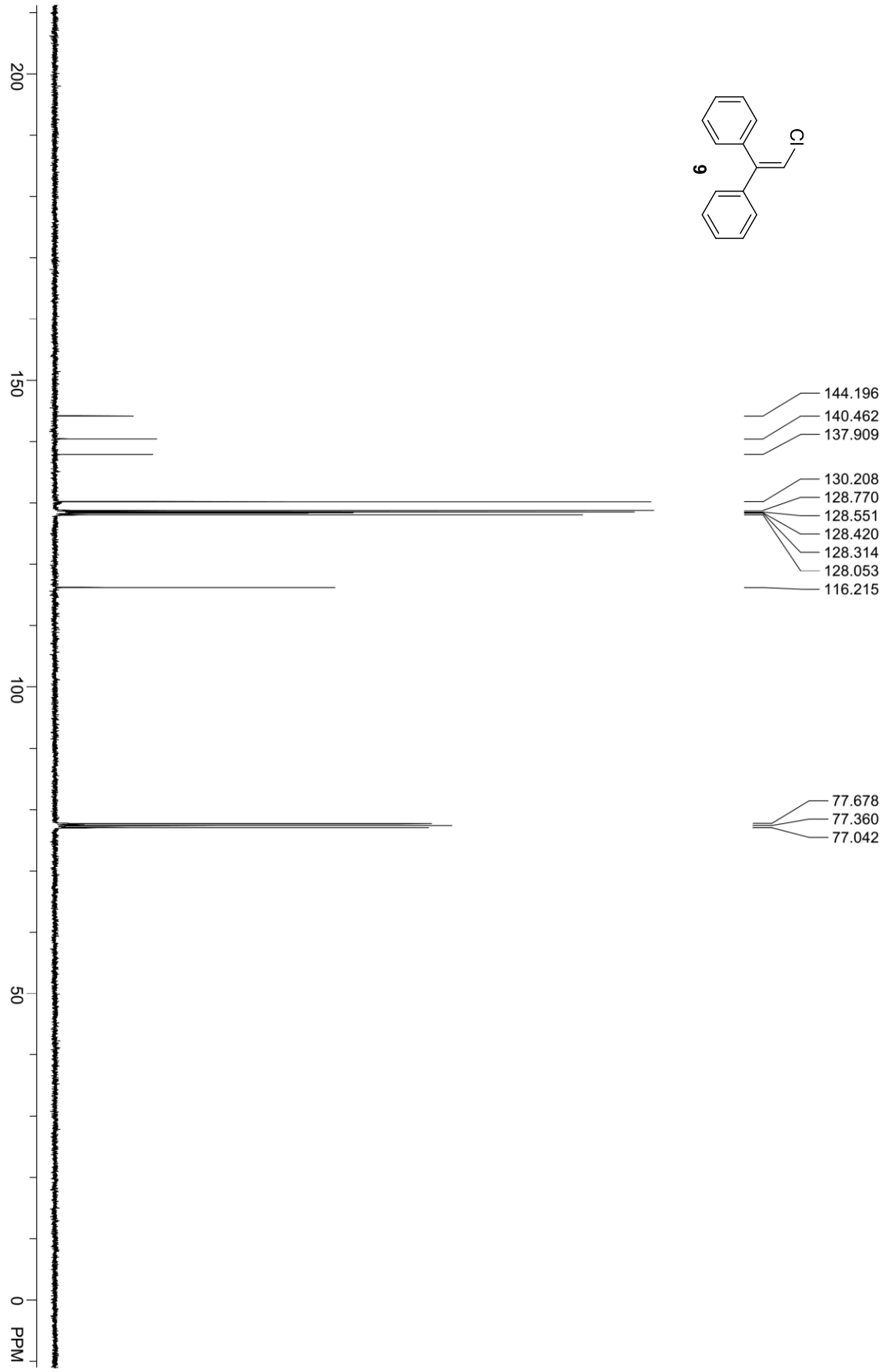

N
O
Cl

2r


3.11
2.06
0.95
1.04
0.21
0.80
2.06
1.08
1.01
1.61
0.91
10
8
6
4
2
0
PPM


2r
N
O
Cl
156.990
156.867
131.403
130.826
130.496
130.446
129.863
129.825
129.064
127.021
127.004
82.011
77.678
77.360
77.270
77.046
44.126
43.841
41.530
40.991
35.546
31.229
200
150
100
50
0
PPM


Cl
9
7.417
7.400
7.382
7.363
7.348
7.330
7.310
7.302
7.293
7.286
7.228
7.214
7.206
7.197
7.192
6.590
8.74
2.08
1.00
10
8
6
4
2
0
PPM


200
150
100
50
0
PPM
6
Cl
144.196
140.462
137.909
130.208
128.770
128.551
128.420
128.314
128.053
116.215
77.678
77.360
77.042