## Supporting Information

# Regioselective *anti*-Silyllithiation of Propargylic Alcohols

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## Instrumentation and Chemicals

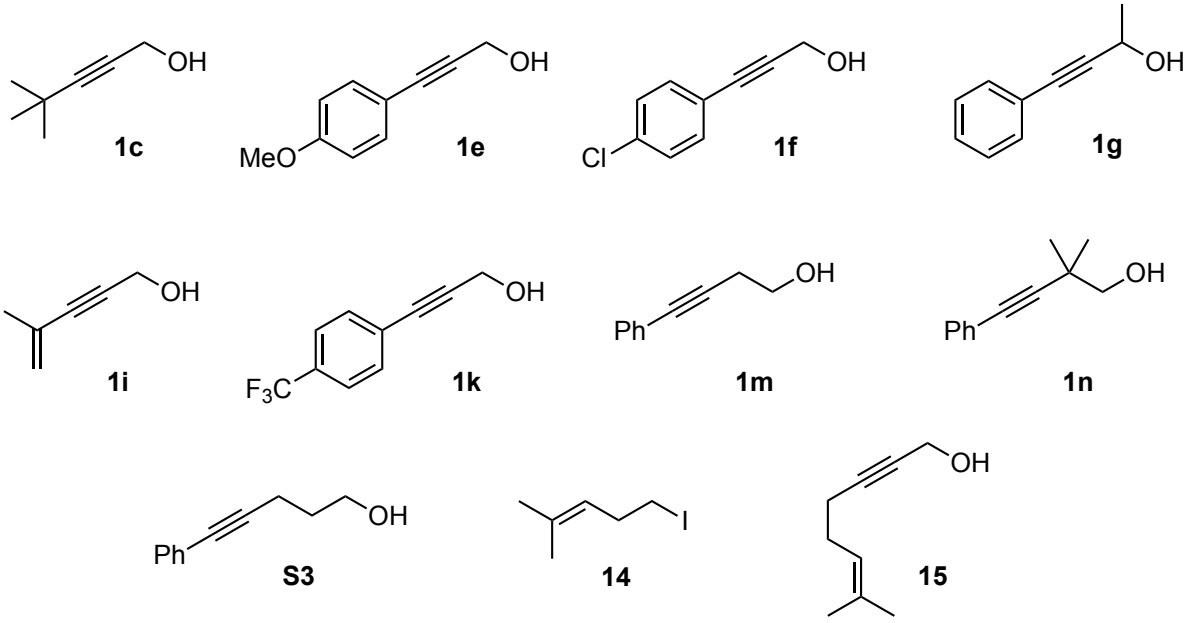
$^{1}$H NMR (600 MHz), $^{13}$C NMR (151 MHz), and spectra were recorded on a JEOL ECA-600 and JEOL ECZ-600 spectrometer (For JEOL ECA-600 and JEOL ECZ-600: $^{1}$H NMR (594 MHz), $^{13}$C NMR (149 MHz). Chemical shifts in $^{1}$H NMR spectra were recorded in delta ($\delta$) units, parts per million (ppm) relative to residual $CHCl_3$ ($\delta$ = 7.26 ppm), DMSO ($\delta$ = 2.50 ppm), $CD_3OD$ ($\delta$ =3.34 ppm). Chemical shifts in $^{13}$C NMR spectra were recorded in delta ($\delta$) units, parts per million (ppm) relative to $CDCl_3$ ($\delta$ = 77.00 ppm), DMSO ($\delta$ = 39.52 ppm), $CD_3OD$ ($\delta$ = 49.86 ppm). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra were recorded on a Thermo Fisher Scientific Nicolet iS5 spectrometer. High resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF II-KR spectrometer in Atmospheric Pressure Chemical Ionization (APCI) method or Electrospray Ionization (ESI) method using "LC/MS tuning mix, for APCI, low concentration" or "LC/MS tuning mix, for ESI, low concentration" (Agilent Technologies, Inc.) as the internal standard. Melting points were determined on a Stanford Research Systems MPA100 melting point apparatus. For all spectroscopic studies, spectroscopic grade solvents were used as purchased unless otherwise noted.

All non-aqueous reactions were carried out under an inert atmosphere of $N_2$ gas in oven-dried glassware unless otherwise noted. Dehydrated solvents (hexane, DMF, 1,4-dioxane) were purchased from FUJIFILM Wako Pure Chemical Corporation and stored under nitrogen atmosphere. Dehydrated Toluene, THF was purchased from Kanto Chemical Co., Inc. and stored under nitrogen atmosphere. *n*BuLi was purchased from Nacalai Tesque Inc. Molarity of *n*BuLi was determined by titration against diphenylacetic acid. Lithium granular (99% trace metal basis) was purchased from Sigma-Aldrich (product No. 499811). But-2-yn-1-ol (**1a**) was purchased from Tokyo Chemical Industry Co., Ltd. (product No. B0712) and distilled over $CaH_2$ before use. 2-Heptyn-1-ol (**1b**) was purchased from Sigma-Aldrich (product No. 630810). 3-Phenyl-2-propyn-1-ol (**1d**) was purchased from Tokyo Chemical Industry Co., Ltd. (product number: P1147). 2-Methyl-4-phenyl-3-butyn-2-ol (**1h**) was purchased from Tokyo Chemical Industry Co., Ltd. (product No. M1415). 3-Trimethylsilyl-2-propyn-1-ol (**1j**) was purchased from Tokyo Chemical Industry Co., Ltd. (product No. T1500). Propargyl alcohol (**1l**) was purchased from Tokyo Chemical Industry Co., Ltd. (product number: P0536). MeLi (1.06 M solution in diethyl ether (Br free)) was purchased from Kanto Chemical Co., Inc. (cat. No. 26103-35). $ZnCl_2$ was purchased from Wako Pure Chemical Industries, Ltd., and stored in a glove box. All other reagents were commercially available and used without further purification unless otherwise noted. Analytical thin layer chromatography (TLC) was performed on Merck

precoated analytical plates, 0.25-mm thick, silica gel 60 $F_{254}$. Preparative flash chromatography was performed using Silica Gel (Wakosil® C-300 purchased from FUJIFILM Wako Pure Chemical Corporation).

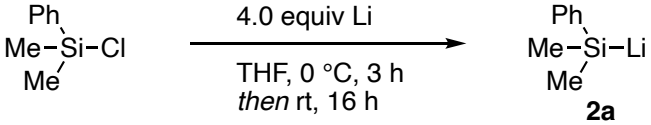
## Preparation of Starting Materials

### Preparation of 1c, 1e, 1f, 1g, 1i, 1k, 1m, 1n, 14, 15, S3




4,4-Dimethylpent-2-yn-1-ol **1c**[1], 3-(4-methoxyphenyl)prop-2-yn-1-ol **1e**[2], 3-(4-chlorophenyl)prop-2-yn-1-ol **1f**[2], 4-phenylbut-3-yn-2-ol **1g**[3], and 2,5-dimethylhex-5-en-3-yn-2-ol **1i**[4], and 3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol **1k**[2] were synthesized according to the literature. 4-Phenylbut-3-yn-1-ol **1m**[2], 2,2-dimethyl-4-phenylbutyn-3-ol **1n**[5], and 5-phenylpent-4-yn-1-ol **S3**[6] were synthesized by similar procedures in the previous reports. 5-Iodo-2-methylpent-2-ene **14**[7] and 7-methyloct-6-en-2-yn-1-ol **15**[8] were synthesized according to the known literature procedure and were distilled before use.

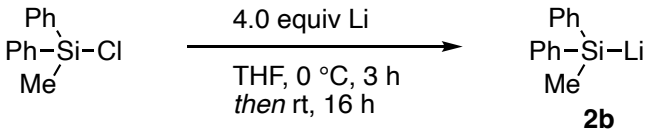
### Preparation of 2a[9]




A 30-mL flask was charged under nitrogen atmosphere with lithium granular (333 mg, 48.0 mmol) and THF (6.0 mL). After the suspension was stirred at 0 °C for 5 min, chlorodimethylphenylsilane (2.05 mL, 12.0 mmol) was slowly added and the resulting mixture was stirred for 3 h at 0 °C. The mixture was then allowed to warm to room temperature and the suspension was stirred for 16 h. The deep red solution thus obtained was used as a solution of

$PhMe_2SiLi$ (**2a**) (1.4 M in THF). The solution was titrated under the modified conditions of Fleming.[10] An aliquot was injected into water, and the alkaline solution was titrated against 0.5 M aqueous oxalic acid using phenolphthalein as an indicator.

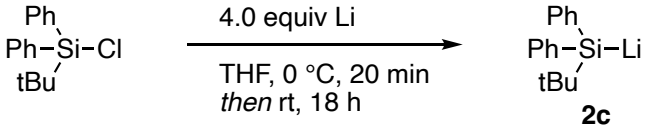
**Preparation of 2b**[9]




**2b**

A 30-mL flask was charged under nitrogen atmosphere with lithium granular (167 mg, 24.0 mmol) and THF (2.7 mL). After the suspension was stirred at 0 °C for 5 min, chloro(methyl)diphenylsilane (1.26 mL, 6.00 mmol) was slowly added and the resulting mixture was stirred for 3 h at 0 °C. The mixture was then allowed to warm to room temperature and the suspension was stirred for 16 h. The black deep-red solution thus obtained was used as a solution of $Ph_2MeSiLi$ (**2b**) (1.5 M in THF). Titration was performed as in **2a**.

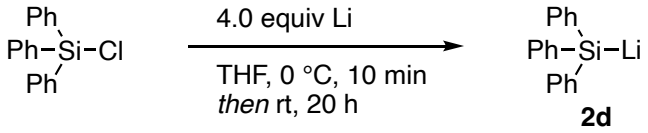
**Preparation of 2c**[9]




**2c**

A 30-mL flask was charged under nitrogen atmosphere with lithium granular (167 mg, 24.0 mmol) and THF (2.4 mL). After the suspension was stirred at 0 °C for 5 min, *tert*-butyl(chloro)diphenylsilane (1.56 mL, 6.00 mmol) was slowly added and the resulting mixture was stirred for 20 min at 0 °C. The mixture was then allowed to warm to room temperature and the suspension was stirred for 18 h. The black-green thick solution thus obtained was used as a solution of $t$BuPh$_2$SiLi (**2c**) (1.5 M in THF). Titration was performed as in **2a**.

**Preparation of 2d**[9]

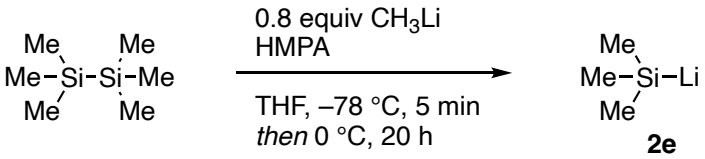



**2d**

A 30-mL flask was charged under nitrogen atmosphere with lithium granular (140 mg, 20.0 mmol) and THF (2.00 mL). After the suspension was stirred at 0 °C for 5 min, chlorotriphenylsilane (1.47 g, 5.00 mmol) in THF (1.53 mL) was slowly added and the resulting mixture was stirred for 10 min at 0 °C. The mixture was then allowed to warm to room temperature and the suspension was stirred for 18 h. The yellowish black thick solution thus

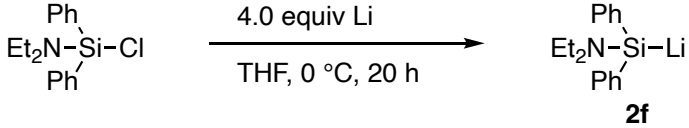
obtained was used as a solution of $Ph_3SiLi$ (**2d**) (0.93 M in THF). Titration was performed as in **2a**.

**Preparation of 2e**[11]




A 30-mL flask was charged under nitrogen atmosphere with HMPA (2.00 mL) and hexamethyldisilane (1.02 mL, 5.00 mmol). After the solution was stirred at –78 ˚C for 5 min (the mixture becomes frozen), methyllithium (Br free, 1.06 M in $Et_2O$, 3.80 mL, 4.00 mmol) and THF (10 ml) was added. The two-phase mixture was kept at –78 ˚C for 5 min and then warmed to 0 ˚C in ice bath. Within two minutes, the solid melted so that stirring was possible. The mixture was stirred for another 20 min at 0 ˚C. The bright red solution obtained was used instantly as a solution of $Me_3SiLi$ (**2e**) (~0.24 M). The solution was used without titration by assuming stoichiometric conversion.

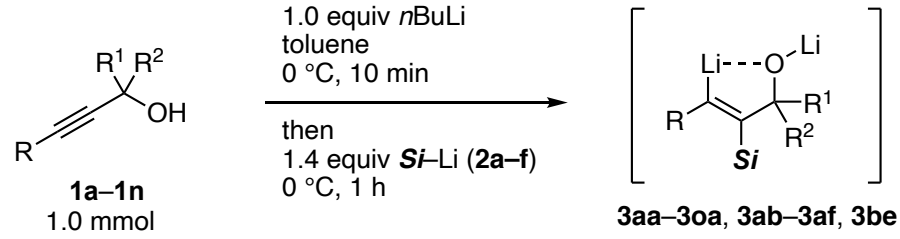
**Preparation of 2f**[12]




A 30-mL flask was charged under nitrogen atmosphere with lithium granular (95.8 mg, 13.8 mmol) and THF (5.80 mL). After the suspension was stirred at 0 °C for 5 min, 1-chloro-*N*,*N*-diethyl-1,1-diphenylsilanamine (1.00 g, 3.44 mmol) was slowly added and the resulting suspension was stirred for 20 h at 0 °C. The black green solution thus obtained was used as a solution of $Ph_2(Et_2N)SiLi$ (**2f**) (~0.50 M). The solution was used without titration by assuming stoichiometric conversion.

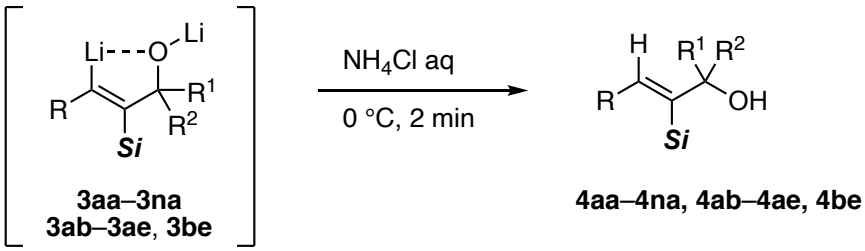
## Experimental Procedures and Characterization Data

### General Procedure for Silyllithiations of Propargylic Alcohols (GP1)



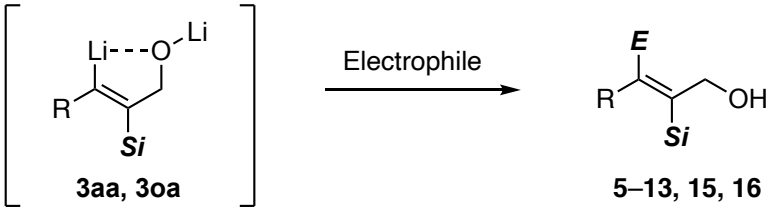

A 30-mL Schlenk tube was charged under $N_2$ atmosphere with propargylic alcohol **1** (1.00 mmol) and toluene (10 mL). After the solution was stirred at 0 °C for 5 min, *n*BuLi (1.31 M in hexane, 765 μL, 1.00 mmol) was slowly added and the resulting mixture was stirred for 10 min at 0 °C. Prepared solution of silyllithium **2** (1.40 mmol) was slowly added to the mixture over 1 min. The resulting solution was stirred at 0 °C for 1 h to give alkenyllithium intermediate **3**.

### General Procedure for Protonation of Alkenyllithium Species (GP2)




Alkenyllithium **3** was quenched with saturated aqueous $NH_4Cl$ (1.0 mL) and the mixture was stirred at 0 °C for 2 min. The mixture was poured into a separatory funnel with $CH_2Cl_2$ (10 mL), water (10 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with $CH_2Cl_2$ (10 mL × 2). The combined organic extract was washed with brine (10 mL), dried over $Na_2SO_4$ (ca. 10 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **4**.

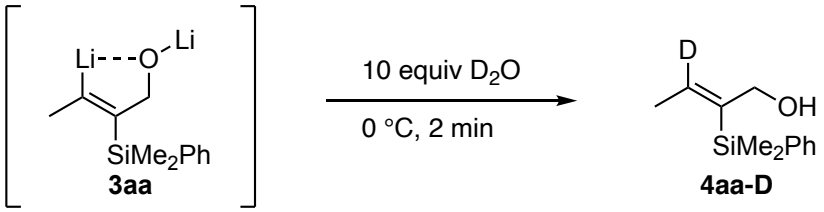
### General Procedure for the Reaction of Alkenyllithium Species with Electrophiles (GP3)




Alkenyllithium **3aa** was reacted with an appropriate electrophile (1.0 mL) and the mixture was stirred under the conditions with the indicated temperature and duration. The

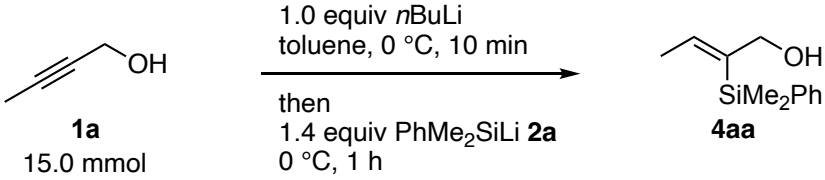
reaction was quenched with saturated aqueous $NH_4Cl$ (1.0 mL) and the mixture was stirred at 0 °C for 2 min. The mixture was poured into a separatory funnel with $CH_2Cl_2$ (10 mL), water (10 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with $CH_2Cl_2$ (20 mL × 3). The combined organic extract was washed with brine (10 mL), dried over $Na_2SO_4$ (ca. 10 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the corresponding adduct (**5–13**, **15**, **16**).

**Optimization of the Reaction Conditions: Deuteration of 3aa and NMR Experiment**




**3aa** was prepared by GP1, with as appropriate deviation as shown in Table 1. The reaction was quenched with $D_2O$ (180 μL, 10 mmol, 10 equiv) and the mixture was stirred at 0 °C for 2 min. The mixture was poured into a separatory funnel with $CH_2Cl_2$ (10 mL), water (10 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with $CH_2Cl_2$ (10 mL × 2). The combined organic extract was washed with brine (10 mL), dried over $Na_2SO_4$ (ca. 10 g), filtered, and concentrated under reduced pressure. 1,3,5-trimethoxybenzene was added as an internal standard and the yield of **4aa-D** and the amount of deuterium incorporation was determined by $^1H$ NMR.

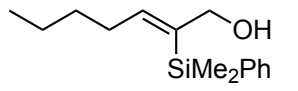
**Gram-scale synthesis of (*Z*)-2-(dimethylphenylsilyl)but-2-en-1-ol (4aa)**




A three-neck 300-mL round-bottomed flask equipped with nitrogen inlet and septum was charged under $N_2$ atmosphere with but-2-yn-1-ol **1a** (1.05 g, 15.0 mmol) and toluene (150 mL). After the solution was stirred at 0 °C for 5 min in an ice bath, *n*BuLi (1.43 M in hexane, 10.5 mL, 15.0 mmol) was slowly added and the resulting mixture was stirred at 0 °C for 10 min. $PhMe_2SiLi$ (**2a**, 1.4 M in THF, 15 mL, 21.0 mmol) was slowly added to the mixture over 5 min. The resulting solution was stirred at 0 °C for 1 h. The reaction mixture was quenched with saturated aqueous $NH_4Cl$ (15 mL) and the mixture was stirred at 0 °C for 2 min. The mixture

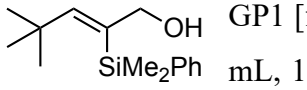
was poured into a separatory funnel with $CH_2Cl_2$ (150 mL), water (150 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with $CH_2Cl_2$ (150 mL × 2). The combined organic extract was washed with brine (150 mL), dried over $Na_2SO_4$ (ca. 100 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane to hexane/EtOAc = 9/1) to give **4aa** (2.82 g, 13.7 mmol, 91%) as a pale yellow oil. $R_f$ = 0.38 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3310, 1619; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.56 (m, 2H), 7.36–7.34 (m, 3H), 6.42 (q, $J$ = 7.0 Hz, 1H), 4.16 (d, $J$ = 6.0 Hz, 2H), 1.67 (d, $J$ = 7.0 Hz, 3H), 1.18–1.14 (m, 1H), 0.46 (s, 6H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 140.6, 139.0, 138.2, 133.7, 128.9, 127.8, 69.3, 17.9, –1.5.; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{12}H_{17}Si$ 189.1094; Found 189.1089.

**(*Z*)-2-(Dimethylphenylsilyl)hept-2-en-1-ol (4ba)**



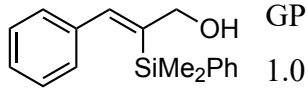

GP1 [from **1b** (112 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)] and GP2 [column chromatography with an eluent (hexane to hexane/EtOAc = 9/1)] afforded **4ba** as a colorless oil (231 mg, 0.928 mmol, 93%). $R_f$ = 0.42 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3316, 2955, 1615; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.57–7.53 (m, 2H), 7.36–7.33 (m, 3H), 6.29 (t, $J$ = 6.9 Hz, 1H), 4.16 (d, $J$ = 4.8 Hz, 2H), 2.02–1.98 (m, 2H), 1.24–1.14 (m, 5H), 0.78 (t, $J$ = 6.9 Hz, 3H), 0.45 (s, 6H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 146.5, 139.2, 136.9, 133.7, 128.8, 127.7, 69.3, 31.7, 31.6, 22.3, 13.8, –1.4; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{15}H_{23}Si$ 231.1564; Found 231.1558.

**(*Z*)-2-(Dimethylphenylsilyl)-4,4-dimethylpent-2-en-1-ol (4ca)**




GP1 [from **1c** (112 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)] and GP2 [column chromatography with an eluent (hexane to hexane/EtOAc = 9/1)] afforded **4ca** as a colorless oil (181 mg, 0.729 mmol, 73%). $R_f$ = 0.44 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3335, 2954, 1594; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.55 (m, 2H), 7.33 (m, 3H), 6.41 (t, $J$ = 1.2 Hz, 1H), 4.18 (dd, $J$ = 6.1, 1.2 Hz, 2H), 1.18 (t, $J$ = 6.1 Hz, 1H), 0.95 (s, 9H), 0.50 (s, 6H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 159.1, 140.7, 133.8, 132.7, 128.7, 127.6, 72.8, 34.3, 30.7, 0.8; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{15}H_{23}Si$ 231.1564; Found 231.1560.

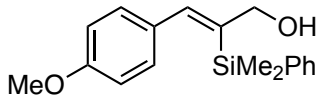
**(*Z*)-2-(dimethylphenylsilyl)-3-phenylprop-2-en-1-ol (4da)**




GP1 [from **1d** (132 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol), reaction time = 40 min] and GP2 [column

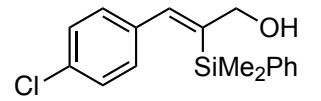
chromatography with an eluent (hexane to hexane/EtOAc = 9/1)] afforded **4da** as a pale yellow oil (241 mg, 0.897 mmol, 90%). $R_f$ = 0.35 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3295, 1594; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.51 (m, 2H), 7.48 (br, 1H), 7.36–7.31 (m, 3H), 7.21–7.19 (m, 3H), 7.12 (m, 2H), 4.34 (dd, $J$ = 6.2, 1.4 Hz, 2H), 1.39 (t, $J$ = 6.2 Hz, 1H), 0.20 (s, 6H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 142.9, 141.2, 139.2, 139.1, 133.7, 128.8, 128.4, 127.7, 127.6, 127.0, 68.6, –1.6; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{17}H_{19}Si$ 251.1251; Found 251.1259.

**(*Z*)-2-(Dimethylphenylsilyl)-3-(4-methoxyphenyl)prop-2-en-1-ol (4ea)**



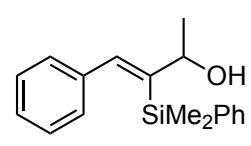

GP1 [from **1e** (162 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)] and GP2 [column chromatography with an eluent (hexane to hexane/EtOAc = 9/1)] afforded **4ea** as a pale yellow oil (279 mg, 0.935 mmol, 93%). $R_f$ = 0.27 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3334, 1608; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.53 (m, 2H), 7.41 (br, 1H), 7.35–7.31 (m, 3H), 7.06 (m, 2H), 6.72 (m, 2H), 4.33 (br, 2H), 3.77 (s, 3H), 1.38 (br, 1H), 0.24 (s, 6H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 158.8, 143.2, 139.8, 139.3, 133.8, 131.6, 129.8, 128.8, 127.8, 113.1, 69.2, 55.1, –1.5; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{18}H_{21}OSi$ 281.1356; Found 281.1353.

**(*Z*)-3-(4-Chlorophenyl)-2-(dimethylphenylsilyl)prop-2-en-1-ol (4fa)**




GP1 [from **1f** (167 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)] and GP2 [column chromatography with an eluent (hexane to hexane/EtOAc = 7/1)] afforded **4fa** as a pale yellow oil (228 mg, 0.754 mmol, 75%). $R_f$ = 0.38 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3305, 1721; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.49–7.47 (m, 2H), 7.39 (s, 1H), 7.36–7.30 (m, 3H), 7.15–7.13 (m, 2H), 7.03–7.01 (m, 2H), 4.35 (d, $J$ = 1.6 Hz, 2H), 1.44 (br, 1H), 0.22 (s, 6H); $^{13}C$ NMR (151 MHz, CDCl3) $\delta$ 142.3, 141.4, 138.8, 137.6, 133.7, 132.9, 129.8, 128.9, 127.8, 68.6, –1.6; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{17}H_{18}ClSi$ 285.0861; Found 285.0862.

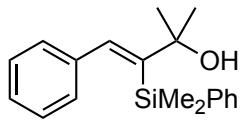
**(*Z*)-3-(Dimethylphenylsilyl)-4-phenylbut-3-en-2-ol (4ga)**




GP1 [from **1g** (146 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)] and GP2 [column chromatography with an eluent (hexane to hexane/EtOAc = 9/1)] afforded **4ga** as a pale yellow oil (251 mg, 0.888 mmol, 89%). $R_f$ = 0.38 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3346, 2967, 1592; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.60 (br, 1H), 7.49 (m, 2H), 7.34–7.29 (m, 3H), 7.20–7.18 (m, 3H),

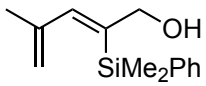
7.12 (m, 2H), 4.55 (m, 1H), 1.50 (m, 1H), 1.36 (d, $J$ = 6.9 Hz, 3H), 0.20 (s, 3H), 0.17 (s, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 146.3, 141.0, 139.5, 139.5, 133.8, 128.7, 128.5, 127.7, 127.6, 126.9, 71.3, 24.4, –0.7, –0.8; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{18}H_{21}Si$ 265.1407; Found 265.1399.

**(*Z*)-3-(Dimethylphenylsilyl)-2-methyl-4-phenylbut-3-en-2-ol (4ha)**



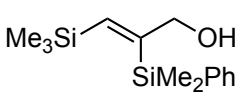

GP1 [from **1h** (160 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)] and GP2 [column chromatography with an eluent (hexane to hexane/EtOAc = 13/1)] afforded **4ha** as a colorless oil (274 mg, 0.925 mmol, 92%). $R_f$ = 0.50 (5% EtOAc/hexane); IR (ATR, cm$^{-1}$) 3456, 2970, 1588; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.52 (m, 2H), 7.45 (s, 1H), 7.32–7.29 (m, 3H), 7.22–7.17 (m, 3H), 7.10 (m, 2H), 1.51 (s, 1H), 1.43 (s, 6H), 0.14 (s, 6H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 151.3, 141.4, 141.2, 140.0, 133.8, 128.5, 128.5, 127.7, 127.6, 126.7, 76.4, 32.1, 1.4; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{19}H_{23}Si$ 279.1564; Found 279.1566.

**(*Z*)-2-(Dimethylphenylsilyl)-4-methylpenta-2,4-dien-1-ol (4ia)**



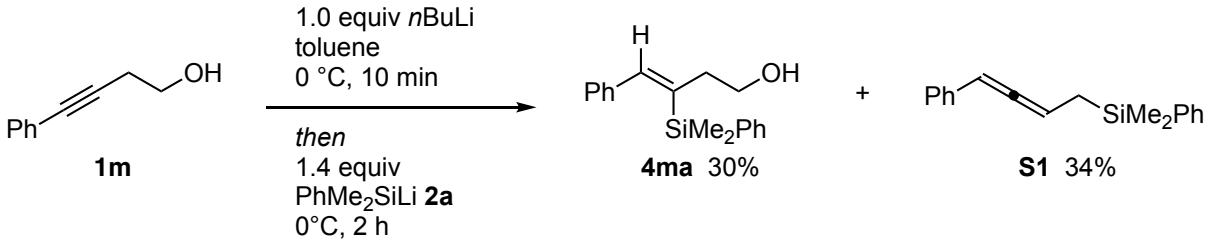

GP1 [from **1i** (96.1 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)] and GP2 [column chromatography with an eluent (hexane to hexane/EtOAc = 13/1)] afforded **4ia** as a colorless oil (177 mg, 0.762 mmol, 76%). Reaction time = 40 min. $R_f$ = 0.43 (20% EtOAc/hexane); IR (ATR, cm$^{-1}$) 3313, 1604; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.53 (m, 2H), 7.34–7.32 (m, 3H), 6.73 (dq, $J$ = 1.7, 0.8 Hz, 1H), 4.75 (br, 1H), 4.74 (br, 1H), 4.19 (d, $J$ = 1.4 Hz, 2H), 1.67 (br, 3H), 0.44 (s, 6H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 145.3, 144.0, 139.5, 138.5, 133.8, 128.7, 127.6, 114.7, 68.5, 22.5, –1.2; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{14}H_{19}Si$ 215.1251; Found 215.1250.

**(*Z*)-2-(Dimethylphenylsilyl)-3-(trimethylsilyl)prop-2-en-1-ol (4ja)**




GP1 [from **1j** (128 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)] and GP2 [column chromatography with an eluent (hexane to hexane/EtOAc = 11/1)] afforded **4ja** as a pale yellow oil (220 mg, 0.832 mmol, 83%). $R_f$ = 0.56 (20% EtOAc/hexane); IR (ATR, cm$^{-1}$) 3313, 2953; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.52 (m, 2H), 7.37–7.32 (m, 3H), 6.70 (t, $J$ = 1.4 Hz, 1H), 4.22 (dd, $J$ = 6.2, 1.4 Hz, 2H), 1.38 (t, $J$ = 6.2 Hz, 1H), 0.44 (s, 6H), –0.01 (s, 9H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 157.3, 143.3, 138.7, 134.1, 129.1, 127.8, 71.2, 0.5, –0.8; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{14}H_{23}Si_2$: 247.1333; Found 247.1331.

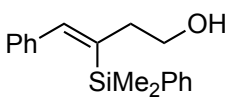
**Reaction of $PhMe_2SiLi$ 2a with 1m**




Formation of allenylsilane **S1** would indicate the deprotonation of the propargylic position and elimination to form an enyne intermediate that would be followed by conjugate addition of silyl group.

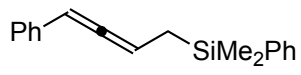
GP1 [from 4-phenylbut-3-yn-1-ol **1m** (146 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.00 mL, 1.40 mmol), the reaction time = 2 h] and GP2 [column chromatography on silica gel (hexane to hexane/EtOAc = 6/1)] afforded **4ma** (85.2 mg, 0.301 mmol, 30%) as a pale yellow oil and allene **S1** (90.8 mg, 0.343 mmol, 34%) as a colorless oil.

**(*Z*)-3-(Dimethylphenylsilyl)-4-phenylbut-3-en-1-ol (4ma)**



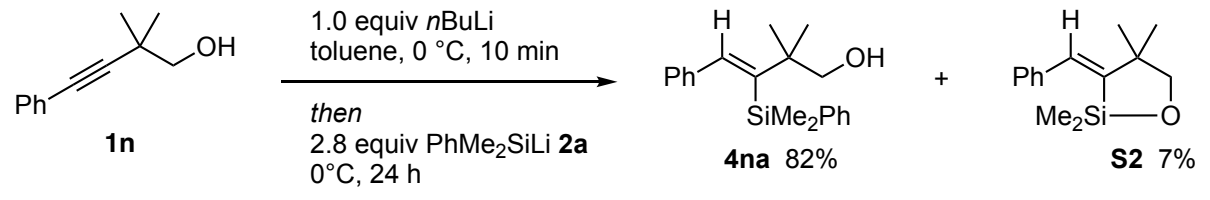

Pale yellow oil. $R_f$ = 0.28 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3324, 1591; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.46 (m, 2H), 7.37 (br, 1H), 7.34–7.30 (m, 3H), 7.20–7.17 (m, 3H), 7.12 (m, 2H), 3.69 (m, 2H), 2.55 (td, $J$ = 6.9, 1.4 Hz, 2H), 1.40 (m, 1H), 0.17 (s, 6H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 146.1, 139.5, 139.3, 138.3, 133.7, 128.8, 128.6, 127.8, 127.7, 127.0, 62.3, 41.9, –1.1; HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{18}H_{22}OSi$ 282.1434; Found 282.1433.

**Dimethylphenyl(4-phenylbuta-2,3-dien-1-yl)silane (S1)**




Colorless oil. $R_f$ = 0.78 (3% EtOAc/hexane); IR (ATR, $cm^{-1}$) 2955, 1703; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.55 (m, 2H), 7.39–7.34 (m, 3H), 7.24 (m, 2H), 7.19–7.14 (m, 3H), 6.06 (m, 1H), 5.52 (m, 1H), 1.72–1.69 (m, 2H), 0.37–0.35 (m, 6H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 205.7, 138.2, 135.2, 133.7, 129.1, 128.4, 127.8, 126.6, 126.5, 94.1, 90.9, 17.1, –3.2, –3.4; HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{18}H_{20}Si$ 264.1329; Found 264.1327.

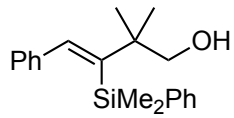
**Reaction of $PhMe_2SiLi$ 2a with 1n**




Cyclic byproduct **S2** would be generated through the cyclization of deprotonated **4na** followed by dearylation from a cyclic silicate intermediate.

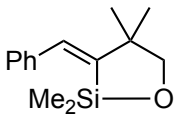
GP1 [from 2,2-dimethyl-4-phenylbut-3-yn-1-ol **1n** (174 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 2.0 mL, 2.8 mmol), the reaction time = 24 h] and GP2 [column chromatography on silica gel (hexane to hexane/EtOAc = 5.6/1)] afforded **4na** (255 mg, 0.820 mmol, 82%) as a colorless oil and **S2** (16.6 mg, 0.071 mmole, 7%) as a colorless oil.

**(*Z*)-3-(Dimethylphenylsilyl)-2,2-dimethyl-4-phenylbut-3-en-1-ol (4na)**



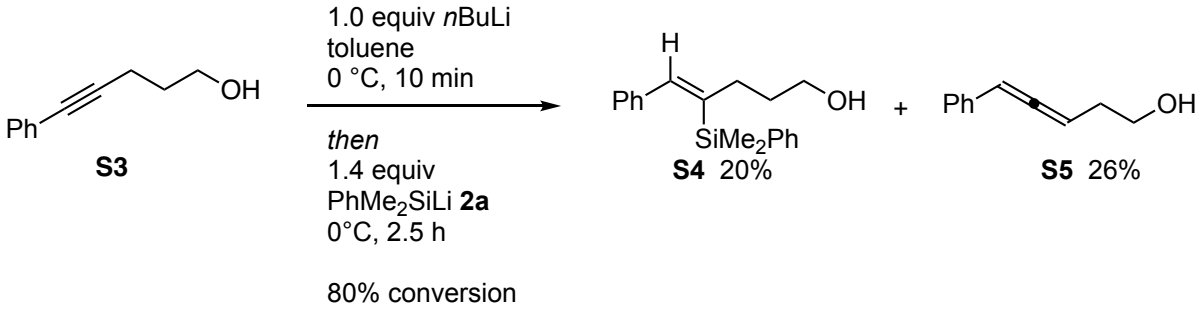

Colorless oil. $R_f$ = 0.41 (10% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3376, 2955, 1427; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.50 (s, 1H), 7.40 (m, 2H), 7.29–7.24 (m, 3H), 7.15–7.13 (m, 3H), 7.02–7.00 (m, 2H), 3.46 (d, $J$ = 6.2 Hz, 2H), 1.33 (t, $J$ = 6.2 Hz, 1H), 1.20 (s, 6H), 0.16 (s, 6H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 146.9, 145.2, 141.2, 140.5, 133.6, 128.5, 128.4, 127.6, 127.6, 126.6, 70.8, 44.0, 26.2, 2.4; HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{20}H_{26}OSi$ 310.1747; Found 310.1750.

**(*Z*)-3-Benzylidene-2,2,4,4-tetramethyl-1,2-oxasilolane (S2)**




Colorless oil. $R_f$ = 0.63 (5% EtOAc/hexane); IR (ATR, $cm^{-1}$) 2957, 2919, 1458; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.54–7.51 (m, 2H), 7.48–7.44 (m, 3H), 3.89 (s, 2H), 1.39 (s, 6H), 0.48 (s, 6H).; $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 151.9, 139.6, 136.0, 128.2, 127.4, 127.3, 77.5, 44.5, 26.2, 0.28; HRMS (APCI-MS, positive): *m/z* $[M+H]^+$ Calcd for $C_{14}H_{21}OSi$ 233.1356; Found 233.1364.

**<u>Reaction of $PhMe_2SiLi$ 2a with S3</u>**

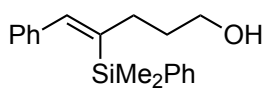



Bishomopropargylic alcohol **S3** gave the product with the same regioselectivity with homopropargylic alcohol and hydrosilylated product **S4** was obtained in 20% yield with concomitant formation of allene **S5** (26%) that also indicated the deprotonation of the propargylic position.

GP1 [from 5-phenylpent-4-yn-1-ol **S3** (160 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)] and GP2 [without column chromatography]. The residue was analyzed by $^1H$ NMR using 1,3,5-trimethoxybenzene as an internal standard. The mixture of **S4** (20% NMR yield), allene **S5** (26% NMR yield) along with unreacted starting material **S3**

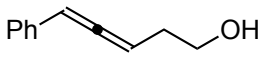
(20% NMR yield) was observed. Small portion of crude material was purified by preparative TLC to get analytical data of **S4** (20%) and **S5** (26%).

**(*Z*)-4-(Dimethylphenylsilyl)-5-phenylpent-4-en-1-ol (S4)**



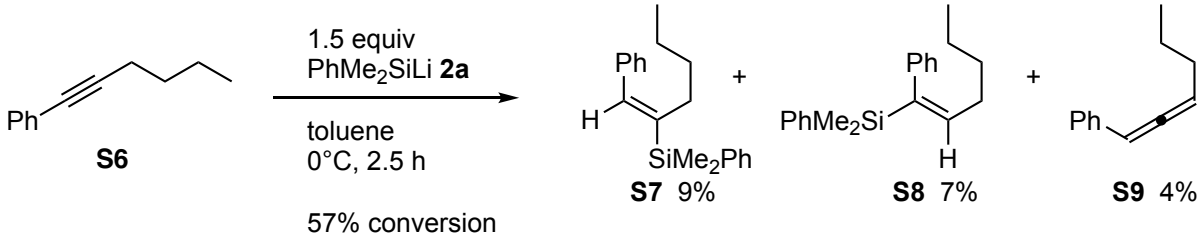

Colorless oil. $R_f$ = 0.26 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3326, 2932, 1591; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.47 (m, 2H), 7.33–7.29 (m, 3H), 7.31 (s, 1H), 7.18–7.15 (m, 3H), 7.11 (m, 2H), 3.64 (t, $J$ = 6.2 Hz, 2H), 2.33 (dt, $J$ = 8.2, 1.4 Hz, 2H), 1.72 (tt, $J$ = 8.2, 6.2 Hz, 2H), 1.15 (br, 1H), 0.16 (s, 6H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 143.7, 141.7, 140.0, 139.7, 133.8, 128.7, 128.6, 127.68, 127.66, 126.8, 62.7, 35.0, 33.4, –1.0; HRMS (APCI-MS, positive): *m/z* $[M+H]^+$ Calcd for $C_{19}H_{25}OSi$ 297.1669; Found 297.1673.

**5-phenylpenta-3,4-dien-1-ol (S5)**




All the resonances in $^1H$ NMR spectra were consistent with reported values.[13]

**Reaction of $PhMe_2SiLi$ with hex-1-yn-1-ylbenzene (S6)**



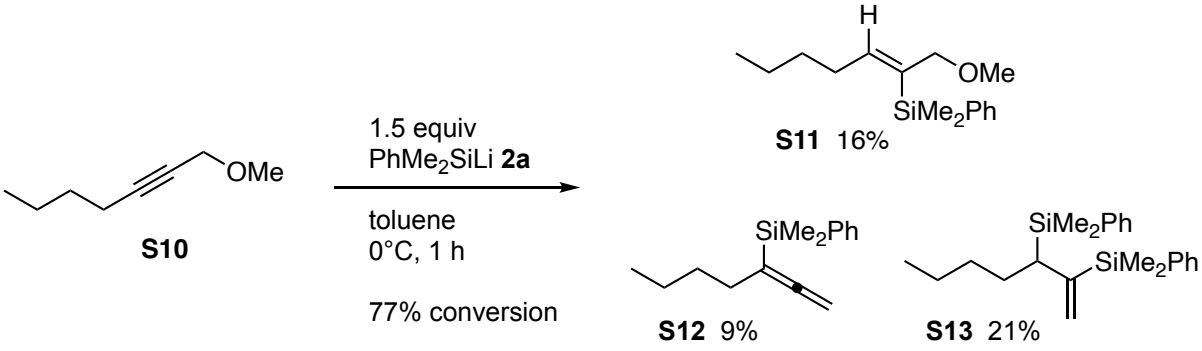

Disappearance of regioselectivity and reduced reactivity was observed for the silyllithation probably because of the absence of an appropriate coordinating functional group close to the triple bond. **S9** would be obtained probably due to the absence of anionic substituent (alkoxide) that would reduce the propensity for the undesired deprotonation of propargylic position.

Simple hexynyl benzene **S6** showed low reactivity and almost no regioselectivity for hydrosilylation. Both regioisomers **S7** and **S8** were obtained in low yields (9% and 7%) with the deprotonation product **S9** in 4%. Notably, the reaction proceeds via the *syn* mode of silyllithiation, which corroborates the importance of the nearby directing hydroxide for successful *anti* formulation and high regioselectivity of the transformation.

A 30-mL Schlenk tube was charged with hex-1-yn-1-ylbenzene **S6** (158 mg, 1.00 mmol), and toluene (10 mL). After the solution was stirred at 0 °C for 5 min, $PhMe_2SiLi$ **2a** (1.40 M in THF, 1.00 mL, 1.40 mmol) was slowly added and the resulting mixture was stirred at 0 °C for 2.5 h. Saturated aqueous $NH_4Cl$ (1.0 mL) was added, and the mixture was stirred

for 2 min at 0 °C. The mixture was poured into a separatory funnel with $CH_2Cl_2$ (10 mL), water (10 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with $CH_2Cl_2$ (10 mL × 2). The combined organic extract was washed with brine (10 mL), dried over $Na_2SO_4$ (ca. 10 g), filtered, and concentrated under reduced pressure. The residue was analyzed by $^1H$ NMR using 1,3,5-trimethoxybenzene as an internal standard. The mixture of silylated product **S7**[14] (9% NMR yield), disilylated product **S8**[14] (7% NMR yield), allene **S9**[15] (4% NMR yield) along with the unreacted ether **S6** (43% by NMR analysis) were observed.

**Reaction of $PhMe_2SiLi$ with 1-Methoxyhept-2-yne (S10)**



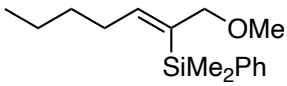

Since methoxide works not only as a directing group but also as a leaving group, the transformation from **S10** is more complex than the cases with alkoxide as a directing group. **S12** would be obtained via the initial silyllithiation of opposite regiochemistry, followed by the elimination of lithium methoxide. **S13** could possibly be obtained from **S11**, through $S_N2'$-type transformation.

In the case of *O*-methylated substrate **S10**, the *anti*-silylated product **S11** was obtained in 16% yield in concomitant with a silylated terminal allene **S12** in 9% yield and a doubly silylated compound **S3** in 21% (*vide supra*). Allene **S12** would be formed via the silylmetalation with opposite regioselectivity followed by the β-elimination of lithium methoxide. **S13** could possibly be obtained through silyllithiation of allene **S12**. Thus, the transformation loses the regioselectivity that was seen in the case of propargylic alkoxides.

A 30-mL Schlenk tube was charged with 1-methoxyhept-2-yne (**S10**, 126 mg, 1.00 mmol), and toluene (10 mL). After the solution was stirred at 0 °C for 5 min, $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.00 mL, 1.40 mmol) was slowly added and the resulting mixture was stirred at 0 °C for 1 h. Saturated aqueous $NH_4Cl$ solution (1.0 mL) was added, and the mixture was stirred at 0 °C for 2 min. The mixture was poured into a separatory funnel with $CH_2Cl_2$ (20 mL), water (20 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with $CH_2Cl_2$ (20 mL × 2). The combined organic extract was washed with brine (10 mL), dried over $Na_2SO_4$ (ca. 10 g), filtered, and concentrated under reduced pressure. The

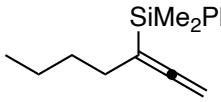
residue was analyzed by $^1$H NMR using 1,3,5-trimethoxybenzene as an internal standard. The mixture of **S11** (16% NMR yield), allene **S12** (9% NMR yield), disilylated product **S13** (21% NMR yield), along with unreacted ether **S10** (23% by NMR analysis) were observed. Small portion of the crude product was purified by preparative TLC to get analytical data of the products **S11**, **S12**, **S13**.

**(*Z*)-(1-Methoxyhept-2-en-2-yl)dimethylphenylsilane (S11)**



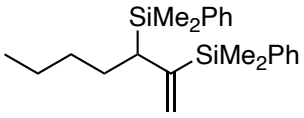

Colorless oil. $R_f$ = 0.48 (3% EtOAc/hexane); IR (ATR, cm$^{-1}$) 2955, 1616; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.54 (m, 2H), 7.33–7.31 (m, 3H), 6.27 (t, $J$ = 7.6 Hz, 1H), 3.92 (br, 2H), 3.24 (s, 3H), 1.96 (dt, $J$ = 7.6, 7.6 Hz, 2H), 1.21–1.10 (m, 4H), 0.76 (t, $J$ = 7.6 Hz, 3H), 0.40 (s, 6H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 148.1, 139.5, 134.0, 133.8, 128.7, 127.6, 79.3, 57.3, 31.8, 31.5, 22.3, 13.9, –1.5; HRMS (APCI-MS, positive): *m/z* [M–OMe]$^+$ Calcd for $C_{15}H_{23}Si$ 231.1564; Found 231.1567.

**Hepta-1,2-dien-3-yl-dimethylphenyl)silane (S12)**



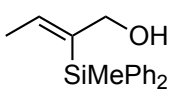

Colorless oil. All the resonances in $^1$H NMR spectra were consistent with the reported values.[16]

**Hept-1-ene-2,3-diylbis(dimethylphenylsilane) (S13)**



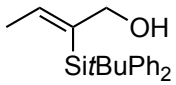

Colorless oil. $R_f$ = 0.80 (3% EtOAc/hexane) ; IR (ATR, cm$^{-1}$) 2955; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.48 (m, 2H), 7.43 (m, 2H), 7.37–7.30 (m, 6H), 5.55 (br, 1H), 5.45 (br, 1H), 1.86 (t, $J$ = 7.6 Hz, 1H), 1.48 (dt, $J$ = 7.6, 7.6 Hz, 2H), 1.19–1.01 (m, 3H), 0.89–0.82 (m, 1H), 0.71 (t, $J$ = 7.6 Hz, 3H), 0.25 (s, 3H), 0.244 (s, 3H), 0.240 (s, 3H), 0.12 (s, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 152.6, 139.0, 138.3, 134.3, 134.2, 128.8, 128.8, 127.6, 127.5, 124.3, 32.4, 31.8, 31.6, 22.7, 13.9, –2.8, –3.2, –3.3, –4.7; HRMS (APCI-MS, positive): *m/z* [M–$CH_3$]$^+$ Calcd for $C_{22}H_{31}Si_2$: 351.1959; Found 351.1971.

**(*Z*)-2-(Methyldiphenylsilyl)but-2-en-1-ol (4ab)**



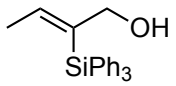

GP1 [from **1a** (70.1 mg, 1.00 mmol) with $Ph_2MeSiLi$ **2b** (1.5 M in THF, 1.0 mL, 1.50 mmol)] and GP2 [column chromatography with an eluent (hexane to hexane/EtOAc = 9/1)] afforded **4ab** as a pale yellow oil (260 mg, 0.969 mmol, 97%). $R_f$ = 0.38 (20% EtOAc/hexane); IR (ATR, cm$^{-1}$) 3318, 1618; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.57–7.55 (m, 4H), 7.40–7.34 (m, 6H), 6.57 (q, $J$ = 7.0 Hz, 1H), 4.11 (dq, $J$ = 6.1 Hz, 2H), 1.61 (d, $J$ = 7.0 Hz, 3H), 1.13 (t, $J$ = 6.1 Hz, 1H), 0.74 (s, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 141.8, 136.5, 136.4, 134.8, 129.2, 127.9, 69.1, 18.5, –2.5; HRMS (APCI-MS, positive): *m/z* [M–OH]$^+$ Calcd for $C_{17}H_{19}Si$ 251.1251; Found 251.1258.

**(*Z*)-2-(*tert*-Butyldiphenylsilyl)but-2-en-1-ol (4ac)**



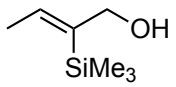

GP1 [from **1a** (70.1 mg, 1.00 mmol) with *t*BuPh$_2$SiLi **2c** (1.5 M in THF, 1.0 mL, 1.5 mmol)] and GP2 [column chromatography with an eluent (hexane to hexane/EtOAc = 9/1)] afforded **4ac** as a white solid (291 mg, 0.936 mmol, 94%). $R_f$ = 0.48 (20% EtOAc/hexane); IR (ATR, cm$^{-1}$) 3342, 2855; mp 81.0–83.0 °C; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.65–7.63 (m, 4H), 7.40–7.33 (m, 6H), 6.66 (q, $J$ = 7.2 Hz, 1H), 4.30 (d, $J$ = 6.3 Hz, 2H), 1.47 (d, $J$ = 7.2 Hz, 3H), 1.17 (m, 10H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 143.5, 135.9, 135.8, 135.3, 129.0, 127.8, 69.7, 29.0, 20.0, 19.2; HRMS (APCI-MS, positive): *m/z* [M–OH]$^+$ Calcd for $C_{20}H_{25}Si$ 293.1720; Found 293.1727.

**(*Z*)-2-(Triphenylsilyl)but-2-en-1-ol (4ad)**



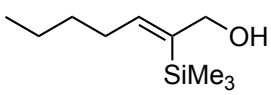

GP1 [from **1a** (70.1 mg, 1.00 mmol) with $Ph_3SiLi$ **2d** (0.93 M in THF, 1.5 mL, 1.4 mmol)] and GP2 [column chromatography with an eluent (hexane to hexane/EtOAc = 9/1)] afforded **4ad** as an off-white solid (236 mg, 0.713 mmol, 71%). $R_f$ = 0.37 (20% EtOAc/hexane); IR (ATR, cm$^{-1}$) 3277, 1611; mp 111.0–113.5 °C; $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 7.53–7.51 (m, 6H), 7.44–7.37 (m, 9H), 6.71 (q, $J$ = 6.9 Hz, 1H), 4.64 (t, $J$ = 4.8 Hz, 1H), 3.81 (m, 2H), 1.45 (d, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (151 MHz, DMSO-$d_6$) $\delta$ 139.1, 135.5, 134.4, 134.3, 129.4, 127.9, 66.2, 19.1; HRMS (APCI-MS, positive): *m/z* [M–OH]$^+$ Calcd for $C_{22}H_{21}Si$ 313.1407; Found 313.1406.

**(*Z*)-2-(trimethylsilyl)but-2-en-1-ol (4ae)**




GP1 [from **1a** (70.1 mg, 1.00 mmol) with $Me_3SiLi$ **2e** (0.24 M in THF, 8.4 mL, 1.50 mmol)] and GP2 [column chromatography with an eluent (hexane to hexane/EtOAc = 9/1)] afforded **4ae** as a colorless oil (46.7 mg, 0.324 mmol, 32%). $R_f$ = 0.40 (20% EtOAc/hexane); IR (ATR, cm$^{-1}$) 3311, 2953; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 6.28 (q, $J$ = 6.9 Hz, 1H), 4.10 (br, 2H), 1.79 (d, $J$ = 6.9 Hz, 3H), 1.26 (s, 1H), 0.18 (s, 9H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 140.2, 138.8, 69.2, 17.4, –0.2; HRMS (APCI-MS, positive): *m/z* [M–H]$^+$ Calcd for $C_7H_{15}OSi$ 143.0892; Found 143.0887.

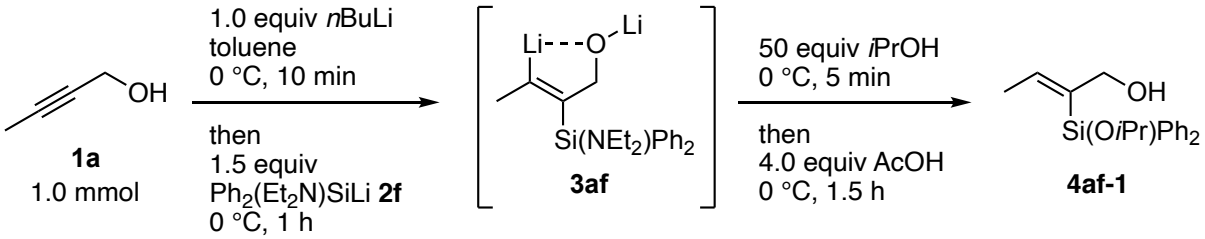
**(*Z*)-2-(trimethylsilyl)hept-2-en-1-ol (4be)**




GP1 [from **1b** (112 mg, 1.00 mmol) with $Me_3SiLi$ **2e** (0.24 M in THF, 8.4 mL, 1.50 mmol)] and GP2 [column chromatography with an eluent (hexane to hexane/EtOAc = 9/1)] afforded **4be** as a pale yellow oil (112 mg, 0.601 mmol, 60%). $R_f$ = 0.48 (20% EtOAc/hexane); IR (ATR, cm$^{-1}$) 3306, 2955, 1616; $^1$H NMR (600 MHz, $CDCl_3$)

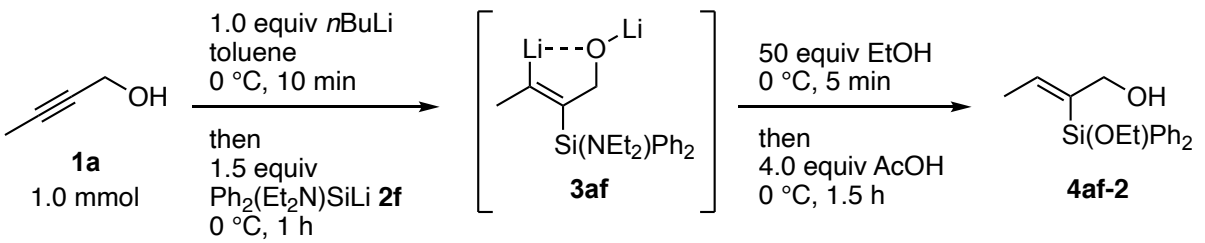
$\delta$ 6.18 (t, $J$ = 7.6 Hz, 1H), 4.13–4.11 (m, 2H), 2.16–2.13 (m, 2H), 1.39–1.30 (m, 4H), 1.10 (m, 1H), 0.92–0.90 (m, 3H), 0.18 (s, 9H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 144.8, 138.8, 69.1, 32.0, 31.5, 22.4, 14.0, 0.0; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{10}H_{21}Si$ 169.1407; Found 169.1407.

**(*Z*)-2-(Isopropoxydiphenylsilyl)but-2-en-1-ol (4af-1)**



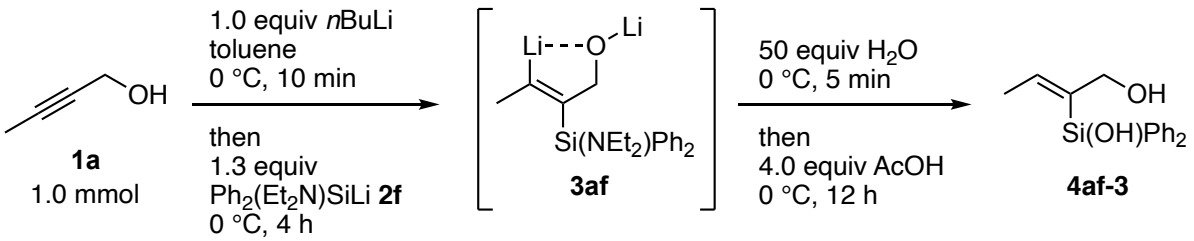

After the sequences in GP1 [from **1a** (70.1 mg, 1.00 mmol) with $Ph_2(NEt_2)SiLi$ **2f** (0.50 M in THF, 3.0 mL, 1.50 mmol)], anhydrous 2-propanol (3.83 mL, 50.0 mmol) was added to the resulting **3ag** and the reaction mixture was stirred at 0 °C for 5 min. AcOH (227 μL, 4.00 mmol) was added to the reaction, and the mixture was stirred at 0 °C for 1.5 h. The reaction was quenched with saturated aqueous $NH_4Cl$ (1.0 mL) and the mixture was poured into a separatory funnel with $CH_2Cl_2$ (10 mL), water (10 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with $CH_2Cl_2$ (10 mL × 2). The combined organic extract was washed with brine (10 mL), dried over $Na_2SO_4$ (ca. 10 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane to hexane/EtOAc = 7/1) to give **4af-1** (167 mg, 0.543 mmol, 54%) as a colorless oil. $R_f$ = 0.42 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3408, 2971, 1621; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.73–7.71 (m, 4H), 7.47–7.44 (m, 2H), 7.43–7.40 (m, 4H), 6.46 (q, $J$ = 6.9 Hz, 1H), 4.29 (d, $J$ = 6.9 Hz, 2H), 4.09 (sept, $J$ = 6.2 Hz, 1H), 2.82 (t, $J$ = 6.9 Hz, 1H), 1.52 (dt, $J$ = 6.9 Hz, 3H), 1.10 (d, $J$ = 6.2 Hz, 6H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 142.0, 136.7, 135.2, 134.4, 130.0, 127.9, 69.7, 66.4, 25.4, 18.4; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{19}H_{23}OSi$ 295.1513; Found 295.1507.

**(*Z*)-2-(Ethoxydiphenylsilyl)but-2-en-1-ol (4af-2)**



After the sequences in GP1 [from **1a** (70.1 mg, 1.00 mmol) with $Ph_2(NEt_2)SiLi$ **2f** (0.50 M in THF, 3.0 mL, 1.50 mmol)], anhydrous ethanol (4.97 mL, 50.0 mmol) was added to **3af**, and the reaction mixture was stirred at 0 °C for 5 min. AcOH (227 μL, 4.00 mmol) was added to the reaction, and the mixture was stirred at 0 °C for 1.5 h. The reaction was quenched with saturated aqueous $NH_4Cl$ (1.0 mL) and the mixture was poured into a separatory funnel with $CH_2Cl_2$ (10 mL), water (10 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with $CH_2Cl_2$ (10 mL × 2). The combined organic extract was washed with brine (10 mL), dried over $Na_2SO_4$ (ca. 10 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane to hexane/EtOAc = 7/1) to give **4af-2** (236 mg, 0.792 mmol, 79%) as a colorless oil. $R_f$ = 0.39 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3352, 1621; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.70–7.68 (m, 4H), 7.47–7.45 (m, 2H), 7.43–7.40 (m, 4H), 6.50 (q, $J$ = 6.9 Hz, 1H), 4.28 (d, $J$ = 6.9 Hz, 2H), 3.74 (q, $J$ = 6.9 Hz, 2H), 2.64 (t, $J$ = 6.9 Hz, 1H), 1.57 (d, $J$ = 6.9 Hz, 4H), 1.17 (t, $J$ = 6.9 Hz, 3H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 142.4, 136.3, 135.1, 133.9, 130.1, 128.0, 69.4, 59.3, 18.3, 18.1; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{18}H_{21}OSi$ 281.1356; Found 281.1346.

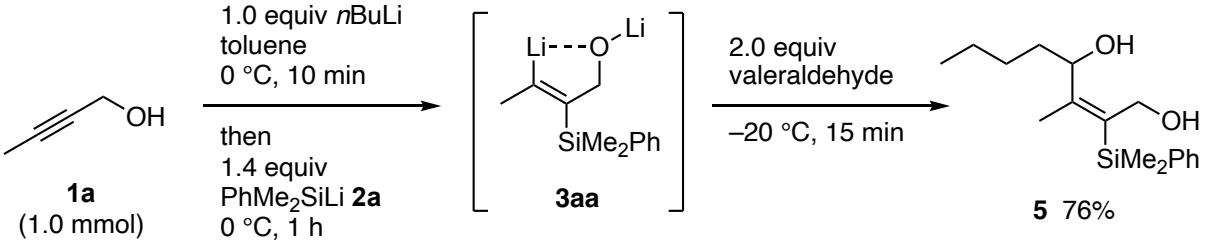
**(*Z*)-(1-hydroxybut-2-en-2-yl)diphenylsilanol (4af-3)**




After the sequences in GP1 [from **1a** (70.1 mg, 1.00 mmol) with $Ph_2(NEt_2)SiLi$ **2f** (0.50 M in THF, 2.60 mL, 1.30 mmol), reaction time = 4 h], ice cooled solution of $H_2O$ (903 μL, 50 mmol) in THF (20.0 mL) was added to **3af** over 30 seconds to the reaction, and the mixture was stirred for 5 min at 0 °C. AcOH (227 μL, 4.00 mmol) was added to the reaction, and the mixture was stirred for 12 h at 0 °C. The reaction mixture was quenched with saturated aqueous $NH_4Cl$ (1.0 mL) and the mixture was poured into a separatory funnel with EtOAc (30 mL), water (30 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with EtOAc (30 mL × 2). The combined organic extract was washed with sequentially with saturated aqueous $NaHCO_3$ solution (30.0 mL), brine (30.0 mL), dried over $Na_2SO_4$ (ca. 10 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane to hexane/EtOAc = 1/1) to give **4af-3** (210 mg, 0.776 mmol, 78%) as a colorless oil which becomes white solid upon standing at room

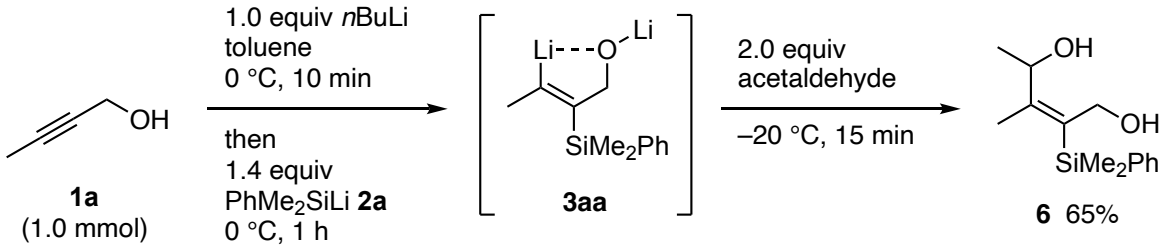
temperature (bath temperature 35 °C). $R_f$ = 0.44 (30% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3292, 1616; mp 84.0–86.0 °C; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.68–7.65 (m, 4H), 7.46–7.43 (m, 2H), 7.41–7.38 (m, 4H), 6.51 (q, $J$ = 6.9 Hz, 1H), 4.33 (d, $J$ = 3.6 Hz, 2H), 3.25 (br, 1H), 1.94 (s, 1H), 1.59 (d, $J$ = 6.9 Hz, 3H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 142.8, 136.5, 135.8, 134.6, 130.0, 127.9, 69.8, 18.5; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{16}H_{17}OSi$ 253.1043; Found 253.1042.

**(*E*)-2-(Dimethylphenylsilyl)-3-methyloct-2-ene-1,4-diol (5)**




GP1 [from but-2-yn-1-ol **1a** (70.1 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)] and GP3 [freshly distilled valeraldehyde (172 mg, 213 μL, 2.00 mmol) at –20 °C for 15 min, column chromatography on silica gel (hexane to hexane/EtOAc = 2.3/1)] afforded **5** (223 mg, 0.763 mmol, 76%) as a light brown oil. $R_f$ = 0.47 (50% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3326, 2954, 1603; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.54 (m, 2H), 7.35–7.33 (m, 3H), 4.75 (dd, $J$ = 7.6, 6.2 Hz, 1H), 4.36 (d, $J$ = 11.0 Hz, 1H), 4.18 (d, $J$ = 11.7 Hz, 1H), 2.08 (br, 1H), 1.71 (s, 3H), 1.69–1.61 (m, 1H), 1.54 (br, 1H), 1.51–1.45 (m, 1H), 1.41–1.32 (m, 3H), 1.25–1.19 (m, 1H), 0.91 (t, $J$ = 7.2 Hz, 3H), 0.46 (s, 3H), 0.45 (s, 3H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 155.1, 139.6, 133.6, 132.7, 128.7, 127.8, 70.4, 59.7, 34.5, 28.1, 22.7, 17.6, 14.0, –0.8, –0.9; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{17}H_{27}OSi$ 275.1826; Found 275.1824.

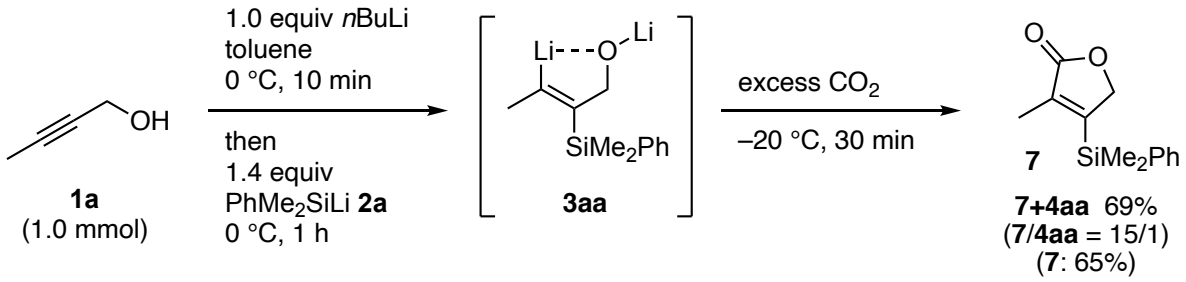
**(*E*)-2-(Dimethylphenylsilyl)-3-methylpent-2-ene-1,4-diol (6)**




A three-neck 300-mL round-bottomed flask equipped with nitrogen inlet and septum was charged under $N_2$ atomosphere with but-2-yn-1-ol **1a** (701 mg, 10.0 mmol) and toluene (100 mL). After the solution was stirred at 0 °C for 10 min in an ice bath, *n*BuLi (1.43 M in hexane, 6.66 mL, 10.0 mmol) was slowly added and the resulting mixture was stirred at 0 °C

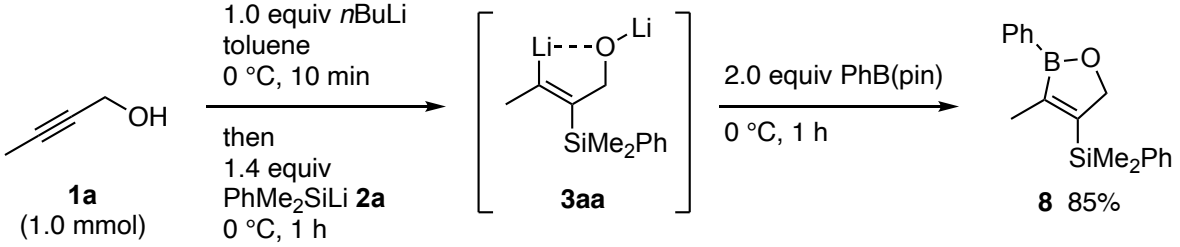
for 10 min. $PhMe_2SiLi$ (**2a**, 1.40 M in THF, 10.0 mL, 14.0 mmol) was slowly added to the mixture over 5 min. The resulting solution was stirred at 0 °C for 1 h. The reaction mixture was cooled to –20 °C and freshly distilled acetaldehyde (1.12 mL, 20.0 mmol) was added and the mixture was stirred at –20 °C for 15 min. The reaction was quenched with saturated aqueous $NH_4Cl$ (10 mL) and the mixture was stirred at 0 °C for 2 min. The mixture was poured into a separatory funnel with $CH_2Cl_2$ (100 mL), water (100 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with $CH_2Cl_2$ (10-0 mL × 2). The combined organic phase was washed with brine (150 mL), dried over $Na_2SO_4$ (ca. 100 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane to hexane/EtOAc = 1/1) to give **6** (1.63 g, 6.49 mmol, 65%) as a colorless oil. $R_f$ = 0.38 (50% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3323, 2971, 1605; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.53 (m, 2H), 7.36–7.33 (m, 3H), 4.98 (q, $J$ = 6.2 Hz, 1H), 4.34 (d, $J$ = 11.7 Hz, 1H), 4.20 (d, $J$ = 11.7 Hz, 1H), 2.09 (br, 1H), 1.75 (s, 3H), 1.61(br, 1H), 1.30 (d, $J$ = 6.9 Hz, 3H), 0.46 (s, 3H), 0.45 (s, 3H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 156.1, 139.5, 133.6, 131.3, 128.7, 127.7, 66.2, 59.4, 21.2, 17.5, –0.8, –1.0; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{14}H_{21}OSi$ 233.1356; Found 233.1353.

**4-(Dimethylphenylsilyl)-3-methylfuran-2(5*H*)-one (7)**



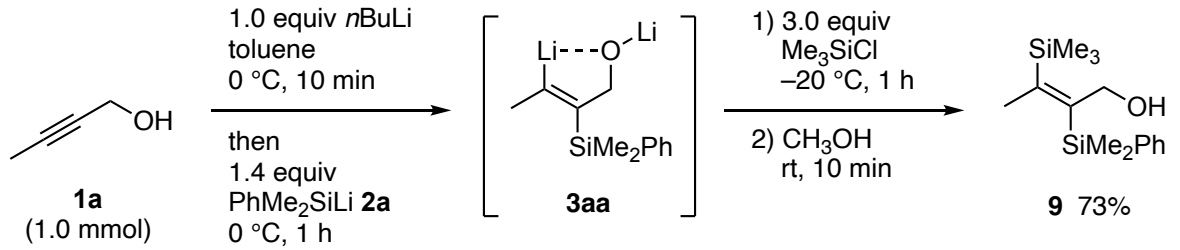

GP1 [from but-2-yn-1-ol **1a** (70.1 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)] and GP3 [dry ice (2.5 g) at –20 °C for 30 min. After quenching with $H_2O$ (10 mL), pH was adjusted to pH = 3 by 1 M HCl aq. at 0 °C, column chromatography on silica gel (hexane to hexane/EtOAc = 6/1)] afforded an inseparable mixture of **7** and **4aa** (**7**:**4aa** = 15:1) (159 mg, 0.685 mmol, 69%, **7**: 65%) as a colorless oil. $R_f$ = 0.38 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 1747; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.49 (m, 2H), 7.45–7.38 (m, 3H), 4.71 (q, $J$ = 2.1 Hz, 2H), 1.88 (t, $J$ = 2.1 Hz, 3H), 0.54 (s, 6H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 175.3, 157.7, 137.3, 134.7, 133.6, 130.0, 128.3, 74.0, 11.4, –3.3; HRMS (APCI-MS, positive): *m/z* $[M+H]^+$ Calcd for $C_{13}H_{17}O_2Si$ 233.0992; Found 233.0995.

**Dimethyl(3-methyl-2-phenyl-2,5-dihydro-1,2-oxaborol-4-yl)phenylsilane (8)**



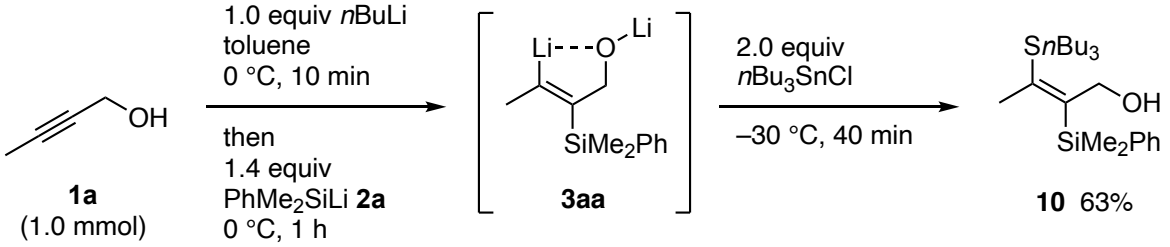

GP1 [from but-2-yn-1-ol **1a** (70.1 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)] and GP3 [phenylboronic acid pinacol ester (204 mg, 2.00 mmol) at 0 °C for 1 h, column chromatography on silica gel (hexane to hexane/EtOAc = 19/1)] afforded **8** (249 mg, 0.850 mmol, 85%) as a colorless oil. $R_f$ = 0.52 (5% EtOAc/hexane); IR (ATR, $cm^{-1}$) 2954, 1599; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.97 (d, $J$ = 6.9 Hz, 2H), 7.54 (m, 2H), 7.48 (m, 1H), 7.42 (t, $J$ = 7.6 Hz, 2H), 7.40–7.35 (m, 3H), 4.91 (br, 2H), 2.18 (m, 3H), 0.52 (s, 6H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 164.2, 137.5, 134.7, 133.7, 130.9, 129.3, 128.0, 127.8, 81.7, 17.0, –2.0 (The carbon atom bearing the boron atom was not observed due to the quadrupolar relaxation mechanism of $^{11}B$ nucleus.); HRMS (APCI-MS, positive): *m/z* $[M+H]^+$ Calcd for $C_{18}H_{22}BOSi$ 293.1527; Found 293.1526.

**(*E*)-2-(Dimethylphenylsilyl)-3-(trimethylsilyl)but-2-en-1-ol (9)**



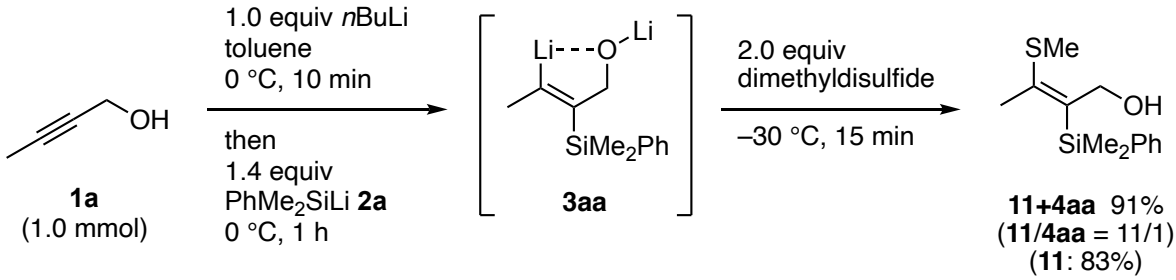

GP1 [from but-2-yn-1-ol **1a** (70.1 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)] and GP3 [TMSCl (326 mg, 381 μL, 3.00 mmol) at –20 °C for 1 h. The crude residue was dissolved in $CH_3OH$ (5 mL) and stirred at room temperature for 10 min. Column chromatography on silica gel (hexane to hexane/EtOAc = 19/1)] afforded **9** (202 mg, 0.725 mmol, 73%) as a colorless oil. $R_f$ = 0.62 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3446, 2952; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.54 (m, 2H), 7.35–7.33 (m, 3H), 4.29 (d, $J$ = 6.2 Hz, 2H), 1.79 (s, 3H), 0.95 (t, $J$ = 6.2 Hz, 1H), 0.46 (s, 6H), 0.19 (s, 9H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 157.5, 149.7, 140.0, 133.6, 128.6, 127.8, 65.9, 24.3, 0.9, –0.6; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{15}H_{25}Si_2$: 261.1489; Found 261.1490.

**(*E*)-2-(Dimethylphenylsilyl)-3-(tributylstannyl)but-2-en-1-ol (10)**



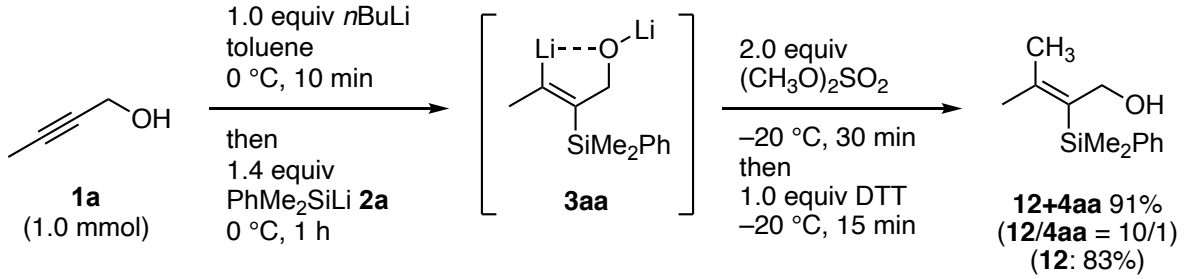

GP1 [from but-2-yn-1-ol **1a** (70.1 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)] and GP3 [tributyltin chloride (651 mg, 543 μL, 2.00 mmol) at –30 °C for 40 min, column chromatography on silica gel (hexane to hexane/EtOAc = 19/1)] afforded **10** (310 mg, 0.625 mmol, 63%) as a pale yellow oil. $R_f$ = 0.38 (5% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3447, 2921; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.55 (m, 2H), 7.35–7.32 (m, 3H), 4.13–4.10 (m, 2H), 1.94 (s, $^3J_{SnH}$ = 46.7 Hz, 3H), 1.50–1.47 (m, 6H), 1.35–1.28 (m, 6H), 0.96–0.93 (m, 7H), 0.90 (t, $J$ = 7.6 Hz, 9H), 0.46 (s, 6H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 162.6, 148.4, 140.1, 133.7, 128.6, 127.8, 71.1, 29.2 (3X, $^3J_{SnC}$ = 20.2 Hz, 3H), 27.4 (3X, $^2J_{SnC}$ = 56.4 Hz), 27.0, 13.7, 11.1 (3X, $^1J_{SnC}$ = 312.1 Hz), –0.5; HRMS (APCI-MS, positive): *m/z* $[M–H]^+$ Calcd for $C_{24}H_{43}OSiSn$ 495.2103; Found 495.2132.

**(*E*)-2-(Dimethylphenylsilyl)-3-(methylthio)but-2-en-1-ol (11)**



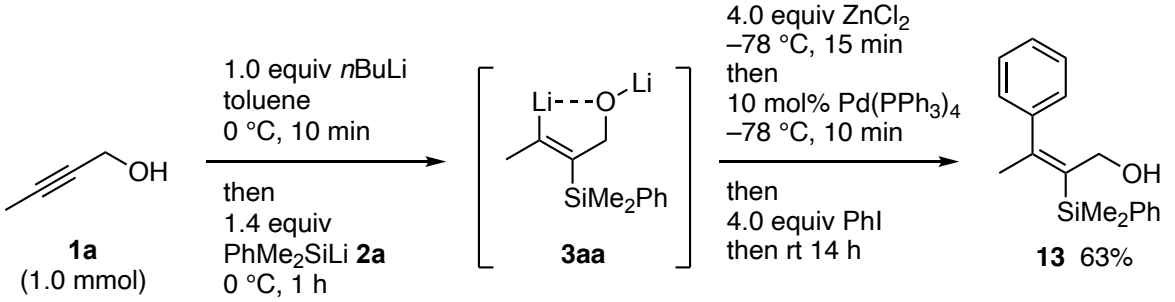

GP1 [from but-2-yn-1-ol **1a** (70.1 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)] and GP3 [dimethyl disulfide (188 mg, 178 μL, 2.00 mmol) at –30 °C for 15 min, column chromatography on silica gel (pretreated by flushing 2% *n*-butyl amine in hexane (200 mL) followed by 100% hexane (500 mL)) (hexane/EtOAc = 7/1)] afforded inseparable mixture of **11** and **4aa** (**11**/**4aa** = 11:1) (225 mg, 0.905 mmol, 91%, **11**: 83%) as a pale yellow oil. $R_f$ = 0.38 (5% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3409, 1560; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.54 (m, 2H), 7.33 (m, 3H), 4.42 (s, 2H), 2.29 (s, 3H), 2.00 (s, 3H), 0.46 (s, 6H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 148.3, 139.5, 133.6, 132.9, 128.8, 127.8, 62.5, 22.5, 14.4, –0.8; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{13}H_{19}SSi$ 235.0971; Found 235.0974.

**2-(Dimethylphenylsilyl)-3-methylbut-2-en-1-ol (12)**




GP1 [from but-2-yn-1-ol **1a** (70.1 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)] and GP3 [dimethyl sulfate (252 mg, 190 μL, 2.00 mmol) at –20 °C for 30 min followed by DL-dithiothreitol (154 mg, 1.00 mmol) in THF (500 μL) at –20 °C for 15 min, column chromatography on silica gel (hexane/EtOAc = 9/1)] afforded an inseparable mixture of **12** and **4aa** (**12**:**4aa** = 10:1) (199 mg, 0.908 mmol, 91%, **12**: 83%) as a colorless oil. $R_f$ = 0.38 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3336, 2910, 1609; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.54 (m, 2H), 7.36–7.33 (m, 3H), 4.24 (d, $J$ = 5.5 Hz, 2H), 1.89 (s, 3H), 1.74 (s, 3H), 0.94 (t, $J$ = 5.5 Hz, 1H), 0.44 (s, 6H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 150.6, 140.1, 133.6, 130.5, 128.6, 127.7, 61.9, 26.0, 21.1, –0.7; HRMS (APCI-MS, positive): $m/z$ $[M–OH]^+$ Calcd for $C_{13}H_{19}Si$ 203.1251; Found 203.1245.

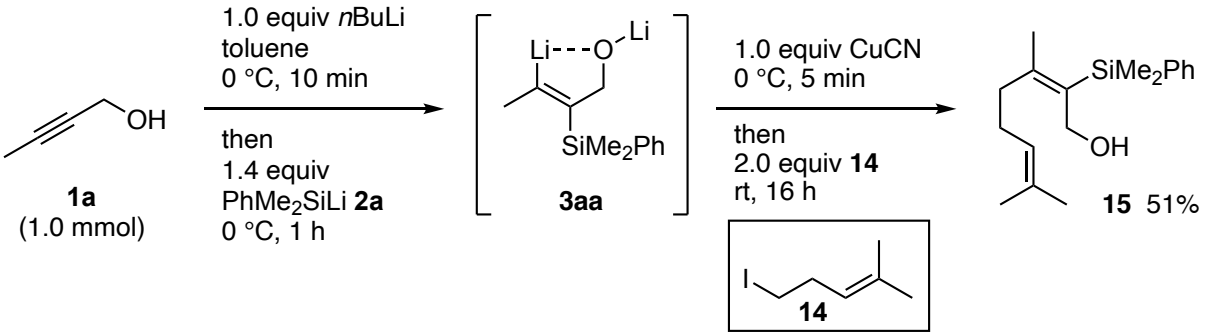
**(*E*)-2-(Dimethylphenylsilyl)-3-phenylbut-2-en-1-ol (13)**




After the sequence of GP1 [from but-2-yn-1-ol **1a** (70.1 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)], the reaction mixture was cooled to –78 °C and $ZnCl_2$ (545 mg, 4.00 mmol, in 2.0 mL THF) was added and the mixture was stirred at –78 °C for 30 min. $Pd(PPh_3)_4$ (116 mg, 0.100 mmol, in 3.0 mL THF) was added to the reaction and the mixture was stirred for 10 min at –78 °C. Iodobenzene (816 mg, 4.00 mmol) was added to the reaction and the mixture was stirred at –78 °C for 1 h. The resulting mixture was warmed to room temperature and stirred for 14 h. After 1 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL), was added. The mixture was poured into a separatory funnel with $CH_2Cl_2$ (20 mL), water (10 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with $CH_2Cl_2$ (20 mL × 2). The combined organic extract

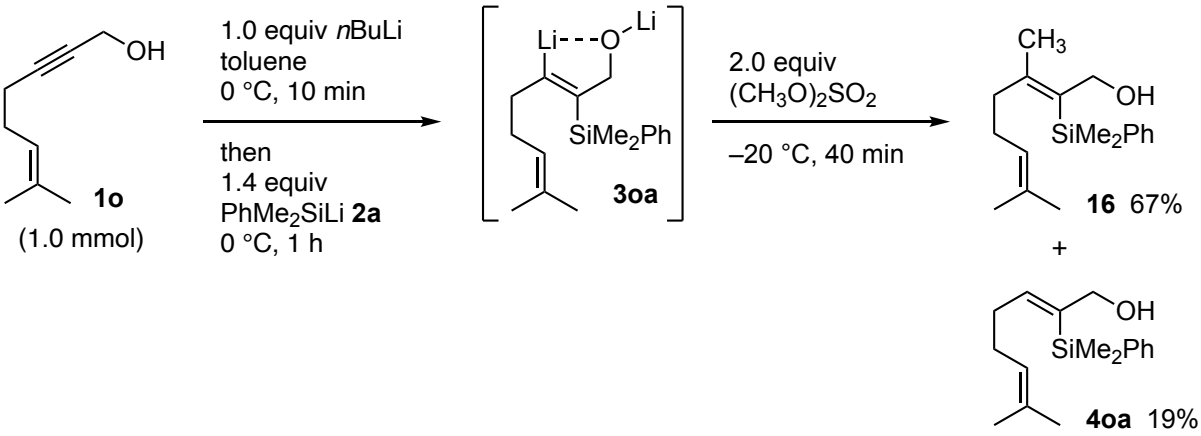
was washed with brine (10 mL), dried over $Na_2SO_4$ (ca. 10 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane to hexane/EtOAc = 9/1) to give **13** (190 mg, 0.673 mmol, 67%) as a colorless oil. $R_f$ = 0.52 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3414, 1592; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.65 (m, 2H), 7.40–7.37 (m, 3H), 7.34 (m, 2H), 7.28–7.25 (m, 1H), 7.15 (m, 2H), 4.05 (d, $J$ = 5.5 Hz, 2H), 1.99 (s, 3H), 1.02 (t, $J$ = 5.5 Hz, 1H), 0.55 (s, 6H).; $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 153.5, 143.9, 139.8, 133.7, 133.4, 128.8, 128.1, 127.9, 127.4, 126.8, 63.7, 26.1, –0.8; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{18}H_{21}Si$ 265.1407; Found 265.1409.

**(*E*)-2-(Dimethylphenylsilyl)-3,7-dimethylocta-2,6-dien-1-ol (15)**



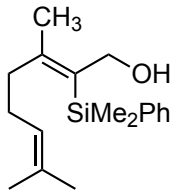

After the sequences in GP1 [from but-2-yn-1-ol **1a** (70.1 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)], CuCN (89.6 mg, 1.00 mmol) was added to the reaction and the mixture was stirred at 0 °C for 10 min. GP3 [5-Iodo-2-methylpent-2-ene **14** (210 mg, 2.00 mmol), at 0 °C for 10 min followed by at room temperature for 16 h. column chromatography on silica gel (hexane to hexane/EtOAc = 9/1)] afforded **15** (146 mg, 0.506 mmol, 51%) as a colorless oil. $R_f$ = 0.60 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3394, 2913, 1604; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.53 (m, 2H), 7.35–7.32 (m, 3H), 5.12 (t, $J$ = 7.6 Hz, 1H), 4.21 (d, $J$ = 5.5 Hz, 2H), 2.28 (t, $J$ = 7.6 Hz, 2H), 2.12 (dt, $J$ = 7.6, 7.6 Hz, 2H), 1.71 (s, 6H), 1.59 (s, 3H), 1.02 (t, $J$ = 5.5 Hz, 1H), 0.44 (s, 6H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 153.5, 140.2, 133.6, 132.7, 131.4, 128.6, 127.7, 123.9, 61.4, 34.6, 27.0, 25.6, 23.7, 17.6, –0.8; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{18}H_{27}Si$ 271.1877; Found 271.1875.

**Reaction of $PhMe_2SiLi$ 2a with 1o**



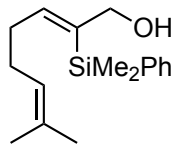

GP1 [from 7-methyloct-6-en-2-yn-1-ol (**1o**, 138 mg, 1.00 mmol) with $PhMe_2SiLi$ **2a** (1.4 M in THF, 1.0 mL, 1.4 mmol)] and GP3 [dimethyl sulfate (252 mg, 190 μL, 2.00 mmol) at –20 °C for 30 min followed by DL-dithiothreitol (154 mg, 1.00 mmol) in THF (500 μL) at –20 °C for 15 min, column chromatography on silica gel (hexane/EtOAc = 9/1)] afforded **16** (195 mg, 0.674 mmol, 67%) as a colorless oil and protonated product **4oa** (52.3 mg, 0.190 mmol, 19%) as a colorless oil

**(*Z*)-2-(Dimethylphenylsilyl)-3,7-dimethylocta-2,6-dien-1-ol (16)**



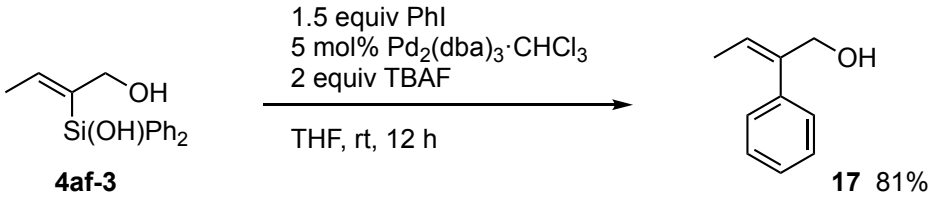

Colorless oil. $R_f$ = 0.43 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3366, 2913, 1602; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.54 (m, 2H), 7.34–7.32 (m, 3H), 4.85 (t, $J$ = 7.6 Hz, 1H), 4.22 (d, $J$ = 4.8 Hz, 2H), 2.10–2.08 (m, 2H), 1.95–1.92 (m, 2H), 1.89 (s, 3H), 1.62 (s, 3H), 1.51 (s, 3H), 0.93 (br, 1H), 0.44 (s, 6H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 154.6, 140.2, 133.7, 131.5, 131.1, 128.6, 127.7, 123.6, 62.0, 39.8, 26.9, 25.6, 18.4, 17.6, –0.4; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{18}H_{27}Si$ 271.1877; Found 271.1878.

**(*Z*)-2-(Dimethylphenylsilyl)-7-methylocta-2,6-dien-1-ol (4oa)**




Colorless oil. $R_f$ = 0.50 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3313, 2912, 1615; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.55 (m, 2H), 7.36–7.33 (m, 3H), 6.29 (t, $J$ = 7.6 Hz, 1H), 4.97 (t, $J$ = 7.6 Hz, 1H), 4.16 (d, $J$ = 5.5, 2H), 2.08–2.02 (m, 2H), 1.96–1.91 (m, 2H), 1.64 (s, 3H), 1.52 (s, 3H), 1.16 (br, 1H), 0.44 (s, 6H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 146.0, 139.1, 137.3, 133.7, 131.9, 128.9, 127.8, 123.5, 69.3, 32.2, 27.8, 25.6, 17.6, –1.3; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{17}H_{25}Si$ 257.1720; Found 257.1717.

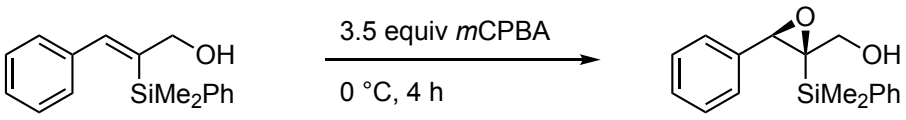
**(*E*)-2-phenylbut-2-en-1-ol (17).**[17]




**4af-3** **17** 81%

A 10-mL round-bottomed flask was charged with **4af-3** (60.0 mg, 0.222 mmol), iodobenzene (67.9 mg, 37 μL, 0.333 mmol), and THF (1.0 mL). $Pd_2(dba)_3{\cdot}CHCl_3$ (11.5 mg, 0.011 mmol) and TBAF (1.0 M in THF, 444 μL, 0.444 mmol) were added to the reaction and the mixture was stirred at room temperature for 12 h. The mixture was diluted with ethyl acetate (10 mL) and filtered through a small pad of silica gel, and the silica pad was washed with ethyl acetate (10 mL). The filtrate was concentrated under reduced pressure, residue was purified by column chromatography on silica gel (hexane to hexane/EtOAc = 4/1) to give **17** (26.7 mg, 0.180 mmol, 81%) as a colorless oil. $R_f$ = 0.50 (30% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3317, 2916; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.37 (t, $J$ = 7.6 Hz, 2H), 7.29 (t, $J$ = 7.6 Hz, 1H), 7.24 (d, $J$ = 7.6 Hz, 2H), 5.84 (q, $J$ = 6.9 Hz, 1H), 4.33 (s, 2H), 1.65 (d, $J$ = 6.9 Hz, 3H), 1.58 (br, 1H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 140.9, 138.2, 128.7, 128.3, 127.0, 123.4, 68.1, 14.4; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{10}H_{11}OSi$ 131.0855; Found 131.0853.

**(2*S**,3*R**)-2-(dimethylphenylsilyl)-2,3-epoxy-3-phenyl-1-propanol (18)**

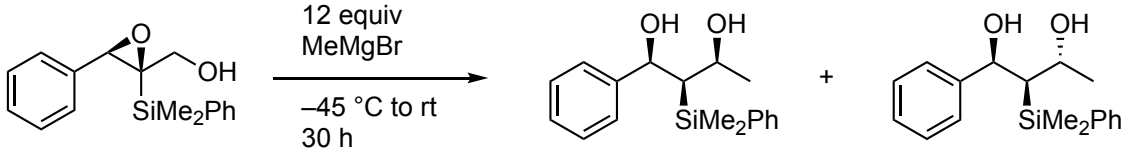



**4da** **18** 81%

A 100-mL three-neck round-bottomed flask was charged with diol **4da** (350 mg, 1.30 mmol) and $CH_2Cl_2$ (21 mL). After the solution was stirred at 0 °C for 5 min, *m*-CPBA (~72%, 1.10 g, 4.56 mmol) was added portionwise over 5 min, and the resulting mixture was stirred at 0 °C for 4 h. 20% aqueous $Na_2SO_3$ solution (60 mL) was added to the reaction, and mixture was stirred at 0 °C for 30 min. The mixture was poured into a separatory funnel with $CH_2Cl_2$ (50 mL), and partitioned. The organic phase was collected, and the aqueous phase was extracted with $CH_2Cl_2$ (50 mL × 2). The combined organic extract was washed with saturated aqueous $NaHCO_3$ solution (50 mL × 3), dried over $Na_2SO_4$ (ca. 70 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane to hexane/EtOAc = 4.5/1) to give epoxide **18** (302 mg, 1.06 mmol, 81%) as a colorless oil. $R_f$ = 0.46 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3419, 3068, 2956; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.38–7.34 (m, 3H), 7.32–7.29 (m, 2H), 7.26–7.23 (m, 5H), 4.29 (s, 1H), 3.78 (dd, $J$ = 13.0, 4.1

Hz, 1H), 3.73 (dd, $J$ = 13.0, 4.1 Hz, 1H) 1.67 (m, 1H), 0.06 (s, 3H), 0.02 (s, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 136.7, 136.0, 133.9, 129.3, 127.9, 127.8, 127.4, 126.4, 64.3, 59.8, 59.7, –3.5, –4.0; HRMS (APCI-MS, positive): *m/z* $[M+H]^+$ Calcd for $C_{17}H_{20}O_2Si$ 285.1305; Found 285.1310.

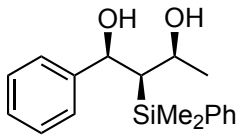
**Reaction of 18 with MeMgBr**




**18** **19** 54% **20** 20%

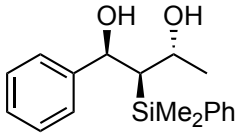
A 20-mL Schlenk tube was charged with $CH_3MgBr$ (3.0 M in THF, 2.8 mL, 8.44 mmol). After the solution was stirred at –45 °C for 5 min, epoxide **18** (200 mg, 0.70 mmol) in $Et_2O$ (15 mL) was slowly added to the reaction. The resulting mixture was allowed to warm to room temperature over 5 h and stirring was continued for 30 h. The reaction mixture was poured slowly into ice cooled solution of saturated aqueous $NH_4Cl$ (20 mL). The mixture was poured into a separatory funnel with $CH_2Cl_2$ (20 mL), water (10 mL), and partitioned. The organic phase was collected, and the aqueous phase was extracted with $CH_2Cl_2$ (20 mL × 2). The combined organic phase was washed with brine (20 mL), dried over $Na_2SO_4$ (ca. 10 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane to hexane/EtOAc = 4/1) to give major isomer **19** (115 mg, 0.381 mmol, 54%) as a colorless oil along with minor isomer **20** (43 mg, 0.144 mmol, 20%) as a colorless oil.

**(1*R**,2*R**,3*S**)-2-(dimethylphenylsilyl)-1-phenylbutane-1,3-diol (19)**




**Major isomer:** Colorless oil. $R_f$ = 0.49 (10% acetone/toluene); IR (ATR, $cm^{-1}$) 3319, 2966, 1427; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.46 (m, 2H), 7.35–7.28 (m, 7H), 7.21 (m, 1H), 5.49 (br, 1H), 4.18 (m, 1H), 3.37 (brd, $J$ = 2.9 Hz, 1H), 2.31 (brd, $J$ = 4.6 Hz, 1H), 1.56 (m, 1H), 1.36 (d, $J$ = 6.9 Hz, 3H), 0.32 (s, 3H), –0.04 (s, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 144.0, 139.3, 133.9, 128.7, 128.0, 127.7, 126.7, 125.6, 72.7, 68.9, 43.1, 23.6, –1.6, –1.7; HRMS (ESI-MS, positive): *m/z* $[M+Na]^+$ Calcd for $C_{18}H_{24}NaO_2Si$ 323.1438; Found 323.1437.

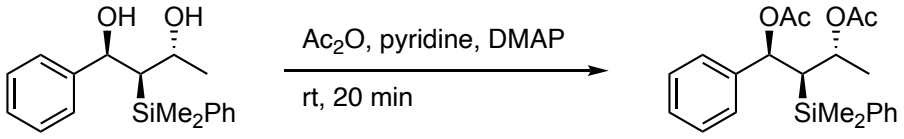
**(1*R**,2*R**,3*R**)-2-(dimethylphenylsilyl)-1-phenylbutane-1,3-diol (20):**




**Minor isomer:** Colorless oil. $R_f$ = 0.43 (50% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3319, 2960, 1450; $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.56 (m, 2H), 7.37–7.34 (m, 3H), 7.31–7.27 (m, 4H), 7.22–7.19 (m, 1H), 5.10 (brd, $J$ = 4.8 Hz, 1H), 4.25 (m, 1H), 3.13 (br, 1H), 2.20 (br, 1H), 1.66 (dd, $J$ = 4.8, 4.1 Hz, 2H), 1.03 (d,

$J$ = 6.9 Hz, 3H), 0.38 (s, 3H), 0.31 (s, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$) $\delta$ 145.8, 138.5, 133.9, 129.1, 128.2, 127.9, 126.9, 125.8, 74.2, 69.2, 41.6, 25.9, –2.6, –3.0; HRMS (APCI-MS, positive): *m/z* $[M+Na]^+$ Calcd for $C_{18}H_{24}NaO_2Si$ 323.1438; Found 323.1424.

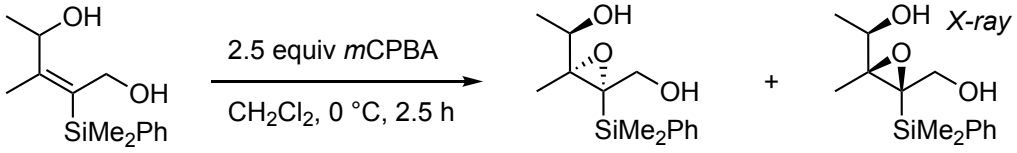
**(1*R**,2*R**,3*R**)-2-(dimethylphenylsilyl)-1-phenylbutane-1,3-diyl diacetate (21)**




**20** **21** 69%

A 10-mL single neck round–bottomed flask was charged with diol 20 (6.00 mg, 0.02 mmol), pyridine (300 μL), $Ac_2O$ (300 μL), and DMAP (cat.). The mixture was stirred at room temperature for 20 min and was concentrated under reduced pressure (bath temp 45 °C). The residue was added toluene (1.0 mL) and concentrated under reduced pressure (bath temp 45 °C). The residue was purified on preparative TLC with an eluent (EtOAc/hexane = 9/1) to give desired diacetate **21** (5.30 mg, 0.014 mmol, 69%) as a light green solid. $R_f$ = 0.46 (20% EtOAc/hexane); IR (ATR, $cm^{-1}$) 2960, 1733, 1227; $^1$H NMR (600 MHz, 600 MHz, $CDCl_3$) $\delta$ 7.47 (m, 2H), 7.34–7.27 (m, 5H), 7.24–7.21 (m, 3H), 6.23 (d, $J$ = 5.5 Hz, 1H), 4.98 (qd, $J$ = 6.4, 4.6 Hz, 1H), 2.00 (dd, $J$ = 5.7, 4.6 Hz, 1H), 1.97 (s, 3H), 1.93 (s, 3H), 1.16 (d, $J$ = 6.4 Hz, 3H), 0.35 (s, 3H), 0.26 (s, 3H); $^{13}$C NMR (151 MHz, 600 MHz, $CDCl_3$) $\delta$ 170.1, 169.6, 141.2, 138.8, 133.7, 128.9, 128.3, 127.7, 127.4, 126.1, 74.5, 70.6, 39.9, 21.3, 21.1, 20.2, –1.3, –1.8; HRMS (APCI-MS, positive): *m/z* $[M–H]^+$ Calcd for $C_{22}H_{27}O_4Si$ 383.1673; Found 383.1671.

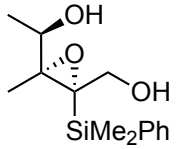
**Reaction of 6 with *m*CPBA**




**6** **26** 9% **27** 82%

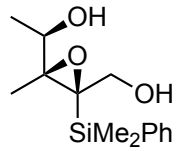
A three-neck 100-mL round-bottomed flask was charged with diol **6** (1.50 g, 5.99 mmol) and $CH_2Cl_2$ (90 mL). After the solution was stirred at 0 °C for 5 min, *m*CPBA (~72%, 3.59 g, 15.0 mmol) was added to the mixture portionwise over 5 min and the resulting mixture was stirred for 2.5 h at 0 °C. 20% aqueous $Na_2SO_3$ solution (90 mL) was added, and reaction mixture was stirred for 30 min at 0 °C. The mixture was poured into a separatory funnel with $CH_2Cl_2$ (90 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with $CH_2Cl_2$ (90 mL × 2). The combined organic extract was washed with saturated aqueous $NaHCO_3$ (50 mL × 3), dried over $Na_2SO_4$ (ca. 100 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane to hexane/EtOAc = 1.8/1) to give minor isomer **26** (149 mg, 0.560 mmol, 9%) as a colorless oil along with major isomer **27** (1.31 g, 4.92 mmol, 82%) as a white solid.

**(2*R**,3*R**,4*R**)-2-(dimethylphenylsilyl)-3-methyl-2,3-epoxy-pentane-1,4-diol (26)**



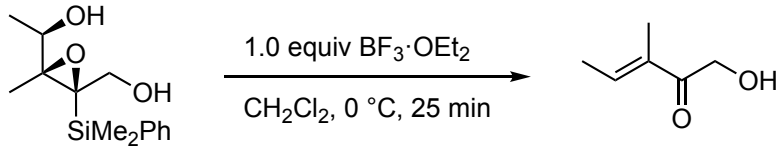

**Minor isomer:** Colorless oil. $R_f$ = 0.54 (50% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3351, 2976, 1428; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.62 (m, 2H), 7.39–7.35 (m, 3H), 3.99 (dd, $J$ = 11.7, 5.5 Hz, 1H), 3.90 (q, $J$ = 6.2 Hz, 1H), 3.64 (m, 1H), 2.60 (br, 1H), 2.13 (br, 1H), 1.30 (d, $J$ = 6.2 Hz, 3H), 1.25 (s, 3H), 0.48 (s, 3H), 0.47 (s, 3H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 137.3, 134.0, 129.3, 127.9, 69.4, 65.7, 64.0, 61.5, 18.2, 15.2, –2.0, –2.7; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{14}H_{21}O_2Si$ 249.1305; Found 249.1302.

**(2*S**,3*S**,4*R**)-2-(dimethylphenylsilyl)-3-methyl-2,3-epoxy-pentane-1,4-diol (27)**




**Major isomer:** White solid. $R_f$ = 0.43 (60% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3416, 2909, 1429; mp 105.0–107.0 °C; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.59 (m, 2H), 7.39–7.36 (m, 3H), 3.90 (q, $J$ = 6.9 Hz, 1H), 3.79 (dd, $J$ = 11.7, 4.1 Hz, 1H), 3.66 (dd, $J$ = 11.7, 4.1 Hz, 1H), 1.94 (br, 1H), 1.57 (br, 1H), 1.24 (s, 3H), 1.22 (d, $J$ = 6.9 Hz, 3H), 0.474 (s, 3H), 0.472 (s, 3H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 137.4, 133.9, 129.3, 127.9, 69.2, 68.4, 62.6, 62.0, 18.9, 14.8, –2.0, –2.5; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_{14}H_{21}O_2Si$ 249.1305; Found 249.1302.

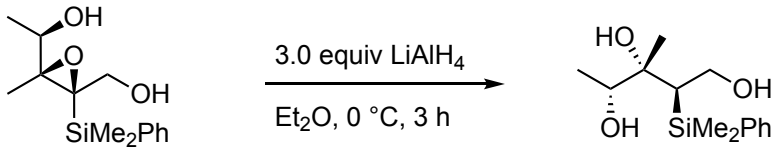
**(*E*)-1-hydroxy-3-methylpent-3-en-2-one (28)**




**27** **28** 62%

An 20-mL Schlenk tube was charged with 1,3-(dimethylphenylsilyl)-3-(hydroxymethyl)-2-methyloxiran-2-yl)ethan-1-ol **27** (266 mg, 1.00 mmol), $CH_2Cl_2$ (10 mL). After the solution was stirred at 0 °C for 5 min, $BF_3{\cdot}OEt_2$ (123 μL, 1.00 mmol) was slowly added to the reaction, and the resulting mixture was stirred at 0 °C for 25 min. The reaction was quenched with saturated aqueous $NH_4Cl$ (2.0 mL) followed by $H_2O$ (10 mL). The mixture was poured into a separatory funnel with $CH_2Cl_2$ (10 mL), and partitioned. The organic phase was collected, and the aqueous phase was extracted with $CH_2Cl_2$ (10 mL × 2). The combined organic extract was washed with brine (10 mL), dried over $Na_2SO_4$ (ca. 10 g), filtered, and concentrated under reduced pressure (bath temperature = 30 °C). The residue was purified by column chromatography on silica gel (hexane to hexane/EtOAc = 4/1) to give **28** (70.2 mg, 0.615 mmol, 62%) as a colorless oil. $R_f$ = 0.51 (40% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3455, 2926, 1667; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 6.69 (qq, $J$ = 6.9, 1.4 Hz, 1H), 4.54 (d, $J$ = 4.8 Hz, 2H), 3.44 (t, $J$ = 4.8 Hz, 1H), 1.89 (m, 3H), 1.85 (m, 3H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 199.1, 138.7, 135.2, 64.1, 14.6, 10.7; HRMS (APCI-MS, positive): *m/z* $[M–OH]^+$ Calcd for $C_6H_9O$ 97.0648; Found 97.0651.

**(2*R**,3*S**,4*R**)-2-(dimethylphenylsilyl)-3-methylpentane-1,3,4-triol (31)**

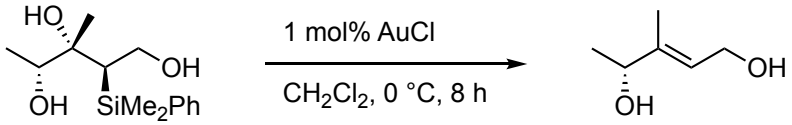



**27** **31** 99%

A 100-mL three neck round-bottomed flask was with charged lithium aluminum hydride (299 mg, 7.88 mmol) and diethyl ether (50 mL). After the solution was stirred at 0 °C for 5 min, a solution of epoxide **27** (700 mg, 2.62 mmol) in diethyl ether (20 mL) was slowly added over 5 min, and the reaction mixture was stirred at 0 °C for 3 h. The reaction was quenched by sequential addition of $H_2O$ (300 μL), 15% aqueous NaOH (300 μL), and $H_2O$, and the slurry was further stirred at 0 °C for 45 min. The mixture was filtered through a Celite plug and the bed was washed with EtOAc (50 mL). The filtrate was poured into a separatory funnel and washed with brine (50 mL), dried over $Na_2SO_4$ (ca. 70 g), filtered, and concentrated under reduced pressure to give desired triol **31** (702 mg, 2.61 mmol, 99%) as a colorless oil. $R_f$ = 0.43

(60% EtOAc/hexane); IR (ATR, $cm^{-1}$) 3400, 2953; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 7.58–7.55 (m, 2H), 7.38–7.35 (m, 3H), 4.03 (m, 1H), 3.90 (ddd, $J$ = 11.7, 7.6, 4.1 Hz, 1H), 3.75 (dq, $J$ = 6.2, 6.2 Hz, 1H), 3.34 (br, 1H), 3.10 (br, 1H), 2.10 (d, $J$ = 6.2 Hz, 1H), 1.75 (dd, $J$ = 7.6, 2.1 Hz, 1H), 1.13 (s, 3H), 1.07 (d, $J$ = 6.2 Hz, 3H), 0.45 (s, 3H), 0.42 (s, 3H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 138.9, 133.7, 129.1, 127.9, 78.8, 71.3, 61.7, 37.1, 22.1, 17.1, –1.1, –1.7; HRMS (APCI-MS, positive): $m/z$ $[M–H]^+$ Calcd for $C_{14}H_{23}O_3Si$ 267.1411; Found 267.1418.

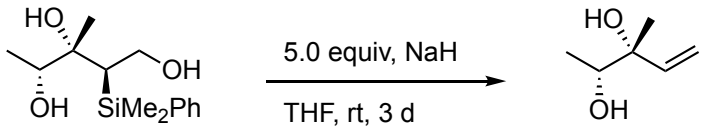
**(*E*)-3-Methylpent-2-ene-1,4-diol (32)**




**31** **32** 74%

A 10-mL Schlenk tube was charged with AuCl (1.16 mg, 0.005 mmol), $CH_2Cl_2$ (1.0 mL). After the solution was stirred at 0 °C for 5 min, **31** (134 mg, 0.500 mmol) in $CH_2Cl_2$ (1.0 mL) was added dropwise, and the resulting mixture was stirred at 0 °C for 8 h. The mixture was diluted with EtOAc (5.0 mL) and filtered through small pad of silica gel, and the bed was washed with EtOAc (10 mL). The filtrate was concentrated under reduced pressure (bath temperature = 30 °C). The residue was purified by column chromatography on silica gel with an eluent (hexane to hexane/EtOAc = 1/9) to provide **33** (43.2 mg, 0.372 mmol, 74%) as a colorless oil. $R_f$ = 0.38 (EtOAc); IR (ATR, $cm^{-1}$) 3300, 2973, 1441; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 5.64 (m, 1H), 4.24–4.16 (m, 3H), 1.89 (br, 1H), 1.79 (br, 1H), 1.67 (s, 3H), 1.27 (d, $J$ = 6.9 Hz, 3H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 141.7, 122.9, 72.3, 58.7, 21.4, 12.0; HRMS (APCI-MS, positive): $m/z$ $[M–OH]^+$ Calcd for $C_6H_{11}O$ 99.0804; Found 99.0802.

**(2R*,3R*)-3-methylpent-4-ene-2,3-diol (33)**

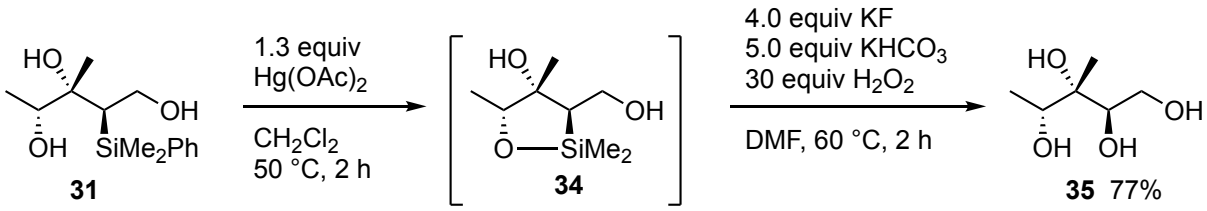



**31** **33** 36%

A 100-mL three neck round-bottomed flask was charged with sodium hydride (hexane-washed, 134 mg, 5.59 mmol) and THF (15 mL). After the solution was stirred at 0 °C for 5 min, a solution of triol **31** (300 mg, 1.12 mmol) in THF (10 mL) over 5 min was added, and the reaction mixture was stirred for 3 h at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3 d. The resulting mixture was cooled to 0 °C, and saturated aqueous $NH_4Cl$ solution (2.0 mL) was added carefully. The mixture was poured into a separatory funnel

with $CH_2Cl_2$ (10 mL), water (20 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with $CH_2Cl_2$ (10 mL × 2). The combined organic extract was washed with brine (20 mL), dried over $Na_2SO_4$ (ca. 25 g), filtered, and concentrated under reduced pressure (bath temperature = 10 °C). The residue was purified by column chromatography on silica gel (hexane to hexane/EtOAc = 1.5/1) to give desired diol **33** (46.9 mg, 0.403 mmol, 36%) as a colorless oil. All the resonances in $^1H$ and $^{13}C$ NMR spectra were consistent with reported values.[18]

**(2*R**,3*S**,4*R**)-3-methylpentane-1,2,3,4-tetraol (35)**




A 50-mL Schlenk tube was charged with triol **31** (300 mg, 1.12 mmol), $Hg(OAc)_2$ (463 mg, 1.45 mmol), and $CH_2Cl_2$ (15 mL). The mixture was stirred at 50 °C for 2 h and the mixture was cooled to room temperature and concentrated under reduced pressure (bath temperature = 20 °C, 60 mmHg) to give crude white residue. An aliquot was purified by recycled GPC (LC–92XX II) with an eluent ($CHCl_3$) to provide cyclic silyl ether **34** as a colorless oil. IR (ATR, $cm^{-1}$) 3372, 2924; $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ 4.01–3.88 (m, 3H), 2.34 (s, 1H), 1.87 (brs, 1H), 1.74 (dd, $J$ = 10.3, 5.5 Hz, 1H), 1.42 (s, 3H), 1.23 (d, $J$ = 6.9 Hz, 3H), 0.29 (s, 3H), 0.17 (s, 3H); $^{13}C$ NMR (151 MHz, $CDCl_3$) $\delta$ 81.3, 79.6, 60.3, 38.5, 24.3, 17.3, 1.7, –1.8; HRMS (APCI-MS, positive): *m/z* $[M+H]^+$ Calcd for $C_8H_{19}O_3Si$ 191.1098; Found 191.1098.

The crude white residue of **34** was dissolved in DMF (10 mL). After the solution was stirred at 0 °C for 5 min, KF (260 mg, 4.48 mmol), $KHCO_3$ (560 mg, 5.60 mmol), and $H_2O_2$ (30% aqueous solution, 3.8 mL, 33.6 mmol) were sequentially added. The mixture was stirred at 0 °C for 15 min and the resulting mixture was warmed to 60 °C and stirred for 2 h. The mixture was cooled to 0 °C, diluted with $H_2O$ (6 mL), and $Na_2SO_3$ (4.25 g) was added portionwise to the reaction. The mixture was stirred at 0 °C for 10 min and warmed to room temperature and stirring was continued for another 20 min. The resulting suspension was filtered through Celite, and the bed was washed with $CH_3OH$ (3 x 20 mL). The filtrate was concentrated under reduced pressure (bath temperature = 50 °C). The residue was purified twice by column chromatography on silica gel with an eluent ($CH_3OH/CH_2Cl_2$ = 6/1) to give tetraol **35** (130 mg, 0.862 mmol, 77%) as a colorless oil. $R_f$ = 0.45 (25% $CH_3OH$ /$CH_2Cl_2$); IR (ATR,

$cm^{-1}$) 3362; $^{1}H$ NMR (600 MHz, $CD_3OD$) $\delta$ 3.84–3.79 (m, 2H), 3.76 (dd, $J$ = 7.3, 3.6 Hz, 1H), 3.60 (dd, $J$ = 10.9, 7.3 Hz, 1H), 1.20 (d, $J$ = 6.4 Hz, 3H), 1.10 (s, 3H); $^{13}C$ NMR (151 MHz, $CD_3OD$) $\delta$ 77.4, 77.0, 72.9, 64.9, 20.0, 18.2; HRMS (APCI-MS, positive): *m/z* $[M+H]^+$ Calcd for $C_6H_{15}O_4$ 151.0965; Found 151.0961.

## X-ray Crystallography

X-ray data were taken at –180 °C with a Rigaku XtaLAB P-200 system by using graphite monochromatic Cu-Kα radiation (λ = 1.54184 Å). The structures were solved by using direct method SHLEXS-2013/1 and refined by SHELXL-2014/7 program.[19] All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically.

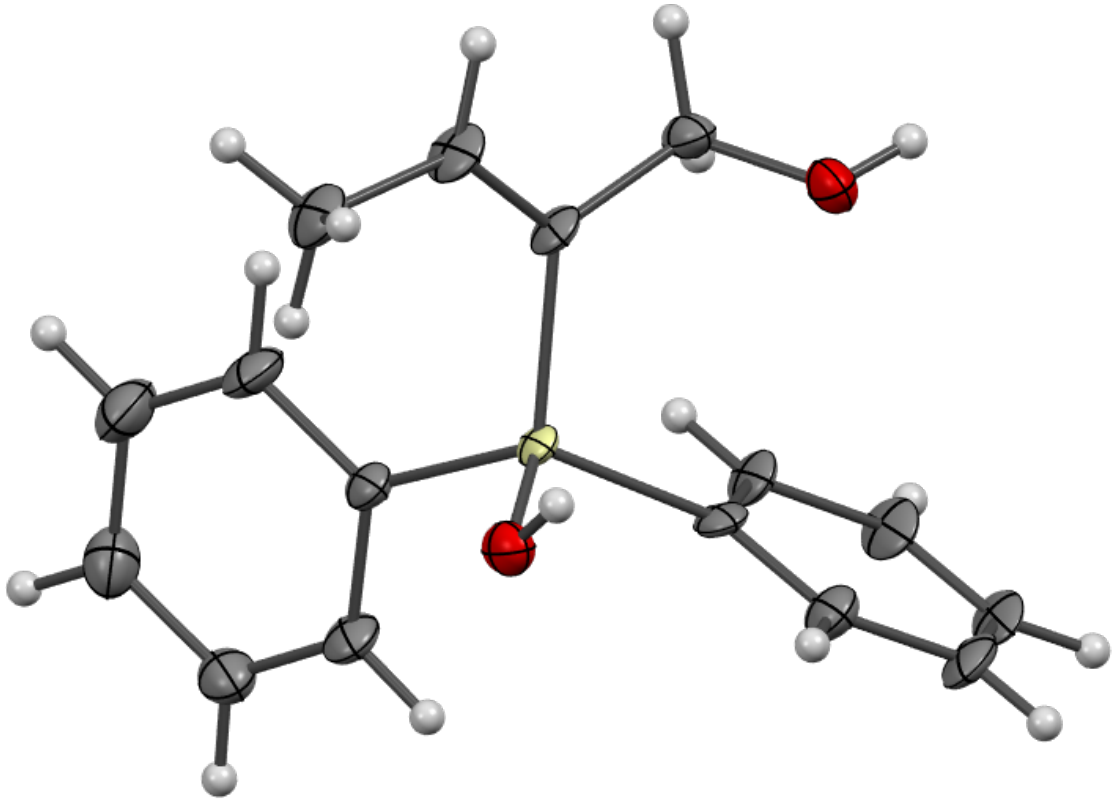


**Figure S1.** ORTEP representation of the crystal structure of **4af-3** (thermal ellipsoid at 50% probability). (color code: white = hydrogen; gray = carbon; yellow = silicon; red = oxygen).

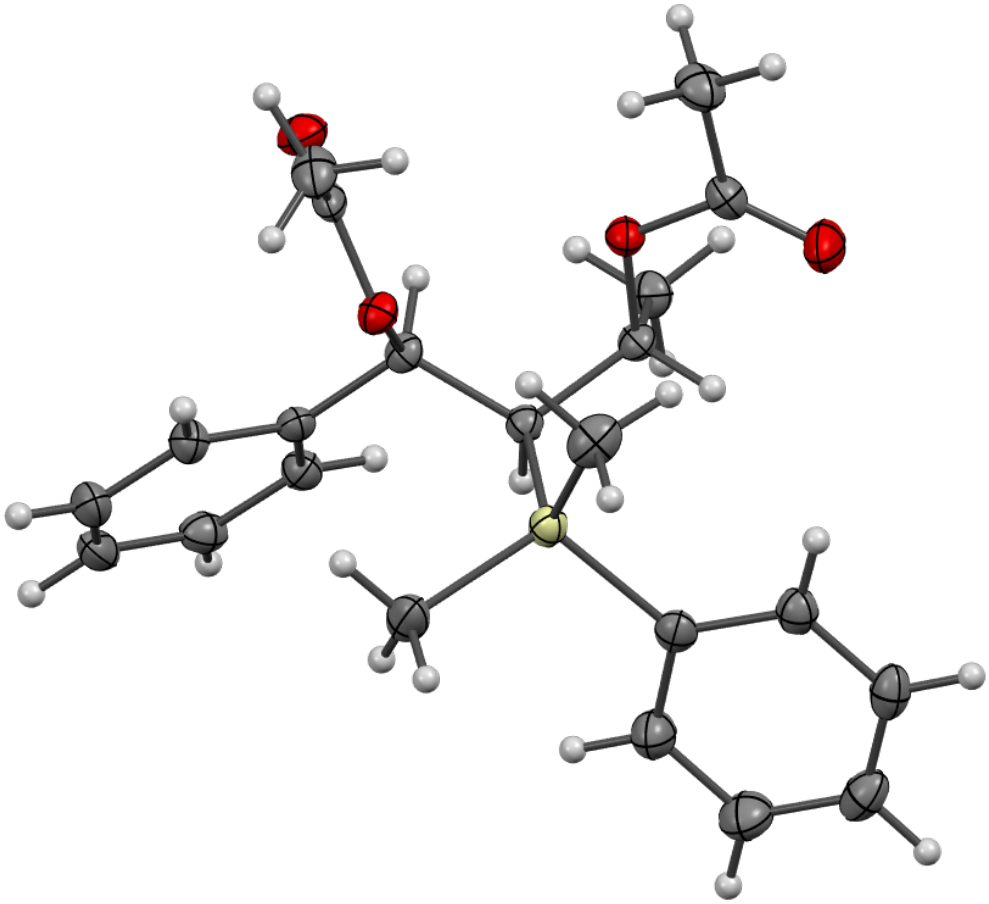


**Figure S2.** ORTEP representation of the crystal structure of **21** (thermal ellipsoid at 50% probability). (color code: white = hydrogen; gray = carbon; yellow = silicon; red = oxygen).

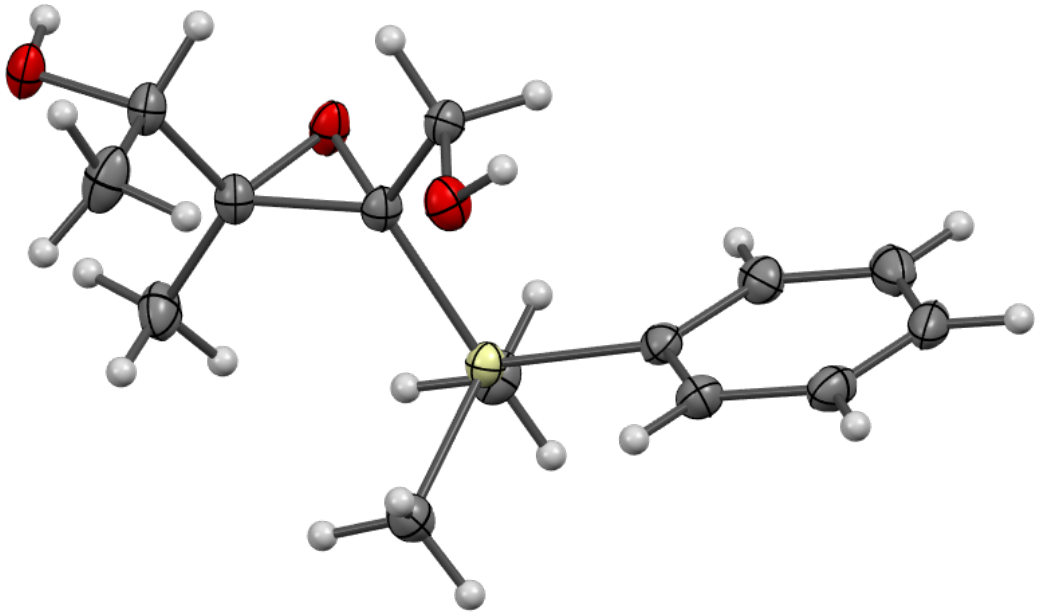


**Figure S3.** ORTEP representation of the crystal structure of **27** (thermal ellipsoid at 50% probability). (color code: white = hydrogen; gray = carbon; yellow = silicon; red = oxygen).

**Table S1.** Crystal parameters and structural refinement data for **4af-3**, **21**, **27**.

| Compound | **4af-3** | **21** | **27** |
|---|---|---|---|
| Formula | $C_{16}H_{18}O_2Si$ | $C_{22}H_{28}O_4Si$ | $C_{14}H_{22}O_3Si$ |
| Solvent | $CHCl_3$ (solvent removal) | $CH_2Cl_2$/hexane (solvent removal) | EtOAc/$CHCl_3$/hexane(solvent removal) |
| Formula weight | 270.39 | 384.53 | 266.41 |
| Temperature / K | 93(2) | 93(2) | 93(2) |
| λ (Å) | 1.54184 | 1.54184 | 1.54184 |
| Crystal size / $mm^3$ | 0.600×0.130×0.010 | 0.230×0.080×0.030 | 0.130×0.100×0.060 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | *P2₁* | $P2_1/a$ | $P2_1/n$ |
| *a* / Å | 9.0548(2) | 8.22670(10) | 10.34820(10) |
| *b* / Å | 6.8785(2) | 16.4329(2) | 12.83180(10) |
| *c* / Å | 12.1843(3) | 15.7770(2) | 11.46370(10) |
| *α* / ° | 90 | 90 | 90 |
| *β* / ° | 99.665(2) | 96.3407(13) | 101.7810(10) |
| *γ* / ° | 90 | 90 | 90 |
| *V* / $Å^3$ | 748.11(3) | 2119.82(5) | 1490.15(2) |
| *Z* | 2 | 4 | 4 |
| *μ* $mm^{-1}$ | 1.344 | 1.167 | 1.383 |
| $D_{calcd.}$ / $g \cdot cm^{-3}$ | 1.200 | 1.205 | 1.178 |
| $\theta_{max}$ | 74.470 | 67.998 | 73.974 |
| Refl./restr./param. | 2699/1/175 | 3837/0/249 | 2999/0/169 |
| Completeness | 0.995 | 0.997 | 0.999 |
| GOF | 1.075 | 1.052 | 1.036 |
| $R_1$ ($I > 2\sigma(I)$) | 0.0901 | 0.0334 | 0.0322 |
| $wR_2$ ($I > 2\sigma(I)$) | 0.2206 | 0.0908 | 0.0832 |
| $R_1$ (all data) | 0.0920 | 0.0377 | 0.0331 |
| $wR_2$ (all data) | 0.2232 | 0.0936 | 0.0838 |
| Largest diff. peak and hole / $e \cdot Å^{-3}$ | 0.689, –1.128 | 0.278, 0.279 | 0.218, –0.305 |
| Absolute structure parameter | 0.03(7) | – | – |
| CCDC number | 2153795 | 2153794 | 2153783 |

## Computational Studies

### Reaction of Propargyl Alkoxide with Silyllithium

Preliminary structures of transition states were automatically explored by MC–AFIR method by using GRRM17 program[20,21,22] associated with Gaussian16 program.[23] For initial search, calculations were carried out at the level of B3LYP[24]/def2–SVP[25] and a phenyl group in **1d** was replaced to a methyl group to reduce calculation costs. During the search, Si, Li (on the Si), and two carbon atoms in the alkyne moiety were chosen as target atoms of the MC–AFIR method. The collision energy parameter $\gamma$ of the AFIR method was set as $\gamma$ = 200.0 kJ/mol and the combinations of artificial forces for each reaction mode (proximal or distal silylation) as described in Figure S4 were employed. The automated search was stopped after finding 10 different pathways for each reaction mode. Of special note is that pathways of silyllithiation with *syn*–configuration was not found in our calculations.

To refine preliminary transition structures obtained in the AFIR search, ωB97X–D[26]/def2–SVP was employed as the calculation level after replacement of a methyl group in each propargyl alkoxide with a phenyl group. All structures were characterized by frequency calculations to confirm their identity as either local minima or first–order saddle points. Free energies including a concentration correction (as the 1 mol $L^{-1}$ standard state, 1.89 kcal $mol^{-1}$ was added to every species) at the optimized structures were calculated by using the ωB97X–D/def2–TZVPPD[27] level of theory at 273.15 K with a solvation effect of THF modeled by SMD[28] method shown in Table S2. Imaginary frequencies of $\mathbf{TS_{prox}}$ and $\mathbf{TS_{dist}}$ are shown in Table S4. All geometries of equilibrium structures and transition states are shown in Table S5.

Although we located **INT1**s corresponding to each transition state, their structures and energies are almost same ($\Delta G$ = 1.7 kcal $mol^{-1}$). To clarify the energy diagram, only the lower **INT1** derived from $\mathbf{TS_{dist}}$ is shown in the main text and Table S2.

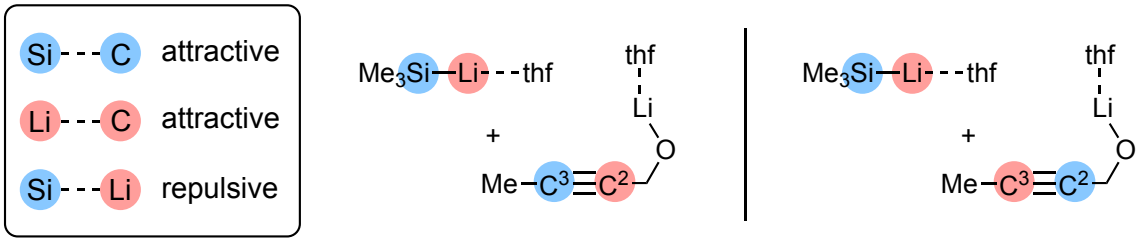



**Figure S4.** Definitions of the combinations of artificial force during initial search.

**Reaction of Methyl Propargyl Ether with Silyllithium**

As well as the case of the propargyl alkoxide, preliminary structures of transition states were automatically explored by MC–AFIR method by using GRRM17 program associated with Gaussian16 program at the level of B3LYP/def2–SVP. During the search, Si, Li, and two carbon atoms in the alkyne moiety were chosen as target atoms of the MC–AFIR method. The collision energy parameter $\gamma$ of the AFIR method was set as $\gamma$ = 200.0 kJ/mol and the combinations of artificial forces for each reaction mode (proximal or distal silylation) as described in Figure S5 were employed. The automated search was stopped after finding 10 different pathways for each reaction mode. In the same way as the case of the propargyl alkoxide, pathways of silyllithiation with *syn*–configuration was not found in our calculations.

To refine preliminary transition structures obtained in the AFIR search, ωB97X–D/def2–SVP was employed as the calculation level. All structures were characterized by frequency calculations to confirm their identity as either local minima or first–order saddle points. Free energies including a concentration correction (as the 1 mol $L^{-1}$ standard state, 1.89 kcal $mol^{-1}$ was added to every species) at the optimized structures were calculated by using the ωB97X–D/def2–TZVPPD level of theory at 273.15 K with a solvation effect of THF modeled by SMD method shown in Table S3. Imaginary frequencies of $\mathbf{TS_{prox\text{-}OMe}}$ and $\mathbf{TS_{dist\text{-}OMe}}$ are shown in Table S4. All geometries of equilibrium structures and transition states are shown in Table S5.

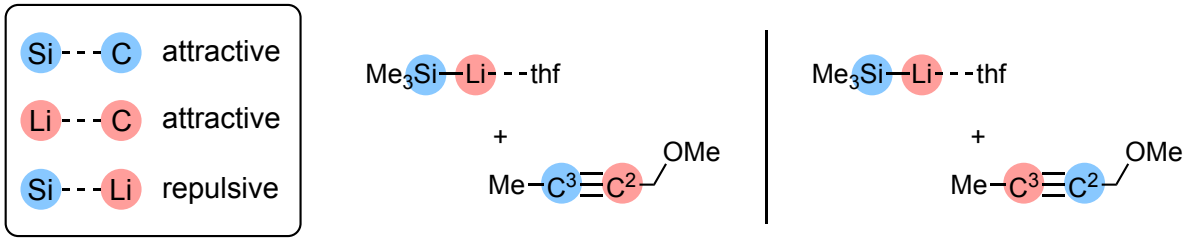
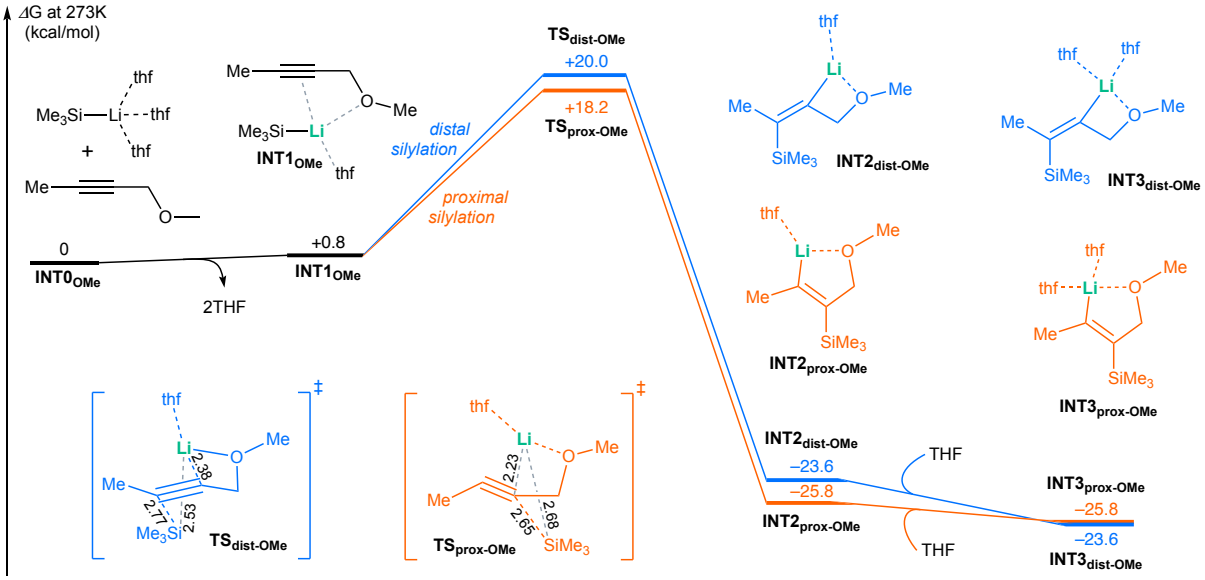



**Figure S5.** Definitions of the combinations of artificial force during initial search.

Our calculated energy diagram for the silyllithiation of *O*-methylated substrate is shown in Chart S1. Our calculation led to the similar diagram from $\mathbf{INT1_{OMe}}$ to $\mathbf{INT2_{OMe}}$ through $\mathbf{TS_{dist\text{-}OMe}}$ or $\mathbf{TS_{prox\text{-}OMe}}$. The diagram indicated the silylation of the proximal carbon center to be favored, though the difference between $\mathbf{TS_{dist\text{-}OMe}}$ and $\mathbf{TS_{prox\text{-}OMe}}$ is only 1.8 kcal $mol^{-1}$. It is also notable that $\mathbf{INT3_{dist\text{-}OMe}}$ and $\mathbf{INT3_{prox\text{-}OMe}}$ show almost the same energy level. These calculated results agree with the fact that the regioselectivity of silyllithiation was mostly lost in the case of *O*-methylated substrate.

Although we located **INT1**s corresponding to each transition state, their structures and energies are almost same ($\Delta G$ = 2.6 kcal mol$^{-1}$). To clarify the energy diagram, only the lower **INT1** derived from **TS$_{dist-OMe}$** is shown in Table S3.

**Chart S1.** Computed Energy Diagram of Proximal and Distal Silyllithiation of Methyl Propargyl Ether.




Energy profile for silyllithiation of methyl propargyl ether **1da** and trimethylsilyllithium (**2e**) at the ωB97X-D/def2-TZVPPD with SMD (THF)//ωB97X-D/def2-SVP/SMD (THF) level of theory at 273.15 K. Bond lengths are given in ångström [Å].

**Table S2.** Calculated energy at 273.15 K for each structure in Hartree.

| Species | Electronic Energy | Thermal Free energy | Corrected Thermal Free Energy |
|---|---|---|---|
| $Me_3SiLi(thf)_3$ | -1114.304406 | -1113.885375 | -1113.882685 |
| **1d**-$Li(thf)_3$ | -1127.423929 | -1126.983495 | -1126.980805 |
| **THF** | -232.477047 | -232.385333 | -232.3826431 |
| **INT1** | -1311.787981 | -1311.355817 | -1311.353127 |
| $\mathbf{TS_{prox}}$ | -1311.753108 | -1311.323549 | -1311.320859 |
| $\mathbf{TS_{dist}}$ | -1311.750243 | -1311.315616 | -1311.312926 |
| $\mathbf{INT2_{prox}}$ | -1311.834897 | -1311.399799 | -1311.397109 |
| $\mathbf{INT2_{dist}}$ | -1311.810724 | -1311.373325 | -1311.370635 |
| $\mathbf{INT3_{prox}}$ | -1776.835178 | -1776.173029 | -1776.170339 |
| $\mathbf{INT3_{dist}}$ | -1776.815841 | -1776.156235 | -1776.153545 |

**Table S3.** Calculated energy at 273.15 K for each structure in Hartree.

| Species | Electronic Energy | Thermal Free energy | Corrected Thermal Free Energy |
|---|---|---|---|
| Ether | -270.511258 | -270.4204814 | -270.4177914 |
| $\mathbf{INT1_{OMe}}$ | -919.842099 | -919.5366652 | -919.5339753 |
| $\mathbf{TS_{prox\text{-}OMe}}$ | -919.812877 | -919.5060039 | -919.503314 |
| $\mathbf{TS_{dist\text{-}OMe}}$ | -919.815199 | -919.5089047 | -919.5062148 |
| $\mathbf{INT2_{prox\text{-}OMe}}$ | -919.889331 | -919.5755178 | -919.5728279 |
| $\mathbf{INT2_{dist\text{-}OMe}}$ | -919.887365 | -919.5790032 | -919.5763133 |
| $\mathbf{INT3_{prox\text{-}OMe}}$ | -1152.387034 | -1151.965425 | -1151.962735 |
| $\mathbf{INT3_{dist\text{-}OMe}}$ | -1152.386085 | -1151.965292 | -1151.962602 |

**Table S4.** Imaginary frequency of each transition state.

| Species | Imaginary Frequency |
|---|---|
| $\mathbf{TS_{prox}}$ | 240.66*i* $cm^{-1}$ |
| $\mathbf{TS_{dist}}$ | 247.07*i* $cm^{-1}$ |
| $\mathbf{TS_{prox\text{-}OMe}}$ | 282.92*i* $cm^{-1}$ |
| $\mathbf{TS_{dist\text{-}OMe}}$ | 228.09*i* $cm^{-1}$ |

**Table S5.** Cartesian coordinates of optimized structures.

<Propargyl Alkoxide>

$Me_3SiLi(thf)_3$

| | | | |
|---|---|---|---|
| Si | -1.403882 | 1.405334 | 1.126898 |
| Li | 0.110872 | 0.069748 | -0.547853 |
| C | -2.523931 | 0.275422 | 2.237352 |
| C | -0.463207 | 2.435481 | 2.470061 |
| C | -2.693187 | 2.710311 | 0.515534 |
| O | 1.134451 | 1.160880 | -1.875143 |
| C | 2.461389 | 0.701688 | -2.073937 |
| C | 1.247454 | 2.496250 | -1.395695 |
| C | 3.290913 | 1.310345 | -0.927445 |
| C | 2.372250 | 2.418280 | -0.366426 |
| H | 1.501916 | 3.168009 | -2.236864 |
| H | 2.823294 | 1.048024 | -3.058953 |
| H | 2.441415 | -0.396226 | -2.080215 |
| H | 0.275027 | 2.780602 | -0.972343 |
| H | 2.885727 | 3.379694 | -0.229982 |
| H | 4.246880 | 1.706858 | -1.297703 |
| H | 3.510739 | 0.554893 | -0.161304 |
| H | 1.942987 | 2.120684 | 0.602475 |
| H | -3.265439 | -0.274249 | 1.629625 |
| H | -1.935366 | -0.483592 | 2.785048 |
| H | -3.086844 | 0.856155 | 2.990472 |
| H | 0.259759 | 1.818688 | 3.033355 |
| H | 0.110381 | 3.259445 | 2.008886 |
| H | -1.151492 | 2.888989 | 3.206413 |
| H | -2.201152 | 3.538328 | -0.024964 |
| H | -3.430879 | 2.272781 | -0.180185 |
| H | -3.257570 | 3.155628 | 1.354852 |
| O | 1.472493 | -0.989375 | 0.418459 |
| O | -0.857762 | -1.383162 | -1.490874 |
| C | 1.528986 | -0.867865 | 1.845431 |
| C | 1.905173 | -2.277037 | 0.001417 |
| C | 2.093073 | -2.195520 | 2.351897 |
| C | 1.724543 | -3.162792 | 1.225472 |

| | | | |
|---|---|---|---|
| H | 1.300667 | -2.571589 | -0.868381 |
| H | 0.509214 | -0.669464 | 2.210010 |
| H | 2.153820 | -0.000252 | 2.107118 |
| H | 2.967821 | -2.233782 | -0.304971 |
| H | 0.672240 | -3.475978 | 1.312613 |
| H | 1.674558 | -2.479594 | 3.326658 |
| H | 3.187701 | -2.139294 | 2.459477 |
| H | 2.350442 | -4.065172 | 1.197593 |
| C | -1.567967 | -2.173473 | -0.530532 |
| C | -1.765815 | -0.797101 | -2.424620 |
| C | -3.044636 | -2.096916 | -0.919491 |
| C | -3.109744 | -0.791150 | -1.713127 |
| H | -1.387497 | 0.204297 | -2.676548 |
| H | -1.391290 | -1.735433 | 0.466067 |
| H | -1.172768 | -3.202035 | -0.548328 |
| H | -1.791221 | -1.407722 | -3.345543 |
| H | -3.160907 | 0.069492 | -1.029516 |
| H | -3.701389 | -2.099393 | -0.039145 |
| H | -3.324531 | -2.951186 | -1.556006 |
| H | -3.959726 | -0.743794 | -2.407594 |

**1d**-Li(thf)$_3$

| | | | |
|---|---|---|---|
| C | -1.592940 | 0.286888 | 1.840810 |
| C | -2.774967 | 0.434108 | 1.043238 |
| C | -0.553654 | 0.131082 | 2.453049 |
| C | 0.845729 | -0.086750 | 2.928854 |
| O | 1.704185 | -0.176488 | 1.885843 |
| H | 1.068931 | 0.750224 | 3.639046 |
| H | 0.816717 | -0.994041 | 3.583211 |
| Li | 1.131081 | -0.142855 | 0.177647 |
| O | -0.065788 | -1.436298 | -0.695830 |
| C | -0.589880 | -2.552245 | 0.024376 |
| C | -0.859759 | -1.137396 | -1.838923 |
| C | -1.629556 | -3.175585 | -0.900847 |
| C | -2.133995 | -1.958452 | -1.677600 |
| H | -1.040634 | -0.053396 | -1.864189 |
| H | -1.035929 | -2.187346 | 0.963345 |
| H | 0.242444 | -3.227608 | 0.273164 |
| H | -0.301371 | -1.423863 | -2.748995 |
| H | -2.871604 | -1.400748 | -1.081745 |
| H | -2.422747 | -3.695898 | -0.347036 |
| H | -1.157449 | -3.901446 | -1.582418 |
| H | -2.595001 | -2.214062 | -2.641476 |
| C | -2.758106 | 1.262440 | -0.093471 |
| C | -3.949931 | -0.275402 | 1.345070 |
| C | -5.072307 | -0.164119 | 0.528226 |
| C | -3.883561 | 1.368680 | -0.905449 |
| C | -5.043864 | 0.655771 | -0.600255 |
| H | -3.968677 | -0.919516 | 2.226335 |
| H | -5.977516 | -0.723918 | 0.774121 |
| H | -1.834879 | 1.789922 | -0.341989 |
| H | -3.853946 | 2.010901 | -1.788801 |
| H | -5.924839 | 0.739481 | -1.240279 |
| O | 0.608763 | 1.677438 | -0.510814 |
| O | 2.866878 | -0.452405 | -0.878800 |
| C | 0.843982 | 2.631693 | 0.539263 |
| C | 1.189688 | 2.114905 | -1.732891 |
| C | 1.560671 | 3.807080 | -0.122428 |
| C | 2.231360 | 3.149580 | -1.329561 |
| H | 1.620295 | 1.239510 | -2.238341 |
| H | 1.451193 | 2.122918 | 1.305844 |
| H | -0.121588 | 2.903996 | 0.991315 |
| H | 0.408876 | 2.560686 | -2.377286 |
| H | 3.161124 | 2.643660 | -1.027515 |
| H | 2.271204 | 4.295871 | 0.558071 |
| H | 0.837787 | 4.567968 | -0.457056 |
| H | 2.470564 | 3.853377 | -2.138826 |
| C | 3.056390 | -1.837662 | -1.109820 |
| C | 3.937409 | -0.014762 | -0.043513 |
| C | 3.504350 | -2.380988 | 0.242622 |
| C | 4.343008 | -1.224954 | 0.816678 |
| H | 4.768463 | 0.340975 | -0.679622 |
| H | 3.831243 | -1.988380 | -1.886815 |
| H | 2.103102 | -2.246528 | -1.469697 |
| H | 3.554365 | 0.809565 | 0.571348 |
| H | 5.422847 | -1.421801 | 0.743218 |
| H | 4.058710 | -3.326360 | 0.157645 |
| H | 2.624436 | -2.536616 | 0.883244 |
| H | 4.067915 | -1.040419 | 1.861490 |

THF

| | | | |
|---|---|---|---|
| C | -1.155694 | -0.432611 | -0.132337 |
| H | -1.530099 | -0.479106 | -1.173161 |
| O | -0.000220 | -1.235559 | -0.000356 |
| C | -0.728893 | 0.989946 | 0.228431 |
| C | 1.155400 | -0.433061 | 0.132783 |
| C | 0.729415 | 0.989508 | -0.228628 |
| H | -1.948892 | -0.823553 | 0.524839 |
| H | -1.345201 | 1.759523 | -0.257131 |
| H | -0.787533 | 1.145426 | 1.317672 |
| H | 0.788159 | 1.144413 | -1.317948 |
| H | 1.949069 | -0.824467 | -0.523527 |
| H | 1.528770 | -0.479430 | 1.174008 |
| H | 1.346113 | 1.758978 | 0.256609 |

**INT1**

| | | | |
|---|---|---|---|
| C | 1.066375 | -0.452588 | 2.441786 |
| C | -0.247483 | -0.892989 | 2.979463 |
| C | 2.007790 | -0.062097 | 1.780131 |
| C | 3.060347 | 0.406496 | 0.923528 |
| H | -0.133991 | -1.945588 | 3.322518 |
| H | -0.446207 | -0.307811 | 3.903657 |
| O | -1.215795 | -0.744975 | 2.019241 |
| Li | -2.533289 | 0.345788 | 1.504264 |
| O | -3.938039 | -0.697343 | 0.658566 |
| C | -4.550159 | -0.320310 | -0.566281 |
| C | -3.564210 | -2.065640 | 0.519359 |
| C | -3.725566 | -1.010986 | -1.659085 |
| C | -3.038522 | -2.179080 | -0.916019 |
| H | -2.807209 | -2.269462 | 1.287787 |
| H | -4.541185 | 0.775550 | -0.629858 |
| H | -5.599394 | -0.667253 | -0.567319 |
| H | -4.454909 | -2.699893 | 0.679478 |
| H | -1.947253 | -2.049684 | -0.932755 |
| H | -2.975643 | -0.315331 | -2.060872 |
| H | -4.361515 | -1.346299 | -2.490130 |
| H | -3.269697 | -3.159885 | -1.354826 |
| Si | -1.566234 | 2.160569 | -0.257664 |
| C | -2.469370 | 2.684119 | -1.873777 |
| C | -0.286331 | 3.583870 | -0.053511 |
| Li | -0.420458 | -0.180114 | 0.392284 |
| C | -2.870652 | 2.700297 | 1.107814 |

| | | | |
|---|---|---|---|
| H | -0.772477 | 4.575330 | -0.075606 |
| H | 0.268487 | 3.503525 | 0.896769 |
| H | 0.457853 | 3.570928 | -0.869097 |
| H | -3.360485 | 2.070852 | -2.089378 |
| H | -2.795494 | 3.738543 | -1.833232 |
| H | -1.796661 | 2.580092 | -2.742281 |
| H | -3.148670 | 3.760074 | 0.981095 |
| H | -3.825683 | 2.139106 | 1.085910 |
| H | -2.456787 | 2.614558 | 2.131942 |
| O | 0.414627 | -1.455493 | -0.783940 |
| C | 0.811175 | -2.736411 | -0.322991 |
| C | 1.124067 | -1.191398 | -1.984756 |
| C | 2.312020 | -2.803848 | -0.606182 |
| C | 2.504776 | -1.842438 | -1.800093 |
| H | 0.575410 | -1.637288 | -2.833880 |
| H | 0.255660 | -3.513642 | -0.881296 |
| H | 0.543651 | -2.805289 | 0.739692 |
| H | 1.154415 | -0.102244 | -2.121080 |
| H | 2.815576 | -2.368547 | -2.713370 |
| H | 2.639743 | -3.829403 | -0.824725 |
| H | 2.874674 | -2.448660 | 0.267541 |
| H | 3.270380 | -1.087932 | -1.574503 |
| C | 4.362276 | -0.111254 | 1.008954 |
| C | 2.769066 | 1.369849 | -0.056808 |
| C | 3.757565 | 1.792338 | -0.940643 |
| C | 5.345895 | 0.316305 | 0.121210 |
| C | 5.046627 | 1.264786 | -0.857768 |
| H | 1.758910 | 1.780945 | -0.117741 |
| H | 3.517696 | 2.541693 | -1.698058 |
| H | 4.592972 | -0.855723 | 1.773494 |
| H | 6.355165 | -0.094585 | 0.193738 |
| H | 5.820735 | 1.596699 | -1.552874 |

**TS$_{prox}$**

| | | | |
|---|---|---|---|
| C | 0.220306 | -0.220799 | -0.770227 |
| C | 1.235225 | 0.844292 | -1.123344 |
| C | -0.923757 | -0.655306 | -1.029887 |
| C | -2.154008 | -1.353191 | -1.001759 |
| H | 2.180835 | 0.313370 | -1.393043 |
| H | 0.885542 | 1.327480 | -2.059642 |
| O | 1.410485 | 1.755415 | -0.095005 |
| Li | 2.576132 | 0.730141 | 0.844486 |
| O | 4.374404 | 0.530346 | 0.259822 |
| C | 4.875006 | -0.774290 | -0.055876 |
| C | 4.739356 | 1.482218 | -0.748045 |
| C | 5.776549 | -0.582795 | -1.272250 |
| C | 5.157948 | 0.642791 | -1.946990 |
| H | 3.865200 | 2.126527 | -0.928221 |
| H | 4.016044 | -1.431780 | -0.275896 |
| H | 5.402875 | -1.173872 | 0.822151 |
| H | 5.573530 | 2.099900 | -0.372896 |
| H | 4.274229 | 0.354949 | -2.537277 |
| H | 5.799669 | -1.471315 | -1.917379 |
| H | 6.809286 | -0.366410 | -0.956930 |
| H | 5.853692 | 1.173404 | -2.610997 |
| Si | 0.871864 | -1.197907 | 1.481116 |
| C | 2.197261 | -1.318198 | 2.900360 |
| C | 0.407110 | -3.004608 | 1.132720 |
| Li | -0.158046 | 1.370824 | 0.822481 |
| C | -0.640539 | -0.482346 | 2.459317 |
| H | 0.123695 | -3.527558 | 2.062167 |
| H | -0.441867 | -3.067359 | 0.435647 |
| H | 1.251942 | -3.550936 | 0.682461 |
| H | 2.490147 | -0.325692 | 3.292664 |
| H | 1.824338 | -1.900309 | 3.763171 |
| H | 3.119312 | -1.812737 | 2.548239 |
| H | -0.908606 | -1.145163 | 3.299356 |
| H | -0.437223 | 0.507545 | 2.915410 |
| H | -1.538380 | -0.398370 | 1.824571 |
| O | -1.781111 | 2.336355 | 0.610321 |
| C | -1.968472 | 2.752872 | -0.752320 |
| C | -2.945096 | 2.586982 | 1.394329 |
| C | -3.242853 | 3.586417 | -0.738275 |
| C | -4.040424 | 2.929181 | 0.389682 |
| H | -3.162039 | 1.693223 | 1.999118 |
| H | -2.062931 | 1.850462 | -1.379757 |
| H | -1.069744 | 3.302592 | -1.065653 |
| H | -2.744179 | 3.430028 | 2.078129 |
| H | -4.528777 | 2.011881 | 0.025854 |
| H | -3.762962 | 3.567539 | -1.705230 |
| H | -3.018095 | 4.636015 | -0.491324 |
| H | -4.813824 | 3.580680 | 0.818478 |
| C | -3.272313 | -0.825806 | -0.314379 |
| C | -2.318369 | -2.592635 | -1.663337 |
| C | -3.536155 | -3.260989 | -1.628950 |
| C | -4.484820 | -1.504570 | -0.287240 |
| C | -4.630731 | -2.727369 | -0.944046 |
| H | -1.470431 | -3.020575 | -2.201675 |
| H | -3.633479 | -4.219086 | -2.145797 |
| H | -3.163317 | 0.127987 | 0.203126 |
| H | -5.328605 | -1.073338 | 0.258159 |
| H | -5.583808 | -3.259312 | -0.921529 |

**INT2$_{prox}$**

| | | | |
|---|---|---|---|
| C | 0.670649 | -0.350681 | -0.938699 |
| C | 1.447975 | 0.714567 | -1.764040 |
| C | -0.424759 | 0.067491 | -0.248942 |
| C | -1.302191 | -0.839115 | 0.488544 |
| H | 2.515850 | 0.686114 | -1.438418 |
| H | 1.491955 | 0.349646 | -2.819324 |
| O | 0.913798 | 1.986059 | -1.664613 |
| Li | 0.699324 | 1.839467 | 0.162967 |
| O | 2.293791 | 1.945578 | 1.216517 |
| C | 2.754605 | 0.762585 | 1.876760 |
| C | 3.357858 | 2.580230 | 0.489947 |
| C | 4.275202 | 0.827907 | 1.810881 |
| C | 4.507013 | 1.578583 | 0.498747 |
| H | 2.978015 | 2.816430 | -0.516667 |
| H | 2.357019 | -0.116282 | 1.341664 |
| H | 2.357724 | 0.754559 | 2.902343 |
| H | 3.628435 | 3.515113 | 1.009764 |
| H | 4.421484 | 0.890904 | -0.356101 |
| H | 4.735561 | -0.169651 | 1.828528 |
| H | 4.674902 | 1.402153 | 2.661565 |
| H | 5.489090 | 2.067544 | 0.444205 |
| Si | 1.395859 | -2.103590 | -0.952192 |
| C | 1.100501 | -3.036207 | 0.660819 |
| C | 3.273649 | -1.974647 | -1.178853 |
| Li | -0.879616 | 1.637896 | -1.693239 |
| C | 0.720087 | -3.120420 | -2.393319 |
| H | 3.727219 | -2.978778 | -1.208647 |
| H | 3.540685 | -1.456911 | -2.113699 |

| | | | |
|---|---|---|---|
| H | 3.741404 | -1.424874 | -0.345478 |
| H | 0.042219 | -3.302016 | 0.797688 |
| H | 1.695352 | -3.964533 | 0.669076 |
| H | 1.401510 | -2.432921 | 1.532081 |
| H | 1.238041 | -4.090318 | -2.470953 |
| H | -0.354388 | -3.321005 | -2.262994 |
| H | 0.853357 | -2.587802 | -3.348463 |
| O | -2.711489 | 2.296339 | -1.513559 |
| C | -3.642144 | 1.220543 | -1.333967 |
| C | -2.843332 | 3.207962 | -0.429646 |
| C | -4.106181 | 1.274387 | 0.130952 |
| C | -3.189267 | 2.328716 | 0.762945 |
| H | -1.894377 | 3.757485 | -0.333995 |
| H | -3.114724 | 0.284220 | -1.566365 |
| H | -4.475862 | 1.343194 | -2.043758 |
| H | -3.642505 | 3.940133 | -0.648516 |
| H | -2.277662 | 1.845718 | 1.144086 |
| H | -4.009530 | 0.297079 | 0.623410 |
| H | -5.159813 | 1.585902 | 0.190822 |
| H | -3.667684 | 2.885684 | 1.580214 |
| C | -1.450164 | -0.739994 | 1.887251 |
| C | -2.110960 | -1.789004 | -0.170178 |
| C | -3.007194 | -2.595898 | 0.527580 |
| C | -2.331258 | -1.557747 | 2.587882 |
| C | -3.124121 | -2.489676 | 1.913803 |
| H | -2.021723 | -1.889559 | -1.255762 |
| H | -3.616899 | -3.321657 | -0.017248 |
| H | -0.848136 | -0.002790 | 2.427929 |
| H | -2.407801 | -1.463231 | 3.674336 |
| H | -3.824473 | -3.122695 | 2.462623 |

**TS$_{dist}$**

| | | | |
|---|---|---|---|
| C | 0.815056 | -0.148194 | -2.191556 |
| C | -0.430236 | -0.235333 | -3.019027 |
| C | 1.181144 | -0.499301 | -1.018804 |
| C | 2.339587 | -0.201494 | -0.161795 |
| H | -0.455929 | 0.613536 | -3.735926 |
| H | -0.323615 | -1.139099 | -3.664154 |
| O | -1.572418 | -0.260113 | -2.233072 |
| Li | -2.307856 | -1.505879 | -1.282694 |
| O | -2.986361 | -0.371173 | 0.166024 |
| C | -2.975265 | -0.425177 | 1.599870 |
| C | -3.802953 | 0.719315 | -0.300279 |
| C | -3.935834 | 0.667786 | 2.062234 |
| C | -3.912035 | 1.653769 | 0.892206 |
| H | -3.300643 | 1.133174 | -1.185328 |
| H | -1.940636 | -0.250287 | 1.938160 |
| H | -3.271796 | -1.433815 | 1.922386 |
| H | -4.789083 | 0.321834 | -0.598611 |
| H | -3.017163 | 2.290159 | 0.938909 |
| H | -3.623686 | 1.114854 | 3.015646 |
| H | -4.948477 | 0.257494 | 2.199149 |
| H | -4.804015 | 2.292831 | 0.845562 |
| Si | 0.101593 | -2.427208 | 0.128096 |
| C | -0.285771 | -3.006457 | 1.924750 |
| C | 1.672004 | -3.422003 | -0.290857 |
| Li | -0.891444 | 0.187121 | -0.529444 |
| C | -1.233190 | -3.447760 | -0.873081 |
| H | 1.544220 | -4.486943 | -0.031288 |
| H | 1.905127 | -3.348921 | -1.364885 |
| H | 2.547030 | -3.041423 | 0.258869 |
| H | -1.264832 | -2.658234 | 2.291299 |
| H | -0.280722 | -4.109382 | 1.987068 |
| H | 0.477216 | -2.640684 | 2.631996 |
| H | -0.981494 | -4.516756 | -0.790120 |
| H | -2.263134 | -3.377059 | -0.465865 |
| H | -1.242515 | -3.226295 | -1.957258 |
| O | -0.770103 | 2.028722 | 0.088651 |
| C | -0.588606 | 2.886977 | -1.036337 |
| C | 0.112413 | 2.459729 | 1.121567 |
| C | 0.910850 | 3.158634 | -1.065231 |
| C | 1.304830 | 3.139023 | 0.424344 |
| H | -0.426529 | 3.159738 | 1.784785 |
| H | -1.178420 | 3.811581 | -0.888841 |
| H | -0.970083 | 2.352767 | -1.918008 |
| H | 0.399737 | 1.573889 | 1.703750 |
| H | 1.454543 | 4.153686 | 0.820762 |
| H | 1.151003 | 4.109830 | -1.559657 |
| H | 1.411186 | 2.342316 | -1.606671 |
| H | 2.234082 | 2.575520 | 0.583573 |
| C | 3.523594 | 0.266968 | -0.761127 |
| C | 2.306697 | -0.290518 | 1.235211 |
| C | 3.402440 | 0.084702 | 2.011565 |
| C | 4.618159 | 0.639860 | 0.011309 |
| C | 4.564467 | 0.556236 | 1.404890 |
| H | 1.394556 | -0.654858 | 1.714792 |
| H | 3.344282 | 0.008526 | 3.100143 |
| H | 3.552063 | 0.338131 | -1.850161 |
| H | 5.525830 | 0.999924 | -0.479265 |
| H | 5.424432 | 0.851081 | 2.010328 |

**INT2$_{dist}$**

| | | | |
|---|---|---|---|
| C | 0.453265 | 1.169370 | 0.371952 |
| C | 0.482258 | 2.486189 | -0.406959 |
| C | 1.541085 | 0.336815 | 0.398389 |
| C | 1.283273 | -1.064050 | 0.860747 |
| H | -0.032605 | 3.289998 | 0.169786 |
| H | 1.482146 | 2.917594 | -0.649893 |
| O | -0.216135 | 2.143197 | -1.585562 |
| Li | 0.582259 | 0.525004 | -1.835967 |
| O | -1.041622 | -0.621338 | -1.983750 |
| C | -1.363868 | -1.874947 | -1.362116 |
| C | -2.012665 | -0.340484 | -2.992715 |
| C | -2.868163 | -2.091972 | -1.611002 |
| C | -3.314948 | -0.836102 | -2.379938 |
| H | -1.971429 | 0.740980 | -3.187193 |
| H | -1.084111 | -1.792374 | -0.303170 |
| H | -0.747986 | -2.669286 | -1.811741 |
| H | -1.757760 | -0.886746 | -3.919043 |
| H | -3.709753 | -0.076322 | -1.689118 |
| H | -3.421662 | -2.215990 | -0.670701 |
| H | -3.031426 | -3.000162 | -2.208717 |
| H | -4.083030 | -1.045578 | -3.136349 |
| Si | 3.286853 | 0.833871 | -0.144388 |
| C | 4.593016 | -0.481251 | 0.233633 |
| C | 3.889640 | 2.408009 | 0.701794 |
| Li | -1.383617 | 1.032960 | -0.621620 |
| C | 3.259368 | 1.079454 | -2.035111 |
| H | 4.899032 | 2.676150 | 0.348890 |
| H | 3.224035 | 3.264999 | 0.529126 |
| H | 3.945461 | 2.241039 | 1.789536 |
| H | 4.514449 | -1.372311 | -0.406671 |

| | | | |
|---|---|---|---|
| H | 5.599754 | -0.055275 | 0.090768 |
| H | 4.514925 | -0.819128 | 1.279336 |
| H | 4.237452 | 1.398644 | -2.428675 |
| H | 3.014532 | 0.127853 | -2.543926 |
| H | 2.522242 | 1.843501 | -2.338049 |
| O | -3.069883 | 1.125975 | 0.346004 |
| C | -3.052942 | 2.453150 | 0.885610 |
| C | -3.039607 | 0.157348 | 1.404551 |
| C | -2.431784 | 2.299527 | 2.264584 |
| C | -3.001877 | 0.951566 | 2.710776 |
| H | -3.924252 | -0.492893 | 1.319209 |
| H | -4.085459 | 2.842333 | 0.932977 |
| H | -2.467458 | 3.086202 | 0.201561 |
| H | -2.125756 | -0.447141 | 1.283556 |
| H | -4.016028 | 1.073552 | 3.122916 |
| H | -2.685285 | 3.127504 | 2.940641 |
| H | -1.338349 | 2.227880 | 2.159567 |
| H | -2.384488 | 0.455660 | 3.472144 |
| C | 0.472104 | -1.305593 | 1.984167 |
| C | 1.736987 | -2.185422 | 0.147225 |
| C | 1.376412 | -3.482938 | 0.513500 |
| C | 0.106619 | -2.597276 | 2.354141 |
| C | 0.551457 | -3.697263 | 1.615917 |
| H | 2.363755 | -2.041200 | -0.737776 |
| H | 1.737175 | -4.331629 | -0.073461 |
| H | 0.121301 | -0.440367 | 2.550757 |
| H | -0.525704 | -2.751734 | 3.232861 |
| H | 0.267776 | -4.711295 | 1.906646 |

**INT3$_{prox}$**

| | | | |
|---|---|---|---|
| C | 0.928309 | -1.120239 | -0.380576 |
| C | 0.053076 | -1.267045 | -1.648408 |
| C | 0.513191 | -0.239087 | 0.566047 |
| C | 1.264047 | 0.100308 | 1.768912 |
| H | 0.724826 | -1.118951 | -2.533319 |
| H | -0.242697 | -2.342553 | -1.743463 |
| O | -1.036140 | -0.428125 | -1.669065 |
| Li | -0.334206 | 1.176630 | -0.924416 |
| O | 0.913594 | 1.919554 | -2.293514 |
| C | 2.316367 | 1.862048 | -2.046654 |
| C | 0.608760 | 1.492406 | -3.626320 |
| C | 2.965082 | 1.766185 | -3.420437 |
| C | 1.921813 | 0.960563 | -4.195803 |
| H | -0.190195 | 0.738097 | -3.557008 |
| H | 2.532530 | 0.970989 | -1.435273 |
| H | 2.610021 | 2.758346 | -1.478990 |
| H | 0.244621 | 2.364360 | -4.197272 |
| H | 2.027684 | -0.111660 | -3.971054 |
| H | 3.951862 | 1.284168 | -3.382792 |
| H | 3.089979 | 2.767876 | -3.861930 |
| H | 1.990360 | 1.088165 | -5.284856 |
| Si | 2.475841 | -2.208545 | -0.306855 |
| C | 2.814493 | -2.847017 | 1.434643 |
| C | 4.021816 | -1.316316 | -0.945127 |
| Li | -1.608809 | -0.517127 | 0.115470 |
| C | 2.259861 | -3.703247 | -1.454634 |
| H | 4.882228 | -2.005406 | -0.964386 |
| H | 3.868064 | -0.949258 | -1.973374 |
| H | 4.291340 | -0.459942 | -0.308920 |
| H | 1.924686 | -3.351463 | 1.844135 |
| H | 3.644593 | -3.572406 | 1.427231 |
| H | 3.075635 | -2.027808 | 2.121076 |
| H | 3.172765 | -4.321240 | -1.450794 |
| H | 1.420172 | -4.349524 | -1.154692 |
| H | 2.076299 | -3.382753 | -2.492812 |
| O | -3.126400 | 0.709702 | 0.164578 |
| C | -4.236874 | 0.536176 | 1.038441 |
| C | -3.544833 | 1.197304 | -1.110491 |
| C | -5.473766 | 0.949008 | 0.234690 |
| C | -5.002586 | 0.775320 | -1.211129 |
| H | -3.433289 | 2.296246 | -1.132215 |
| H | -4.090911 | 1.150816 | 1.941521 |
| H | -4.265427 | -0.523428 | 1.339786 |
| H | -2.879407 | 0.743966 | -1.859411 |
| H | -5.574233 | 1.376820 | -1.931242 |
| H | -5.724626 | 2.004098 | 0.425976 |
| H | -6.356567 | 0.344676 | 0.485011 |
| H | -5.067888 | -0.280607 | -1.518020 |
| C | 2.485666 | 0.807555 | 1.720434 |
| C | 0.740458 | -0.155763 | 3.056024 |
| C | 1.410264 | 0.230323 | 4.212051 |
| C | 3.148306 | 1.212315 | 2.877207 |
| C | 2.621139 | 0.923899 | 4.135952 |
| H | -0.223573 | -0.666917 | 3.137208 |
| H | 0.977039 | -0.001882 | 5.188768 |
| H | 2.913850 | 1.045769 | 0.744374 |
| H | 4.092375 | 1.757743 | 2.793340 |
| H | 3.140838 | 1.238034 | 5.043478 |
| O | -2.454920 | -2.206048 | 0.686122 |
| C | -1.748651 | -3.092777 | 1.542655 |
| C | -2.848433 | -2.881779 | -0.516400 |
| C | -1.086261 | -4.082662 | 0.600592 |
| C | -2.150736 | -4.250309 | -0.487835 |
| H | -3.946942 | -2.975376 | -0.535531 |
| H | -2.453773 | -3.590302 | 2.234934 |
| H | -1.030680 | -2.499666 | 2.125372 |
| H | -2.525326 | -2.246618 | -1.357810 |
| H | -2.861590 | -5.044192 | -0.210865 |
| H | -0.809561 | -5.026369 | 1.090356 |
| H | -0.177116 | -3.624062 | 0.188039 |
| H | -1.719711 | -4.512596 | -1.463615 |
| O | -0.900073 | 2.841599 | 0.039279 |
| C | -1.132594 | 2.703886 | 1.442177 |
| C | -0.130975 | 4.014257 | -0.165612 |
| C | 0.005125 | 3.466105 | 2.149913 |
| C | 0.857467 | 4.008521 | 0.992507 |
| H | 0.324812 | 3.940895 | -1.161388 |
| H | -1.129395 | 1.629553 | 1.662573 |
| H | -2.124916 | 3.121866 | 1.685472 |
| H | -0.785701 | 4.906804 | -0.132029 |
| H | 1.680691 | 3.311396 | 0.775253 |
| H | 0.586282 | 2.806681 | 2.808861 |
| H | -0.397764 | 4.287096 | 2.761648 |
| H | 1.289334 | 4.998562 | 1.195344 |

**INT3$_{dist}$**

| | | | |
|---|---|---|---|
| C | 0.976698 | 0.099773 | -0.817517 |
| C | -0.078739 | 0.626926 | -1.775588 |
| C | 2.159570 | 0.719523 | -0.573116 |
| C | 3.010601 | 0.094205 | 0.487801 |
| H | -0.093045 | 1.746332 | -1.847788 |
| H | 0.179137 | 0.288993 | -2.809417 |

| | | | |
|---|---|---|---|
| O | -1.335972 | 0.139258 | -1.392704 |
| Li | -2.321129 | 0.219524 | 0.090120 |
| O | -1.342653 | -0.874270 | 1.494832 |
| C | -1.797073 | -2.103771 | 2.058928 |
| C | -0.269151 | -0.391604 | 2.310973 |
| C | -0.555303 | -2.748031 | 2.704872 |
| C | 0.522260 | -1.645420 | 2.642921 |
| H | 0.298053 | 0.329969 | 1.707364 |
| H | -2.240837 | -2.690222 | 1.243945 |
| H | -2.580255 | -1.888221 | 2.806561 |
| H | -0.690726 | 0.087859 | 3.214273 |
| H | 1.241256 | -1.823796 | 1.830051 |
| H | -0.240921 | -3.647093 | 2.158165 |
| H | -0.771761 | -3.053481 | 3.738314 |
| H | 1.099056 | -1.543591 | 3.571248 |
| Si | 2.867542 | 2.200934 | -1.500111 |
| C | 2.050324 | 3.855435 | -1.063997 |
| C | 2.680540 | 1.968440 | -3.367160 |
| Li | -0.495056 | -1.222955 | -0.358388 |
| C | 4.714427 | 2.371591 | -1.129949 |
| H | 3.185032 | 2.780043 | -3.917029 |
| H | 3.125355 | 1.011715 | -3.684532 |
| H | 1.621578 | 1.960485 | -3.666810 |
| H | 2.114820 | 4.063465 | 0.016124 |
| H | 2.544858 | 4.683009 | -1.599170 |
| H | 0.987035 | 3.856542 | -1.349753 |
| H | 5.164630 | 3.180152 | -1.728927 |
| H | 4.896940 | 2.591442 | -0.066364 |
| H | 5.245980 | 1.435110 | -1.363980 |
| O | -0.488386 | -3.084355 | -0.980486 |
| C | 0.714507 | -3.768693 | -0.616253 |
| C | -0.542088 | -2.901469 | -2.401784 |
| C | 1.500539 | -3.986032 | -1.912176 |
| C | 0.913598 | -2.921379 | -2.840521 |
| H | -1.121872 | -3.725281 | -2.856442 |
| H | 0.456202 | -4.713067 | -0.110602 |
| H | 1.270780 | -3.126206 | 0.084820 |
| H | -1.051370 | -1.943095 | -2.584943 |
| H | 1.035414 | -3.155885 | -3.906979 |
| H | 1.316984 | -4.994997 | -2.313959 |
| H | 2.583279 | -3.877114 | -1.759663 |
| H | 1.368908 | -1.940783 | -2.632131 |
| C | 3.459895 | -1.231416 | 0.368492 |
| C | 3.332453 | 0.777309 | 1.671178 |
| C | 4.036190 | 0.155949 | 2.703616 |
| C | 4.170683 | -1.856361 | 1.391237 |
| C | 4.456419 | -1.167560 | 2.571552 |
| H | 2.999898 | 1.813763 | 1.788433 |
| H | 4.257681 | 0.709840 | 3.619946 |
| H | 3.227688 | -1.767305 | -0.555117 |
| H | 4.508305 | -2.889260 | 1.267523 |
| H | 5.011886 | -1.654533 | 3.376521 |
| O | -2.811816 | 1.956523 | 0.833580 |
| C | -2.103322 | 2.933816 | 0.070371 |
| C | -2.637588 | 2.250594 | 2.212046 |
| C | -0.830618 | 3.160124 | 0.872305 |
| C | -1.317093 | 3.040181 | 2.326625 |
| H | -3.497004 | 2.841243 | 2.574240 |
| H | -2.714597 | 3.851587 | -0.013073 |
| H | -1.933014 | 2.500641 | -0.924989 |
| H | -2.627777 | 1.293542 | 2.754771 |
| H | -1.499675 | 4.029892 | 2.769568 |
| H | -0.360877 | 4.128501 | 0.658330 |
| H | -0.098594 | 2.374839 | 0.622485 |
| H | -0.582065 | 2.528749 | 2.962657 |
| O | -3.971596 | -0.794333 | -0.214091 |
| C | -4.236047 | -0.684536 | -1.611975 |
| C | -5.130097 | -0.342707 | 0.463447 |
| C | -4.983256 | 0.643345 | -1.745607 |
| C | -5.682966 | 0.819211 | -0.379465 |
| H | -5.858541 | -1.171000 | 0.536734 |
| H | -4.853279 | -1.542868 | -1.934812 |
| H | -3.259605 | -0.682652 | -2.116648 |
| H | -4.834314 | -0.050216 | 1.480967 |
| H | -6.778219 | 0.768810 | -0.456160 |
| H | -5.685380 | 0.640768 | -2.590649 |
| H | -4.256153 | 1.450083 | -1.916219 |
| H | -5.416704 | 1.783263 | 0.072913 |

<Methyl Propargyl Ether>

**Ether**

| | | | |
|---|---|---|---|
| C | -1.614040 | 2.871205 | 0.000000 |
| C | -0.726751 | 1.712206 | 0.000000 |
| H | -2.666609 | 2.550931 | 0.000000 |
| H | -1.450399 | 3.495955 | 0.890753 |
| H | -1.450399 | 3.495955 | -0.890753 |
| C | 0.000000 | 0.746404 | 0.000000 |
| C | 0.901525 | -0.406497 | 0.000000 |
| H | 1.565237 | -0.348521 | -0.888617 |
| H | 1.565237 | -0.348521 | 0.888617 |
| O | 0.178774 | -1.604234 | 0.000000 |
| C | 0.998563 | -2.731655 | 0.000000 |
| H | 1.650396 | -2.772115 | -0.895641 |
| H | 1.650396 | -2.772115 | 0.895641 |
| H | 0.350162 | -3.617671 | 0.000000 |

**INT1$_{OMe}$**

| | | | |
|---|---|---|---|
| Si | -2.290844 | 0.375469 | -0.359106 |
| C | -2.952607 | -1.374354 | 0.163012 |
| C | -3.522679 | 0.808754 | -1.776520 |
| Li | 0.266230 | 0.562302 | -0.747444 |
| C | -2.959549 | 1.474340 | 1.082795 |
| H | -4.574192 | 0.698694 | -1.454326 |
| H | -3.386549 | 1.848157 | -2.121346 |
| H | -3.372872 | 0.155834 | -2.653767 |
| H | -2.486032 | -1.757149 | 1.089038 |
| H | -4.043085 | -1.350472 | 0.340592 |
| H | -2.768815 | -2.132388 | -0.619391 |
| H | -4.034775 | 1.299040 | 1.269427 |
| H | -2.424220 | 1.297554 | 2.032174 |
| H | -2.834630 | 2.544977 | 0.845129 |
| O | 1.260099 | -1.020816 | -1.344589 |
| C | 2.447890 | -1.402994 | -0.669038 |
| C | 0.451826 | -2.189482 | -1.436312 |
| C | 2.020495 | -2.460330 | 0.367043 |
| C | 0.582727 | -2.828462 | -0.057701 |
| H | -0.568418 | -1.870414 | -1.685214 |
| H | 2.888257 | -0.498359 | -0.229271 |
| H | 3.163673 | -1.821410 | -1.398988 |
| H | 0.844637 | -2.844758 | -2.235813 |
| H | -0.158422 | -2.371447 | 0.614178 |

| | | | |
|---|---|---|---|
| H | 2.047969 | -2.048426 | 1.385155 |
| H | 2.694991 | -3.327869 | 0.343399 |
| H | 0.399626 | -3.911213 | -0.075924 |
| C | -0.099327 | -0.497607 | 2.938736 |
| C | 0.747686 | 0.435028 | 2.207311 |
| H | 0.406047 | -1.459928 | 3.106413 |
| H | -0.383255 | -0.076976 | 3.914135 |
| H | -1.020097 | -0.676155 | 2.362810 |
| C | 1.414955 | 1.235442 | 1.592356 |
| C | 2.095699 | 2.201361 | 0.735346 |
| H | 1.794297 | 3.229094 | 1.012132 |
| H | 3.194613 | 2.134155 | 0.848811 |
| O | 1.731808 | 1.932575 | -0.605878 |
| C | 2.244883 | 2.842879 | -1.546240 |
| H | 1.883527 | 3.866873 | -1.347819 |
| H | 3.349089 | 2.842763 | -1.536993 |
| H | 1.894514 | 2.524835 | -2.535724 |

**TS$_{prox\text{-}OMe}$**

| | | | |
|---|---|---|---|
| Si | -1.167887 | -1.372518 | -0.291983 |
| C | -0.785466 | -2.798914 | 0.923023 |
| C | -0.617729 | -2.114461 | -1.991565 |
| Li | 0.013814 | 1.022392 | -0.541291 |
| C | -3.080638 | -1.414719 | -0.431742 |
| H | -1.144474 | -3.064912 | -2.193646 |
| H | -0.831904 | -1.434224 | -2.834104 |
| H | 0.463721 | -2.335617 | -2.007595 |
| H | -1.072134 | -2.533425 | 1.953154 |
| H | -1.343543 | -3.709024 | 0.640816 |
| H | 0.286280 | -3.058521 | 0.933456 |
| H | -3.427906 | -2.408025 | -0.765998 |
| H | -3.559482 | -1.210372 | 0.540868 |
| H | -3.460971 | -0.672107 | -1.154546 |
| O | 1.873604 | 1.184216 | -0.946794 |
| C | 2.709802 | 1.404788 | 0.196391 |
| C | 2.417535 | 0.120837 | -1.725778 |
| C | 3.588675 | 0.148840 | 0.337648 |
| C | 3.000516 | -0.825729 | -0.690847 |
| H | 1.602436 | -0.313613 | -2.321119 |
| H | 2.047086 | 1.568522 | 1.059748 |
| H | 3.307226 | 2.316488 | 0.037468 |
| H | 3.190770 | 0.516205 | -2.409306 |
| H | 2.185392 | -1.419840 | -0.247447 |
| H | 3.564823 | -0.255876 | 1.358003 |
| H | 4.636026 | 0.382583 | 0.095745 |
| H | 3.744966 | -1.515765 | -1.110220 |
| C | 0.860321 | -0.387934 | 2.793415 |
| C | -0.207859 | 0.517498 | 2.354943 |
| H | 1.211128 | -1.018675 | 1.947027 |
| H | 1.723210 | 0.146981 | 3.221543 |
| H | 0.489374 | -1.067455 | 3.577099 |
| C | -1.021595 | 0.654147 | 1.400752 |
| C | -2.055826 | 1.570664 | 0.863485 |
| H | -2.996252 | 1.039187 | 0.642100 |
| H | -2.258171 | 2.371013 | 1.596599 |
| O | -1.556632 | 2.151545 | -0.344086 |
| C | -2.519755 | 2.815594 | -1.116894 |
| H | -2.977101 | 3.648603 | -0.554653 |
| H | -2.016949 | 3.222398 | -2.003895 |
| H | -3.318235 | 2.123779 | -1.439410 |

**INT2$_{prox\text{-}OMe}$**

| | | | |
|---|---|---|---|
| Si | 0.026153 | 2.570916 | -0.303623 |
| C | 1.896768 | 2.551882 | -0.591071 |
| C | -0.418606 | 3.971867 | 0.884805 |
| Li | -1.120307 | -1.591656 | 1.283020 |
| C | -0.756986 | 3.025380 | -1.972715 |
| H | -0.077225 | 4.943251 | 0.490449 |
| H | -1.511239 | 4.024031 | 1.017173 |
| H | 0.028235 | 3.831086 | 1.879891 |
| H | 2.157125 | 1.781145 | -1.334743 |
| H | 2.248022 | 3.524196 | -0.974195 |
| H | 2.455724 | 2.326793 | 0.329400 |
| H | -0.392196 | 4.011701 | -2.303150 |
| H | -0.502643 | 2.299636 | -2.762094 |
| H | -1.855632 | 3.084780 | -1.910522 |
| O | 0.060562 | -3.137646 | 1.057746 |
| C | 0.410919 | -3.317298 | -0.321106 |
| C | 1.235305 | -2.874647 | 1.831702 |
| C | 1.924561 | -3.109081 | -0.411414 |
| C | 2.220364 | -2.280986 | 0.839848 |
| H | 0.957556 | -2.181520 | 2.638578 |
| H | -0.141446 | -2.564774 | -0.905370 |
| H | 0.094574 | -4.320506 | -0.646601 |
| H | 1.606360 | -3.817885 | 2.271769 |
| H | 1.966952 | -1.222286 | 0.671977 |
| H | 2.217514 | -2.605551 | -1.342567 |
| H | 2.452838 | -4.074455 | -0.369064 |
| H | 3.263715 | -2.352347 | 1.175893 |
| C | 0.661998 | 0.896254 | 2.403915 |
| C | -0.286158 | 0.244635 | 1.425183 |
| H | 1.128749 | 1.853900 | 2.102037 |
| H | 0.137493 | 1.084426 | 3.357592 |
| H | 1.490989 | 0.211788 | 2.664260 |
| C | -0.616525 | 0.884317 | 0.270931 |
| C | -1.598090 | 0.253080 | -0.703520 |
| H | -2.506600 | 0.879641 | -0.818010 |
| H | -1.159935 | 0.160639 | -1.719316 |
| O | -2.021234 | -1.052010 | -0.302752 |
| C | -2.948325 | -1.639240 | -1.169748 |
| H | -2.533094 | -1.752725 | -2.188556 |
| H | -3.201432 | -2.634891 | -0.779073 |
| H | -3.872989 | -1.038223 | -1.238483 |

**TS$_{dist\text{-}OMe}$**

| | | | |
|---|---|---|---|
| Si | -2.231774 | -0.304107 | -0.368610 |
| C | -2.823993 | -2.113429 | -0.574715 |
| C | -2.420044 | 0.451550 | -2.135140 |
| Li | 0.162230 | 0.511614 | -0.523161 |
| C | -3.606898 | 0.563715 | 0.632895 |
| H | -3.456123 | 0.355299 | -2.507343 |
| H | -2.170530 | 1.527199 | -2.145232 |
| H | -1.760278 | -0.049310 | -2.864789 |
| H | -2.826587 | -2.656920 | 0.384404 |
| H | -3.850911 | -2.153229 | -0.979013 |
| H | -2.173424 | -2.672618 | -1.268400 |
| H | -4.596760 | 0.428063 | 0.162962 |
| H | -3.673937 | 0.184171 | 1.665626 |
| H | -3.410209 | 1.646522 | 0.699461 |
| O | 1.624124 | -0.596689 | -1.149859 |
| C | 2.948231 | -0.186720 | -0.798859 |
| C | 1.421097 | -1.966280 | -0.793157 |

| | | | |
|---|---|---|---|
| C | 3.583723 | -1.369477 | -0.058997 |
| C | 2.367823 | -2.192264 | 0.373252 |
| H | 0.355485 | -2.085371 | -0.547263 |
| H | 2.866060 | 0.707975 | -0.161801 |
| H | 3.498563 | 0.090113 | -1.711672 |
| H | 1.666474 | -2.614254 | -1.653720 |
| H | 1.927900 | -1.774825 | 1.292390 |
| H | 4.207474 | -1.044519 | 0.784607 |
| H | 4.219471 | -1.954478 | -0.741335 |
| H | 2.596864 | -3.253471 | 0.540272 |
| C | -0.853461 | -1.254988 | 2.315595 |
| C | -0.356432 | -0.025436 | 1.653237 |
| H | -0.599619 | -2.155954 | 1.737521 |
| H | -0.404593 | -1.337318 | 3.318616 |
| H | -1.947729 | -1.236646 | 2.423766 |
| C | 0.406028 | 0.962419 | 1.801544 |
| C | 0.902989 | 2.233238 | 1.289998 |
| H | 0.365601 | 3.068174 | 1.777635 |
| H | 1.982778 | 2.377802 | 1.491545 |
| O | 0.707418 | 2.321899 | -0.136681 |
| C | 1.065958 | 3.547319 | -0.712565 |
| H | 0.465184 | 4.375175 | -0.296202 |
| H | 2.135942 | 3.770816 | -0.546077 |
| H | 0.878579 | 3.480697 | -1.792145 |

**INT2**$_{\text{dist-OMe}}$

| | | | |
|---|---|---|---|
| Si | -2.775969 | -0.243512 | 0.221616 |
| C | -2.638550 | 0.788699 | 1.804362 |
| C | -3.589332 | -1.882517 | 0.703289 |
| Li | 1.798626 | 0.715358 | -1.408076 |
| C | -3.946587 | 0.666258 | -0.954201 |
| H | -4.565285 | -1.711211 | 1.185942 |
| H | -3.757523 | -2.522553 | -0.177178 |
| H | -2.958080 | -2.446448 | 1.409246 |
| H | -2.412086 | 1.846324 | 1.600050 |
| H | -3.596896 | 0.756688 | 2.348313 |
| H | -1.858106 | 0.395684 | 2.475654 |
| H | -4.929488 | 0.852419 | -0.490976 |
| H | -3.520713 | 1.637198 | -1.253940 |
| H | -4.108209 | 0.079260 | -1.872409 |
| O | 3.296372 | -0.295087 | -0.713153 |
| C | 3.530895 | 0.091609 | 0.649297 |
| C | 2.986154 | -1.690961 | -0.778706 |
| C | 3.260100 | -1.150880 | 1.503152 |
| C | 2.396036 | -2.015059 | 0.582145 |
| H | 2.277368 | -1.840294 | -1.605860 |
| H | 2.837644 | 0.915772 | 0.882665 |
| H | 4.563070 | 0.462273 | 0.746147 |
| H | 3.908447 | -2.263568 | -0.984211 |
| H | 1.347211 | -1.678877 | 0.601004 |
| H | 2.761801 | -0.899730 | 2.449248 |
| H | 4.202707 | -1.665802 | 1.745921 |
| H | 2.438548 | -3.086044 | 0.822559 |
| C | -1.028808 | -1.915149 | -1.331328 |
| C | -1.127173 | -0.564119 | -0.638770 |
| H | -1.861076 | -2.087427 | -2.038766 |
| H | -0.089710 | -1.979189 | -1.904972 |
| H | -1.055962 | -2.758910 | -0.617417 |
| C | -0.098674 | 0.305999 | -0.753962 |
| C | -0.122036 | 1.660149 | -0.110344 |
| H | -0.943220 | 2.323003 | -0.458183 |
| H | -0.156323 | 1.632177 | 0.997565 |
| O | 1.129640 | 2.306475 | -0.473387 |
| C | 1.293945 | 3.597372 | 0.032925 |
| H | 1.270794 | 3.605285 | 1.139071 |
| H | 2.267734 | 3.980147 | -0.303046 |
| H | 0.501132 | 4.277408 | -0.329656 |

**INT3**$_{\text{prox-OMe}}$

| | | | |
|---|---|---|---|
| Si | -0.020645 | 1.886196 | 0.064547 |
| C | 1.782356 | 1.357420 | -0.159756 |
| C | -0.086690 | 3.509474 | 1.034766 |
| Li | -2.443735 | -1.367082 | 2.399429 |
| C | -0.671893 | 2.282883 | -1.674436 |
| H | 0.494463 | 4.297949 | 0.528624 |
| H | -1.129080 | 3.857850 | 1.117822 |
| H | 0.307617 | 3.397613 | 2.055710 |
| H | 1.834526 | 0.445280 | -0.776106 |
| H | 2.363806 | 2.143916 | -0.668692 |
| H | 2.274023 | 1.137125 | 0.799405 |
| H | -0.046728 | 3.059169 | -2.145242 |
| H | -0.652781 | 1.399701 | -2.333359 |
| H | -1.706227 | 2.662503 | -1.650762 |
| O | -1.784865 | -3.257830 | 2.477333 |
| C | -1.520399 | -3.771347 | 1.168339 |
| C | -0.586343 | -3.239059 | 3.252183 |
| C | -0.046964 | -4.176512 | 1.157522 |
| C | 0.541371 | -3.264662 | 2.233961 |
| H | -0.590440 | -2.325489 | 3.863953 |
| H | -1.722634 | -2.968279 | 0.442176 |
| H | -2.202684 | -4.612030 | 0.967797 |
| H | -0.562859 | -4.121256 | 3.917789 |
| H | 0.687866 | -2.248274 | 1.836091 |
| H | 0.414191 | -4.038132 | 0.170116 |
| H | 0.069313 | -5.234635 | 1.441159 |
| H | 1.489420 | -3.630238 | 2.651778 |
| C | 0.182969 | 0.514183 | 2.999126 |
| C | -0.924792 | 0.007603 | 2.103098 |
| H | -0.251191 | 0.983972 | 3.902482 |
| H | 0.788982 | -0.328010 | 3.382762 |
| H | 0.898615 | 1.248103 | 2.578600 |
| C | -1.079919 | 0.534568 | 0.858671 |
| C | -2.207264 | 0.044473 | -0.036550 |
| H | -2.856335 | 0.884140 | -0.363446 |
| H | -1.814024 | -0.413676 | -0.969416 |
| O | -3.037839 | -0.918999 | 0.603848 |
| C | -4.094962 | -1.380367 | -0.184471 |
| H | -3.729618 | -1.874446 | -1.104416 |
| H | -4.666946 | -2.109214 | 0.406581 |
| H | -4.768684 | -0.555205 | -0.482082 |
| O | -3.770051 | -0.706125 | 3.747665 |
| C | -3.039931 | -0.456563 | 4.951052 |
| C | -4.368123 | 0.498544 | 3.272409 |
| C | -3.207630 | 1.033097 | 5.258851 |
| C | -3.544951 | 1.619852 | 3.887135 |
| H | -4.329030 | 0.480272 | 2.174941 |
| H | -1.982173 | -0.705679 | 4.763220 |
| H | -3.424013 | -1.108990 | 5.750473 |
| H | -5.424379 | 0.538551 | 3.597120 |
| H | -2.632132 | 1.765954 | 3.290242 |
| H | -2.302141 | 1.467601 | 5.704211 |
| H | -4.039767 | 1.192536 | 5.962829 |

| | | | |
|---|---|---|---|
| H | -4.093763 | 2.570257 | 3.943288 |

**INT3**$_{\text{dist-OMe}}$

| | | | |
|---|---|---|---|
| Si | -2.320465 | -0.458805 | 0.083954 |
| C | -3.453639 | 0.840298 | 0.869878 |
| C | -3.227994 | -2.116860 | 0.184416 |
| Li | 2.006554 | 1.175085 | 1.962751 |
| C | -2.128840 | -0.015801 | -1.747431 |
| H | -4.208448 | -2.061043 | -0.316079 |
| H | -2.650072 | -2.921906 | -0.296678 |
| H | -3.400748 | -2.411837 | 1.232274 |
| H | -3.139229 | 1.868449 | 0.634162 |
| H | -4.482195 | 0.715153 | 0.493287 |
| H | -3.480521 | 0.736450 | 1.966493 |
| H | -3.104580 | 0.063293 | -2.254501 |
| H | -1.605200 | 0.946522 | -1.864353 |
| H | -1.534070 | -0.781475 | -2.271035 |
| O | 2.401830 | 0.806442 | 3.876002 |
| C | 1.458812 | 1.478111 | 4.719294 |
| C | 2.271966 | -0.609344 | 4.011917 |
| C | 0.726475 | 0.384035 | 5.496082 |
| C | 0.878598 | -0.828658 | 4.576859 |
| H | 2.404316 | -1.055933 | 3.015183 |
| H | 0.775751 | 2.050838 | 4.071149 |
| H | 1.999976 | 2.181932 | 5.370338 |
| H | 3.062127 | -0.988140 | 4.686462 |
| H | 0.152783 | -0.779316 | 3.750421 |
| H | -0.321637 | 0.647760 | 5.692865 |
| H | 1.217129 | 0.201785 | 6.465473 |
| H | 0.775526 | -1.790306 | 5.098055 |
| C | -0.073396 | -1.998671 | 1.026847 |
| C | -0.624170 | -0.585581 | 0.897997 |
| H | 0.012372 | -2.512405 | 0.050486 |
| H | 0.931952 | -1.968641 | 1.478327 |
| H | -0.707386 | -2.648198 | 1.657508 |
| C | 0.146621 | 0.455006 | 1.293676 |
| C | -0.329656 | 1.871332 | 1.188253 |
| H | -0.640797 | 2.188572 | 0.168439 |
| H | -1.166410 | 2.105258 | 1.878964 |
| O | 0.785913 | 2.712091 | 1.572198 |
| C | 0.534503 | 4.082618 | 1.522492 |
| H | -0.291047 | 4.370092 | 2.201739 |
| H | 1.446566 | 4.612490 | 1.830973 |
| H | 0.263071 | 4.410092 | 0.501220 |
| O | 3.614007 | 0.621375 | 1.030176 |
| C | 4.849651 | 0.259793 | 1.618576 |
| C | 3.395399 | -0.231988 | -0.084988 |
| C | 4.976143 | -1.263647 | 1.427715 |
| C | 3.891270 | -1.600901 | 0.381332 |
| H | 2.320290 | -0.199203 | -0.311438 |
| H | 4.821233 | 0.578295 | 2.669742 |
| H | 5.671224 | 0.795449 | 1.109574 |
| H | 3.974371 | 0.138490 | -0.951288 |
| H | 3.061624 | -2.156696 | 0.840969 |
| H | 4.799071 | -1.799650 | 2.370560 |
| H | 5.984390 | -1.534508 | 1.084410 |
| H | 4.273582 | -2.207135 | -0.451153 |

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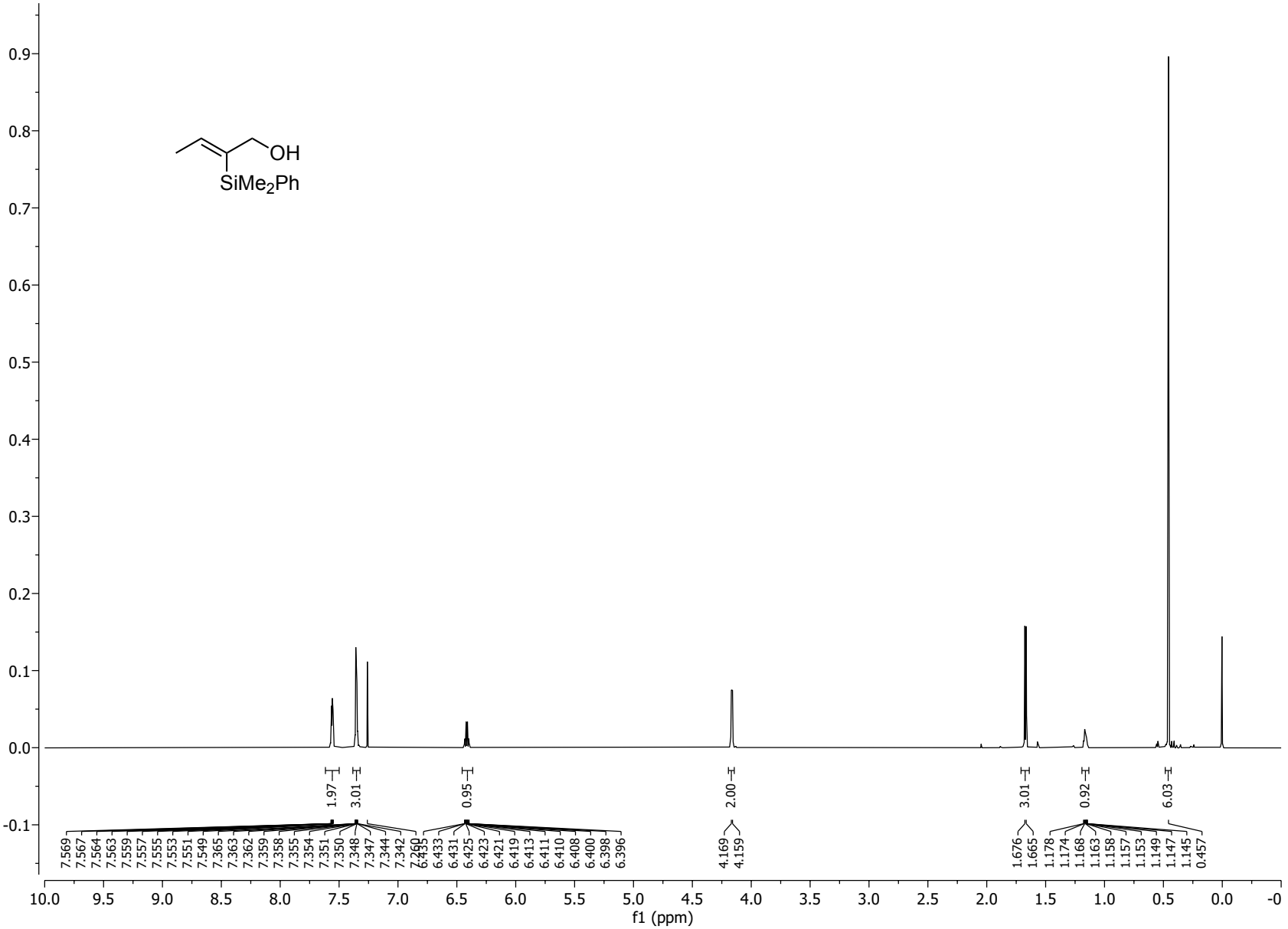


**Figure S6.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **4aa**

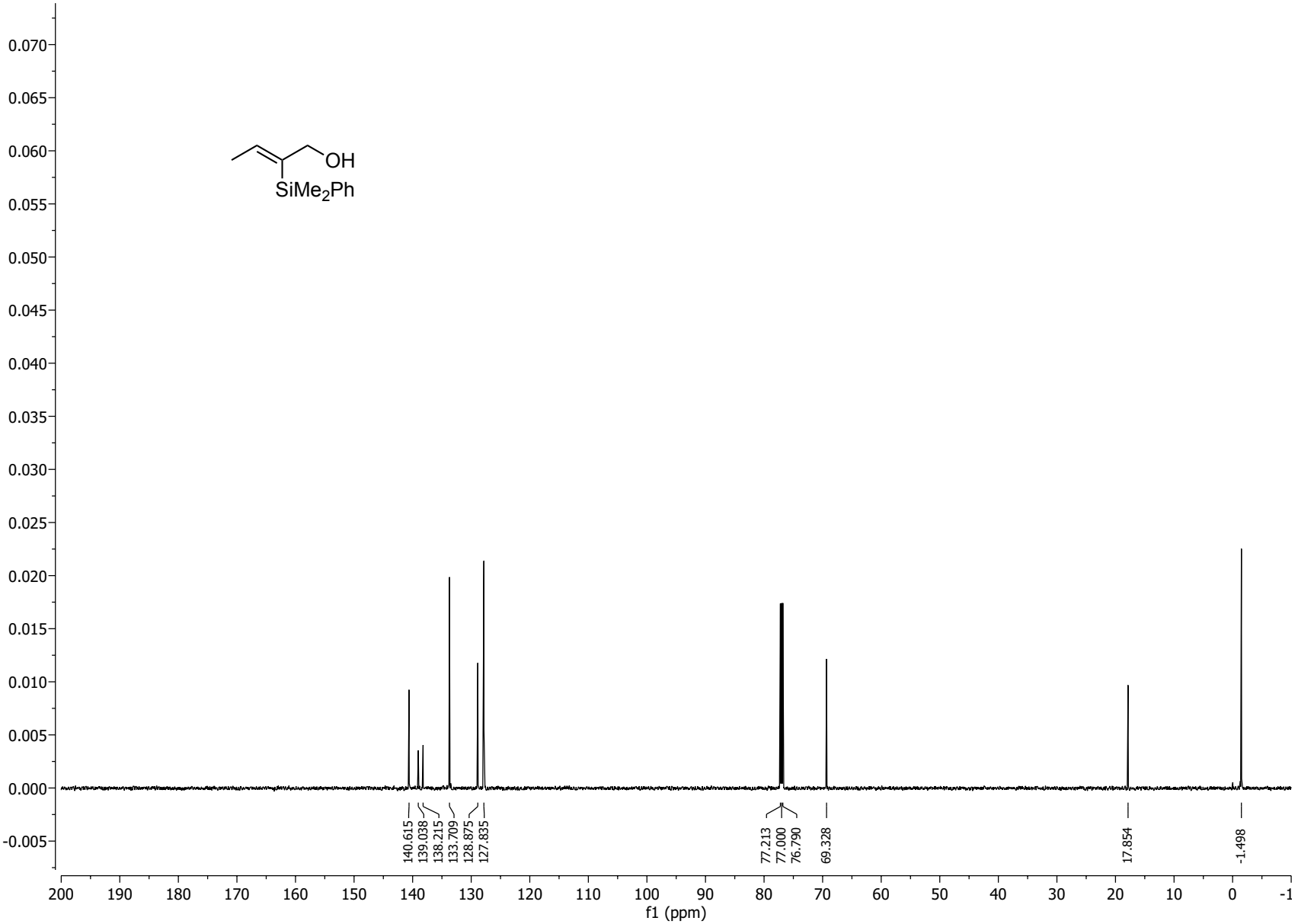


**Figure S7.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4aa**

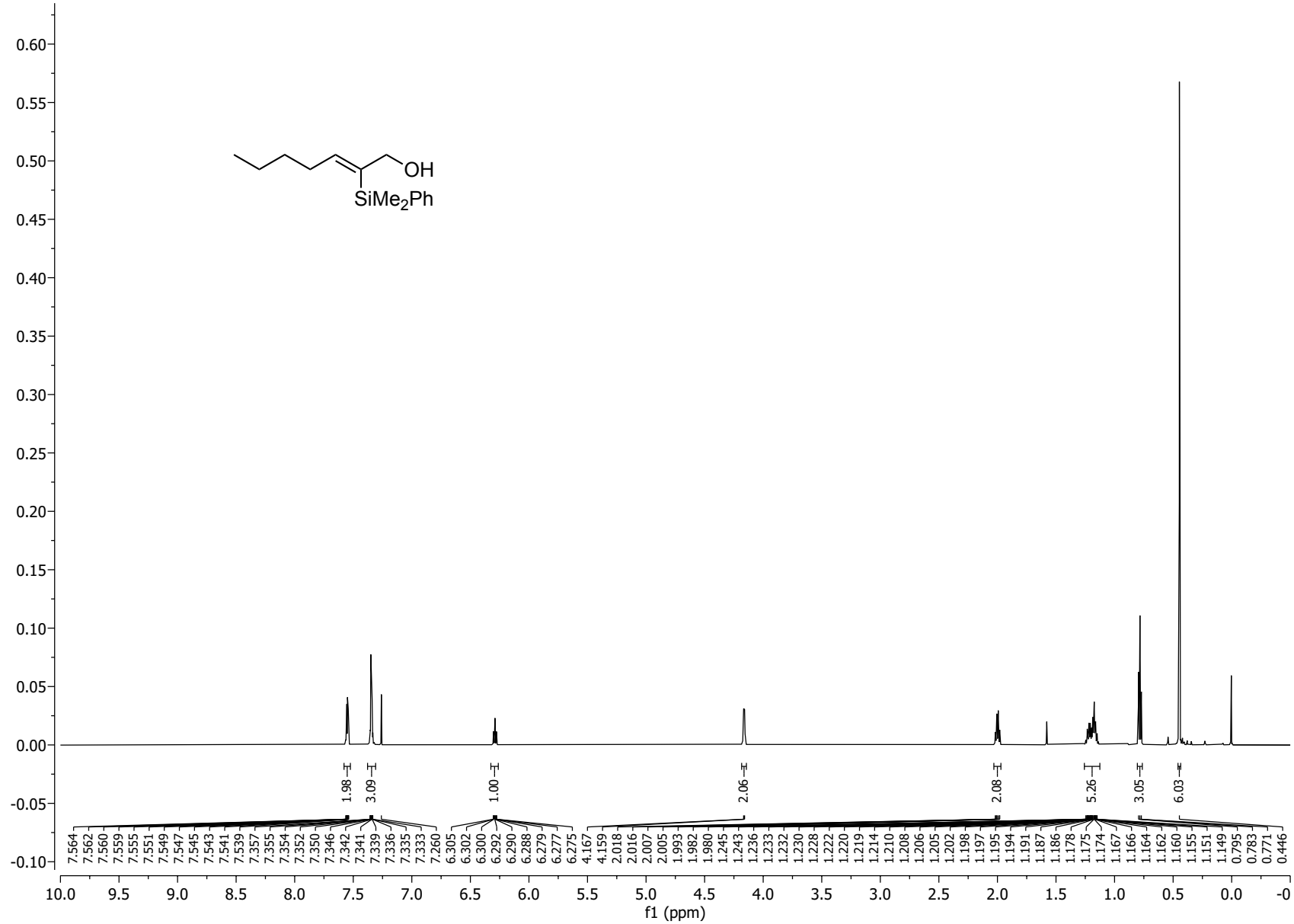


**Figure S8.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of **4ba**

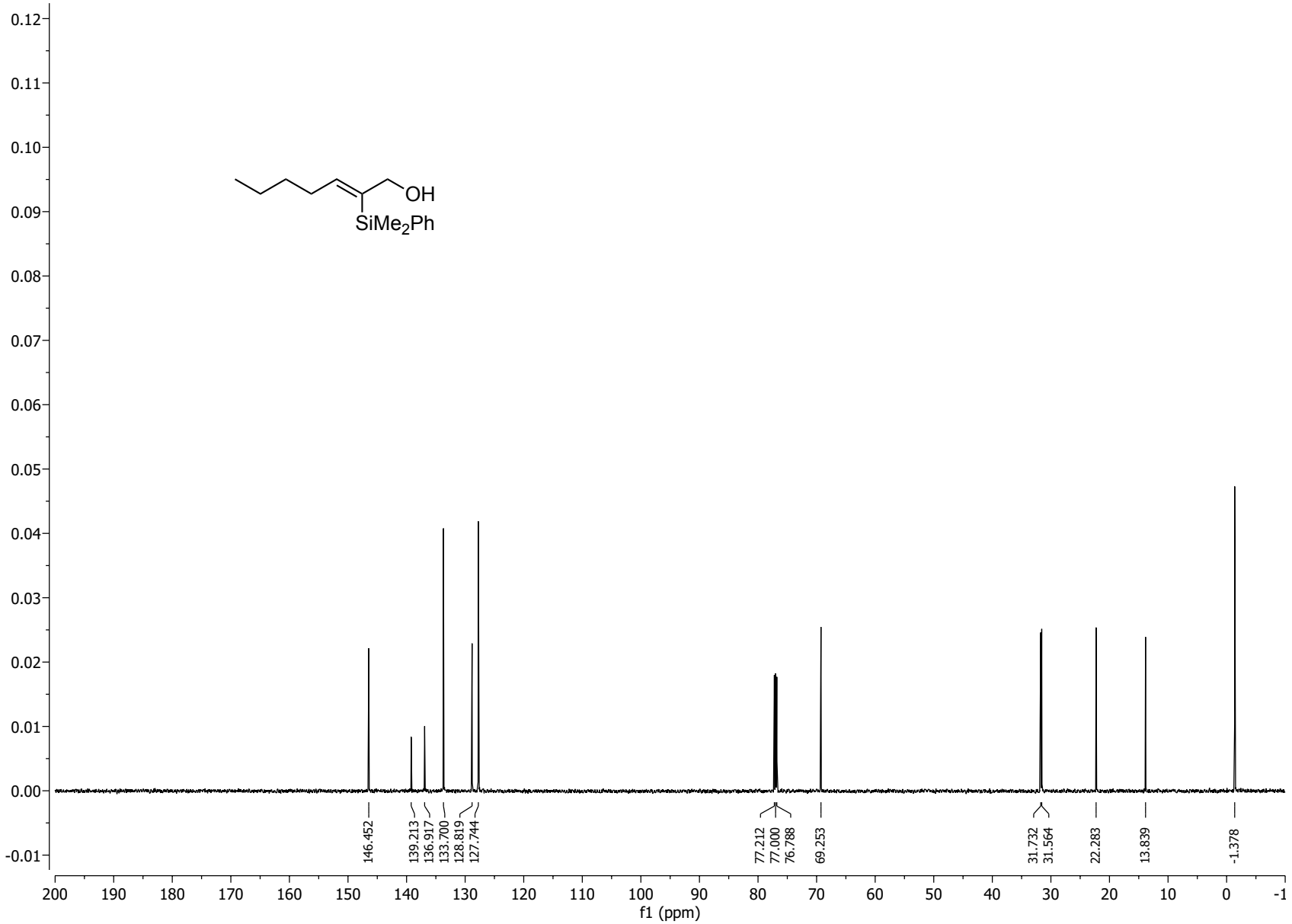


**Figure S9.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4ba**

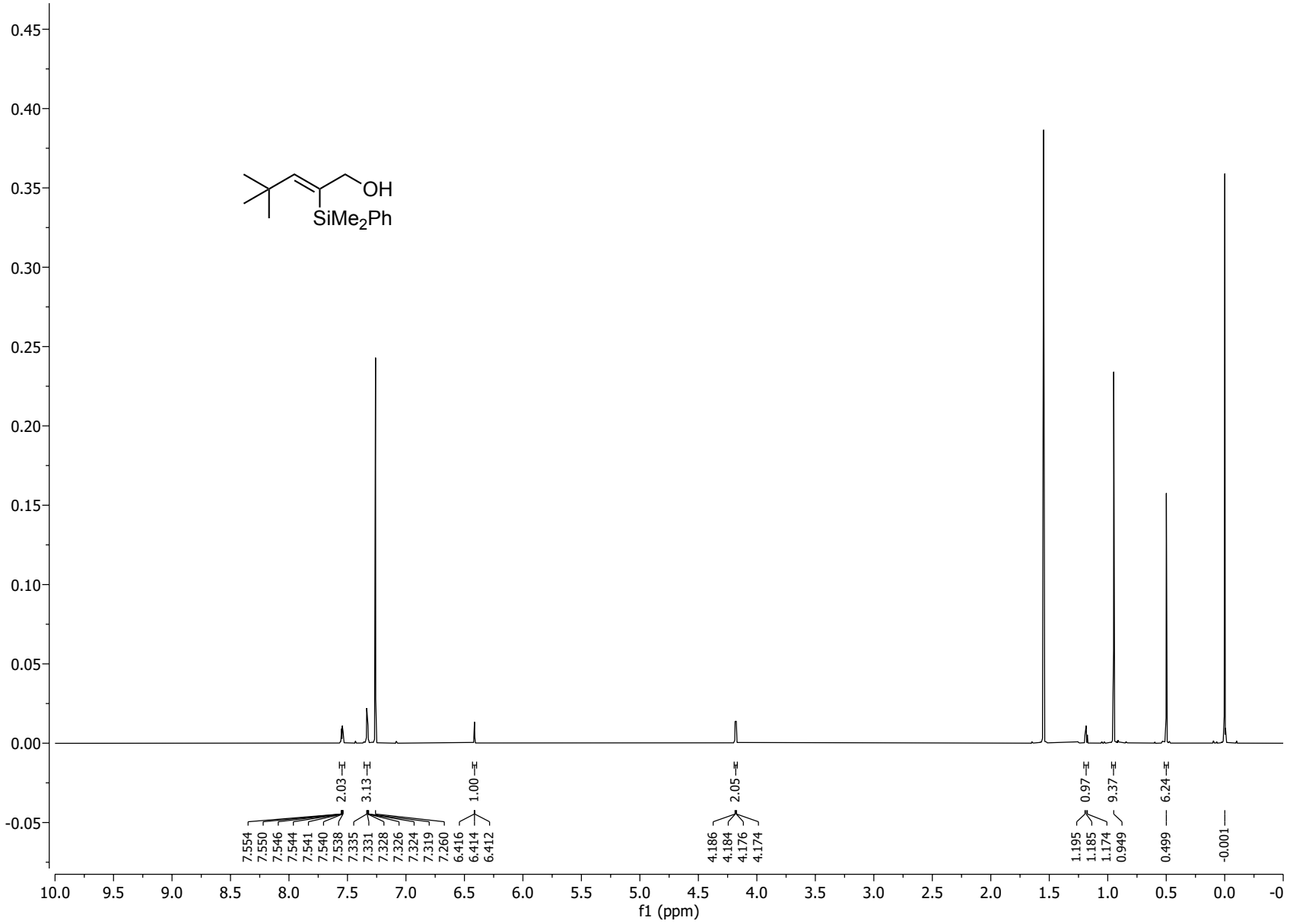


**Figure S10.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **4ca**

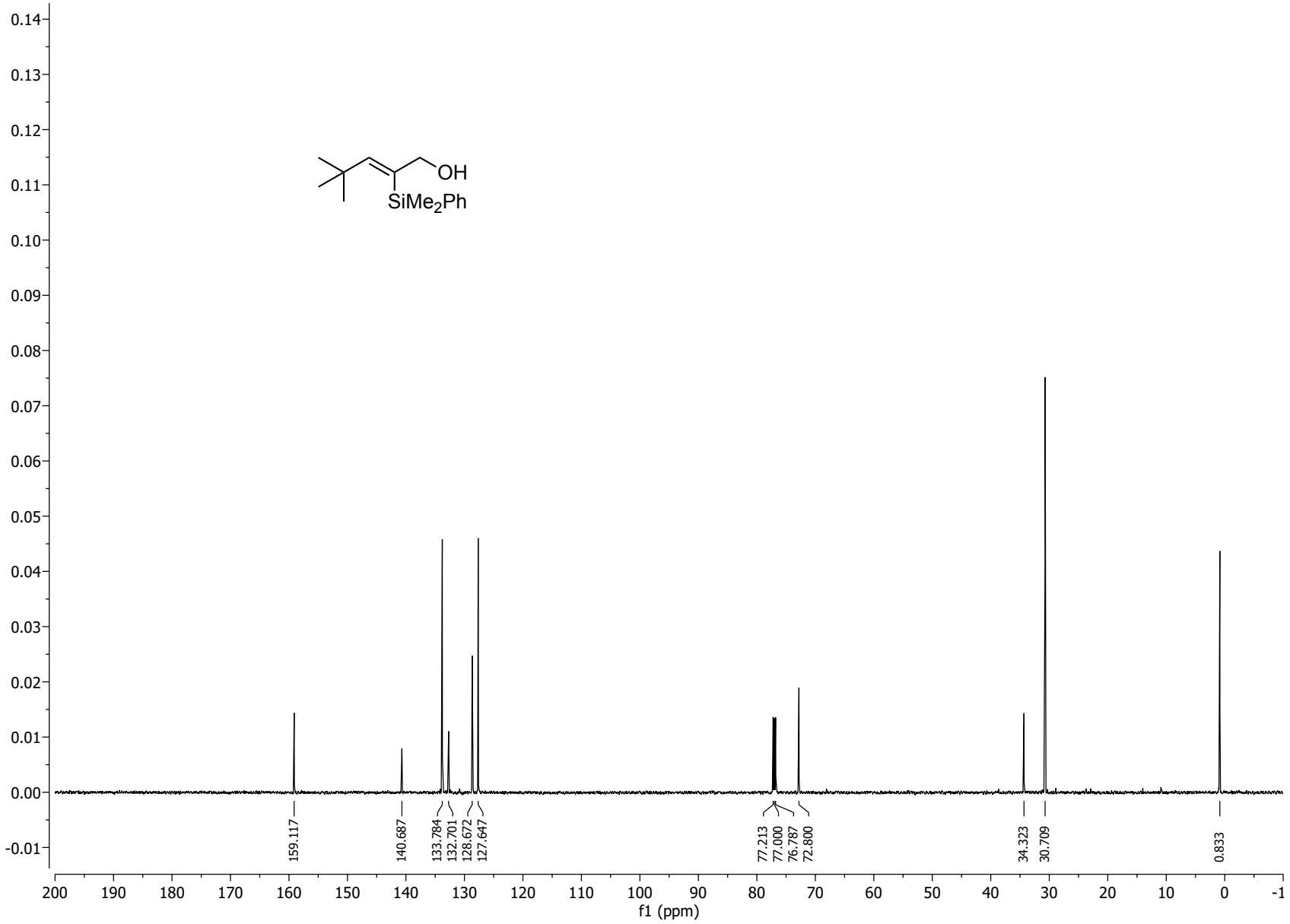


**Figure S11.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4ca**

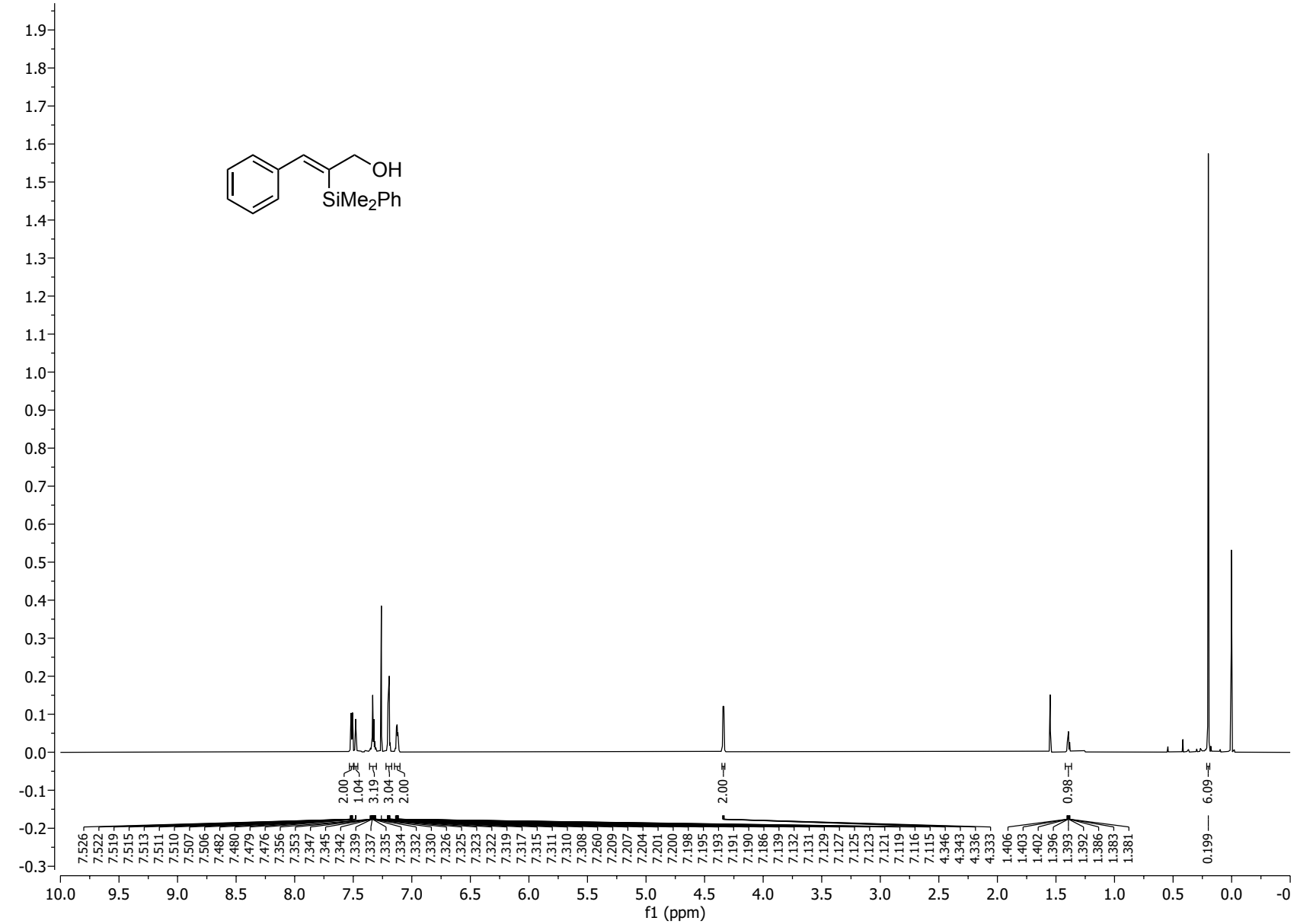


**Figure S12.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of **4da**

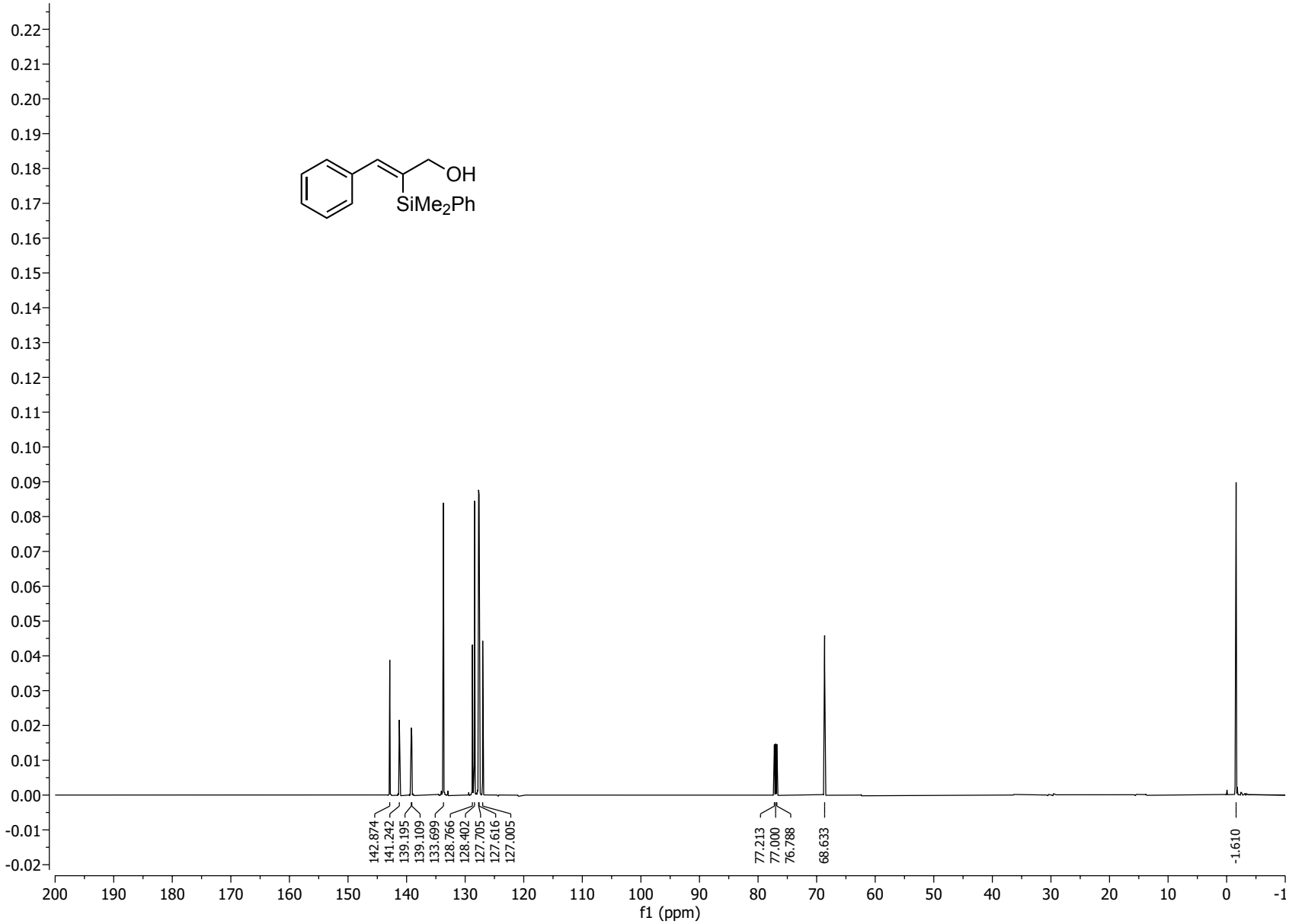


**Figure S13.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4da**

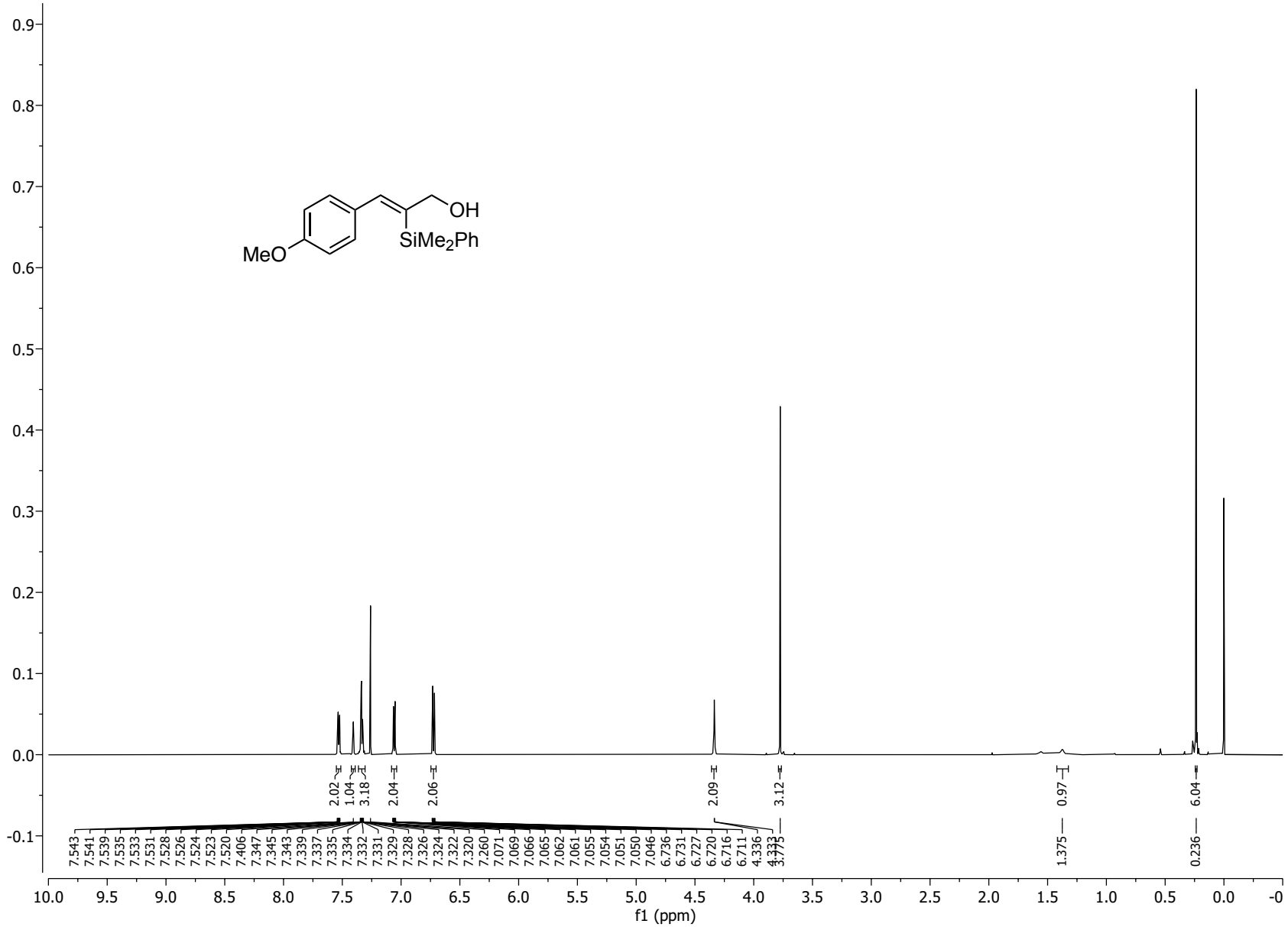


**Figure S14.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **4ea**

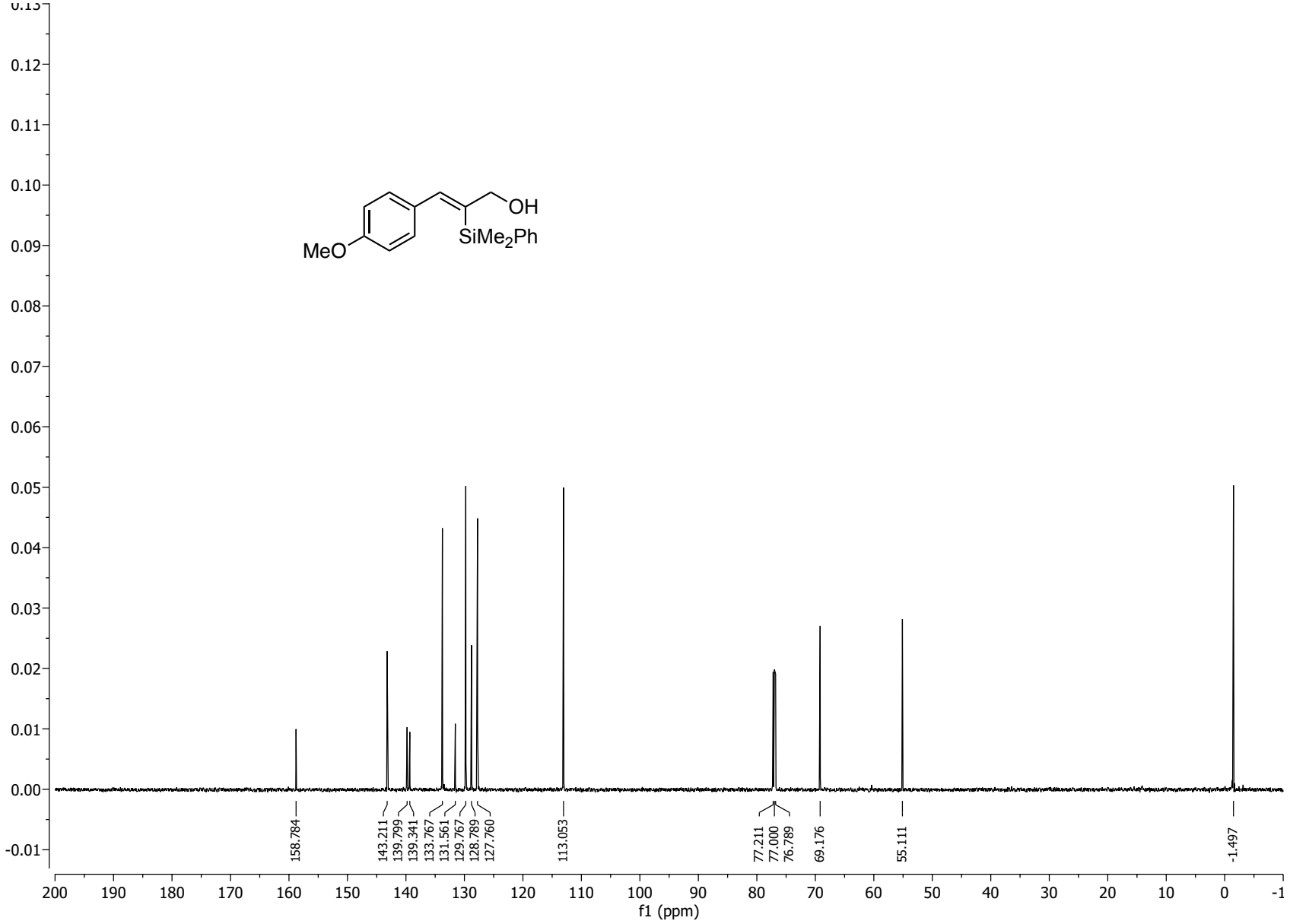


**Figure S15.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4ea**

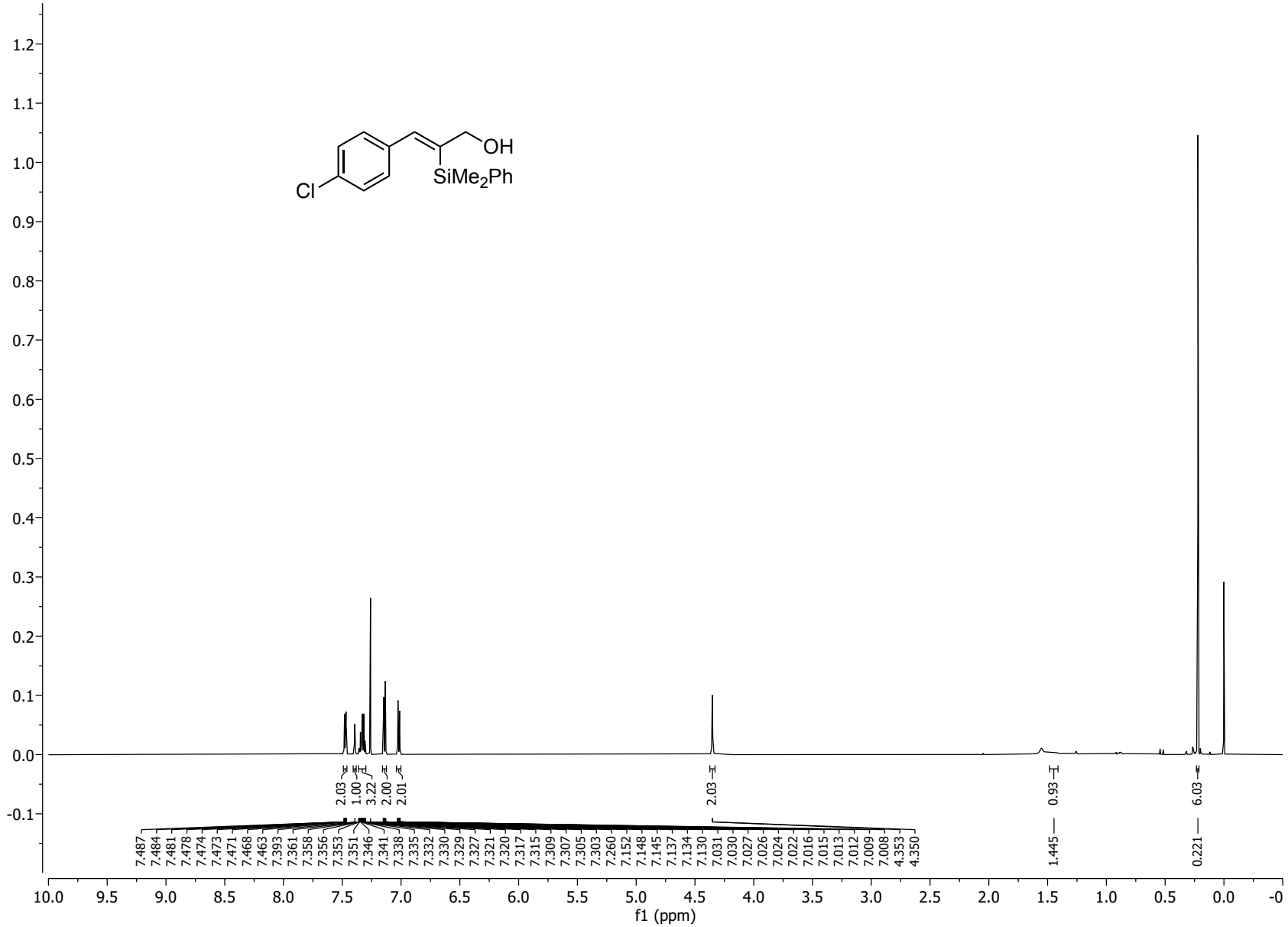


**Figure S16.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **4fa**

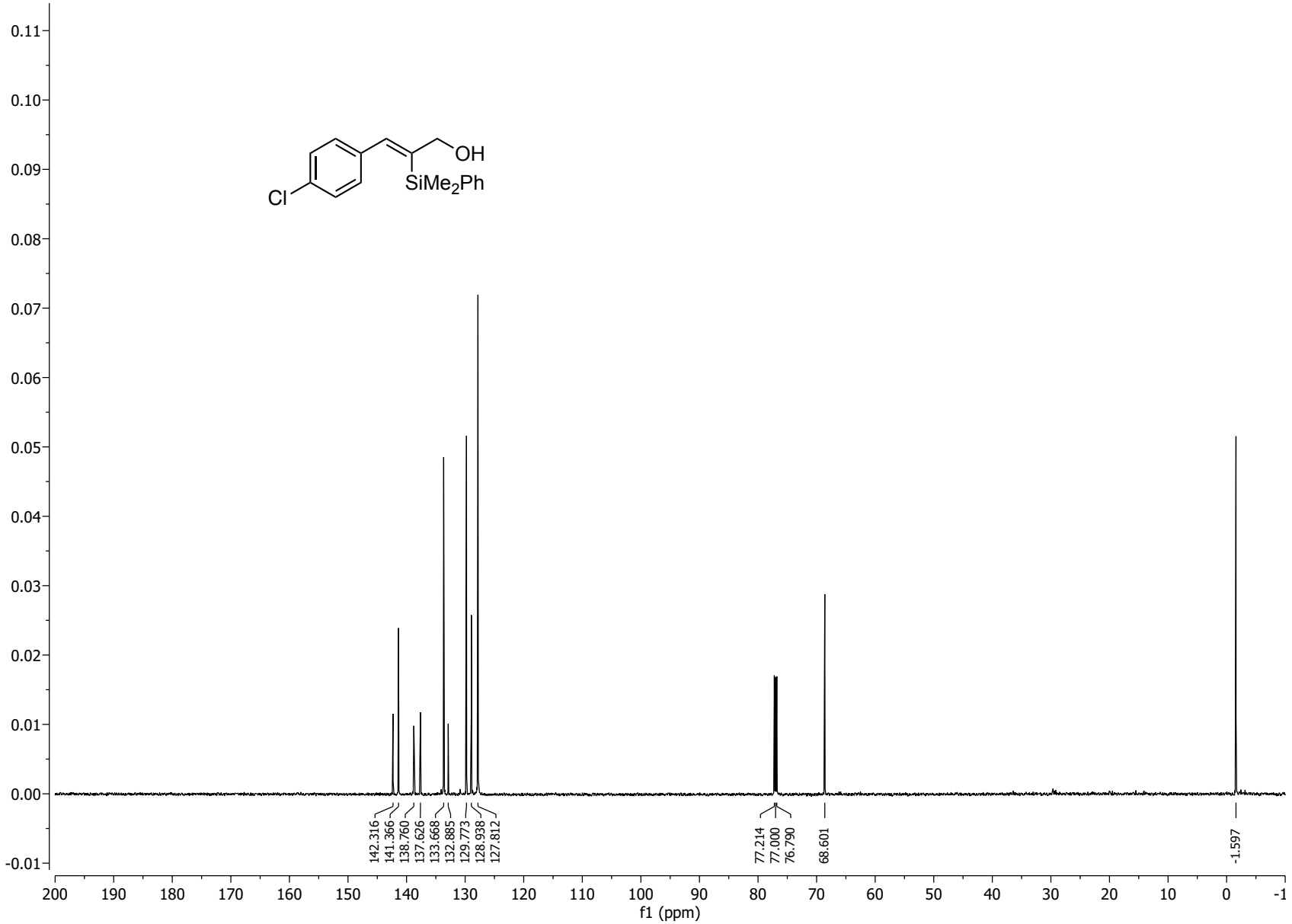


**Figure S17.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4fa**

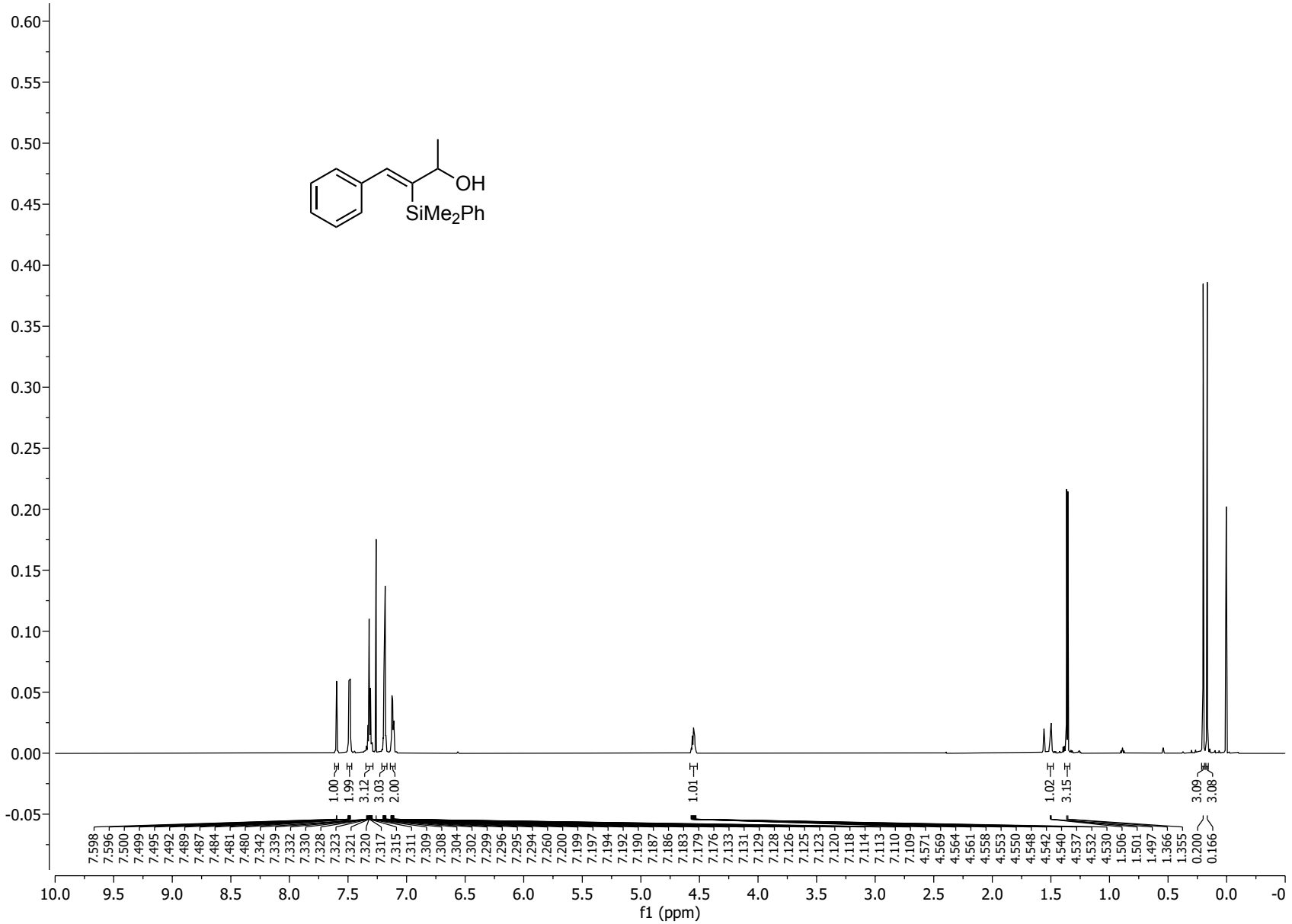


**Figure S18.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of **4ga**

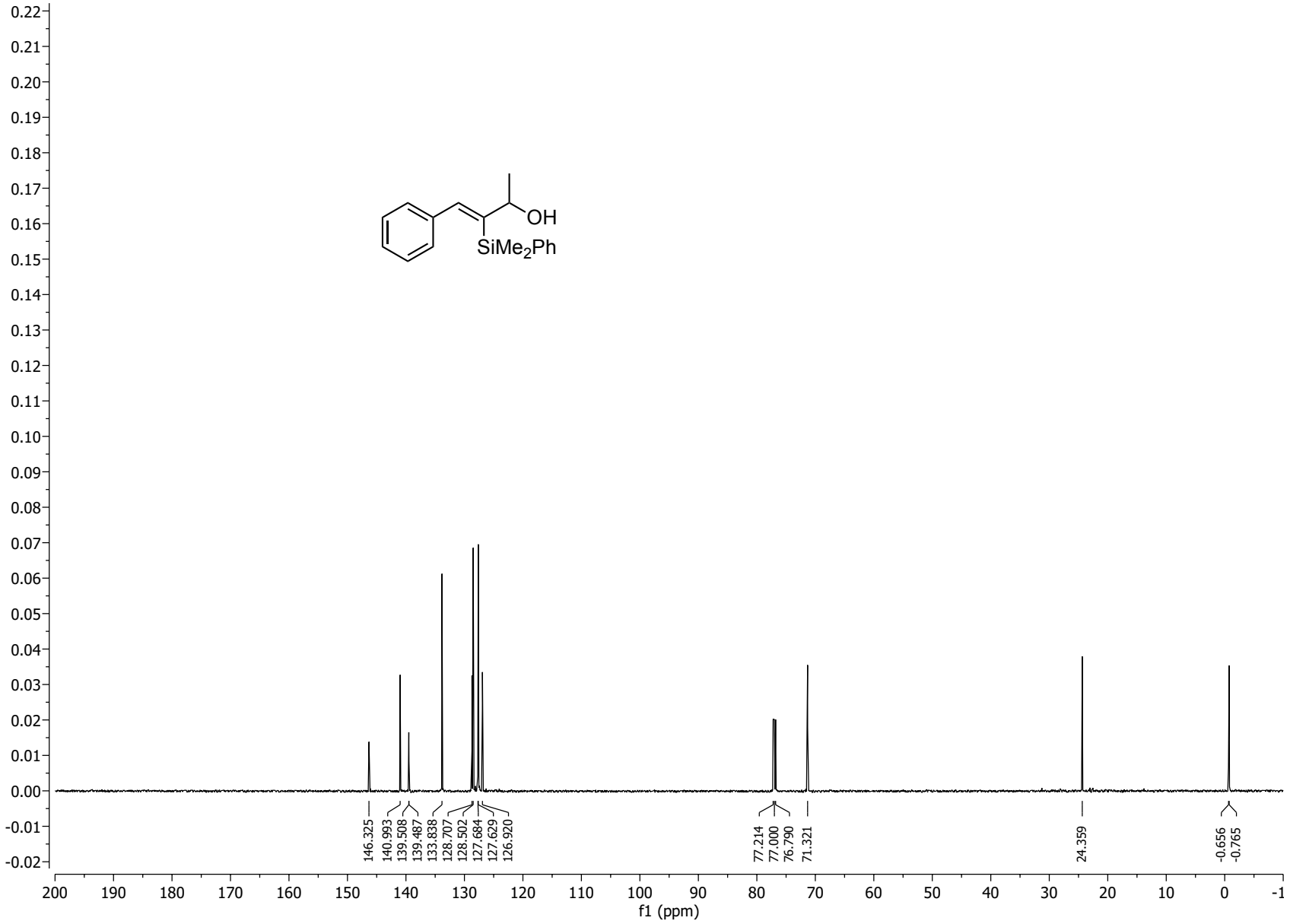


**Figure S19.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4ga**

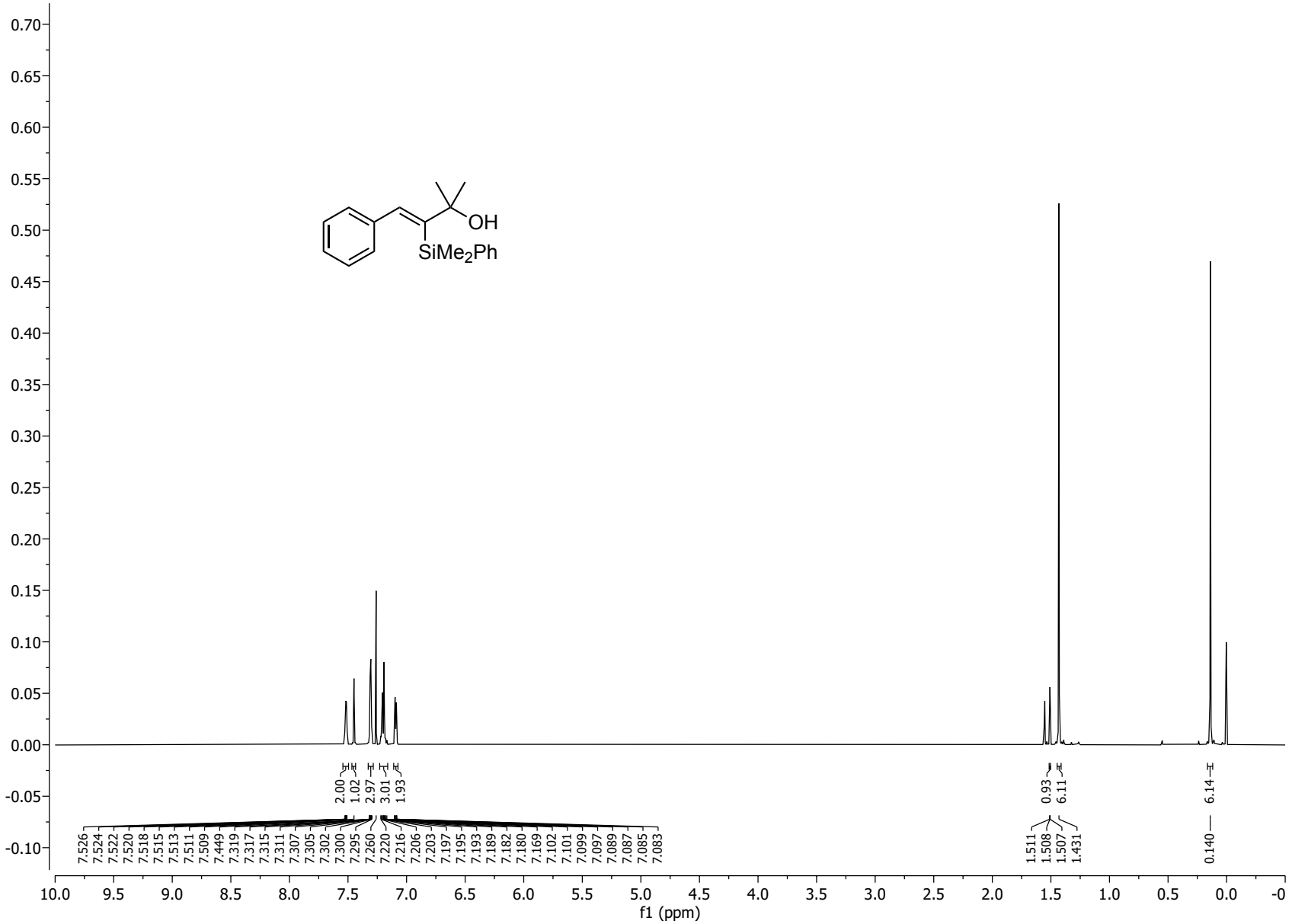


**Figure S20.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **4ha**

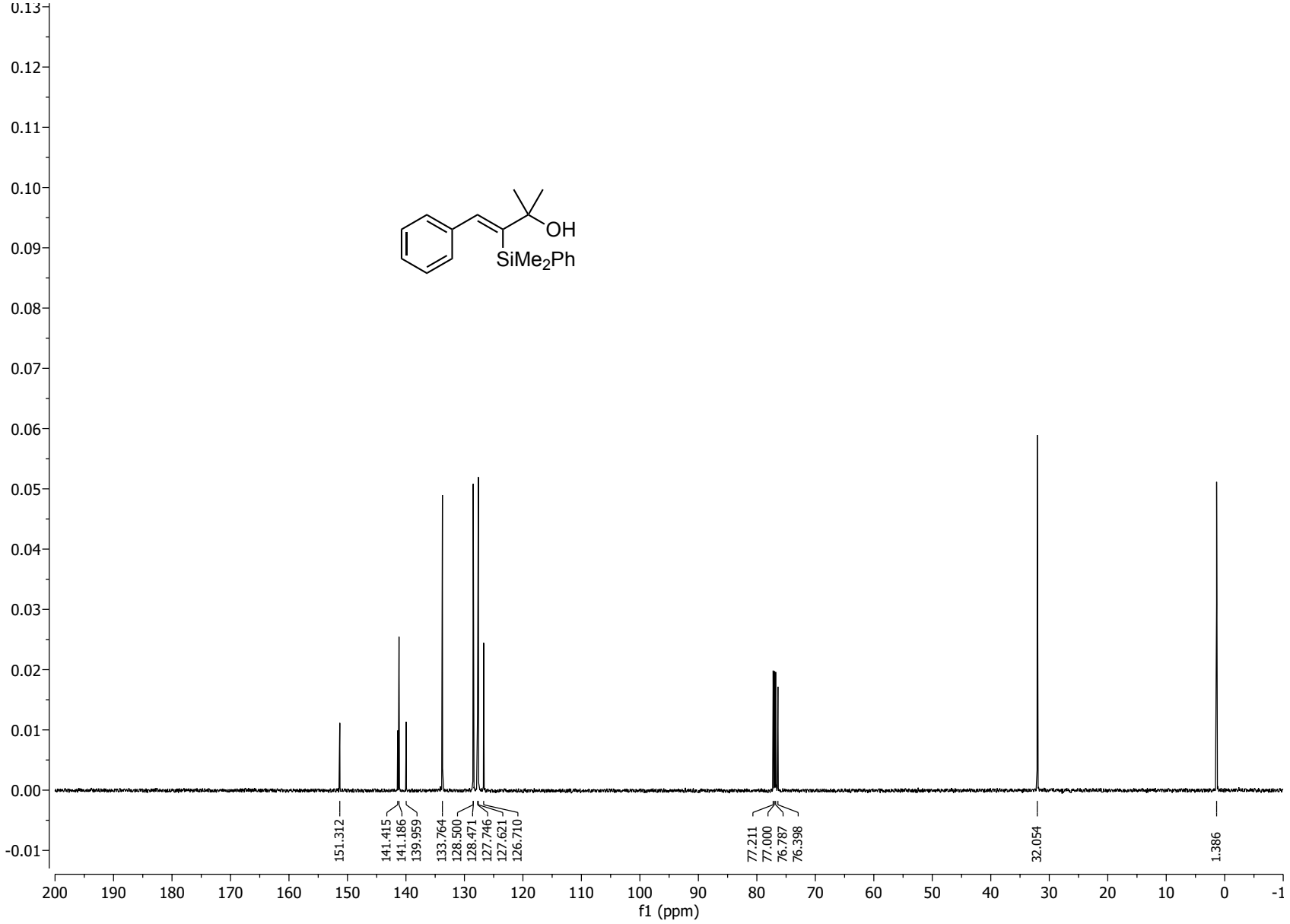


**Figure S21.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4ha**

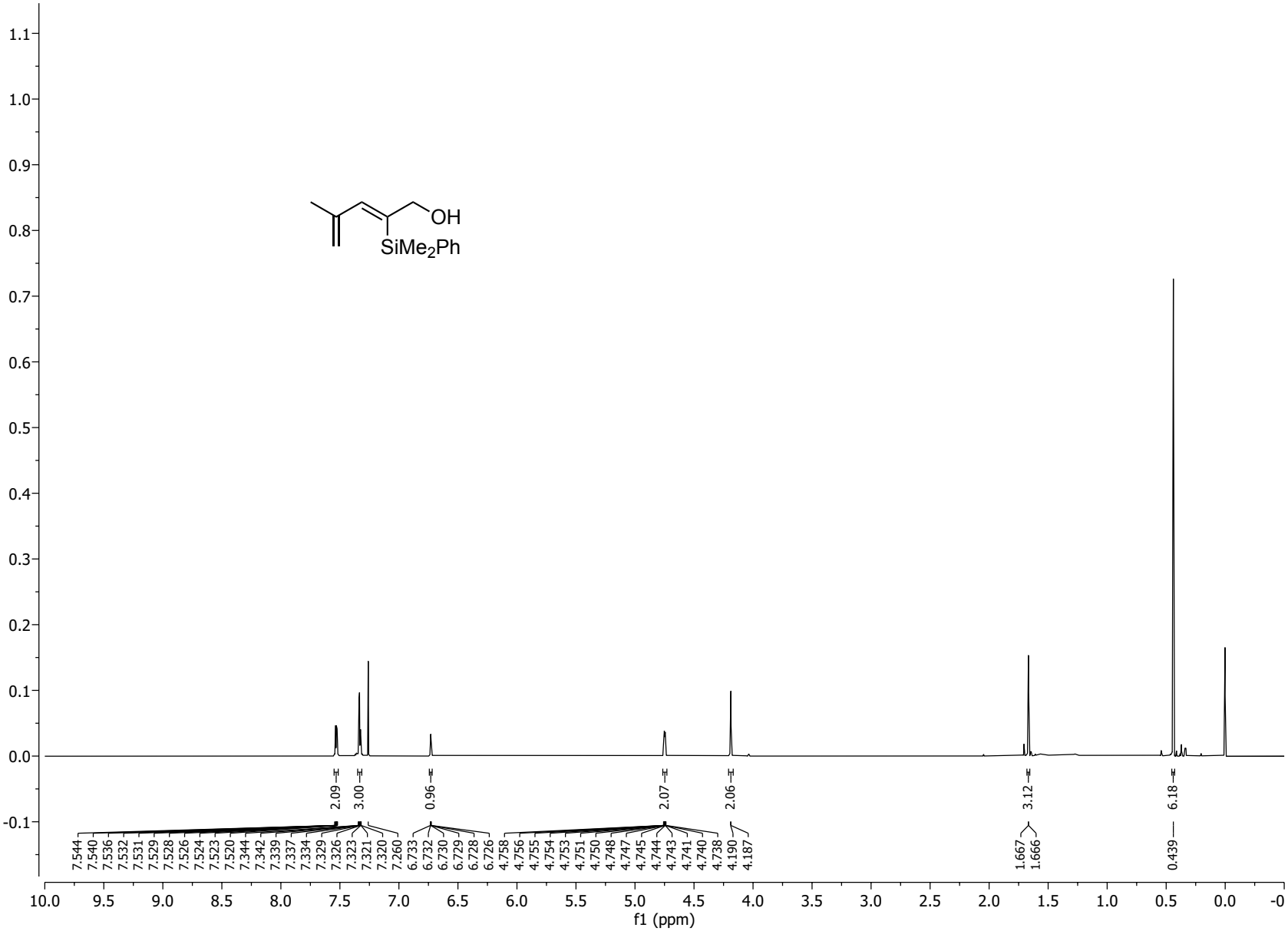


**Figure S22.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **4ia**

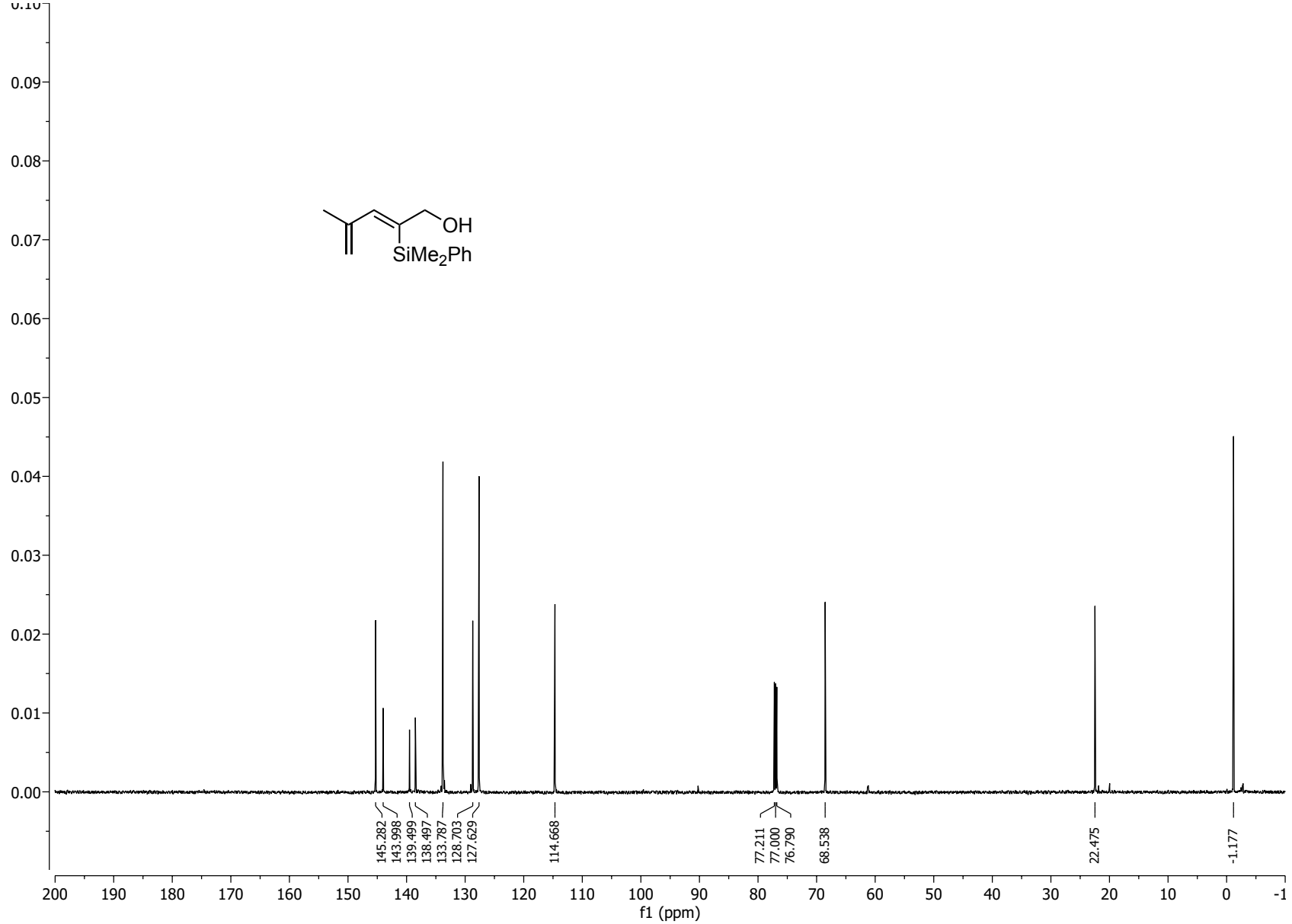


**Figure S23.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4ia**

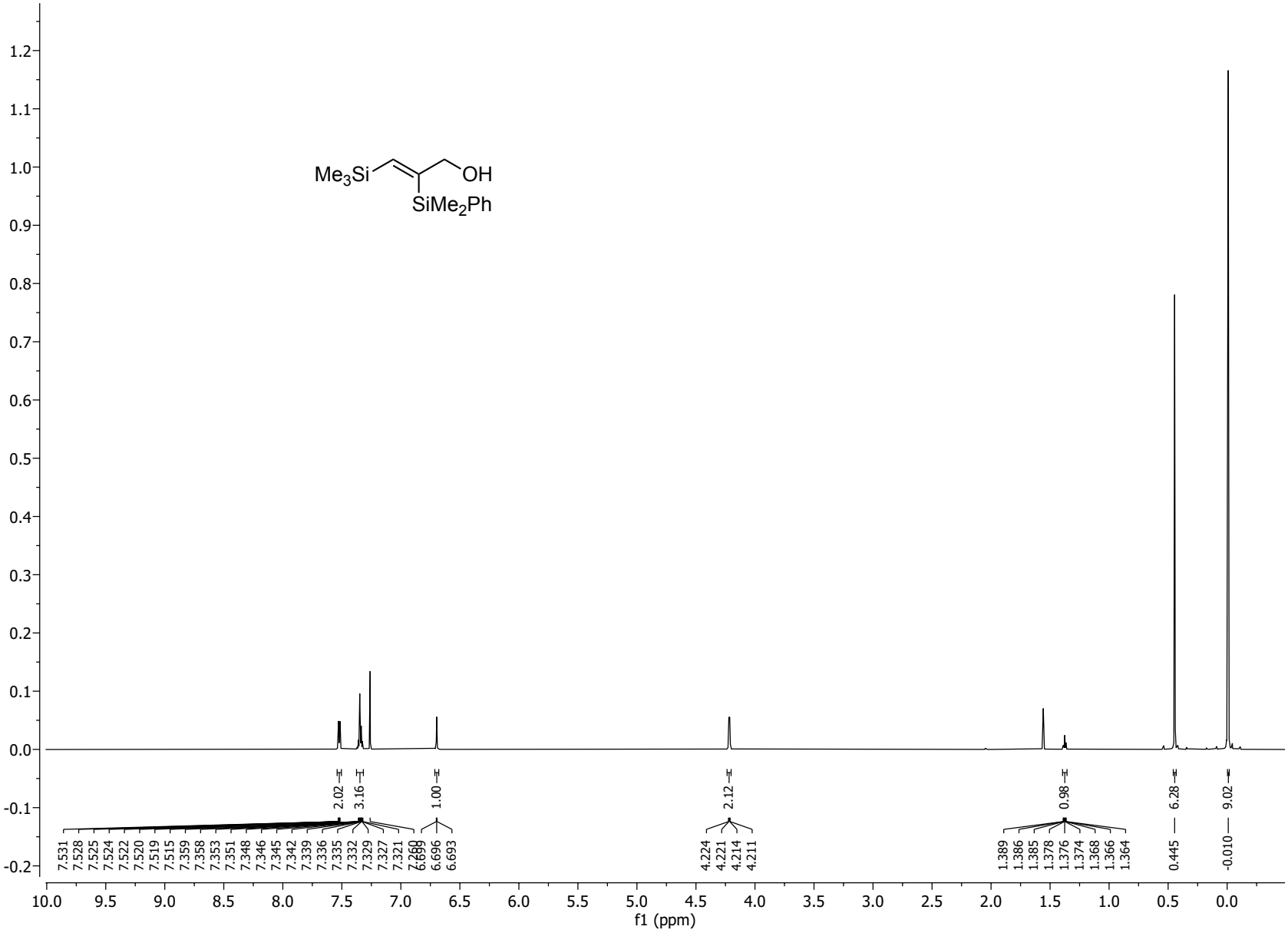


**Figure S24.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **4ja**

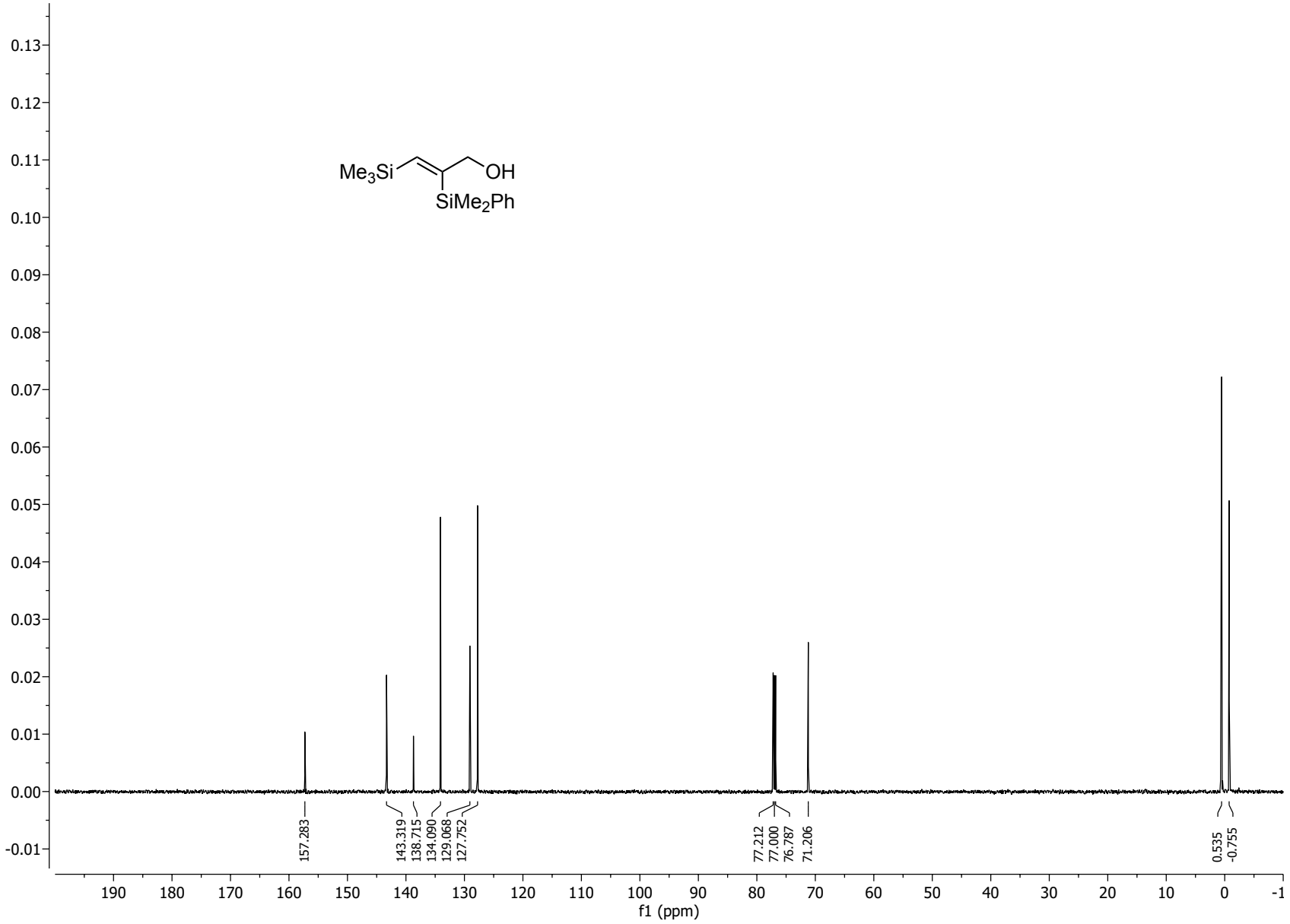


**Figure S25.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4ja**

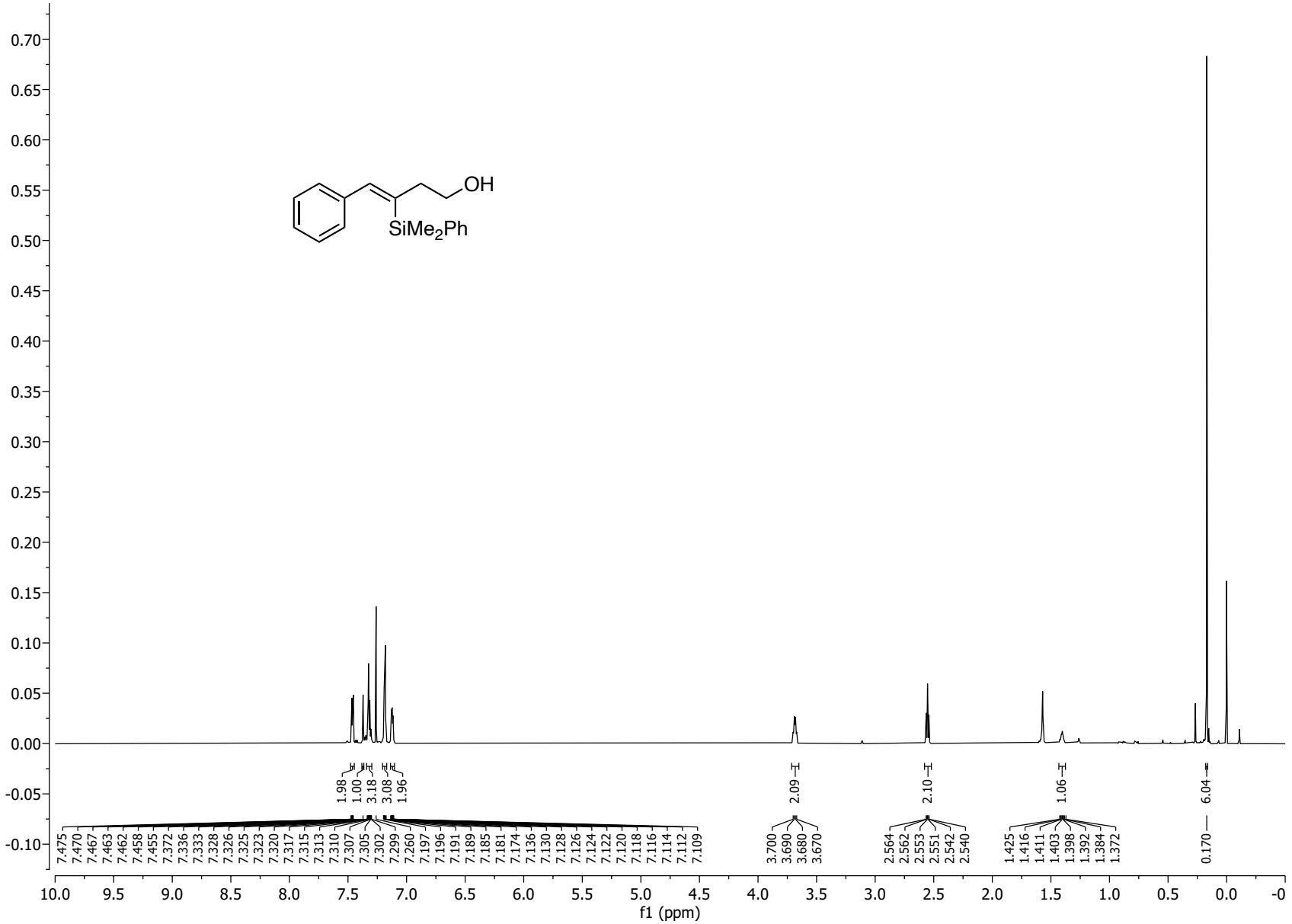


**Figure S26.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **4ma**

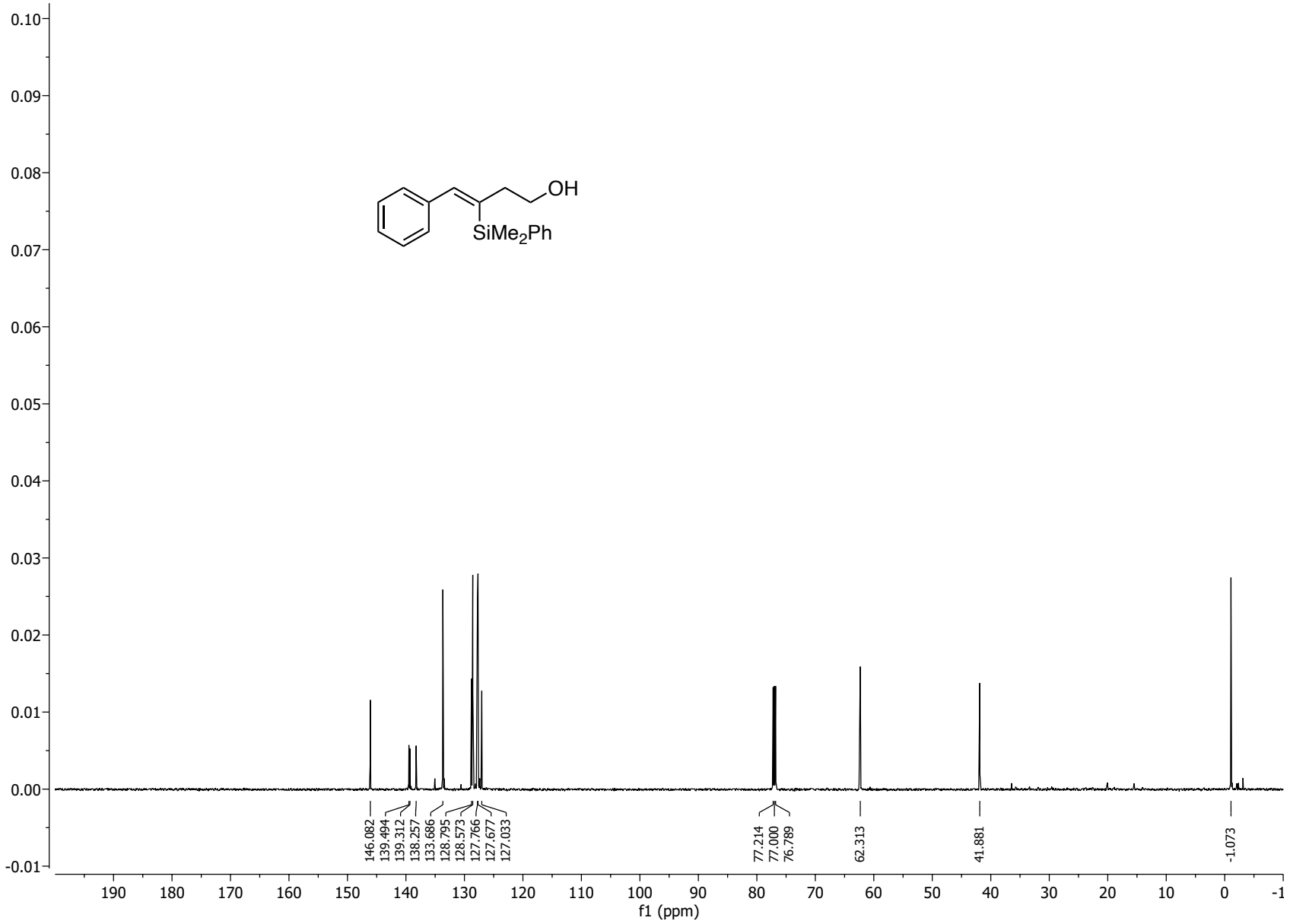


**Figure S27.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4ma**

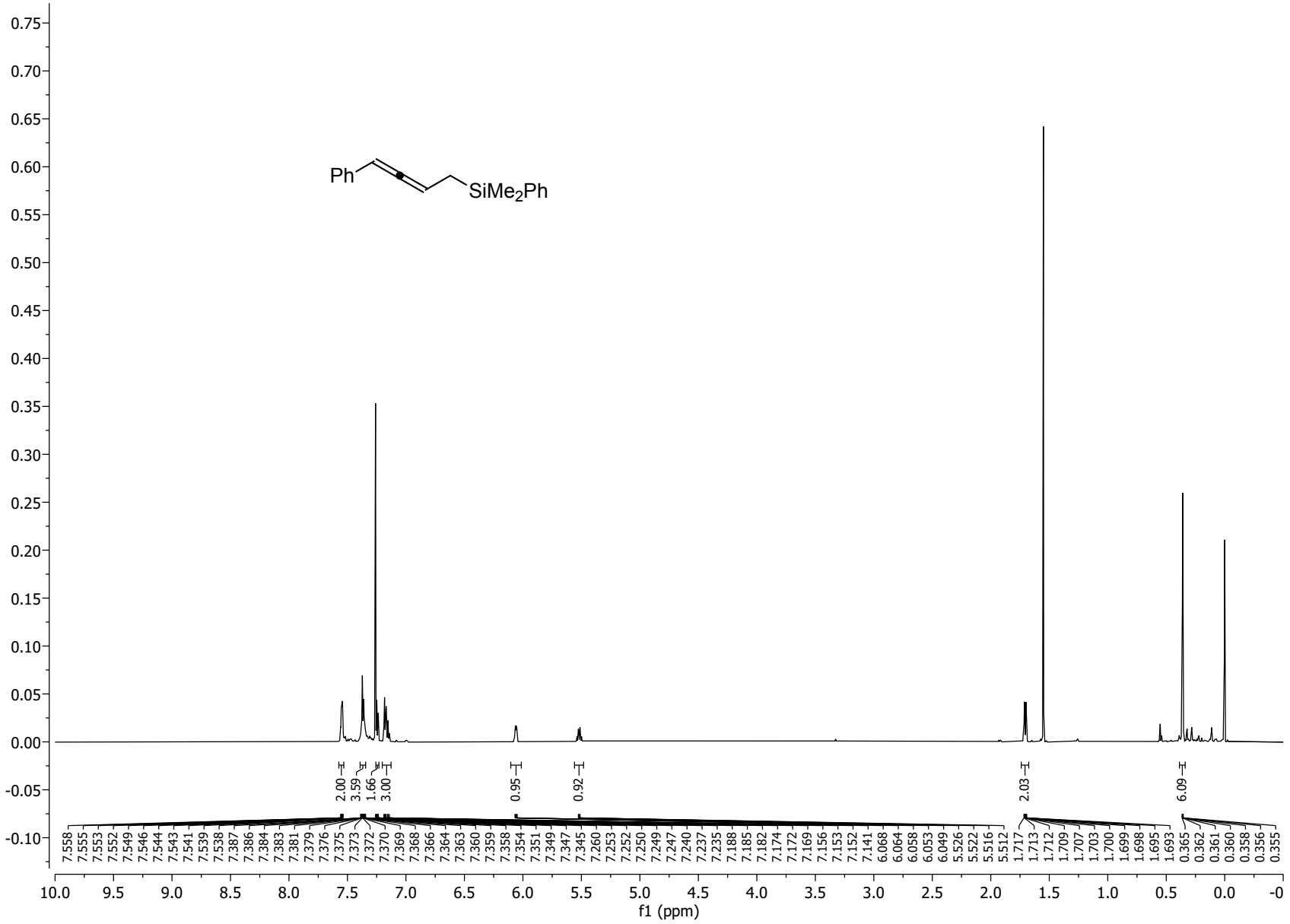


**Figure S28.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **S1**

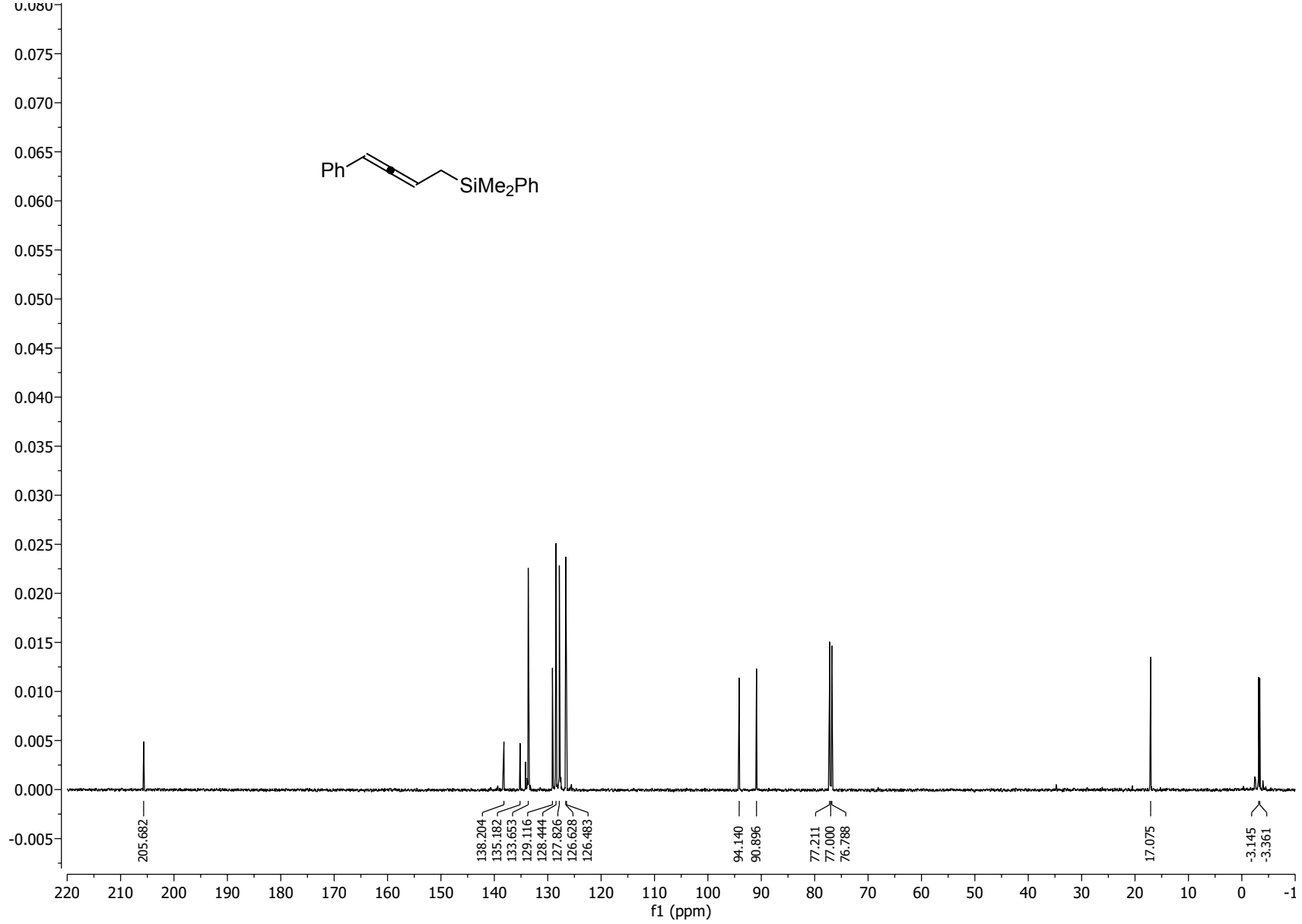


**Figure S29.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **S1**

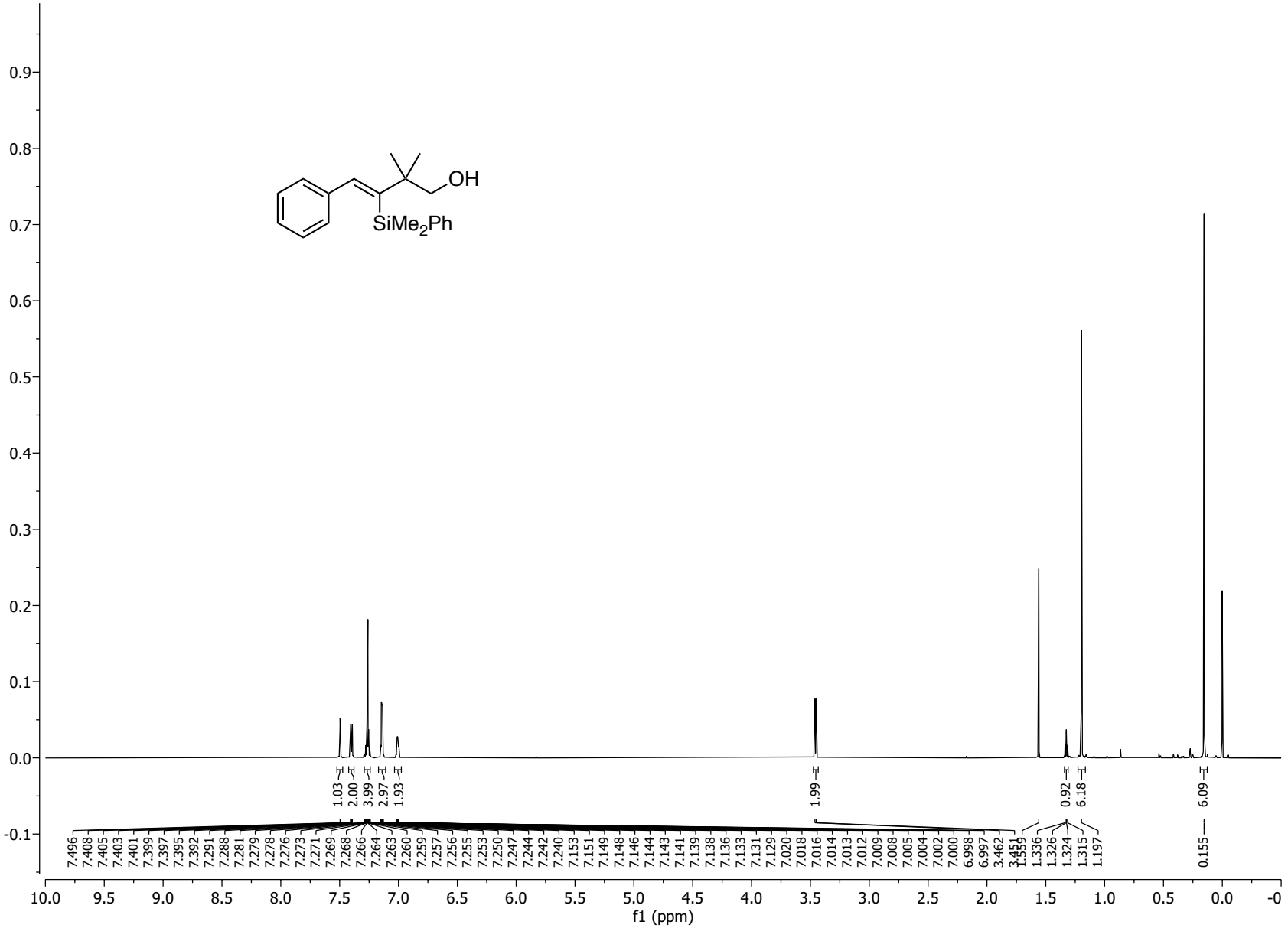


**Figure S30.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of **4na**

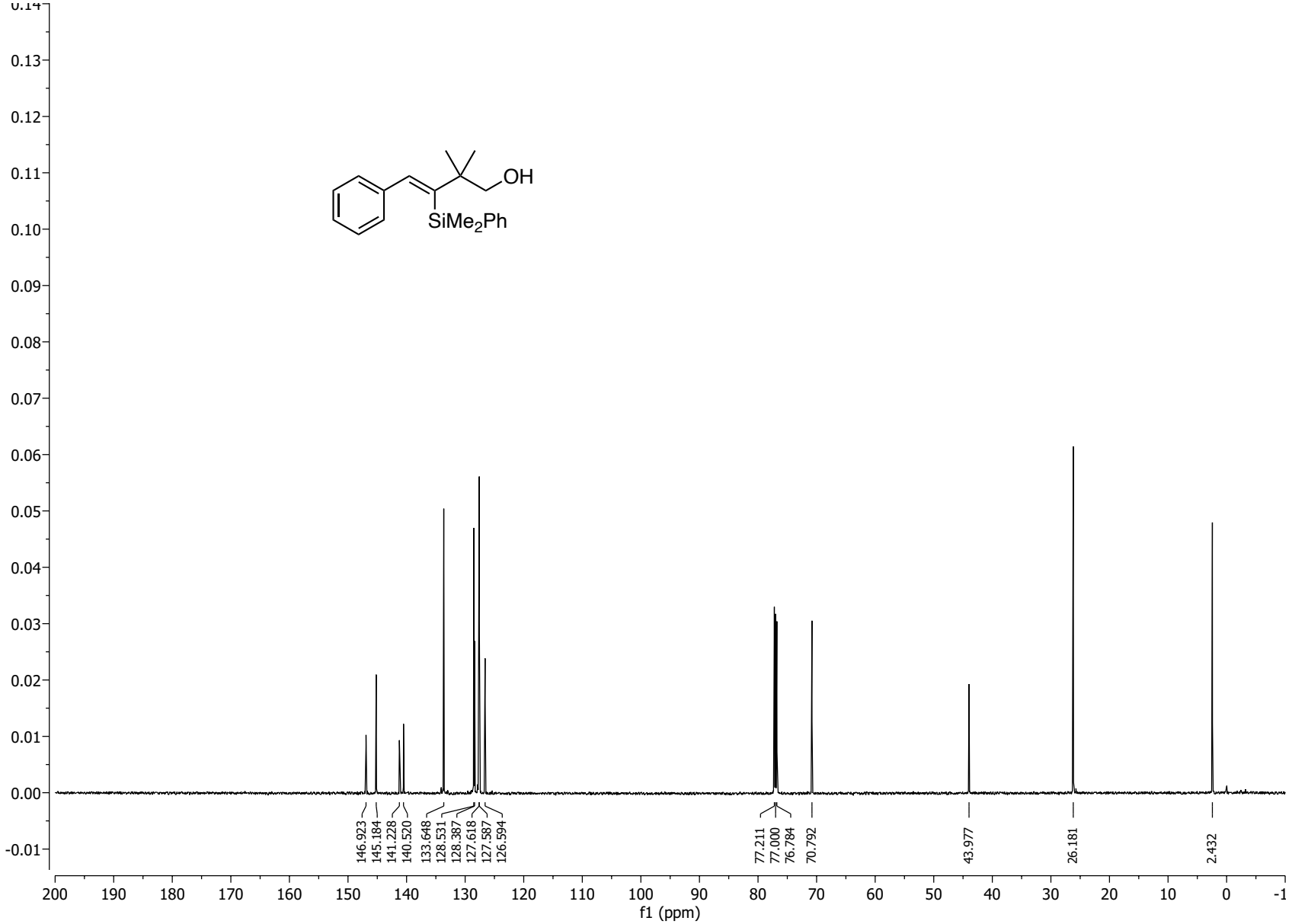


**Figure S31.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4na**

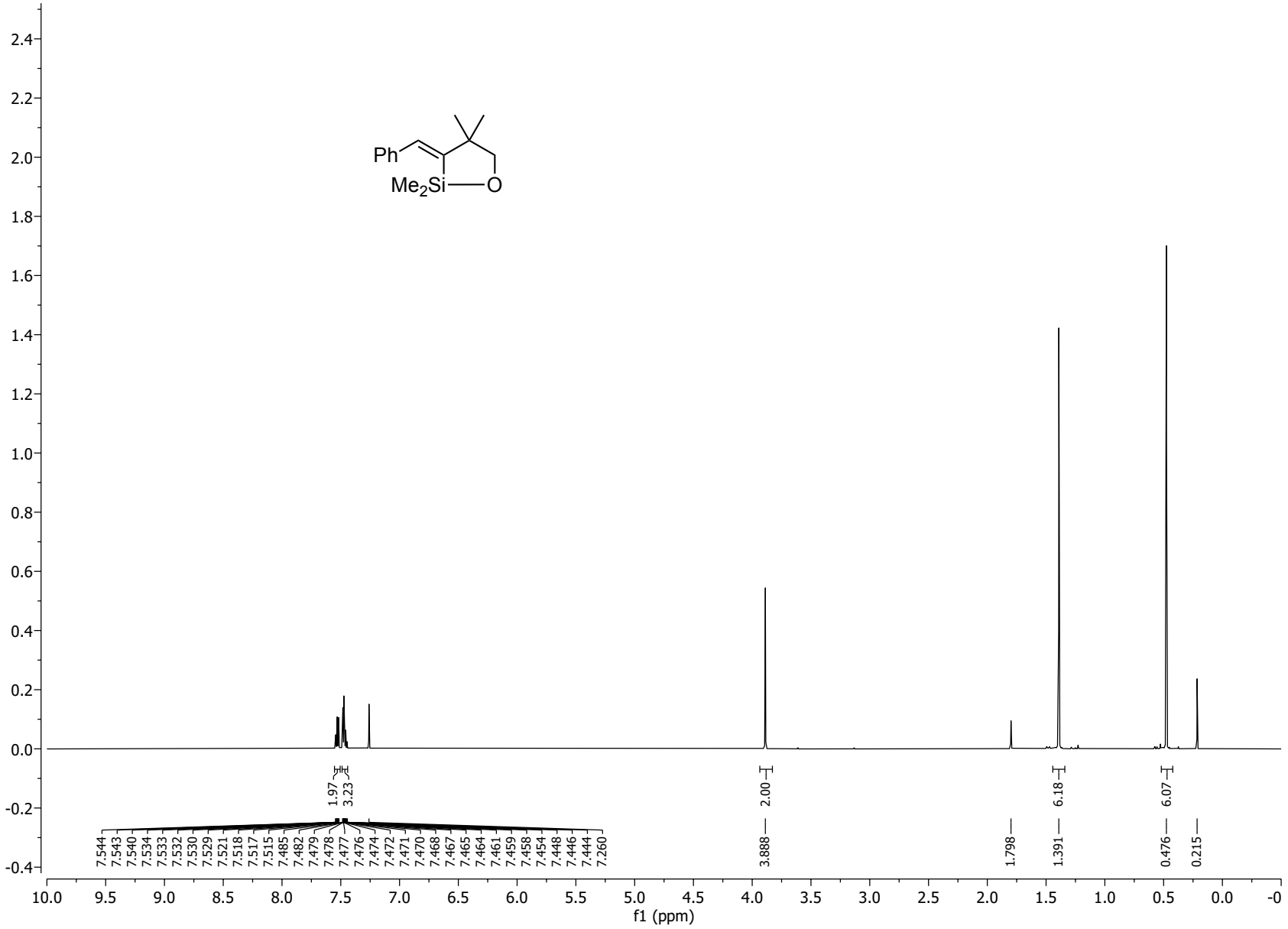


**Figure S32.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **S2**

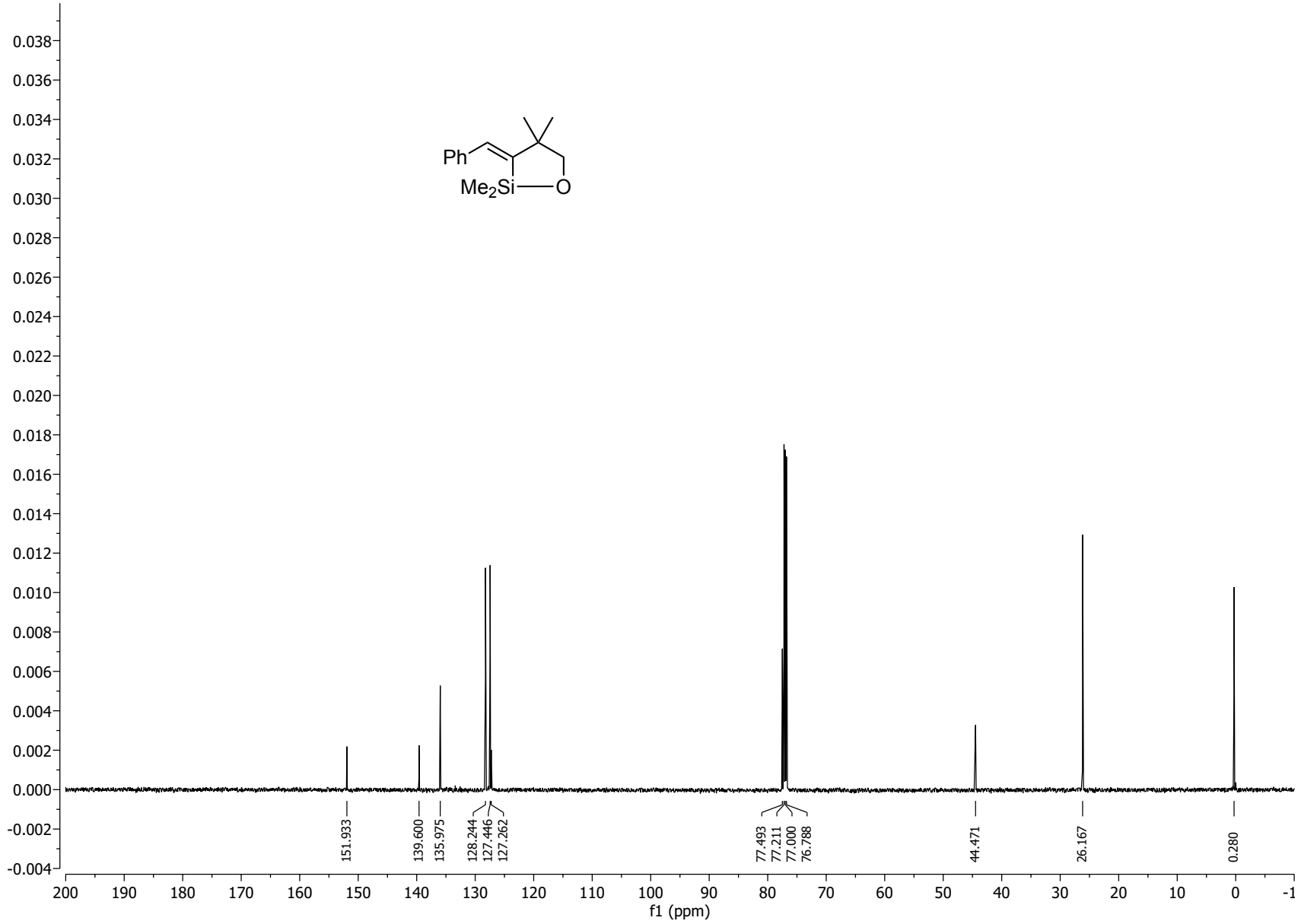


**Figure S33.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **S2**

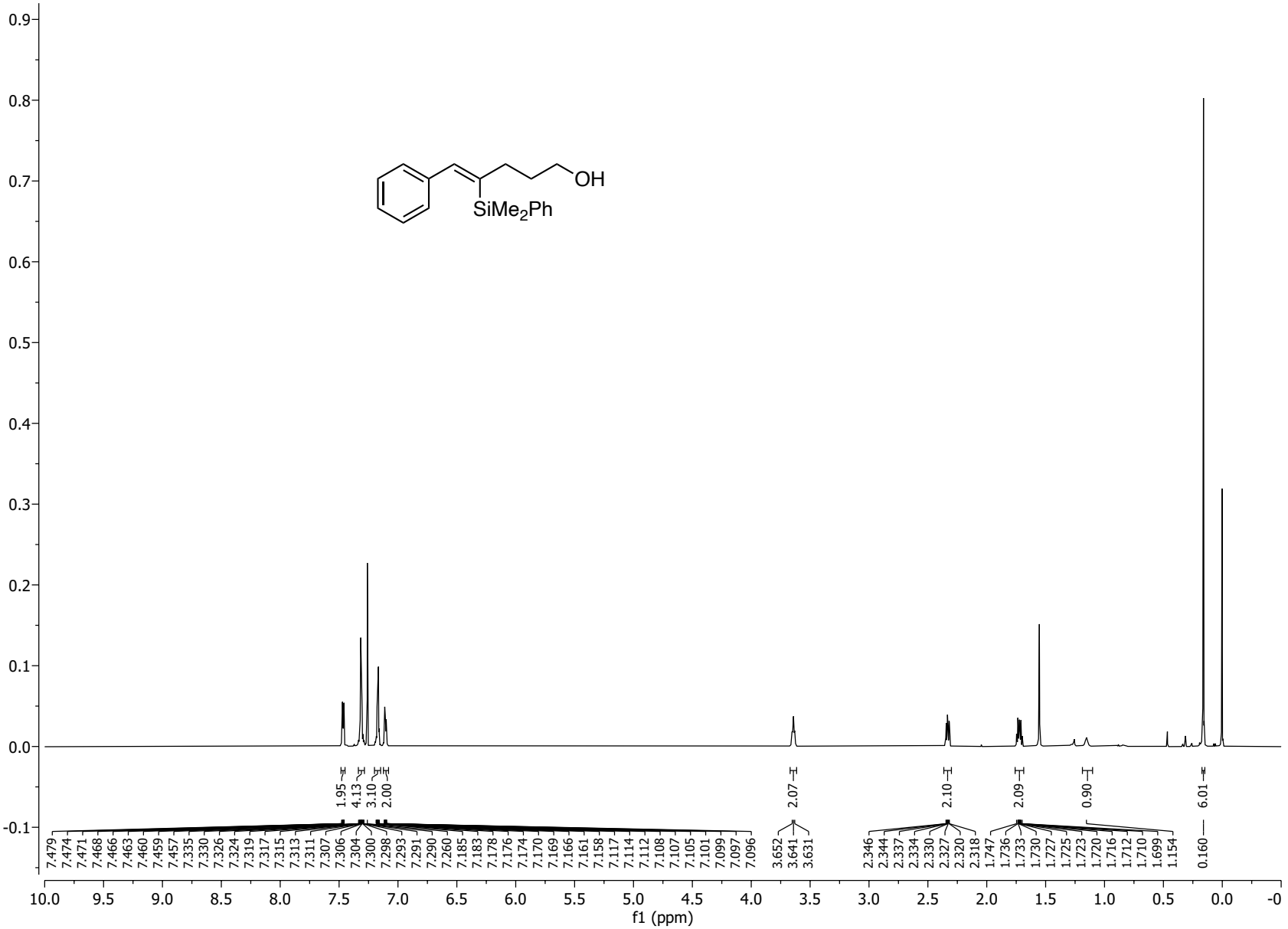


**Figure S34.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **S4**

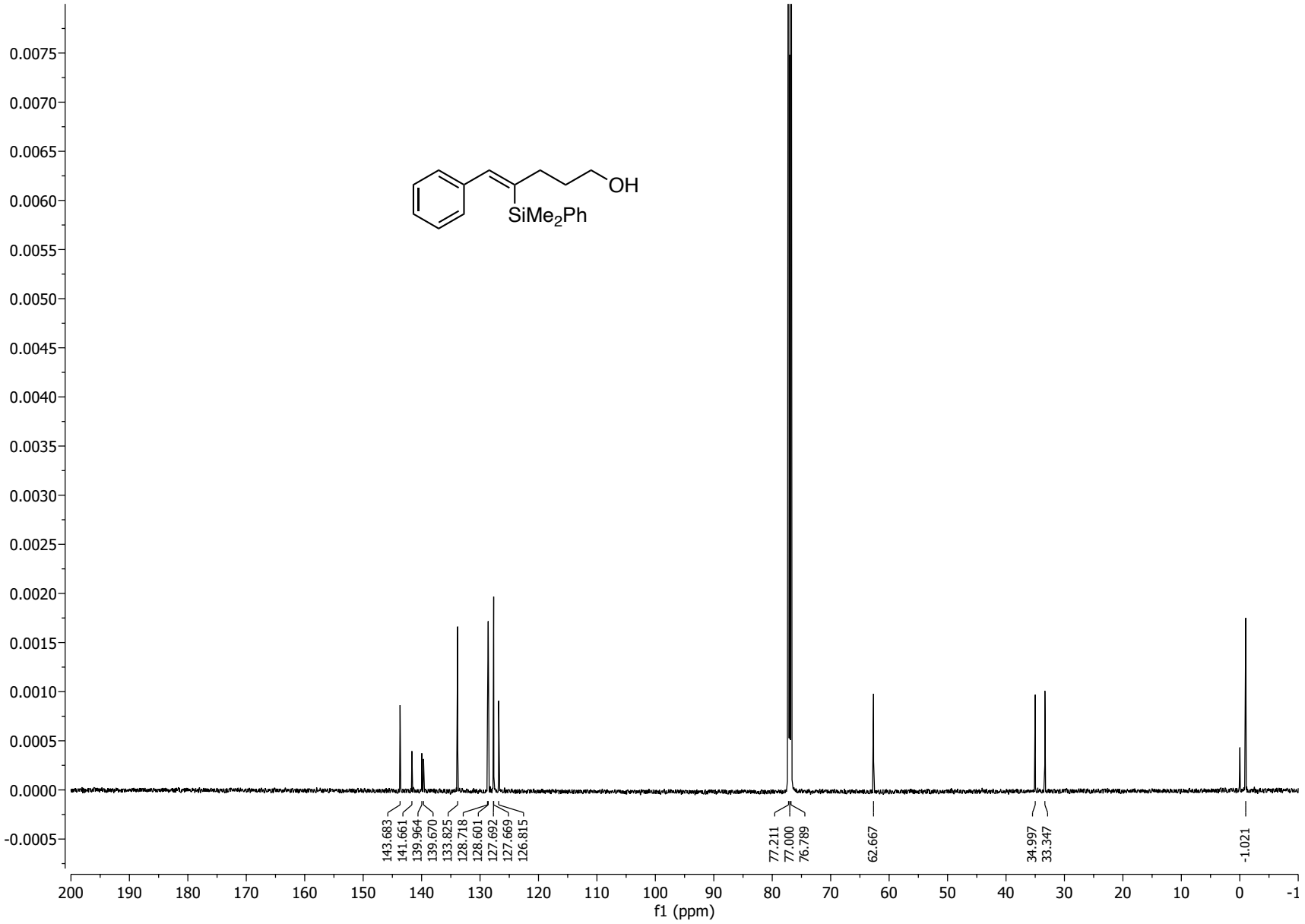


**Figure S35.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **S4**

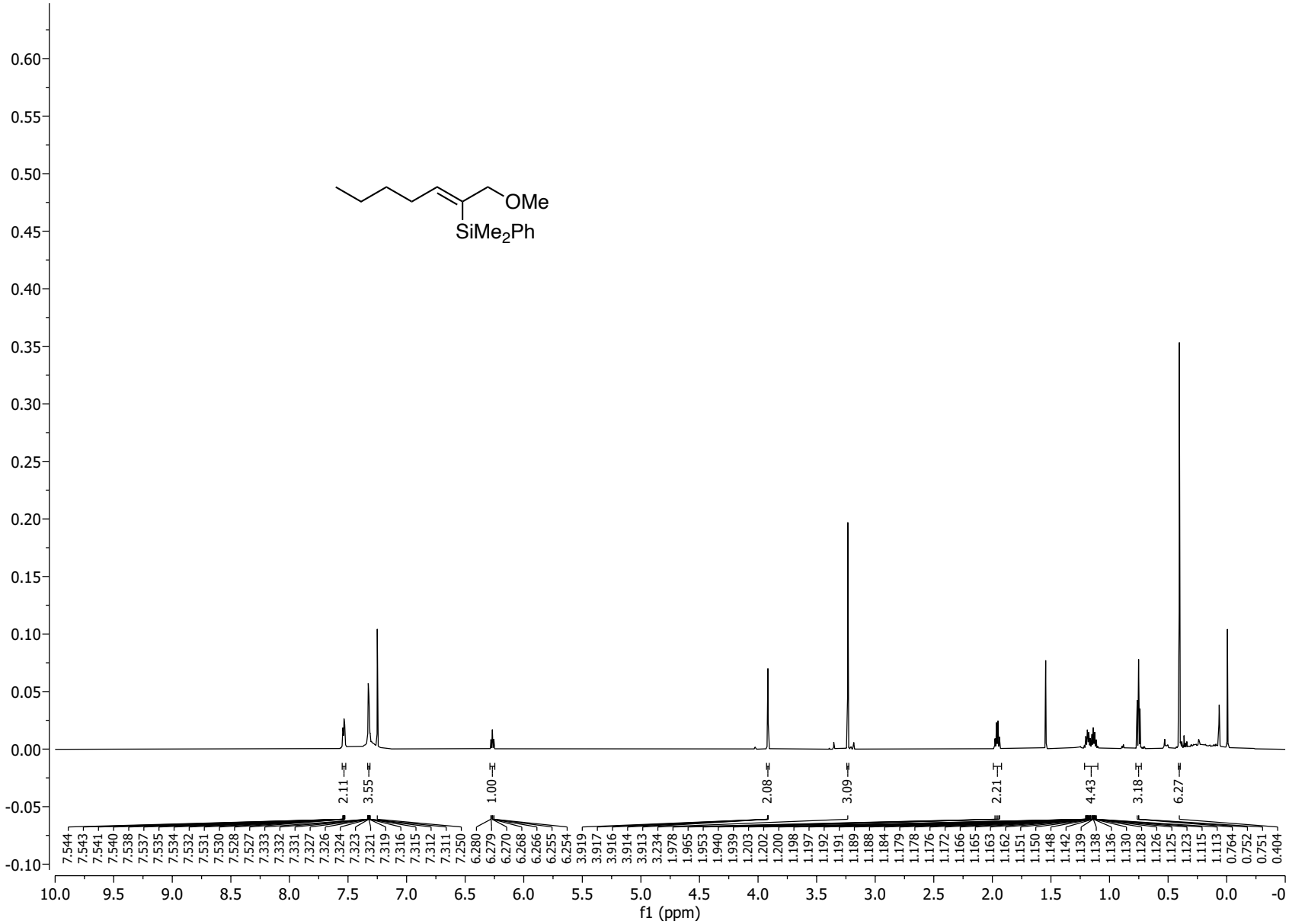


**Figure S36.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **S11**

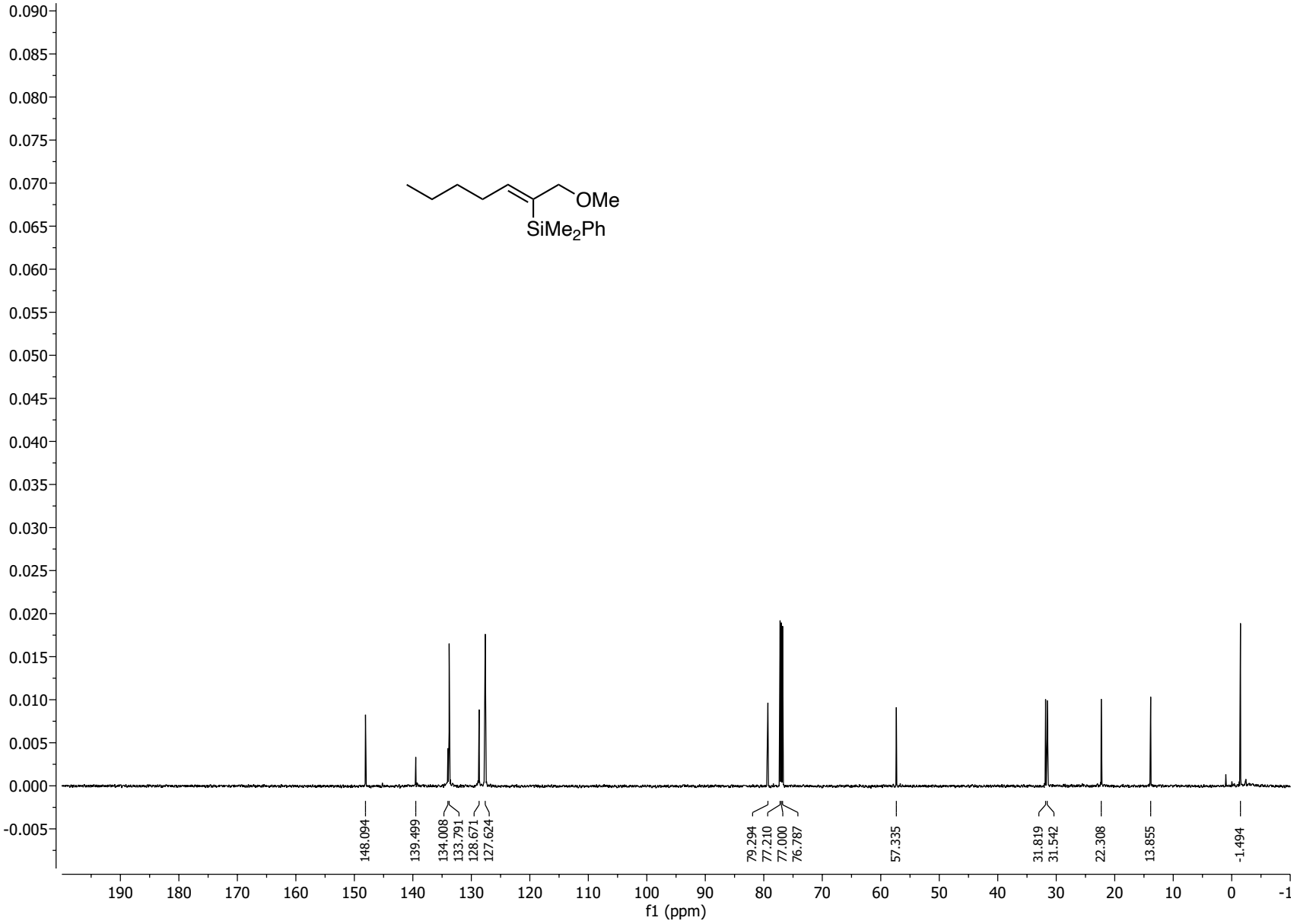


**Figure S37.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **S11**

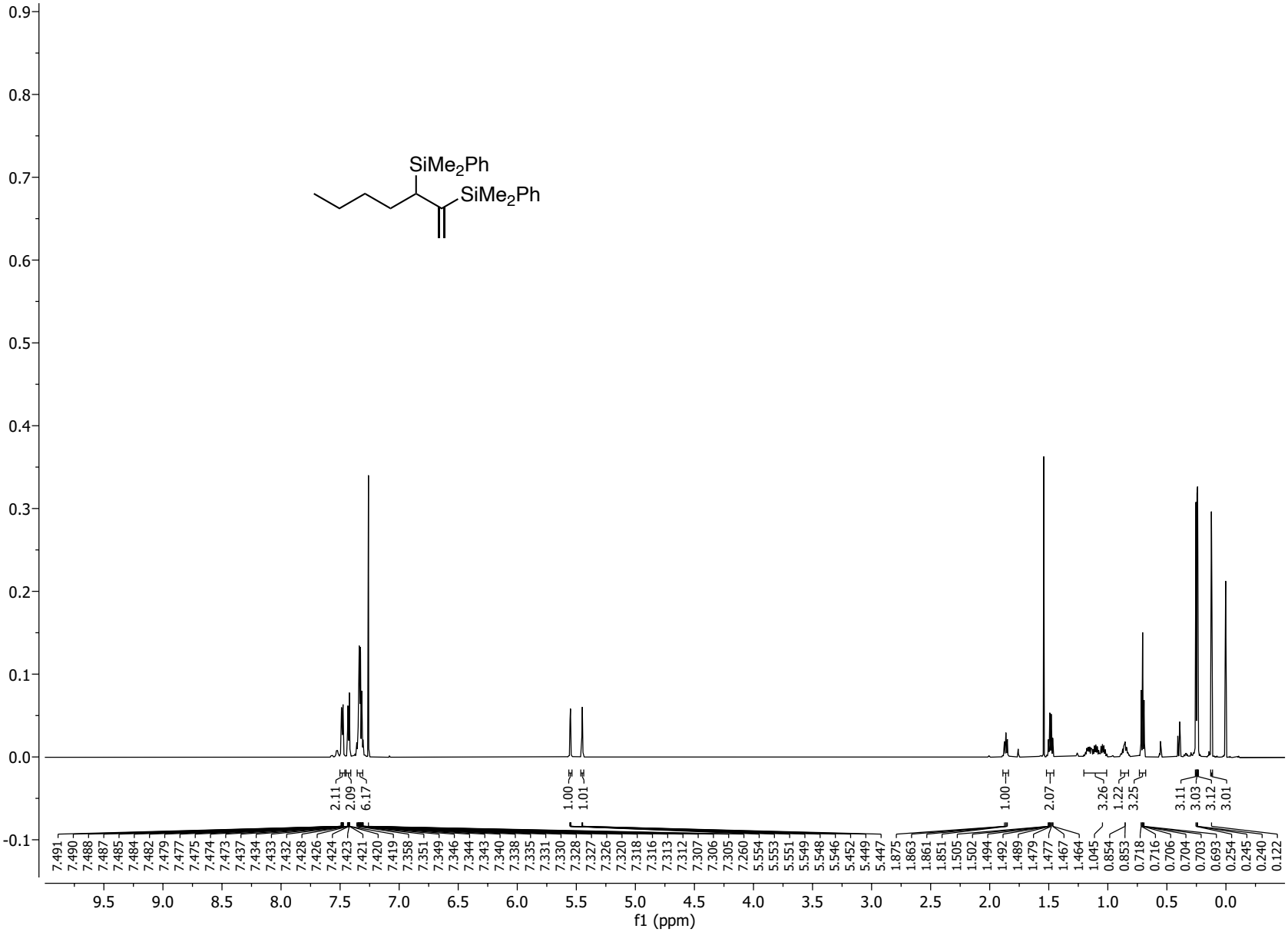


**Figure S38.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **S13**

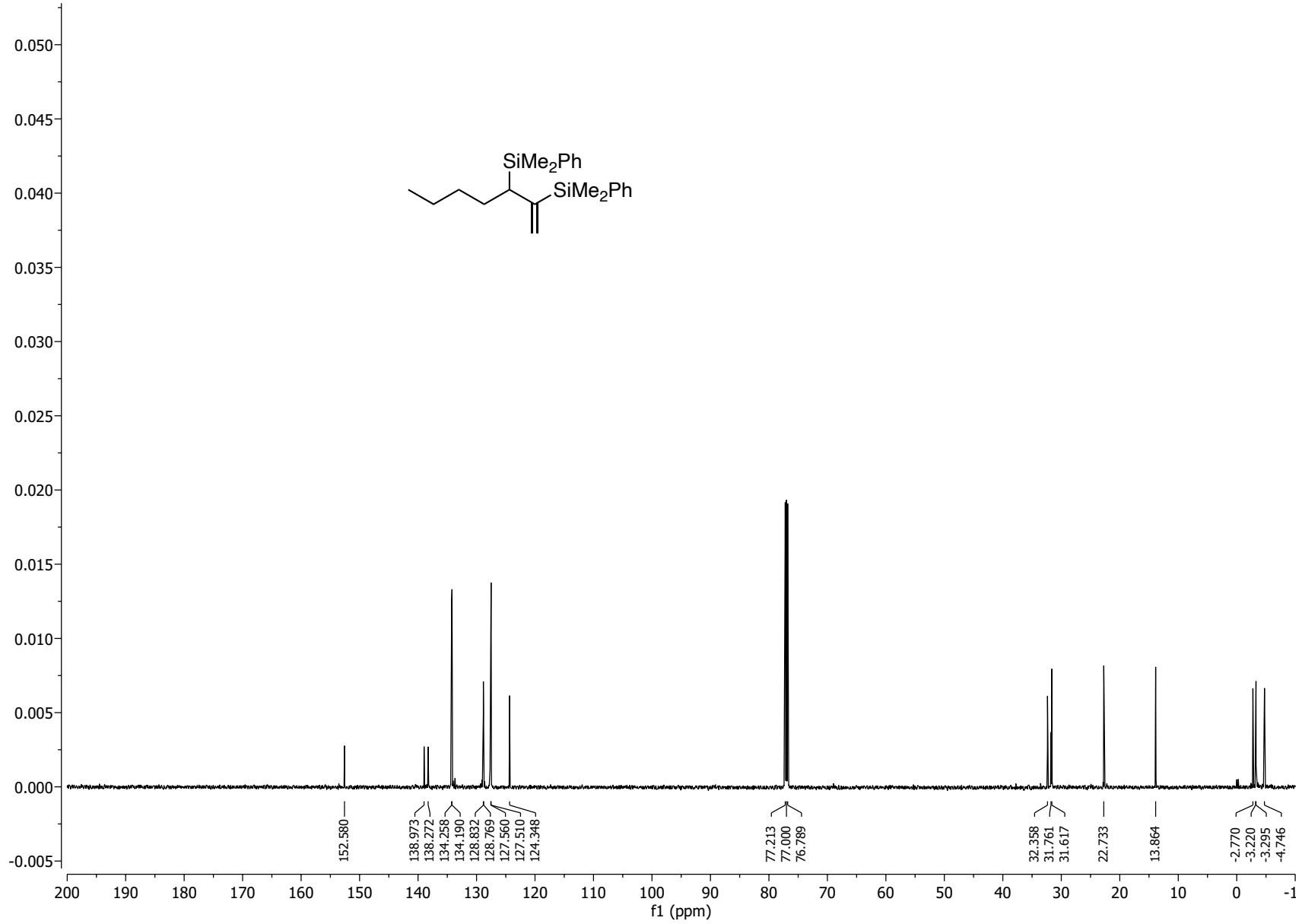


**Figure S39.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **S13**

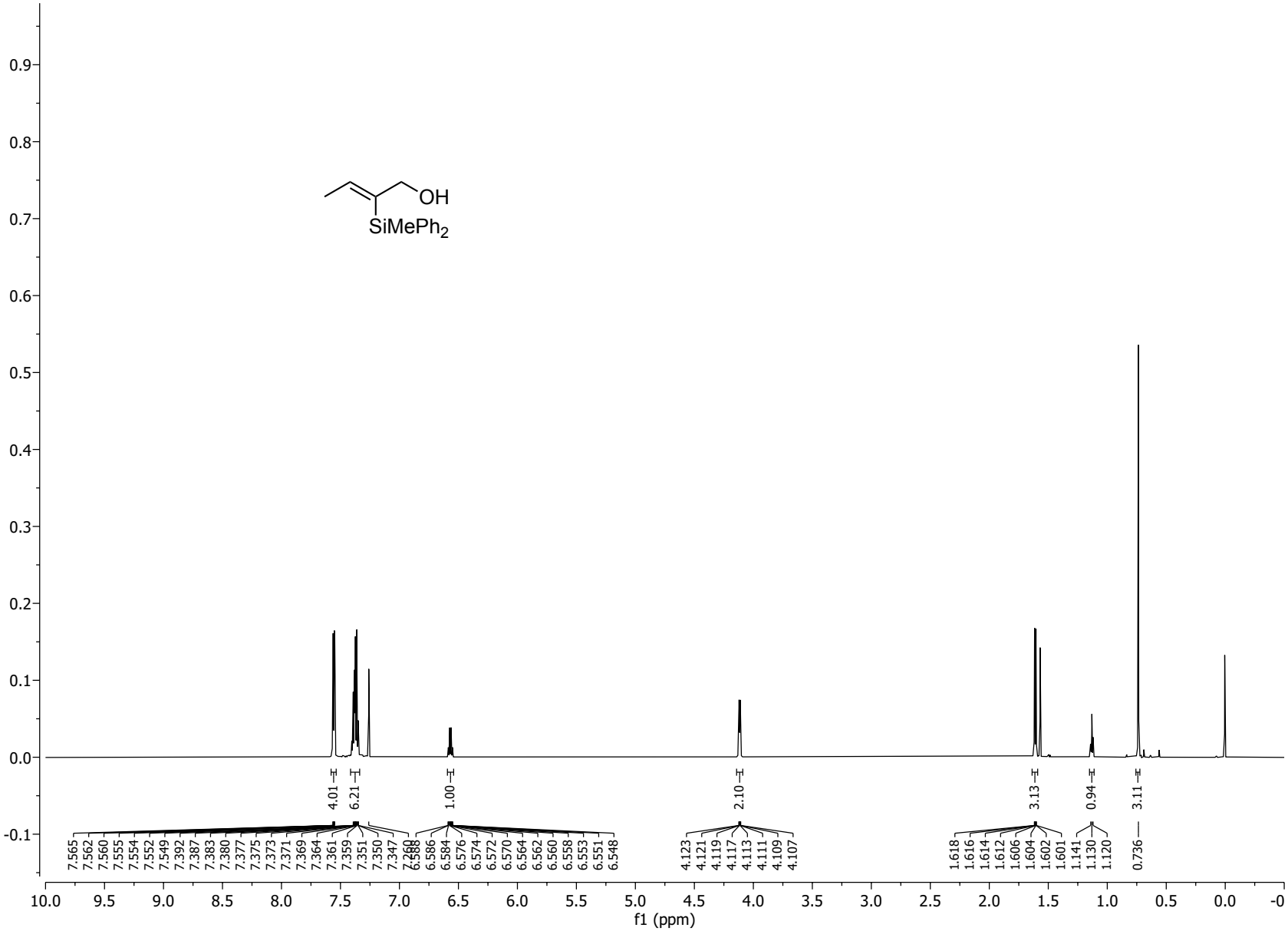


**Figure S40.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of **4ab**

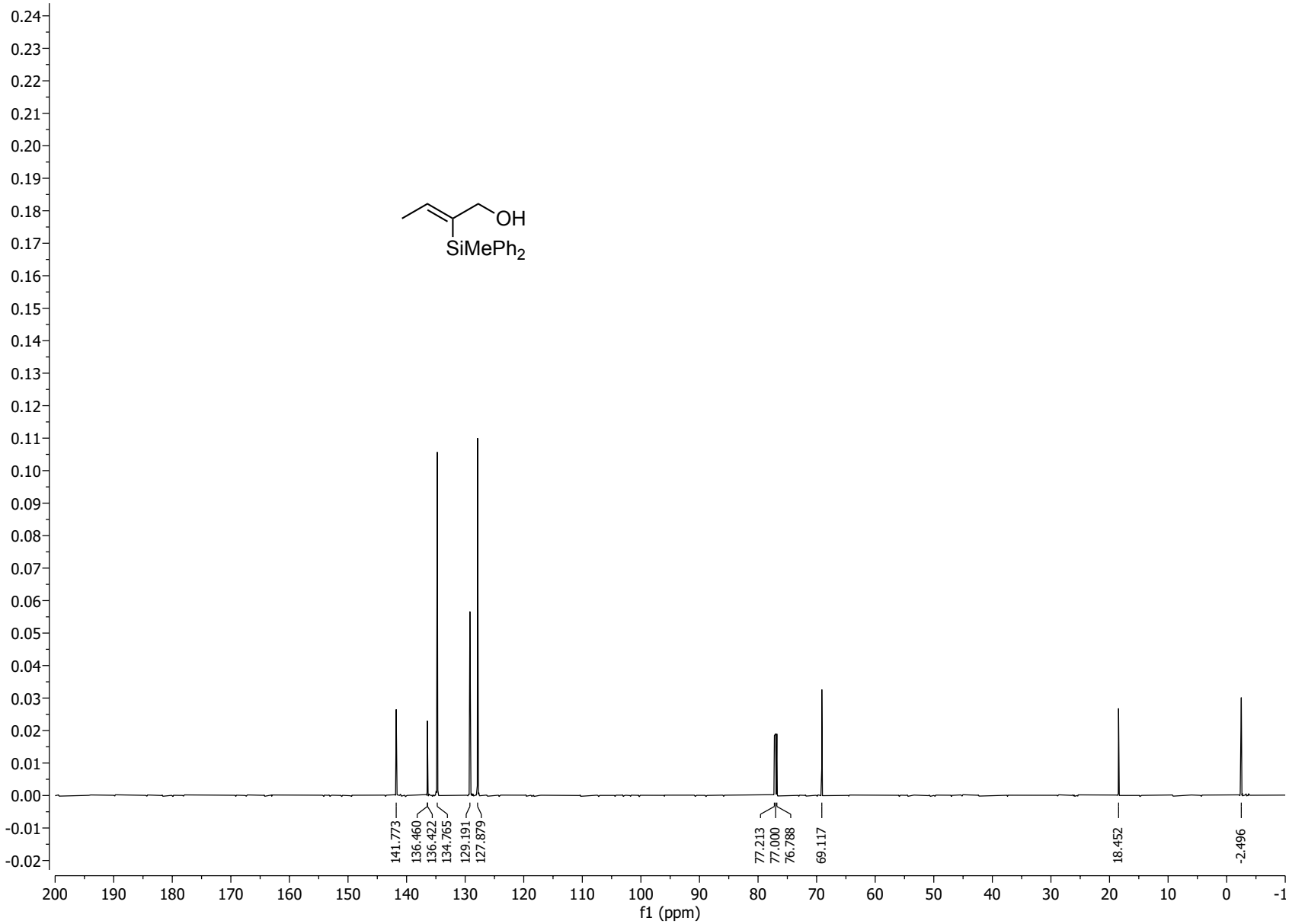


**Figure S41.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4ab**

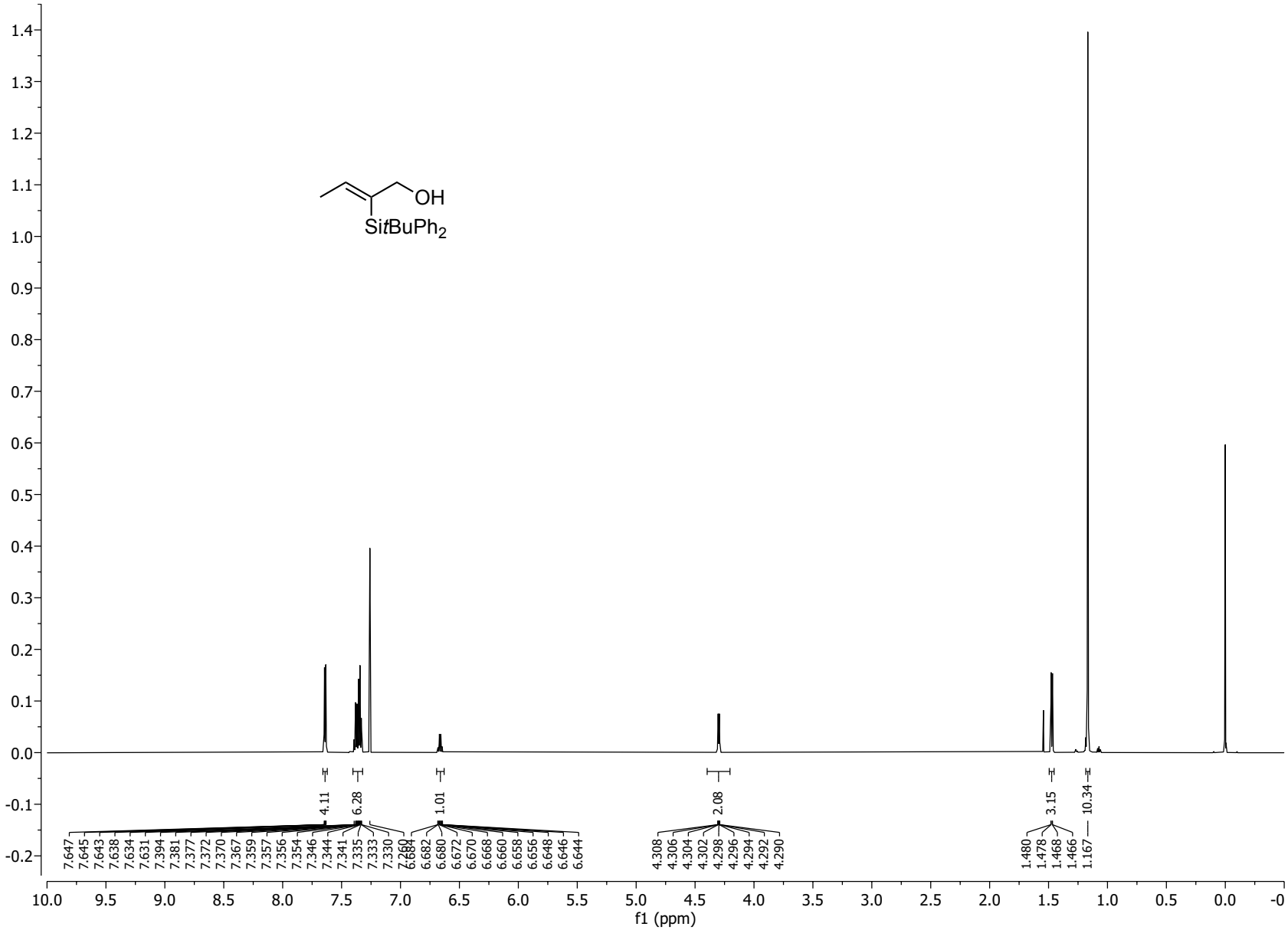


**Figure S42.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of **4ac**

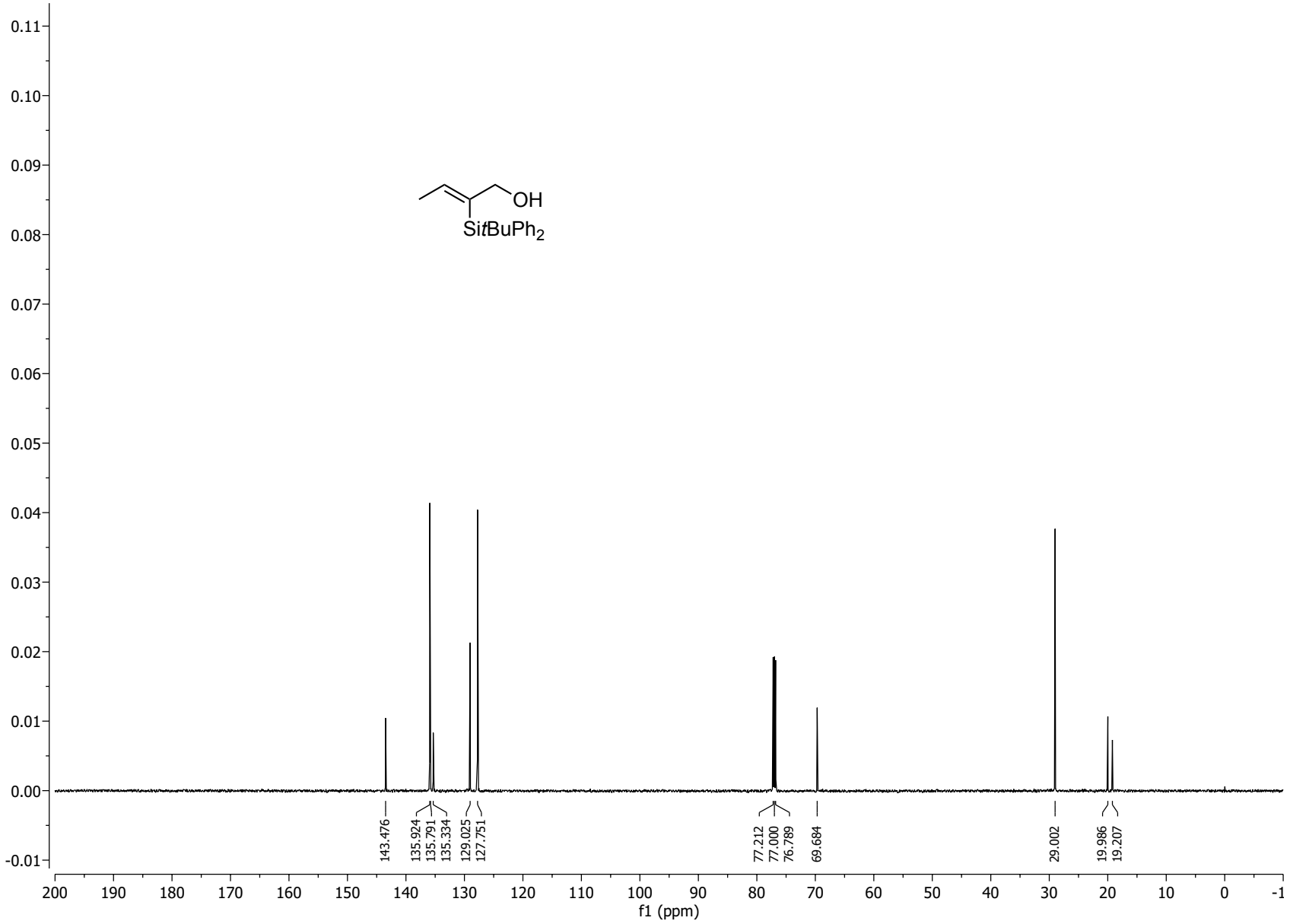


**Figure S43.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4ac**

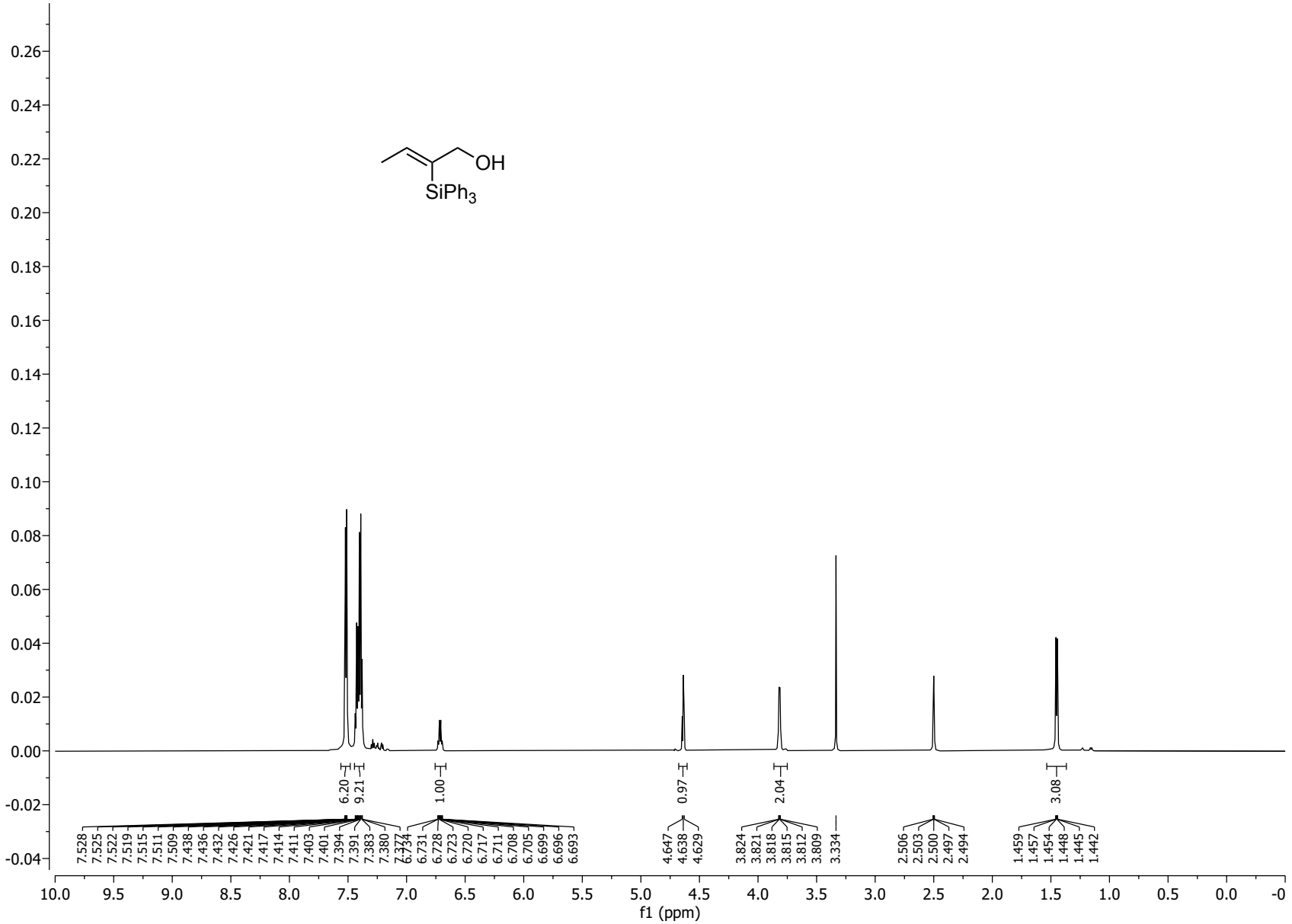


**Figure S44.** $^{1}$H NMR (600 MHz, DMSO-$d_6$) spectrum of **4ad**

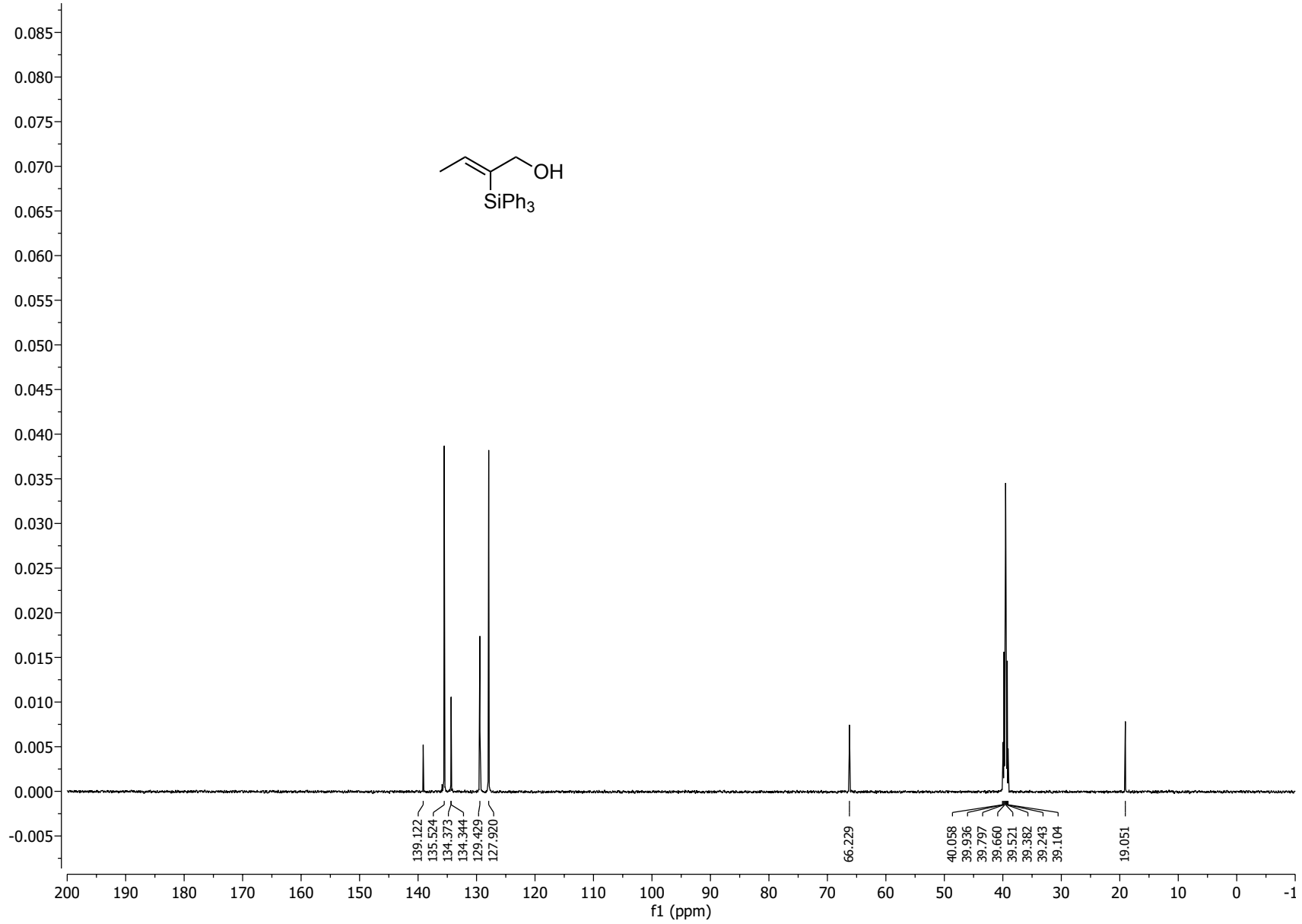


**Figure S45.** $^{13}$C NMR (151 MHz, DMSO-$d_6$) spectrum of **4ad**

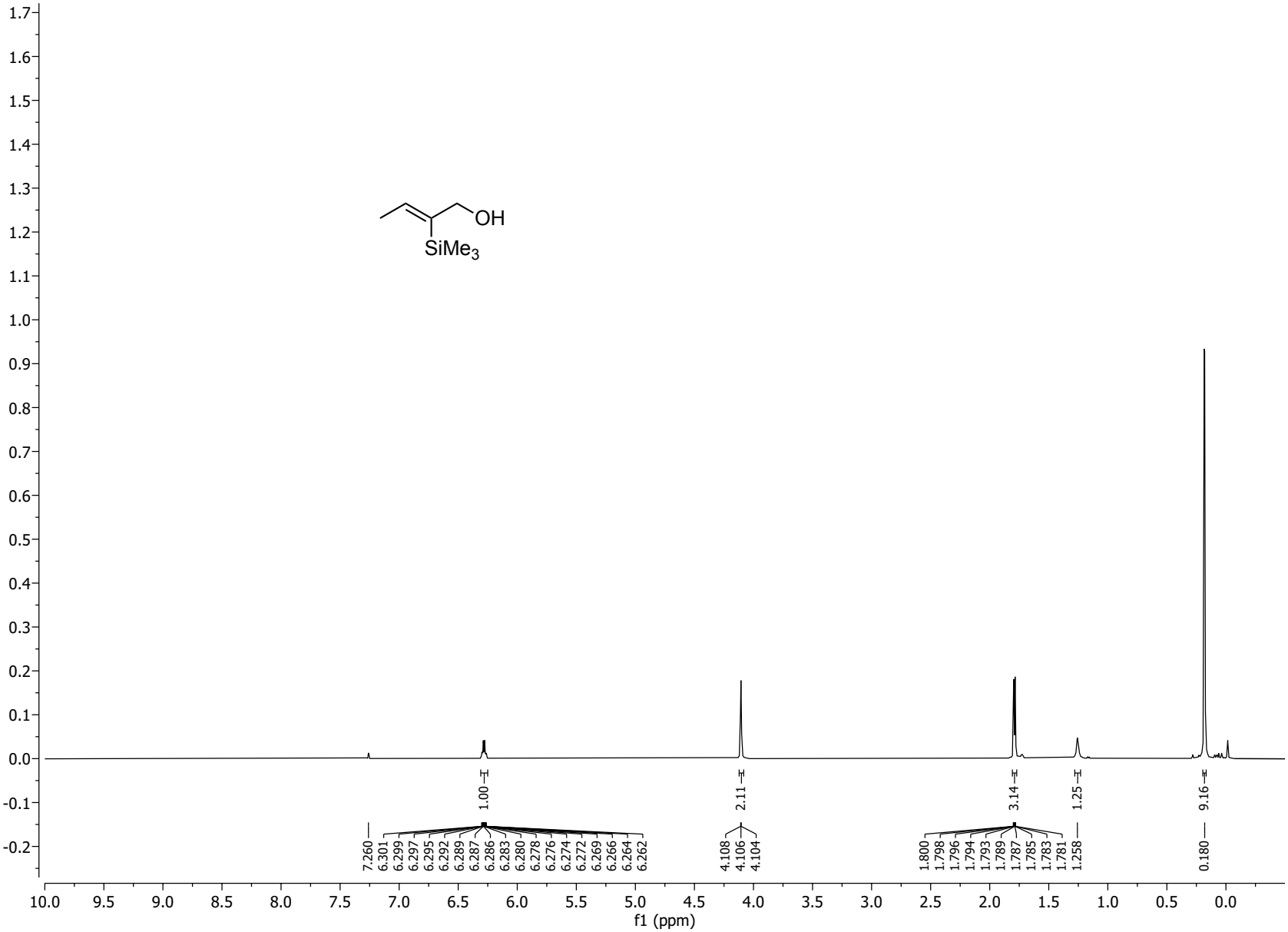


**Figure S46.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **4ae**

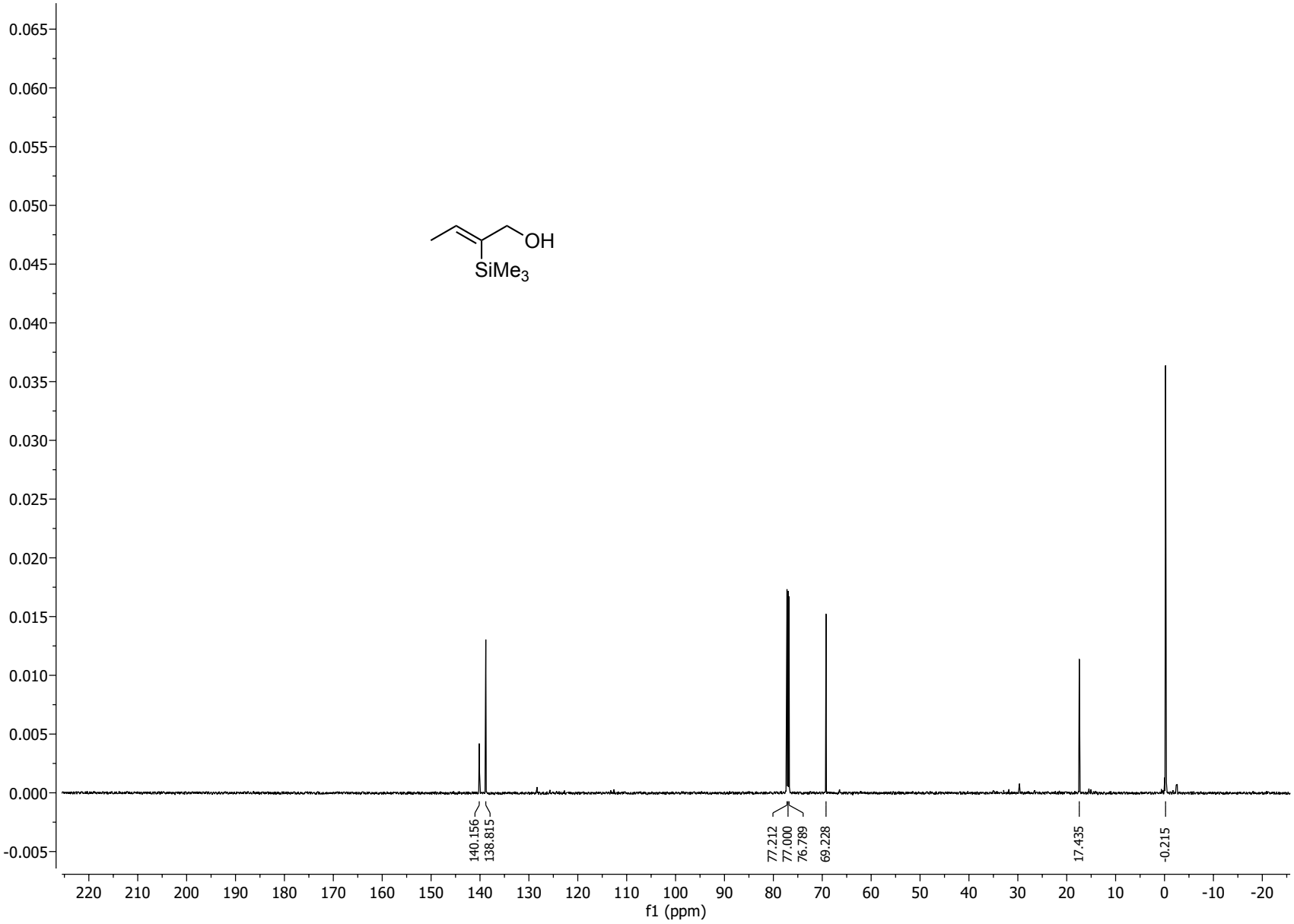


**Figure S47.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4ae**

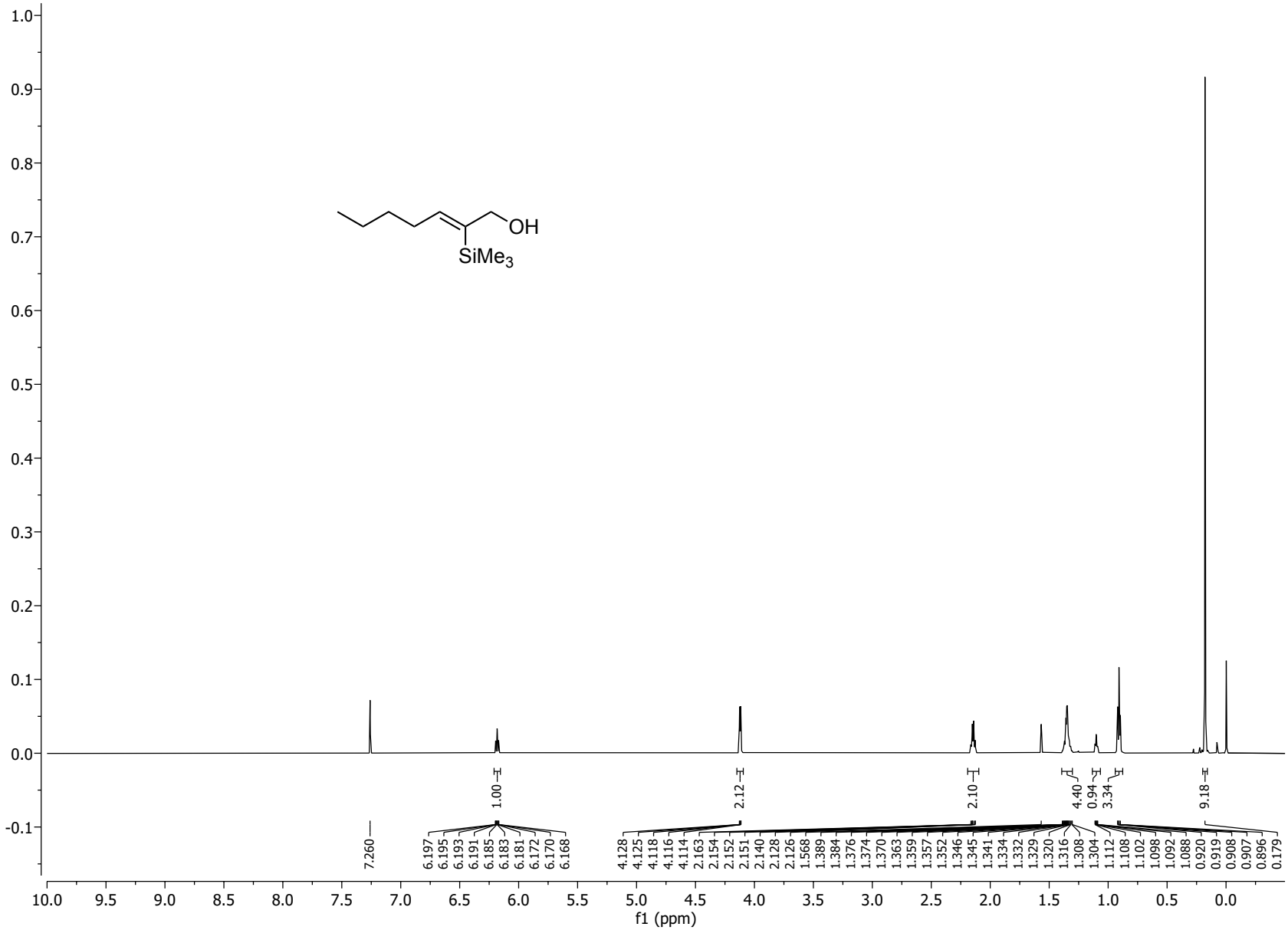


**Figure S48.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of **4be**

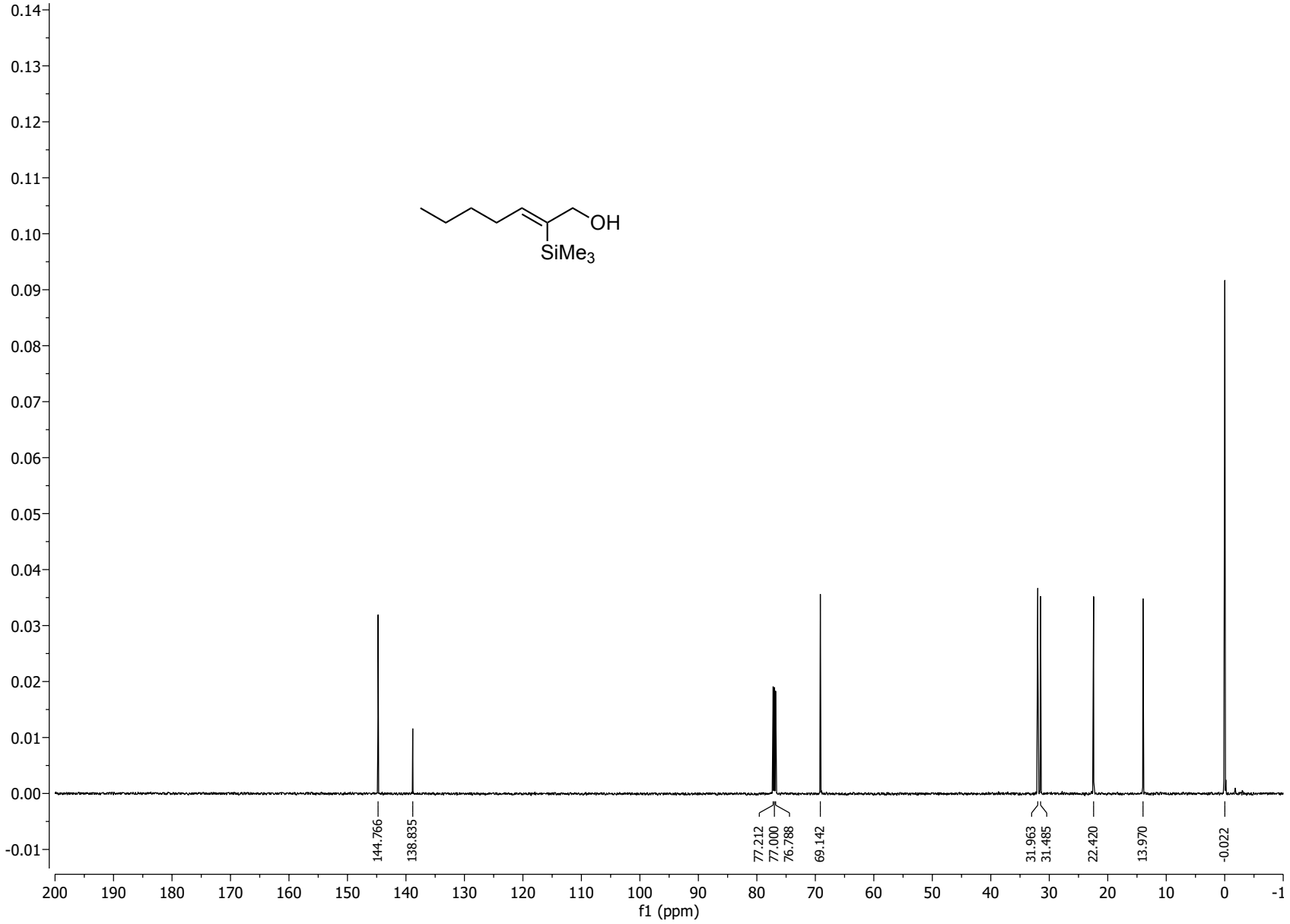


**Figure S49.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4be**

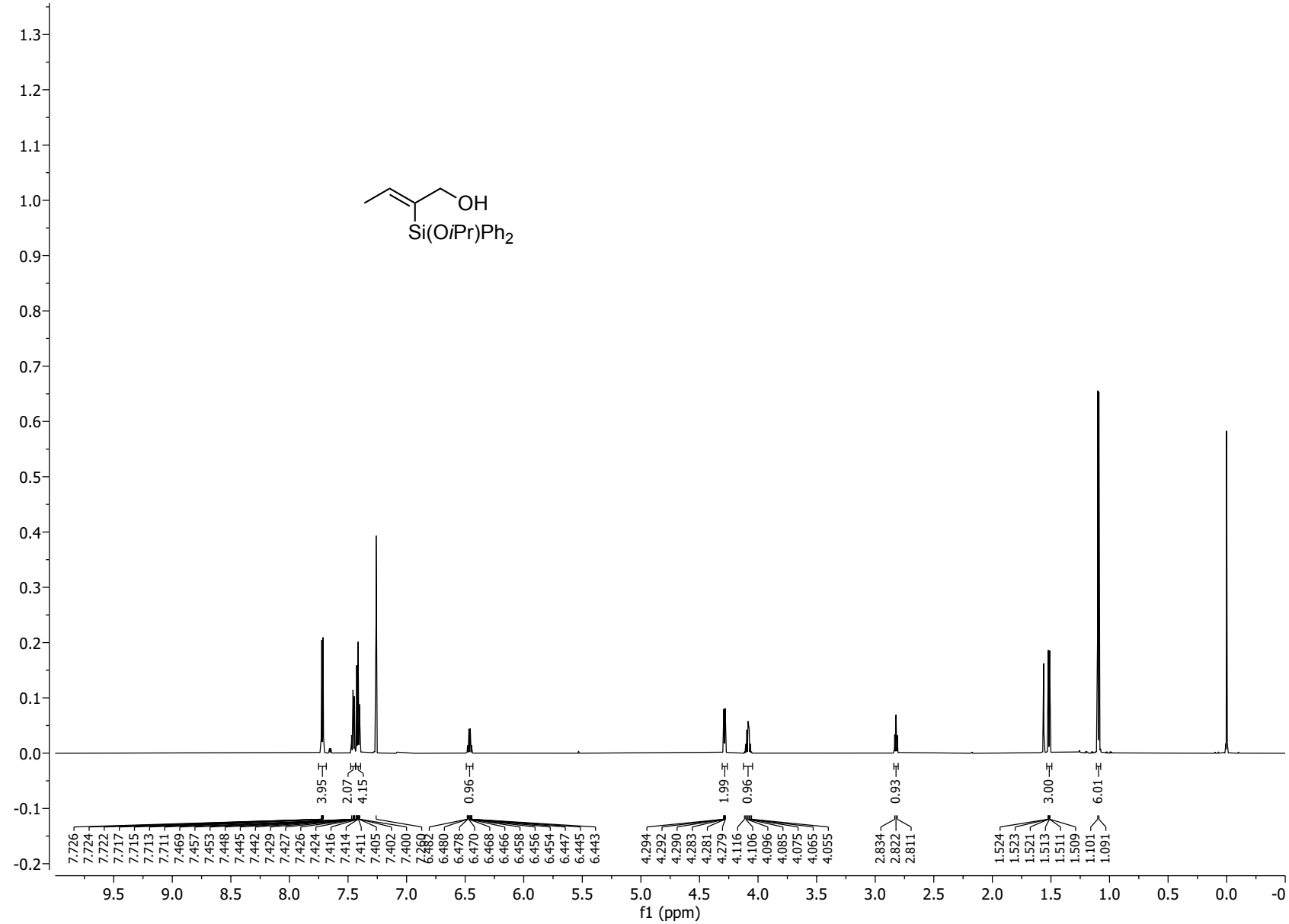


**Figure S50.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **4af-1**

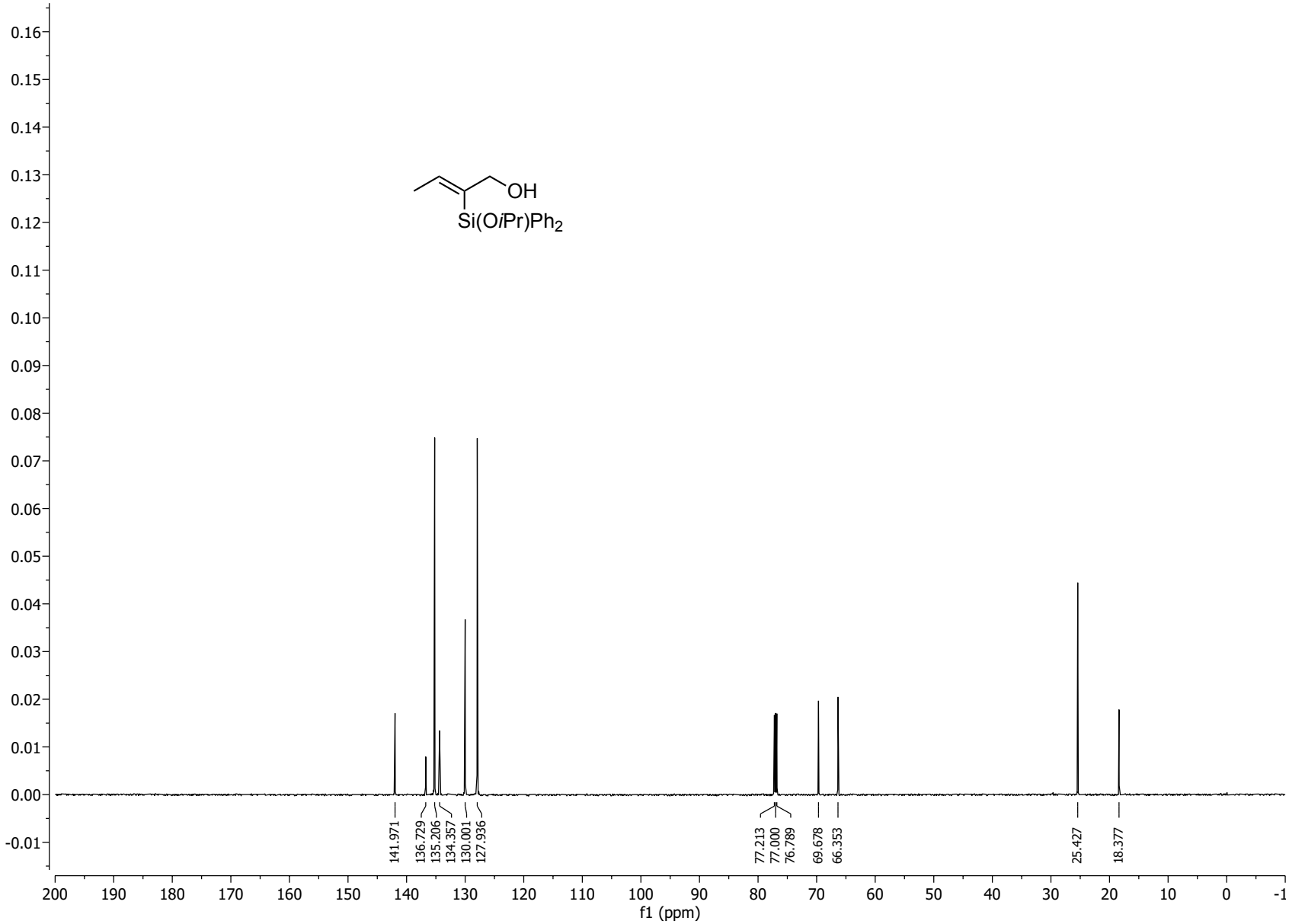


**Figure S51.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4af-1**

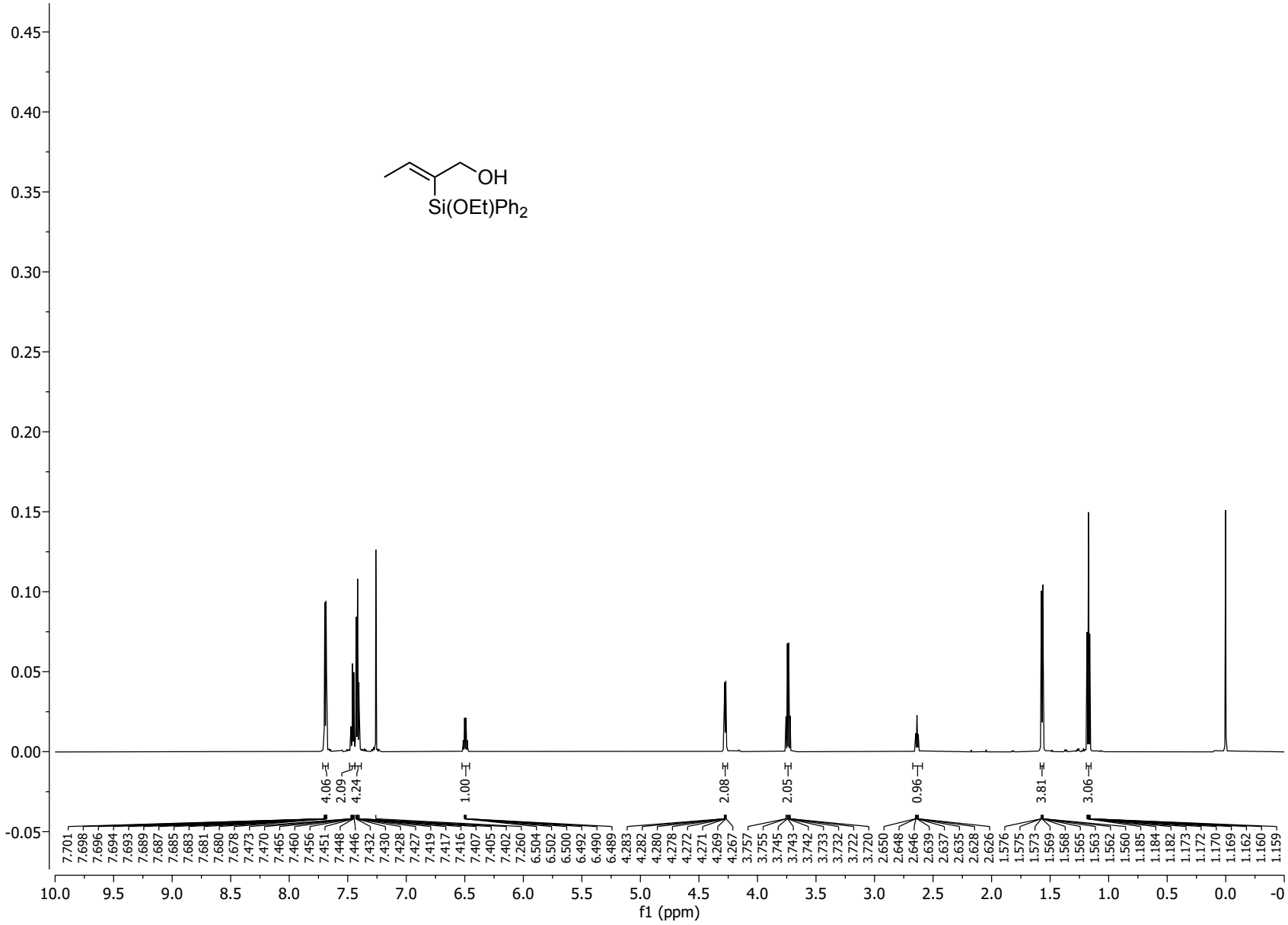


**Figure S52.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **4af-2**

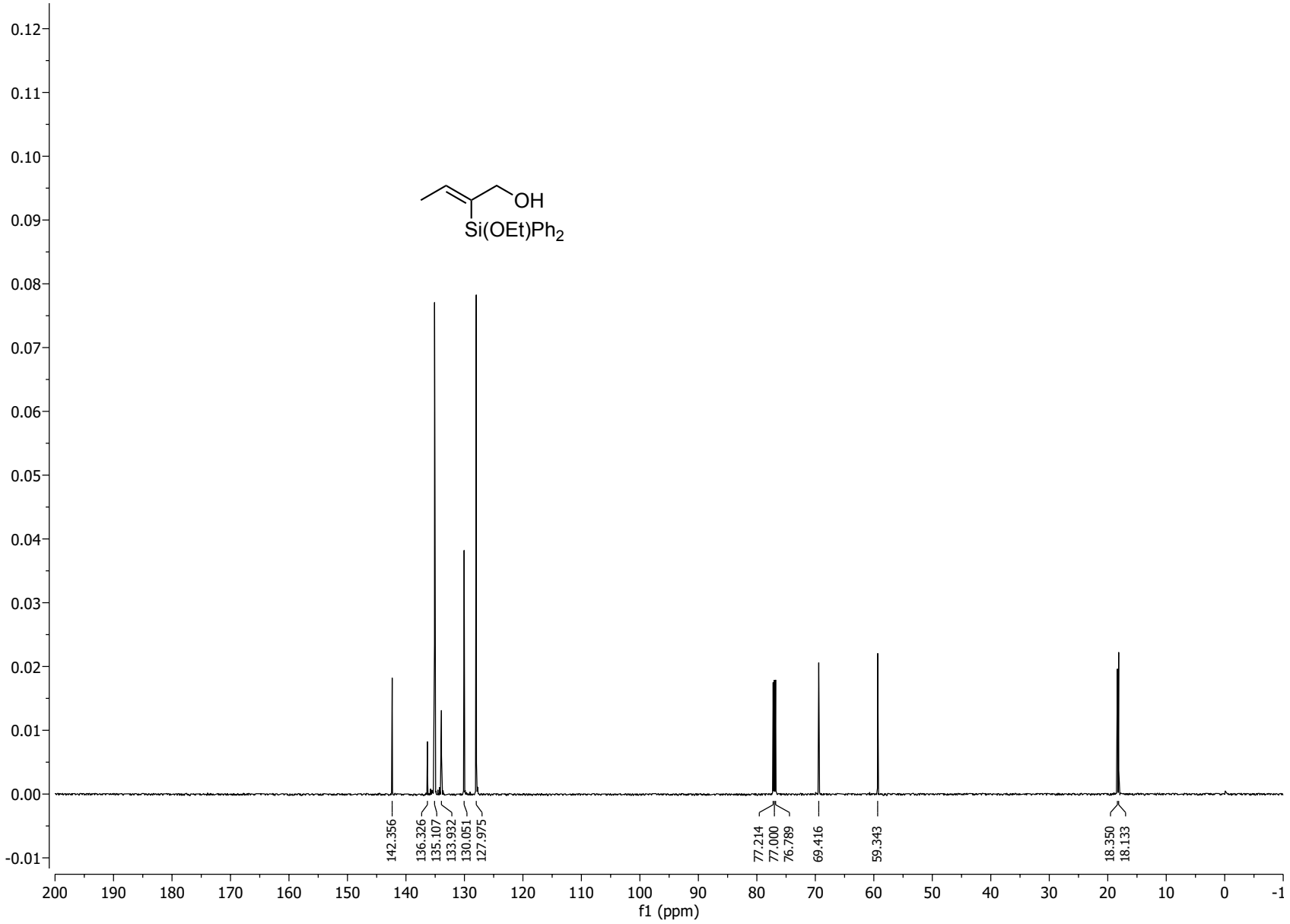


**Figure S53.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4af-2**

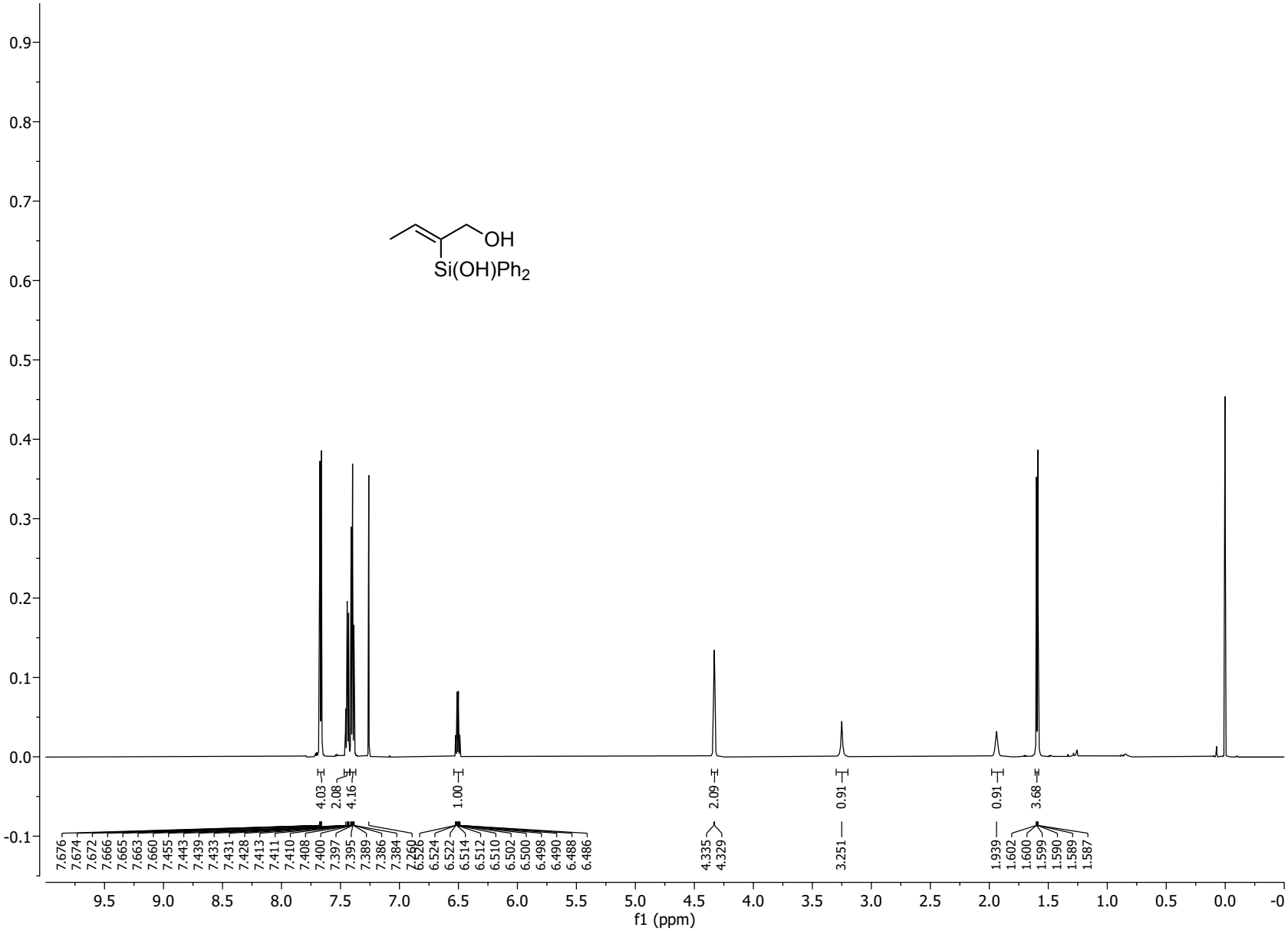


**Figure S54.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **4af-3**

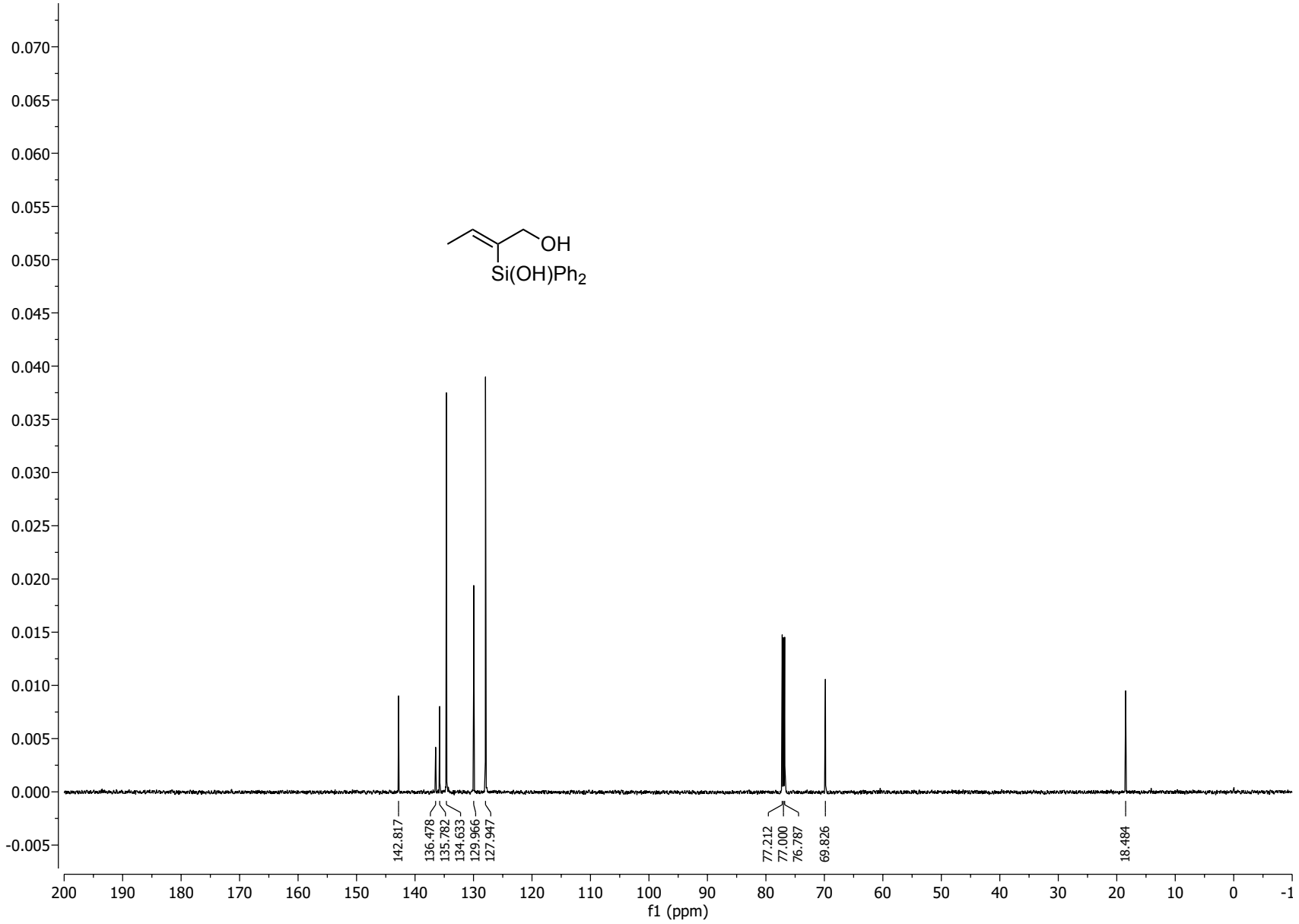


**Figure S55.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4af-3**

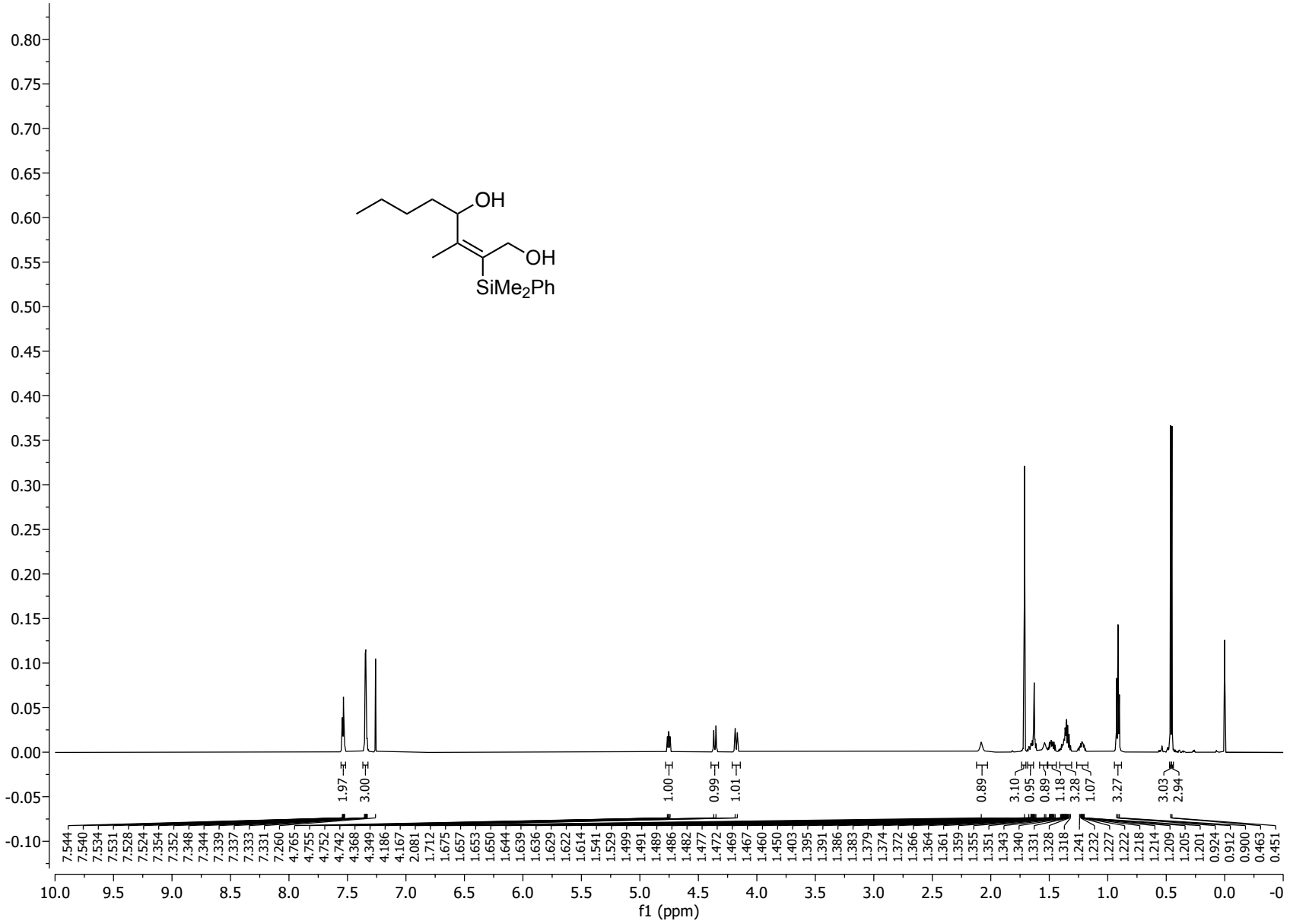


**Figure S56.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **5**

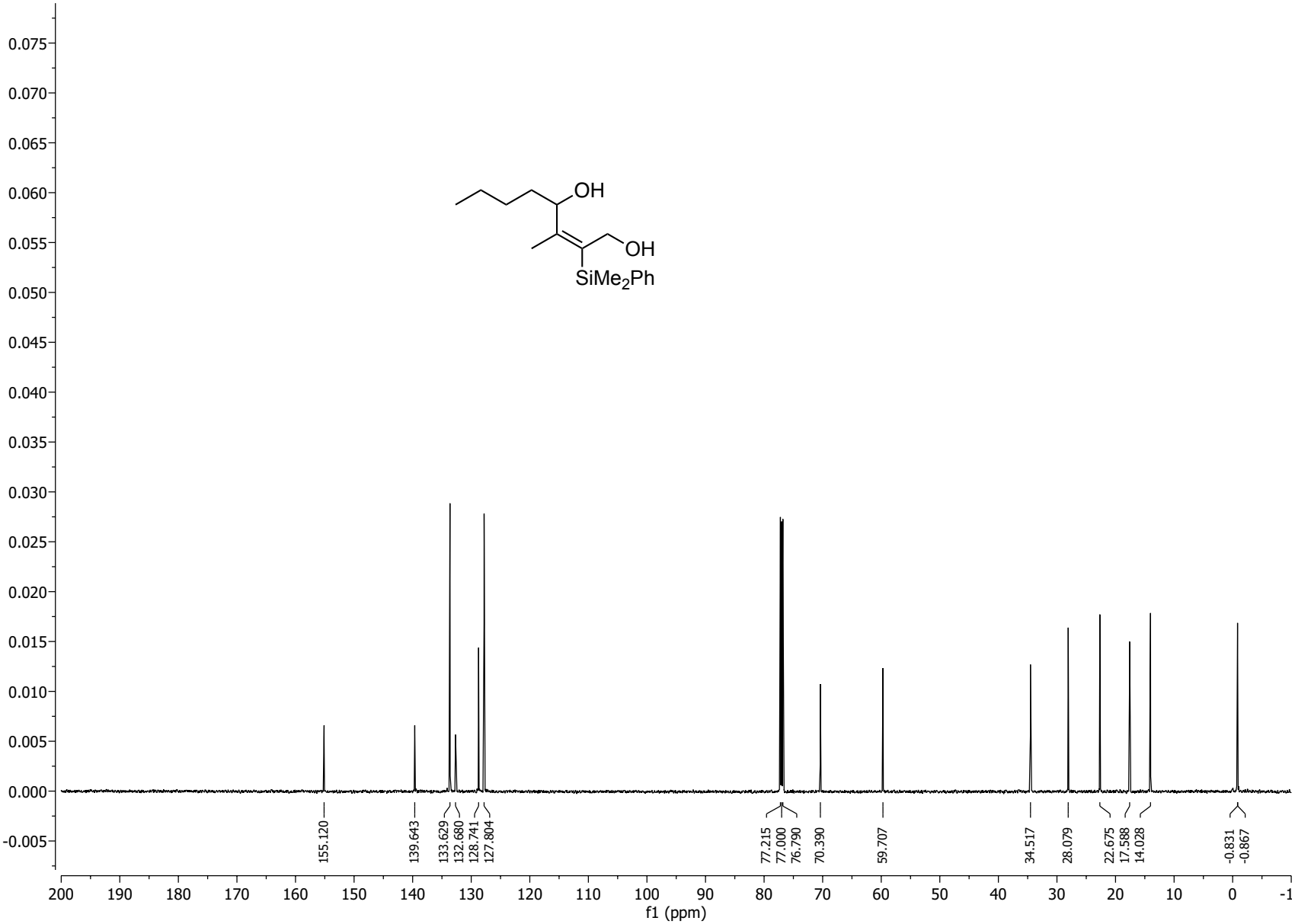


**Figure S57.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **5**

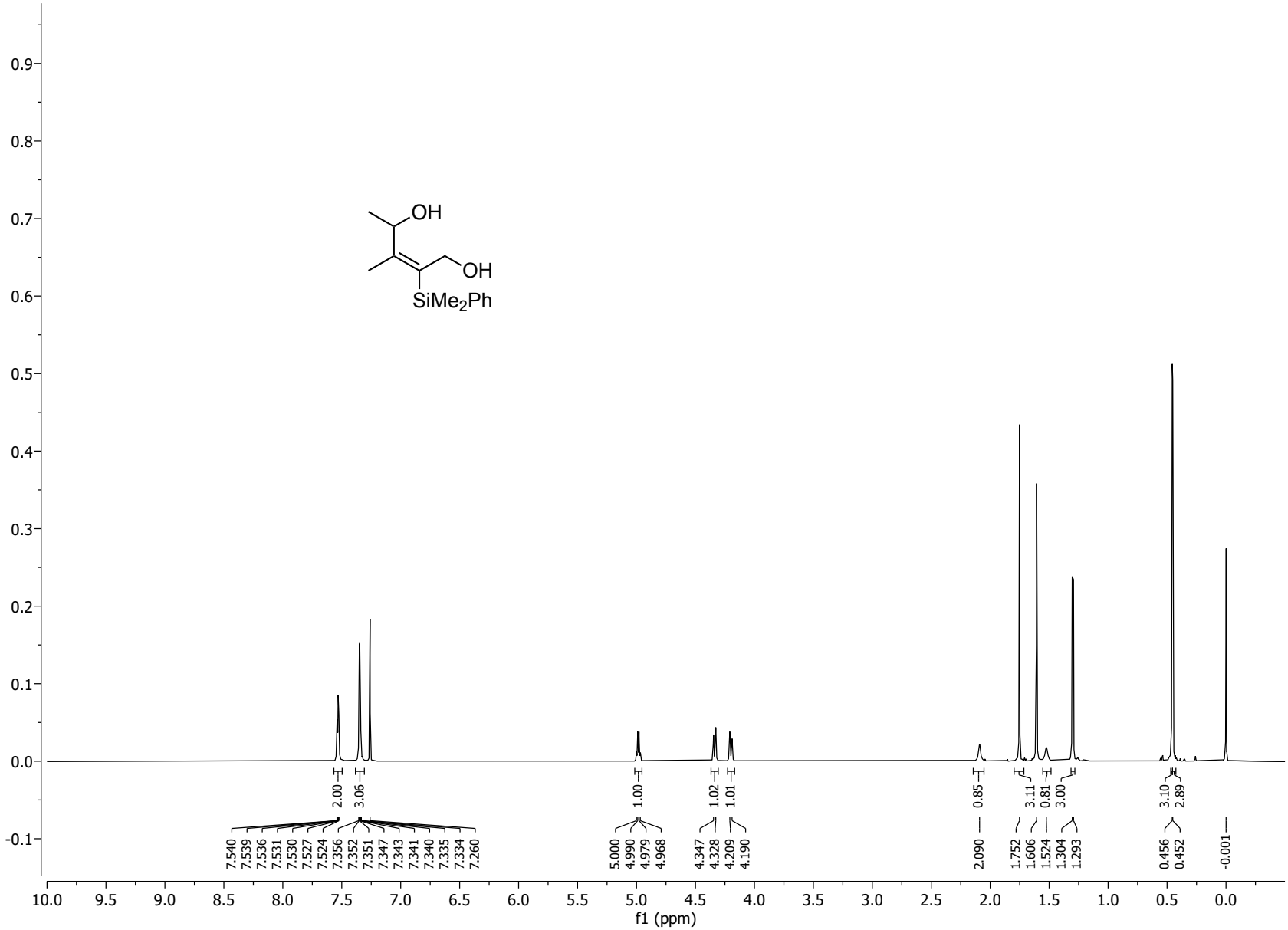


**Figure S58.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **6**

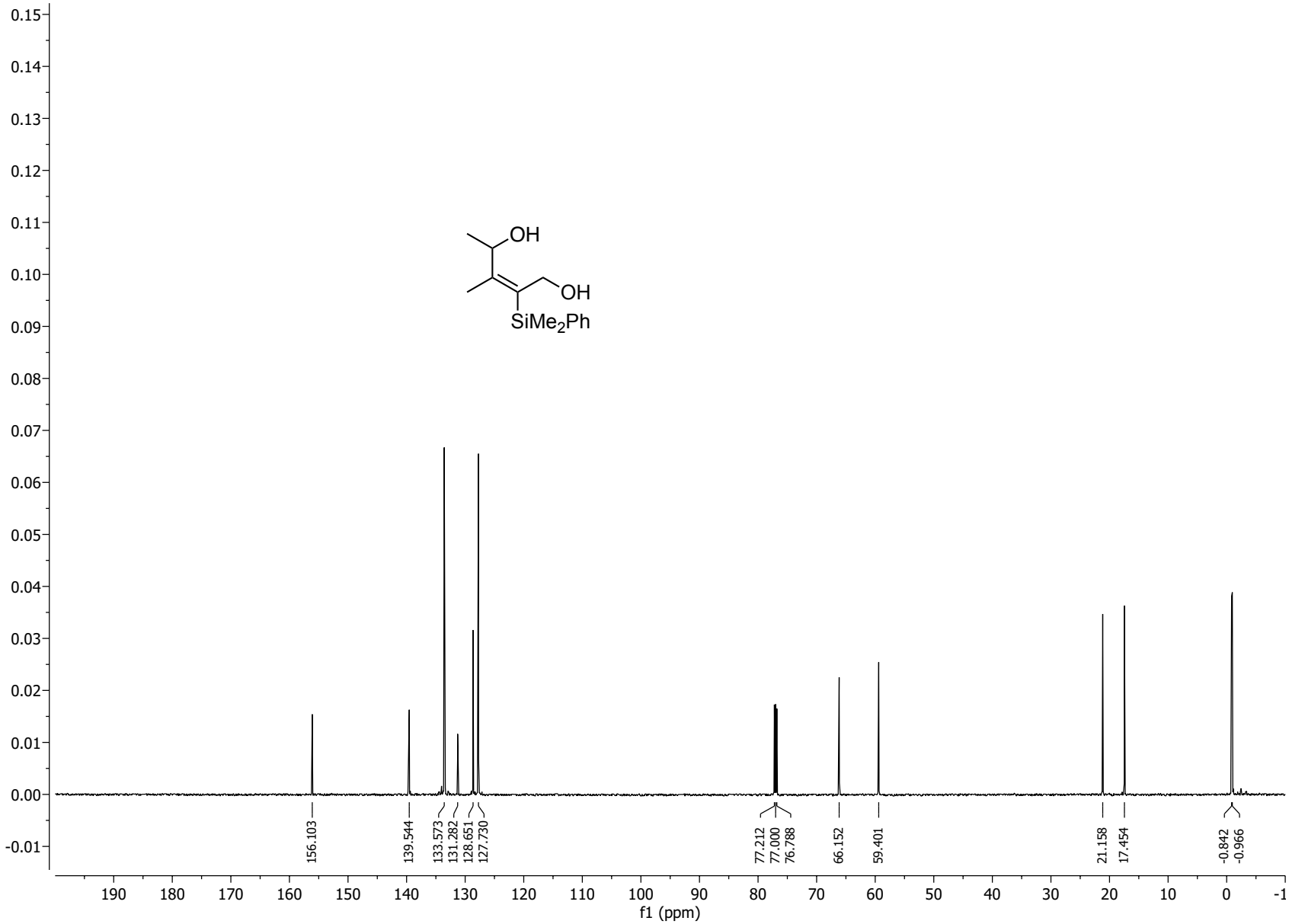


**Figure S59.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **6**

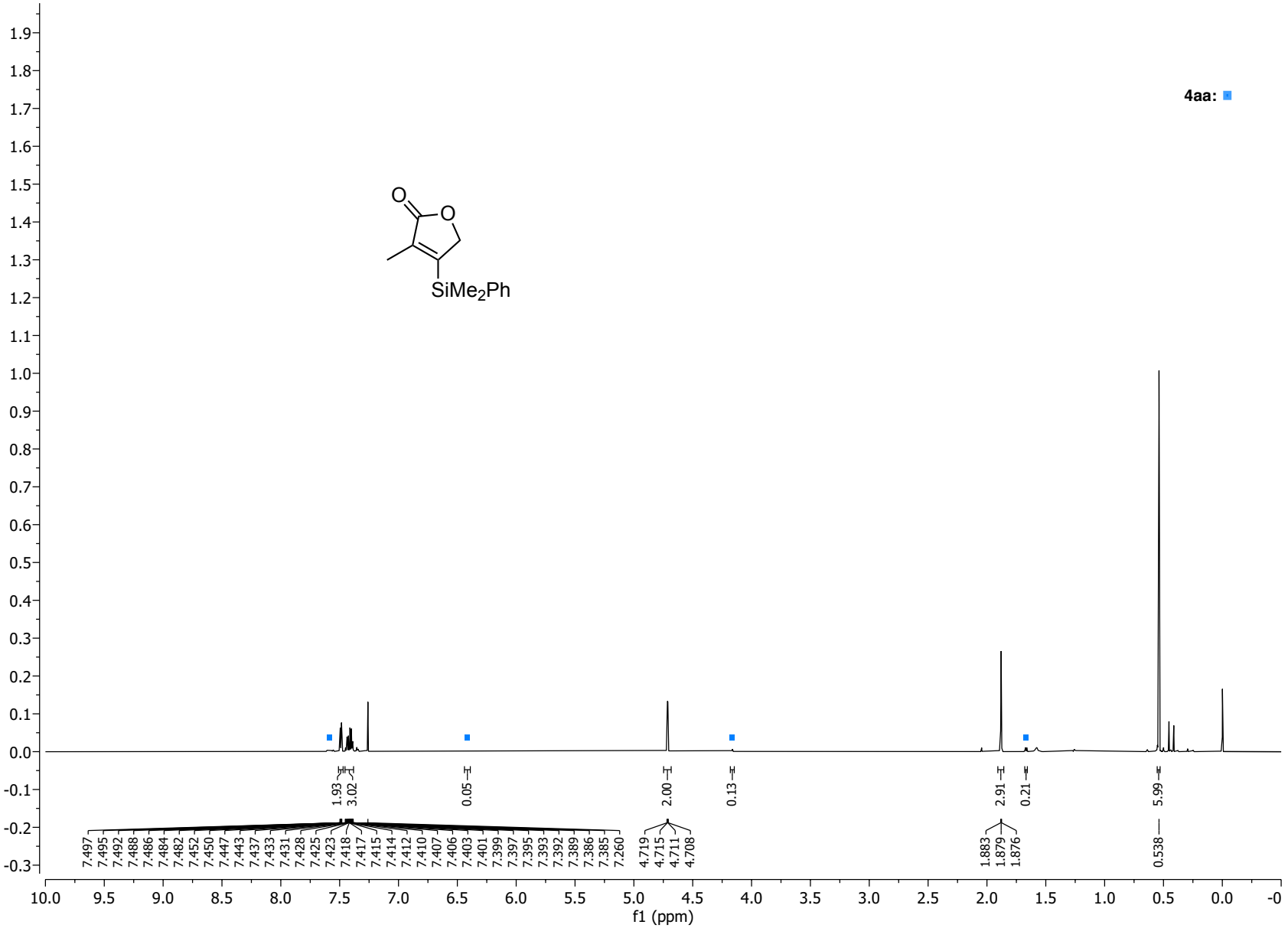


**Figure S60.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **7**

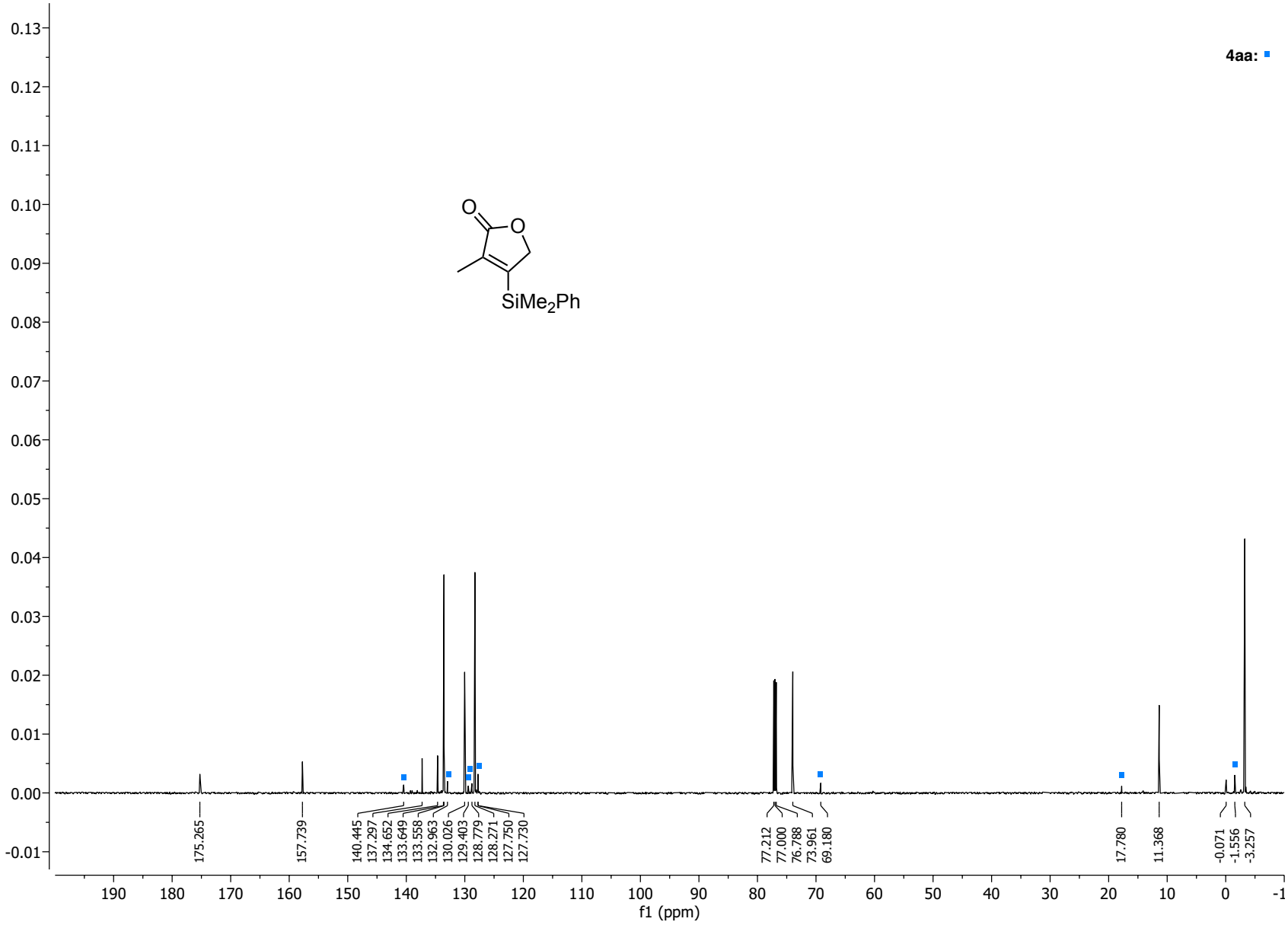


**Figure S61.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **7**

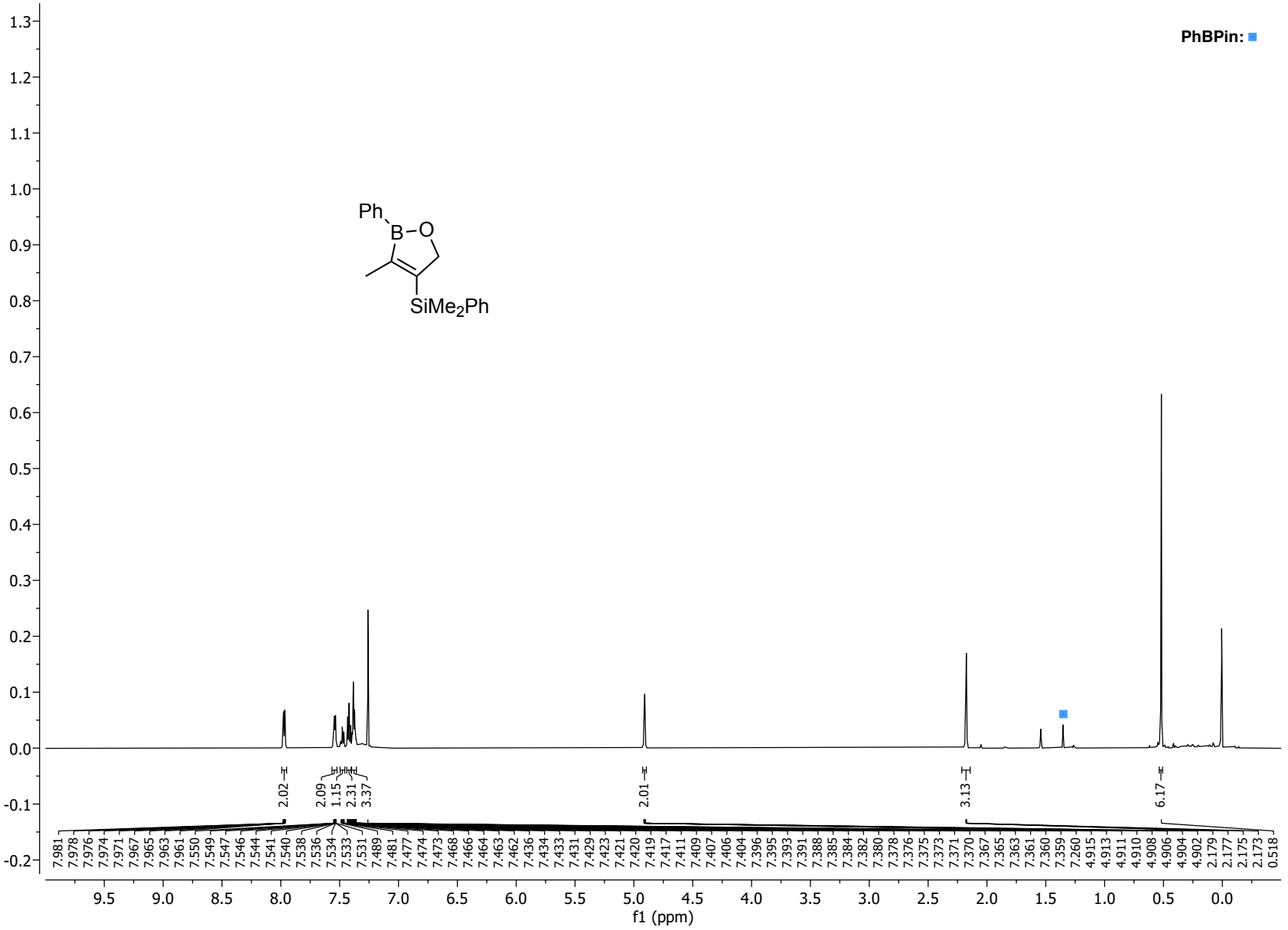


**Figure S62.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of **8**

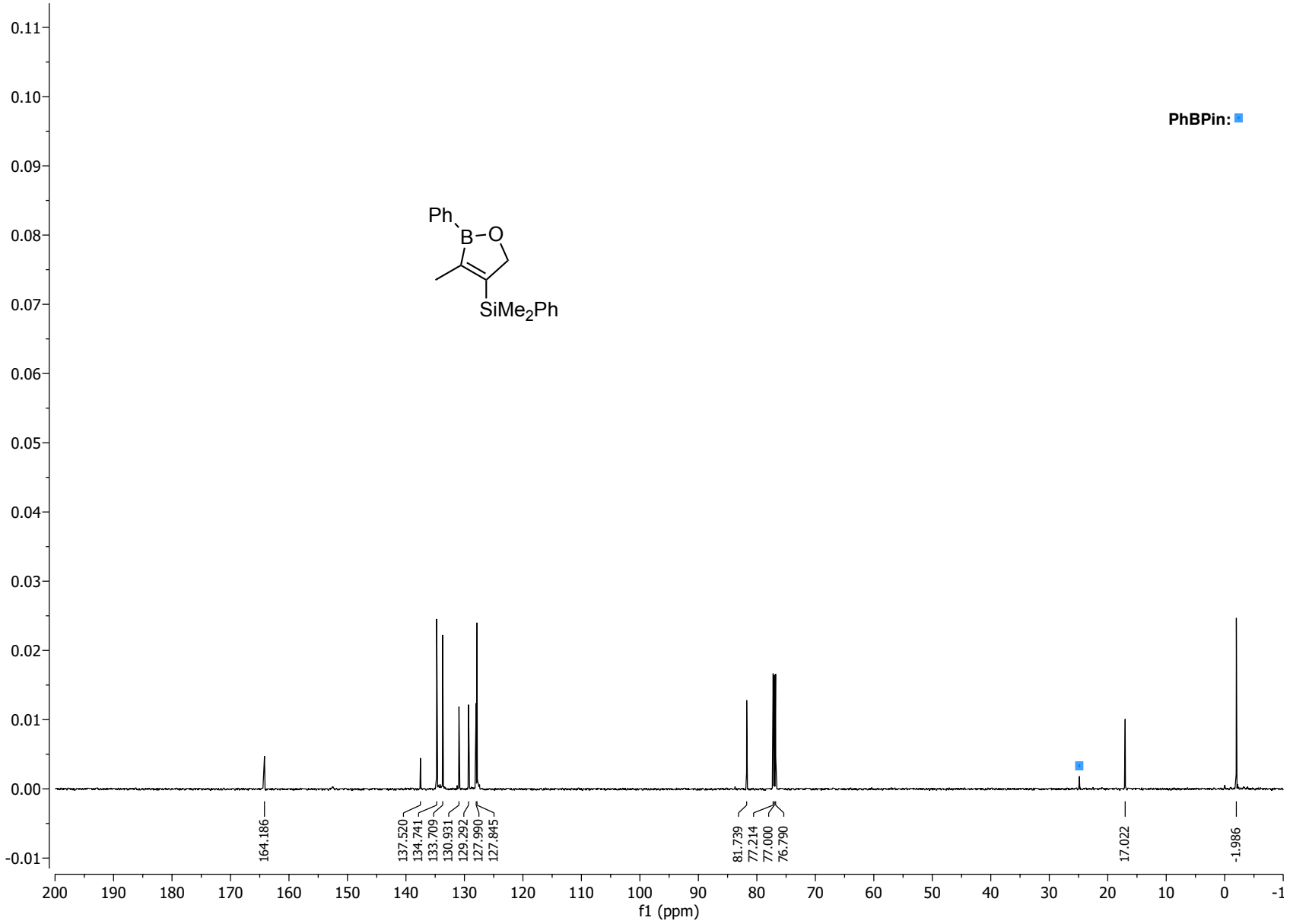


**Figure S63.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **8**

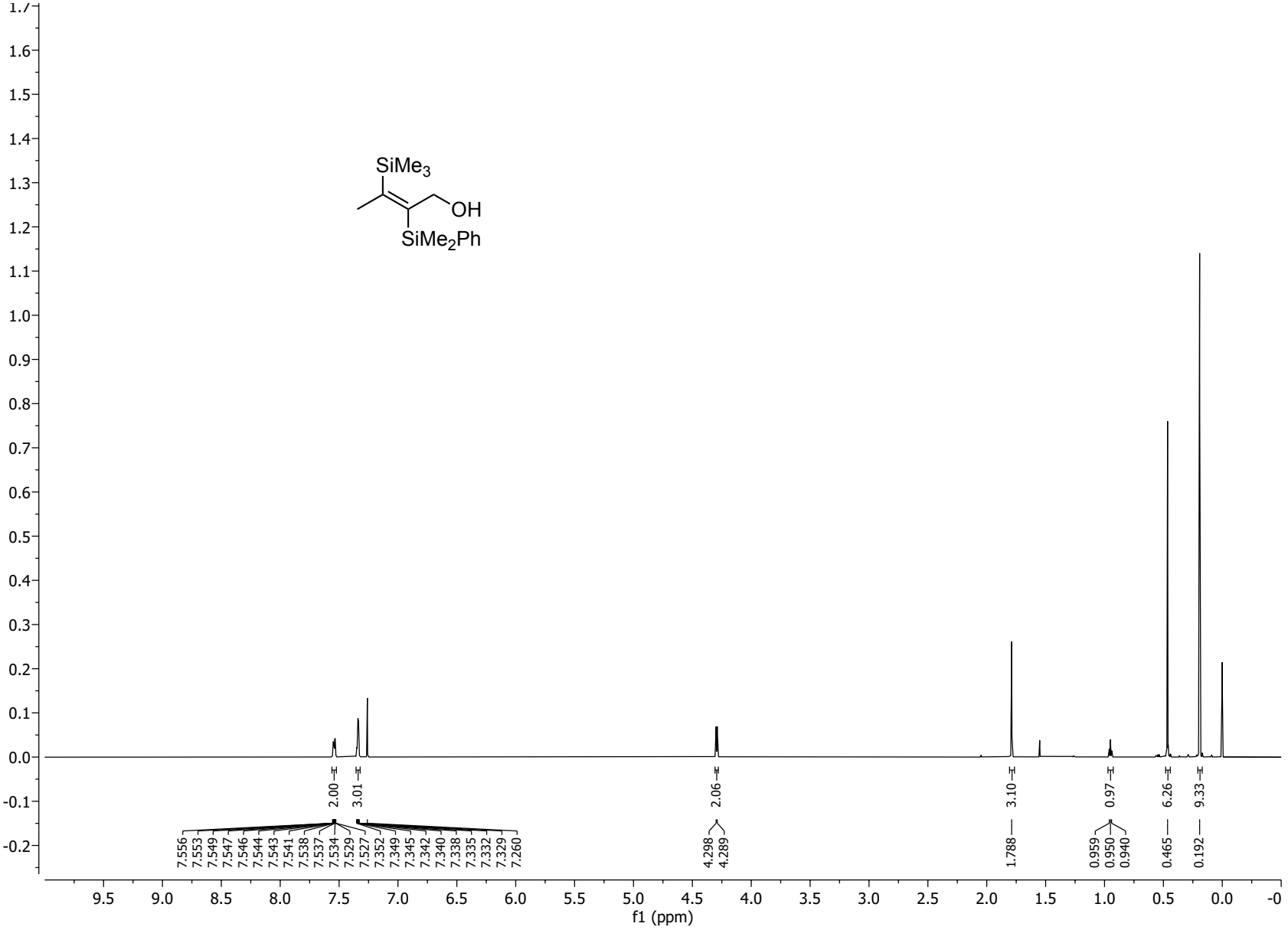


**Figure S64.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **9**

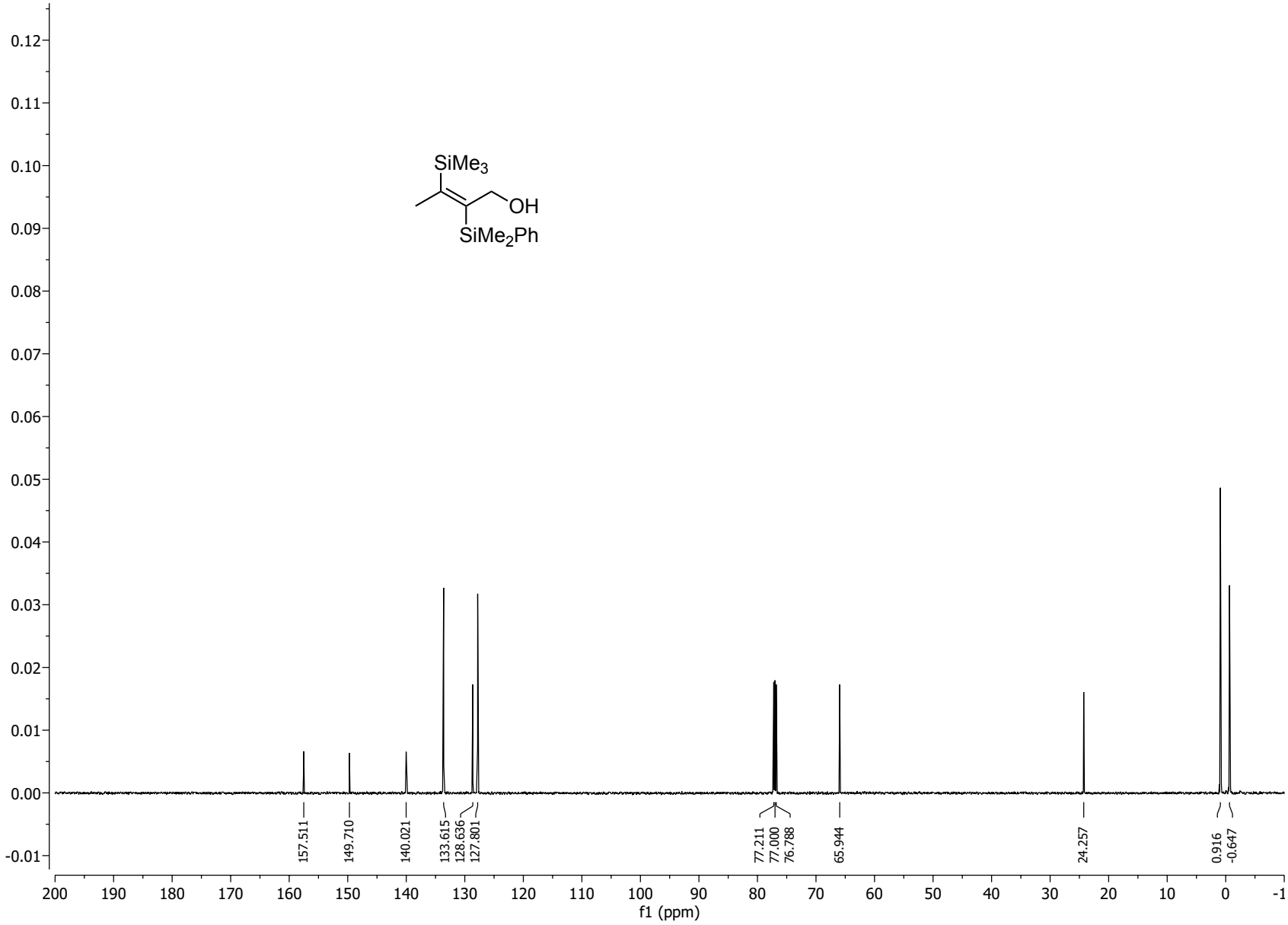


**Figure S65.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **9**

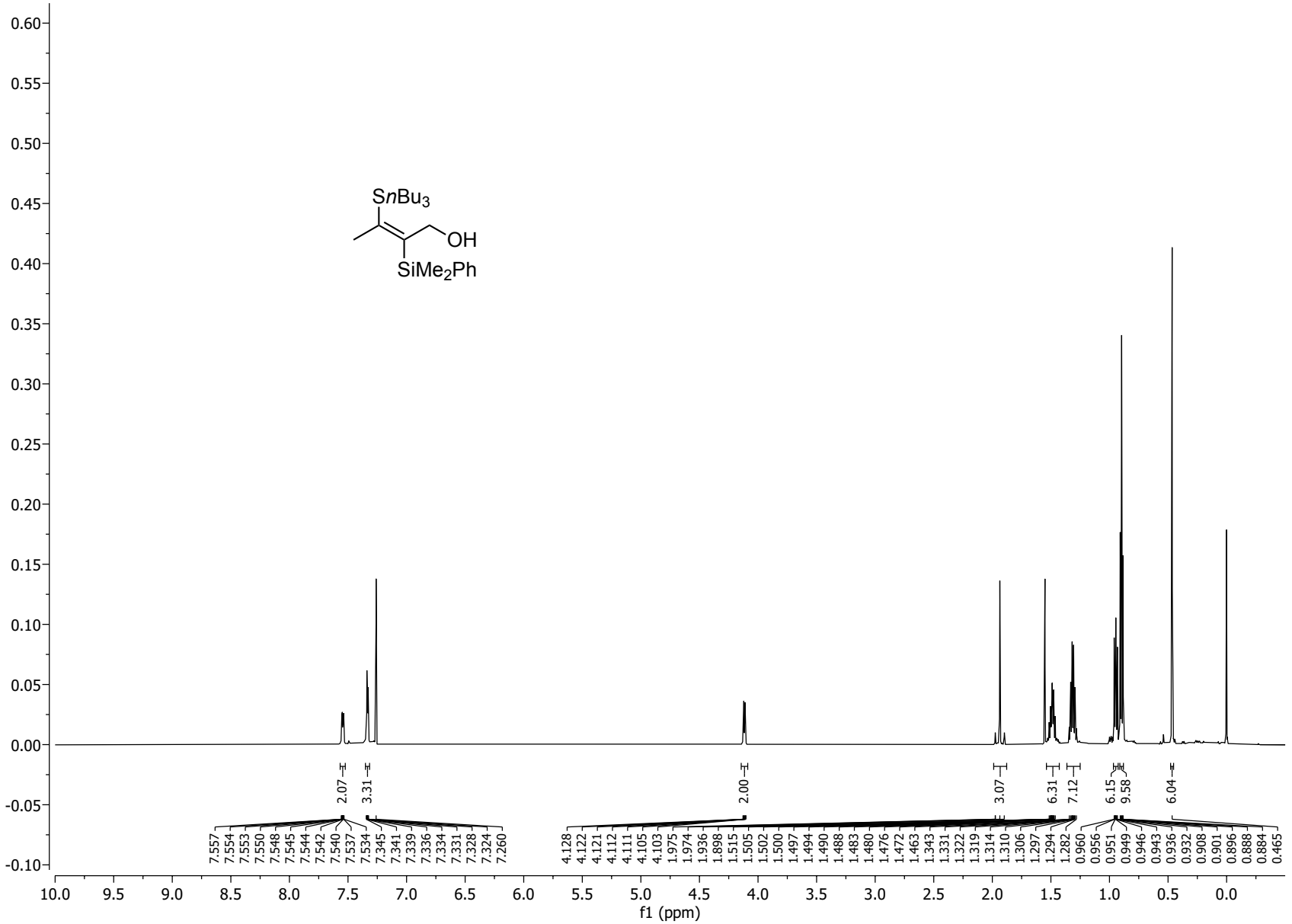


**Figure S66.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **10**

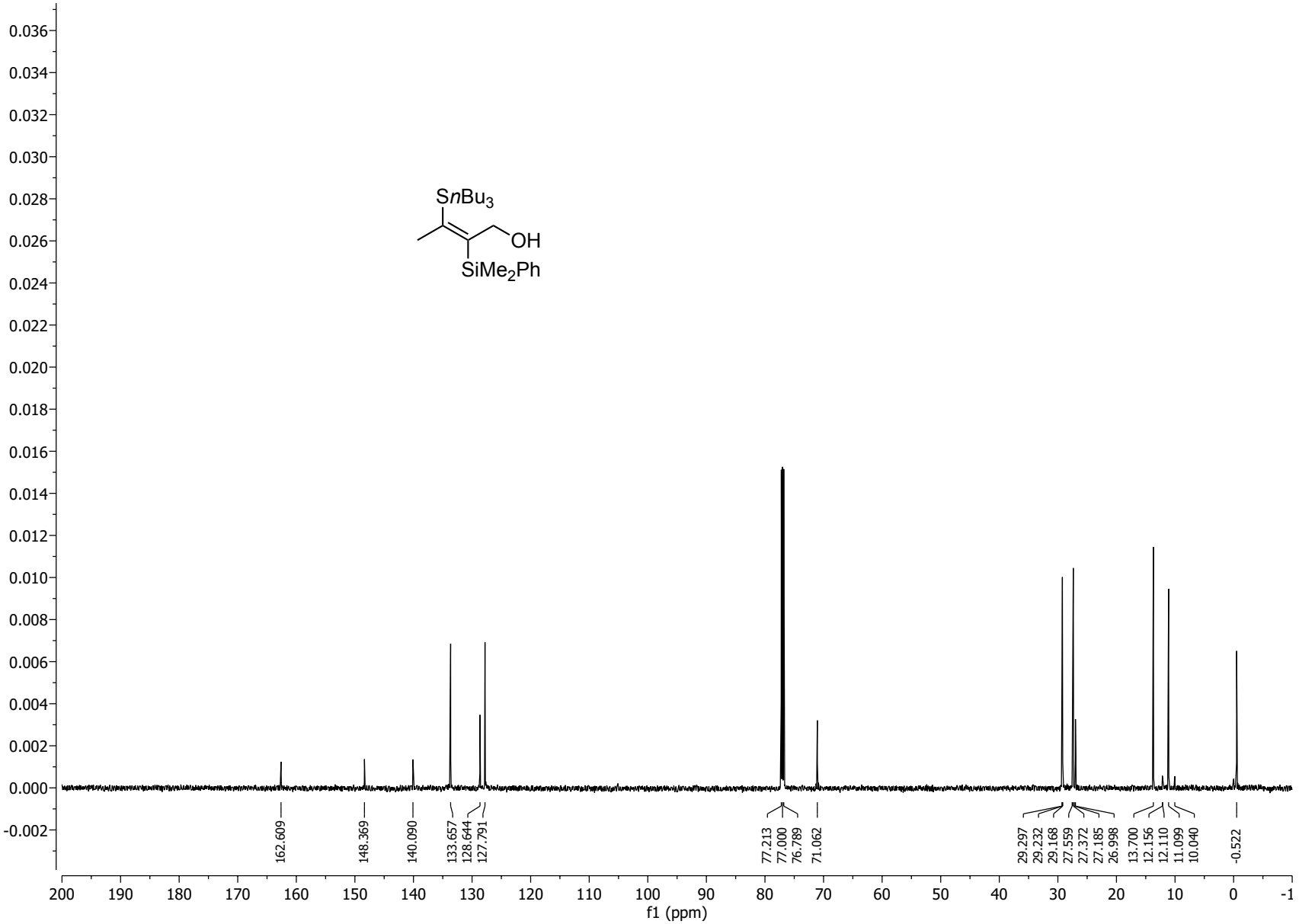


**Figure S67.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **10**

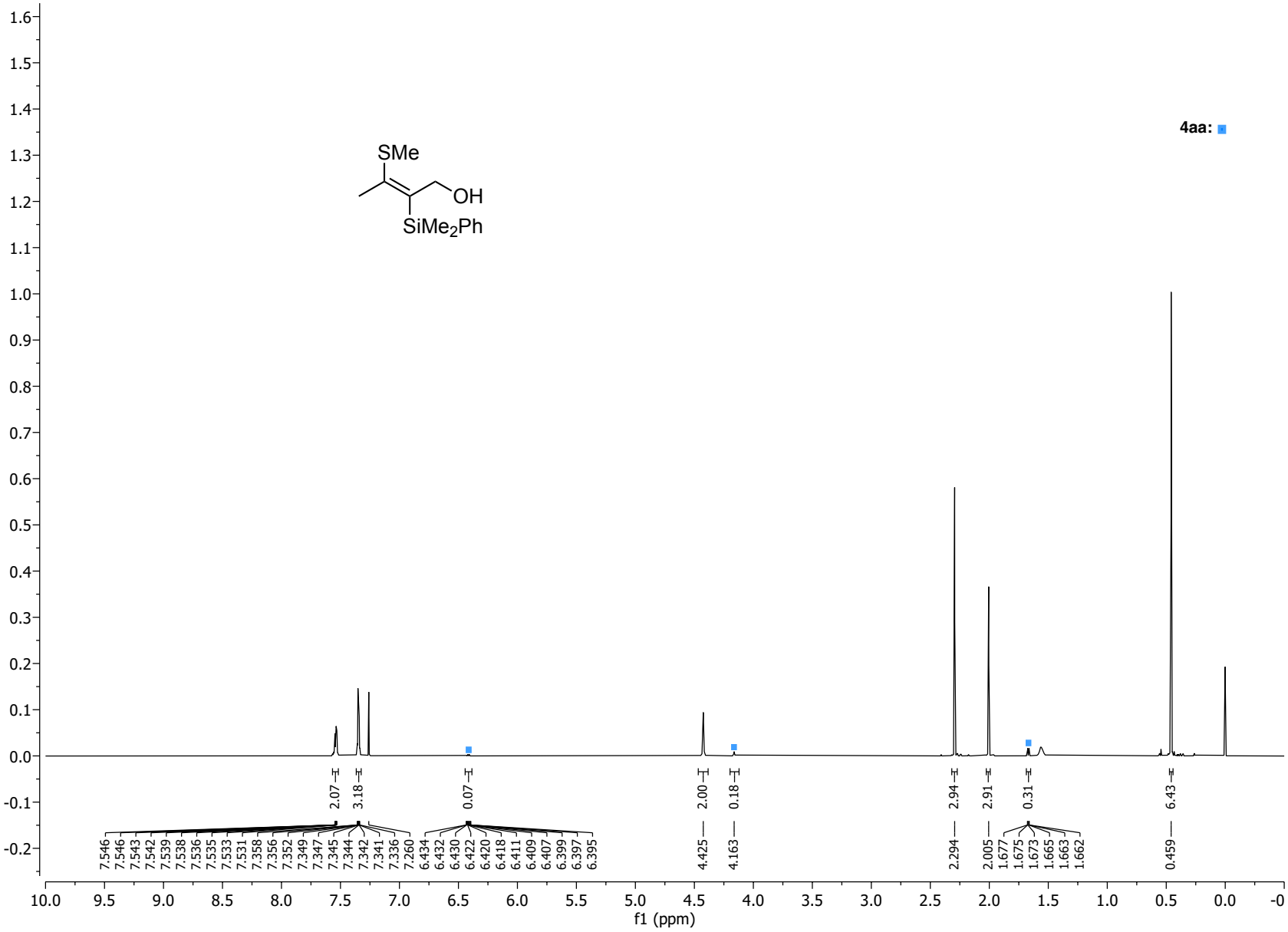


**Figure S68.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **11**

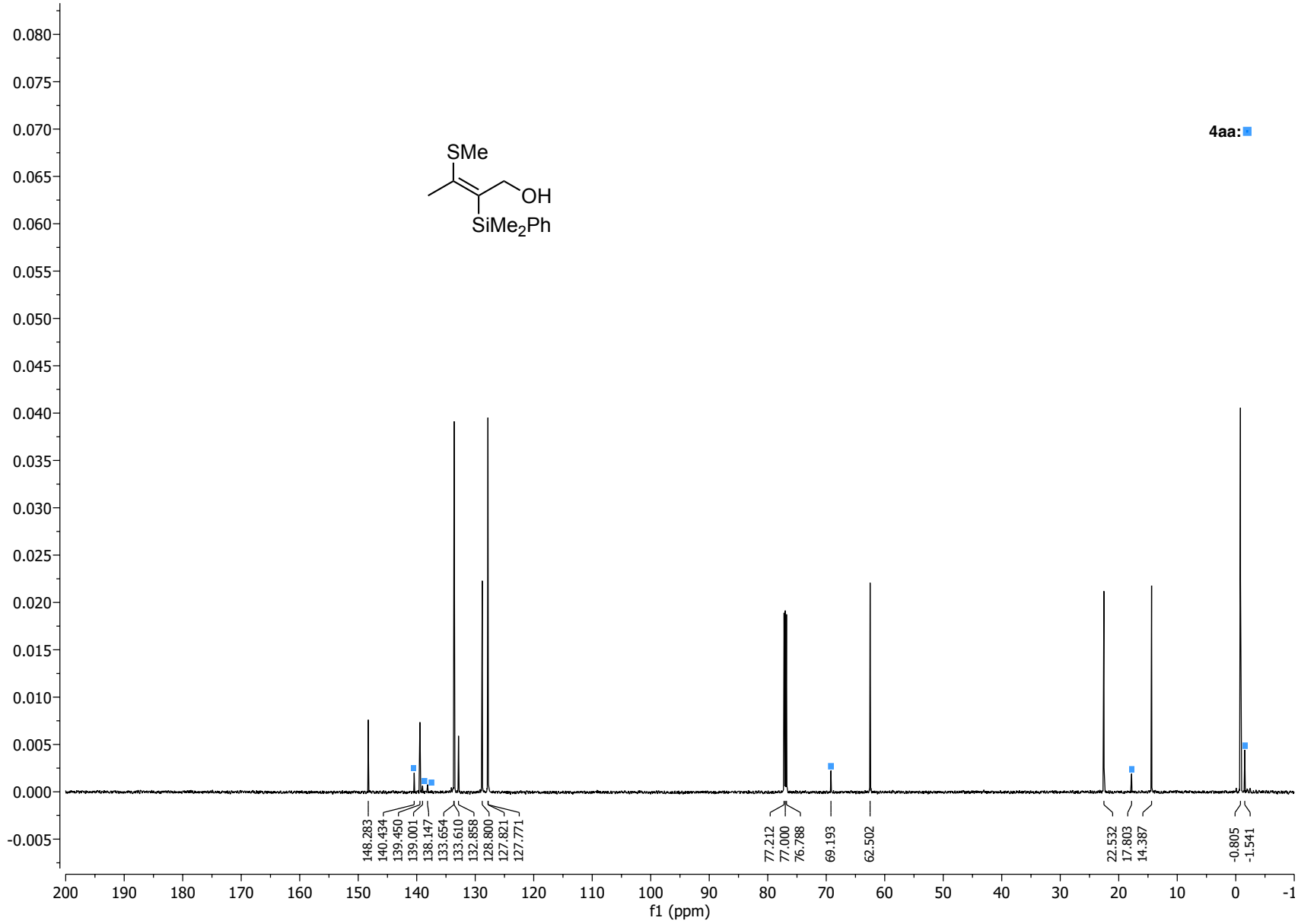


**Figure S69.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **11**

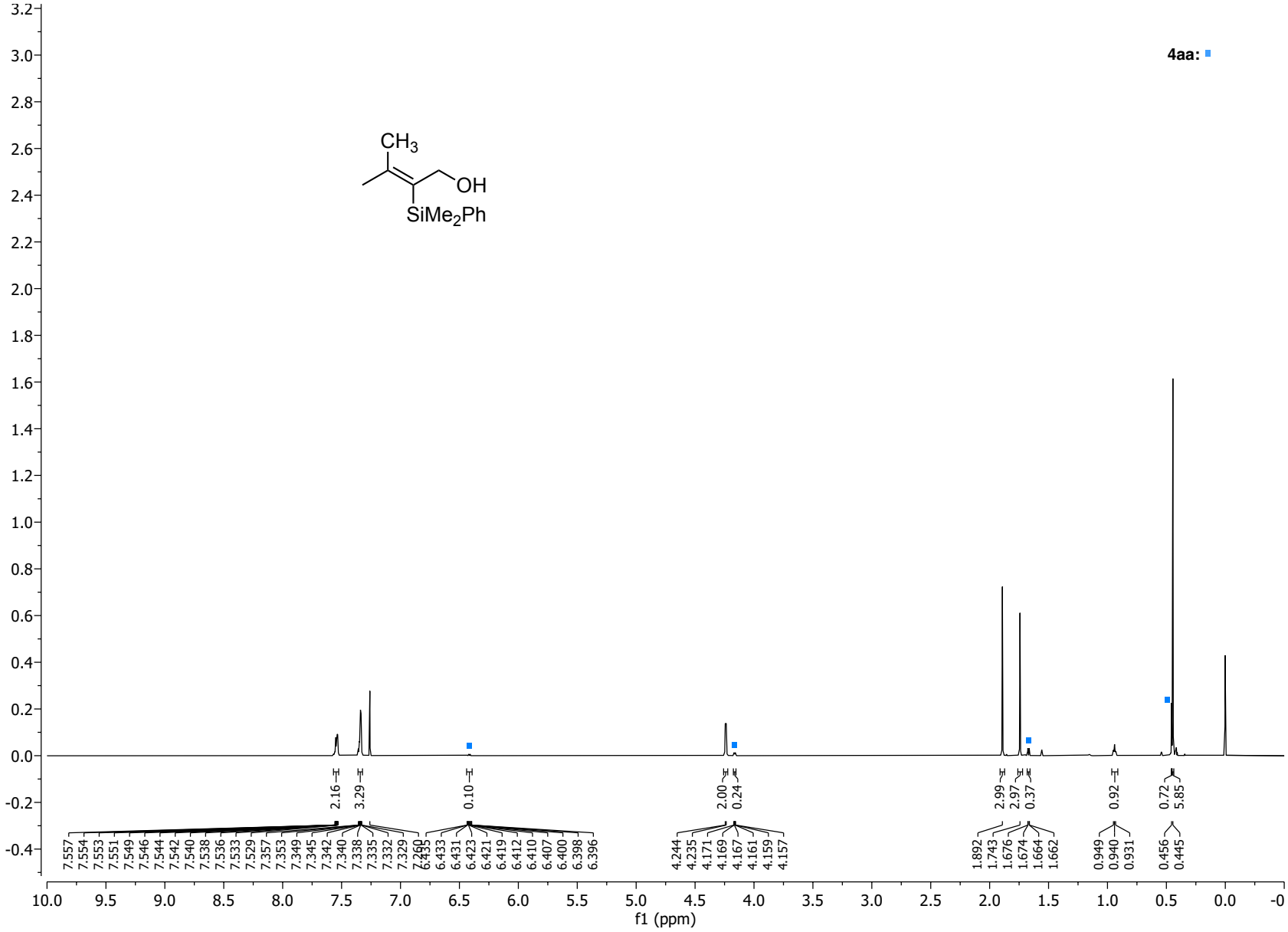


**Figure S70.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of **12**

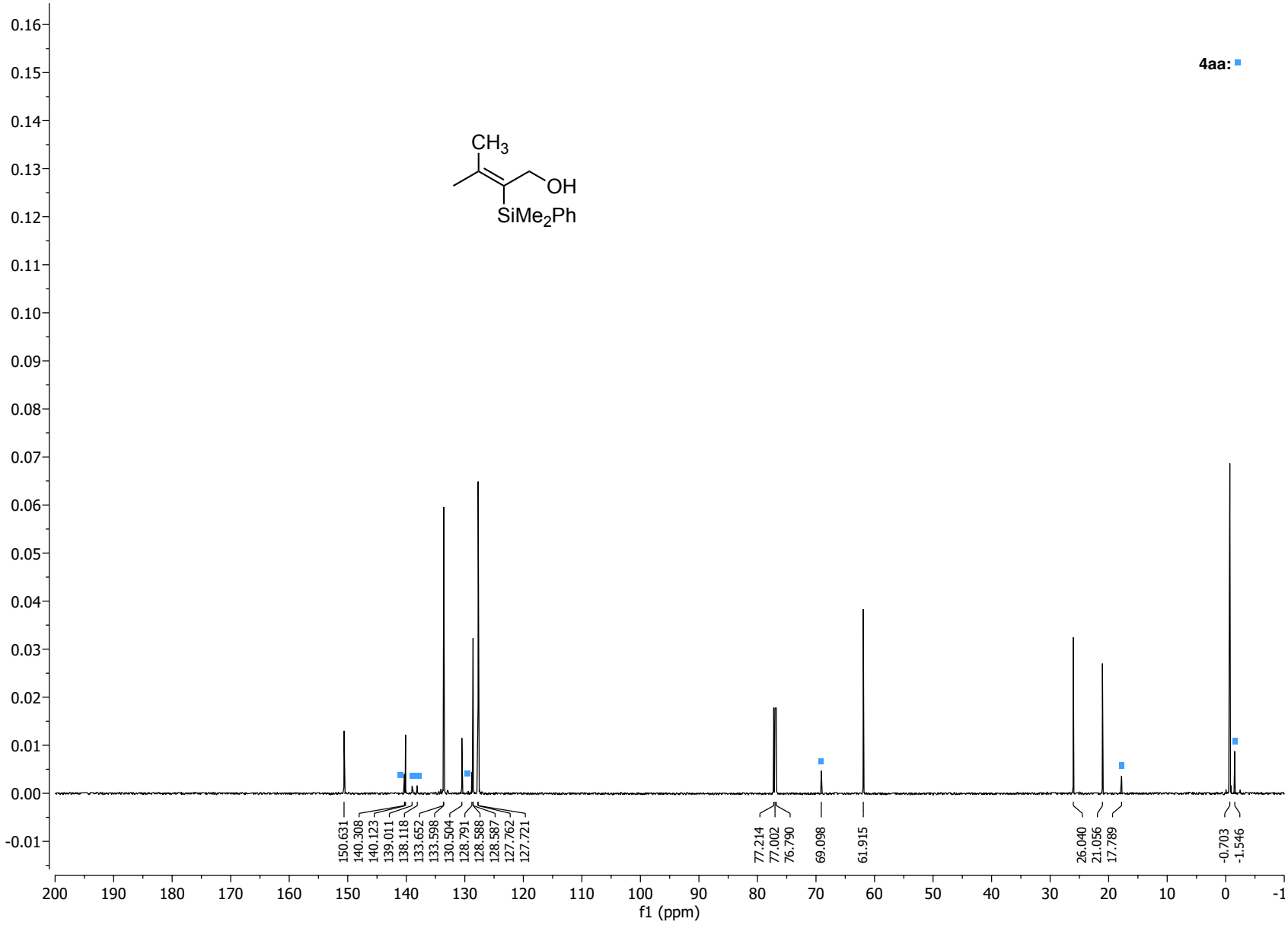


**Figure S71.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **12**

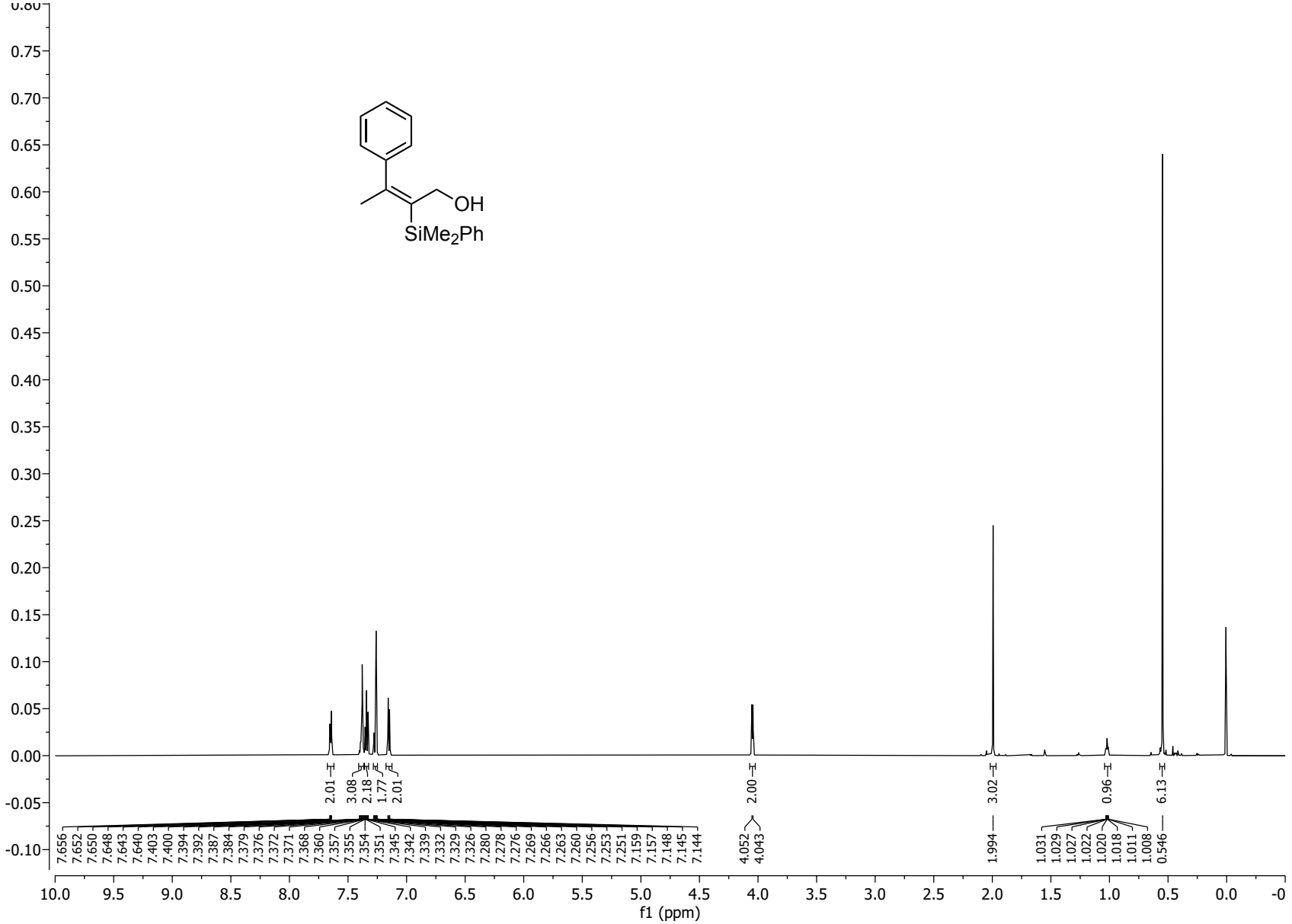


**Figure S72.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **13**

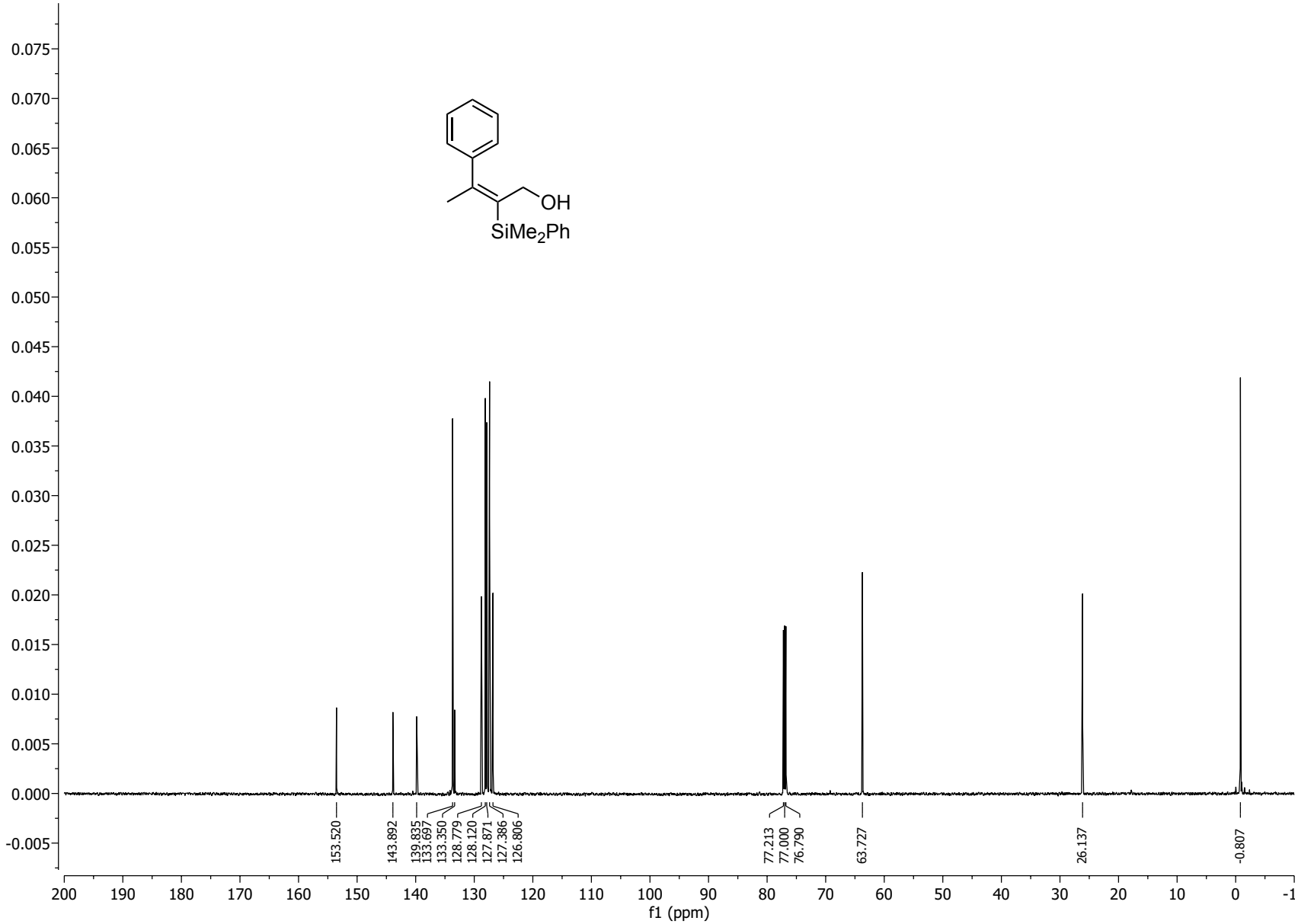


**Figure S73.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **13**

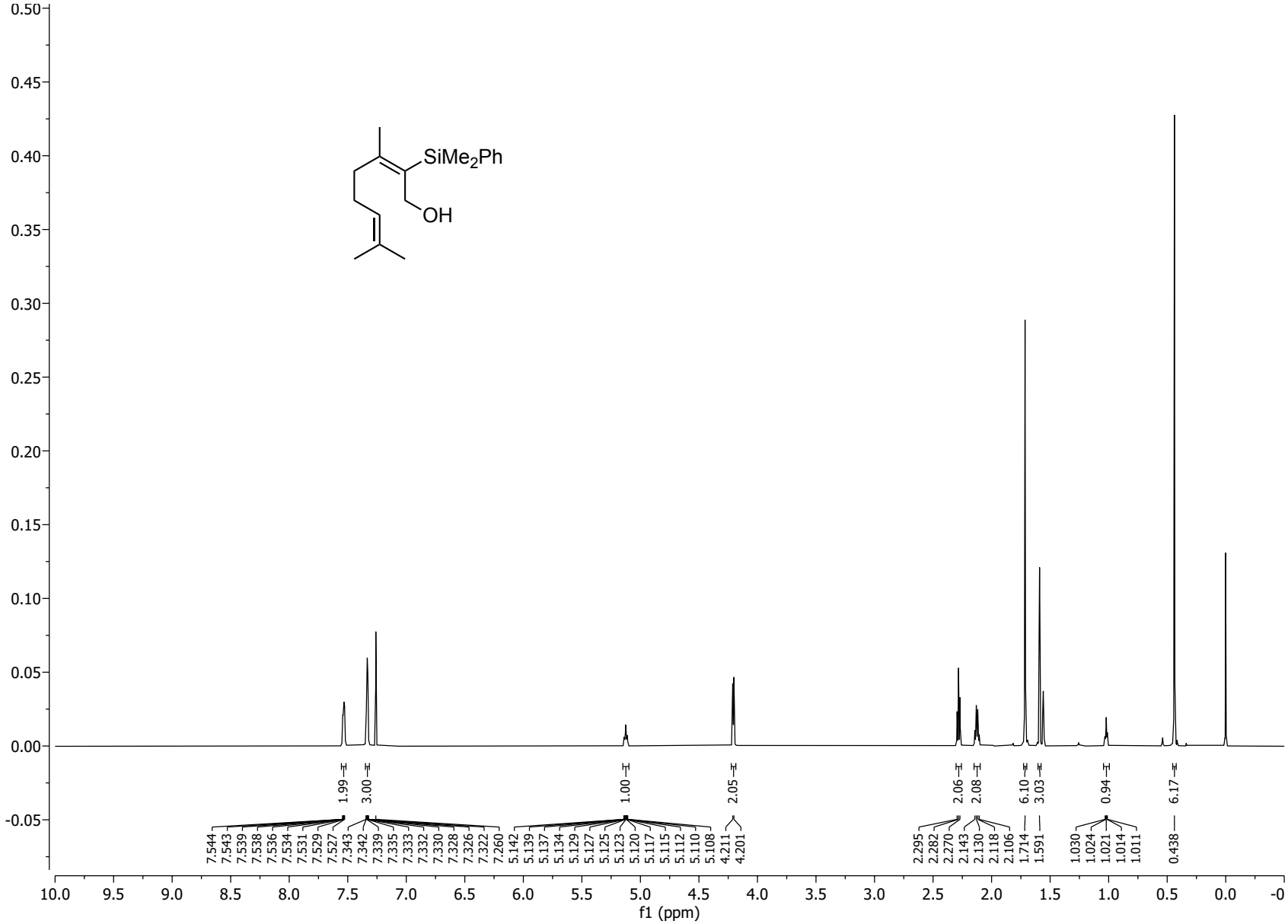


**Figure S74.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **15**

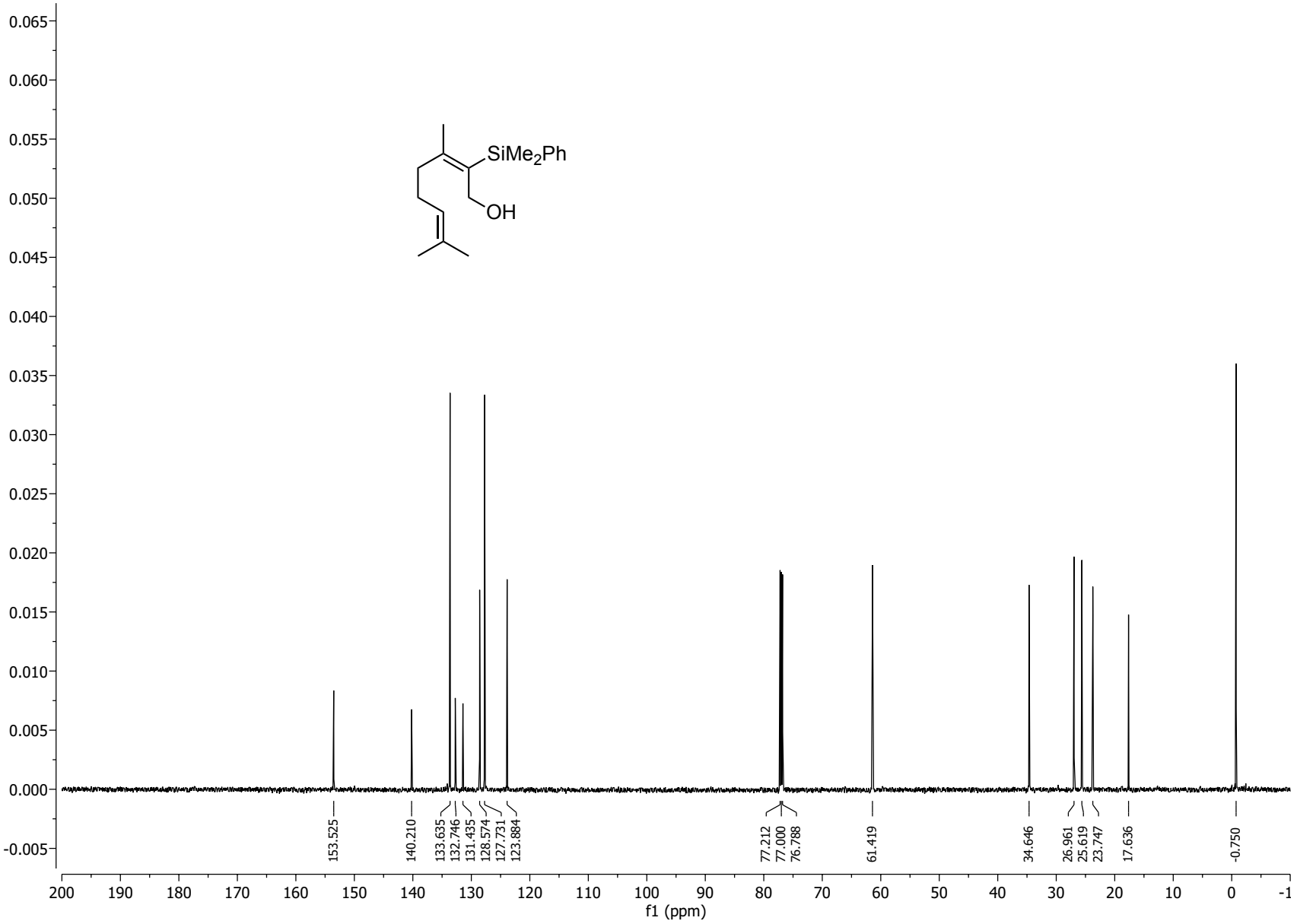


**Figure S75.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **15**

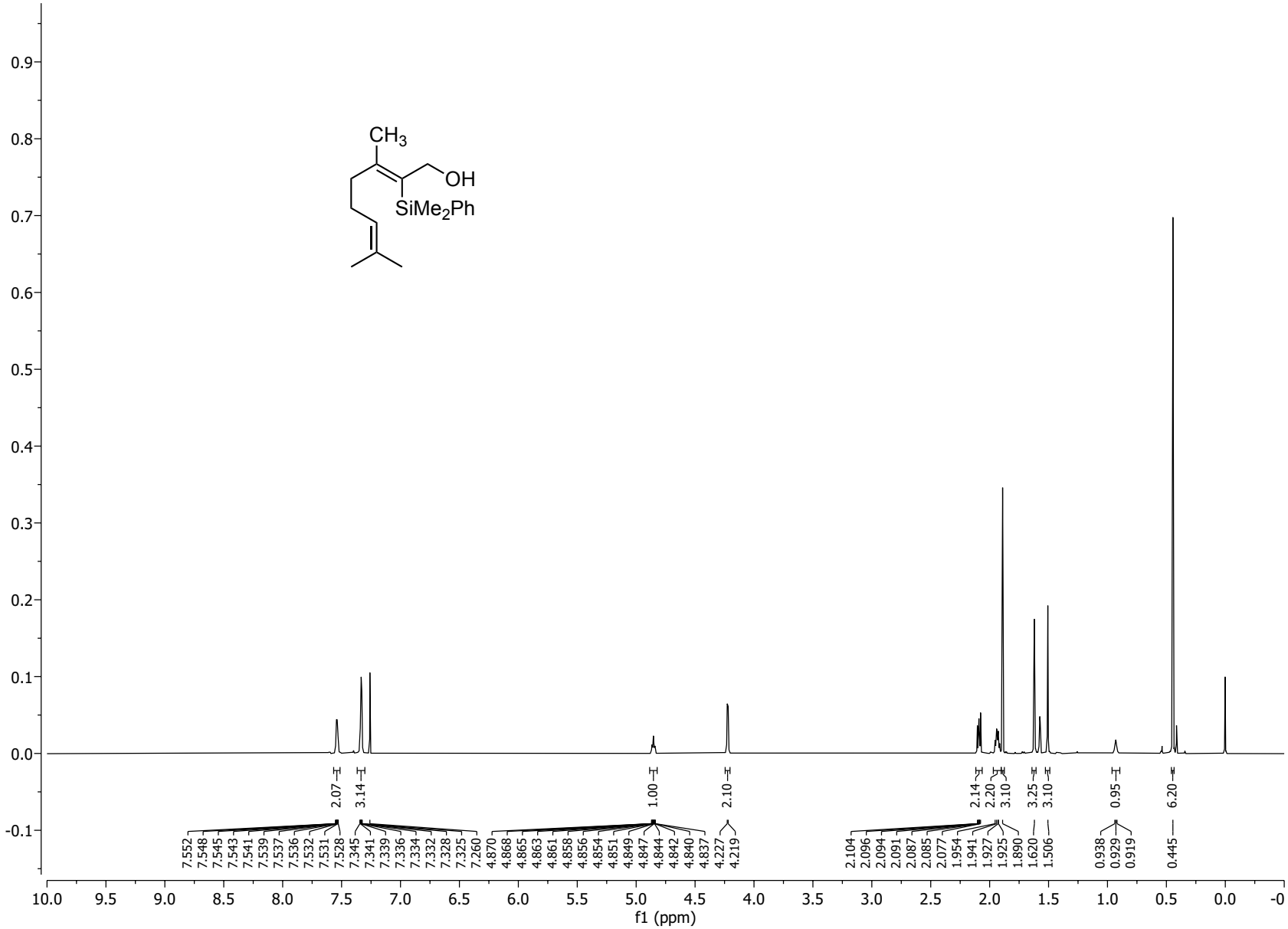


**Figure S76.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **16**

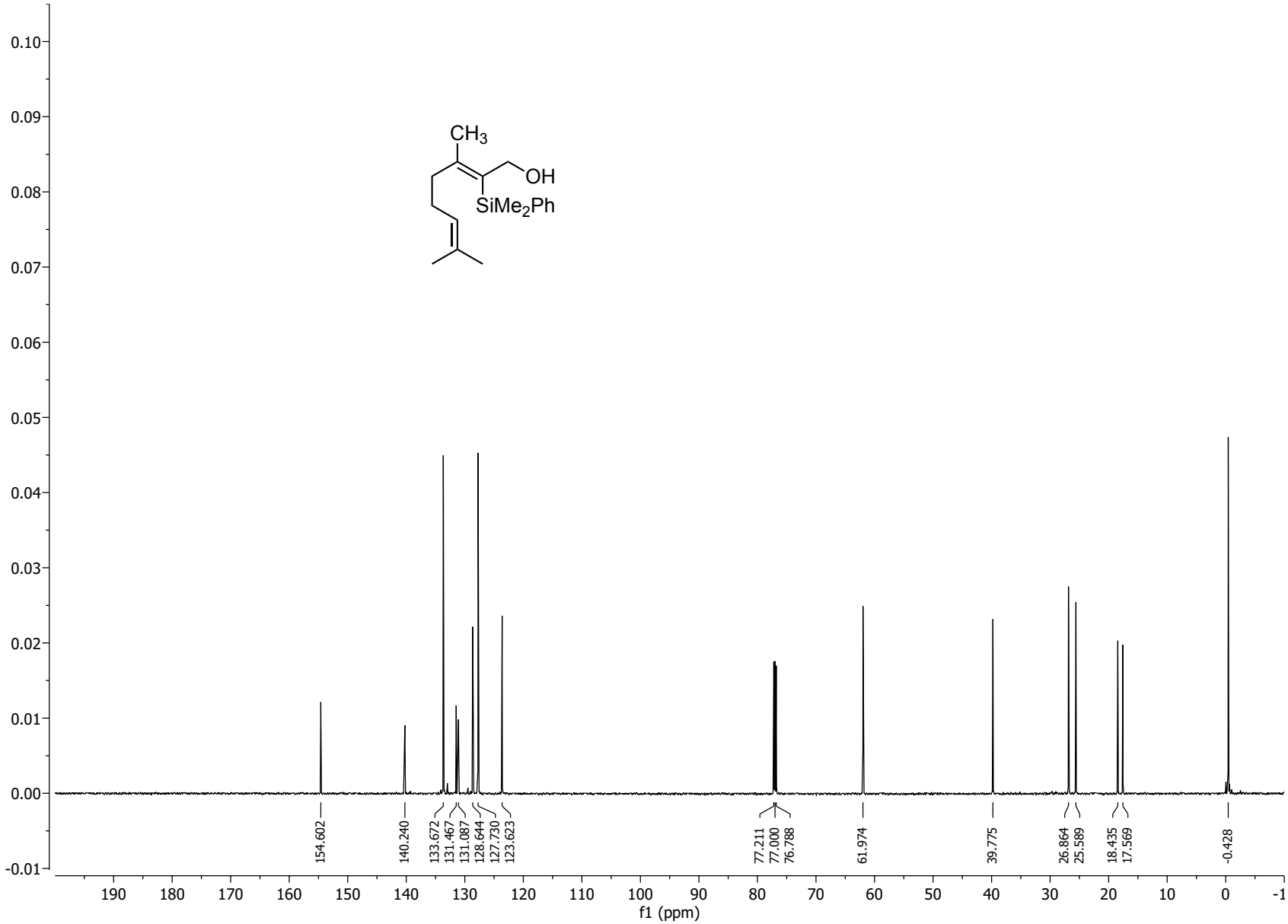


**Figure S77.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **16**

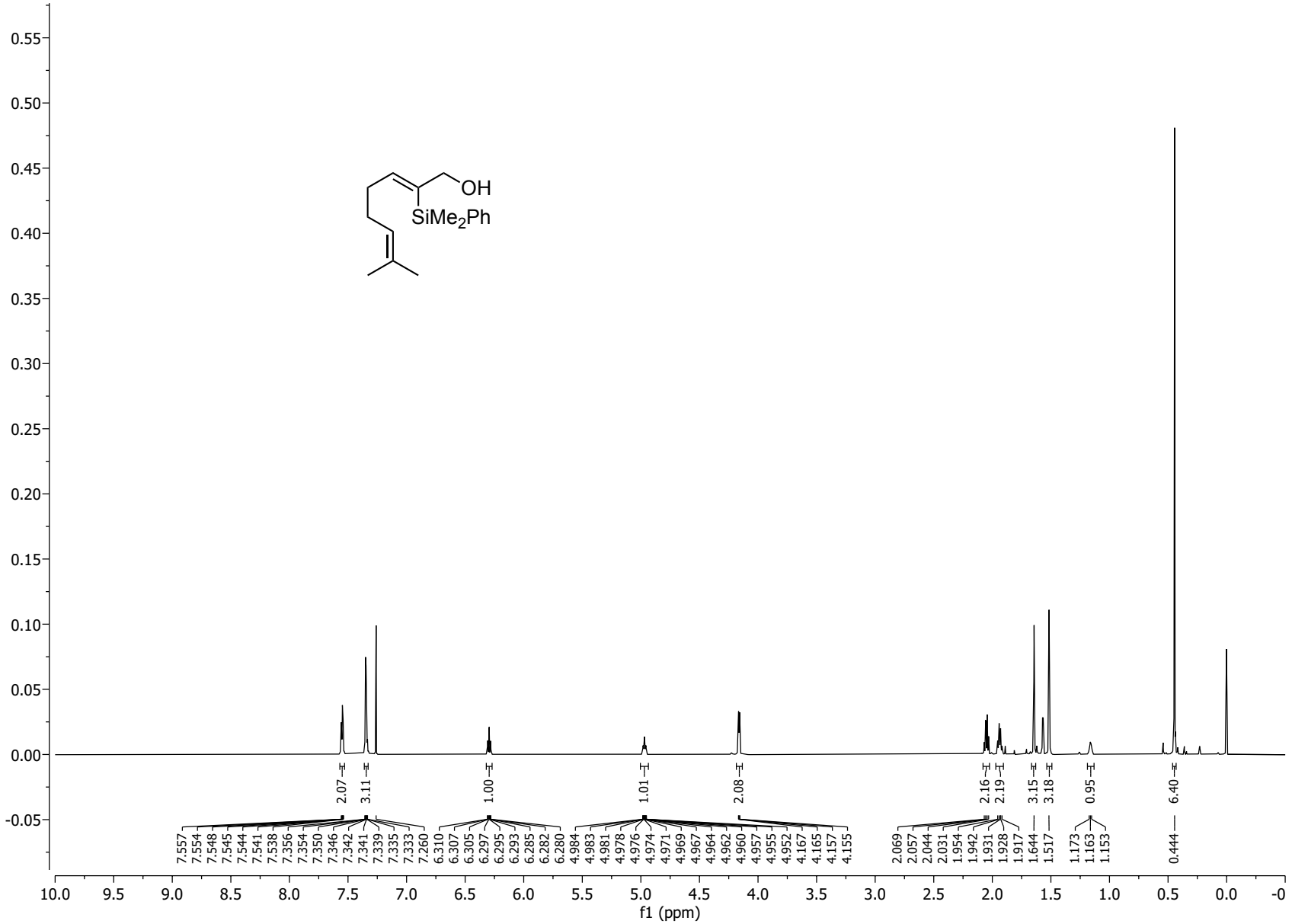


**Figure S78.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **4oa**

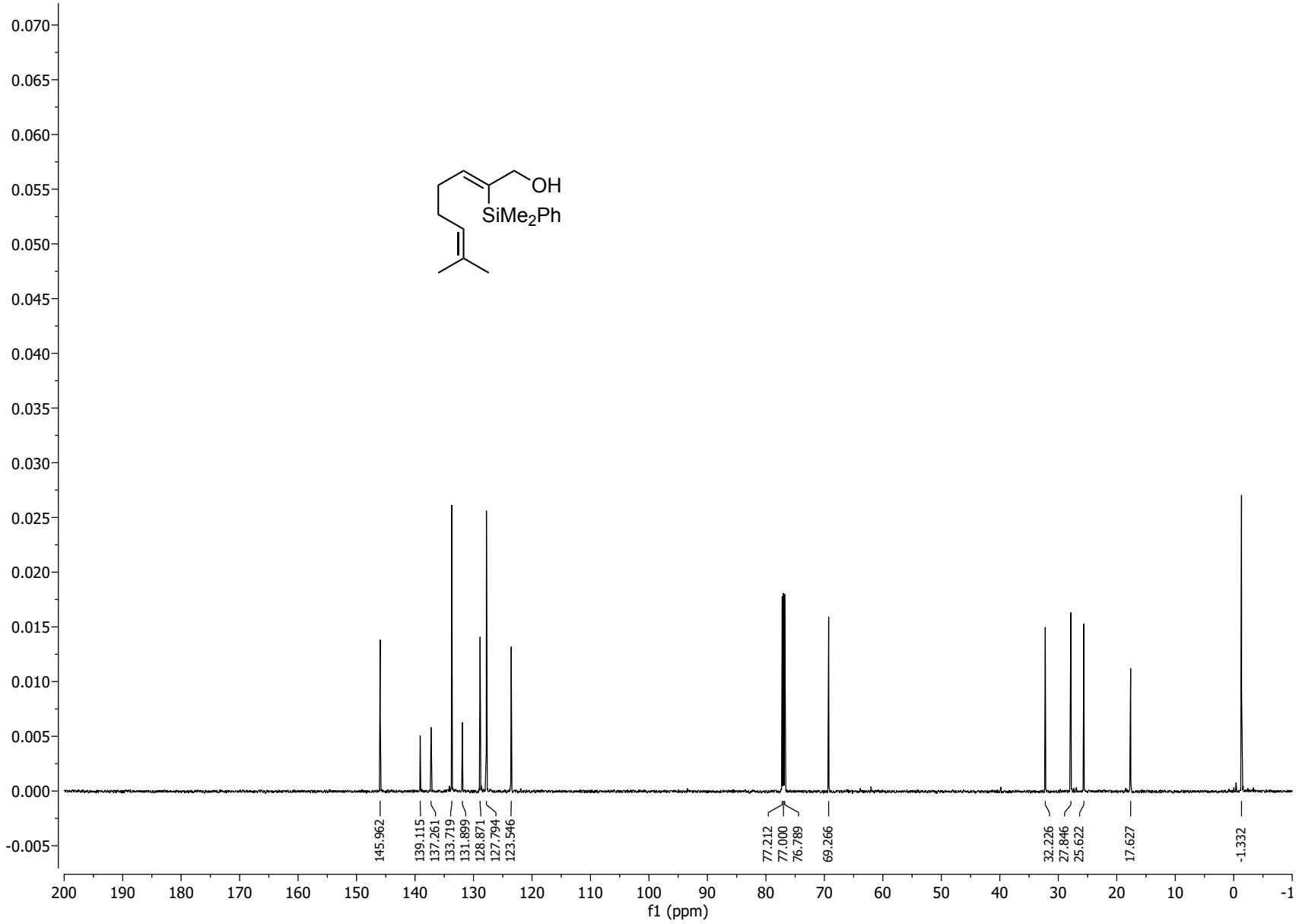


**Figure S79.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **4oa**

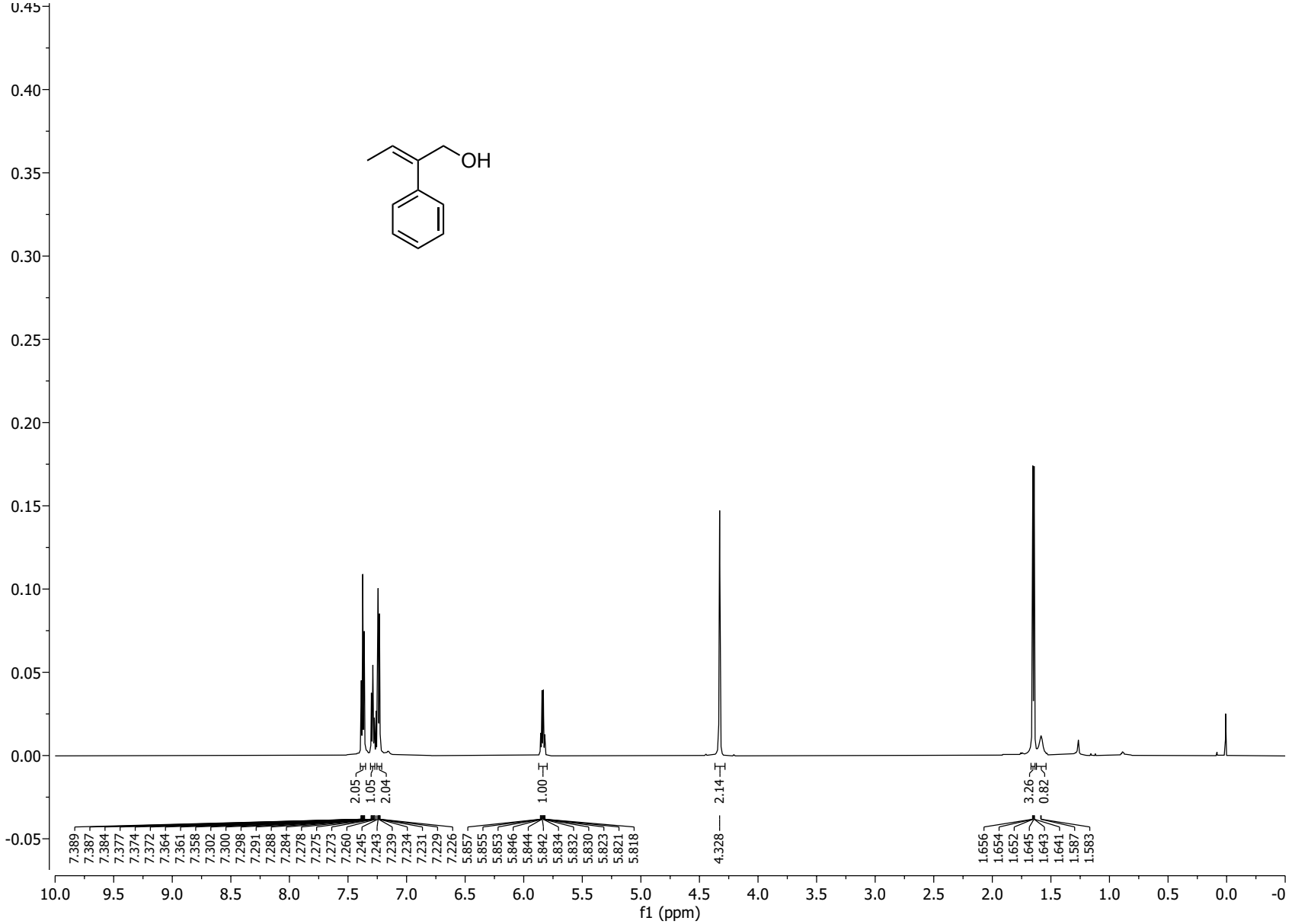


**Figure S80.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **17**

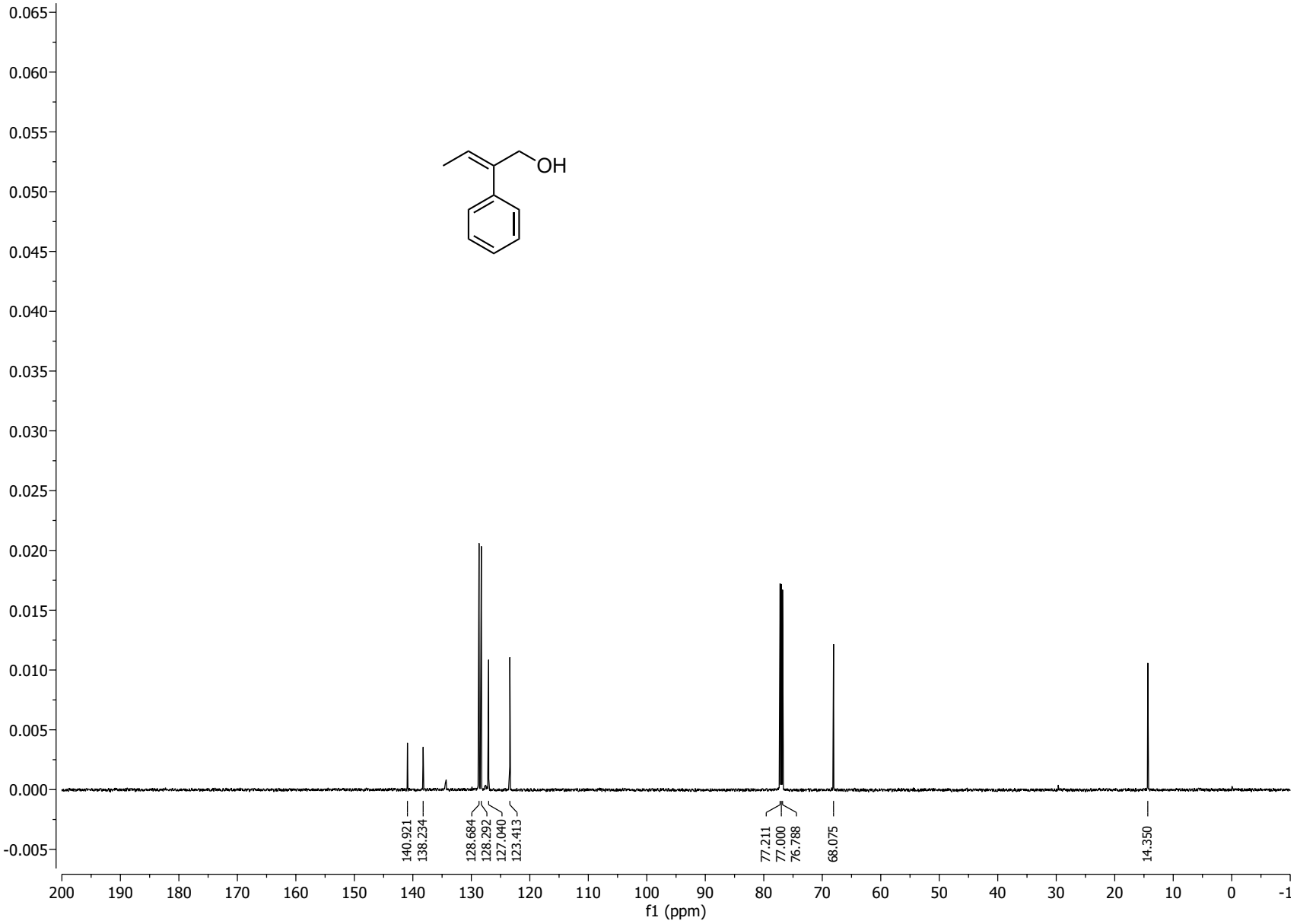


**Figure S81.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **17**

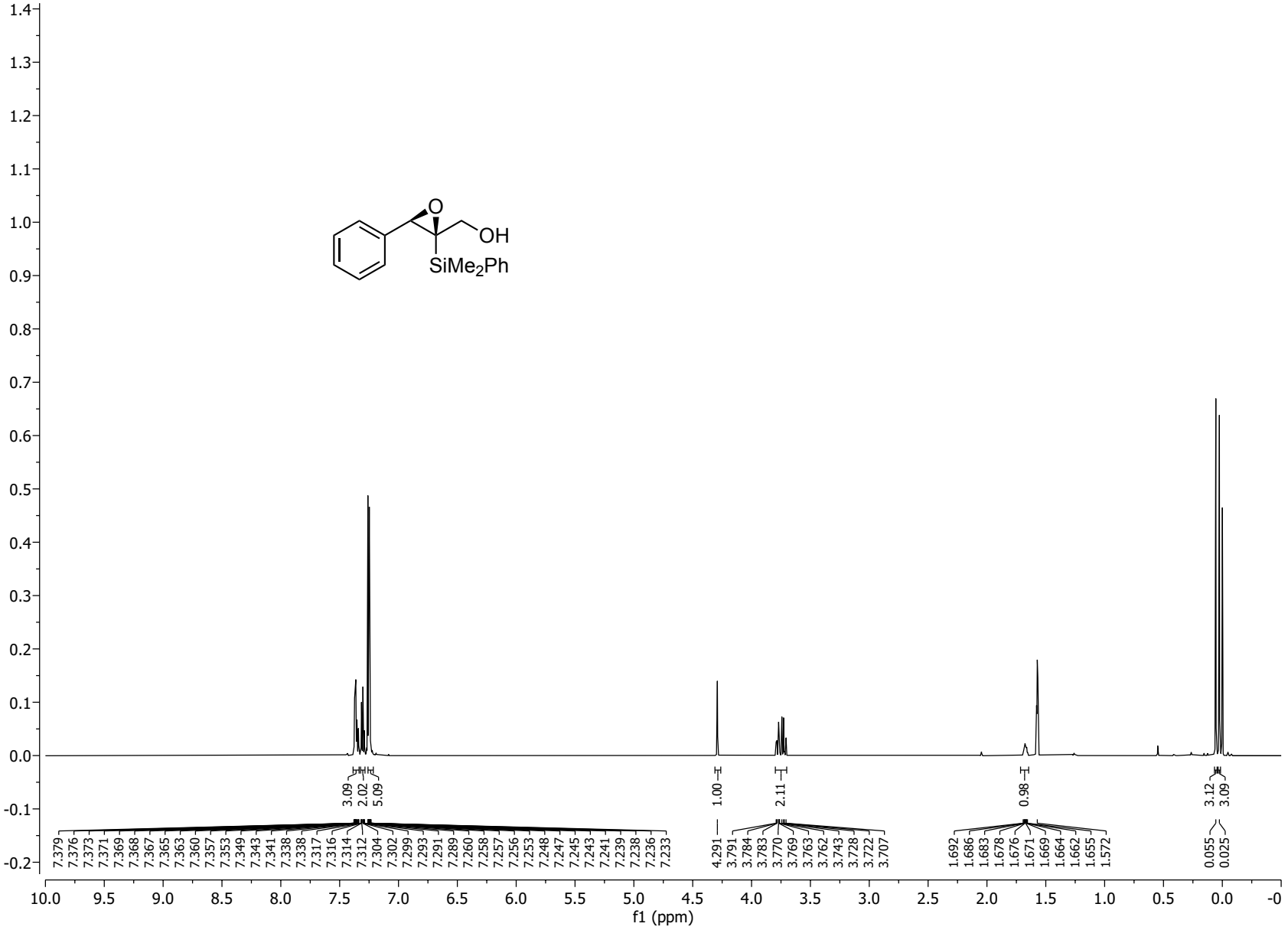


**Figure S82.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **18**

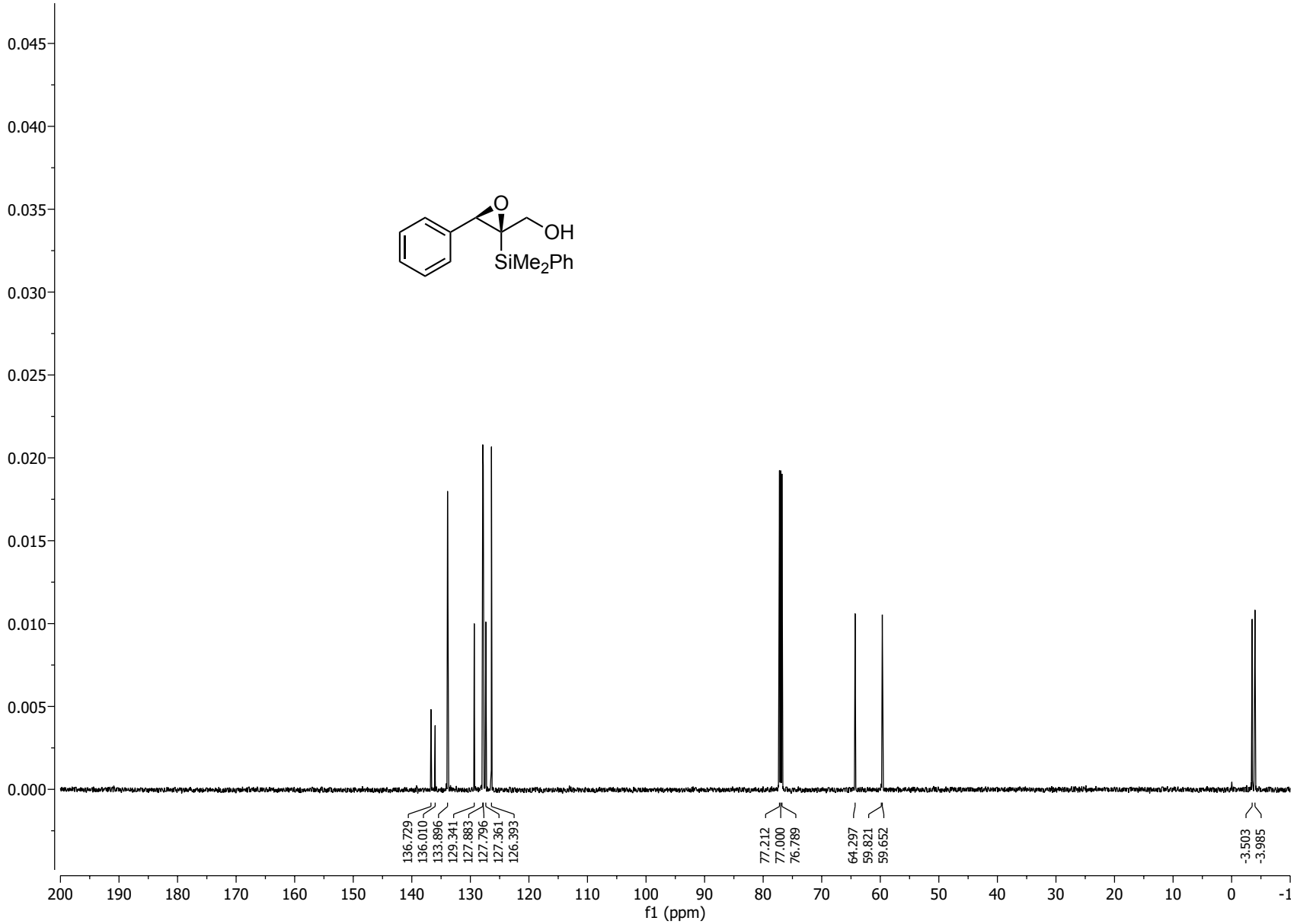


**Figure S83.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **18**

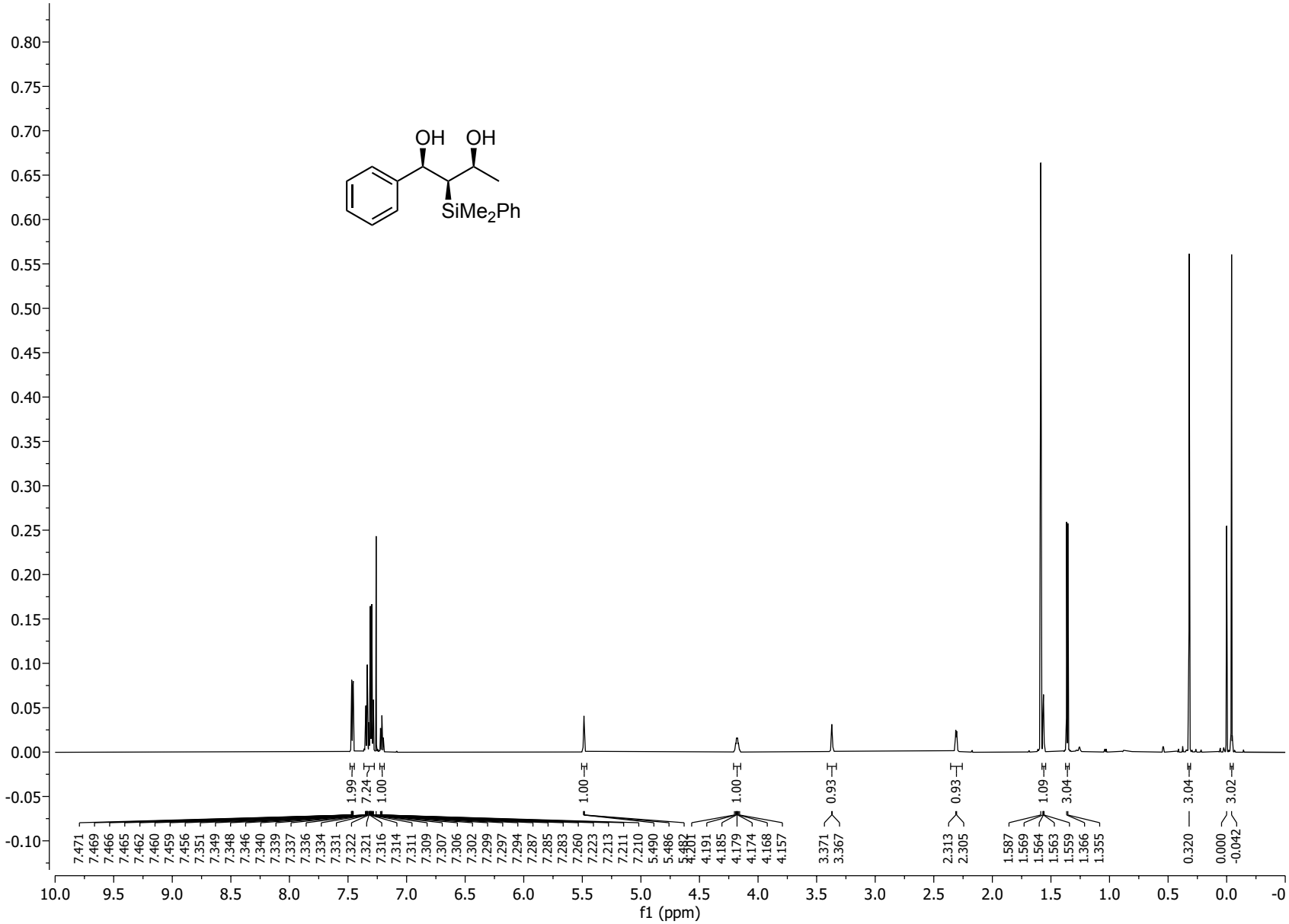


**Figure S84.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **19**

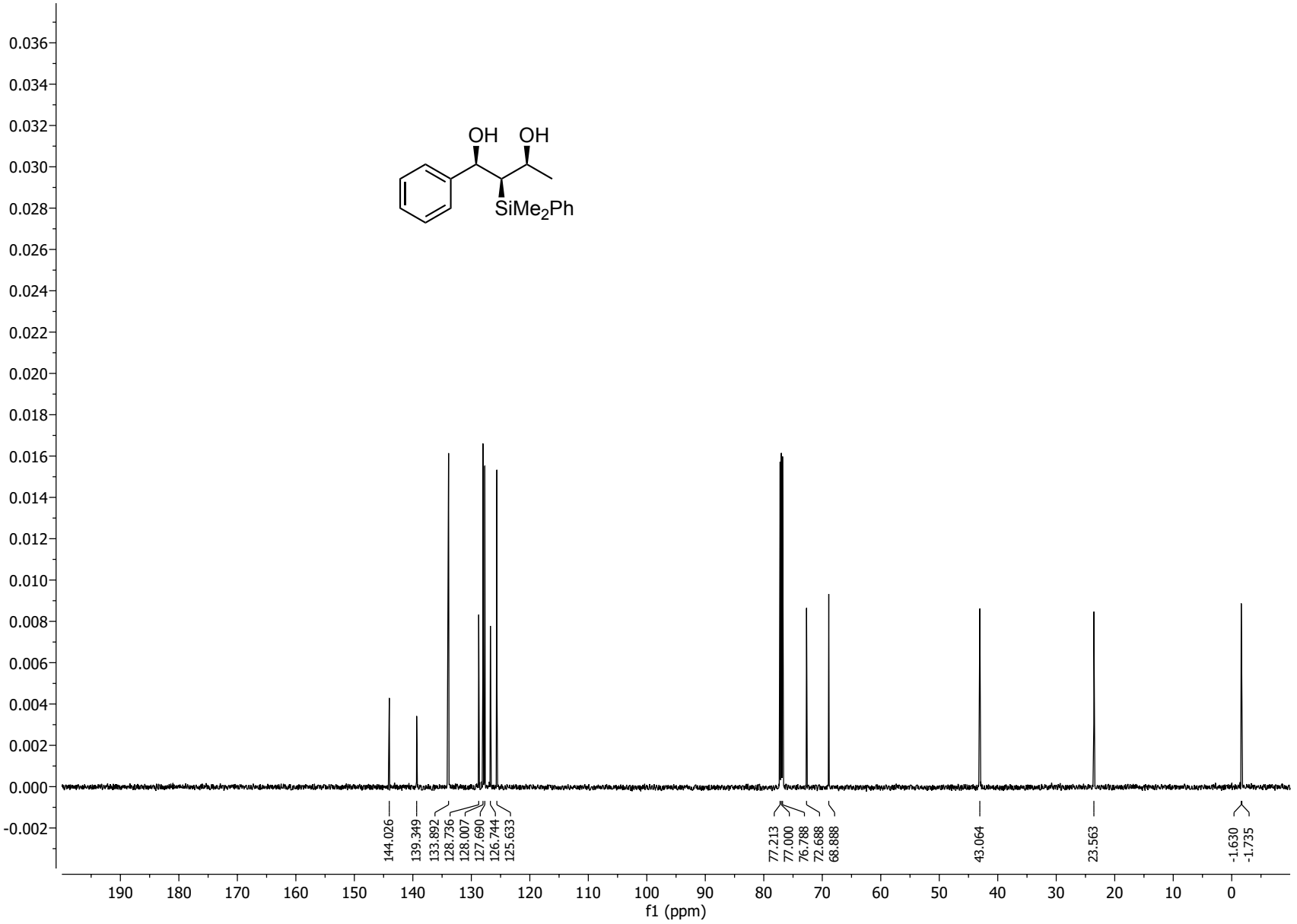


**Figure S85.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **19**

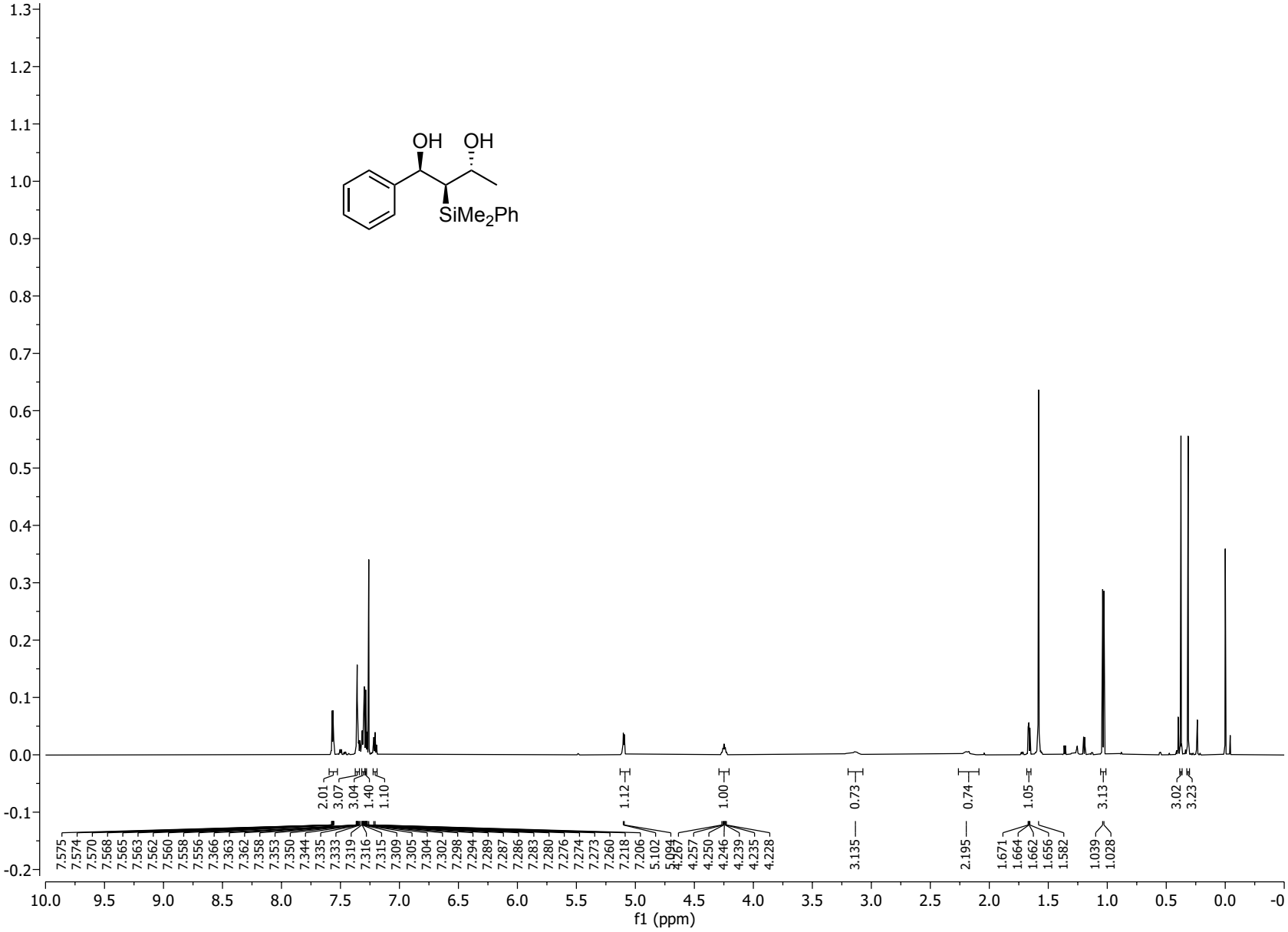


**Figure S86.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **20**

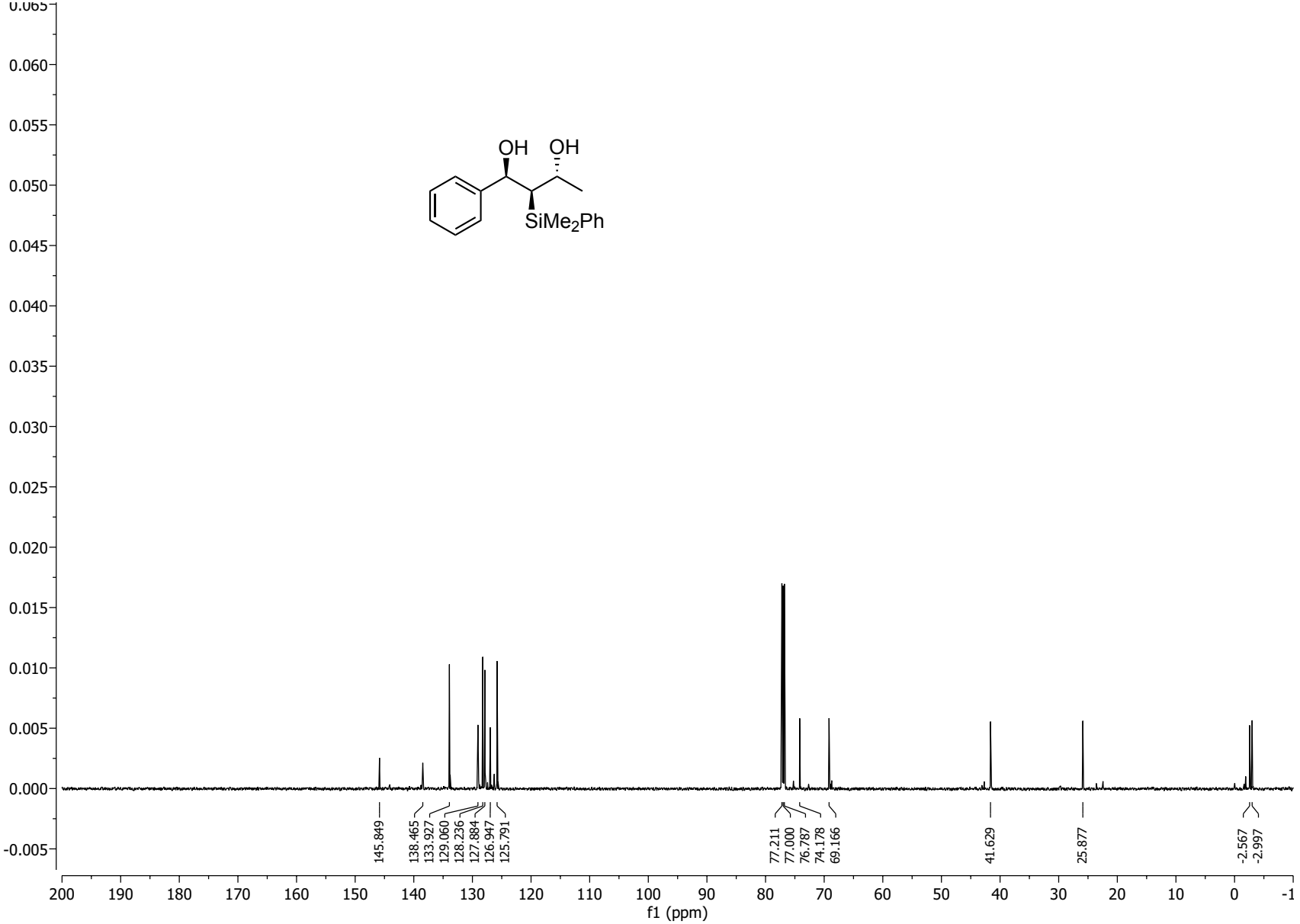


**Figure S87.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **20**

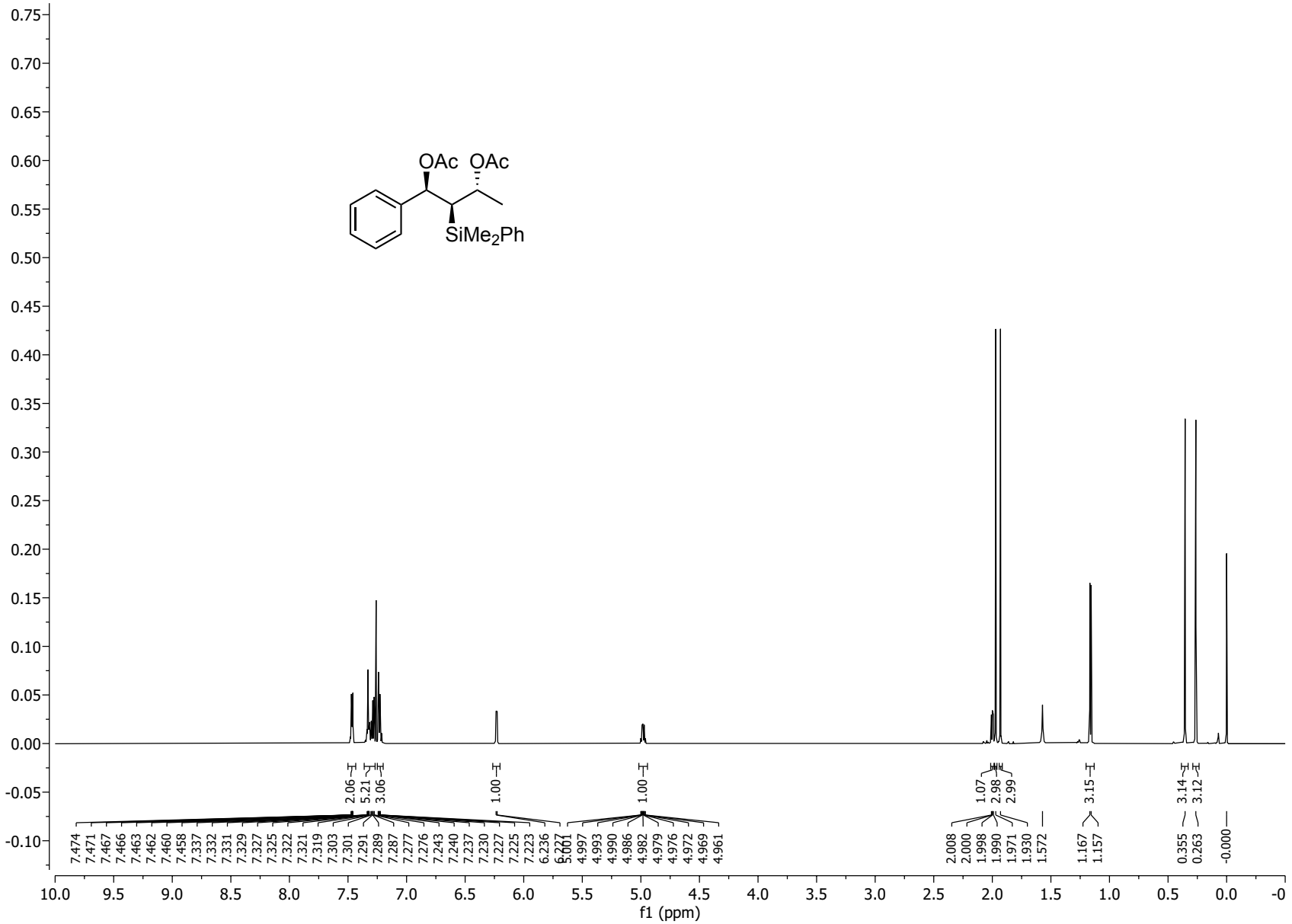


**Figure S88.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **21**

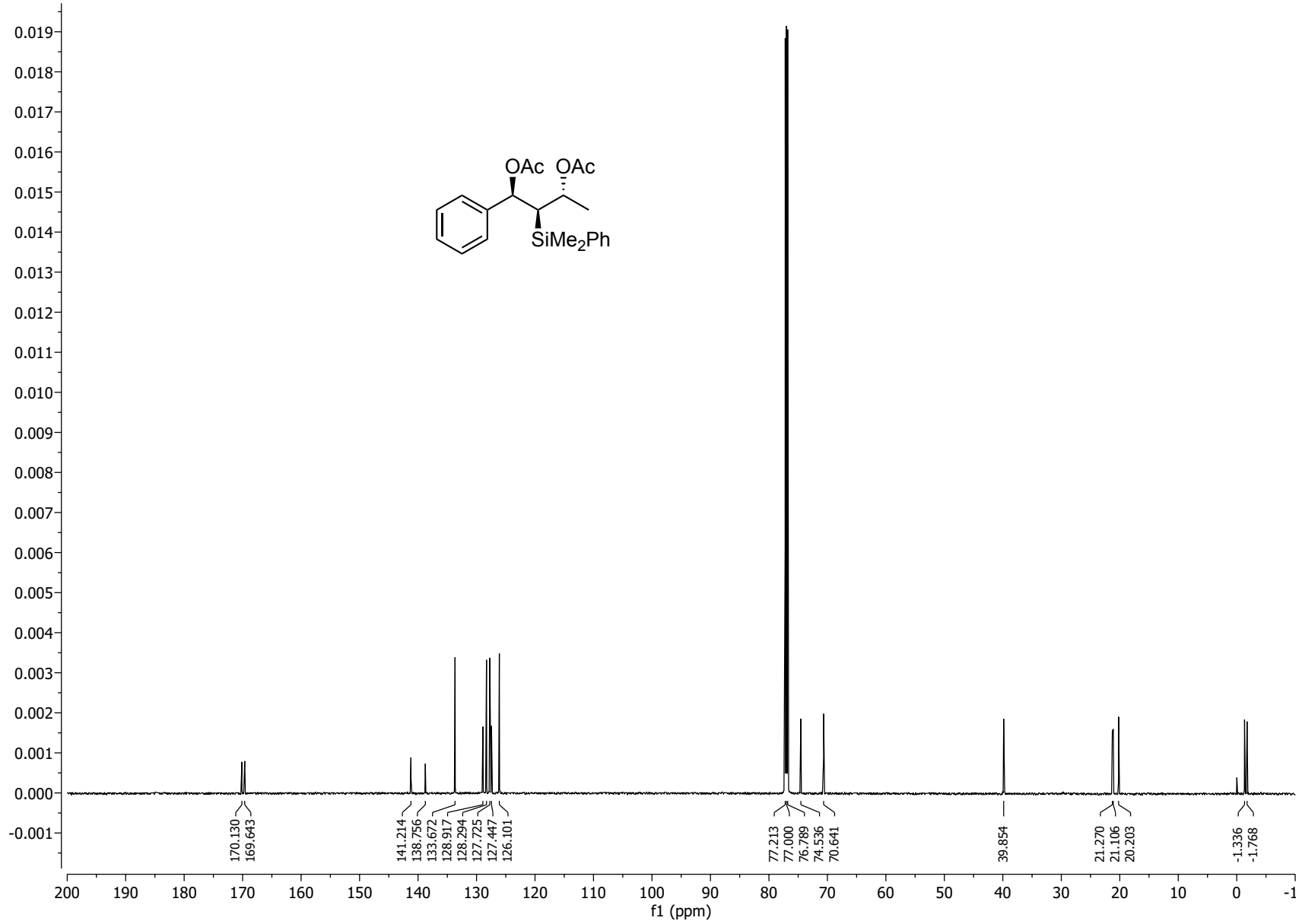


**Figure S89.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **21**

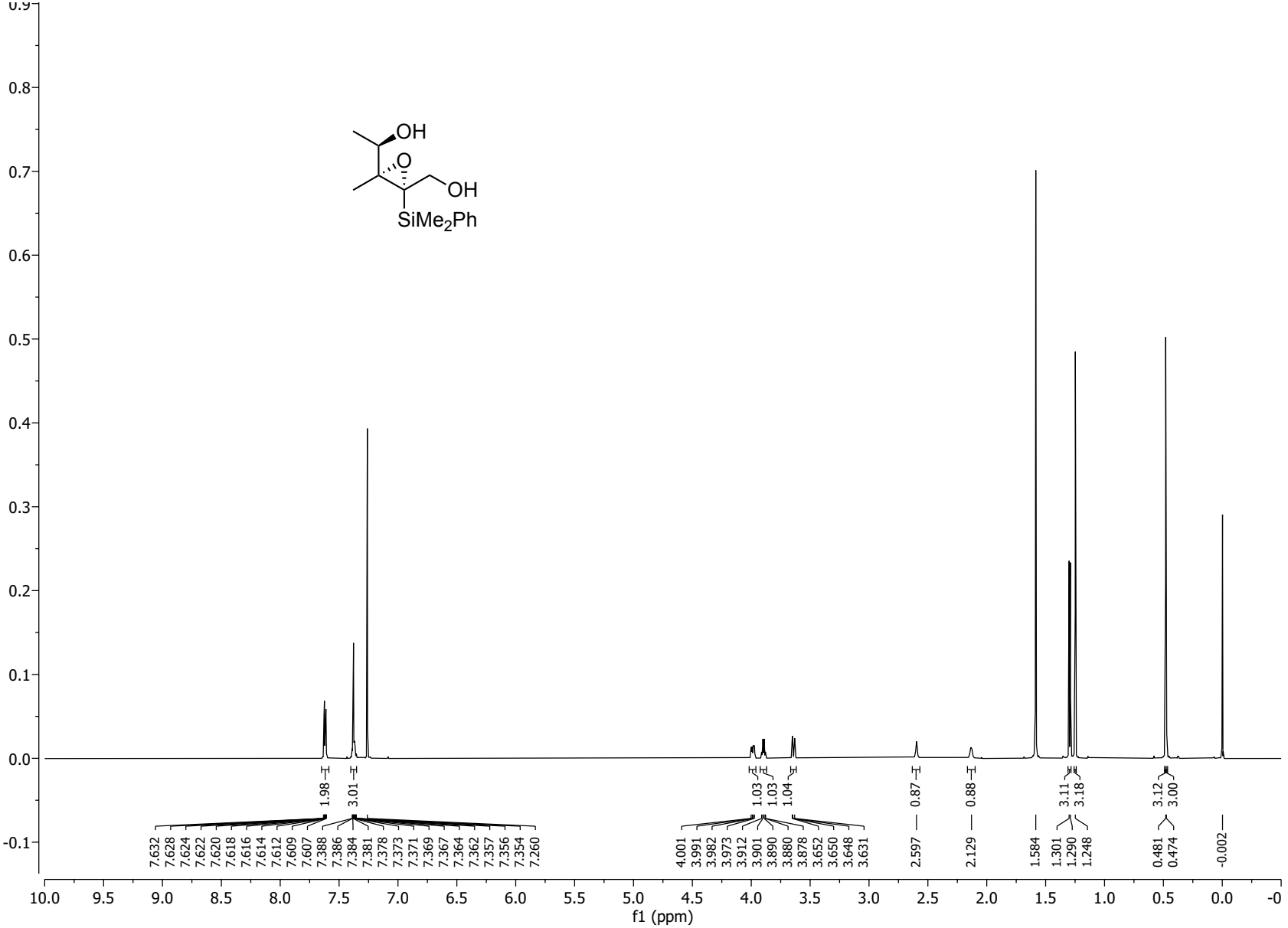


**Figure S90.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **26**

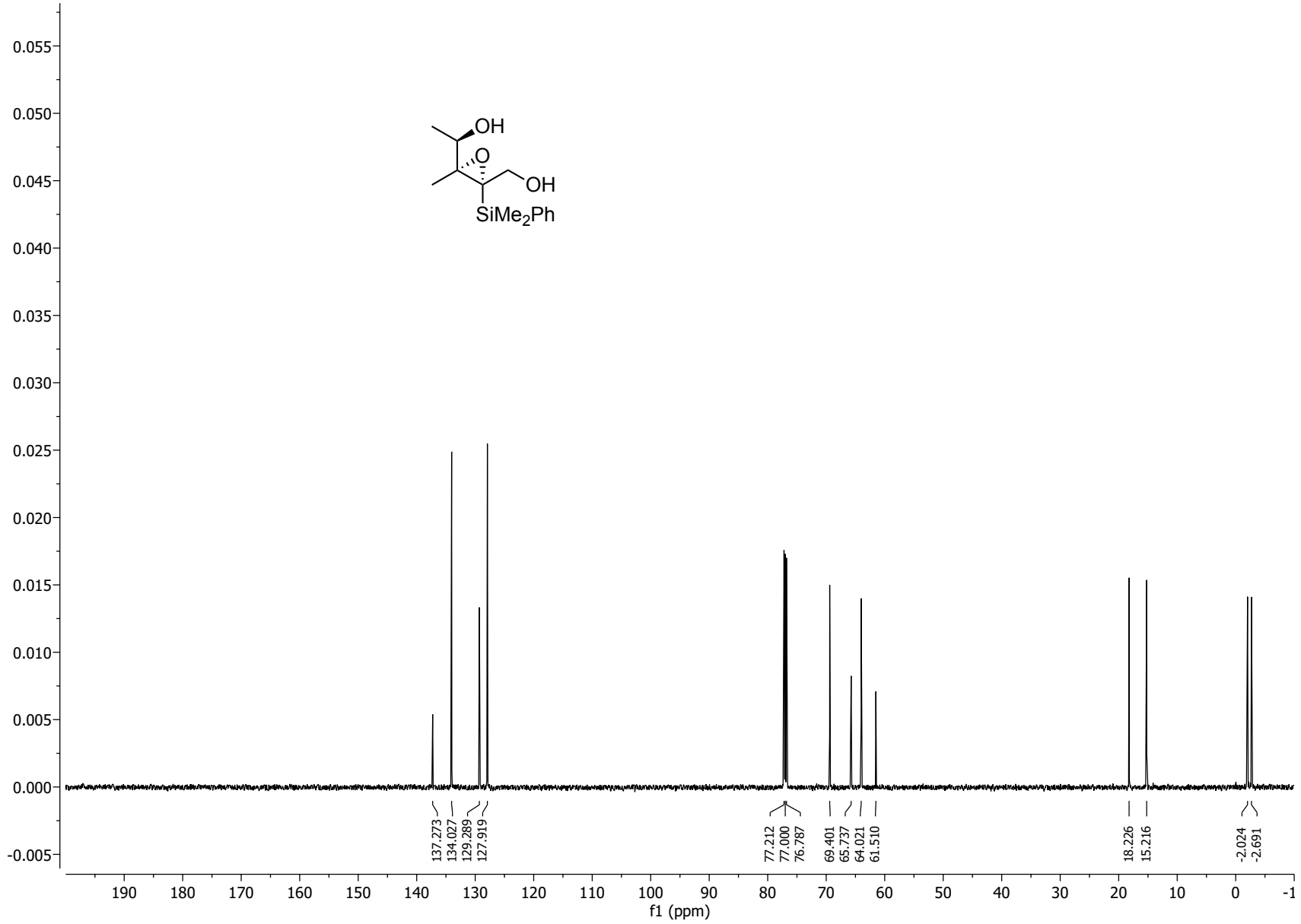


**Figure S91.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **26**

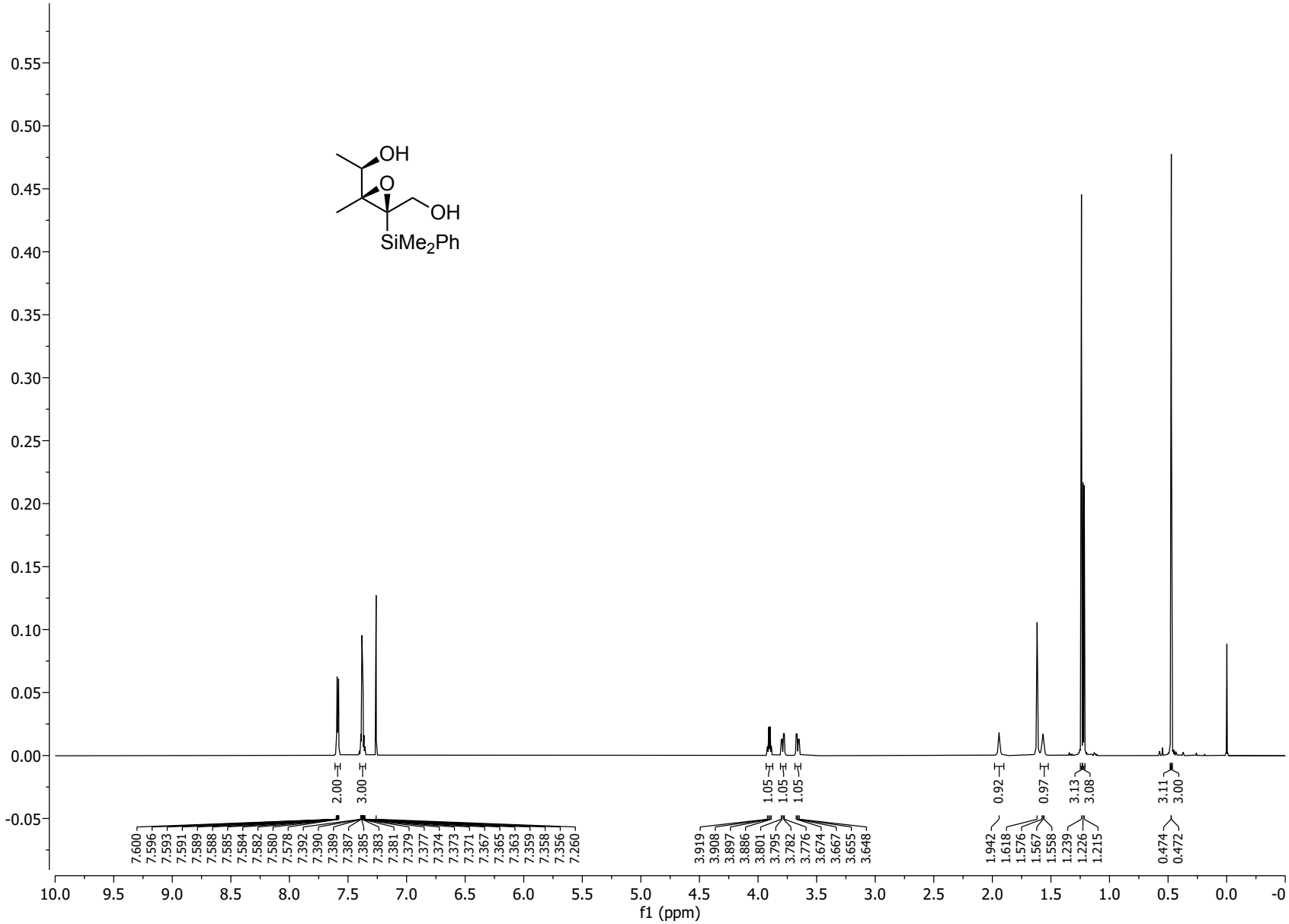


**Figure S92.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **27**

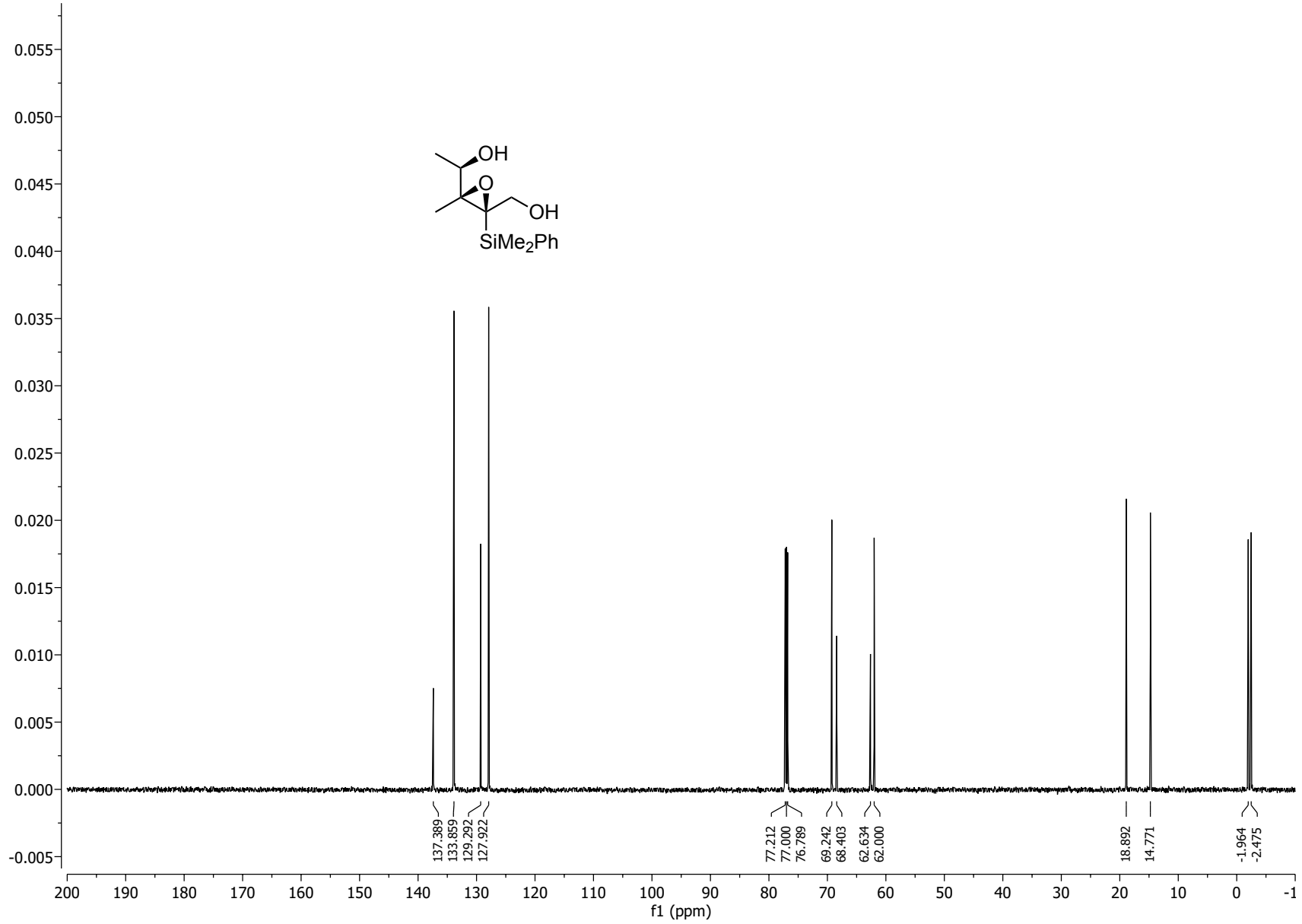


**Figure S93.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **27**

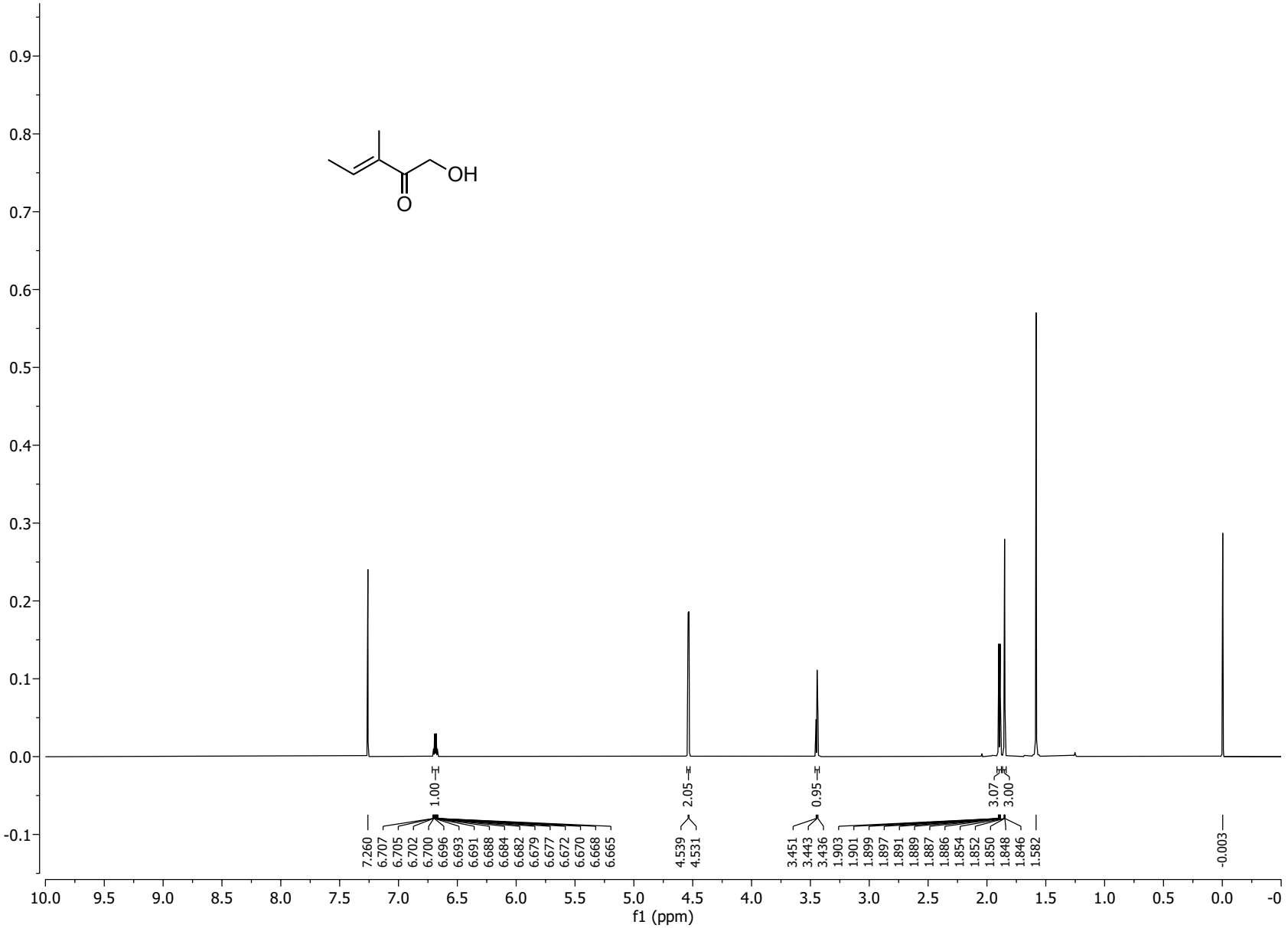


**Figure S94.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **28**

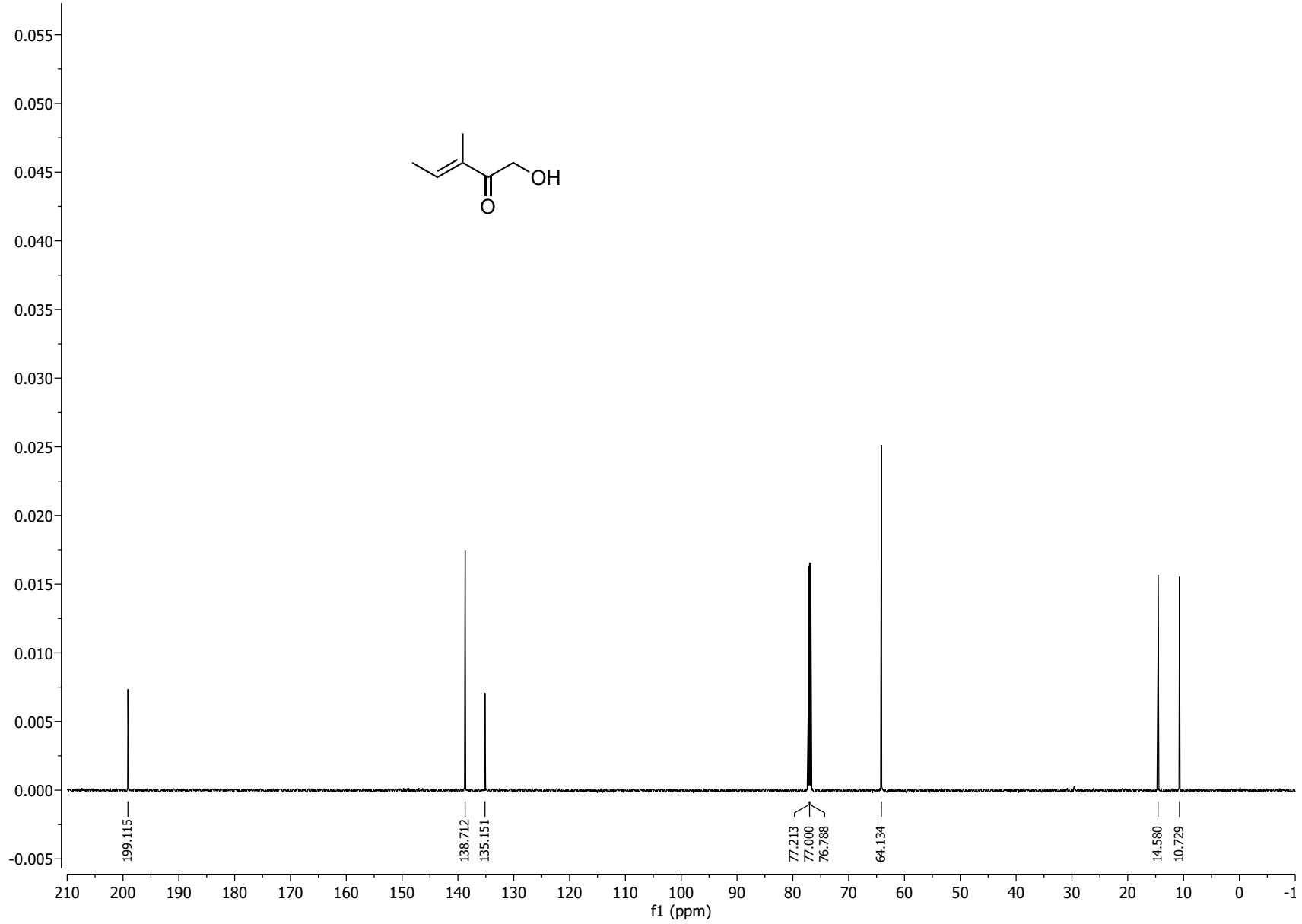


**Figure S95.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **28**

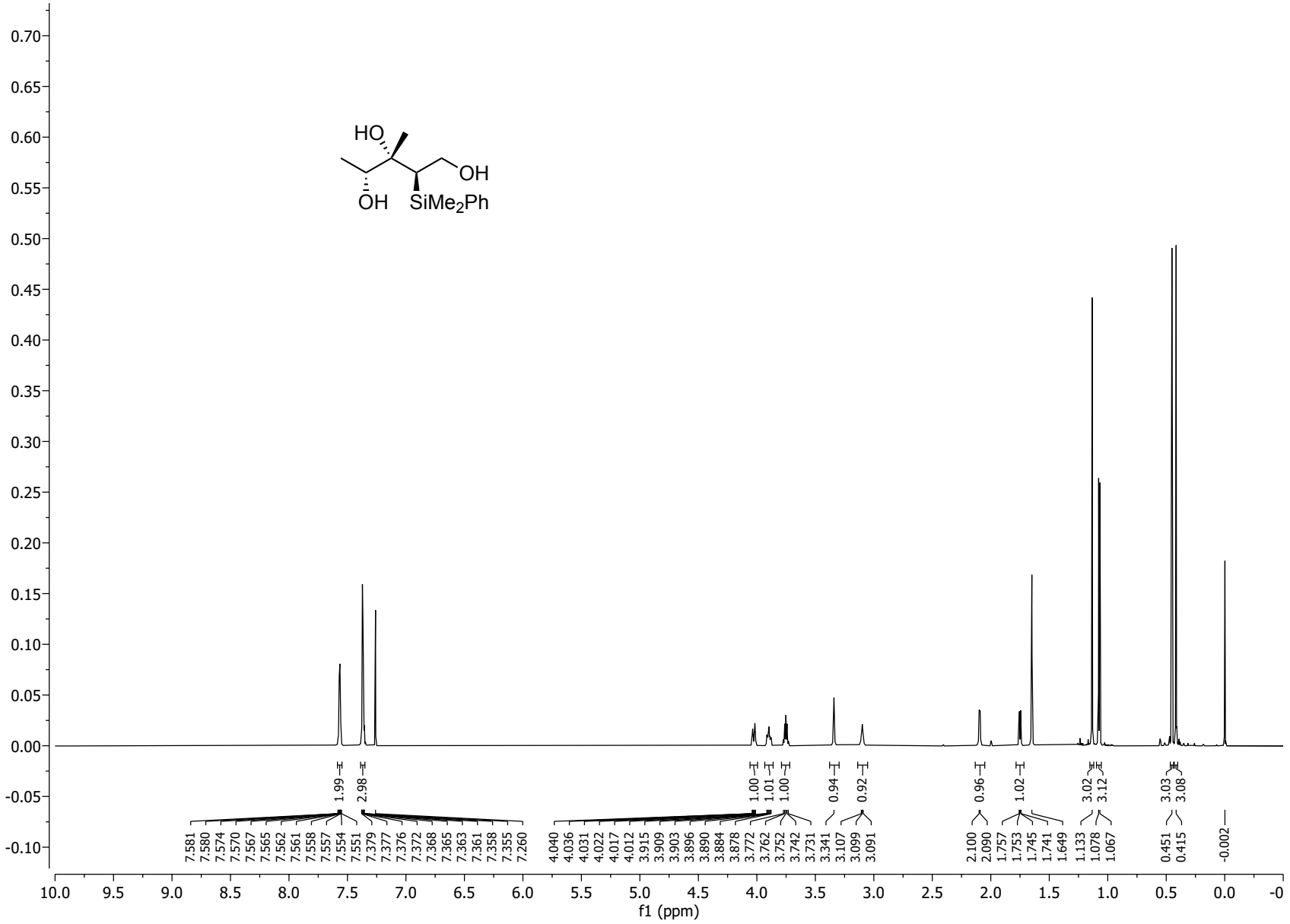


**Figure S96.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **31**

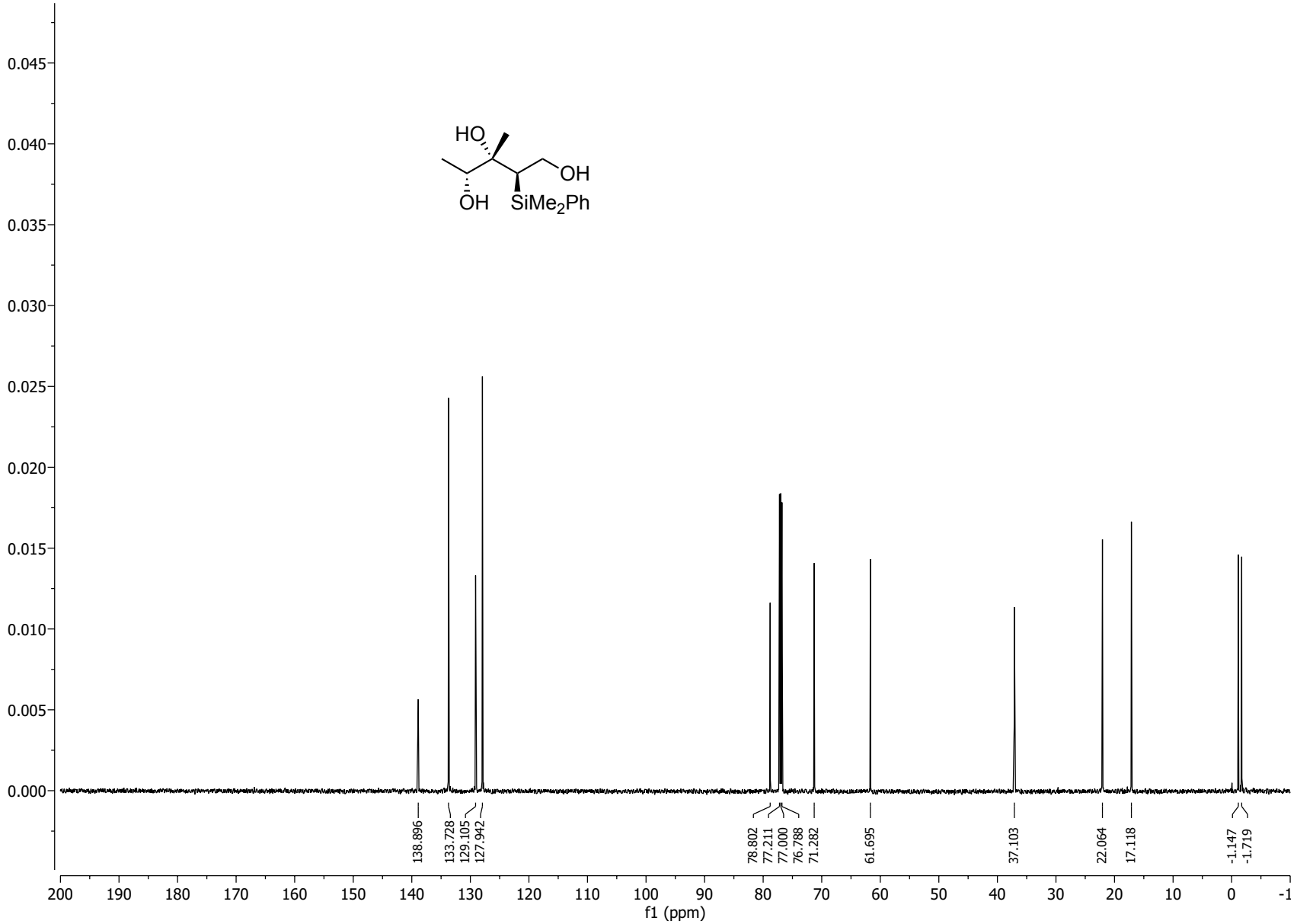


**Figure S97.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **31**

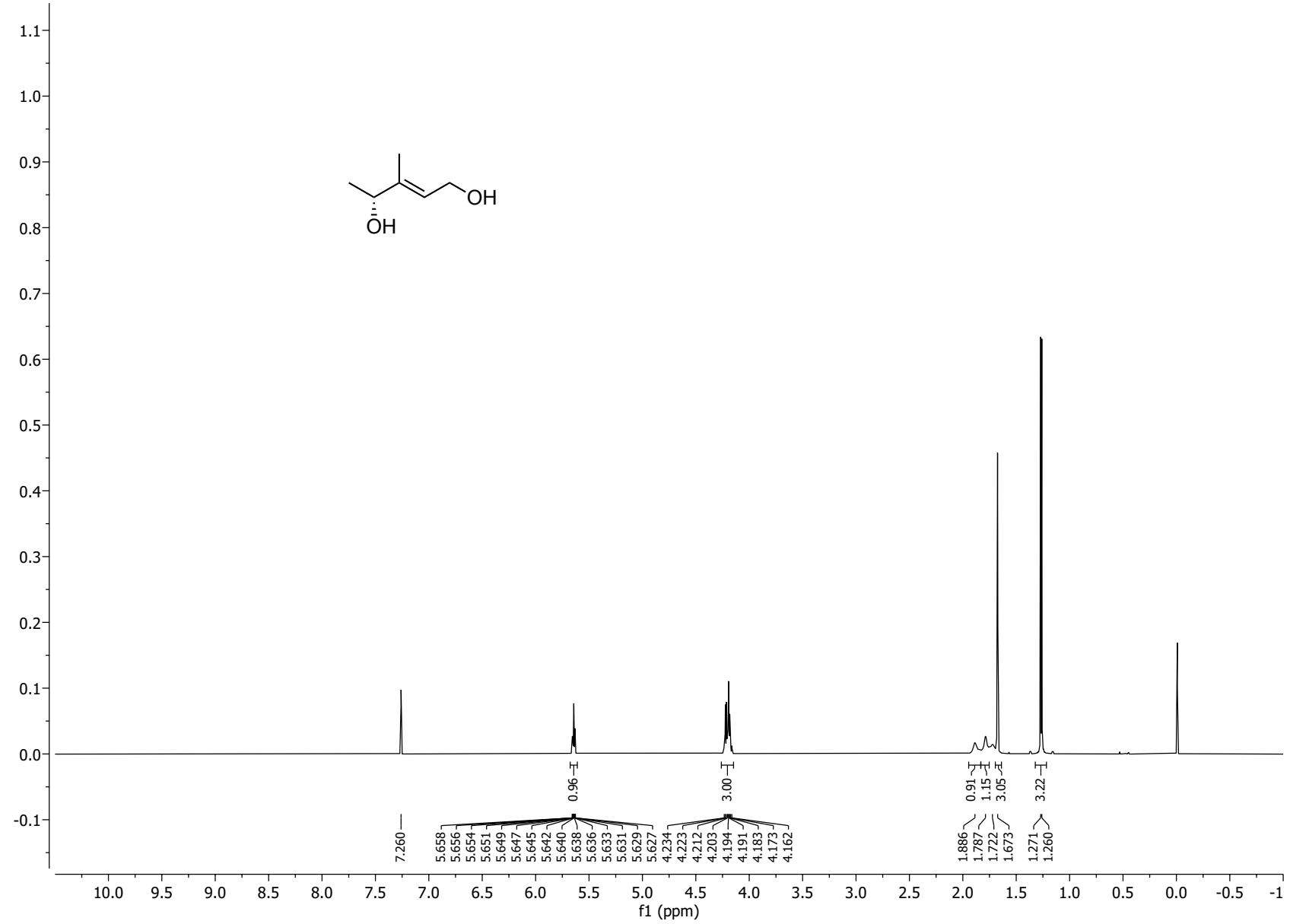


**Figure S98.** $^{1}H$ NMR (600 MHz, $CDCl_3$) spectrum of **32**

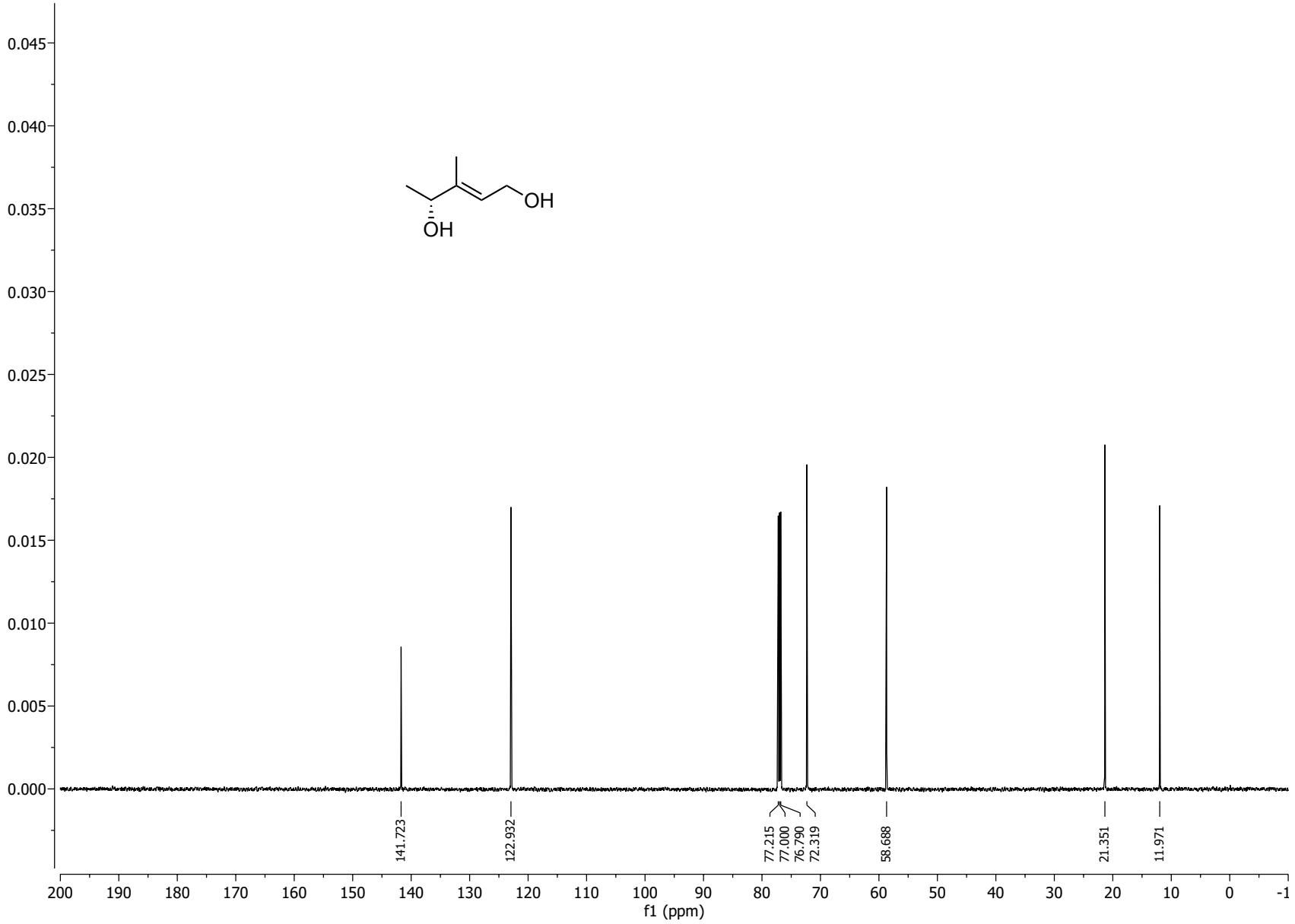


**Figure S99.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **32**

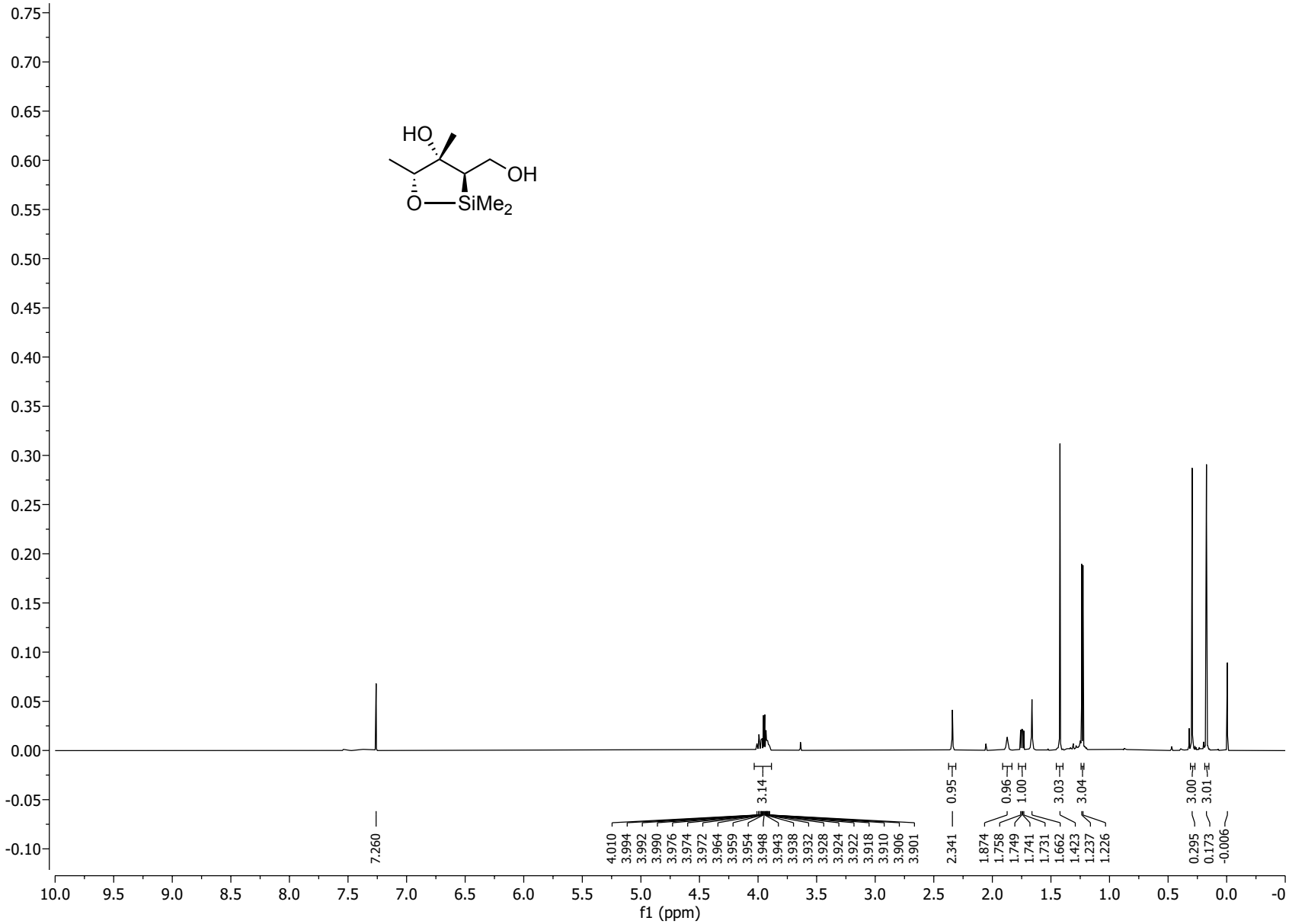


**Figure S100.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectrum of **34**

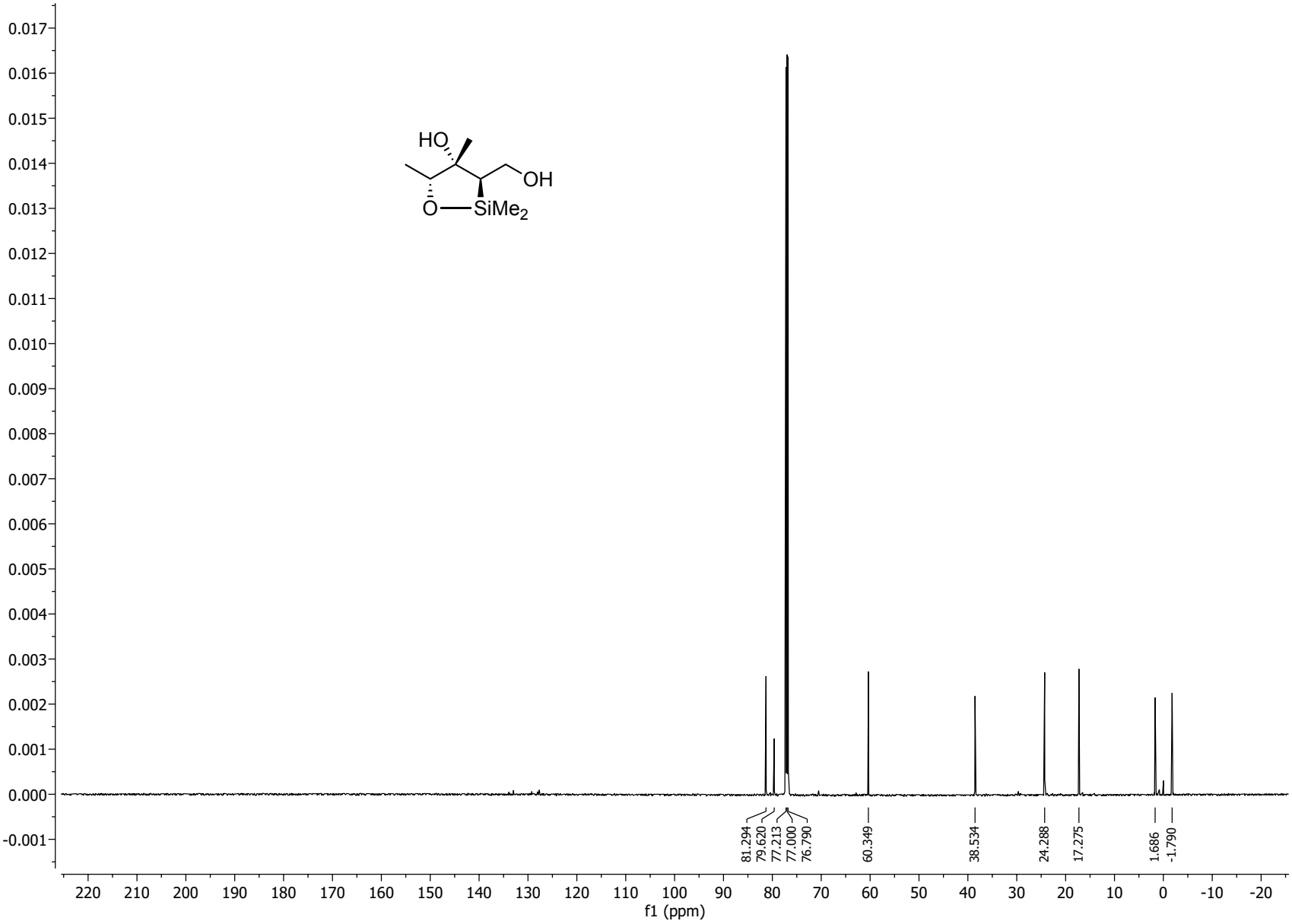


**Figure S101.** $^{13}C$ NMR (151 MHz, $CDCl_3$) spectrum of **34**

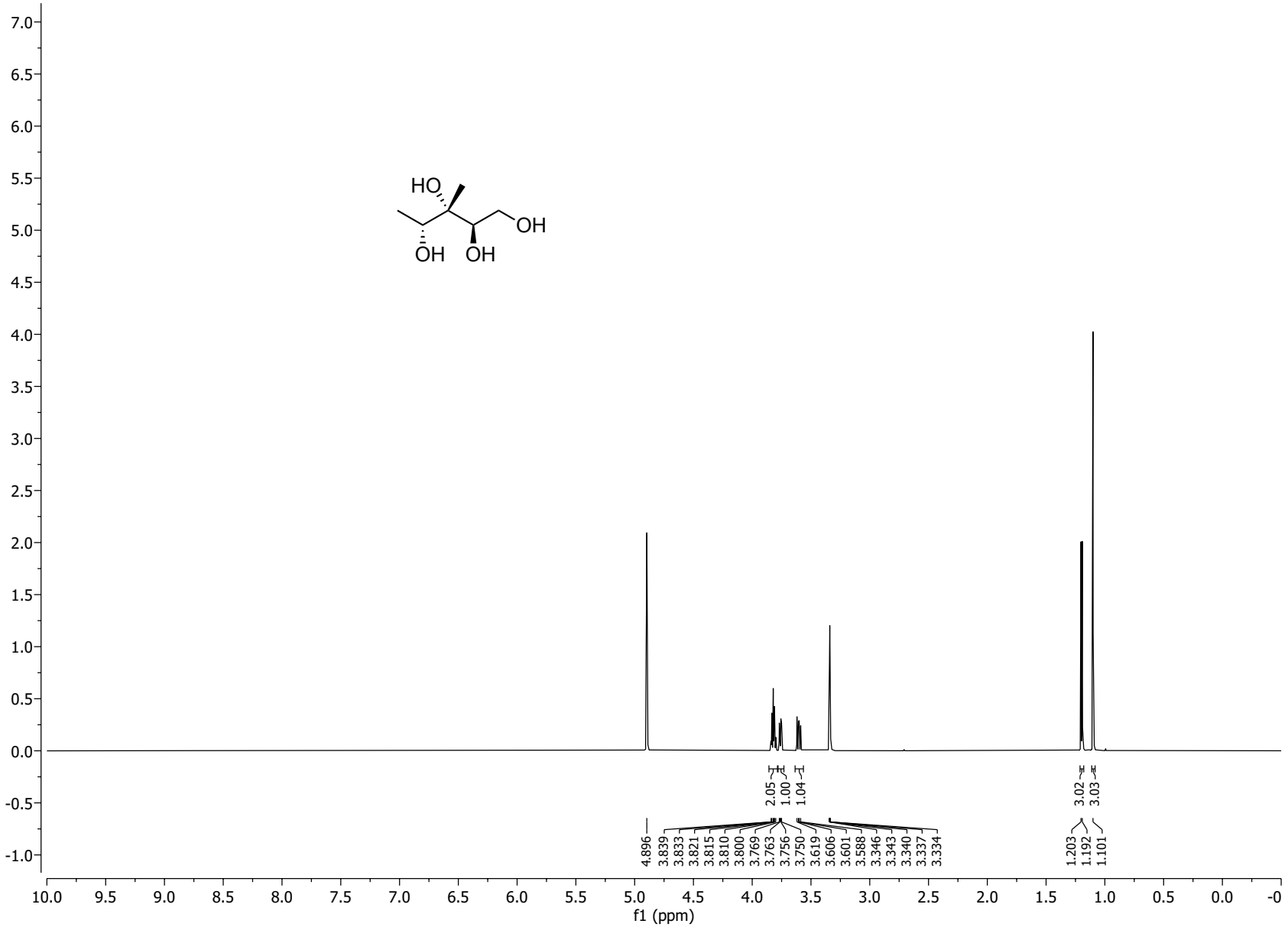


**Figure S102.** $^{1}$H NMR (600 MHz, $CD_3OD$) spectrum of **35**

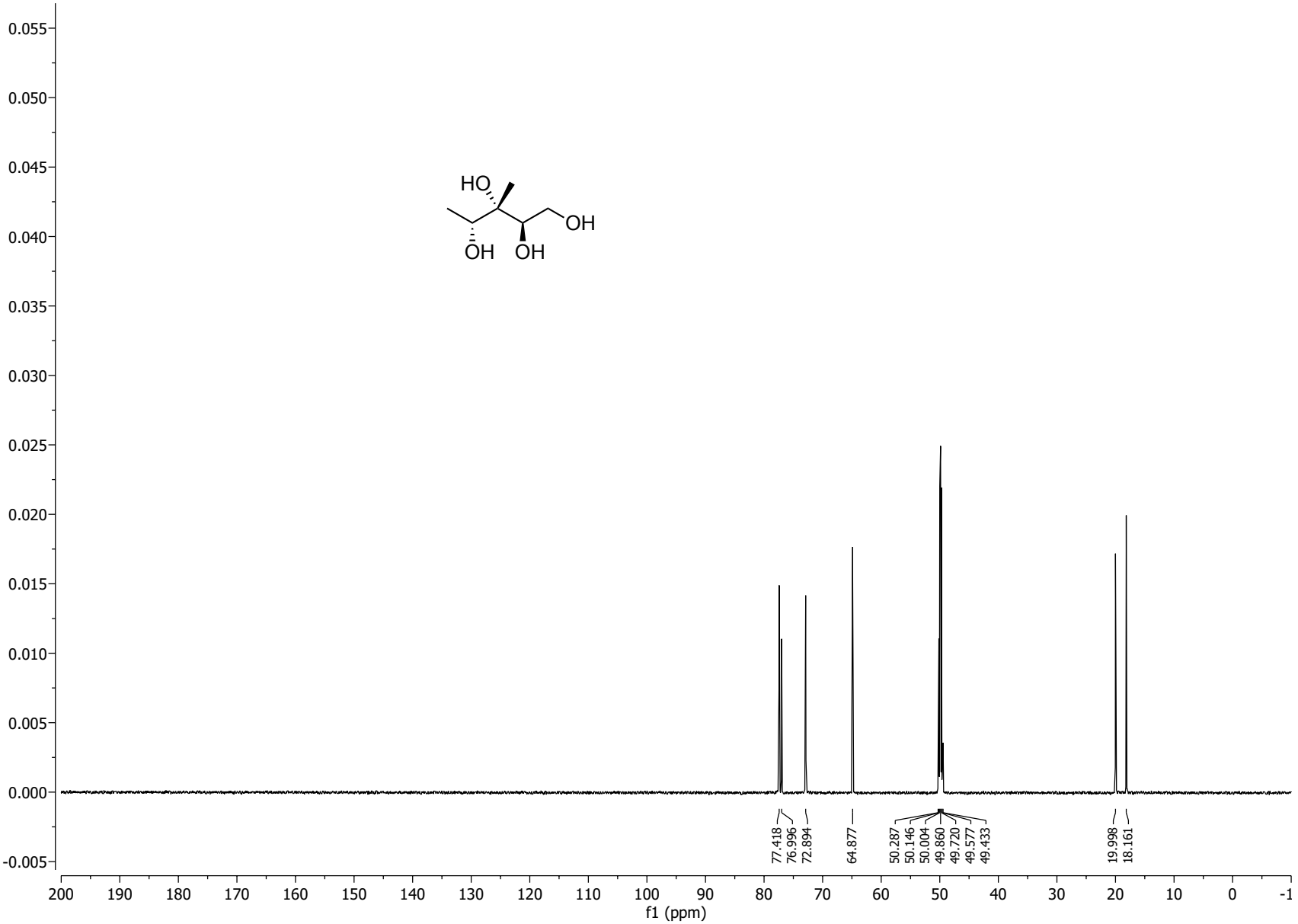


**Figure S103.** $^{13}C$ NMR (151 MHz, $CD_3OD$) spectrum of **35**