Catalytic, Nucleophilic Allylation of Aldehydes with 2-Substituted Allylic Acetates: Carbon-Carbon Bond Formation Driven by the Water-Gas Shift Reaction

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SUPPORTING INFORMATION

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General Experimental

Reaction Setup: All carbonylation reactions were performed in a six-well autoclave (Figure S1), which allows for independent control of gas pressure in each well via the individual valves, equipped with a temperature probe connected to a magnetic stirrer bearing a heat control element. All other reactions were performed in oven (160 °C) and/or flame dried glassware under an atmosphere of dry argon unless otherwise noted. Room temperature (rt) was approximately 23 °C.

NMR Spectroscopy: ^{1}H and ^{13}C spectra were recorded 400 MHz, ^{1}H (100 MHz, ^{13}C) and 500 MHz, 1H (126 MHz, ^{13}C), spectrometers. Spectra were referenced to residual chloroform (7.26 ppm, ^{1}H; 77.16 ppm, ^{13}C) or when the chloroform peak is obscured in the ^{1}H NMR spectrum, to isolated singlets in the product spectrum corroborated with a more diluted sample. Chemical shifts are reported in parts per million (ppm), multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), and br (broad). Coupling constants, *J*, are reported in Hertz with integration provided and assignments indicated. Assignments are corroborated by 2D experiments (COSY, HMQC, HMBC).

***Infrared Spectroscopy*:** Infrared spectra (IR) were recorded in NaCl cells or using an FT-IR instrument. Peaks are reported in cm^{-1} with indicated relative intensities: s (strong, 67-100%); m (medium, 34-66%); w (weak, 0-33%).

Mass Spectrometry: Electron Impact (EI) spectra were performed at 70 eV using methane as the carrier gas, with a time-of-flight (TOF) mass analyzer. Chemical Ionization (CI) spectra were performed with methane reagent gas, with a TOF mass analyzer. Electrospray Ionization (ESI) spectra were performed using TOF mass analyzer. Data are reported in the form of m/z (intensity relative to the base peak = 100).

Melting Points: Melting points (mp) were determined in vacuum-sealed capillary tubes and are corrected.

Elemental Analysis: Elemental analysis data is the average of 2 runs.

Distillation: Bulb-to-bulb distillation was performed on a Kugelrohr, with boiling points (bp) corresponding to uncorrected air-bath temperatures (ABT). A vacuum of 10^{-5} torr was achieved using a diffusion pump.

Liquid Chromatography: Analytical thin-layer chromatography was performed on silica gel 60 F254 plates. Visualization was accomplished with UV light and/or potassium permanganate ($KMnO_4$) solution, Cerium-ammonium-molybdate (CAM), or 4-anisaldehyde (PA) solution. Retention factor (*Rf*) values reported were measured using a 10 × 2 cm TLC plate in a developing chamber containing the solvent system described. Flash column chromatography was performed using 40-63 μm particle size (230-400 mesh, 60 Å pore size) SiO_2. Preparative, radial, centrifugally accelerated, thin-layer chromatography was performed using glass-backed, circular TLC plates prepared with silica gel (high-purity grade, pore size 60 Å, 2-25 μm particle size, without binder, with fluorescent indicator, pore volume 0.75 cm3/g) and calcium sulfate hemihydrate (≥99%).

Gas Chromatography: Analytical gas chromatography (GC) was performed using a flame ionization detector. GC methods were used in the analysis of the products.

Solvents: Reaction solvent dioxane (HPLC grade) was distilled from sodium. Reaction solvents tetrahydrofuran (HPLC grade), diethyl ether (Et_2O) (ACS grade, BHT stabilized), and dichloromethane (HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Triethylamine (ACS grade) and pyridine (ACS grade) were distilled from CaH_2. Solvents for chromatography were: hexanes (Optima

Grade), ethyl acetate (ACS Grade), diethyl ether (ACS Grade), and dichloromethane (ACS Grade).

Chemicals: Ruthenium (III) chloride hydrate was purchased from Strem Chemicals. Triruthenium dodecacarbonyl was obtained from Sigma Aldrich and sublimed prior to use and subsequently stored in the glove box. Carbon monoxide gas was CP grade. Methallyl alcohol, benzaldehyde, 4-methoxybenzaldehyde, 4-trifluoromethylbenzaldhyde, *(E)*-cinnamaldehyde, hydrocinnamaldehyde, pivalaldehyde, isovaleraldehyde, 2-tolualdehyde, 3-chloro-2-methylprop-1-ene, and acetyl chloride were distilled prior to use. 4-Nitrobenzaldehyde was sublimed prior to use. "Brine" refers to a saturated solution of sodium chloride in water. All other reagents were used as received.

Literature Preparations

The following compounds were prepared according to literature procedures and had spectroscopic data consistent with literature: 3-(hydroxymethyl)but-3-en-2-one,[1] 2-(diethoxymethyl)prop-2-en-1-ol,[2] 2-methallyl acetate **2b**,[3] ethyl 2-(acetoxymethyl)acrylate **2l**,[4] tert-butyl 2-(acetoxymethyl)acrylate **2m**,[5] 2-phenylallyl acetate **2o**,[6] ((2-methylallyl)oxy)benzene **2k**,[7] 2-methylallyl 2-chloroacetate **2d**,[8] and 2-methylallyl 2,2,2-trichloroacetate **2c**.[9]

GC Analysis and Response Factors

Retention times (t_R) and integrated ratios were obtained from reporting integrators. Response factors for quantitative GC analysis were obtained using the following equation: response factor of compound = (area compound × mmol tetradecane)/(mmol compound × area tetradecane). Under the conditions employed, the retention time for tetradecane was 7.174 min. Three to five samples with internal standard were prepared and dissolved in EtOAc. A small

portion of each sample was diluted further to ~1.5 mL. And aliquot of each sample was injected into the GC in triplicate. The average of the 9-15 response factors was used to calculate the amount of compounds by equation 2.

GC Method: Injections were made onto a Hewlett-Packard HP-1 (30 meter) capillary column. Injector temperature was 250 °C; the detector temperature was 300 °C with a H_2 carrier gas flow of 16.7 mL/min. The column oven temperature program is as follows: 75 °C for 0 minutes, 75 °C to 250 °C ramp at 30 °C/minute, 250 °C for 6.2 minutes. Total run time is 12 minutes.

GC Method Parameters

Compound	Response Factor	t_R, min
benzaldehyde (**1a**)	1.872	3.099
trans-cinnamaldehyde (**1b**)	1.790	6.264
hydrocinnamaldehyde (**1c**)	1.850	5.489
2-methallyl acetate (**2b**)	2.513	2.452
2-methylallyl 2,2,2-trichloroacetate (**2c**)	3.024	5.436
2-methylallyl 2-chloroacetate (**2d**)	2.656	4.098
2-methylallyl 2-chlorobenzoate (**2e**)	1.333	5.436
ethyl (2-methylallyl) carbonate (**2f**)	2.976	3.630
2-methylallyl benzoate (**2g**)	1.439	6.781
1,3,5-trichloro-2-((2-methylallyl)oxy)benzene (**2h**)	1.465	7.531
1,3-dichloro-5-((2-methylallyl)oxy)benzene (**2i**)	1.483	8.043
1-((2-methylallyl)oxy)-4-(trifluoromethyl)benzene (**2j**)	1.458	5.795
((2-methylallyl)oxy)benzene (**2k**)	1.437	5.593
tert-butyl 2-(acetoxymethyl)acrylate (**2m**)	1.824	2.927
2-methylene-3-oxobutyl acetate (**2n**)	2.601	4.549
2-phenylallyl acetate (**2o**)	1.359	6.713
3-methyl-1-phenylbut-3-en-1-ol (**3ab**)	1.306	6.598
5-hydroxy-3-methylene-5-phenylpentan-2-one (**3an**)	1.534	7.927
Tetradecane	--	7.174

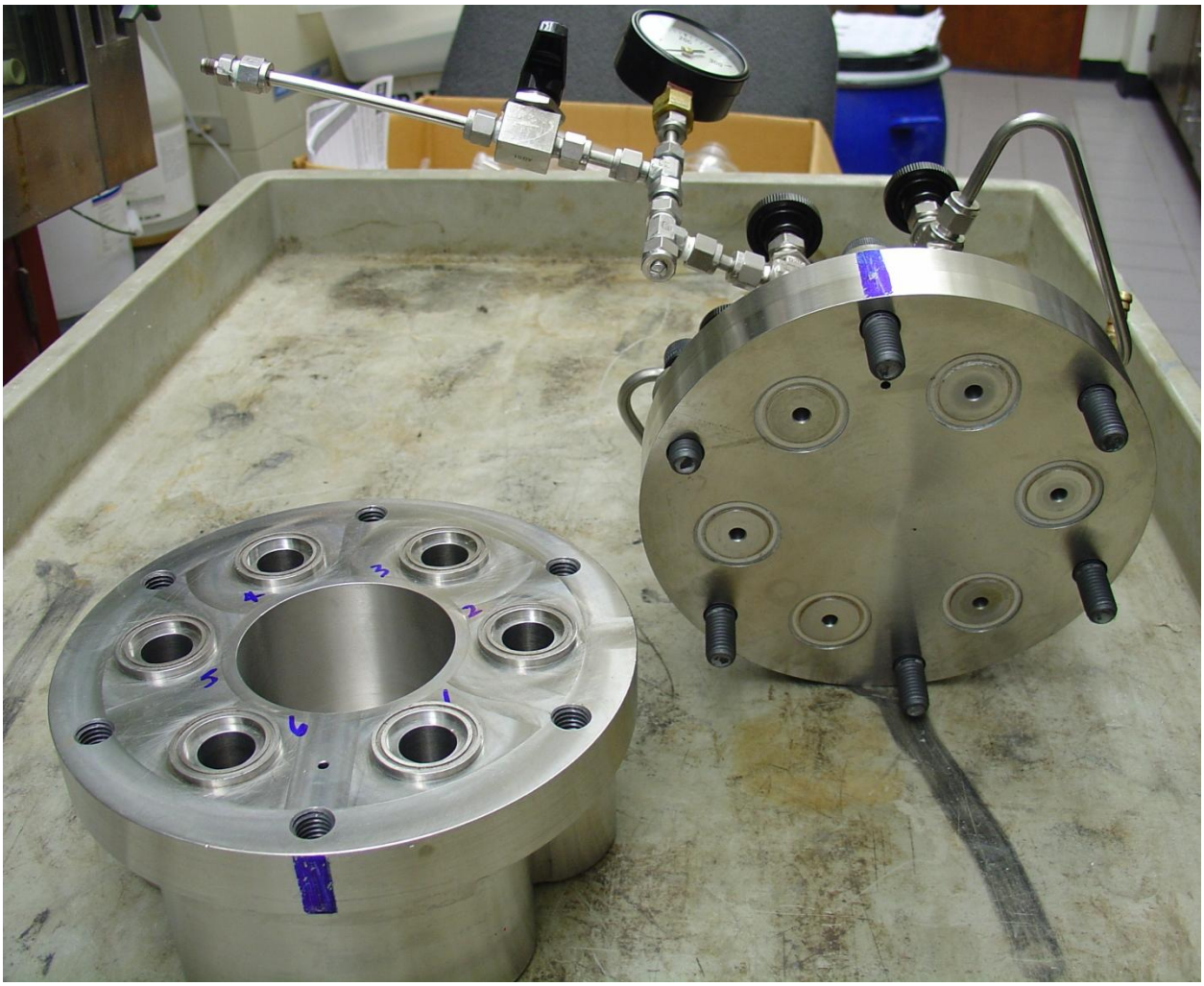


FIGURE S1(A). The six-well autoclave: open

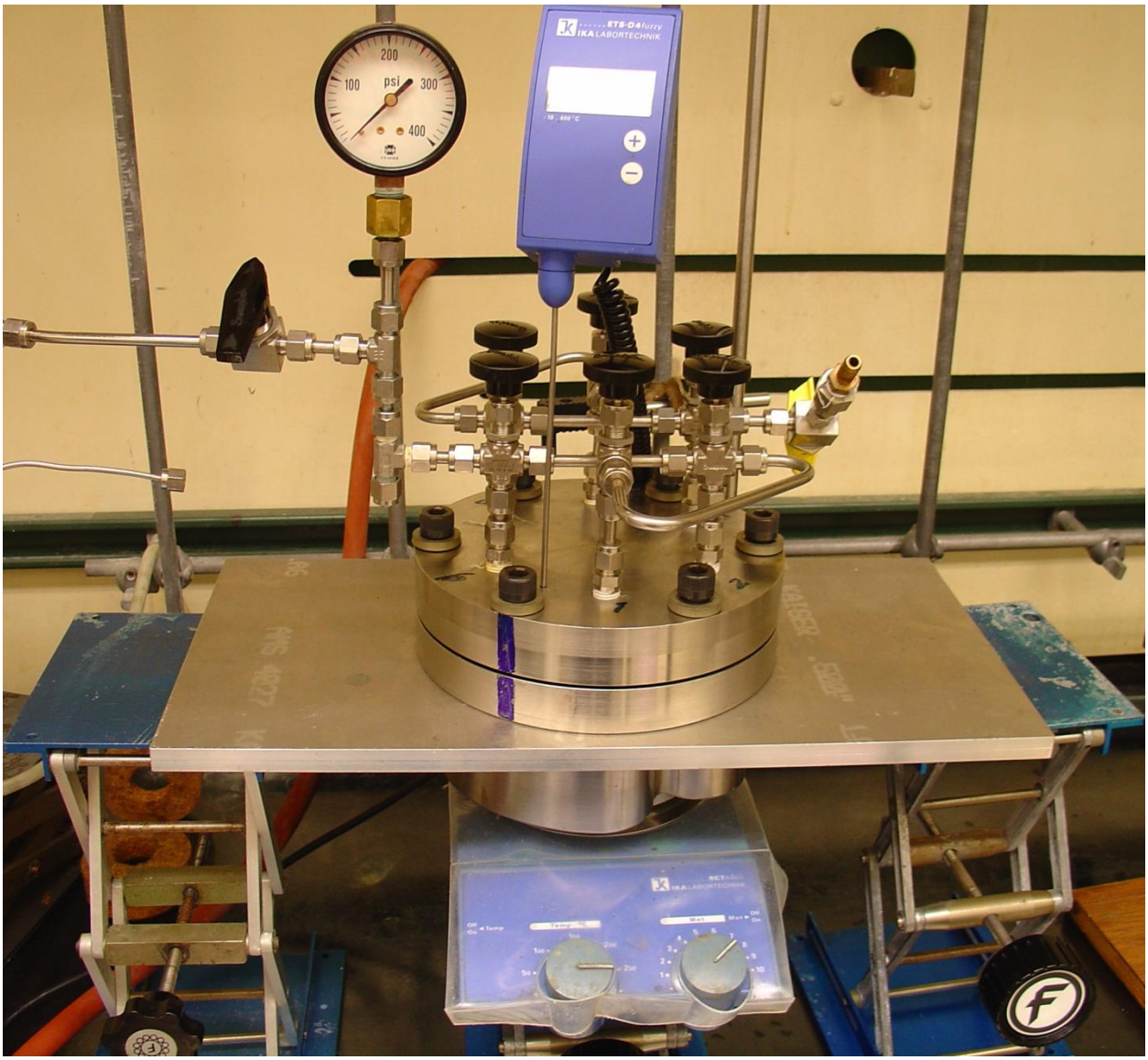


FIGURE S2(B). The six-well autoclave: closed

Optimization Studies

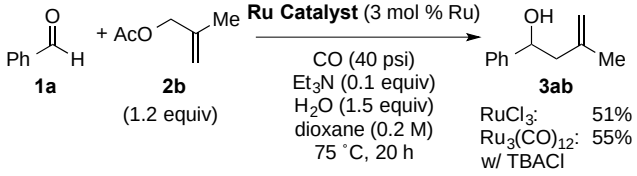
In all cases, product distributions were assessed by GC (see General Experimental section for details), employing tetradecane as the internal standard, and the observed retention times of products **3** were compared to those of their authentic samples.

General Procedure

All reactions were run in a 10-mL, flat-bottomed, glass tube (1.5 x 6.5 cm) containing a Teflon-coated, magnetic stir bar. In the glovebox, the tube was charged with $RuCl_3 \bullet xH_2O$ or $Ru_3(CO)_{12}$/TBACl before being covered with a rubber septa and removed from the glovebox. Outside the glovebox, the tube was charged sequentially with 1,4-dioxane, H_2O, Et_3N, allyl donor **2**, tetradecane, and aldehyde **1 (**1.0 equiv) *via* syringe. The tube was placed in a six-well autoclave that allows six separate reactions to be conducted at the same time. The autoclave was sealed and connected to a carbon monoxide gas cylinder. The autoclave was charged with CO gas (100 psi) and pressure was released to a vented hood four times before the CO gas was maintained at 40 psi and the valves for each cell were closed. The autoclave was mounted onto a magnetic stirrer with a temperature probe inserted into the metal block of the autoclave. The temperature was set at 75 °C and stirring was started. The temperature reached 75 °C within 30 min and was maintained for the indicated time. The autoclave was removed from the stirrer and chilled in an ice/water bath. The temperature reached ~20 °C within 40 min. The outlet was connected to a vented hood and the pressure in the autoclave was gently released. The inlet was then connected to a nitrogen line and the system was purged by N_2 (which was passed through a drying tube filled with Drierite) for 15 min before the autoclave was opened.

1. Catalytic Nucleophilic Allylation with 2-Methallyl Acetate. 1.1. Optimization of Catalyst. (Scheme S1)

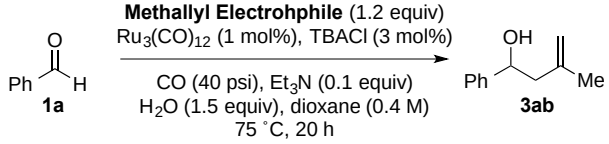
Scheme S1



According to the General Procedure either $RuCl_3 \bullet xH_2O$ or $Ru_3(CO)_{12}$ (1 mol %) and TBACl (3 mol %) was combined with 1,4-dioxane (5.0 mL), H_2O (27 μL, 1.5 mmol, 1.5 equiv), Et_3N (14 μL, 0.10 mmol, 0.1 equiv), **2b** (158.0 μL, 137.0 mg, 1.2 mmol, 1.2 equiv), and **1a** (102 μL, 106 mg, 1.0 mmol, 1.0 equiv) and reacted for 20 h. Reaction contents transferred to a 20 mL glass scintillation vial and then concentrated in vacuo (20 – 23 °C, 10 mmHg). The crude product was purified by flash column chromatography (25 g SiO_2, 2.0 cm column) $RuCl_3$: Et_2O:Hex (1:9, 400 mL then 1:4, 200 mL); $Ru_3(CO)_{12}$: Et_2O:Hex (1:9, 200 mL then 1:3, 300 mL).

1.2. Optimization of Leaving Group (Table S1). According to the General Procedure $Ru_3(CO)_{12}$ (1 mol %), TBACl (3 mol %), 1,4-dioxane (1.0 mL), H_2O (10.8 μL, 0.6 mmol, 1.5 equiv), Et_3N (5.6 μL, 0.04 mmol, 0.1 equiv), allyl donor **2** (1.2 equiv), tetradecane (50 μL, 0.192 mmol, 0.48 equiv), and **1a** (42.4 mg, 40.8 μL, 0.40 mmol, 1.0 equiv) were combined and reacted for 20 h. A 30 μL aliquot of the reaction mixture was passed through a plug of Fluorosil (ca. 1 cm) in Pasteur pipettes and washed with EtOAc (1.0 mL) into a fresh GC vial for analysis.

Table S1. Effect of Nucleofuge on Methallyl Electrophile and 3ab Conversion



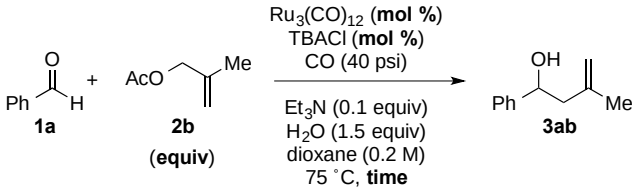
Entry	Methallyl Electrophile	pK_a of Electrophile Conjugate Acid (H_2O)	Methallyl Electrophile Recovery (%)[c]	**3ab** Conversation (%)[c]
1	**2c**	0.65	38	0
2	**2d**	2.86	4	15
3	**2e**	2.94	0	26
4	**2f**	3.60[b]	11	55
5	**2g**	4.20	0	38
6	**2b**	4.76	6	60
7	**2h**	6.35	0	27
8	**2i**	8.18	18	60
9	**2j**	8.74	21	51
10	**2k**	9.95	87	9

[a] Determined by GC analysis using tetradecane as the internal standard. [b] pK_a value of carbonic acid

1.3. Optimization of Reaction Conditions (Table S2). According to the General Procedure According to the General Procedure, $Ru_3(CO)_{12}$ (1 or 2 mol %), TBACl (3 or 6 mol %), 1,4-dioxane (1.0 mL for 0.4 M or 2.0 mL for 0.2 M), H_2O (10.8 μL, 0.6 mmol, 1.5 equiv), Et_3N (5.6 μL, 0.04 mmol, 0.1 equiv), allyl donor **2b** (1.2, 1.4, 2.0, or 3.0 equiv), tetradecane (50 μL, 0.192 mmol, 0.48 equiv), and **1a** (42.4 mg, 40.8 μL, 0.40 mmol, 1.0 equiv) were combined and reacted for 20 or 40 h. A 30 μL aliquot of the reaction mixture was passed through a plug of

Fluorosil (ca. 1 cm) in Pasteur pipettes and washed with EtOAc (1.0 mL) into a fresh GC vial for analysis.

Table S2. Effect of 2ab Equivalents, Catalyst Loading, and Time on Yield of 3ab



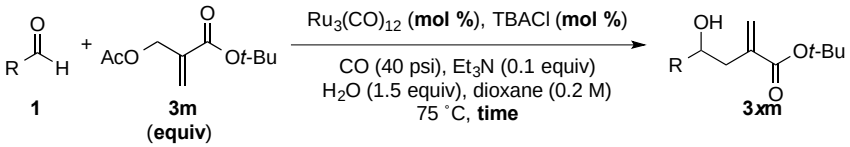
entry	$Ru_3(CO)_{12}$ mol %[a]	time (h)	**2b** (equiv)	**2b** recovery (%)[b,c]	**3ab** yield (%)[b]
1	1	20	1.2	0	53
2	1	20	2.0	6	60
3	1	40	1.4	2	49
4	1	40	2.0	0	52
5	2	20	1.2	0	39
6	2	20	2.0	10	55
7	2	20	3.0	36	61
8	2	40	2.0	11	53

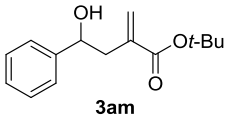
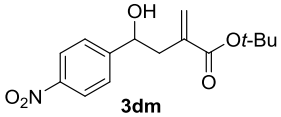
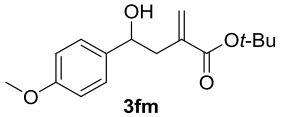
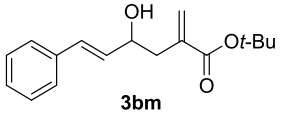
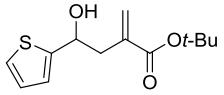
[a] TBACl loading 3 mol % w.r.t $Ru_3(CO)_{12}$. [b] Determined by GC using tetradecane as the internal standard. [c] Percentage recovered with respect to the total equiv of **2b**.

2. Catalytic Nucleophilic Allylation with *tert*-Butyl 2-(acetoxymethyl)acrylate. 2.1. Optimization of Catalyst Loading and Reaction Time (Table S3). According to the General Procedure, $Ru_3(CO)_{12}$ (1 or 2 mol %), TBACl (3 or 6 mol %), 1,4-dioxane (2.0 mL), H_2O (10.8 μL, 0.6 mmol, 1.5 equiv), Et_3N (5.6 μL, 0.04 mmol, 0.1 equiv), allyl donor **2m** (1.2, 1.4, 1.5, or 1.6 equiv), tetradecane (50 μL, 0.192 mmol, 0.48 equiv), and aldehyde **1** (0.40 mmol, 1.0 equiv) were combined and reacted for 20 or 36 h. A 30 μL aliquot of the reaction mixture was passed through a plug of Fluorosil (ca. 1 cm) in Pasteur pipettes and washed with EtOAc (1.0 mL) into a fresh GC vial for analysis. The remainder of the solution was transferred to a 20-mL, glass scintillation vial with the aid of 3 mL of diethyl ether. The solvent was removed under reduced

pressure by rotary evaporation (25 °C, 20 mmHg). A ^{1}H NMR sample (in $CDCl_3$) was made of this concentrated reaction mixture and the relative ratios of product to aldehyde peaks (assumed mass balance) were integrated to determine the conversion of **1**.

Table S3. Effect of $Ru_3(CO)_{12}$ Catalyst Loading and Reaction Time on Allylation with 2m

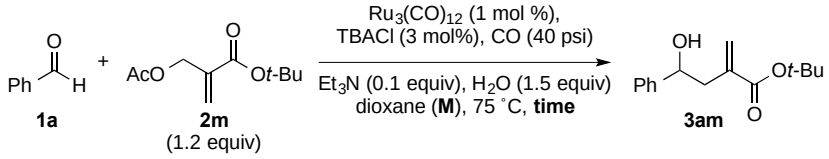


entry	product **3*x*m**	$Ru_3(CO)_{12}$ mol %[a]	time (h)	**2m** (equiv)	**1** conversion (%)[b]	**2m** recovery (%)[c]
1	 **3am**	1	20	1.6	76	28
2		2	20	1.6	99	14
3	 **3dm**	1	36	1.2	93	27
4		2	20	1.2	96	19
5	 **3fm**	1	36	1.5	91	1
6		2	20	1.6	96	25
7	 **3bm**	1	20	1.4	67	33
8		2	20	1.4	91	22
9	 **3jm**	1	20	1.4	79	21
10		2	20	1.4	91	22

[a] TBACl mol % = 3 equivalents w.r.t. $Ru_3(CO)_{12}$ [b] Determined via ^{1}H NMR integration of aldehyde and product peaks. [c] Determined by GC analysis using tetradecane as the internal standard.

2.2. Optimization of Concentration and Reaction Time (Table S4). According to the General Procedure, $Ru_3(CO)_{12}$ (1 mol %), TBACl (3 mol %), 1,4-dioxane (1.0 mL for 0.4 M or 2.0 mL for 0.2 M), H_2O (10.8 μL, 0.6 mmol, 1.5 equiv), Et_3N (5.6 μL, 0.04 mmol, 0.1 equiv), allyl donor **2m** (96.1 mg, 0.48 mmol, 1.2 equiv), tetradecane (50 μL, 0.192 mmol, 0.48 equiv), and aldehyde **1** (42.4 mg, 40.8 μL, 0.40 mmol, 1.0 equiv) were combined and reacted for 4, 12, or 16 h. A 30 μL aliquot of the reaction mixture was passed through a plug of Fluorosil (ca. 1 cm) in Pasteur pipettes and washed with EtOAc (1.0 mL) into a fresh GC vial for analysis.

Table S4. Effect of Reaction Time and Concentration on Allylation with 2m.

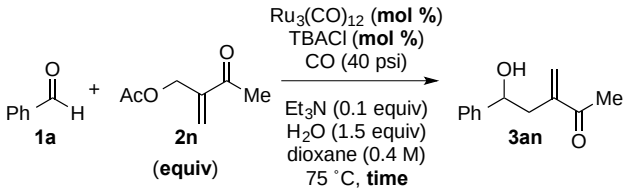


entry	**1a** concentration	time (h)	**1a** recovery (%)[a]
1	0.2 M	4	67
2	0.2 M	12	28
3	0.2 M	16	30
4	0.4 M	4	28
5	0.4 M	12	23
6	0.4 M	16	23

[a] Determined by GC analysis using tetradecane as the internal standard

3. Catalytic Nucleophilic Allylation 2-Methylene-3-oxobutyl Acetate. 3.1. Optimization of Reaction Conditions (Table S5). According to the General Procedure, $Ru_3(CO)_{12}$ (1 or 2 mol %), TBACl (3 or 6 mol %), 1,4-dioxane (1.0 mL), H_2O (10.8 μL, 0.6 mmol, 1.5 equiv), Et_3N (5.6 μL, 0.04 mmol, 0.1 equiv), allyl donor **2n** (1.2, 1.6, or 2.0 equiv), tetradecane (50 μL, 0.192 mmol, 0.48 equiv), and aldehyde **1a** (42.4 mg, 40.8 μL, 0.40 mmol, 1.0 equiv) were combined and reacted for 20 or 40 h. A 30 μL aliquot of the reaction mixture was passed through a plug of Fluorosil (ca. 1 cm) in Pasteur pipettes and washed with EtOAc (1.0 mL) into a fresh GC vial for analysis.

Table S5. Effect of Catalyst Loading, Reaction Time, and 2n Equivalents on Allylation of 1a.

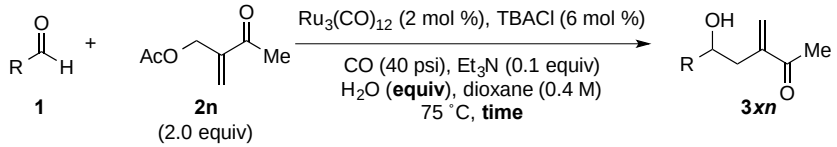


entry	$Ru_3(CO)_{12}$ mol %[a]	time (h)	**2n** (equiv)	**2n** recovery (%)[b,c]	**3an** yield (%)[b]
1	1	20	1.2	0	51
2	1	20	1.6	18	58
3	1	20	2.0	28	73
4	1	40	2.0	24	71
5	2	20	2.0	23	94

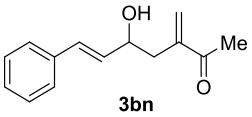
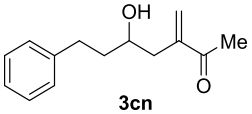
[a] TBACl loading 3 mol % w.r.t $Ru_3(CO)_{12}$. [b] Determined by GC analysis using tetradecane as the internal standard.[c] Percentage recovered is with respect to the total equiv of **2n**

3.2. Optimization of Water Loading (Table S6). According to the General Procedure $Ru_3(CO)_{12}$ (2 mol %), TBACl (6 mol %), 1,4-dioxane (1.0 mL), H_2O (2.5, 3.0, or 3.5 equiv), Et_3N (5.6 μL, 0.04 mmol, 0.1 equiv), allyl donor **2n** (113.7 mg, 0.80 mmol, 2.0 equiv), tetradecane (50 μL, 0.192 mmol, 0.48 equiv), and aldehyde **1** (0.40 mmol, 1.0 equiv) were combined and reacted for 24 or 48 h. A 30 μL aliquot of the reaction mixture was passed through a plug of Fluorosil (ca. 1 cm) in Pasteur pipettes and washed with EtOAc (1.0 mL) into a fresh GC vial for analysis.

Table 6. Effect of H_2O Loading on Allylation with 2n



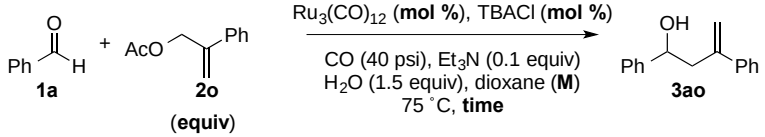
1 **2n** (2.0 equiv) **3*xn***

entry	product **3*x*n**	H_2O (equiv)	time (h)	**1** recovery (%)[a]	**2n** recovery (%)[a,b]
1		2.5	48	20	14
2	 **3bn**	3.0	24	40	26
3		3.5	24	39	24
4		3.5	48	18	8
5	 **3cn**	3.0	24	11	4
6		3.5	24	2	15

[a] Determined by GC analysis using tetradecane as the internal standard. [b] Percentage recovered is with respect to the total equiv of **2n** added.

4. Catalytic Nucleophilic Allylation 2-Phenylallyl Acetate. 4.1. Reaction Optimization (Table S7). According to the General Procedure, $Ru_3(CO)_{12}$ (1 or 2 mol %), TBACl (3 or 6 mol %), 1,4-dioxane (1.0 mL for 0.4 M or 2.0 mL for 0.2 M), H_2O (10.8 μL, 0.6 mmol, 1.5 equiv), Et_3N (5.6 μL, 0.04 mmol, 0.1 equiv), allyl donor **2o** (1.2, 1.5, or 1.8 equiv), tetradecane (50 μL, 0.192 mmol, 0.48 equiv), and aldehyde **1a** (42.4 mg, 40.8 μL, 0.40 mmol, 1.0 equiv) were combined and reacted for 20 or 40 h. A 30 μL aliquot of the reaction mixture was passed through a plug of Fluorosil (ca. 1 cm) in Pasteur pipettes and washed with EtOAc (1.0 mL) into a fresh GC vial for analysis.

Table 7. Effect of Concentration, Time, Catalyst, and 2o Loading on the Allylation of 1a

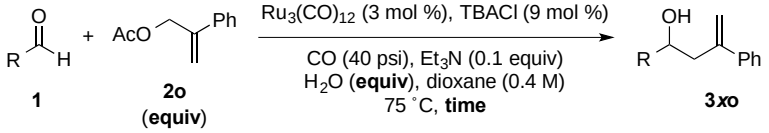


entry	$Ru_3(CO)_{12}$ mol %[a]	**1a** concentration	time (h)	**2o** (equiv)	**1a** recovery (%)[b]	**2o** recovery (%)[b,c]
1	1	0.2 M	20	1.2	47	0
2	1	0.2 M	40	1.5	25	0
3	1	0.4 M	40	1.5	18	1
4	2	0.4 M	20	1.8	23	26

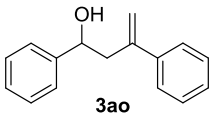
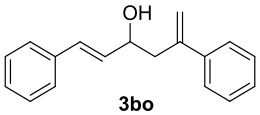
[a] TBACl loading 3 mol % w.r.t $Ru_3(CO)_{12}$. [b] Determined by GC analysis using tetradecane as the internal standard. [c] Percentage recovered is with respect to the total equiv of **2o** added.

4.2. Optimization of Water Loading (Table S8). According to the General Procedure $Ru_3(CO)_{12}$ (3 mol %), TBACl (9 mol %), 1,4-dioxane (1.0 mL), H_2O (2.0, 2.5, 3.0, or 3.5 equiv), Et_3N (5.6 μL, 0.04 mmol, 0.1 equiv), allyl donor **2o** (2.4 or 2.8 equiv), tetradecane (50 μL, 0.192 mmol, 0.48 equiv), and aldehyde **1** (0.40 mmol, 1.0 equiv) were combined and reacted for 24 or 48 h. A 30 μL aliquot of the reaction mixture was passed through a plug of Fluorosil (ca. 1 cm) in Pasteur pipettes and washed with EtOAc (1.0 mL) into a fresh GC vial for analysis.

Table 8. Effect of Time and H_2O and 2o Loading on Allylation of 1



1 **2o** (**equiv**) **3*x*o**

entry	product **3*x*o**	H_2O (equiv)	**2o** (equiv)	time (h)	**1** recovery (%)[a]	**2o** recovery (%)[a,b]
1	 **3ao**	2.0	2.8	24	16	40
2		2.0	2.8	48	17	37
3		2.5	2.8	24	12	11
4		2.5	2.8	48	11	7
5		3.0	2.4	24	17	0
6		3.5	2.4	24	19	1
7	 **3bo**	2.5	2.8	24	22	12
8		3.5	2.4	24	18	0
9		3.5	2.8	24	22	0
10		3.5	2.8	48	18	0

[a] Determined by GC analysis using tetradecane as the internal standard.
[b] Percentage recovered is with respect to the total equiv of **2o** added.

References

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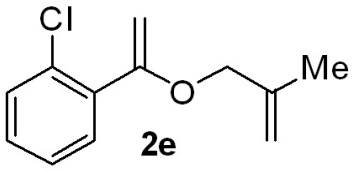
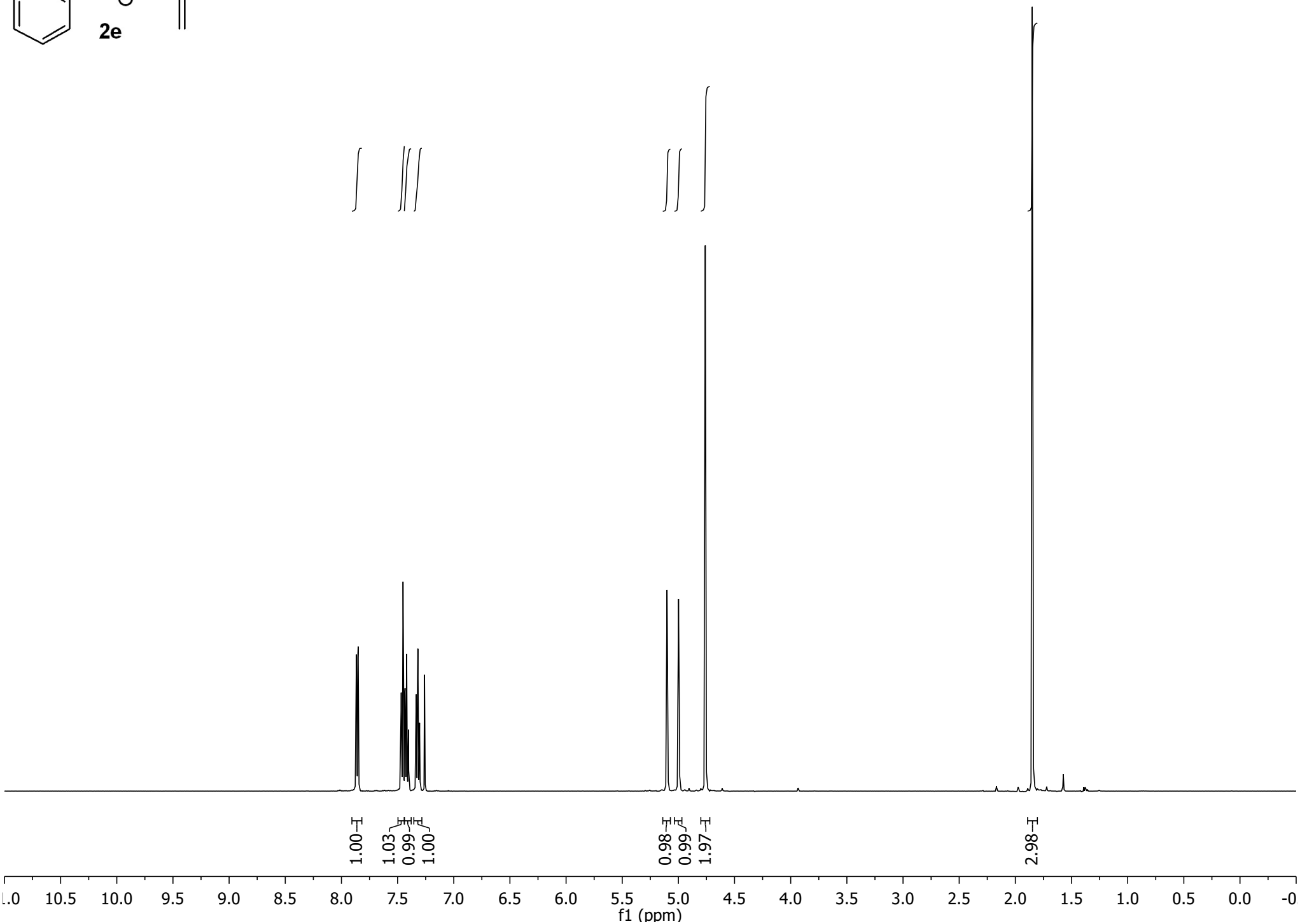
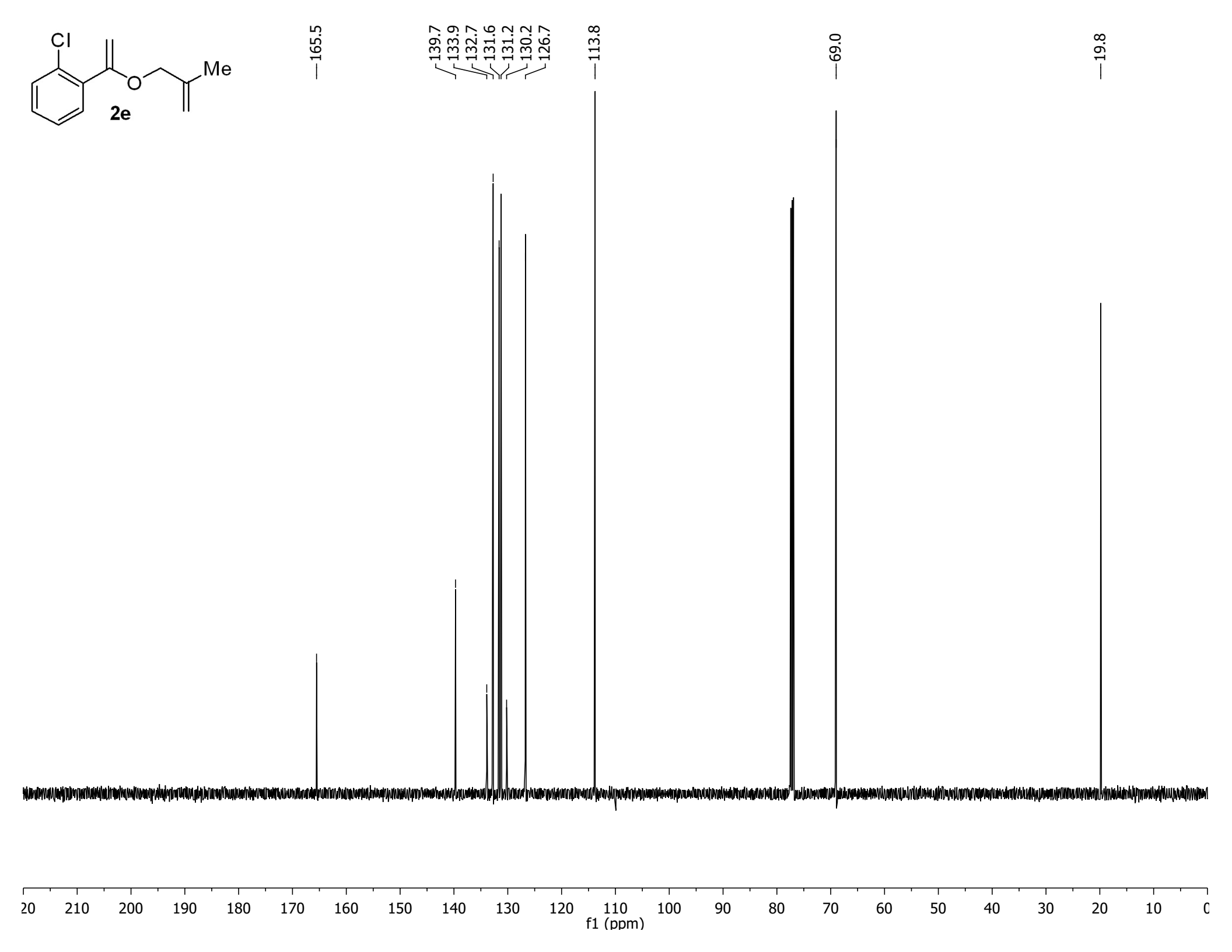


2e

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132.7
131.6
131.2
130.2
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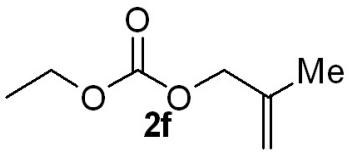
113.8
69.0
19.8
f1 (ppm)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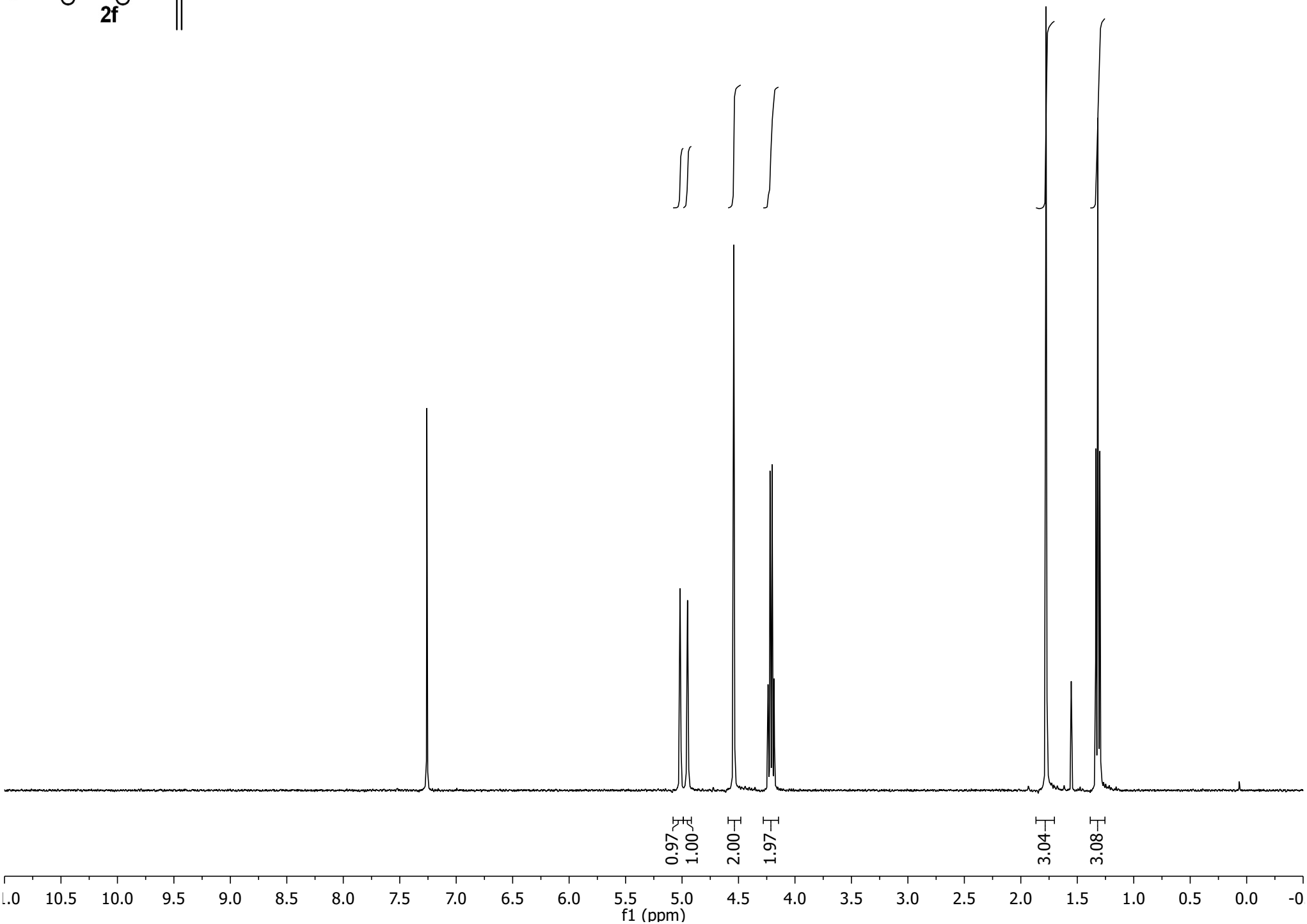
O
O
Me
2f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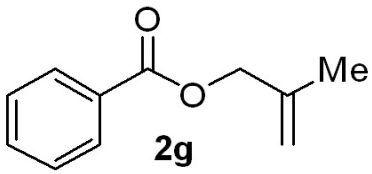
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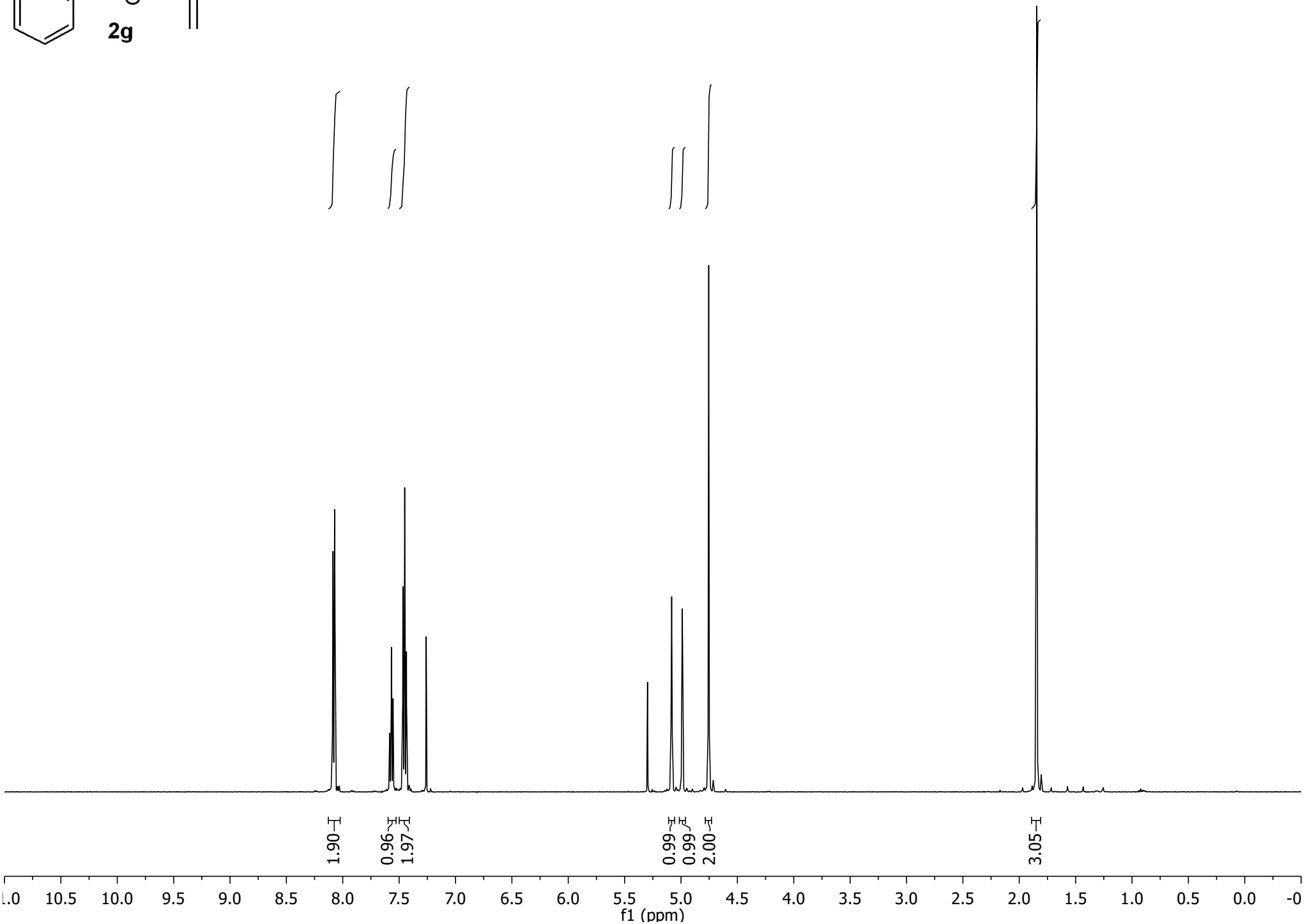
O
Me

2g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6.5
6.0
5.5
5.0
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2.0
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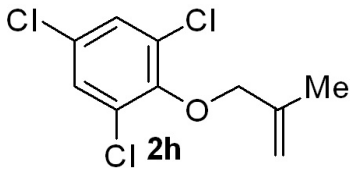
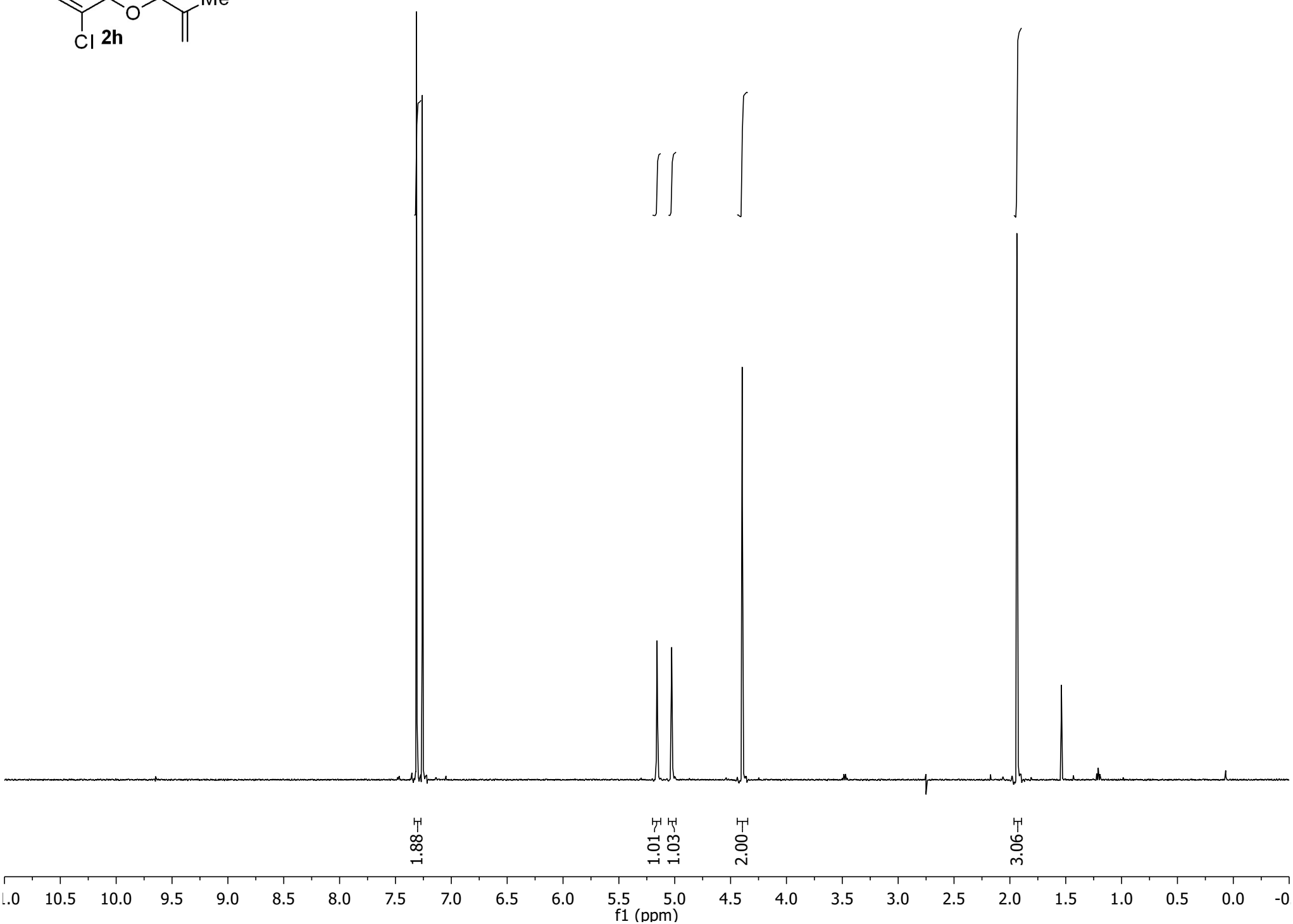
0.0
f1 (ppm)


Cl
Cl
Me
O
Cl
2h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6.5
6.0
5.5
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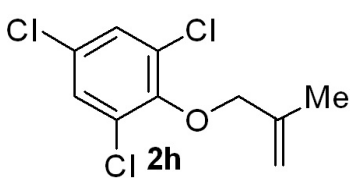
f1 (ppm)


Cl
Cl
O
Me
Cl
2h

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130.3
129.6
128.9
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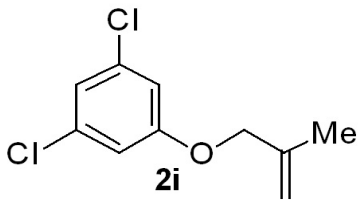
77.2
19.8
f1 (ppm)


Cl
Cl
O
Me

2i

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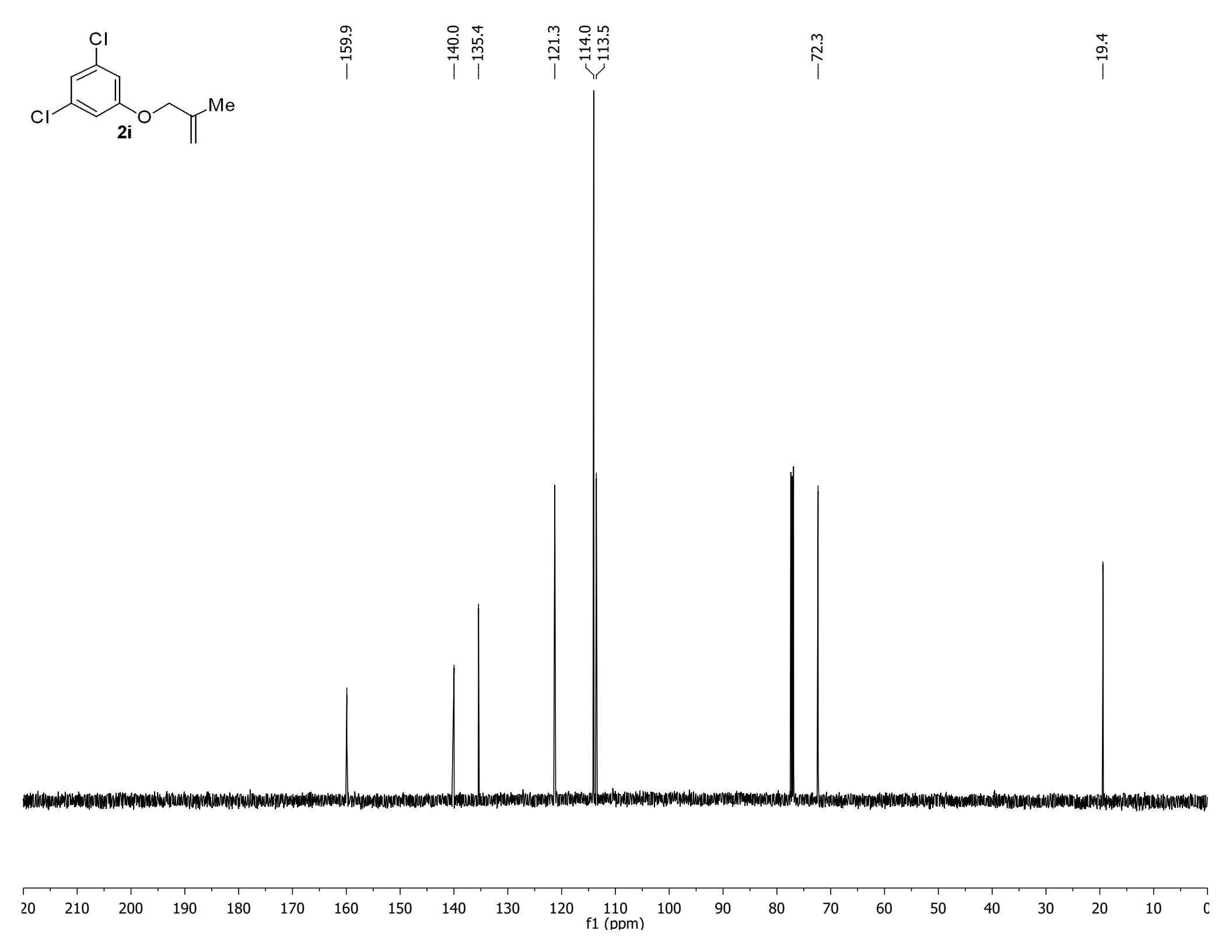
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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121.3
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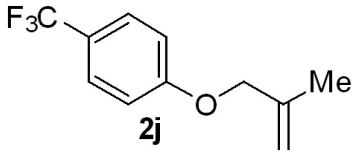
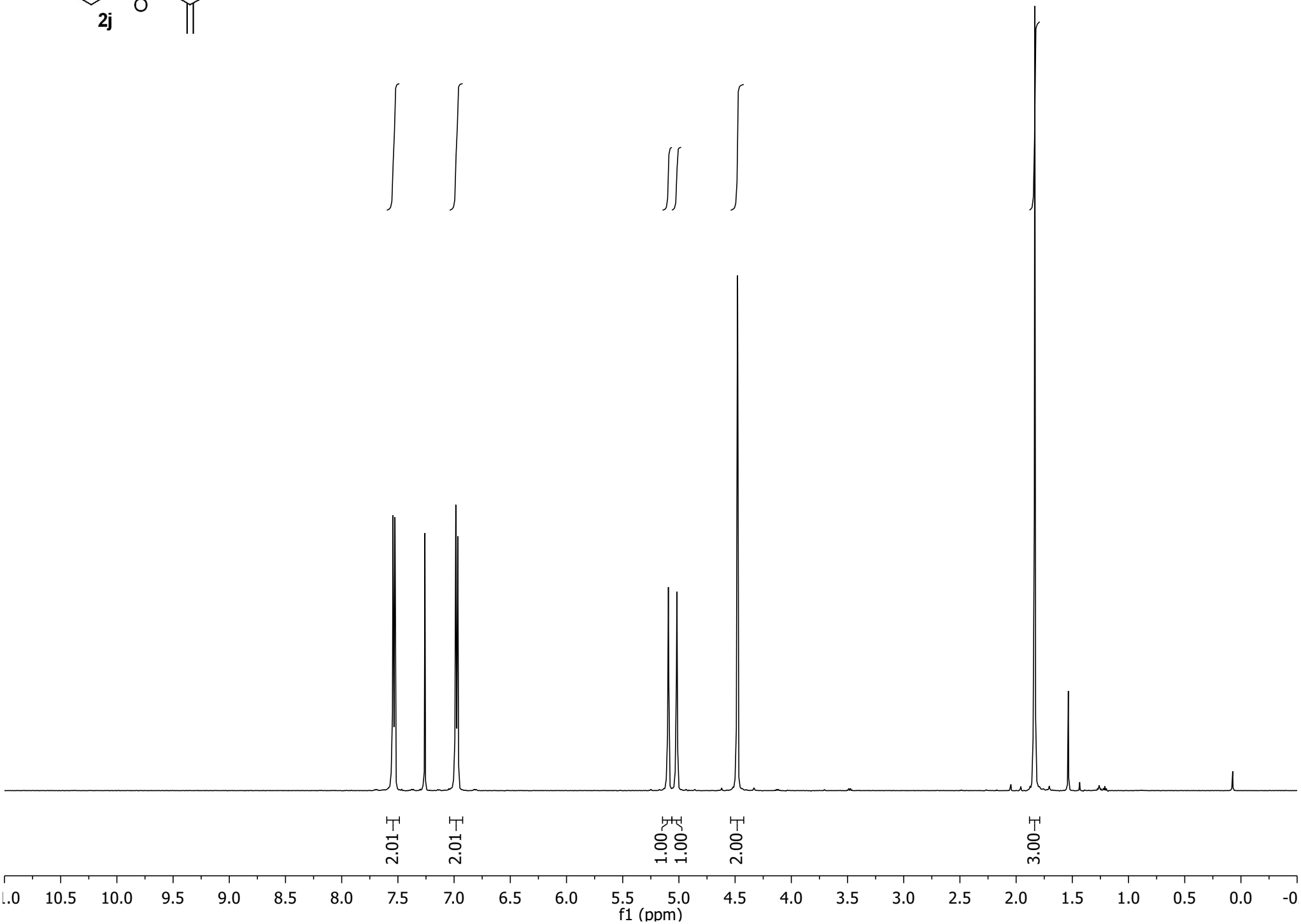
113.5
72.3
19.4
f1 (ppm)


F3C
Me
O

2j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6.5
6.0
5.5
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2.5
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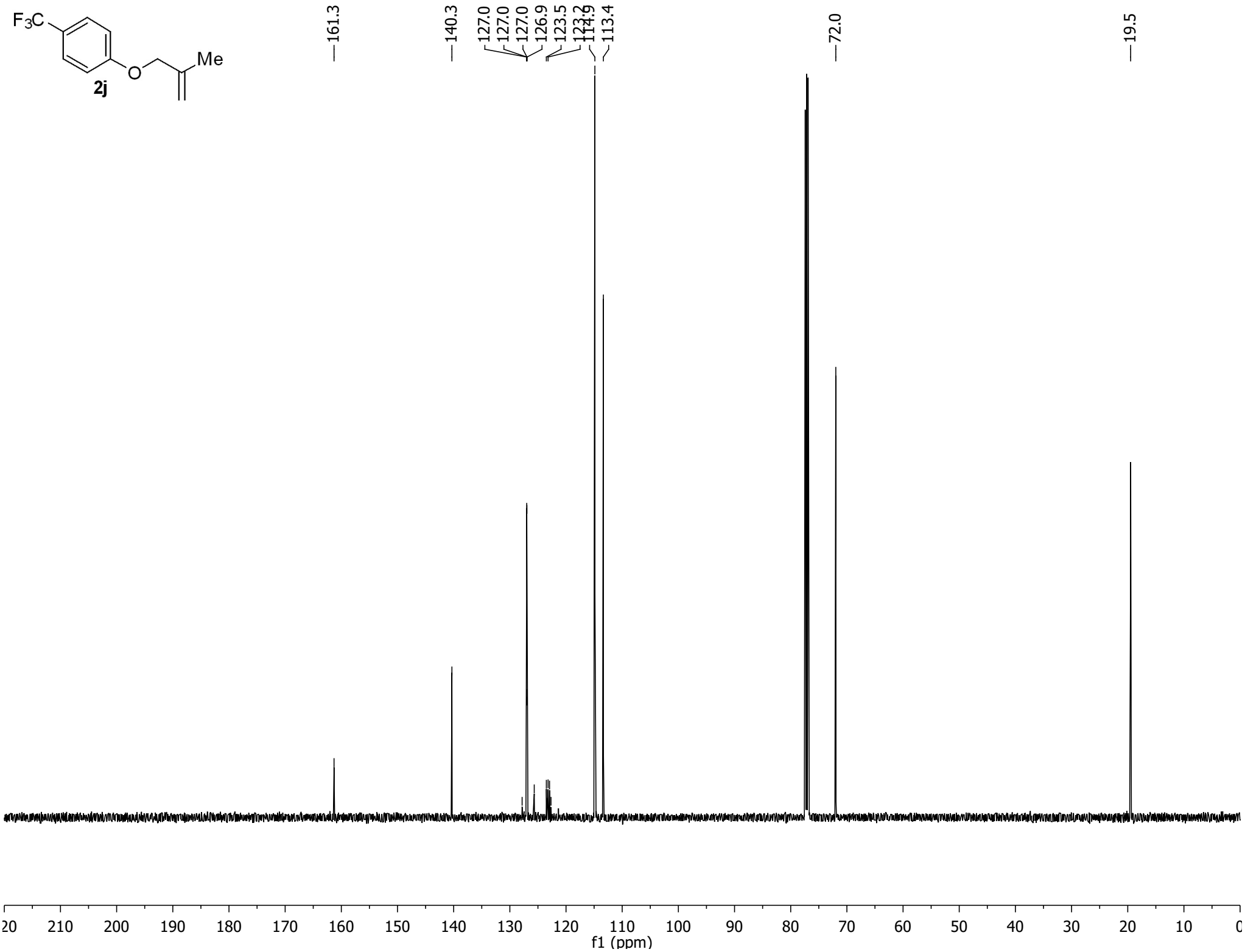
1.5
1.0
0.5
0.0
f1 (ppm)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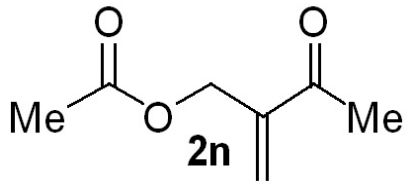
f1 (ppm)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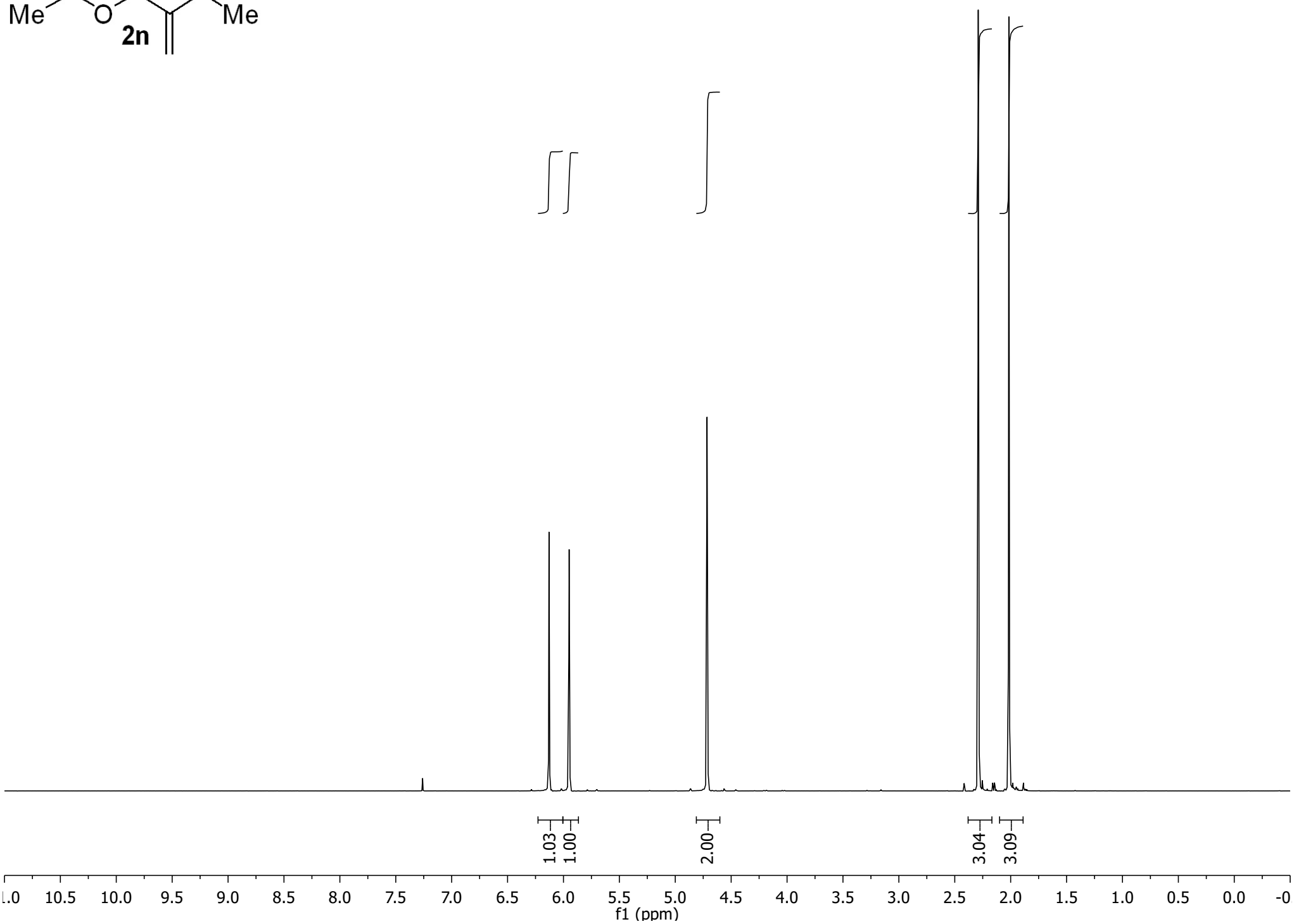
O
Me
O
Me
2n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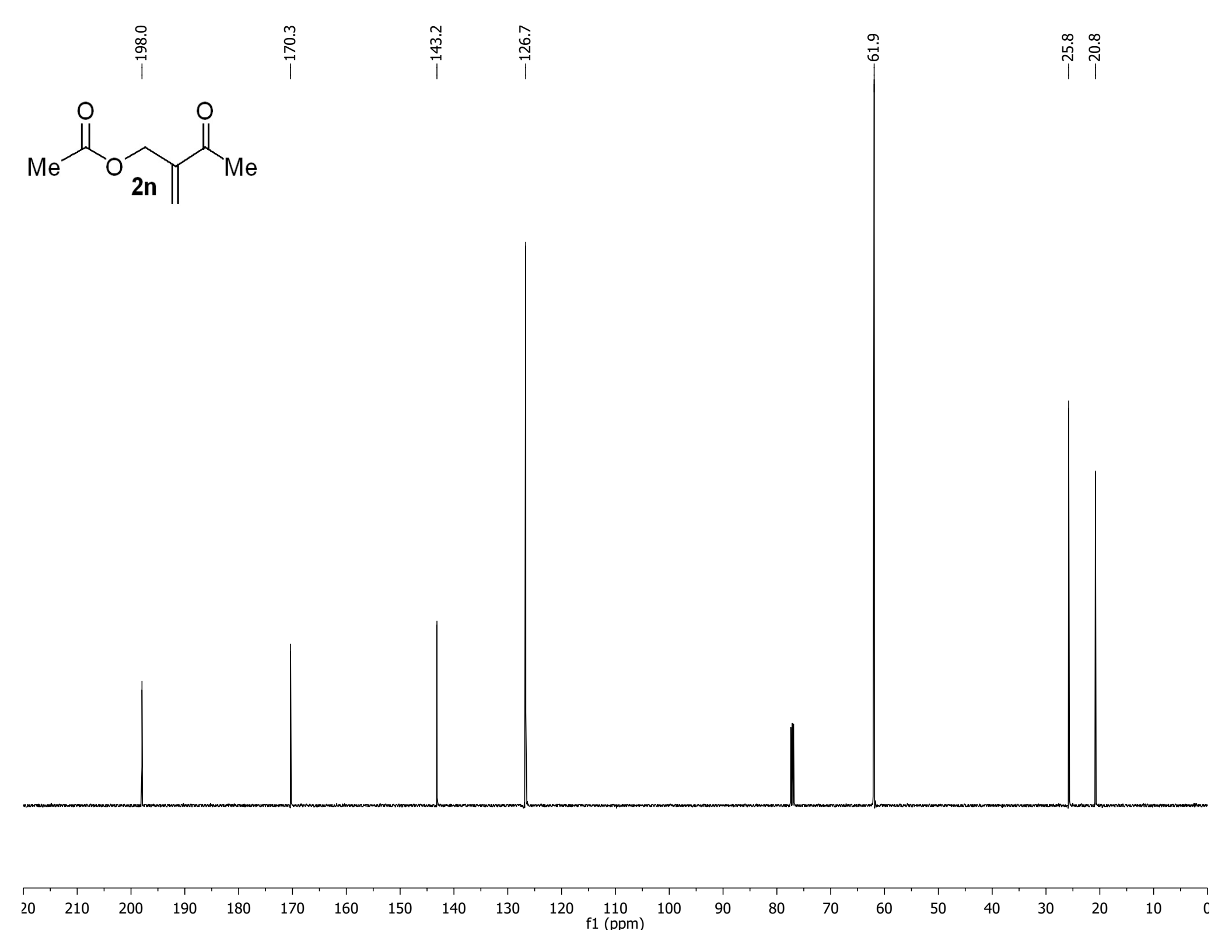
0.0
f1 (ppm)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Me
O
O
O
Me
2n
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200
190
180
170
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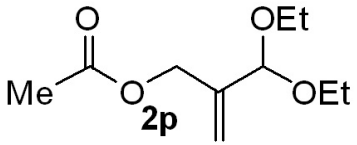
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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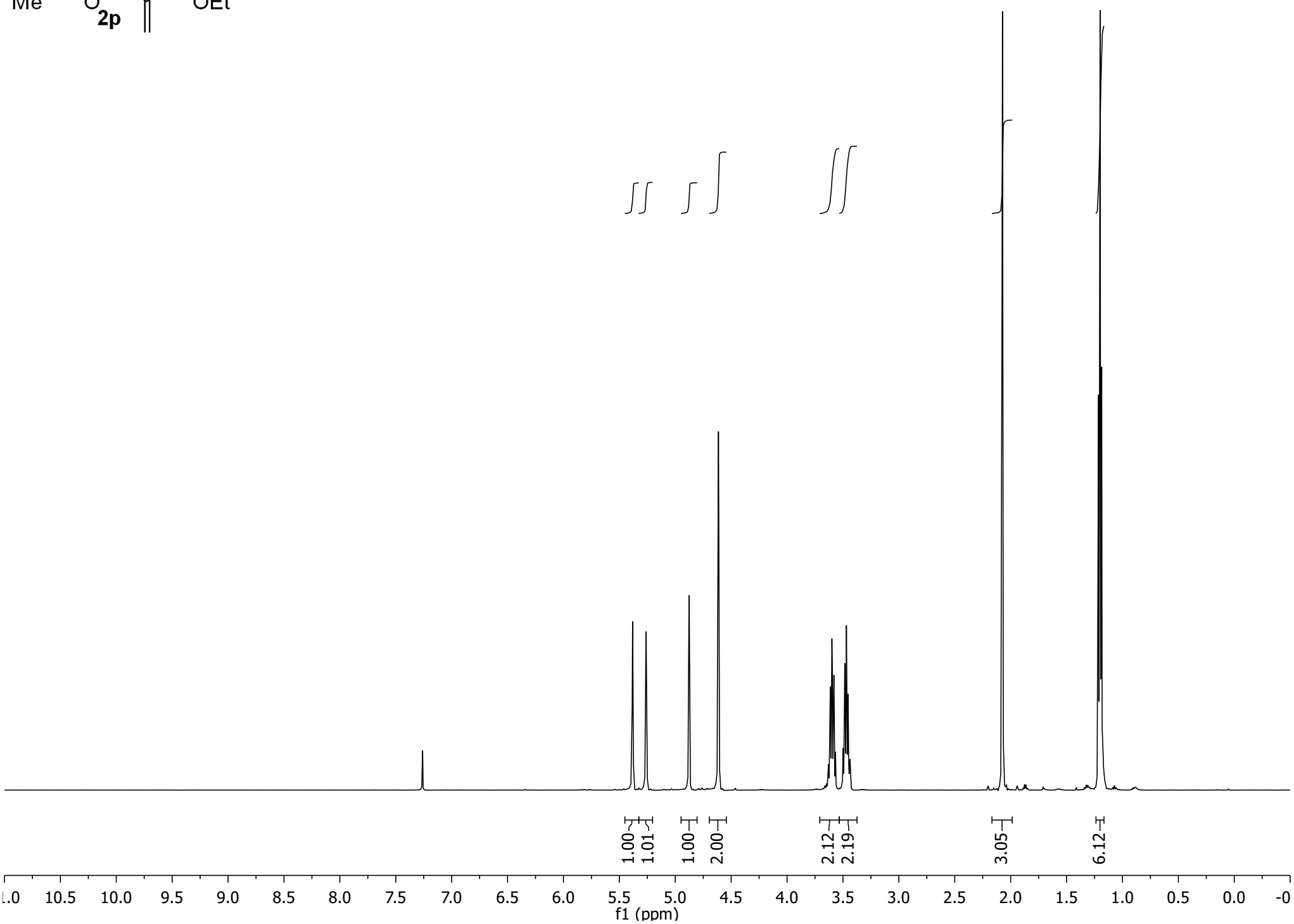
OEt
Me
O
OEt
2p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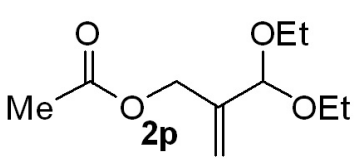
0.0
f1 (ppm)


O
OEt
Me
O
OEt
2p

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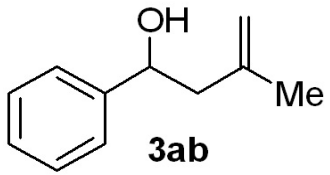
15.2
f1 (ppm)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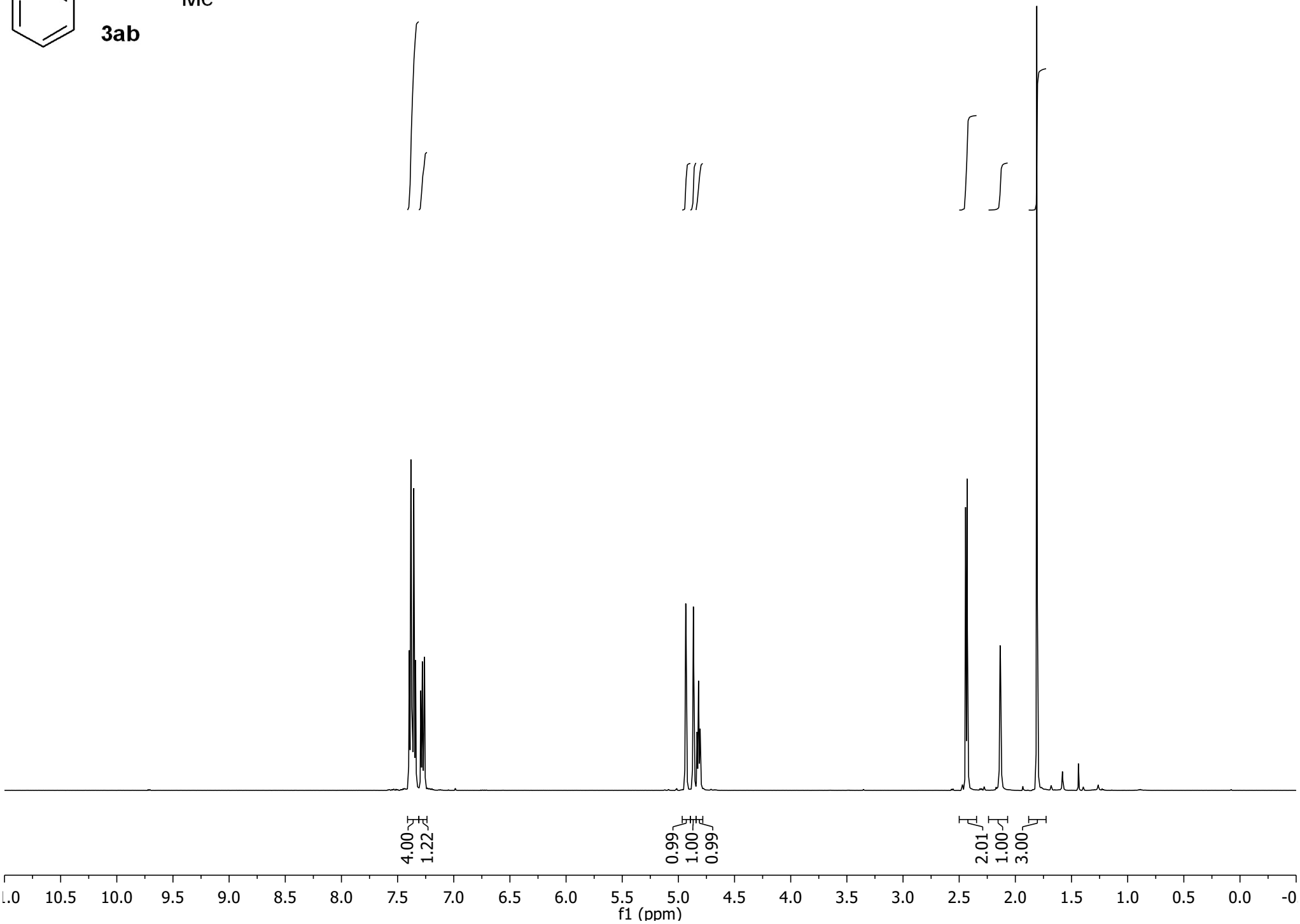
Me

3ab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7.5
7.0
6.5
6.0
5.5
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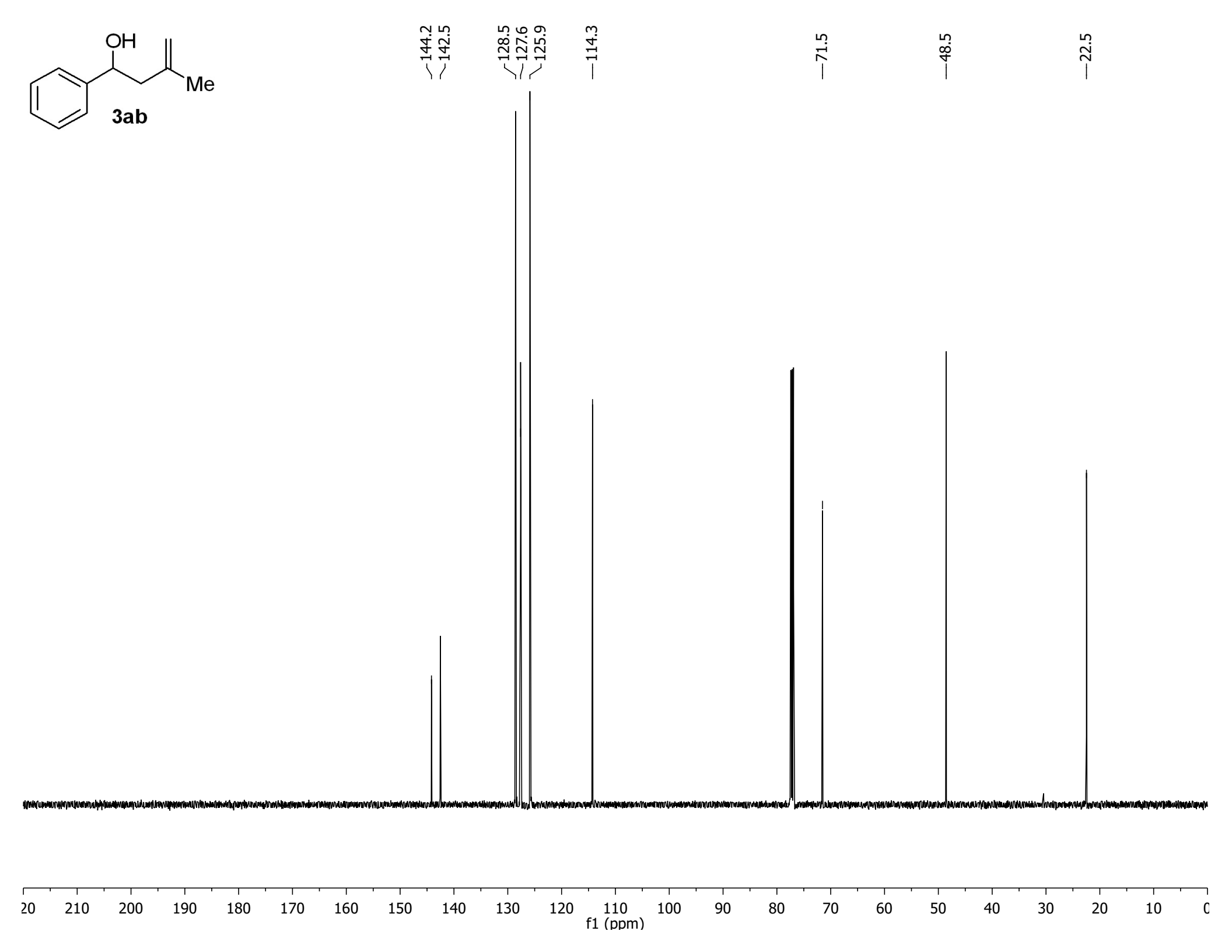
f1 (ppm)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Me
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71.5
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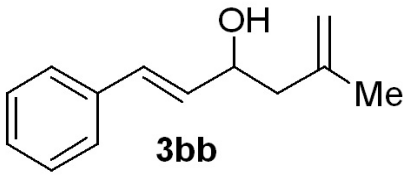
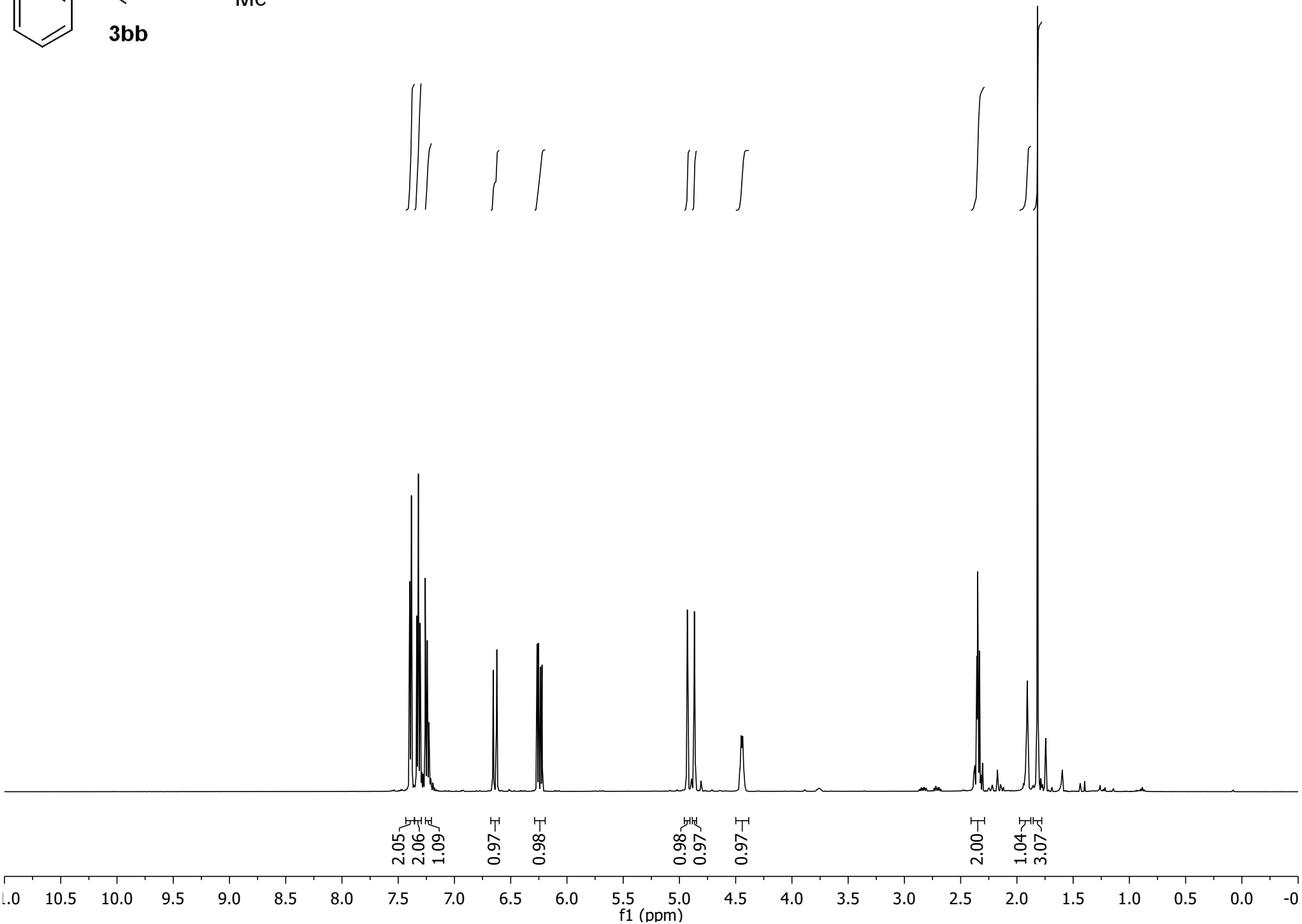
22.5
f1 (ppm)


OH
Me

3bb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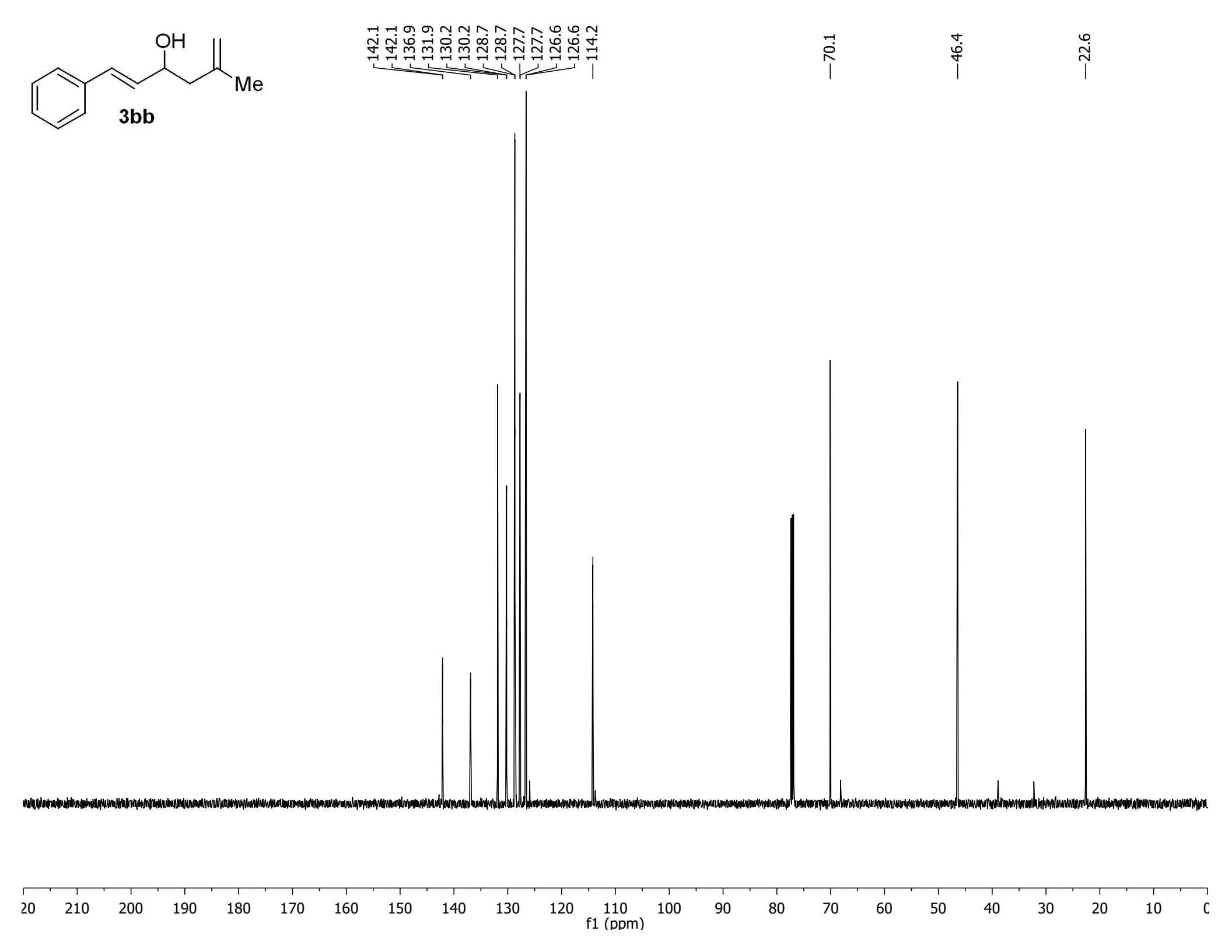
f1 (ppm)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Me
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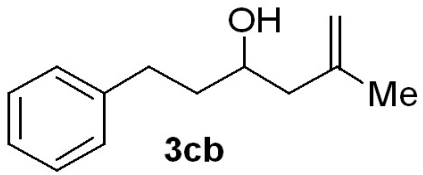
114.2
70.1
46.4
22.6
f1 (ppm)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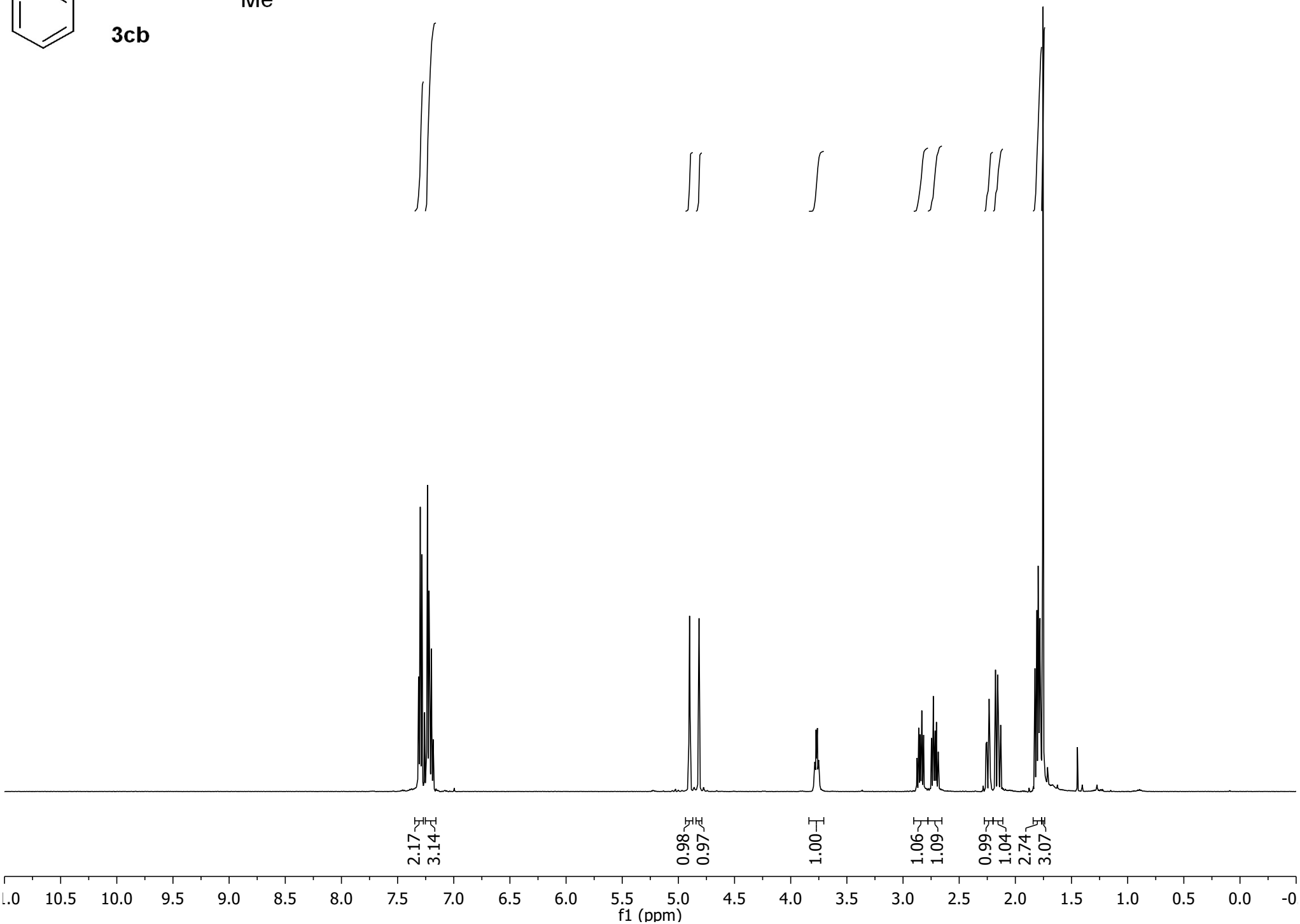
Me

3cb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3.07
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9.0
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8.0
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7.0
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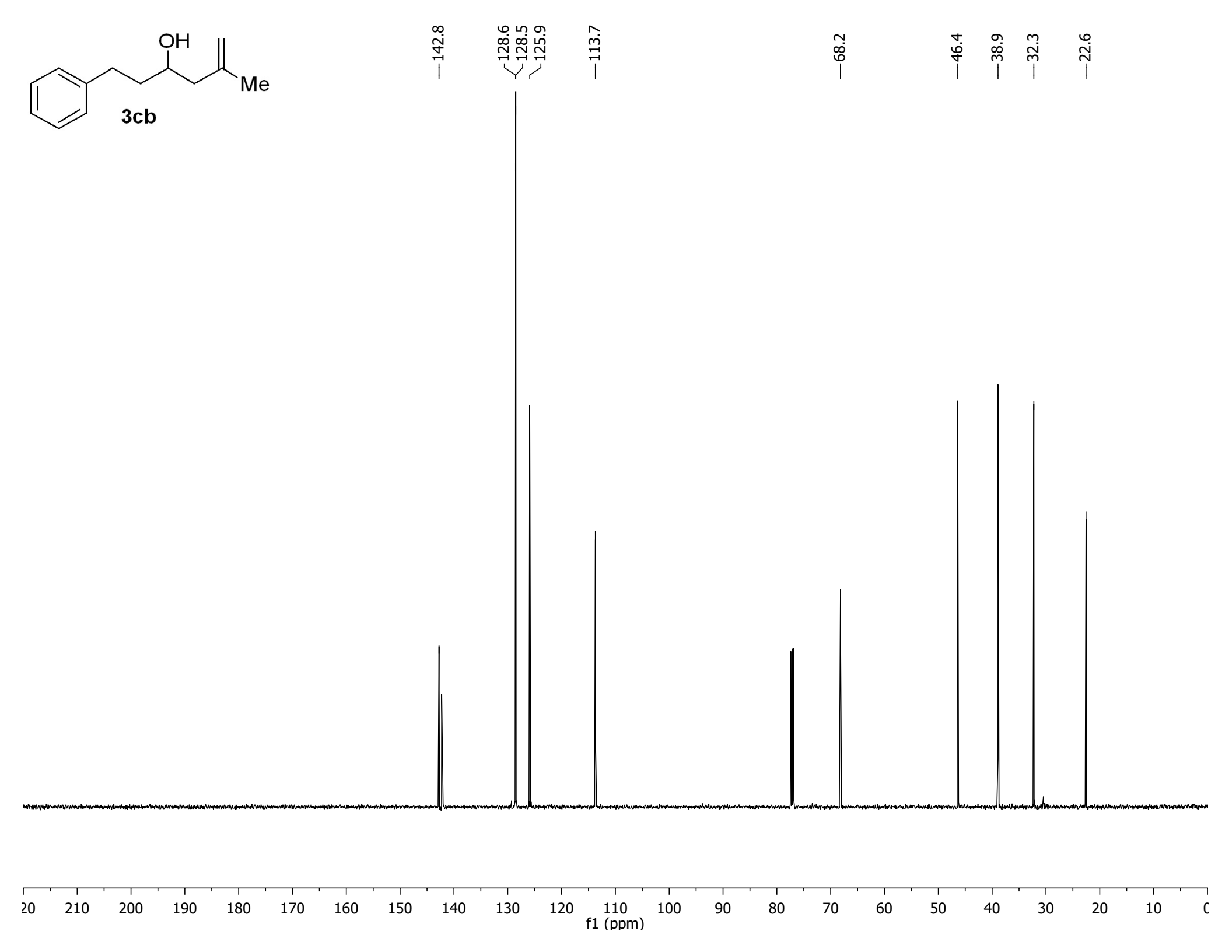
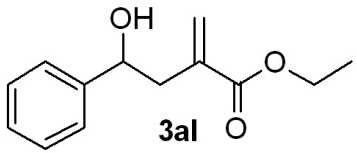
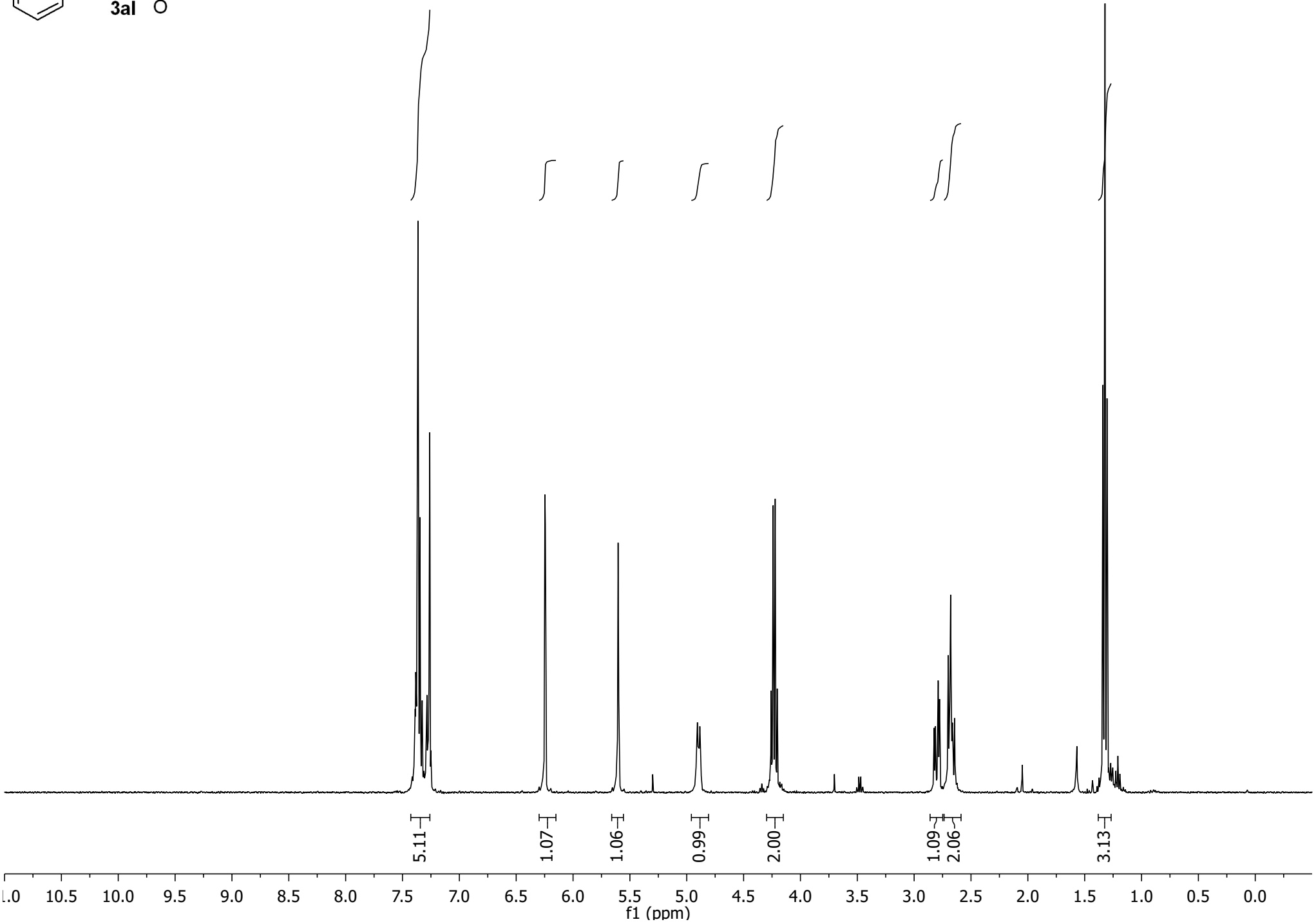
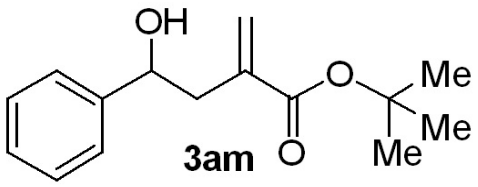
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

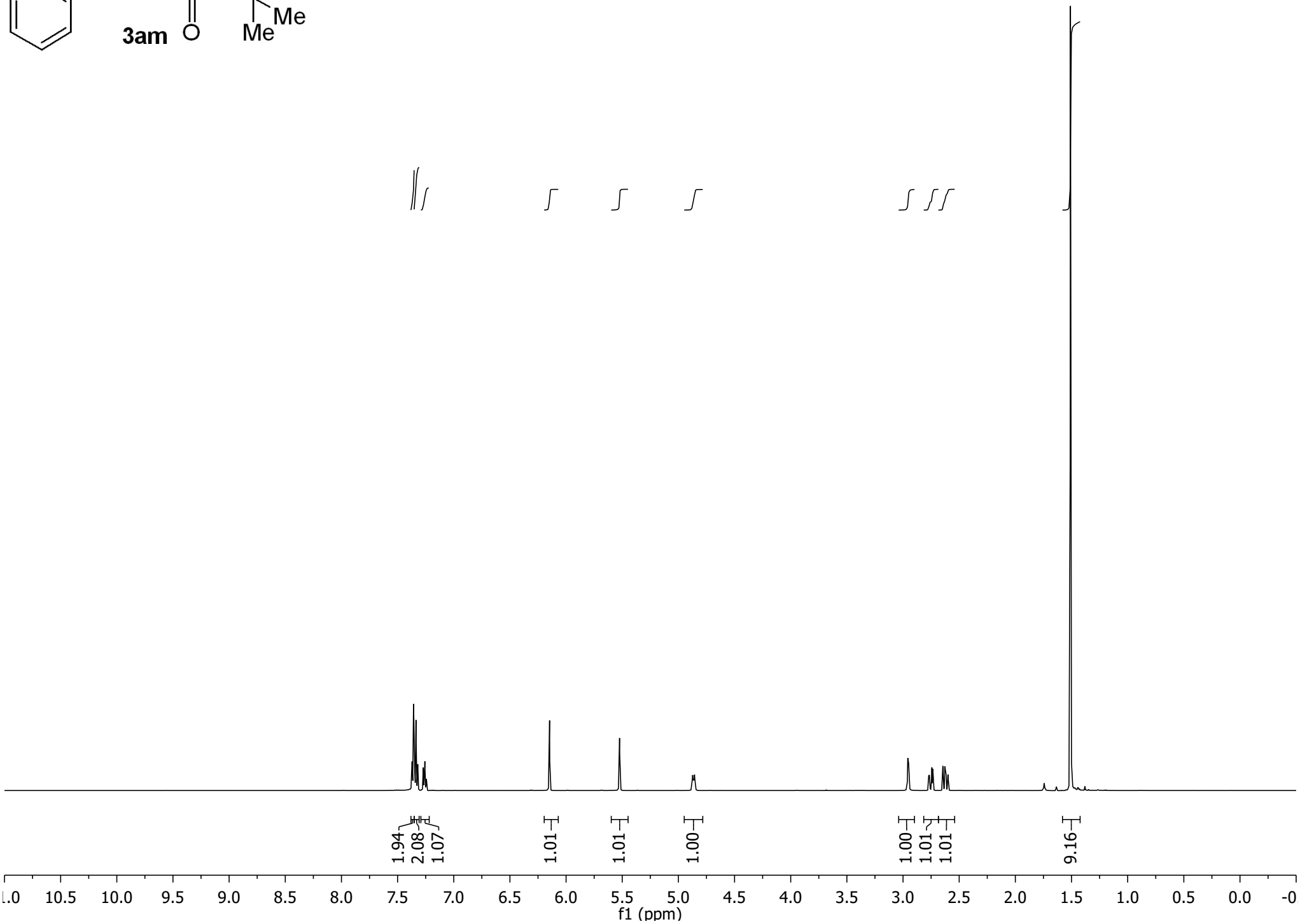

OH
Me
3cb
142.8
128.6
128.5
125.9
113.7
68.2
46.4
38.9
32.3
22.6
f1 (ppm)

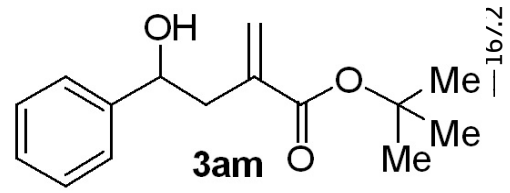

OH
O
O
3al


5.11
1.07
1.06
0.99
2.00
1.09
2.06
3.13
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

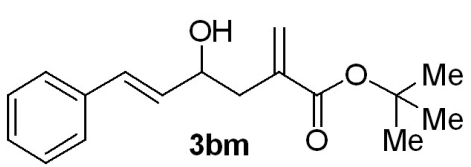

OH
O
Me
Me
Me
O
O

3am

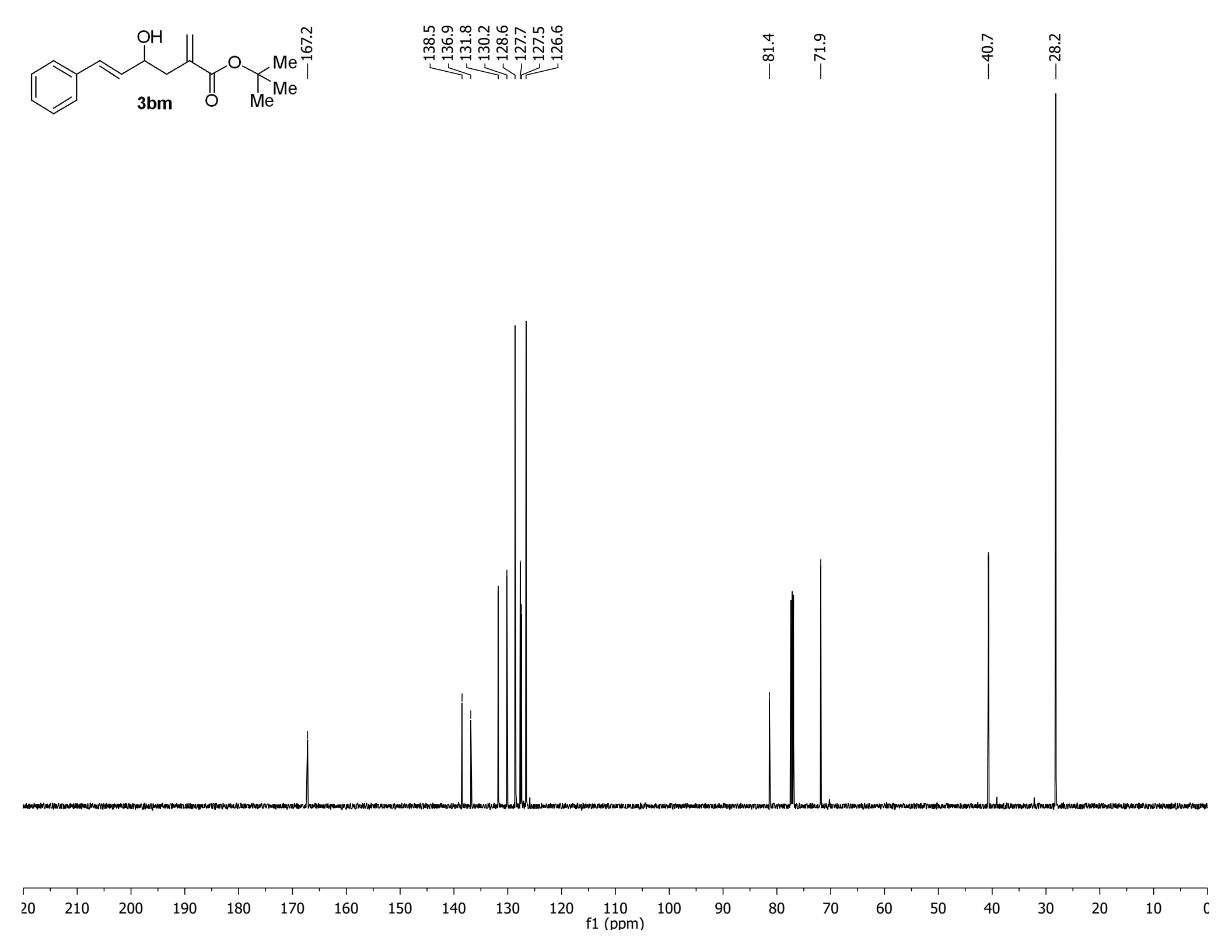

1.94
2.08
1.07
1.01
1.01
1.00
1.00
1.01
1.01
9.16
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

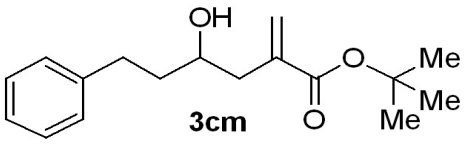

OH
O
Me
Me
Me
O
O
3am

144.2
138.7
128.4
127.6
127.5
125.8
81.4
73.4
42.8
28.2
f1 (ppm)

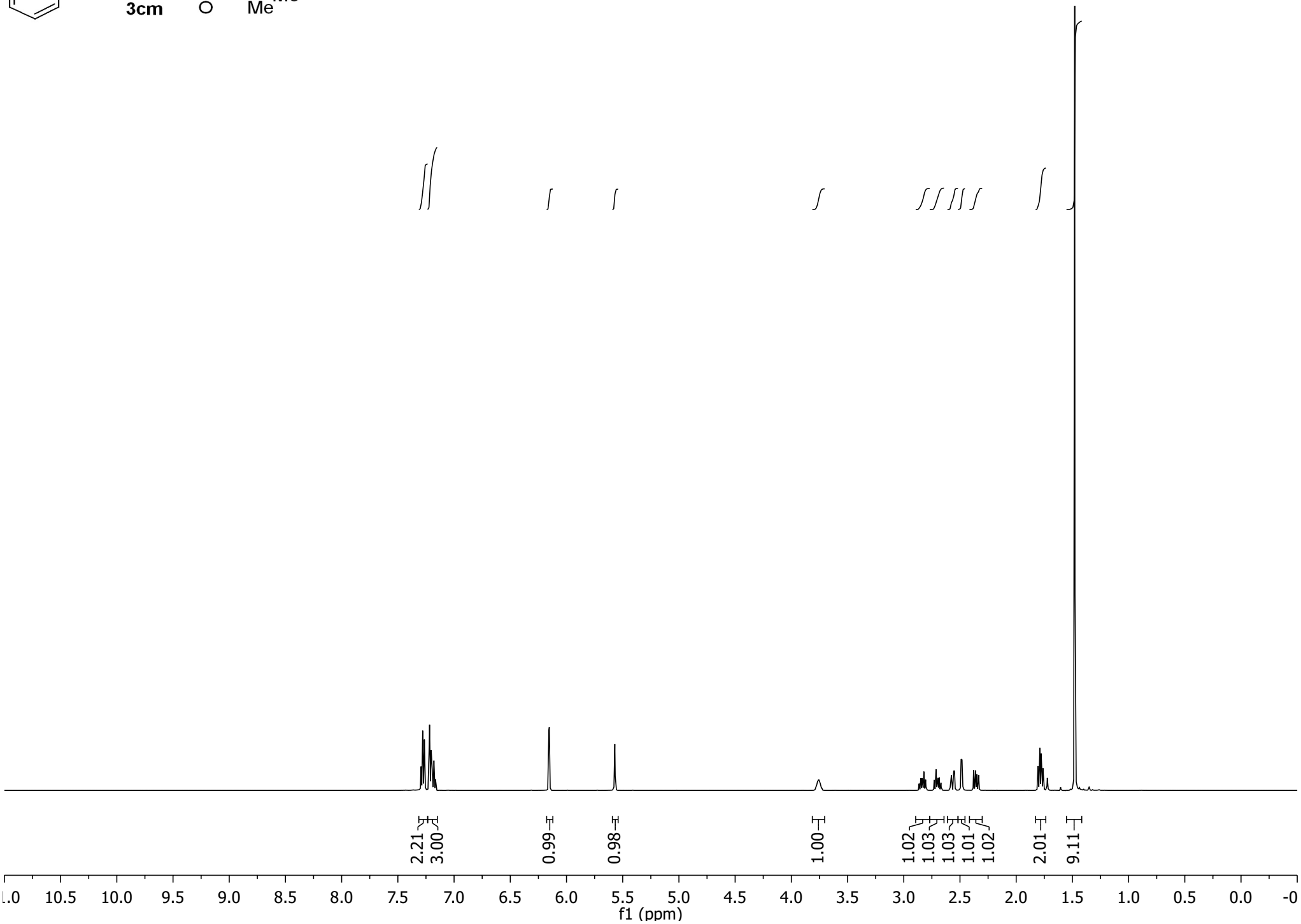

OH
O
Me
Me
Me
O
3bm

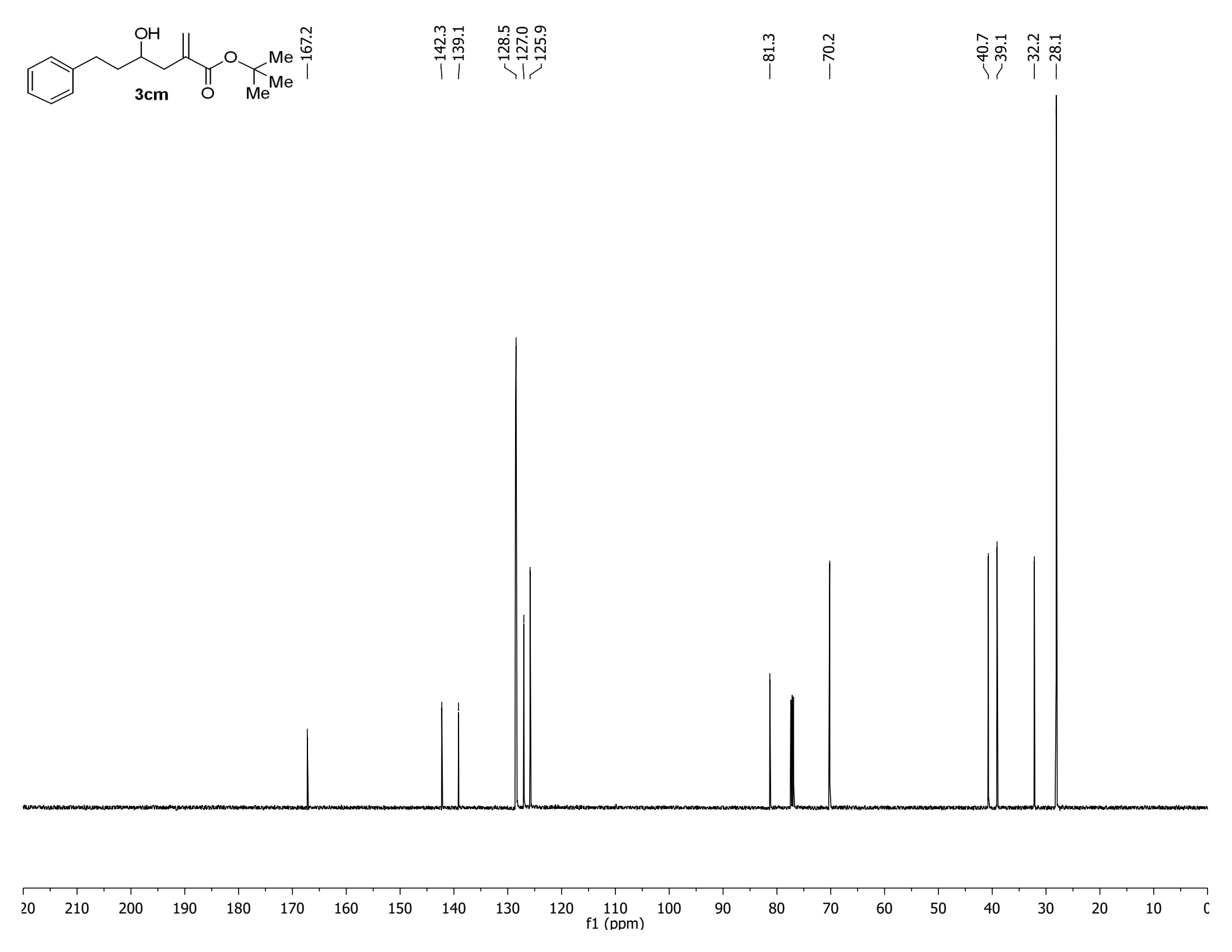
1.94
1.99
1.00
0.94
0.97
0.91
0.92
0.92
0.96
1.92
8.92
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

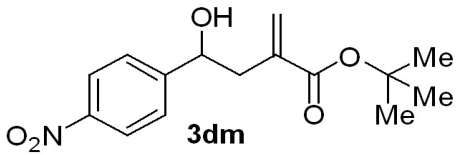

OH
O
O
Me
Me
Me
3bm
167.2
138.5
136.9
131.8
130.2
128.6
127.7
127.5
126.6
81.4
71.9
40.7
28.2
f1 (ppm)


OH
O
Me
Me
Me
O

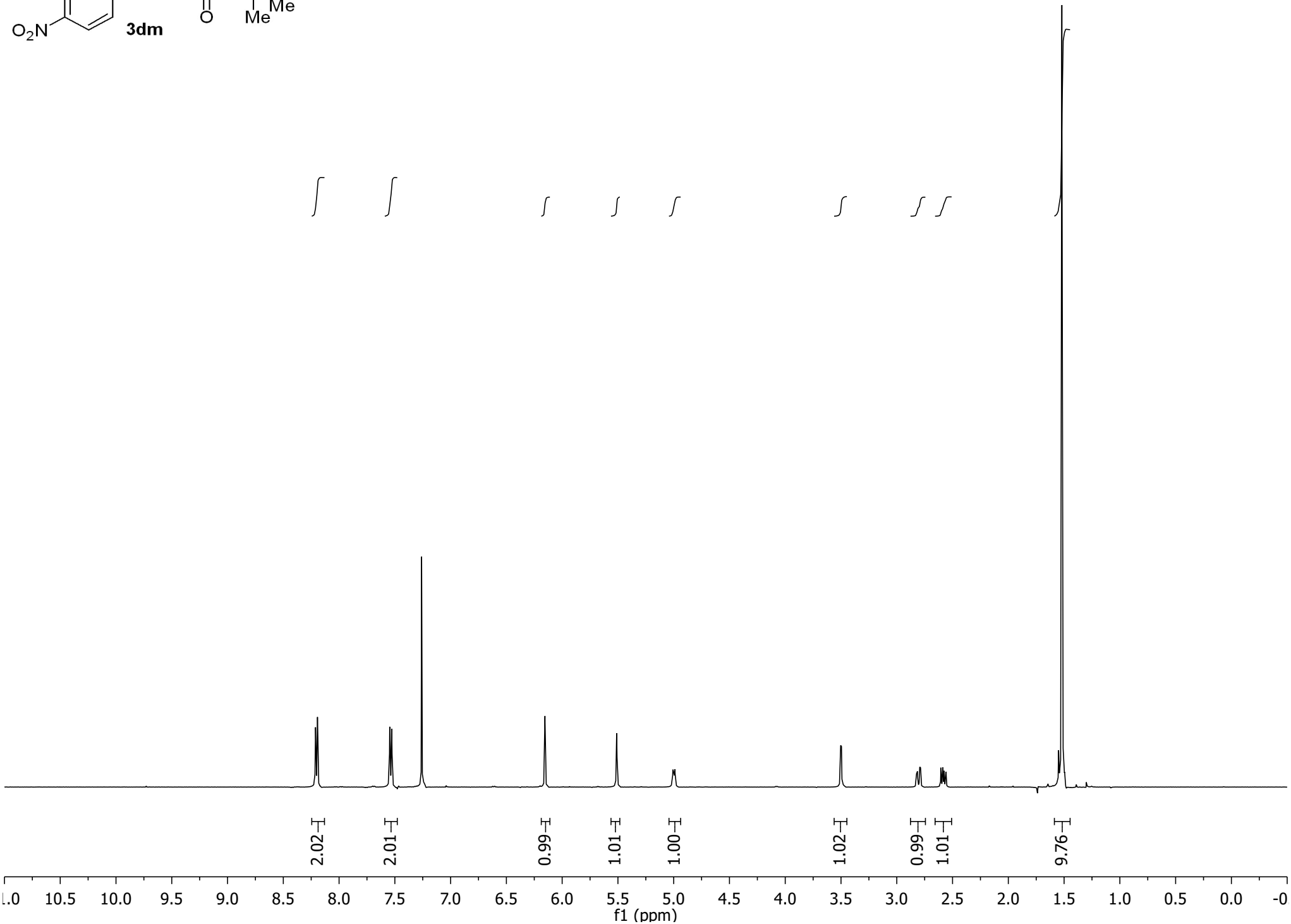
3cm

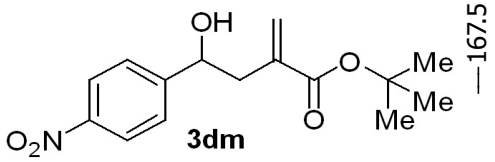

2.21
3.00
0.99
0.98
1.00
1.02
1.03
1.03
1.01
1.02
2.01
9.11
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OH
O
Me
Me
Me
O
3cm
167.2
142.3
139.1
128.5
127.0
125.9
81.3
70.2
40.7
39.1
32.2
28.1
f1 (ppm)

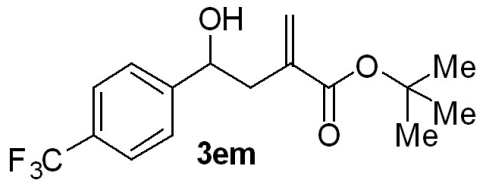

OH
O
Me
Me
Me
O
O_2N

3dm

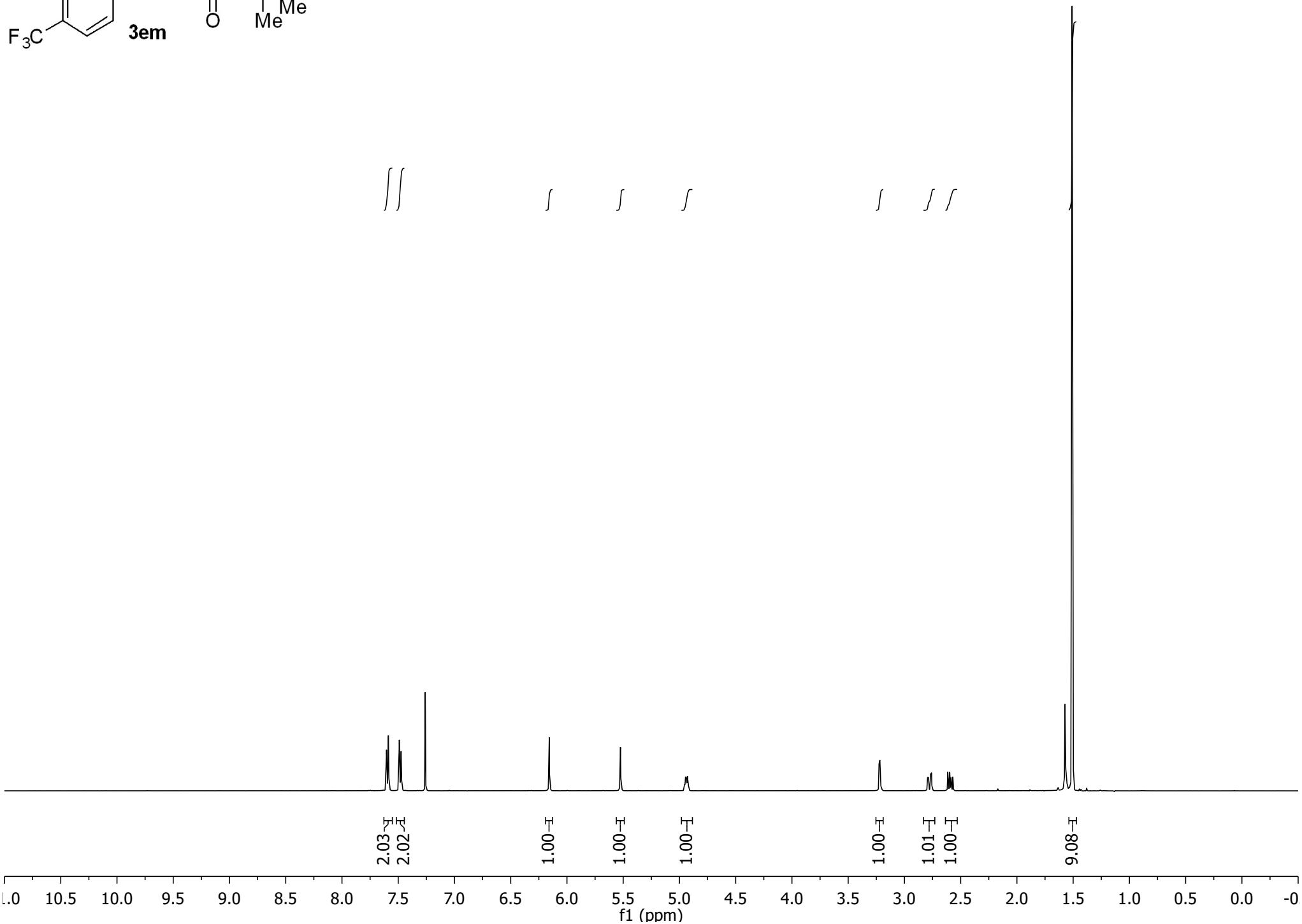

2.02
2.01
0.99
1.01
1.00
1.02
0.99
1.01
9.76
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

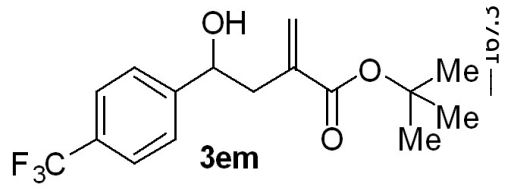

OH
O
Me
Me
Me
O
O_2N
3dm

167.5
151.5
147.3
137.8
128.5
126.6
123.7
82.0
72.7
42.9
28.1
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

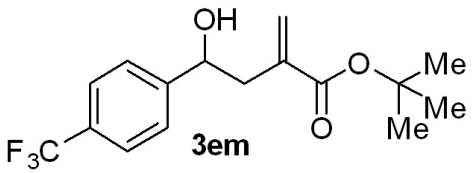


3em



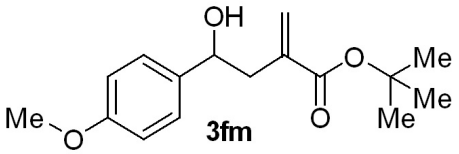

OH
O
Me
Me
Me
O
F3C
3em

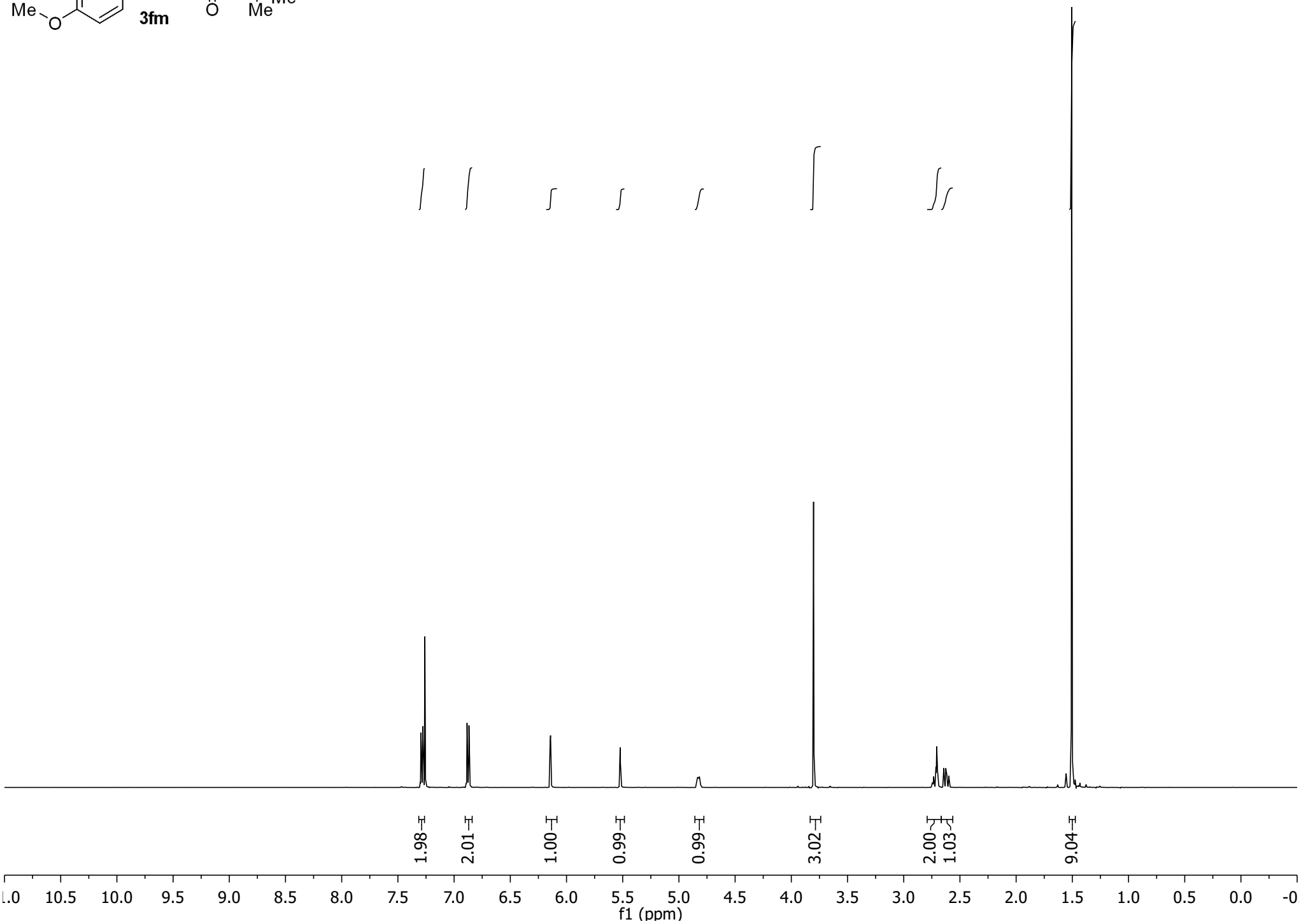
167.3
148.2
138.1
128.1
126.1
125.4
125.4
125.3
125.3
81.7
72.9
42.8
28.1
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

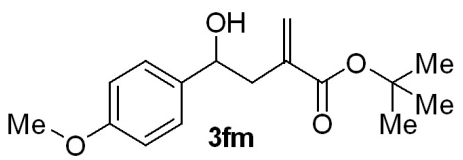


3em

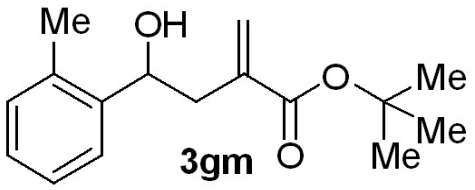
External $BF_3 \bullet OEt_2$ standard

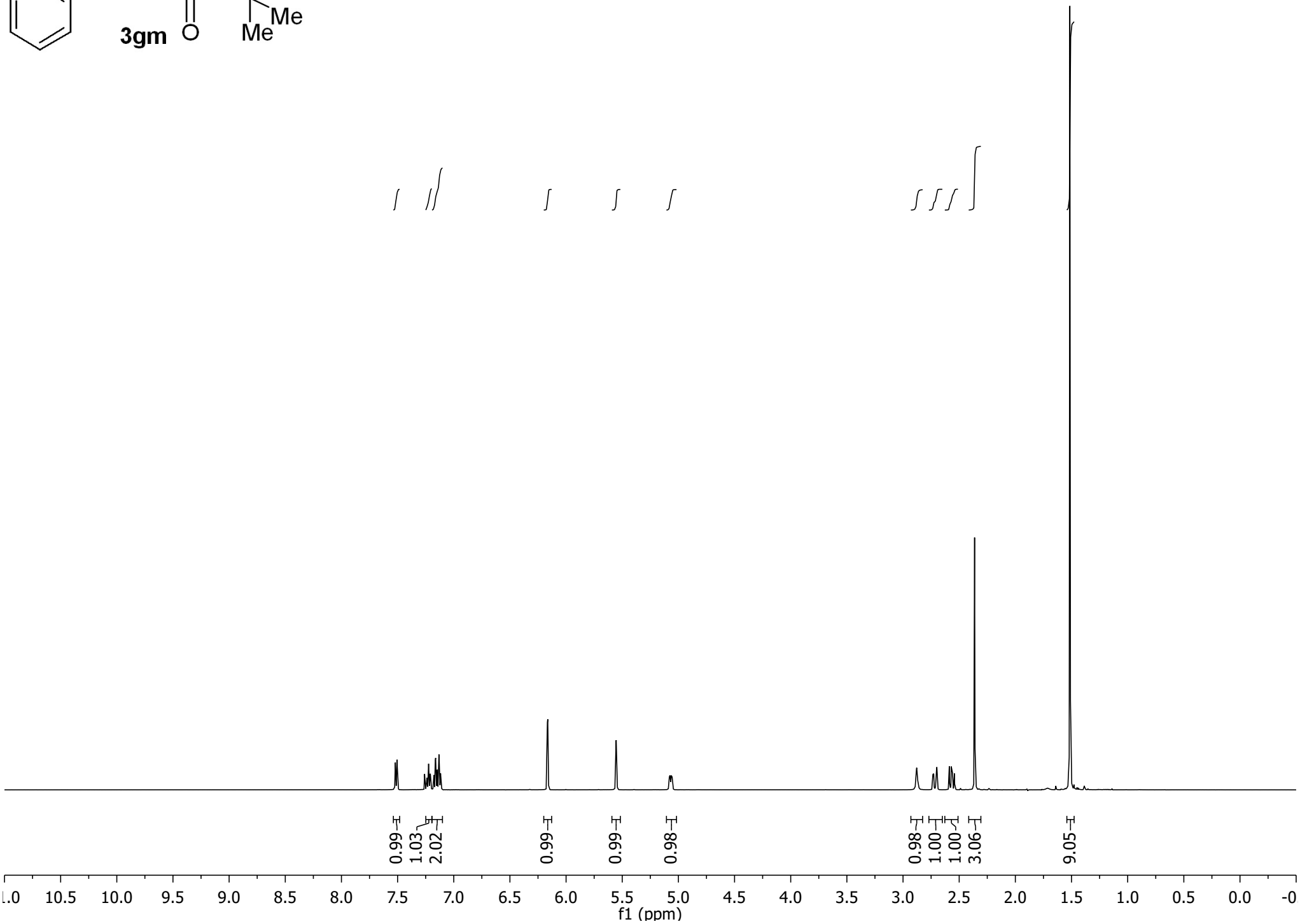

OH
Me
O
Me
Me
O
O
Me
3fm

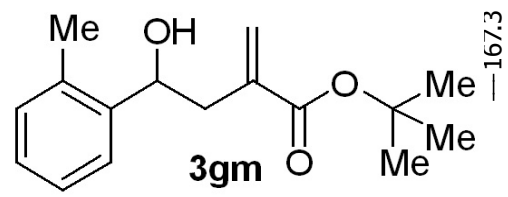

1.98
2.01
1.00
0.99
0.99
3.02
2.00
1.03
9.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



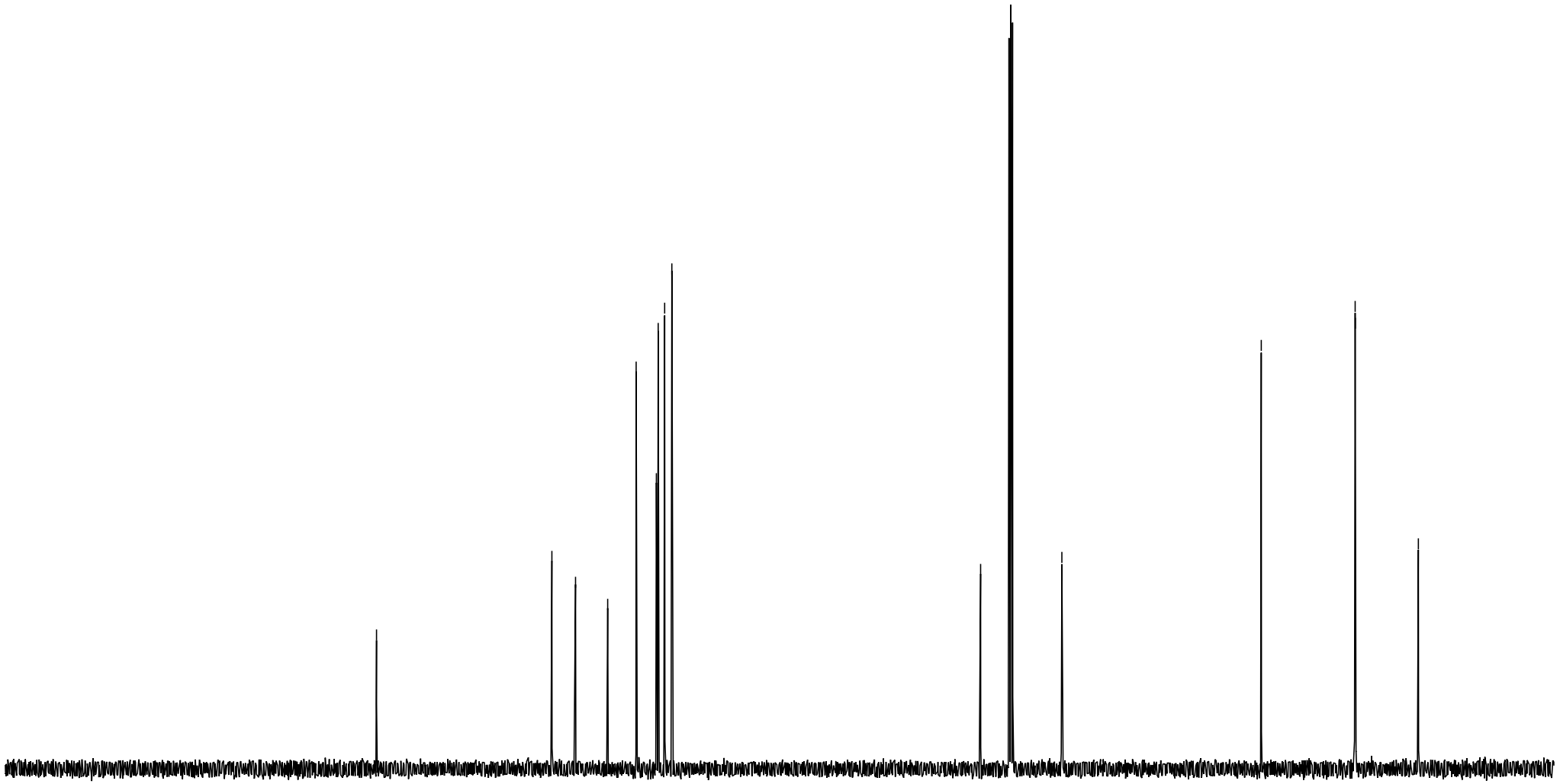
167.2
159.1
138.9
136.4
127.4
127.1
113.9
81.3
73.1
73.1
55.5
55.4
55.4
55.4
42.8
28.2
28.2


Me
OH
O
Me
Me
Me
O
3gm


0.99
1.03
2.02
0.99
0.99
0.98
0.98
1.00
1.00
3.06
9.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

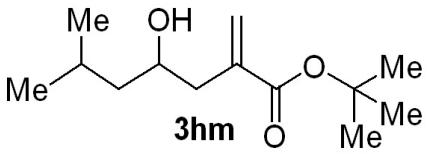


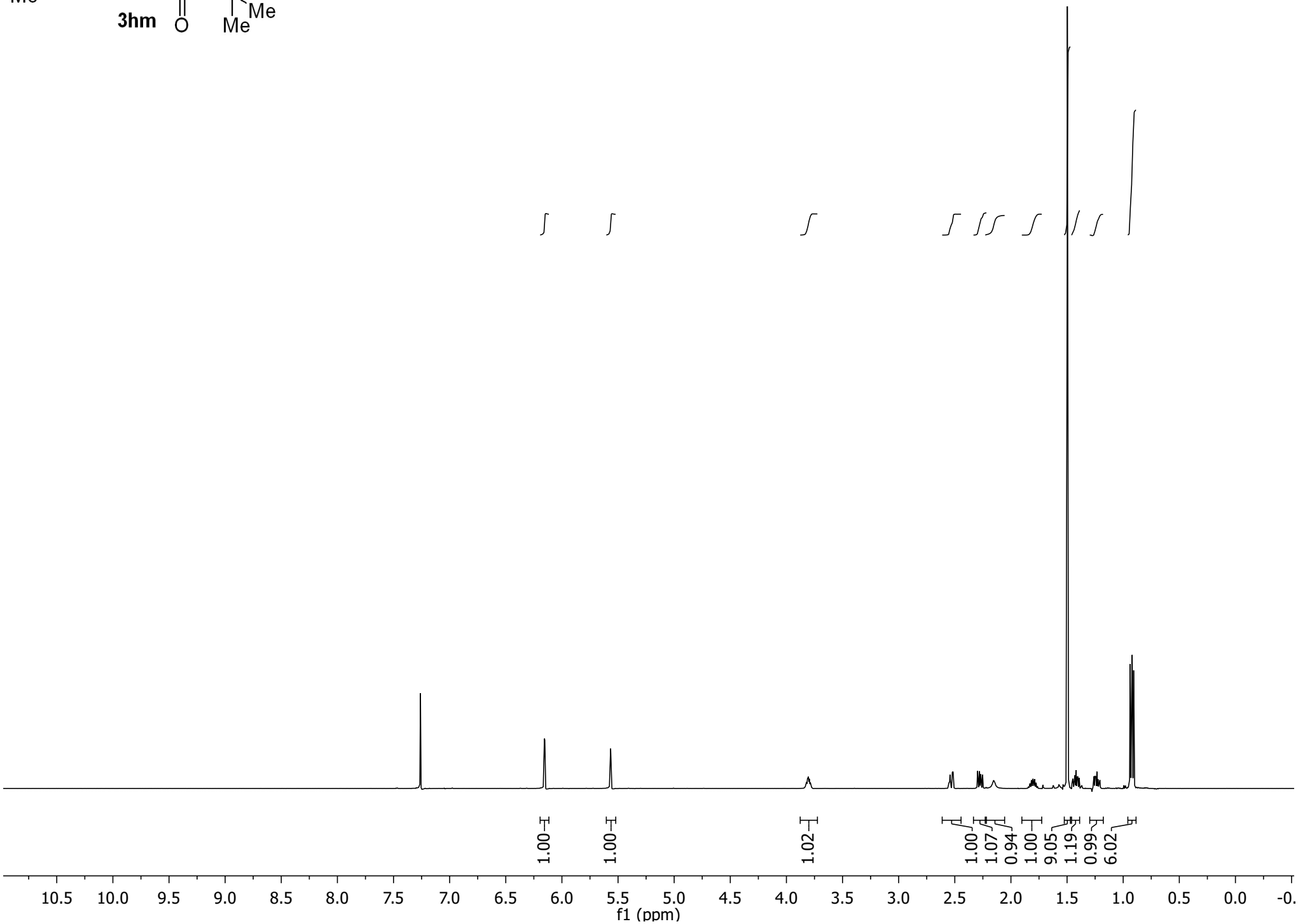
167.3
142.4
139.0
134.4
130.4
127.5
127.3
126.3
125.3
81.4
69.9
69.9
41.6
28.2
28.2
19.2

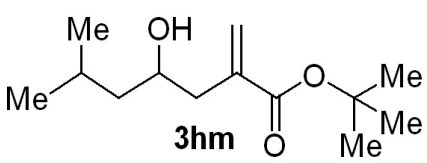


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)


Me
OH
Me
O
Me
Me
Me
O
3hm

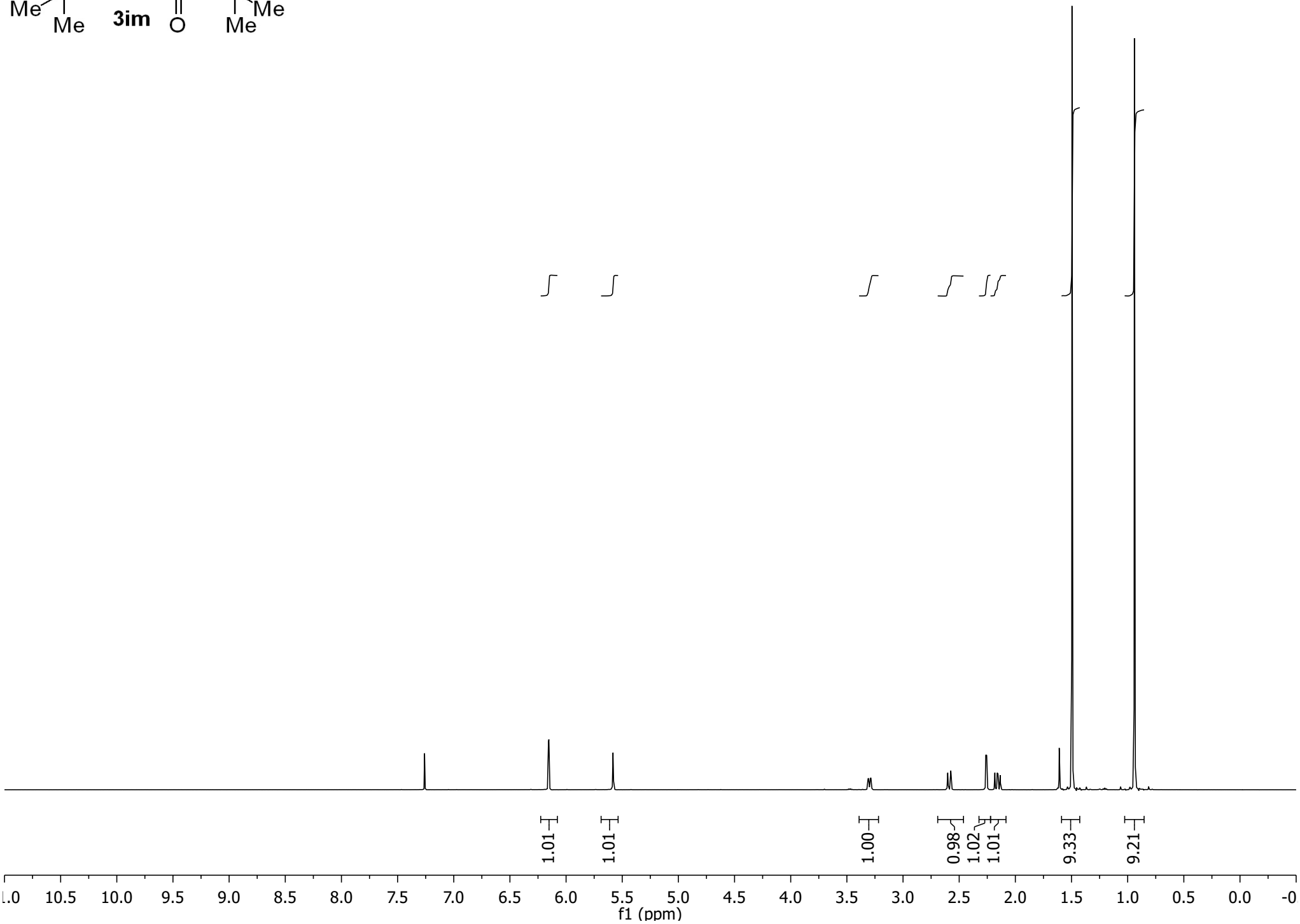

1.00
1.00
1.02
1.00
1.07
0.94
1.00
9.05
1.19
0.99
6.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

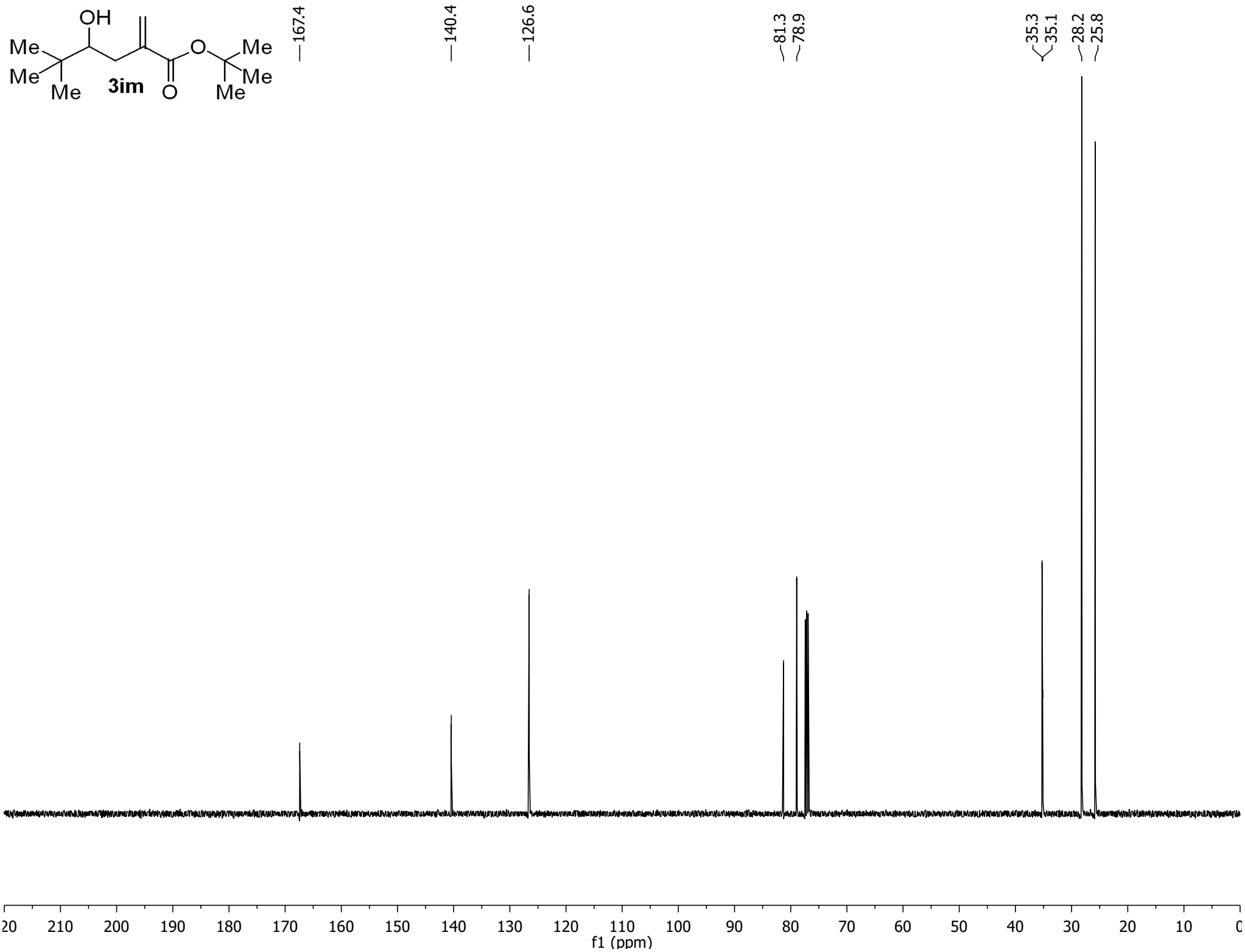

Me
OH
Me
O
Me
Me
O
Me

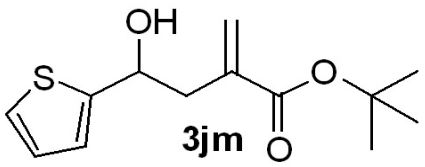
3hm

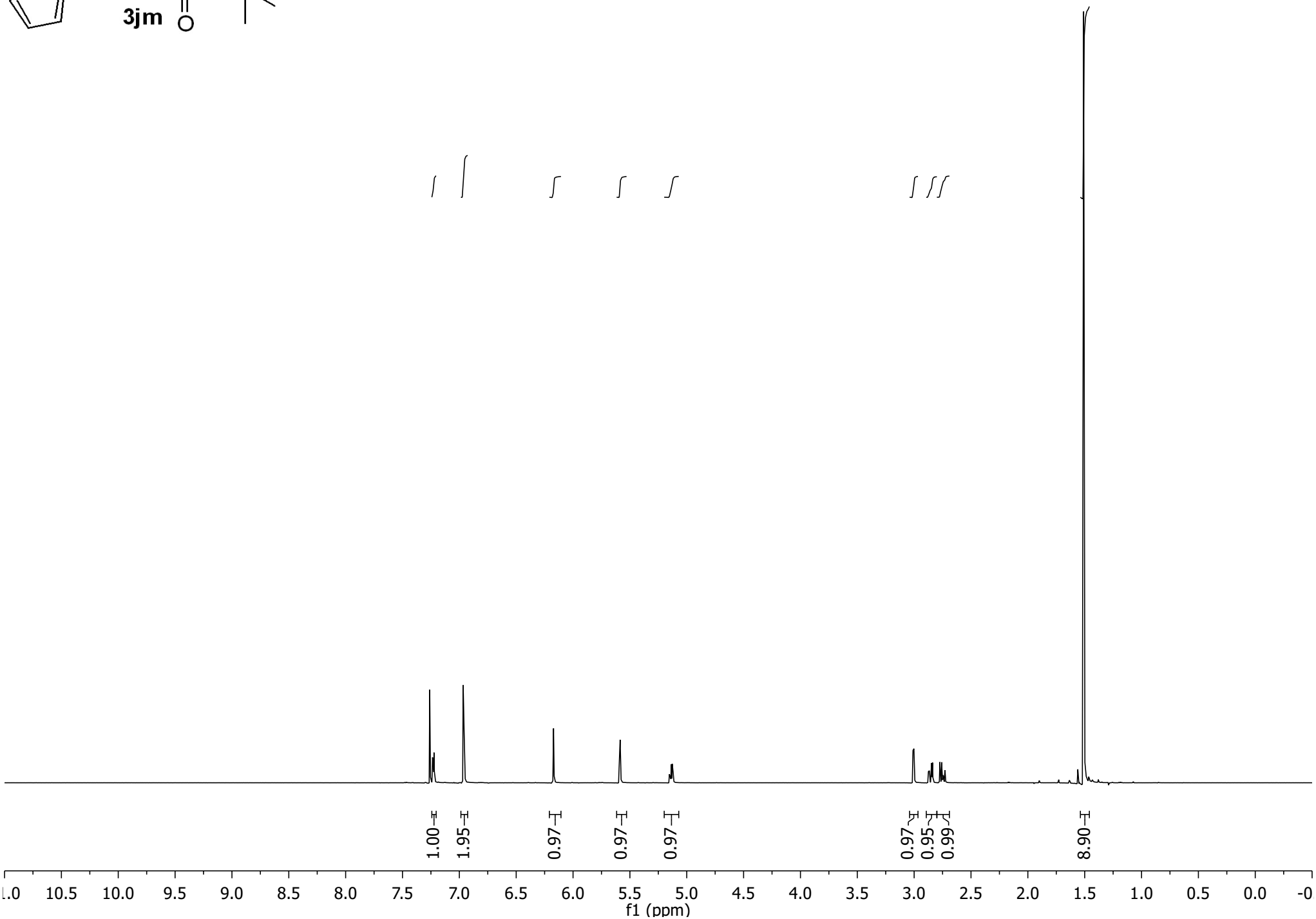
167.2
139.3
126.8
81.2
68.8
46.6
41.1
28.1
24.7
23.5
22.2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

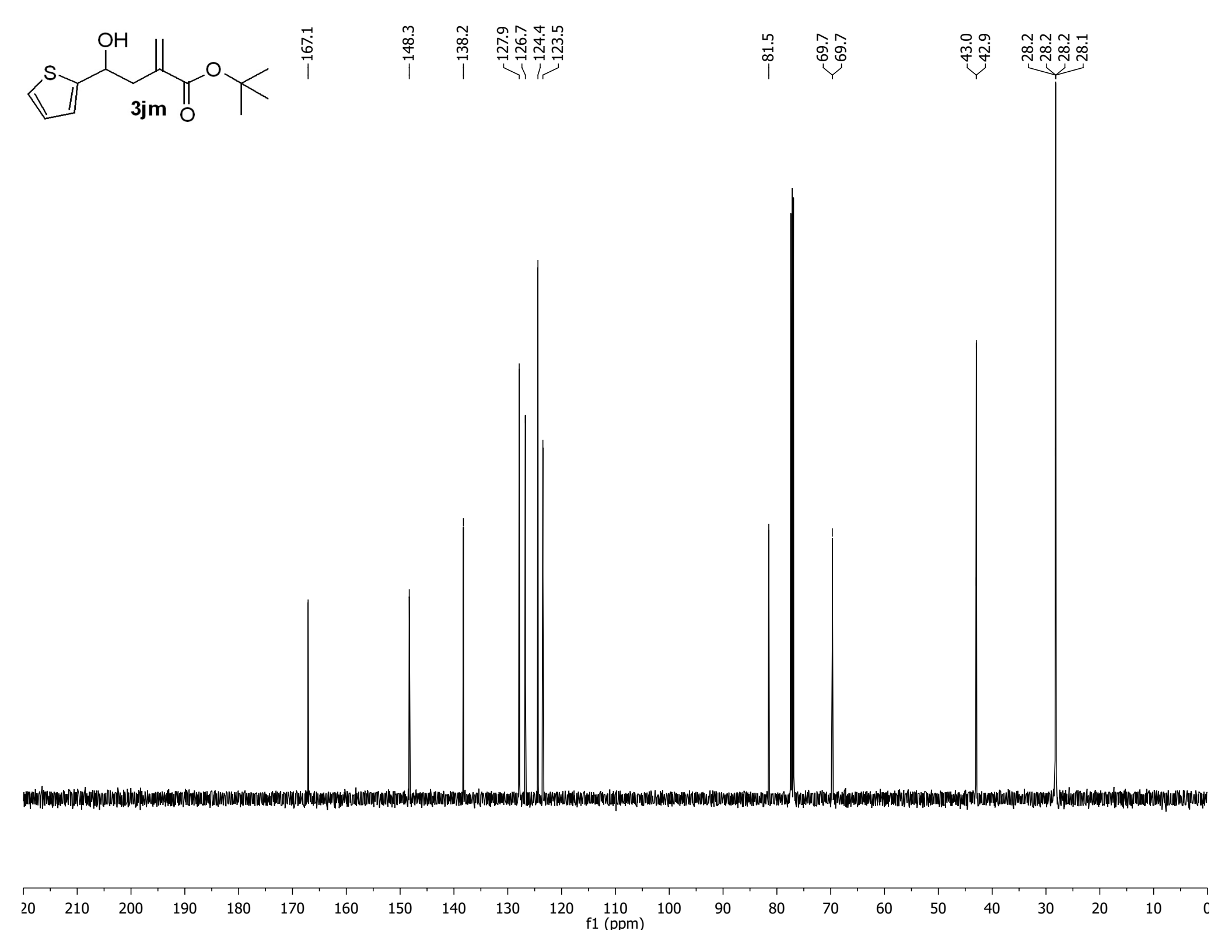

OH
Me
Me
Me
3im
O
O
Me
Me
Me

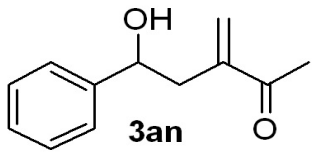

1.01
1.01
1.00
0.98
1.02
1.01
9.33
9.21
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OH
Me
Me
Me
3im
O
O
Me
Me
Me
167.4
140.4
126.6
81.3
78.9
35.3
35.1
28.2
25.8
f1 (ppm)

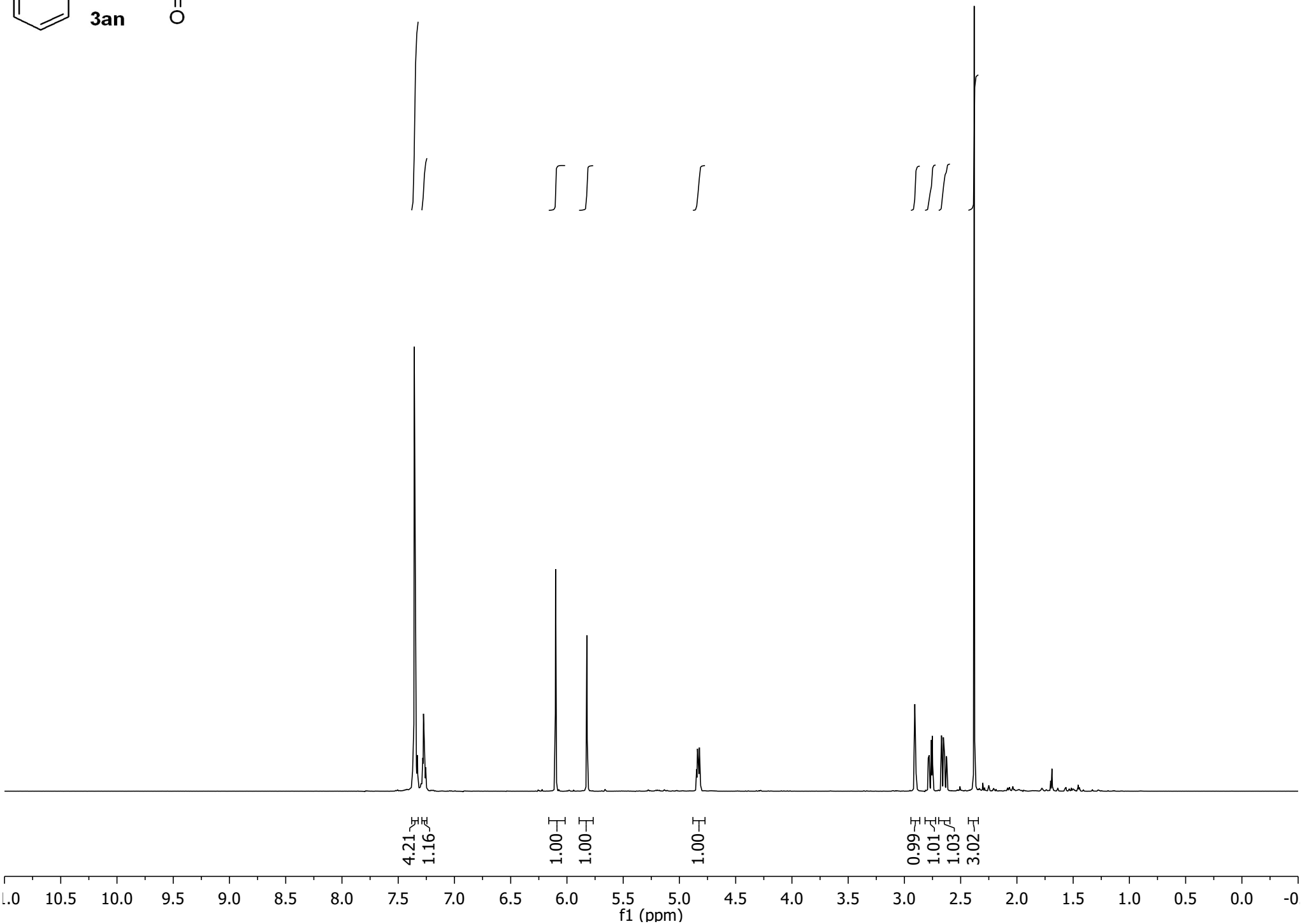

OH
S
O
O
3jm

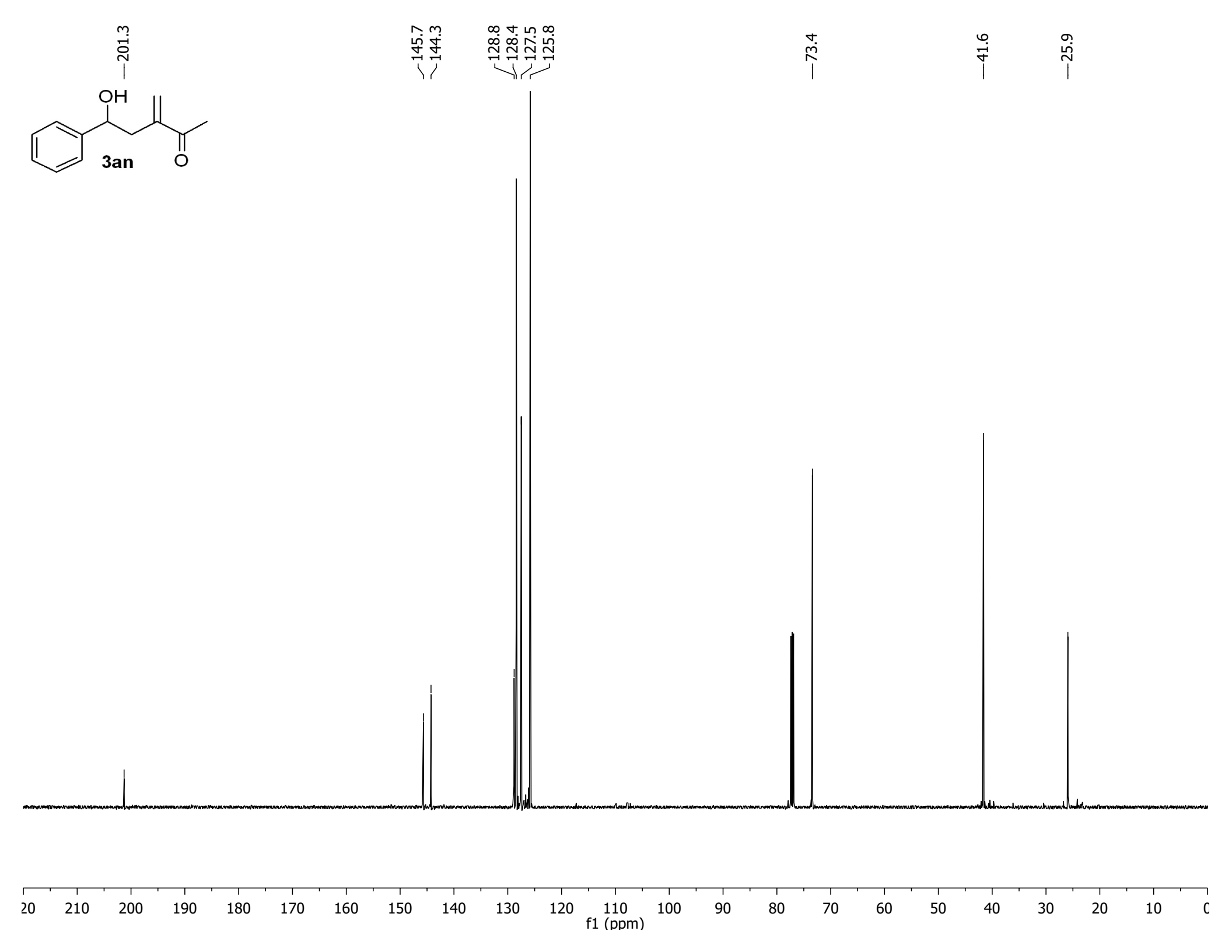

1.00
1.95
0.97
0.97
0.97
0.97
0.95
0.99
8.90
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

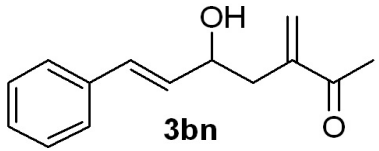

OH
S
O
O
3jm
167.1
148.3
138.2
127.9
126.7
124.4
123.5
81.5
69.7
69.7
43.0
42.9
28.2
28.2
28.2
28.1
f1 (ppm)


OH
O

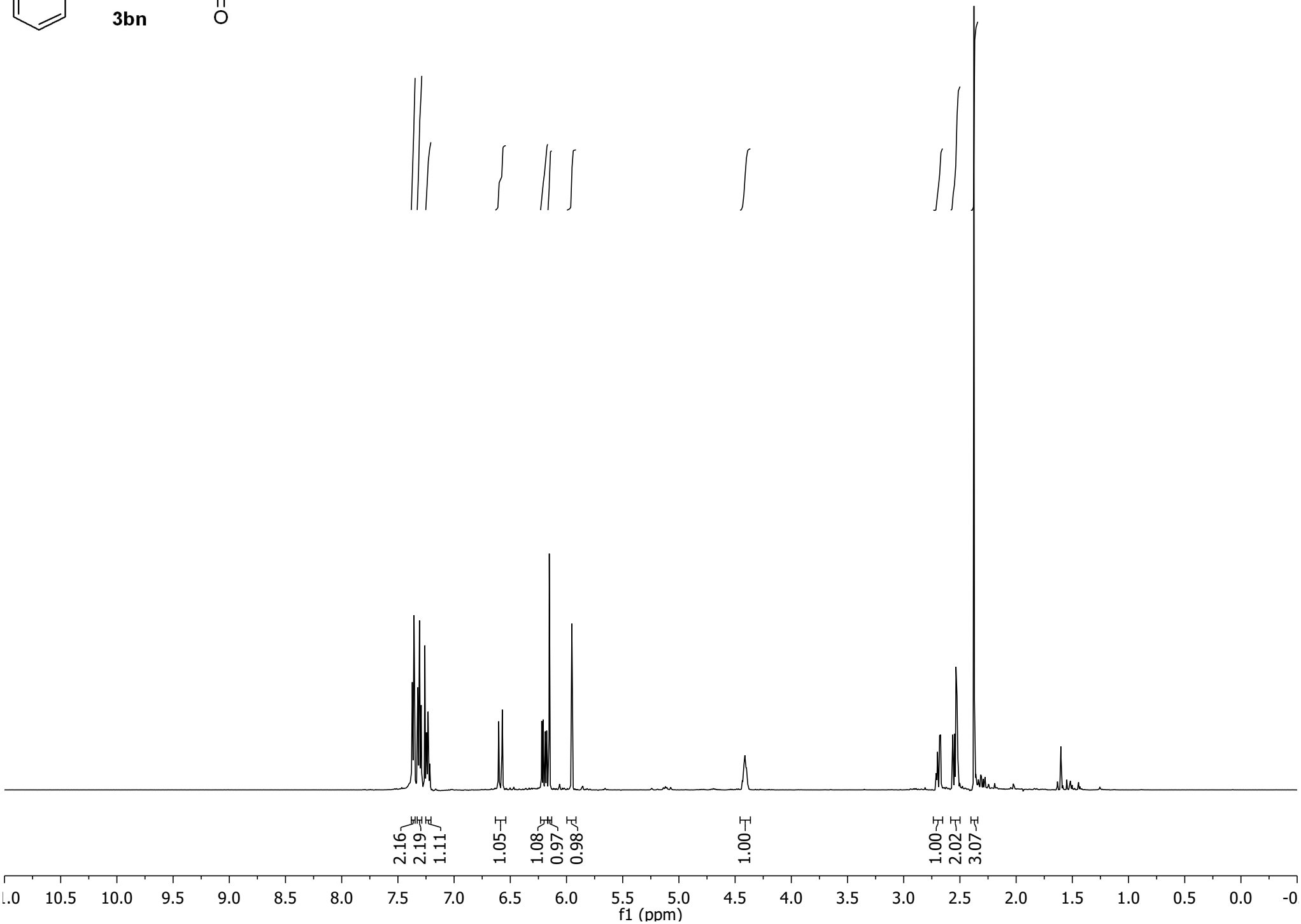
3an

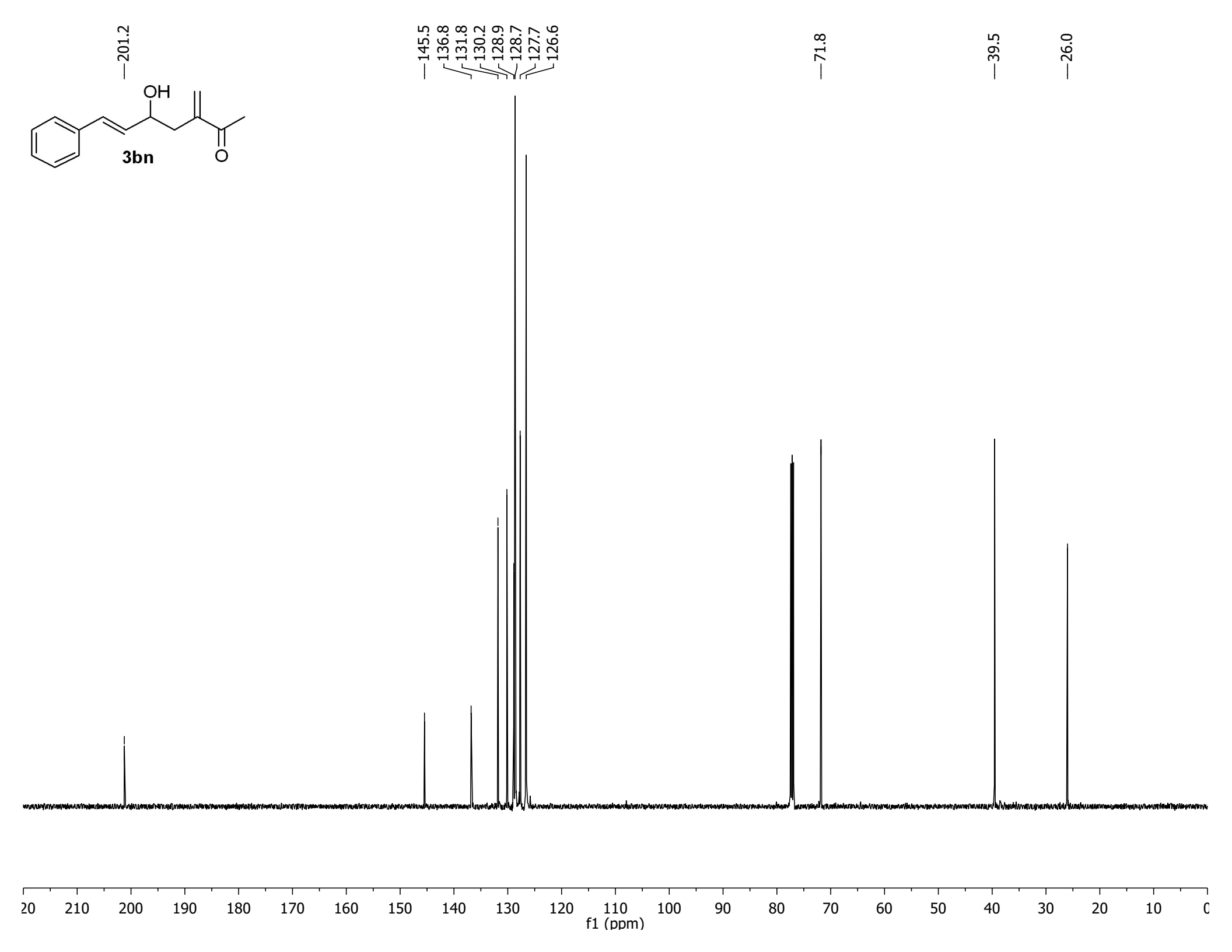

4.21
1.16
1.00
1.00
1.00
0.99
1.01
1.03
3.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

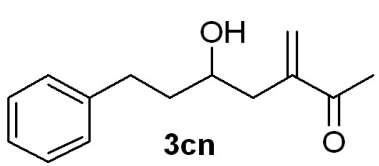

201.3
145.7
144.3
128.8
128.4
127.5
125.8
73.4
41.6
25.9
OH
O
3an
f1 (ppm)


OH
O

3bn

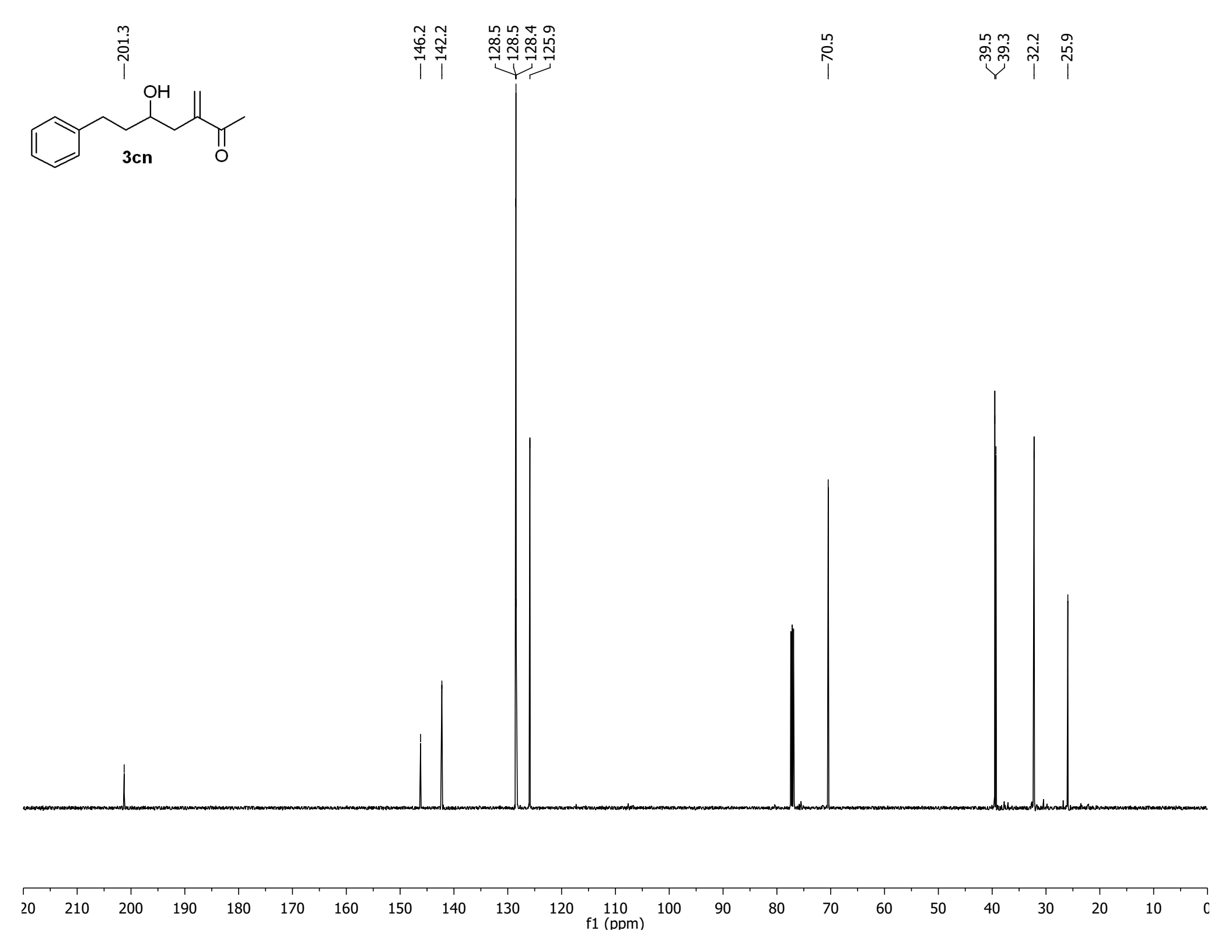

2.16
2.19
1.11
1.05
1.08
0.97
0.98
1.00
1.00
2.02
3.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

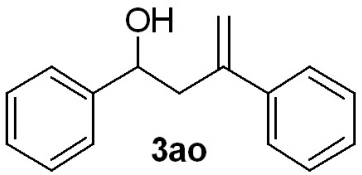

201.2
145.5
136.8
131.8
130.2
128.9
128.7
127.7
126.6
71.8
39.5
26.0
OH
O
3bn
f1 (ppm)


OH
O

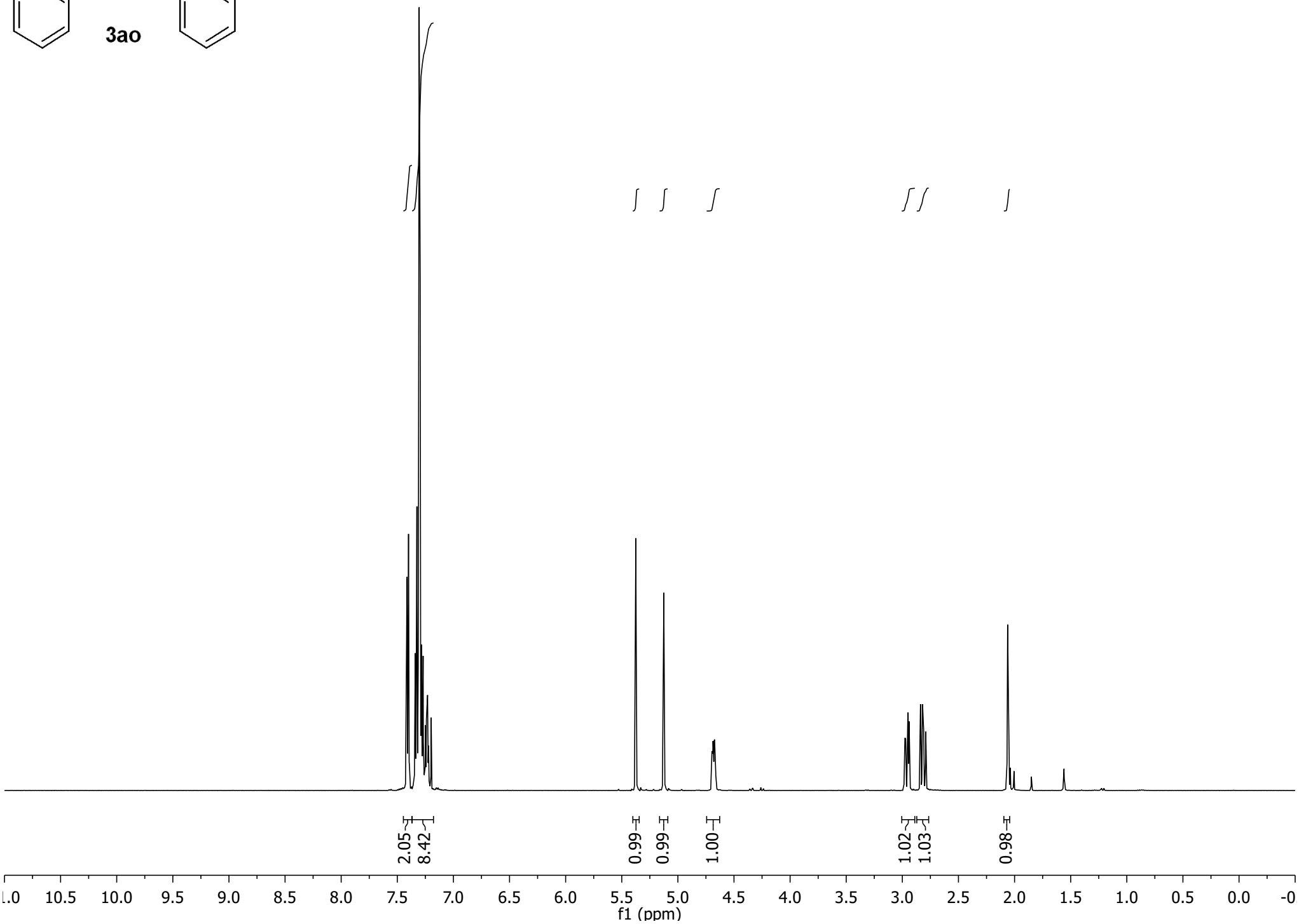
3cn

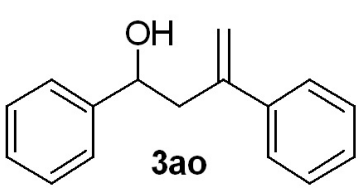
2.14
3.32
0.97
0.97
1.00
1.05
1.29
1.06
4.99
2.11
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


201.3
146.2
142.2
128.5
128.5
128.4
125.9
70.5
39.5
39.3
32.2
25.9
OH
O
3cn
f1 (ppm)

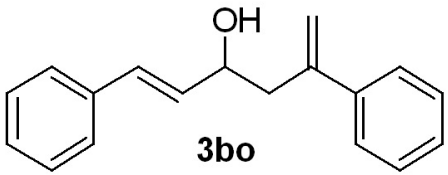


3ao

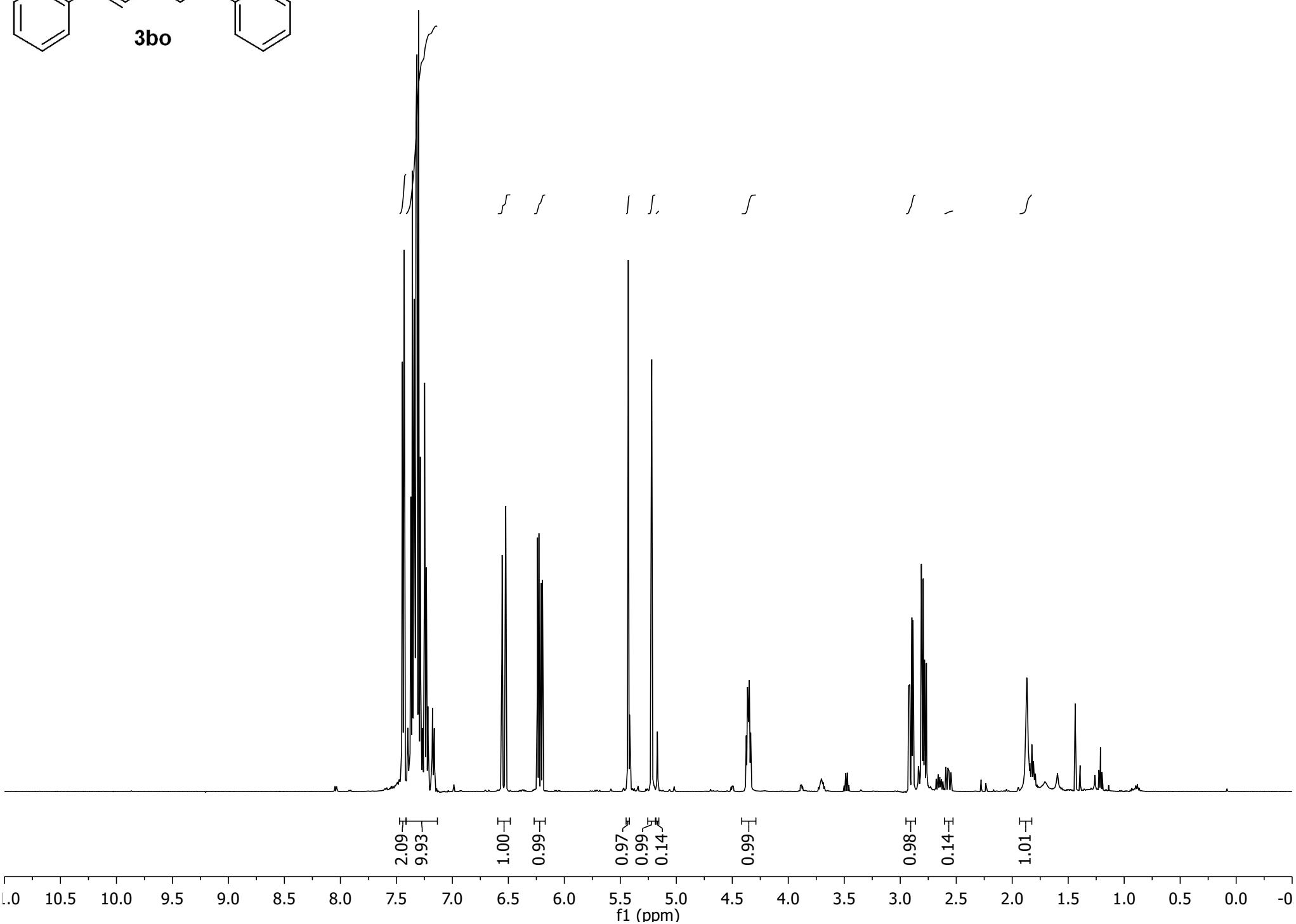


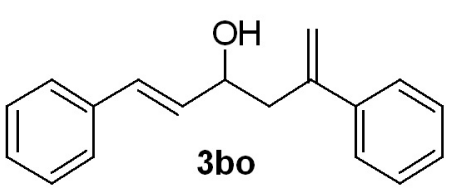


3ao


OH

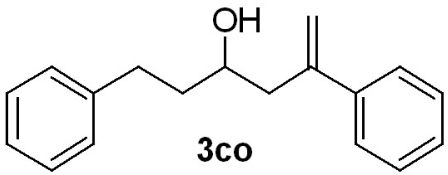
3bo


2.09
9.93
1.00
0.99
0.97
0.99
0.14
0.99
0.98
0.14
1.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

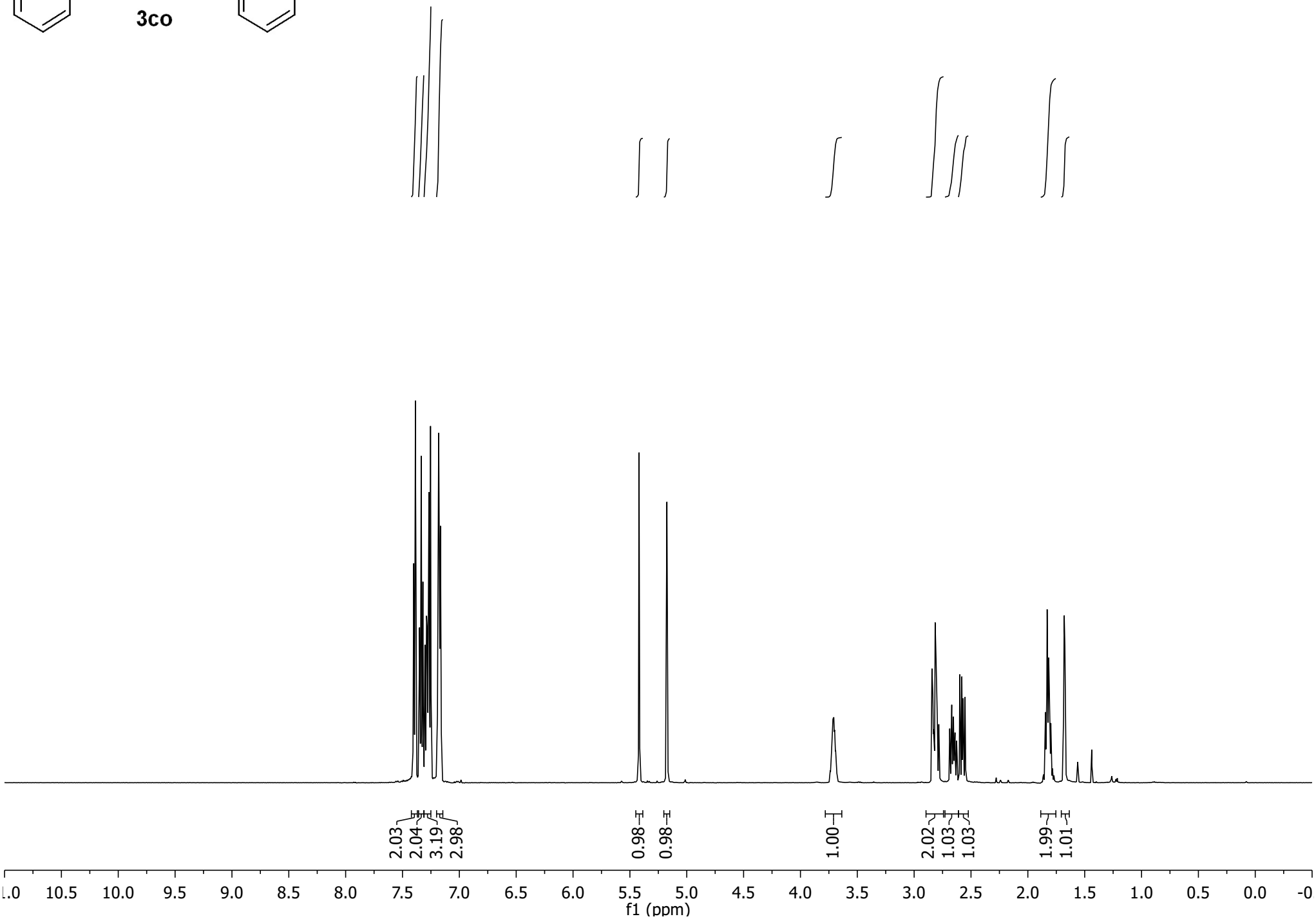

OH

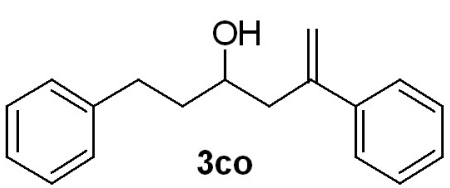
3bo

144.6
140.3
136.6
131.4
130.1
128.4
128.4
127.6
127.5
126.3
126.2
115.7
70.5
43.8
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH

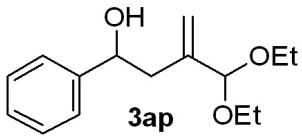
3co


2.03
2.04
3.19
2.98
0.98
0.98
1.00
2.02
1.03
1.03
1.99
1.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

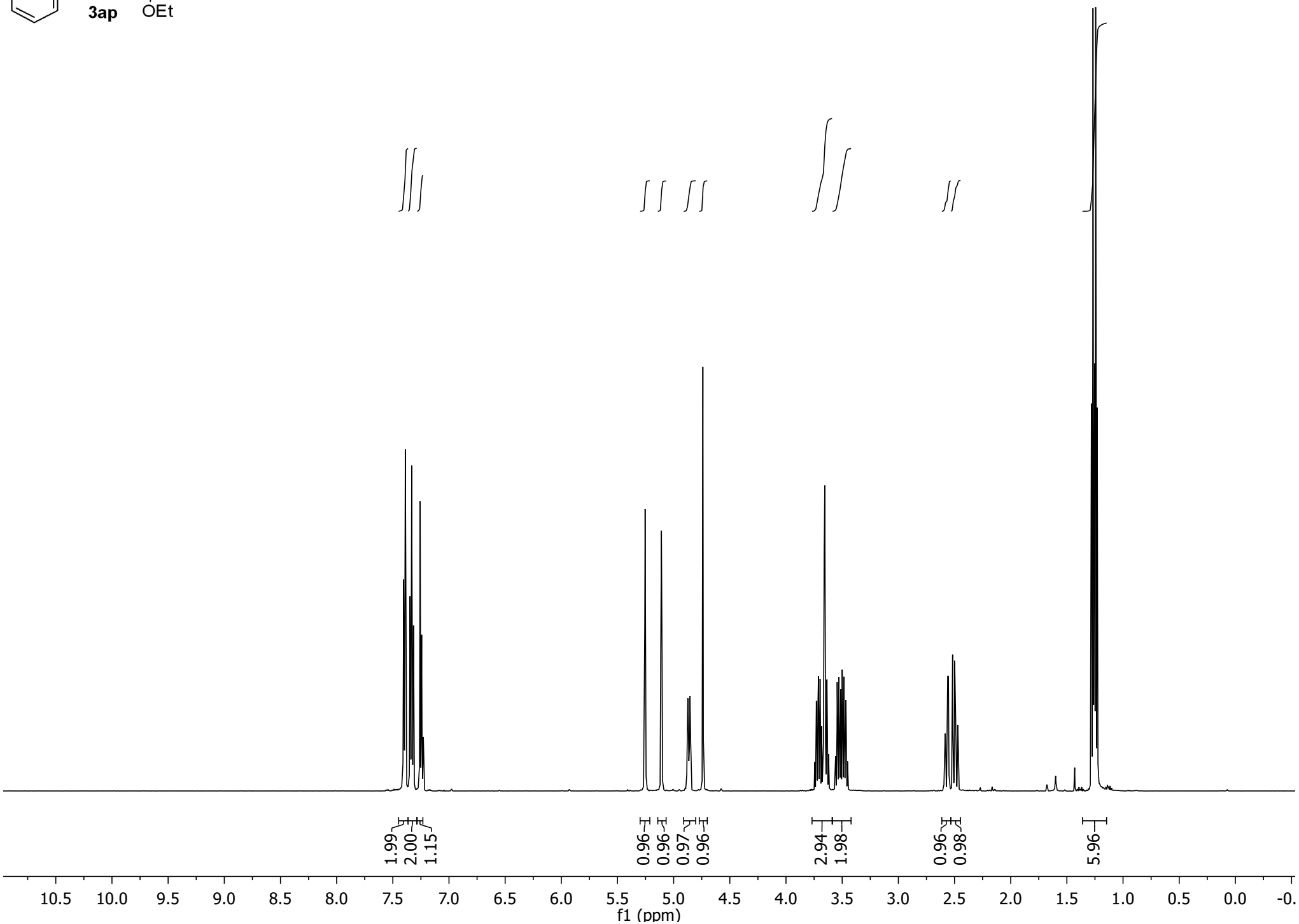

OH

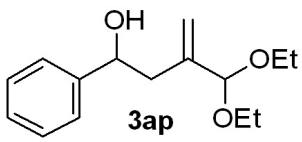
3co

145.5
142.2
140.7
128.6
128.5
127.9
126.4
125.9
115.5
69.2
44.0
38.8
32.2
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
OEt
OEt

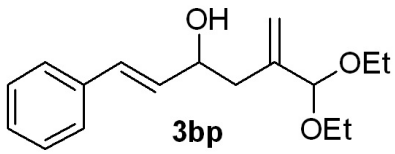
3ap


1.99
2.00
1.15
0.96
0.96
0.97
0.96
2.94
1.98
0.96
0.98
5.96
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

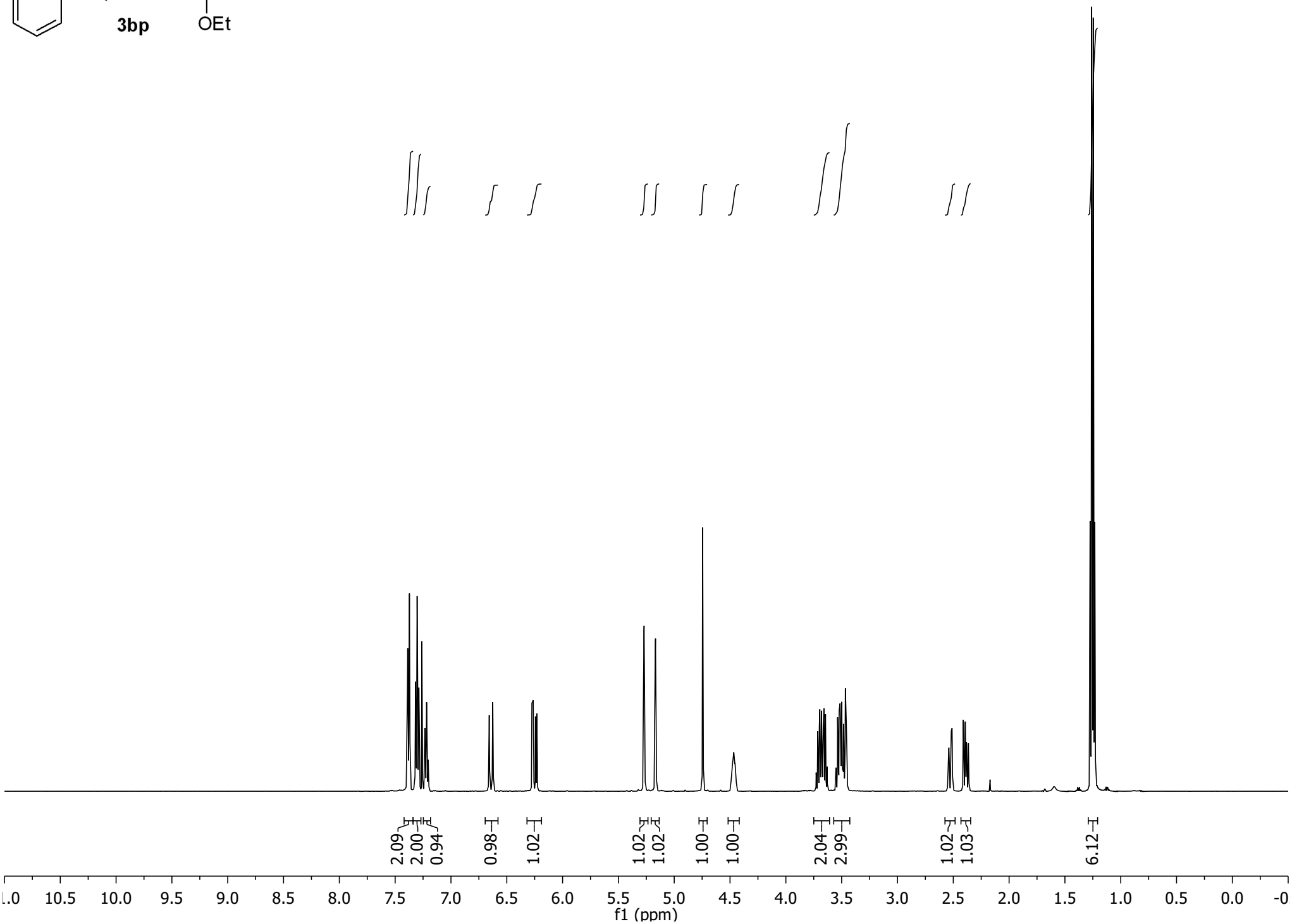

OH
OEt
OEt

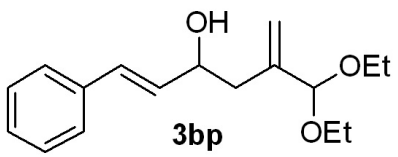
3ap

144.7
143.3
128.3
127.2
125.9
117.8
104.7
73.8
63.0
62.6
42.1
15.2
15.2
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
OEt
OEt

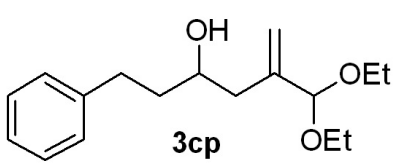
3bp


2.09
2.00
0.94
0.98
1.02
1.02
1.02
1.00
1.00
2.04
2.99
1.02
1.03
6.12
f1 (ppm)


OH
OEt
OEt

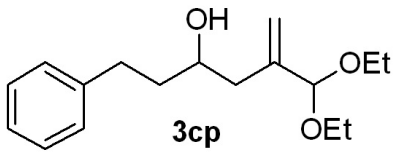
3bp

143.1
137.3
132.4
129.6
128.6
127.5
126.6
117.8
104.7
71.8
62.9
62.7
40.0
15.2
15.2
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

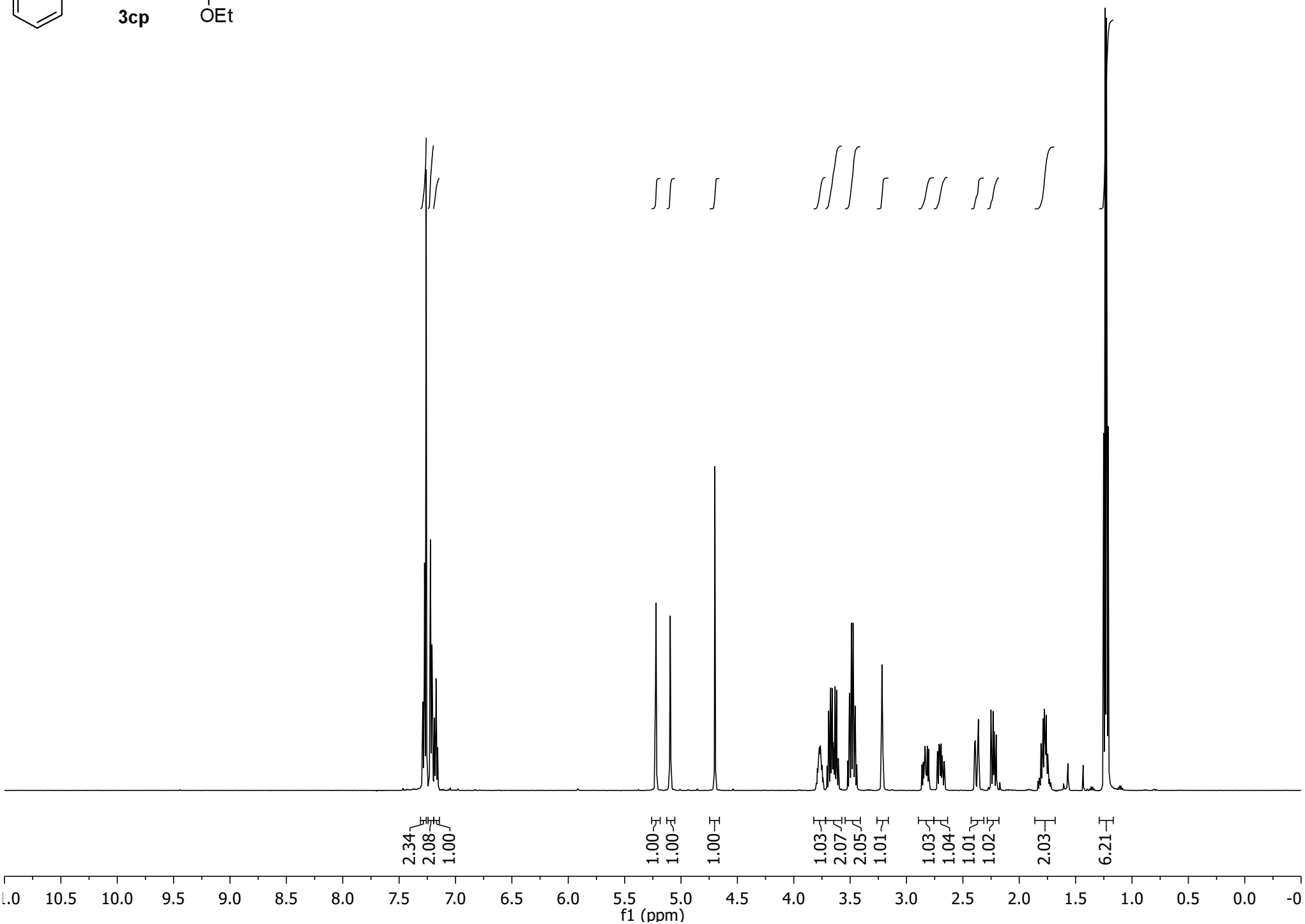

OH
OEt
OEt

3cp

143.7
142.6
128.6
128.4
125.8
117.3
104.8
70.4
63.0
62.6
39.8
39.3
32.4
15.2
15.2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OH
OEt
OEt

3cp


2.34
2.08
1.00
1.00
1.00
1.00
1.03
2.07
2.05
1.01
1.03
1.04
1.01
1.02
2.03
6.21
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)