A Phosphate Tether-Mediated, One-pot, Sequential Ring-Closing Metathesis/ Cross-Metathesis/Chemoselective Hydrogenation Protocol

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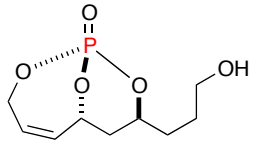
General Experimental Methods

All air and moisture sensitive reactions were carried out in flame or oven-dried glassware under argon atmosphere using standard gas-tight syringes, canellas, and septa. Stirring was achieved with oven-dried magnetic stir bars. Solvents were purified by passage through the Solv-Tek purification system employing activated Al_2O_3 (Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Organometallics **1996**, *15*, 1518-1520). Solvents (CH_2Cl_2 and 1,2-dichloroethane) were also purified by distilling over CaH_2 and degassing using freeze-degas-thaw technique for optimization studies. Et_3N was purified by passage over basic alumina and stored over KOH. All olefin metathesis catalysts were acquired from Materia and used without further purification. Flash column chromatography was performed with Mallinckrodt Chemicals (V120-25, Silica Gel, 60 A, 40-63 μm) and thin layer chromatography was performed on silica gel 60F254 plates (EMD-5715-7). Deuterated solvents were purchased from Cambridge Isotope Laboratories. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ (unless otherwise mentioned) on a Bruker DRX-500 spectrometer operating at 500 MHz, 125 MHz respectively and calibrated to the solvent peak. ^{13}P NMR spectra were 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 TOF MS ES+ (MeOH). FTIR spectroscopy was performed using a Shimadzu FTIR-8400S instrument. Observed rotations at 589 nm, were measured using AUTOPOL IV Model automatic polarimeter.

General procedure for RCM/CM/hydrogenation with Type I olefins (Table 1)

To a stirring solution of triene (*R*,*R*)-**1** (50 mg, 0.217 mmol) in freshly distilled, freeze-degas-thawed CH_2Cl_2 (31 mL, 0.007 M) was added Hoveyda-Grubbs 2nd Gen. catalyst (8 mg, 0.013 mmol) and the reaction was refluxed for 45 min. After completion of RCM, type I olefin cross partner [1–1.5 equiv with respect to the triene (*R*,*R*)-**1**] was added, followed by addition of Hoveyda-Grubbs 2nd Gen. catalyst (5 mg, 0.008 mmol). The reaction was refluxed with simultaneous evaporation of excess CH_2Cl_2 to reach optimal concentration for CM reaction (4 mL, 0.05 M). Reflux was continued for an additional 2–3 h upon which the reaction showed the CM product formation along with some trace amounts of RCM starting material (*R*,*R*,R_P)-**2**. Reflux was stopped and *o*-nitrobenzenesulfonyl hydrazine (*o*-NBSH) (538 mg, 2.17 mmol) and Et_3N (1.07 mL, at 2 mL/g of *o*-NBSH) were added, upon which the reaction was stirred at RT overnight. Excess *o*-NBSH (269 mg, 1.08 mmol) and Et_3N (0.538 mL, at 2 mL/g of *o*-NBSH) were added and the reaction was stirred for an additional 8 h. The reaction mixture was diluted with EtOAc (10 mL) and extracted with sat. $NaHCO_3$ (10 mL). The aqueous layer was washed with EtOAc (2x5 mL) and the combined organic layers were dried (Na_2SO_4), concentrated under reduced pressure and purified using flash column chromatography.

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



R_f = 0.25 (9:1 EtOAc:MeOH);

FTIR (neat): 3415, 3033, 2925, 2889, 1286 cm^{-1};

Optical Rotation: $[\alpha]_D = -73.4$ (c = 0.47, $CHCl_3$);

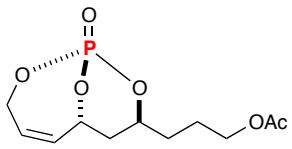
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 6.04 (dddd, J = 11.9, 6.7, 3.1, 2.2 Hz, 1H), 5.60 (ddd, J = 11.8, 3.9, 2.6 Hz, 1H), 5.20 (br.d, J_{PH} = 24.5 Hz, 1H), 5.01 (dddd, J = 11.4, 8.4, 5.7, 2.7 Hz, 1H), 4.66–4.60 (m, 1H), 4.37 (ddd, J = 27.7, 14.8, 6.8 Hz, 1H), 3.69 (ddd, J = 22.2, 10.6, 5.7 Hz, 2H), 2.21 (ddd, J = 14.6, 11.9, 6.3 Hz, 1H), 1.86–1.63 (m, 5H);

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 129.8, 127.9, 77.2 (d, J_{CP} = 6.6 Hz), 76.5 (d, J_{CP} = 6.7 Hz), 62.9 (d, J_{CP} = 6.5 Hz), 62.0, 34.8 (d, J_{CP} = 6.2 Hz), 32.0 (d, J_{CP} = 9.6 Hz), 27.6;

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) -3.08;

HRMS: Calculated for $C_9H_{15}O_5PNa$ $(M+Na)^+$ 257.0555; found 257.0557 (TOF MS ES^+).

3-((1*R*,6*R*,8*S*)-1-oxido-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-en-8-yl)propyl acetate (5b)



R_f = 0.18 (1:3 Hexane:EtOAc);

FTIR (neat): 3029, 2958, 2925, 1735, 1461, 1298, 1247 cm^{-1};

Optical Rotation: $[\alpha]_D = -59.19$ ($c = 0.74$, $CHCl_3$);

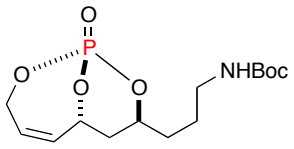
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 6.04 (dddd, J = 11.9, 6.7, 3.0, 2.3 Hz, 1H), 5.60 (ddd, J = 11.8, 3.9, 2.5 Hz, 1H), 5.20 (br.d, J_{PH} = 24.5 Hz, 1H), 5.01 (dddd, J = 11.3, 8.4, 5.7, 2.7 Hz, 1H), 4.63-4.57 (m, 1H), 4.37 (ddd, J = 27.8, 14.8, 6.7 Hz, 1H), 4.09 (ddd, J = 20.1, 17.0, 5.7 Hz, 2H), 2.20 (ddd, J = 14.5, 11.9, 6.2 Hz, 1H), 2.05 (s, 3H), 1.91–1.61 (m, 5H);

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 171.1, 129.7, 127.9, 77.1 (d, J_{CP} = 6.7 Hz), 76.0 (d, J_{CP} = 6.7 Hz), 63.7, 62.9 (d, J_{CP} = 6.7 Hz), 34.8 (d, J_{CP} = 6.1Hz), 32.2 (d, J_{CP} = 9.6 Hz), 23.8, 20.9;

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) -3.23;

HRMS : Calculated for $C_{11}H_{17}O_6PNa$ $(M+Na)^+$ 299.0660; found 299.0659 (TOF MS ES^+).

***tert*-Butyl (3-((1*R*,6*R*,8*S*)-1-oxido-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-en-8-yl)propyl)carbamate (5c)**



R_f = 0.18 (1:3 Hexane:EtOAc);

FTIR (neat): 3350, 3055, 2974, 2929, 1693, 1525, 1288 cm^{-1};

Optical Rotation: $[\alpha]_D = -46.85$ ($c = 0.715$, $CHCl_3$);

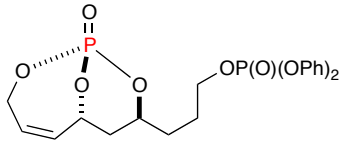
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 6.03 (dddd, J = 11.9, 6.7, 3.0, 2.2 Hz, 1H), 5.59 (ddd, J = 11.8, 3.9, 2.6 Hz, 1H), 5.19 (br.d, J_{PH} = 24.5 Hz, 1H), 5.00 (dddd, J = 11.3, 8.4, 5.7, 2.8 Hz, 1H), 4.63–4.55 (m, 1H), 4.36 (ddd, J = 27.8, 14.8, 6.6 Hz, 1H), 3.18–3.10 (m, 2H), 2.18 (ddd, J = 14.7, 11.9, 6.2 Hz, 1H), 1.81–1.54 (m, 5H), 1.44 (s, 9H);

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 156.0, 129.8, 127.9, 79.2, 77.1 (d, J_{CP} = 6.6 Hz), 76.3 (d, J_{CP} = 6.6 Hz), 62.9 (d, J_{CP} = 6.4 Hz), 39.9, 34.8 (d, J_{CP} = 5.9 Hz), 32.7 (d, J_{CP} = 9.4 Hz), 28.3 (3C), 25.3;

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) -3.17;

HRMS: Calculated for $C_{14}H_{24}NO_6PNa$ $(M+Na)^+$ 356.1239; found 356.1237 (TOF MS ES^+).

3-((1*R*,6*R*,8*S*)-1-oxido-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-en-8-yl)propyl diphenyl phosphate (5d)



R_f = 0.3 (9:1 EtOAc:MeOH);

FTIR (neat): 3066, 3041, 2960, 2925, 1589, 1487, 1296, 956, 773, 690 cm^{-1};

Optical Rotation $[\alpha]_D = -32.90$ (c = 1.17, $CHCl_3$);

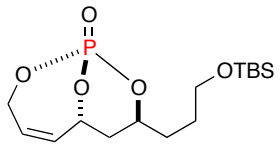
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.35 (t, J = 8.03 Hz, 4H), 7.23-7.18 (m, 6H), 6.00 (dddd, J = 11.9, 6.7, 3.0, 2.2 Hz, 1H), 5.55 (ddd, J = 11.9, 3.9, 2.6 Hz, 1H), 5.17 (dr.d, J_{PH} = 24.5 Hz, 1H), 4.98 (dddd, J = 11.3, 8.4, 5.7, 2.7 Hz, 1H), 4.59–4.53 (m, 1H), 4.39–4.23 (m, 3H), 2.17–2.09 (m, 1H), 2.01–1.90 (m, 1H), 1.86–1.62 (m, 4H);

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 150.4 (d, J_{CP} = 7.1 Hz, 2C), 129.8 (4C), 129.6, 127.9, 125.4 (2C), 120.0 (2C), 119.9 (2C), 77.07 (d, J_{CP} = 6.7 Hz), 75.80 (d, J_{CP} = 6.7 Hz), 68.4 (d, J_{CP}= 6.5 Hz), 62.9 (d, J_{CP} = 6.4 Hz), 34.7 (d, J_{CP} = 5.8 Hz), 31.4 (d, J_{CP} = 9.4 Hz), 25.3 (d, J_{CP} = 6.9 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) -3.24, -11.31;

HRMS: : Calculated for $C_{21}H_{24}O_8P_2Na$ $(M+Na)^+$ 489.0844; found 489.0843 (TOF MS ES^+).

(1*R*,6*R*,8*S*)-8-(3-((*tert*-butyldimethylsilyl)oxy)propyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5e)



R_f = 0.25 (1:3 Hexane:EtOAc);

FTIR (neat): 2952, 2925, 2854, 1299, 1257 cm^{-1};

Optical Rotation: $[\alpha]_D = -29.14$ (c = 0.35, $CHCl_3$);

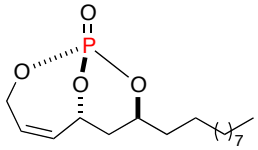
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 6.04 (dddd, J = 11.9, 6.7, 3.1, 2.2 Hz, 1H), 5.60 (ddd, J = 11.8, 3.9, 2.6 Hz, 1H), 5.20 (br.d, J_{PH} = 24.5 Hz, 1H), 5.01 (dddd, J = 11.3, 8.4, 5.7, 2.7 Hz, 1H), 4.66–4.60 (m, 1H), 4.37 (ddd, J = 27.7, 14.8, 6.8 Hz, 1H), 3.63 (ddd, J = 22.3, 10.7, 5.7 Hz, 2H), 2.19 (ddd, J = 14.6, 11.9, 6.3 Hz, 1H), 1.85–1.55 (m, 5H), 0.89 (s, 9H), 0.05 (s, 6H);

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 129.9, 127.9, 77.2 (d, J_{CP} = 6.7 Hz), 76.6 (d, J_{CP} = 6.7 Hz), 62.9 (d, J_{CP} = 6.4 Hz), 62.3, 34.9 (d, J_{CP} = 5.9 HZ), 32.7 (d, J_{CP} = 9.4 Hz), 29.7, 27.6, 25.9 (3C), 18.3, -5.4 (d, J = 2.9 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) -3.06;

HRMS: Calculated for $C_{15}H_{29}O_5PSiNa$ $(M+Na)^+$ 371.1420; found 371.1424 (TOF MS ES+).

(1*R*,6*R*,8*S*)-8-decyl-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5f)



R_f = 0.3 (1:3 Hexane:EtOAc);

M.P: 78–80 ºC;

FTIR (thinfilm): 3026, 2933, 2914, 2846, 1467, 1286 cm^{-1};

Optical Rotation: $[\alpha]_D = -57.02$ (*c* = 0.84, $CHCl_3$);

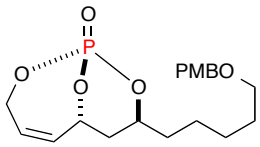
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 6.03 (dddd, *J* = 11.9, 6.7, 3.0, 2.2 Hz, 1H), 5.59 (ddd, *J* = 11.8, 3.9, 2.6 Hz, 1H), 5.18 (br.d, J_{PH} = 24.5 Hz, 1H), 5.00 (dddd, *J* = 11.3, 8.3, 5.6, 2.7 Hz, 1H), 4.59–4.52 (m, 1H), 4.36 (ddd, *J* = 27.7, 14.7, 6.8 Hz, 1H), 2.17 (ddd, *J* = 14.5, 11.9, 6.3 Hz, 1H), 1.78–1.68 (m, 2H), 1.61–1.43 (m, 2H), 1.39-1.22 (m, 15H), 0.88 (t, *J* = 6.8 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 129.9, 127.8, 77.2 (d, J_{CP} = 7.0 Hz), 76.8 (d, J_{CP} = 7.0 Hz), 62.9 (d, J_{CP} = 6.9 Hz), 35.6 (d, J_{CP} = 9.2 Hz), 34.8 (d, J_{CP} = 5.9 Hz), 31.8, 29.6, 29.5, 29.4, 29.3, 29.1, 24.5, 22.6, 14.1;

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) -3.01;

HRMS: Calculated for $C_{16}H_{29}O_4PNa$ $(M+Na)^+$ 339.1701; found 339.1688 (TOF MS ES^+).

(1*R*,6*R*,8*S*)-8-(5-((4-methoxybenzyl)oxy)pentyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5g)



R_f = 0.2 (1:3 Hexane:EtOAc)

FTIR (neat) 2936, 1612, 1512, 1300, 1247, cm^{-1};

Optical Rotation: $[\alpha]_D$ = –50.3 (c = 5.4, CH_2Cl_2);

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.28, (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.03 (dddd, *J* = 11.9, 6.7, 3.0, 2.1 Hz, 1H), 5.59 (ddd, *J* = 11.8, 3.8, 2.5 Hz, 1H), 5.18 (d, J_{PH} = 24.3 Hz, 1H), 4.98–5.05 (m, 1H), 4.55–4.61 (m, 1H), 4.45 (s, 2H), 4.37 (ddd, *J* = 27.6, 14.7, 6.7 Hz, 1H), 3.82 (s, 3H), 3.45 (t, *J* = 6.5 Hz, 2H), 2.18 (ddd, *J* = 14.6, 11.9, 6.3 Hz, 1H), 1.68–1.81 (m, 2H), 1.35–1.80 (m, 7H);

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 158.9, 130.5, 129.7, 129.0 (2C), 127.5, 113.5 (2C), 77.1 (d, J_{CP} = 6.6 Hz), 76.5 (d, J_{CP} = 6.7 Hz), 72.3, 69.6, 62.7 (d, J_{CP} = 6.4 Hz), 55.0, 35.4 (d, J_{CP} = 9.4 Hz), 34.6 (d, J_{CP} = 5.9 Hz), 29.3, 25.6, 24.2;

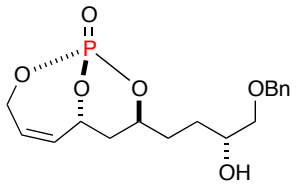
^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) -2.96;

HRMS calculated for $C_{19}H_{27}O_6P$ $(M+Na)^+$ 405.1443; found 405.1427 (TOF MS ES+)..

General procedure for RCM/CM/hydrogenation with Type II olefins (Table 2)

To a stirring solution of triene (*R*,*R*)-**1** (50 mg, 0.217 mmol) in freshly distilled, freeze-degas-thawed CH_2Cl_2 (31 mL, 0.007 M) was added Hoveyda-Grubbs 2nd Gen. catalyst (8 mg, 0.013 mmol) and the reaction was refluxed for 45 min. After completion of RCM, type II olefin cross partner [2–4 equiv with respect to triene (*R*,*R*)-**1**] was dissolved in freshly distilled, freeze-degas-thawed 1,2-dichloroethane (4 mL, 0.05 M) and added to the crude reaction mixture, followed by addition of Hoveyda-Grubbs 2nd Gen. catalyst (5 mg, 0.008 mmol). The reaction was continued at 70 ºC with simultaneous evaporation of the excess CH_2Cl_2 from the previous reaction to reach optimal concentration for CM reaction (4 mL, 0.05 M). The reaction was continued (at 70 ºC) for an additional 4–6 h upon which the reaction showed the CM product formation along with trace amount of unreacted RCM starting material (*R*,*R*,R_P)-**2**. The reaction was stopped and to the reaction mixture was added *o*-NBSH (538 mg, 2.17 mmol) and Et_3N (1.07 mL, at 2 mL/g of *o*-NBSH). The reaction was stirred at RT overnight, after which excess *o*-NBSH (269 mg, 1.08 mmol) and Et_3N (0.538 mL, at 2 mL/g of *o*-NBSH) were added and the crude mixture was stirred for an additional 8 h. The reaction mixture was diluted with EtOAc (10 mL) and extracted with sat. $NaHCO_3$ (10 mL). The aqueous layer was washed with EtOAc (2x5 mL) and the combined organic layers were dried (Na_2SO_4), concentrated under reduced pressure and purified using flash column chromatography.

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



R_f = 0.4 (9:1 EtOAc:MeOH);

FTIR (neat): 3415, 3029, 2920, 2858, 1452, 1290, 773, 740, 700 cm^{-1};

Optical Rotation: $[\alpha]_D = -44.34$ (c = 0.654, CH_2Cl_2);

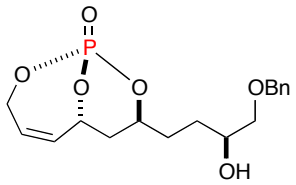
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.40–7.29 (m, 5H), 6.02 (dddd, J = 11.9, 6.7, 3.0, 2.3 Hz, 1H), 5.58 (ddd, J = 11.9, 3.9, 3.0 Hz, 1H), 5.18 (br.d, J_{PH} = 24.5 Hz, 1H), 5.00 (dddd, J = 11.3, 8.3., 5.7, 2.7 Hz, 1H), 4.60-4.56 (m, 1H), 4.56 (s, 2H), 4.35 (ddd, J = 27.8, 14.8, 6.8 Hz, 1 H), 3.81–3.76 (m, 1H), 3.52-3.31 (m, 2H), 2.18 (ddd, J = 14.7, 11.9, 6.2 Hz, 1H), 1.92–1.82 (m, 1H), 1.82–1.69 (m, 4H), 1.50–1.41 (m, 1H);

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 137.7, 129.8, 128.4 (2C), 127.8 (d, J = 2.6 Hz, 2C), 127.7 (2C), 77.1 (t, J_{CP} = 6.4 Hz 2C), 74.4, 73.3, 70.2, 62.9 (d, J_{CP} = 6.4 Hz), 35.0 (d, J_{CP} = 6.1 Hz), 32.2 (d, J_{CP} = 8.8 Hz), 28.5;

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) -3.09;

HRMS: Calculated for $C_{17}H_{23}O_6PNa$ $(M+Na)^+$ 377.1130; found 377.1128 (TOF MS ES^+).

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



R_f = 0.4 (9:1 EtOAc:MeOH) ;

FTIR (neat): 3415, 3029, 2923, 2856, 1292, 775, 742, 700 cm^{-1};

Optical Rotation: $[\alpha]_D = -32.43$ ($c = 0.595$, $CHCl_3$);

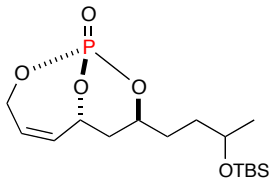
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.40-7.30 (m, 5H), 6.02 (dddd, J = 11.8, 6.6, 3.0, 2.3 Hz, 1H), 5.58 (ddd, J = 11.8, 3.8, 2.6 Hz, 1H), 5.18 (br.d, J_{PH} = 24.5 Hz, 1H), 5.00 (dddd, J = 11.3, 8.4, 5.7, 2.8 Hz, 1H), 4.69–4.61 (m, 1H), 4.56 (s, 2H), 3.85 (m, 1H), 3.51–3.31(m, 2H), 2.39 (br.s, 1H), 2.19 (ddd, J = 14.6, 11.9, 6.2 Hz, 1H), 1.89 (ddd, J = 21.7, 14.3, 7.6 Hz, 2H), 1.80–1.69 (m, 2H), 1.61 (dd, J = 13.5, 7.2 Hz, 2H);

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 137.7, 129.8, 128.4 (2C), 127.9 (2C), 127.8 (2C), 77.2 (d, J_{CP} = 2.8 Hz), 75.9 (d, J_{CP} = 6.9 Hz), 74.4, 73.4, 69.1, 62.9 (d, J_{CP} = 6.4 Hz), 34.7 (d, J_{CP} = 6.1Hz), 31.0 (d, J_{CP} = 9.4 Hz), 27.3;

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) -3.00;

HRMS: Calculated for $C_{17}H_{23}O_6PNa$ $(M+Na)^+$ 377.1130; found 377.1124 (TOF MS ES^+).

(1*R*,6*R*,8*S*)-8-(3-((*tert*-butyldimethylsilyl)oxy)butyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5j): (pair of diastereomers based on ^{13}C NMR)



R_f = 0.5 (1:3 Hexane:EtOAc);

FTIR (neat): 2960, 2927, 2889, 2854, 1292, 1068 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 6.03 (dddd, *J* = 11.8, 6.6, 3.1, 2.1 Hz, 1H), 5.59 (ddd, *J* = 11.8, 3.8, 2.6 Hz, 1H), 5.19 (br.d, J_{PH} = 24.5 Hz, 1H), 5.00 (ddq, *J* = 13.0, 5.6, 2.7, 2.6, 2.6 Hz, 1H), 4.63–4.52 (m, 1H), 4.37 (ddd, *J* = 27.8, 14.8, 6.8 Hz, 1H), 3.81 (m, 1H), 2.18 (ddt, *J* = 14.5, 12.0, 6.1, 6.1 Hz, 1H), 1.86–1.38 (m, 5H), 2.83 (dd, *J* = 6.1, 1.8 Hz, 3H), 0.87 (d, *J* = 2.5 Hz, 9H), 0.04 (dd, *J* = 6.4, 3.4 Hz, 6H);

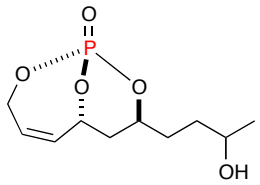
^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 129.9, 127.9, 77.2 (d, J_{CP} = 6.5 Hz), 76.5 (d, J_{CP} = 6.7 Hz), 68.2, 62.9 (d, J_{CP} = 6.7 Hz), 34.9 (d, J_{CP} = 5.9 Hz), 34.6, 32.3 (d, J_{CP} = 9.4 Hz), 25.8 (3C), 23.9, 18.0, -4.3 (d, *J* = 6.9 Hz, 2C);

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 129.9, 127.9, 77.1 (d, J_{CP} = 6.5 Hz), 76.5 (d, J_{CP} = 6.7 Hz), 67.5, 62.9 (d, J_{CP} = 6.7 Hz), 34.8 (d, J_{CP} = 5.8 Hz), 33.8, 31.3 (d, J_{CP} = 9.0 Hz), 25.8 (3C), 23.7, 18.0, -4.8 (d, *J* = 11.0 Hz, 2C);

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm): -3.10;

HRMS: Calculated for $C_{16}H_{31}O_5PSiNa$ $(M+Na)^+$ 385.1576; found 385.1570 (TOF MS ES+).

(1*R*,6*R*,8*S*)-8-(3-hydroxybutyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5k): (pair of diastereomers based on ^{13}C NMR)



R_f = 0.4 (9:1 EtOAc:MeOH);

FTIR (neat): 3421, 2966, 2929, 2854, 1288, 1068 cm^{-1};

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 6.06-6.01 (m, 1H), 5.59 (ddd, J = 11.8, 3.6, 2.8 Hz, 1H), 5.19 (br.d, J_{PH} = 24.5 Hz, 1H), 5.00 (dddd, J = 11.3, 8.4, 5.7, 2.7 Hz, 1H), 4.67–4.56 (m, 1H), 4.37 (ddd, J = 27.7, 14.8, 6.8 Hz, 1H), 3.88–3.78 (m, 1H), 2.24–2.16 (m, 2H), 1.90–1.66 (m, 4H), 1.64–1.58 (m, 1H), 1.21 (d, J = 6.2 Hz, 3H);

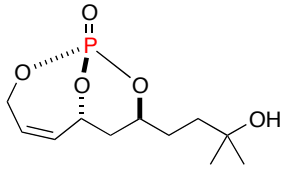
^{13}C NMR (126 MHz, $CDCl_3$) δ 129.9, 127.9, 77.1 (d, J_{CP} = 5.6 Hz), 76.3 (d, J_{CP} = 6.9 Hz), 67.7, 62.9 (d, J_{CP} = 7.3 Hz), 35.0 (d, J_{CP} = 5.62 Hz), 34.3, 32.2 (d, J_{CP} = 9.5 Hz), 23.9;

^{13}C NMR (126 MHz, $CDCl_3$) δ 129.9, 127.9, 77.1 (d, J_{CP} = 5.6 Hz), 76.3 (d, J_{CP} = 6.9 Hz), 67.1, 62.9 (d, J_{CP} = 7.3 Hz), 34.8 (d, J_{CP} = 5.6 Hz), 33.5, 31.4 (d, J_{CP} = 9.5 Hz), 23.7;

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) -3.02;

HRMS: Calculated for $C_{10}H_{17}O_5PNa$ $(M+Na)^+$ 271.0711; found 270.0710 (TOF MS ES+).

(1*R*,6*R*,8*S*)-8-(3-hydroxy-3-methylbutyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5l)



R_f = 0.25 (9:1 EtOAc:MeOH);

FTIR (neat): 3421, 2966, 2929, 2854, 1288, 1068 cm^{-1};

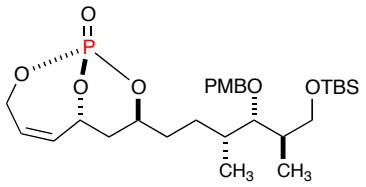
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 6.02 (dddd, *J* = 11.9, 6.6, 3.0, 2.2 Hz, 1H), 5.58 (ddd, *J* = 11.8, 3.8, 2.6 Hz, 1H), 5.19 (br.d, J_{PH} = 24.5 Hz, 1H), 4.98 (dddd, *J* = 11.3, 8.4, 5.7, 2.8 Hz, 1H), 4.60–4.54 (m, 1H), 4.35 (ddd, *J* = 27.8, 14.8, 6.8 Hz, 1H), 2.19 (ddd, *J* = 14.6, 11.9, 6.2 Hz, 1H), 1.86–1.78 (m, 2H), 1.77–1.75 (m, 1H), 1.74–1.70 (m, 2H), 1.21 (d, *J* = 7.5, 6H);

^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 141.5, 129.8, 127.8, 77.2 (d, J_{CP} = 6.7 Hz), 70.3, 62.9 (d, J_{CP} = 7.0 Hz), 38.3, 34.8 (d, J_{CP} = 5.9 Hz), 30.4 (d, J_{CP} = 9.6), 29.6, 28.9;

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm): -3.05;

HRMS: Calculated for $C_{11}H_{19}O_5PNa$ $(M+Na)^+$ 285.0868; found 285.0864 (TOF MS ES+).

(1*R*,6*R*,8*S*)-8-((3*R*,4*S*,5*R*)-6-((*tert*-butyldimethylsilyl)oxy)-4-((4-methoxybenzyl)oxy)-3,5-dimethylhexyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5m)



R_f = 0.3 (1:3 Hexane:EtOAc);

FTIR (neat) 2954, 2929, 2883, 1514, 1461, 1249 1072 cm^{-1};

Optical Rotation: $[\alpha]_D$ = 20.00 (*c* = 0.46, CH_2Cl_2);

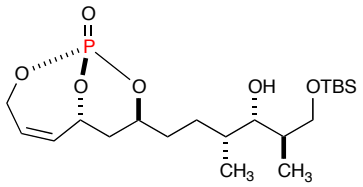
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.27 (d, *J* = 7.6 Hz, 2 H), 6.88 (d, *J* = 8.5 Hz, 2 H), 6.04 (dddd, *J* = 11.8, 6.5, 2.8, 2.6 Hz, 1 H), 5.59 (ddd, *J* = 11.8, 4.0, 2.5 Hz, 1 H), 5.11–5.21 (m, 1 H), 5.01 (dddd, *J* = 11.8, 8.6, 5.2, 2.8 Hz, 1 H), 4.57 (d, *J* = 11.4 Hz, 1 H), 4.44–4.51 (m, 1 H), 4.46 (d, *J* = 11.0 Hz, 1 H), 4.37 (ddd, J_{PH} = 27.7, 14.8, 6.6 Hz, 1 H), 3.81 (s, 3 H), 3.74 (dd, *J* = 9.8, 5.0 Hz, 1 H), 3.63 (dd, *J* = 9.8, 3.5 Hz, 1 H), 3.26 (dd, *J* = 8.8, 2.5 Hz, 1 H), 2.09 (ddd, *J* = 14.5, 12.0, 6.3 Hz, 1 H), 1.71–1.86 (m, 2 H), 1.55–1.70 (m, 3 H), 1.34–1.54 (m, 2 H), 0.92 (s, 9 H), 0.90 (d, *J* = 4.1 Hz, 3 H), 0.88 (d, *J* = 6.6 Hz, 3 H), 0.06 (s, 3 H), 0.06 (s, 3 H);

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 158.9, 131.5, 129.9, 129.4, 129.1(2C), 127.9, 113.7 (2C), 83.0, 77.2, 76.8, 74.1, 64.9, 62.9, 55.3, 38.5, 34.9, 34.6, 33.8, 25.9 (3C), 18.3, 14.7, 13.3, -5.3, -5.4;

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) -3.12;

HRMS: Calculate for $C_{28}H_{51}NO_7PSi$ $(M+NH_4)^+$ 572.3172; found 572.3163 (TOF MS ES+).

(1*R*,6*R*,8*S*)-8-((3*R*,4*S*,5*R*)-6-((*tert*-butyldimethylsilyl)oxy)-4-hydroxy-3,5-dimethylhexyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5n)



R_f = 0.25 (1:3 Hexane:EtOAc);

FTIR (neat): 3450, 2956, 2929, 1296, 1070, 973 cm^{-1};

Optical Rotation: $[\alpha]_D = -61.70$ (c = 0.235, $CHCl_3$);

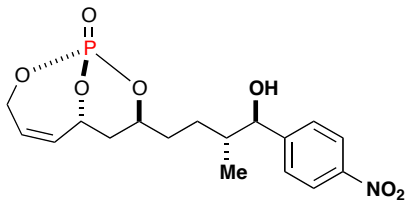
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 6.02 (dddd, J = 11.9, 6.7, 3.1, 2.2 Hz, 1H), 5.58 (ddd, J = 11.8, 3.9, 2.5 Hz, 1H), 5.19 (d, J_{PH} = 24.4 Hz, 1H), 5.00 (dddd, J = 11.3, 8.4, 5.7, 2.8 Hz, 1H), 4.57 (ddd, J = 12.4, 6.5, 5.6 Hz, 1H), 4.36 (ddd, J = 27.7, 14.9, 6.7 Hz, 1H), 4.04 (dd, J = 2.0. 0.8 Hz, 1H), 3.77 (dd, J = 9.9, 3.9 Hz, 1H), 3.58 (t, J = 9.3 Hz, 1H), 3.43 (dt, J = 8.7, 2.3 Hz, 1H), 2.17 (ddd, J = 14.5, 11.9, 6.2, 1H), 1.88–1.58 (m, 4H), 1.55 (dt, J = 18.6, 7.4 Hz, 1H), 1.41–1.25 (m, 2H), 0.91 (s, 9H), 0.89 (d, J = 6.7 Hz, 3H), 0.75 (d, J = 6.9 Hz, 3H), 0.09 (s, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 129.9, 127.8, 79.8, 77.2 (2C), 69.7, 62.9 (d, J_{CP} = 6.0 Hz), 37.1, 35.2, 34.7 (d, J_{CP}= 5.8 Hz), 33.8 (d, J_{CP} = 9.4 Hz), 29.2, 25.8 (3C), 18.2, 13.0, 11.9, -5.62 (2C);

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) -3.13;

HRMS: Calculated for $C_{20}H_{39}O_6PSiNa$ $(M+Na)^+$ 457.2151; found 457.2148 (TOF MS ES+).

(1*R*,6*R*,8*S*)-8-((3*R*,4*R*)-4-hydroxy-3-methyl-4-(4-nitrophenyl)butyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxiden (5o)



R_f = 0.18 (1:3Hexane:EtOAc)

FTIR (neat): 3415, 2962, 2929, 1517, 1346, 1284, 973, 775, 754 cm^{-1};

Optical Rotation: $[\alpha]_D = -30.00$ ($c = 0.25$, $CHCl_3$);

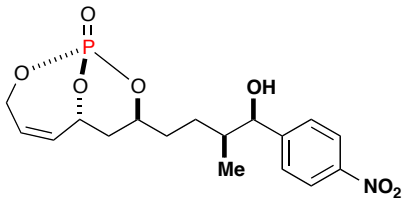
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.23 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 6.04 (dddd, J = 11.9, 6.7, 3.1, 2.2 Hz, 1H), 5.59 (ddd, J = 11.8, 3.9, 2.5 Hz, 1H), 5.19 (br.d, J_{PH} = 24.5 Hz,1H), 4.99 (dddd, J = 11.3, 8.4, 5.7, 2.8 Hz, 1H), 4.62 (d, J = 4.9 Hz, 1H), 4.56–4.50 (m, 1H), 4.35 (ddd, J = 27.7, 14.7, 6.8 Hz, 1H), 3.37 (s, 1H), 2.26 (d, J = 2.4 Hz, 1H), 2.19 (ddd, J = 14.6, 12.0, 6.2 Hz, 1H), 1.92–1.77 (m, 2H), 1.71 (m, J = 6.4, 4.5, 2.8 Hz, 2H), 1.27–1.17 (m, 1H), 0.85 (d, J = 6.8 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 150.6, 147.3, 129.8, 127.9, 127.4 (2C), 123.5 (2C), 77.7, 77.2 (d, J_{CP} = 5.2 Hz), 77.1 (d, J_{CP} = 2.3 Hz), 63.0 (d, J_{CP} = 6.4 Hz), 39.9, 34.8 (d, J_{CP} = 5.9 Hz), 33.1 (d, J_{CP} = 9.4 Hz), 26.9, 15.7;

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) -3.17;

HRMS: Calculated for $C_{17}H_{22}NO_7PNa$ $(M+Na)^+$ 406.1032; found 406.1040 (TOF MS ES+).

(1*R*,6*R*,8*S*)-8-((3*S*,4*R*)-4-hydroxy-3-methyl-4-(4-nitrophenyl)butyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5p)



R_f = 0.18 (1:3 Hexane:EtOAc);

FTIR (neat): 3402, 2960, 2929, 1517, 1346, 1286, 977, 750 cm^{-1};

Optical Rotation: $[\alpha]_D = -49.14$ ($c = 0.35$, $CHCl_3$);

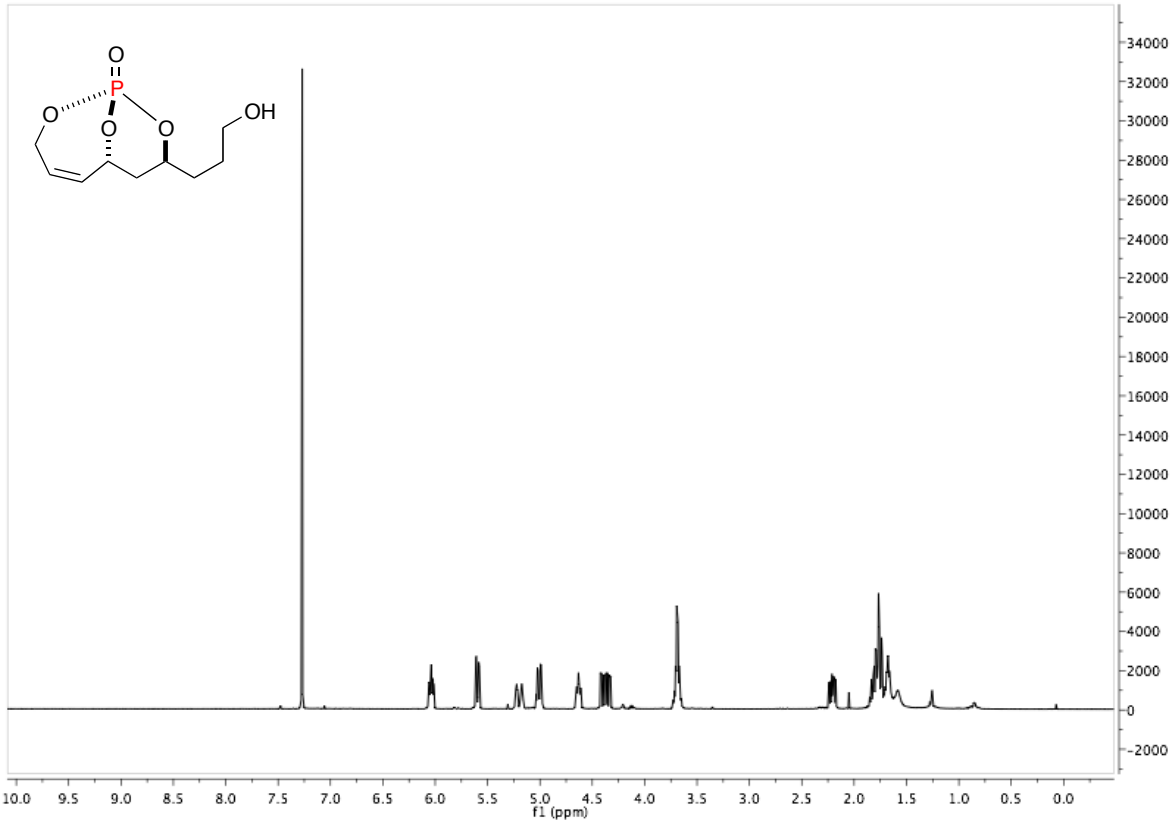
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.21 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 6.03 (dddd, J = 11.9, 6.6, 3.1, 2.1 Hz, 1H), 5.58 (ddd, J = 11.9, 3.9, 2.6 Hz, 1H), 5.19 (br.d, J_{PH} = 24.5 Hz, 1H), 4.99 (ddt, J = 14.7, 8.3, 2.7 Hz, 1H), 4.75 (d, J = 4.5 Hz, 1H), 4.57–4.50 (m, 1H), 4.36 (ddd, J = 27.8, 14.8, 6.7 Hz, 1H), 2.33 (s, 1H), 2.20 (ddd, J = 14.6, 11.8, 6.5 Hz, 1H), 1.90–1.78 (m, 2H), 1.71 (ddd, J = 9.8, 3.3, 1.6 Hz, 1H), 1.67–1.55 (m, 1H), 1.56–1.49 (m, 1H), 1.43 (dddd, J = 20.8, 16.9, 10.4, 5.5 Hz, 1H), 0.85 (d, J = 6.8 Hz, 3H);

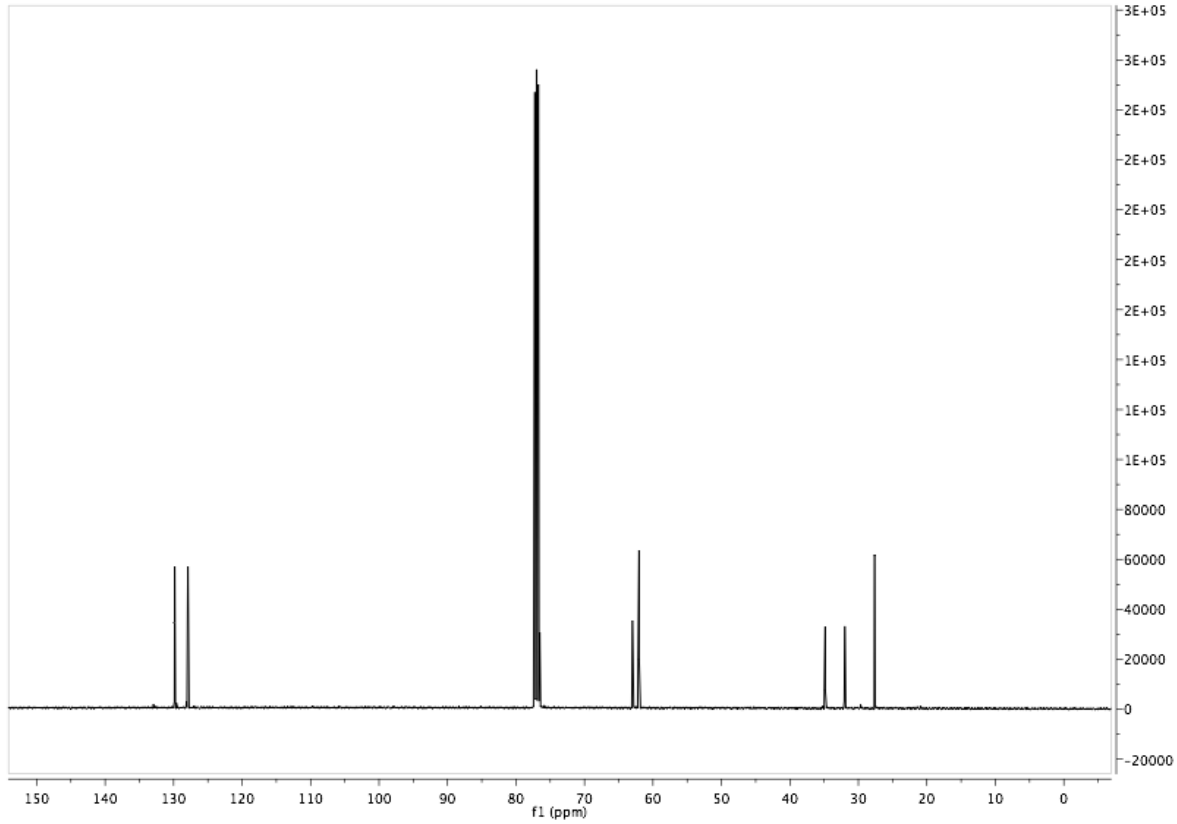
^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 151.10, 147.11, 129.77, 127.96, 127.02 (2C), 123.43 (2C), 77.2 (d, J_{CP} = 7.1 Hz), 76.67, 76.25, 63.0 (d, J_{CP} = 6.3 Hz), 39.87, 34.8 (d, J_{CP} = 5.9 Hz), 33.3 (d, J_{CP} = 9.3 Hz), 28.18, 13.49;

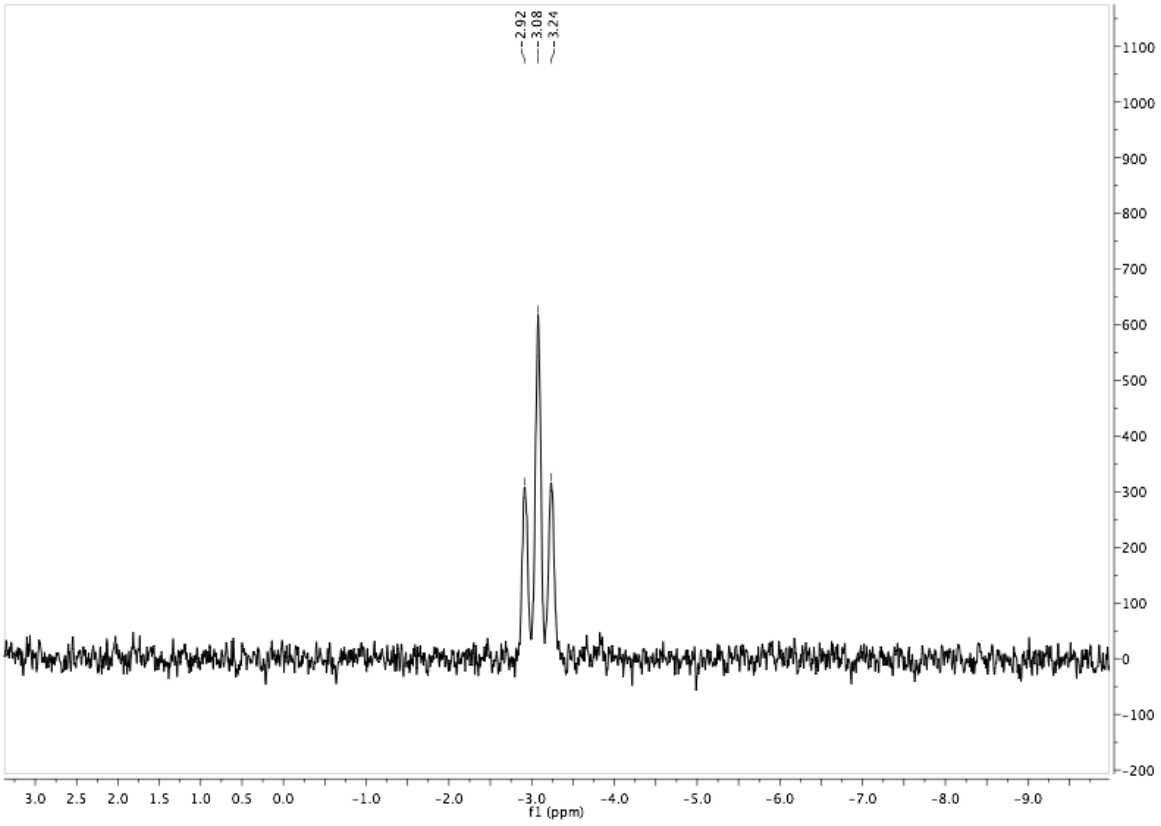
^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) -3.15

HRMS: Calculated for $C_{17}H_{22}NO_7PNa$ $(M+Na)^+$ 406.1032; found 406.1040 (TOF MS ES+).

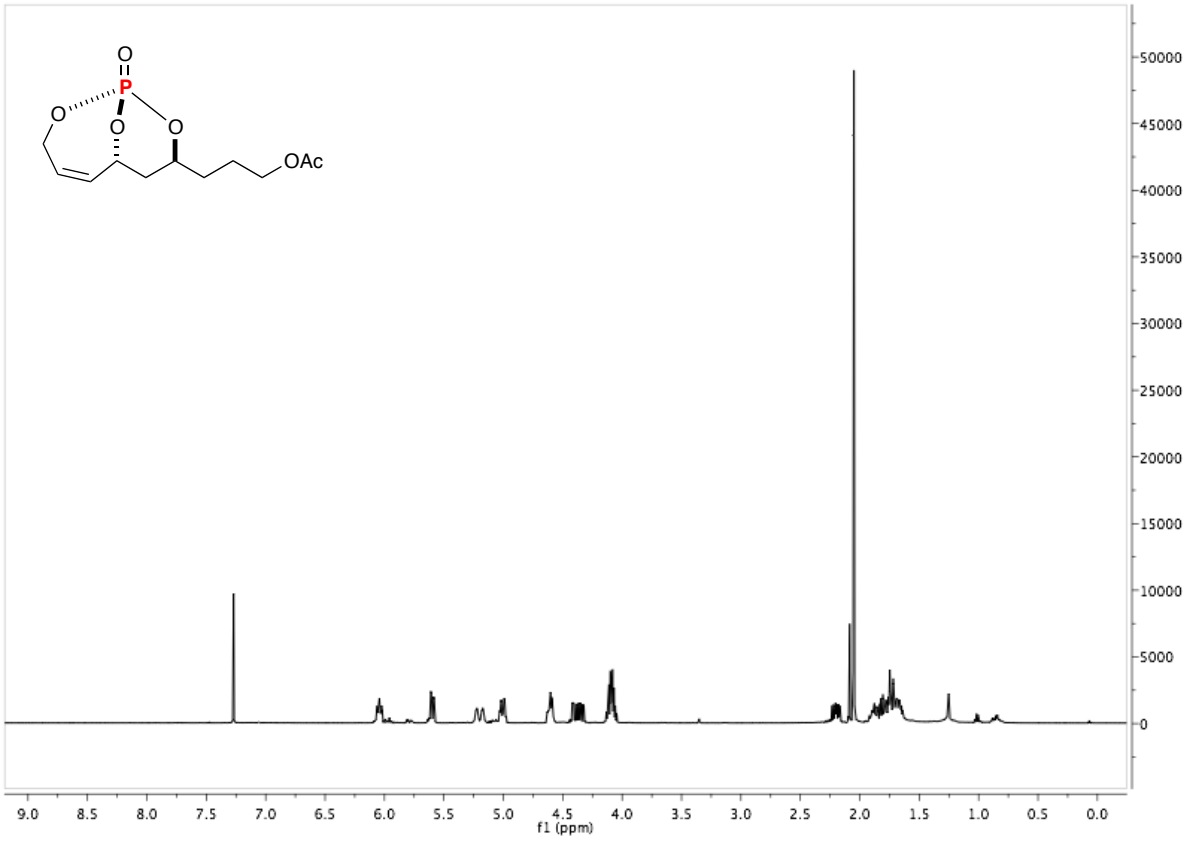
(1*R*,6*R*,8*S*)-8-(3-hydroxypropyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5a)

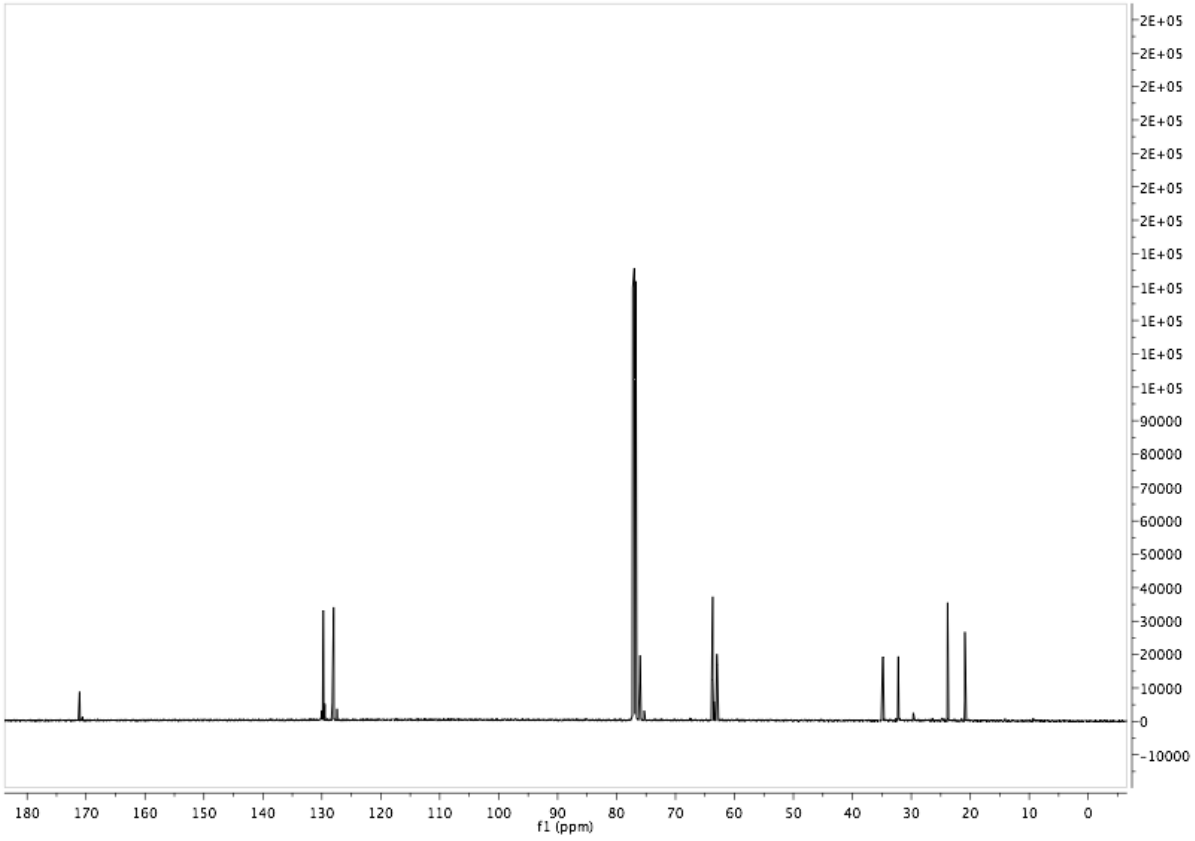


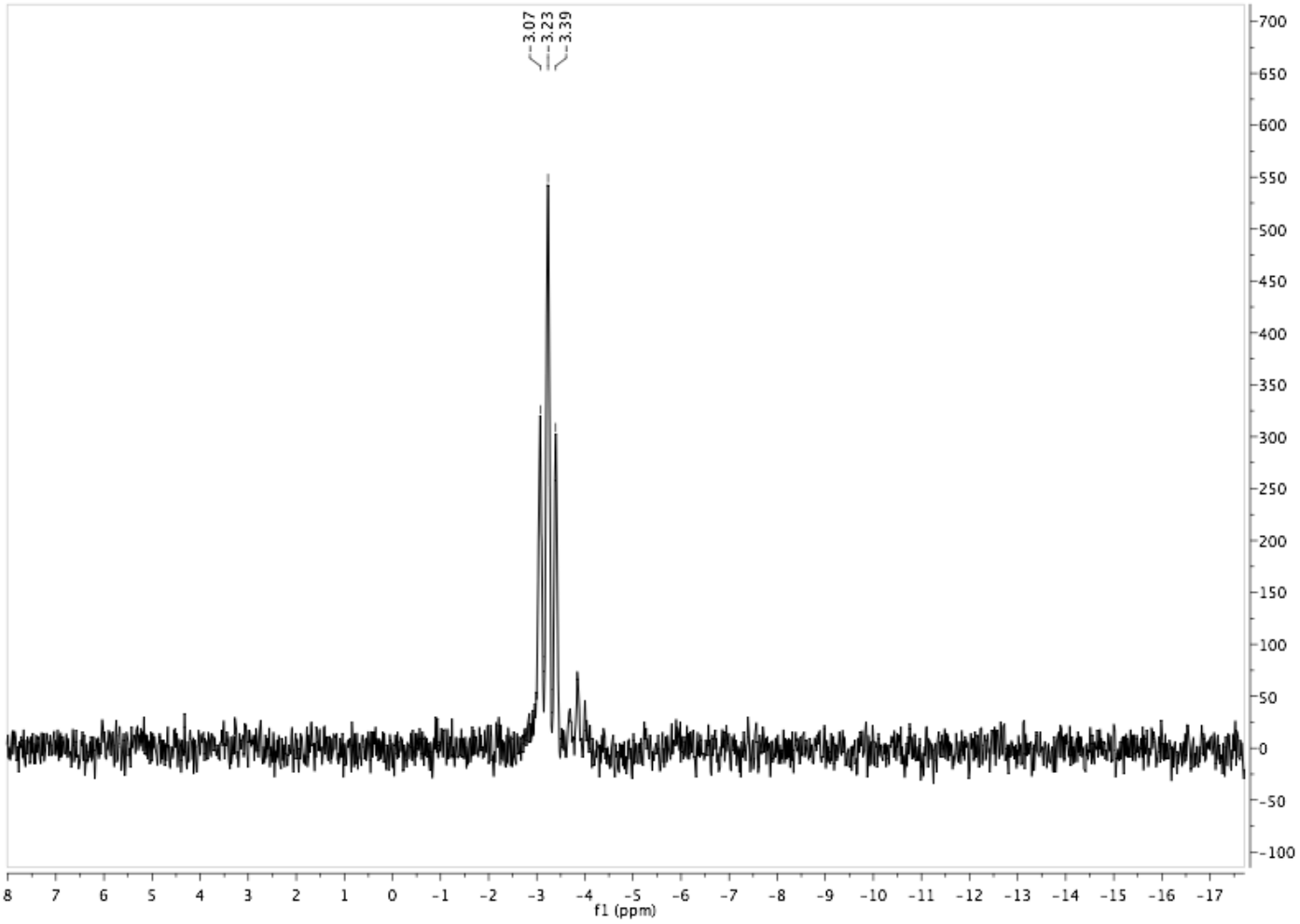



2.92
3.08
3.24
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
f1 (ppm)

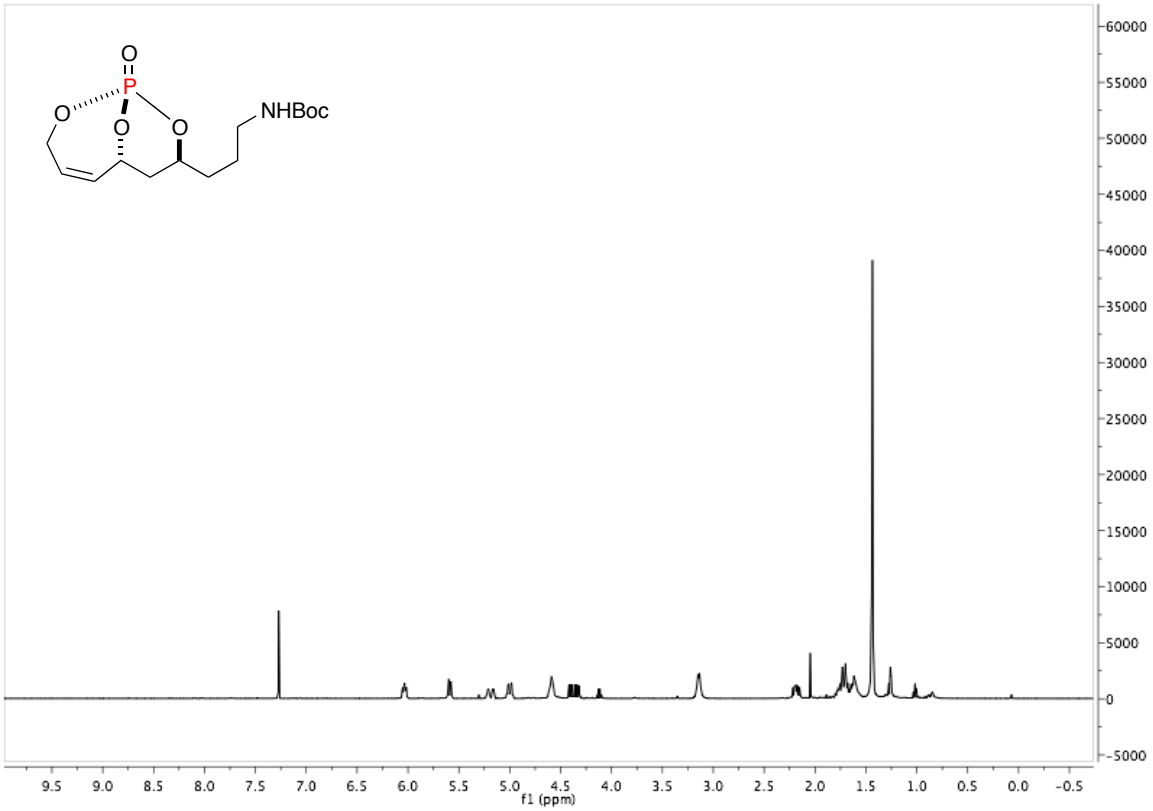
3-((1*R*,6*R*,8*S*)-1-oxido-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-en-8-yl)propyl acetate (5b)

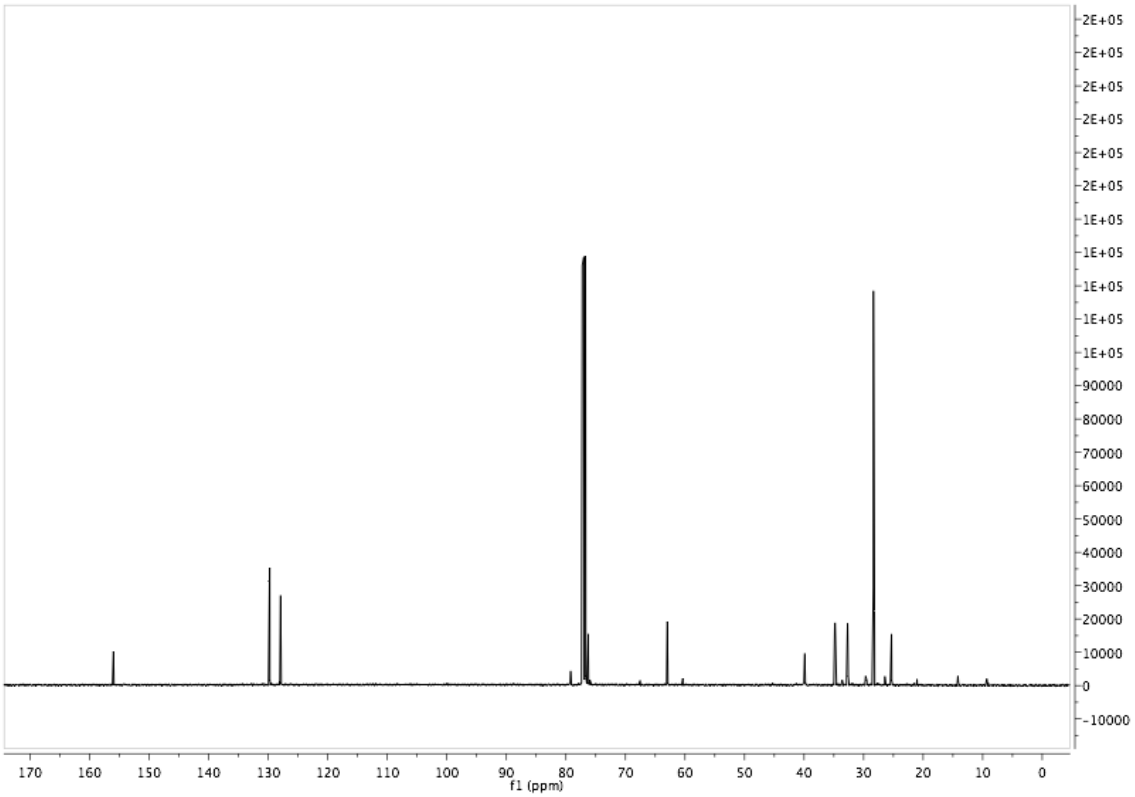


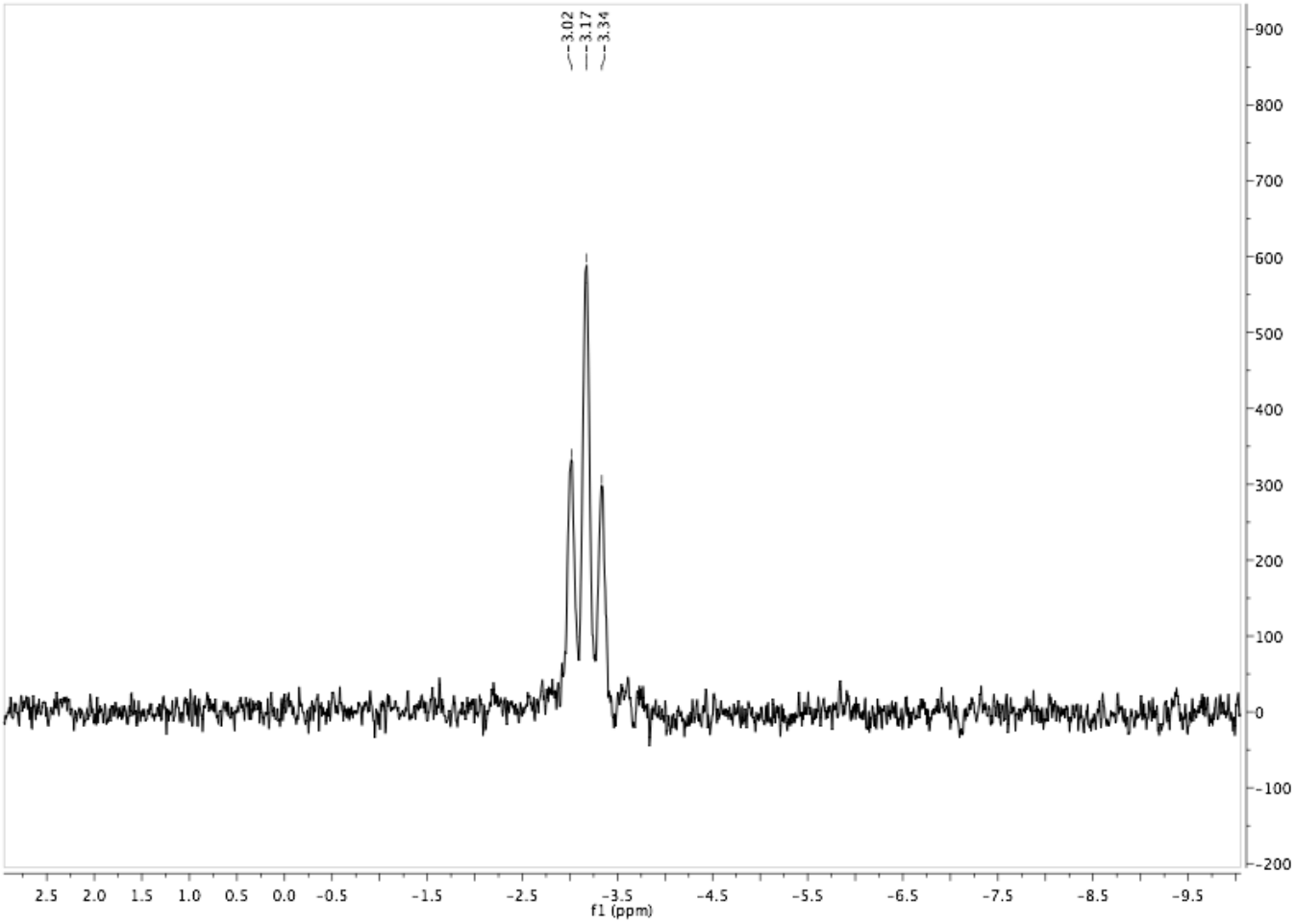



3.07
3.23
3.39
f1 (ppm)

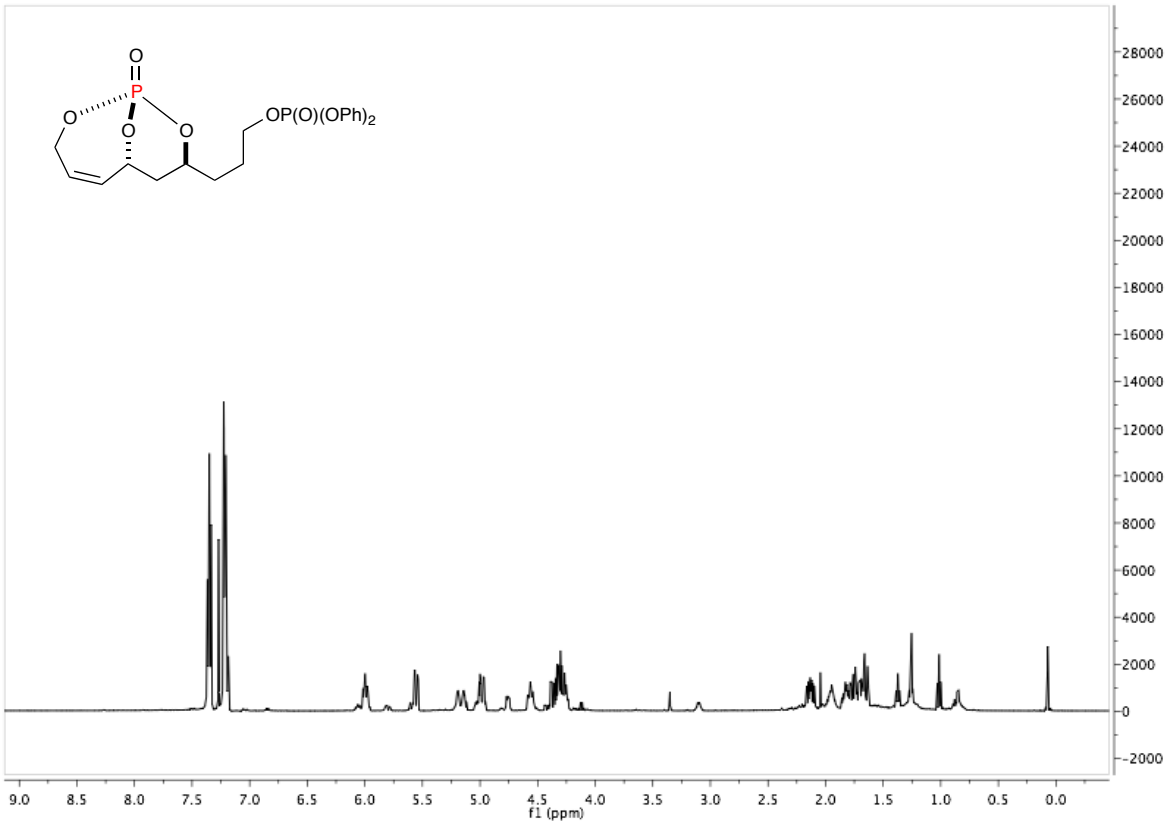
***tert*-Butyl (3-((1*R*,6*R*,8*S*)-1-oxido-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-en-8-yl)propyl)carbamate (5c)**

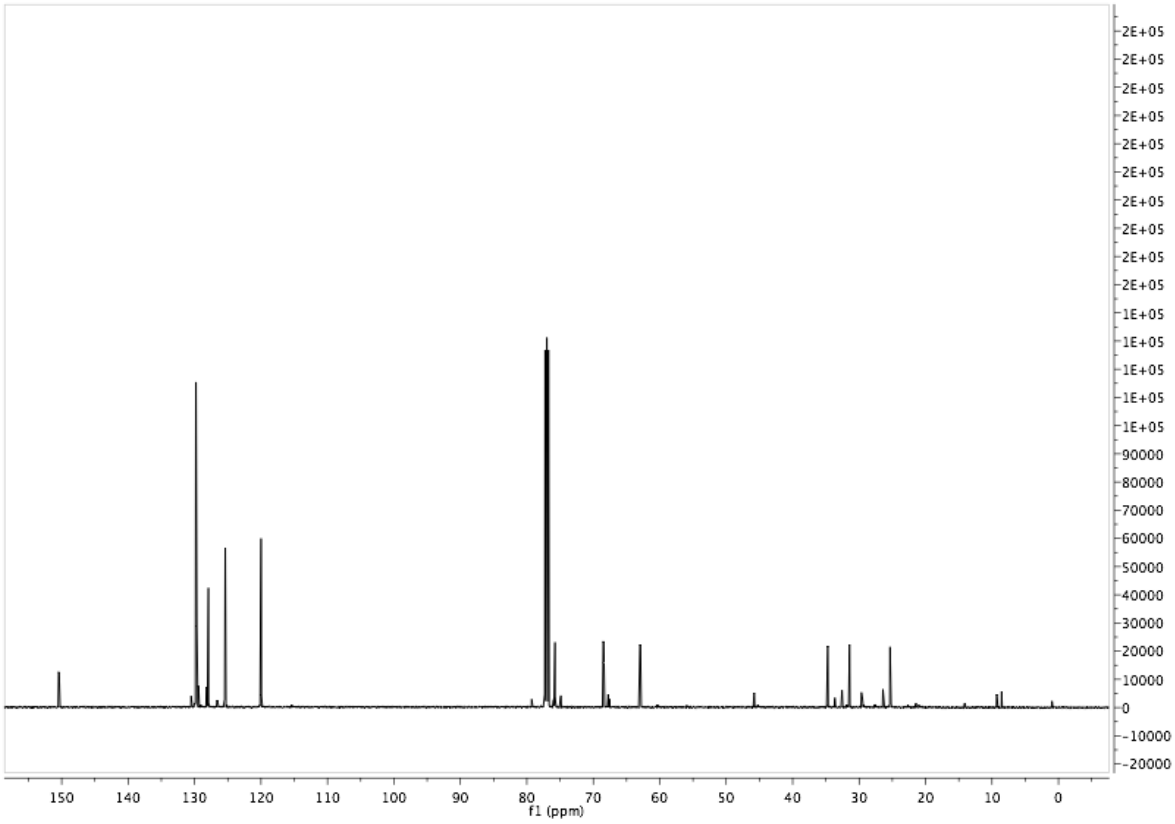


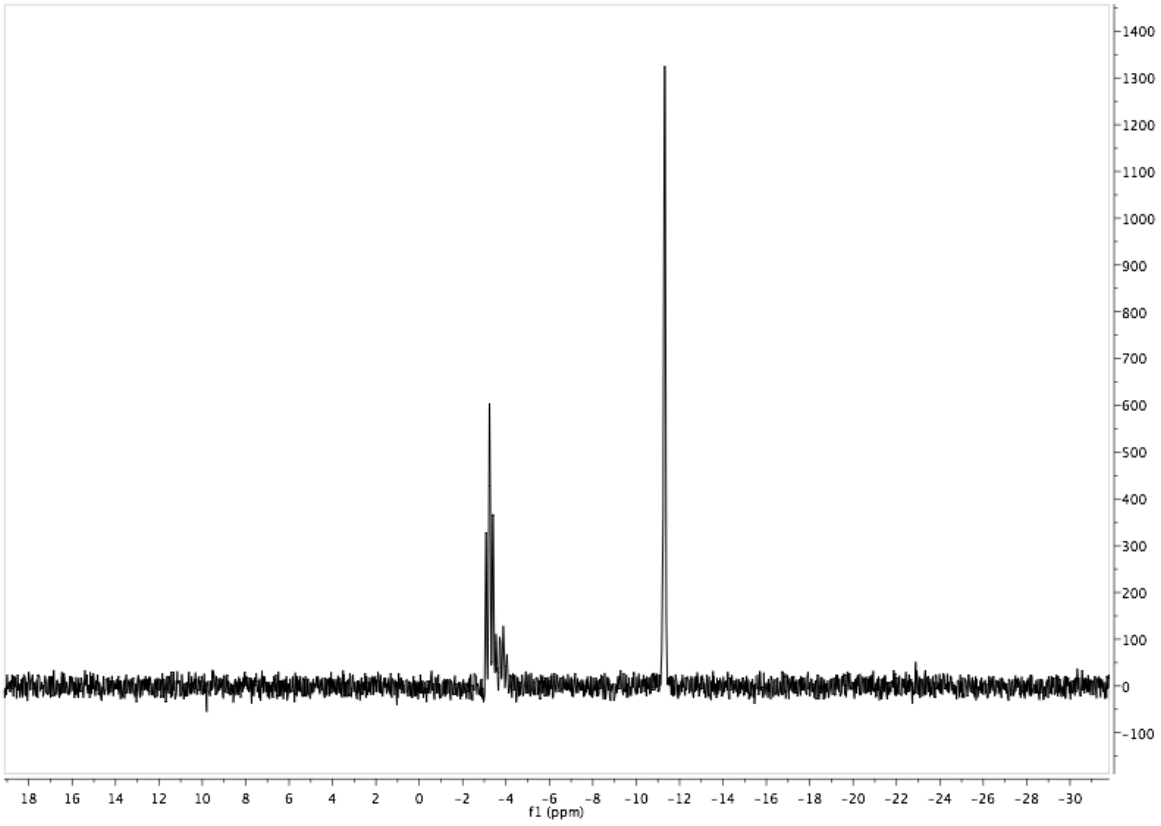



3.02
3.17
3.34
900
800
700
600
500
400
300
200
100
0
-100
-200
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.5
-2.5
-3.5
-4.5
-5.5
-6.5
-7.5
-8.5
-9.5
f1 (ppm)

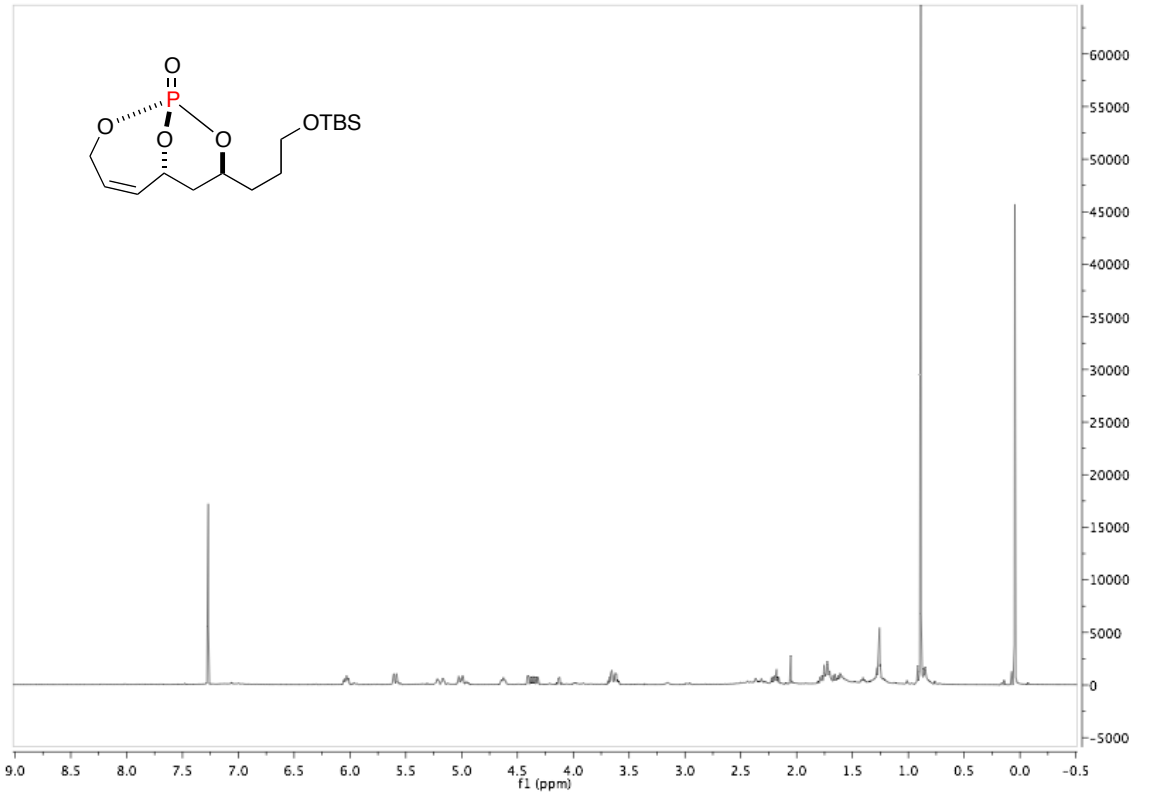
3-((1*R*,6*R*,8*S*)-1-oxido-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-en-8-yl)propyl diphenyl phosphate (5d)

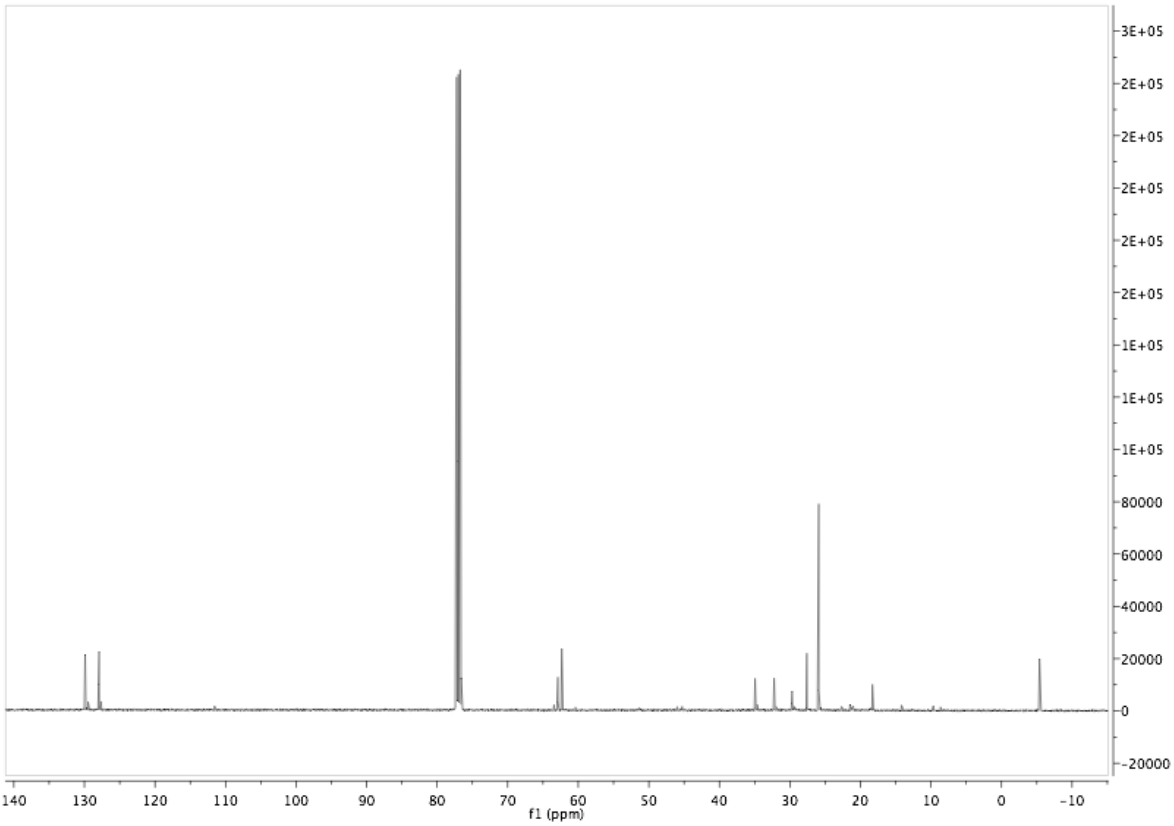


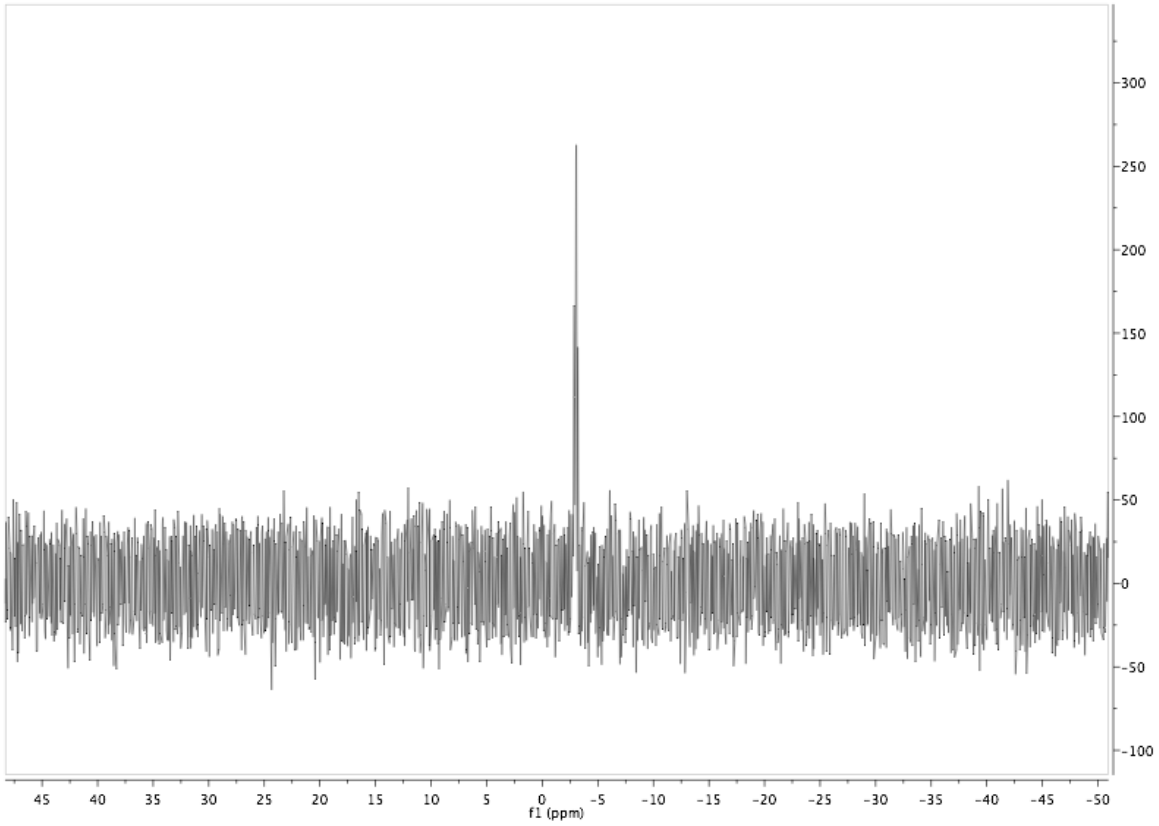



1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8 -10 -12 -14 -16 -18 -20 -22 -24 -26 -28 -30
f1 (ppm)

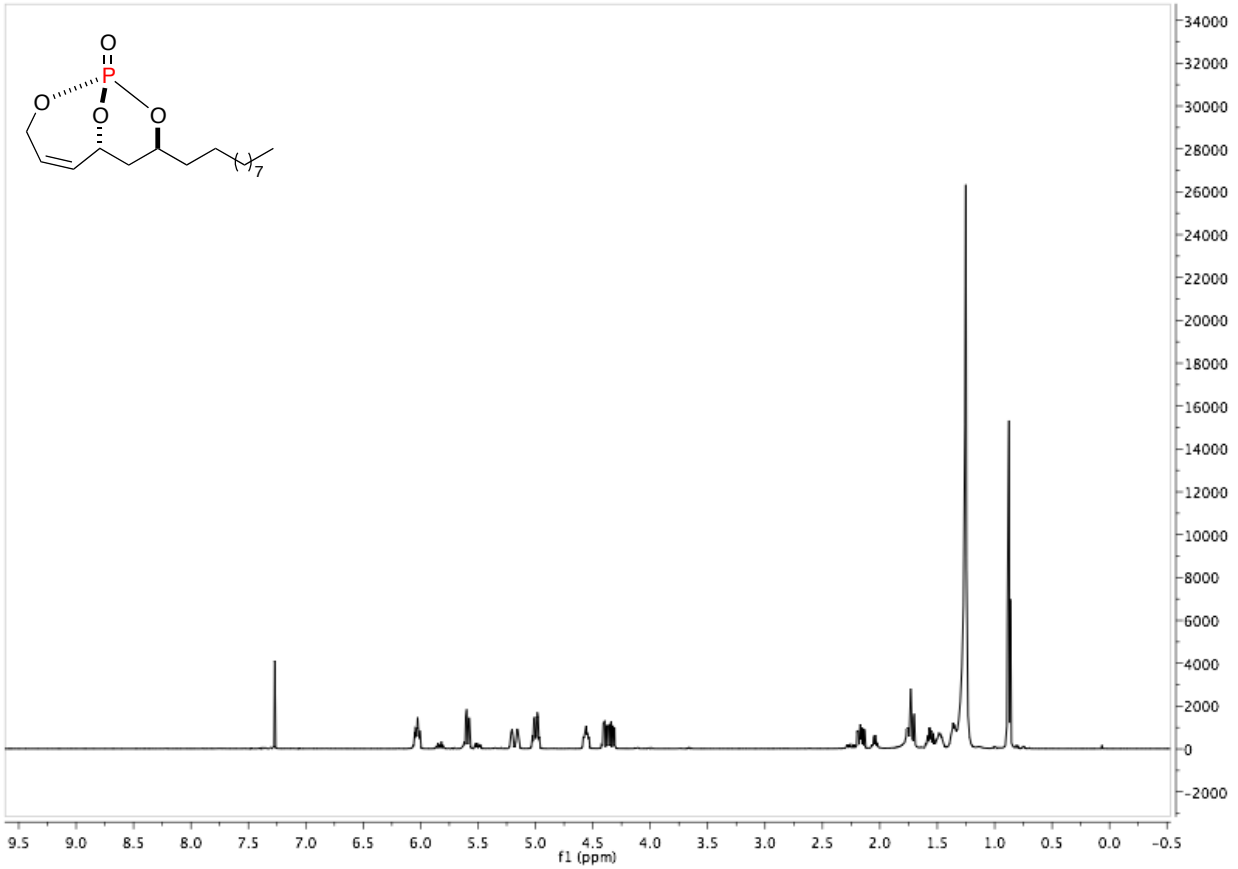
(1*R*,6*R*,8*S*)-8-(3-((*tert*-butyldimethylsilyl)oxy)propyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5e)

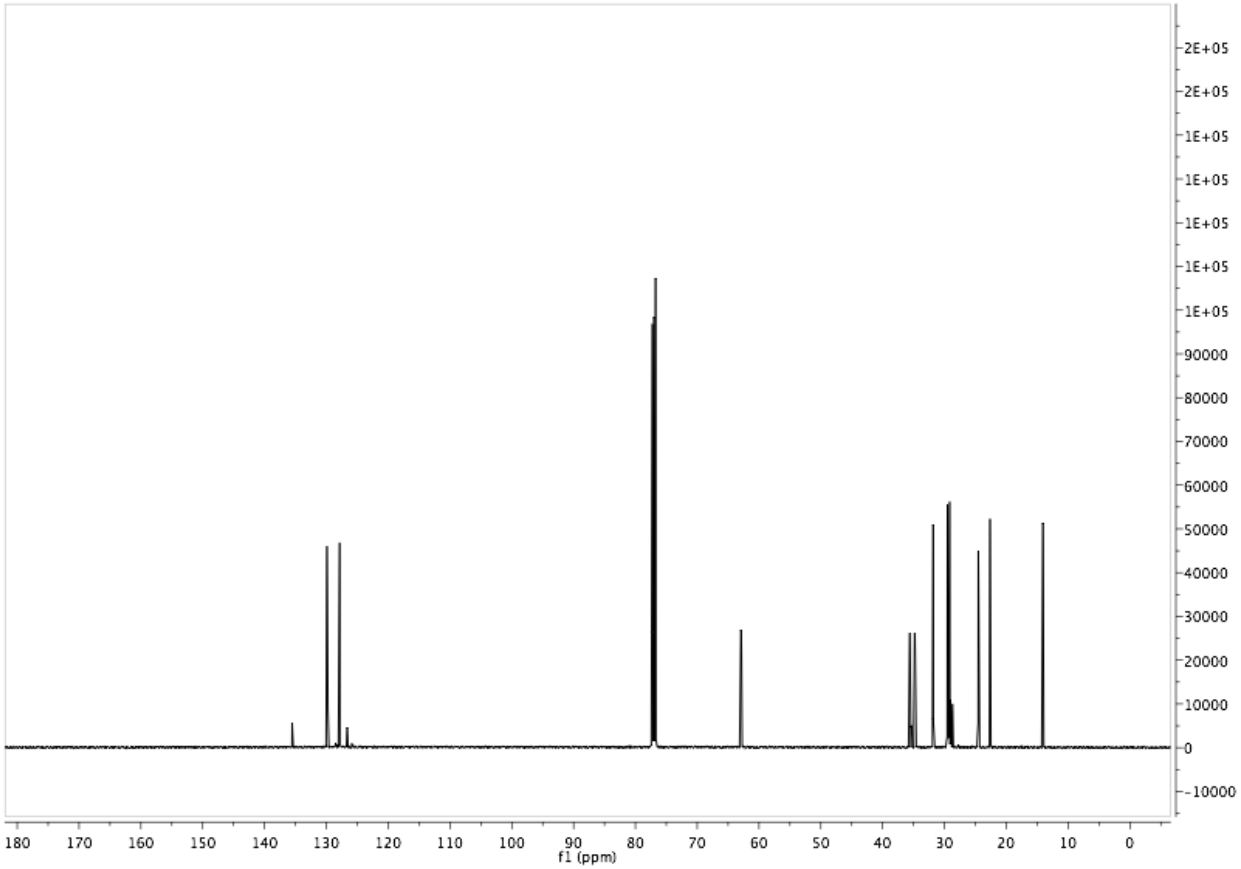


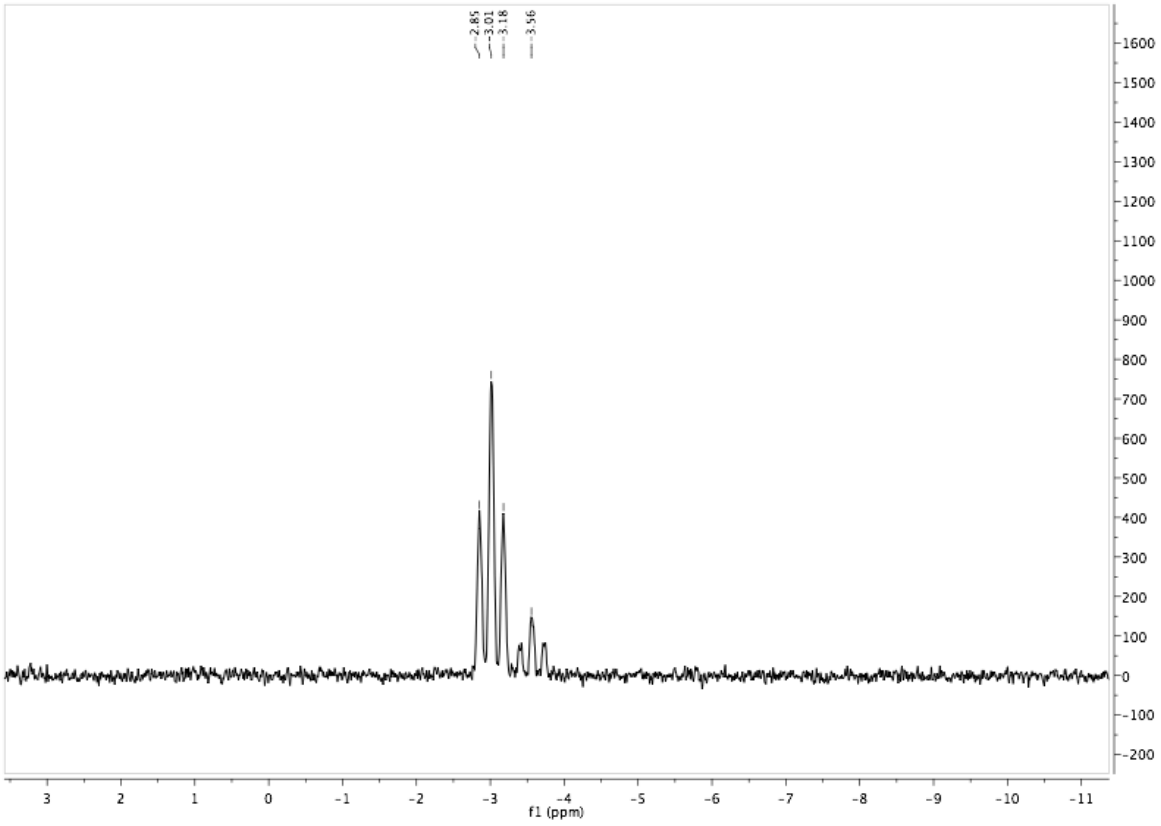



300
250
200
150
100
50
0
-50
-100
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

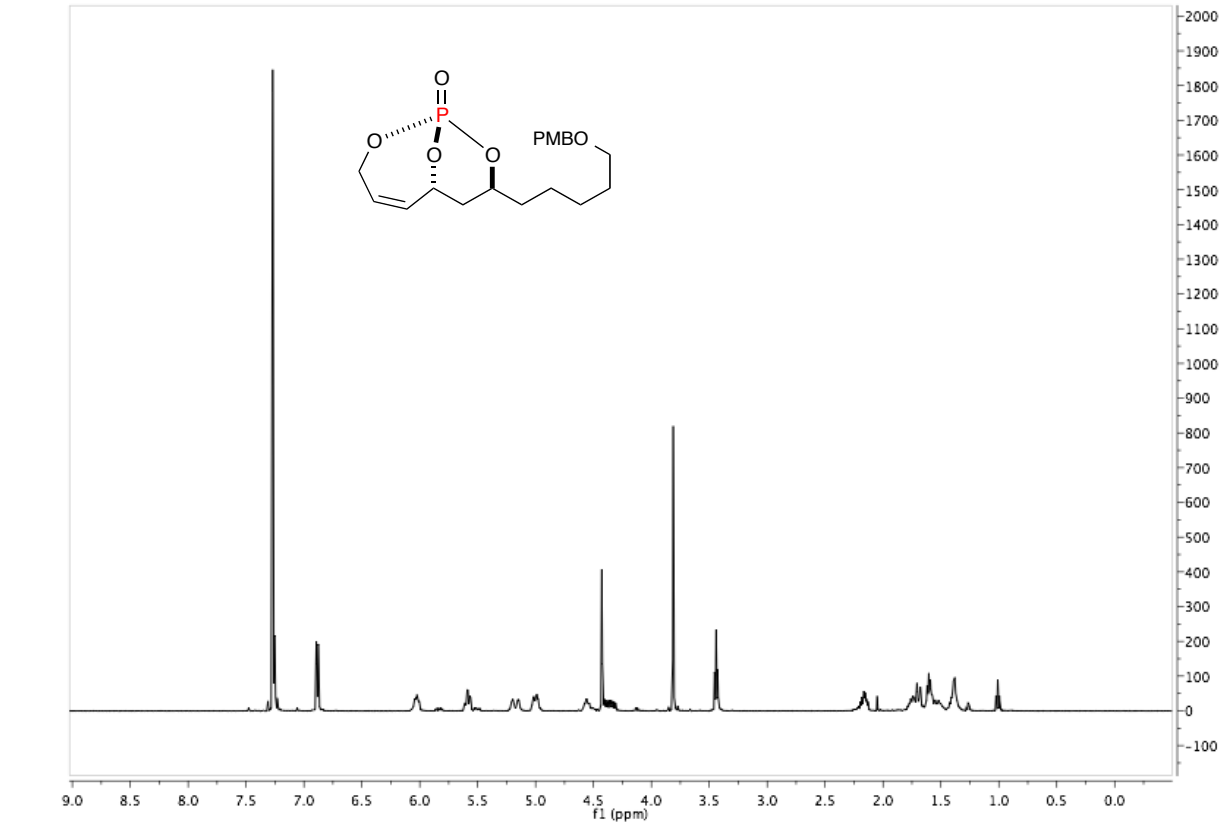
(1*R*,6*R*,8*S*)-8-decyl-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5f)

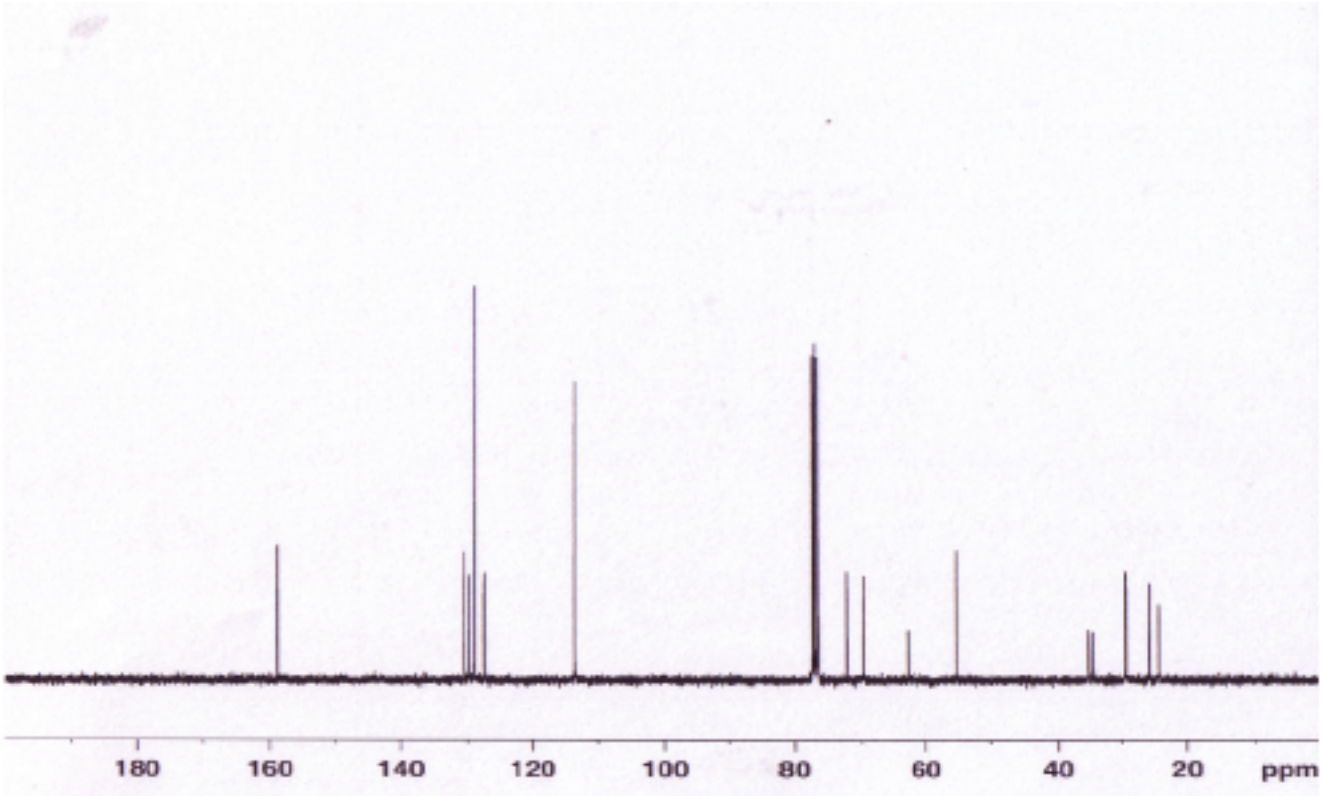


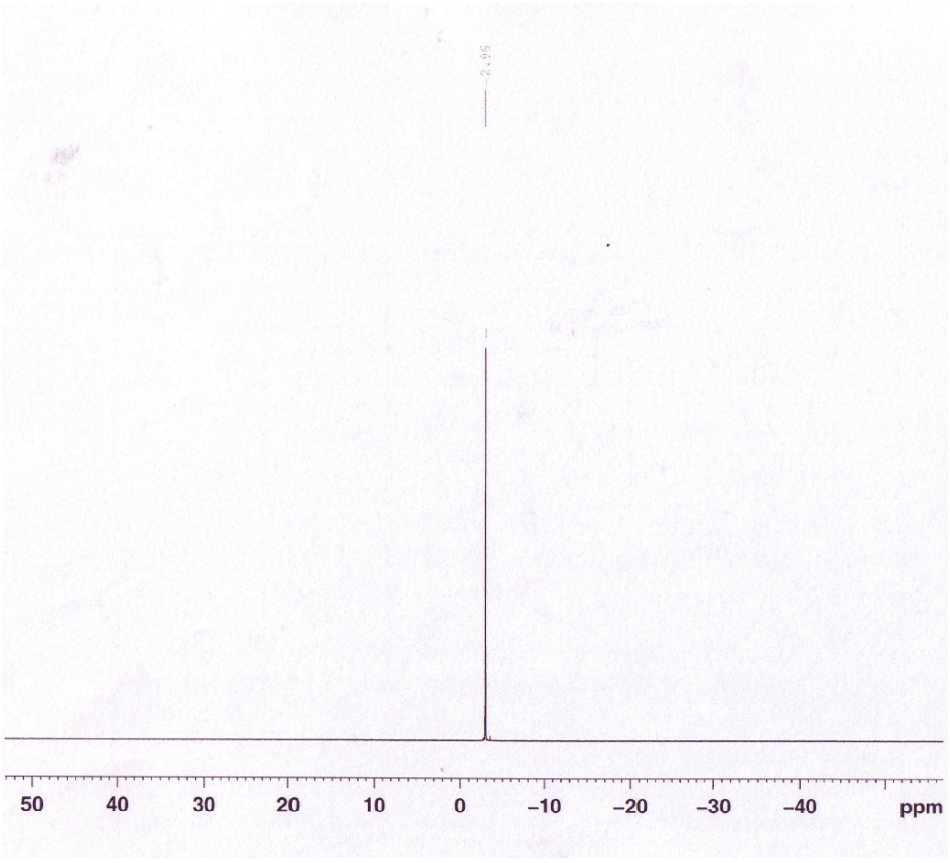



-2.85
-3.01
-3.18
-3.56
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
f1 (ppm)

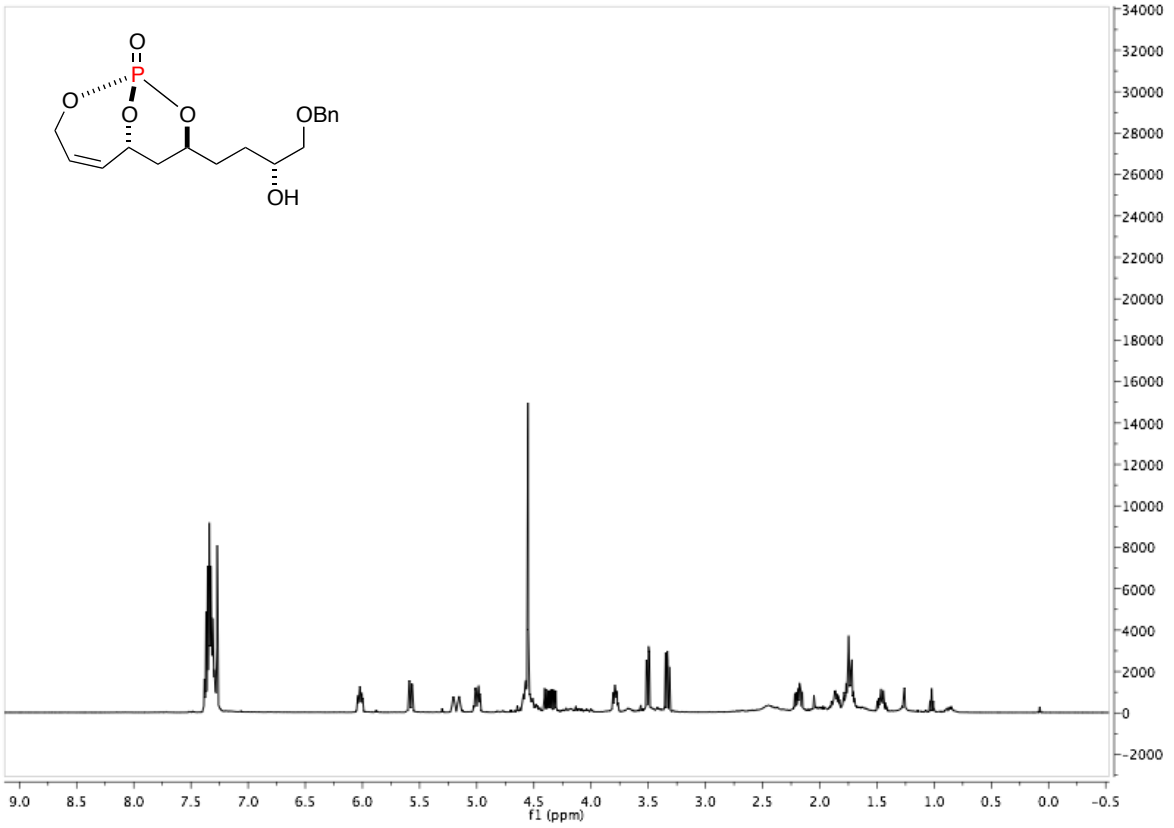
(1*R*,6*R*,8*S*)-8-(5-((4-methoxybenzyl)oxy)pentyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5g)

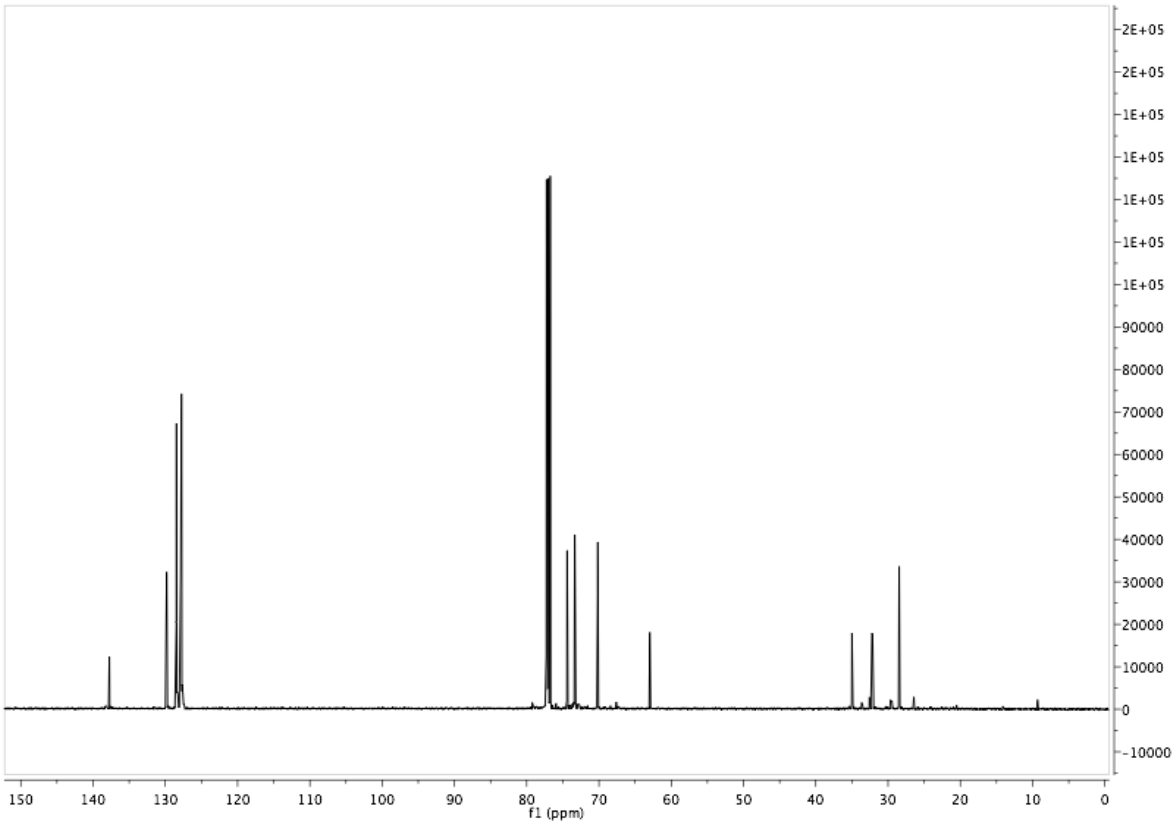


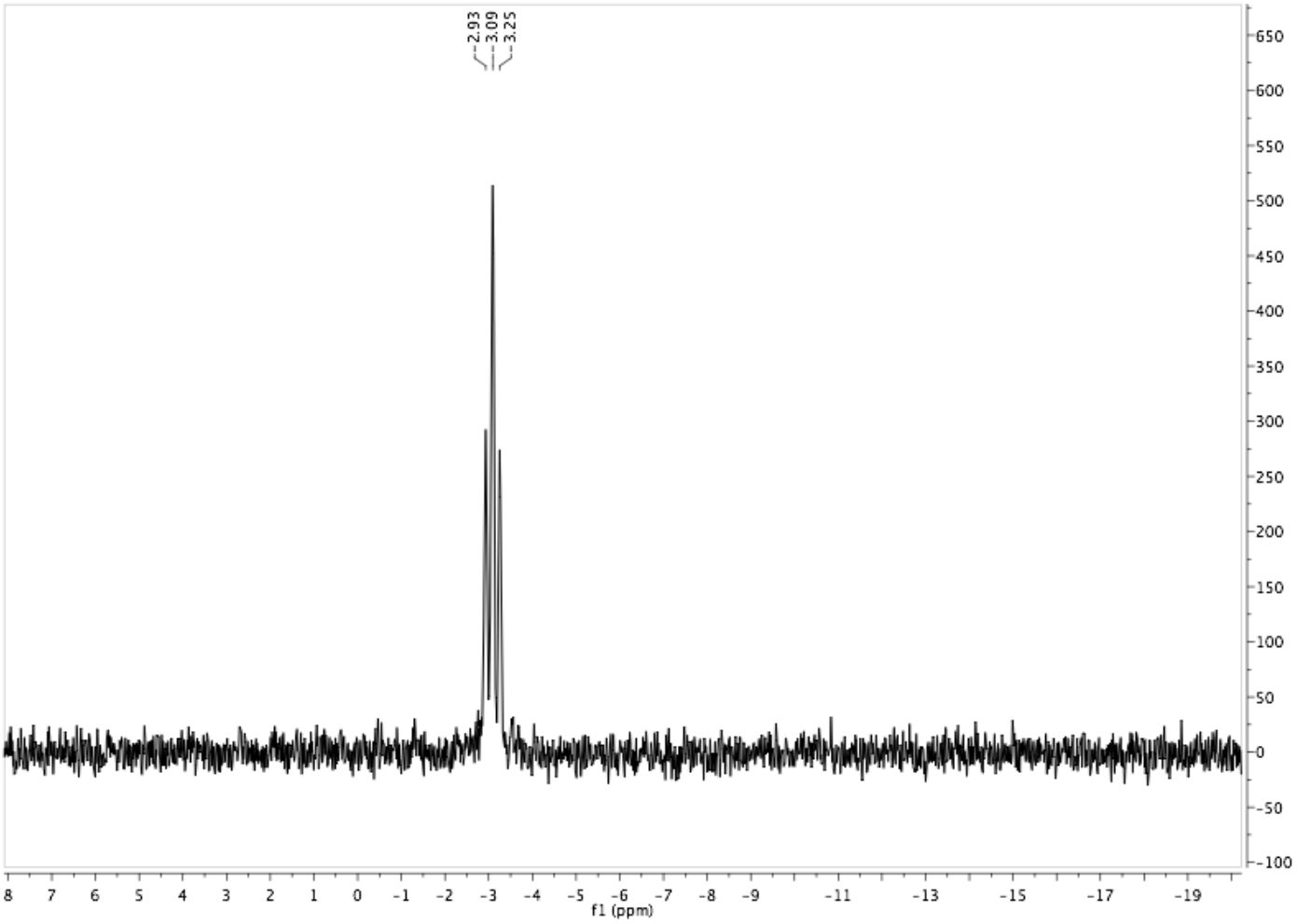



2.95
50
40
30
20
10
0
−10
−20
−30
−40
ppm

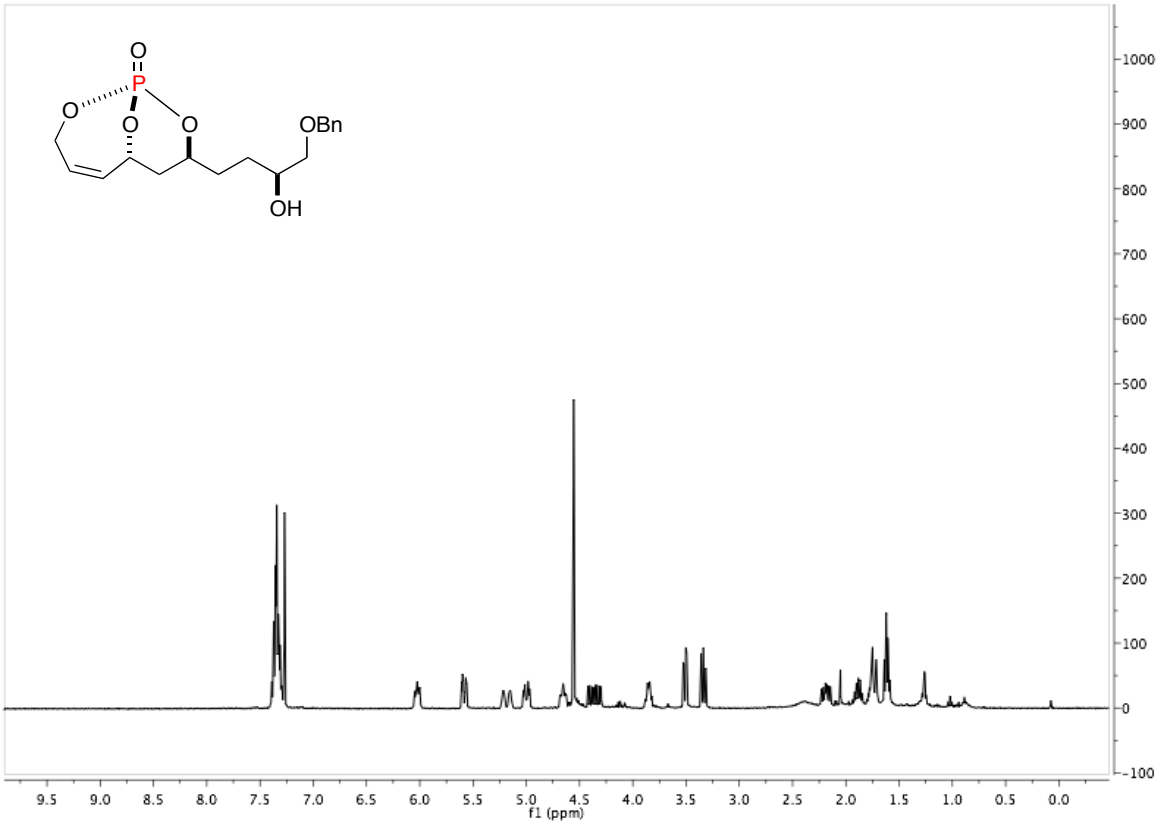
(1*R*,6*R*,8*S*)-8-((*R*)-4-(benzyloxy)-3-hydroxybutyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5h)

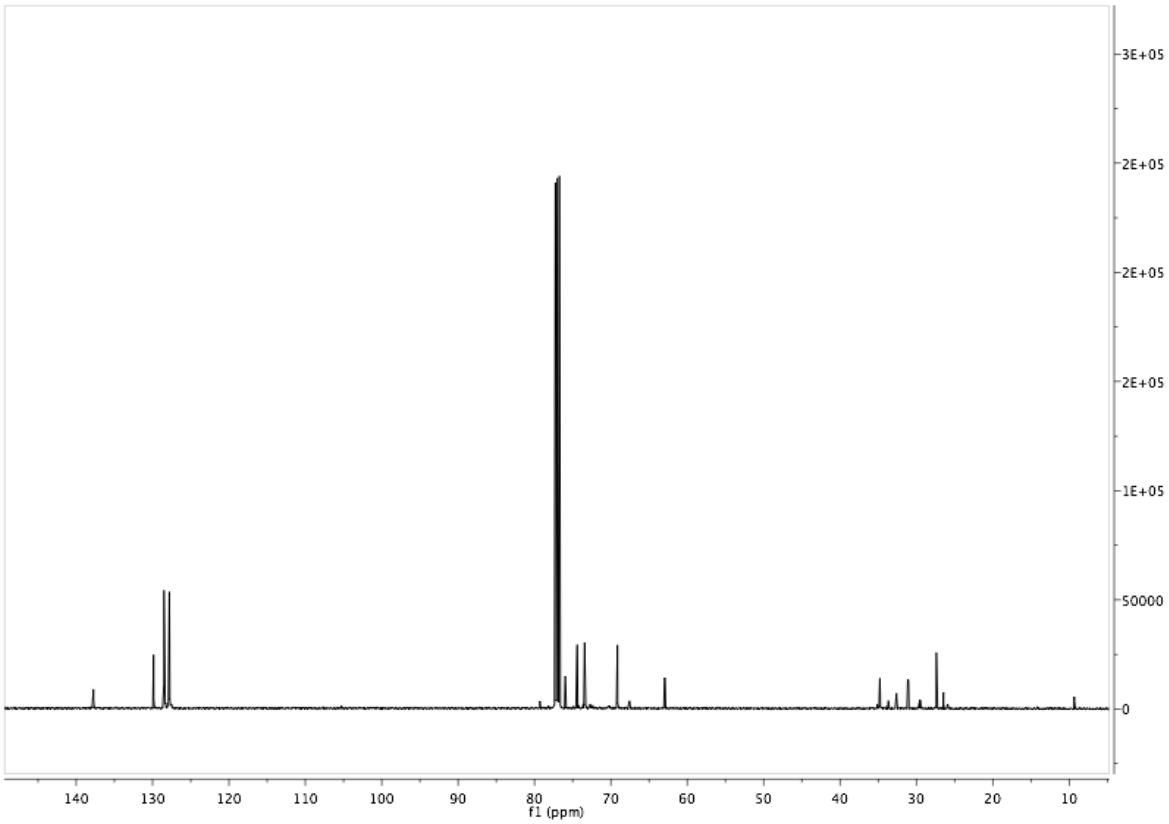


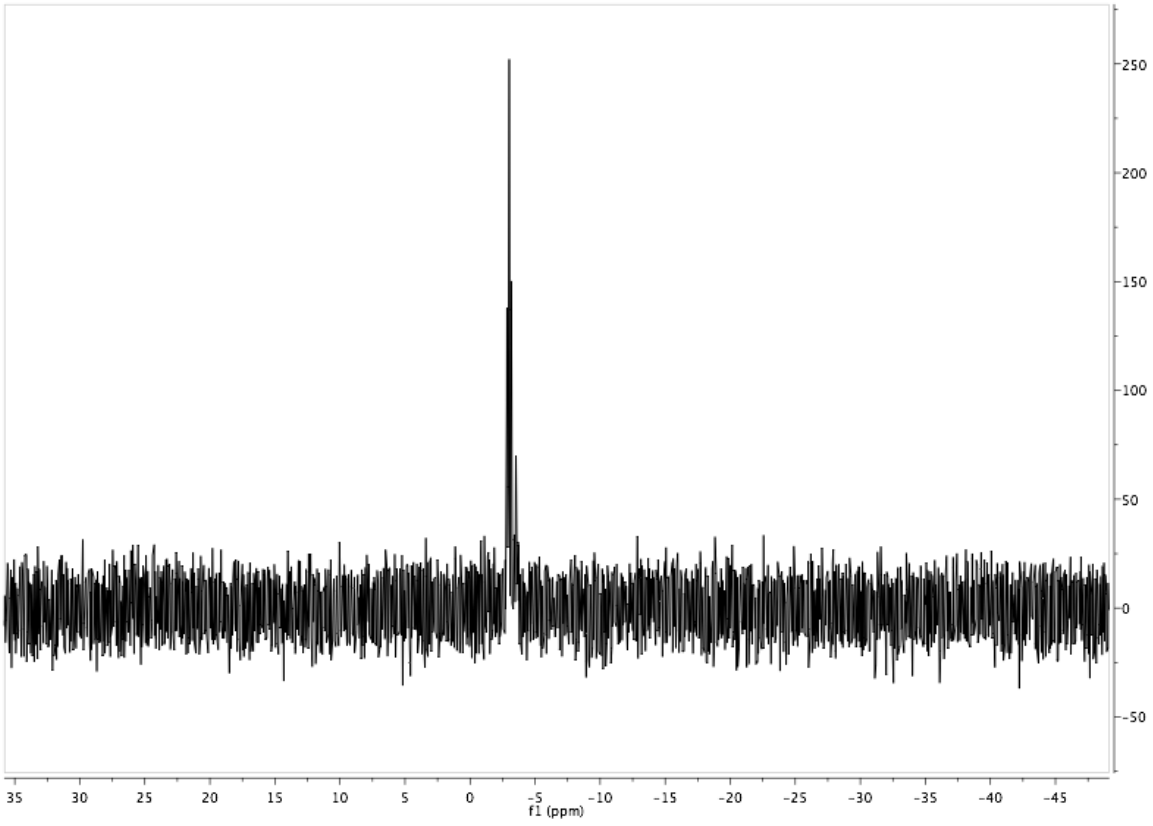



2.93
3.09
3.25
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -11 -13 -15 -17 -19
f1 (ppm)

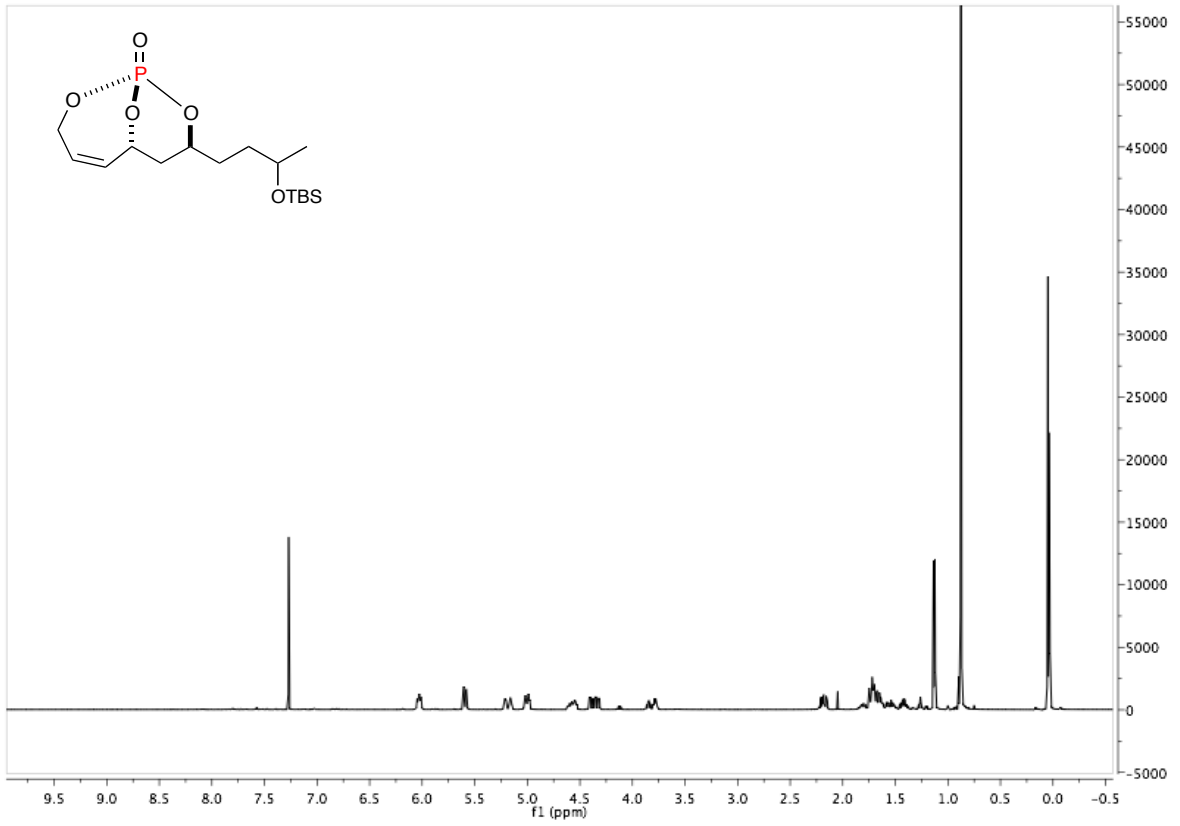
(1*R*,6*R*,8*S*)-8-((*S*)-4-(benzyloxy)-3-hydroxybutyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5i)

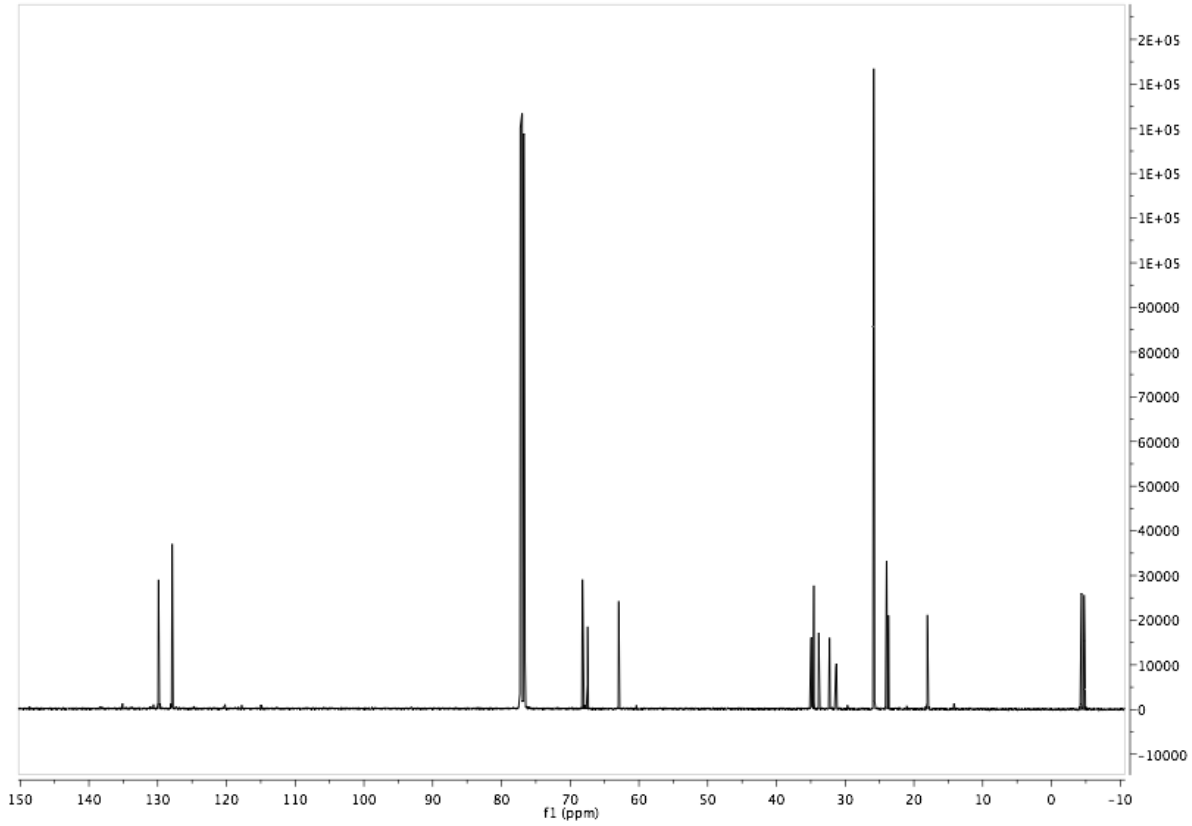


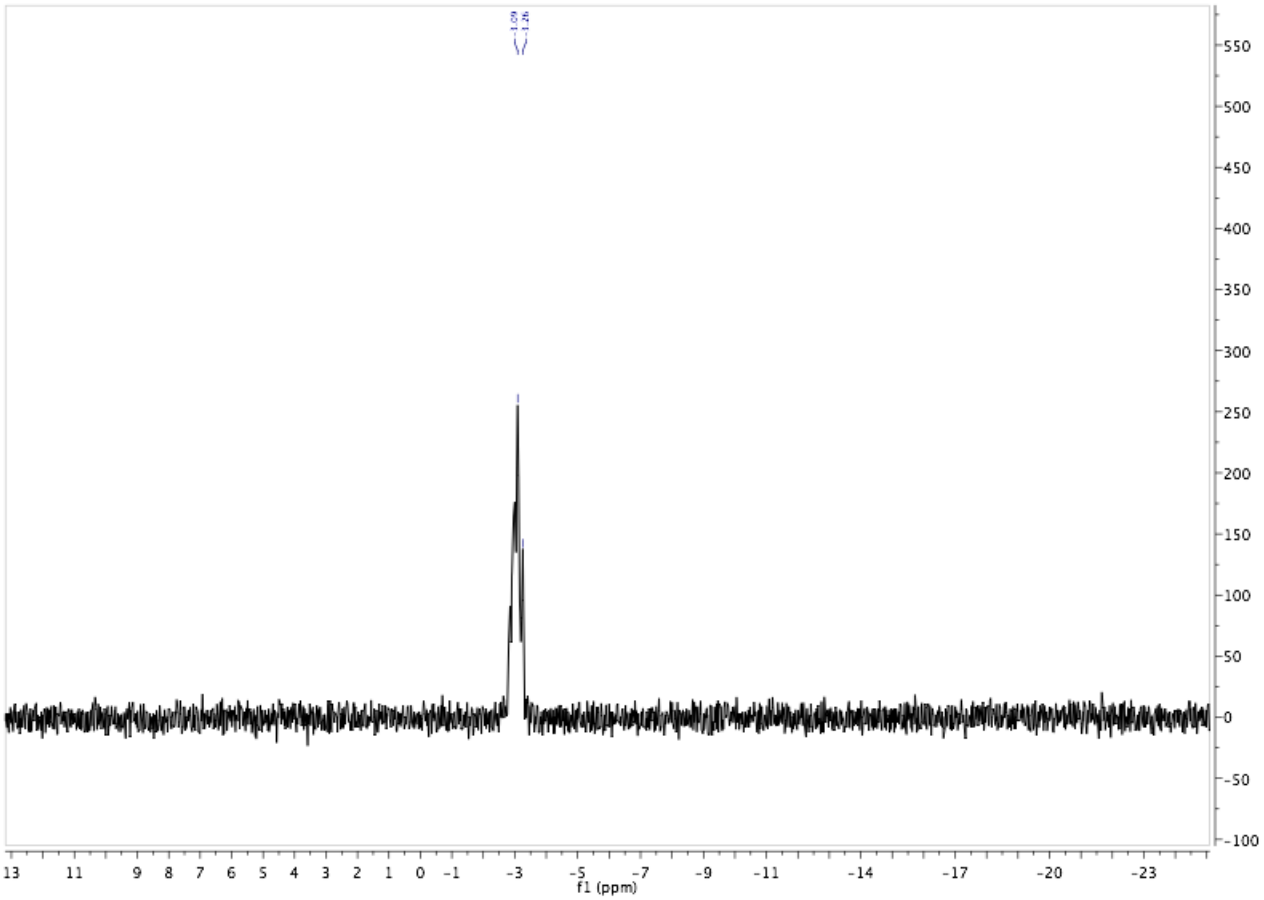



250
200
150
100
50
0
-50
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

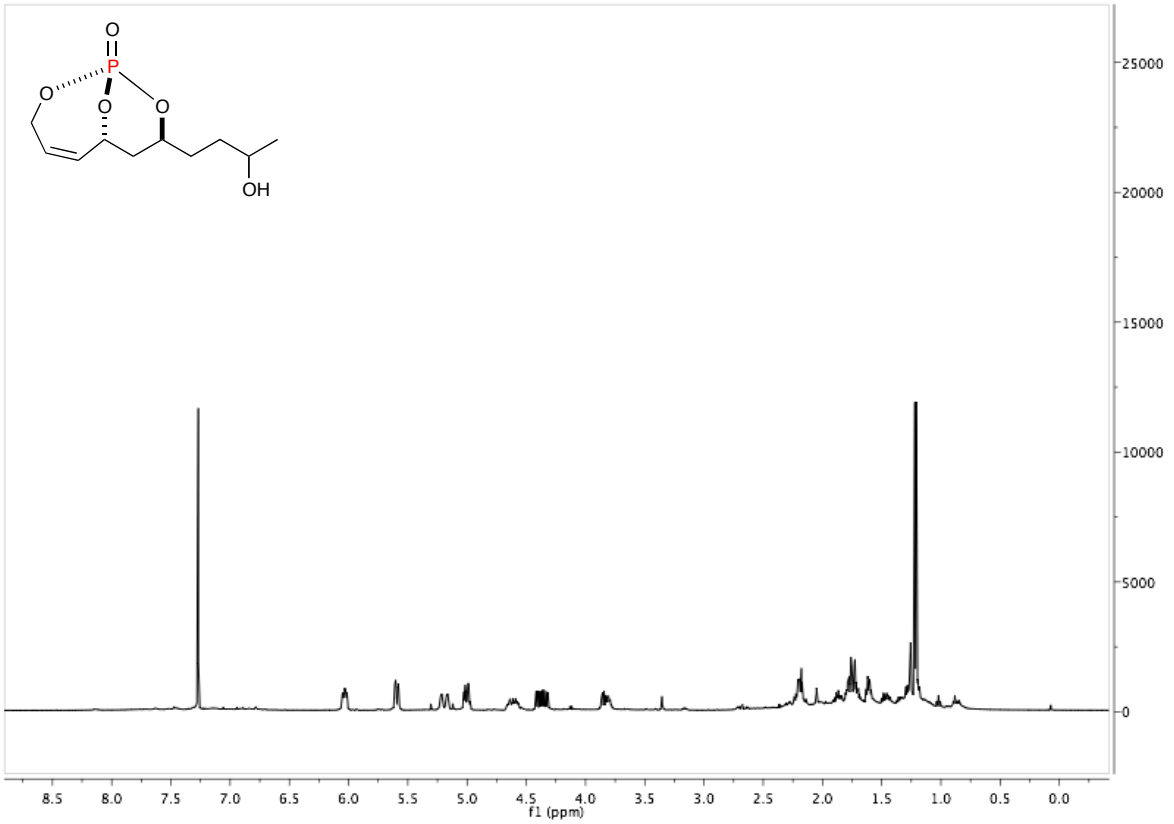
(1*R*,6*R*,8*S*)-8-(3-((*tert*-butyldimethylsilyl)oxy)butyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5j)

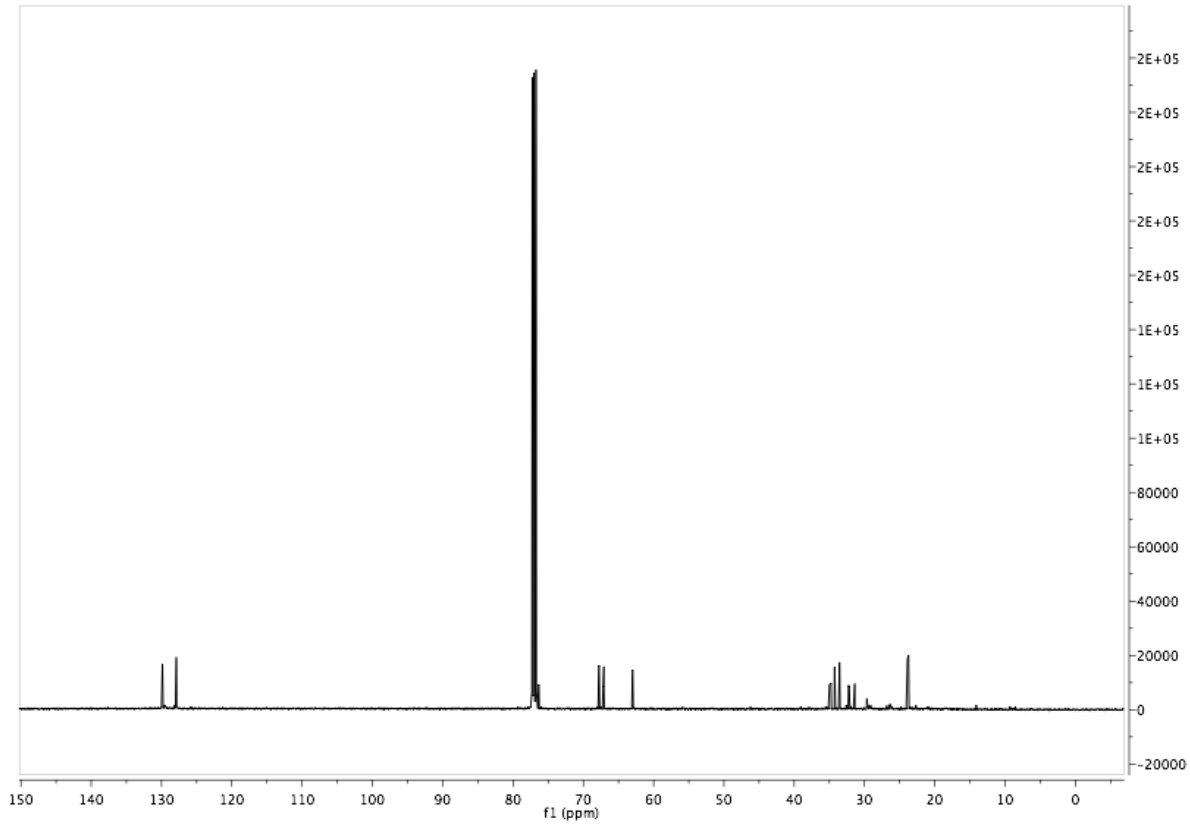


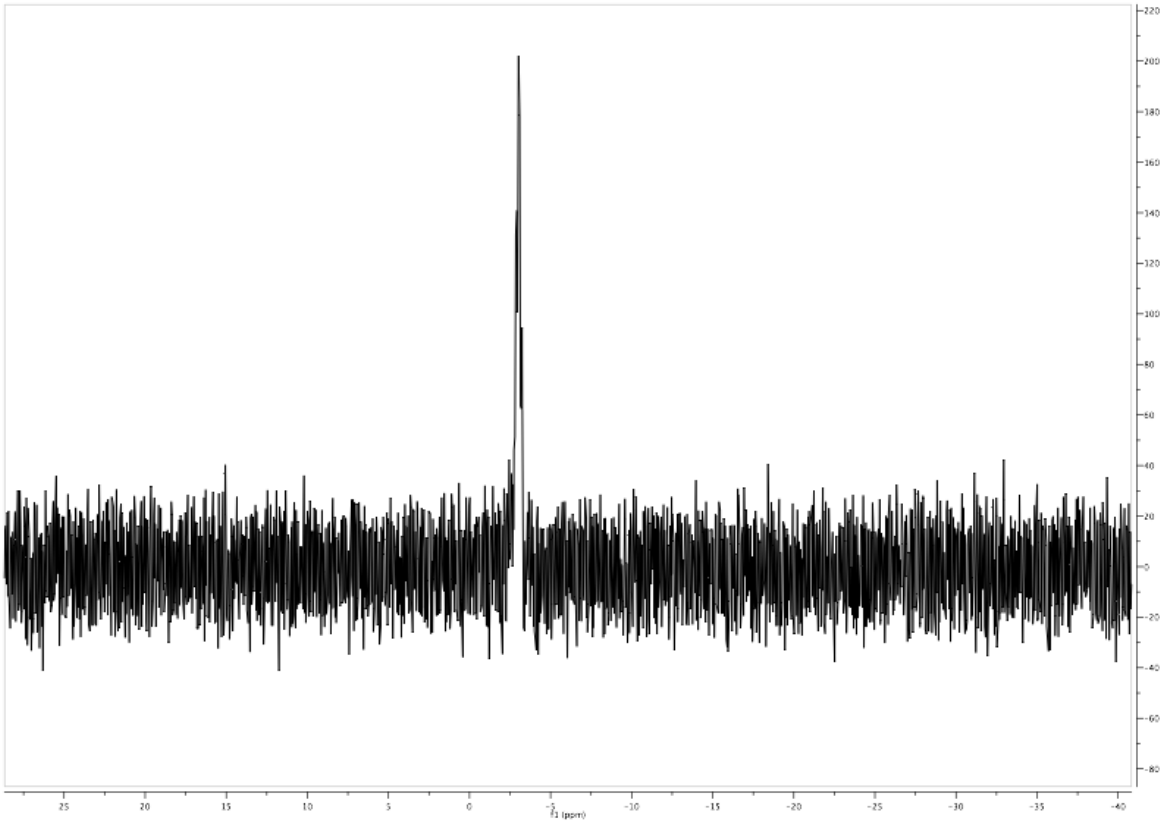



550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
13
11
9
8
7
6
5
4
3
2
1
0
-1
-3
-5
-7
-9
-11
-14
-17
-20
-23
f1 (ppm)

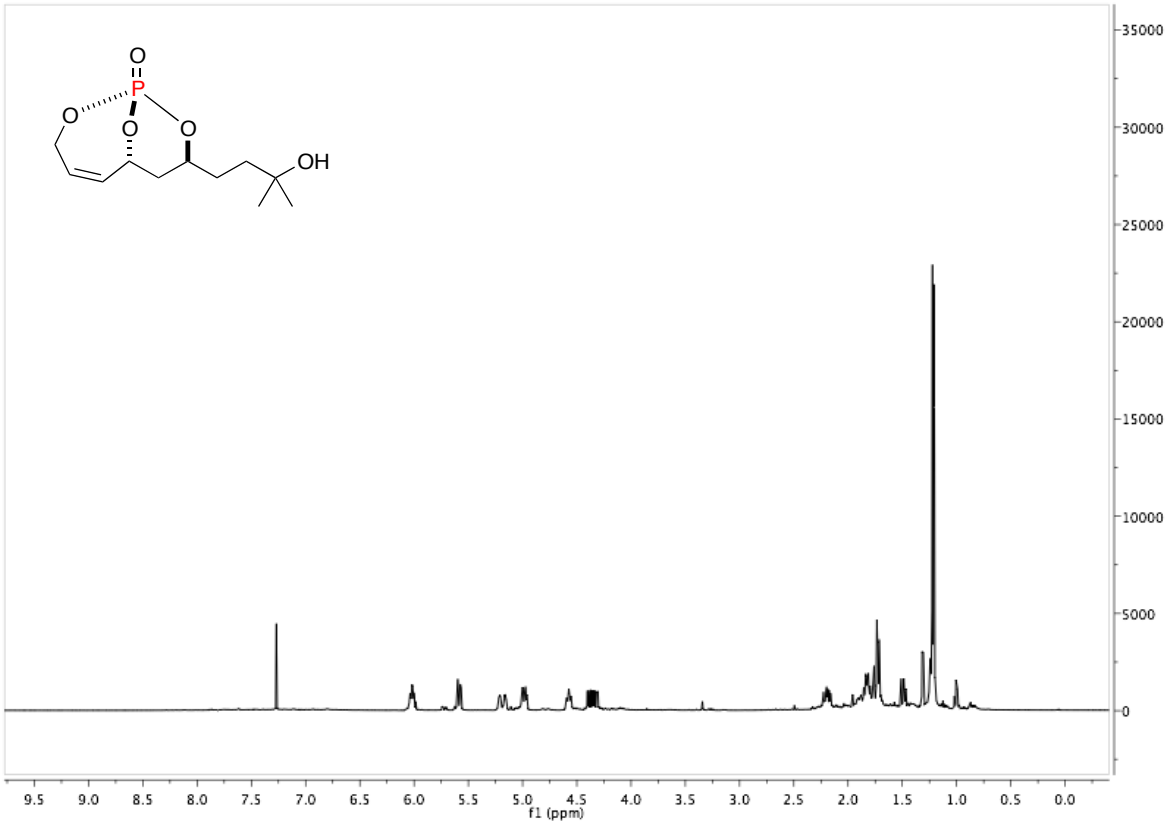
(1*R*,6*R*,8*S*)-8-(3-hydroxybutyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5k)

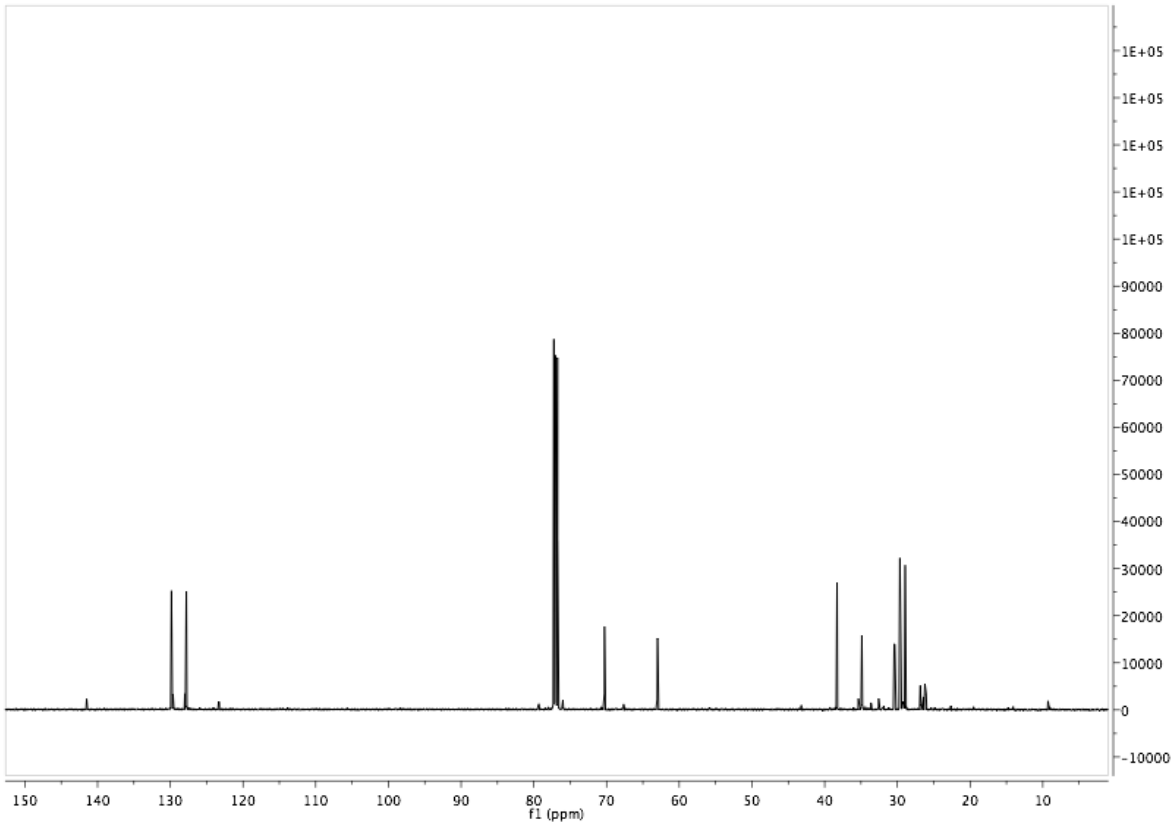


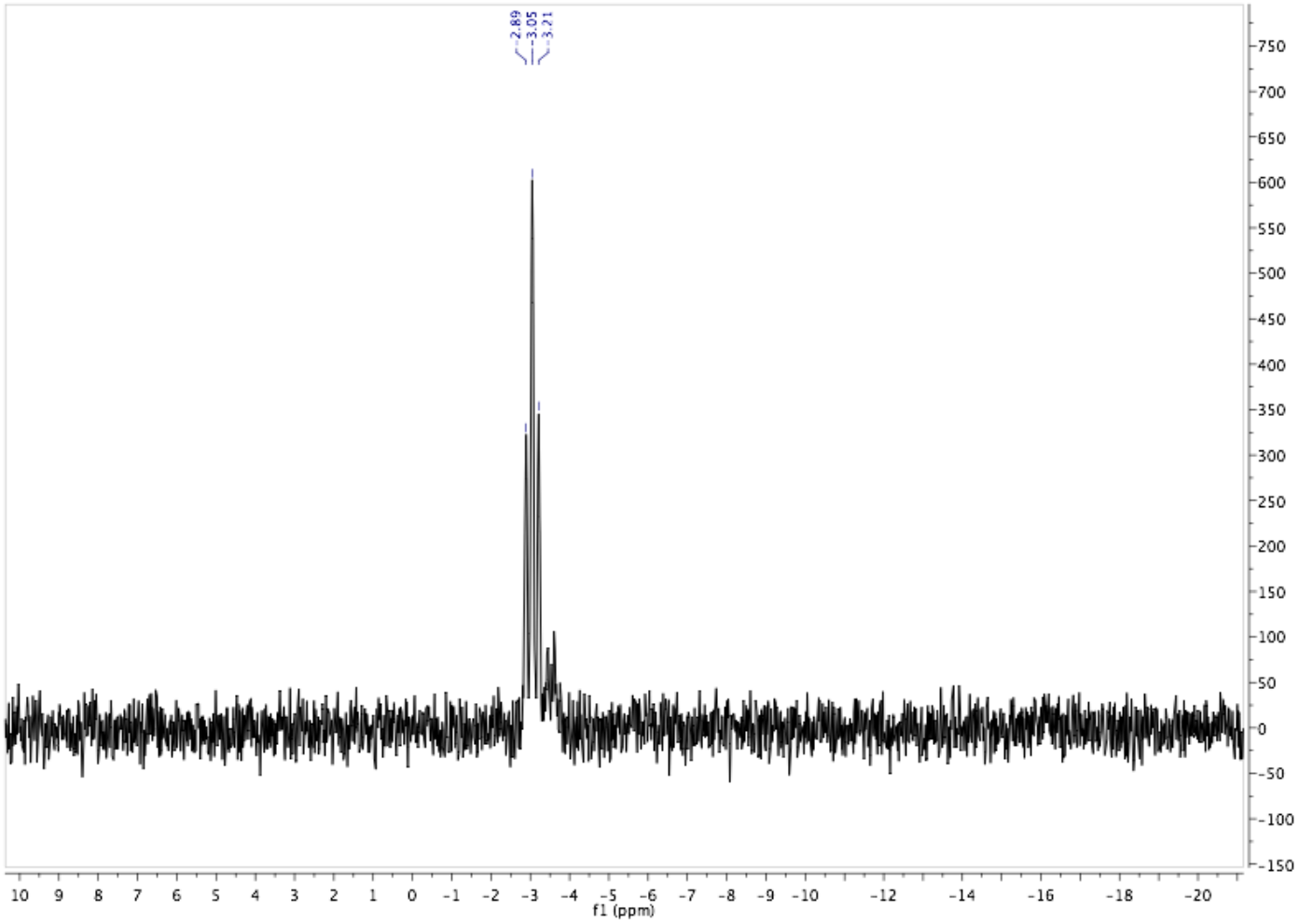



220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
f1 (ppm)

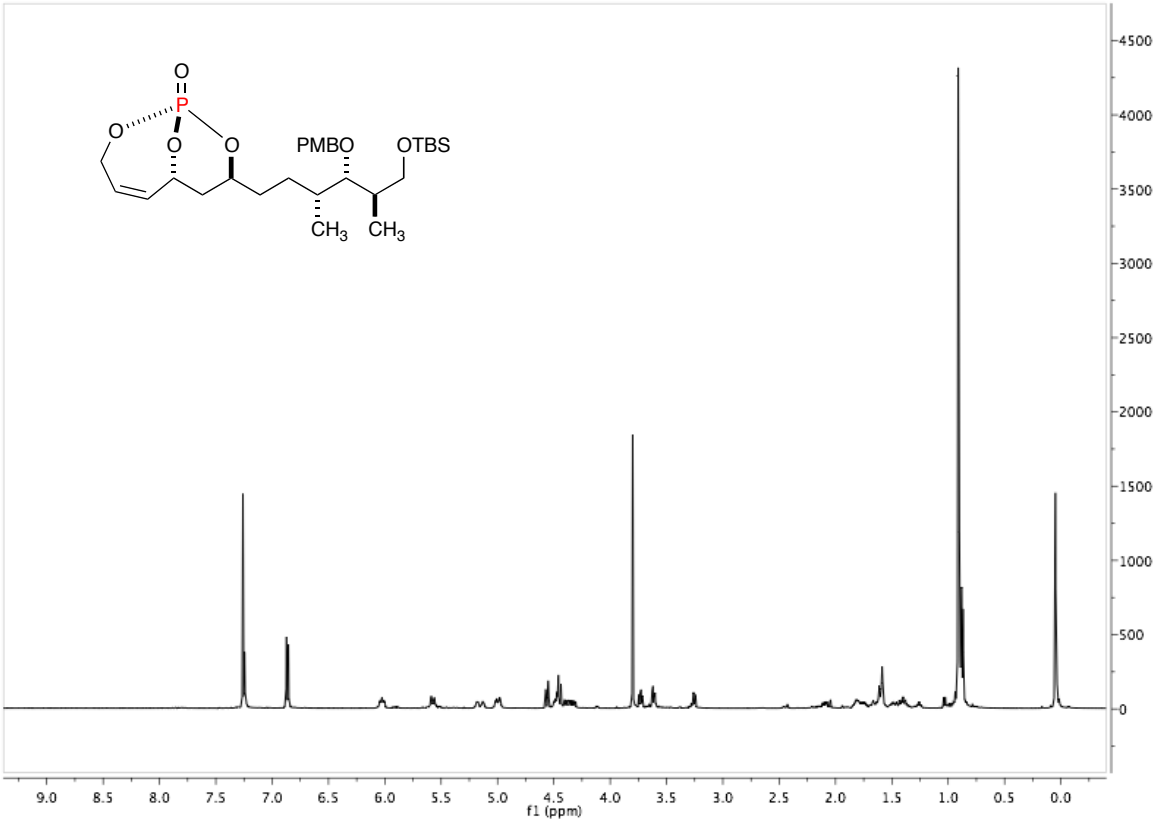
(1*R*,6*R*,8*S*)-8-(3-hydroxy-3-methylbutyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5l)

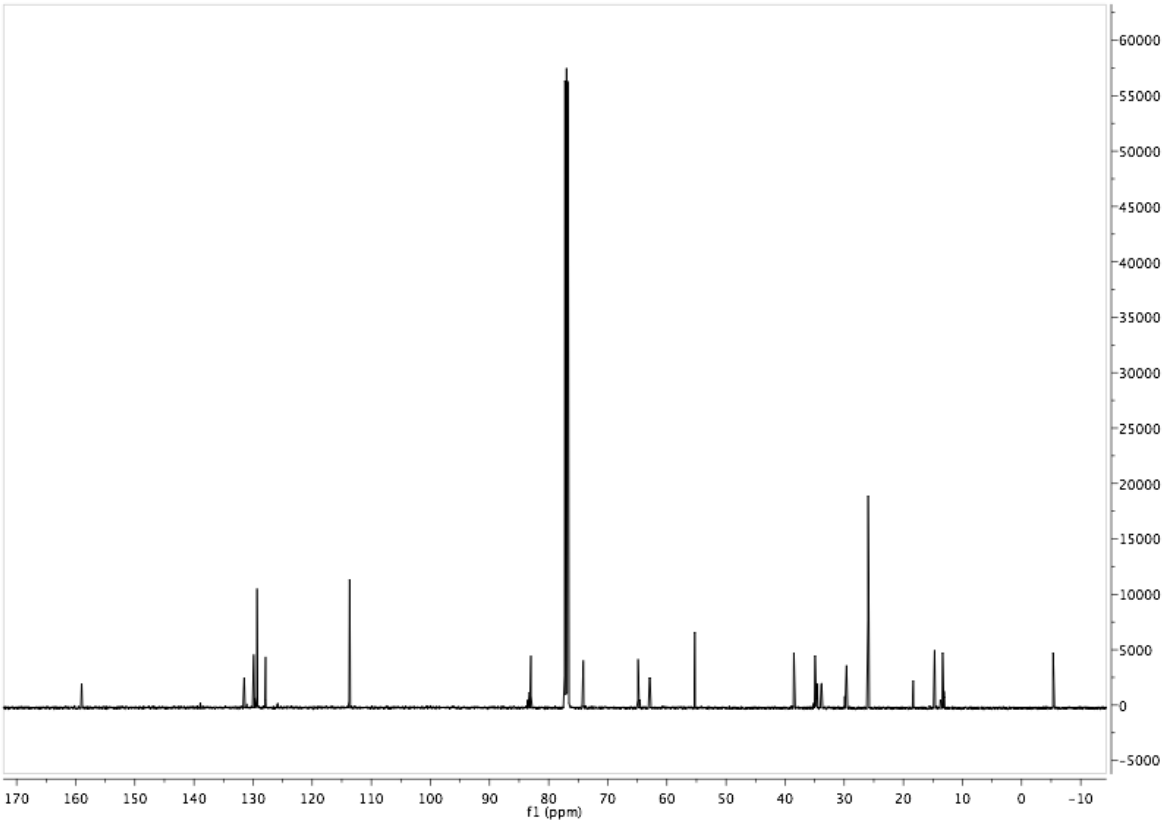


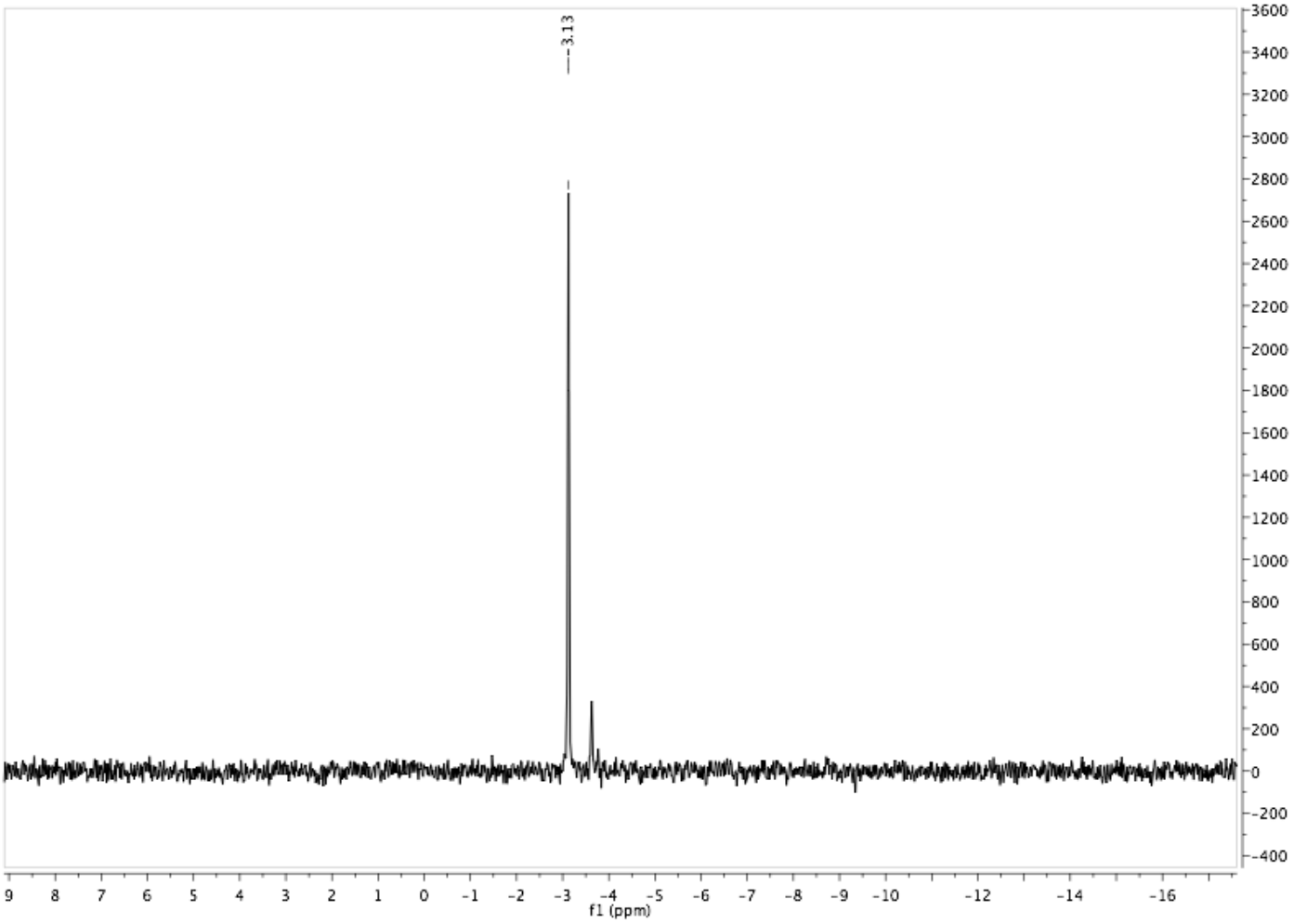



2.89
3.05
3.21
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -10 -12 -14 -16 -18 -20
f1 (ppm)

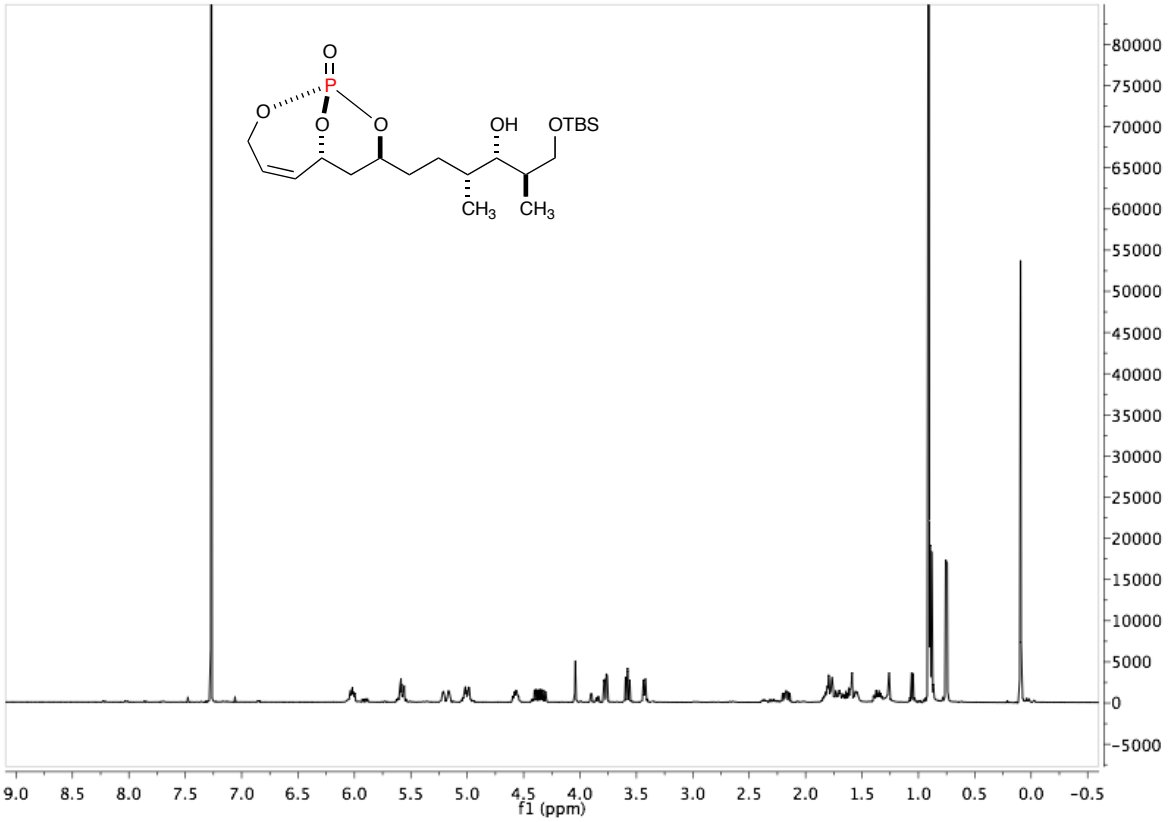
(1*R*,6*R*,8*S*)-8-((3*R*,4*S*,5*R*)-6-((*tert*-butyldimethylsilyl)oxy)-4-((4-methoxybenzyl)oxy)-3,5-dimethylhexyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5m)

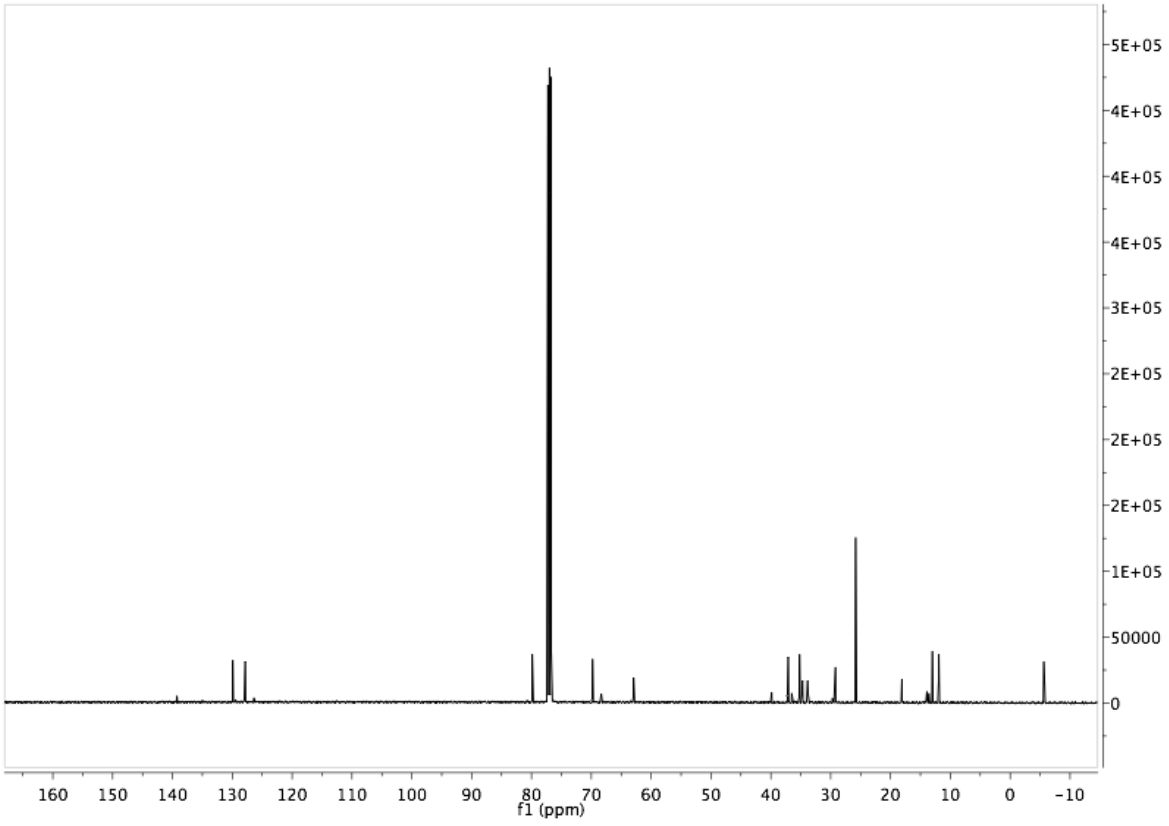


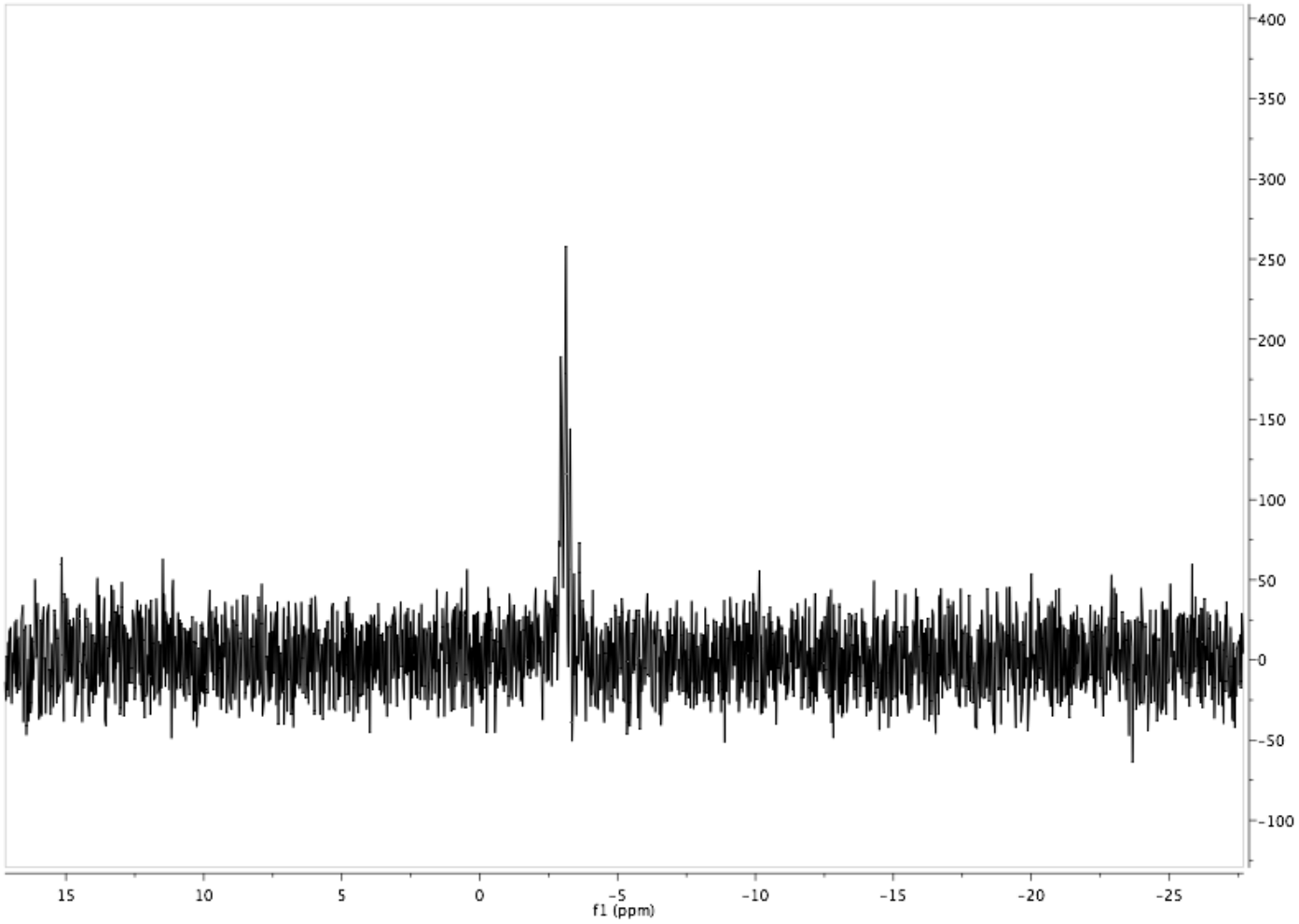



3.13
f1 (ppm)

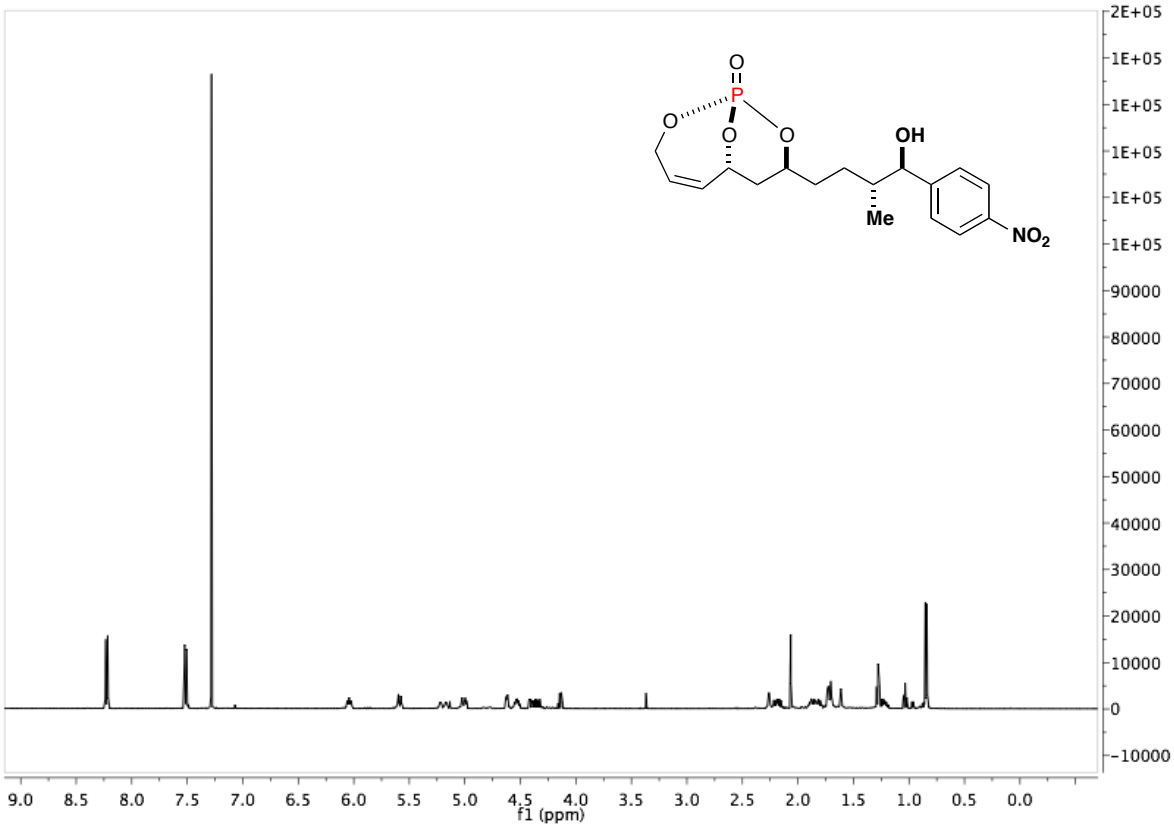
(1*R*,6*R*,8*S*)-8-((3*R*,4*S*,5*R*)-6-((*tert*-butyldimethylsilyl)oxy)-4-hydroxy-3,5-dimethylhexyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5n)

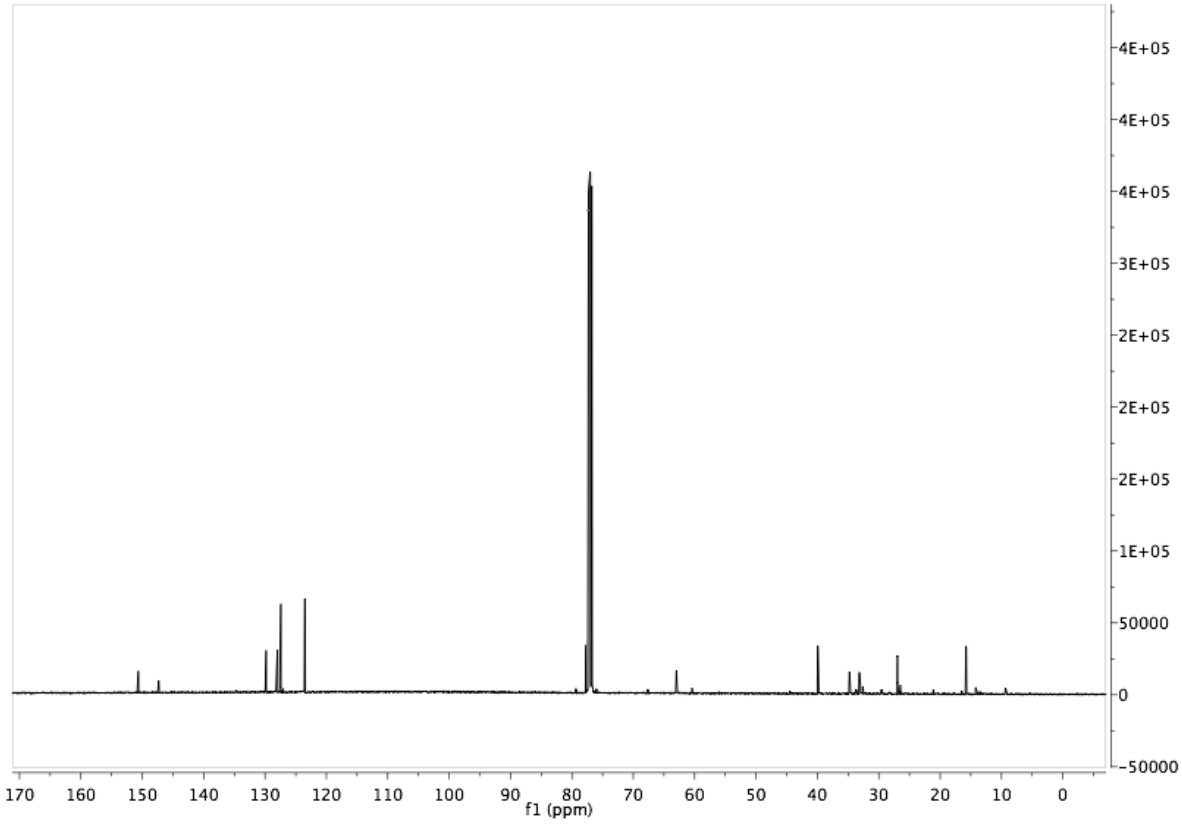


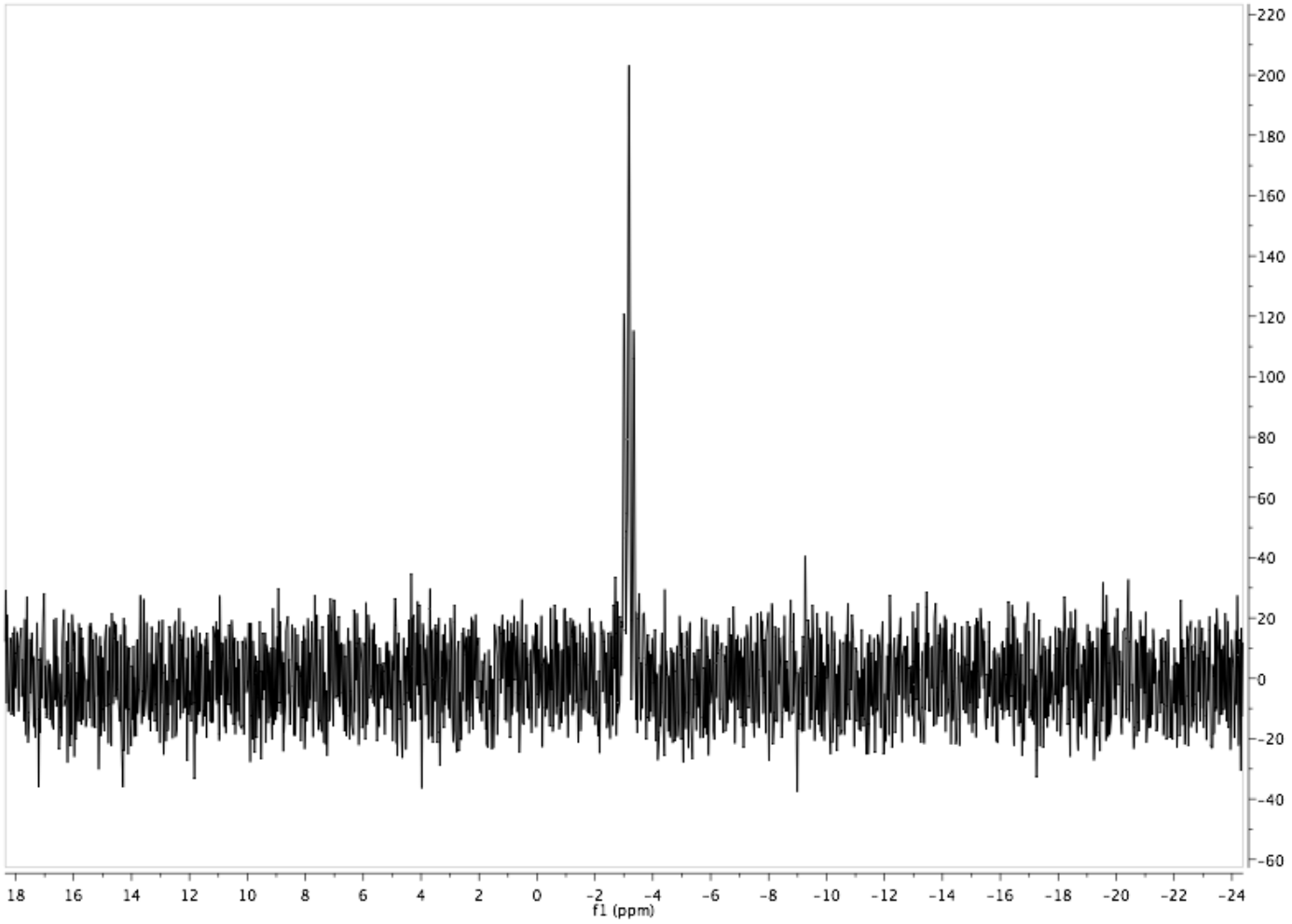



400
350
300
250
200
150
100
50
0
-50
-100
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

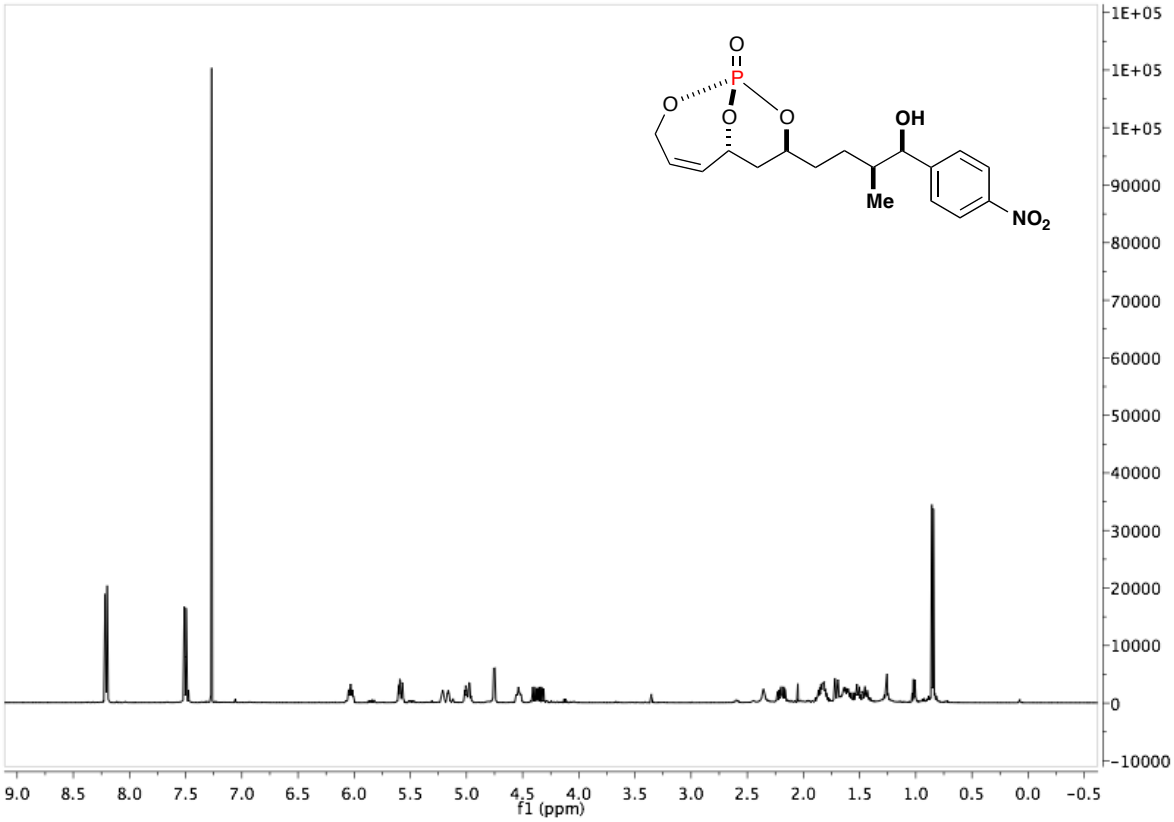
(1*R*,6*R*,8*S*)-8-((3*R*,4*R*)-4-hydroxy-3-methyl-4-(4-nitrophenyl)butyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5o)

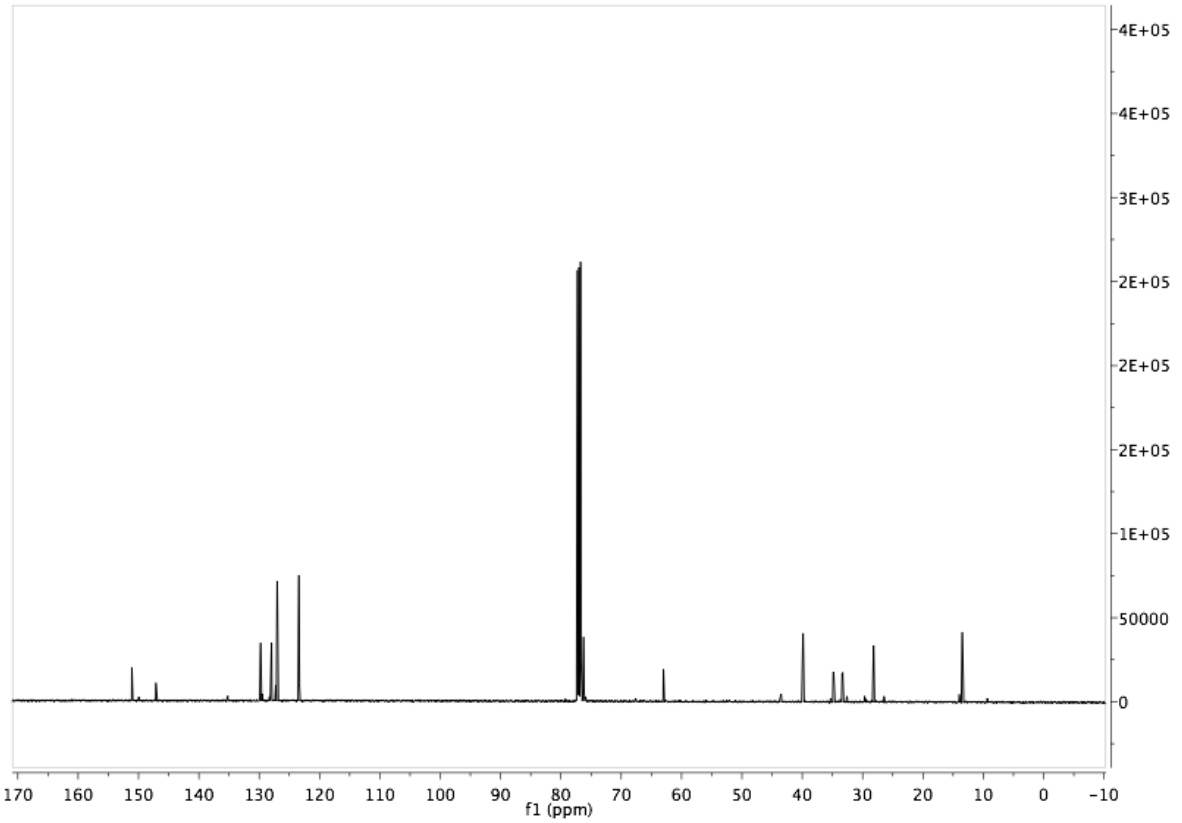


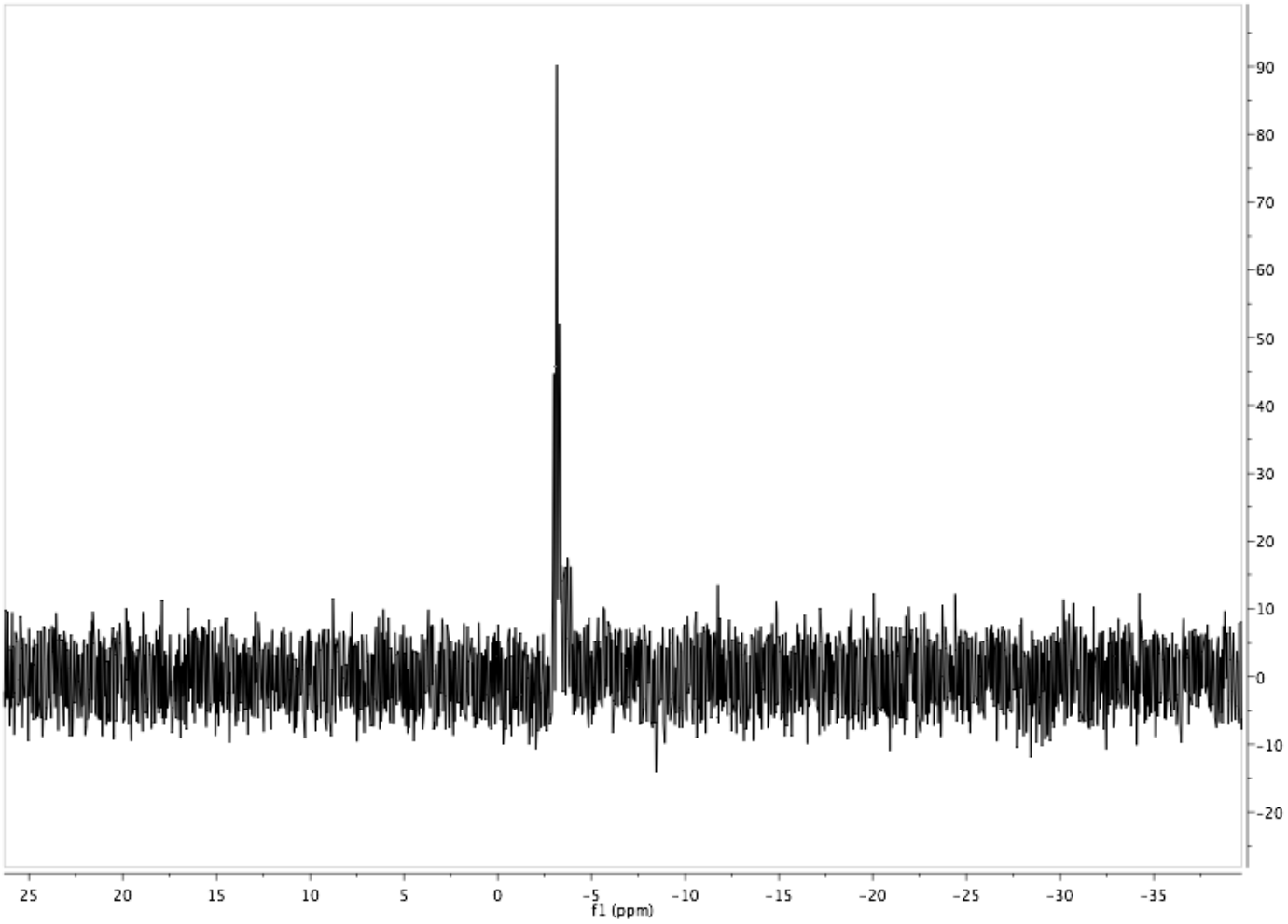



220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
18
16
14
12
10
8
6
4
2
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
-22
-24
f1 (ppm)

(1*R*,6*R*,8*S*)-8-((3*S*,4*R*)-4-hydroxy-3-methyl-4-(4-nitrophenyl)butyl)-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (5p)






90
80
70
60
50
40
30
20
10
0
-10
-20
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
f1 (ppm)