One-pot one-base for two shots: organocatalyzed tandem isomerization-olefination of allylic alcohols

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1. General information

Solvents were pre-dried over activated 4 Å molecular sieves and heated to reflux over sodium (toluene, octane, THF) or calcium hydride (DMF, DMA, 1,4-dioxane, DMSO) under an argon atmosphere and collected by distillation. ^{1}H, ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer; Chemical shifts are reported in δ units relative to $CDCl_3$ [^{1}H δ = 7.26, ^{13}C δ = 77.36].

2. General procedures

2.1. Screening reaction conditions (Table S1)

1a (0.5 mmol, 105 mg), **3a** (0.2 mmol, 18 mg), Ph_3PCH_3Br (1.25 mmol, 446 mg) were weighed directly into a Schlenk tube and dried under high vacuum for 15 min. Then solvent (toluene, 2 mL) was added and stirred. The base was then added and stirred at 70 °C and the reaction was monitored by TLC. The reaction mixture was

directly examined on ^{1}H NMR spectrometer to determine the conversion and selectivity by using 1,4-dioxane (10.7 μL) as internal standards.

Table S1. Screening reaction conditions

entry	Ph_3PCH_3Br	^{t}BuONa	T/℃	t/h	conv(%)
1	1.5	1.55	90	24	46
2	1.5	2.0	90	24	38
3	2.0	2.20	90	24	66
4	2.0	2.20	70	24	81
5	2.5	2.70	70	12	85[a]
6	3.0	3.2	70	12	90[a]
7	2.5	2.7	70	4	93[a]

[a] Isolated yield.

2. 2. Scope of solvents (Table S2)

1a (0.5 mmol, 105 mg), **3a** (0.2 mmol, 18 mg), Ph_3PCH_3Br (1.25 mmol, 446 mg) were weighed directly into a Schlenk tube and dried under high vacuum for 15 min. Then solvent (toluene, THF, DME, 1,4-dioxane, CH_3CN, DMF, or DMSO, 2 mL) was added and stirred. ^{t}BuONa (1.35 mmol, 135 mg) was then added and stirred at 70 °C and the resulting reaction mixture was monitored by TLC. The crude reaction mixture was directly examined on ^{1}H NMR spectrometer to determine the conversion and selectivity by using 1,4-dioxane (10.7 μL) or 1,3-dimethoxybenzene (22 μL) as internal standards.

Table S2. Solvents

entry	Solvent	t/h	conv (%)
1	toluene	4	93
2	THF	4	63
3	1,4-dioxane	4	49
4	DMSO	4	52
5	DMF	4	45
6	DMA	4	76

7	octane	4	93

2. 3. Effect of base (Table S3)

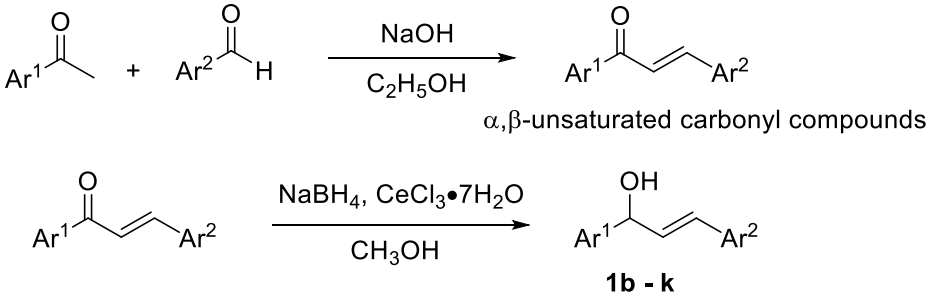
1a (0.5 mmol, 105mg), **3a** (0.2 mmol, 18mg), Ph_3PCH_3Br (1.25 mmol, 446mg) were weighed directly into a Schlenk tube and dried under high vacuum for 15 min. Then solvent (toluene 2mL) was added and stirred. The base (1.35 mmol) was then added and stirred at 70 °C and the resulting reaction mixture was monitored by TLC. The crude reaction mixture was directly examined on ^{1}H NMR spectrometer to determine the conversion and selectivity by using 1,4-dioxane (10.7 μL) or 1,3-dimethoxybenzene (22 μL) as internal standards.

Table S3 Effect of base

entry	Base	t/h	conv(%)
1	^{t}BuONa	4	93
2[a]	^{t}BuONa	4	56
3	KOH	4	trace
4	NaOH	4	trace
5	NaH	4	88
6	KHMDS	4	60
7	LiHMDS	4	10
8	^{n}BuLi	4	trace

[a] no phenanthroline

2.4. Preparation of general materials

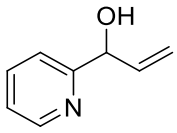


Compounds 1b-k were prepared as described in a reported protocol.1,2 General procedures: corresponding benzaldehyde (10 mmol) was dissolved in ethanol (20 mL). Then aqueous NaOH (2.0 equiv) was added dropwise followed by the slow addition of the corresponding ketone (10 mmol). The reaction mixture was stirred at room

temperature until the complete consumption of the starting materials (monitored by TLC). The reaction mixture was diluted with water. The precipitate was collected by filtration and washed with water and EtOH. Allylic Alcohols were prepared by reduction of α,β-unsaturated carbonyl compounds with $NaBH_4$ or $LiAlH_4$ in the presence of $CeCl_3$. The reduction was quenched by addition of a mixed solution of saturated NH_4Cl and 1 M HCl and extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, concentrated and purified on silica gel chromatography to give the allylic alcohols.

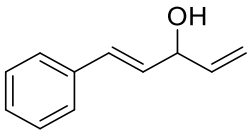
1l - q

Compounds **1l-q** were prepared as described in a reported protocol.3 General procedure: vinyl magnesium bromide (2.0 equiv., 1.0 M in THF) was added slowly to a stirred solution of freshly distilled aldehyde (1.0 equiv) in dry THF (0.5 M), which was maintained an internal temperature below 5 ˚C. After 15 min, the reaction was allowed to warm to r.t. and stirred for additional 1-3 h. Then the reaction was quenched by adding saturated NH_4Cl aq. and extracted with Et_2O. The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, concentrated and purified on silica gel chromatography (EtOAc/petroleum ether as eluent) to give the allylic alcohol.



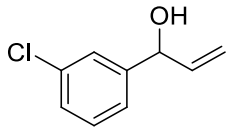
1-(pyridin-2-yl)prop-2-en-1-ol (**1b**)

Prepared according to the general procedure method 1 h, yellow oil, 427 mg, 63%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55–8.53 (m, 1H), 7.69 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.31–7.29 (m, 1H), 7.23–7.19 (m, 1H), 5.97 (ddd, *J* = 17.2, 10.0, 6.4 Hz, 1H), 5.45 (dt, *J* = 17.2, 1.2 Hz, 1H), 5.24 (dt, *J* = 10.0, 1.2 Hz, 1H), 5.18 (d, *J* = 6.0 Hz, 1H), 4.79 (s, 1H).[4]



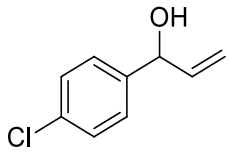
(*E*)-1-phenylpenta-1,4-dien-3-ol (**1c**)

Prepared according to the general procedure method 4 h, yellow oil, 1.19 g, 74%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.36 (m, 2H), 7.32–7.28 (m, 2H), 7.25–7.21 (m, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.22 (dd, *J* = 16.0, 6.4 Hz, 1H), 5.97 (ddd, *J* = 17.2, 10.4, 6.0 Hz, 1H), 5.33 (dt, *J* = 17.2, 1.2 Hz, 1H), 5.18 (dt, *J* = 10.4, 1.2 Hz, 1H), 4.79 (br s, 1H), 1.97 (br s, 1H).[5]



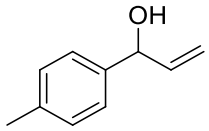
1-(3-chlorophenyl)prop-2-en-1-ol (**1d**)

Prepared according to the general procedure method 3 h, yellow oil, 856 mg, 98%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38–7.37 (m, 1H), 7.30–7.23 (m, 3H), 6.04–5.96 (m, 1H), 5.36 (dt, *J*= 16.8, 1.2 Hz, 1H), 5.22 (dt, *J*= 10.4, 1.2 Hz, 1H), 5.18 (br s, 1H), 2.10 (brs, 1H).[6]



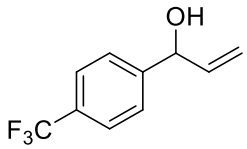
1-(4-chlorophenyl)prop-2-en-1-ol (**1e**)

Prepared according to the general procedure method 1 h, yellow oil, 665 mg, 66%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.28 (m, 4H), 6.04–5.95 (m, 1H), 5.36–5.30 (m, 1H), 5.22–5.16(m, 2H), 2.14 (brs, 1H).[7]



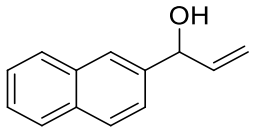
1-(*p*-tolyl)prop-2-en-1-ol (**1f**)

Prepared according to the general procedure method 3 h, yellow oil, 616 mg, 62%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.02 (ddd, *J*= 16.8, 10.4, 5.8 Hz, 1H), 5.34 (dt, *J* = 16.8, 1.4 Hz, 1H), 5.20–5.17 (m, 2H), 2.35 (s, 3H), 1.93 (d, *J* = 3.6 Hz, 1H).[8]



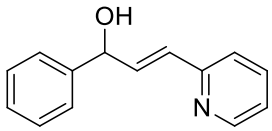
1-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (**1g**)

Prepared according to the general procedure method 3 h, yellow oil, 696 mg, 69%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.50–7.48 (m, 2H), 6.05–5.95 (m, 1H), 5.39–5.33 (m, 1H), 5.25–5.21 (m, 1H), 2.40 (br s, 1H).[8]



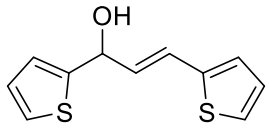
1-(naphthalen-2-yl)prop-2-en-1-ol (**1h**)

Prepared according to the general procedure method 1 h, colorless oil, 1.026 g, 56%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87–7.82 (m, 4H), 7.53–7.47 (m, 3H), 6.13 (ddd, *J* = 16.4, 10.4, 6.0 Hz, 1H), 5.41 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.34 (s, 1H), 5.25 (dt, *J* = 10.4, 1.4 Hz, 1H), 2.60 (br s, 1H).[9]



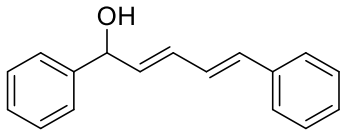
(*E*)-1-phenyl-3-(pyridin-2-yl)prop-2-en-1-ol (**1j**)

Prepared according to the general procedure method 1 h, yellow oil, 1.3153 g, 48%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (dt, *J* = 0.8, 4.8 Hz, 1H), 7.61 (td, *J* = 7.6, 1.9 Hz, 1H), 7.46–7.43 (m, 2H), 7.38–7.34 (m, 2H), 7.32–7.27 (m, 2H), 7.12 (ddd, *J* = 7.2, 4.8, 1.2 Hz, 1H), 6.91–6.78 (m, 2H), 5.44 (d, *J* = 5.6 Hz, 1H), 3.32 (s, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.2, 149.4, 142.5, 136.6, 136.5, 129.5, 128.6, 127.8, 126.5, 122.3, 121.8, 74.5. **HRMS (ESI)** calcd for $C_{14}H_{14}NO$ $[M+H]^+$ 212.1075, found 212.1078.



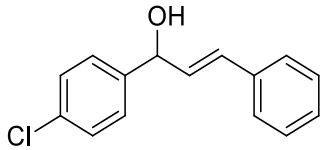
(*E*)-1,3-di(thiophen-2-yl)prop-2-en-1-ol (**1k**)

Prepared according to the general procedure method 1 h, purple oil, 203 mg, 18%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 4.8 Hz, 1H), 7.18 (d, *J* = 4.8 Hz, 1H), 7.04–6.96 (m, 4H), 6.85 (d, *J* = 15.6 Hz, 1H), 6.28 (dd, *J* = 6.4, 16.0 Hz, 1H), 5.58 (d, *J* = 6.4 Hz, 1H), 2.02 (br s, 1H).[10]



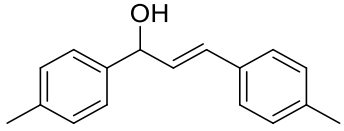
(2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-ol (**1l**)

Prepared according to the general procedure method 1 h, yellow solid, 1.60 g, 84%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43–7.28(m, 9H), 7.25–7.21 (m, 1H), 6.79 (dd, *J* = 15.6, 9.8 Hz, 1H), 6.59 (d, *J* = 15.6, 1H), 6.48 (dd, *J* = 15.6, 10.8 Hz, 1H), 6.01 (dd, *J* = 15.2, 6.8 Hz, 1H), 6.32 (d, *J* = 6.8, 1H), 2.03 (s, 1H).[11]



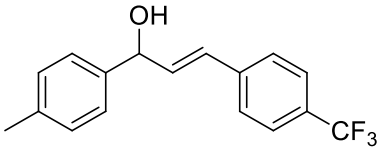
(*E*)-1-(4-chlorophenyl)-3-phenylprop-2-en-1-ol (**1m**)

Prepared according to the general procedure method 10 min, colorless oil, 574 mg, 79%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.23 (m, 9H), 6.64 (d, *J* = 15.6 Hz, 1H), 6.30 (dd, *J* = 15.6, 6.6 Hz, 1H), 5.32 (t, *J* = 7.0 Hz, 1H), 2.21 (br s, 1H).[12]



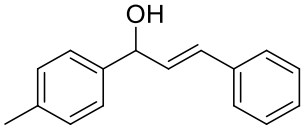
(*E*)-1, 3-di-*p*-tolylprop-2-en-1-ol（**1n**）

Prepared according to the general procedure method 15 min, white solid, 636 mg, 90%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (q, *J* = 7.2 Hz 4H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.32 (dd, *J* = 16.0, 6.4 Hz, 1H), 5.33 (d, *J* = 6.0 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H), 2.02 (d, *J* = 2.8 Hz, 1H).[13]



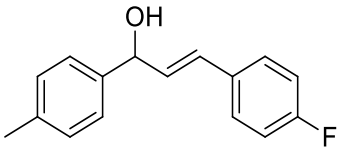
(*E*)-1-(*p*-tolyl)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (**1o**)

Prepared according to the general procedure method 1 h, white solid, 709 mg, 81%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.32 - 7.30 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 15.6 Hz, 1H), 6.47 (dd, *J* = 15.6, 5.8 Hz, 1H), 5.38 (d, *J* = 5.6 Hz, 1H), 2.36 (s, 3H), 2.02 (br s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.3, 139.6, 138.0, 134.4, 129.6 (t, *J* = 128.4 Hz), 128.7, 126.9, 126.5, 125.6 (q, *J* = 15.6 Hz), 123.0, 74.8, 21.3. **HRMS (EI)** calcd for $C_{17}H_{15}F_3O^+$ 292.1075, found 292.1081.



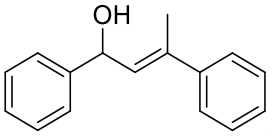
(*E*)-3-phenyl-1-(*p*-tolyl)prop-2-en-1-ol (**1p**)

Prepared according to the general procedure method 1 h, white solid, 664 mg, 98%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.16 (m, 9H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.37 (dd, *J* = 16.0, 6.4 Hz, 1H), 5.34 (dd, *J* = 6.4, 2.4 Hz, 1H), 2.34 (s, 3H), 2.04 (d, *J* = 3.2 Hz, 1H).[14]



(*E*)-3-(4-fluorophenyl)-1-(*p*-tolyl)prop-2-en-1-ol (**1q**)

Prepared according to the general procedure method 1 h, white solid, 824 mg, 45%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.31 (m, 4H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.02–6.96 (m, 2H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.30 (dd, *J* = 16.0, 6.4 Hz, 1H), 5.36–5.33 (m, 1H), 2.36 (s, 3H), 2.08–2.05 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.6, 161.2, 139.9, 137.7, 132.8 (d, *J* = 13.2 Hz), 131.5 (d, *J* = 8.0 Hz), 129.4, 129.1, 128.1 (d, *J* = 32.4 Hz), 126.3, 115.6, 115.4, 74.9, 21.2. **HRMS (ESI)** calcd for $C_{16}H_{15}FONa$ $[M+Na]^+$ 265.1005, found 265.1009.



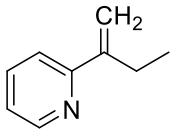
(*E*)-1, 3-diphenylbut-2-en-1-ol (**1s**)

Prepared according to the general procedure method 1 h, yellow oil, 1.950 g, 61%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 - 7.23 (m, 10H), 6.01 (dq, *J* = 8.6, 1.3 Hz, 1H), 5.65

(d, *J* = 8.8 Hz, 1H), 2.20 (d, *J* = 1.2 Hz, 3H), 2.00 (s, 1H).[14]

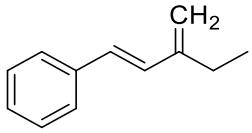
2.3. General procedure of base catalyzed olefination of allylic alcohols

1a (0.5 mmol, 105 mg), **3a** (0.2 mmol, 18 mg), Ph_3PCH_3Br (1.25 mmol, 446 mg) were introduced into a Schlenk tube and then dried under vacuum for 15 min. After that, solvent (toluene, 2 mL) was added under stirring in the presence of argon atmosphere followed by the addition of ^{t}BuONa (1.35 mmol). The reaction mixture was stirred at 70 °C and was monitored by TLC analysis. After completion, the reaction mixture was subjected to run a silica gel column to give the target product.



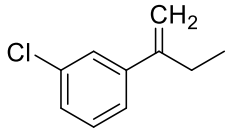
2-(but-1-en-2-yl)pyridine (**2b**)

Prepared according to the general procedure method, 5 h, yellow oil, 58.9mg, 68%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59–8.57 (m, 1H), 7.66–7.61 (m, 1H), 7.46 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.17–7.13 (m, 1H), 5.75 (s, 1H), 5.28–5.27 (m, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.15 (t, *J* = 7.4 Hz, 3H).[16]



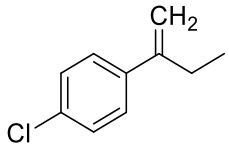
(*E*)-(3-methylenepent-1-en-1-yl)benzene (**2c**)

Prepared according to the general procedure method, 5 h, colorless oil, 58.6 mg, 74%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.43 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 16.0 Hz, 1H), 6.59 (d, *J* = 16.4 Hz, 1H), 5.13 (s, 1H), 5.08 (s, 1H), 2.36 (q, *J* = 7.2 Hz, 2H), 1.17 (td, *J* = 7.2, 1.0 Hz, 3H).[17]



1-(but-1-en-2-yl)-3-chlorobenzene (**2d**)

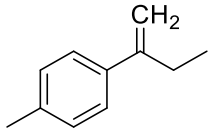
Prepared according to the general procedure method, 4 h, colorless oil, 76.1 mg 92%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.38 (m, 1H), 7.29–7.23 (m, 3H), 5.27 (s, 1H), 5.09 (q, *J* = 1.2 Hz, 1H), 2.47 (q, *J* = 7.4 Hz, 2H), 1.09 (t, *J* = 7.4 Hz, 3H). [18]



1-(but-1-en-2-yl)-4-chlorobenzene (**2e**)

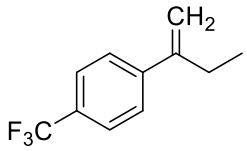
Prepared according to the general procedure method, 4 h, colorless oil, 59.9 mg, 72%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.32 (m, 2H), 7.31–7.25 (m, 2H), 5.25 (s, 1H), 5.07 (q, *J* = 1.2 Hz, 1H), 2.48 (q, *J* = 7.4 Hz, 2H), 1.09 (t, *J* = 7.4 Hz, 3H).[18]



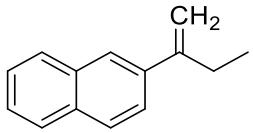
1-(but-1-en-2-yl)-4-methylbenzene (**2f**)

Prepared according to the general procedure method, 4 h, colorless oil, 50.8 mg, 71%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 5.26 (s, 1H), 5.02 (s, 1H), 2.51 (q, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 1.13–1.09 (m, 3H).[18]



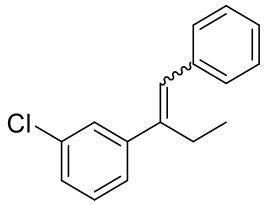
1-(but-1-en-2-yl)-4-(trifluoromethyl)benzene (**2g**)

Prepared according to the general procedure method, 4 h, colorless oil, 80.1 mg, 80%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 5.33 (s, 1H), 5.15 (s, 1H), 2.52 (q, *J* = 7.2 Hz, 2H), 1.12–1.07 (m, 3H).[18]



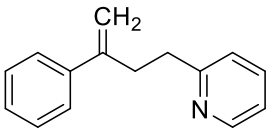
2-(but-1-en-2-yl)naphthalene (**2h**)

Prepared according to the general procedure method, 5 h, colorless oil, 82.7 mg, 92%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 13.8, 8.6 Hz, 4H), 7.60 - 7.57 (m, 1H), 7.46–7.41 (m, 2H), 5.42 (s, 1H), 5.16 (q, *J* = 1.2 Hz, 1H), 2.63 (q, *J* = 7.2 Hz, 2H), 1.15 (td, *J* = 7.2, 1.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.9, 138.7, 133.4, 132.8, 128.2, 127.7, 127.5, 126.1, 125.7, 124.7, 124.5, 111.6, 28.1, 13.1. **HRMS (ESI)** calc. for $C_{14}H_{15}$ $[M+H]^+$ 183.1174, found 183.1174.



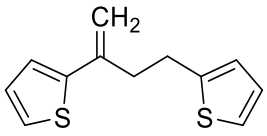
(*Z*/*E*)-1-chloro-3-(1-phenylbut-1-en-2-yl)benzene (**2i**)

Prepared according to the general procedure method, 4 h, colorless oil, 108.2 mg, 68%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46–6.46 (m, 10H), 2.72 (q, *J* = 7.6 Hz, 1.21H), 2.50 (q, *J* = 7.6 Hz, 0.87H), 1.09–1.05 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.7, 143.4, 143.3 (two peaks), 137.9, 137.0, 134.3 (two peaks), 129.8, 129.6, 129.1, 129.0, 128.9, 128.7, 128.6, 128.5, 128.3, 128.2, 127.9, 127.2, 127.1, 127.0, 126.9, 126.8, 126.4, 126.0, 124.8, 33.3, 23.2, 13.4, 12.8. **HRMS (EI)** calcd for $C_{16}H_{15}Cl^+$ 242.0862, found 242.0855.



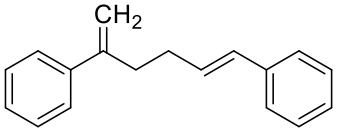
2-(3-phenylbut-3-en-1-yl)pyridine (**2j**)

Prepared according to the general procedure method, 4 h, colorless oil, 98.3 mg, 94%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.0 Hz, 1H), 7.55 (td, *J* = 7.6, 2.0 Hz, 1H), 7.45–7.43 (m, 2H), 7.35–7.31 (m, 2H), 7.28–7.25 (m, 1H), 7.10–7.06 (m, 2H), 5.29 (d, *J* = 1.2Hz, 1H), 5.07 (s, 1H), 2.95 (s, 4H). **^{13}C NMR** (100MHz, $CDCl_3$) δ 161.5, 149.3, 147.7, 141.0, 136.2, 128.4, 127.4, 126.2, 123.0, 121.1, 112.8, 37.1, 35.3. **HRMS (ESI)** calcd for $C_{15}H_{16}N$ $[M+H]^+$ 210.1283, found 210.1286.



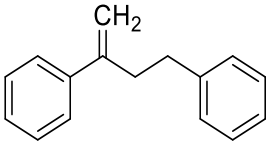
2,2'-(but-3-ene-1,3-diyl)dithiophene (**2k**)

Prepared according to the general procedure method, 5 h, yellow oil, 80.8 mg, 78%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.12–7.10 (m, 1H), 7.06–7.05 (m, 1H), 6.99 – 6.96 (m, 1H), 6.93–6.90 (m, 1H), 6.81–6.80 (m, 1H), 5.42 (d, *J* = 2.4 Hz, 1H), 4.97 (s, 1H), 3.11–3.07 (m, 2H), 2.85–2.81 (m, 2H). **^{13}C NMR** (100MHz, $CDCl_3$) δ 144.9, 144.4, 140.6, 127.4, 126.8, 124.4 (two peaks), 123.4, 123.2, 111.7, 37.7, 29.1. **HRMS (ESI)** calcd for $C_{12}H_{12}S_2$ $[M+H]^+$ 221.0453, found 221.0456.



(*E*)-hexa-1,5-diene-1,5-diyldibenzene (**2l**)

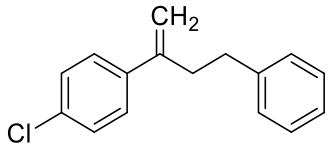
Prepared according to the general procedure method, 4 h, yellow oil, 60.0 mg, 51%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44–7.41 (m, 2H), 7.36–7.26 (m, 7H), 7.19 (tt, *J* = 7.0, 1.8 Hz, 1H), 6.36 (d, *J* = 15.6 Hz, 1H), 6.24–6.19 (m, 1H), 5.30 (d, *J* = 1.6 Hz, 1H), 5.11 (q, *J* = 1.4 Hz, 1H), 2.68 (t, J = 7.4Hz, 2H), 2.40–2.34 (m, 2H).[19]



but-3-ene-1,3-diyldibenzene (**2a**)

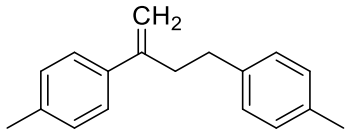
Prepared according to the general procedure method, 4 h, colorless oil, 96.6 mg, 93%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45–7.43 (m, 2H), 7.37–7.32 (m, 2H), 7.28 (t, *J* = 7.2 Hz, 3H), 7.20–7.16 (m, 3H), 5.29 (d, *J* = 0.8 Hz, 1H), 5.06 (d, *J* = 1.2 Hz, 1H), 2.84–2.74 (m, 4H).[20]

For gram scale reaction： **1a** (6 mmol), 1,10-Phenanthroline (1.2 mmol), Ph_3PCH_3Br (15 mmol), toluene (12 mL) and tBuONa (16.2 mmol) were used according to the standard procedure. After 6 hours, it affords the target product **2a** as a colorless oil in 88% yield (1.1 g).



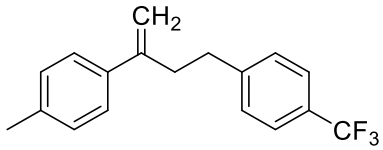
1-chloro-4-(4-phenylbut-1-en-2-yl)benzene (**2m**)

Prepared according to the general procedure method, 5 h, colorless oil, 93.2 mg, 77%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.24 (m, 6H), 7.21–7.15 (m, 3H), 5.27 (s, 1H), 5.07 (m, 1H), 2.80–2.72 (m, 4H).[21]



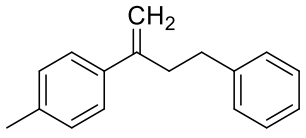
4, 4'-(but-3-ene-1,3-diyl)bis(methylbenzene) (**2n**)

Prepared according to the general procedure method, 12 h, colorless oil, 109.1 mg, 92%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 9.0 Hz, 4H), 5.27 (s, 1H), 5.02 (s, 1H), 2.79–2.70(m, 4H), 2.35 (s, 3H), 2,31(s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.7, 139.0, 138.2, 137.2, 135.3, 1129.1, 129.0, 128.3, 126.1, 111.8, 37.5, 34.4, 21.1 (two peaks). **HRMS (EI)** calcd for $C_{18}H_{20}^+$ 236.1565, found 236.1575.



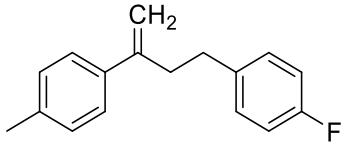
1-methyl-4-(4-(4-(trifluoromethyl)phenyl)but-1-en-2-yl)benzene (**2o**)

Prepared according to the general procedure method, 5 h, colorless oil, 130 mg, 90%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.32 (dd, *J* = 8.0, 2.2 Hz, 2H), 7.27–7.25 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 5.27 (s, 1H), 4.99 (s, 1H), 2.82 (s, 4H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, CDCl3) δ 147.2, 146.2, 138.0, 137.5, 129.3, 128.9, 126.2, 125.3 (q, *J* = 14.4 Hz), 112.52, 37.0, 34.6, 21.2. **HRMS (ESI)** calcd for $C_{18}H_{18}F_3$ $[M+H]^+$ 291.1361, found 291.1360.



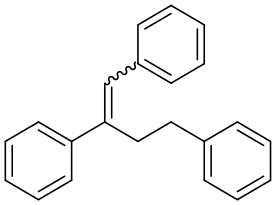
1-methyl-4-(4-phenylbut-1-en-2-yl)benzene (**2p**)

Prepared according to the general procedure method, 5 h, colorless oil, 90 mg, 81%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.14 (m, 9H), 5.27 (d, *J* = 1.2 Hz, 1H), 5.02 (d, *J* = 1.2 Hz, 1H), 2.81–2.73 (m, 4H), 2.35 (s, 3H).[21]



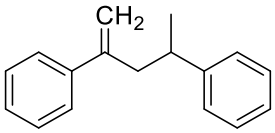
1-fluoro-4-(3-(*p*-tolyl)but-3-en-1-yl)benzene (**2q**)

Prepared according to the general procedure method, 5 h, colorless oil, 91.2 mg, 76%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.13–7.08 (m, 2H), 6.98–6.92 (m, 2H), 5.25 (d, *J* = 1.2 Hz, 1H), 4.98 (d, *J* = 0.8 Hz, 1H), 2.79–2.70 (m, 4H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.5, 160.1, 147.4, 138.1, 137.6 (d, *J* = 12.4 Hz), 137.3, 129.8 (d, *J* = 29.6 Hz), 129.2, 126.1, 115.2, 114.9, 112.2, 37.4, 33.9, 21.2. **HRMS (EI)** calcd for $C_{17}H_{15}F^+$ 240.1314, found 240.1317.



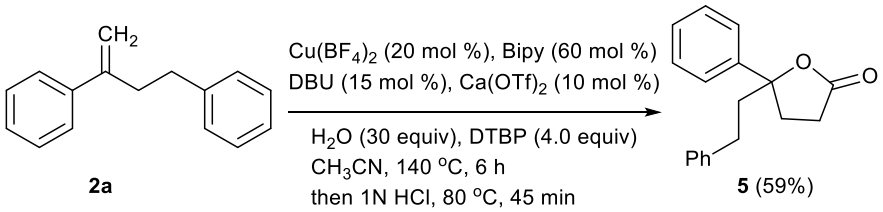
(*Z*/*E*)-but-1-ene-1,2,4-triyltribenzene (**2r**)

Prepared according to the general procedure method, 5 h, colorless oil, 98.0 mg, 69%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52–6.88 (m, 15H), 6.76 (s, 0.57H), 6.40 (s, 0.38 H), 3.03–2.99 (m, 1.21H), 2.82–2.78 (m, 0.81H), 2.74–2.70 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.7, 142.3, 142.1, 141.9, 141.8, 141.0, 138.1, 137.4, 129.1, 129.0, 128.9, 128.7, 128.6, 128.5 (two peaks), 128.4, 128.3 (two peaks), 128.2, 127.8, 127.6, 127.4, 127.0, 126.9, 126.7 (two peaks), 126.5, 126.2, 125.9, 125.8, 34.7, 34.5, 32.1. **HRMS (ESI)** calcd for $C_{22}H_{20}$ $[M+Na]^+$ 307.1463, found 307.1461.



pent-1-ene-2,4-diyldibenzene (**2s**)

Prepared according to the general procedure method, 4 h, colorless oil, 78.2 mg, 70%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40–7.26 (m, 10H), 7.20–7.14 (m, 3H), 5.26 (d, *J* = 1.6, 1H), 4.96 (q, J = 1.2 Hz, 1H), 2.90–2.76 (m, 2H), 2.66 (qd, J = 4.0, 0.8 Hz, 1H), 1.21 (d, *J* = 6.8 Hz). [22]



In the glovebox, **2a** (0.5 mmol), $Cu(BF_4)_2$ (20 mol%), 2,2'-bipyridine (60 mol%), $Ca(OTf)_2$ (20 mol%), and DBU (15 mol%) were dissolved in degassed MeCN (0.025 M) in a sealed tube. DTBP (4 equiv) and H_2O (30 equiv) were then added and the tube was sealed and heated to 140 °C. After 6 h, the reaction mixture was cooled down to room temperature, and an aqueous HCl solution (1 M, 5 mL) was added. After heating at 80 °C for 45 minutes, the resulting mixture was cooled down, diluted with water, extracted with EtOAc. The combined organic extracts were washed with brine, dried

over anhydrous $MgSO_4$, filtered, concentrated and purified on silica gel chromatography to give the product **5,** yellow oil, 79 mg, 59%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43–7.38 (m, 4H), 7.34–7.30 (m, 1H), 7.26–7.22 (m, 2H), 7.17–7.13 (m, 1H), 7.09–7.06 (m, 2H), 2.73–2.66 (m, 1H), 2.64–2.42 (m, 4H), 2.37–2.20 (m, 3H).[23]

3. Isotope labelling experiments (Scheme 1)

3.1. Deuterium labeling experiments

1a-D (0.5 mmol), Ph_3PCH_3Br, 1, 10-phenanthroline, ^{t}BuONa were weighed directly into a Schlenk tube and dried under high vacuum for 15 min. Then the solvent (toluene, 1ml) was added and stirred at 70 °C, the reaction mixture was monitored by TLC. After completion, the mixture was subjected to run a silica gel column to give the target product.

3.2. Kinetic isotope effect

Two parallel reactions with **1a** and **1a**-*d* were ran at same time. **1a** or **1a**-*d* (0.5 mmol), 1,10-phenanthroline, Ph_3PCH_3Br were weighed directly into a Schlenk tube and dried under vacuum for 15 min. Then solvent (toluene, 2 mL) was added and stirred. ^{t}BuONa was then added and 1,3-dimethoxybenzene (22 μL) was added as internal standard, the resulting mixture was stirred at 70 ˚C. The sample mixture was used to collect ^{1}H NMR (400 MHz ^{1}H NMR) data. The recovery of **1a**/**1a**-*d* was determined by 1,3-dimethoxybenzene from the ^{1}H NMR spectra.

4. ICP-AES analysis

^{t}BuONa was dissolved in aqua regia and ICP-AES was used to determine the trace metals and suspected metals were not detected (Pd, Ir, Ru, Ni, Rh, Pt, Fe, Co, and Os). After the reaction mixture baked at 1173 K, the residue was dissolved in aqua regia and ICP-AES was used to determine the trace metals and all suspected metals were not found (Pd, Ir, Ru, Ni, Rh, Pt, Co, and Os).

Table S4.

Metallic elements	Content of elements (μg/mg)	
	^{t}BuONa	Reaction system
Pd	0.01	N. D.
Ir	0.03	N.D
Ru	0.0003	N. D.
Rh	0.001.	N. D.
Fe	0.08	N.D.
Ni	0.007	N. D.
Co	0.0007	N. D.
Os	0.0007.	N.D
Mo	0.001	N.D

5. References

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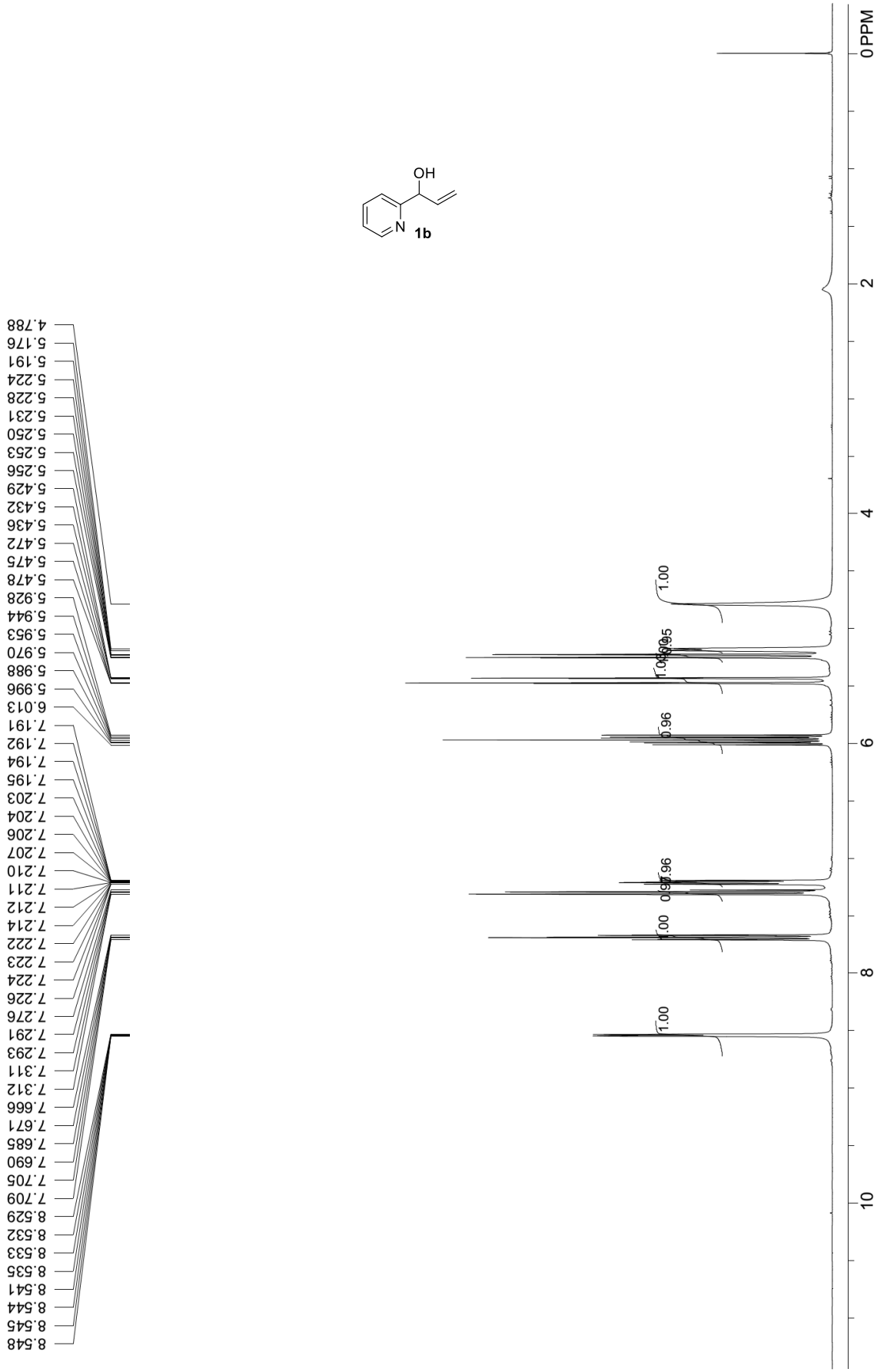
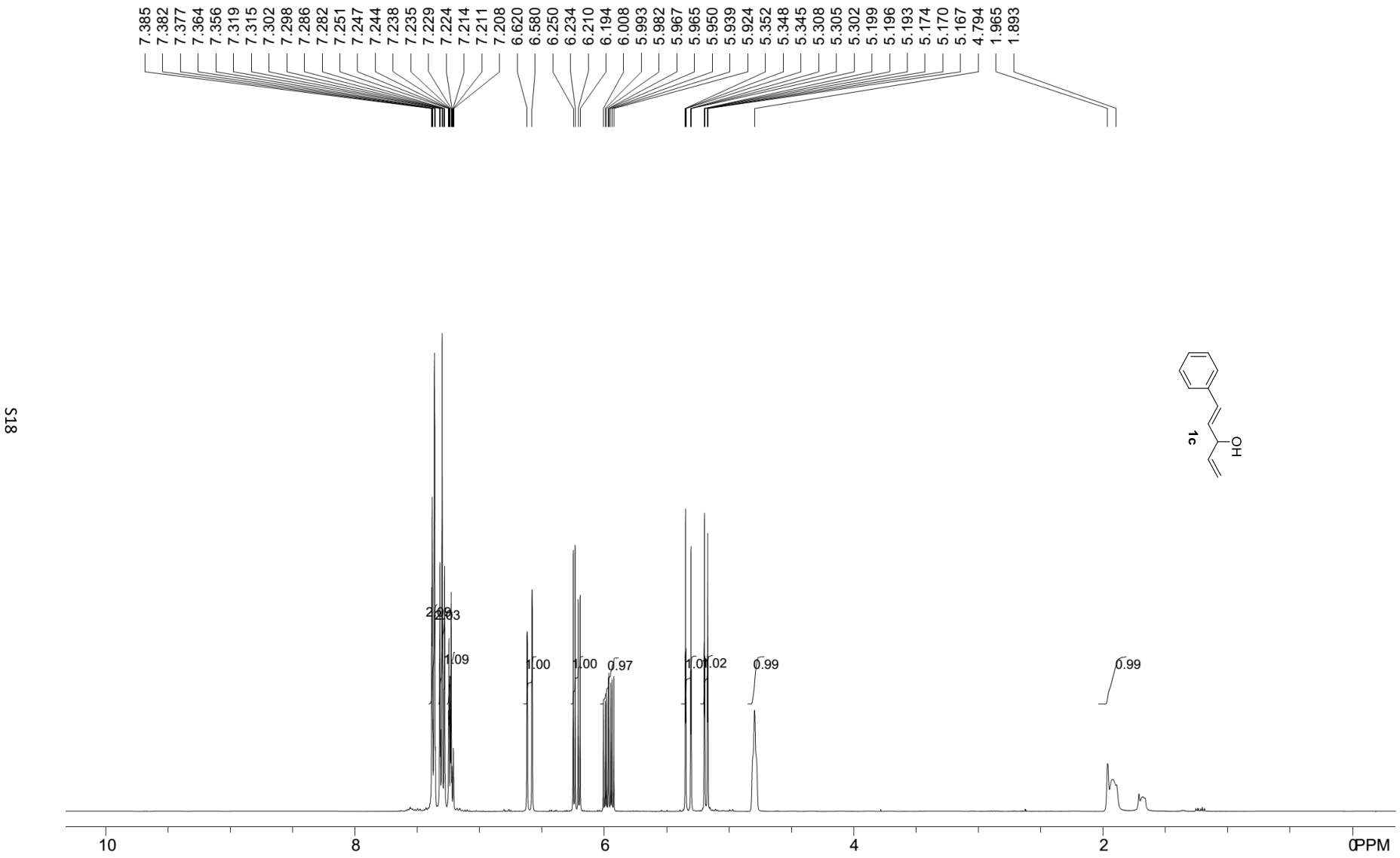
6. NMR spectra.

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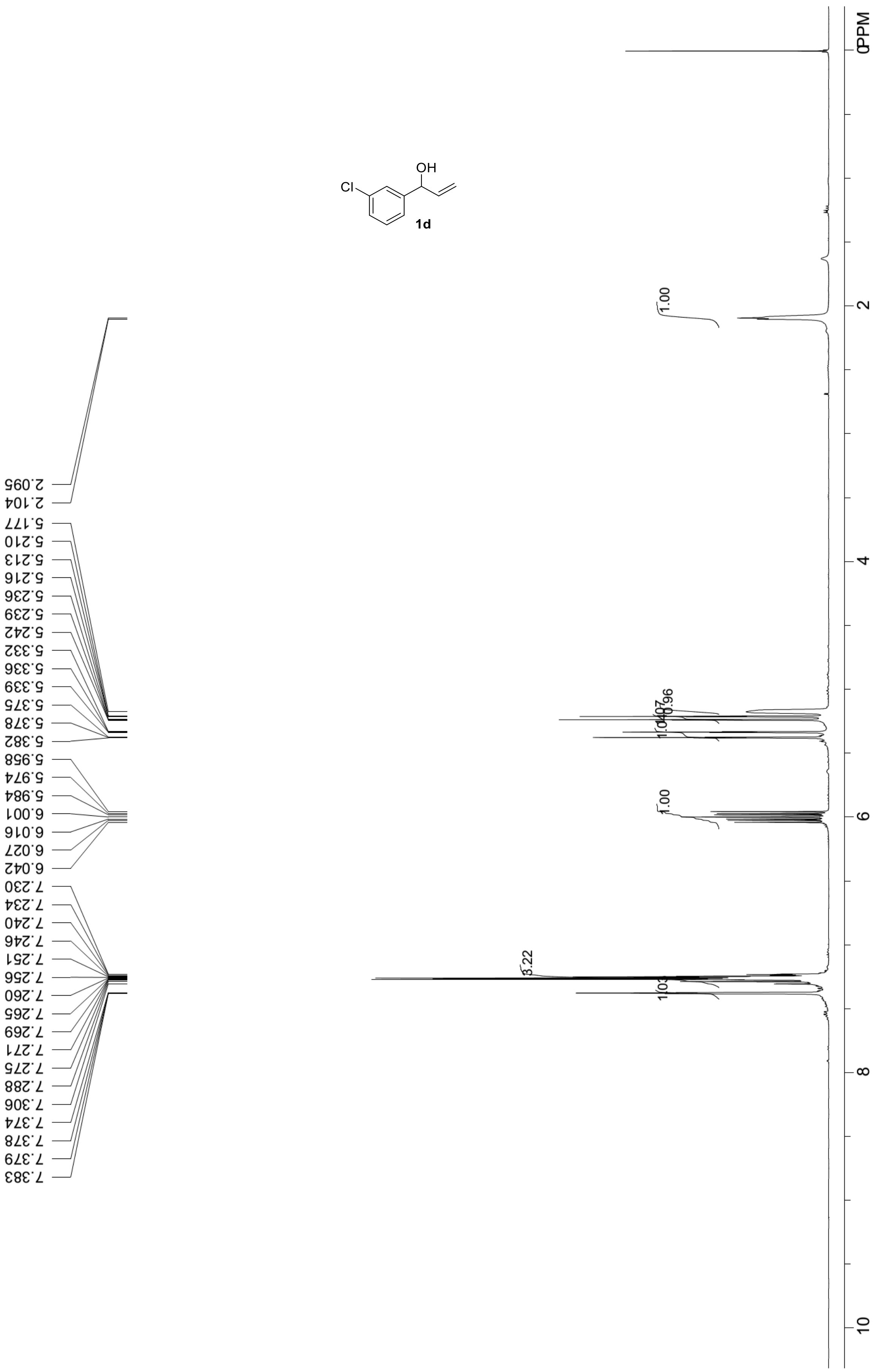
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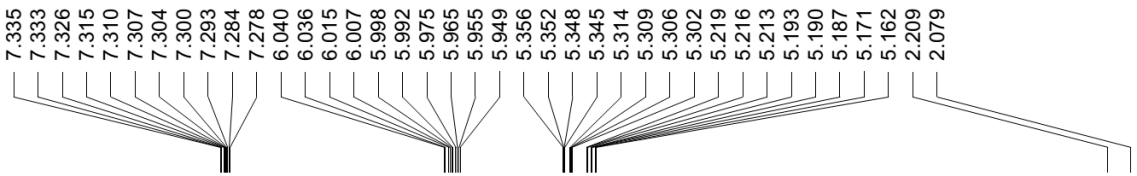
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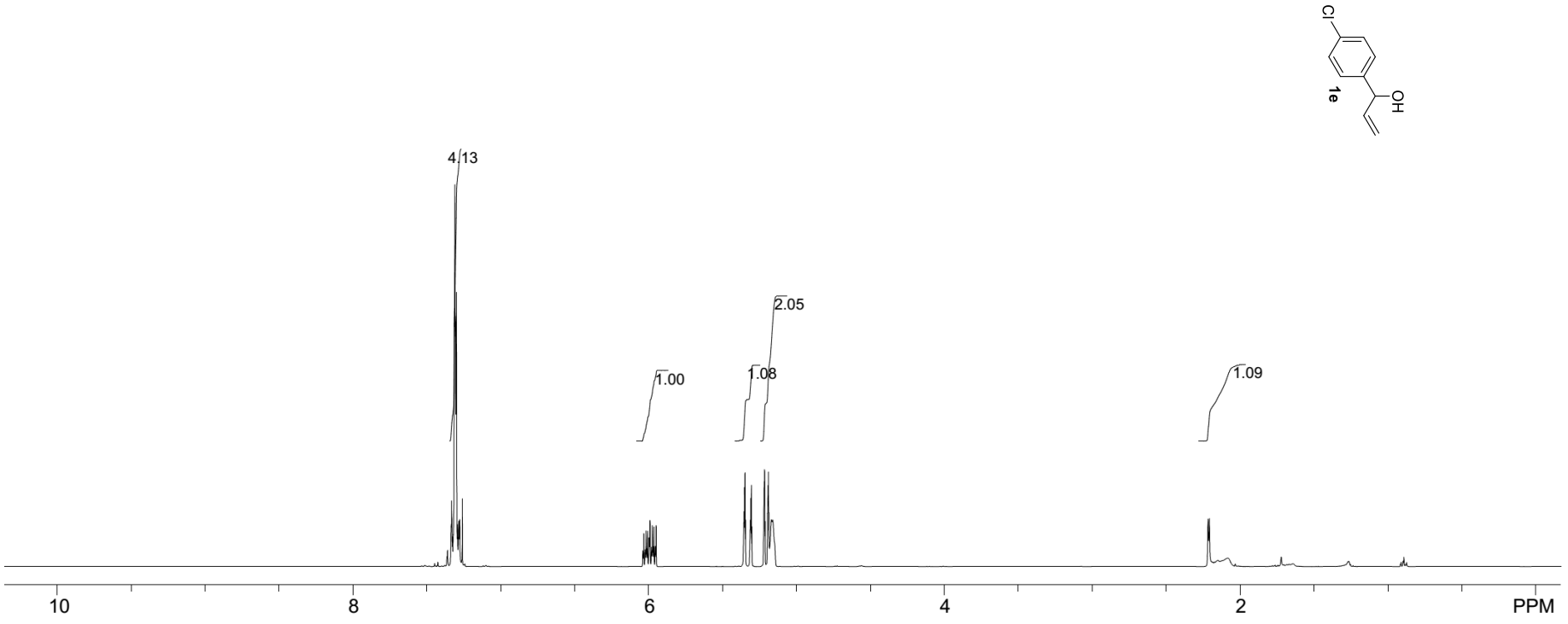
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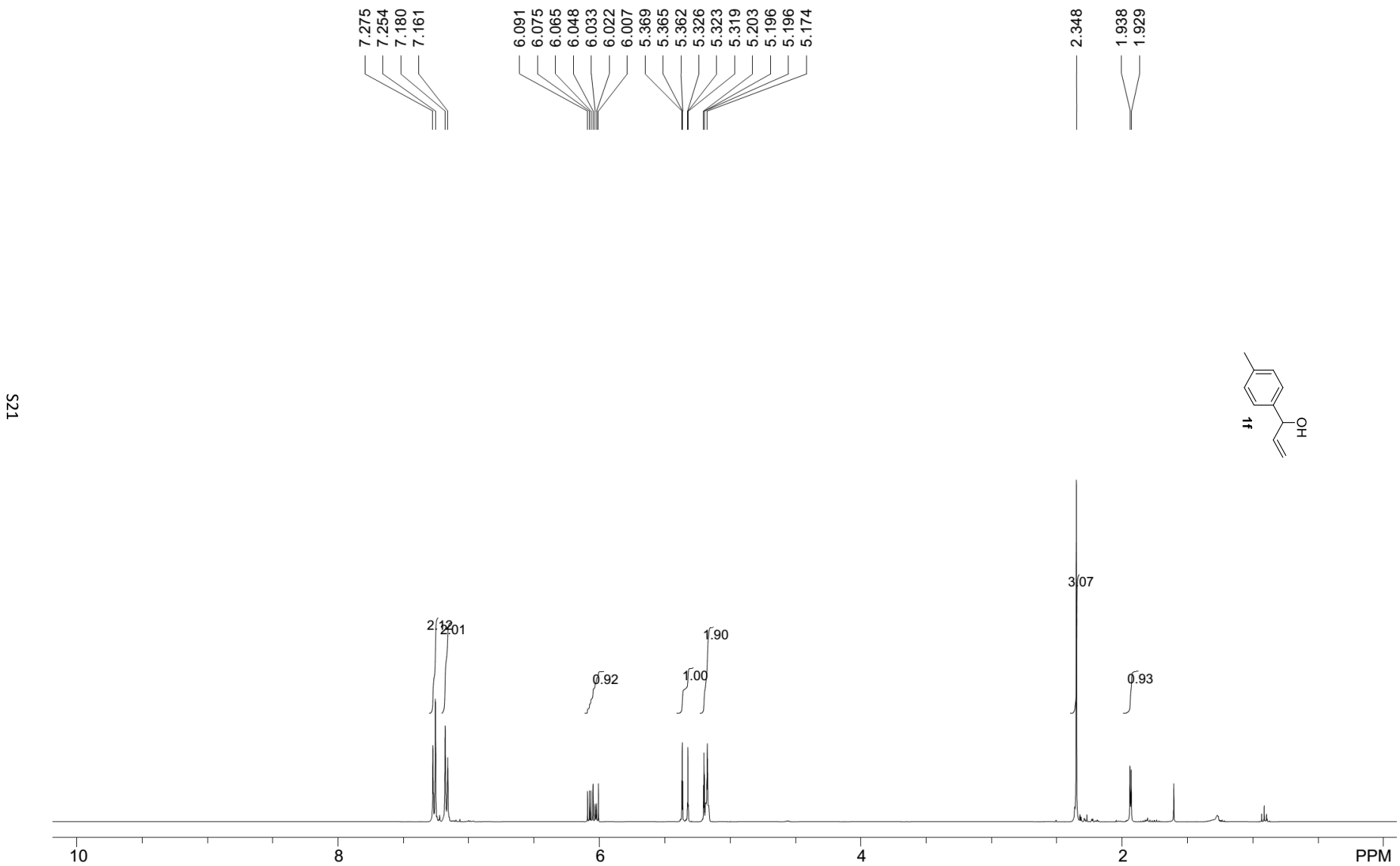
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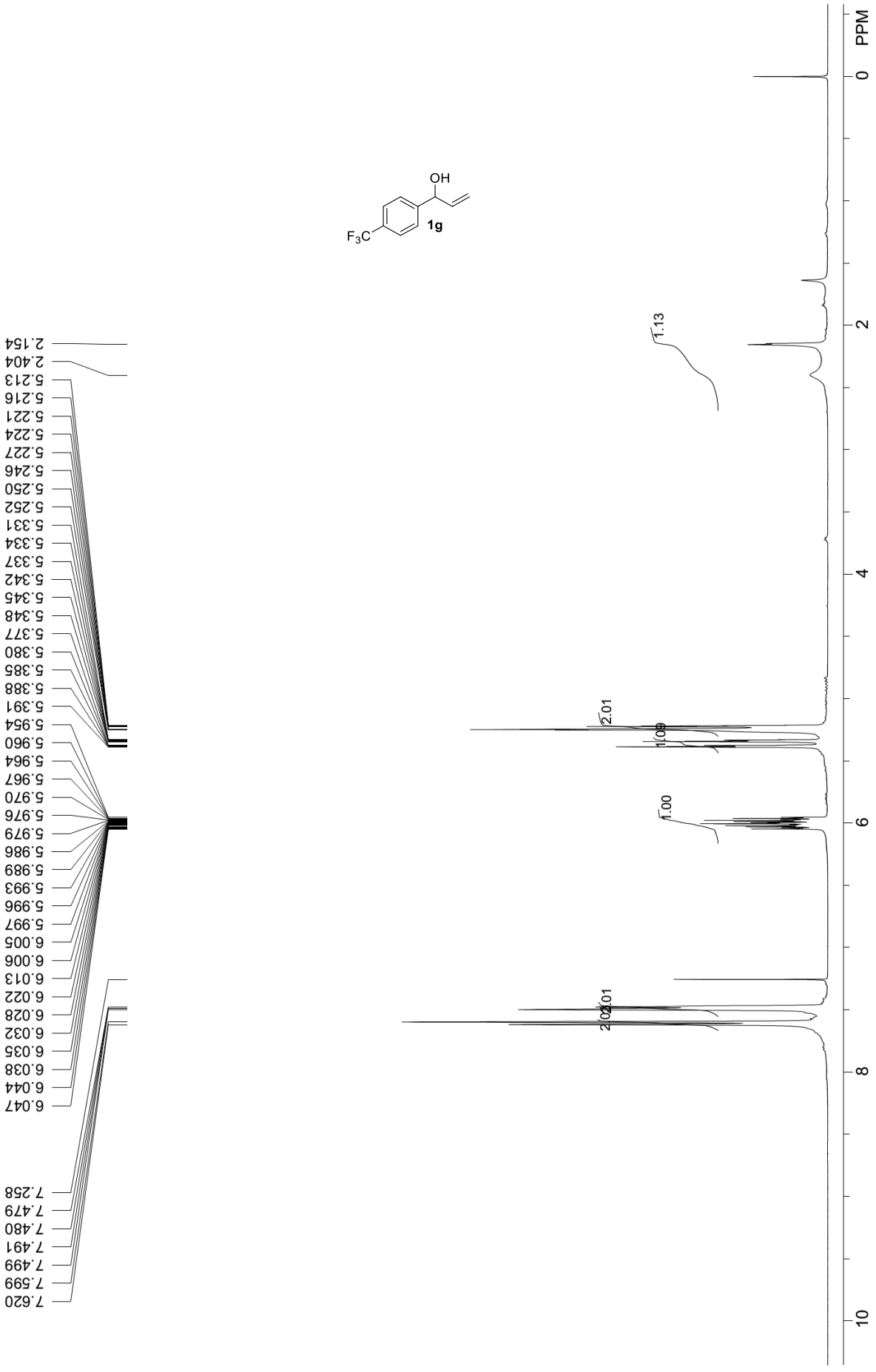
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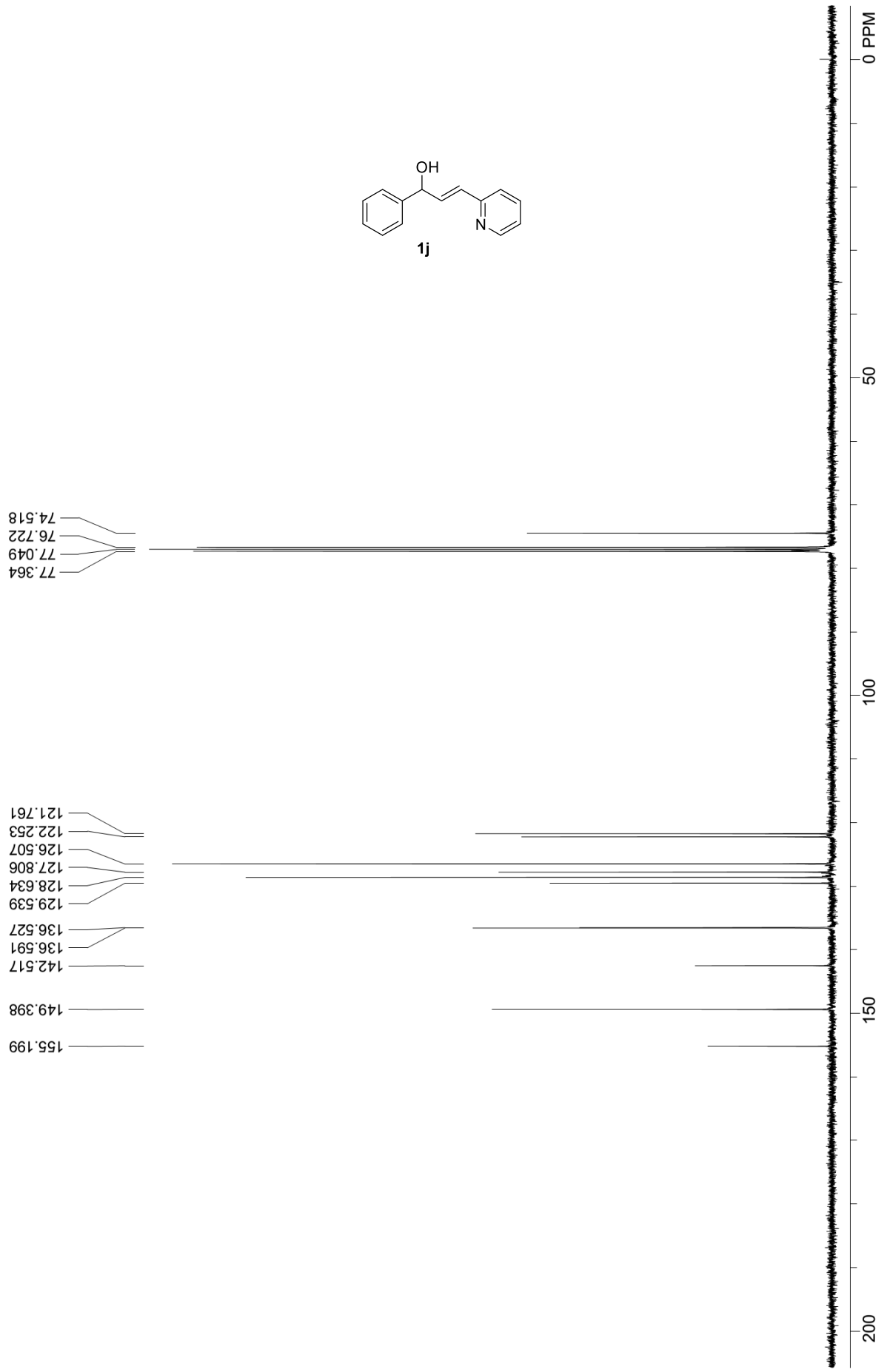
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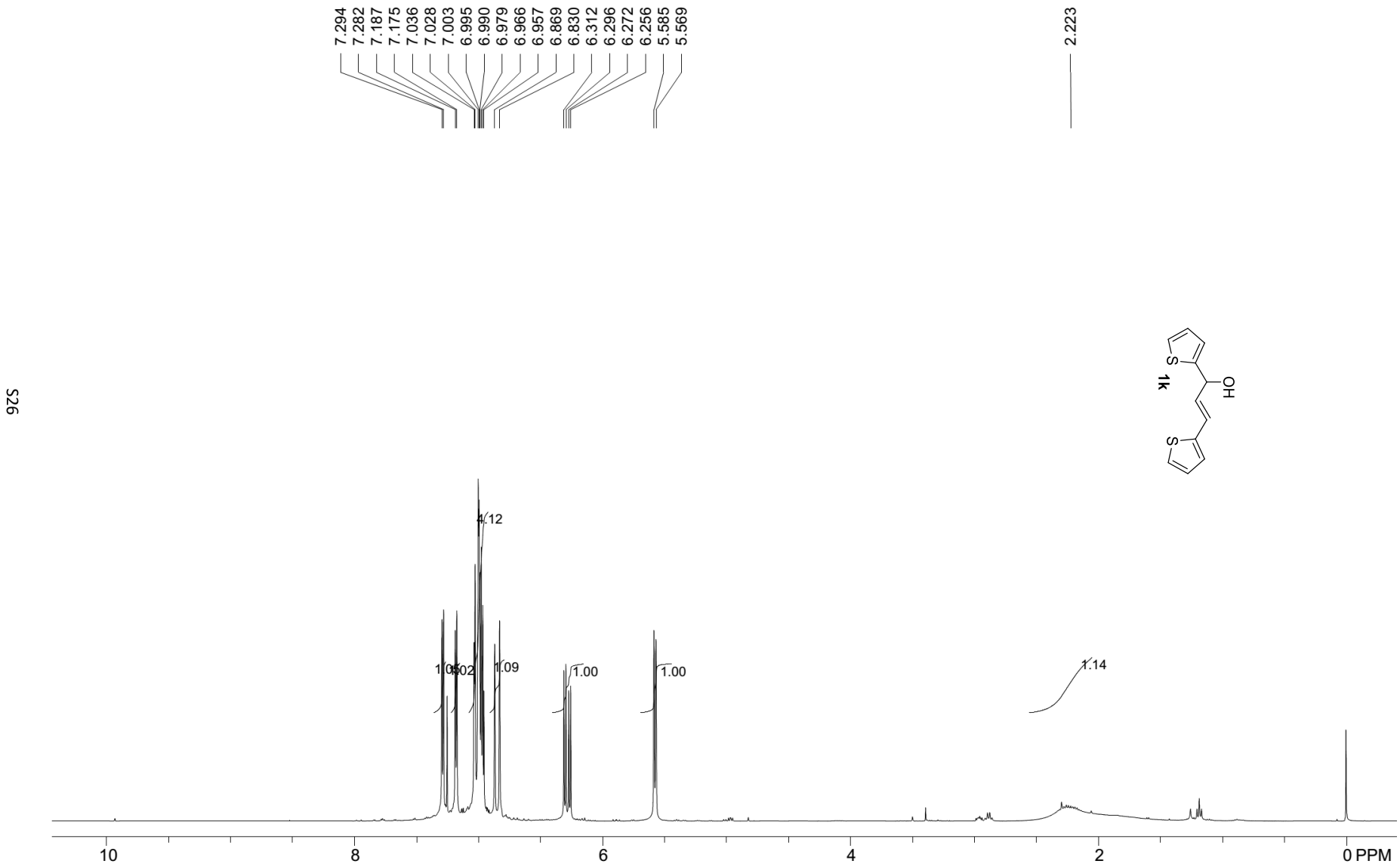
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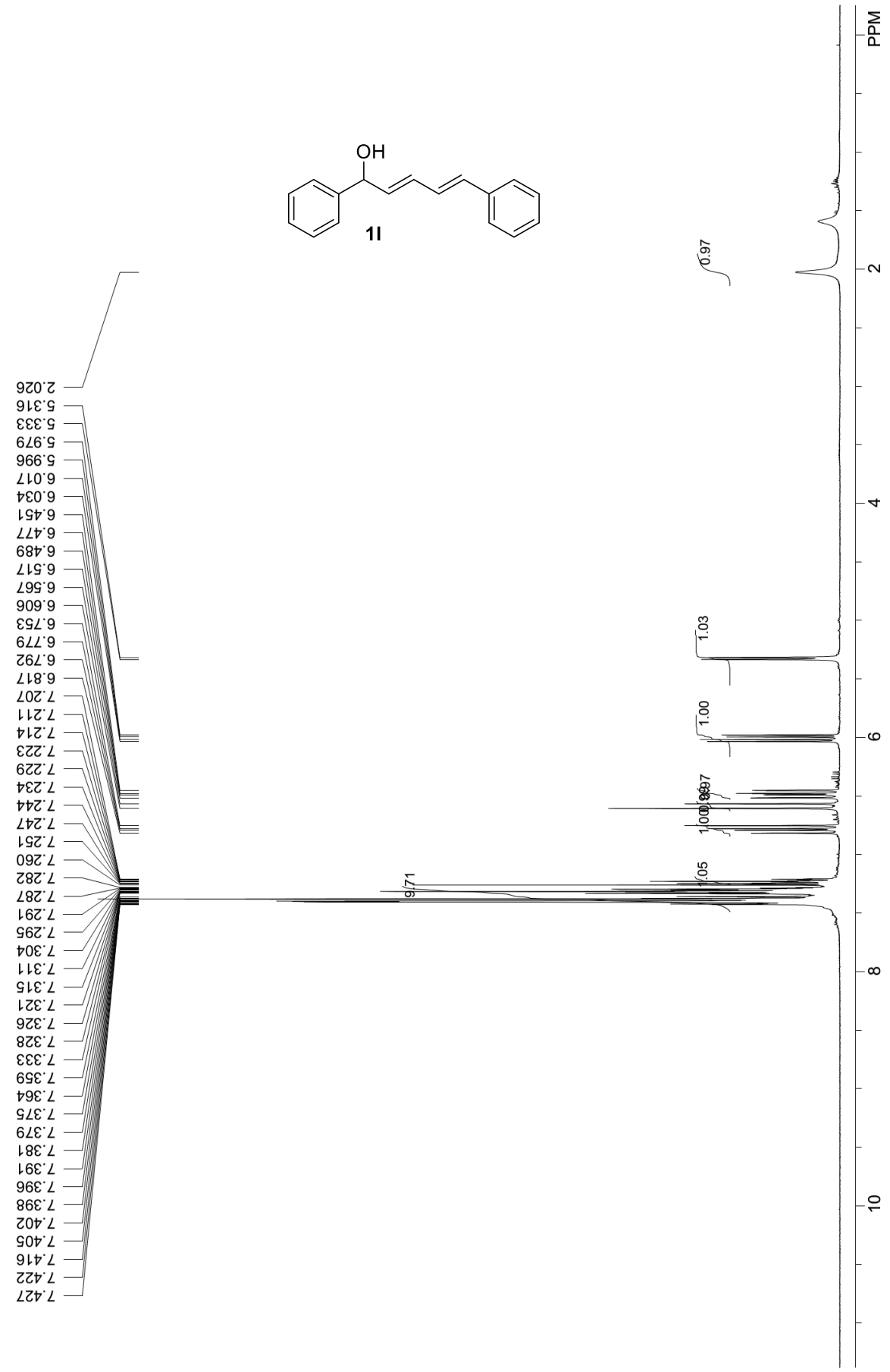
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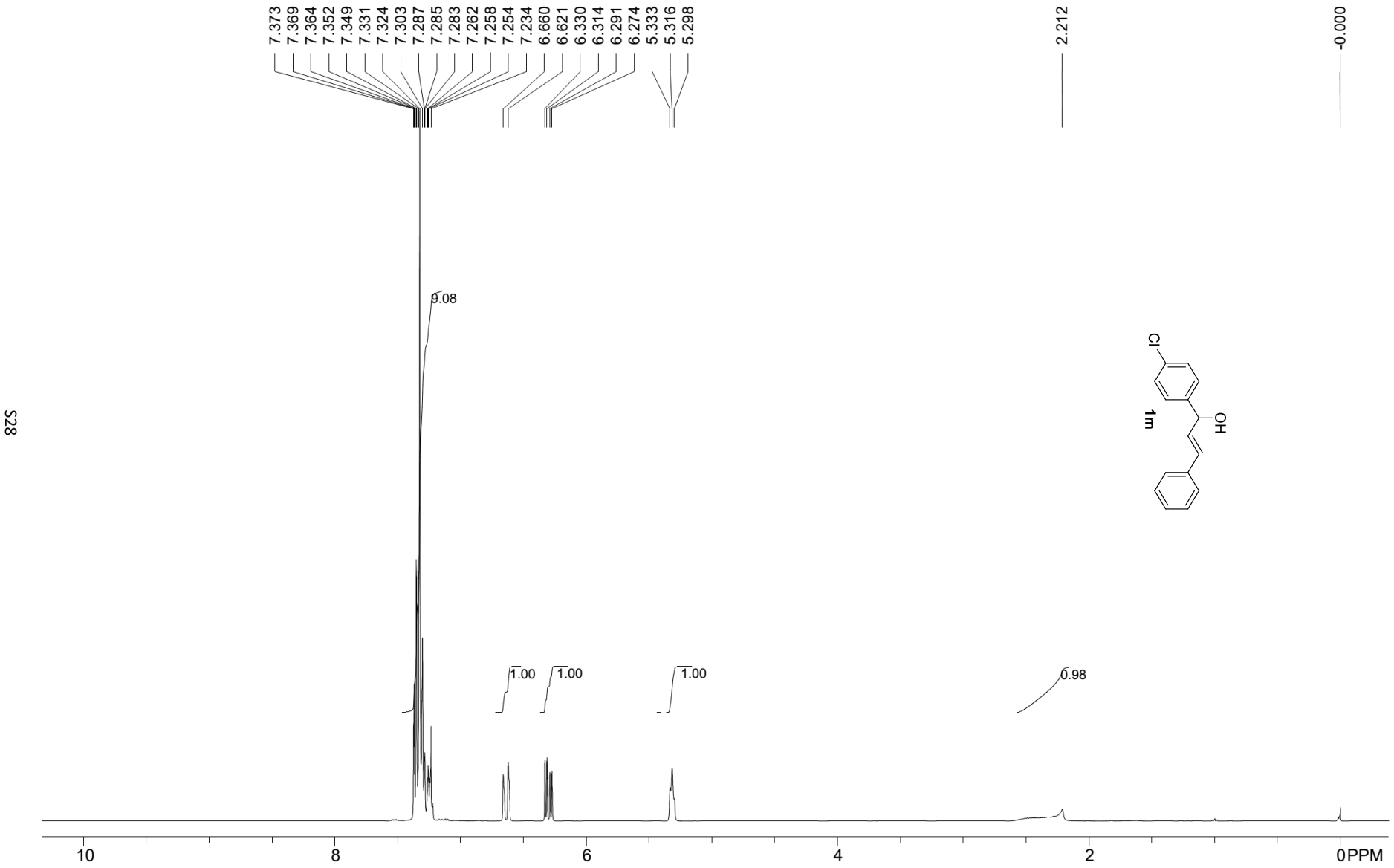
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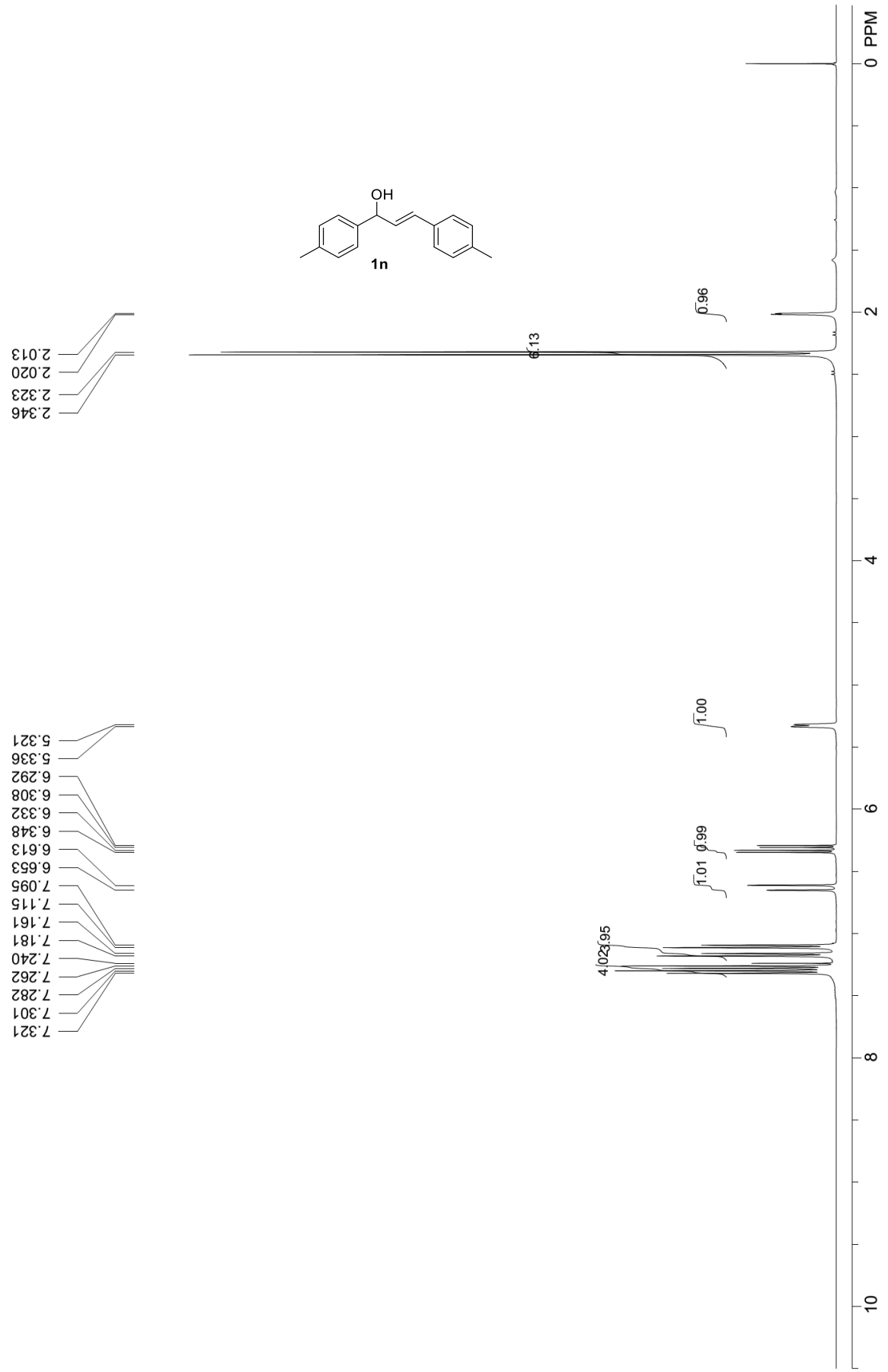
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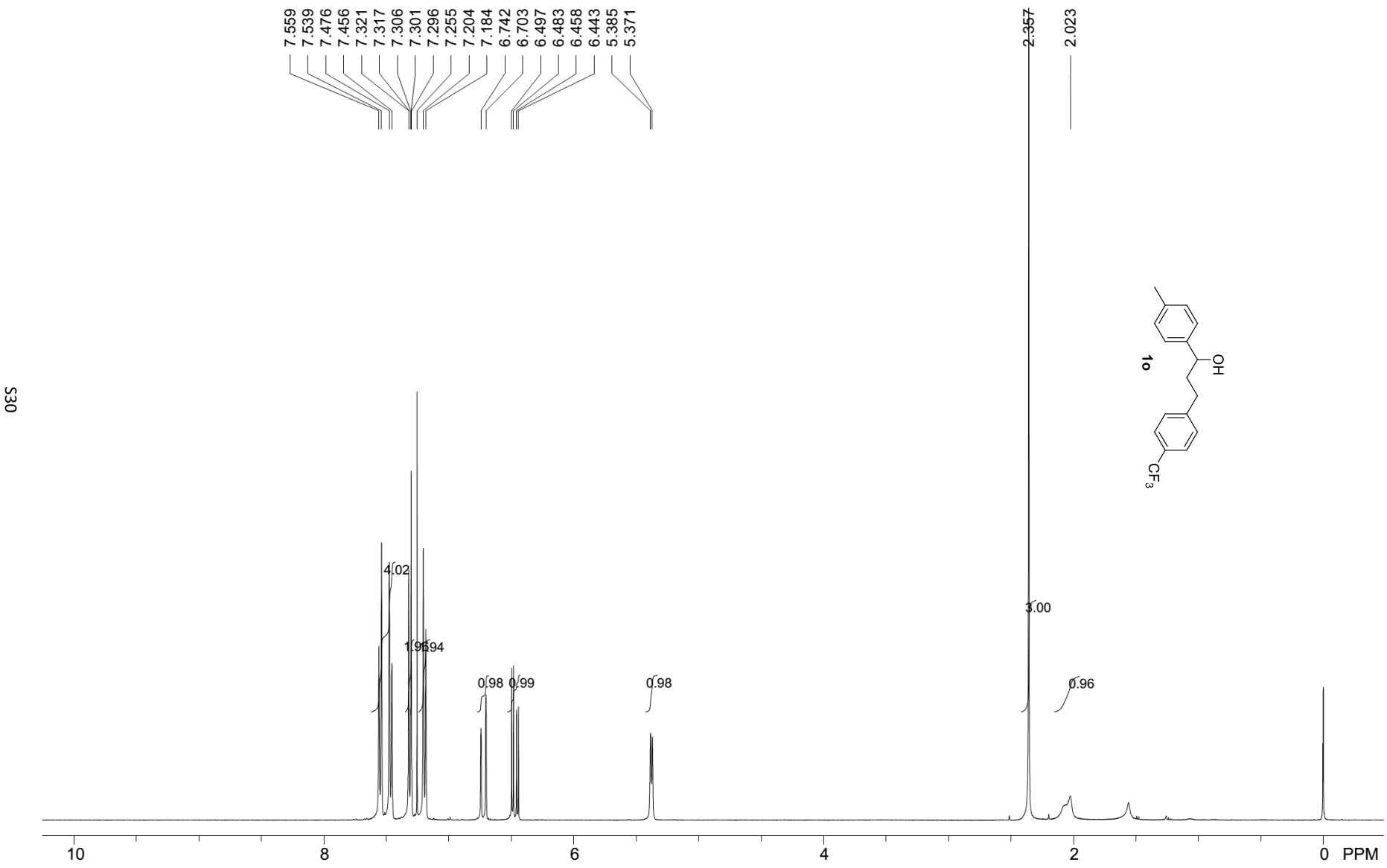
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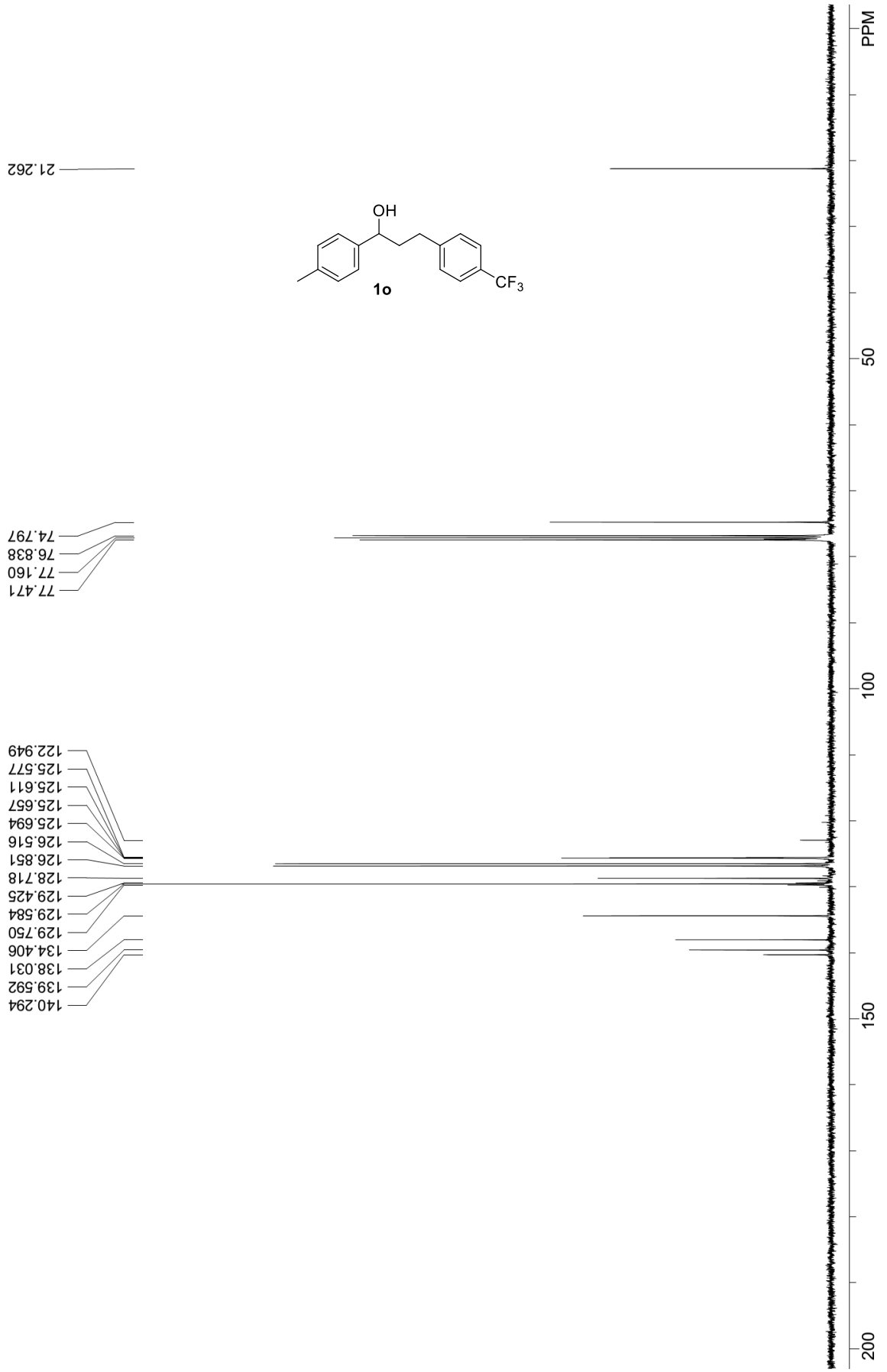
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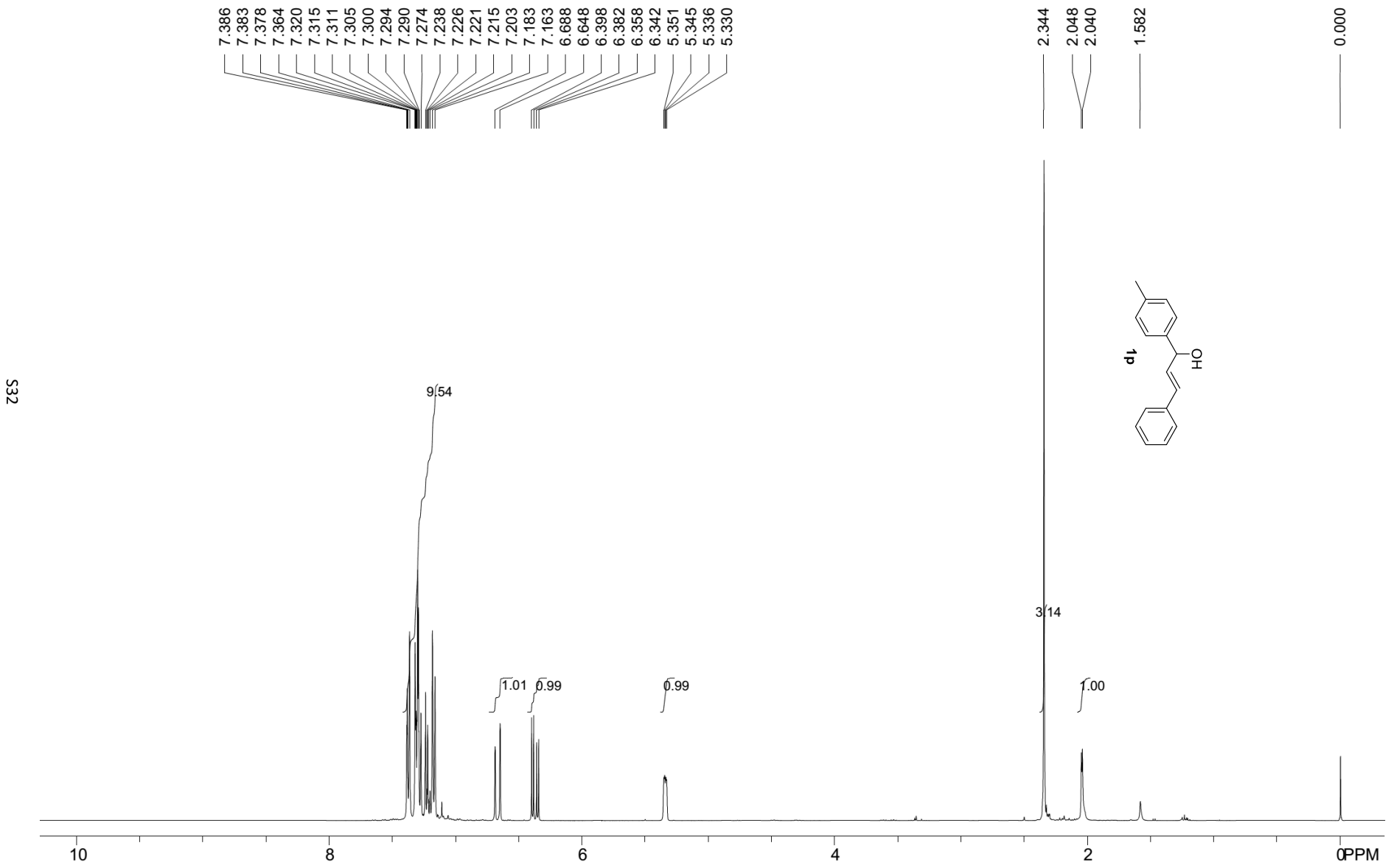
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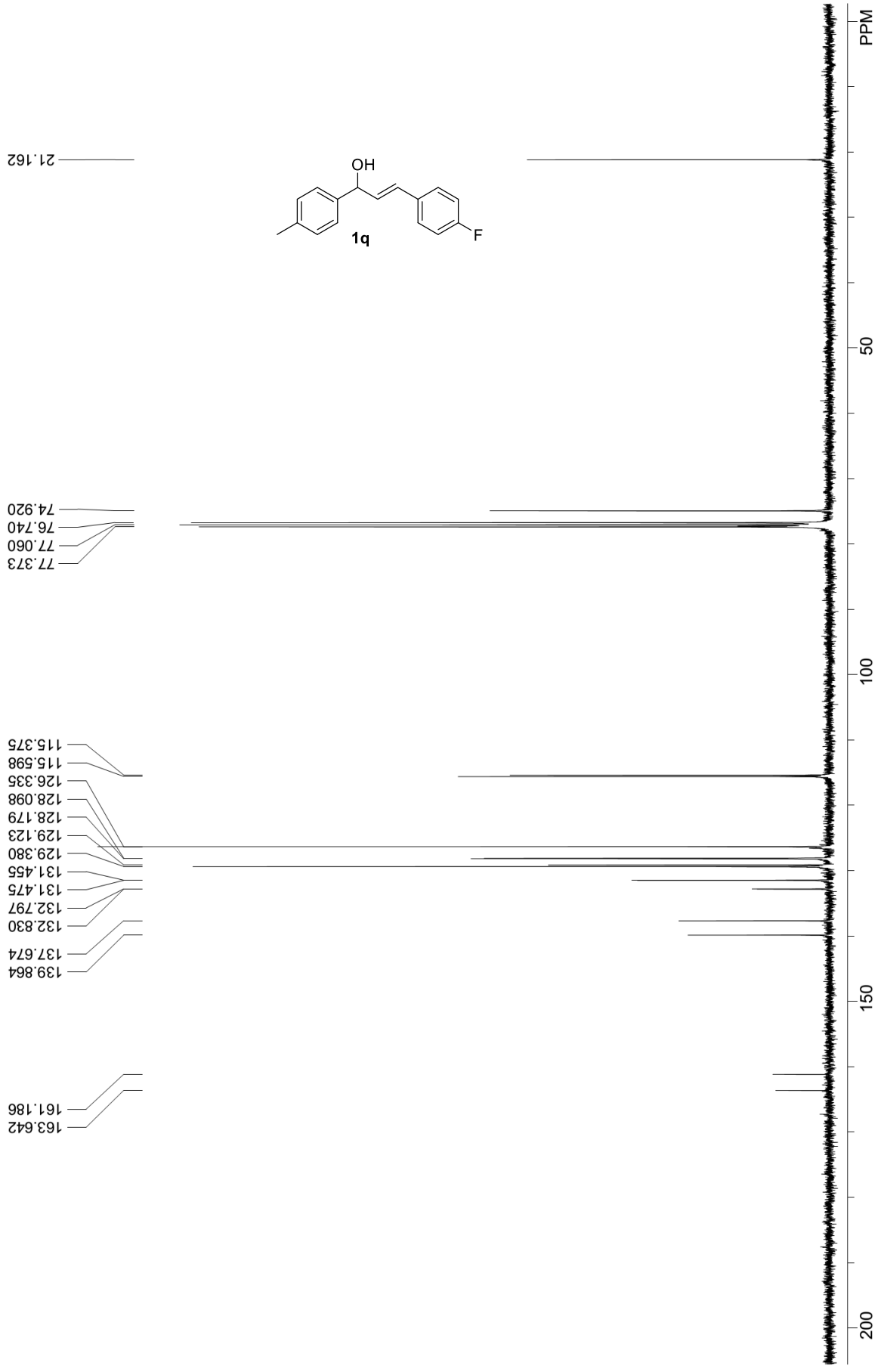
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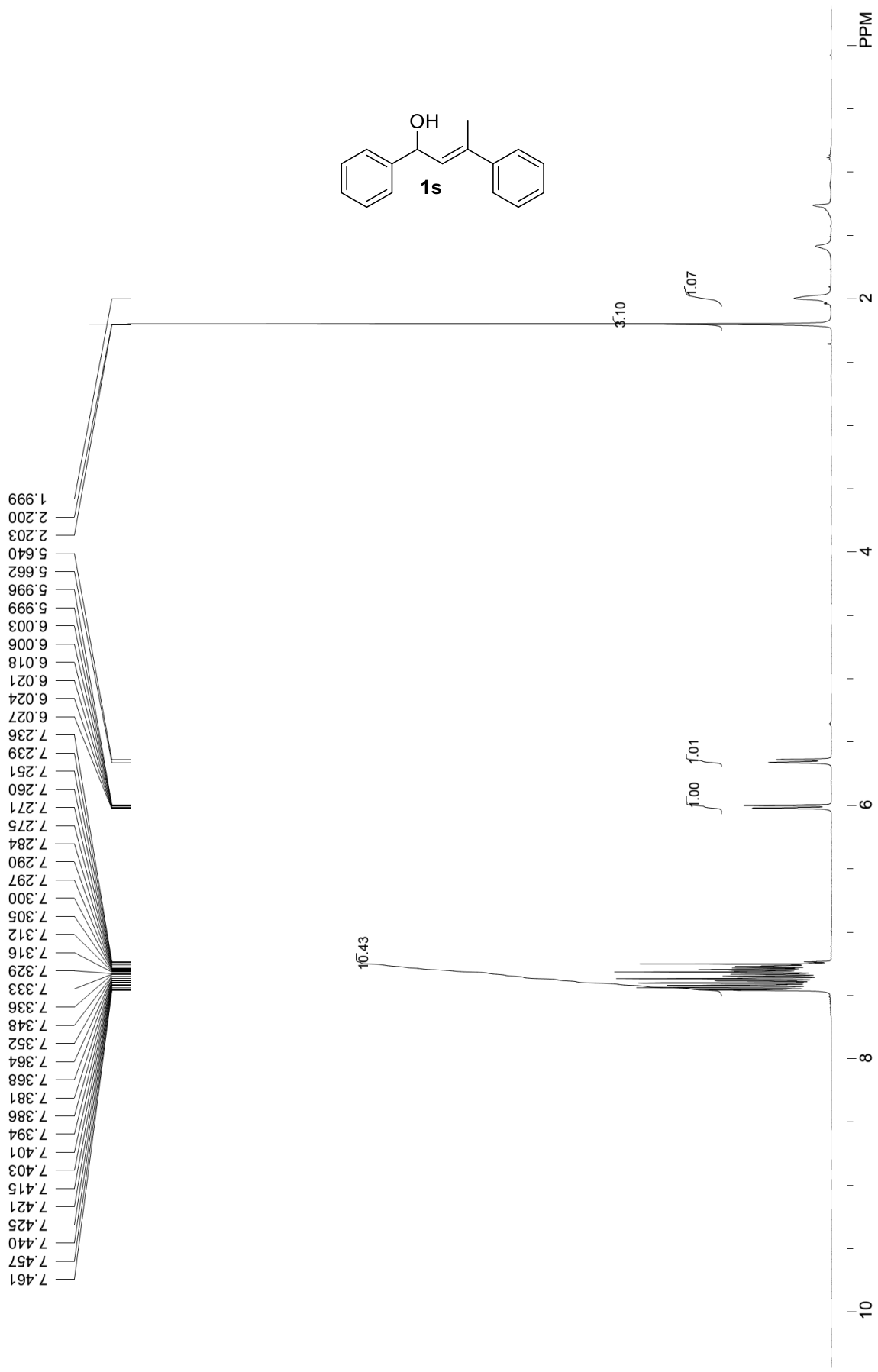
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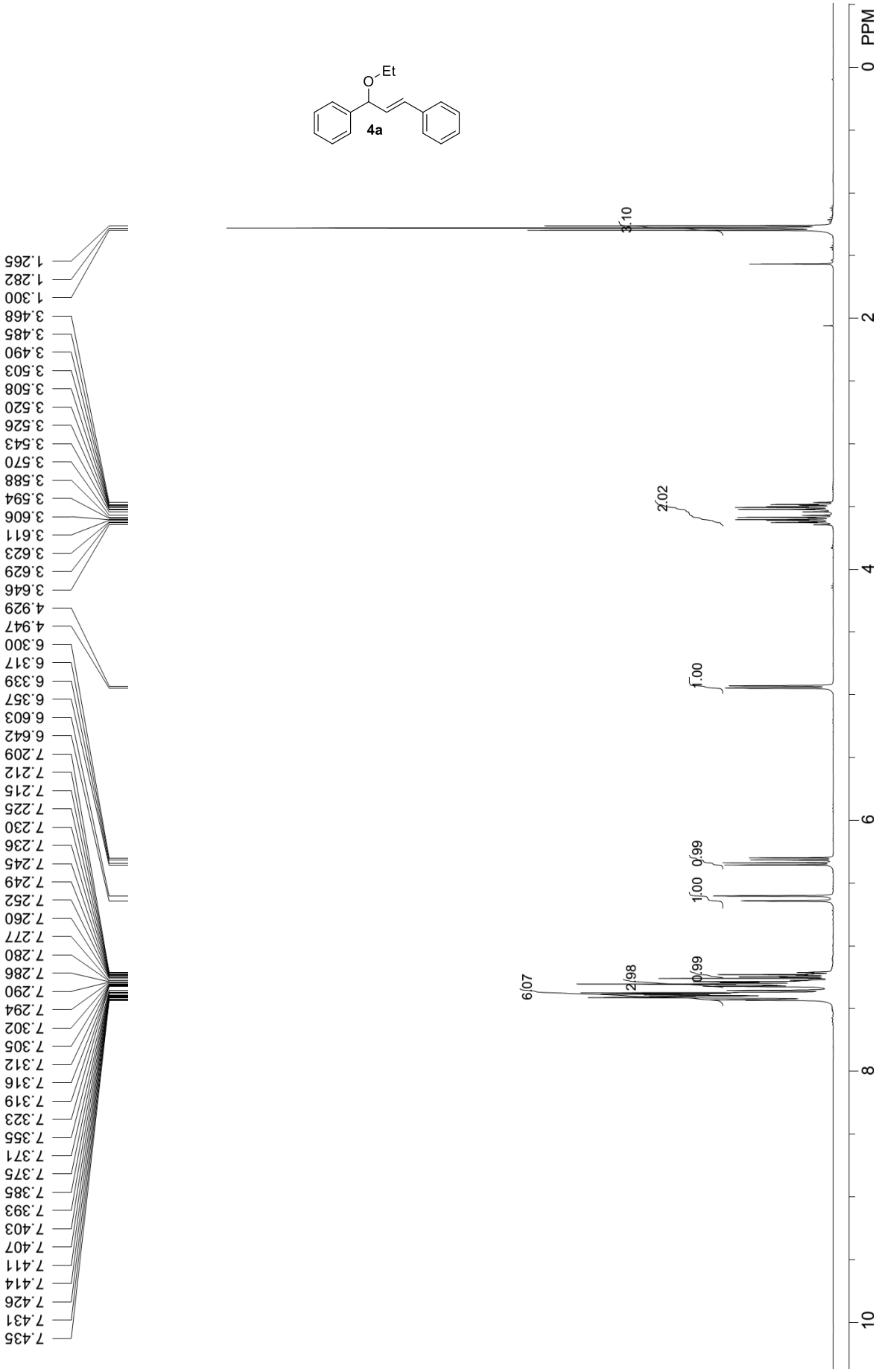
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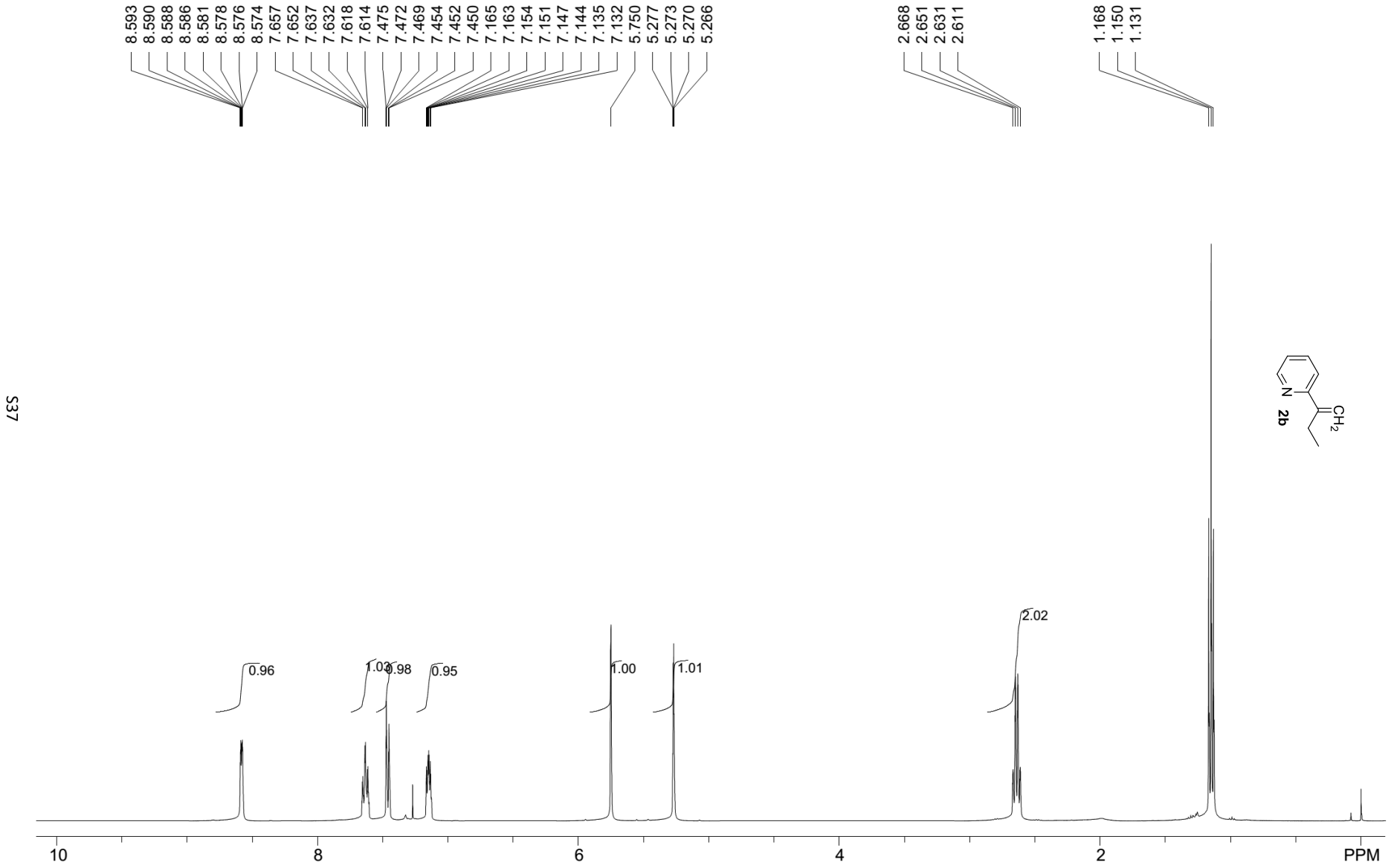
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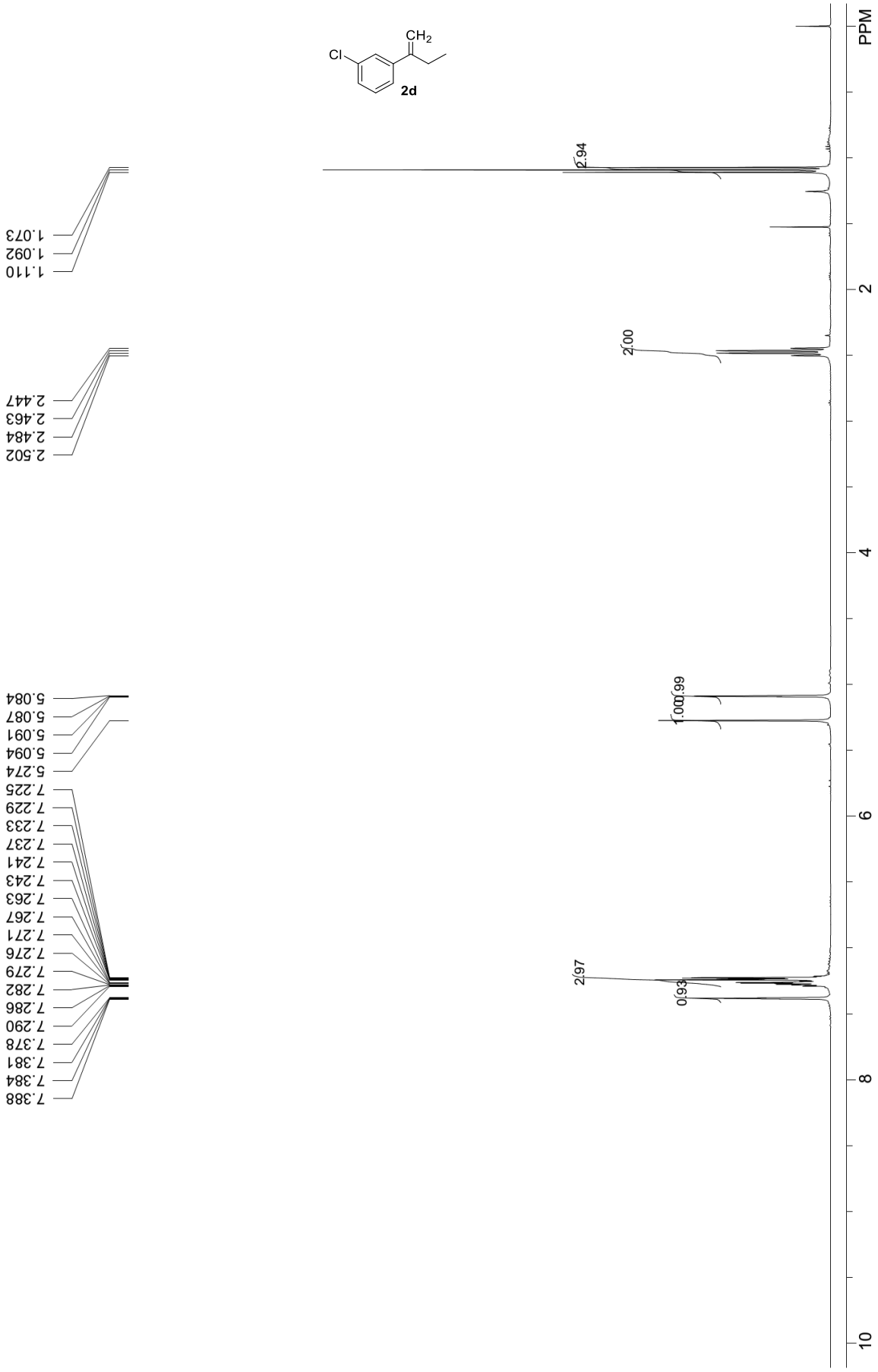
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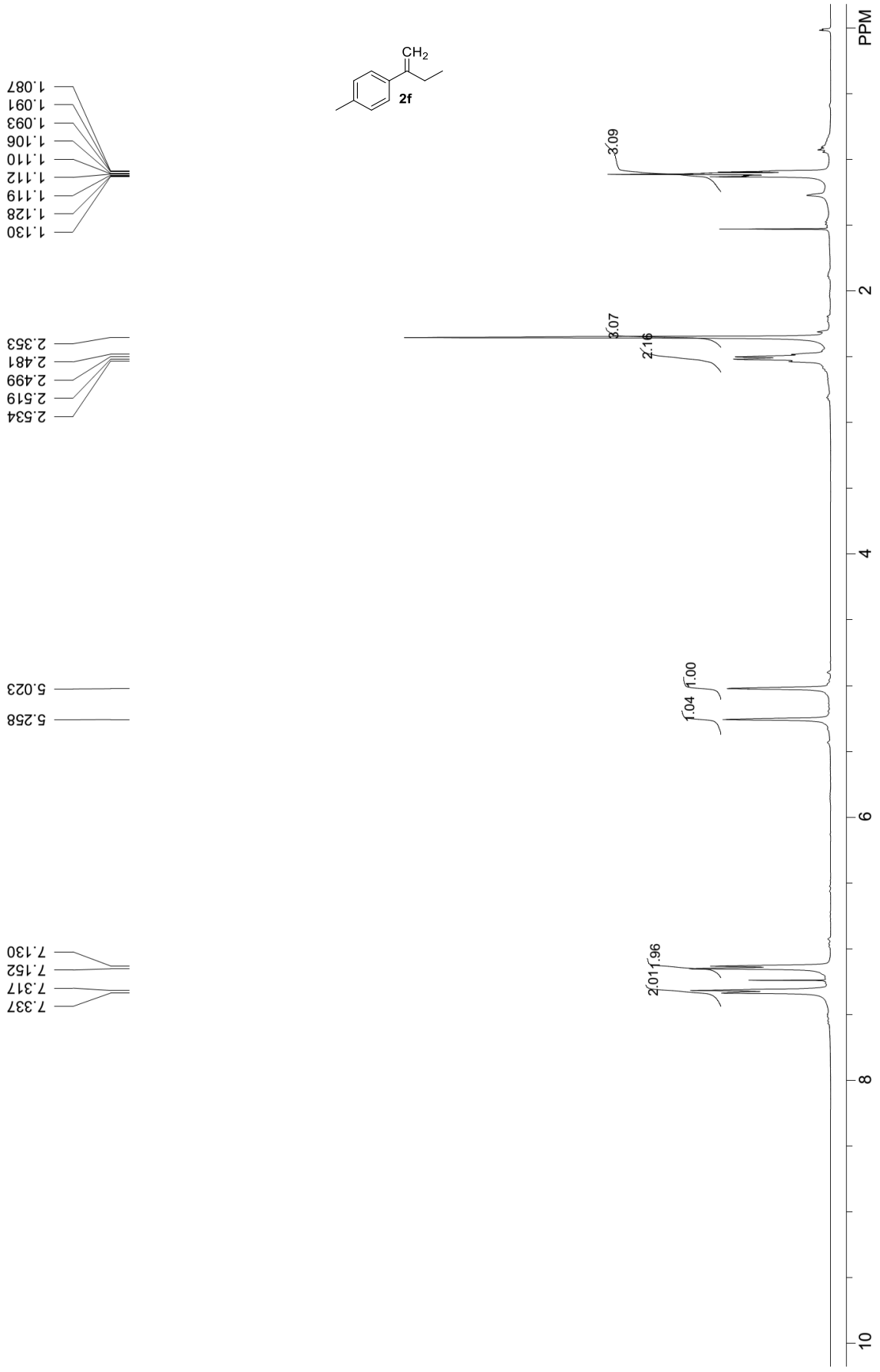
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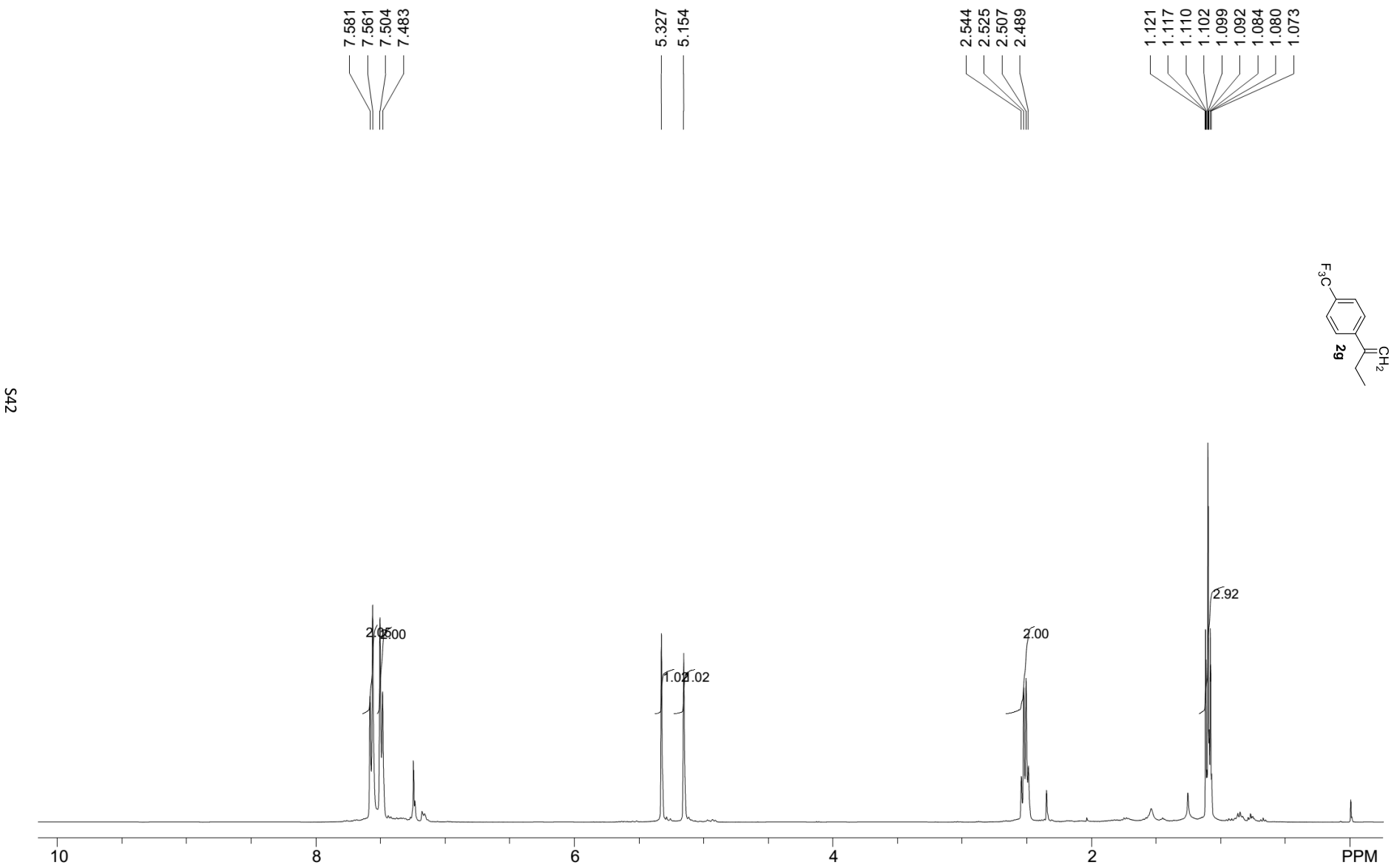
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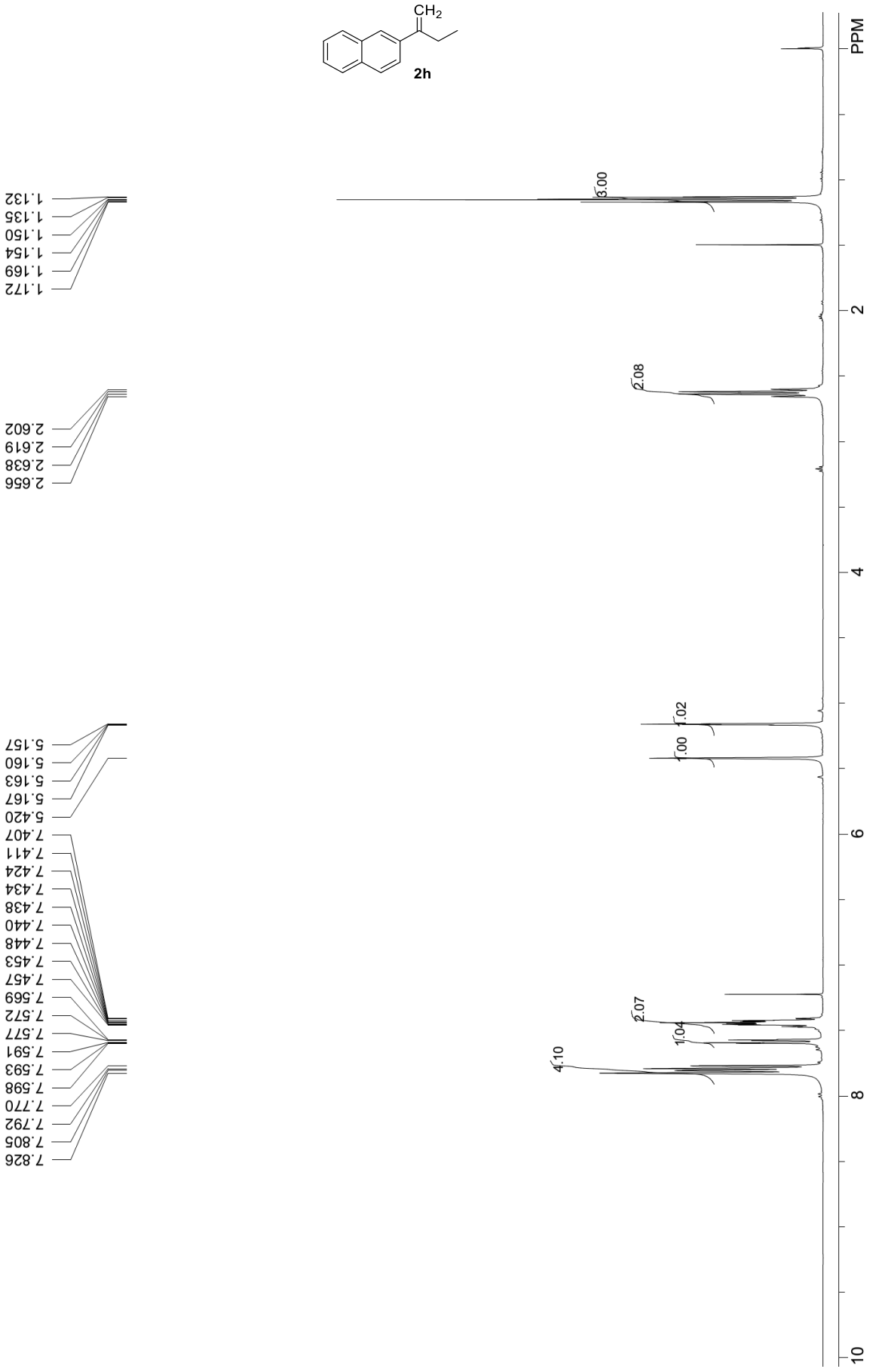
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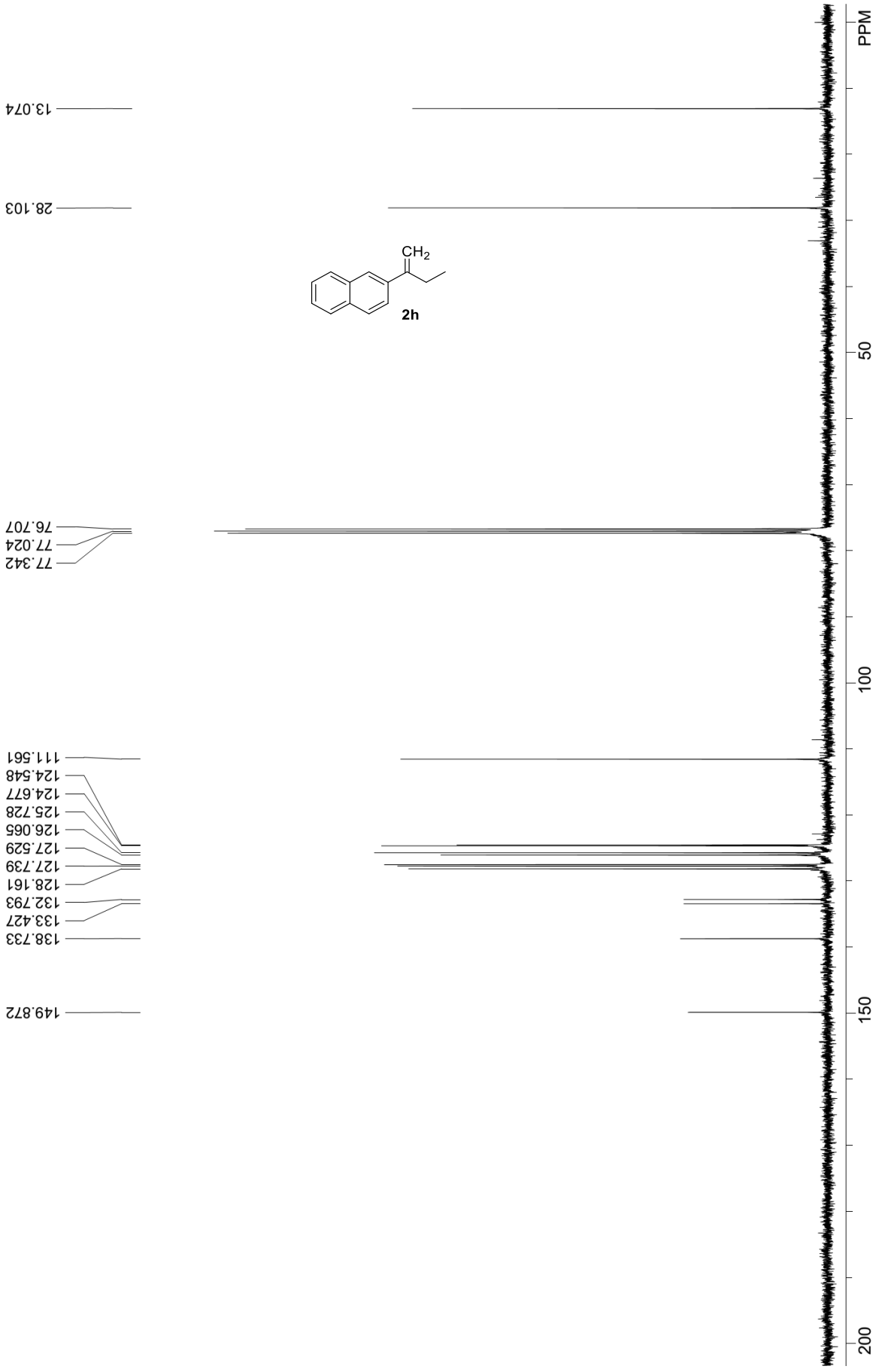
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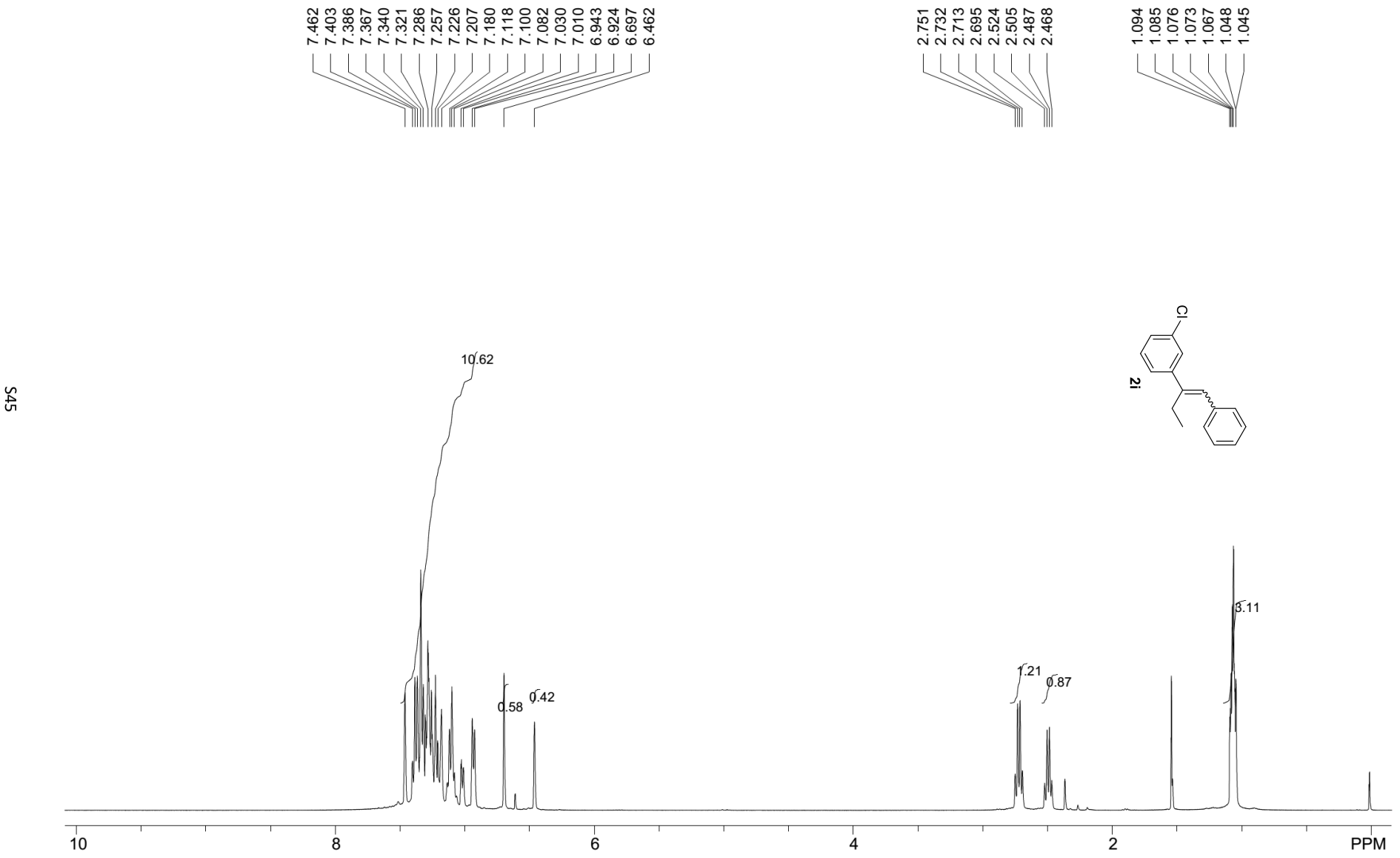
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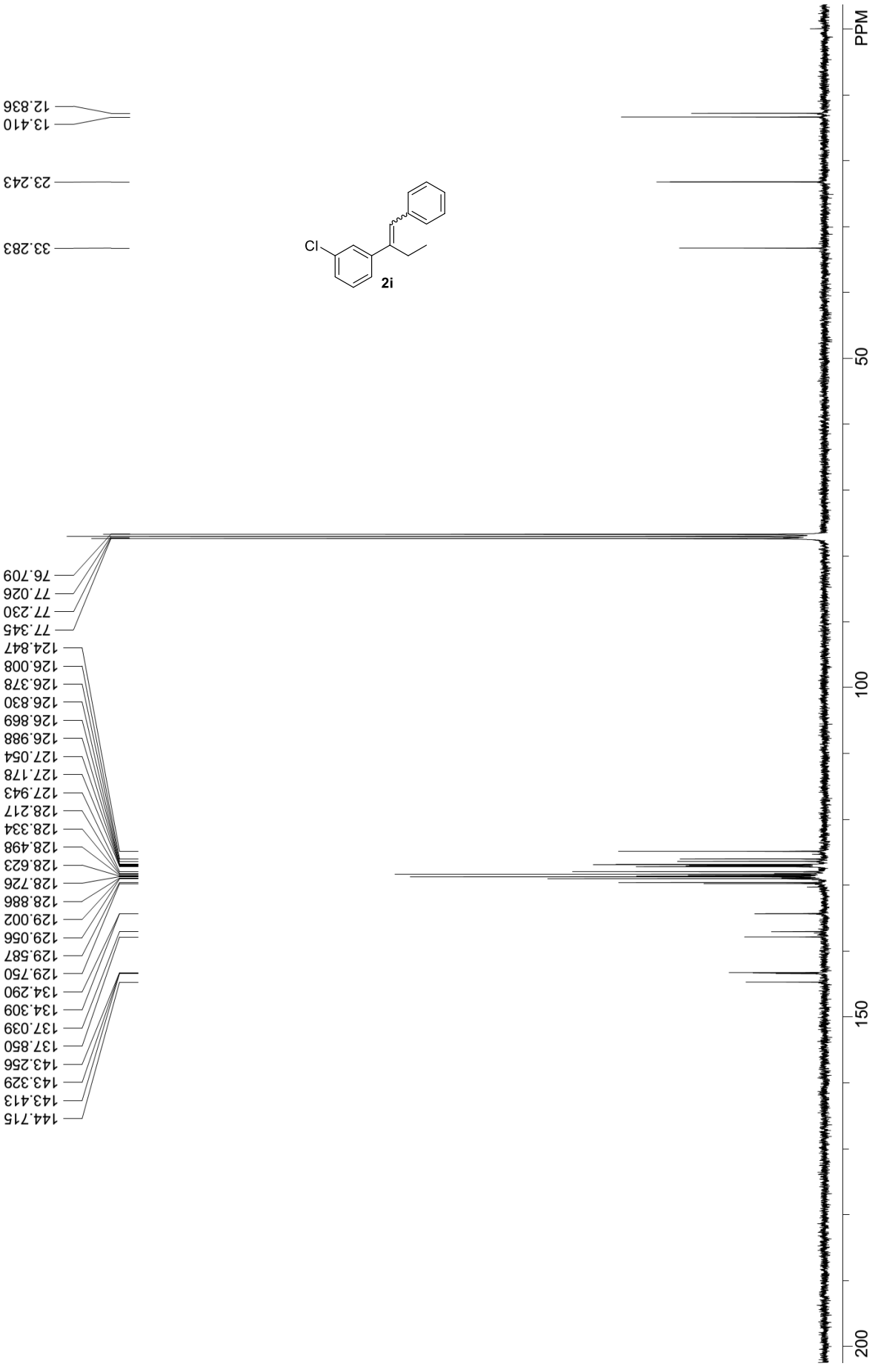
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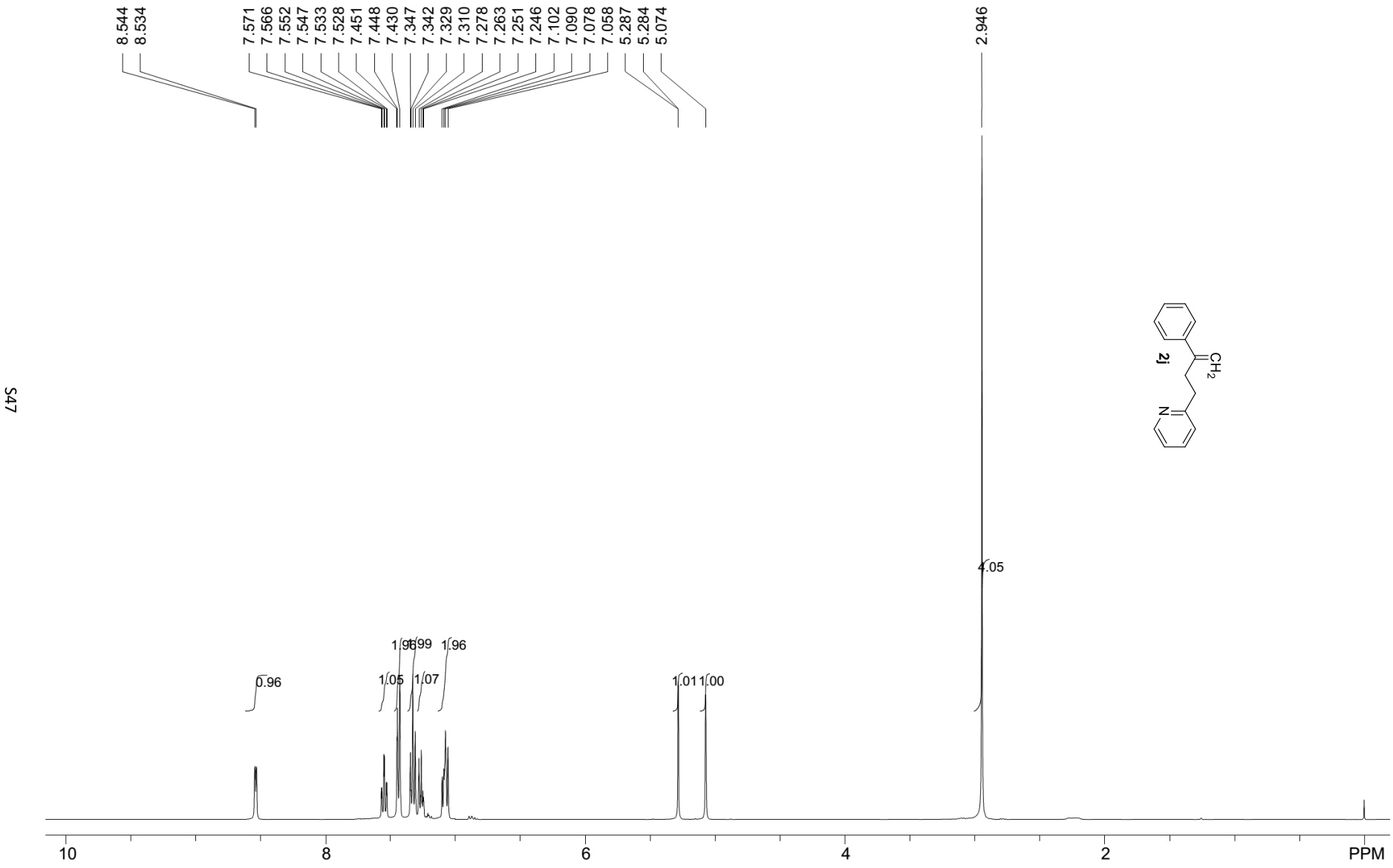
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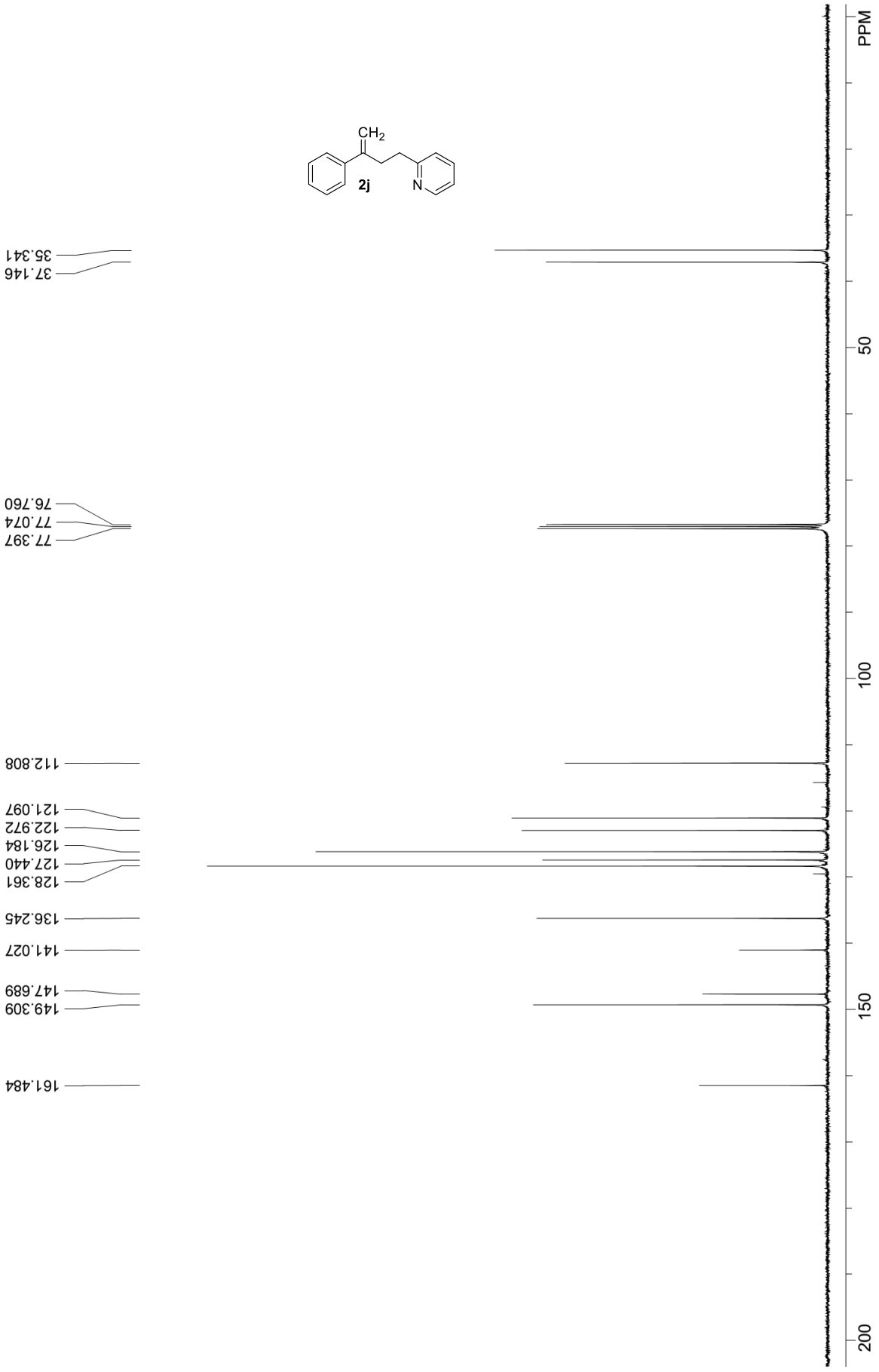
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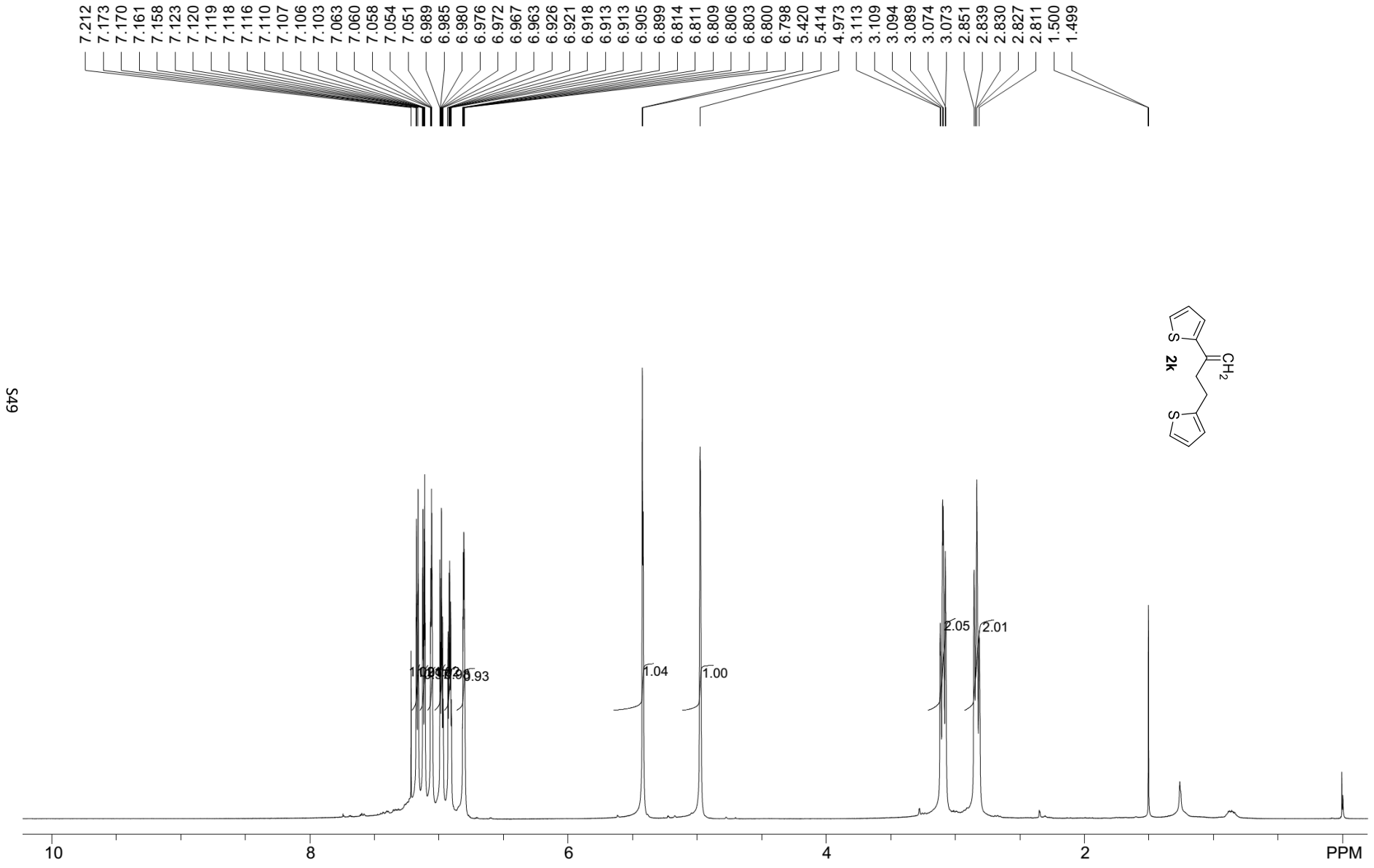
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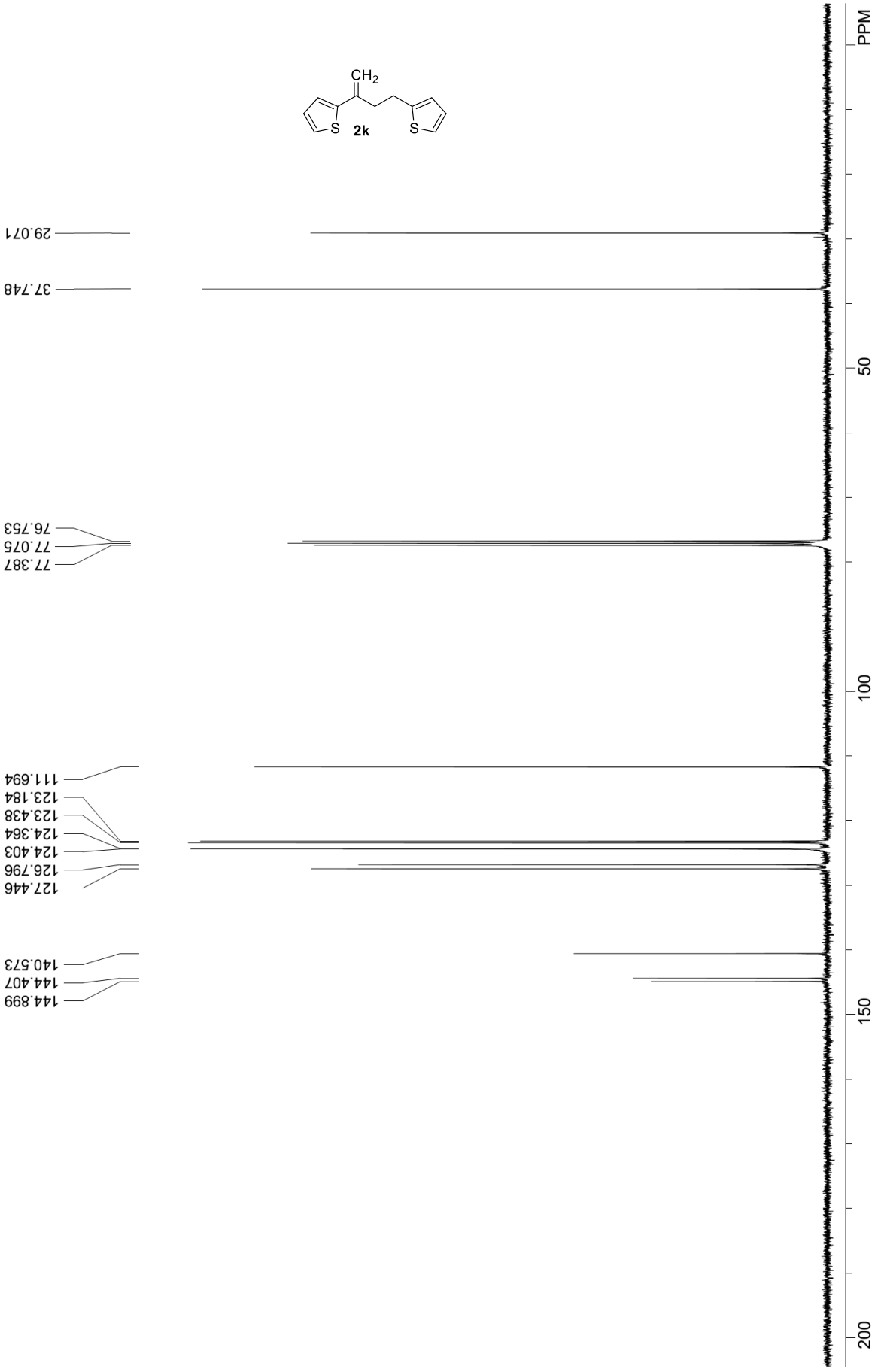
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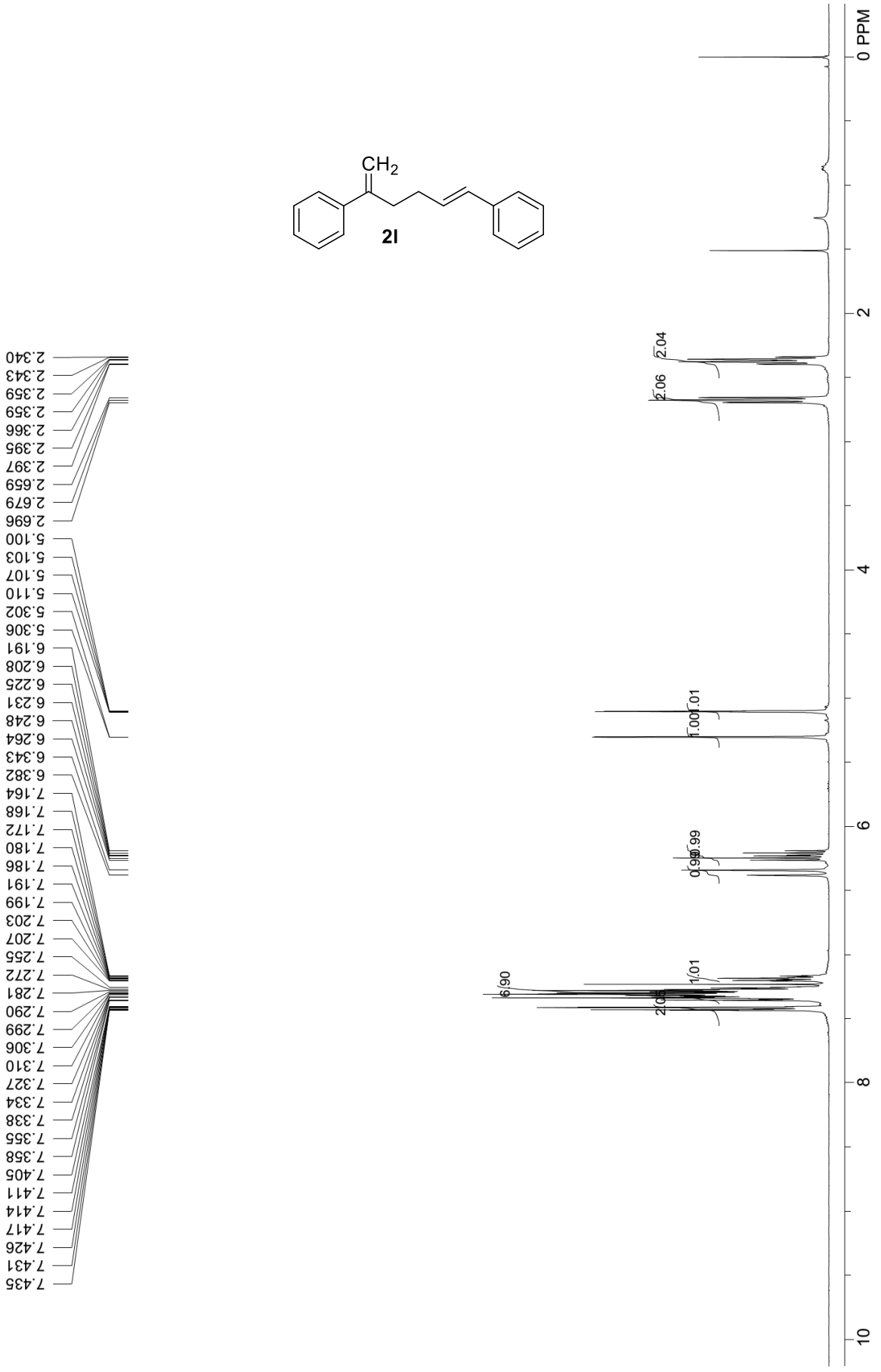
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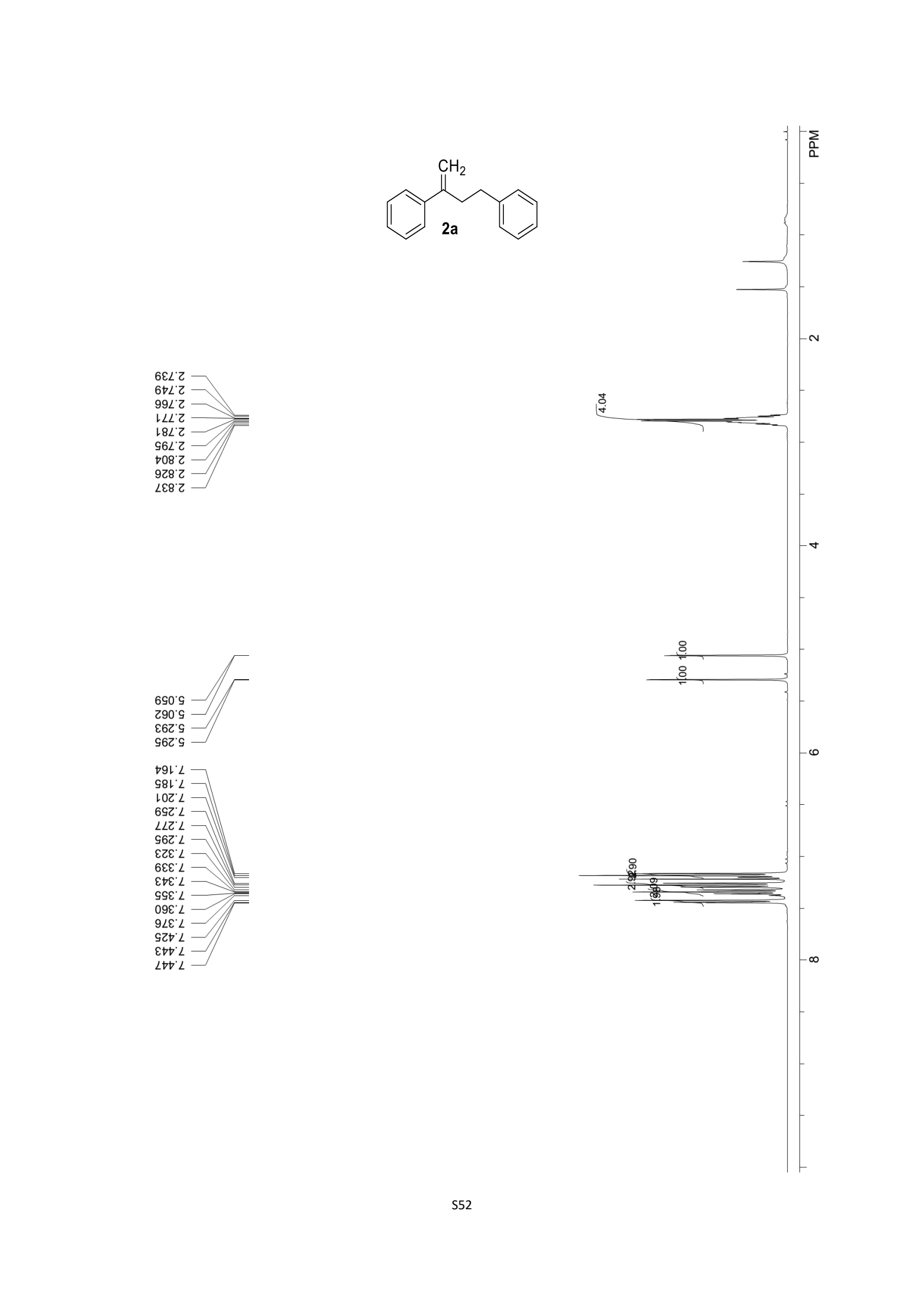
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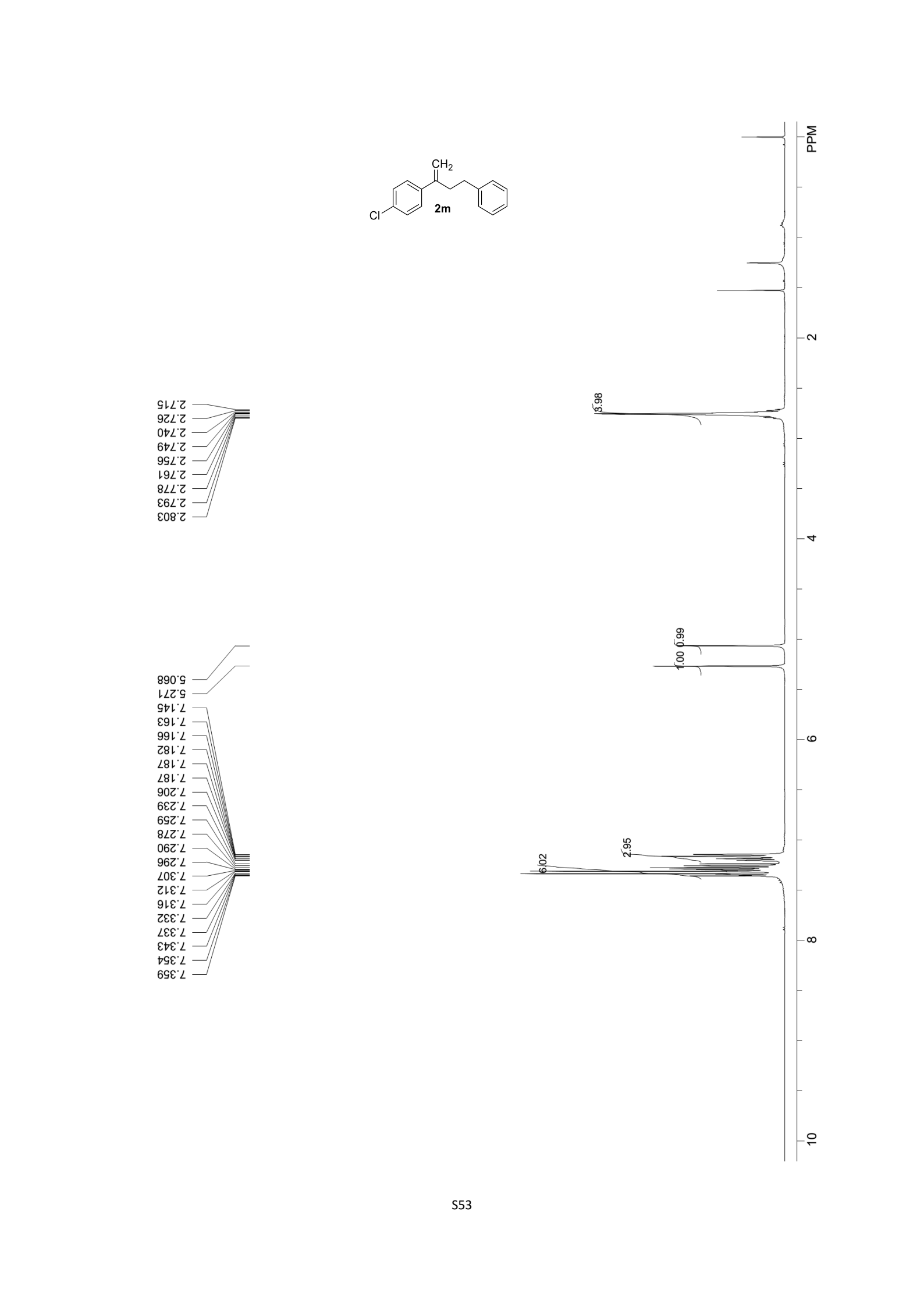
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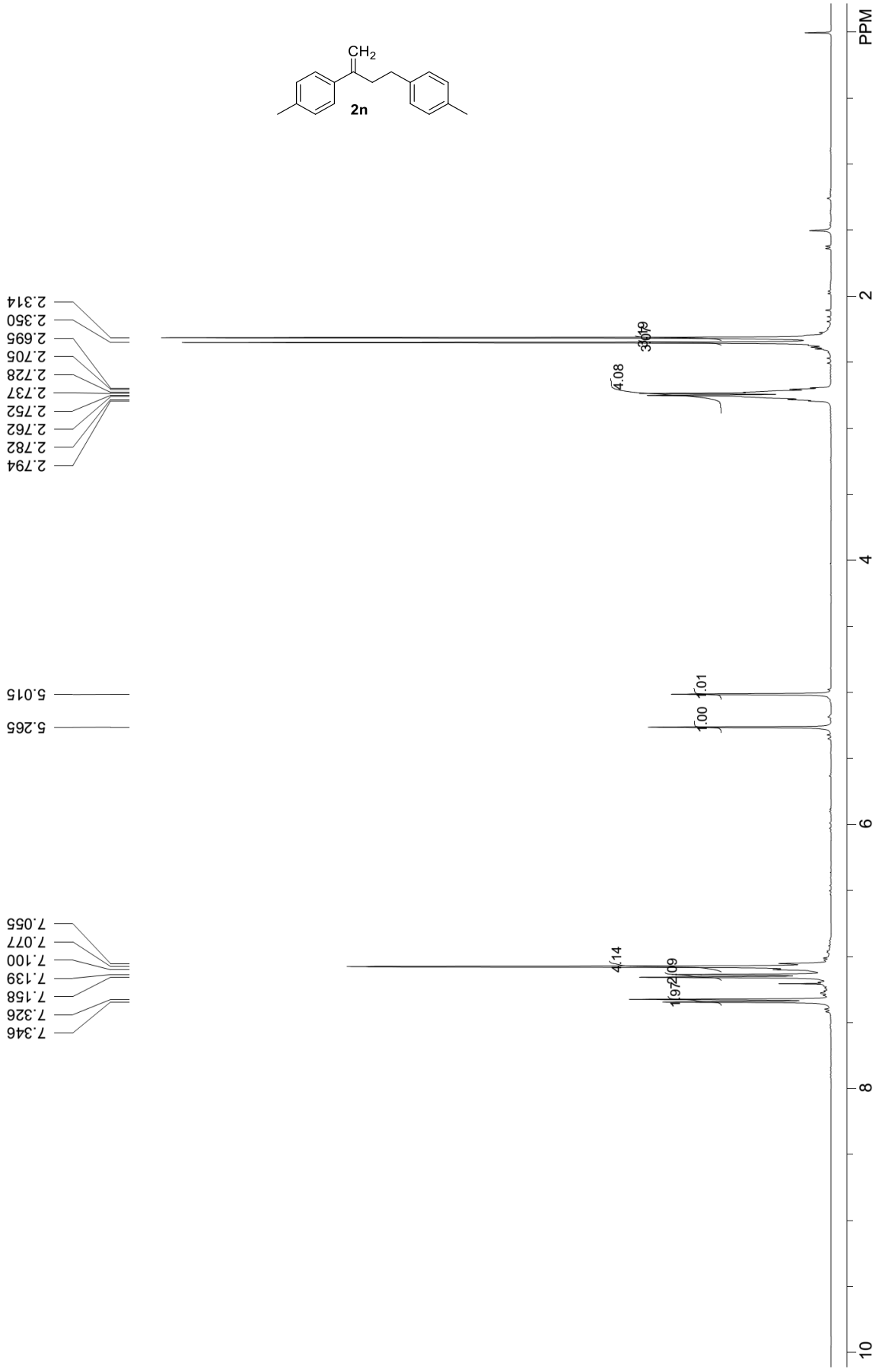
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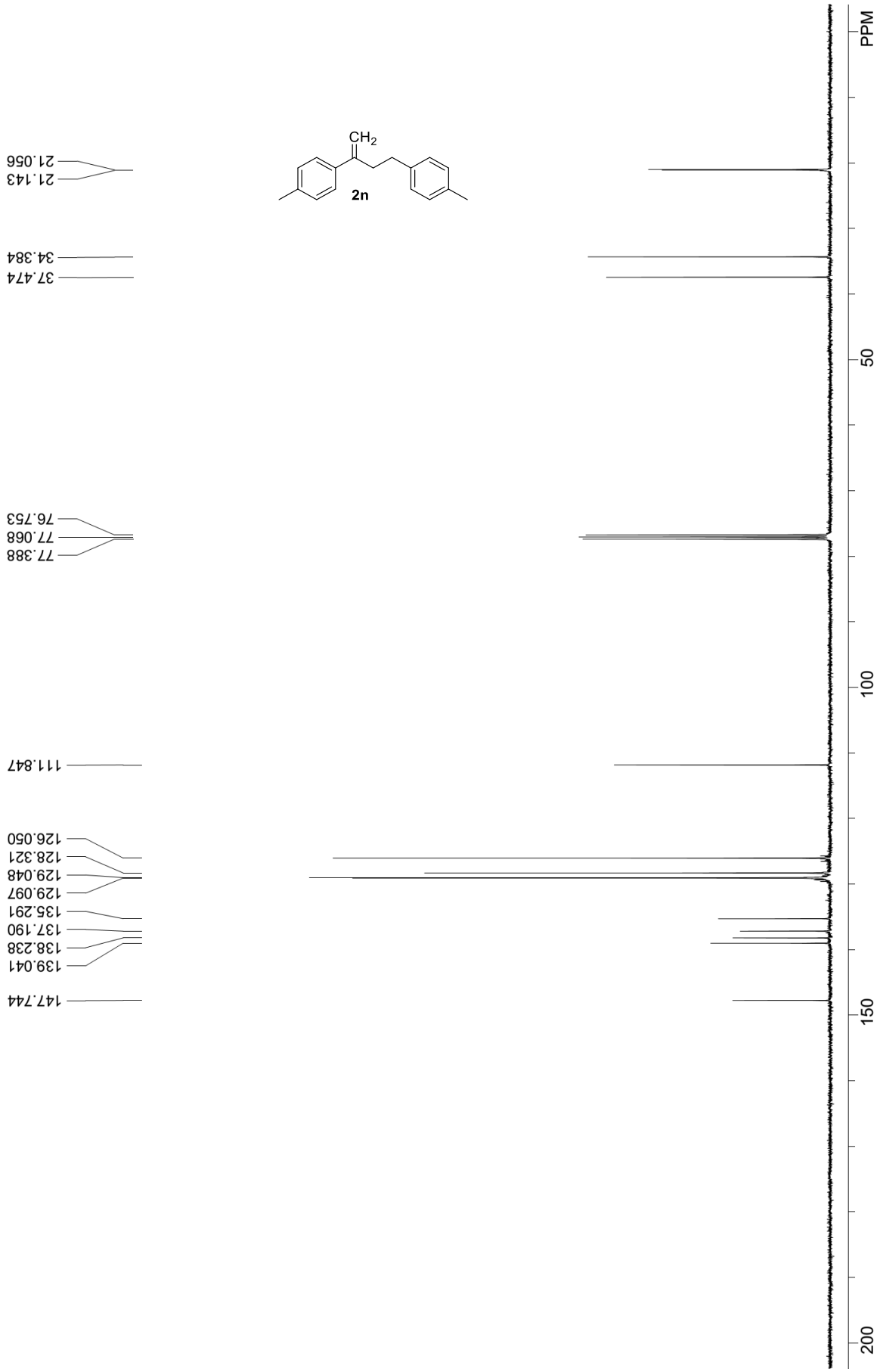
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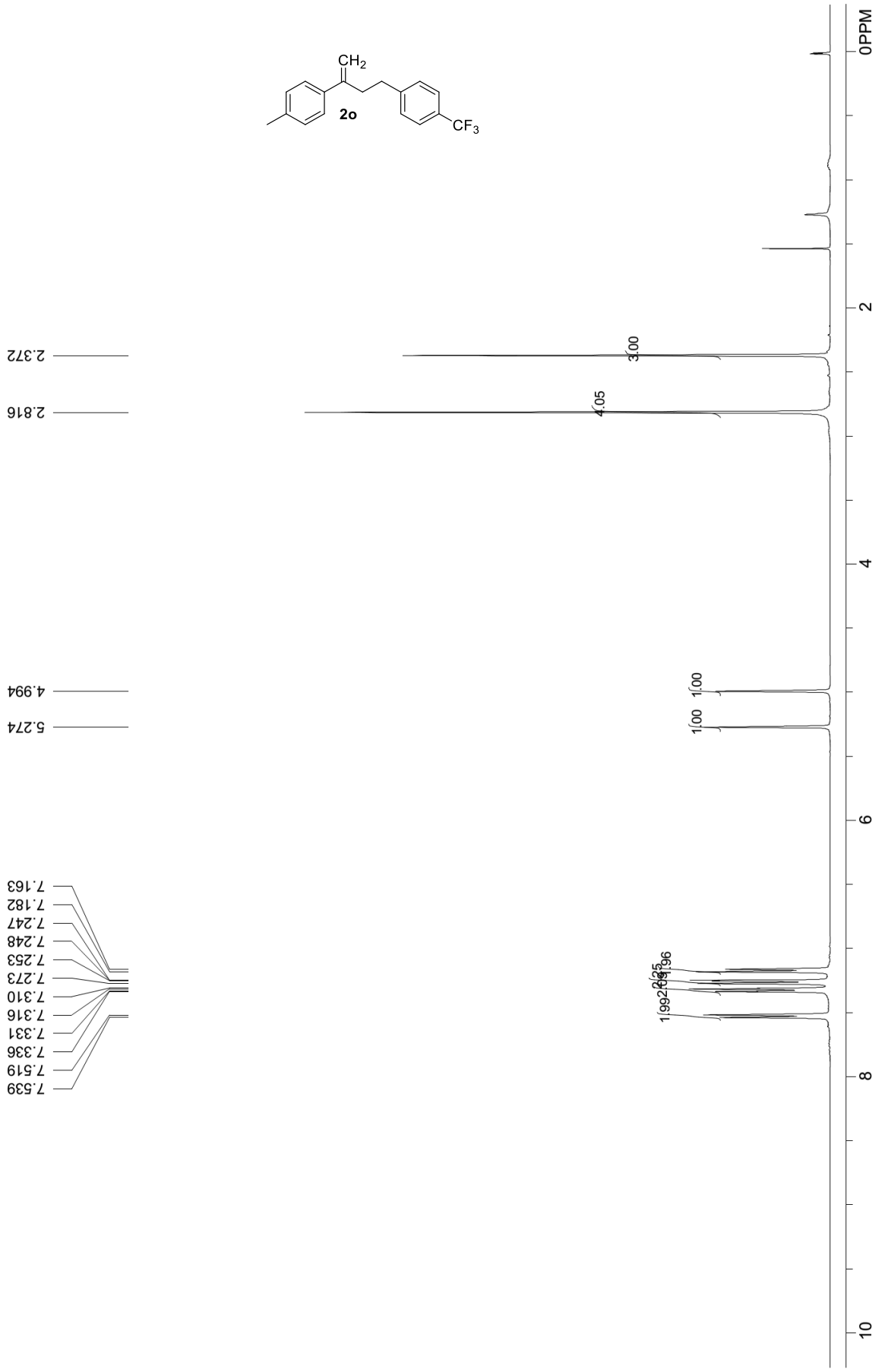
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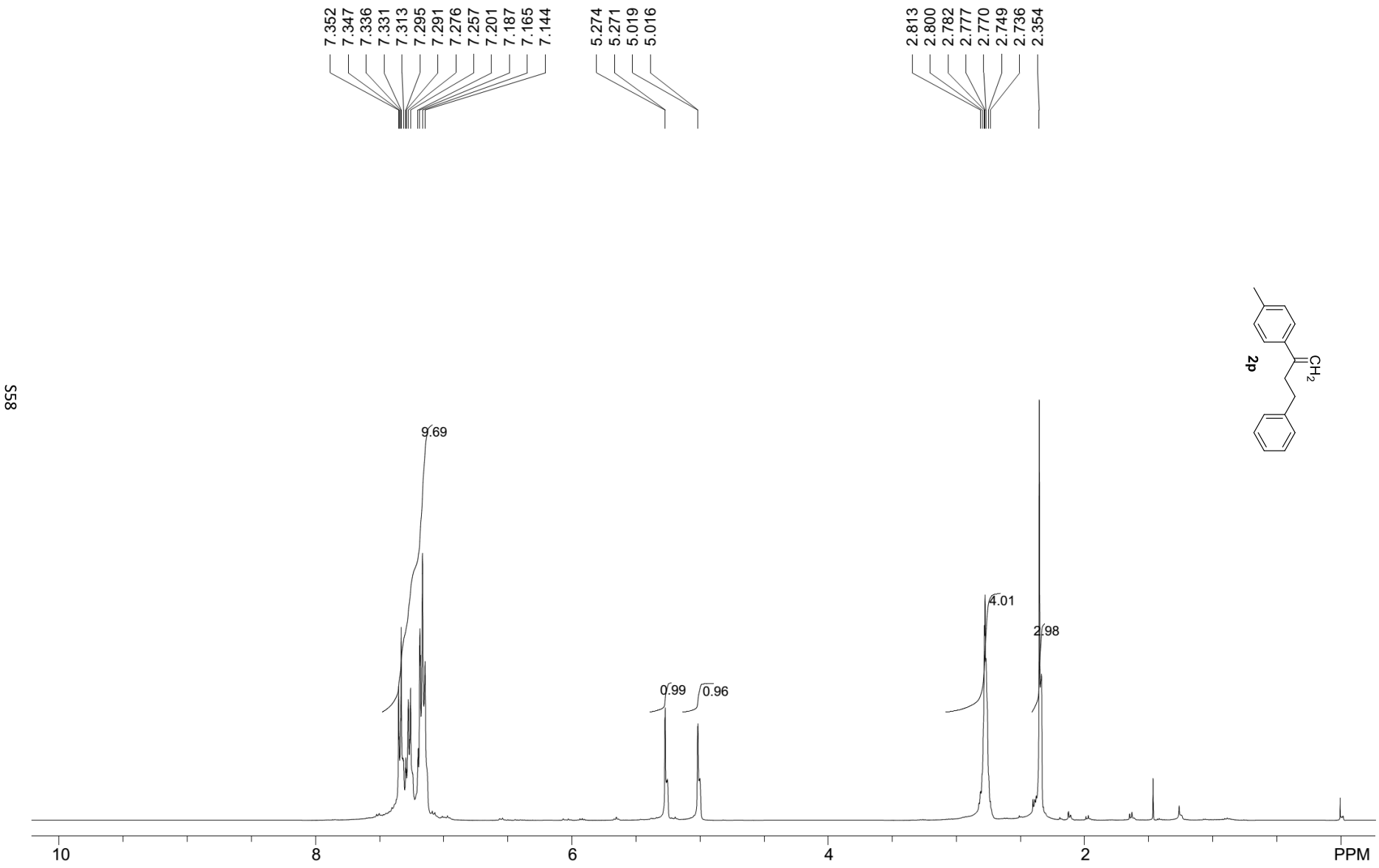
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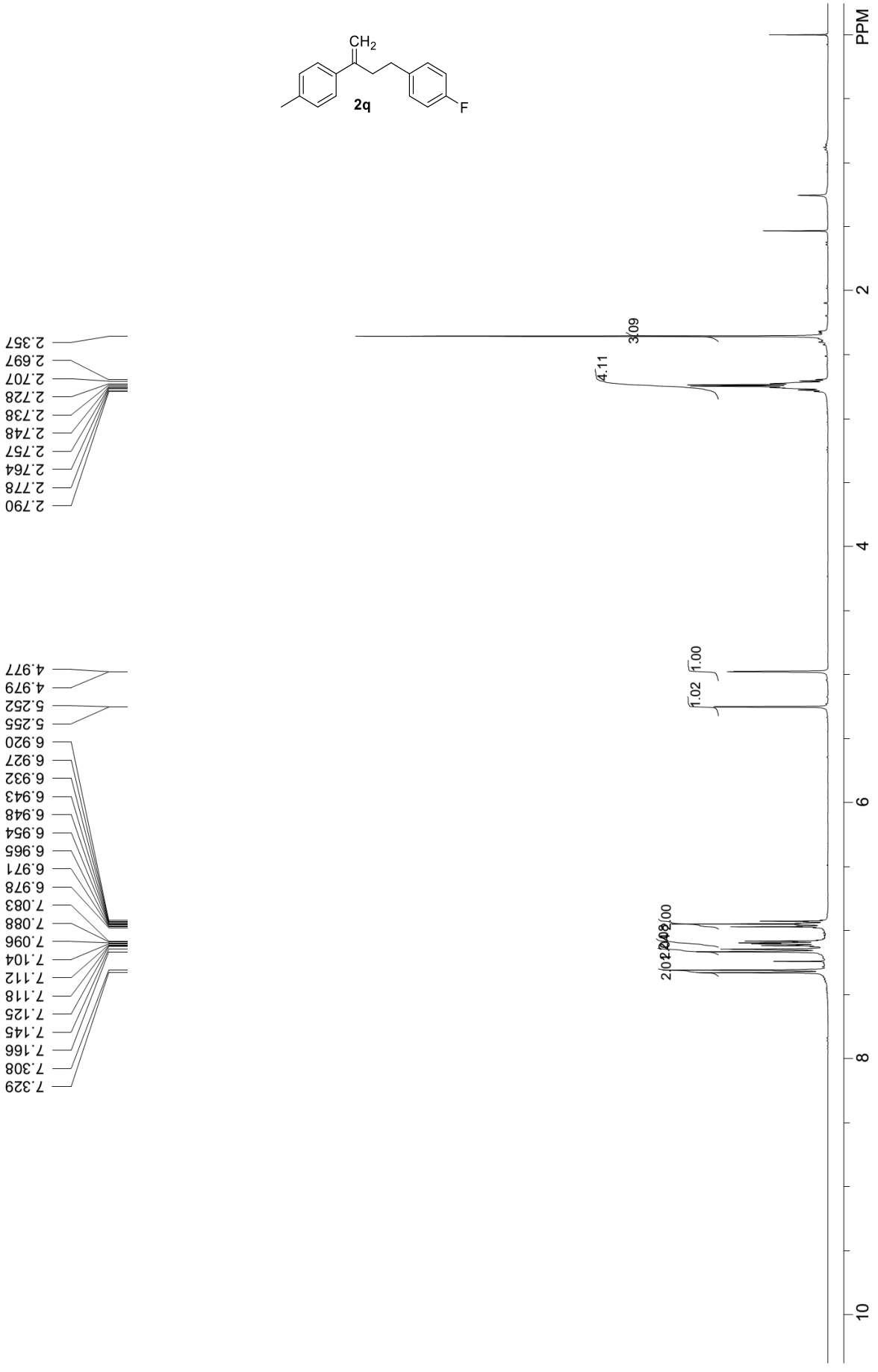
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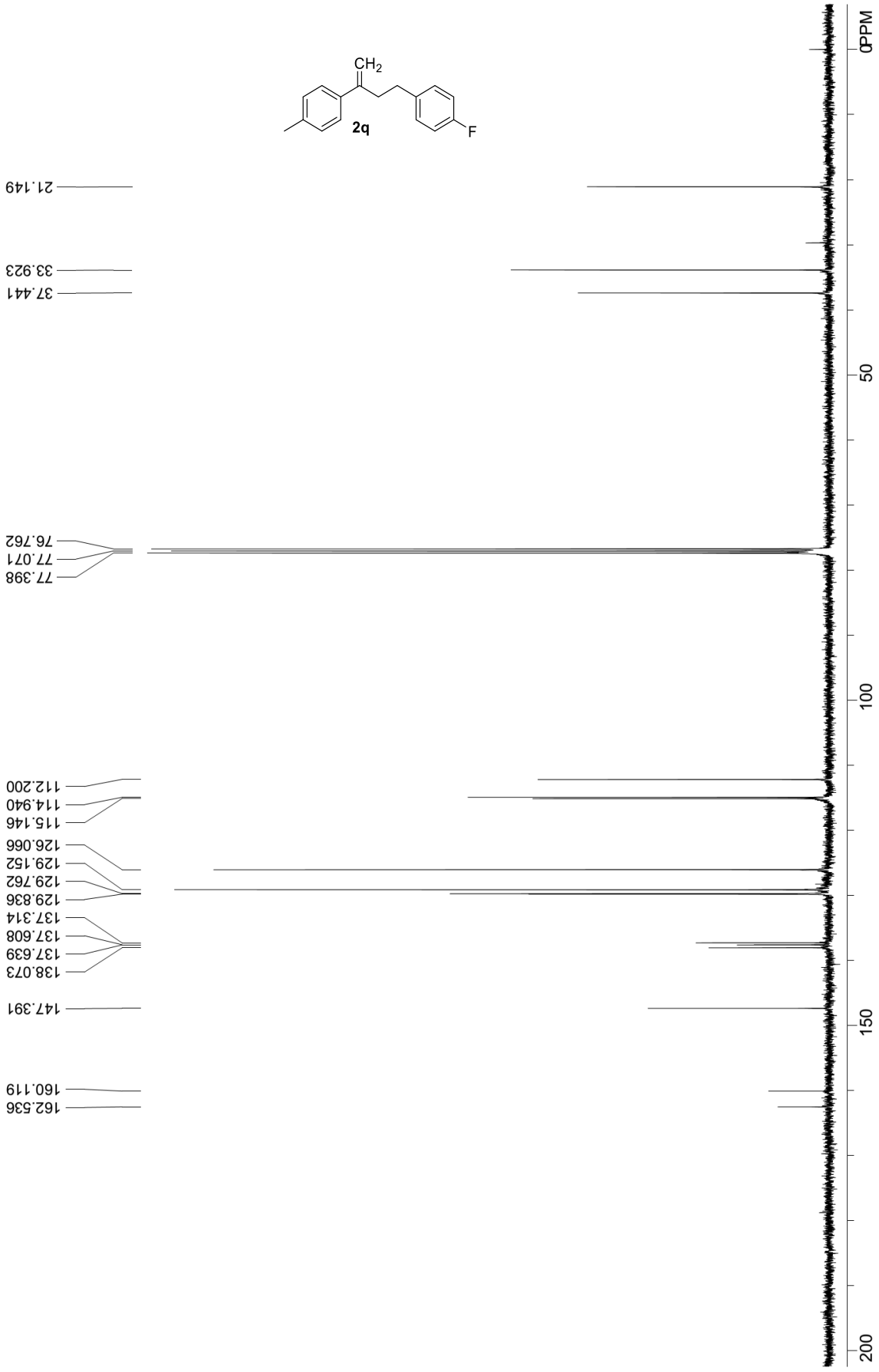
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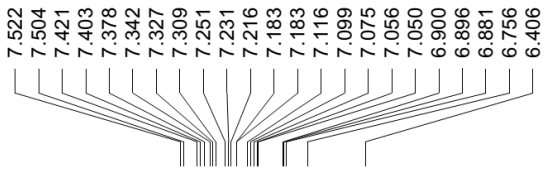
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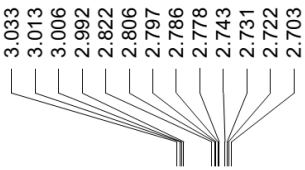
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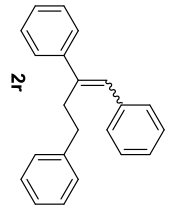
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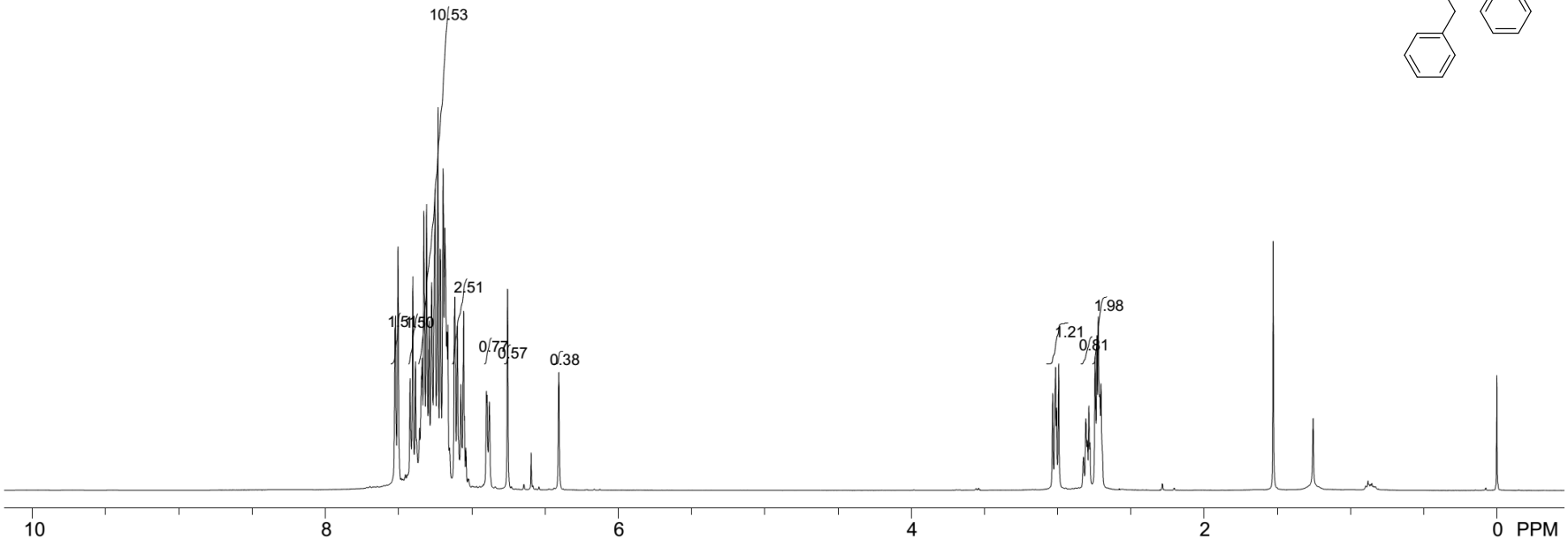
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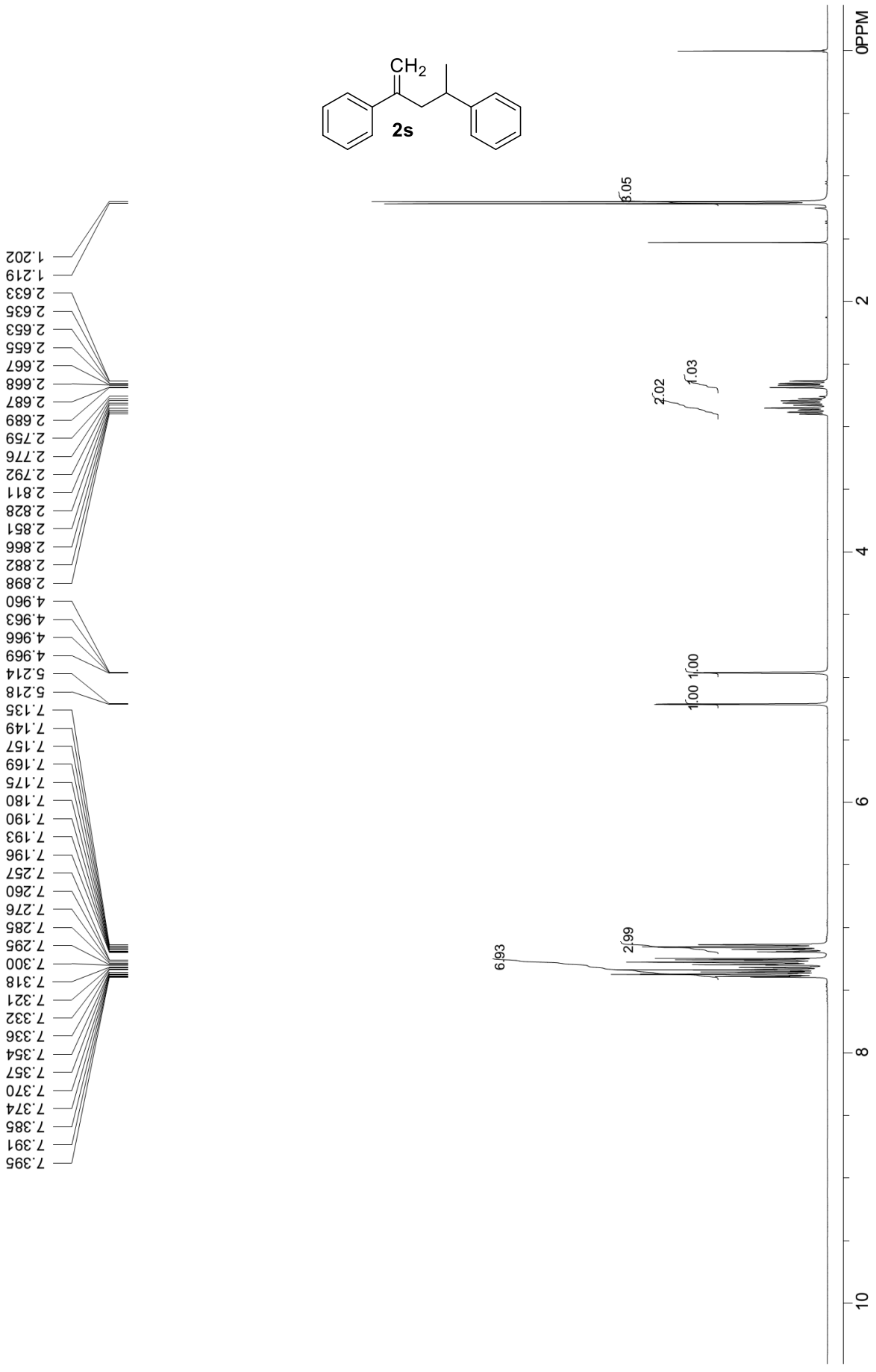
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