Electronic Supplementary Information for

(*E*)-Specific Direct Julia-Olefination of Aryl Alcohols without Extra Reducing Agents Promoted by Bases

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Contents

1. General information

Solvents were pre-dried over activated 4 Å molecular sieves and heated to reflux over sodium (toluene, THF, Et_2O) or calcium hydride ($CHCl_3$, DCM) under a nitrogen atmosphere and collected by distillation. ICP-AES and elemental analysis were tested by the services at University of Science and Technology of China. ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer. Chemical shifts are reported in δ units relative to $CHCl_3$ [^1H δ = 7.26, ^{13}C δ = 77.36]. All alcohols and sulfones (**2a**, **2b**, **2d**-**2e**) were purchased from commercial sources. Sulfone **2f** was prepared by literature procedure.[1]

2. Experiments

2.1. Screening reaction conditions (Table 1)

To the solution of methyl phenyl sulfone (1 mmol) in benzyl alcohol (1 mL, 10 mmol) in a 25 mL Schlenk tube was added 1.5 mmol of the base [*t*BuOK, *t*BuONa, LiHMDS, KOH, MeONa, *n*BuLi, and NaH (60% dispersion in mineral oil, 0.5-2.5 mmol)]. The Schlenk tube was equipped with a finger-shape condenser and the homogeneous reaction mixture was stirred under argon at 135 ℃ (oil bath) for the desired time. After cooling to room temperature, the reaction mixture was filtrated through a thin pad of silica gel, followed by washing with light petroleum ether (b.p. 30-60) and dichloromethane. After concentrated by a rotary evaporator under reduced pressure, the crude reaction residue was examined on ^1H

NMR spectrometer to determine the conversion using 1,4-dioxane and dimethylsulfoxide as internal standards.

Table S1. Sreening reaction conditions (some data shown in Table 1 were omitted here)

NaH (equiv·)	temp./°C	time (h)	conv.(%)[a]
0.5	130	24	33
1.0	130	24	71
1.5	130	24	78
2.0	130	24	74
2.5	130	24	82
2.5	135	24	85
2.5	135	12	82
2.5	135	8	85
2.5	135	5	87
3.0	135	5	87

[a] Conversions were determined by ^{1}H NMR (400 MHz) using dioxane and dimethylsulfoxide as the internal standards.

2.2. Isotope labelling experiments (Scheme 1)

Sulfone **2a** (0.5 mmol) was weighed into a Schlenk tube. After dried *in vacuo* for 15 min, $PhCH_2OH$ **1a** (or **1a-2D,** $PhCD_2OH$**)** (5 mmol) and 8-Methylquinoline (0.33 mmol, 45.8 μL) (as internal standard) were added. The reaction mixture was vigorously stirred under an argon atmosphere at 135 ℃ (oil bath). After solid disappeared, NaH (60% dispersion in mineral oil, 100 mg, 2.5 equiv) was added. The Schlenk tube was equipped with a finger-shape condenser and the mixture was stirred at 135 ℃ for 30 min. After cooling to room temperature, the reaction mixture was diluted with dichloromethane and analyzed by GC. The reactions for **1a** and **1a-2D** were parallelly done and the k_H/k_D was 2.7:1.

2.3. Reaction of 6a to 3a with or without 1a (Scheme 3, Eq. 2)

Preparation of β-Phenyl-β-hydroxyethyl Phenyl Sulfone (**6a**): A solution of methyl phenyl sulfone (1.56 g, 10 mmol) in 15 mL toluene was added to methylmagnesium bromide (4.7 mL, 14 mmol, 3 M in Et_2O) over 10 minutes. The mixture was stirred for 20 minutes at RT and then heated rapidly to 80 ℃ for 3 minutes. After cooling quickly back to RT in a water bath, a solution of benzaldehyde in 5 mL toluene was added into the mixture and stirred for one additional hour at RT. Aqueous hydrochloric acid solution 20 mL (1 M) was added, and then extracted with ethyl acetate (2 × 30 mL). The purification on silica gel by column chromatography gave the pure product **6a** as a white solid (1.36 g, 52% yield). **^{1}H NMR** (400

MHz, $CDCl_3$) δ 7.99 - 7.96 (m, 2H), 7.67 - 7.62 (m, 3H), 7.70 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.62 - 7.58 (m, 2H), 7.35 - 7.26 (m, 5H), 5.29 (dt, *J* = 10.0, 2.0 Hz, 1 H), 3.67 (d, *J* = 2.0 Hz, 1 H), 3.51 (dd, *J* = 14.2, 10.2 Hz, 1 H), 3.66 (dd, *J* = 14.4, 2.0 Hz, 1 H).[2,3]

To the solution of **6a** (131 mg, 0.5 mmol) in benzyl alcohol (0.5 mL, 5 mmol) and toluene (0.3 mL)was added NaH (60% dispersion in mineral oil, 50 mg, 2.5 equiv) under argon atmosphere at 135 ℃. The Schlenk tube was equipped with a finger-shape condenser and the mixture was stirred for 21 hours. After cooling to room temperature, the reaction mixture was filtrated through a thin pad of silica gel, followed by washing with light petroleum ether/ethyl acetate. After concentrated by a rotary evaporator under reduced pressure, the crude reaction residue was examined on ^{1}H NMR spectrometer to determine conversion using CH_3NO_3 and *t*BuOMe as internal standards (91% styrene). In the experiment without benzyl alcohol got only 1% styrene.

2.4. Reaction of 9 to 3a (Scheme 3, Eq. 4)

Preparation of **9**: To a suspension of sodium benzenesulfonate (4.92 g, 30.0 mmol, 3.00 equiv) and NaOAc (1.23 g, 15.0 mmol, 1.50 equiv) in MeCN (40 mL) was added styrene (1.16 mL, 10.0 mmol, 1.00 equiv) and iodine (3.81 g, 15.0 mmol, 1.50 equiv). The mixture was heated to reflux for 1 h before cooling down and the excess iodine was quenched with 10% aq. sodium thiosulfate. Sat. aq. $NaHCO_3$ was added and the product extracted into EtOAc (20 mL x 3). The combined organic phases were washed with H_2O, brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography gave the pure product **9** as a white solid (2.0 g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 - 7.95 (m, 2H), 7.70 (d, *J* = 15.4 Hz, 1H), 7.66 - 7.62 (m, 1H), 7.59 - 7.55 (m, 2H), 7.50 (dd, *J* = 10.0, 2.0 Hz, 2 H), 7.45 - 7.39 (m, 3 H).[25]

To the solution of **9** (244 mg, 0.5 mmol) in benzyl alcohol (1.0 mL, 5 mmol) and toluene (1 mL) was added NaH (60% dispersion in mineral oil, 100 mg, 2.5 equiv) under argon atmosphere at 135 ℃. The Schlenk tube was equipped with a finger-shape condenser and the mixture was stirred for 5 hours. After cooling to room temperature, the reaction mixture was filtrated through a thin pad of silica gel, followed by washing with light petroleum ether/ethyl acetate. After concentrated by a rotary evaporator under reduced pressure, the crude reaction residue was examined on ^{1}H NMR spectrometer to determine conversion using CH_3NO_3 and *t*BuOMe as internal standards (64% styrene).

2.5. Reaction of 10 to 3a (Scheme 3, Eq. 5)

Preparation of **10**: Under argon, a 100 mL round-bottom flask was charged with sodium benzenesulfonate (3.28 g, 20.0 mmol) and dry ethanol (40 mL). To the stirred solution, 2-phenylethyl bromide (3.70g, 20.1 mmol) was added over 10 minutes *via* a syringe. The reaction mixture was refluxed for 3 hours and then

cooled down to 25 ℃. Ethanol was removed on a rotary evaporator and water (20 mL) was added to the residue. The aqueous layer was extracted with diethyl ether (20 mL x 3) and concentrated on a rotary evaporator. The residue was purified by silica gel flash chromatography (5:1 petroleum/ethyl acetate) to give the desired product **10** as a white solid (3.35 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 - 7.93 (m, 2H), 7.69 - 7.65 (m, 1H), 7.60 - 7.56 (m, 2H), 7.28 - 7.24 (m, 2H), 7.22 - 7.18 (m, 1 H), 7.12 - 7.10 (m, 2 H), 3.38 - 3.34 (m, 2H), 3.08 - 3.03 (m, 2H).[26]

To the solution of **10** (244 mg, 0.5 mmol) in benzyl alcohol (1.0 mL, 5 mmol) and toluene (1 mL)was added NaH (60% dispersion in mineral oil, 100 mg, 2.5 equiv) under argon atmosphere at 135 ℃. The Schlenk tube was equipped with a finger-shape condenser and the mixture was stirred for 5 hours. After cooling to room temperature, the reaction mixture was filtrated through a thin pad of silica gel, followed by washing with light petroleum ether/ethyl acetate. After concentrated by a rotary evaporator under reduced pressure, the crude reaction residue was examined on ^{1}H NMR spectrometer to determine conversion using CH_3NO_3 and *t*BuOMe as internal standards (91% styrene).

2.6. ICP-AES analysis of NaH and reaction mixture for trace metals.

The experiments was carried out on inductively coupled plasma atomic emission spectrometer (Optima 7300DV, Perkin Elmer Corporation) [N.D. refers to **N**ot **D**etected].

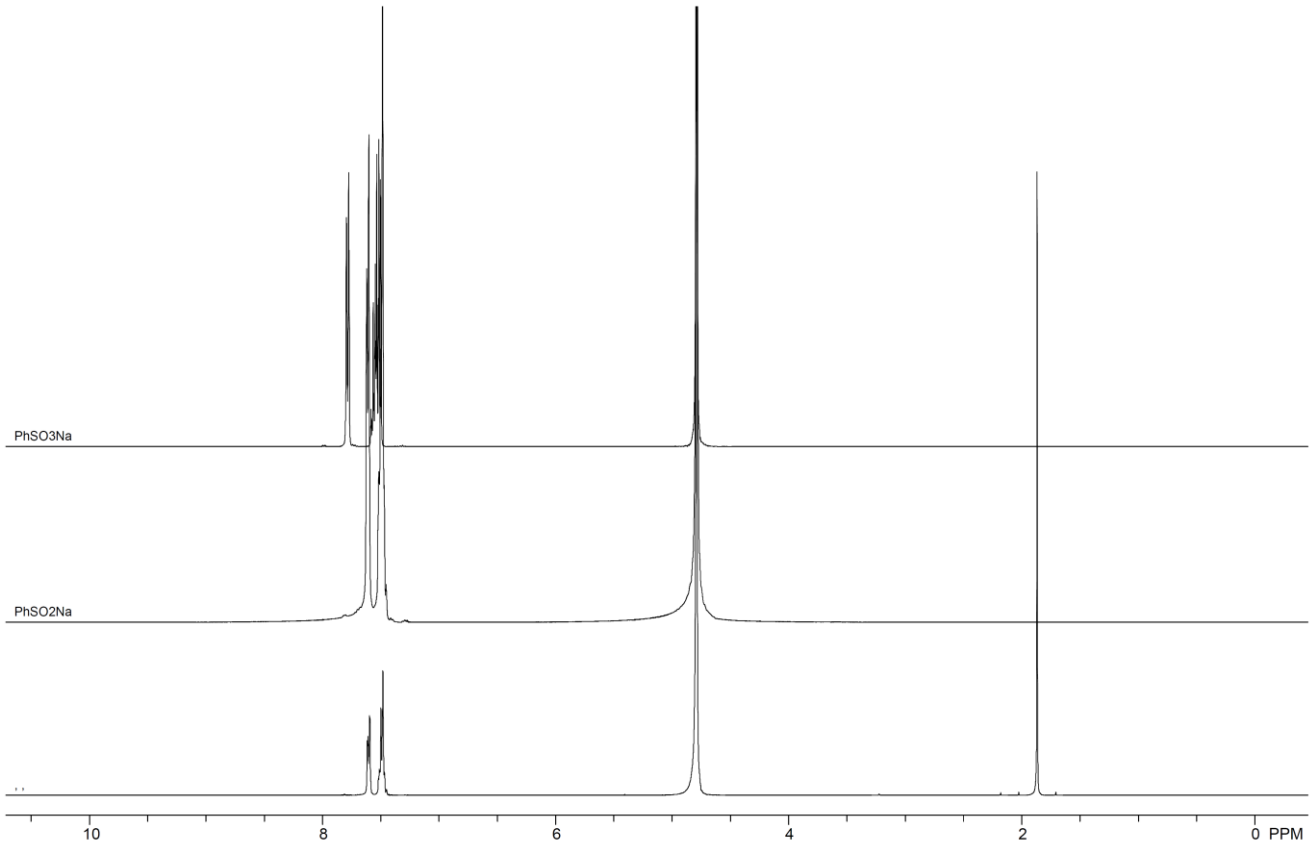
metals	content of elements (μg/g)	
	NaH	reaction mixture
Pd	N.D.	N.D.
Ru	N.D.	N.D.
Rh	N.D.	N.D.
Ir	N.D.	N.D.
Pt	N.D.	N.D.
Cu	N.D.	N.D.
Fe	N.D.	N.D.
Al	0.008	0.010
Ni	0.01	N.D.
Zn	N.D.	N.D.
Co	N.D.	N.D.
Sn	0.002	N.D.

2.7. Identification of $PhSO_2Na$

The precipitate generated in the later stage of the reaction mixture was collected by filtration and

washing with DCM quickly. The white solid was kept under argon and examined by ^{1}H NMR and HRMS (anion). The results show that the precipitate was $PhSO_2Na$ (Note: Exposure in air will result in the formation of $PhSO_3Na$). **^{1}H NMR** (400 MHz, D_2O): δ 7.62 - 7.60 (m, 2H), 7.52 -7.47 (m, 3H); HRMS (ESI) calcd for $C_6H_5O_2S^-$ 141.0005, found 141.0016.

The comparison of the precipitate with standard $PhSO_2Na$ and $PhSO_3Na$ (^{1}H NMR):

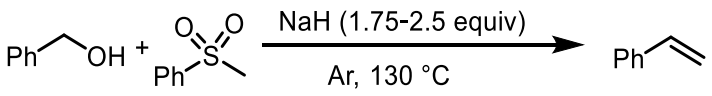


2.8. Exploring the transformation between $PhSO_3Na$ and $PhSO_2Na$

$PhSO_3Na$ (1 mmol) was weighed into a 25 mL Schlenk tube. After dried *in vacuo* for 15 min, benzyl alcohol (1mL, 10 mmol) was added under argon atmosphere. NaH (60% dispersion in mineral oil N/A, 100 mg, 2.5 equiv) was added. The Schlenk tube was equipped with a finger-shape condenser and the mixture was stirred under argon for 24 h at 135 ℃. After cooling to room temperature, the reaction mixture was filtrated to collect solid, followed by washing with dichloromethane. The solid was still $PhSO_3Na$ and no $PhSO_2Na$ was observed.

When the mixture of $PhSO_2Na$ and $PhCH_2OH$ was exposed in air for hours, $PhSO_3Na$ was observed. Consequently, $PhSO_3Na$ probably formed from the oxidation of $PhSO_2Na$ in the work-up procedure.

2.9. Experiments for kinetic study (Fig. 1A and 1B)



All data were collected by GC analysis using 8-Methylquinoline as an internal standard. The initial rates in **Fig. S5** were obtained as the slopes of time zero.

2.9.1. Initial rate v.s. the amount of base (NaH)

2a (2 mmol, 312.4 mg) was weighed into a 25 mL Schlenk tube. After dried *in vacuo* for 15 min, 2 mL of **1a** and 8-methylquinoline (2 mmol, 272.2 μL) (as an internal standard) were added. The reaction mixture was vigorously stirred (350 rpm) at 130 ℃. After solids dissolved, NaH (60% dispersion in mineral oil, 1.75 - 2.5 equiv, 140 - 200 mg) was added. At each sampling time, 10 μL reaction mixture was sampled from the Schlenk tube and detected by GC. The production of styrene was determined by GC using 8-Methylquinoline as an internal standard. The initial rates were calculated from the slopes of time zero from the curves of [styrene] - time. The results were demonstrated in Fig. S1-5 and Table S2.

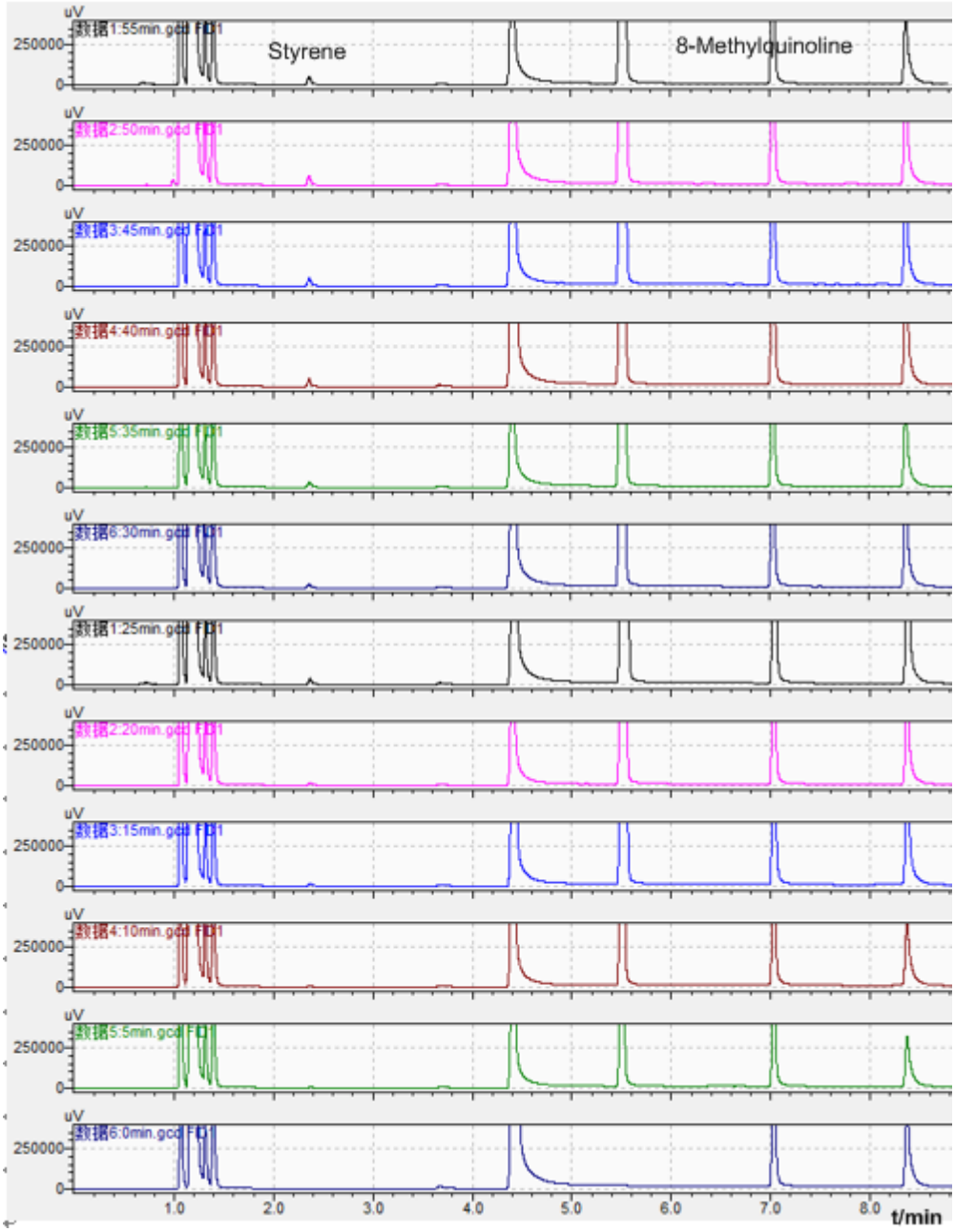


Figure S1. Conditions: **2a** (2 mmol, 312.4 mg), **1a** (19.2 mmol, 2 mL), NaH (60% dispersion in mineral oil, **1.75 equiv**, 140 mg), 130 ºC, 8-methylquinoline (2 mmol, 272.2 μL) as an internal standard.

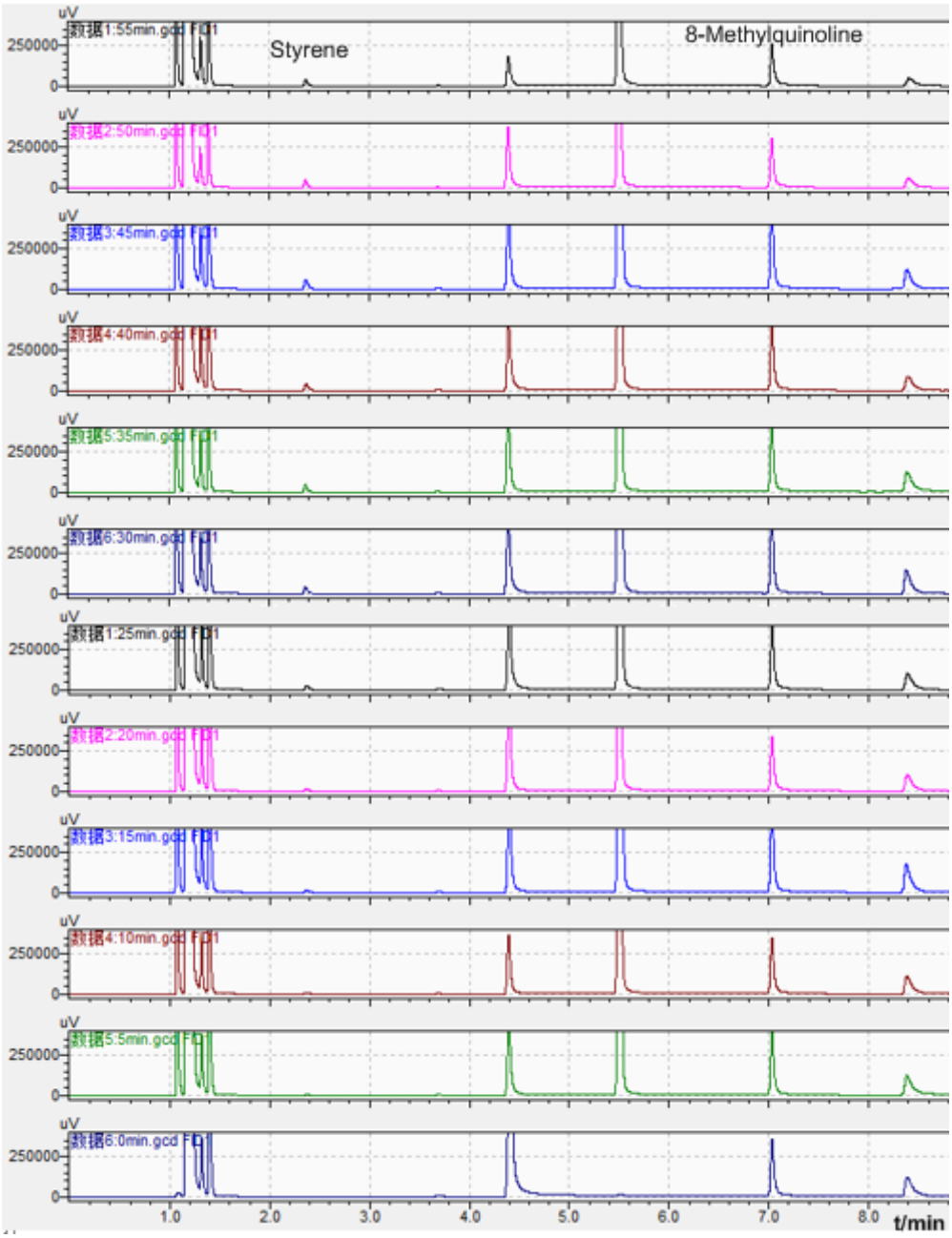


Figure S2. Conditions: **2a** (2 mmol, 312.4 mg), **1a** (19.2 mmol, 2 mL), NaH (60% dispersion in mineral oil, **2.0 equiv**, 160 mg), 130 ºC, 8-methylquinoline (2 mmol, 272.2 μL) as an internal standard.

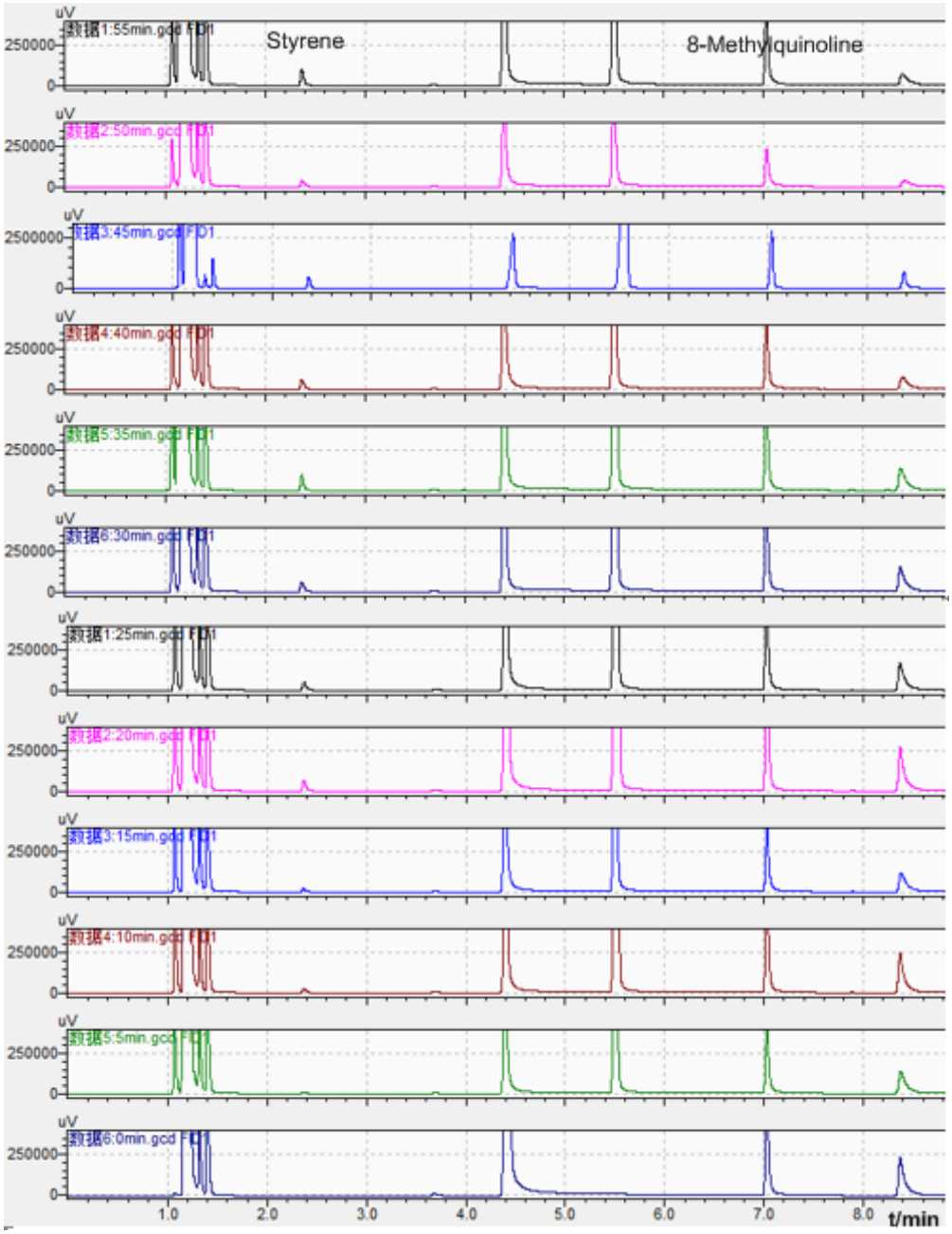


Figure S3. Conditions: **2a** (2 mmol, 312.4 mg), **1a** (19.2 mmol, 2 mL), NaH (60% dispersion in mineral oil, **2.25 equiv**, 180 mg), 130 ºC, 8-methylquinoline (2 mmol, 272.2 μL) as an internal standard.

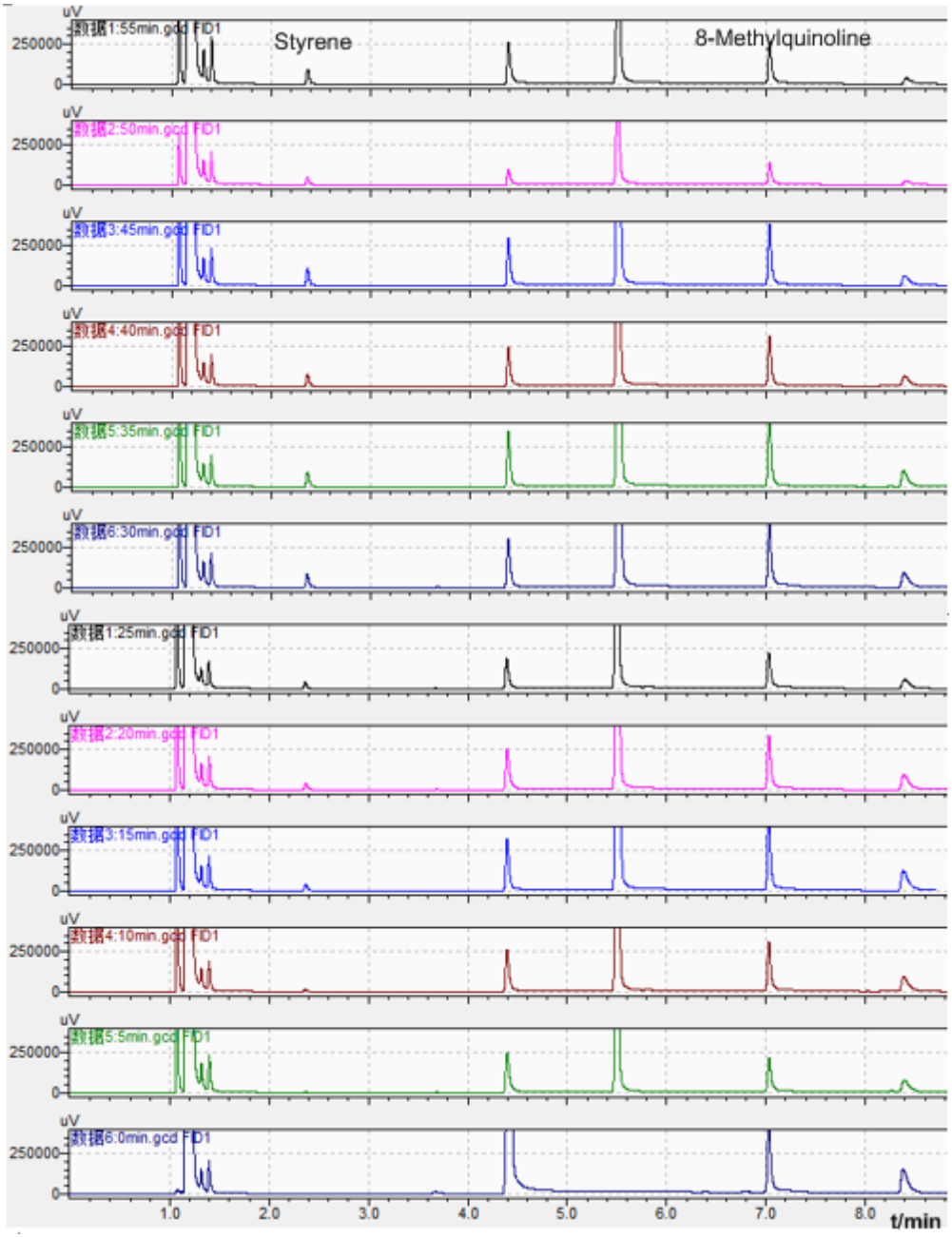


Figure S4. Conditions: **2a** (2 mmol, 312.4 mg), **1a** (19.2 mmol, 2 mL), NaH (60% dispersion in mineral oil, **2.5 equiv**, 200 mg), 130 ºC, 8-methylquinoline (2 mmol, 272.2 μL) as an internal standard.

Table S2. [Styrene] *v.s.* time.[a]

Time (min)	Styrene (M)			
	1.75 equiv	2.0 equiv	2.25 equiv	2.75 equiv
0	0.000	0.000	0.000	0.000
5	0.006	0.016	0.027	0.012
10	0.010	0.034	0.044	0.037

15	0.014	0.041	0.064	0.079
20	0.018	0.052	0.093	0.117
25	0.023	0.070	0.103	0.148
30	0.025	0.087	0.129	0.185
35	0.030	0.108	0.159	0.201
40	0.030	0.123	0.176	0.229
45	0.038	0.124	0.194	0.257
50	0.040	0.141	0.187	0.286
55	0.045	0.153	0.221	0.305

[a] Conditions: **2a** (2 mmol, 312.4 mg), **1a** (19.2 mmol, 2 mL), NaH (60% dispersion in mineral oil, 1.75 - 2.5 equiv, 140 - 200 mg), 130 °C, 8-methylquinoline (2 mmol, 272.2 μL) as an internal standard.

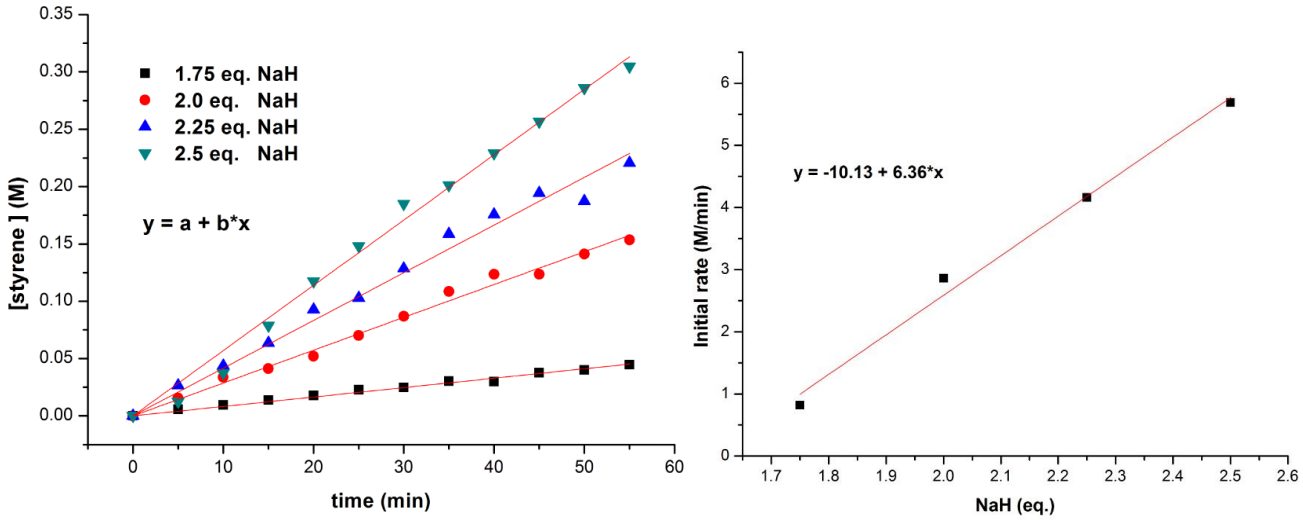


Figure S5. Polts of [Styrene] *v.s.* time using NaH (L) and dependence of the initial rate on NaH (R).

2.9.2. Initial rate v.s. the amount of sulfone 2a

Methyl phenyl sulfone **2a** (1.6 - 2.8 mmol, 249.9 - 437.4 mg) was weighed into a 25 mL Schlenk tube. After dried *in vacuo* for 15 min, 2 mL of **1a** and 8-methylquinoline (2 mmol, 272.2 μL) (as an internal standard) were added. The reaction mixture was vigorously stirred (350 rpm) at 130 ℃. After solids dissolved, NaH (60% dispersion in mineral oil, 5 mmol, 200 mg) was added. At each sampling time,

10 μL reaction mixture was sampled from the Schlenk tube and detected by GC. The production of styrene was determined by GC using 8-methylquinoline as an internal standard. The initial rates were calculated from the slopes of time zero. The results were demonstrated in Fig. S6-10 and Table S3.

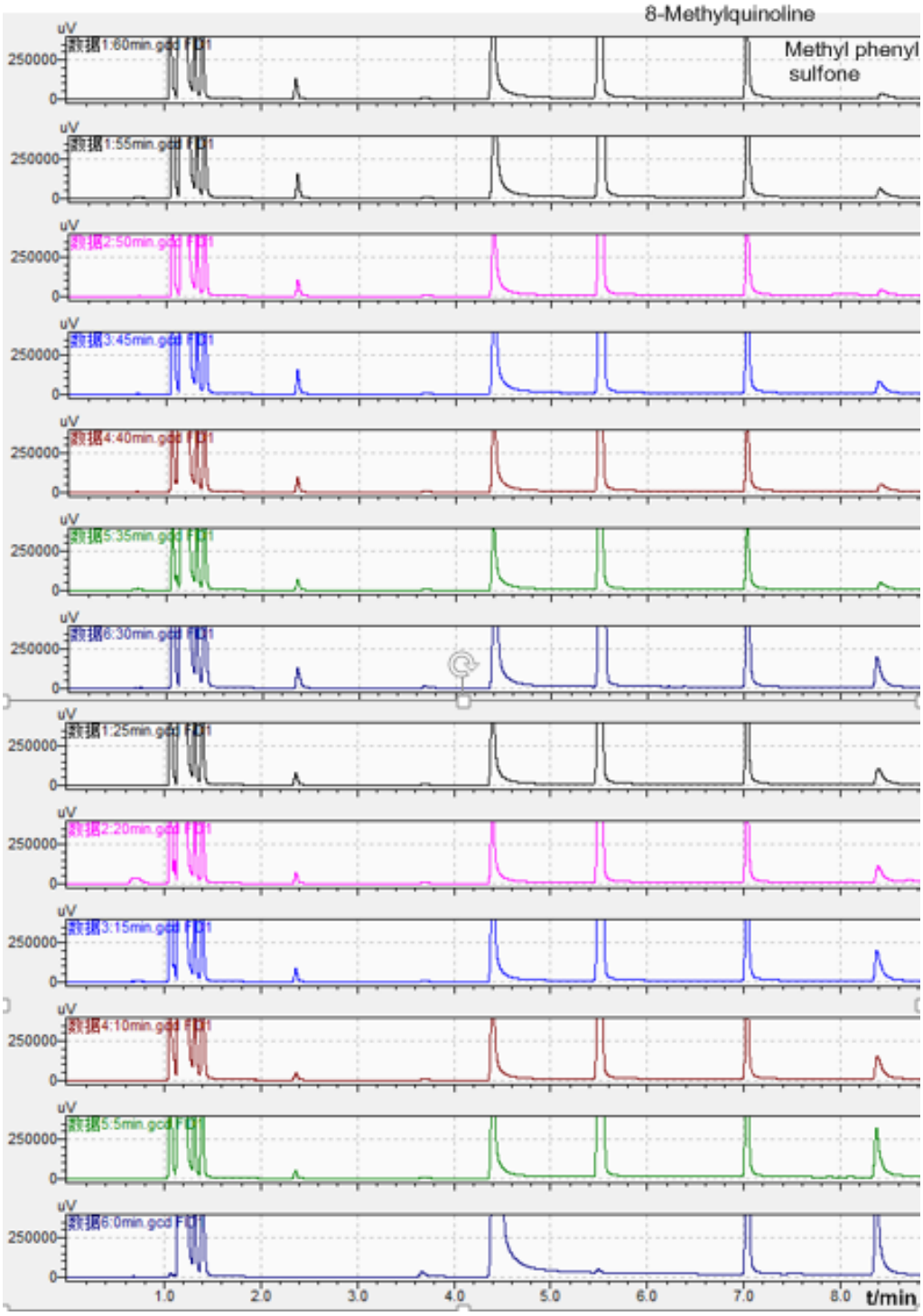


Figure S6. Conditions: Methyl phenyl sulfone (**1.6 mmol**, 249.9 mg), **1a** (19.2 mmol, 2 mL), NaH (60% dispersion in mineral oil, 5 mmol, 200 mg), 130 °C, 8-methylquinoline (2 mmol, 272.2 μL) as an internal standard.

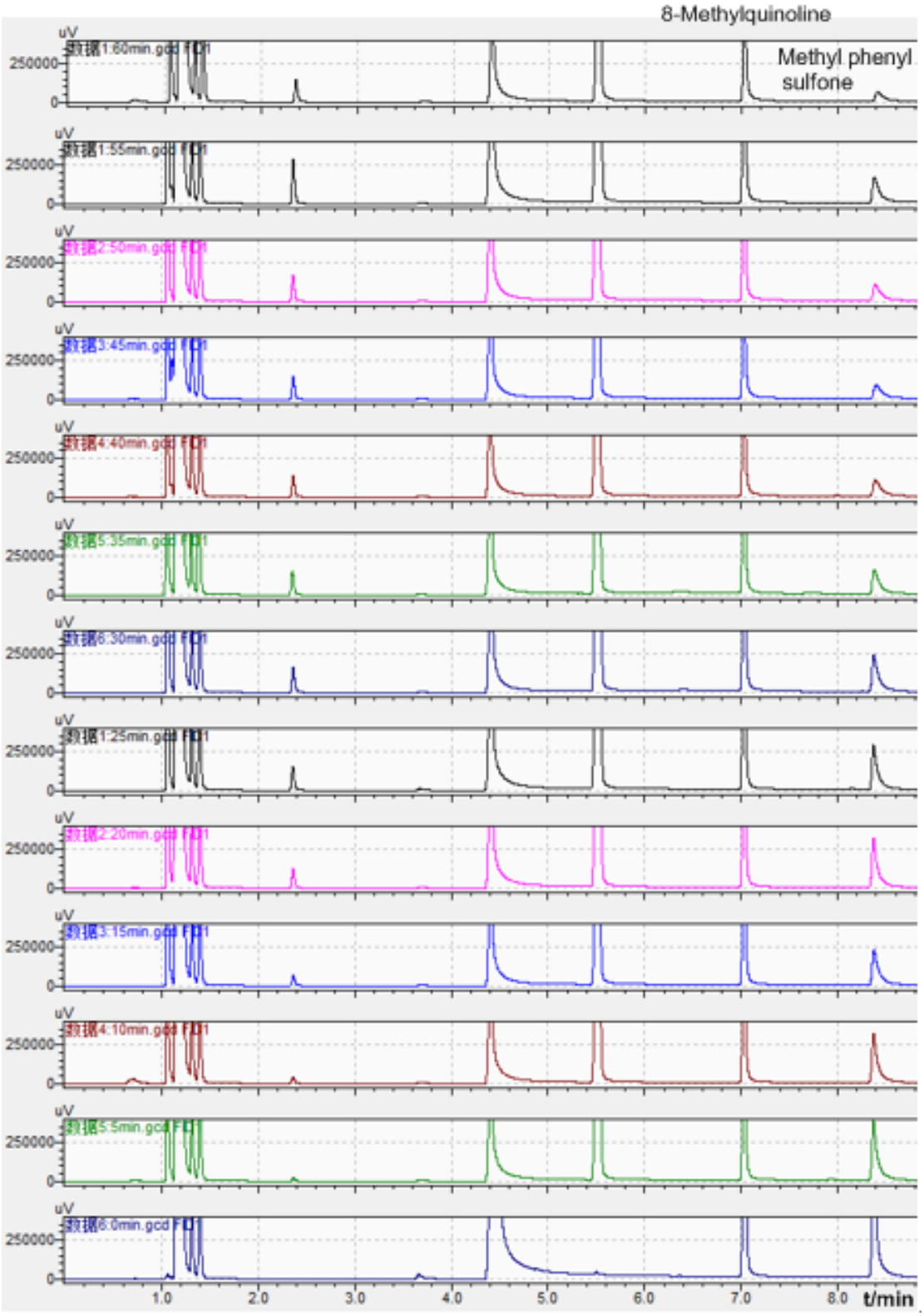


Figure S7. Conditions: Methyl phenyl sulfone (**2.0 mmol**, 312.4 mg), **1a** (19.2 mmol, 2 mL), NaH (60% dispersion in mineral oil, 5 mmol, 200 mg), 130 ºC, 8-methylquinoline (2 mmol, 272.2 µL) as an internal standard.

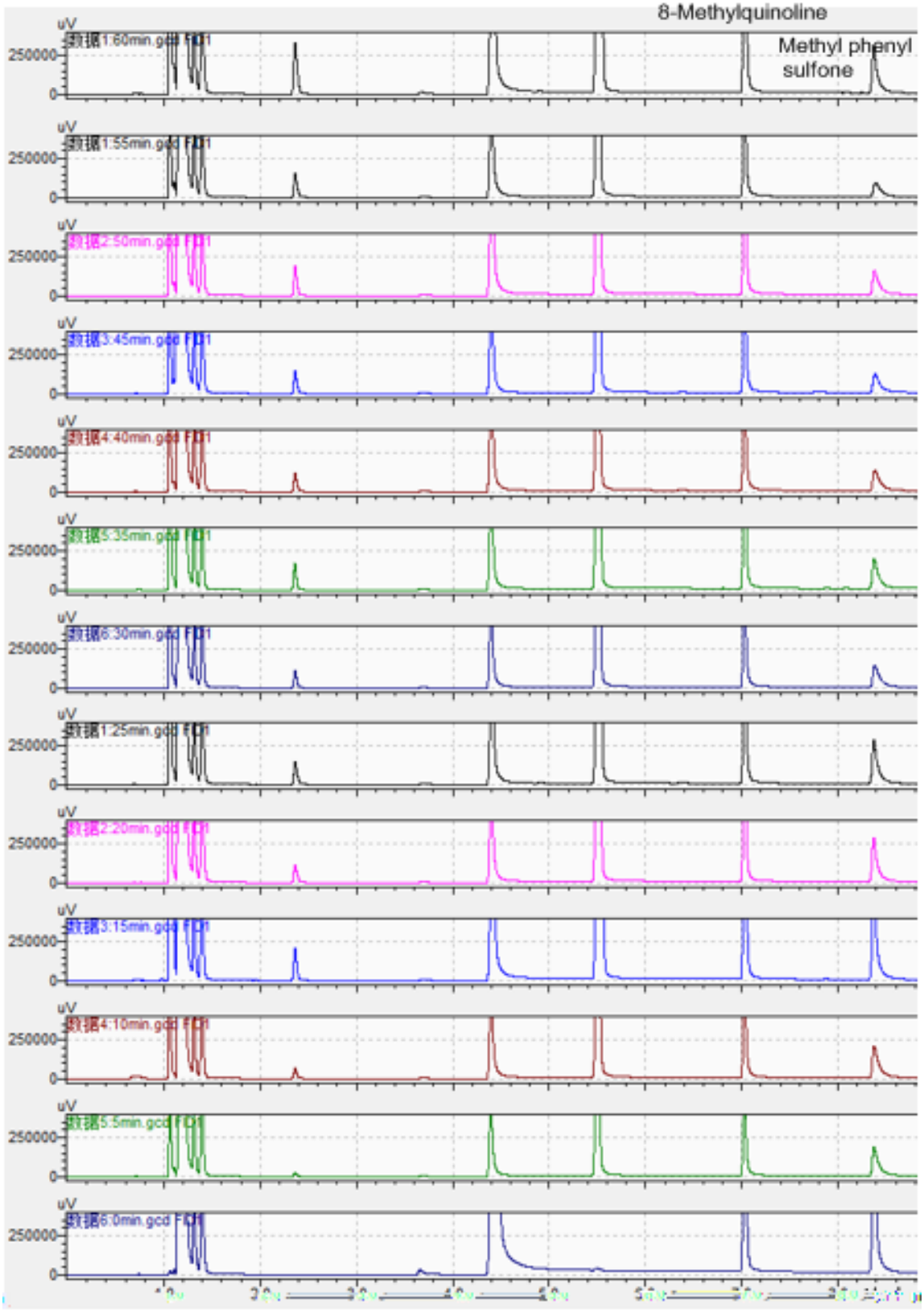


Figure S8. Conditions: Methyl phenyl sulfone (**2.4 mmol**, 374.9 mg), **1a** (19.2 mmol, 2 mL), NaH (60% dispersion in mineral oil, 5 mmol, 200 mg), 130 ^{o}C, 8-methylquinoline (2 mmol, 272.2 μL) as an internal standard.

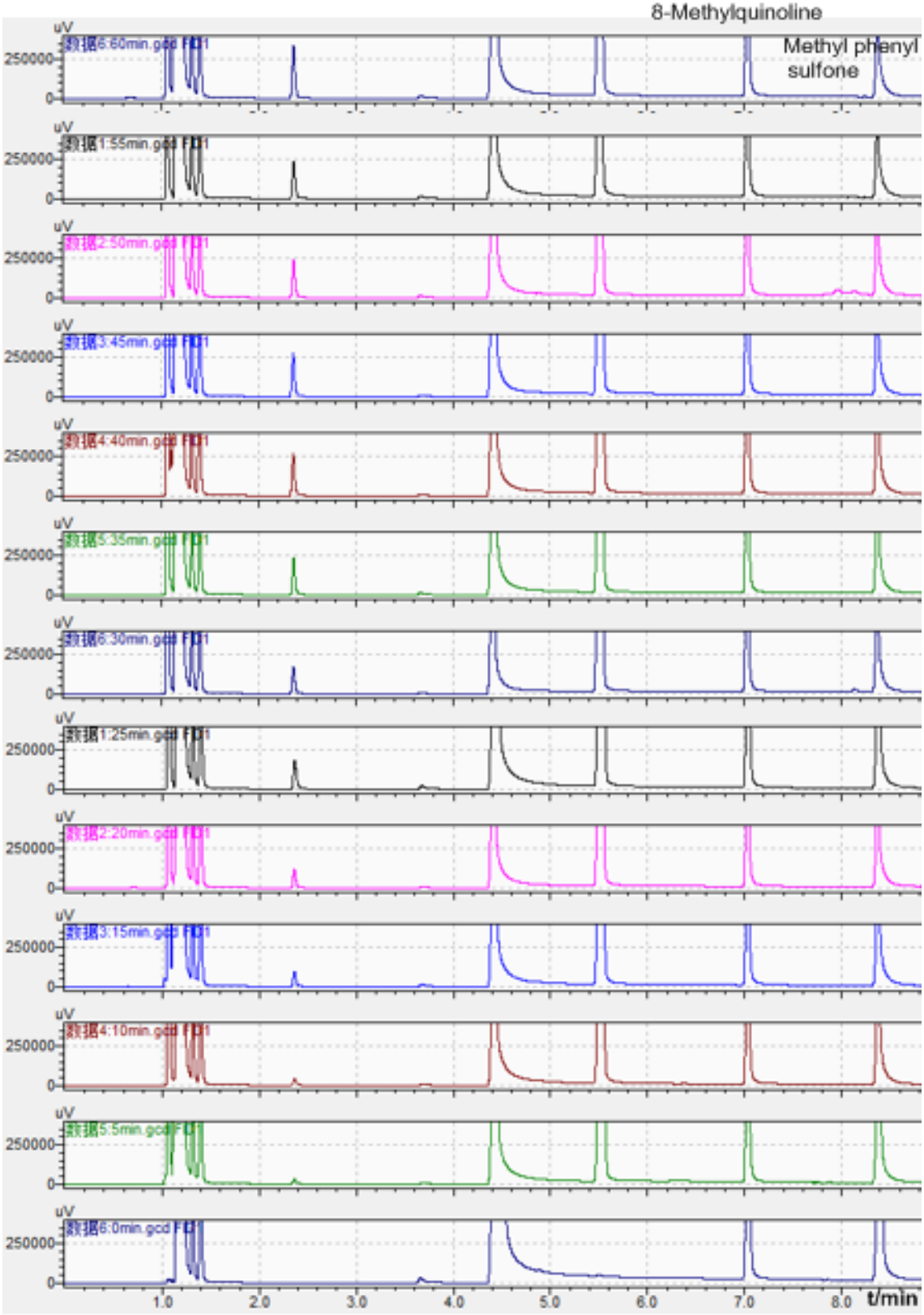


Figure S9. Conditions: Methyl phenyl sulfone (**2.8 mmol**, 437.4 mg), **1a** (19.2 mmol, 2 mL), NaH (60% dispersion in mineral oil, 5 mmol, 200 mg), 130 ºC, 8-methylquinoline (2 mmol, 272.2 µL) as an internal standard.

Table S3. [Methyl phenyl sulfone] *v.s.* time.[a]

Time (min)	Methyl phenyl sulfone (M)			
	0.8 M	1.0 M	1.2 M	1.4 M
0	0.800	1.000	1.200	1.400
5	0.682	0.883	1.032	1.284
10	0.586	0.783	0.950	1.205
15	0.526	0.693	0.868	1.099
20	0.453	0.635	0.815	1.010
25	0.404	0.530	0.712	0.952
30	0.359	0.491	0.707	0.926
35	0.282	0.454	0.631	0.825
40	0.257	0.385	0.599	0.791
45	0.212	0.345	0.534	0.755
50	0.174	0.321	0.501	0.710
55	0.158	0.291	0.452	0.685
60	0.126	0.268	0.439	0.613

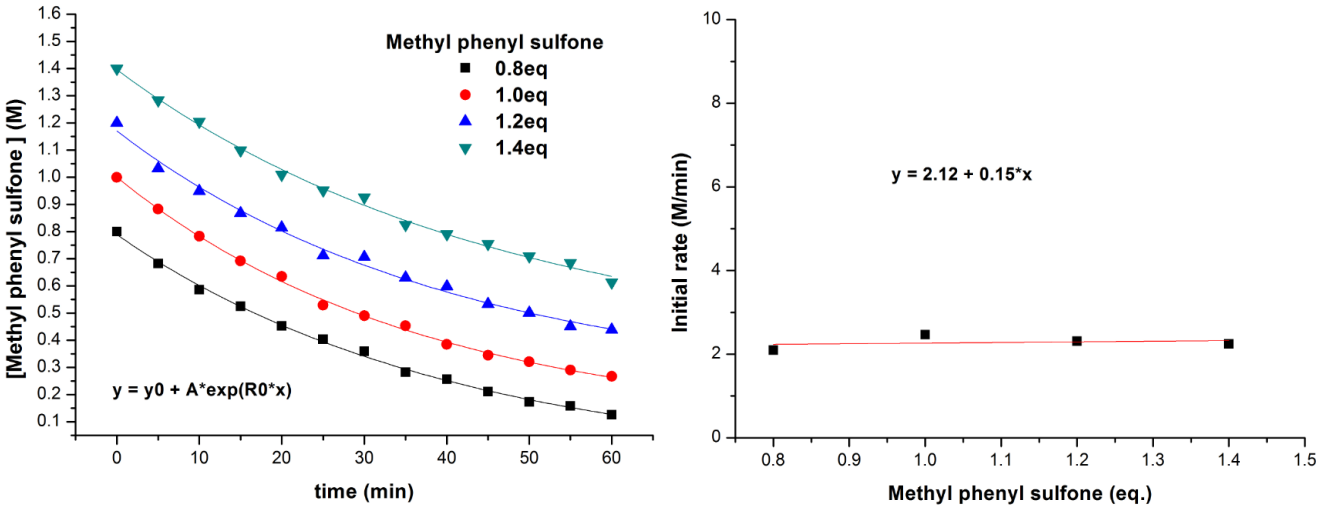
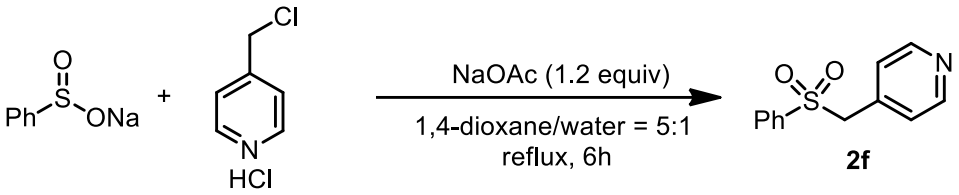


Figure S10. Polts of [Methyl phenyl sulfone] *v.s.* time (L) and dependence of the initial rate on [Methyl phenyl sulfone] (R).

3. General reaction procedures (Tables 2-3)

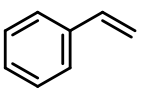
3.1. Preparation of 2f



A mixture of 4-(chloromethyl)pyridine hydrochloride (8.2 g, 50 mmol), NaOAc (4.9 g, 60 mmol), sodium phenylsulfinate (10.7 g, 65 mmol) in the solution (4-dioxane/water = 5:1, 60 mL) was refluxed for 6 h. The reaction mixture was cooled to room temperature and poured into a mixture of ethyl acetate (100 mL), sat. aq. K_2CO_3 (20 mL) and water (30 mL). Then the mixture was extracted with ethyl acetate (2 ×100 mL). The organic phases were combined and washed with brine (1 ×80 mL), dried over $MgSO_4$. After concentration *in vacuo*, the crude product was recrystallized with ethanol to afford pure product **2f** as a colorless solid (5.74 g, 25% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 4.6, 1.4 Hz, 2H), 7.67 - 7.62 (m, 3H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 6.0 Hz, 2 H), 4.29 (s, 2 H).[1]

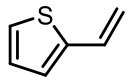
3.2. General procedure for direct olefination of alcohols to terminal alkenes.

Methyl phenyl sulfone (1 mmol) was weighed into a 25 mL Schlenk tube. After dried *in vacuo* for 15 min, an alcohol (10 mmol) was added under argon atmosphere (Some solid alcohols need adding 1 mL of toluene to improve solubility). The reaction mixture was vigorously stirred at 135 ℃. After solids dissolved, NaH (60% dispersion in mineral oil, 100 mg, 2.5 equiv) was added. The Schlenk tube was equipped with a finger-shape condenser and the mixture was stirred under argon at 135 ℃ (oil bath). The reaction was monitored by TLC. After cooling to room temperature, the reaction mixture was filtrated through a thin pad of silica gel, followed by washing with light petroleum ether/ethyl acetate. After concentrated by a rotary evaporator under reduced pressure, the crude reaction residue was examined on ^{1}H NMR spectrometer to determine conversion and selectivity using dioxane and dimethylsulfoxide as internal standards. The purification on silica gel column with light petroleum ether (b.p. 30-60) and the careful removal of solvents by rotary evaporation afforded the olefin product.



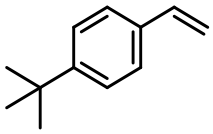
styrene (3a)[4]

Colorless oil, 87%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 - 7.45(m, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.32 - 7.28 (m, 1H), 6.77 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.80 (d, *J* = 17.6 Hz, 1H), 5.29 (d, *J* = 11.2 Hz, 1H).



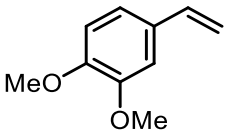
2-vinylthiophene (3b)[5]

Colorless oil, 84%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 4.4, 1H), 7.00 - 6.98 (m, 2H), 6.85 (ddd, *J* = 17.2, 10.8 Hz, 1H), 5.60 (d, *J* = 17.2 Hz, 1H), 5.17 (d, *J* = 108 Hz, 1H).



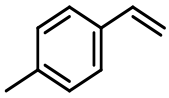
1-(*tert*-butyl)-4-vinylbenzene (3c)[6]

Colorless oil, 88%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (s, 4H), 6.71 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.72 (d, *J* = 17.6 Hz, 1H), 5.20 (d, *J* = 10.8 Hz, 1H), 1.33 (s, 9H).



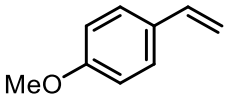
1,2-dimethoxy-4-vinylbenzene (3d)[7]

Colorless oil, 85%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.98 - 6.94 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.66 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.62 (d, *J* = 17.6 Hz, 1H), 5.15 (d, *J* = 10.8 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H).



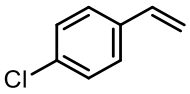
1-methyl-4-vinylbenzene (3e)[8]

Colorless oil, 99%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 6.79 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.80 (d, *J* = 17.6 Hz, 1H), 5.28 (d, *J* = 10.8 Hz, 1H), 2.43 (s, 3H).



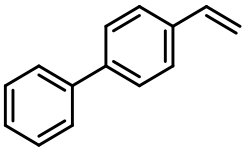
1-methoxy-4-vinylbenzene (3f) [4]

Colorless oil, 95%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.69 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.64 (d, *J* = 17.6 Hz, 1H), 5.16 (d, *J* = 10.8 Hz, 1H), 3.83 (s, 3H).



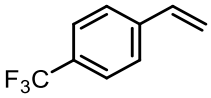
1-chloro-4-vinylbenzene (3g)[8]

Colorless oil, 79%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 6.68 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.74 (d, *J* = 17.6 Hz, 1H), 5.28 (d, *J* = 10.8 Hz, 1H).



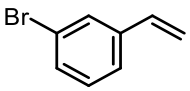
4-vinyl-1,1'-biphenyl (3h)[7]

White solid, 75%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 - 7.56 (m, 4H), 7.50 - 7.42 (m, 4H), 7.36 - 7.33 (m, 1H), 6.76 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.80 (d, *J* = 17.6 Hz, 1H), 5.28 (d, *J* = 10.8 Hz, 1H).



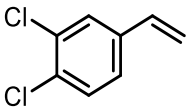
1-(trifluoromethyl)-4-vinylbenzene (3i)[8]

Colorless oil, 52%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 6.75 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.85 (d, *J* = 17.6 Hz, 1H), 5.39 (d, *J* = 11.2 Hz, 1H).



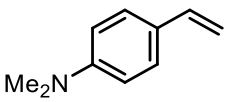
1-bromo-3-vinylbenzene (3j)[10]

Colorless oil, 81%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 6.65 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.77 (d, *J* = 17.6 Hz, 1H), 5.31 (d, *J* = 10.8 Hz, 1H).



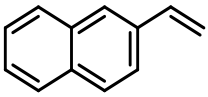
1,2-dichloro-4-vinylbenzene (3k)[11]

Colorless oil, 77%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 2.0 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.22 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.61 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.75 (d, *J* = 17.6 Hz, 1H), 5.33 (d, *J* = 10.8 Hz, 1H).



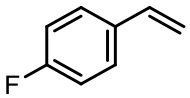
***N*,*N*-dimethyl-4-vinylaniline (3l)**[12]

Colorless oil, 60%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.8 Hz, 2H), 6.71 (d, J= 8.8 Hz, 2H), 6.68 (dd, J= 17.6, 11.2 Hz, 1H), 5.56 (d, *J* = 17.6 Hz, 1H), 5.04 (d, *J* = 11.2 Hz, 1H), 2.98 (s, 6H).



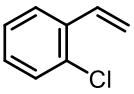
2-vinylnaphthalene (3m)[7]

White solid, 92%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 - 7.75 (m, 4H), 7.64 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.48 - 7.42 (m, 2H), 6.89 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.88 (d, *J* = 17.6 Hz, 1H), 5.34 (d, *J* = 10.8 Hz, 1H).



1-fluoro-4-vinylbenzene (3n)[8]

Colorless oil, 60%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 - 7.36 (m, 2H), 7.04 - 7.00 (m, 2H), 6.69 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.68 (d, *J* = 17.6 Hz, 1H), 5.23 (d, *J* = 10.8 Hz, 1H).

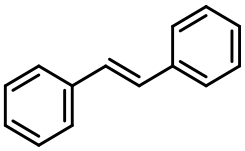


1-chloro-2-vinylbenzene (3o)[13]

Colorless oil, 95%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.34 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.23 - 7.14 (m, 2H), 7.10 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.72 (d, *J* = 17.2 Hz, 1H), 5.37 (dd, *J* = 10.8, 0.8 Hz, 1H).

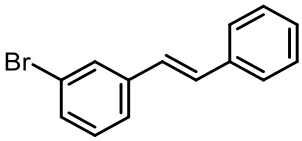
3.3. General procedure for direct olefination of alcohols to internal alkenes. A sulfone (1 mmol) was weighed into a 25 mL Schlenk tube. After dried *in vacuo* for 15 min, an alcohol (1mL, 10 mmol) was added under argon atmosphere (Some solid alcohols need adding 1 mL of toluene to improve solubility). The reaction mixture was vigorously stirred at 135 ℃. After solids dissolved, NaH (60% dispersion in mineral oil, 100 mg, 2.5 equiv) was added. The Schlenk tube was equipped with a finger-shape condenser and the mixture was stirred under argon at 135 ℃ (oil bath). The reaction was monitored by TLC. After cooling to room temperature, the reaction mixture was filtrated through a thin pad of silica gel, followed by washing with light petroleum ether/ethyl acetate. After concentrated by a rotary evaporator under re-

duced pressure, the crude reaction residue was examined on ^{1}H NMR spectrometer to determine conversion and selectivity using dioxane and dimethylsulfoxide as internal standards. The purification on silica gel column with light petroleum ether (b.p. 30-60) and the careful removal of solvents by rotary evaporation afforded the olefin product.



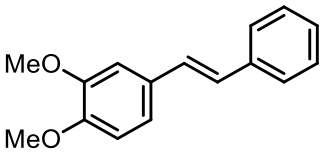
(*E*)-1,2-diphenylethene (4a)[14]

White solid, 90%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* =7.2 Hz, 4H), 7.36 (t, *J* =7.6 Hz, 4H), 7.28 - 7.24 (m, 2H), 7.11 (s, 2H).



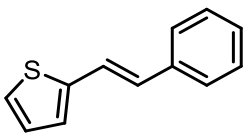
(*E*)-1-bromo-3-styrylbenzene (4b)[15]

White solid, 93%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (t, *J* = 1.8 Hz, 1H), 7.51 - 7.49 (m, 2H), 7.41 - 7.35 (m, 4H), 7.28 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.24 - 7.19 (m, 1H), 7.09 (d, *J* = 16.4 Hz, 1H), 6.70 (d, *J* = 16.4 Hz, 1H).



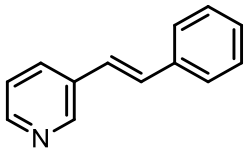
(*E*)-1,2-dimethoxy-4-styrylbenzene (4c)[17]

White solid, 90%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* =7.6 Hz, 2H), 7.34 (t, *J* =7.6 Hz, 2H), 7.24 - 7.21 (m, 1H), 7.07 - 6.94 (m, 4H), 6.85 (d, *J* =8.4 Hz, 2H), 3.94 (s, 3H), 3.89 (s, 3H).



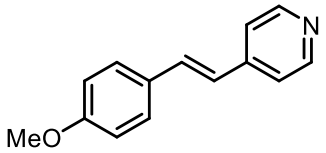
(*E*)-2-styrylthiophene (4d)[17]

White solid, 82%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.28 - 7.20 (m, 3H), 7.09 (d, *J* = 3.6 Hz, 1H), 7.02 (dd, *J* = 5.0, 3.4 Hz, 1H), 6.95 (d, *J* = 16.0 Hz, 1H).



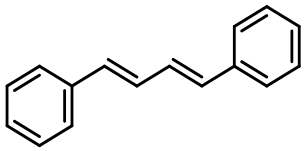
(*E*)-3-styrylpyridine (4e)[18]

White solid, 95%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 2.0 Hz, 1H), 8.48 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.81 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.53 - 7.51 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.31 - 7.25 (m, 2H), 7.16 (d, *J* = 16.4 Hz, 1H), 7.06 (d, *J* = 16.4 Hz, 1H).



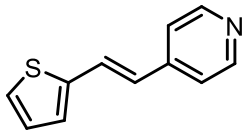
(*E*)-4-(4-methoxystyryl)pyridine (4f)[19]

Light yellow solid, 95%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 5.6, 1.6 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.33 (dd, *J* = 4.8, 1.2 Hz, 2H), 7.26 (d, *J* =16.4 Hz, 1H), 6.92 (dd, *J* = 6.8, 2.0 Hz, 2H), 6.88 (d, J = 16.4 Hz, 1H), 3.85 (s, 3H).



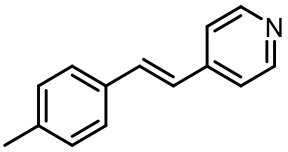
(*1E,3E*)-1,4-diphenylbuta-1,3-diene (4g)[20]

White solid, 58%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 - 7.41 (m, 4H), 7.35 - 7.31(m, 4H), 7.25 - 7.21 (m, 2H), 6.96 (dd, *J* = 11.8, 2.6 Hz, 2H); 6.68 (dd, *J* = 11.8, 2.6 Hz, 2H)



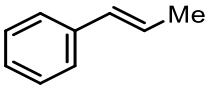
(*E*)-4-(2-(thiophen-2-yl)vinyl)pyridine (4h)[21]

White solid, 59%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.42 (d, *J* = 16.4 Hz, 1H), 7.30 (d, *J* = 4.4 Hz, 1.4 H), 7.28 (d, *J* = 4.8 Hz, 1H), 7.16 (d, *J* = 3.6 Hz, 1H), 7.04 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.82 (d, *J* = 16.0 Hz, 1H).



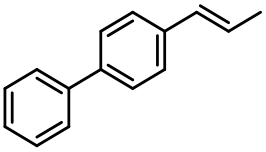
(*E*)-4-(4-methylstyryl)pyridine (4i)[22]

White solid, 95%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 6.0, 1.2 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 6.0 Hz, 2H), 7.28 (d, *J* =16.0 Hz, 1H,), 7.20 (d, *J* = 8 Hz, 2H), 6.97 (d, *J* = 16.0 Hz, 1H), 2.38 (s, 3H).



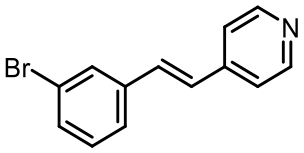
(*E*)-prop-1-en-1-ylbenzene (4j)[23]

Colorless oil, 75%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 - 7.23 (m, 4H), 7.20 - 7.16 (m, 1H), 6.40 (dd, *J* = 15.6, 2.0 Hz, 1H), 6.23 (dq, *J* = 15.6, 6.8 Hz, 1H), 1.88 (dd, *J* = 6.8, 2.0 Hz, 3H).



(*E*)-4-(prop-1-en-1-yl)-1,1'-biphenyl (4k)[24]

White solid, 95%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.2 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.46 -7.40 (m, 4H), 7.34 (t, *J* = 7.2 Hz, 1H), 6.45 (d, *J* = 16.0 Hz, 1H)， 6.30 (dq, *J* = 16.0, 6.8 Hz, 1H), 1.92 (dd, *J* = 6.8, 1.2 Hz, 3H).



(*E*)-4-(3-bromostyryl)pyridine (4l)

White solid, 95%: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 7.6 Hz, 2H), 7.69 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 5.6 Hz, 2H), 7.28 - 7.19 (m, 2H), 7.00 (d, *J* = 16.4, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.6, 144.3, 138.6, 131.8 (2 peaks), 130.6, 130.0, 127.7, 126.0, 123.3, 121.2. **HRMS (ESI)** Calcd for $C_{13}H_{11}NBr$ $[M+H]^+$ 260.0075, found 260.0076.

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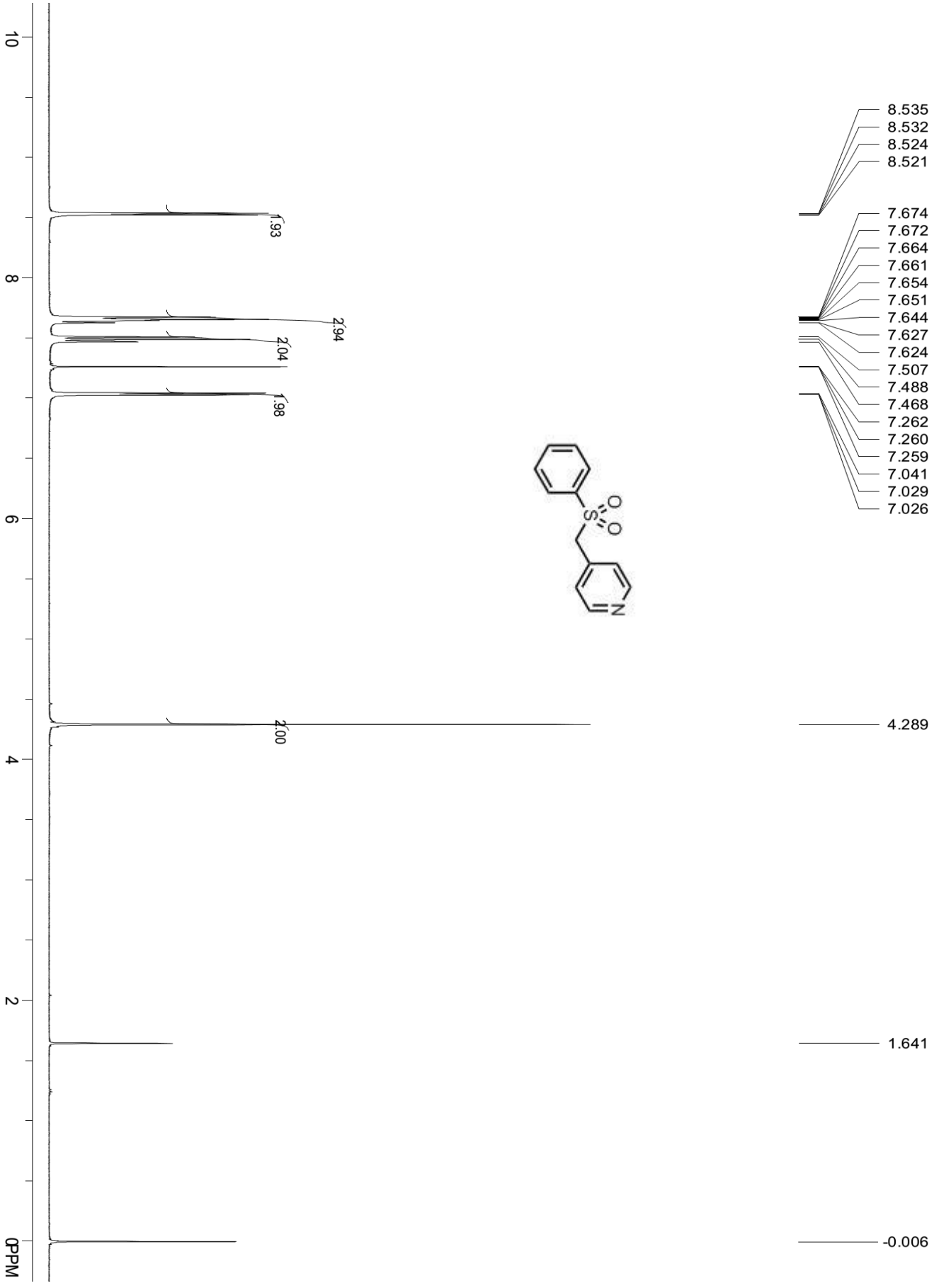
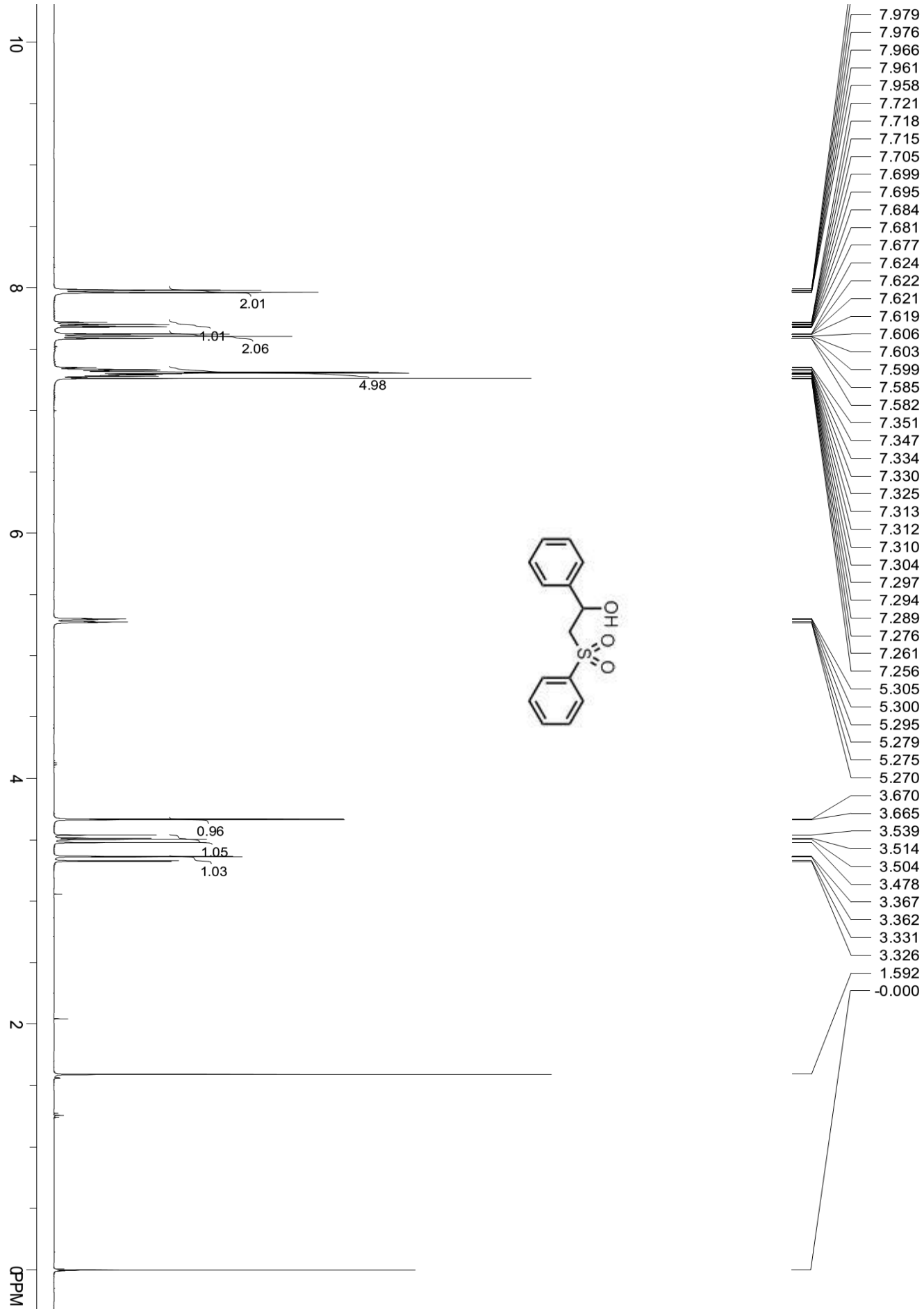
5. NMR spectra

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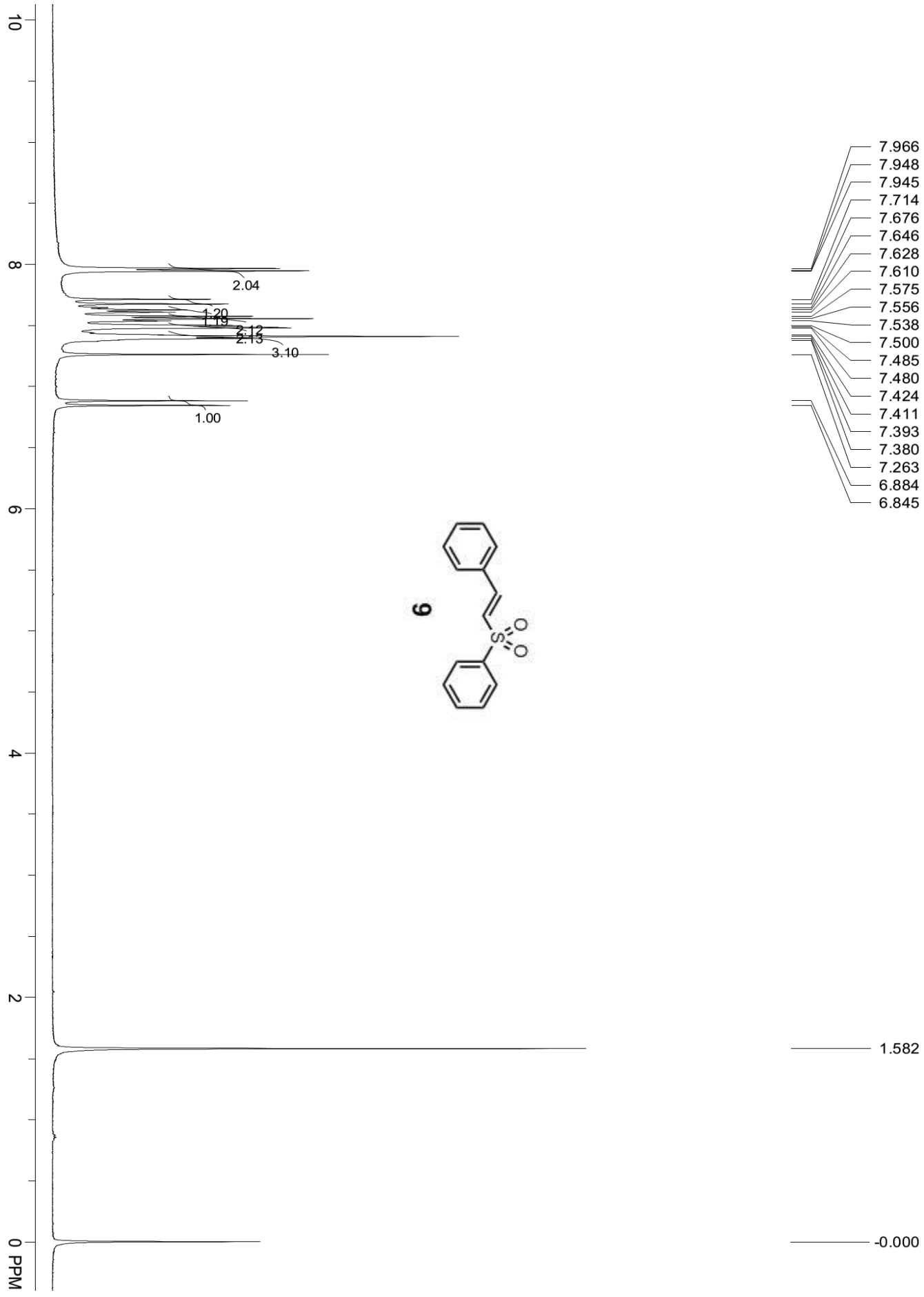
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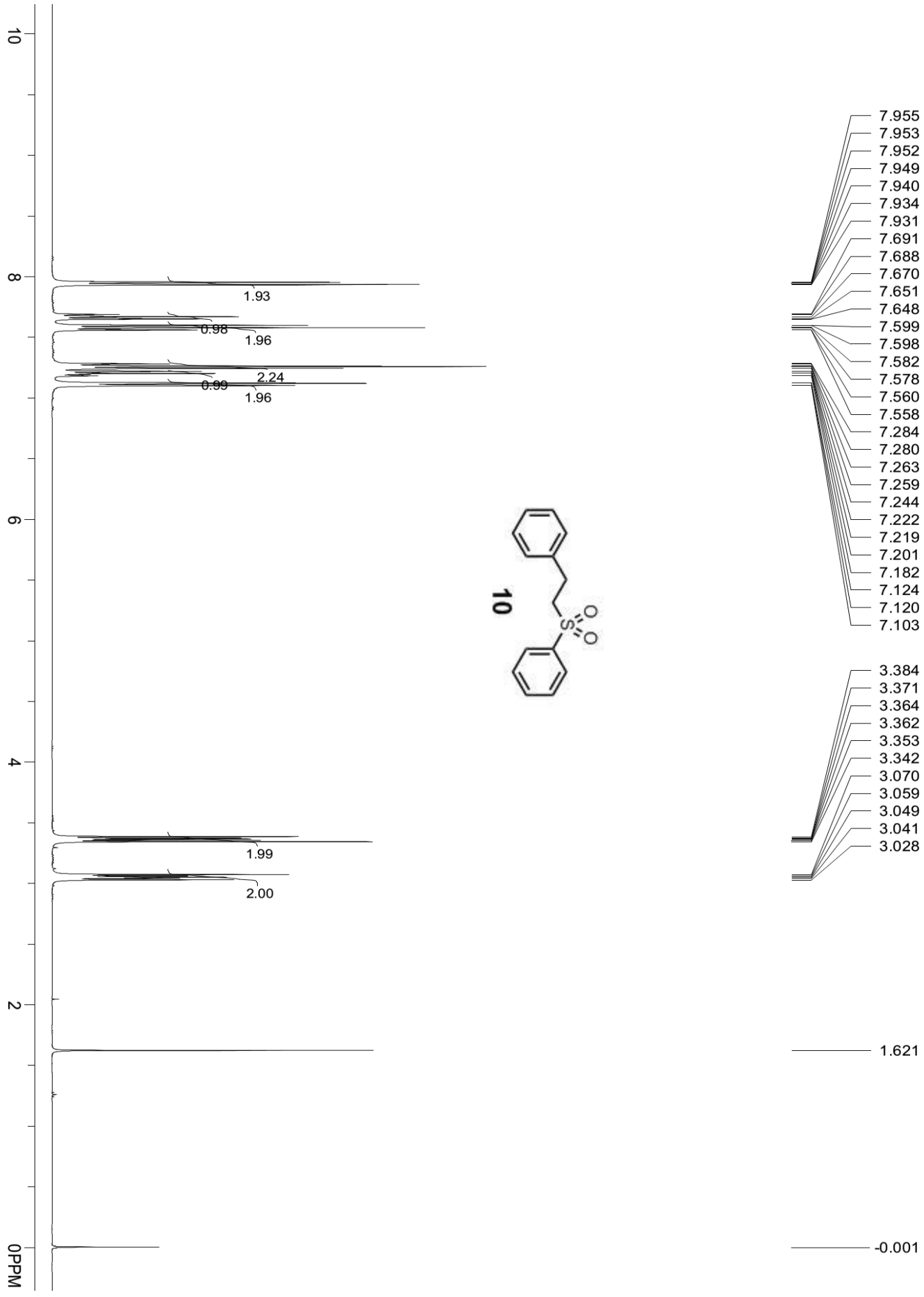
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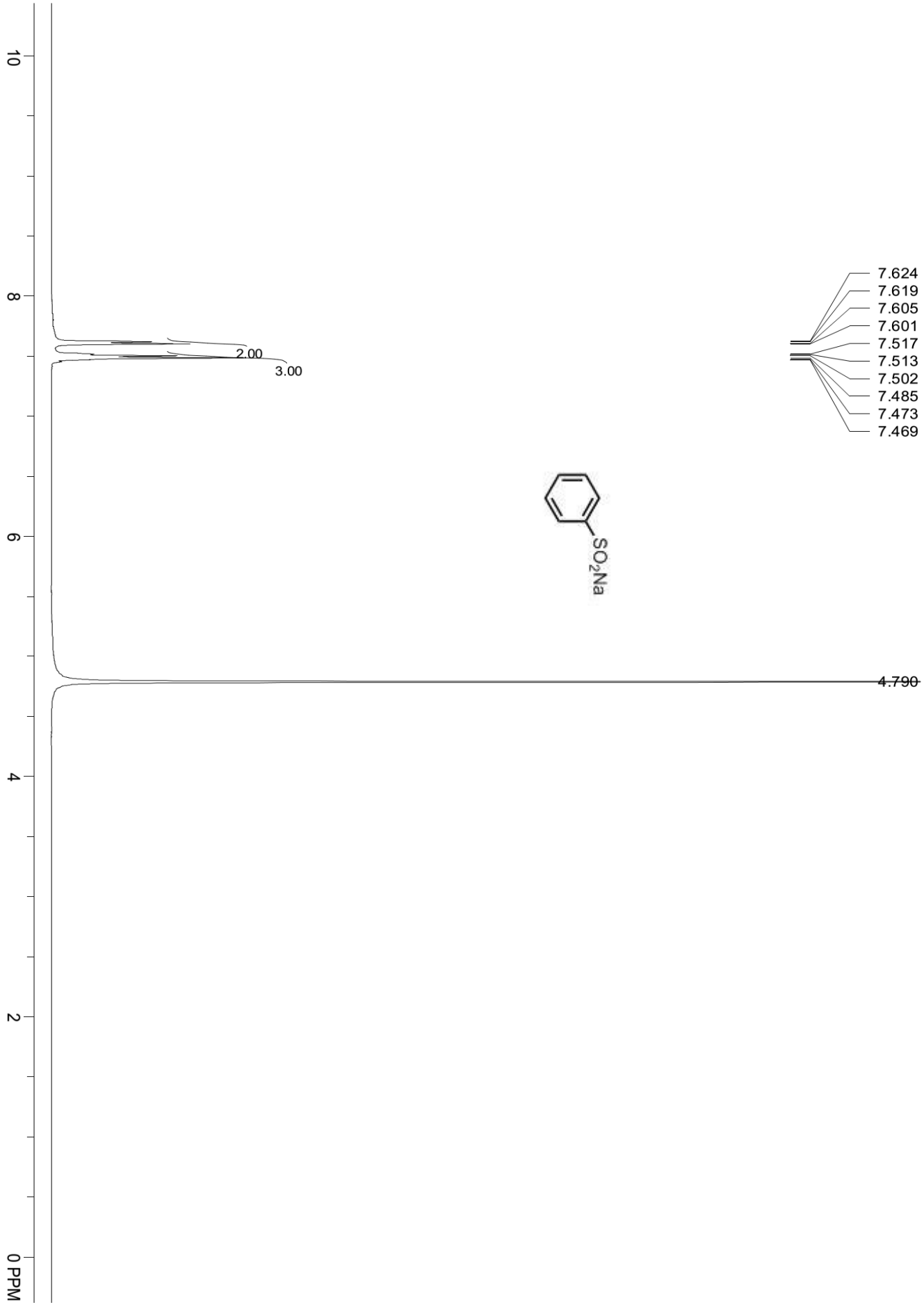
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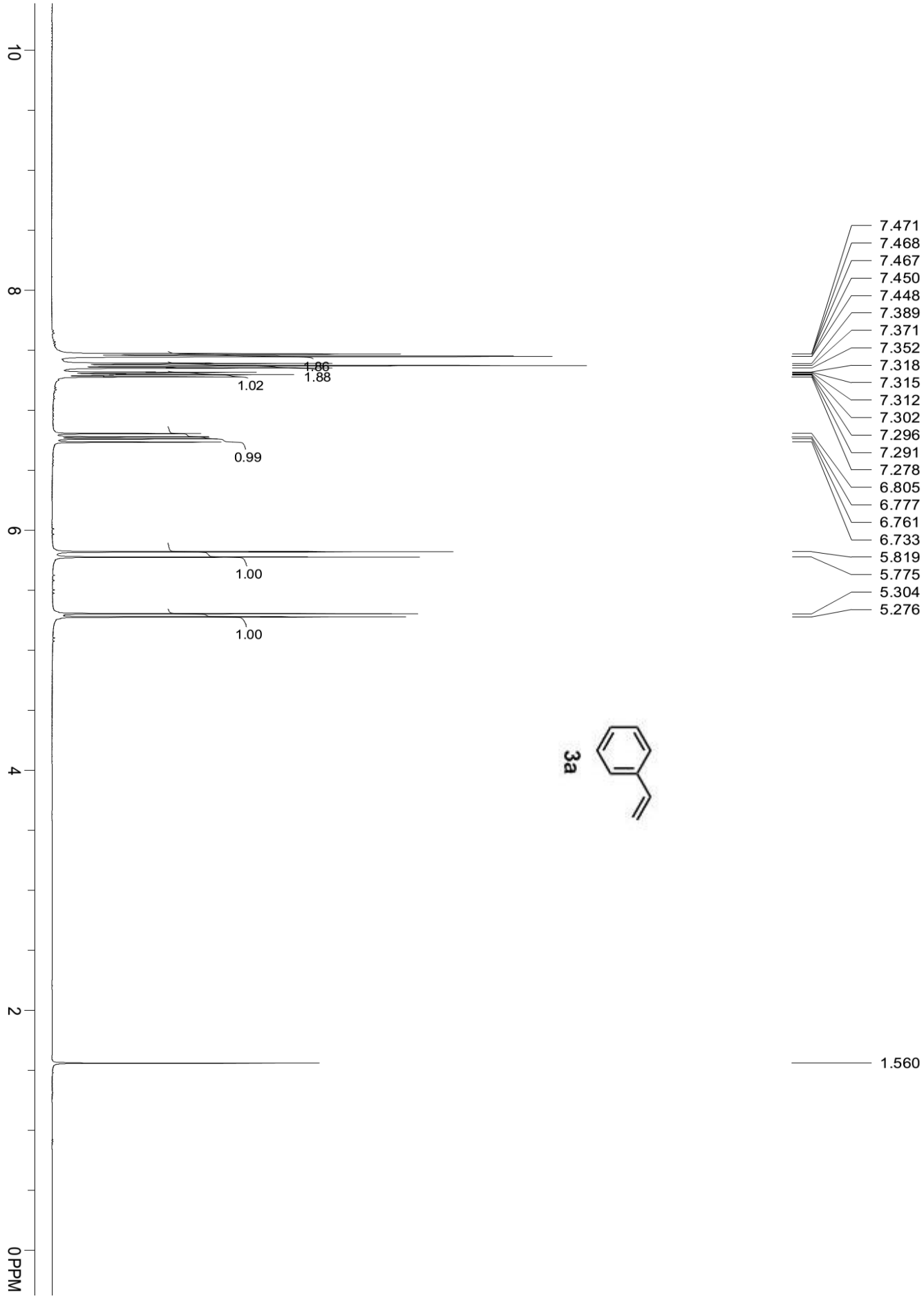
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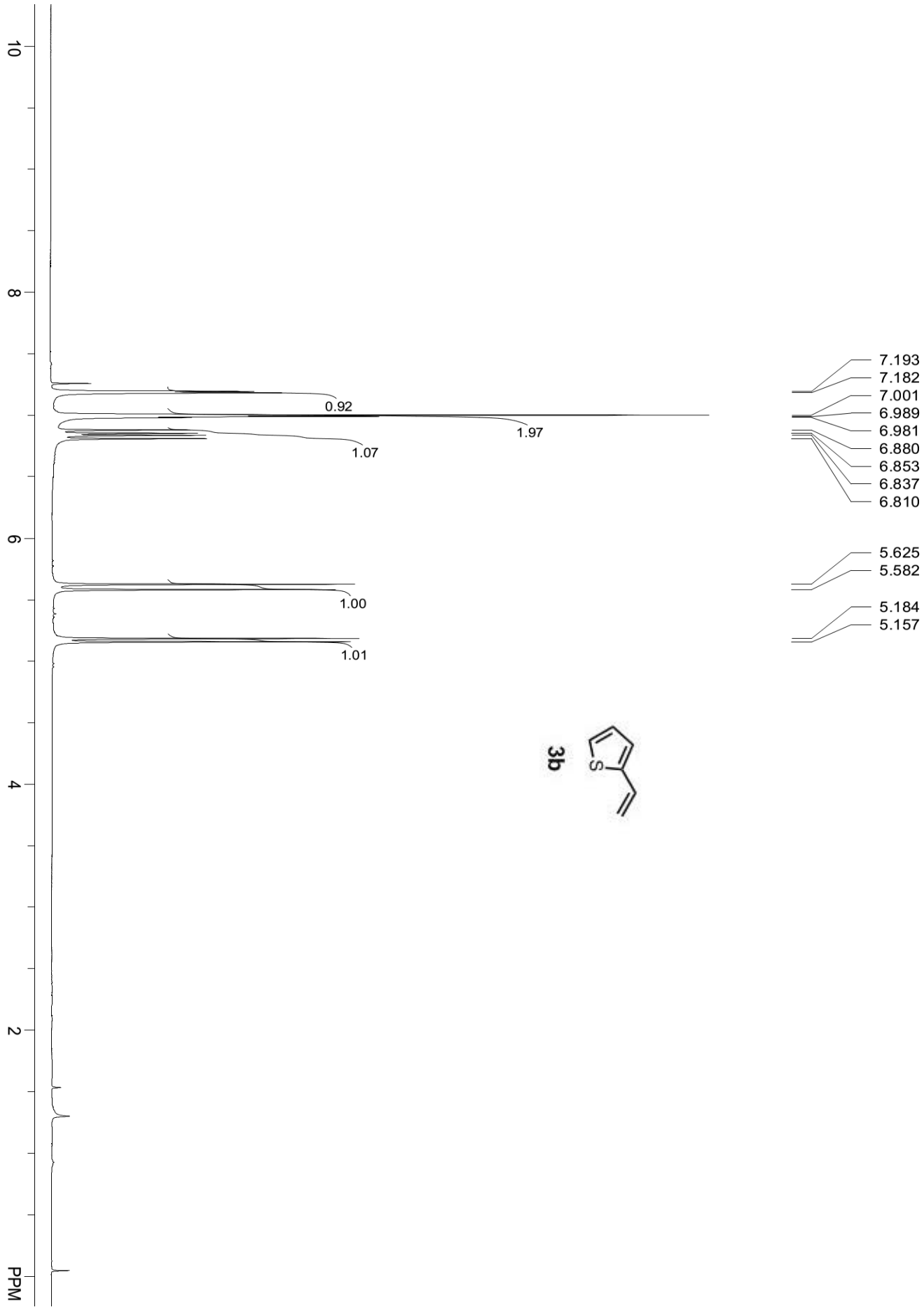
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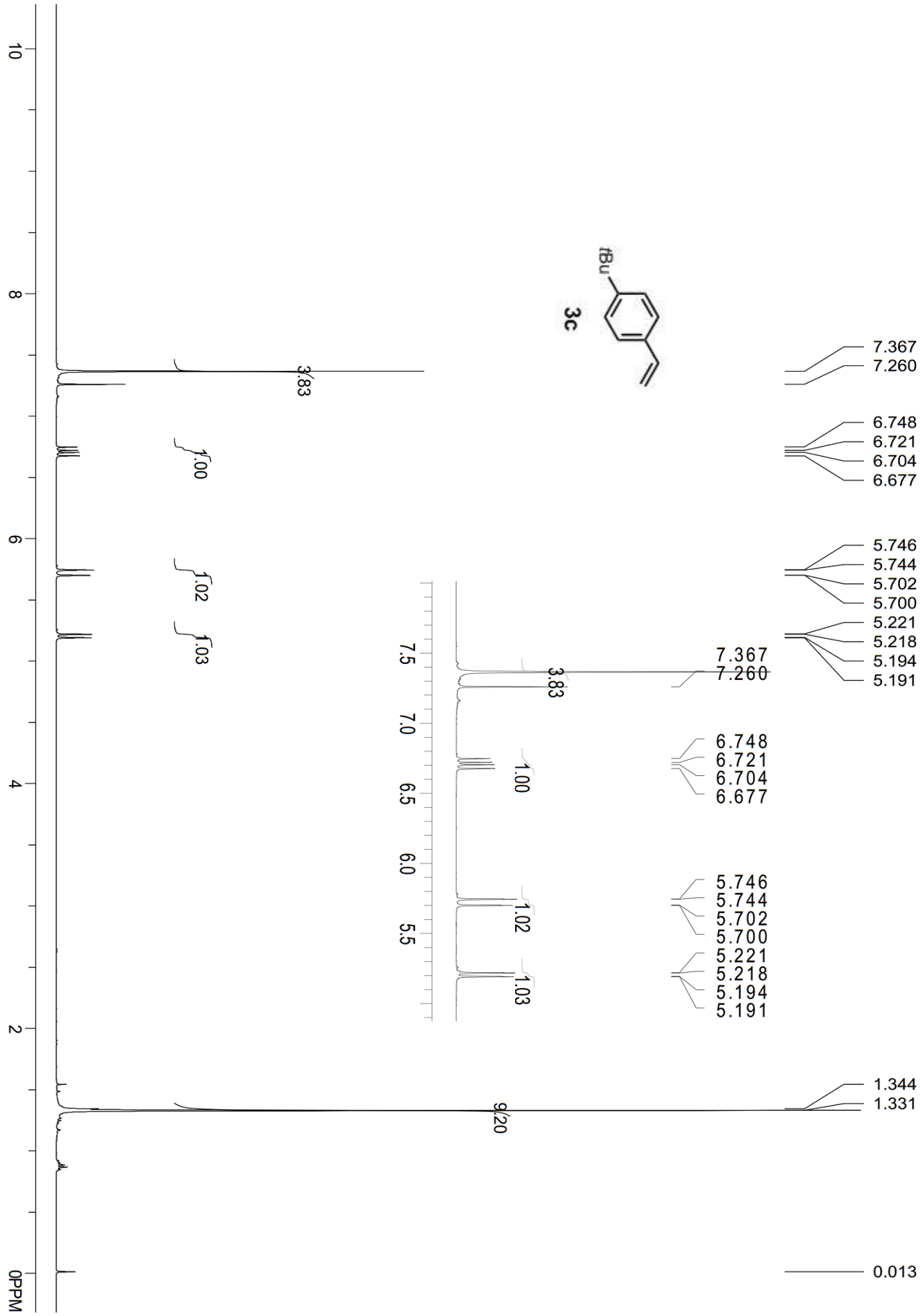
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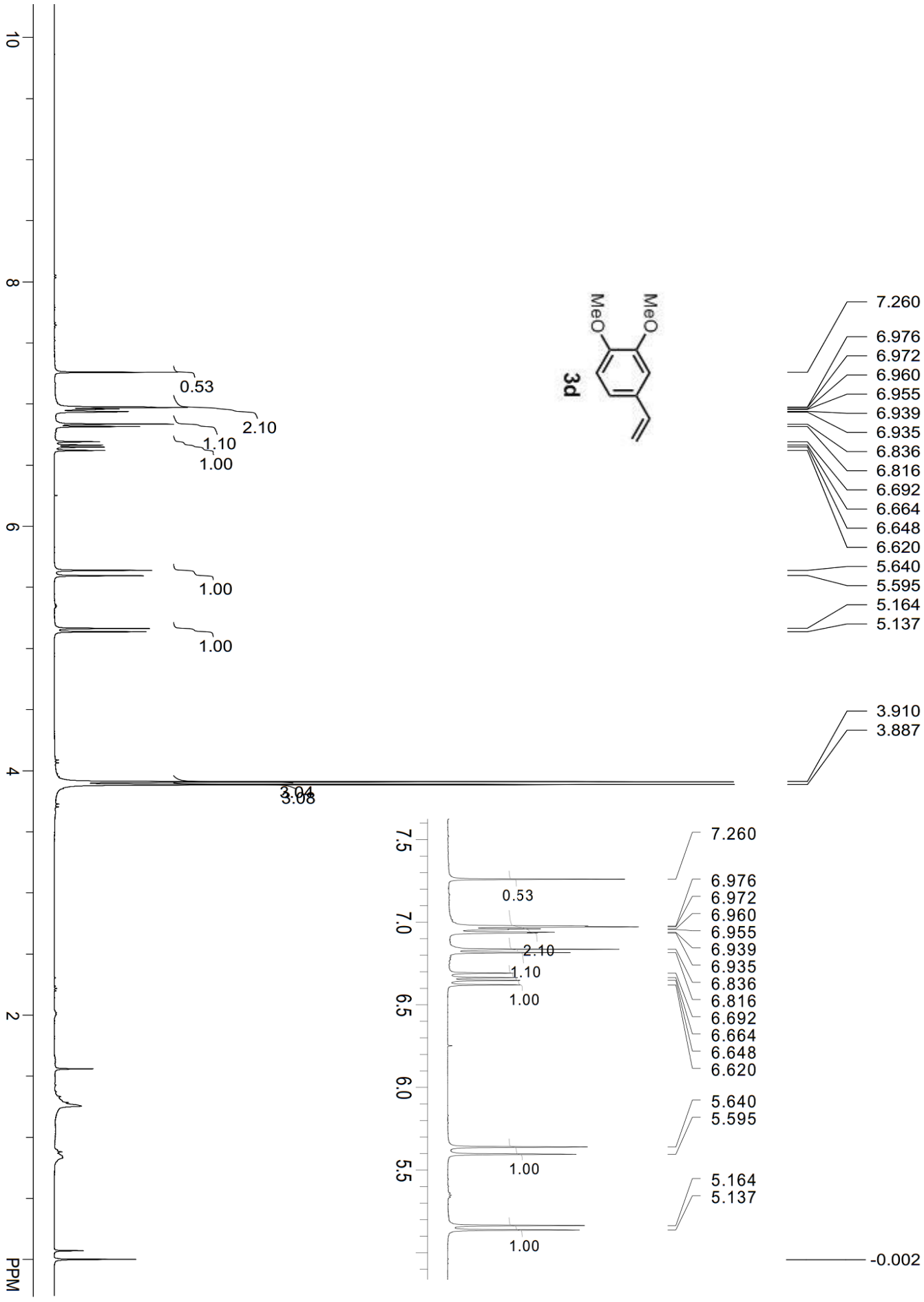
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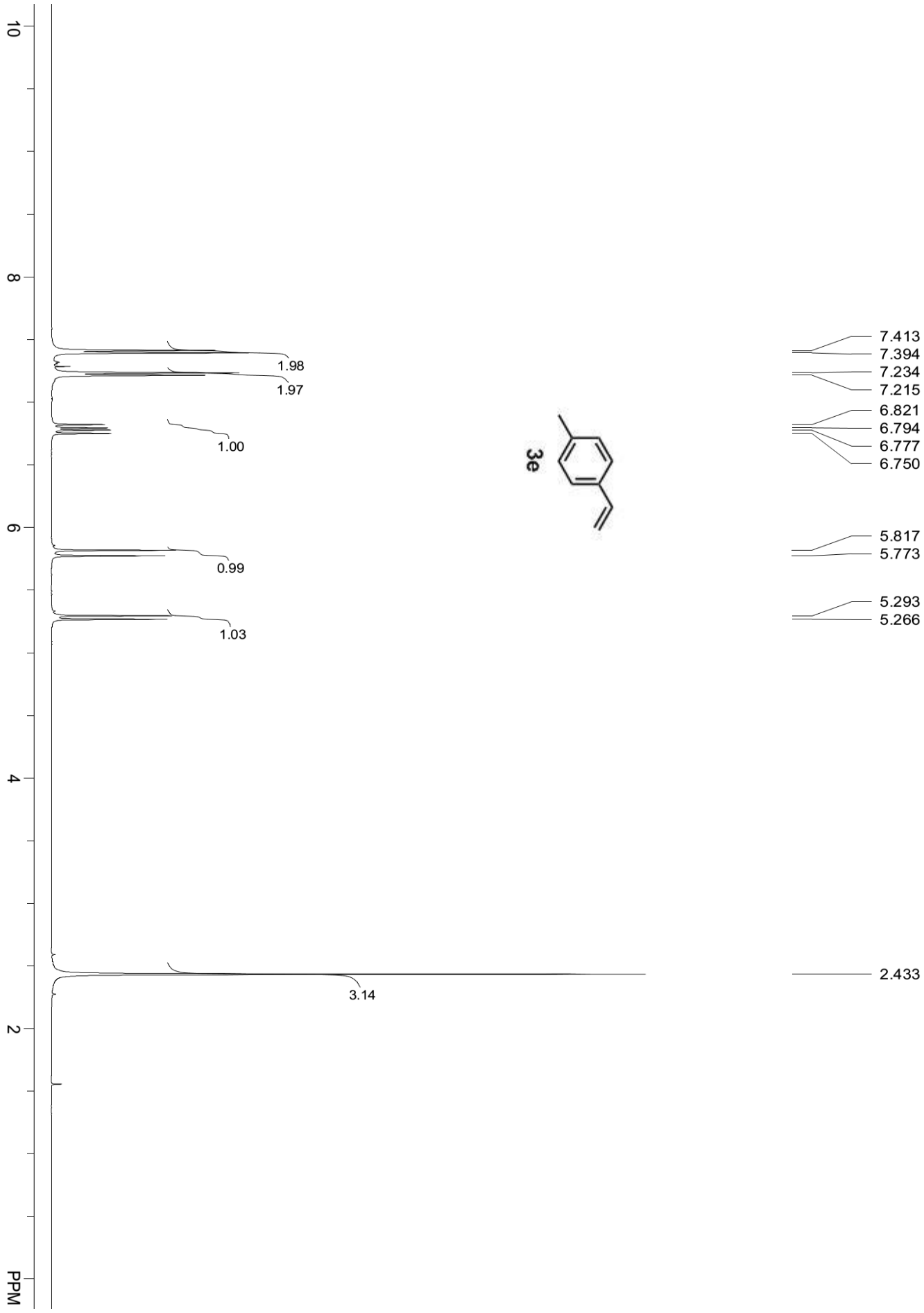
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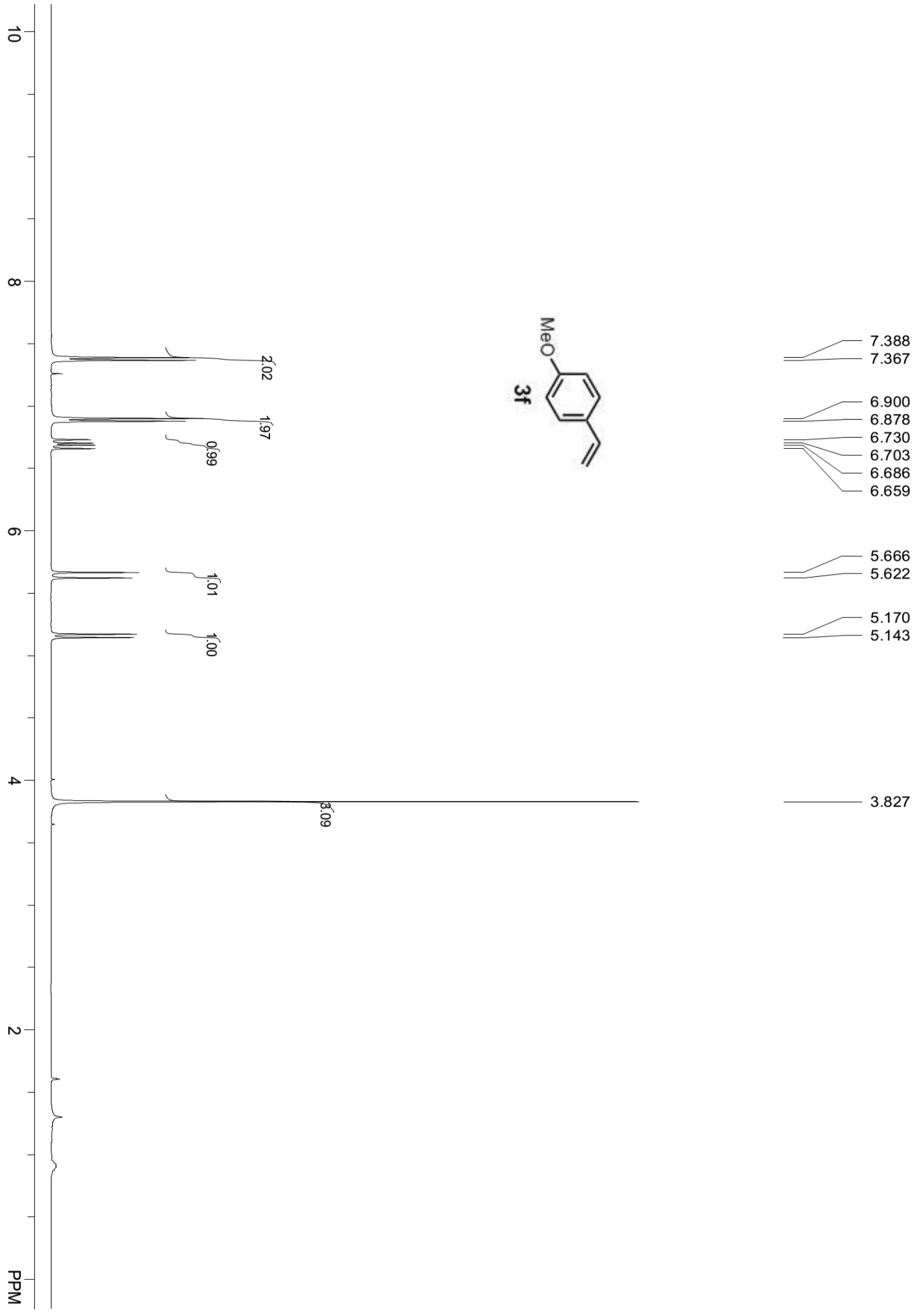
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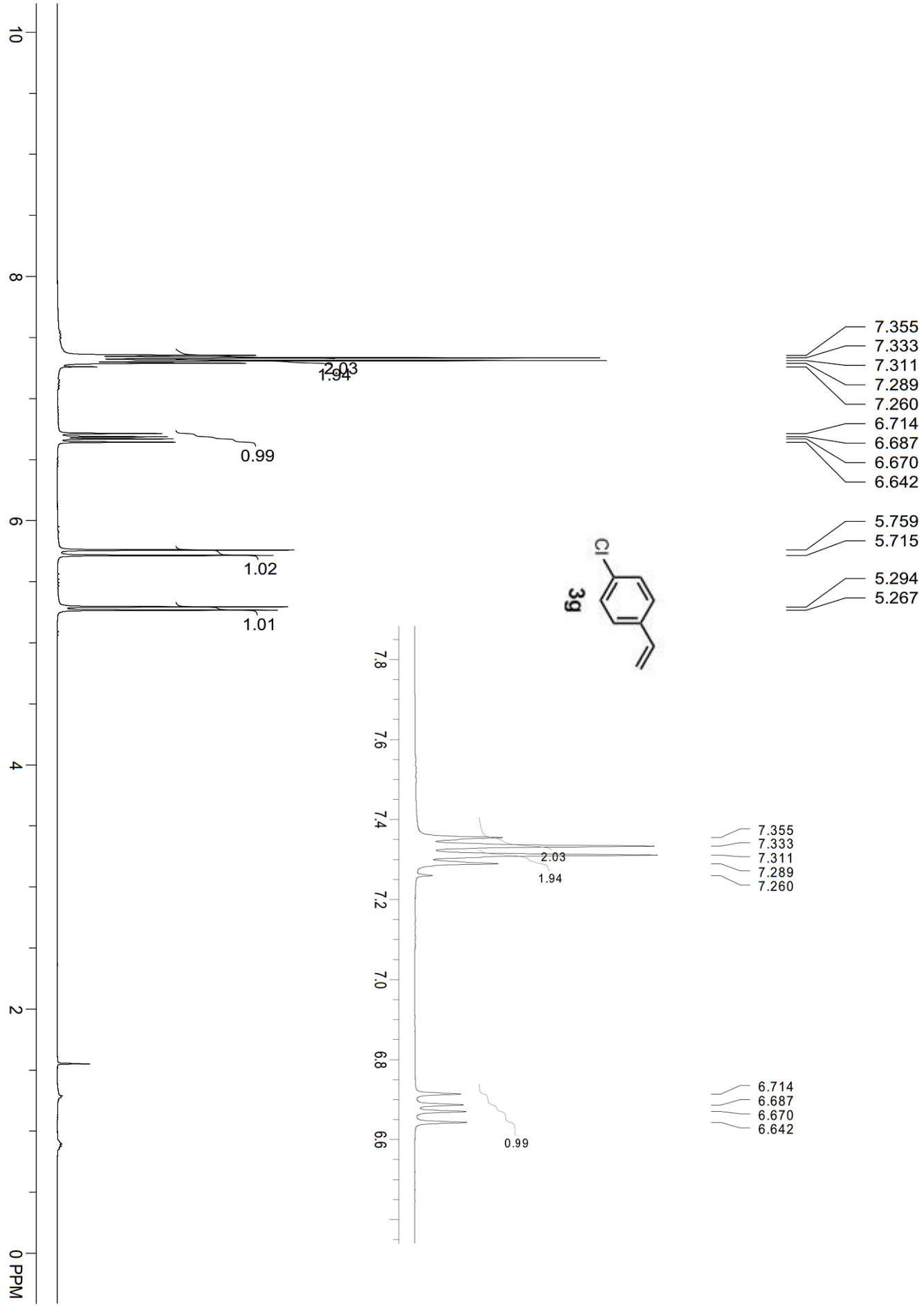
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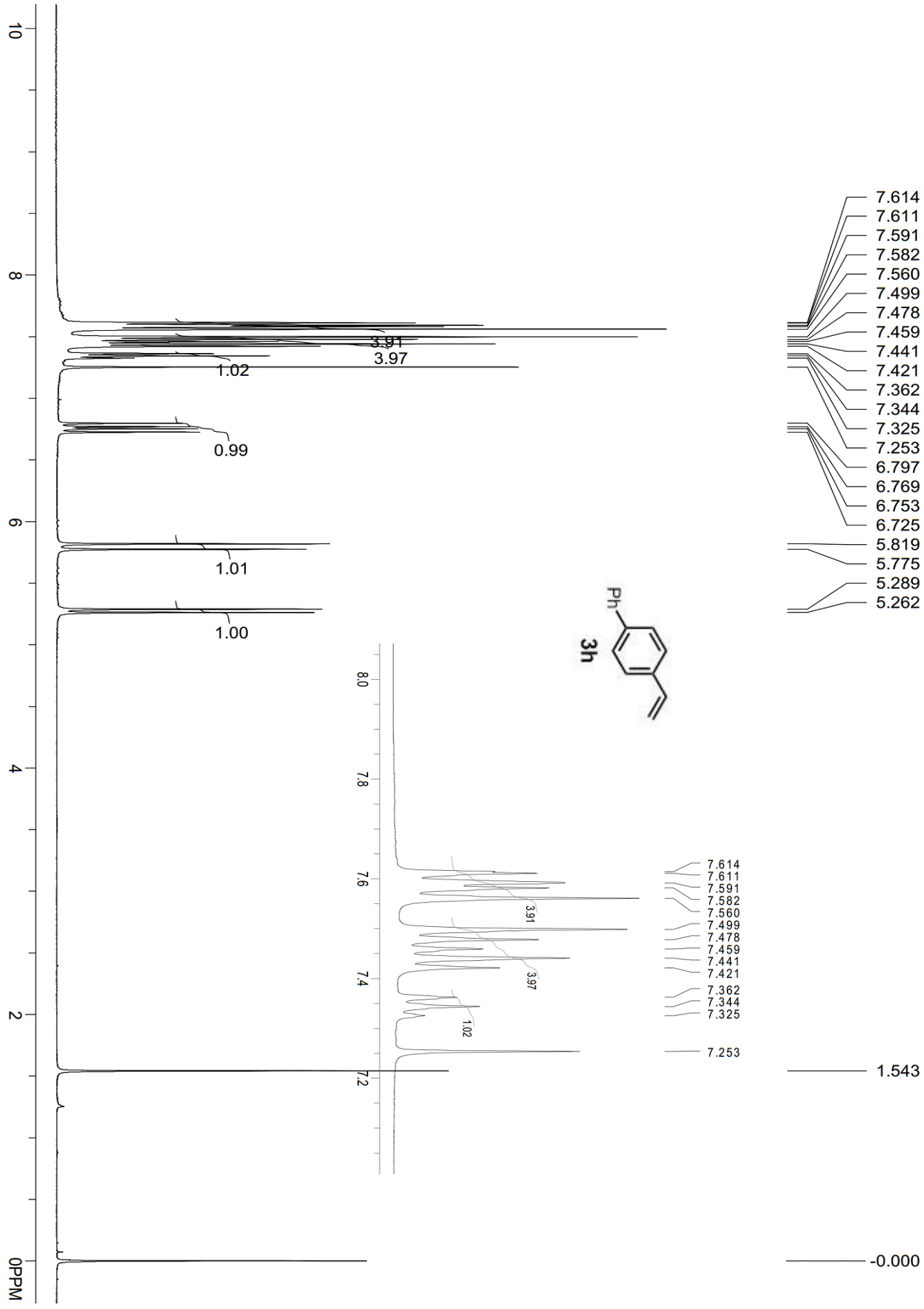
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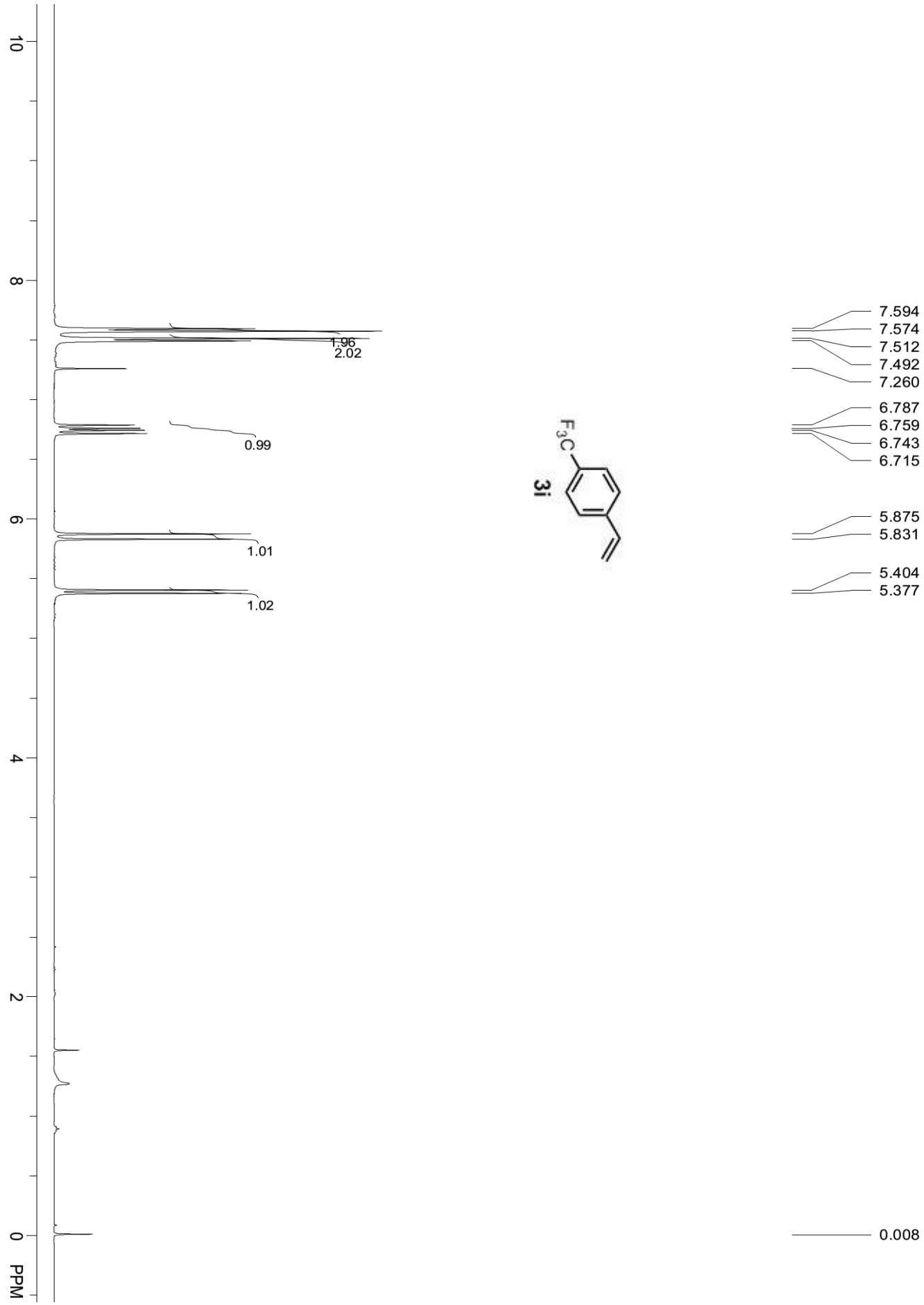
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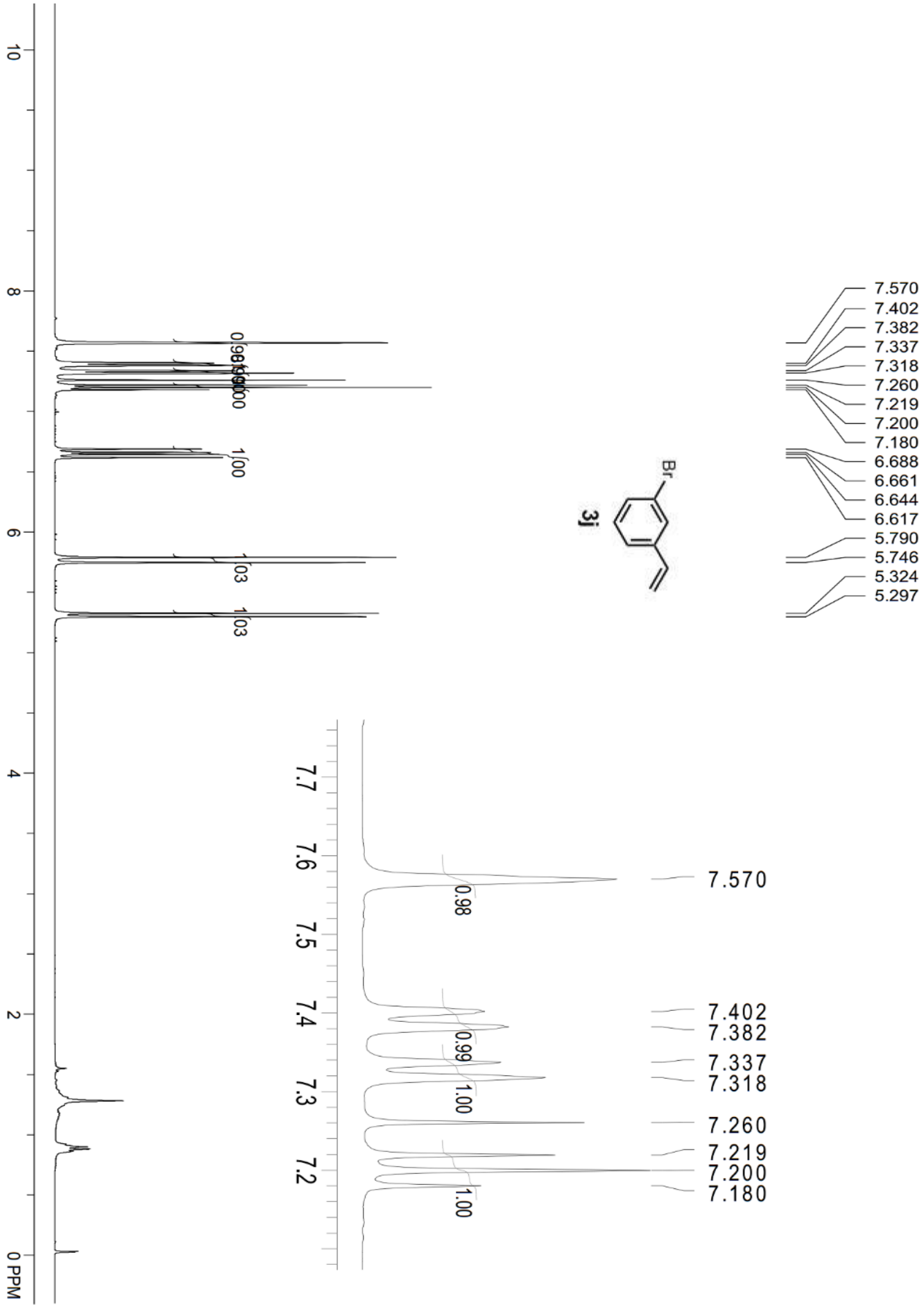
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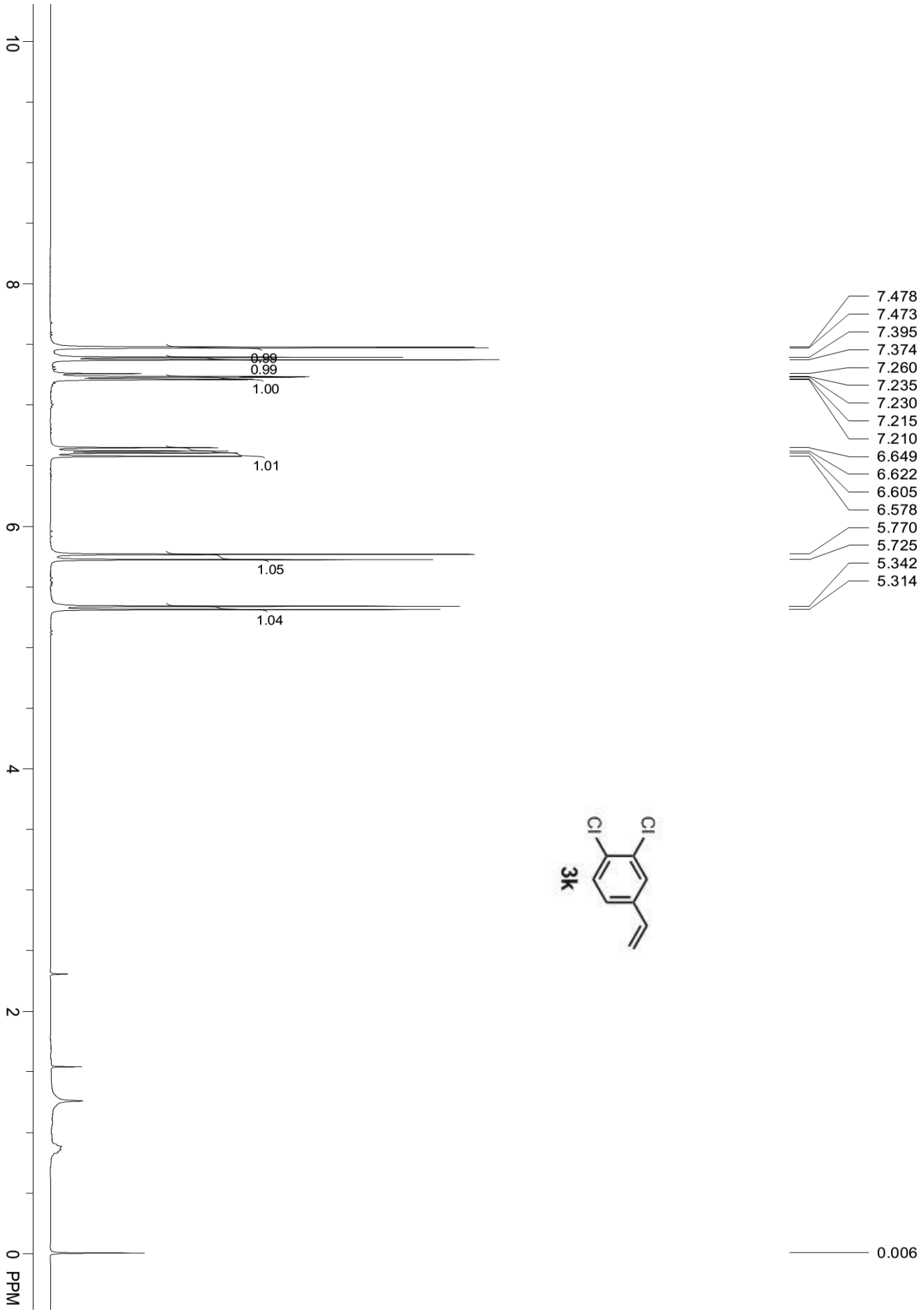
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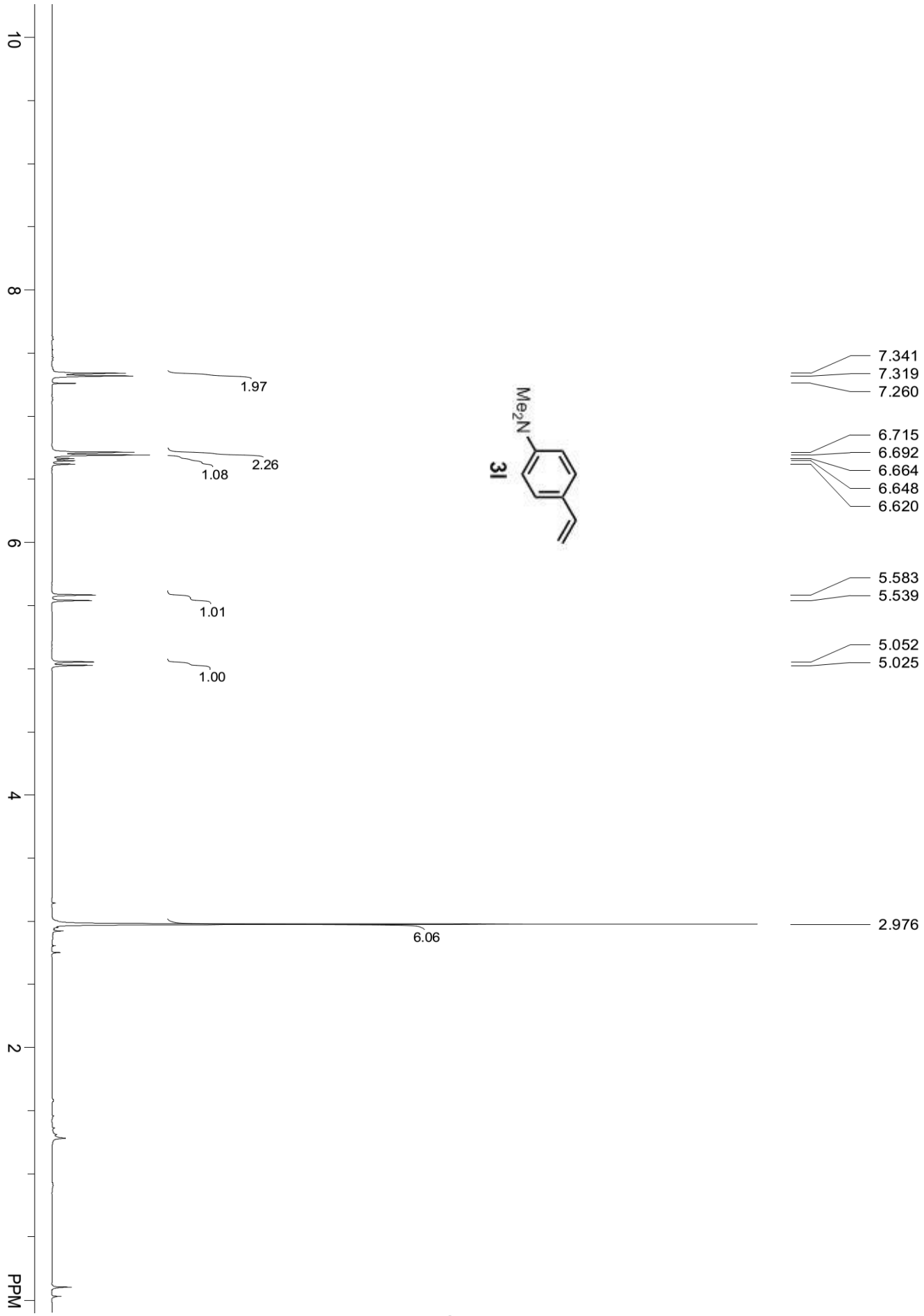
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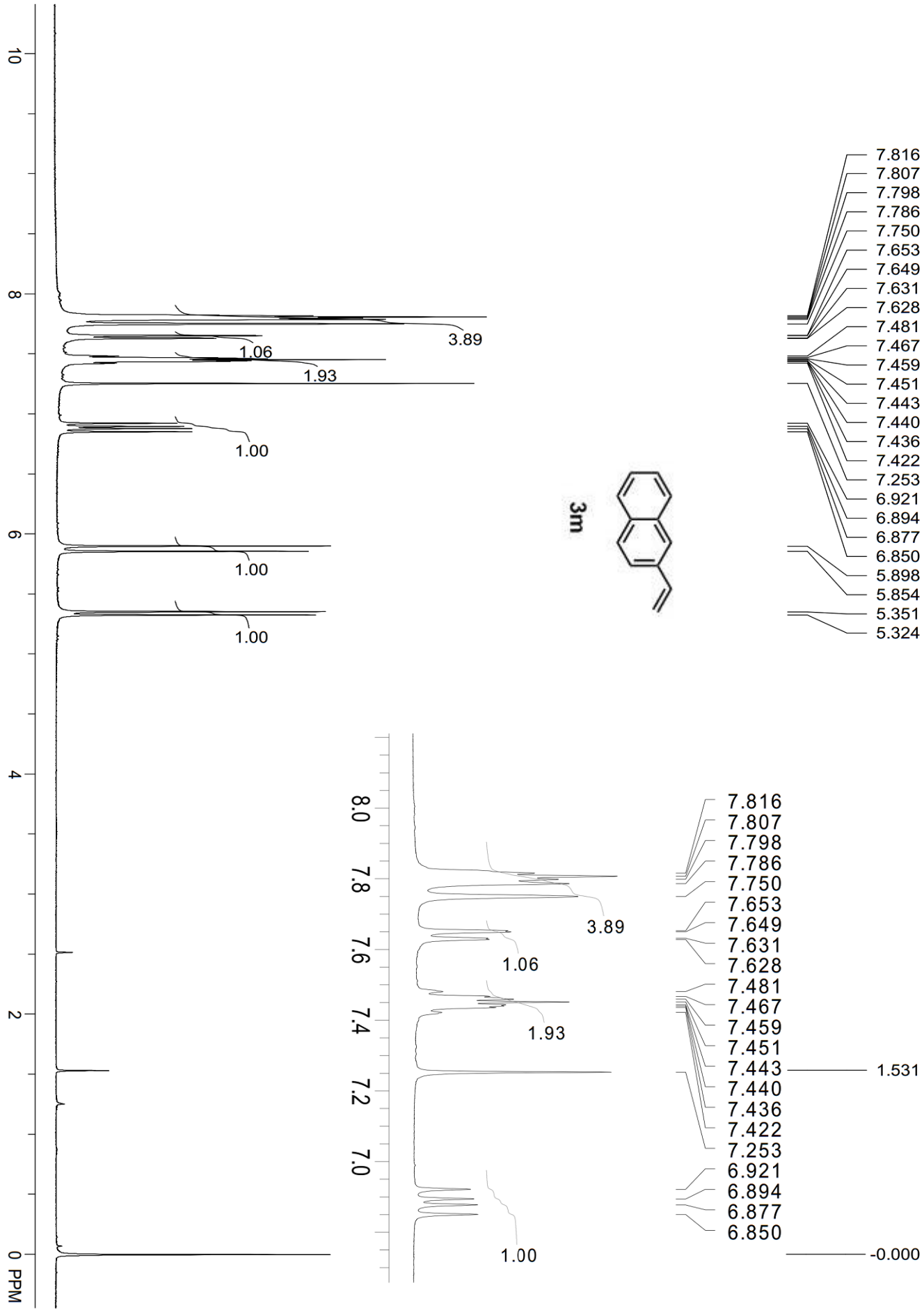
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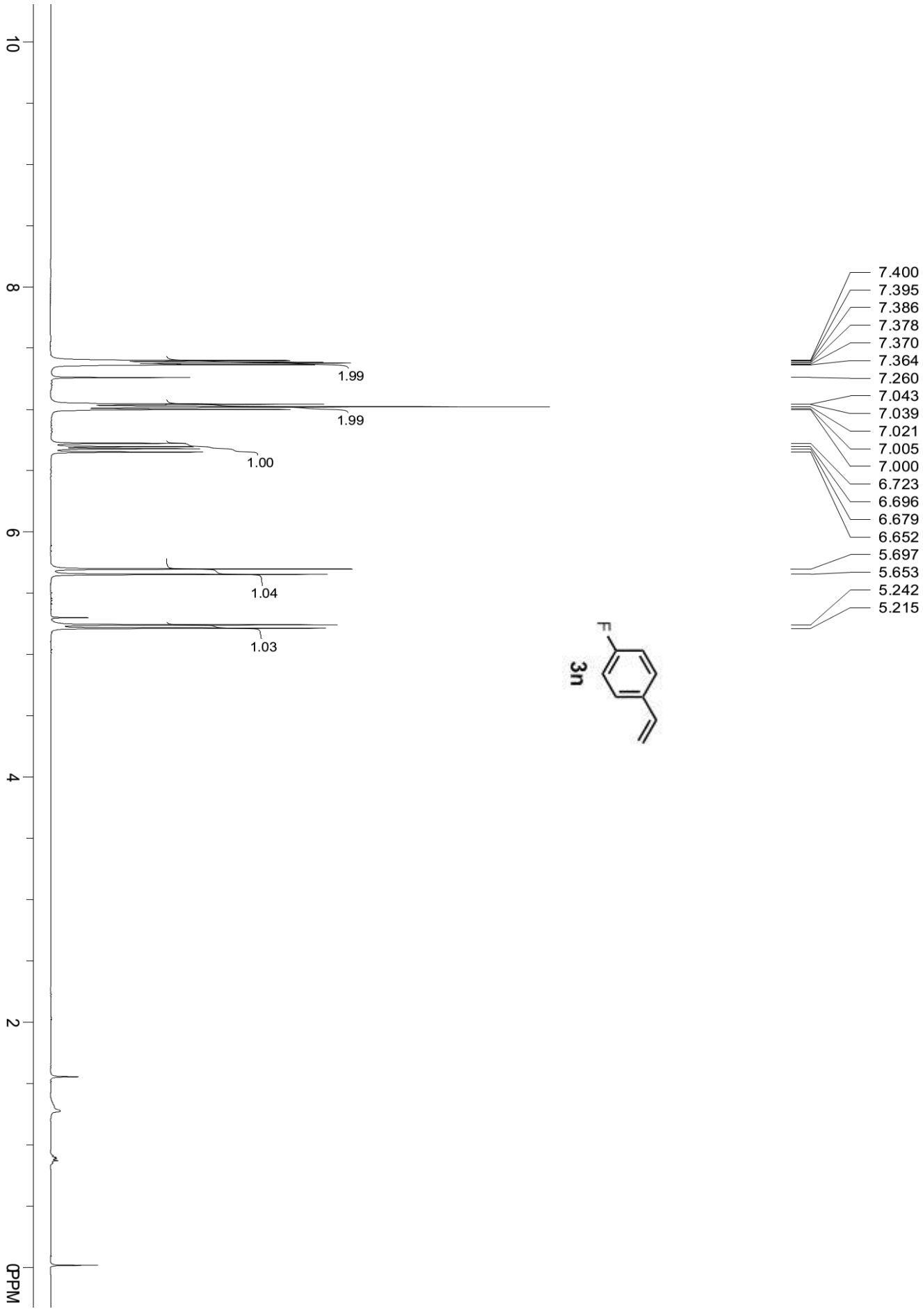
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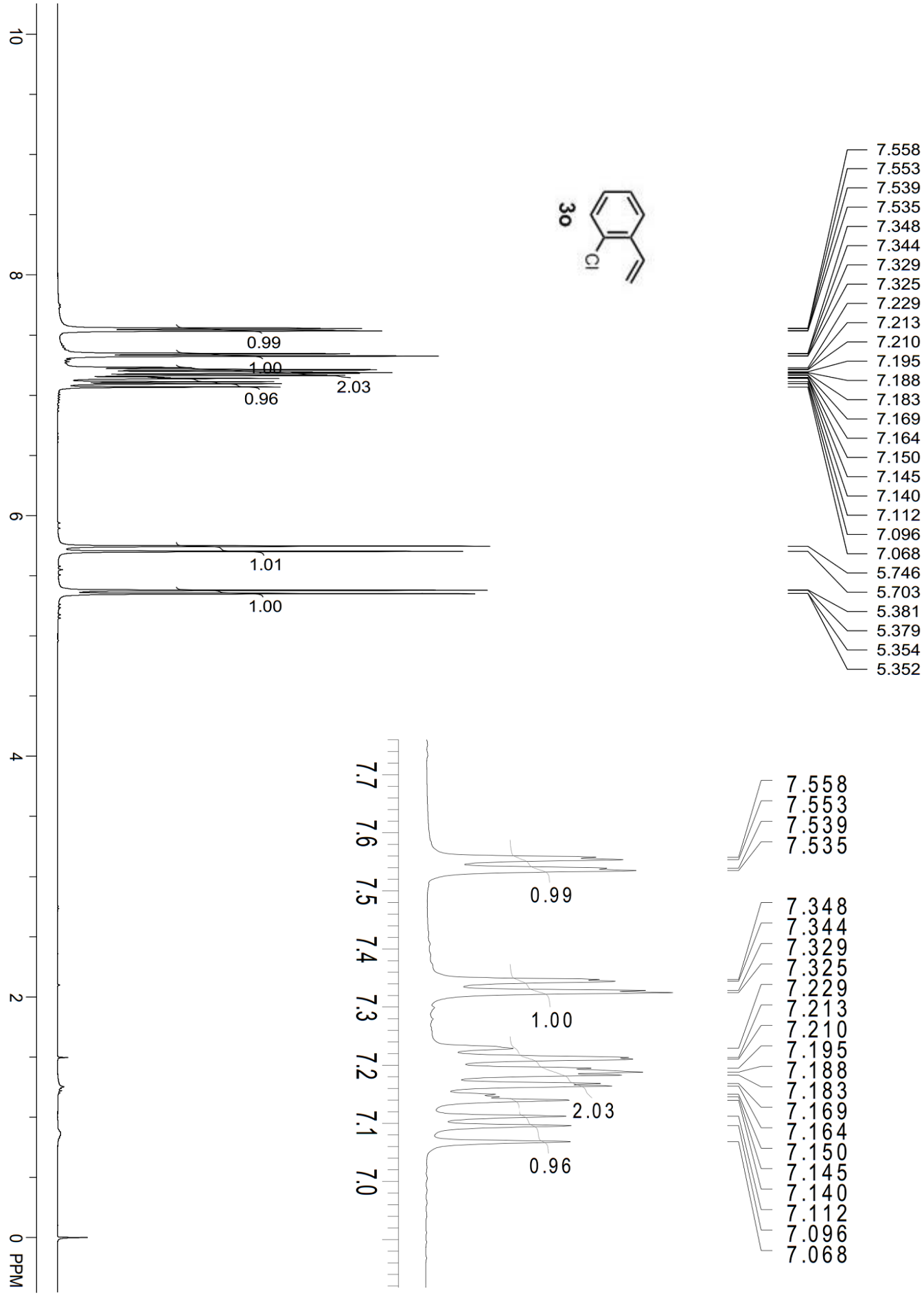
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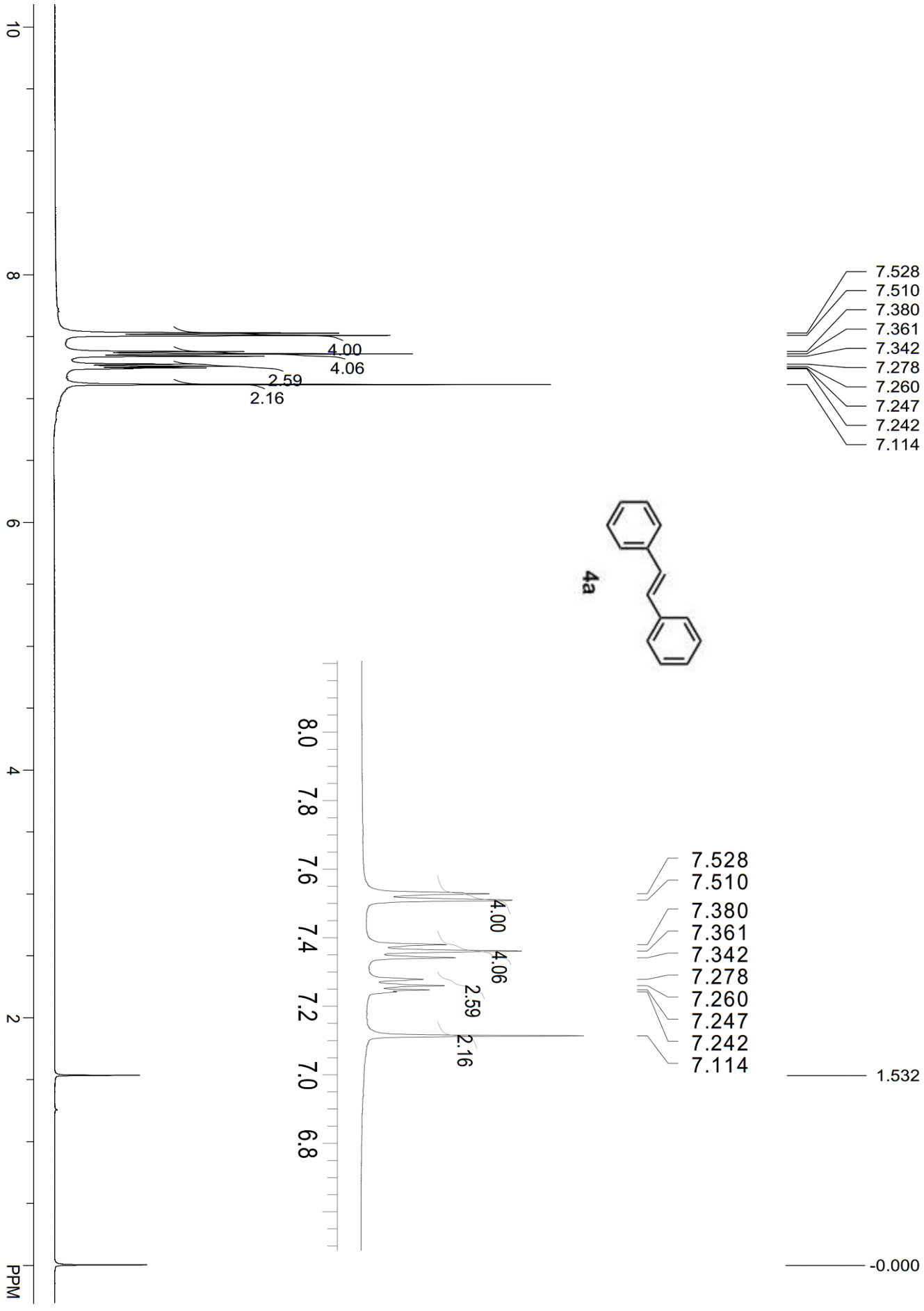
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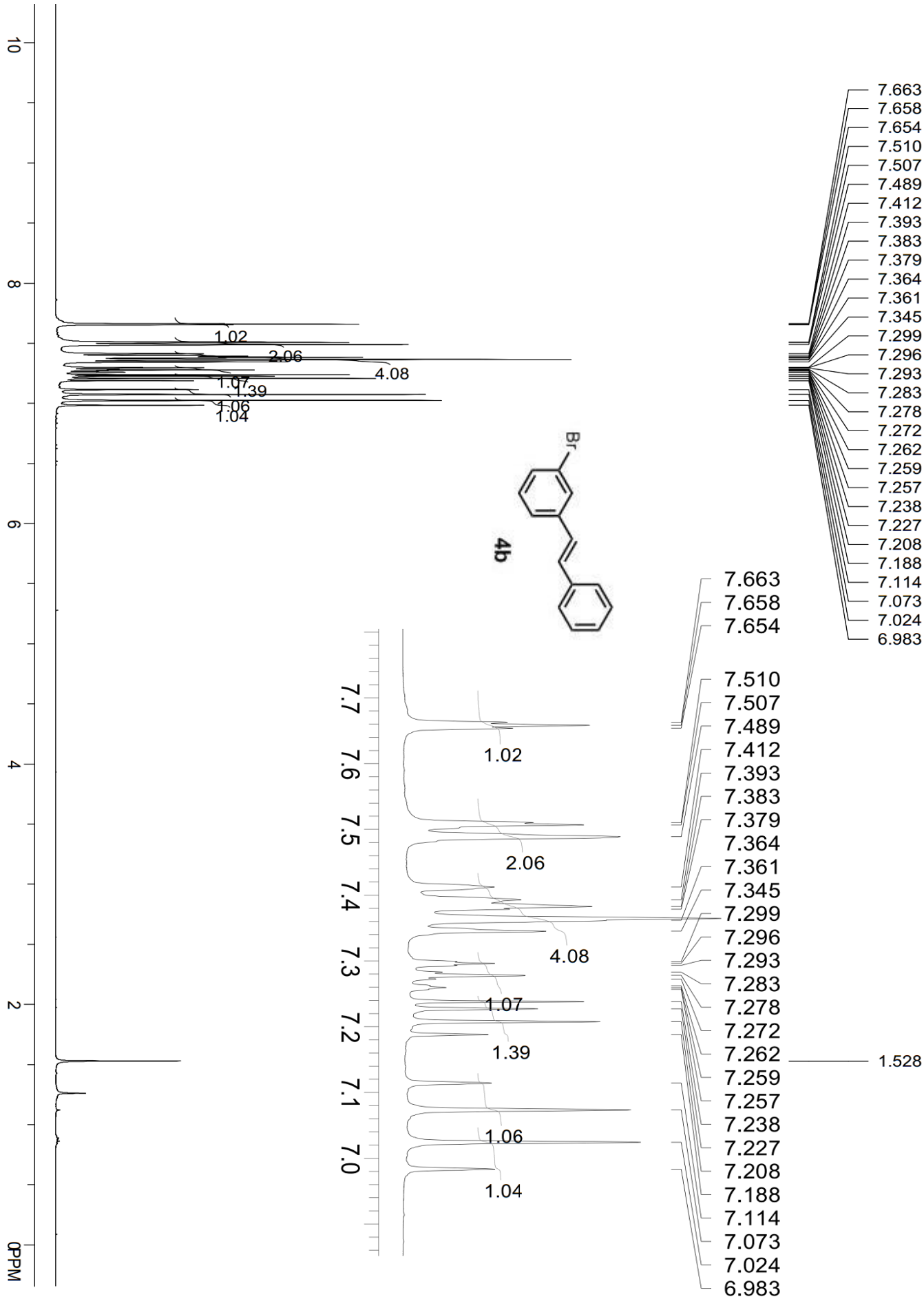
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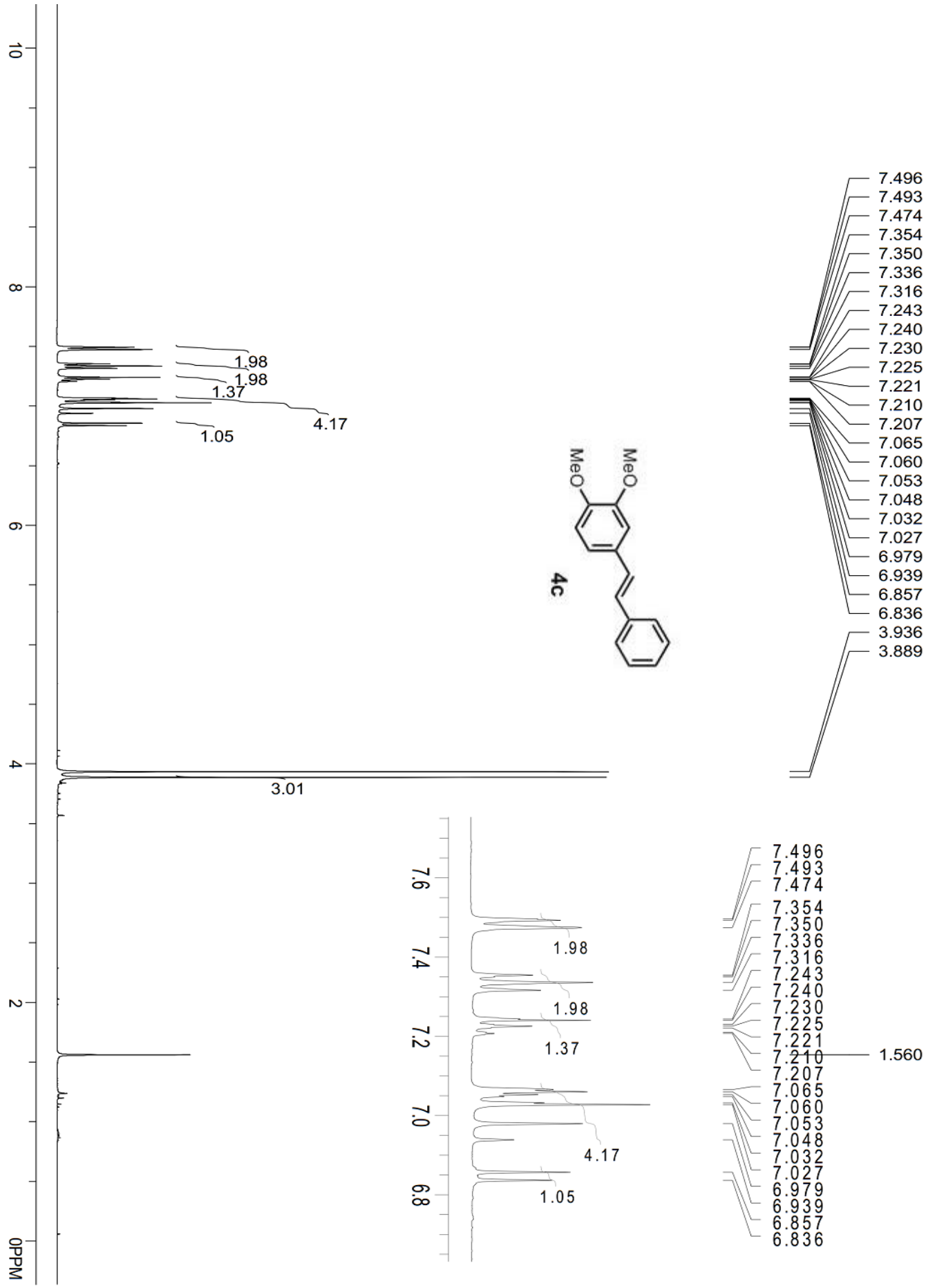
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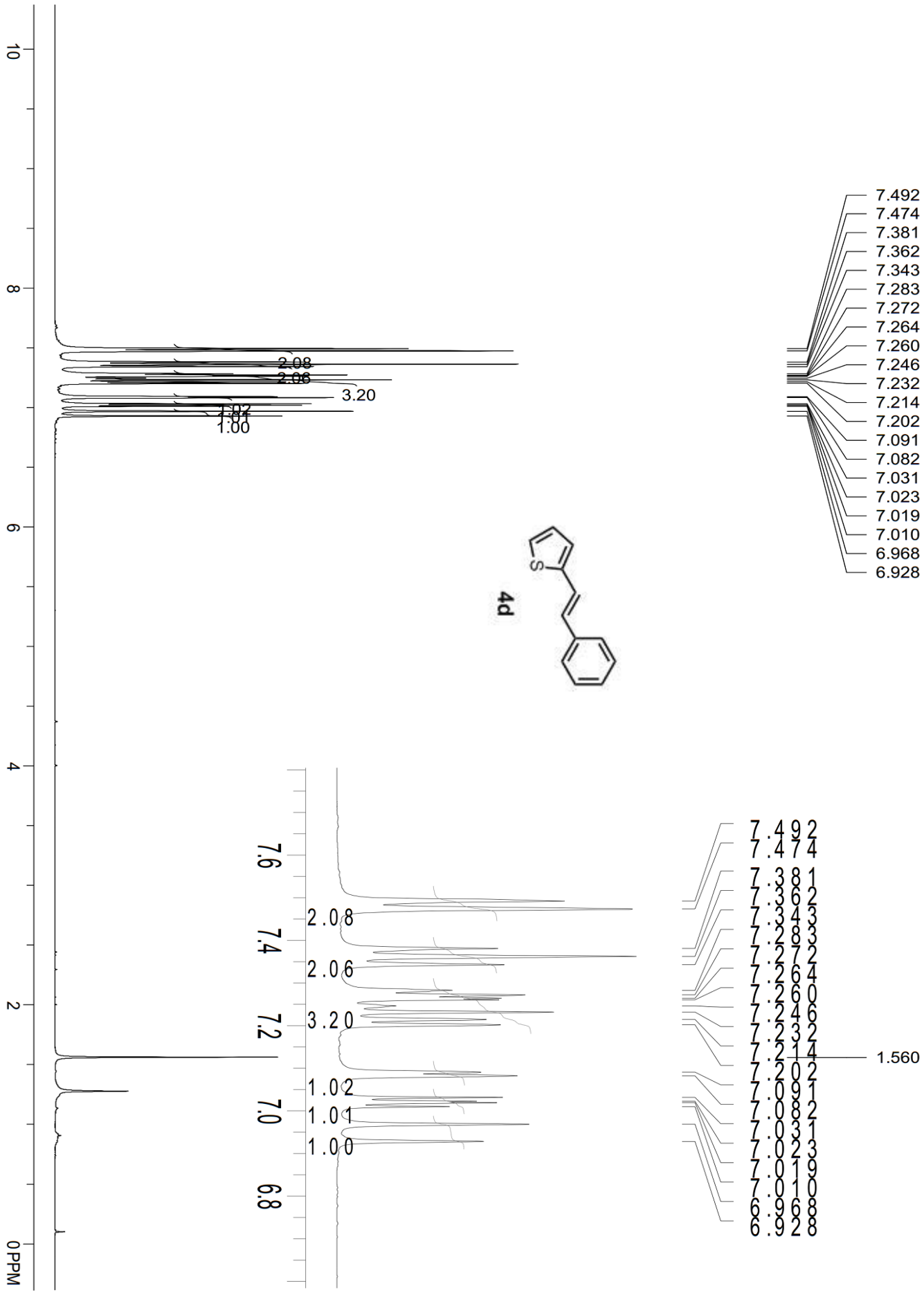
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2.08
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3.20
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1.01
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7.492
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7.232
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7.010
6.968
6.928
4d
S
7.6
7.4
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1.02
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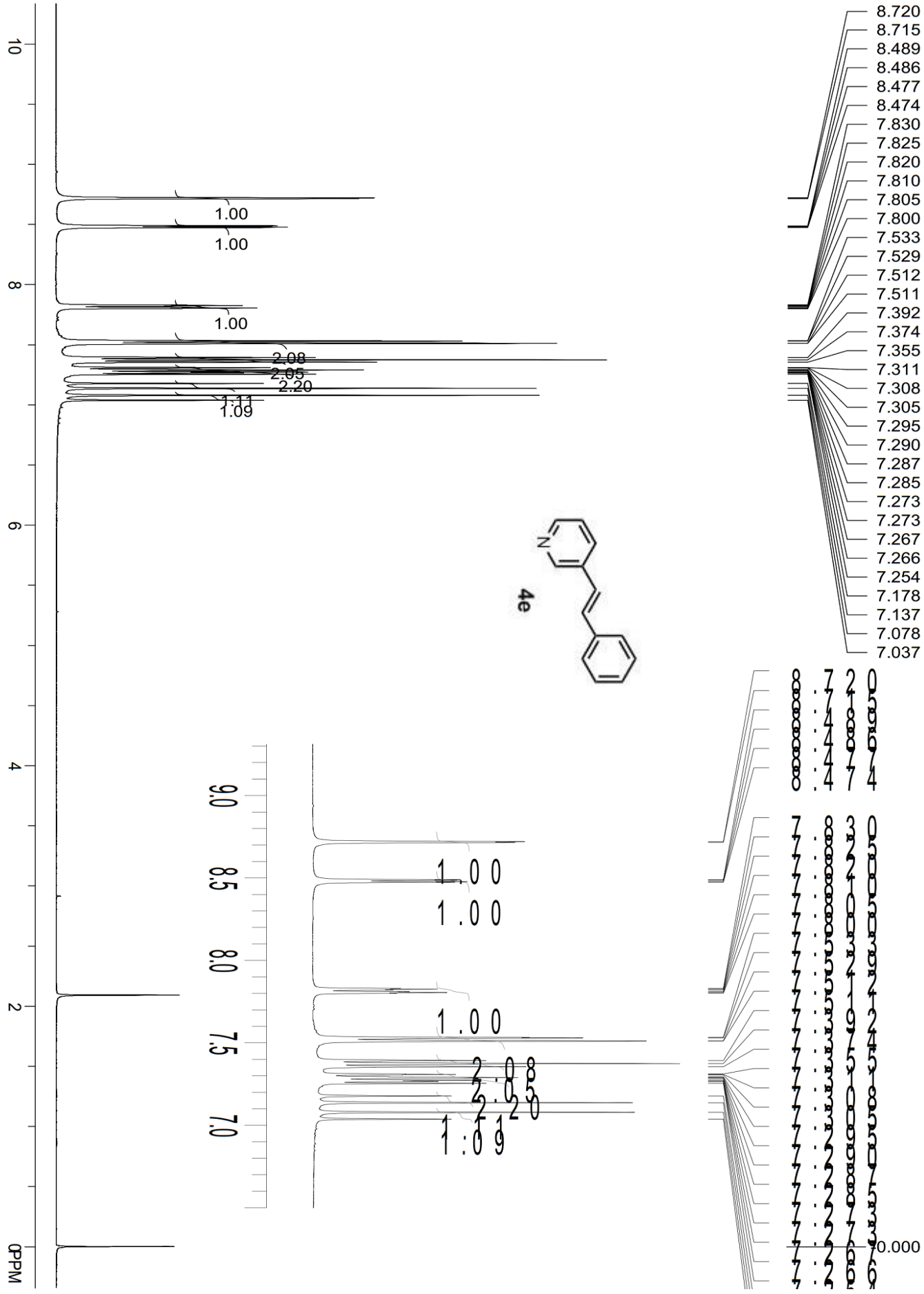
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7.078
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1.00
1.00
2.08
2.05
2.20
1.11
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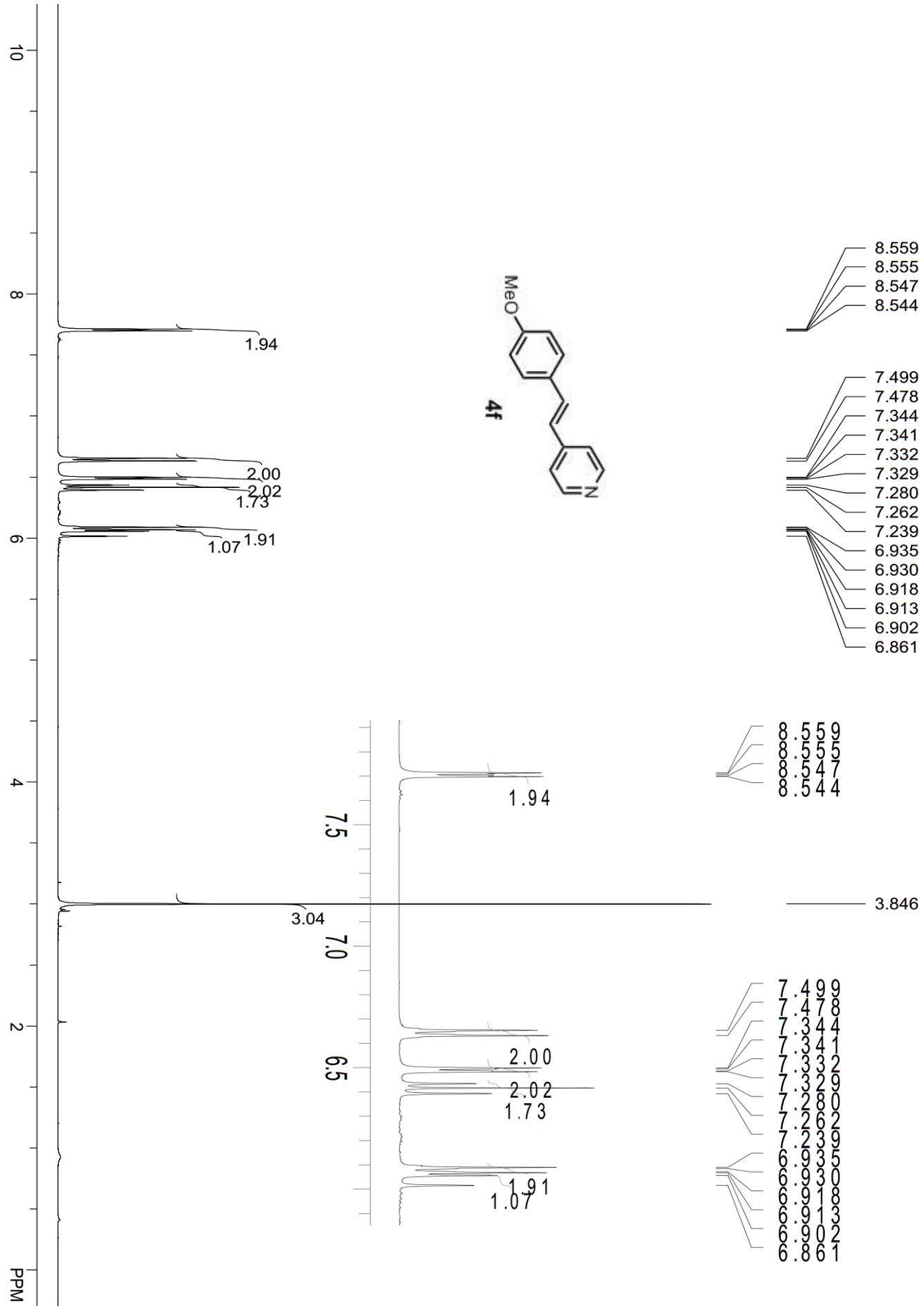
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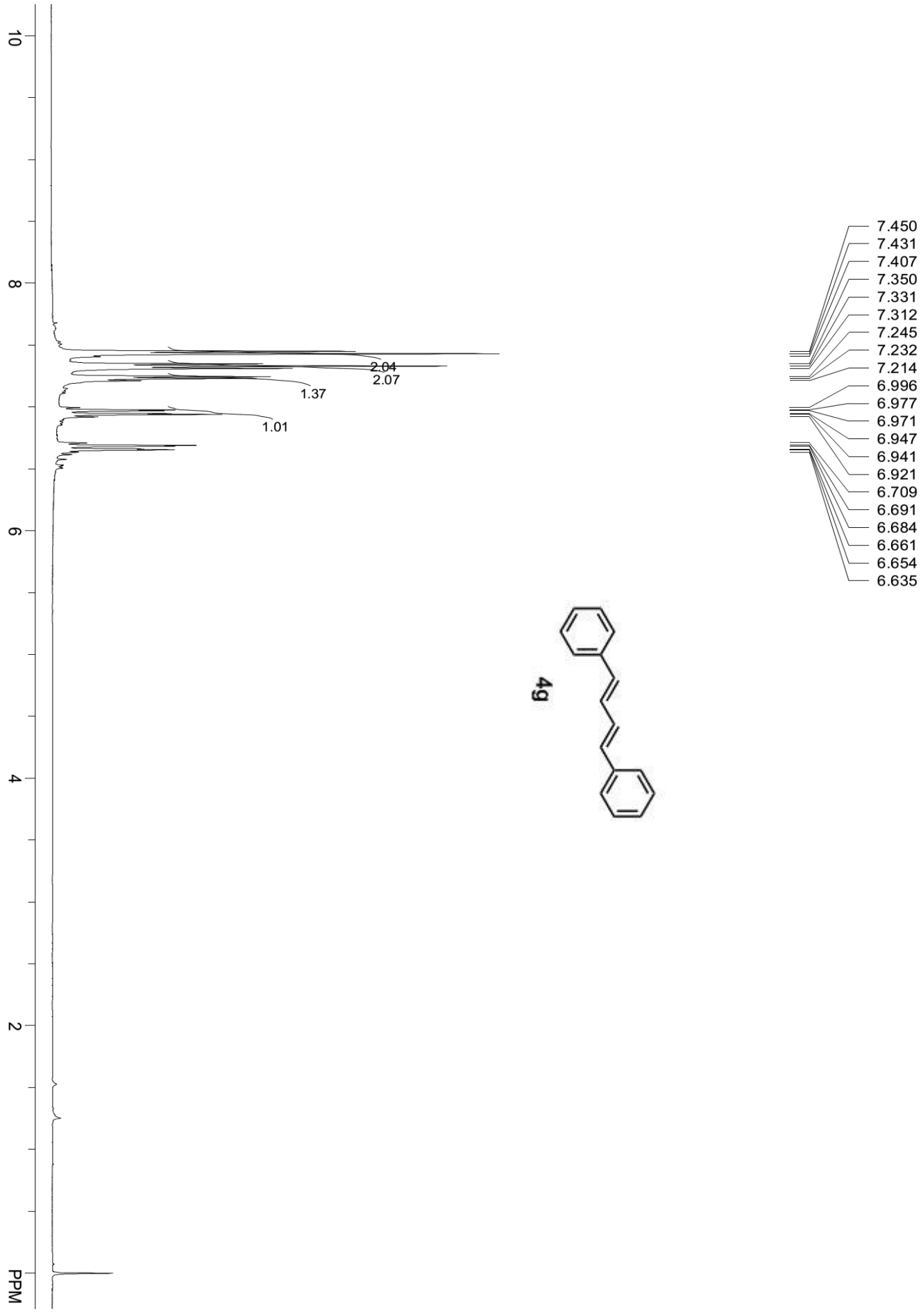
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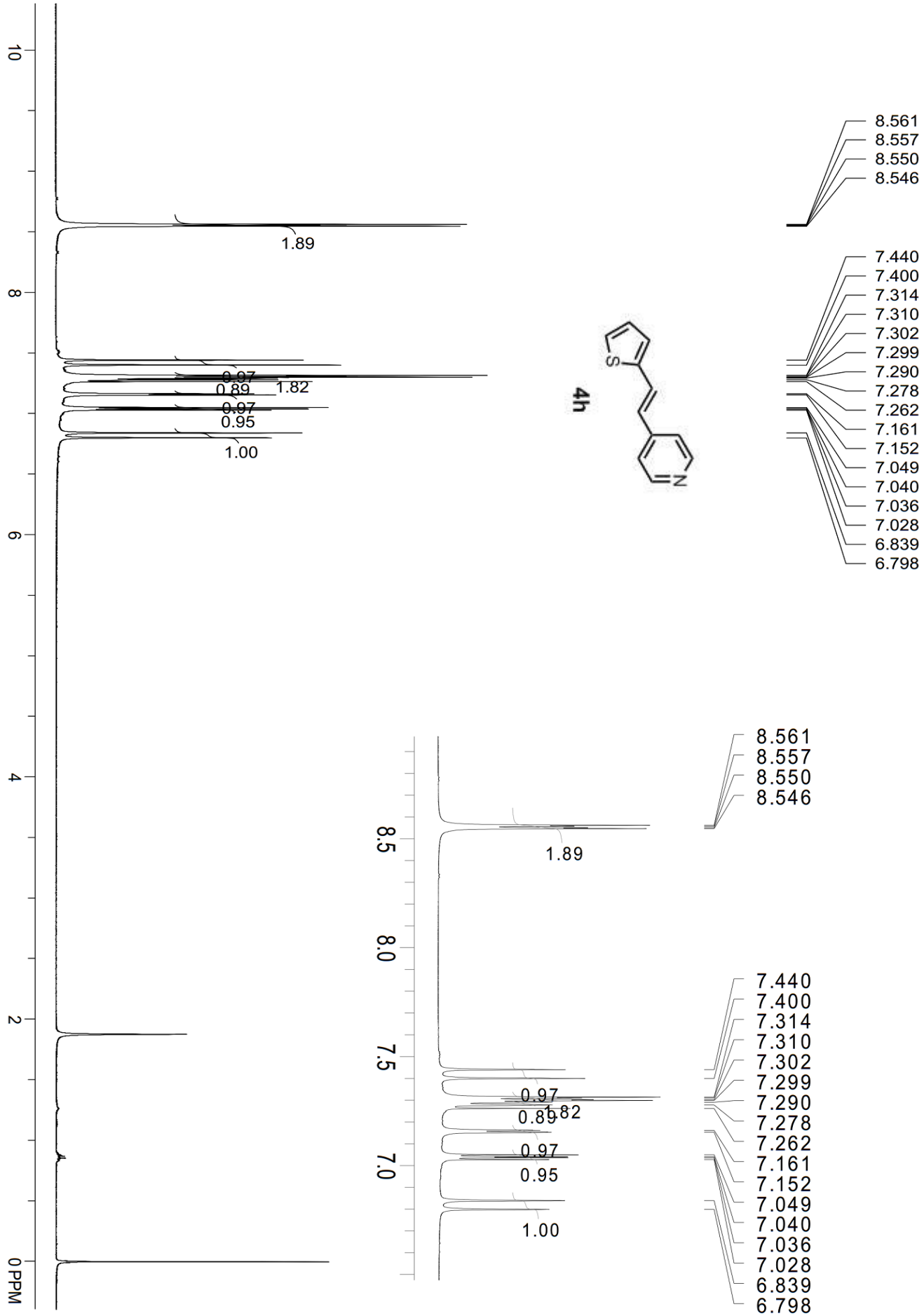
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8.550
8.546
7.440
7.400
7.314
7.310
7.302
7.299
7.290
7.278
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7.040
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S
N
4h
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7.5
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0.89
1.82
0.97
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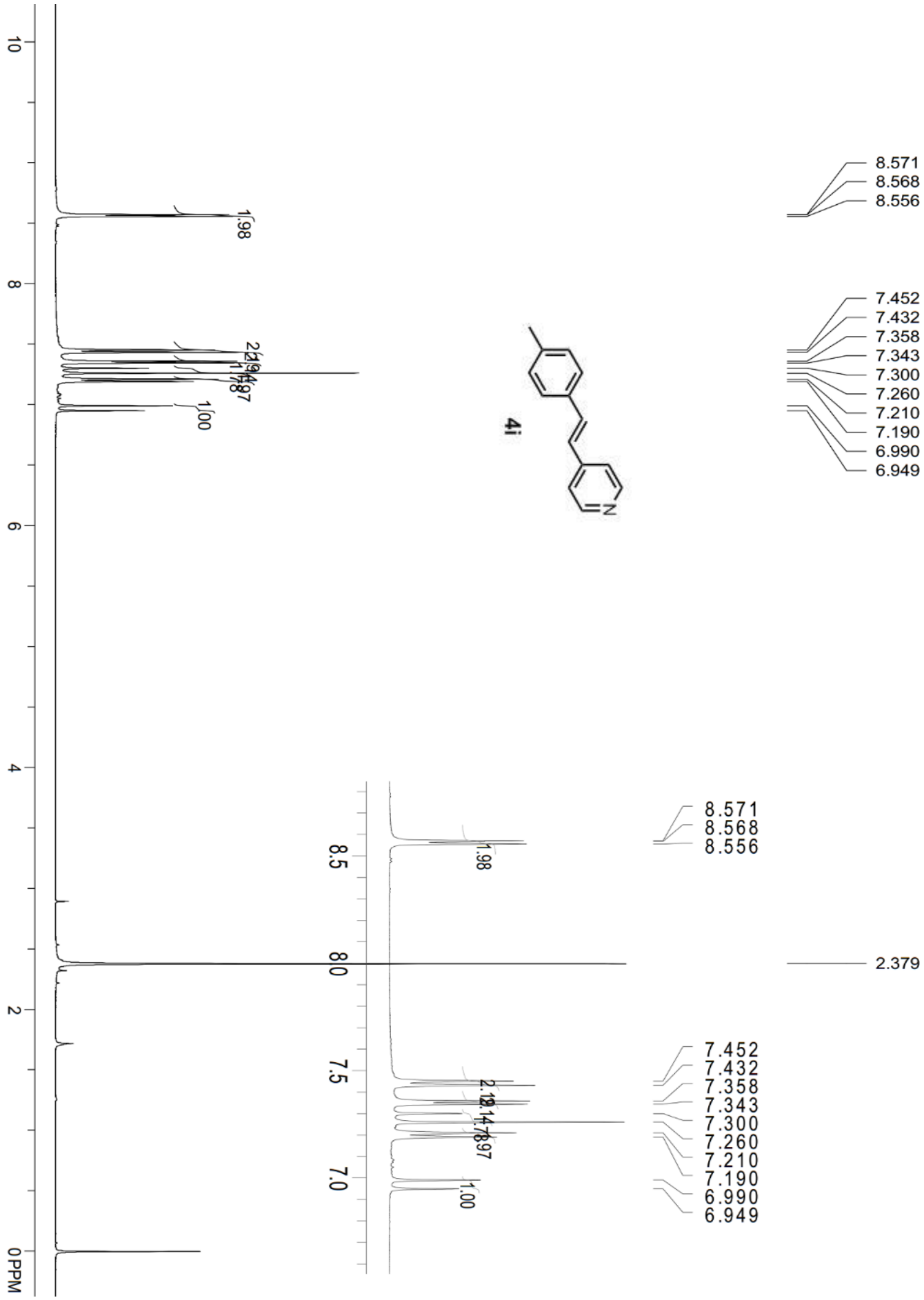
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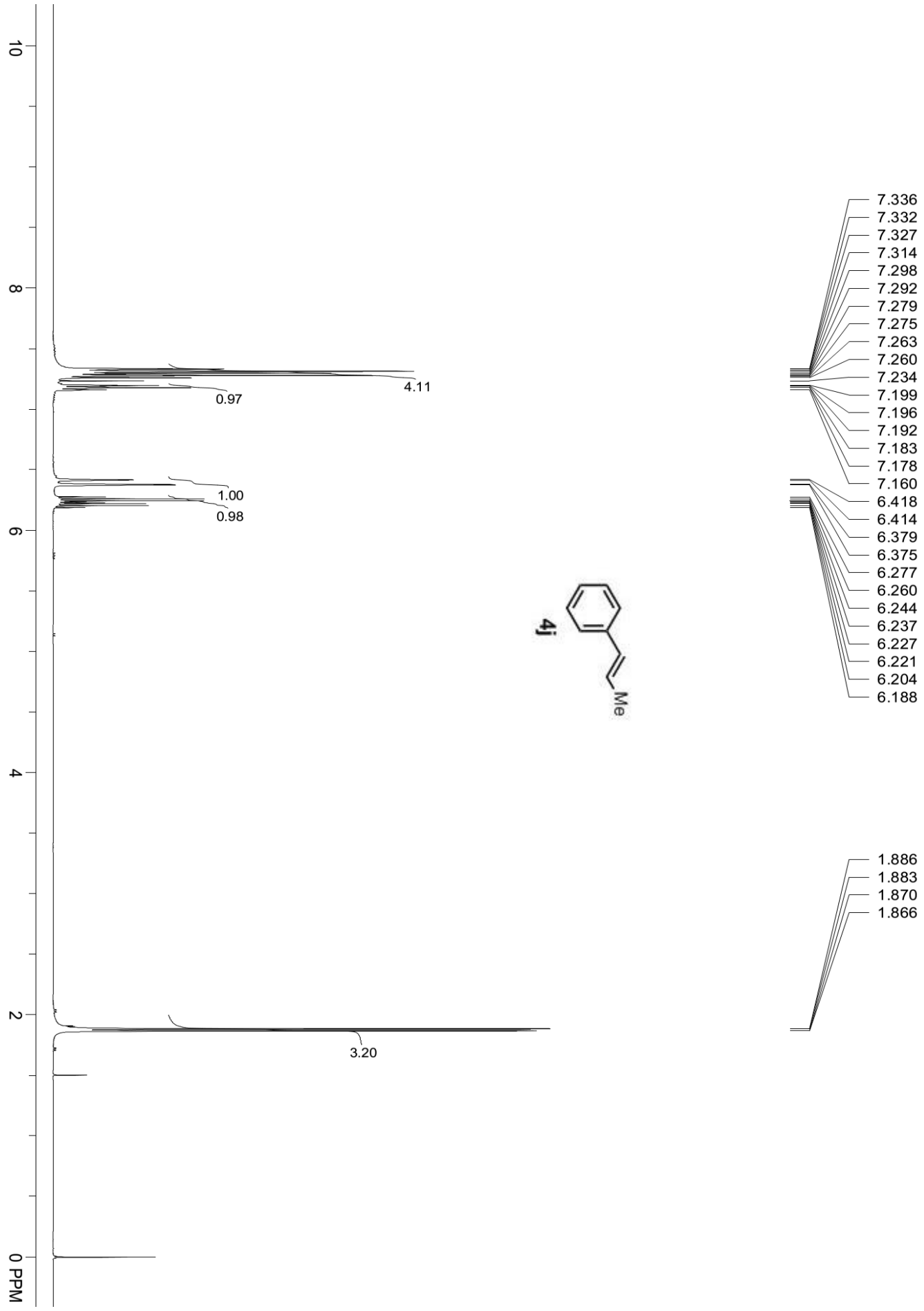
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4j
Me
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7.183
7.178
7.160
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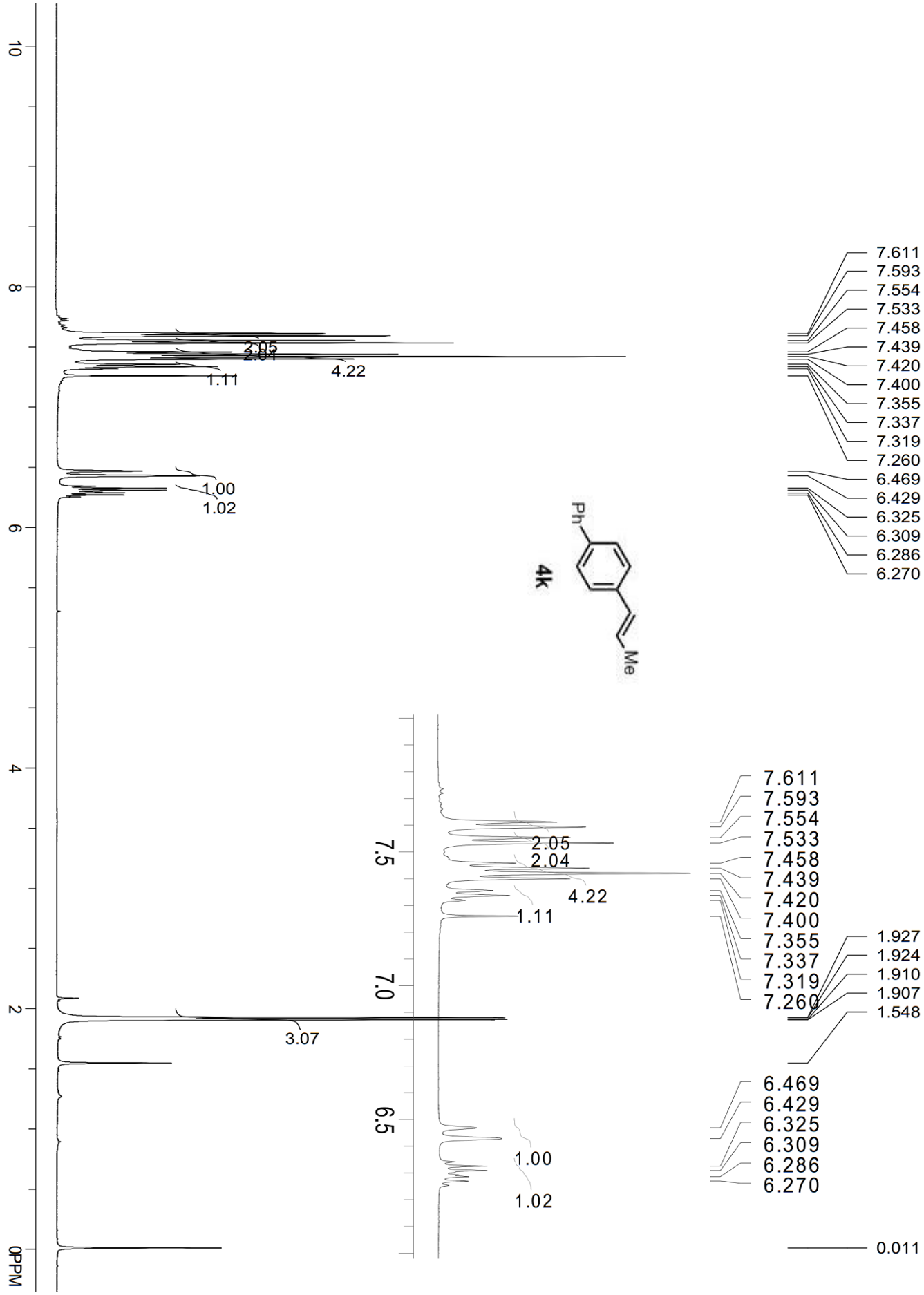
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3.07
Ph
Me
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7.439
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7.400
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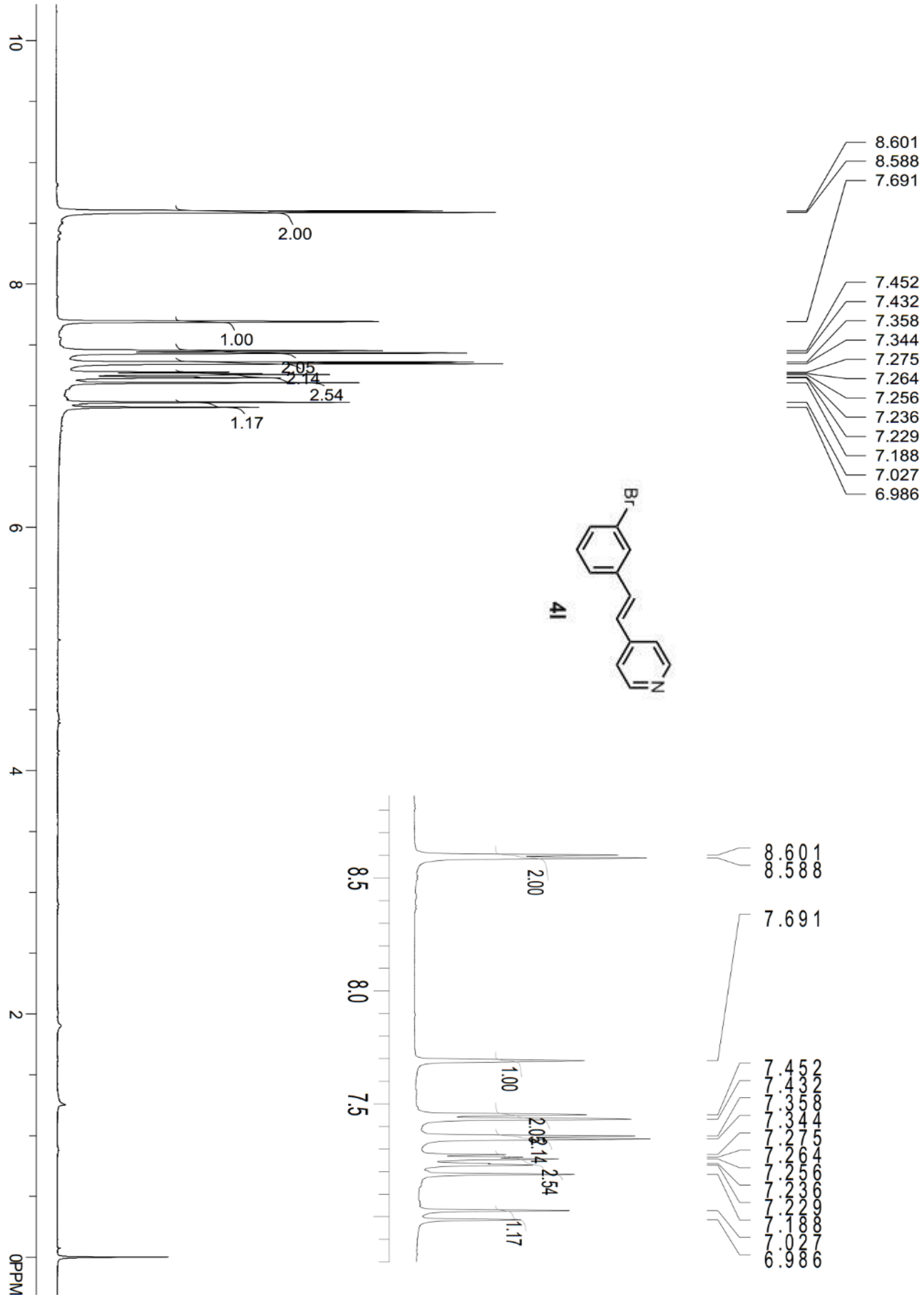
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Br
N
4l
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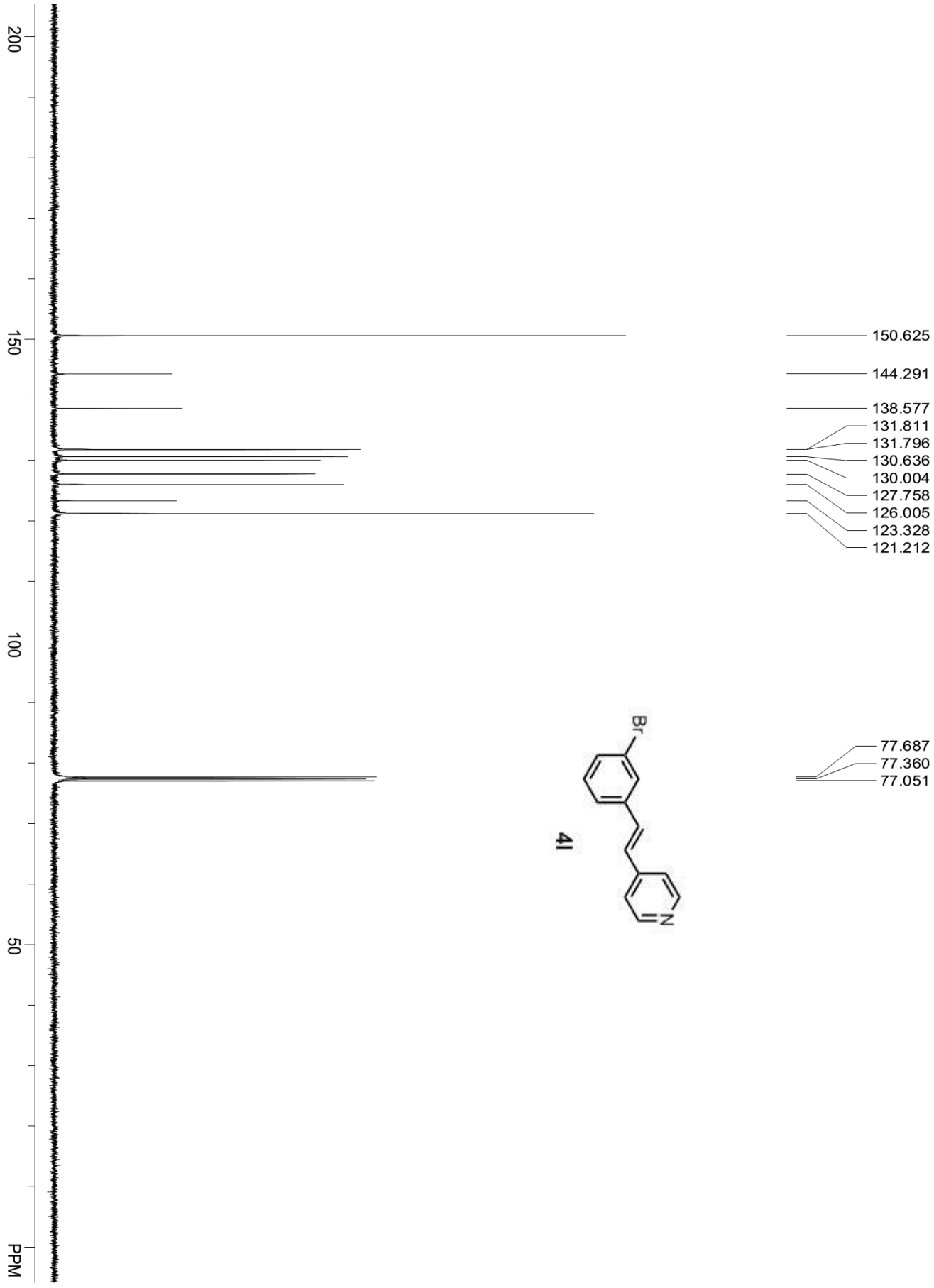
7.5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77.360
77.051
Br
N
4l

The End