Supplementary Information

Chiral Brønsted Acid-Catalysed Enantioselective Allylboration of Sterically Hindered Aldehydes Enabled by Multiple Hydrogen Bonding Interactions

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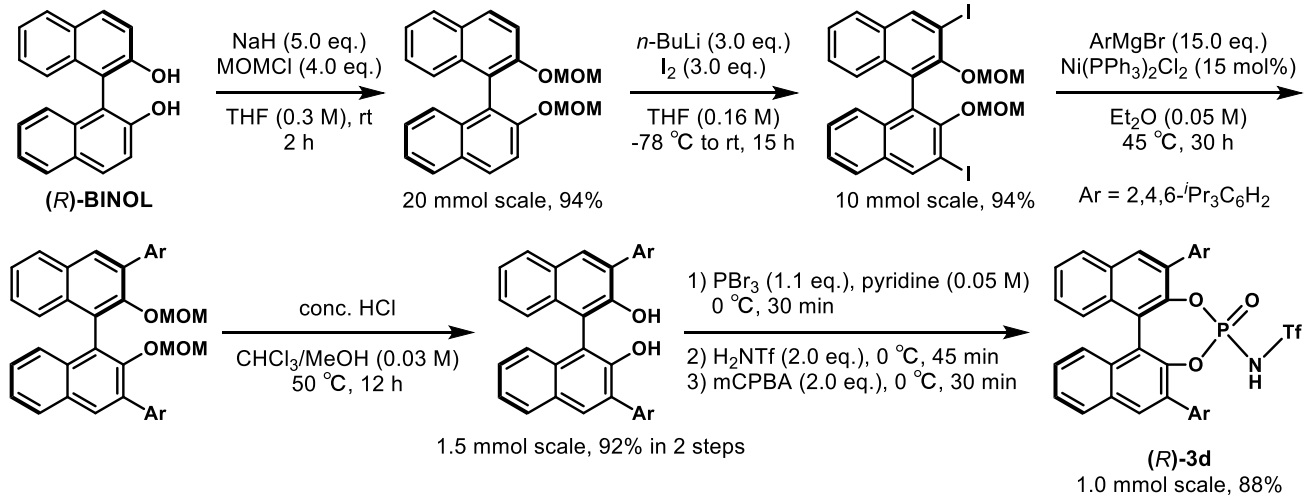
Contents

1. General Information

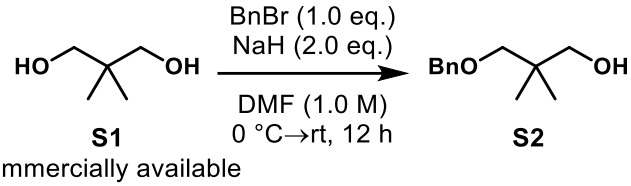
All reactions were conducted under a nitrogen atmosphere in flame-dried glassware. Dichloromethane (DCM), diethyl ether (Et_2O), toluene, and tetrahydrofuran (THF) were supplied from KANTO Chemical Co., Inc. as "Dehydrated solvent system". Other solvents and reagents were purchased from commercial suppliers and used without further purification. Aldehydes especially not mentioned were commercially available, each of which was freshly distilled before use. Allyl boronic acid pinacol ester was purchased from Combi-Blocks Inc. Purification of reaction products was conducted by flash column chromatography using silica gel 60 N (Merck 40-63 am). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF 254, 0.25 mm). ^{1}H NMR spectra were recorded on a JEOL ECA-600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane or solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm, TMS: 0.00 ppm). ^{13}C NMR spectra were recorded on a JEOL ECA-600 (151 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). Infrared spectra were recorded on a Jasco FT/IR-4100 spectrometer. Chiral stationary phase HPLC analysis was performed on a Jasco LC-2000 Plus Series system with DACIEL chiral analytical column (4.6 mmΦ* 250 mm length). Optical rotations were measured on a Jasco P1020 digital polarimeter with a sodium lamp and reported as follows; [α]T ºCD (c = g/100 mL, solvent). Mass spectra analysis using ESI ionization method was performed on a Bruker Daltonics solariX 9.4T spectrometer and the FD method was performed using a JEOL JMS-T100GC spectrometer at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

2. Catalyst Synthesis

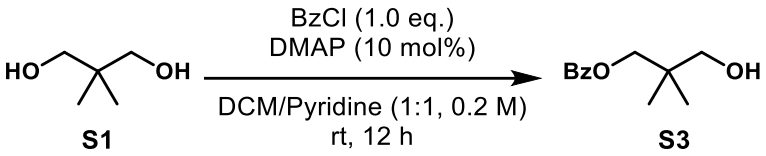


3. Preparation of Substrates

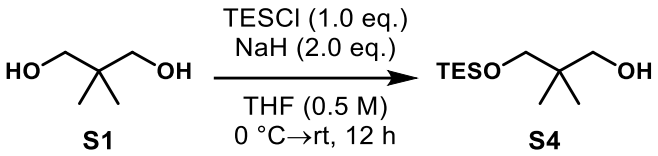
Preparation of mono-protected neopentyl glycol



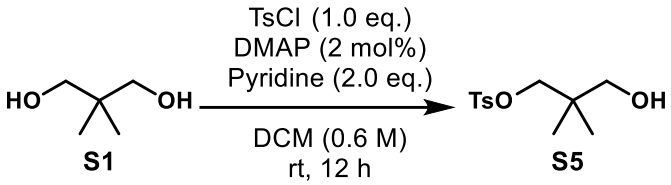
To a solution of **S1** (1.25 g, 12 mmol, 1.2 eq.) in DMF (12 mL, 0.8 M) was added NaH (800 mg, 20 mmol, 2.0 eq.) at 0 °C. After stirring the mixture for an hour, BnBr (1.2 mL, 10 mmol, 1.0 eq.) was slowly added at the same temperature. The reaction was warmed up to room temperature and stirred for 12 h. The reaction was cooled to 0 °C and quenched with aq. NH_4Cl. The resulting mixture was extracted with Et_2O, and the combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Hexane/EtOAc = 5/1 to 2/1) to give **S2** (1.5g, 8.0 mmol) in 80% yield as a colorless oil. All spectroscopic data for **S2** was known.[1]



To a solution of **S1** (2.6 g, 25 mmol, 5.0 eq.), DMAP (61 mg, 0.5 mmol, 10 mol%) in DCM and pyridine (1:1, 25 mL, 0.2 M) was added BzCl (580 μL, 5.0 mmol, 1.0 eq.) at room temperature. The reaction was stirred for 12 h. The reaction was cooled to 0 °C and quenched with aq. NH_4Cl. The resulting mixture was extracted with EtOAc, and the combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Hexane/EtOAc = 5/1 to 2/1) to give **S3** (972.7 mg, 4.7 mmol) in 94% yield as a colorless oil. All spectroscopic data for **S3** was known.[2]

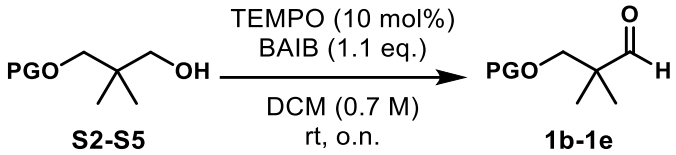


To a solution of **S1** (2.6 g, 25 mmol, 5.0 eq.) in THF (10 mL, 0.5 M) was added NaH (400 mg, 10 mmol, 2.0 eq.) at 0 °C. After stirring the mixture for an hour, TESCl (837 μL, 5.0 mmol, 1.0 eq.) was slowly added at the same temperature. The reaction was warmed up to room temperature and stirred for 4 h. The reaction was cooled to 0 °C and quenched with aq. NH_4Cl. The resulting mixture was extracted with Et_2O, and the combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Hexane/EtOAc = 10/1 to 5/1) to give **S4** (1.03 g, 4.75 mmol) in 95% yield as a colorless oil.

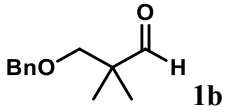


A solution of **S1** (2.6 g, 25 mmol, 5.0 eq.), DMAP (61 mg, 0.1 mmol, 2 mol%) and pyridine (807 μL, 2.0 eq.) in DCM (12.2 mL, 0.4 M) was stirred for 15 minutes, then TsCl (953.2 mg, 5.0 mmol, 1.0 eq.) was added to the mixture at room temperature. The reaction was stirred for 12 h. The reaction was quenched with H_2O. The resulting mixture was extracted with DCM, and the combined extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Hexane/EtOAc = 5/1 to 1/1) to give **S5** (1.26 g, 5.0 mmol) in quantitative yield as a colorless oil. All spectroscopic data for **S5** was known.[3]

Preparation of aldehyde **1b-1e**



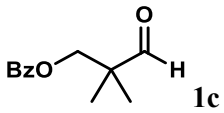
General Procedure: To a solution of alcohol and TEMPO (10 mol%) in DCM (0.7 M) was added phenyliodine(III) diacetate (PIDA) (1.1 eq.) at room temperature. The reaction was stirred overnight at room temperature. The reaction was cooled at 0 °C, added aq. $Na_2S_2O_3$ (5 mL) and aq. $NaHCO_3$ (5 mL), and stirred vigorously for 10 minutes at the same temperature. Then, the resulting mixture was extracted with Et_2O for 3 times. The organic layers were combined, washed with aq. $NaHCO_3$ for twice and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Hexane/EtOAc) to give the corresponding aldehyde.



1b

80% yield; red oil; Hexane/ Ether = 20/1

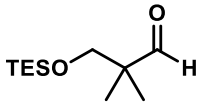
All spectroscopic data for **1b** was known.[4]



1c

83% yield; red oil; Hexane/EtOAc = 1/0 to 20/1

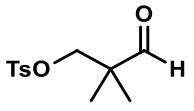
All spectroscopic data for **1c** was known.[5]



1d

90% yield; red oil; Hexane/EtOAc = 1/0 to 10/1

All spectroscopic data for **1d** was known.[6]



1e

52% yield; white solid; Hexane/EtOAc = 50/1 to 5/1

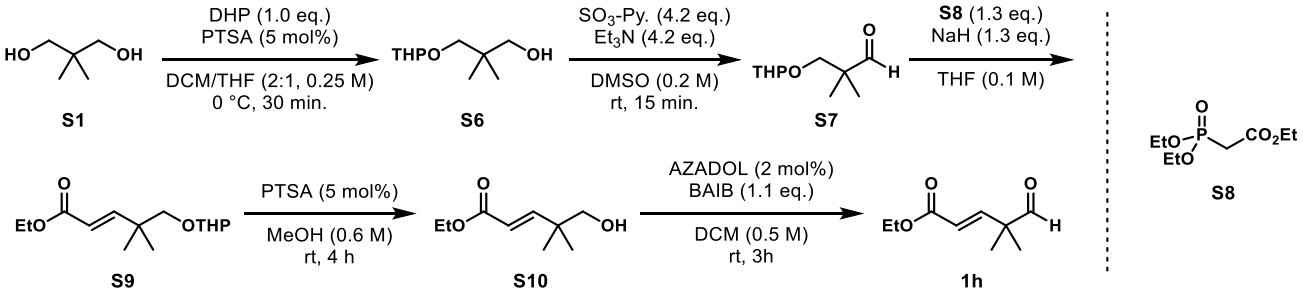
R_f = 0.34 (Hexane/EtOAc = 3/1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 4.00 (s, 2H), 2.46 (s, 3H), 1.10 (s, 6H).

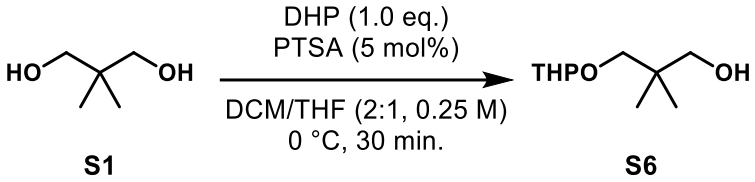
^{13}C NMR (151 MHz, $CDCl_3$) δ 202.5 (1C), 145.2 (1C), 132.4 (1C), 130.0 (2C), 128.1 (2C), 73.2 (1C), 46.3 (1C), 21.7 (1C), 18.9 (2C).

HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{12}H_{16}O_4SNa$ 279.0661, Found 279.0661.

Preparation of aldehyde **1h**

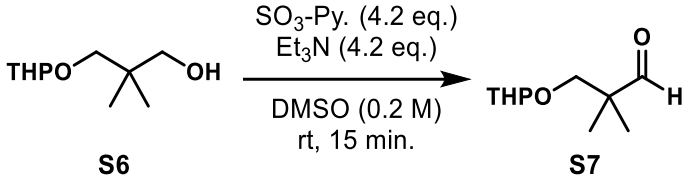


2,2-dimethyl-3-((tetrahydro-2H-pyran-2-yl)oxy)propan-1-ol（S6）



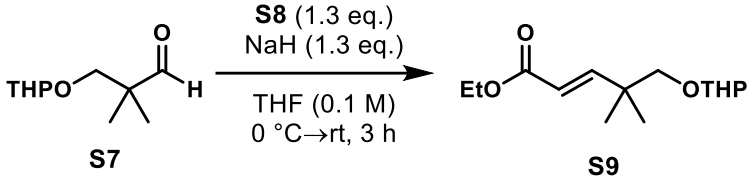
To a solution of **S1** (2.6 g, 25 mmol, 5.0 eq.) and 3,4-dihydro-2H-pyran (DHP) (457 μL, 5.0 mmol, 1.0 eq.) in DCM and THF (2:1, 2.0 mL, 0.25 M) was added *p*-toluenesulfonic acid (PTSA) (47.6 mg, 0.25 mmol, 5 mol%) at 0 °C. The reaction was stirred for 30 minutes. The reaction was quenched with aq. $NaHCO_3$ at the same temperature. The resulting mixture was extracted with DCM, and the combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Hexane/EtOAc = 9/1 to 3/1) to give **S6** (733 mg, 3.9 mmol) in 78% yield as a colorless oil. All spectroscopic data for **S6** was known.[7]

2,2-dimethyl-3-((tetrahydro-2H-pyran-2-yl)oxy)propanal (**S7**)



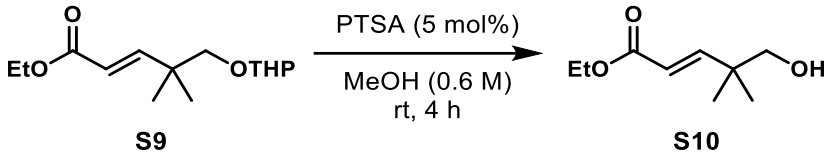
To a solution of **S6** (560.5 mg, 3 mmol, 1.0 eq.) and Et_3N (1.86 mL, 13.4 mmol, 4.2 eq.) in DMSO (15 mL, 0.2 M) was added SO_3-Pyridine (2.0 g, 13.4 mmol, 4.2 eq.) at room temperature. The reaction was stirred for 15 minutes. The reaction was quenched with 1 N HCl aq. at the same temperature. The resulting mixture was extracted with Et_2O, and the combined extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Hexane/EtOAc = 15/1 to 10/1) to give **S7** (516.4 mg, 2.8 mmol) in 92% yield as a colorless oil. All spectroscopic data for **S7** was known.[8]

ethyl (*E*)-4,4-dimethyl-5-((tetrahydro-2H-pyran-2-yl)oxy)pent-2-enoate (**S9**)



To a suspension of NaH (400 mg, 10 mmol, 1.3 eq.) in THF (70 mL, 0.1 M) was added **S8** (2 mL, 10 mmol, 1.3 eq.) at 0 °C. After stirring the mixture for 30 minutes, **S7** (1.43 g, 7.7 mmol, 1.0 eq.) in THF (7 mL) was slowly added at the same temperature. The reaction was warmed up to room temperature and stirred until TLC showed complete conversion of starting material. The reaction was cooled to 0 °C and quenched with aq. NH_4Cl. The resulting mixture was extracted with EtOAc, and the combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The product was directly used in the next step without further purification.

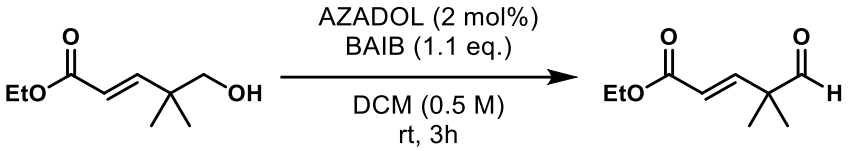
ethyl (*E*)-5-hydroxy-4,4-dimethylpent-2-enoate (**S10**)



S9 **S10**

To a crude of **S9** in MeOH (12.8 mL, 0.6 M) was added PTSA (672 mg, 0.39 mmol, 5 mol%) at 0 °C and the mixture was warmed to room temperature. The reaction was stirred for 4 h at the same temperature and then was quenched with aq. $NaHCO_3$. The resulting mixture was extracted with EtOAc, and the combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Hexane/EtOAc = 15/1 to 10/1) to give **S10** (1.31 g, 7.7 mmol) in quantitative yield as a colorless oil. All spectroscopic data for **S10** was known.[9]

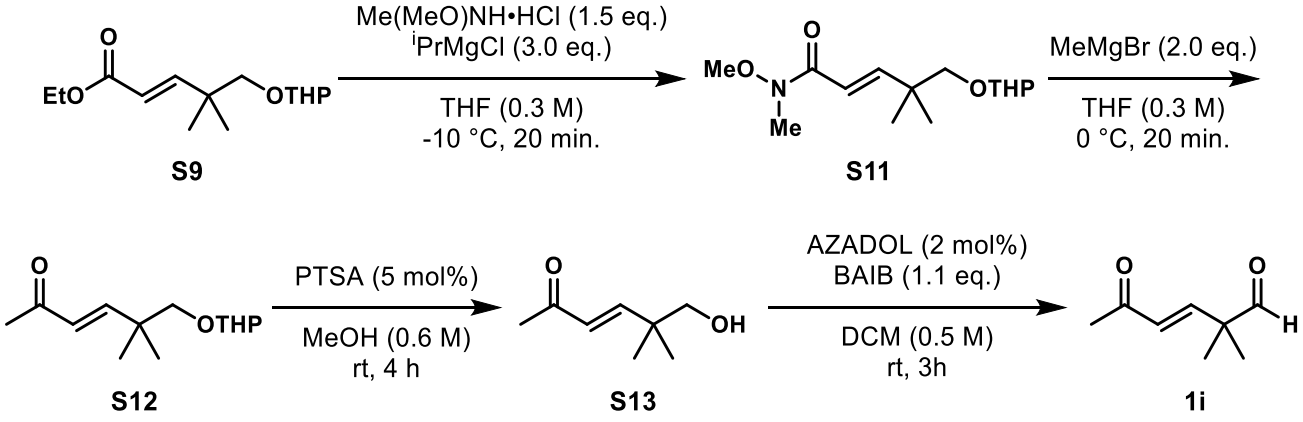
ethyl (*E*)-4,4-dimethyl-5-oxopent-2-enoate (**1h**)



S10 **1h**

To a solution of **S10** (172.2 mg, 2.0 mmol, 1.0 eq.) and AZADOL® (3.0 mg, 0.04 mmol, 2 mol%) in DCM (5.0 mL 0.5 M) was added phenyliodine(III) diacetate (PIDA) (354.3 mg, 2.2 mmol, 1.1 eq.) at room temperature. The reaction was stirred until TLC showed complete conversion of starting material. The reaction was cooled at 0 °C, added aq. $Na_2S_2O_3$ (5 mL) and aq. $NaHCO_3$ (5 mL), and stirred vigorously for 10 minutes at the same temperature. Then, the resulting mixture was extracted with Et_2O for 3 times. The organic layers were combined, washed with aq. $NaHCO_3$ for 2 times and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Hexane/EtOAc = 15/1 to 10/1) to give **1h** (322.4 mg, 1.9 mmol) in 95% yield as a colorless oil. All spectroscopic data for **1h** was known.[9]

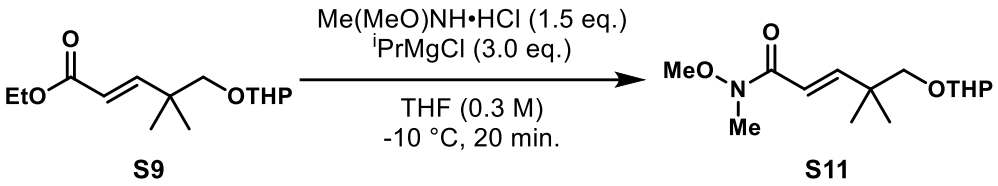
Preparation of aldehyde **1i**



S9 **S11**

S12 **S13** **1i**

(*E*)-N-methoxy-N,4,4-trimethyl-5-((tetrahydro-2H-pyran-2-yl)oxy)pent-2-enamide (**S11**)



To a solution of **S9** (151.5 mg, 0.6 mmol, 1.0 eq.) and Me(MeO)NH·HCl (87.8 mg, 0.9 mmol, 1.5 eq.) in THF (2 mL, 0.3 M) was added ^{i}PrMgCl (2.0 M in THF, 900 μL, 3.0 eq.) at -10 °C. The reaction was stirred for 20 minutes. The reaction was quenched with aq. NH_4Cl at the same temperature. The resulting mixture was extracted with EtOAc, and the combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Hexane/EtOAc = 5/1 to 1/1) to give **S11** (149 mg, 0.55 mmol) in 92% yield as a colorless oil.

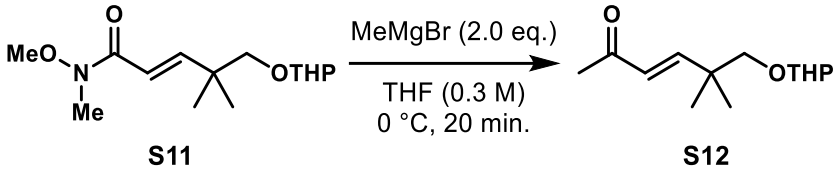
R_f = 0.39 (Hexane/EtOAc = 1/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 (d, *J* = 15.8 Hz, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 4.58 (t, *J* = 3.3 Hz, 1H), 3.84-3.81 (ddd, 1H), 3.70 (s, 3H), 3.60 (d, *J* = 9.3 Hz, 1H), 3.52-3.49 (ddd, 1H), 3.25 (s, 3H), 3.17 (d, *J* = 9.3 Hz, 1H), 1.84-1.78 (m, 1H), 1.70-1.65 (m, 1H), 1.61-1.50 (m, 6H), 1.14-1.09 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.3 (1C), 154.2 (1C), 116.0 (1C), 98.9 (1C), 75.5 (1C), 61.9 (1C), 61.7 (1C), 38.0 (1C), 32.5 (1C), 30.5 (1C), 25.6 (1C), 24.2 (1C), 24.2 (1C), 19.3 (1C).

HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{25}NO_4Na$ 294.1676, Found 294.1676.

(*E*)-5,5-dimethyl-6-((tetrahydro-2H-pyran-2-yl)oxy)hex-3-en-2-one



To a solution of **S11** (149 mg, 0.55 mmol, 1.0 eq.) in THF (1.83 mL, 0.3 M) was added MeMgBr (3.0 M in Et_2O, 370 μL, 2.0 eq.) at 0 °C. The reaction was stirred for 20 minutes. The reaction was quenched with aq. NH_4Cl at the same temperature. The resulting mixture was extracted with EtOAc, and the combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Hexane/EtOAc = 10/1 to 4/1) to give **S12** (98.1 mg, 0.43 mmol) in 78% yield as a colorless oil.

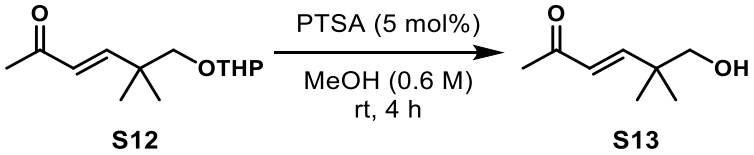
R_f = 0.18 (Hexane/EtOAc = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.86 (d, *J* = 16.5 Hz, 1H), 6.07 (d, *J* = 16.2 Hz, 1H), 4.57 (t, *J* = 3.3 Hz, 1H), 3.83-3.79 (ddd, 1H), 3.60 (d, *J* = 9.3 Hz, 1H), 3.53-3.49 (m, 1H), 3.16 (d, *J* = 9.3 Hz, 1H), 2.26 (s, 3H), 1.84-1.78 (m, 1H), 1.72-1.67 (m, 1H), 1.62-1.50 (m, 5H), 1.12 (d, *J* = 7.6 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 199.2 (1C), 154.9 (1C), 128.4 (1C), 99.0 (1C), 75.5 (1C), 62.0 (1C), 38.0 (1C), 30.5 (1C), 27.0 (1C), 25.5 (1C), 24.0 (1C), 23.9 (1C), 19.4 (1C).

HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{13}H_{22}O_3Na$ 249.1461, Found 249.1461.

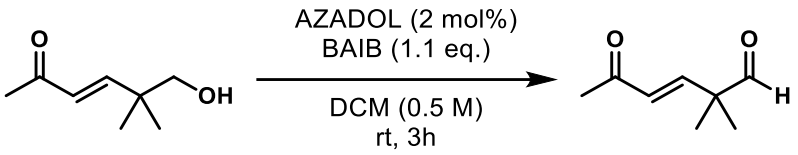
(E)-6-hydroxy-5,5-dimethylhex-3-en-2-one (**S13**)



S12 **S13**

To a solution of **S12** (1.2 mmol, 1.0 eq.) in MeOH (2.0 mL, 0.6 M) was added PTSA (10.3 mg, 0.06 mmol, 5 mol%) at 0 °C. The reaction was stirred for 4 h. The reaction was quenched with aq. $NaHCO_3$ at the same temperature. The resulting mixture was extracted with EtOAc, and the combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The product was directly used in the next step without further purification.

(E)-2,2-dimethyl-5-oxohex-3-enal (**1i**)

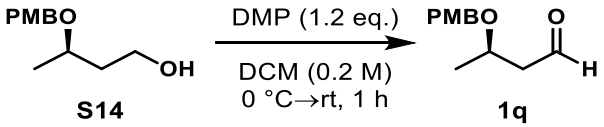


S13 **1i**

To a crude of **S13** and AZADOL® (3.7 mg, 0.024 mmol, 2 mol%) in DCM (2.4 mL 0.5 M) was added phenyliodine(III) diacetate (PIDA) (425.2 mg, 1.32 mmol, 1.1 eq.) at room temperature. The reaction was stirred until TLC showed complete conversion of starting material. The reaction was cooled at 0 °C, added aq. $Na_2S_2O_3$ (5 mL) and aq. $NaHCO_3$ (5 mL), and stirred vigorously for 10 minutes at the same temperature. Then, the resulting mixture was extracted with Et_2O for 3 times. The organic layers were combined, washed with aq. $NaHCO_3$ for 2 times and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Hexane/EtOAc = 10/1 to 5/1) to give **1i** (132.9 mg, 0.95 mmol) in 82% yield in 2 steps as a colorless oil. All spectroscopic data for **1i** was known.[10]

Preparation of aldehyde **1q**

(*R*)-3-((4-methoxybenzyl)oxy)butanal (**1q**)



S14 **1q**

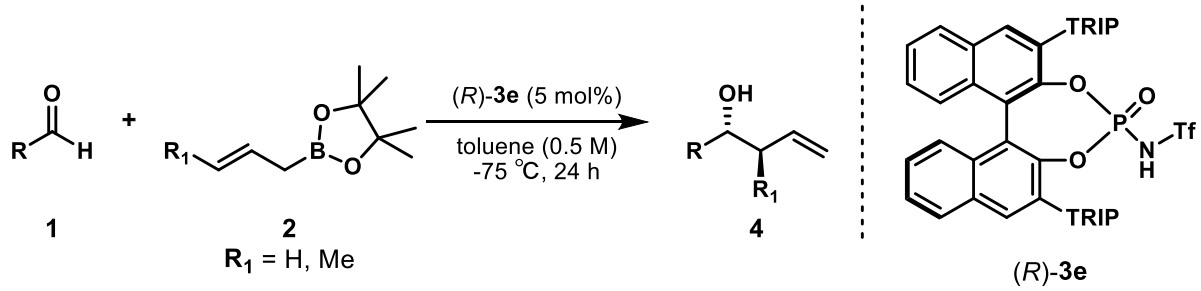
To a solution of known alcohol **S14**[1] (210.3 mg, 1.0 mmol, 1.0 eq.) in DCM (5.0 mL, 0.2 M) was added to Dess-Martin periodinane (DMP) (509 mg, 1.2 mmol, 1.2 eq.) at 0 °C. The reaction was carefully warmed up to room temperature. The reaction was quenched with 1:1 mixture of aq. $Na_2S_2O_3$ and aq. $NaHCO_3$. The resulting mixture was extracted with EtOAc, and the combined extracts were washed with brine, dried over $MgSO_4$, filtered, and

concentrated in vacuo. The residue was quickly purified by flash column chromatography on silica gel (Hexane/EtOAc = 10/1 to 1/1) to give **1q** (207 mg, 1.0 mmol) in quantitative yield as a colorless oil. All spectroscopic data for **1q** was known.[11]

Preparation of aldehyde **1o, 1p, 1u**

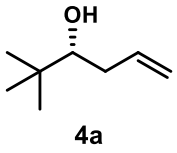
The aldehyde was prepared according to the procedure reported in the literature. [12]

3. Asymmetric Allylation/Crotylation Reactions with Chiral Phosphoramide



General Procedure: To a solution of **1** (0.2 mmol, 1.0 eq.), (*R*)-**3e** (8.8 mg, 0.01 mmol, 5 mol%) in toluene (200 μL) was added to boron reagent **2**[13] (0.24 mmol, 1.5 eq.) in toluene (200 μL) at -75 °C under an atmosphere of nitrogen. The reaction was stirred for 24 h. The reaction was quenched with aq. $NaHCO_3$ at the same temperature. The aqueous phase was extracted with EtOAc, the organic layers were combined, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Hexane/EtOAc) to give a homoallylic alcohol **4**.

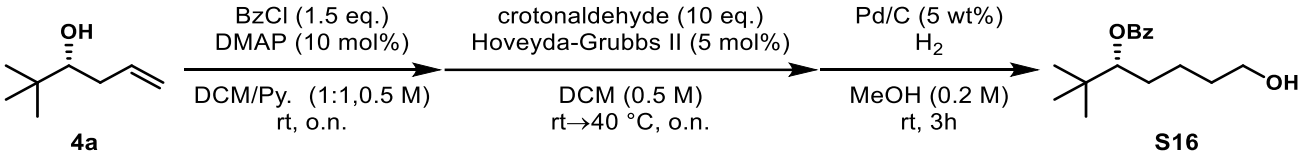
(*R*)-2,2-dimethylhex-5-en-3-ol (**4a**)



Purification with column chromatography on silica gel (Hexane/EtOAc = 20/1 to 5/1); quantitative yield (46.9 mg); colorless oil; $[\alpha]_D^{25.0}$: +3.2 (c = 8.0, $CHCl_3$); Literature date[14]; $[\alpha]_D^{20.0}$: +2.6 (c = 10.0, $CHCl_3$); R_f = 0.35 (Hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.90-5.83 (m, 1H), 5.17-5.14 (m, 2H), 3.26 (dd, *J* = 10.2, 1.8 Hz, 1H), 2.39-2.35 (m, 1H), 2.01-1.96 (m, 1H), 0.93 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.7 (1C), 117.7 (1C), 78.2 (1C), 36.6 (1C), 34.7 (1C), 25.8 (3C).

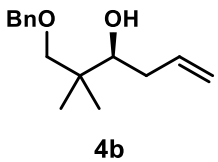
All spectroscopic data for **4b** was known.[14]

Enantiomeric excess of **4a** was determined by HPLC analysis of benzoate derivative **S16** according to the below scheme.



HPLC analysis: Chiralcel AD-3 column (Hexane/^{i}PrOH = 97/3, 1.0 mL/min, 40 °C, 254 nm), tR major = 17.950 min, tR minor = 16.308 min; 95% ee,

(*S*)-1-(benzyloxy)-2,2-dimethylhex-5-en-3-ol (**4b**)

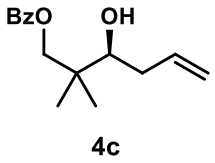


Purification with column chromatography on silica gel (Hexane/EtOAc = 20/1 to 5/1); 85% yield (46.9 mg); colorless oil; $[\alpha]_D^{23.5}$: -12.3 (c = 0.13, $CHCl_3$); R_f = 0.26 (Hexane/EtOAc = 10/1); HPLC analysis: Chiralcel AD-3 column (Hexane/^{i}PrOH = 98/2, 0.7 mL/min, 30 °C, 254 nm), tR major = 11.000 min, tR minor = 10.400 min; 90% ee; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.27 (m, 5H), 5.96-5.89 (m, 1H), 5.13-5.07 (m, 2H), 4.51 (s, 2H), 3.54 (d, *J* = 10.8 Hz, 1H), 3.39 (d, *J* = 8.4 Hz, 1H), 3.30 (d, *J* = 8.4 Hz, 1H), 3.09 (s, 1H), 2.30-2.26 (m, 1H), 2.09-2.04 (m, 1H), 0.94 (s, 3H), 0.92 (s, 3H); ^{13}C

NMR (151 MHz, $CDCl_3$) δ 138.0 (1C), 136.9 (1C), 128.5 (2C), 127.8 (1C), 127.6 (2C) , 116.7 (1C), 79.7 (1C), 77.6 (1C), 73.7 (1C), 38.5 (1C), 36.6 (1C), 22.7 (1C), 19.7 (1C).

All spectroscopic data for **4b** was known.[15]

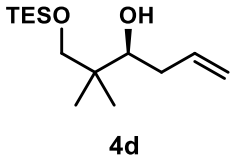
(*S*)-3-hydroxy-2,2-dimethylhex-5-en-1-yl benzoate (**4c**)



4c

Purification with column chromatography on silica gel (Hexane/EtOAc = 20/1 to 5/1); 95% yield (47.2 mg); colorless oil; $[\alpha]_D^{26.7}$: -4.11 (c = 0.125, $CHCl_3$); R_f = 0.17 (Hexane/EtOAc = 10/1); HPLC analysis: Chiralcel AD-3 column (Hexane/^{i}PrOH = 98/2, 0.7 mL/min, 30 °C, 254 nm), tR major = 26.392 min, tR minor = 25.425 min; 92% ee; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.59-7.56 (dt, *J* = 7.2, 1.2 1H), 7.46 (dd, *J* = 8.4, 7.2 Hz, 2H), 5.91-5.84 (m, 1H), 5.18-5.14 (m, 2H), 4.41 (d, *J* = 10.2 Hz, 1H), 4.06 (d, *J* = 11.4 Hz, 1H), 3.54 (d, *J* = 10.8 Hz, 1H), 2.39 (m, 1H), 2.14-2.09 (m, 2H), 1.05 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9 (1C), 136.2 (1C), 133.1 (1C), 130.3 (1C), 129.7 (2C), 128.5 (2C), 118.1 (1C), 74.1 (1C), 71.1 (1C), 38.7 (1C), 36.2 (1C), 21.9 (1C), 19.4 (1C); HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{20}O_3Na$ 271.1304, Found 271.1304.

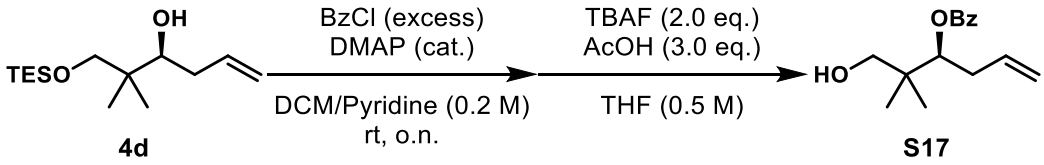
(*S*)-2,2-dimethyl-1-((triethylsilyl)oxy)hex-5-en-3-ol (**4d**)



4d

Purification with column chromatography on silica gel (Hexane/EtOAc = 1/0 to 10/1); quantitative yield (56.2 mg); colorless oil; $[\alpha]_D^{25.7}$: -10.4 (c = 0.100, $CHCl_3$); R_f = 0.39 (Hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.98-5.92 (m, 1H), 5.13-5.07 (m, 2H), 3.55 (dd, *J* = 10.3, 2.4 Hz, 1H), 3.50 (d, *J* = 9.6 Hz, 1H), 3.48 (d, *J* = 9.6 Hz, 1H), 2.29-2.25 (m, 1H), 2.13-2.08 (m, 1H), 0.96 (t, *J* = 7.8 Hz, 9H), 0.92 (s, 3H), 0.84 (s, 3H), 0.61 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.0 (1C), 116.4 (1C), 78.6 (1C), 73.2 (1C), 38.4 (1C), 36.8 (1C), 22.4 (1C), 18.9 (1C), 6.8 (3C), 4.2 (3C); HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{14}H_{30}O_2SiNa$ 281.1913, Found 281.1907.

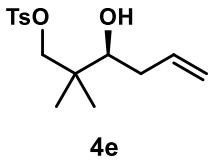
Enantiomeric excess of **4d** was determined by HPLC analysis of benzoate derivative **S17** according to the below scheme.



4d **S17**

HPLC analysis: Chiralcel AD-3 column (Hexane/^{i}PrOH = 95/5, 1.0 mL/min, 30 °C, 254 nm), tR major = 10.367 min, tR minor = 11.283 min; 92% ee

(*S*)-3-hydroxy-2,2-dimethylhex-5-en-1-yl 4-methylbenzenesulfonate (**4e**)

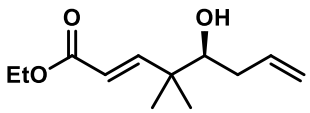


4e

Purification with column chromatography on silica gel (Hexane/EtOAc = 20/1 to 5/1); 75% yield (44.5 mg); colorless oil; $[\alpha]_D^{27.1}$: -3.14 (c = 0.285, $CHCl_3$); R_f = 0.35 (Hexane/EtOAc = 5/1); HPLC analysis: Chiralcel AD-3 column (Hexane/^{i}PrOH = 98/2, 0.7 mL/min, 30 °C, 254 nm), tR major = 11.000 min, tR minor = 10.400 min; 90% ee; ^{1}H NMR (600 MHz, $CDCl_3$)δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 5.83-5.76 (m, 1H), 5.15-5.11 (m, 2H), 4.01 (d, *J* = 9.3 Hz, 1H),

3.73 (d, *J* = 9.3 Hz, 1H), 3.47 (d, *J* = 10.7 Hz, 1H), 2.45 (s, 3H), 2.28 (dd, *J* = 14.1, 5.5 Hz, 1H), 2.00-1.95 (m, 1H), 1.76 (s, 1H), 0.92 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.8 (1C), 135.7 (1C), 133.0 (1C), 129.9 (2C), 128.0 (2C), 118.5 (1C), 76.4 (1C), 73.1 (1C), 38.6 (1C), 36.0 (1C), 21.7 (1C), 21.5 (1C), 18.5 (1C); HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{22}O_4SNa$ 321.1131, Found 321.1131.

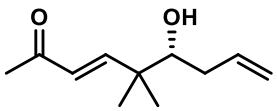
ethyl (*S*,*E*)-5-hydroxy-4,4-dimethylocta-2,7-dienoate (**4f**)



4f

Purification with column chromatography on silica gel (Hexane/EtOAc = 20/1 to 5/1); quantitative yield (47.0 mg); colorless oil; $[\alpha]_D^{25.1}$: +6.06 (c = 0.165, $CHCl_3$); R_f = 0.35 (Hexane/EtOAc = 5/1); HPLC analysis: Chiralcel OD-3 column (Hexane/^{i}PrOH = 95/5, 1.0 mL/min, 30 °C, 254 nm), tR major = 6.833 min, tR minor = 5.533 min; 95% ee; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.03 (d, *J* = 15.8 Hz, 1H), 5.85-5.78 (m, 2H), 5.16-5.14 (m, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.43 (d, *J* = 9.6 Hz, 1H), 2.33 (dd, *J* = 13.7, 4.8 Hz, 1H), 2.00-1.95 (m, 1H), 1.69 (s, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.11 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.0 (1C), 155.0 (1C), 135.6 (1C), 119.7 (1C), 118.5 (1C), 76.7 (1C), 60.4 (1C), 41.5 (1C), 37.0 (1C), 23.0 (1C), 22.5, (1C) 14.4 (1C); HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{12}H_{20}O_3Na$ 235.1304, Found 235.1305.

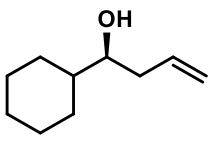
(*R*,*E*)-6-hydroxy-5,5-dimethylnona-3,8-dien-2-one (**4g**)



4g

Purification with column chromatography on silica gel (Hexane/EtOAc = 20/1 to 5/1); 81% yield (46.9 mg); colorless oil; $[\alpha]_D^{26.7}$: +27.2 (c = 0.13, $CHCl_3$); R_f = 0.21 (Hexane/EtOAc = 5/1); HPLC analysis: Chiralcel OD-3 column (Hexane/^{i}PrOH = 95/5, 1.0 mL/min, 30 °C, 254 nm), tR major = 6.292 min, tR minor = 6.925 min; 95% ee; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.89 (d, *J* = 16.5 Hz, ^{1}H), 6.08 (d, *J* = 16.2 Hz, 1H), 5.85-5.78 (m, 1H), 5.18-5.14 (m, 2H), 3.44 (d, *J* = 10.3 Hz, 1H), 2.33 (m, 1H), 2.28 (s, 3H), 1.99-1.94 (m, 1H), 1.75 (s, 1H), 1.12 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.0 (1C), 154.1 (1C), 135.5 (1C), 129.0 (1C), 118.7 (1C), 76.7 (1C), 41.4 (1C), 37.1 (1C), 27.3 (1C), 23.0 (1C), 22.8 (1C); HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{11}H_{18}O_2Na$ 205.1199, Found 205.1199.

(*S*)-1-cyclohexylbut-3-en-1-ol (**4h**)

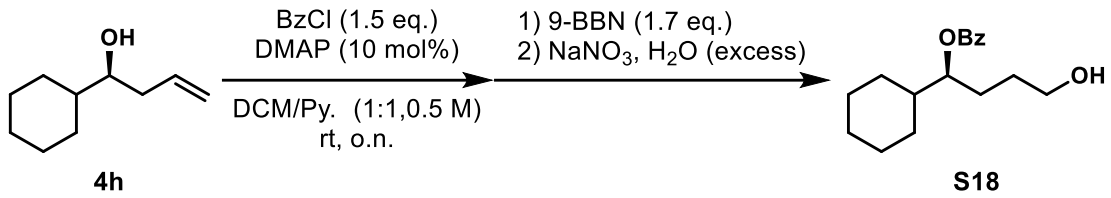


4h

Purification with column chromatography on silica gel (Hexane/EtOAc = 30/1 to 10/1); 91% yield (27.8 mg); colorless oil; $[\alpha]_D^{23.5}$: -1.48 (c = 0.12, $CHCl_3$); R_f = 0.28 (Hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.88-5.81 (m, 1H), 5.16-5.13 (m, 2H), 3.41-3.38 (m, 1H), 2.32-2.36 (m, 1H), 2.16-2.10 (m, 1H), 1.85-1.88 (m, 1H), 1.79-1.73 (m, 2H), 1.70-1.65 (m, 2H), 1.39-1.33 (m, 1H), 1.28-1.19 (m, 2H), 1.13-1.18 (m, 1H), 0.99-1.10 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.6 (1C), 118.1 (1C), 77.3 (1C), 77.1 (1C), 76.9 (1C), 74.8 (1C), 43.2 (1C), 38.9 (1C), 29.2 (1C), 28.2 (1C), 26.6 (1C), 26.4 (1C), 26.2 (1C).

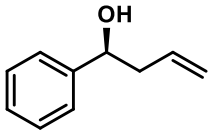
All spectroscopic data for **4h** was known.[16]

Enantiomeric excess of **4h** was determined by HPLC analysis of benzoate derivative **S18** according to the below scheme.



HPLC analysis: Chiralcel AD-3 column (Hexane/^{i}PrOH = 97/3, 1.0 mL/min, 30 °C, 254 nm), tR major = 25.650 min, tR minor = 24.242 min; 89% ee

(*R*)-1-phenylbut-3-en-1-ol (**4i**)

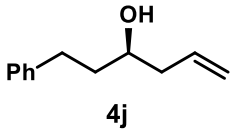


4i

Purification with column chromatography on silica gel (Hexane/EtOAc = 20/1 to 10/1); 90% yield (27.8 mg); colorless oil; $[\alpha]_D^{26.4}$: +28.4 (c = 0.08, $CHCl_3$); R_f = 0.19 (Hexane/EtOAc = 5/1); HPLC analysis: Chiralcel OD-3 column (Hexane/^{i}PrOH = 98/2, 0.7 mL/min, 30 °C, 254 nm), tR major = 21.500 min, tR minor = 18.542 min; 90% ee; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39-7.33 (m, 4H), 7.30-7.26 (m, 1H), 5.85-5.78 (m, 1H), 5.19-5.14 (m, 2H), 4.75 (d, *J* = 7.8, 4.8, 2.4 Hz, 1H), 2.57-2.47 (m, 2H), 2.03 (brs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ144.1 (1C), 134.6 (1C), 128.5 (2C), 127.6 (1C), 126.0 (2C), 118.4 (1C), 73.5 (1C), 43.9 (1C).

All spectroscopic data for **4i** was known.[16]

(*R*)-1-phenylhex-5-en-3-ol (**4j**)

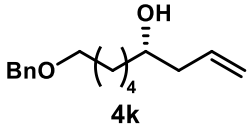


4j

Purification with column chromatography on silica gel (Hexane/EtOAc = 10/1 to 3/1); 85% yield (30.1 mg); colorless oil; $[\alpha]_D^{24.8}$: +9.72 (c = 0.200, $CHCl_3$); R_f = 0.18 (Hexane/EtOAc = 3/1); HPLC analysis: Chiralcel OD-3 column (Hexane/^{i}PrOH = 95/5, 1.0 mL/min, 30 °C, 254 nm), tR major = 6.292 min, tR minor = 6.925 min; 95% ee; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.7 Hz, 2H), 7.20 (dd, *J* = 16.0, 7.4 Hz, 3H), 5.85-5.79 (m, 1H), 5.16-5.14 (m, 2H), 3.68 (s, 1H), 2.81 (ddd, *J* = 14.4, 9.0, 6.0 Hz, 1H), 2.67-2.72 (m, 1H), 2.35-2.31 (m, 1H), 2.21-2.16 (m, 1H), 1.83-1.76 (m, 2H), 1.57 (d, *J* = 4.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.1 (1C), 134.7 (1C), 128.5 (2C), 128.5 (2C), 125.9 (1C), 118.5 (1C), 77.3 (1C), 77.1 (1C), 76.9 (1C), 70.0 (1C), 42.2 (1C), 38.5 (1C), 32.1 (1C).

All spectroscopic data for **4j** was known.[16]

(*S*)-9-(benzyloxy)non-1-en-4-ol (**4k**)

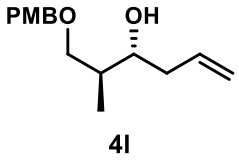


4k

Purification with column chromatography on silica gel (Hexane/EtOAc = 20/1 to 10/1); 96% yield (47.7 mg); colorless oil; $[\alpha]_D^{25}$: -7.96 (c = 0.300, $CHCl_3$); R_f = 0.29 (Hexane/EtOAc = 5/1); SFC analysis: Chiralpak IF-3/SFC 4.6×150 mm (CO_2/MeOH = 95/5, 3.0 mL/min, 220 nm, 40 °C), tR major = 5.978 min, tR minor = 5.523 min; 95% ee; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35-7.27 (m, 5H), 5.86-5.79 (m, 1H), 5.15-5.11 (m, 2H), 4.50 (s, 2H), 3.66-3.62 (m, 1H), 3.47 (t, *J* = 6.5 Hz, 2H), 2.32-2.27 (m, 1H), 2.17-2.11 (m, 1H), 1.66-1.33 (m, 8H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.6 (1C), 134.9 (1C), 128.4 (2C), 127.7 (2C), 127.5 (1C), 118.2 (1C), 77.2 (1C), 77.0 (1C), 76.8 (1C), 72.9 (1C), 70.6 (1C), 70.3

(1C), 42.0 (1C), 36.7 (1C), 29.7 (1C), 26.2 (1C), 25.5 (1C); HRMS (FD) m/z: [M+Na]+ Calcd for $C_{16}H_{24}NaO_2$ 271.1668; Found 271.1668.

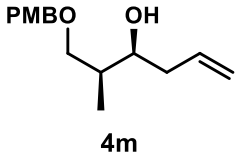
(2*S*,3*R*)-1-((4-methoxybenzyl)oxy)-2-methylhex-5-en-3-ol (**4l**)



4l

Purification with column chromatography on silica gel (Hexane/EtOAc = 20/1 to 5/1); 95% yield (47.8 mg); colorless oil; $[\alpha]_D^{26.4}$: +1.96 (c = 0.100, $CHCl_3$); R_f = 0.16 (Hexane/EtOAc = 5/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.87-5.80 (m, 1H), 5.13-5.07 (m, 2H), 4.44 (s, 2H), 3.83-3.79 (m, 4H), 3.50 (d, *J* = 5.5 Hz, 2H), 2.57 (brs, 1H), 2.26-2.17 (m, 2H), 1.92-1.86 (m, 1H), 0.95 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3 (1C), 135.7 (1C), 130.2 (1C), 129.3 (2C), 117.3 (1C), 113.9 (2C), 74.4 (1C), 73.2 (1C), 73.1 (1C), 55.4 (1C), 38.9 (1C), 37.5 (1C), 10.8 (1C); HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{22}O_3Na$ 273.1467, Found 273.1461.

(2*S*,3*S*)-1-((4-methoxybenzyl)oxy)-2-methylhex-5-en-3-ol (**4m**)

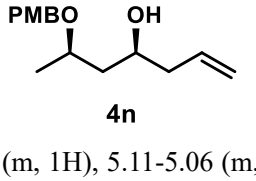


4m

Purification with column chromatography on silica gel (Hexane/EtOAc = 20/1 to 5/1); 94% yield (47.2 mg); colorless oil; $[\alpha]_D^{27.2}$: -5.63 (c = 0.12, $CHCl_3$); R_f = 0.25 (Hexane/EtOAc = 5/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.93-5.86 (m, 1H), 5.12-5.09 (m, 2H), 4.45 (s, 2H), 3.80 (s, 3H), 3.60-3.56 (m, 2H), 3.46 (dd, *J* = 9.3, 7.2 Hz, 1H), 3.45 (brs, 1H), 2.36-2.32 (m, 1H), 2.21-2.15 (m, 1H), 1.90-1.84 (m, 1H), 0.90 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4 (1C), 135.3 (1C), 130.0 (1C), 129.4 (2C), 117.3 (1C), 113.9 (2C), 75.2 (1C), 74.6 (1C), 73.2 (1C), 55.4 (1C), 39.5 (1C), 37.9 (1C), 13.9 (1C).

All spectroscopic data for **4m** was known.[17]

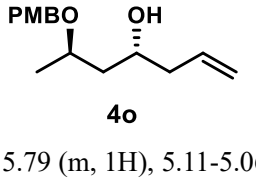
(4*S*,6*R*)-6-((4-methoxybenzyl)oxy)hept-1-en-4-ol (**4n**)



4n

Purification with column chromatography on silica gel (Hexane/EtOAc = 10/1 to 3/1); 90% yield (45.3 mg); colorless oil; $[\alpha]_D^{24.6}$: -25.7 (c = 0.200, $CHCl_3$); R_f = 0.30 (Hexane/EtOAc = 3/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 5.82 (m, 1H), 5.11-5.06 (m, 2H), 4.60 (d, *J* = 10.8 Hz, 1H), 4.35 (d, *J* = 10.8 Hz, 1H), 3.86-3.80 (m, 5H), 3.77 (s, 1H), 2.25-2.15 (m, 2H), 1.68-1.58 (m, 2H), 1.24 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4 (1C), 135.1 (1C), 130.1 (1C), 129.5 (2C), 117.3 (1C), 114.0 (2C), 75.8 (1C), 71.2 (1C), 70.1 (1C), 55.4 (1C), 43.2 (1C), 42.1 (1C), 19.7 (1C); HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{22}O_3Na$ 273.1467, Found 273.1461.

(4*R*,6*R*)-6-((4-methoxybenzyl)oxy)hept-1-en-4-ol (**4o**)

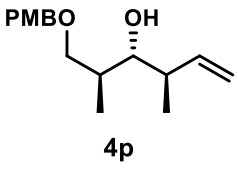


4o

Purification with column chromatography on silica gel (Hexane/EtOAc = 10/1 to 3/1); 89% yield (44.6 mg); colorless oil; $[\alpha]_D^{25.3}$: -24.8 (c = 0.165, $CHCl_3$); R_f = 0.39 (Hexane/EtOAc = 3/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 5.86-5.79 (m, 1H), 5.11-5.06 (m, 2H), 4.55 (d, *J* = 11.4 Hz, 1H), 4.39 (d, *J* = 11.4 Hz, 1H), 3.99-3.95 (m, 1H), 3.89-3.83 (m, 1H), 3.80 (s, 3H), 2.24-2.17 (m, 2H), 1.68-1.58 (m, 2H), 1.24 (t, *J* = 5.7 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$)

δ 159.3 (1C), 135.2 (1C), 130.6 (1C), 129.5 (2C), 117.5 (1C), 114.0 (2C), 72.3 (1C), 70.3 (1C), 67.8 (1C), 55.4 (1C), 42.4 (1C), 42.1 (1C), 19.4 (1C); HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{22}O_3Na$ 273.1467, Found 273.1461.

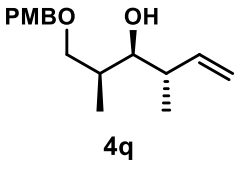
(2*S*,3*R*,4*R*)-1-((4-methoxybenzyl)oxy)-2,4-dimethylhex-5-en-3-ol (**4p**)



4p

Purification with column chromatography on silica gel (Hexane/EtOAc = 20/1 to 5/1); 85% yield (48.8 mg); colorless oil; $[\alpha]_D^{27.1}$: -2.77 (c = 0.12, $CHCl_3$); R_f = 0.60 (Hexane/EtOAc = 5/1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 5.85-5.79 (m, 1H), 4.99-4.96 (m, 2H), 4.36 (s, 2H), 3.72 (s, 3H), 3.47 (dd, *J* = 9.0, 4.2 Hz, 1H), 3.40 (t, *J* = 8.4 Hz, 2H), 3.28 (dd, *J* = 7.2, 3.6 Hz, 1H), 2.28-2.24 (m, 1H), 1.85-1.81 (m, 1H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.79 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4 (1C), 139.9 (1C), 129.9 (1C), 129.4 (2C), 115.2 (1C), 113.9 (2C), 79.9 (1C), 75.3 (1C), 73.2 (1C), 55.4 (1C), 41.2 (1C), 36.3 (1C), 17.8 (1C), 14.0 (1C); HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{24}O_3Na$ 287.1623, Found 287.1618.

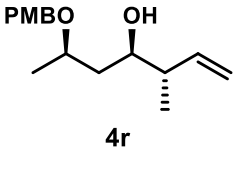
(2*S*,3*S*,4*S*)-1-((4-methoxybenzyl)oxy)-2,4-dimethylhex-5-en-3-ol (**4q**)



4q

Purification with column chromatography on silica gel (Hexane/EtOAc = 20/1 to 5/1); 70% yield (37.3 mg); colorless oil; $[\alpha]_D^{24.4}$: +2.77 (c = 0.24, $CHCl_3$); R_f = 0.54 (Hexane/EtOAc = 5/1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.82-5.76 (m, 1H), 5.12-5.08 (m, 2H), 4.44 (s, 2H), 3.80 (s, 3H), 3.53 (dd, *J* = 8.9, 6.2 Hz, 1H), 3.50-3.46 (m, 2H), 2.33 (brs, 1H), 2.26 (td, *J* = 15.1, 7.2 Hz, 1H), 1.97-1.93 (m, 1H), 0.95 (t, *J* = 7.6 Hz, 6H)
^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2 (1C), 142.0 (1C), 130.5 (1C), 129.3 (2C), 115.7 (1C), 113.9 (2C), 75.8 (1C), 74.6 (1C), 73.1 (1C), 55.4 (1C), 42.0 (1C), 35.0 (1C), 16.7 (1C), 9.9 (1C).
All spectroscopic data for **4q** was known.[18]

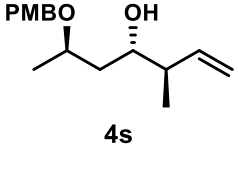
(3*S*,4*R*,6*R*)-6-((4-methoxybenzyl)oxy)-3-methylhept-1-en-4-ol (**4r**)



4r

Purification with column chromatography on silica gel (Hexane/EtOAc = 20/1 to 3/1); 72% yield (38.0 mg); colorless oil; $[\alpha]_D^{24.4}$: +2.77 (c = 0.24, $CHCl_3$); R_f = 0.37 (Hexane/EtOAc = 3/1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.9 Hz, 3H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.84-5.78 (m, 1H), 5.06-5.02 (m, 2H), 4.59 (d, *J* = 10.8 Hz, 1H), 4.36 (d, *J* = 10.8 Hz, 1H), 3.81-3.77 (m, 4H), 3.70-3.68 (m, 1H), 2.24-2.20 (m, 1H), 1.66-1.57 (m, 3H), 1.24 (d, *J* = 5.4 Hz, 3H), 1.03 (d, *J* = 7.2 Hz, 3H);^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3 (1C), 140.7 (1C), 130.2 (1C), 129.6 (2C), 115.1 (1C), 114.0 (2C), 76.1 (1C), 75.0 (1C), 70.1 (1C), 55.4 (1C), 43.9 (1C), 40.6 (1C), 19.8 (1C), 15.5 (1C).
All spectroscopic data for **4r** was known.[11]

(3*R*,4*S*,6*R*)-6-((4-methoxybenzyl)oxy)-3-methylhept-1-en-4-ol (**4s**)

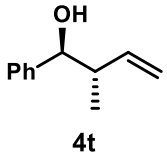


4s

Purification with column chromatography on silica gel (Hexane/EtOAc = 20/1 to 3/1); 80% yield (45.9 mg); colorless oil; $[\alpha]_D^{24.8}$: -35.8 (c = 0.13, $CHCl_3$); R_f = 0.37 (Hexane/EtOAc = 5/1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.84-5.78 (m, 1H), 5.08-5.05 (m, 2H), 4.54 (d, *J* = 11.3 Hz, 1H), 4.39 (d, *J* = 11.0 Hz, 1H), 3.88-

3.83 (m, 1H), 3.80-3.75 (m, 4H), 2.15-2.23 (m, 1H), 1.65-1.56 (m, 2H), 1.24 (d, *J* = 6.2 Hz, 3H), 1.02 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2 (1C), 140.8 (1C), 130.7 (1C), 129.4 (2C), 115.5 (1C), 113.9 (2C), 72.3 (1C), 71.3 (1C), 70.4 (1C), 55.4 (1C), 44.2 (1C), 40.3 (1C), 19.4 (1C), 16.2 (1C); HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{24}O_3Na$ 287.1623, Found 287.1618.

(1*S*,2*S*)-2-methyl-1-phenylbut-3-en-1-ol (**4t**)

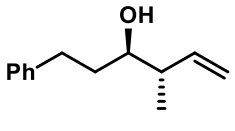


4t

Purification with column chromatography on silica gel (Hexane/EtOAc = 20/1 to 5/1); 98% yield (31.2 mg); colorless oil; $[\alpha]_D^{24.6}$: -122.7 (c = 0.200, $CHCl_3$); R_f = 0.38 (Hexane/EtOAc = 5/1); HPLC analysis: Chiralcel OD-3 column (Hexane/^{i}PrOH = 90/10, 1.0 mL/min, 30 °C, 254 nm), tR major = 7.917 min, tR minor = 9.150 min; 96% ee ; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.27 (m, 5H), 5.84-5.78 (m, 1H), 5.23-5.18 (m, 2H), 4.36 (d, *J* = 7.8 Hz, 1H), 2.52-2.45 (m, 1H), 2.14 (s, 1H), 0.87 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.5 (1C), 140.7 (1C), 128.3 (2C), 127.8 (1C), 126.9 (2C), 117.0 (1C), 77.9 (1C), 46.4 (1C), 16.6 (1C).

All spectroscopic data for **4t** was known.[19]

(3*R*,4*S*)-4-methyl-1-phenylhex-5-en-3-ol (**4u**)

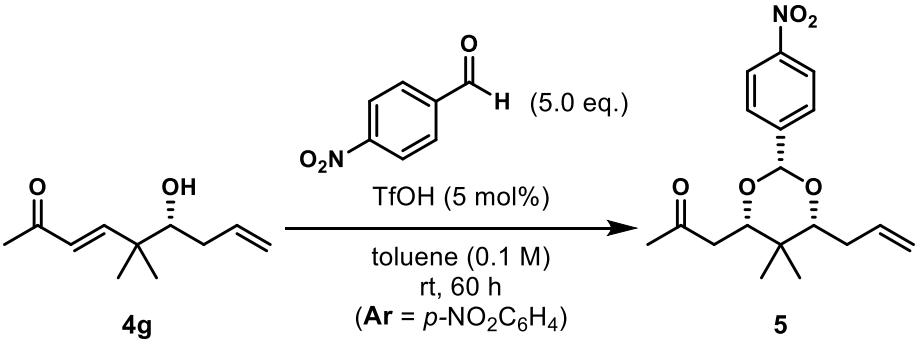


4u

Purification with column chromatography on silica gel (Hexane/EtOAc = 20/1 to 5/1); 85% yield (32.2 mg); colorless oil; $[\alpha]_D^{24.9}$: +13.8 (c = 0.25, $CHCl_3$); R_f = 0.35 (Hexane/EtOAc = 5/1); HPLC analysis: Chiralcel OD-3 column (Hexane/^{i}PrOH = 95/5, 1.0 mL/min, 30 °C, 254 nm), tR major = 12.208 min, tR minor = 7.958 min; 93% ee ^{1}H NMR (600 MHz, $CDCl_3$) δ7.30-7.18 (m, 5H), 5.77-5.71 (m, 1H), 5.14-5.08 (m, 2H), 3.42 (ddd, *J* = 8.4, 6.0, 3.0 Hz, 1H), 2.85 (ddd, *J* = 13.2, 10.2, 5.4, Hz, 1H), 2.67 (ddd, *J* = 13.8, 10.2, 6.6 Hz, 1H), 2.22 (q, *J* = 7.1 Hz, 1H), 1.87-1.81 (m, 1H), 1.70 (dddd, *J* = 14.4, 9.6, 9.6, 5.4 Hz, 1H), 1.60 (s, 1H), 1.03 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.4 (1C), 140.3 (1C), 128.6 (2C), 128.5 (2C), 125.9 (1C), 116.7 (1C), 74.1 (1C), 44.5 (1C), 36.2 (1C), 32.2 (1C), 16.3 (1C).

All spectroscopic data for **4u** was known.[19]

5. Derivatization of Products



To a solution of **4g** (91.1 mg, 0.5 mmol, 1.0 eq.) and *p*-nitrobenzaldehyde (377.8 mg, 2.5 mmol, 5.0 eq.) in toluene (4.9 mL, 0.1 M overall) was added TfOH (0.5 M in toluene, 100 μL, 10 mol%) at room temperature. The reaction was stirred until TLC showed complete conversion of starting material. The reaction was cooled to 0 °C, quenched

with Et_3N (100 μL), and then concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Hexane/EtOAc = 20/1 to 1/1) to give **5** (144.7 mg, 0.43 mmol) in 87% yield as a colorless oil.

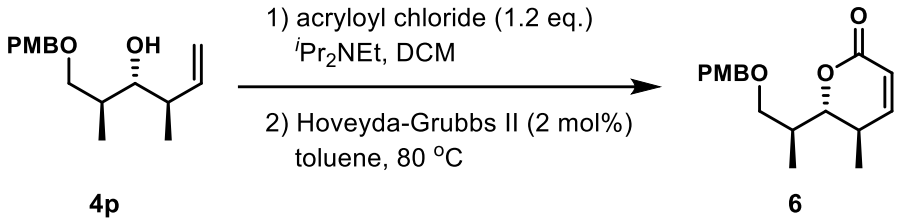
R_f = 0.51 (Hexane/EtOAc = 3/1).

$[\alpha]_D^{25.2}$: +6.20 (c = 0.100, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.9 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 5.96-5.89 (m, 1H), 5.65 (s, 1H), 5.15-5.08 (m, 2H), 4.13 (dd, *J* = 9.6, 1.7 Hz, 1H), 3.59 (dd, *J* = 9.6, 2.7 Hz, 1H), 2.75 (dd, *J* = 16.2, 10.0 Hz, 1H), 2.50 (dd, *J* = 16.2, 1.7 Hz, 1H), 2.35-2.23 (m, 5H), 0.99 (s, 3H), 0.84 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 206.8 (1C), 148.1 (1C), 145.1 (1C), 135.6 (1C), 127.2 (2C), 123.4 (2C), 116.8 (1C), 99.6 (1C), 85.9 (1C), 81.9 (1C), 43.2 (1C), 35.5 (1C), 33.7 (1C), 31.5 (1C), 20.8 (1C), 14.2 (1C).

HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{18}H_{23}NO_5Na$ 356.1468, Found 356.1468.



To a solution of **4p** (86.1 mg, 0.3 mmol, 1.0 eq.) and ^{i}Pr$_2$NEt (76.5 μL, 0.45 mmol, 1.5 eq.) in DCM (0.6 mL, 0.2 M) was added acryloyl chloride (29.1 μL, 0.36 mmol, 1.2 eq.) at room temperature. The reaction was stirred until TLC showed complete conversion of starting material. The reaction was quenched with aq. NH_4Cl. The aqueous phase was extracted with EtOAc, the organic layers were combined, dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The crude material was used to the next reaction without further purification.

To a crude ester in toluene (3 mL, 0.1 M) was added Hoveyda-Grubbs II catalyst (3.8 mg, 2 mol%) and the mixture was heated to 80 °C. The reaction mixture was stirred for 12 h and the reaction mixture was concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel (Hexane/EtOAc=20/1 to 8/1) to give a lactone **6** in 91% yied (2 steps).

R_f = 0.26 (Hexane/EtOAc = 3/1).

$[\alpha]_D^{25.8}$: +11.6 (c = 0.13, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24-7.21 (m, 2H), 6.89-6.86 (m, 2H), 6.66 (dd, *J* = 10.2, 3.0 Hz, 1H), 5.94 (dd, *J* = 9.6, 2.4 Hz, 1H), 4.41 (s, 2H), 4.05 (dd, *J* = 9.3, 3.4 Hz, 1H), 3.81 (s, 3H), 3.67 (dd, *J* = 9.5, 6.6 Hz, 1H), 3.37 (dd, *J* = 9.6, 5.4 Hz, 1H), 2.89-2.83 (m, 1H), 2.25-2.19 (m, 1H), 1.15 (d, *J* = 7.2 Hz, 3H), 1.08 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.4 (1C), 159.2 (1C), 152.3 (2C), 130.5 (1C), 129.2 (1C), 119.8 (2C), 113.9 (1C), 86.3 (1C), 73.0 (1C), 70.7 (1C), 55.4 (1C), 35.0 (1C), 31.3 (1C), 16.8 (1C), 15.5 (1C).

HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{17}H_{22}O_4Na$ 313.1410, Found 313.1410.

6. References

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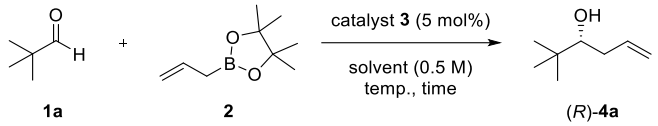
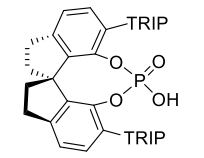
7. Optimization of allylboration of pivalaldehyde

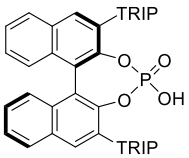
Table S1. Optimization of reaction condition[a]



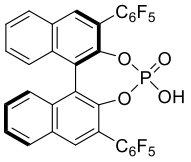
Entry	Catalyst	Solvent	Temp./ °C	Time / h	Yield /% [b]	Ee / %
1	(*S*)-**3a**	toluene	-75	24	90	40
2	(*R*)-**3b**	toluene	-75	24	80	67
3	(*R*)-**3c**	toluene	-75	24	38	39
4	(*R*)-**3d**	toluene	-75	72	98	84
5	(*R*)-**3e**	toluene	-75	24	quant.	95
6	(*R*)-**3f**	toluene	-75	72	no reaction	nd
7	(*R*)-**3g**	toluene	-75	72	no reaction	nd
8	(*R*)-**3h**	toluene	-75	72	no reaction	nd
9[c]	(*R*)-**3d**	toluene	-75	72	quant.	95
10	(*R*)-**3i**	toluene	-75	24	84	93
11	(*R*)-**3j**	toluene	-75	24	48	21
12	(*R*)-**3k**	toluene	-75	24	no reaction	nd
13	(*R*)-**3e**	Et_2O	-75 to -40	48	92	95
14	(*R*)-**3e**	THF	-40	48	no reaction	nd
15	(*R*)-**3e**	MeCN	-40	48	trace	nd
16	(*R*)-**3e**	EtOAc	-75 to -40	48	quant.	89
17	(*R*)-**3e**	DCM	-75	24	quant.	78
18	(*R*)-**3e**	toluene	-40	12	quant.	93
19	(*R*)-**3e**	toluene	25	<0.1	quant.	87
20[d]	(*R*)-**3e**	toluene	-75	48	83	73



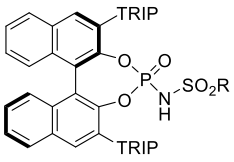
(*S*)-**3a**
TRIP = 2,4,6-^{i}Pr$_3$-C$_6$H$_2$



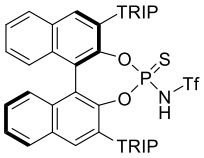
(*R*)-**3b**



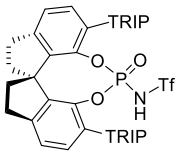
(*R*)-**3c**



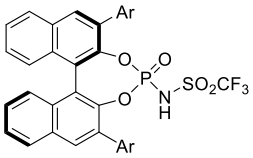
(*R*)-**3d**: R = C$_6$F$_5$
(*R*)-**3e**: R = CF$_3$
(*R*)-**3f**: R = Me



(*R*)-**3g**



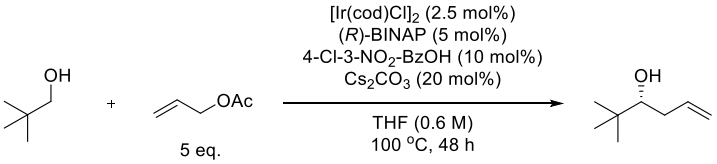
(*S*)-**3h**



(*R*)-**3i**: Ar = 2,4,6-Me$_3$-C$_6$H$_2$
(*R*)-**3j**: Ar = Ph
(*R*)-**3k**: Ar = C$_6$F$_5$

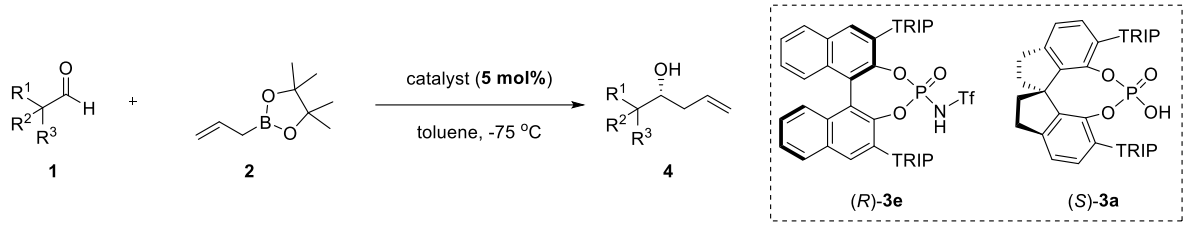
[a] Unless otherwise specified, all reactions were carried out using 0.20 mmol of **1a**, 0.24 mmol (1.2 eq.) of **2**, 0.010 mmol (5 mol%) of catalyst. [b] Isolated yield. [c] Catalyst loading was 0.5 mol% and 2 g of pivalaldehyde was employed. [d] In 2.5 M in toluene.

·Our attempt of Ir-catalyzed allylation reaction of neopentyl alcohol using BINAP ligand

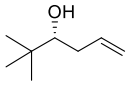


(*R*)-**4a**
55%, 77% ee

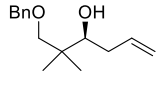
8. Comparison of enantioselectivities in substrate scope



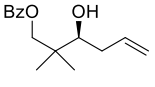
selected examples of the present allylboration



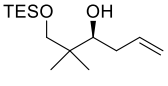
(*R*)-**3e**: quant., 95% ee
(*S*)-**3a**: 90%, 40% ee



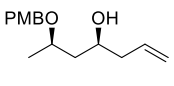
(*S*)-**3e**: 85%, 90% ee
(*R*)-**3a**: 7%, 33% ee



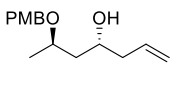
(*S*)-**3e**: 95%, 92% ee
(*R*)-**3a**: 9%, 62% ee



(*S*)-**3e**: quant., 92% ee
(*R*)-**3a**: no reaction



(*S*)-**3e**: 90%, dr=5.3:1
(*R*)-**3a**: 83%, dr=3:1



(*R*)-**3e**: 89%, dr=7.1:1
(*S*)-**3a**: 78%, dr=2:1

9. DFT calculation

9-1. Cartesian coordinates of intermediates and transition states

TS Re_A (B3LYP)
B3LYP/6-31g(d); E(RB3LYP) = -4248.127703 hartree
Sum of electronic and thermal Free Energies= -4246.866565 hartree
Thermal correction to Gibbs Free Energy= 1.261139 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.927491	3.116483	0.236316
2	6	0	-1.729254	1.995299	0.086061
3	6	0	-3.125759	1.985767	0.387746
4	6	0	-3.623880	3.086475	1.052211
5	1	0	-4.686232	3.131698	1.272396
6	6	0	2.895917	3.608055	-1.700412
7	6	0	0.370638	3.262114	-0.487596
8	6	0	1.385620	2.329553	-0.370042
9	6	0	2.682384	2.477570	-0.937708
10	1	0	3.879289	3.769510	-2.133250
11	8	0	-1.222699	0.839159	-0.515963
12	15	0	0.149205	0.055287	-0.171095
13	8	0	1.143542	1.186982	0.413792
14	6	0	-5.927703	-0.985094	-1.083864
15	6	0	-5.178883	-0.189714	-1.952407
16	6	0	-4.258432	0.762129	-1.499632
17	6	0	-4.053721	0.910845	-0.103084
18	6	0	-4.810714	0.121103	0.800791
19	6	0	-5.725552	-0.806497	0.286135
20	1	0	-5.340531	-0.295629	-3.023046
21	1	0	-6.310646	-1.396833	0.985827
22	6	0	6.125643	-0.092949	-0.435146
23	6	0	5.358682	-0.136181	-1.601043
24	6	0	4.207190	0.641646	-1.770066
25	6	0	3.812718	1.509548	-0.723668
26	6	0	4.562891	1.559343	0.476008
27	6	0	5.699654	0.752083	0.591878
28	1	0	5.668610	-0.788204	-2.413170
29	1	0	6.287240	0.794323	1.504881
30	8	0	0.563518	-0.764901	-1.325189
31	1	0	0.322905	-1.932103	1.083773
32	7	0	-0.012584	-0.937259	1.198529
33	16	0	-0.511628	-0.552199	2.736914
34	8	0	-0.830230	-1.807691	3.407007
35	8	0	-1.432362	0.576141	2.681323
36	6	0	0.998641	0.120162	3.639726
37	9	0	2.070016	-0.646086	3.403315
38	9	0	1.252224	1.368096	3.258463
39	9	0	0.724205	0.099111	4.942889
40	6	0	1.872859	4.550207	-1.970870
41	6	0	0.581623	4.377891	-1.377529
42	6	0	-1.433783	4.194425	1.046803
43	6	0	-2.800261	4.163560	1.466414
44	6	0	-1.152151	-5.214414	1.386699
45	6	0	-2.106959	-4.185323	1.058651
46	6	0	-2.869745	-4.179252	-0.082647
47	8	0	1.235868	-5.880029	0.623554
48	5	0	0.269889	-4.847875	0.495000
49	8	0	-0.267211	-4.804722	-0.935791
50	8	0	0.912737	-3.582574	0.868641
51	6	0	-1.053893	-3.889210	-1.373941
52	6	0	2.260472	-3.895595	1.328184
53	6	0	2.535181	-5.273261	0.621100
54	6	0	3.010602	-5.112195	-0.834691
55	6	0	3.496991	-6.199920	1.368357
56	6	0	3.205269	-2.768091	0.915501
57	6	0	2.219568	-4.029853	2.858037
58	1	0	-0.833082	-5.203064	2.431183
59	1	0	-1.442992	-6.220971	1.074556
60	1	0	-2.050970	-3.265294	1.639800
61	1	0	-3.102242	-5.113623	-0.586707
62	1	0	-3.520857	-3.337324	-0.297417
63	1	0	-0.905550	-2.868404	-1.018998
64	1	0	2.373436	-4.419748	-1.391570
65	1	0	2.960853	-6.088668	-1.327187
66	1	0	4.043615	-4.750584	-0.888146
67	1	0	3.611808	-7.132573	0.805886
68	1	0	3.118637	-6.453715	2.361138
69	1	0	4.489057	-5.744747	1.474081
70	1	0	2.976062	-1.849625	1.462922
71	1	0	3.134447	-2.549662	-0.151972
72	1	0	4.242797	-3.034833	1.147909
73	1	0	1.590041	-4.871418	3.160345
74	1	0	1.804395	-3.120806	3.298835
75	1	0	3.222133	-4.181670	3.273101
76	6	0	-1.546709	-4.026723	-2.810291
77	6	0	-1.833790	-5.488168	-3.186796
78	1	0	-2.691776	-5.885956	-2.633419
79	1	0	-2.067779	-5.556022	-4.255169
80	1	0	-0.971602	-6.127606	-2.979964
81	6	0	-0.348104	-3.499641	-3.654008
82	1	0	-0.622081	-3.508040	-4.715437
83	1	0	-0.080449	-2.475812	-3.372624
84	1	0	0.532297	-4.135487	-3.518402
85	6	0	-2.768564	-3.134792	-3.082949
86	1	0	-2.622032	-2.117422	-2.705500
87	1	0	-2.942069	-3.066985	-4.162913
88	1	0	-3.677034	-3.538771	-2.626567
89	6	0	4.213716	2.532705	1.603512
90	1	0	3.141128	2.745243	1.546469
91	6	0	3.446817	0.548309	-3.094268
92	1	0	2.491266	1.067237	-2.973165
93	6	0	7.411171	-0.898925	-0.292846
94	1	0	7.766802	-0.758643	0.737272
95	6	0	-3.594376	1.662227	-2.545429
96	1	0	-2.901634	2.336483	-2.037166
97	6	0	-4.717275	0.261109	2.321697
98	1	0	-3.870248	0.908484	2.556010
99	6	0	-6.979062	-1.945749	-1.626554
100	1	0	-6.813431	-2.024096	-2.710006
101	6	0	-6.869128	-3.363908	-1.040306
102	1	0	-7.606174	-4.028210	-1.506643
103	1	0	-5.874460	-3.791244	-1.207167
104	1	0	-7.057689	-3.371358	0.039441
105	6	0	-8.398089	-1.378632	-1.417802
106	1	0	-8.626056	-1.276781	-0.349992
107	1	0	-8.500455	-0.389070	-1.876334
108	1	0	-9.151210	-2.041307	-1.861155
109	6	0	-4.642546	2.556364	-3.240082
110	1	0	-5.364058	1.961295	-3.811810
111	1	0	-5.204253	3.149579	-2.509826
112	1	0	-4.152940	3.247378	-3.936898
113	6	0	-2.771608	0.871988	-3.579354
114	1	0	-1.980673	0.292322	-3.093935
115	1	0	-3.398395	0.181749	-4.156181
116	1	0	-2.298900	1.559755	-4.290993
117	6	0	-5.990032	0.918743	2.896295
118	1	0	-6.874130	0.293518	2.721981
119	1	0	-5.890430	1.062281	3.978950
120	1	0	-6.187299	1.896389	2.442566
121	6	0	-4.459209	-1.082513	3.028617
122	1	0	-3.560344	-1.572846	2.645543
123	1	0	-4.313669	-0.919208	4.102527
124	1	0	-5.299100	-1.777530	2.912353
125	6	0	4.218986	1.251053	-4.229462
126	1	0	3.647561	1.211094	-5.164679
127	1	0	4.413686	2.303830	-3.997473
128	1	0	5.186675	0.766400	-4.407160
129	6	0	3.114642	-0.903126	-3.487223
130	1	0	2.512857	-0.910385	-4.404137
131	1	0	4.017278	-1.493090	-3.686112
132	1	0	2.537501	-1.396031	-2.701264
133	6	0	8.508948	-0.365551	-1.234693
134	1	0	8.219786	-0.486549	-2.285512
135	1	0	8.697018	0.699631	-1.061098
136	1	0	9.449252	-0.908852	-1.081397
137	6	0	7.196357	-2.408245	-0.504020
138	1	0	6.450488	-2.805037	0.192813
139	1	0	6.851988	-2.626625	-1.521678
140	1	0	8.133895	-2.955053	-0.347857
141	6	0	4.960481	3.870195	1.417643
142	1	0	6.045419	3.715936	1.460789
143	1	0	4.724574	4.331372	0.453219
144	1	0	4.687611	4.579098	2.209056
145	6	0	4.478499	1.970778	3.011463
146	1	0	4.021967	0.986510	3.145624
147	1	0	5.550054	1.879266	3.222692
148	1	0	4.058890	2.646520	3.765638
149	6	0	2.106350	5.651482	-2.838295
150	1	0	3.097883	5.770811	-3.268072
151	6	0	-0.442312	5.299052	-1.734236
152	1	0	-1.439293	5.168675	-1.332240
153	6	0	-0.190380	6.344796	-2.594828
154	1	0	-0.993588	7.027678	-2.857647
155	6	0	1.098863	6.535748	-3.143800
156	1	0	1.285076	7.370244	-3.814039
157	6	0	-0.623989	5.280288	1.477451
158	1	0	0.422548	5.305549	1.195089
159	6	0	-3.311894	5.223668	2.261016
160	1	0	-4.355662	5.188250	2.563438
161	6	0	-2.502651	6.263794	2.656701
162	1	0	-2.900892	7.064135	3.274083
163	6	0	-1.143243	6.282762	2.267650
164	1	0	-0.499971	7.093530	2.598548

TS Re_E (B3LYP)
B3LYP/6-31g(d); E(RB3LYP) = -4248.121262 hartree
Sum of electronic and thermal Free Energies= -4246.862435 hartree
Thermal correction to Gibbs Free Energy= 1.258826 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	-2.378151	3.638164	-0.161646
2	6	0	-0.871731	4.441022	-0.002753
3	6	0	-1.112988	5.413614	1.037131
4	6	0	-1.042892	5.131547	2.377900

5	1	0	-0.685172	4.880256	-0.985645
6	1	0	-0.122042	3.686863	0.246140
7	1	0	-1.596535	6.343780	0.736662
8	1	0	-1.305920	5.887892	3.111897
9	1	0	-0.425836	4.310296	2.726406
10	8	0	-3.439445	4.564022	-0.439645
11	6	0	-4.347255	3.925687	-1.352078
12	8	0	-2.409468	2.597928	-1.169418
13	6	0	-3.383622	2.997385	-2.176488
14	6	0	-5.391435	3.132175	-0.545867
15	1	0	-4.923172	2.322860	0.021889
16	1	0	-5.881389	3.810369	0.161505
17	1	0	-6.163757	2.699463	-1.191182
18	6	0	-5.052264	5.011823	-2.167058
19	1	0	-5.688958	5.610453	-1.506285
20	1	0	-4.334188	5.685072	-2.640435
21	1	0	-5.689878	4.574864	-2.944639
22	6	0	-4.044584	1.747872	-2.754669
23	1	0	-4.416823	1.088827	-1.966044
24	1	0	-3.323329	1.190881	-3.357920
25	1	0	-4.884072	2.023005	-3.404817
26	6	0	-2.649161	3.763219	-3.288058
27	1	0	-2.216816	4.693767	-2.908295
28	1	0	-1.844848	3.139556	-3.683887
29	1	0	-3.325887	4.012144	-4.113331
30	8	0	-2.520803	2.999621	1.231050
31	6	0	-2.847861	3.747909	2.219766
32	1	0	-3.505174	4.593628	2.003455
33	8	0	-0.293224	-1.269162	0.781367
34	15	0	0.341334	0.102598	0.180015
35	8	0	1.794984	-0.335244	-0.370099
36	8	0	0.219653	1.172266	1.187488
37	6	0	-0.042520	-2.556051	0.301616
38	6	0	1.260317	-3.034502	0.261173
39	6	0	-1.181076	-3.364627	-0.000456
40	6	0	1.493778	-4.311782	-0.362105
41	6	0	-0.936205	-4.639544	-0.469323
42	6	0	0.371400	-5.122622	-0.720202
43	1	0	-1.779228	-5.292781	-0.676663
44	6	0	2.675969	-0.978795	0.516393
45	6	0	2.392999	-2.283982	0.878564
46	6	0	3.834957	-0.264651	0.933024
47	6	0	3.224429	-2.900422	1.881251
48	6	0	4.675955	-0.914748	1.813410
49	6	0	4.387302	-2.200314	2.335944
50	1	0	5.580810	-0.410872	2.141931
51	6	0	4.167520	1.113878	0.439786
52	6	0	4.011962	2.227613	1.294817
53	6	0	4.706278	1.284483	-0.861170
54	6	0	4.379666	3.493552	0.819260
55	6	0	5.052780	2.569978	-1.281077
56	6	0	4.892054	3.691818	-0.460875
57	1	0	4.260277	4.355799	1.471080
58	1	0	5.460770	2.702648	-2.278226
59	6	0	-2.590925	-2.905800	0.230399
60	6	0	-3.498418	-2.791458	-0.854654
61	6	0	-3.046902	-2.672664	1.551274
62	6	0	-4.817728	-2.404374	-0.593366
63	6	0	-4.377332	-2.287965	1.749801
64	6	0	-5.281718	-2.142127	0.697447
65	1	0	-5.507603	-2.319549	-1.429177
66	1	0	-4.729787	-2.119507	2.765042
67	7	0	-0.414282	0.442222	-1.308395
68	1	0	-1.219943	1.108752	-1.243598
69	16	0	0.306124	0.619125	-2.826852
70	8	0	-0.787553	0.963075	-3.730761
71	8	0	1.538113	1.394498	-2.793469
72	6	0	0.804624	-1.142349	-3.314096
73	9	0	-0.041488	-2.033679	-2.795318
74	9	0	2.042489	-1.425112	-2.921828
75	9	0	0.742596	-1.193985	-4.643618
76	6	0	-2.976763	3.109088	3.597459
77	6	0	-1.752775	2.259950	3.980523
78	1	0	-0.916783	2.888490	4.303884
79	1	0	-2.006546	1.596777	4.815158
80	1	0	-1.410665	1.651242	3.139684
81	6	0	-4.219567	2.180816	3.464292
82	1	0	-4.448026	1.739548	4.441157
83	1	0	-5.105074	2.734069	3.129105
84	1	0	-4.026804	1.373956	2.751569
85	6	0	-3.269903	4.176463	4.665251
86	1	0	-4.123945	4.805091	4.383823
87	1	0	-3.514096	3.693231	5.617713
88	1	0	-2.407796	4.828200	4.835667
89	6	0	0.587079	-6.394246	-1.316656
90	1	0	-0.278370	-7.001347	-1.570921
91	6	0	2.794891	-4.797911	-0.667846
92	1	0	3.657759	-4.183107	-0.439655
93	6	0	2.926317	-4.157427	2.476395
94	1	0	2.029749	-4.687197	2.177820
95	6	0	5.226466	-2.798219	3.314737
96	1	0	6.111600	-2.256326	3.638765
97	6	0	1.859895	-6.840812	-1.585495
98	1	0	2.014269	-7.810238	-2.050974
99	6	0	2.971334	-6.025260	-1.268208
100	1	0	3.974994	-6.367838	-1.504494
101	6	0	3.748836	-4.701209	3.438303
102	1	0	3.492366	-5.657947	3.884890
103	6	0	4.919183	-4.024923	3.854831
104	1	0	5.563334	-4.469600	4.608257
105	6	0	3.498249	2.105762	2.730154
106	1	0	3.112112	1.091721	2.869113
107	6	0	4.998986	0.087683	-1.768000
108	1	0	4.285298	-0.705070	-1.521845
109	6	0	5.263158	5.087915	-0.943349
110	1	0	5.058627	5.779487	-0.114306
111	6	0	-2.177549	-2.922933	2.784552
112	1	0	-1.163274	-3.158201	2.452915
113	6	0	-3.122001	-3.113759	-2.302781
114	1	0	-2.057332	-3.350098	-2.336696
115	6	0	-6.732448	-1.762780	0.965472
116	1	0	-6.816783	-1.556202	2.041375
117	6	0	2.333512	3.066050	3.030503
118	1	0	2.634592	4.117072	2.950370
119	1	0	1.503232	2.883196	2.344425
120	1	0	1.974723	2.904820	4.054940
121	6	0	4.643939	2.309240	3.742701
122	1	0	4.279296	2.177715	4.768819
123	1	0	5.460461	1.596909	3.579410
124	1	0	5.066153	3.318259	3.663225
125	6	0	4.393340	5.528053	-2.136213
126	1	0	4.559050	4.884465	-3.008111
127	1	0	3.327943	5.480097	-1.887271
128	1	0	4.632269	6.557475	-2.430055
129	6	0	6.762039	5.203690	-1.278978
130	1	0	7.015644	6.231376	-1.566013
131	1	0	7.383431	4.925631	-0.420457
132	1	0	7.035293	4.548881	-2.114941
133	6	0	4.830767	0.380333	-3.268677
134	1	0	4.900252	-0.555115	-3.836374
135	1	0	3.861745	0.839872	-3.478702
136	1	0	5.617822	1.042957	-3.647912
137	6	0	6.413620	-0.463367	-1.488065
138	1	0	6.532311	-0.760405	-0.440770
139	1	0	6.617949	-1.340273	-2.114961
140	1	0	7.173839	0.295309	-1.710208
141	6	0	-2.074975	-1.692298	3.702202
142	1	0	-1.676189	-0.831269	3.159088
143	1	0	-3.050132	-1.413750	4.119361
144	1	0	-1.405572	-1.903639	4.544875
145	6	0	-2.683403	-4.155079	3.563171
146	1	0	-2.710918	-5.044629	2.923794
147	1	0	-2.025179	-4.367253	4.414512
148	1	0	-3.695029	-3.994374	3.954078
149	6	0	-7.153980	-0.485583	0.217110
150	1	0	-6.499566	0.355880	0.467439
151	1	0	-7.114842	-0.626866	-0.869495
152	1	0	-8.182464	-0.208049	0.477608
153	6	0	-7.687638	-2.929221	0.645280
154	1	0	-8.721234	-2.664734	0.899330
155	1	0	-7.660093	-3.181805	-0.421425
156	1	0	-7.416686	-3.829209	1.208084
157	6	0	-3.340207	-1.923465	-3.252605
158	1	0	-2.763523	-1.051819	-2.933977
159	1	0	-3.020086	-2.186258	-4.268053
160	1	0	-4.394480	-1.628291	-3.304975
161	6	0	-3.880415	-4.357385	2.810442
162	1	0	-3.707268	-5.228240	-2.167660
163	1	0	-4.962273	-4.182392	-2.840355
164	1	0	-3.556452	-4.614851	-3.826069

TS Si_A (B3LYP)

B3LYP/6-31g(d); E(RB3LYP) = -4248.120157 hartree

Sum of electronic and thermal Free Energies= -4246.859715 hartree

Thermal correction to Gibbs Free Energy= 1.260442 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	1.039528	-4.519935	-0.563647
2	6	0	-0.506161	-4.575757	-1.301998
3	6	0	-1.467720	-3.947376	-0.425789
4	6	0	-1.999641	-4.554707	0.684994
5	1	0	-0.385744	-4.070753	-2.263503
6	1	0	-0.680024	-5.645094	-1.450659
7	1	0	-1.629304	-2.875786	-0.532161
8	1	0	-2.683560	-4.007884	1.325099
9	1	0	-2.024198	-5.638712	0.755404
10	8	0	1.643089	-3.186488	-0.536246
11	8	0	1.963706	-5.407075	-1.181462
12	6	0	3.126420	-4.681424	-1.594645
13	6	0	3.679024	-3.622018	0.707661
14	1	0	3.276293	-4.524386	1.174700
15	1	0	3.438471	-2.764386	1.345072
16	1	0	4.769347	-3.717515	0.661098
17	6	0	3.697142	-2.152269	-1.317903
18	1	0	3.620506	-1.298149	-0.637039
19	1	0	3.203773	-1.895018	-2.256258
20	1	0	4.762332	-2.314519	-1.519430
21	6	0	4.354495	-5.570165	-1.371607
22	1	0	4.408549	-5.929349	-0.341043
23	1	0	4.291213	-6.445491	-2.026708
24	1	0	5.283279	-5.037394	-1.609436
25	6	0	2.987290	-4.368125	-3.094548
26	1	0	2.145514	-3.698030	-3.288333
27	1	0	2.806693	-5.307499	-3.627387
28	1	0	3.894781	-3.910668	-3.505485

29	8	0	0.748587	-5.066576	0.843486
30	6	0	0.003009	-4.471452	1.702907
31	1	0	-0.002753	-3.378013	1.720676
32	1	0	-5.253381	2.377532	1.644852
33	6	0	-4.200654	2.530652	1.423491
34	6	0	-3.534756	1.579873	0.676181
35	6	0	-3.553575	3.670808	1.960060
36	6	0	-2.163416	1.837380	0.391719
37	6	0	-2.177204	3.906674	1.648594
38	6	0	-1.501276	2.995814	0.758367
39	8	0	-1.460386	0.884163	-0.369233
40	6	0	-0.136897	3.317655	0.250007
41	15	0	-0.273918	0.045441	0.333835
42	6	0	0.940644	2.456669	0.415620
43	6	0	0.096881	4.585076	-0.394567
44	8	0	0.730830	1.173659	0.927886
45	8	0	-0.581542	-0.939538	1.390809
46	6	0	2.298252	2.863157	0.225232
47	6	0	1.443607	5.005800	-0.619577
48	6	0	2.502718	4.147762	-0.240230
49	1	0	3.521482	4.506706	-0.350519
50	7	0	0.443016	-0.648550	-1.042612
51	1	0	0.974365	-1.537383	-0.845770
52	16	0	-0.123531	-0.692360	-2.628048
53	8	0	0.859737	-1.471273	-3.373893
54	8	0	-1.547201	-0.995154	-2.708038
55	6	0	0.073758	1.088043	-3.239297
56	9	0	0.263489	1.018947	-4.554912
57	9	0	1.132011	1.664021	-2.665329
58	9	0	-1.013798	1.809649	-2.987668
59	6	0	3.489197	2.005565	0.539426
60	6	0	3.737377	1.582937	1.869862
61	6	0	4.445085	1.719135	-0.475118
62	6	0	4.907325	0.866152	2.146030
63	6	0	5.599715	1.006696	-0.132341
64	6	0	5.856849	0.569340	1.168563
65	1	0	5.101936	0.554528	3.169777
66	1	0	6.329760	0.799817	-0.910562
67	6	0	-4.250746	0.346843	0.210397
68	6	0	-4.639066	0.217072	-1.147919
69	6	0	-4.595356	-0.654264	1.145885
70	6	0	-5.316595	-0.937465	-1.543814
71	6	0	-5.280088	-1.789619	0.690679
72	6	0	-5.637622	-1.961191	-0.645015
73	1	0	-5.605362	-1.043599	-2.584498
74	1	0	-5.546720	-2.565247	1.405349
75	6	0	-0.185719	-5.181728	3.042805
76	6	0	1.150746	-4.910485	3.794154
77	1	0	1.996881	-5.357210	3.264097
78	1	0	1.340044	-3.836449	3.903991
79	1	0	1.098052	-5.348028	4.797680
80	6	0	-1.333359	-4.574056	3.863214
81	1	0	-2.310824	-4.812137	3.434642
82	1	0	-1.310932	-4.975059	4.882910
83	1	0	-1.246294	-3.484433	3.930037
84	6	0	-0.367041	-6.698496	2.874636
85	1	0	-0.339005	-7.186955	3.855251
86	1	0	-1.330734	-6.939565	2.413436
87	1	0	0.424579	-7.124097	2.252482
88	6	0	-4.423732	1.355271	-2.147400
89	1	0	-3.505004	1.881389	-1.868025
90	6	0	-4.293331	-0.533836	2.640402
91	1	0	-3.671273	0.351795	2.793883
92	6	0	-6.356245	-3.223651	-1.103163
93	1	0	-6.537022	-3.833339	-0.207000
94	6	0	2.842196	1.962345	3.051194
95	1	0	1.965424	2.490612	2.670873
96	6	0	4.313127	2.186750	-1.929423
97	1	0	3.348033	2.682089	-2.048230
98	6	0	7.151885	-0.144828	1.534002
99	1	0	7.061690	-0.456752	2.583584
100	6	0	3.078565	-3.394820	-0.689055
101	6	0	-3.492819	-1.728555	3.183329
102	1	0	-3.265461	-1.577882	4.245969
103	1	0	-4.053068	-2.667743	3.100592
104	1	0	-2.547498	-1.832087	2.644369
105	6	0	-5.589652	-0.330051	3.450857
106	1	0	-5.359791	-0.194934	4.514747
107	1	0	-6.145599	0.550496	3.109306
108	1	0	-6.257151	-1.195393	3.359991
109	6	0	-7.727052	-2.915746	-1.734012
110	1	0	-8.246849	-3.844430	-1.998375
111	1	0	-8.364469	-2.351709	-1.044025
112	1	0	-7.620734	-2.323756	-2.650586
113	6	0	-5.480153	-4.056198	-2.058840
114	1	0	-5.262889	-3.503449	-2.980306
115	1	0	-4.522893	-4.314367	-1.593373
116	1	0	-5.989270	-4.986690	-2.338137
117	6	0	-5.583460	2.370881	-2.054683
118	1	0	-5.421094	3.204793	-2.748735
119	1	0	-6.535203	1.893346	-2.317124
120	1	0	-5.682392	2.784202	-1.045719
121	6	0	-4.243904	0.896172	-3.604009
122	1	0	-3.473462	0.126182	-3.688878
123	1	0	-5.176109	0.503334	-4.027477
124	1	0	-3.947815	1.750732	-4.223747
125	6	0	3.569962	2.945601	3.991694
126	1	0	4.457847	2.488874	4.444235
127	1	0	3.895108	3.842808	3.452901
128	1	0	2.904526	3.259415	4.805127
129	6	0	2.329368	0.734228	3.825822
130	1	0	1.767178	0.060313	3.173080
131	1	0	3.152291	0.168501	4.278704
132	1	0	1.663541	1.051621	4.637332
133	6	0	8.358224	0.810557	1.440179
134	1	0	8.212305	1.696090	2.068371
135	1	0	9.277071	0.307695	1.765128
136	1	0	8.510691	1.153465	0.409791
137	6	0	7.392072	-1.413380	0.696321
138	1	0	6.557436	-2.115525	0.791546
139	1	0	7.511138	-1.176095	-0.367512
140	1	0	8.305864	-1.922489	1.024944
141	6	0	4.336729	1.025506	-2.940537
142	1	0	3.515896	0.326878	-2.763948
143	1	0	4.234085	1.415735	-3.960302
144	1	0	5.274777	0.460639	-2.896612
145	6	0	5.405589	3.217850	-2.282866
146	1	0	6.405445	2.770578	-2.238395
147	1	0	5.256893	3.598797	-3.300405
148	1	0	5.400472	4.072232	-1.596569
149	6	0	-4.242586	4.569321	2.819171
150	1	0	-5.291484	4.379743	3.033494
151	6	0	-1.533138	5.013137	2.268347
152	1	0	-0.479877	5.186798	2.083647
153	6	0	-3.594409	5.642104	3.384426
154	1	0	-4.127369	6.318305	4.046962
155	6	0	-2.221756	5.852865	3.115696
156	1	0	-1.702555	6.683150	3.586353
157	6	0	-0.952083	5.435375	-0.841537
158	1	0	-1.981339	5.119376	-0.718232
159	6	0	1.694920	6.267594	-1.223368
160	1	0	2.727032	6.574363	-1.374137
161	6	0	0.657017	7.072968	-1.629872
162	1	0	0.857683	8.031047	-2.101095
163	6	0	-0.678023	6.641404	-1.448440
164	1	0	-1.496876	7.265595	-1.795368

TS Si_E (B3LYP)

B3LYP/6-31g(d); E(RB3LYP) = -4248.123720 hartree

Sum of electronic and thermal Free Energies= -4246.866448 hartree

Thermal correction to Gibbs Free Energy= 1.257273 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	-0.269059	4.245361	-0.800570
2	6	0	-0.896986	3.801189	-2.330851
3	6	0	-2.013599	4.694318	-2.529707
4	6	0	-3.263538	4.488431	-2.001995
5	1	0	-0.072121	3.968121	-3.027569
6	1	0	-1.151802	2.741076	-2.278285
7	1	0	-1.787907	5.685830	-2.924722
8	1	0	-4.045207	5.229785	-2.138239
9	1	0	-3.587387	3.483117	-1.750544
10	8	0	0.147895	5.616778	-0.780100
11	6	0	1.353919	5.704128	-0.000801
12	8	0	0.845941	3.433550	-0.346177
13	6	0	2.009586	4.297321	-0.249499
14	6	0	0.982016	5.929283	1.475498
15	1	0	0.442911	5.072295	1.888749
16	1	0	0.336255	6.811631	1.544068
17	1	0	1.867415	6.109139	2.095461
18	6	0	2.169147	6.892580	-0.513784
19	1	0	1.629190	7.823300	-0.308279
20	1	0	2.330885	6.830835	-1.592601
21	1	0	3.143463	6.951423	-0.014300
22	6	0	2.907135	3.801677	0.880731
23	1	0	2.350188	3.679432	1.811847
24	1	0	3.348079	2.836574	0.613105
25	1	0	3.731598	4.504097	1.053230
26	6	0	2.763341	4.218989	-1.585897
27	1	0	2.160476	4.613118	-2.408922
28	1	0	2.998374	3.172000	-1.802011
29	1	0	3.703022	4.781319	-1.548369
30	8	0	-1.472522	3.975556	0.117160
31	6	0	-2.450218	4.808931	0.097976
32	1	0	-2.201288	5.850442	-0.119331
33	1	0	-3.824501	-4.114408	-1.730748
34	6	0	-2.809558	-3.894147	-1.411790
35	6	0	-2.562690	-2.699529	-0.764030
36	6	0	-1.787882	-4.829380	-1.708616
37	6	0	-1.223561	-2.472349	-0.339832
38	6	0	-0.455375	-4.582031	-1.249699
39	6	0	-0.200569	-3.395542	-0.473148
40	8	0	-0.930283	-1.256111	0.303750
41	6	0	1.133646	-3.177210	0.158210
42	15	0	-0.022292	-0.197972	-0.515235
43	6	0	1.894388	-2.047153	-0.111777
44	6	0	1.687024	-4.178176	1.032547
45	8	0	1.344101	-1.009320	-0.862525
46	8	0	-0.546803	0.418943	-1.746725
47	6	0	3.281079	-1.943702	0.218912
48	6	0	3.062111	-4.079672	1.410841
49	6	0	3.829462	-2.988387	0.936964
50	1	0	4.889977	-2.962960	1.169797
51	6	0	-3.706634	-1.758330	-0.513086
52	6	0	-4.299531	-1.701227	0.772870

53	6	0	-4.278903	-1.041423	-1.588464
54	6	0	-5.464868	-0.949353	0.939195
55	6	0	-5.455206	-0.312058	-1.364494
56	6	0	-6.073761	-0.261319	-0.115639
57	1	0	-5.931884	-0.909563	1.919963
58	1	0	-5.898384	0.221019	-2.200178
59	6	0	4.159497	-0.807390	-0.217466
60	6	0	4.836036	-0.015214	0.747875
61	6	0	4.409957	-0.590013	-1.597066
62	6	0	5.714932	0.980716	0.304306
63	6	0	5.304339	0.416647	-1.976664
64	6	0	5.971874	1.216309	-1.046884
65	1	0	6.234030	1.587144	1.043478
66	1	0	5.500560	0.560014	-3.035376
67	7	0	0.342288	0.899838	0.730777
68	1	0	0.634838	1.849642	0.375315
69	16	0	-0.357629	1.059770	2.245871
70	8	0	0.252164	2.248076	2.836884
71	8	0	-1.803780	0.870930	2.244757
72	6	0	0.323435	-0.412707	3.219446
73	9	0	-0.478365	-1.467508	3.109950
74	9	0	1.544625	-0.739603	2.792371
75	9	0	0.386009	-0.035645	4.495824
76	6	0	-3.631755	4.576467	1.028314
77	6	0	-4.124598	3.122135	1.031962
78	1	0	-4.892838	2.998891	1.803965
79	1	0	-4.573796	2.845000	0.073328
80	1	0	-3.316666	2.420513	1.247044
81	6	0	-4.778287	5.550634	0.706042
82	1	0	-5.286474	5.287818	-0.226526
83	1	0	-5.523408	5.523718	1.508566
84	1	0	-4.419900	6.584220	0.621411
85	6	0	-3.063729	4.923447	2.437296
86	1	0	-2.258904	4.237064	2.714203
87	1	0	-2.675872	5.948382	2.476837
88	1	0	-3.866515	4.838431	3.178441
89	6	0	3.631527	-5.074376	2.251095
90	1	0	4.682044	-4.988722	2.518173
91	6	0	0.923206	-5.255564	1.560452
92	1	0	-0.130246	-5.328563	1.316218
93	6	0	0.561113	-5.504951	-1.621941
94	1	0	1.585041	-5.317480	-1.322089
95	6	0	-2.063214	-6.001089	-2.464433
96	1	0	-3.084328	-6.177153	-2.793725
97	6	0	2.868001	-6.111798	2.733110
98	1	0	3.309501	-6.862110	3.383060
99	6	0	1.497210	-6.191647	2.392389
100	1	0	0.889054	-6.997405	2.794223
101	6	0	0.266503	-6.620858	-2.373737
102	1	0	1.063397	-7.303993	-2.654524
103	6	0	-1.059874	-6.883208	-2.789565
104	1	0	-1.278797	-7.771822	-3.375029
105	6	0	3.824396	-1.472142	-2.701810
106	1	0	3.127139	-2.181205	-2.250364
107	6	0	4.698234	-0.214436	2.260804
108	1	0	3.948698	-0.986660	2.440049
109	6	0	7.011375	2.251575	-1.459911
110	1	0	7.141676	2.931485	-0.606332
111	6	0	-3.754129	-2.512828	1.948942
112	1	0	-2.692246	-2.703232	1.765737
113	6	0	-7.406693	0.442463	0.119837
114	1	0	-7.413167	0.769841	1.169244
115	6	0	-3.683961	-1.049504	-2.997877
116	1	0	-2.710358	-1.545892	-2.953146
117	6	0	-3.839320	-1.780654	3.299348
118	1	0	-3.304784	-2.355552	4.064872
119	1	0	-3.388451	-0.786787	3.239875
120	1	0	-4.874507	-1.672788	3.644270
121	6	0	-4.459617	-3.882939	2.031204
122	1	0	-4.341738	-4.452911	1.103333
123	1	0	-4.047109	-4.481611	2.852803
124	1	0	-5.533789	-3.755539	2.212683
125	6	0	-8.573834	-0.552355	-0.055762
126	1	0	-8.616183	-0.920370	-1.088113
127	1	0	-8.458696	-1.419997	0.602739
128	1	0	-9.533689	-0.073287	0.173569
129	6	0	-7.630417	1.688041	-0.751035
130	1	0	-8.556840	2.193772	-0.455103
131	1	0	-6.807214	2.403311	-0.651412
132	1	0	-7.728029	1.430519	-1.812251
133	6	0	-3.428800	0.371488	-3.533559
134	1	0	-2.948858	0.319405	-4.518080
135	1	0	-4.359727	0.938975	-3.651732
136	1	0	-2.761732	0.921122	-2.865417
137	6	0	-4.569585	-1.846516	-3.976914
138	1	0	-4.714714	-2.880282	-3.643899
139	1	0	-5.561485	-1.389246	-4.076801
140	1	0	-4.111972	-1.873317	-4.973201
141	6	0	3.032835	-0.665188	-3.747776
142	1	0	2.215264	-0.106932	-3.282920
143	1	0	3.674416	0.045711	-4.282008
144	1	0	2.599182	-1.340914	-4.494746
145	6	0	4.930727	-2.313255	-3.372192
146	1	0	5.666151	-1.679273	-3.881236
147	1	0	5.468330	-2.921901	-2.636226
148	1	0	4.496870	-2.987485	-4.120556
149	6	0	6.590441	3.104382	-2.667975
150	1	0	6.513543	2.503616	-3.581796
151	1	0	5.621623	3.585643	-2.501003
152	1	0	7.334013	3.887627	-2.856475
153	6	0	8.373611	1.575080	-1.719536
154	1	0	9.140362	2.322271	-1.958167
155	1	0	8.708714	1.008336	-0.843996
156	1	0	8.307380	0.877557	-2.563287
157	6	0	6.022505	-0.711669	2.877379
158	1	0	6.816685	0.037210	2.775825
159	1	0	5.893119	-0.916852	3.946919
160	1	0	6.376482	-1.630453	2.396023
161	6	0	4.213638	1.050162	2.993674
162	1	0	4.105922	0.843378	4.065341
163	1	0	4.920327	1.881285	2.888350
164	1	0	3.243592	1.384784	2.617989

TS Re_A (M06-2X)

M06-2X/6-31g(d); E(RM062X) = -4246.641581 hartree
Sum of electronic and thermal Free Energies= -4245.358770 hartree
Thermal correction to Gibbs Free Energy= 1.282811 hartree
smd(toluene)/MN15/6-31g(d); E(RMN15) = -4243.889016 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.982648	3.035993	0.247060
2	6	0	-1.740266	1.911008	0.010165
3	6	0	-3.136339	1.832263	0.271468
4	6	0	-3.698874	2.871289	0.967280
5	1	0	-4.767122	2.854502	1.171942
6	6	0	2.845994	3.494317	-1.669498
7	6	0	0.336293	3.216989	-0.418665
8	6	0	1.325469	2.267005	-0.318176
9	6	0	2.600165	2.363458	-0.930036
10	1	0	3.823158	3.620442	-2.129717
11	8	0	-1.179812	0.811100	-0.630283
12	15	0	0.111376	0.004425	-0.119901
13	8	0	1.081590	1.139763	0.466117
14	6	0	-5.610678	-1.319913	-1.337227
15	6	0	-4.907187	-0.449630	-2.169330
16	6	0	-4.078496	0.553760	-1.673852
17	6	0	-3.963800	0.712369	-0.272808
18	6	0	-4.683753	-0.138054	0.587752
19	6	0	-5.485677	-1.143661	0.036067
20	1	0	-4.999131	-0.575268	-3.247790
21	1	0	-6.020747	-1.806101	0.712098
22	6	0	5.865791	-0.422323	-0.747940
23	6	0	4.990069	-0.417807	-1.831472
24	6	0	3.878526	0.425472	-1.880443
25	6	0	3.652972	1.305757	-0.804795
26	6	0	4.480095	1.268974	0.333667
27	6	0	5.579691	0.409747	0.332718
28	1	0	5.178620	-1.086102	-2.668874
29	1	0	6.238502	0.384087	1.197050
30	8	0	0.591033	-0.891376	-1.178852
31	1	0	0.233998	-1.832623	1.311906
32	7	0	-0.192646	-0.842220	1.300919
33	16	0	-0.591728	-0.244557	2.779680
34	8	0	-0.702037	-1.389316	3.659322
35	8	0	-1.629337	0.755292	2.651889
36	6	0	0.875056	0.713212	3.413186
37	9	0	2.007323	0.144758	3.019210
38	9	0	0.836450	1.967626	3.000053
39	9	0	0.811339	0.686988	4.735183
40	6	0	1.859270	4.491861	-1.872569
41	6	0	0.577509	4.349148	-1.271315
42	6	0	-1.556274	4.059707	1.072579
43	6	0	-2.925022	3.962251	1.442563
44	6	0	-0.763985	-5.068723	1.889761
45	6	0	-1.779162	-4.066903	1.652895
46	6	0	-2.651142	-4.086864	0.602372
47	8	0	1.652133	-5.426406	0.969263
48	5	0	0.507109	-4.600027	0.879042
49	8	0	-0.147999	-4.692983	-0.496138
50	8	0	0.955595	-3.215940	1.102136
51	6	0	-0.962591	-3.777723	-0.845377
52	6	0	2.369437	-3.247848	1.389978
53	6	0	2.788611	-4.597970	0.732242
54	6	0	2.996167	-4.449948	-0.779187
55	6	0	4.004838	-5.251791	1.370982
56	6	0	3.045945	-2.025650	0.788326
57	6	0	2.524507	-3.263238	2.909748
58	1	0	-0.350155	-5.041711	2.899804
59	1	0	-1.049840	-6.082857	1.602691
60	1	0	-1.689048	-3.145426	2.229602
61	1	0	-2.887818	-5.026186	0.107907
62	1	0	-3.331902	-3.254737	0.435380
63	1	0	-0.783644	-2.764937	-0.481281
64	1	0	2.165146	-3.903060	-1.236536
65	1	0	3.039530	-5.448460	-1.223361
66	1	0	3.925618	-3.918034	-1.009464
67	1	0	4.252375	-6.169642	0.829957
68	1	0	3.803700	-5.513606	2.411894
69	1	0	4.874233	-4.585858	1.333432
70	1	0	2.716023	-1.110256	1.288571
71	1	0	2.826282	-1.920992	-0.276129
72	1	0	4.132171	-2.090689	0.918356
73	1	0	2.089512	-4.174265	3.331500
74	1	0	1.998013	-2.403257	3.334649
75	1	0	3.576745	-3.203985	3.205745

76	6	0	-1.613860	-3.881399	-2.204792
77	6	0	-2.000207	-5.314902	-2.562316
78	1	0	-2.830463	-5.674054	-1.945823
79	1	0	-2.320920	-5.356131	-3.608187
80	1	0	-1.152720	-5.992377	-2.430757
81	6	0	-0.493286	-3.392342	-3.156338
82	1	0	-0.878822	-3.381958	-4.181380
83	1	0	-0.164070	-2.382500	-2.891659
84	1	0	0.369995	-4.063875	-3.113066
85	6	0	-2.799982	-2.924633	-2.304543
86	1	0	-2.561891	-1.945937	-1.869322
87	1	0	-3.069427	-2.763645	-3.354524
88	1	0	-3.681827	-3.316449	-1.788978
89	6	0	4.214821	2.174296	1.528363
90	1	0	3.128428	2.300262	1.614908
91	6	0	2.961450	0.379639	-3.094917
92	1	0	2.007427	0.840274	-2.816135
93	6	0	7.100036	-1.304686	-0.744183
94	1	0	7.600459	-1.163194	0.222439
95	6	0	-3.371046	1.451260	-2.682082
96	1	0	-2.764671	2.185831	-2.145432
97	6	0	-4.604822	-0.047055	2.103632
98	1	0	-3.926629	0.763959	2.370306
99	6	0	-6.501159	-2.385351	-1.950359
100	1	0	-6.019831	-2.703072	-2.885807
101	6	0	-6.675015	-3.622721	-1.068345
102	1	0	-7.205788	-4.405736	-1.618131
103	1	0	-5.711233	-4.027248	-0.739578
104	1	0	-7.266046	-3.394231	-0.174981
105	6	0	-7.868644	-1.785049	-2.305559
106	1	0	-8.373966	-1.438422	-1.397366
107	1	0	-7.761620	-0.928735	-2.978018
108	1	0	-8.507955	-2.529773	-2.791126
109	6	0	-4.392061	2.241656	-3.511315
110	1	0	-5.017138	1.572495	-4.112354
111	1	0	-5.052016	2.828783	-2.865408
112	1	0	-3.879236	2.925717	-4.195324
113	6	0	-2.429404	0.652076	-3.591912
114	1	0	-1.675934	0.112970	-3.009803
115	1	0	-2.986012	-0.076062	-4.193186
116	1	0	-1.911543	1.326158	-4.282411
117	6	0	-5.972849	0.252359	2.726375
118	1	0	-6.692177	-0.546567	2.515486
119	1	0	-5.882817	0.342228	3.813743
120	1	0	-6.392088	1.186717	2.338533
121	6	0	-4.005416	-1.333240	2.680126
122	1	0	-3.070853	-1.570907	2.164134
123	1	0	-3.783328	-1.220258	3.745926
124	1	0	-4.680765	-2.188322	2.556691
125	6	0	3.558234	1.174184	-4.264093
126	1	0	2.902321	1.119643	-5.139322
127	1	0	3.698148	2.228596	-4.008867
128	1	0	4.534511	0.762241	-4.544375
129	6	0	2.655764	-1.056218	-3.537414
130	1	0	1.857803	-1.047994	-4.287606
131	1	0	3.529795	-1.532494	-3.995454
132	1	0	2.321531	-1.664368	-2.693353
133	6	0	8.076868	-0.882339	-1.848117
134	1	0	7.623805	-1.017905	-2.836400
135	1	0	8.354065	0.170975	-1.747349
136	1	0	8.988998	-1.486838	-1.810340
137	6	0	6.743822	-2.788627	-0.877741
138	1	0	6.066450	-3.106356	-0.078911
139	1	0	6.250056	-2.989065	-1.835163
140	1	0	7.644973	-3.408684	-0.830448
141	6	0	4.843354	3.559216	1.317174
142	1	0	5.928397	3.461849	1.199524
143	1	0	4.446974	4.052971	0.426051
144	1	0	4.650510	4.204252	2.181072
145	6	0	4.711124	1.582742	2.851883
146	1	0	4.420336	0.534791	2.963724
147	1	0	5.801927	1.644255	2.930953
148	1	0	4.293085	2.148244	3.690826
149	6	0	2.124671	5.614227	-2.700789
150	1	0	3.114123	5.709554	-3.139912
151	6	0	-0.419378	5.315299	-1.579230
152	1	0	-1.417335	5.200157	-1.172803
153	6	0	-0.137374	6.380365	-2.396538
154	1	0	-0.915660	7.102079	-2.623434
155	6	0	1.152152	6.544533	-2.953771
156	1	0	1.360979	7.397010	-3.592133
157	6	0	-0.797359	5.158598	1.553709
158	1	0	0.254928	5.226269	1.296486
159	6	0	-3.498905	4.975051	2.253655
160	1	0	-4.548478	4.890725	2.522278
161	6	0	-2.744036	6.028619	2.699897
162	1	0	-3.189448	6.793996	3.327308
163	6	0	-1.376164	6.113881	2.350977
164	1	0	-0.777923	6.940110	2.721944

TS Re_E (M06-2X)

M06-2X/6-31g(d); E(RM062X) = -4246.622898 hartree
Sum of electronic and thermal Free Energies= -4245.336090 hartree
Thermal correction to Gibbs Free Energy= 1.286808 hartree
smd(toluene)/MN15/6-31g(d); E(RMN15) = -4243.871348 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	-3.221314	2.115913	-0.539616
2	6	0	-2.065902	3.325055	-0.410985
3	6	0	-2.383031	4.051570	0.807837
4	6	0	-1.995676	3.644640	2.049331
5	1	0	-2.195050	3.923381	-1.316382
6	1	0	-1.074413	2.867750	-0.382823
7	1	0	-3.120803	4.852921	0.735584
8	1	0	-2.299092	4.203656	2.929705
9	1	0	-1.189061	2.920742	2.149770
10	8	0	-4.550952	2.636058	-0.683138
11	6	0	-5.261179	1.707954	-1.502804
12	8	0	-3.004562	1.149943	-1.594716
13	6	0	-4.144505	1.206723	-2.469491
14	6	0	-5.798471	0.571799	-0.624407
15	1	0	-4.974764	-0.018114	-0.208293
16	1	0	-6.371035	1.005080	0.202966
17	1	0	-6.457201	-0.098965	-1.186193
18	6	0	-6.412079	2.434693	-2.182229
19	1	0	-7.156531	2.724501	-1.434271
20	1	0	-6.059953	3.339945	-2.680656
21	1	0	-6.901373	1.789467	-2.920295
22	6	0	-4.398413	-0.168208	-3.068083
23	1	0	-4.450481	-0.933718	-2.288069
24	1	0	-3.587572	-0.424523	-3.755598
25	1	0	-5.341333	-0.172921	-3.627025
26	6	0	-3.853043	2.220937	-3.575690
27	1	0	-3.740410	3.224951	-3.155331
28	1	0	-2.923004	1.940430	-4.074515
29	1	0	-4.659126	2.242134	-4.316590
30	8	0	-3.078605	1.351257	0.796283
31	6	0	-3.538572	1.922349	1.828684
32	1	0	-4.358615	2.633850	1.686977
33	8	0	0.551669	-1.227740	0.742043
34	15	0	0.411068	0.224927	0.056472
35	8	0	1.848931	0.435248	-0.625998
36	8	0	-0.094436	1.194808	1.030327
37	6	0	1.145012	-2.296572	0.080444
38	6	0	2.492455	-2.258855	-0.211176
39	6	0	0.321190	-3.444133	-0.130052
40	6	0	3.036508	-3.335228	-0.988924
41	6	0	0.899149	-4.520631	-0.754110
42	6	0	2.228916	-4.475350	-1.249986
43	1	0	0.330103	-5.438412	-0.875698
44	6	0	2.983076	0.157883	0.141771
45	6	0	3.345630	-1.157145	0.314900
46	6	0	3.676790	1.269091	0.700507
47	6	0	4.507996	-1.428440	1.119389
48	6	0	4.843634	0.997057	1.366132
49	6	0	5.283575	-0.333275	1.594645
50	1	0	5.423260	1.817781	1.782406
51	6	0	3.028117	2.613340	0.644455
52	6	0	2.406611	3.121387	1.806559
53	6	0	2.930716	3.293433	-0.582442
54	6	0	1.603419	4.252789	1.668757
55	6	0	2.122414	4.426963	-0.662627
56	6	0	1.424033	4.899521	0.445522
57	1	0	1.087660	4.655598	2.536697
58	1	0	2.021629	4.935760	-1.615154
59	6	0	-1.067046	-3.463290	0.428815
60	6	0	-2.200870	-3.628884	-0.400243
61	6	0	-1.225887	-3.313470	1.823381
62	6	0	-3.467894	-3.553293	0.184012
63	6	0	-2.514977	-3.250731	2.352625
64	6	0	-3.649144	-3.355781	1.552577
65	1	0	-4.343349	-3.670945	-0.444714
66	1	0	-2.642056	-3.139961	3.429356
67	7	0	-0.484253	0.020715	-1.360745
68	1	0	-1.519197	0.113891	-1.267927
69	16	0	-0.105110	0.709234	-2.835543
70	8	0	-1.167028	0.331042	-3.742240
71	8	0	0.344872	2.077401	-2.699803
72	6	0	1.380573	-0.270689	-3.427119
73	9	0	1.497810	-1.422513	-2.785393
74	9	0	2.488043	0.434269	-3.282582
75	9	0	1.182866	-0.506125	-4.714027
76	6	0	-3.484473	1.196584	3.150484
77	6	0	-2.197683	0.399680	3.325189
78	1	0	-1.326547	1.056379	3.389529
79	1	0	-2.259466	-0.187604	4.247814
80	1	0	-2.039798	-0.285024	2.486921
81	6	0	-4.671394	0.208018	3.044440
82	1	0	-4.755933	-0.347509	3.984798
83	1	0	-5.622207	0.722499	2.864331
84	1	0	-4.495994	-0.504336	2.231975
85	6	0	-3.723156	2.148682	4.323188
86	1	0	-4.566841	2.821433	4.129521
87	1	0	-3.953792	1.571668	5.224145
88	1	0	-2.837173	2.753908	4.530540
89	6	0	2.770662	-5.554648	-1.995617
90	1	0	2.145402	-6.425024	-2.175832
91	6	0	4.348416	-3.293454	-1.530420
92	1	0	4.959361	-2.412031	-1.364961
93	6	0	4.900678	-2.741220	1.496997
94	1	0	4.294093	-3.586603	1.194152
95	6	0	6.454660	-0.584179	2.356571
96	1	0	7.039972	0.265494	2.697705
97	6	0	4.046181	-5.493627	-2.493409
98	1	0	4.448237	-6.319737	-3.071126

99	6	0	4.837080	-4.343275	-2.266617
100	1	0	5.838088	-4.289149	-2.682656
101	6	0	6.028683	-2.950771	2.249921
102	1	0	6.305869	-3.962187	2.529824
103	6	0	6.828000	-1.863942	2.671897
104	1	0	7.722263	-2.045578	3.259416
105	6	0	2.629183	2.493213	3.184719
106	1	0	3.699237	2.269238	3.263842
107	6	0	3.779347	2.846674	-1.763719
108	1	0	3.736547	1.753227	-1.815256
109	6	0	0.543459	6.134579	0.386981
110	1	0	-0.308789	5.945181	1.053572
111	6	0	-0.050017	-3.351966	2.794255
112	1	0	0.883450	-3.337091	2.226386
113	6	0	-2.077471	-3.907785	-1.899321
114	1	0	-1.320138	-4.688260	-2.027705
115	6	0	-5.022752	-3.385366	2.199969
116	1	0	-4.969843	-2.755253	3.097948
117	6	0	1.873078	1.175780	3.402189
118	1	0	0.796338	1.339891	3.315676
119	1	0	2.144866	0.405296	2.674644
120	1	0	2.092160	0.783616	4.401782
121	6	0	2.298099	3.449024	4.334817
122	1	0	2.632943	3.013921	5.281298
123	1	0	2.784619	4.421293	4.211358
124	1	0	1.217822	3.614676	4.416376
125	6	0	-0.006644	6.428862	-1.008510
126	1	0	0.784759	6.778255	-1.681204
127	1	0	-0.462076	5.539256	-1.453334
128	1	0	-0.762118	7.219291	-0.956943
129	6	0	1.306623	7.351715	0.928810
130	1	0	0.668820	8.242227	0.931991
131	1	0	1.661690	7.177229	1.949110
132	1	0	2.179919	7.558336	0.299958
133	6	0	3.322557	3.394574	-3.115735
134	1	0	3.898583	2.919114	-3.916150
135	1	0	2.262168	3.204940	-3.292143
136	1	0	3.502390	4.473694	-3.183386
137	6	0	5.242903	3.248342	-1.518622
138	1	0	5.636480	2.806475	-0.598869
139	1	0	5.874855	2.924270	-2.352503
140	1	0	5.322050	4.337755	-1.432936
141	6	0	-0.012260	-2.163232	3.757830
142	1	0	0.015703	-1.214538	3.214551
143	1	0	-0.884175	-2.158834	4.421567
144	1	0	0.880930	-2.224442	4.388916
145	6	0	-0.075646	-4.678776	3.567333
146	1	0	-0.060530	-5.532318	2.882366
147	1	0	0.791807	-4.751733	4.231633
148	1	0	-0.979980	-4.755786	4.181058
149	6	0	-6.145034	-2.847335	1.310931
150	1	0	-5.912136	-1.854482	0.913984
151	1	0	-6.334376	-3.514087	0.462604
152	1	0	-7.075701	-2.778217	1.882713
153	6	0	-5.345040	-4.816789	2.653816
154	1	0	-6.313273	-4.855547	3.164112
155	1	0	-5.387186	-5.485343	1.786754
156	1	0	-4.577828	-5.197721	3.334511
157	6	0	-1.600804	-2.674611	-2.670068
158	1	0	-0.607219	-2.362752	-2.347400
159	1	0	-1.563627	-2.880318	-3.745493
160	1	0	-2.285643	-1.836370	-2.512621
161	6	0	-3.363838	-4.441644	-2.534486
162	1	0	-3.768643	-5.299638	-1.988818
163	1	0	-4.137943	-3.667668	-2.584777
164	1	0	-3.155345	-4.756601	-3.561070

TS Si_A (M06-2X)

M06-2X/6-31g(d); E(RM062X) = -4246.634493 hartree
Sum of electronic and thermal Free Energies= -4245.351055 hartree
Thermal correction to Gibbs Free Energy= 1.283437 hartree
smd(toluene)/MN15/6-31g(d); E(RMN15) = -4243.883554 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	1.626370	-4.085428	-0.371890
2	6	0	0.141725	-4.389604	-1.094512
3	6	0	-0.918795	-3.873411	-0.237913
4	6	0	-1.359197	-4.514543	0.879945
5	1	0	0.177886	-3.906613	-2.076308
6	1	0	0.100130	-5.476014	-1.213991
7	1	0	-1.272016	-2.853286	-0.399612
8	1	0	-2.125007	-4.065027	1.502638
9	1	0	-1.144946	-5.570596	1.025506
10	8	0	1.955144	-2.658257	-0.334743
11	8	0	2.740650	-4.763976	-0.933617
12	6	0	3.726690	-3.814981	-1.321702
13	6	0	3.972197	-2.641116	0.964466
14	1	0	3.766303	-3.613496	1.421738
15	1	0	3.511411	-1.856099	1.574870
16	1	0	5.055101	-2.478328	0.962725
17	6	0	3.725064	-1.233196	-1.089079
18	1	0	3.416441	-0.414969	-0.428731
19	1	0	3.211483	-1.127762	-2.046664
20	1	0	4.802731	-1.136519	-1.258440
21	6	0	5.109713	-4.394912	-1.049860
22	1	0	5.200439	-4.733090	-0.015434
23	1	0	5.276743	-5.255405	-1.704063
24	1	0	5.891746	-3.653710	-1.253489
25	6	0	3.559579	-3.546516	-2.818391
26	1	0	2.589543	-3.087572	-3.029172
27	1	0	3.610507	-4.504656	-3.343241
28	1	0	4.346820	-2.892727	-3.208503
29	8	0	1.435808	-4.614173	1.058152
30	6	0	0.662990	-4.003656	1.858613
31	1	0	0.496092	-2.929103	1.721397
32	1	0	-5.681311	1.407474	1.342624
33	6	0	-4.665208	1.767225	1.198330
34	6	0	-3.787132	1.009164	0.464632
35	6	0	-4.270347	2.971698	1.834351
36	6	0	-2.481295	1.538116	0.285147
37	6	0	-2.941472	3.451869	1.671334
38	6	0	-2.048526	2.737702	0.800539
39	8	0	-1.585651	0.787069	-0.486125
40	6	0	-0.705301	3.276260	0.454247
41	15	0	-0.432538	0.021854	0.326653
42	6	0	0.445152	2.524611	0.604824
43	6	0	-0.584732	4.610088	-0.065734
44	8	0	0.368436	1.212854	1.052953
45	8	0	-0.777099	-1.010773	1.315787
46	6	0	1.752967	3.056289	0.419652
47	6	0	0.709217	5.176794	-0.210643
48	6	0	1.844318	4.385267	0.078969
49	1	0	2.831187	4.828919	-0.029523
50	7	0	0.496436	-0.524083	-0.961894
51	1	0	1.138639	-1.353274	-0.724153
52	16	0	-0.020658	-0.659435	-2.525995
53	8	0	1.078175	-1.251290	-3.261477
54	8	0	-1.363054	-1.190598	-2.629446
55	6	0	-0.116398	1.129426	-3.082634
56	9	0	0.504284	1.216646	-4.247125
57	9	0	0.475009	1.934468	-2.209208
58	9	0	-1.377724	1.490779	-3.228691
59	6	0	3.014589	2.262458	0.539514
60	6	0	3.386212	1.647670	1.752161
61	6	0	3.912365	2.247524	-0.557337
62	6	0	4.645189	1.046811	1.846744
63	6	0	5.172534	1.674017	-0.390060
64	6	0	5.565154	1.071484	0.803620
65	1	0	4.936194	0.580449	2.786501
66	1	0	5.864327	1.685137	-1.230431
67	6	0	-4.122039	-0.350342	-0.054000
68	6	0	-4.250978	-0.573706	-1.441688
69	6	0	-4.248271	-1.413797	0.857053
70	6	0	-4.426884	-1.876943	-1.894432
71	6	0	-4.432701	-2.703561	0.349821
72	6	0	-4.486099	-2.960446	-1.015225
73	1	0	-4.495381	-2.060636	-2.962201
74	1	0	-4.523022	-3.539653	1.040730
75	6	0	0.555263	-4.552854	3.265422
76	6	0	1.899478	-4.118527	3.900320
77	1	0	2.738433	-4.616310	3.406662
78	1	0	2.045782	-3.034619	3.828899
79	1	0	1.898666	-4.393343	4.959941
80	6	0	-0.586163	-3.900223	4.040357
81	1	0	-1.560916	-4.242959	3.684066
82	1	0	-0.504267	-4.159289	5.101001
83	1	0	-0.550625	-2.808754	3.951187
84	6	0	0.456129	-6.077710	3.292221
85	1	0	0.601309	-6.436334	4.316302
86	1	0	-0.528604	-6.416478	2.957139
87	1	0	1.218427	-6.529953	2.652831
88	6	0	-4.280055	0.601287	-2.408240
89	1	0	-3.492029	1.302481	-2.110308
90	6	0	-4.236999	-1.208967	2.365314
91	1	0	-3.844429	-0.210983	2.577520
92	6	0	-4.636032	-4.379032	-1.529348
93	1	0	-4.440889	-5.050877	-0.682838
94	6	0	2.524831	1.685332	3.007035
95	1	0	1.596421	2.215227	2.784239
96	6	0	3.566478	2.790657	-1.941234
97	1	0	2.562308	3.216036	-1.915149
98	6	0	6.969610	0.528107	0.993184
99	1	0	6.987268	-0.000630	1.955072
100	6	0	3.390699	-2.564785	-0.447873
101	6	0	-3.325123	-2.199265	3.087038
102	1	0	-3.256865	-1.947671	4.151437
103	1	0	-3.706449	-3.225738	3.021205
104	1	0	-2.323072	-2.160445	2.655585
105	6	0	-5.666105	-1.289566	2.918436
106	1	0	-5.673501	-1.107622	3.998438
107	1	0	-6.327747	-0.560342	2.440578
108	1	0	-6.088618	-2.284650	2.738135
109	6	0	-6.067367	-4.629869	-2.019669
110	1	0	-6.187158	-5.664193	-2.358987
111	1	0	-6.796474	-4.437655	-1.226801
112	1	0	-6.302842	-3.968124	-2.860847
113	6	0	-3.620351	-4.703634	-2.629263
114	1	0	-3.815021	-4.117371	-3.533560
115	1	0	-2.598964	-4.485963	-2.303186
116	1	0	-3.680874	-5.762217	-2.902185
117	6	0	-5.630518	1.327472	-2.297181
118	1	0	-5.661573	2.185445	-2.977309
119	1	0	-6.443380	0.645658	-2.570579
120	1	0	-5.817577	1.688796	-1.282314
121	6	0	-4.031209	0.220671	-3.868420

122	1	0	-3.124728	-0.377693	-3.980274
123	1	0	-4.876915	-0.344022	-4.277074
124	1	0	-3.926174	1.128851	-4.470427
125	6	0	3.228168	2.469030	4.123800
126	1	0	4.152914	1.973404	4.437527
127	1	0	3.483941	3.479984	3.792145
128	1	0	2.576454	2.547880	5.000056
129	6	0	2.155613	0.274630	3.481344
130	1	0	1.623841	-0.280349	2.702023
131	1	0	3.052271	-0.291528	3.760597
132	1	0	1.506643	0.327364	4.361930
133	6	0	7.971471	1.688013	1.072028
134	1	0	7.697886	2.391216	1.863950
135	1	0	8.982029	1.316026	1.270125
136	1	0	7.992543	2.239474	0.125280
137	6	0	7.387083	-0.464579	-0.095652
138	1	0	6.727119	-1.336557	-0.117632
139	1	0	7.366541	0.000143	-1.087617
140	1	0	8.408215	-0.816498	0.083008
141	6	0	3.537941	1.662890	-2.979453
142	1	0	2.809722	0.895398	-2.703674
143	1	0	3.261549	2.057821	-3.962804
144	1	0	4.514937	1.174862	-3.070833
145	6	0	4.529252	3.902065	-2.376064
146	1	0	5.552524	3.525485	-2.478971
147	1	0	4.226092	4.308213	-3.346387
148	1	0	4.551268	4.723375	-1.652253
149	6	0	-5.173048	3.682698	2.668829
150	1	0	-6.187056	3.305995	2.772139
151	6	0	-2.546296	4.603738	2.404064
152	1	0	-1.524241	4.957037	2.326198
153	6	0	-4.769861	4.805063	3.342214
154	1	0	-5.464224	5.338755	3.983204
155	6	0	-3.435746	5.258623	3.217327
156	1	0	-3.110813	6.130778	3.775702
157	6	0	-1.705723	5.388770	-0.465548
158	1	0	-2.699374	4.958904	-0.410258
159	6	0	0.847276	6.509457	-0.682371
160	1	0	1.847499	6.924451	-0.774007
161	6	0	-0.253529	7.243560	-1.034294
162	1	0	-0.142206	8.258379	-1.402423
163	6	0	-1.541820	6.665807	-0.938261
164	1	0	-2.410488	7.237632	-1.248894

TS Si_E (M06-2X)

M06-2X/6-31g(d); E(RM062X) = -4246.635557 hartree
Sum of electronic and thermal Free Energies= -4245.352082 hartree
Thermal correction to Gibbs Free Energy= 1.283476 hartree
smd(toluene)/MN15/6-31g(d); E(RMN15) = -4243.884321 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	0.631441	3.869879	-0.977511
2	6	0	0.034282	3.668790	-2.527691
3	6	0	-0.894621	4.778504	-2.666675
4	6	0	-2.193701	4.743076	-2.265191
5	1	0	0.903430	3.748717	-3.185966
6	1	0	-0.426531	2.681120	-2.599317
7	1	0	-0.462784	5.749616	-2.910522
8	1	0	-2.812097	5.634121	-2.316458
9	1	0	-2.702768	3.793680	-2.126401
10	8	0	1.186930	5.175331	-0.782255
11	6	0	2.251811	5.048888	0.159775
12	8	0	1.609694	2.902115	-0.509608
13	6	0	2.804945	3.626587	-0.159651
14	6	0	1.679200	5.145078	1.577266
15	1	0	1.018918	4.301872	1.803744
16	1	0	1.103706	6.073719	1.655186
17	1	0	2.471557	5.168398	2.332323
18	6	0	3.249368	6.174111	-0.076829
19	1	0	2.790953	7.131563	0.188179
20	1	0	3.548096	6.218811	-1.126155
21	1	0	4.143055	6.039796	0.542625
22	6	0	3.471296	2.920428	1.006110
23	1	0	2.801793	2.846764	1.867080
24	1	0	3.751232	1.909939	0.695360
25	1	0	4.384207	3.446593	1.311052
26	6	0	3.715877	3.613103	-1.385976
27	1	0	3.257171	4.160199	-2.215741
28	1	0	3.867276	2.573011	-1.691701
29	1	0	4.691740	4.060594	-1.166452
30	8	0	-0.635356	3.649394	-0.127931
31	6	0	-1.469942	4.600803	-0.054078
32	1	0	-1.078482	5.620378	-0.125152
33	1	0	-4.571030	-3.133514	-1.630345
34	6	0	-3.513857	-3.152582	-1.376227
35	6	0	-2.991437	-2.108419	-0.648859
36	6	0	-2.721456	-4.235749	-1.828911
37	6	0	-1.618244	-2.195873	-0.310230
38	6	0	-1.345501	-4.291819	-1.476361
39	6	0	-0.807774	-3.259179	-0.638766
40	8	0	-1.046245	-1.138433	0.407197
41	6	0	0.590557	-3.319652	-0.137331
42	15	0	-0.121781	-0.172562	-0.489753
43	6	0	1.476380	-2.285048	-0.363185
44	6	0	1.043372	-4.463116	0.601042
45	8	0	1.046084	-1.143775	-1.027626
46	8	0	-0.736822	0.561151	-1.599943
47	6	0	2.859593	-2.363387	-0.038862
48	6	0	2.423091	-4.571215	0.920297
49	6	0	3.300178	-3.524646	0.550965
50	1	0	4.358666	-3.624052	0.780591
51	6	0	-3.896084	-0.982547	-0.258241
52	6	0	-4.356272	-0.873226	1.068193
53	6	0	-4.422861	-0.151571	-1.265542
54	6	0	-5.401032	0.010964	1.341229
55	6	0	-5.479245	0.702382	-0.944348
56	6	0	-5.999383	0.781062	0.345204
57	1	0	-5.782276	0.086914	2.356332
58	1	0	-5.909605	1.319894	-1.731302
59	6	0	3.837880	-1.264851	-0.298004
60	6	0	4.578013	-0.732035	0.784844
61	6	0	4.114680	-0.836997	-1.610049
62	6	0	5.582233	0.195158	0.516539
63	6	0	5.128211	0.103576	-1.819588
64	6	0	5.878936	0.631182	-0.774892
65	1	0	6.137785	0.622353	1.350712
66	1	0	5.331239	0.422252	-2.838106
67	7	0	0.565876	0.759397	0.733037
68	1	0	1.060426	1.632547	0.367191
69	16	0	-0.107828	0.995347	2.216868
70	8	0	0.675348	2.036285	2.854592
71	8	0	-1.554099	1.054410	2.200661
72	6	0	0.300791	-0.610359	3.098200
73	9	0	-0.808033	-1.301213	3.293665
74	9	0	1.155382	-1.343786	2.398229
75	9	0	0.840367	-0.302745	4.266991
76	6	0	-2.746908	4.367865	0.712599
77	6	0	-3.356202	2.998564	0.403698
78	1	0	-4.009546	2.679130	1.221388
79	1	0	-3.960630	3.034277	-0.508684
80	1	0	-2.587830	2.229962	0.283095
81	6	0	-3.749988	5.498529	0.478380
82	1	0	-4.204269	5.434202	-0.514195
83	1	0	-4.553783	5.434419	1.218714
84	1	0	-3.278001	6.482605	0.584174
85	6	0	-2.269259	4.421672	2.186270
86	1	0	-1.570901	3.610156	2.402079
87	1	0	-1.782271	5.376907	2.414639
88	1	0	-3.139513	4.316212	2.841533
89	6	0	2.894526	-5.711903	1.623071
90	1	0	3.955598	-5.778967	1.848191
91	6	0	0.165937	-5.489114	1.048022
92	1	0	-0.896787	-5.403285	0.849589
93	6	0	-0.555639	-5.351440	-2.000166
94	1	0	0.504117	-5.386094	-1.773444
95	6	0	-3.276584	-5.256542	-2.645644
96	1	0	-4.332437	-5.201148	-2.896710
97	6	0	2.028296	-6.694406	2.022397
98	1	0	2.393344	-7.560174	2.565575
99	6	0	0.646778	-6.570740	1.740782
100	1	0	-0.040854	-7.337959	2.082349
101	6	0	-1.116758	-6.314171	-2.799498
102	1	0	-0.495765	-7.110459	-3.197496
103	6	0	-2.495193	-6.276922	-3.118199
104	1	0	-2.924685	-7.050165	-3.747111
105	6	0	3.405826	-1.392177	-2.836900
106	1	0	2.651589	-2.114025	-2.515565
107	6	0	4.314262	-1.086081	2.244749
108	1	0	3.507540	-1.818647	2.289864
109	6	0	6.991997	1.646551	-0.977906
110	1	0	6.785598	2.482998	-0.293519
111	6	0	-3.810111	-1.771713	2.167687
112	1	0	-2.763693	-1.991719	1.934028
113	6	0	-7.208096	1.647485	0.650653
114	1	0	-7.382378	1.596337	1.733185
115	6	0	-3.877047	-0.139791	-2.686779
116	1	0	-2.982629	-0.769096	-2.717994
117	6	0	-3.825161	-1.115909	3.550399
118	1	0	-3.283653	-1.747025	4.262020
119	1	0	-3.345456	-0.133865	3.524483
120	1	0	-4.845708	-1.002067	3.931743
121	6	0	-4.583572	-3.097862	2.198236
122	1	0	-4.530466	-3.616896	1.236269
123	1	0	-4.180026	-3.761638	2.970422
124	1	0	-5.639417	-2.911918	2.425463
125	6	0	-8.452589	1.092641	-0.054102
126	1	0	-8.329231	1.135871	-1.142018
127	1	0	-8.628136	0.048912	0.222075
128	1	0	-9.341047	1.676364	0.208660
129	6	0	-6.992230	3.118008	0.278491
130	1	0	-7.886358	3.706183	0.510179
131	1	0	-6.147600	3.547014	0.824318
132	1	0	-6.789908	3.228430	-0.793044
133	6	0	-3.433523	1.272776	-3.083432
134	1	0	-2.964706	1.260741	-4.073051
135	1	0	-4.282216	1.966685	-3.123156
136	1	0	-2.698263	1.643631	-2.365502
137	6	0	-4.895911	-0.693671	-3.689102
138	1	0	-5.173779	-1.725795	-3.453060
139	1	0	-5.812163	-0.092304	-3.686103
140	1	0	-4.484324	-0.674830	-4.703496
141	6	0	2.688526	-0.283454	-3.616405
142	1	0	1.987157	0.262008	-2.978863
143	1	0	3.406794	0.434536	-4.028788
144	1	0	2.128410	-0.711368	-4.454087

145	6	0	4.391133	-2.148463	-3.738145
146	1	0	5.164829	-1.479615	-4.130131
147	1	0	4.888921	-2.953491	-3.188619
148	1	0	3.864464	-2.587259	-4.591892
149	6	0	7.070000	2.208483	-2.396417
150	1	0	7.347368	1.426143	-3.112091
151	1	0	6.118874	2.643707	-2.717641
152	1	0	7.835767	2.988206	-2.447873
153	6	0	8.345628	1.038275	-0.582869
154	1	0	9.144645	1.781416	-0.672450
155	1	0	8.337907	0.666112	0.445510
156	1	0	8.584582	0.196675	-1.242142
157	6	0	5.548467	-1.715108	2.902225
158	1	0	6.386754	-1.010537	2.928067
159	1	0	5.324544	-2.004936	3.933998
160	1	0	5.882679	-2.605744	2.359964
161	6	0	3.844245	0.138520	3.037822
162	1	0	3.608058	-0.143883	4.069057
163	1	0	4.613874	0.918414	3.068148
164	1	0	2.948423	0.579017	2.590683

pivalaldehyde (1a) (B3LYP)

B3LYP/6-31g(d); E(RB3LYP) = -271.773728 hartree
Sum of electronic and thermal Free Energies= -271.663424 hartree
Thermal correction to Gibbs Free Energy= 0.110304 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	2.088464	-0.096837	0.000082
2	6	0	1.023341	-0.659984	0.000282
3	1	0	0.971922	-1.773522	0.000587
4	6	0	-0.329782	0.027053	-0.000027
5	6	0	-0.148292	1.541018	-0.000218
6	1	0	-1.123169	2.039193	-0.000498
7	1	0	0.410382	1.865218	0.882134
8	1	0	0.410724	1.864978	-0.882445
9	6	0	-1.081423	-0.443270	-1.254129
10	1	0	-1.170081	-1.535279	-1.279834
11	1	0	-2.092897	-0.023998	-1.259822
12	1	0	-0.571226	-0.117992	-2.166374
13	6	0	-1.081809	-0.442852	1.254070
14	1	0	-1.170621	-1.534844	1.279967
15	1	0	-0.571750	-0.117430	2.166339
16	1	0	-2.093206	-0.023414	1.259430

2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2) (B3LYP)

B3LYP/6-31g(d); E(RB3LYP) = -528.590975 hartree
Sum of electronic and thermal Free Energies= -528.377916 hartree
Thermal correction to Gibbs Free Energy= 0.213059 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.306528	-0.197871	-0.995888
2	6	0	3.214638	0.432913	0.023595
3	6	0	4.186739	-0.201022	0.673112
4	8	0	-0.105237	-1.141560	-0.684763
5	5	0	0.801418	-0.123327	-0.540198
6	8	0	0.257966	0.992150	0.048215
7	6	0	-1.169785	0.790312	0.103500
8	6	0	-1.285302	-0.767769	0.058950
9	6	0	-1.157941	-1.410108	1.439164
10	6	0	-2.514050	-1.298518	-0.661766
11	6	0	-1.713040	1.436221	1.367930
12	6	0	-1.760956	1.463534	-1.134018
13	1	0	2.393744	0.346017	-1.948255
14	1	0	2.599232	-1.234397	-1.190334
15	1	0	3.018398	1.480934	0.247816
16	1	0	4.406407	-1.248816	0.482373
17	1	0	4.797783	0.301806	1.415904
18	1	0	-0.280809	-1.025292	1.968805
19	1	0	-1.035946	-2.489259	1.314695
20	1	0	-2.046282	-1.226254	2.050837
21	1	0	-2.503752	-2.391778	-0.644744
22	1	0	-2.536070	-0.973921	-1.703780
23	1	0	-3.428314	-0.956212	-0.164970
24	1	0	-1.586698	2.520705	1.307730
25	1	0	-1.185106	1.080055	2.254425
26	1	0	-2.781076	1.220855	1.480931
27	1	0	-1.386311	0.995453	-2.049774
28	1	0	-1.461332	2.514805	-1.139515
29	1	0	-2.853787	1.411058	-1.136249

(*R*)-3d (B3LYP)

B3LYP/6-31g(d); E(RB3LYP) = -3447.760690 hartree
Sum of electronic and thermal Free Energies= -3446.877656 hartree
Thermal correction to Gibbs Free Energy= 0.883033 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.711888	1.688483	0.749783
2	6	0	-1.579116	0.765211	0.185923
3	6	0	-2.988491	0.770663	0.420366
4	6	0	-3.447937	1.606159	1.416384
5	1	0	-4.515876	1.662497	1.604666
6	6	0	3.245732	2.497887	-0.764520
7	6	0	0.634313	1.966787	0.166101
8	6	0	1.573192	0.968630	-0.023284
9	6	0	2.908824	1.194360	-0.460185
10	1	0	4.262138	2.715768	-1.080563
11	8	0	-1.118869	-0.144634	-0.771179
12	15	0	0.172112	-1.114840	-0.684129
13	8	0	1.205752	-0.351130	0.295600
14	6	0	-5.896631	-1.240088	-2.097996
15	6	0	-5.043617	-0.257893	-2.603354
16	6	0	-4.088115	0.390958	-1.813260
17	6	0	-3.957737	0.021098	-0.449231
18	6	0	-4.820618	-0.967556	0.090882
19	6	0	-5.765134	-1.572541	-0.748239
20	1	0	-5.147696	0.033607	-3.646336
21	1	0	-6.430741	-2.318356	-0.322648
22	6	0	6.128875	-1.675363	-0.795053
23	6	0	5.432106	-1.239773	-1.923853
24	6	0	4.349636	-0.356006	-1.841814
25	6	0	3.954316	0.119290	-0.568383
26	6	0	4.632796	-0.320607	0.593778
27	6	0	5.701745	-1.211861	0.451162
28	1	0	5.744175	-1.588875	-2.904404
29	1	0	6.235001	-1.544028	1.337682
30	8	0	0.596965	-1.509514	-2.040605
31	1	0	0.131760	-3.423553	-0.212111
32	7	0	-0.140107	-2.507555	0.237857
33	16	0	-0.702612	-2.646281	1.796154
34	8	0	-1.147270	-4.024736	1.966254
35	8	0	-1.537762	-1.495517	2.115933
36	6	0	0.793806	-2.466986	2.926038
37	9	0	1.821629	-3.190554	2.466800
38	9	0	1.155863	-1.191489	3.021050
39	9	0	0.440872	-2.920984	4.127419
40	6	0	2.308652	3.559423	-0.714838
41	6	0	0.975296	3.301541	-0.262405
42	6	0	-1.189813	2.452138	1.873882
43	6	0	-2.577846	2.393666	2.211870
44	6	0	4.285040	0.220590	1.981867
45	1	0	3.235162	0.531223	1.970244
46	6	0	3.665447	0.087947	-3.136102
47	1	0	2.742702	0.611502	-2.868780
48	6	0	7.344464	-2.587532	-0.907830
49	1	0	7.646526	-2.849472	0.115616
50	6	0	-3.301599	1.540381	-2.449702
51	1	0	-2.595452	1.930584	-1.713535
52	6	0	-4.809110	-1.379653	1.564493
53	1	0	-3.934758	-0.931521	2.040033
54	6	0	-6.977706	-1.854267	-2.979351
55	1	0	-6.753204	-1.560775	-4.014195
56	6	0	-7.001902	-3.391832	-2.931848
57	1	0	-7.753991	-3.783673	-3.626706
58	1	0	-6.031098	-3.817292	-3.208156
59	1	0	-7.254974	-3.762027	-1.931661
60	6	0	-8.363883	-1.276646	-2.627639
61	1	0	-8.647887	-1.537357	-1.601027
62	1	0	-8.369580	-0.184170	-2.707804
63	1	0	-9.133245	-1.673663	-3.300953
64	6	0	-4.241566	2.708414	-2.814179
65	1	0	-4.967054	2.416817	-3.582422
66	1	0	-4.803522	3.053172	-1.938941
67	1	0	-3.664225	3.555303	-3.204336
68	6	0	-2.475146	1.096183	-3.670394
69	1	0	-1.756933	0.317018	-3.397821
70	1	0	-3.112612	0.709493	-4.474216
71	1	0	-1.913967	1.946711	-4.076086
72	6	0	-6.065301	-0.858844	2.294765
73	1	0	-6.978629	-1.304219	1.881979
74	1	0	-6.021114	-1.114145	3.360380
75	1	0	-6.166613	0.229016	2.211863
76	6	0	-4.687864	-2.902914	1.755880
77	1	0	-3.803860	-3.302850	1.252175
78	1	0	-4.596036	-3.140675	2.821793
79	1	0	-5.565502	-3.437565	1.373934
80	6	0	4.551277	1.075494	-3.922750
81	1	0	4.035606	1.416203	-4.828704
82	1	0	4.804350	1.958595	-3.325963
83	1	0	5.491886	0.602737	-4.230390
84	6	0	3.257452	-1.098365	-4.029198
85	1	0	2.712721	-0.730989	-4.907396
86	1	0	4.127240	-1.656241	-4.396090
87	1	0	2.601355	-1.784359	-3.488155
88	6	0	8.531164	-1.853898	-1.563727
89	1	0	8.297872	-1.572434	-2.597569
90	1	0	8.782000	-0.938138	-1.017300
91	1	0	9.420569	-2.495304	-1.583822
92	6	0	7.038407	-3.901814	-1.647951
93	1	0	6.226317	-4.452340	-1.161360
94	1	0	6.741388	-3.718028	-2.687138
95	1	0	7.924642	-4.547259	-1.666700
96	6	0	5.132693	1.468387	2.306785
97	1	0	6.199750	1.215902	2.326513
98	1	0	4.987679	2.257610	1.562106
99	1	0	4.862720	1.874599	3.289354
100	6	0	4.425198	-0.820932	3.106049
101	1	0	3.894186	-1.746291	2.867424
102	1	0	5.473200	-1.072846	3.304676
103	1	0	4.009036	-0.419896	4.037424

104	6	0	2.669689	4.870806	-1.126756
105	1	0	3.691112	5.047638	-1.454643
106	6	0	0.041061	4.373898	-0.300786
107	1	0	-0.984888	4.197002	-0.002949
108	6	0	0.416194	5.629523	-0.725461
109	1	0	-0.320428	6.427727	-0.753794
110	6	0	1.746197	5.889356	-1.129885
111	1	0	2.029796	6.886812	-1.453818
112	6	0	-0.333865	3.243240	2.687414
113	1	0	0.726951	3.275825	2.465576
114	6	0	-3.061375	3.146739	3.314626
115	1	0	-4.121343	3.097396	3.551684
116	6	0	-2.207054	3.907540	4.079231
117	1	0	-2.585076	4.470968	4.927730
118	6	0	-0.828722	3.944789	3.765346
119	1	0	-0.151713	4.528855	4.382730

Int-1 (B3LYP)

B3LYP/6-31g(d); E(RB3LYP) = -4248.145003 hartree

Sum of electronic and thermal Free Energies= -4246.897101 hartree

Thermal correction to Gibbs Free Energy= 1.247901 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.947785	3.104920	-0.229126
2	6	0	1.743784	1.979969	-0.077664
3	6	0	3.139611	1.961513	-0.379510
4	6	0	3.642382	3.058752	-1.046939
5	1	0	4.704614	3.096932	-1.268857
6	6	0	-2.878588	3.612803	1.693750
7	6	0	-0.350968	3.254637	0.491666
8	6	0	-1.370276	2.327718	0.366557
9	6	0	-2.668342	2.482231	0.929818
10	1	0	-3.862912	3.779187	2.122568
11	8	0	1.226901	0.826796	0.525319
12	15	0	-0.140430	0.048862	0.157649
13	8	0	-1.130256	1.187334	-0.422209
14	6	0	5.949629	-0.994683	1.100927
15	6	0	5.190858	-0.206948	1.966974
16	6	0	4.266206	0.739263	1.511335
17	6	0	4.064688	0.885747	0.114389
18	6	0	4.828289	0.099983	-0.787555
19	6	0	5.750777	-0.818119	-0.270043
20	1	0	5.351365	-0.310884	3.037947
21	1	0	6.344522	-1.402735	-0.967678
22	6	0	-6.128335	-0.064632	0.419880
23	6	0	-5.362213	-0.115452	1.585986
24	6	0	-4.206598	0.655983	1.757513
25	6	0	-3.805048	1.522308	0.712612
26	6	0	-4.553762	1.578906	-0.487801
27	6	0	-5.696160	0.779753	-0.605306
28	1	0	-5.677058	-0.766607	2.396996
29	1	0	-6.283482	0.826844	-1.518298
30	8	0	-0.573444	-0.785989	1.295328
31	1	0	-0.267274	-1.919989	-1.126659
32	7	0	0.028746	-0.922577	-1.227397
33	16	0	0.516584	-0.519439	-2.768151
34	8	0	0.824878	-1.766350	-3.455523
35	8	0	1.432962	0.611054	-2.704492
36	6	0	-1.006326	0.155192	-3.645909
37	9	0	-2.072816	-0.615832	-3.396273
38	9	0	-1.259960	1.400872	-3.258316
39	9	0	-0.749824	0.137731	-4.952522
40	6	0	-1.852335	4.549631	1.969370
41	6	0	-0.559477	4.370283	1.382064
42	6	0	1.459535	4.180789	-1.038484
43	6	0	2.825232	4.141013	-1.459924
44	6	0	1.147970	-5.295429	-1.368969
45	6	0	2.187998	-4.225149	-1.231020
46	6	0	3.312945	-4.315801	-0.513646
47	8	0	-1.291723	-5.911620	-0.796036
48	5	0	-0.316221	-4.933090	-0.852981
49	8	0	0.247983	-4.913430	1.150185
50	8	0	-0.899384	-3.650683	-1.015262
51	6	0	0.713294	-3.931184	1.705097
52	6	0	-2.313420	-3.876539	-1.340398
53	6	0	-2.580662	-5.271523	-0.669462
54	6	0	-2.946008	-5.173521	0.820178
55	6	0	-3.611220	-6.145688	-1.386151
56	6	0	-3.151159	-2.724881	-0.794251
57	6	0	-2.406742	-3.940830	-2.871735
58	1	0	1.024400	-5.531671	-2.443033
59	1	0	1.480410	-6.224433	-0.888551
60	1	0	1.989765	-3.302953	-1.777755
61	1	0	3.573303	-5.225651	0.025976
62	1	0	4.023156	-3.495517	-0.460556
63	1	0	0.610688	-2.933073	1.249416
64	1	0	-2.257856	-4.525091	1.364574
65	1	0	-2.887451	-6.173313	1.261858
66	1	0	-3.965019	-4.795820	0.956426
67	1	0	-3.697637	-7.103489	-0.864477
68	1	0	-3.320108	-6.353103	-2.416851
69	1	0	-4.599385	-5.672885	-1.387640
70	1	0	-2.944849	-1.799709	-1.338697
71	1	0	-2.950537	-2.544396	0.262960
72	1	0	-4.217371	-2.940641	-0.912942
73	1	0	-1.847287	-4.793674	-3.266289
74	1	0	-1.985435	-3.031884	-3.304870
75	1	0	-3.447424	-4.025165	-3.203802
76	6	0	1.366244	-3.982511	3.067288
77	6	0	1.651429	-5.432423	3.478364
78	1	0	2.337090	-5.912310	2.774105
79	1	0	2.107885	-5.459796	4.473688
80	1	0	0.733364	-6.025760	3.504390
81	6	0	0.348409	-3.318215	4.030742
82	1	0	0.785279	-3.247975	5.033981
83	1	0	0.085981	-2.307179	3.700300
84	1	0	-0.572076	-3.907624	4.100412
85	6	0	2.660432	-3.145241	3.024719
86	1	0	2.472885	-2.126476	2.671507
87	1	0	3.094181	-3.077857	4.029647
88	1	0	3.401770	-3.599023	2.359228
89	6	0	-4.194431	2.548284	-1.615108
90	1	0	-3.118944	2.746194	-1.560090
91	6	0	-3.451480	0.560080	3.084710
92	1	0	-2.494540	1.077453	2.967854
93	6	0	-7.420383	-0.859755	0.275014
94	1	0	-7.773154	-0.715644	-0.755548
95	6	0	3.601500	1.642144	2.554591
96	1	0	2.915700	2.321098	2.043068
97	6	0	4.732956	0.235688	-2.308694
98	1	0	3.888226	0.885812	-2.543714
99	6	0	7.005370	-1.948661	1.646477
100	1	0	6.875305	-1.980964	2.737100
101	6	0	6.850028	-3.386769	1.122107
102	1	0	7.600745	-4.043184	1.578170
103	1	0	5.859104	-3.790823	1.354969
104	1	0	6.984663	-3.437639	0.035357
105	6	0	8.425760	-1.415934	1.370005
106	1	0	8.624780	-1.366281	0.292808
107	1	0	8.558603	-0.408955	1.780065
108	1	0	9.180974	-2.071443	1.820321
109	6	0	4.651310	2.530069	3.254864
110	1	0	5.370729	1.930775	3.824613
111	1	0	5.215556	3.124725	2.527764
112	1	0	4.162860	3.219526	3.954205
113	6	0	2.768542	0.857448	3.584382
114	1	0	1.974264	0.286099	3.094820
115	1	0	3.387447	0.160222	4.161026
116	1	0	2.300171	1.548105	4.296136
117	6	0	6.006727	0.886555	-2.888451
118	1	0	6.888350	0.257922	-2.714322
119	1	0	5.905219	1.026579	-3.971421
120	1	0	6.209749	1.865074	-2.438818
121	6	0	4.467580	-1.109711	-3.009827
122	1	0	3.571991	-1.599262	-2.618536
123	1	0	4.316107	-0.949463	-4.083435
124	1	0	5.306787	-1.805827	-2.896284
125	6	0	-4.226889	1.264190	4.216953
126	1	0	-3.660496	1.220741	5.155043
127	1	0	-4.416344	2.318014	3.985410
128	1	0	-5.197589	0.783443	4.389037
129	6	0	-3.124043	-0.891994	3.478893
130	1	0	-2.532335	-0.900972	4.402276
131	1	0	-4.028888	-1.481782	3.666886
132	1	0	-2.538412	-1.383142	2.698099
133	6	0	-8.515434	-0.317390	1.214867
134	1	0	-8.230858	-0.443154	2.266372
135	1	0	-8.691853	0.749987	1.042787
136	1	0	-9.460937	-0.850369	1.057613
137	6	0	-7.219710	-2.371160	0.485120
138	1	0	-6.483463	-2.775618	-0.217796
139	1	0	-6.870542	-2.593575	1.500223
140	1	0	-8.163574	-2.908671	0.335029
141	6	0	-4.922685	3.895955	-1.428312
142	1	0	-6.009731	3.756867	-1.469567
143	1	0	-4.678514	4.354363	-0.464720
144	1	0	-4.641417	4.600488	-2.220651
145	6	0	-4.469712	1.990248	-3.022620
146	1	0	-4.031244	0.997740	-3.156479
147	1	0	-5.542821	1.918222	-3.233436
148	1	0	-4.038177	2.657679	-3.777311
149	6	0	-2.084084	5.652733	2.835128
150	1	0	-3.076874	5.777611	3.260423
151	6	0	0.467654	5.286383	1.742552
152	1	0	1.465615	5.150688	1.344781
153	6	0	0.217145	6.334453	2.600657
154	1	0	1.022550	7.013700	2.866047
155	6	0	-1.073639	6.532450	3.143752
156	1	0	-1.258735	7.368744	3.812040
157	6	0	0.656957	5.273525	-1.464937
158	1	0	-0.388794	5.305559	-1.180570
159	6	0	3.343009	5.199727	-2.252680
160	1	0	4.386065	5.157834	-2.556693
161	6	0	2.540989	6.247201	-2.643388
162	1	0	2.944306	7.046551	-3.258751
163	6	0	1.182334	6.275064	-2.252112
164	1	0	0.544553	7.091755	-2.579021

Int-2 (B3LYP)

B3LYP/6-31g(d); E(RB3LYP) = -4248.190779 hartree

Sum of electronic and thermal Free Energies= -4246.932756 hartree

Thermal correction to Gibbs Free Energy= 1.258023 hartree

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	-0.915656	3.126300	0.238636
2	6	0	-1.721195	2.008907	0.081819
3	6	0	-3.116594	1.998568	0.387584
4	6	0	-3.609830	3.096660	1.060601
5	1	0	-4.671186	3.141760	1.285397
6	6	0	2.910951	3.602923	-1.694253
7	6	0	0.383858	3.269656	-0.482994
8	6	0	1.396096	2.335205	-0.360481
9	6	0	2.692972	2.473939	-0.930197
10	1	0	3.894268	3.759688	-2.128936
11	8	0	-1.215568	0.856293	-0.529934
12	15	0	0.153166	0.073872	-0.180854
13	8	0	1.143240	1.197380	0.426835
14	6	0	-5.932101	-0.953854	-1.091571
15	6	0	-5.177878	-0.162038	-1.958250
16	6	0	-4.252758	0.783841	-1.503136
17	6	0	-4.048606	0.928528	-0.106110
18	6	0	-4.811333	0.142021	0.795946
19	6	0	-5.732059	-0.777622	0.278794
20	1	0	-5.337321	-0.267544	-3.029095
21	1	0	-6.321418	-1.366039	0.976568
22	6	0	6.125049	-0.114955	-0.434362
23	6	0	5.356266	-0.153628	-1.599207
24	6	0	4.208512	0.630776	-1.766793
25	6	0	3.818979	1.499494	-0.718864
26	6	0	4.569753	1.542584	0.480899
27	6	0	5.703334	0.730214	0.594573
28	1	0	5.662322	-0.805279	-2.413161
29	1	0	6.292693	0.768107	1.506746
30	8	0	0.592103	-0.744170	-1.324878
31	1	0	0.284705	-1.902790	1.050281
32	7	0	-0.025365	-0.918721	1.190697
33	16	0	-0.517080	-0.547751	2.736440
34	8	0	-0.828603	-1.809899	3.396723
35	8	0	-1.433250	0.583244	2.693449
36	6	0	0.999076	0.111502	3.638730
37	9	0	2.063724	-0.666346	3.400063
38	9	0	1.265740	1.357221	3.262392
39	9	0	0.725341	0.087361	4.941841
40	6	0	1.892752	4.550739	-1.963456
41	6	0	0.600009	4.384134	-1.371866
42	6	0	-1.417795	4.201442	1.054369
43	6	0	-2.783536	4.171000	1.476546
44	6	0	-1.788042	-5.340179	1.787457
45	6	0	-2.160265	-4.228473	1.127762
46	6	0	-2.583087	-4.199888	-0.314846
47	8	0	1.326855	-5.848026	0.386160
48	5	0	0.548319	-4.753951	0.067376
49	8	0	-0.362885	-4.855014	-0.919913
50	8	0	1.012218	-3.579523	0.675134
51	6	0	-1.376512	-3.903041	-1.239465
52	6	0	2.301649	-3.913700	1.303429
53	6	0	2.641267	-5.288842	0.610353
54	6	0	3.285292	-5.116928	-0.776645
55	6	0	3.460325	-6.263252	1.449985
56	6	0	3.282711	-2.786783	0.992373
57	6	0	2.077526	-4.054116	2.811646
58	1	0	-1.471326	-5.295113	2.824568
59	1	0	-1.832476	-6.321912	1.323324
60	1	0	-2.100158	-3.279203	1.650797
61	1	0	-3.008107	-5.170023	-0.595014
62	1	0	-3.353007	-3.436757	-0.466030
63	1	0	-1.006383	-2.891707	-1.033007
64	1	0	2.734092	-4.407398	-1.400964
65	1	0	3.288233	-6.086177	-1.283721
66	1	0	4.321177	-4.767409	-0.699338
67	1	0	3.619836	-7.186789	0.883990
68	1	0	2.945311	-6.522719	2.378726
69	1	0	4.441964	-5.842309	1.698519
70	1	0	2.982191	-1.866500	1.500202
71	1	0	3.342774	-2.576395	-0.077126
72	1	0	4.285013	-3.046827	1.354666
73	1	0	1.379166	-4.868533	3.025308
74	1	0	1.651367	-3.133237	3.214610
75	1	0	3.019350	-4.252291	3.333302
76	6	0	-1.643297	-4.008385	-2.771158
77	6	0	-1.934562	-5.462380	-3.190505
78	1	0	-2.850389	-5.848188	-2.726882
79	1	0	-2.073666	-5.514301	-4.277326
80	1	0	-1.110235	-6.126408	-2.917194
81	6	0	-0.383186	-3.513785	-3.514147
82	1	0	-0.539702	-3.553703	-4.599176
83	1	0	-0.139579	-2.481931	-3.238251
84	1	0	0.481372	-4.141612	-3.275164
85	6	0	-2.832704	-3.110580	-3.155262
86	1	0	-2.700891	-2.085130	-2.792028
87	1	0	-2.932386	-3.066331	-4.246415
88	1	0	-3.779616	-3.489318	-2.754727
89	6	0	4.223181	2.512345	1.611794
90	1	0	3.150882	2.726639	1.556239
91	6	0	3.449544	0.543330	-3.092351
92	1	0	2.495099	1.064089	-2.970930
93	6	0	7.408299	-0.925074	-0.294389
94	1	0	7.763545	-0.789600	0.736513
95	6	0	-3.586287	1.685499	-2.546252
96	1	0	-2.893206	2.357444	-2.035257
97	6	0	-4.717994	0.276179	2.317325
98	1	0	-3.870260	0.921258	2.555061
99	6	0	-6.983566	-1.913139	-1.635753
100	1	0	-6.821278	-1.986357	-2.719970
101	6	0	-6.864776	-3.333257	-1.055374
102	1	0	-7.599761	-3.999875	-1.521745
103	1	0	-5.867916	-3.753428	-1.227652
104	1	0	-7.049396	-3.345255	0.025101
105	6	0	-8.403677	-1.351943	-1.419875
106	1	0	-8.629068	-1.256799	-0.350801
107	1	0	-8.511621	-0.360532	-1.873103
108	1	0	-9.155428	-2.015719	-1.864009
109	6	0	-4.633386	2.584076	-3.237032
110	1	0	-5.359530	1.991946	-3.805839
111	1	0	-5.190244	3.179402	-2.504656
112	1	0	-4.143657	3.273172	-3.935784
113	6	0	-2.765002	0.899070	-3.584040
114	1	0	-1.977307	0.311931	-3.102927
115	1	0	-3.393638	0.215544	-4.166179
116	1	0	-2.289696	1.590682	-4.290275
117	6	0	-5.989496	0.933455	2.894892
118	1	0	-6.873900	0.309364	2.718560
119	1	0	-5.889595	1.072938	3.978150
120	1	0	-6.186436	1.912933	2.444831
121	6	0	-4.462672	-1.071205	3.018580
122	1	0	-3.569613	-1.566251	2.628188
123	1	0	-4.311381	-0.912447	4.092476
124	1	0	-5.306496	-1.761582	2.903831
125	6	0	4.225964	1.247909	-4.223802
126	1	0	3.657393	1.208936	-5.160721
127	1	0	4.420228	2.300545	-3.990466
128	1	0	5.194273	0.763512	-4.399257
129	6	0	3.114818	-0.905852	-3.491866
130	1	0	2.511081	-0.907776	-4.407131
131	1	0	4.016935	-1.494705	-3.696348
132	1	0	2.536900	-1.402112	-2.708638
133	6	0	8.508580	-0.391826	-1.233348
134	1	0	8.219422	-0.506502	-2.284844
135	1	0	8.700138	0.671857	-1.054726
136	1	0	9.447131	-0.938755	-1.082309
137	6	0	7.189898	-2.433195	-0.511182
138	1	0	6.436822	-2.828541	0.178921
139	1	0	6.853156	-2.647493	-1.532347
140	1	0	8.124011	-2.984166	-0.349310
141	6	0	4.971490	3.849735	1.430619
142	1	0	6.056348	3.694777	1.473152
143	1	0	4.735648	4.314200	0.467830
144	1	0	4.699162	4.556197	2.224378
145	6	0	4.487806	1.944839	3.017524
146	1	0	4.031638	0.959726	3.147883
147	1	0	5.559370	1.852905	3.228601
148	1	0	4.067857	2.617280	3.774365
149	6	0	2.131917	5.652824	-2.828330
150	1	0	3.123995	5.768480	-3.257892
151	6	0	-0.419508	5.310476	-1.726912
152	1	0	-1.417214	5.183772	-1.325562
153	6	0	-0.161744	6.357298	-2.584215
154	1	0	-0.961168	7.045034	-2.845813
155	6	0	1.129010	6.543009	-3.131635
156	1	0	1.319866	7.378211	-3.799693
157	6	0	-0.605173	5.284546	1.485954
158	1	0	0.440435	5.308968	1.200196
159	6	0	-3.291479	5.230533	2.274450
160	1	0	-4.334686	5.196480	2.578955
161	6	0	-2.479890	6.268805	2.670086
162	1	0	-2.875888	7.068559	3.289681
163	6	0	-1.121108	6.286523	2.278720
164	1	0	-0.476097	7.095998	2.609414

product 4a (B3LYP)

B3LYP/6-31g(d); E(RB3LYP) = -800.419849 hartree

Sum of electronic and thermal Free Energies= -800.068357 hartree

Thermal correction to Gibbs Free Energy= 0.351492 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.390277	3.227272	-0.692216
2	6	0	0.990718	2.507015	0.251740
3	6	0	2.200183	1.647995	0.017631
4	8	0	-1.405419	-0.438635	-1.321492
5	5	0	-0.411598	-0.206945	-0.400258
6	8	0	0.899307	-0.210132	-0.735984
7	8	0	-0.889345	-0.035443	0.884453
8	6	0	1.880124	0.163064	0.228977
9	6	0	-2.321526	0.075192	0.771600
10	6	0	-2.605227	-0.685726	-0.566408
11	6	0	-2.709413	-2.197470	-0.368382
12	6	0	-3.800130	-0.169610	-1.351521
13	6	0	-2.963684	-0.539837	2.004474
14	6	0	-2.654683	1.562878	0.679471
15	1	0	-0.486383	3.831585	-0.478763
16	1	0	0.762949	3.242235	-1.713410
17	1	0	0.582612	2.498879	1.262980
18	1	0	2.561728	1.794078	-1.006104
19	1	0	3.000511	1.944394	0.706282
20	1	0	1.459061	0.034450	1.237038
21	1	0	-1.861831	-2.572264	0.214669
22	1	0	-2.691051	-2.681490	-1.348293

23	1	0	-3.636138	-2.474803	0.143008
24	1	0	-3.920854	-0.760880	-2.263433
25	1	0	-3.663925	0.874806	-1.638222
26	1	0	-4.717744	-0.259164	-0.760028
27	1	0	-2.714239	0.058879	2.885067
28	1	0	-2.607044	-1.558024	2.171528
29	1	0	-4.053944	-0.558781	1.900758
30	1	0	-2.213639	2.001908	-0.220328
31	1	0	-2.233029	2.073088	1.550580
32	1	0	-3.735762	1.731569	0.664778
33	6	0	3.078224	-0.799176	0.095243
34	6	0	3.712732	-0.696978	-1.295455
35	1	0	4.198294	0.272611	-1.448617
36	1	0	4.477848	-1.471443	-1.417362
37	1	0	2.956439	-0.833366	-2.073959
38	6	0	2.561343	-2.227391	0.312184
39	1	0	3.392188	-2.940621	0.286515
40	1	0	2.065446	-2.319931	1.286122
41	1	0	1.844985	-2.505389	-0.465167
42	6	0	4.120485	-0.481177	1.173109
43	1	0	3.670642	-0.479830	2.173253
44	1	0	4.909748	-1.240348	1.163339
45	1	0	4.598242	0.489953	1.010567

pivalaldehyde (1a) (M06-2X)

M06-2X/6-31g(d); E(RM062X) = -271.637576 hartree
Sum of electronic and thermal Free Energies= -271.525525 hartree
Thermal correction to Gibbs Free Energy= 0.112051 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.362237	-0.160592	-2.385899
2	6	0	-0.452355	0.754668	-2.735138
3	1	0	-0.273408	1.767454	-2.371042
4	6	0	-1.103624	0.650992	-4.094553
5	6	0	-1.489971	-0.782511	-4.452077
6	1	0	-2.320227	-1.141663	-3.835584
7	1	0	-1.810684	-0.823740	-5.497948
8	1	0	-0.642484	-1.459986	-4.320518
9	6	0	0.016950	1.140049	-5.046099
10	1	0	-0.368586	1.150433	-6.071141
11	1	0	0.346166	2.149891	-4.781420
12	1	0	0.880231	0.468516	-5.002827
13	6	0	-2.289746	1.607758	-4.194304
14	1	0	-2.051655	2.586454	-3.759083
15	1	0	-2.559191	1.768746	-5.244285
16	1	0	-3.171591	1.215942	-3.678739

2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2) (M06-2X)

M06-2X/6-31g(d); E(RM062X) = -528.350484 hartree
Sum of electronic and thermal Free Energies= -528.134194 hartree
Thermal correction to Gibbs Free Energy= 0.216290 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.763985	-5.068723	1.889761
2	6	0	-1.779162	-4.066903	1.652895
3	6	0	-2.651142	-4.086864	0.602372
4	8	0	1.652133	-5.426406	0.969263
5	5	0	0.507109	-4.600027	0.879042
6	8	0	0.955595	-3.215940	1.102136
7	6	0	2.369437	-3.247848	1.389978
8	6	0	2.788611	-4.597970	0.732242
9	6	0	2.996167	-4.449948	-0.779187
10	6	0	4.004838	-5.251791	1.370982
11	6	0	3.045945	-2.025650	0.788326
12	6	0	2.524507	-3.263238	2.909748
13	1	0	-0.350155	-5.041711	2.899804
14	1	0	-1.049840	-6.082857	1.602691
15	1	0	-1.689048	-3.145426	2.229602
16	1	0	-2.887818	-5.026186	0.107907
17	1	0	-3.331902	-3.254737	0.435380
18	1	0	2.165146	-3.903060	-1.236536
19	1	0	3.039530	-5.448460	-1.223361
20	1	0	3.925618	-3.918034	-1.009464
21	1	0	4.252375	-6.169642	0.829957
22	1	0	3.803700	-5.513606	2.411894
23	1	0	4.874233	-4.585858	1.333432
24	1	0	2.716023	-1.110256	1.288571
25	1	0	2.826282	-1.920992	-0.276129
26	1	0	4.132171	-2.090689	0.918356
27	1	0	2.089512	-4.174265	3.331500
28	1	0	1.998013	-2.403257	3.334649
29	1	0	3.576745	-3.203985	3.205745

(*R*)-3d (M06-2X)

M06-2X/6-31g(d); E(RM062X) = -3446.607067 hartree
Sum of electronic and thermal Free Energies= -3445.708017 hartree
Thermal correction to Gibbs Free Energy= 0.899051 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.715706	1.896620	-0.111277
2	6	0	-1.543874	0.800964	-0.208072
3	6	0	-2.954975	0.862961	-0.039396
4	6	0	-3.474788	2.042967	0.427031
5	1	0	-4.551399	2.133929	0.553351
6	6	0	3.245236	1.754982	-1.794320
7	6	0	0.650958	1.869567	-0.700388
8	6	0	1.554527	0.887559	-0.368332
9	6	0	2.867280	0.789839	-0.893362
10	1	0	4.255150	1.732877	-2.196992
11	8	0	-1.034244	-0.429033	-0.609897
12	15	0	0.156524	-1.218900	0.122608
13	8	0	1.176105	-0.066328	0.576212
14	6	0	-5.568554	-2.348582	-1.264820
15	6	0	-4.750117	-1.686310	-2.179283
16	6	0	-3.876309	-0.669679	-1.802535
17	6	0	-3.833794	-0.276725	-0.444221
18	6	0	-4.668758	-0.913411	0.493638
19	6	0	-5.512731	-1.943839	0.063974
20	1	0	-4.786760	-1.992028	-3.224515
21	1	0	-6.137858	-2.440519	0.801991
22	6	0	5.886833	-2.134013	-0.003736
23	6	0	5.080799	-2.260168	-1.133048
24	6	0	4.043979	-1.365764	-1.405244
25	6	0	3.824209	-0.297926	-0.514055
26	6	0	4.576047	-0.190607	0.671189
27	6	0	5.602721	-1.108599	0.896165
28	1	0	5.266122	-3.075645	-1.828795
29	1	0	6.204402	-1.026966	1.797872
30	8	0	0.626928	-2.316114	-0.731061
31	1	0	0.048108	-2.781480	1.850741
32	7	0	-0.297881	-1.781875	1.640680
33	16	0	-0.736754	-0.909570	2.963433
34	8	0	-0.989362	-1.872964	4.014372
35	8	0	-1.682956	0.119900	2.592553
36	6	0	0.760143	0.043548	3.529976
37	9	0	1.865789	-0.659689	3.321674
38	9	0	0.845192	1.206179	2.908058
39	9	0	0.615327	0.253095	4.829030
40	6	0	2.354006	2.765618	-2.235092
41	6	0	1.031220	2.816516	-1.713142
42	6	0	-1.255545	3.084997	0.484418
43	6	0	-2.647450	3.145773	0.765068
44	6	0	4.311576	0.925296	1.672235
45	1	0	3.235227	1.137063	1.656902
46	6	0	3.200694	-1.561486	-2.657697
47	1	0	2.270850	-0.996254	-2.531329
48	6	0	7.045393	-3.082946	0.239585
49	1	0	7.496471	-2.808611	1.201910
50	6	0	-3.041220	-0.011716	-2.894429
51	1	0	-2.412252	0.762962	-2.447716
52	6	0	-4.674043	-0.564404	1.973696
53	1	0	-3.951393	0.233366	2.147317
54	6	0	-6.501668	-3.442579	-1.751148
55	1	0	-5.991544	-3.950461	-2.581519
56	6	0	-6.824938	-4.492268	-0.686766
57	1	0	-7.381696	-5.321903	-1.132662
58	1	0	-5.917437	-4.896864	-0.224868
59	1	0	-7.448719	-4.072032	0.109427
60	6	0	-7.793905	-2.823198	-2.301633
61	1	0	-8.323995	-2.290074	-1.504702
62	1	0	-7.579689	-2.106722	-3.100196
63	1	0	-8.459512	-3.596712	-2.698812
64	6	0	-3.945283	0.688307	-3.917885
65	1	0	-4.583851	-0.032115	-4.440349
66	1	0	-4.594587	1.422219	-3.430821
67	1	0	-3.340112	1.206325	-4.669033
68	6	0	-2.112449	-1.018963	-3.584367
69	1	0	-1.440020	-1.497372	-2.865919
70	1	0	-2.687509	-1.801955	-4.092065
71	1	0	-1.502663	-0.512220	-4.339832
72	6	0	-6.049185	-0.069650	2.435387
73	1	0	-6.815166	-0.843037	2.311546
74	1	0	-6.017793	0.202616	3.495310
75	1	0	-6.369595	0.808544	1.865019
76	6	0	-4.213348	-1.767327	2.802332
77	1	0	-3.271093	-2.153681	2.403549
78	1	0	-4.047435	-1.484988	3.846734
79	1	0	-4.945232	-2.583545	2.777176
80	6	0	3.927222	-1.025359	-3.898321
81	1	0	3.322771	-1.187874	-4.796903
82	1	0	4.134066	0.045627	-3.816434
83	1	0	4.883130	-1.544515	-4.032816
84	6	0	2.810128	-3.028777	-2.870885
85	1	0	2.061757	-3.098253	-3.667573
86	1	0	3.669901	-3.635332	-3.176583
87	1	0	2.379038	-3.456240	-1.962351
88	6	0	8.116913	-2.926539	-0.846062
89	1	0	7.714729	-3.202017	-1.827239
90	1	0	8.469551	-1.892837	-0.905806
91	1	0	8.974752	-3.574959	-0.639929
92	6	0	6.582222	-4.540090	0.334510
93	1	0	5.835235	-4.667144	1.124308
94	1	0	6.132580	-4.871168	-0.608276
95	1	0	7.427341	-5.201393	0.551840
96	6	0	5.058634	2.206648	1.275120
97	1	0	6.137756	2.017629	1.254926
98	1	0	4.756523	2.562542	0.286646
99	1	0	4.865619	3.004196	2.000546
100	6	0	4.679473	0.542192	3.109538

101	1	0	4.300971	-0.448174	3.376330
102	1	0	5.765016	0.543237	3.256106
103	1	0	4.257611	1.272363	3.807576
104	6	0	2.756098	3.705594	-3.220414
105	1	0	3.774550	3.656097	-3.596229
106	6	0	0.133701	3.778673	-2.252359
107	1	0	-0.892811	3.803562	-1.905929
108	6	0	0.547152	4.663155	-3.216016
109	1	0	-0.156929	5.384685	-3.618192
110	6	0	1.876710	4.640504	-3.697783
111	1	0	2.189881	5.352338	-4.454783
112	6	0	-0.442797	4.197616	0.825769
113	1	0	0.625088	4.148524	0.637988
114	6	0	-3.187537	4.320925	1.348420
115	1	0	-4.254716	4.355466	1.550430
116	6	0	-2.380287	5.383197	1.662888
117	1	0	-2.800970	6.274579	2.117093
118	6	0	-0.991477	5.314182	1.404947
119	1	0	-0.353450	6.150490	1.672668

Int-1 (M06-2X)

M06-2X/6-31g(d); E(RM062X) = -4246.647360 hartree

Sum of electronic and thermal Free Energies= -4245.366354 hartree

Thermal correction to Gibbs Free Energy= 1.281006 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.984361	3.042136	-0.220703
2	6	0	1.745957	1.920119	0.014814
3	6	0	3.143587	1.846492	-0.237740
4	6	0	3.707595	2.894288	-0.918971
5	1	0	4.777114	2.883118	-1.116854
6	6	0	-2.864160	3.475556	1.660598
7	6	0	-0.340852	3.211202	0.434962
8	6	0	-1.324652	2.256764	0.322462
9	6	0	-2.606686	2.348254	0.919797
10	1	0	-3.847131	3.597204	2.109581
11	8	0	1.184535	0.814302	0.644918
12	15	0	-0.091653	0.000718	0.113333
13	8	0	-1.070953	1.132134	-0.463401
14	6	0	5.566167	-1.363921	1.332391
15	6	0	4.863650	-0.502666	2.174857
16	6	0	4.056697	0.523783	1.691580
17	6	0	3.962530	0.714698	0.293105
18	6	0	4.684097	-0.124010	-0.577805
19	6	0	5.464583	-1.152714	-0.038114
20	1	0	4.942295	-0.651597	3.251507
21	1	0	6.001249	-1.805630	-0.722374
22	6	0	-5.869964	-0.436643	0.691651
23	6	0	-5.001952	-0.440773	1.781439
24	6	0	-3.890494	0.401500	1.844705
25	6	0	-3.657376	1.290469	0.777846
26	6	0	-4.477224	1.263899	-0.365992
27	6	0	-5.576463	0.404226	-0.380165
28	1	0	-5.197960	-1.114926	2.612372
29	1	0	-6.229597	0.386453	-1.249006
30	8	0	-0.565947	-0.912597	1.161549
31	1	0	-0.158687	-1.821091	-1.341936
32	7	0	0.228503	-0.825164	-1.315462
33	16	0	0.628876	-0.203438	-2.787713
34	8	0	0.748372	-1.332274	-3.683982
35	8	0	1.655732	0.803791	-2.638826
36	6	0	-0.849316	0.750462	-3.402207
37	9	0	-1.975230	0.173787	-3.000942
38	9	0	-0.812883	2.002623	-2.981493
39	9	0	-0.798074	0.732798	-4.724667
40	6	0	-1.882706	4.474996	1.879175
41	6	0	-0.594555	4.338762	1.290507
42	6	0	1.559961	4.074074	-1.034440
43	6	0	2.932803	3.985832	-1.391672
44	6	0	0.809465	-5.094119	-1.853473
45	6	0	1.908660	-4.092305	-1.744883
46	6	0	2.954643	-4.176616	-0.917025
47	8	0	-1.630023	-5.439355	-1.031807
48	5	0	-0.477542	-4.631223	-0.990648
49	8	0	0.140459	-4.737824	0.569441
50	8	0	-0.906942	-3.242589	-1.125191
51	6	0	0.742096	-3.775716	1.043310
52	6	0	-2.324707	-3.246568	-1.406428
53	6	0	-2.762384	-4.607664	-0.785972
54	6	0	-2.995618	-4.499945	0.725004
55	6	0	-3.976185	-5.236013	-1.455963
56	6	0	-2.985671	-2.031805	-0.774307
57	6	0	-2.479837	-3.219214	-2.926201
58	1	0	0.476348	-5.186110	-2.894300
59	1	0	1.139311	-6.083109	-1.516057
60	1	0	1.788672	-3.191235	-2.348920
61	1	0	3.123479	-5.071180	-0.316829
62	1	0	3.692195	-3.380187	-0.834413
63	1	0	0.671150	-2.804117	0.545959
64	1	0	-2.180903	-3.958511	1.215541
65	1	0	-3.040737	-5.509628	1.142800
66	1	0	-3.933060	-3.979980	0.950177
67	1	0	-4.245320	-6.158831	-0.934048
68	1	0	-3.759604	-5.484145	-2.496977
69	1	0	-4.837491	-4.559417	-1.423360
70	1	0	-2.643514	-1.108224	-1.251030
71	1	0	-2.768443	-1.956392	0.292843
72	1	0	-4.072360	-2.079791	-0.908808
73	1	0	-2.046239	-4.118430	-3.374045
74	1	0	-1.950727	-2.349522	-3.326862
75	1	0	-3.531861	-3.148525	-3.220063
76	6	0	1.450538	-3.828849	2.358945
77	6	0	1.782388	-5.263209	2.759418
78	1	0	2.460088	-5.724618	2.033557
79	1	0	2.269561	-5.267992	3.738991
80	1	0	0.877977	-5.875100	2.815351
81	6	0	0.443517	-3.197937	3.350455
82	1	0	0.906930	-3.163953	4.341441
83	1	0	0.173762	-2.182071	3.047835
84	1	0	-0.469498	-3.797597	3.413670
85	6	0	2.698175	-2.942656	2.278956
86	1	0	2.467910	-1.963929	1.840579
87	1	0	3.097449	-2.770299	3.285223
88	1	0	3.481964	-3.406055	1.671182
89	6	0	-4.206519	2.182498	-1.549086
90	1	0	-3.120443	2.317629	-1.623099
91	6	0	-2.982307	0.349198	3.065746
92	1	0	-2.025468	0.809737	2.795825
93	6	0	-7.103087	-1.320285	0.672202
94	1	0	-7.598371	-1.169654	-0.295634
95	6	0	3.354363	1.413339	2.710598
96	1	0	2.760587	2.164499	2.182580
97	6	0	4.636791	0.011750	-2.092144
98	1	0	3.955896	0.823600	-2.348505
99	6	0	6.438459	-2.449983	1.935708
100	1	0	5.937067	-2.789123	2.853043
101	6	0	6.624003	-3.665291	1.026738
102	1	0	7.155257	-4.458316	1.561228
103	1	0	5.664495	-4.066088	0.683322
104	1	0	7.219558	-3.413821	0.142805
105	6	0	7.800993	-1.864629	2.333308
106	1	0	8.322148	-1.491896	1.446640
107	1	0	7.685404	-1.030255	3.028885
108	1	0	8.429891	-2.624235	2.805688
109	6	0	4.381624	2.175545	3.558256
110	1	0	5.000590	1.486526	4.143113
111	1	0	5.047131	2.771182	2.925896
112	1	0	3.875027	2.848377	4.258093
113	6	0	2.396388	0.613487	3.602502
114	1	0	1.648509	0.082857	3.004848
115	1	0	2.940631	-0.121461	4.207940
116	1	0	1.871231	1.286280	4.289485
117	6	0	6.016699	0.348731	-2.668549
118	1	0	6.747608	-0.434749	-2.436709
119	1	0	5.960328	0.442545	-3.758633
120	1	0	6.400853	1.291221	-2.262039
121	6	0	4.069595	-1.259428	-2.731673
122	1	0	3.139934	-1.550969	-2.234437
123	1	0	3.849503	-1.096731	-3.791440
124	1	0	4.766999	-2.101818	-2.653065
125	6	0	-3.586993	1.139246	4.233831
126	1	0	-2.941217	1.074941	5.116084
127	1	0	-3.717126	2.196191	3.983622
128	1	0	-4.569133	0.731756	4.500220
129	6	0	-2.680400	-1.088293	3.504176
130	1	0	-1.903030	-1.081477	4.275932
131	1	0	-3.562690	-1.574521	3.934695
132	1	0	-2.320018	-1.686347	2.663294
133	6	0	-8.087138	-0.911242	1.774723
134	1	0	-7.643386	-1.064763	2.764738
135	1	0	-8.358857	0.144876	1.688469
136	1	0	-9.001665	-1.510895	1.719430
137	6	0	-6.744389	-2.804814	0.792290
138	1	0	-6.065409	-3.113580	-0.008854
139	1	0	-6.251273	-3.013068	1.748447
140	1	0	-7.644197	-3.426344	0.738339
141	6	0	-4.847146	3.560613	-1.329733
142	1	0	-5.932642	3.454614	-1.225086
143	1	0	-4.464063	4.047419	-0.429039
144	1	0	-4.649431	4.216316	-2.184343
145	6	0	-4.685216	1.600838	-2.883418
146	1	0	-4.385213	0.556433	-3.003226
147	1	0	-5.775565	1.655202	-2.973106
148	1	0	-4.262906	2.178097	-3.712174
149	6	0	-2.160088	5.592593	2.709881
150	1	0	-3.154443	5.683203	3.138820
151	6	0	0.396386	5.306257	1.613333
152	1	0	1.398757	5.195963	1.216535
153	6	0	0.102992	6.366256	2.433170
154	1	0	0.876849	7.088937	2.671785
155	6	0	-1.192717	6.524135	2.977698
156	1	0	-1.410526	7.372995	3.617855
157	6	0	0.799880	5.171913	-1.515982
158	1	0	-0.255064	5.232656	-1.268031
159	6	0	3.509032	5.006715	-2.190932
160	1	0	4.561398	4.929133	-2.450455
161	6	0	2.752745	6.058734	-2.638403
162	1	0	3.200011	6.830038	-3.257182
163	6	0	1.381165	6.134800	-2.302173
164	1	0	0.782227	6.960110	-2.674017

Int-2 (M06-2X)

M06-2X/6-31g(d); E(RM062X) = -4246.703069 hartree

Sum of electronic and thermal Free Energies= -4245.420090 hartree

Thermal correction to Gibbs Free Energy= 1.282979 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.868083	2.991403	0.331669
2	6	0	-1.665622	1.906975	0.038633
3	6	0	-3.064572	1.875994	0.290310
4	6	0	-3.578333	2.891768	1.057677
5	1	0	-4.647010	2.906875	1.260735
6	6	0	2.967458	3.450903	-1.559838
7	6	0	0.451031	3.168148	-0.332713
8	6	0	1.421181	2.197588	-0.262969
9	6	0	2.704704	2.301334	-0.854654
10	1	0	3.950948	3.581004	-2.005176
11	8	0	-1.137717	0.815760	-0.647344
12	15	0	0.142592	-0.033041	-0.182965
13	8	0	1.139116	1.043891	0.469966
14	6	0	-5.988682	-0.717674	-1.526480
15	6	0	-5.146525	0.073285	-2.300145
16	6	0	-4.144366	0.870955	-1.741776
17	6	0	-3.984032	0.877917	-0.340702
18	6	0	-4.800121	0.050963	0.461088
19	6	0	-5.785076	-0.725275	-0.147511
20	1	0	-5.280236	0.075299	-3.380519
21	1	0	-6.406604	-1.364717	0.476829
22	6	0	6.016256	-0.427947	-0.666829
23	6	0	5.190932	-0.384938	-1.788417
24	6	0	4.061464	0.436061	-1.844804
25	6	0	3.761705	1.247579	-0.734061
26	6	0	4.536207	1.165522	0.439937
27	6	0	5.655677	0.333069	0.444103
28	1	0	5.440325	-0.993475	-2.655642
29	1	0	6.277864	0.280013	1.333945
30	8	0	0.620267	-0.893600	-1.266960
31	1	0	0.146717	-1.909706	1.160819
32	7	0	-0.187769	-0.924374	1.216534
33	16	0	-0.584677	-0.389630	2.725100
34	8	0	-0.724296	-1.570696	3.549555
35	8	0	-1.591969	0.641411	2.630918
36	6	0	0.900931	0.495901	3.412257
37	9	0	2.017611	-0.106818	3.024606
38	9	0	0.917841	1.761845	3.037130
39	9	0	0.807692	0.432936	4.731144
40	6	0	1.995418	4.466940	-1.738733
41	6	0	0.711429	4.326009	-1.142421
42	6	0	-1.395718	3.990446	1.214122
43	6	0	-2.762385	3.919545	1.595519
44	6	0	-1.211263	-5.391506	2.670986
45	6	0	-1.846735	-4.396488	2.055025
46	6	0	-2.518153	-4.523754	0.716927
47	8	0	1.778503	-5.438088	-0.035248
48	5	0	0.702894	-4.588021	0.006447
49	8	0	-0.508189	-4.920976	-0.477416
50	8	0	1.033712	-3.336917	0.522068
51	6	0	-1.591938	-3.999249	-0.388076
52	6	0	2.412753	-3.411832	0.963945
53	6	0	2.947868	-4.613907	0.120913
54	6	0	3.375728	-4.187344	-1.283409
55	6	0	4.038070	-5.423912	0.801055
56	6	0	3.106664	-2.093651	0.668568
57	6	0	2.375025	-3.696637	2.462551
58	1	0	-0.707598	-5.237902	3.620895
59	1	0	-1.183184	-6.393565	2.248654
60	1	0	-1.842225	-3.405330	2.508534
61	1	0	-2.738692	-5.574874	0.501484
62	1	0	-3.461904	-3.967514	0.706360
63	1	0	-1.203930	-3.013476	-0.095918
64	1	0	2.578244	-3.613776	-1.768470
65	1	0	3.566687	-5.083645	-1.879634
66	1	0	4.279202	-3.570683	-1.266418
67	1	0	4.358970	-6.232933	0.139341
68	1	0	3.678286	-5.865222	1.732747
69	1	0	4.906816	-4.793439	1.019740
70	1	0	2.688320	-1.293420	1.283338
71	1	0	2.996916	-1.803036	-0.378297
72	1	0	4.174798	-2.165148	0.903265
73	1	0	1.880626	-4.652159	2.663670
74	1	0	1.804249	-2.908138	2.964531
75	1	0	3.382167	-3.717906	2.889411
76	6	0	-2.226411	-3.819308	-1.779173
77	6	0	-3.001256	-5.070871	-2.200226
78	1	0	-3.882214	-5.233218	-1.568795
79	1	0	-3.347450	-4.969284	-3.234930
80	1	0	-2.363144	-5.959053	-2.139743
81	6	0	-1.108501	-3.535863	-2.791508
82	1	0	-1.544192	-3.269209	-3.761123
83	1	0	-0.481611	-2.699912	-2.458052
84	1	0	-0.472580	-4.414514	-2.931452
85	6	0	-3.157292	-2.606161	-1.725645
86	1	0	-2.614212	-1.695129	-1.437381
87	1	0	-3.599455	-2.422339	-2.711816
88	1	0	-3.981461	-2.739764	-1.016627
89	6	0	4.205447	2.008881	1.663515
90	1	0	3.114368	2.100423	1.720028
91	6	0	3.213922	0.445817	-3.109726
92	1	0	2.273031	0.959638	-2.885494
93	6	0	7.286410	-1.258419	-0.654917
94	1	0	7.744259	-1.139261	0.335493
95	6	0	-3.298607	1.709131	-2.691301
96	1	0	-2.601339	2.318366	-2.110043
97	6	0	-4.572426	-0.107258	1.955219
98	1	0	-3.865586	0.655116	2.284144
99	6	0	-7.086398	-1.551105	-2.160636
100	1	0	-7.067230	-1.350563	-3.239652
101	6	0	-6.848634	-3.052046	-1.956227
102	1	0	-7.654263	-3.634798	-2.414902
103	1	0	-5.899594	-3.368676	-2.398397
104	1	0	-6.821629	-3.299837	-0.888647
105	6	0	-8.465704	-1.144240	-1.629339
106	1	0	-8.546123	-1.351955	-0.556695
107	1	0	-8.646917	-0.075957	-1.778970
108	1	0	-9.255842	-1.705412	-2.138688
109	6	0	-4.164973	2.683682	-3.499270
110	1	0	-4.857990	2.150317	-4.158307
111	1	0	-4.755301	3.325690	-2.838250
112	1	0	-3.532863	3.321009	-4.126261
113	6	0	-2.467546	0.812654	-3.618624
114	1	0	-1.818475	0.142713	-3.046842
115	1	0	-3.116783	0.199618	-4.254267
116	1	0	-1.838789	1.424797	-4.273962
117	6	0	-5.850997	0.052808	2.782175
118	1	0	-6.586499	-0.725588	2.553173
119	1	0	-5.618756	-0.018519	3.849483
120	1	0	-6.323347	1.023355	2.598472
121	6	0	-3.913399	-1.468737	2.210549
122	1	0	-3.042303	-1.597782	1.554800
123	1	0	-3.580372	-1.560589	3.249993
124	1	0	-4.611745	-2.287808	1.996853
125	6	0	3.924208	1.210352	-4.234200
126	1	0	3.307870	1.221837	-5.138958
127	1	0	4.133243	2.246149	-3.949944
128	1	0	4.878749	0.731004	-4.480067
129	6	0	2.850162	-0.969420	-3.571732
130	1	0	2.182685	-0.915047	-4.437926
131	1	0	3.735845	-1.539501	-3.873538
132	1	0	2.328334	-1.509957	-2.779290
133	6	0	8.284001	-0.744966	-1.700116
134	1	0	7.876538	-0.856813	-2.710888
135	1	0	8.507796	0.314125	-1.543553
136	1	0	9.221077	-1.309071	-1.650798
137	6	0	7.004172	-2.748687	-0.865801
138	1	0	6.314130	-3.131223	-0.106593
139	1	0	6.556130	-2.927379	-1.849733
140	1	0	7.930409	-3.329888	-0.810524
141	6	0	4.798567	3.419576	1.533431
142	1	0	5.889405	3.358961	1.449776
143	1	0	4.417587	3.941189	0.651649
144	1	0	4.557350	4.019225	2.417602
145	6	0	4.677442	1.376684	2.977034
146	1	0	4.421148	0.315532	3.034366
147	1	0	5.761936	1.472516	3.097825
148	1	0	4.210531	1.890031	3.823798
149	6	0	2.278942	5.611744	-2.529489
150	1	0	3.269327	5.705606	-2.966747
151	6	0	-0.269064	5.319844	-1.412152
152	1	0	-1.267718	5.207967	-1.005937
153	6	0	0.030455	6.406706	-2.193631
154	1	0	-0.734734	7.150034	-2.393540
155	6	0	1.321652	6.566040	-2.749003
156	1	0	1.543891	7.435600	-3.359152
157	6	0	-0.594019	5.037045	1.741271
158	1	0	0.456687	5.084394	1.472901
159	6	0	-3.292074	4.904159	2.469282
160	1	0	-4.340909	4.840753	2.746256
161	6	0	-2.496231	5.905522	2.961644
162	1	0	-2.907576	6.649883	3.635866
163	6	0	-1.130705	5.965610	2.597151
164	1	0	-0.501138	6.751351	3.002653

product-4a (M06-2X)

M06-2X/6-31g(d); E(RM062X) = -800.064212 hartree

Sum of electronic and thermal Free Energies= -799.707167 hartree

Thermal correction to Gibbs Free Energy= 0.357045 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.051941	-0.560331	1.520551
2	6	0	3.984078	-1.118300	0.939140
3	6	0	3.927768	-1.556882	-0.500877
4	8	0	5.239237	2.494066	0.235840
5	5	0	4.333736	1.533119	-0.158126
6	8	0	4.588842	0.643692	-1.136759
7	8	0	3.050093	1.808781	0.326758
8	6	0	3.615435	-0.359169	-1.414835
9	6	0	3.061079	3.181323	0.791640
10	6	0	4.431831	3.687781	0.222321
11	6	0	4.324351	4.113892	-1.245487
12	6	0	5.109872	4.766765	1.043272
13	6	0	1.839392	3.868830	0.201399
14	6	0	3.019277	3.173435	2.314397
15	1	0	5.016626	-0.225400	2.552586
16	1	0	5.994512	-0.443715	0.990995
17	1	0	3.068034	-1.216657	1.518547
18	1	0	4.893082	-1.981959	-0.799403
19	1	0	3.156873	-2.323540	-0.628194

20	1	0	2.622147	0.032221	−1.166526
21	1	0	3.817877	3.350017	−1.844922
22	1	0	5.335517	4.238609	−1.640679
23	1	0	3.780100	5.056188	−1.358339
24	1	0	6.047799	5.054518	0.560858
25	1	0	5.336967	4.413138	2.050943
26	1	0	4.471477	5.653930	1.112582
27	1	0	0.924076	3.465841	0.643821
28	1	0	1.777061	3.707441	−0.875995
29	1	0	1.863870	4.945943	0.403253
30	1	0	3.887987	2.650909	2.725329
31	1	0	2.119114	2.655965	2.658124
32	1	0	2.992288	4.192851	2.710085
33	6	0	3.609141	−0.629821	−2.931743
34	6	0	4.994304	−1.049858	−3.430360
35	1	0	5.299745	−2.017909	−3.017699
36	1	0	4.985140	−1.145388	−4.521887
37	1	0	5.745761	−0.304133	−3.155455
38	6	0	3.186194	0.666495	−3.639262
39	1	0	3.092973	0.494666	−4.717430
40	1	0	2.220486	1.016552	−3.257215
41	1	0	3.933056	1.452002	−3.484532
42	6	0	2.572935	−1.717491	−3.231835
43	1	0	1.595576	−1.444791	−2.812563
44	1	0	2.455272	−1.835953	−4.314772
45	1	0	2.865982	−2.687672	−2.816459

9-2. Calculation results of transition states by B3LYP

We calculated four transition states for *re*-face attack and *si*-face attack considering axial and equatorial models respectively (Figure S1). DFT calculation was performed using Gaussian 16. We first optimized geometries of four transition states using the B3LYP density function and 6-31G(d) basis set, in which the level of theory was used in previous works by Goodman and Houk. As a result, the transition state Re_A, which was *re*-face attack with a bidentate chelation via hydrogen bonding of the phosphoryl oxygen of the catalyst with the hydrogen atom of the formyl group (2.58 Å) and the hydrogen bond between axial boronate oxygen and hydrogen atom (N-H) of the catalyst (1.77 Å), gave the lowest energy. However, Re_A is found to be favored of only 0.1 kcal/mol lower in energy than the transition state Si_E, which was *si*-face attack via the equatorial coordination model to give the minor enantiomer. The energy difference between Re_A and Si_E is not in good agreement with the enantioselectivity observed experimentally (95% ee, theoretically ca. 2.2 kcal/mol). Interestingly, in the case of the transition state Re_E, unlike the Houk's results using benzaldehyde as a substrate, the hydrogen bonding between the hydrogen atom of the olefin in allylboronic reagent and the phosphoryl oxygen of the catalyst was observed. Moreover, DFT calculation showed that hydrogen bonding between the methylene hydrogen atom of the allylboronic reagent and the phosphoryl oxygen is formed (2.46 Å) in the transition state Si_E. As shown above, several hydrogen bonds were observed in our system that were not found in the benzaldehyde system reported by Goodman and Houk. As opposed to chiral phosphoric acid catalysts, chiral phosphoramide catalyst (*R*)-**3e** possesses a sulfonic moiety and a CF_3 group that can interact with pivalaldehyde and pinacol boronic acid ester through weak hydrogen bonding. Furthermore, pivalaldehyde does not have an acidic sp^2 hydrogen atom like phenyl group, which plays an important role for stabilization of the equatorial transition state in Houk model. We thought that weak interactions such as C-F···H interaction between phosphoramide catalyst (*R*)-**3e** and allyboronic agent **2** would be important in the calculations because our allylation reaction was found to be different to well-studied allylation reactions with benzaldehyde using chiral phosphoric acid in the preliminary DFT calculation. Thus, we performed optimization of geometries again by M06-2X/6-31G(d) level of theory (See the main text).

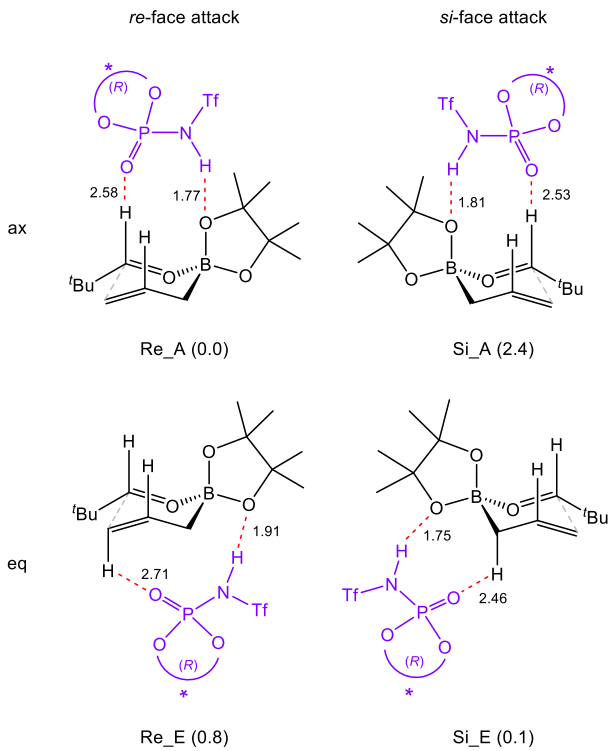


Figure S1. Schematic optimized transition state models of different mechanisms (Goodman and Houk model) at the B3LYP/6-31G(d) level of theory. Bond lengths are given in Å. Relative energies (kcal/mol) are shown in parentheses.

9-3. Potential energy surface of the allylboration

We prepared an energy diagram for comparison of B3LYP vs. M06-2X with 6-31G(d) basis set to understand the effect of weak interactions for calculation results in detail (Figure 4). When B3LYP was used, the transition structure Re_A are found to be high in free energy exhibiting barrier of 32.9 kcal/mol. This energy barrier is too high for such a fast reaction at 25 °C (<0.1 h) in Table 1, entry 18. On the other hand, when M06-2X was used in the calculation, the relative energies of transition states Re_A and Si_E are considerably lower with barriers of 5.6 kcal/mol and 9.8 kcal/mol, respectively. These results are much more reasonable for the present phosphoramide catalyzed reaction that proceeds within only 10 min at 25 °C. These results indicate that M06-2X is a much better function than B3LYP for finding transition states and comparing Gibbs free energies of the corresponding transitions states in the present enantioselective allylation reaction using the chiral phosphamide catalyst with several functional groups that can interact with pivalaldehyde (**1**) and allylboron reagent **2** in multiple manner.

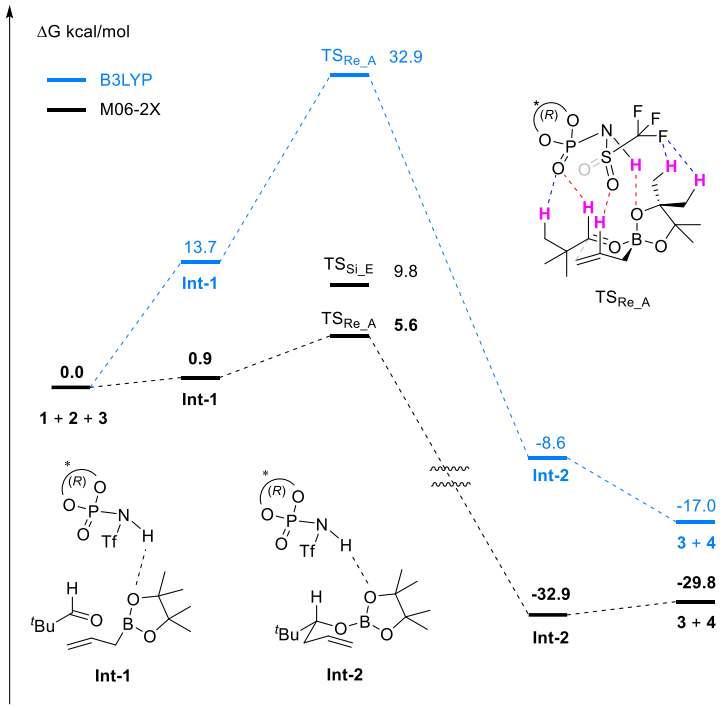


Figure S2. Potential energy surface displaying the free energies (ΔG) of the enantioselective allylation pathway with (black) and without dispersion (blue). Level of theory: M06-2X/6-31g(d) and B3LYP/6-31g(d). Energies are given in kcal/mol.

9-4. Summary of other calculation methods

M06-2X/6-31G(d)	Re_A	Si_A	Re_E	Si_E
ΔΔG (kcal/mol)	0.0	4.8	14.2	4.2

MN15-2X/6-31G(d)+SMD (toluene)	Re_A	Si_A	Re_E	Si_E
ΔΔG (kcal/mol)	0.0	3.4	11.1	3.0

B3LYP-D3(BJ)/6-311G(d,p)	Re_A	Si_A	Re_E	Si_E
ΔΔG (kcal/mol)	0.0	5.9	17.1	5.4

ωB97XD/6-31G(d)	Re_A	Si_A	Re_E	Si_E
ΔΔG (kcal/mol)	0.0	5.2	14.1	4.7

Similar tendency of energy differences as with M06-2X or MN15 was observed by using B3LYP-D3(BJ)/6-311G(d,p) and ωB97XD/6-31G(d).

9-5. Fig 3. with schematic models

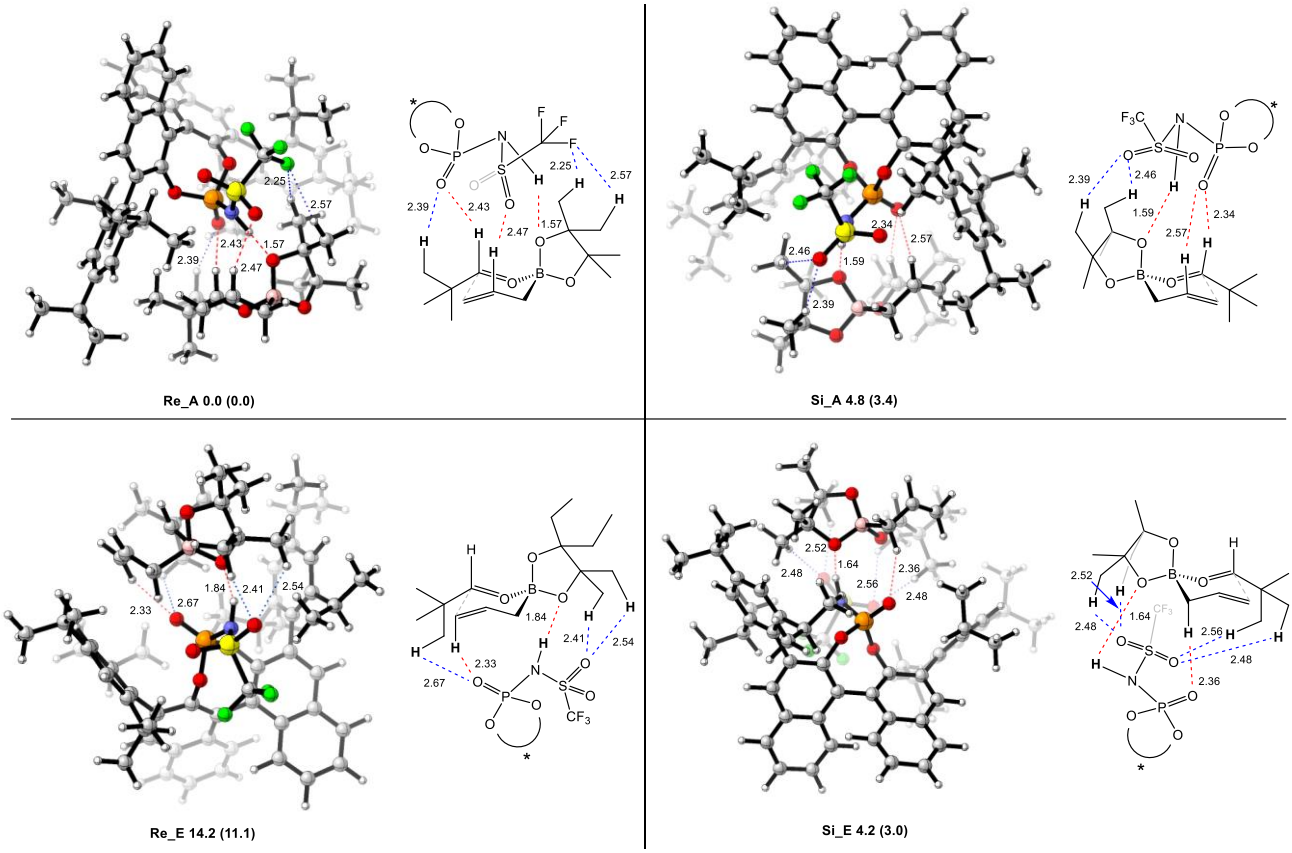
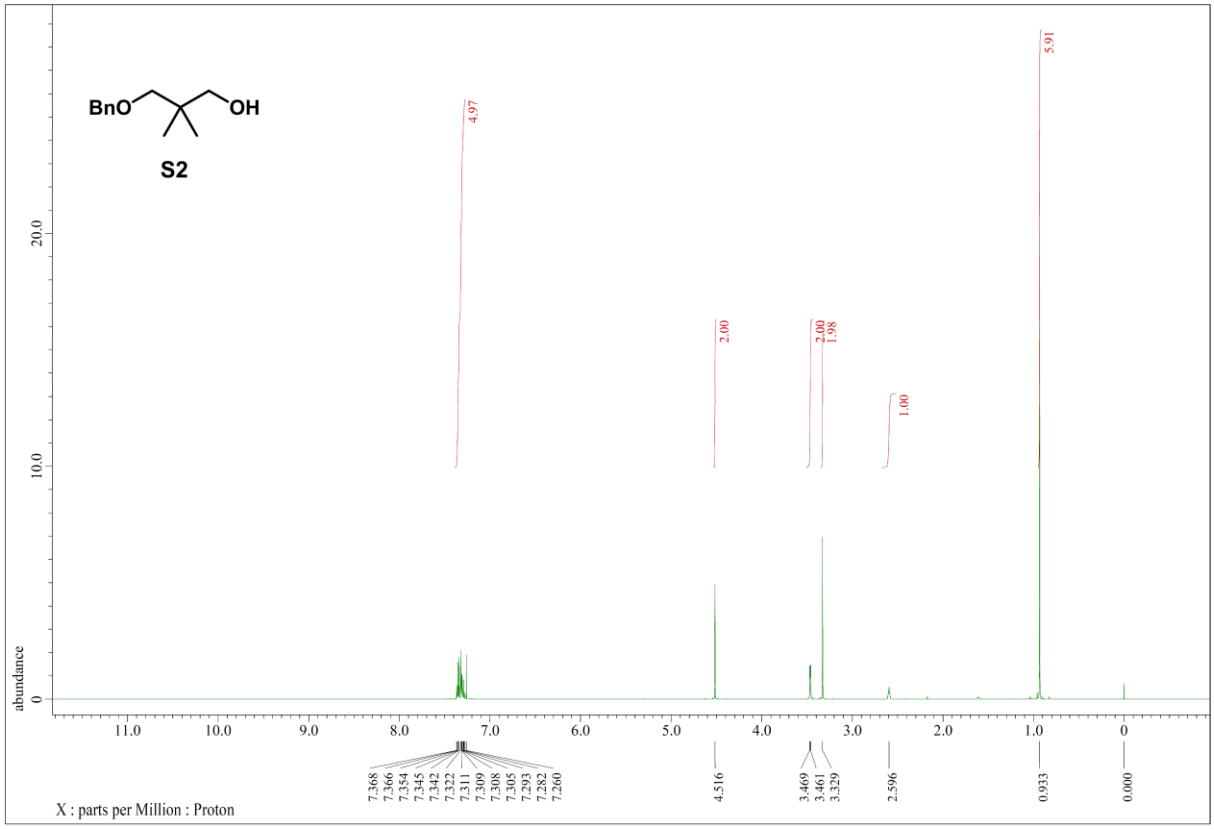
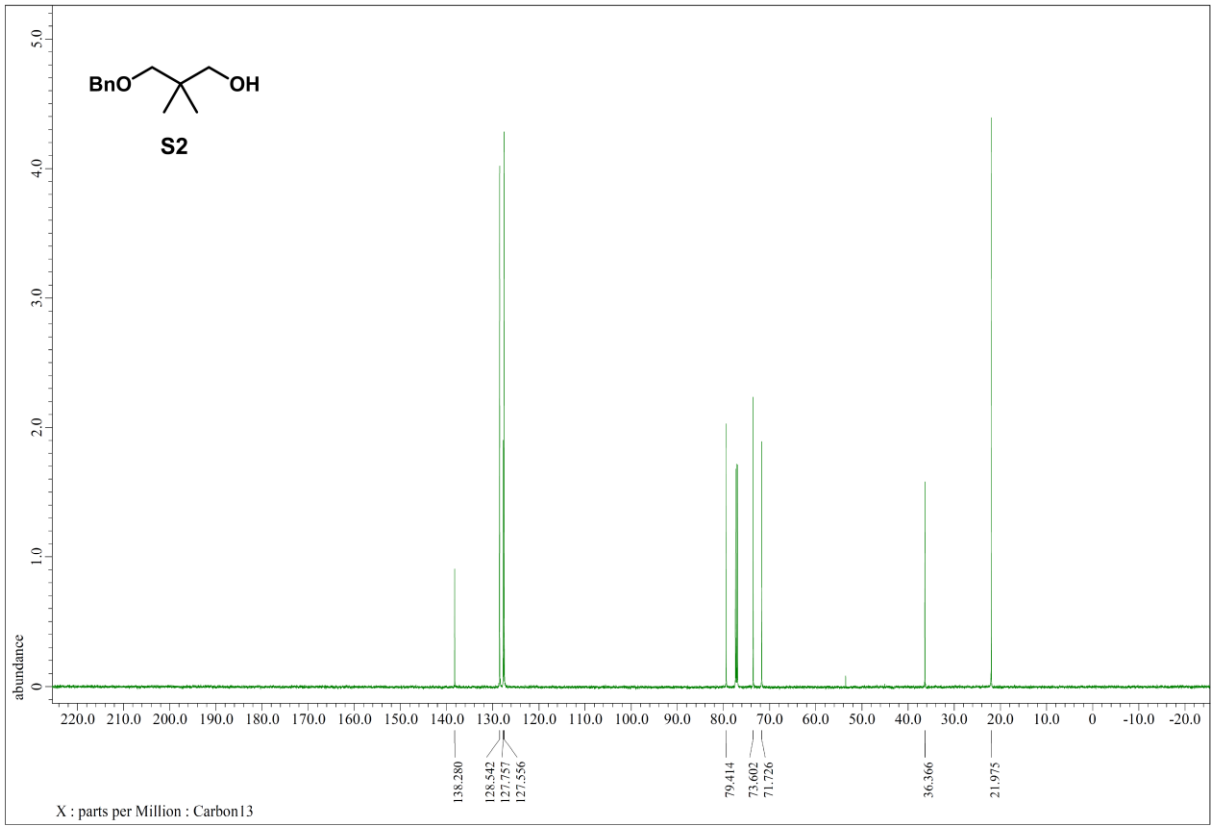


Fig. 3 Optimized transition states of Re_A, Re_E, Si_A, and Se_E at the M06-2X/6-31G(d) level of theory. Bond lengths are given in Å. Values enclosed in parentheses are energies relative to "Re_A" calculated by MN15/6-31g(d)+SDM (toluene). Energy differences are given in kcal/mol.

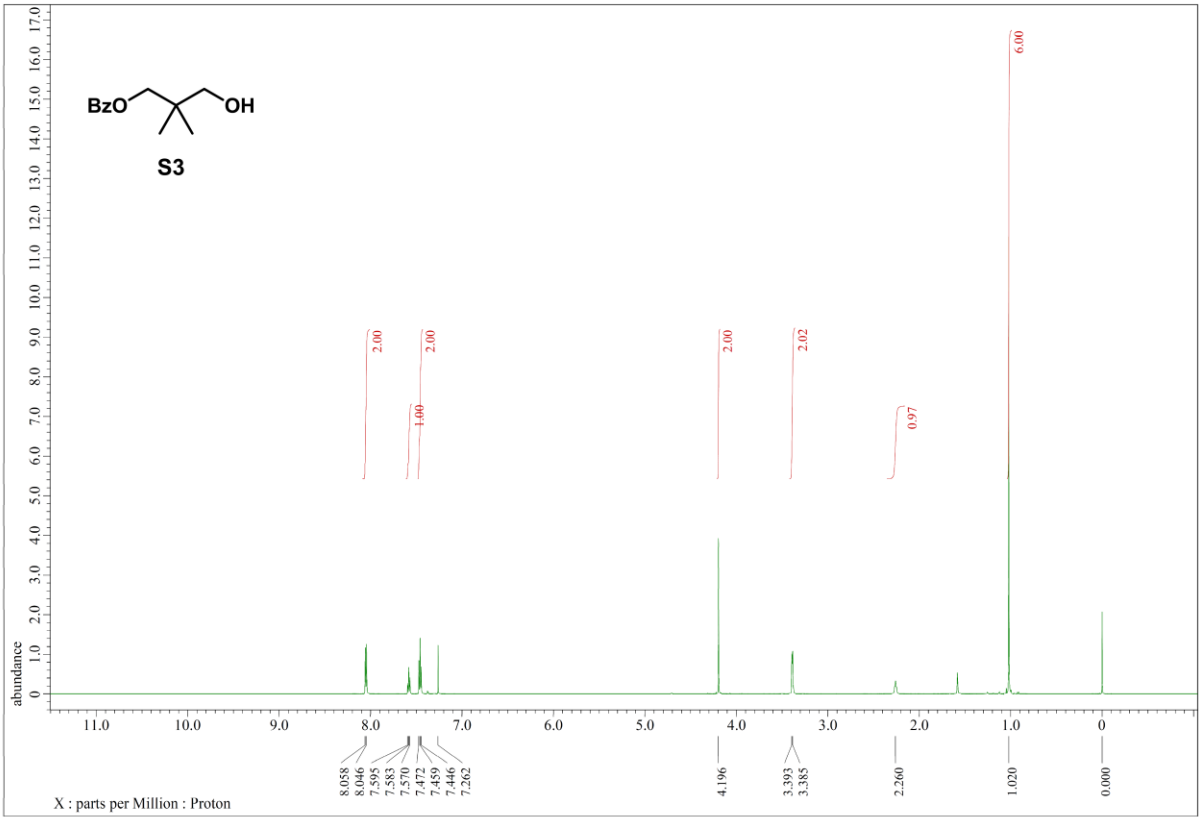
10. NMR Spectra

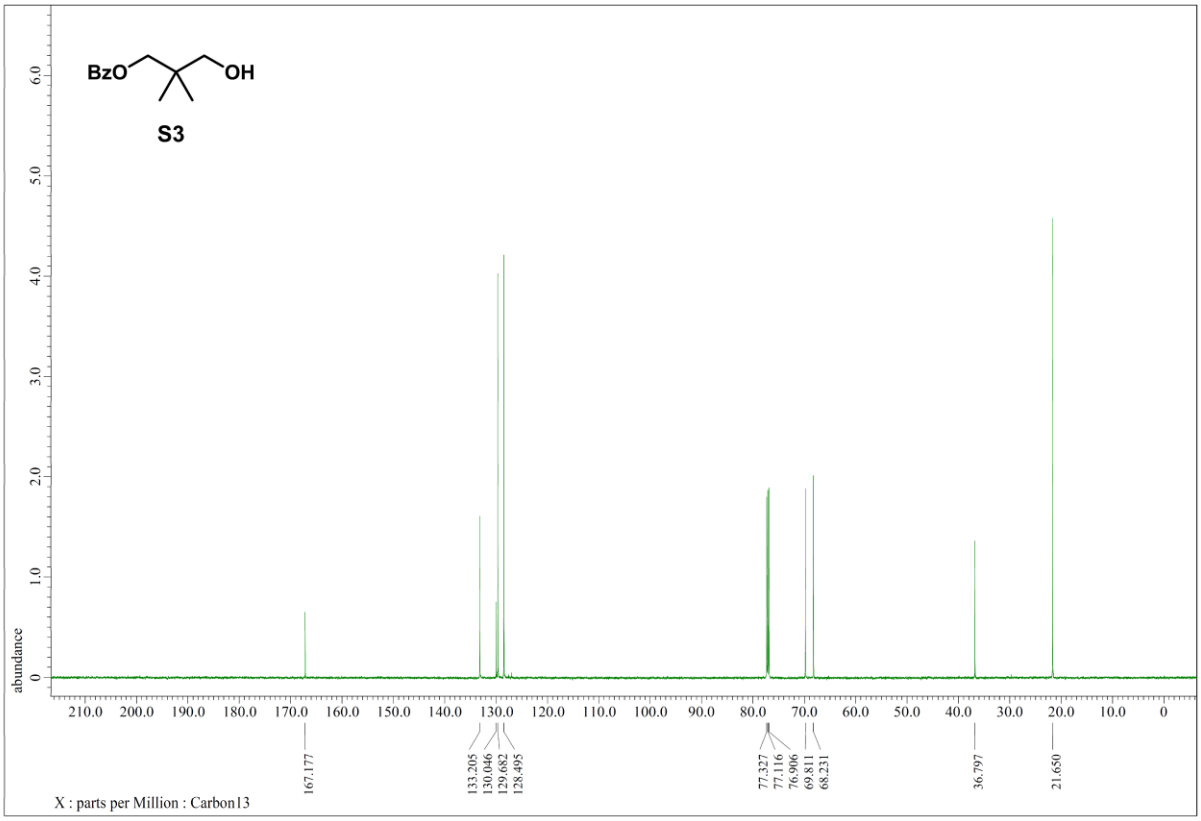
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **S2**



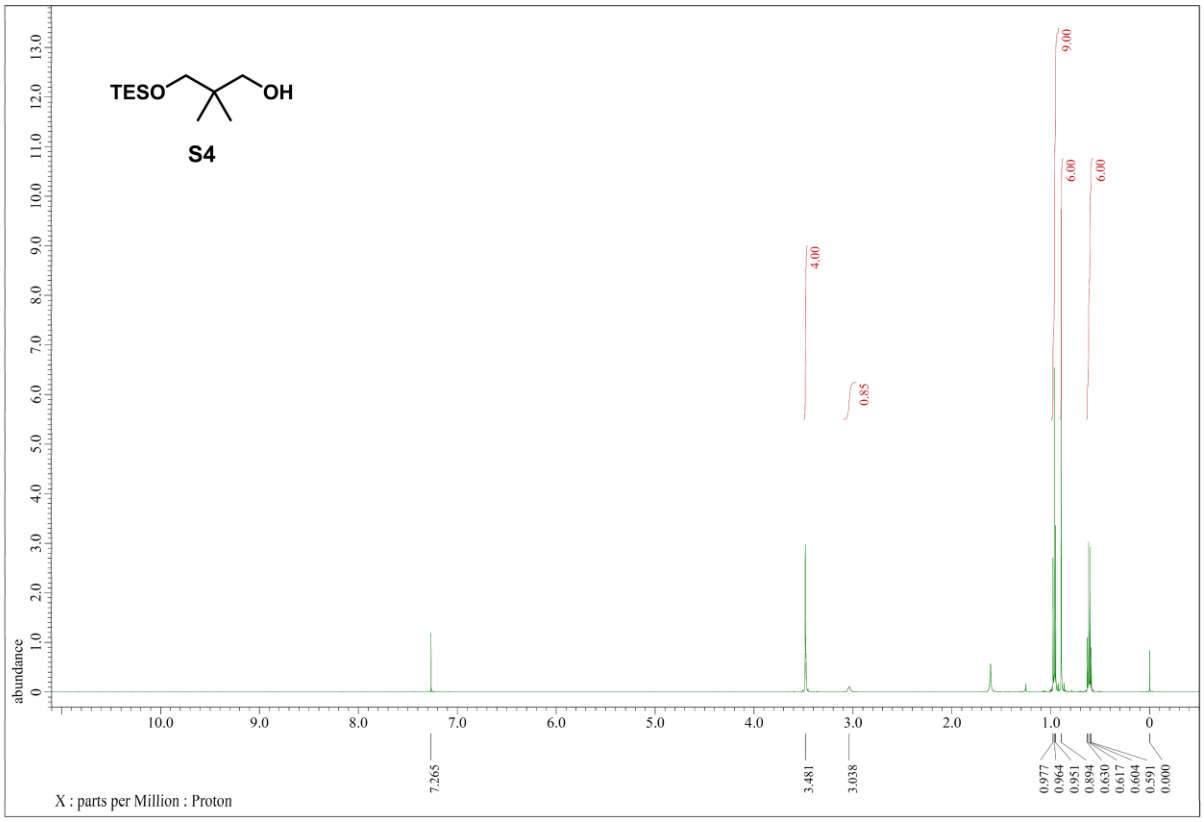


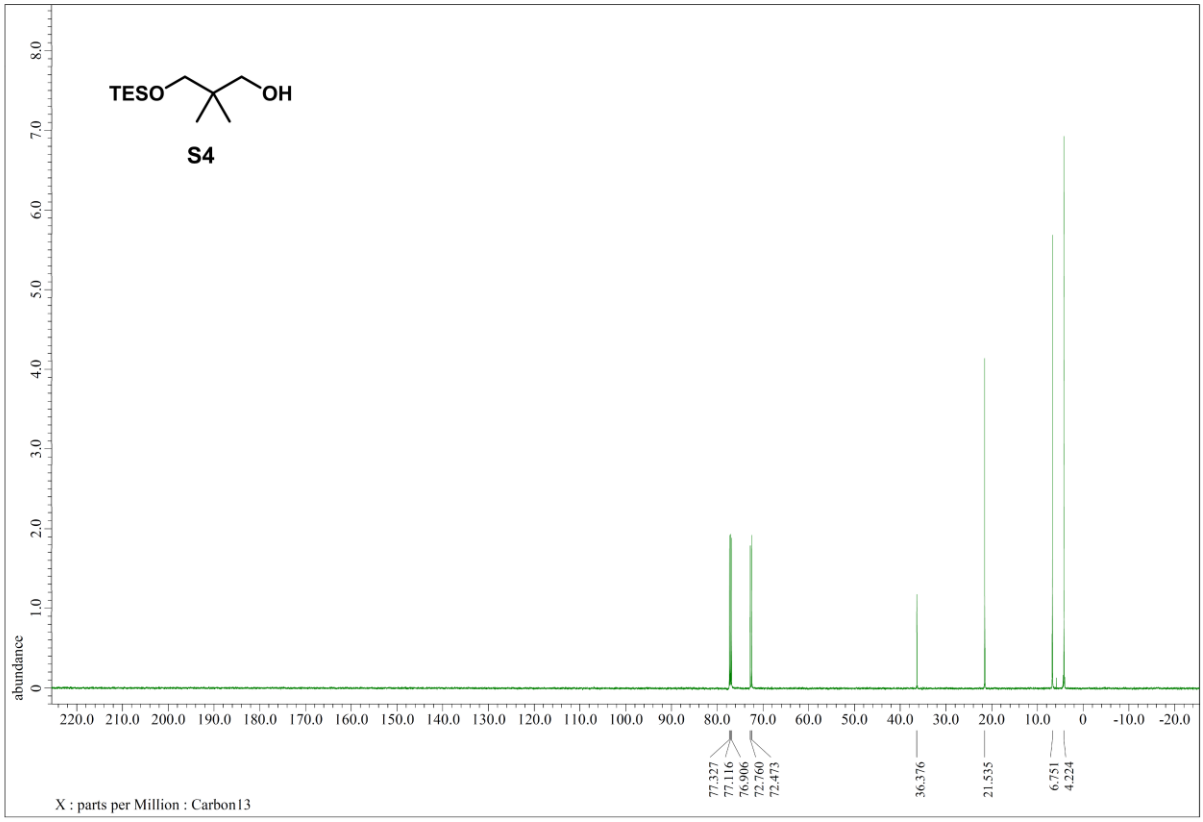
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **S3**



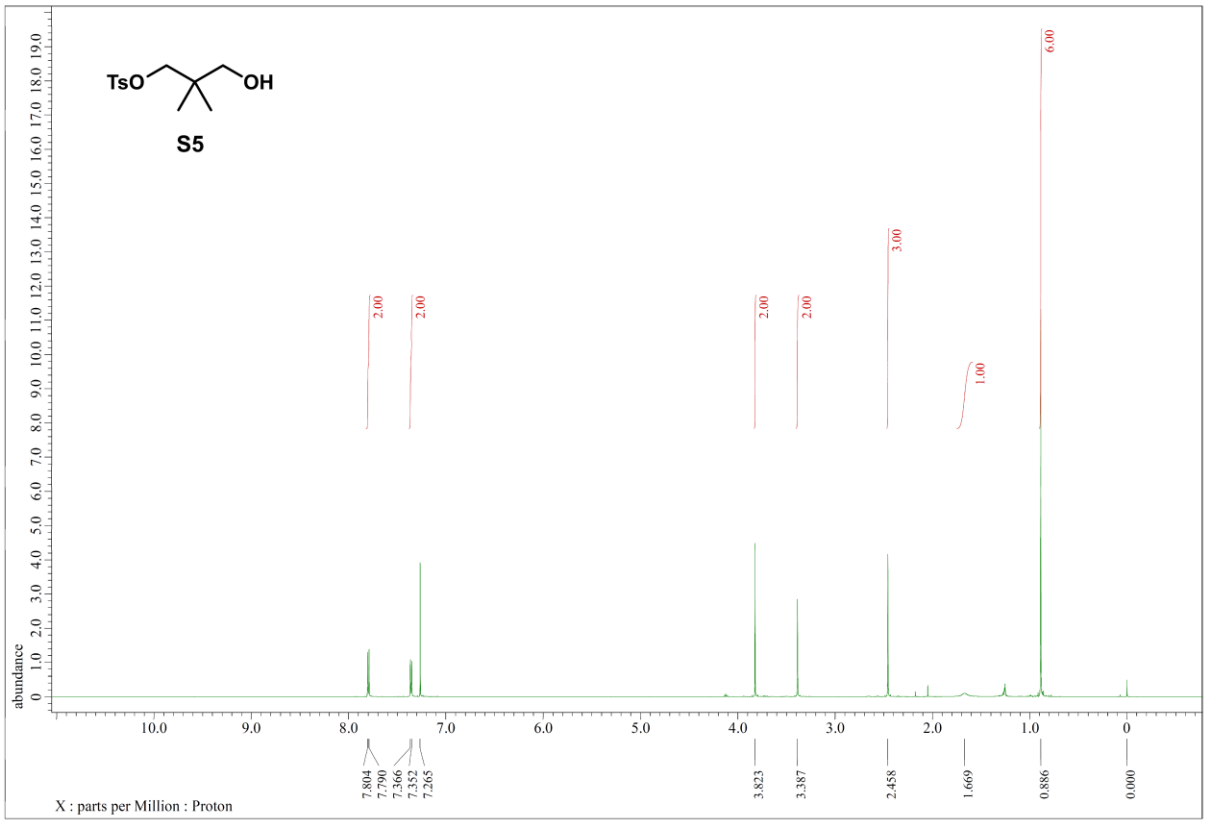


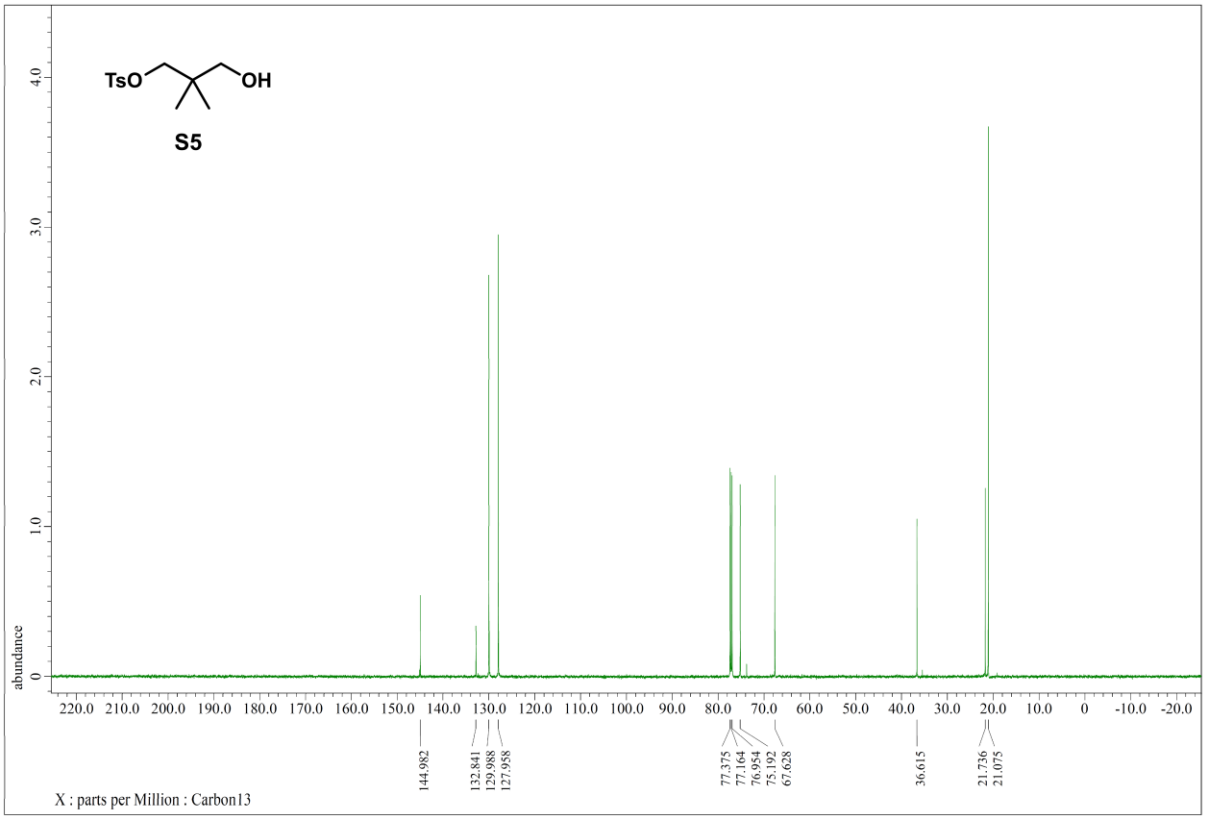
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **S4**



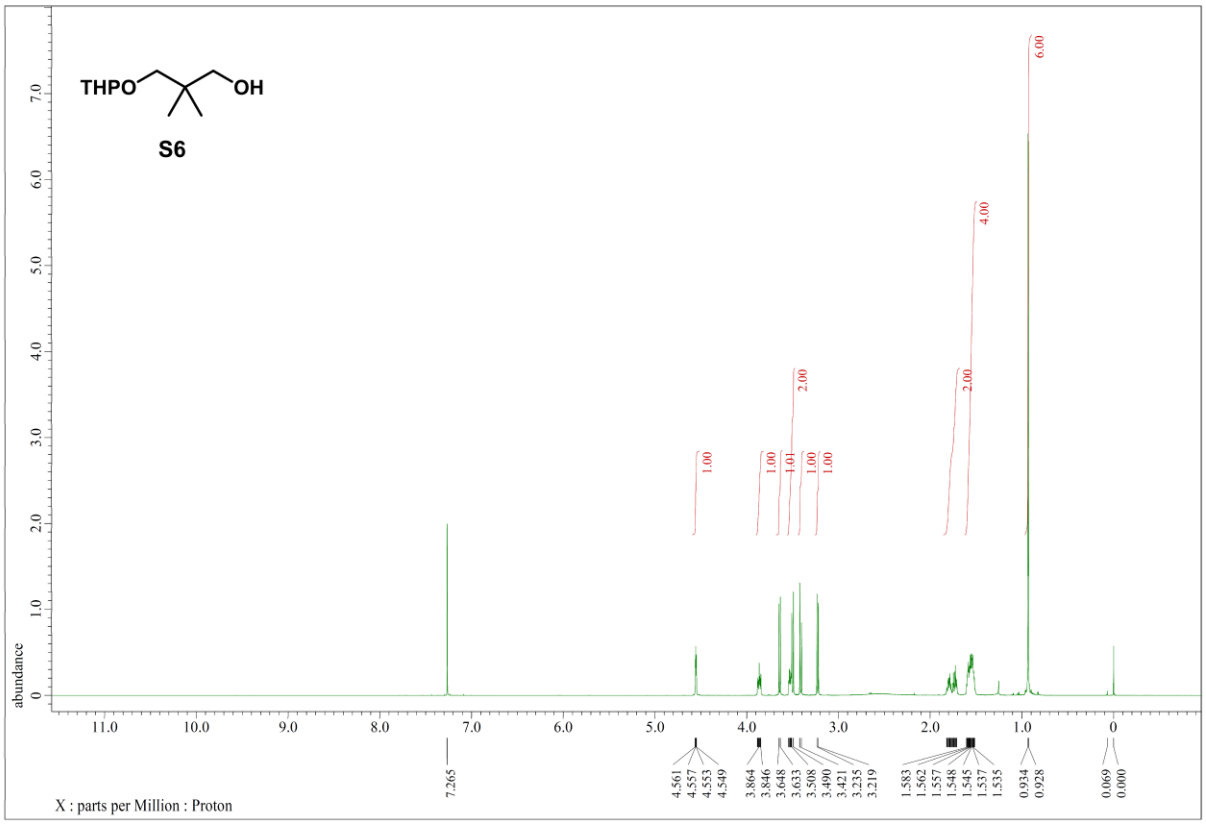


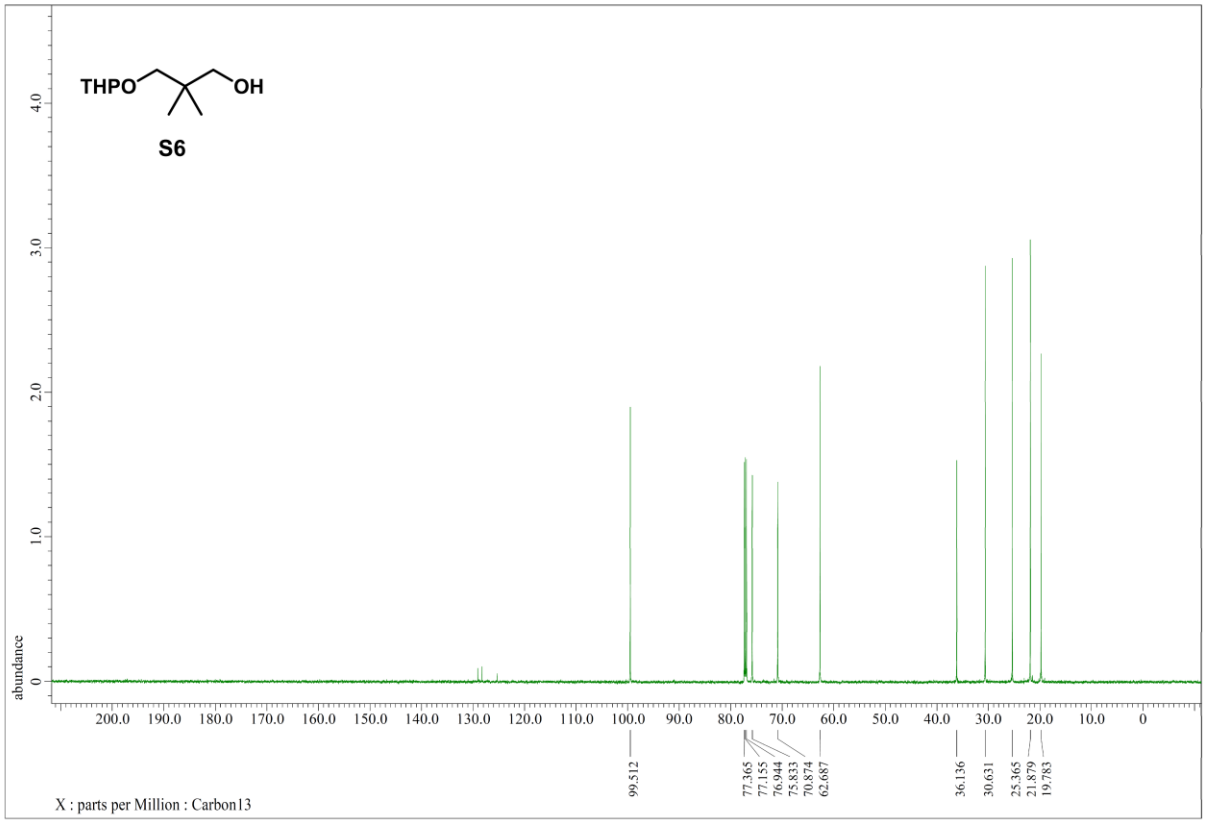
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **S5**



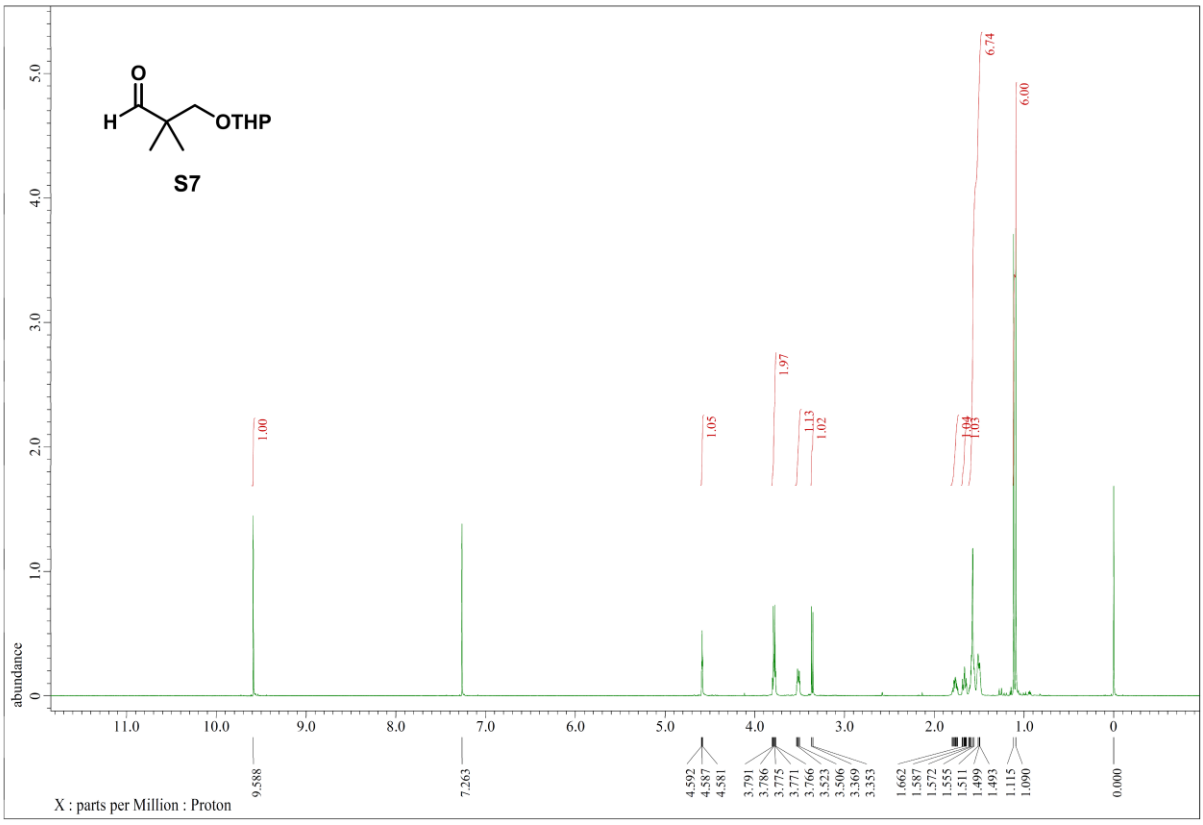


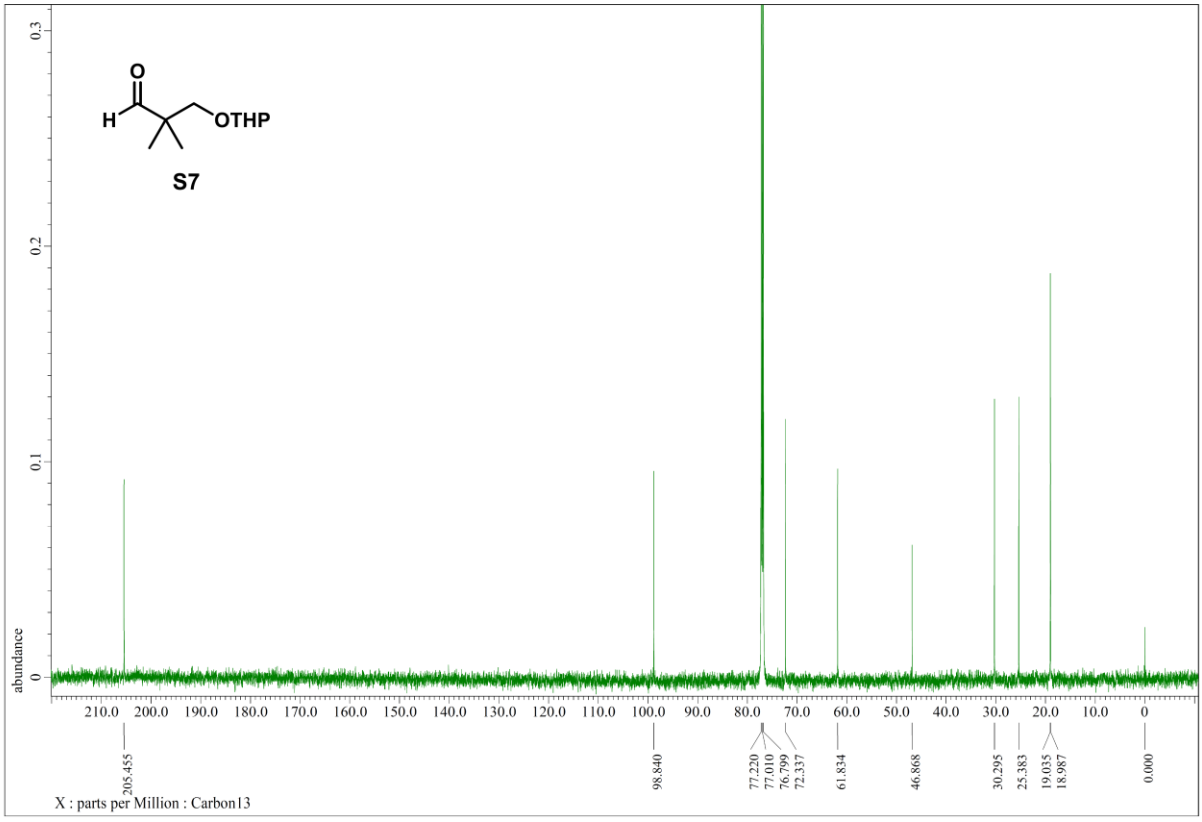
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **S6**



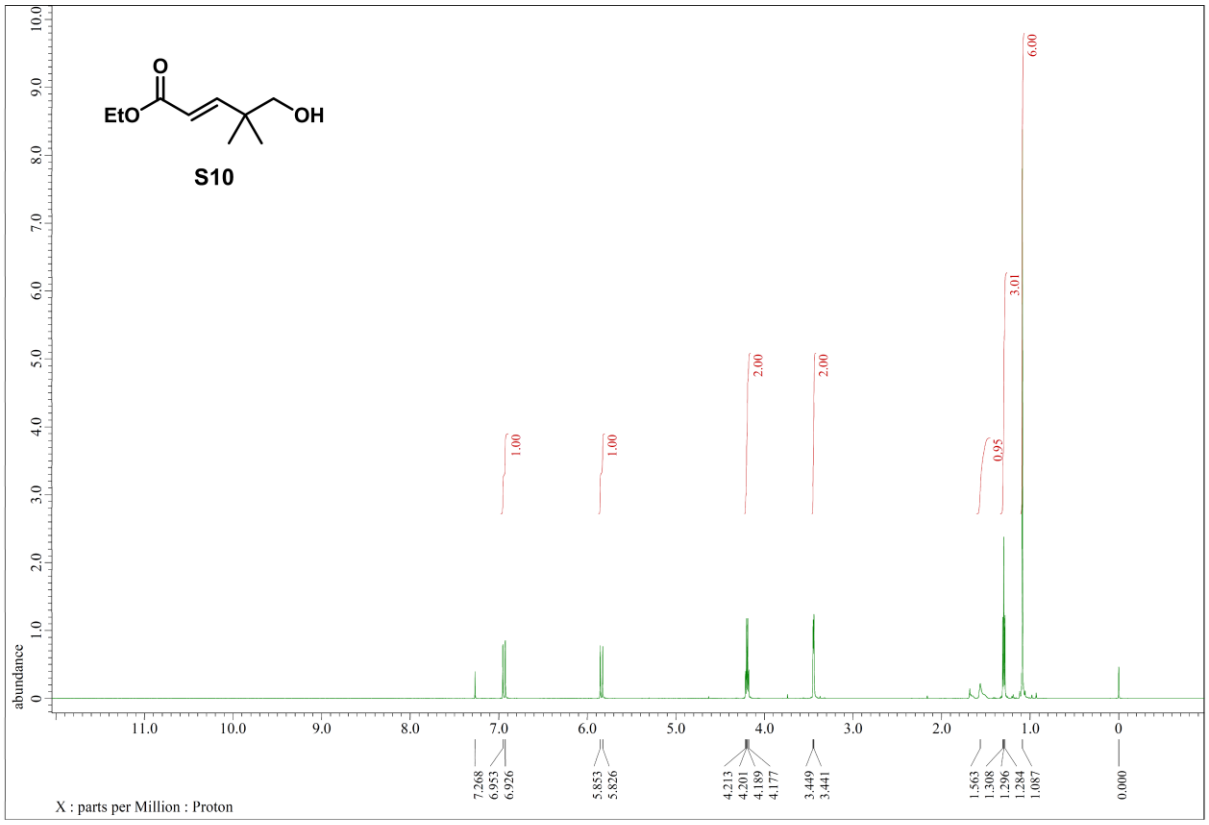


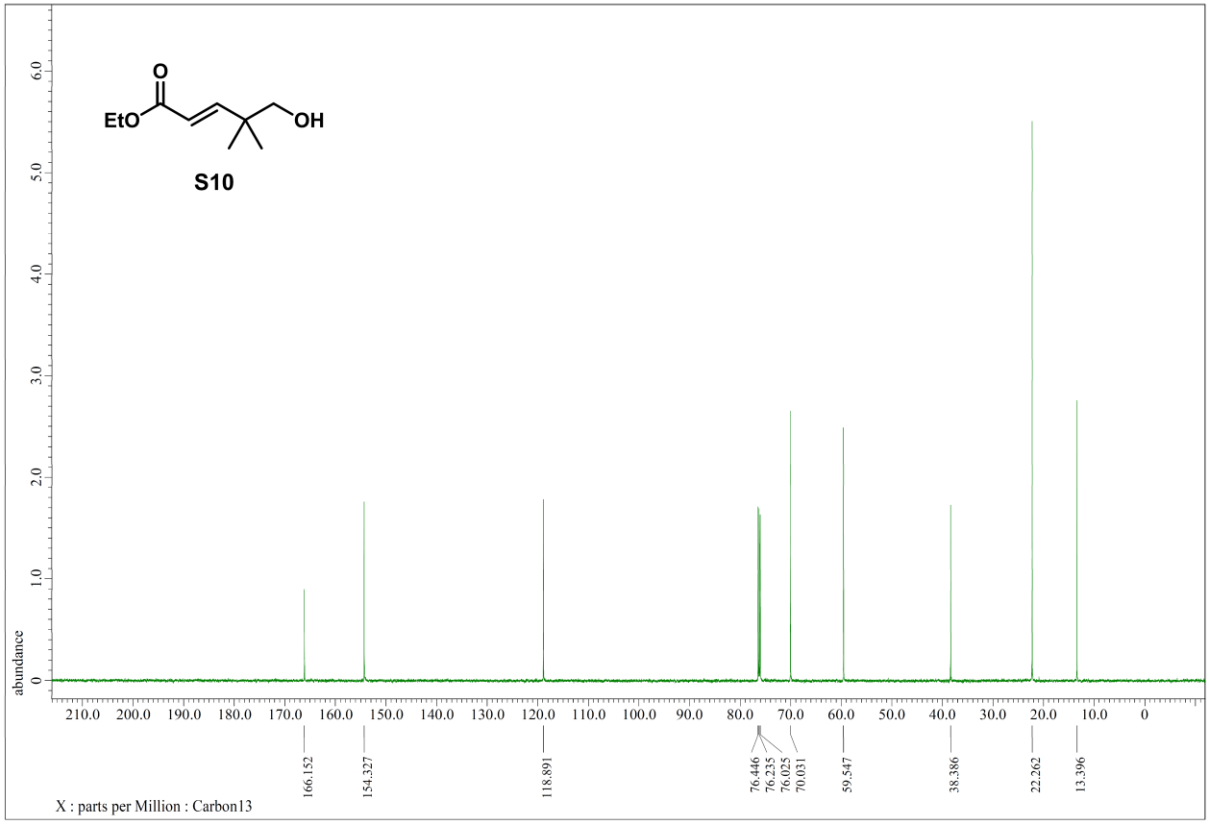
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **S7**



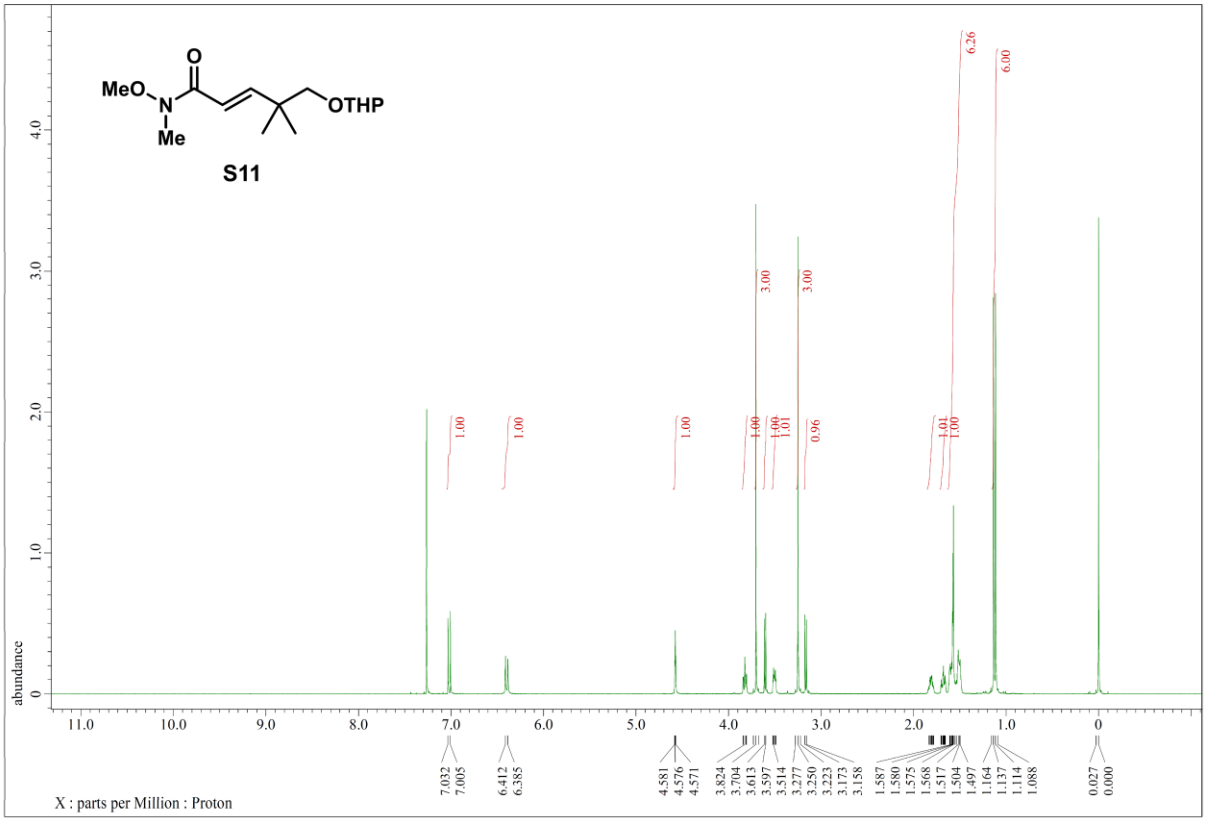


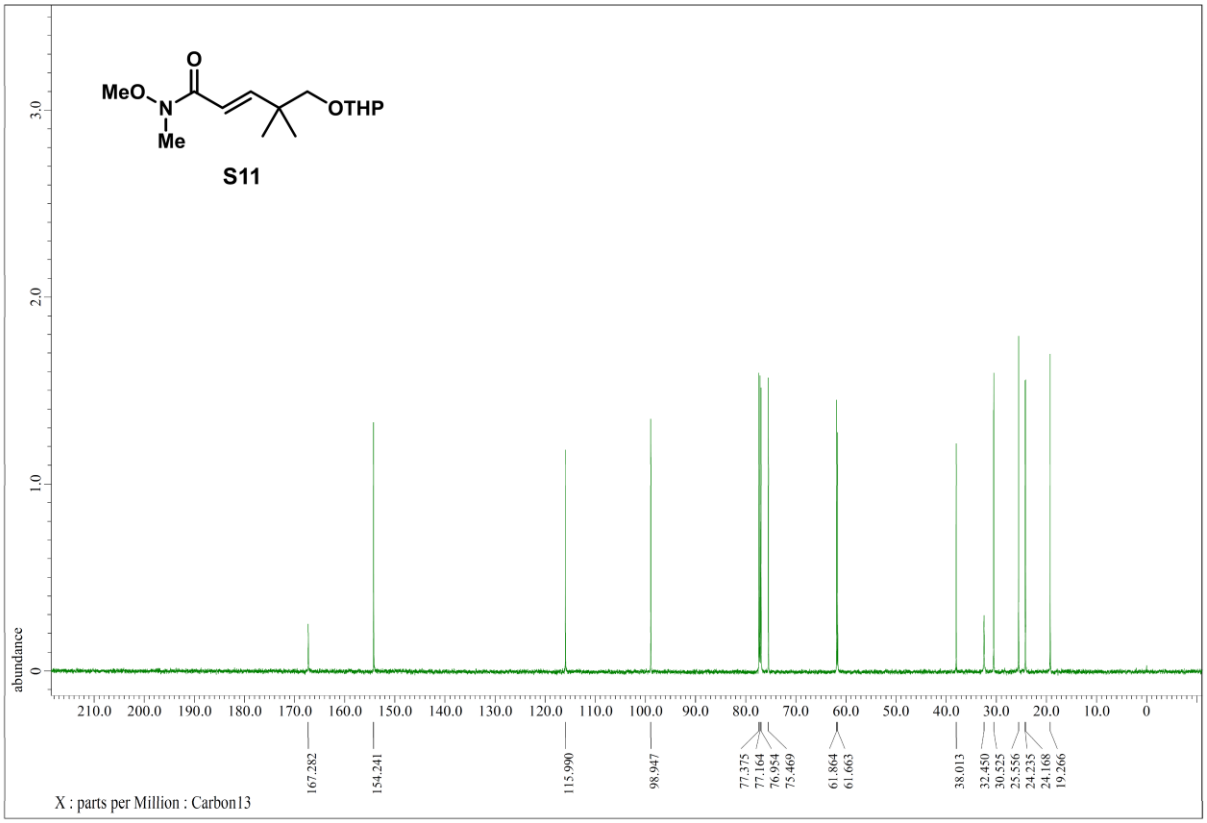
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **S10**



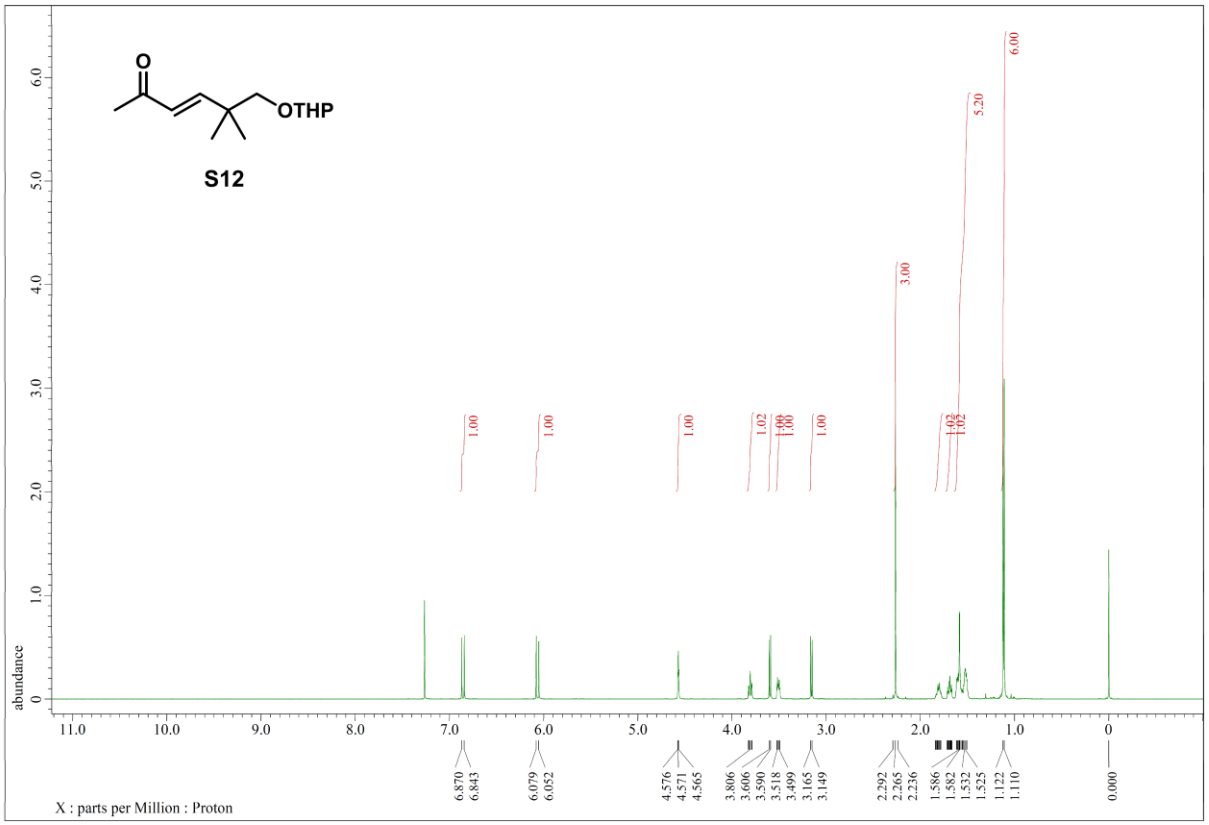


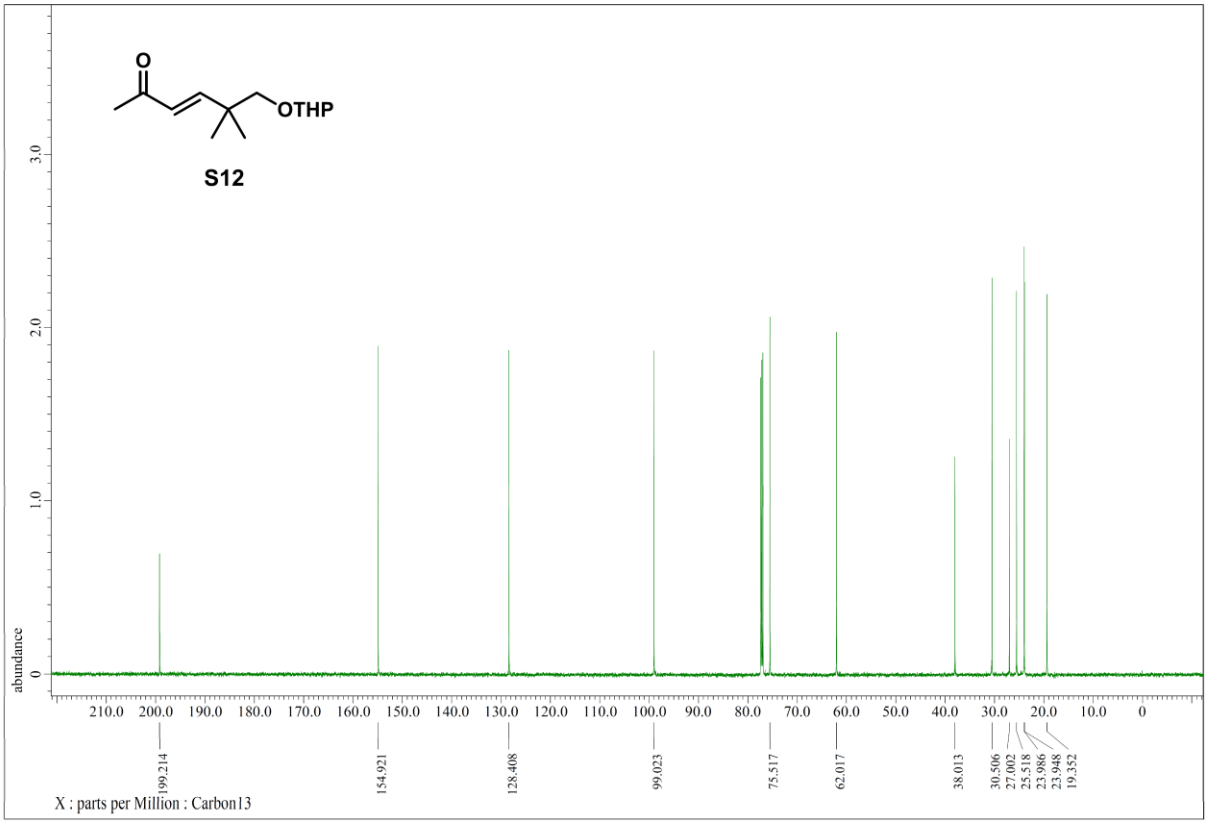
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **S11**



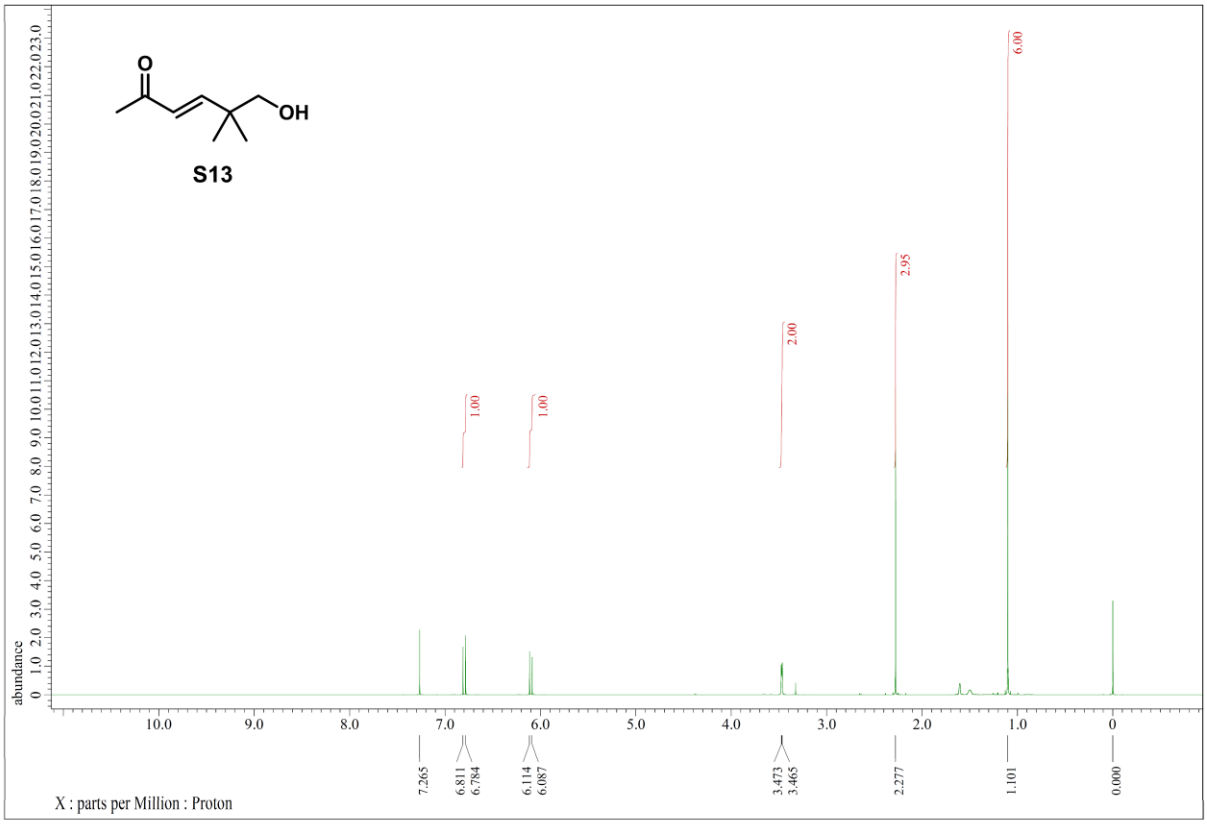


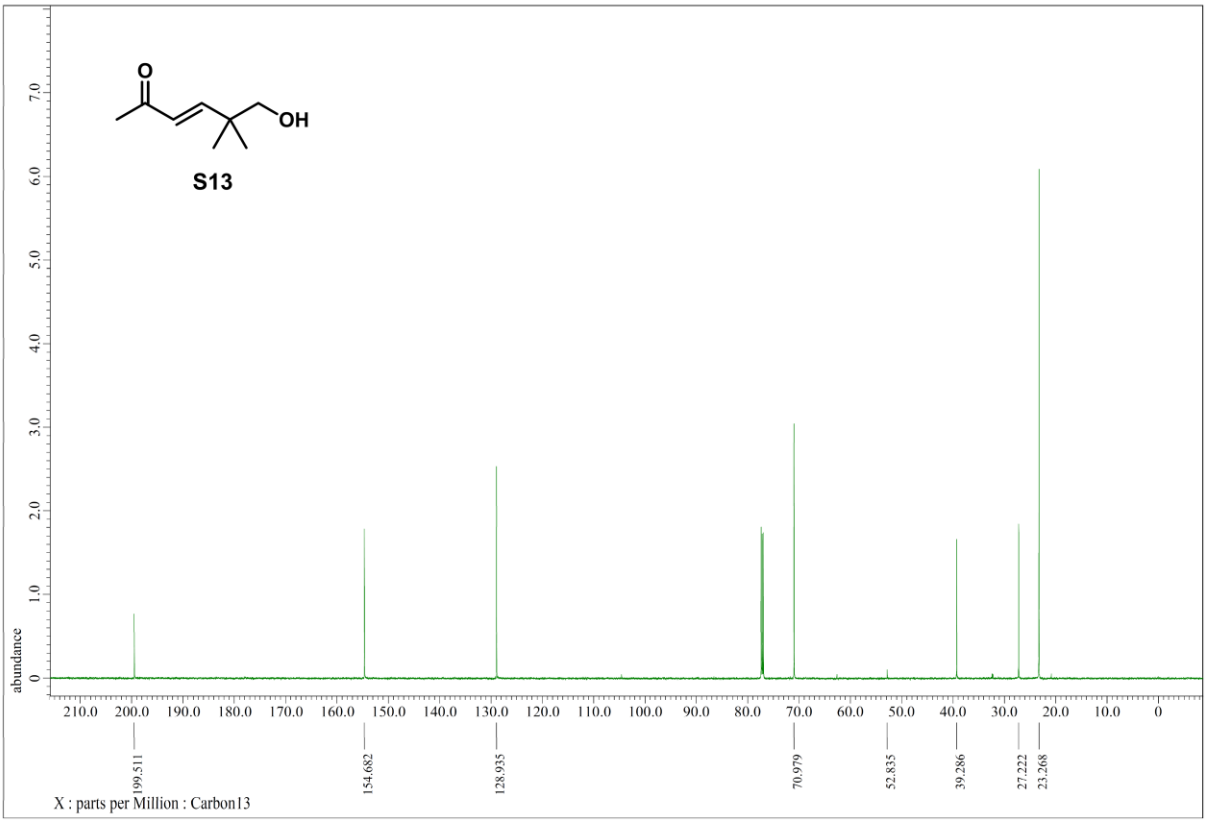
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **S12**



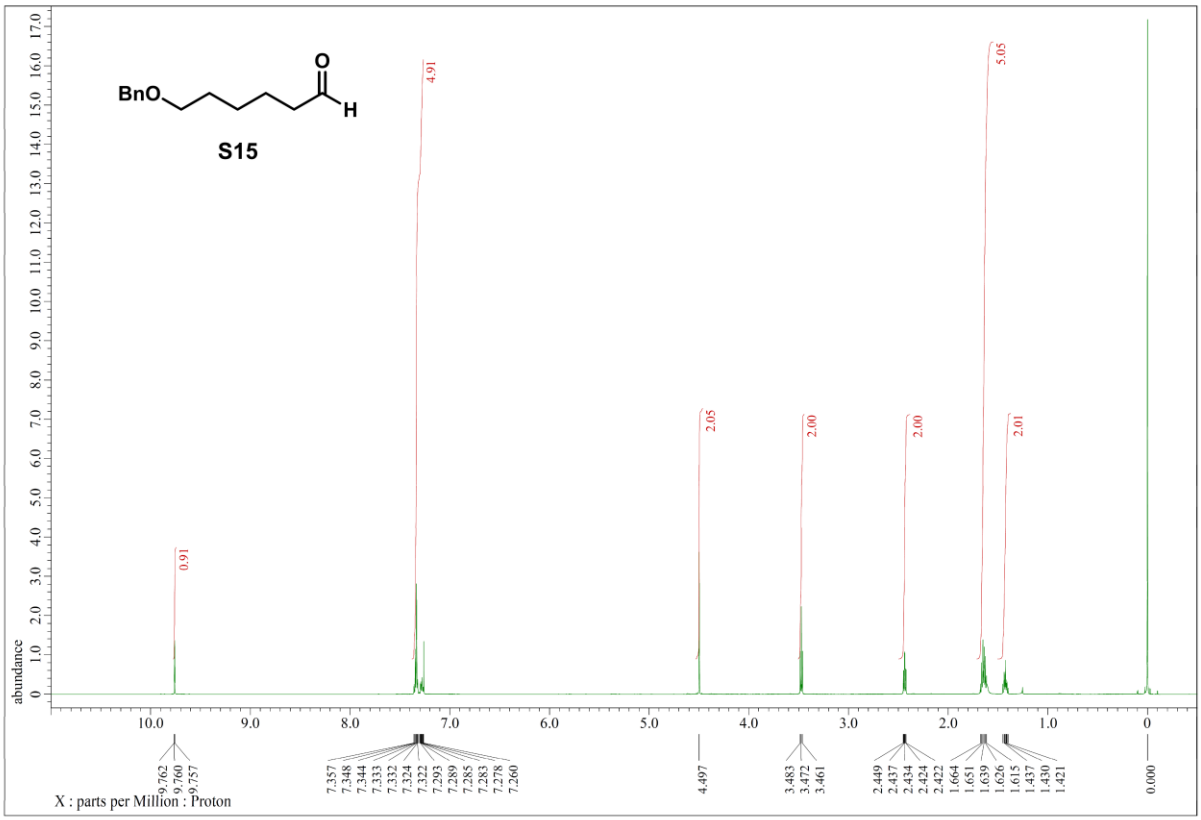


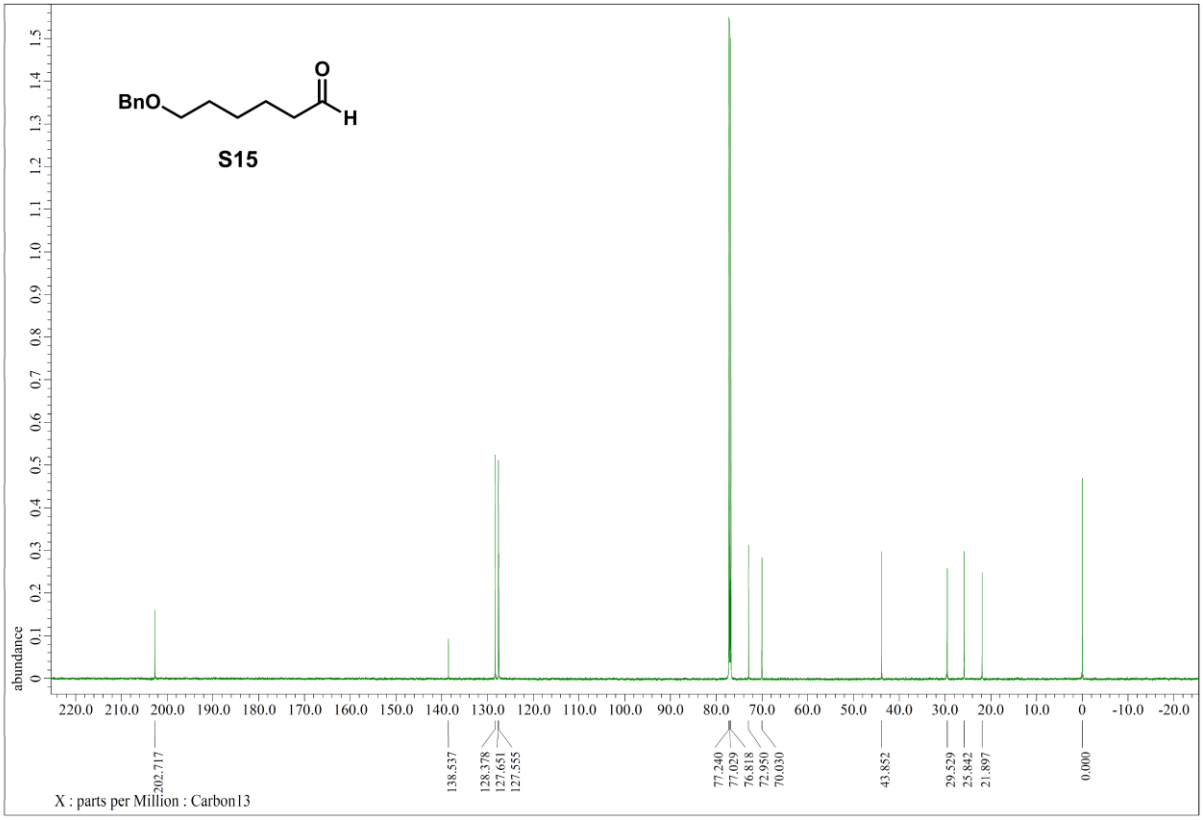
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **S13**



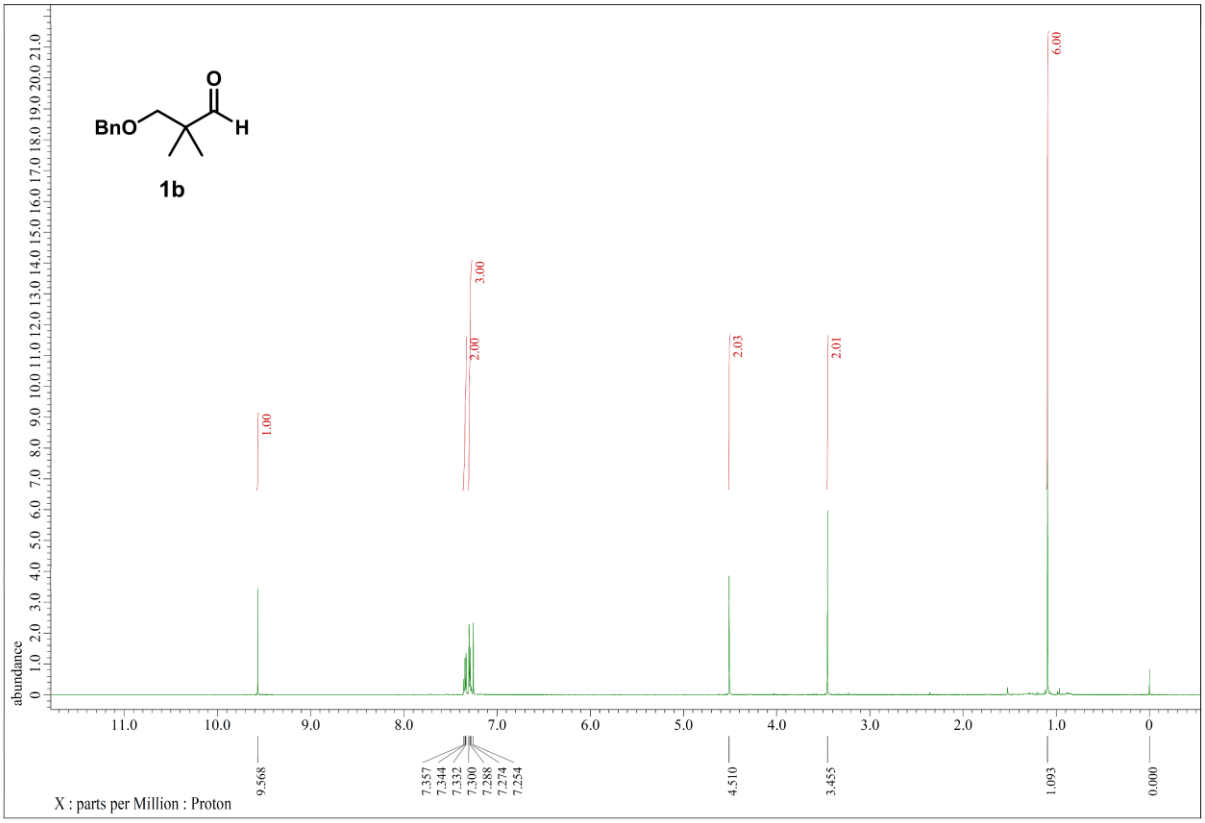


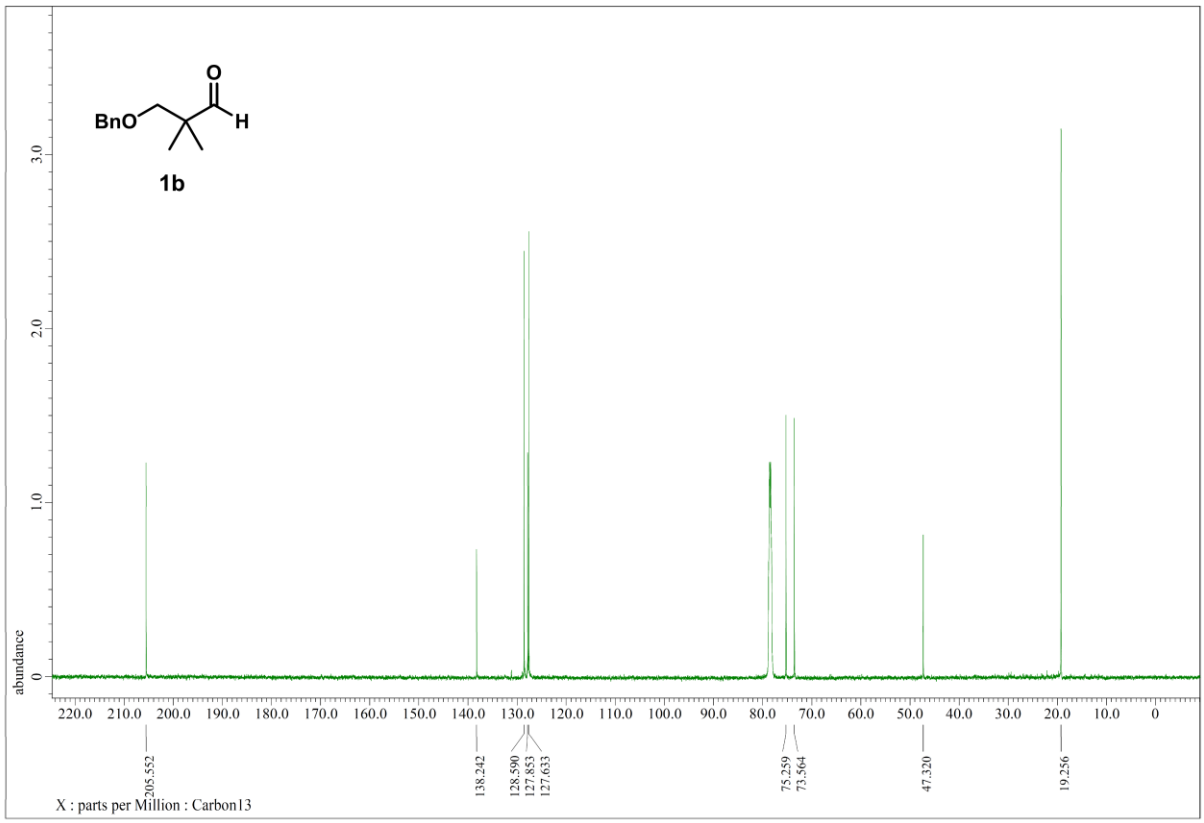
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **S15**



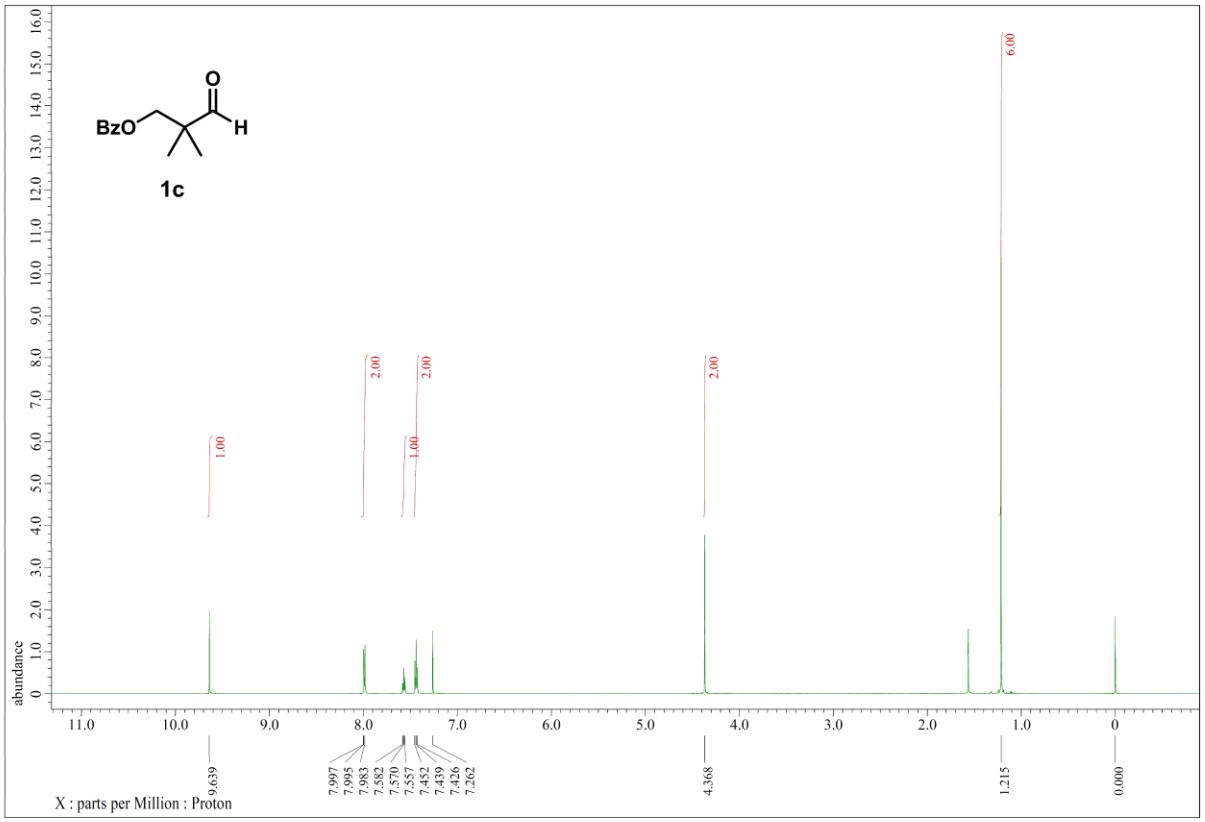


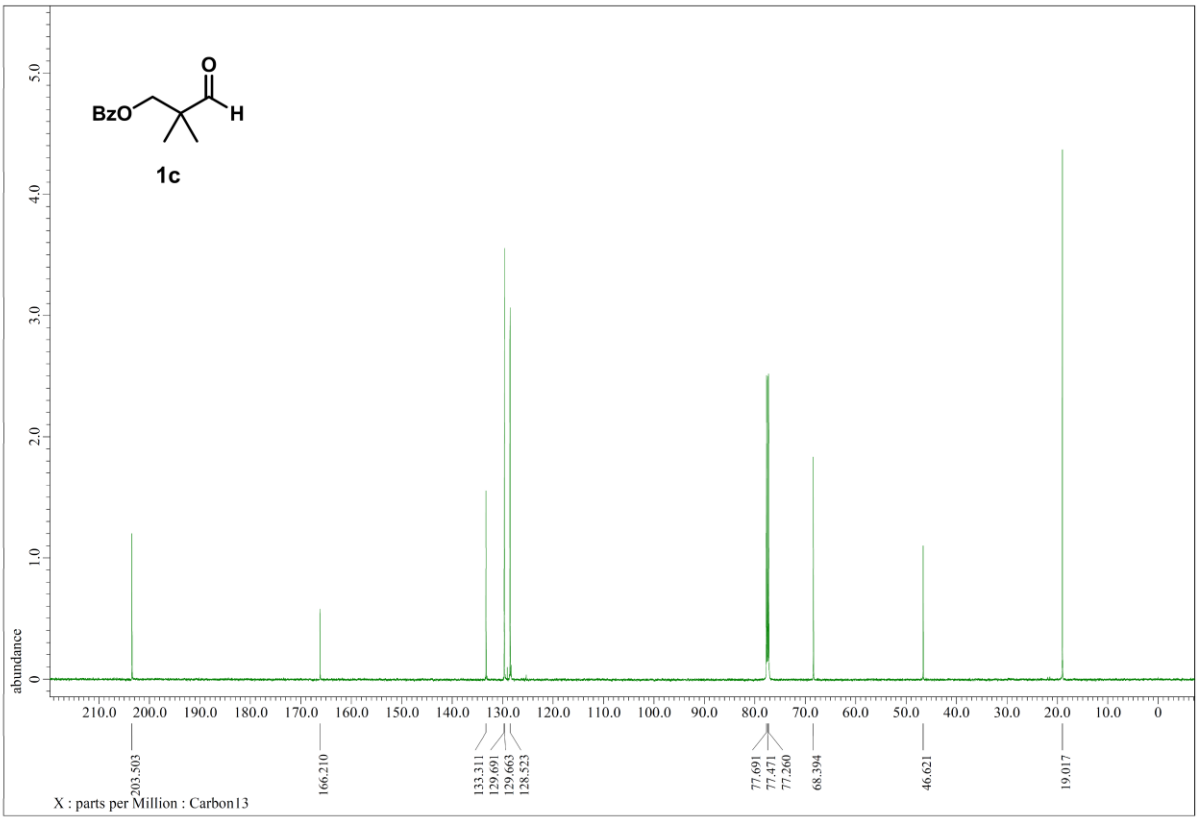
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **1b**



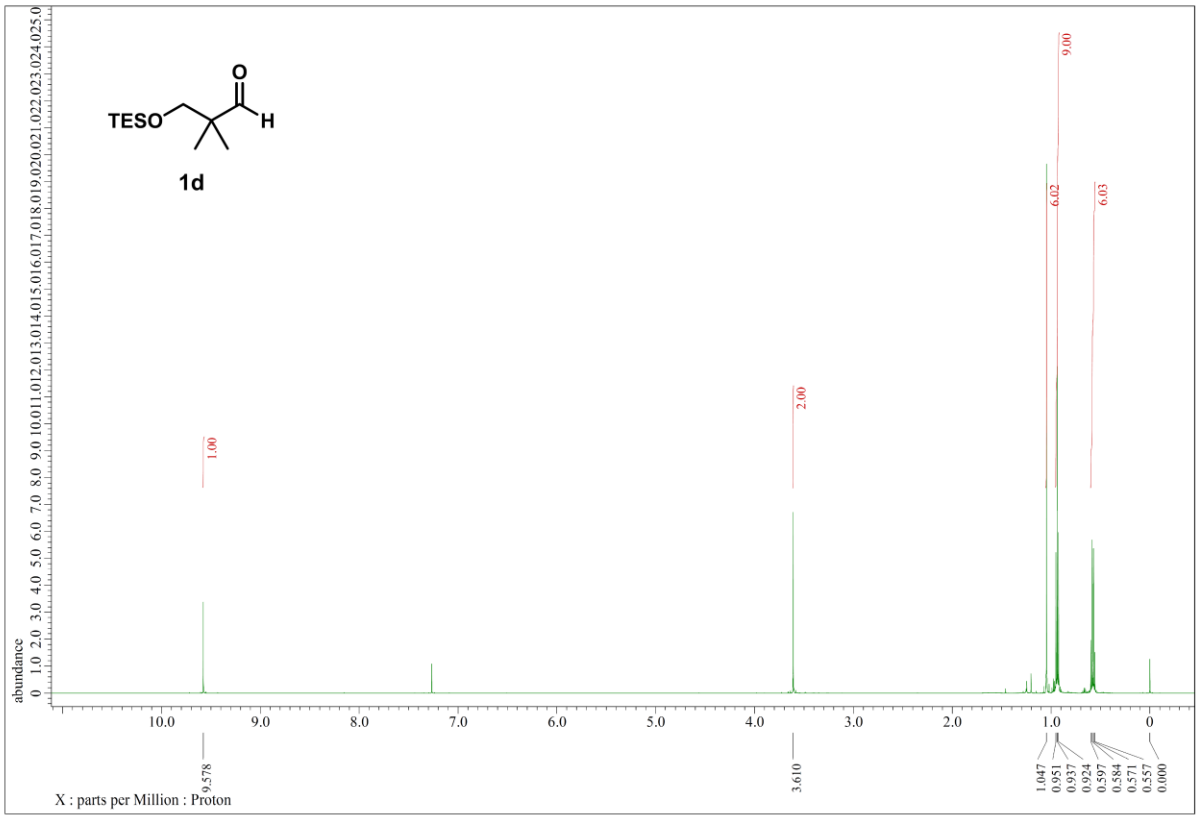


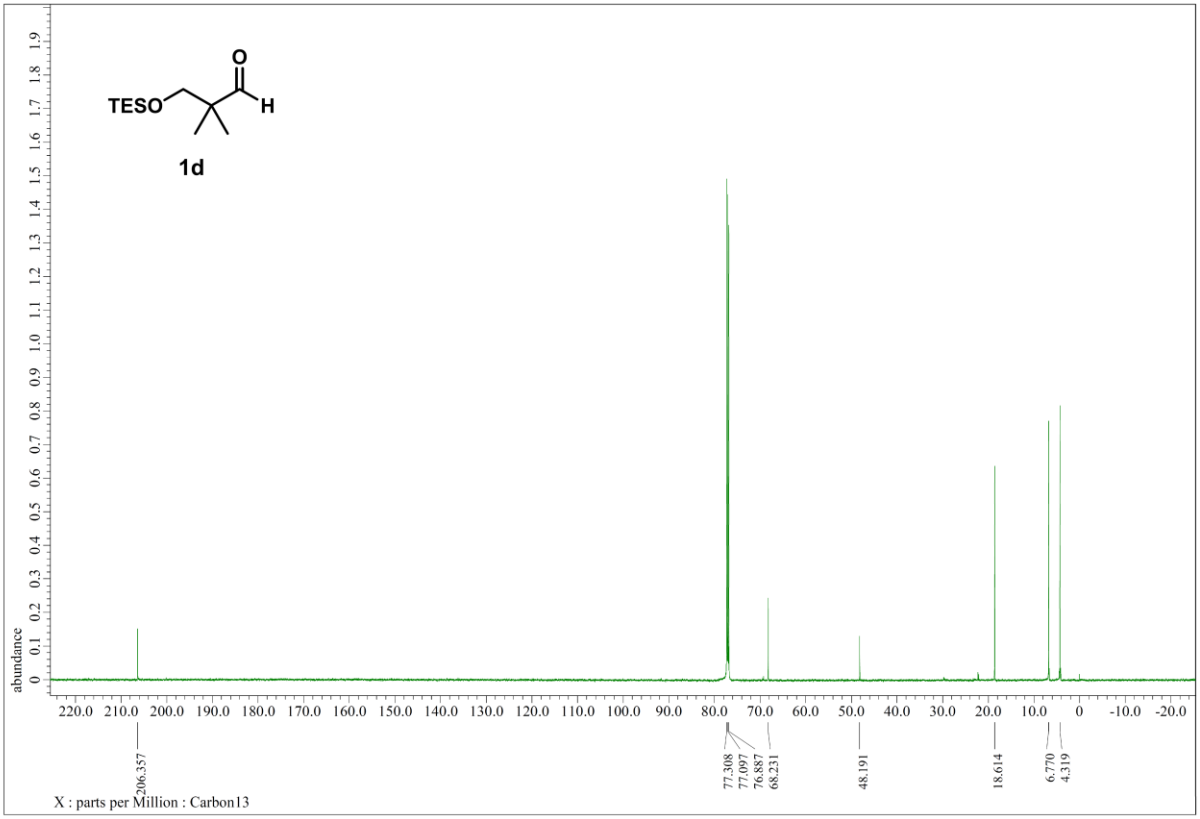
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **1c**



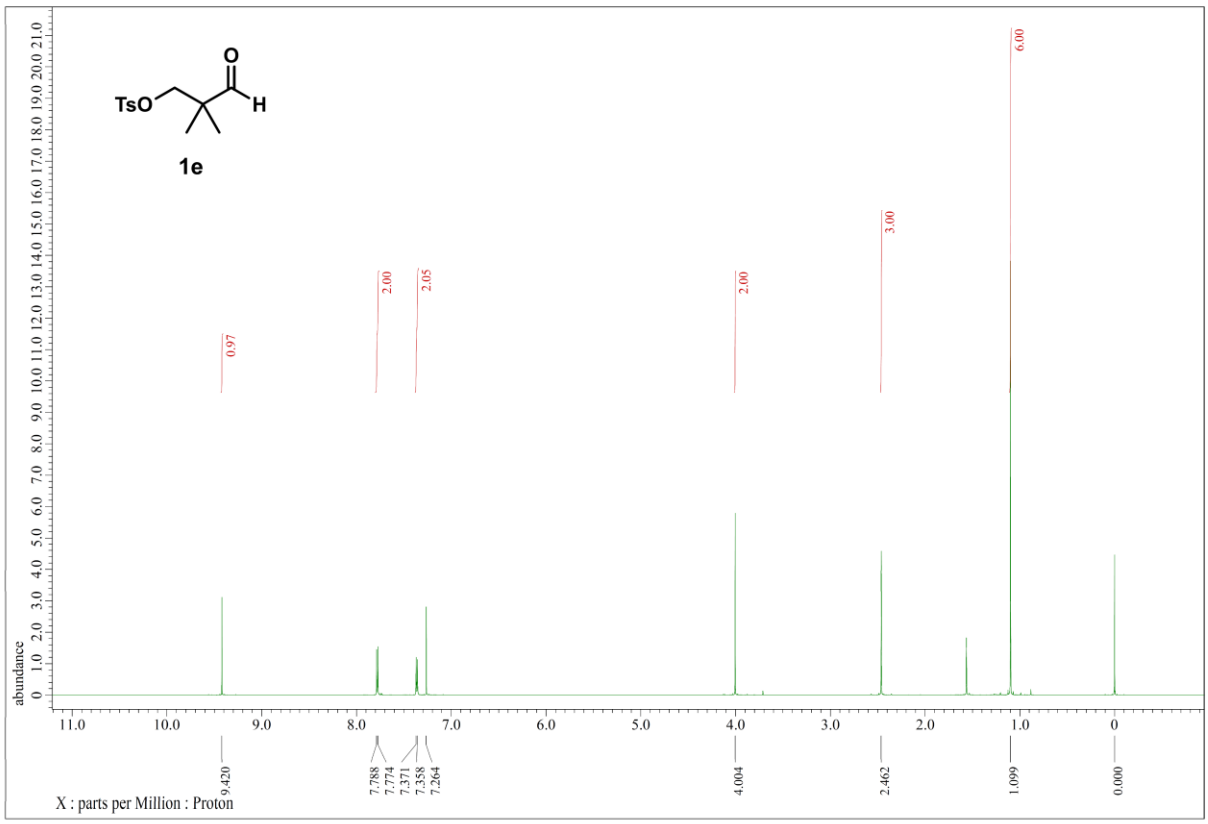


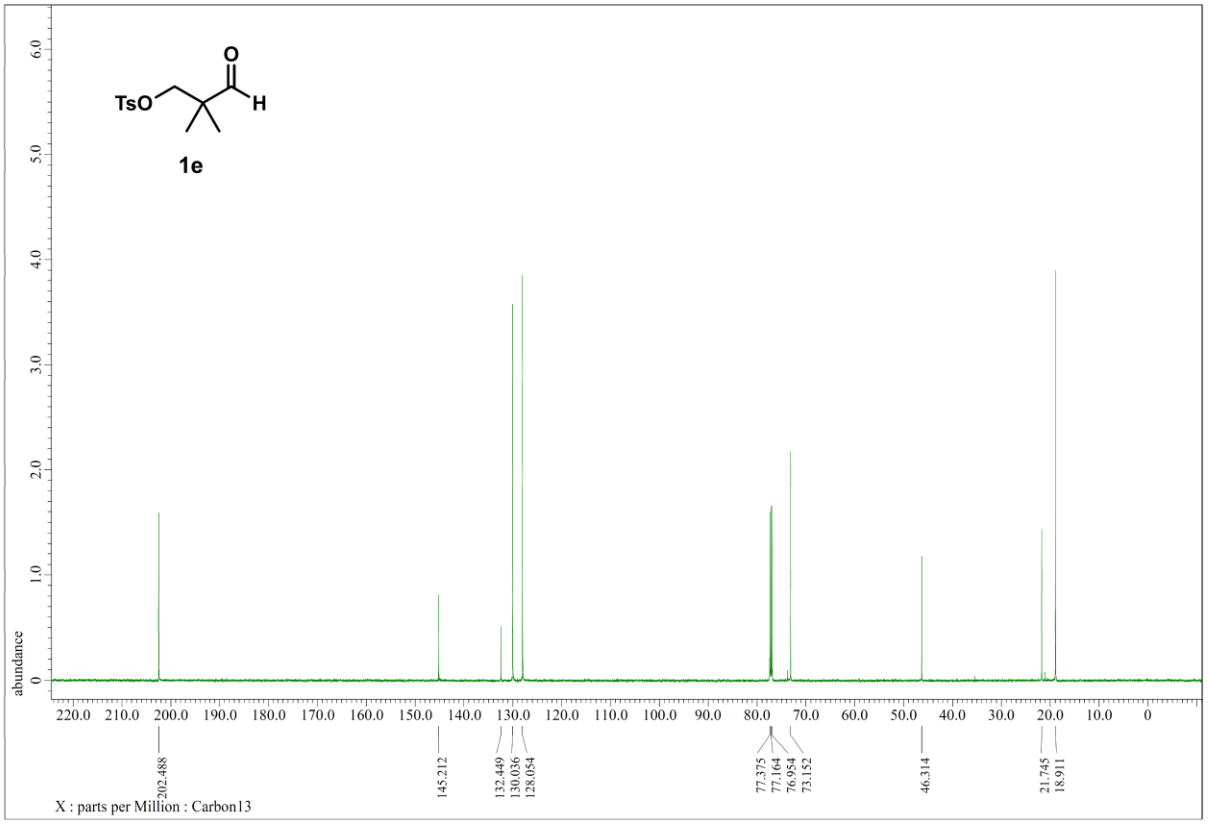
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **1d**



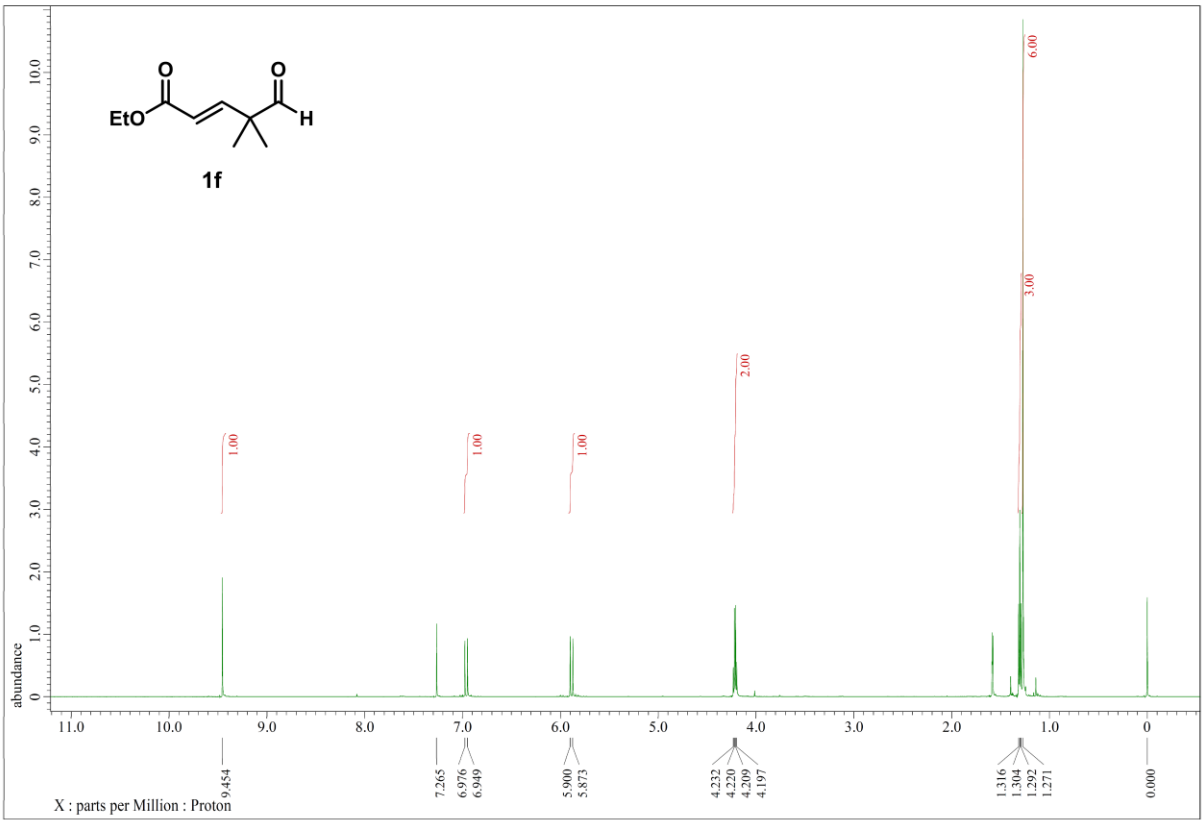


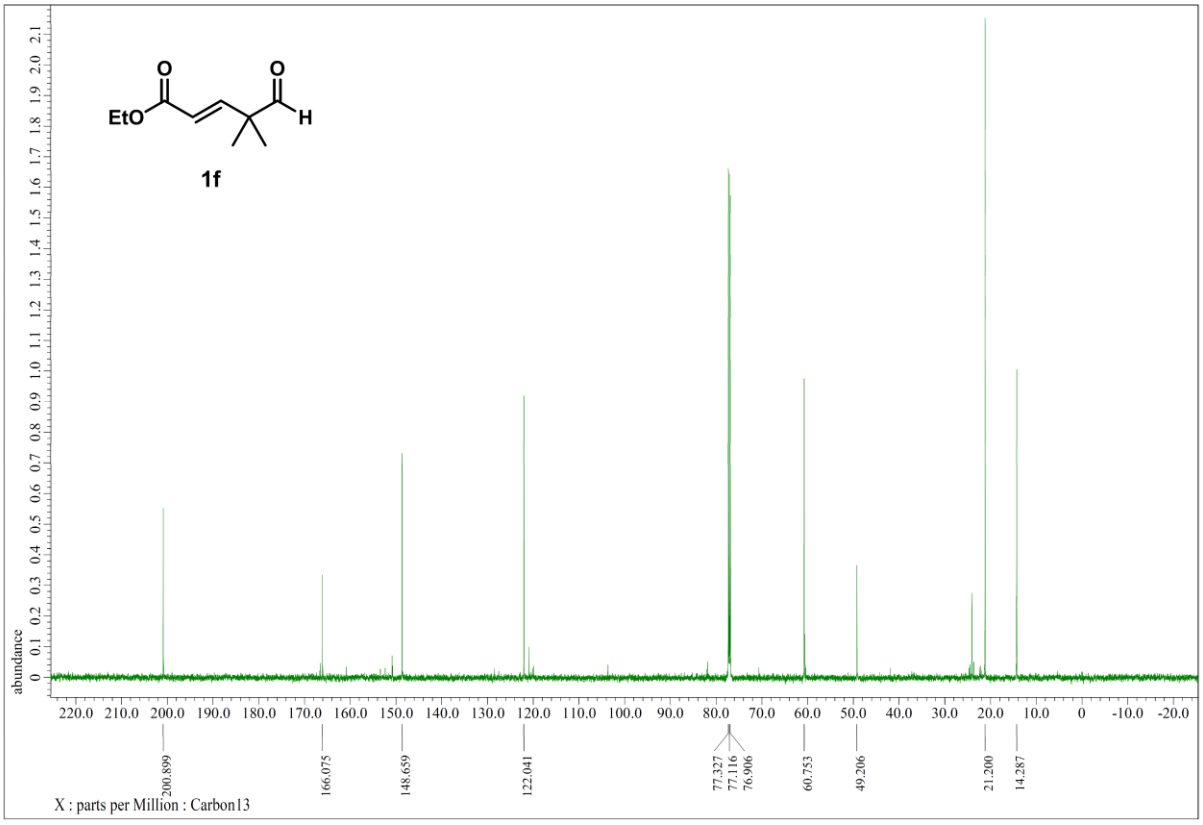
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **1e**



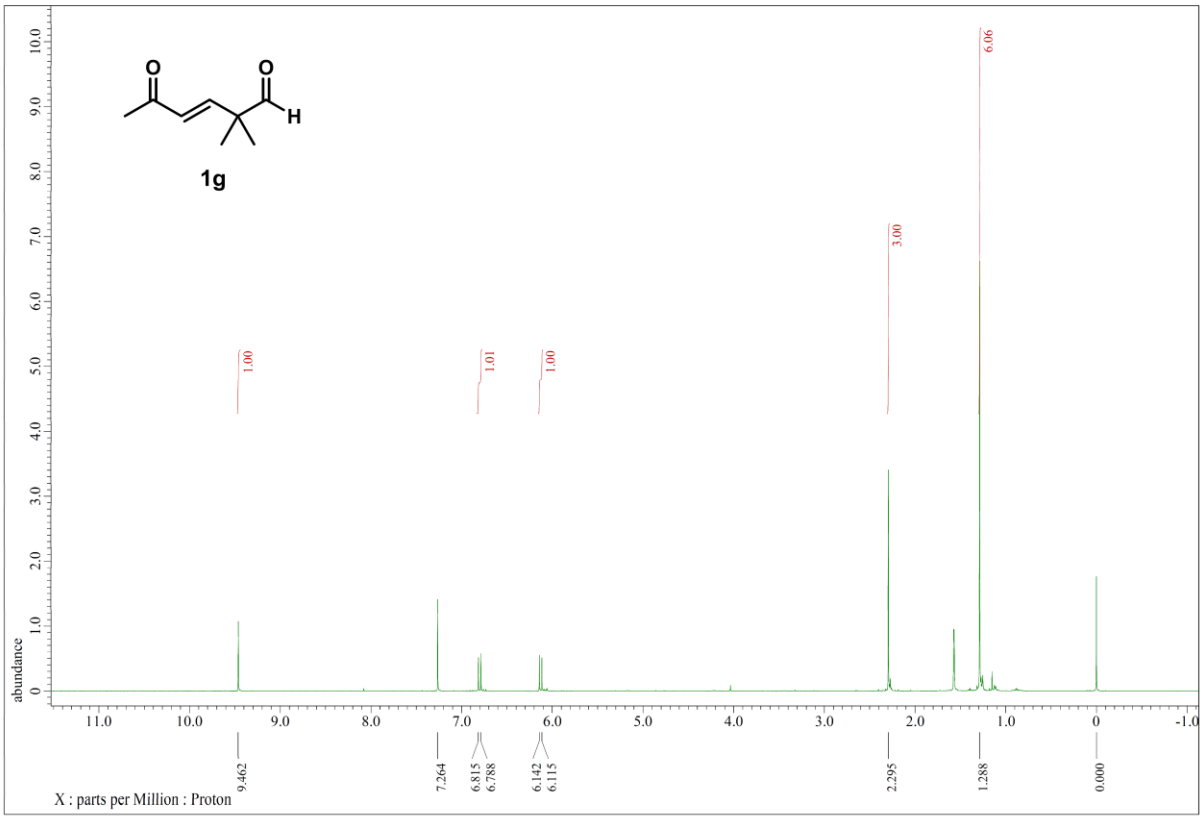


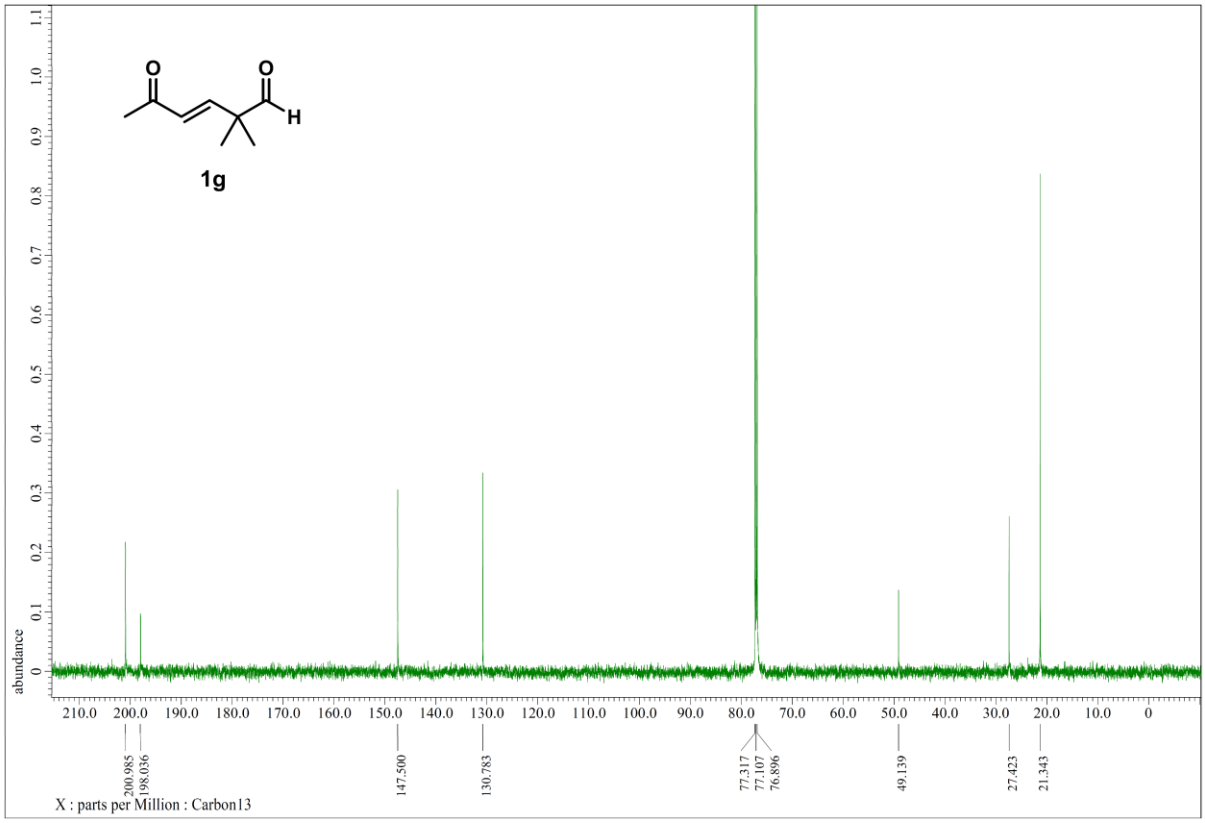
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **1f**



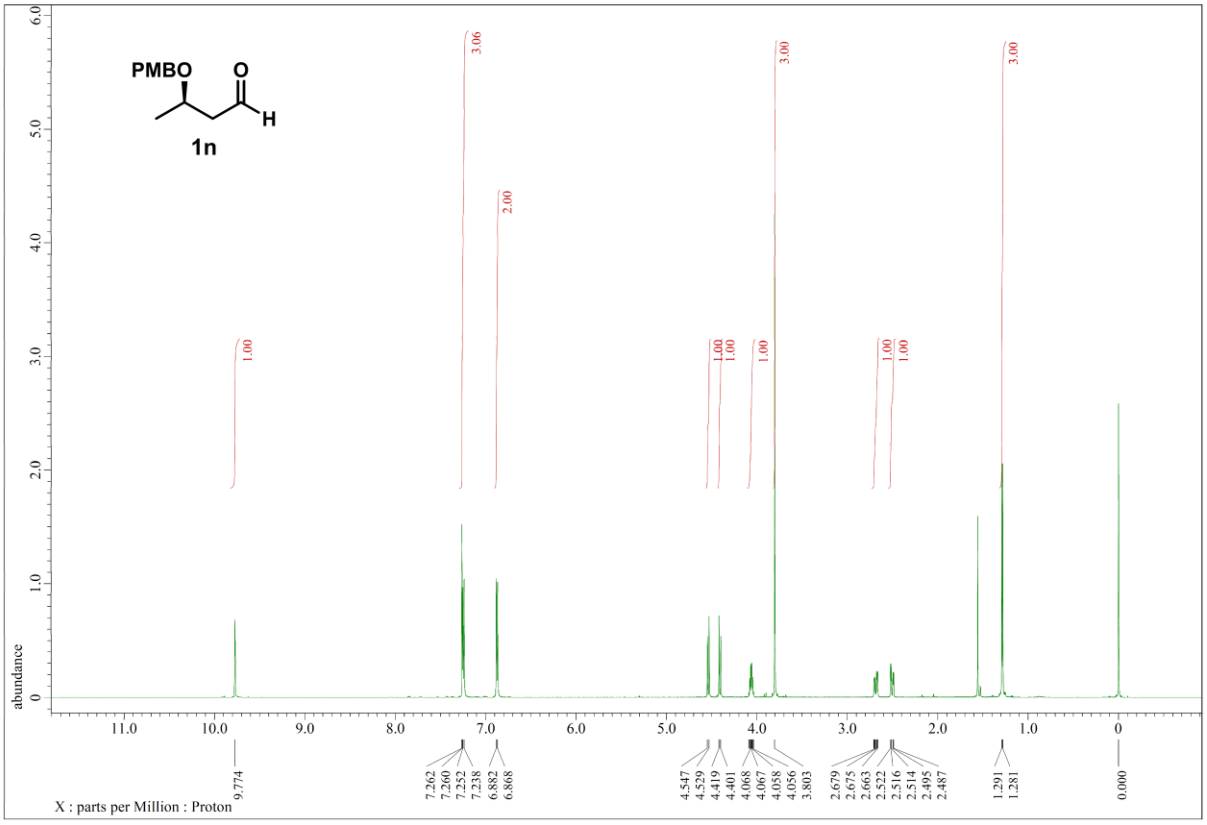


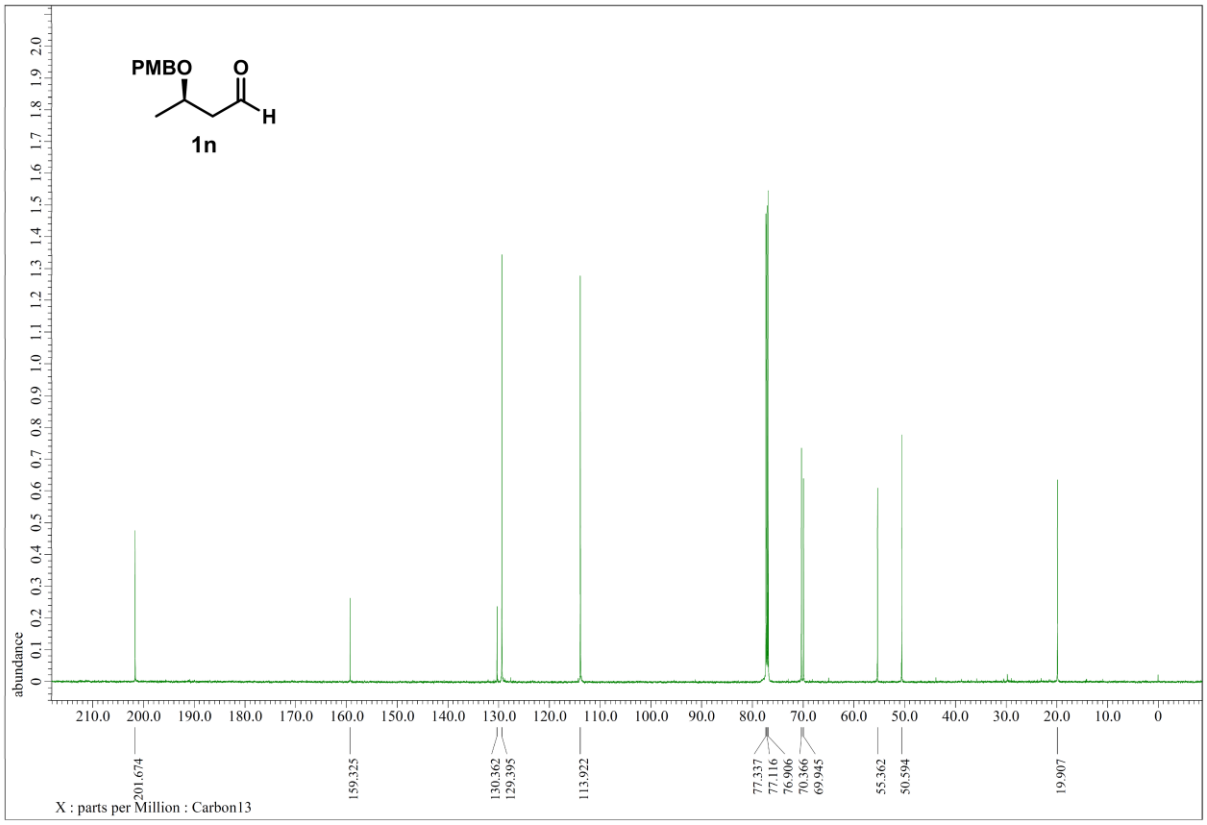
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **1g**



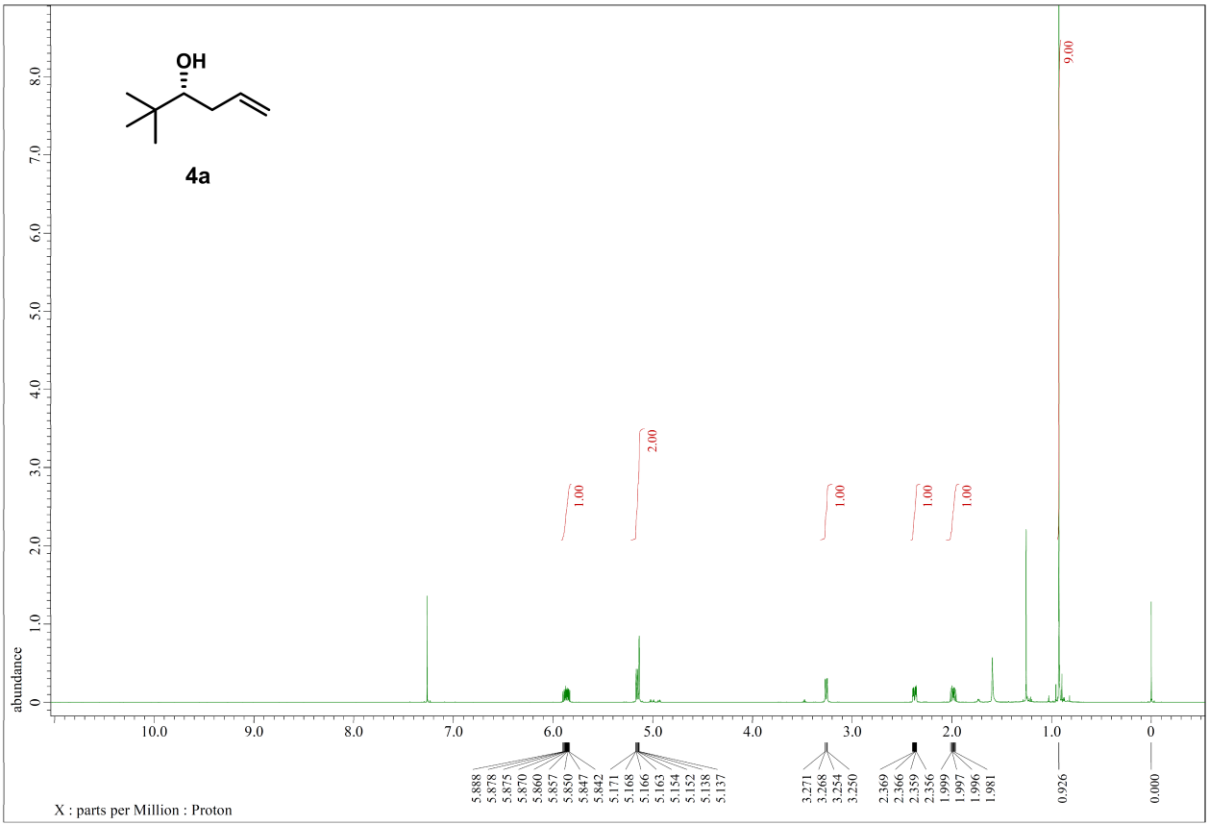


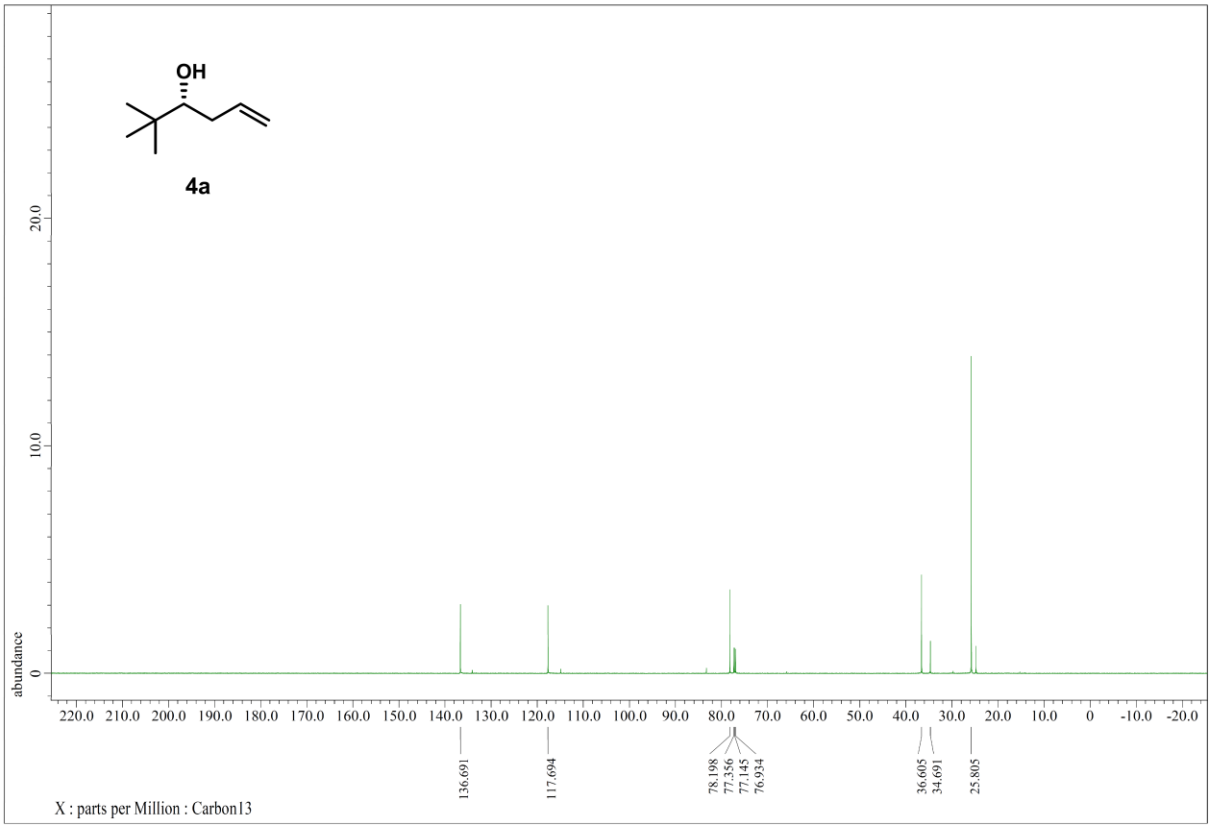
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **1n**



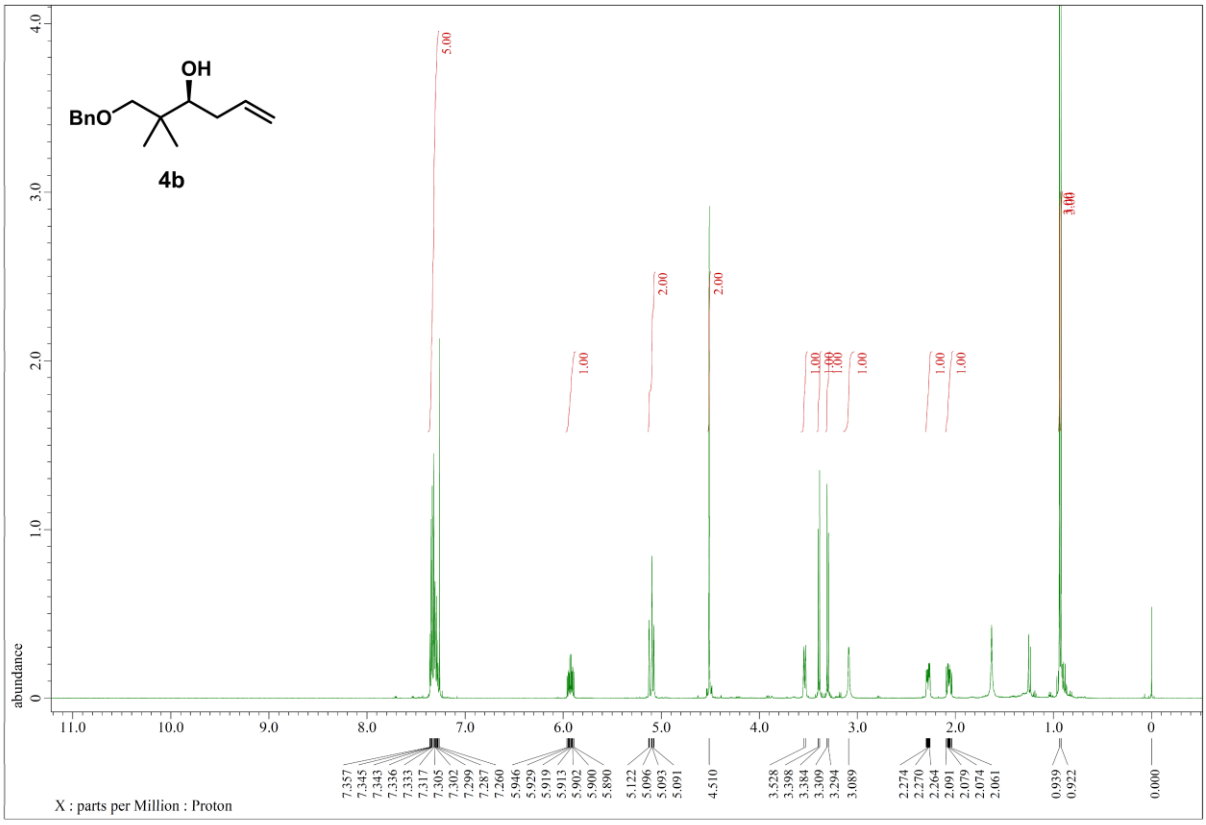


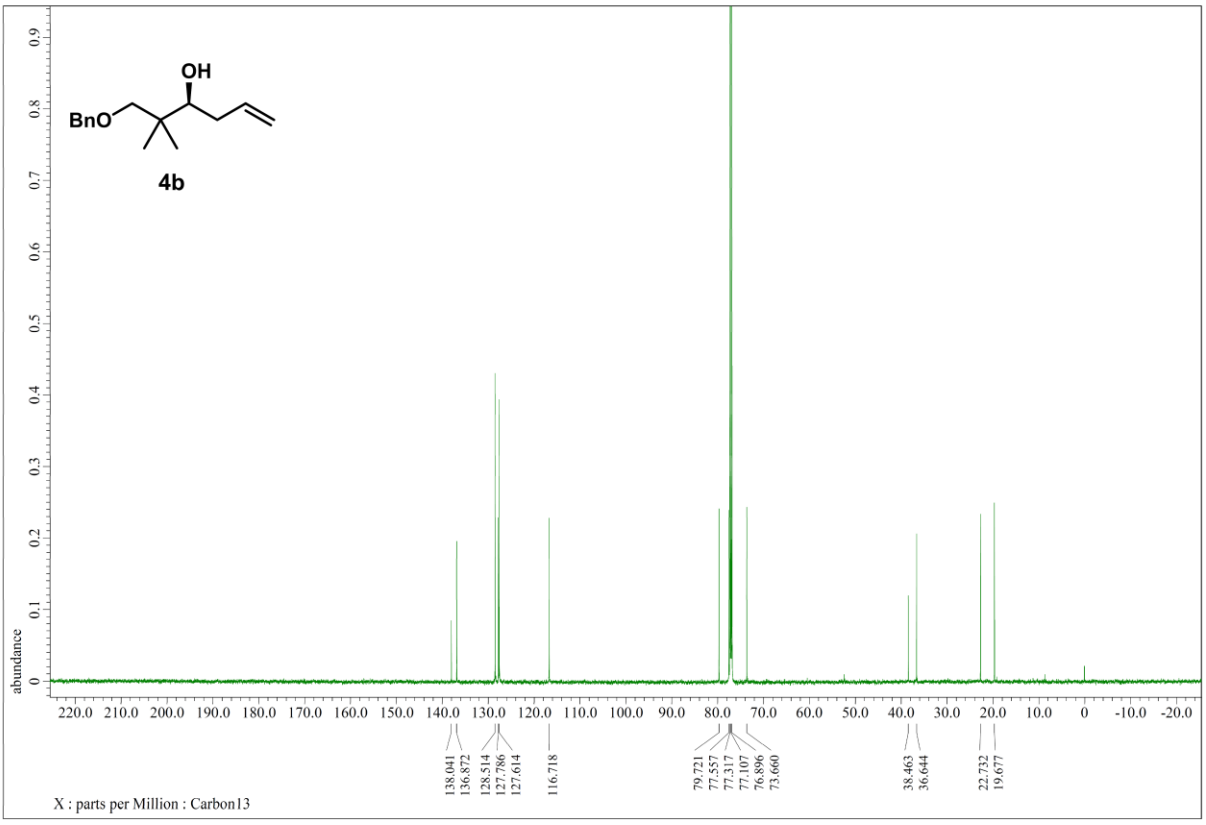
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4a**



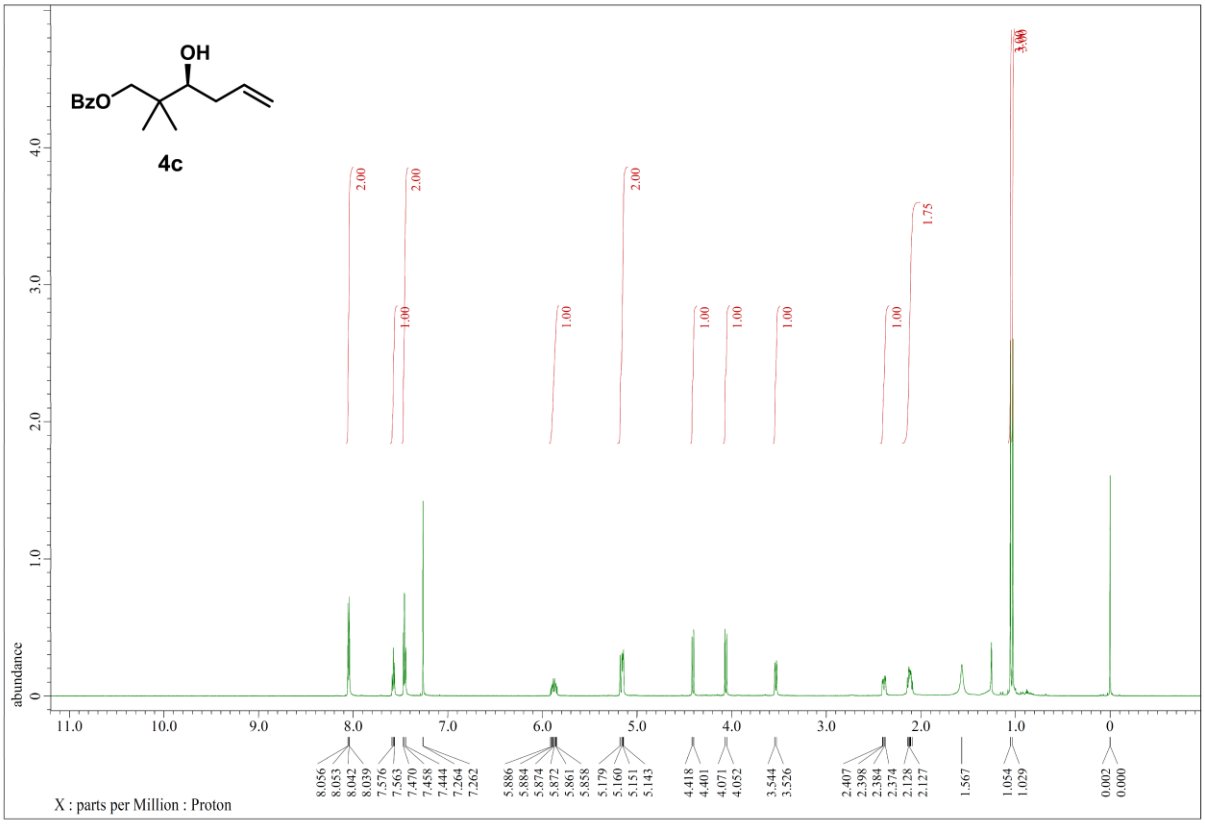


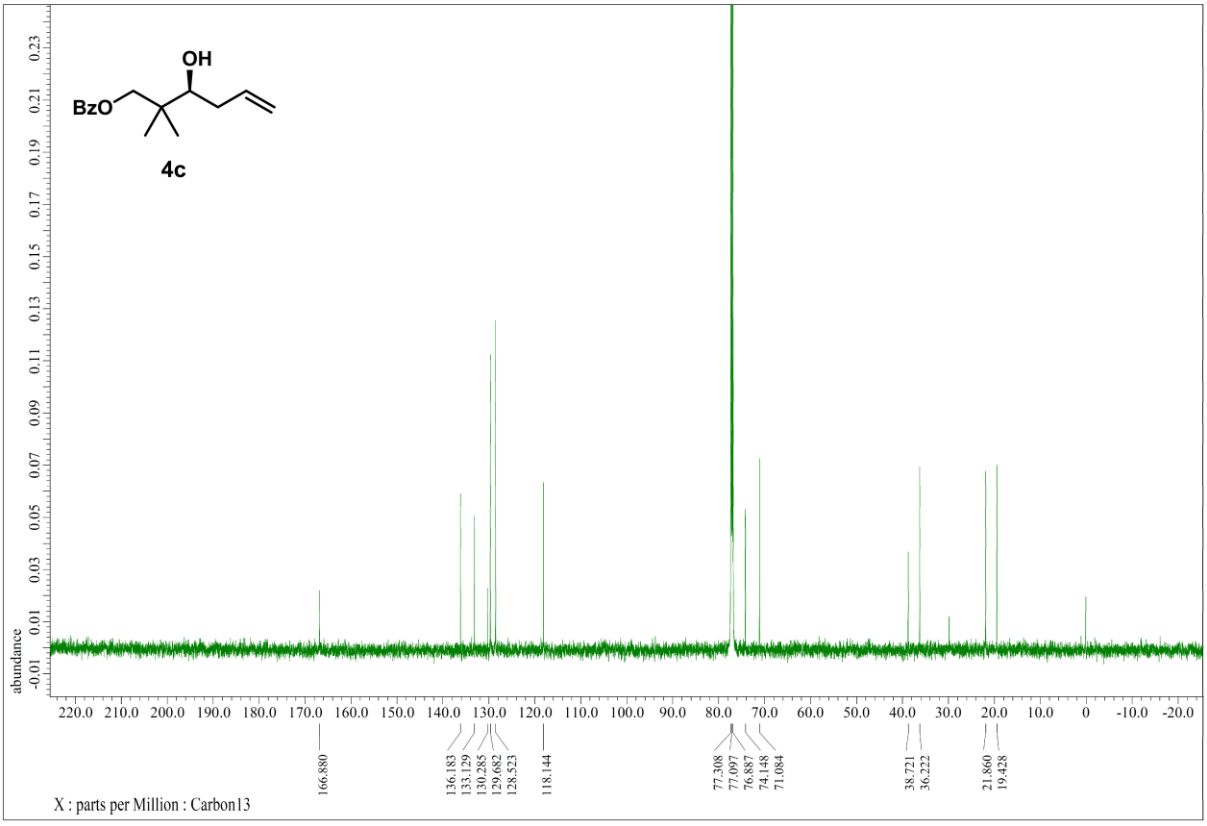
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4b**



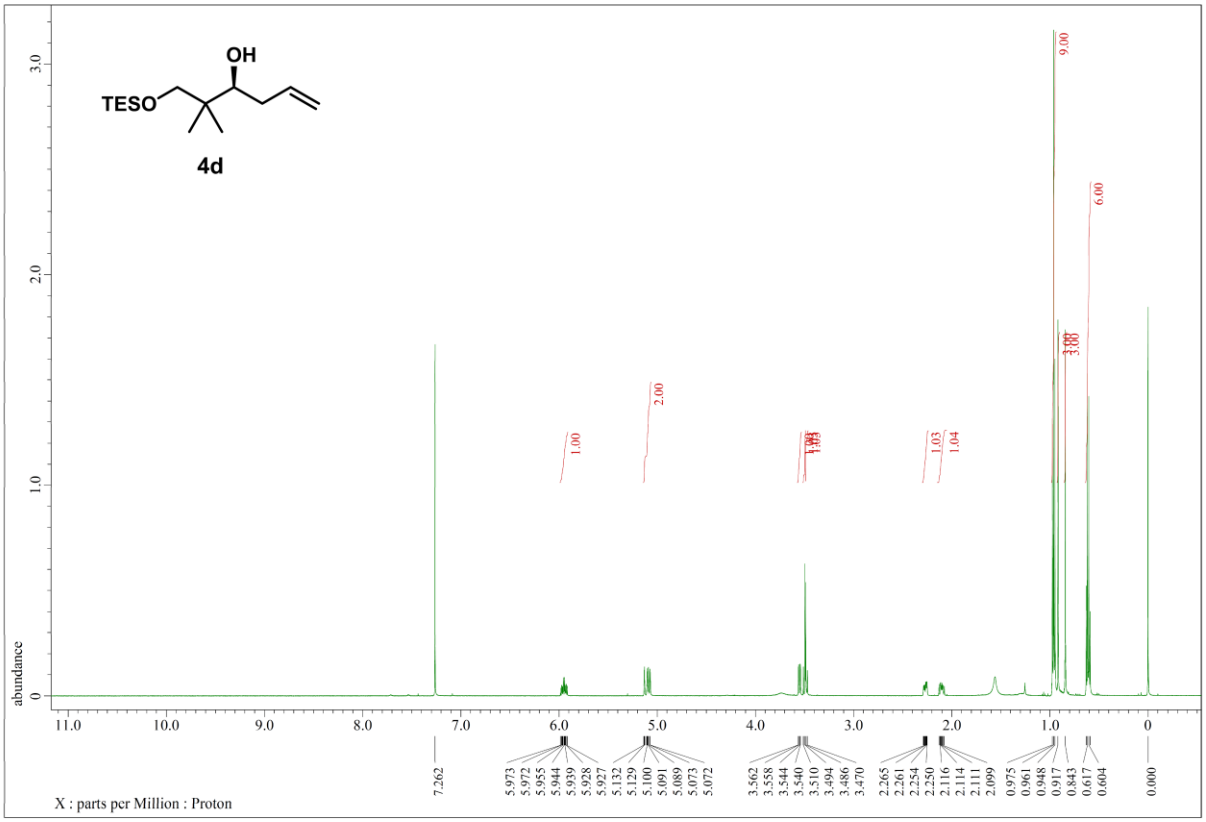


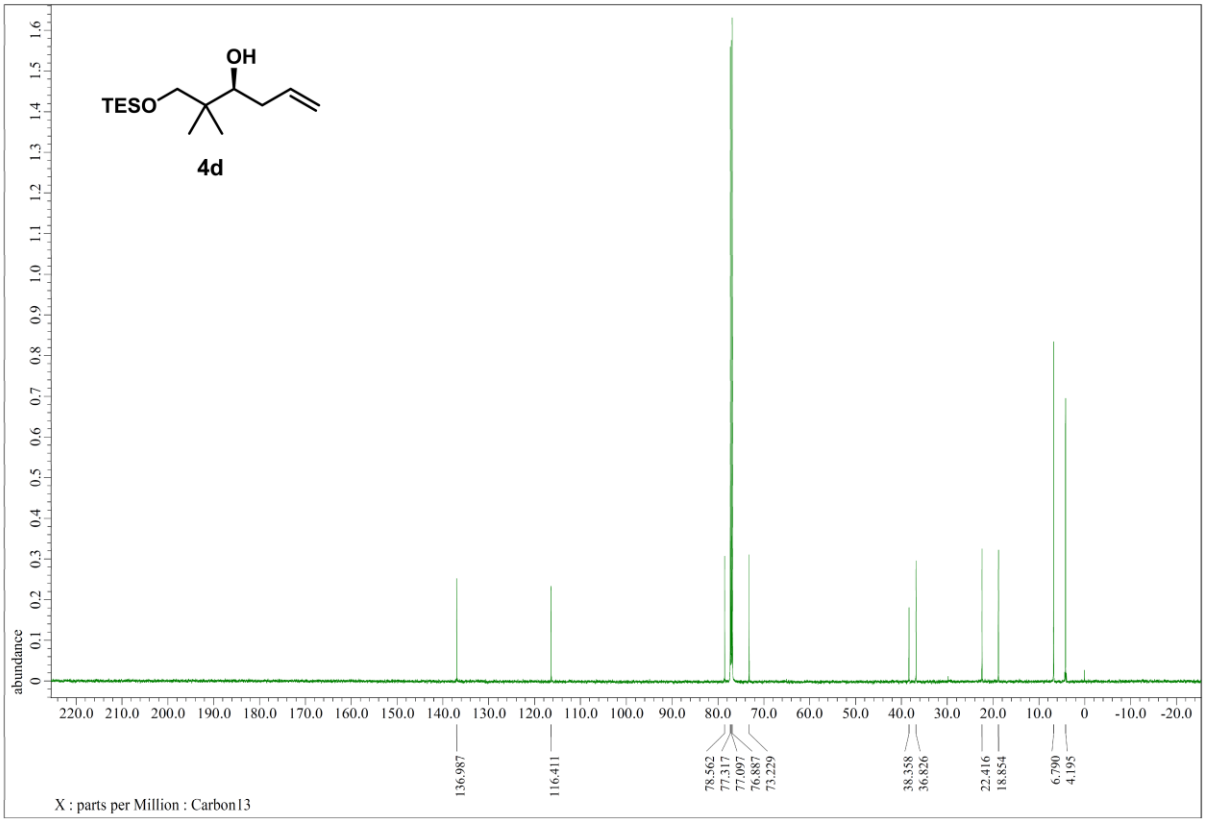
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4c**



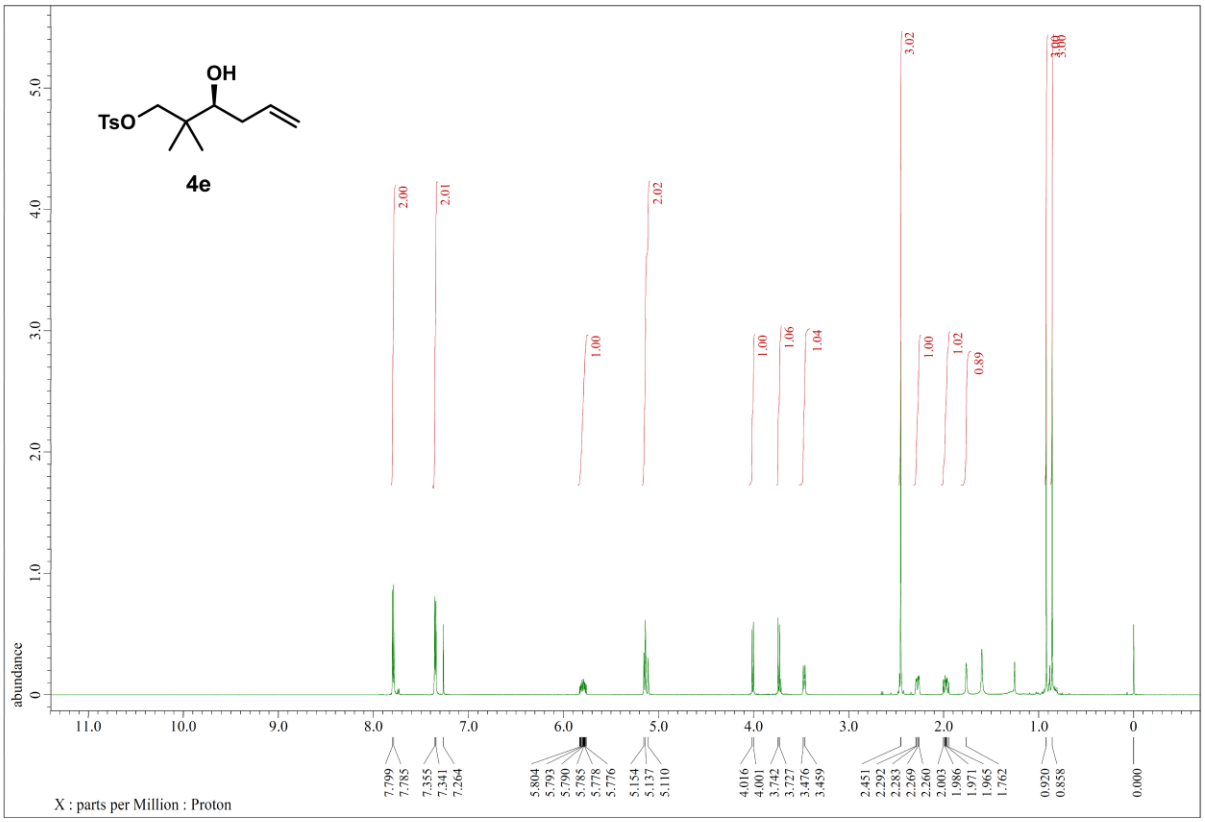


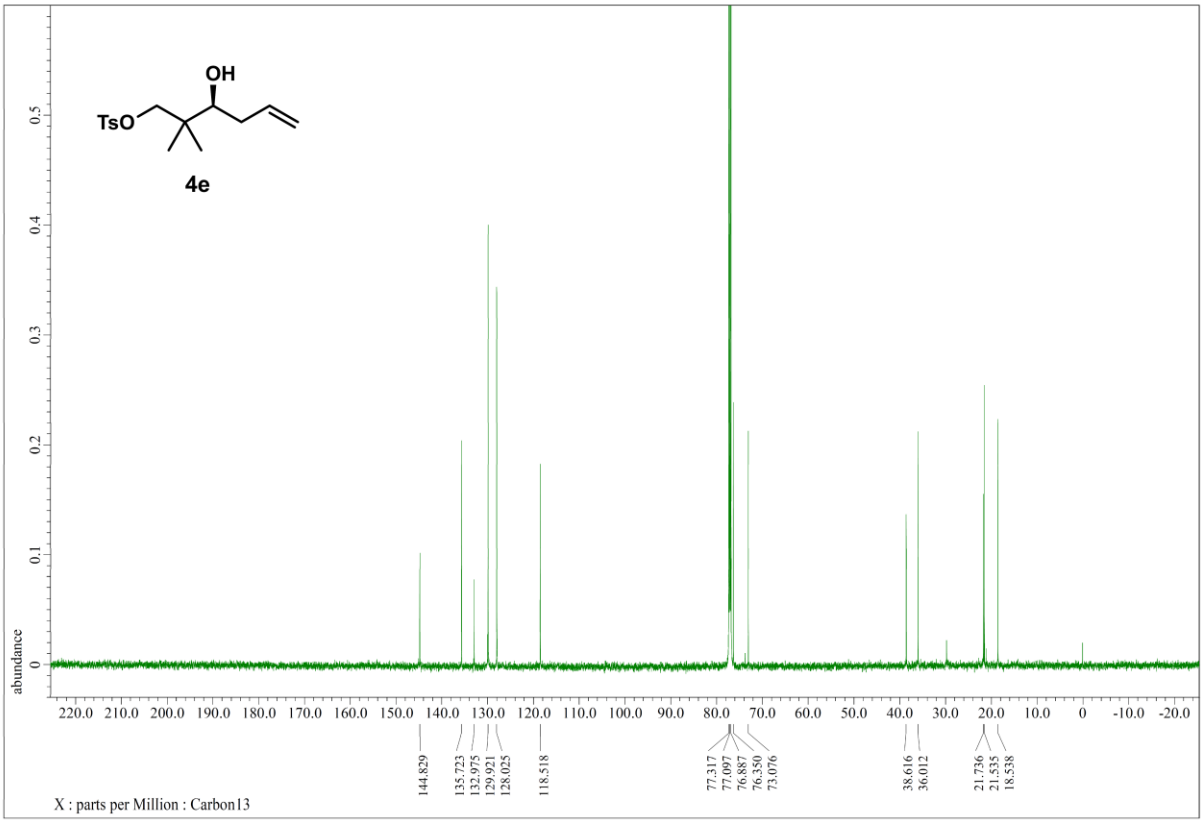
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4d**



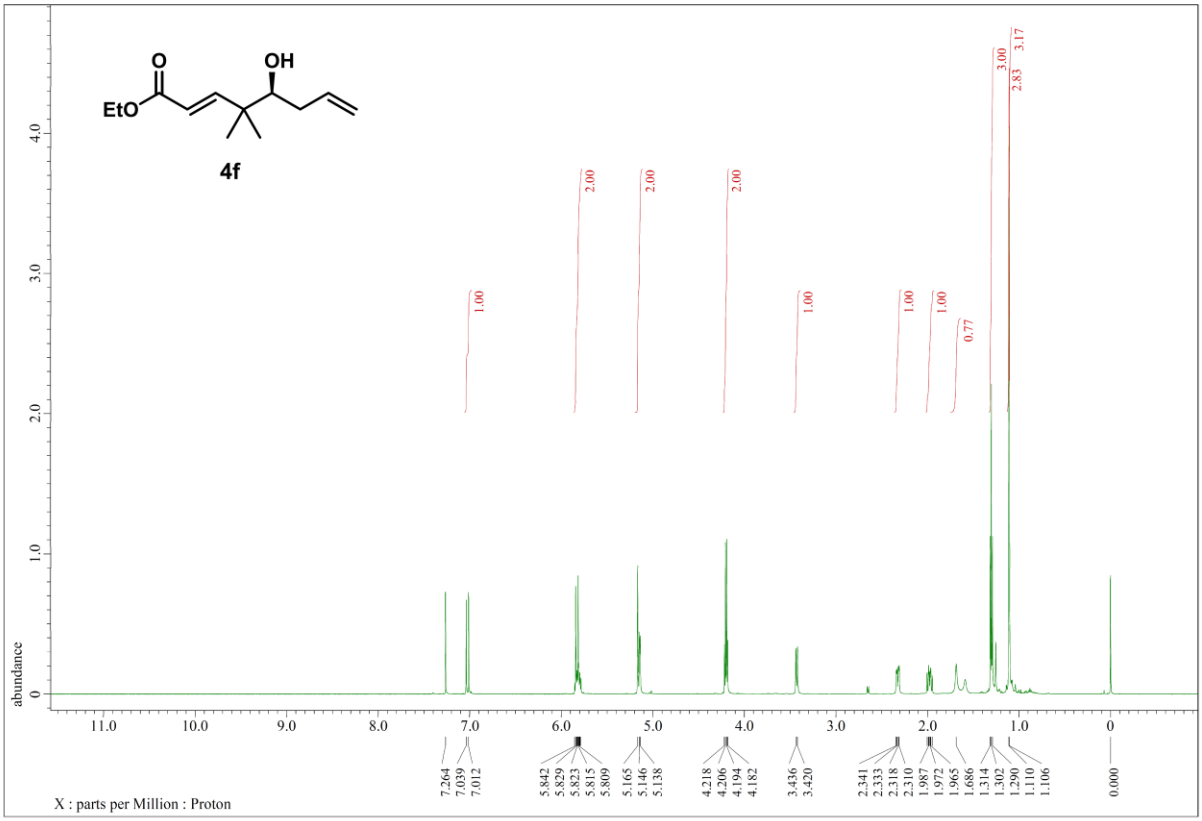


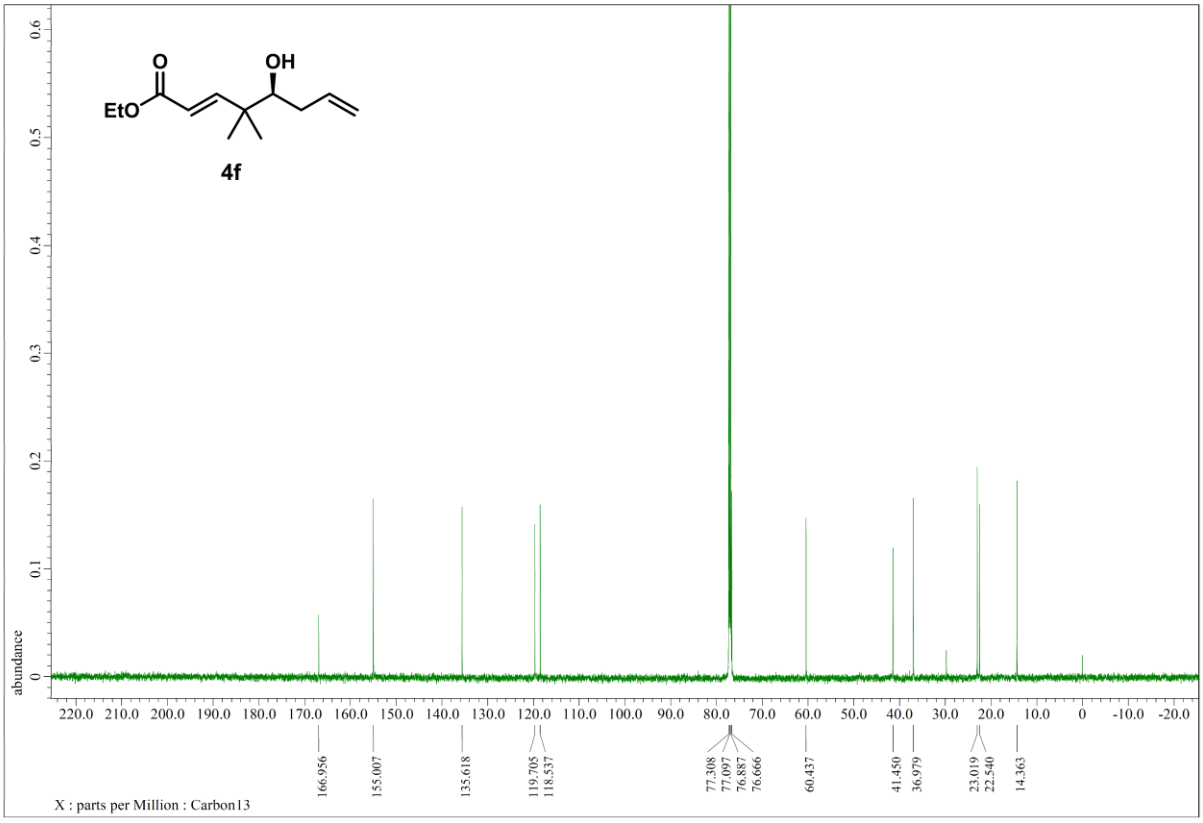
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4e**



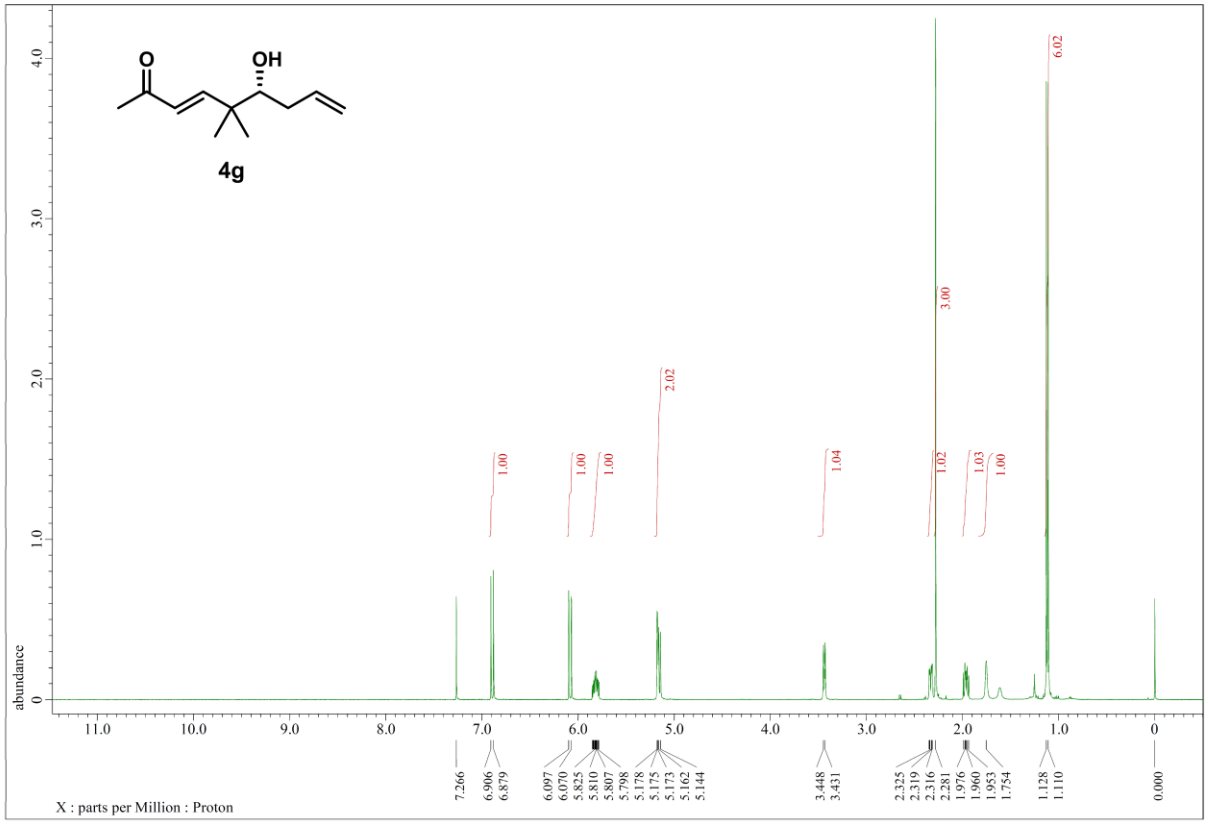


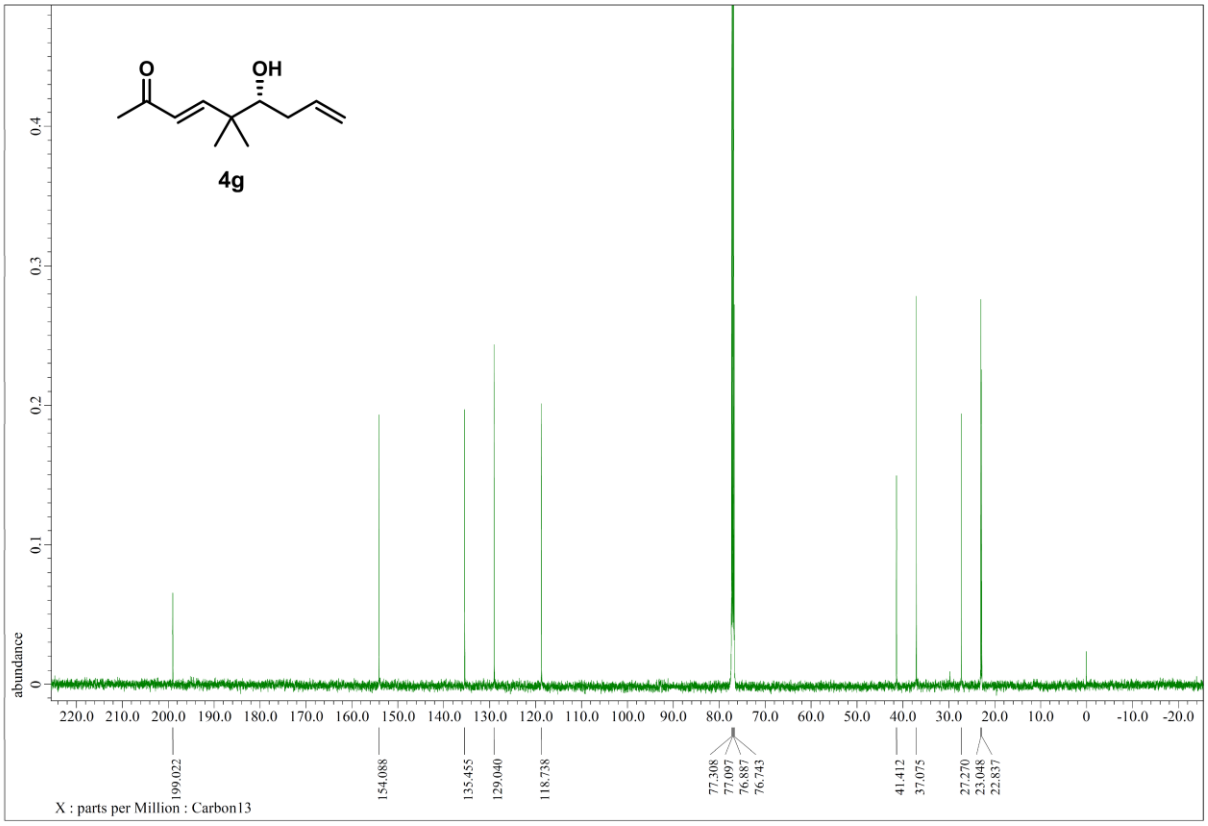
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4f**



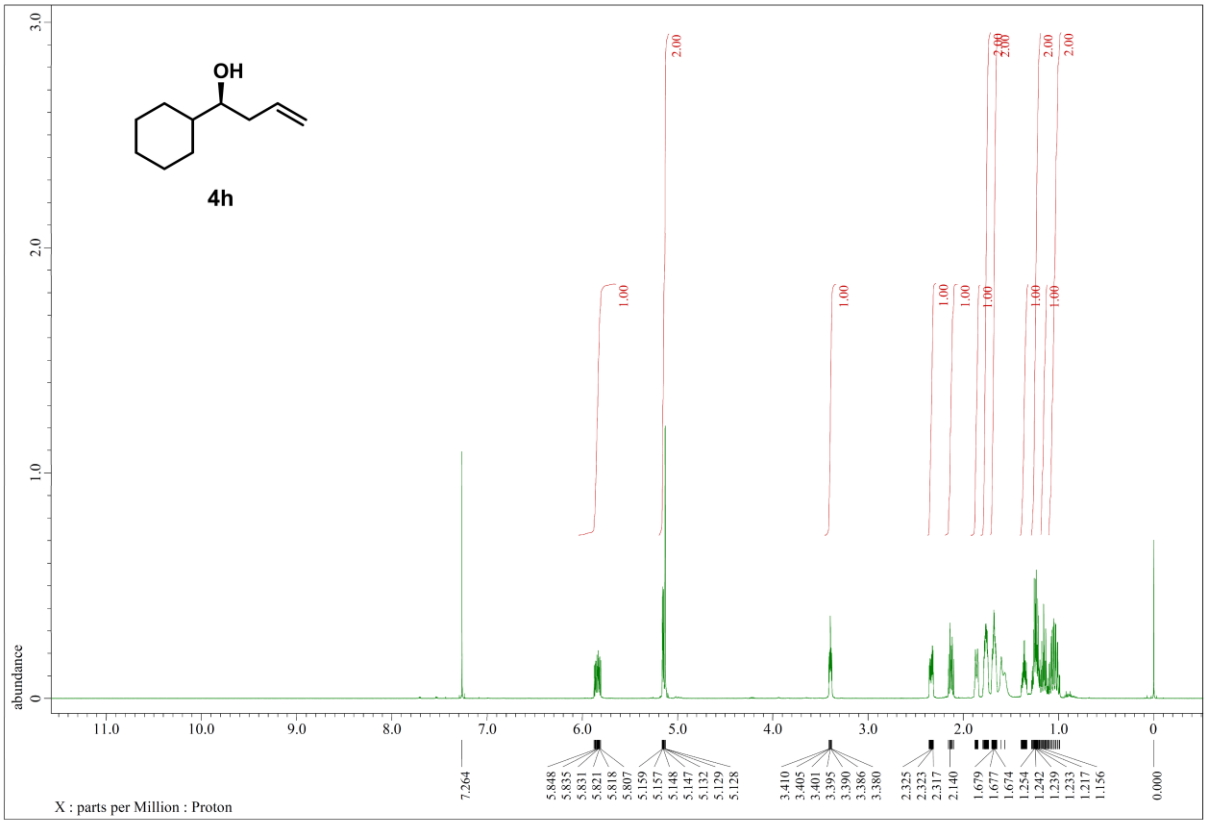


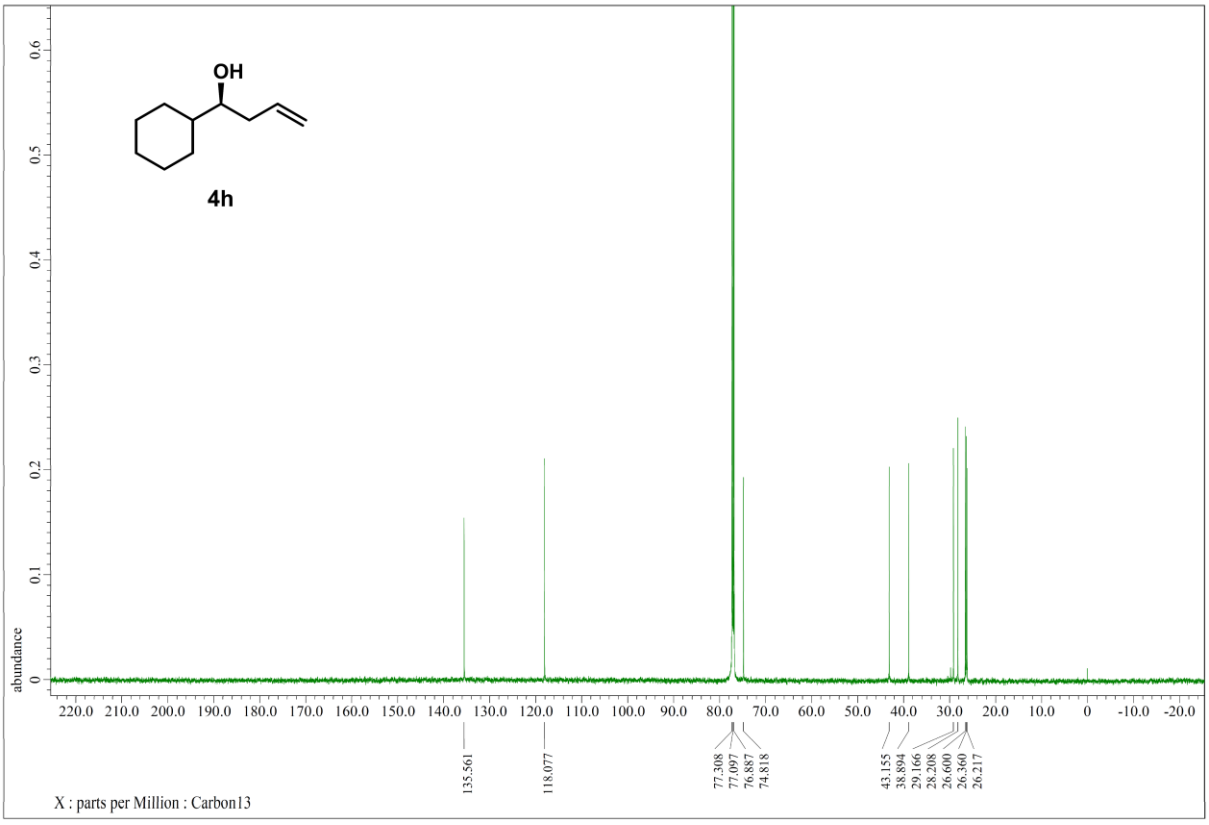
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4g**



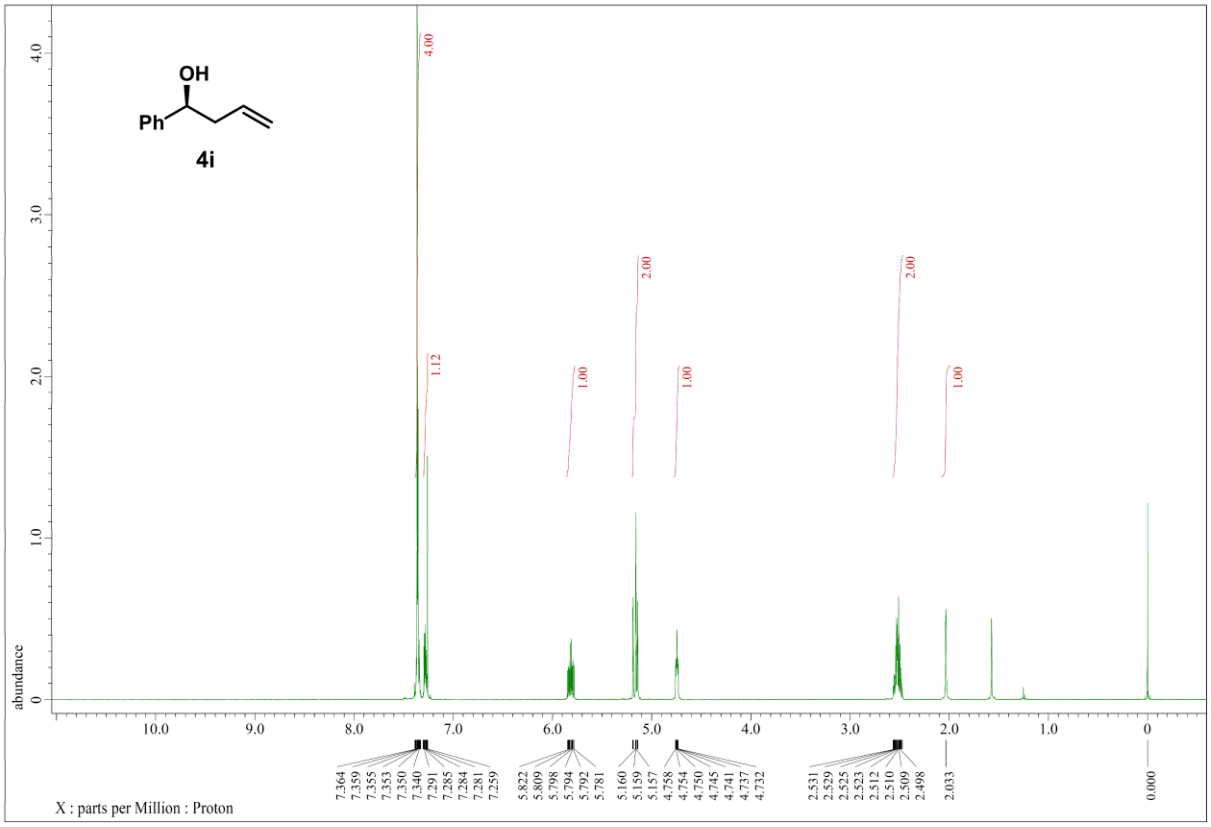


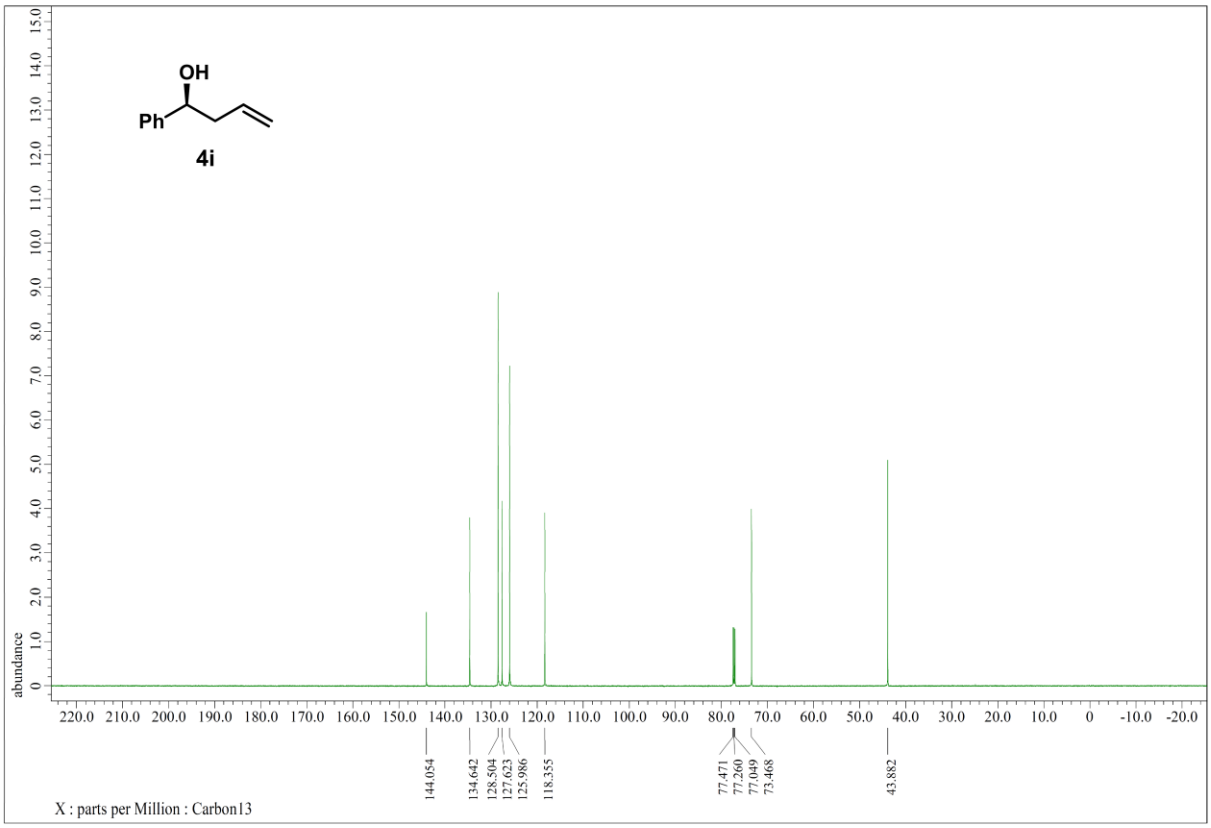
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4h**



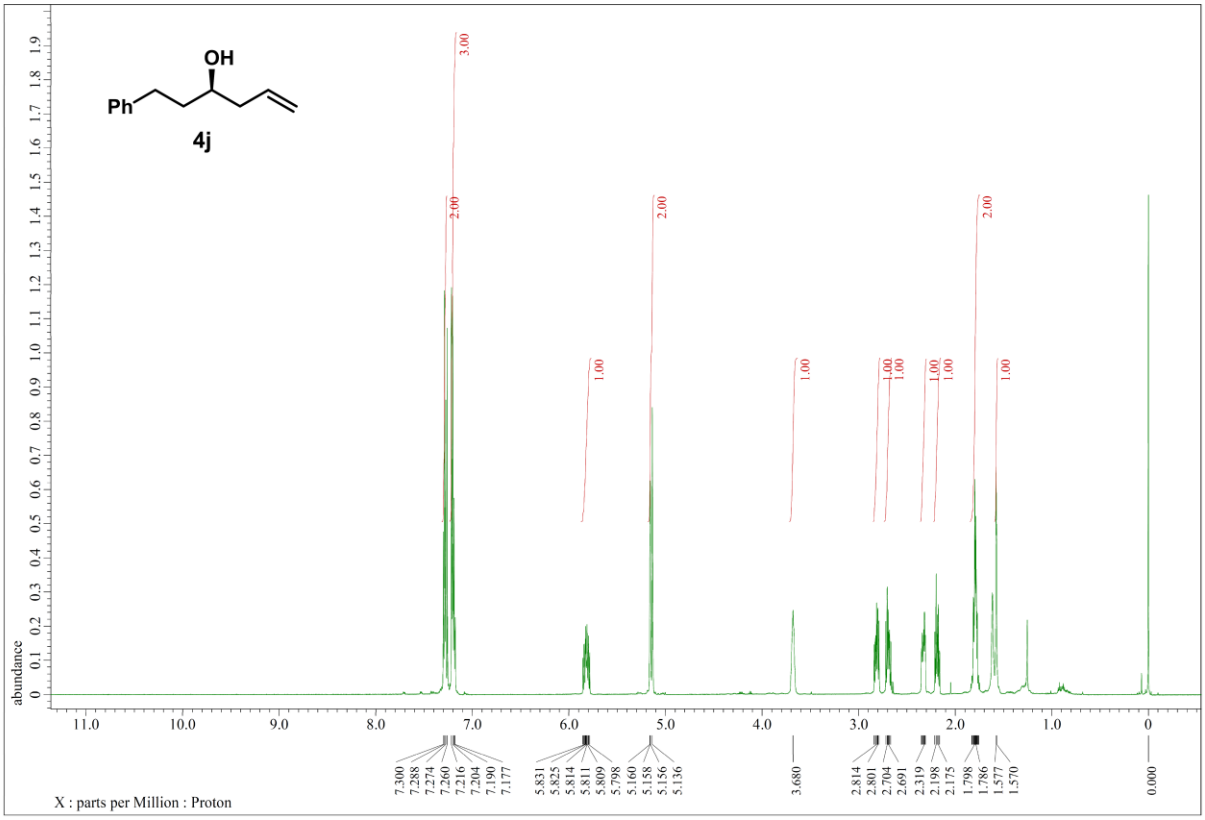


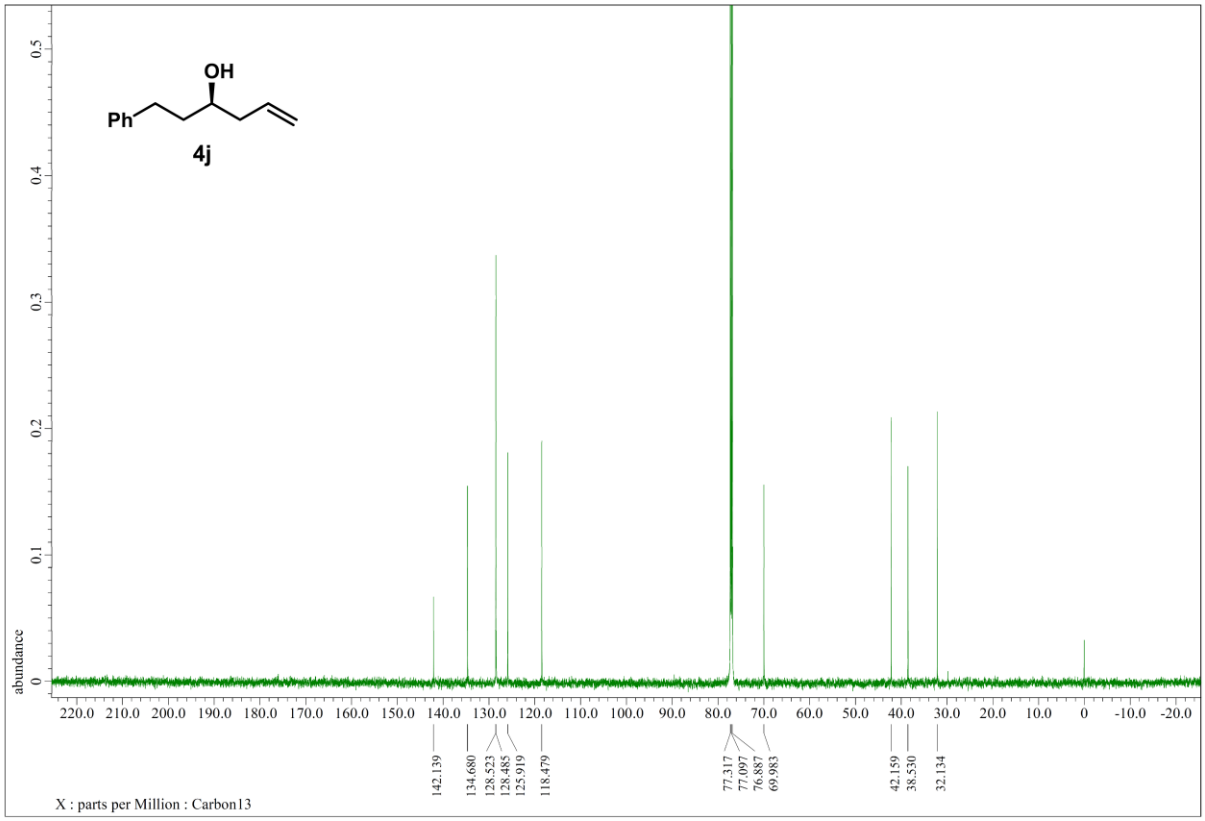
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4i**



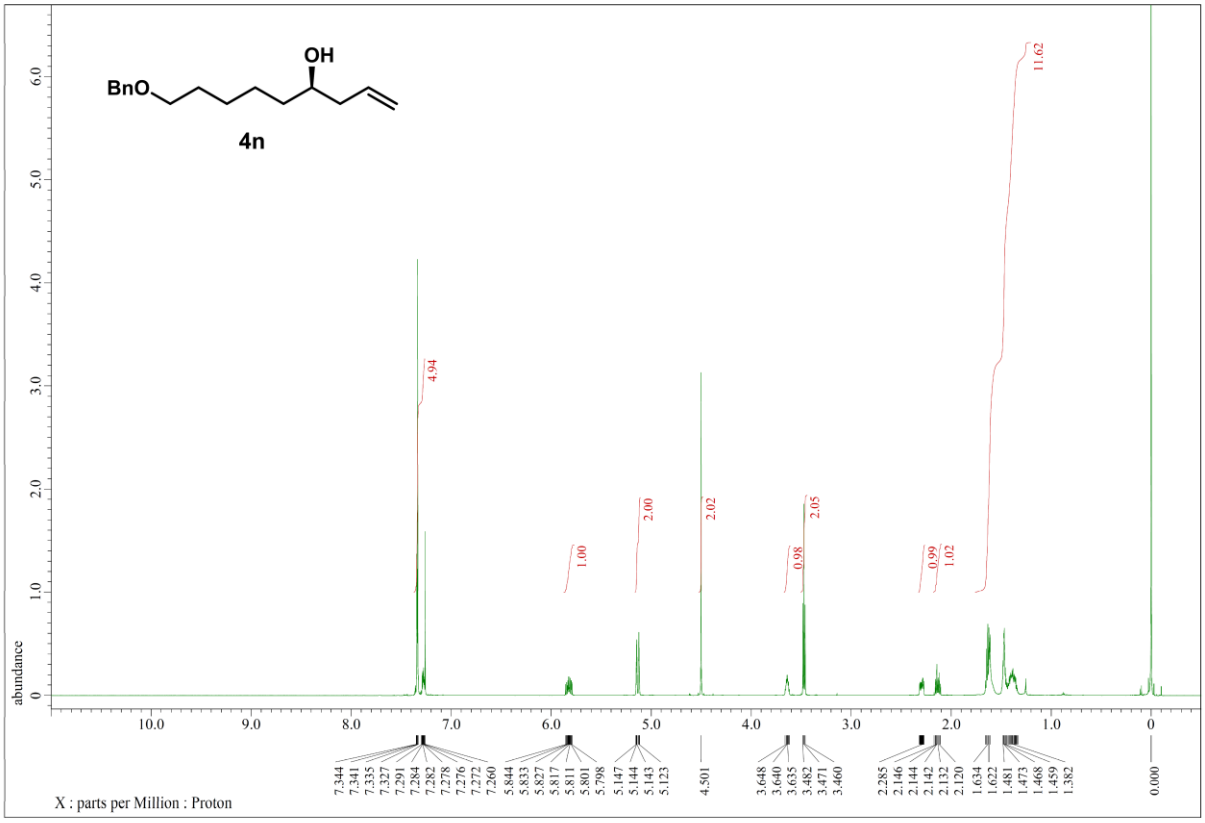


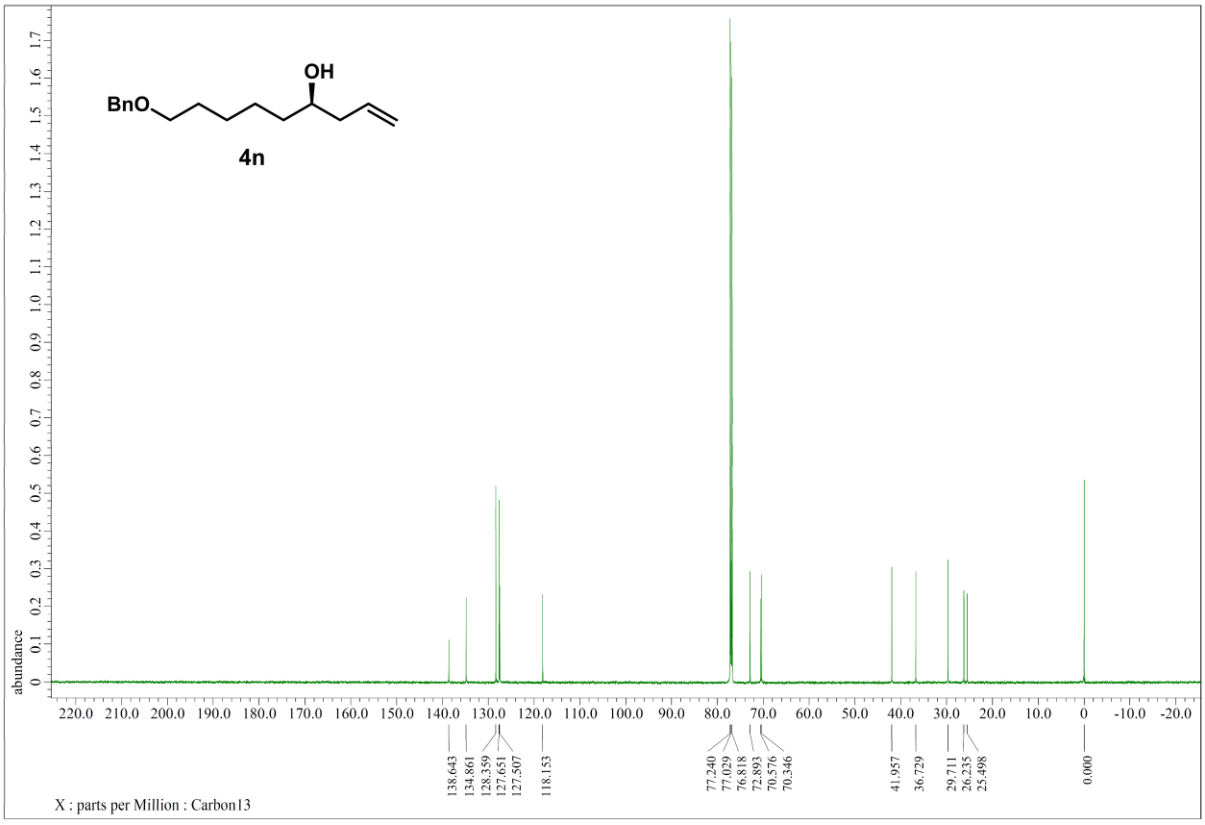
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4j**



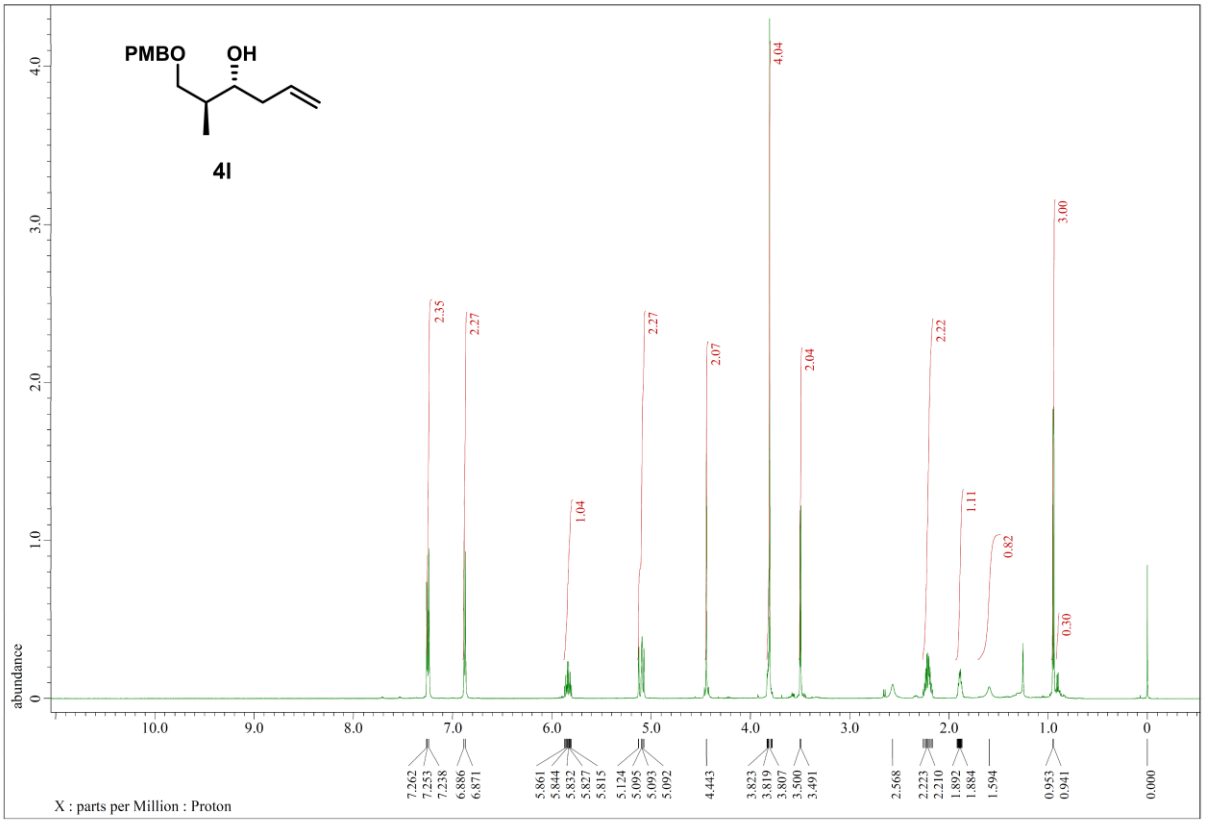


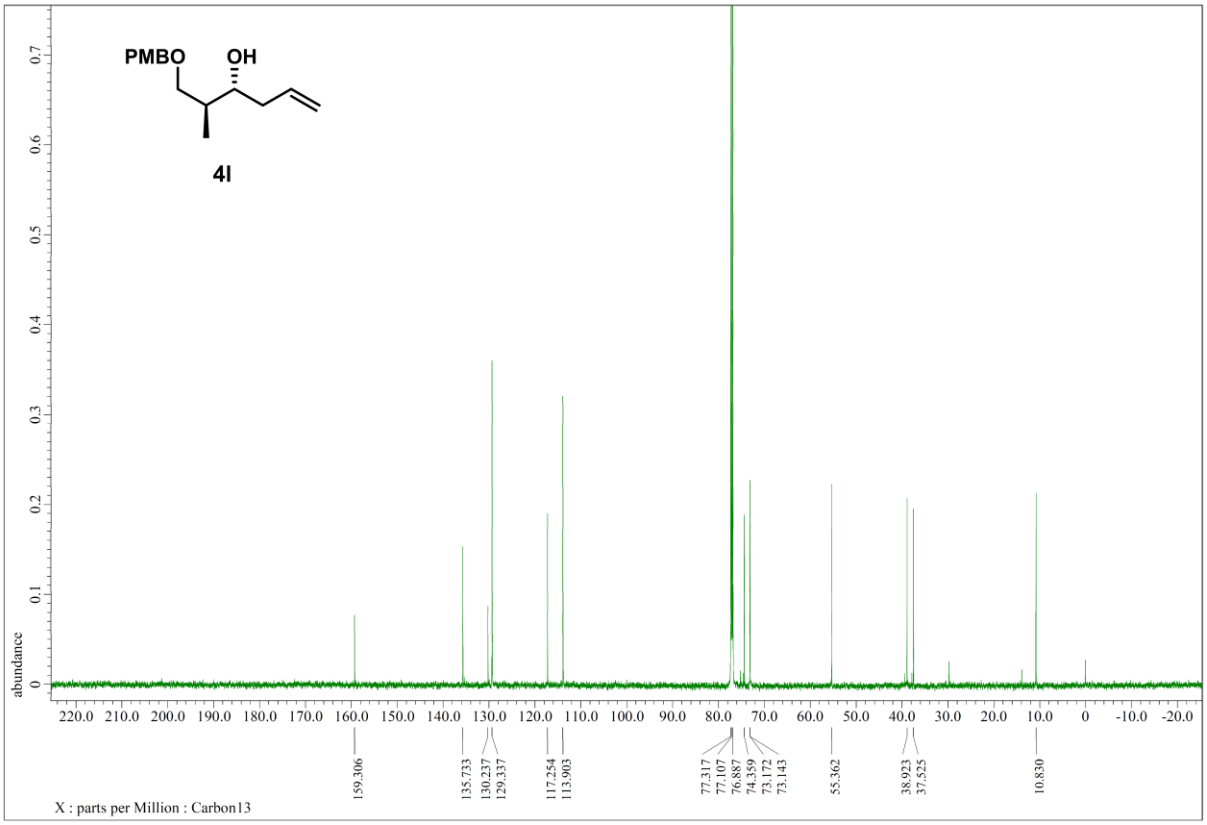
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4n**



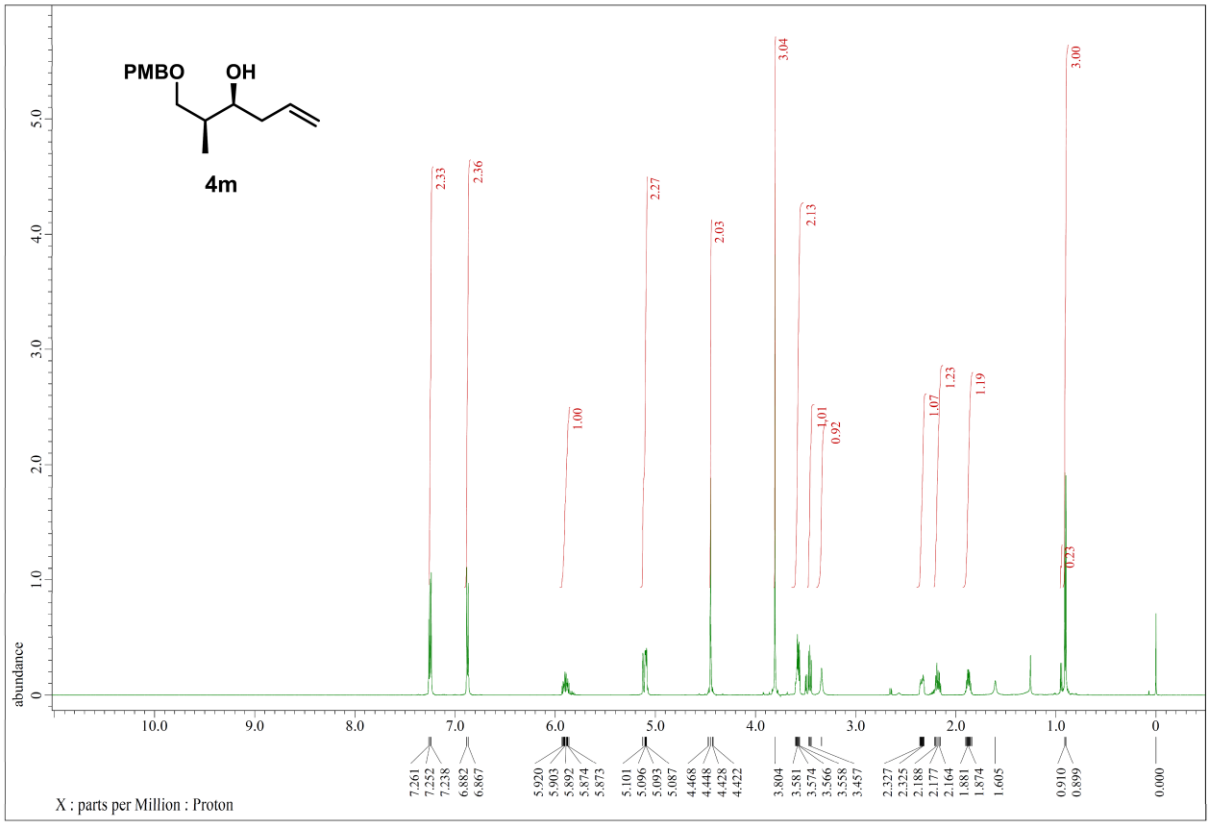


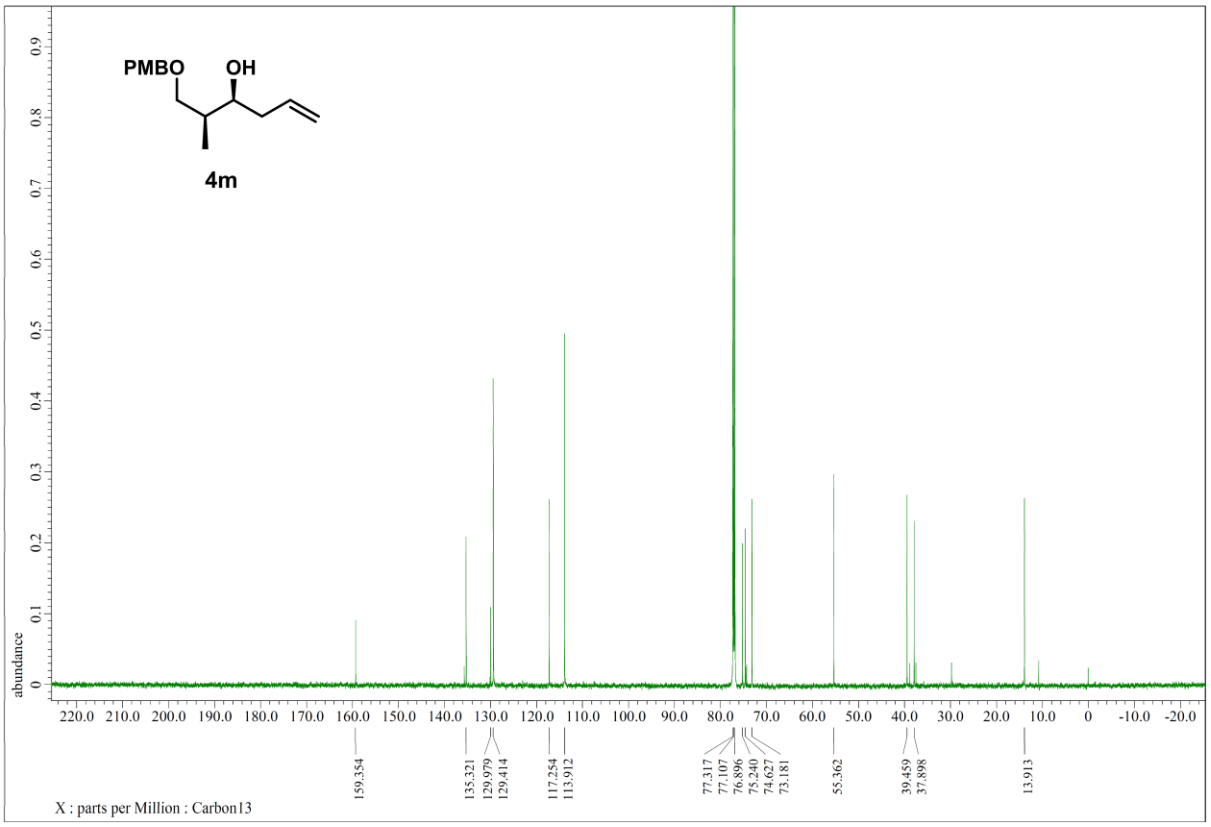
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4l**



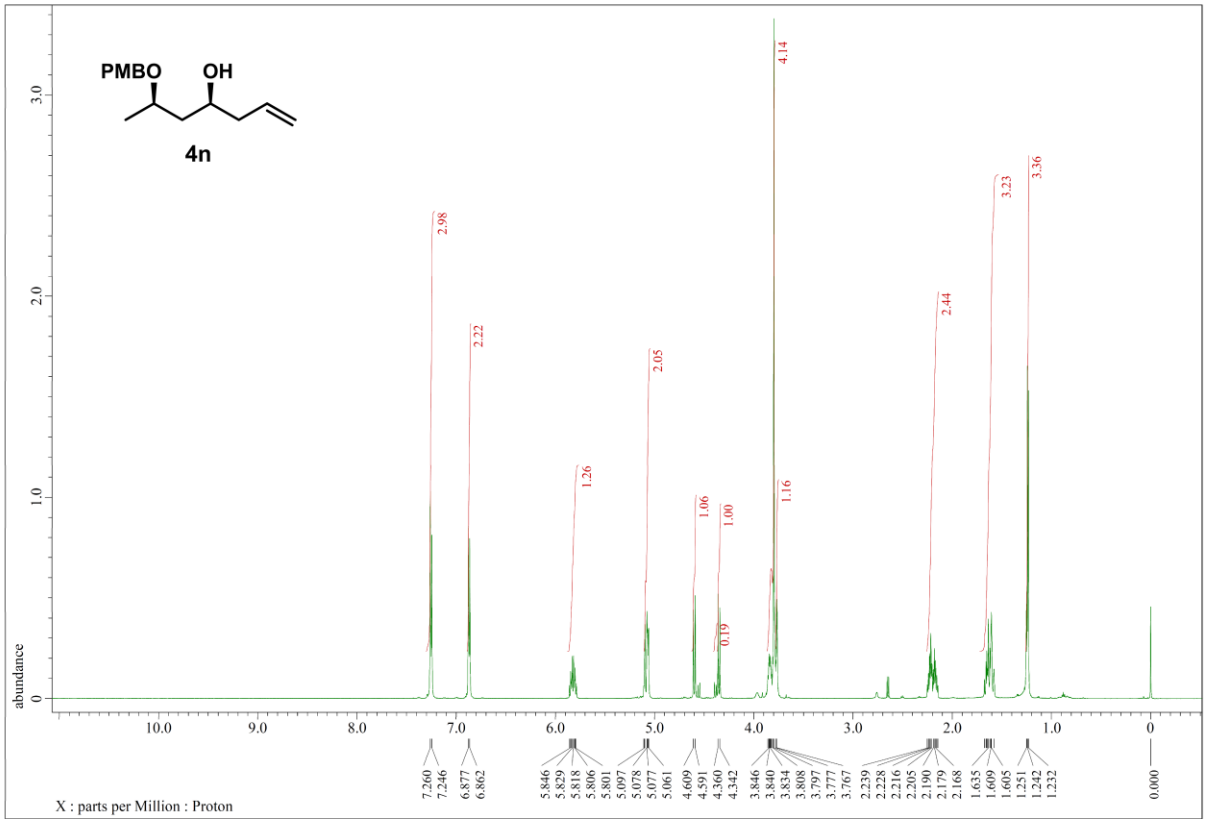


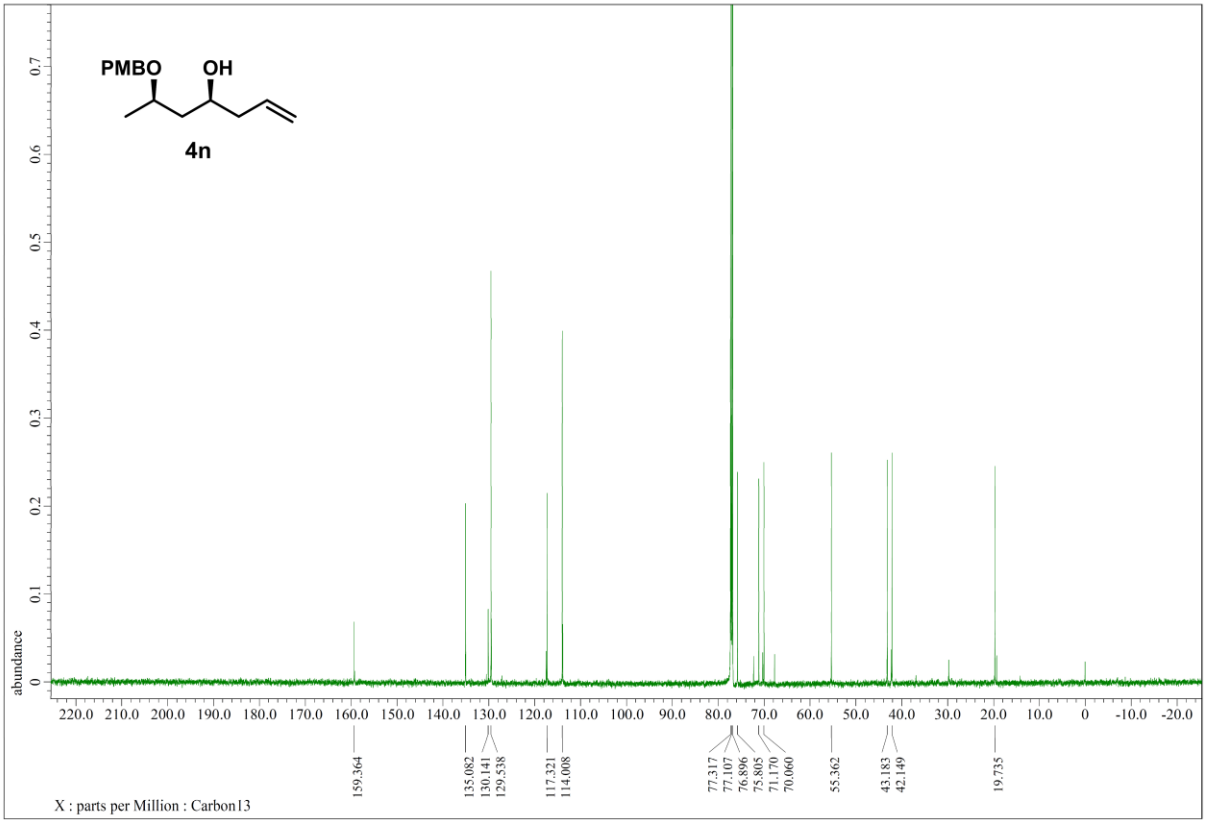
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4m**



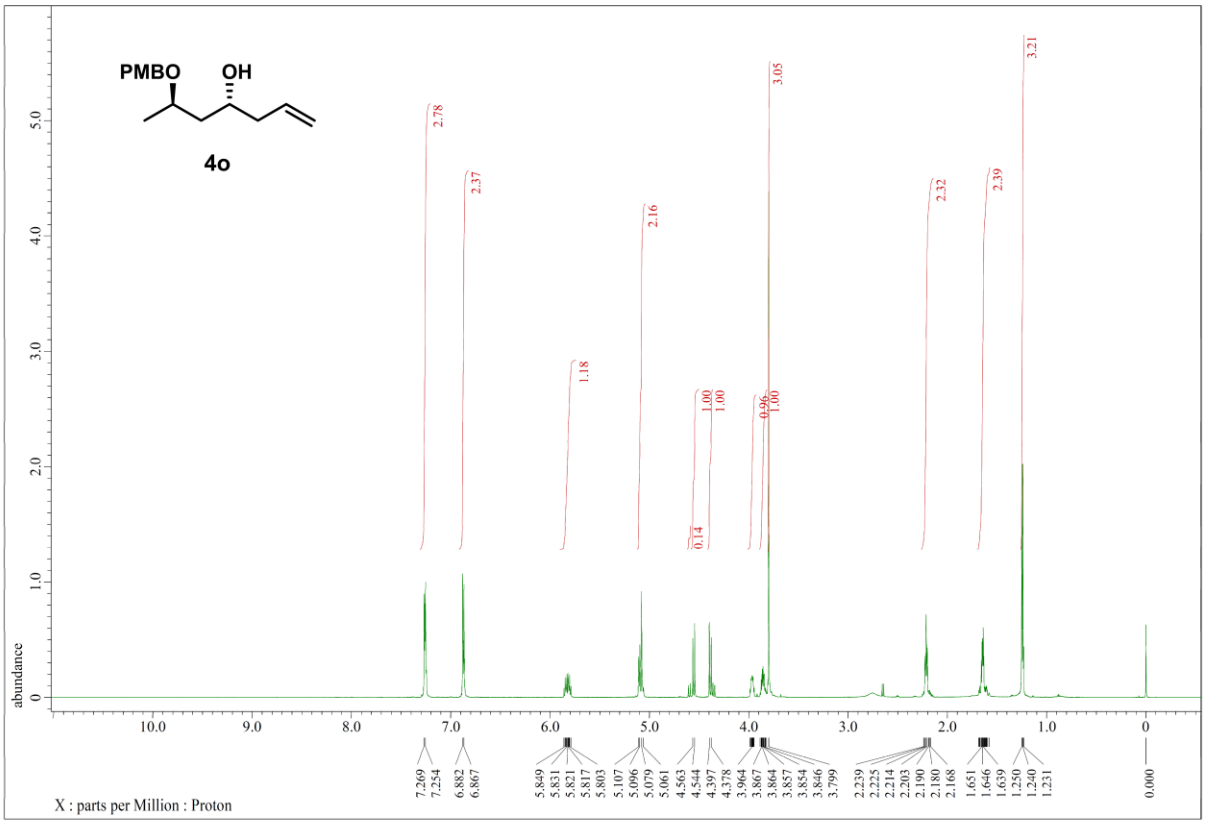


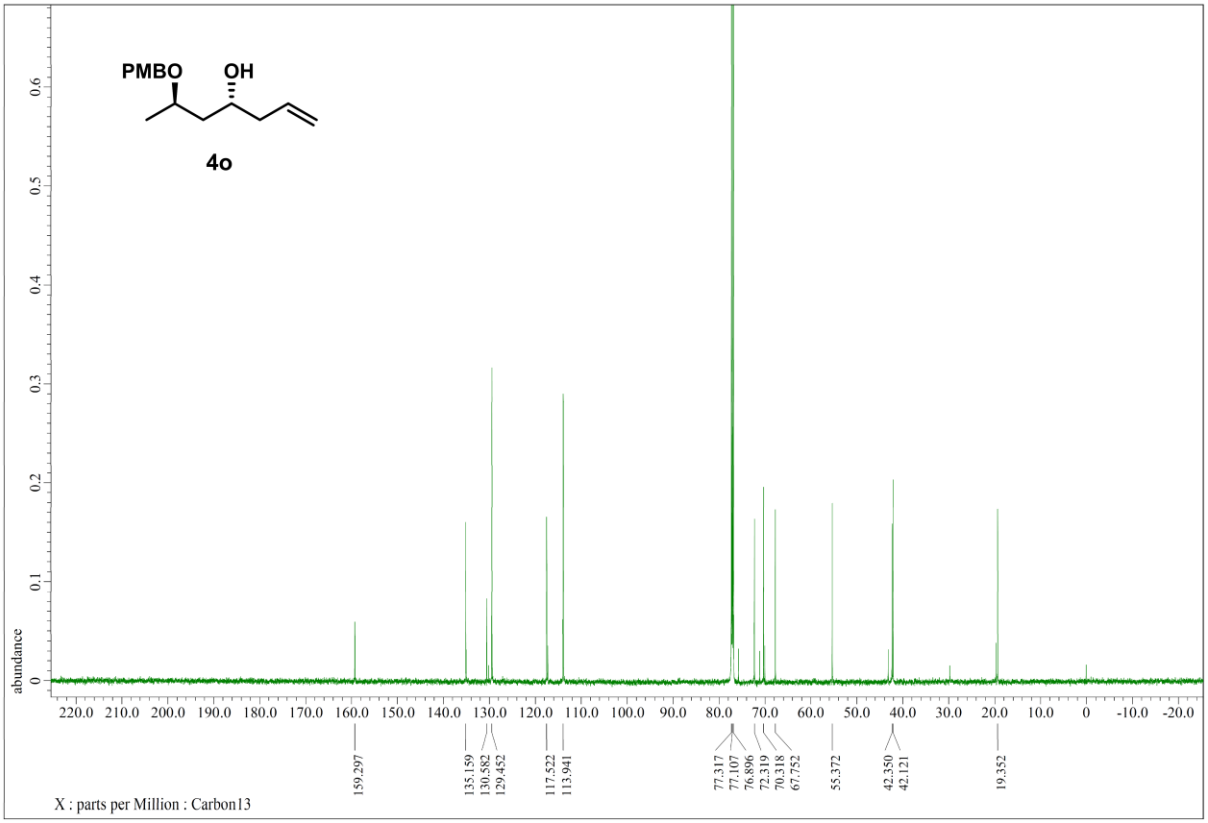
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4n**



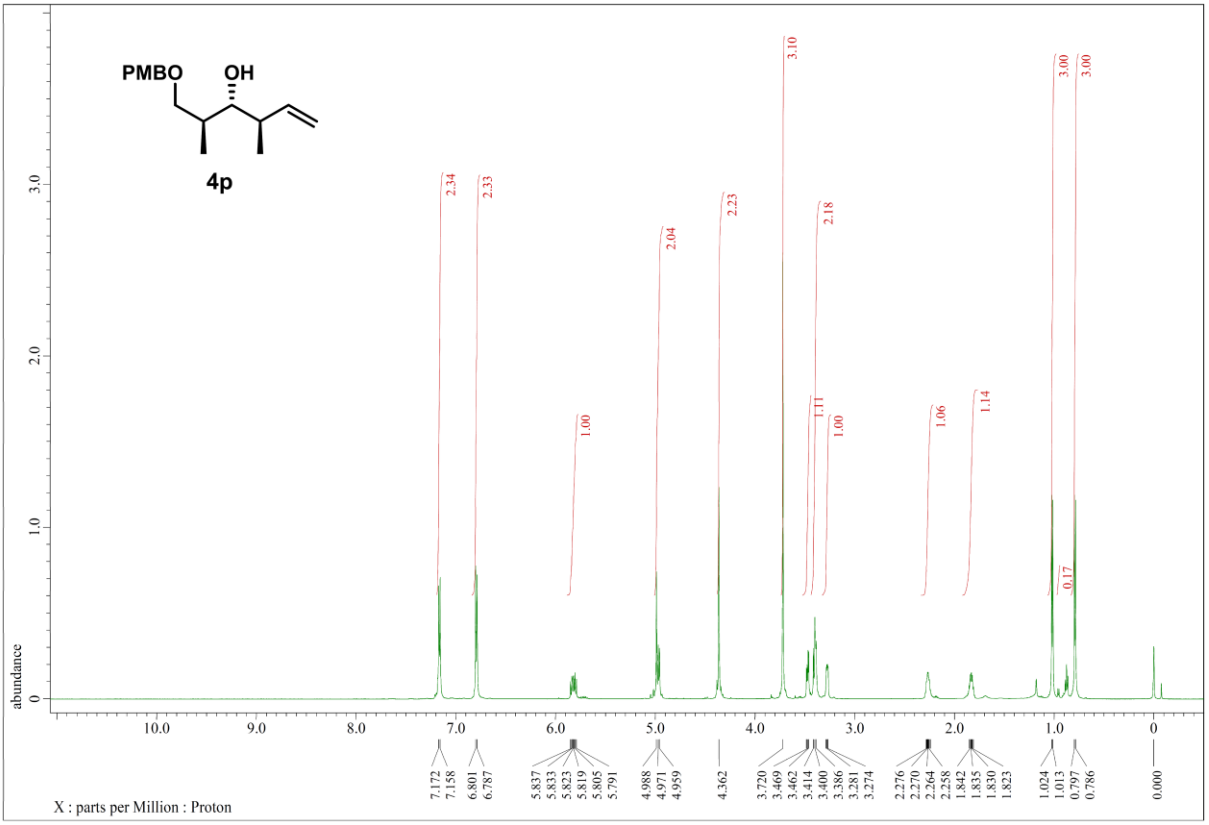


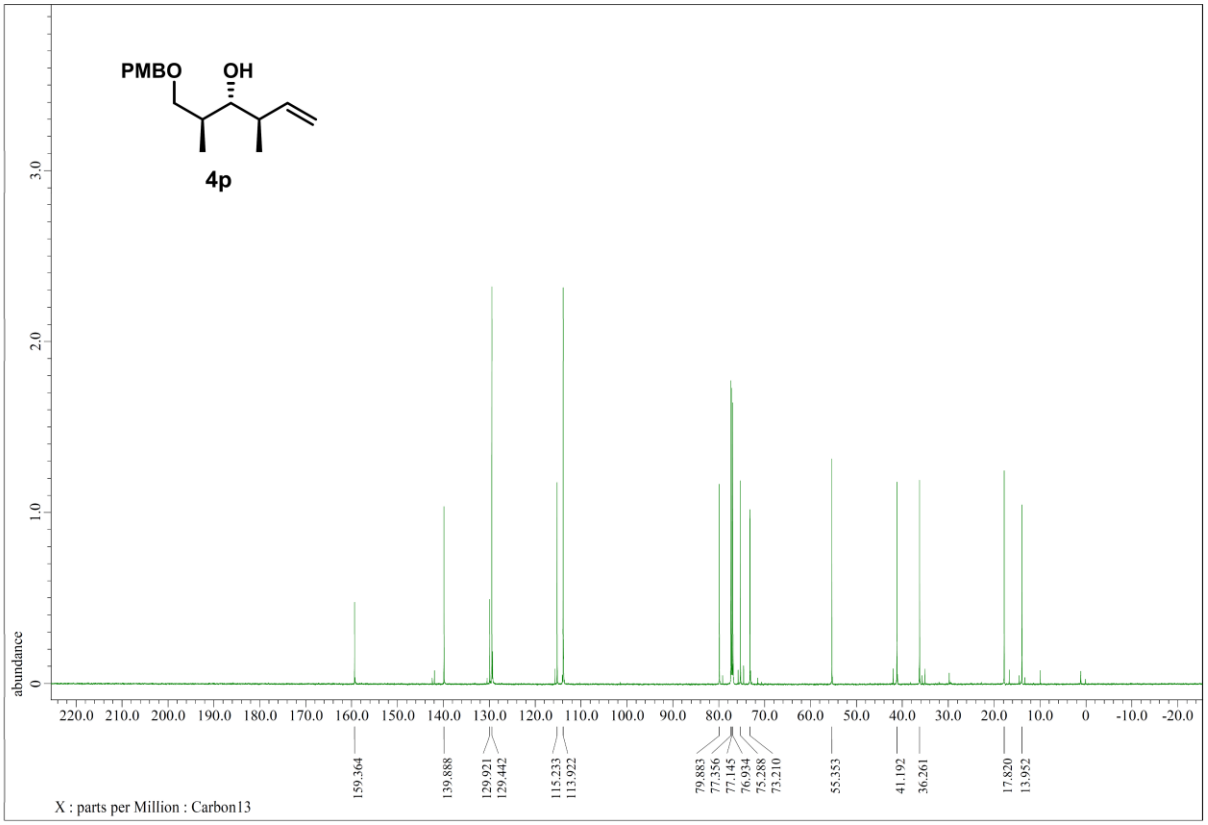
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4o**



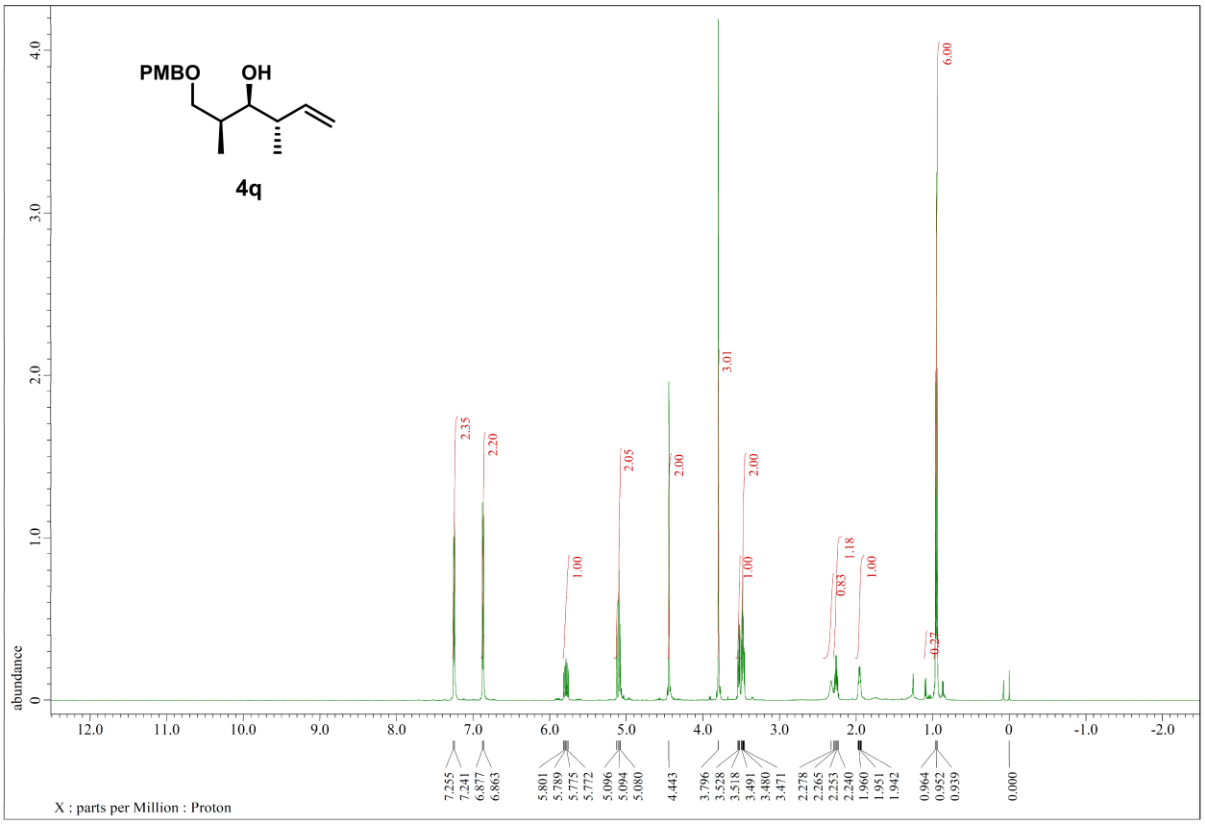


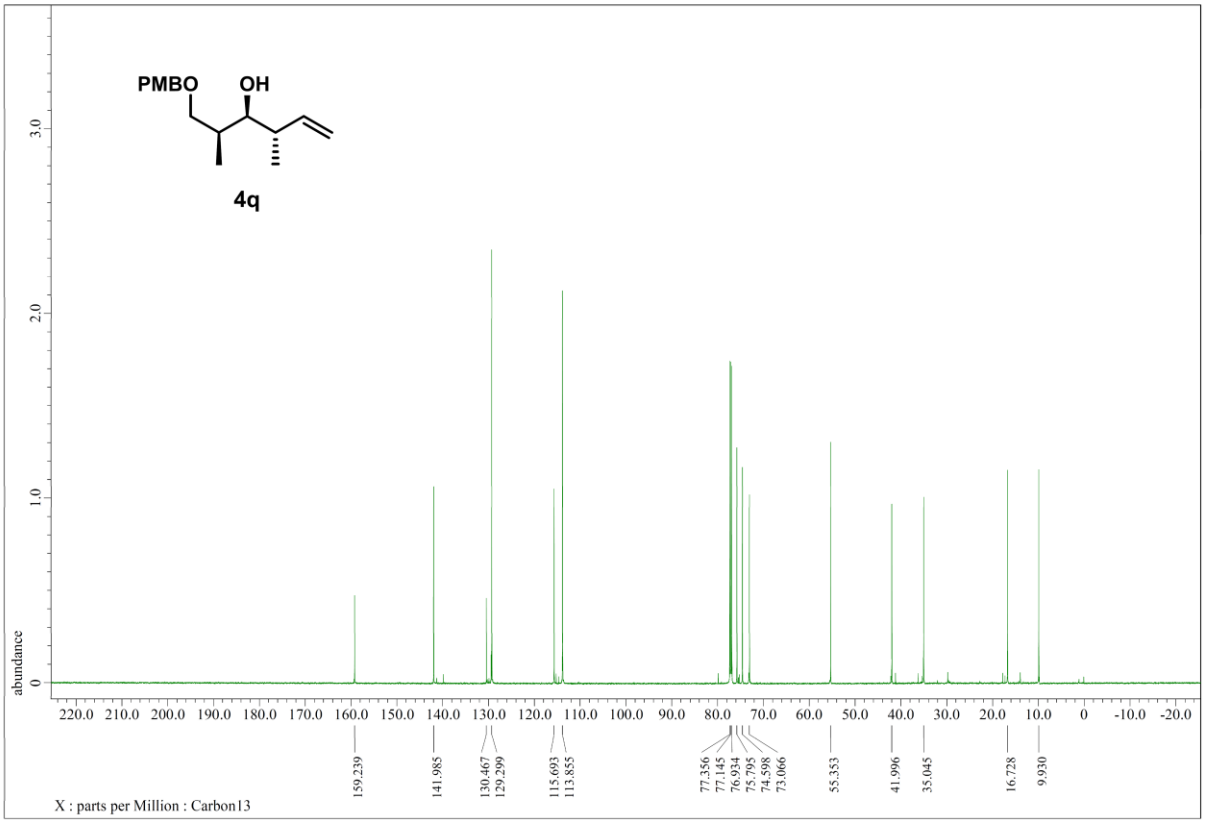
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4p**



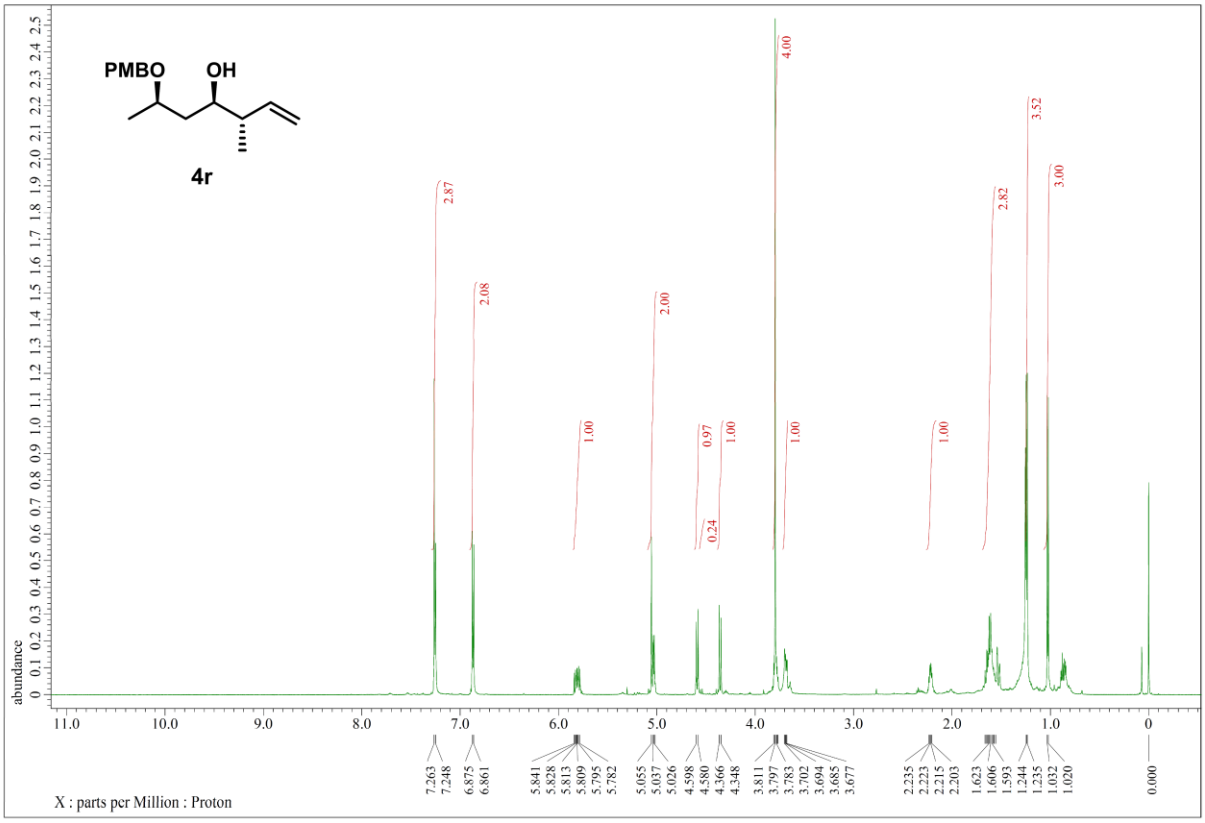


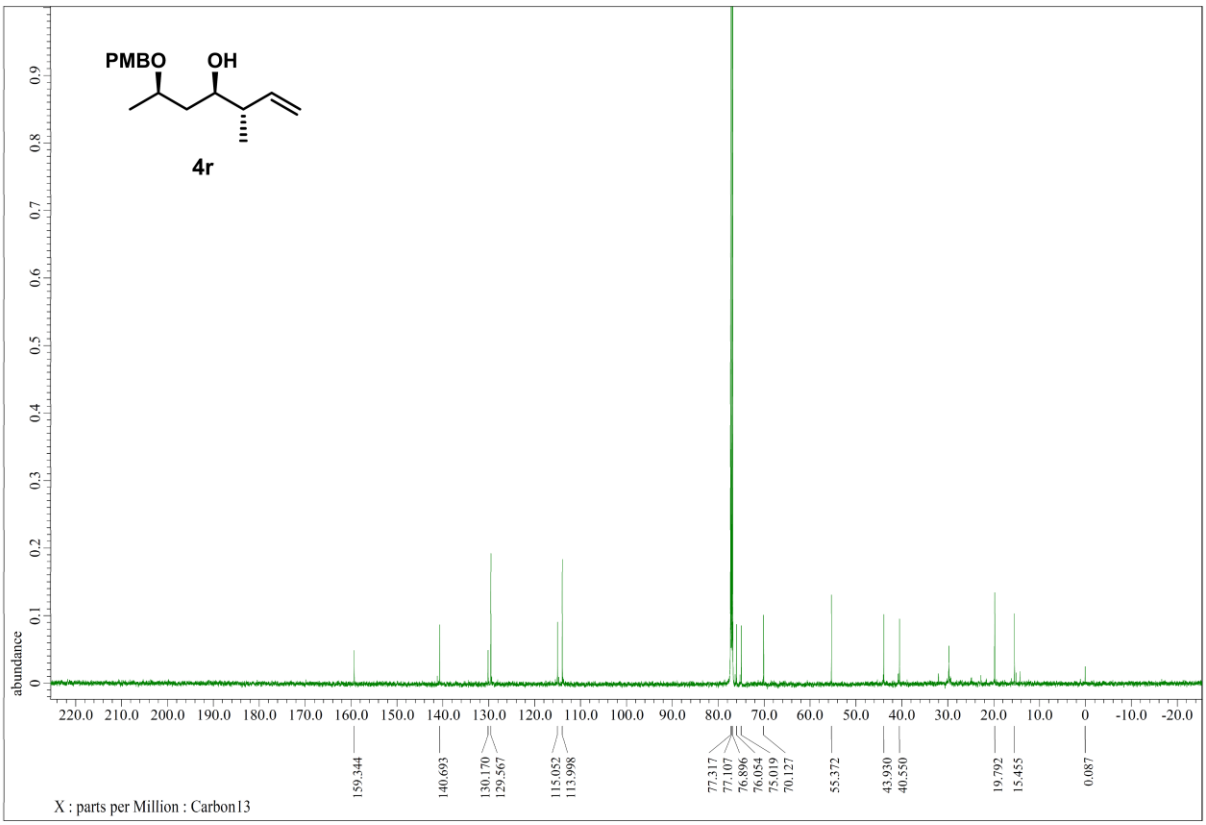
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4q**



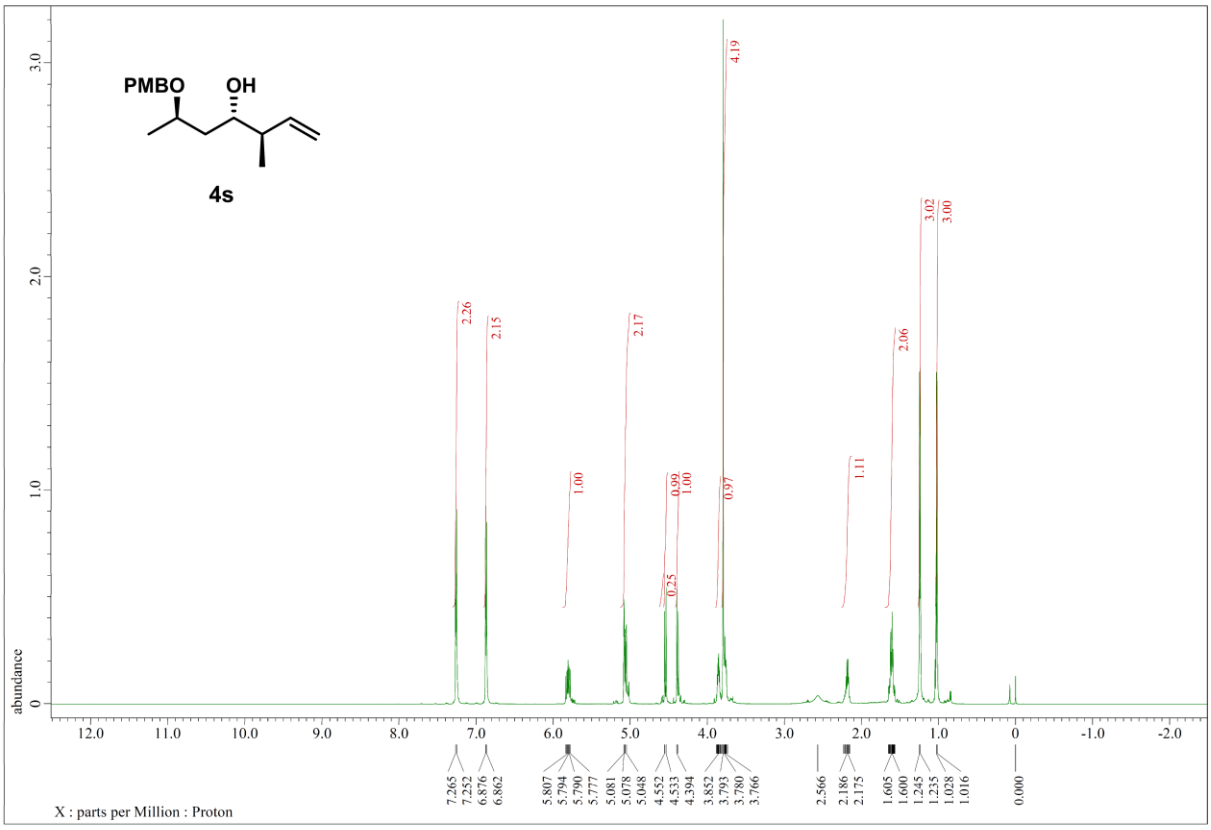


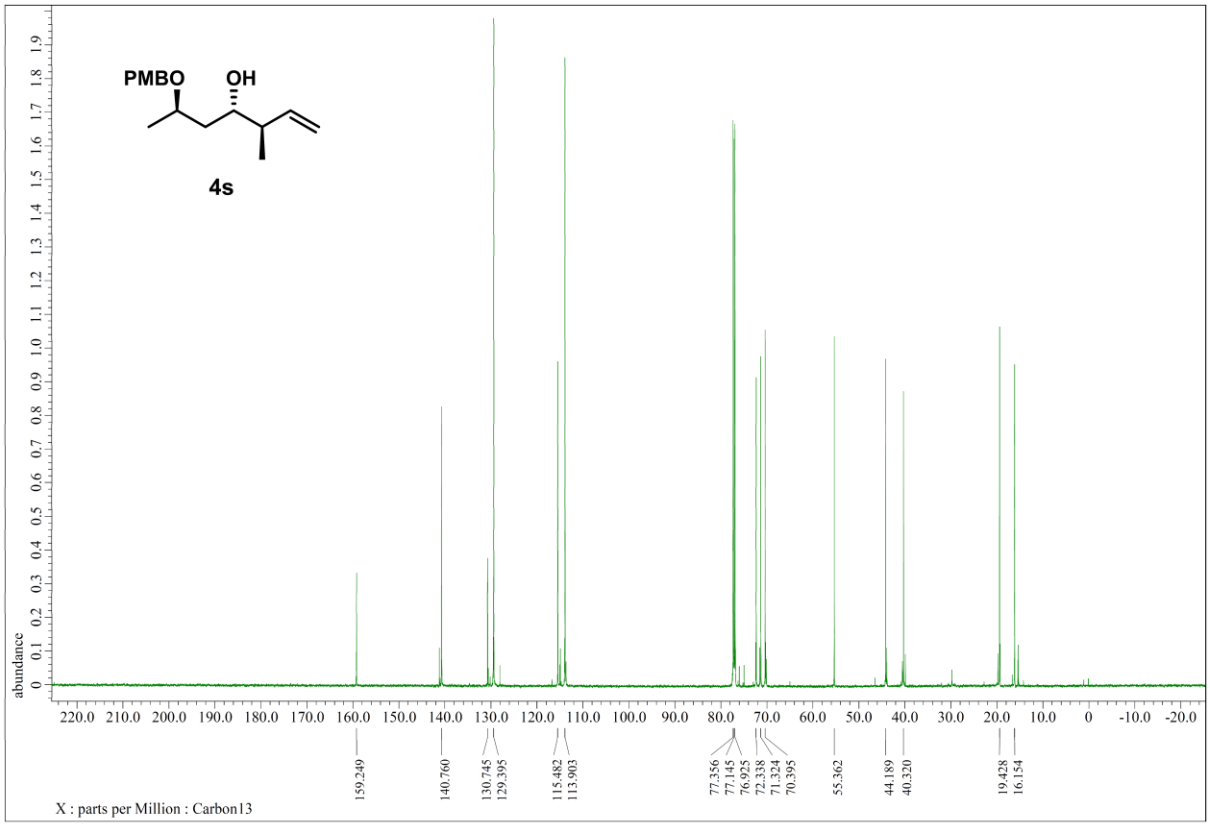
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4r**



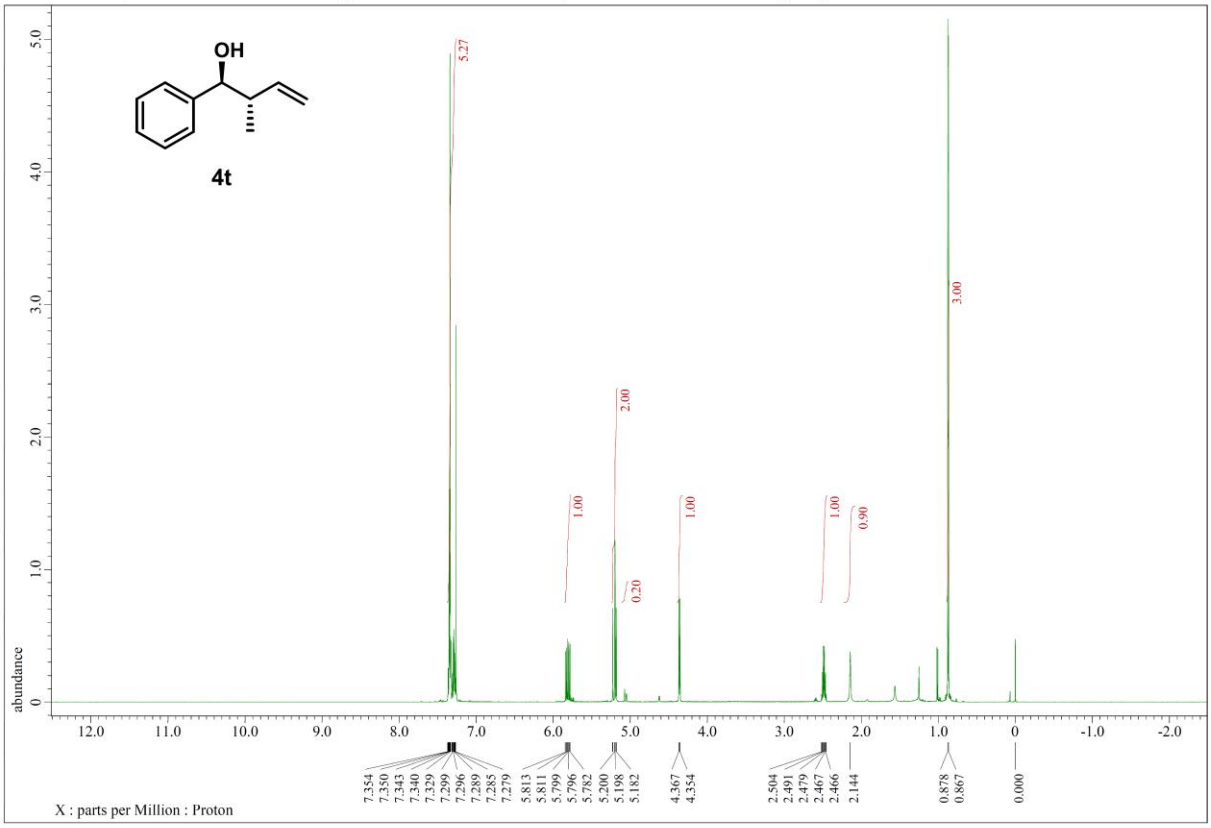


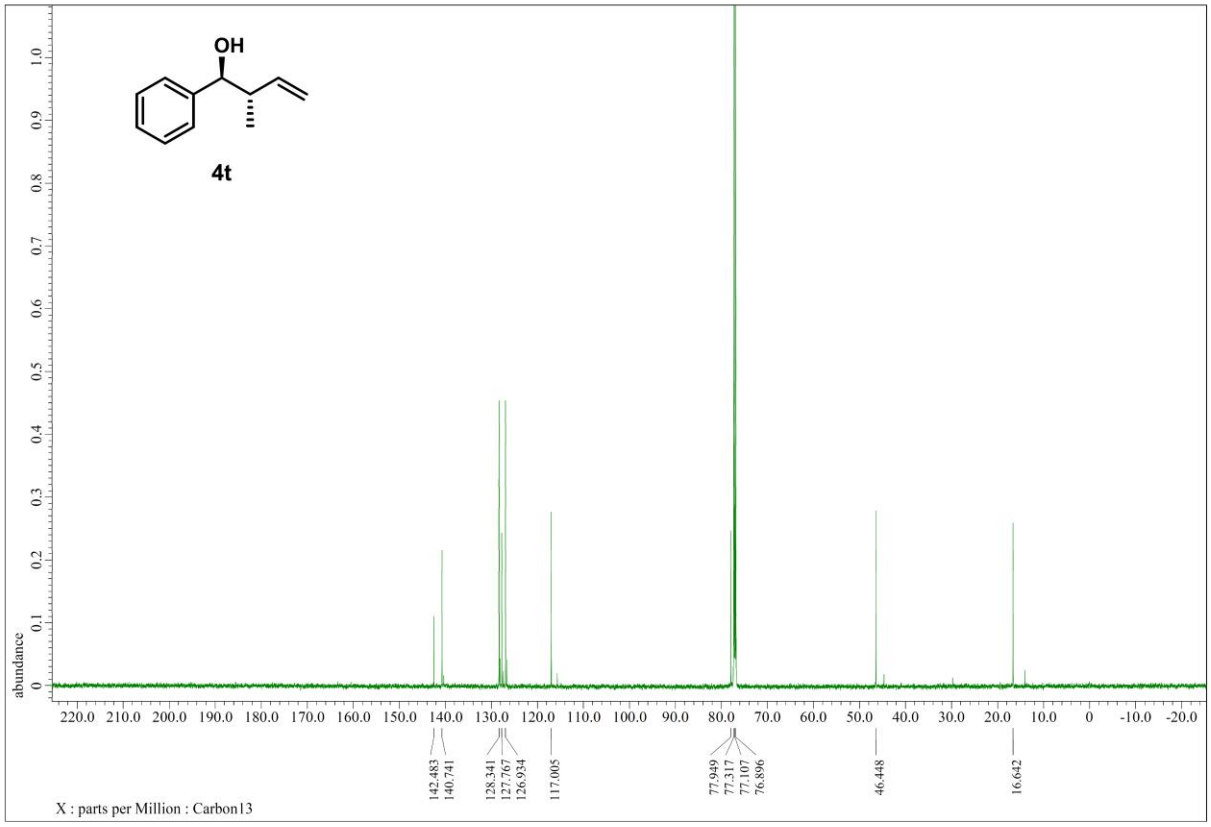
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4s**



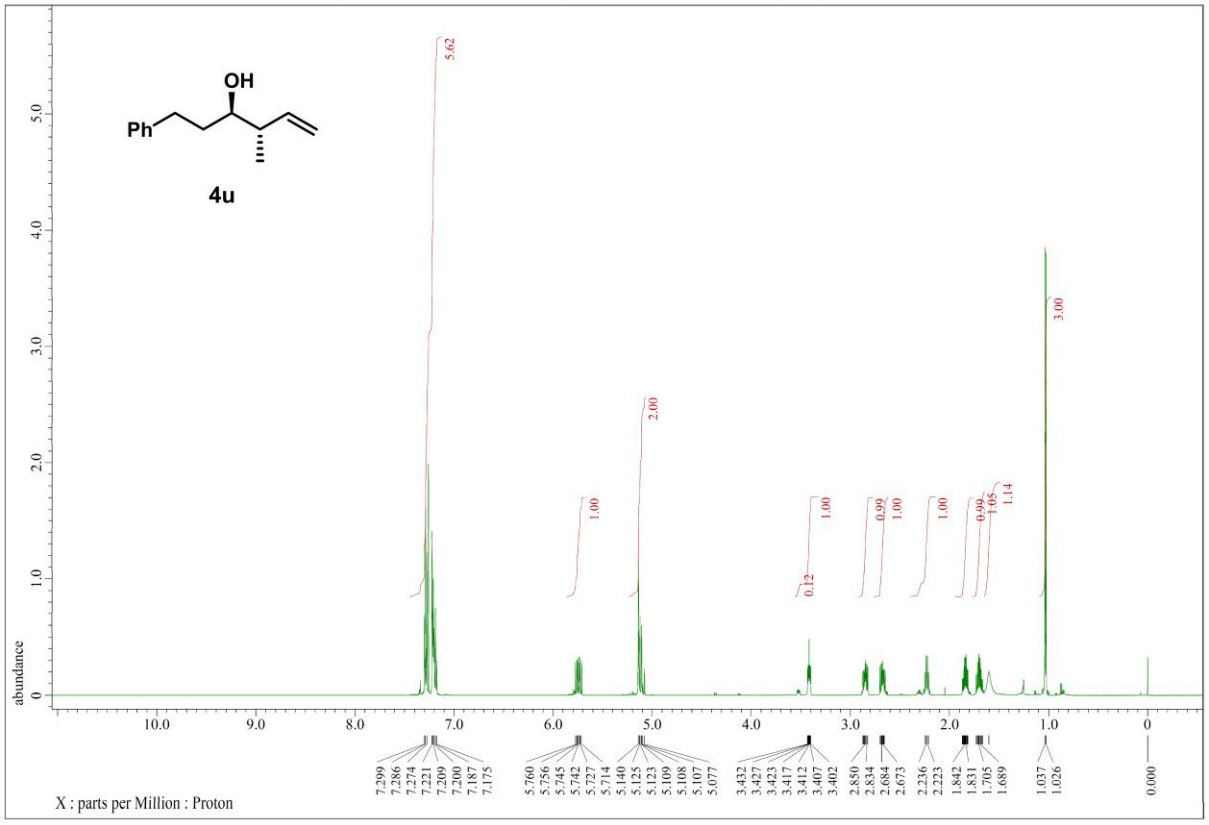


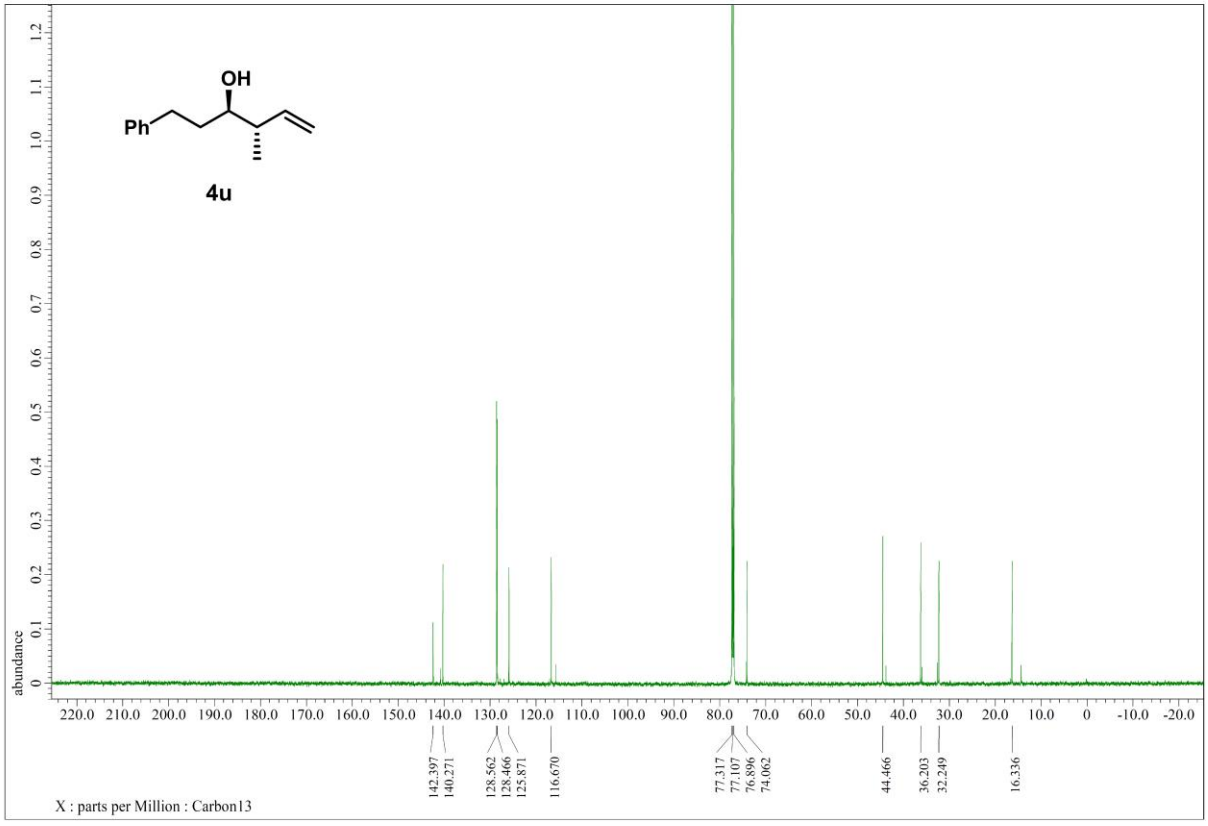
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4t**



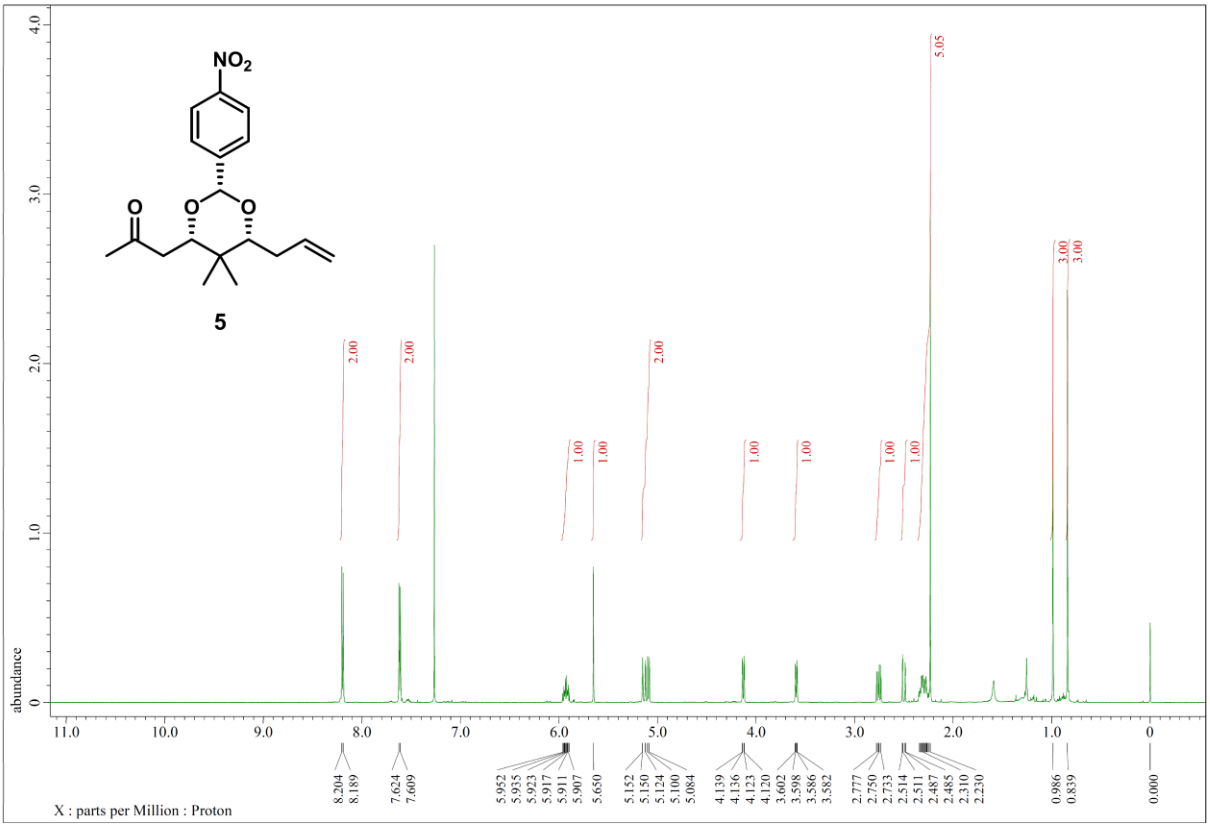


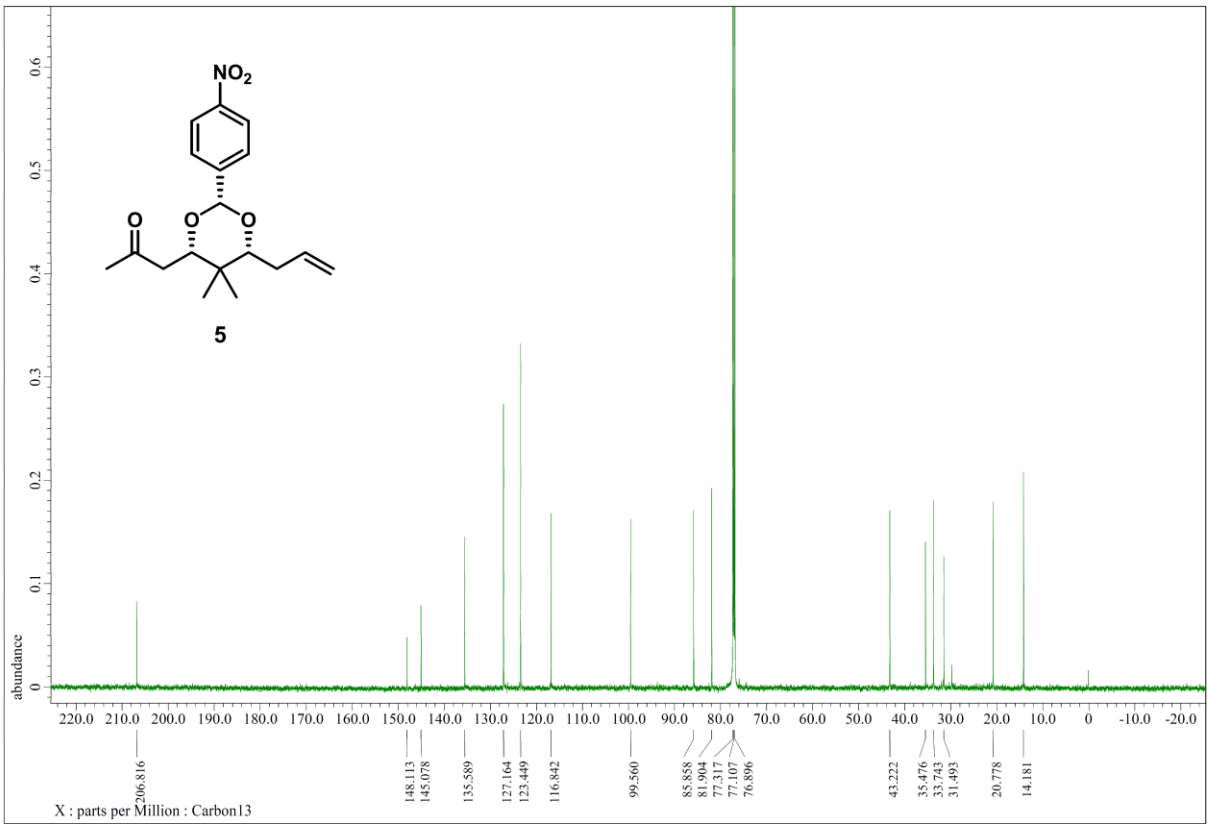
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **4u**



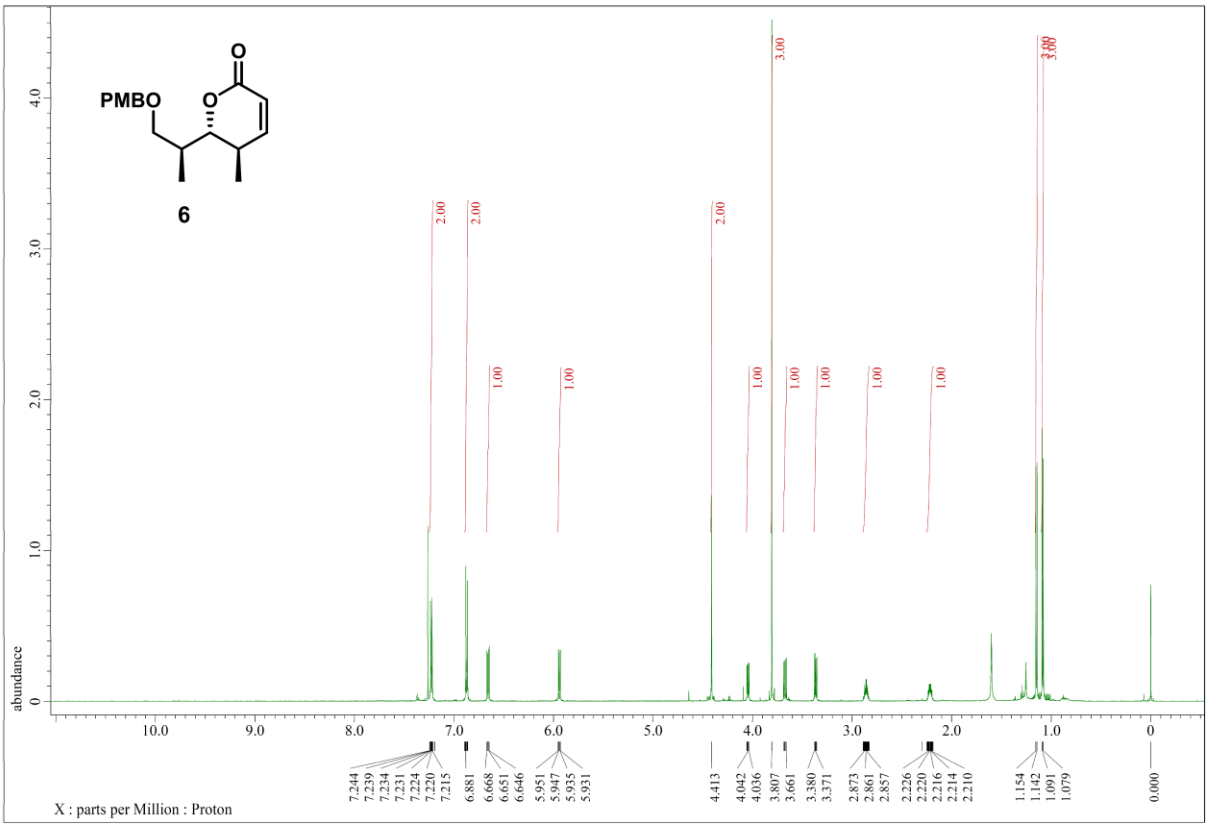


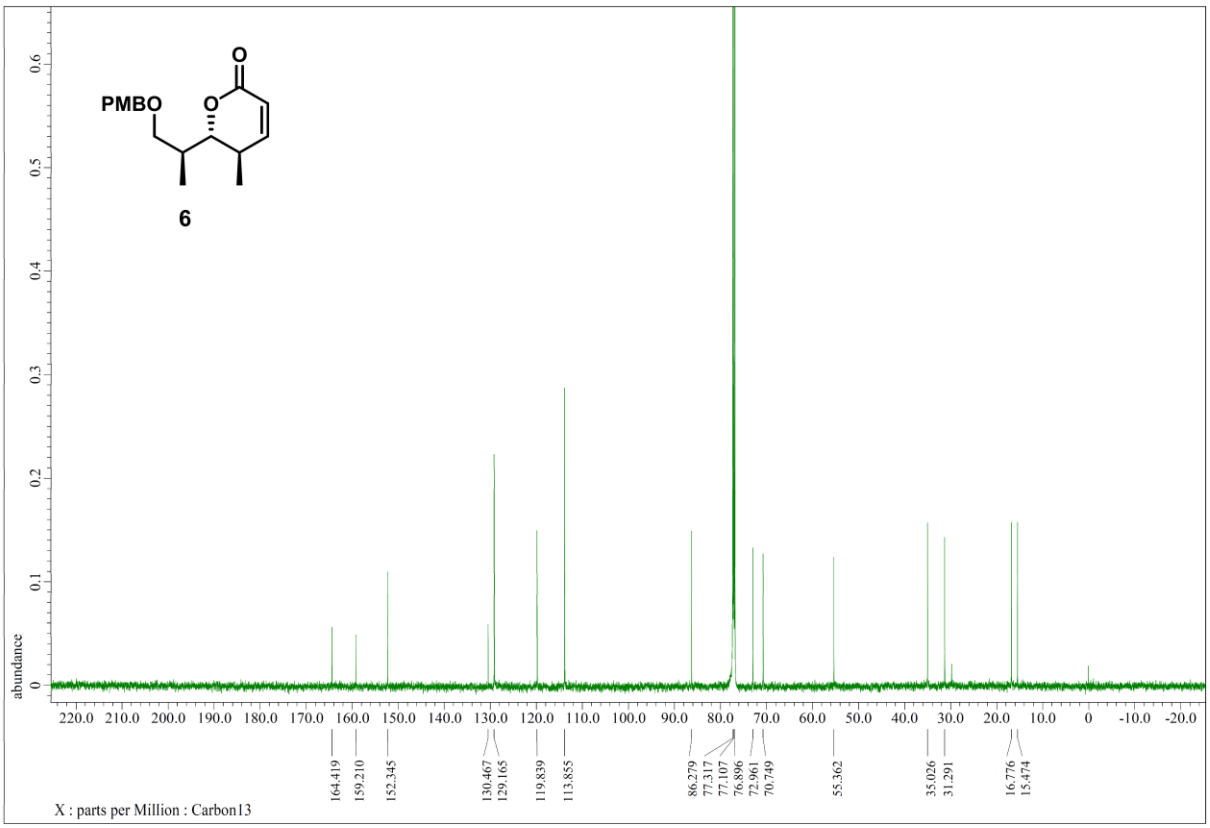
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **5**



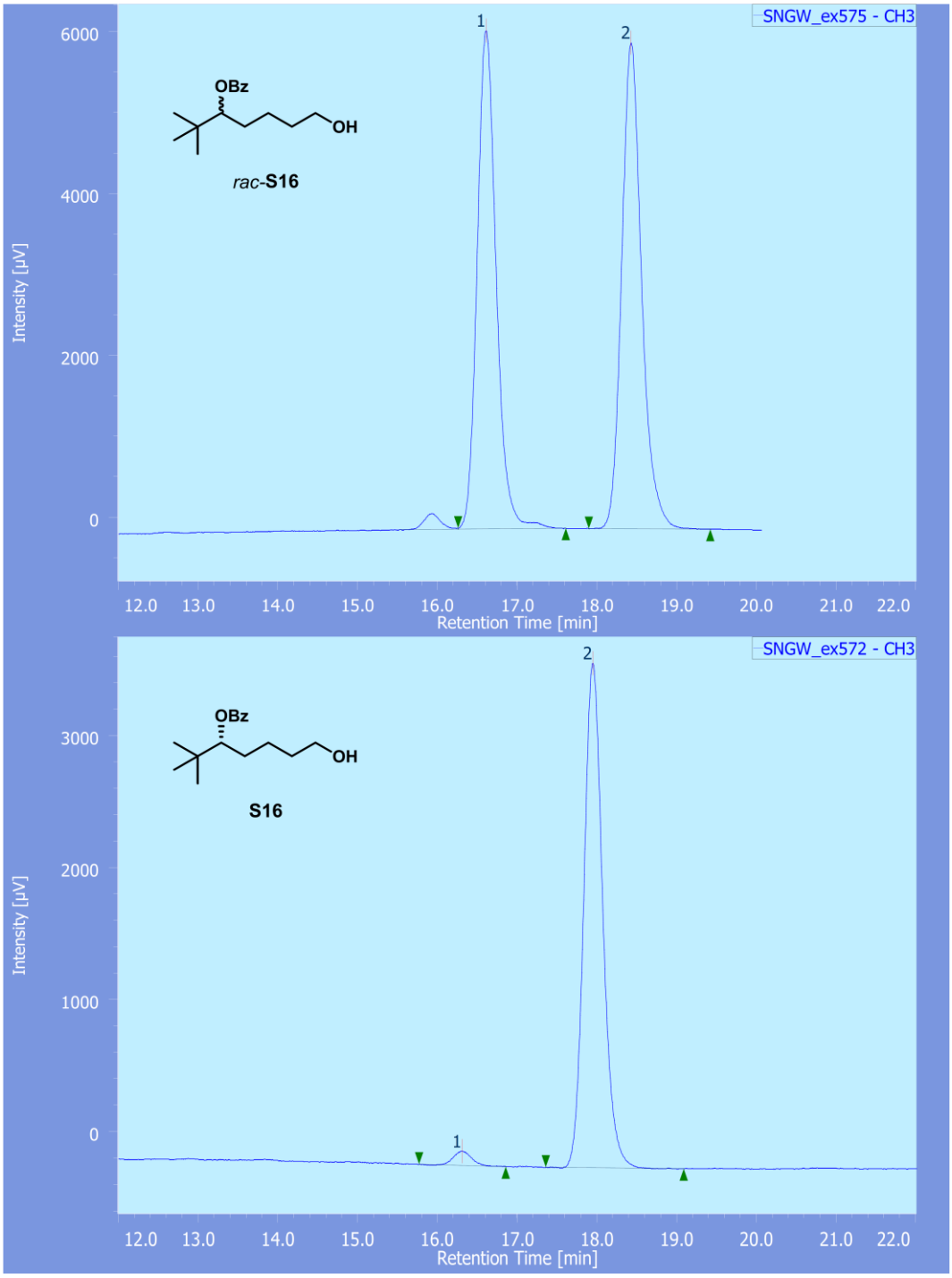


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **6**

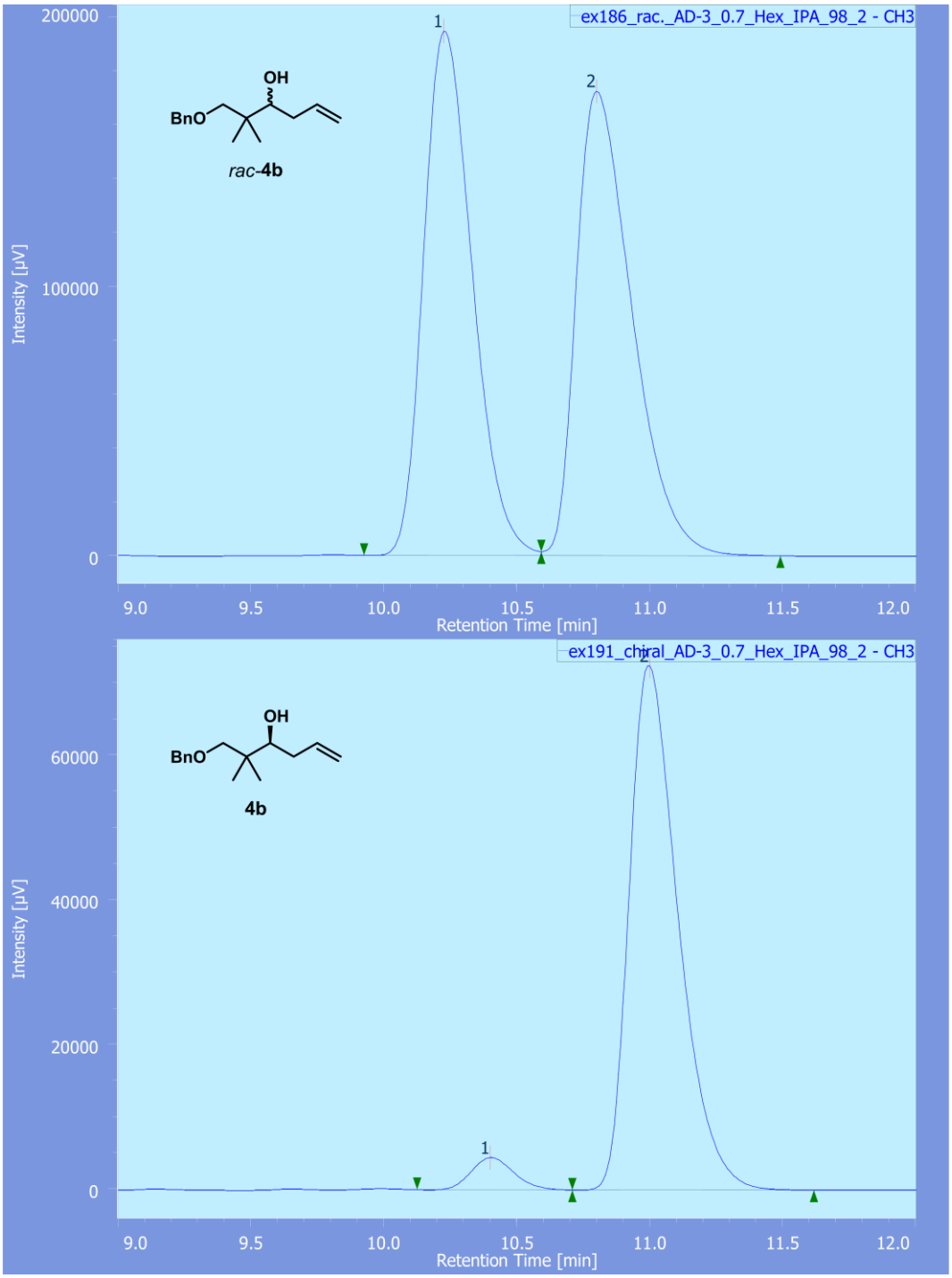




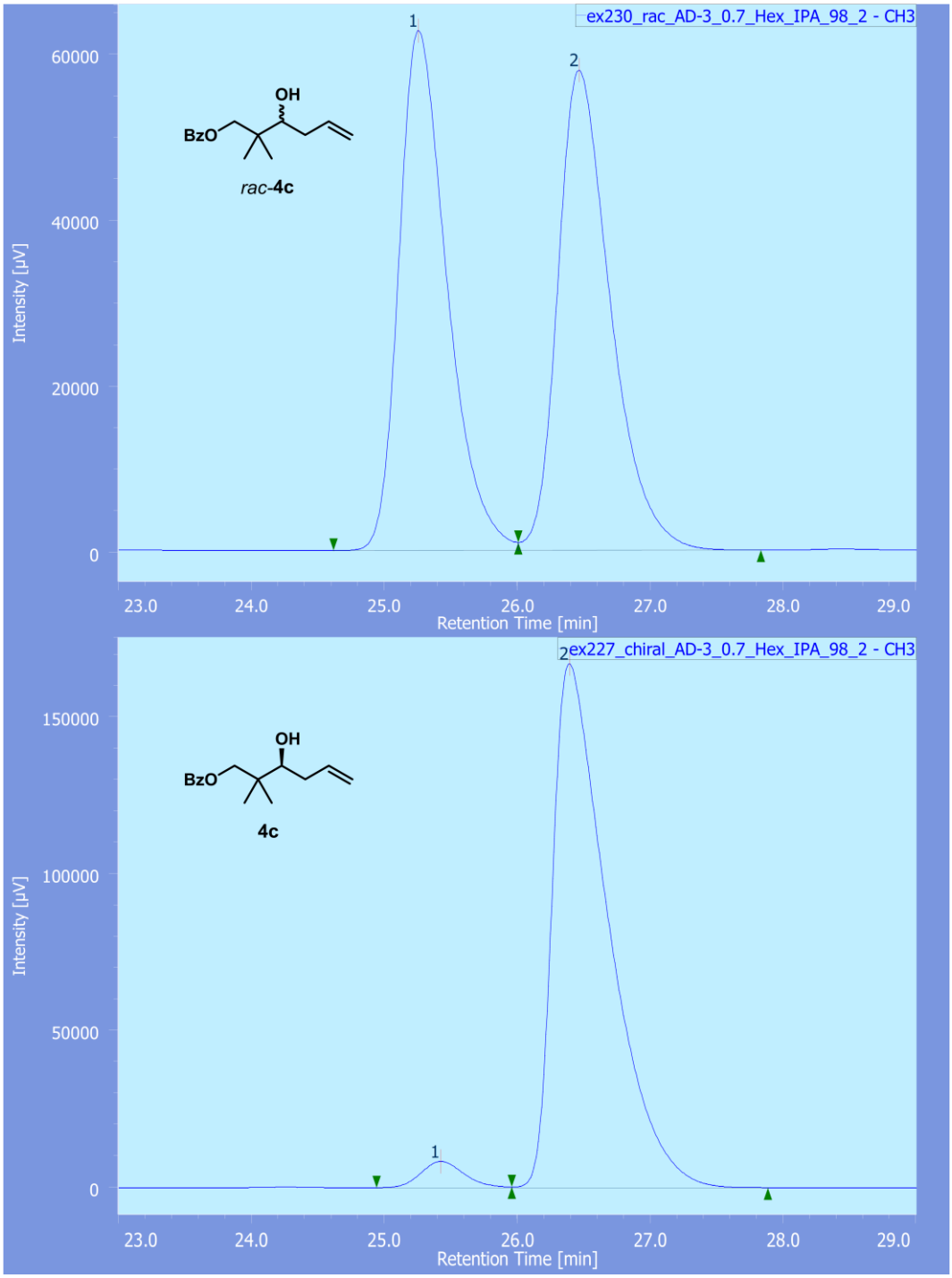
11. HPLC and SFC Charts



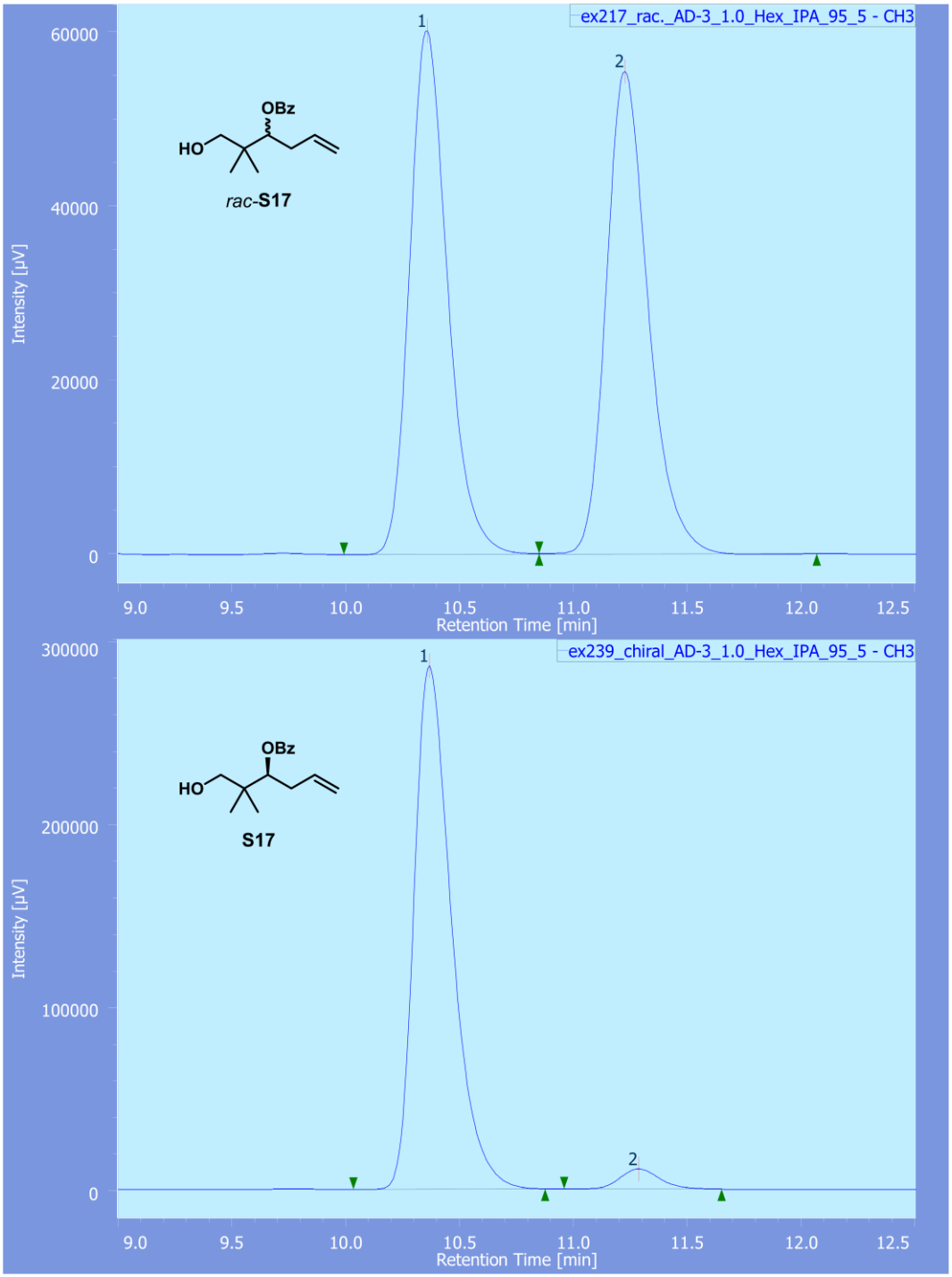
	Retention time (1)	Retention time (2)	% area (1)	% area (2)
rac-**S16**	16.608	18.425	49.548	50.452
S16	16.308	17.950	2.622	97.378



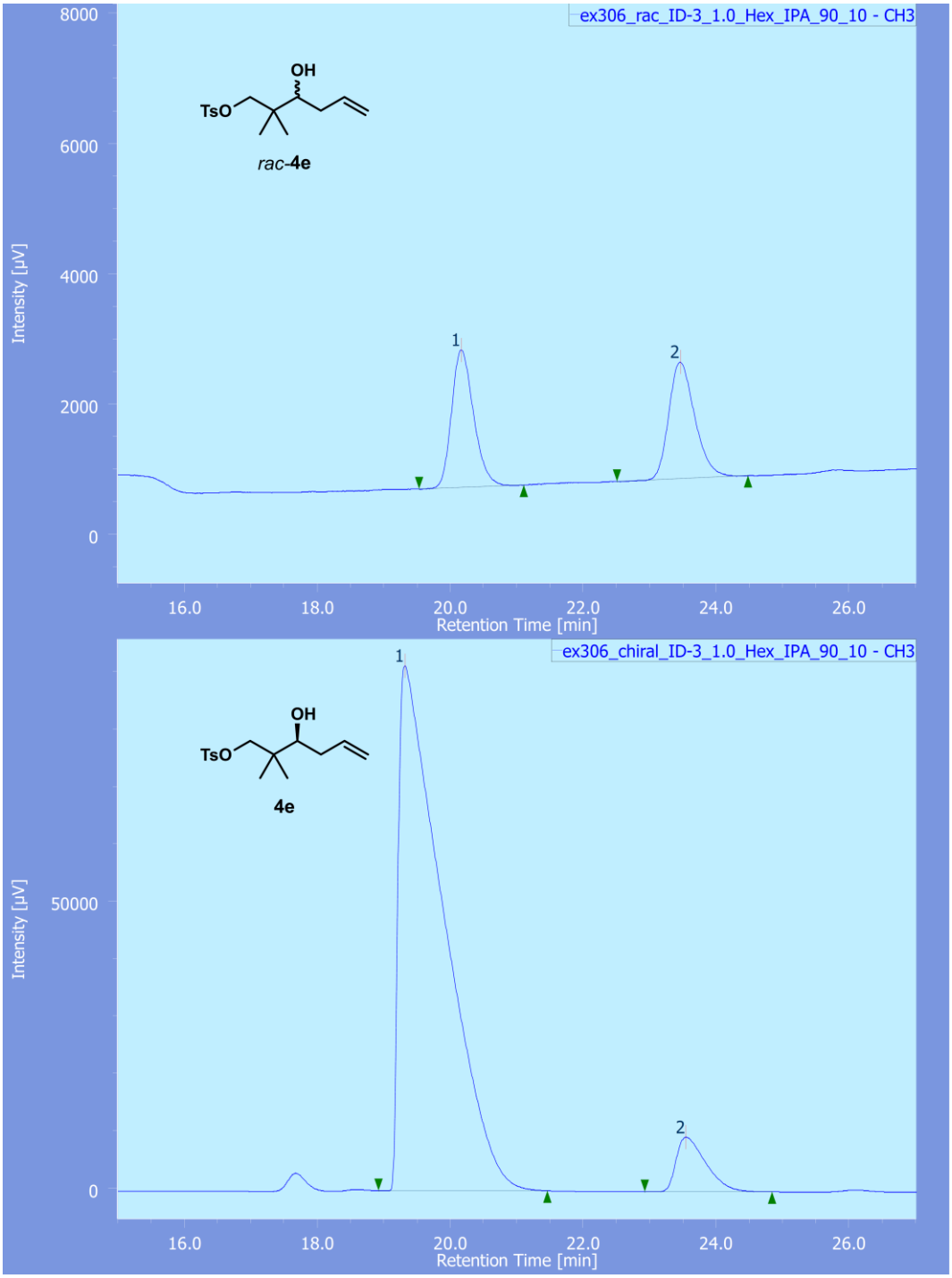
	Retention time (1)	Retention time (2)	% area (1)	% area (2)
rac-**4b**	10.225	10.800	49.786	50.214
4b	10.400	11.000	5.041	94.959



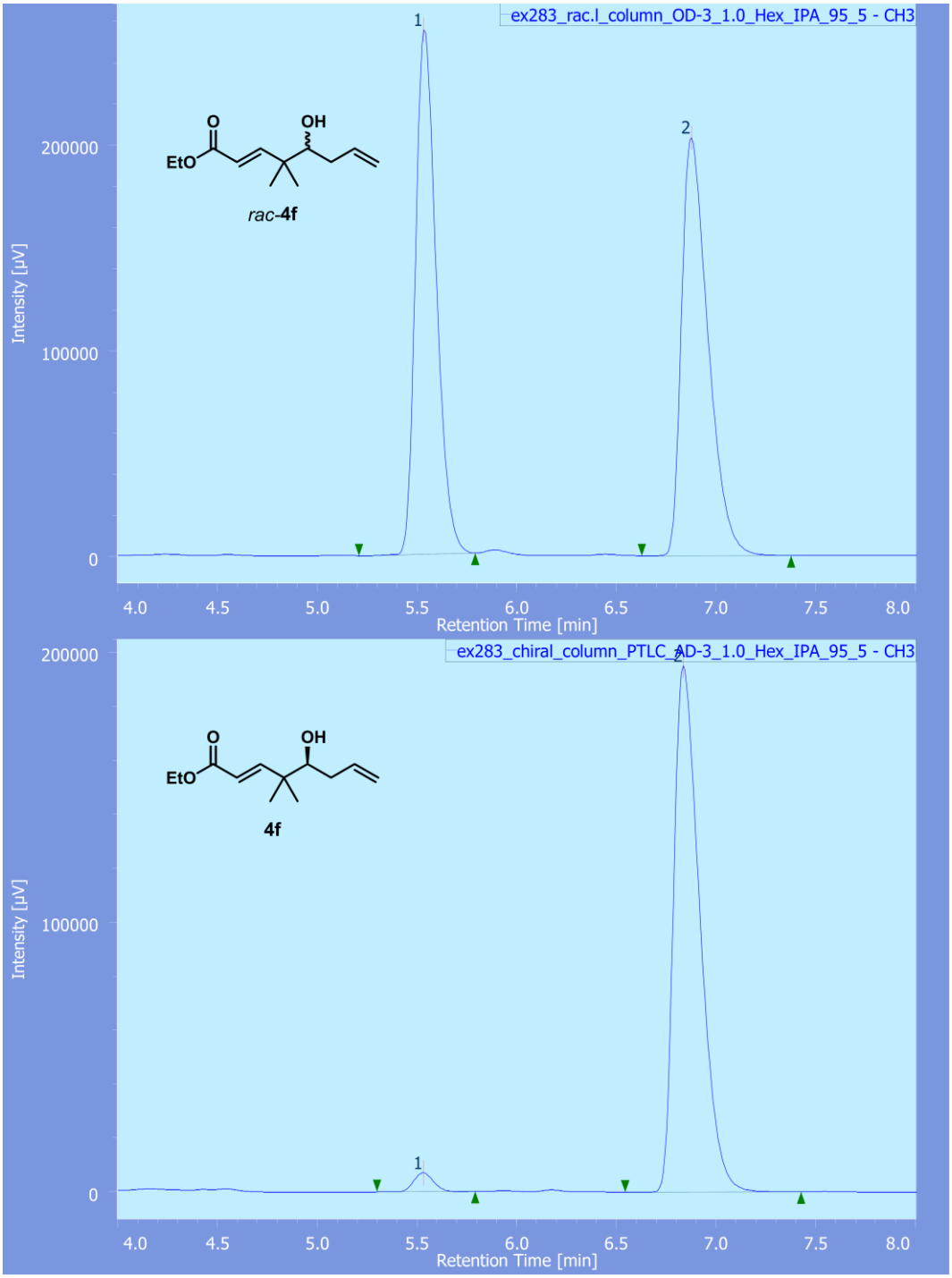
	Retention time (1)	Retention time (2)	% area (1)	% area (2)
rac-**4c**	25.258	26.467	49.744	50.256
4c	25.425	26.392	3.639	96.361



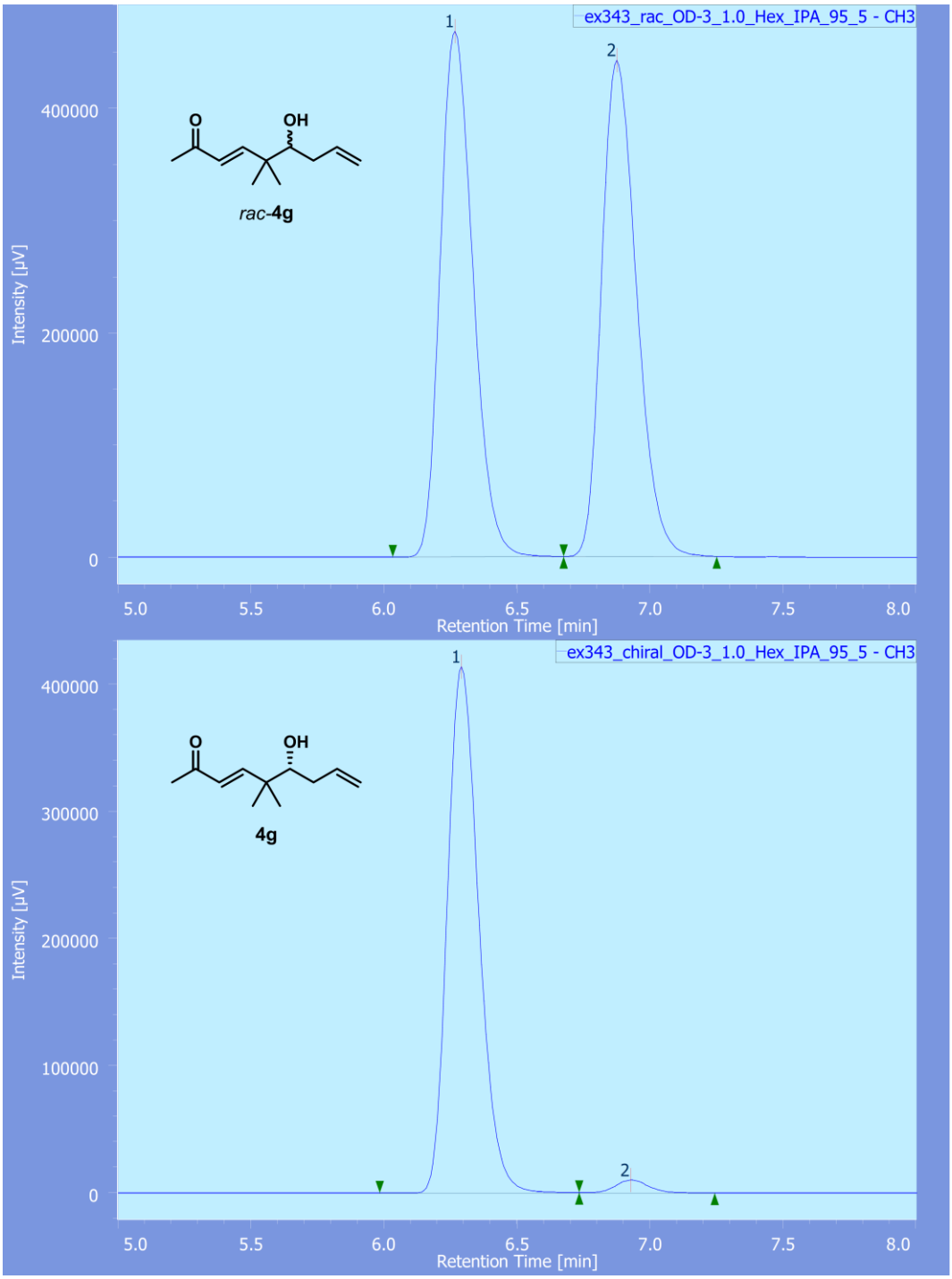
	Retention time (1)	Retention time (2)	% area (1)	% area (2)
rac-**S17**	10.358	11.225	49.731	50.269
S17	10.367	11.283	96.064	3.936



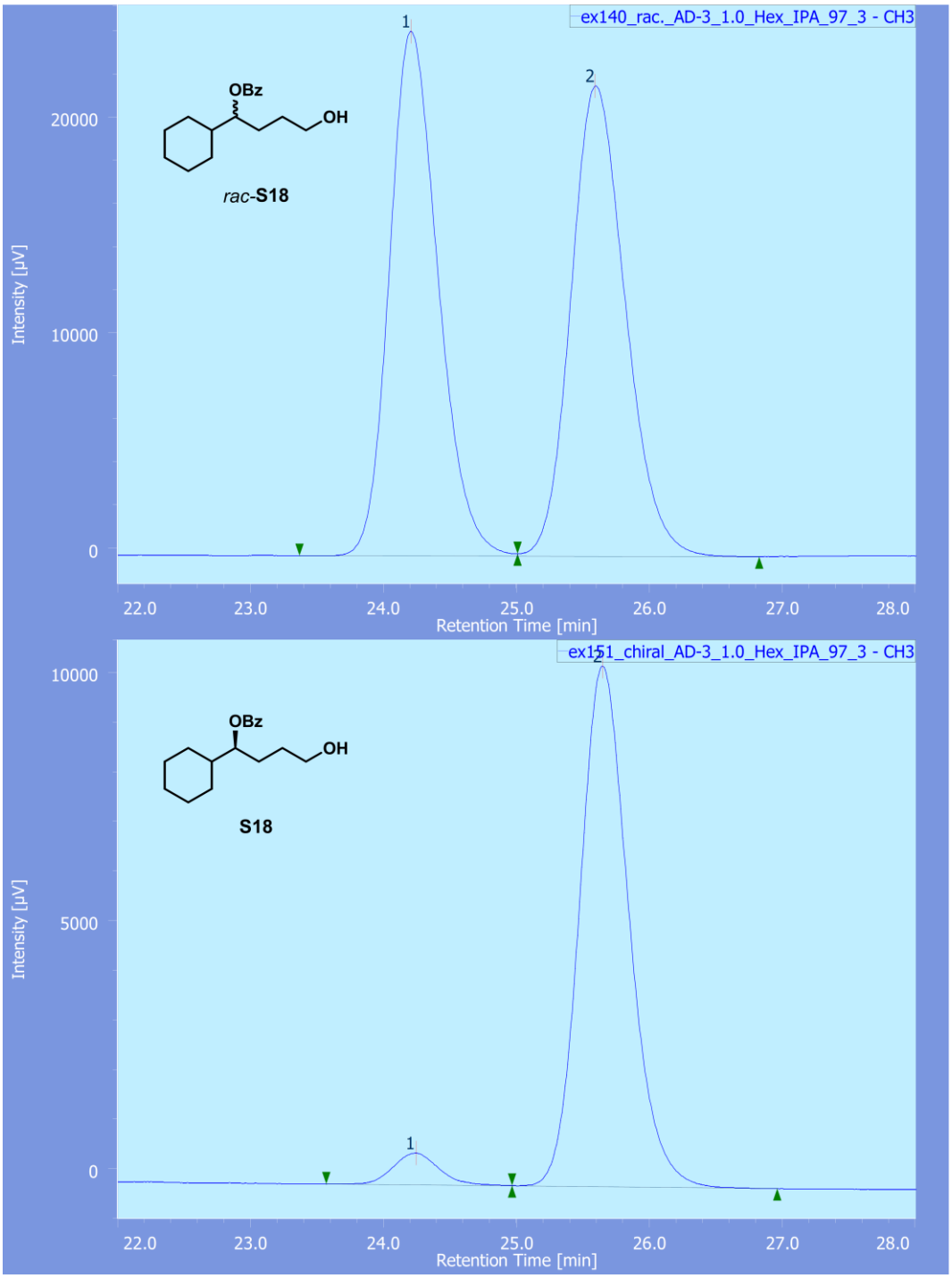
	Retention time (1)	Retention time (2)	% area (1)	% area (2)
rac-**4e**	20.167	23.458	54.110	45.890
4e	19.317	23.542	93.520	6.480



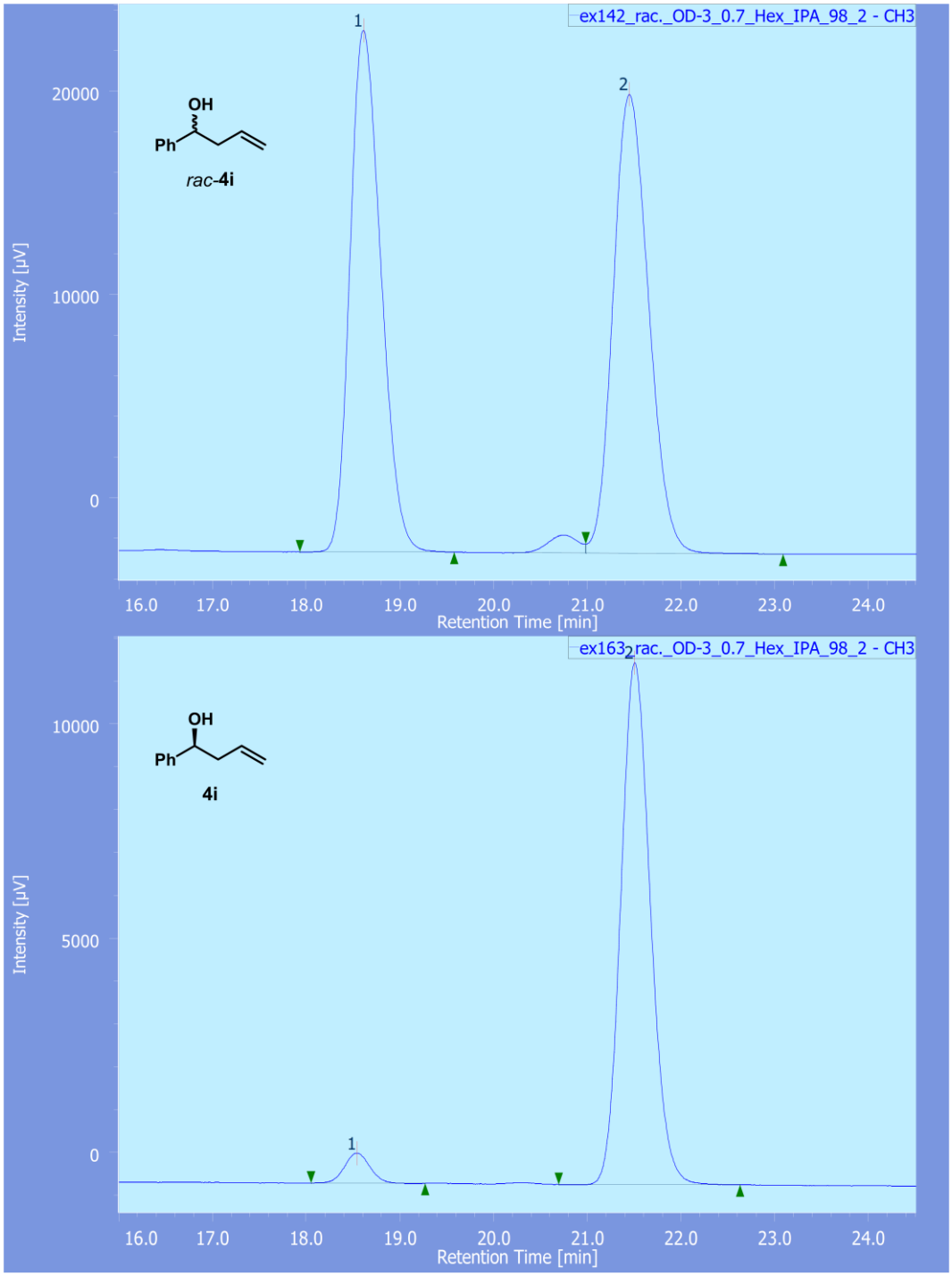
	Retention time (1)	Retention time (1)	% area (1)	% area (2)
rac-**4f**	5.533	6.875	49.596	50.404
4f	5.533	6.833	2.596	97.404



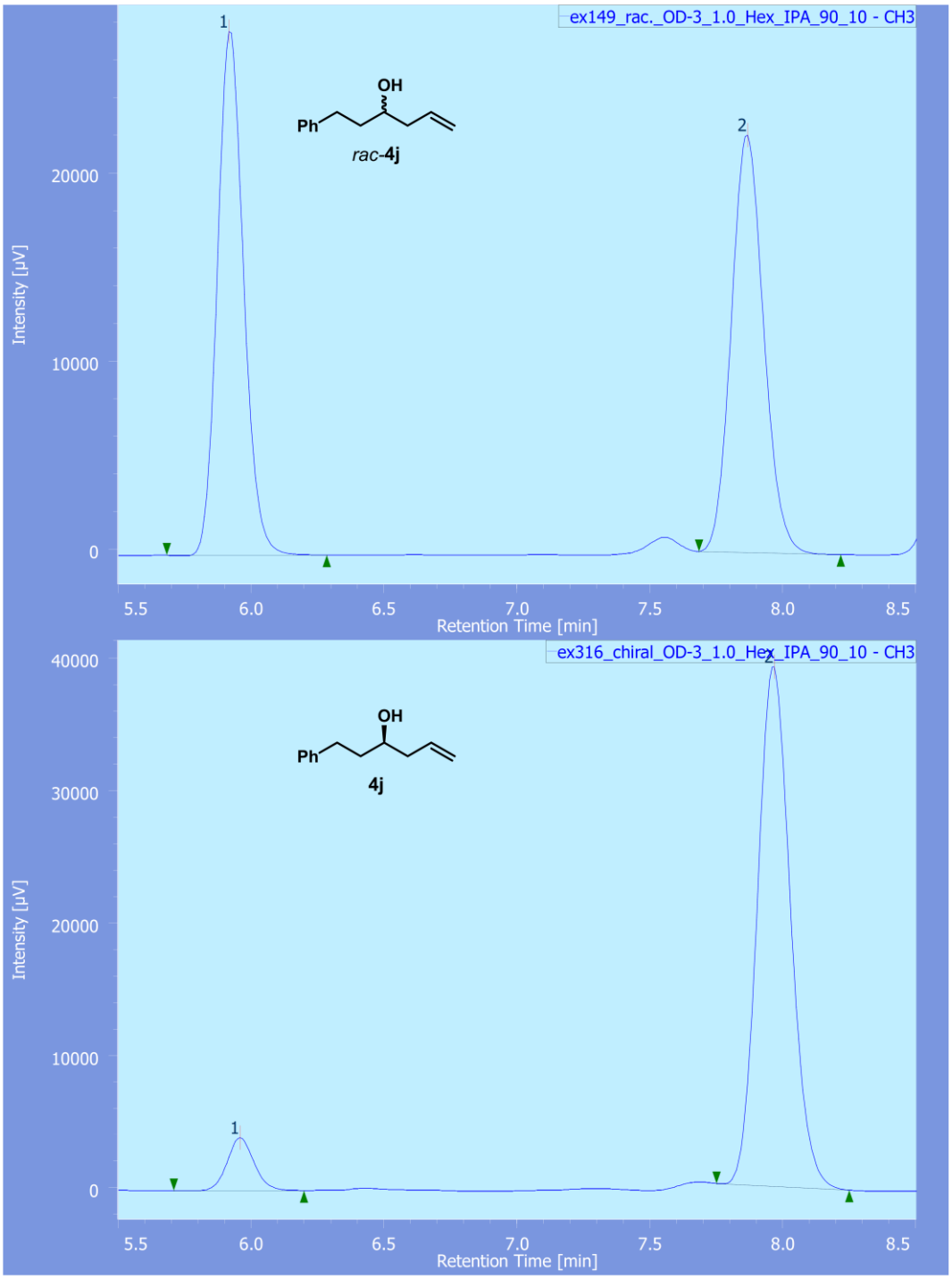
	Retention time (1)	Retention time (2)	% area (1)	% area (2)
rac-**4g**	6.267	6.875	49.933	50.067
4g	6.292	6.925	97.434	2.566



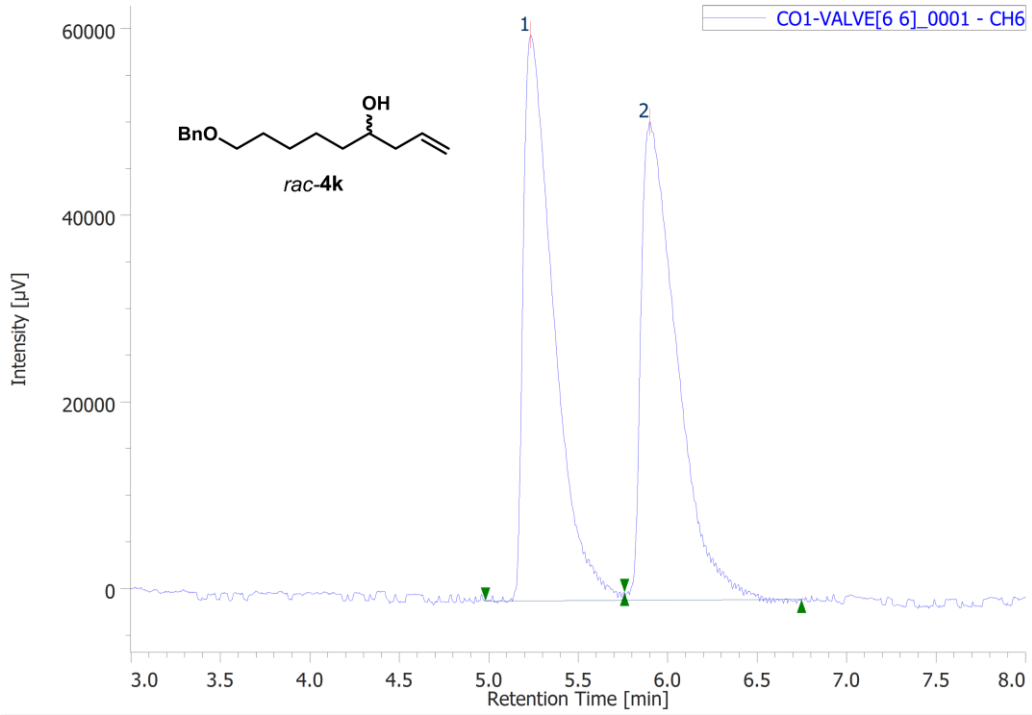
	Retention time (1)	Retention time (2)	% area (1)	% area (2)
rac-**S18**	24.208	25.592	49.994	50.006
S18	24.242	25.650	5.765	94.235

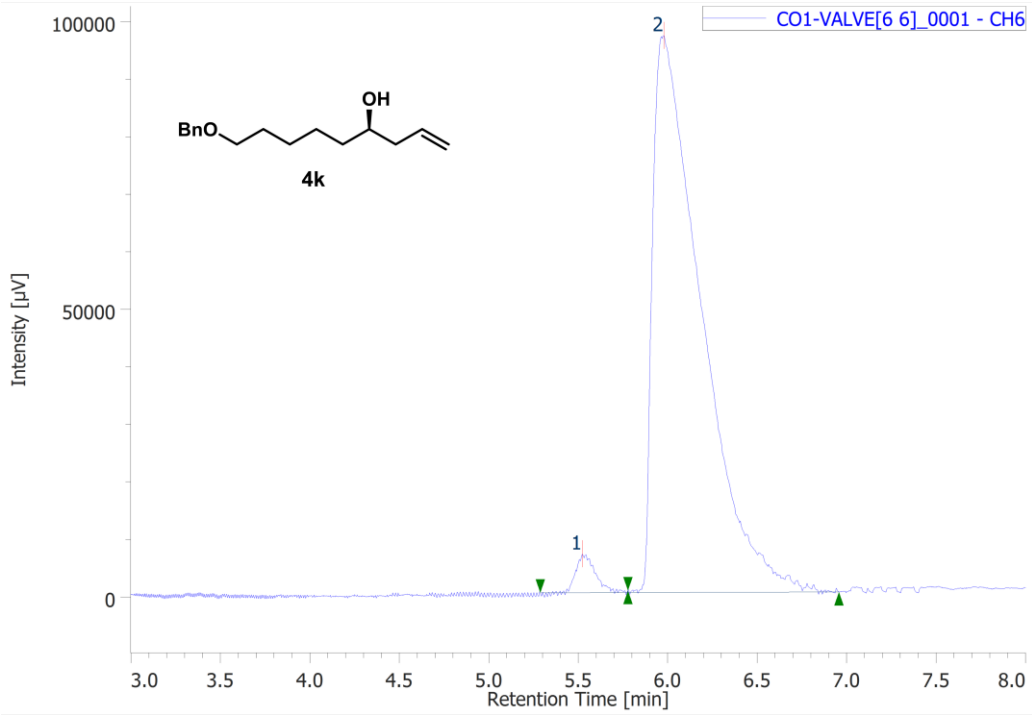


	Retention time (1)	Retention time (2)	% area (1)	% area (2)
rac-**4i**	18.608	21.442	49.869	50.131
4i	18.542	21.500	4.760	94.557

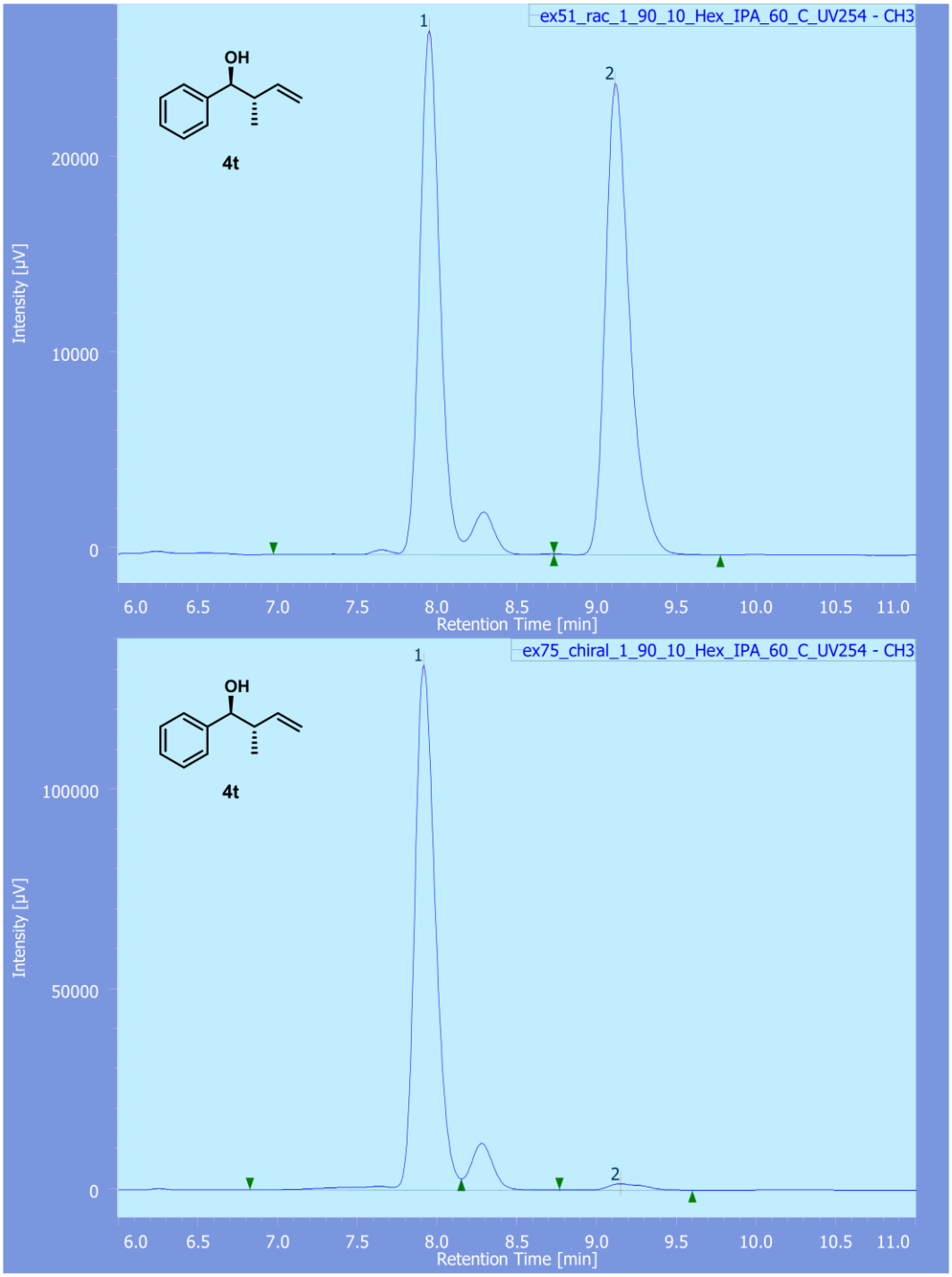


	Retention time (1)	Retention time (2)	% area (1)	% area (2)
rac-**4j**	5.917	7.867	50.408	49.592
4j	5.958	7.967	7.653	92.347

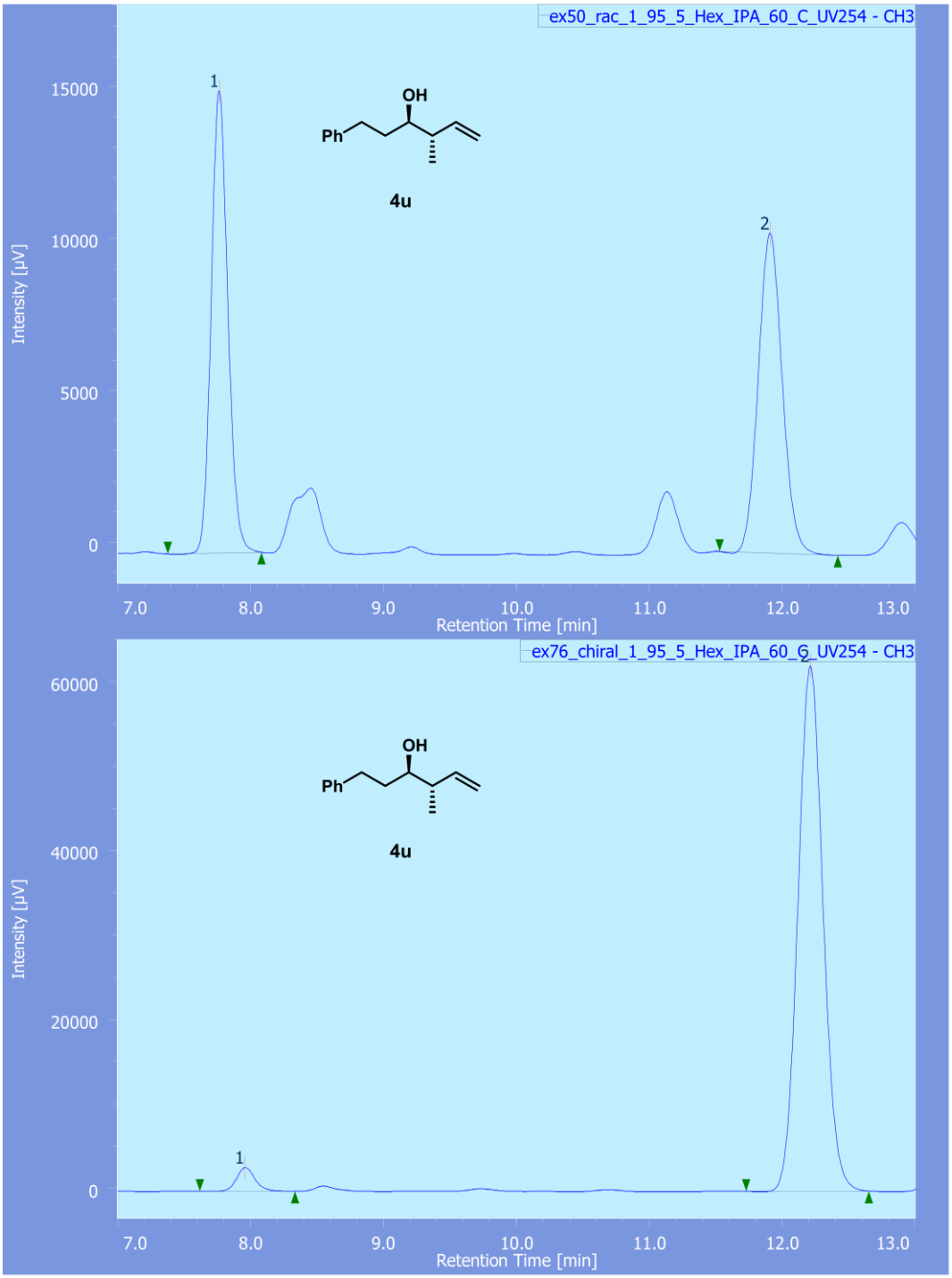




	Retention time (1)	Retention time (2)	% area (1)	% area (2)
rac-**4k**	5.233	5.900	50.137	49.863
4k	5.523	5.978	2.727	97.273



	Retention time (1)	Retention time (2)	% area (1)	% area (2)
rac-**4t**	7.950	9.117	50.330	49.670
4t	7.917	9.150	97.963	2.037



	Retention time (1)	Retention time (2)	% area (1)	% area (2)
rac-**4u**	7.767	11.908	50.179	49.821
4u	7.958	12.208	3.270	96.730