Supplementary Information (SI) for Organic & Biomolecular Chemistry.
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Supporting Information

Diastereoselective oxidative cyclization of 1,4-dienes for the synthesis of oxetanes

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Table of contents

1. Materials and Methods S2
2. Investigation of Oxidative Cyclization Conditions S3
3. Structure Determination of Oxidative Cyclization Products S4
4. Preparation and Characterization of Substrates S5
5. General Methods for Oxidative Cyclization S12
6. Characterization of Oxidative Cyclization Products S13
7. Derivatization of Oxidation Cyclization Products S16
8. References S18
9. X-ray Crystal Data S19
10. Selected NMR Spectra S20

1. Materials and Methods

General

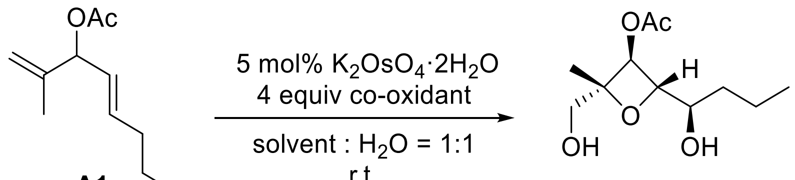
^{1}H, ^{13}C NMR spectra were recorded on Bruker Avance III 400 (400MHz) (100 MHz) or Jeol (400 MHz) (100 MHz) spectrometer. Chemical shifts are recorded as δ in units of parts per million (ppm). The residual solvent peak was used as an internal reference. High resolution mass spectra (HRMS) were obtained on a Waters LC-TOF mass spectrometer (Xevo G2-XS QTof) using electrospray ionization (ESI) and reported in units of mass of charge ratio (m/z). IR spectra were obtained with KBr plates by using an IS10 FT-IR Spectrometer (ThermoFisher Corporation) and reported in wave numbers (cm^{-1}). X-ray crystallography analysis was performed on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. Flash chromatography was performed with Qingdao Haiyang flash silica gel (200–300 mesh). Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. Visualization was performed using a UV lamp, potassium permanganate stain or phosphomolybdic acid stain.

Materials

THF were distilled over sodium/benzophenone under N_2 atmosphere. Grignard reagents (isopropenylmagnesium bromide, cas: 13291-18-4; vinylmagnesium bromide, cas: 1826-67-1), aldehydes (hex-2-enal, cinnamaldehyde, crotonaldehyde) and sodium periodate were purchased from commercial suppliers. Potassium osmium dihydrate is in powder form. Solvents for oxidative cyclization reaction were commercial grade and used as supplied without further purification.

2. Investigation of Asymmetric Permanganate Oxidation Conditions

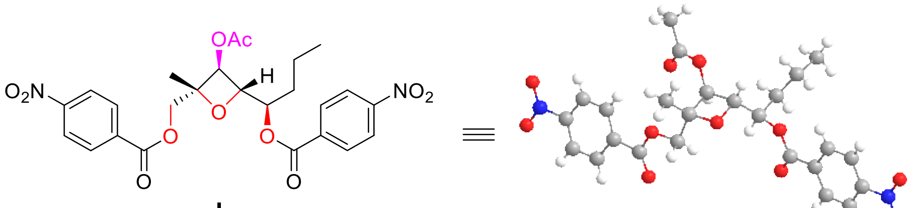
Table S1. Screening of Oxidative Cyclization Conditions of A1[a]



entry	solvent	additive	co-oxidant	yield
1	THF	none	$NaIO_4$	18%
2	MeCN	none	$NaIO_4$	9%
3	Acetone	none	$NaIO_4$	25%
4	*t*BuOH	none	$NaIO_4$	/
5	MeOH	none	$NaIO_4$	/
6	DMF	none	$NaIO_4$	/
7	DCM	none	$NaIO_4$	/
8	toluene	none	$NaIO_4$	/
9	TBME	none	$NaIO_4$	/
10	3-Pentanone	none	$NaIO_4$	24%
11[b]	Acetone	none	$NaIO_4$	**28%**
12[c]	Acetone	none	$NaIO_4$	17%
13[b]	Acetone	5 eq AcOH	$NaIO_4$	20%
14[b]	Acetone	5 eq HCl	$NaIO_4$	/
15[b]	Acetone	5 eq $CeCl_3$	$NaIO_4$	18%
16[b]	Acetone	5 eq Et_3N	$NaIO_4$	14%
17[b]	Acetone	5 eq K_2CO_3	$NaIO_4$	12%
18[b,d]	Acetone	none	$NaIO_4$	16%
19[b]	Acetone	0.5 eq TBAB	$NaIO_4$	24%
20	Acetone	none	$K_3Fe(CN)_6$	12%
21	Acetone	none	H_2O_2	/
22	Acetone	none	Oxone	/
23	Acetone	none	NMO	/
24	Acetone	none	TBHP	/
25[b,e]	Acetone	none	$NaIO_4$	27%
26[b,f]	Acetone	none	$NaIO_4$	27%
27[b,g]	Acetone	none	$NaIO_4$	/

[a]The reaction was conducted on 0.2 mmol scale in 2.0 mL solvent and 2.0 mL H_2O with 0.8 mmol co-oxidant and 0.01 mmol $K_2OsO_4 \cdot 2H_2O$. [b]With 1.0 mL H_2O. [c]With 0.5 mL H_2O. [d]Reaction at 0 °C. [e]2 mol% $K_2OsO_4 \cdot 2H_2O$. [f]1 mol% $K_2OsO_4 \cdot 2H_2O$. [g]Without $K_2OsO_4 \cdot 2H_2O$.

3. Structure Determination of Oxidative Cyclization Products



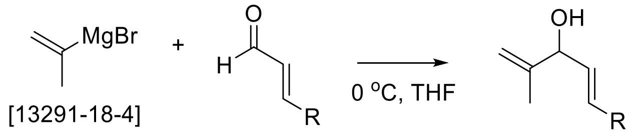
I

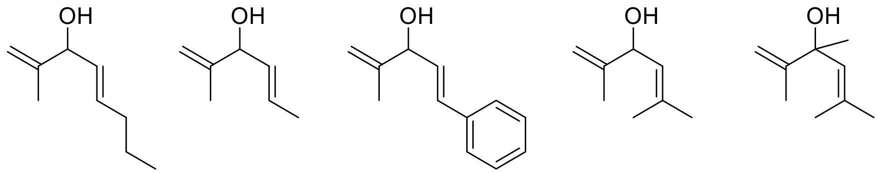
CCDC 2502003

Figure S1. Structure Determination of Oxidative Cyclization Products. CCDC 2502003 for compound **I**. The relative configuration of oxidative cyclization product **A1** was determined to be 3-*trans*-2,4-*cis*. All the other oxidative cyclization product were assigned by analogy. The relative configuration of compounds **II**, **III** and **IV** was determined based on the configuration of compound **I**.

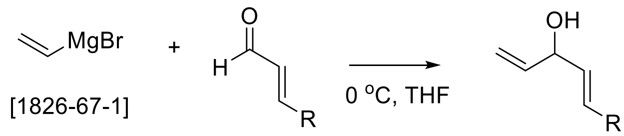
4. Preparation and Characterization of Substrates

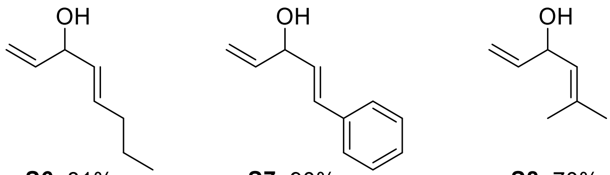
Preparation of 3-hydroxy-1,4-dienes





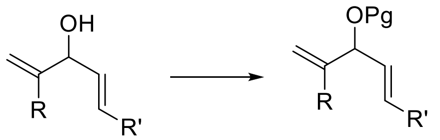
S1, 89% **S2**, 42% **S3**, 83% **S4**, 77% **S5**, 56%

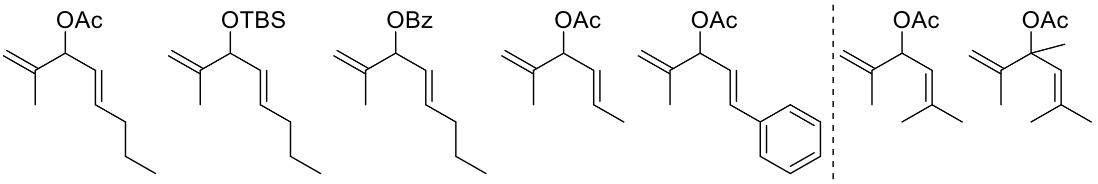




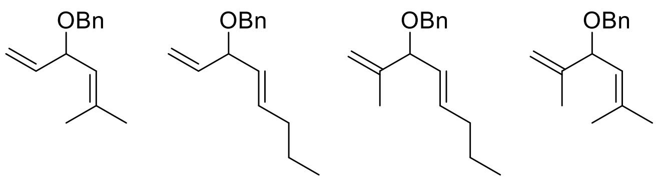
S6, 81% **S7**, 90% **S8**, 70%

Protection of 3-hydroxy-1,4-dienes





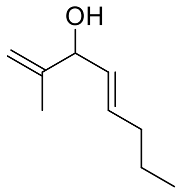
A1,80% **A2**,81% **A3**,61% **A4**,63% **A5**, 85% **A6** **A7**



A9, 70% **A10**, 85% **A11**, 87% **A12**, 51%

Preparation of 3-hydroxy-1,4-dienes using Grignard reagents [1]

To a stirred solution of 2-hexenal (981 mg, 10 mmol) in THF (10 mL) at 0 °C was added isopropenylmagnesium bromide (15 mL, 15 mmol, 1.0 mol/L in THF). The reaction was warmed to room temperature over 1 h and then quenched with saturated aqueous NH_4Cl (10 mL) at 0 °C. The organic layer was separated and the aqueous layer was extracted with EtOAc (10 mL × 3). The organic layers were combined and washed with brine (30 mL), dried with anhydrous Na_2SO_4 and then concentrated in vacuo. The residue was purified by column chromatography on silica gel affording the desired product **S1** in 89% yield (1.25 g) as a colorless liquid.

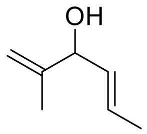


S1

(*E*)-2-methylocta-1,4-dien-3-ol (S1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 – 5.60 (m, 1H), 5.46 (ddt, *J* = 15.4, 7.0, 1.4 Hz, 1H), 5.05 – 5.00 (m, 1H), 4.84 (td, *J* = 1.6, 0.8 Hz, 1H), 4.48 (d, *J* = 7.0 Hz, 1H), 2.03 (q, *J* = 7.4 Hz, 2H), 1.72 (s, 3H), 1.41 (h, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

SMILES:OC(C(C)=C)/C=C/CCC

InChI=1S/C9H16O/c1-4-5-6-7-9(10)8(2)3/h6-7,9-10H,2,4-5H2,1,3H3/b7-6+

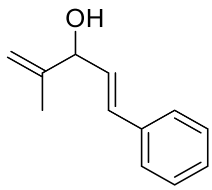


S2

(*E*)-2-methylhexa-1,4-dien-3-ol (S2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 – 5.68 (m, 1H), 5.51 (ddq, *J* = 15.2, 7.0, 1.7 Hz, 1H), 5.03 (s, 1H), 4.87 (s, 1H), 4.50 (d, *J* = 7.1 Hz, 1H), 1.78 – 1.71 (m, 6H).

SMILES:OC(C(C)=C)/C=C/C

InChI=1S/C7H12O/c1-4-5-7(8)6(2)3/h4-5,7-8H,2H2,1,3H3/b5-4+

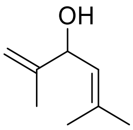


S3

(*E*)-4-methyl-1-phenylpenta-1,4-dien-3-ol (S3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.35 – 7.29 (m, 2H), 7.27 – 7.22 (m, 1H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 15.9, 6.6 Hz, 1H), 5.11 (d, *J* = 0.9 Hz, 1H), 4.95 – 4.90 (m, 1H), 4.73 (d, *J* = 6.5 Hz, 1H), 1.78 (s, 3H).

SMILES:OC(C(C)=C)/C=C/C1=CC=CC=C1

InChI=1S/C12H14O/c1-10(2)12(13)9-8-11-6-4-3-5-7-11/h3-9,12-13H,1H2,2H3/b9-8+

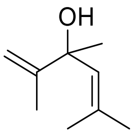


S4

2,5-dimethylhexa-1,4-dien-3-ol (S4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.18 (dp, *J* = 8.7, 1.4 Hz, 1H), 5.04 – 4.99 (m, 1H), 4.81 (h, *J* = 1.5 Hz, 1H), 4.77 (d, *J* = 8.7 Hz, 1H), 1.74 (d, *J* = 1.4 Hz, 3H), 1.73 – 1.69 (m, 6H).

SMILES:OC(C(C)=C)/C=C(C)/C

InChI=1S/C8H14O/c1-6(2)5-8(9)7(3)4/h5,8-9H,3H2,1-2,4H3

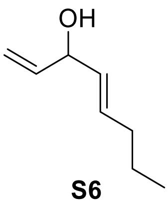


S5

2,3,5-trimethylhexa-1,4-dien-3-ol (S5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35 (p, *J* = 1.4 Hz, 1H), 5.09 (dd, *J* = 1.7, 0.9 Hz, 1H), 4.82 (p, *J* = 1.5 Hz, 1H), 1.76 (d, *J* = 0.7 Hz, 3H), 1.73 (d, *J* = 1.3 Hz, 3H), 1.71 (d, *J* = 1.5 Hz, 3H), 1.42 (s, 3H).

SMILES:OC(C(C)=C)(C)/C=C(C)/C

InChI=1S/C9H16O/c1-7(2)6-9(5,10)8(3)4/h6,10H,3H2,1-2,4-5H3

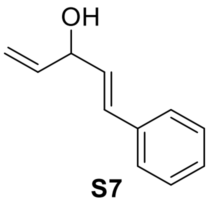


S6

(*E*)-octa-1,4-dien-3-ol (S6): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (ddd, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.75 – 5.63 (m, 1H), 5.56 – 5.45 (m, 1H), 5.25 (dt, *J* = 17.3, 1.5 Hz, 1H), 5.12 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.58 (t, *J* = 6.4 Hz, 1H), 2.02 (q, *J* = 6.7 Hz, 2H), 1.62 (s, 1H), 1.41 (h, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

SMILES:OC(C=C)/C=C/CCC

InChI=1S/C8H14O/c1-3-5-6-7-8(9)4-2/h4,6-9H,2-3,5H2,1H3/b7-6+

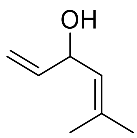


S7

(*E*)-1-phenylpenta-1,4-dien-3-ol (S7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.36 – 7.28 (m, 2H), 7.28 – 7.22 (m, 1H), 6.62 (d, *J* = 17.3 Hz, 1H), 6.24 (dd, *J* = 15.9, 6.4 Hz, 1H), 5.99 (ddd, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.35 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.20 (dt, *J* = 10.3, 1.3 Hz, 1H), 4.86 – 4.77 (m, 1H).

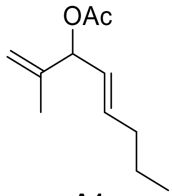
SMILES:OC(C=C)/C=C/C1=CC=CC=C1

InChI=1S/C11H12O/c1-2-11(12)9-8-10-6-4-3-5-7-10/h2-9,11-12H,1H2/b9-8+



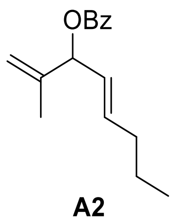
S8

5-methylhexa-1,4-dien-3-ol (S8): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 5.88 (ddd, *J* = 17.2, 10.3, 5.8 Hz, 1H), 5.27 – 5.14 (m, 2H), 5.08 (dt, *J* = 10.3, 1.4 Hz, 1H), 4.85 (t, *J* = 7.3 Hz, 1H), 1.74 (d, *J* = 1.4 Hz, 3H), 1.71 (d, *J* = 1.4 Hz, 3H).
SMILES:OC(C=C)/C=C(C)/C
InChI=1S/C7H12O/c1-4-7(8)5-6(2)3/h4-5,7-8H,1H2,2-3H3



A1

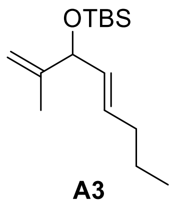
(*E*)-2-methylocta-1,4-dien-3-yl acetate (A1): Acetic acid (1.2 mmol) was added to a solution of (*E*)-2-methylocta-1,4-dien-3-ol (140 mg, 1 mmol) in DCM (5 mL) at room temperature, followed by the addition of DMAP (24.4 mg, 0.2 mmol) and EDCI (287.6 mg, 1.5 mmol) successively. The reaction was then carried out at room temperature overnight and then quenched with water. The organic layer was washed with water for three times and then dried with anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by column chromatography on silica gel affording the desired product **A1** in 80% yield (145.6 mg) as a colorless oil.
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 5.73 (dtd, *J* = 14.8, 6.8, 1.0 Hz, 1H), 5.56 (d, *J* = 7.2 Hz, 1H), 5.42 (ddt, *J* = 15.3, 7.2, 1.5 Hz, 1H), 4.98 (s, 1H), 4.88 (s, 1H), 2.07 (s, 3H), 2.06 – 1.96 (m, 2H), 1.72 (s, 3H), 1.40 (h, *J* = 7.3 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 169.96, 143.12, 134.94, 126.77, 111.95, 77.57, 34.23, 22.05, 21.27, 18.74, 13.59; **HRMS** (ESI) calcd for $C_{11}H_{19}O_2$ *m/z* $[M+H]^+$: 183.1380; found: 183.1386.
SMILES:CCC/C=C/C(C(C)=C)OC(C)=O
InChI=1S/C11H18O2/c1-5-6-7-8-11(9(2)3)13-10(4)12/h7-8,11H,2,5-6H2,1,3-4H3/b8-7+



A2

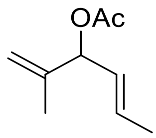
(*E*)-2-methylocta-1,4-dien-3-yl benzoate (A2): colorless oil; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.12 – 8.03 (m, 2H), 7.60 – 7.51 (m, 1H), 7.44 (dd, *J* = 8.4, 7.0 Hz, 2H), 5.88 – 5.79 (m, 2H), 5.55 (ddt, *J* = 15.4, 7.0, 1.5 Hz, 1H), 5.09 (s, 1H), 4.94 (s, 1H), 2.05 (q, *J* = 7.1 Hz, 2H), 1.81 (s, 3H), 1.42 (h, *J* = 7.3 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 165.46, 143.16, 135.04, 132.84, 130.62, 129.60, 128.33,

126.78, 112.20, 78.11, 34.28, 22.06, 18.78, 13.61, 1.00; **HRMS** (ESI) calcd for $C_{16}H_{21}O_2$ *m/z* [M+H]$^+$: 245.1536; found: 245.1542.
SMILES:CCC/C=C/C(C(C)=C)OC(C1=CC=CC=C1)=O
InChI=1S/C16H20O2/c1-4-5-7-12-15(13(2)3)18-16(17)14-10-8-6-9-11-14/h6-12,15H,2,4-5H2,1,3H3/b12-7+



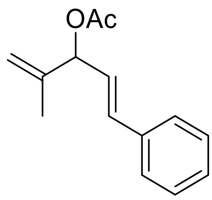
A3

(*E*)-tert-butyldimethyl ((2-methylocta-1,4-dien-3-yl)oxy) silane (A3): [2] colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.61 (dtd, *J* = 15.0, 6.8, 1.2 Hz, 1H), 5.36 (ddt, *J* = 15.3, 6.3, 1.4 Hz, 1H), 4.96 (dt, *J* = 2.1, 1.0 Hz, 1H), 4.78 – 4.73 (m, 1H), 4.44 (d, *J* = 6.2 Hz, 1H), 2.00 (q, *J* = 6.9 Hz, 2H), 1.44 – 1.35 (m, 2H), 0.89 (s, 13H), 0.04 (d, *J* = 1.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.5, 132.0, 130.9, 109.6, 34.2, 25.8, 22.4, 18.3, 18.0, 13.6, –4.7, –4.9.
SMILES:CCC/C=C/C(C(C)=C)O[Si](C)(C)C(C)(C)C
InChI=1S/C15H30OSi/c1-9-10-11-12-14(13(2)3)16-17(7,8)15(4,5)6/h11-12,14H,2,9-10H2,1,3-8H3/b12-11+



A4

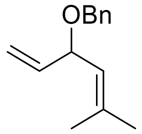
(*E*)-2-methylhexa-1,4-dien-3-yl acetate (A4): colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.82 – 5.70 (m, 1H), 5.55 (d, *J* = 7.4 Hz, 1H), 5.45 (ddq, *J* = 15.3, 7.3, 1.7 Hz, 1H), 4.98 (t, *J* = 1.8 Hz, 1H), 4.88 (t, *J* = 1.7 Hz, 1H), 2.07 (s, 3H), 1.74 – 1.69 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.9, 144.1, 131.5, 127.9, 112.0, 77.5, 21.2, 18.7, 17.7; **HRMS** (ESI) calcd for $C_9H_{15}O_2$ *m/z* [M+H]$^+$: 155.1067; found: 155.1063.
SMILES:C/C=C/C(C(C)=C)OC(C)=O
InChI=1S/C9H14O2/c1-5-6-9(7(2)3)11-8(4)10/h5-6,9H,2H2,1,3-4H3/b6-5+



A5

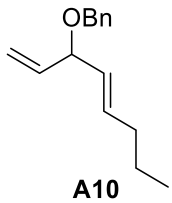
(*E*)-4-methyl-1-phenylpenta-1,4-dien-3-yl acetate (A5): colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.22 (m, 7H), 6.64 (d, *J* = 14.7 Hz, 1H), 6.16 (dd, *J* = 15.9, 7.1 Hz, 1H), 5.83 – 5.74 (m, 1H), 5.09 (s, 1H), 4.97 (s, 1H), 2.12 (s, 3H), 1.79 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.93, 142.63, 128.56, 128.00, 126.97, 126.61, 126.05, 112.77, 77.39, 21.24, 18.74; **HRMS** (ESI) calcd for $C_{14}H_{17}O_2$ *m/z* [M+H]$^+$: 217.1223; found: 217.1232.

SMILES:C=C(C)C(OC(C)=O)/C=C/C1=CC=CC=C1
InChI=1S/C14H16O2/c1-11(2)14(16-12(3)15)10-9-13-7-5-4-6-8-13/h4-10,14H,1H2,2-3H3/b10-9+



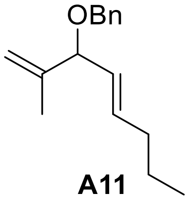
A9

(((5-methylhexa-1,4-dien-3-yl)oxy)methyl)benzene (A9): [3] To a suspension of NaH (240 mg, 6 mmol, 60 wt%) in dry THF (25 mL) under argon at 0 °C was added dropwise a solution of (*E*)-2-methylocta-1,4-dien-3-ol (560 mg, 5 mmol) in dry THF (25 mL). After stirring for 5 minutes, benzyl bromide (860 mg, 5 mmol) was added to the mixture at 0 °C. The reaction was then refluxed for 5 hours, cooled to room temperature and quenched with water (10 mL approximately). The organic layer was separated and aqueous layer was then extracted with EtOAc (6 mL×4). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel affording the desired product **A9** in 70% yield (707 mg) as a light-yellow oil.
light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 5H), 5.83 (ddd, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.27 – 5.19 (m, 2H), 5.16 (dt, *J* = 10.3, 1.4 Hz, 1H), 4.55 – 4.47 (m, 3H), 1.77 (d, *J* = 1.4 Hz, 3H), 1.63 (d, *J* = 1.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.68, 138.07, 136.39, 128.28, 127.80, 127.38, 124.31, 115.81, 76.58, 69.30, 25.93, 18.33.
SMILES:C/C(C)=C/C(C=C)OCC1=CC=CC=C1
InChI=1S/C14H18O/c1-4-14(10-12(2)3)15-11-13-8-6-5-7-9-13/h4-10,14H,1,11H2,2-3H3



A10

(*E*)-((octa-1,4-dien-3-yloxy)methyl)benzene (A10): light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 5H), 5.86 (ddd, *J* = 17.0, 10.4, 6.4 Hz, 1H), 5.74 – 5.62 (m, 1H), 5.45 (dd, *J* = 15.5, 7.2 Hz, 1H), 5.30 – 5.16 (m, 2H), 4.58 – 4.46 (m, 2H), 4.24 (t, *J* = 6.9 Hz, 1H), 2.05 (q, *J* = 7.9, 7.1 Hz, 2H), 1.43 (h, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.7, 138.3, 134.1, 129.4, 128.3, 127.7, 127.4, 116.2, 80.7, 69.5, 34.4, 22.2, 13.7; **HRMS** (ESI) calcd for $C_{15}H_{21}O$ *m/z* $[M+H]^+$: 217.1587; found: 217.1589.
SMILES:C=CC(OCC1=CC=CC=C1)/C=C/CCC
InChI=1S/C15H20O/c1-3-5-7-12-15(4-2)16-13-14-10-8-6-9-11-14/h4,6-12,15H,2-3,5,13H2,1H3/b12-7+

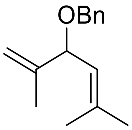


A11

(*E*)-(((2-methylocta-1,4-dien-3-yl)oxy)methyl)benzene (A11): light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.23 (m, 7H), 5.69 (dt, *J* = 14.3, 6.7 Hz, 1H), 5.51 – 5.41 (m, 1H), 5.03 (s, 1H), 4.93 (s, 1H), 4.51 – 4.43 (m, 2H), 4.18 (d, *J* = 6.9 Hz, 1H), 2.05 (q, *J* = 7.1 Hz, 2H), 1.73 (s, 3H), 1.43 (h, *J* = 7.3 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 140.0, 133.6, 130.4, 128.3, 127.6, 127.3, 112.3, 86.3, 69.5, 33.6, 23.8, 18.7, 14.6; **HRMS** (ESI) calcd for $C_{16}H_{23}O$ *m/z* $[M+H]^+$: 231.1743; found: 231.1732.

SMILES:C=C(C)C(OCC1=CC=CC=C1)/C=C/CCC

InChI=1S/C16H22O/c1-4-5-7-12-16(14(2)3)17-13-15-10-8-6-9-11-15/h6-12,16H,2,4-5,13H2,1,3H3/b12-7+



A12

(((2,5-dimethylhexa-1,4-dien-3-yl)oxy)methyl)benzene (A12): light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 6H), 6.30 (d, *J* = 16.1 Hz, 1H), 5.74 (d, *J* = 16.2 Hz, 1H), 5.00 (s, 2H), 4.38 (s, 2H), 1.86 (s, 3H), 1.41 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.6, 139.8, 135.5, 132.0, 128.3, 127.4, 127.1, 116.5, 75.5, 65.0, 27.1, 19.7; **HRMS** (ESI) calcd for $C_{15}H_{21}O$ *m/z* $[M+H]^+$: 217.1587; found: 217.1588.

SMILES:C=C(C)C(OCC1=CC=CC=C1)/C=C(C)/C

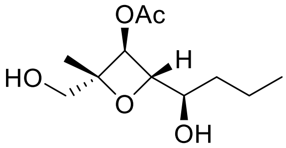
InChI=1S/C15H20O/c1-12(2)10-15(13(3)4)16-11-14-8-6-5-7-9-14/h5-10,15H,3,11H2,1-2,4H3

5. General Methods for Oxidative Cyclization.

Method A: 0.2 mmol scale for optimization of oxidative cyclization conditions. To a mixture of acetone (2 mL) and H_2O (1 mL) was added potassium osmium dihydrate aqueous solution (50 mg/mL) (74 μL, 0.01 mmol). After stirring the mixture for 5 minutes, (*E*)-2-methylocta-1,4-dien-3-yl acetate **A1** (36.4 mg, 0.2 mmol) and sodium periodate (170.4 mg, 0.8 mmol) was added successively at room temperature and the reaction was allowed to react for 12 h. The reaction was then quenched with a saturated solution of sodium thiosulfate, extracted with DCM, dried with anhydrous sodium sulfate and concentrated in vacuo. The residue was then purified by column chromatography on silica gel (CH_2Cl_2:MeOH = 100:1) affording pure oxidative cyclization product **P1** as a colorless oil.

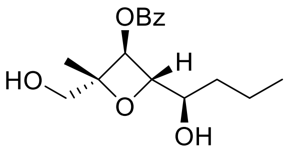
Method B: 0.5 mmol scale for oxidative cyclization of 1,4-dienes **A**. To a mixture of acetone (5 mL) and H_2O (2.5 mL) was added potassium osmium dihydrate aqueous solution (50 mg/mL) (184 μL, 0.025 mmol). After stirring the mixture for 5 minutes, 1,4-dienes **A** (0.5 mmol) and sodium periodate (428 mg, 2.0 mmol) was added successively at room temperature and the reaction was allowed to react for 12 h. The reaction was then quenched with a saturated solution of sodium thiosulfate, extracted with DCM, dried with anhydrous sodium sulfate and concentrated in vacuo. The residue was then purified by column chromatography on silica gel (CH_2Cl_2:MeOH = 100:1) affording pure oxidative cyclization product **P**.

6. Characterization of Oxidative Cyclization Products.



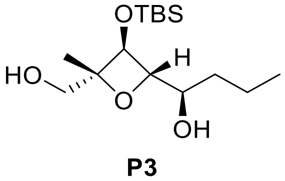
P1

4-(1-hydroxybutyl)-2-(hydroxymethyl)-2-methyloxetan-3-yl acetate (P1): 28% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.41 (d, *J* = 6.0 Hz, 1H), 4.45 (dd, *J* = 6.1, 3.5 Hz, 1H), 3.83 – 3.75 (m, 1H), 3.61 (s, 2H), 3.39 (s, 1H), 3.18 (s, 1H), 2.10 (s, 3H), 1.56 – 1.44 (m, 2H), 1.44 – 1.32 (m, 3H), 1.30 (s, 3H), 0.93 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.6, 86.6, 83.3, 71.5, 69.2, 67.4, 34.5, 20.5, 18.7, 17.3, 13.9; **IR**: 3393, 2934, 2363, 1741, 1448, 1372, 1234, 1067 cm^{-1}; **HRMS** (ESI) calcd for $C_{11}H_{21}O_5$ *m/z* $[M+H]^+$: 233.1389; found: 233.1388.
SMILES:[H][C@@]1([C@H](O)CCC)O[C@](C)(CO)[C@H]1OC(C)=O
InChI=1S/C11H20O5/c1-4-5-8(14)9-10(15-7(2)13)11(3,6-12)16-9/h8-10,12,14H,4-6H2,1-3H3/t8-,9-,10-,11+/m0/s1



P2

4-(1-hydroxybutyl)-2-(hydroxymethyl)-2-methyloxetan-3-yl benzoate (P2): 18% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 2H), 7.63 – 7.57 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 5.68 (d, *J* = 5.9 Hz, 1H), 4.62 (dd, *J* = 5.9, 3.5 Hz, 1H), 3.91 (dt, *J* = 8.3, 3.9 Hz, 1H), 3.70 (s, 2H), 3.65 – 3.18 (m, 1H), 1.64 – 1.41 (m, 4H), 1.40 (s, 3H), 0.93 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 133.6, 129.7, 129.0, 128.5, 86.9, 83.6, 71.6, 69.7, 67.5, 34.5, 18.7, 17.6, 14.0; **IR**: 3403, 2924, 1723, 1450, 1279, 1118, 1069, 710 cm^{-1}; **HRMS** (ESI) calcd for $C_{16}H_{23}O_5$ *m/z* $[M+H]^+$: 295.1545; found: 295.1547.
SMILES:[H][C@@]1([C@H](O)CCC)O[C@](C)(CO)[C@H]1OC(C2=CC=CC=C2
)=O
InChI=1S/C16H22O5/c1-3-7-12(18)13-14(16(2,10-17)21-13)20-15(19)11-8-5-4-6-9-11/h4-6,8-9,12-14,17-18H,3,7,10H2,1-2H3/t12-,13-,14-,16+/m0/s1

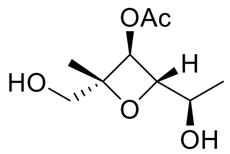


P3

1-(3-((tert-butyldimethylsilyl)oxy)-4-(hydroxymethyl)-4-methyloxetan-2-yl)butan-1-ol (P3): 16% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.71 (d, *J* = 5.7 Hz, 1H), 4.27 (dd, *J* = 5.7, 3.9 Hz, 1H), 3.68 (dd, *J* = 8.1, 4.0 Hz, 1H), 3.56 (d, *J* = 12.6 Hz, 1H), 3.45 (d, *J* = 12.6 Hz, 1H), 3.10 (s, 2H), 1.47 (dd, *J* = 16.5, 6.6 Hz, 2H), 1.44 – 1.35 (m, 3H), 1.29 (s, 3H), 0.96 – 0.91 (m, 5H), 0.89 (s, 9H), 0.04 (d, *J* = 4.0 Hz, 6H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 88.6, 87.6, 71.8, 67.3, 66.8, 34.8, 25.7, 25.6, 18.7, 17.9, 17.4, 14.0, –4.8, –4.9; **IR**: 3421, 2924, 2364, 1463, 1257, 1145, 880, 831 cm^{-1}; **HRMS** (ESI) calcd for $C_{15}H_{33}O_4Si$ *m/z* $[M+H]^+$: 305.2148; found: 305.2150.

SMILES:[H][C@@]1([C@H](O)CCC)O[C@](C)(CO)[C@H]1O[Si](C)(C)C(C)(C)C

InChI=1S/C15H32O4Si/c1-8-9-11(17)12-13(15(5,10-16)18-12)19-20(6,7)14(2,3)4/h11-13,16-17H,8-10H2,1-7H3/t11-,12-,13-,15+/m0/s1

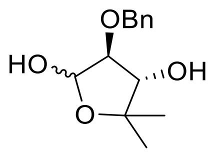


P4

4-(1-hydroxyethyl)-2-(hydroxymethyl)-2-methyloxetan-3-yl acetate (P4): 9% yield; colorless oil; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 5.36 (d, J = 6.0 Hz, 1H), 4.39 (dd, J = 6.0, 3.9 Hz, 1H), 4.03 – 3.93 (m, 1H), 3.61 (s, 2H), 2.11 (s, 3H), 1.31 (s, 3H), 1.19 (d, J = 6.5 Hz, 3H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 170.6, 86.1, 84.3, 69.2, 68.0, 67.4, 20.5, 18.1, 17.3; **IR**: 3368, 2915, 2848, 2359, 1745, 1369, 1248, 1055 cm^{-1}; **HRMS** (ESI) calcd for $C_9H_{17}O_5$ *m/z* $[M+H]^+$: 205.1076; found: 205.1075.

SMILES:[H][C@@]1([C@H](O)C)O[C@](C)(CO)[C@H]1OC(C)=O

InChI=1S/C9H16O5/c1-5(11)7-8(13-6(2)12)9(3,4-10)14-7/h5,7-8,10-11H,4H2,1-3H3/t5-,7+,8+,9-/m1/s1

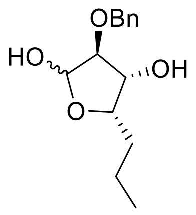


P9 dr = 1:1

3-(benzyloxy)-5,5-dimethyltetrahydrofuran-2,4-diol (P9): 33% yield; light yellow oil; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 10H), 5.36 (d, J = 2.3 Hz, 1H), 5.28 (dd, J = 9.1, 4.5 Hz, 2H), 4.80 – 4.57 (m, 4H), 4.06 – 3.98 (m, 3H), 3.85 (t, J = 4.8 Hz, 1H), 3.76 (d, J = 9.2 Hz, 1H), 3.37 (d, J = 3.0 Hz, 1H), 2.85 (d, J = 5.0 Hz, 1H), 2.73 (d, J = 7.1 Hz, 1H), 1.39 (s, 3H), 1.34 (s, 3H), 1.26 (s, 3H), 1.17 (s, 3H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 137.1, 137.0, 128.6, 128.6, 128.3, 128.2, 128.1, 127.8, 99.2, 95.8, 84.5, 84.2, 82.9, 78.4, 76.1, 75.7, 72.9, 72.6, 28.8, 28.3, 24.1, 23.2; **IR**: 1796, 1666, 1464, 1379, 1087, 850, 694 cm^{-1}; **HRMS** (ESI) calcd for $C_{13}H_{18}O_4$ *m/z* $[M+H]^+$: 239.1283; found: 239.1274.

SMILES:OC1OC(C)(C)[C@@H](O)[C@@H]1OCC2=CC=CC=C2

InChI=1S/C13H18O4/c1-13(2)11(14)10(12(15)17-13)16-8-9-6-4-3-5-7-9/h3-7,10-12,14-15H,8H2,1-2H3/t10-,11-,12?/m0/s1



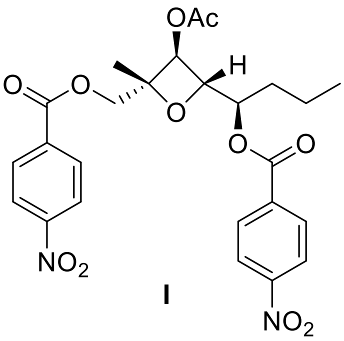
P10 dr = 2:1

3-(benzyloxy)-5-propyltetrahydrofuran-2,4-diol (P10): 26% yield; light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 15H), 5.43 (t, J = 3.0 Hz, 2H), 5.25 (dd, J = 9.7, 4.4 Hz, 1H), 4.80 – 4.61 (m, 6H), 4.14 (h, J = 3.6 Hz, 5H), 3.98 (dd, J = 4.8, 2.9 Hz, 2H), 3.91 – 3.84 (m, 2H), 3.69 (d, J = 9.7 Hz, 1H), 2.99 (d, J = 3.2 Hz, 2H), 2.64 (d, J = 3.9 Hz, 1H), 2.55 (d, J = 3.8 Hz, 2H), 1.77 – 1.59 (m, 10H), 1.43 (tq, J = 14.6, 6.7 Hz, 7H), 0.95 (t, J = 7.4 Hz, 10H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.0, 128.7, 128.6, 128.3, 128.2, 128.0, 100.3, 95.3, 85.5, 80.9, 80.2, 78.9, 72.8, 72.1, 71.1, 70.8, 32.5, 30.7, 19.1, 19.0, 14.1, 14.1; **IR**:1778, 1453, 1369, 1189, 1141, 1079, 741, 693 cm^{-1}; **HRMS** (ESI) calcd for $C_{14}H_{20}O_4$ *m/z* [M+H]$^+$: 253.1440; found: 253.1440.

SMILES:OC1OC(CCC)[C@@H](O)[C@@H]1OCC2=CC=CC=C2

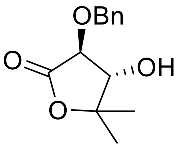
InChI=1S/C14H20O4/c1-2-6-11-12(15)13(14(16)18-11)17-9-10-7-4-3-5-8-10/h3-5,7-8,11-16H,2,6,9H2,1H3/t11?,12-,13+,14?/m1/s1

7. Derivatization of Oxidative Cyclization Products



I

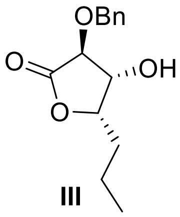
((2*R*,3*S*,4*S*)-3-acetoxy-2-methyl-4-((*R*)-1-((4-nitrobenzoyl)oxy)butyl)oxetan-2-yl)methyl 4-nitrobenzoate (I): colorless solid; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.34 – 8.29 (m, 4H), 8.24 (d, *J* = 8.8 Hz, 2H), 8.18 – 8.13 (m, 2H), 7.21 (s, 5H), 6.49 (d, *J* = 2.4 Hz, 1H), 5.43 (d, *J* = 5.1 Hz, 1H), 4.69 – 4.58 (m, 3H), 1.59 (s, 2H), 1.50 (d, *J* = 4.9 Hz, 6H), 1.42 (s, 1H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 164.2, 163.8, 151.3, 137.1, 135.1, 135.0, 131.1, 131.0, 128.6, 128.2, 127.8, 123.8, 123.8, 101.2, 85.8, 82.5, 78.2, 73.5, 28.5, 27.1, 23.9; **HRMS** (ESI) calcd for $C_{25}H_{27}N_2O_{11}$ *m/z* $[M+H]^+$: 531.1609; found: 531.1610.
SMILES:[H][C@@]1([C@H](OC(C2=CC=C([N+]([O-])=O)C=C2)=O)CCC)O[C@](C)(COC(C3=CC=C([N+]([O-])=O)C=C3)=O)[C@H]1OC(C)=O
InChI=1S/C25H26N2O11/c1-4-5-20(37-24(30)17-8-12-19(13-9-17)27(33)34)21-22(36-15(2)28)25(3,38-21)14-35-23(29)16-6-10-18(11-7-16)26(31)32/h6-13,20-22H,4-5,14H2,1-3H3/t20-,21+,22+,25-/m1/s1



II

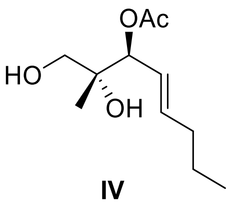
3-(benzyloxy)-4-hydroxy-5,5-dimethyldihydrofuran-2(*3H*)-one (II):[4] To a solution of compound **P9** (23.8 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) at 0 °C under argon was added a solution of NIS (56 mg, 0.25 mmol) and Bu_4NI (44 mg, 0.12 mmol) in CH_2Cl_2 (3.5 mL). The reaction mixture was stirred at room temperature for 21 h. The mixture was poured into a saturated aqueous solution of $Na_2S_2O_3$ and extracted with CH_2Cl_2 (5 mL × 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 1:1) affording pure lactone **II** product in 65% yield (15.3 mg) as a light-yellow oil.
^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 5H), 5.06 (d, *J* = 11.7 Hz, 1H), 4.82 (d, *J* = 11.8 Hz, 1H), 4.33 (d, *J* = 5.1 Hz, 1H), 3.96 (d, *J* = 5.1 Hz, 1H), 2.75 (s, 1H), 1.46 (s, 3H), 1.33 (s, 3H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 172.8, 136.2, 128.8, 128.6, 128.3, 85.1, 74.7, 73.1, 73.1, 25.7, 22.0; **IR**: 1783, 1673, 1459, 1265, 1079, 1039, 729, 701 cm^{-1}; **HRMS** (ESI) calcd for $C_{13}H_{16}O_4$ *m/z* $[M+H]^+$: 237.1127; found: 237.1133.
SMILES:O=C1OC(C)(C)C(O)C1OCC2=CC=CC=C2

InChI=1S/C13H16O4/c1-13(2)11(14)10(12(15)17-13)16-8-9-6-4-3-5-7-9/h3-7,10-11,14H,8H2,1-2H3



III

3-(benzyloxy)-4-hydroxy-5-propyldihydrofuran-2(*3H*)-one (III): 60% yield; light yellow oil; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 5H), 5.04 (d, *J* = 11.9 Hz, 1H), 4.85 (d, *J* = 11.9 Hz, 1H), 4.26 – 4.18 (m, 3H), 2.48 (s, 1H), 1.92 – 1.81 (m, 1H), 1.78 – 1.66 (m, 1H), 1.53 – 1.40 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 173.2, 136.2, 129.4, 128.6, 127.8, 80.2, 75.6, 72.9, 69.0, 30.2, 18.3, 13.9; **IR**: 1789, 1448, 1265, 1144, 1079, 896, 729, 690 cm^{-1}; **HRMS** (ESI) calcd for $C_{14}H_{18}O_4$ *m/z* $[M+H]^+$: 251.1283; found: 251.1275.
SMILES:O=C1OC(CCC)C(O)C1OCC2=CC=CC=C2
InChI=1S/C14H18O4/c1-2-6-11-12(15)13(14(16)18-11)17-9-10-7-4-3-5-8-10/h3-5,7-8,11-13,15H,2,6,9H2,1H3



IV

(*E*)-1,2-dihydroxy-2-methyloct-4-en-3-yl acetate (IV): ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 5.84 – 5.72 (m, 1H), 5.53 (ddt, *J* = 15.4, 7.1, 1.4 Hz, 1H), 5.23 (dd, *J* = 7.1, 1.0 Hz, 1H), 3.53 (d, *J* = 11.8 Hz, 1H), 3.35 (dd, *J* = 11.3, 4.7 Hz, 1H), 2.48 (s, 2H), 2.11 (s, 3H), 2.09 – 2.02 (m, 2H), 1.41 (h, *J* = 7.5 Hz, 3H), 1.11 (s, 3H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 170.9, 136.7, 123.6, 76.7, 73.4, 66.7, 34.4, 22.0, 21.2, 19.3, 13.6; **HRMS** (ESI) calcd for $C_{11}H_{21}O_4$ *m/z* $[M+H]^+$: 217.1434; found: 217.1432.
SMILES:CCC/C=C/C(OC(C)=O)C(CO)(O)C
InChI=1S/C11H20O4/c1-4-5-6-7-10(15-9(2)13)11(3,14)8-12/h6-7,10,12,14H,4-5,8H2,1-3H3/b7-6+

8. Reference

1. W. Xia, Y. Yang, X. Zhang, L. Hu and Y. Xiong, Electrochemical synthesis of γ-keto sulfones containing a β-quaternary carbon center via 1,2-migration. *Green Chem.*, 2023, **25**, 8273−8279.
2. W. J. Leigh, R. Boukherroub and C. Kerst, Substituent Effects on the Reactivity of the Silicon−Carbon Double Bond. Resonance, Inductive, and Steric Effects of Substituents at Silicon on the Reactivity of Simple 1-Methylsilenes. *J. Am. Chem. Soc.*, 1998, **120**, 9504−9512.
3. P. Bertus, L. Drouin, C. Laroche and J. Szymoniak, *Tetrahedron*, 2004, **60**, 1375−1383.
4. H. Sugimura, S. Sato, K. Tokudome and T. Yamada, Stereoselective Formation of Tetrahydrofuran Rings via [3 + 2] Annulation: Total Synthesis of Plakortone L. *Org. Lett.*, 2014, **16**, 3384−3387.

9. X-ray Crystal Data

Table S2. Sample And Crystal Data for 4062 (I, CCDC 2502003)

Identification code	4062	
Chemical formula	$C_{25}H_{26}N_2O_{11}$	
Formula weight	530.48 g/mol	
Temperature	303.10 K	
Wavelength	1.54178 Å	
Crystal size	0.15 × 0.12 × 0.1 mm^3	
Crystal habit	colorless block	
Crystal system	triclinic	
Space group	P –1	
Unit cell dimensions	a = 7.5470(4) Å	α = 71.305(3)°
	b = 11.1144(7) Å	β = 87.165(2)°
	c = 16.8902(10) Å	γ = 73.744(2)°
Volume	1287.09(13) $Å^3$	
Z	2	
Density (calculated)	1.369 g/cm^3	
Absorption coefficient	0.925 mm^{-1}	
F(000)	566.0	

10. Selected NMR Spectra

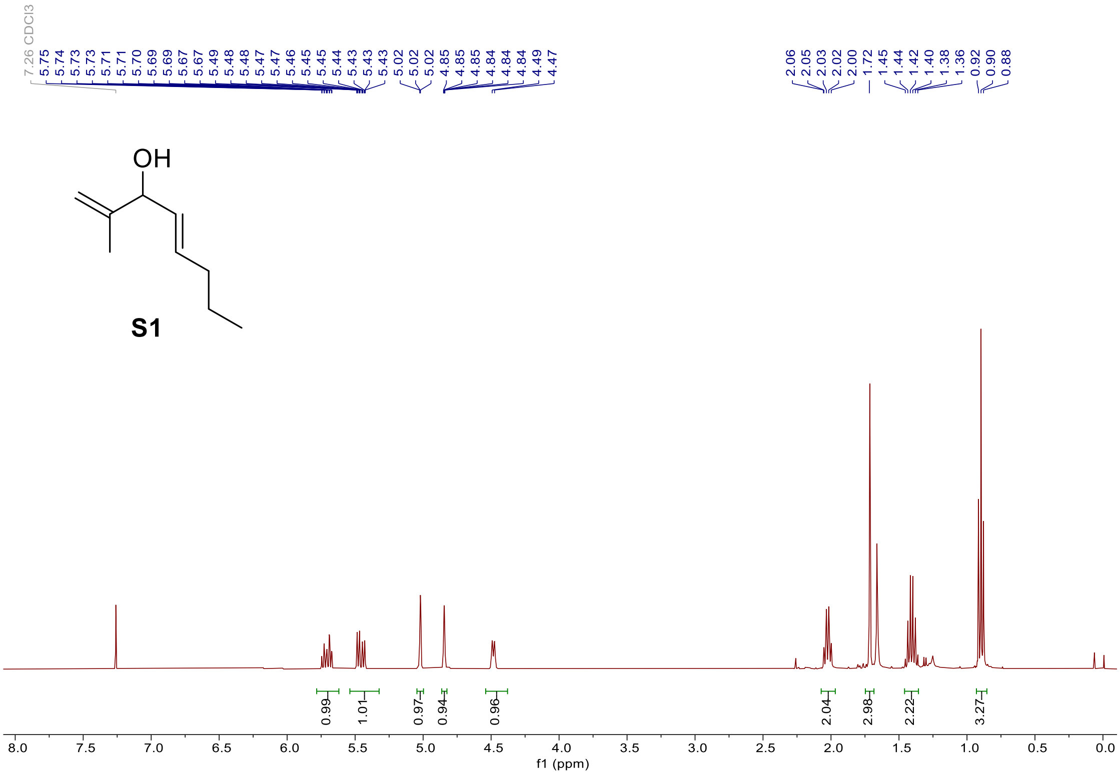


Figure S2. ^1H NMR (400 MHz) spectra of **S1** in $CDCl_3$.

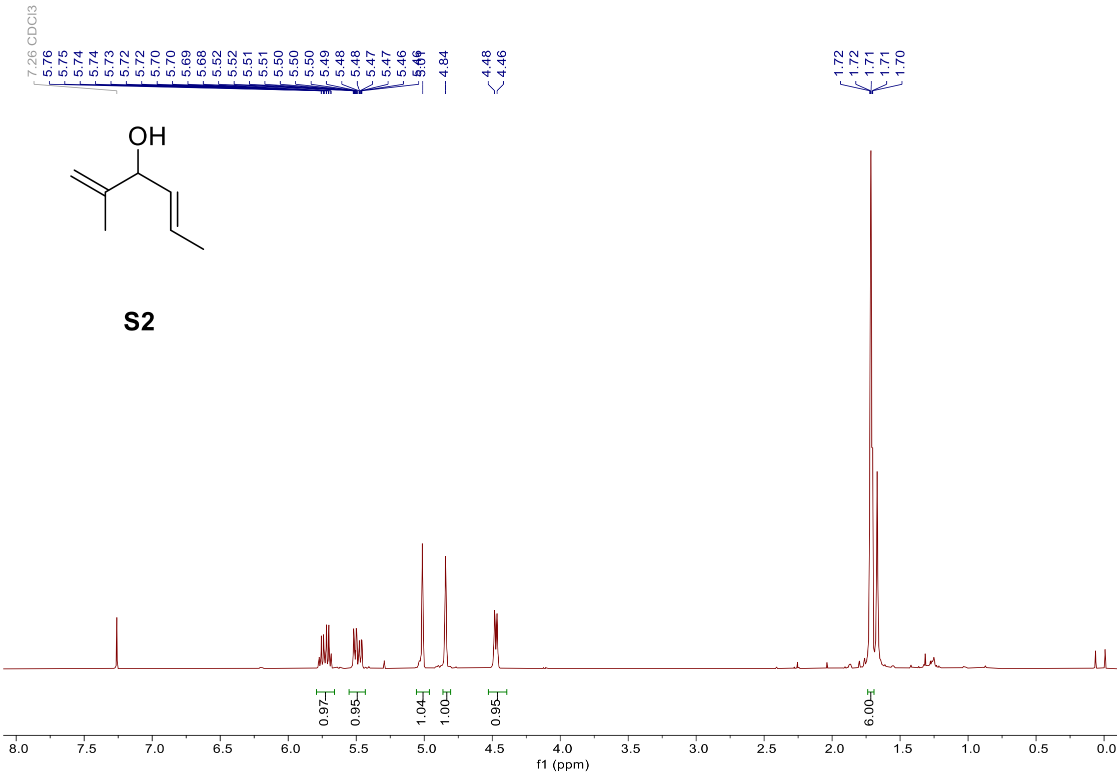


Figure S3. ^1H NMR (400 MHz) spectra of **S2** in $CDCl_3$.

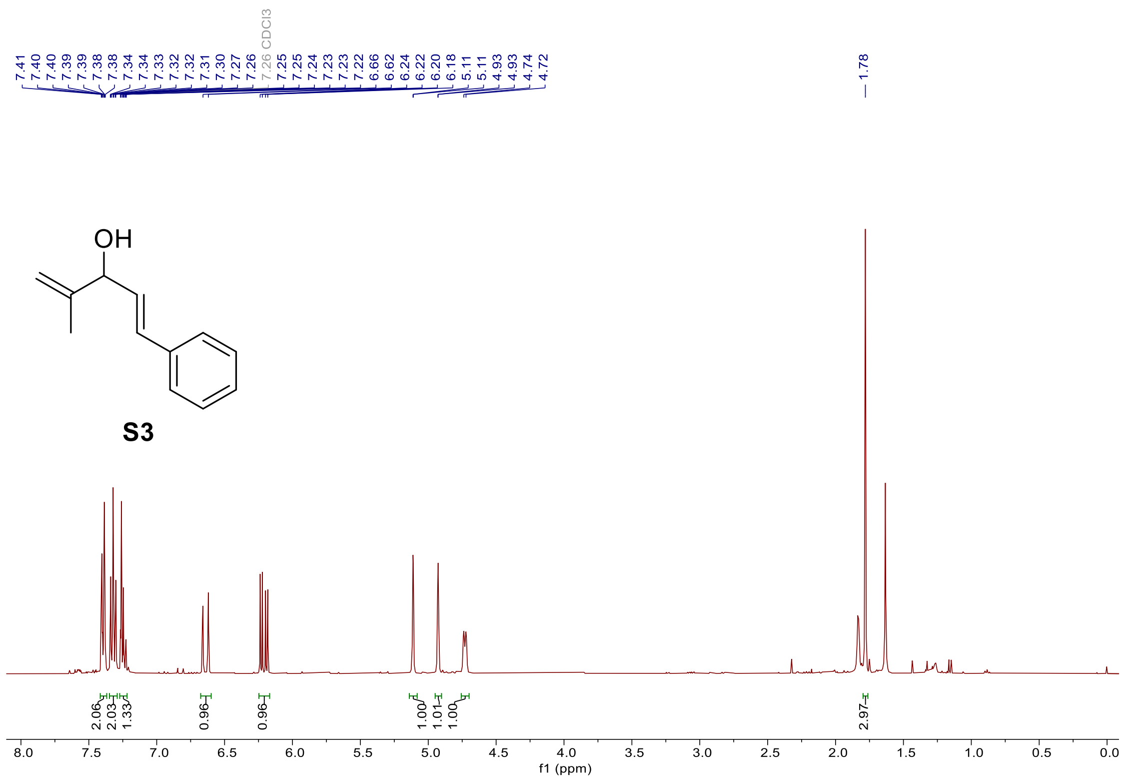


Figure S4. ^{1}H NMR (400 MHz) spectra of **S3** in $CDCl_3$.

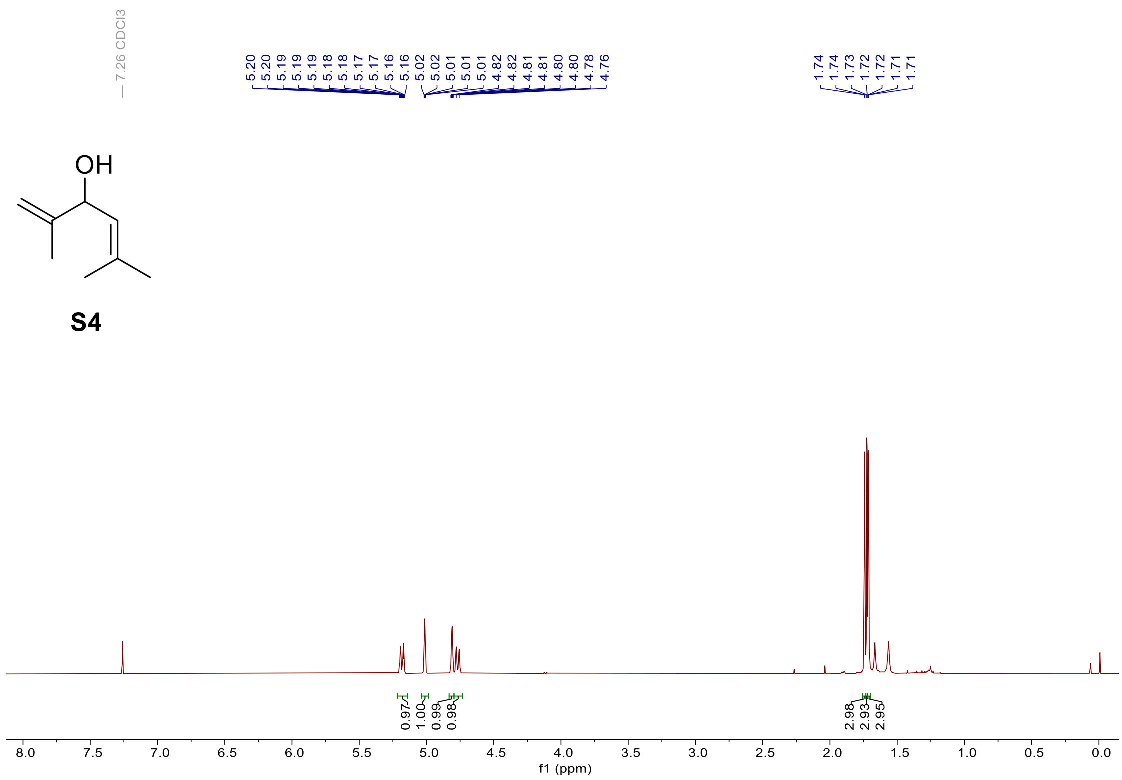


Figure S5. ^{1}H NMR (400 MHz) spectra of **S4** in $CDCl_3$.

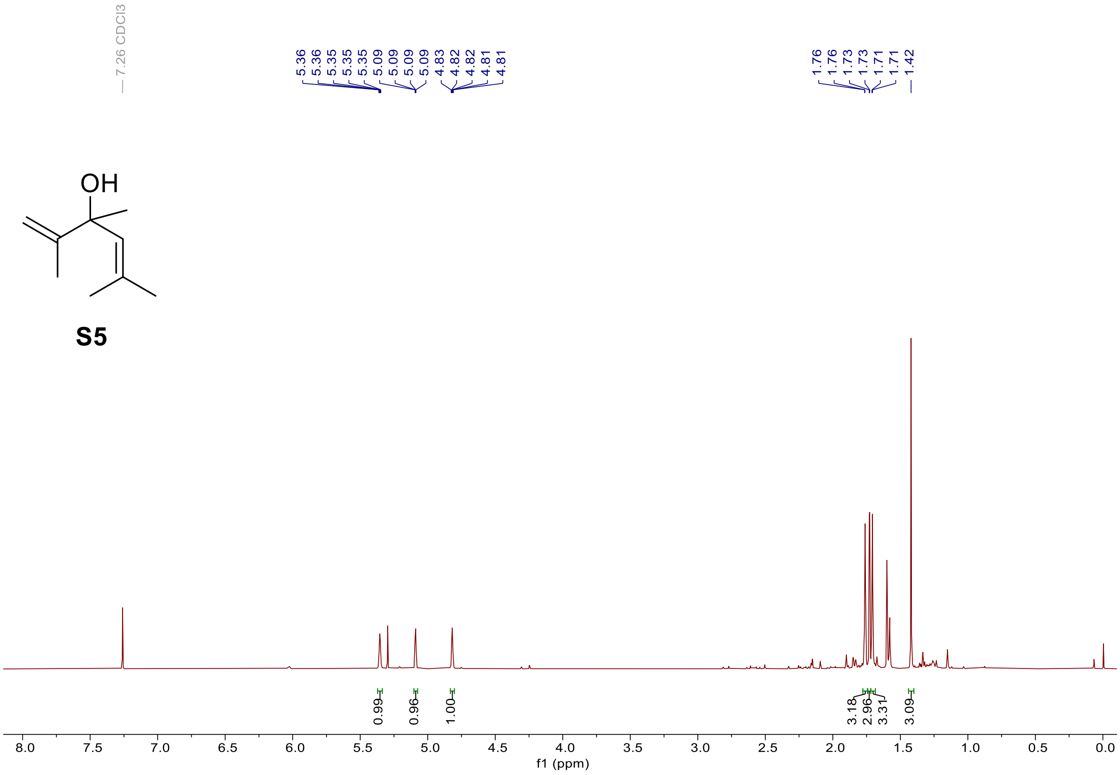


Figure S6. ^{1}H NMR (400 MHz) spectra of **S5** in $CDCl_3$.

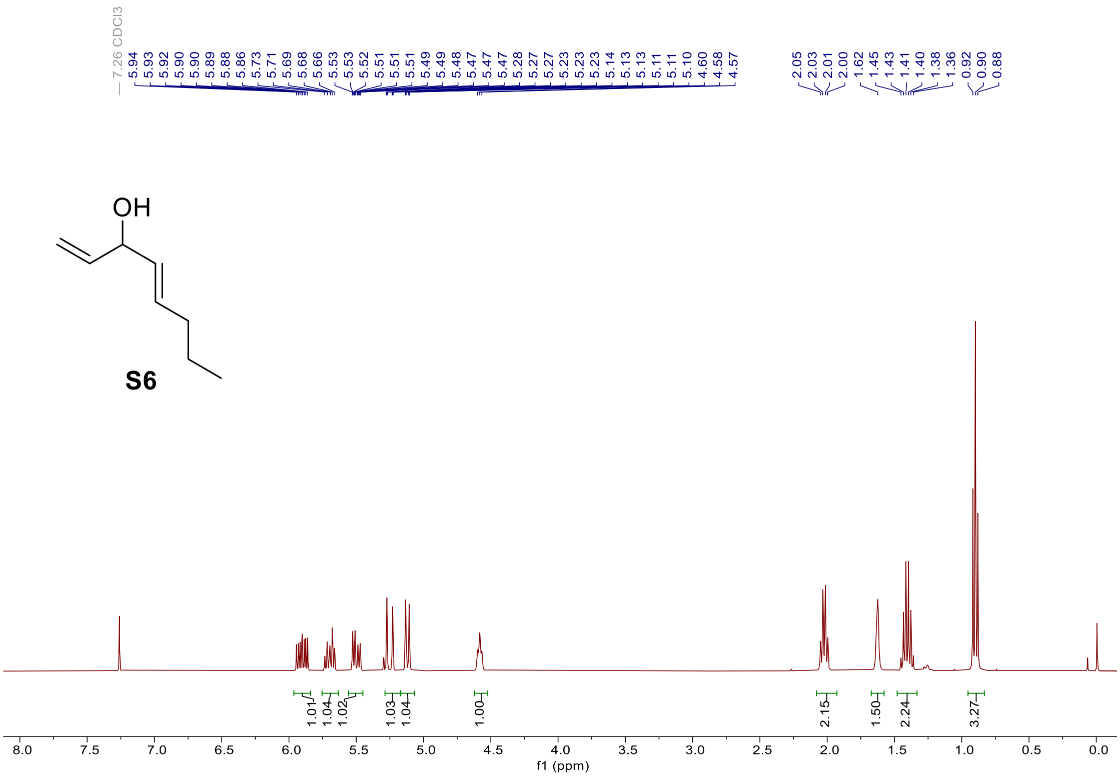


Figure S7. ^{1}H NMR (400 MHz) spectra of **S6** in $CDCl_3$.

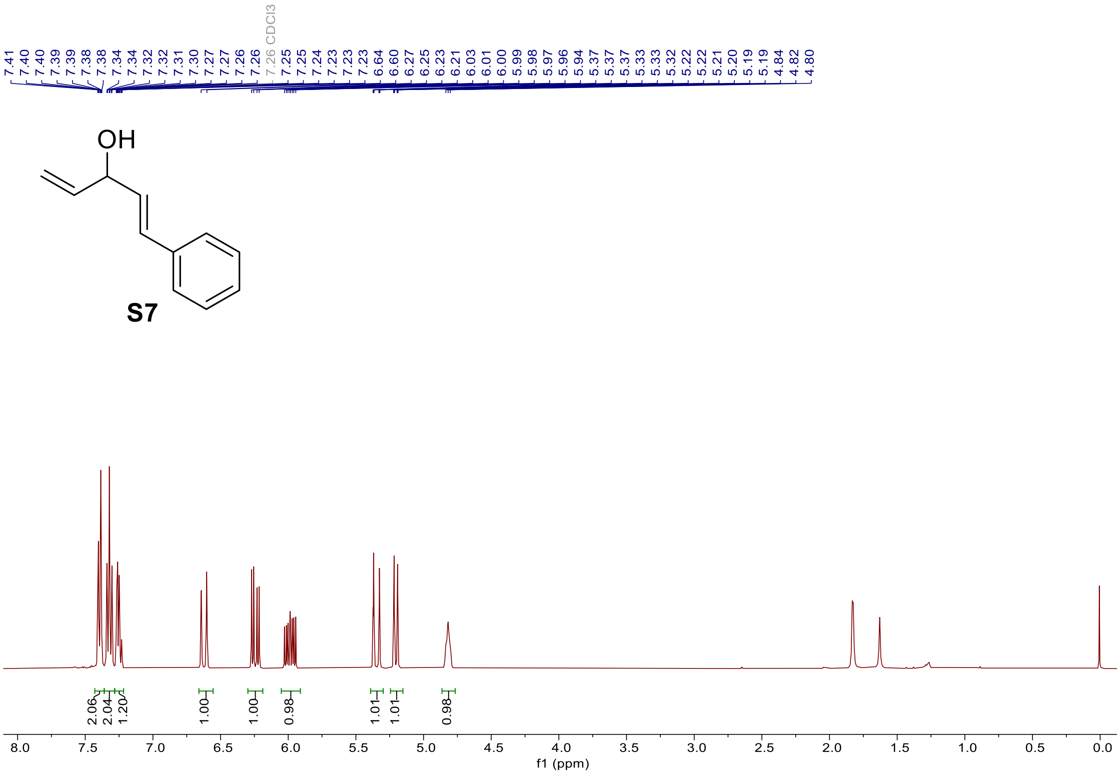


Figure S8. ^{1}H NMR (400 MHz) spectra of **S7** in $CDCl_3$.

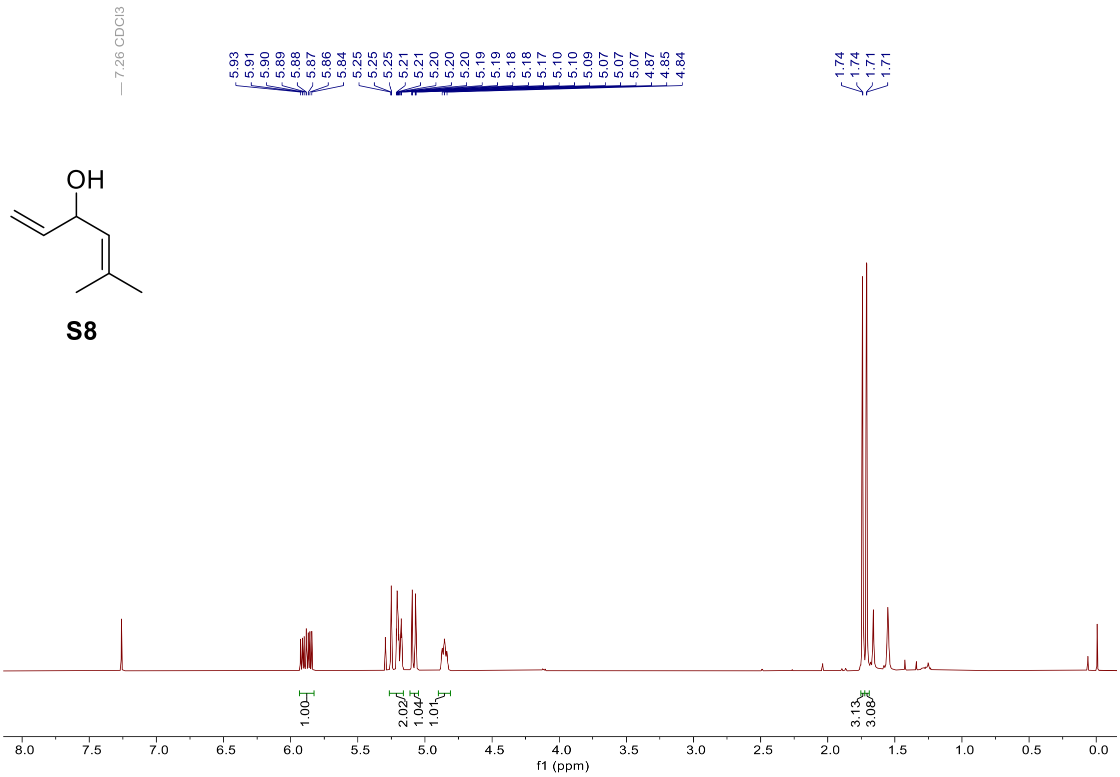
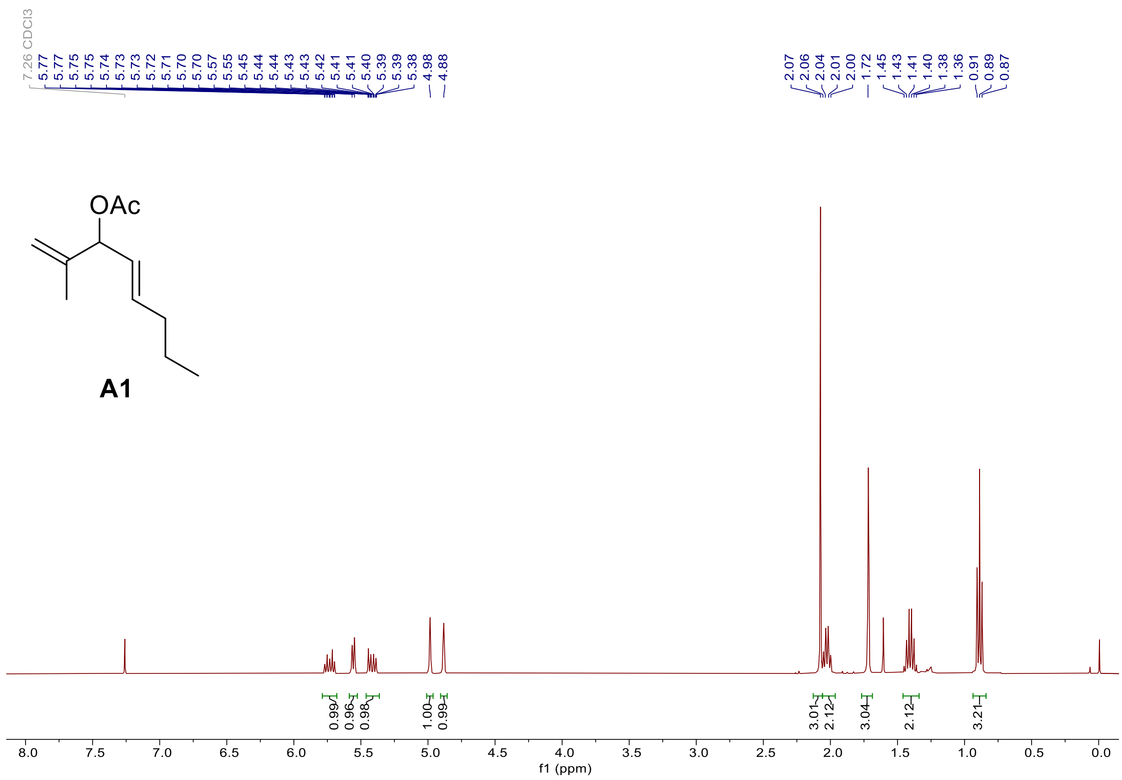


Figure S9. ^{1}H NMR (400 MHz) spectra of **S8** in $CDCl_3$.



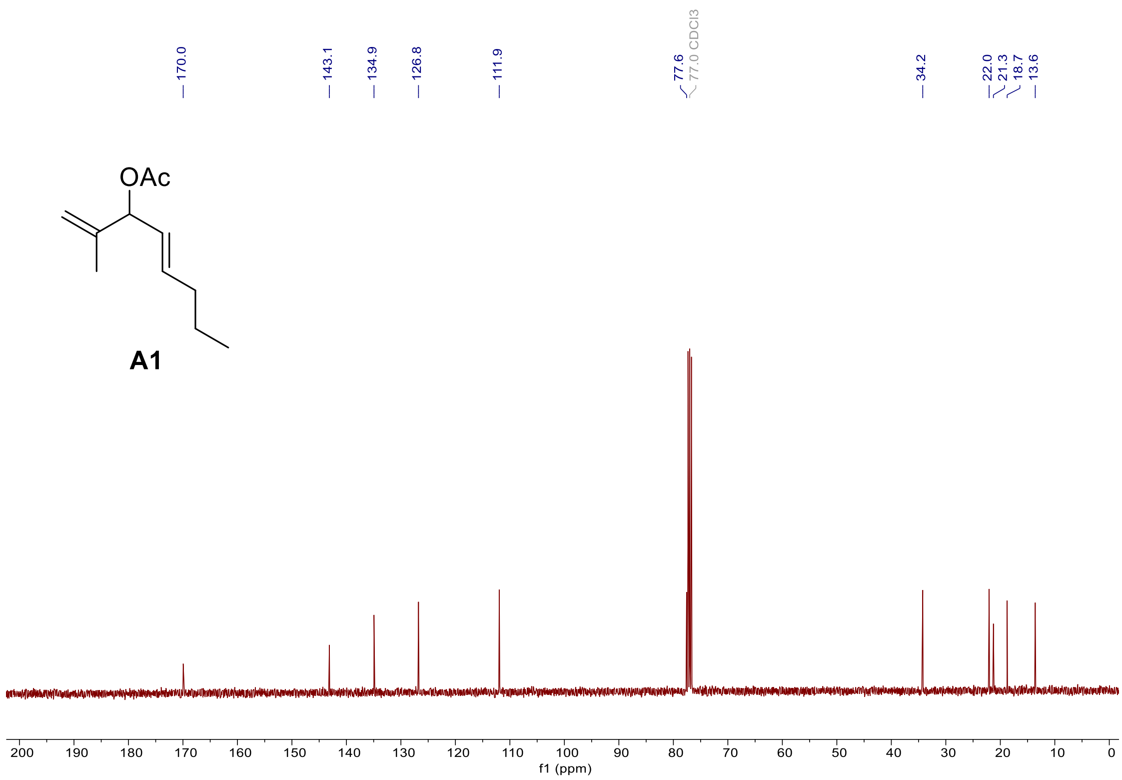
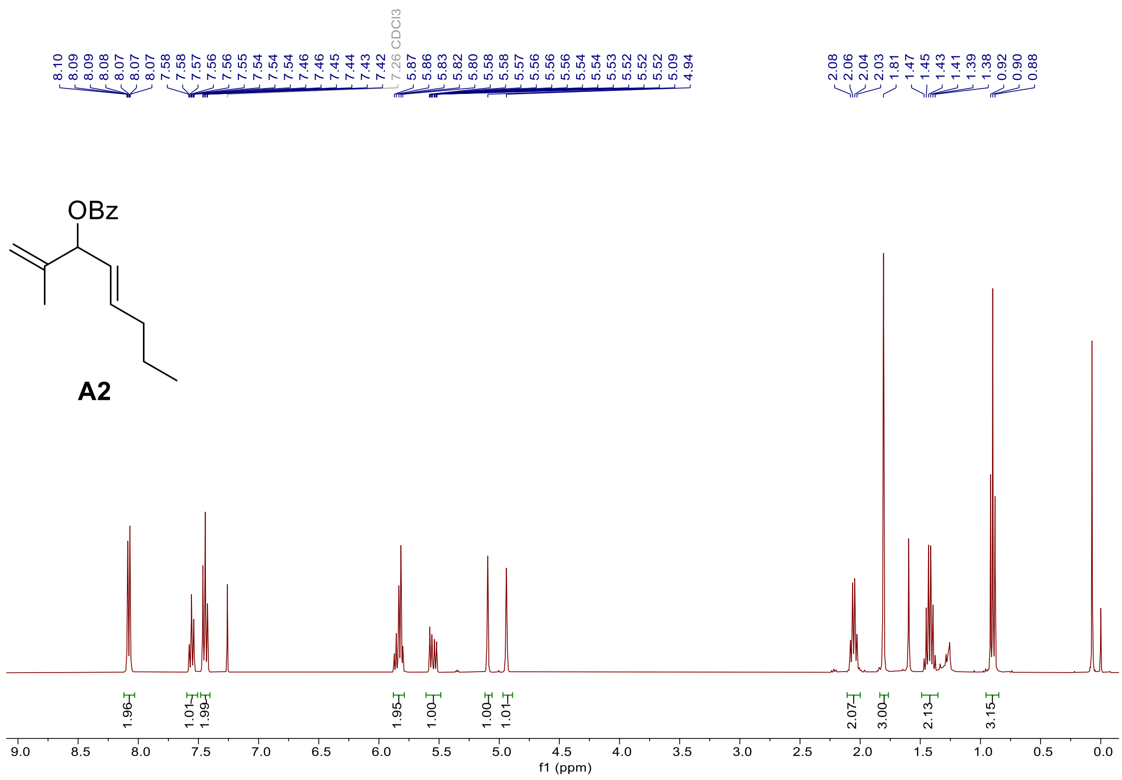


Figure S10. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **A1** in $CDCl_3$.



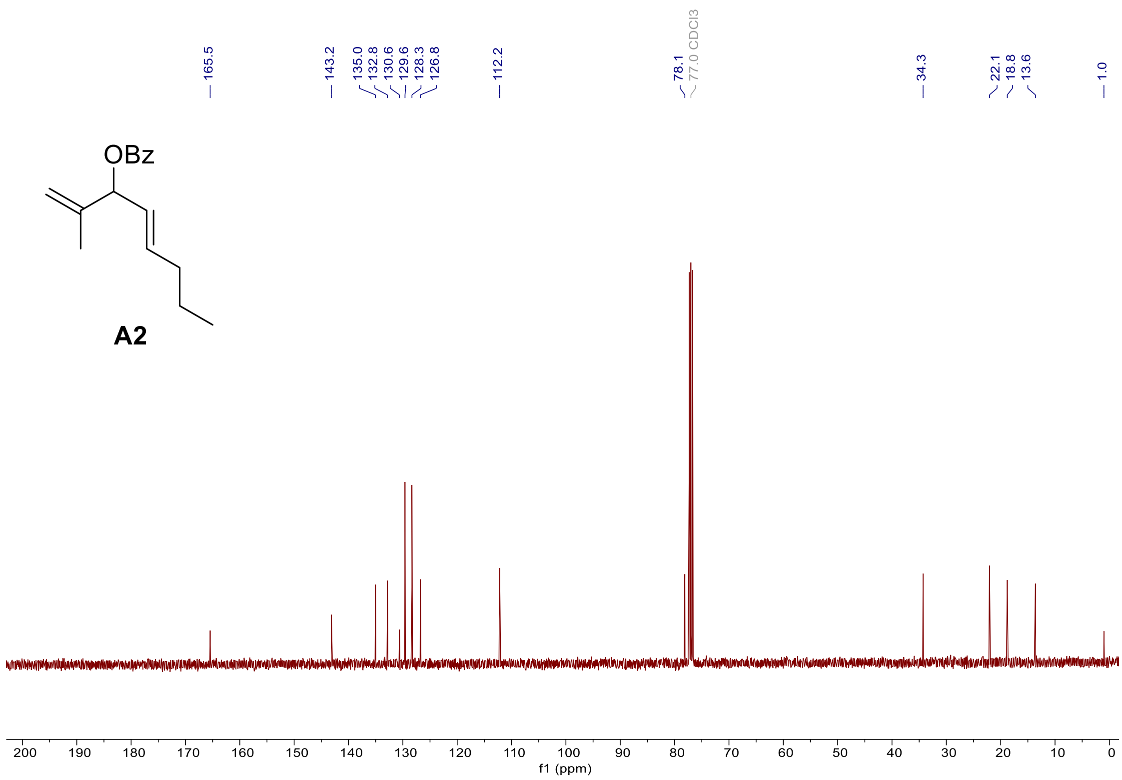
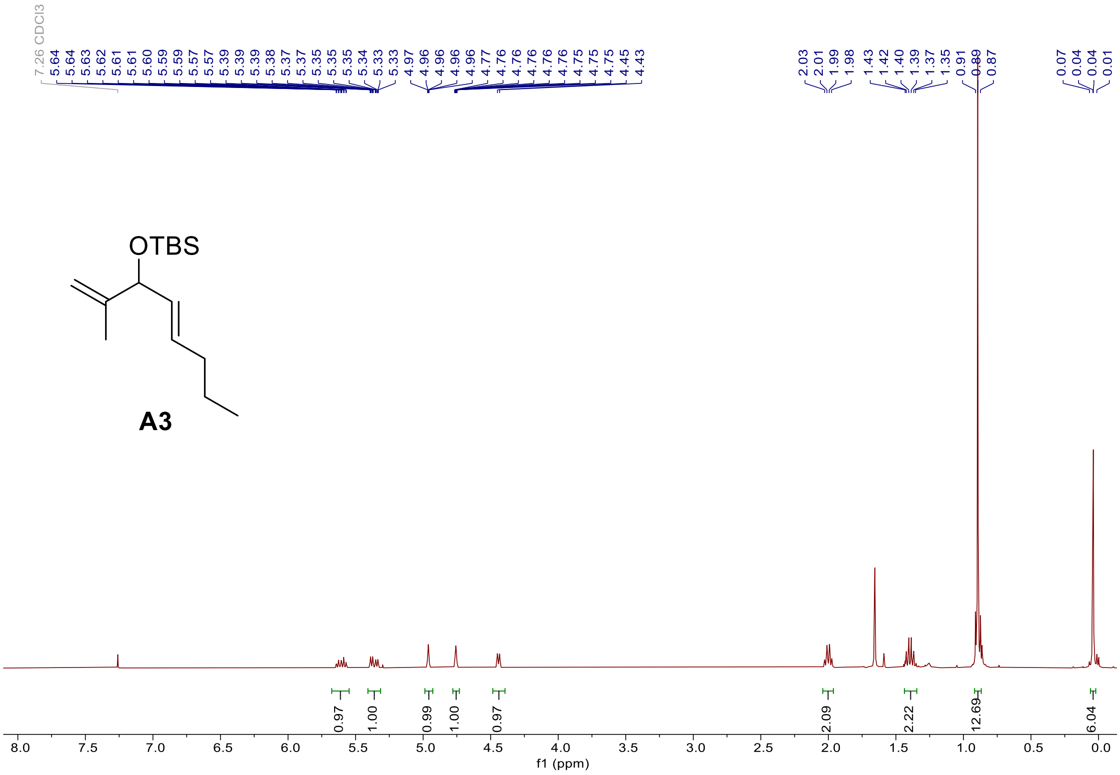


Figure S11. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **A2** in $CDCl_3$.



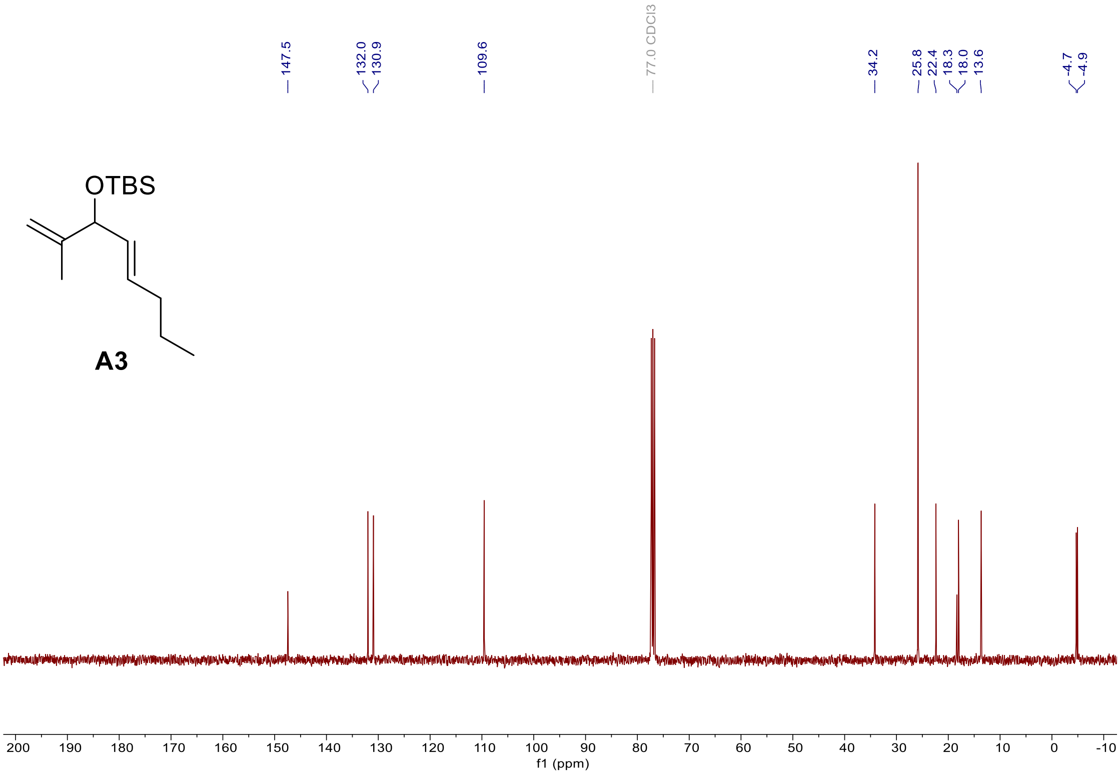
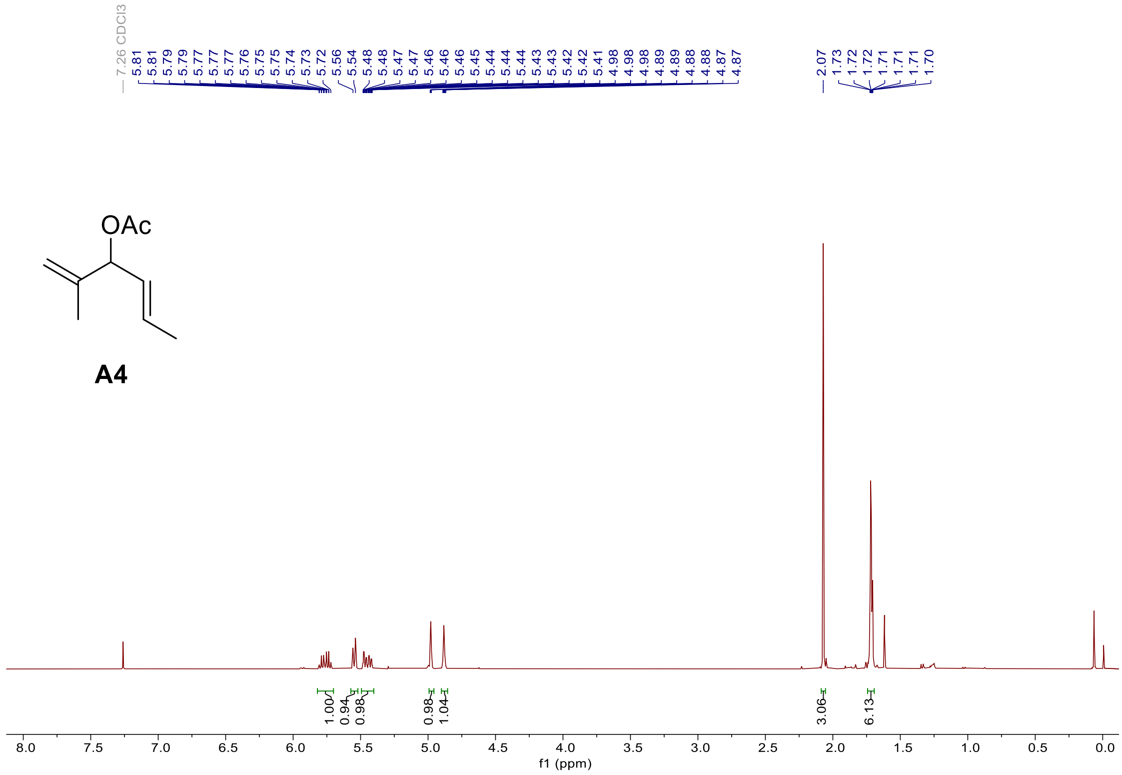


Figure S12. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **A3** in $CDCl_3$.



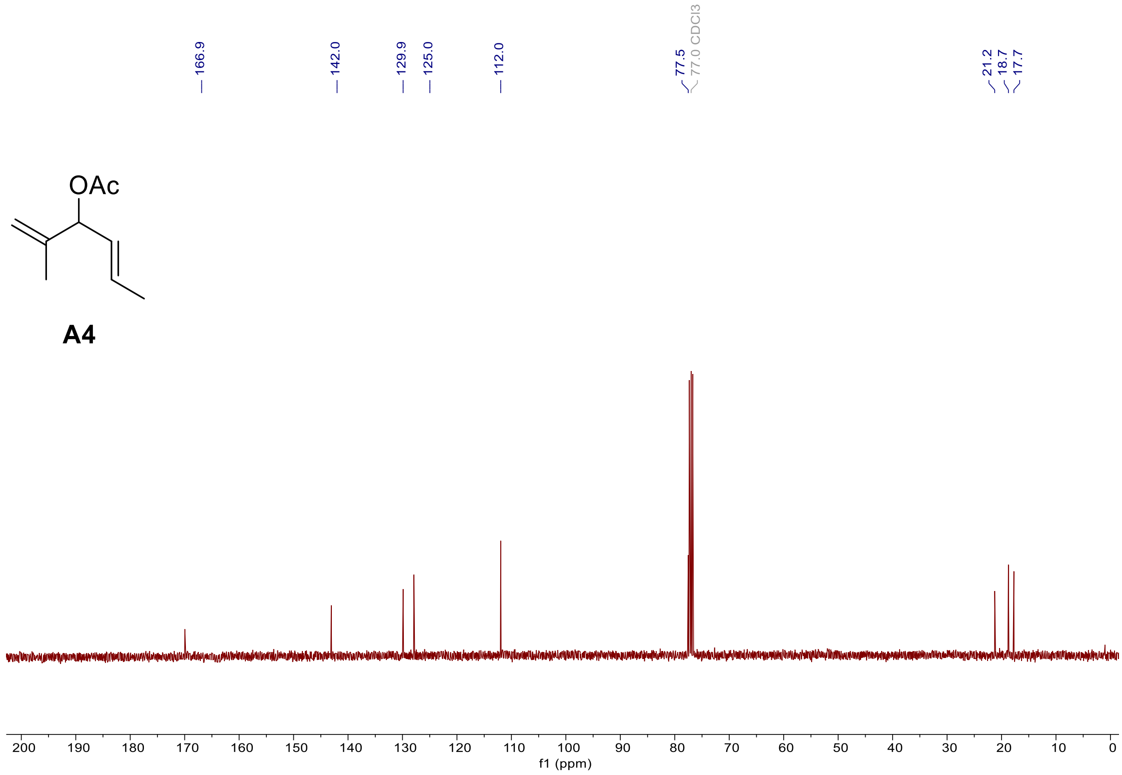
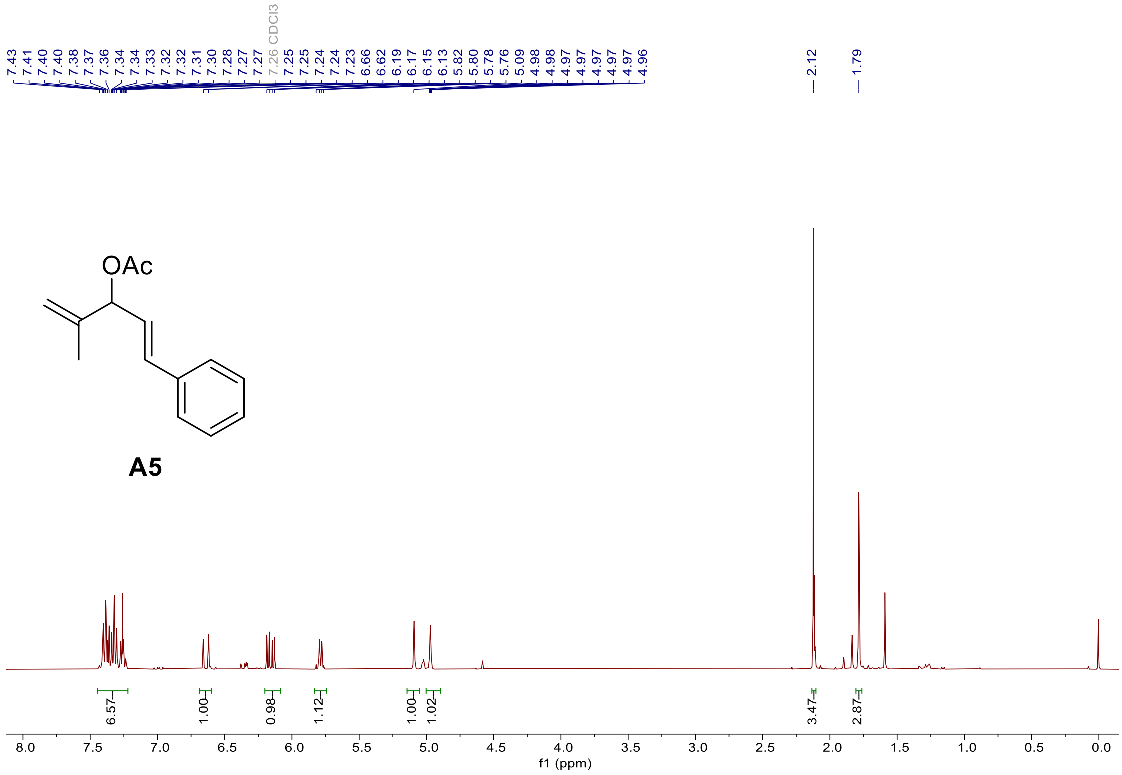


Figure S13. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **A4** in $CDCl_3$.



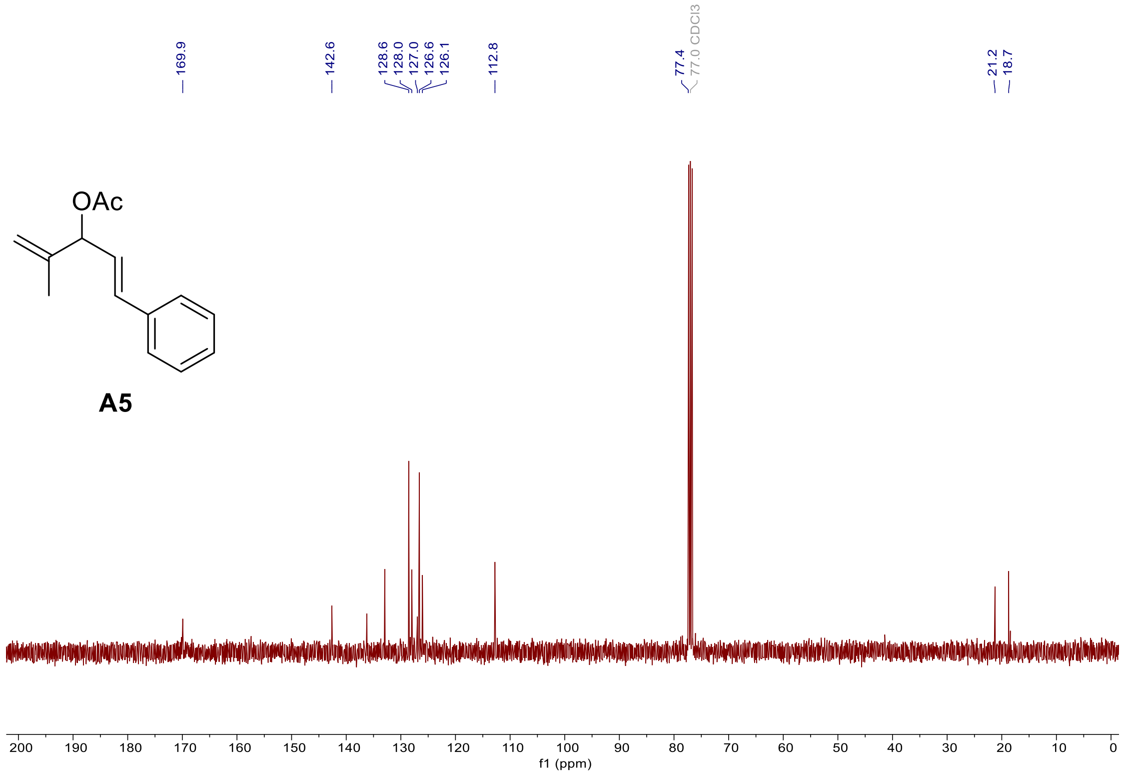
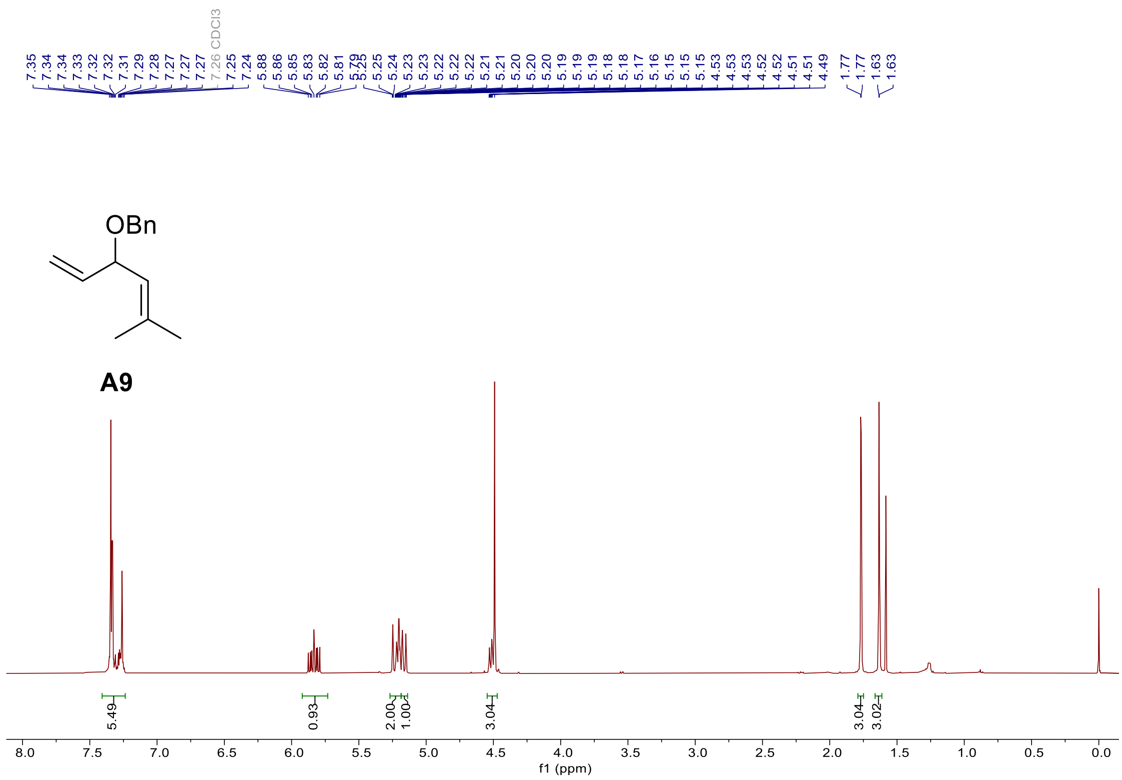


Figure S14. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **A5** in $CDCl_3$.



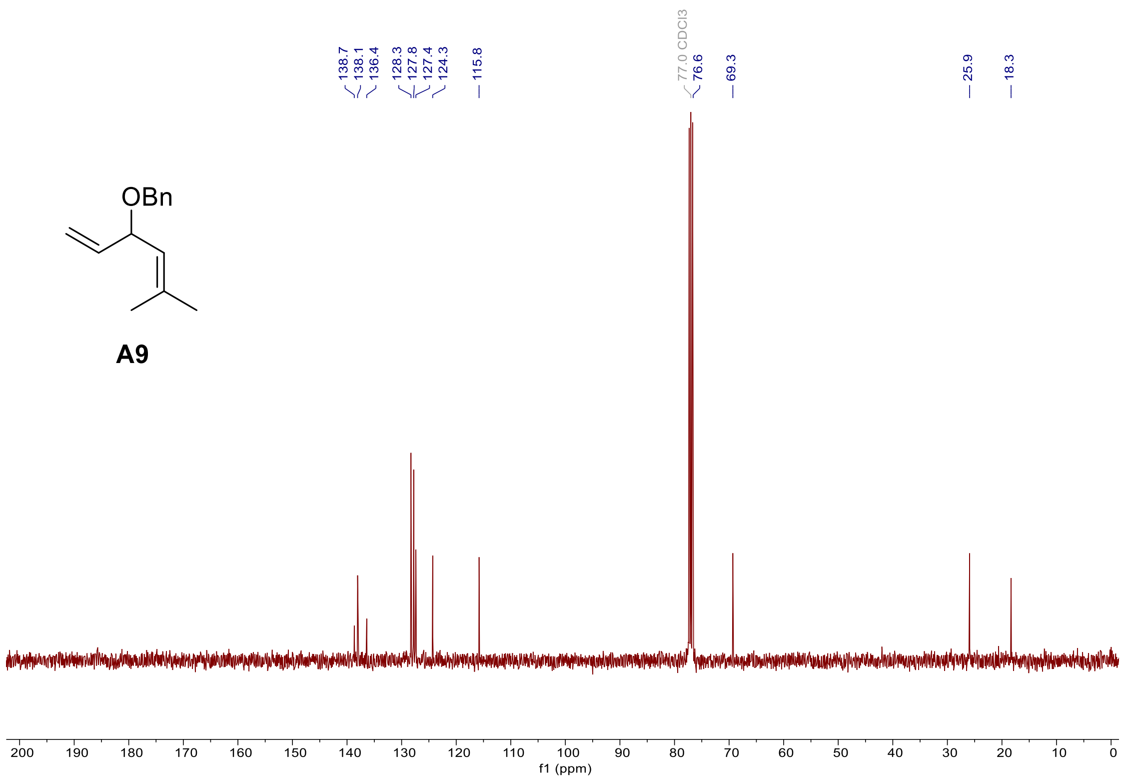
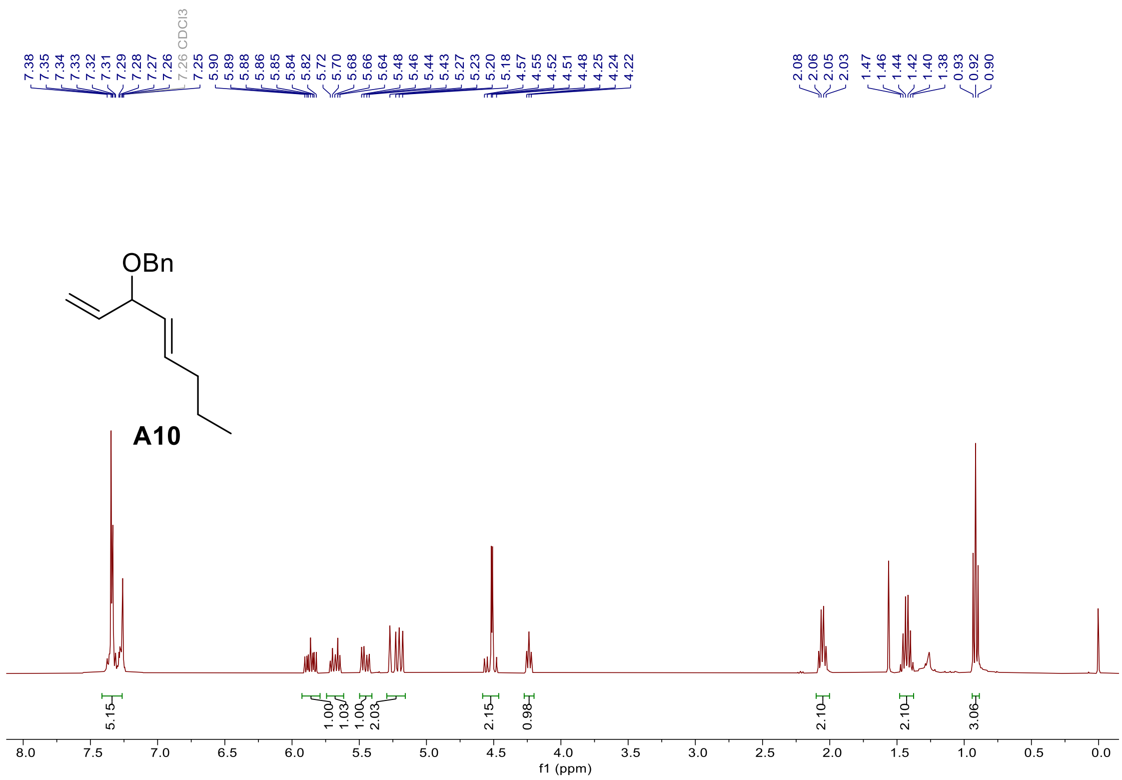


Figure S15. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **A9** in $CDCl_3$.



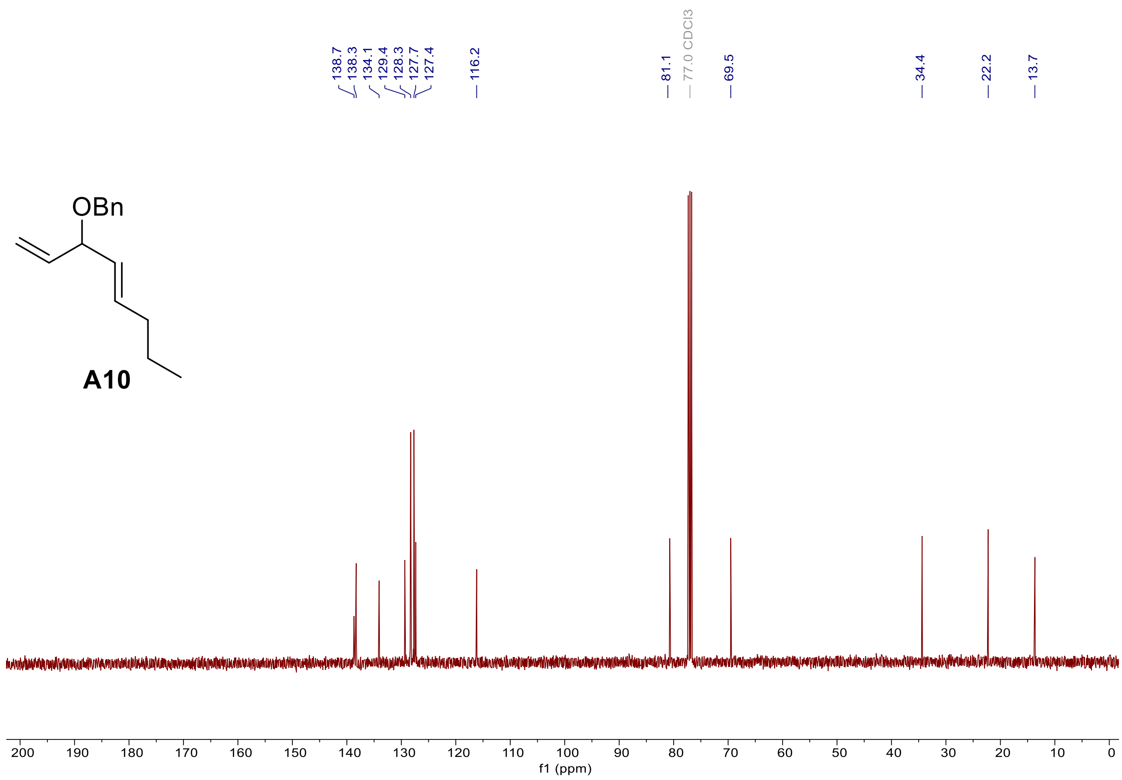
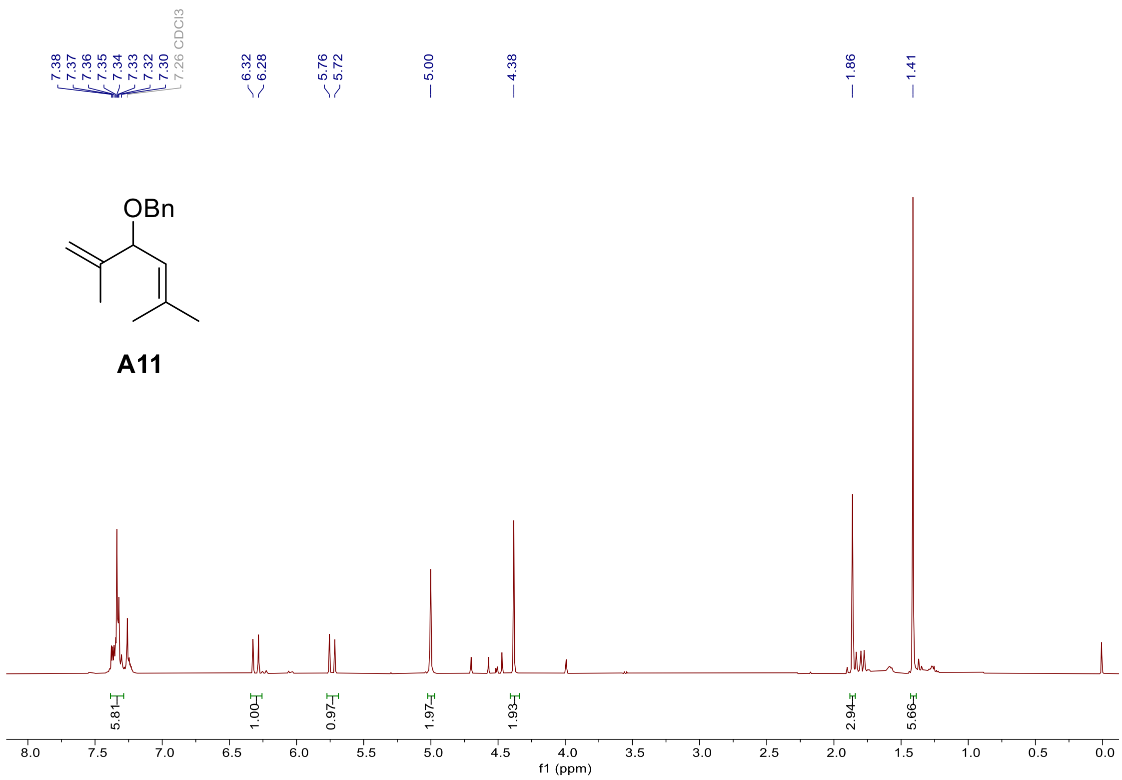


Figure S16. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **A10** in $CDCl_3$.



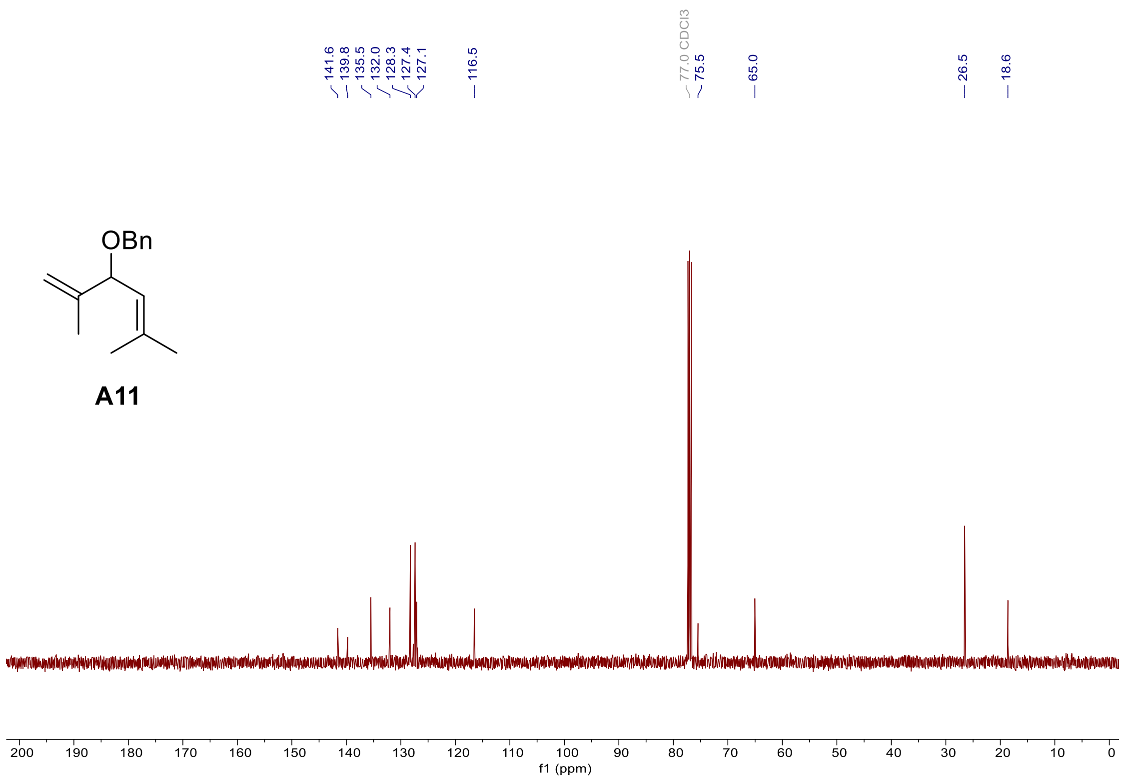
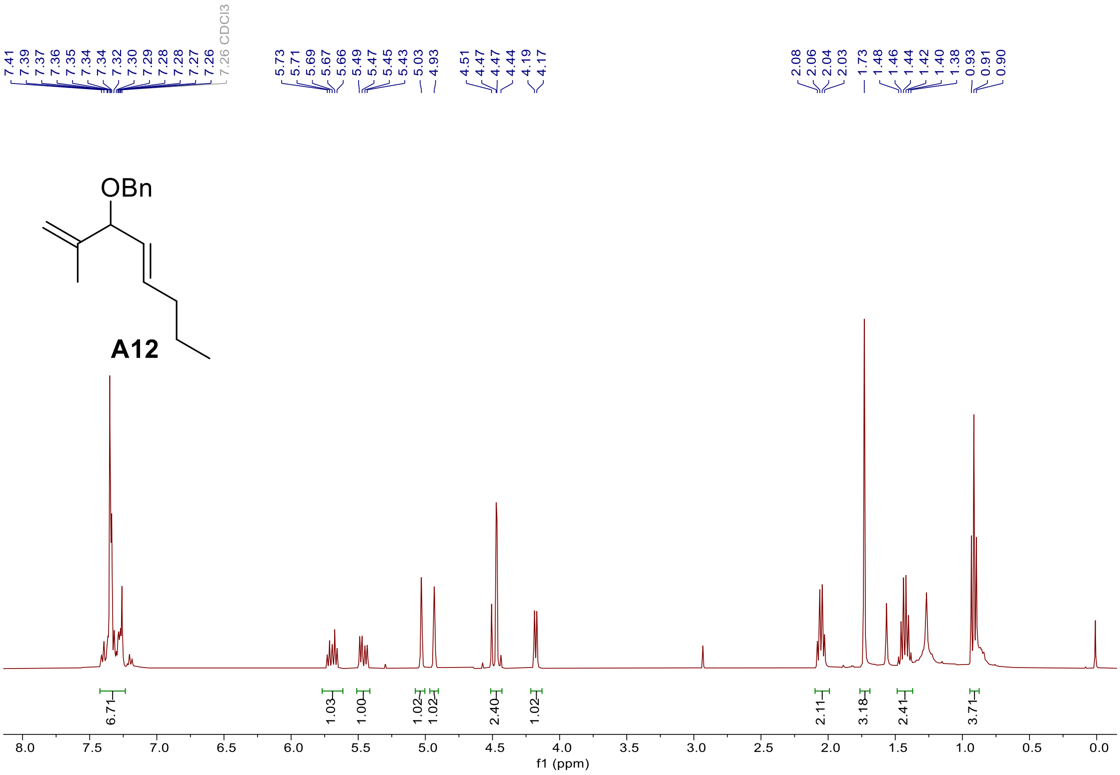


Figure S17. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **A11** in $CDCl_3$.



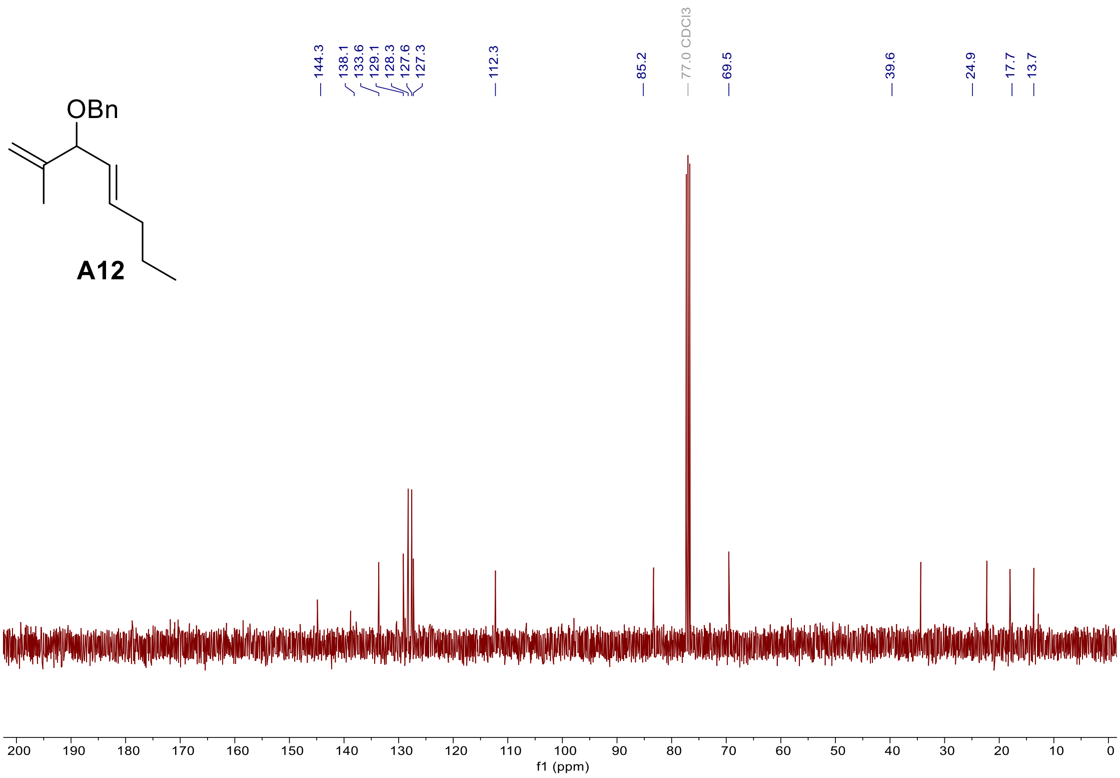


Figure S18. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **A12** in $CDCl_3$.

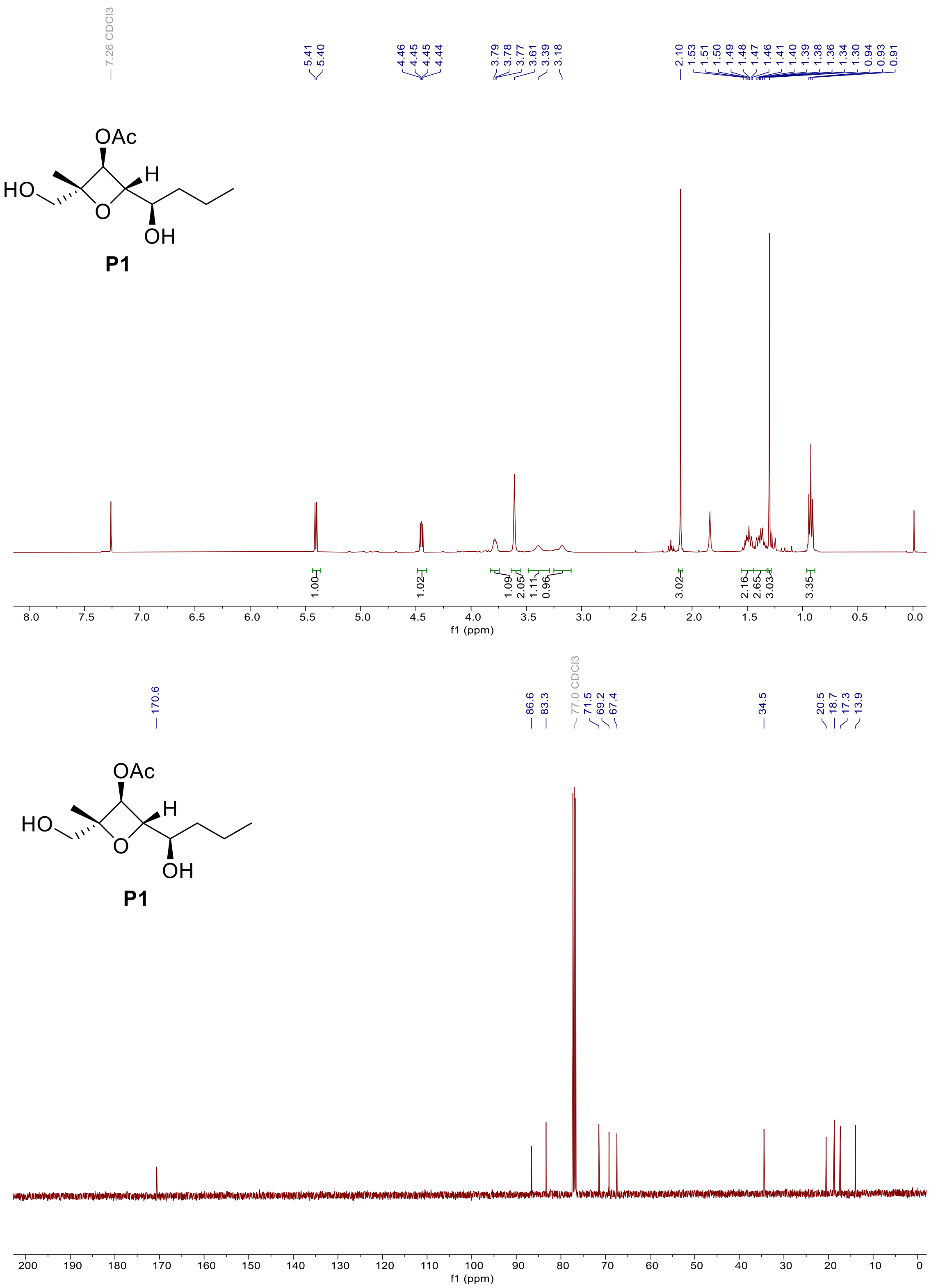


Figure S19. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **P1** in $CDCl_3$.

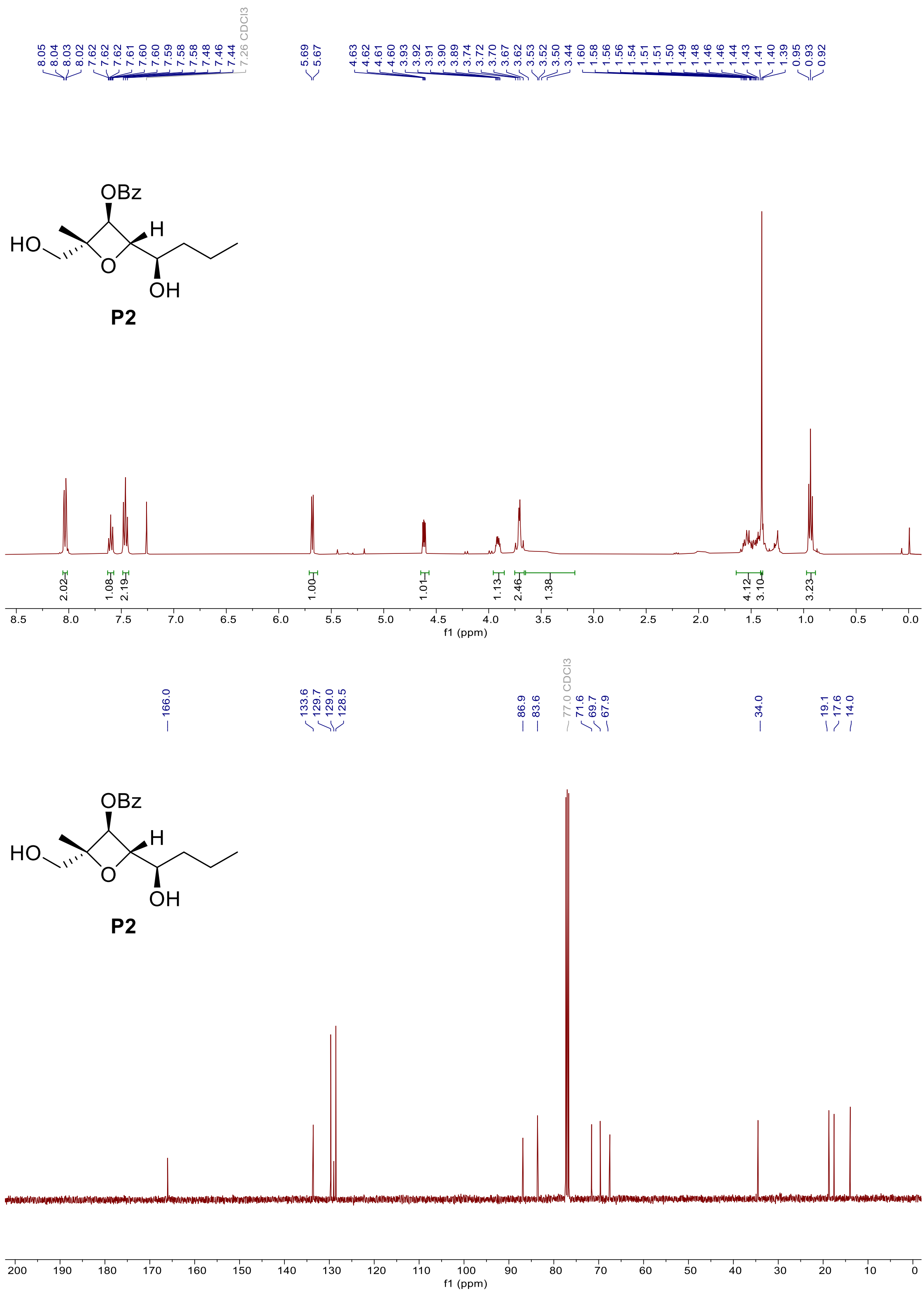
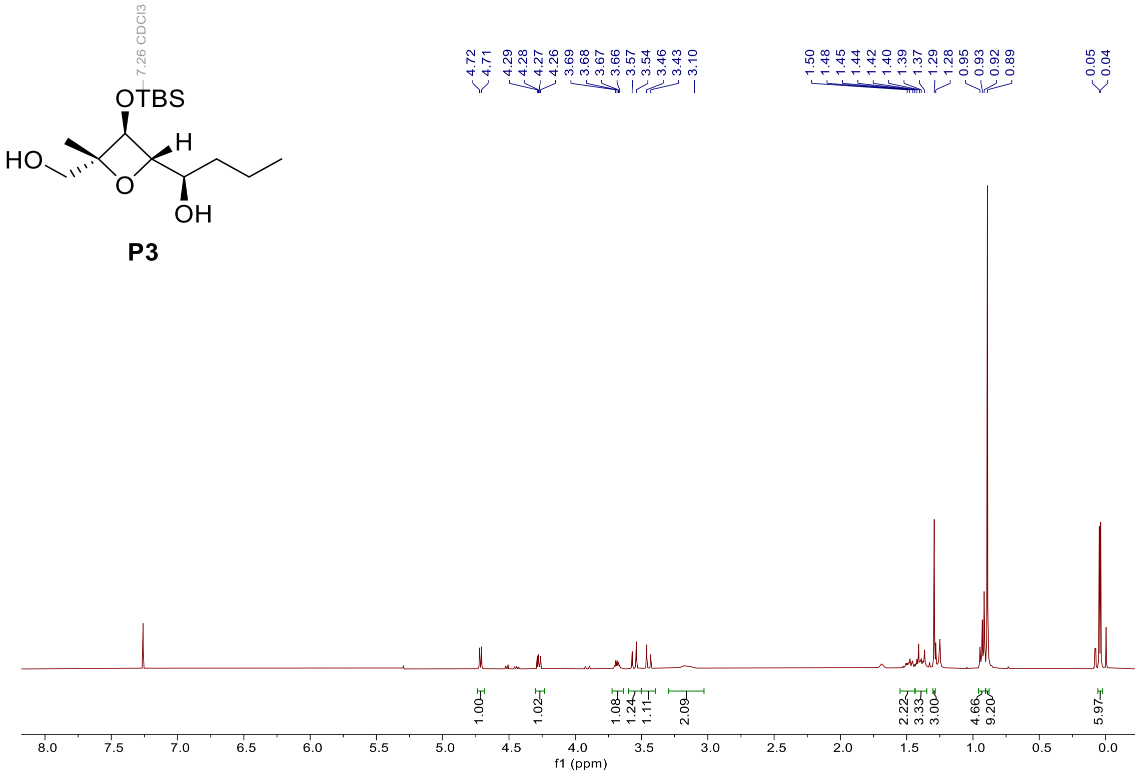


Figure S20. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **P2** in $CDCl_3$.



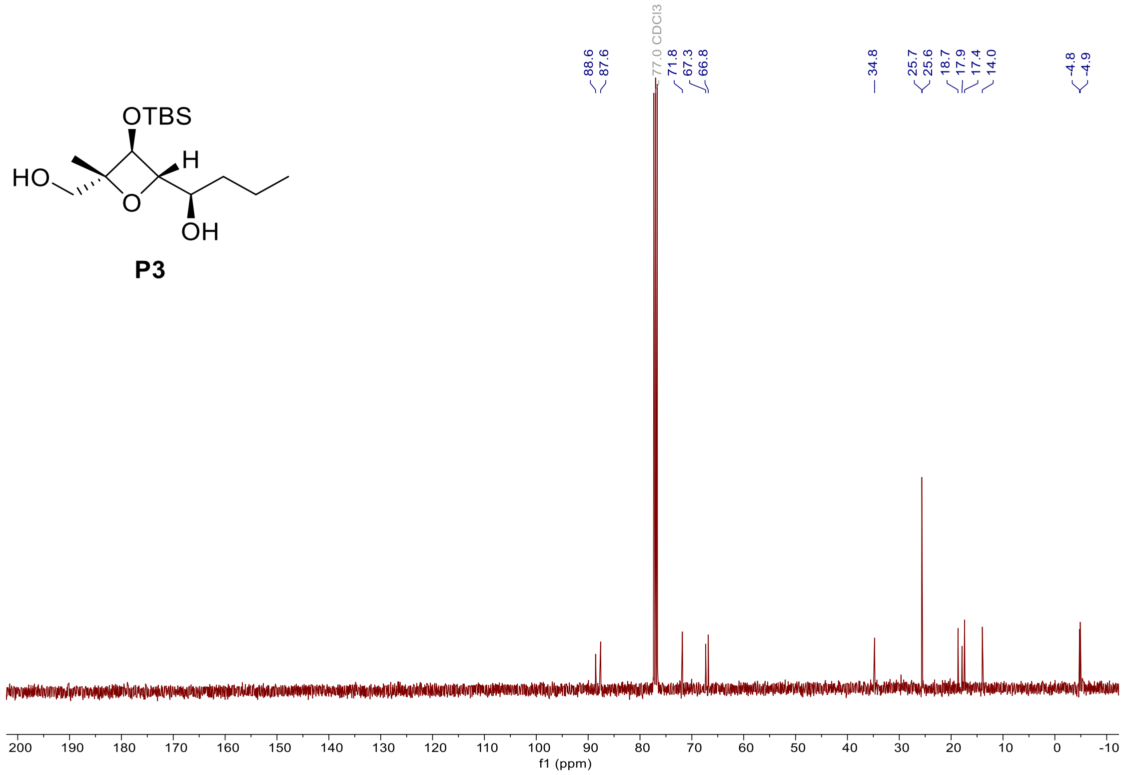
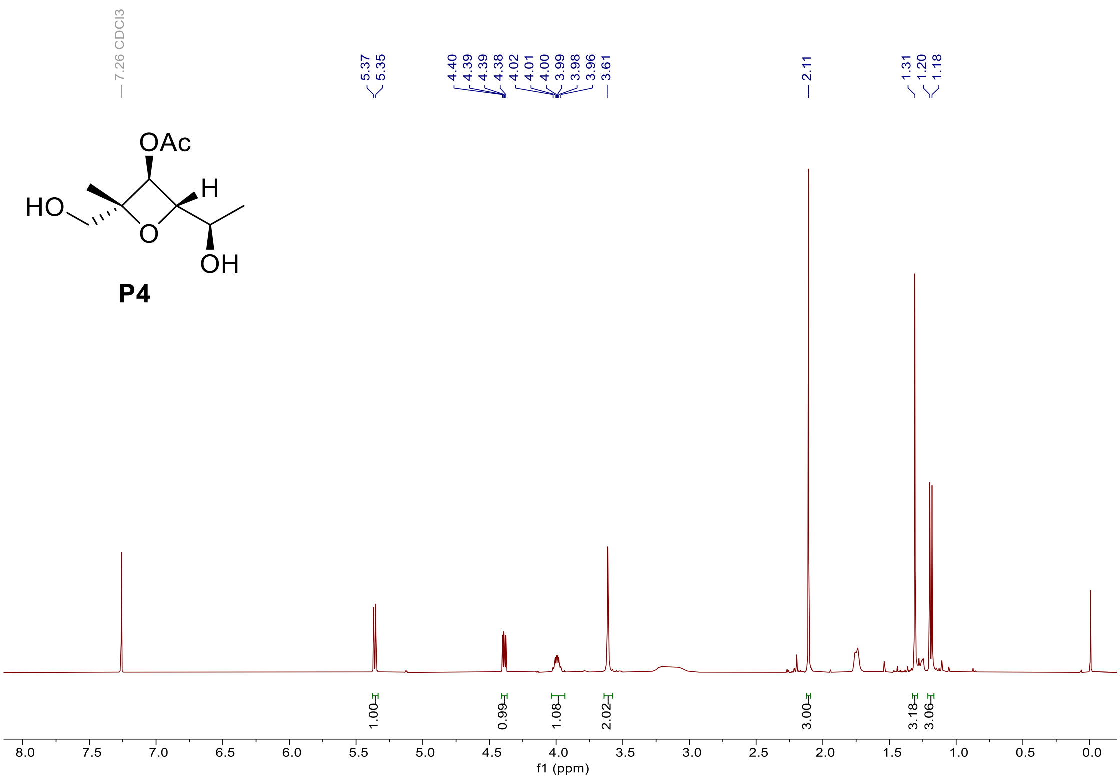


Figure S21. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **P3** in $CDCl_3$.



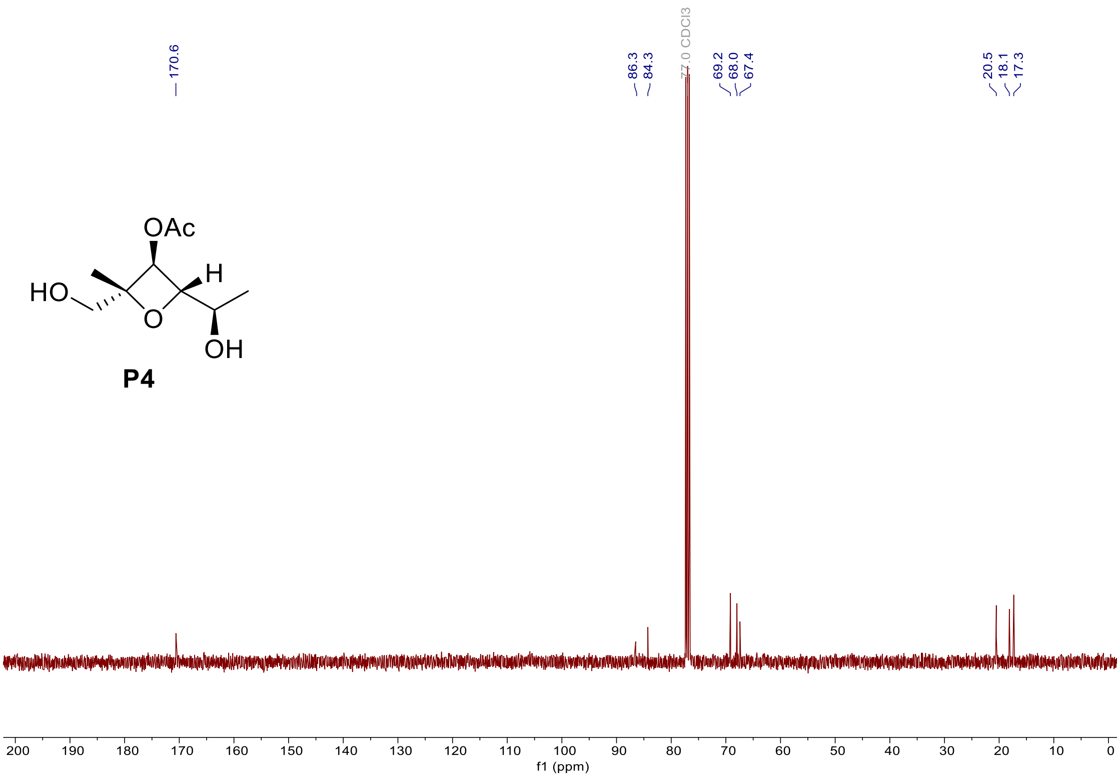


Figure S22. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **P4** in $CDCl_3$.

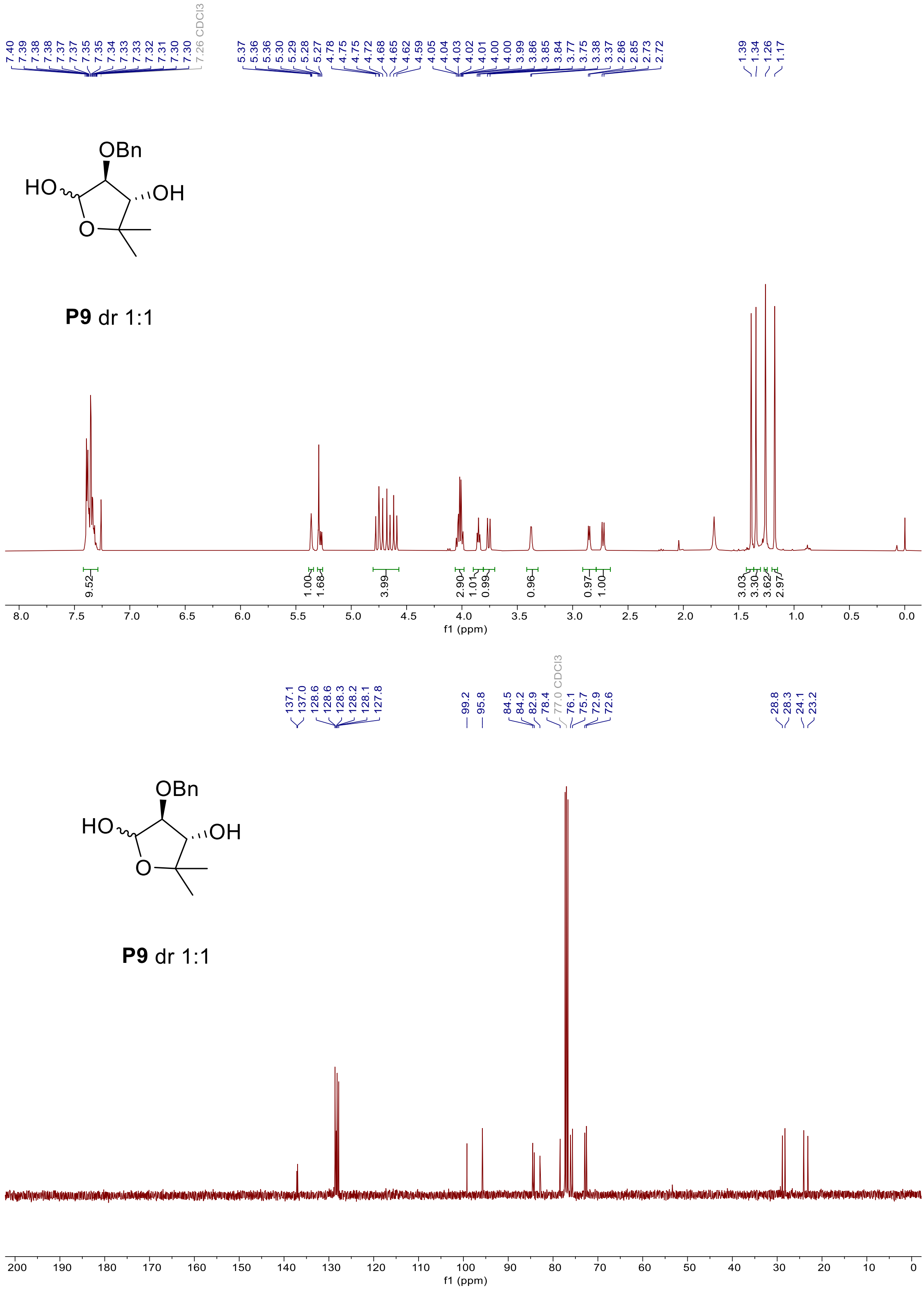
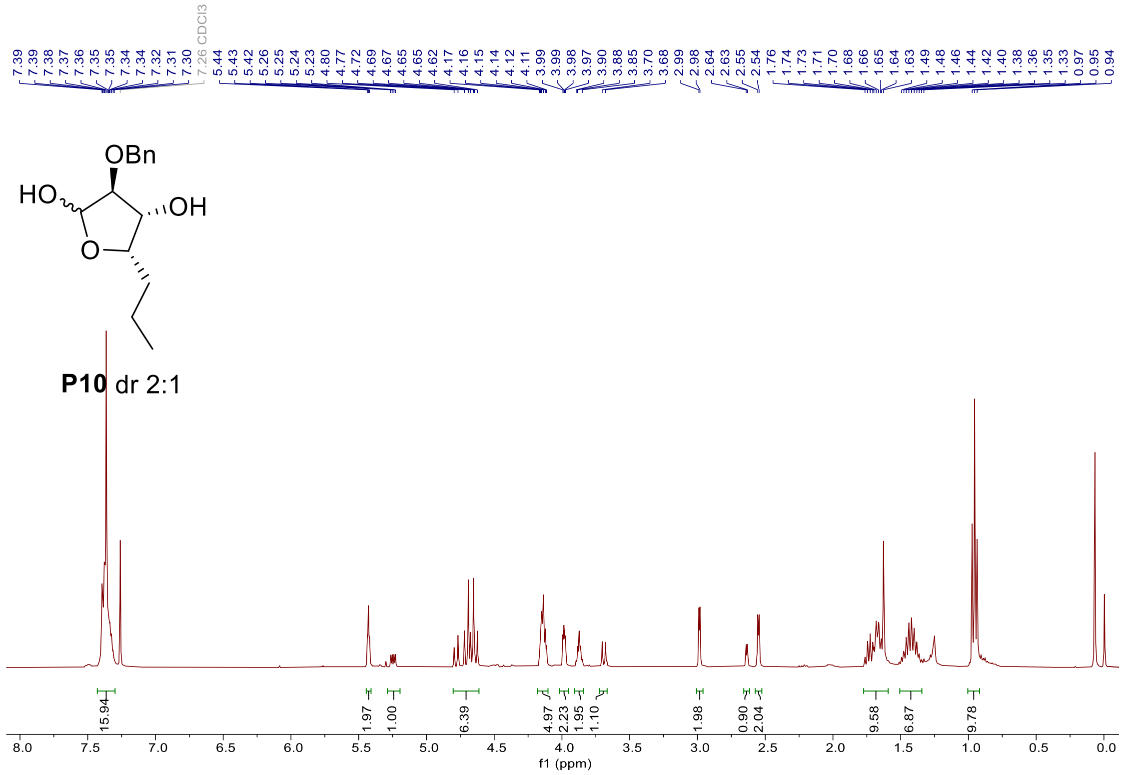


Figure S23. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **P9** in $CDCl_3$.



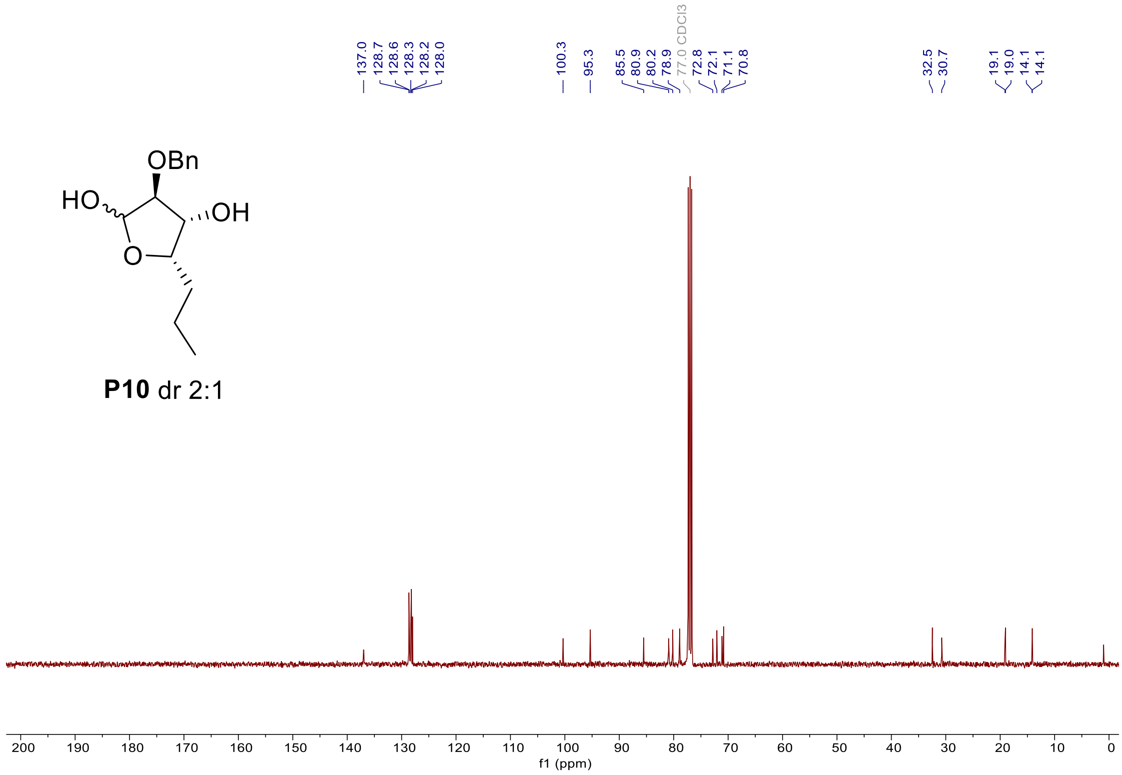
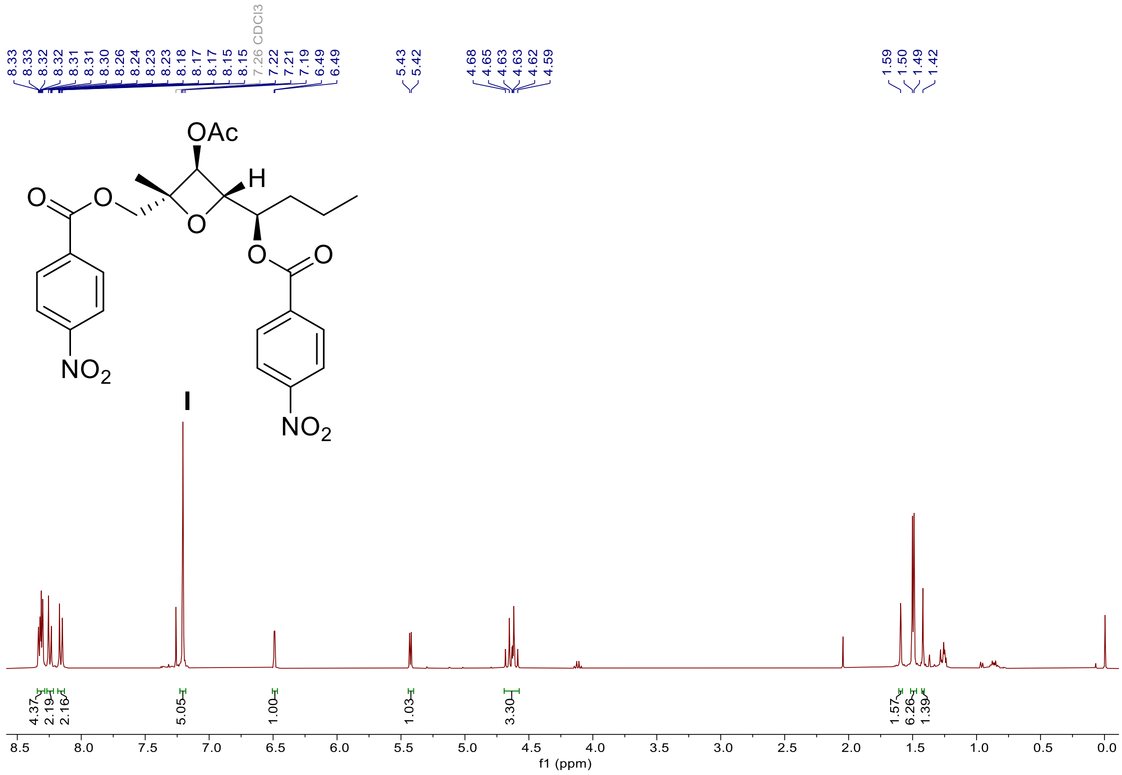


Figure S24. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **P10** in $CDCl_3$.



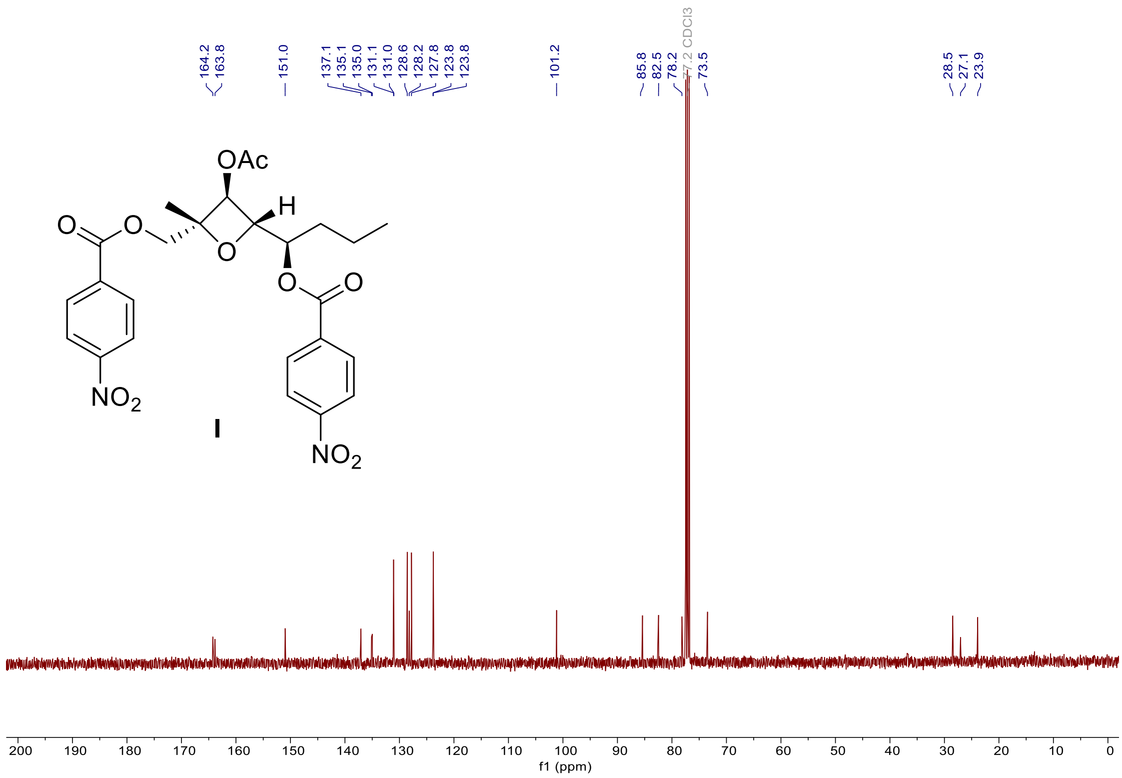
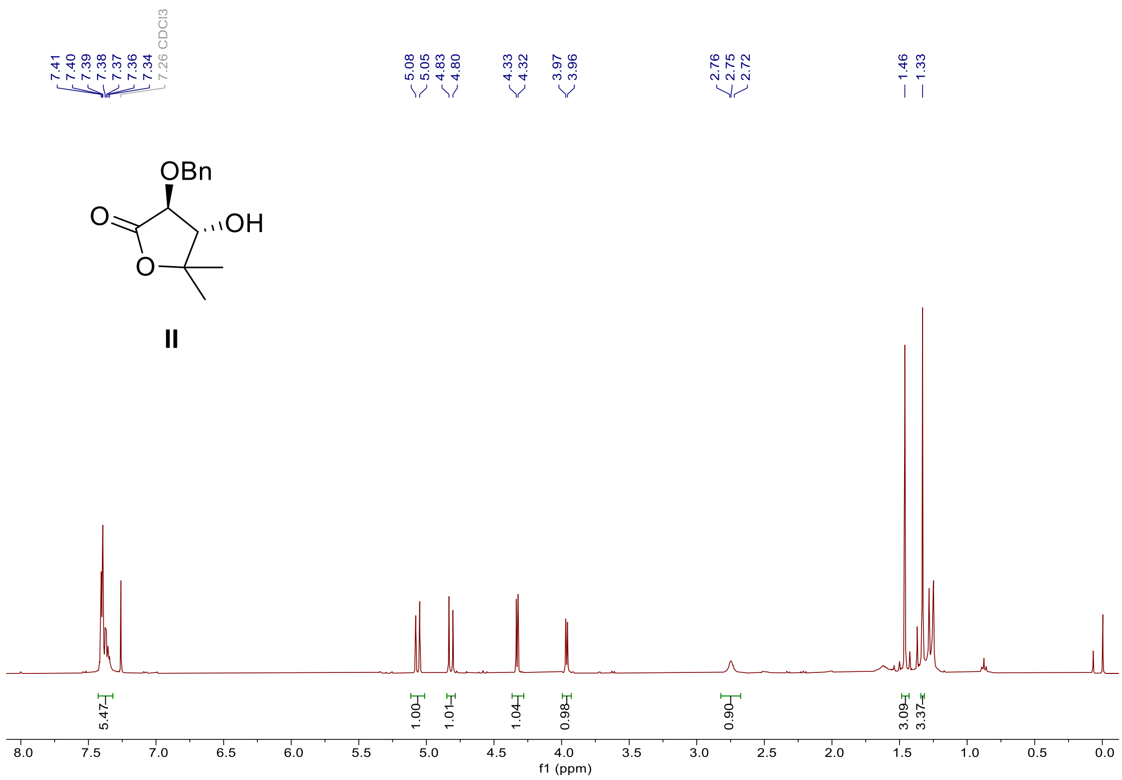


Figure S25. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **I** in $CDCl_3$.



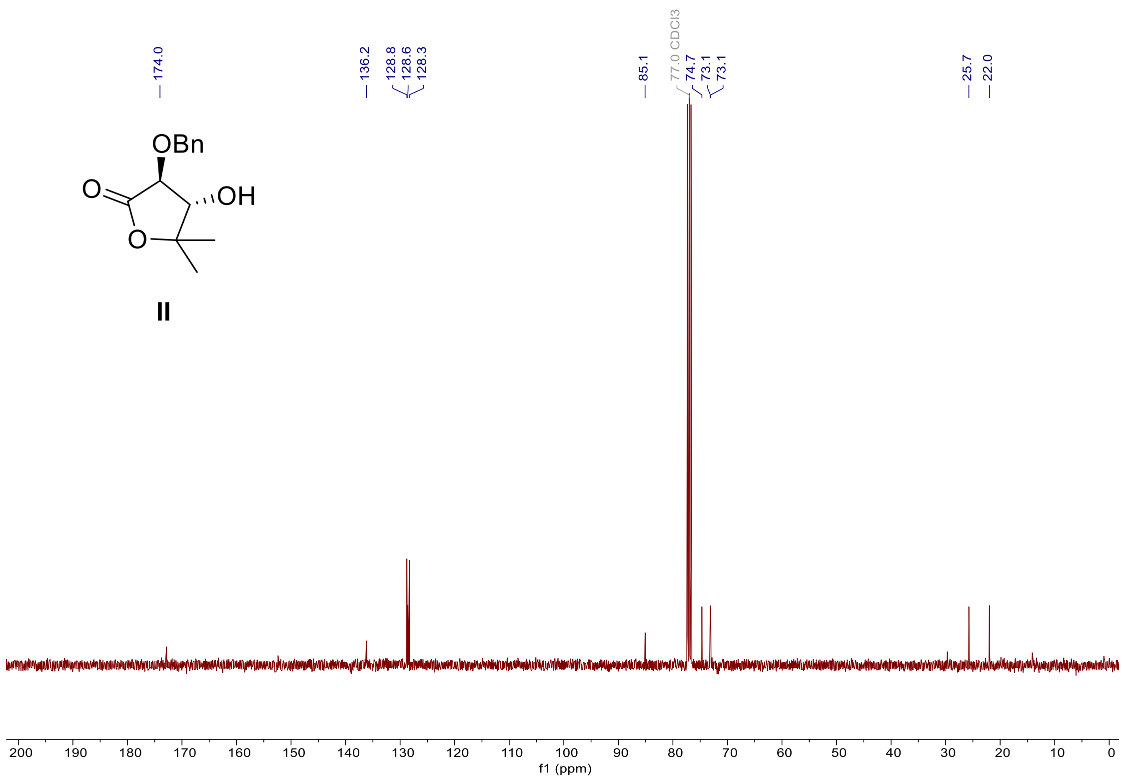


Figure S26. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **II** in $CDCl_3$.

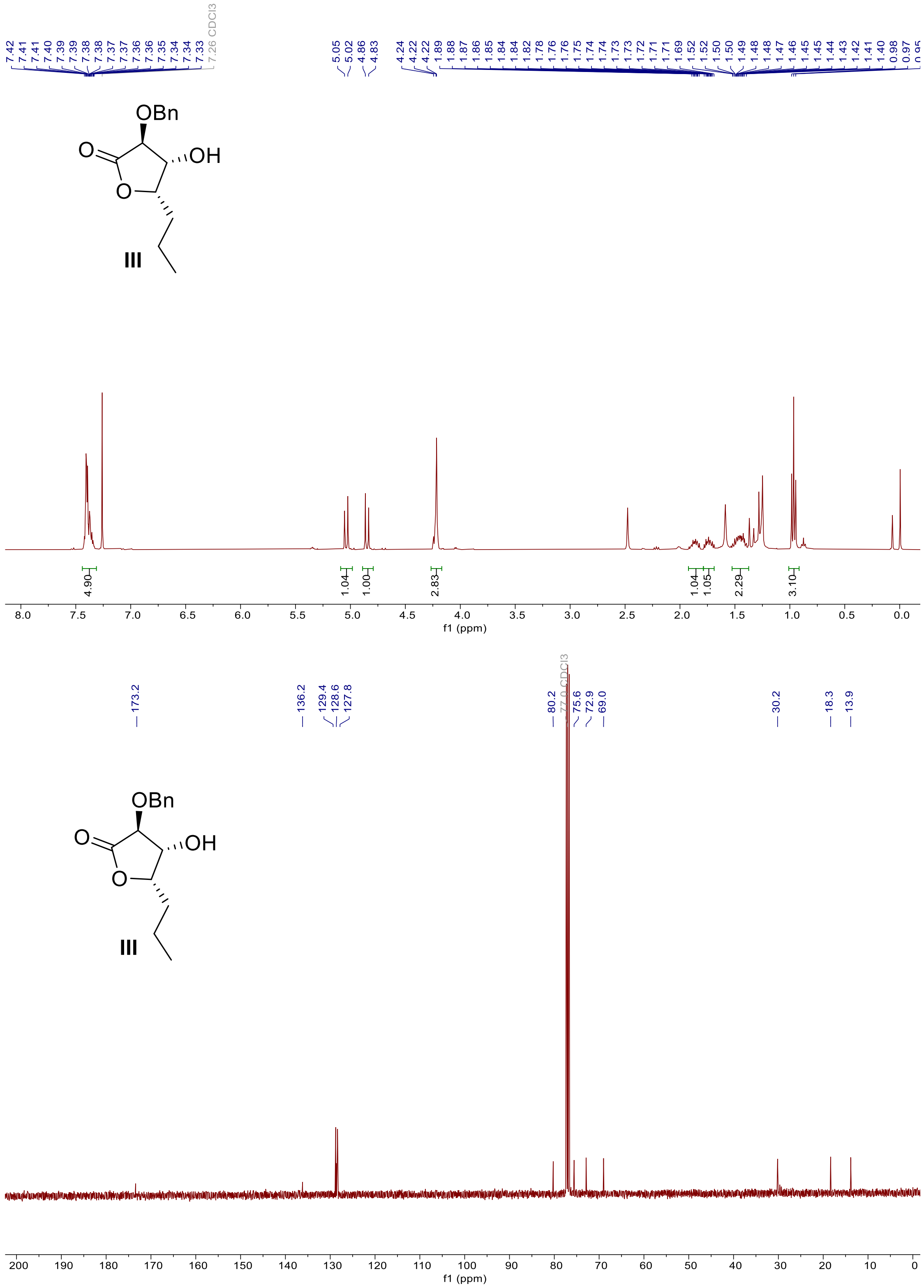
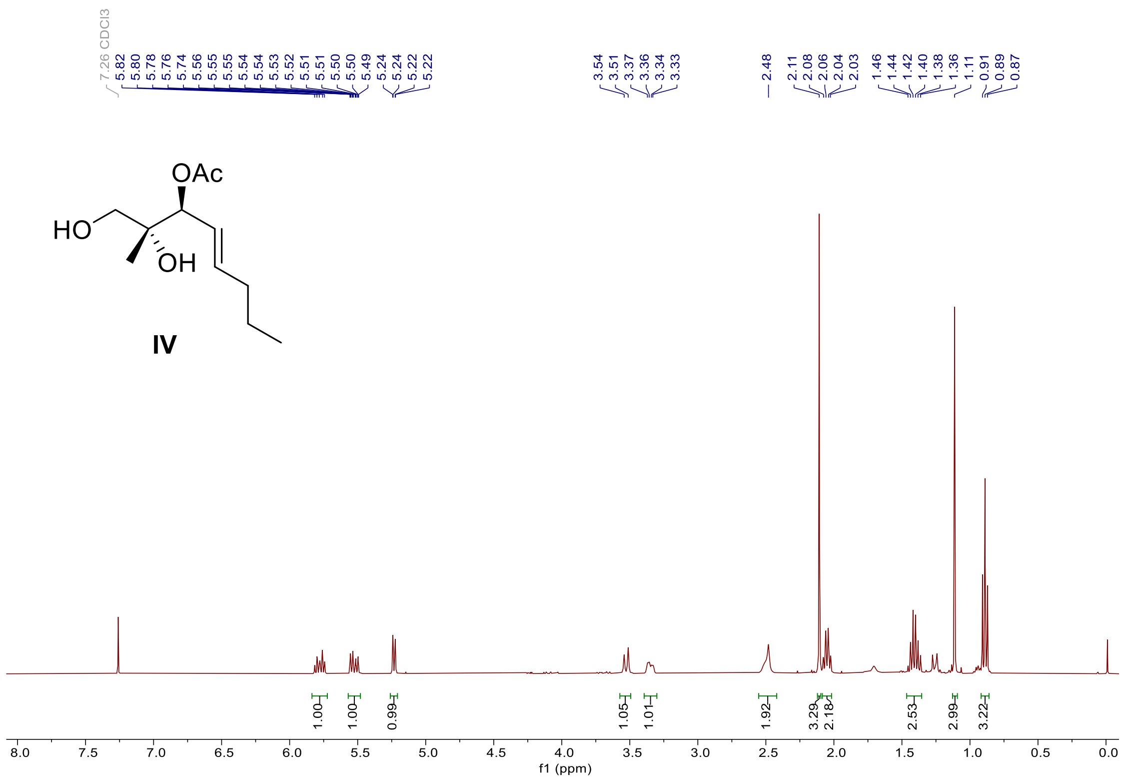


Figure S27. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **III** in $CDCl_3$.



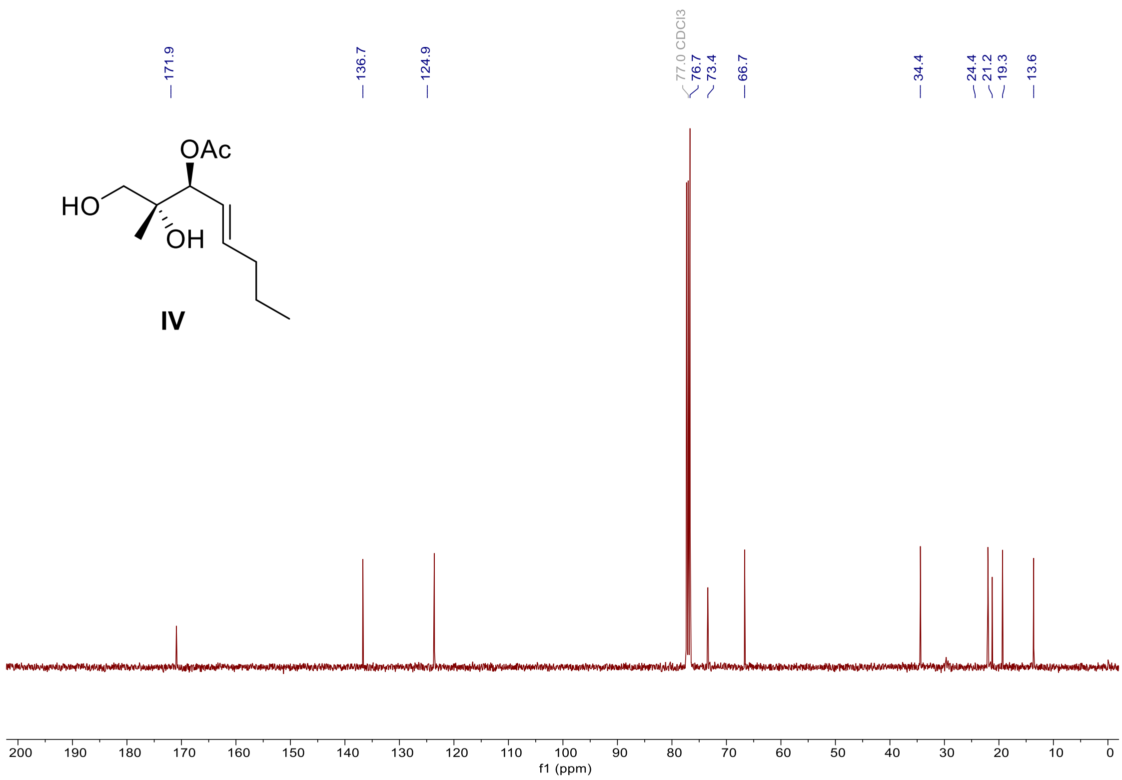


Figure S28. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of **IV** in $CDCl_3$.