

# Intramolecular Hydroalkoxylation of Unactivated Alkenes Using Silane-Iodine Catalytic System

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## Supporting Information

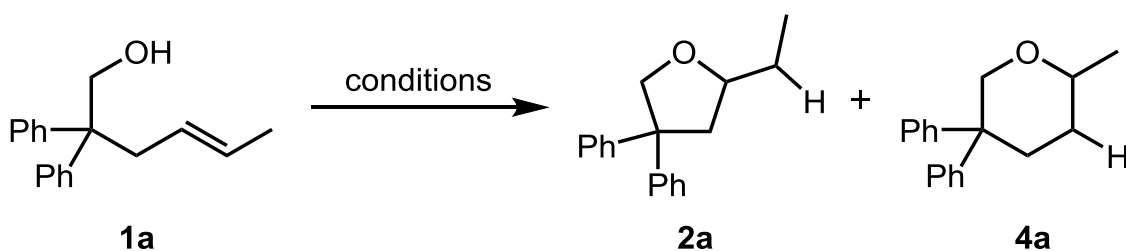
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### 1. General considerations

Reagents were purchased from commercial suppliers and used without purification. Alcohol **1x** was purchased from Sigma-Aldrich and used as received. Column chromatography was performed on neutral silica gel (Cica silica gel 60N) with solvents specified below. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained in CDCl<sub>3</sub> solutions at 25 °C. <sup>1</sup>H NMR chemical shifts are reported in terms of chemical shift (δ, ppm) relative to the singlet at δ 7.26 ppm for chloroform or δ 0.00 ppm for tetramethylsilane as an internal standard. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet. Coupling constants are reported in Hz. <sup>13</sup>C NMR spectra were fully decoupled and are reported in terms of chemical shift (δ, ppm) relative to the triplet at δ 77.0 ppm for CDCl<sub>3</sub>.

## 2. Intramolecular Hydroalkoxylation of 1a under the reported conditions

**Table S1**



entry	conditions	temp. (°C)	time	<b>2a</b> (%)	<b>4a</b> (%)
1	I <sub>2</sub> (10 mol%), PhSiH <sub>3</sub> (20 mol%) CH <sub>2</sub> Cl <sub>2</sub>	rt	1 h	95%	0%
2 <sup>a</sup>	[PtCl <sub>2</sub> (H <sub>2</sub> C=CH <sub>2</sub> ) <sub>2</sub> ] (2 mol%) P(4-F <sub>3</sub> CC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> (4 mol%) Cl <sub>2</sub> CHCHCl <sub>2</sub>	80	48 h	49%	14%
3 <sup>b</sup>	AgOTf (5 mol%) ClCH <sub>2</sub> CH <sub>2</sub> Cl	83	15 h	81%	8%
4 <sup>c</sup>	FeCl <sub>3</sub> (10 mol%), AgOTf (30 mol%) ClCH <sub>2</sub> CH <sub>2</sub> Cl	80	45 min	86%	8%
5 <sup>d</sup>	Bu <sub>4</sub> NPF <sub>6</sub> /Ca(NTf <sub>2</sub> ) <sub>2</sub> (5 mol%) CH <sub>2</sub> Cl <sub>2</sub>	35	24 h	82%	no data
6 <sup>e</sup>	TfOH (10 mol%), CH <sub>2</sub> Cl <sub>2</sub>	rt	24 h	5%	0%

<sup>a</sup> Widenhoefer, R. A. *et al. J. Am. Chem. Soc.* **2004**, 126, 9536.

<sup>b</sup> He, C. *et al. Org. Lett.* **2005**, 7, 4553.

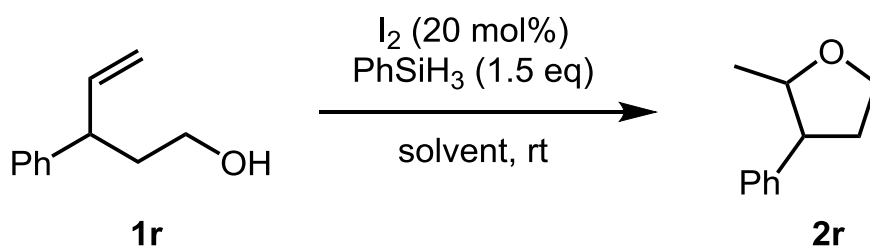
<sup>c</sup> Takaki, K. *et al. Tetrahedron Lett.* **2007**, 48, 3259.

<sup>d</sup> Niggemann, M *et al. Tetrahedron Lett.* **2012**, 53, 6629.

<sup>e</sup> NMR yield.

### 3. Solvent screening

**Table S2**



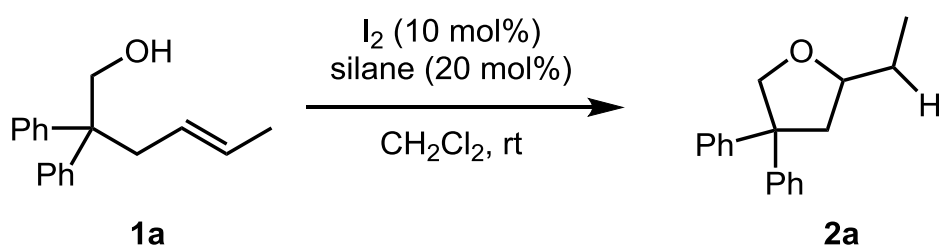
entry	solvent	time (h) <sup>a</sup>	<b>2r</b> (%)
1	toluene	29	63
2	$CH_3CN$	30	29
3	MeOH	24	no reaction
4	$CHCl_3$	24	44 <sup>b</sup>
5	trifluoromethylbenzene	24	61 <sup>b</sup>
6	chlorobenzene	24	80 <sup>b</sup>
7	$ClH_2CCH_2Cl$	3	94 <sup>b</sup>
8	$CH_2Cl_2$	3	83

<sup>a</sup> The reaction mixture was treated with 1.0 equiv of TBAF after the reaction time and stirred for additional 30 min at rt.

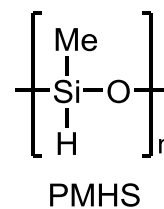
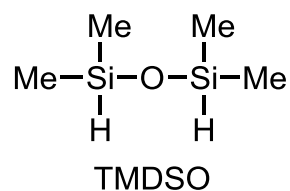
<sup>b</sup> NMR yield.

## 4. Screening of silanes

**Table S3**



entry	silane	time (h)	<b>2a</b> (%)
1	PhSiH <sub>3</sub>	1	95
2	Ph <sub>2</sub> SiH <sub>2</sub>	2	84
3	Ph <sub>3</sub> SiH	24	71 <sup>a</sup>
4	PhSiMe <sub>2</sub> H	1.5	95 <sup>b</sup>
5	PhSiH <sub>2</sub> Cl	1.5	97 <sup>b</sup>
6	PhSiHCl <sub>2</sub>	2	84 <sup>b, c</sup>
7	<i>n</i> BuSiH <sub>3</sub>	2	96 <sup>b</sup>
8	Et <sub>2</sub> SiH <sub>2</sub>	2	97 <sup>b</sup>
9	Et <sub>3</sub> SiH	1.5	93 <sup>b, d</sup>
10	(TMS) <sub>3</sub> SiH	13	96 <sup>b</sup>
11	TMDSO	6	93 <sup>e</sup>
12	PMHS	24	11 <sup>b</sup>



<sup>a</sup> Iodoether **3a** (14%) and tetrahydropyran **4a** (5%) were obtained.

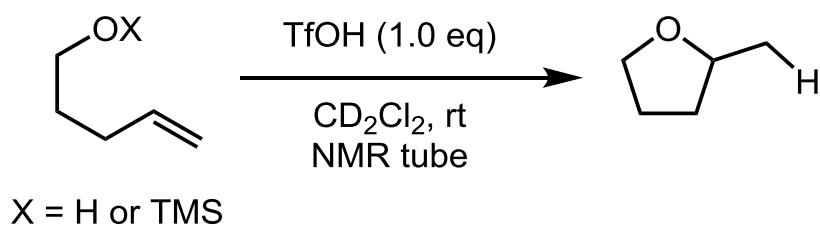
<sup>b</sup> NMR yield.

<sup>c</sup> Iodoether **3a** (6%) and tetrahydropyran **4a** (5%) were obtained.

<sup>d</sup> Iodoether **3a** (0.4%) was obtained.

<sup>e</sup> I<sub>2</sub> (5 mol%) and PhSiH<sub>3</sub> (10 mol%) were used.

## 5. Cyclization of 4-penten-1-ol and the corresponding TMS ether

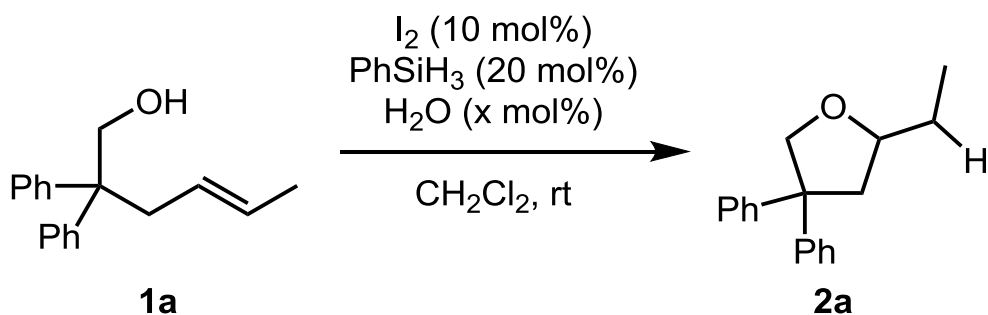


	time (h)	20	30	48
	yield (%) (conversion)	15	20	28

	time (h)	20	30	48
	yield (%) (conversion)	74	83	91

## 6. The effect of H<sub>2</sub>O under I<sub>2</sub>/PhSiH<sub>3</sub> condition

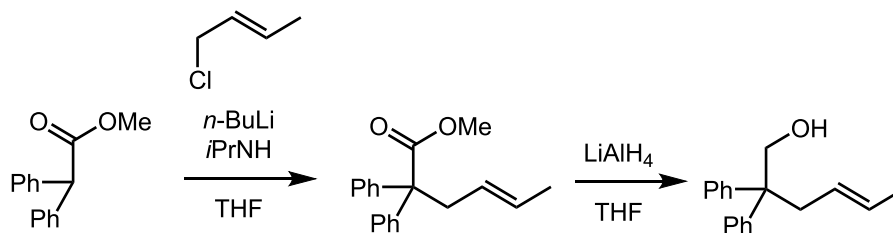
**Table S4**



x	time (h)	<b>2a</b> (%) <sup>a</sup>	
anhydrous condition	1	94	in glovebox dry CH <sub>2</sub> Cl <sub>2</sub> (water <10 ppm)
0	1	95	standard condition
10	24	88	
100	24	19	

<sup>a</sup> Isolated yield.

## 7. Preparation of alcohols



### (*E*)-2,2-Diphenylhex-4-en-1-ol (**1a**)<sup>1</sup>

A solution of methyl diphenylacetate (1.32 g, 5.82 mmol) in THF (7.6 mL) was added slowly to a solution of LDA [generated from diisopropylamine (0.98 mL, 6.98 mmol) and *n*-BuLi (4.4 mL, 1.6 M in hexane, 6.98 mmol) in THF (10 mL) at  $-78\text{ }^{\circ}\text{C}$ ] over 30 min at  $-78\text{ }^{\circ}\text{C}$  and the resulting solution was stirred for additional 15 min. Crotyl chloride (*cis*- and *trans*- mixture) (6.40 mmol) was added over 10 min and the resulting mixture was warmed up to  $0\text{ }^{\circ}\text{C}$ , stirred overnight, quenched with saturated aqueous  $\text{NH}_4\text{Cl}$ , and extracted with EtOAc. The organic layer was then washed with brine, dried over  $\text{MgSO}_4$ , and concentrated under reduced pressure. The product was used for next step without further purification.

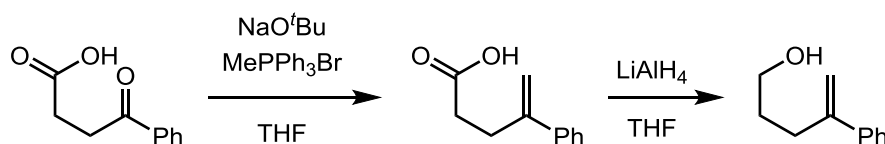
To a solution of  $\text{LiAlH}_4$  (266 mg, 7.00 mmol) in THF (7.5 mL), methyl 2,2-diphenyl-4-pentenoate (5.82 mmol) in THF (7.0 mL) was slowly added at  $0\text{ }^{\circ}\text{C}$ . After stirred for 1 h, the reaction mixture was carefully quenched with  $\text{H}_2\text{O}$  (0.27 mL), 10%  $\text{NaOH}$  (0.40 mL), and  $\text{H}_2\text{O}$  (0.81 mL) at  $0\text{ }^{\circ}\text{C}$ , and filtered through a pad of Celite. The filtrate was extracted with EtOAc, washed with brine, dried over  $\text{MgSO}_4$  and concentrated under reduced pressure. The residue was purified by flash column chromatography ( $\text{SiO}_2$ , 10:1 hexane: EtOAc) to give a *E*:*Z* = 25:1 mixture of alcohols (0.85 g, 58%, 2 steps) as a colorless oil. *E* isomer **1a** was isolated by flash column chromatography ( $\text{SiO}_2$ , 20:1 hexane: EtOAc).

<sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.28 (m, 4H), 7.23-7.17 (m, 6H), 5.51 (dtq, 1H,  $J = 15.0, 6.8, 1.6$  Hz), 5.06 (dq, 1H,  $J = 15.0, 6.4$  Hz), 4.14 (d, 2H,  $J = 6.8$  Hz), 2.89 (d, 2H,  $J = 6.8$  Hz), 1.57 (dd, 3H,  $J = 6.4, 1.6$  Hz), 1.16 (t, 1H,  $J = 6.8$  Hz);

<sup>13</sup>C NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.5, 128.7, 128.2, 128.1, 126.6, 126.2, 68.1, 51.7, 39.7, 18.0;

IR (neat,  $\text{cm}^{-1}$ ): 3549, 3434;

HRMS (ESI,  $m/z$ ) Calcd. for  $\text{C}_{18}\text{H}_{20}\text{NaO}$ : 275.1412 ( $[\text{M}+\text{Na}]^+$ ), found 275.1408( $[\text{M}+\text{Na}]^+$ ).



### 4-Phenylpent-4-en-1-ol (**1b**)<sup>2</sup>

<sup>1</sup> Qian, H.; Han, X.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2004**, *126*, 9536.

<sup>2</sup> Takemiya, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 6042.

To a suspension of methyltriphenylphosphonium bromide (13.0 g, 36.4 mmol) in THF (50 mL), sodium *tert*-butoxide (7.0 g, 72.8 mmol) was added at 0 °C. The mixture was then stirred for 30 min and changed from a colorless suspension to yellow suspension. After 3-Benzoylpropionic acid (5.00 g, 28.0 mmol) was added to the reaction mixture at 0 °C, the mixture was allowed to warm up to ambient temperature, and stirred for 2 h. After evaporation of THF, CH<sub>2</sub>Cl<sub>2</sub> and 10% aqueous NaOH were added. The aqueous layer was washed with CH<sub>2</sub>Cl<sub>2</sub>. 10% aqueous HCl was then added until ca. pH 2. The aqueous layer was then extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with brine, dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The product was used for next step without further purification.

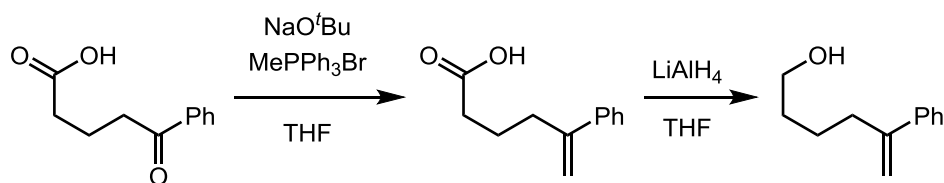
To a solution of LiAlH<sub>4</sub> (3.2 g, 84.0 mmol) in THF (25 mL), a solution of 4-phenylpent-4-enoic acid (28.0 mmol) in THF (25 mL) was slowly added at 0 °C. The reaction mixture was stirred for 30 min. The reaction mixture was slowly quenched with H<sub>2</sub>O (3.2 mL), and 10% aqueous NaOH (4.8 mL), and H<sub>2</sub>O (9.6 mL) at 0 °C, and filtered through a pad of Celite. The filtrate was extracted with EtOAc, washed with brine, dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO<sub>2</sub>, 5:1 hexane: EtOAc) to give alcohol **1b** (4.04 g, 83%, 2 steps) as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42-7.39 (m, 2H), 7.35-7.26 (m, 3H), 5.30 (d, 1H, *J* = 1.2 Hz), 5.10 (d, 1H, *J* = 1.2 Hz), 3.67 (t, 2H, *J* = 6.4 Hz), 2.61 (t, 2H, *J* = 8.0 Hz), 1.73 (tt, 2H, *J* = 8.0, 6.4 Hz), 1.36 (br s, 1H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 147.9, 141.0, 128.3, 127.4, 126.1, 112.5, 62.4, 31.5, 31.1;

IR (neat, cm<sup>-1</sup>): 3347;

HRMS (DART, *m/z*) Calcd. for C<sub>11</sub>H<sub>15</sub>O: 163.1123([M+H]<sup>+</sup>), found 163.1144 ([M+H]<sup>+</sup>).



### 5-Phenylhex-5-en-1-ol (**1c**)

Compound **1c**<sup>3</sup> (567 mg, 23%, 2 steps) was synthesized from 4-benzoylbutanoic acid (2.69 g, 14.0 mmol) according to the preparation procedure of **1b**.

Colorless oil;

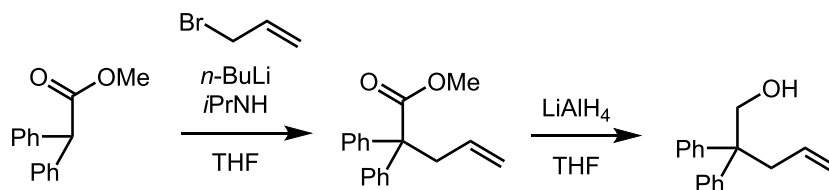
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40-7.38 (m, 2H), 7.35-7.31 (m, 2H), 7.28-7.24 (m, 1H), 5.27 (d, 1H, *J* = 1.2 Hz), 5.07 (d, 1H, *J* = 1.2 Hz), 3.64 (t, 2H, *J* = 6.0 Hz), 2.54 (t, 2H, *J* = 7.6 Hz), 1.65-1.49 (m, 4H), 1.20 (brs, 1H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 148.2, 141.1, 128.2, 127.3, 126.0, 112.3, 62.6, 35.0, 32.2, 24.3;

<sup>3</sup> Oh, C. H.; Jung, H. H.; Kim, K. S.; Kim, N. *Angew. Chem. Int. Ed.* **2003**, *42*, 805.

IR (neat,  $\text{cm}^{-1}$ ): 3347;

HRMS (DART,  $m/z$ ) Calcd. for  $\text{C}_{12}\text{H}_{17}\text{O}$ : 177.1279 ( $[\text{M}+\text{H}]^+$ ), found 177.1266 ( $[\text{M}+\text{H}]^+$ ).



### 2,2-Diphenylpent-4-en-1-ol (**1d**)<sup>1</sup>

Compound **1d** (419 mg, 76%, 2 steps) was synthesized from methyl diphenyl acetate (523 mg, 2.31 mmol) and allyl bromide according to the preparation procedure of **1a**.

White solid;

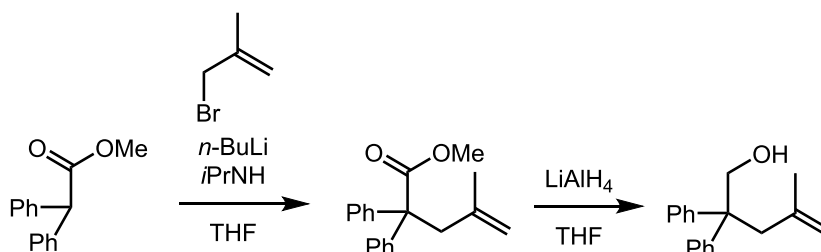
mp 46-47 °C;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.17 (m, 10H), 5.48-5.37 (ddt, 1H,  $J = 17.2, 10.0, 6.8$  Hz), 5.09 (d, 1H,  $J = 17.2$  Hz), 4.98 (d, 1H,  $J = 10.0$  Hz), 4.14 (d, 2H,  $J = 6.8$  Hz), 2.97 (d, 2H,  $J = 6.8$  Hz), 1.16 (t, 1H,  $J = 6.8$  Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.2, 134.5, 128.2, 128.1, 126.4, 118.1, 67.9, 51.5, 41.0;

IR (neat,  $\text{cm}^{-1}$ ): 3549, 3434;

HRMS (ESI,  $m/z$ ) Calcd. for  $\text{C}_{17}\text{H}_{18}\text{NaO}$ : 261.1255 ( $[\text{M}+\text{Na}]^+$ ), found 261.1245 ( $[\text{M}+\text{Na}]^+$ ).



### 4-Methyl-2,2-diphenylpent-4-en-1-ol (**1e**)<sup>4</sup>

Compound **1e** (1.35 g, 92%, 2 steps) was synthesized from methyl diphenyl acetate (1.32 g, 5.82 mmol) and 3-bromo-2-methylprop-1-ene according to the preparation procedure of **1a**.

Colorless oil;

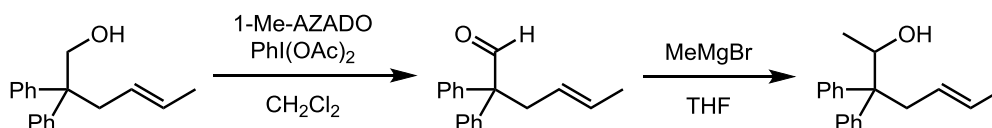
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31-7.27 (m, 4H), 7.24-7.18 (m, 6H), 4.86-4.84 (m, 1H), 4.68-4.67 (m, 1H), 4.25 (d, 2H,  $J = 7.2$  Hz), 2.96 (s, 2H), 1.12 (s, 3H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.9, 142.6, 128.3, 128.1, 126.4, 115.6, 67.2, 51.4, 43.8, 24.3;

IR (neat,  $\text{cm}^{-1}$ ): 3549;

<sup>4</sup> Jeong, Y.; Kim, D. Y.; Choi, Y.; Ryu, J. S. *Org. Biomol. Chem.* **2011**, *9*, 374.

HRMS (ESI, m/z) Calcd. for C<sub>18</sub>H<sub>20</sub>NaO: 275.1412 ([M+Na]<sup>+</sup>), found 275.1387 ([M+Na]<sup>+</sup>).



### 3,3-Diphenylhept-5-en-2-ol (**1f**)

To a solution of **1a** (*E:Z* = 25:1 mixture) (786.4 mg, 3.116 mmol) and 1-Me-AZADO (25.9 mg, 0.156 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was added PhI(OAc)<sub>2</sub> (1.5 g, 4.674 mmol) at room temperature. The mixture was quenched aqueous NaHCO<sub>3</sub>, followed by saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The product was used for next step without further purification.

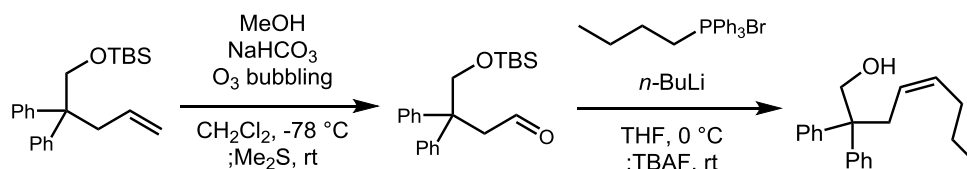
to a solution of aldehyde (3.116 mmol) in THF (15.6 mL), MeMgBr (1.25 mL of a 1.0 M solution in THF, 1.25 mmol) was slowly added and the resulting solution was stirred for 1 h at 0 °C. The reaction mixture was carefully quenched with saturated aqueous NH<sub>4</sub>Cl, the layer was separated and the aqueous layer was extracted with EtOAc. The organic layer was then washed with brine, dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO<sub>2</sub>, 4:1 hexane: EtOAc) to give alcohol **1f** (1.05 g, 76%, 2 steps) as a colorless oil. (25:1 of *E:Z* isomers)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *E* isomer) δ 7.31-7.22 (m, 10H), 5.40 (dq, 1H, *J* = 15.4, 6.8 Hz), 5.06-4.98 (m, 1H), 4.65-4.58 (m, 1H), 2.89 (dd, 1H, *J* = 14.0, 6.8 Hz), 2.79 (dd, 1H, *J* = 14.0, 7.2 Hz), 1.53 (dd, 3H, *J* = 6.4, 1.2 Hz), 1.38 (d, 1H, *J* = 8.0 Hz), 1.02 (d, 3H, *J* = 6.8 Hz);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *E* isomer) δ 144.7, 143.8, 129.7, 129.5, 128.2, 127.6, 127.5, 126.8, 126.2, 126.1, 69.5, 55.8, 41.5, 18.9, 18.0;

IR (neat, cm<sup>-1</sup>): 3567, 3455;

HRMS (ESI, m/z) Calcd. for C<sub>19</sub>H<sub>22</sub>NaO: 289.1568 ([M+Na]<sup>+</sup>), found 289.1565 ([M+Na]<sup>+</sup>).



### (*Z*)-2,2-Diphenyloct-4-en-1-ol (**1g**)

Ozone was bubbled through a solution of *tert*-butyl (2,2-diphenylpent-4-en-1-yl)oxy dimethylsilane<sup>5</sup> (synthesized from **1d**) (2.26 g, 6.42 mmol) in MeOH (3.8 mL) and CH<sub>2</sub>Cl<sub>2</sub> (17 mL) buffered with NaHCO<sub>3</sub> (808 mg, 9.63 mmol) at -78 °C until

<sup>5</sup> Shigehisa, H.; Aoki, T.; Yamaguchi, S.; Shimizu, N.; Hiroya, K. *J. Am. Chem. Soc.* **2013**, *135*, 10306.

the appearance of a persistent deep blue color. The reaction mixture was subsequently purged with a flow of dry Ar, treated with Me<sub>2</sub>S (4.75 mL, 64.17 mmol) at -78 °C, slowly warmed up to ambient temperature and stirred for 7 h. The volatiles were concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO<sub>2</sub>, 50:1 hexane: EtOAc) to give aldehyde (1.79 g, 78%) as a colorless oil.

#### 4-*tert*-Butyldimethylsilyloxy-3,3-diphenylbutanal

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.42 (br s, 1H), 7.32-7.20 (m, 10H), 4.12 (s, 2H), 3.18 (d, 2H, *J* = 2.4 Hz), 0.85 (s, 9H), 0.00 (s, 6H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 202.7, 144.8, 128.4, 127.8, 126.6, 70.2, 50.7, 50.6, 25.7, 18.2, -5.8;

IR (neat, cm<sup>-1</sup>): 1718;

HRMS (ESI, *m/z*) Calcd. for C<sub>22</sub>H<sub>30</sub>NaO<sub>2</sub>Si: 377.1913 ([M+Na]<sup>+</sup>), found 377.1914 ([M+Na]<sup>+</sup>).

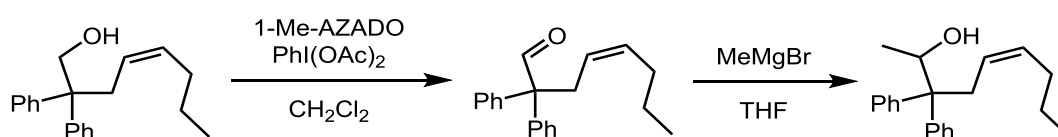
To a suspension of butyltriphenylphosphonium bromide (3.03 g, 7.58 mmol) in THF (17 mL) was added *n*-BuLi (4.7 mL, 1.6 M hexane, 7.58 mmol) at 0 °C. The mixture was then stirred for 30 min to result in a yellow suspension. 4-*tert*-butyldimethylsilyloxy-3,3-diphenylbutanal (1.79 g, 5.05 mmol) was then added to the reaction mixture at 0 °C. The mixture was then stirred for 2 h, quenched with saturated aqueous NH<sub>4</sub>Cl, filtered through a pad of Celite and washed with hexane. The organic layer was then washed with brine, dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. A solution of the product in THF (17 mL) was added TBAF (6.0 mL, 1.0 M THF) and stirred for 9 h. The resulting mixture was then quenched with H<sub>2</sub>O and extracted with EtOAc. The organic layer was then washed with brine, dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO<sub>2</sub>, 25:1 hexane: EtOAc) to give alcohol **1g** (632 mg, 45%) as a colorless oil (a mixture of 1:15 of *E/Z* isomers).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *Z* isomer) δ 7.32-7.28 (m, 4H), 7.24-7.19 (m, 6H), 5.43-5.36 (m, 1H), 5.11-5.04 (m, 1H), 4.14 (s, 2H), 2.96-2.94 (dd, 2H, *J* = 7.2, 1.2 Hz), 1.99 (qd, 2H, *J* = 7.2, 1.2 Hz), 1.39-1.26 (sext, 2H, *J* = 7.2 Hz), 0.87 (t, 3H, *J* = 7.2 Hz);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *Z* isomer) δ 145.4, 132.8, 128.3, 128.2, 126.3, 124.9, 68.2, 52.0, 34.1, 29.5, 22.7, 13.8;

IR (neat, cm<sup>-1</sup>): 3435;

HRMS (ESI, *m/z*) Calcd. for C<sub>20</sub>H<sub>24</sub>NaO: 303.1725 ([M+Na]<sup>+</sup>), found 303.1700 ([M+Na]<sup>+</sup>).



#### (*Z*)-3,3-Diphenylnon-5-en-2-ol (**1h**)

Compound **1h** (278 mg, 82%, 2 steps) was synthesized from 2,2-diphenyloct-4-en-1-ol (323 mg, 1.153 mmol, a mixture of 1:15 of *E/Z* isomers) according to the preparation procedure of **1f**.

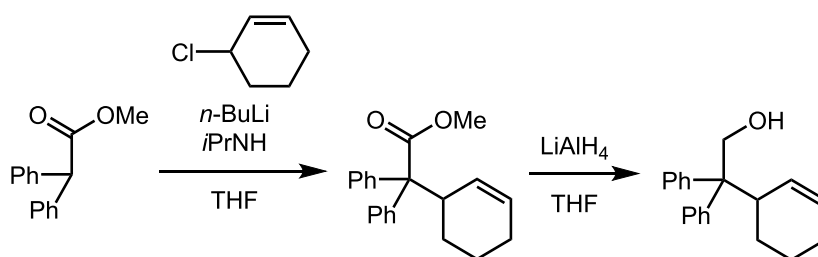
Colorless oil;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33-7.19 (m, 10H), 5.35-5.29 (m, 1H), 5.12-5.06 (m, 1H), 4.64 (q, 1H,  $J = 6.4$  Hz), 2.94 (dd, 1H,  $J = 15.2, 7.6$  Hz), 2.87 (dd, 1H,  $J = 15.2, 6.8$  Hz), 1.88 (q, 2H,  $J = 7.2$  Hz), 1.24 (sext, 2H,  $J = 7.2$  Hz), 1.04 (d, 3H,  $J = 6.4$  Hz), 0.84 (t, 3H,  $J = 7.2$ Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.4, 143.6, 132.3, 129.7, 129.5, 127.7, 127.5, 126.2, 126.1, 125.0, 70.0, 56.0, 35.7, 29.5, 22.6, 19.1, 13.8;

IR (neat,  $\text{cm}^{-1}$ ): 3455;

HRMS (ESI,  $m/z$ ) Calcd. for  $\text{C}_{21}\text{H}_{26}\text{NaO}$ : 317.1881 ( $[\text{M}+\text{Na}]^+$ ), found 317.1876 ( $[\text{M}+\text{Na}]^+$ )



### 2-(Cyclohex-2-en-1-yl)-2,2-diphenylethan-1-ol (**1i**)<sup>1</sup>

Compound **1i** (203 mg, 13%, 2 steps) was synthesized from methyl diphenyl acetate (1.32 g, 5.82 mmol) and 3-chlorocyclohex-1-ene according to the preparation procedure of **1a**.

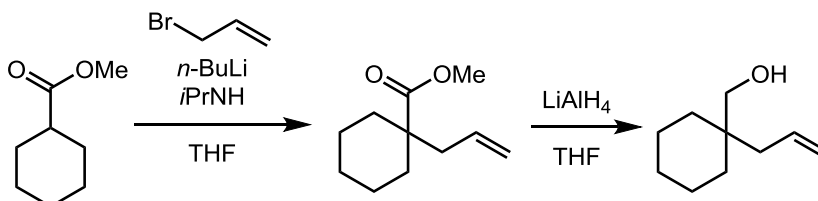
Colorless oil;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31-7.21 (m, 10H), 5.81 (br d, 1H,  $J = 10.4$  Hz), 5.70-5.64 (m, 1H), 4.22 (dd, 2H,  $J = 6.8, 2.0$  Hz), 3.38-3.28 (m, 1H), 1.92-1.53 (m, 5H), 1.18 (t, 1H,  $J = 6.8$  Hz), 1.06 (qd, 1H,  $J = 12.4, 3.6$  Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.1, 142.3, 129.4, 129.3, 129.0, 128.9, 127.8, 127.3, 126.2, 126.1, 68.0, 55.6, 39.0, 24.9, 24.8, 22.3;

IR (neat,  $\text{cm}^{-1}$ ): 3545, 3417;

HRMS (ESI,  $m/z$ ) Calcd. for  $\text{C}_{20}\text{H}_{22}\text{NaO}$ : 301.1568 ( $[\text{M}+\text{Na}]^+$ ), found 301.1553 ( $[\text{M}+\text{Na}]^+$ ).



### (1-Allylcyclohexyl)methanol (**1j**)<sup>6</sup>

<sup>6</sup> Zheng, T.; Narayan, R. S.; Schomaker, J. M.; Borhan, B. *J. Am. Chem. Soc.* **2005**, *127*, 6946.

A solution of methylcyclohexane carboxylate (1.42 g, 10.0 mmol) in THF (15 mL) was added slowly to a solution of LDA [generated from diisopropylamine (1.7 mL, 12.0 mmol) and *n*-BuLi (7.5 mL, 1.6 M in hexanes, 12.0 mmol) in THF (10 mL) at  $-78\text{ }^{\circ}\text{C}$ ] over 30 min at  $-78\text{ }^{\circ}\text{C}$  and the resulting solution was stirred for additional 15 min. Allyl bromide (0.95 mL, 11.0 mmol) was slowly added over 10 min and the resulting mixture was warmed up to  $0\text{ }^{\circ}\text{C}$ , stirred for 12 h, quenched with saturated aqueous  $\text{NH}_4\text{Cl}$ , and extracted with  $\text{Et}_2\text{O}$ . The organic layer was then washed with brine, dried over  $\text{MgSO}_4$ , and concentrated under reduced pressure. The product was used for next step without further purification.

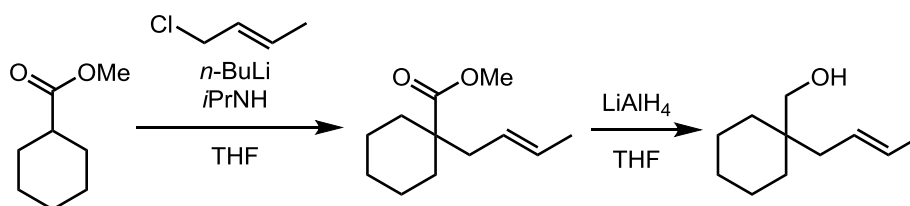
$\text{LiAlH}_4$  (455 mg, 12.0 mmol) was dissolved in THF (13 mL) and a solution of methyl 1-allylcyclohexane-1-carboxylate (1.82 g, 10.0 mmol) in THF (12 mL) was then slowly added at  $0\text{ }^{\circ}\text{C}$ . The reaction mixture was stirred for 3 h. The reaction mixture was slowly quenched with  $\text{H}_2\text{O}$  (0.45 mL), 10% aqueous  $\text{NaOH}$  (0.68 mL),  $\text{H}_2\text{O}$  (1.35 mL) at  $0\text{ }^{\circ}\text{C}$ , filtered through a pad of Celite. The filtrate was extracted with  $\text{EtOAc}$ , washed with brine, dried over  $\text{MgSO}_4$  and concentrated under reduced pressure. The residue was purified by flash column chromatography ( $\text{SiO}_2$ , 5:1 hexane:  $\text{EtOAc}$ ) to give alcohol **1j** (1.30 g, 84%, 2 steps) as a colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.86 (ddt, 1H,  $J = 17.6, 10.2, 7.6$  Hz), 5.10-5.03 (m, 2H), 3.41 (d, 2H,  $J = 6.0$  Hz), 2.11 (dt, 2H,  $J = 7.6, 1.2$  Hz), 1.45-1.30 (m, 10H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.3, 117.0, 68.7, 39.9, 37.7, 32.2, 26.3, 21.4;

IR (neat,  $\text{cm}^{-1}$ ): 3357;

HRMS (DART,  $m/z$ ) Calcd. for  $\text{C}_{10}\text{H}_{22}\text{NO}$ : 172.1701 ( $[\text{M}+\text{NH}_4]^+$ ), found 172.1712 ( $[\text{M}+\text{NH}_4]^+$ ).



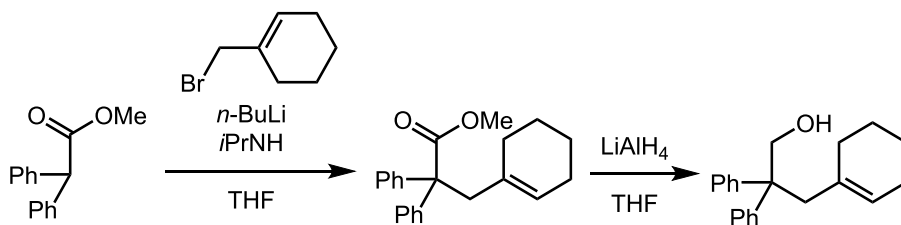
**(E)-1-(But-2-en-1-yl)cyclohexylmethanol (1k)**<sup>7</sup>

Compound **1k** (1.04 g, 52%, 2 steps) was synthesized from methylcyclohexane carboxylate (1.75 g, 8.84 mmol) and crotyl chloride according to the preparation procedure of **1a**.

Colorless oil (a mixture of 9:1 of *E/Z* isomers);

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.51-5.47 (m, 2H), 3.41 (s, 2H), 2.04 (dd, 2H,  $J = 4.8, 1.2$  Hz), 1.67 (d, 3H,  $J = 4.8$  Hz), 1.44-1.29 (m, 10H);

<sup>7</sup> Adrio, L. A.; Quek, L. S.; Raylor, J. G.; Hii, K. K. M. *Tetrahedron* **2009**, 65, 10334.



### 3-(Cyclohex-1-en-1-yl)-2,2-diphenylpropan-1-ol (**11**)<sup>1</sup>

Compound **11** (495 mg, 52%, 2 steps) was synthesized from methyl diphenyl acetate (1.00 g, 4.42 mmol) and 1-(bromomethyl)cyclohex-1-ene according to the preparation procedure of **1a**.

White solid;

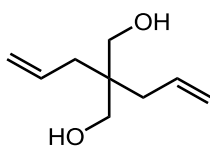
mp 57-59 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30-7.26 (m, 4H), 7.22-7.17 (m, 6H), 5.40 (s, 1H), 4.22 (d, 2H, *J* = 6.8 Hz), 2.84 (s, 2H), 1.95 (br s, 2H), 1.43-1.37 (m, 2H), 1.32-1.27 (m, 2H), 1.11 (br s, 3H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 146.1, 134.5, 128.4, 128.0, 126.7, 126.3, 67.3, 51.7, 44.4, 30.2, 25.5, 23.1, 22.1;

IR (neat, cm<sup>-1</sup>): 3446;

HRMS (ESI, *m/z*) Calcd. for C<sub>21</sub>H<sub>24</sub>NaO: 315.1725 ([M+Na]<sup>+</sup>), found 315.1731 ([M+Na]<sup>+</sup>).



### 2,2-Diallylpropane-1,3-diol (**1m**)<sup>7</sup>

**1m** (297 mg, 85%) was synthesized from diethyl 2, 2-diallylmalonate (537 mg, 2.24 mmol) according to a literature procedure.

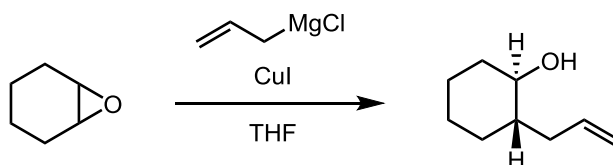
Colorless oil;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.90-5.80 (m, 2H), 5.14-5.09 (m, 4H), 3.59 (d, 4H, *J* = 5.6 Hz), 2.22 (br s, 2H), 2.09 (d, 4H, *J* = 7.6 Hz);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 133.9, 118.1, 68.2, 42.1, 36.1;

IR (neat, cm<sup>-1</sup>): 3364;

HRMS (ESI, *m/z*) Calcd. for C<sub>9</sub>H<sub>16</sub>NaO<sub>2</sub>: 179.1048 ([M+Na]<sup>+</sup>), found 179.1072 ([M+Na]<sup>+</sup>).



### *trans*-2-Allylcyclohexanol (**1n**)<sup>8</sup>

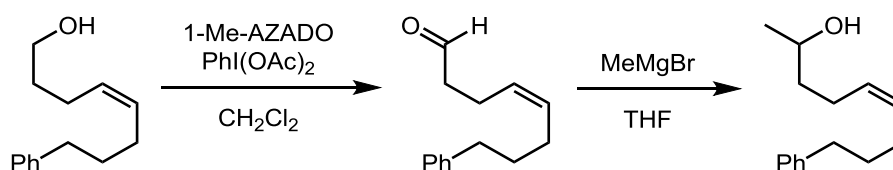
Allylmagnesium chloride (3.60 mL of a 2.0 M solution in THF, 7.20 mmol) was added dropwise to a solution of cyclohexene oxide (0.610 mL, 6.00 mmol) and CuI (172 mg, 0.90 mmol) in THF (10 mL) at -20 °C. The reaction was allowed to warm up to ambient temperature. After 1 h, the reaction was quenched with aqueous saturated NH<sub>4</sub>Cl and extracted with Et<sub>2</sub>O. The combined organic layer was then washed with brine, dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO<sub>2</sub>, 15:1 hexane: EtOAc) to give alcohol **1n** (505 mg, 60%) as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.84 (ddt, 1H, *J* = 17.2, 9.6, 7.2 Hz), 5.05 (dd, 1H, *J* = 16.8, 1.6 Hz), 5.00 (dd, 1H, *J* = 10.4, 1.6 Hz), 3.24 (m, 1H), 2.49-2.41 (m, 1H), 2.00-1.92 (m, 2H), 1.78-1.70 (m, 3H), 1.63-1.59 (m, 1H), 1.35-1.09 (m, 4H), 0.92 (dq, 1H, *J* = 12.8, 3.6 Hz);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.5, 116.0, 74.6, 44.8, 37.4, 35.5, 30.3, 25.5, 24.9;

IR (neat, cm<sup>-1</sup>): 3348, 1639;

HRMS (DART, *m/z*) Calcd. for C<sub>9</sub>H<sub>20</sub>NO: 158.1545 ([M+NH<sub>4</sub>]<sup>+</sup>), found 158.1567 ([M+NH<sub>4</sub>]<sup>+</sup>).



### (*Z*)-9-Phenylnon-5-en-2-ol (**1o**)

Compound **1o** was synthesized (257 mg, 80%, 2 steps) from (*Z*)-8-phenyloct-4-en-1-ol<sup>9</sup> (306 mg, 1.50 mmol) according to the preparation procedure of **1f**.

Colorless oil (a mixture of 1:9 of *E/Z* isomers);

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *Z* isomer) δ 7.28-7.26 (m, 2H), 7.19-7.16 (m, 3H), 5.43-5.40 (m, 2H), 3.80 (sext, 1H, *J* = 6.0 Hz), 2.63 (br t, 2H, *J* = 7.8 Hz), 2.16-2.07 (m, 4H), 1.69 (quin, 2H, *J* = 7.4 Hz), 1.53-1.46 (m, 2H), 1.19 (d, 3H, *J* = 6.0 Hz);

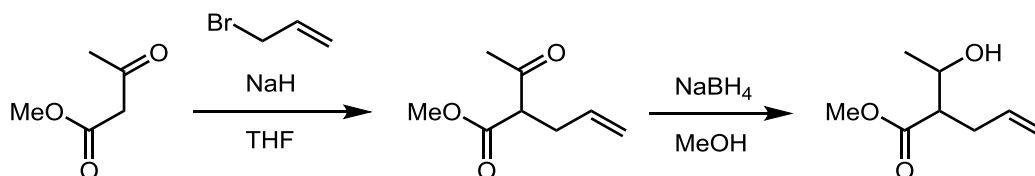
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, *Z* isomer) δ 142.4, 130.0, 129.6, 128.4, 128.2, 125.7, 67.8, 39.0, 35.4, 31.3, 26.7, 23.7, 23.4;

IR (neat, cm<sup>-1</sup>): 3364;

HRMS (ESI, *m/z*) Calcd. for C<sub>15</sub>H<sub>22</sub>NaO: 241.1568 ([M+Na]<sup>+</sup>), found 241.1574 ([M+Na]<sup>+</sup>).

<sup>8</sup> Wang, L.; Thai, K.; Gravel, M. *Org. Lett.* **2009**, *11*, 891.

<sup>9</sup> Kwon, H. Y.; Park, C. M.; Lee, S. B.; Youn, J. H.; Kang, S. H. *Chem. -Eur. J.* **2008**, *14*, 1023.



### Methyl 2-(1-hydroxyethyl)pent-4-enoate (**1p**)

To a suspension of NaH (60% dispersion in mineral oil, 10.4 g, 260 mmol) in dry THF (20 mL), and methyl 3-oxobutanoate (2.33 g, 20.0 mmol) was then slowly added at 0 °C. After the resulting solution was stirred for additional 15 min, allyl bromide (2.94 mL, 20.0 mmol) was added over 10 min. The resulting mixture was warmed up to ambient temperature, stirred for 4 h, quenched with 10% aqueous HCl (20 mL), and extracted with Et<sub>2</sub>O. The organic layer was then washed with brine, dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The product<sup>10</sup> was used for next step without further purification.

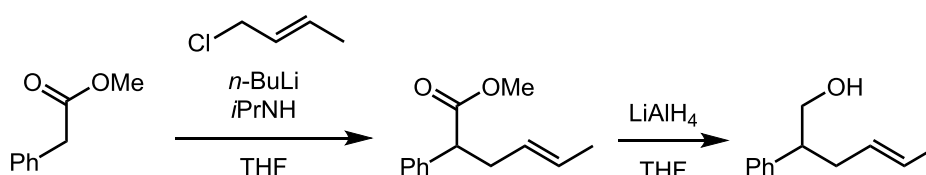
NaBH<sub>4</sub> (189.2 mg, 5.0 mmol) was dissolved in MeOH (20 mL) and a solution of methyl 2-acetylpent-4-enoate (20.0 mmol) in MeOH (13 mL) was then slowly added at 0 °C. The reaction mixture was stirred for 9 h. The reaction mixture was then concentrated under reduced pressure, quenched with H<sub>2</sub>O and washed with Et<sub>2</sub>O. The organic layer was then washed with brine, dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO<sub>2</sub>, 5:1 hexane: EtOAc) to give alcohol **1p** (1.75 g, 56%, 2 steps) as a colorless oil, obtained as an inseparable mixture of isomers (ratio 13.6:1, by integration of methyl signals).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, major isomer) δ 5.77-5.66 (m, 1H), 5.06 (dq, 1H, *J* = 16.8, 1.6 Hz), 5.02-4.98 (m, 1H), 3.91 (sext, 1H, *J* = 6.8 Hz), 3.68 (s, 3H), 2.68 (d, 1H, *J* = 6.8 Hz), 2.46 (m, 1H), 2.40-2.34 (m, 2H), 1.21 (d, 3H, *J* = 6.8 Hz);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, major isomer) δ 175.1, 134.7, 117.1, 67.8, 52.3, 51.5, 33.5, 21.3;

IR (neat, cm<sup>-1</sup>): 3454, 1737;

HRMS (ESI, *m/z*) Calcd. for C<sub>8</sub>H<sub>14</sub>NaO<sub>3</sub>: 181.0841 ([M+Na]<sup>+</sup>), found 181.0824 ([M+Na]<sup>+</sup>).



### (*E*)-2-Phenylhex-4-en-1-ol (**1q**)

Compound **1q** was synthesized (868 mg, 37%, 2 steps) from methyl 2-phenylacetate (2.00 g, 13.3 mmol) and crotyl chloride according to the preparation procedure of **1a**.

Colorless oil (a mixture of 11:1 of *E/Z* isomers);

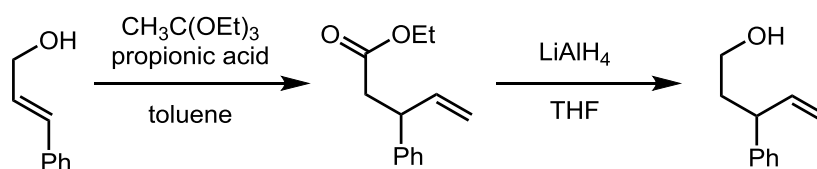
<sup>10</sup> Welch, S. C.; Assercq, J. M.; Loh, J. P.; Glase, S. A. *J. Org. Chem.* **1987**, *52*, 1440.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , *E* isomer)  $\delta$  7.35-7.31 (m, 2H) 7.26-7.21 (m, 3H), 5.51-5.42 (m, 1H) 5.38-5.31 (m, 1H) 3.83-3.70 (m, 2H), 2.84 (dt, 1H,  $J = 13.2, 7.2$  Hz), 2.43-2.28 (m, 2H), 1.60 (dd, 3H,  $J = 6.4, 1.6$  Hz), 1.31 (t, 1H,  $J = 6.4$  Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , *E* isomer)  $\delta$  142.2, 128.7, 128.6, 128.0, 126.9, 126.7, 67.0, 48.5, 35.5, 17.9;

IR (neat,  $\text{cm}^{-1}$ ): 3357;

HRMS (ESI,  $m/z$ ) Calcd. for  $\text{C}_{12}\text{H}_{16}\text{NaO}$ : 199.1099 ( $[\text{M}+\text{Na}]^+$ ), found 199.1089 ( $[\text{M}+\text{Na}]^+$ ).



### 3-Phenylpent-4-en-1-ol (**1r**)<sup>11</sup>

To a solution of cinnamyl alcohol (1.00 g, 7.50 mmol) and triethyl orthoacetate (6.0 g, 37.40 mmol) in toluene (30 mL) was added propionic acid (27.7 mg, 0.374 mmol). The reaction was then heated at 150 °C and stirred for 15 h. The reaction mixture was then cooled down to ambient temperature and concentrated under reduced pressure. The residue was purified by flash column chromatography ( $\text{SiO}_2$ , 10:1 hexane: EtOAc) to give ethyl 3-phenylpent-4-enoate (1.51 g, 99%) as a colorless oil.

### Ethyl 3-phenylpent-4-enoate

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.18 (m, 5H), 5.99 (ddd, 1H  $J = 17.6, 10.2, 7.2$  Hz), 5.10-5.06 (m, 2H), 4.07 (q, 2H,  $J = 7.2$  Hz), 2.74 (dd, 1H,  $J = 14.8, 8.0$  Hz), 2.69 (dd, 1H,  $J = 15.2, 7.2$  Hz), 1.16 (t, 3H,  $J = 7.2$  Hz);

To a suspension of  $\text{LiAlH}_4$  (673 mg, 17.7 mmol) in THF (15 mL), a solution of ethyl 3-phenylpent-4-enoate (1.51 g, 7.39 mmol) in THF (15 mL) was then slowly added at 0 °C. The reaction mixture was stirred for 20 min. The reaction mixture was quenched with  $\text{H}_2\text{O}$  (0.67 mL), and 10% aqueous NaOH (1.0 mL), and  $\text{H}_2\text{O}$  (2.0 mL) at 0 °C, and filtered through a pad of Celite and washed with EtOAc. The filtrate was extracted with EtOAc, washed with brine, dried over  $\text{MgSO}_4$  and concentrated under reduced pressure. The residue was purified by flash column chromatography ( $\text{SiO}_2$ , 3:1 hexane: EtOAc) to give alcohol **1r** (1.00 g, 86%) as a colorless oil.

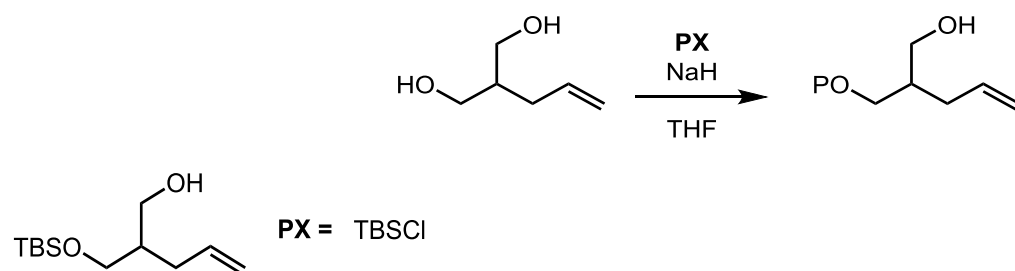
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33-7.29 (m, 2H), 7.22-7.20 (m, 3H), 5.98 (ddd, 1H,  $J = 17.2, 10.0, 7.6$  Hz), 5.09 (d, 1H,  $J = 17.2$  Hz), 5.06 (d, 1H,  $J = 10.0$  Hz), 3.68-3.62 (m, 2H), 3.47 (q, 1H,  $J = 7.6$  Hz), 2.07-1.92 (m, 2H), 1.27 (br s, 1H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.6, 141.8, 128.6, 127.5, 126.4, 114.4, 61.0, 46.3, 37.9;

IR (neat,  $\text{cm}^{-1}$ ): 3335;

<sup>11</sup> Heuger, G.; Kalsow, S.; Göttlich, R. *Eur. J. Org. Chem.* **2002**, 1848.

HRMS (ESI, m/z) Calcd. for C<sub>11</sub>H<sub>14</sub>NaO: 185.0942 ([M+Na]<sup>+</sup>), found 185.0944 ([M+Na]<sup>+</sup>).



### 2-(*tert*-Butyldimethylsilyloxymethyl)pent-4-en-1-ol (**1s**)

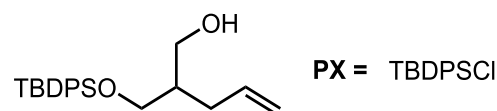
To a suspension of NaH (60% dispersion in mineral oil, 62.1 mg, 1.55 mmol) in dry THF (3 mL), and 2-allyl-1,3-propane diol (180.3 mg, 1.55 mmol) was then slowly added at 0 °C and the resulting solution was stirred for additional 15 min. TBSCl (233.9 mg, 1.55 mmol) was added and the resulting mixture was warmed up to ambient temperature, stirred for 4 h, quenched with H<sub>2</sub>O, and extracted with Et<sub>2</sub>O. The organic layer was then washed with brine, dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO<sub>2</sub>, 10:1 hexane: EtOAc) to give alcohol **1s** (264.7 mg, 74%) as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.78 (ddt, 1H, *J* = 17.2, 9.8, 7.2 Hz), 5.05 (dt, 1H, *J* = 17.2, 1.6 Hz), 5.02 (d, 1H, *J* = 9.8 Hz), 3.79 (dd, 1H, *J* = 10.4, 4.0 Hz), 3.74 (dd, 1H, *J* = 10.4, 3.6 Hz), 3.64 (dd, 1H, *J* = 12.0, 6.8 Hz), 3.61 (dd, 1H, *J* = 12.0, 7.2 Hz), 2.04 (t, 2H, *J* = 7.2 Hz), 1.83 (m, 1H), 0.90 (s, 9H), 0.07 (s, 6H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 136.4, 116.4, 66.5, 66.1, 41.7, 32.4, 25.8, 18.1, -5.61, -5.65;

IR (neat, cm<sup>-1</sup>): 3376;

HRMS (DART, m/z) Calcd. for C<sub>12</sub>H<sub>27</sub>O<sub>2</sub>Si: 231.1780 ([M+H]<sup>+</sup>), found 231.1772 ([M+H]<sup>+</sup>).



### 2-(*tert*-Butyldiphenylsilyloxymethyl)pent-4-en-1-ol (**1t**)<sup>12</sup>

Compound **1t** was synthesized (531 mg, 83%) from 2-allyl-1,3-propane diol (209 mg, 1.80 mmol) and TBDPSCl according to the preparation procedure of **1s**.

Colorless oil;

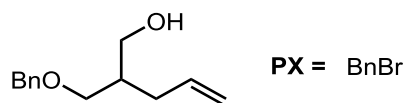
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68-7.67 (d, 4H, *J* = 6.0 Hz), 7.45-7.38 (m, 6H), 5.71 (ddt, 1H, *J* = 17.2, 10.0, 7.2 Hz), 5.00 (d, 1H, *J* = 17.2 Hz), 4.95 (d, 1H, *J* = 10.0 Hz), 3.80-3.64 (m, 4H), 2.05 (t, 2H, *J* = 6.8 Hz), 1.92-1.83 (m, 1H), 1.06 (s, 9H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 136.3, 135.6, 133.1, 129.8, 127.8, 116.4, 66.5, 65.4, 42.1, 32.4, 26.8, 19.1;

<sup>12</sup> Rej, R.; Jana, N.; Kar, S.; Nanda, S. *Tetrahedron: Asymmetry* **2012**, *23*, 364.

IR (neat,  $\text{cm}^{-1}$ ): 3434;

HRMS (ESI,  $m/z$ ) Calcd. for  $\text{C}_{22}\text{H}_{30}\text{NaO}_2\text{Si}$ : 377.1913 ( $[\text{M}+\text{Na}]^+$ ), found 377.1929 ( $[\text{M}+\text{Na}]^+$ ).



### 2-(Benzyloxymethyl)pent-4-en-1-ol (**1u**)

Compound **1u** was synthesized (357 mg, 70%) from 2-allyl-1,3-propane diol (287 mg, 2.47 mmol) and BnBr according to the preparation procedure of **1s**.

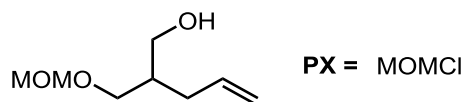
Colorless oil;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34-7.28 (m, 5H), 5.78 (ddt, 1H,  $J = 16.8, 9.6, 6.8$  Hz), 5.05 (d, 1H,  $J = 16.8$  Hz), 5.02 (d, 1H,  $J = 9.6$  Hz), 4.54 (d, 1H,  $J = 12.0$  Hz), 4.50 (d, 1H,  $J = 12.0$  Hz), 3.74-3.61 (m, 2H), 3.62 (dd, 1H,  $J = 9.6, 4.4$  Hz), 3.49 (dd, 1H,  $J = 9.6, 6.8$  Hz), 2.49 (br s, 1H), 2.09 (t, 2H,  $J = 6.8$  Hz), 1.97 (m, 1H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.9, 136.2, 128.4, 127.7, 127.6, 116.5, 73.4, 73.1, 65.5, 40.3, 32.7;

IR (neat,  $\text{cm}^{-1}$ ): 3419;

HRMS (ESI,  $m/z$ ) Calcd. for  $\text{C}_{13}\text{H}_{18}\text{NaO}_2$ : 229.1205 ( $[\text{M}+\text{Na}]^+$ ), found 229.1208 ( $[\text{M}+\text{Na}]^+$ ).



### 2-(Methoxymethoxymethyl)pent-4-en-1-ol (**1v**)

Compound **1v** was synthesized (139 mg, 68%) from 2-allyl-1,3-propane diol (150 mg, 1.29 mmol) and MOMCl according to the preparation procedure of **1s**.

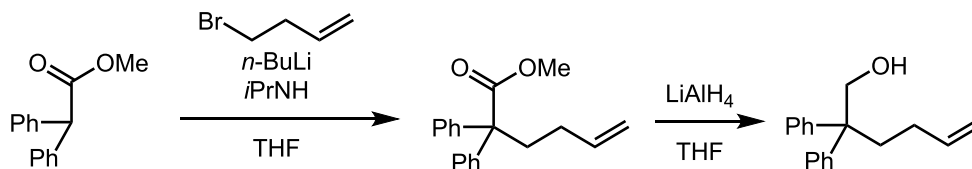
Colorless oil;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.80 (ddt, 1H,  $J = 16.8, 9.6, 7.2$  Hz), 5.06 (d, 1H,  $J = 16.8$  Hz), 5.04 (d, 1H,  $J = 9.6$  Hz), 4.62 (s, 2H), 3.72 (d, 1H,  $J = 10.8, 4.0$  Hz), 3.67-3.62 (m, 2H), 3.55 (dd, 1H,  $J = 9.6, 7.2$  Hz), 3.37 (s, 3H), 2.11 (t, 2H,  $J = 7.2$  Hz), 1.93 (m, 1H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.1, 116.6, 96.7, 70.1, 65.1, 55.3, 40.4, 32.8;

IR (neat,  $\text{cm}^{-1}$ ): 3433;

HRMS (ESI,  $m/z$ ) Calcd. for  $\text{C}_8\text{H}_{16}\text{NaO}_3$ : 183.0997 ( $[\text{M}+\text{Na}]^+$ ), found 183.0989 ( $[\text{M}+\text{Na}]^+$ ).



### 2,2-Diphenylhex-5-en-1-ol (**1w**)<sup>1</sup>

Compound **1w** was synthesized (774 mg, 12%, 2 steps) from methyl diphenyl acetate (5.00 g, 22.1 mmol) and 3-bromo-1-propene according to the preparation procedure of **1a**.

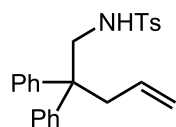
Colorless oil;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33-7.29 (m, 4H), 7.25-7.19 (m, 6H), 5.79 (ddt, 1H, *J* = 16.8, 10.4, 6.4 Hz), 4.98 (dq, 1H, *J* = 16.8, 2.0 Hz), 4.91 (dd, 1H, *J* = 10.4, 2.0 Hz), 4.17 (d, 2H, *J* = 6.8 Hz), 2.28-2.24 (m, 2H), 1.85-1.79 (m, 2H), 1.09 (t, 1H, *J* = 6.8 Hz);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 145.4, 138.7, 128.2, 128.19, 126.4, 114.4, 68.1, 51.9, 35.5, 28.7;

IR (neat, cm<sup>-1</sup>): 3425;

HRMS (ESI, *m/z*) Calcd. for C<sub>18</sub>H<sub>20</sub>NaO: 275.1412 ([M+Na]<sup>+</sup>), found 275.1390 ([M+Na]<sup>+</sup>).



### *N*-(2,2-Diphenylpent-4-en-1-yl)-4-methylbenzenesulfonamide (**6a**)<sup>13</sup>

**6a** (380 mg, 19%, 3 steps) was synthesized from diphenylacetonitrile (987 mg, 5.11 mmol) according to a literature procedure.

White solid;

mp 132-135 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59 (d, 2H, *J* = 8.6 Hz), 7.28-7.19 (m, 8H), 7.05 (d, 2H, *J* = 8.6 Hz), 7.05 (d, 2H, *J* = 6.8 Hz), 5.26 (ddt, 1H, *J* = 16.0, 11.6, 7.2 Hz), 4.94 (d, 1H, *J* = 16.0 Hz), 4.93 (d, 1H, *J* = 11.6 Hz), 3.82 (t, 1H, *J* = 6.4 Hz), 3.52 (d, 2H, *J* = 6.4 Hz), 2.90 (d, 2H, *J* = 7.2 Hz), 2.43 (s, 3H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.5, 143.4, 136.2, 133.1, 129.7, 128.4, 127.7, 127.1, 126.7, 119.1, 49.4, 49.2, 41.2, 21.5;

IR (neat, cm<sup>-1</sup>): 3286, 1331, 1164;

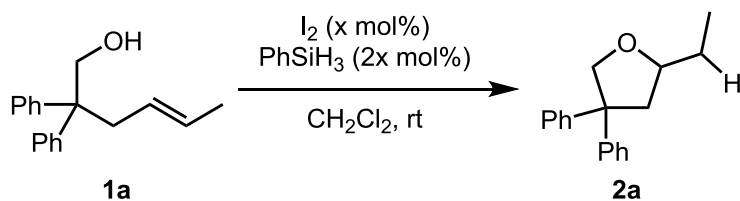
HRMS (ESI, *m/z*) Calcd. for C<sub>24</sub>H<sub>25</sub>N<sub>1</sub>Na<sub>1</sub>O<sub>2</sub>S<sub>1</sub>: 414.1504 ([M+Na]<sup>+</sup>), found 414.1476 ([M+Na]<sup>+</sup>).

<sup>13</sup> Zhang, J.; Yang, C.-G.; He, C. *J. Am. Chem. Soc.* **2006**, *128*, 1798.

## 8. Cyclization of alcohols to cyclic ethers

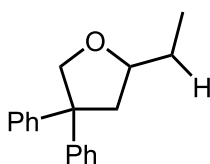
### Typical procedure for intramolecular hydroalkoxylation by catalytic I<sub>2</sub> and PhSiH<sub>3</sub>.

Typical catalytic intramolecular hydroalkoxylation reactions were performed in 10 mL round bottom flask with a PP cap.



A solution of I<sub>2</sub> (5.1 mg, 0.02 mmol) and PhSiH<sub>3</sub> (4.9 μL, 0.04 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was stirred for 15 ~30 min and hydroxy alkene **1a** (50.4 mg, 0.2 mmol) was then added under air. The resulting mixture was quenched with saturated aqueous Na<sub>2</sub>CO<sub>3</sub> and extracted with EtOAc or Et<sub>2</sub>O. The organic layer was washed with brine, dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO<sub>2</sub>, hexane:EtOAc = 50:1) to give cyclic ether **2a** (47.9 mg, 95%) as colorless oil.

### 2-Methyl-4,4-diphenyltetrahydrofuran (**2a**)



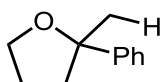
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32-7.24 (m, 6H), 7.22-7.15 (m, 4H), 4.61 (dd, 1H, *J* = 8.8, 0.8 Hz), 4.11 (d, 1H, *J* = 8.8 Hz), 3.95 (ddt, 1H, *J* = 12.0, 9.6, 6.4 Hz), 2.60 (ddd, 1H, *J* = 12.0, 6.4, 0.8 Hz), 2.27 (dd, 1H, *J* = 12.0, 9.6 Hz), 1.73-1.63 (m, 1H), 1.60-1.49 (m, 1H), 0.93 (t, 3H, *J* = 7.2 Hz);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 146.4, 146.1, 128.3, 128.2, 127.12, 127.09, 126.3, 126.1, 80.1, 76.7, 56.0, 44.4, 28.9, 10.3;

IR (neat, cm<sup>-1</sup>): 2963;

HRMS (DART, *m/z*) Calcd. for C<sub>18</sub>H<sub>24</sub>NO: 270.1858 ([M+NH<sub>4</sub>]<sup>+</sup>), found 270.1845 ([M+NH<sub>4</sub>]<sup>+</sup>).

### 2-Methyl-2-phenyltetrahydrofuran (**2b**)



Title compound (30.8 mg, 95%) was obtained from **1b** as colorless oil.

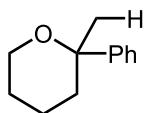
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42-7.39 (m, 2H), 7.34-7.30 (m, 2H), 7.24-7.20 (m, 1H), 4.02 (dt, 1H, *J* = 7.2, 6.0 Hz), 3.92 (m, 1H), 2.24-2.14 (m, 1H), 2.06-1.97 (m, 2H), 1.87-1.76 (m, 1H), 1.53 (s, 3H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 148.2, 128.1, 126.3, 124.7, 84.2, 67.5, 39.5, 29.7, 25.8;

IR (neat, cm<sup>-1</sup>): 2972;

HRMS (DART, *m/z*) Calcd. for C<sub>11</sub>H<sub>18</sub>NO: 180.1388 ([M+NH<sub>4</sub>]<sup>+</sup>), found 180.1413 ([M+NH<sub>4</sub>]<sup>+</sup>).

## 2-Methyl-2-phenyltetrahydro-2H-pyran (2c)



Title compound (31.4 mg, 89%) was obtained from **1c** as colorless oil.

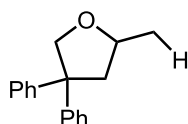
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.34 (d, 2H,  $J = 7.6$  Hz), 7.36-7.33 (t, 2H,  $J = 7.6$  Hz), 7.24-7.20 (t, 1H,  $J = 7.6$  Hz), 3.72 (br d, 1H,  $J = 11.2$  Hz), 3.48 (td, 1H,  $J = 11.2, 3.2$  Hz), 2.29 (dt, 1H,  $J = 13.2, 3.2$  Hz), 1.77-1.40 (m, 5H), 1.38 (s, 3H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.3, 128.4, 126.4, 125.9, 75.9, 62.7, 34.5, 32.7, 25.9, 20.0;

IR (neat,  $\text{cm}^{-1}$ ): 2937;

HRMS (DART,  $m/z$ ) Calcd. for  $\text{C}_{12}\text{H}_{17}\text{O}$ : 177.1279 ( $[\text{M}+\text{H}]^+$ ), found 177.1283 ( $[\text{M}+\text{H}]^+$ ).

## 2-Methyl-4,4-diphenyltetrahydrofuran (2d)



Title compound (45.3 mg, 95%) was obtained from **1d** as colorless oil.

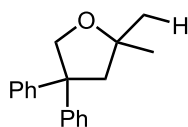
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31-7.28 (m, 6H), 7.22-7.16 (m, 4H), 4.58 (d, 1H,  $J = 8.8$  Hz), 4.21-4.13 (m, 1H), 4.17 (d, 1H,  $J = 8.8$  Hz), 2.63 (dd, 1H,  $J = 12.0, 5.6$  Hz), 2.27 (dd, 1H,  $J = 12.0, 9.6$  Hz), 1.30 (d, 3H,  $J = 5.6$  Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.4, 146.2, 128.4, 128.3, 127.1, 127.1, 126.4, 126.2, 76.8, 74.7, 56.4, 46.6, 21.3;

IR (neat,  $\text{cm}^{-1}$ ): 2968;

HRMS (DART,  $m/z$ ) Calcd. for  $\text{C}_{17}\text{H}_{22}\text{NO}$ : 256.1701 ( $[\text{M}+\text{NH}_4]^+$ ), found 256.1699 ( $[\text{M}+\text{NH}_4]^+$ ).

## 2,2-Dimethyl-4,4-diphenyltetrahydrofuran (2e)



Title compound (48.5 mg, 96%) was obtained from **1e** as colorless oil.

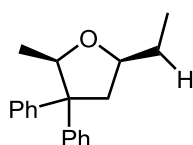
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28-7.25 (m, 8H), 7.19-7.14 (m, 2H), 4.43 (s, 2H), 2.60 (s, 2H), 1.18 (s, 6H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.8, 128.3, 127.2, 126.1, 81.3, 75.4, 56.7, 51.4, 29.2;

IR (neat,  $\text{cm}^{-1}$ ): 2969;

HRMS (DART,  $m/z$ ) Calcd. for  $\text{C}_{18}\text{H}_{24}\text{NO}$ : 270.1858 ( $[\text{M}+\text{NH}_4]^+$ ), found 270.1876 ( $[\text{M}+\text{NH}_4]^+$ ).

## 2,5-Dimethyl-3,3-diphenyltetrahydrofuran (2f)



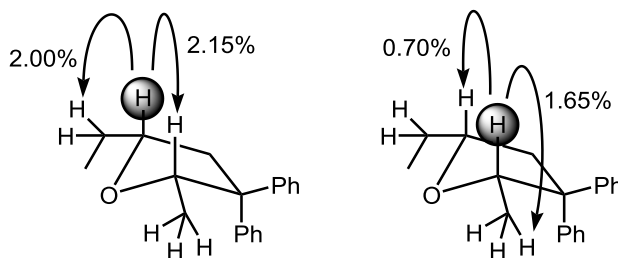
Title compound (48.5 mg, 91%, a mixture of isomers (*syn:anti* = 93:7)) was obtained from **1f** as colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , *syn* isomer)  $\delta$  7.29-7.16 (m, 8H), 7.1-7.08 (m, 2H), 4.88 (q, 1H,  $J = 6.4$  Hz), 3.77 (ddt, 1H,  $J = 10.0, 6.4, 6.0$ ), 2.54 (dd, 1H,  $J = 12.0, 10.0$  Hz), 2.29 (dd, 1H,  $J = 12.0, 6.0$  Hz), 1.76 (dq, 1H,  $J = 14.0, 7.2$  Hz), 1.62 (dq, 1H,  $J = 14.0, 7.2$  Hz), 0.95 (t, 3H,  $J = 7.2$  Hz), 0.87, (d, 3H,  $J = 6.4$  Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , *syn* isomer)  $\delta$  148.2, 145.6, 128.5, 128.1, 128.0, 127.8, 126.2, 126.0, 80.2, 78.8, 58.9, 43.0, 29.5, 20.1, 10.5;

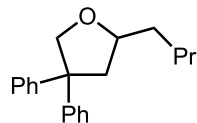
IR (neat,  $\text{cm}^{-1}$ ): 2968;

HRMS (DART,  $m/z$ ) Calcd. for  $\text{C}_{19}\text{H}_{26}\text{NO}$ : 284.2014 ( $[\text{M}+\text{NH}_4]^+$ ), found 284.2022 ( $[\text{M}+\text{NH}_4]^+$ ).



NOE of **2f**

## 2-Butyl-4,4-diphenyltetrahydrofuran (**2g**)



Title compound (53.3 mg, 95%) was obtained from **1g** as colorless oil.

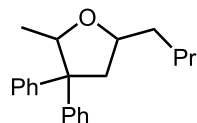
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34-7.28 (m, 6H), 7.24-7.18 (m, 4H), 4.63 (d, 1H,  $J = 8.4$  Hz), 4.14 (d, 1H,  $J = 8.4$  Hz), 4.07-4.00 (m, 1H), 2.63 (dd, 1H,  $J = 12.4, 6.0$  Hz), 2.30 (dd, 1H,  $J = 12.4, 10.0$  Hz), 1.74-1.66 (m, 1H), 1.58-1.51 (m, 1H), 1.45-1.29 (m, 4H), 0.91 (t, 3H,  $J = 6.4$  Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.4, 146.2, 128.3, 128.2, 127.13, 127.11, 126.3, 126.1, 78.9, 76.7, 56.0, 44.9, 35.8, 28.4, 22.8, 14.0;

IR (neat,  $\text{cm}^{-1}$ ): 2928;

HRMS (ESI,  $m/z$ ) Calcd. for  $\text{C}_{20}\text{H}_{24}\text{NaO}$ : 303.1725 ( $[\text{M}+\text{Na}]^+$ ), found 303.1695 ( $[\text{M}+\text{Na}]^+$ ).

## 5-Butyl-2-methyl-3,3-diphenyltetrahydrofuran (**2h**)



Title compound (54.8 mg, 93%, a mixture of diastereomers (96:4)) was obtained from **1h** as colorless oil.

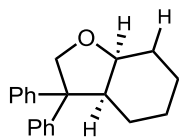
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , major isomer)  $\delta$  7.32-7.16 (m, 8H), 7.10-7.07 (m, 2H), 4.87 (q, 1H,  $J = 6.4$  Hz), 3.81 (ddt, 1H,  $J = 10.0, 6.4, 6.0$  Hz), 2.54 (dd, 1H,  $J = 12.0, 10.4$  Hz), 2.31 (dd, 1H,  $J = 12.0, 6.0$  Hz), 1.80-1.71 (m, 1H), 1.63-1.55 (m, 1H), 1.41-1.28 (m, 4H), 0.90 (t, 3H,  $J = 6.8$  Hz), 0.87 (d, 3H,  $J = 6.4$  Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , major isomer)  $\delta$  148.2, 146.0, 128.4, 128.1, 127.9, 127.8, 126.1, 126.0, 80.2, 77.5, 58.8, 43.6, 36.5, 28.5, 22.8, 20.8, 14.0;

IR (neat,  $\text{cm}^{-1}$ ): 2929;

HRMS (ESI,  $m/z$ ) Calcd. for  $\text{C}_{21}\text{H}_{26}\text{NaO}$ : 317.1881 ( $[\text{M}+\text{Na}]^+$ ), found 317.1884 ( $[\text{M}+\text{Na}]^+$ ).

### (3*aS*,7*aS*)-3,3-Diphenyloctahydrobenzofuran (2i)



Title compound (52.9 mg, 95%) was obtained from **1i** as colorless oil.

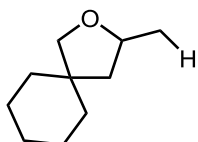
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48-7.46 (m, 2H), 7.31-7.25 (m, 4H), 7.19-7.14 (m, 4H), 4.81 (d, 1H,  $J = 8.6$  Hz), 4.68 (d, 1H,  $J = 8.6$  Hz), 4.21-4.18 (m, 1H), 2.80 (ddd, 1H,  $J = 11.8, 5.6, 4.0$  Hz), 2.00 (br d, 1H,  $J = 14.4$  Hz), 1.76-1.65 (m, 2H), 1.56-1.40 (m, 3H), 1.29-1.14 (m, 1H), 1.07-0.88 (m, 1H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.4, 143.5, 128.4, 128.1, 128.1, 126.8, 126.0, 125.9, 76.2, 74.4, 59.5, 44.4, 28.9, 25.7, 24.5, 20.1;

IR (neat,  $\text{cm}^{-1}$ ): 2931

HRMS (DART,  $m/z$ ) Calcd. for  $\text{C}_{20}\text{H}_{26}\text{NO}$ : 296.2014 ( $[\text{M}+\text{NH}_4]^+$ ), found 296.2037 ( $[\text{M}+\text{NH}_4]^+$ ).

### 3-Methyl-2-oxaspiro[4.5]decane (2j)



Title compound (26.8 mg, 87%) was obtained from **1j** as colorless oil.

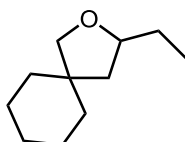
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.06-3.97 (m, 1H), 3.63 (d, 1H,  $J = 8.6$  Hz), 3.47 (d, 1H,  $J = 8.6$  Hz), 1.86 (dd, 1H,  $J = 12.4, 6.4$  Hz), 1.44-1.40 (m, 10H), 1.24 (d, 3H,  $J = 6.0$  Hz), 1.22 (dd, 1H,  $J = 12.4, 9.2$  Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  78.6, 74.8, 46.4, 44.1, 37.4, 35.8, 25.9, 23.9, 23.6, 21.4;

IR (neat,  $\text{cm}^{-1}$ ): 2967;

HRMS (DART,  $m/z$ ) Calcd. for  $\text{C}_{10}\text{H}_{22}\text{NO}$ : 172.1701 ( $[\text{M}+\text{NH}_4]^+$ ), found 172.1711 ( $[\text{M}+\text{NH}_4]^+$ ).

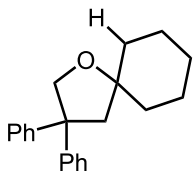
### 3-Ethyl-2-oxaspiro[4.5]decane (2k)<sup>7</sup>



Title compound (31.0 mg, 92%) was obtained from **1k** as colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.80 (ddt, 1H,  $J = 9.2, 6.4, 6.4$  Hz), 3.59 (d, 1H,  $J = 8.4$  Hz), 3.48 (d, 1H,  $J = 8.4$  Hz), 1.82 (dd, 1H,  $J = 12.4, 6.4$  Hz), 1.64-1.56 (m, 1H), 1.51-1.39 (m, 1H), 1.51-1.39 (m, 10H), 1.22 (dd, 1H,  $J = 12.4, 9.2$  Hz), 0.91 (t, 3H,  $J = 7.6$  Hz);

### 3,3-Diphenyl-1-oxaspiro[4.5]decane (2l)



Title compound (52.6 mg, 90%) was obtained from **1l** as colorless oil.

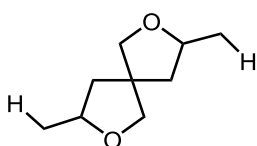
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30-7.24 (m, 8H), 7.18-7.14 (m, 2H), 4.42 (s, 2H), 2.54 (s, 2H), 1.63 (br s, 2H), 1.51-1.27 (m, 8H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.1, 128.3, 127.2, 126.0, 83.3, 74.8, 56.0, 49.6, 37.9, 37.9, 25.4, 23.7, 23.7;

IR (neat,  $\text{cm}^{-1}$ ): 2931;

HRMS (DART,  $m/z$ ) Calcd. for  $\text{C}_{21}\text{H}_{28}\text{NO}$ : 310.2171 ( $[\text{M}+\text{NH}_4]^+$ ), found 310.2166 ( $[\text{M}+\text{NH}_4]^+$ ).

### 3,8-Dimethyl-2,7-dioxaspiro[4.4]nonane (2m)



Title compound (25.9 mg, 83%, an inseparable mixture of diastereomers) was obtained from **1m** as colorless oil.

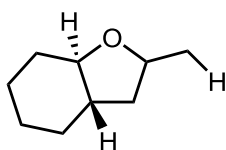
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.09-3.98 (m, 2H), 3.85-3.51 (m, 4H), 2.12-2.01 (m, 2H), 1.57-1.44 (m, 2H), 1.26-1.22 (m, 6H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  77.8, 77.5, 76.9, 76.7, 76.4, 75.3, 75.2, 75.2, 51.9, 51.87, 45.1, 45.0, 44.1, 22.2;

IR (neat,  $\text{cm}^{-1}$ ): 2968;

HRMS (DART,  $m/z$ ) Calcd. for  $\text{C}_9\text{H}_{20}\text{NO}_2$ : 174.1494 ( $[\text{M}+\text{NH}_4]^+$ ), found 174.1506 ( $[\text{M}+\text{NH}_4]^+$ ).

### (3a*R*,7a*S*)-2-Methyloctahydrobenzofuran (2n)



Title compound (25.8 mg, 92%, a mixture of diastereomers (92:8)<sup>14</sup>) was obtained from **1n** as colorless oil.

<sup>14</sup> Schuch, D.; Fries, P.; Dönges, M.; Pérez, B. M.; Hartung, J. *J. Am. Chem. Soc.* **2009**, *131*, 12918.

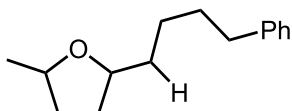
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 2*S*, major isomer)  $\delta$  4.23-4.14 (m, 1H), 3.15 (td, 1H,  $J = 10.0, 3.6$  Hz), 2.15-2.06 (m, 2H), 1.91 (br d, 1H,  $J = 11.6$  Hz), 1.80 (br d, 1H,  $J = 8.4$  Hz), 1.70 (br d, 1H,  $J = 11.2$  Hz), 1.50-1.39 (m, 1H), 1.26 (d, 3H,  $J = 6.4$  Hz), 1.31-1.04 (m, 5H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , major isomer)  $\delta$  81.9, 74.3, 46.6, 39.8, 31.4, 29.0, 25.7, 24.3, 22.3;

IR (neat,  $\text{cm}^{-1}$ ): 2861;

HRMS (DART,  $m/z$ ) Calcd. for  $\text{C}_9\text{H}_{17}\text{O}$ : 141.1279 ( $[\text{M}+\text{H}]^+$ ), found 141.1303 ( $[\text{M}+\text{H}]^+$ ).

## 2-Methyl-5-(4-phenylbutyl)tetrahydrofuran (2o)



Title compound (30.6 mg, 70%, a mixture of diastereomers (78:22)) was obtained from **1o** as colorless oil.

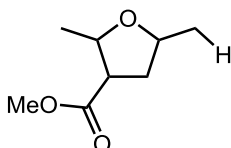
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , major isomer)  $\delta$  7.30-7.26 (m, 2H), 7.19-7.16 (m, 3H), 4.09 (sext, 1H,  $J = 6.0$  Hz), 4.01-3.95 (m, 1H), 2.63 (t, 2H,  $J = 8.0$  Hz), 2.08-2.00 (m, 2H), 1.69-1.60 (m, 3H), 1.54-1.34 (m, 5H), 1.22 (d, 3H,  $J = 6.0$  Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , major isomer)  $\delta$  142.7, 128.4, 128.2, 125.6, 78.6, 74.4, 36.0, 35.9, 34.0, 32.3, 31.6, 25.9, 21.3;

IR (neat,  $\text{cm}^{-1}$ ): 2965;

HRMS (DART,  $m/z$ ) Calcd. for  $\text{C}_{15}\text{H}_{26}\text{NO}$ : 236.2014 ( $[\text{M}+\text{NH}_4]^+$ ), found 236.2005 ( $[\text{M}+\text{NH}_4]^+$ ).

## Methyl 2,5-dimethyltetrahydrofuran-3-carboxylate (2p)



Title compound (25.6 mg, 81%, an inseparable mixture of isomers (ratio 1:1, by integration of methyl signals)) was obtained from **1p** as colorless oil.

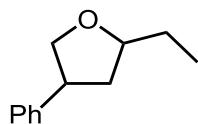
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 2 isomers):  $\delta$  4.45-4.36 (m, 2H), [4.20-4.13 (m, 1H), 3.98-3.90 (m, 1H)], 3.69 (s, 6H), [3.18-3.13 (m, 1H), 3.11 (q, 1H,  $J = 8.0$  Hz)], [2.47-2.41 (m, 1H), 2.19-2.12 (m, 1H), 1.96-1.88 (m, 1H), 1.70-1.63 (m, 1H)], [1.34 (d, 3H,  $J = 6.0$  Hz), 1.22 (d, 3H,  $J = 6.0$  Hz)], [1.19 (d, 3H,  $J = 6.4$  Hz), 1.15 (d, 3H,  $J = 6.4$  Hz)];

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 2 isomers):  $\delta$  173.6, 173.2, 76.1, 75.3, 75.1, 74.0, 51.6, 51.6, 48.5, 48.4, 36.3, 36.0, 21.7 20.5 17.4 17.2;

IR (neat,  $\text{cm}^{-1}$ ): 2974, 1738;

HRMS (DART,  $m/z$ ) Calcd. for  $\text{C}_8\text{H}_{15}\text{O}_3$ : 159.1021 ( $[\text{M}+\text{H}]^+$ ), found 159.1050 ( $[\text{M}+\text{H}]^+$ ).

## 2-Ethyl-4-phenyltetrahydrofuran (2q)



Title compound (32.8 mg, 93%, a mixture of diastereomers (85:15)) was obtained from **1q** as colorless oil.

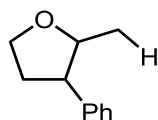
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , major isomer)  $\delta$  7.33-7.30 (m, 2H), 7.27-7.20 (m, 3H), 4.16 (t, 1H,  $J = 8.4$  Hz), 3.96 (ddt, 1H,  $J = 10.4, 6.0, 5.6$  Hz), 3.81 (t, 1H,  $J = 8.4$  Hz), 3.46 (ddt, 1H,  $J = 10.0, 8.4, 8.0$  Hz), 2.45 (tt, 1H,  $J = 6.8, 5.2$  Hz), 1.81-1.53 (m, 3H), 1.00 (t, 3H,  $J = 7.6$  Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , major isomer)  $\delta$  142.7, 128.5, 127.2, 126.4, 81.8, 74.2, 45.5, 40.6, 28.6, 10.4;

IR (neat,  $\text{cm}^{-1}$ ): 2963;

HRMS (ESI,  $m/z$ ) Calcd. for  $\text{C}_{12}\text{H}_{16}\text{NaO}$ : 199.1099 ( $[\text{M}+\text{Na}]^+$ ), found 199.1074 ( $[\text{M}+\text{Na}]^+$ ).

## 2-Methyl-3-phenyltetrahydrofuran (2r)



Title compound (31.1 mg, 96%, a mixture of diastereomers (93:7)) was obtained from **1r** as colorless oil.

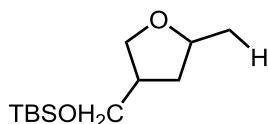
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , major isomer) :  $\delta$  7.35-7.30 (m, 2H), 7.26-7.24 (m, 3H), 4.05 (d, 1H,  $J = 8.4$  Hz), 4.03 (d, 1H,  $J = 8.4$  Hz), 3.87 (dq, 1H,  $J = 8.8, 6.0$  Hz), 2.80 (q, 1H,  $J = 8.8$  Hz), 2.44-2.36 (m, 1H), 2.19-2.09 (m, 1H), 1.23 (d, 3H,  $J = 6.0$  Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , major isomer) :  $\delta$  141.5, 128.6, 127.6, 126.6, 82.2, 67.4, 53.0, 35.4, 19.0;

IR (neat,  $\text{cm}^{-1}$ ): 2969;

HRMS (DART,  $m/z$ ) Calcd. for  $\text{C}_{11}\text{H}_{18}\text{NO}$ : 180.1388 ( $[\text{M}+\text{NH}_4]^+$ ), found 180.1407 ( $[\text{M}+\text{NH}_4]^+$ ).

## *tert*-Butyldimethyl(5-methyltetrahydrofuran-3-yl)methoxysilane (2s)



Title compound (37.3 mg, 81%, a mixture of diastereomers (76:24)) was obtained from **1s** as colorless oil.

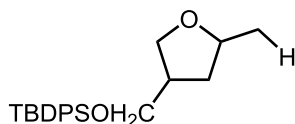
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , major isomer):  $\delta$  3.94-3.86 (m, 1H), 3.77-3.68 (m, 2H), 3.55-3.47 (m, 2H), 2.55-2.38 (m, 1H), 2.09-2.02 (m, 1H), 1.24 (d, 3H,  $J = 6.0$  Hz), 1.06 (dt, 1H,  $J = 12.4, 8.4$  Hz), 0.87 (s, 9H), 0.03 (s, 6H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , major isomer) :  $\delta$  75.7, 70.3, 65.5, 42.6, 36.6, 25.6, 20.9, 18.2, -5.4;

IR (neat,  $\text{cm}^{-1}$ ): 2956;

HRMS (DART,  $m/z$ ) Calcd. for  $\text{C}_{12}\text{H}_{27}\text{O}_2\text{Si}$ : 231.1780 ( $[\text{M}+\text{H}]^+$ ), found 231.1775 ( $[\text{M}+\text{H}]^+$ ).

**tert-Butyl(5-methyltetrahydrofuran-3-yl)methoxydiphenylsilane (2t)**



Title compound (60.3 mg, 85%, a mixture of diastereomers (73:27)) was obtained from **1t** as colorless oil.

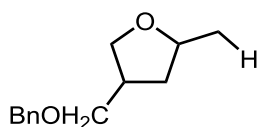
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , major isomer):  $\delta$  7.66 (d, 4H,  $J = 7.6$  Hz), 7.45-7.35 (m, 6H), 3.97-3.80 (m, 1H), 3.83-3.76 (m, 2H), 3.60-3.58 (m, 2H), 2.57-2.48 (m, 1H), 2.10-2.03 (m, 1H), 1.23 (d, 3H,  $J = 6.0$  Hz), 1.06 (s, 9H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , major isomer):  $\delta$  135.7, 133.9, 129.7, 127.8, 75.8, 70.4, 62.3, 42.6, 36.7, 26.9, 21.0, 19.4;

IR (neat,  $\text{cm}^{-1}$ ): 2962;

HRMS (DART,  $m/z$ ) Calcd. for  $\text{C}_{22}\text{H}_{34}\text{NO}_2\text{Si}$ : 372.2359 ( $[\text{M}+\text{NH}_4]^+$ ), found 372.2367 ( $[\text{M}+\text{NH}_4]^+$ ).

**4-Benzyloxymethyl-2-methyltetrahydrofuran (2u)**



Title compound (32.6 mg, 79%, a mixture of diastereomers (70:30)) was obtained from **1u** as colorless oil.

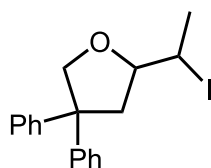
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , major isomer):  $\delta$  7.36-7.25 (m, 5H), 4.50 (s, 2H), 3.90 (ddt, 1H,  $J = 15.6, 6.4, 5.6$  Hz), 3.79 (dd, 1H,  $J = 8.8, 6.4$  Hz), 3.72 (dd, 1H,  $J = 8.8, 6.4$  Hz), 3.39 (dd, 2H,  $J = 6.4, 4.0$  Hz), 2.64-2.53 (m, 1H), 2.13 (ddd, 1H,  $J = 12.4, 8.4, 6.0$  Hz), 1.24 (d, 3H,  $J = 6.0$  Hz), 1.09 (m, 1H);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , major isomer):  $\delta$  138.3, 128.4, 127.62, 127.60, 75.6, 73.2, 73.1, 70.7, 40.1, 37.1, 20.8;

IR (neat,  $\text{cm}^{-1}$ ): 2967;

HRMS (ESI,  $m/z$ ) Calcd. for  $\text{C}_{13}\text{H}_{18}\text{NaO}_2$ : 229.1205 ( $[\text{M}+\text{Na}]^+$ ), found 229.1190 ( $[\text{M}+\text{Na}]^+$ ).

**2-(Iodomethyl)-4,4-diphenyltetrahydrofuran (3a)**



Colorless oil;

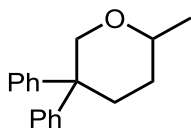
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34-7.18 (m, 10H), 4.76 (dd, 1H,  $J = 8.8, 1.2$  Hz), 4.23 (quin, 1H,  $J = 6.8$  Hz), 4.21 (d, 1H,  $J = 8.8$  Hz), 3.83-3.77 (m, 1H), 2.80 (ddd, 1H,  $J = 12.0, 6.0, 1.2$  Hz), 2.52 (dd, 1H,  $J = 12.0, 9.6$  Hz), 1.90 (d, 3H,  $J = 6.8$  Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.9, 144.8, 128.5, 128.4, 127.1, 126.9, 126.6, 126.4, 83.0, 77.3, 56.0, 45.2, 33.3, 24.8;

IR (neat,  $\text{cm}^{-1}$ ): 2923, 2867;

HRMS (ESI,  $m/z$ ) Calcd. for  $\text{C}_{18}\text{H}_{19}\text{INO}$ : 401.0378 ( $[\text{M}+\text{Na}]^+$ ), found 401.0390 ( $[\text{M}+\text{Na}]^+$ ).

### 2-Methyl-5,5-diphenyltetrahydro-2H-pyran (4a)



Title compound (23.2 mg, 46%) was obtained from **1w** as white solid.

mp 46-50°C

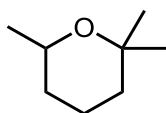
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46-7.44 (m, 2H), 7.32-7.25 (m, 4H), 7.21-7.17 (m, 4H), 4.66 (dd, 1H,  $J = 12.0, 2.8$  Hz), 3.58 (m, 2H), 2.52-2.39 (m, 2H), 1.60-1.54 (m, 1H), 1.30-1.21 (m, 1H), 1.19 (d, 3H,  $J = 6.4$  Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.8, 145.8, 128.9, 128.2, 127.9, 127.0, 126.2, 125.6, 75.0, 74.0, 45.7, 34.8, 29.7, 21.7;

IR (neat,  $\text{cm}^{-1}$ ):2969;

HRMS (ESI,  $m/z$ ) Calcd. for  $\text{C}_{18}\text{H}_{20}\text{NaO}$ : 275.1436 ( $[\text{M}+\text{Na}]^+$ ), found 275.1428 ( $[\text{M}+\text{Na}]^+$ ).

### 2,2,6-Trimethyltetrahydro-2H-pyran (4x)



Title compound (2.0 mg, 8%) was obtained from **1x** as colorless oil.

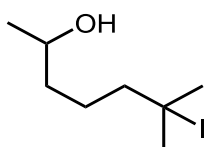
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.67 (dq, 1H,  $J = 12.4, 6.4, 2.4$  Hz), 1.67-1.26 (m, 6H), 1.20 (s, 3H), 1.19 (s, 3H), 1.11 (d, 3H,  $J = 6.4$  Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  71.6, 66.3, 36.0, 33.4, 32.0, 22.7, 22.0, 20.1;

IR (neat,  $\text{cm}^{-1}$ ):2924;

HRMS (ESI,  $m/z$ ) Calcd. for  $\text{C}_8\text{H}_{16}\text{NaO}$ : 151.1099 ( $[\text{M}+\text{Na}]^+$ ), found 151.1124 ( $[\text{M}+\text{Na}]^+$ ).

### 6-Iodo-6-methylheptan-2-ol (5)



Title compound (3.1 mg, 6%) was obtained from **1x** as yellow oil.

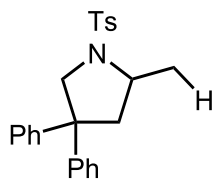
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.85 (sext, 1H,  $J = 6.4$  Hz), 1.93 (s, 3H), 1.92 (s, 3H), 1.72-1.48 (m, 6H), 1.22 (d, 3H,  $J = 6.4$  Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  68.0, 52.4, 50.4, 38.8, 38.1, 37.9, 24.8, 23.6;

IR (neat,  $\text{cm}^{-1}$ ):3357;

HRMS (DART,  $m/z$ ) Calcd. for  $\text{C}_8\text{H}_{21}\text{INO}$ : 274.0668 ( $[\text{M}+\text{NH}_4]^+$ ), found 274.0675 ( $[\text{M}+\text{NH}_4]^+$ ).

**2-Methyl-4,4-diphenyl-1-tosylpyrrolidine (7a)**



Title compound (76.7 mg, 98%) was obtained from **6a** as colorless oil.

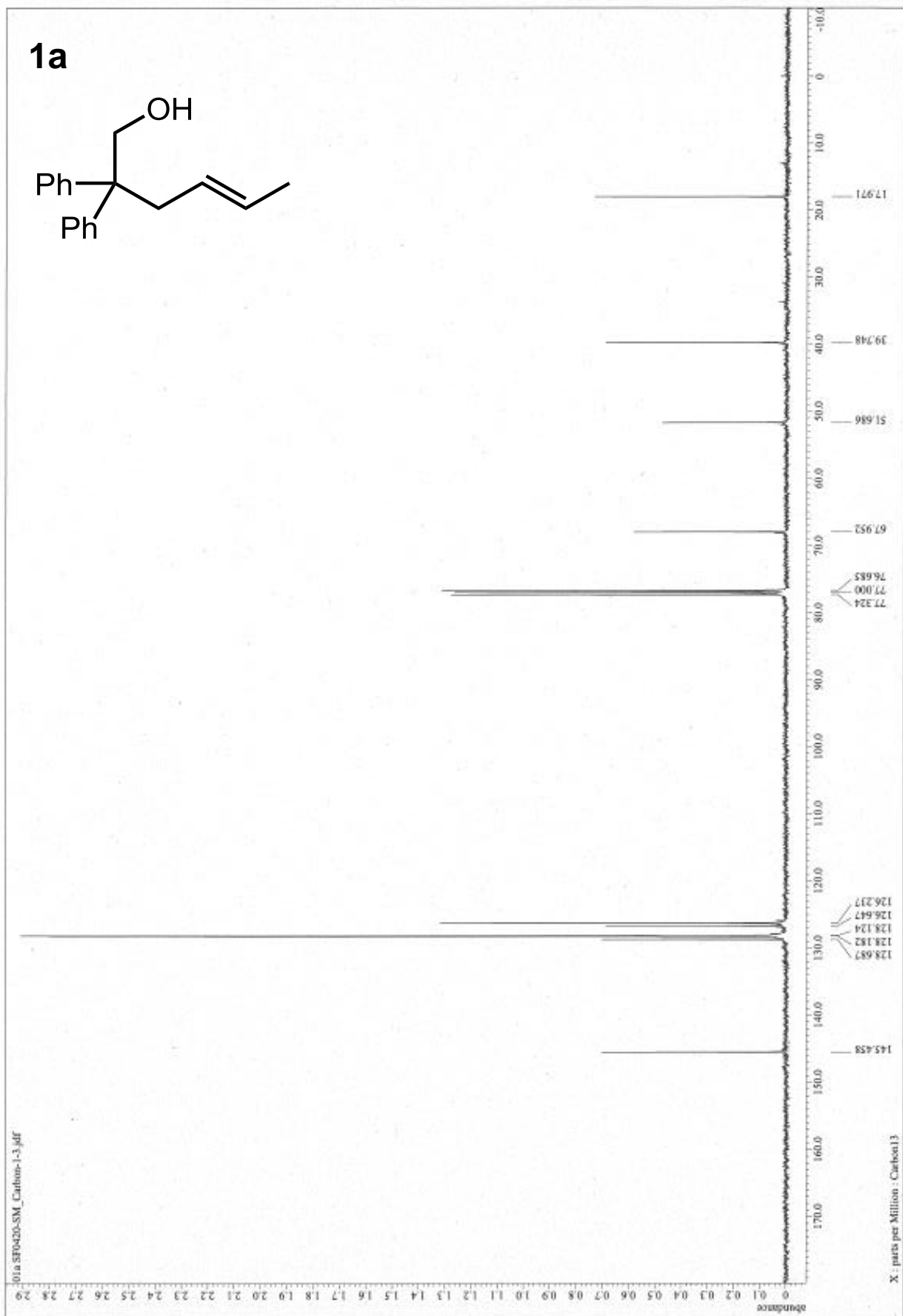
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (d, 2H,  $J = 8.0$  Hz), 7.28-7.08 (m, 12H), 4.18 (d, 1H,  $J = 10.4$  Hz), 3.95 (dd, 1H,  $J = 10.4, 0.8$  Hz), 3.79 (sext, 1H,  $J = 6.4$  Hz), 2.79 (ddd, 1H,  $J = 12.4, 7.2, 0.8$  Hz), 2.39 (s, 3H), 2.27 (dd, 1H,  $J = 12.4, 7.2$  Hz), 1.26 (d, 3H,  $J = 6.8$  Hz);

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.6, 144.8, 142.6, 135.4, 129.5, 128.4, 128.4, 127.2, 126.7, 126.4, 126.4, 126.2, 58.4, 55.4, 52.3, 46.0, 22.1, 21.4;

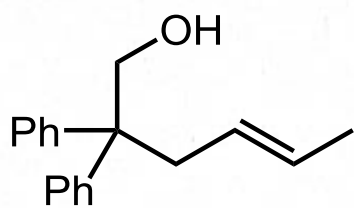
IR (neat,  $\text{cm}^{-1}$ ): 1338, 1162;

HRMS (ESI,  $m/z$ ) Calcd. for  $\text{C}_{24}\text{H}_{25}\text{N}_1\text{Na}_1\text{O}_2\text{S}_1$ : 414.1504 ( $[\text{M}+\text{Na}]^+$ ), found 414.1489 ( $[\text{M}+\text{Na}]^+$ ).

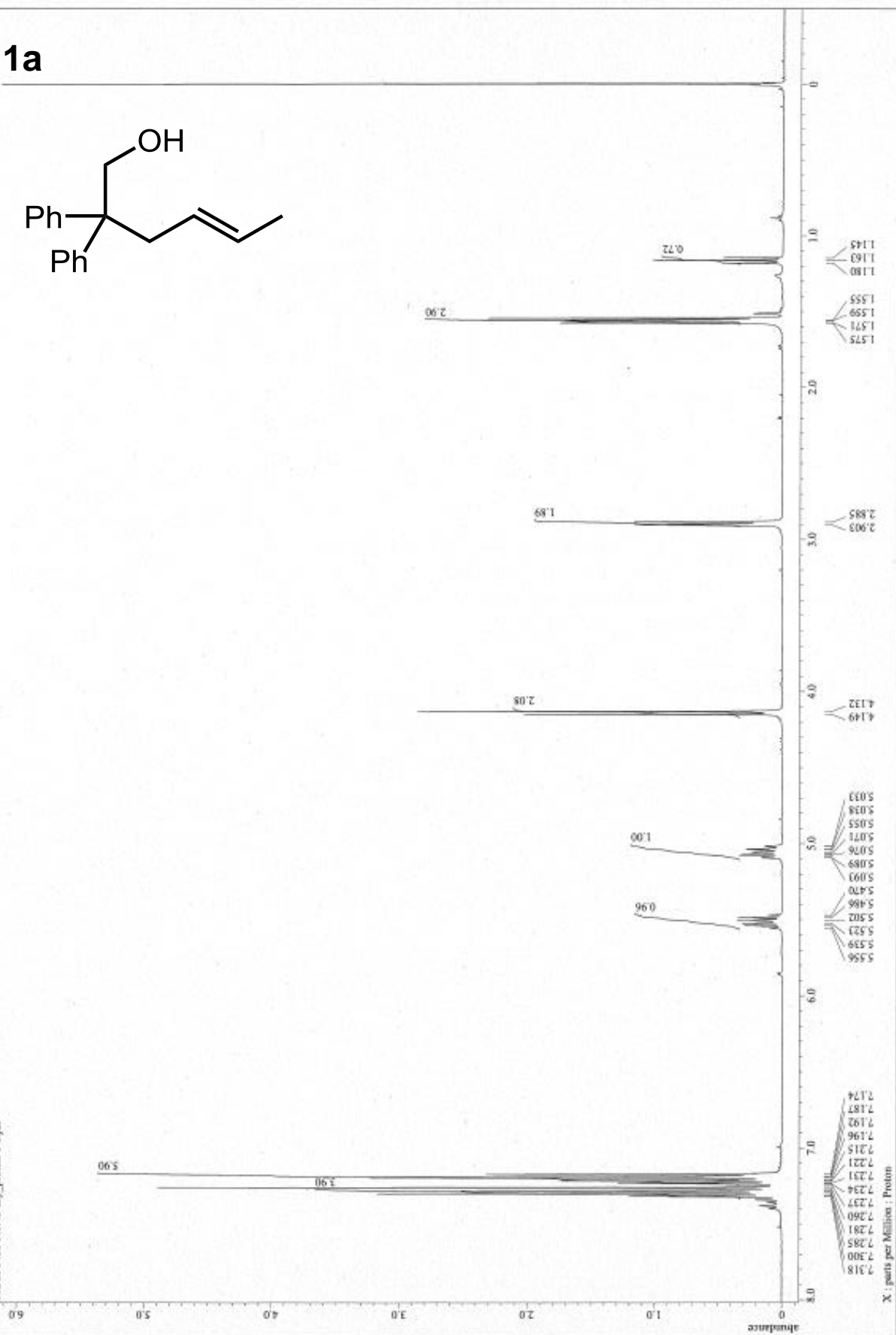
## 9. NMR charts (alcohols)



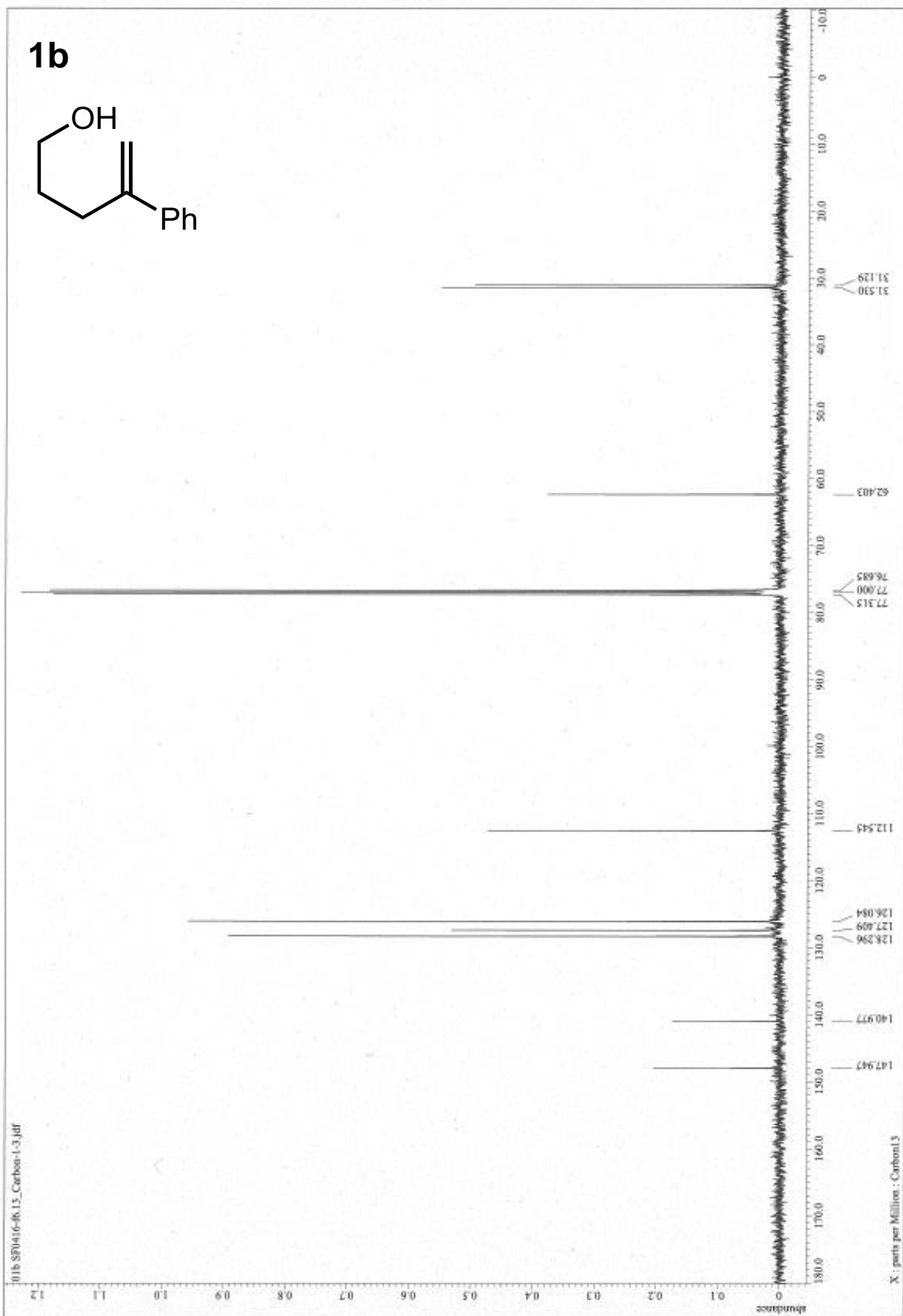
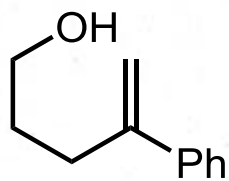
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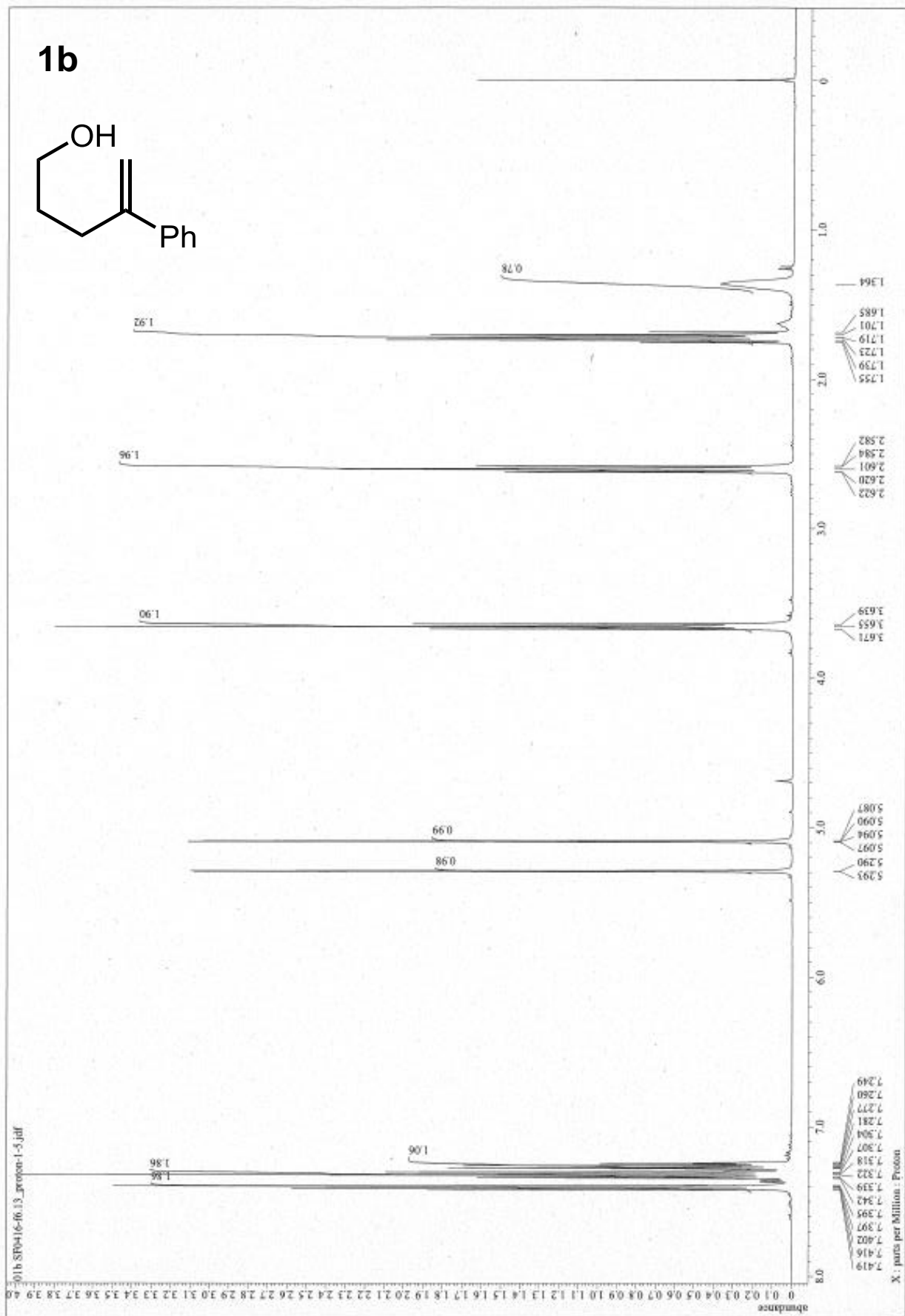
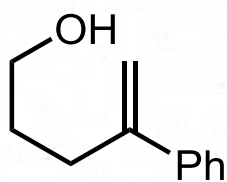
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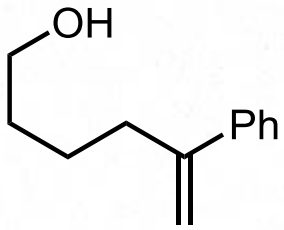
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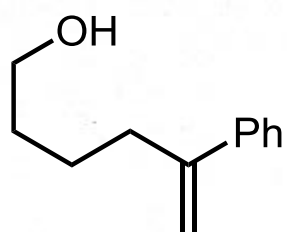
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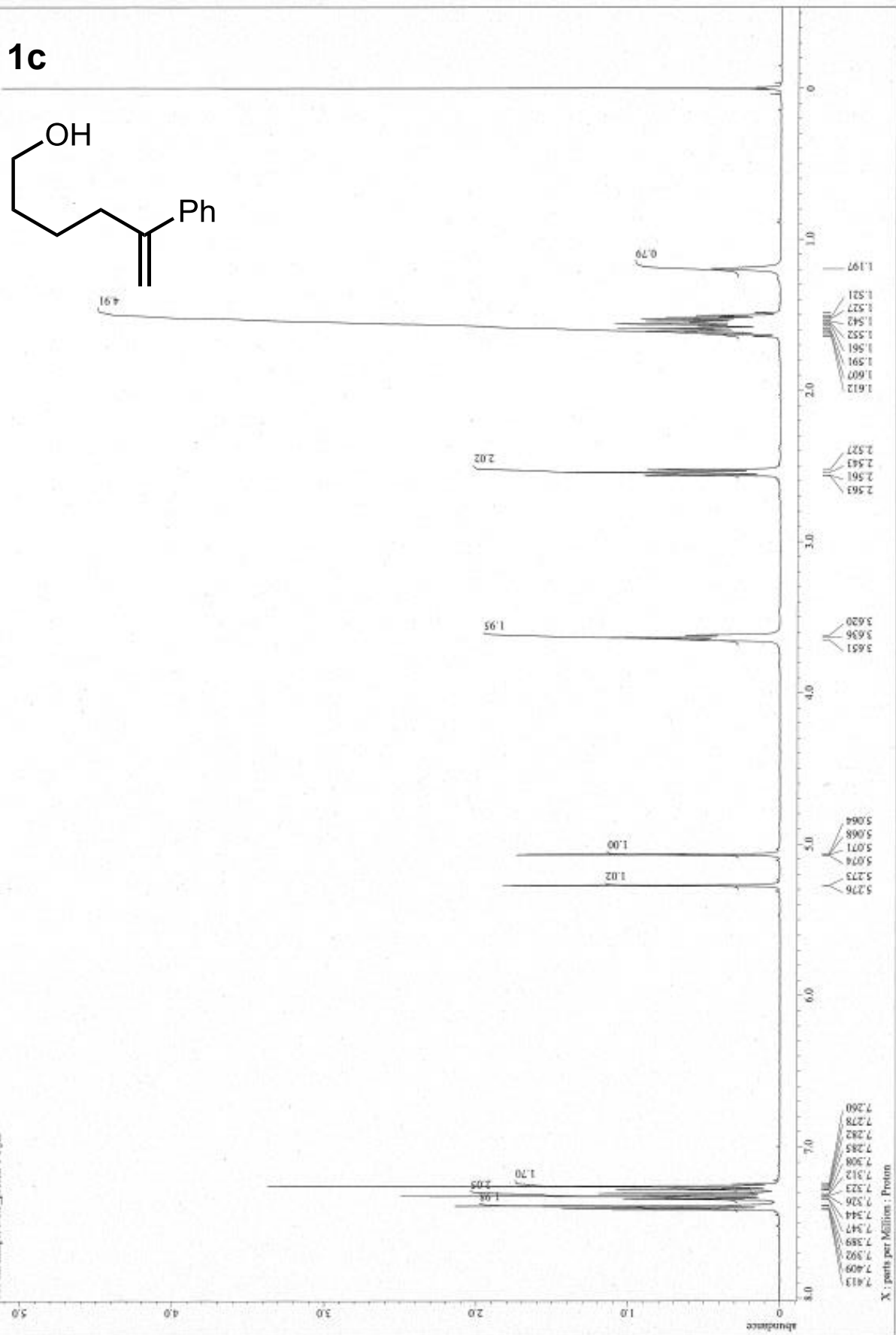
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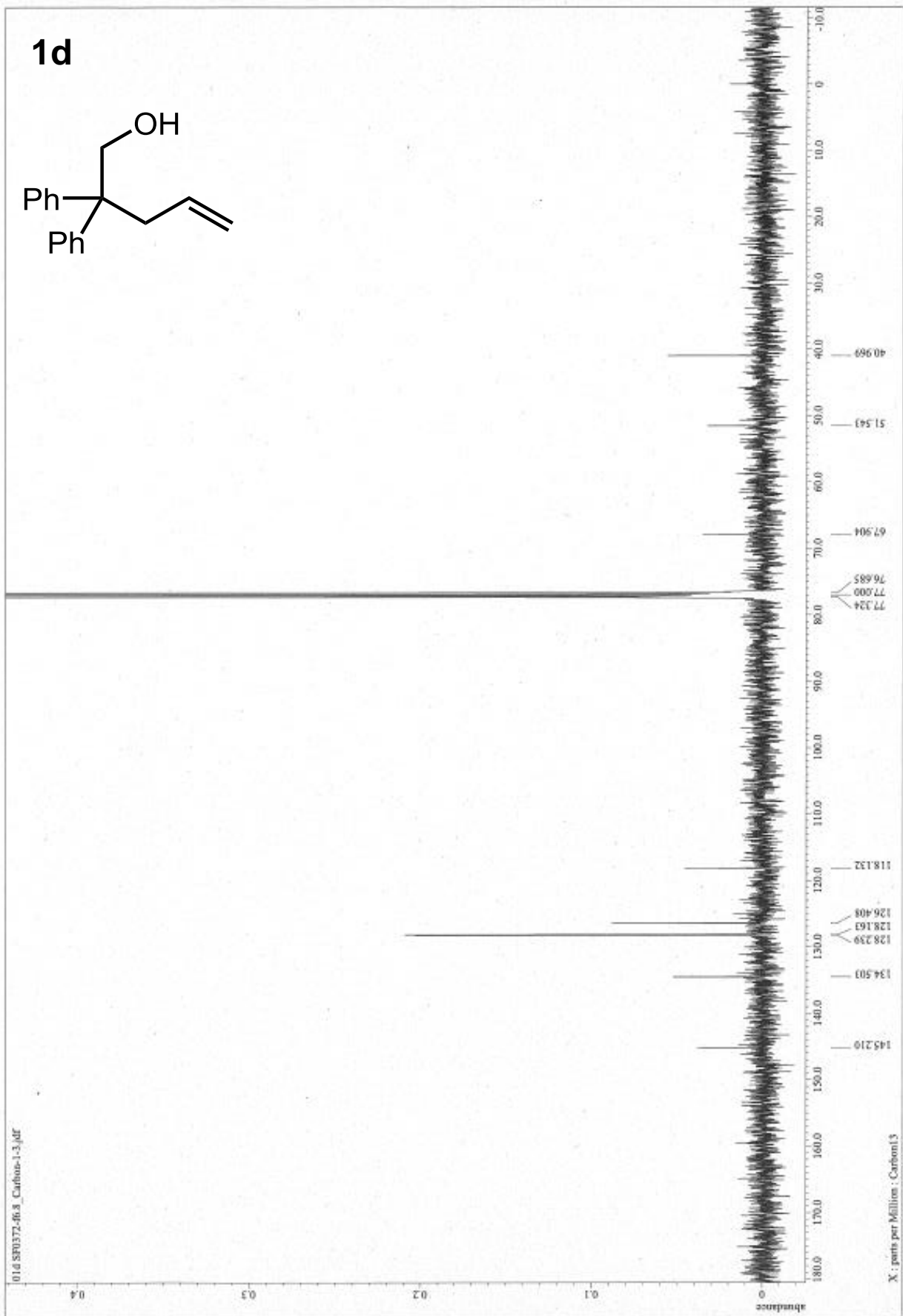
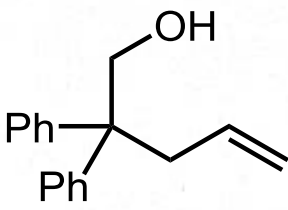
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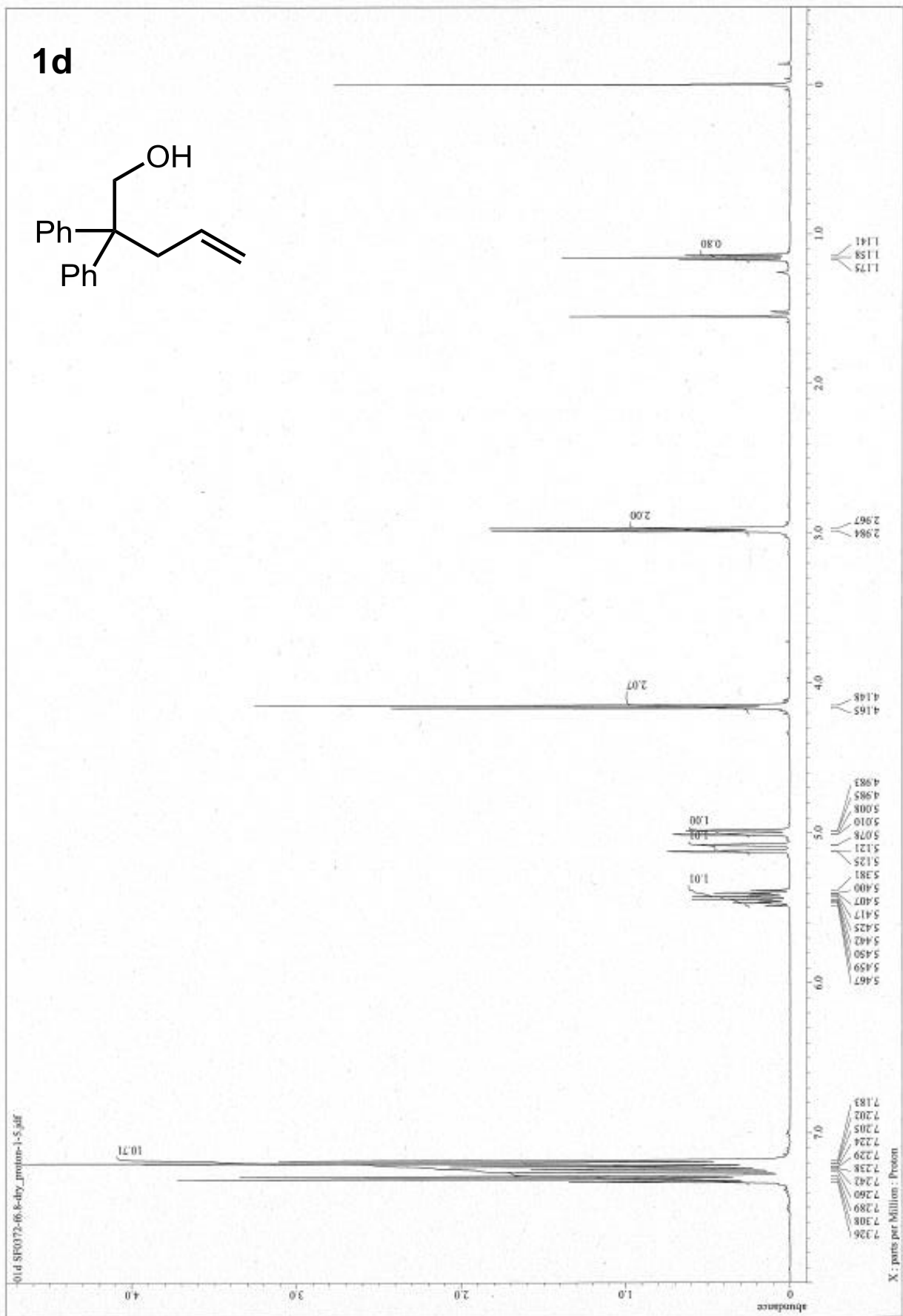


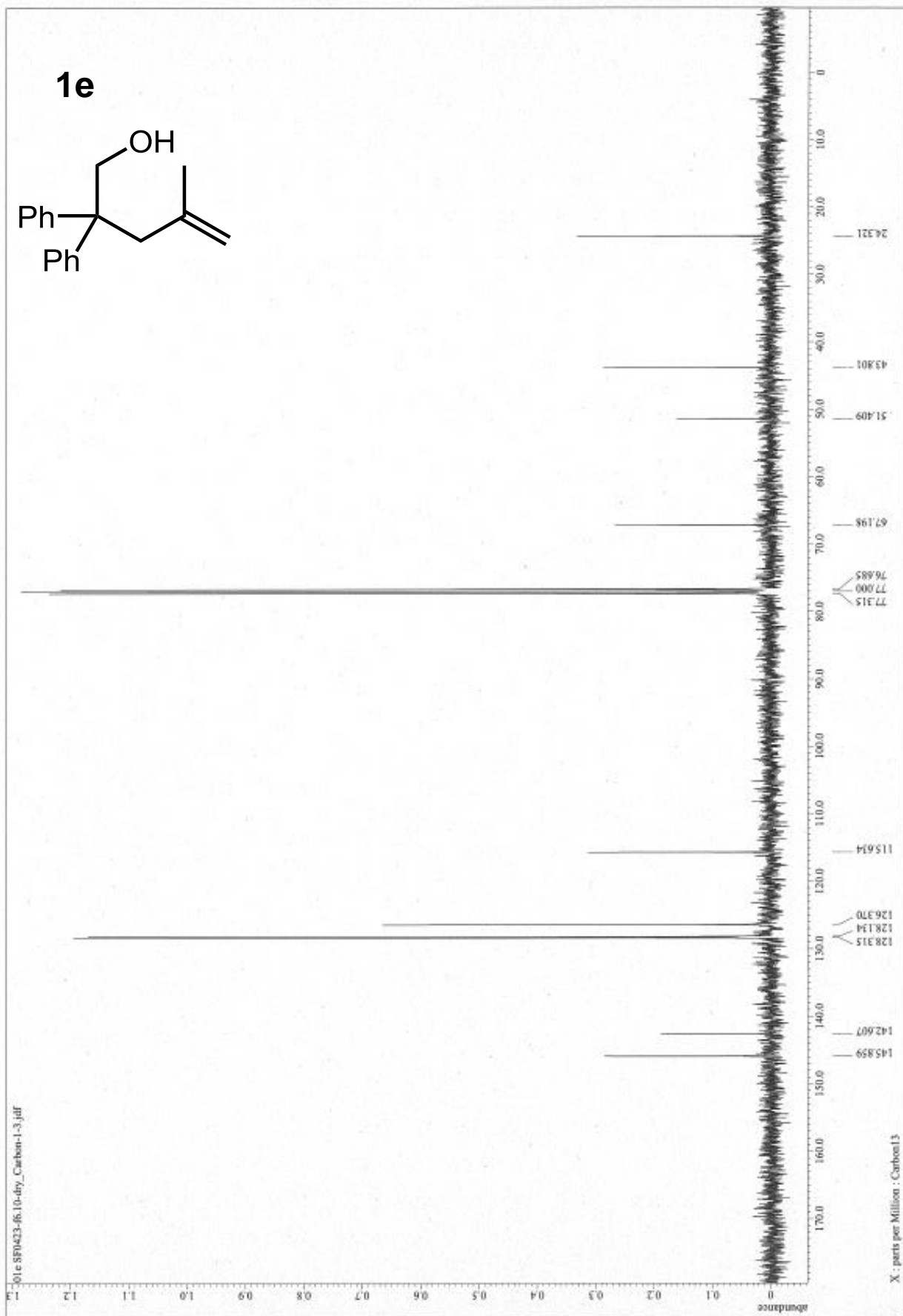
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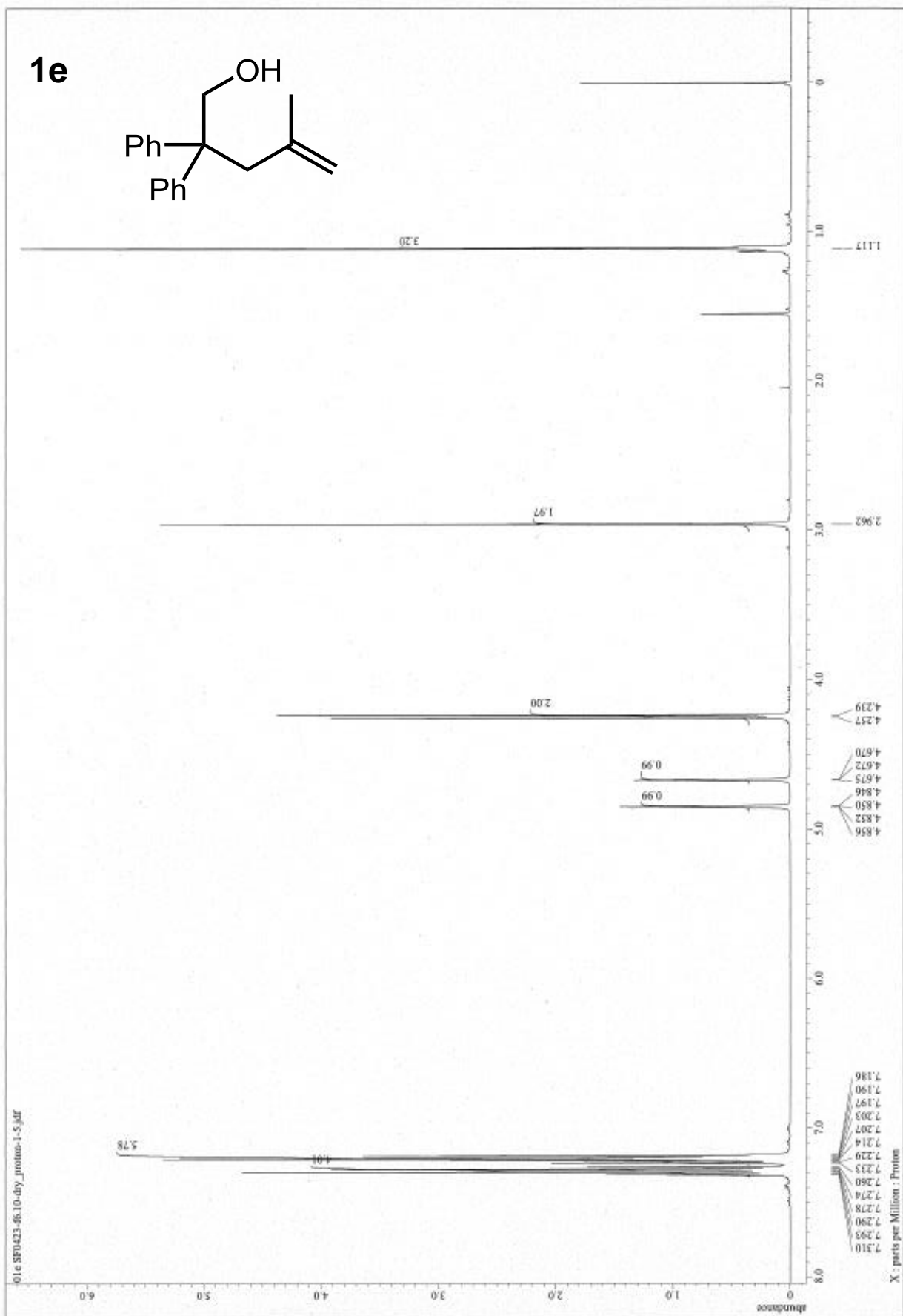
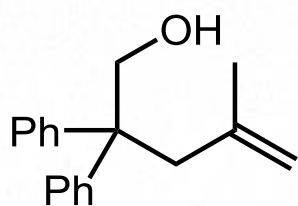
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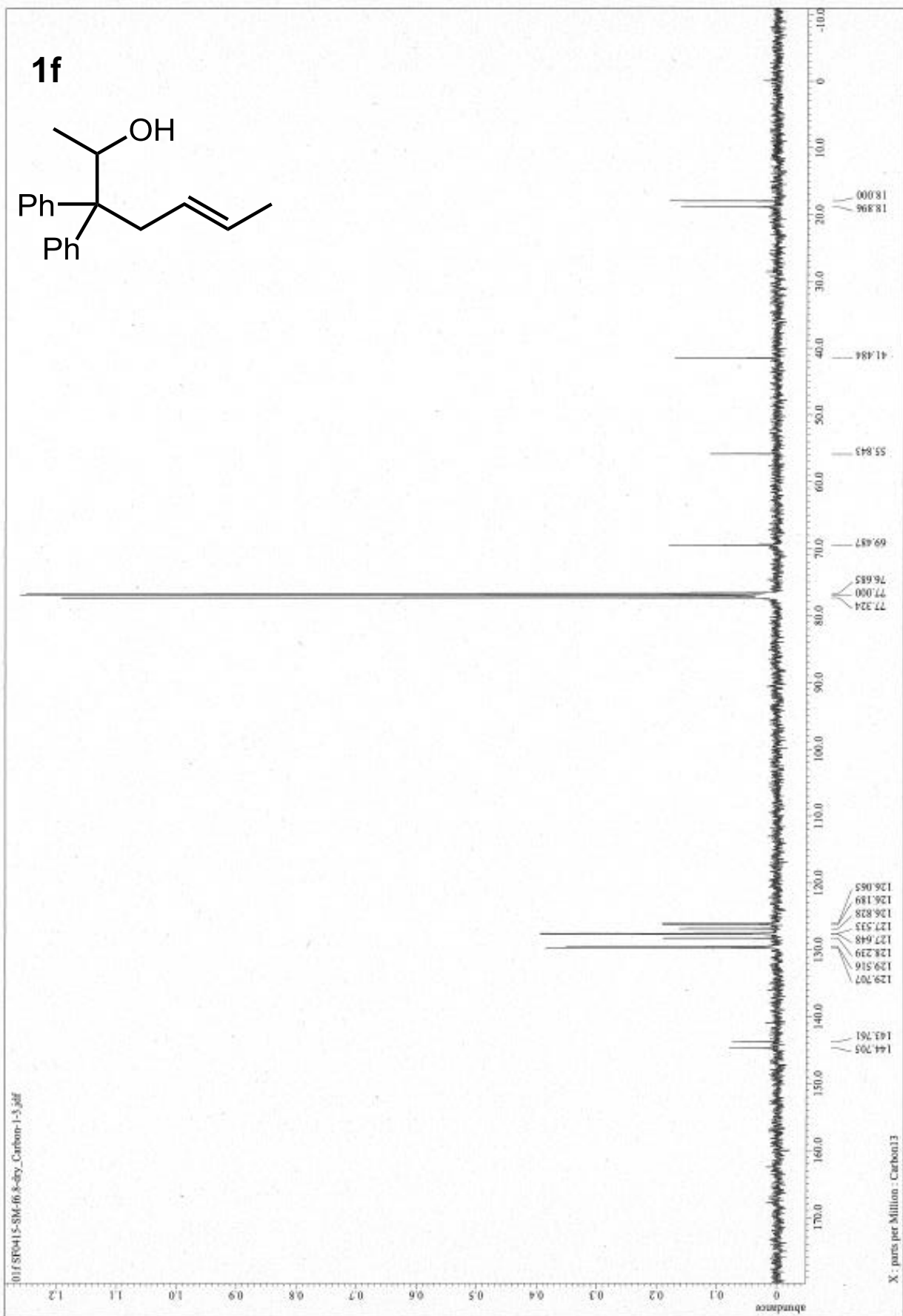




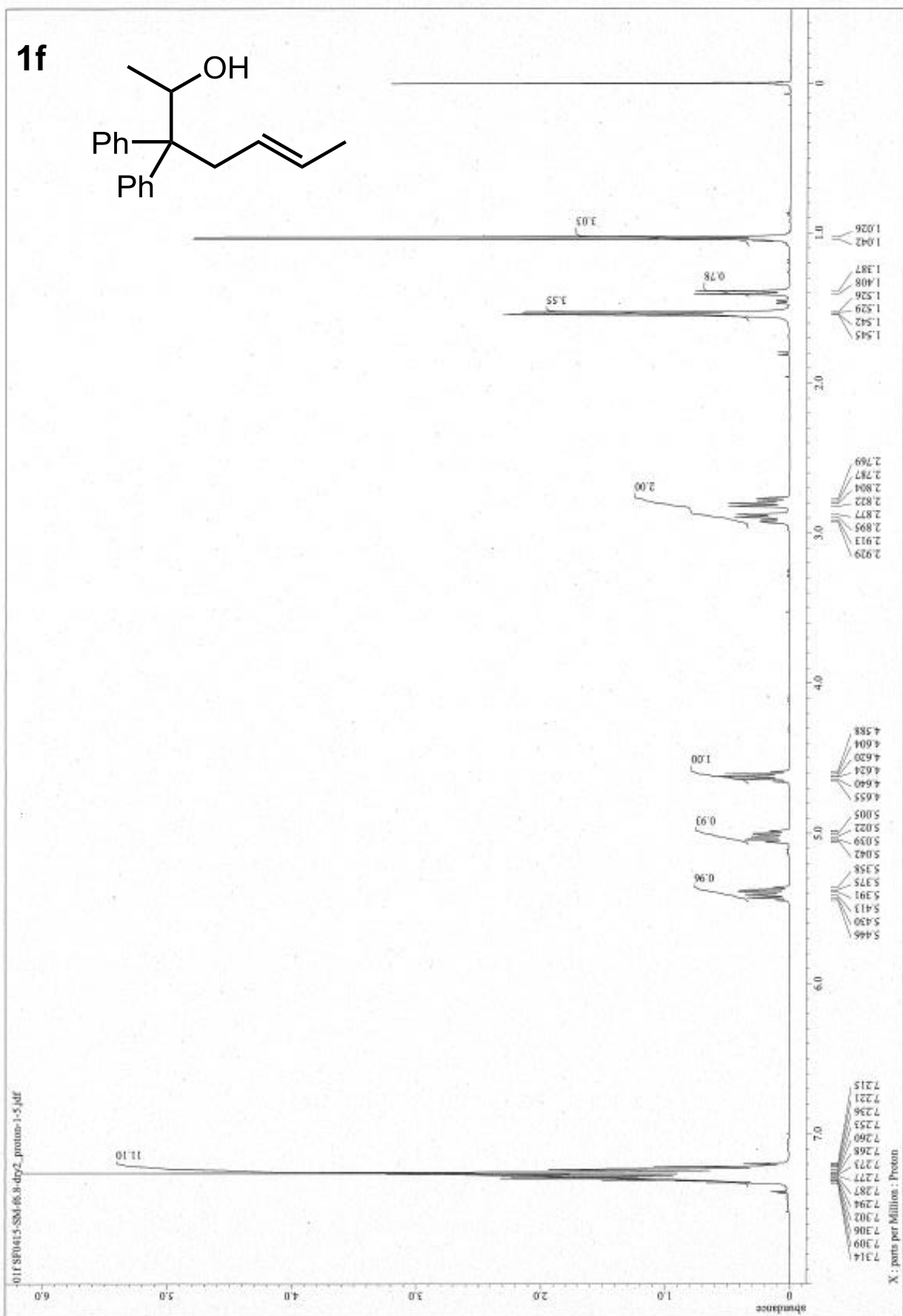
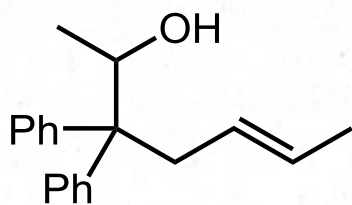


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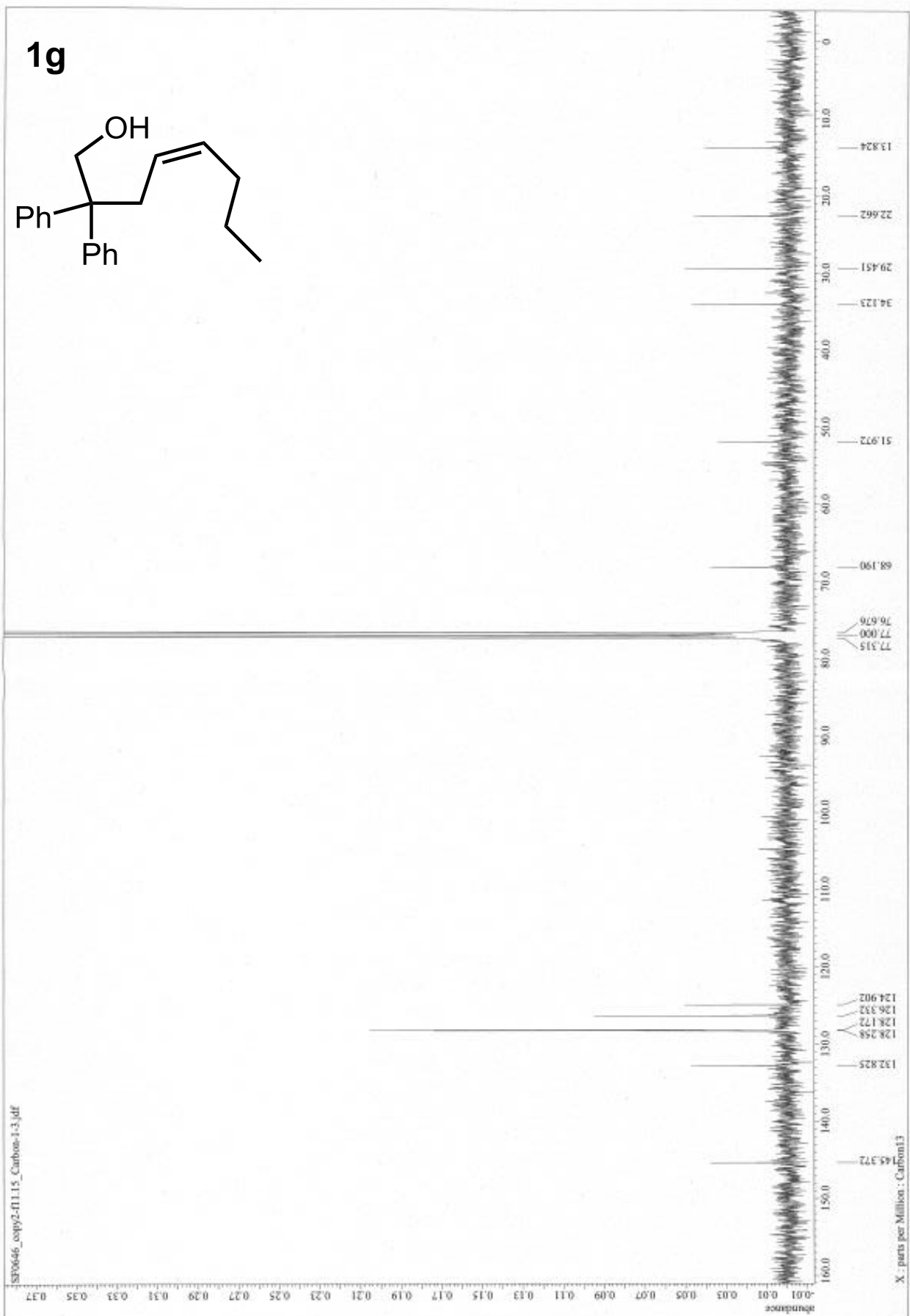
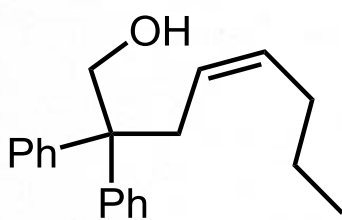




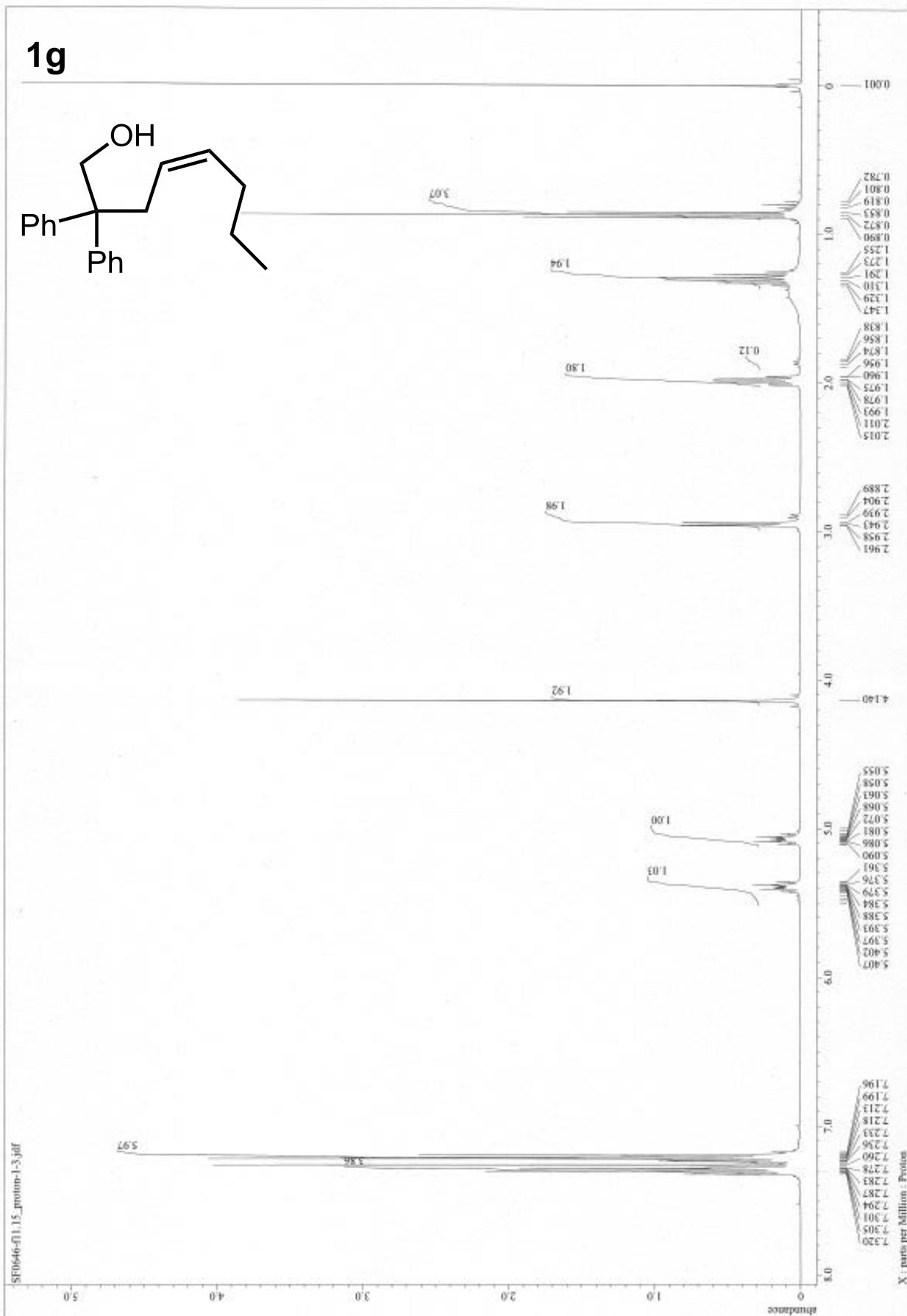
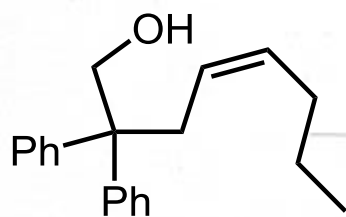
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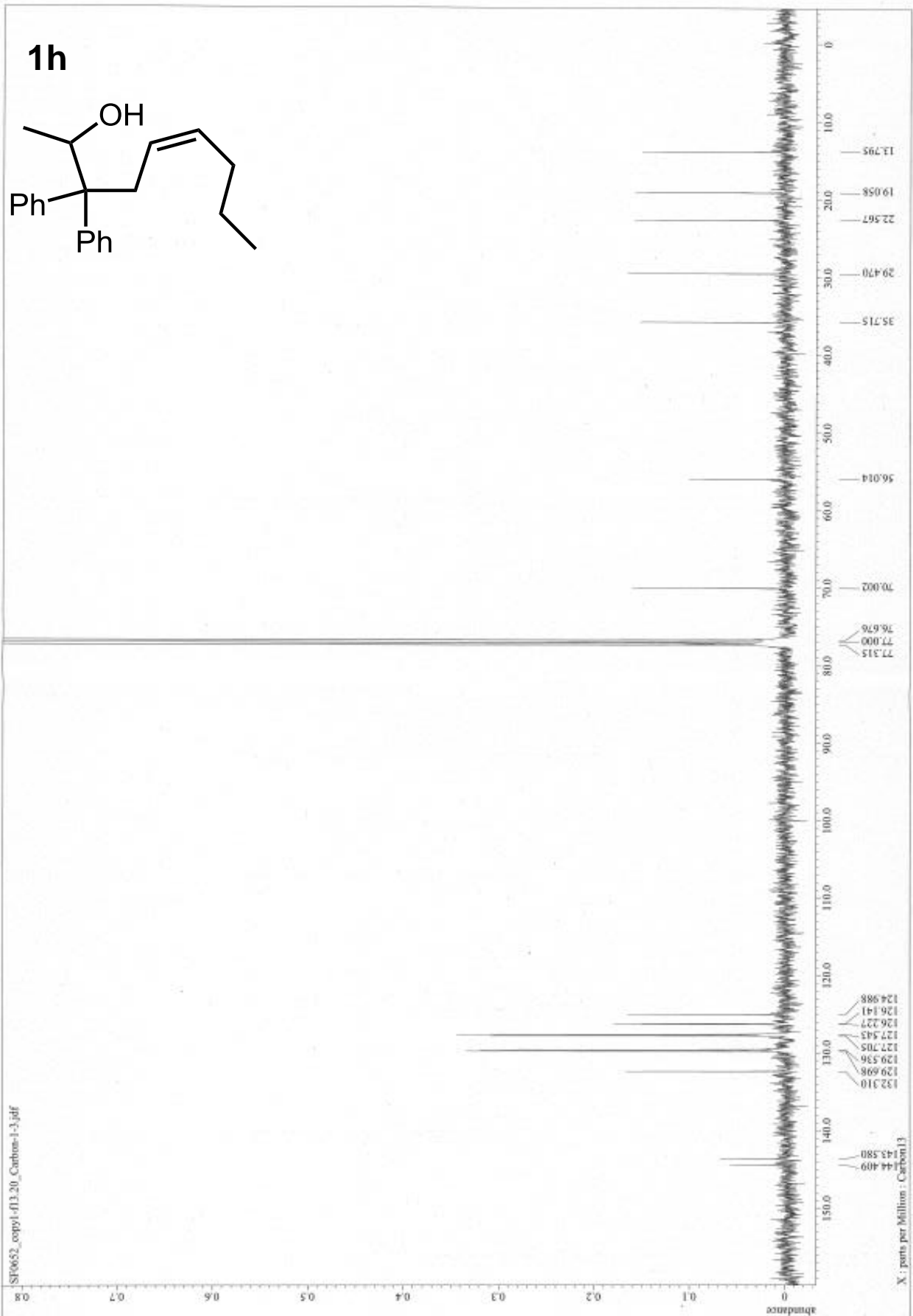


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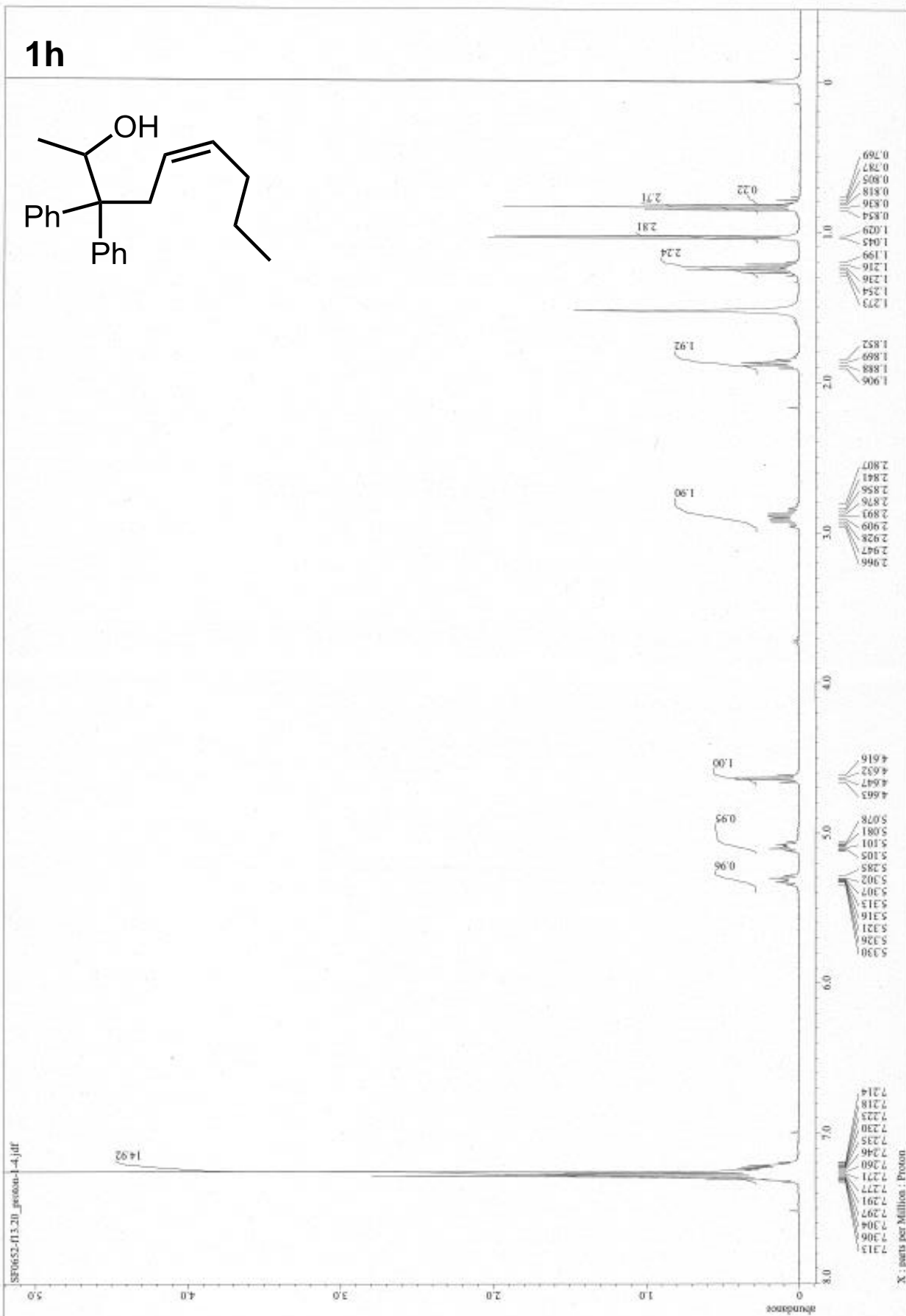
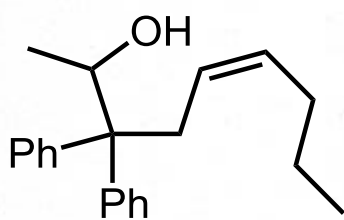


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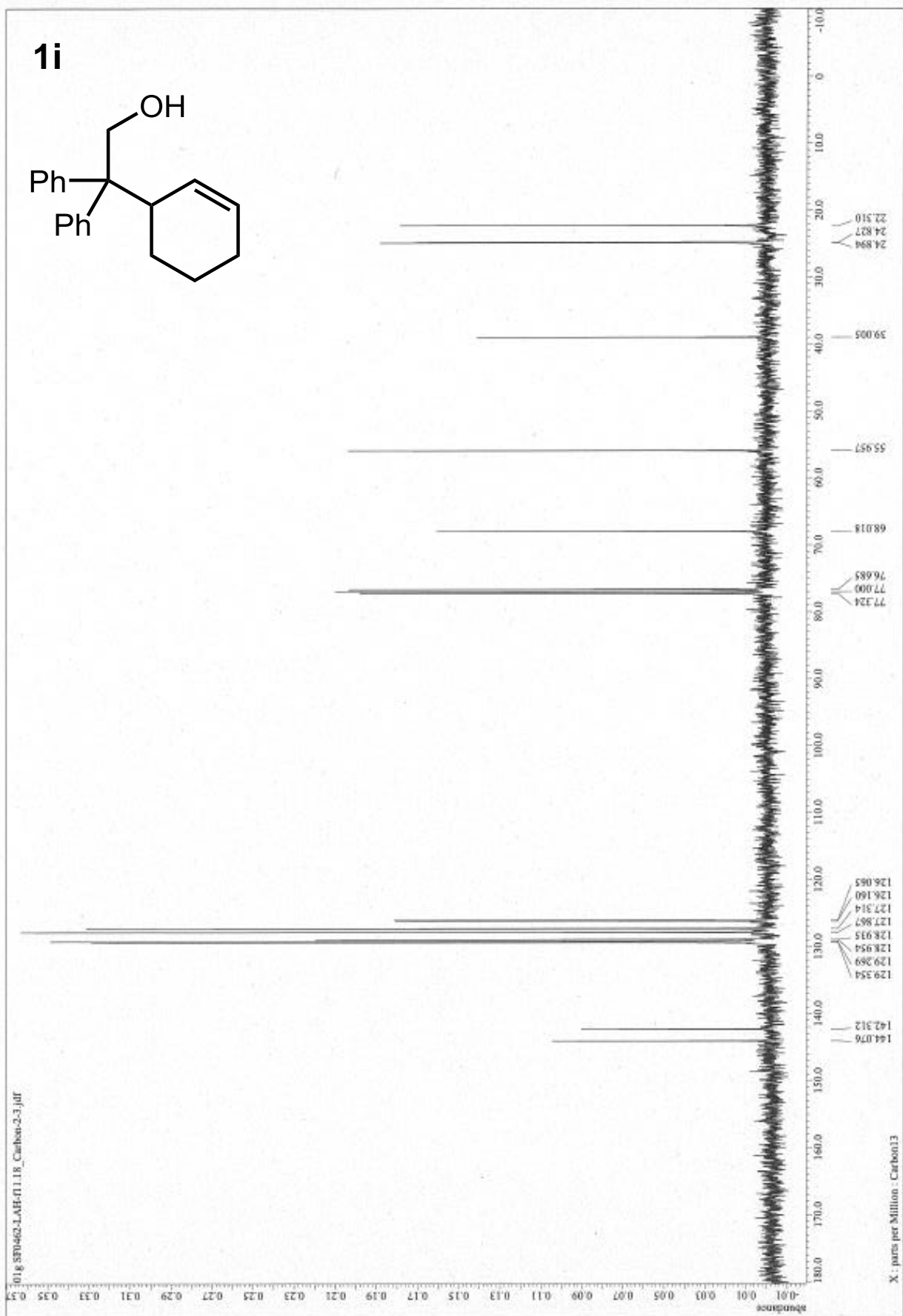
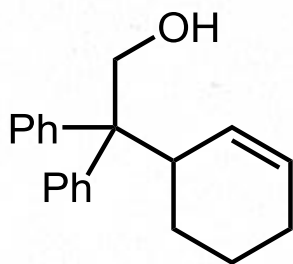




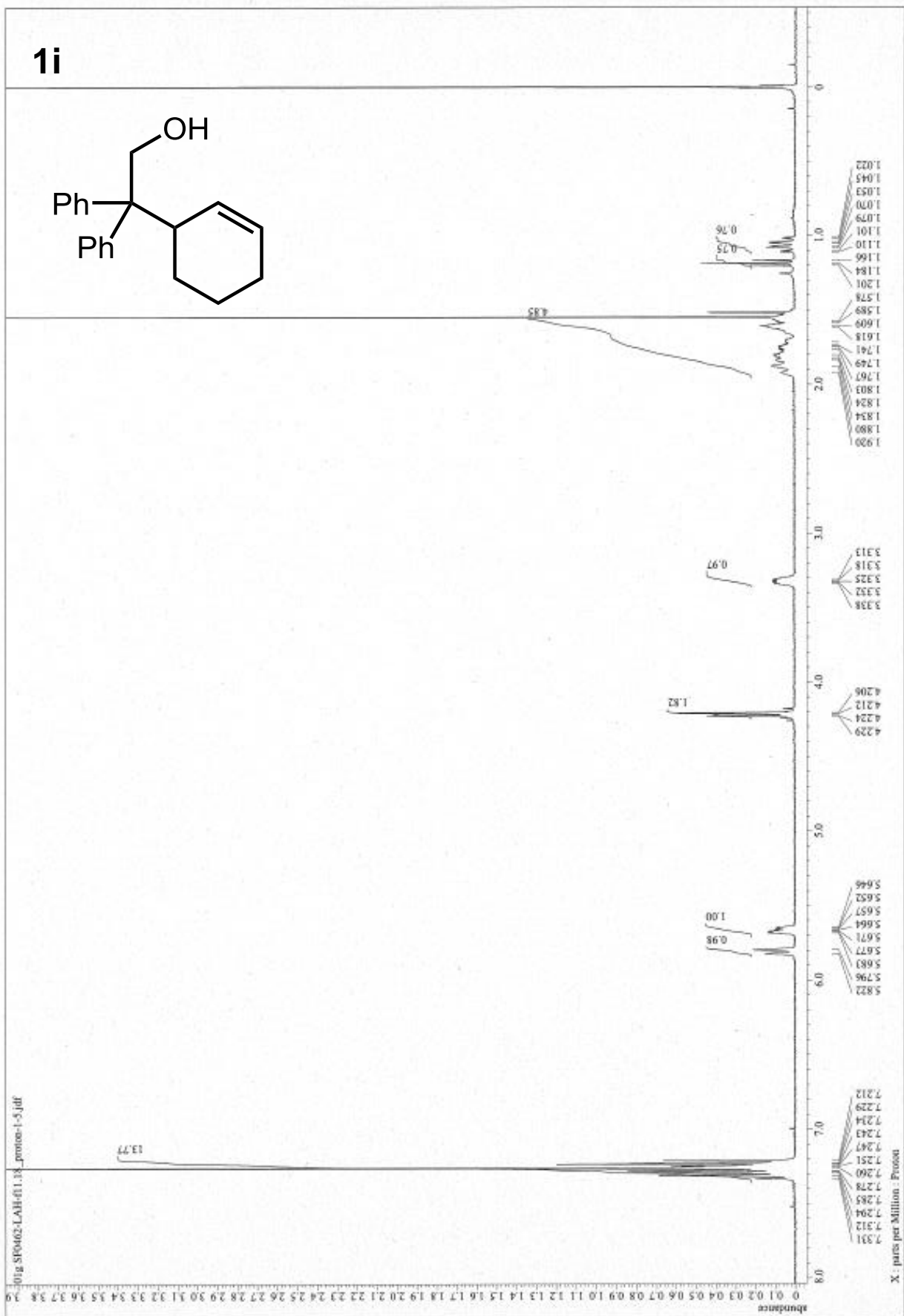
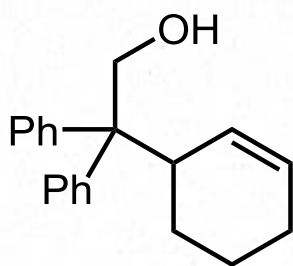
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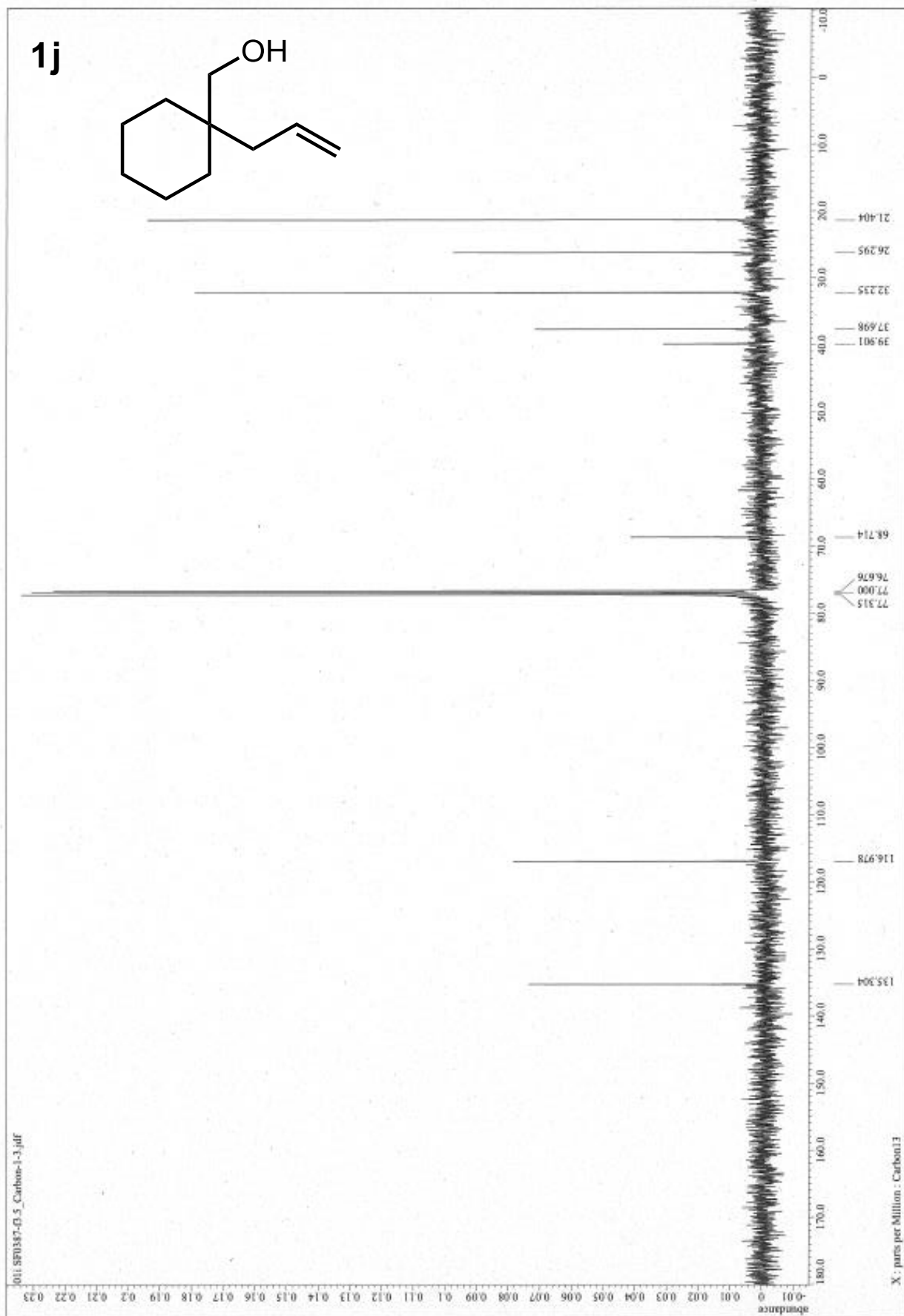


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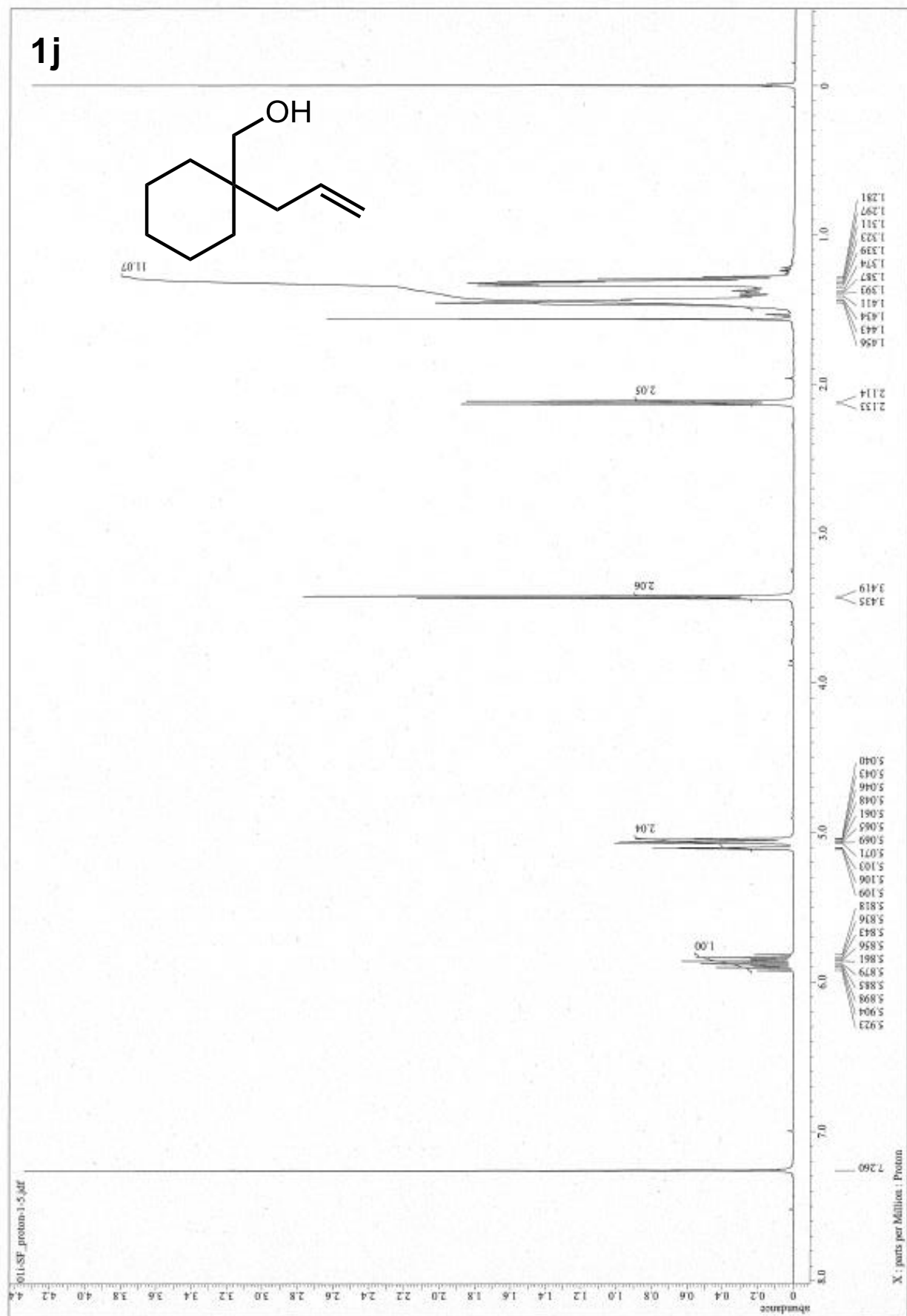
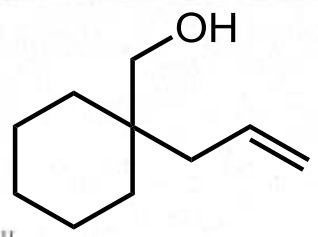


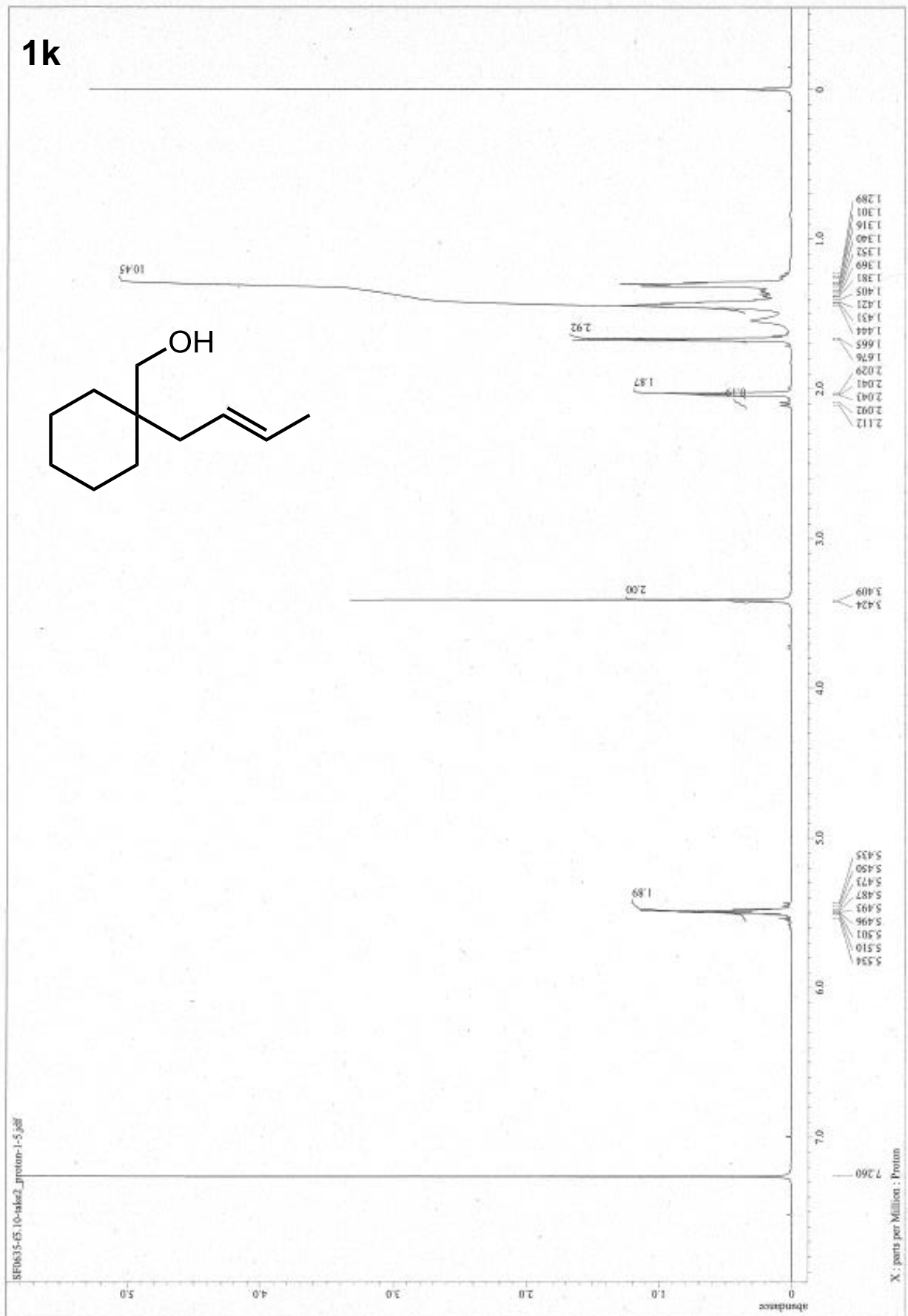
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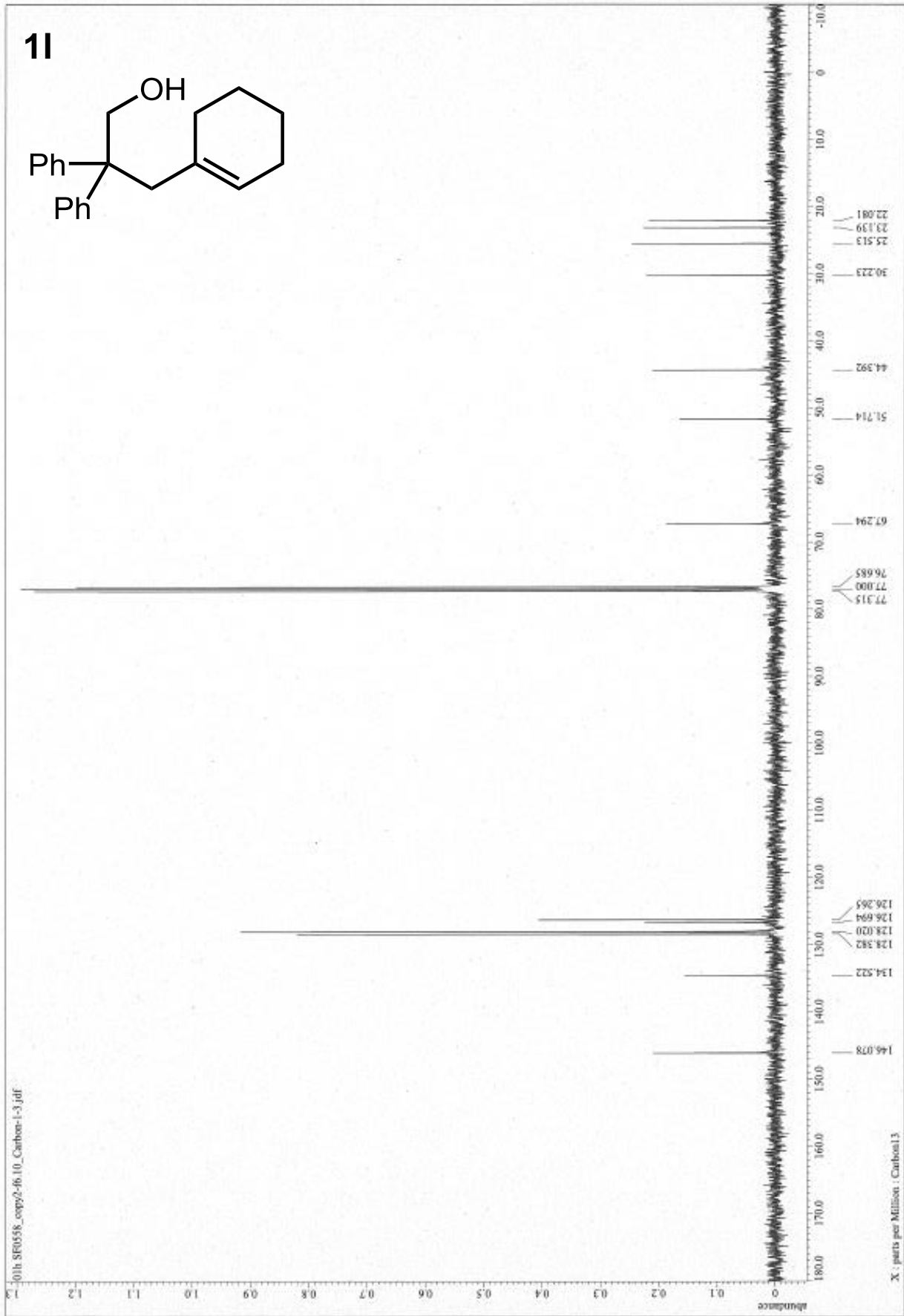
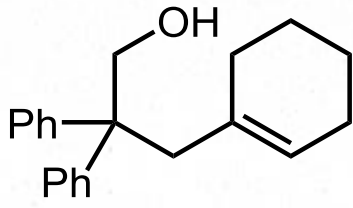


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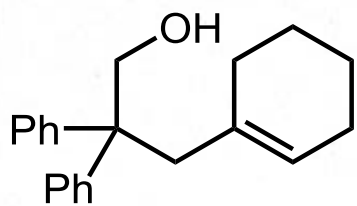




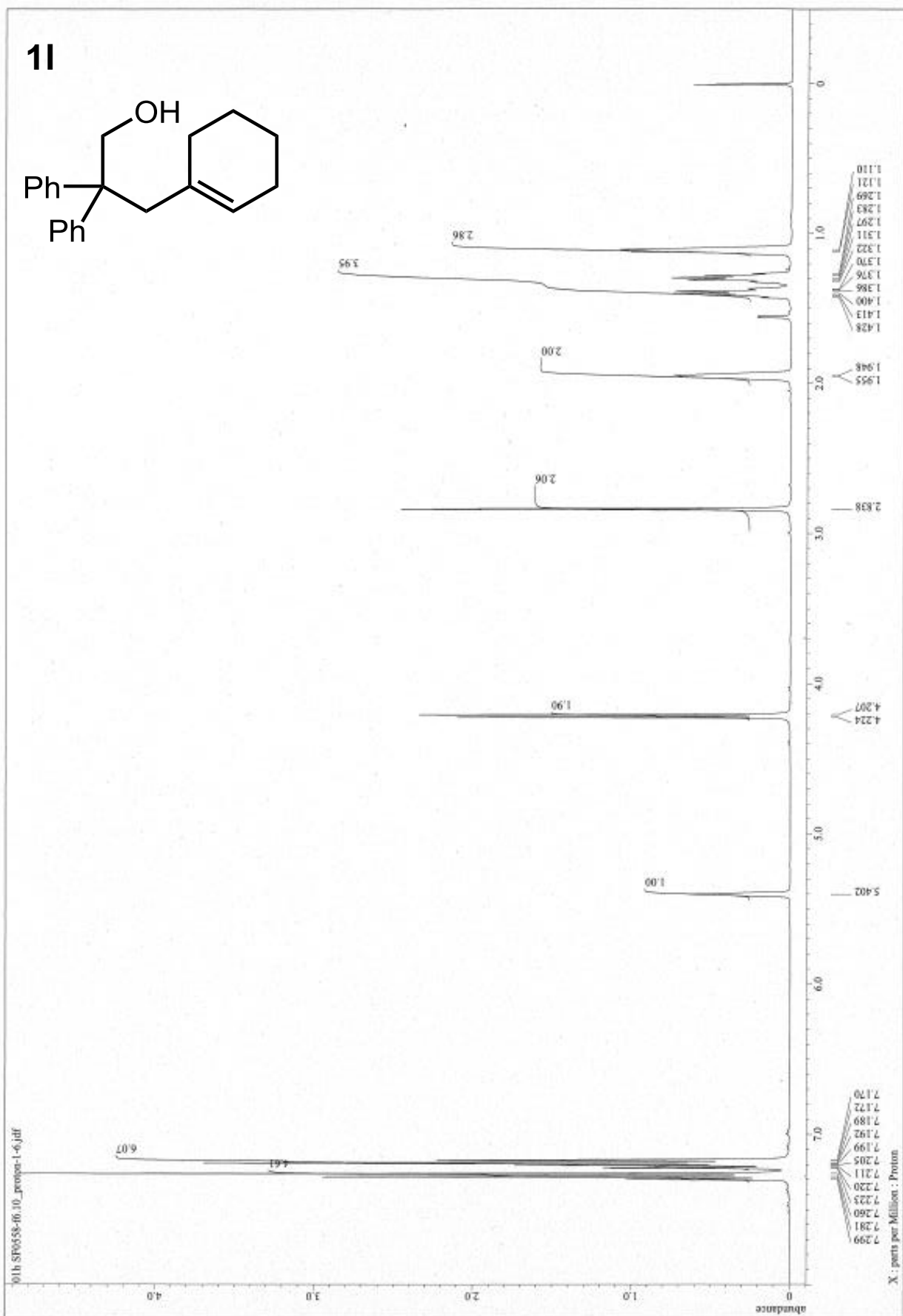
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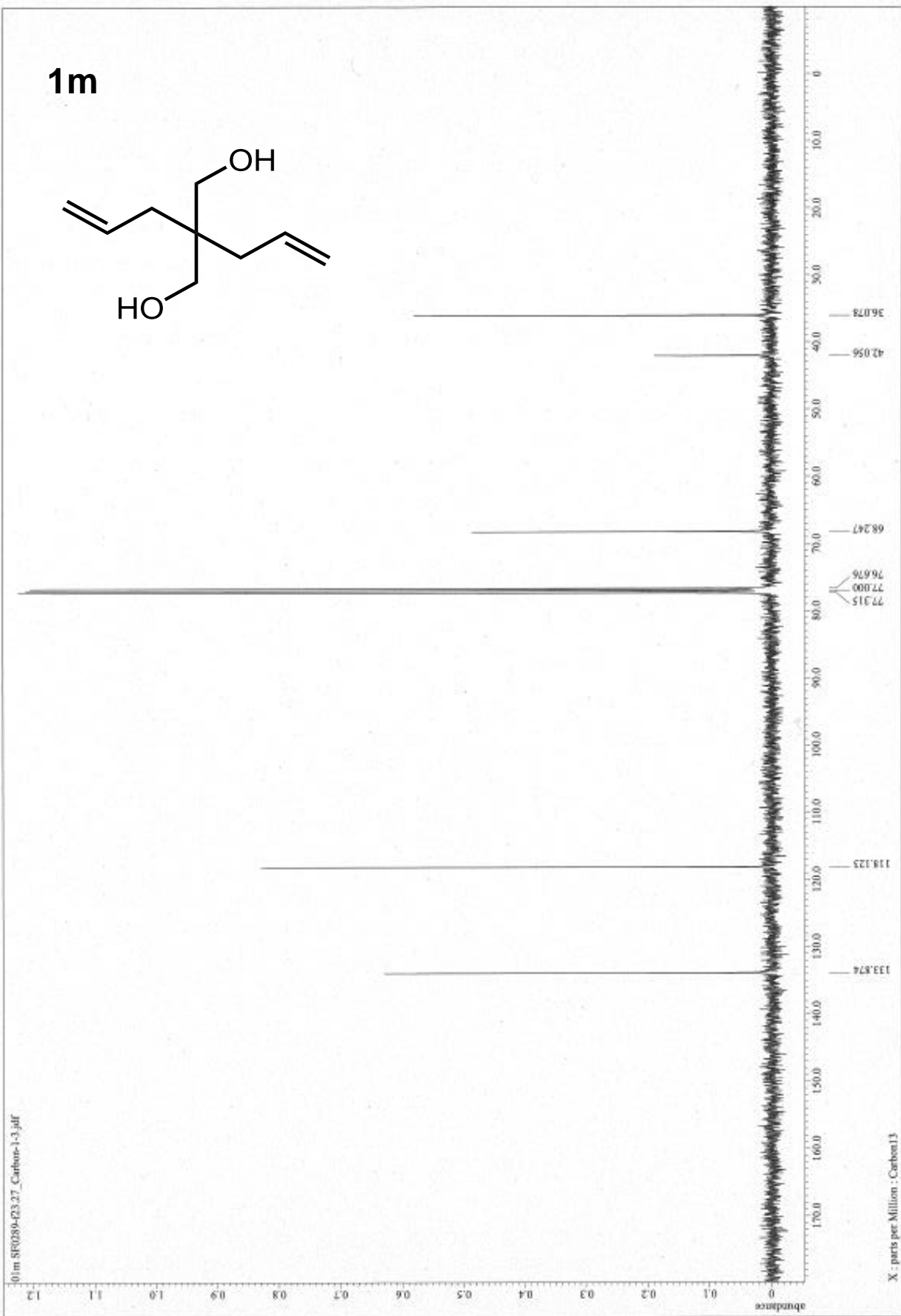
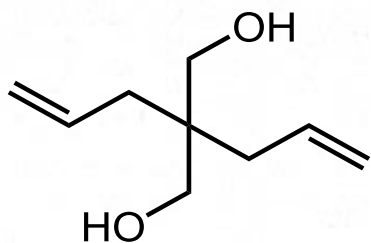
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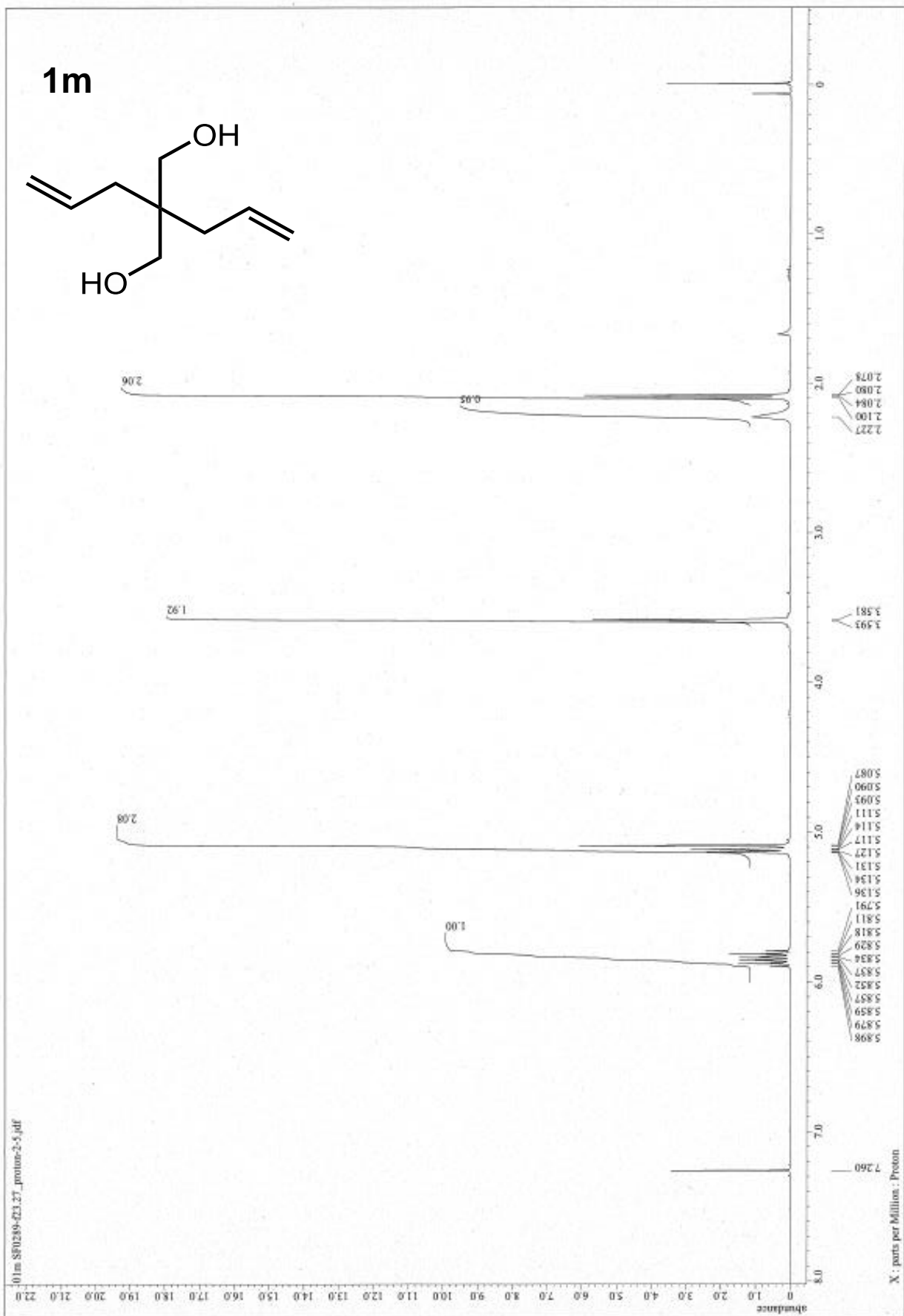


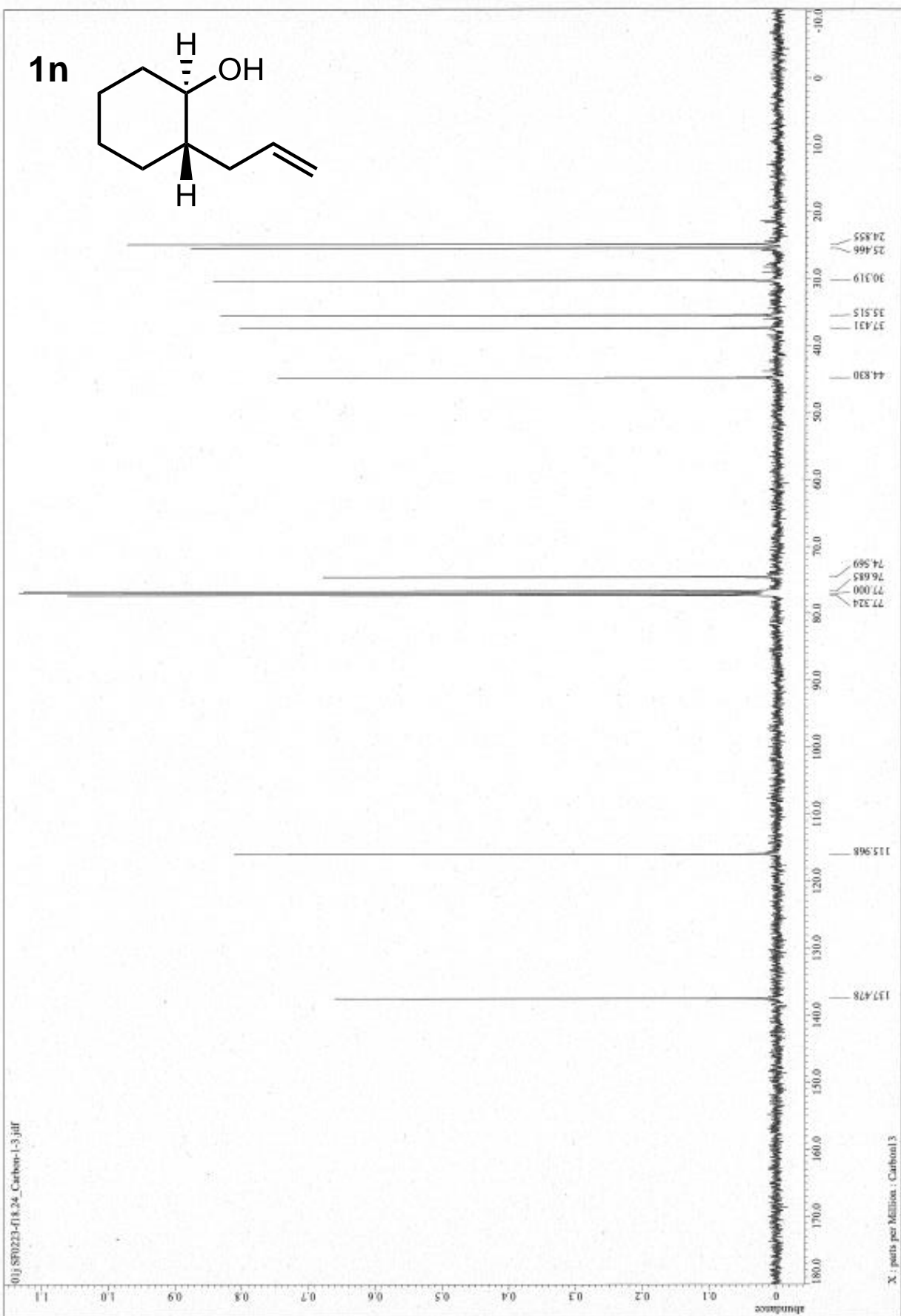
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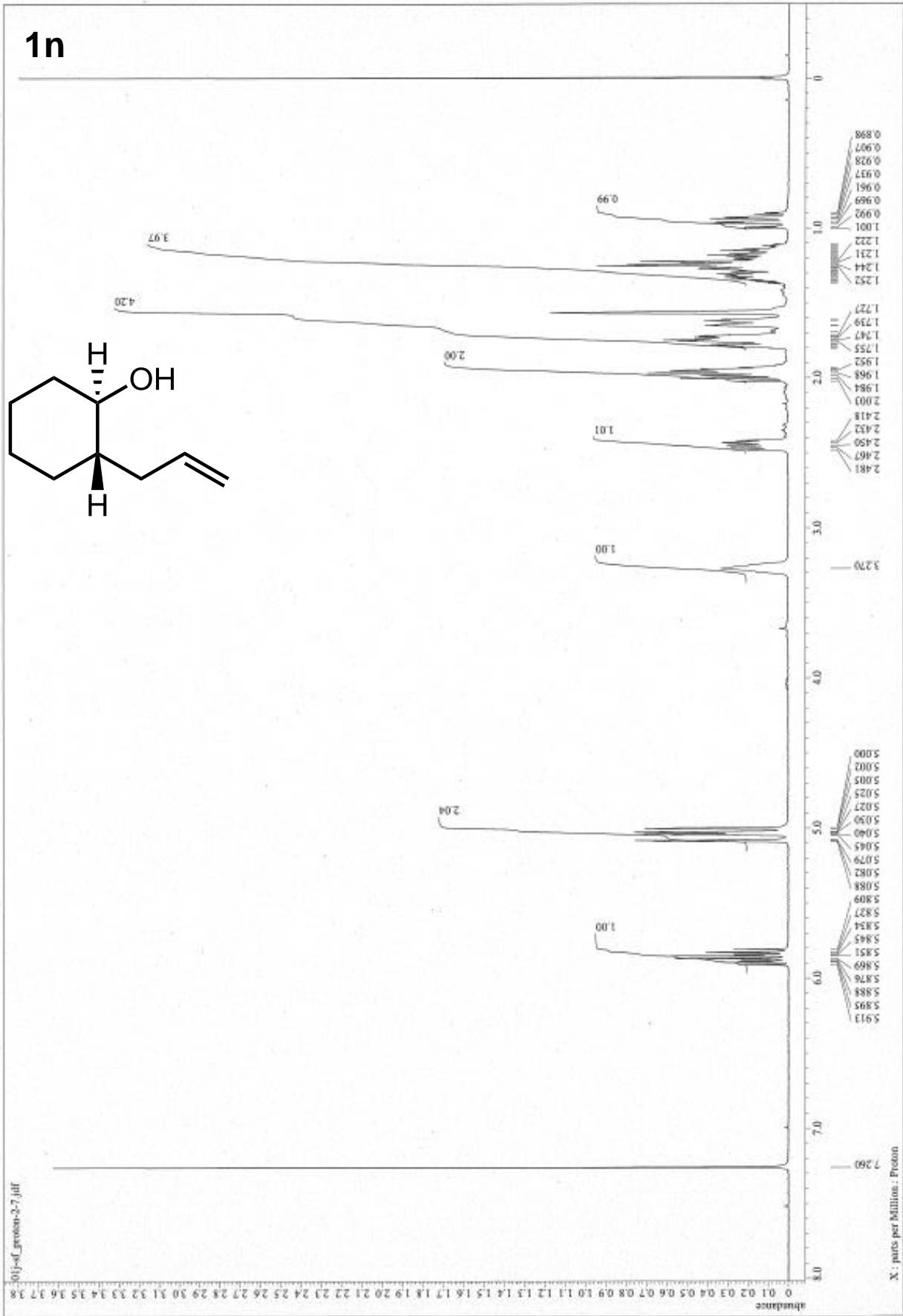


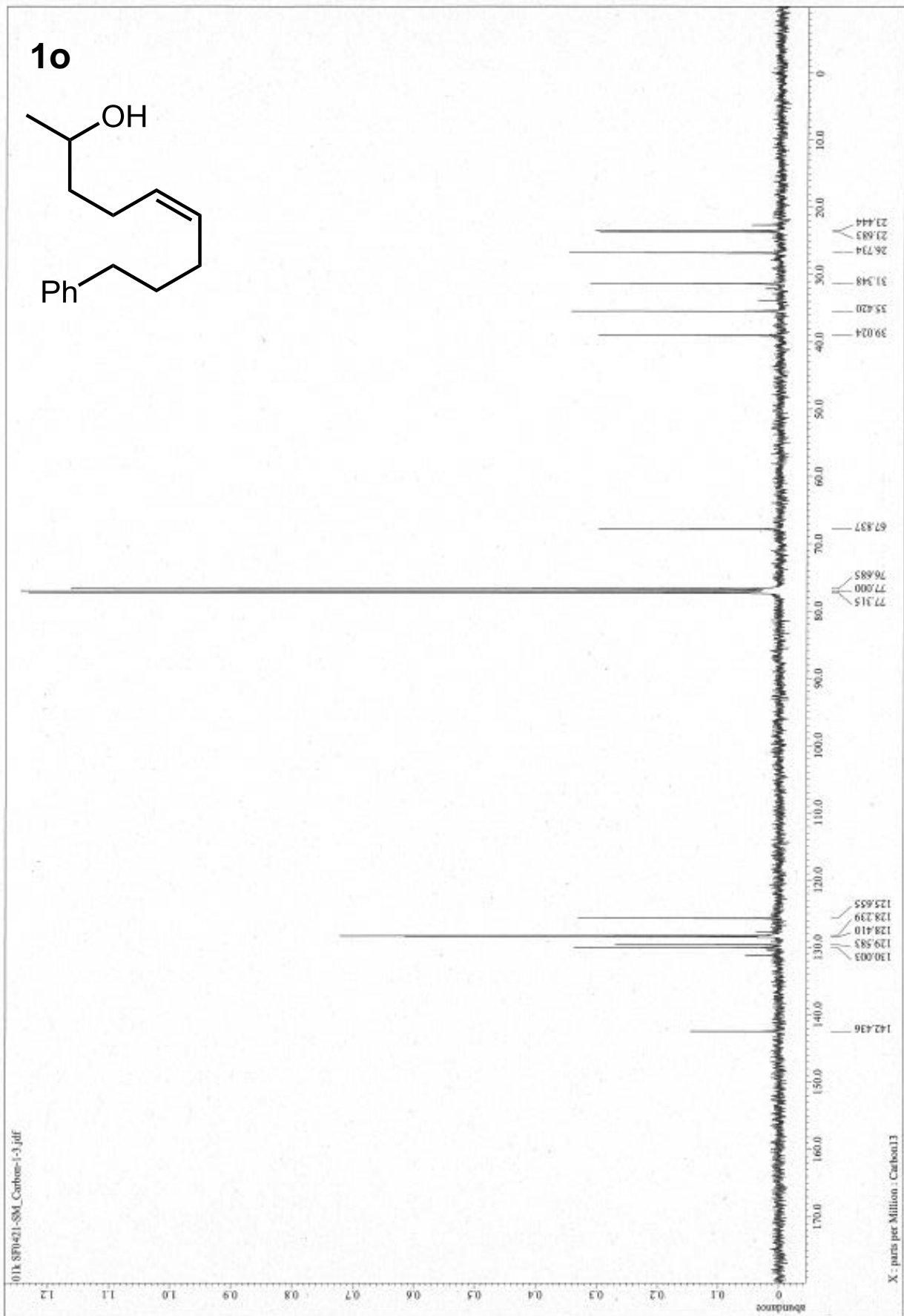
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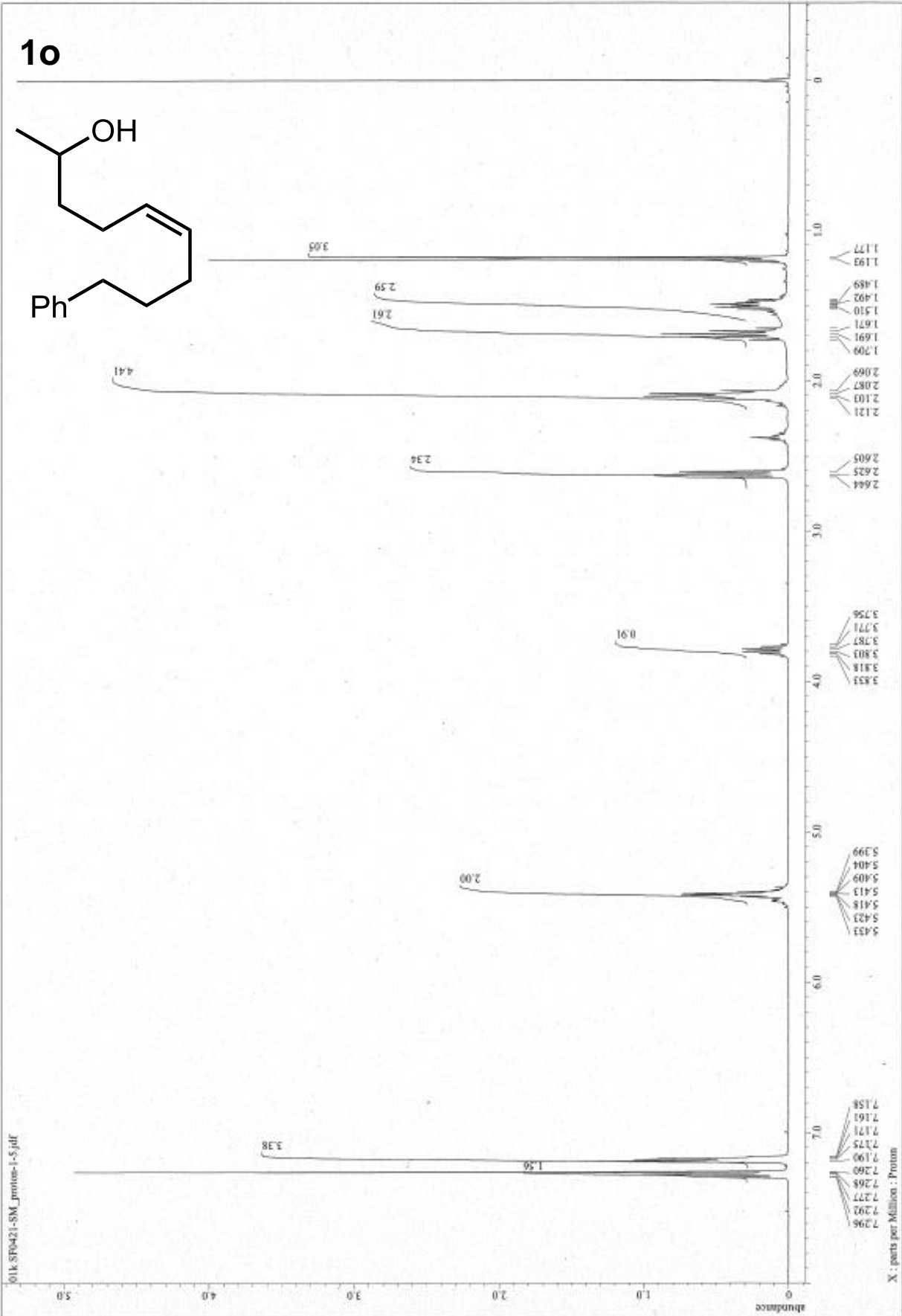
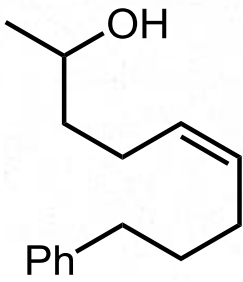




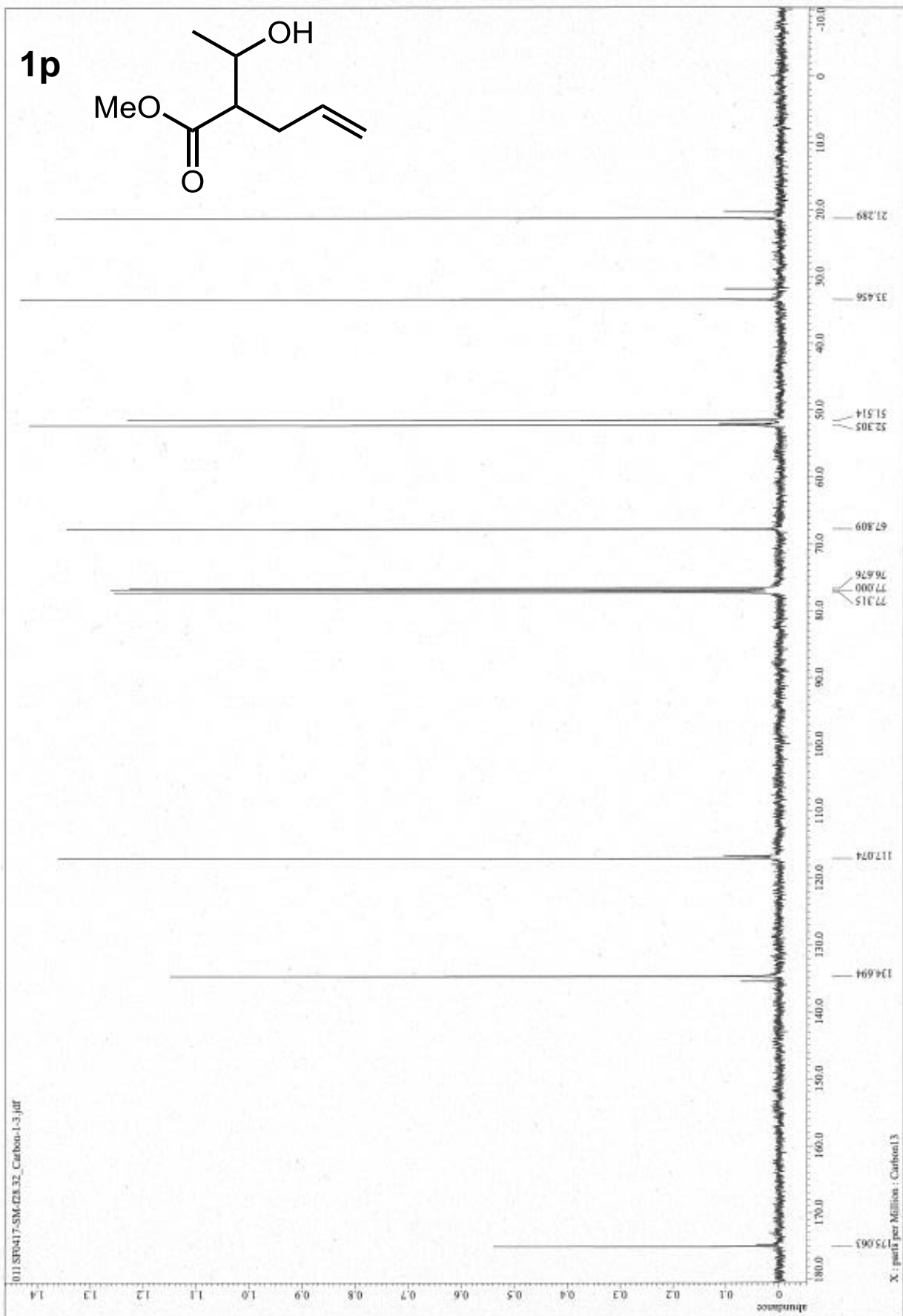
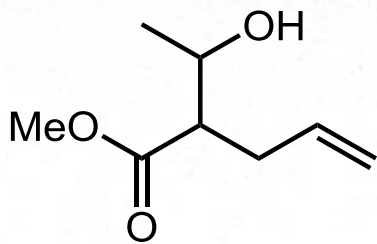




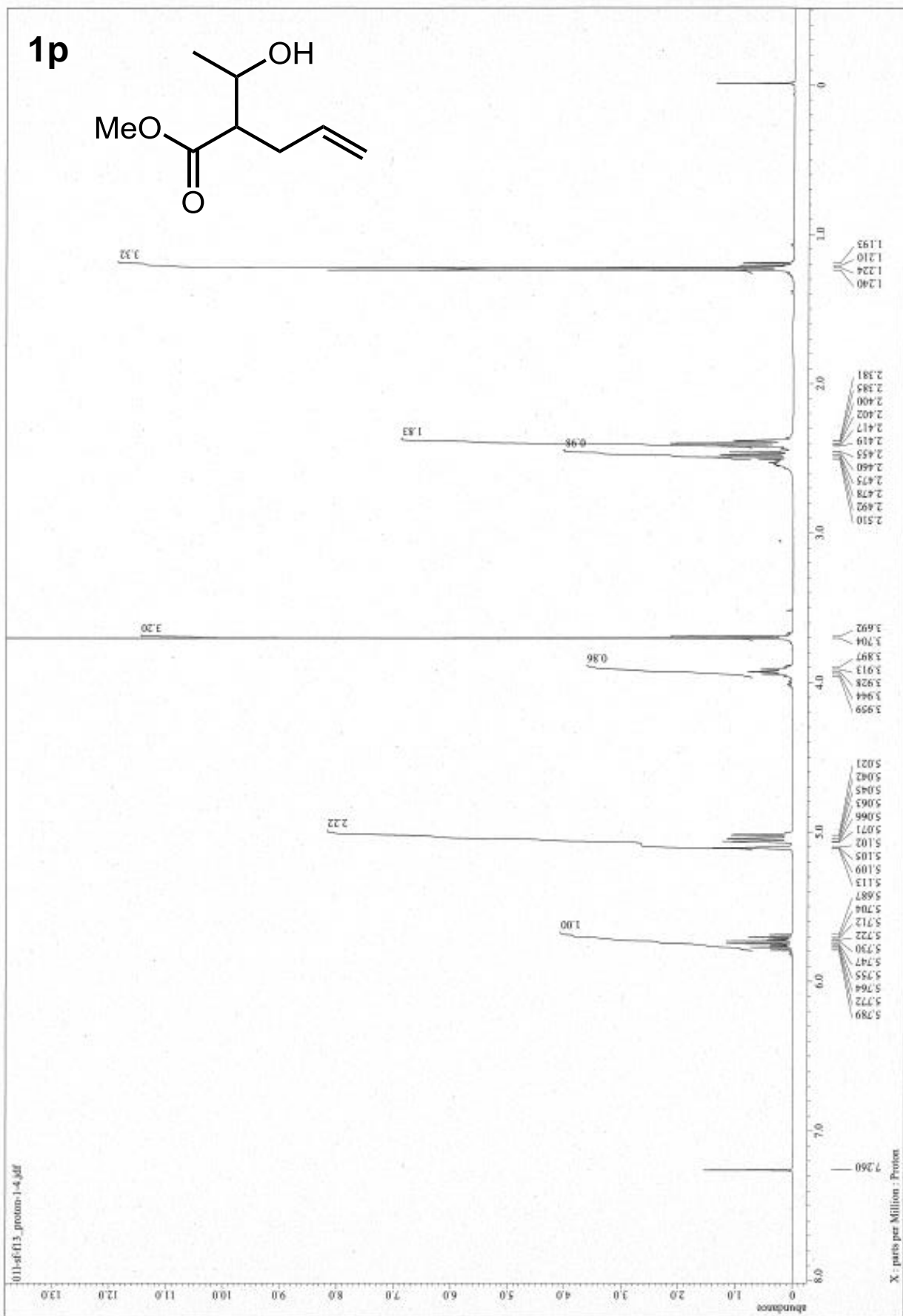
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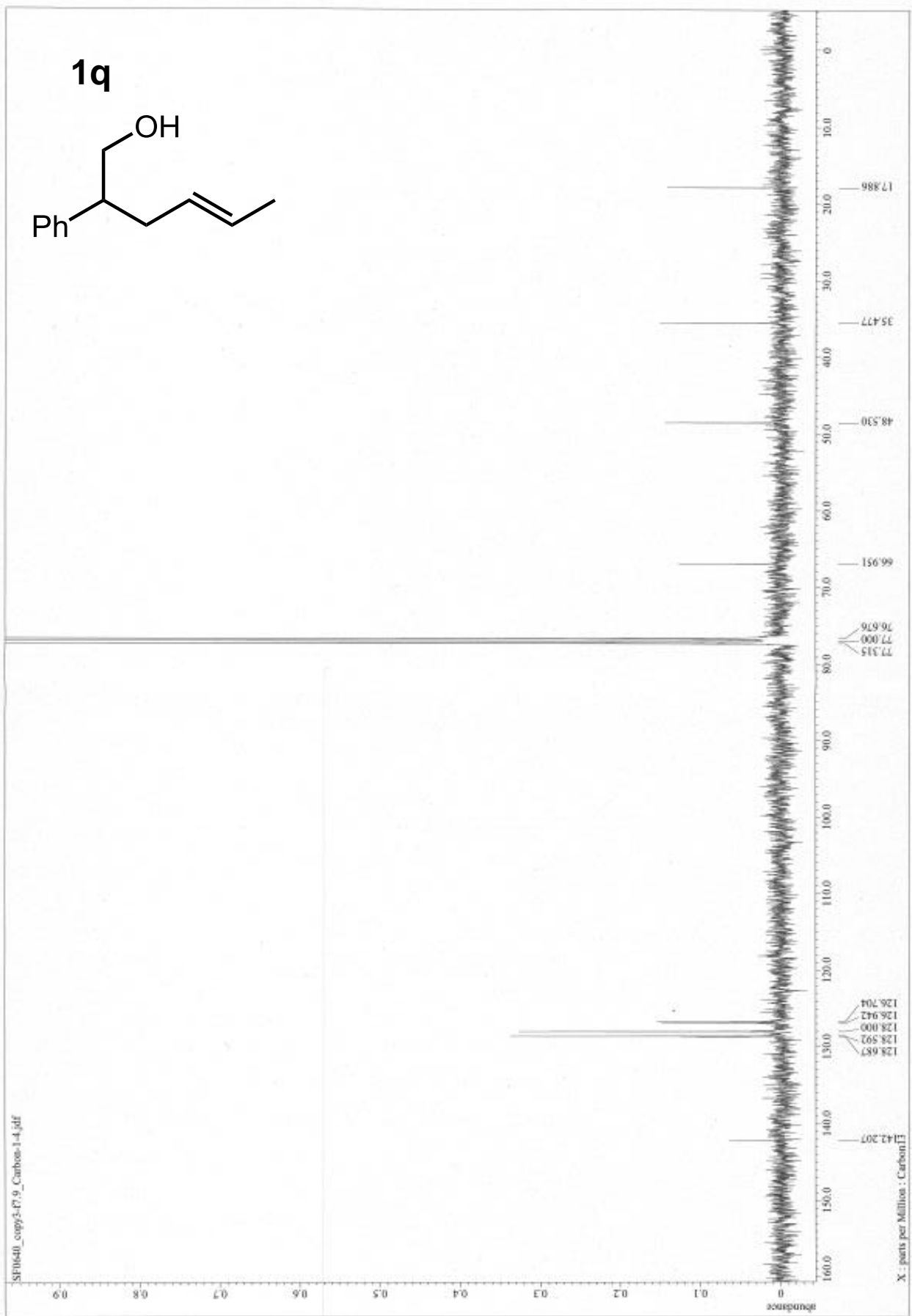


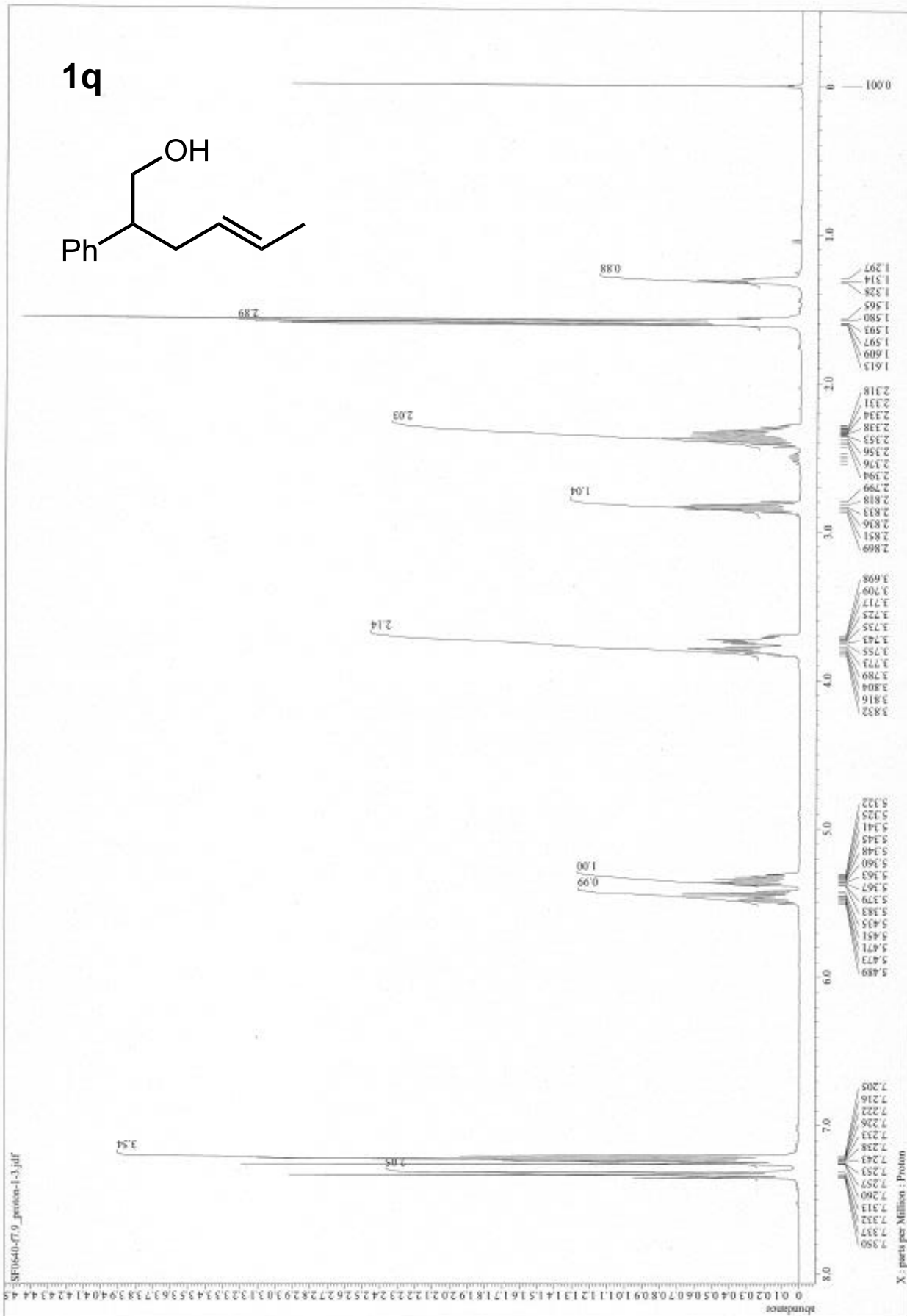
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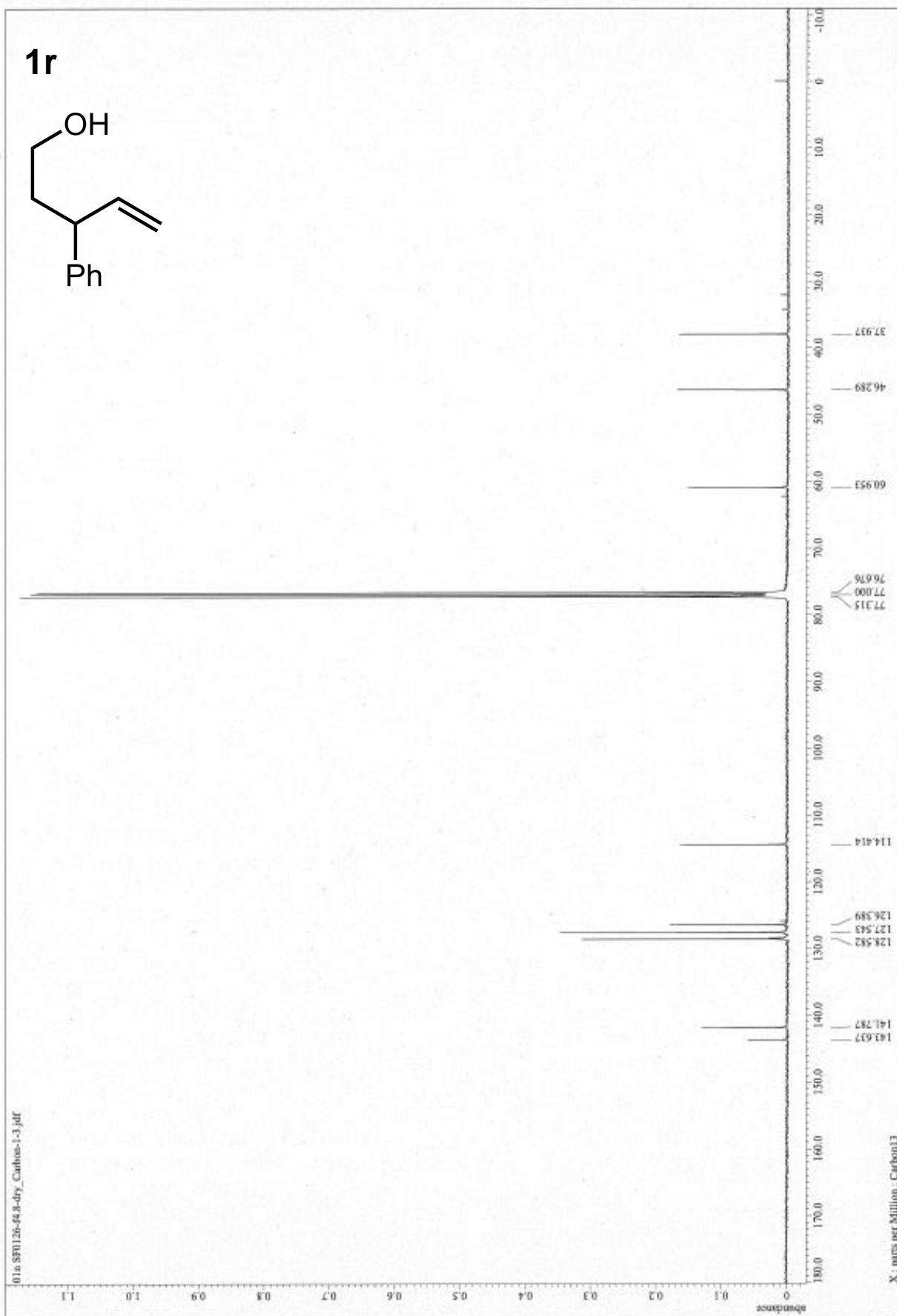
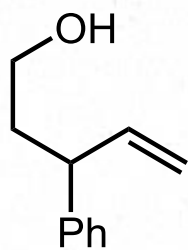
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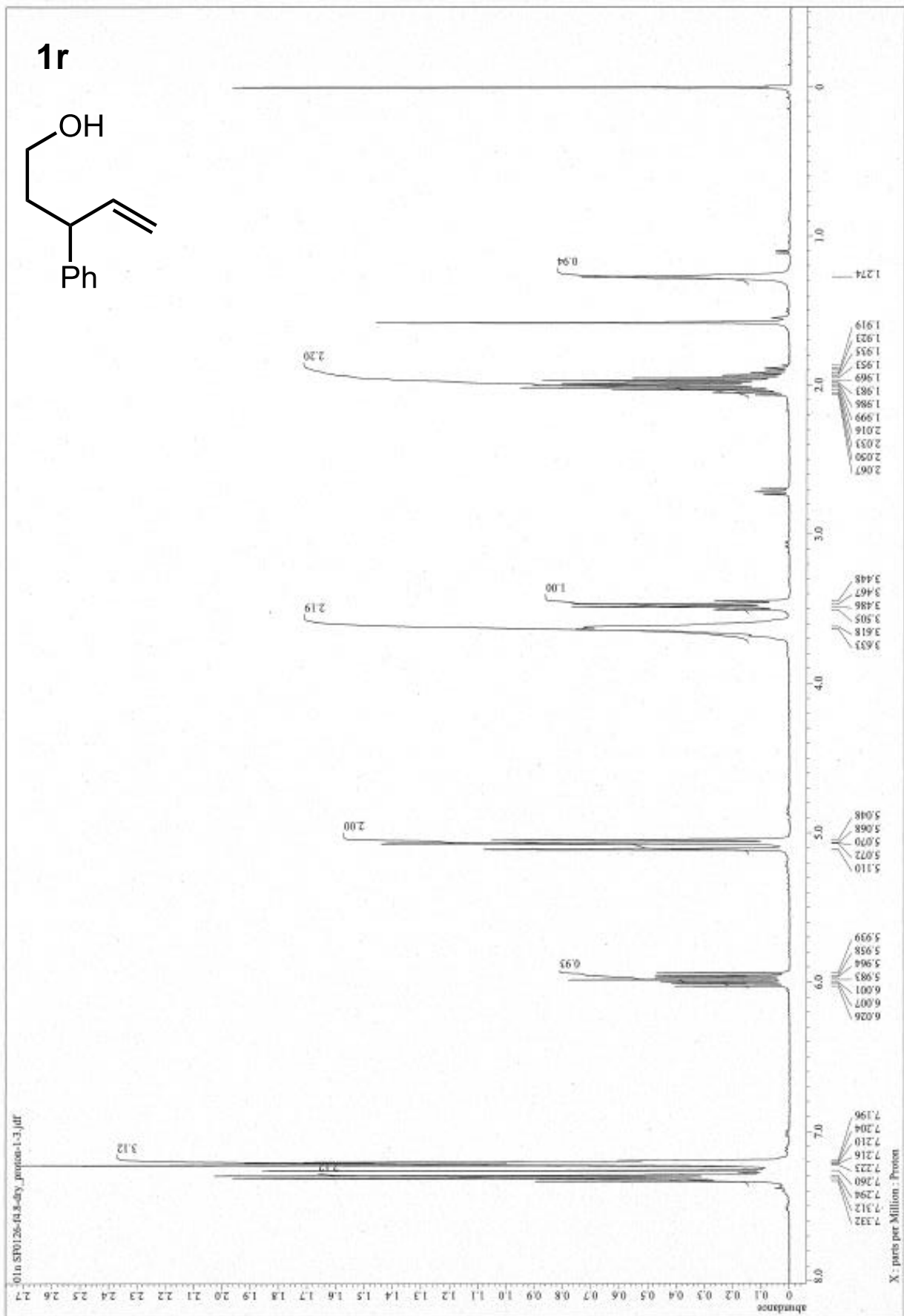


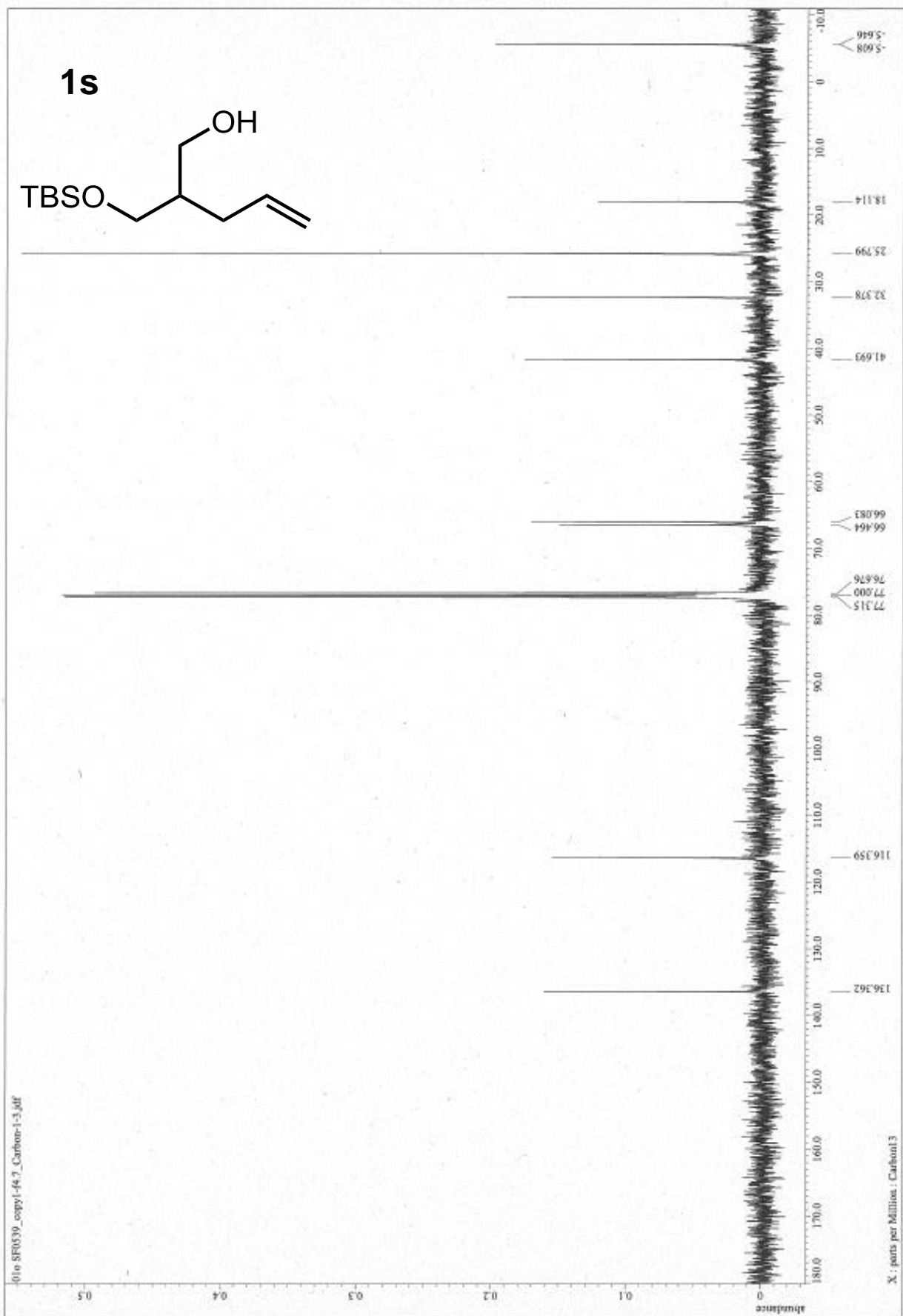


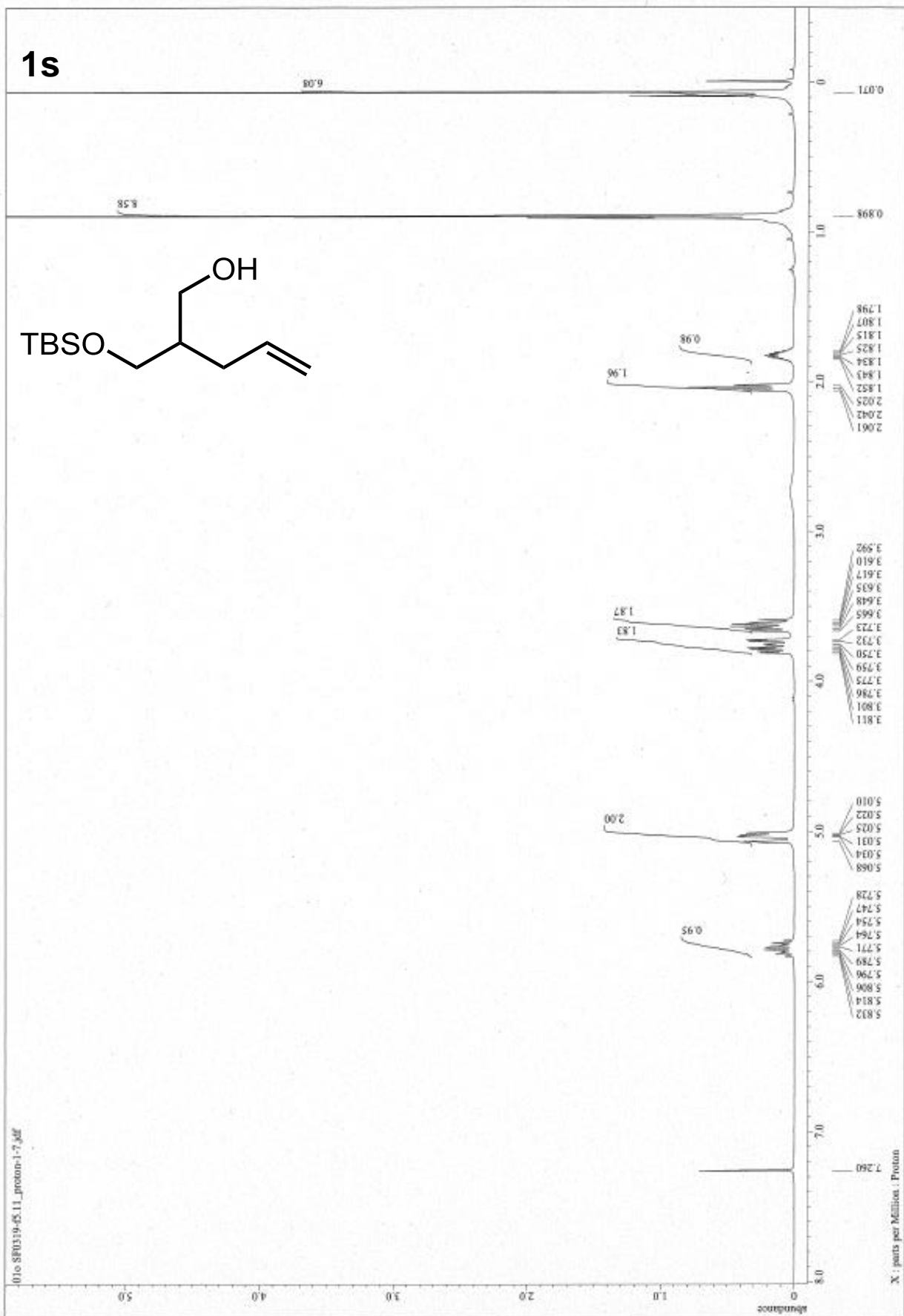


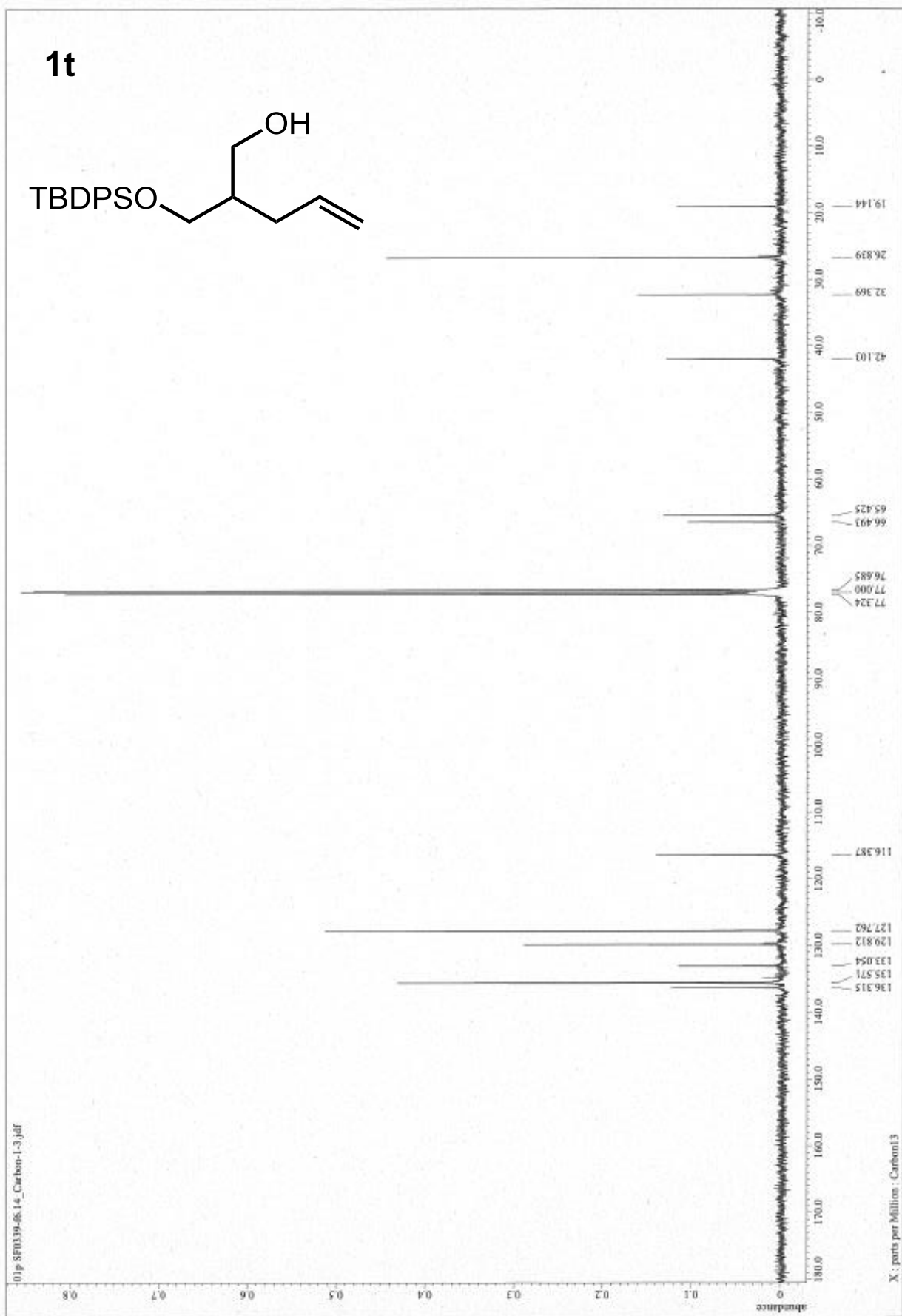
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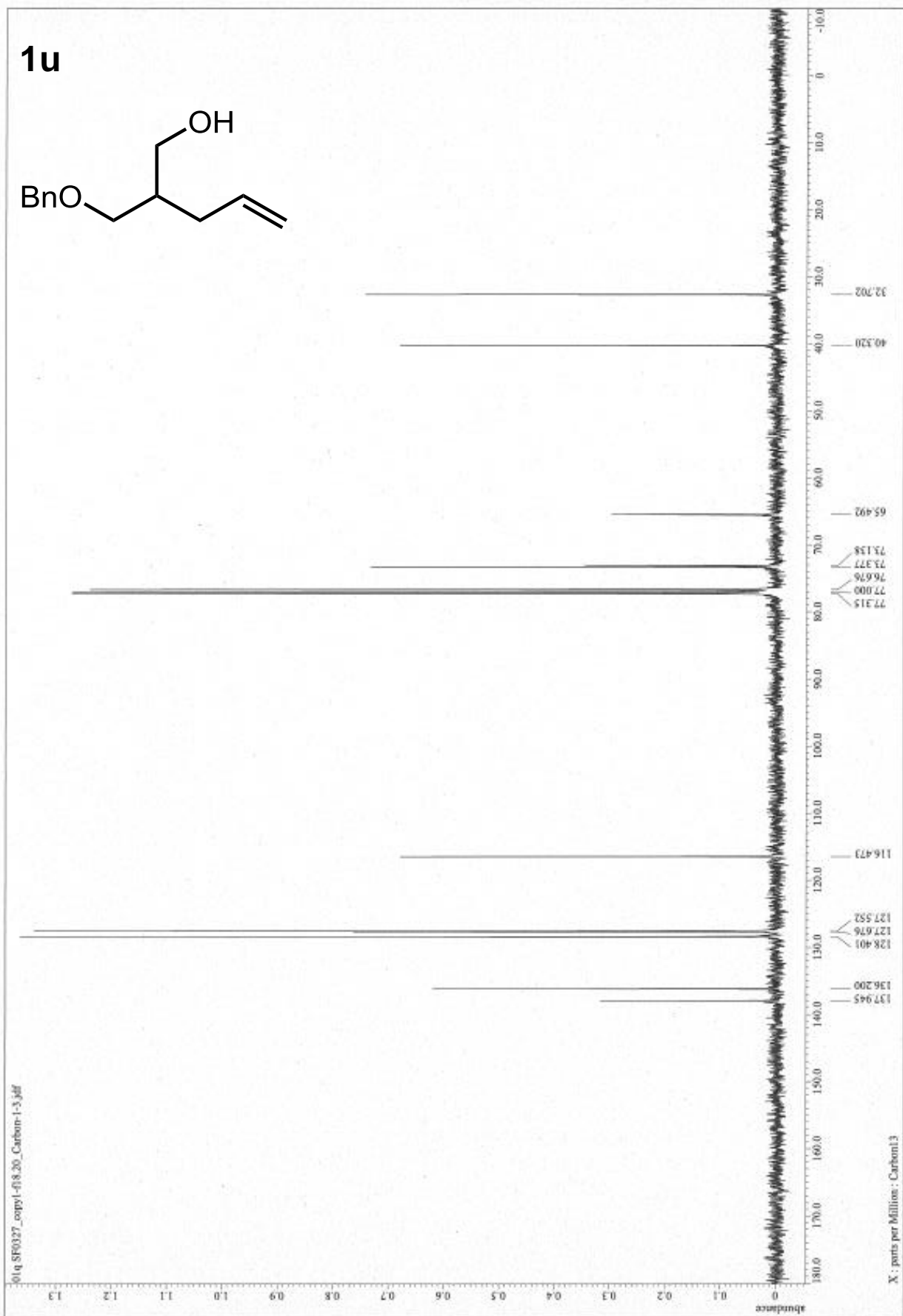
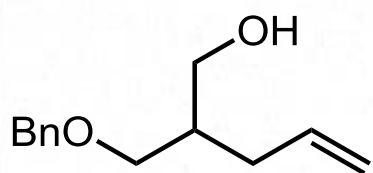


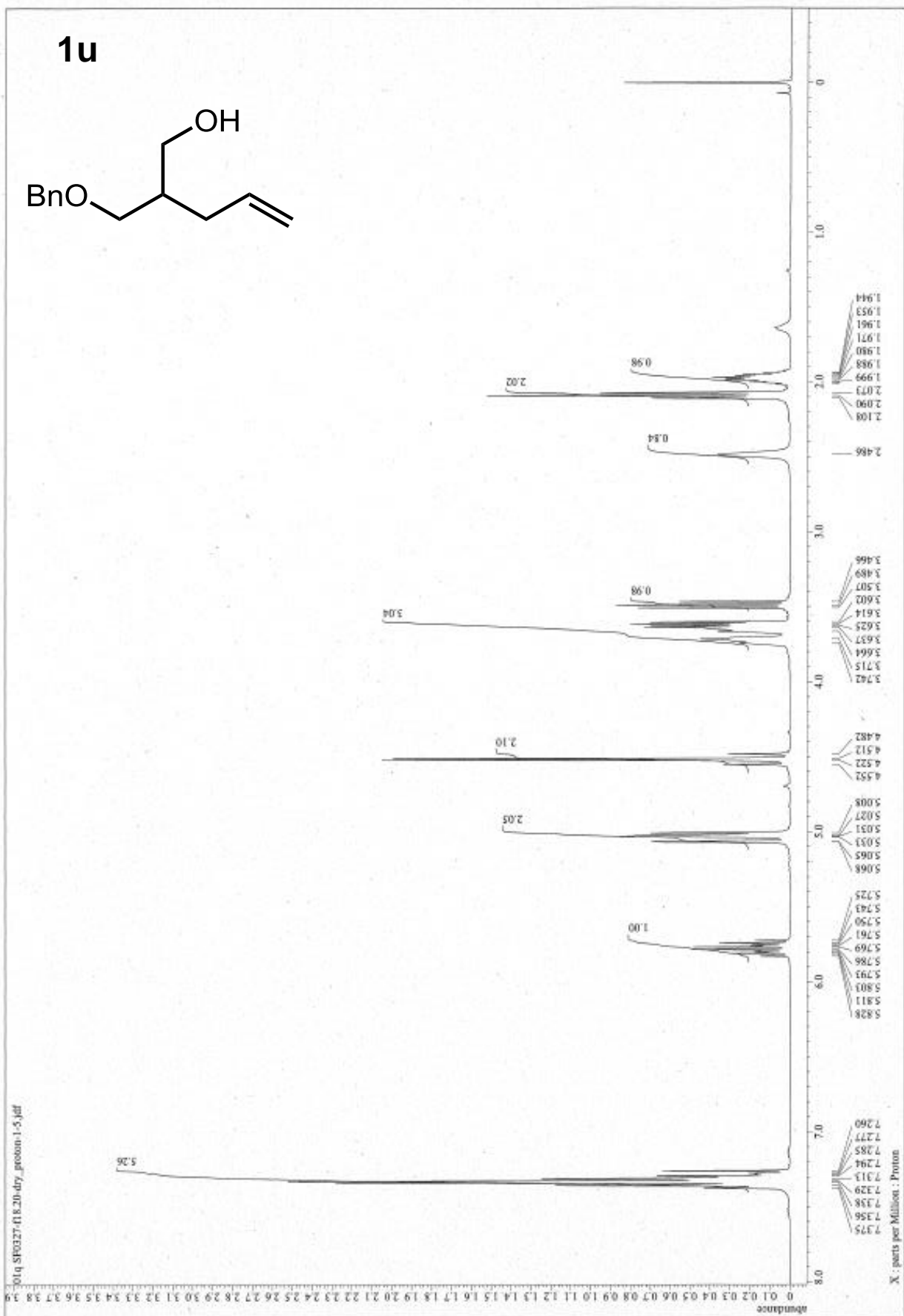




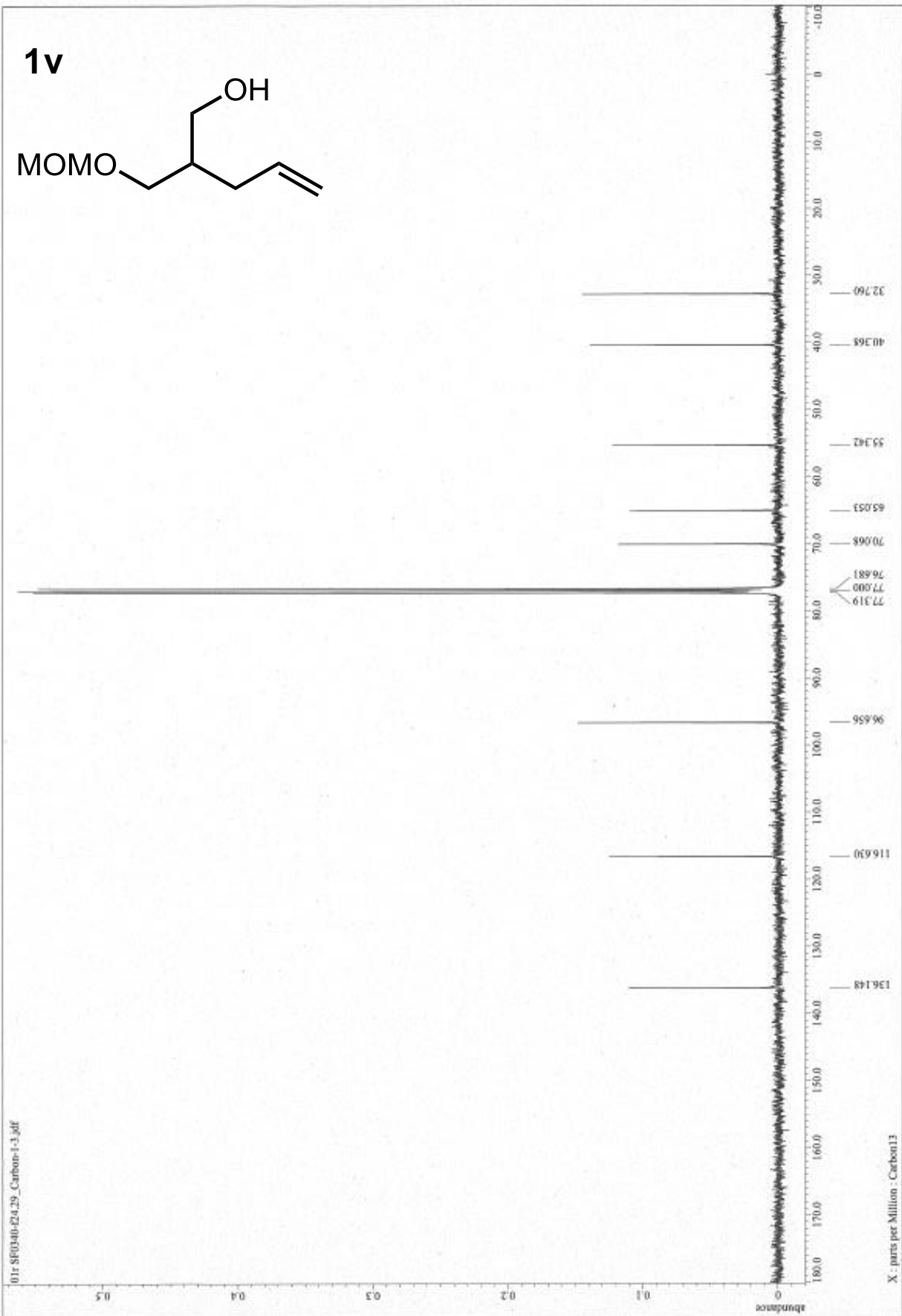
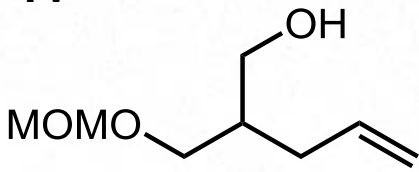


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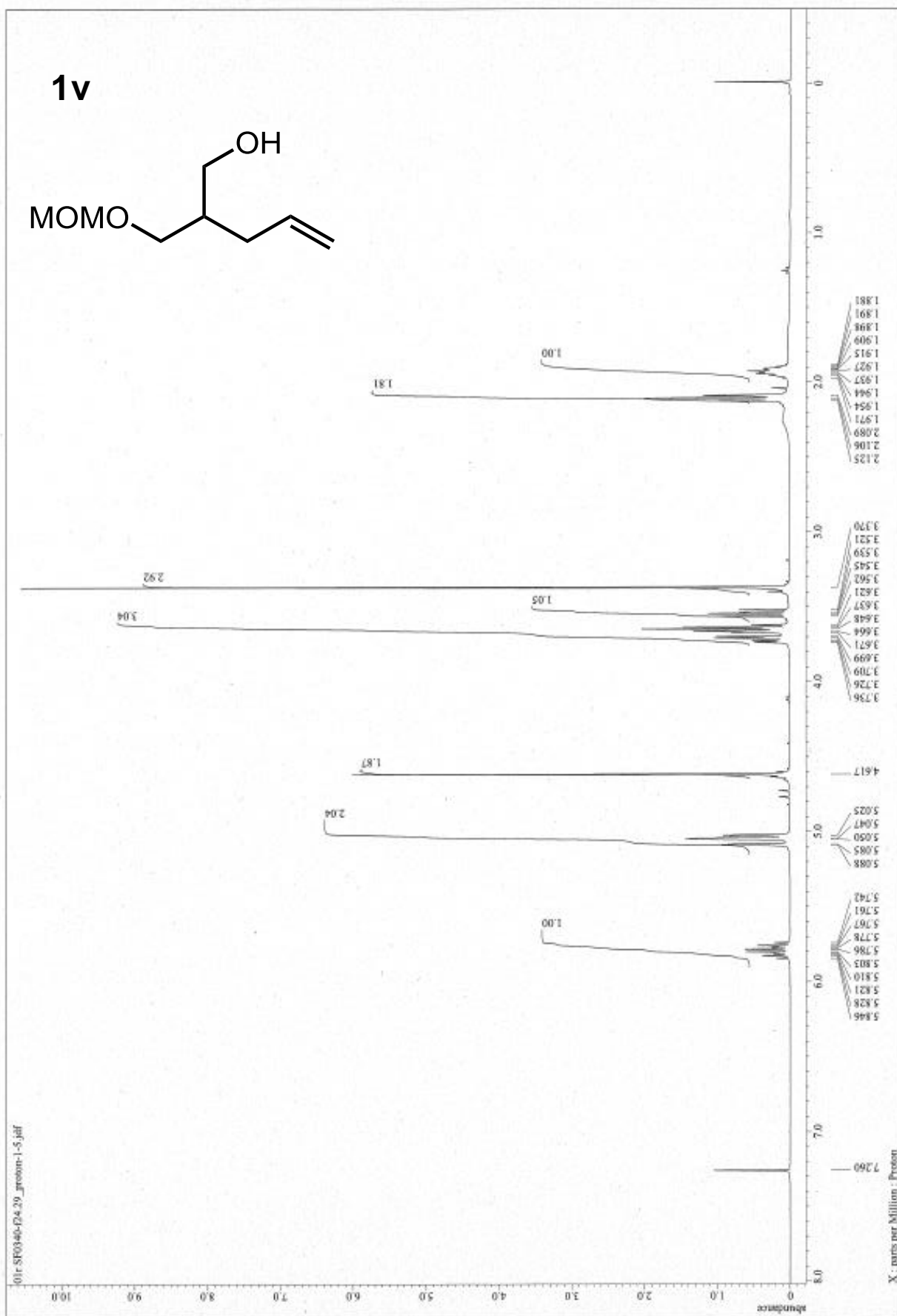
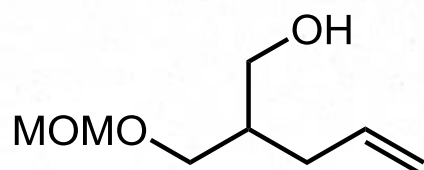


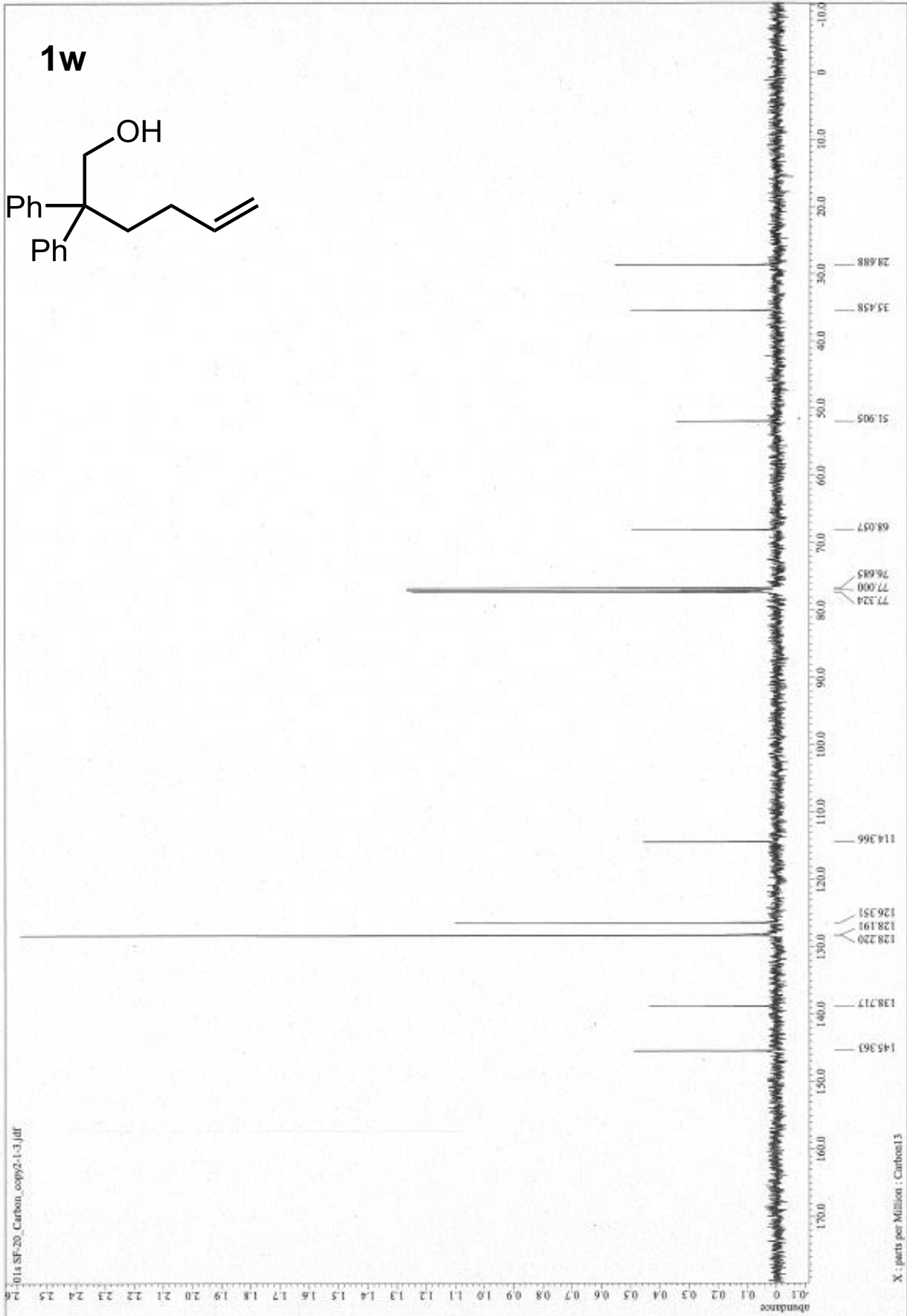


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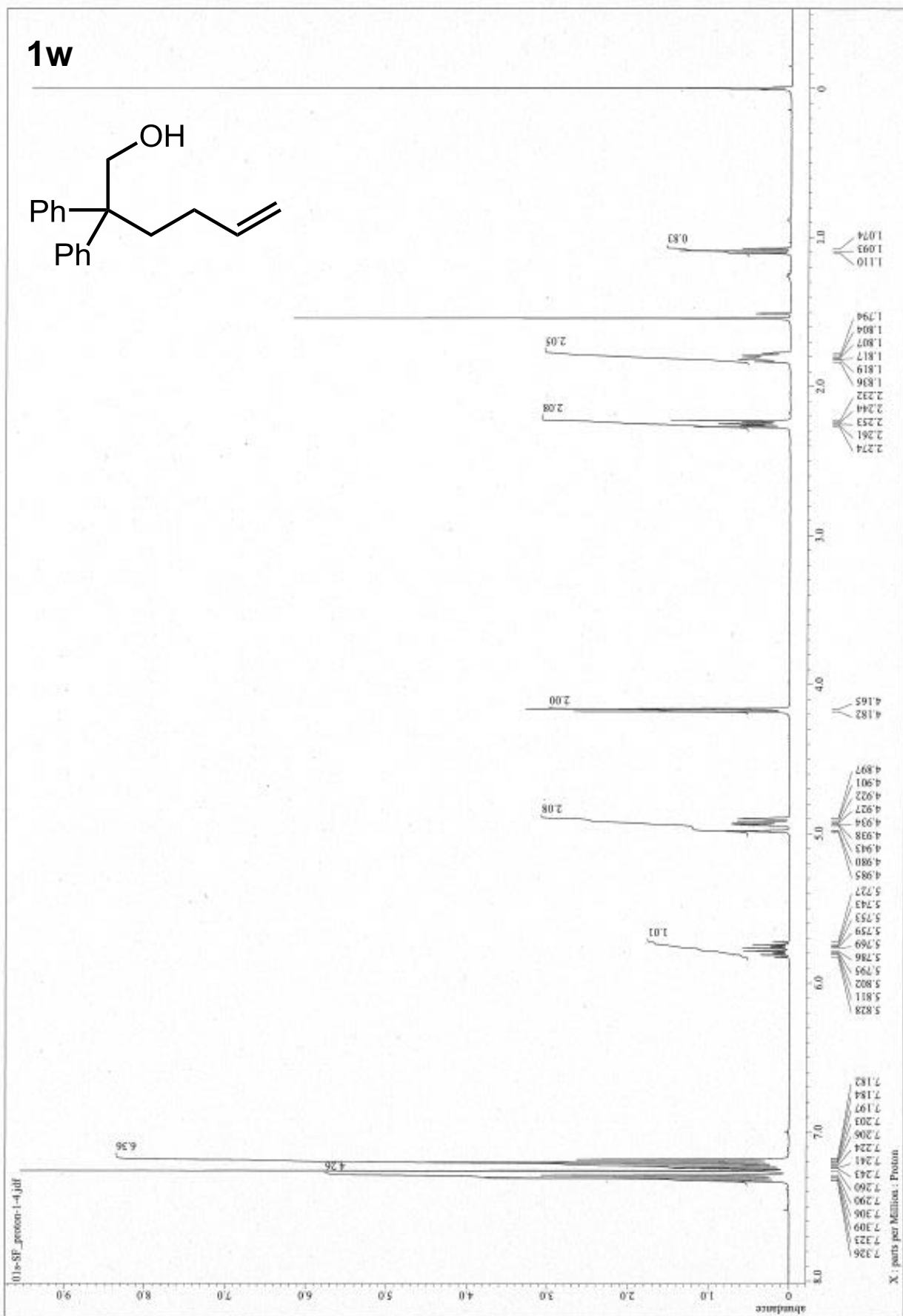
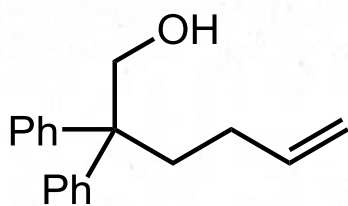


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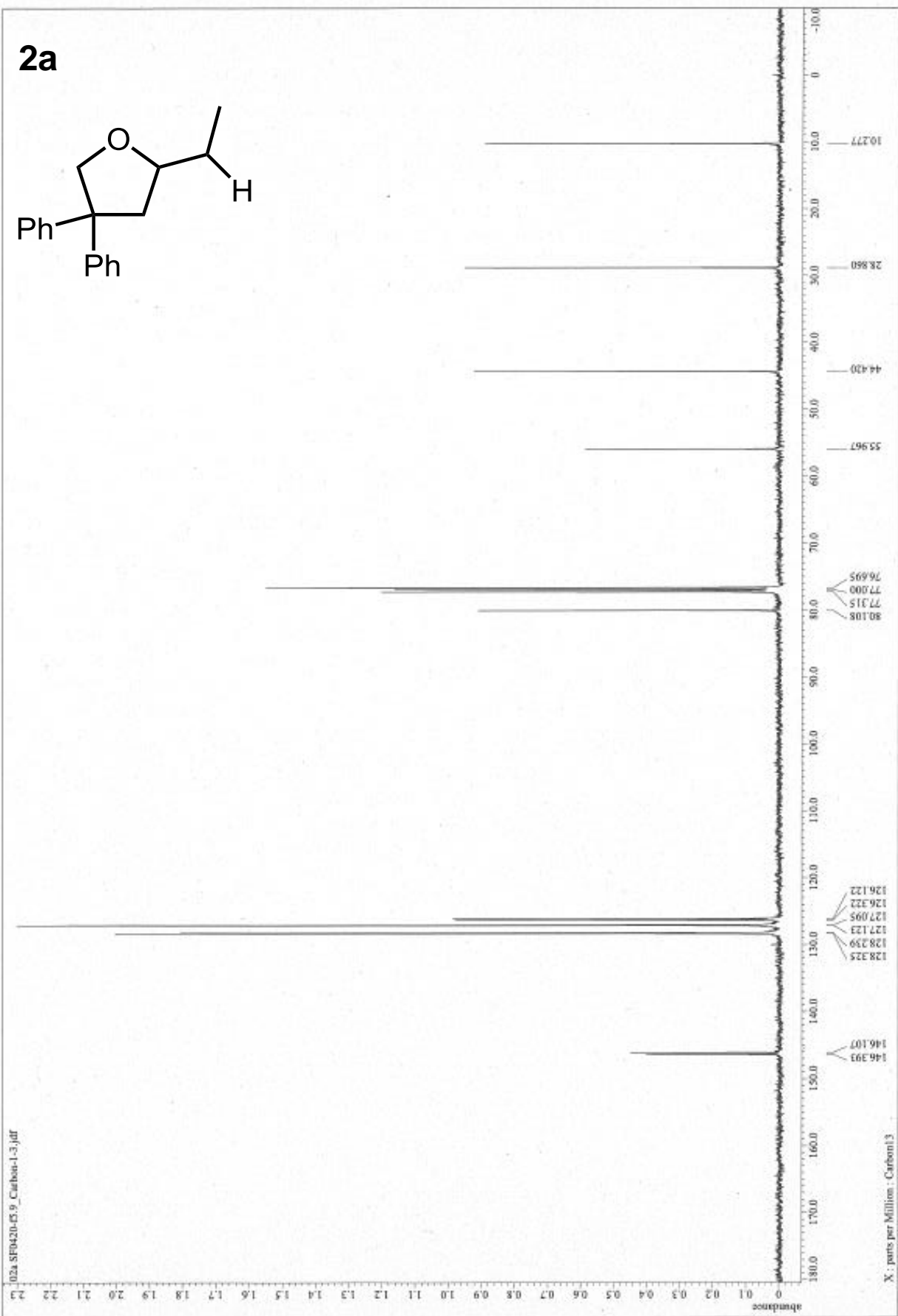
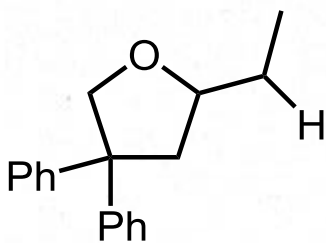




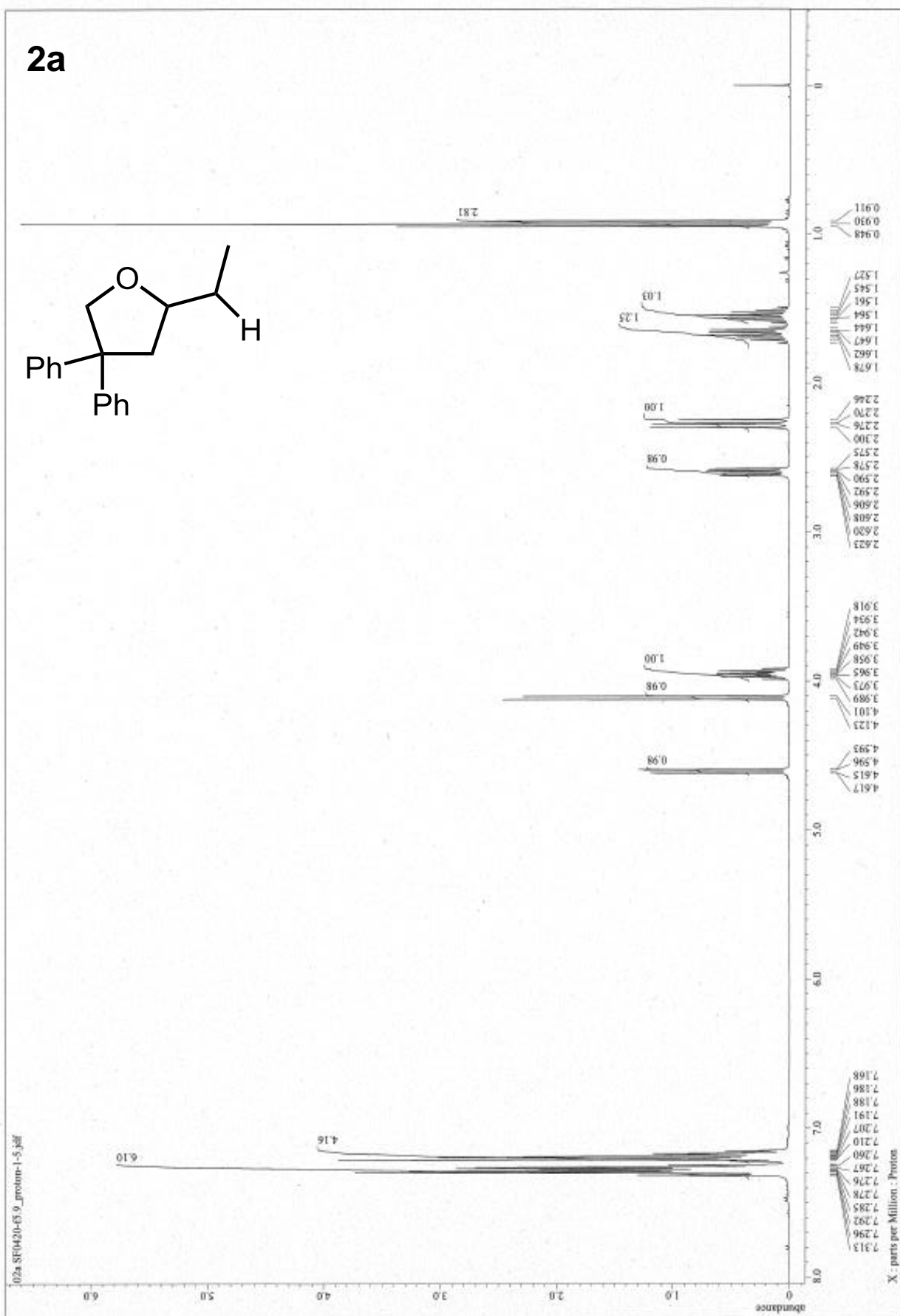
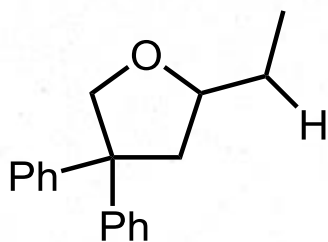
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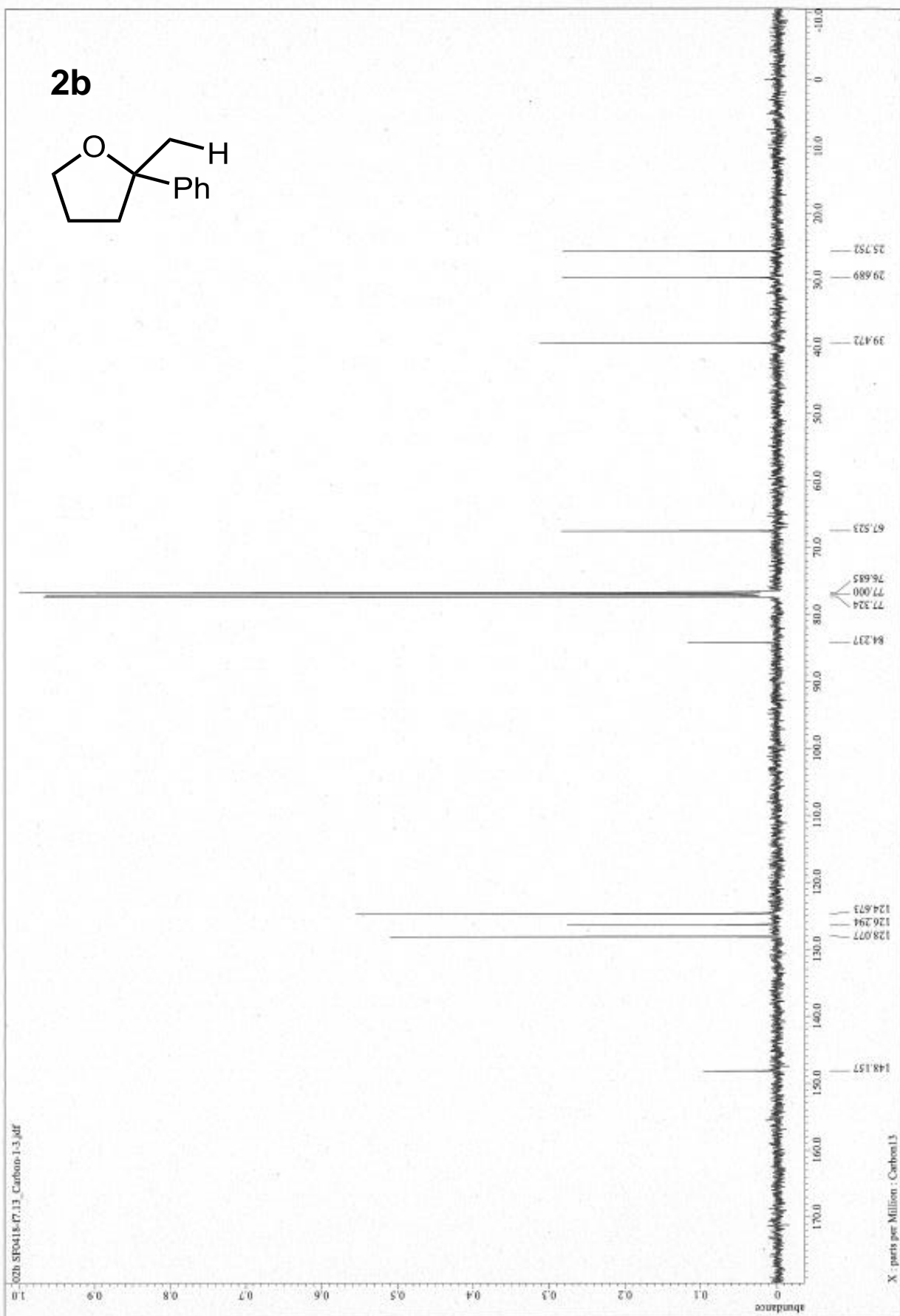
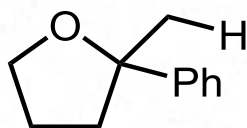
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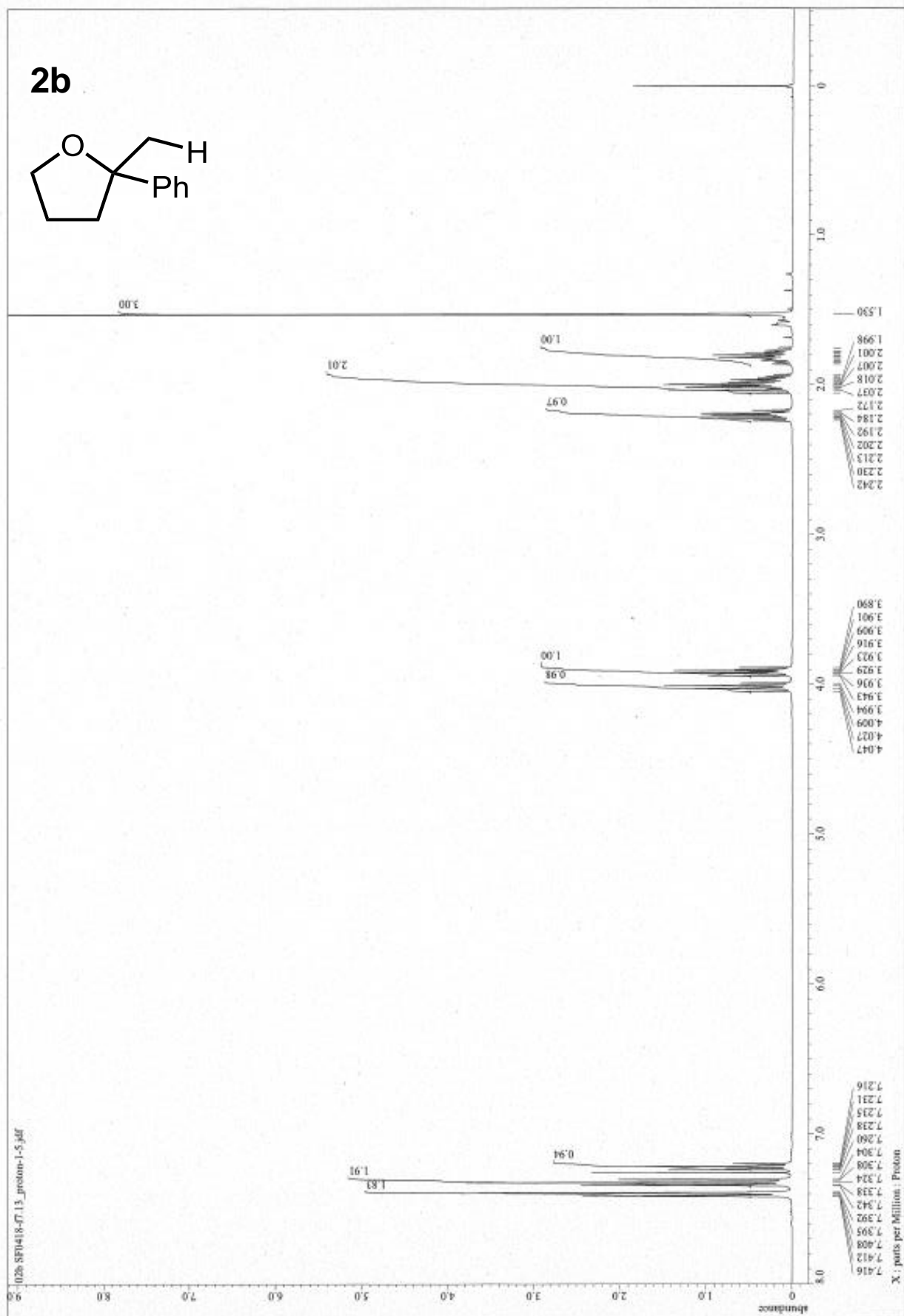
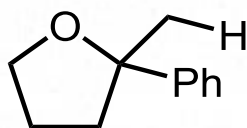
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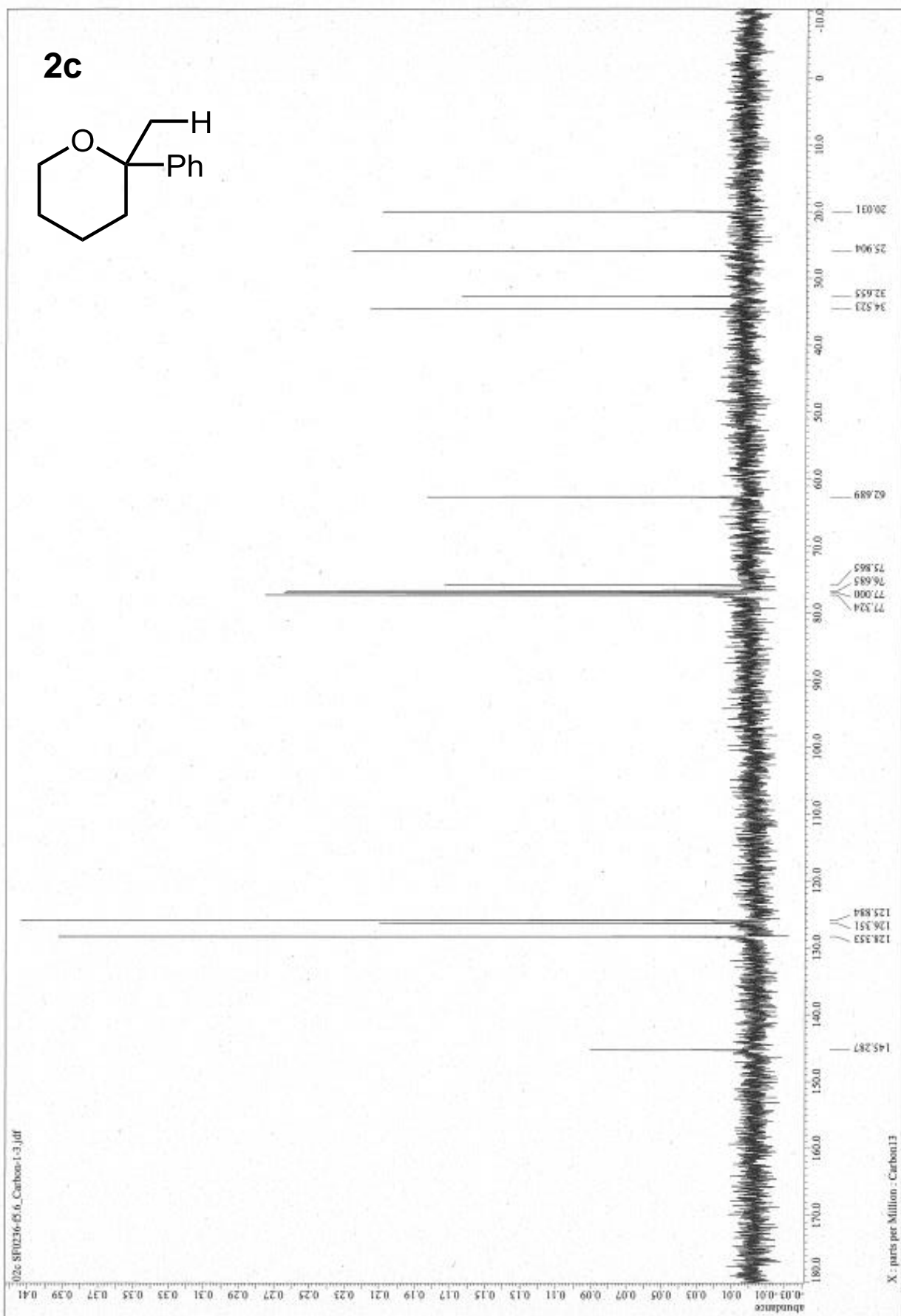
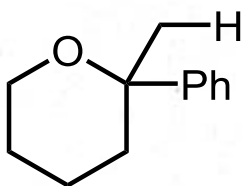
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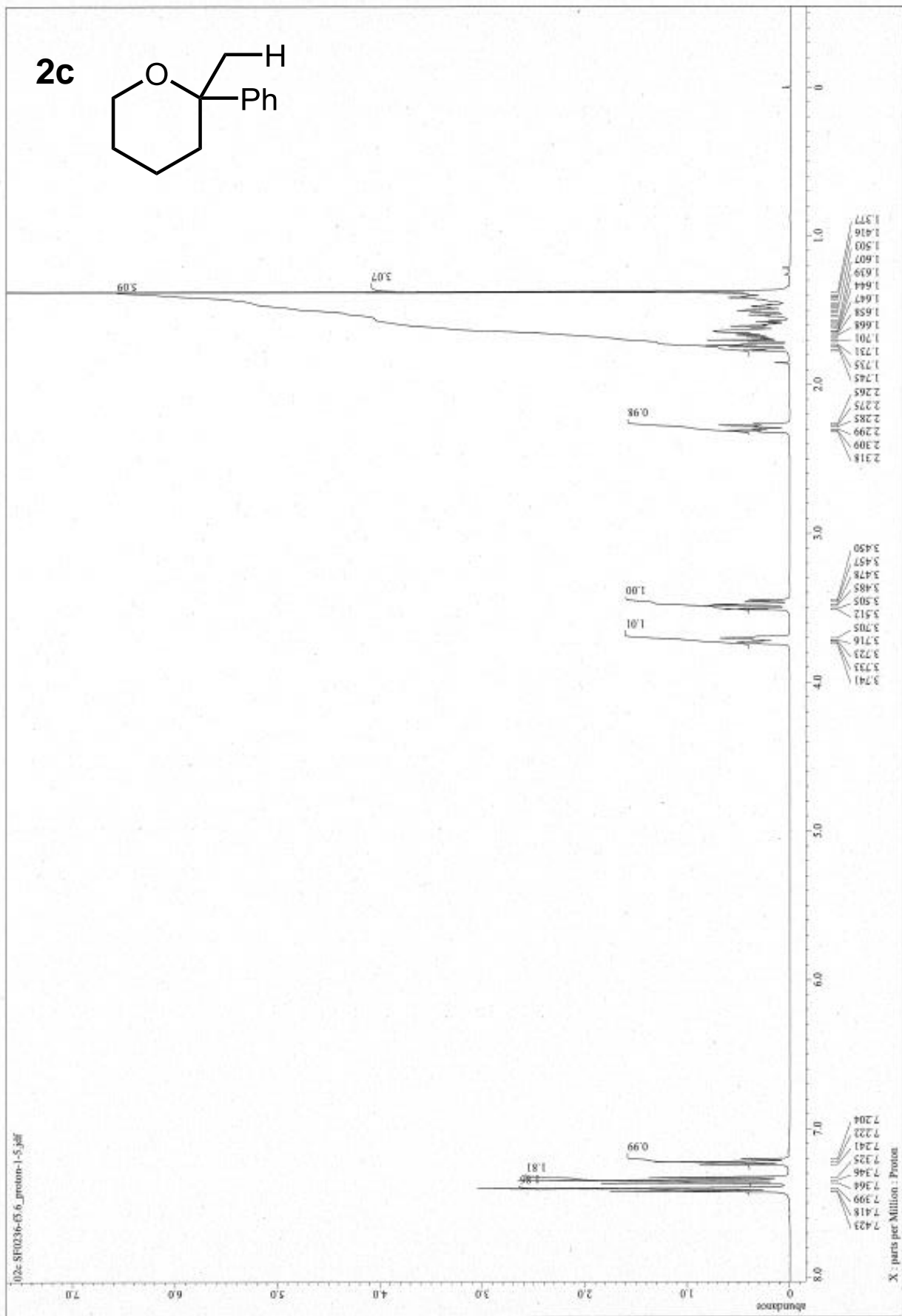
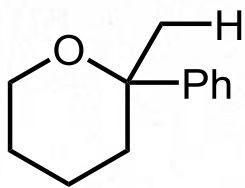
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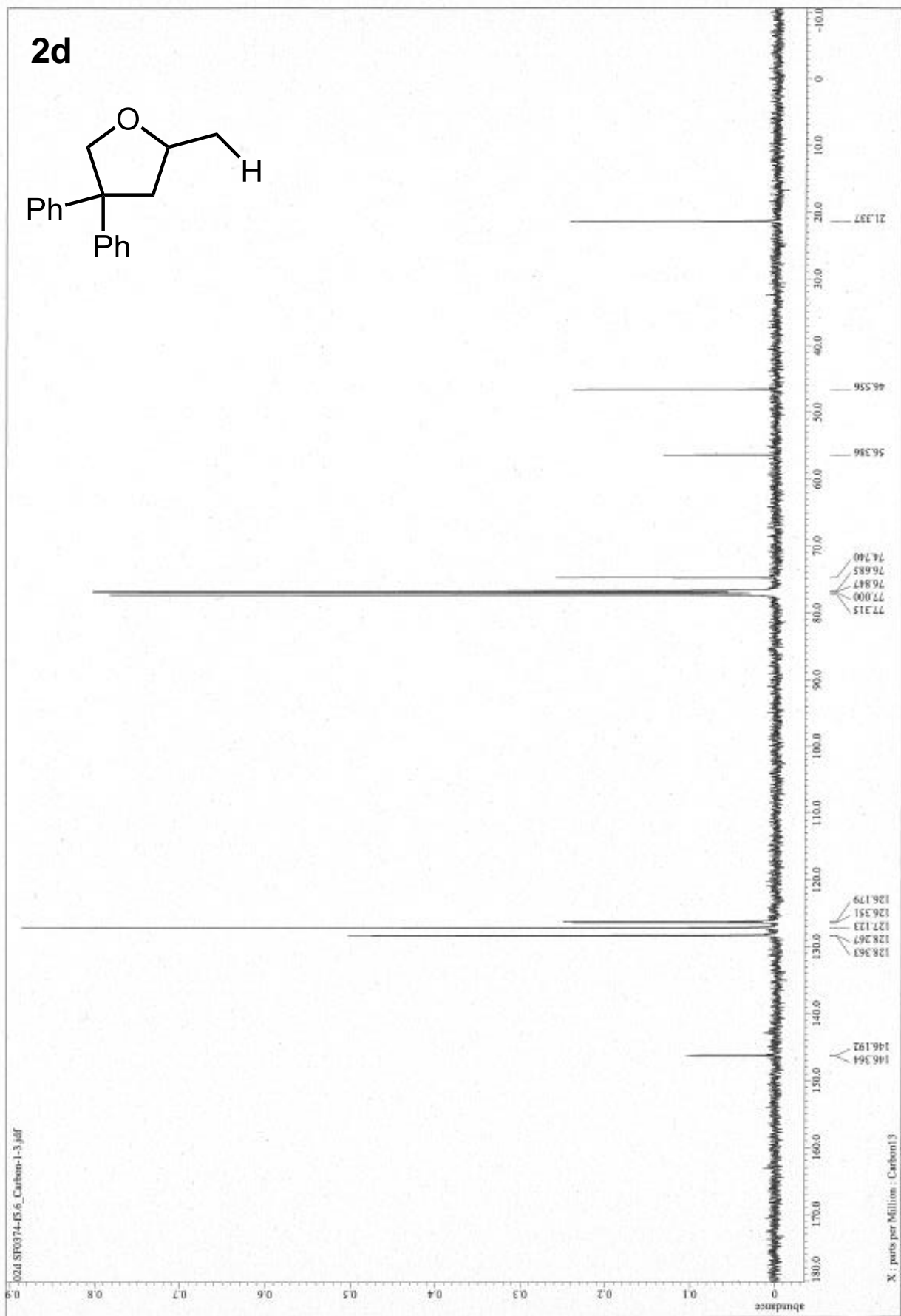
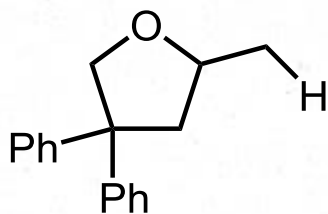
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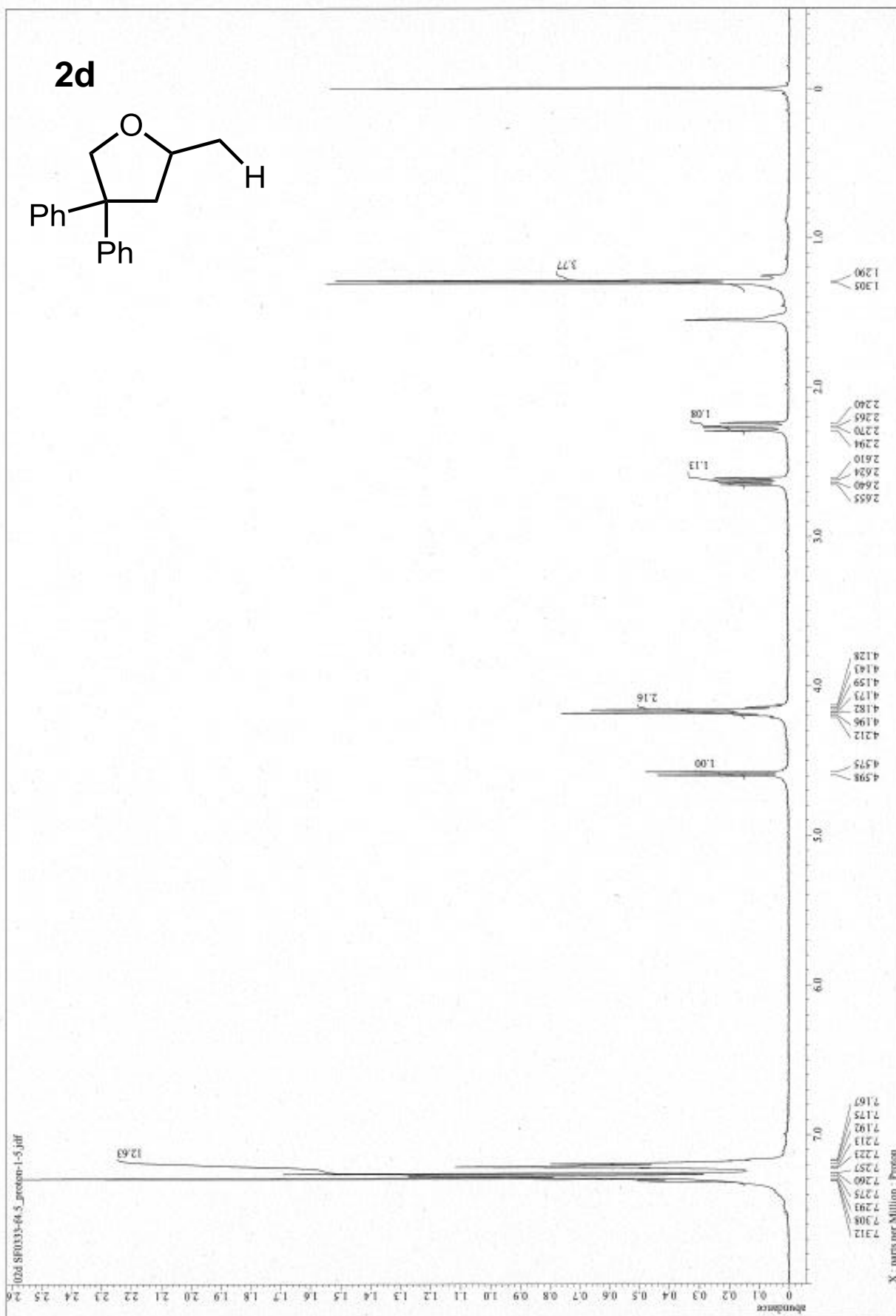


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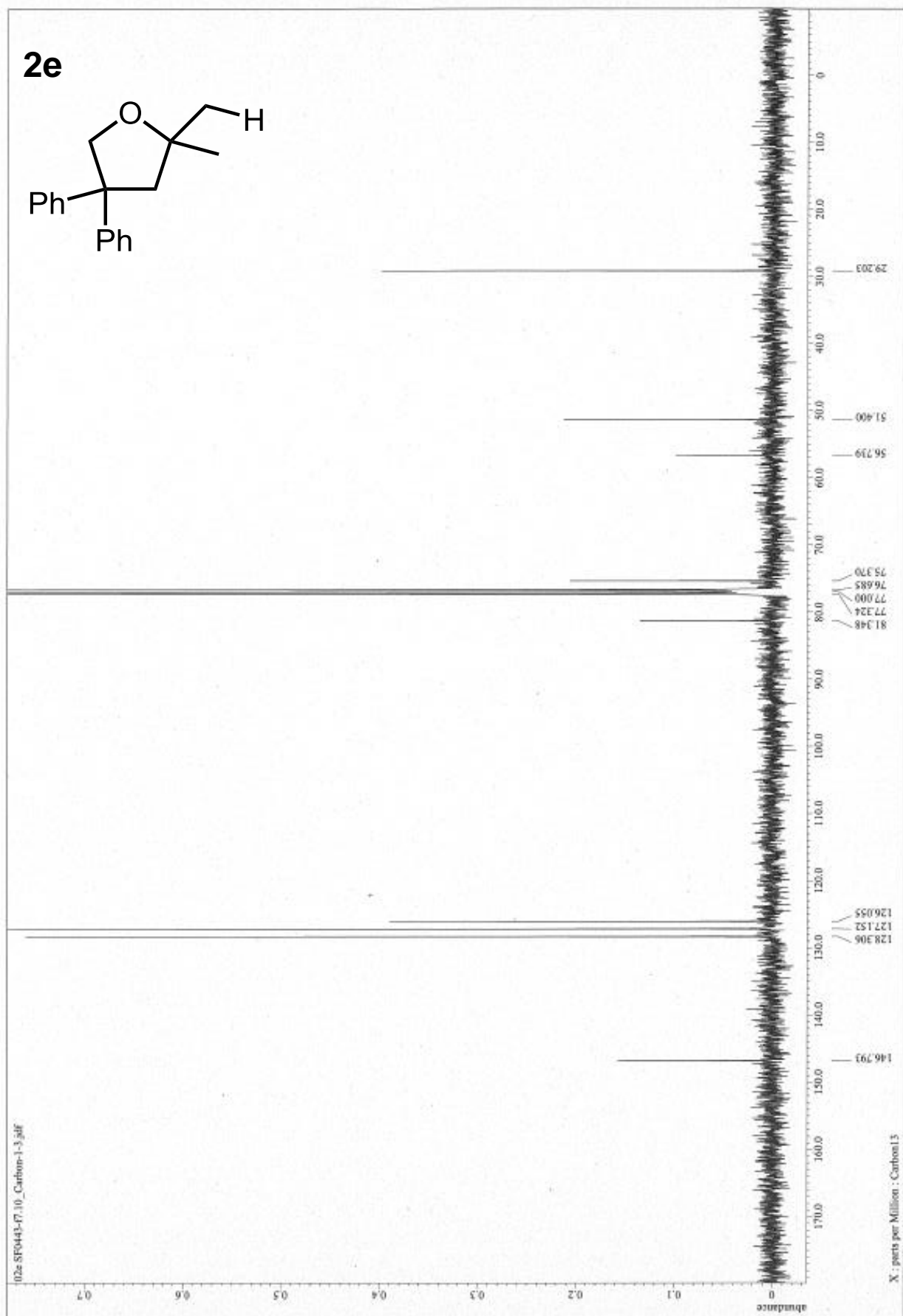
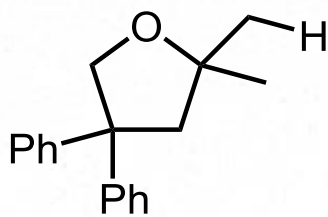


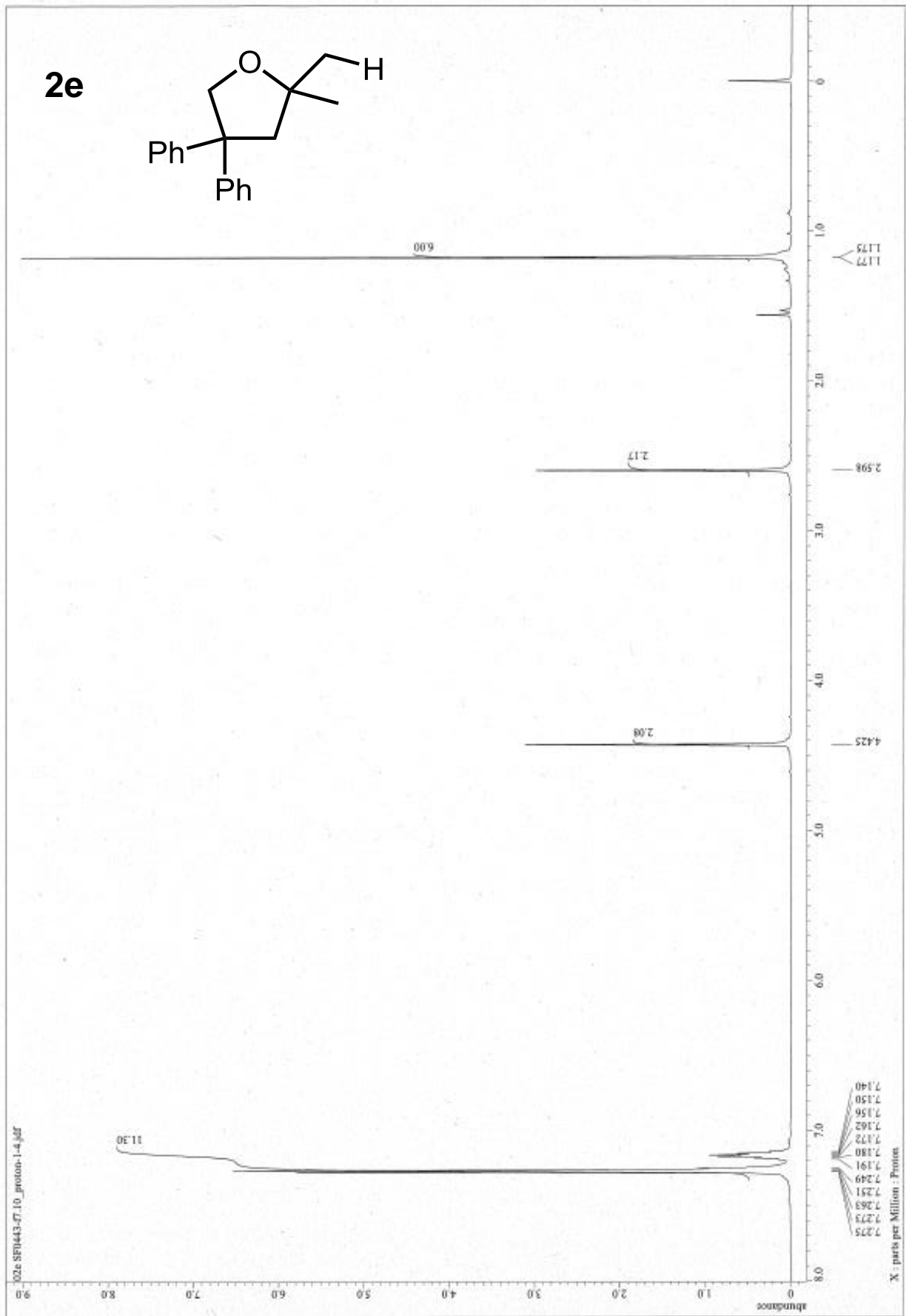
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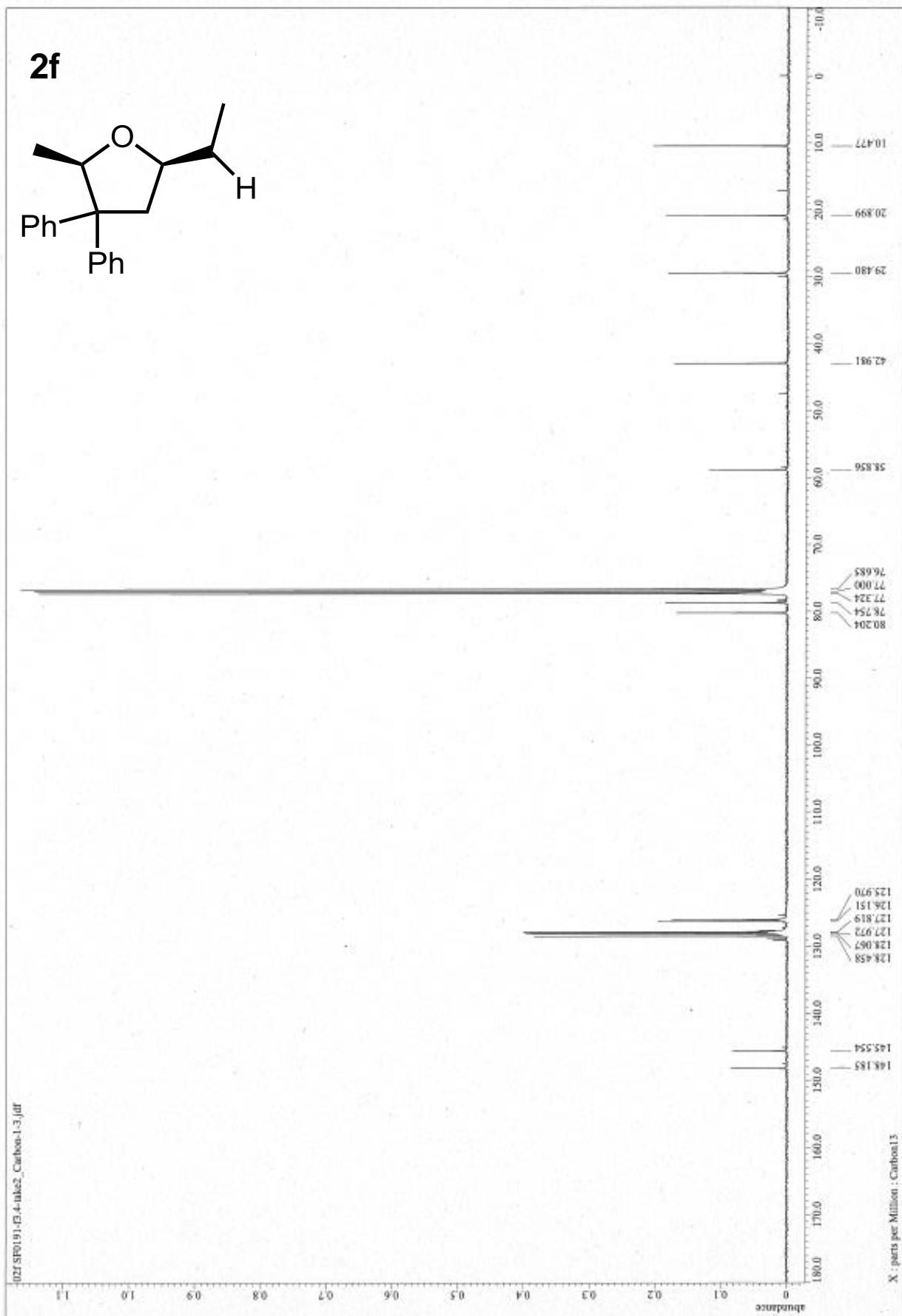


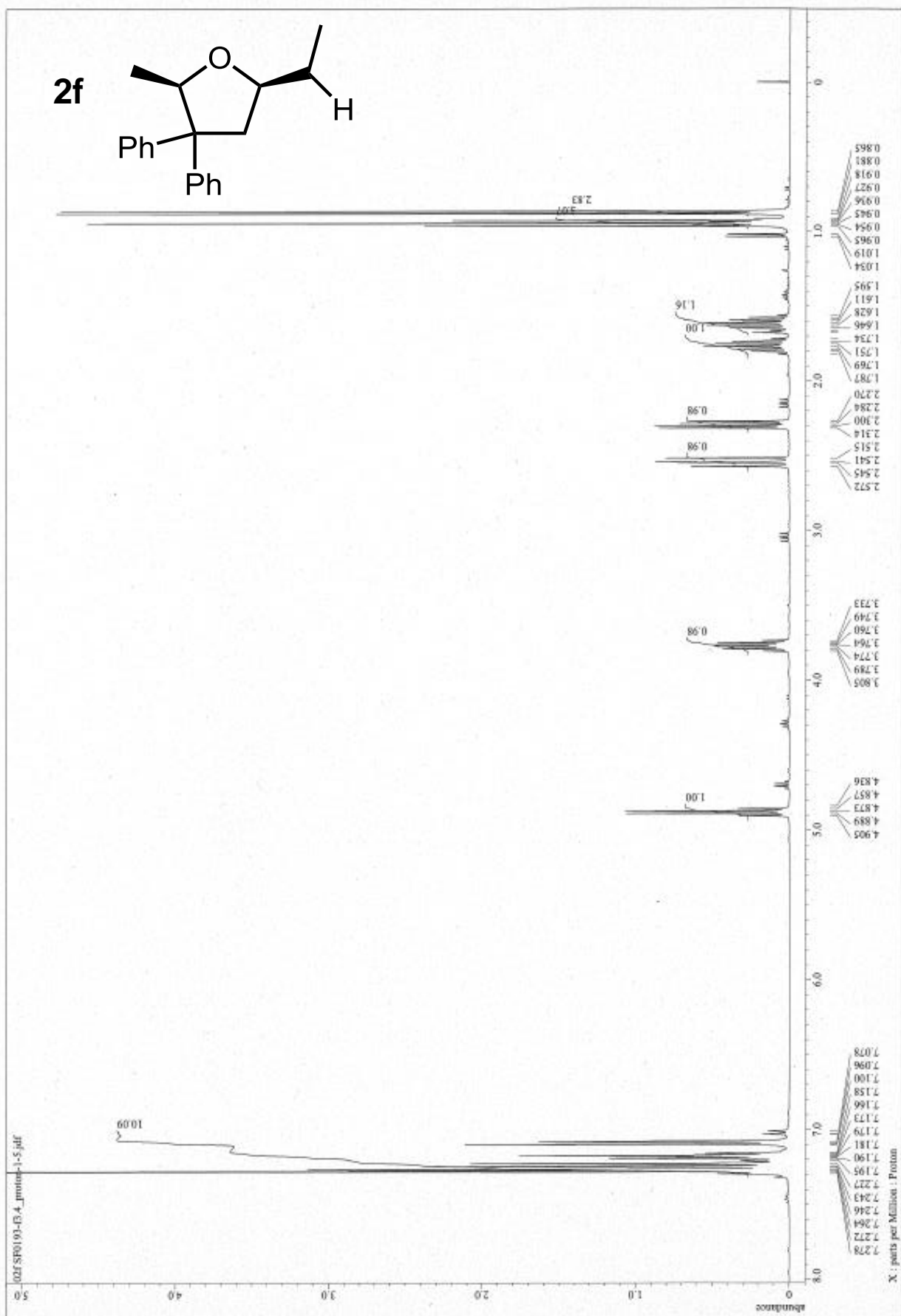


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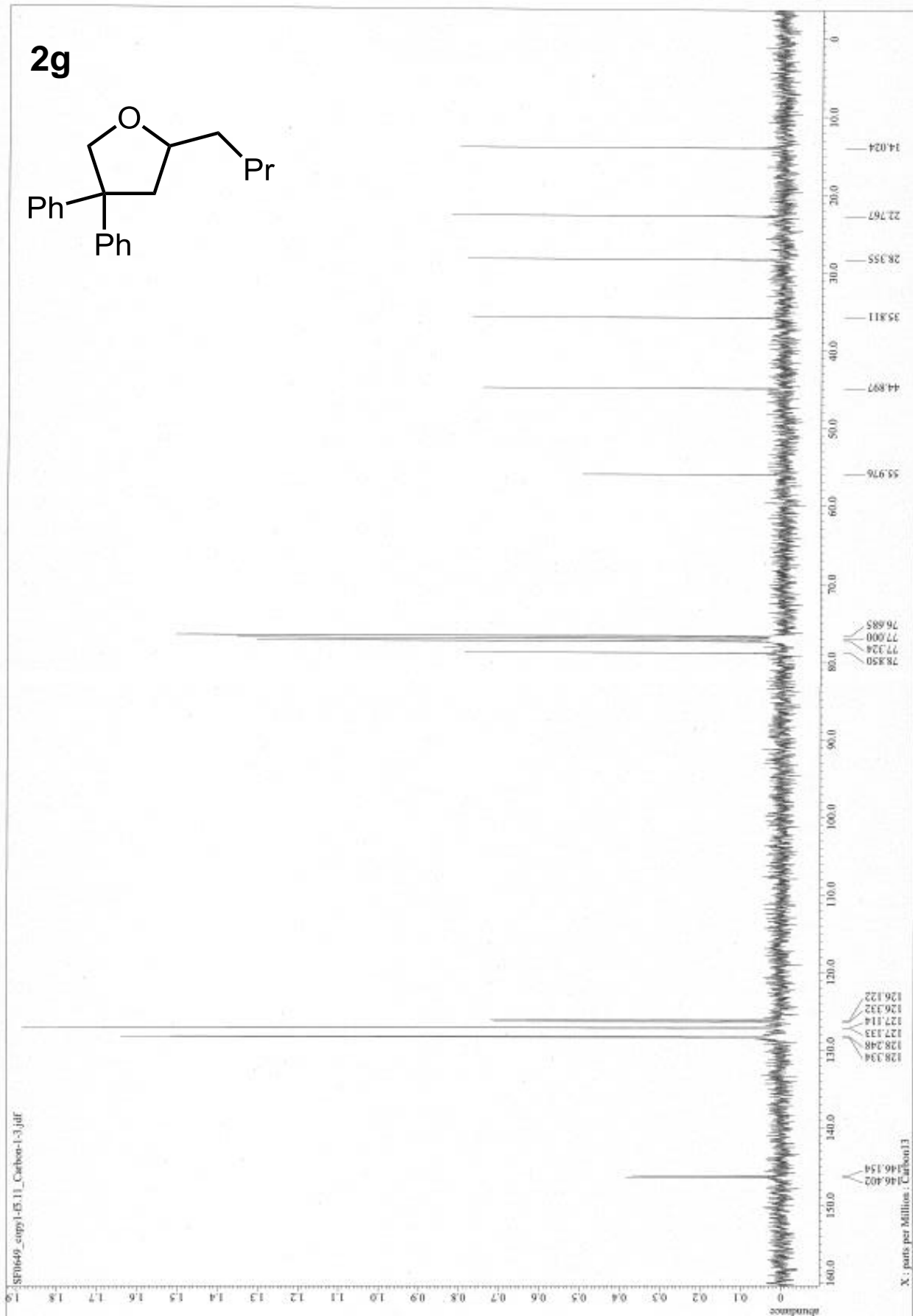
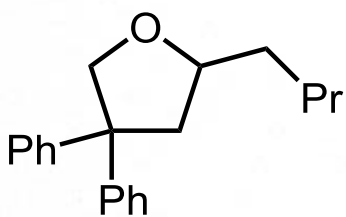


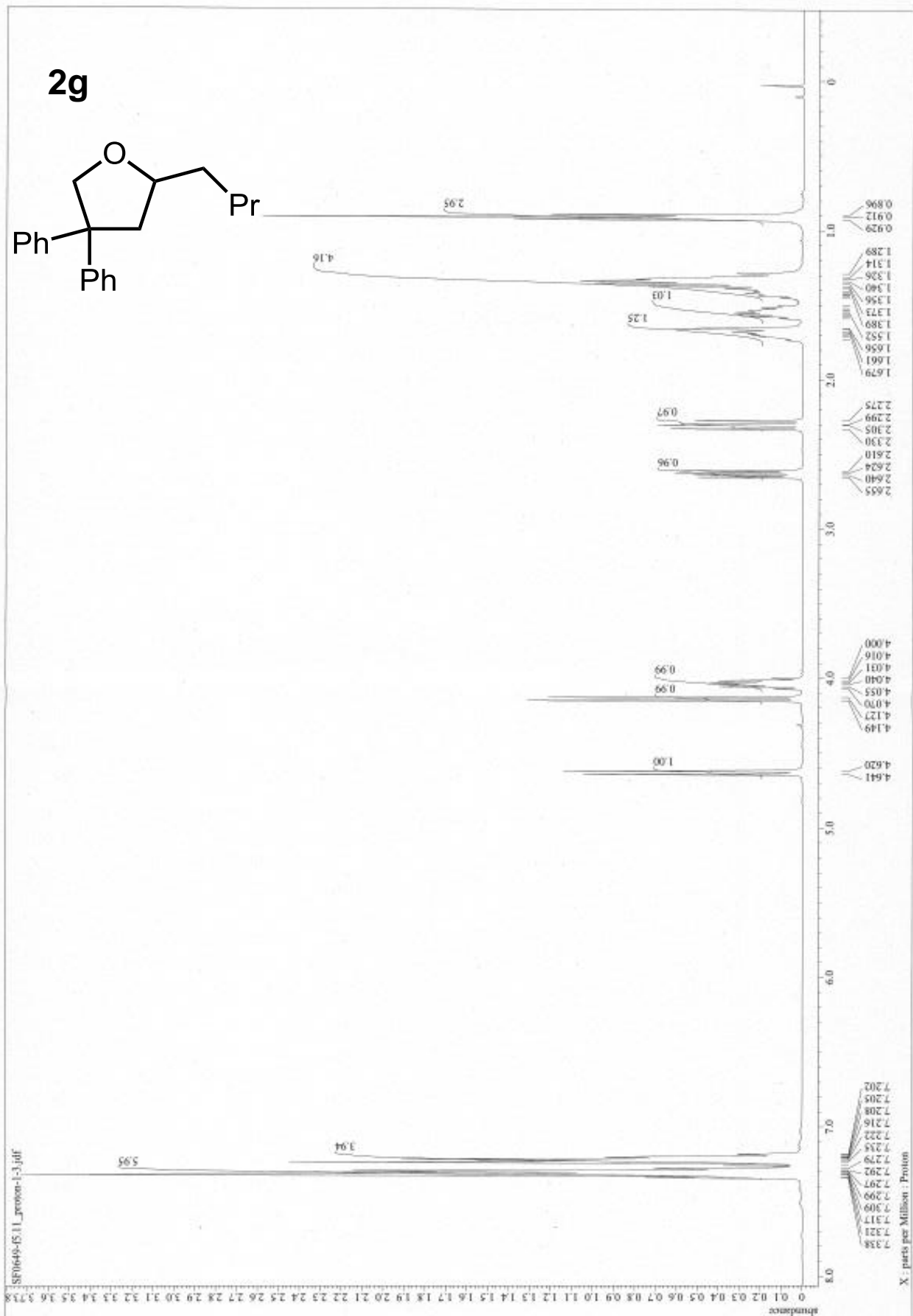




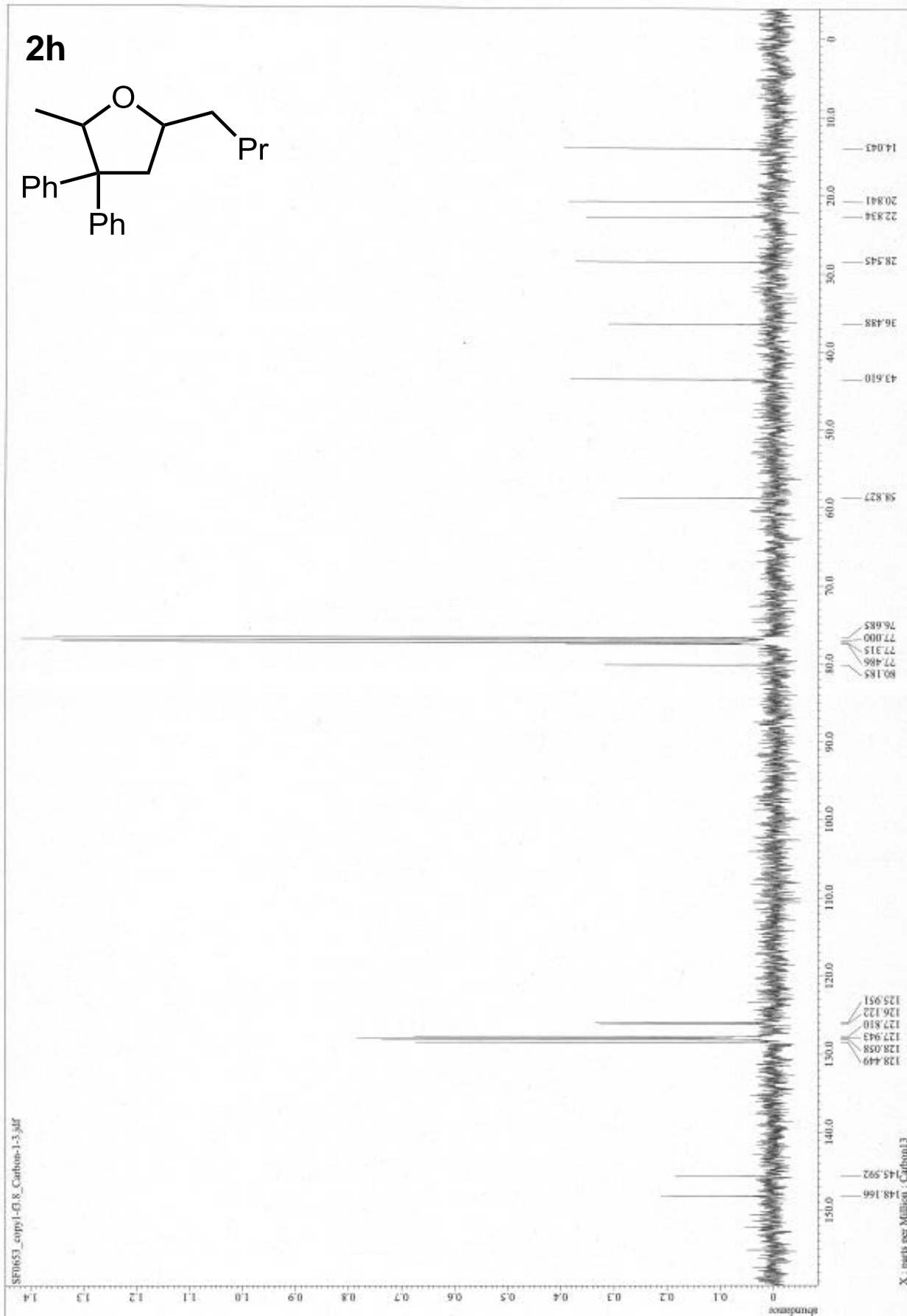
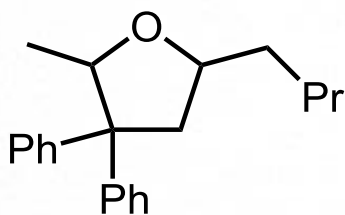


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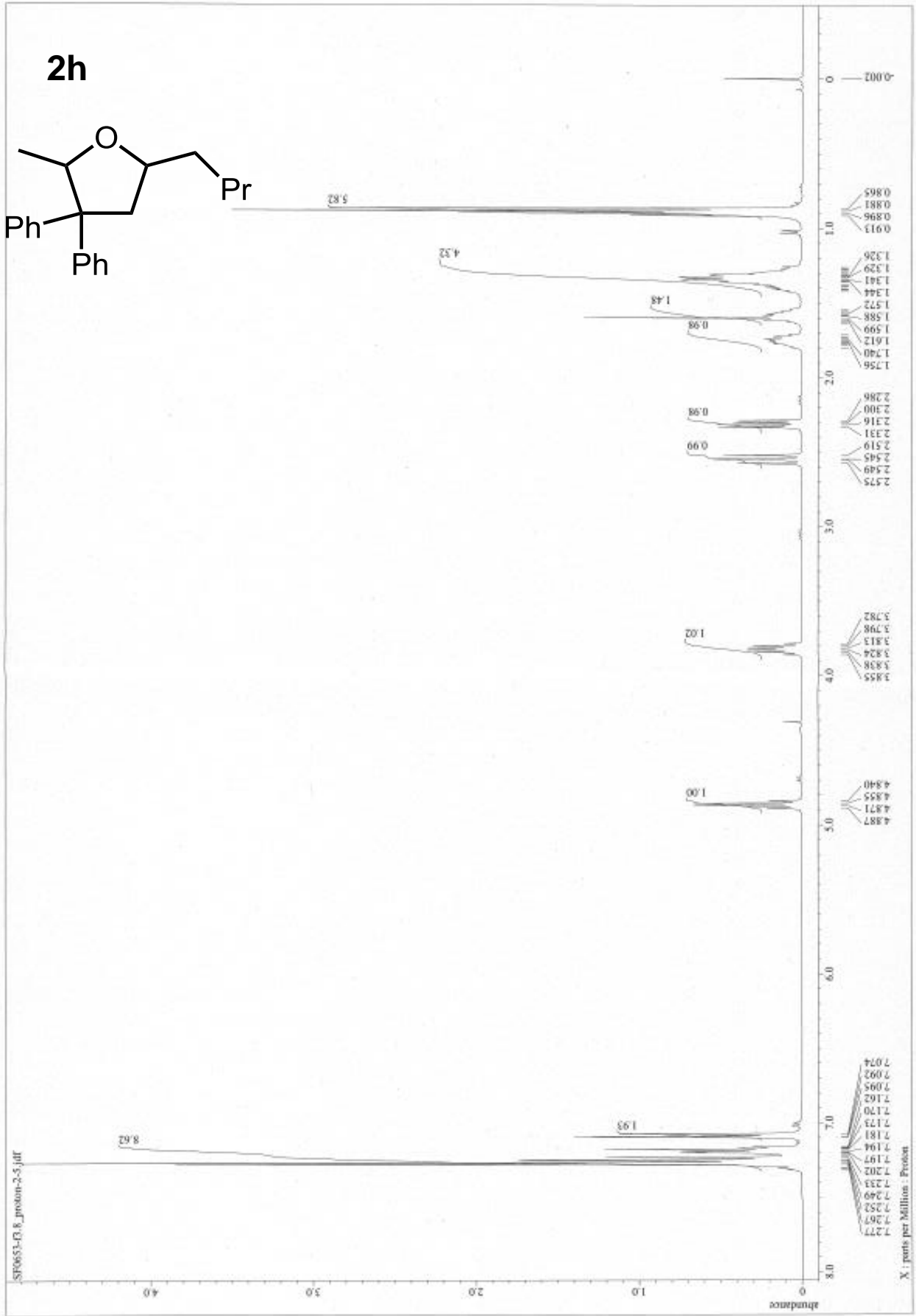




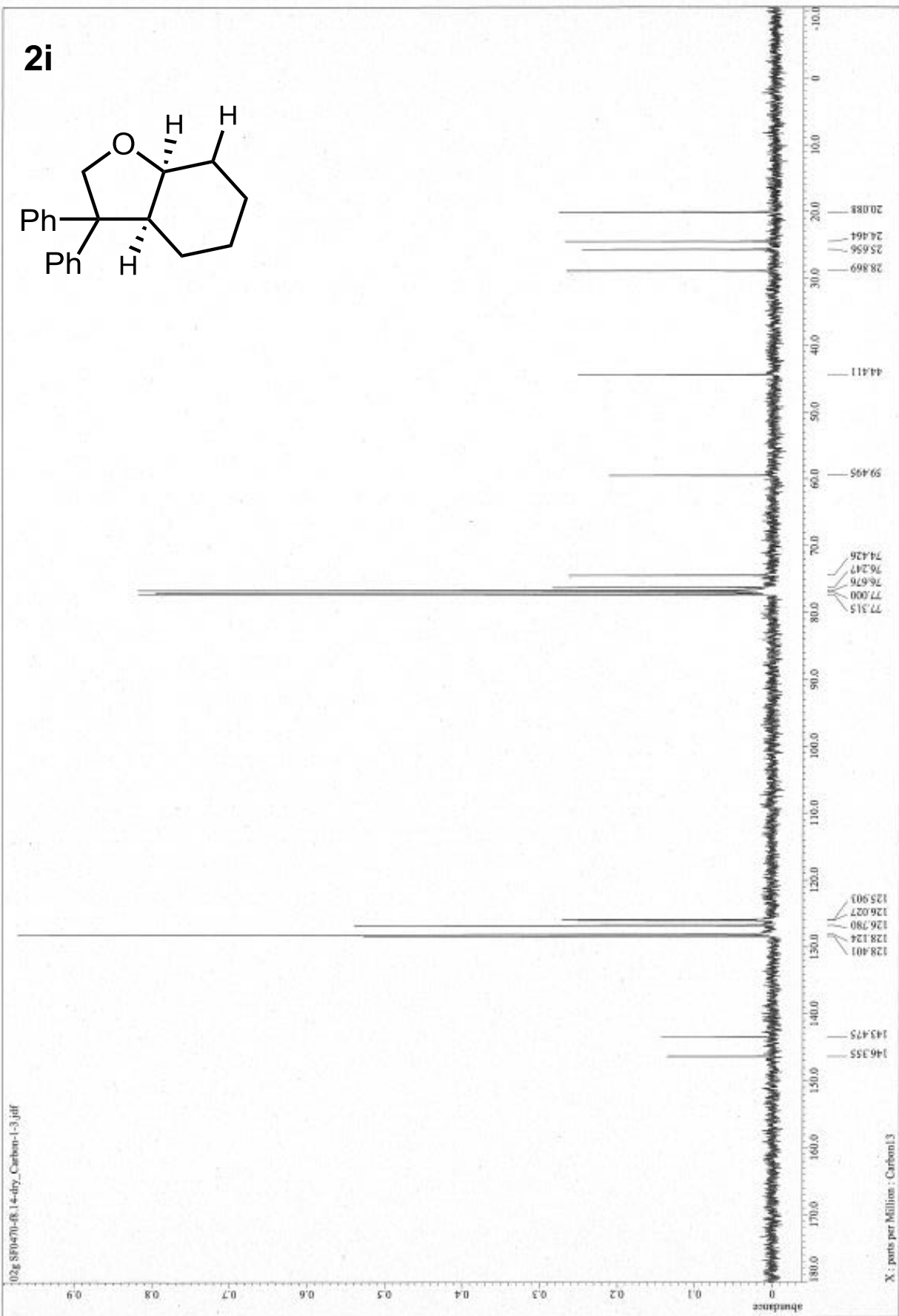
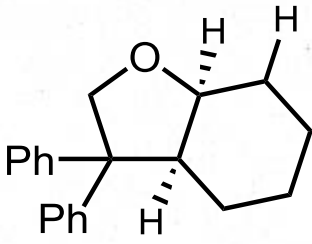
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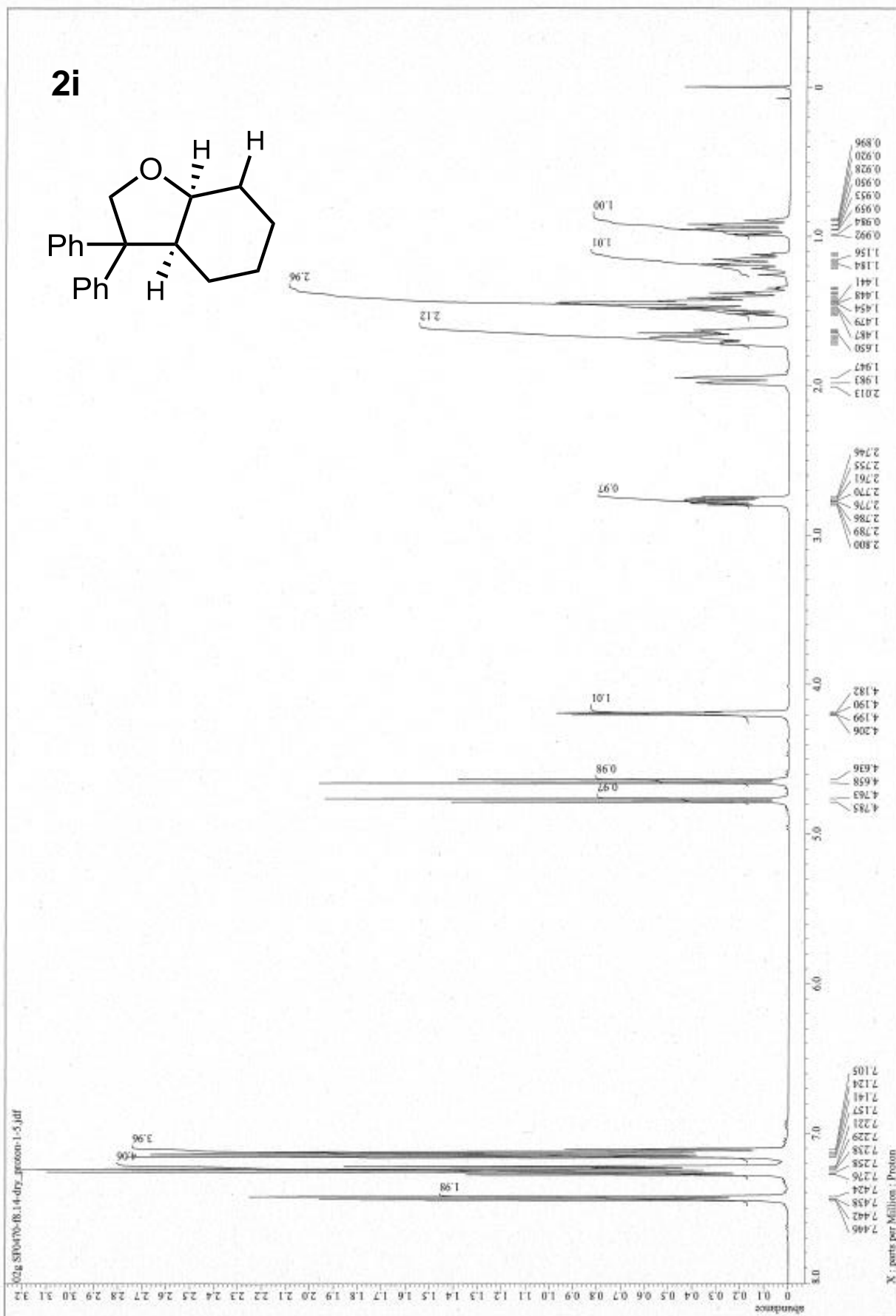


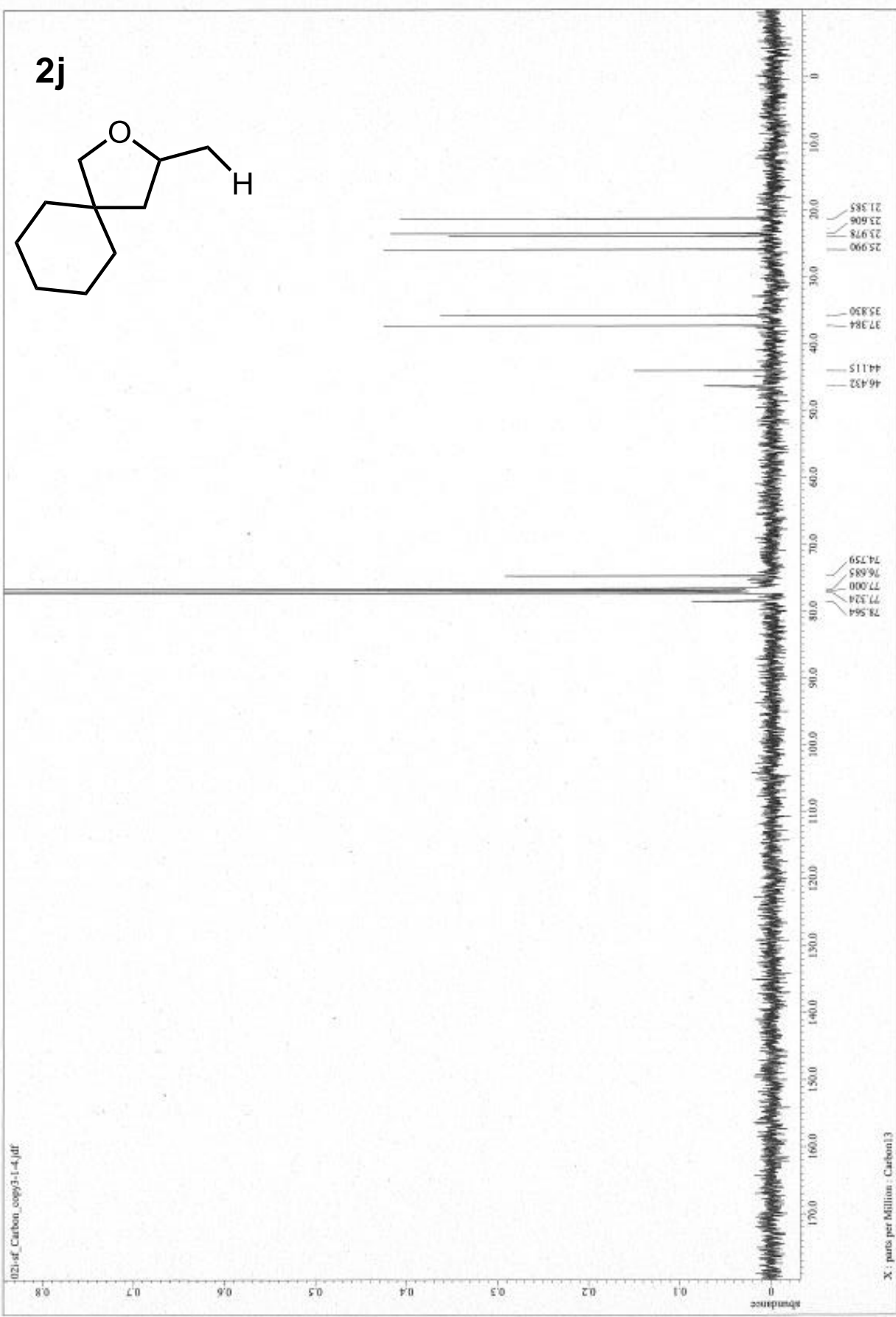
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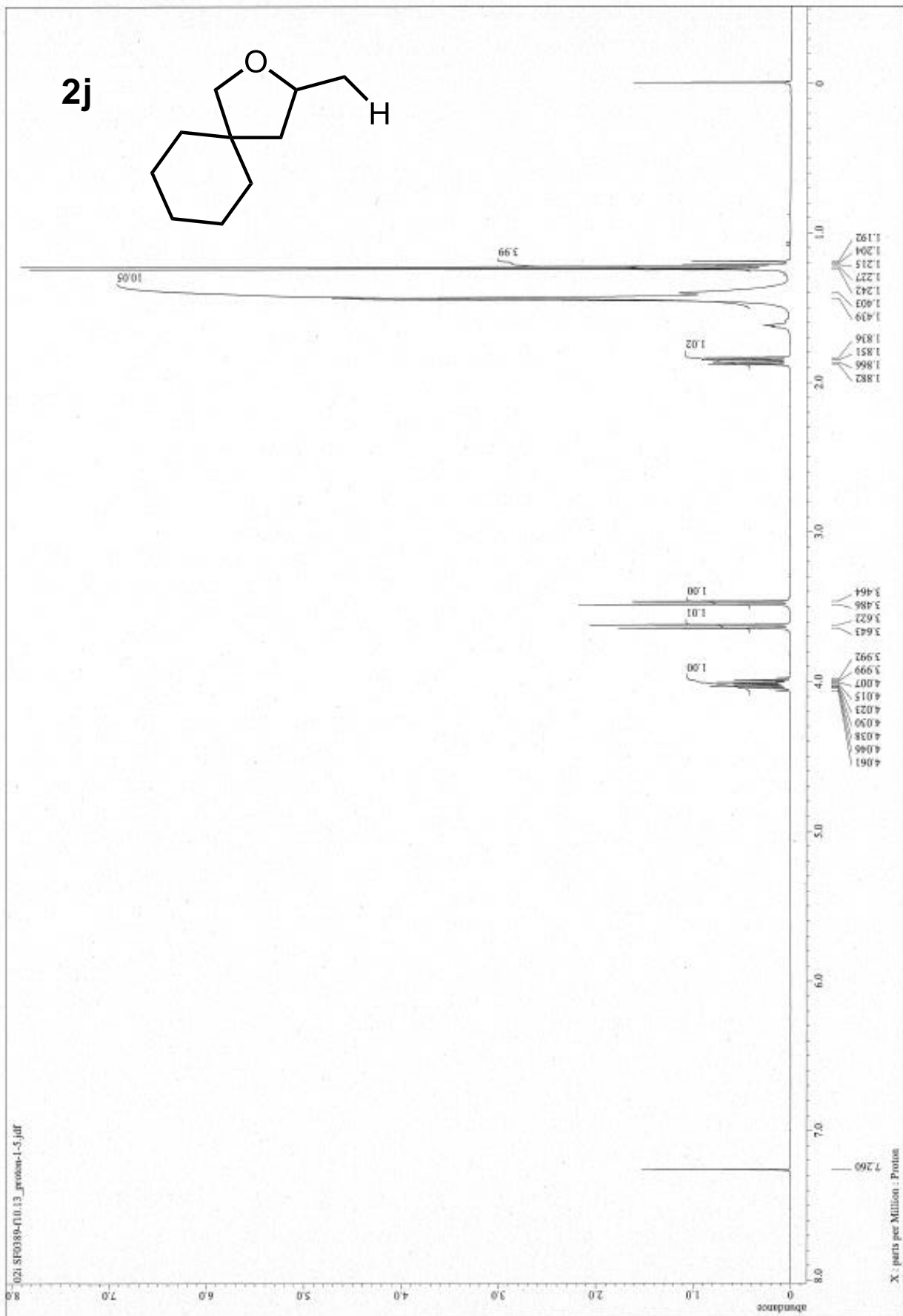


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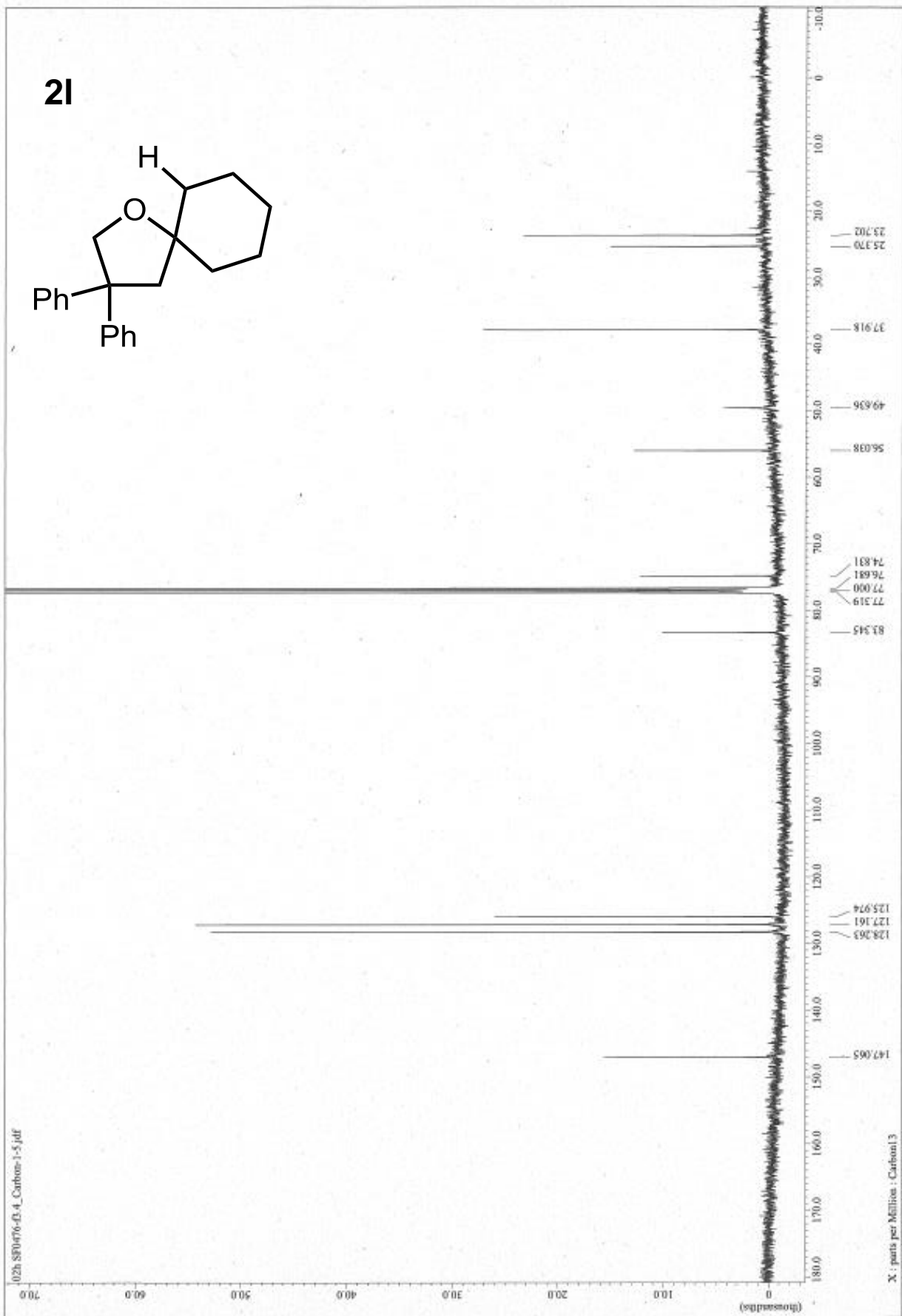


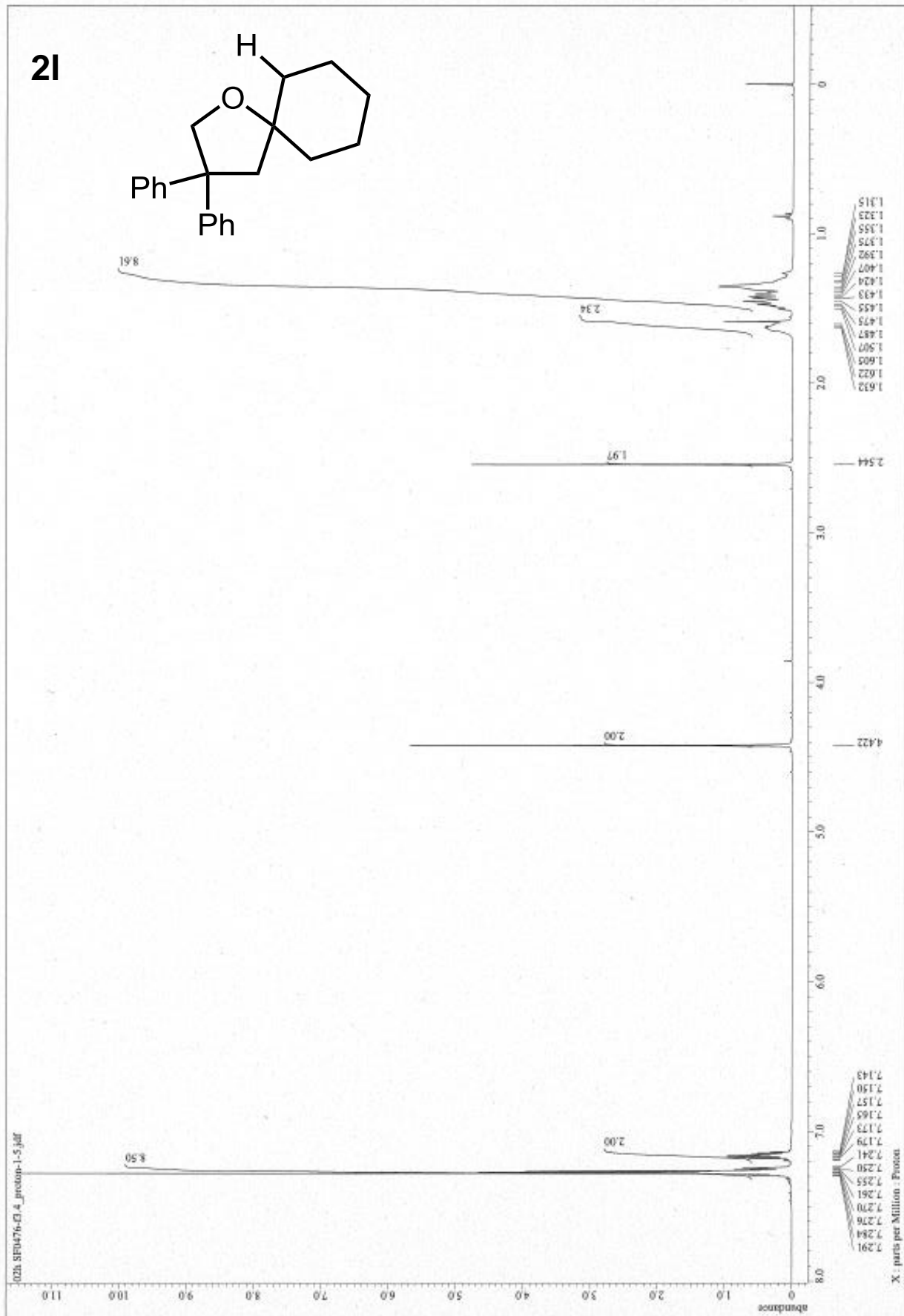


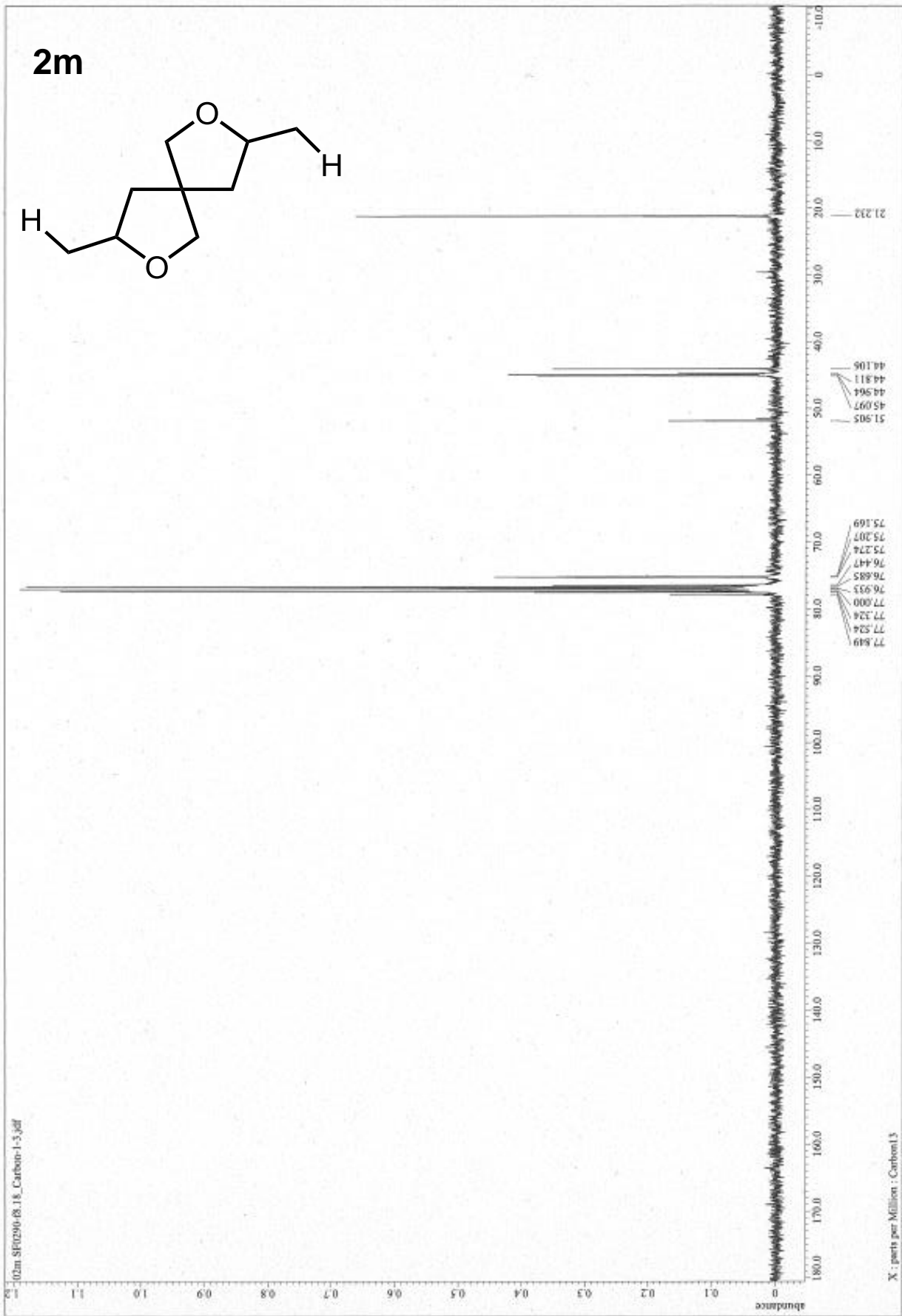


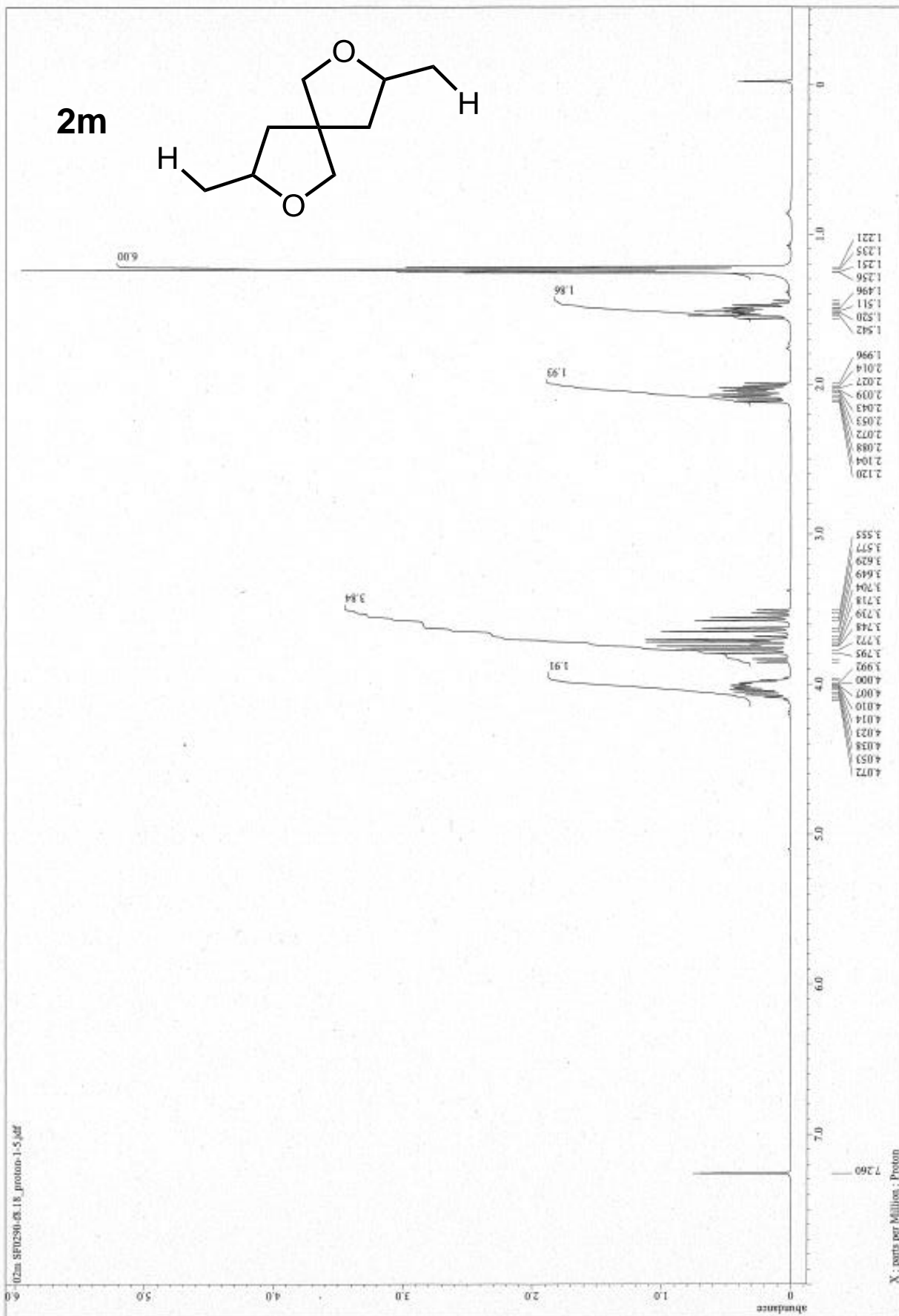


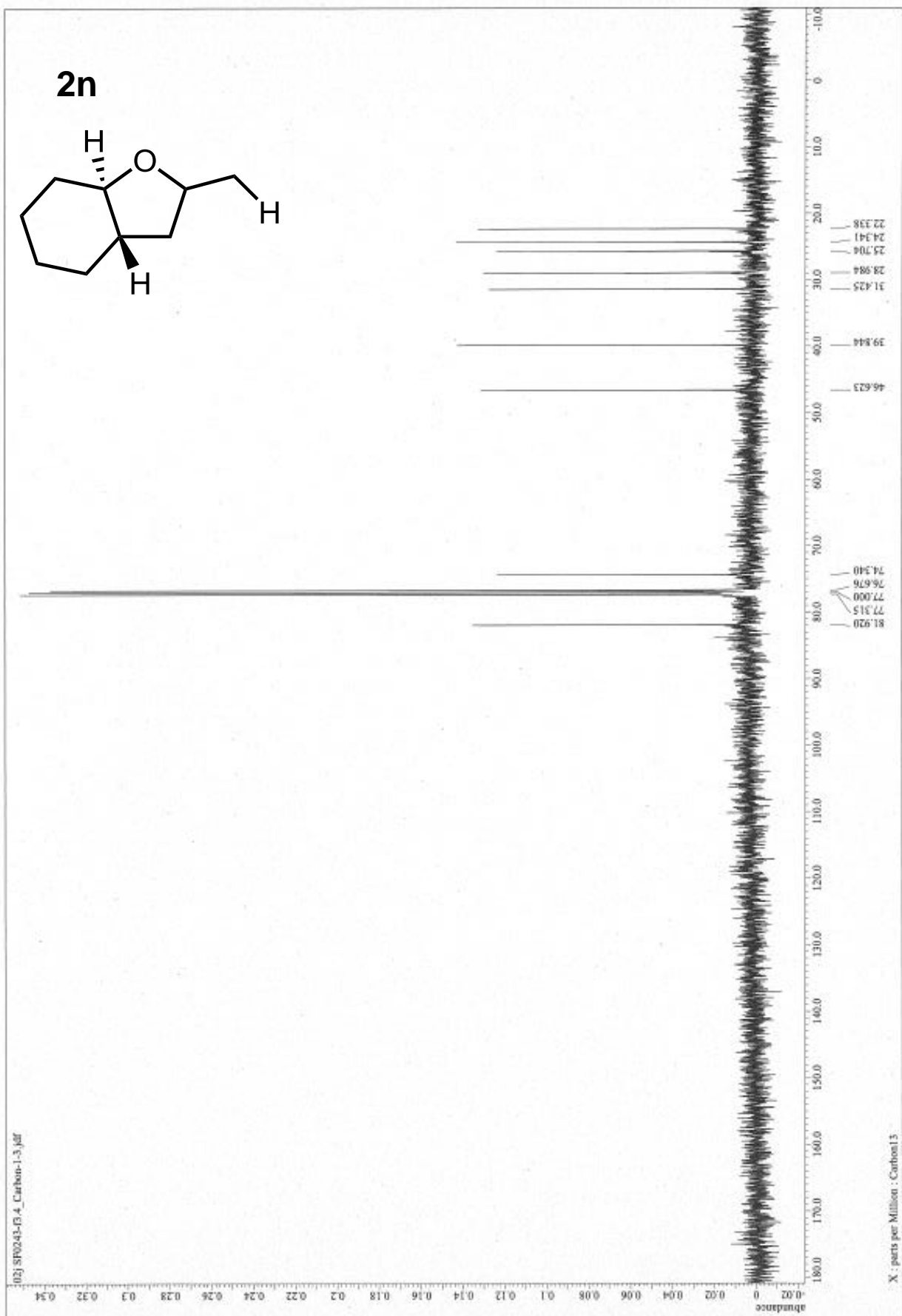




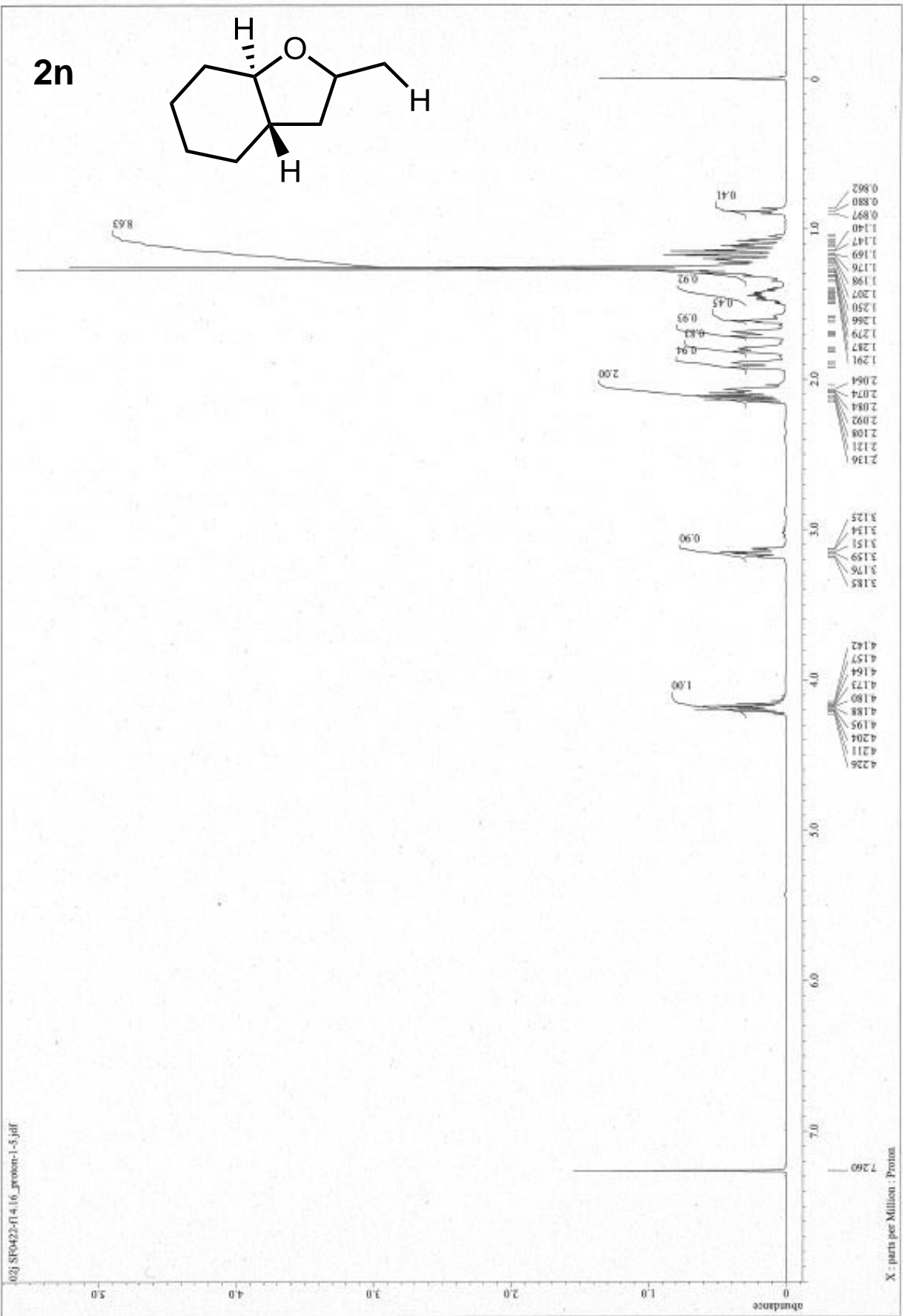
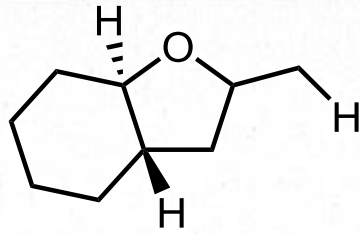


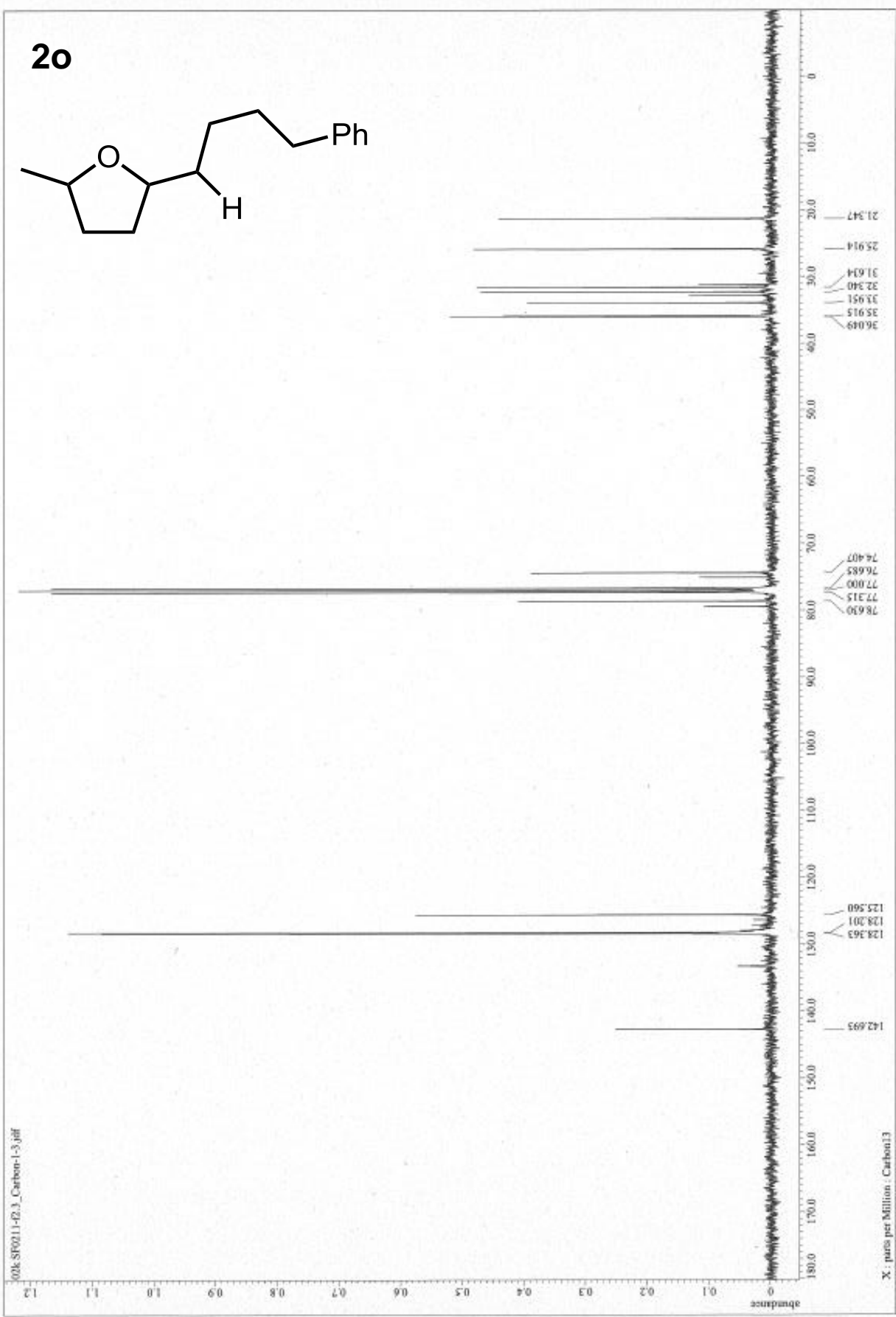


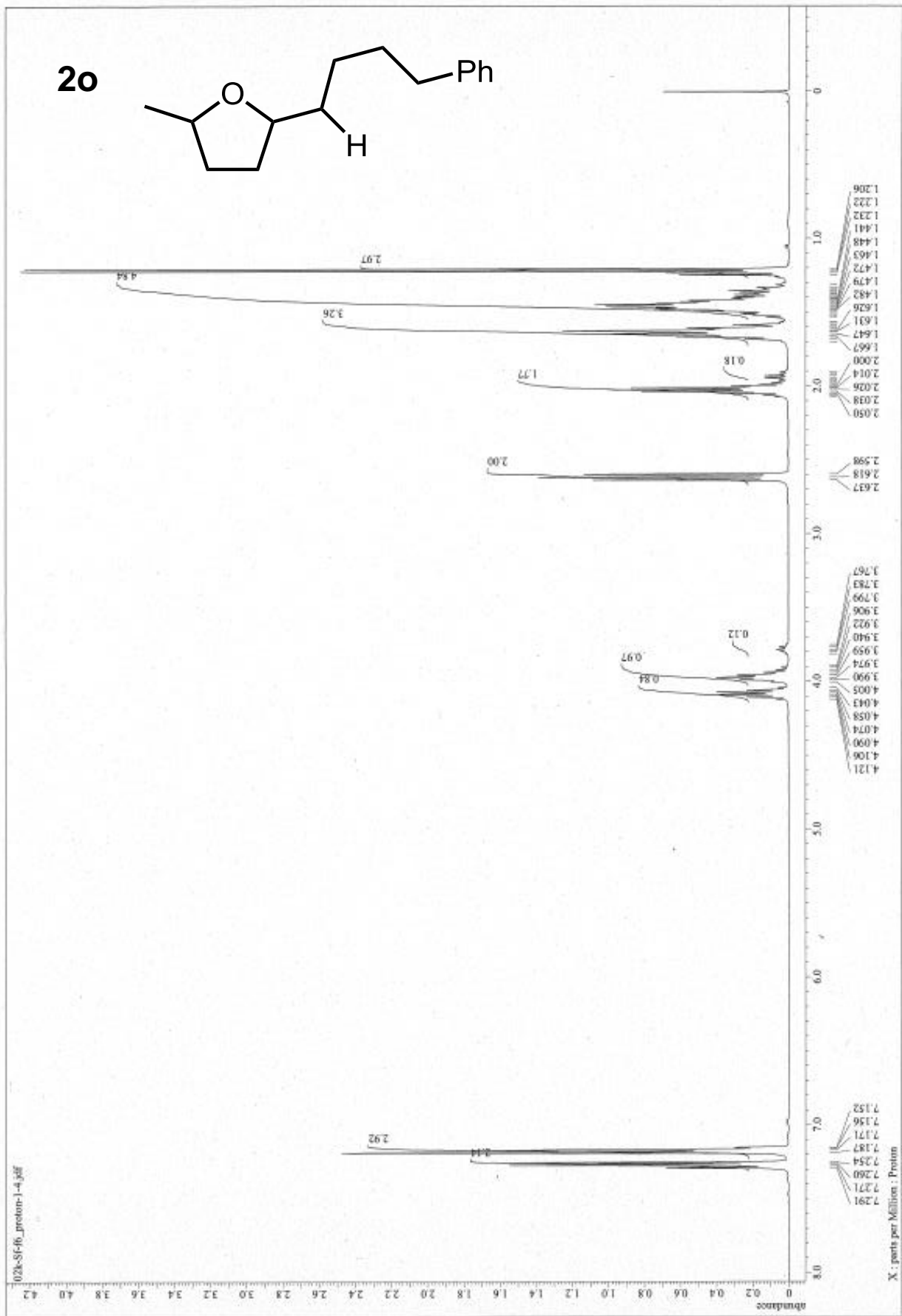


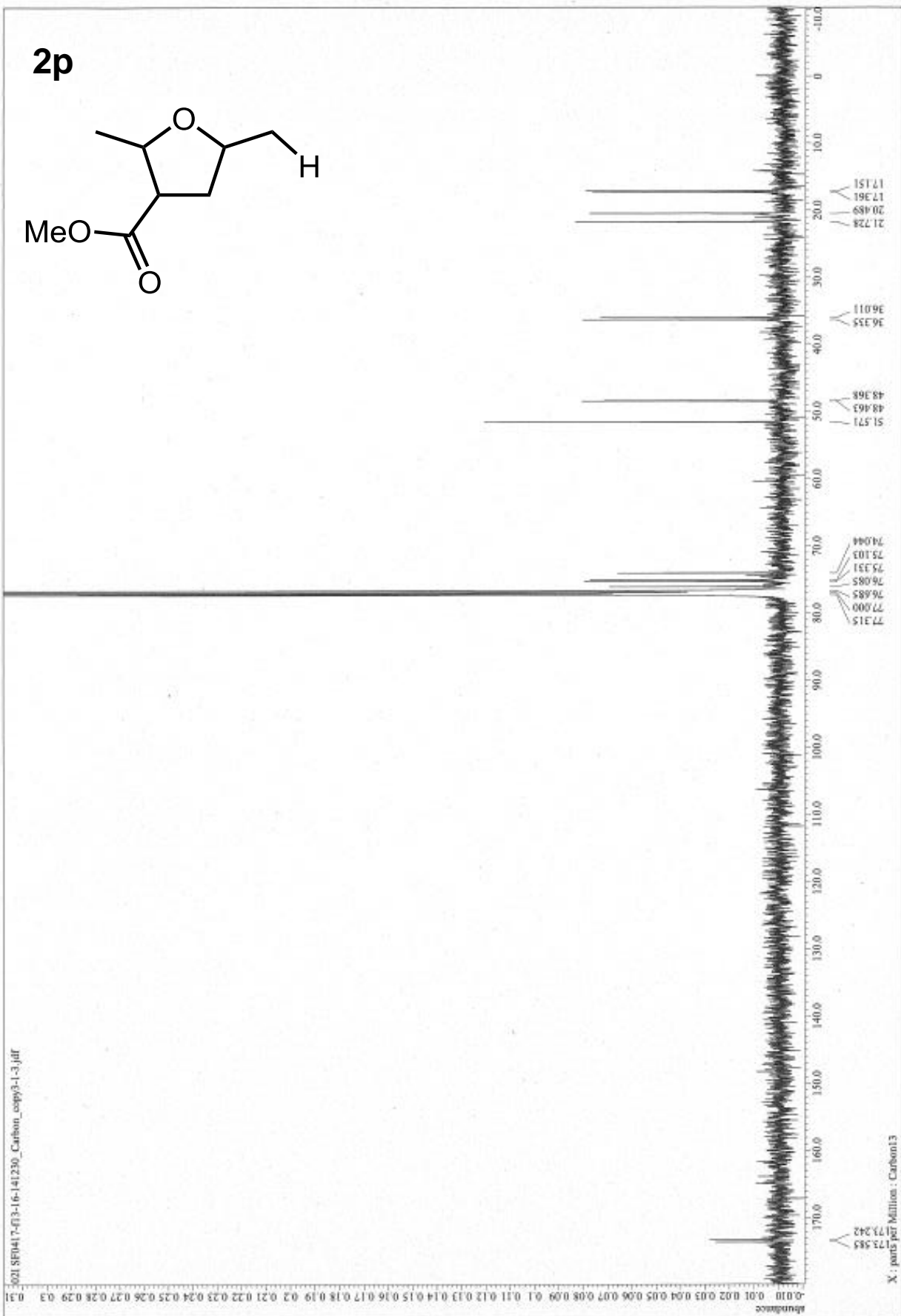


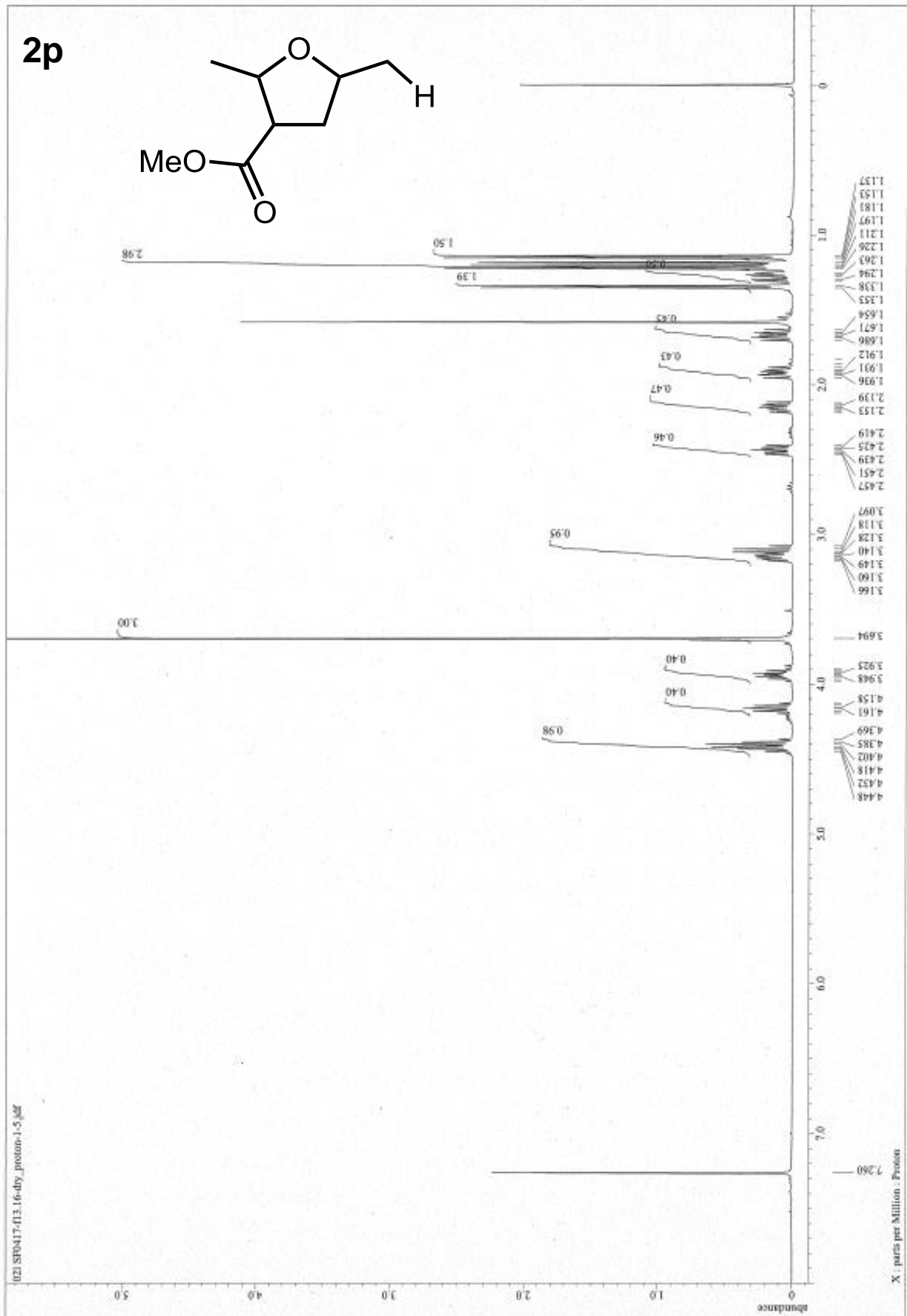
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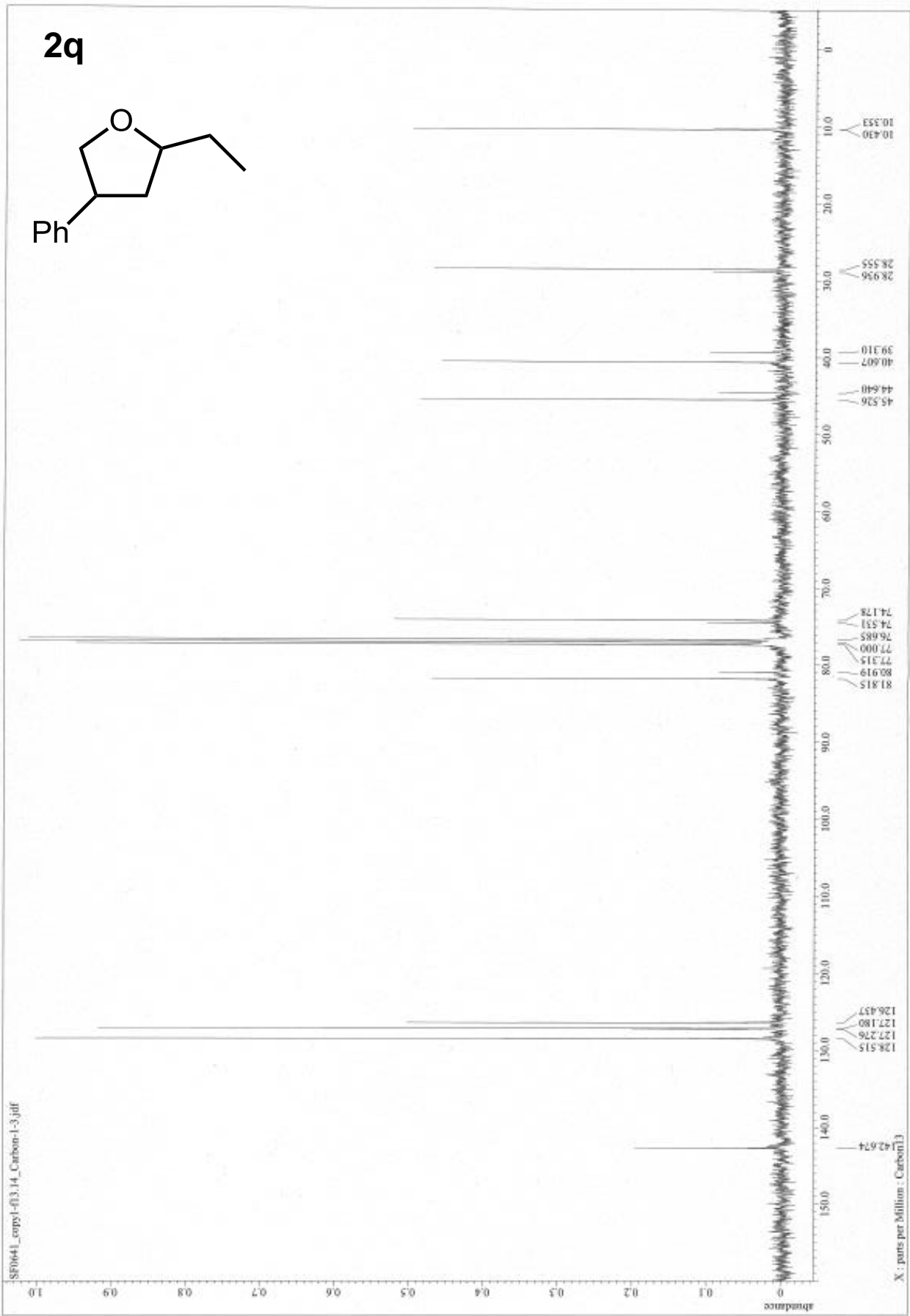
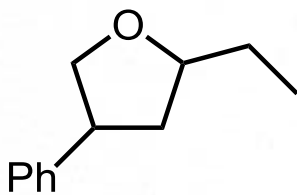




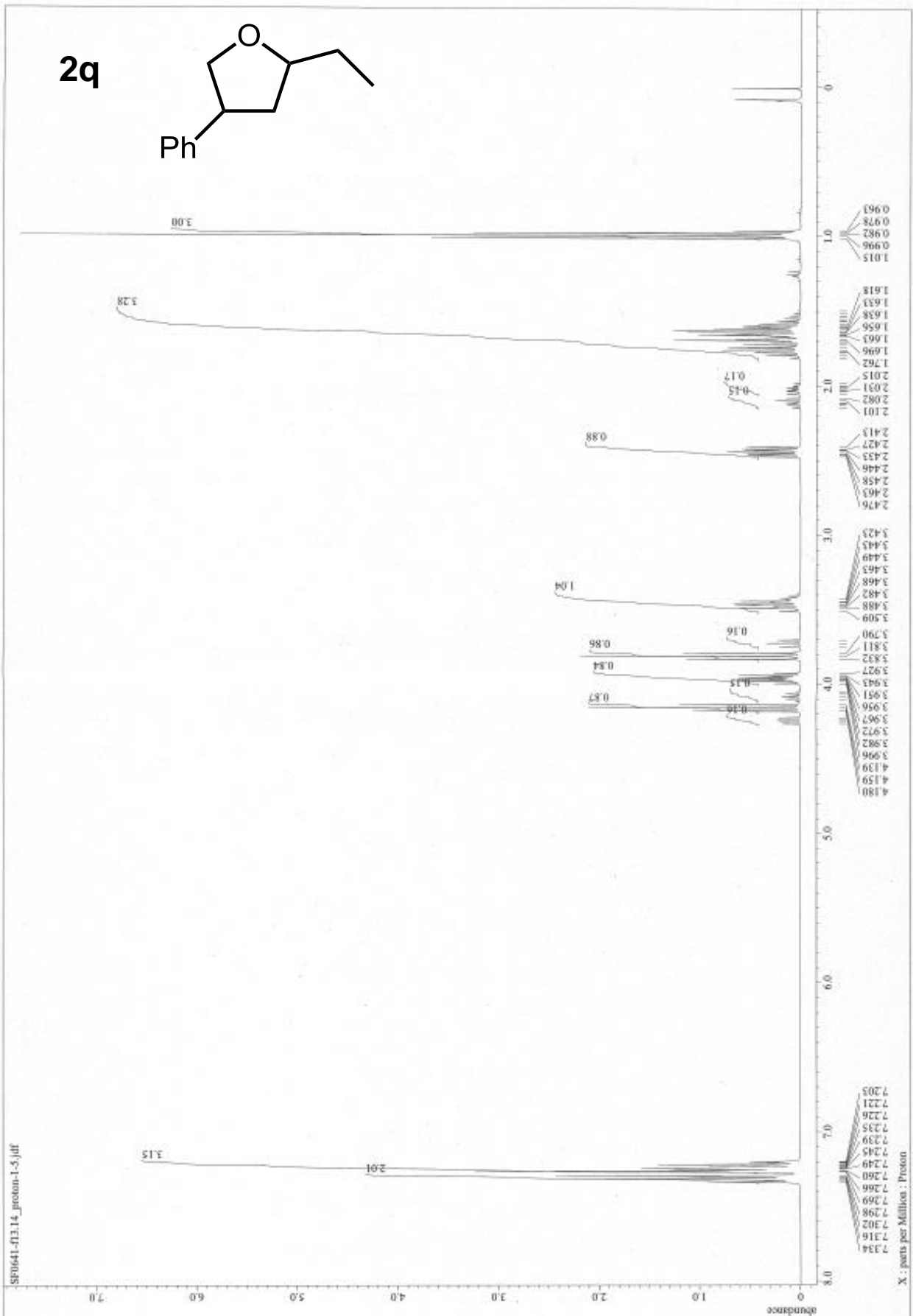
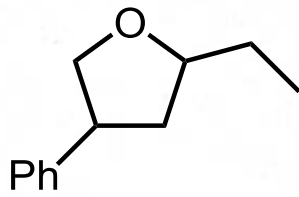




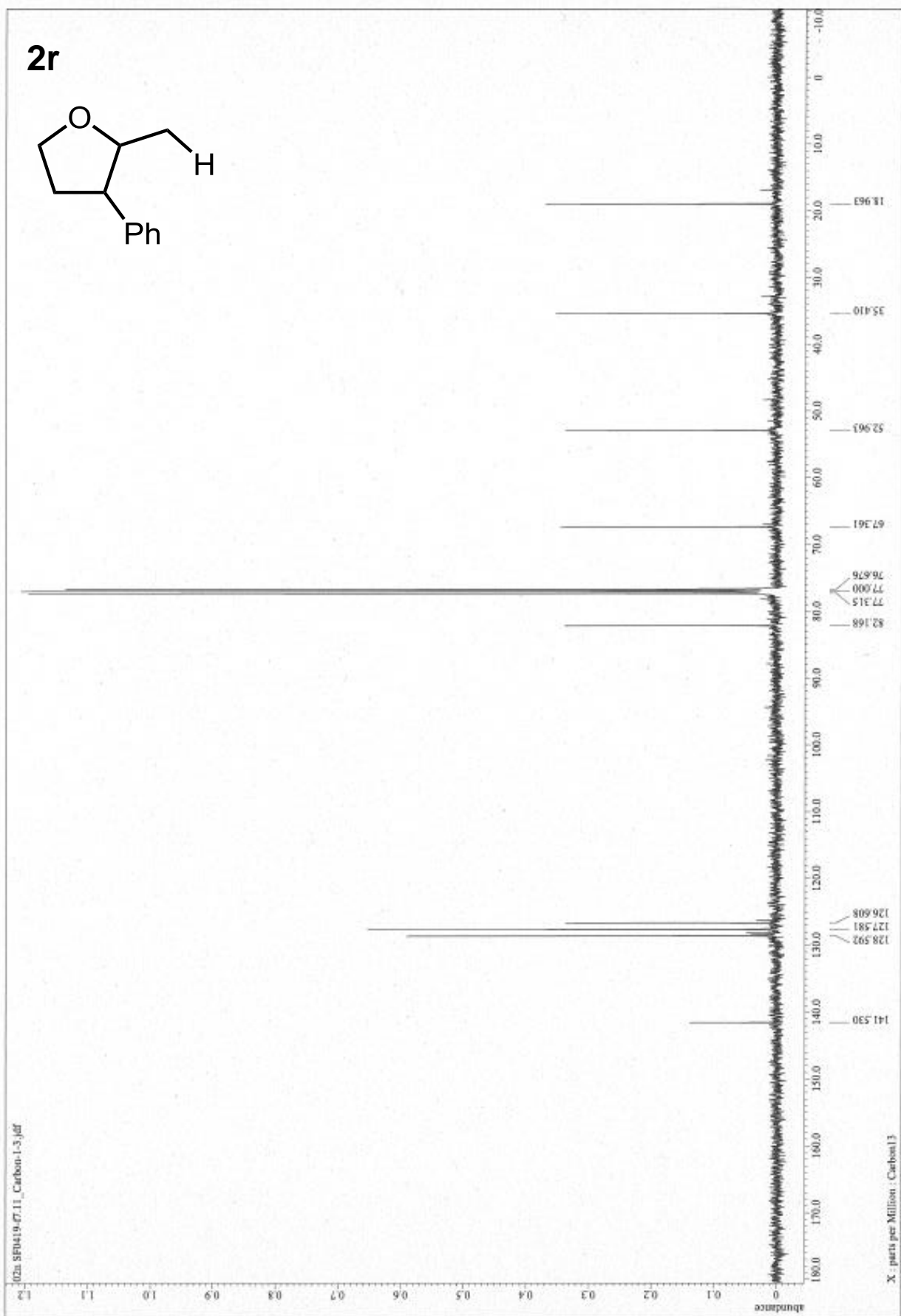
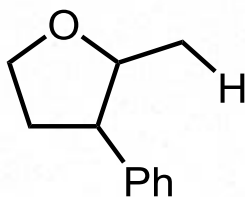
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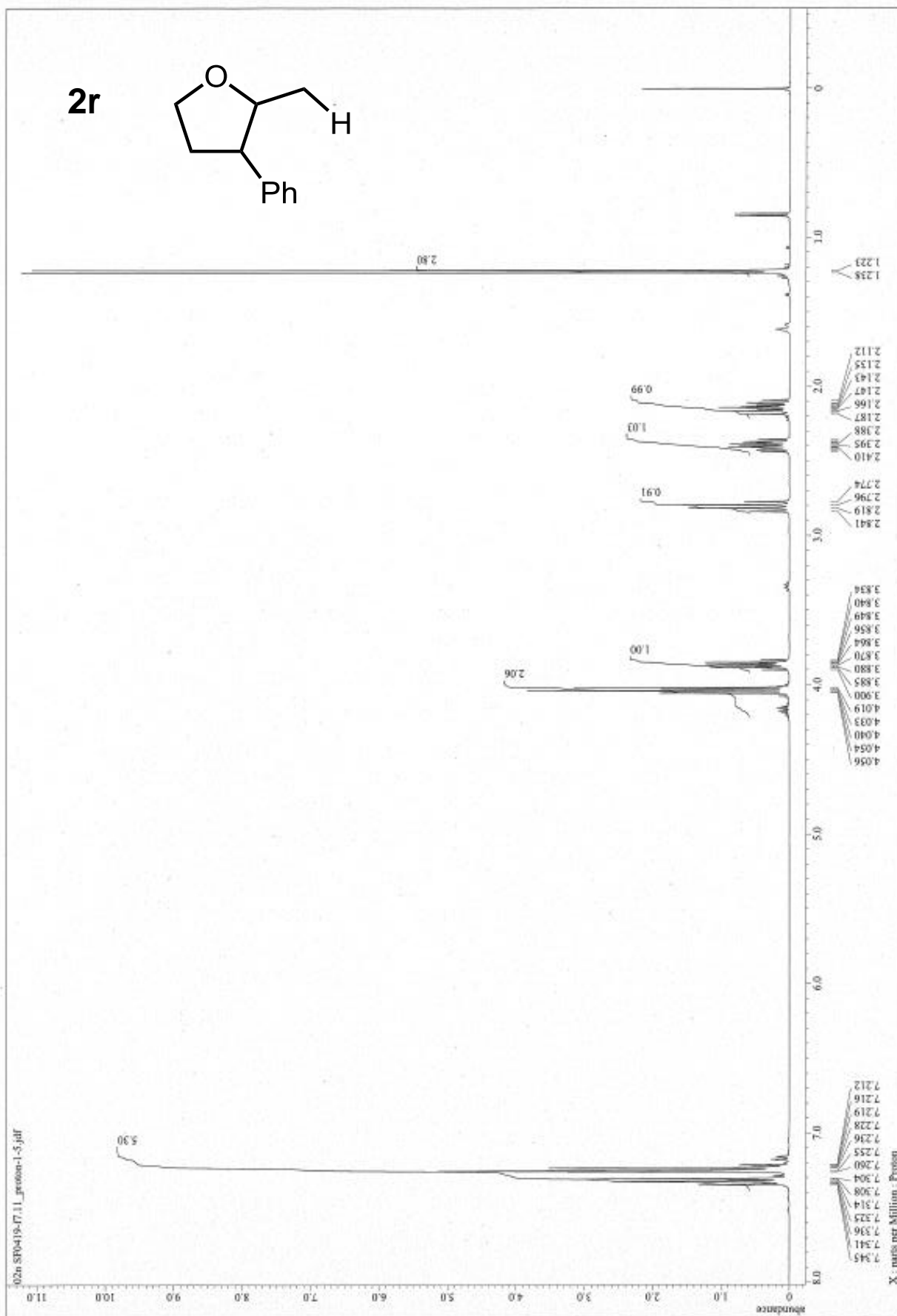


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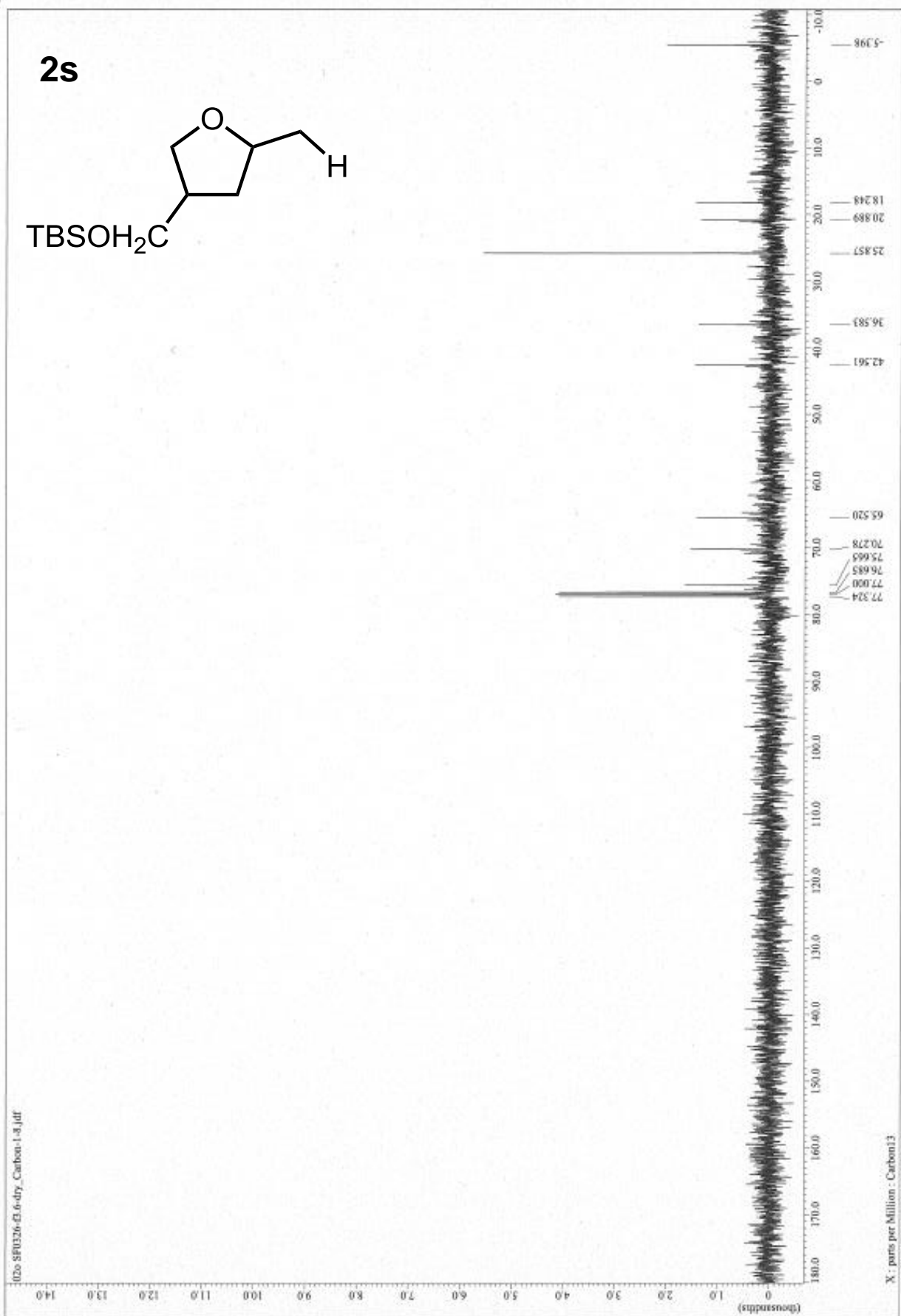
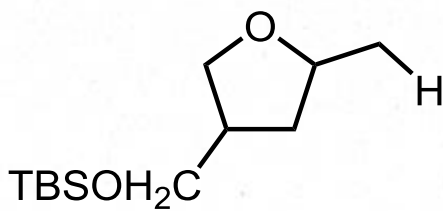


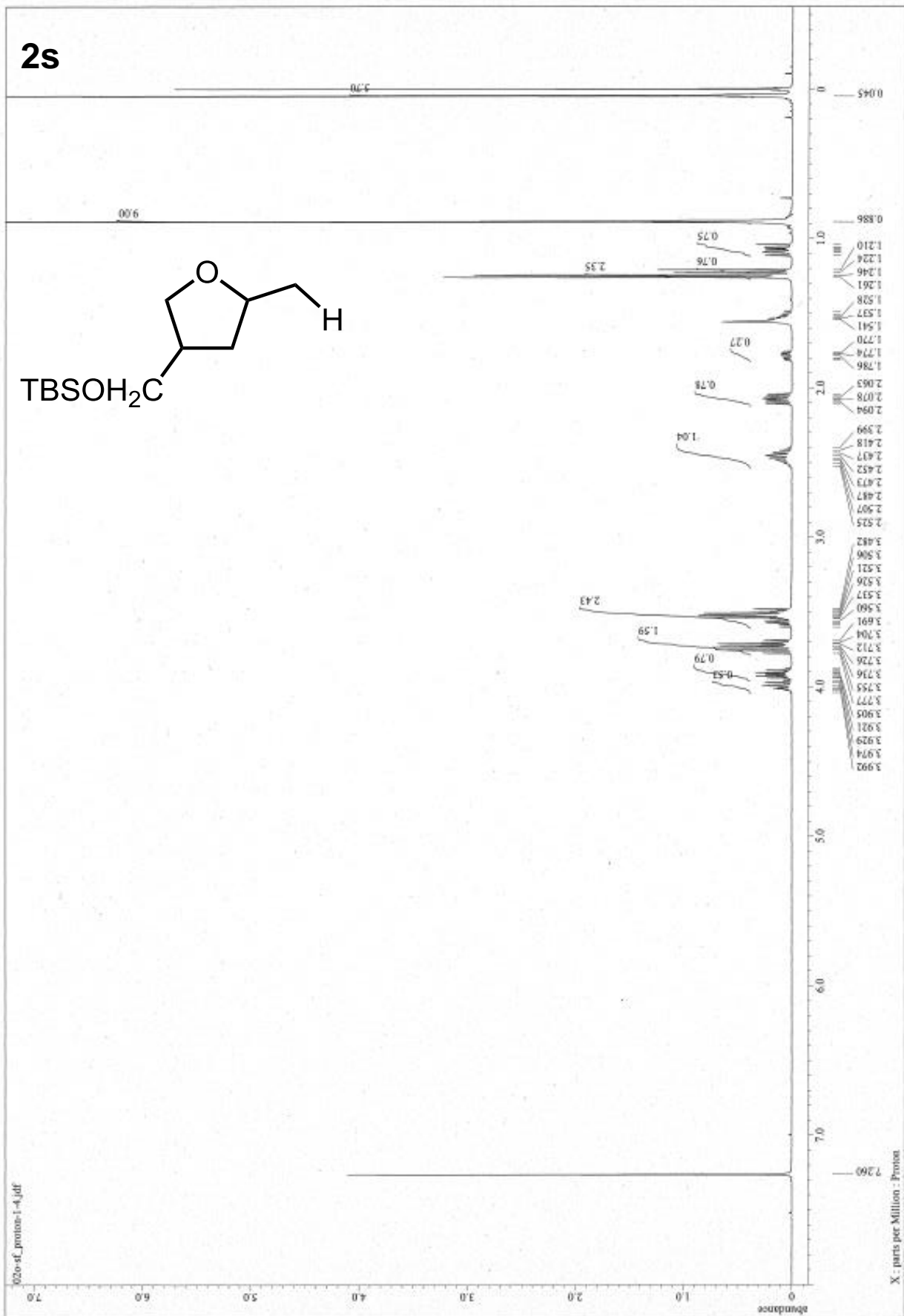
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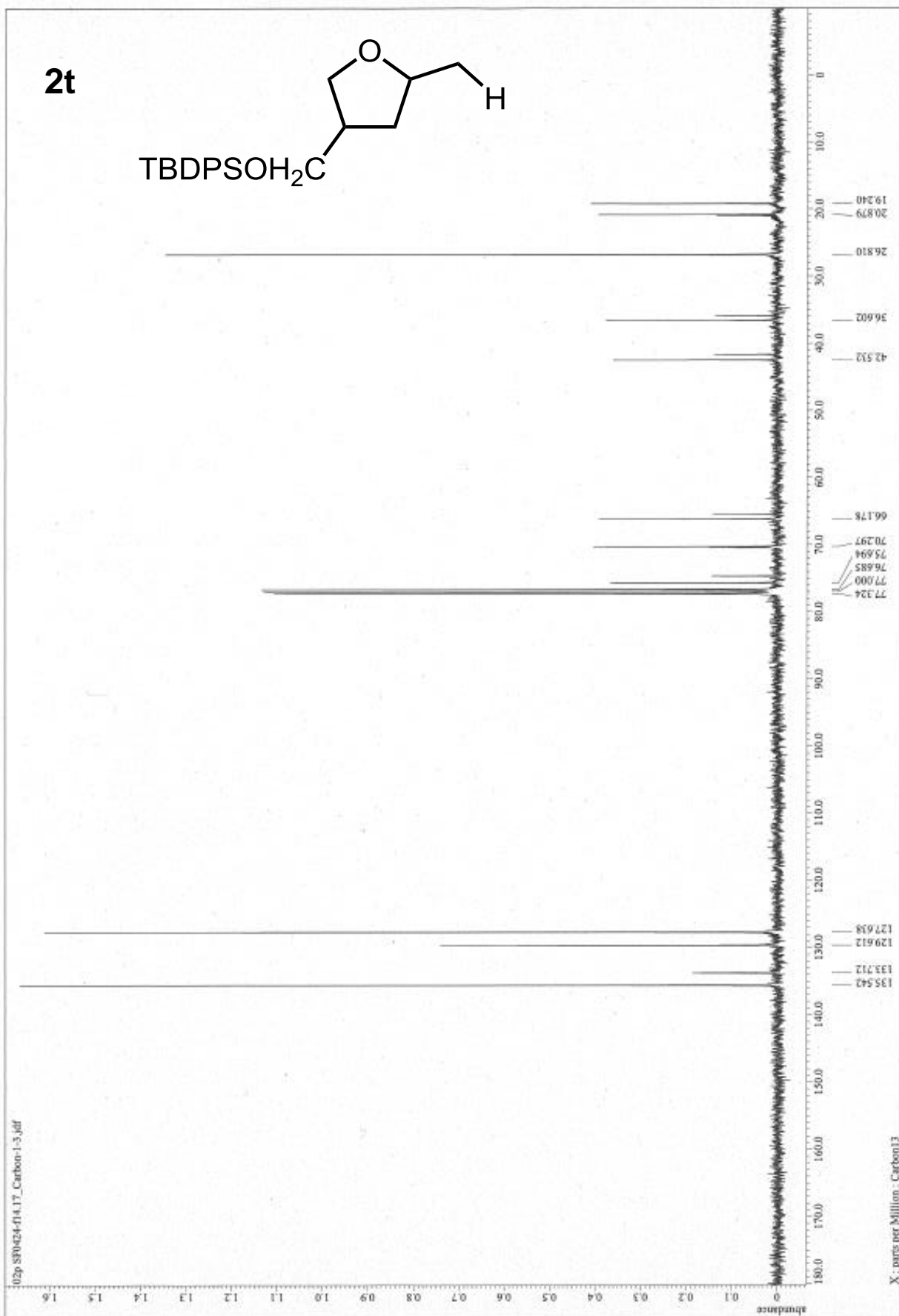




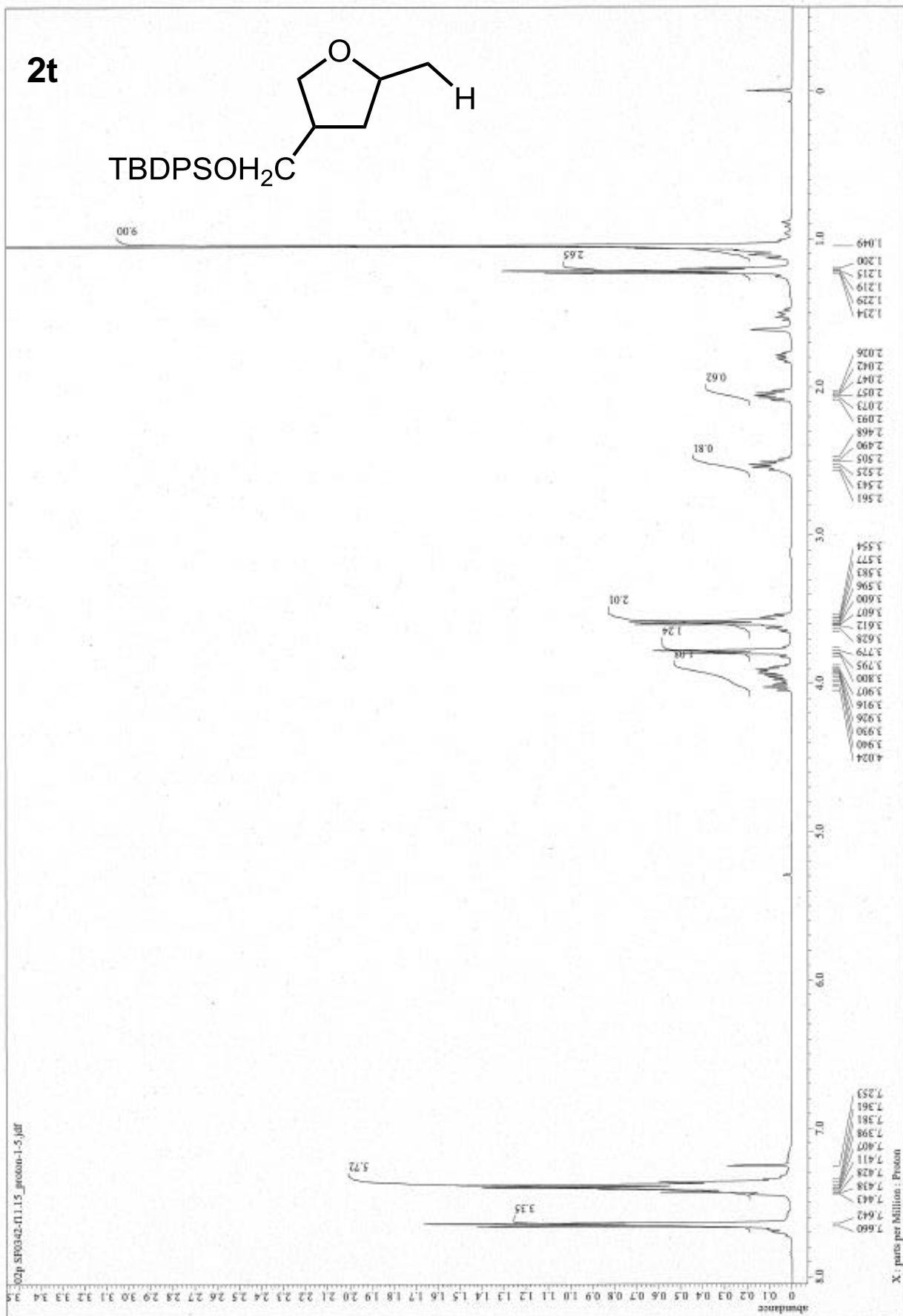
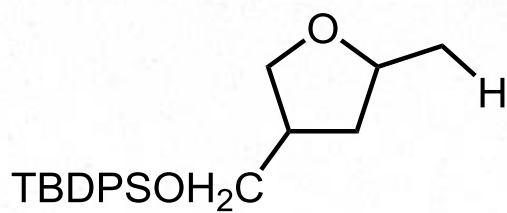
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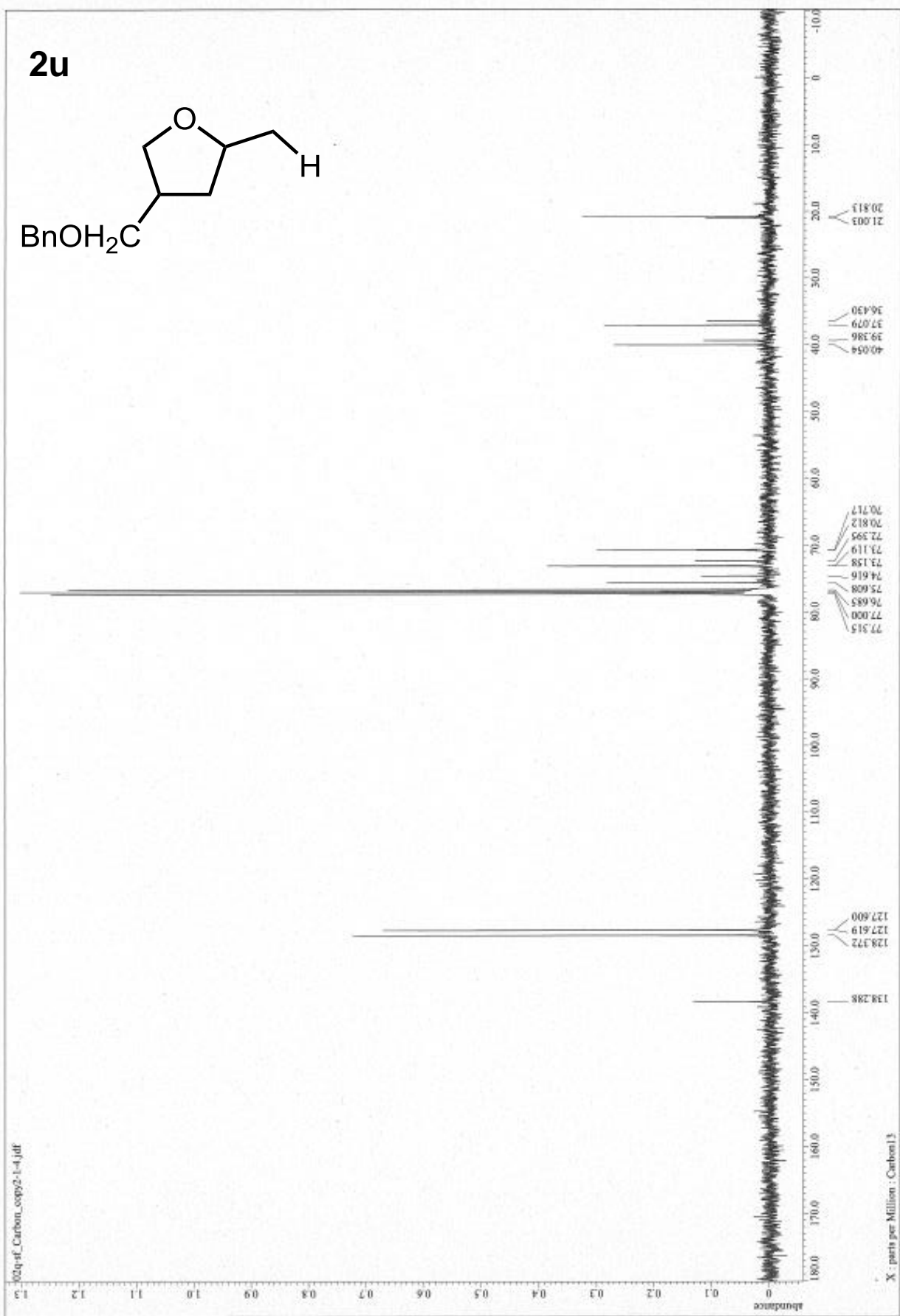
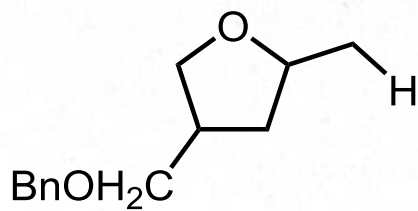




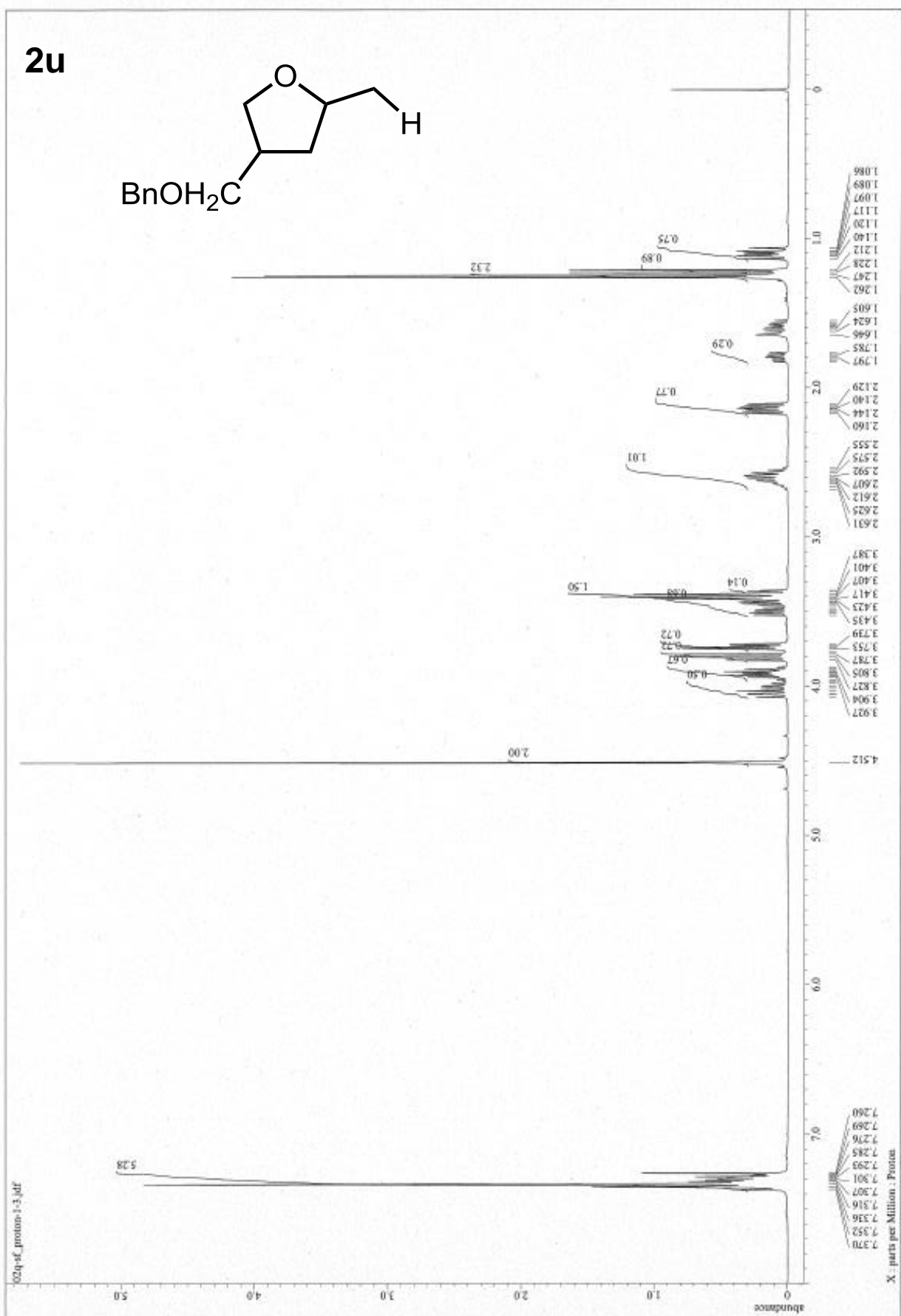
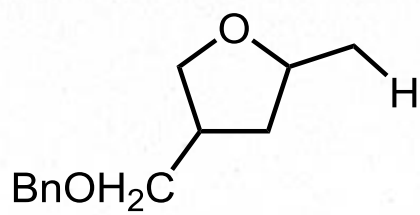
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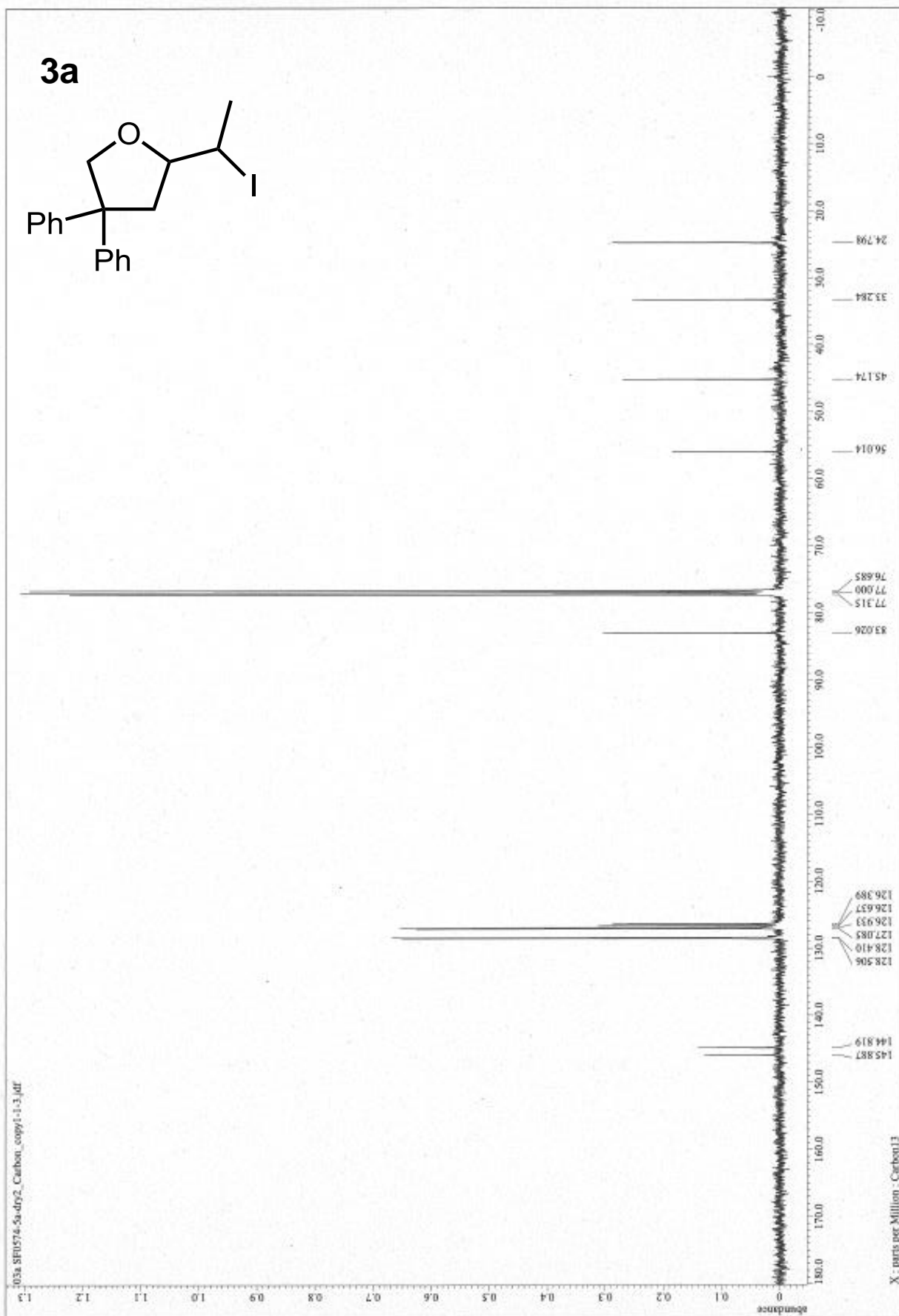


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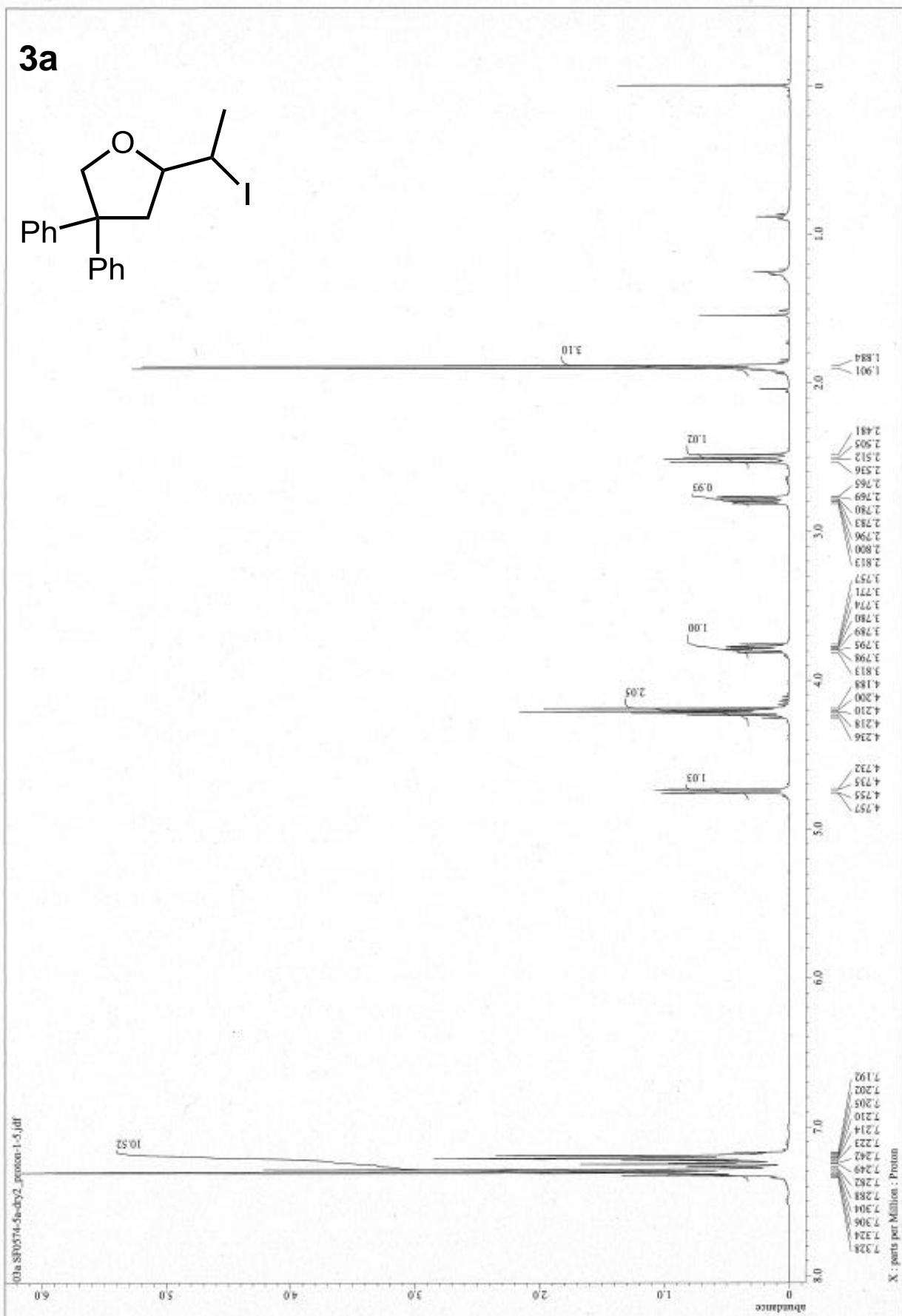
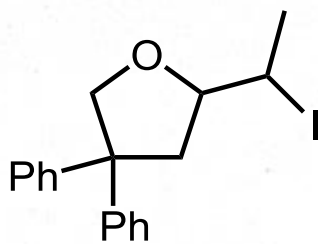


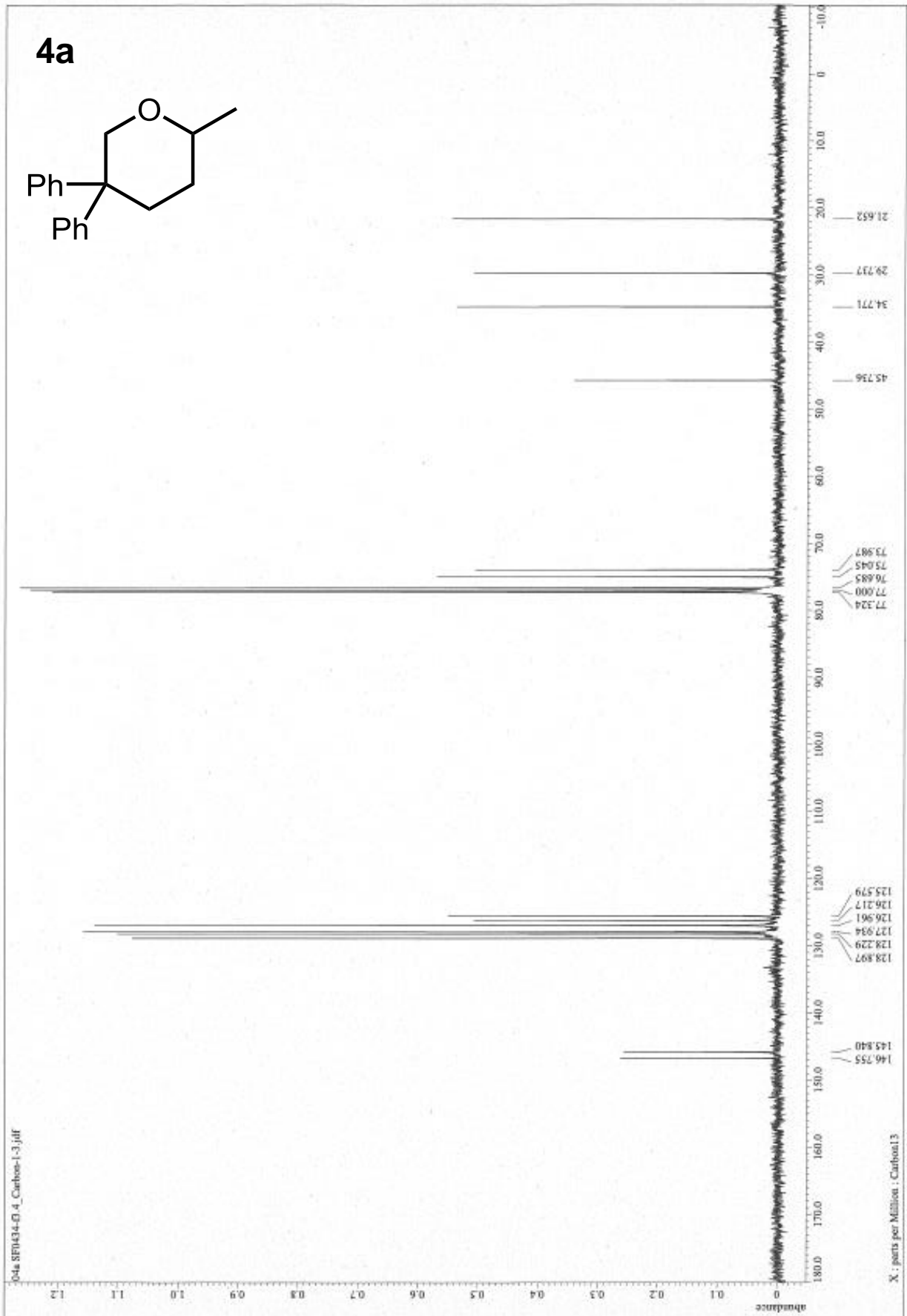
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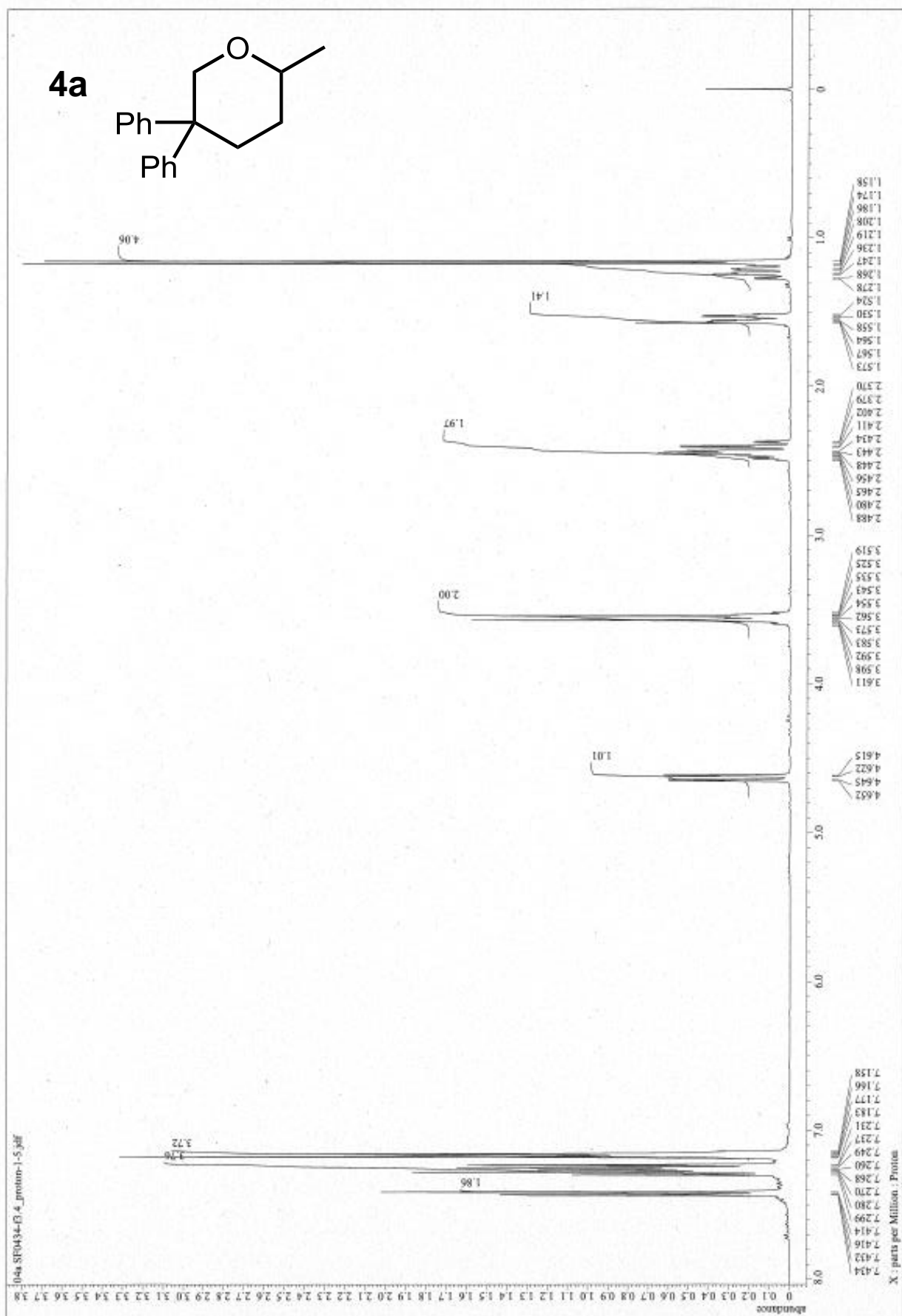




3a







4x

