Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

Palladium-Catalyzed Alkene Chain-Running Isomerization

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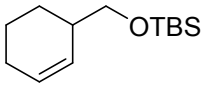
General Considerations

Reactions were performed using standard glassware or were run in 2-dram vials with PTFE/Liner screw caps. Column chromatography was performed on 60Å silica gel (Silicycle). The ^{1}H, ^{13}C, ^{19}F and 2D-NMR spectra were recorded on JEOL EC-400, JEOL EC-500, or JEOL EC-600 spectrometers using residual solvent peak as a reference. Analytical thin layer chromatography was performed on silica gel TLC Al foils with fluorescent indicator (254 nm) from Fluka. Low temperature reactions were performed using Cryo Immersion Cooler FC100 with Flexi Probe from SP Scientific. All procedures were performed under ambient air unless otherwise noted. Reagents and starting materials were obtained from commercial sources and used without further purification unless otherwise noted. Complex **3**[1] and NaBArF (sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate)[2] were prepared according to literature procedure. Hexene was distilled from sodium under nitrogen. Methylene chloride was purified on a Glasscontour solvent purification system.

Synthesis of New Starting Materials

3-tert-Butyldimethylsiloxymethylcyclohexene



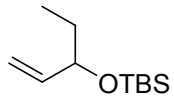
Intermediate alcohol was produced by a known procedure.[3] In a glove box KOtBu (1.68 g, 15 mmol) was added to a 100 mL oven dried round bottom flask equipped with a stir bar. Outside the glovebox, cyclohexene (19.5 mL) was added via syringe and the suspension was cooled to 0 ºC. nBuLi (10.3 mL of a 1.6 M solution in hexanes, 16.5 mmol) was added slowly and the mixture was stirred for 2 hours, warmed to room temperature, and stirred overnight. The solution was heated to 60 ºC and paraformaldehyde (495 mg, 16.5 mmol) was added slowly in 3 portions. The mixture was heated for 3 h at 60 ºC. The reaction was quenched at 0 ºC by addition of NH_4Cl (aq) and the organic layer was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude mixture was dissolved in CH_2Cl_2 (30 mL) and cooled to 0 ºC. Imidazole (1.12 g, 16.5 mmol) was added with stirring followed by TBSCl (2.49 g, 16.5 mmol). The mixture was stirred overnight at room temperature and quenched by addition of NH_4Cl (aq). The organic layer was separated, dried over Na_2SO_4, and concentrated. The mixture was concentrated on silica and purified by column chromatography on silica gel (eluent: pentane) to give 1.14 g of 3-tert-butyldimethylsiloxymethylcyclohexene (34%) as a clear liquid. R_f (pentane) = 0.40

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 5.78 – 5.55 (m, 2H), 3.45 (qd, J = 9.7, 7.1 Hz, 2H), 2.31-2.19 (m, 1H), 2.05 – 1.89 (m, 2H), 1.81 – 1.62 (m, 2H), 1.56 – 1.43 (m, 2H), 1.35-1.22 (m, 1H), 0.89 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 128.5, 67.4, 38.4, 26.1, 25.7, 25.6, 20.9, 18.5, 14.2, -5.2.

HR-MS (ESI) calcd. for $C_{13}H_{26}OSi$ $[M-H]^+$ 225.1675; found: 225.1680

tert-Butyldimethyl(pent-4-en-3-yloxy)silane



1-Penten-3-ol (2.05 mL, 20 mmol) was dissolved in CH_2Cl_2 (20 mL) and the solution was cooled to 0 ºC. Imidazole (1.5 g, 22 mmol) was added in one portion and the mixture was stirred for 10 minutes. TBSCl (3.32 g, 22 mmol) was added at 0 ºC and then

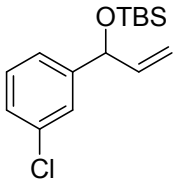
the solution was warmed to room temperature and stirred overnight. The reaction was quenched with NH_4Cl (aq) and the organic layer was separated and dried over Na_2SO_4. The mixture was concentrated to give 3.32 g of 3-tert-butyldimethyl(pent-4-en-3-yloxy)silane (83%) as a clear liquid.

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.84 – 5.70 (m, 1H), 5.02 (d, J = 10.4 Hz, 1H), 4.01 (q, J = 6.1 Hz, 1H), 4.01 (q, *J* = 6.1, 1H), 1.53 – 1.44 (m, 1H), 0.89 (s, 6H), 0.86 (t, *J* = 7.4 Hz, 3H), 0.05 (s, 3H), 0.03 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 141.7, 113.6, 75.1, 30.9, 26.0, 18.4, 9.7, -4.3, -4.8.

HR-MS (ESI) calcd. for $C_{11}H_{24}OSi$ $[M]^+$ 200.1596; found: 200.1599

tert-Butyldimethyl(1-*m*-chlorophenyl-prop-2-en-1-yloxy)silane



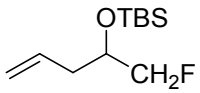
In a 200 mL flame dried round bottom flask *m*-chlorobenzaldehyde (1.13 mL, 10 mmol) was dissolved in THF (50 mL) and cooled to 0 ºC. Vinyl magnesium bromide solution (10.0 mL of a 1M solution in THF) was added dropwise at 0 °C. The solution was warmed to room temperature and stirred for 3 hours. The reaction was quenched with aqueous 1M HCl and extracted with ethyl acetate (3 x 25 mL). The extra was dried with Na_2SO_4 and concentrated. The crude product was redissolved in CH_2Cl_2 (20 mL) and cooled to 0 ºC. Imidazole (750 mg, 11 mmol) was added and the mixture was stirred for 5 minutes. TBSCl (1.65 g, 11 mmol) was added and the mixture was allowed to warm to room temperature and was stirred overnight. The reaction was quenched with water (20 mL) and the organic layer was separated and dried with Na_2SO_4. The mixture was concentrated on silica and purified by column chromatography on silica gel (eluent: hexane) to give 1.45 g of tert-buytldimethyl(1-m-chlorophenyl-prop-2-en-1-yloxy)silane (51%) as a clear liquid. R_f (pentane) = 0.66.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.30 – 7.08 (m, 4H), 5.98 – 5.65 (m, 1H), 5.33 – 5.05 (m, 3H), 0.91 (s, 9H), 0.07 (s, 3H), 0.01 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 146.0, 141.1, 134.2, 129.6, 127.2, 126.2, 124.2, 114.1, 75.4, 25.9, 18.4, -4.6, -4.8.

HR-MS (ESI) calcd. for $C_{15}H_{23}ClOSi$ $[M-H]^+$ 282.1128; found: 282.1132

tert-Butyldimethyl(1-fluoropent-4-en-2-yloxy)silane



Using a modified procedure,[4] InI_3 (990 mg, 2 mmol) was added to a 100 mL oven dried round bottom flask inside a glovebox. The flask was sealed with a rubber septum and taken outside the glovebox. Dichloromethane (10 mL) was added via syringe followed by allyltrimethylsilane (6.24 mL, 40 mmol) and ethyl 2-fluoroacetate (0.98 mL, 10 mmol; CAUTION-TOXIC). In a separate 25 mL oven-dried round bottom flask methyldiphenylsilane (3.96 mL, 20 mmol) was dissolved in CH_2Cl_2 (20 mL). This solution was added dropwise using canula over 2 hours to the mixture of allylsilane and fluoroacetate followed by stirring for additional 15 minutes. TBAF (1M in THF, 50 mL, 50 mmol) was added at 0 ºC. The reaction was quenched with 1M HCl and then extracted with Et_2O (3 x 25 mL). The organic layer was separated and dried with Na_2SO_4. The mixture was concentrated on silica and purified by column chromatography on silica gel (eluent: hexanes then 5:1 hexanes: ethyl acetate). All fractions containing 5-fluoro-1-penten-4-ol were combined, concentrated, and dissolved in CH_2Cl_2 (50 mL). Imidazole (1.30 g, 20 mmol) was added and the mixture was stirred for 5 minutes followed by addition of TBSCl (2.26 g, 15 mmol). The mixture was stirred overnight. The reaction was quenched with water and the organic layer was separated and dried with Na_2SO_4. The mixture was concentrated on silica and purified by column chromatography on silica gel (eluent: pentane) to give 172 mg of tert-butyldimethyl(1-fluoropent-4-en-2-yloxy)silane (8%) as a clear liquid. R_f (pentane) = 0.36.

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.80 (ddt, J = 17.4, 10.3, 7.2 Hz, 1H), 5.16 – 4.99 (m, 2H), 4.42 – 4.11 (m, 2H), 3.92 (ddd, J = 15.2, 6.1, 4.4 Hz, 1H), 2.34 – 2.13 (m, 2H), 0.88 (s, 9H), 0.07 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 134.0, 117.8, 86.3 (d, J = 171.9 Hz), 70.8 (d, J = 19.6 Hz), 38.2 (d, J = 6.5 Hz), 25.9, 18.2, -4.6, -4.7.

^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -224.59 (td, J = 47.4, 15.2 Hz).

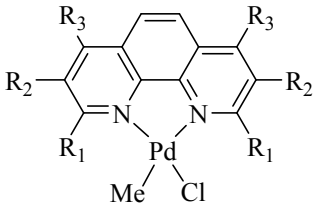
HR-MS (ESI) calcd. for $C_{11}H_{23}FOSi$ $[M+H]^+$ 219.1580; found: 219.1574

Reaction Optimization

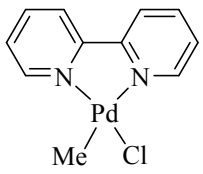
General Procedure for Optimization Reactions

A 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar was charged with $NaB[(C_6H_4(CF_3)_2]_4$ (7 mg, 8 μmol) and tert-butyldimethyl(allyloxy)silane[5] (1.0 mmol). A freshly prepared solution of catalyst (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed, placed in cooling bath at 0 ºC and allowed to stir for the specified time. After the reaction had finished, a solution of nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. An internal standard, 1,4-bis(trifluoromethyl)benzene (7.8 μL, 0.050 mmol) was added to the vial and the whole reaction mixture was transferred to an NMR tube. Yields were determined by NMR. Spectra were taken with relaxation time of 20 seconds.

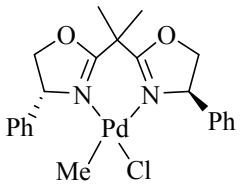
Figure S1. Palladium Complexes Used in Optimization



3: R_1= Me, R_2= H, R_3=H
S1: R_1= H, R_2= H, R_3=H
S2: R_1= Me, R_2= H, R_3=Ph
S3: R_1= Me, R_2= H, R_3=Cl
S4: R_1= Me, R_2= p$CF_3C_6H_4$, R_3=H

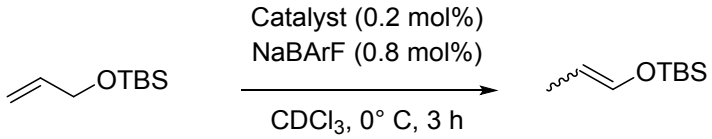


S5



S6

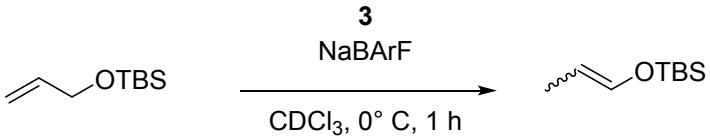
Table S1. Catalyst Optimization Results[a]



Entry	Catalyst	Yield
1	**S1**	36%
2[b]	**3**	79%
3	**S2**	7%
4	**S3**	27%
5	**S4**	28%
6	**S5**	49%
7	**S6**	5%

[a)] Olefin (1.0 mmol, 1 equiv), catalyst (0.002 mmol, 0.2 mol%), NaBArF (0.008 mmol, 0.8 mol%), $CDCl_3$ (0.5 mL), 0 °C, 3 h, yields measured by NMR. [b)] Catalyst (0.1 mol%)

Table S2. Optimization of Reaction Conditions and Control Experiments[a]



Entry	Catalyst Loading	NaBArF	[Olefin]	Yield
1	1 mol%	4 mol%	0.4 M	12%
2	1 mol%	4 mol%	0.67 M	7%
3	1 mol%	4 mol%	2 M	31%
4[b]	1 mol%	4 mol%	2 M	86%
5	-------	4 mol%	0.4 M	0%
6	1 mol%	-------	0.4 M	2%

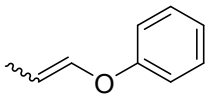
[a)] Olefin (1.0 mmol, 1 eq), catalyst (0.002 mmol, 0.2 mol%), NaBArF (0.008 mmol, 0.8 mol%), $CDCl_3$ (0.5 mL), 0 °C, 1 h, yields measured by NMR. [b)] Reaction time: 3 h

Isomerization of Olefins

General Procedure for Isomerization of Olefins

A 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar was charged with $NaB[(C_6H_4(CF_3)_2]_4$ (7 mg, 8 μmol) and olefin (0.2 mmol). A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed, placed in cooling bath at the indicated temperature and allowed to stir for the specified time. After the reaction had finished, a solution of nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. An internal standard, 1,4-bis(trifluoromethyl)benzene (7.8 μL, 0.050 mmol) was added to the vial and the whole reaction mixture was transferred to an NMR tube. Either the allylic $-CH_3$, allylic $-CH_2$, or the olefin signal was used for quantification based on the best resolution in the spectra. Spectra were taken with relaxation time of 20 seconds. The signal used for quantification is designated in bold in each entry.

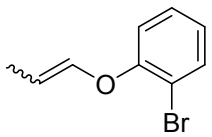
(Prop-1-enyloxy)benzene (Table 1, Entry 1)



Allyl phenyl ether (27.4 μL, 0.20 mmol) and $NaB[(C_6H_4(CF_3)_2]_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed and placed in a cooling bath at 0 ºC for 16 h. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed formation of 90% (prop-1-enyloxy)benzene (E:Z = 2.7:1). This product is known.[6]

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.35 – 7.26 (m, 2H), 7.02 (m, 3H), 6.43 (Z, dd, J = 12.1, 1.5 Hz, 1H), 6.39 (E, dd, J = 5.8, 1.7 Hz, 1H), **5.39 (Z, dq, J = 12.1, 6.9 Hz, 1H), 4.93 – 4.82 (E, m, 1H),** 1.73 (E, dd, J = 6.9, 1.7 Hz, 3H), 1.68 (Z, dd, J = 7.0, 1.5 Hz, 3H).

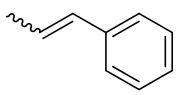
(Prop-1-enyloxy)-2-bromobenzene (Table 1, Entry 2)



o-Allyl-2-bromophenol (43 mg, 0.20 mmol) and $NaB[(C_6H_4(CF_3)_2]_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed and placed in cooling bath at 0 ºC for 16 hrs. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed formation of 94% (prop-1-enyloxy)benzene (E:Z = 1.1:1). This product is known.[7]

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.54 (m, 1H), 7.25 (m, 1H), 7.02 – 6.94 (m, 1H), 6.92 – 6.79 (m, 1H), 6.42 – 6.26 (m, 1H), **5.44 (Z, dq, J = 12.1, 6.9 Hz, 1H), 5.03 – 4.92 (E, m, 1H),** 1.75 (E. dd, J = 6.9, 1.7 Hz, 3H), 1.67 (Z, dd, J = 6.9, 1.7 Hz, 3H).

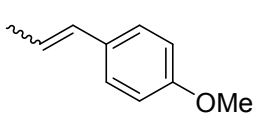
1-Propenylbenzene (Table 1, Entry 3)



Allylbenzene (26.5 μL, 0.20 mmol) and $NaB[(C_6H_4(CF_3)_2]_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed and placed in a cooling bath at 0 ºC for 2 h. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed formation of 90% 1-propenylbenzene (E:Z = >50:1). This product is known.[8]

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.41 – 7.16 (m, 5H), 6.41 (dd, J = 15.7, 1.5 Hz, 1H), **6.25 (dq, J = 15.7, 6.6 Hz, 1H)**, 1.89 (dd, J = 6.5, 1.6 Hz, 3H). (Only E isomer is visible in reaction mixture)

1-(4'-Methoxyphenyl)prop-1-ene (Table 1, Entry 4)

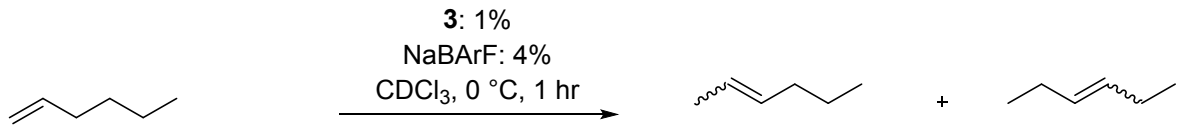


Allylanisole (30.7 μL, 0.20 mmol) and $NaB[(C_6H_4(CF_3)_2]_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed and placed in a cooling bath at 0 ºC for 16 h. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv

relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed 100% 1-(4'-methoxyphenyl)prop-1-ene (E:Z = 22.5:1). This product is known.[8]

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.29 – 7.17 (m, 2H), 6.87 – 6.76 (m, 2H), 6.34 (dd, J = 15.8, 1.7 Hz, 1H), 6.09 (dq, J = 15.8, 6.5 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), **1.89 (Z, dd, J = 7.2, 1.8 Hz, 3H), 1.86 (E, dd, J = 6.5, 1.7 Hz, 3H).** Not all Z isomer signals are resolvable.

1-Hexene Isomerization (Table 1, Entry 5)



1-Hexene (25.0 μL, 0.20 mmol) and $NaB[(C_6H_4(CF_3)_2]_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed and placed in a cooling bath at 0 ºC for 1 h. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed 57% 2-hexene and 23% 3-hexene. This product is known.[8]

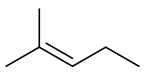
2-Hexene:

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.50 – 5.26 (m, 2H, 2-hexene and 3-hexene signals overlap), 2.03 – 1.87 (m, 2H, 2-hexene and 3-hexene signals overlap), 1.68 – 1.52 (m, 3H), 1.43 – 1.31 (m, 2H), **0.99 – 0.91 (m, 3H).**

3-Hexene:

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.50 – 5.26 (m, 2H, 2-hexene and 3-hexene signals overlap), 2.03 – 1.87 (m, 4H, 2-hexene and 3-hexene signals overlap), **0.88 – 0.83 (m, 6H).**

2-Methyl-2-pentene (Table 1, Entry 6)

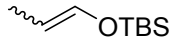


2-Methyl-1-pentene (24.8 μL, 0.20 mmol) and $NaB[(C_6H_4(CF_3)_2]_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was

added to the vial. The vial was sealed and placed in a cooling bath at 0 ºC for 3 h. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed 84% 2-methyl-2-pentene. This product is known.[8]

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ **5.14 – 5.08 (m, 1H)**, 1.98 (p, J = 7.4 Hz, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 0.97 – 0.89 (m, 3H).

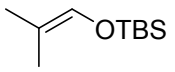
tert-Butyldimethyl(prop-1-en-1-yloxy)silane (Table 2, Entry 1)



tert-Butyldimethyl(allyloxy)silane[5] (34 mg, 0.20 mmol) and NaB[($C_6H_4(CF_3)_2$]$_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed and placed in a cooling bath at 0 ºC for 2 h. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed 86% tert-butyldimethyl(prop-1-en-1-yloxy)silane (E:Z = 1.4:1). This product is known[5].

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.20 (m, 1H, E and Z signals overlap), **4.98 (*E*, dq, *J* = 11.9, 6.8 Hz, 1H), 4.55 – 4.41 (*Z*, m, 1H)**, 1.57 (*Z*, dd, J = 6.7, 1.7 Hz, 3H), 1.51 (*E*, dd, J = 6.8, 1.5 Hz, 3H), 0.92 (*Z*, s, 9H), 0.91 (*E*, s, 9H), 0.12 (*Z*, s, 6H), 0.12 (*E*, s, 6H).

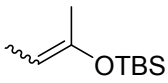
tert-Butyldimethyl(2-methylprop-1-en-1-yloxy)silane (Table 2, Entry 2)



tert-Butyldimethyl((2-methylallyloxy)silane[5] (37.0 mg, 0.200 mmol) and NaB[($C_6H_4(CF_3)_2$]$_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was filled with ethylene and then sealed and placed in a cooling bath at 0 ºC for 16 h. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed 87% tert-butyldimethyl(2-methylprop-1-en-1-yloxy)silane. This product is known.[5]

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ **6.03 (s, 1H)**, 1.59 (s, 3H), 1.53 (s, 3H), 0.92 (s, 9H), 0.10 (s, 6H).

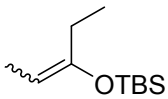
tert-Butyldimethyl(but-2-en-2-yloxy)silane (Table 2, Entry 3)



tert-Butyldimethyl(but-1-en-3-yloxy)silane[9] (37 mg, 0.20 mmol) and $NaB[(C_6H_4(CF_3)_2]_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed and placed in a cooling bath at 0 ºC for 3 h. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed 60% of tert-butyldimethyl(but-2-en-2-yloxy)silane (E:Z = 4.4:1). This product is known.[10]

^{1}H NMR (400 MHz, $CDCl_3$, ppm) **δ 4.65 (Z, q, J = 6.9 Hz, 1H), 4.45 (E, q, J = 6.8 Hz, 1H),** 1.74 (E, s, 3H), 1.70 (Z, s, 3H), 1.52 – 1.46 (m, 3H, E and Z signals overlap), 0.94 (E, s, 9H), 0.90 (Z, s, 9H), 0.12 (E, s, 6H), 0.10 (Z, s, 6H).

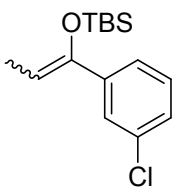
tert-Buytldinethyl(pent-2-en-3-yloxy)silane (Table 2, Entry 4)



tert-Butyldimethyl(pent-1-en-3-yloxy)silane (40 mg, 0.20 mmol) and $NaB[(C_6H_4(CF_3)_2]_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed and placed in a cooling bath at 0 ºC for 3 h. After the reaction was finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed 77% tert-buytldinethyl(pent-2-en-3-yloxy)silane (E:Z = 4.1:1). This product is known.[11]

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ **4.57 (Z, q, J = 6.9 Hz, 1H), 4.48 (E, q, J = 6.6 Hz, 1H)**, 2.11 – 1.94 (m, 2H), 1.57 – 1.43 (m, 3H), 1.09 – 0.96 (m, 3H), 0.94 (s, 9H), 0.11 (E, s, 6H), 0.11 (Z s, 6H).

tert-Buytldimethyl[1-(3-Chlorophenyl)prop-1-enyloxy]silane (Table 2, Entry 5)

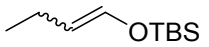


tert-Butyldimethyl(1-m-chlorophenyl-prop-2-en-1-yloxy)silane (57 mg, 0.20 mmol) and $NaB[(C_6H_4(CF_3)_2]_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial.

The vial was sealed and placed in a cooling bath at -30 ºC for 22 h. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed 87% tert-buytldimethyl[1-(3-chlorophenyl)prop-1-enyloxy]silane (E:Z = 1.6:1). This product is known.[12]

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.41 – 7.11 (m, 4H), 5.34 – 4.99 (m, 1H), **1.71 (Z, d, J = 6.9 Hz, 3H), 1.68 (E, d, J = 7.4 Hz, 3H)**, 0.98 (Z, s, 9H), 0.90 (E, s, 9H), 0.02 (E, s, 6H), -0.05 (Z, s, 6H).

tert-Butyldimethyl(but-1-en-1-yloxy)silane (Table 2, Entry 6)



tert-Butyldimethyl(but-2-en-1-yloxy)silane[13] (37 mg, 0.20 mmol) and NaB[(C$_6$H$_4$(CF$_3$)$_2$]$_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed and placed in a cooling bath at 0 ºC for 48 h. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed 93% 1- tert-butyldimethyl(but-1-en-1yloxy)silane (E:Z = 2.0:1). This product is known.[14]

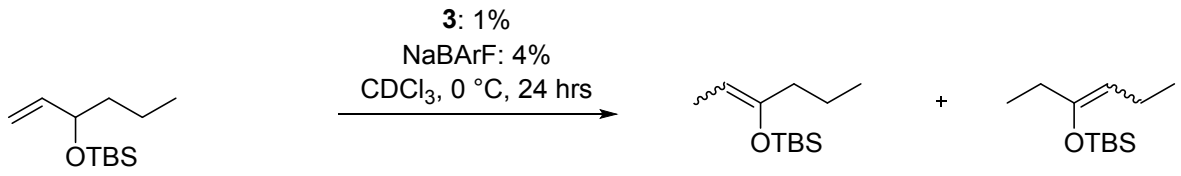
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.22 (Z, dt, J = 12.0, 1.3 Hz, 1H), 6.13 (E, dt, J = 5.8, 1.6 Hz, 2H), **5.01 (Z, dt, J = 12.0, 7.2 Hz, 1H), 4.44 (E, td, J = 7.0, 5.8 Hz, 1H),** 2.08 (E, pd, J = 7.0, 1.6 Hz, 2H), 1.89 (Z, pd, J = 7.2, 1.3 Hz, 2H), 1.02 – 0.92 (m, 3H), 0.91 (E, s, 9H), 0.90 (Z, s, 9H), 0.11 (Z, s, 6H), 0.11 (E, s, 6H).

1,4-Bis(tert-butyldimethylsilyloxy)-1-butene (Table 2, Entry 7)

(E)-1,4-Bis(tert-butyldimethylsilyloxy)-2-butene[15] (63 mg, 0.20 mmol) and NaB[(C$_6$H$_4$(CF$_3$)$_2$]$_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed and placed in a cooling bath at 0 ºC for 3 h. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed 62% 1,4-bis(tert-butyldimethylsilyloxy)-1-butene (E:Z = 1.3:1). This product is known.[15]

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.27 – 6.22 (E, m, 1H), 6.20 (Z, dt, J = 5.9, 1.2 Hz, 1H), **4.94 (E, dt, J = 12.0, 7.7 Hz, 1H)**, **4.45 (Z, td, J = 7.1, 5.9 Hz, 1H),** 3.58 – 3.49 (m, 2H, E and Z signals overlap), 2.29 (Z, m, 2H), 2.08 (E, m, 2H), 0.90 – 0.87 (m, 9H, E and Z signals overlap), 0.11 – 0.01 (m, 9H, E and Z signals overlap).

Isomerization of tert-Butyldimethyl(hex-1-en-3-yloxy)silane (Table 2, entry 8)



tert-Butyldimethyl(hex-1-en-3-yloxy)silane[16] (44 mg, 0.20 mmol) and $NaB[(C_6H_4(CF_3)_2]_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed and placed in a cooling bath at 0 ºC for 24 h. After the reaction had finished, $n$$Bu_4NCl$ in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed 51% tert-butyldimethyl(hex-2-en-3-yloxy)silane (E:Z = 4.7:1) and 20% tert-butyldimethyl(hex-3-en-3-yloxy)silane (E:Z 5.6:1). These products are known.[17,18]

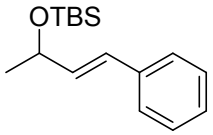
tert-Butyldimethyl(hex-2-en-3-yloxy)silane:

^{1}H NMR (400 MHz, $CDCl_3$, ppm) **δ 4.62 (q, J = 6.9 Hz, 1H, E), 4.47 (q, J = 6.4 Hz, 1H, Z)**, 2.03 – 1.99 (m, 3H, E), 1.97 – 1.93 (m, 3H, Z), 1.53 – 1.48 (m, 5H, E and Z signals overlap), 0.94 (s, 9H, E and Z signals overlap), 0.93 – 0.83 (m, 3H, E and Z signals overlap), 0.11 (s, 6H, E and Z signals overlap).

tert-Butyldimethyl(hex-3-en-3-yloxy)silane:

^{1}H NMR (400 MHz, $CDCl_3$, ppm) **δ 4.56 (t, J = 7.5 Hz, 1H, Z), 4.40 (t, J = 6.8 Hz, 1H, E),** 2.08 – 1.86 (m, 4H, E and Z signals overlap), 0.94 (s, 9H, E and Z signals overlap), 0.92 – 0.86 (m, 6H, E and Z signals overlap), 0.11 (s, 6H, E and Z signals overlap).

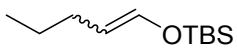
tert-Butyldimethyl(4-phenylbut-3-en-2-yloxy)silane (Table 2, Entry 9)



tert-Butyldimethyl(4-phenylbut-1-en-4-yloxy)silane[9] (52 μL, 0.20 mmol) and $NaB[(C_6H_4(CF_3)_2]_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed and stirred at 0 °C for 24 h. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed 49% tert-butyldimethyl(4-phenylbut-3-en-2-yloxy)silane (E:Z = >50:1). This product is known.[19]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.18 (m, 5H), 6.52 (d, J = 16.0 Hz, 1H), 6.23 (dd, J = 16.0, 5.6 Hz, 1H), 4.55-4.41 (m, 1H), 1.31 (d, J = 6.3 Hz, 3H), 0.94 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H).

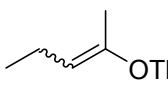
tert-Butyldimethyl(pent-1-en-1-yloxy)silane (Table 3, Entry 1)



tert-Butyldimethyl(pent-4-en-1yloxy)silane[20] (40 mg, 0.20 mmol) and $NaB[(C_6H_4(CF_3)_2]_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed and placed in a cooling bath at 0 ºC for 48 h. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed 66% tert-butyldimethyl(pent-1-en-1yloxy)silane (E:Z = 2:1). This product is known.[19]

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.19 (Z, dt, J = 11.9, 1.1 Hz, 1H), 6.15 (E, dt, J = 6.1, 1.6 Hz, 2H), **4.96 (Z, dt, J = 11.9, 7.5 Hz, 1H), 4.42 (E, td, J = 7.3, 6.1 Hz, 1H),** 2.06-2.00 (E, m, 2H), 1.86-1.80 (Z, m, 2H), 1.45-1.29 (m, 2H, E and Z signals overlap), 0.89 (E, s, 9H), 0.88 (Z, s, 9H), 0.86 (m, 3H, E and Z signals overlap), 0.10 (E, s, 6H), 0.09 (Z, s, 6H).

tert-Butyldimethyl(pent-2-en-2-yloxy)silane (Table 3, Entry 2)

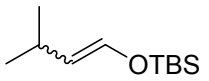


tert-Butyldimethyl(pent-4-en-2-yloxy)silane[22] (40 mg, 0.20 mmol) and $NaB[(C_6H_4(CF_3)_2]_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20

mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed and placed in a cooling bath at 0 ºC for 16 h. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed 64% tert-butyldimethyl(pent-2-en-2-yloxy)silane (E:Z = 3.3:1). This product is known.[23]

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ **4.64 (Z, t, J = 7.4 Hz, 1H), 4.38 (E, dt, J = 7.7, 3.9 Hz, 1H),** 2.03 – 1.95 (E, m, 2H), 1.94 – 1.89 (Z, m, 2H), 1.74 (E, dd, J = 2.1, 1.0 Hz, 3H), 1.70 (Z, s, 3H), 0.96 (t, J = 7.4 Hz, 3H), 0.93 (E, s, 9H), 0.85 (Z, s, 9H), 0.11 (E, s, 6H), 0.10 (Z, s, 6H).

tert-Butyldimethyl(3-methylbut-1-en-1-yloxy)silane (Table 3, Entry 3)



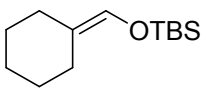
tert-Butyldimethyl(3-methylbut-3-en-1-yloxy)silane[24] (400 mg, 2.0 mmol and NaB[(C$_6$H$_4$(CF$_3$)$_2$]$_4$ (35 mg, 40 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in $CDCl_3$, 1.0 mL, 20 μmol) was added to the vial. The vial was sealed and stirred at room temperature for 24 h. The mixture was concentrated on silica and purified by column chromatography on silica gel (eluent: pentane) to give 319 mg of tert-butyldimethyl(3-methylbut-1-en-1-yloxy)silane (80%, E:Z 1.3:1). Rf (pentane) = 0.34.

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ **6.23 – 6.15 (Z, m, 1H), 6.04 (E, dd, J = 5.8, 0.9 Hz, 1H),** 4.94 (Z, dd, J = 12.0, 7.9 Hz, 1H), 4.28 (E, dd, J = 8.9, 5.8 Hz, 1H), 2.82 – 2.71 (E, m, 1H), 2.24 – 2.14 (Z, m, 1H), 0.99 – 0.91 (m, 6H), 0.90 (E, s, 9H), 0.89 (Z, s, 9H), 0.10 (Z, s, 6H), 0.09 (E, s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm; isomer mixture) δ 138.4, 136.7, 119.5, 118.5, 77.4, 77.1, 76.9, 27.3, 25.8, 25.7, 23.7, 23.6, 23.3, 18.4, -5.2, -5.3.

HR-MS (ESI) calcd. for $C_{11}H_2OSi$ $[M+H]^+$ 201.1675; found: 201.1679

(tert-Butyldimethylsiloxymethylidene)cyclohexane (Table 3, Entry 4)

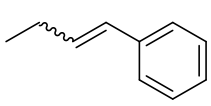


3-tert-Butyldimethylsiloxymethylcyclohexene (40 mg, 0.20 mmol) and NaB[(C$_6$H$_4$(CF$_3$)$_2$]$_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20

mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed and placed in a cooling bath at 0 ºC for 48 h. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed 80% (tert-butyldimethylsiloxymethylidene)cyclohexane (E:Z = 1.7:1). This product is known.[12]

^{1}H NMR (500 MHz, $CDCl_3$, ppm) **δ 6.00 (d, J = 1.0 Hz, 1H),** 2.18 – 2.15 (m, 2H), 1.92 – 1.88 (m, 2H), 1.52 – 1.35 (m, 6H), 0.97 (t, J = 7.3 Hz, 9H), 0.89 (s, 9H), 0.08 (s, 6H).

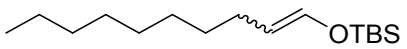
1-Phenylbut-1-ene (Table 3, Entry 5)



1-Phenyl-3-butene (30 μL, 0.20 mmol) and NaB[$(C_6H_4(CF_3)_2]_4$ (7.0 mg, 8.0 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in $CDCl_3$, 0.1 mL, 2 μmol) was added to the vial. The vial was sealed and stirred at room temperature for 48 h. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. ^{1}H NMR analysis revealed 56% 1-phenylbut-1-ene (E:Z = >50:1). This product is known.[8]

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.38 – 7.14 (m, 5H), **6.38 (d, J = 15.9 Hz, 1H),** 6.28 (dt, J = 15.9, 6.4 Hz, 1H), 2.29 – 2.20 (m, 2H), 1.10 (t, J = 7.5 Hz, 3H).

tert-Butyldimethyl(dec-1-en-1-yloxy)silane (Table 3, Entry 6)



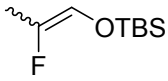
tert-Butyldimethyl(dec-9-en-1-yloxy)silane (1.26 g, 4.6 mmol) and NaB[$(C_6H_4(CF_3)_2]_4$ (8.8 mg mg, 10 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in CH_2Cl_2, 0.115 mL, 2.3 μmol) was added to the vial. The vial was sealed and stirred at room temperature for 24 hours. The reaction was poured into hexanes (10 mL) and filtered. The mixture was concentrated on silica and purified by column chromatography on silica gel (eluent: pentane) to give 962 mg of tert-butyldimethyl(dec-1-en-1-yloxy)silane (76%, E:Z = 2.6:1). The two isomers can be separated by column chromatography, Rf (pentane) = 0.74 (spot 1), 0.56 (spot 2).

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.20 (Z, d, J = 11.8 Hz, 1H), 6.15 (E, dt, J = 6.0, 1.5 Hz, 1H), 4.97 **(Z, dt, J = 11.8, 7.5 Hz, 1H), 4.43 (E, td, J = 7.2, 6.0 Hz, 1H),** 2.09 – 2.01 (Z, m, 2H), 1.85 (E, dt, J = 7.7, 4.0 Hz, 2H), 1.34 – 1.18 (m, 12H), 0.98 – 0.93 (m, 3H), 0.91 (E, s, 9H), 0.90 (Z, s, 9H), 0.11 (Z, s, 6H), 0.11 (E, s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 140.0, 138.4, 111.8, 111.0, 32.0, 30.5, 29.8, 29.6, 29.5, 29.4, 29.2, 27.4, 25.8, 25.7, 23.7, 22.8, 18.4, 14.2, -5.1, -5.3.

HR-MS (ESI) calcd. for $C_{16}H_{34}OSi$ $[M+H]^+$ 271.2457; found: 271.2452

tert-Butyldimethyl(2-fluoroprop-1-en-1-yloxy)silane (5, Scheme 2)



A modified procedure was used. tert-Butyldimethyl((2-fluoroallyl)oxy)silane[25] (38 mg, 0.20 mmol), $NaB[(C_6H_4(CF_3)_2]_4$ (7.0 mg, 8.0 μmol), and solution of **3** (0.1 mL of a 20 mM solution in $CDCl_3$, 2.0 μmol) were cooled -30 ºC. Phenylsilane (0.7 μL, 6.0 μmol) was added via syringe and the reaction mixture was stirred for 16 h at -30 ºC. After the reaction had finished, nBu$_4$NCl in $CDCl_3$ (>20 equiv relative to catalyst) was added and the mixture was shaken to terminate the reaction. An internal standard (1,4-bis(trifluoromethyl)benzene (7.8 μL, 0.050 mmol) was added to the vial and the whole reaction mixture was transferred to an NMR tube. ^{1}H NMR analysis revealed 78% tert-butyldimethyl(2-fluoroprop-1-en-1-yloxy)silane (E:Z = 1.7:1). This product was isolated via column chromatography (pentane) as well to confirm its structure. The two isomers are separable by column chromatography, Rf (pentane) = 0.62 (spot 1), 0.46 (spot 2).

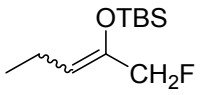
^{1}H NMR (500 MHz, $CDCl_3$, ppm) **δ 6.48 (Z, dd, J = 7.2, 1.1 Hz, 1H), 5.57 (E, dd, J = 21.7, 1.1 Hz, 1H),** 1.92 (Z, dd, J = 17.4, 1.1 Hz, 3H), 1.78 (E, dd, J = 16.8, 1.1 Hz, 3H), 0.92 (E, s, 9H), 0.91 (Z, s, 9H), 0.13 (Z, s, 6H), 0.11 (E, s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm; list of signals, C-F couplings not resolved) δ 152.4, 150.6, 146.6, 144.7, 126.1, 125.7, 120.8, 120.8, 25.7, 25.7, 18.5, 18.2, 14.3, 14.1, 12.3, 12.1, -5.3, -5.4.

^{19}F NMR (470 MHz, $CDCl_3$, ppm) δ -128.1 (dq, J = 21.7, 16.8 Hz), -147.8 (qd, J = 17.4, 7.2 Hz).

HR-MS (ESI) calcd. for $C_9H_{19}FOSi$ $[M]^+$ 190.1189; found: 190.1200

tert-Butyldimethyl(1-fluoropent-2-en-2-yloxy)silane (7, Scheme 2)



tert-Butyldimethyl(1-fluoropent-4-en-2-yloxy)silane (109 mg, 0.5 mmol) and $NaB[(C_6H_4(CF_3)_2]_4$ (35 mg, 40 μmol) were added to a 2-dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar. A freshly prepared solution of **3** (20 mM in $CDCl_3$, 2.0 mL, 40 μmol) was added to the vial. The vial was sealed and cooled to 0 ºC and stirred for 30 hours. The reactions mixture was poured into pentane (20 mL) and filtered through celite. The mixture was concentrated on silica and purified by column chromatography on silica gel (eluent: pentane) to give 50 mg of tert-butyldimethyl(1-fluoropent-2-en-2-yloxy)silane (46%, E:Z 2.2:1). The two isomers are separable by column chromatography, Rf (pentane) = 0.66 (spot 1), 0.44 (spot 2).

^{1}H NMR (400 MHz,$CDCl_3$, ppm) δ 4.96 (td, *J* = 7.9, 3.9 Hz, 1H, E), 4.88 – 4.80 (m, 1H, Z), 4.78 (d, *J* = 50.4 Hz, 2H, Z), 4.62 (d, *J* = 46.2 Hz, 2H, E), 2.15 – 1.94 (m, 2H, E and Z signals overlap), 1.00 – 0.93 (m, 3H, E and Z signals overlap), 0.95 (s, 9H, E), 0.92 (s, 9H, Z), 0.14 (s, 6H, Z), 0.14 (s, 6H, E).

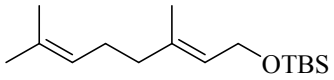
^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 145.7 (d, *J* = 13.2 Hz), 145.1 (d, *J* = 14.8 Hz), 117.0 (d, *J* = 9.8 Hz), 116.8 (d, *J* = 8.7 Hz), 84.6 (d, *J* = 166.1 Hz), 79.5 (d, *J* = 163.8 Hz), 25.9, 25.7, 20.1, 18.5, 18.4, 18.1, 15.4 (d, *J* = 3.0 Hz), 13.9 (d, *J* = 3.6 Hz), -4.3, -4.5.

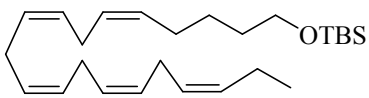
^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ -209.05 (t, J = 50.4 Hz), -215.93 (t, J = 46.2 Hz).

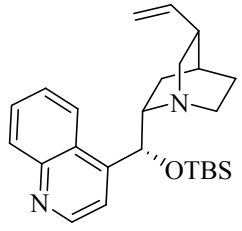
HR-MS (ESI) calcd. for $C_{11}H_{23}FOSi$ $[M+H]^+$ 219.1580; found: 219.1578

The substrates listed below did not give acceptable yields of isomerization products.

Figure S2. Substrates Giving Non-Acceptable Yields







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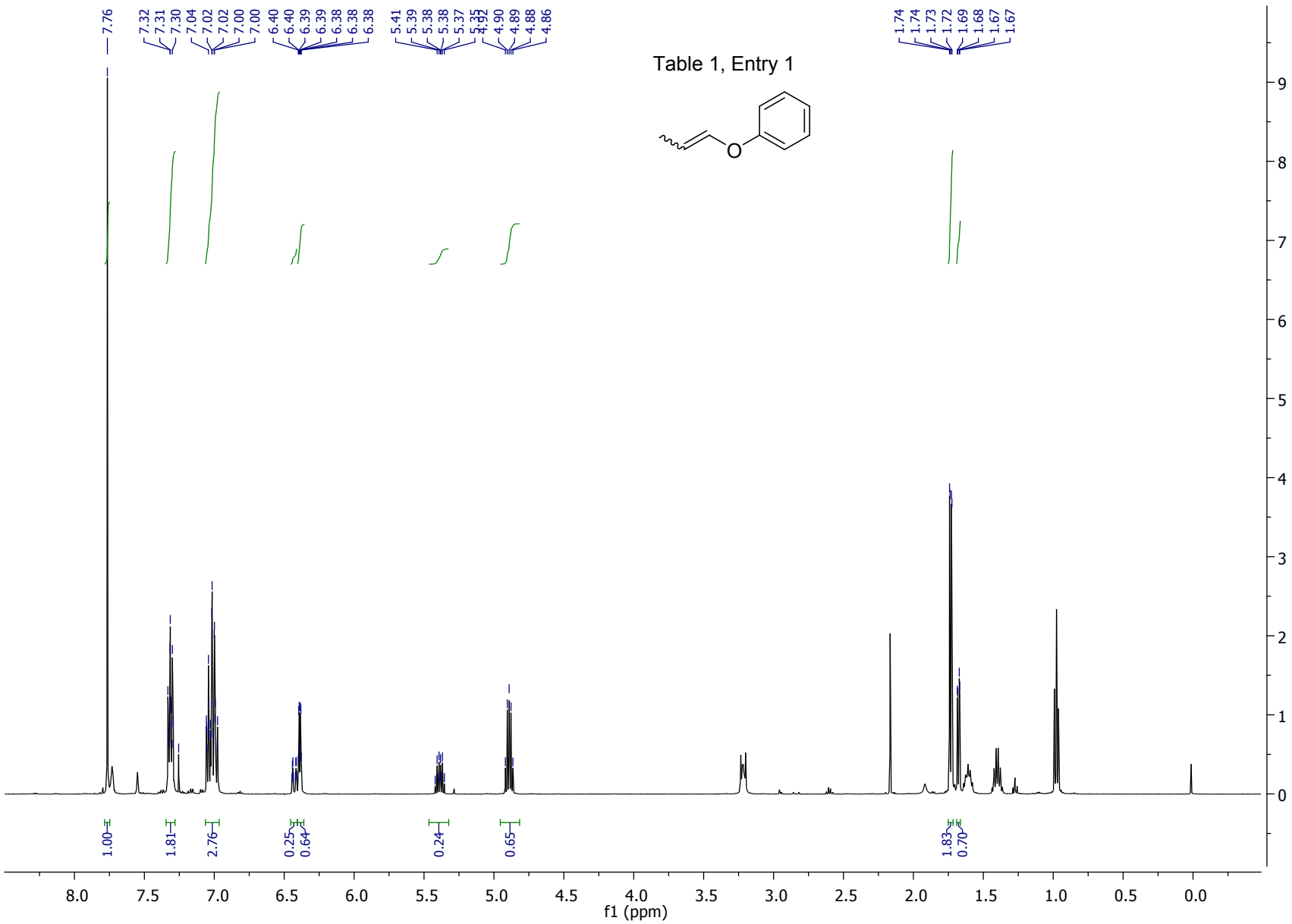
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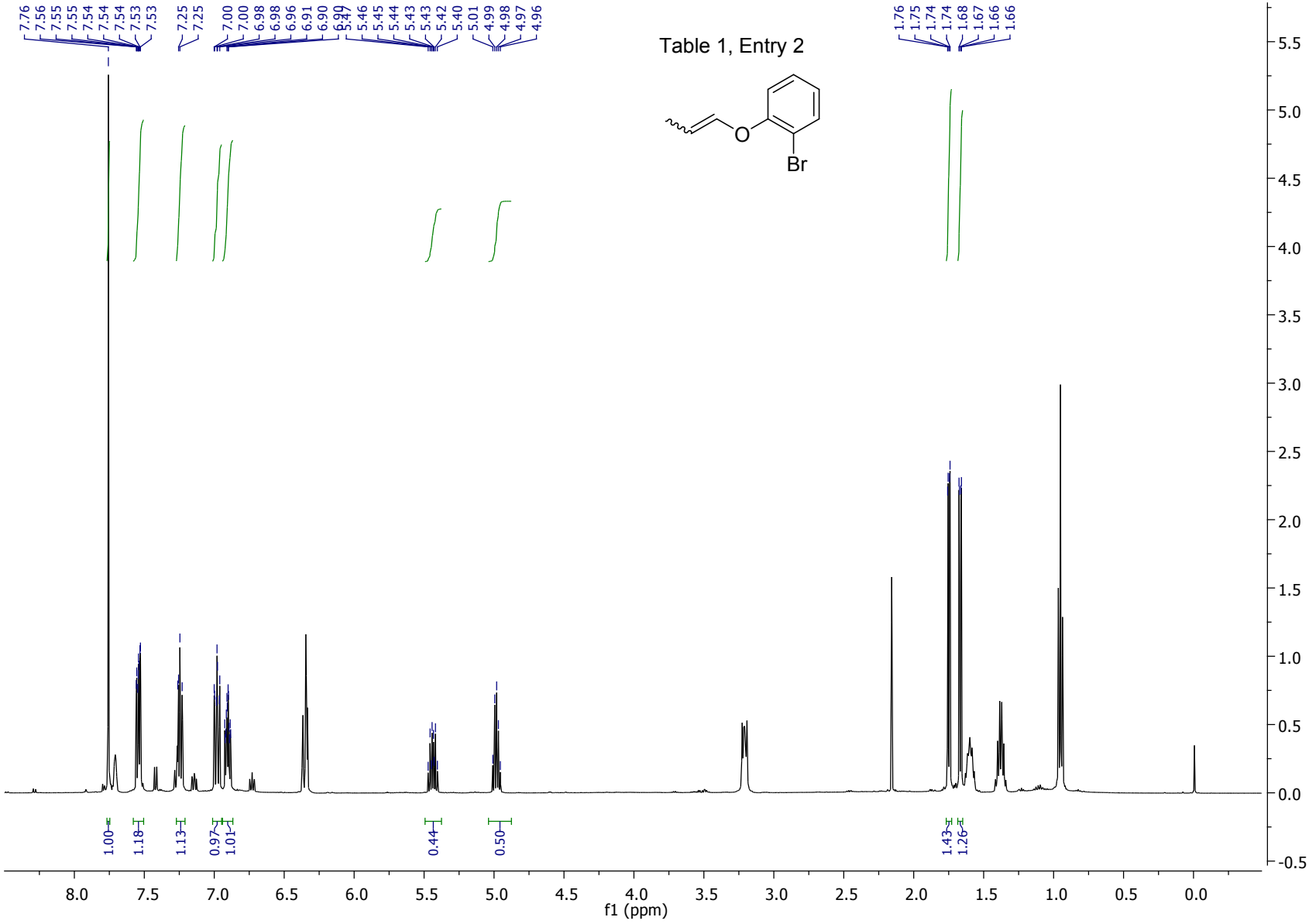
7.31
7.30
7.04
7.02
7.02
7.00
7.00
6.40
6.40
6.39
6.39
6.38
6.38
6.38
5.41
5.39
5.38
5.38
5.37
4.92
4.90
4.89
4.88
4.86
1.74
1.74
1.73
1.72
1.69
1.68
1.67
1.67
1.00
1.81
2.76
0.25
0.64
0.24
0.65
1.83
0.70
f1 (ppm)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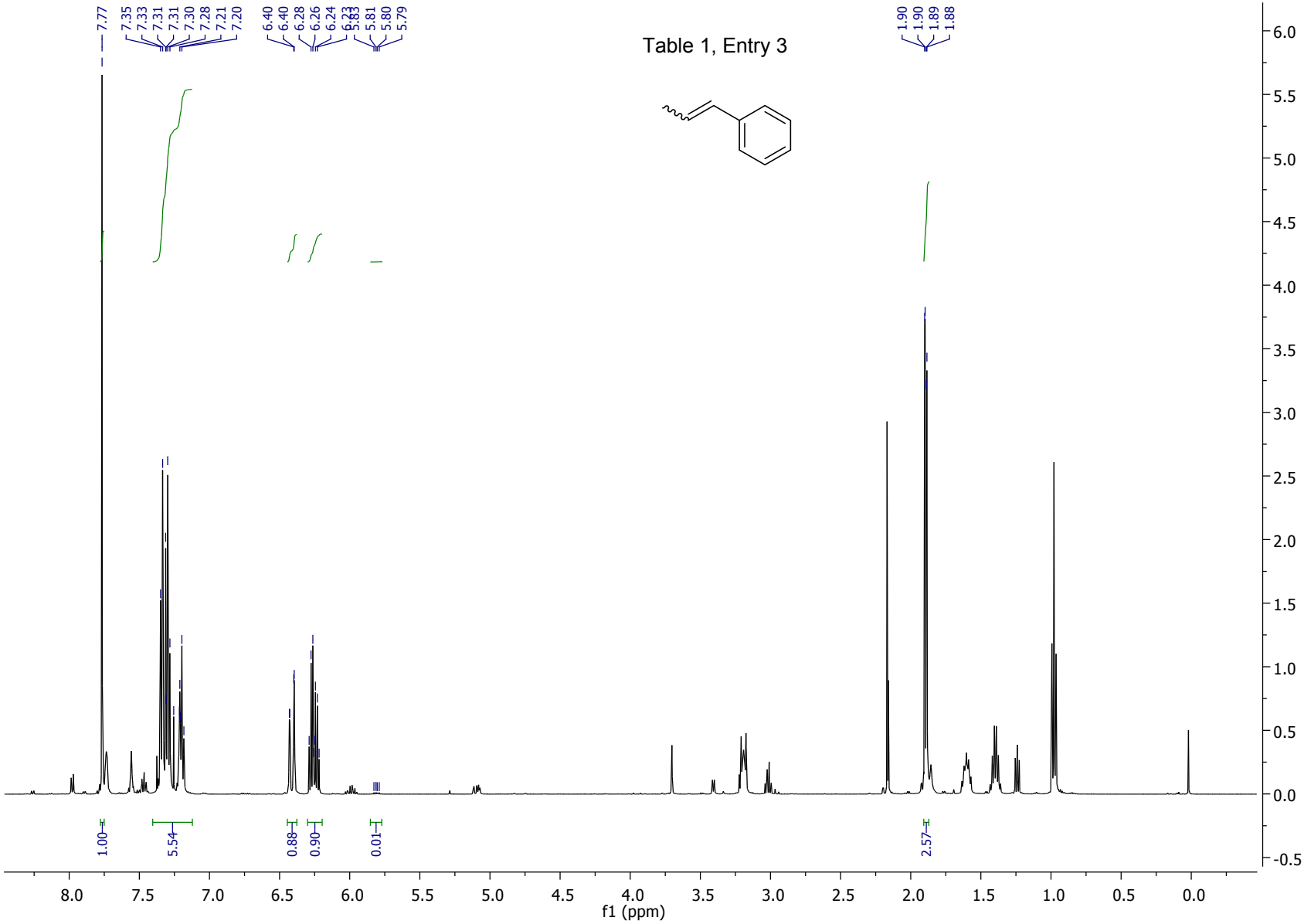
Br
f1 (ppm)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7.20
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6.26
6.24
5.81
5.80
5.79
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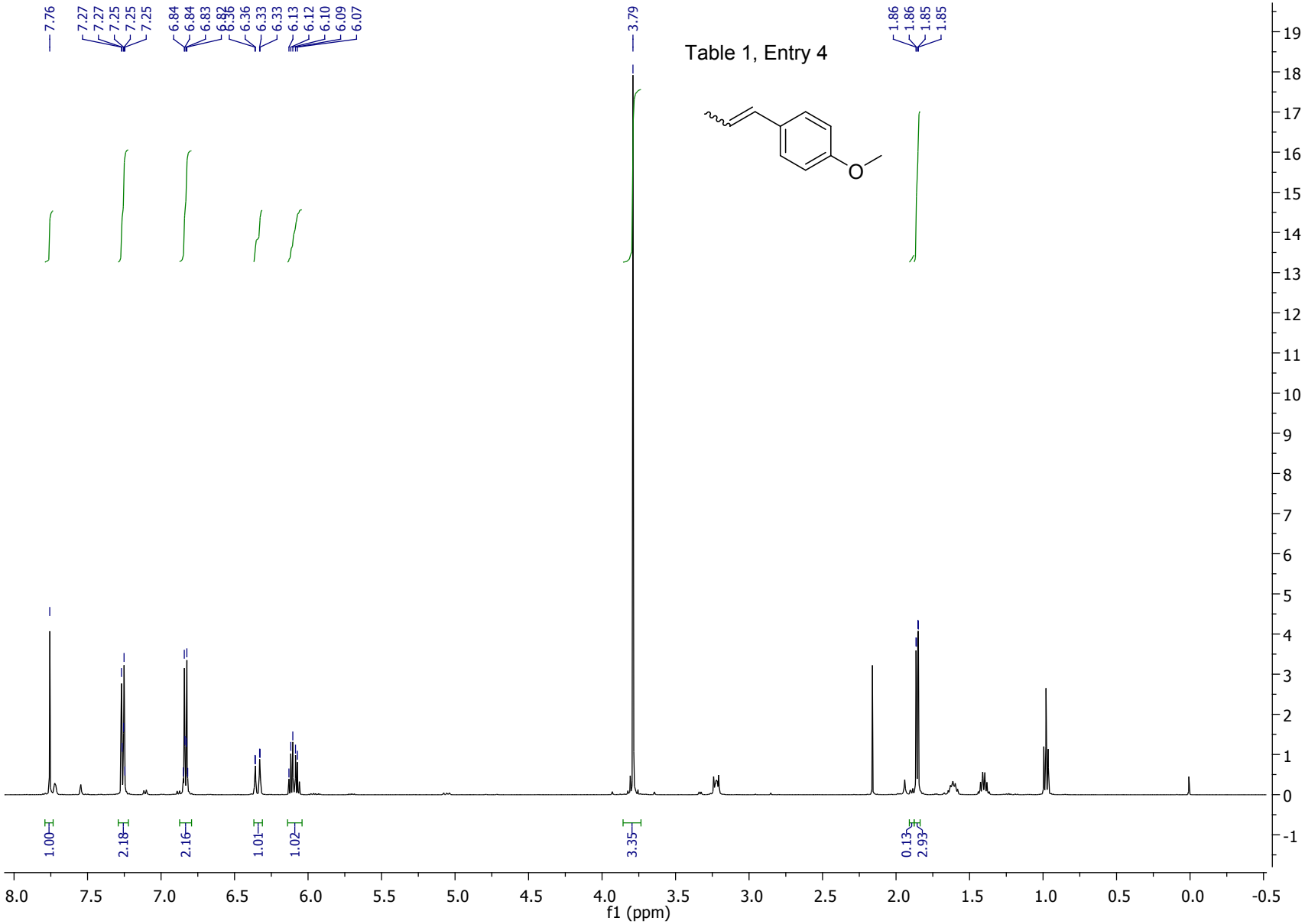
f1 (ppm)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7.27
7.27
7.25
7.25
7.25
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6.84
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6.36
6.36
6.33
6.33
6.13
6.12
6.10
6.09
6.07
3.79
1.86
1.86
1.85
1.85
1.00
2.18
2.16
1.01
1.02
3.35
0.13
2.93
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
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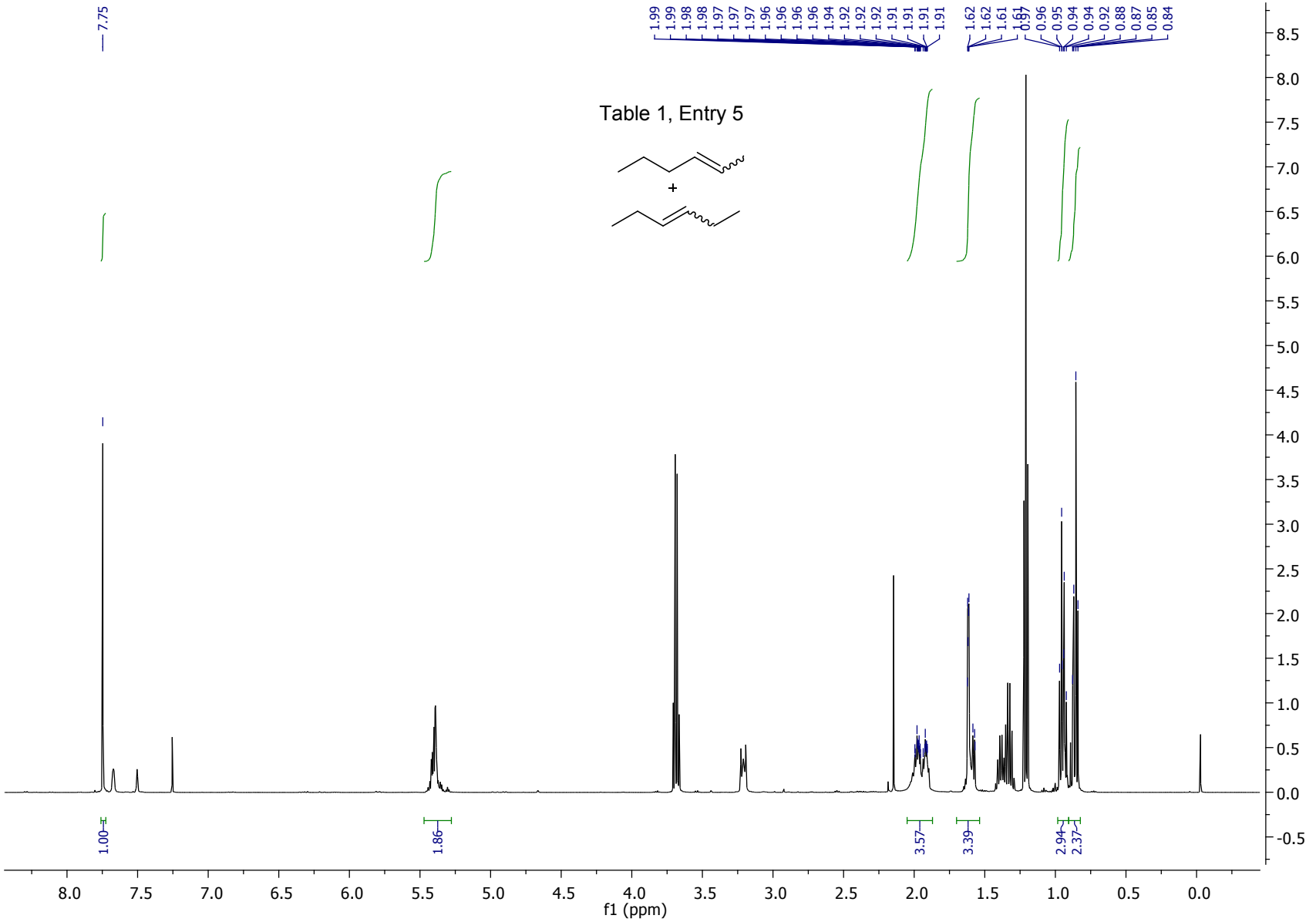
0.5
0.0
-0.5
f1 (ppm)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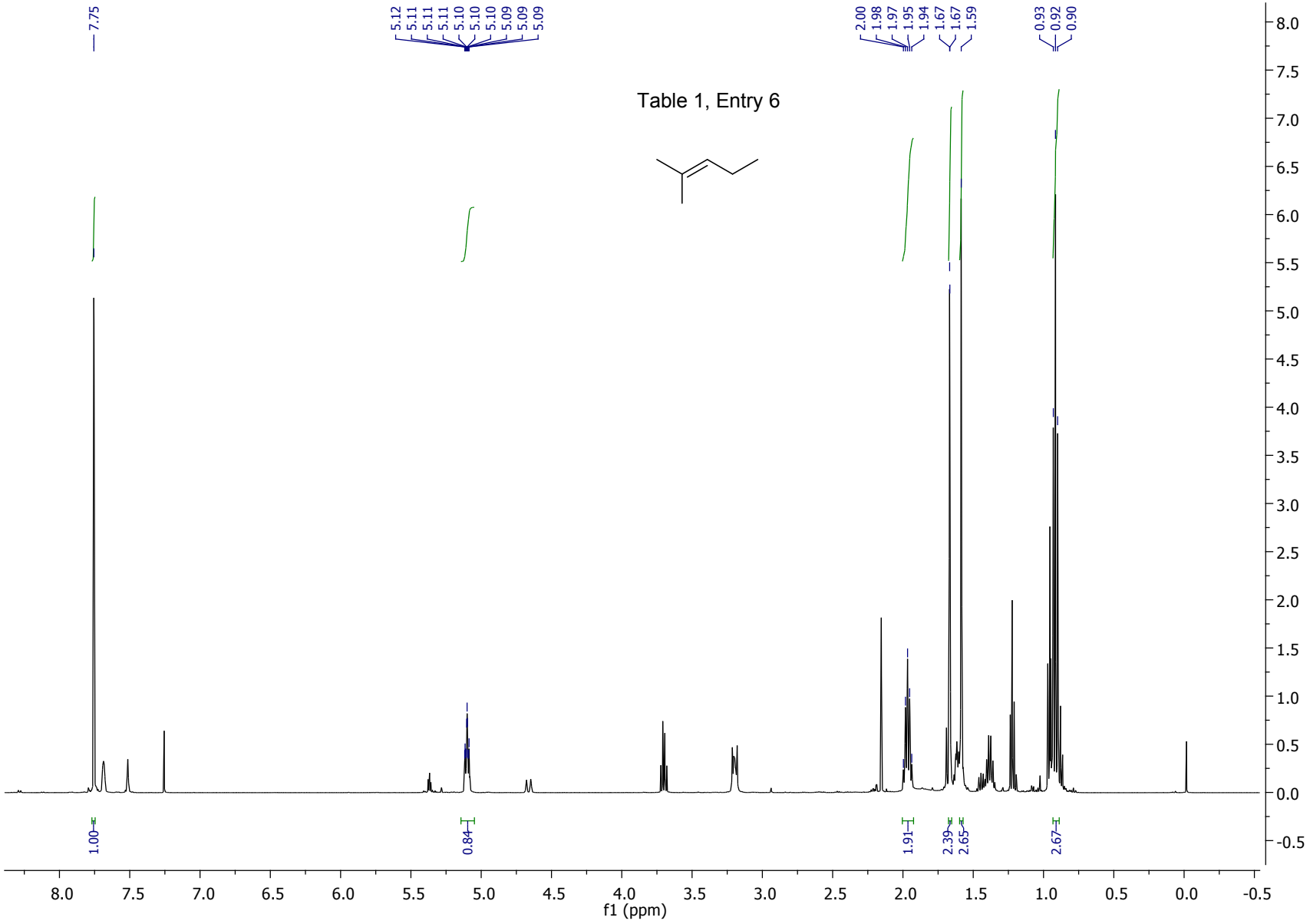
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5.09
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1.98
1.97
1.95
1.94
1.67
1.67
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1.00
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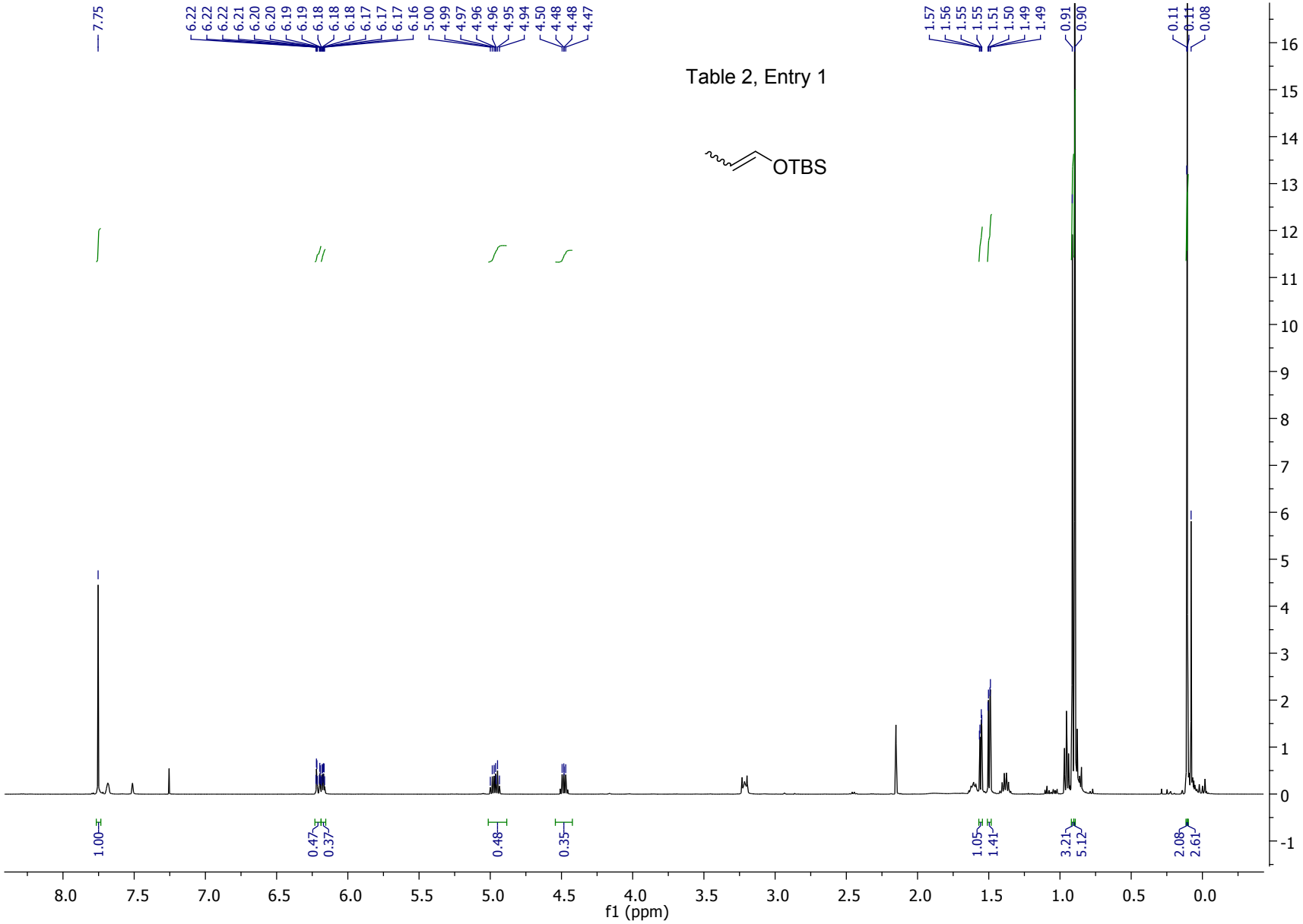
2.39
2.65
2.67
f1 (ppm)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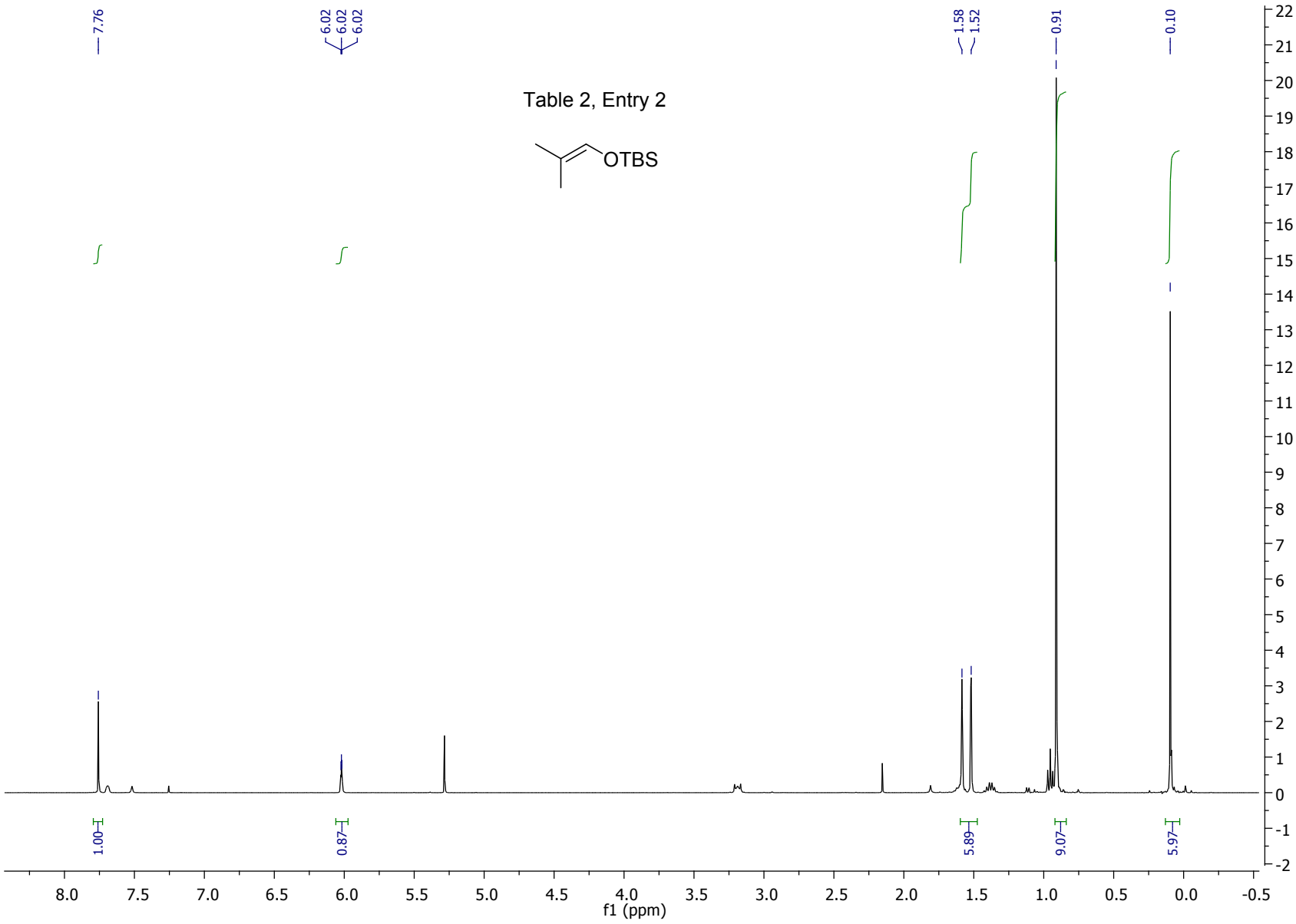
f1 (ppm)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6.02
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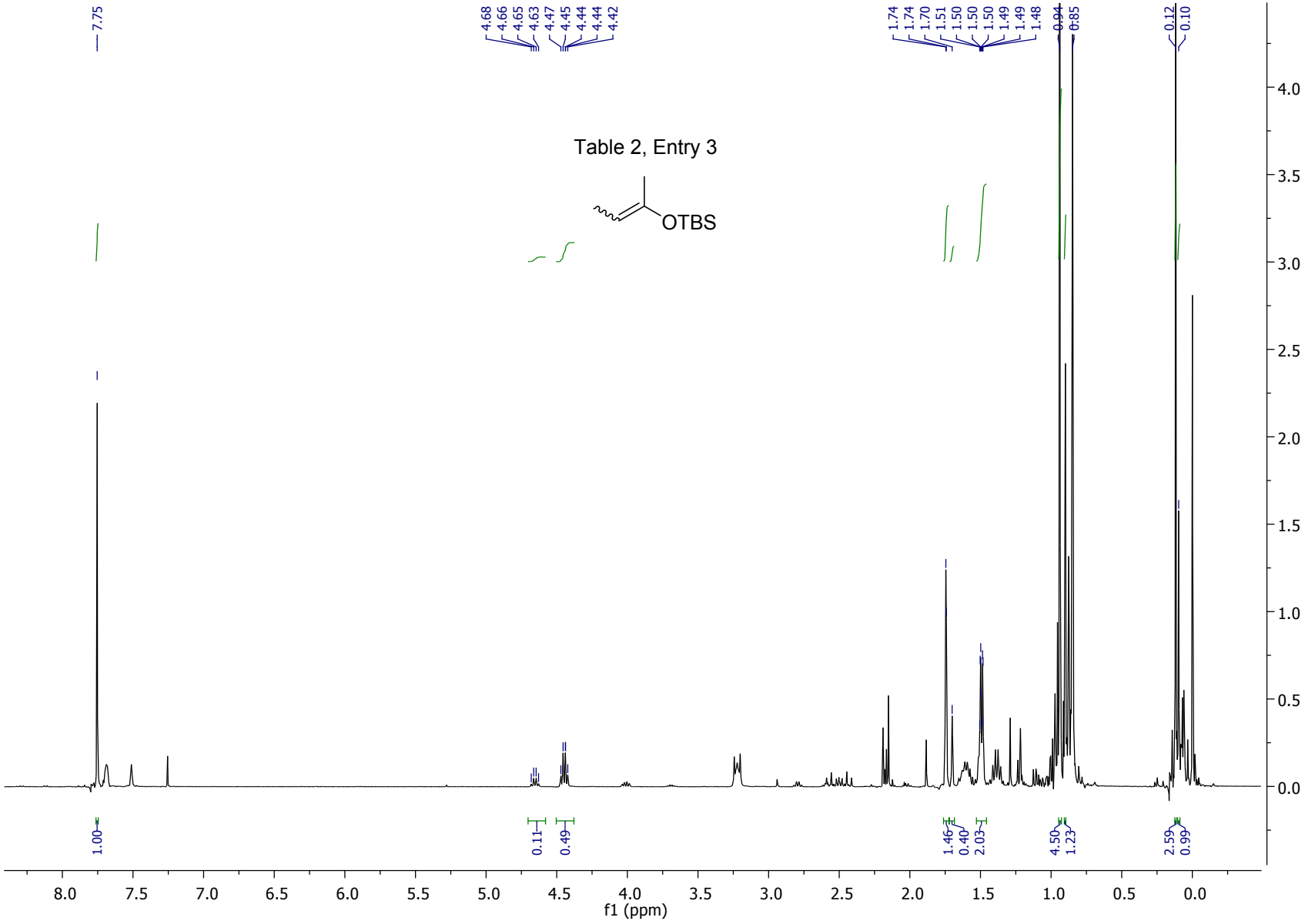
5.97
f1 (ppm)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1.74
1.70
1.51
1.50
1.50
1.50
1.49
1.49
1.48
0.94
0.85
0.12
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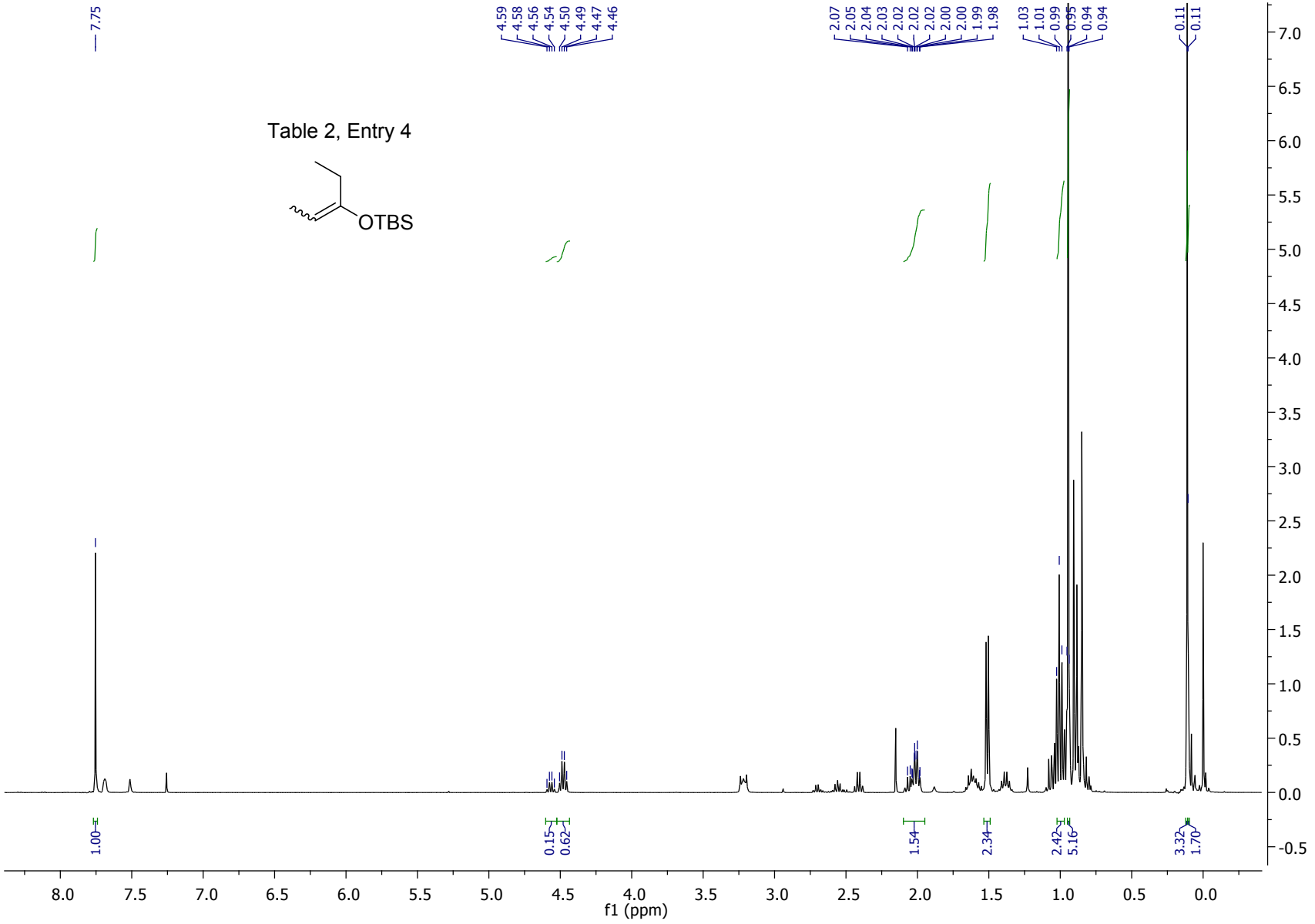
f1 (ppm)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2.04
2.03
2.02
2.02
2.02
2.00
2.00
1.99
1.98
1.03
1.01
0.99
0.95
0.94
0.94
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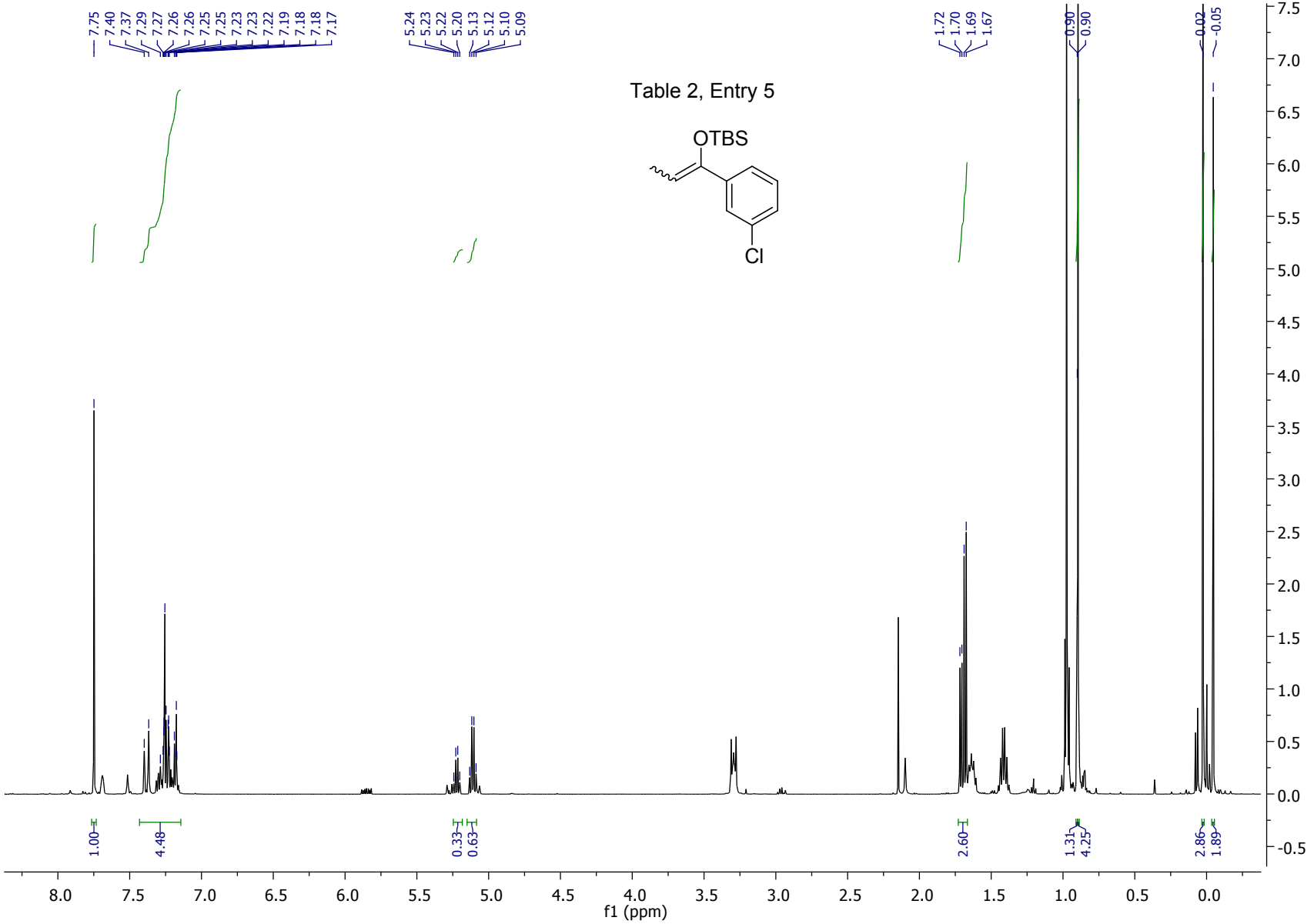
f1 (ppm)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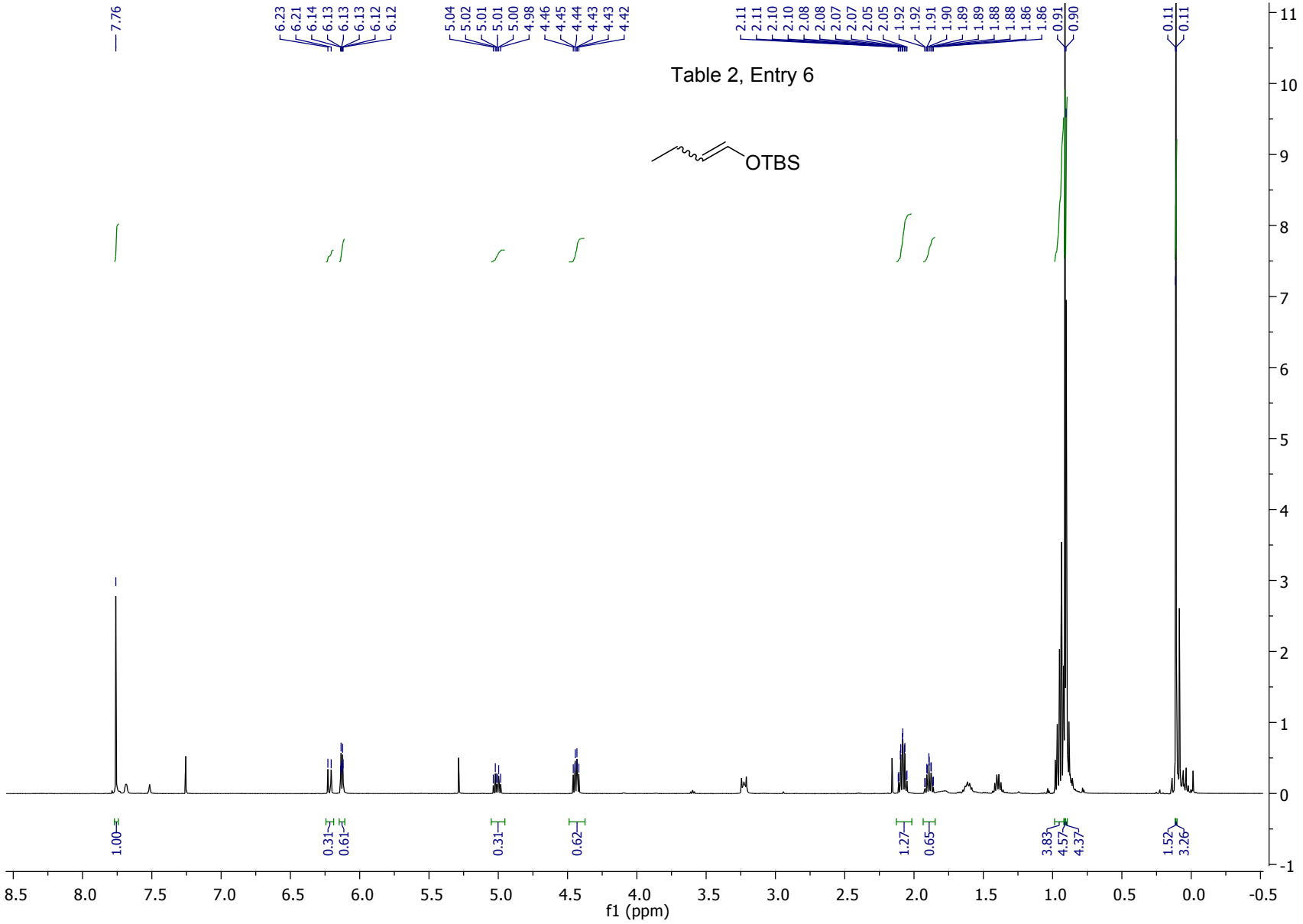
OTBS
Cl
f1 (ppm)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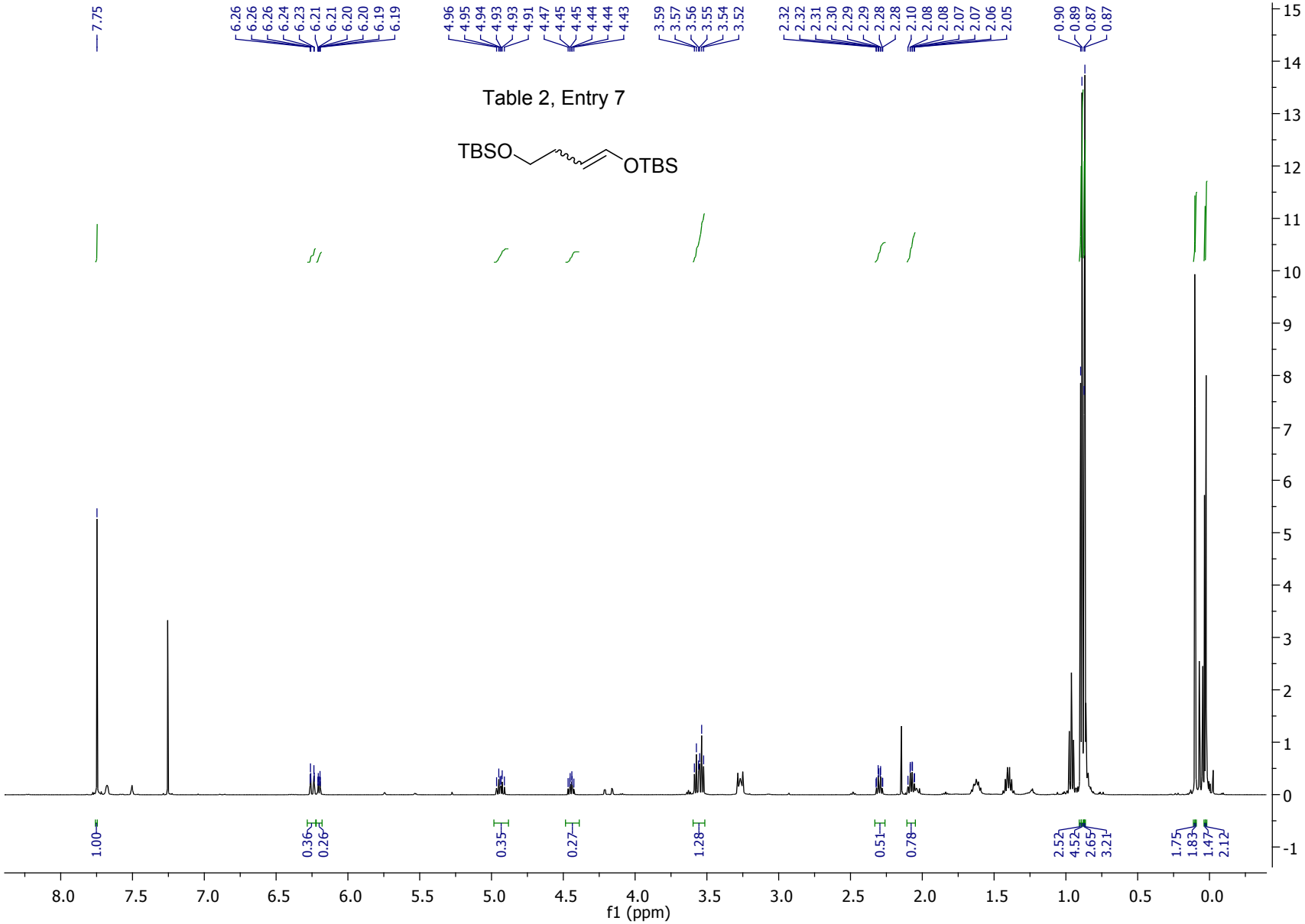
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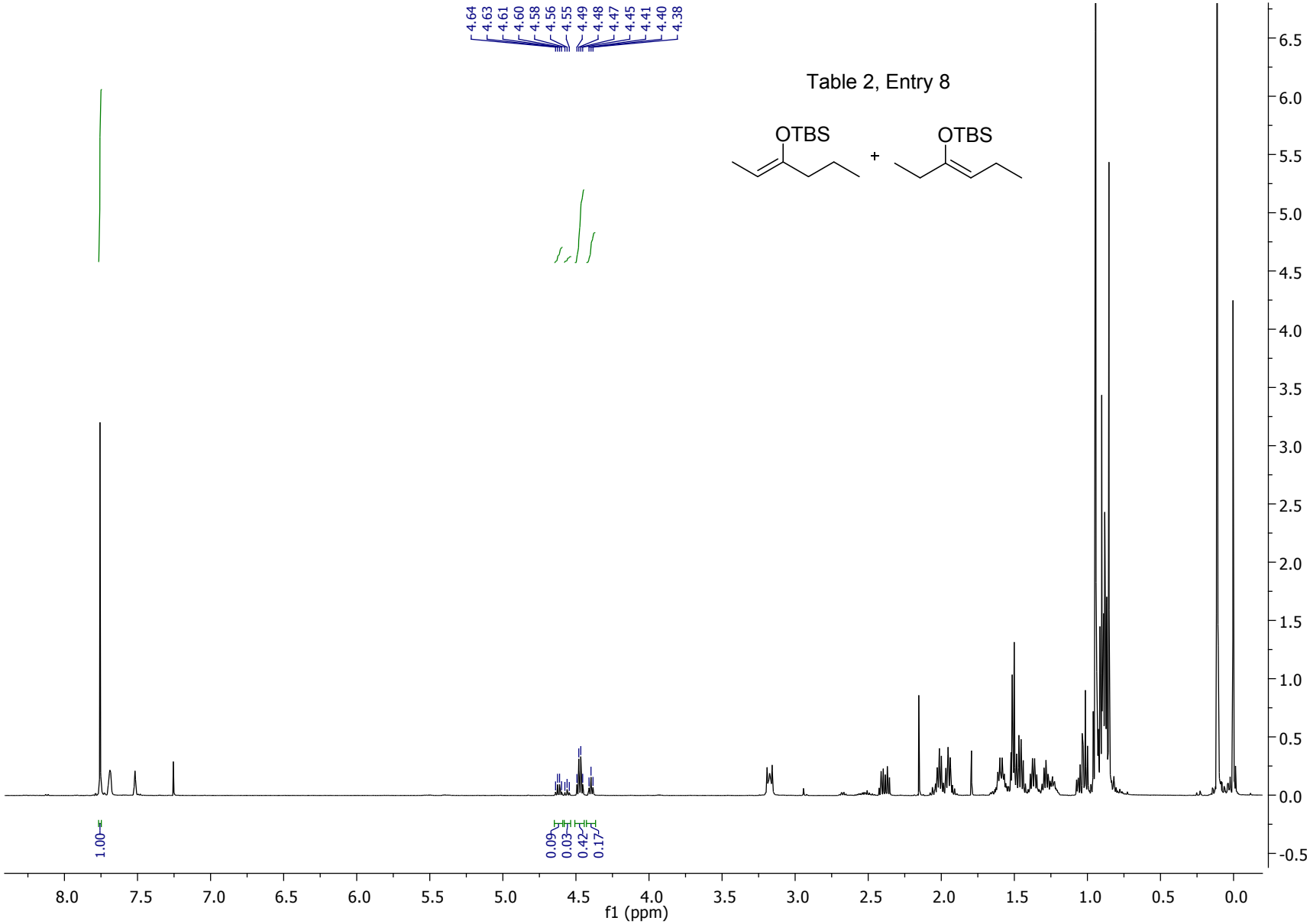
OTBS
f1 (ppm)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4.58
4.56
4.55
4.49
4.48
4.47
4.45
4.41
4.40
4.38
Table 2, Entry 8
OTBS
+
OTBS
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0.09
0.03
0.42
0.17
f1 (ppm)

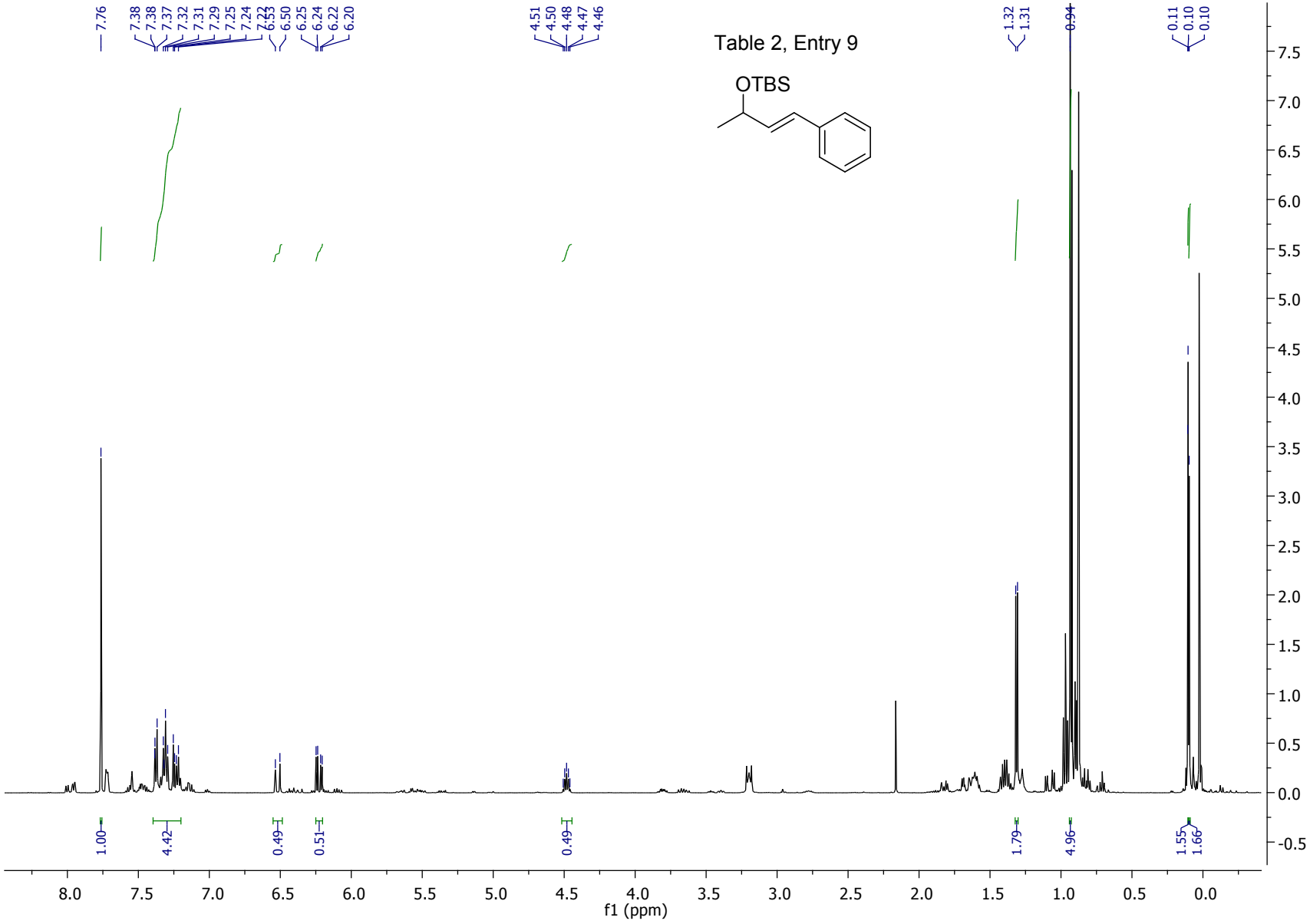


Table 2, Entry 9
OTBS
7.76
7.38
7.38
7.37
7.32
7.31
7.29
7.25
7.24
6.53
6.50
6.25
6.24
6.22
6.20
4.51
4.50
4.48
4.47
4.46
1.32
1.31
0.94
0.11
0.10
0.10
1.00
4.42
0.49
0.51
0.49
1.79
4.96
1.55
1.66
f1 (ppm)

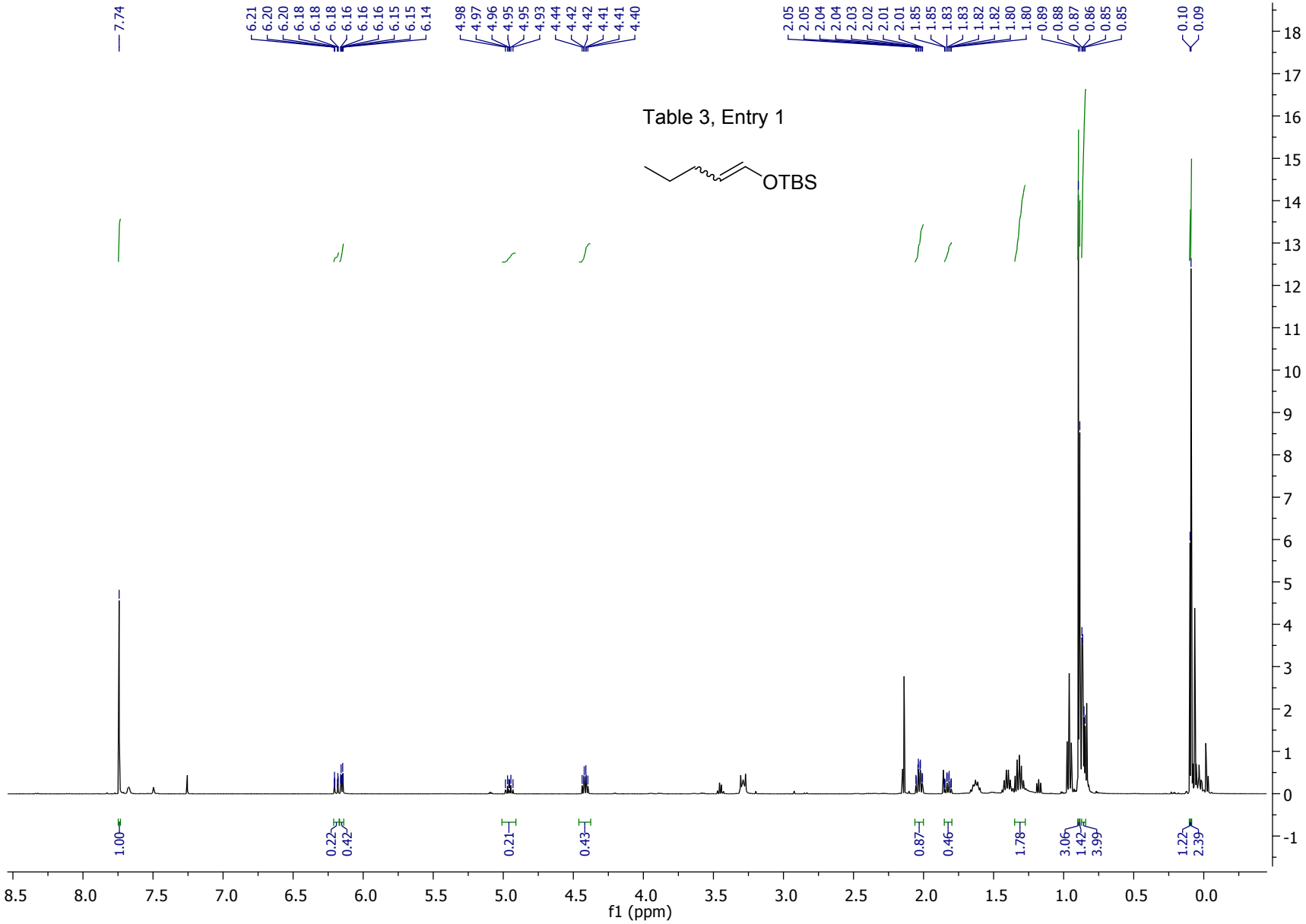


Table 3, Entry 1
OTBS
f1 (ppm)

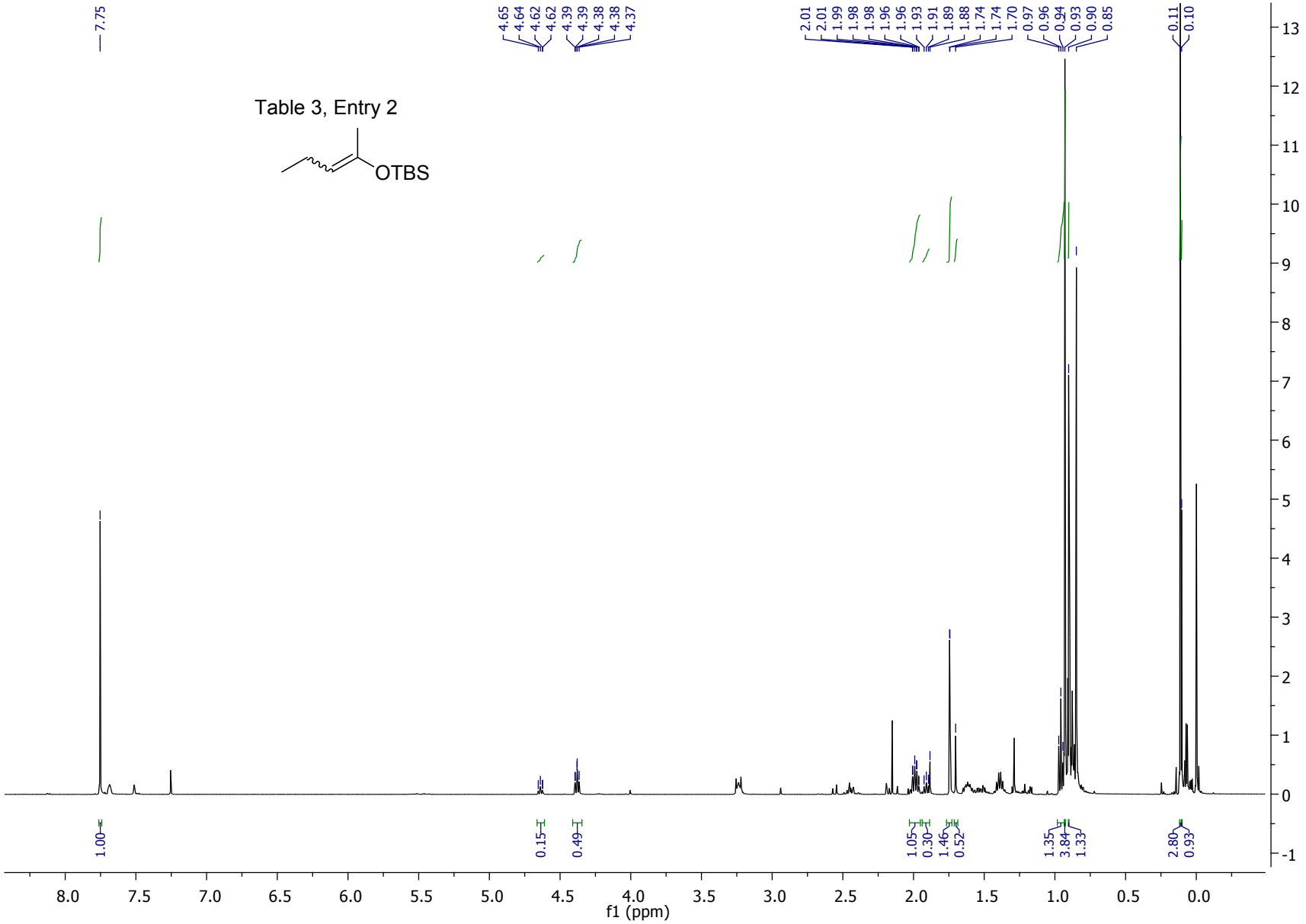


Table 3, Entry 2
OTBS
7.75
4.65
4.64
4.62
4.62
4.39
4.39
4.38
4.38
4.37
2.01
2.01
1.99
1.98
1.98
1.96
1.96
1.93
1.91
1.89
1.88
1.74
1.74
1.70
0.97
0.96
0.94
0.93
0.90
0.85
0.11
0.10
1.00
0.15
0.49
1.05
0.30
1.46
0.52
1.35
3.84
1.33
2.80
0.93
f1 (ppm)

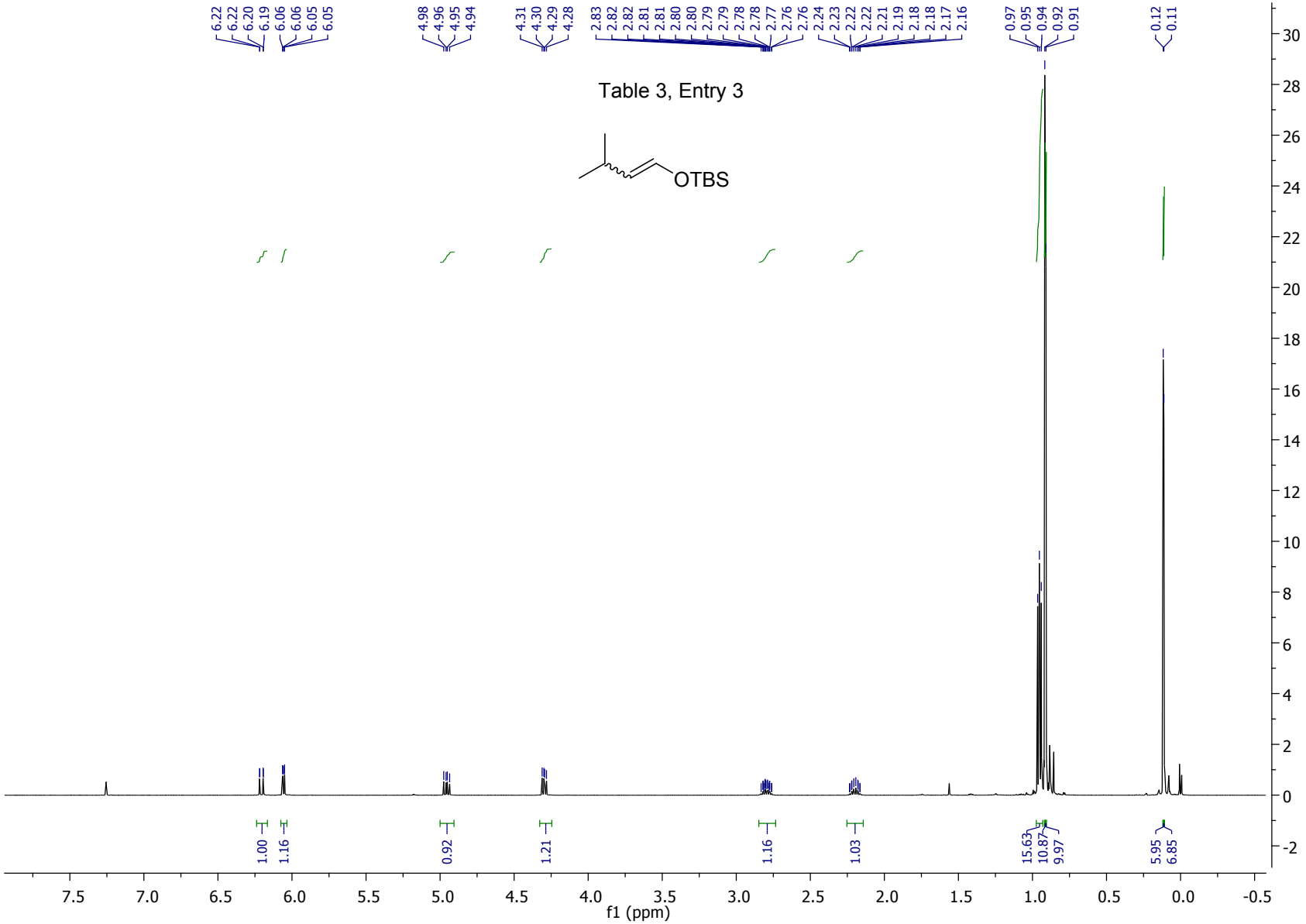
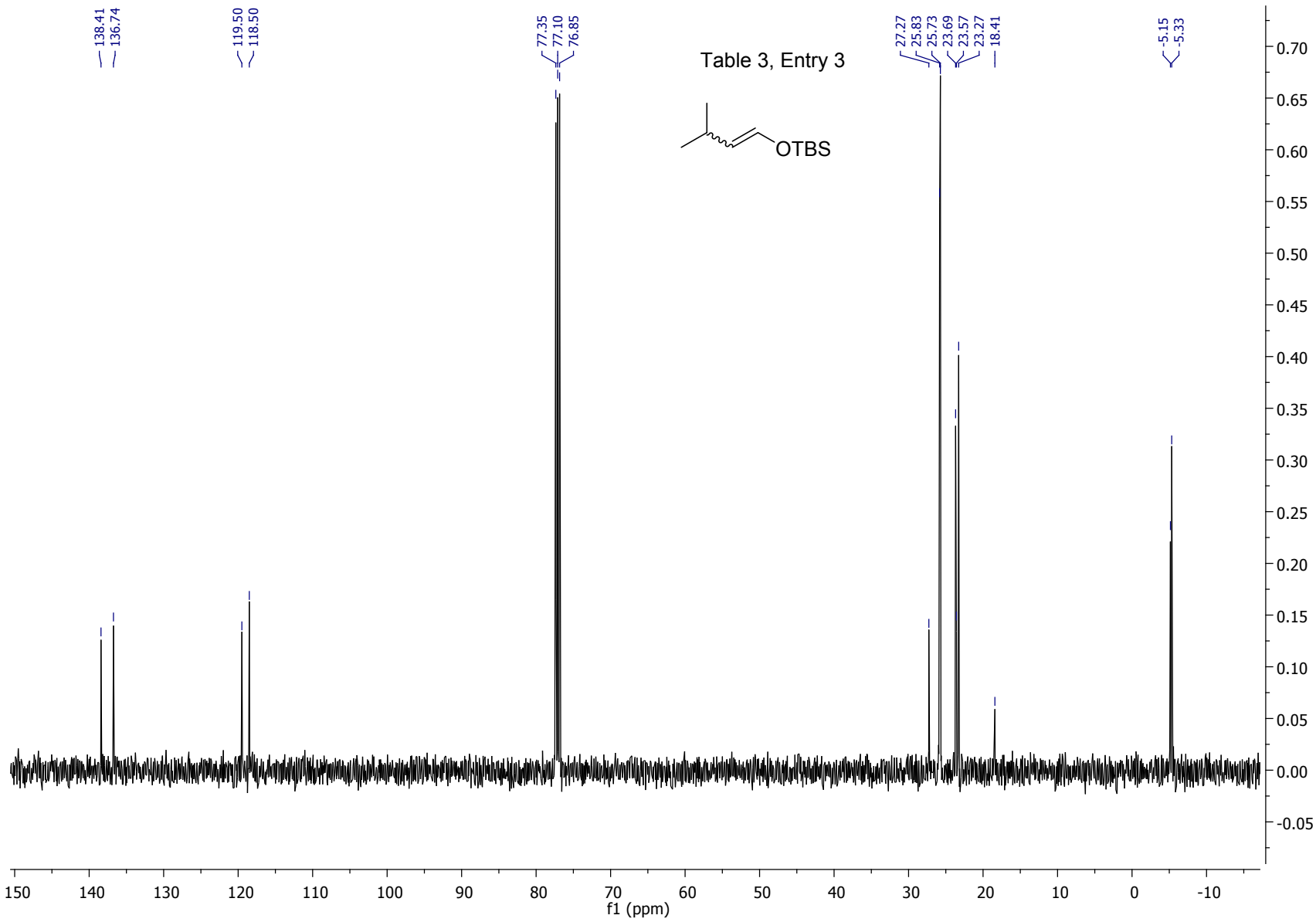


Table 3, Entry 3
OTBS
6.22 6.22 6.20 6.19 6.06 6.06 6.05 6.05
4.98 4.96 4.95 4.94
4.31 4.30 4.29 4.28
2.83 2.82 2.82 2.81 2.81 2.80 2.80 2.79 2.79 2.78 2.78 2.77 2.76 2.76
2.24 2.23 2.22 2.22 2.21 2.19 2.18 2.18 2.17 2.16
0.97 0.95 0.94 0.92 0.91
0.12 0.11
1.00 1.16 0.92 1.21 1.16 1.03 15.63 10.87 9.97 5.95 6.85
f1 (ppm)


138.41
136.74
119.50
118.50
77.35
77.10
76.85
27.27
25.83
25.73
23.69
23.57
23.27
18.41
-5.15
-5.33
Table 3, Entry 3
OTBS
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

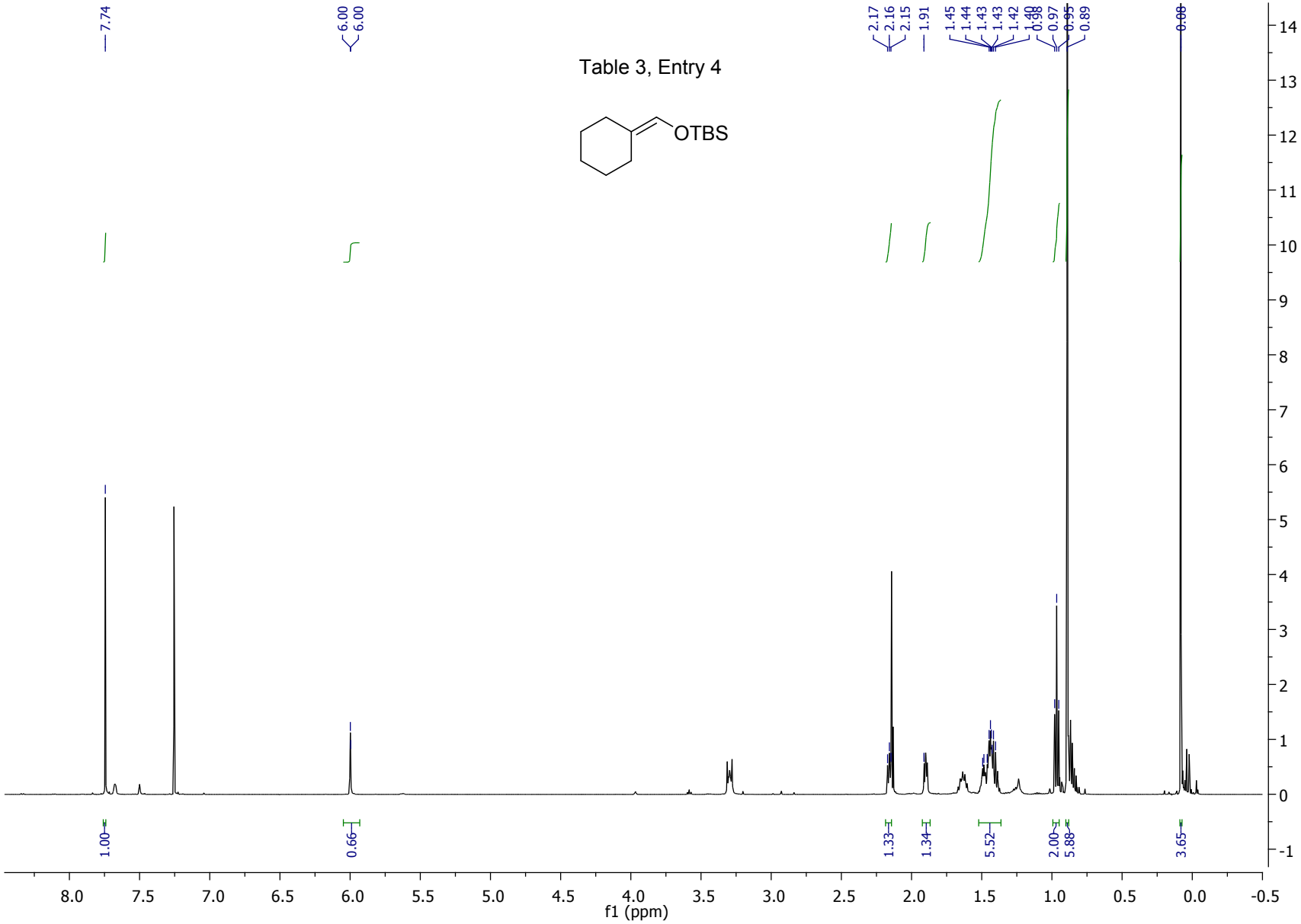


Table 3, Entry 4
OTBS
7.74
6.00
6.00
2.17
2.16
2.15
1.91
1.45
1.44
1.43
1.43
1.42
1.40
0.98
0.97
0.95
0.89
0.00
1.00
0.66
1.33
1.34
5.52
2.00
5.88
3.65
f1 (ppm)

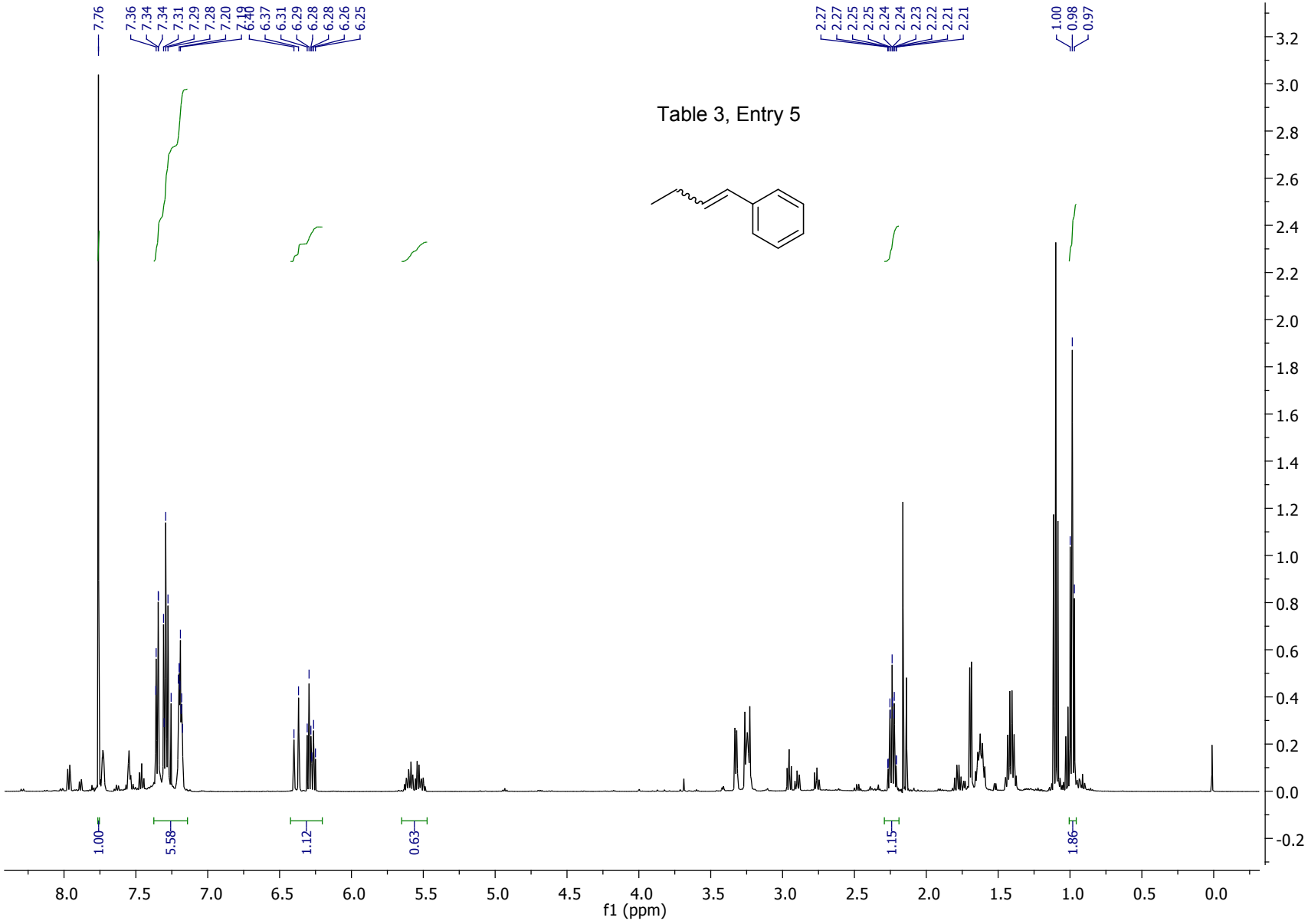


Table 3, Entry 5
7.76
7.36
7.34
7.34
7.31
7.29
7.28
7.20
7.19
6.37
6.31
6.29
6.28
6.28
6.26
6.25
2.27
2.27
2.25
2.25
2.24
2.24
2.23
2.22
2.21
2.21
1.00
0.98
0.97
1.00
5.58
1.12
0.63
1.15
1.86
f1 (ppm)

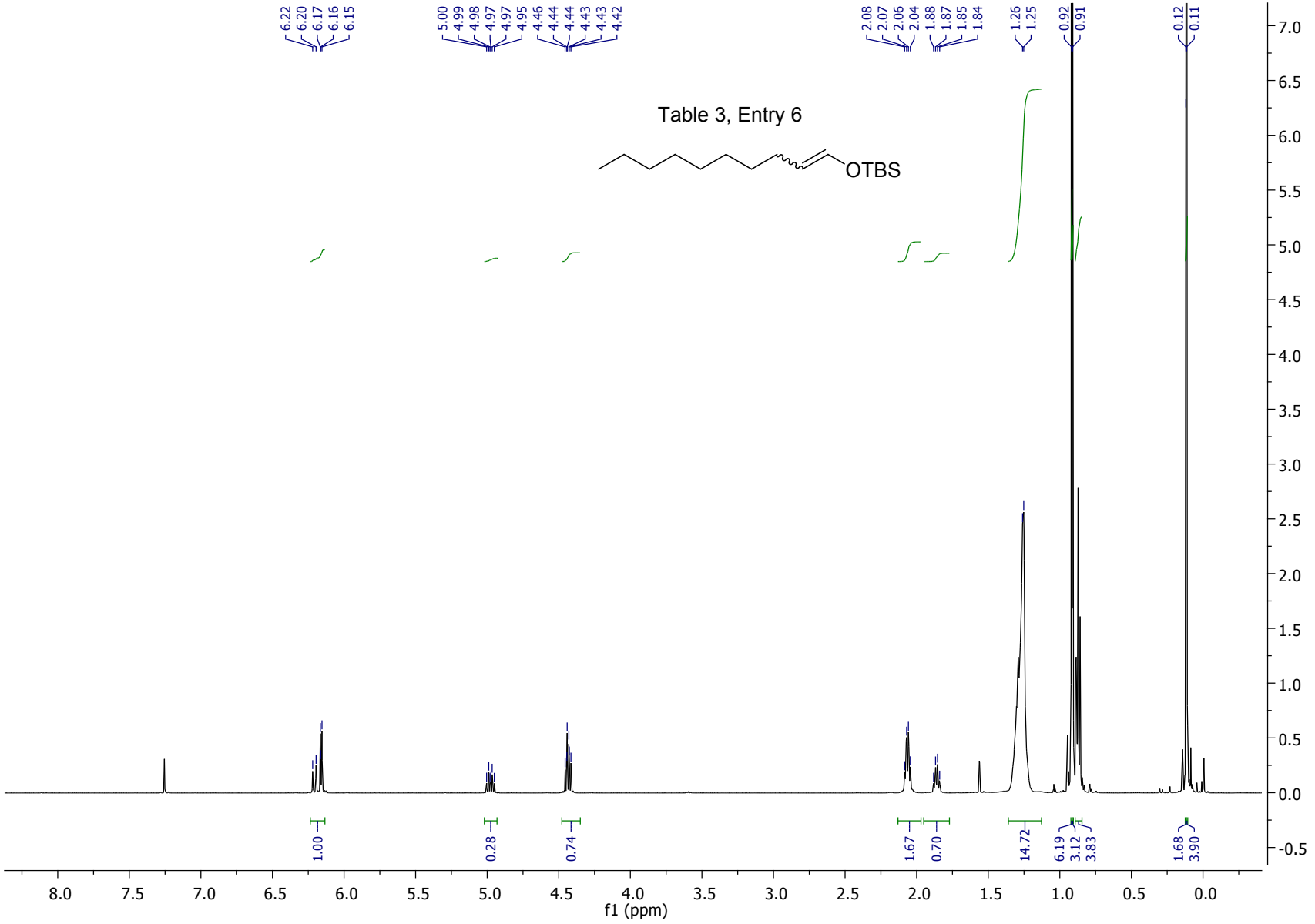
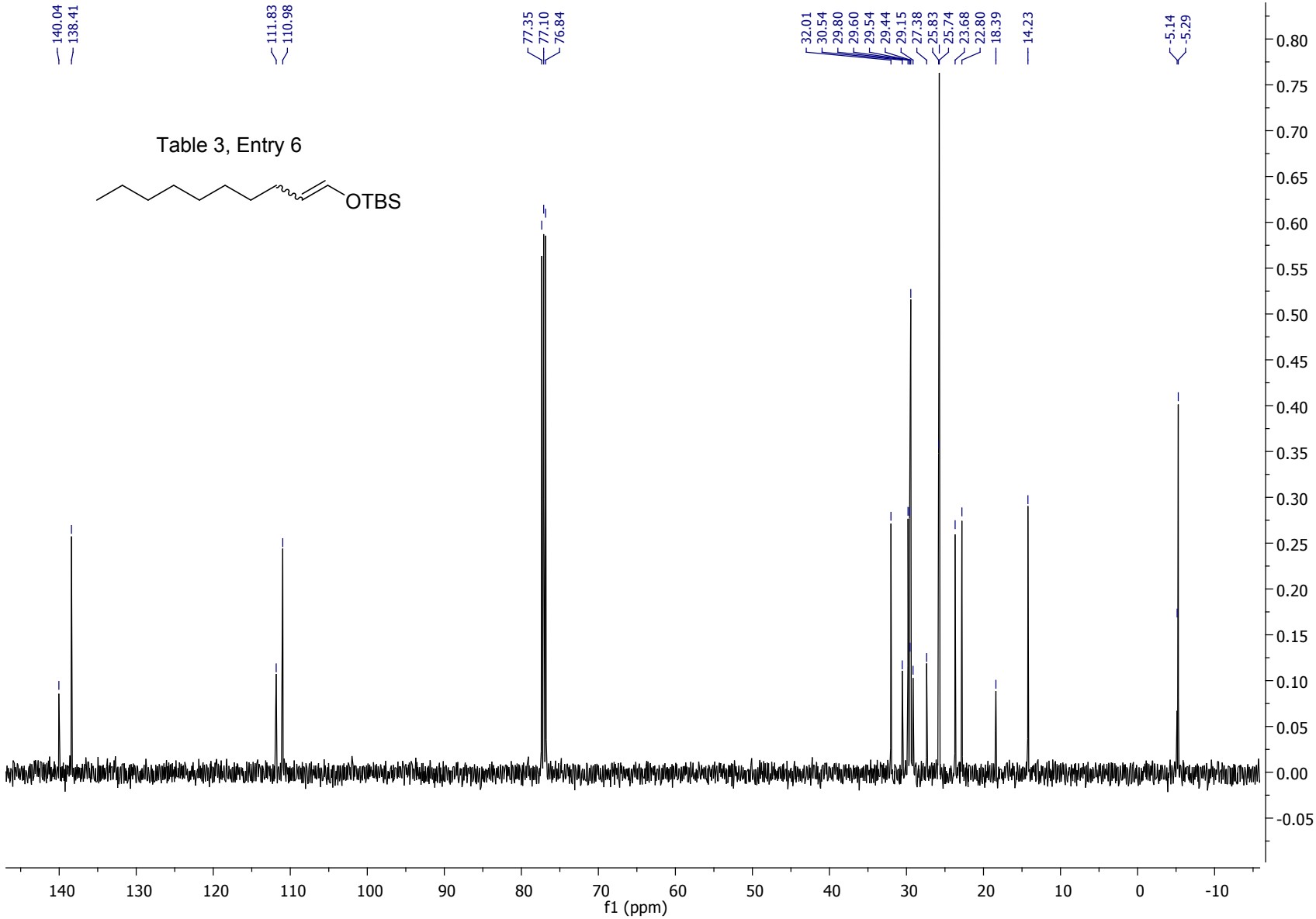
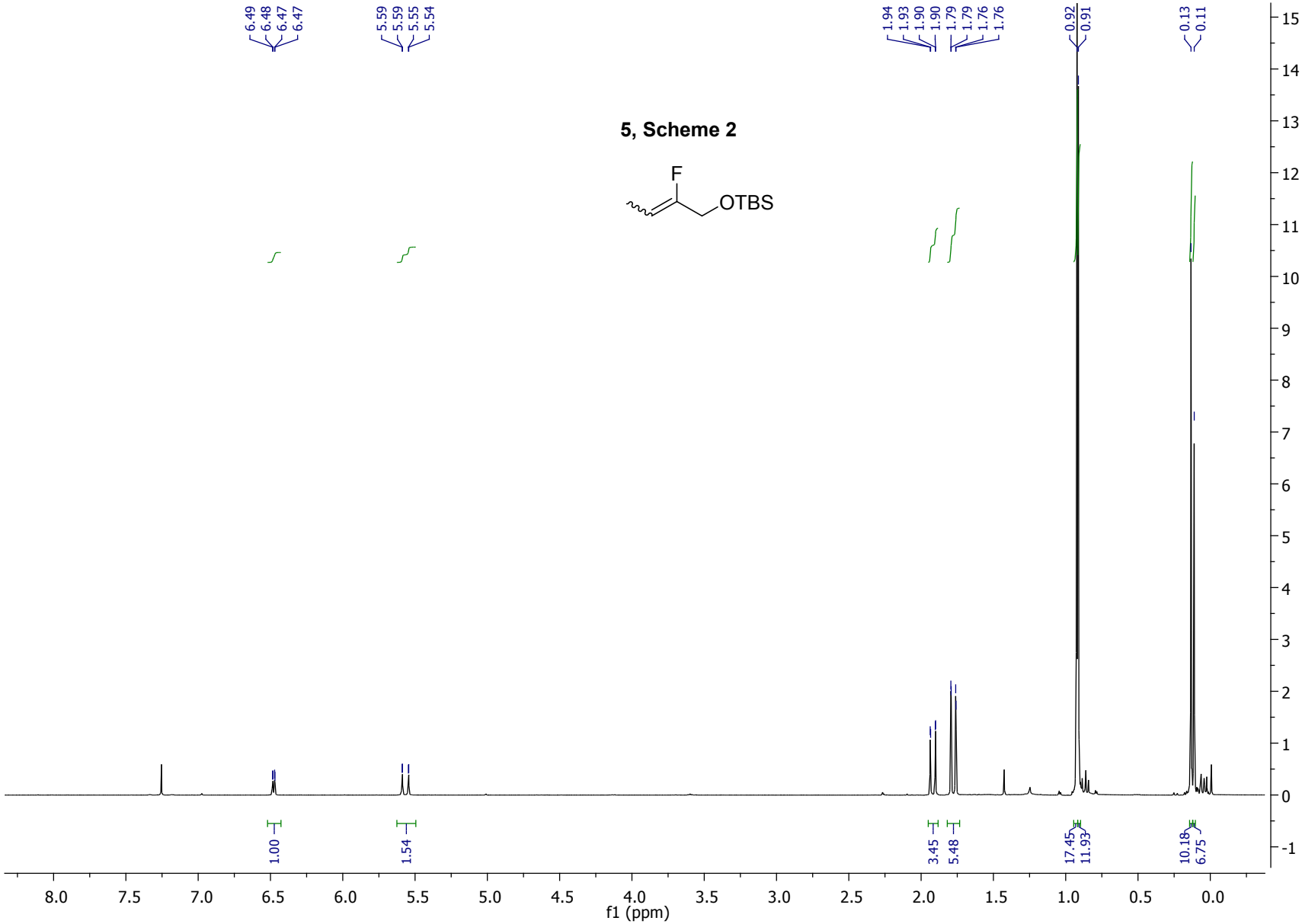
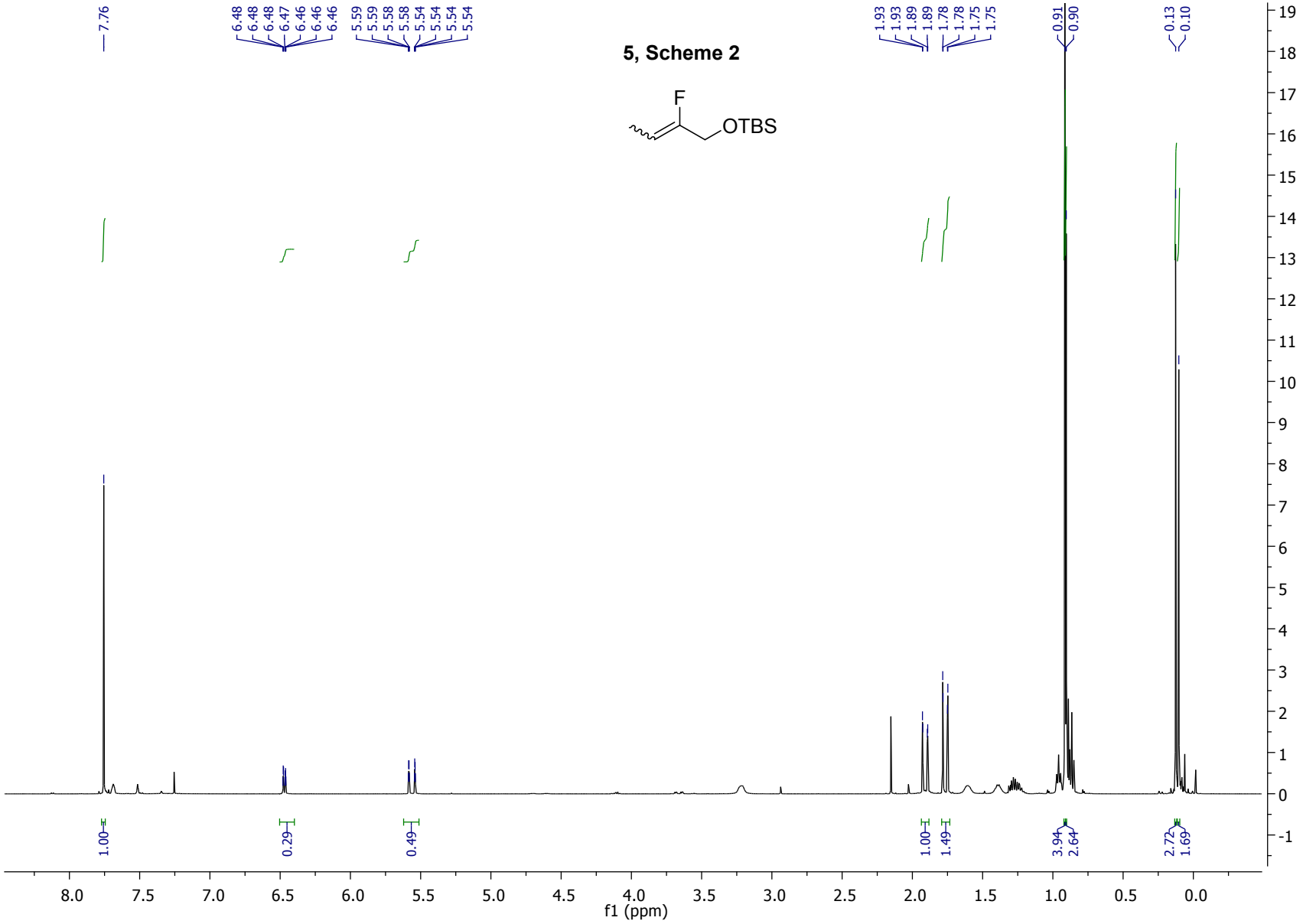
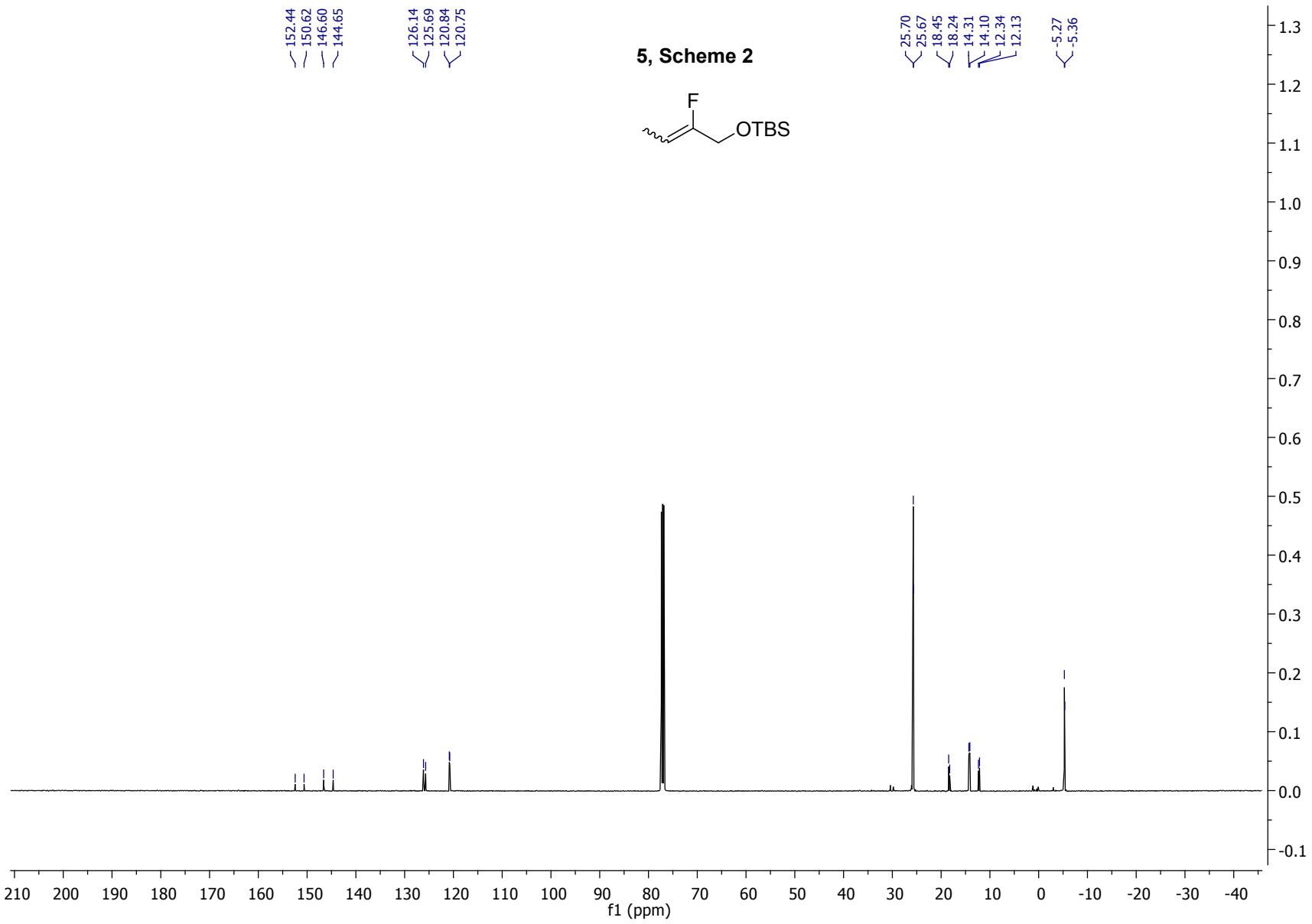


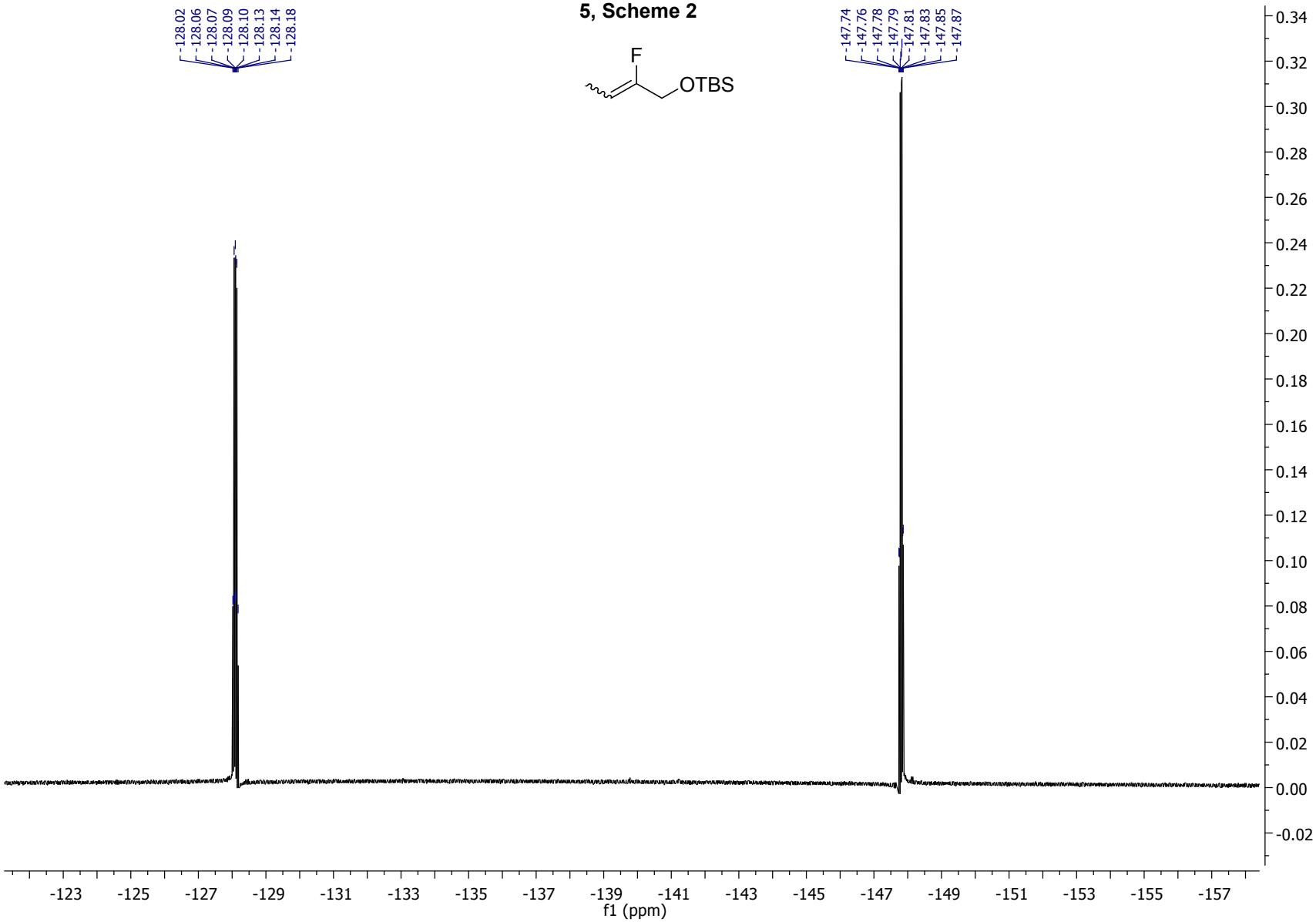
Table 3, Entry 6
OTBS
6.22
6.20
6.17
6.16
6.15
5.00
4.99
4.98
4.97
4.97
4.95
4.46
4.44
4.44
4.43
4.43
4.42
2.08
2.07
2.06
2.04
1.88
1.87
1.85
1.84
1.26
1.25
0.92
0.91
0.12
0.11
1.00
0.28
0.74
1.67
0.70
14.72
6.19
3.12
3.83
1.68
3.90
f1 (ppm)


140.04
138.41
111.83
110.98
77.35
77.10
76.84
32.01
30.54
29.80
29.60
29.54
29.44
29.15
27.38
25.83
25.74
23.68
22.80
18.39
14.23
-5.14
-5.29
Table 3, Entry 6
OTBS
f1 (ppm)

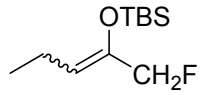

6.49
6.48
6.47
6.47
5.59
5.59
5.55
5.54
1.94
1.93
1.90
1.90
1.79
1.79
1.76
1.76
0.92
0.91
0.13
0.11
5, Scheme 2
F
OTBS
1.00
1.54
3.45
5.48
17.45
11.93
10.18
6.75
f1 (ppm)


5, Scheme 2
F
OTBS
7.76
6.48
6.48
6.48
6.47
6.46
6.46
6.46
5.59
5.59
5.58
5.58
5.54
5.54
5.54
5.54
1.93
1.93
1.89
1.89
1.78
1.78
1.75
1.75
0.91
0.90
0.13
0.10
1.00
0.29
0.49
1.00
1.49
3.94
2.64
2.72
1.69
f1 (ppm)

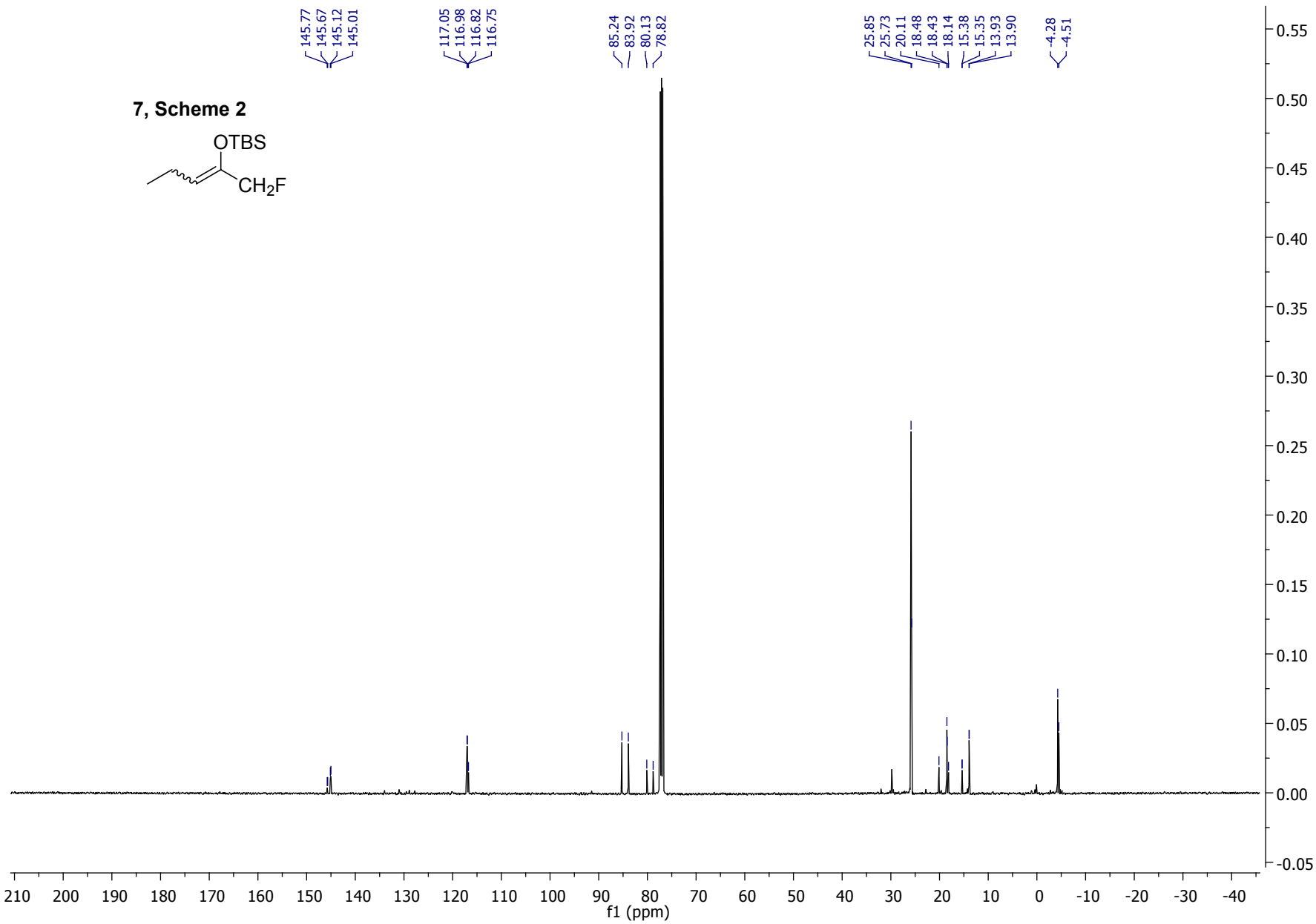

152.44
150.62
146.60
144.65
126.14
125.69
120.84
120.75
25.70
25.67
18.45
18.24
14.31
14.10
12.34
12.13
-5.27
-5.36
5, Scheme 2
F
OTBS
f1 (ppm)

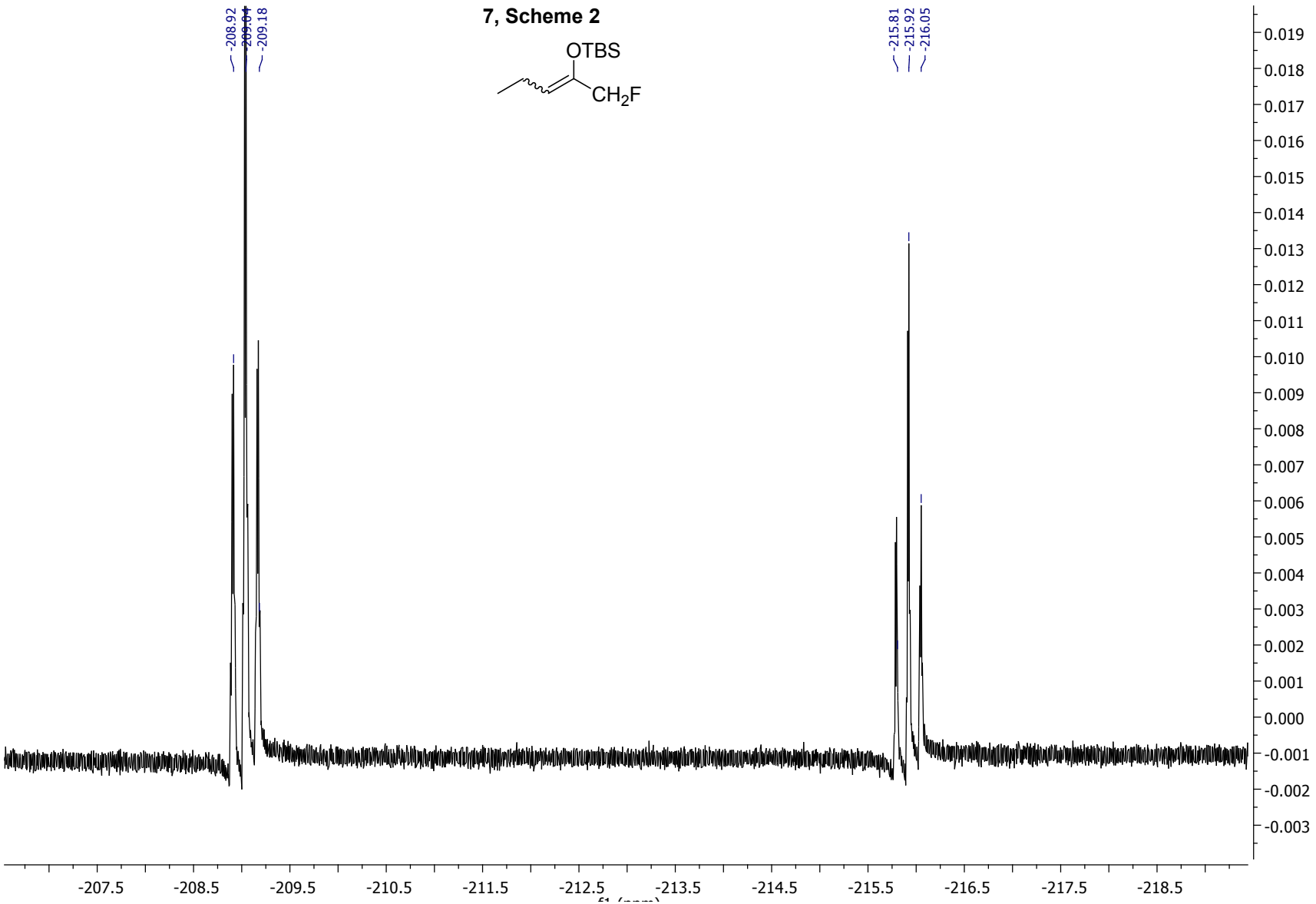

5, Scheme 2
F
OTBS
-128.02
-128.06
-128.07
-128.09
-128.10
-128.13
-128.14
-128.18
-147.74
-147.76
-147.78
-147.79
-147.81
-147.83
-147.85
-147.87
0.34
0.32
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-123
-125
-127
-129
-131
-133
-135
-137
-139
-141
-143
-145
-147
-149
-151
-153
-155
-157
f1 (ppm)

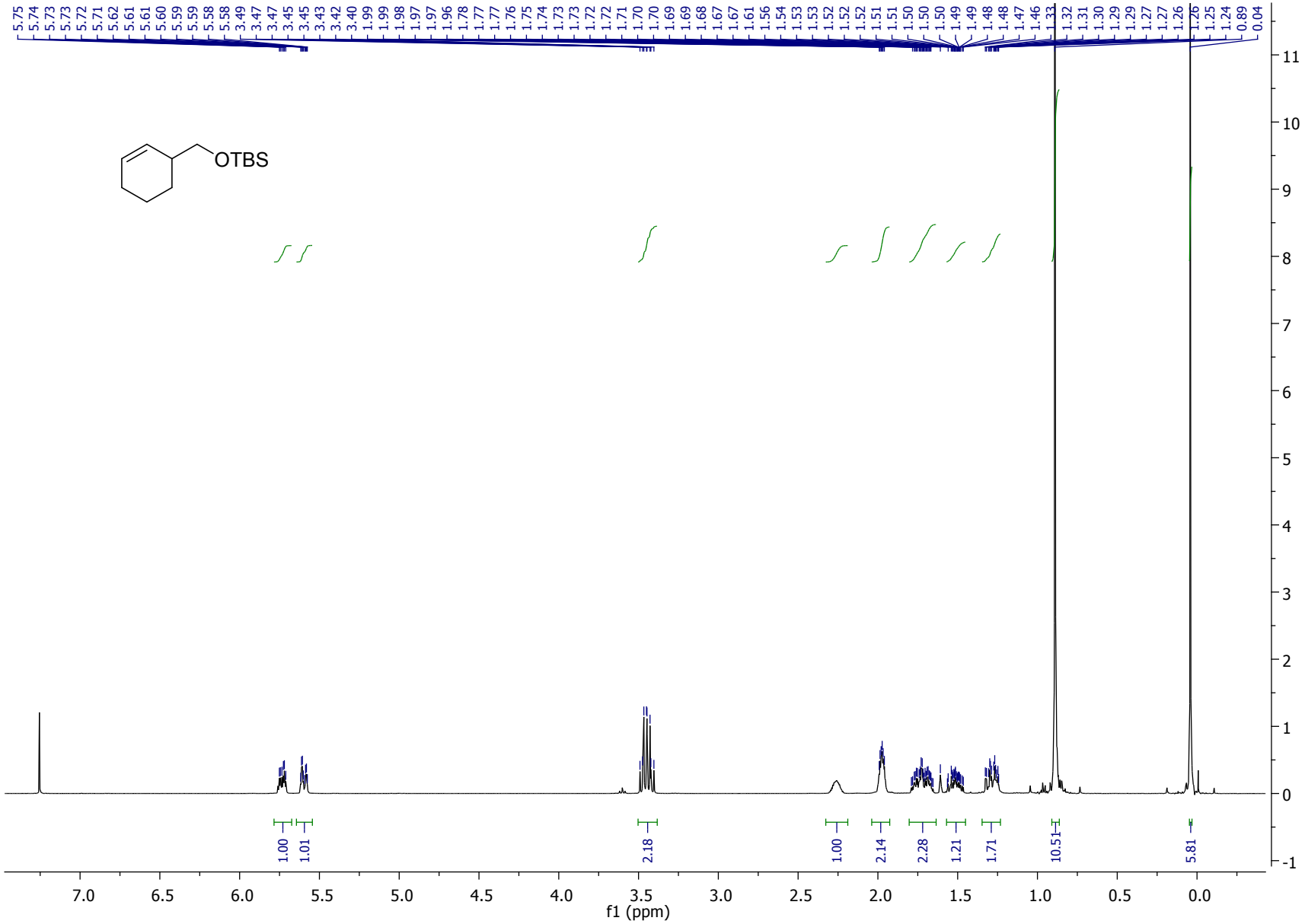
7, Scheme 2

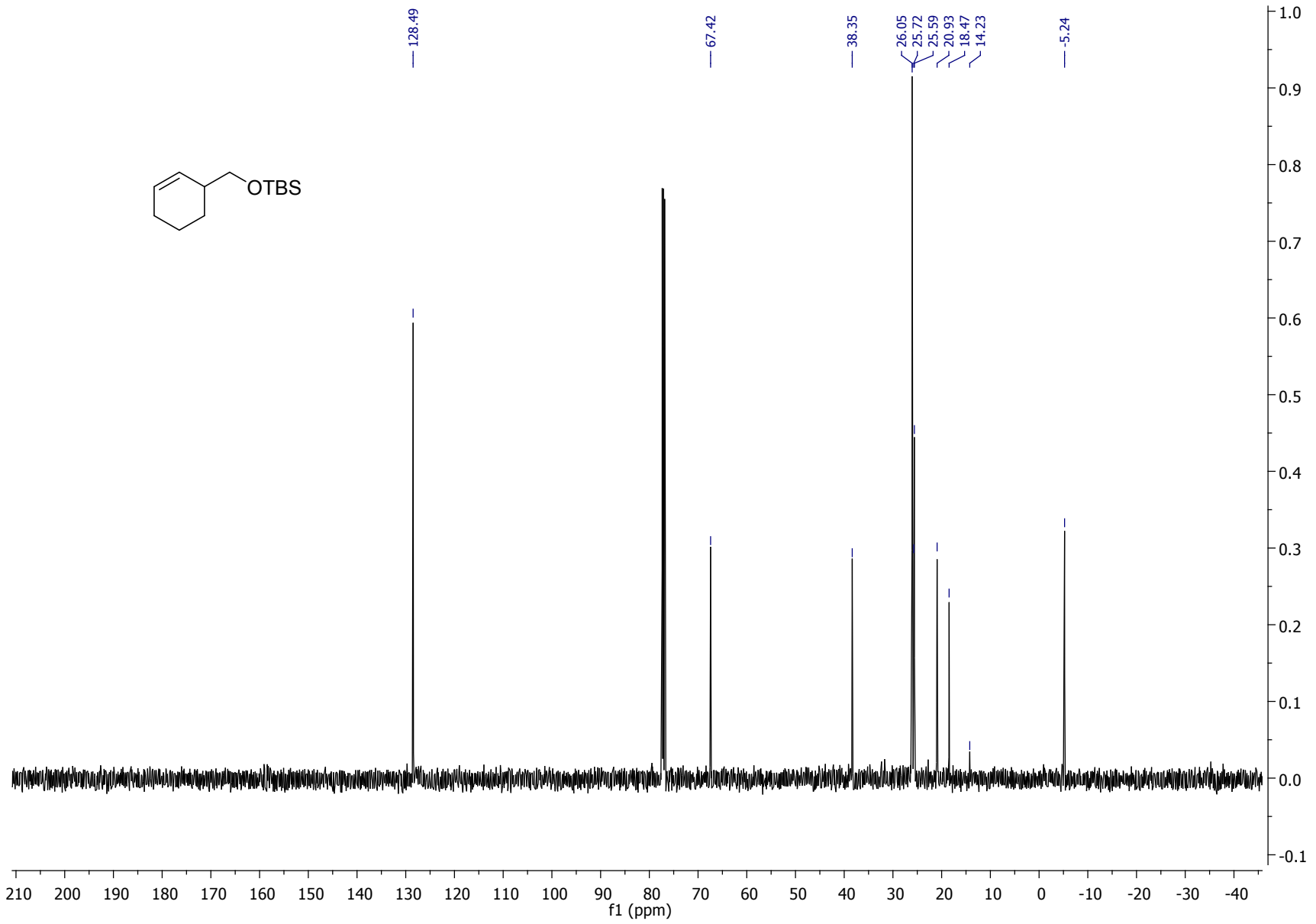

OTBS
CH2F

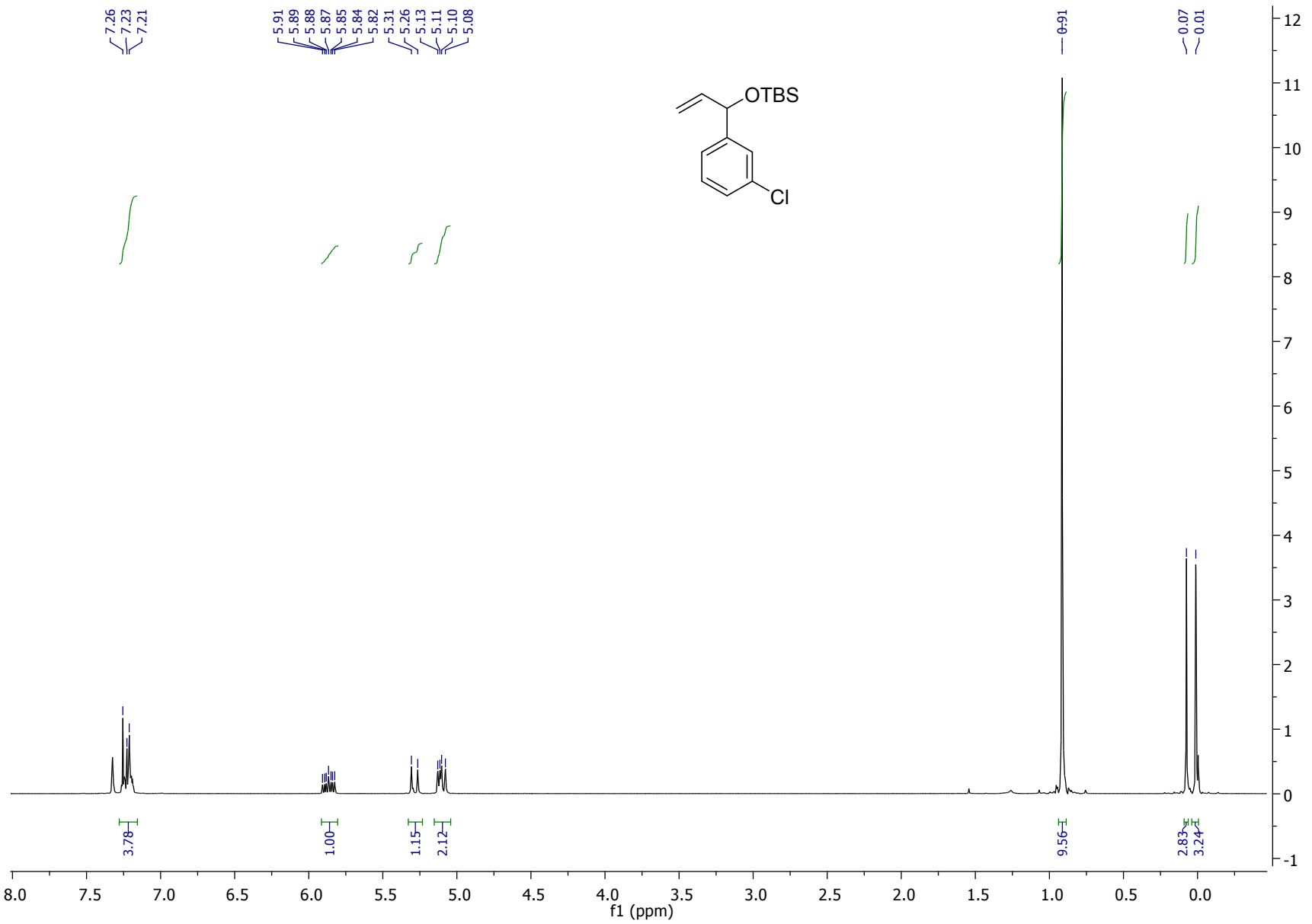
4.98
4.97
4.96
4.96
4.94
4.94
4.86
4.85
4.84
4.83
4.82
4.72
4.68
4.56
2.12
2.10
2.08
2.07
2.05
2.05
2.03
2.03
2.01
2.01
0.99
0.97
0.95
0.95
0.93
0.93
0.92
0.14
0.14
0.14
1.00
3.01
0.98
2.17
2.20
6.03
7.63
20.65
10.08
10.65
6.30
f1 (ppm)

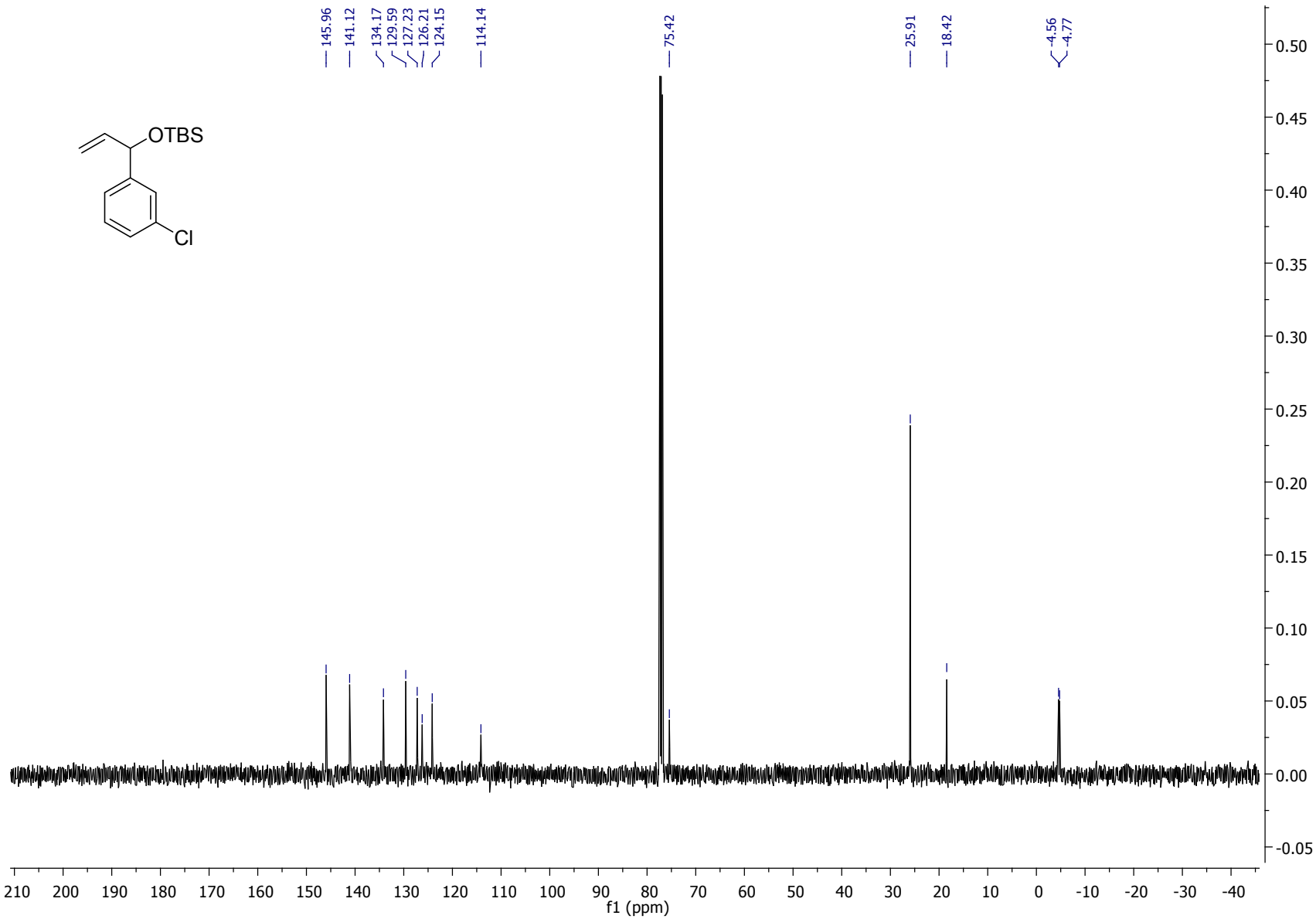

145.77
145.67
145.12
145.01
117.05
116.98
116.82
116.75
85.24
83.92
80.13
78.82
25.85
25.73
20.11
18.48
18.43
18.14
15.38
15.35
13.93
13.90
-4.28
-4.51
7, Scheme 2
OTBS
CH2F
f1 (ppm)

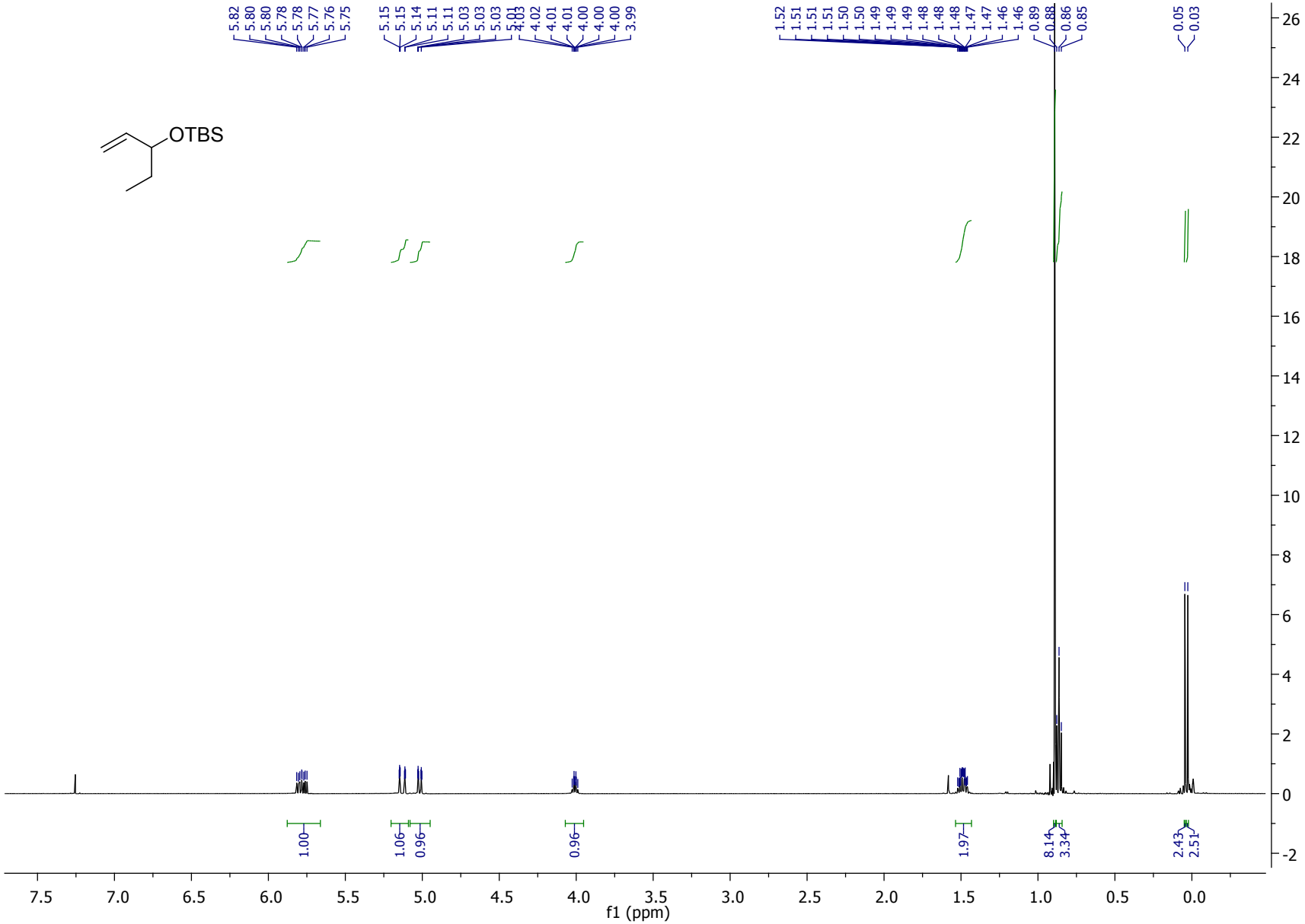

7, Scheme 2
OTBS
CH2F
-208.92
-209.04
-209.18
-215.81
-215.92
-216.05
0.019
0.018
0.017
0.016
0.015
0.014
0.013
0.012
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
-0.001
-0.002
-0.003
-207.5
-208.5
-209.5
-210.5
-211.5
-212.5
-213.5
-214.5
-215.5
-216.5
-217.5
-218.5

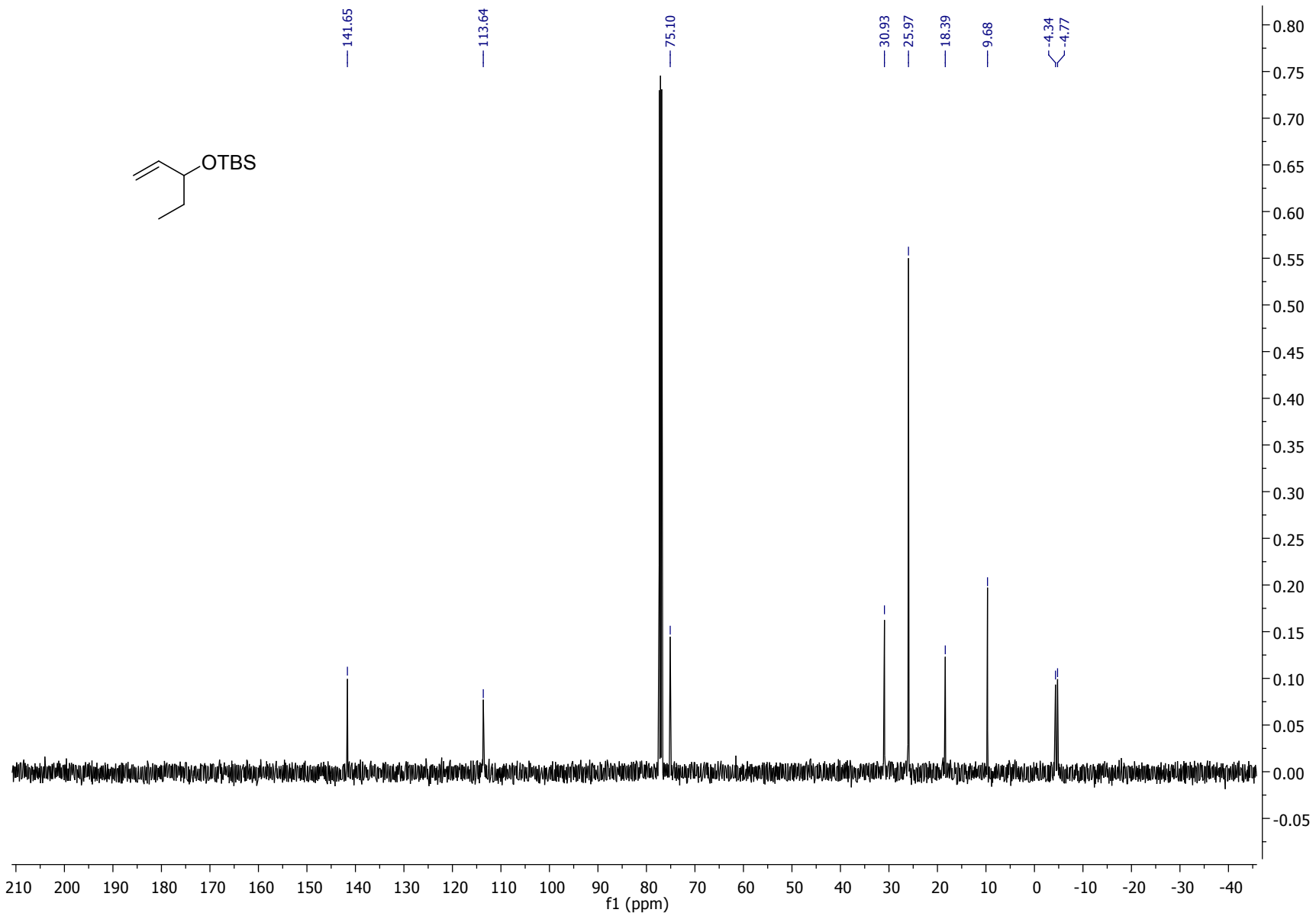

OTBS
f1 (ppm)

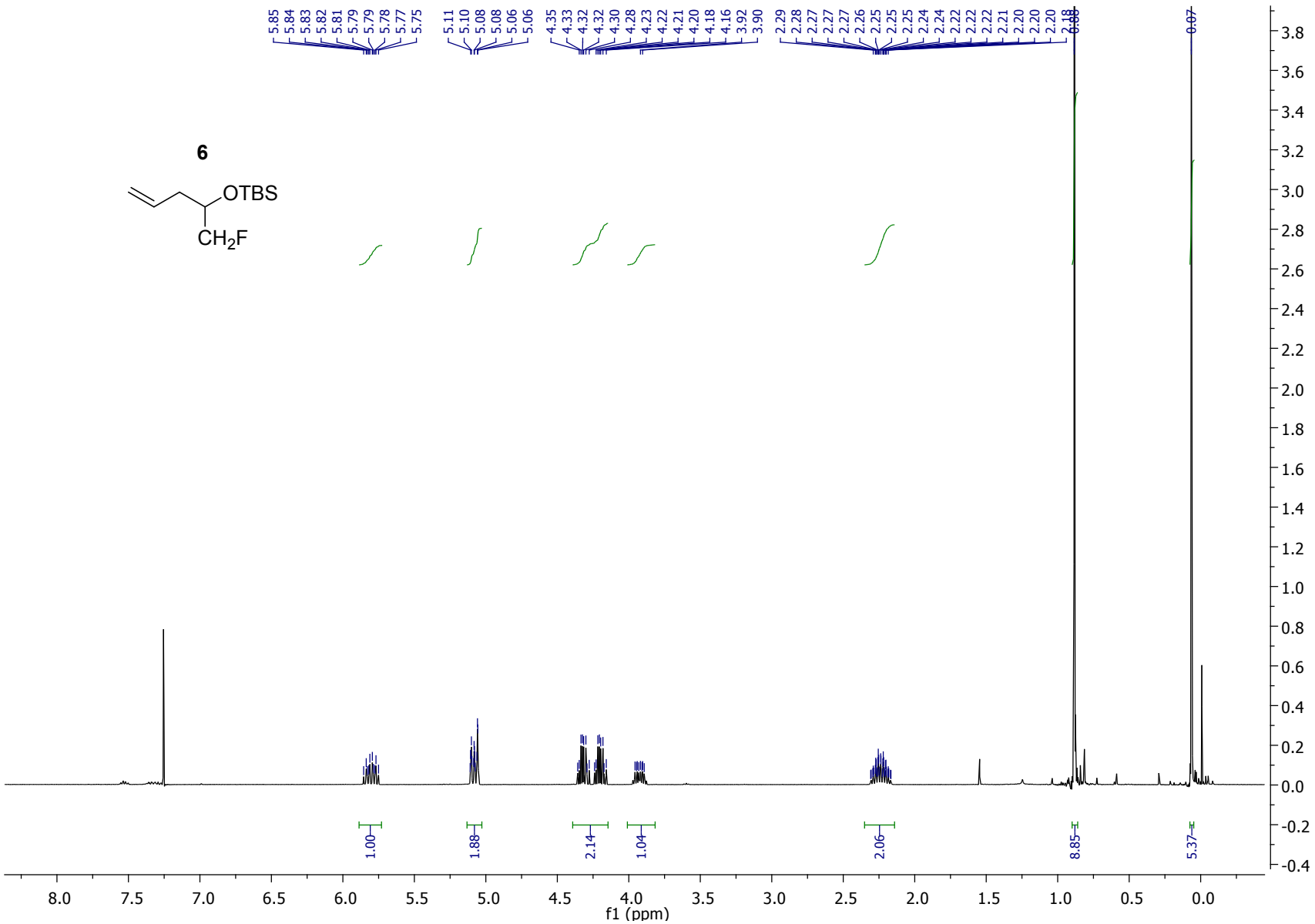

128.49
67.42
38.35
26.05
25.72
25.59
20.93
18.47
14.23
-5.24
OTBS
f1 (ppm)

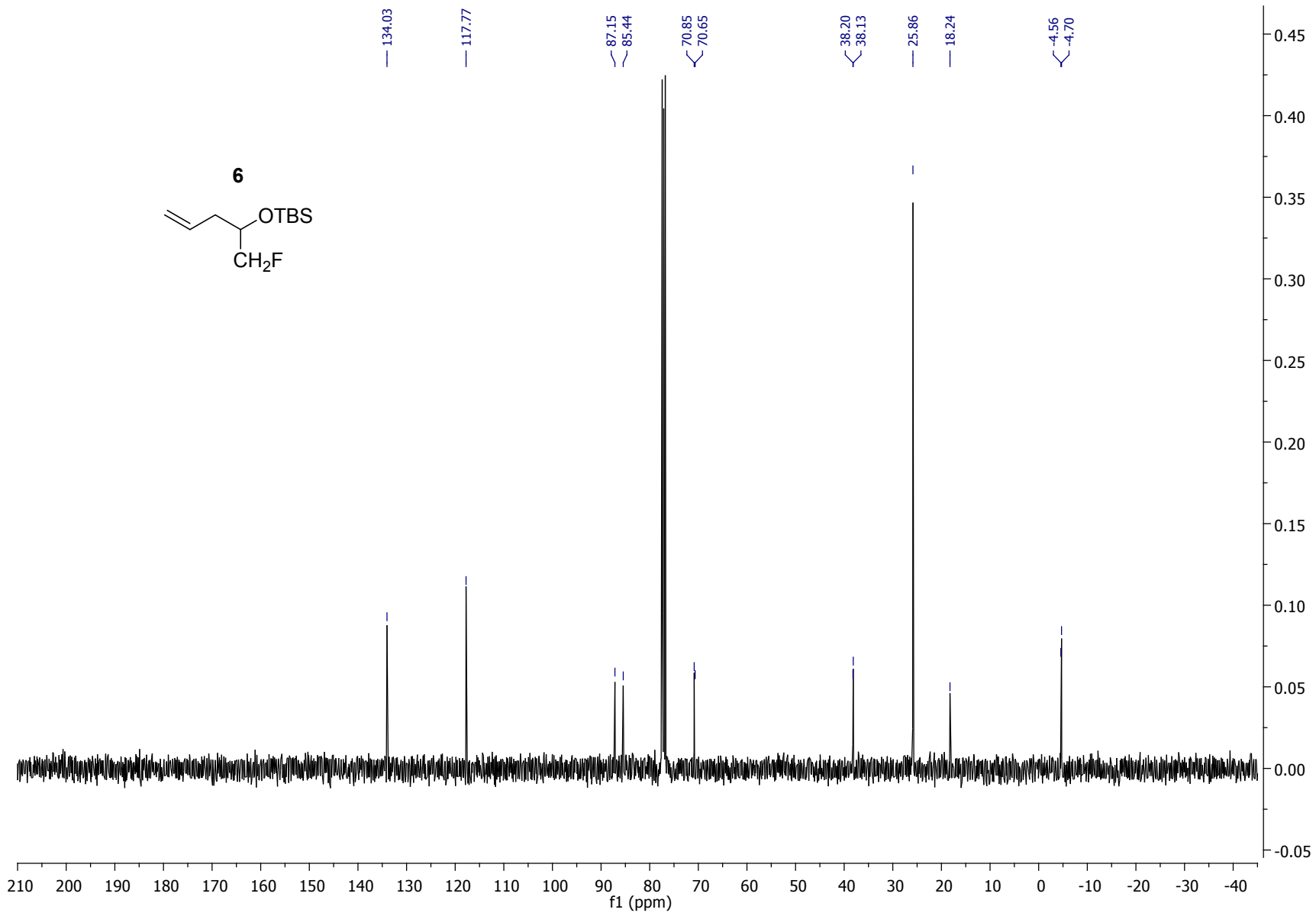

7.26
7.23
7.21
5.91
5.89
5.88
5.87
5.85
5.84
5.82
5.31
5.26
5.13
5.11
5.10
5.08
0.91
0.07
0.01
OTBS
Cl
3.78
1.00
1.15
2.12
9.56
2.83
3.24
f1 (ppm)

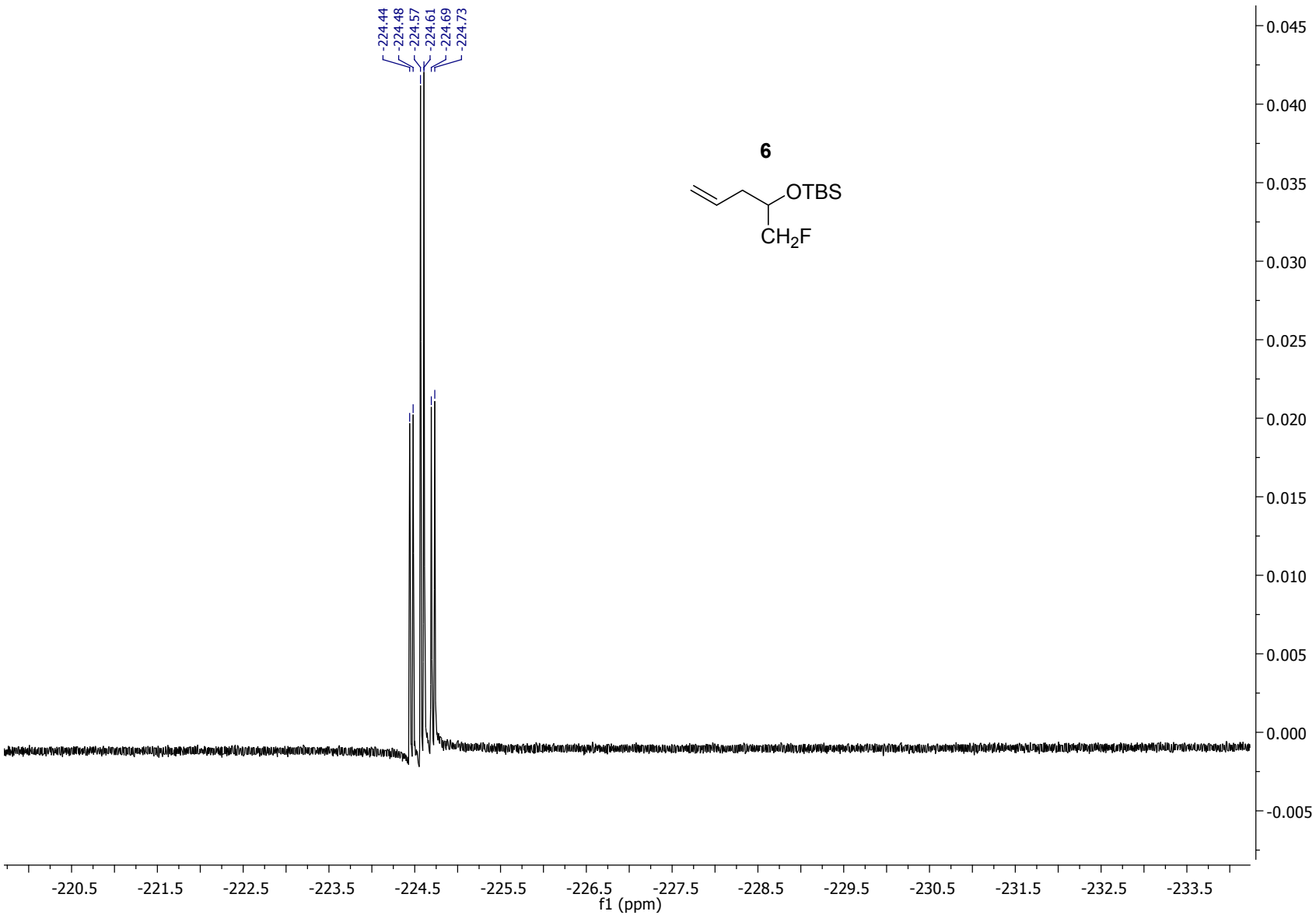

145.96
141.12
134.17
129.59
127.23
126.21
124.15
114.14
75.42
25.91
18.42
-4.56
-4.77
OTBS
Cl
f1 (ppm)


OTBS
5.82 5.80 5.80 5.78 5.78 5.77 5.76 5.75
5.15 5.15 5.14 5.11 5.11 5.03 5.03 5.03 5.01 5.01 4.03 4.02 4.01 4.01 4.00 4.00 4.00 3.99
1.52 1.51 1.51 1.51 1.50 1.50 1.49 1.49 1.49 1.48 1.48 1.48 1.47 1.47 1.46 1.46
0.89 0.88 0.86 0.85
0.05 0.03
1.00 1.06 0.96 0.96 1.97 8.14 3.34 2.43 2.51
f1 (ppm)


141.65
113.64
75.10
30.93
25.97
18.39
9.68
-4.34
-4.77
OTBS
f1 (ppm)


6
OTBS
CH2F
f1 (ppm)


6
OTBS
CH2F
134.03
117.77
87.15
85.44
70.85
70.65
38.20
38.13
25.86
18.24
-4.56
-4.70
f1 (ppm)


-224.44
-224.48
-224.57
-224.61
-224.69
-224.73
6
OTBS
CH2F
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
-220.5
-221.5
-222.5
-223.5
-224.5
-225.5
-226.5
-227.5
-228.5
-229.5
-230.5
-231.5
-232.5
-233.5
f1 (ppm)