A *SeCSe*-Pd(II) Pincer Complex as Highly Efficient Catalyst for Allylation of Aldehydes with Allyltributyltin

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CONTENTS

Experimental Section

General. Aldehydes were obtained from commercial sources. Their purity was checked by ^{1}H NMR and, whenever necessary, purified by distillation or chromatography to ensure no carboxylic acid was present. Allyltributyltin was purchased from Aldrich and used as received. THF was distilled from sodium/benzophenone under a nitrogen atmosphere prior to use. *N*,*N*-Dimethylformamide (DMF) (anhydrous; Sure-Seal bottle) was purchased from Aldrich. *N*,*N*-Dimethylacetamide (DMA) and DMSO were dried and freshly distilled over molecular sieves. THF-d_8 was purchased from Cambridge Chemicals and dried over flamed dried molecular sieves prior to use. Unless otherwise indicated, ^{1}H and ^{13}C NMR spectra were recorded at 25 ^{o}C in $CDCl_3$ at 500 and 125 MHz, respectively. Chemical shifts (ppm) were obtained by referencing to $CDCl_3$ as a standard. Flash chromatography was performed on grade 60 silica gel (32-63μm) obtained from commercial sources. All reactions were performed under an argon atmosphere by standard Schlenk techniques. All reactions were performed in duplicate.

Synthesis of the *SeCSe*-Pd(II) Pincer Complex 4. An oven-dried flask was charged with bis-selenide ligand **5**[11] (435 mg, 1.045 mmol) and 1 mL of glacial HOAc. Palladium acetate (236 mg, 1.05 mmol) was then added followed by an additional 1 mL of HOAc. The reaction mixture was heated to 116°C and maintained at gentle reflux for 3h. After the reaction was cooled to rt and HOAc removed in vacuo, the crude reaction product was dissolved in dichloromethane (2 mL). Hexanes (10 mL) were then added and the product precipitated as a yellow crystalline solid. The precipitates were allowed to settle and the solvent was decanted. This process was repeated three times and the purified product was dried on vacuum line overnight to give pure **4** (498 mg, 82%) as a bright yellow solid, m.p. 185-188 ^{o}C. Spectroscopic analysis showed that this material exists as a diastereomeric mixture in a ratio of 3:2. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.98 (dd, J = 1.86 and 7.7 Hz, major diastereomer) and 7.91 (d, J = 7.2 Hz, minor diastereomer)

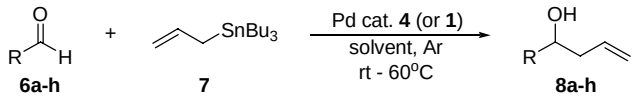
(4 H in total), 7.33-7.41 (m, 6H), 6.87-6.94 (m, 3H), 4.573 (minor, d, *J* = 14.2 Hz) and 4.568 (d, *J* = 13.7 Hz, major diastereomer) (2 H in total), 4.32 (d, *J* = 13.7 Hz, major) and 4.21 (d, *J* = 14.1 Hz, minor diastereomer) (2 H in total), 1.84 (bs, minor diastereomer) and 1.71 (bs, major diastereomer) (3 H in total). ^{13}C NMR (125Hz, $CDCl_3$): δ 177.2 (minor diastereomer) and 176.9 (major diastereomer), 152.7 (minor diastereomer) and 152.3 (major diastereomer), 150.7 (minor diastereomer) and 150.1 (major diastereomer), 133.3 (major diastereomer) and 133.2 (minor diastereomer), 130.0, 129.8, 129.59, 129.56 and 129.4 (isomeric peaks of 3 C), 124.5 (major diastereomer) and 124.3 (minor diastereomer), 123.7 (minor diastereomer) and 123.6 (major diastereomer), 43.0 (major diastereomer) and 42.4 (minor diastereomer), 23.6 (minor diastereomer) and 23.5 (major diastereomer). Anal. Calcd. for $C_{22}H_{20}O_2PdSe_2$: C, 45.50; H, 3.47. Found: C, 45.45; H, 3.48.

Allylation of Aldehydes with Allyltributyltin in the Presence of the *SeCSe*-Pd(II) Pincer Catalyst 4. ***Representative Procedure:*** *Allylation of 4-bromobenzaldehyde* ***(6a)*** *with allyltributyltin* ***(7)*** *in the presence of* ***4*** (Table 1, entry 6). A flame-dried Schlenk flask was charged with aldehyde **6a** (92.5 mg, 0.5 mmol), DMF (0.5 mL) and catalyst **4** (2.9 mg, 0.0050 mmol) under argon. Allyltributyltin (**7**) (186 μL, 199 mg, 0.6 mmol) was then added via syringe. The flask was sealed and heated to 40 ^{o}C (bath temperature) for 18 h. After cooling to rt, the reaction mixture was poured into water and extracted with ether. The combined extracts were stirred with aqueous KF (10%, w/v) overnight. The organic layer was then separated, washed with brine, dried (Na_2SO_4) and concentrated. The crude product was purified by flash column chromatography (hexanes/EtOAc 8:1) to give the known homoallyl alcohol **8a**[1] (106 mg, 93%) as a colorless oil. The reaction was repeated one more time and the product was isolated in 95% yield. ^{1}H NMR (200 MHz): δ 7.48 (d, 2 H, *J* = 8.5 Hz,), 7.22 (d, 2 H *J* = 8.3 Hz), 5.68-5.88 (m, 1

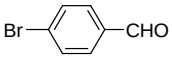
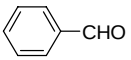
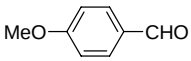
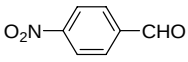
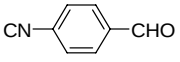
H), 5.10-5.21 (m, 2 H), 4.67 (t, 1 H, J = 6.4 Hz), 2.64 (bs, 1 H, alcohol), 2.44-2.51(m, 2 H). ^{13}C NMR (50 MHz): δ 142.84, 133.97, 131.43, 127.61, 121.21, 118.69, 72.65, 43.69.

Reactions (each in duplicate) of other aldehydes under a variety of conditions were performed according to the general procedure with appropriate adjustment of the solvent used and the reaction time and temperature. The results were given in Table S-1.

TABLE S-1. Allylation of Aldehydes with Allyltributyltin **7** Using the Pd-Complex **4** as Catalyst

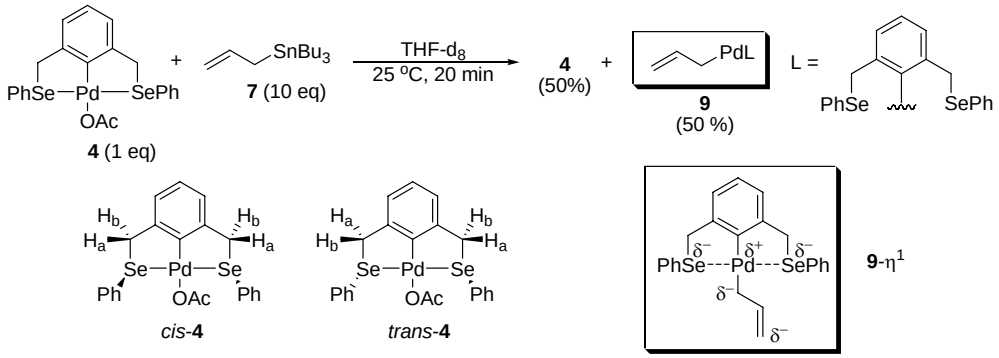


6a-h **7** **8a-h**

entry	aldehyde	mmol	mol % **4**	Solvent	conditions	yield[b, c]
1	 **6a**	1.0	1	THF (1 mL)	rt (18h)	86.5
2		0.5	1	THF ((0.5 mL)	rt (24h)	92.5
3		1.0	1	THF (1 mL)	40 °C (18h)	67.5
4		0.5	1	THF (0.5 mL)	60 °C (18h)	64
5		0.5	1	DMF (0.5 mL)	rt (18h)	77
6		0.5	1	DMF (0. 5 mL)	40 °C (18h)	94
7		0.5	1	DMF (0.5 mL)	60 °C (18h)	96
8		0.5	1	DMSO (0.5 mL)	rt (18h)	86.5
9		0.5	1	DMSO (0.5 mL)	40 °C (18h)	96.5
10		0.5	1	DMSO (0.5 mL)	60 °C (18h)	97
11	 **6b**	1.0	1	DMF (1 mL)	rt (36h)	87.5
12		1.0	1	DMF (1 mL)	40 °C (2h)	66.5
13		1.0	1	DMF (1 mL)	40 °C (4h)	77.5
14		1.0	1	DMF (1 mL)	40 °C (6h)	87
15		0.5	1	DMF (0.5 mL)	40 °C (18h)	92.5
16		2.0	0.25	DMF (1 mL)	40 °C (24h)	92
17		2.0	0.02	DMF (1 mL)	40 °C (40h)	95.5
18		1.0	1 (**1**)[d]	DMF (1 mL)	40 °C (18h)	54
19		1.0	none[e]	DMF (0.5 mL)	40 °C (18h)	<1[f]
20		1.0	1 (**2**)[g]	DMF (1 mL)	40 °C (18h)	74
21	 **6c**	0.5	1	DMF (0.5 mL)	60 °C (18h)	58.5
22		0.5	1	DMSO (0.5 mL)	60 °C (18h)	22.5
23		2.0	1	DMA (1 mL)	60 °C (18h)	64.5
24	 **6d**	1.0	1	DMF (0.5 mL)	rt (24h)	95
25		1.0	1	DMF (0.5 mL)	40 °C (6h)	95.5
26		2.0	0.25	DMF (1 mL)	40 °C (18h)	95.5
27		4.0	0.1	DMF (2 mL)	40 °C (40h)	95.5
28		2.0	0.02	DMF (1 mL)	40 °C (24h)	95.5
29		2.0	0.005	DMF(2 mL)	40 °C (40h)	73.5
30		2.0	0.005	DMF(2 mL)	40 °C (96h)	79.5
31	 **6e**	1.0	1	DMF (0.5 mL)	rt (24h)	94.5
32		4.0	0.1	DMF (2 mL)	40 °C (40h)	95.5
33	$PhCH_2CH_2CHO$ **6f**	1.0	1	DMF (0.5 mL)	40 °C (40h)	66.5
34	$CH_3(CH_2)_5CH_2CHO$ **6g**	1.0	1	DMF (0.5 mL)	40 °C (18h)	47
35		2.0	1	DMF (1 mL)	60 °C (24h)	59

[a] All reactions were performed with 1 eq of **6** and 1.2 eq of **7** under conditions as indicated. [b] Referred to isolated yield after column chromatography on silica gel. [c] Average of two runs. [d] The *SeCSe*-Pd(II) pincer complex **1** was used. [e] This control reaction was performed in the absence of any catalyst. [f] Not detected by ^{1}H NMR. [g] The *Se*-palladacycle **2** was used.

^{1}H NMR Spectroscopic Study on the Reaction of the Pd Complex 4 with Allyltributyltin 7: *Identification of the Transmetalation Product 9*. An NMR tube (5 mm) was charged with **4** (4.6 mg, 0.008 mmol) and 600 μL of degassed THF-d_8 was added under an Ar atmosphere. The NMR tube was cooled to -5°C and ^{1}H NMR spectrum (at 500 MHz with d1 = 10s) was recorded. Due to the chiral nature of the Pd-bound selenium, there exist two diastereomers, *cis*- and *trans*-**4** (**Scheme S-1**) as evidenced by the two diastereotopic $SeCH_2$ groups corresponding to each of the diastereomers. Each of the $SeCH_2$ groups appears as two doublets (**Figure S-1**). Allyltributyltin **7** (24.5 μL, 26.5 mg, 0.080 mmol) was then added and the temperature of the NMR probe was raised to 25 ^{o}C. After 20 min at this temperature, **4** was converted to a new compound in about 50% conversion. This new compound was identified as the transmetalation product **9**-η^1. The ^{1}H NMR spectrum of the reaction mixture at -5°C was shown in **Figure S-2**. The spectrum assignments for compounds **4**, **7** and **9** were shown in **Figure S-3**. The 2D proton COSY NMR spectra of the reaction mixture were shown in **Figures S-4.A** and **S-4.B**.



SCHEME S-1. Reaction of Pd Complex **4** with Allyltributyltin **7** in THF-d_8.

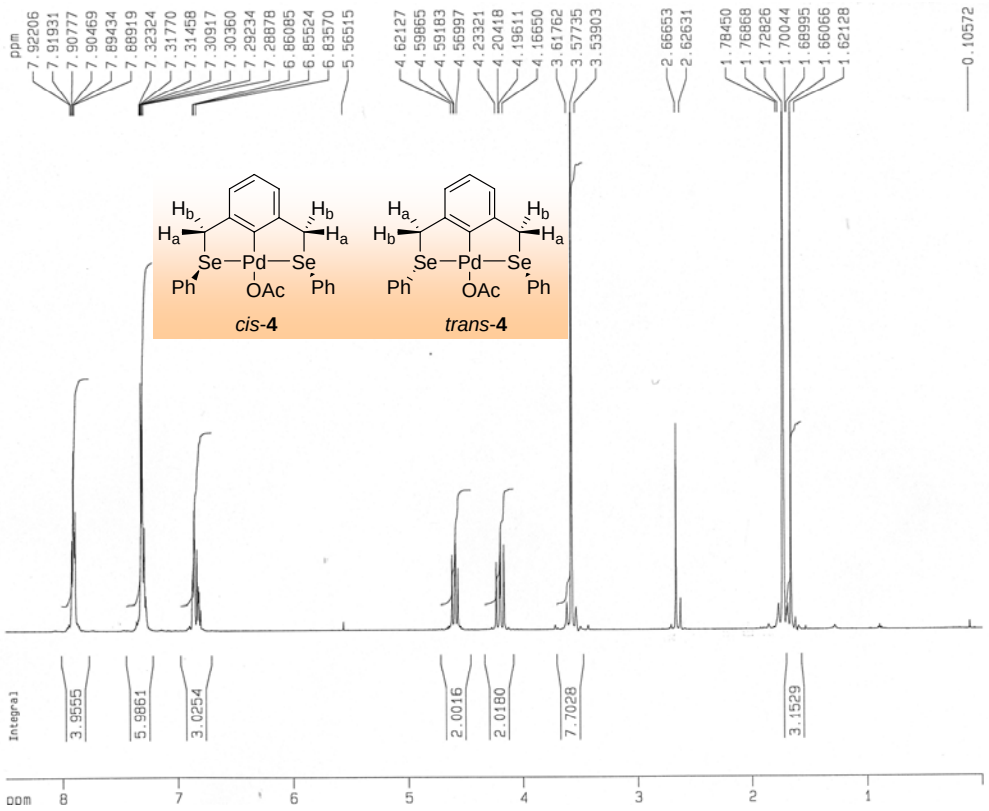


FIGURE S-1. ^{1}H NMR Spectrum of **4** in THF-d_8 to 25 ^{o}C.

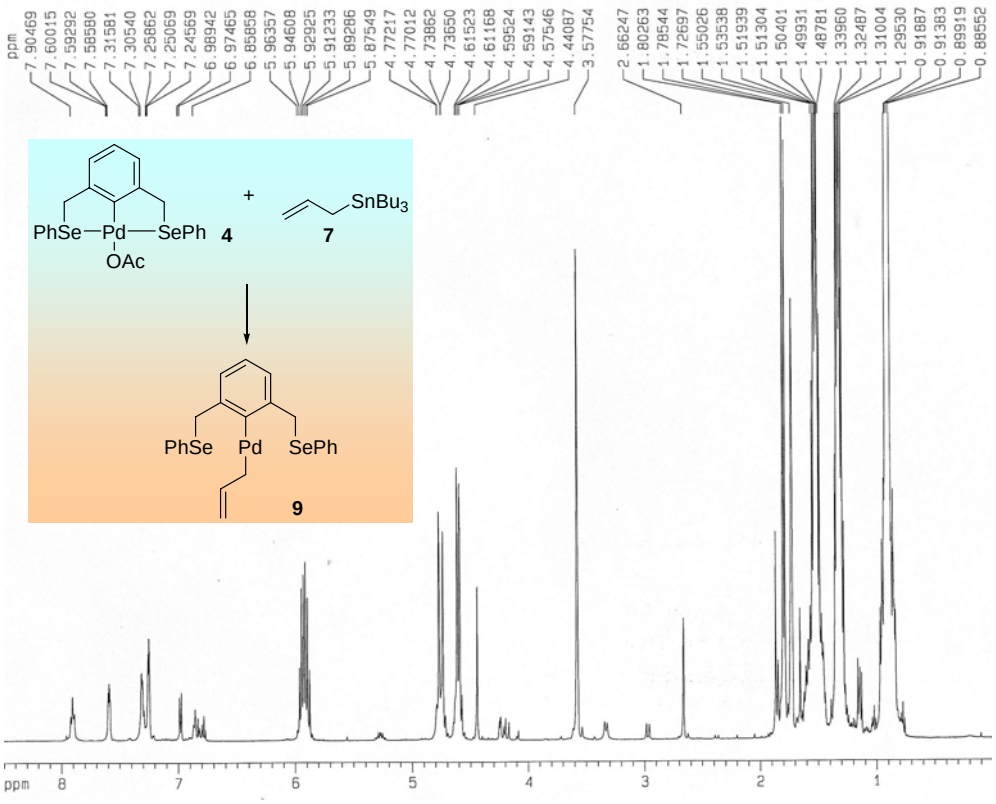


FIGURE S-2. ^{1}H NMR Spectrum of the Reaction Mixture of **4** and **7**.

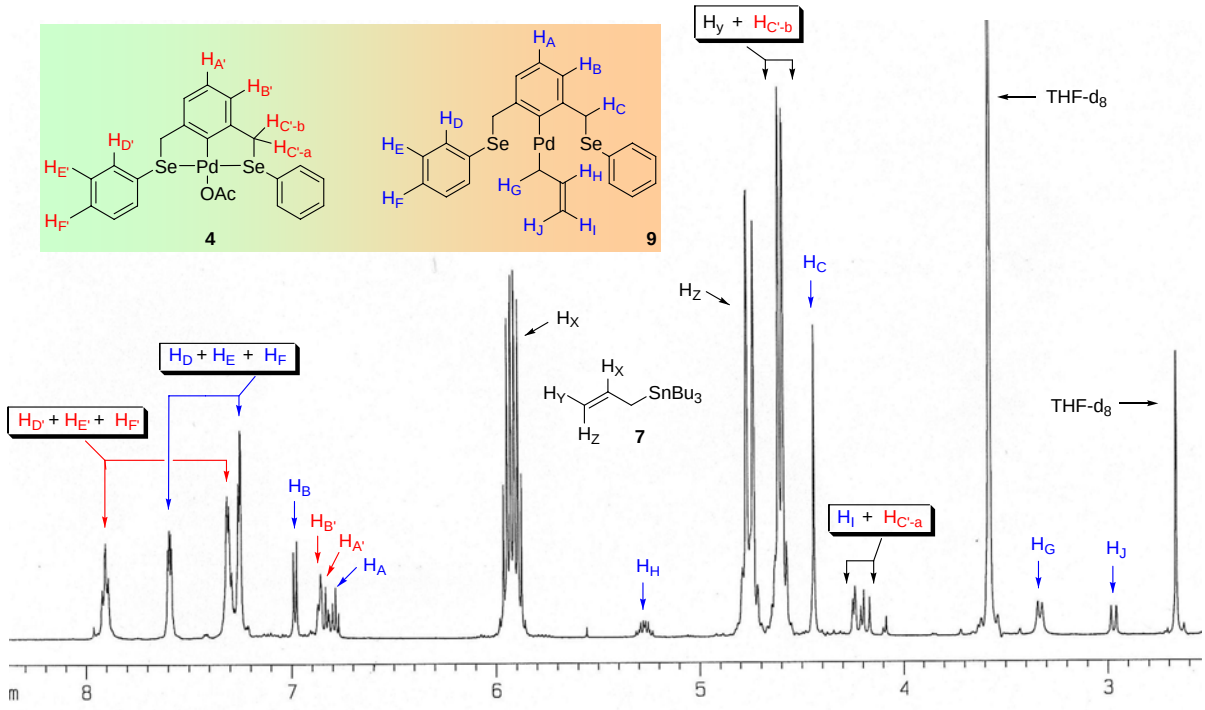


FIGURE S-3. Partial 500 MHz ^{1}H NMR Spectrum and Spectrum Assignments for the Crude Reaction Mixture Containing **4**, **7** and the Allyl-Pd(II) Complex **9**[14] in THF-d_8 at -5 ^{o}C.

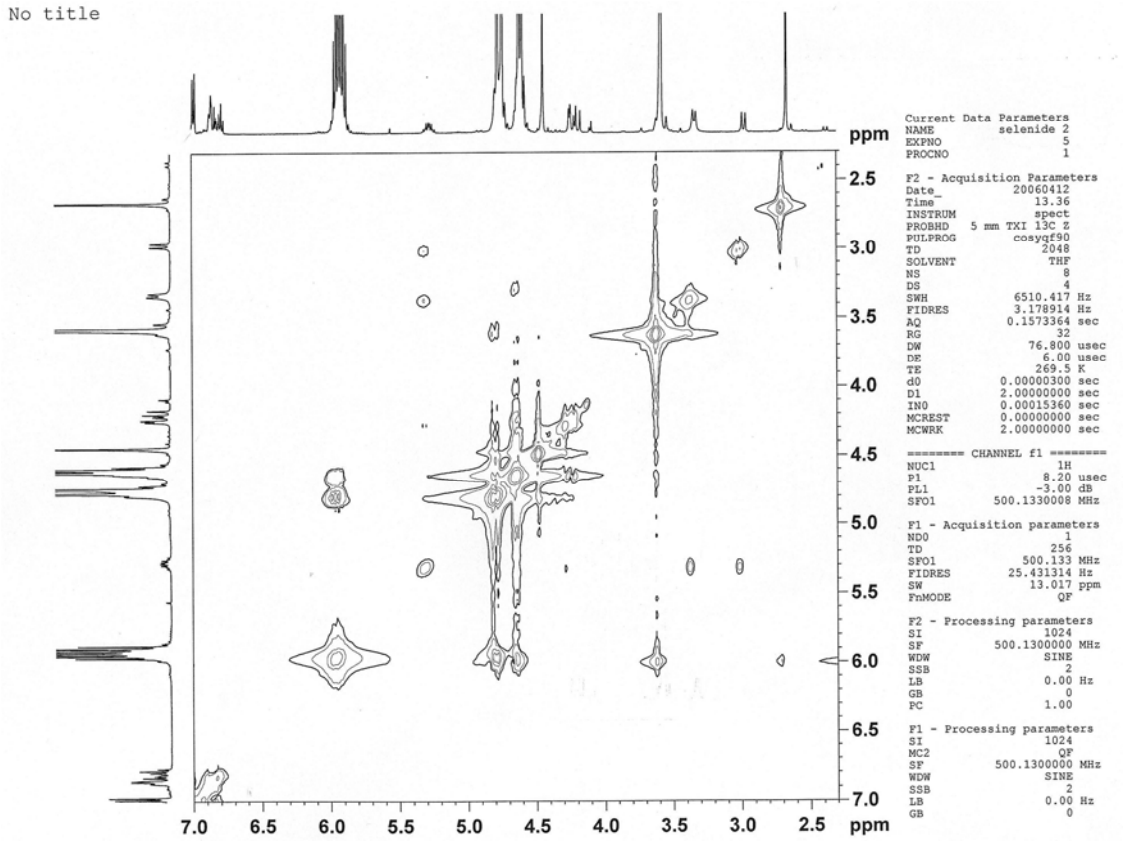


FIGURE S-4. A. 2D COSY Spectrum (Plot A) of the Crude Reaction Mixture of **4** and **7.**

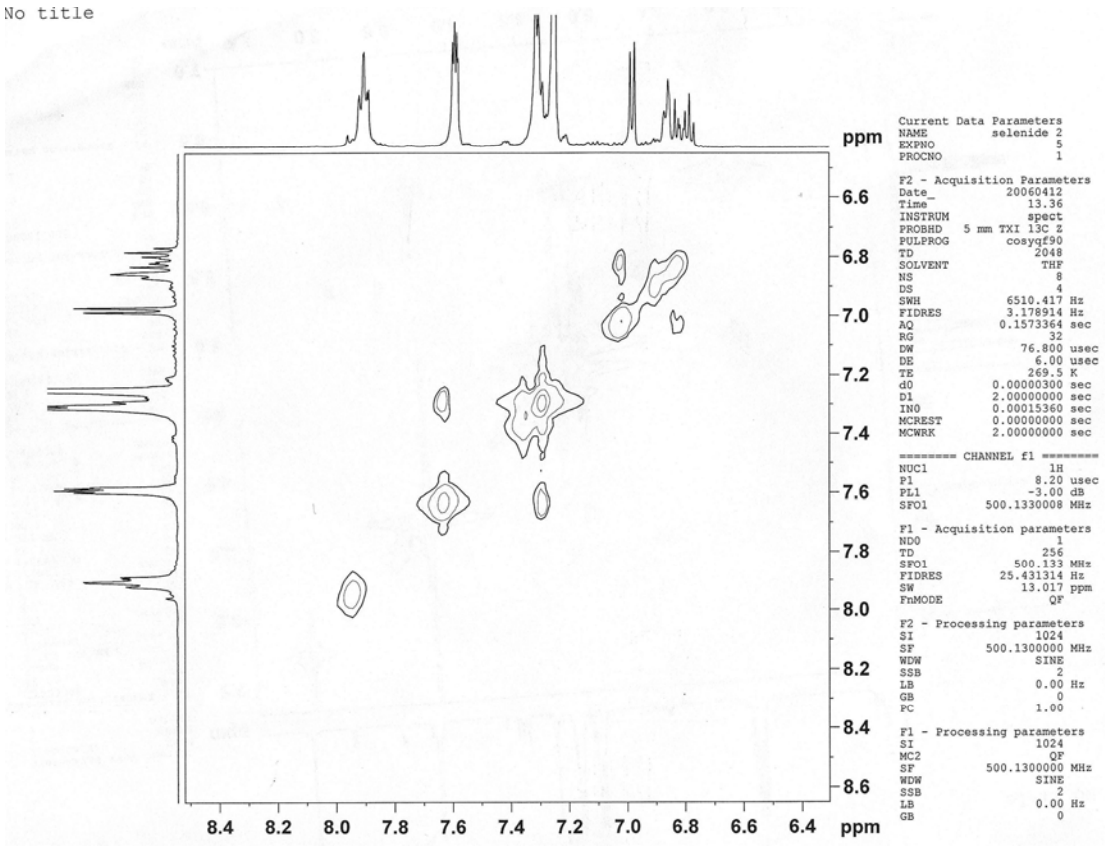
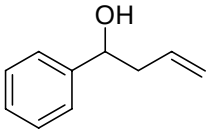


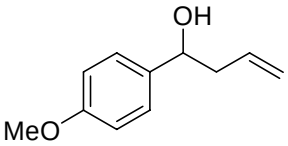
Figure S-4. B. 2D COSY Spectrum (Plot B) of the Reaction Mixture of **4** and **7**.

Phenylbut-3-en-1-ol (8b)[2]



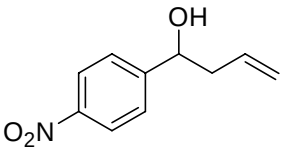
^{1}H NMR: δ 7.29-7.41 (m, 5 H), 5.79-5.88 (m, 1 H), 5.15-5.20 (m, 2H), 4.71 (t, 1H *J* = 6.5 Hz), 2.79 (bs, 1 H alcohol), 2.54 (t, 2 H, *J* = 6.8). ^{13}C NMR: δ 144.22, 134.74, 128.39, 127.47, 126.08, 117.85, 73.56, 43.72.

1-(4-Methoxyphenyl)but-3-en-1-ol (8c)[1,3]



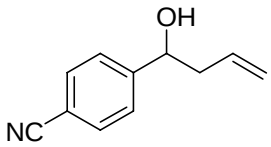
^{1}H NMR: δ 7.30 (d, 2 H, *J* = 8.5 Hz), 6.90 (d, 2 H, *J* = 8.5 Hz), 5.78-5.86 (m, 1 H), 5.13-5.18 (m, 2 H), 4.69 (t, 1 H, *J* = 6.5 Hz), 3.82 (s, 3 H), 2.52 (t, 2H, *J* = 7.0 Hz), 2.18 (bs, 1 H, alcohol). ^{13}C NMR: δ 159.07, 136.14, 134.65, 127.09, 118.11, 113.64, 73.03, 55.28, 43.64.

1-(4-Nitrophenyl)but-3-en-1-ol (8d)[1b,3c]



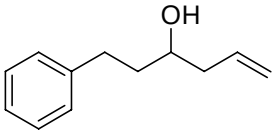
^{1}H NMR: δ 8.14 (d, 2 H, *J* = 8.5 Hz), 7.52 (d, 2 H, *J* = 8.5 Hz), 5.74-5.82 (m, 1 H), 5.11-5.15 (m, 2 H), 4.87 (t, 1 H, *J* = 6.0 Hz), 3.17 (bs, 1H, alcohol), 2.45-2.56 (m, 2 H). ^{13}C NMR: δ 151.52, 147.067, 133.36, 126.65, 123.46, 118.96, 72.35, 43.61.

4-(1-Hydroxybut-3-enyl)benzonitrile (8e)[3c]



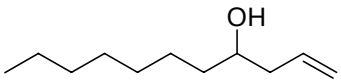
^{1}H NMR: δ 7.56 (d, 2 H, *J* = 8.0 Hz), 7.43 (d, 2 H, *J* = 7.5 Hz), 5.69-5.77 (m, 1 H), 5.07-5.11 (m, 2H), 4.75 (t, *J* = 6.1 Hz), 3.08 (bs, 1H, alcohol), 2.39-2.50 (m, 2H). ^{13}C NMR: δ 149.56, 133.50, 132.12, 126.61, 118.9, 110.81, 72.48, 43.62.

Phenyl-5-hexen-3-ol (8f)[4]



^{1}H NMR: δ 7.20-7.38 (m, 5 H), 5.78-5.90 (m, 1 H), 5.13-5.19 (m, 2 H), 3.71 (m, 1 H), 2.67-2.89 (m, 2 H), 2.18-2.40 (m, 2 H), 1.76-1.86 (m, 2H), 1.66 (bs, 1 H, alcohol). ^{13}C NMR: δ 142.07, 134.63, 128.48, 128.44, 125.87, 118.51, 69.88, 42.12, 38.48, 32.08

Undec-1-en-4-ol (8g)[1b,5]



^{1}H NMR: δ 5.81-5.88 (m, 1 H), 5.02-5.18 (m, 2 H), 3.60-3.67 (m, 1H), 2.25-2.29 (m, 1 H), 2.20-2.11 (m, 2 H), 1.71 (bs, 1 H, alcohol), 1.49-1.28 (m, 12 H), 0.89 (t, 1 H, J = 7.0Hz). ^{13}C NMR: δ 134.94, 117.66, 70.75, 41.91, 36.84, 31.77, 29.58, 29.20, 25.60, 22.56, 13.93.

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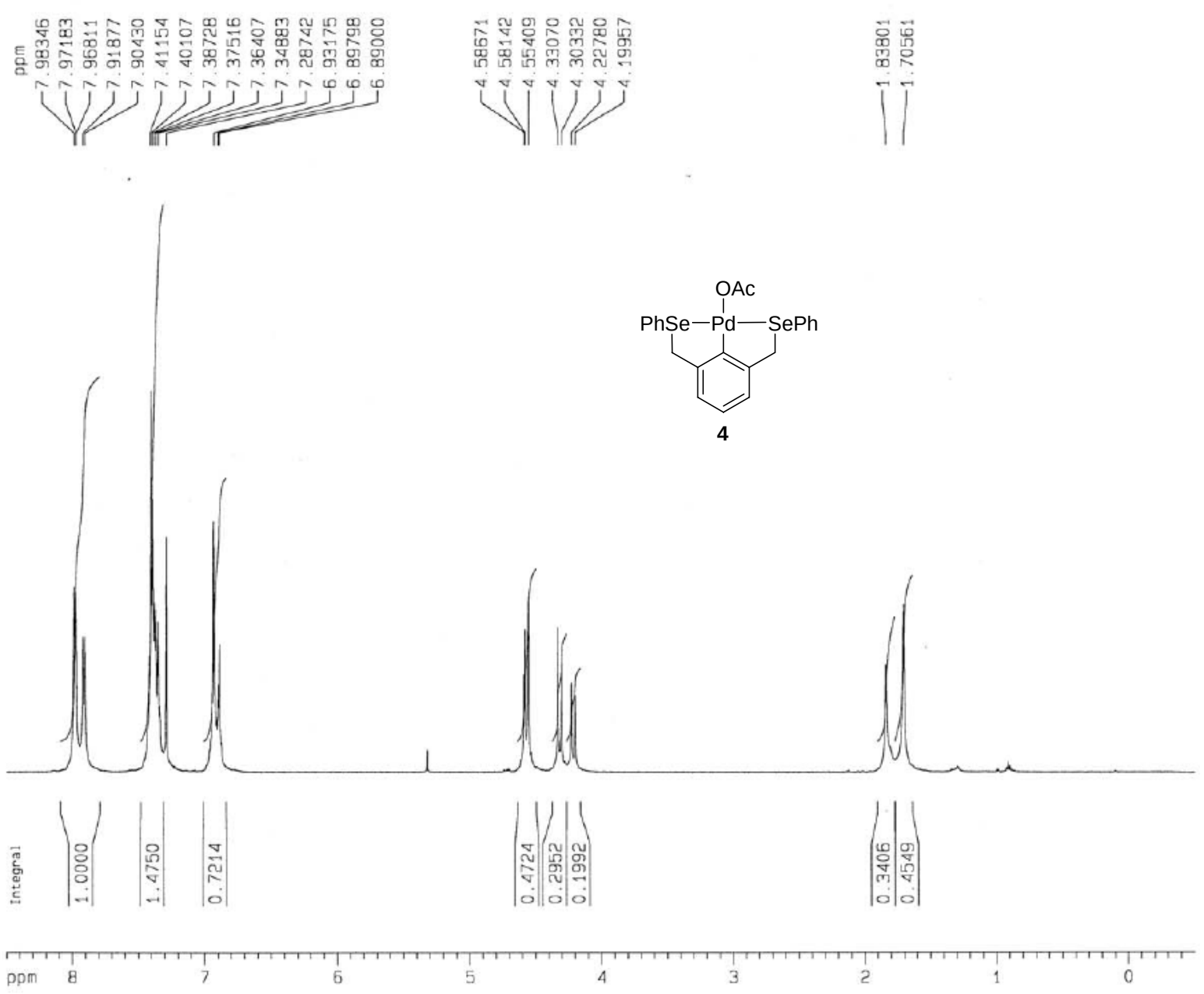
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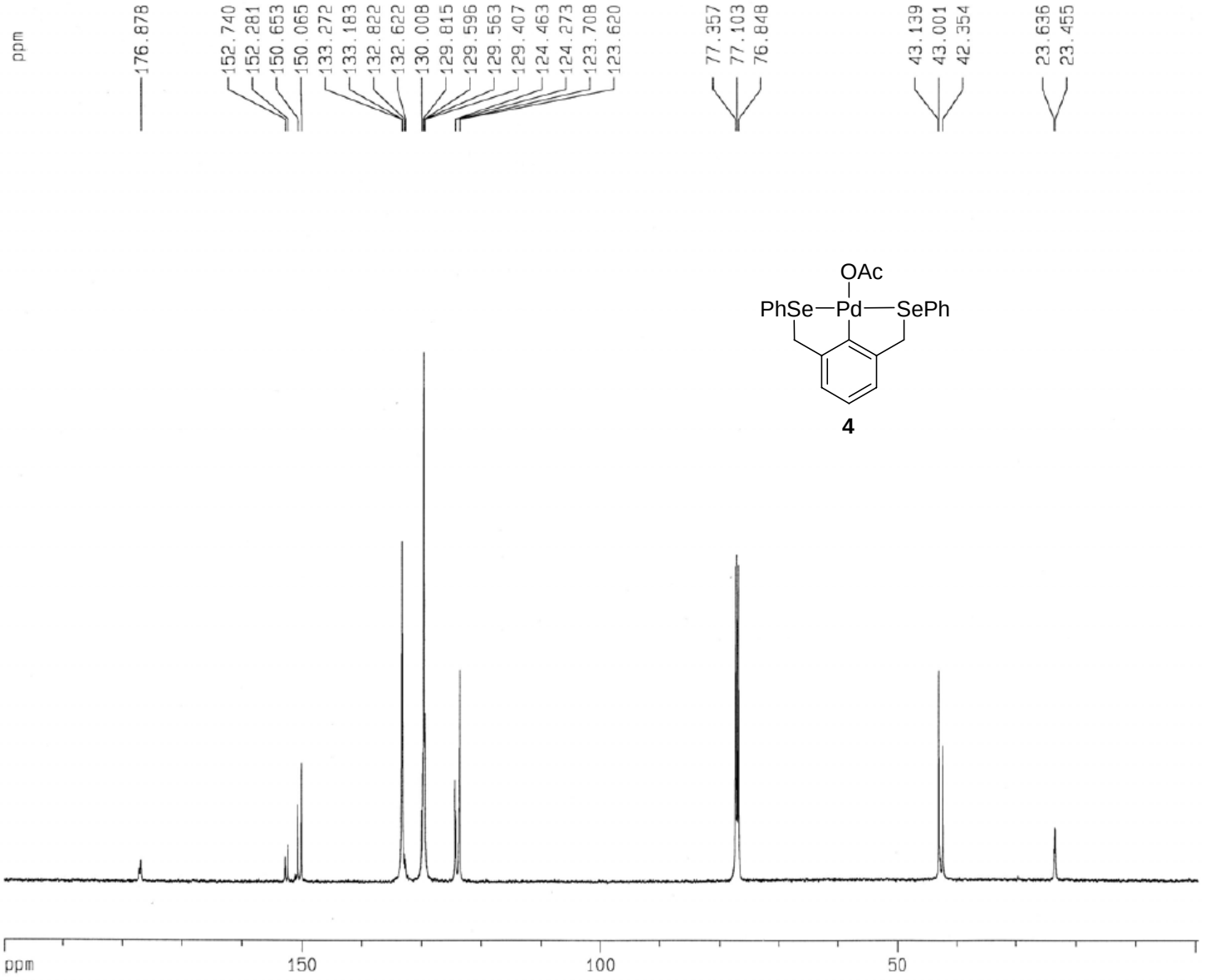
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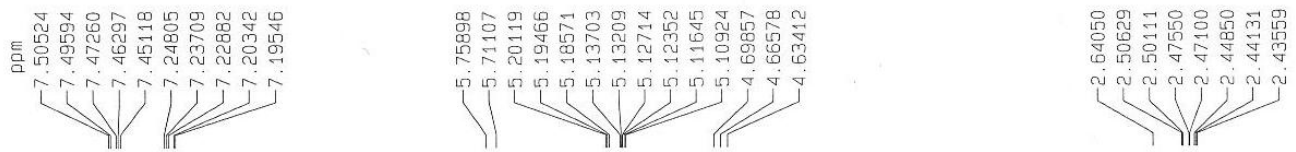
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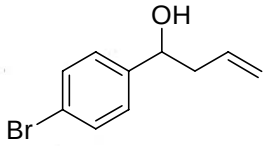
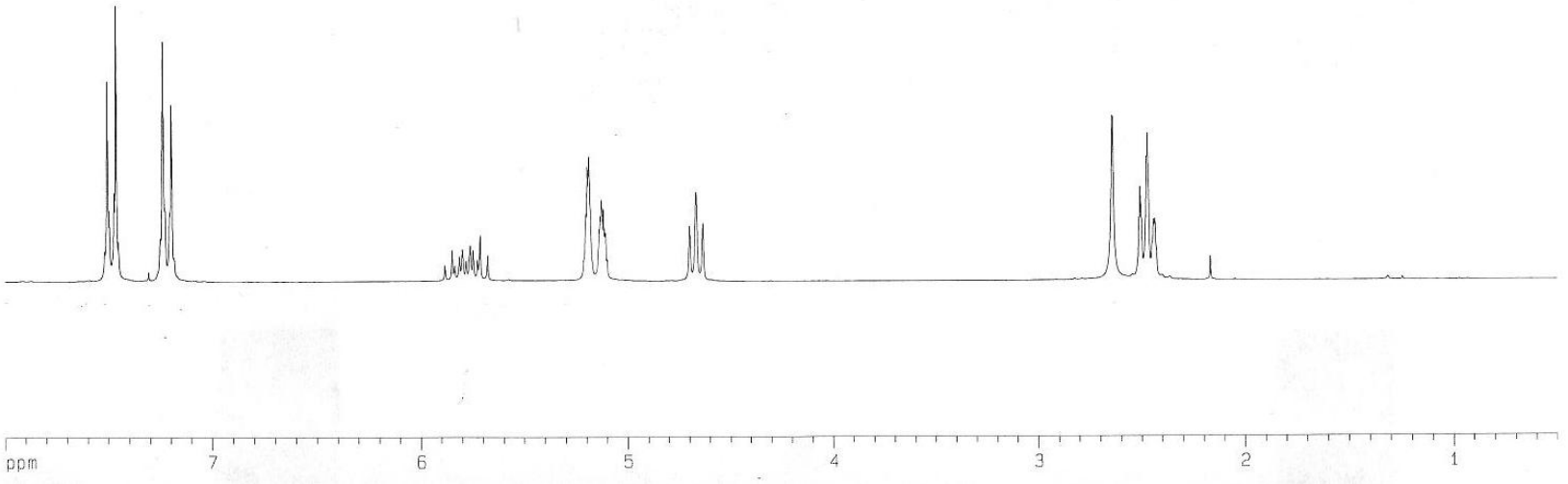
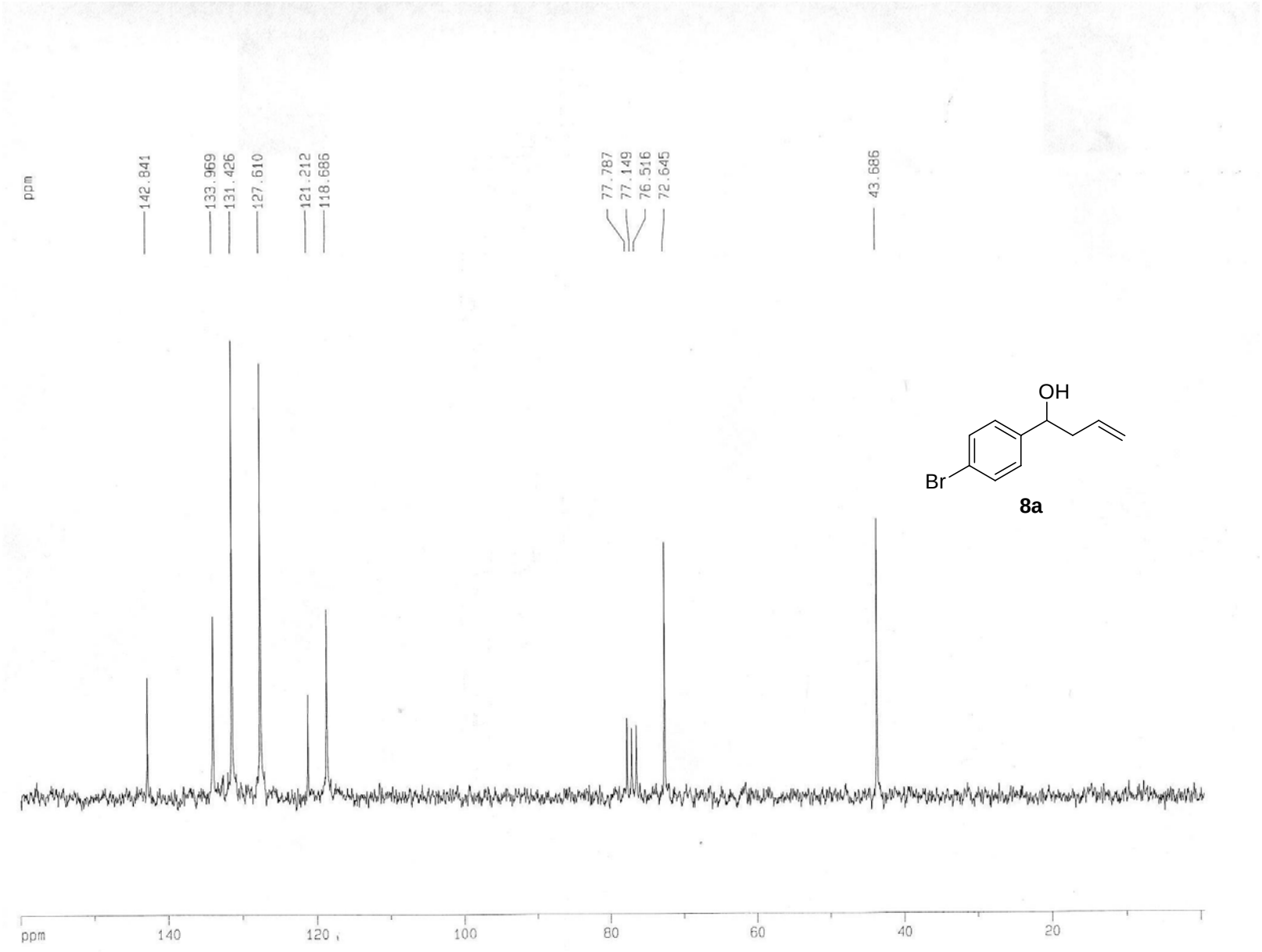
5.75898
5.71107
5.20119
5.19466
5.18571
5.13703
5.13209
5.12714
5.12352
5.11645
5.10924
4.69857
4.66578
4.63412
2.64050
2.50629
2.50111
2.47550
2.47100
2.44850
2.44131
2.43559


OH
Br

8a


ppm
7
6
5
4
3
2
1


ppm
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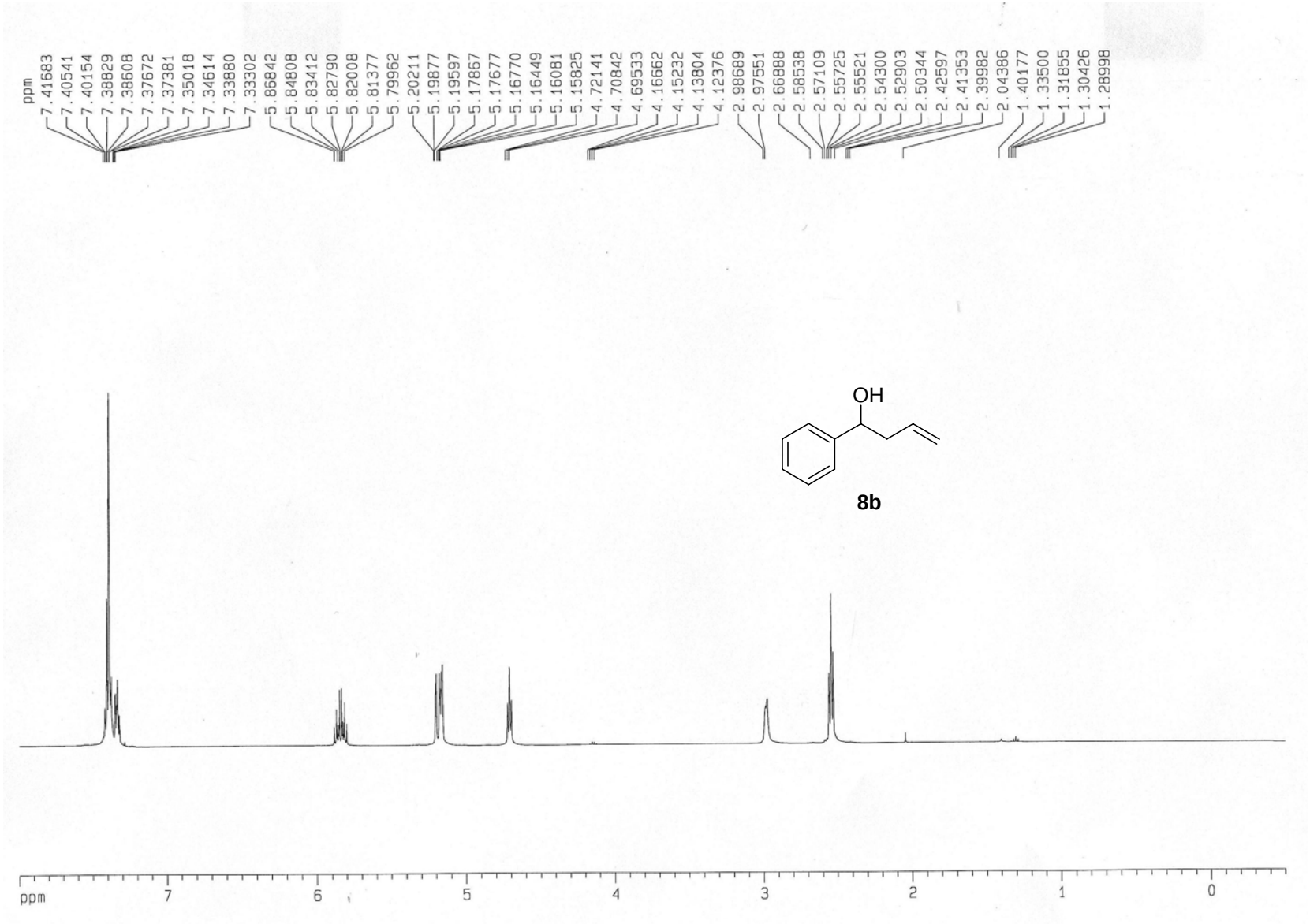
133.969
131.426
127.610
121.212
118.686
77.787
77.149
76.516
72.645
43.686
OH
Br
8a
ppm
140
120
100
80
60
40
20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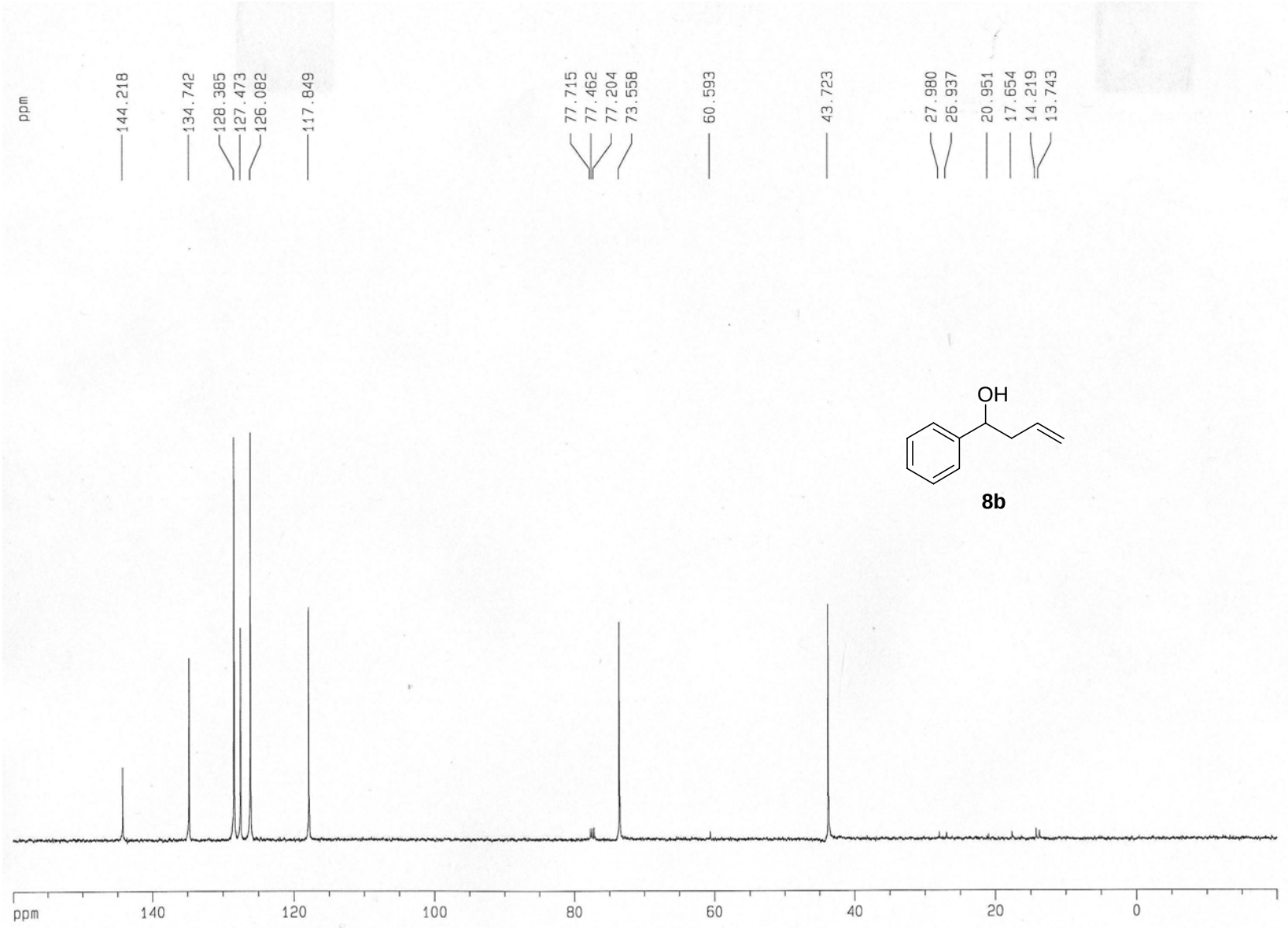
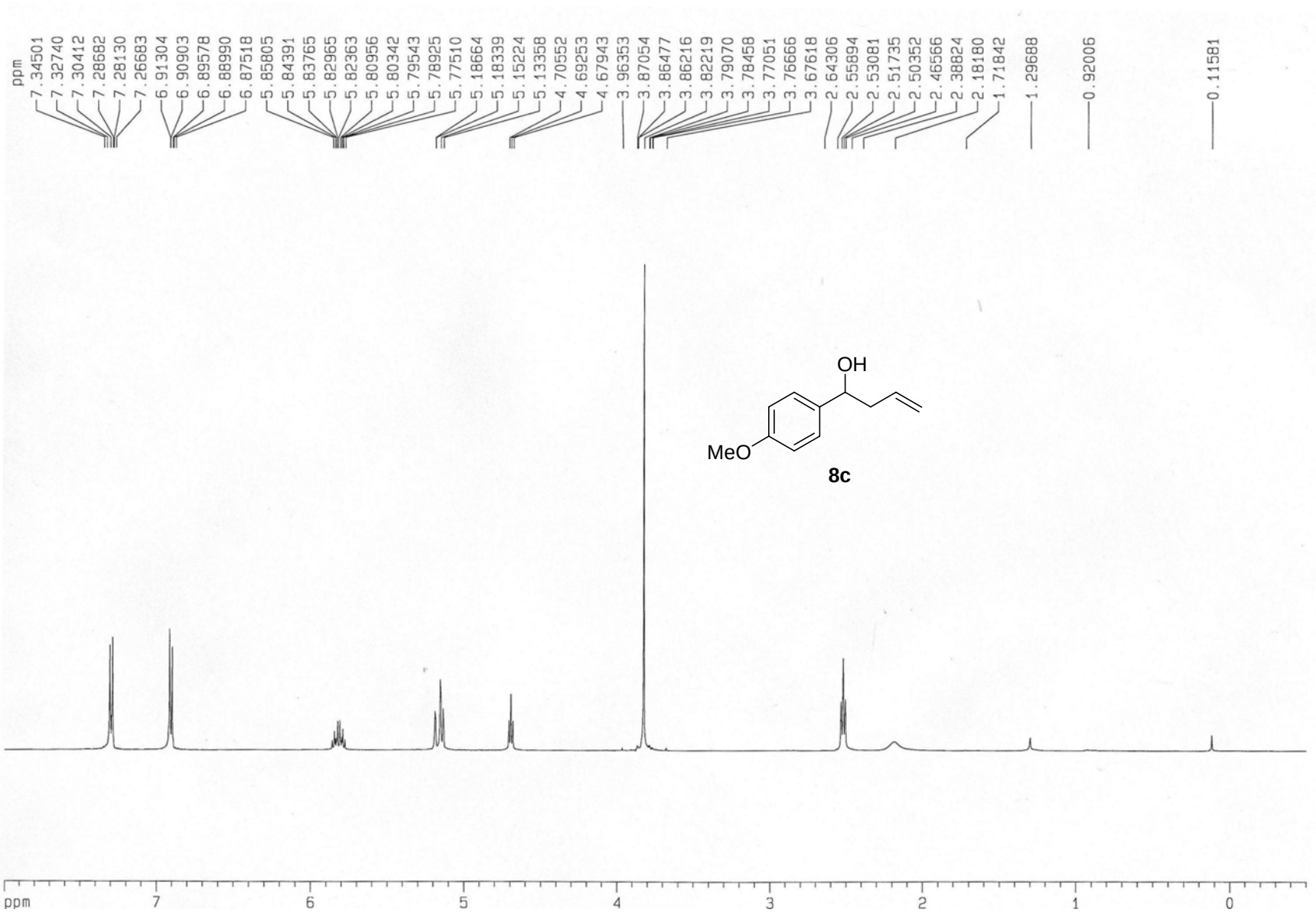
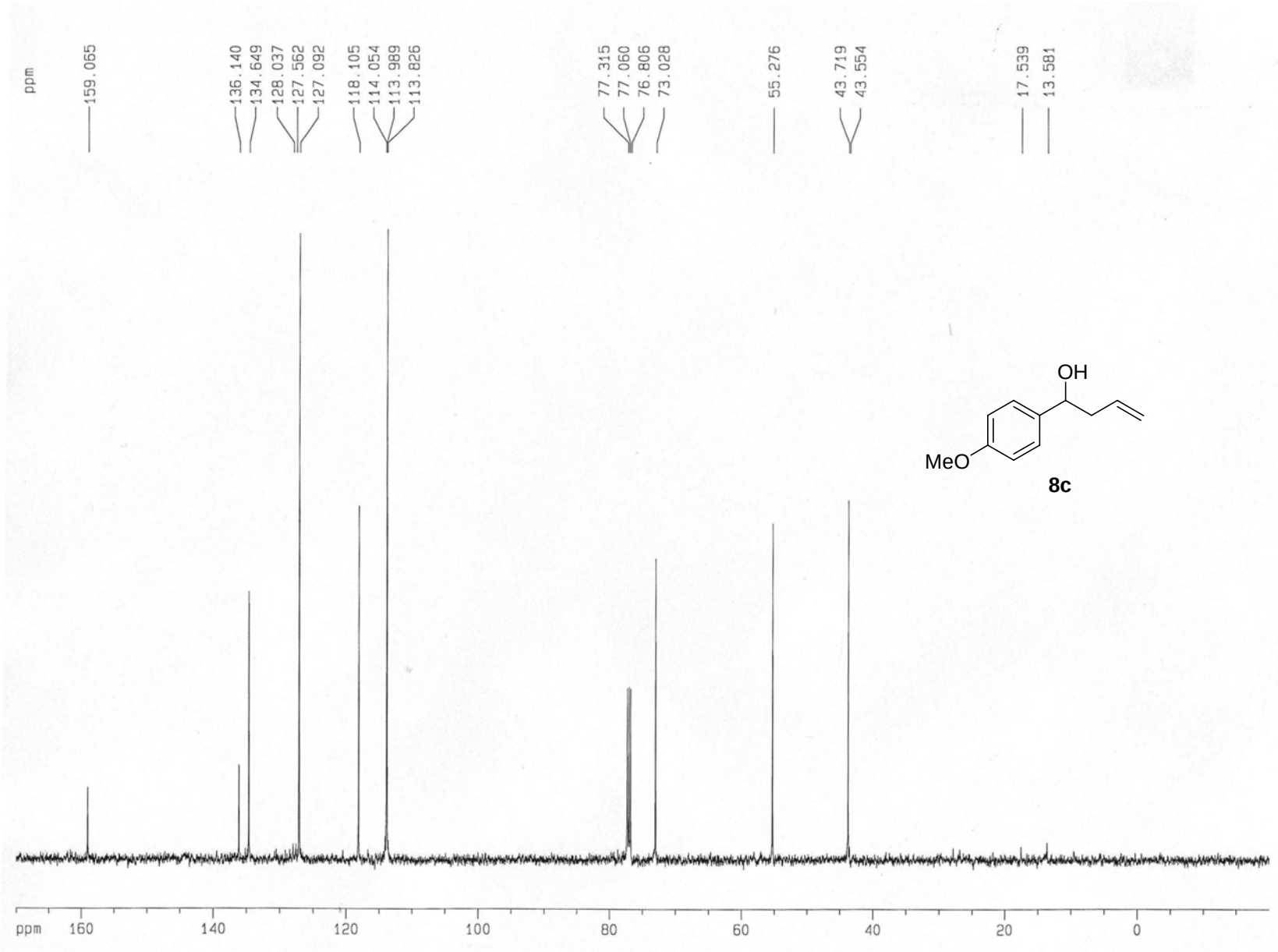
7.41683
7.40541
7.40154
7.38829
7.38608
7.37672
7.37381
7.35018
7.34614
7.33880
7.33302
5.86842
5.84808
5.83412
5.82790
5.82008
5.81377
5.79962
5.20211
5.19877
5.19597
5.17867
5.17677
5.16770
5.16449
5.16081
5.15825
4.72141
4.70842
4.69533
4.16662
4.15232
4.13804
4.12376
2.98689
2.97551
2.66888
2.58538
2.57109
2.55725
2.55521
2.54300
2.52903
2.50344
2.42597
2.41353
2.39982
2.04386
1.40177
1.33500
1.31855
1.30426
1.28998
OH
8b
ppm
7
6
5
4
3
2
1
0

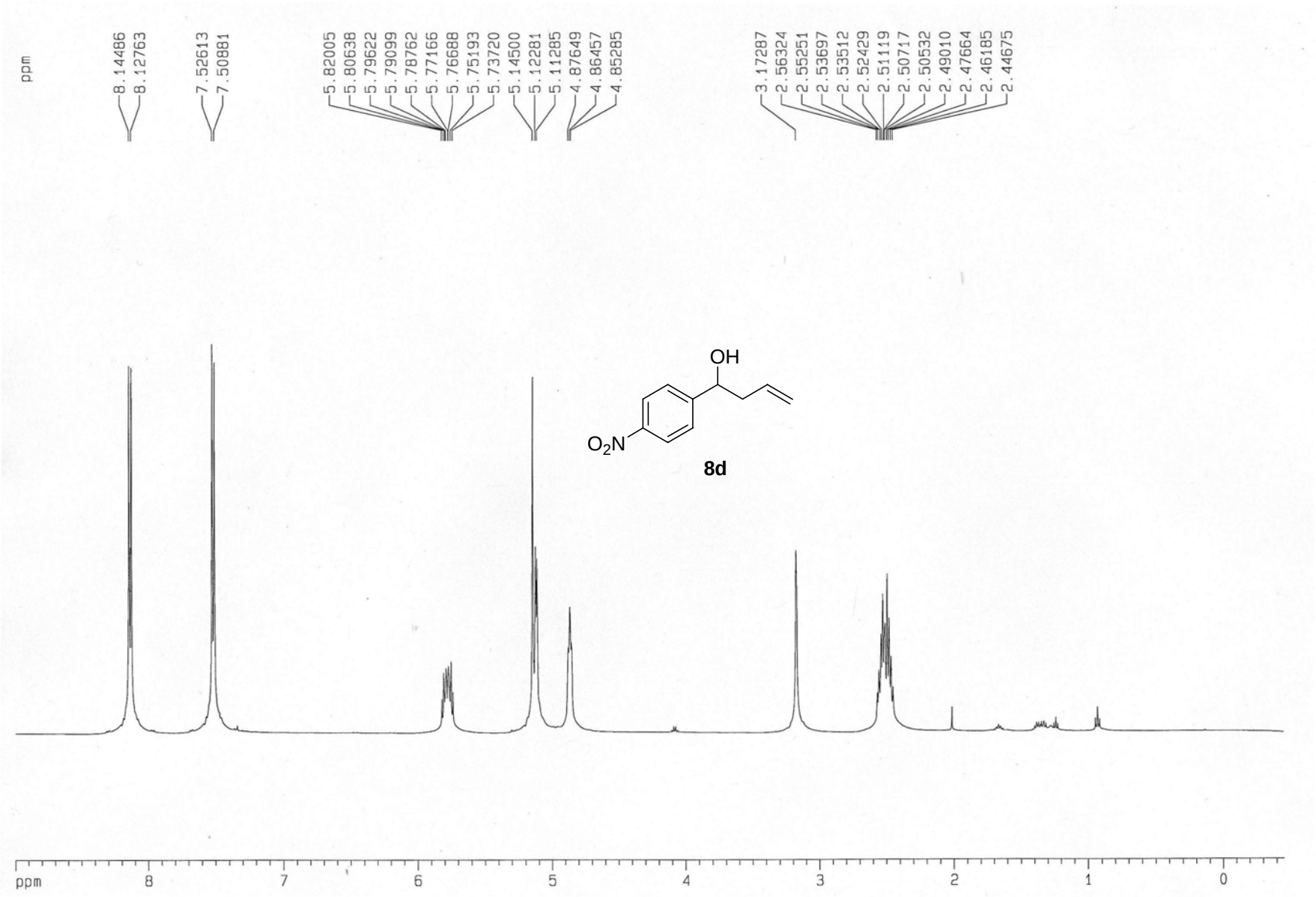

ppm
144.218
134.742
128.385
127.473
126.082
117.849
77.715
77.462
77.204
73.558
60.593
43.723
27.980
26.937
20.951
17.654
14.219
13.743
OH
ppm
140
120
100
80
60
40
20
0

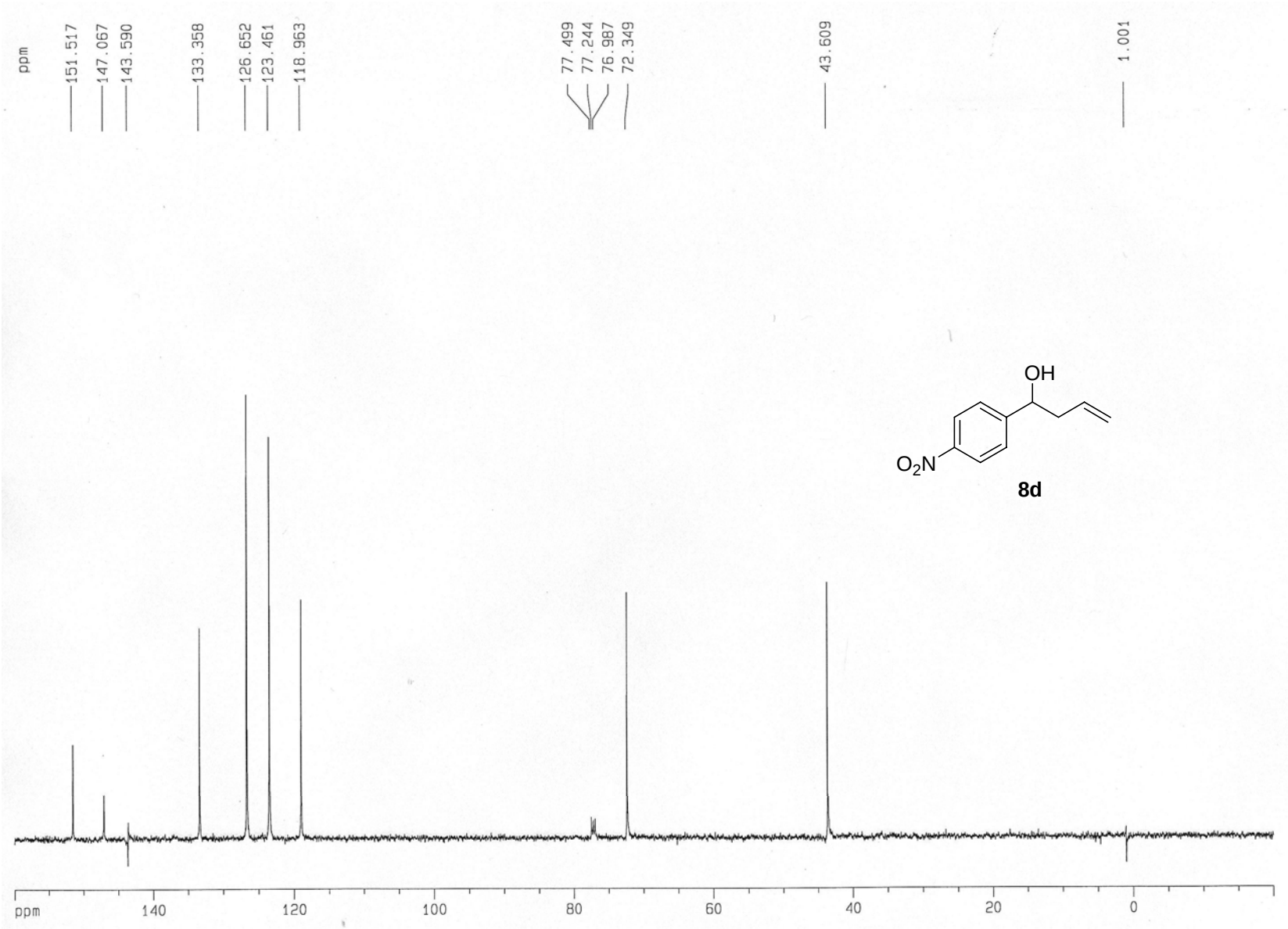
8b

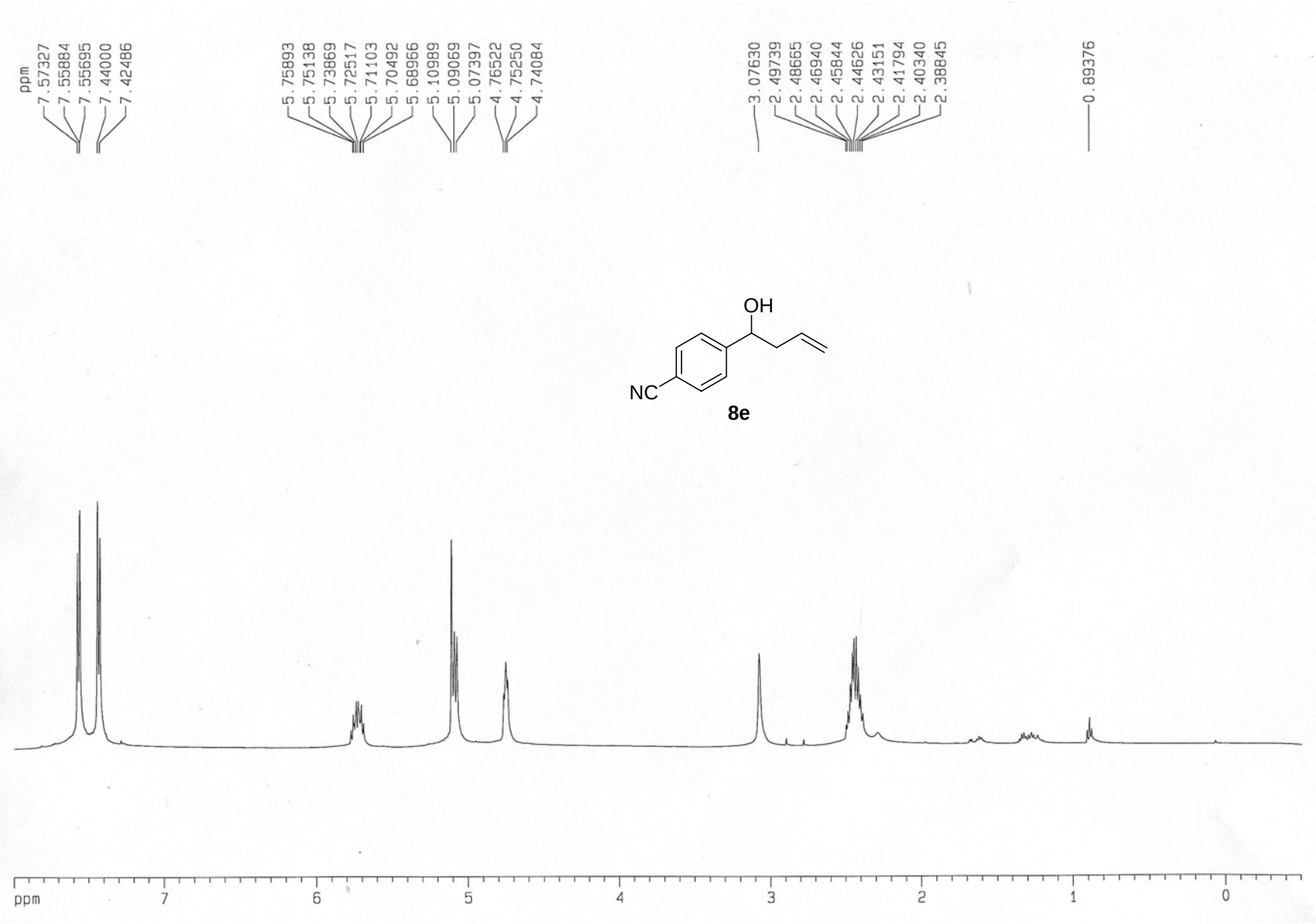

ppm
7.34501
7.32740
7.30412
7.28682
7.28130
7.26683
6.91304
6.90903
6.89578
6.88990
6.87518
5.85805
5.84391
5.83765
5.82965
5.82363
5.80956
5.80342
5.79543
5.78925
5.77510
5.18664
5.18339
5.15224
5.13358
4.70552
4.69253
4.67943
3.96353
3.87054
3.86477
3.86216
3.82219
3.79070
3.78458
3.77051
3.76666
3.67618
2.64306
2.55894
2.53081
2.51735
2.50352
2.46566
2.38824
2.18180
1.71842
1.29688
0.92006
0.11581
OH
MeO
8c
ppm
7
6
5
4
3
2
1
0

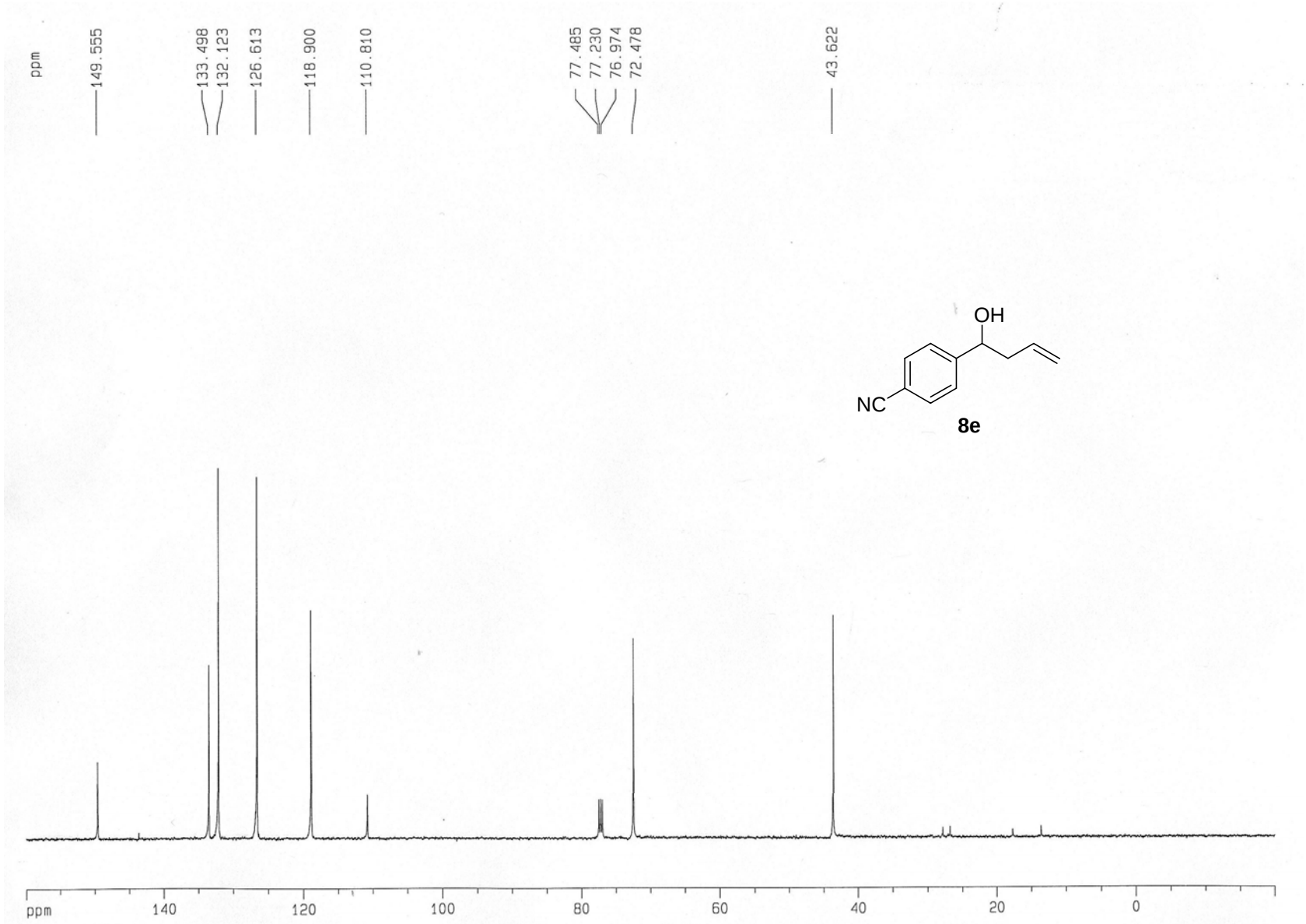

ppm
159.065
136.140
134.649
128.037
127.562
127.092
118.105
114.054
113.989
113.826
77.315
77.060
76.806
73.028
55.276
43.719
43.554
17.539
13.581
OH
MeO
ppm 160 140 120 100 80 60 40 20 0

8c


ppm
8.14486
8.12763
7.52613
7.50881
5.82005
5.80638
5.79622
5.79099
5.78762
5.77166
5.76688
5.75193
5.73720
5.14500
5.12281
5.11285
4.87649
4.86457
4.85285
3.17287
2.56324
2.55251
2.53697
2.53512
2.52429
2.51119
2.50717
2.50532
2.49010
2.47664
2.46185
2.44675
OH
O2N
8d
ppm
8
7
6
5
4
3
2
1
0


ppm
151.517
147.067
143.590
133.358
126.652
123.461
118.963
77.499
77.244
76.987
72.349
43.609
1.001
OH
O2N
8d
ppm
140
120
100
80
60
40
20
0


ppm
7.57327
7.55884
7.55695
7.44000
7.42486
5.75893
5.75138
5.73869
5.72517
5.71103
5.70492
5.68966
5.10989
5.09069
5.07397
4.76522
4.75250
4.74084
3.07630
2.49739
2.48665
2.46940
2.45844
2.44626
2.43151
2.41794
2.40340
2.38845
0.89376
OH
NC
8e
ppm
7
6
5
4
3
2
1
0


ppm
149.555
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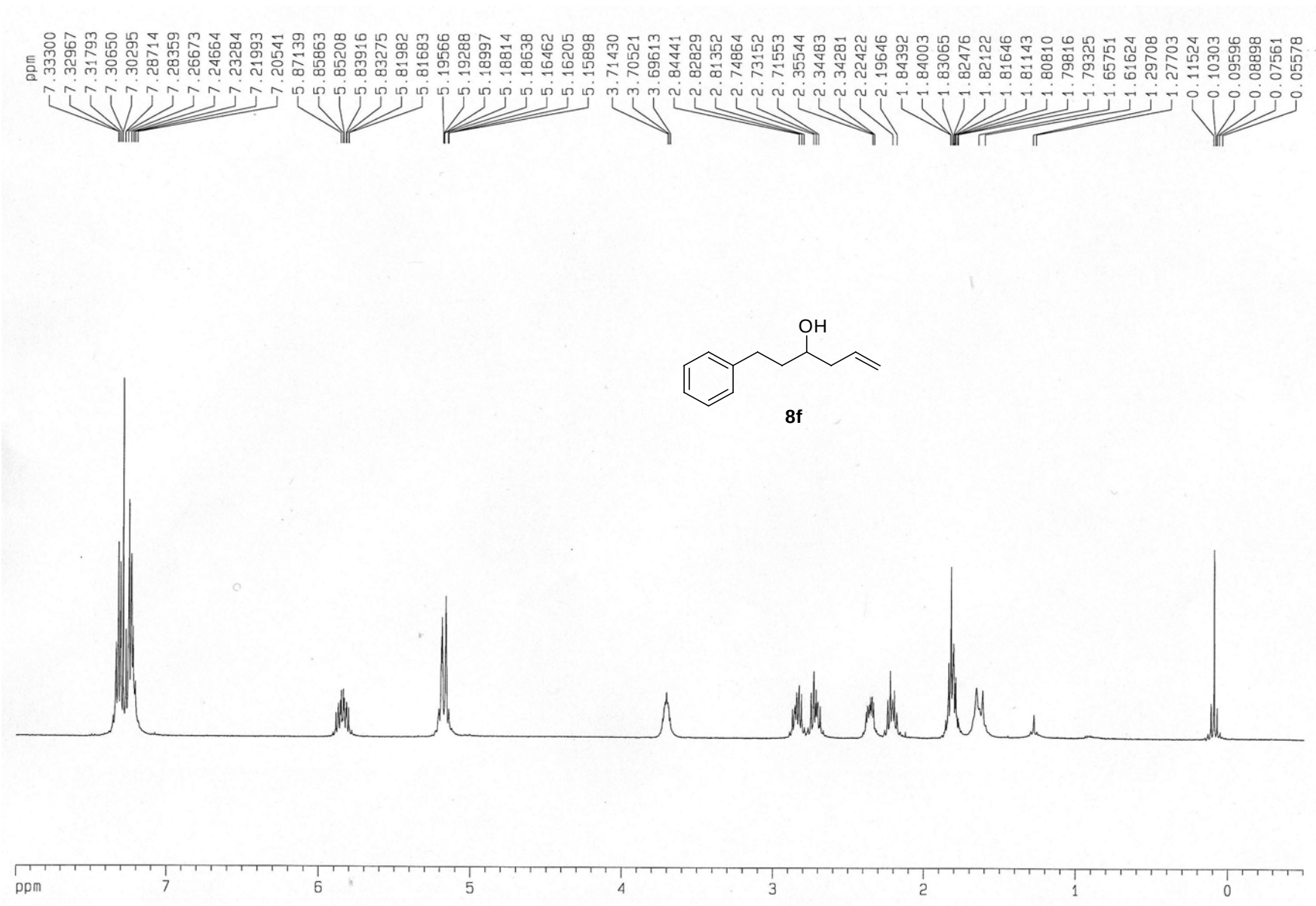
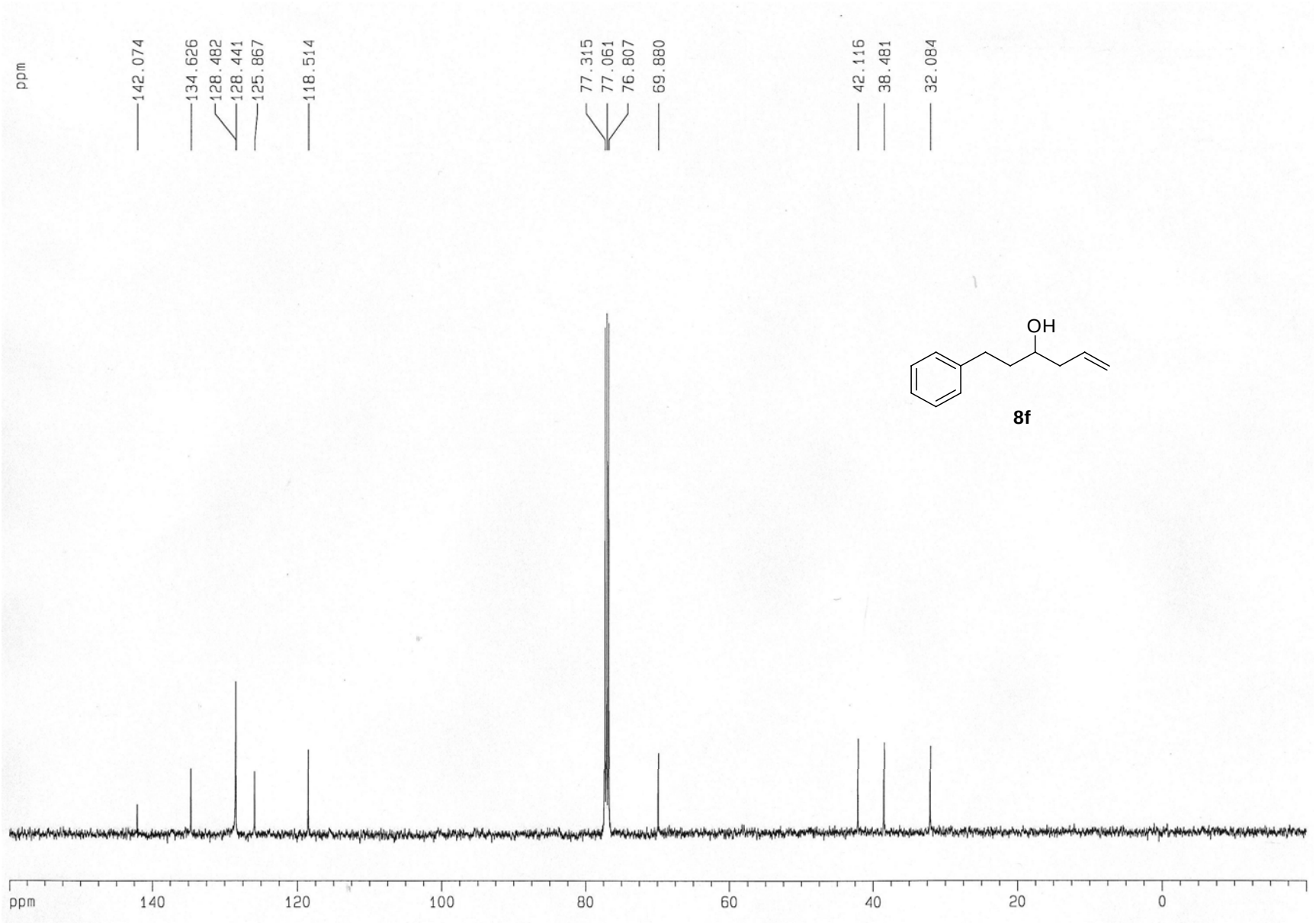
132.123
126.613
118.900
110.810
77.485
77.230
76.974
72.478
43.622
OH
NC
8e
ppm
140
120
100
80
60
40
20
0


ppm
7.33300
7.32967
7.31793
7.30650
7.30295
7.28714
7.28359
7.26673
7.24664
7.23284
7.21993
7.20541
5.87139
5.85863
5.85208
5.83916
5.83275
5.81982
5.81683
5.19566
5.19288
5.18997
5.18814
5.18638
5.16462
5.16205
5.15898
3.71430
3.70521
3.69613
2.84441
2.82829
2.81352
2.74864
2.73152
2.71553
2.35544
2.34483
2.34281
2.22422
2.19646
1.84392
1.84003
1.83065
1.82476
1.82122
1.81646
1.81143
1.80810
1.79816
1.79325
1.65751
1.61624
1.29708
1.27703
0.11524
0.10303
0.09596
0.08898
0.07561
0.05578
OH
8f
ppm
7
6
5
4
3
2
1
0


ppm
142.074
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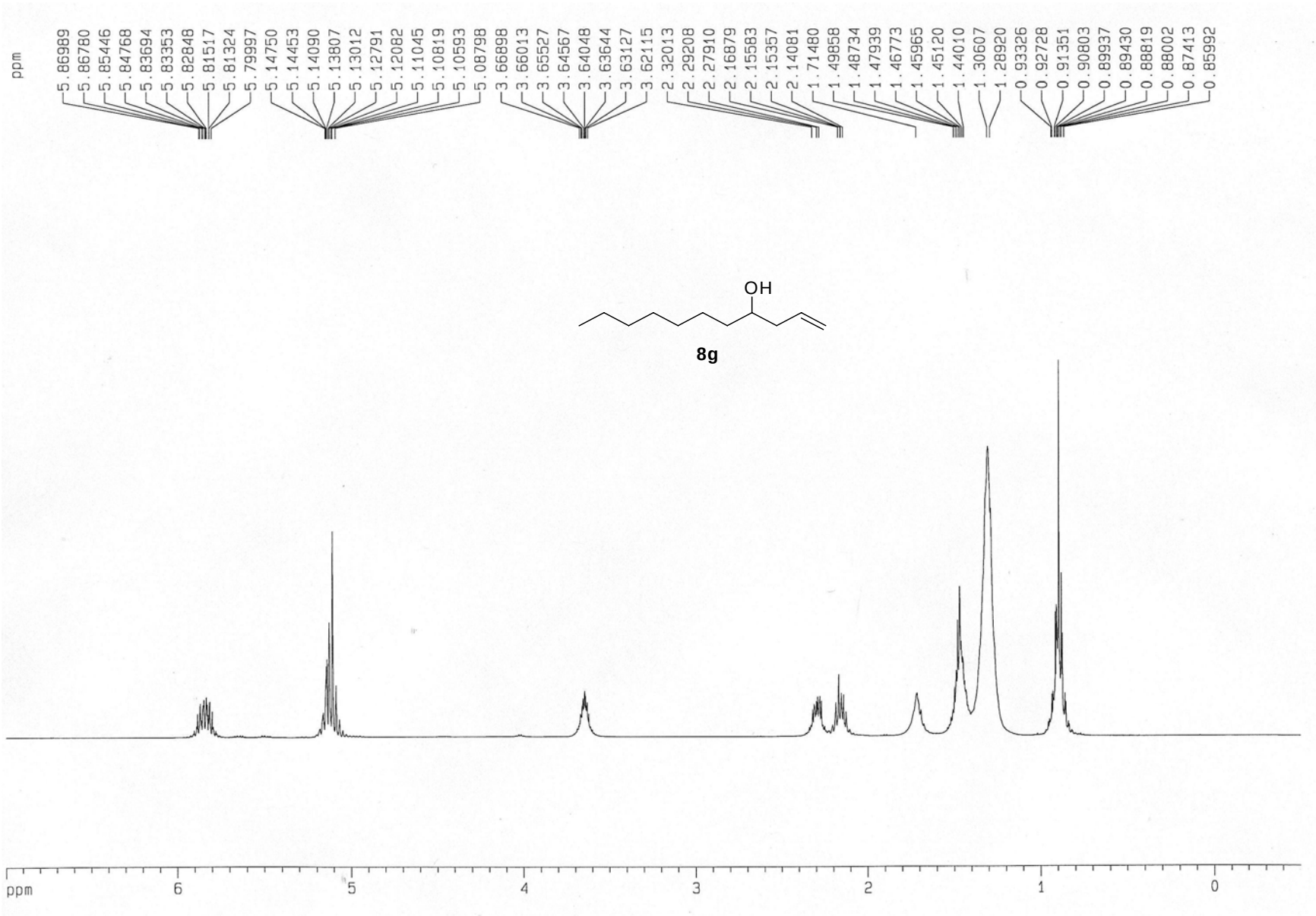
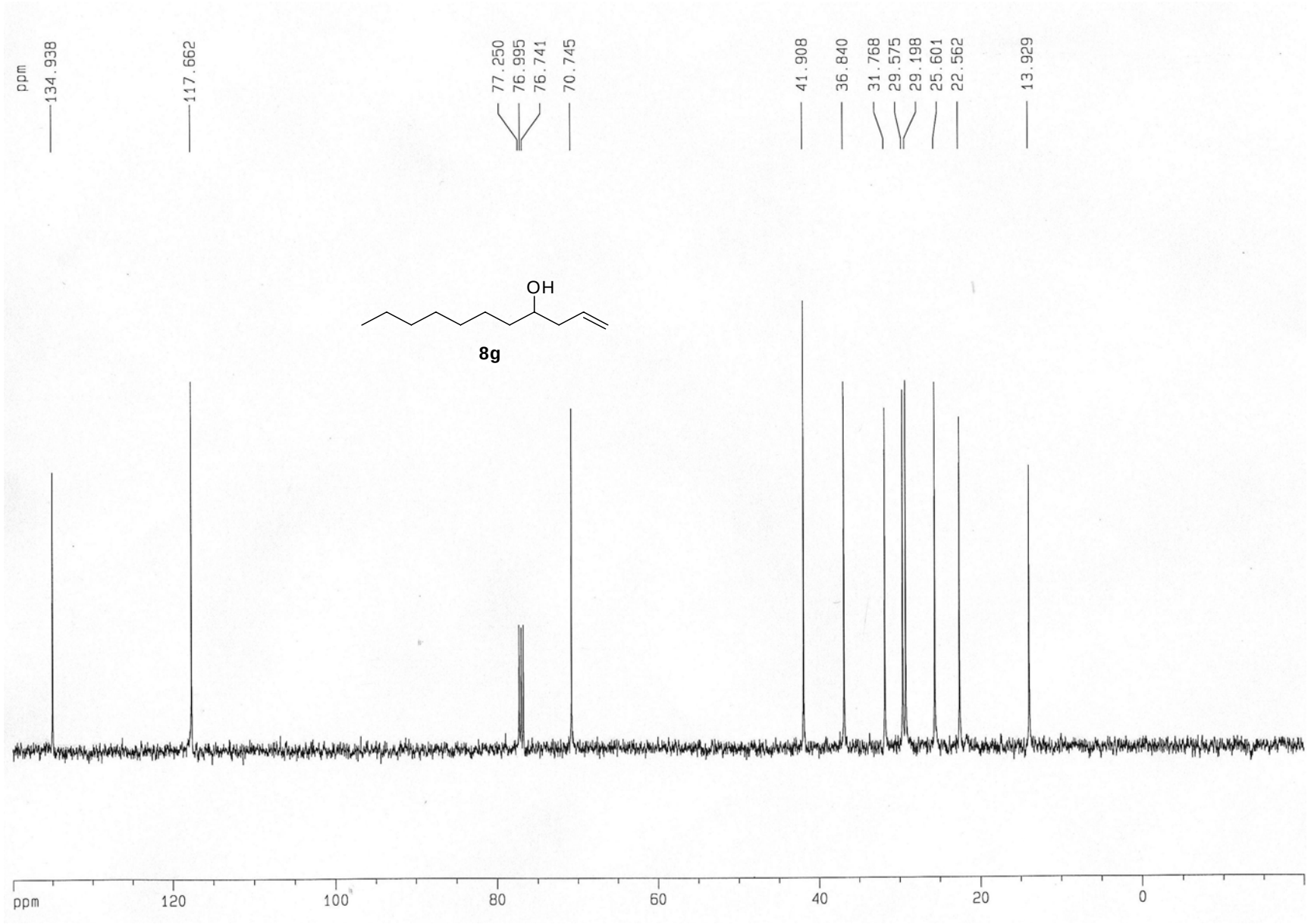
128.482
128.441
125.867
118.514
77.315
77.061
76.807
69.880
42.116
38.481
32.084
OH
8f
ppm
140
120
100
80
60
40
20
0


ppm
5.86989
5.86780
5.85446
5.84768
5.83694
5.83353
5.82848
5.81517
5.81324
5.79997
5.14750
5.14453
5.14090
5.13807
5.13012
5.12791
5.12082
5.11045
5.10819
5.10593
5.08798
3.66898
3.66013
3.65527
3.64567
3.64048
3.63644
3.63127
3.62115
2.32013
2.29208
2.27910
2.16879
2.15583
2.15357
2.14081
1.71480
1.49858
1.48734
1.47939
1.46773
1.45965
1.45120
1.44010
1.30607
1.28920
0.93326
0.92728
0.91351
0.90803
0.89937
0.89430
0.88819
0.88002
0.87413
0.85992
OH
8g
ppm
6
5
4
3
2
1
0


ppm
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76.995
76.741
70.745
41.908
36.840
31.768
29.575
29.198
25.601
22.562
13.929
OH
8g
ppm
120
100
80
60
40
20
0