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Supporting Information

Stereoselective allylic reduction via one-pot palladium-catalyzed allylic sulfonation and sulfinyl retro-ene reactions

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I. General Information

All solvents were obtained by passing through activated alumina columns of solvent purification systems from Glass Contour. Commercially available reagents were obtained from Sigma-Aldrich, Alfa Aesar, Strem, Acros or TCI and used without further purification.

NMR spectra were obtained on an Agilent 400-MR DD2 Magnetic Resonance System (400 MHz) and a Varian/Oxford As-500 (500 MHz) spectrophotometer. Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard unless otherwise indicated, and coupling constants in Hertz. The following abbreviations (or combinations thereof) were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. IR spectra were measured on a Thermo Scientific Nicolet 6700 spectrometer. High resolution mass spectra were recorded from the Organic Chemistry Research Center at Sogang University (Seoul) on a Brucker Compact or ThermoFisher Scientific using electrospray ionization (ESI) method. Specific rotations were obtained on a JASCO P-1030 polarimeter. Chiral HPLC spectra were obtained on a HPLC Hewlett Packard 1100 Series.

The progress of reaction was checked on thin layer chromatography (TLC) plates (Merck 5554 Kiesel gel 60 F254), and the spots were visualized under 254 nm UV and/or charring after dipping the TLC plate into a vanillin solution (15.0 g of vanillin and 2.5 mL of concentrated sulfuric acid in 250 mL of ethanol), a $KMnO_4$ solution (3.0 g of potassium permanganate, 20.0 g of potassium carbonate, and 5.0 mL of 5% sodium hydroxide solution in 300 mL of water), or a ceric ammonium sulfate (CAM) solution (5 g of cerium sulfate, 25 g of ammonium molybdate tetrahydrate, 50 mL of concentrated sulfuric acid in 450 mL of water). Column chromatography was performed on silica gel (Merck 9385 Kiesel gel 60) using an appropriate eluent system.

II. Preparation of Sulfinate (TBSOMS-Na) from Rongalite™

To an argon-purged flask were added 80 mmol of TBSCl (4.0 equiv) and 20 mmol of Rongalite™ (1.0 equiv) and the solid mixture was gently stirred and cooled to 0 °C with an ice-water bath. Pyridine (1 M with respect to Rongalite™) was added to the flask over a few minutes. The resulting mixture was stirred for 12 h at room temperature under inert atmosphere. Pyridine was removed *in vacuo* and pyridinium salt was filterated through Celite with hexanes. The filterate was concentrated *in vacuo*, and a solution of the corresponding filterate in DCM (60 mL) was prepared under inert atmosphere at 0 °C. To the solution was dropwise added 19 mmol of sodium methoxide (1.0 M or 5.4 M in MeOH; 0.95 equiv). The reaction mixture was vigorously stirred at room temperature until the solution turned into a heterogeneous white solution. Solvent was removed under reduced pressure and the white precipitate was gathered, washed several times with hexanes and dried for a day under vacuum (or under a stream of nitrogen) to provide the corresponding sulfinate salt (54%).

III. General Procedure for the Preparation of Substrates

To a solution of allylic alcohol (1.0 equiv) in THF (0.5 M), which was prepared in a way reported in the corresponding literature, were added base (pyridine or ^{n}BuLi; 1.1 equiv) and a corresponding reagent (acetyl chloride for the preparation of acetate, methyl chloroformate for the preparation of methyl carbonate and Boc anhydride for the preparation of *tert*-butyldimethyl carbonate; 1.1 equiv) at -78 °C or 0 °C. Reaction mixture was stirred at room temperature. After full conversion of allylic alcohol, which was observed by TLC monitoring, reaction was quenched with *sat. aq.* NH_4Cl solution. Organic fractions were extracted by dichloromethane or ethyl acetate, washed with H_2O and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography with an appropriate eluent system to give corresponding allylic acetate or carbonate.

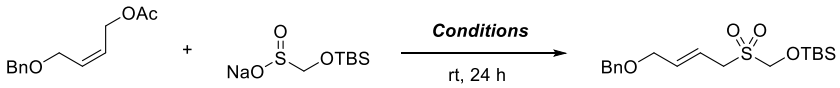
IV. General Procedure for the Tandem *S*-Allylation-Rearrangement Reaction

To an argon-purged flask with a stir bar were added 0.275 mmol of sulfinate (1.1 equiv) and 0.4 mL of H_2O. The aqueous solution was degassed by argon bubbling for 30 minutes. To another argon-purged flask were added 0.25 mmol of allylic carbonate (1.0 equiv), 0.0375 mmol of PPh_3 (0.15 equiv), 0.00625 mmol of [(η^3-

allyl)PdCl]$_2$ and 1.6 mL of THF. The organic solution in THF was transferred into the aqueous solution by cannulation, and the reaction mixture was stirred at room temperature for 12 h under inert atmosphere. 0.75 mmol of TFA (3.0 equiv.) was then directly added to the solution and the reaction mixture was kept stirring at 70 °C for additional 12 h. After the reaction mixture was cooled to room temperature, the mixture was filtered through Celite. The filterate was washed with *sat. aq.* $NaHCO_3$ solution, H_2O and brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography with an appropriate eluent system to give corresponding alkene.

V. Screening Experiments for the Optimization of Reaction Conditions

Table S1. Primary screening of palladium catalyzed *S*-allylation

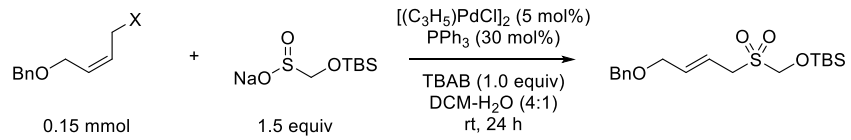


0.15 mmol 1.5 equiv

catalyst[a]	additive[b]	solvent[c]	results[d]
$Pd(PPh_3)_4$	-	DCM-H_2O (4:1)	No Reaction
$Pd(PPh_3)_4$	TBAB	DCM-H_2O (4:1)	No Reaction
$Pd(PPh_3)_4$	TBAB	DCM-MeOH (4:1)	No Reaction
$Pd_2(dba)_3$	TBAB	DCM-H_2O (4:1)	No Reaction
$Pd(dba)_2$	TBAB	DCM-H_2O (4:1)	No Reaction
$[(C_3H_5)PdCl]_2$ / PPh_3	TBAB	DCM-H_2O (4:1)	74%

[a] 10 mol% of palladium catalyst (with 30 mol% of phosphine ligand, if necessary)
[b] 1.0 equiv
[c] 2.0 mL of total volume
[d] isolated yield

Table S2. Leaving group screening of palladium catalyzed *S*-allylation

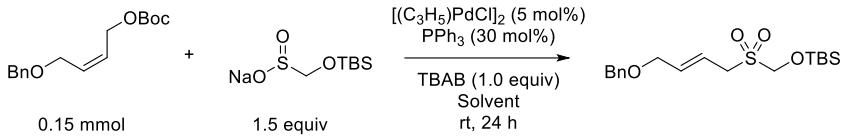


0.15 mmol 1.5 equiv

Leaving group (X)	results[a]
OAc	74%
OCO_2Me	85%
OBoc	95%

[a] isolated yield

Table S3. Solvent screening of palladium catalyzed *S*-allylation

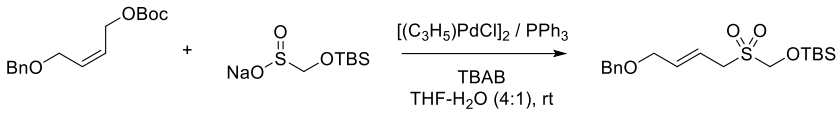


0.15 mmol 1.5 equiv

Solvent	results[a]
DCM-H_2O (4:1)	95%
DCE-H_2O (4:1)	58%
MeOH	46%
DCM	64%
THF	19%
THF-H_2O (1:1)	12%
THF-H_2O (4:1)	98%

[a] isolated yield

Table S4. Equivalent screening of palladium catalyzed *S*-allylation



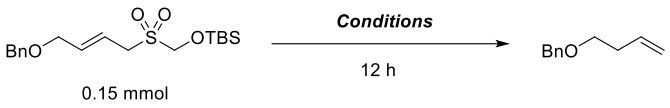
0.15 mmol TBSOMS-Na

$[(C_3H_5)PdCl]_2$ / PPh_3	TBSOMS-Na	TBAB	results[a]
5 mol% / 30 mol%	1.5 equiv	1.0 equiv	98%
5 mol% / 30 mol%	1.5 equiv	-	84%
2.5 mol% / 15 mol%	1.5 equiv	-	79%
1.25 mol% / 7.5 mol%	1.5 equiv	-	71%
2.5 mol% / 15 mol%	1.1 equiv	-	90%
2.5 mol% / 15 mol%	1.1 equiv	-	97%[b]

[a] isolated yield

[b] 0.25 mmol instead of 0.15 mmol

Table S5. Screening of allylic sulfinic acid rearrangement

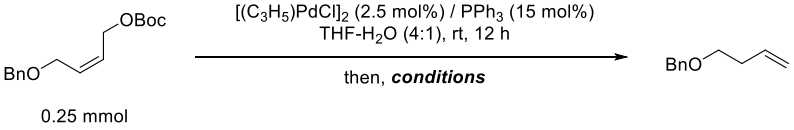


0.15 mmol

acid[a]	temperature	solvent[b]	results[c]
HCl / MeOH	50 °C	DCM-H_2O (4:1)	-
HCl / MeOH	50 °C	DCE	40%
HCl / MeOH	50 °C	THF-H_2O (4:1)	70%
AcOH	50 °C	THF-H_2O (4:1)	50%
AcOH	70 °C	THF-H_2O (4:1)	71%
TFA	70 °C	THF-H_2O (4:1)	87%

[a] amount of acid: HCl (2.0 equiv), AcOH (20 vol%), TFA (3.0 equiv)
[b] 2.0 mL of total volume
[c] isolated yield

Table S6. Screening of one-pot allylic reduction

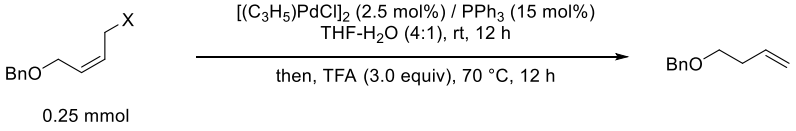


0.25 mmol

acid[a]	temperature	reaction time	results[b]
HCl / MeOH	50 °C	12 h	-
AcOH	70 °C	12 h	-
citric acid	70 °C	12 h	-
tartaric acid	70 °C	12 h	-
conc. HCl (aq.)	50 °C	12 h	65%
conc. HCl (aq.)	50 °C	24 h	48%
TFA	70 °C	12 h	69%

[a] amount of acid: HCl (2.0 equiv), AcOH (20 vol%), TFA (3.0 equiv), citric acid (5.0 equiv), tartaric acid (5.0 equiv)
[b] isolated yield

Table S7. Leaving group screening of one-pot allylic reduction



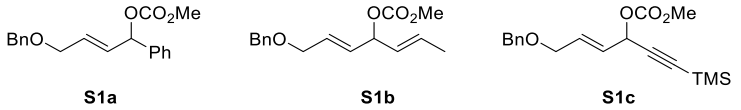
0.25 mmol

Leaving group (X)	results[a]
OAc	69%
OCO_2Me	80%
OBoc	69%

[a] isolated yield

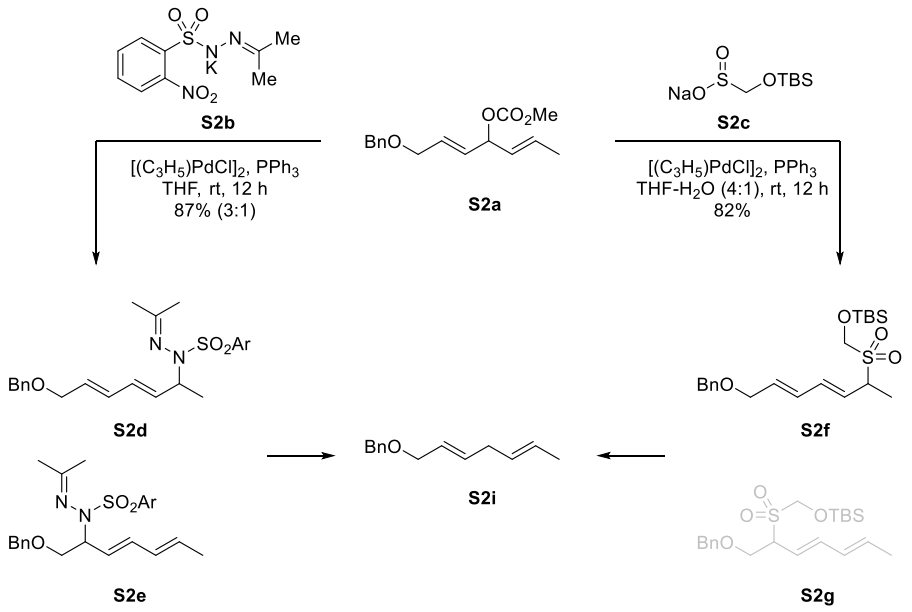
VI. Comparison with Other Allylic Reduction Methodology

Figure S1. Carbonates flanked by two π-systems



Doubly activated carbonates (Figure S1) are sensitive in that they are not suited for traditional reduction. For instance, carbonate **S1c** under conventional formate reduction conditions afforded deoxygenated alkene as a minor product with significant decomposition of starting material, while exposure to free-radical mediated conditions gave complex mixture with no trace of product.[1] Conventional reduction by formate or sodium borohydride gave regioisomeric alkenes even for simpler allylic carbonate **3b.** It is also noteworthy that allylic thiocarbonyl derivatives often suffer from the regioselectivity issue, significantly diminishing the utility of free-radical mediate reduction in allylic compounds.[2]

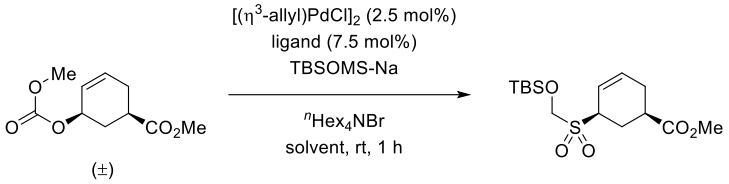
Scheme S1. Allylic Reduction of Bis-Allylic Carbonate



Reduction of *bis*-allylic carbonate (**S2a**) either with potassium sulfonylhydrazide (**S2b**) or with sulfinate (**S2c**) afforded the same skipped diene (**S2i**) through S_N2-type reductive displacement. Palladium-catalyzed allylation of sulfonylhydrazone salt led to the regioisomeric mixtures in a 3:1 ratio (**S2d**:**S2e**)[1] while *S*-allylation with TBSOMS-Na (**S2c**) gave the single isomer **S2f**, demonstrating the enhanced selectivity of palladium catalysis with heteroatom nucleophile.

VII. Asymmetric Allylic Reduction

Table S8. Asymmetric *S*-allylation of cyclic *cis*-carbonate

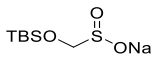


ligand	TBSOMS-Na	$^{n}Hex_4NBr$	solvent	yield (dr)	*ee*	note[a]
PPh_3	1.1	-	THF-H_2O (4:1)	94% (1:2.37)	-	-
PPh_3	1.1	1.1	DCM-H_2O (3:1)	99% (1:1.37)	-	-
(*R*,*R*)	5.0	5.0	DCM-H_2O (3:1)	97% (10:1)	-	24 h
(*S*,*S*)	5.0	5.0	DCM-H_2O (3:1)	75% (10:1)	-	36 h
(*R*,*R*)	1.1	-	THF-H_2O (4:1)	94% (10:1)	-	-
(*R*,*R*)	1.1	1.1	DCM-H_2O (3:1)	99%	98%	-
(*R*,*R*)	1.1	0.25	DCM-H_2O (3:1)	99%	98%	2 h
(*S*,*S*)	1.1	0.25	DCM-H_2O (3:1)	99%	98%	2 h
(*R*,*R*)	1.1	0.25	DCM-H_2O (3:1)	91% (10:1)	-	2 h (1.5 mmol)
(*S*,*S*)	1.1	0.25	DCM-H_2O (3:1)	76% (10:1)	-	2 h (1.5 mmol)

[a] 0.1 mmol of carbonate in 2.0 mL of solvent unless specified.

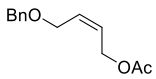
The feasibility of asymmetric *S*-allylation of cyclic *cis*-carbonate using Trost's diamide ligands was probed (Table S8). It should be noted that a diastereomer possibly derived from palladium-coordination followed by reductive elimination, which has been proposed by Trost and others (*J. Am. Chem. Soc.* **1995**, *117*, 9662.), was observed as a byproduct. Formation of the byproduct also depends on the concentration, solvent, scale and degassing.

VIII. Compound Characterization



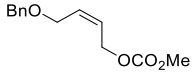
sodium ((*tert*-butyldimethylsilyl)oxy)methanesulfinate (S1)

white solid; ^{1}H NMR (400 MHz, CD_3OD) δ 3.86 (s, 2H), 0.93 (s, 9H), 0.13 (s, 6H); ^{13}C NMR (100 MHz, CD_3OD) δ 88.07, 26.35, 19.26, -4.92; IR (neat, ν_{max}) 3860, 3635, 3331, 2798, 2513, 2226, 2044, 1668, 1419, 1114, 1010, 769 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_7H_{17}NaO_3SSi$ $[M+H]^+$: 233.0638, found: 233.06392; HRMS (ESI) *m/z* calc. for $C_7H_{17}NaO_3SSi$ $[M+Na]^+$: 255.0458, found: 255.04588; HRMS (ESI) *m/z* calc. for $C_7H_{17}NaO_3SSi$ $[M-Na]^-$: 209.0673, found: 209.06626.



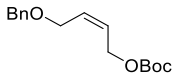
(*Z*)-4-(benzyloxy)but-2-en-1-yl acetate (S2)

clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H), 5.82 (dt, *J* = 11.2, 6.3 Hz, 1H), 5.70 (dt, *J* = 11.2, 6.7 Hz, 1H), 4.62 (d, *J* = 6.7 Hz, 2H), 4.52 (s, 2H), 4.12 (d, *J* = 6.2 Hz, 2H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.93, 138.10, 130.97, 128.56, 127.94, 127.87, 126.77, 72.59, 65.78, 60.44, 21.05; IR (neat, ν_{max}) 3332, 2958, 2835, 1701, 1410, 1097, 1040, 1024, 742, 679, 653 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{13}H_{16}O_3$ $[M+Na]^+$: 243.0992, found: 243.0989.



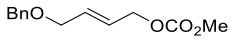
(*Z*)-4-(benzyloxy)but-2-en-1-yl methyl carbonate (S3)[3]

clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H), 5.85 (dt, *J* = 11.4, 6.1 Hz, 1H), 5.73 (dt, *J* = 11.3, 6.6 Hz, 1H), 4.69 (d, *J* = 6.6 Hz, 2H), 4.50 (s, 2H), 4.13 (d, *J* = 6.1 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.77, 138.05, 131.52, 128.56, 127.93, 127.87, 126.17, 72.59, 65.78, 63.75, 54.98; IR (neat, ν_{max}) 2254, 1793, 1748, 1445, 1381, 1273, 1091, 912, 744, 650 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{13}H_{16}O_4$ $[M+Na]^+$: 259.0941, found: 259.0940.



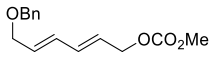
(*Z*)-4-(benzyloxy)but-2-en-1-yl *tert*-butyl carbonate (S4)

clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 5.83 (dt, *J* = 12.2, 6.5 Hz, 1H), 5.74 (dt, *J* = 11.4, 6.5 Hz, 1H), 4.62 (d, *J* = 6.5 Hz, 2H), 4.51 (s, 2H), 4.13 (d, *J* = 6.0 Hz, 2H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.46, 138.10, 131.05, 128.55, 127.92, 127.84, 126.62, 82.37, 72.52, 65.78, 62.76, 27.89; IR (neat, ν_{max}) 3414, 3275, 1913, 1856, 1780, 1685, 1568, 1423, 1299, 1080, 891, 767, 712 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{16}H_{22}O_4$ [M+Na]$^+$: 301.1410, found: 301.1416.



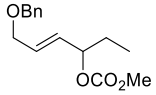
(*E*)-4-(benzyloxy)but-2-en-1-yl methyl carbonate (S5)[4]

clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 5.91 (tdd, *J* = 15.6, 10.7, 5.1 Hz, 2H), 4.65 (d, *J* = 5.5 Hz, 2H), 4.52 (s, 2H), 4.05 (d, *J* = 4.8 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.73, 138.19, 131.90, 128.56, 127.88, 127.83, 125.97, 72.53, 69.77, 67.82, 54.97; IR (neat, ν_{max}) 3028, 2858, 2254, 1748, 1381, 1444, 1271, 1094, 913, 742, 651 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{13}H_{16}O_4$ [M+Na]$^+$: 259.0941, found: 259.0940.



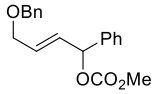
(2*E*,4*E*)-6-(benzyloxy)hexa-2,4-dien-1-yl methyl carbonate (S6)

clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 6.31 (dt, *J* = 25.6, 10.6 Hz, 2H), 5.86 (dt, *J* = 14.3, 5.8 Hz, 1H), 5.77 (dt, *J* = 14.3, 5.8 Hz, 1H), 4.66 (d, *J* = 6.5 Hz, 2H), 4.52 (s, 2H), 4.07 (d, *J* = 6.0 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.74, 138.28, 134.24, 131.77, 131.24, 128.55, 127.88, 127.80, 126.17, 72.36, 70.19, 68.10, 54.97; IR (neat, ν_{max}) 2859, 2740, 1747, 1444, 1271, 1071, 993, 911, 740, 650 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{15}H_{18}O_4$ [M+Na]$^+$: 285.1097, found: 285.1096.



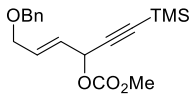
(*E*)-6-(benzyloxy)hex-4-en-3-yl methyl carbonate (S7)

clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 5.88 (dt, *J* = 15.6, 5.4 Hz, 1H), 5.71 (dd, *J* = 15.6, 7.0 Hz, 1H), 5.03 (q, *J* = 6.7 Hz, 1H), 4.51 (s, 2H), 4.03 (d, *J* = 4.9 Hz, 2H), 3.77 (s, 3H), 1.70 (dtd, *J* = 27.8, 14.0, 6.9 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.42, 138.25, 130.37, 130.13, 128.55, 127.89, 127.80, 79.76, 72.39, 69.85, 54.77, 27.56, 9.57; IR (neat, ν_{max}) 2972, 3029, 2855, 1747, 1442, 1267, 1075, 971, 949, 793, 740, 699 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{15}H_{20}O_4$ $[M+Na]^+$: 287.1254, found: 287.1254.



(*E*)-4-(benzyloxy)-1-phenylbut-2-en-1-yl methyl carbonate (S8)

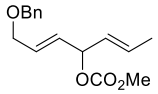
clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 10H), 6.11 (d, *J* = 6.0 Hz, 1H), 5.97 (dd, *J* = 15.5, 6.0 Hz, 1H), 5.89 (dt, *J* = 15.6, 5.0 Hz, 1H), 4.50 (s, 2H), 4.04 (d, *J* = 5.0 Hz, 2H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.10, 138.57, 138.15, 130.37, 130.13, 128.75, 128.52, 127.87, 127.79, 127.12, 79.66, 72.50, 69.73, 54.95; IR (neat, ν_{max}) 3390, 3342, 3306, 3091, 2860, 2735, 1056, 1000, 738 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{19}H_{20}O_4$ $[M+Na]^+$: 335.1254, found: 335.1256.



(*E*)-6-(benzyloxy)-1-(trimethylsilyl)hex-4-en-1-yn-3-yl methyl carbonate (S9)

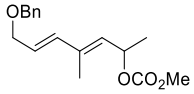
clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 6.12 (dt, *J* = 15.3, 5.2 Hz, 1H), 5.86 (dd, *J* = 15.3, 5.9 Hz, 1H), 5.77 (d, *J* = 6.1 Hz, 1H), 4.53 (s, 2H), 4.07 (d, *J* = 5.1 Hz, 2H), 3.81 (s, 3H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.84, 138.09, 132.62, 128.57, 127.92, 127.87, 126.46, 99.60, 93.42, 72.60, 69.35, 68.10, 55.18, -0.15; IR (neat, ν_{max}) 3156, 3029, 2962, 2856, 2792, 2254, 1749, 1469, 1385, 1262, 1090, 989, 648 cm^{-1};

HRMS (ESI) *m/z* calc. for $C_{18}H_{24}O_4Si$ $[M+Na]^+$: 355.1336, found: 355.1335.



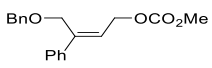
(2*E*,5*E*)-1-(benzyloxy)hepta-2,5-dien-4-yl methyl carbonate (S10)

clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 5H), 6.28 (dt, *J* = 24.3, 10.6 Hz, 2H), 5.85 (dt, *J* = 13.9, 6.0 Hz, 1H), 5.68 (dd, *J* = 14.3, 7.0 Hz, 1H), 5.24 (m, 1H), 4.52 (s, 2H), 4.07 (d, *J* = 5.7 Hz, 2H), 3.77 (s, 3H), 1.38 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.21, 138.32, 131.93, 131.70, 131.46, 128.52, 127.86, 127.76, 74.95, 72.31, 70.23, 54.74, 20.42; IR (neat, ν_{max}) 3688, 3535, 3159, 3031, 2855, 2793, 2257, 1740, 1603, 1444, 1058, 1000, 645 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{16}H_{20}O_4$ $[M+Na]^+$: 299.1254, found: 299.1252.



(3*E*,5*E*)-7-(benzyloxy)-4-methyl-hepta-3,5-dien-2-yl methyl carbonate (S11)

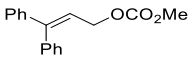
clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 5H), 6.26 (d, *J* = 15.7 Hz, 1H), 5.85 (dt, *J* = 15.7, 6.0 Hz, 1H), 5.56 (dq, *J* = 12.7, 6.4 Hz, 1H), 5.45 (d, *J* = 8.9 Hz, 1H), 4.52 (s, 2H), 4.09 (d, *J* = 6.0 Hz, 2H), 3.75 (s, 3H), 1.86 (s, 3H), 1.36 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.31, 138.38, 136.40, 136.10, 130.66, 128.54, 127.91, 127.77, 126.53, 72.36, 72.11, 70.79, 20.82, 13.03; IR (neat, ν_{max}) 2954, 2852, 1741, 1441, 1330, 1258, 1149, 1113, 1070, 1034, 968, 940, 864, 791, 737, 698 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{17}H_{22}O_4$ $[M+Na]^+$: 313.1410, found: 313.14114.



(*Z*)-4-(benzyloxy)-3-phenylbut-2-en-1-yl methyl carbonate (S12)

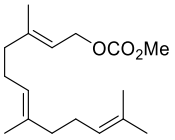
clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 10H), 6.06 (t, *J* = 6.8 Hz, 1H), 4.88 (d, *J* = 6.8 Hz, 2H), 4.52 (s, 2H), 4.46 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.82, 141.31, 140.28, 137.94, 128.55, 128.50,

128.05, 127.95, 127.92, 126.63, 125.77, 125.74, 72.44, 67.06, 64.53, 54.98; IR (neat, ν_{max}) 3157, 3030, 2860, 2254, 1747, 146, 1381, 1271, 1091, 913, 746, 650 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{19}H_{20}O_4$ $[M+Na]^+$: 335.1254, found: 335.1255.



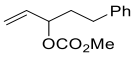
3,3-diphenylallyl methyl carbonate (S13)

white solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.15 (m, 10H), 6.19 (t, *J* = 7.0 Hz, 1H), 4.68 (d, *J* = 6.9 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.86, 147.15, 141.47, 138.62, 129.82, 128.49, 128.36, 128.11, 128.02, 127.85, 121.71, 66.12, 54.97; IR (neat, ν_{max}) 3413, 3400, 3377, 3012, 2858, 2809, 1444, 1267, 1058, 1005, 906, 733, 650 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{17}H_{16}O_3$ $[M+Na]^+$: 291.0992, found: 291.0991.



methyl ((2*E*,6*E*)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl) carbonate (S14)

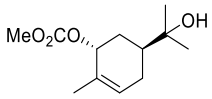
clear oil; ^1H NMR (400 MHz, $CDCl_3$) δ 5.38 (t, *J* = 6.7 Hz, 1H), 5.09 (t, *J* = 5.8 Hz, 2H), 4.66 (d, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 2.08 (dt, *J* = 15.2, 7.4 Hz, 6H), 1.99 – 1.95 (m, 2H), 1.72 (s, 3H), 1.68 (s, 3H), 1.60 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.03, 143.42, 135.67, 131.49, 124.44, 123.69, 117.83, 64.88, 54.79, 39.83, 39.66, 26.86, 26.30, 25.85, 17.84, 16.68, 16.16; IR (neat, ν_{max}) 3483, 3412, 3031, 2973, 2860, 2790, 1745, 1272, 1059, 1001, 908, 738, 651 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{17}H_{28}O_3$ $[M+Na]^+$: 303.1931, found: 303.1929.



methyl (5-phenylpent-1-en-3-yl) carbonate (S15)[5]

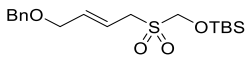
white solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.26 (m, 2H), 7.21 – 7.19 (m, 3H), 5.83 (ddd, *J* = 17.2, 10.5, 6.7 Hz, 1H), 5.29 (dd, *J* = 31.7, 13.9 Hz, 2H), 5.09 (dd, *J* = 13.1, 6.6 Hz, 1H), 3.79 (s, 3H), 2.69 (dd, *J* = 15.3,

8.8 Hz, 2H), 2.05 (ddd, J = 13.8, 11.8, 6.9 Hz, 1H), 1.93 (ddt, J = 12.6, 9.8, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.36, 141.25, 135.88, 128.61, 128.50, 126.19, 117.96, 78.69, 54.81, 36.01, 31.41. IR (neat, ν_{max}) 3060, 2984, 2305, 1743, 1443, 1421, 1263, 939, 860, 735 cm^{-1}



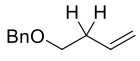
(1*RS*,5*SR*)-5-(2-hydroxypropan-2-yl)-2-methylcyclohex-2-en-1-yl methyl carbonate (S16)

clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (d, J = 5.4 Hz, 1H), 5.10 (s, 1H), 3.79 (s, 3H), 2.15 (t, J = 15.0 Hz, 2H), 1.85 – 1.77 (m, 2H), 1.73 (s, 3H), 1.49 (td, J = 13.5, 3.7 Hz, 1H), 1.20 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.95, 130.32, 128.57, 75.33, 72.13, 54.79, 39.30, 29.87, 27.82, 27.01, 26.55, 20.76; IR (neat, ν_{max}) 3155, 2973, 2878, 2254, 1739, 1442, 1384, 1270, 1079, 1163, 980, 917, 745, 650 cm^{-1} HRMS (ESI) *m/z* calc. for $C_{12}H_{20}O_4$ [M+Na]$^+$: 251.1254, found: 251.1256.



(*E*)-(((4-(benzyloxy)but-2-en-1-yl)sulfonyl)methoxy)(*tert*-butyl)dimethylsilane (S17)

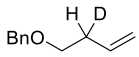
yellow oil (*E*:*Z* = 10:1); R_f = 0.62 (hexanes: EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 6.00 (dt, J = 15.5, 5.4 Hz, 1H), 5.82 (m, 1H), 4.52 (d, J = 5.0 Hz, 4H), 4.07 (d, J = 5.3 Hz, 2H), 3.74 (d, J = 7.4 Hz, 2H), 0.93 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.99, 137.12, 128.59, 127.91, 127.89, 118.53, 72.65, 69.70, 52.60, 25.69, 18.35, -5.21; IR (neat, ν_{max}) 3543, 3252, 3088, 2858, 2743, 1794, 1470, 1049, 1012, 647 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{18}H_{30}O_4SSi$ [M+Na]$^+$: 393.1526, found: 393.1526



((but-3-en-1-yloxy)methyl)benzene (S18)[1]

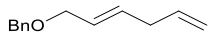
clear oil; R_f = 0.68 (hexanes: EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 5H), 5.84 (ddt, J = 17.0,

10.2, 6.7 Hz, 1H), 5.08 (ddd, *J* = 29.6, 14.2, 5.9 Hz, 2H), 4.52 (s, 2H), 3.53 (t, *J* = 6.8 Hz, 2H), 2.38 (q, *J* = 6.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.61, 135.41, 128.50, 127.79, 127.68, 116.50, 73.05, 69.76, 34.39.



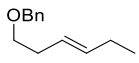
(((but-3-en-1-yl-2-*d*)oxy)methyl)benzene (S19)

clear oil; R_f = 0.55 (hexanes: EA = 10 :1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 5H), 5.85 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.06 (ddd, *J* = 14.5, 14.0, 4.7 Hz, 2H), 4.52 (s, 2H), 3.52 (d, *J* = 6.4 Hz, 2H), 2.37 (dt, *J* = 6.9, 3.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.59, 135.35, 128.49, 127.77, 127.67, 116.53, 73.04, 69.70, 34.37, 34.23, 34.03, 33.83; IR (neat, ν_{max}) 3686, 3157, 3085, 2860, 2790, 2256, 1455, 1061, 999, 645 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{11}H_{13}DO$ $[M+Na]^+$: 186.1000, found: 186.0997.



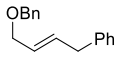
(*E*)-((hexa-2,5-dien-1-yloxy)methyl)benzene (S20)[1]

clear oil; R_f = 0.59 (hexanes: EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 5H), 5.85 (ddd, *J* = 16.8, 10.0, 5.1 Hz, 1H), 5.75 (m, 1H), 5.64 (dtd, *J* = 7.3, 5.9, 1.2 Hz, 1H), 5.04 (m, 2H), 4.51 (s, 2H), 4.00 (d, *J* = 5.9 Hz, 2H), 2.82 (t, *J* = 5.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.52, 136.47, 132.16, 128.51, 127.93, 127.70, 127.60, 115.70, 72.14, 70.87, 36.57.



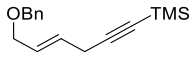
(*E*)-((hex-3-en-1-yloxy)methyl)benzene (S21)[1,6]

clear oil (*E*:*Z* = 3.3:1); R_f = 0.52 (hexanes: EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 5H), 5.55 (m, 1H), 5.41 (m, 1H), 4.52 (s, 2H), 3.48 (t, *J* = 6.6 Hz, 2H), 2.32 (dd, *J* = 13.6, 6.8 Hz, 2H), 2.03 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.73, 134.31, 128.49, 127.79, 127.64, 125.35, 72.98, 70.43, 33.20, 25.80, 13.93.



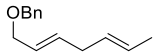
(*E*)-(4-(benzyloxy)but-2-en-1-yl)benzene (S22)[1,7]

clear oil (*E*:*Z* = 7.2:1); R_f = 0.57 (hexanes: EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.15 (m, 10H), 5.88 (m, 1H), 5.67 (dt, *J* = 15.3, 6.1 Hz, 1H), 4.50 (s, 2H), 4.00 (d, *J* = 6.0 Hz, 2H), 3.40 (d, *J* = 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.13, 138.48, 133.18, 128.73, 128.56, 128.49, 127.92, 127.89, 127.69, 126.23, 72.17, 70.79, 38.69.



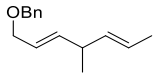
(*E*)-(6-(benzyloxy)hex-4-en-1-yn-1-yl)trimethylsilane (S23)[1]

clear oil (*E*:*Z* = 8.1:1); R_f = 0.49 (hexanes: EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 5H), 5.88 (dt, *J* = 15.0, 5.9 Hz, 1H), 5.70 (ddd, *J* = 17.2, 11.1, 5.1 Hz, 1H), 4.52 (s, 2H), 4.03 (d, *J* = 5.1 Hz, 2H), 3.02 (d, *J* = 5.1 Hz, 2H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.42, 128.53, 128.38, 127.94, 127.76, 127.66, 103.66, 87.03, 72.27, 70.36, 23.07, 0.25.



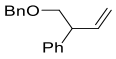
((((2*E*,5*E*)-hepta-2,5-dien-1-yl)oxy)methyl)benzene (S24)[1]

clear oil (*E*:*Z* = 2.5:1); R_f = 0.58 (hexanes: EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 5H), 5.72 (m, 1H), 5.62 (m, 1H), 5.55 - 5.40 (m, 2H), 4.50 (s, 2H), 3.98 (d, *J* = 6.0 Hz, 2H), 2.73 (m, 2H), 1.66 (d, *J* = 4.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.55, 133.22, 128.87, 128.47, 127.91, 127.65, 126.90, 126.32, 72.11, 70.94, 35.43, 18.03.



((((2*E*,5*E*)-4-methylhepta-2,5-dien-1-yl)oxy)methyl)benzene (S25)

clear oil (*E*:*Z* = 9.5:1); R_f = 0.59 (hexanes: EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 5H), 5.67 (dd, *J* = 15.5, 6.4 Hz, 1H), 5.56 (dt, *J* = 11.3, 5.9 Hz, 1H), 5.48 – 5.35 (m, 2H), 4.50 (s, 2H), 3.98 (d, *J* = 6.0 Hz, 2H), 2.83 (dd, *J* = 12.7, 6.5 Hz, 1H), 1.66 (d, *J* = 5.4 Hz, 3H), 1.08 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.12, 138.57, 135.22, 128.50, 127.97, 127.68, 124.70, 123.98, 72.12, 71.09, 39.28, 20.32, 18.09. IR (neat, ν_{max}) 3028, 2962, 2925, 2853, 1736, 1496, 1452, 1360, 1204, 1099, 1073, 1027, 968, 905, 735, 696 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{15}H_{20}O$ [M+Na]$^+$: 239.1406, found: 239.14064.

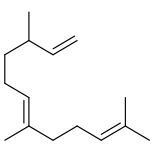


(1-(benzyloxy)but-3-en-2-yl)benzene (S26)[8]

clear oil; R_f = 0.57 (hexanes: EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 10H), 6.04 (ddd, *J* = 17.1, 10.4, 6.6 Hz, 1H), 5.12 (m, 2H), 4.51 (s, 2H), 3.68 (m, 3H); ^{13}C NMR (101 MHz, cdcl$_3$) δ 141.58, 139.13, 138.46, 128.59, 128.46, 128.18, 127.72, 127.65, 126.72, 116.13, 73.74, 73.18, 49.90; IR (neat, ν_{max}) 2961, 1660, 1511, 1473, 1429, 1347, 1141, 1036, 948, 777, 717, 697 cm^{-1}; HRMS (ESI) *m/z* calc. for $C_{17}H_{18}O$ [M+Na]$^+$: 261.1250, found: 261.1248.

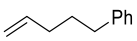
prop-2-ene-1,1-diyldibenzene (S27)[9]

clear oil; R_f = 0.18 (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 10H), 6.30 (m, 1H), 5.22 (d, *J* = 10.0 Hz, 1H), 4.99 (d, *J* = 17.0 Hz, 1H), 4.73 (d, *J* = 5.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.43, 140.78, 128.74, 128.54, 126.48, 116.49, 55.15.



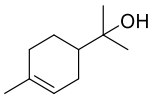
(*E*)-3,7,11-trimethyldodeca-1,6,10-triene (S28)[1]

clear oil; R_f = 0.88 (hexanes: EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70 (ddd, *J* = 17.5, 10.3, 7.6 Hz, 1H), 5.10 (m, 2H), 4.98 – 4.90 (m, 2H), 2.16 – 1.95 (m, 7H), 1.68 (s, 3H), 1.60 (s, 3H), 1.59 (s, 3H), 1.32 (m, 2H), 0.99 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.94, 135.02, 131.41, 124.71, 124.55, 112.59, 39.90, 37.47, 36.89, 26.86, 25.85, 25.77, 20.31, 17.84, 16.14.



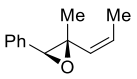
pent-4-en-1-ylbenzene (S29)[1]

clear oil; R_f = 0.85 (hexanes: EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.20 – 7.18 (m, 3H), 5.84 (dddd, *J* = 16.9, 13.3, 6.6, 3.3 Hz, 1H), 5.03 (dd, *J* = 17.1, 1.6 Hz, 1H), 4.99 (m, 1H), 2.63 (t, *J* = 7.7 Hz, 2H), 2.10 (d, *J* = 7.4 Hz, 2H), 1.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.60, 138.75, 128.59, 128.41, 125.82, 114.84, 35.47, 33.44, 30.77.



2-(4-methylcyclohex-3-en-1-yl)propan-2-ol (S30)[10]

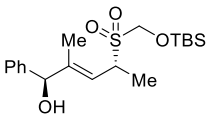
clear oil; R_f = 0.60 (hexanes: EA = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (s, 1H), 2.06 – 1.97 (m, 2H), 1.92 – 1.85 (m, 1H), 1.85 – 1.74 (m, 1H), 1.65 (s, 3H), 1.50 (tdd, *J* = 12.0, 4.9, 2.4 Hz, 1H), 1.32 – 1.23 (m, 2H), 1.19 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.15, 120.67, 72.89, 45.12, 31.14, 27.59, 27.02, 26.40, 24.10, 23.49.



(2*S*,3*S*)-2-methyl-3-phenyl-2-((*Z*)-prop-1-en-1-yl)oxirane (S31)

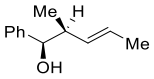
yellow oil; 98% *ee*[11]; R_f = 0.12 (hexanes: EA = 50:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 5.74

(dd, J = 11.0, 1.4 Hz, 1H), 5.61 (dq, J = 11.1, 6.9 Hz, 1H), 4.01 (s, 3H), 1.83 (dd, J = 6.9, 1.5 Hz, 3H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.28, 131.34, 128.26, 127.66, 126.99, 126.58, 64.98, 62.02, 17.44, 14.45; IR (neat, ν_{max}) 3021, 2963, 1655, 1603, 1495, 1448, 1377, 1247, 1279, 1247, 1208, 1117, 1073, 1048, 1027, 991. 935, 899, 849, 816, 756, 697 cm^{-1}; $[\alpha]^{20}{}_D$ = +27.3 (c 1.02, $CHCl_3$); HRMS (ESI) m/z calc. for $C_{12}H_{14}O$ $[M+Na]^+$: 197.0937, found: 197.09369.



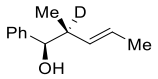
(1*R*,4*R*,*E*)-4-((((*tert*-butyldimethylsilyl)oxy)methyl)sulfonyl)-2-methyl-1-phenylpent-2-en-1-ol (S32)

yellow oil; 97% *ee*; R_f = 0.23 (hexanes: EA = 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 5H), 5.73 (d, J = 10.5 Hz, 1H), 5.20 (d, J = 2.9 Hz, 1H), 4.54 (d, J = 11.6 Hz, 1H), 4.34 (d, J = 11.6 Hz, 1H), 4.16 (dq, J = 10.5, 7.0 Hz, 1H), 2.08 (d, J = 3.4 Hz, 1H), 1.51 (d, J = 7.0 Hz, 3H), 0.85 (s, 9H), 0.14 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.80, 141.48, 128.69, 128.01, 126.23, 119.46, 76.62, 75.55, 52.85, 25.63, 18.36, 12.97, 12.55, -5.09, -5.53; IR (neat, ν_{max}) 3494, 2952, 2927, 2956, 1493, 1451, 1361, 1332, 1298, 1255, 1151, 1113, 1059, 1020, 937, 831, 782, 738, 701, 666 cm^{-1}; $[\alpha]^{20}{}_D$ = +11.8 (c 0.91, $CHCl_3$); HRMS (ESI) m/z calc. for $C_{19}H_{32}O_4SSi$ $[M+Na]^+$: 407.1683, found: 407.16827. (CHIRALPACK IA, Hex:IPA = 98:2, 1.0 mL/min, t_R (minor) = 38.942 min, t_R (major) = 47.326 min)



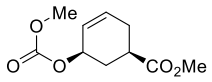
(1*R*,2*S*,*E*)- 2-methyl-1-phenylpent-3-en-1-ol (S33)[1]

yellow oil; 97% *ee*[11]; R_f = 0.21 (hexanes: EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 5H), 5.48 (dt, J = 21.1, 6.0 Hz, 1H), 5.35 (dd, J = 15.4, 6.9 Hz, 1H), 4.58 (d, J = 4.7 Hz, 1H), 2.52 (dd, J = 12.6, 6.3 Hz, 1H), 1.98 (s, 1H), 1.65 (d, J = 6.0 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.79, 132.94, 128.08, 127.29, 126.63, 126.53, 77.50, 43.79, 18.24, 14.65; $[\alpha]^{20}{}_D$ = +0.92 (c 0.89, $CHCl_3$); The absolute stereochemistry was determined by chiral HPLC analysis based on the previous report.[12] (CHIRALCEL OD-H, Hex:IPA = 99.8:0.2, 1.0 mL/min, t_R (major) = 57.693 min, t_R (minor) = 72.808 min)



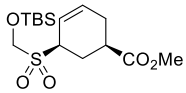
(1*R*,2*S*,*E*)- 2-methyl-1-phenylpent-3-en-2-*d*-1-ol (S34)

yellow oil; R_f = 0.24 (hexanes: EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 5H), 5.48 (m, 1H), 5.35 (d, *J* = 15.5 Hz, 1H), 2.00 (s, 1H), 1.65 (d, *J* = 6.1 Hz, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.81, 132.90, 128.07, 127.28, 126.63, 126.51, 77.47, 43.54, 43.34, 43.15, 18.22, 14.58; IR (neat, ν_{max}) 3395, 3027, 2962, 2918, 2852, 1603, 1493, 1451, 1375, 1249, 1198, 1084, 1054, 1022, 965, 910, 758, 700 cm^{-1}; $[\alpha]^{20}{}_D$ = +24.2 (*c* 0.98, $CHCl_3$); HRMS (ESI) *m/z* calc. for $C_{12}H_{15}DO$ $[M+Na]^+$: 200.1156, found: 200.11561.



Methyl (1*RS*,5*RS*)-5-((methoxycarbonyl)oxy)cyclohex-3-ene-1-carboxylate (S35)[13]

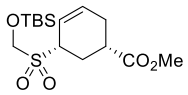
clear oil; R_f = 0.34 (hexanes: EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (dtd, *J* = 9.9, 3.7, 1.8 Hz, 1H), 5.73 – 5.69 (m, 1H), 5.28 – 5.24 (m, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 2.73 (tdd, *J* = 10.7, 7.8, 3.0 Hz, 1H), 2.46 – 2.42 (m, 1H), 2.32 (ddd, *J* = 8.5, 5.9, 2.8 Hz, 2H), 1.84 (td, *J* = 12.3, 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.48, 155.47, 129.81, 126.19, 73.07, 54.80, 52.00, 37.73, 30.51, 27.25.



Methyl (1*R*,5*R*)-5-((((*tert*-butyldimethylsilyl)oxy)methyl)sulfonyl)cyclohex-3-ene-1-carboxylate (36a)

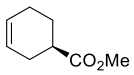
clear oil; 98% *ee*[11]; R_f = 0.24 (hexanes: EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 – 6.12 (m, 1H), 5.88 (d, *J* = 10.1 Hz, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 4.56 (d, *J* = 11.9 Hz, 1H), 3.97 (m, 1H), 3.72 (s, 3H), 2.83 – 2.59 (m, 1H), 2.53 – 2.49 (m, 1H), 2.44 – 2.39 (m, 1H), 2.34 – 2.29 (m, 1H), 2.10 (dd, *J* = 24.6, 12.8 Hz, 1H), 0.92 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.36, 132.94, 118.13, 76.70, 57.88, 52.20, 38.42, 27.43, 25.67, 24.85, 18.33, -5.18, -5.31; IR (neat, ν_{max}) 2953, 2931, 2857, 1733, 1463, 1436, 1363, 1302, 1255, 1209, 1150, 1112, 1058, 1005, 939, 917, 886, 831, 783, 732 cm^{-1}; $[\alpha]^{20}{}_D$ = +24.6 (*c* 0.26, CH_3OH); HRMS (ESI) *m/z*

calc. for $C_{15}H_{28}O_5SSi$ $[M+Na]^+$: 371.1319, found: 371.1322.



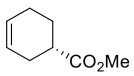
Methyl (1*S*,5*S*)-5-((((*tert*-butyldimethylsilyl)oxy)methyl)sulfonyl)cyclohex-3-ene-1-carboxylate (36b)

clear oil; 98% *ee*[11]; R_f = 0.24 (hexanes: EA = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 – 6.12 (m, 1H), 5.88 (d, *J* = 10.1 Hz, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 4.56 (d, *J* = 11.9 Hz, 1H), 3.97 (m, 1H), 3.72 (s, 3H), 2.83 – 2.59 (m, 1H), 2.53 – 2.49 (m, 1H), 2.44 – 2.39 (m, 1H), 2.34 – 2.29 (m, 1H), 2.10 (dd, *J* = 24.6, 12.8 Hz, 1H), 0.92 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.36, 132.94, 118.13, 76.70, 57.88, 52.20, 38.42, 27.43, 25.67, 24.85, 18.33, -5.18, -5.31; IR (neat, ν_{max}) 2953, 2931, 2857, 1733, 1463, 1436, 1363, 1302, 1255, 1209, 1150, 1112, 1058, 1005, 939, 917, 886, 831, 783, 732 cm^{-1}; $[\alpha]^{20}{}_D$ = -13.7 (*c* 0.25, CH_3OH); HRMS (ESI) *m/z* calc. for $C_{15}H_{28}O_5SSi$ $[M+Na]^+$: 371.1319, found: 371.1322.



Methyl (*R*)-cyclohex-3-ene-1-carboxylate (S37a)[1]

yellow oil; 96% *ee*[11]; R_f = 0.29 (hexanes: EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 – 5.66 (m, 2H), 3.69 (s, 3H), 2.60 – 2.54 (m, 1H), 2.26 – 2.24 (m, 2H), 2.12 – 2.08 (m, 2H), 2.01 (ddd, *J* = 12.4, 9.8, 6.3 Hz, 1H), 1.69 (dddd, *J* = 12.8, 11.3, 9.5, 6.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.35, 126.72, 125.26, 51.67, 39.31, 27.53, 25,17, 24.52.



Methyl (*S*)-cyclohex-3-ene-1-carboxylate (S37b)[14]

yellow oil; 96% *ee*[11]; R_f = 0.29 (hexanes: EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 – 5.66 (m, 2H), 3.69 (s, 3H), 2.60 – 2.54 (m, 1H), 2.26 – 2.24 (m, 2H), 2.12 – 2.08 (m, 2H), 2.01 (ddd, *J* = 12.4, 9.8, 6.3 Hz, 1H),

1.69 (dddd, J = 12.8, 11.3, 9.5, 6.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.35, 126.72, 125.26, 51.67, 39.31, 27.53, 25,17, 24.52.

VIII. References

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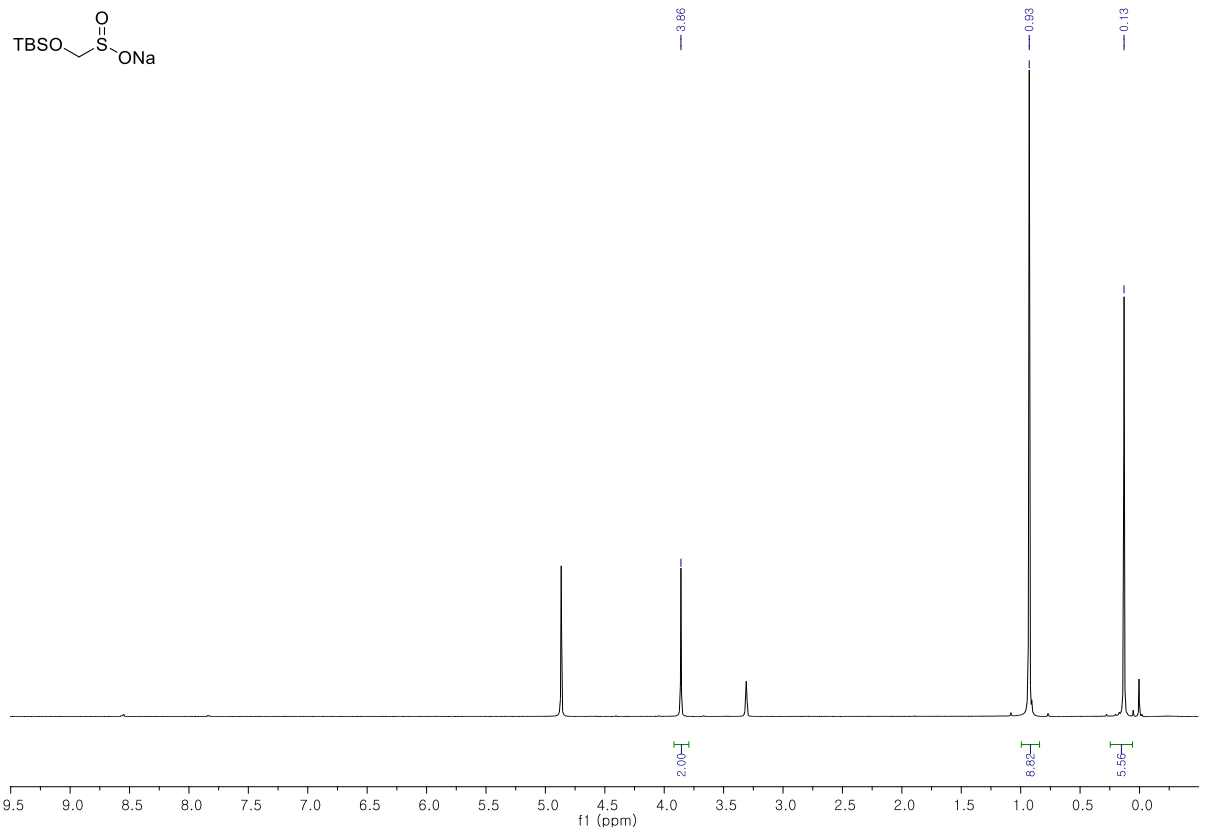
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O
S
ONa
3.86
0.93
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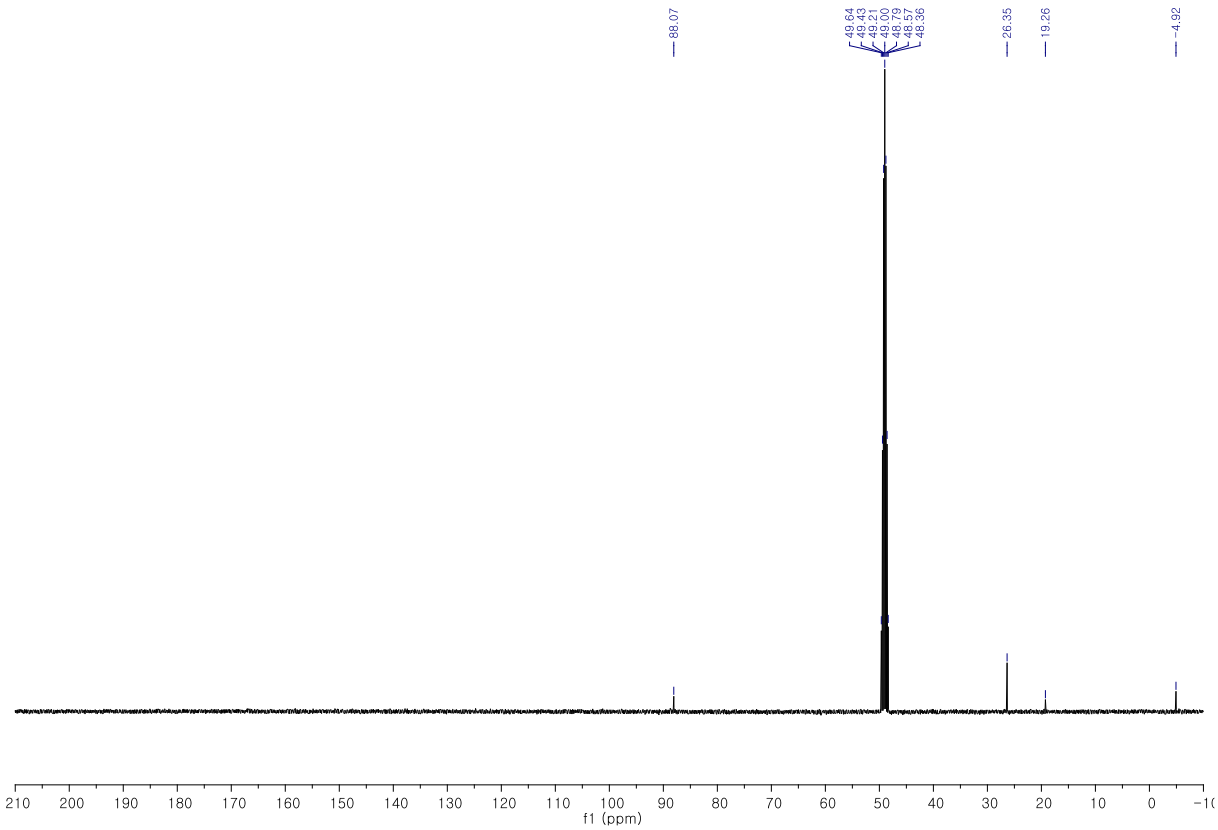
2.00
8.82
5.56
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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49.43
49.21
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-4.92
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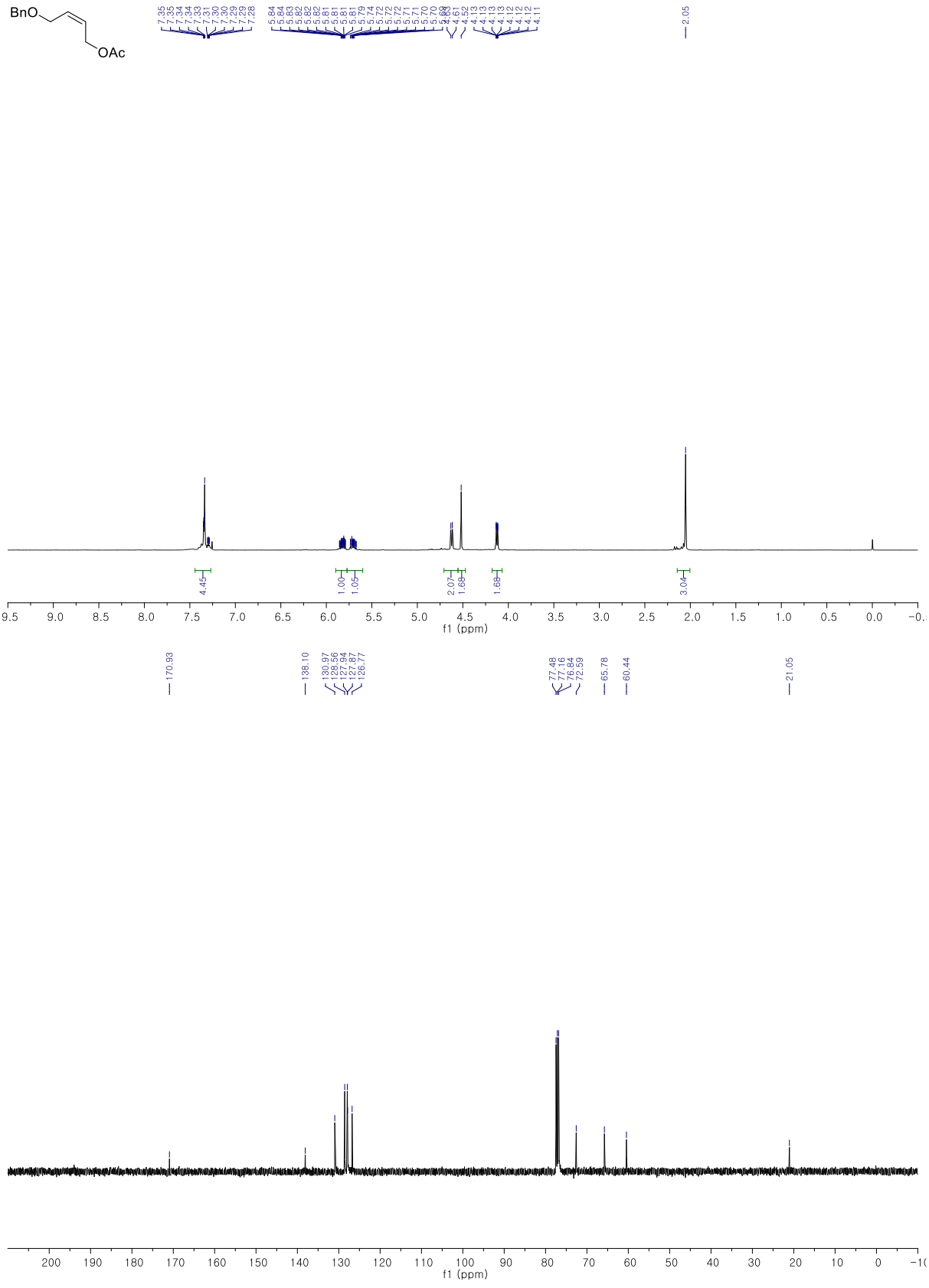
f1 (ppm)


BnO
OAc
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7.35
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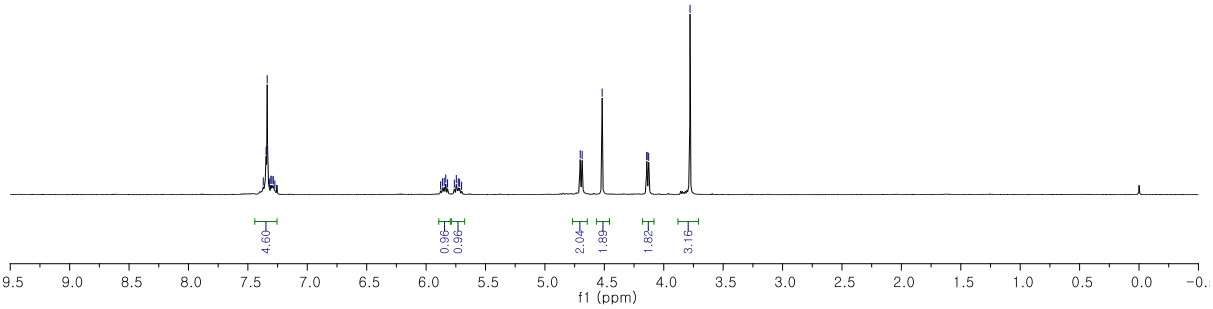
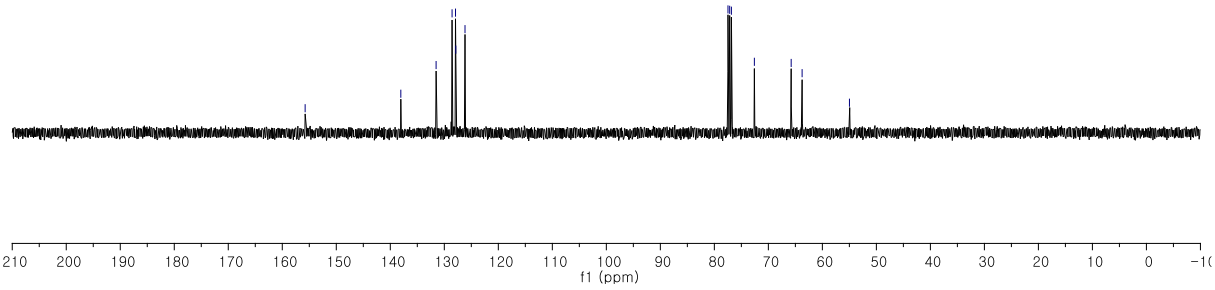
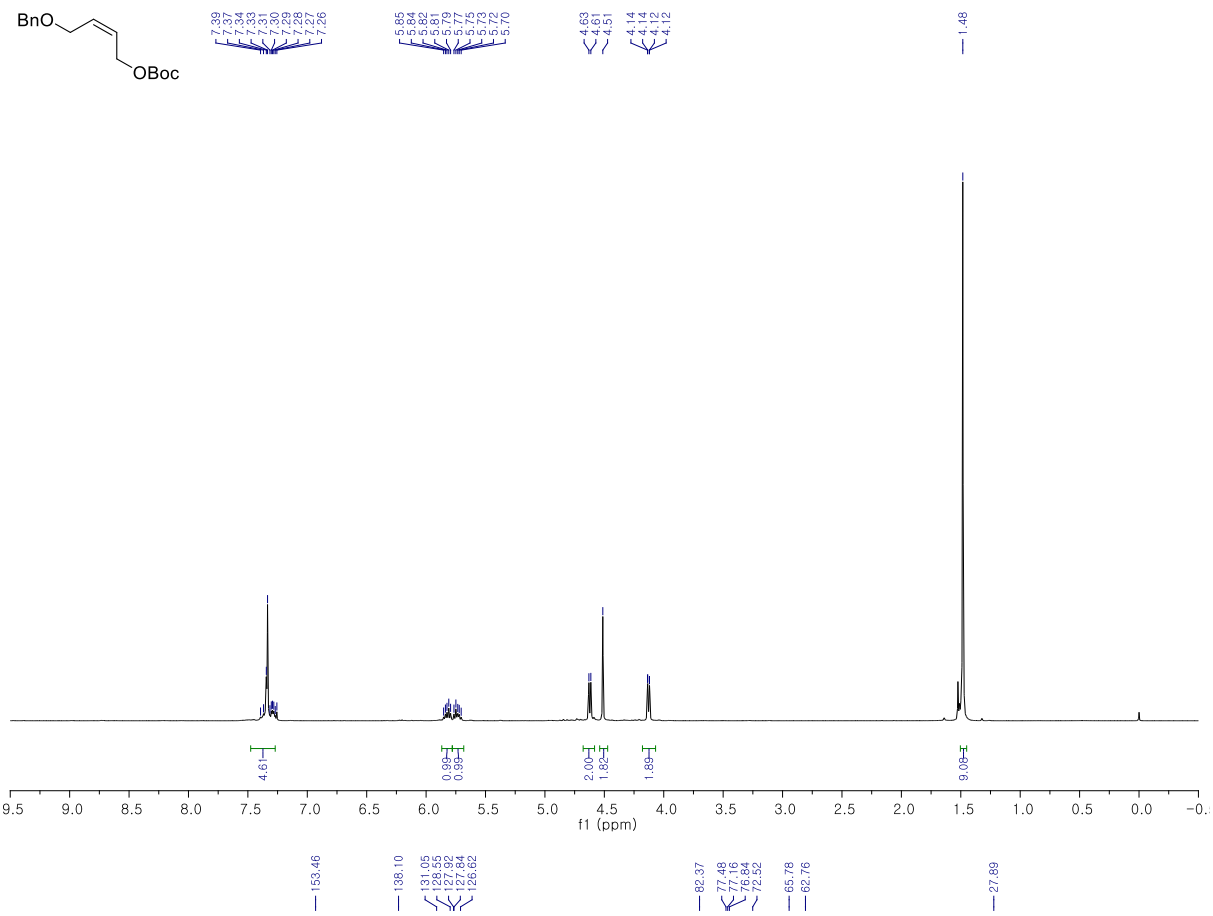
5.81
5.81
5.81
5.79
5.74
5.72
5.72
5.72
5.71
5.71
5.70
5.70
4.61
4.52
4.13
4.13
4.13
4.12
4.12
4.12
4.12
4.11
2.05
4.45
1.00
1.05
2.07
1.68
1.68
3.04
f1 (ppm)
170.93
138.10
130.97
129.56
127.94
127.87
126.77
77.48
77.16
76.84
72.59
65.78
60.44
21.05
f1 (ppm)

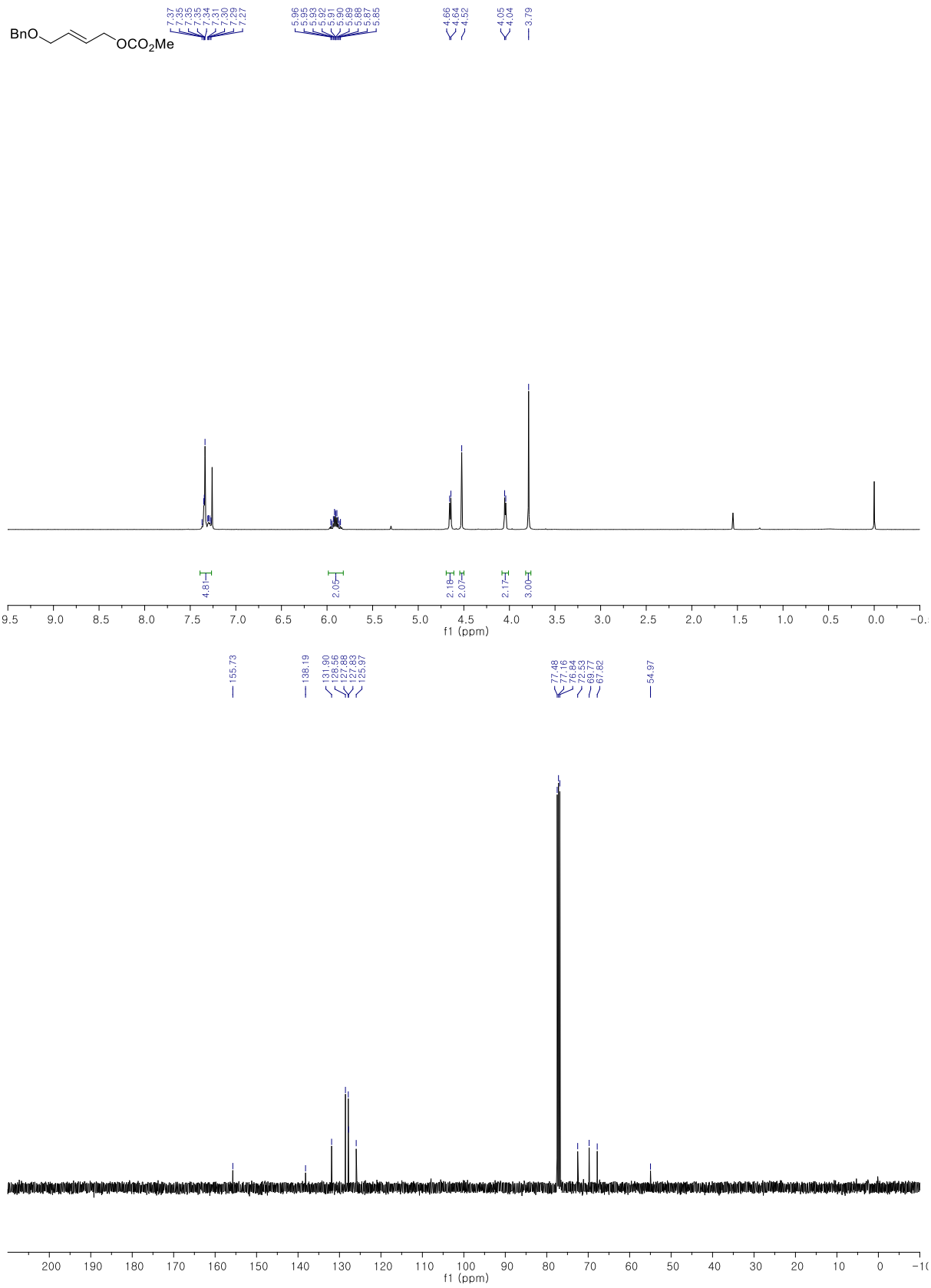

BnO
OCO2Me
7.37
7.35
7.34
7.32
7.31
7.30
7.29
7.27
5.88
5.86
5.85
5.83
5.82
5.76
5.75
5.73
5.72
5.70
4.70
4.69
4.62
4.14
4.14
4.13
3.78


4.60
0.96
0.96
2.04
1.89
1.82
3.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

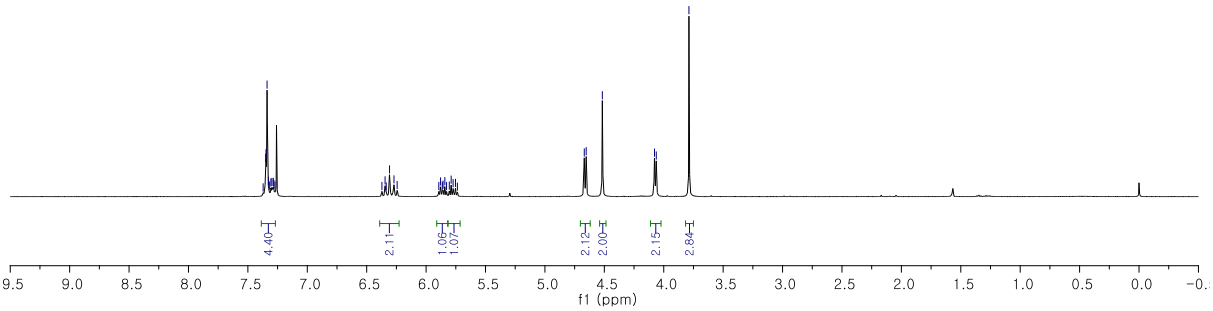

155.77
138.05
131.52
129.56
127.98
127.87
126.17
77.48
77.16
76.84
72.59
65.78
63.75
54.98


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

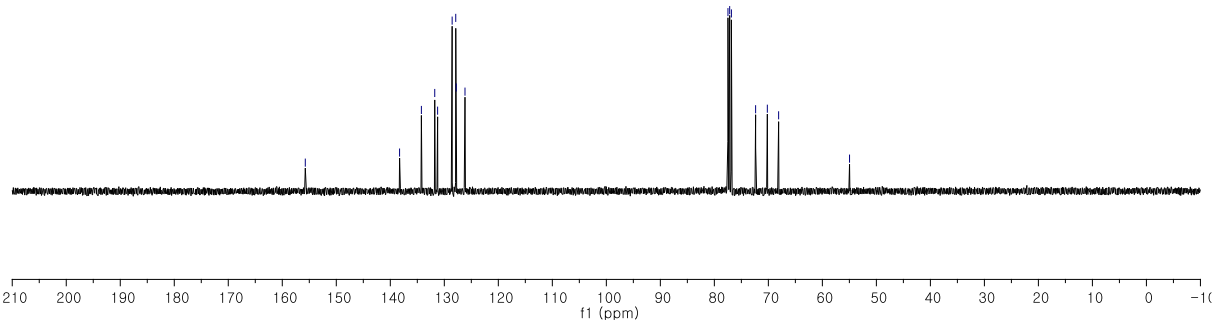

BnO
OBoc
7.39
7.37
7.34
7.33
7.31
7.30
7.29
7.28
7.27
7.26
5.85
5.84
5.82
5.81
5.79
5.77
5.75
5.73
5.72
5.70
4.63
4.61
4.51
4.14
4.14
4.12
4.12
1.48
4.61
0.99
0.99
2.00
1.82
1.89
9.08
f1 (ppm)
153.46
138.10
131.05
129.55
127.92
127.84
126.62
82.37
77.48
77.16
76.84
72.52
65.78
62.76
27.89
f1 (ppm)

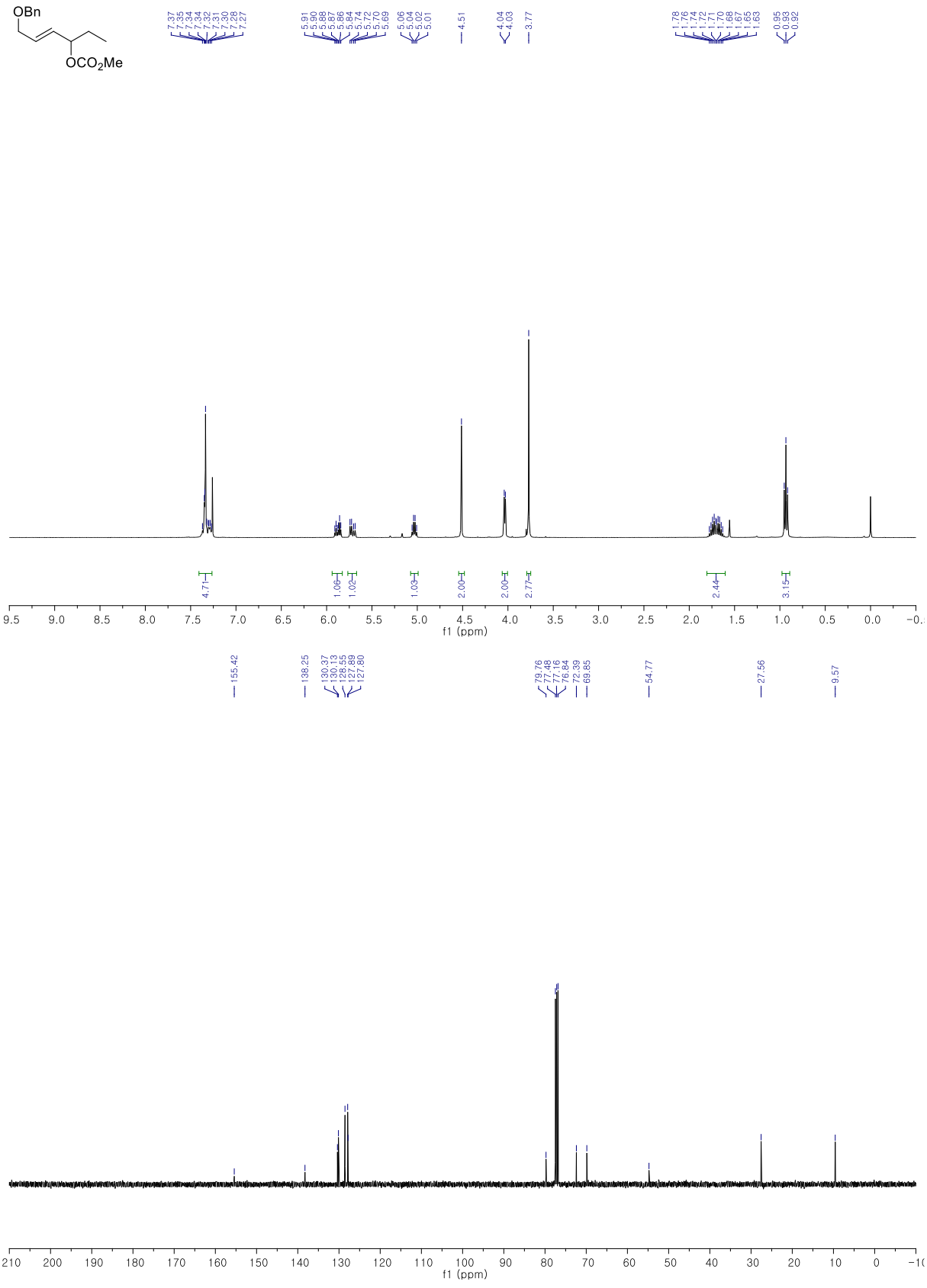

BnO
OCO2Me
7.37
7.35
7.35
7.35
7.34
7.31
7.30
7.29
7.27
5.96
5.95
5.93
5.92
5.91
5.90
5.89
5.88
5.87
5.85
4.66
4.64
4.52
4.05
4.04
3.79
4.81
2.05
2.18
2.07
2.17
3.00
f1 (ppm)
155.73
138.19
131.90
128.55
127.88
127.83
125.97
77.48
77.16
76.84
72.53
69.77
67.82
54.97
f1 (ppm)

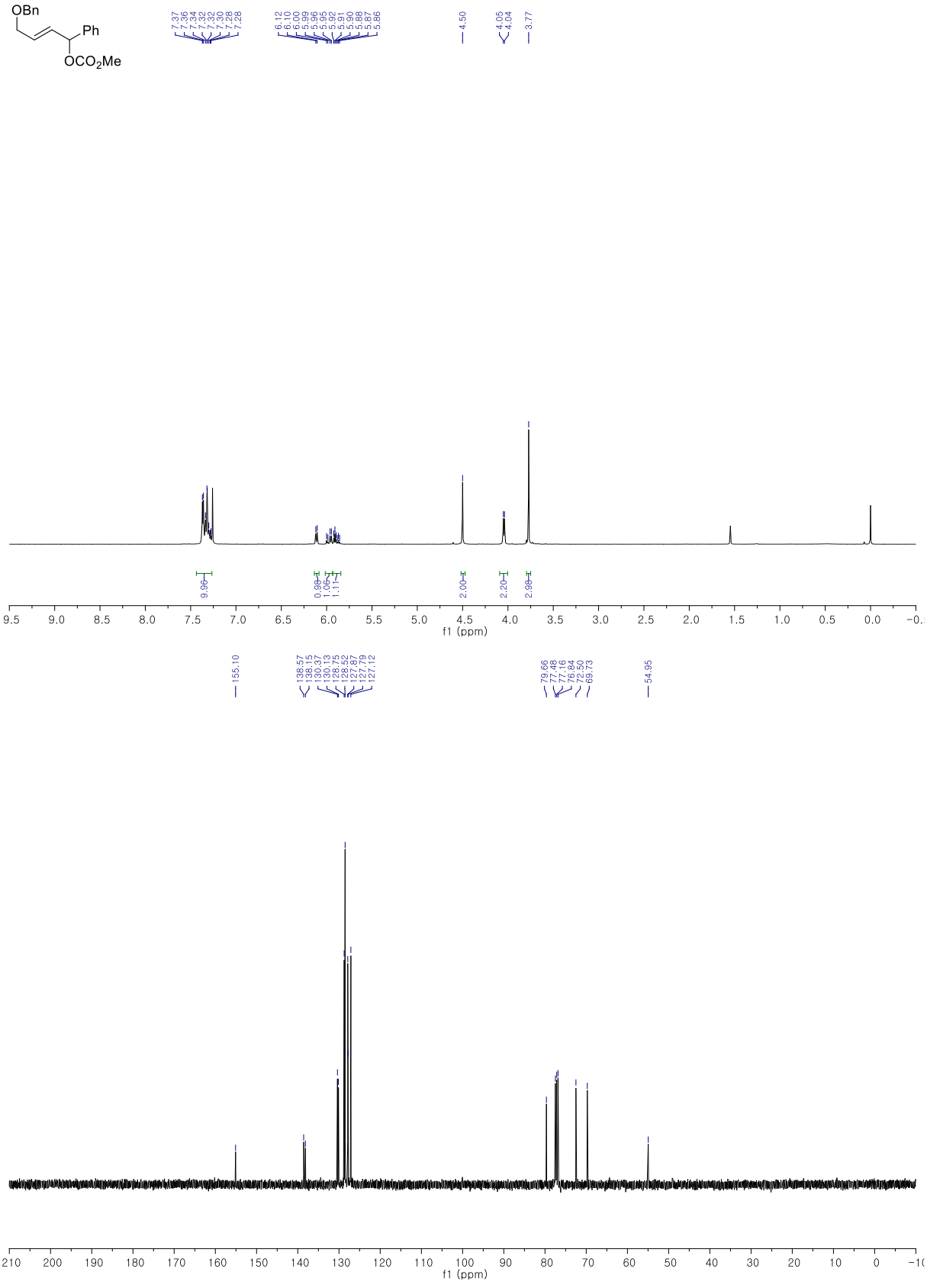

OBn
OCO2Me
7.37
7.35
7.35
7.34
7.33
7.32
7.31
7.30
7.29
7.28
7.27
6.37
6.35
6.34
6.31
6.27
6.24
5.89
5.88
5.86
5.84
5.83
5.80
5.79
5.77
5.75
5.74
4.67
4.65
4.52
4.08
4.06
3.79

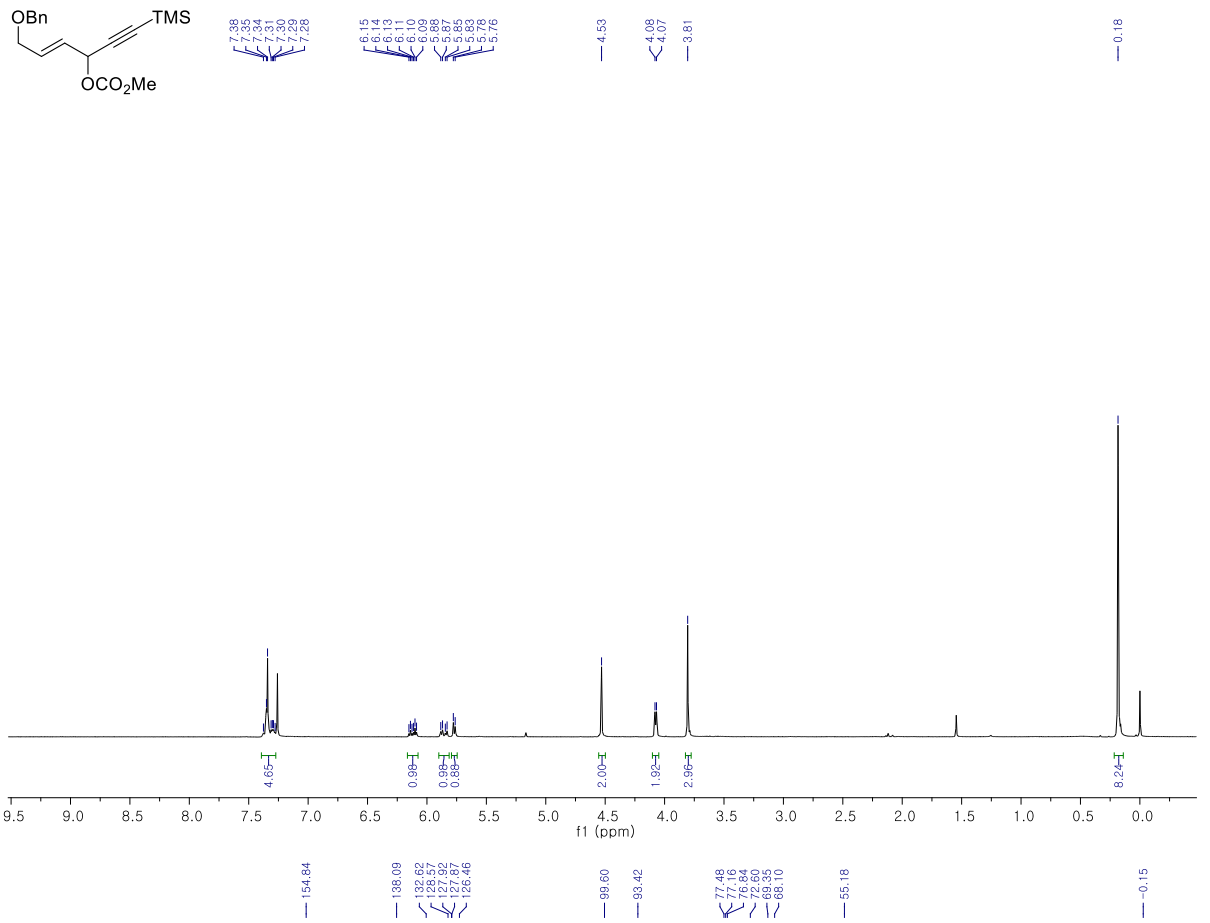

4.40
2.11
1.06
1.07
2.12
2.00
2.15
2.84
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

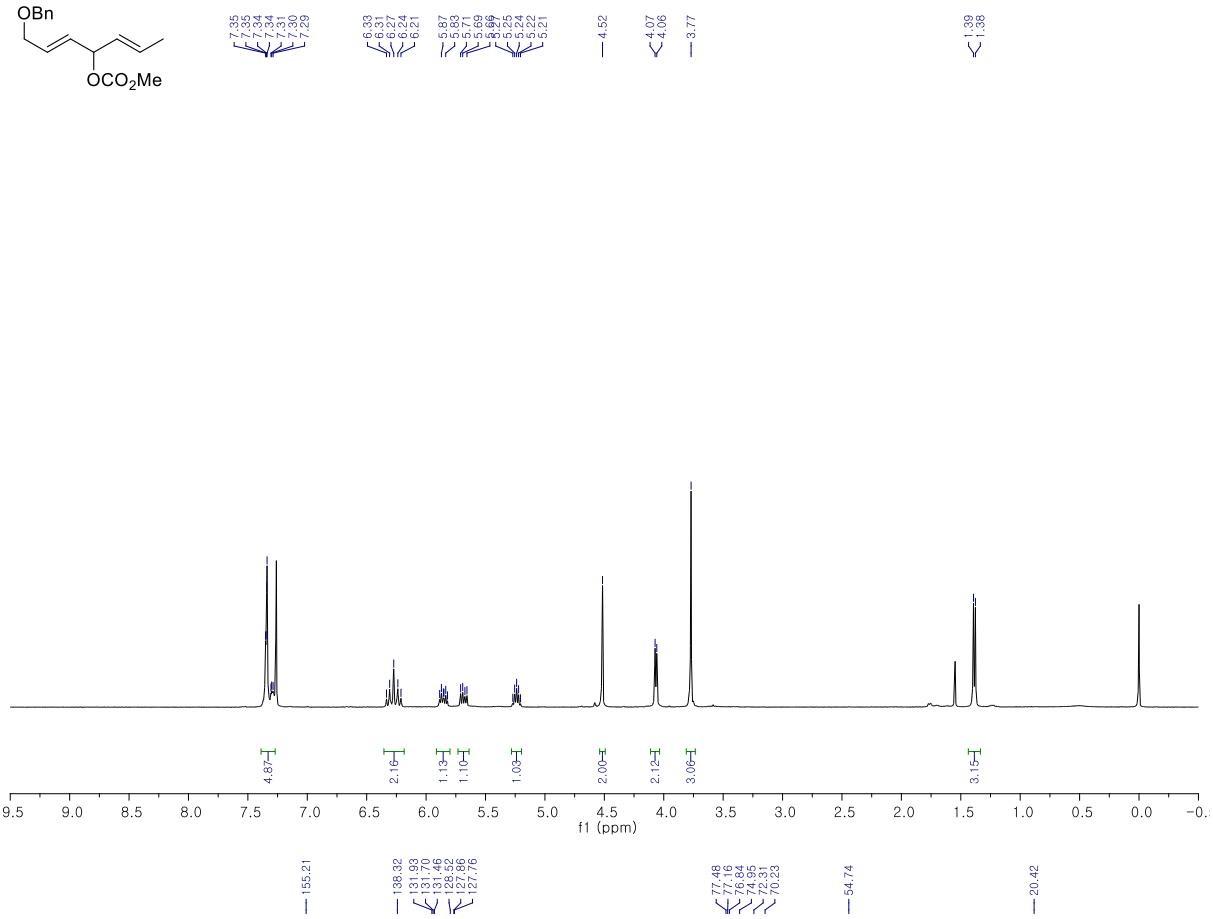

155.74
138.28
134.24
131.77
131.24
128.55
127.88
127.80
126.17
77.48
77.16
76.84
72.36
70.19
68.10
54.97

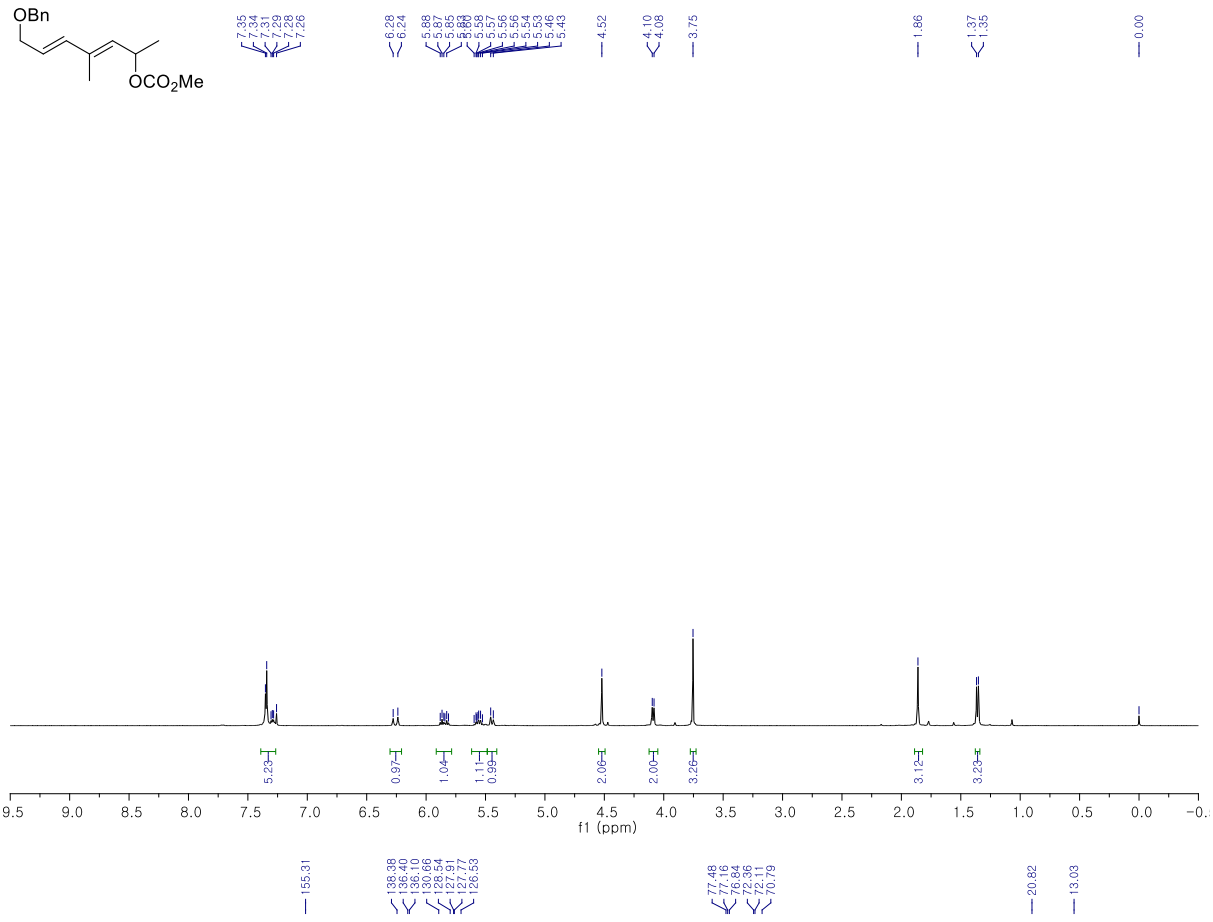

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

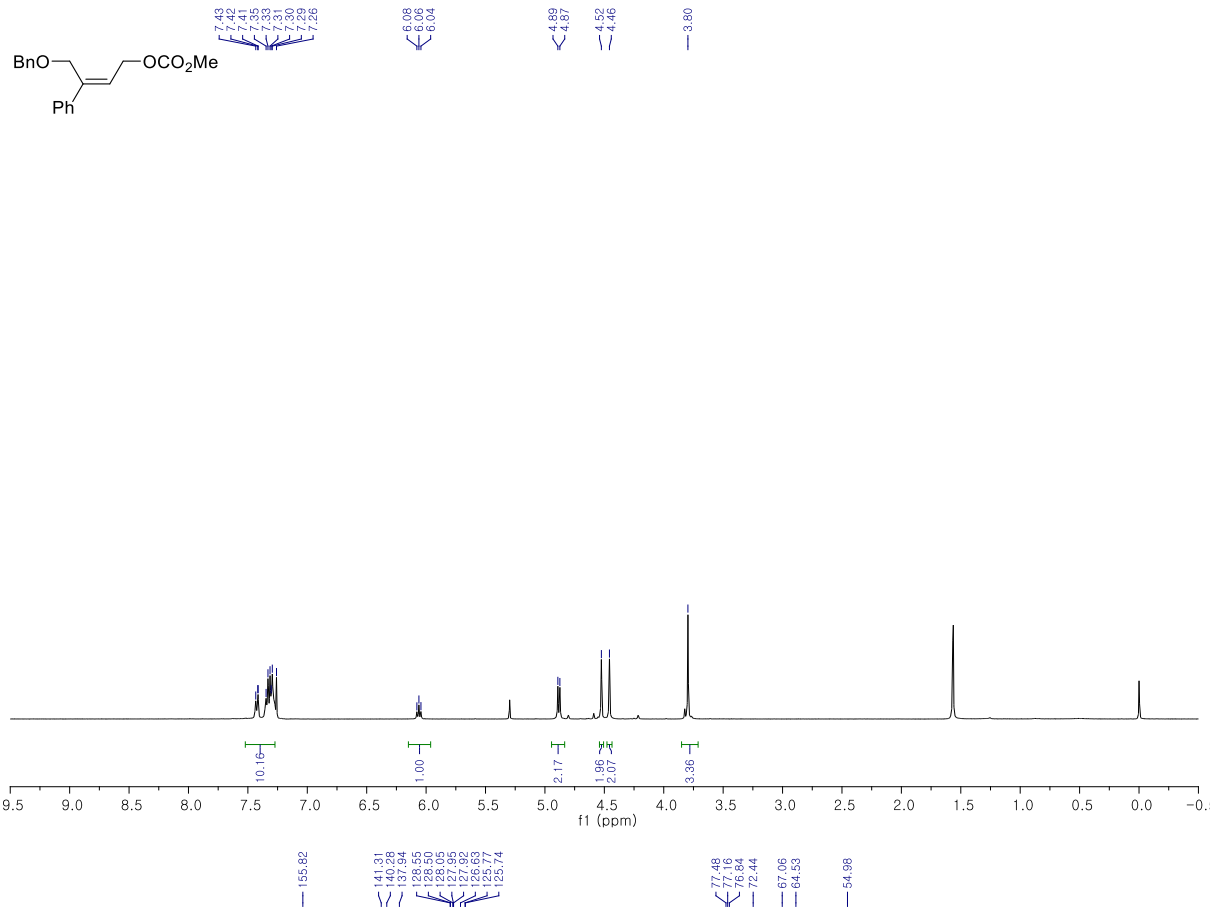

OBn
OCO2Me
7.37
7.35
7.34
7.34
7.32
7.31
7.30
7.28
7.27
5.91
5.90
5.89
5.87
5.86
5.84
5.74
5.72
5.70
5.69
5.06
5.04
5.02
5.01
4.51
4.04
4.03
3.77
1.78
1.76
1.74
1.72
1.71
1.70
1.68
1.67
1.65
1.63
0.95
0.93
0.92
4.71
1.06
1.02
1.03
2.00
2.00
2.77
2.44
3.15
f1 (ppm)
155.42
138.25
130.37
130.13
128.55
127.89
127.80
79.76
77.48
77.16
76.84
72.39
69.85
54.77
27.56
9.57
f1 (ppm)

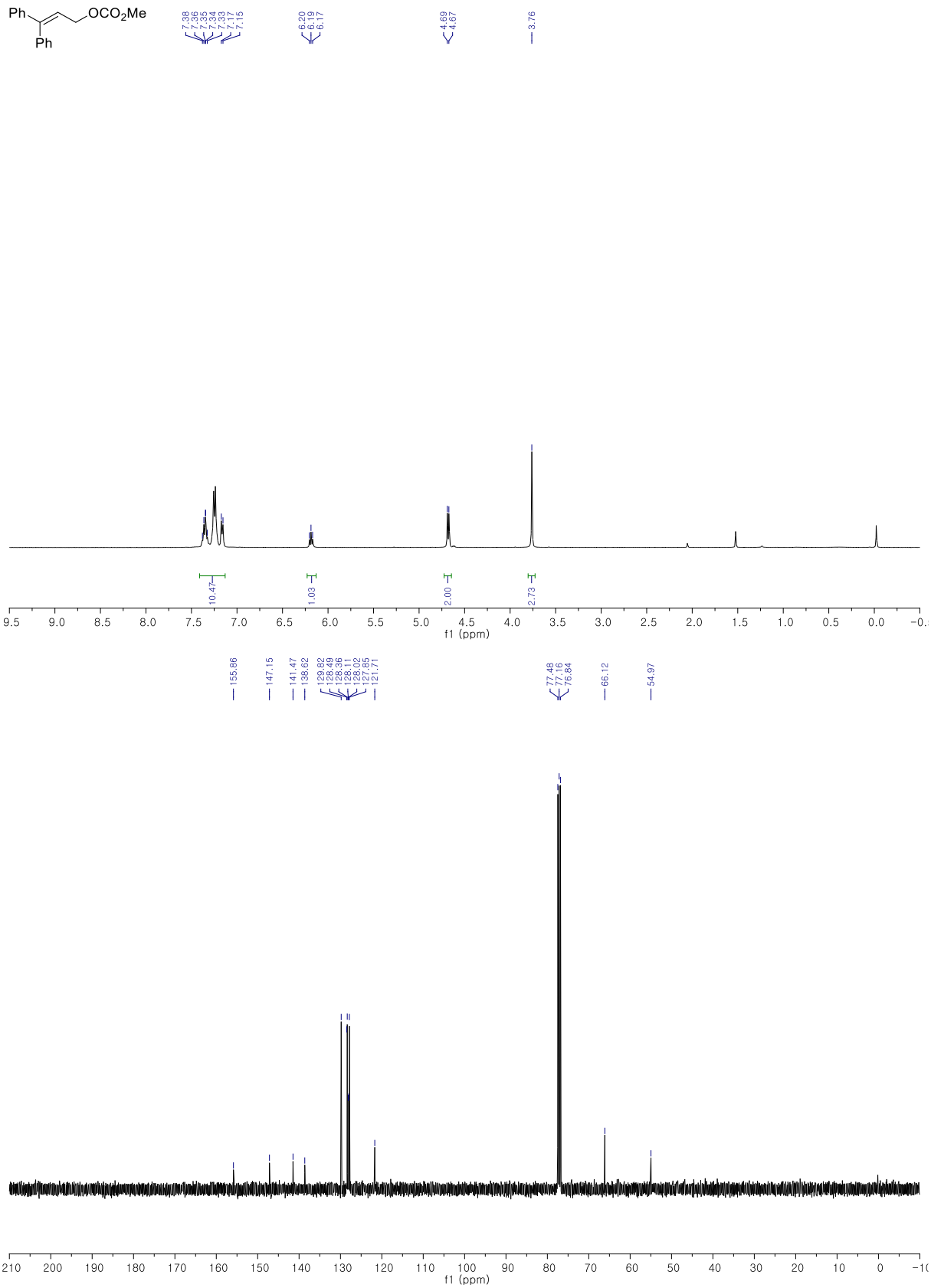

OBn
Ph
OCO2Me
7.37
7.36
7.34
7.32
7.32
7.30
7.28
7.28
6.12
6.10
6.00
5.99
5.96
5.95
5.92
5.91
5.90
5.88
5.87
5.86
4.50
4.05
4.04
3.77
9.96
0.98
1.06
1.11
2.00
2.20
2.98
f1 (ppm)
155.10
138.57
138.15
130.37
130.13
128.75
128.52
127.87
127.79
127.12
79.66
77.48
77.16
76.84
72.50
69.73
54.95
f1 (ppm)

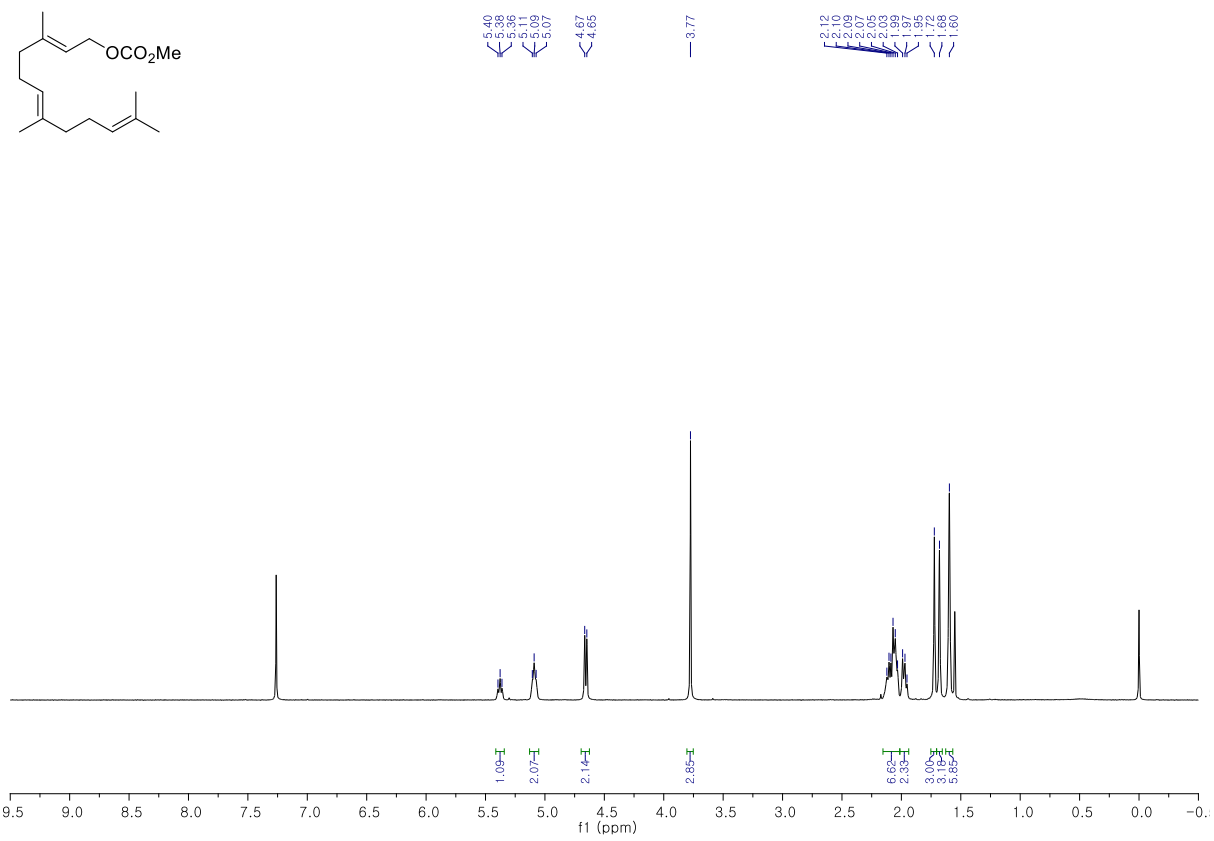

OBn
TMS
OCO2Me
7.38
7.35
7.34
7.31
7.30
7.29
7.28
6.15
6.14
6.13
6.11
6.10
6.09
5.89
5.87
5.85
5.83
5.78
5.76
4.53
4.08
4.07
3.81
0.18
4.65
0.98
0.98
0.88
2.00
1.92
2.96
8.24
f1 (ppm)
154.84
138.09
132.62
128.57
127.92
127.87
126.46
99.60
93.42
77.48
77.16
76.84
72.60
69.35
68.10
55.18
-0.15
f1 (ppm)

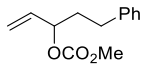

OBn
OCO2Me
7.35
7.35
7.34
7.34
7.31
7.30
7.29
6.33
6.31
6.27
6.24
6.21
5.87
5.83
5.71
5.69
5.25
5.24
5.22
5.21
4.52
4.07
4.06
3.77
1.39
1.38
4.87
2.16
1.13
1.10
1.03
2.00
2.12
3.06
3.15
f1 (ppm)
155.21
138.32
131.93
131.70
131.46
128.52
127.86
127.76
77.48
77.16
76.84
74.95
72.31
70.23
54.74
20.42
f1 (ppm)


OBn
OCO2Me
7.35
7.34
7.31
7.29
7.28
7.26
6.28
6.24
5.88
5.87
5.85
5.83
5.60
5.58
5.57
5.56
5.56
5.54
5.53
5.46
5.43
4.52
4.10
4.08
3.75
1.86
1.37
1.35
0.00
5.23
0.97
1.04
1.11
0.99
2.06
2.00
3.26
3.12
3.23
f1 (ppm)
155.31
138.38
136.40
136.10
130.66
129.54
128.91
127.77
126.53
77.48
77.16
76.84
72.36
72.11
70.79
20.82
13.03
f1 (ppm)

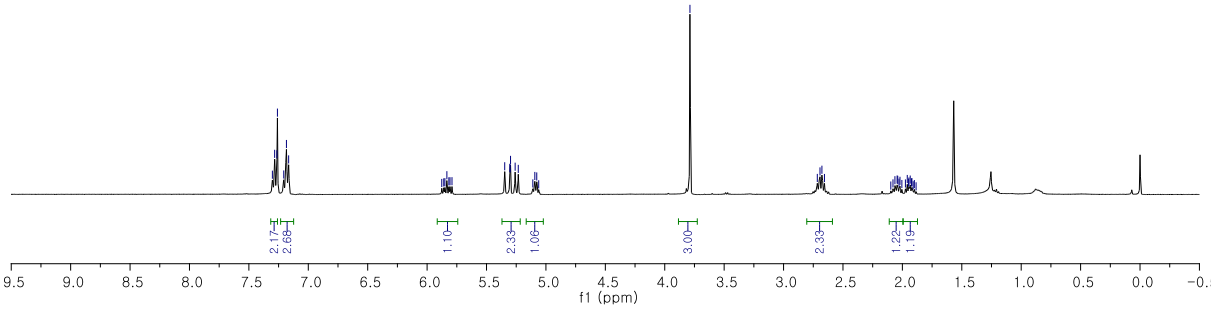

BnO
OCO2Me
Ph
7.43
7.42
7.41
7.35
7.33
7.31
7.30
7.29
7.26
6.08
6.06
6.04
4.89
4.87
4.52
4.46
3.80
10.16
1.00
2.17
1.96
2.07
3.36
f1 (ppm)
155.82
141.31
140.28
137.94
128.55
128.50
128.05
127.95
127.82
126.63
125.77
125.74
77.48
77.16
76.84
72.44
67.06
64.53
54.98
f1 (ppm)


Ph
OCO2Me
Ph
7.38
7.36
7.35
7.34
7.33
7.17
7.15
6.20
6.19
6.17
4.69
4.67
3.76
10.47
1.03
2.00
2.73
f1 (ppm)
155.86
147.15
141.47
138.62
129.82
128.49
128.36
128.11
127.02
127.85
121.71
77.48
77.16
76.84
66.12
54.97
f1 (ppm)

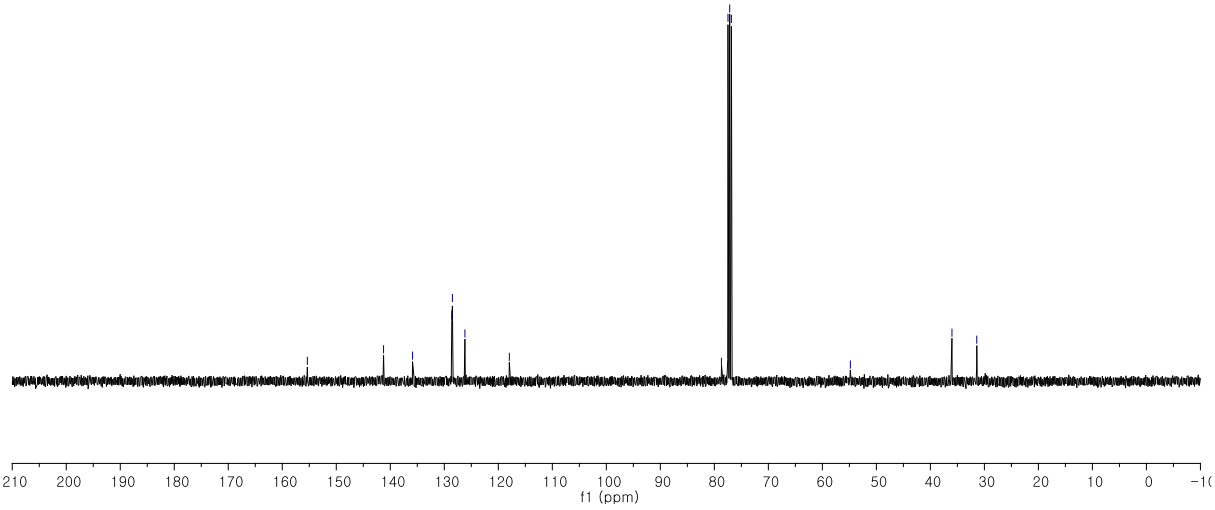

OCO2Me
5.40
5.38
5.36
5.11
5.09
5.07
4.67
4.65
3.77
2.12
2.10
2.09
2.07
2.05
2.03
1.99
1.97
1.95
1.72
1.68
1.60
1.09
2.07
2.14
2.85
6.62
2.33
3.00
3.18
3.82
f1 (ppm)
156.03
143.42
135.67
131.49
124.44
123.69
117.83
77.48
77.16
76.84
64.88
54.79
39.83
39.66
26.86
26.30
25.85
17.84
16.68
16.16
f1 (ppm)

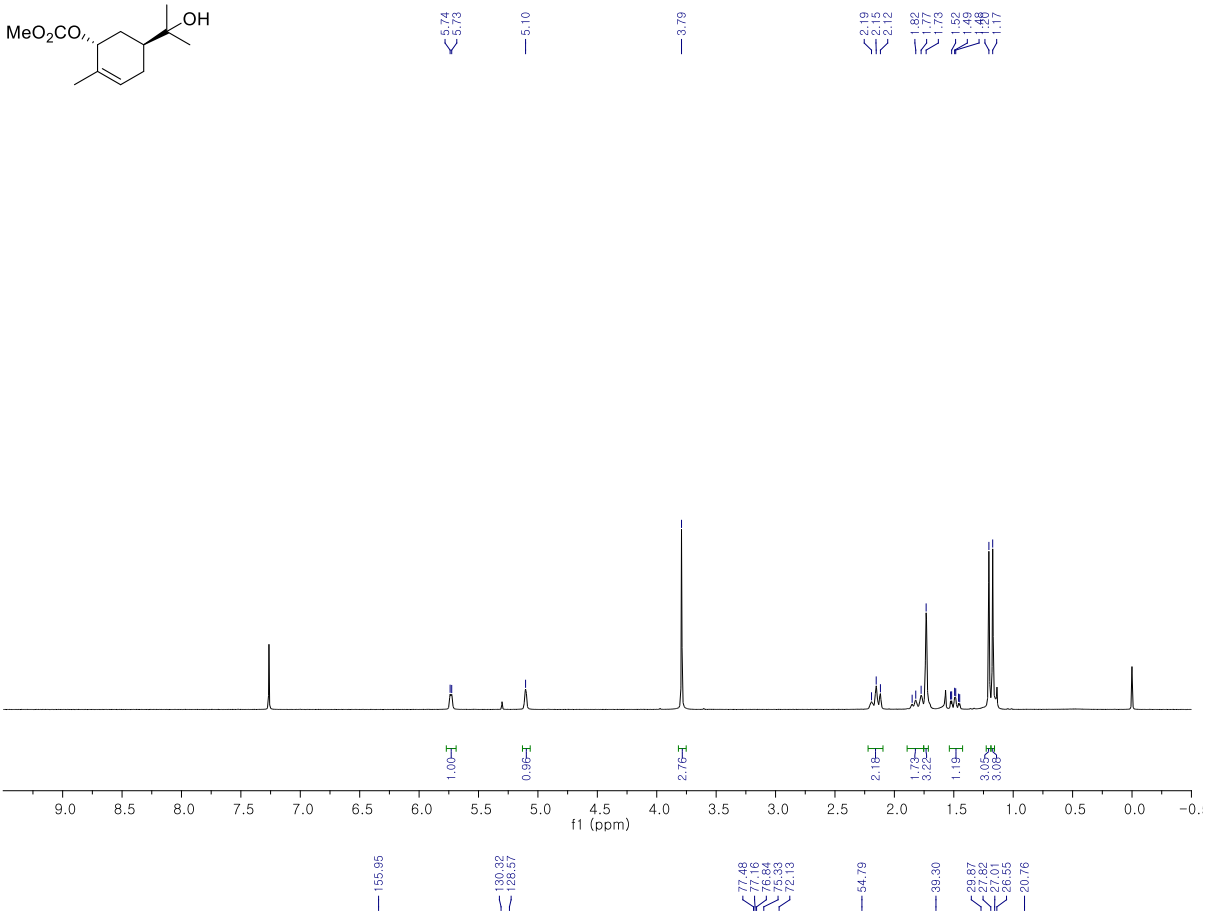

Ph
OCO2Me

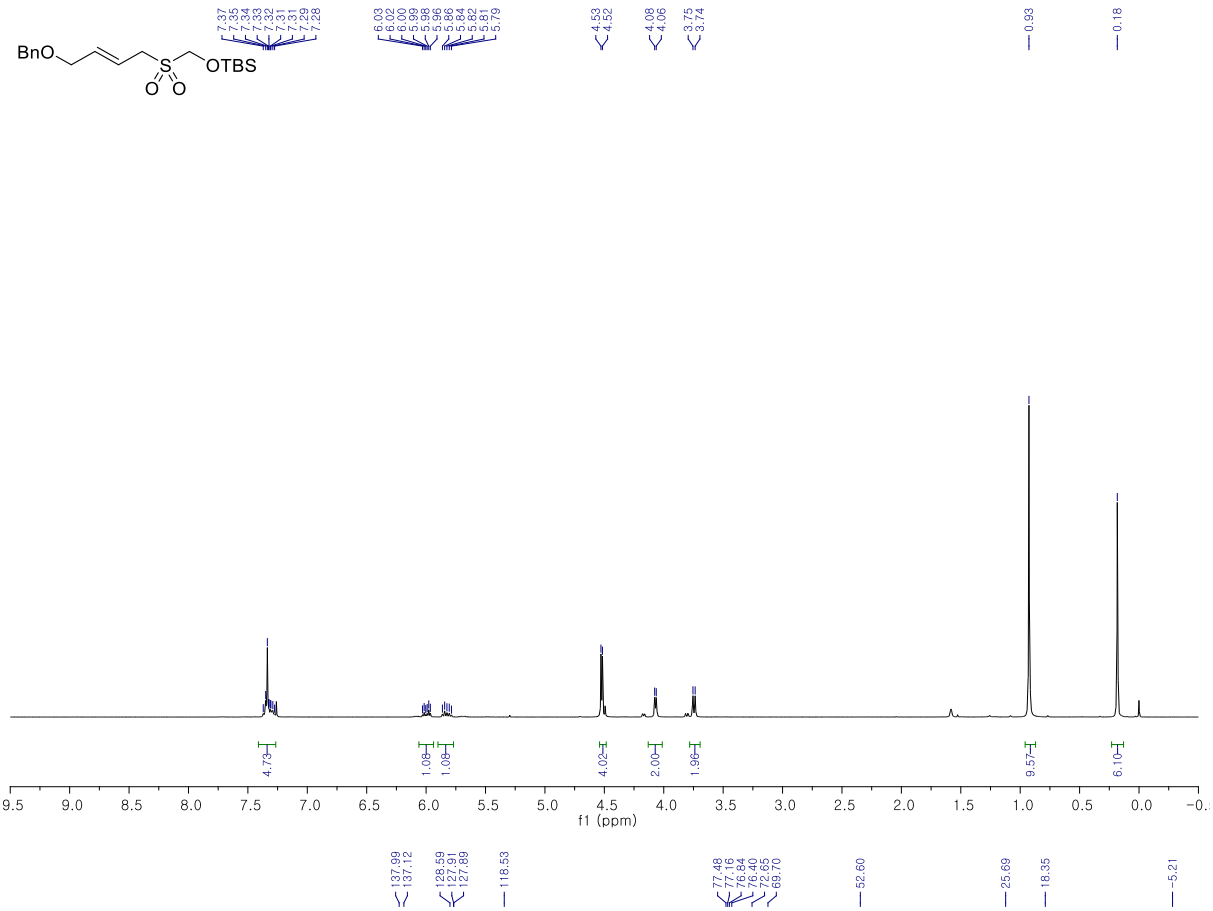

7.30
7.28
7.26
7.26
7.21
7.18
7.17
5.88
5.86
5.85
5.83
5.82
5.81
5.79
5.35
5.30
5.30
5.30
5.26
5.23
5.11
5.09
5.08
5.06
3.79
2.72
2.69
2.68
2.66
2.10
2.08
2.06
2.04
2.04
2.03
2.02
2.00
1.97
1.96
1.95
1.94
1.93
1.92
1.92
1.91
1.90
1.88

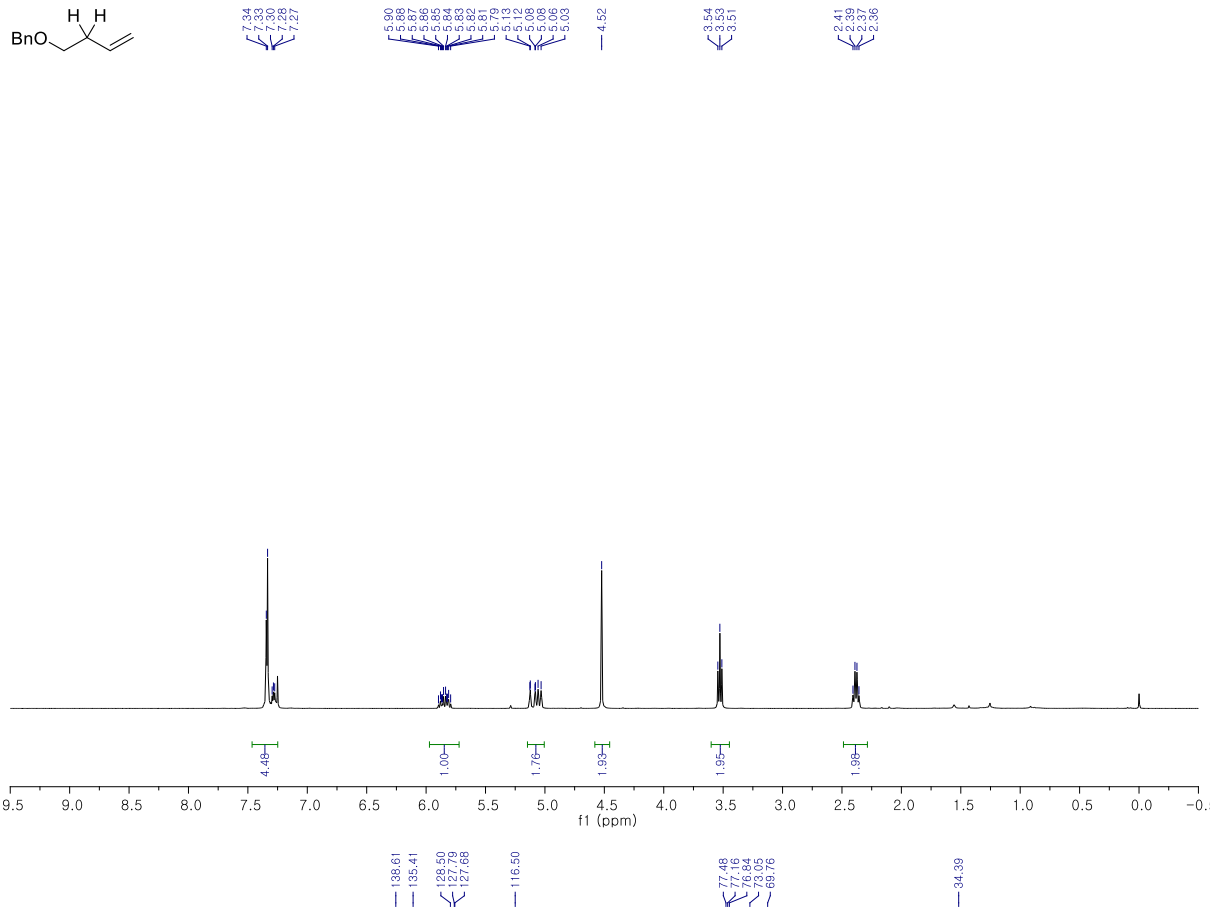

2.17
2.68
1.10
2.33
1.06
3.00
2.33
1.22
1.19
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

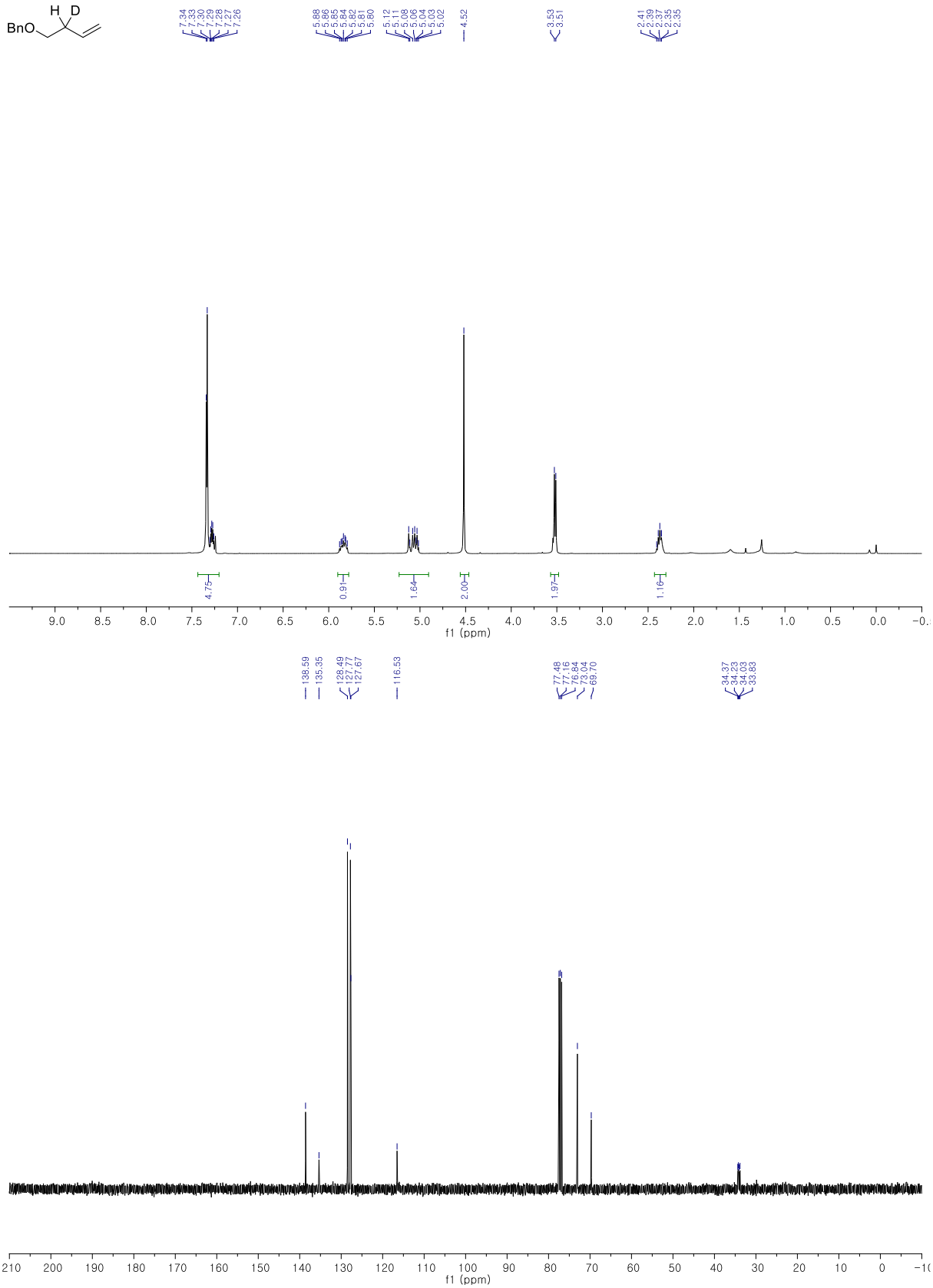

155.36
141.25
135.88
128.61
128.50
126.19
117.96
78.69
77.48
77.16
76.84
54.81
36.01
31.41


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MeO2CO
OH
5.74
5.73
5.10
3.79
2.19
2.15
2.12
1.82
1.77
1.73
1.52
1.49
1.48
1.17
1.00
0.96
2.76
2.16
1.73
3.22
1.19
3.05
3.08
f1 (ppm)
155.95
130.32
128.57
77.48
77.16
76.84
75.33
72.13
54.79
39.30
29.87
27.82
27.01
26.55
20.76
f1 (ppm)


BnO
S
O
O
OTBS
7.37
7.35
7.34
7.33
7.32
7.31
7.31
7.29
7.28
6.03
6.02
6.00
5.99
5.98
5.86
5.84
5.82
5.81
5.79
4.53
4.52
4.08
4.06
3.75
3.74
0.93
0.18
4.73
1.08
1.08
4.02
2.00
1.96
9.57
6.10
f1 (ppm)
137.99
137.12
128.59
128.01
127.89
118.53
77.48
77.16
76.84
76.40
72.65
69.70
52.60
25.69
18.35
-5.21
f1 (ppm)


BnO
H H
7.34
7.33
7.30
7.28
7.27
5.90
5.88
5.87
5.86
5.85
5.84
5.83
5.82
5.81
5.79
5.13
5.12
5.08
5.08
5.06
5.03
4.52
3.54
3.53
3.51
2.41
2.39
2.37
2.36
4.48
1.00
1.76
1.93
1.95
1.98
f1 (ppm)
138.61
135.41
129.50
127.79
127.68
116.50
77.48
77.16
76.84
73.65
69.76
34.39
f1 (ppm)


H D
BnO
7.34
7.33
7.30
7.29
7.28
7.27
7.26
5.88
5.86
5.85
5.84
5.82
5.81
5.80
5.12
5.11
5.08
5.06
5.04
5.03
5.02
4.52
3.53
3.51
2.41
2.39
2.37
2.35
2.35
4.75
0.91
1.64
2.00
1.97
1.16
f1 (ppm)
138.59
135.35
128.49
127.77
127.67
116.53
77.48
77.16
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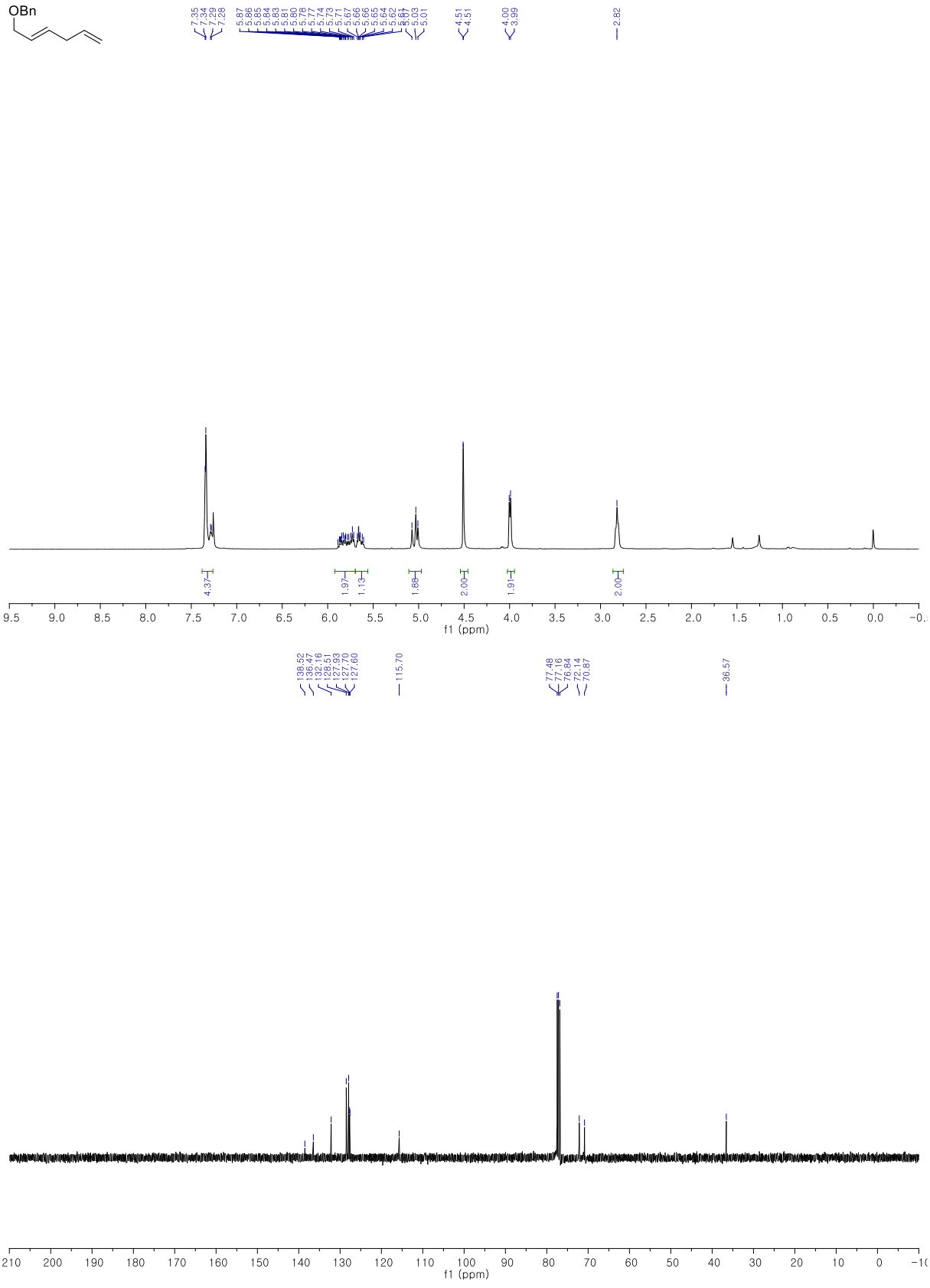
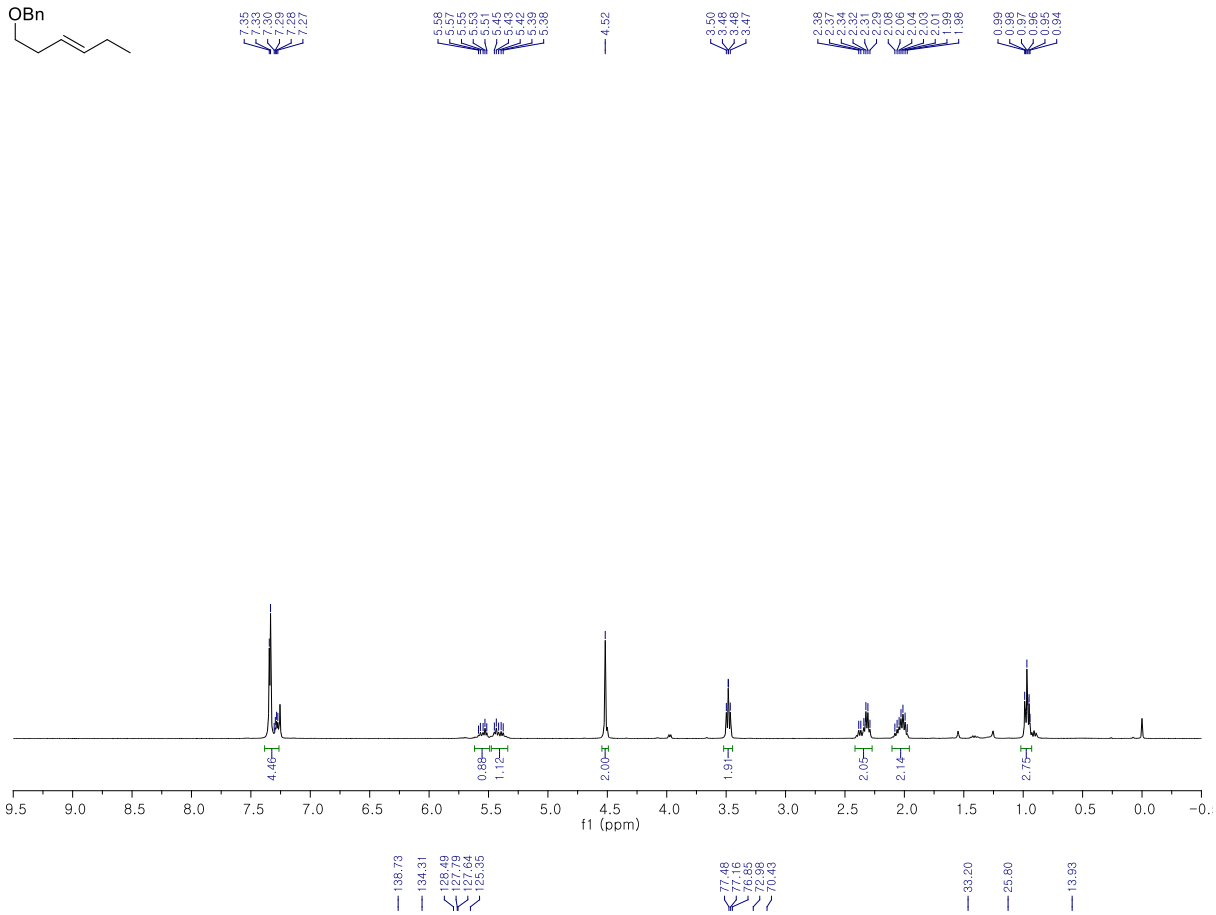
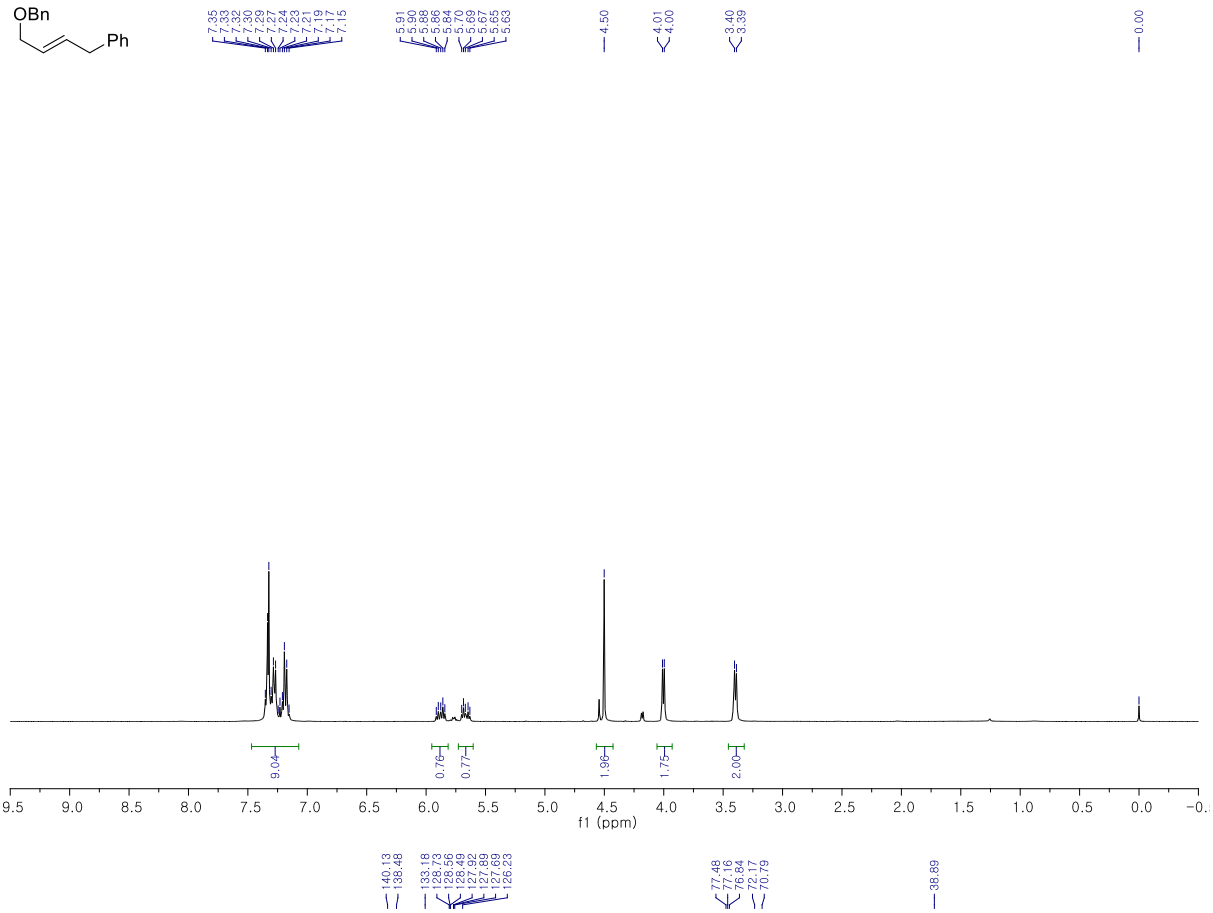
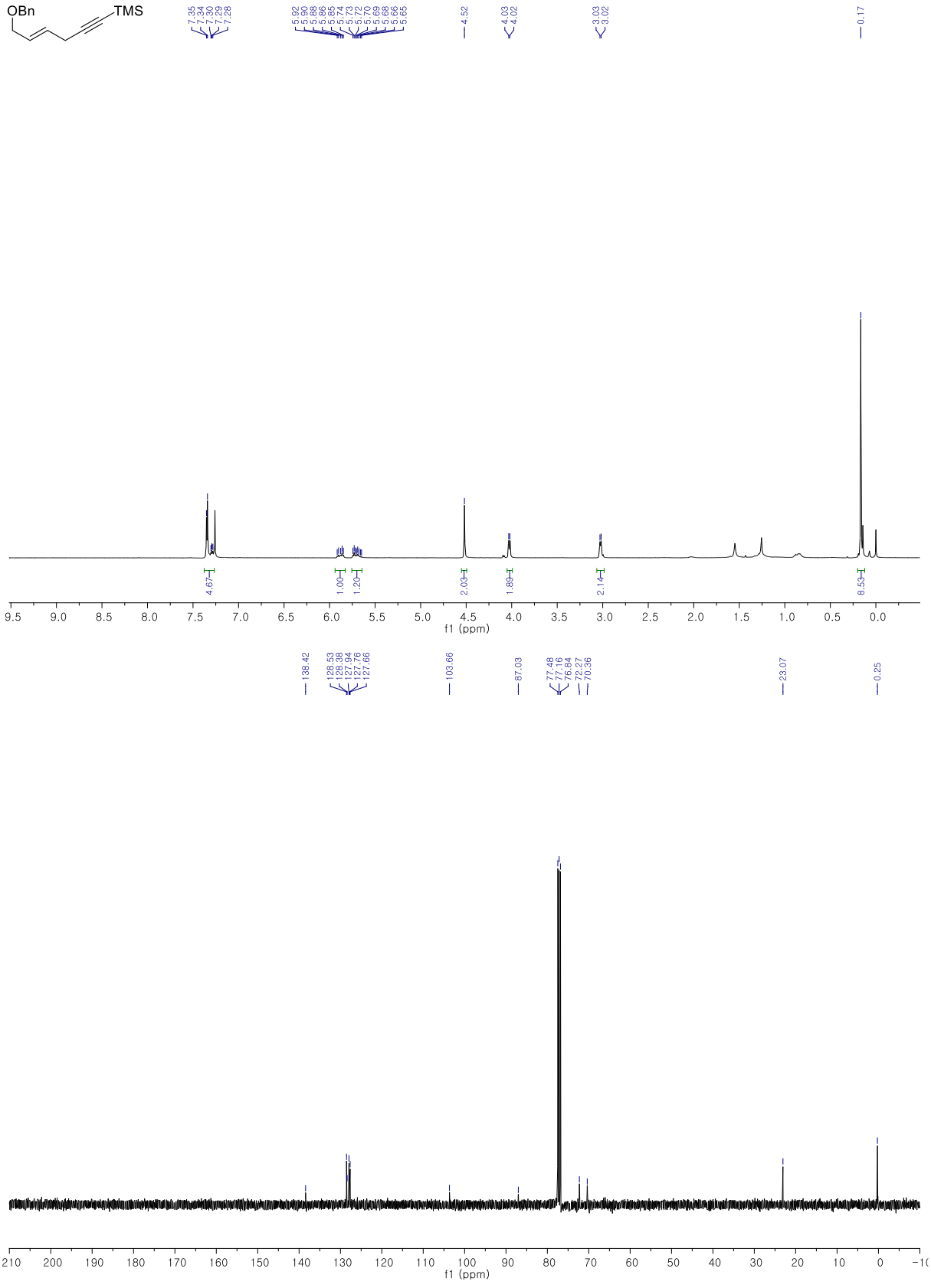
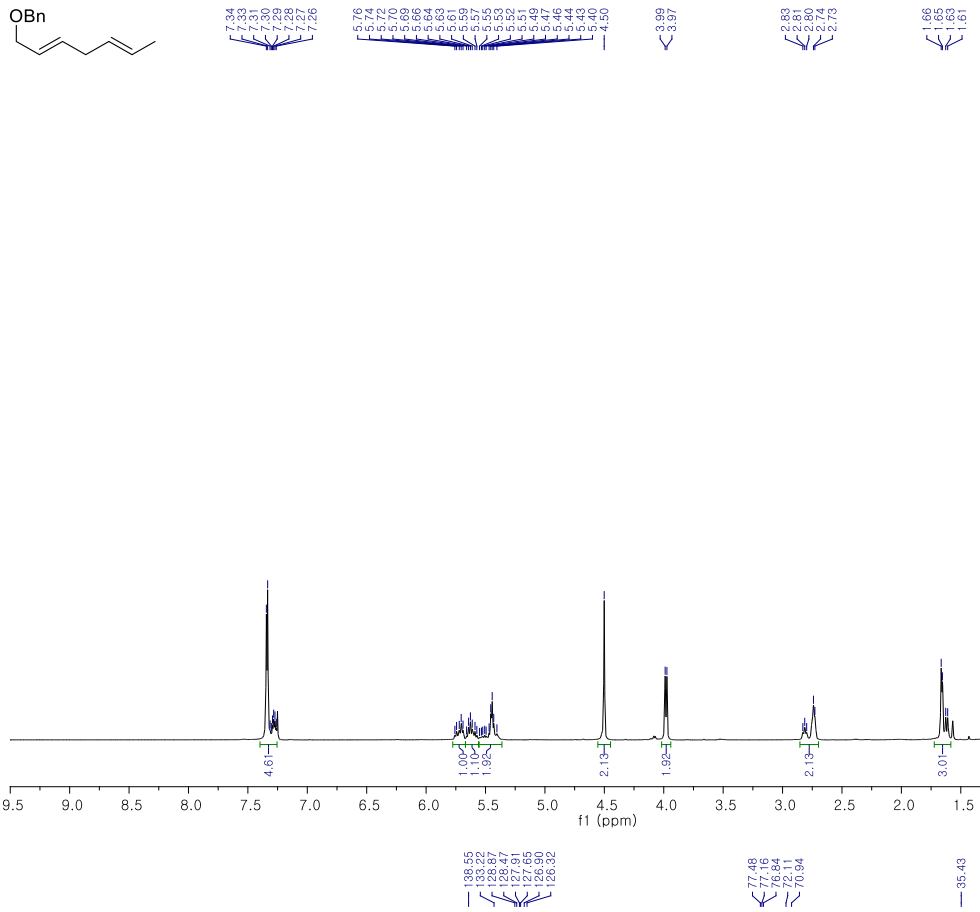
69.70
34.37
34.23
34.03
33.83
f1 (ppm)

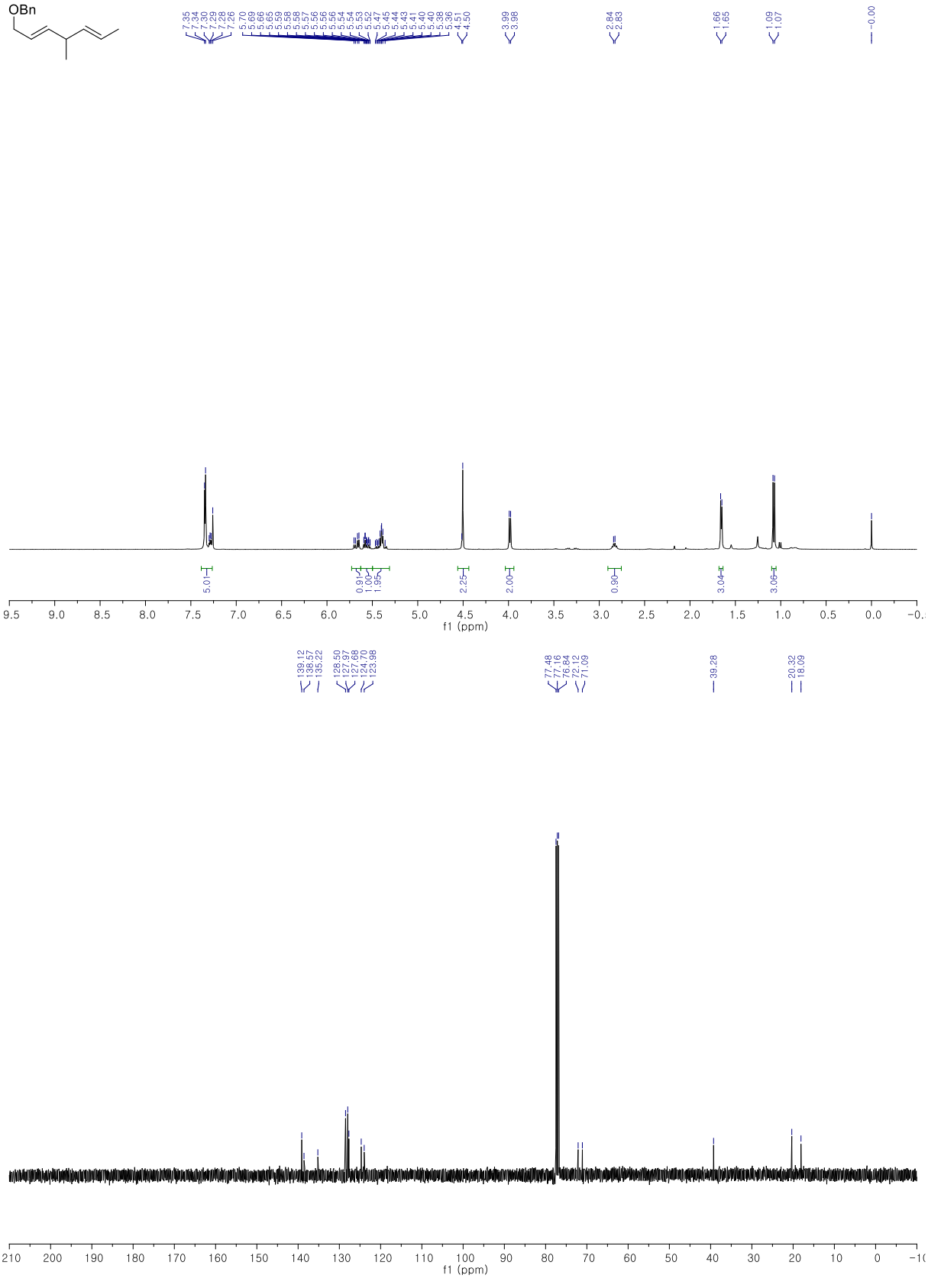

OBn
7.35
7.34
7.29
7.28
5.87
5.86
5.85
5.84
5.83
5.81
5.80
5.79
5.77
5.74
5.73
5.71
5.67
5.66
5.65
5.64
5.62
5.03
5.01
4.51
4.51
4.00
3.99
2.82
4.37
1.97
1.13
1.88
2.00
1.91
2.00
f1 (ppm)
138.52
136.47
132.16
129.51
128.63
127.70
127.60
115.70
77.48
77.16
76.84
72.14
70.87
36.57
f1 (ppm)

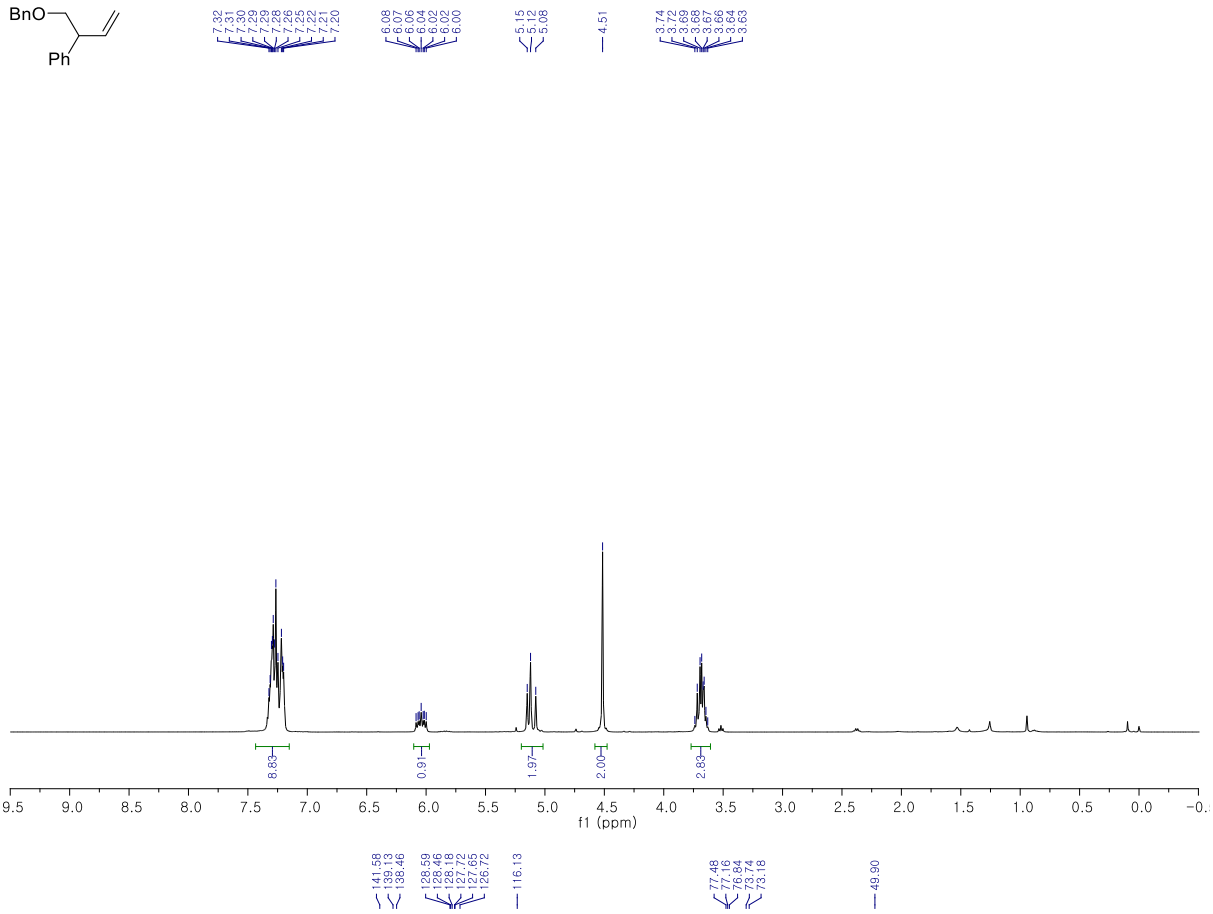

OBn
7.35
7.33
7.30
7.29
7.28
7.27
5.58
5.57
5.55
5.53
5.51
5.45
5.43
5.42
5.39
5.38
4.52
3.50
3.48
3.47
2.38
2.37
2.34
2.32
2.31
2.29
2.06
2.04
2.03
2.01
1.99
1.98
0.99
0.98
0.97
0.96
0.95
0.94
4.46
0.88
1.12
2.00
1.91
2.05
2.14
2.75
f1 (ppm)
138.73
134.31
128.49
127.79
127.64
125.85
77.48
77.16
76.85
72.99
70.43
33.20
25.80
13.93
f1 (ppm)

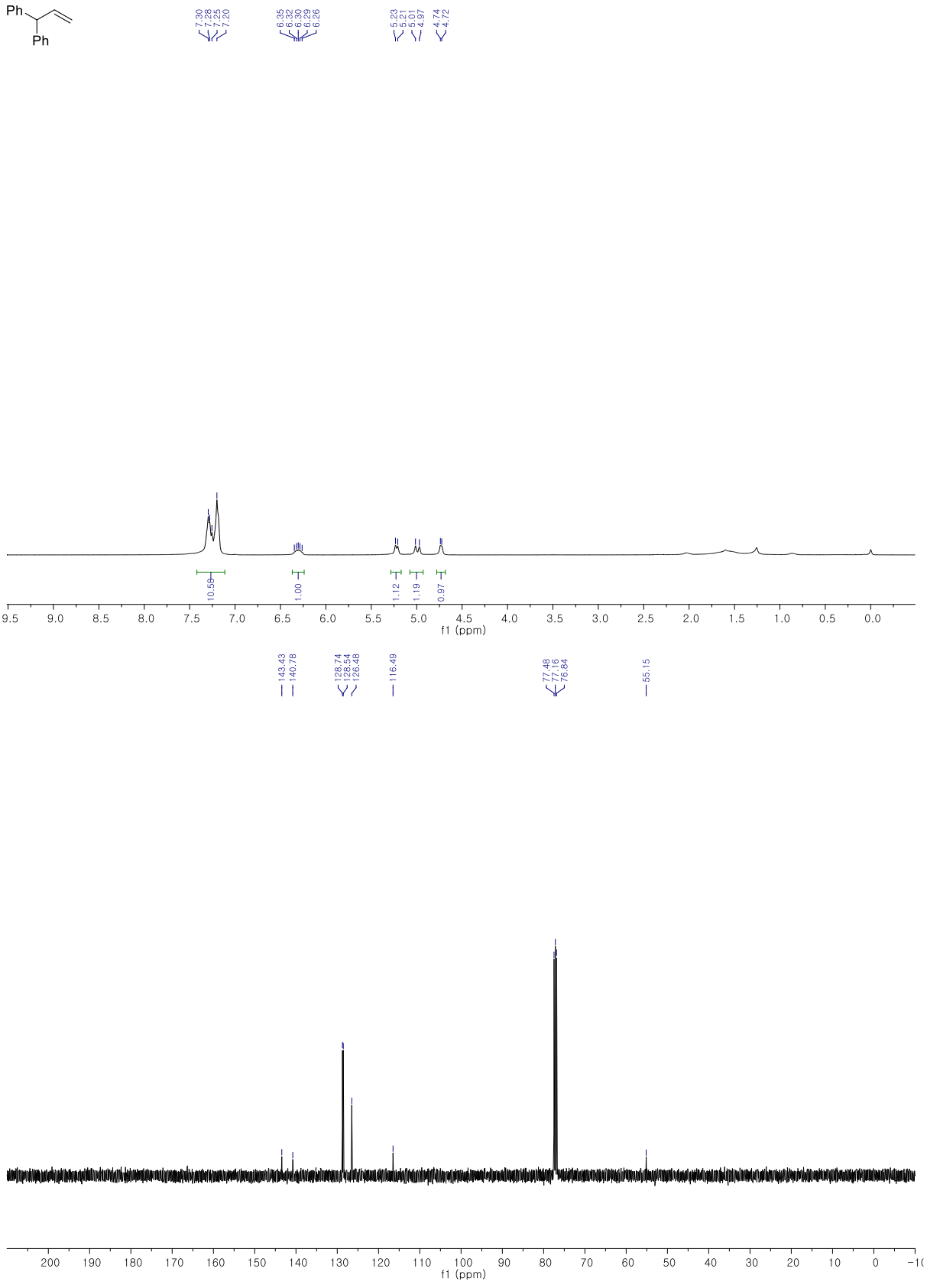

OBn
Ph
7.35
7.33
7.32
7.30
7.29
7.27
7.24
7.23
7.21
7.19
7.17
7.15
5.91
5.90
5.88
5.86
5.84
5.70
5.69
5.67
5.65
5.63
4.50
4.01
4.00
3.40
3.39
0.00
9.04
0.76
0.77
1.96
1.75
2.00
f1 (ppm)
140.13
138.48
133.18
129.73
128.56
128.49
127.92
127.89
127.69
126.23
77.48
77.16
76.84
72.17
70.79
38.89
f1 (ppm)

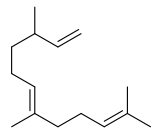

OBn
TMS
7.35
7.34
7.30
7.29
7.28
5.92
5.90
5.88
5.86
5.85
5.74
5.73
5.72
5.70
5.69
5.68
5.66
5.65
4.52
4.03
4.02
3.03
3.02
0.17
4.67
1.00
1.20
2.03
1.89
2.14
8.53
f1 (ppm)
138.42
128.53
128.38
127.94
127.76
127.66
103.66
87.03
77.48
77.16
76.84
72.27
70.36
23.07
0.25
f1 (ppm)


OBn
7.34
7.33
7.31
7.30
7.29
7.28
7.27
7.26
5.76
5.74
5.72
5.70
5.69
5.66
5.64
5.63
5.61
5.59
5.57
5.55
5.53
5.52
5.51
5.49
5.47
5.46
5.44
5.43
5.40
4.50
3.99
3.97
2.83
2.81
2.80
2.74
2.73
1.66
1.65
1.63
1.61
4.61
1.00
1.10
1.92
2.13
1.92
2.13
3.01
f1 (ppm)
138.55
138.22
128.87
128.47
127.91
127.65
126.90
126.32
77.48
77.16
76.84
72.11
70.94
35.43
18.03
f1 (ppm)

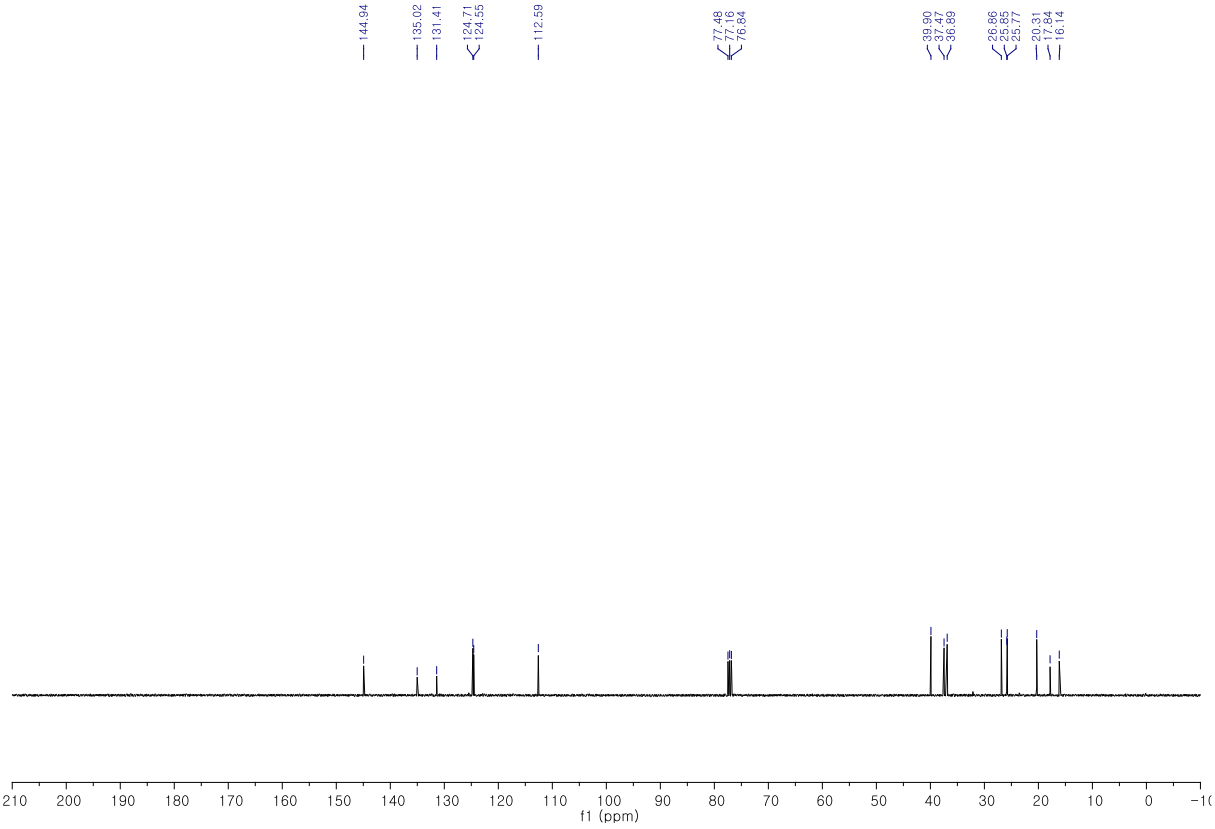

OBn
7.35
7.34
7.30
7.29
7.28
7.26
5.70
5.69
5.66
5.60
5.59
5.58
5.58
5.57
5.56
5.56
5.56
5.54
5.54
5.53
5.52
5.47
5.45
5.44
5.43
5.41
5.40
5.40
5.38
5.36
4.51
4.50
3.99
3.98
2.84
2.83
1.66
1.65
1.09
1.07
0.00
5.01
0.91
1.00
1.95
2.25
2.00
0.90
3.04
3.06
f1 (ppm)
139.12
138.57
135.22
129.50
128.97
127.68
124.70
123.98
77.48
77.16
76.84
72.12
71.09
39.28
20.32
18.09
f1 (ppm)

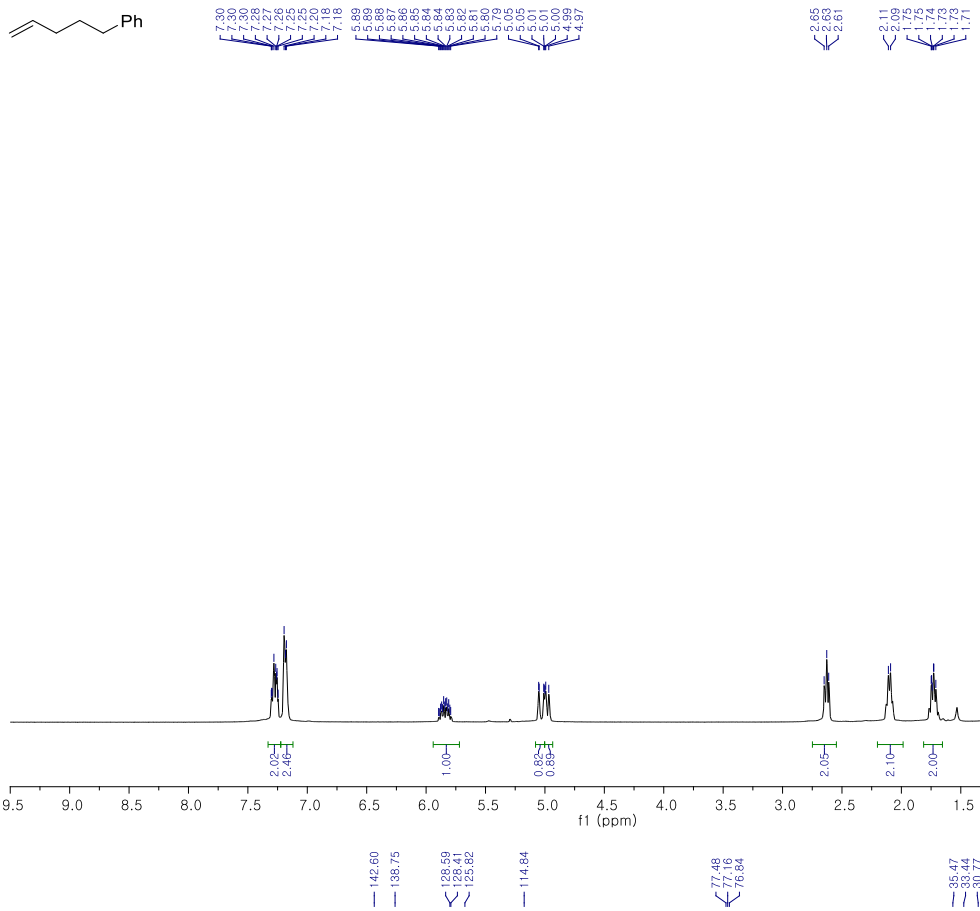

BnO
Ph
7.32
7.31
7.30
7.29
7.28
7.26
7.25
7.22
7.21
7.20
6.08
6.07
6.06
6.04
6.02
6.02
6.00
5.15
5.12
5.08
4.51
3.74
3.72
3.69
3.68
3.67
3.66
3.64
3.63
8.83
0.91
1.97
2.00
2.83
f1 (ppm)
141.58
139.13
138.46
128.59
128.46
128.18
127.72
127.65
126.72
116.13
77.48
77.16
76.84
73.74
73.18
49.90
f1 (ppm)

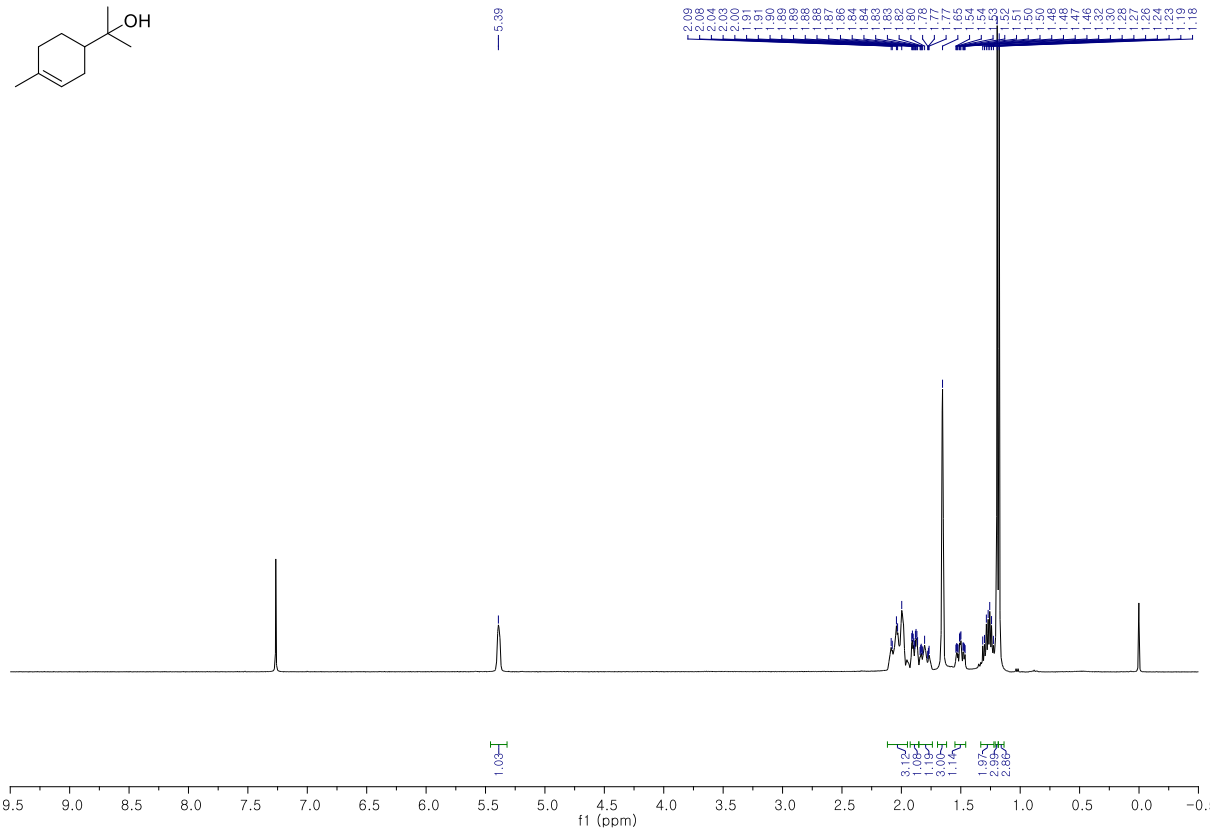

Ph
Ph
7.30
7.28
7.25
7.20
6.35
6.32
6.30
6.29
6.26
5.23
5.21
5.01
4.97
4.74
4.72
10.58
1.00
1.12
1.19
0.97
f1 (ppm)
143.43
140.78
128.74
128.54
126.48
116.49
77.48
77.16
76.84
55.15
f1 (ppm)

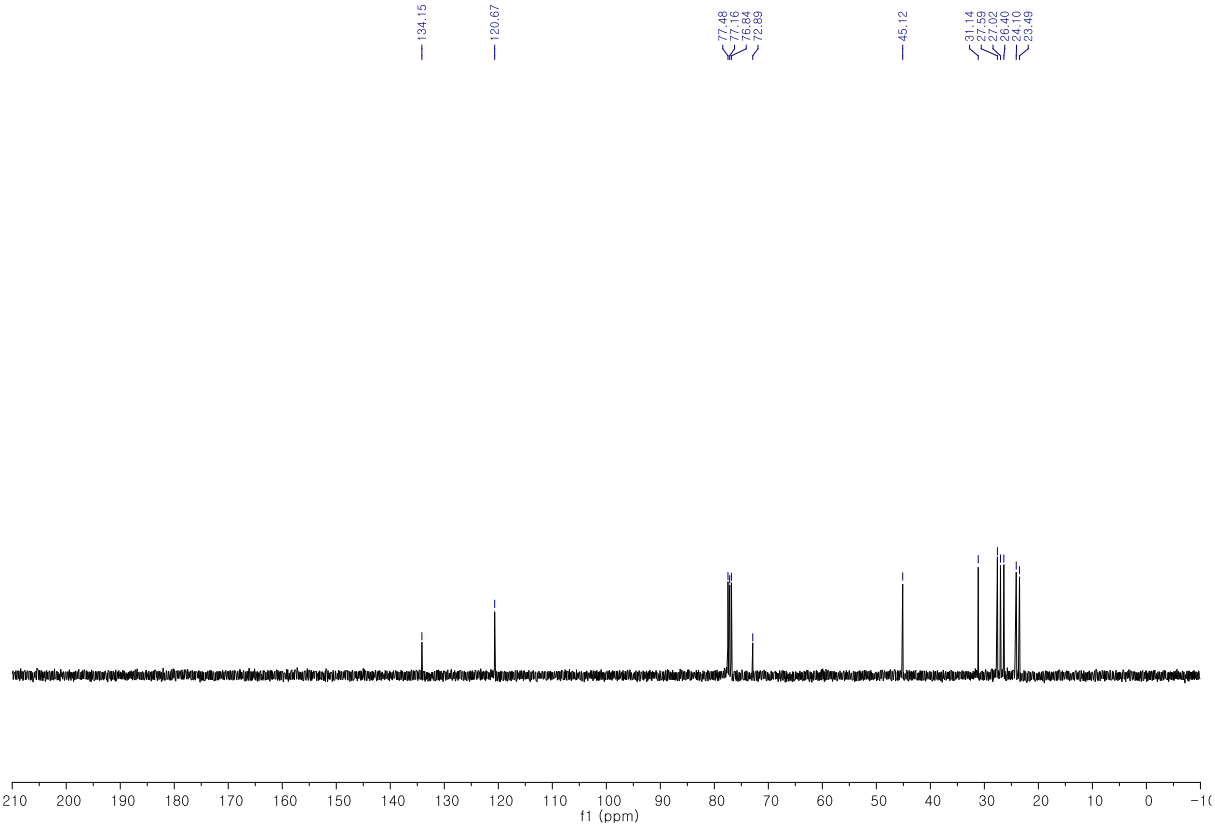


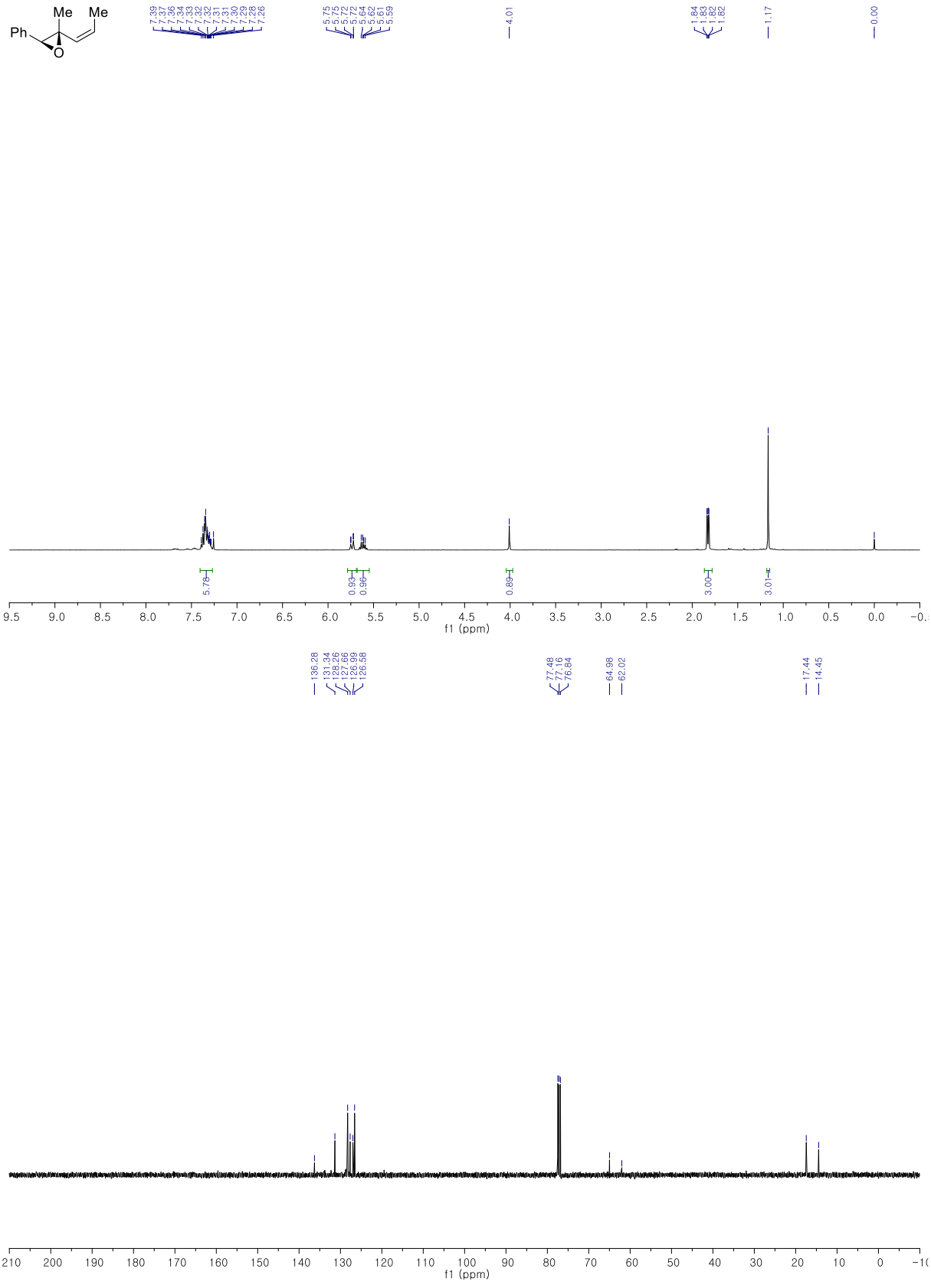
5.74
5.72
5.72
5.70
5.68
5.67
5.66
5.12
5.11
5.09
5.08
5.08
4.98
4.97
4.97
4.97
4.93
4.93
4.90
4.90
4.90
4.90
2.16
2.14
2.13
2.11
2.09
2.08
2.06
2.04
2.03
2.00
1.98
1.96
1.95
1.68
1.60
1.59
1.33
1.33
1.32
1.31
1.30
0.98
1.00
1.91
1.97
7.10
3.01
2.60
2.69
1.97
2.94
f1 (ppm)

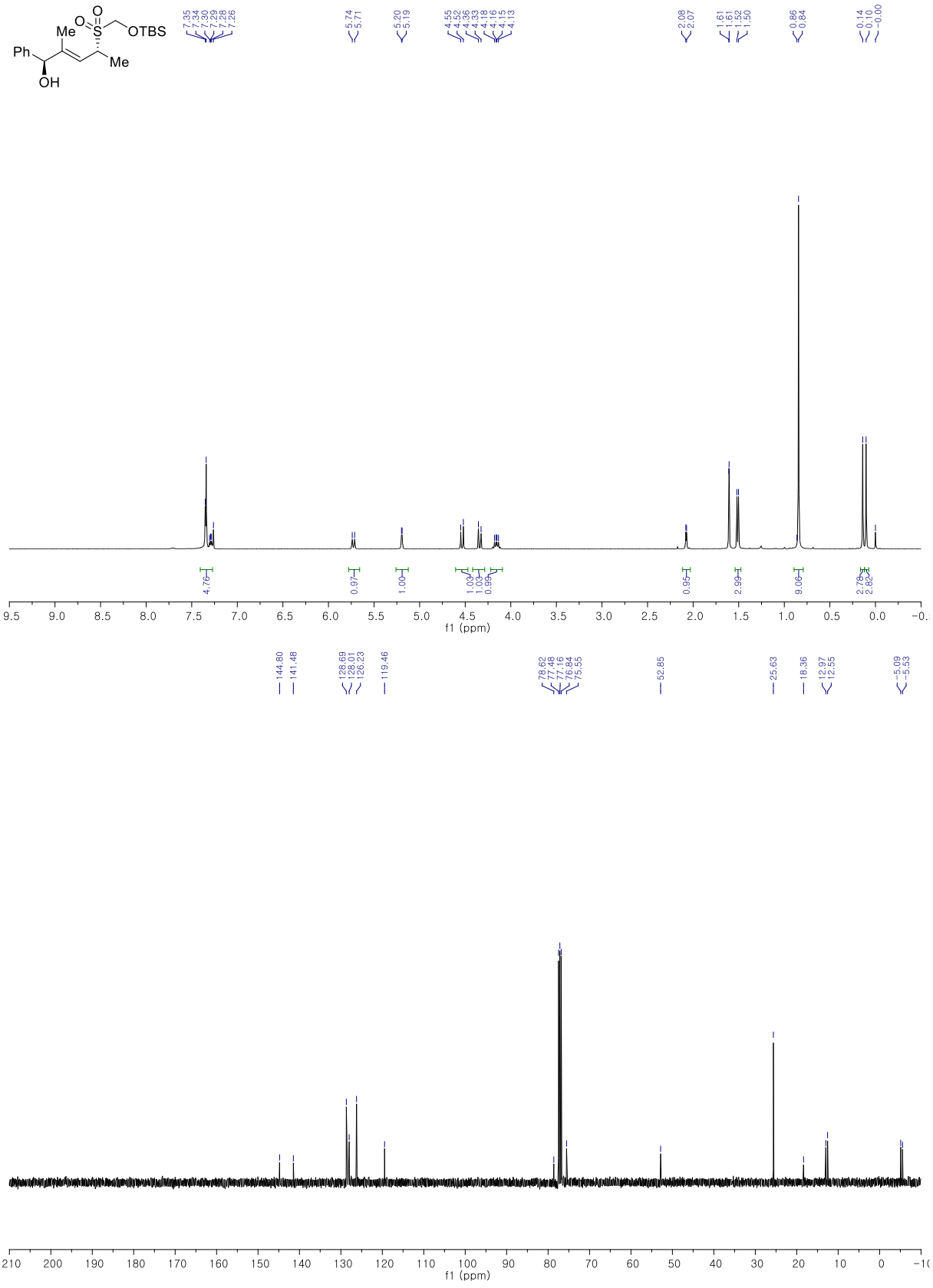

144.94
135.02
131.41
124.71
124.55
112.59
77.48
77.16
76.84
39.90
37.47
36.89
26.86
25.85
25.77
20.31
17.84
16.14
f1 (ppm)


Ph
7.30
7.30
7.30
7.28
7.27
7.26
7.25
7.25
7.20
7.18
7.18
5.89
5.88
5.88
5.87
5.86
5.85
5.84
5.83
5.82
5.81
5.80
5.79
5.05
5.05
5.01
5.01
5.00
4.99
4.97
2.65
2.63
2.61
2.11
2.09
1.75
1.75
1.74
1.73
1.73
1.71
2.02
2.46
1.00
0.82
0.89
2.05
2.10
2.00
f1 (ppm)
142.60
138.75
128.59
128.41
125.82
114.84
77.48
77.16
76.84
35.47
33.44
30.77
f1 (ppm)

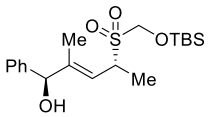

OH
5.39
1.03
f1 (ppm)


134.15
120.67
77.48
77.16
76.84
72.89
45.12
31.14
27.59
27.02
26.40
24.10
23.49
f1 (ppm)

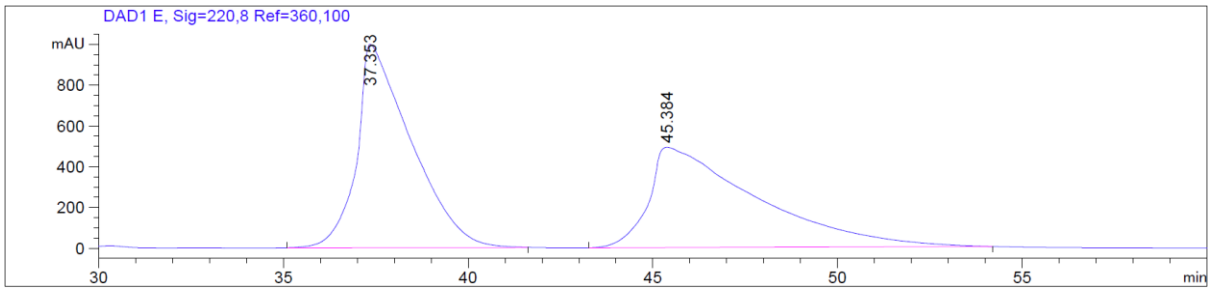

Me
Me
Ph
O
7.39
7.37
7.36
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.28
7.26
5.75
5.75
5.72
5.72
5.64
5.62
5.61
5.59
4.01
1.84
1.83
1.82
1.82
1.17
0.00
5.78
0.93
0.96
0.89
3.00
3.01
f1 (ppm)
136.28
131.34
128.26
127.66
126.99
126.58
77.48
77.16
76.84
64.98
62.02
17.44
14.45
f1 (ppm)


Me
O
O
S
OTBS
Ph
Me
OH
7.35
7.34
7.30
7.29
7.28
7.26
5.74
5.71
5.20
5.19
4.55
4.52
4.36
4.33
4.18
4.16
4.15
4.13
2.08
2.07
1.61
1.61
1.52
1.50
0.86
0.84
0.14
0.10
-0.00
4.76
0.97
1.00
1.03
1.03
0.99
0.95
2.99
9.06
2.78
2.82
f1 (ppm)
144.80
141.48
128.69
128.01
126.23
119.46
78.62
77.48
77.16
76.84
75.55
52.85
25.63
18.36
12.97
12.55
-5.09
-5.53
f1 (ppm)

Chiral HPLC Analysis

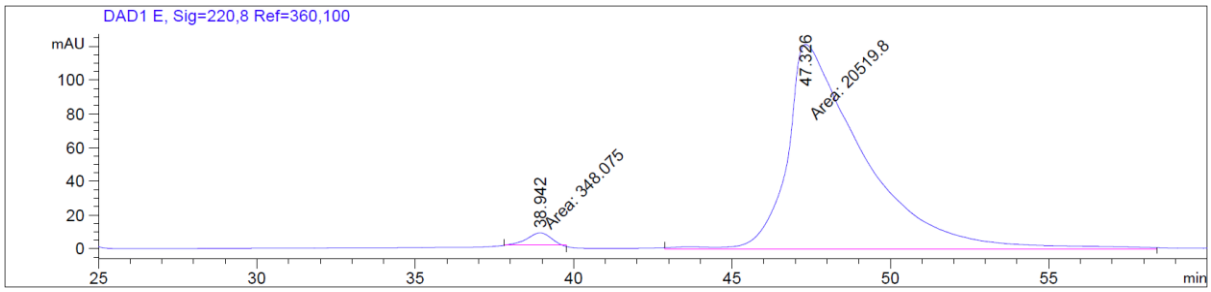


CHIRALPACK IA | Hex:IPA = 98:2 | Flow rate: 1.0 mL/min



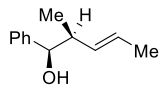
Signal 5: DAD1 E, Sig=220,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.353	BB	1.3755	1.02431e5	997.92517	50.5523
2	45.384	BB	2.5391	1.00193e5	492.16513	49.4477



Signal 5: DAD1 E, Sig=220,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.942	MM	0.8244	348.07510	7.03685	1.6680
2	47.326	MM	2.8162	2.05198e4	121.43780	98.3320



7.34
7.32
7.31
7.28
7.27
7.25
7.23

5.51
5.49
5.47
5.45
5.38
5.36
5.34
5.33

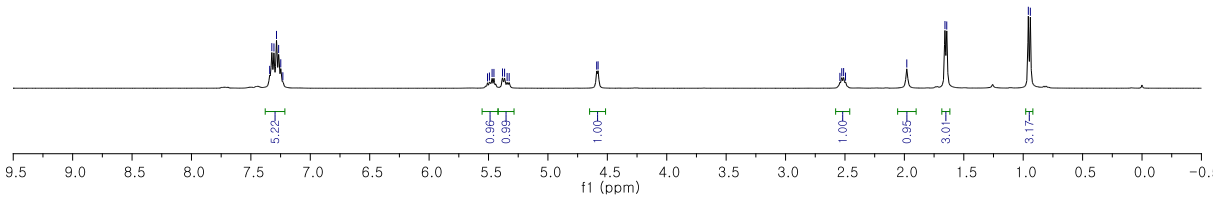
4.59
4.58

2.54
2.53
2.51
2.50

1.98

1.66
1.64

0.96
0.94



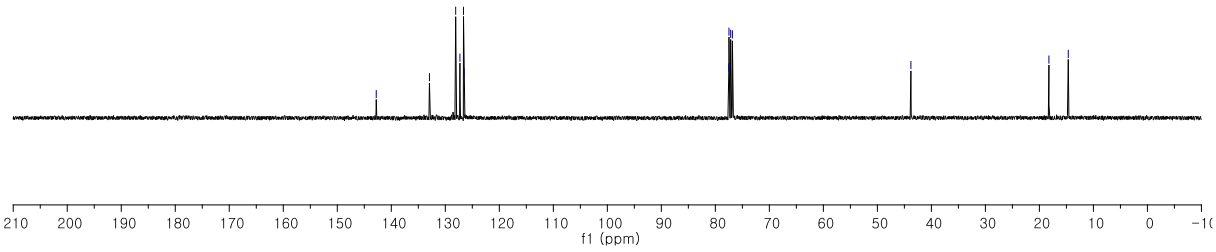
142.79

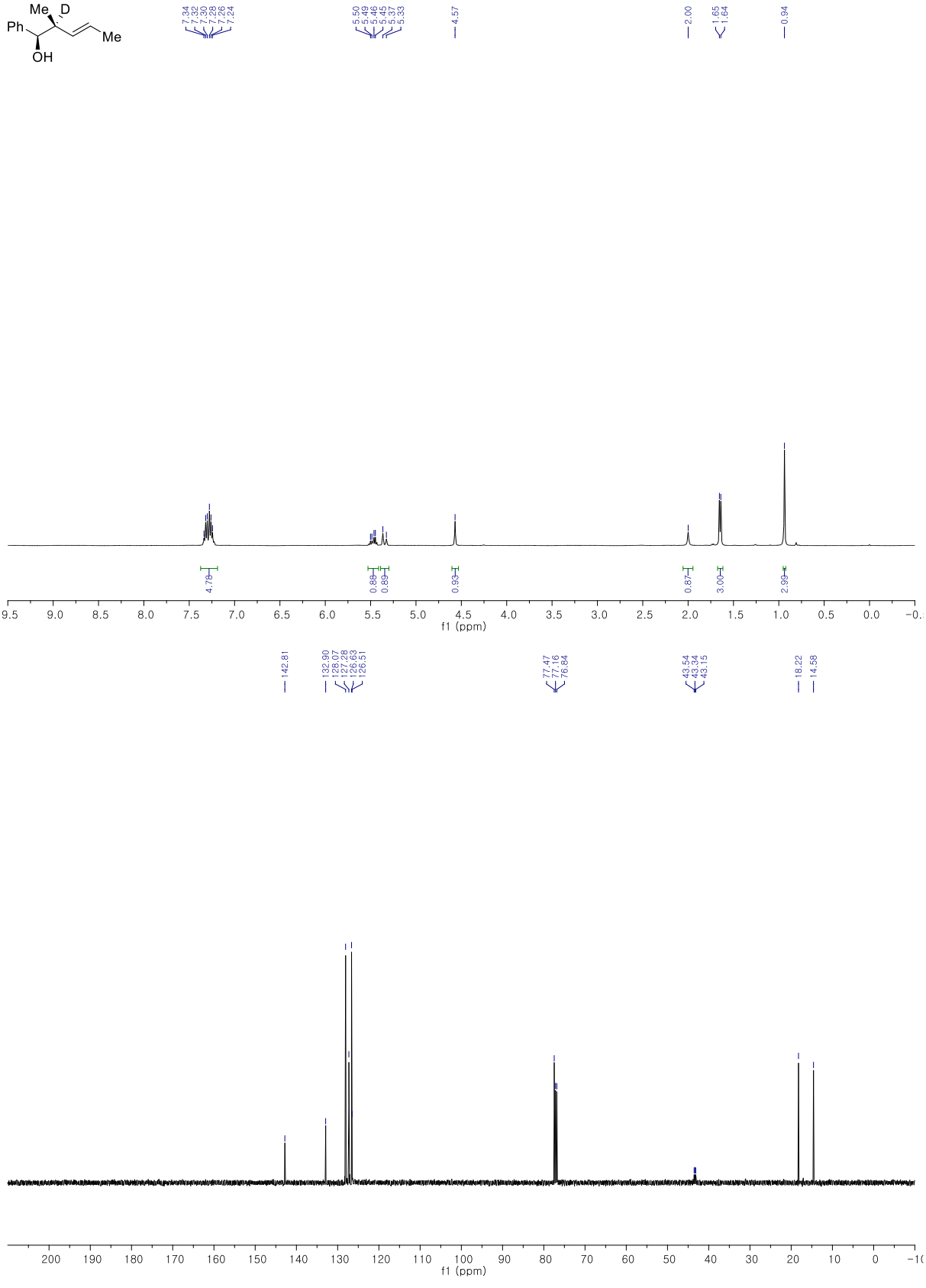
132.94
128.08
127.29
126.63
126.53

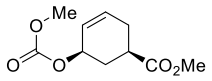
77.50
77.48
77.16
76.84

43.79

18.24
14.65

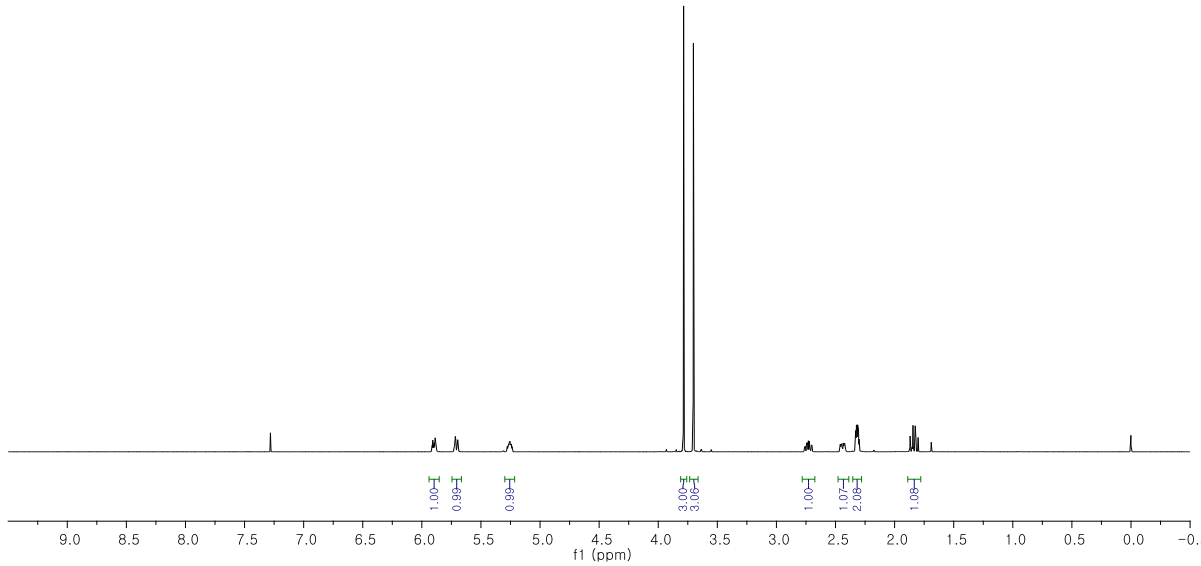



Me
D
Ph
Me
OH
7.34
7.32
7.30
7.28
7.26
7.24
5.50
5.49
5.46
5.45
5.37
5.33
4.57
2.00
1.65
1.64
0.94
4.78
0.88
0.89
0.93
0.87
3.00
2.99
f1 (ppm)
142.81
132.90
129.07
128.28
126.63
126.51
77.47
77.16
76.84
43.54
43.34
43.15
18.22
14.58
f1 (ppm)

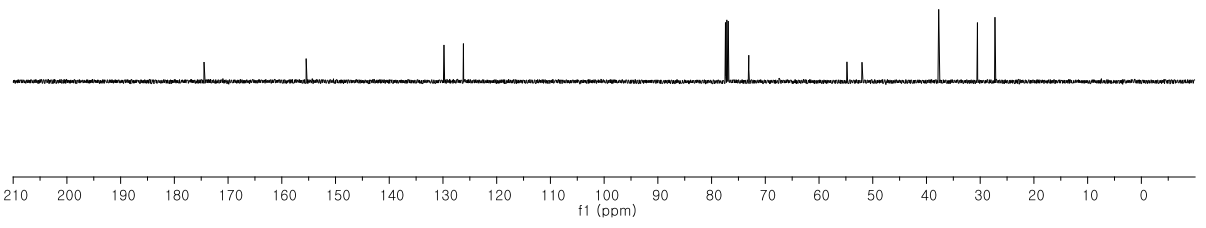

Me
O
O
O
CO2Me

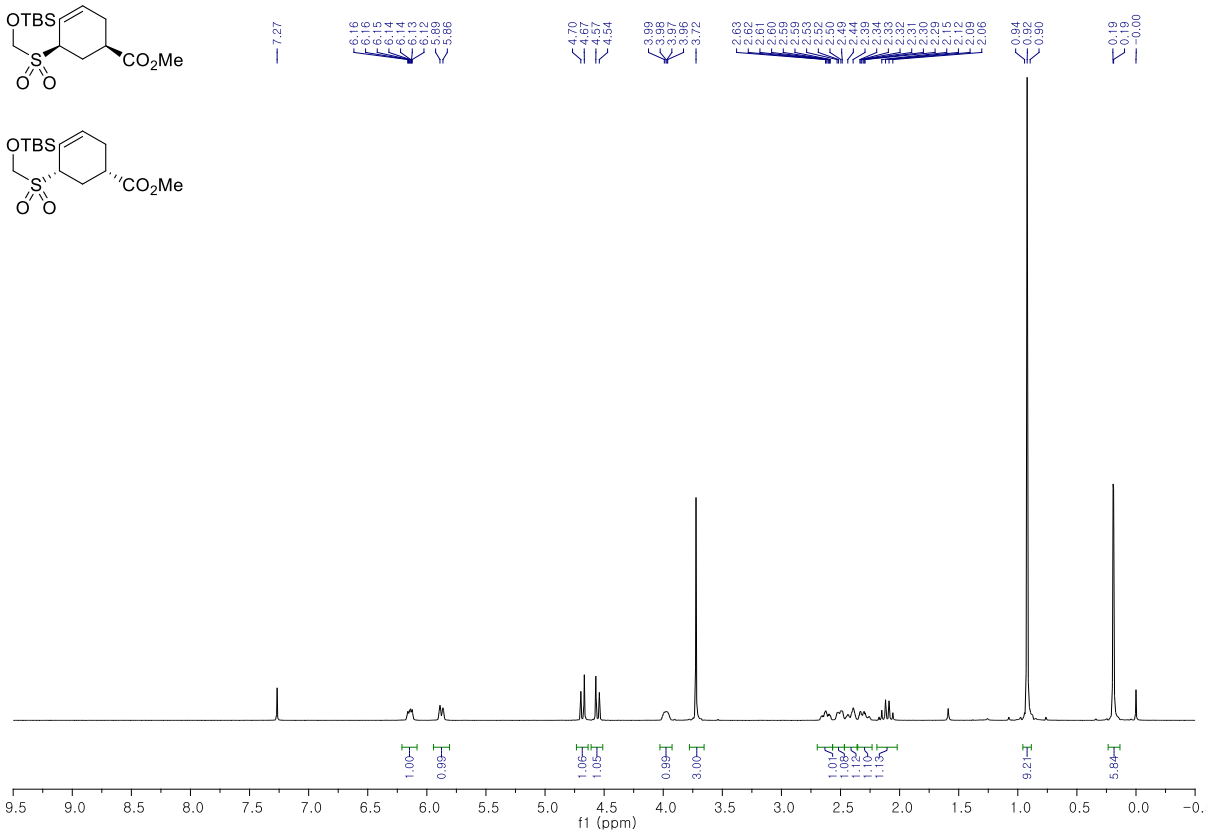

7.28
5.91
5.90
5.90
5.90
5.89
5.89
5.88
5.88
5.88
5.72
5.72
5.72
5.71
5.70
5.70
5.68
5.27
5.26
5.25
5.25
5.25
5.24

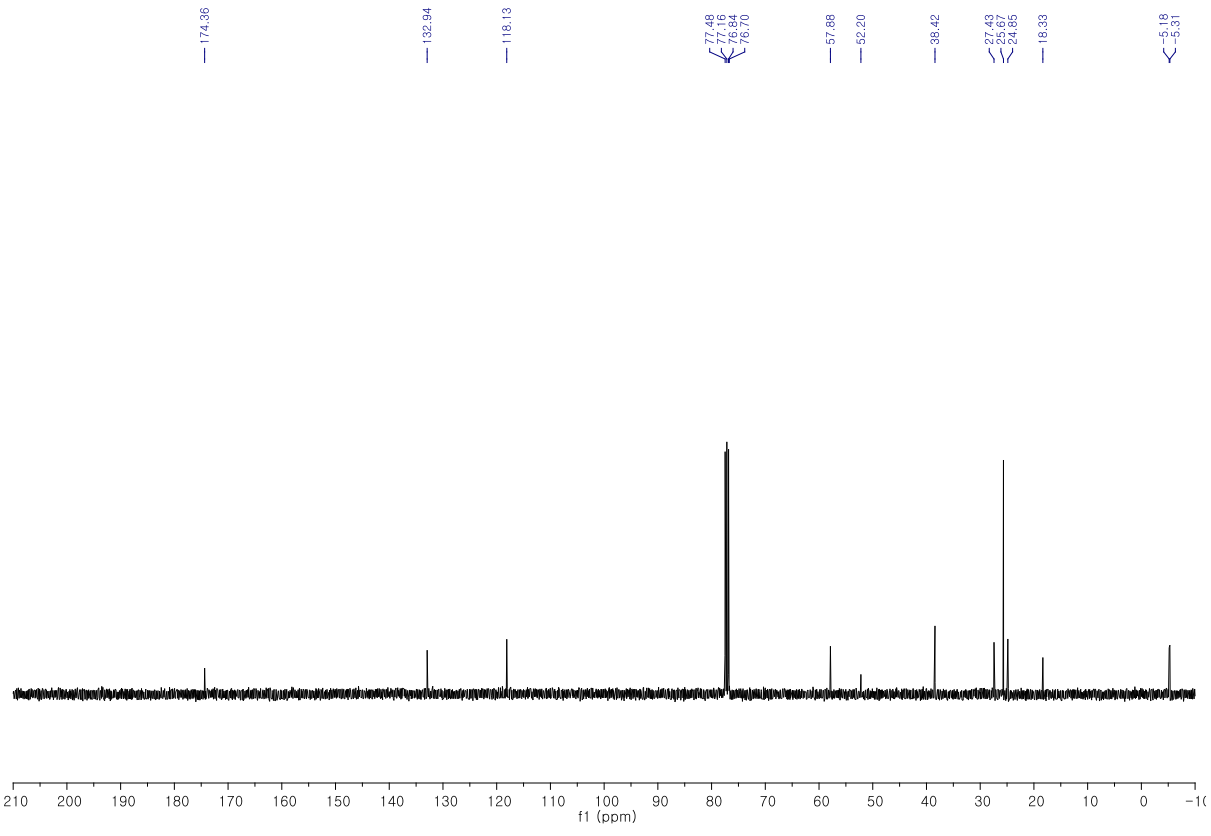

3.79
3.70
2.76
2.75
2.74
2.74
2.73
2.72
2.72
2.71
2.70
2.33
2.32
2.32
2.31
1.87
1.85
1.84
1.83
1.82
1.80

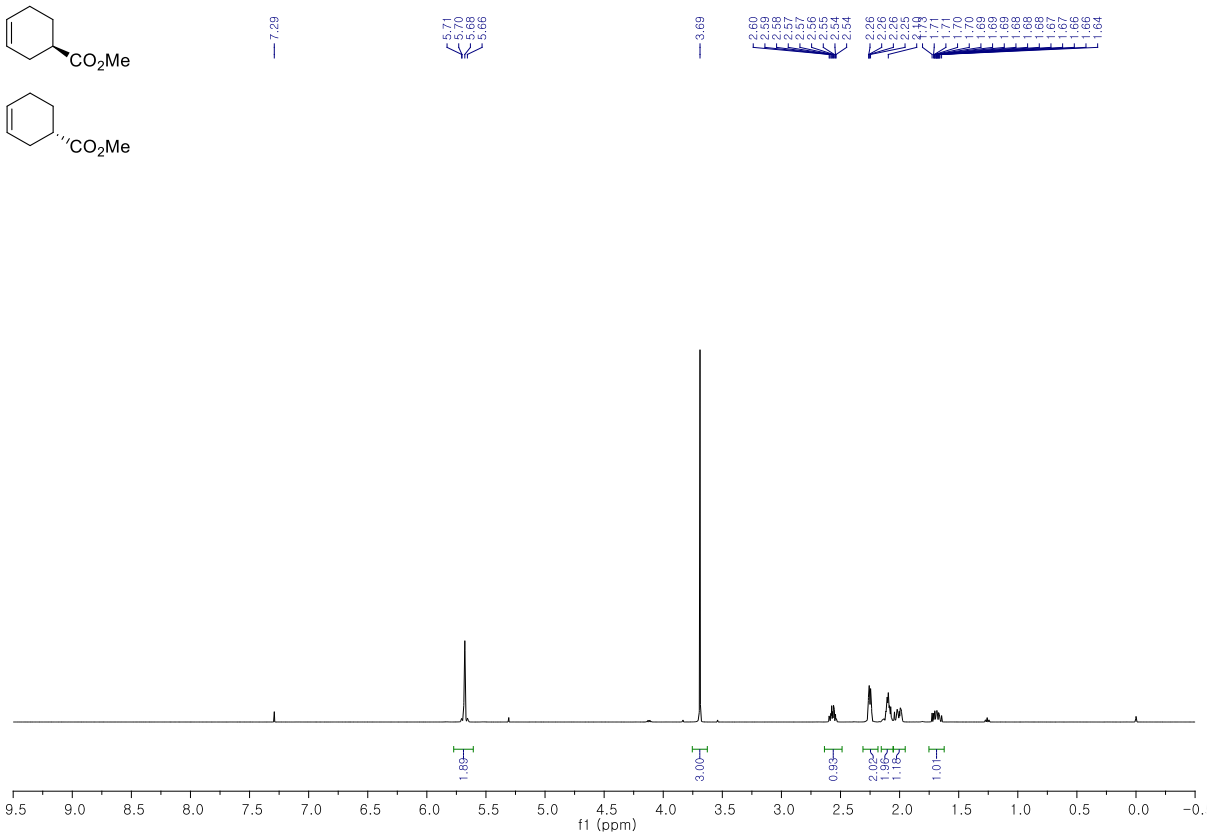

1.00
0.99
0.99
3.00
3.06
1.00
1.07
2.08
1.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


174.48
155.47
129.81
126.19
77.41
77.16
76.91
73.07
54.80
52.00
37.73
30.51
27.25


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OTBS
CO2Me
OTBS
CO2Me
f1 (ppm)


f1 (ppm)


CO2Me
CO2Me
7.29
5.71
5.70
5.68
5.66
3.69
2.60
2.59
2.58
2.57
2.57
2.56
2.55
2.54
2.54
2.26
2.26
2.26
2.25
2.24
1.73
1.71
1.71
1.70
1.70
1.69
1.69
1.69
1.68
1.68
1.68
1.67
1.67
1.66
1.66
1.64
1.89
3.00
0.93
2.02
1.96
1.18
1.01
f1 (ppm)
176.35
126.72
125.26
77.41
77.16
76.90
51.67
39.31
27.53
25.17
24.52
f1 (ppm)