## Supporting Information

**for**

# A modular phosphate tether-mediated divergent strategy to complex polyols

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## Experimental section

General Methods: S1 to S5
Experimental Data: S6 to S14
$^{1}H$ NMR, $^{13}C$ NMR, $^{31}P$ NMR spectra: S15 to S32

All reactions were carried out in an oven- or flame-dried glassware under argon atmosphere using standard gas-tight syringes, cannulae, and septa. Stirring was achieved with oven-dried magnetic stir bars. $Et_2O$, THF and $CH_2Cl_2$ were purified by passage through a purification system (Solv-Tek) employing activated $Al_2O_3$ (Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Safe and Convenient Procedure for Solvent Purification *Organometallics*, **1996**, *15*, 1518–1520). $Et_3N$ was purified by passage over basic alumina and stored over KOH. Butyllithium was purchased from Aldrich and titrated prior to use. All olefin metathesis catalysts were acquired from Materia and used without further purification. Flash column chromatography was performed with Sorbent Technologies (30930M-25, Silica Gel 60A, 40-63 μm) and thin layer chromatography was performed on silica gel $60F_{254}$ plates (EM-5717, Merck). Deuterated solvents were purchased from Cambridge Isotope laboratories. $^{1}H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ (unless otherwise mentioned) on a Bruker DRX-500 spectrometer operating at 500 MHz, and 125 MHz, respectively and calibrated to the solvent peak. $^{31}P$ NMR spectra was recorded on Bruker DRX-400 spectrometer operating at 162 MHz. High-resolution mass spectrometry (HRMS) was recorded on a LCT Premier Spectrometer (Micromass UK Limited) operating on ESI (MeOH). Observed rotations at 589 nm, were measured using AUTOPOL IV Model automatic polarimeter. IR was recorded on Shimadzu FTIR-8400S instrument.

**General procedure for RCM/CM/hydrogenation (Procedure A)**

To a stirring solution of triene (*S*,*S*) in freshly distilled, freeze-degas-thawed dichloroethane [1] (0.007 M) was added Hoveyda-Grubbs 2nd Gen. catalyst (HG-II) (3 mol %) and the reaction was refluxed for 2 hours. After completion of RCM (monitored by TLC), the solvent was removed under reduced pressure and olefin cross partner [3–5 equivalent with respect to the triene (*S*,*S*)] dissolved in freeze-degas-thawed $CH_2Cl_2$ (0.1 M) was introduced , followed by addition of HG-II (3–5 mol %). It should be noted that the use of dichloromethane was critical for successful cross-metathesis reaction in order to avoid the formation of isomerized ketone byproducts. Cross-metathesis (CM) reaction in dichloroethane provided the isomerized ketone byproduct (confirmed by $^1H$ and $^{13}C$ spectra) and the cross-metathesis product with 1:1 ratio both at 70 ºC and 90 ºC. The reaction was refluxed for an additional 2–3 hours upon which the reaction showed the CM product formation along with some amounts of RCM starting material (*S*,*S*,$S_P$). The reaction mixture was cooled to RT and *o*-nitrobenzenesulfonylhydrazine (*o*-NBSH) (12 equiv.) and $Et_3N$ (2 mL/g of *o*-NBSH) were added, upon which the reaction was stirred at RT overnight. The reaction mixture was quenched with sat. $NaHCO_3$ (1 mL), and diluted with $CH_2Cl_2$ (10 mL). The aqueous layer was washed with $CH_2Cl_2$ (3x5 mL) and the combined organic layers were dried ($Na_2SO_4$), concentrated under reduced pressure and purified using flash column chromatography.

**General procedure for RCM/CM/hydrogenation (Procedure B)**

To a stirring solution of triene (*S*,*S*) in freshly distilled, freeze-degas-thawed $CH_2Cl_2$ (0.007 M) was added HG-II (3 mol %) and the reaction was refluxed for 2 hours. After completion of RCM (monitored by TLC), the solvent was removed and olefin cross partner [3 equivalent with respect to the triene (*S*,*S*)] dissolved in freeze-degas-thawed $CH_2Cl_2$ (0.1 M) was introduced, followed by addition of HG-II (3 mol %). It should be noted that the use of dichloromethane was critical for successful CM reaction in order to avoid the formation of isomerized ketone byproducts. Cross-metathesis reaction in dichloroethane provided the isomerized ketone byproduct (confirmed by $^1H$ and $^{13}C$ spectra) and the CM product with 1:1 ratio both at 70 ºC and 90 ºC. The reaction was refluxed for an additional 2–3 hours upon which the reaction showed the CM product formation along with some amounts of RCM starting material (*S*,*S*,$S_P$). The reaction mixture was cooled to RT and *o*-nitrobenzenesulfonyl hydrazine (*o*-NBSH) (12 equiv.) and $Et_3N$ (2 mL/g of *o*-NBSH) were added, upon which the reaction was stirred at RT overnight. The

[1] In $CH_2Cl_2$, the RCM appeared to be slower in the presence of HG-II.

reaction mixture was quenched with sat. $NaHCO_3$ (1 mL), and diluted with $CH_2Cl_2$ (10 mL). The aqueous layer was washed with $CH_2Cl_2$ (3x5 mL) and the combined organic layers were dried ($Na_2SO_4$), concentrated under reduced pressure and purified using flash column chromatography.

**General procedure for RCM/CM/hydrogenation and subsequent reduction with $LiAlH_4$ (Procedure C)**

The above-mentioned procedure for one-pot RCM/CM/hydrogenation was followed and the crude product was purified using flash column chromatography [2]. To a stirring solution of the hydrogenated product in dry THF (0.5 M), $LiAlH_4$ (2–4 equiv.) was added portion wise at 0 ºC and the reaction was stirred at 0 ºC for 2 hours. After the completion of reduction, the reaction was quenched via slow sequential addition of $H_2O$ (1 mL/g of $LiAlH_4$), 10% NaOH (1 mL/g of $LiAlH_4$), and $H_2O$ (3 mL/g of $LiAlH_4$) [Feiser workup] [3], and the ice bath was removed and the reaction was stirred for 2 h. The reaction was filtered through Celite® and washed with EtOAc (2x5 mL). The combined organic layers were concentrated under reduced pressure and purified using flash column chromatography.

**General procedure for RCM/CM/$LiAlH_4$ reduction (Procedure D)**

To a stirring solution of triene (*S*,*S*) in freshly distilled, freeze-degas-thawed dichloroethane (0.007 M) was added HG-II (3 mol %) and the reaction was refluxed for 2 hours. After completion of RCM (monitored by TLC), the solvent was removed and olefin cross partner [3–5 equivalent with respect to the triene (*S*,*S*)] dissolved in freeze-degas-thawed $CH_2Cl_2$ (0.1 M) was introduced, followed by addition of HG-II (3–6 mol %). The reaction was refluxed for an additional 2–3 hours upon which the reaction showed the CM product formation along with some amounts of RCM starting material (*S*,*S*,$S_P$). After the completion of CM, the solvent was evaporated under reduced pressure. The crude reaction mixture was then dissolved in dry THF (0.5 M) and cooled to 0 ºC. To this solution $LiAlH_4$ (4 equiv.) was added portion wise and the reaction was stirred at 0 ºC for 2 hours. After the completion of reduction, the reaction was quenched via slow sequential addition of $H_2O$ (1 mL/g of $LiAlH_4$), 10% NaOH (1 mL/g of $LiAlH_4$), and $H_2O$ (3 mL/g of $LiAlH_4$) [Feiser workup], and the ice bath was removed and the reaction was

[2] Purification was necessary at this stage for subsequent successful LAH reduction.
[3] Fieser, L.F.; Fieser, M. Reagents for Organic Synthesis Vol. 1, Wiley, New York 1967, pp 581–595.

stirred for 2 h. The reaction was filtered through Celite® and washed with EtOAc (2x5 mL). The combined organic layers were concentrated under reduced pressure and purified using flash column chromatography.

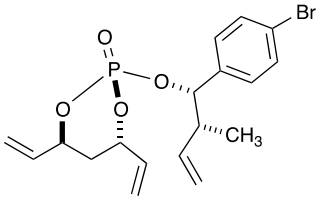
**General procedure for RCM/CM/$LiAlH_4$ reduction (Procedure E)**

To a stirring solution of triene (*S*,*S*) in freshly distilled, freeze-degas-thawed $CH_2Cl_2$ (0.007 M) was added HG-II (3 mol %) and the reaction was refluxed for 2 hours. After completion of RCM (monitored by TLC), the solvent was removed and olefin cross partner [3 equivalent with respect to the triene (*S*,*S*)] dissolved in freeze-degas-thawed $CH_2Cl_2$ (0.1 M) was introduced, followed by addition of Hoveyda-Grubbs 2nd Gen. catalyst (3 mol %). The reaction was refluxed for an additional 2–3 hours upon which the reaction showed the CM product formation along with some amounts of RCM starting material (*S*,*S*,$S_P$). After the completion of CM, the solvent was evaporated under reduced pressure. The crude reaction mixture was then dissolved in dry THF (0.5 M) and cooled to 0 ºC. To this solution $LiAlH_4$ (4 equiv.) was added portion wise and the reaction was stirred at 0 ºC for 2 hours. After the completion of reduction, the reaction was quenched via slow sequential addition of $H_2O$ (1 mL/g of $LiAlH_4$), 10% NaOH (1 mL/g of $LiAlH_4$), and $H_2O$ (3 mL/g of $LiAlH_4$) [Feiser workup], and the ice bath was removed and the reaction was stirred for 2 h. The reaction was filtered through Celite® and washed with EtOAc (2x5 mL). The combined organic layers were concentrated under reduced pressure and purified using flash column chromatography.

**General procedure for RCM/CM/ $LiAlH_4$ reduction and subsequent global hydrogenation (Procedure F)**

The above-mentioned procedure (D or E) was followed to obtain the reduced product and the crude product was dissolved in $CH_2Cl_2$ (0.1 M) and *o*-nitrobenzenesulfonyl hydrazine (*o*-NBSH) (20 equiv.) and $Et_3N$ (2 mL/g of *o*-NBSH) were added, upon which the reaction was stirred at RT overnight. The reaction mixture was quenched with sat. $NaHCO_3$ (1 mL) and diluted with $CH_2Cl_2$ (10 mL). The aqueous layer was washed with $CH_2Cl_2$ (3x5 mL) and the combined organic layers were dried ($Na_2SO_4$), concentrated under reduced pressure and purified using flash column chromatography. At this stage, purification was performed twice in order to remove all the byproducts arising from the use of *o*-NBSH.

**(4*S*,6*S*)-2-(((1*S*,2*R*)-1-(4-bromophenyl)-2-methylbut-3-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (5)**




Synthesized by following the literature precedence [4].
**Yield :** 75%

**FTIR** (neat): 2962, 2927, 2349,1724, 1593, 1488, 1283, 1120, 1070, 997 $cm^{-1}$;
**Optical Rotation**: $[\alpha]_D$ = + 26.7 (*c* = 0.075, $CHCl_3$);

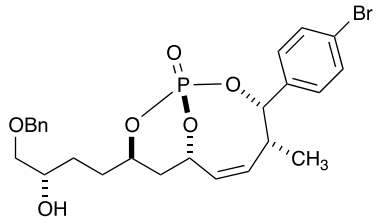
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H, aromatic), 7.17 (d, *J* = 8.4 Hz, 2H, aromatic), 6.00 (dddd, *J* = 17.1, 10.6, 5.5, 0.9 Hz, 1H, $H_2C$=C<u>H</u>CH(OP)$CH_2$), 5.68 (dddd, *J* = 17.3, 10.6, 5.4, 1.6 Hz, 1H, $H_2C$=C<u>H</u>CH(OP)$CH_2$), 5.58 (ddd, *J* = 17.1, 10.5, 7.4 Hz, 1H, $H_2C$=C<u>H</u>CH($CH_3$)CH(OP)Ar), 5.39–5.30 (m, 2H, <u>$H_2$</u>C=CHCH(OP)$CH_2$), 5.18–5.12 (m, 2H, <u>$H_2$</u>C=CHCH(OP)$CH_2$), 5.10 (d, *J* = 1.3 Hz, 1H, $H_2C$=CHCH($CH_3$)C<u>H</u>(OP)Ar), 5.05 (dddd, *J* = 14.3, 6.8, 3.3, 1.4 Hz, 1H, $H_2C$=CHC<u>H</u>(OP)$CH_2$), 5.01–4.93 (m, 2H, <u>$H_2$</u>C=CHCH($CH_3$)CH(OP)Ar), 4.52–4.45 (m, 1H, $H_2C$=CHC<u>H</u>(OP)$CH_2$), 2.78–2.65 (m, 1H, $H_2C$=CHC<u>H</u>($CH_3$)CH(OP)Ar), 2.09 (dddd, *J* = 14.7, 8.3, 5.0, 1.5 Hz, 1H, $H_2C$=CHCH(OP)C<u>$H_2$</u>CH(OP)CH), 1.93 (dddd, *J* = 14.8, 5.2, 3.5, 1.9 Hz, 1H, $H_2C$=CHCH(OP)C<u>$H_2$</u>CH(OP)CH), 1.13 (d, *J* = 6.8 Hz, 3H, $H_2C$=CHCH(C<u>$H_3$</u>)CH(OP)Ar).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 137.9, 137.8 (d, *J* = 2.3 Hz), 135.2 (d, *J* = 3.0 Hz), 134.7 (d, *J* = 7.9 Hz), 131.3 (2C), 129.0 (2C), 122.2, 117.8, 117.6, 116.7, 83.5 (d, *J* = 6.2 Hz), 78.0 (d, *J* = 6.8 Hz), 75.7 (d, *J* = 6.0 Hz), 44.1 (d, *J* = 6.8 Hz), 35.0 (d, *J* = 7.4 Hz), 15.8.

**$^{31}$P NMR** (162 MHz, $CDCl_3$) δ -6.85;

**HRMS:** cald. for $C_{18}H_{22}BrO_4PNa$ $(M+Na)^+$ 435.0337; found 435.0325 (TOF MS ES+).

**(1*S*,3*S*,4*R*,7*S*,9*R*,*Z*)-9-((*S*)-4-(benzyloxy)-3-hydroxybutyl)-3-(4-bromophenyl)-4-methyl-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-5-ene 1-oxide (8)**




Synthesized by following procedure B

**Yield:** 33% over 3 reactions (70% avg/rxn)

**FTIR** (neat): 3411, 2962, 2927, 2873,1593, 1454, 1488, 1284, 1105, 1007, 979 $cm^{-1}$;

**Optical Rotation**: $[\alpha]_D$ = - 18.3 (*c* = 0.59, $CHCl_3$);

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 13.6 Hz, 2H aromatic), 7.34–7.11 (m, 5H, aromatic), 7.03 (d, *J* = 13.6 Hz, 2H, aromatic), 5.47 (dt, *J* = 11.8, 1.8 Hz, 1H, CHOPC<u>H</u>=CHCH$CH_3$CHOPAr ), 5.26–5.16 (m, 3H,

[4] Chegondi, R.; Maitra, S.; Markley, J. L. Hanson, P. R. *Chem. Eur. J.* **2013**, *19*, 8088–8093.

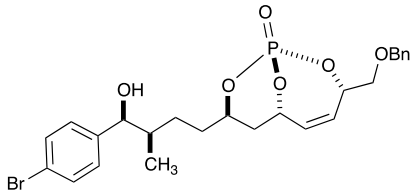
$CH_2C\underline{H}OPCH{=}C\underline{H}CHCH_3C\underline{H}OPAr$ ), 4.70 (t, $J$ = 11.5 Hz, 1H, $CH_2C\underline{H}OPCH_2CHOP$), 4.46 (s, 2H, $CH_2OC\underline{H}_2Ph$), 4.01–3.92 (m, 1H, $CH{=}CHC\underline{H}CH_3CHOPAr$), 3.77–3.68 (m, 1H, $CH_2C\underline{H}OHCH_2OCH_2Ph$), 3.41 (dd, $J$ = 9.4, 3.2 Hz, 1H $CHOHC\underline{H}_2OCH_2Ph$), 3.24 (dd, $J$ = 9.5, 7.9 Hz, 1H, $CHOHC\underline{H}_2OCH_2Ph$), 2.34 (s, 1H, OH), 2.15 (ddd, $J$ = 14.4, 11.8, 6.1 Hz, 1H, $CH_2CHOPC\underline{H}_2CHOP$), 1.89–1.76 (m, 2H, $CHOHCH_2C\underline{H}_2CHOPC\underline{H}_2CHOP$), 1.74–1.60 (m, 2H, $CHOHC\underline{H}_2C\underline{H}_2CHOPCH_2CHOP$), 1.42–1.34 (m, 1H, $CHOHC\underline{H}_2CH_2CHOPCH_2CHOP$), 0.69 (d, $J$ = 6.9 Hz, 3H, $CH{=}CHCHC\underline{H}_3CHOHAr$);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 137.7, 135.6 (d, $J_{CP}$ = 13.6 Hz), 132.0, 131.1 (2C), 130.4, 129.0 (2C), 128.5 (2C), 127.9, 127.8 (2C), 122.4, 79.1 (d, $J_{CP}$ = 4.0 Hz), 78.7 (d, $J$ = 6.9 Hz), 78.5 (d, $J_{CP}$ = 7.4 Hz), 74.5, 73.4, 70.3, 36.4 (d, $J_{CP}$ = 6.5 Hz), 34.2, 32.6 (d, $J_{CP}$ = 9.3 Hz), 28.5, 16.9;

**$^{31}$P NMR** (162 MHz, $CDCl_3$) δ -8.89;

**HRMS:** cald. for $C_{25}H_{30}BrO_6PNa$ $(M+Na)^+$ 559.0861; found 559.0865 (TOF MS ES+).

**(1*S*,3*S*,6*S*,8*R*)-3-((benzyloxy)methyl)-8-((3*R*,4*S*)-4-(4-bromophenyl)-4-hydroxy-3-methylbutyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (9):**




Synthesized by following procedure A

**Yield:** 40% over 3 reactions (72% avg/rxn)

**FTIR** (neat): 3400, 2974, 2285, 1630, 1288, 1209, 1101, 977, 848 $cm^{-1}$;

**Optical Rotation**: $[\alpha]_D$ = + 17.34(*c* = 1, $CHCl_3$);

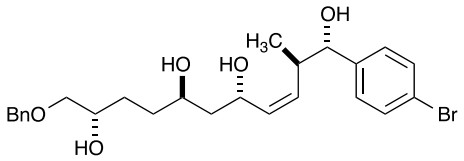
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.50–7.43 (m, 2H, aromatic), 7.40–7.29 (m, 5H, aromatic), 7.21–7.16 (m, 2H, aromatic), 6.01 (ddd, $J$ = 11.9, 3.0, 2.1 Hz, 1H, $CH{=}C\underline{H}CHOPCH_2OBn$), 5.56 (ddd, $J$ = 11.9, 3.9, 2.4 Hz, 1H, $C\underline{H}{=}CHCHOPCH_2OBn$), 5.27 (dddd, $J$ = 5.3, 5.3, 2.6, 2.6 Hz, 1H, $CH{=}CHC\underline{H}OPCH_2OBn$), 5.18 (dddd, $J_{PH,}$ = 24.6, $J_{HH}$ =6.2, 4.1, 1.9 Hz, 1H, $CH_2C\underline{H}OPCH{=}CH$), 4.65–4.58 (m, 2H, $CH_2OC\underline{H}_2Ph$), 4.58–4.47 (m, 2H, 4-$BrC_6H_4C\underline{H}OH$, $CH_2CH_2C\underline{H}OP$), 3.71 (ddd, $J$ = 10.3, 5.1, 1.2 Hz, 1H, $C\underline{H}_2OBn$), 3.61 (dd, $J$ = 10.2, 6.0 Hz, 1H, $C\underline{H}_2OBn$), 2.16 (ddd, $J$ = 14.7, 12.0, 6.2 Hz, 1H, $CHOPC\underline{H}_2CHOP$), 1.88 (d, $J$ = 3.5 Hz, 1H, OH), 1.87–1.71 (m, 2H, 4-$BrC_6H_4CHOHC\underline{H}(CH_3)CH_2$, $C\underline{H}_2CHOPCH_2CHOP$), 1.67 (ddd, $J$ = 14.6, 3.5, 2.0 Hz, 1H, $CHOPC\underline{H}_2CHOP$), 1.58–1.48 (m, 1H, $C\underline{H}_2CHOPCH_2CHOP$), 1.48–1.40 (m, 1H, $C\underline{H}_2CH_2CHOPCH_2CHOP$), 1.39–1.30 (m, 1H, $C\underline{H}_2CH_2CHOPCH_2CHOP$), 0.88 (d, $J$ = 6.7 Hz, 3H, 4-$BrC_6H_4CHOHCH(C\underline{H}_3)CH_2$)

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 142.4, 137.5, 131.3 (2C), 129.9, 129.6, 128.5 (2C), 128.0 (2C), 127.9, 127.7 (2C), 121.1, 77.3 (d, $J_{CP}$ = 6.8 Hz), 77.0, 76.8 (d, $J_{CP}$ = 7.2 Hz), 73.5, 72.2 (d, $J_{CP}$ = 6.1 Hz), 71.2 (d, $J_{CP}$ = 12.2 Hz), 39.9, 34.8 (d, $J_{CP}$ = 6.0 Hz), 33.5 (d, $J_{CP}$ = 9.3 Hz), 27.9, 14.0;

**$^{31}$P NMR** (162 MHz, $CDCl_3$) δ -5.30;

**HRMS:** cald. for $C_{25}H_{30}BrO_6P$ $(M+Na)^+$ 559.0861; found (TOF MS ES+) 559.0856.

**(1*S*,2*R*,5*S*,7*R*,10*S*,*Z*)-11-(benzyloxy)-1-(4-bromophenyl)-2-methylundec-3-ene-1,5,7,10-tetraol (10)**




Synthesized by following procedure C

**Yield:** 24% over 4 reactions (70% avg/rxn)

**FTIR** (neat): 3367, 3335, 3061, 2921, 2852, 1595, 1519, 1456, 1093, 1072, 1026, 910 $cm^{-1}$;

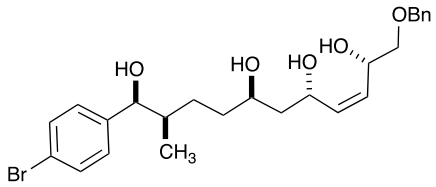
**Optical Rotation**: $[\alpha]_D$ =-32.3 (*c* = 0.33, $CHCl_3$);

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.8 Hz, 2H, aromatic), 7.38–7.28 (m, 5H, aromatic), 7.16 (d, *J* = 7.8 Hz, 2H, aromatic), 5.64 (dd, *J* =8.5, 10.4 Hz, 1H, CHOHC<u>H</u>=CHCHCH$_3$CHOHAr), 5.03 (dd, *J* =10.5, 10.6 Hz, 1H, CHOHCH=C<u>H</u>CHCH$_3$CHOHAr), 4.70 (dd, *J* = 7.3, 10.7 Hz, 1H, C<u>H</u>OHCH=CHCHCH$_3$CHOHAr), 4.60 (d, *J* = 4.6 Hz, 1H, CHOHCH=CHCHCH$_3$C<u>H</u>OHAr ), 4.50 (s, 2H, $CH_2OC\underline{H}_2Ph$), 4.06–3.93 (m, 1H, OH), 3.87 (m, 1H, $CH_2C\underline{H}OHCH_2CHOH$), 3.71 (dd, *J* = 5.7, 5.7 Hz, 1H, $CH_2C\underline{H}OHCH_2OCH_2Ph$), 3.51 (dd, *J* = 3.2, 9.4 Hz, 1H, CHOHC$\underline{H}_2$OCH$_2$Ph), 3.37 (dd, *J* = 8.9, 8.9 Hz, 1H, CHOHC$\underline{H}_2$OCH$_2$Ph), 3.07 (dq, *J* = 12.8, 6.4 Hz, 1H, CH=CHC<u>H</u>CH$_3$CHOHAr ), 2.92 (s, 1H, OH), 1.78–1.44 (m, 8H, OH, CHOHC$\underline{H}_2$C$\underline{H}_2$CHOHC$\underline{H}_2$CHOH), 0.95 (d, *J* = 6.8 Hz, 3H, CH=CHCHC$\underline{H}_3$CHOHAr);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 139.8, 137.9, 133.7, 133.4, 130.9(2C), 128.9(2C), 128.4(2C), 127.8(2C), 127.2, 121.5, 77.7, 74.4, 73.2, 70.3, 68.7, 64.3, 42.1, 38.2, 33.4, 29.8, 17.4;

**HRMS:** cald. for $C_{25}H_{33}BrO_5$ $(M+Na)^+$ 515.1409; found 515.1397 (TOF MS ES+).

**(1*S*,2*R*,5*R*,7*S*,10*S*,*Z*)-11-(benzyloxy)-1-(4-bromophenyl)-2-methylundec-8-ene-1,5,7,10-tetraol (11)**




Synthesized by following procedure C

**Yield:** 26% over 4 reactions (71% avg/rxn)

**FTIR** (neat): 3365, 3294, 2943, 2872, 2349, 2872, 1631, 1485, 1454, 1070, 1028, 827, 750, 698 $cm^{-1}$;

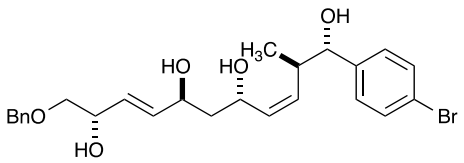
**Optical Rotation**: $[\alpha]_D$ = + 5.0 (*c* = 0.12, $CHCl_3$);

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.50–7.44 (m, 2H, aromatic), 7.39–7.28 (m, 5H, aromatic), 7.22–7.17 (m, 2H, aromatic), 5.71 (ddd, *J* = 11.5, 7.3, 1.4 Hz, 1H, CHOHC<u>H</u>=CHCHOHCH$_2$OBn), 5.50 (ddd, *J* = 11.4, 7.3, 1.3 Hz, 1H, CHOHCH=C<u>H</u>CHOHCH$_2$OBn), 4.85–4.77 (m, 1H, C<u>H</u>OHCH=CHCHOHCH$_2$OBn), 4.75–4.69 (m, 1H, CHOHCH=CHC<u>H</u>OHCH$_2$OBn), 4.62–4.54 (m, 3H, 4-Br$C_6H_4$C<u>H</u>OHCH(CH$_3$)CH$_2$, $CH_2OC\underline{H}_2Ph$), 3.88 (bs, 1H, OH), 3.76–3.68 (m, 1H, $CH_2C\underline{H}OHCH_2CHOHCH{=}CH$), 3.50 (dd, J = 9.4, 4.1 Hz, 1H, C$\underline{H}_2$OBn), 3.45 (dd, J = 9.4, 7.6 Hz, 1H, C$\underline{H}_2$OBn), 1.84–1.74 (m, 1H, 4-Br$C_6H_4$CHOHC<u>H</u>(CH$_3$)CH$_2$), 1.72–1.68 (m, 1H, OH), 1.67–1.62 (m, 2H, CHOHC$\underline{H}_2$CHOH), 1.46–1.37 (m, 2H, $CH_2C\underline{H}_2CHOHCH_2CHOH$), 1.26 (s, 4H, OH, C$\underline{H}_2$CH$_2$CHOHCH$_2$CHOH), 0.88 (d, *J* = 6.8 Hz, 3H, 4-Br$C_6H_4$CHOHCH(C$\underline{H}_3$)CH$_2$).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 142.5, 137.5, 136.5, 131.2 (2C), 129.2, 128.5 (2C), 128.0 (2C), 127.99, 127.9 (2C), 120.9, 76.9, 73.6, 73.5, 67.3, 66.2, 62.9, 42.6, 40.0, 28.9, 28.8, 14.3.

**HRMS:** cald. for $C_{25}H_{33}BrO_5$ $(M+Na)^+$ 515.1409; found (TOF MS ES+) 515.1398.

**(1*S*,2*R*,3*Z*,5*S*,7*S*,8*E*,10*S*)-11-(benzyloxy)-1-(4-bromophenyl)-2-methylundeca-3,8-diene-1,5,7,10-tetraol (12)**




Synthesized by following procedure E

**Yield:** 38% over 3 reactions (73% avg/rxn)

**FTIR** (neat): 3377, 3330, 2962, 2926, 2868, 1865, 1591, 1454, 1215, 1101, 1070, 1009, 976 $cm^{-1}$;

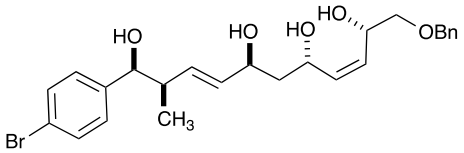
**Optical Rotation**: $[\alpha]_D$ =-38.8 (*c* = 0.45, $CHCl_3$);

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H, aromatic), 7.40–7.29 (m, 5H, aromatic), 7.15 (d, *J* = 8.4 Hz, 2H, aromatic), 5.91 (ddd, *J* = 15.6, 5.6, 1.4 Hz, 1H, CHOHCH=C<u>H</u>CHOHCH$_2$CHOH), 5.74 (ddd, *J* = 15.6, 5.8, 1.4 Hz, 1H, CHOHC<u>H</u>=CHCHOHCH$_2$), 5.63 (ddd, *J* = 10.9, 8.2, 0.9 Hz, 1H, CH$_2$CHOHC<u>H</u>=CHCHCH$_3$), 4.97 (td, *J* = 10.6, 1.2 Hz, 1H, CHOHCH=C<u>H</u>CHCH3), 4.65 (ddd, *J* = 11.4, 6.3, 2.2 Hz, 1H, CH$_2$C<u>H</u>OHCH=CHCHCH$_3$), 4.58 (d, *J* = 2.9 Hz, 4H, OH, PhC<u>H$_2$</u>OCH$_2$CHOHCH=CHCHOHCH$_2$CHOHCH=CHCHCH$_3$C<u>H</u>OHAr), 4.48 (s, 1H PhCH$_2$OCH$_2$CHOHCH=CHC<u>H</u>OHCH$_2$CHOH), 4.40 (s, 1H PhCH$_2$OCH$_2$C<u>H</u>OHCH=CH), 3.56 (dd, *J* = 9.6, 3.3 Hz, 1H, PhCH$_2$OC<u>H$_2$</u>CHOH), 3.38 (dd, *J* = 9.6, 8.1 Hz, 1H, PhCH$_2$OC<u>H$_2$</u>CHOH), 3.13 (s, 1H, OH), 3.12–3.01 (m, 1H, CHOHCH=CHC<u>H</u>CH$_3$), 2.62 (s, 1H, OH), 1.87 (ddd, *J* = 14.4, 8.7, 3.6 Hz, 1H, CH=CHCHOHC<u>H$_2$</u>CHOH), 1.70 (ddd, *J* = 14.3, 7.5, 3.3 Hz, 1H, CH=CHCHOHC<u>H$_2$</u>CHOH), 1.61 (s, 1H, OH), 0.9 (s, 3H, CH=CHCHC<u>H$_3$</u>);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 139.6, 137.7, 134.8, 133.8, 133.5, 130.9 (2C), 128.9 (2C), 128.5 (2C), 128.4, 127.90, 127.8 (2C), 121.6, 76.9, 74.1, 73.4, 70.7, 69.5, 64.1, 41.9, 38.2, 17.4;

**HRMS:** cald. for $C_{25}H_{31}BrO_5$ $(M+Na)^+$513.1253; found 513.1255 (TOF MS ES+).

**(1*S*,2*R*,3*E*,5*S*,7*S*,8*Z*,10*S*)-11-(benzyloxy)-1-(4-bromophenyl)-2-methylundeca-3,8-diene-1,5,7,10-tetraol (13)**




Synthesized by following procedure D

**Yield:** 35% over 3 reactions (70% avg/rxn)

**FTIR** (neat): 3440, 3417, 3386, 2390, 1643, 1633, 1054, 698, 522 $cm^{-1}$;

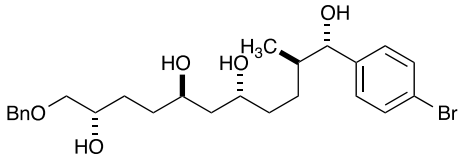
**Optical Rotation**: $[\alpha]_D$ = - 4.81 (*c* = 0.22, $CHCl_3$)

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.47–7.43 (m, 2H, aromatic), 7.37–7.29 (m, 5H, aromatic), 7.18–7.12 (m, 2H, aromatic), 5.68 (ddd, *J* = 11.4, 7.6, 1.4 Hz, 1H, CHOHC<u>H</u>=CH$_{cis}$CHOHCH$_2$OBn), 5.61 (ddd, *J* = 15.6, 7.0, 1.0 Hz, 1H, C<u>H</u>=CH$_{trans}$CHOHCH$_2$CHOH), 5.53 (d, *J* = 6.2 Hz, 1H, CH=C<u>H</u>$_{trans}$CHOHCH$_2$CHOH), 5.48 (ddd, *J* = 11.4, 7.4, 1.3 Hz, 1H, CH=CH$_{cis}$C<u>H</u>OHCH$_2$CHOH), 4.76 (dd, *J* = 7.9, 2.9 Hz, 1H, C<u>H</u>OHCH=CHCHOHCH$_2$OBn), 4.68 (ddd, *J* = 7.5, 4.1, 1.4 Hz, 1H, CHOHCH=CHC<u>H</u>OHCH$_2$OBn ), 4.59 (d, *J* = 5.1 Hz, 1H, 4-BrC$_6$H$_4$C<u>H</u>OHCH(CH$_3$)CH$_2$), 4.56 (bs, 2H, C<u>H$_2$</u>OBn ), 4.35 (dd, *J* = 6.6, 10.4 Hz, 1H, CH=CHC<u>H</u>OHCH$_2$CHOH), 3.55 (s, 1H, OH), 3.48 (dd, *J* = 9.5, 4.1 Hz, 1H, C<u>H$_2$</u>OBn), 3.44 (dd, *J* = 9.5, 7.5 Hz, 1H, C<u>H$_2$</u>OBn), 3.16 (s, 1H, OH), 2.90 (s, 1H, OH), 2.52 (dd, *J* = 12.6, 6.7 Hz, 1H, 4-BrC$_6$H$_4$CHOHC<u>H</u>(CH$_3$)CH$_2$ ), 2.46 (s, 1H, OH), 1.74 (ddd, *J* = 14.4, 8.7, 3.8 Hz, 1H, CHOHC<u>H$_2$</u>CHOH), 1.61 (ddd, *J* = 14.3, 7.5, 3.3 Hz, 1H, CHOHC<u>H$_2$</u>CHOH), 0.96 (d, *J* = 6.8 Hz, 3H, 4-BrC$_6$H$_4$CHOHCH(C<u>H$_3$</u>)CH$_2$)

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 141.6, 137.5, 136.3, 133.8, 132.5, 131.1 (2C), 129.2, 128.5 (2C), 128.1 (2C), 127.9, 127.9 (2C), 121.0, 76.6, 73.6, 73.5, 70.1, 67.2, 65.7, 43.3, 42.8, 14.0.

**HRMS:** cald. for $C_{25}H_{31}BrO_5$ $(M+Na)^+$513.1253; found (TOF MS ES+) 513.1237.

**(1*S*,2*R*,5*R*,7*R*,10*S*)-11-(benzyloxy)-1-(4-bromophenyl)-2-methylundecane-1,5,7,10-tetraol (14)**




Synthesized by following procedure F

**Yield:** 26% over 4 reactions (72% avg/rxn)

**FTIR** (neat): 3377, 3330, 2962, 2926, 2868, 1865, 1454, 1215, 1070, 1009, 976 cm$^{-1}$;

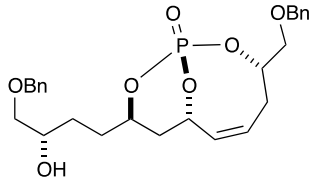
**Optical Rotation**: $[\alpha]_D$ = -11.4 (*c* = 0.285, $CHCl_3$);

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.3 Hz, 2H, aromatic), 7.38–7.28 (m, 5H, aromatic), 7.2 (d, *J* = 8.3 Hz, 2H, aromatic), 4.60 (d, *J* = 4.9 Hz, 1H, CH$_2$CHCH$_3$C<u>H</u>OHAr), 4.56 (s, 2H, PhC<u>H$_2$</u>OCH$_2$CHOH), 4.06–3.93 (m, 1H, CH$_2$C<u>H</u>OHCH$_2$CHOH), 3.92–3.85 (m, 2H, PhCH$_2$OCH$_2$C<u>H</u>OHCH$_2$CH$_2$CHOHCH$_2$C<u>H</u>OH), 3.50 (dd, *J* = 9.3, 3.5 Hz, 1H, PhCH$_2$OC<u>H$_2$</u>CHOH), 3.37 (m, 1H, PhCH$_2$OC<u>H$_2$</u>CHOH), 1.84–1.74 (m, 1H CH$_2$C<u>H</u>CH$_3$CHOHAr), 1.65–1.55 (m, 11H, OH, aliphatic), 1.46–1.37 (m, 2H, aliphatic), 1.28–1.21 (m, 1H, aliphatic), 0.95 (d, *J* = 6.8 Hz, 3H, CH$_2$CH$_2$CHC<u>H$_3$</u>CHOHAr);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 142.6, 137.7, 131.2, 128.5(2C), 128.1(2C), 127.8(2C), 126.4(2C), 121.0, 77.1, 74.3, 73.4, 70.3, 69.4, 69.0, 42.4, 40.0, 34.8, 33.4, 29.0, 28.9, 14.3;

**HRMS:** cald. for $C_{25}H_{35}BrO_5$ $(M+Na)^+$ 517.1566; found 517.1584 (TOF MS ES+).

**(1*S*,3*S*,7*S*,9*R*,*Z*)-9-((*S*)-4-benzyloxy-3-hydroxybutyl)-3-((benzyloxy)methyl)-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-5-ene 1-oxide (15)**




Synthesized by following procedure B

**Yield:** 40% over 3 reactions (72% avg/rxn)

**FTIR** (neat): 3413, 3028, 2923, 2858, 1679, 1452, 1363, 1288, 1101, 979 $cm^{-1}$;

**Optical Rotation**: $[\alpha]_D$ = +7.6 (*c* = 0.41, $CHCl_3$);

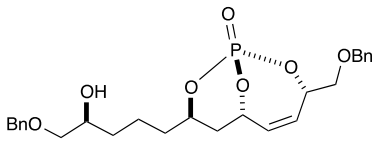
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.40–7.30 (m, 10H, aromatic), 5.69 (dtd, *J* = 11.8, 8.8, 2.9 Hz, 1H, CHOPCH=C<u>H</u>$CH_2$CHOP), 5.45 (dt, *J* = 11.8, 1.7 Hz, 1H, CHOPC<u>H</u>=$CHCH_2$CHOP), 5.25 (dd, *J* = 25.0, 4.3 Hz, 1H, $CH_2C$<u>H</u>$OPCH_2$CHOPCH=CH), 4.76–4.65 (m, 1H, CH=$CHCH_2C$<u>H</u>$OPCH_2$OBn), 4.59–4.52 (m, 5H, $OC$<u>$H_2$</u>Ph, $CHOPCH_2C$<u>H</u>OPCH=CH), 3.79 (ddd, *J* = 11.4, 8.9, 3.1Hz, 1H, $PhCH_2OCH_2C$<u>H</u>$OHCH_2$), 3.51 (ddd, *J* = 11.3, 9.7, 4.2 Hz, 2H, $PhCH_2OC$<u>$H_2$</u>$CHOHC_2H_4CHOPCH_2CHOPCH$=$CHCH_2CHOPC$<u>$H_2$</u>$OCH_2$Ph), 3.43 (dd, *J* = 9.4, 7.4 Hz, 1H, CH=$CHCH_2CHOPC$<u>$H_2$</u>OBn), 3.36–3.29 (m, 2H, $BnOC$<u>$H_2$</u>$CHOHC_2H_4CHOPCH_2CHOPCH$=$CHC$<u>$H_2$</u>CHOP), 2.36 (dd, *J* = 13.9, 8.5 Hz, 1H, CH=$CHC$<u>$H_2$</u>$CHOPCH_2$OBn), 2.14 (ddd, *J* = 14.5, 11.7, 6.0 Hz, 1H, $CHOPC$<u>$H_2$</u>$CHOPCH$=CH), 1.91–1.79 (m, 1H, $CHOHCH_2C$<u>$H_2$</u>$CHOPCH_2CHOP$), 1.78–1.65 (m, 3H, $CHOHC$<u>$H_2$</u>$C$<u>$H_2$</u>$CHOPC$<u>$H_2$</u>CHOP), 1.62 (s, 1H, OH), 1.44 (dddd, *J* = 15.2, 12.9, 7.5, 3.0 Hz, 1H, $CHOHC$<u>$H_2$</u>$CH_2CHOPCH_2$CHOP);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 137.8, 137.7, 131.5, 128.5 (2C), 128.5 (2C), 127.9, 127.8, 127.7 (2C), 127.6 (2C), 125.03, 78.4 (d, $J_{CP}$ = 7.1 Hz), 78.1 (d, $J_{CP}$ = 7.2 Hz) 74.4, 73.4, 73.2, 72.3 (d, $J_{CP}$ = 4.9 Hz), 70.4 (d, $J_{CP}$ = 15.5 Hz), 70.2, 36.2 (d, $J_{CP}$ = 6.5 Hz), 32.4 (d, $J_{CP}$ = 8.8 Hz), 28.5, 27.4;

**$^{31}$P NMR** (162 MHz, $CDCl_3$) δ –8.2;

**HRMS:** cald. for $C_{26}H_{33}O_7P$ $(M+Na)^+$ 511.1862; found 511.1855 (TOF MS ES+).

**(1*S*,3*S*,6*S*,8*R*)-8-((*S*)-5-benzyloxy-4-hydroxypentyl)-3-((benzyloxy)methyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (16)**




Synthesized by following procedure A

**Yield:** 35% over 3 reactions (70% avg/rxn)

**FTIR** (neat): 3520, 3444, 2395, 1633, 1286, 1101, 973, 734 $cm^{-1}$;

**Optical Rotation**: $[\alpha]_D$ = + 21.57(*c* = 0.26, $CHCl_3$);

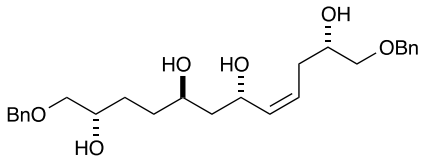
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.42–7.28 (m, 10H, aromatic), 6.02 (ddd, *J* = 11.9, 3.0, 2.1 Hz, 1H, CH=C<u>H</u>$CHOPCH_2$OBn), 5.57 (ddd, *J* = 11.9, 3.9, 2.4 Hz, 1H, C<u>H</u>=$CHCHOPCH_2$OBn), 5.28 (ddddd, *J* = 5.3, 5.3, 2.7, 2.7, 2.7 Hz, 1H, CH=$CHC$<u>H</u>$OPCH_2$OBn), 5.19 (ddddd, $J_{PH}$= 24.5, $J_{HH}$= 6.2, 4.1, 1.8, 1.8 Hz, 1H, $CH_2C$<u>H</u>OPCH=CH), 4.66–4.52 (m, 5H, $CH_2OC$<u>$H_2$</u>Ph, $CH_2CH_2CH_2C$<u>H</u>OP), 3.84–3.77 (m, 1H, $CH_2C$<u>H</u>$OHCH_2$OBn), 3.72 (ddd, *J* = 10.2, 5.1, 1.1 Hz, 1H, C<u>$H_2$</u>OBn), 3.61 (dd, *J* = 10.2, 6.1 Hz, 1H, C<u>$H_2$</u>OBn), 3.50 (dd, *J* = 9.4, 3.1 Hz, 1H, C<u>$H_2$</u>OBn), 3.32 (dd, *J* = 9.4, 7.9 Hz, 1H, C<u>$H_2$</u>OBn), 2.34 (d, *J* = 3.4 Hz, 1H, $BnOCH_2CHO$<u>H</u>$CH_2CH_2CH_2$CHOP), 2.22–2.12 (m, 2H, $CHOPC$<u>$H_2$</u>CHOP), 1.83–1.55 (m, 4H, $BnOCH_2CHOHCH_2C$<u>$H_2$</u>$C$<u>$H_2$</u>CHOP), 1.52–1.37 (m, 2H, $BnOCH_2CHOHC$<u>$H_2$</u>$CH_2CH_2$CHOP).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 137.8, 137.5, 129.9, 129.6, 128.5 (4C), 127.9, 127.8, 127.7 (4C), 77.3 (d, $J_{CP}$ = 6.7 Hz), 76.6 (d, $J_{CP}$ = 6.8 Hz), 74.4, 73.5, 73.4, 72.1 (d, $J_{CP}$ = 6.0 Hz), 71.2 (d, $J_{CP}$ = 12.2 Hz), 70.0, 35.4 (d, $J_{CP}$ = 9.3 Hz), 34.7 (d, $J_{CP}$ = 6.0 Hz), 32.4, 20.5.

**$^{31}$P NMR** (162 MHz, $CDCl_3$) δ -5.46 ;

**HRMS:** cald. for $C_{26}H_{33}O_7PNa$ $(M+Na)^+$ 511. 1862; found (TOF MS ES+) 511.1847.

**(2*S*,5*R*,7*S*,11*S*,*Z*)-1,12-bis(benzyloxy)dodec-8-ene-2,5,7,11-tetraol (17)**




Synthesized by following procedure C

**Yield:** 24% over 4 reactions (70% avg/rxn)

**FTIR** (neat): 3367, 2914, 2858, 2914,2331, 1093, 1076, 698 $cm^{-1}$;

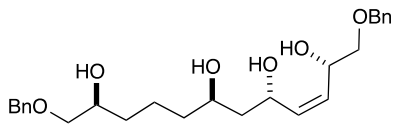
**Optical Rotation**: $[\alpha]_D$ = + 6.8 (*c* = 0.44, $CHCl_3$);

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.40–7.30 (m, 10H, aromatic), 5.70 (ddt, *J* = 11.0, 8.2, 1.4 Hz, 1H, CHOHC<u>H</u>=CHCH$_2$CHOH), 5.51 (dddd, *J* = 11.0, 8.6, 7.5, 1.1 Hz, 1H, CHOHCH=C<u>H</u>CH$_2$CHOH), 4.79 (dt, *J* = 7.6, 5.6 Hz, 1H, CHOHCH$_2$C<u>H</u>OHCH=CHCH$_2$CHOH), 4.60–4.53 (m, 4H, CH$_2$OC<u>H$_2$</u>Ph), 4.01–3.93 (m, 1H, CH$_2$C<u>H</u>OCH$_2$CHOCH=CH), 3.93 (ddd, *J* = 11.2, 5.1, 3.5 Hz 1H, CH=CHCH$_2$C<u>H</u>OHCH$_2$OBn), 3.89–3.82 (m, 1H, CH$_2$CH$_2$C<u>H</u>OHCH$_2$OBn), 3.51(td, *J* = 9.4, 3.3 Hz, 2H, CH=CHCH$_2$CHOHC<u>H$_2$</u>OBn), 3.45–3.33 (m, 2H, CH$_2$CH$_2$CHOHC<u>H$_2$</u>OBn), 3.15 (bs, 1H, OH), 2.90 (bs, 2H, OH), 2.43 (dddd, *J* = 14.5, 8.6, 5.1, 1.1 Hz, 1H, CH=CHC<u>H$_2$</u>CHOHCH$_2$OBn), 2.30 (dddd, *J* = 14.2, 7.7, 6.5, 1.3 Hz, 1H, CH=CHC<u>H$_2$</u>CHOHCH$_2$OBn), 1.77–1.67 (m, 2H, CHOHC<u>H$_2$</u>CHOHCH=CHCH$_2$CHOH), 1.67–1.49 (m, 4H, CHOHC<u>H$_2$</u>C<u>H$_2$</u>CHOHCH$_2$CHOH ), 1.30 (s, 1H, OH);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 137.9, 137.7, 135.6, 128.5 (2C), 128.4 (2C), 127.9, 127.8 (3C), 127.7 (2C), 126.4, 74.4, 73.6, 73.5, 73.3, 70.4, 69.6, 68.9, 65.3, 42.5, 33.5, 31.2, 29.2;

**HRMS:** cald. for $C_{26}H_{36}O_6$ $(M+Na)^+$ 467.2410; found 467.2390 (TOF MS ES+).

**(2*S*,5*S*,7*R*,11*S*,*Z*)-1,12-bis(benzyloxy)dodec-3-ene-2,5,7,11-tetraol (18)**




Synthesized by following procedure C

**Yield:** 23% over 4 reactions (69% avg/rxn)

**FTIR** (neat): 3400, 3290, 2943, 2350, 1631, 1480, 1070, 750, 698$cm^{-1}$;

**Optical Rotation**: $[\alpha]_D$ = + 6.32(*c* = 0.19, $CHCl_3$);

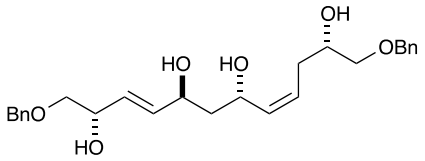
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.40–7.28 (m, 10H, aromatic), 5.70 (ddd, *J* = 11.5, 7.5, 1.4 Hz, 1H, CHOHC<u>H</u>=CHCHOHCH$_2$OBn), 5.48 (ddd, *J* = 11.4, 7.4, 1.4 Hz, 1H, CHOHCH=C<u>H</u>CHOHCH$_2$OBn), 4.80 (ddd, *J* = 10.4, 7.3, 3.4 Hz, 1H, C<u>H</u>OHCH=CHCHOHCH$_2$OBn), 4.75–4.67 (m, 1H, CHOHCH=CHC<u>H</u>OHCH$_2$OBn), 4.59–4.53 (m, 4H, CH$_2$OC<u>H$_2$</u>Ph), 3.97–3.88 (m, 1H, CH$_2$C<u>H</u>OHCH$_2$CHOHCH=CH), 3.88–3.79 (m, 1H,

BnOCH$_2$C<u>H</u>OHCH$_2$CH$_2$CH$_2$), 3.56–3.41 (m, 4H, C<u>H$_2$</u>OBn), 3.40–3.29 (m, 2H, BnOC<u>H$_2$</u>CHOHCH$_2$CH$_2$CH$_2$), 1.66 (ddd, *J* = 14.5, 7.5, 2.6 Hz, 1H, CHOHC<u>H$_2$</u>CHOH), 1.63–1.57 (m, 3H, CHOHC<u>H$_2$</u>CHOH, BnOCH$_2$CHOHC<u>H$_2$</u>CH$_2$CH$_2$, O<u>H</u>), 1.53–1.35 (m, 6H, BnOCH$_2$CHOHC<u>H$_2$</u>C<u>H$_2$</u>C<u>H$_2$</u>CHOH).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 137.9, 137.6, 136.5, 129.2, 128.5 (2C), 128.46 (2C), 127.9, 127.85 (2C), 127.8, 127.7 (2C), 74.5, 73.6, 73.4, 73.3, 70.23, 68.8, 67.1, 66.1, 42.7, 37.2, 32.8, 21.5.

**HRMS:** cald. for $C_{26}H_{36}O_6$ $(M+Na)^+$ 467.2410; found (TOF MS ES+) 467.2413.

**(2*S*,3*E*,5*S*,7*S*,8*Z*,11*S*)-1,12-bis(benzyloxy)dodeca-3,8-diene-2,5,7,11-tetraol (19)**




Synthesized by following procedure E

**Yield:** 42% over 3 reactions (75% avg/rxn)

**FTIR** (neat): 3377, 3361, 3028, 2916, 2858, 1602, 1452, 1101 $cm^{-1}$;

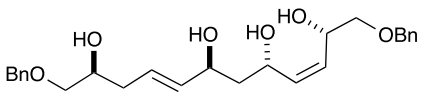
**Optical Rotation**: $[\alpha]_D$ = +10.4 (*c* = 0.67, $CHCl_3$);

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.40–7.29 (m, 10H, aromatic), 5.89 (ddd, *J* = 15.5, 5.4, 1.3 Hz, 1H, CHOHCH=C<u>H</u>CHOHCH$_2$), 5.77–5.64 (m, 2H, CHOHC<u>H</u>=CHCHOHCH$_2$CHOHC<u>H</u>=CHCH$_2$), 5.53–5.48 (m, 1H, CHOHCH=C<u>H</u>CH$_2$CHOHCH$_2$OBn), 4.71 (td, *J* = 2.1 Hz, 1H, CHOHCH$_2$C<u>H</u>OHCH=CHCH$_2$), 4.57 (d, *J* = 2.1 Hz, 2H, CH$_2$OC<u>H$_2$</u>Ph), 4.55 (d, *J* = 3.8 Hz, 2H, CH$_2$OC<u>H$_2$</u>Ph), 4.46 (bs, 1H, CHOHCH=CHC<u>H</u>OHCH$_2$), 4.38 (bs, 1H, PhCH$_2$OCH$_2$C<u>H</u>OHCH=CHCHOH), 3.91 (ddt, *J* = 11.0, 6.7, 3.4 Hz, 1H, CH=CHCH$_2$C<u>H</u>OHCH$_2$OBn), 3.54 (ddd, *J* = 9.5, 3.4, 2.2 Hz, 1H, CH=CHCHOHC<u>H$_2$</u>OBn), 3.51 (dd, *J* = 9.5, 3.4 Hz, 1H, CH=CHCH$_2$CHOHC<u>H$_2$</u>OBn), 3.45–3.32 (m, 2H, C<u>H$_2$</u>OBn ), 3.06 (s, 1H, OH), 2.82 (s, 1H, OH), 2.60 (s, 1H, OH) 2.42 (dddd, *J* = 13.9, 8.7, 5.1, 1.3 Hz, 1H, CH=CHC<u>H$_2$</u>CHOHCH$_2$OBn), 2.28 (dddd, *J* = 14.1, 7.6, 6.3, 1.3 Hz, 1H, CH=CHC<u>H$_2$</u>CHOHCH$_2$OBn), 1.85 (ddd, *J* = 14.3, 8.1, 3.6 Hz, 1H, CHOHC<u>H$_2$</u>CHOHCH=CHCH$_2$ ), 1.70 (ddd, *J* = 14.3, 7.6, 3.7 Hz, 1H, CHOHC<u>H$_2$</u>CHOHCH=CHCH$_2$), 1.64 (s, 1H, OH);

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 137.7, 137.6, 135.4, 134.9, 128.51 (2C), 128.5, 128.48 (2C), 128.4, 127.92, 127.89, 127.86, 127.8 (2C), 126.6, 74.1, 73.5, 73.4, 73.36, 70.7, 69.6, 69.5, 64.9, 42.4, 31.1;

**HRMS:** cald. for $C_{26}H_{34}O_6$ $(M+Na)^+$ 465.2253; found 465.2241 (TOF MS ES+).

**(2*S*,3*Z*,5*S*,7*S*,8*E*,11*S*)-1,12-bis(benzyloxy)dodeca-3,8-diene-2,5,7,11-tetraol (20)**




Synthesized by following procedure D

**Yield:** 40% over 3 reactions (72% avg/rxn)

**FTIR** (neat): 3408, 3402, 3385, 2918, 2852, 2349, 1637, 1632, 1072, 1027, 972, 737, 698 $cm^{-1}$;

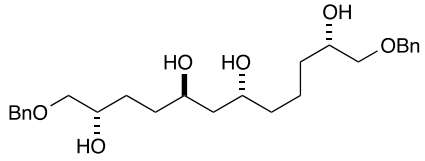
**Optical Rotation**: $[\alpha]_D$ = + 5.92(*c* = 0.14, $CHCl_3$);

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.42–7.28 (m, 10H, aromatic), 5.75–5.64 (m, 2H, CHOHC<u>H</u>=C<u>H</u>CHOHCH$_2$OBn), 5.62–5.53 (m, 1H, BnOCH$_2$CHOHCH$_2$CH=C<u>H</u>CHOH), 5.48 (ddd, *J* = 11.3, 7.4, 1.3 Hz, 1H, BnOCH$_2$CHOHCH$_2$C<u>H</u>=CHCHOH), 4.78 (ddd, *J* = 7.8, 7.8, 3.0 Hz, 1H, C<u>H</u>OHCH=CHCHOHCH$_2$OBn), 4.70 (dddd, *J* = 7.5, 7.5, 4.3, 1.4 Hz, 1H, CHOHCH$_2$CHOHCH=CHC<u>H</u>OHCH$_2$OBn), 4.59–4.52 (m, 4H, CH$_2$OC<u>H</u>$_2$Ph), 4.42–4.35 (m, 1H, CHOHCH$_2$CH=CHC<u>H</u>OH), 3.90–3.82 (m, 1H, BnOCH$_2$C<u>H</u>OHCH$_2$CH=CH), 3.54–3.40 (m, 4H, BnOC<u>H</u>$_2$CHOH, OH), 3.36 (dd, *J* = 9.5, 7.3 Hz, 2H, BnOC<u>H</u>$_2$CHOH), 2.30–2.13 (m, 4H, BnOCH$_2$CHOHC<u>H</u>$_2$CH=CH ), 1.77 (ddd, *J* = 14.3, 8.6, 3.6 Hz, 1H, CHOHC<u>H</u>$_2$CHOH), 1.64 (ddd, *J* = 14.4, 7.7, 3.3 Hz, 1H, CHOHC<u>H</u>$_2$CHOH).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 137.8, 137.6, 136.3, 135.5, 129.3, 128.5 (2C), 128.4 (2C), 127.9, 127.85 (2C), 127.8, 127.7 (2C), 126.7, 77.2, 73.9, 73.6, 73.4, 73.3, 69.9, 67.1, 65.6, 42.6, 36.2;

**HRMS:** cald. for $C_{26}H_{34}O_6$ $(M+Na)^+$ 465.2253; found (TOF MS ES+) 465.2236.

**(2*S*,5*R*,7*R*,11*S*)-1,12-bis(benzyloxy)dodecane-2,5,7,11-tetraol (21)**




Synthesized by following procedure F

**Yield:** 34% over 4 reactions (77% avg/rxn)

**FTIR** (neat): 3283, 2943, 2394, 1454, 1093, 1076, 737 cm$^{-1}$;

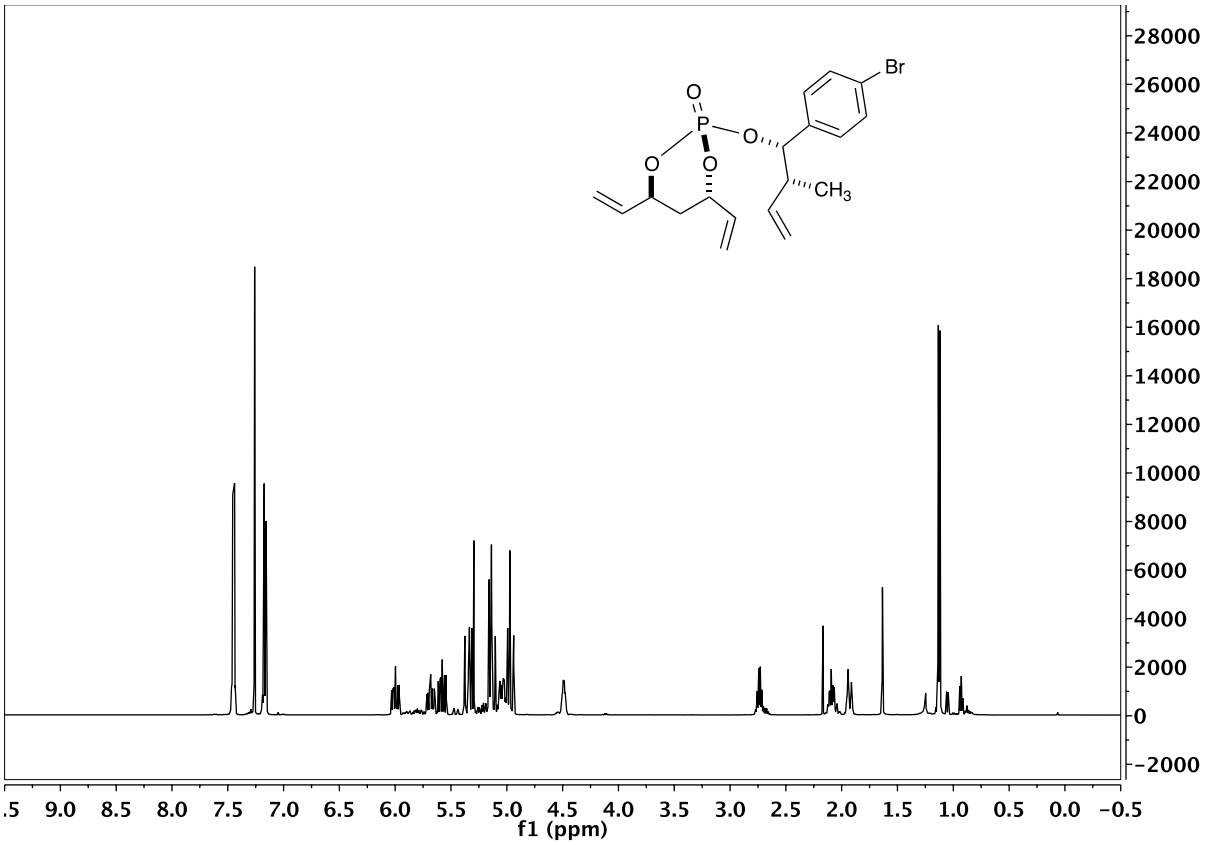
**Optical Rotation**: $[\alpha]_D$ = + 2.80 (*c* = 0.25, $CHCl_3$);

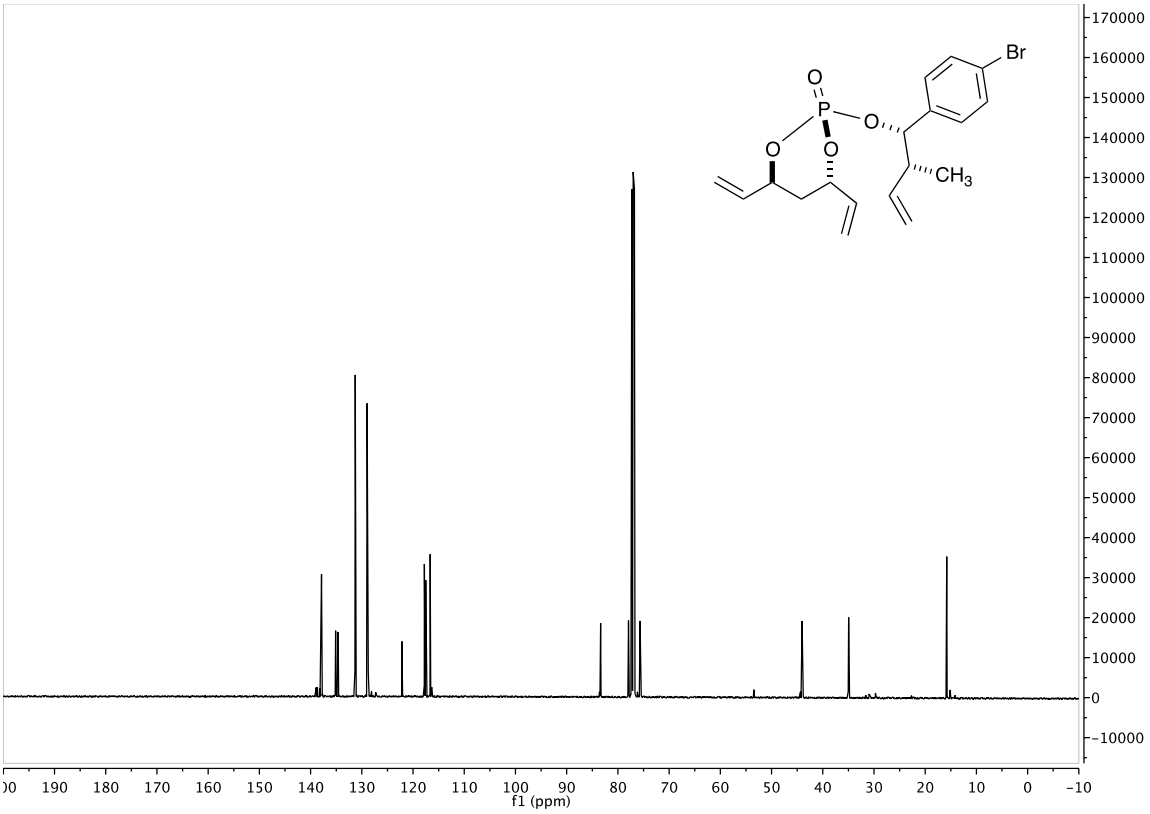
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.40–7.29 (m, 10H, aromatic), 4.60–4.52 (m, 4H, CH$_2$OC<u>H</u>$_2$Ph), 4.04–3.91 (m, 2H, C<u>H</u>OHCH$_2$C<u>H</u>OH), 3.92–3.76 (m, 2H, C<u>H</u>OHCH$_2$OBn), 3.51 (ddd, *J* = 9.5, 4.9, 3.2 Hz, 2H, BnOC<u>H</u>$_2$CHOH), 3.36 (ddd, *J* = 17.2, 9.4, 8.0 Hz, 2H, BnOC<u>H</u>$_2$CHOH), 2.80 (s, 1H, OH), 2.61 (s, 1H, OH), 2.40 (bs, 1H, OH), 1.70–1.37 (m, 13H, aliphatic, OH).

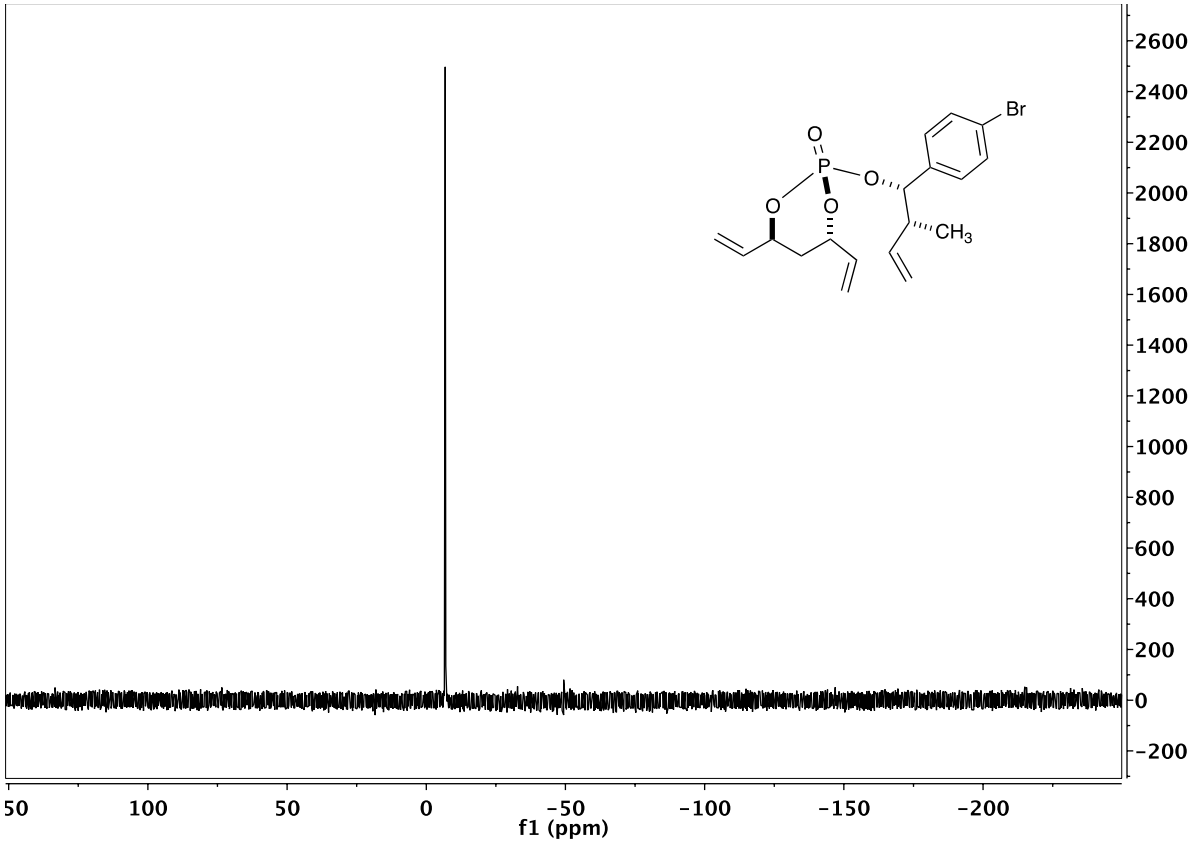
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 137.9, 137.8, 128.5 (4C), 127.9, 127.8, 127.77 (2C), 127.75 (2C), 74.3, 74.5, 73.3 (2C), 70.4, 70.3, 69.3, 69.0, 42.3, 37.2, 33.5, 32.8, 29.1, 21.6.

**HRMS:** cald. for $C_{26}H_{38}O_6$ $(M+Na)^+$ 469.2566; found (TOF MS ES+) 469.2567.

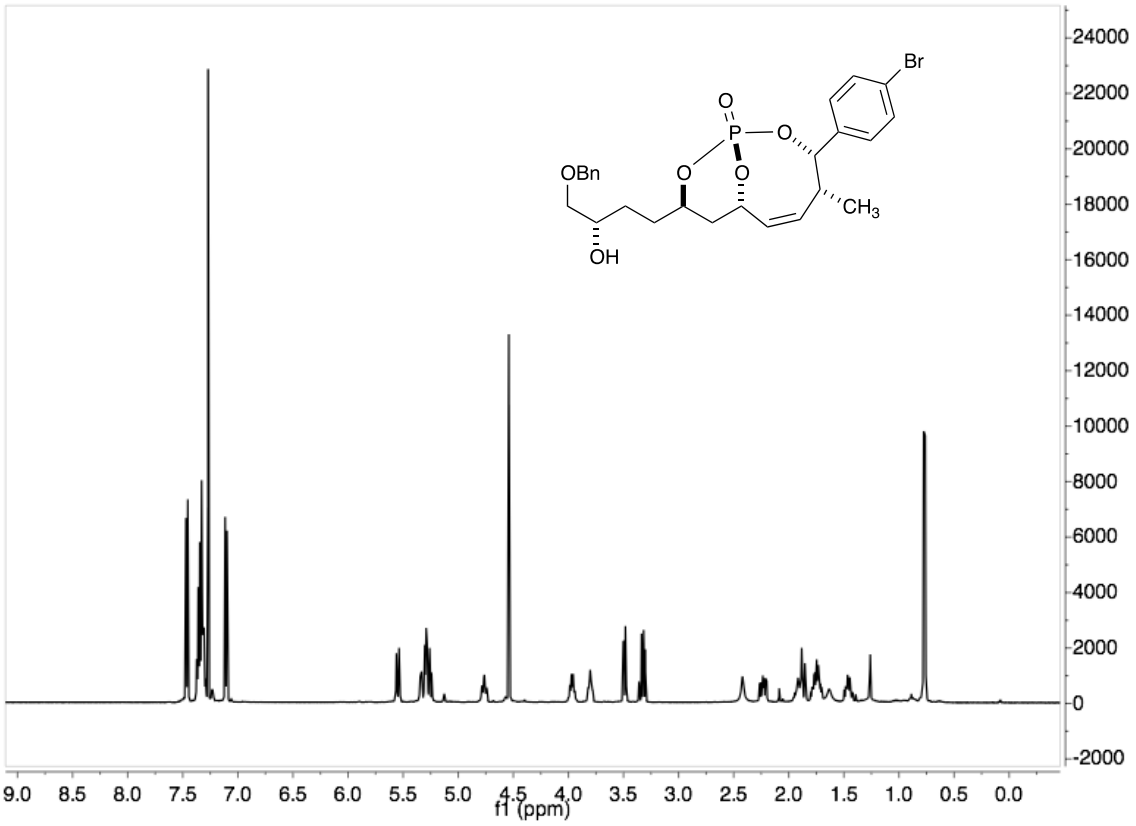
**(4*S*,6*S*)-2-(((1*S*,2*R*)-1-(4-bromophenyl)-2-methylbut-3-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (5)**

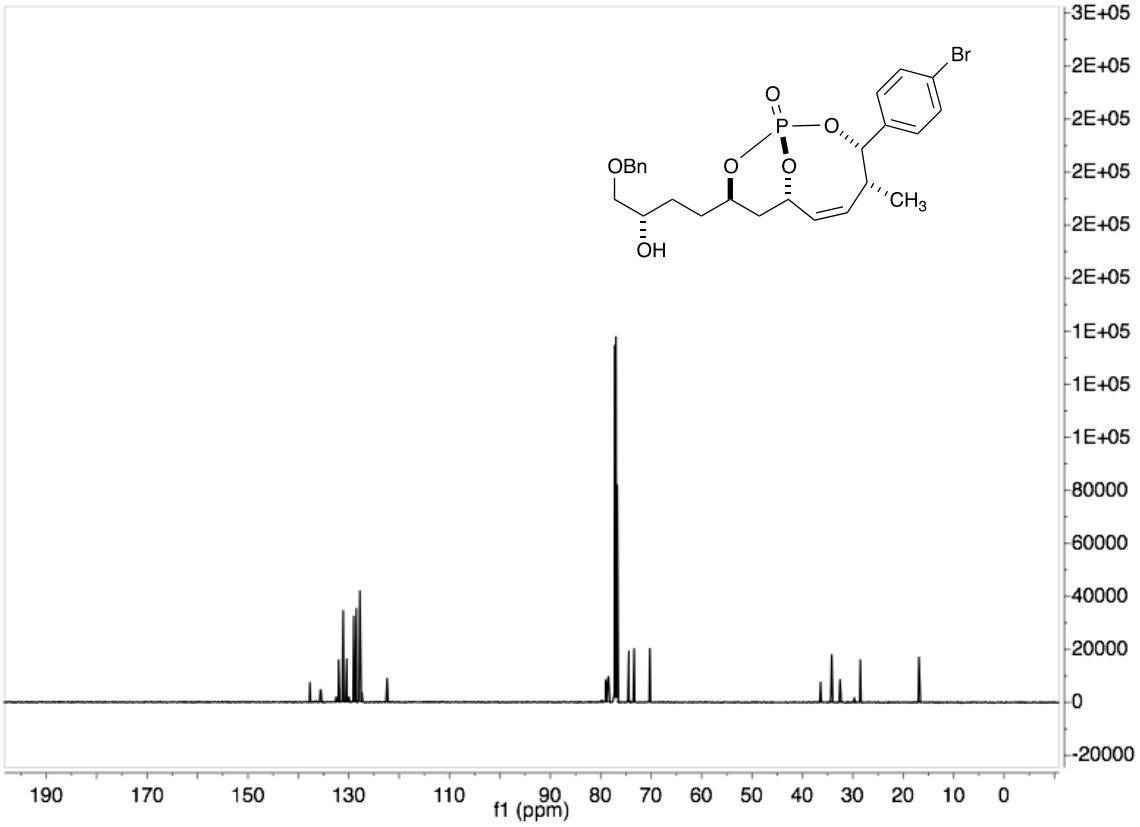


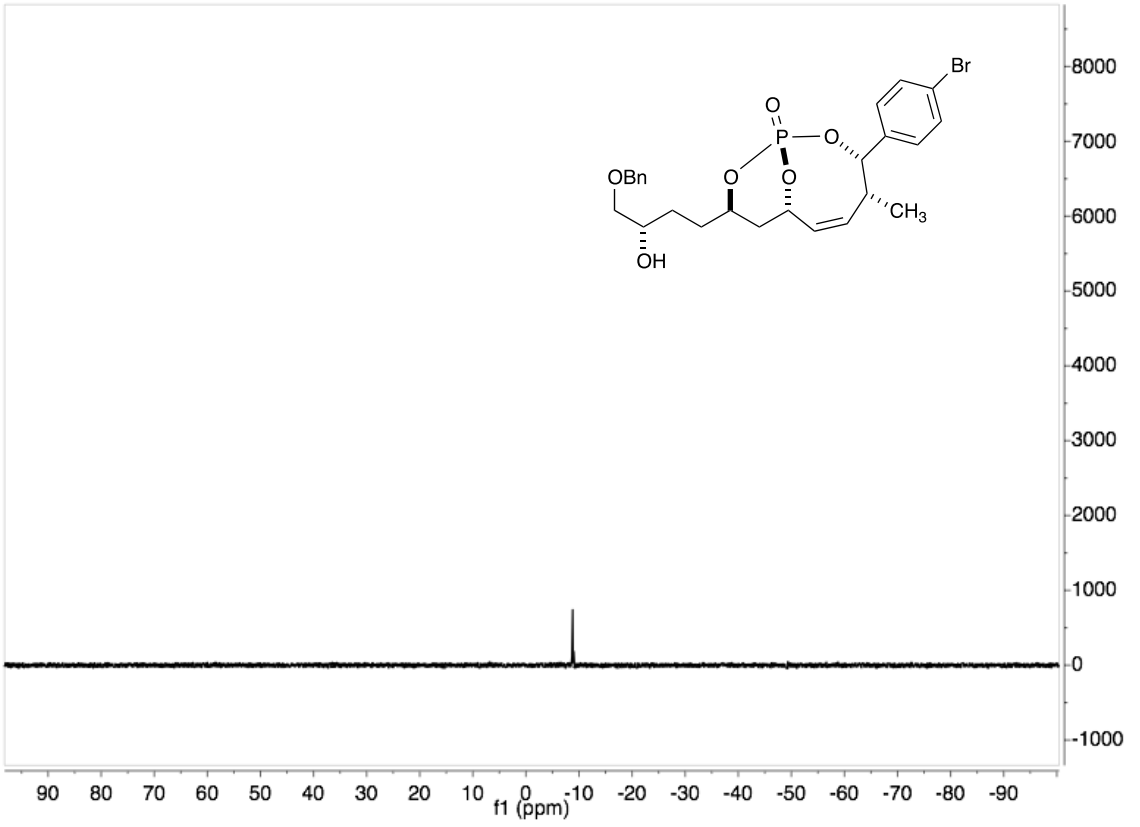





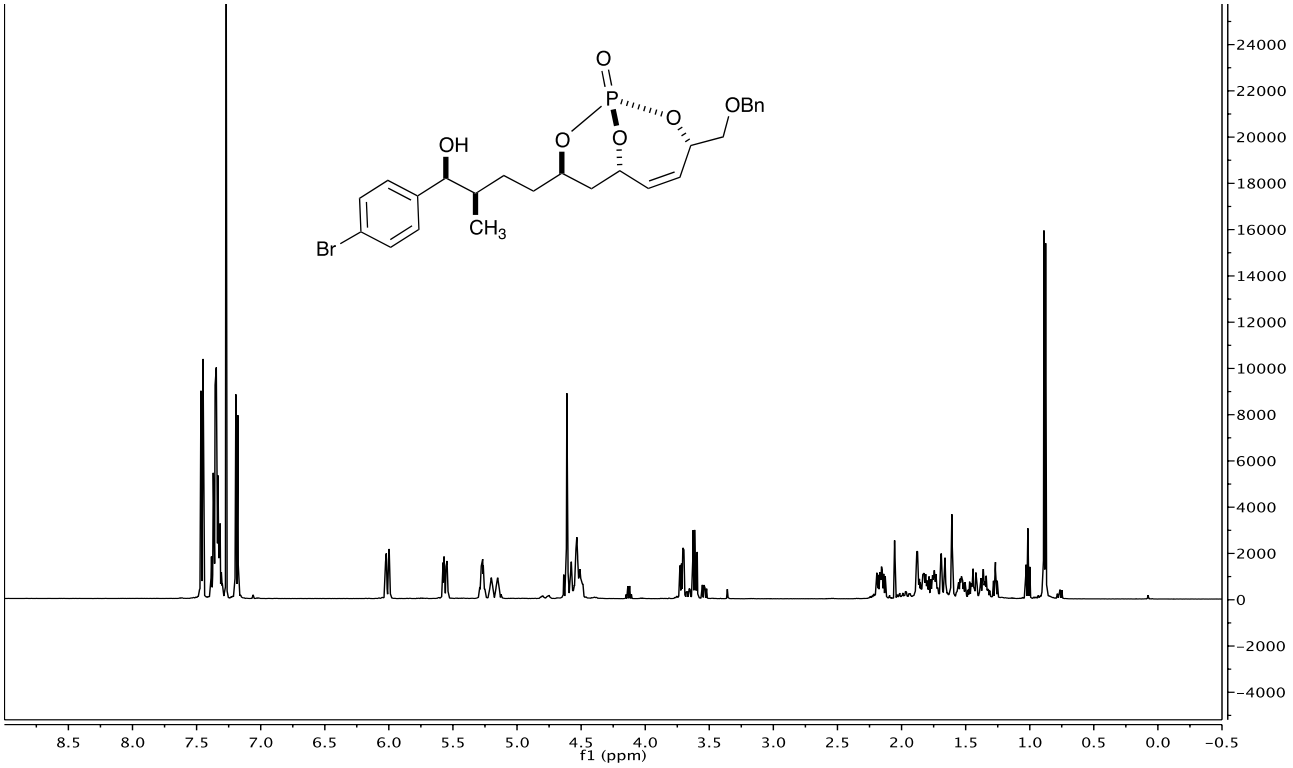

**(1*S*,3*S*,4*R*,7*S*,9*R*,*Z*)-9-((*S*)-4-(benzyloxy)-3-hydroxybutyl)-3-(4-bromophenyl)-4-methyl-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-5-ene 1-oxide (8)**

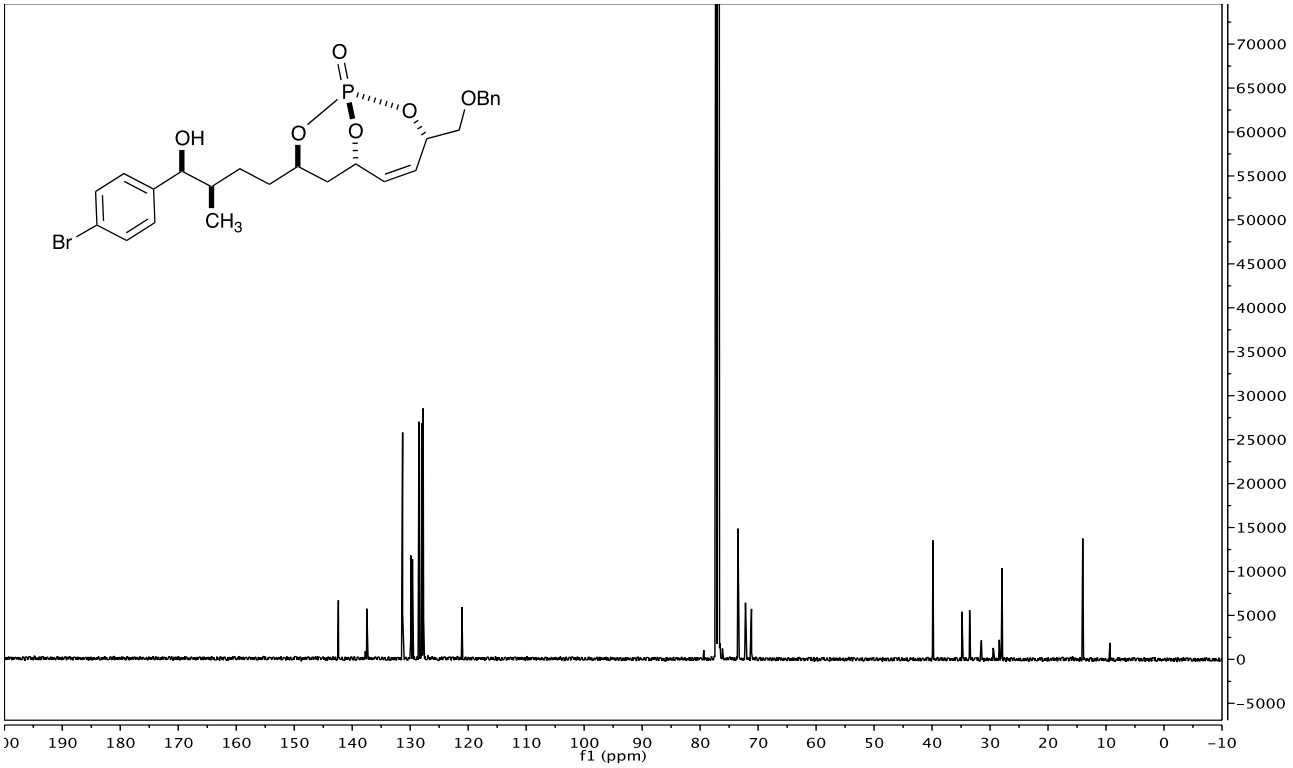


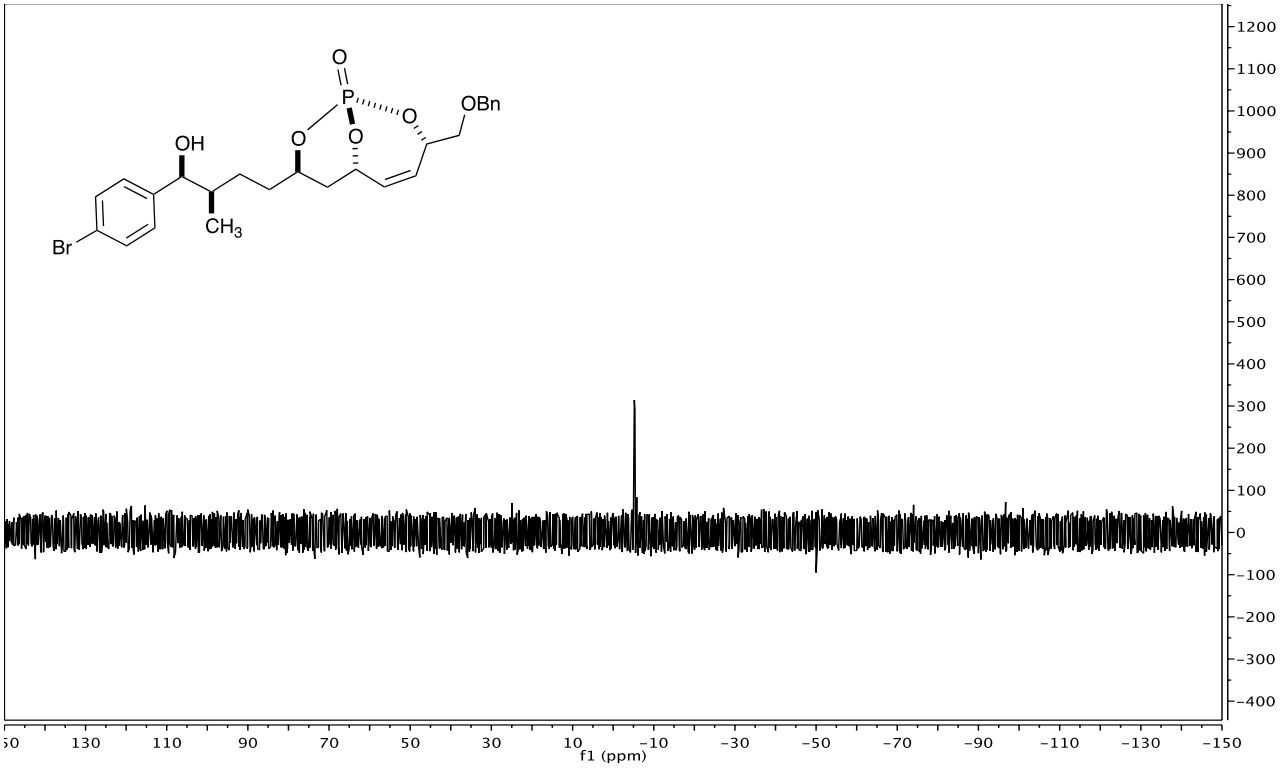

Br
O
P
O
O
O
OBn
O
CH3
OH
3E+05
2E+05
2E+05
2E+05
2E+05
2E+05
1E+05
1E+05
1E+05
80000
60000
40000
20000
0
-20000
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Br
O
P
O
O
O
OBn
O
CH3
OH
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

**(1*S*,3*S*,6*S*,8*R*)-3-((benzyloxy)methyl)-8-((3*R*,4*S*)-4-(4-bromophenyl)-4-hydroxy-3-methylbutyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (9)**




O
P
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O
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OBn
OH
CH3
Br
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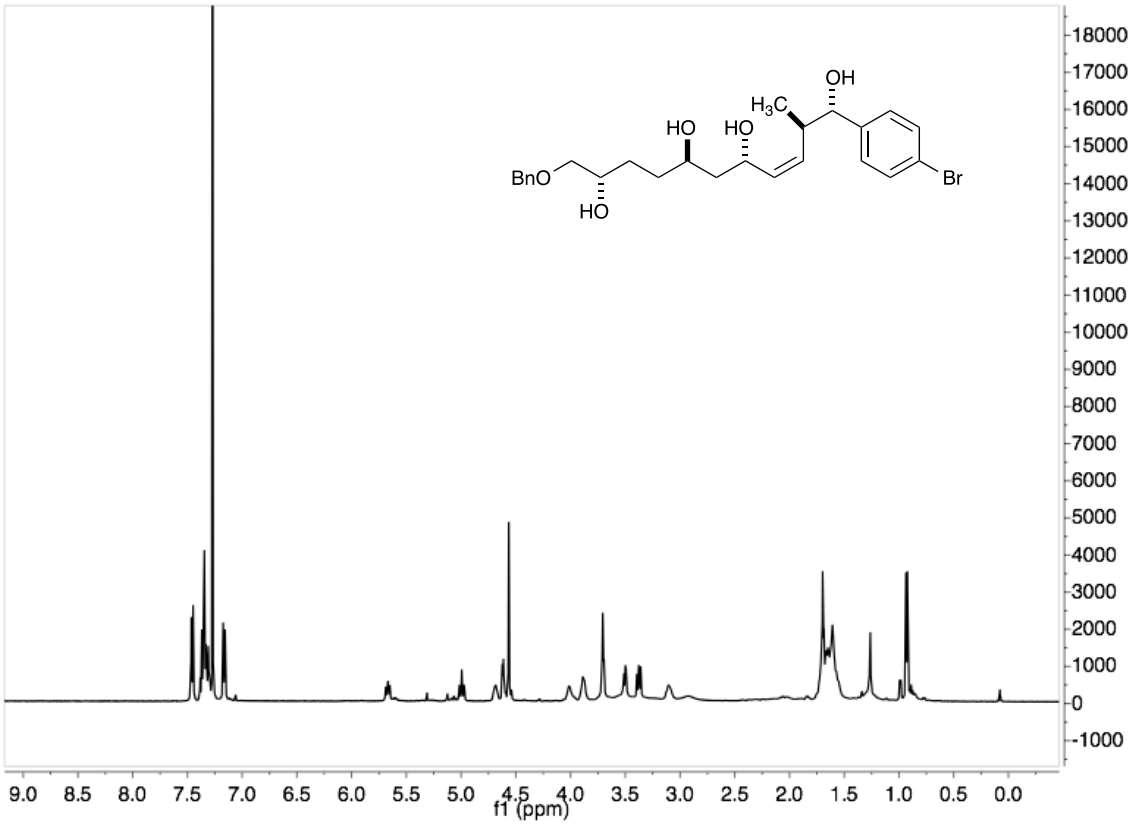
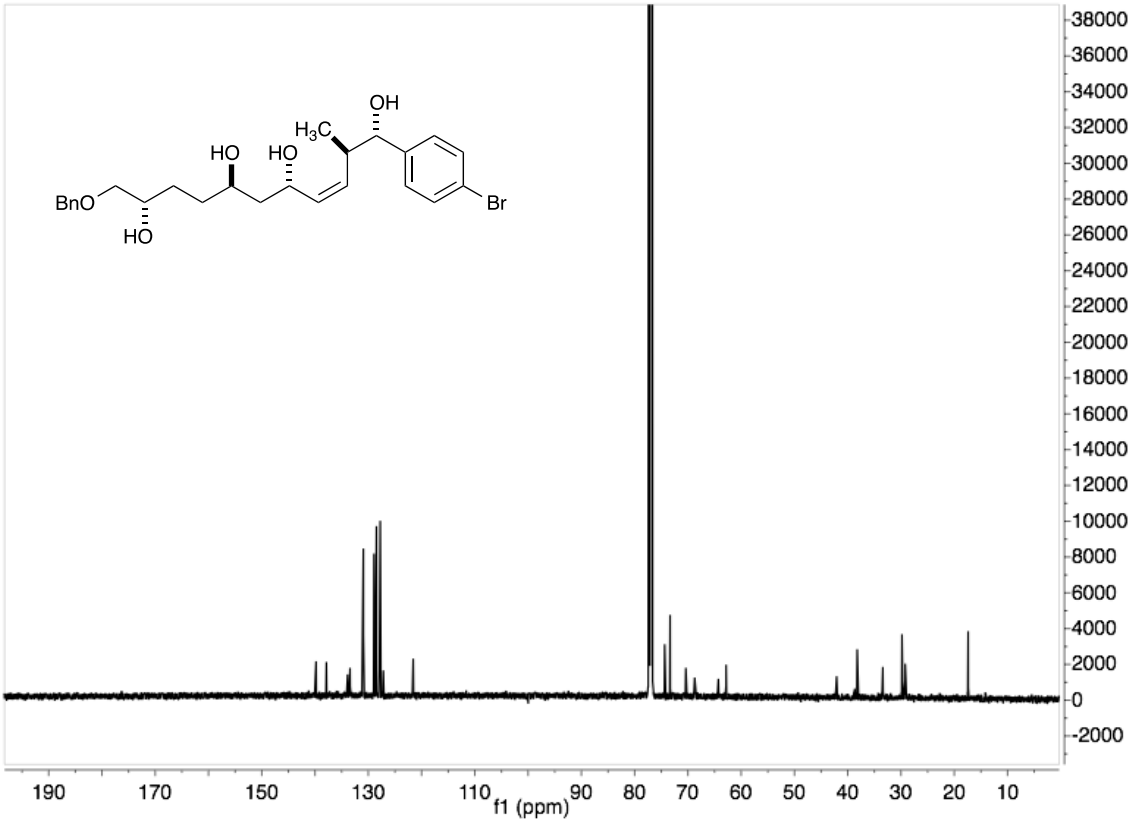
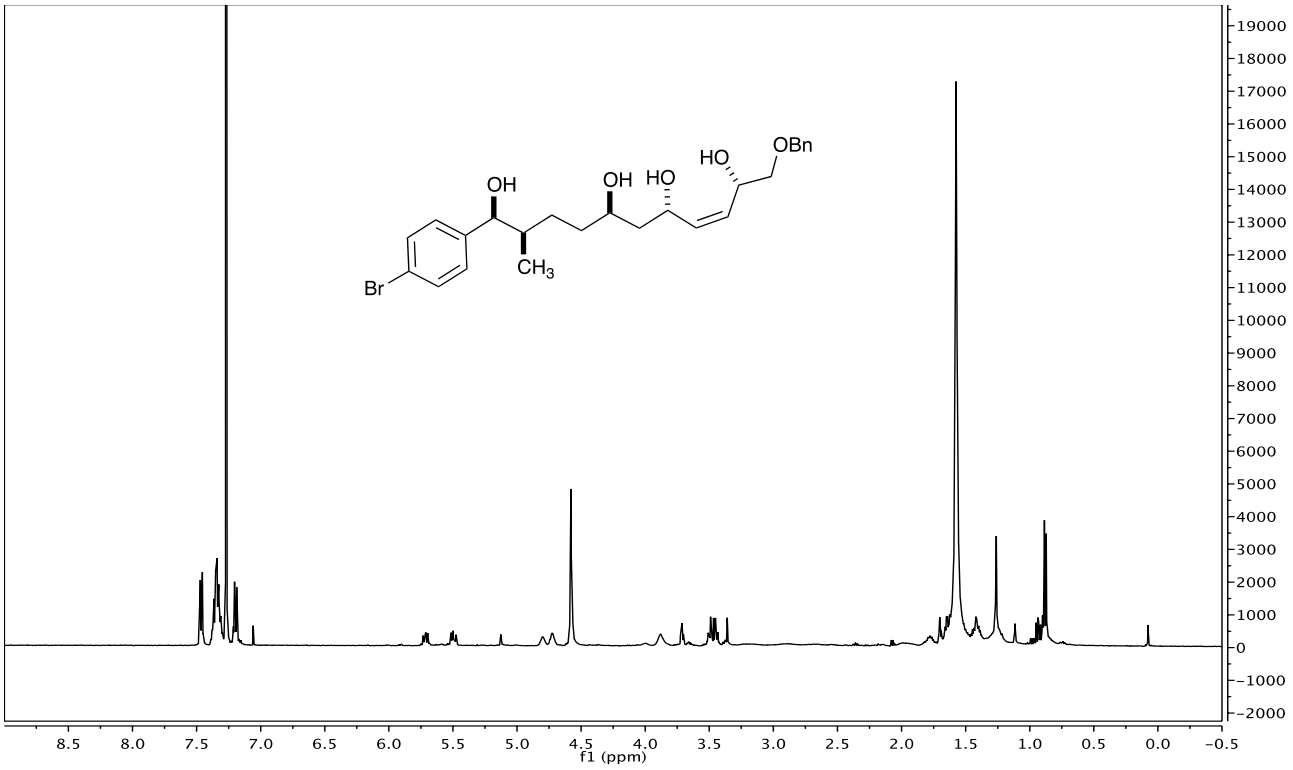
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
−300
−400
130
110
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
f1 (ppm)

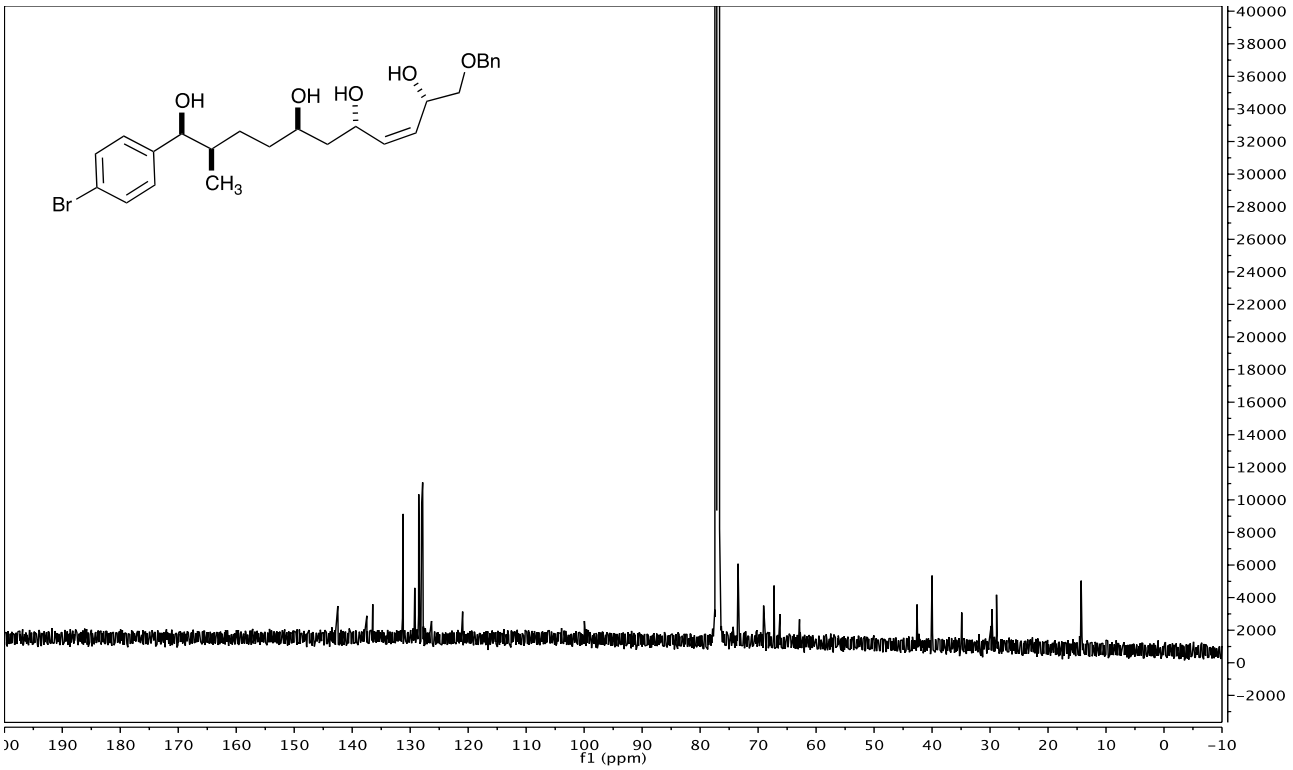
**(1*S*,2*R*,5*S*,7*R*,10*S*,*Z*)-11-(benzyloxy)-1-(4-bromophenyl)-2-methylundec-3-ene-1,5,7,10-tetraol (10)**



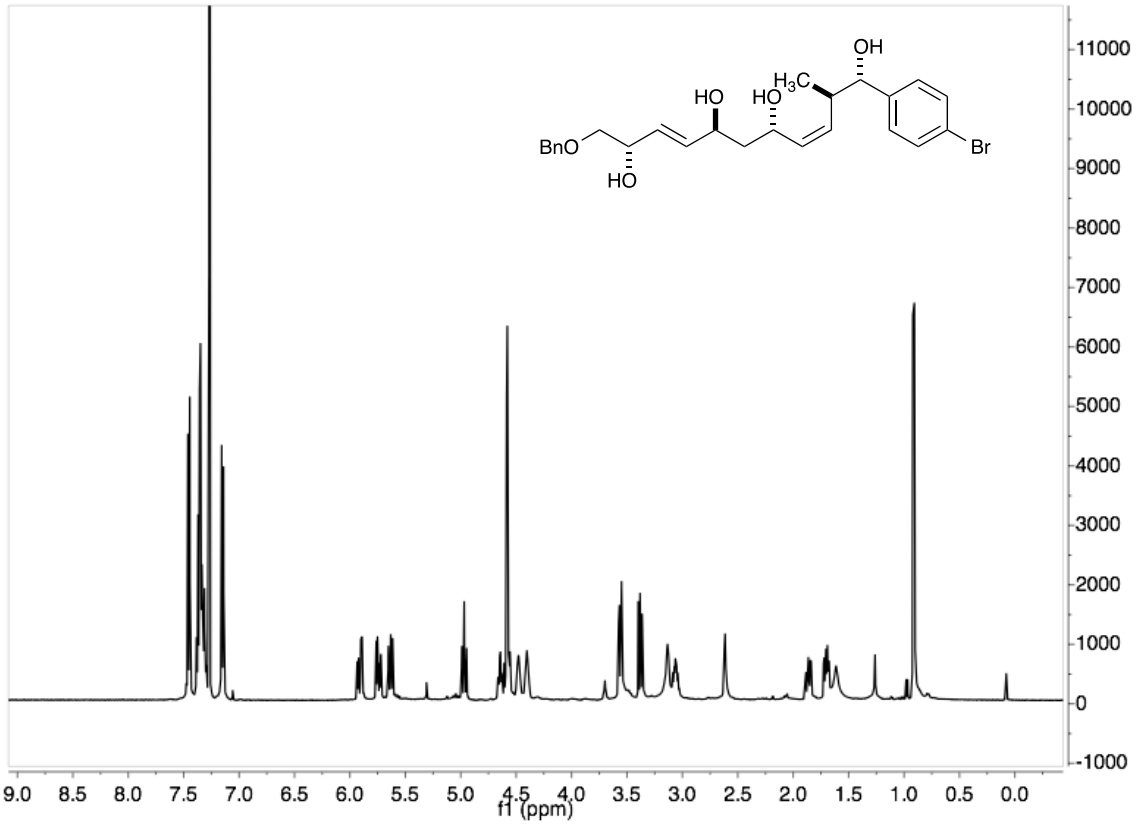



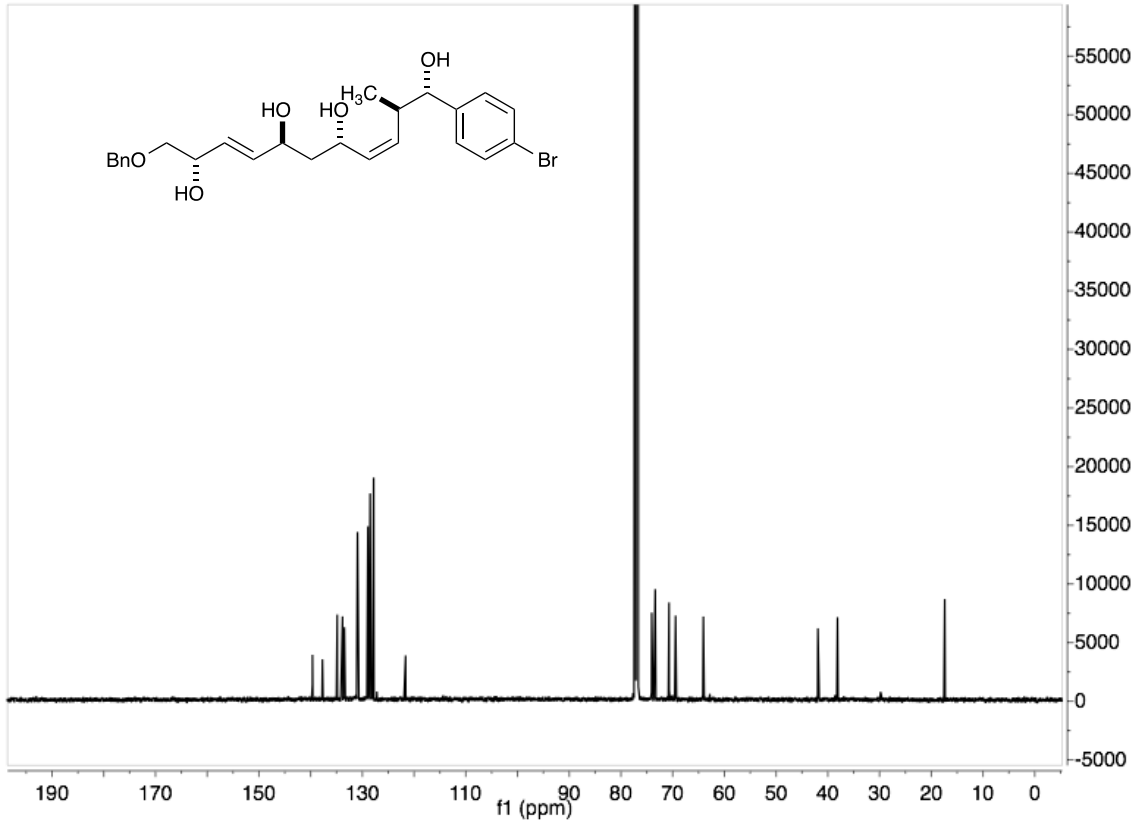
**(1*S*,2*R*,5*R*,7*S*,10*S*,*Z*)-11-(benzyloxy)-1-(4-bromophenyl)-2-methylundec-8-ene-1,5,7,10-tetraol (11)**



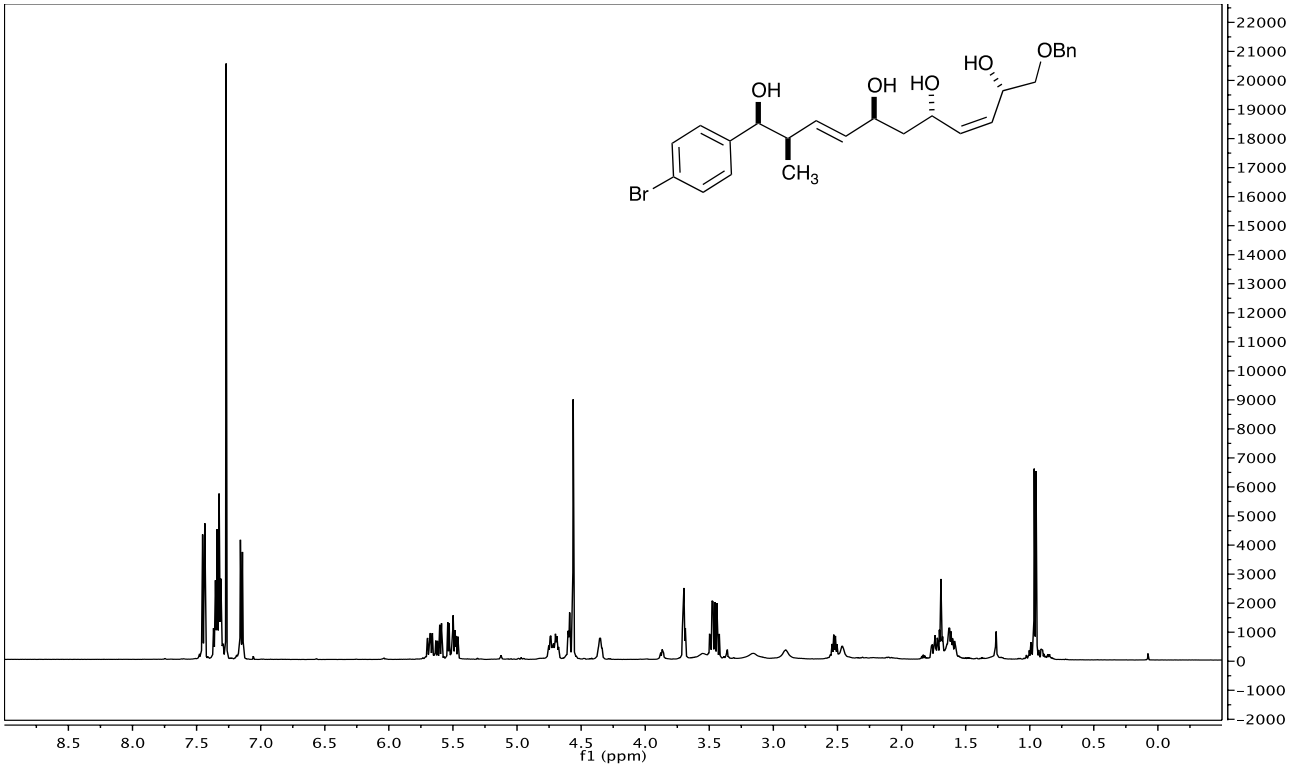



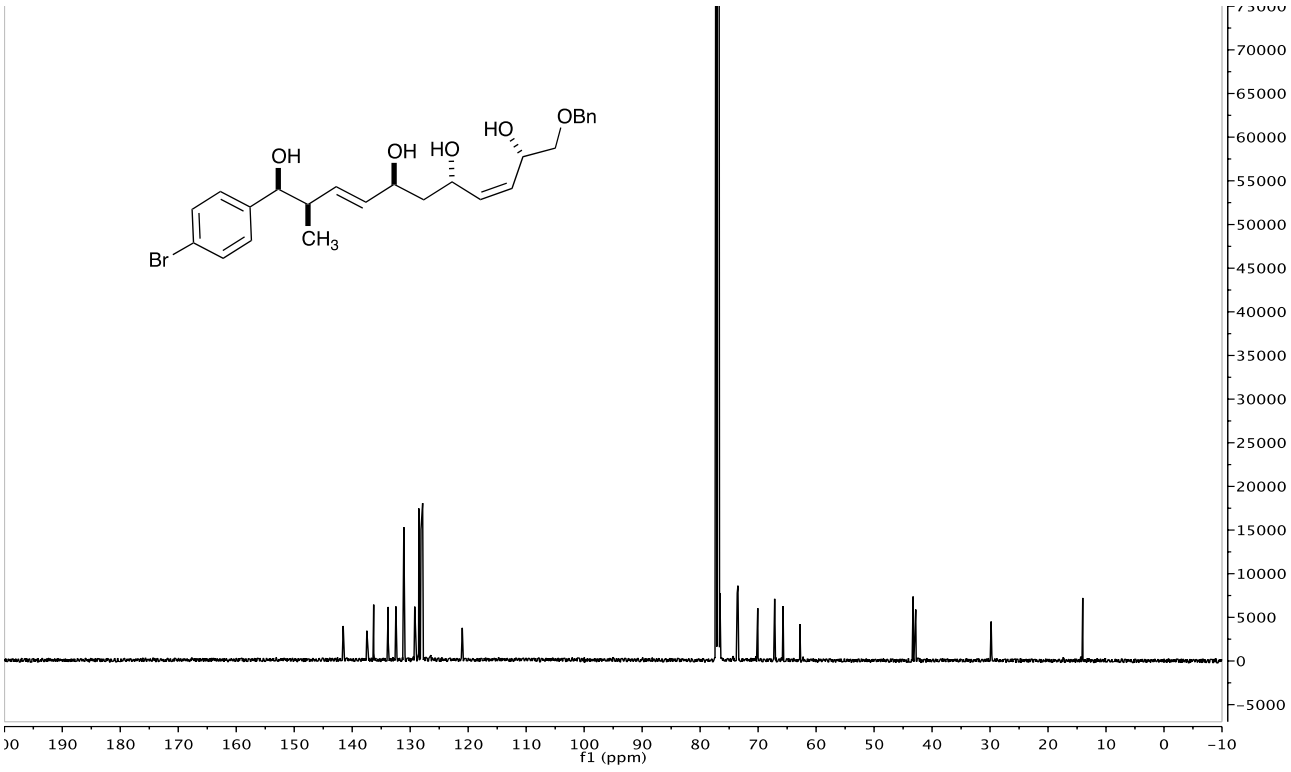
**(1*S*,2*R*,3*Z*,5*S*,7*S*,8*E*,10*S*)-11-(benzyloxy)-1-(4-bromophenyl)-2-methylundeca-3,8-diene-1,5,7,10-tetraol (12)**



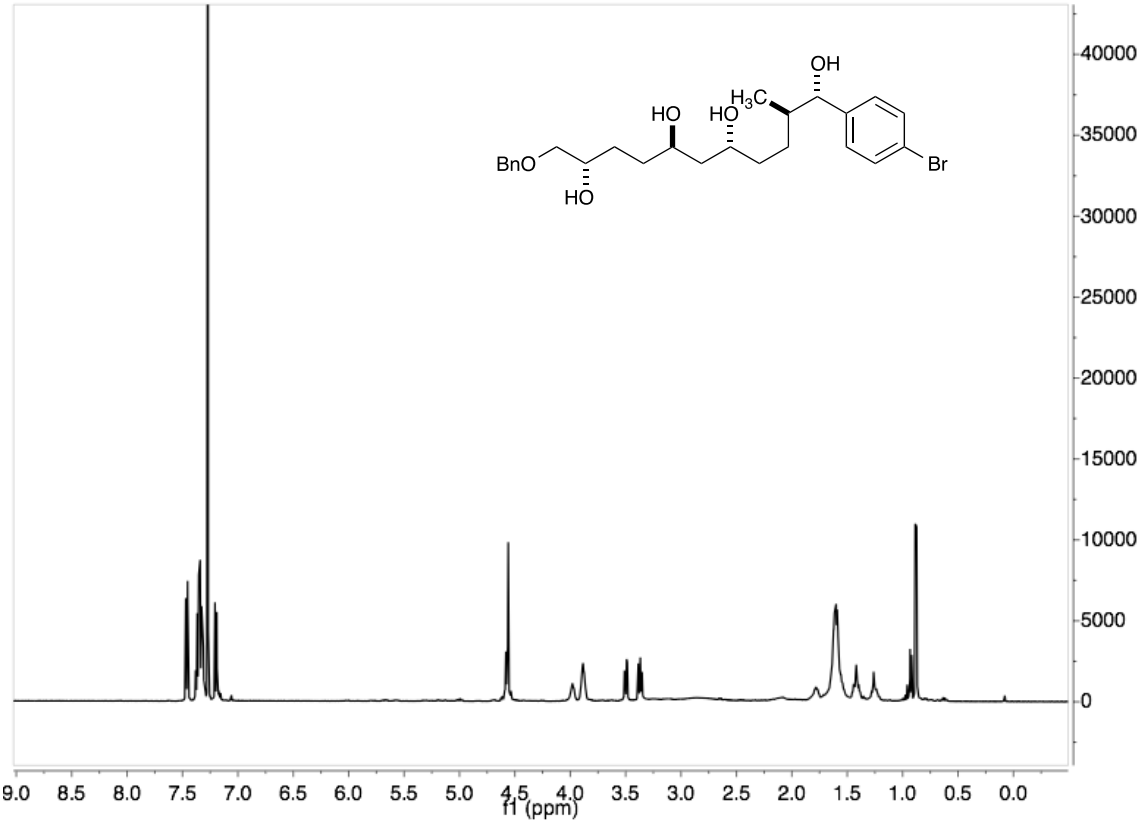



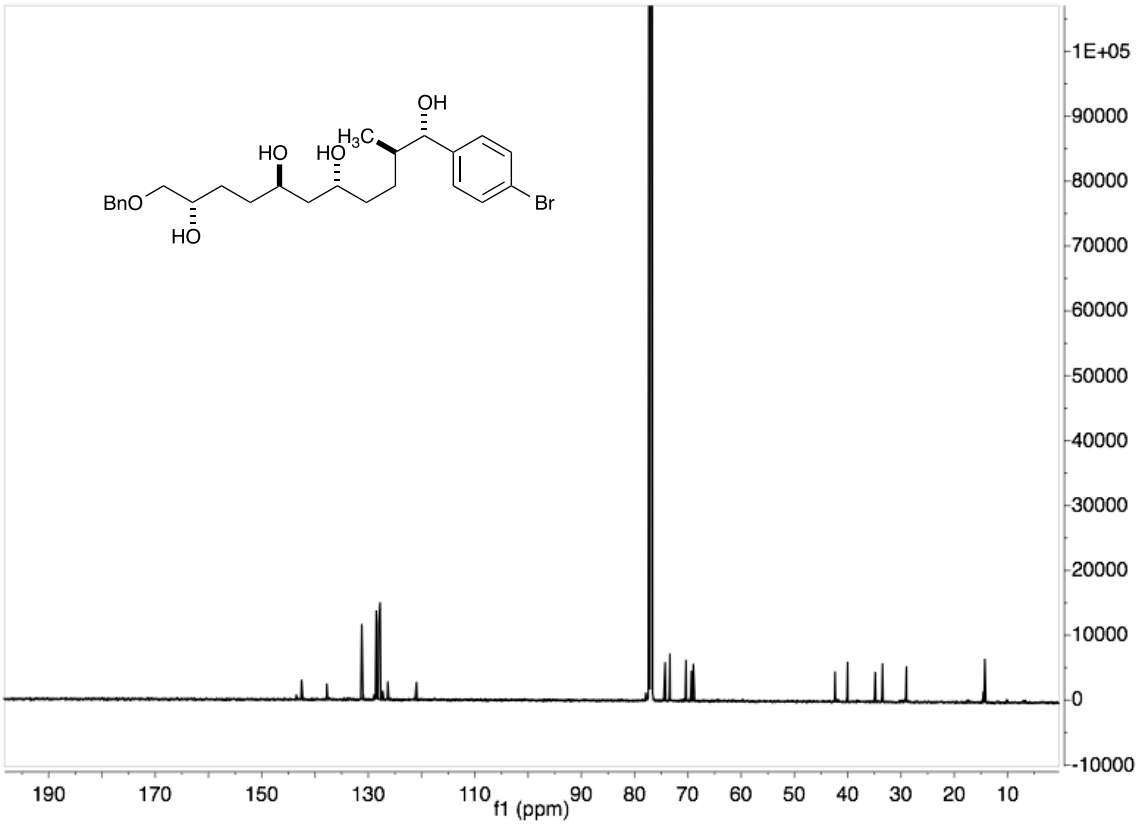
**(1*S*,2*R*,3*E*,5*S*,7*S*,8*Z*,10*S*)-11-(benzyloxy)-1-(4-bromophenyl)-2-methylundeca-3,8-diene-1,5,7,10-tetraol (13)**



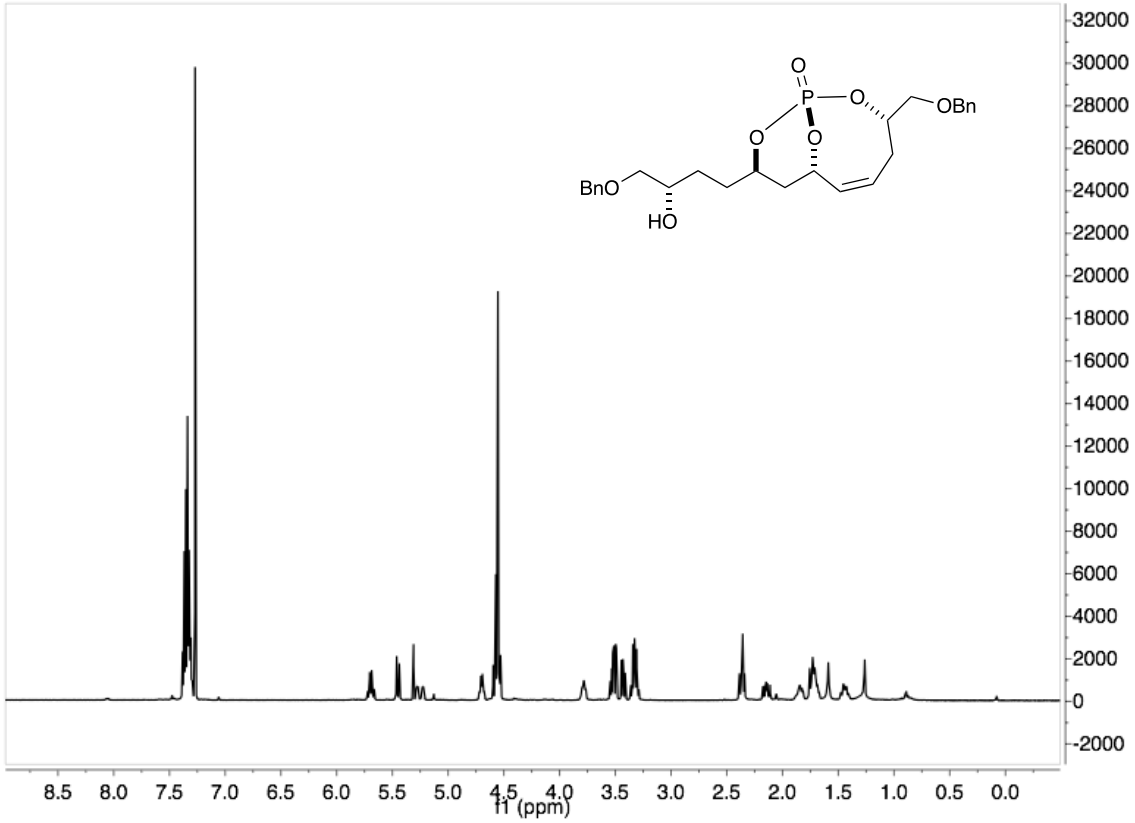



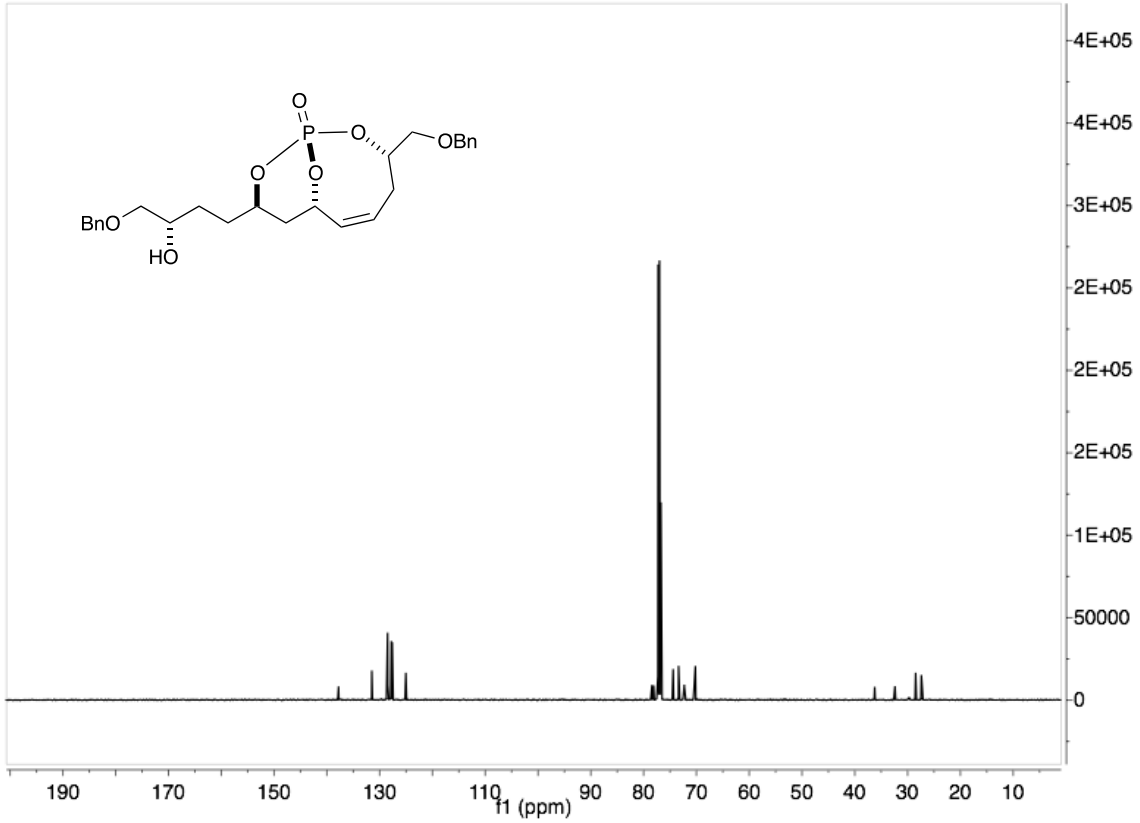
**(1*S*,2*R*,5*R*,7*R*,10*S*)-11-(benzyloxy)-1-(4-bromophenyl)-2-methylundecane-1,5,7,10-tetraol (14)**

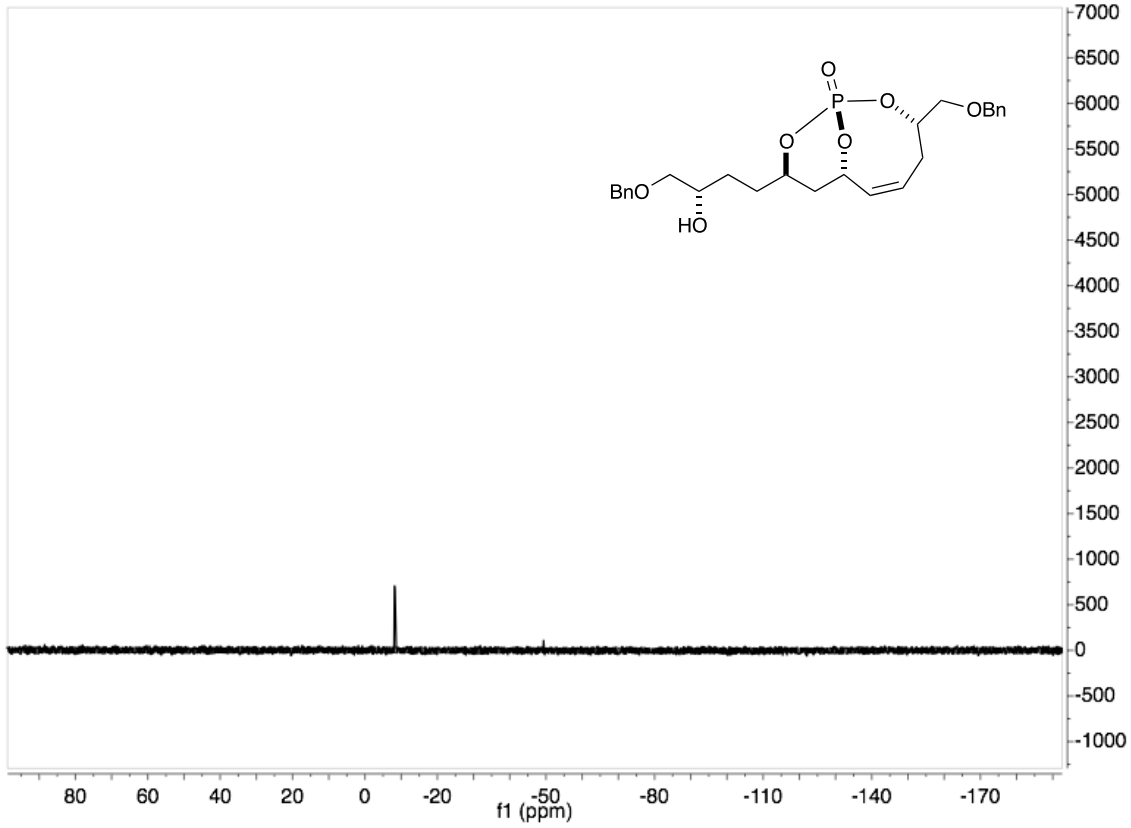


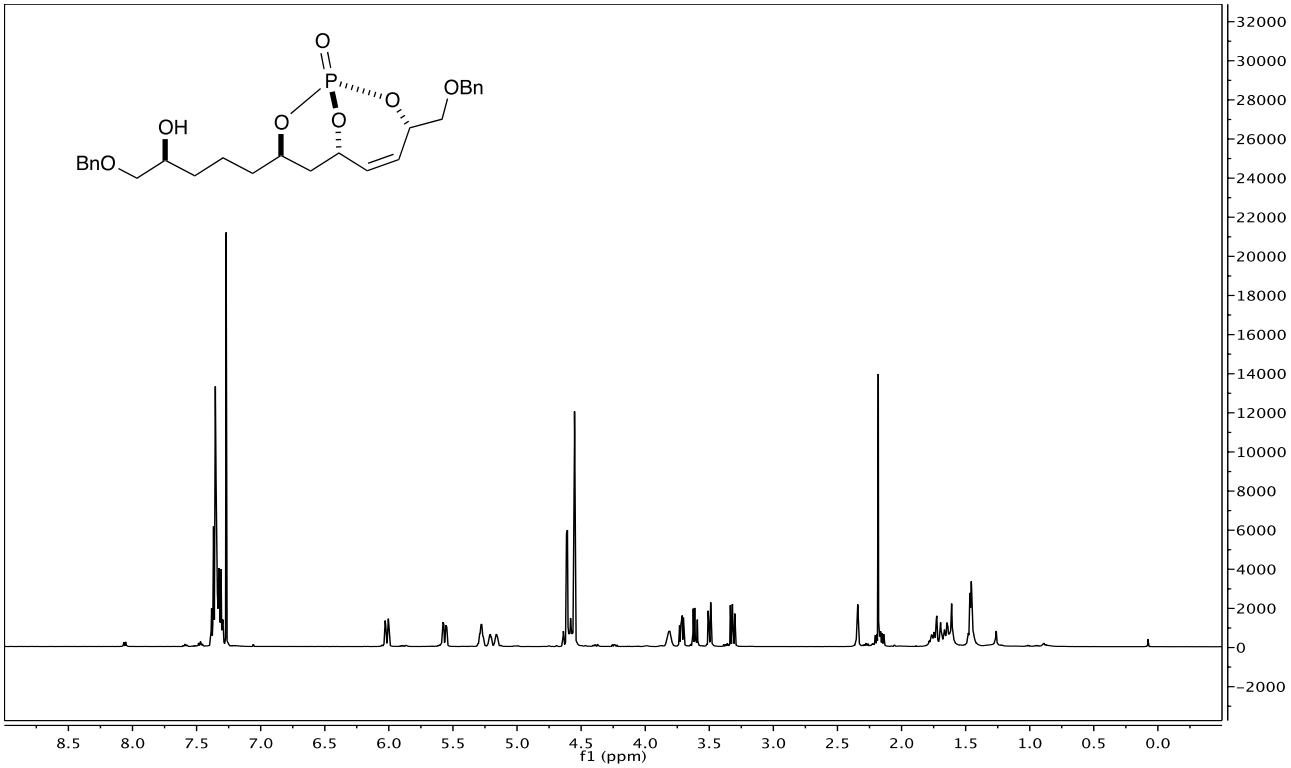
**(1*S*,3*S*,7*S*,9*R*,*Z*)-9-((*S*)-4-(benzyloxy)-3-hydroxybutyl)-3-((benzyloxy)methyl)-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-5-ene 1-oxide (15)**

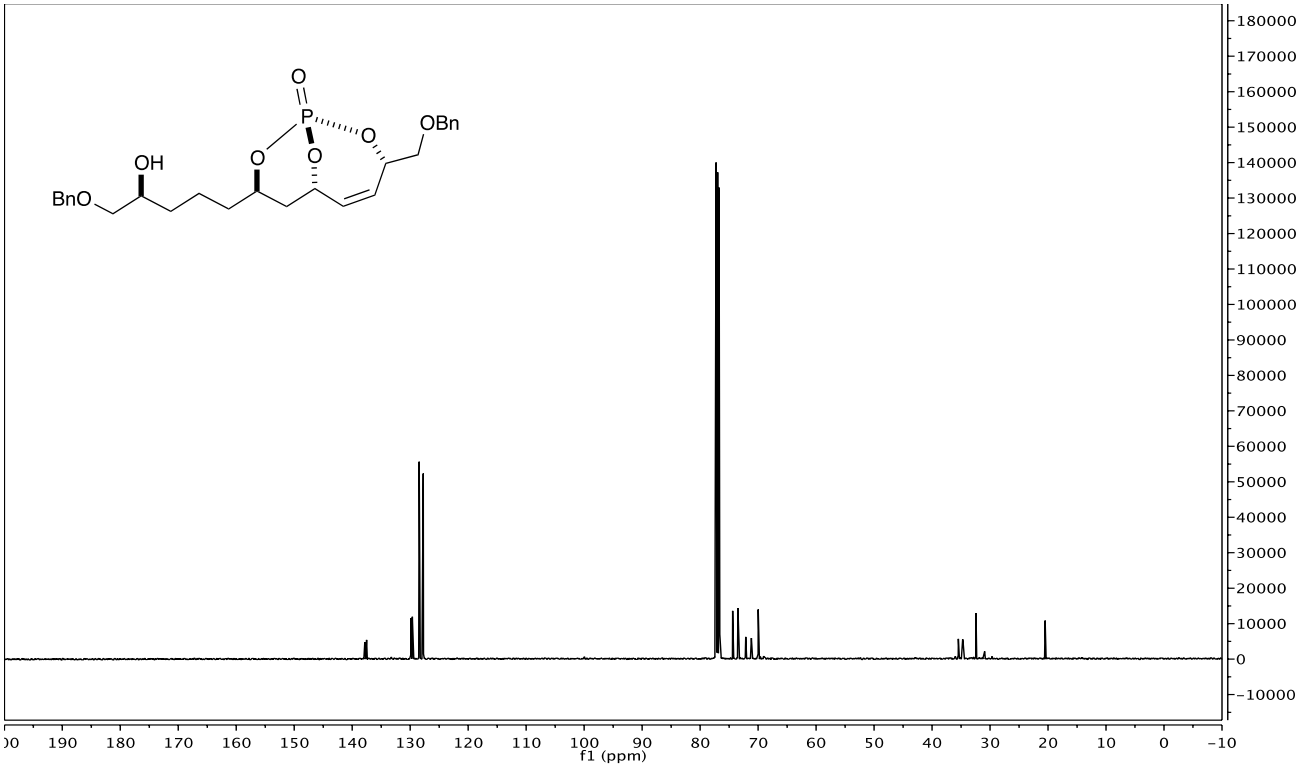


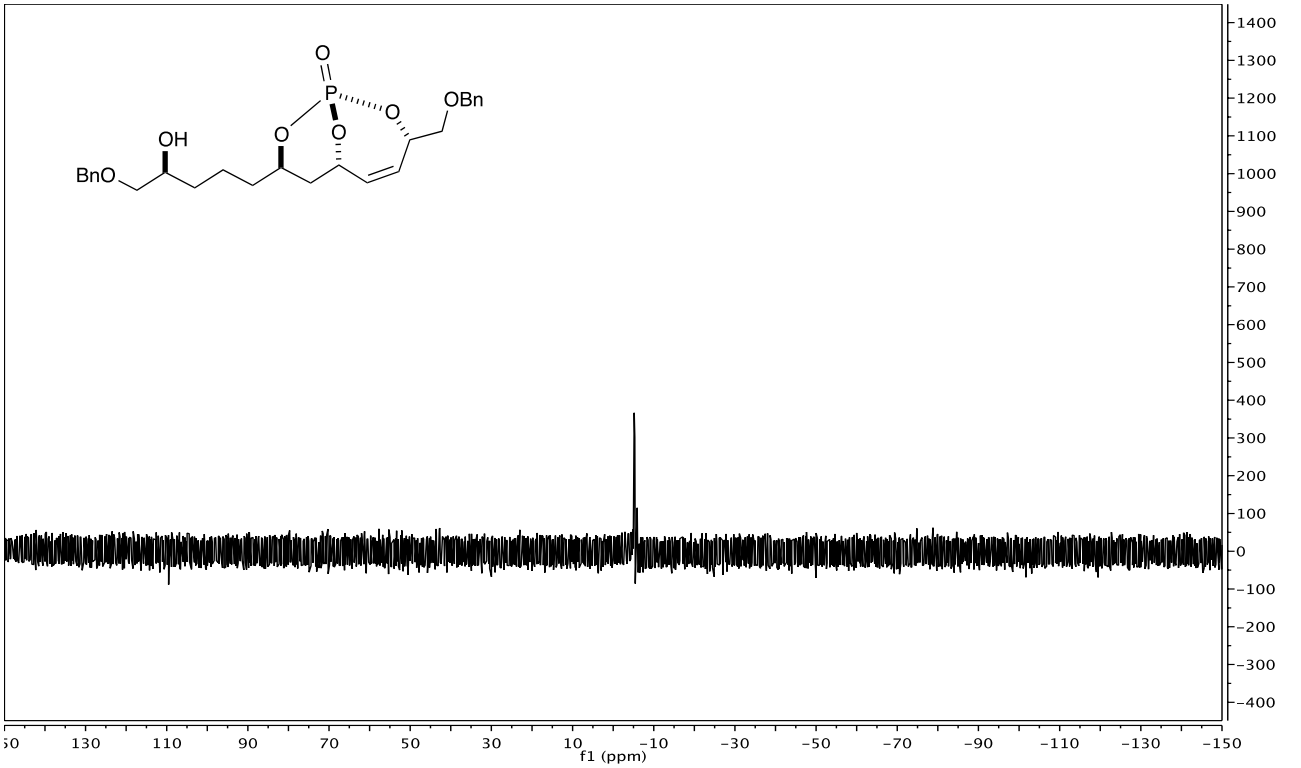





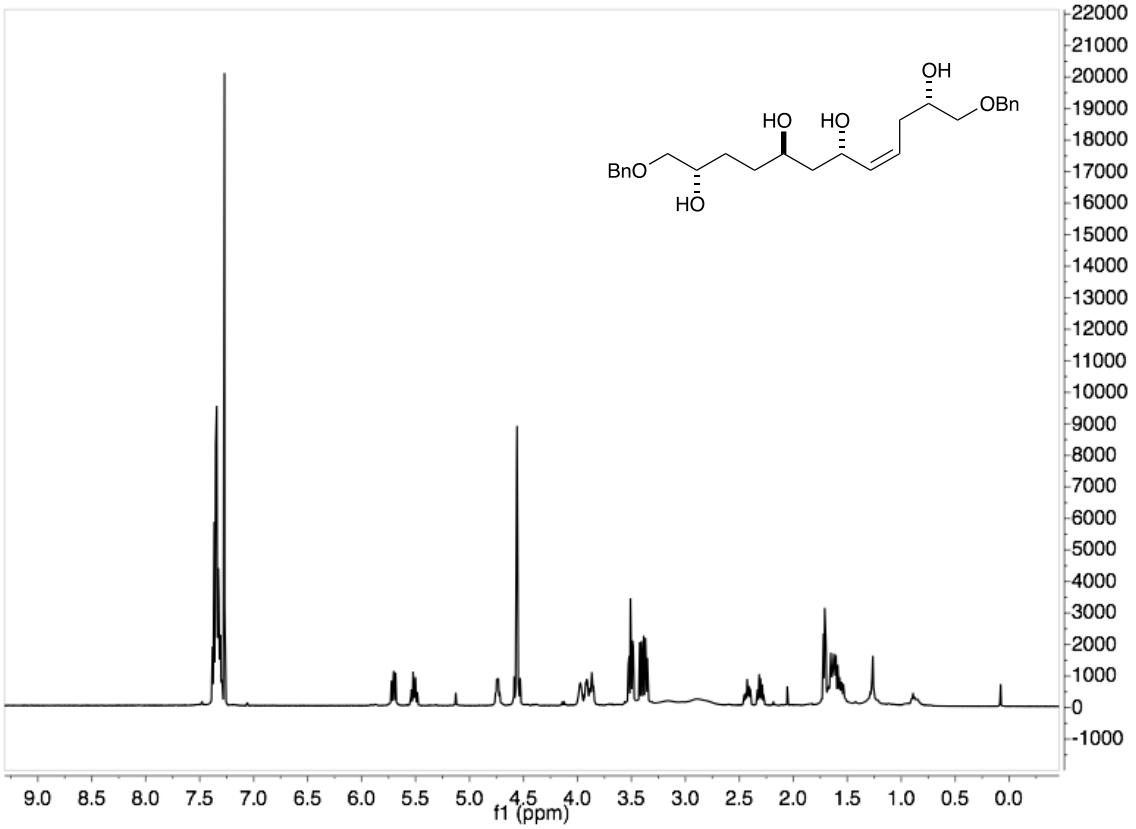

**(1*S*,3*S*,6*S*,8*R*)-8-((*S*)-5-(benzyloxy)-4-hydroxypentyl)-3-((benzyloxy)methyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (16)**

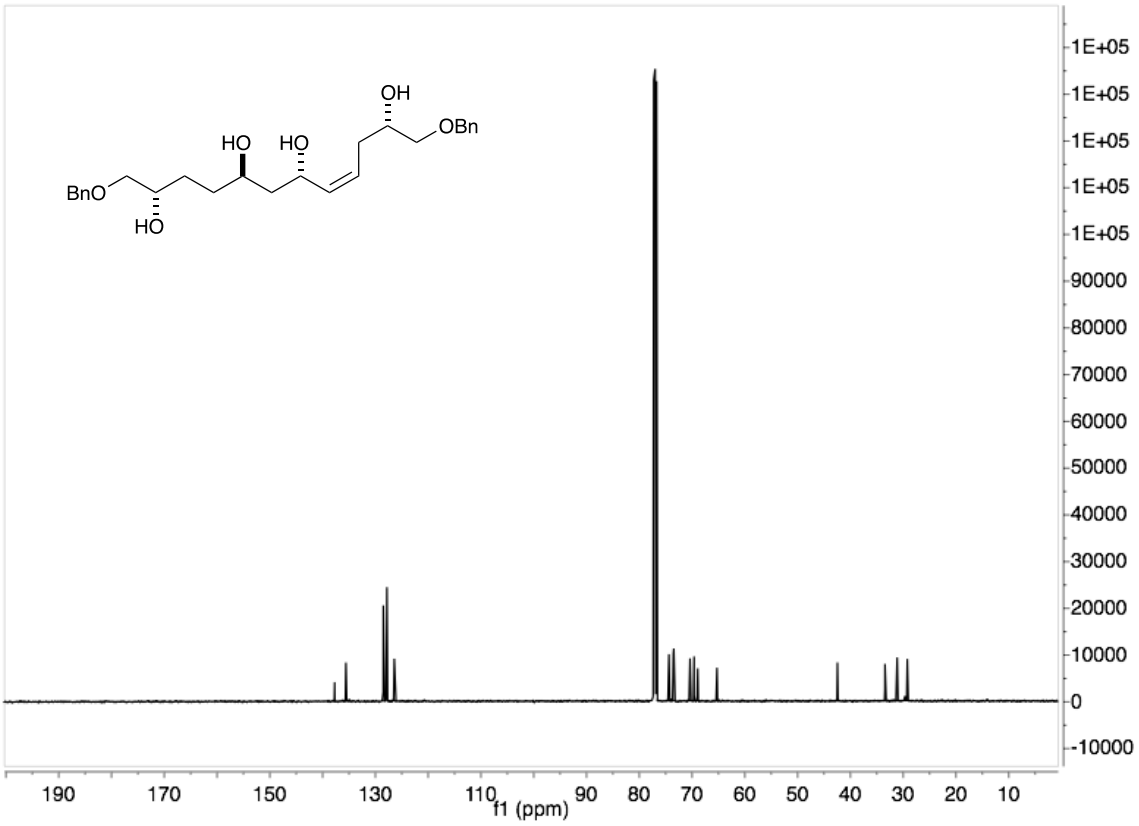



O
P
O
OBn
OH
O
O
BnO
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
−10000
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

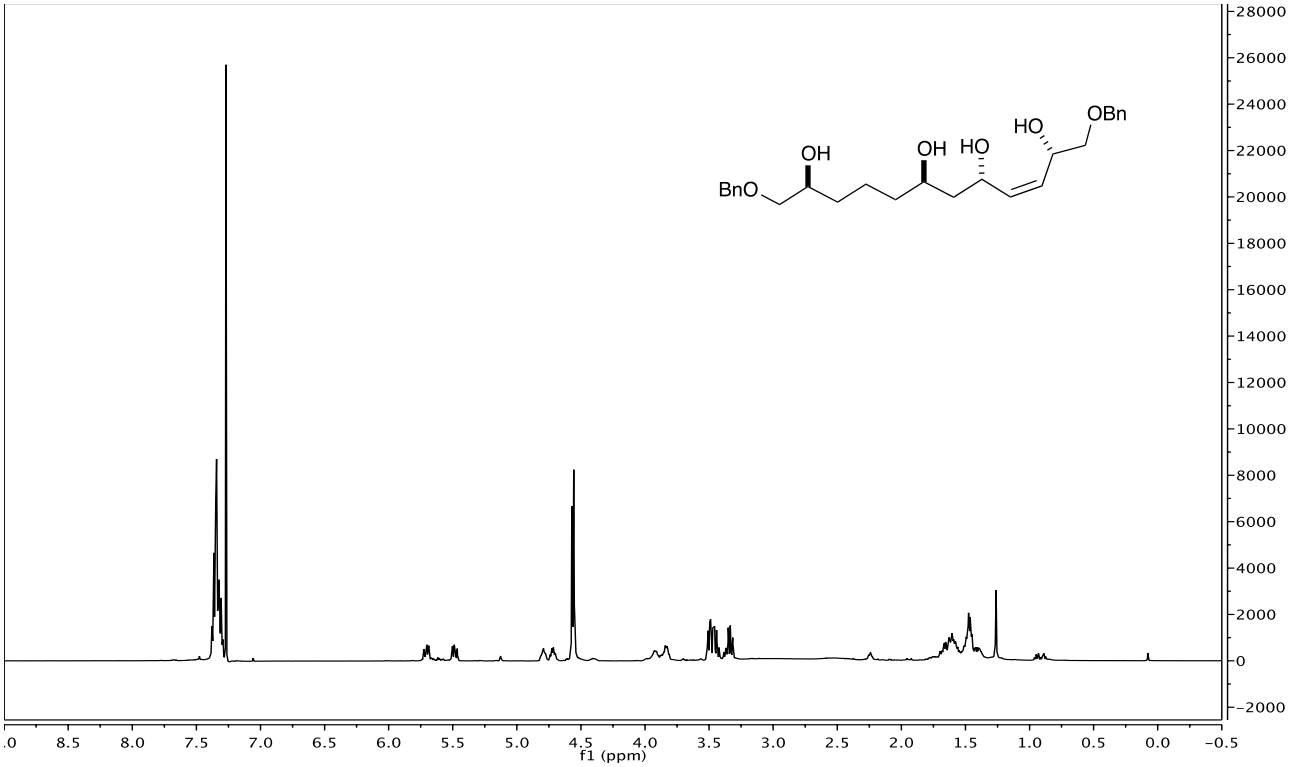

O
P
O
OBn
OH
O
O
BnO
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
−300
−400
130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150
f1 (ppm)

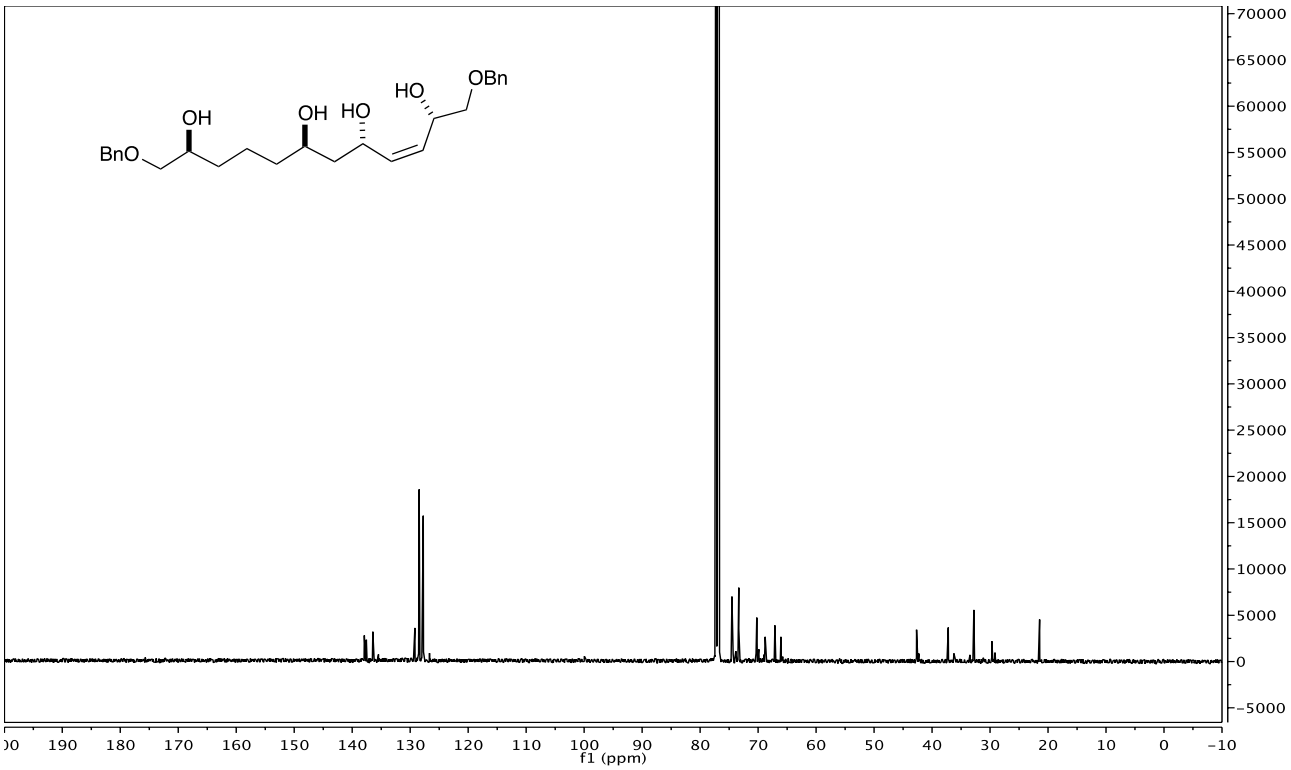
**(2*S*,5*R*,7*S*,11*S*,*Z*)-1,12-bis(benzyloxy)dodec-8-ene-2,5,7,11-tetraol (17)**



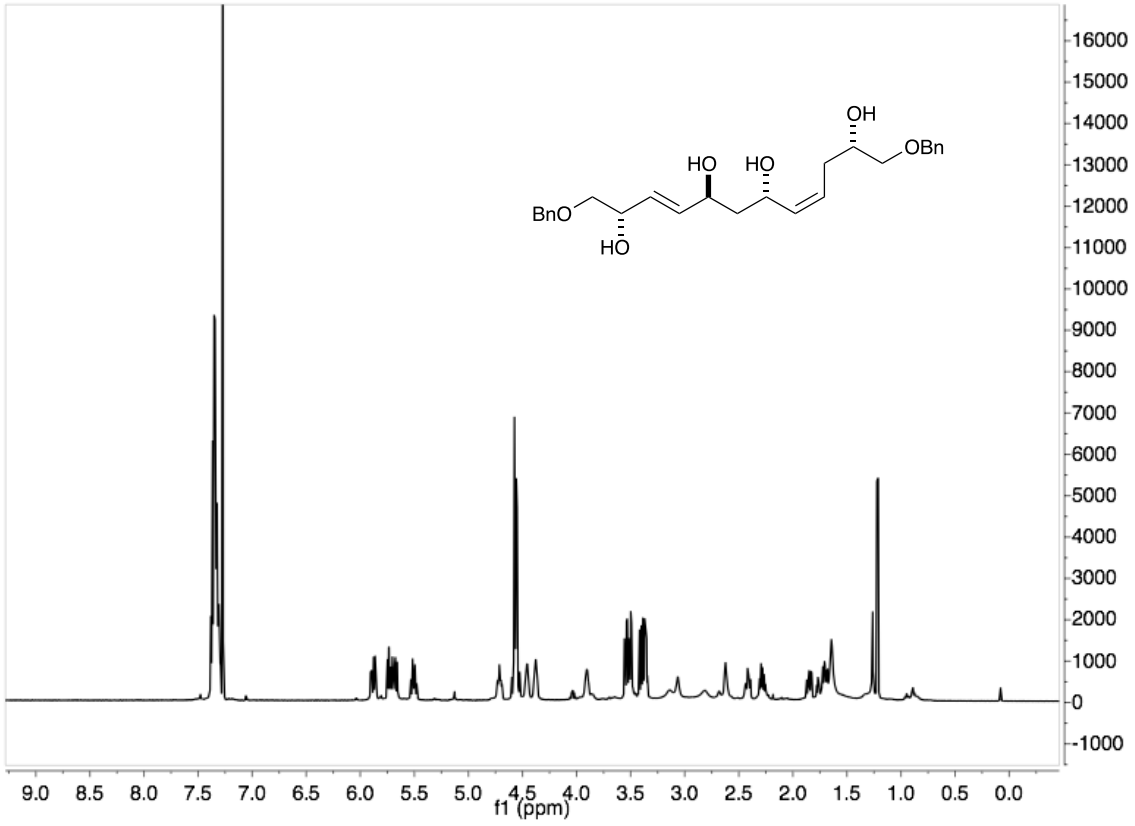



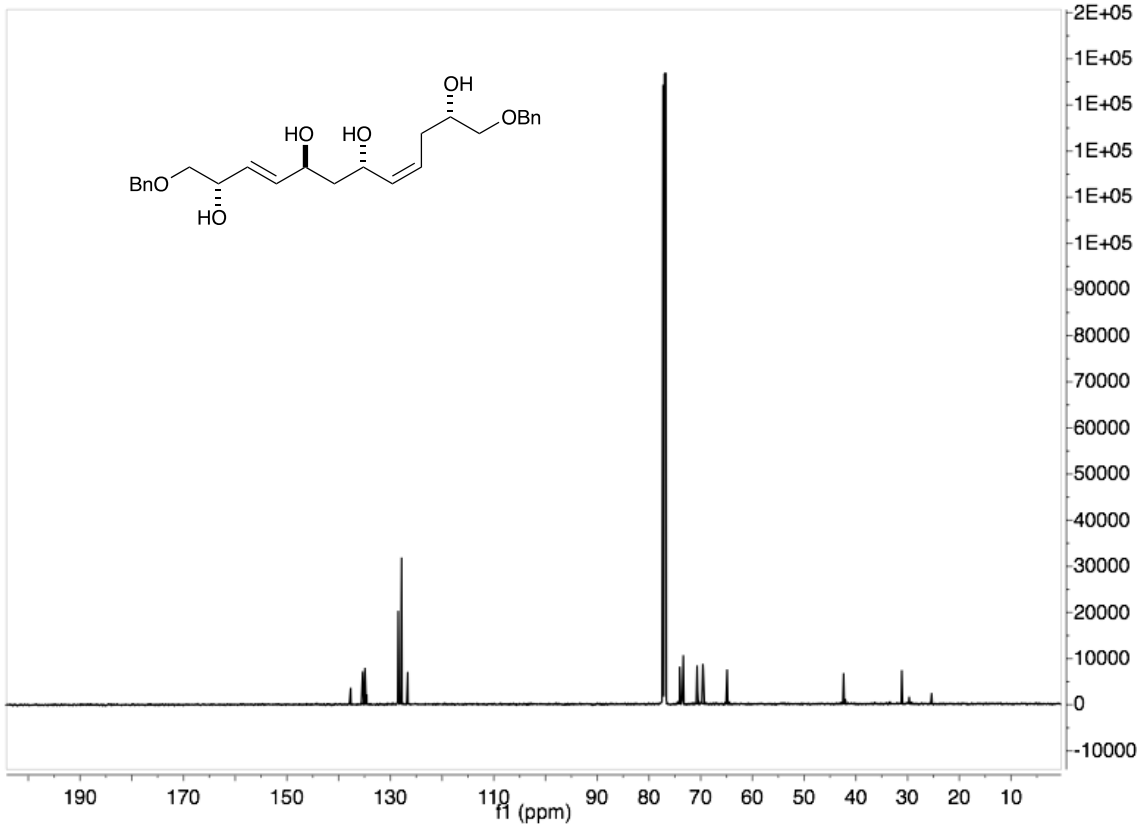
**(2*S*,5*S*,7*R*,11*S*,*Z*)-1,12-bis(benzyloxy)dodec-3-ene-2,5,7,11-tetraol (18)**



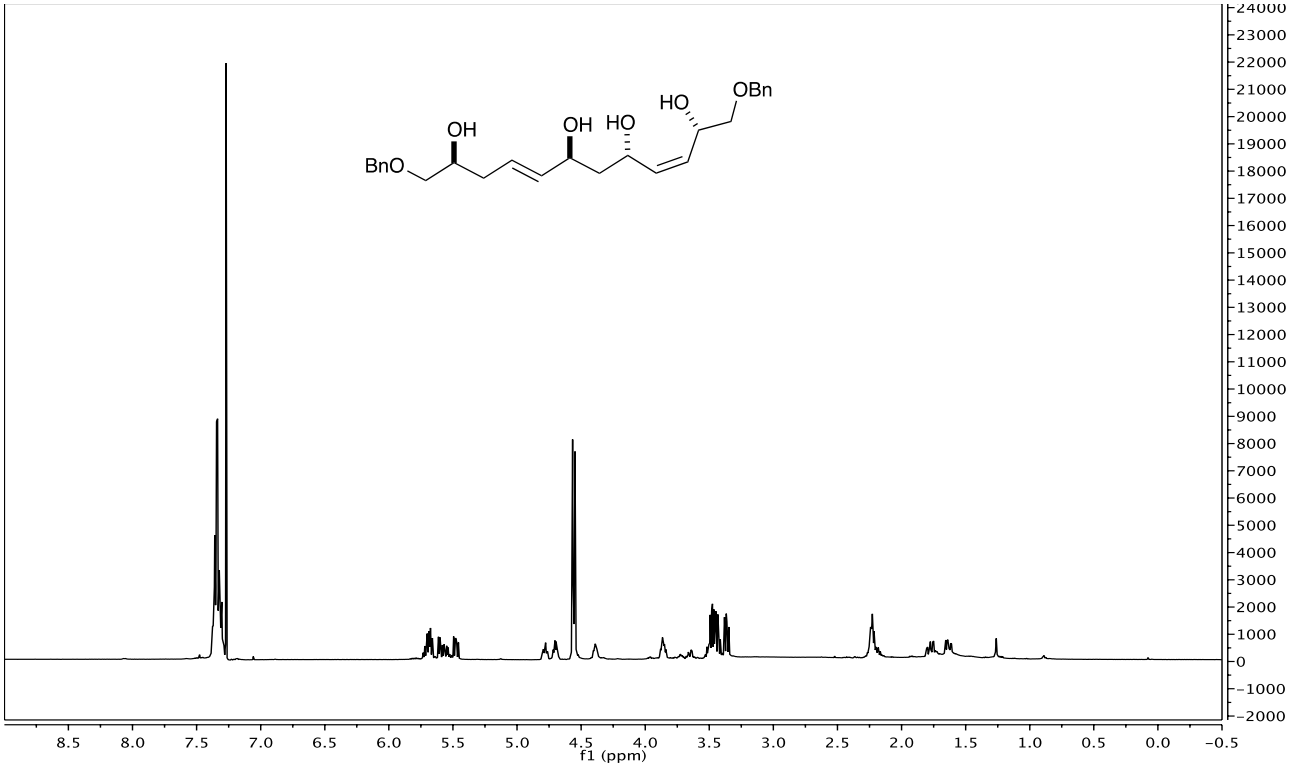



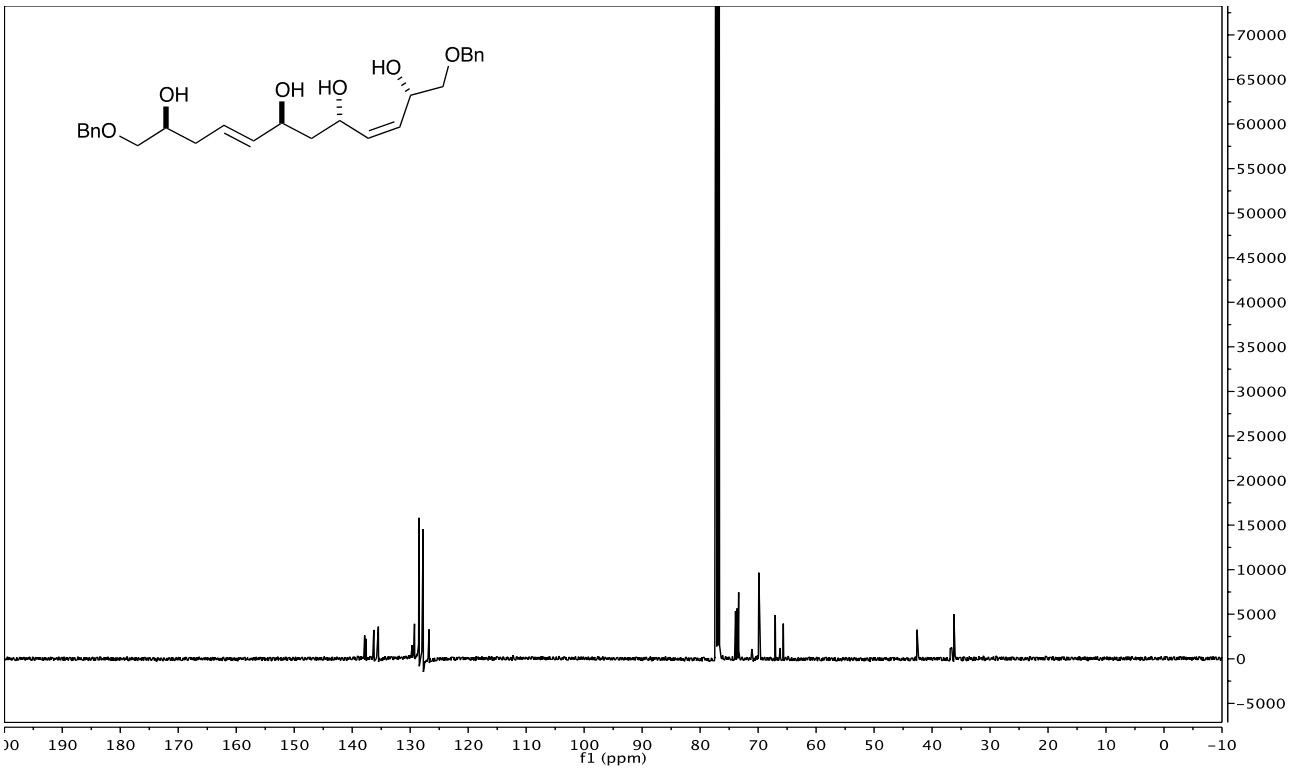
**(2*S*,3*E*,5*S*,7*S*,8*Z*,11*S*)-1,12-bis(benzyloxy)dodeca-3,8-diene-2,5,7,11-tetraol (19)**



**(2*S*,3*Z*,5*S*,7*S*,8*E*,11*S*)-1,12-bis(benzyloxy)dodeca-3,8-diene-2,5,7,11-tetraol (20)**



**(2*S*,5*R*,7*R*,11*S*)-1,12-bis(benzyloxy)dodecane-2,5,7,11-tetraol (21)**