Phosphate Tether-Mediated Ring-Closing Metathesis Studies to Complex 1,3-*anti*-Diol-Containing Subunits

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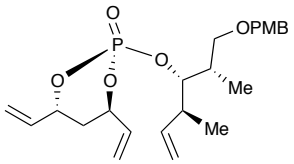
General Methods. All reactions were carried out in oven- or flame-dried glassware under argon atmosphere using standard gas-tight syringes, cannulas, and septa. Stirring was achieved with oven dried magnetic stir bars. Et_2O, THF and CH_2Cl_2 were purified by passage through a purification system (Solv-Tek) employing activated Al_2O_3 (Grubbs, R. H.; Rosen. R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520). Et_3N was purified by passage over basic alumina and stored over KOH. Butyl lithium 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 um) and thin layer chromatography was performed on silica gel 60F254 plates (EM-5717, Merck). Deuterated solvents were purchased from Cambridge Isotope laboratories. All NMR spectra were recorded in $CDCl_3$ (unless otherwise mentioned) on a Bruker DRX (500 or 400 MHz) spectrometers and calibrated to the solvent peak. 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.

Experimental data

(4*R*,6*R*)-2-(((2*S*,3*S*,4*S*)-1-((4-methoxybenzyl)oxy)-2,4-dimethylhex-5-en-3-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (10):



FTIR (neat): 2978, 2962, 1610, 1521, 1278, 1249, 1000, 836, 746 cm^{-1};

Optical Rotation: $[\alpha]_D$ = -26.2 (*c* = 1, $CHCl_3$);

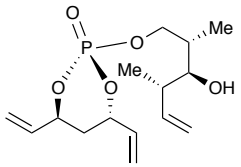
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.00 (dddd, *J* = 17.1, 10.5, 6.2, 0.8 Hz, 1H), 5.90 (dddd, *J* = 17.1, 10.7, 5.1, 1.7 Hz, 1H), 5.85–5.79 (m, 1H), 5.44 (ddd, *J* = 17.1, 1.5, 1.2 Hz, 1H), 5.35 (ddd, *J* = 17.2, 1.3, 1.0 Hz, 1H), 5.27 (dddd, *J* = 10.7, 4.8, 1.3, 1.0 Hz, 2H), 5.06–5.00 (m, 3H), 4.96 (ddt, *J* = 9.6, 7.9, 5.0 Hz, 1H), 4.55 (dddd, *J* = 9.7, 6.5, 4.3 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.38 (d, *J* = 11.5 Hz, 1H), 3.80 (s, 3H), 3.49 (dd, *J* = 9.2, 6.2 Hz, 1H), 3.35 (dd, *J* = 9.2, 6.6 Hz, 1H), 2.53–2.43 (m, 1H), 2.14 (dddd, *J* = 14.5, 7.9, 4.8, 1.5 Hz, 1H), 2.10–2.05 (m, 1H), 2.02 (dddd, *J* = 14.6, 5.6, 3.9, 1.7 Hz, 1H), 1.04 (d, *J* = 6.4 Hz, 3H), 1.00 (d, *J* = 5.8 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 140.0, 135.4 (d, J_{CP} = 3.9 Hz), 135.3 (d, J_{CP} = 7.6 Hz), 130.7, 129.4, 117.7, 117.1, 115.6, 113.7, 85.0 (d, J_{CP} = 7.4 Hz), 77.4 (d, J_{CP} = 6.7 Hz), 75.5 (d, J_{CP} = 6.2 Hz), 72.8, 72.6, 55.3, 41.2 (d, J_{CP} = 3.5 Hz), 36.2 (d, J_{CP} = 3.9 Hz), 35.2 (d, J_{CP} = 7.3 Hz), 17.5, 11.8;

^{31}P NMR (162 MHz, $CDCl_3$) δ -6.64;

HRMS: cald. for $C_{23}H_{33}O_6PNa$ $(M+Na)^+$ 459.1912; found 459.1895 (TOF MS ES+).

(4*S*,6*S*)-2-(((2*S*,3*S*,4*S*)-3-hydroxy-2,4-dimethylhex-5-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (13a):



FTIR (neat): 2959, 2910, 1650, 1392, 1272, 1118, 1012, 927, 877 cm^{-1};

Optical Rotation: $[\alpha]_D$ = +56.2 (*c* = 1.5, $CHCl_3$);

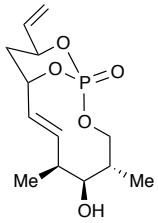
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.97 (ddd, *J* = 16.7, 10.6, 6.0 Hz, 1H), 5.85 (dddd, *J* = 17.3, 10.6, 5.2, 1.6 Hz, 1H), 5.71 (ddd, *J* = 17.3, 10.2, 8.4 Hz, 1H), 5.41 (dd, *J* = 17.1, 1.1 Hz, 1H), 5.32 (dd, *J* = 17.2, 1.0 Hz, 1H), 5.25 (ddd, *J* = 10.6, 6.6, 1.0 Hz, 2H), 5.09–5.03 (m, 2H), 5.02–4.91 (m, 2H), 4.11–4.05 (m, 1H), 3.92 (ddd, *J* = 10.0, 7.7, 6.1 Hz, 1H), 3.38 (dd, *J* = 8.8, 2.8 Hz, 1H), 2.25–2.17 (m, 1H), 2.12 (dddd, *J* = 14.6, 8.1, 4.8, 1.5 Hz, 2H), 2.03–1.97 (m, 2H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.9 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 135.0 (d, J_{CP} = 1.8 Hz), 135.0 (d, J_{CP} = 3.1 Hz), 118.2, 117.6, 116.2, 77.6 (d, J_{CP} = 6.7 Hz), 76.4 (d, J_{CP} = 6.0 Hz), 72.6, 70.3 (d, J_{CP} = 6.0 Hz), 41.8, 35.5 (d, J_{CP} = 6.1 Hz), 35.1 (d, J_{CP} = 7.7 Hz), 16.4, 8.8;

^{31}P NMR (162 MHz, $CDCl_3$) δ -6.62;

HRMS: cald. for $C_{15}H_{26}O_5P$ $(M+H)^+$ 317.1518; found 317.1513 (TOF MS ES+).

(1*S*,4*S*,5*S*,6*S*,9*S*,11*S*,*E*)-5-hydroxy-4,6-dimethyl-11-vinyl-2,12,13-trioxa-1-phosphabicyclo[7.3.1]tridec-7-ene 1-oxide (14a):



FTIR (neat): 2962, 2958, 1459, 1245, 1012 cm^{-1};

Optical Rotation: $[\alpha]_D$ = +47.6 (*c* = 0.105, $CHCl_3$);

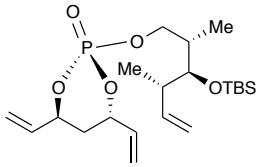
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.21 (ddd, *J* = 16.1, 8.7, 1.8 Hz, 1H), 5.87 (dddd, *J* = 17.9, 9.9, 4.8, 1.7 Hz, 1H), 5.83 (dd, *J* = 15.4, 4.6 Hz, 1H), 5.44 (ddd, *J* = 17.1, 1.1, 1.1 Hz, 1H), 5.29 (ddd, *J* = 10.7, 1.1, 1.0 Hz, 1H), 5.19–5.07 (m, 2H), 4.28 (dd, *J* = 10.9, 5.6 Hz, 1H), 3.95 (dd, *J* = 11.1, 5.0 Hz, 1H), 3.73 (d, *J* = 5.9 Hz, 1H), 2.71–2.61 (m, 1H), 2.24 (ddd, *J* = 14.6, 12.1, 5.2 Hz, 1H), 2.06–1.97 (m, 1H), 1.83 (ddd, *J* = 14.6, 3.7, 2.1 Hz, 1H), 1.69 (s, 1H), 1.16 (d, *J* = 7.1 Hz, 3H), 1.11 (d, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.9, 135.3 (d, J_{CP} = 10.1 Hz), 127.7, 117.1, 79.4, 77.2, 76.3 (d, J_{CP} = 6.4 Hz), 75.1 (d, J_{CP} = 7.0 Hz), 64.2, 39.4, 37.3 (d, J_{CP} = 10.1 Hz), 35.5 (d, J_{CP} = 5.6 Hz), 13.6;

^{31}P NMR (162 MHz, $CDCl_3$) δ -7.10;

HRMS: cald. for $C_{13}H_{21}O_5PNa$ $(M+Na)^+$ 311.1024; found 311.0998 (TOF MS ES+).

(4*S*,6*S*)-2-(((2*S*,3*S*,4*S*)-3-((*tert*-butyldimethylsilyl)oxy)-2,4-dimethylhex-5-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (13b):



FTIR (neat): 2951, 2919, 1491, 1256, 1231, 1109, 1000, 919, 853, 829 cm^{-1};

Optical Rotation: $[\alpha]_D$ = +37.0 (*c* = 1.1, $CHCl_3$);

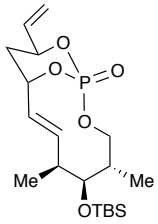
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.01 (ddd, *J* = 16.6, 10.6, 5.8 Hz, 1H), 5.92 (dddd, *J* = 15.9, 10.6, 5.2, 1.5 Hz, 1H), 5.82 (ddd, *J* = 17.9, 10.2, 8.0 Hz, 1H), 5.46 (ddd, *J* = 17.2, 1.3, 0.8 Hz, 1H), 5.38 (dd, *J* = 17.2, 0.9 Hz, 1H), 5.30 (dd, *J* = 10.6, 0.9 Hz, 2H), 5.09–5.02 (m, 1H), 5.04–4.97 (m, 2H), 5.01–4.93 (m, 1H), 4.03–3.93 (m, 2H), 3.63 (dd, *J* = 4.5, 3.7 Hz, 1H), 2.37 (dq, *J* = 14.0, 7.0 Hz, 1H), 2.18 (dddd, *J* = 14.5, 8.1, 4.8, 1.5 Hz, 1H), 2.04 (dddd, *J* = 14.3, 5.2, 3.7, 1.7 Hz, 2H), 1.01 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.90 (s, 9H), 0.06 (s, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 135.1 (d, J_{CP} = 3.2 Hz), 135.0 (d, J_{CP} = 7.1 Hz), 117.9, 117.5, 114.6, 77.4 (d, J_{CP} = 6.7 Hz), 76.1 (d, J_{CP} = 6.1 Hz), 75.3, 70.6 (d, J_{CP} = 6.0 Hz), 42.5, 38.0 (d, J_{CP} = 6.7 Hz), 35.1 (d, J_{CP} = 7.6 Hz), 26.0, 18.3, 17.3, 11.8, -3.8, -4.1;

^{31}P NMR (162 MHz, $CDCl_3$) δ -7.05;

HRMS: cald. for $C_{21}H_{39}O_5PSiNa$ $(M+Na)^+$ 453.2202; found 453.2189 (TOF MS ES+).

(1*S*,4*S*,5*S*,6*S*,9*S*,11*S*,*E*)-5-((*tert*-butyldimethylsilyl)oxy)-4,6-dimethyl-11-vinyl-2,12,13-trioxa-1-phosphabicyclo[7.3.1]tridec-7-ene 1-oxide (14b):



FTIR (neat): 2956, 2929, 1471, 1276, 1257, 1103, 1001, 927, 862, 837 cm^{-1};

Optical Rotation: $[\alpha]_D$ = +36.5 (*c* = 3.75, $CHCl_3$);

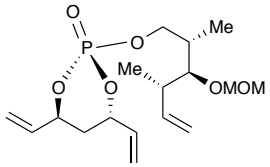
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.22 (dd, *J* = 15.5, 9.7 Hz, 1H), 5.87 (dddd, *J* = 17.4, 9.9, 4.8, 1.8 Hz, 1H), 5.75 (dd, *J* = 16.0, 4.7 Hz, 1H), 5.45 (ddd, *J* = 17.0, 1.2, 1.0 Hz, 1H), 5.27 (d, *J* = 10.6 Hz, 1H), 5.18–5.04 (m, 2H), 4.34 (s, 1H), 3.91 (dd, *J* = 11.2, 6.6 Hz, 1H), 3.68 (dd, *J* = 5.9, 2.1 Hz, 1H), 2.49 (s, 1H), 2.22 (ddd, *J* = 14.6, 12.2, 5.2 Hz, 1H), 2.10–1.96 (m, 1H), 1.81 (dd, *J* = 14.5, 1.5 Hz, 1H), 1.09 (d, *J* = 6.9 Hz, 3H), 1.01 (d, *J* = 7.4 Hz, 3H), 0.92 (s, 9H), 0.08 (s, 3H), 0.03 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.4 (d, J_{CP} = 10.0 Hz), 127.1, 116.9, 80.0, 77.2 (d, J_{CP} = 6.1 Hz), 76.1 (d, J_{CP} = 6.5 Hz), 75.1 (d, J_{CP} = 7.0 Hz), 70.6 (d, J_{CP} = 5.9 Hz), 42.5, 39.5, 35.6 (d, J_{CP} = 5.7 Hz), 29.6, 26.0, 25.9, 18.1, -4.2, -4.8;

^{31}P NMR (162 MHz, $CDCl_3$) δ -7.16;

HRMS: cald. for $C_{19}H_{35}O_5PSiNa$ $(M+Na)^+$ 425.1889; found 425.1885 (TOF MS ES+).

(4*S*,6*S*)-2-(((2*S*,3*S*,4*S*)-3-(methoxymethoxy)-2,4-dimethylhex-5-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (13c):



FTIR (neat): 2961, 2926, 1456, 1221, 1076, 1006, 939 cm^{-1};

Optical Rotation: $[\alpha]_D$ = +65.7 (*c* = 1.0, $CHCl_3$);

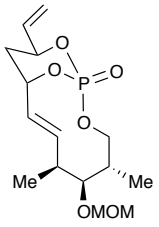
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.03 (ddd, *J* = 16.6, 10.6, 5.7 Hz, 1H), 5.91 (ddd, *J* = 15.9, 10.6, 5.2 Hz, 1H), 5.81 (ddd, *J* = 17.7, 10.0, 8.6, 1H), 5.46 (dd, *J* = 17.1, 0.5 Hz, 1H), 5.38 (d, *J* = 17.2 Hz, 1H), 5.30 (ddd, *J* = 10.6, 5.6, 0.5 Hz, 2H), 5.09–4.98 (m, 2H), 5.06 (d, *J* = 17.3 Hz, 1H), 5.01 (d, *J* = 8.3 Hz, 1H), 4.60 (s, 2H), 4.01 (t, *J* = 6.6 Hz, 2H), 3.42 (dd, *J* = 6.6, 3.0 Hz, 1H), 3.36 (d, *J* = 0.6, 3H), 2.48–2.39 (m, 1H), 2.21–2.14 (m, 1H), 2.13–2.00 (m, 2H), 1.01 (d, *J* = 6.9, 3H), 0.95 (d, *J* = 6.9, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 135.1, 135.1 (d, J_{CP} = 4.8 Hz), 117.9, 117.3, 114.8, 98.2, 82.4, 77.7 (d, J_{CP} = 6.8 Hz), 76.0 (d, J_{CP} = 6.1 Hz), 70.0 (d, J_{CP} = 5.9 Hz), 56.0, 41.1, 36.3 (d, J_{CP} = 7.3 Hz), 35.1 (d, J_{CP} = 7.6 Hz), 17.2, 10.8;

^{31}P NMR (162 MHz, $CDCl_3$) δ -7.02;

HRMS: cald. for $C_{17}H_{29}O_6PNa$ $(M+Na)^+$ 383.1599; found 383.1571 (TOF MS ES+).

(1*S*,4*S*,5*S*,6*S*,9*S*,11*S*,*E*)-5-(methoxymethoxy)-4,6-dimethyl-11-vinyl-2,12,13-trioxa-1-phosphabicyclo[7.3.1]tridec-7-ene 1-oxide (14c):



FTIR (neat): 2964, 2929, 2904, 1451, 1226, 1091, 1016, 927 cm^{-1};

Optical Rotation: $[\alpha]_D$ = +40.0 (*c* = 0.43, $CHCl_3$);

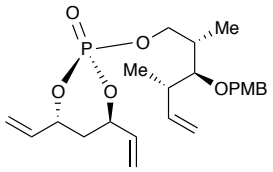
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.18 (ddd, *J* = 16.1, 8,7, 1.3 Hz, 1H), 5.89 (ddd, *J* = 9.9, 4.8, 1.8 Hz, 1H), 5.81 (dd, *J* = 16.2, 4.8 Hz, 1H), 5.45 (dd, *J* = 17.1, 0.9 Hz, 1H), 5.28 (d, *J* = 10.6 Hz, 1H), 5.18–5.07 (m, 2H), 4.68 (s, 2H), 4.26 (s, 1H), 3.95 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.52 (dd, *J* = 7.1, 3.0 Hz, 1H), 3.39 (s, 3H), 2.70 (s, 1H), 2.22 (ddd, *J* = 14.6, 12.2, 5.2 Hz, 1H), 2.15 (s, 1H), 1.83 (d, *J* = 14.6 Hz, 1H), 1.14 (d, *J* = 7.0 Hz, 3H), 1.07 (d, *J* = 7.2 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.2, 135.3 (d, J_{CP} = 10 Hz), 128.7, 127.5, 117.0 (d, J_{CP} = 0.7 Hz), 96.9, 86.0, 77.2 (d, J_{CP} = 6.2 Hz), 76.2 (d, J_{CP} = 6.3 Hz), 75.1 (d, J_{CP} = 7.0 Hz), 60.4, 55.9, 35.5, 21.0, 14.2;

^{31}P NMR (162 MHz, $CDCl_3$) δ -7.01;

HRMS: cald. for $C_{15}H_{25}O_6PNa$ $(M+Na)^+$ 355.1286; found 355.1280 (TOF MS ES+).

(4*R*,6*R*)-2-(((2*S*,3*S*,4*S*)-3-((4-methoxybenzyl)oxy)-2,4-dimethylhex-5-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (15):



FTIR (neat): 2971, 1651, 1521, 1282, 1249, 1112, 1008, 964, 927, 827 cm^{-1};

Optical Rotation: $[\alpha]_D$ = -16.4 (*c* = 1.8, $CHCl_3$);

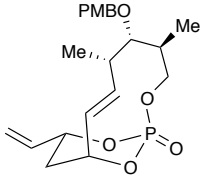
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.05–5.87 (m, 3H), 5.46 (ddd, *J* = 17.1, 1.5, 0.9 Hz, 1H), 5.37 (ddd, *J* = 17.1, 1.5 0.9 Hz, 1H), 5.29 (dddd, *J* = 10.8, 9.1, 1.1, 1.1 Hz, 2H), 5.11 (ddd, *J* = 17.3, 1.7, 1.4 Hz, 1H), 5.08–5.04 (m, 1H), 5.04 (ddd, *J* = 10.3, 1.6, 1.1 Hz, 1H), 4.98–4.89 (m, 1H), 4.50 (dd, *J* = 31.2, 10.5 Hz, 2H), 4.28–4.07 (m, 2H), 3.80 (s, 3H), 3.27 (dd, *J* = 6.9, 4.9 Hz, 1H), 2.52–2.42 (m, 1H), 2.16 (dddd, *J* = 14.0, 7.7, 4.7, 1.5 Hz, 1H), 2.10–2.00 (m, 2H), 1.06 (d, *J* = 7.0 Hz, 3H), 1.05 (d, *J* = 7.1 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 142.1, 135.1 (d, J_{CP} = 3.5 Hz), 135.0 (d, J_{CP} = 6.8 Hz), 130.74, 129.3, 117.8, 117.5, 114.3, 113.7, 83.8, 77.3 (d, J_{CP} = 4.1 Hz), 76.1 (d, J_{CP} = 6.1 Hz), 74.3, 70.1 (d, J_{CP} = 6.1 Hz), 55.2, 40.1, 37.0 (d, J_{CP} = 7.6 Hz), 35.1 (d, J_{CP} = 7.6 Hz), 14.6, 14.1;

^{31}P NMR (162 MHz, $CDCl_3$) δ -6.81;

HRMS: cald. for $C_{23}H_{33}O_6PNa$ $(M+Na)^+$ 459.1912; found 459.1908 (TOF MS ES+).

(1*R*,4*S*,5*S*,6*S*,9*R*,11*R*,*E*)-5-((4-methoxybenzyl)oxy)-4,6-dimethyl-11-vinyl-2,12,13-trioxa-1-phosphabicyclo[7.3.1]tridec-7-ene 1-oxide (16):



FTIR (neat): 2979, 1659, 1515, 1279, 1239, 1111, 1002, 957, 922, 821 cm^{-1};

Optical Rotation: $[\alpha]_D$ = -18.5 (*c* = 0.26, $CHCl_3$);

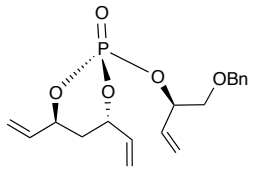
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 5.88–5.77 (m, 2H), 5.73 (dd, *J* = 15.8, 3.9 Hz, 1H), 5.36 (d, *J* = 17.0 Hz, 1H), 5.24 (d, *J* = 10.5 Hz, 1H), 5.12 (ddd, *J* = 24.4, 5.1, 3.8 Hz, 1H), 5.04 (d, *J* = 7.6 Hz, 1H), 4.51 (d, *J* = 10.7 Hz, 1H) 4.40 (d, *J* = 10.7, 1H), 4.18 (dd, *J* = 10.4, 8.5 Hz, 1H), 3.90 (dd, *J* = 11.0, 6.6 Hz, 1H), 3.82 (s, 3H), 3.11 (d, *J* = 7.2, 1H), 2.55 (br.s, 1H), 2.33 (br.s, 1H), 2.20 (ddd, *J* = 14.5, 12.2, 5.3 Hz, 1H), 1.78 (d, *J* = 14.4 Hz, 1H), 1.12 (d, *J* = 6.6 Hz, 3H), 1.07 (d, *J* = 7.3 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 139.0, 135.3 (d, J_{CP} = 9.9 Hz), 130.2, 129.5, 127.0, 117.0, 113.8, 87.4, 77.2 (d, J_{CP} = 6.1 Hz), 76.4 (d, J_{CP} = 6.4 Hz), 75.3 (d, J_{CP} = 6.0 Hz), 72.0, 65.7, 55.3, 35.6 (d, J_{CP} = 3.2 Hz), 35.5, 34.60 (d, J_{CP} = 8.9 Hz), 17.9;

^{31}P NMR (162 MHz, $CDCl_3$) δ -8.02;

HRMS: cald. for $C_{21}H_{29}O_6PNa$ $(M+Na)^+$ 431.1599; found 431.1605 (TOF MS ES+).

(4*S*,6*S*)-2-(((*R*)-1-(benzyloxy)but-3-en-2-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (18):



FTIR (neat): 2924, 2856, 1454, 1281, 1009, 741 cm^{-1};

Optical Rotation: $[\alpha]_D$ = +47.6 (*c* = 0.38, $CHCl_3$);

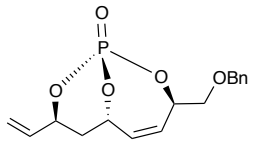
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.26 (m, 5H), 6.05 (ddd, J = 16.9, 10.6, 6.0 Hz, 1H), 5.99–5.85 (m, 1H), 5.94 (ddd, *J* = 17.1, 10.6, 6.5 Hz, 1H), 5.46 (d, *J* = 6.7 Hz, 1H), 5.42 (d, *J* = 6.8 Hz, 1H), 5.37 (d, *J* = 17.1 Hz, 1H), 5.32 (d, *J* = 4.6 Hz, 1H), 5.29 (d, *J* = 4.6 Hz, 1H), 5.26 (d, *J* = 10.6 Hz, 1H), 5.11–4.95 (m, 3H), 4.62 (d, *J* = 12.1 Hz, 1H), 4.57 (d, *J* = 12.1 Hz, 1H), 3.71–3.61 (m, 2H), 2.12 (ddddd, J = 16.4, 14.8, 10.8, 5.2, 1.7 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9 (s), 135.2 (d, J_{CP} = 3.3 Hz), 135.0 (s), 135.0 (s), 133.8 (d, J_{CP} = 4.1 Hz), 128.3, 127.6, 118.7, 117.8, 117.4, 78.2 (d, J_{CP} = 5.6 Hz), 77.9 (d, J_{CP} = 6.7 Hz), 76.0 (d, J_{CP} = 6.1 Hz), 73.2, 72.2 (d, J_{CP} = 5.9 Hz), 35.2 (d, J_{CP} = 7.7 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -8.23;

HRMS: cald. for $[C_{18}H_{23}O_5P]_2Na$ $(2M+Na)^+$ 723.2464; found 723.2456 (TOF MS ES+).

(1*S*,3*R*,6*S*,8*S*)-3-((benzyloxy)methyl)-8-vinyl-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (*trans*-19):



FTIR (neat): 2924, 2866, 1454, 1300, 1086, 741 cm^{-1};

Optical Rotation: $[\alpha]_D$ = +146.0 (*c* = 0.49, $CHCl_3$);

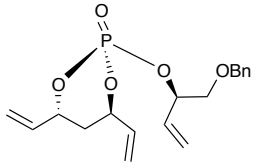
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.28 (m, 5H), 6.02 (ddd, *J* = 12.3, 5.9, 1.8 Hz, 1H), 5.86 (dddd, *J* = 17.1, 10.5, 5.2, 1.7 Hz, 1H), 5.66 (dd, *J* = 12.5, 4.4 Hz, 1H), 5.44 (d, *J* = 17.1 Hz, 1H), 5.28 (d, *J* = 10.6 Hz, 1H), 5.15 (ddd, *J* = 24.6, 4.2, 4.2 Hz, 1H), 5.02 (dd, *J* = 11.6, 4.6 Hz, 1H), 4.92 (ddd, *J* = 29.2, 12.5, 6.0 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.06 (dd, *J* = 10.3, 7.0 Hz, 1H), 3.84 (dd, *J* = 10.3, 5.9 Hz, 1H), 2.26 (ddd, *J* = 14.5, 11.9, 6.1 Hz, 1H), 1.79 (d, *J* = 14.6 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.6, 134.7 (d, J_{CP} = 10.4 Hz), 129.8, 128.9, 128.4, 127.9, 127.8, 117.5, 76.3 (d, J_{CP} = 7.8 Hz), 75.9 (d, J_{CP} = 6.6 Hz), 75.8 (d, J_{CP} = 6.8 Hz), 73.7, 72.0, 34.4 (d, J_{CP} = 5.7 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -7.86;

HRMS: cald. for $[C_{16}H_{19}O_5P]_2Na$ $(2M+Na)^+$ 667.1838; found 667.1848 (TOF MS ES+).

(4*R*,6*R*)-2-(((*R*)-1-(benzyloxy)but-3-en-2-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (20):



FTIR (neat): 3085, 2922, 1427, 1285, 1007, 739 cm^{-1};

Optical Rotation: $[\alpha]_D$ = -53.9 (*c* = 1.7, $CHCl_3$);

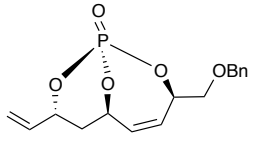
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.27 (m, 5H), 6.09 (dddd, *J* = 17.1, 10.6, 6.4, 0.8 Hz, 1H), 5.91 (ddd, *J* = 17.0, 10.7, 6.2 Hz, 1H), 5.82 (dddd, *J* = 17.3, 10.6, 5.2, 1.7 Hz, 1H), 5.46 (ddd, *J* = 17.2, 1.2, 1.2 Hz, 1H), 5.38 (ddd, *J* = 4.7, 1.0, 1.0 Hz, 1H), 5.34 (ddd, *J* = 4.7, 1.1, 1.1 Hz, 1H), 5.31 (d, *J* = 10.9 Hz, 1H), 5.28 (ddd, *J* = 10.8, 1.0, 1.0 Hz, 1H), 5.23 (ddd, *J* = 10.7, 1.0, 1.0 Hz, 1H), 5.10 – 4.97 (m, 3H), 4.61 (d, *J* = 11.9 Hz, 1H), 4.54 (d, *J* = 11.9 Hz, 1H), 3.64–3.61 (m, 2H), 2.12 (dddd, *J* = 14.5, 8.0, 4.9, 1.6 Hz, 1H), 2.03 (dddd, *J* = 14.8, 5.5, 3.7, 1.8 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 135.2, 135.2 (d, J_{CP} = 4.8 Hz), 133.4 (d, J_{CP} = 4.0 Hz), 128.4, 127.8, 127.7, 118.6, 118.0, 117.1, 78.2 (d, J_{CP} = 6.8 Hz), 77.8 (d, J_{CP} = 5.5 Hz), 75.9 (d, J_{CP} = 6.1 Hz), 73.2 (s), 72.3 (d, J_{CP} = 5.8 Hz), 35.3 (d, J_{CP} = 7.7 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -8.37;

HRMS: cald. for $[C_{18}H_{23}O_5P]_2Na$ $(2M+Na)^+$ 723.2464; found 723.2400 (TOF MS ES+).

(1*R*,3*R*,6*R*,8*R*)-3-((benzyloxy)methyl)-8-vinyl-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (*cis*-21):



FTIR (neat): 2924, 2854, 1454, 1298, 968, 764 cm^{-1};

Optical Rotation: $[\alpha]_D$ = -17.6 (*c* = 0.42, $CHCl_3$);

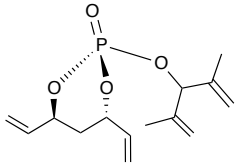
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.28 (m, 5H), 6.04 (ddd, *J* = 11.9, 2.5, 2.5 Hz, 1H), 5.84 (ddd, *J* = 10.6, 5.9, 2.0 Hz, 1H), 5.61 (ddd, *J* = 11.9, 3.9, 2.4 Hz, 1H), 5.43 (d, *J* = 17.2 Hz, 1H), 5.33–5.27 (m, 1H), 5.27 (d, *J* = 10.6 Hz, 1H), 5.27–5.16 (m, 1H), 5.04 (dd, *J* = 11.9, 5.3 Hz, 1H), 4.64 (dd, *J* = 12.1 Hz, 1H), 4.59 (dd, *J* = 12.1 Hz, 1H), 3.72 (ddd, *J* = 10.2, 5.0, 1.0 Hz, 1H), 3.63 (dd, *J* = 10.3, 6.0 Hz, 1H), 2.23 (ddd, *J* = 14.7, 12.1, 6.2 Hz, 1H), 1.80 (dd, *J* = 14.4, 2.0 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.5, 134.7 (d, J_{CP} = 10.4 Hz), 130.1, 129.4, 128.5, 127.9, 127.7, 117.4, 77.1, 76.2 (d, J_{CP} = 6.0 Hz), 73.5, 72.2 (d, J_{CP} = 5.9 Hz), 71.2 (d, J_{CP} = 12.1 Hz), 34.9 (d, J_{CP} = 5.9 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -5.74;

HRMS: cald. for $[C_{16}H_{19}O_5P]_2Na$ $(2M+Na)^+$ 667.1838; found 667.1835 (TOF MS ES+).

(4*S*,6*S*)-2-((2,4-dimethylpenta-1,4-dien-3-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (22):



FTIR (thin film): 2922, 1827, 1649, 1448, 1375, 1281, 1140, 1119, 1003, 928 cm^{-1};

Optical Rotation: $[\alpha]_D$ = +48.40 (*c* = 0.75, $CHCl_3$);

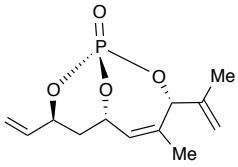
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (ddd, *J* = 16.7, 10.7, 5.5 Hz 1H), 5.90 (dddd, *J* = 17.3, 10.6, 5.1, 1.5 Hz, 1H), 5.45 (d, *J* = 22.0 Hz, 1H), 5.39 (d, *J* = 21.6 Hz, 1H), 5.33–5.27 (m, 2H), 5.20–5.11 (m, 3H), 5.11–5.03 (m, 1H), 5.01 (s, 2H), 4.99–4.92 (m, 1H), 2.17 (dddd, *J* = 12.8, 7.8, 4.8, 1.4 Hz, 1H), 2.07 (dddd, *J* = 14.7, 5.4, 3.7, 1.8 Hz, 1H), 1.66 (s, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.3 (d, J_{CP} = 4.3 Hz), 141.1 (d, J_{CP} = 5.3 Hz), 135.2 (d, J_{CP} = 3.2 Hz), 135.1 (d, J_{CP} = 7.5 Hz), 117.7, 117.5, 114.4, 113.5, 84.7 (d, J_{CP} = 5.2 Hz), 77.6 (d, J_{CP} = 6.8 Hz), 76.0 (d, J_{CP} = 6.1 Hz), 35.1 (d, J_{CP} = 7.7 Hz), 18.0, 17.4;

^{31}P NMR (162 MHz, $CDCl_3$) δ -8.58;

HRMS cald for $C_{14}H_{21}O_4PNa$ $(M+Na)^+$ 307.1075; found 307.1067 (TOF MS ES+).

(1*S*,3*R*,6*S*,8*S*)-4-methyl-3-(prop-1-en-2-yl)-8-vinyl-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (*cis*-23):



FTIR (thin film): 2922, 1726, 1298, 1026, 966, 768 cm^{-1};

Optical Rotation: $[\alpha]_D$ = + 103.14(*c* = 0.17, $CHCl_3$);

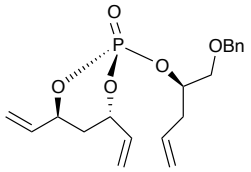
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.89 (dddd, *J* = 17.2, 10.8, 5.1, 2.1 Hz 1H), 5.59 (d, *J* = 5.3 Hz, 1H), 5.45 (d, *J* = 17.2 Hz, 1H), 5.43–5.39 (m, 1H), 5.28 (d, *J* = 10.7 Hz, 1H), 5.12 (d, *J* = 21.5 Hz, 1H), 5.09–5.03 (m, 3H), 2.19 (ddd, *J* = 14.5, 12.1, 6.2 Hz, 1H), 1.93–1.81 (m, 1H), 1.79 (s, 3H), 1.75 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1 (d, J_{CP} = 10.1 Hz), 138.1, 135.0 (d, J_{CP} = 10.2 Hz), 124.9, 117.1 (d, J_{CP} = 1.0 Hz), 116.6, 80.6 (d, J_{CP} = 5.7 Hz), 76.7 (d, J_{CP} = 6.2 Hz), 76.5 (d, J_{CP} = 6.2 Hz), 35.3 (d, J_{CP} = 6.2 Hz), 22.2, 17.5;

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) -5.91;

HRMS cald for $(C_{12}H_{17}O_4P)_2Na(2M+Na)^+$ 535.1627; found 536.1624 (TOF MS ES+).

(4*S*,6*S*)-2-(((*R*)-1-(benzyloxy)pent-4-en-2-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (26):



FTIR (neat): 2924, 2858, 1454, 1283, 1007, 739 cm^{-1};

Optical Rotation: $[\alpha]_D$ = +37.9 (*c* = 0.33, $CHCl_3$);

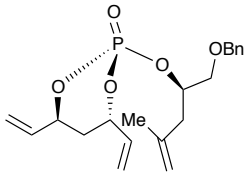
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.27 (m, 5H), 6.04 (ddd, *J* = 17.2, 10.7, 6.1 Hz, 1H), 5.90 (dddd, *J* = 17.3, 10.6, 5.2, 1.7 Hz, 1H), 5.80 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.45 (ddd, *J* = 17.2, 1.3, 1.3 Hz, 1H), 5.35 (ddd, *J* = 17.2, 1.3, 1.3 Hz, 1H), 5.30 (ddd, *J* = 10.6, 1.2, 1.2 Hz, 1H), 5.23 (ddd, *J* = 10.6, 1.2, 1.2 Hz, 1H), 5.15 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.12–5.08 (m, 1H), 5.08–4.96 (m, 2H), 4.71–4.62 (m, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 3.70–3.59 (m, 2H), 2.62–2.45 (m, 2H), 2.18–2.02 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.0, 135.2 (d, J_{CP} = 3.2 Hz), 135.1, 135.0, 133.0, 128.3, 127.6, 118.4, 117.8, 117.3, 77.9 (d, J_{CP} = 6.8 Hz), 77.2, 75.9 (d, J_{CP} = 6.1 Hz), 73.22, 71.2 (d, J_{CP} = 4.4 Hz), 36.7 (d, J_{CP} = 4.9 Hz), 35.2 (d, J_{CP} = 7.6 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -8.26;

HRMS: cald. for $[C_{19}H_{25}O_5P]_2Na$ $(2M+Na)^+$ 751.2777; found 751.2770 (TOF MS ES+).

(4*S*,6*S*)-2-(((*R*)-1-(benzyloxy)-4-methylpent-4-en-2-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane-2-oxide (27):



FTIR (thin film): 2920, 2359,1827, 1649, 1454, 1283, 1121, 1097, 999, 929, 739 cm^{-1};

Optical Rotation: $[\alpha]_D$ = +40.72 (*c* = 1.04, $CHCl_3$);

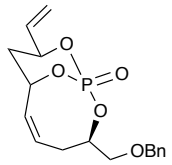
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.27 (m, 5H), 6.06 (ddd, *J* = 17.1, 10.6, 6.2 Hz, 1H), 5.89 (dddd, *J* = 17.2, 10.6, 5.2, 1.7 Hz, 1H), 5.43 (ddd, *J* = 17.1, 1.3, 1.1 Hz, 1H), 5.35 (ddd, *J* = 17.2, 1.4, 1.0 Hz, 1H), 5.28 (dd, *J* = 11.7, 1.1 Hz, 1H), 5.23 (dd, *J* = 10.6, 1.1 Hz, 1H), 5.08–4.95 (m, 2H), 4.86–4.80 (m, 2H), 4.80–4.71 (m, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 3.71–3.63 (m, 2H), 2.53–2.40 (m, 2H), 2.14 (dddd, *J* = 14.6, 8.1, 4.9, 1.5 Hz, 1H), 2.04 (dddd, *J* = 14.7, 5.4, 3.8, 1.8 Hz, 1H), 1.77 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 138.1, 135.3 (d, J_{CP} = 3.0 Hz), 135.2 (d, J_{CP} = 7.8 Hz), 128.3, 127.7, 127.6 (d, J_{CP} = 5.8 Hz), 117.9 117.2, 113.9, 78.1 (d, J_{CP} = 6.9 Hz), 76.1 (d, J_{CP} = 6.3 Hz), 75.8 (d, J_{CP} = 6.2 Hz), 73.3, 71.8 (d, J_{CP} = 3.2 Hz), 40.9 (d, J_{CP} = 5.8 Hz), 35.3 (d, J_{CP} = 7.6 Hz), 22.2;

^{31}P NMR (162 MHz, $CDCl_3$) δ -8.20;

HRMS cald for $C_{20}H_{27}O_5PNa$ $(M+Na)^+$ 401.1494; found 401.1512 (TOF MS ES+).

(1*S*,3*R*,7*S*,9*S*,*Z*)-3-((benzyloxy)methyl)-9-vinyl-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-5-ene 1-oxide (*trans*-28):



FTIR (neat): 2926, 2854, 1454, 1283, 1020, 756 cm^{-1};

Optical Rotation: $[\alpha]_D$ = +61.8 (*c* = 0.45, $CHCl_3$);

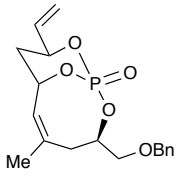
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.28 (m, 5H), 5.89–5.80 (m, 2H), 5.53 (d, *J* = 11.8 Hz, 1H), 5.41 (ddd, *J* = 17.0, 1.1, 1.1 Hz, 1H), 5.35–5.23 (m, 1H), 5.26 (ddd, *J* = 10.5, 0.9, 0.9 Hz, 1H), 5.06–4.99 (m, 1H), 4.67 (d, *J* = 11.9 Hz, 1H), 4.58 (d, *J* = 11.9 Hz, 1H), 4.16 (dddt, *J* = 30.8, 13.0, 6.4, 3.3 Hz, 1H), 4.07 (dd, *J* = 9.7, 6.1 Hz, 1H), 3.74 (dd, *J* = 9.8, 6.4 Hz, 1H), 3.17–3.07 (m, 1H), 2.36 (ddd, *J* = 14.0, 8.7, 2.9 Hz, 1H), 2.20 (ddd, *J* = 14.5, 11.9, 6.0 Hz, 1H), 1.81 (ddd, *J* = 14.5, 3.7, 1.9 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 135.0 (d, J_{CP} = 10.2 Hz), 131.2, 128.4, 127.8, 127.7, 126.8, 117.2 (d, J_{CP} = 1.4 Hz), 78.3 (d, J_{CP} = 7.2 Hz), 76.9 (d, J_{CP} = 6.0 Hz), 76.0 (d, J_{CP} = 5.9 Hz), 73.6, 72.2, 36.0 (d, J_{CP} = 6.4 Hz), 29.5;

^{31}P NMR (162 MHz, $CDCl_3$) δ -10.79;

HRMS: cald. for $[C_{17}H_{21}O_5P]_2Na$ $(2M+Na)^+$ 695.2151; found 695.2125 (TOF MS ES+).

(1*S*,3*R*,7*S*,9*S*,*Z*)-3-((benzyloxy)methyl)-5-methyl-9-vinyl-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-5-ene 1-oxide (*trans*-29):



FTIR (thin film): 2918, 2849, 1718, 1582, 1364, 1333, 1283, 1126, 1090, 1001, 901 cm^{-1};

Optical Rotation: $[\alpha]_D$ = + 24.51(*c* =0.16, $CHCl_3$);

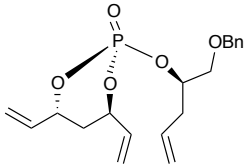
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.27 (m, 5H), 5.84 (dddd, *J* = 17.2, 10.6, 5.4, 2.1 Hz, 1H), 5.42 (ddd, *J* = 17.1, 5.8, 4.6 Hz, 1H), 5.34–5.16 (m, 2H), 5.24 (m, ddd, *J* = 10.7, 1.2, 1.1 Hz, 1H), 5.02 (dd, *J* = 11.7, 5.4 Hz, 1H), 4.68 (dd, *J* = 11.9, 4.3 Hz, 1H), 4.60 (dd, *J* = 11.9, 5.1 Hz, 1H), 4.08 (dd, *J* = 10.0, 6.2 Hz, 1H), 3.75 (dd, *J* = 10.0, 6.5 Hz, 1H), 3.38–3.26 (m, 1H), 2.21–2.14 (m, 1H), 2.09 (dd, *J* = 13.9, 3.1 Hz, 1H), 1.92–1.89 (m, 1H), 1.88 (dd, *J* = 2.4, 1.4 Hz, 3H), 1.76 (ddd, *J* = 14.5, 3.9, 1.9 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 135.5, 128.8, 128.4, 127.9, 127.7, 124.6, 117.2, 77.6 (d, J_{CP} = 7.4 Hz), 75.3 (d, J_{CP} = 5.8 Hz), 73.7, 72.3, 36.7 (d, J_{CP} = 6.6 Hz), 34.7, 34.1, 29.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) -10.34;

HRMS cald for $C_{18}H_{23}O_5PNa$ $(M+Na)^+$ 373.1181; found 373.1176 (TOF MS ES+).

(4*R*,6*R*)-2-(((*R*)-1-(benzyloxy)but-3-en-2-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (30):



FTIR (neat): 2924, 2862, 1454, 1283, 1004, 740 cm^{-1};

Optical Rotation: $[\alpha]_D$ = -57.6 (*c* = 0.46, $CHCl_3$);

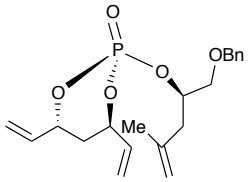
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.26 (m, 5H), 6.08 (ddd, *J* = 17.0, 10.6, 6.2 Hz, 1H), 5.87–5.74 (m, 2H), 5.36 (d, *J* = 11.0 Hz, 1H), 5.32 (d, *J* = 11.0 Hz, 1H), 5.28 (d, *J* = 10.6 Hz, 1H), 5.22 (d, *J* = 10.6 Hz, 1H), 5.13 (dd, *J* = 17.03, 1.6 Hz, 1H), 5.10 (d, *J* = 9.8, 1H), 5.07–4.96 (m, 2H), 4.68–4.60 (m, 1H), 4.58 (d, *J* = 11.8 Hz, 1H), 4.50 (d, *J* = 11.8 Hz, 1H), 3.65–3.55 (m, 2H), 2.60–2.47 (m, 2H), 2.09 (ddd, *J* = 8.1, 4.9, 1.6 Hz, 1H), 2.01 (dddd, *J* = 14.7, 5.4, 3.9, 1.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8, 135.2 (d, J_{CP} = 6.4 Hz), 135.2 (d, J_{CP} = 1.0 Hz), 132.7, 128.3, 127.7, 127.7, 118.4, 117.9, 117.0, 78.1 (d, J_{CP} = 6.8 Hz), 77.0 (d, J_{CP} = 6.3 Hz), 75.7 (d, J_{CP} = 6.0 Hz), 73.2, 71.3 (d, J_{CP} = 4.9 Hz), 36.7 (d, J_{CP} = 4.3 Hz), 35.3 (d, J_{CP} = 7.6 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -8.19;

HRMS: cald. for $[C_{19}H_{25}O_5P]_2Na$ $(2M+Na)^+$ 751.2777; found 751.2760 (TOF MS ES+).

(4*R*,6*R*)-2-(((*R*)-1-(benzyloxy)-4-methylpent-4-en-2-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (31):



FTIR (thin film): 2924, 1827, 1645, 1454, 1285, 1120, 1003, 926 cm^{-1};

Optical Rotation: $[\alpha]_D$ = - 53.0 (*c* = 2.61, $CHCl_3$);

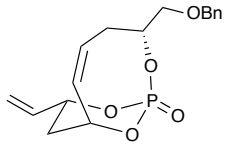
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.28 (m, 5H), 6.08 (dddd, *J* = 17.2, 10.6, 6.3, 0.8 Hz, 1H), 5.82 (dddd, *J* = 17.4, 10.6, 5.2, 1.7 Hz, 1H), 5.37(ddd, *J* = 7.4, 1.4, 1.2 Hz, 1H), 5.32 (ddd, *J* = 7.2, 1.4, 1.1 Hz, 1H),), 5.27 (ddd, *J* = 10.5, 1.2, 1.0 Hz, 1H), 5.22 (ddd, *J* = 10.6, 1.3, 1.1 Hz, 1H), 5.06–4.97 (m, 2H), 4.86–4.78 (m, 2H), 4.77–4.71 (m, 1H), 4.58 (d, *J* = 11.9 Hz, 1H), 4.52 (d, *J* = 11.8 Hz, 1H) 3.66 (ddd, *J* = 10.7, 3.5, 1.7 Hz, 1H), 3.58 (dd, *J* = 10.7, 5.8 Hz, 1H), 2.55 (dd, *J* = 14.2, 6.6 Hz, 1H), 2.43 (dd, *J* = 14.1, 7.1 Hz, 1H), 2.10 (dddd, *J* = 14.4, 8.0, 4.8, 1.6 Hz, 1H), 2.01 (dddd, *J* = 14.7, 5.5, 3.9, 1.8 Hz, 1H), 1.79 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.9, 137.9, 135.3, 135.3 (d, J_{CP} = 3.0 Hz), 128.3, 127.8, 127.7 (d, J_{CP} = 5.4 Hz), 117.8, 117.0, 114.0, 78.1 (d, J_{CP} = 6.8 Hz), 76.1 (d, J_{CP} = 6.1 Hz), 75.71 (d, J_{CP} = 6.0 Hz), 73.3, 71.6 (d, J_{CP} = 4.3 Hz), 40.6 (d, J_{CP} = 4.8 Hz), 35.3 (d, J_{CP} = 7.6 Hz), 22.6;

^{31}P NMR (162 MHz, $CDCl_3$) δ -8.09;

HRMS cald for $C_{20}H_{27}O_5PNa$ $(M+Na)^+$ 401.1494; found 401.1479 (TOF MS ES+).

(1R,3R,7R,9R,Z)-3-((benzyloxy)methyl)-9-vinyl-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-5-ene 1-oxide (*cis*-32):



FTIR (neat): 2924, 2854, 1454, 1292, 1018, 743 cm^{-1};

Optical Rotation: $[\alpha]_D$ = +3.5 (*c* = 0.46, $CHCl_3$);

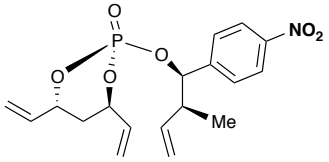
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.28 (m, 5H), 5.84 (dddd, *J* = 17.1, 10.7, 5.3, 2.1 Hz, 1H), 5.73 (ddd, *J* = 20.5, 8.7, 2.8 Hz, 1H), 5.50 (dd, *J* = 11.8, 1.8 Hz, 1H), 5.41 (dd, *J* = 17.2, 1.3 Hz, 1H), 5.34–5.23 (m, 1H), 5.26 (dd, *J* = 10.7, 1.0 Hz, 1H), 5.03 (dd, *J* = 11.9, 5.0 Hz, 1H), 4.73 (ddd, *J* = 12.7, 6.8, 2.3 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 3.55 (dd, *J* = 10.0, 5.4 Hz, 1H), 3.45 (ddd, *J* = 9.9, 7.1, 0.7 Hz, 1H), 3.38–3.29 (m, 1H), 2.38 (dd, *J* = 14.1, 8.7 Hz, 1H), 2.19 (ddd, *J* = 14.6, 12.0, 5.9 Hz, 1H), 1.81 (dd, *J* = 14.6, 1.9 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 135.0 (d, J_{CP} = 10.0 Hz), 131.2, 128.4, 127.8, 127.6, 125.3, 117.2 (d, J_{CP} = 1.3 Hz), 78.3 (d, J_{CP} = 7.1 Hz), 77.1 (d, J_{CP} = 6.1 Hz), 73.2, 72.4 (d, J_{CP} = 4.8 Hz), 70.4 (d, J_{CP} = 15.1 Hz), 36.2 (d, J_{CP} = 6.5 Hz), 27.4;

^{31}P NMR (162 MHz, $CDCl_3$) δ -9.29;

HRMS: cald. for $[C_{17}H_{21}O_5P]_2Na$ $(2M+Na)^+$ 695.2151; found 695.2162 (TOF MS ES+).

(4*R*,6*R*)-2-(((1*R*,2*S*)-2-methyl-1-(4-nitrophenyl)but-3-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (36):



FTIR (neat): 3080, 2969, 2913, 1617, 1525, 1339, 1281, 1102, 1019, 921, 879, 751 cm^{-1};

Optical Rotation: $[\alpha]_D$ = –44.8 (*c* = 0.5, $CHCl_3$);

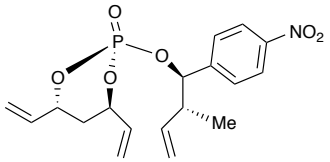
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 6.01 (ddd, *J* = 16.4, 10.7, 5.4 Hz, 1H), 5.72 (ddd, *J* = 15.9, 10.6, 5.3 Hz, 1H), 5.61 (ddd, *J* = 17.8, 9.0, 5.5 Hz, 1H), 5.43–5.31 (m, 3H), 5.18 (ddd, *J* = 6.0, 2.7, 0.9 Hz, 2H), 5.14–5.06 (m, 1H), 5.02 (d, *J* = 10.3 Hz, 1H), 4.97 (dd, *J* = 17.2, 1.0 Hz, 1H), 4.69–4.62 (m, 1H), 2.81–2.73 (m, 1H), 2.17–2.10 (m, 1H), 2.01 (dddd, *J* = 14.8, 5.3, 3.6, 1.8 Hz, 1H), 1.14 (d, *J* = 6.8 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 145.9 (d, J_{CP} = 2.3 Hz), 137.3, 134.9 (d, J_{CP} = 3.2 Hz), 134.4 (d, J_{CP} = 7.3 Hz), 127.9, 123.3 (d, J_{CP} = 5.1 Hz), 118.0 (d, J_{CP} = 14.5 Hz), 117.6, 117.2, 82.8 (d, J_{CP} = 6.0 Hz), 77.9 (d, J_{CP} = 6.8 Hz), 75.9 (d, *J* = 6.1 Hz), 44.2 (d, J_{CP} = 6.7 Hz), 34.9 (d, J_{CP} = 7.7 Hz), 15.6;

^{31}P NMR (162 MHz, $CDCl_3$) δ -7.54;

HRMS: cald. for $C_{18}H_{22}NO_6PNa$ $(M+Na)^+$ 402.1082; found 402.1069 (TOF MS ES+).

(4*R*,6*R*)-2-(((1*R*,2*R*)-2-methyl-1-(4-nitrophenyl)but-3-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (37):



FTIR (neat): 2972, 2933, 1610, 1521, 1348, 1282, 1112, 1004, 927, 885, 750 cm^{-1};

Optical Rotation: $[\alpha]_D$ = -32.8 (*c* = 0.6, $CHCl_3$);

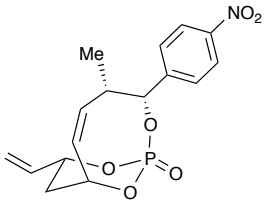
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 6.01 (dddd, *J* = 17.0, 10.7, 5.3, 0.7 Hz, 1H), 5.81–5.70 (m, 2H), 5.43–5.38 (m, 2H), 5.36 (d, *J* = 10.9 Hz, 1H), 5.21 (d, *J* = 17.0 Hz, 1H), 5.19 (d, *J* = 10.9 Hz, 1H), 5.11 (d, *J* = 10.3 Hz, 1H), 5.13–5.06 (m, 1H), 5.02 (d, *J* = 17.1 Hz, 1H), 4.76–4.69 (m, 1H), 2.77–2.68 (m, 1H), 2.15 (dddd, *J* = 9.5, 8.0, 4.5, 2.1 Hz, 1H), 2.03 (dddd, *J* = 14.8, 5.4, 3.6, 1.8 Hz, 1H), 1.01 (d, *J* = 6.9 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 146.1 (d, J_{CP} = 2.5 Hz), 137.7, 135.0 (d, J_{CP} = 3.2 Hz), 134.5 (d, J_{CP} = 7.2 Hz), 127.7, 123.5, 117.9, 117.7, 117.1, 82.8 (d, J_{CP} = 6.0 Hz), 77.9 (d, J_{CP} = 6.8 Hz), 76.1 (d, J_{CP} = 6.1 Hz), 44.4 (d, J_{CP} = 6.5 Hz), 34.9 (d, J_{CP} = 7.7 Hz), 15.8;

^{31}P NMR (162 MHz, $CDCl_3$) δ -7.61;

HRMS: cald. for $C_{18}H_{22}NO_6PNa$ $(M+Na)^+$ 402.1082; found 402.1074 (TOF MS ES+).

(1*R*,3*R*,4*S*,7*R*,9*R*,*Z*)-4-methyl-3-(4-nitrophenyl)-9-vinyl-2,10,11-trioxa-1 phosphabicyclo[5.3.1]undec-5-ene 1-oxide (*cis*,*syn*-38):



FTIR (neat): 2982, 2923, 1613, 1545, 1324, 1295, 1012, 975, 814, 759 cm^{-1};

Optical Rotation: $[\alpha]_D$ = +70.4 (*c* = 1.05, $CHCl_3$);

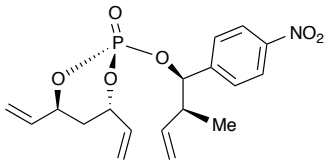
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 5.91 (dddd, *J* = 17.2, 10.7, 5.1, 2.3 Hz, 1H), 5.67 (d, *J* = 11.7 Hz, 1H), 5.51–5.44 (m, 2H), 5.38 (dd, *J* = 25.2, 4.8 Hz, 1H), 5.32 (ddd, *J* = 10.7, 1.1, 1.0 Hz, 1H), 5.30–5.21 (m, 2H), 4.09–4.01 (m, 1H), 2.31 (ddd, *J* = 14.7, 12.0, 6.1 Hz, 1H), 1.99 (ddd, *J* = 14.7, 3.7, 2.1 Hz, 1H), 0.80 (d, *J* = 6.9 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 143.4 (d, J_{CP} = 13.6 Hz), 134.7 (d, J_{CP} = 10.0 Hz), 131.6, 130.7, 128.2, 123.2, 117.5 (d, J_{CP} = 1.0 Hz), 78.4 (d, J_{CP} = 3.7 Hz), 78.3 (d, J_{CP} = 7.3 Hz), 77.7 (d, J_{CP} = 6.3 Hz), 36.2 (d, J_{CP} = 6.6 Hz), 34.2, 16.8;

^{31}P NMR (162 MHz, $CDCl_3$) δ -9.46;

HRMS: cald. for $2(C_{16}H_{18}NO_6P)Na$ $(2M+Na)^+$ 725.1641; found 725.1623 (TOF MS ES+).

(4*S*,6*S*)-2-(((1*R*,2*S*)-2-methyl-1-(4-nitrophenyl)but-3-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (40):



FTIR (neat): 3059, 2952, 2931, 1617, 1501, 1331, 1269, 1139, 1024, 927, 739 cm^{-1};

Optical Rotation: $[\alpha]_D$ = +32.9 (*c* = 0.93, $CHCl_3$);

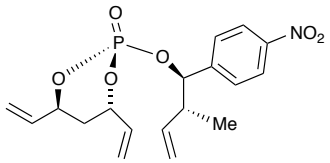
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 5.96–5.85 (m, 2H), 5.66 (ddd, *J* = 17.5, 8.8, 5.6 Hz, 1H), 5.48 (d, *J* = 17.1 Hz, 1H), 5.42 (dd, *J* = 8.5, 6.0 Hz, 1H), 5.33 (d, *J* = 10.7 Hz, 1H), 5.29 (d, *J* = 17.2 Hz, 1H), 5.25 (d, *J* = 10.6 Hz, 1H), 5.07–4.98 (m, 4H), 2.79–2.71 (m, 1H), 2.18 (dddd, *J* = 14.1, 7.6, 4.7, 1.6 Hz, 1H), 2.08 (dddd, *J* = 14.8, 5.6, 3.8, 1.8 Hz, 1H), 1.07 (d, *J* = 6.8 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 145.9 (d, J_{CP} = 3.1 Hz), 137.7, 134.8 (d, J_{CP} = 3.6 Hz), 134.7 (d, J_{CP} = 7.1 Hz), 127.8, 123.3, 118.0, 117.7, 116.9, 82.8 (d, J_{CP} = 6.0 Hz), 77.6 (d, J_{CP} = 6.8 Hz), 76.4 (d, J_{CP} = 6.3 Hz), 44.0 (d, J_{CP} = 6.1 Hz), 35.0 (d, J_{CP} = 7.9 Hz), 14.8;

^{31}P NMR (162 MHz, $CDCl_3$) δ -7.82;

HRMS: cald. for $C_{18}H_{22}NO_6PNa$ $(M+Na)^+$ 402.1082; found 402.1072 (TOF MS ES+).

(4*S*,6*S*)-2-(((1*R*,2*R*)-2-methyl-1-(4-nitrophenyl)but-3-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (41):



FTIR (neat): 2954, 2931, 1608, 1529, 1319, 1289, 1136, 1015, 920, 875, 751 cm^{-1};

Optical Rotation: $[\alpha]_D$ = +41.1 (*c* = 1.24, $CHCl_3$);

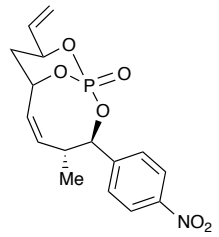
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 5.96–5.88 (m, 2H), 5.73 (ddd, *J* = 17.9, 10.3, 7.8Hz, 1H), 5.48 (d, *J* = 17.0 Hz, 1H), 5.39 (dd, *J* = 8.6, 6.2 Hz, 1H), 5.33 (d, *J* = 4.2 Hz, 1H), 5.30 (d, *J* = 11.1 Hz, 1H), 5.27 (d, *J* = 10.6 Hz, 1H), 5.09 (d, *J* = 10.3 Hz, 1H), 5.07–4.99 (m, 3H), 2.75–2.67 (m, 1H), 2.18 (dddd, *J* = 14.1, 7.6, 4.7, 1.5 Hz, 1H), 2.08 (dddd, *J* = 14.8, 5.6, 3.8, 1.8 Hz, 1H), 0.99 (d, *J* = 6.9 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 146.1 (d, J_{CP} = 2.9 Hz), 137.9, 134.7 (d, J_{CP} = 3.4 Hz), 134.7 (d, J_{CP} = 7.2 Hz), 127.6, 123.3, 118.0, 117.7, 117.0, 82.9 (d, J_{CP} = 5.9 Hz), 77.7 (d, J_{CP} = 6.8 Hz), 76.3 (d, J_{CP} = 6.3 Hz), 44.4 (d, J_{CP} = 6.2 Hz), 35.0 (d, J_{CP} = 7.8 Hz), 15.8;

^{31}P NMR (162 MHz, $CDCl_3$) δ -7.82;

HRMS: cald. for $C_{18}H_{22}NO_6PNa$ $(M+Na)^+$ 402.1082; found 402.1064 (TOF MS ES+).

(1*S*,3*R*,4*R*,7*S*,9*S*,*Z*)-4-methyl-3-(4-nitrophenyl)-9-vinyl-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-5-ene 1-oxide (*trans*,*anti*-43):



FTIR (neat): 2984, 2914, 1623, 1523, 1349, 1290, 1004, 970, 852, 750 cm^{-1};

Optical Rotation: $[\alpha]_D$ = +151.2 (*c* = 0.4, $CHCl_3$);

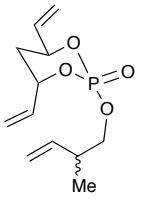
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.8 Hz, 2H), 7.74(d, *J* = 8.8 Hz, 2H), 5.86 (dddd, *J* = 17.1, 10.6, 5.5, 2.0 Hz, 1H), 5.66–5.58 (m, 2H), 5.40 (d, *J* = 17.2 Hz, 1H), 5.38 (dd, *J* = 24.8, 5.6 Hz, 1H), 5.27 (d, *J* = 10.6 Hz, 1H), 5.04 (dd, *J* = 11.8, 5.5 Hz, 1H), 4.59 (dd, *J* = 29.6, 11.7 Hz, 1H), 4.04–3.90 (m, 1H), 2.26 (ddd, *J* = 14.6, 12.0, 5.8 Hz, 1H), 1.87 (ddd, *J* = 14.6, 3.8, 1.8 Hz, 1H), 0.85 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.3, 142.9, 134.9 (d, J_{CP} = 10.3 Hz), 134.6, 130.1, 130.0, 123.8, 117.5 (d, J_{CP} = 1.3 Hz), 83.2 (d, J_{CP} = 6.6 Hz), 78.2 (d, J_{CP} = 7.3 Hz), 77.1 (d, J_{CP} = 6.5 Hz), 36.2 (d, J_{CP} = 6.4 Hz), 34.5, 18.3;

^{31}P NMR (162 MHz, $CDCl_3$) δ -11.71;

HRMS: cald. for $2(C_{16}H_{18}NO_6P)Na$ $(2M+Na)^+$ 725.1641; found 725.1647 (TOF MS ES+).

(4*S*,6*S*)-2-((2-methylbut-3-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (45a): *(pair of diastereomers detected by ^{13}C NMR)*



FTIR (thin film): 2964, 2926, 1647, 1458, 1283, 1140, 1119, 1013, 926 cm^{-1};

Optical Rotation: $[\alpha]_D$ = + 62.02(*c* = 1.24, $CHCl_3$);

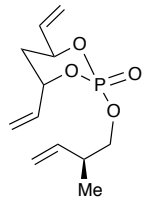
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (ddd, *J* = 16.6, 10.6, 6.2 Hz, 1H), 5.90 (ddddd, *J* = 17.7, 10.6, 5.2, 1.7, 0.7 Hz, 1H), 5.75 (dddd, *J* = 17.4, 10.2, 7.0, 2.7 Hz, 1H), 5.46 (ddd, *J* = 17.2, 1.1, 1.1 Hz, 1H), 5.37 (ddd, *J* = 17.2, 1.2, 0.9 Hz, 1H), 5.33 – 5.27 (m, 2H), 5.14–5.01 (m, 3H), 5.00–4.93 (m, 1H), 4.03–3.97 (m, 1H), 3.95 (ddd, *J* = 13.3, 6.4, 3.9 Hz, 1H), 2.70–2.47 (m, 1H), 2.17 (dddd, *J* = 14.6, 8.3, 4.9, 1.5 Hz, 1H), 2.10–1.98 (m, 1H), 1.06 (d, *J* = 6.8 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.4 (d, J_{CP} = 5.7 Hz), 135.0 (d, J_{CP} = 3.0 Hz), 135.0, 118.1 (d, J_{CP} = 1.6 Hz), 117.4, 115.4 (d, J_{CP} = 7.1 Hz), 77.8 (d, J_{CP} = 6.8 Hz), 76.0 (d, J_{CP} = 1.1 Hz), 75.9 (d, J_{CP} = 1.0 Hz), 71.6 (d, J_{CP} = 6.2 Hz), 38.2 (d, J_{CP} = 7.3 Hz), 38.1 (d, J_{CP} = 7.1 Hz), 35.2 (d, J_{CP} = 1.1 Hz), 35.1 (d, J_{CP} = 1.1 Hz), 16.0 (d, J_{CP} = 6.0 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ -7.61;

HRMS cald for $C_{12}H_{19}O_4PNa$ $(M+Na)^+$ 281.0919; found 281.0913 (TOF MS ES+).

(4*S*,6*S*)-2-(((*S*)-2-methylbut-3-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (45b):



FTIR (thin film): 2968, 2920, 1625, 1456, 1280, 1145, 1016, 925 cm^{-1};

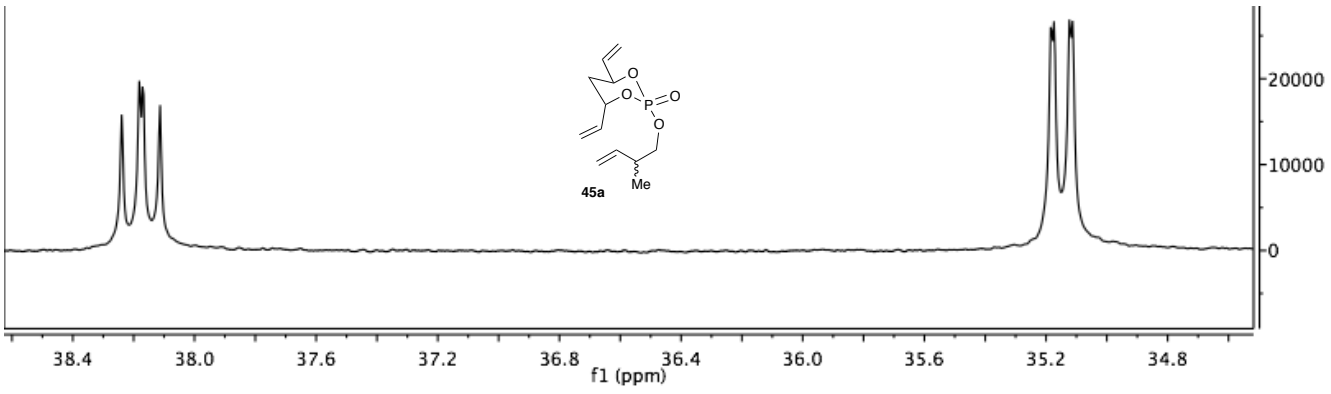
Optical Rotation: $[\alpha]_D$ = + 83.91(*c* = 0.44, $CHCl_3$);

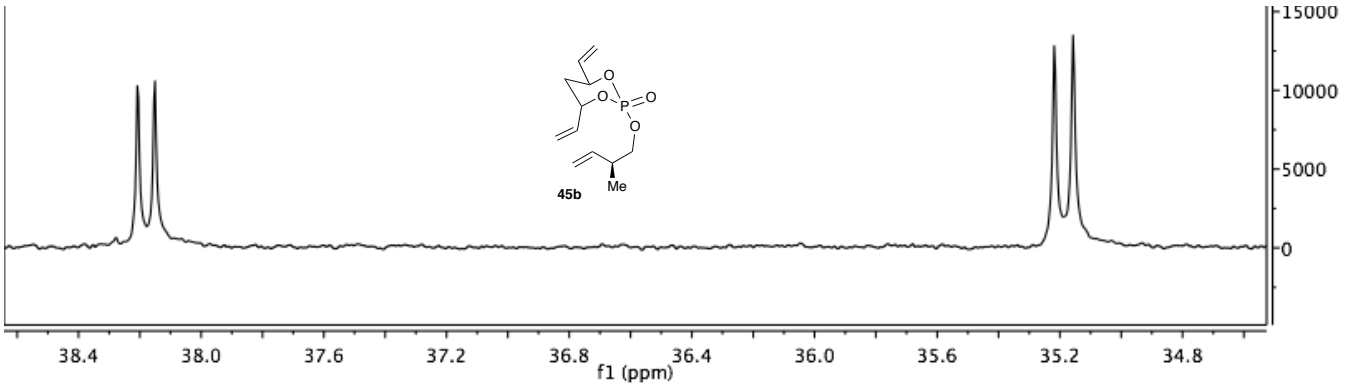
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (ddd, *J* = 17.0, 10.6, 6.0 Hz, 1H), 5.91 (dddd, *J* = 17.3, 10.5, 5.1, 1.2 Hz, 1H), 5.76 (ddd, *J* = 14.1, 10.4, 7.0 Hz, 1H), 5.46 (d, *J* = 17.1 Hz, 1H), 5.38 (d, *J* = 17.2 Hz, 1H), 5.31 (ddd, *J* = 10.6, 1.9, 1.0 Hz, 2H), 5.16–5.06 (m, 2H), 5.06–5.01 (m, 1H), 5.01–4.95 (m, 1H), 4.03–3.95 (m, 2H), 2.57 (dt, *J* = 13.4, 6.7 Hz, 1H), 2.17 (dddd, *J* = 14.7, 8.1, 4.7, 1.3 Hz, 1H), 2.08–2.01 (m, 1H), 1.07 (d, *J* = 6.8 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.5, 135.1 (d, J_{CP} = 2.9 Hz), 135.0, 118.1, 117.4, 115.4, 77.8 (d, J_{CP} = 6.8 Hz), 76.0 (d, J_{CP} = 6.1 Hz), 71.6 (d, J_{CP} = 6.1 Hz), 38.2 (d, J_{CP} = 7.0 Hz), 35.2 (d, J_{CP} = 7.7 Hz), 16.0;

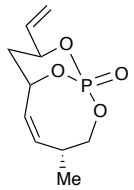
^{31}P NMR (162 MHz, $CDCl_3$) δ -7.61;

HRMS cald for $C_{12}H_{19}O_4PNa$ $(M+Na)^+$ 281.0919; found 281.0914 (TOF MS ES+).





(1*S*,4*R*,7*S*,9*S*,*Z*)-4-methyl-9-vinyl-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-5-ene 1-oxide (46):



FTIR (thin film): 2922, 1827, 1649, 1448, 1375, 1281, 1140, 1119, 1003, 928 cm^{-1};

Optical Rotation: $[\alpha]_D$ = + 122.98 (*c* = 0.57, $CHCl_3$);

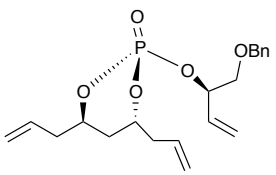
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (dddd, *J* = 18.0, 10.6, 5.4, 2.1 Hz, 1H), 5.48–5.45 (m, 2H), 5.45–5.39 (m, 1H), 5.33–5.22 (m, 2H), 5.07 (dd, *J* = 11.7, 5.3 Hz, 1H), 4.33 (ddd, *J* = 10.8, 6.2, 2.1 Hz, 1H), 3.64–3.52 (m, 1H), 3.34 (ddd, *J* = 30.9, 12.5, 10.8 Hz, 1H), 2.26–2.15 (m, 1H), 1.82 (ddd, *J* = 14.5, 3.7, 2.0 Hz, 1H), 1.01 (d, *J* = 6.6 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.0 (d, J_{CP} = 10.1 Hz), 134.1, 129.3, 117.3 (d, J_{CP} = 1.1 Hz), 77.9 (d, J_{CP} = 7.1 Hz), 77.1 (d, J_{CP} = 6.2 Hz), 68.2 (d, J_{CP} = 5.0 Hz), 36.2 (d, J_{CP} = 6.5 Hz), 31.2, 16.6;

^{31}P NMR (162 MHz, $CDCl_3$) δ -8.05;

HRMS cald for $C_{10}H_{15}O_4PNa$ $(M+Na)^+$ 253.0606; found 253.0617 (TOF MS ES+).

(4*R*,6*R*)-4,6-diallyl-2-(((*R*)-1-(benzyloxy)but-3-en-2-yl)oxy)-1,3,2-dioxaphosphinane 2-oxide (50):



FTIR (thin film): 2924, 1643, 1431, 1366, 1286, 1095, 1011, 976, 922 cm^{-1};

Optical Rotation: $[\alpha]_D$ = + 41.66 (*c* = 0.71, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.28 (m, 5H), 5.94 (ddd, *J* = 17.2, 10.5, 6.7 Hz, 1H), 5.84 – 5.77 (m, 1H), 5.77–5.70 (m, 1H), 5.44 (ddd, *J* = 17.2, 1.1,1.1 Hz, 1H), 5.31 (ddd, *J* = 10.5, 1.1, 1.1 Hz, 1H), 5.18–5.12 (m, 3H),

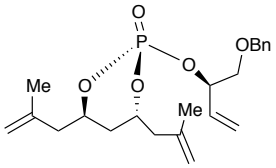
5.12–5.09 (m, 1H), 5.07–5.00 (m, 1H), 4.67–4.55 (m, 3H), 4.55–4.48 (m, 1H), 3.67 (dd, *J* = 10.5, 5.6 Hz, 1H), 3.63 (ddd, *J* = 10.5, 4.7, 1.1 Hz, 1H), 2.66 (dt, *J* = 13.2, 6.5 Hz, 1H), 2.54 (ddd, *J* = 7.6, 6.6, 3.3 Hz, 1H), 2.44–2.33 (m, 2H), 2.00 (dddd, *J* = 13.5, 8.4, 5.0, 1.2 Hz, 1H), 1.89 (dddd, *J* = 14.6, 5.4, 3.8, 1.8 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 133.9 (d, J_{CP} = 3.9 Hz), 132.6 (d, J_{CP} = 5.7 Hz), 132.3, 128.4 (d, J_{CP} = 9.9 Hz), 127.8 (d, J_{CP} = 2.7 Hz), 127.6, 118.7 (d, J_{CP} = 2.6 Hz), 78.0 (d, J_{CP} = 5.6 Hz), 77.3, 75.3 (d, J_{CP} = 6.7 Hz), 73.3 (d, J_{CP} = 6.1 Hz), 72.2 (d, J_{CP} = 6.0 Hz), 40.0 (d, J_{CP} = 7.7 Hz), 40.0 (d, J_{CP} = 3.5 Hz), 33.0 (d, J_{CP} = 6.8 Hz), 31.0;

^{31}P NMR (162 MHz, $CDCl_3$) δ -7.34;

HRMS cald for $C_{20}H_{27}O_5PNa$ $(M+Na)^+$ 401.1494; found 401.1493 (TOF MS ES+).

(4*R*,6*R*)-2-(((*R*)-1-(benzyloxy)but-3-en-2-yl)oxy)-4,6-bis(2-methylallyl)-1,3,2-dioxaphosphinane 2-oxide (51):



FTIR (thin film): 3076, 2964, 2926, 2359, 1827, 1649, 1454, 1364, 1288, 1099, 1074, 1007, 982, 739 cm^{-1};

Optical Rotation: $[\alpha]_D$ = + 44.04 (*c* = 1.3, $CHCl_3$);

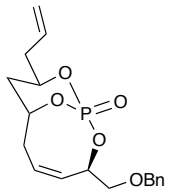
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 4.4 Hz, 3H), 7.32–7.28 (m, 2H), 5.95 (ddd, *J* = 17.2, 10.5, 6.7 Hz, 1H), 5.44 (ddd, *J* = 17.2, 1.3, 1.3 Hz, 1H), 5.31 (ddd, *J* = 10.6, 1.1, 1.2 Hz, 1H), 5.08–4.99 (m, 1H), 4.85 (ddd, *J* = 7.04, 1.6, 1.6 Hz, 2H), 4.77 (d, *J* = 9.8 Hz, 2H), 4.74–4.59 (m, 3H), 4.56 (d, *J* = 12.0 Hz, 1H), 3.67 (dd, *J* = 10.5, 5.6 Hz, 1H), 3.63 (ddd, *J* = 10.6, 4.9, 1.0 Hz, 1H), 2.62 (dd, *J* = 14.2, 6.7 Hz, 1H), 2.53 (dd, *J* = 14.1, 6.7 Hz, 1H), 2.37 (dd, *J* = 14.1, 7.8 Hz, 1H), 2.32 (dd, *J* = 13.6, 6.5 Hz, 1H), 1.98 (dddd, *J* = 13.0, 8.0, 4.9, 1.2 Hz, 1H), 1.89 (dddd, *J* = 14.6, 5.4, 3.9, 1.9 Hz, 1H), 1.75 (s, 3H), 1.73 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 140.2, 139.8, 137.9, 134.0 (d, J_{CP} = 4.1 Hz), 128.3, 127.6, 118.7, 114.6 (d, J_{CP} = 3.7 Hz), 114.2 (d, J_{CP} = 4.8 Hz), 78.0 (d, J_{CP} = 5.6 Hz), 76.1 (d, J_{CP} = 6.9 Hz), 74.4 (d, J_{CP} = 6.6 Hz), 73.2, 72.2 (d, J_{CP} = 5.8 Hz), 43.8 (d, J_{CP} = 7.5 Hz), 42.8 (d, J_{CP} = 3.4 Hz), 33.2 (d, J_{CP} = 6.8 Hz), 22.6, 22.3;

^{31}P NMR (162 MHz, $CDCl_3$) δ -7.09;

HRMS cald for $C_{22}H_{31}O_5PNa$ $(M+Na)^+$ 429.1807; found 429.1802 (TOF MS ES+).

(1*S*,3*R*,7*R*,9*R*,*Z*)-9-allyl-3-((benzyloxy)methyl)-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-4-ene 1-oxide (*trans*-52):



FTIR (thin film): 2920, 1364, 1288, 1113, 1092, 1022, 972, 928 cm^{-1};

Optical Rotation: $[\alpha]_D$ = + 61.6 (*c* = 0.38, $CHCl_3$);

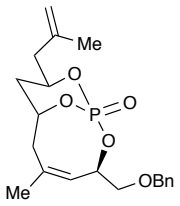
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.28 (m, 5H), 5.89–5.78 (m, 3H), 5.19 (dd, *J* = 4.2, 2.8 Hz, 1H), 5.15 (s, 1H), 5.03 (ddd, *J* = 28.5, 7.1 Hz, 1H), 4.83–4.73 (m, 1H), 4.68 (d, *J* = 11.8 Hz, 1H), 4.59 (d, *J* = 11.8 Hz, 1H), 4.52–4.37 (m, 1H), 4.03 (dd, *J* = 9.8, 6.9 Hz, 1H), 3.79 (dd, *J* = 9.8, 7.2 Hz, 1H), 3.17 (ddd, *J* = 13.6, 10.4, 6.2 Hz, 1H), 2.59 – 2.50 (m, 1H), 2.41 (dt, *J* = 14.3, 6.7 Hz, 1H), 2.27 (ddd, *J* = 14.6, 11.9, 5.2 Hz, 1H), 2.21–2.13 (m, 1H), 1.69 (dd, *J* = 14.6, 1.1 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8, 132.1, 130.1, 128.4 (d, J_{CP} = 7.3 Hz), 128.0, 127.7 (d, J_{CP} = 12.6 Hz), 126.4, 119.0, 75.8 (d, J_{CP} = 7.4 Hz), 73.6, 73.1 (d, J_{CP} = 6.4 Hz), 71.8 (d, J_{CP} = 2.1 Hz), 40.6 (d, J_{CP} = 8.6 Hz), 33.5 (d, J_{CP} = 6.3 Hz), 31.1 (d, J_{CP} = 32.0 Hz), 29.7;

^{31}P NMR (162 MHz, $CDCl_3$) δ -10.75;

HRMS cald for $C_{18}H_{23}O_5PNa$ $(M+Na)^+$ 373.1181; found 373.1173 (TOF MS ES+).

(1*S*,3*R*,7*R*,9*R*,*Z*)-3-((benzyloxy)methyl)-5-methyl-9-(2-methylallyl)-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-4-ene 1-oxide (*trans*-53):



FTIR (thin film): 2924, 2853, 1718, 1649, 1452, 1246, 1175, 1095, 1013, 899, 818, 748 cm^{-1};

Optical Rotation: $[\alpha]_D$ = + 50.10 (*c* = 1.3, $CHCl_3$);

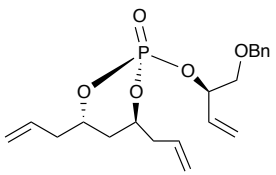
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.28 (m, 5H), 5.57 (s, 1H), 4.98 (dd, *J* = 25.2, 1.7 Hz, 1H), 4.93–4.84 (m, 2H), 4.82 (s, 1H), 4.67 (d, *J* = 11.9 Hz, 1H), 4.58 (d, *J* = 11.9 Hz, 1H), 4.56–4.45 (m, 1H), 3.94 (dd, *J* = 9.9, 7.0 Hz, 1H), 3.72 (dd, *J* = 9.9, 6.6 Hz, 1H), 3.29 (t, *J* = 12.8 Hz, 1H), 2.57 (dd, *J* = 14.0, 6.6 Hz, 1H), 2.33 (ddd, *J* = 14.0, 6.8, 1.4 Hz, 1H), 2.24 (ddd, *J* = 14.6, 11.7, 5.3 Hz, 1H), 1.97 (dd, *J* = 13.1, 5.2 Hz, 1H), 1.86 (t, *J* = 1.6 Hz, 3H), 1.78 (s, 3H), 1.73 (d, *J* = 14.6 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 137.8, 137.1, 128.4, 127.8 (d, J_{CP} = 26.9 Hz), 123.6, 114.4, 76.1 (d, J_{CP} = 7.7 Hz), 75.2 (d, J_{CP} = 7.4 Hz), 73.6, 72.3 (d, J_{CP} = 6.4 Hz), 72.1 (d, J_{CP} = 3.7 Hz), 44.7 (d, J_{CP} = 7.7 Hz), 36.5, 33.7 (d, J_{CP} = 6.6 Hz), 29.7, 24.3, 22.8;

^{31}P NMR (162 MHz, $CDCl_3$) δ -4.06;

HRMS cald for $C_{20}H_{27}O_5PNa$ $(M+Na)^+$ 401.1494; found 401.1495 (TOF MS ES+).

(4*S*,6*S*)-4,6-diallyl-2-(((*R*)-1-(benzyloxy)but-3-en-2-yl)oxy)-1,3,2-dioxaphosphinane 2-oxide (56):



FTIR (thin film): 2922, 1641, 1364, 1286, 1095, 1119, 1007, 920 cm^{-1};

Optical Rotation: $[\alpha]_D$ = - 44.31 (*c* = 0.24, $CHCl_3$);

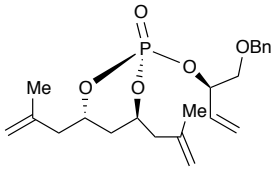
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.28 (m, 5H), 5.90 (ddd, *J* = 16.9, 10.6, 6.0 Hz, 1H), 5.81–5.72 (m, 1H), 5.72–5.62 (m, 1H), 5.45 (ddd, *J* = 17.2, 1.2 Hz, 1H), 5.31 (ddd, *J* = 10.6, 1.2 Hz, 1H), 5.15–5.10 (m, 3H), 5.10–5.07 (m, 1H), 5.02 (td, *J* = 11.6, 5.5 Hz, 1H), 4.63 – 4.54 (m, 4H), 3.62 (dd, *J* = 5.5, 0.8 Hz, 2H), 2.70 (dt, *J* = 13.3, 6.7 Hz, 1H), 2.49–2.43 (m, 1H), 2.39 (dd, *J* = 14.5, 7.3 Hz, 1H), 2.34–2.26 (m, 1H), 2.02–1.93 (m, 1H), 1.87–1.79 (m, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 133.4 (d, J_{CP} = 3.8 Hz), 132.8, 132.3, 128.4, 127.7 (d, J_{CP} = 7.8 Hz), 118.7 (d, J_{CP} = 8.5 Hz), 118.5, 77.7 (d, J_{CP} = 7.1 Hz), 77.6 (d, J_{CP} = 5.5 Hz), 75.0 (d, J_{CP} = 6.6 Hz), 73.2, 72.4 (d, J_{CP} = 6.0 Hz), 40.0 (d, J_{CP} = 8.0 Hz), 38.8 (d, J_{CP} = 2.8 Hz), 32.9 (d, J_{CP} = 6.9 Hz), 30.9;

^{31}P NMR (162 MHz, $CDCl_3$) δ -7.59;

HRMS cald for $C_{20}H_{27}O_5PNa$ $(M+Na)^+$ 401.1494; found 401.1491 (TOF MS ES+).

(4*S*,6*S*)-2-(((*R*)-1-(benzyloxy)but-3-en-2-yl)oxy)-4,6-bis(2-methylallyl)-1,3,2-dioxaphosphinane 2-oxide (57):



FTIR (thin film): 2918, 1827, 1649, 1448, 1290, 1092, 1074, 1007, 976 cm^{-1};

Optical Rotation: $[\alpha]_D$ = - 40.69 (*c* = 1.4, $CHCl_3$);

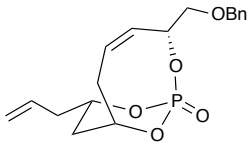
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.28 (m, 5H), 5.90 (ddd, *J* = 16.9, 10.6, 6.1 Hz, 1H), 5.44 (d, *J* = 17.2 Hz, 1H), 5.30 (d, *J* = 10.6 Hz, 1H), 5.01 (dq, *J* = 12.4, 6.1 Hz, 1H), 4.85 (ddd, *J* = 10.6, 1.4, 1.4 Hz, 2H), 4.79–4.68 (m, 4H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 3.66–3.57 (m, 2H), 2.65 (dd, *J* = 14.1, 6.9 Hz, 1H), 2.49 (dd, *J* = 14.1, 6.4 Hz, 1H), 2.39 (dd, *J* = 14.2, 7.7 Hz, 1H), 2.29 (dd, *J* = 14.1, 7.3 Hz, 1H), 1.97 (dddd, *J* = 14.7, 8.2, 5.1,1.3 Hz, 1H), 1.87 (dddd, *J* = 14.6, 5.3, 3.7,1.9 Hz, 1H), 1.74 (s, 3H), 1.69 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ140.5, 140.3, 137.7, 133.5 (d, J_{CP} = 3.8 Hz), 128.4 (d, J_{CP} = 2.7 Hz), 128.4, 127.8 (d, J_{CP} = 5.0 Hz), 127.7 (d, J_{CP} = 9.0 Hz), 118.5, 114.1 (d, J_{CP} = 2.9 Hz), 77.7 (d, J_{CP} = 5.5 Hz), 76.3 (d, J_{CP} = 7.0 Hz), 74.3 (d, J_{CP} = 6.7 Hz), 73.2, 72.3 (d, J_{CP} = 6.1 Hz), 43.8 (d, J_{CP} = 7.7 Hz), 42.7 (d, J_{CP} = 3.0 Hz), 33.1 (d, J_{CP} = 7.1 Hz), 22.6, 22.3;

^{31}P NMR (162 MHz, $CDCl_3$) δ -7.58;

HRMS cald for $C_{22}H_{31}O_5PNa$ $(M+Na)^+$ 429.1807; found 429.1794 (TOF MS ES+).

(1*R*,3*R*,7*S*,9*S*,*Z*)-9-allyl-3-((benzyloxy)methyl)-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-4-ene 1-oxide (*cis*-58):



FTIR (thin film): 2924, 2363, 1641, 1497, 1452, 1364, 1292, 1103, 978, 928 cm^{-1};

Optical Rotation: $[\alpha]_D$ = + 43.30(*c* = 1.03, $CHCl_3$);

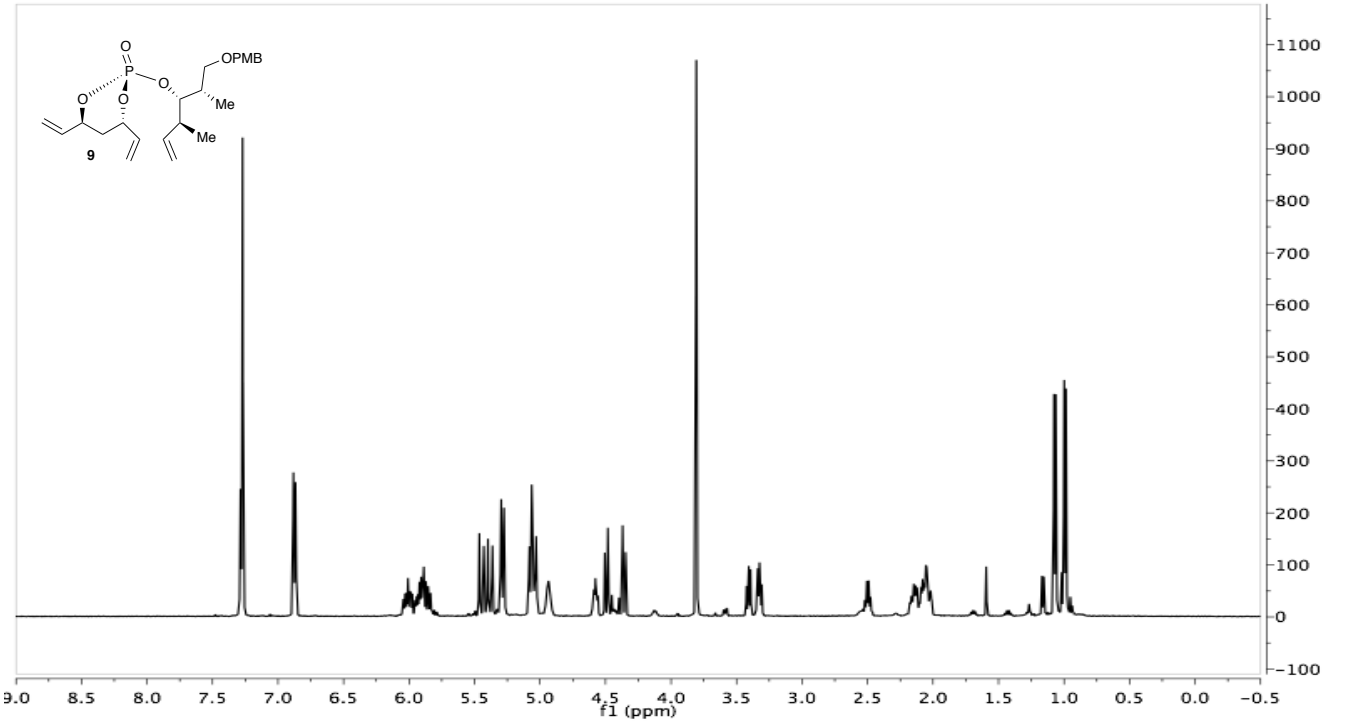
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.27 (m, 5H), 5.89–5.81 (m, 1H), 5.81–5.74 (m, 1H), 5.68 (dd, *J* = 11.9, 3.0 Hz, 1H), 5.25–5.17 (m, 2H), 5.16 (d, *J* = 1.1 Hz, 1H), 4.79 (dddd, *J* = 12.5, 6.2, 6.2, 2.7 Hz, 1H), 4.63 (d, *J* = 12.3 Hz, 1H), 4.59 (d, *J* = 12.2 Hz, 1H), 4.56–4.41 (m, 1H), 3.70–3.61 (m, 2H), 3.31 (td, *J* = 13.1, 8.4 Hz, 1H), 2.53 (ddd, *J* = 12.9, 7.1, 1.3 Hz, 1H), 2.47 – 2.36 (m, 1H), 2.24 (ddd, *J* = 14.6, 12.2, 5.2 Hz, 1H), 2.07 (ddd, *J* = 13.7, 8.4, 5.3 Hz, 1H), 1.65 (d, *J* = 14.7 Hz, 1H);

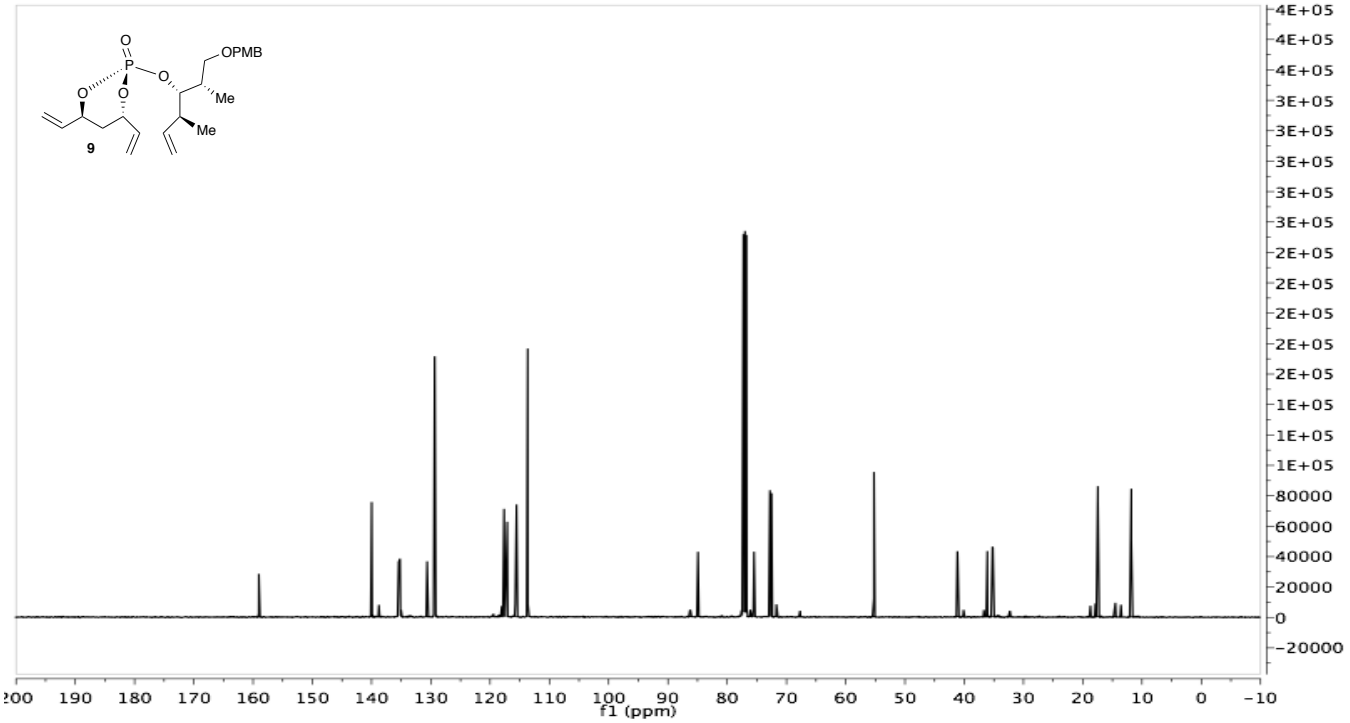
^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8, 132.0, 130.3, 128.3, 127.6 (d, J_{CP} = 15.2 Hz), 126.2, 124.2, 119.0, 77.2 (d, J_{CP} = 5.5 Hz), 76.0 (d, J_{CP} = 7.3 Hz), 74.3 (d, J_{CP} = 6.4 Hz), 73.1, 71.4 (d, J_{CP} = 12.0 Hz), 40.4 (d, J_{CP} = 9.2 Hz), 33.8 (d, J_{CP} = 6.3 Hz), 30.2 (d, J_{CP} = 10.3 Hz);

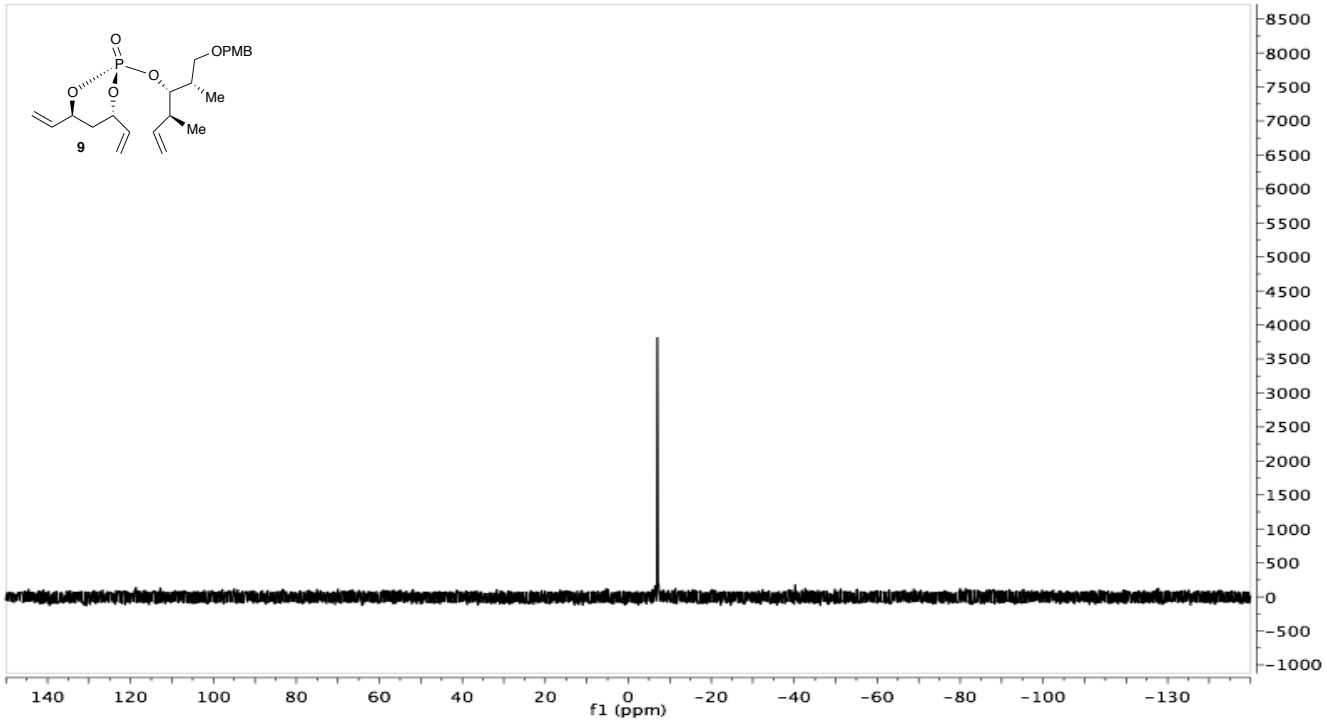
^{31}P NMR (162 MHz, $CDCl_3$) δ -7.60;

HRMS cald for $C_{18}H_{23}O_5PNa$ $(M+Na)^+$ 373.1181; found 373.1174 (TOF MS ES+).

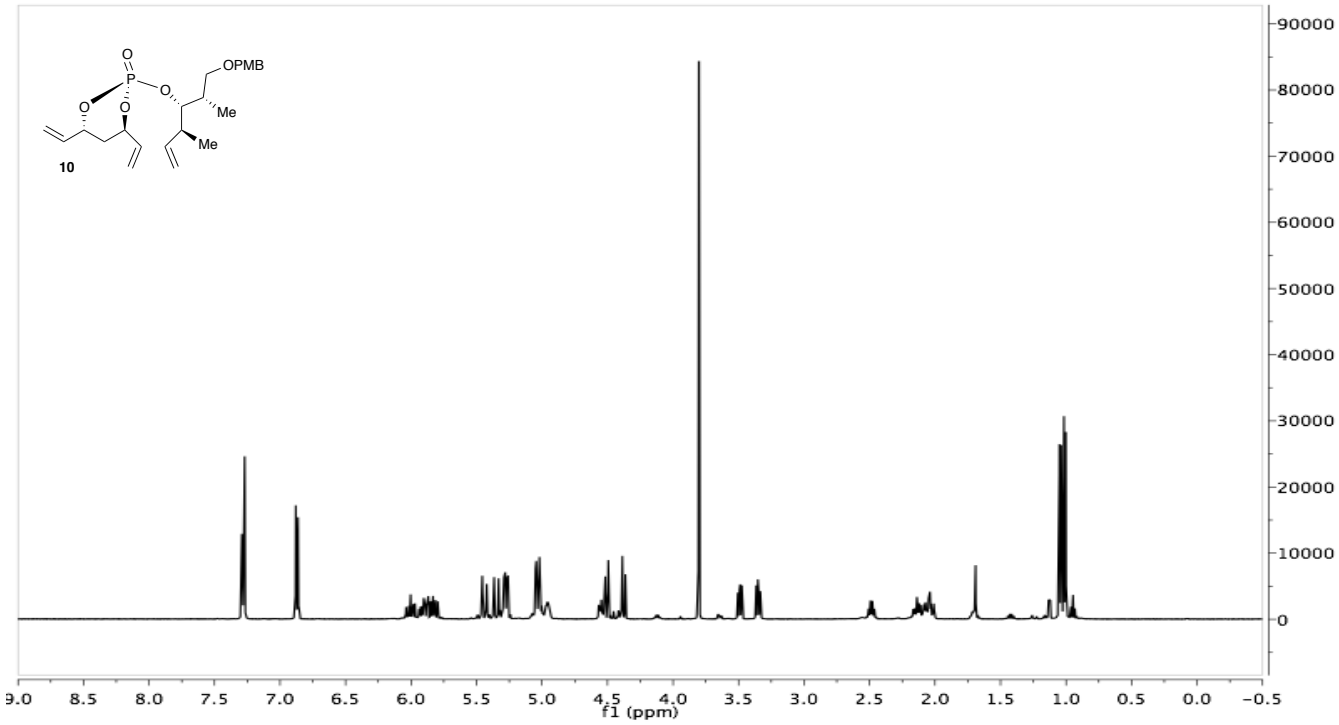
(4*S*,6*S*)-2-(((2*S*,3*S*,4*S*)-1-((4-methoxybenzyl)oxy)-2,4-dimethylhex-5-en-3-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (9):

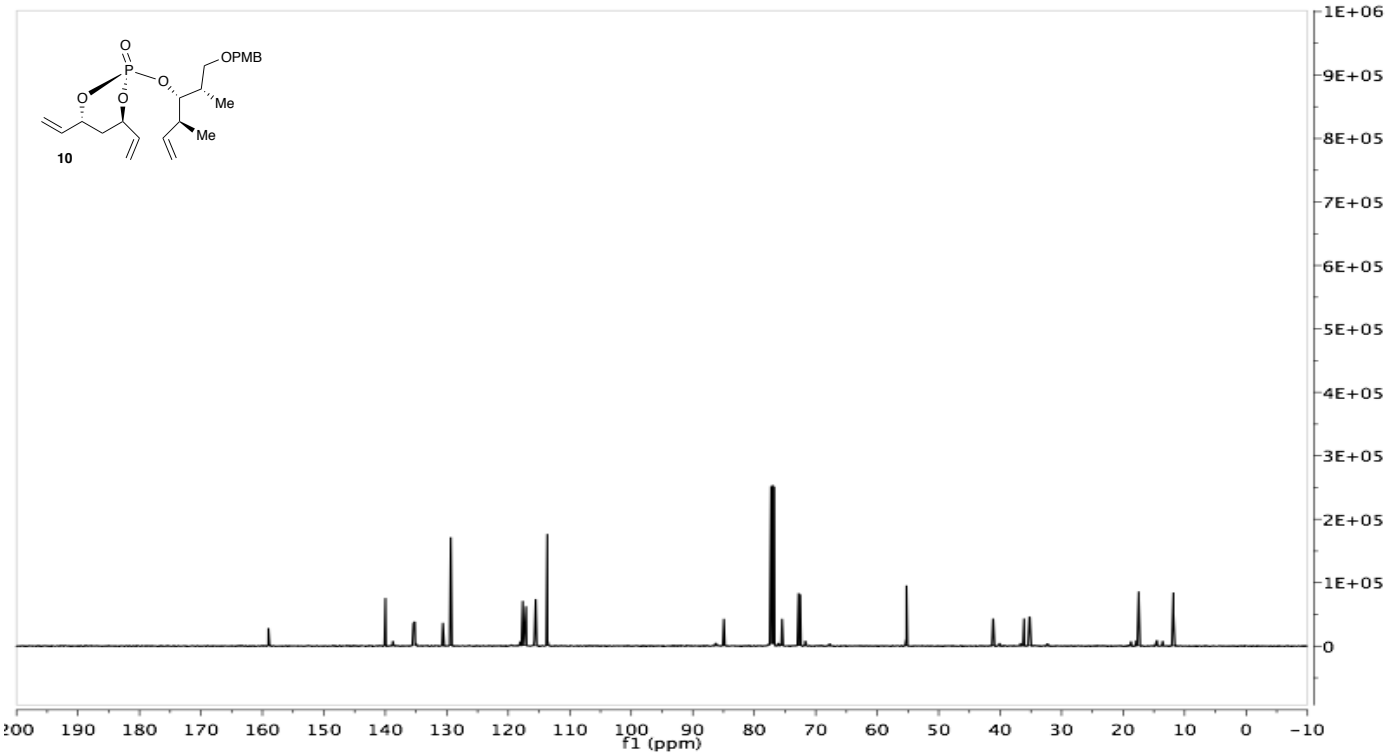


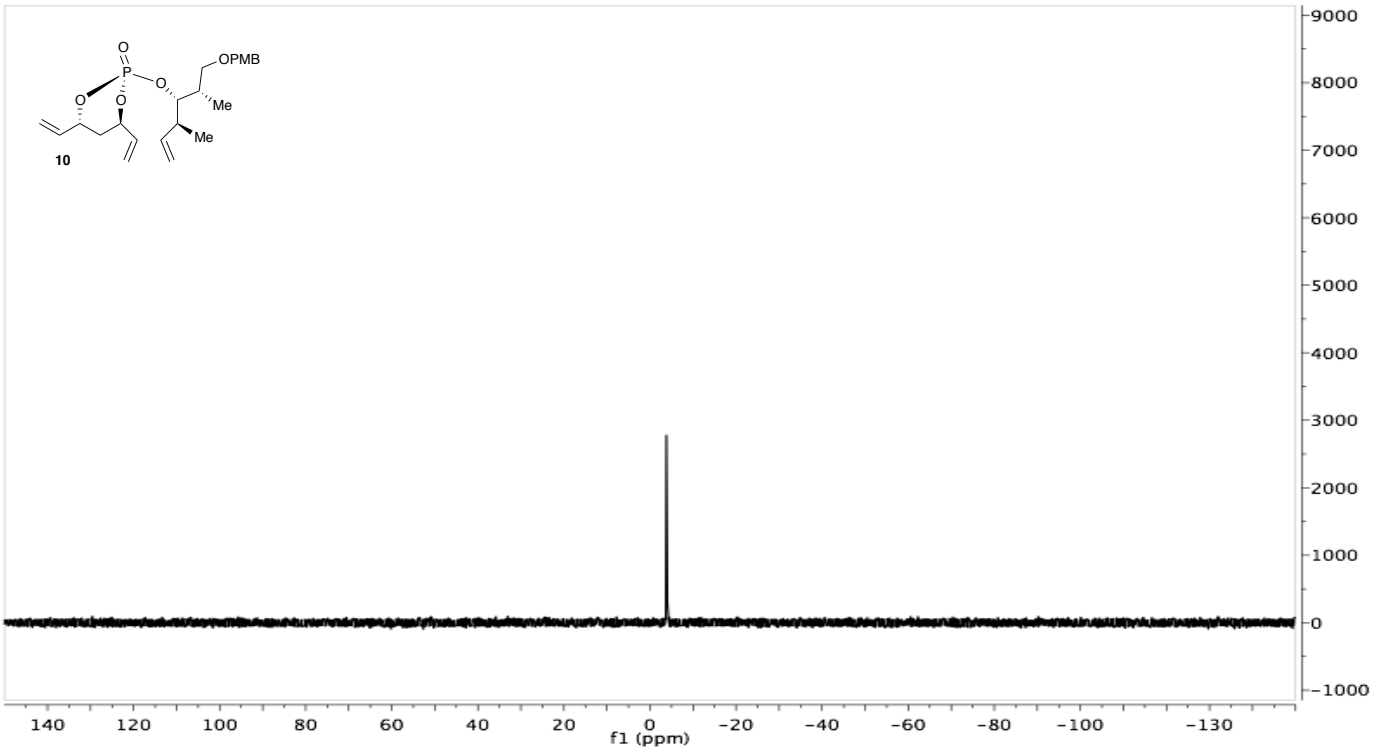




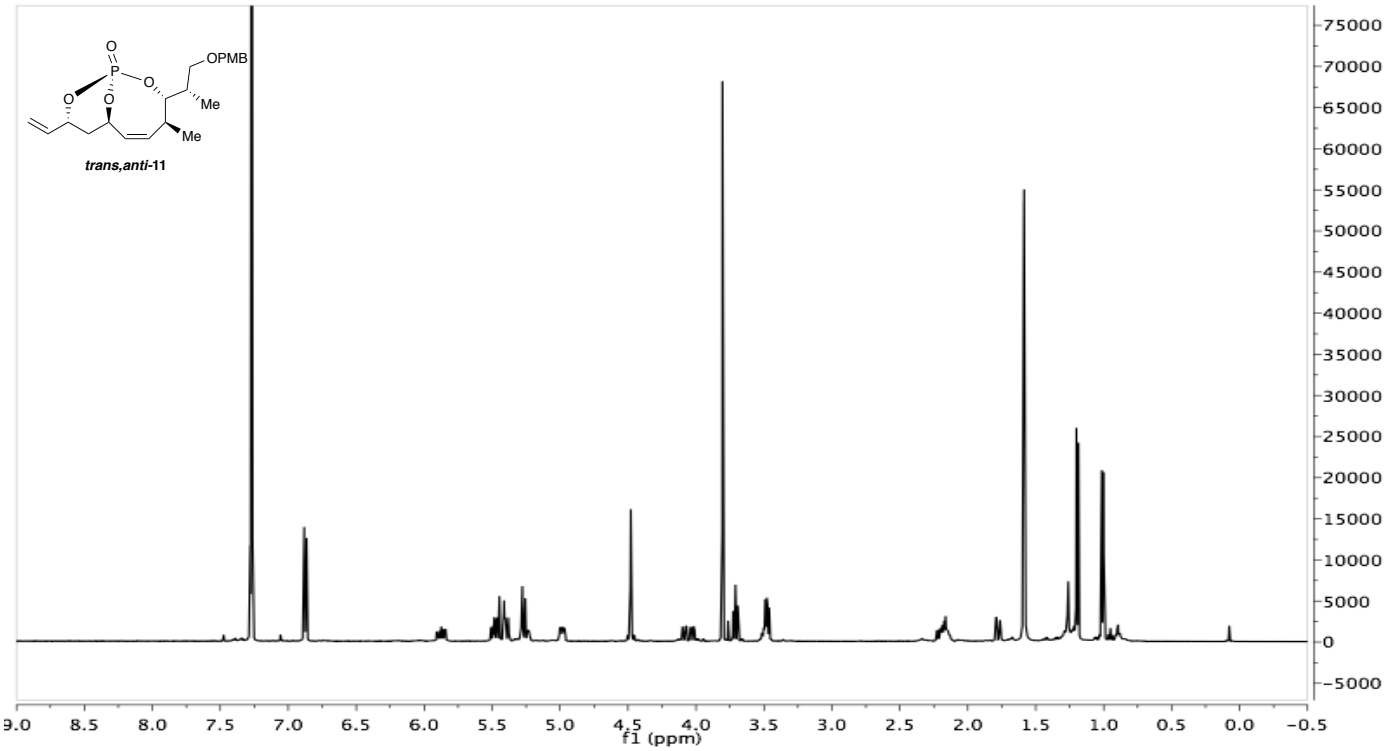
(4*R*,6*R*)-2-(((2*S*,3*S*,4*S*)-1-((4-methoxybenzyl)oxy)-2,4-dimethylhex-5-en-3-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (10):

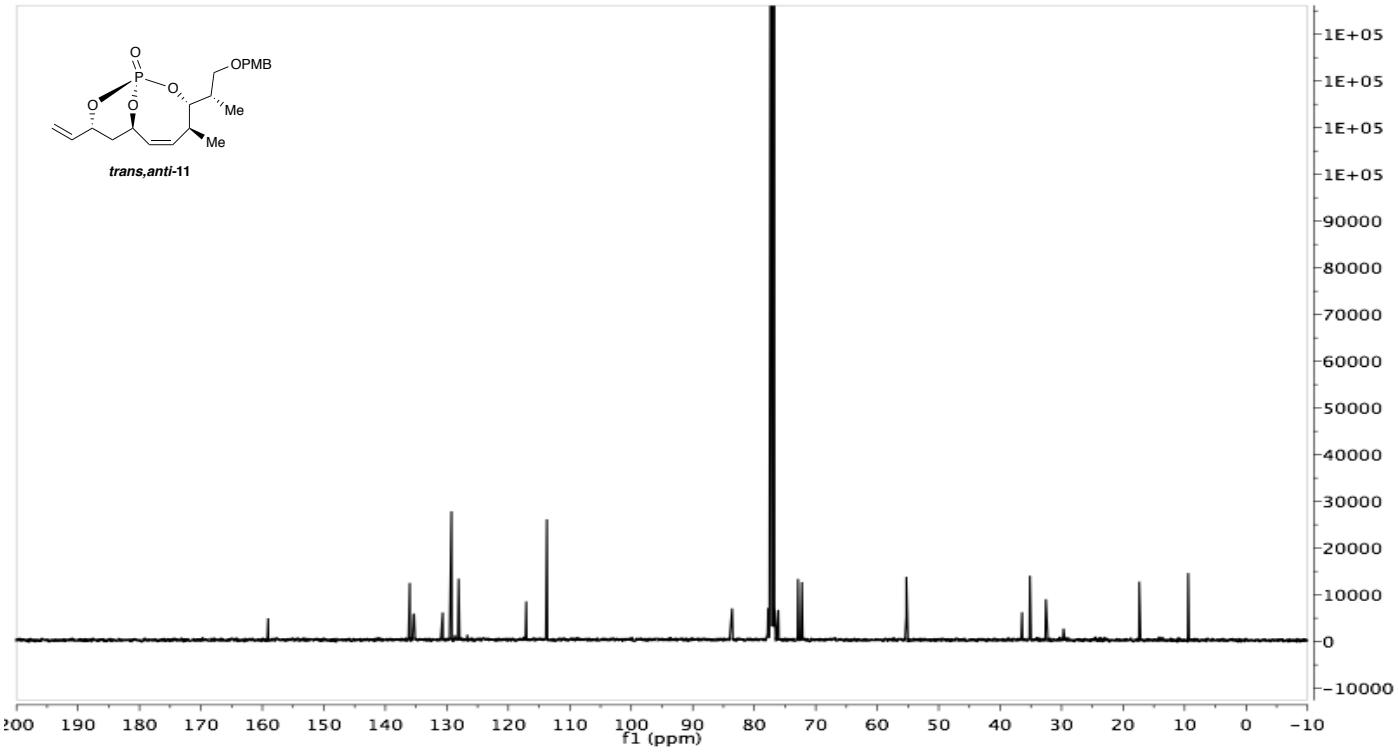


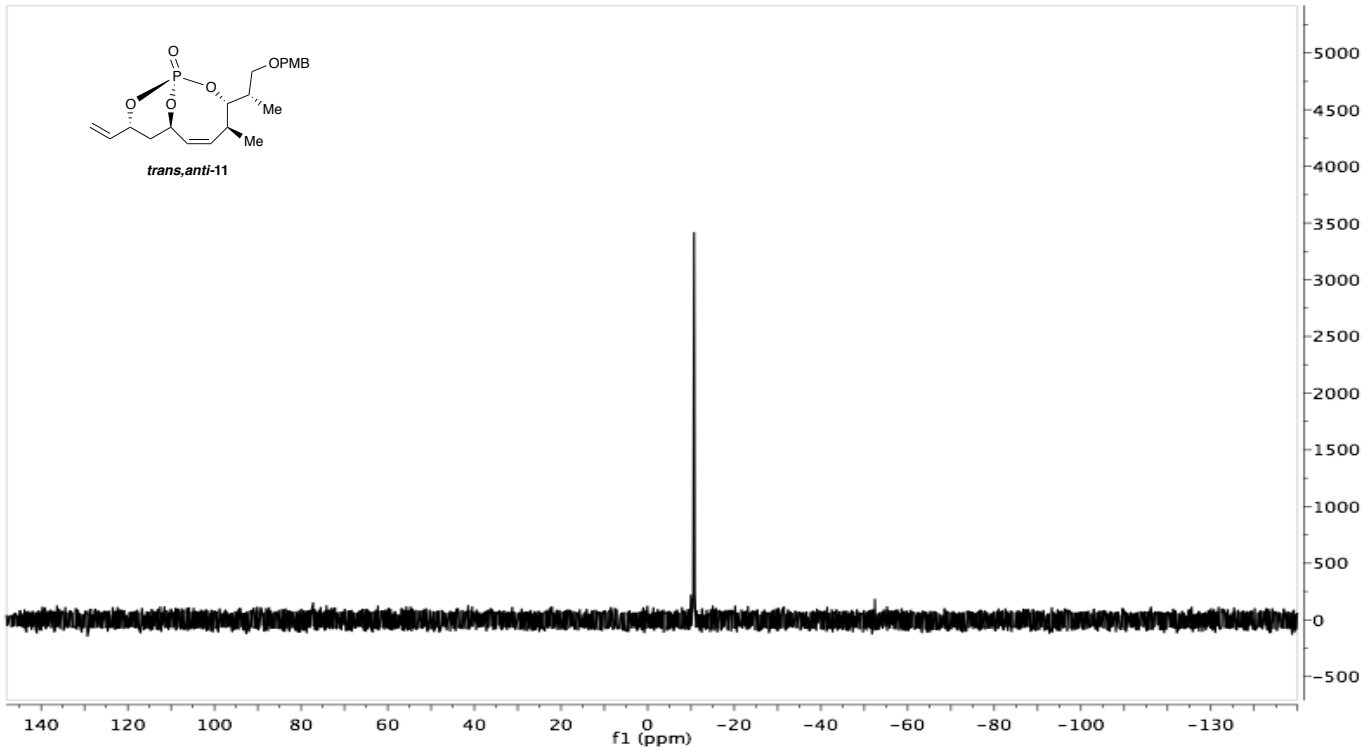

OPMB
Me
Me
10
1E+06
9E+05
8E+05
7E+05
6E+05
5E+05
4E+05
3E+05
2E+05
1E+05
0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OPMB
Me
Me
10
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -130
f1 (ppm)

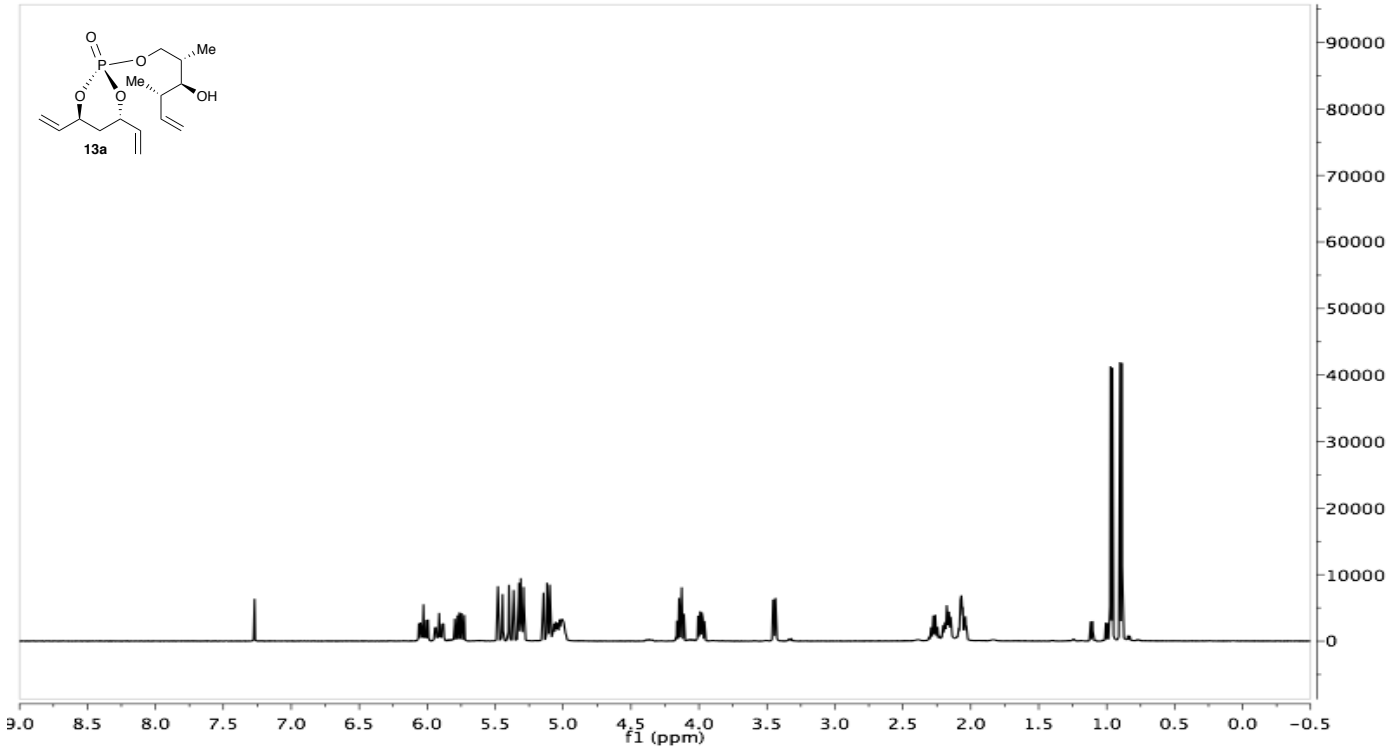
(1*R*,3*S*,4*S*,7*R*,9*R*,*Z*)-3-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)-4-methyl-9-vinyl-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-5-ene 1-oxide (*trans,anti*-11):

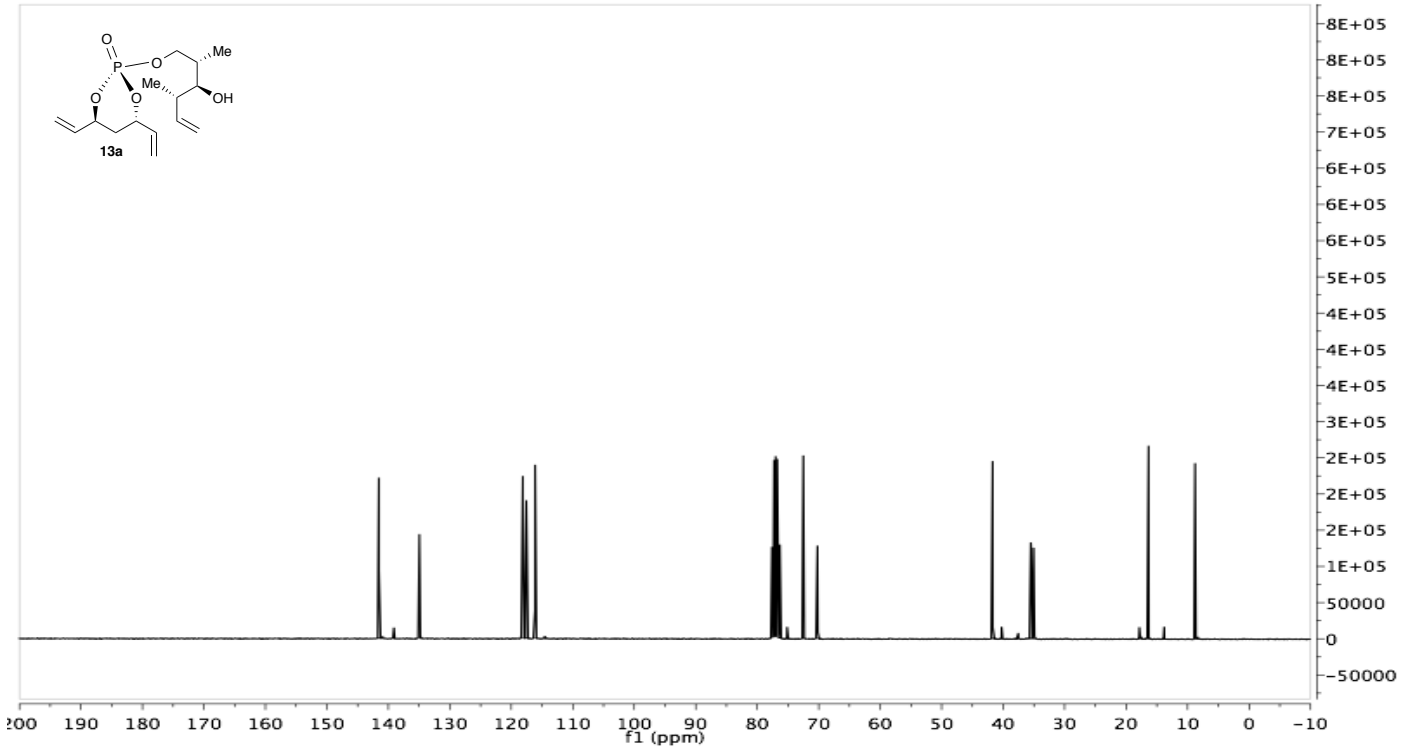


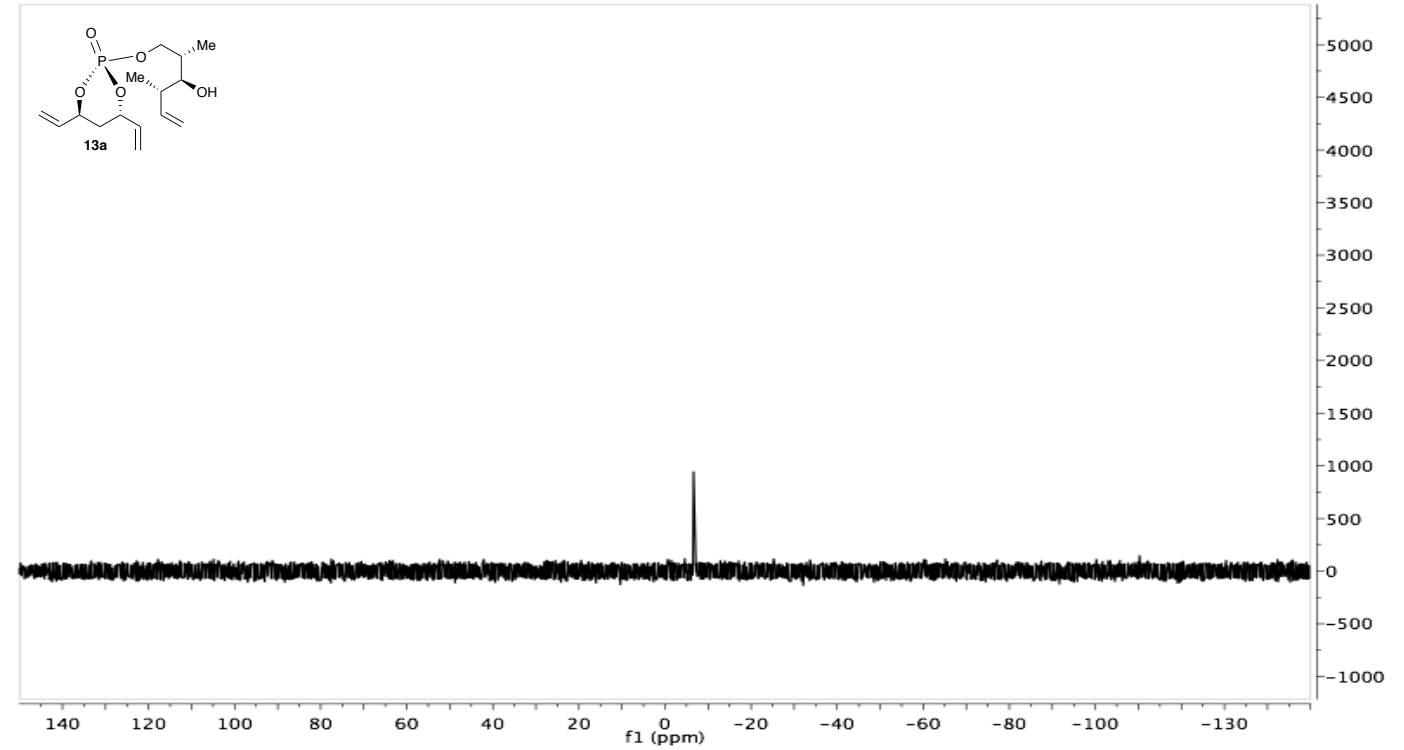




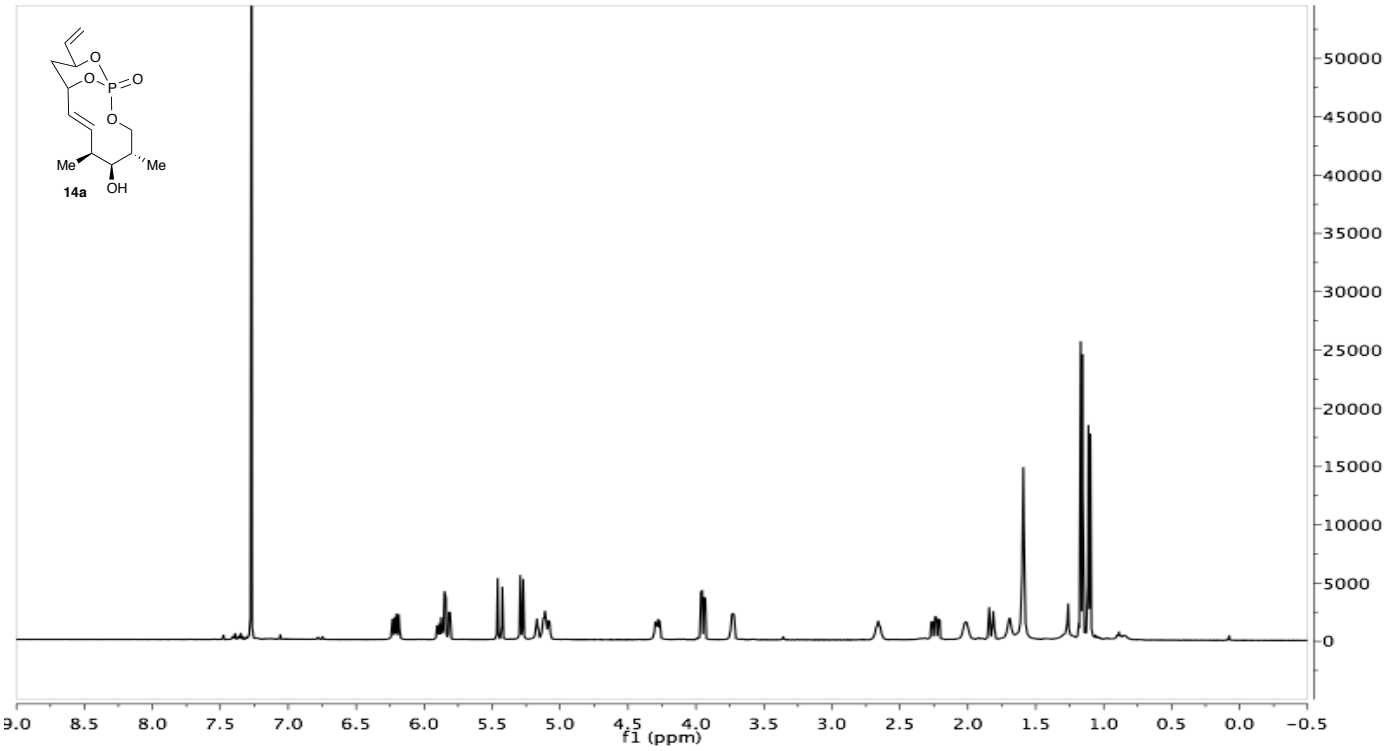
(4*S*,6*S*)-2-(((2*S*,3*S*,4*S*)-3-hydroxy-2,4-dimethylhex-5-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (13a):

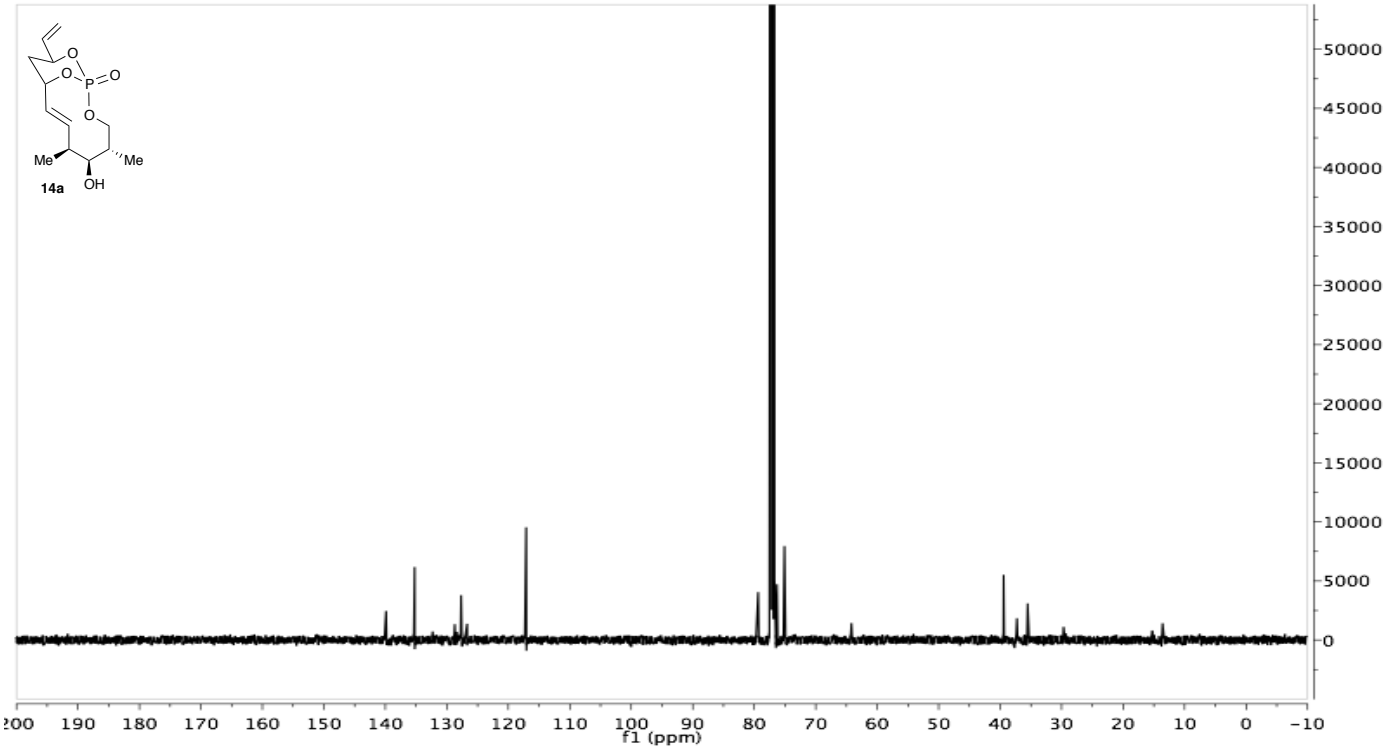


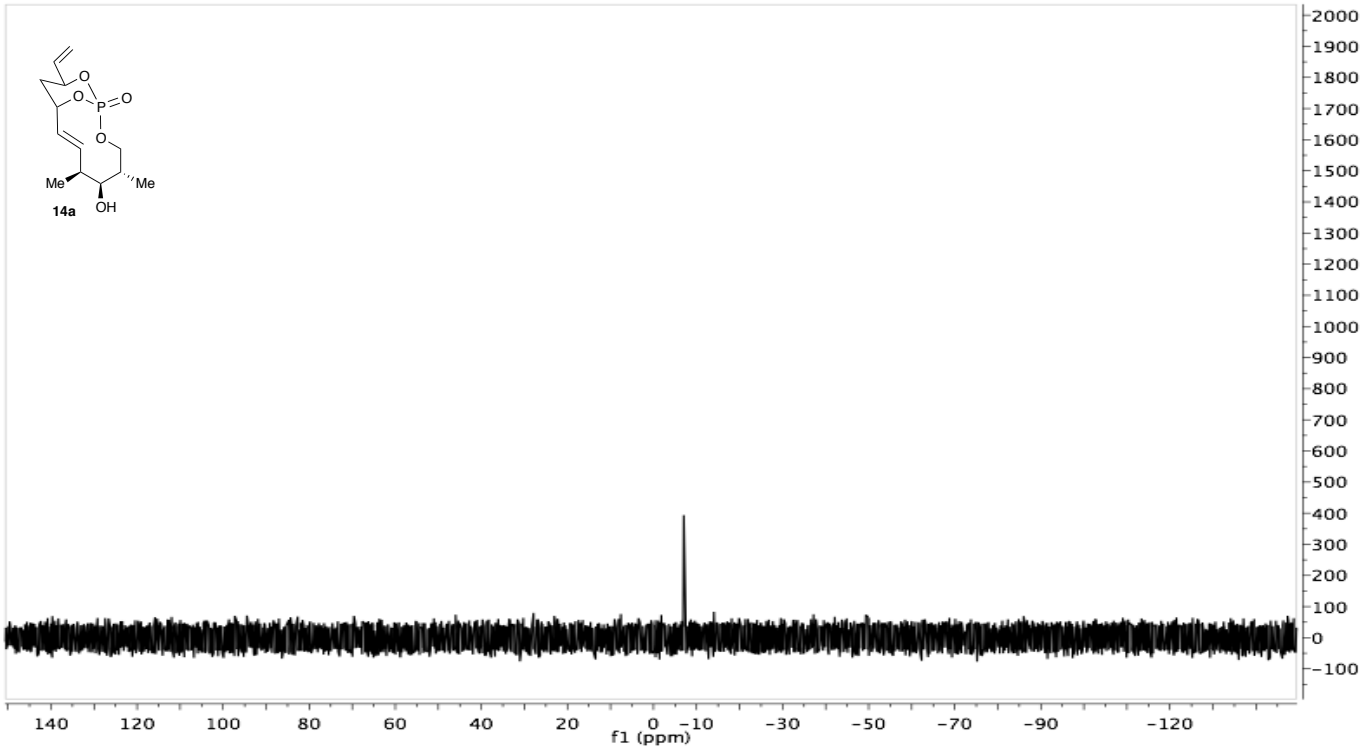

13a
f1 (ppm)


13a
f1 (ppm)

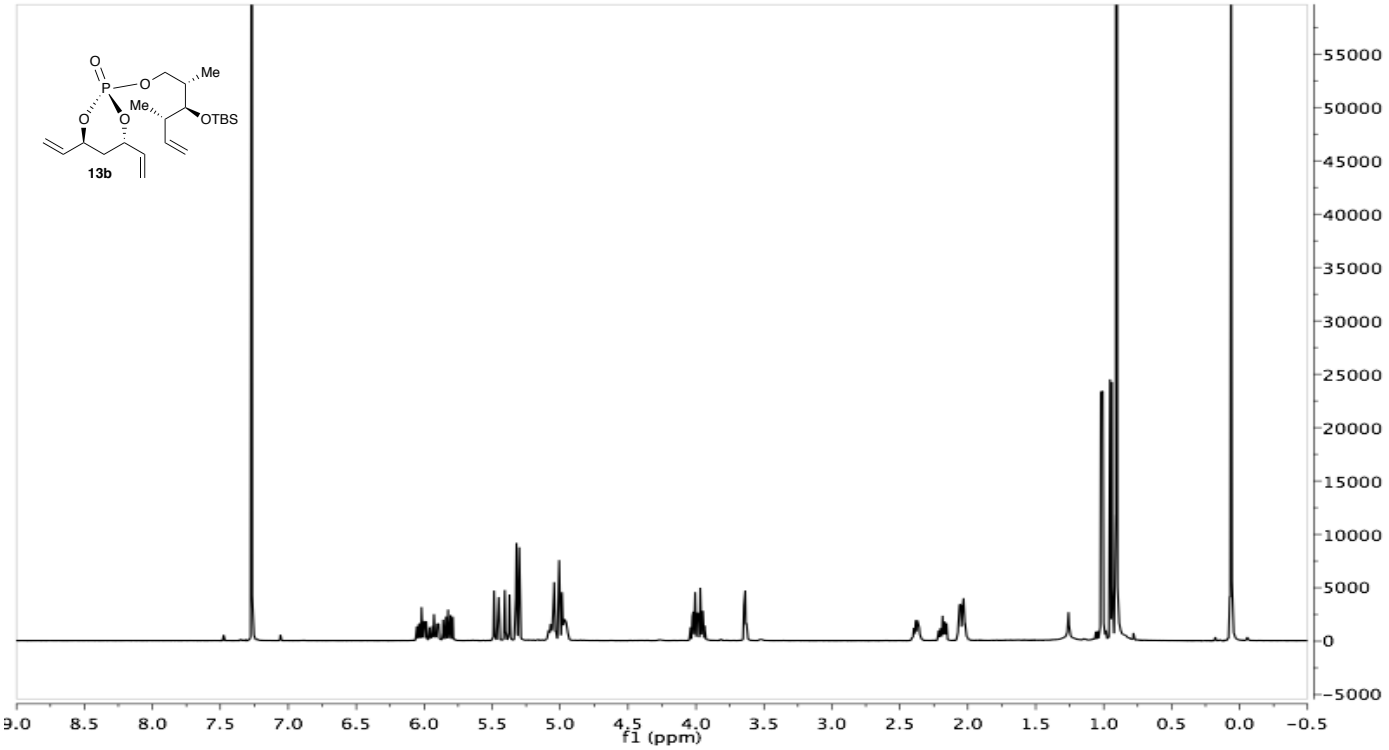
(1*S*,4*S*,5*S*,6*S*,9*S*,11*S*,*E*)-5-hydroxy-4,6-dimethyl-11-vinyl-2,12,13-trioxa-1-phosphabicyclo[7.3.1]tridec-7-ene 1-oxide (14a):

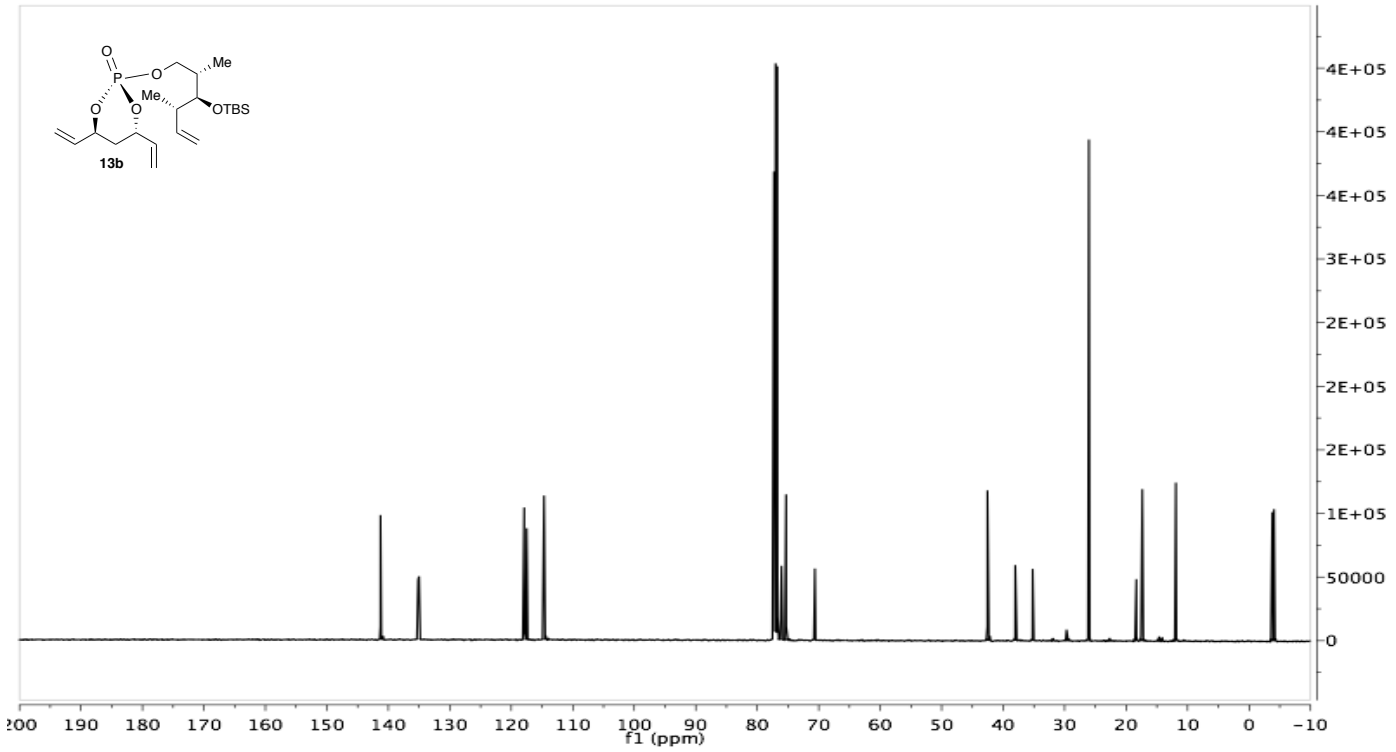


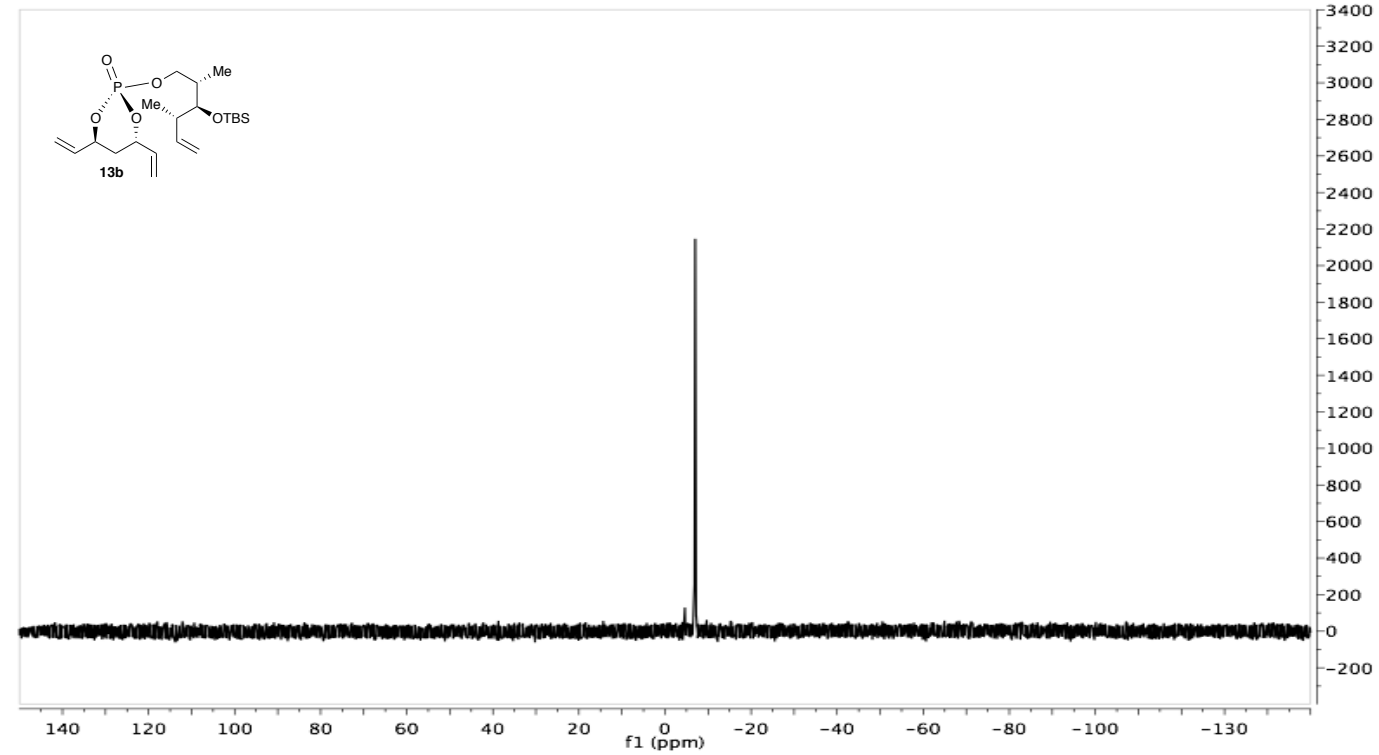




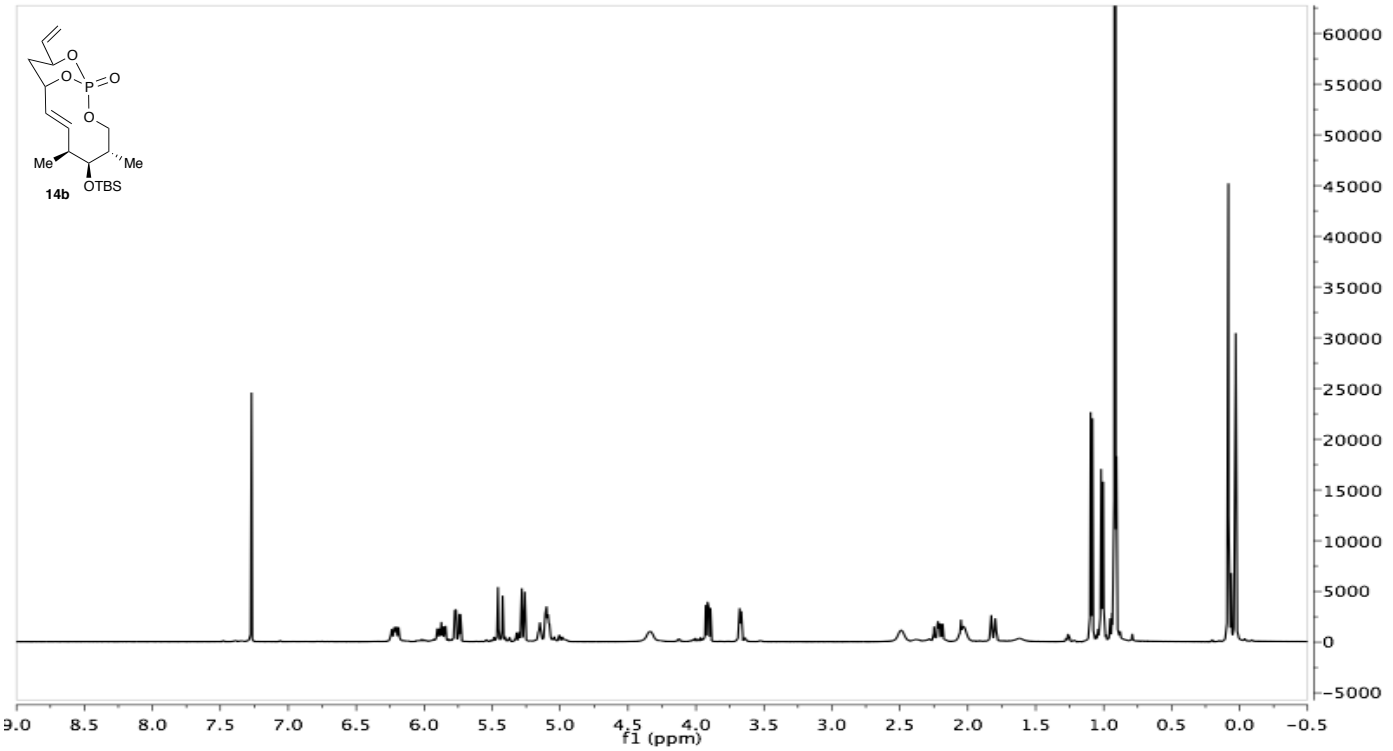
(4*S*,6*S*)-2-(((2*S*,3*S*,4*S*)-3-((*tert*-butyldimethylsilyl)oxy)-2,4-dimethylhex-5-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (13b):

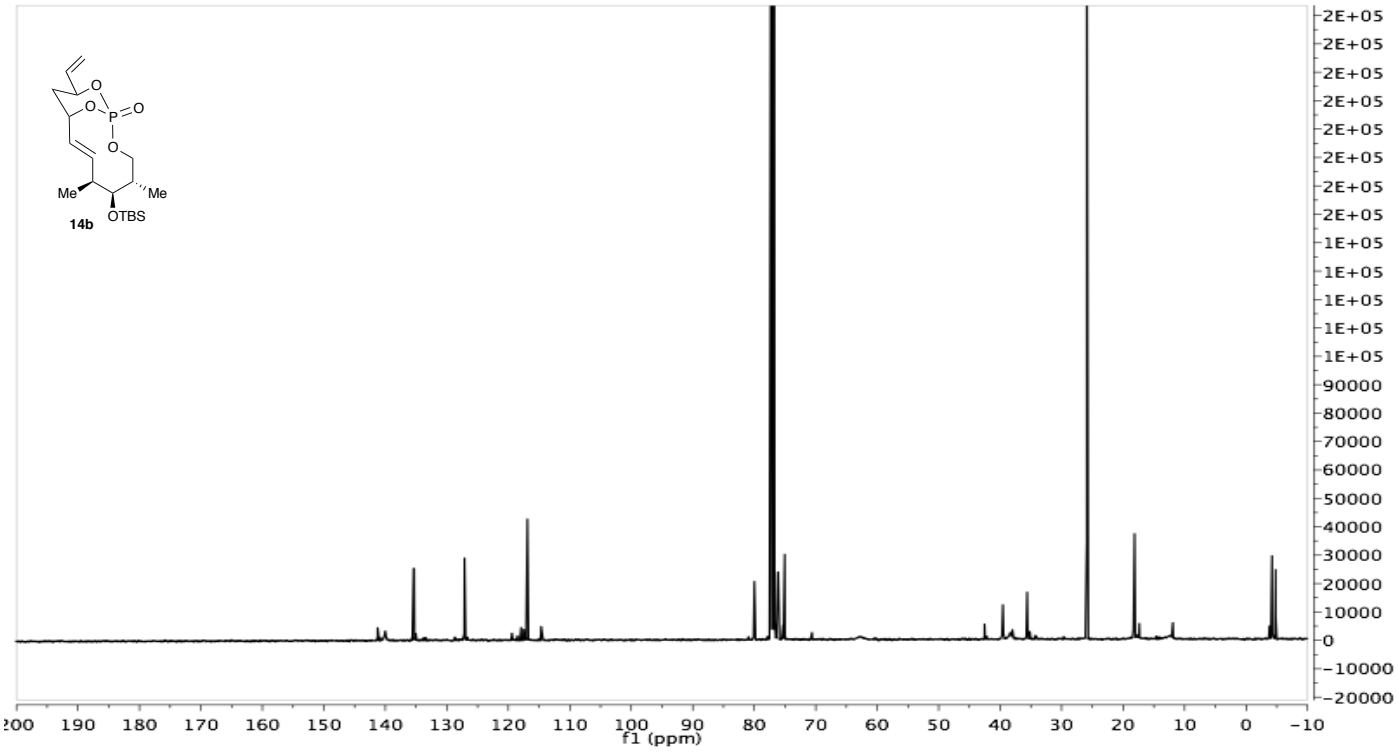


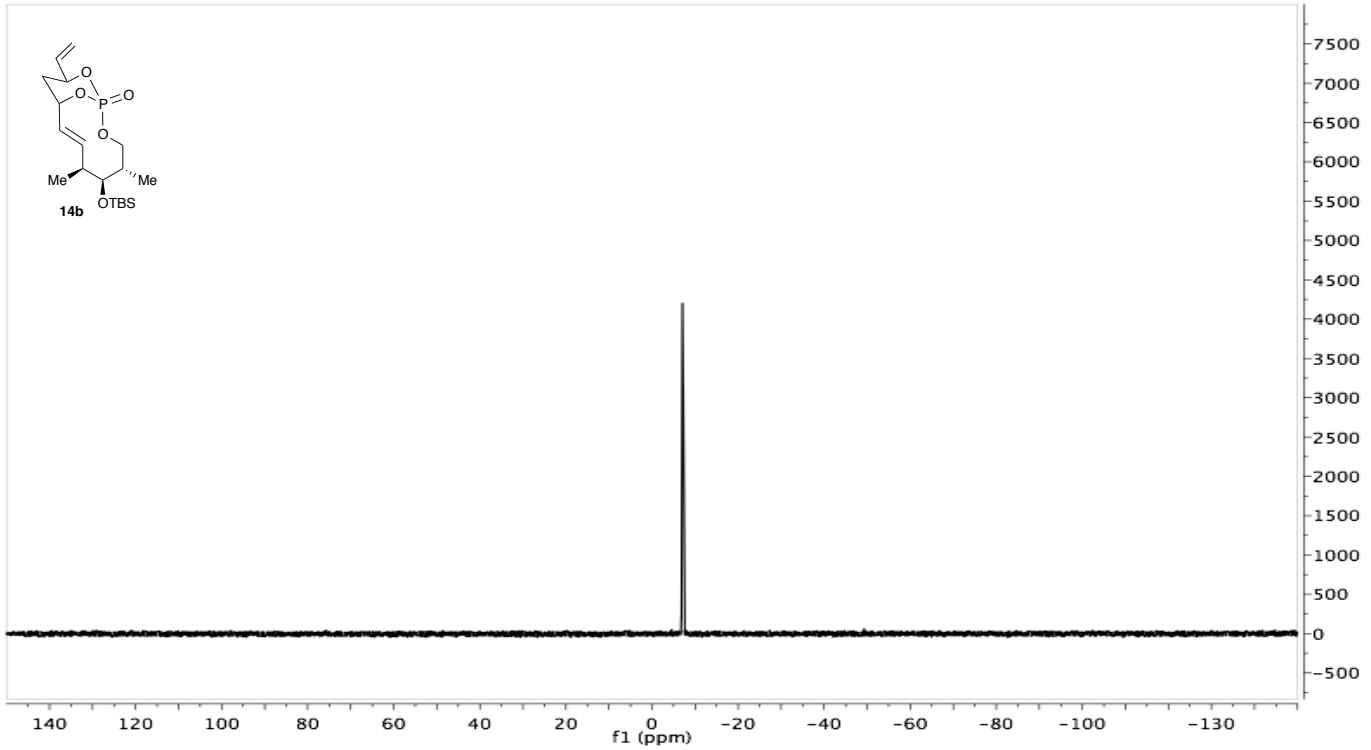

13b
Me
OTBS
4E+05
3E+05
2E+05
1E+05
50000
0
f1 (ppm)


13b
Me
OTBS
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
f1 (ppm)

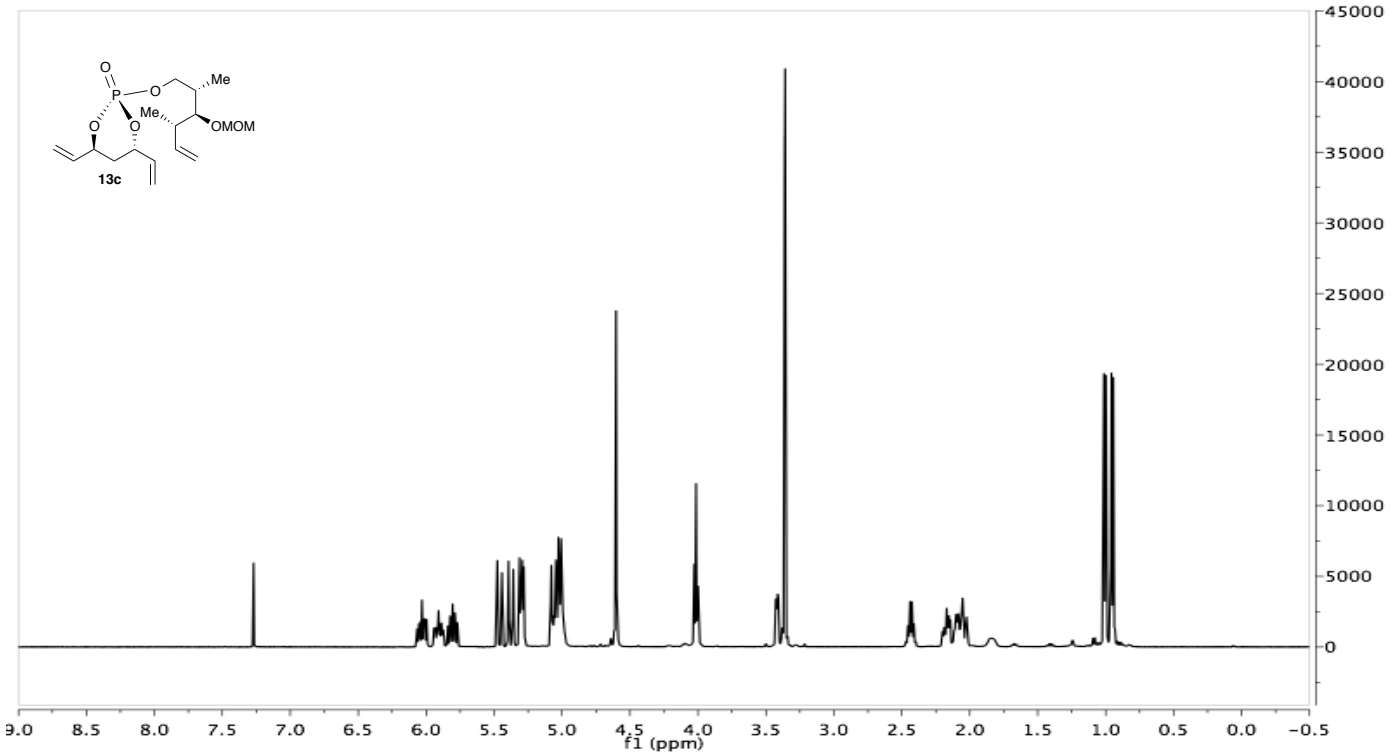
(1*S*,4*S*,5*S*,6*S*,9*S*,11*S*,*E*)-5-((*tert*-butyldimethylsilyl)oxy)-4,6-dimethyl-11-vinyl-2,12,13-trioxa-1-phosphabicyclo[7.3.1]tridec-7-ene 1-oxide (14b):

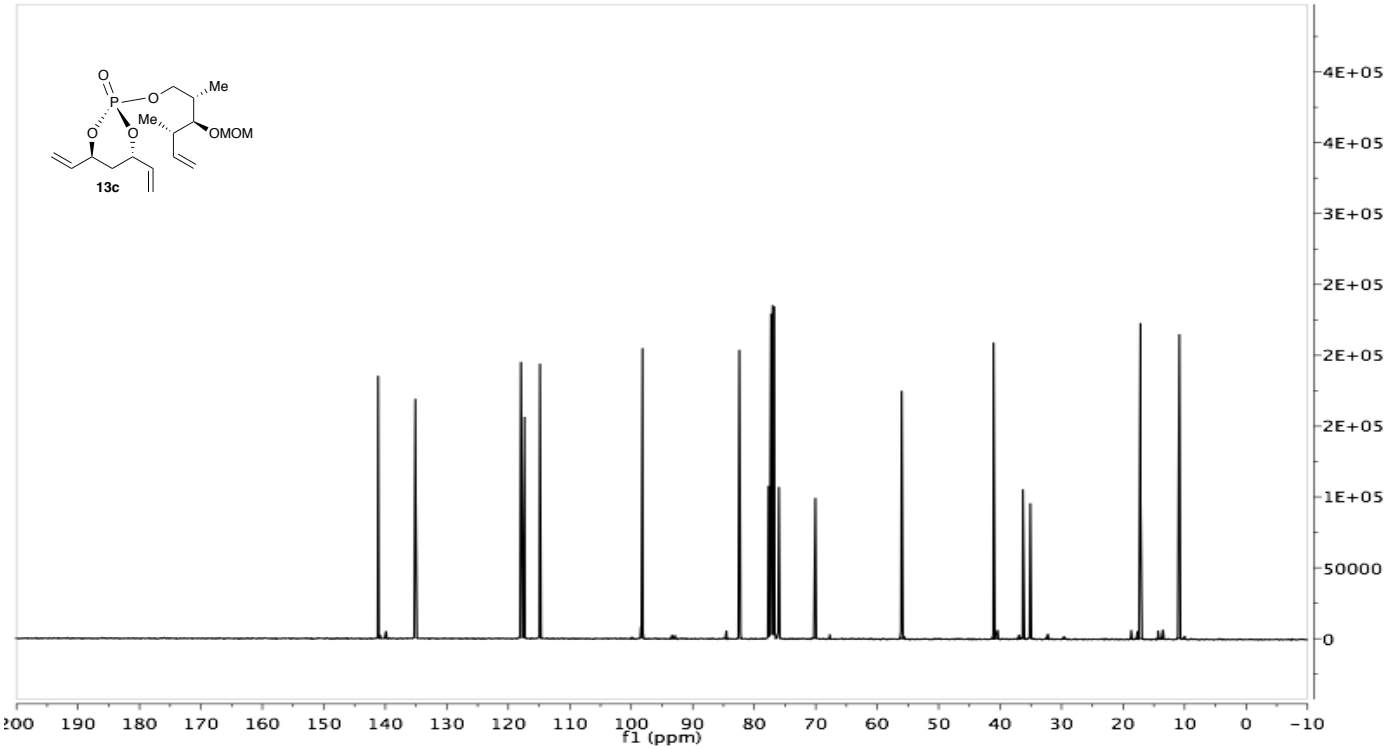


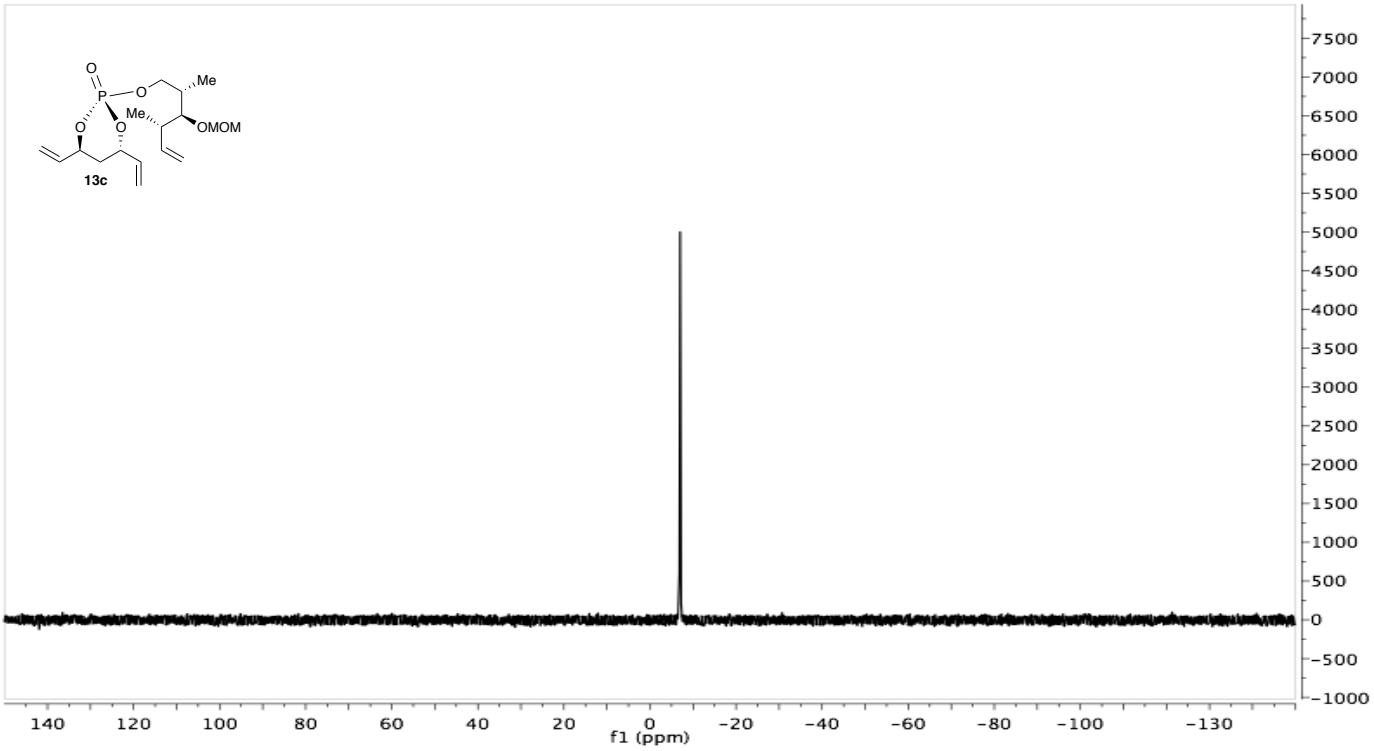




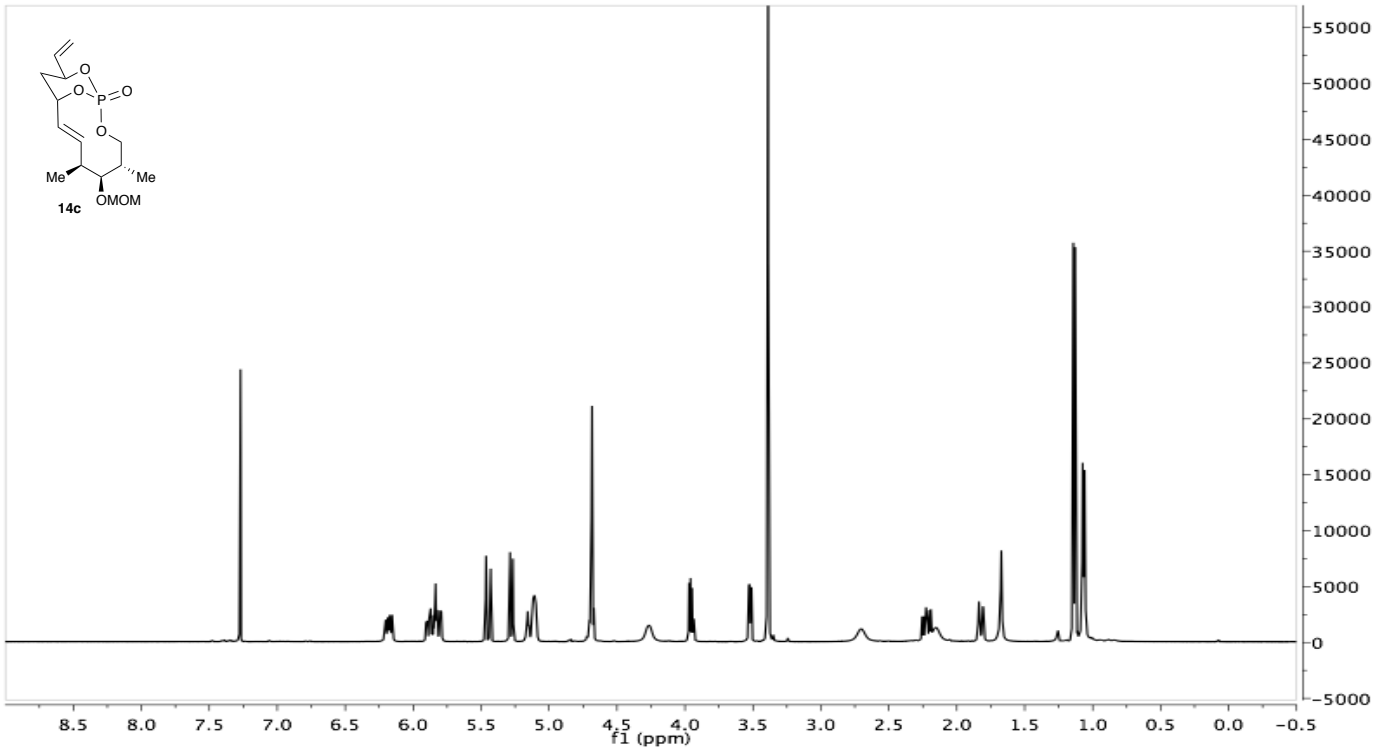
(4*S*,6*S*)-2-(((2*S*,3*S*,4*S*)-3-(methoxymethoxy)-2,4-dimethylhex-5-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (13c):

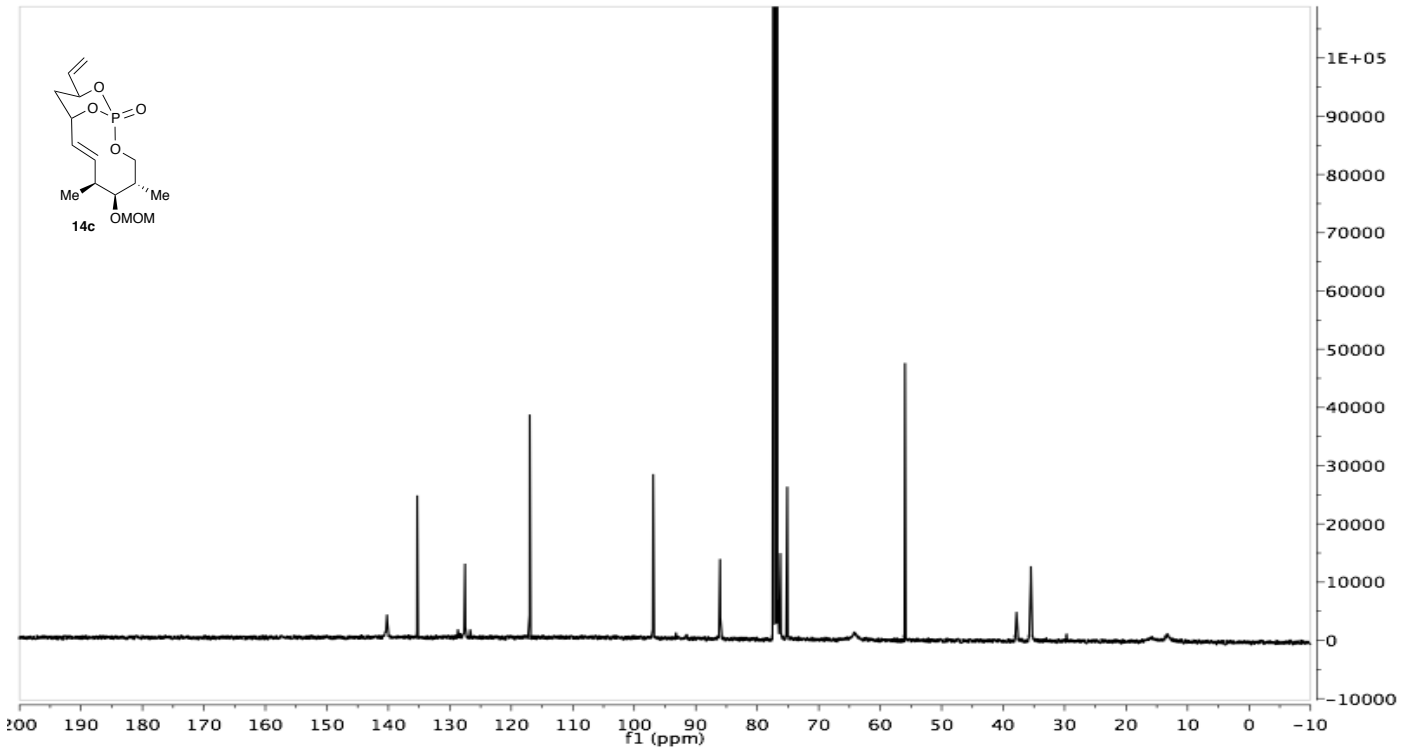


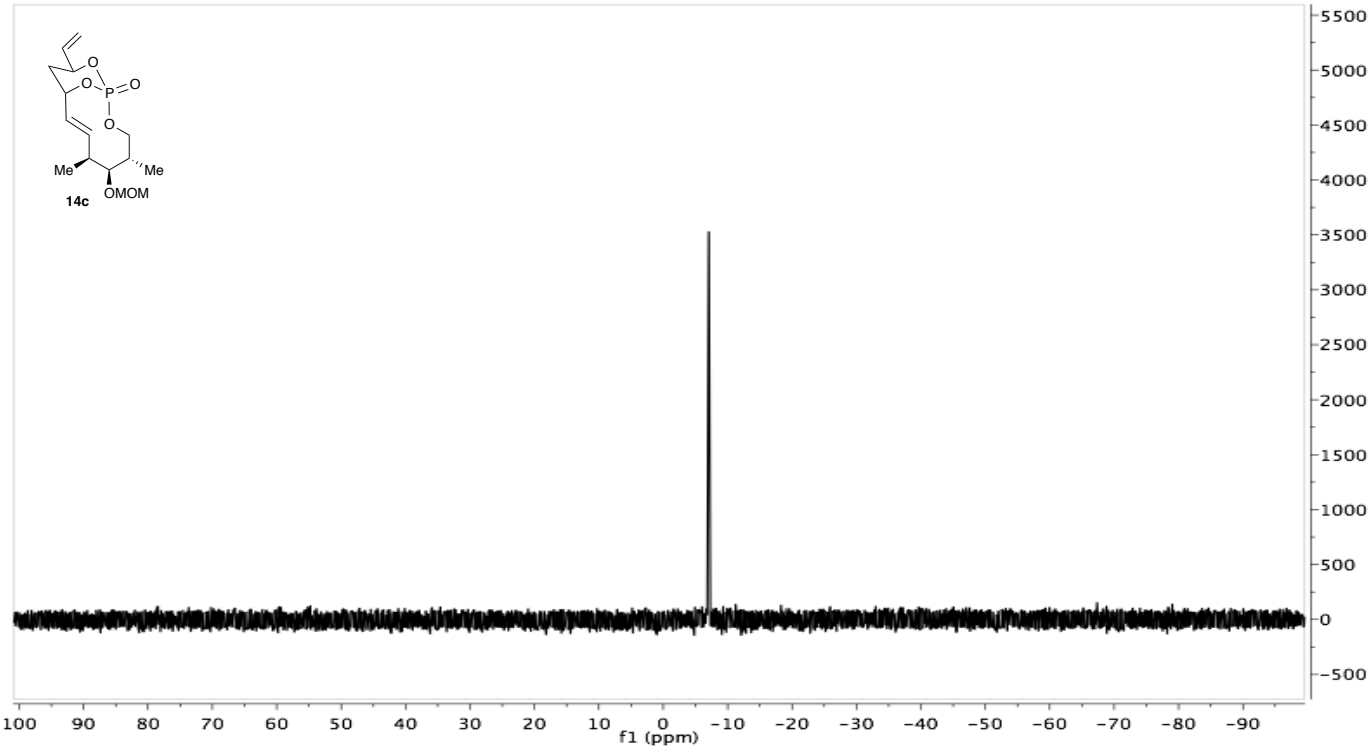

13c
Me
OMOM
4E+05
3E+05
2E+05
1E+05
50000
0
f1 (ppm)


13c
Me
OMOM
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
f1 (ppm)

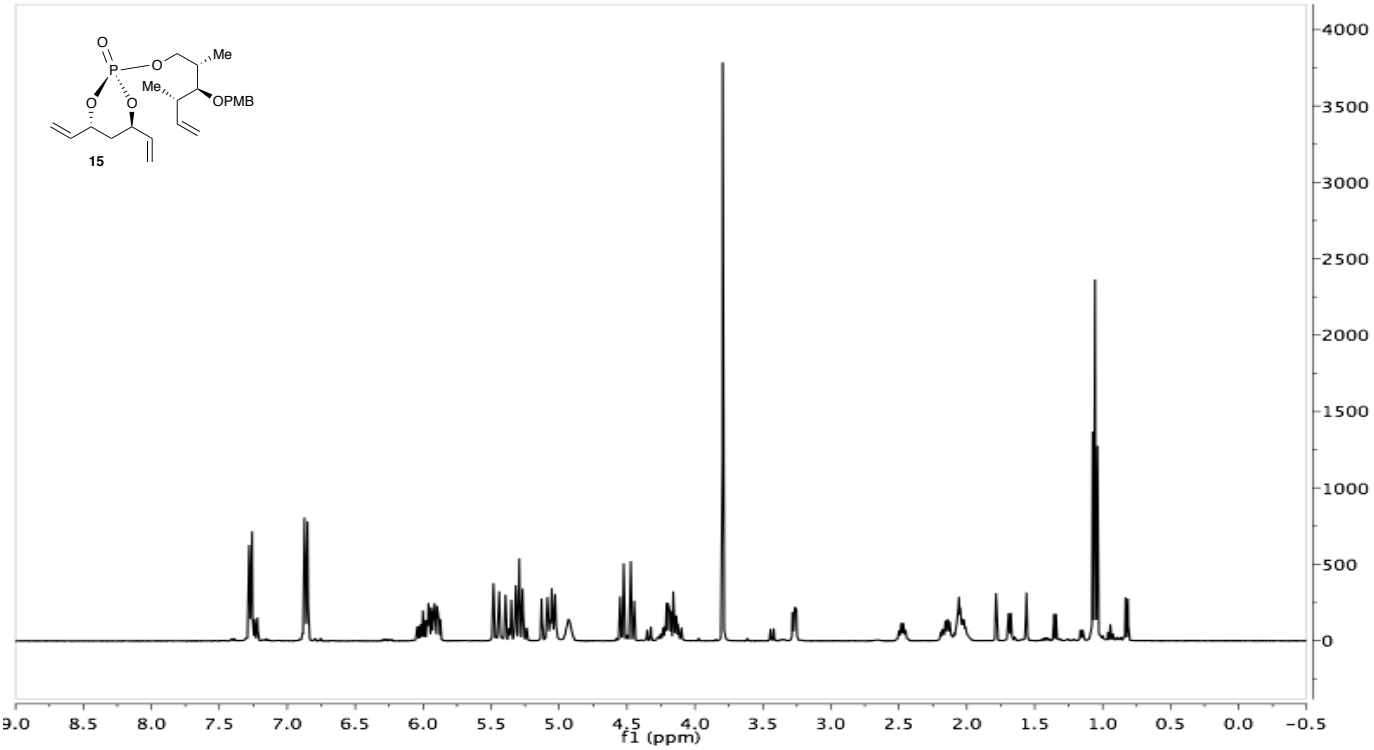
(1*S*,4*S*,5*S*,6*S*,9*S*,11*S*,*E*)-5-(methoxymethoxy)-4,6-dimethyl-11-vinyl-2,12,13-trioxa-1-phosphabicyclo[7.3.1]tridec-7-ene 1-oxide (14c):

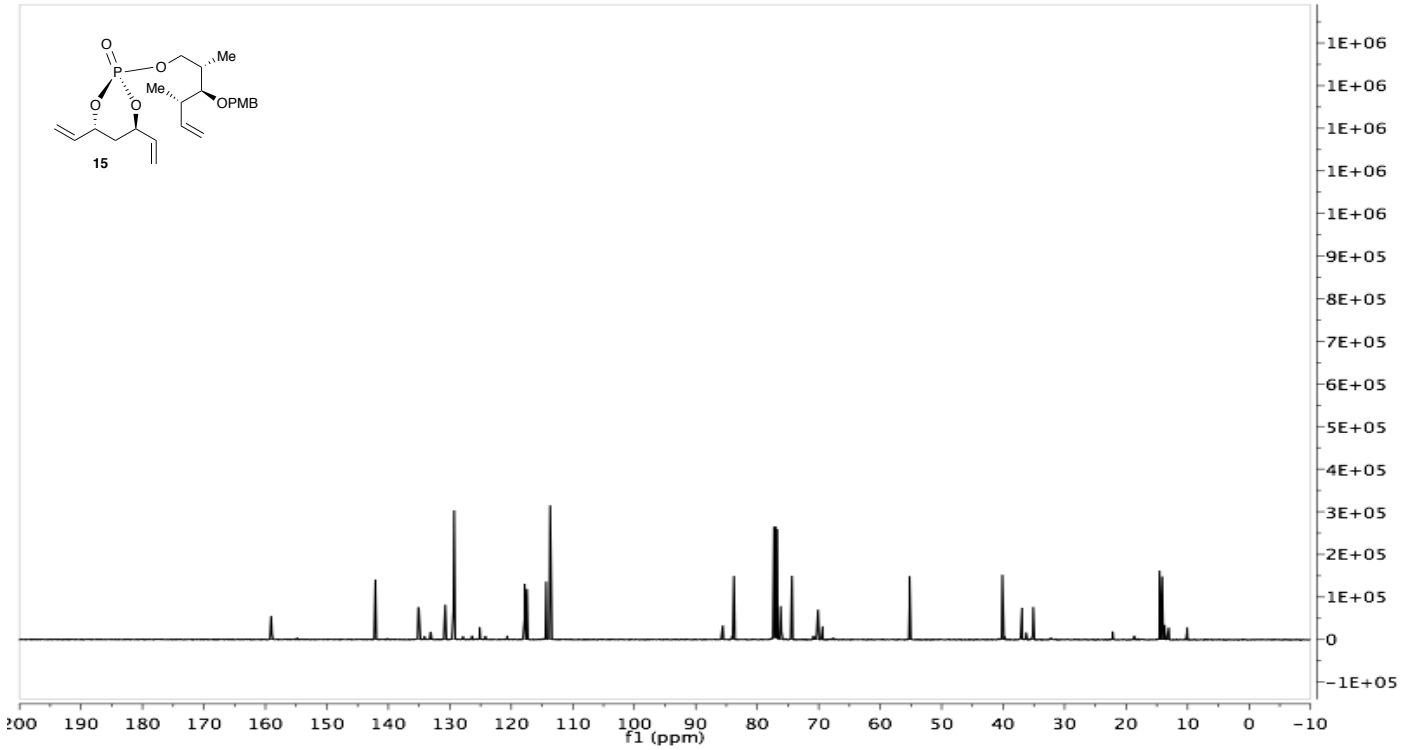


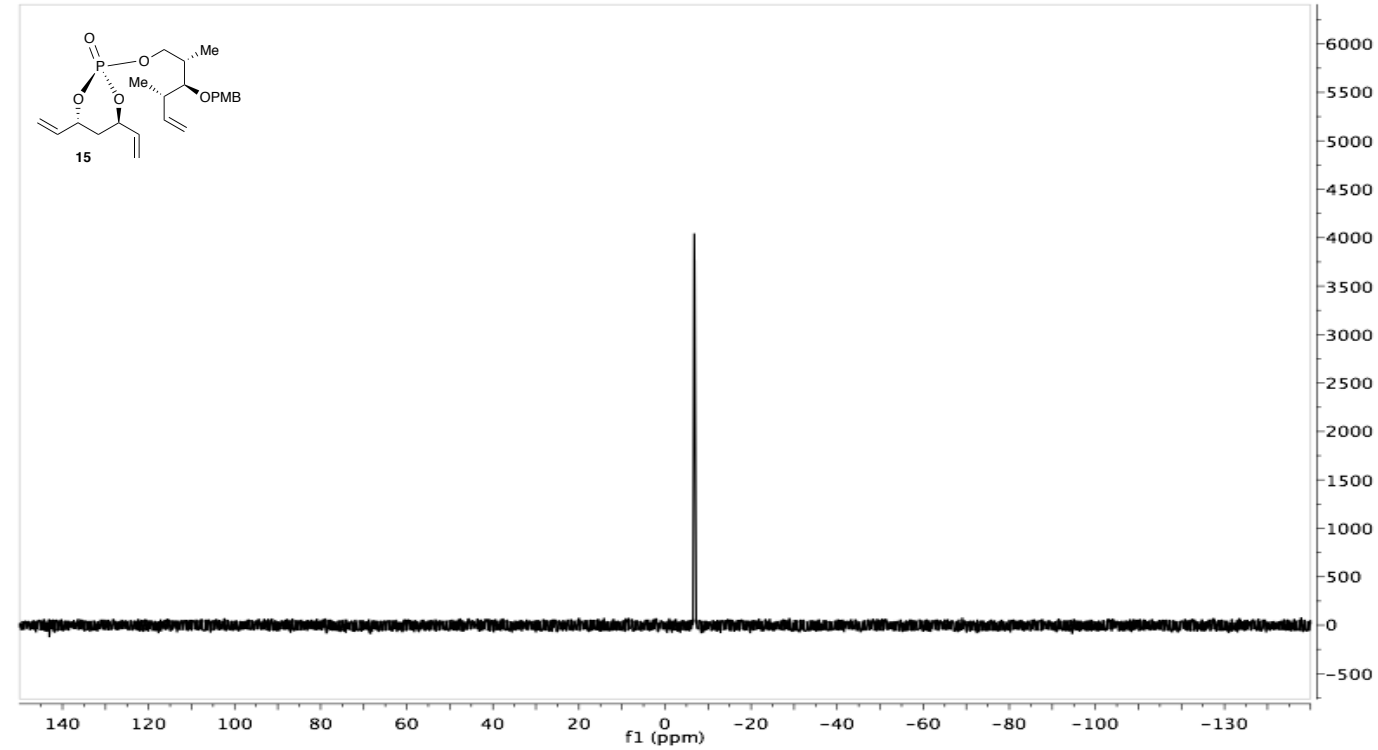




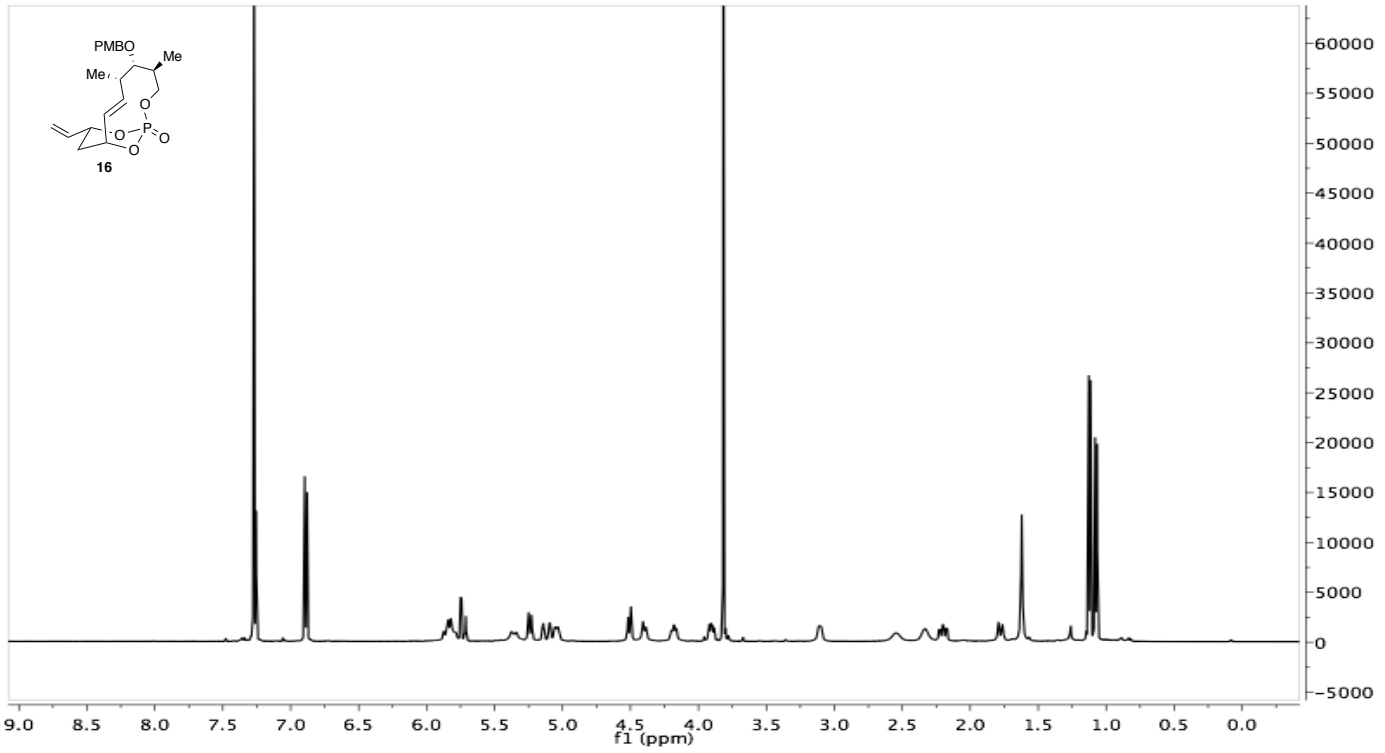
(4*R*,6*R*)-2-(((2*S*,3*S*,4*S*)-3-((4-methoxybenzyl)oxy)-2,4-dimethylhex-5-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (15):

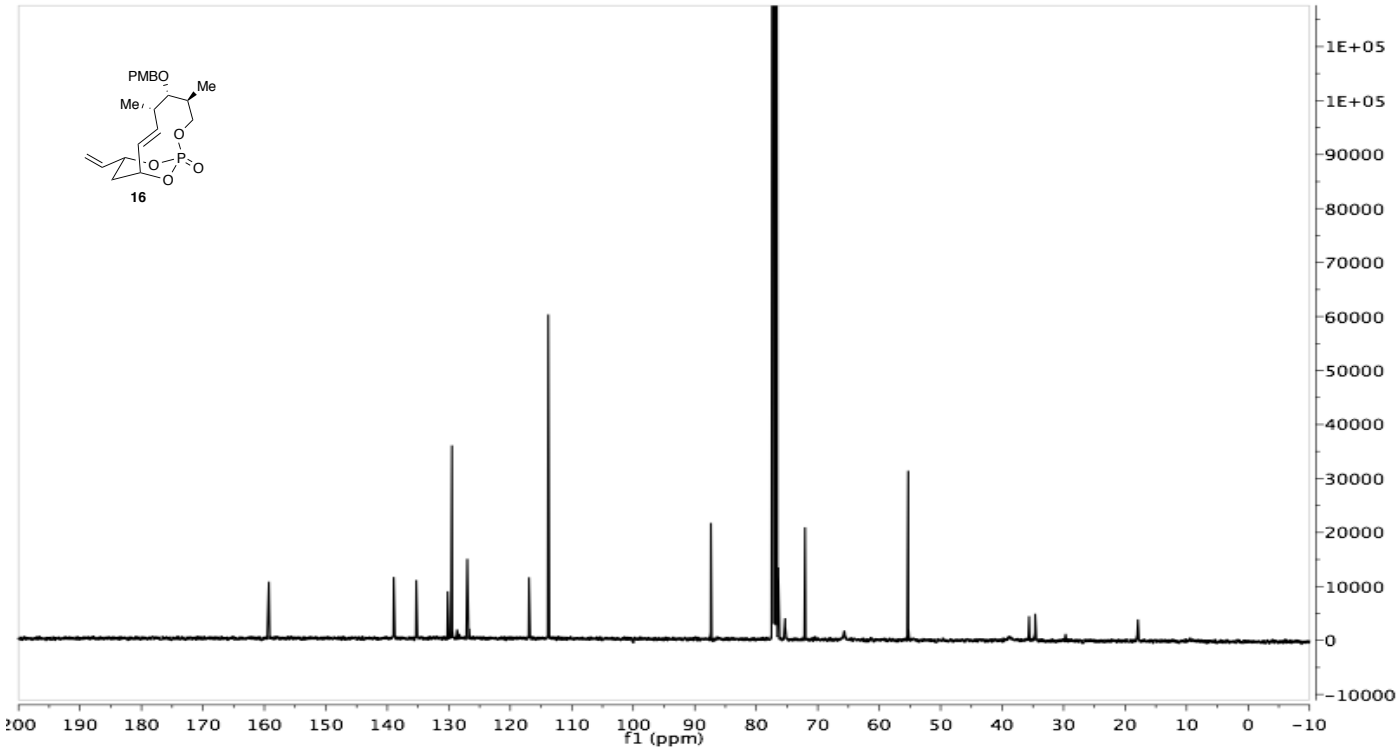


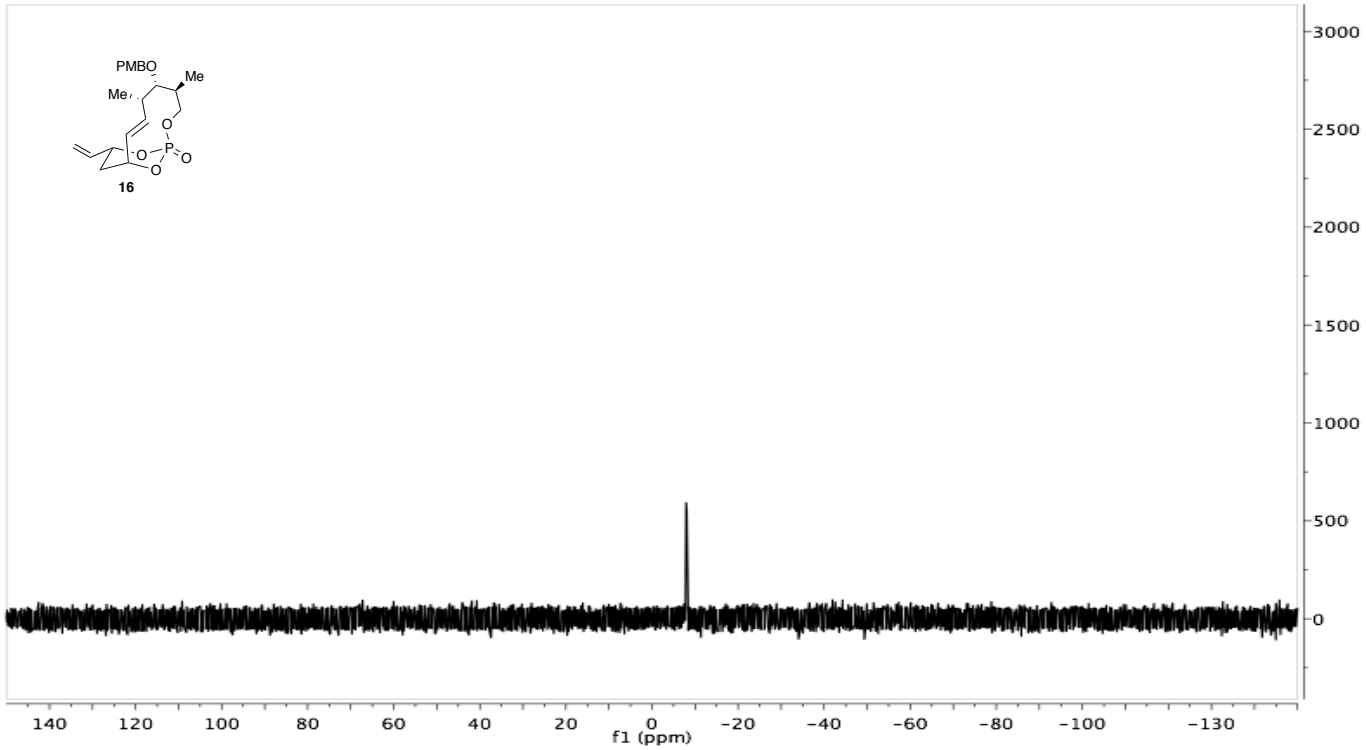

15
Me
OPMB
Me
1E+06
9E+05
8E+05
7E+05
6E+05
5E+05
4E+05
3E+05
2E+05
1E+05
0
-1E+05
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


15
Me
OPMB
Me
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -130
f1 (ppm)

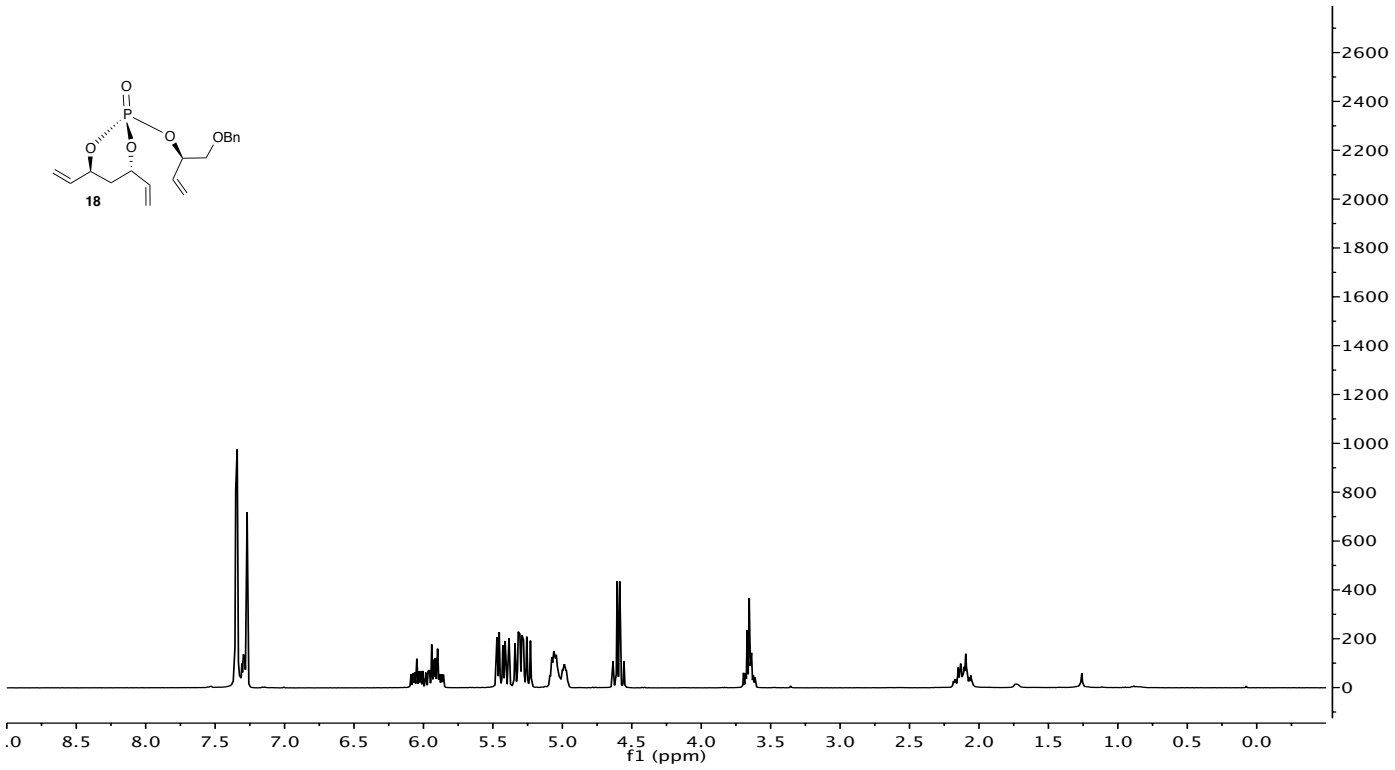
(1*R*,4*S*,5*S*,6*S*,9*R*,11*R*,*E*)-5-((4-methoxybenzyl)oxy)-4,6-dimethyl-11-vinyl-2,12,13-trioxa-1-phosphabicyclo[7.3.1]tridec-7-ene 1-oxide (16):

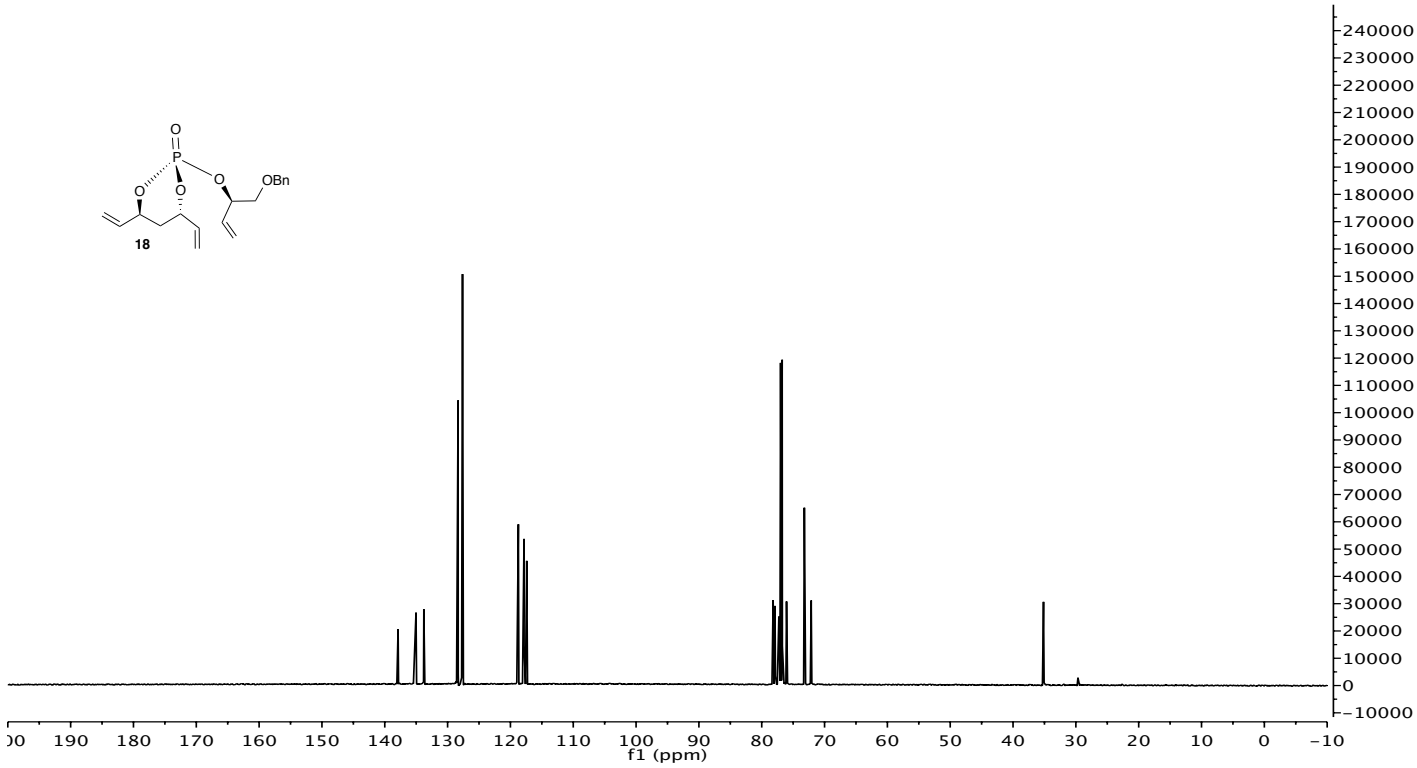


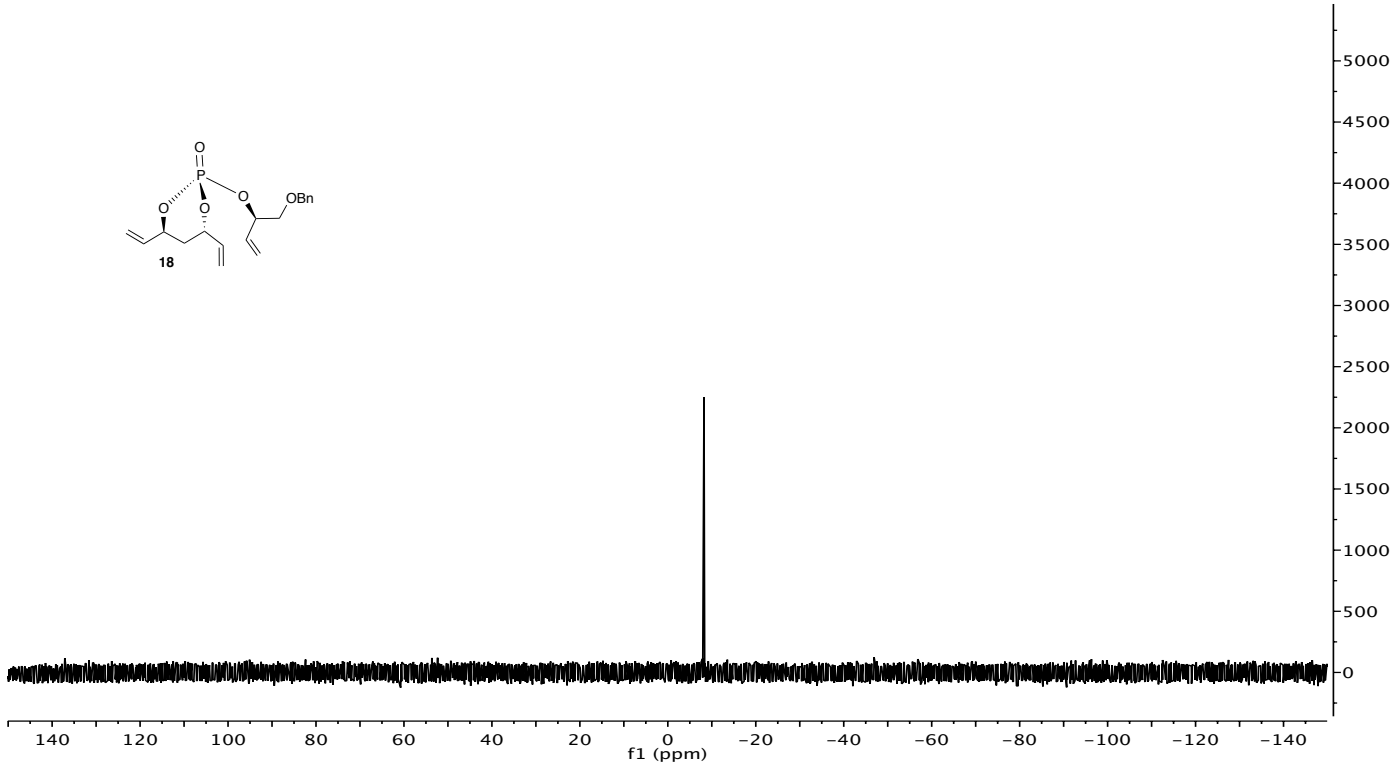




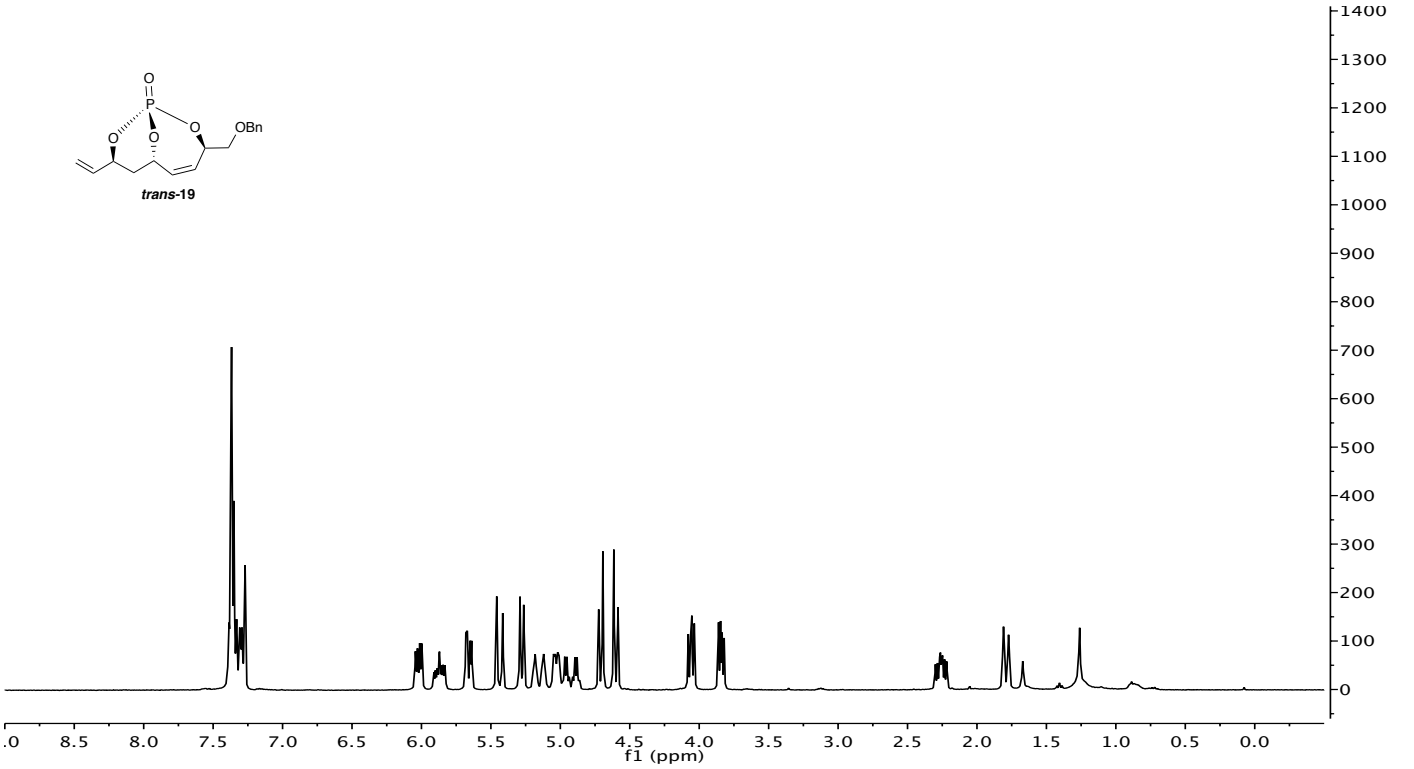
(4*S*,6*S*)-2-(((*R*)-1-(benzyloxy)but-3-en-2-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (18):

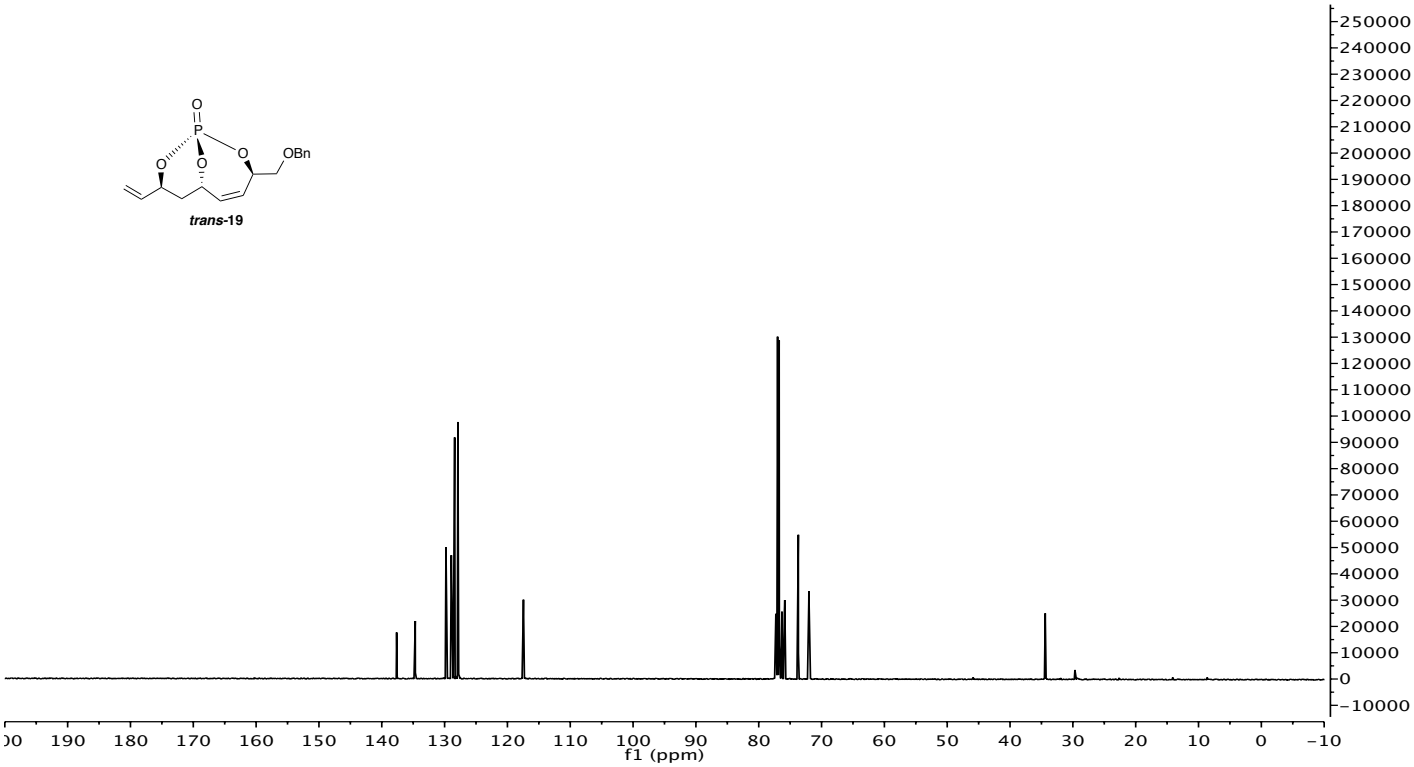


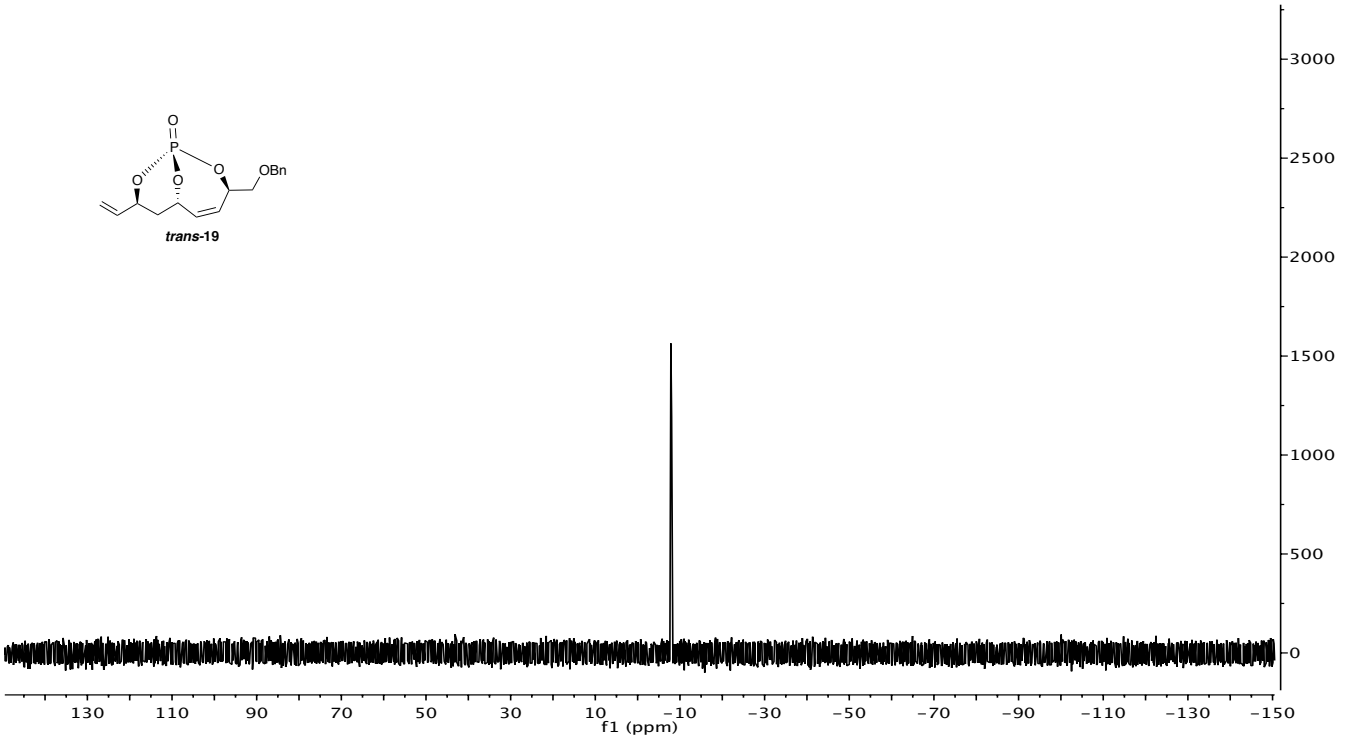

O
P
O
O
O
OBn
18
240000
230000
220000
210000
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
−10000
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


O
P
O
O
O
OBn
18
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140
f1 (ppm)

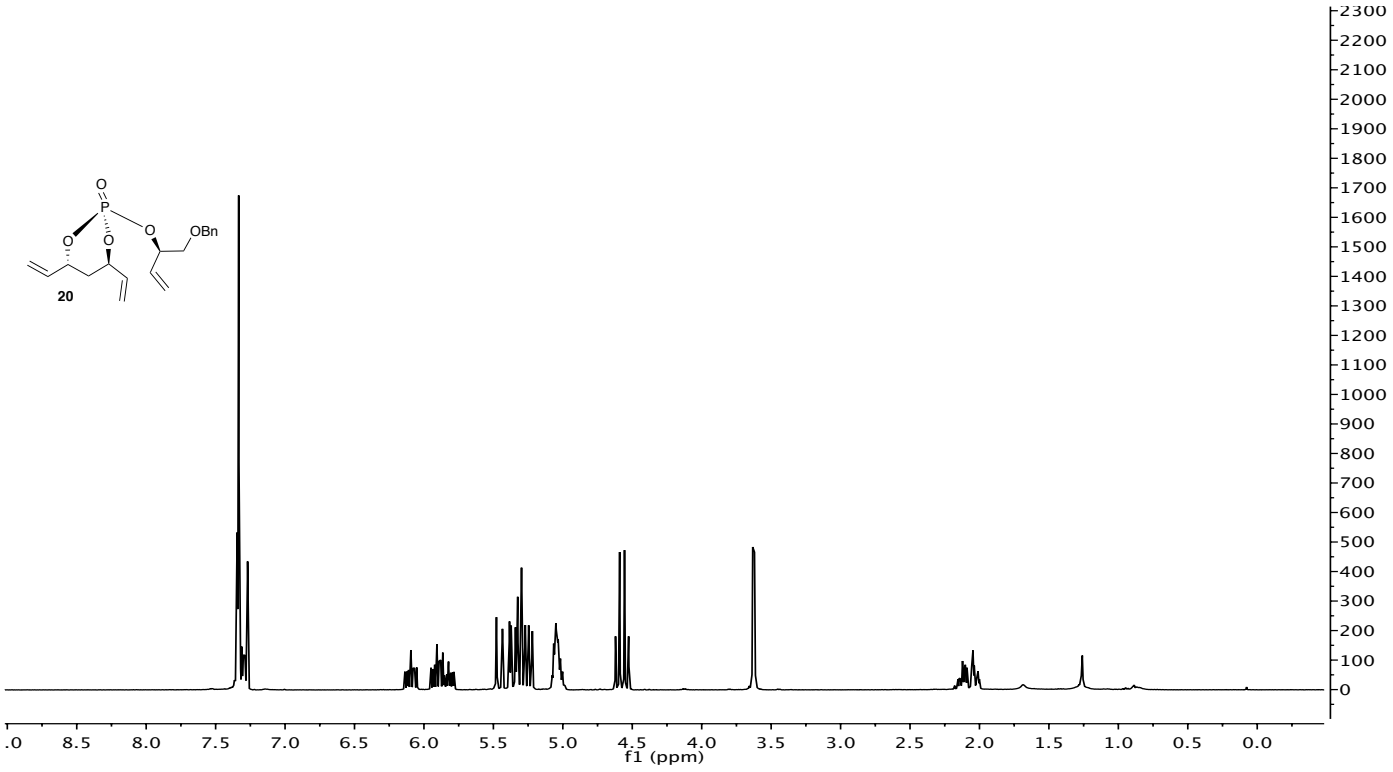
(1*S*,3*R*,6*S*,8*S*)-3-((benzyloxy)methyl)-8-vinyl-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (*trans*-19):

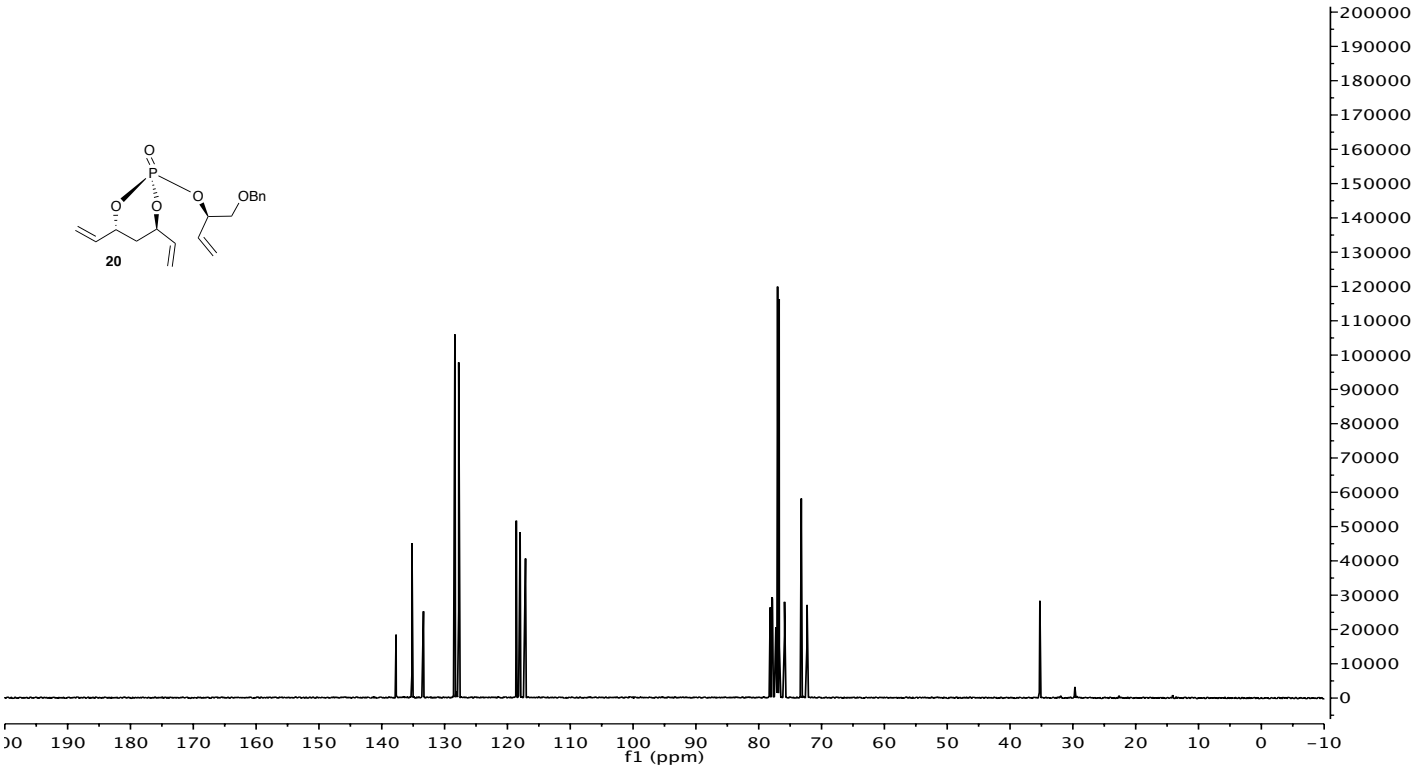


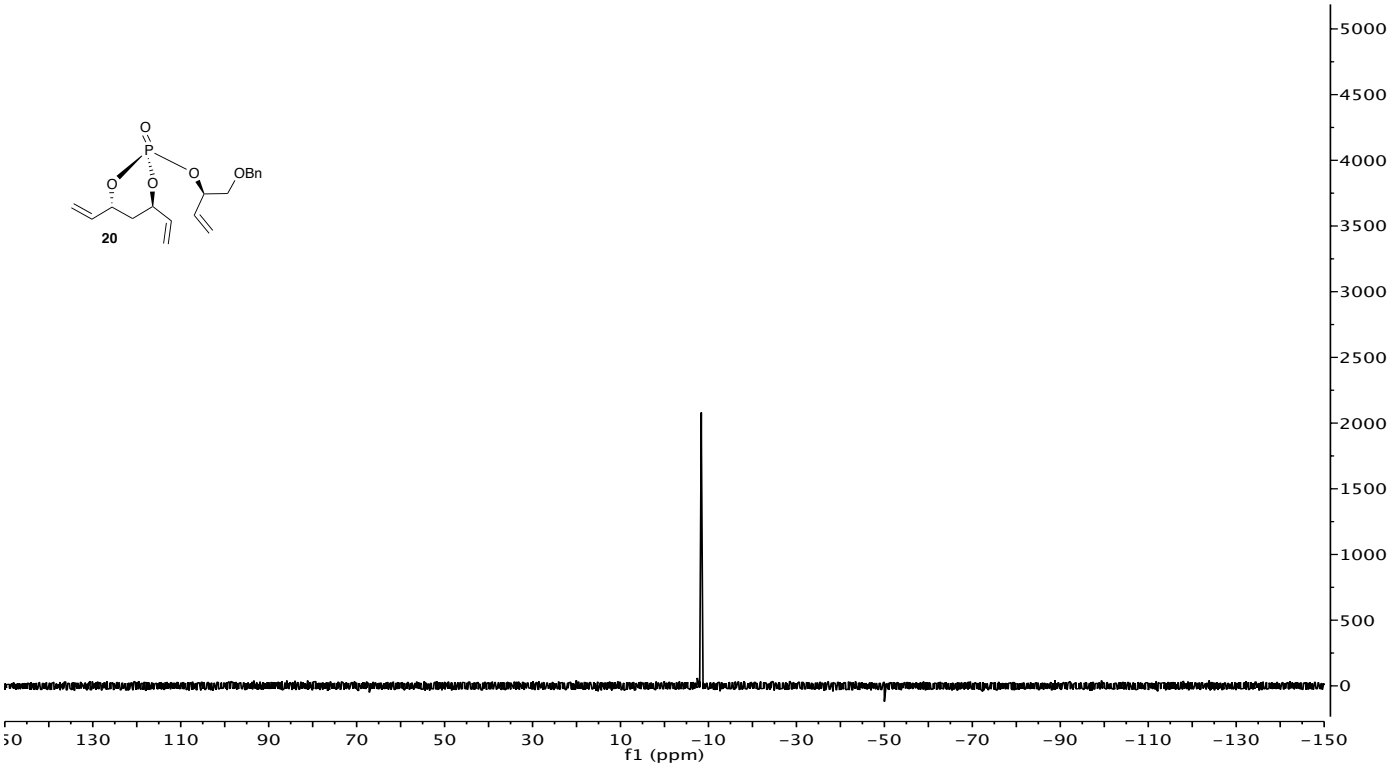




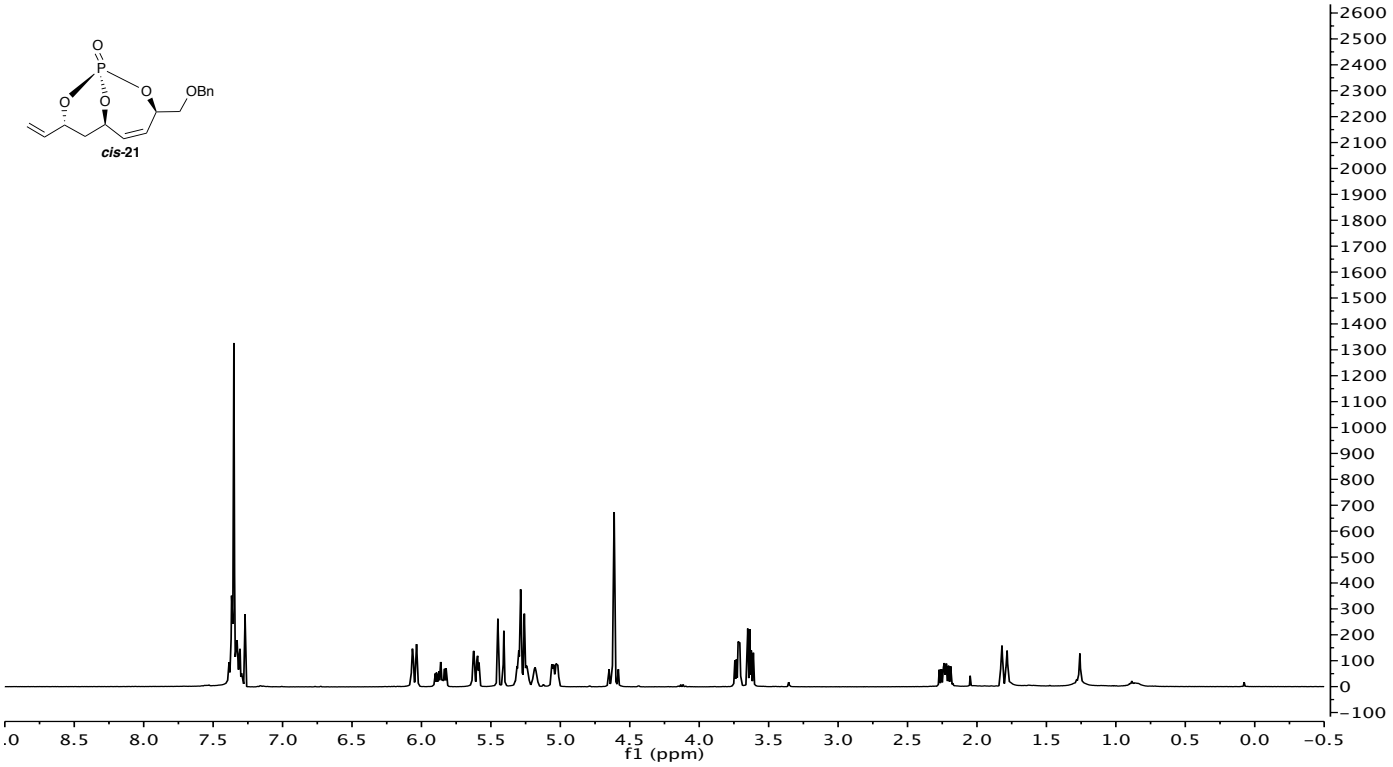
(4*R*,6*R*)-2-(((*R*)-1-(benzyloxy)but-3-en-2-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (20):

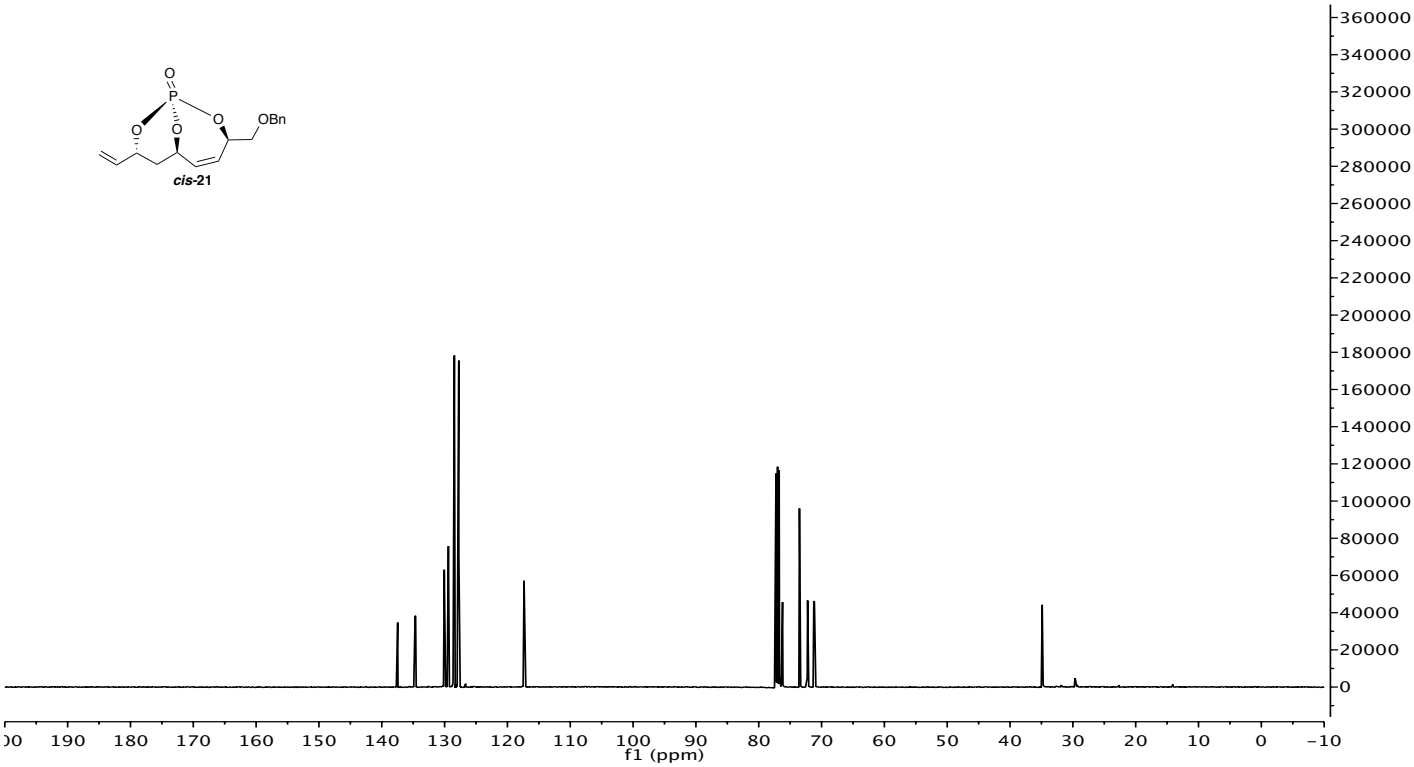


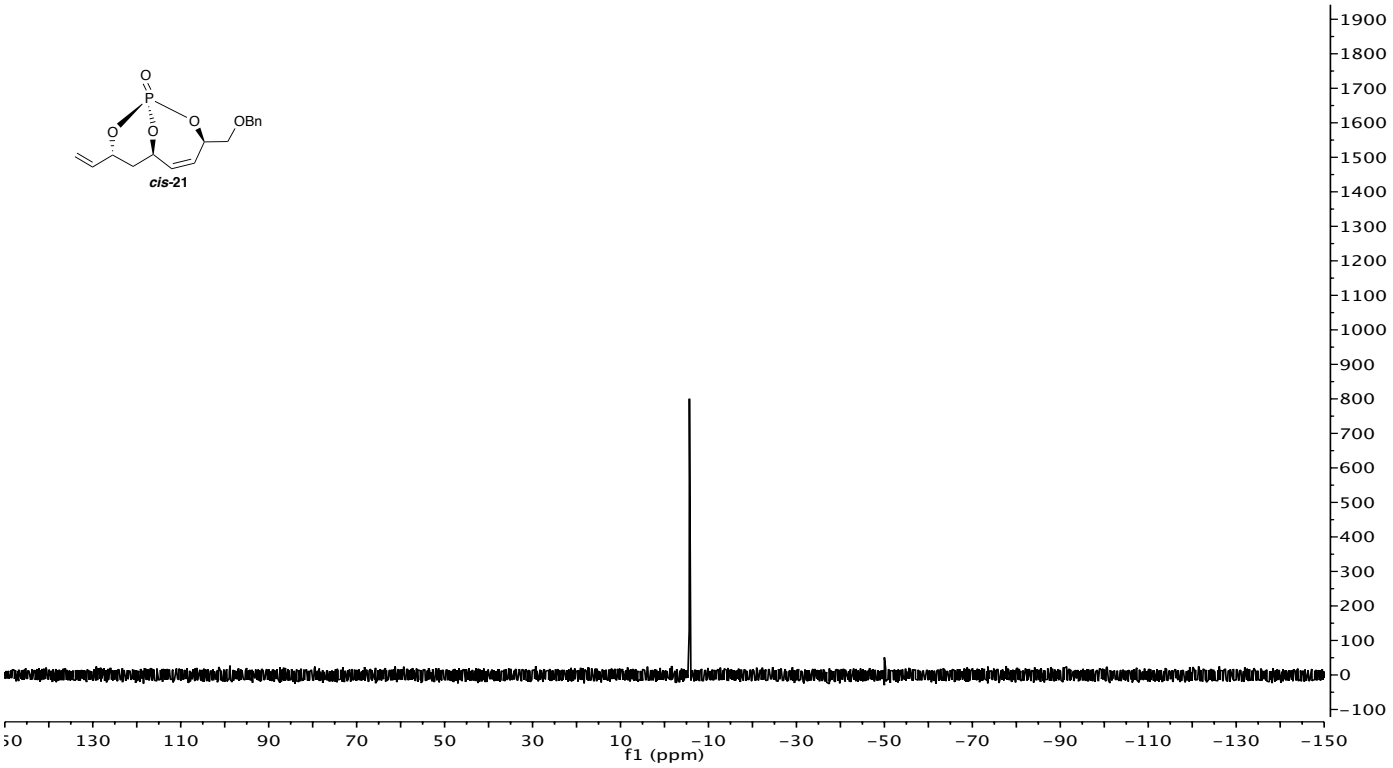

O
P
O
O
O
OBn
20
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


O
P
O
O
O
OBn
20
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150
f1 (ppm)

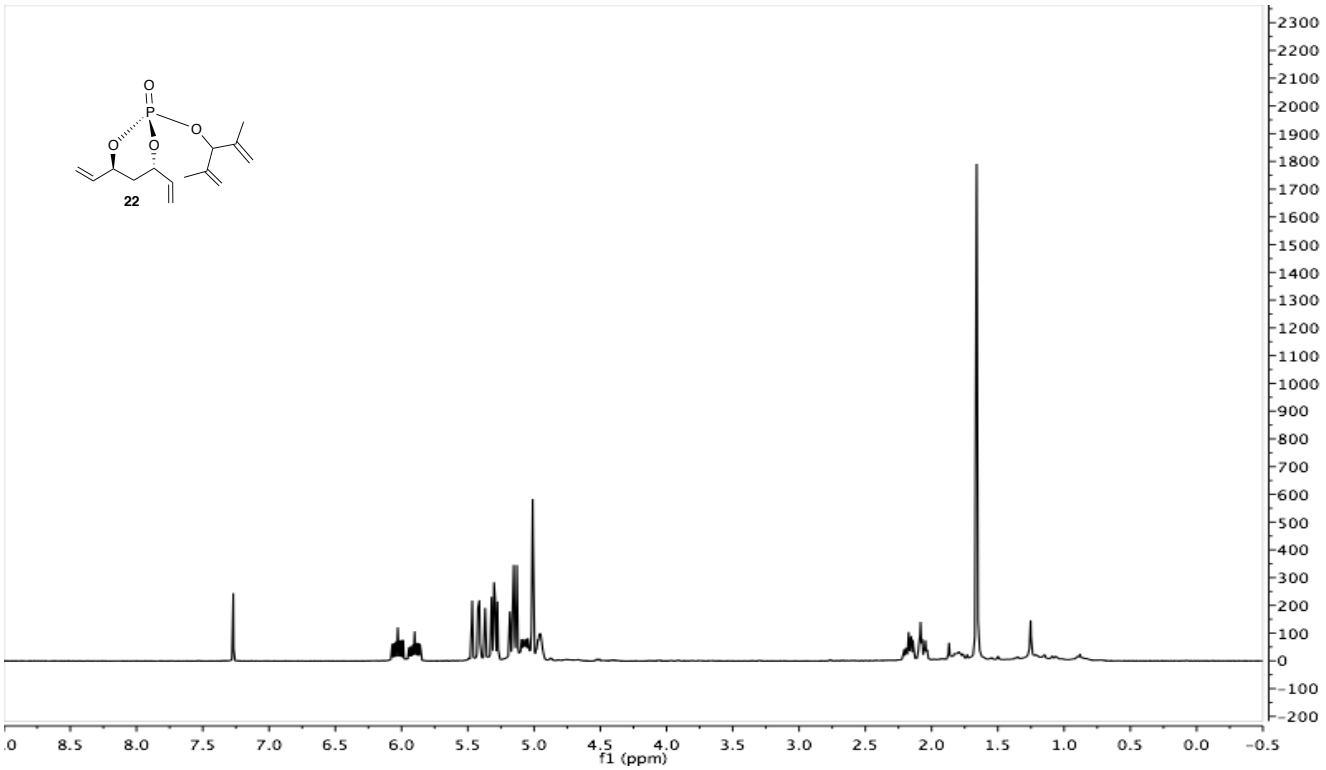
(1*R*,3*R*,6*R*,8*R*)-3-((benzyloxy)methyl)-8-vinyl-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (*cis*-21):

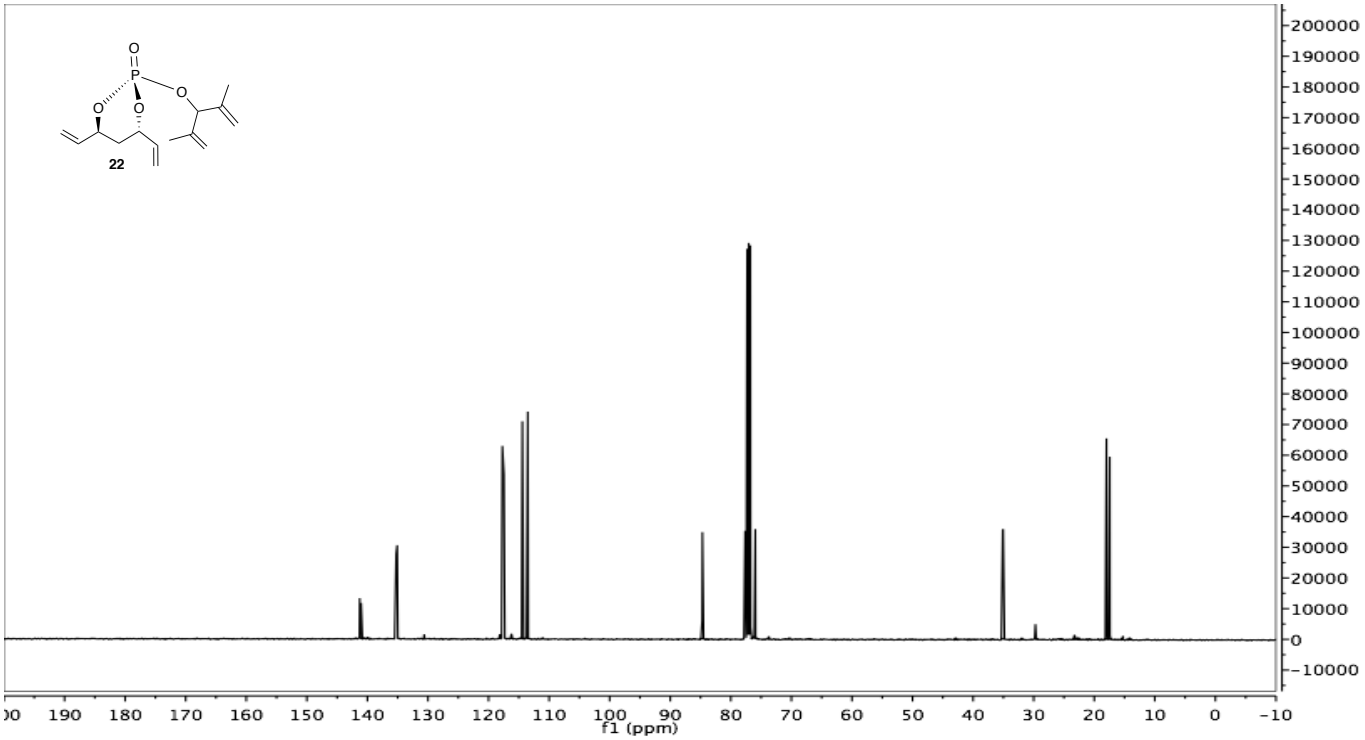


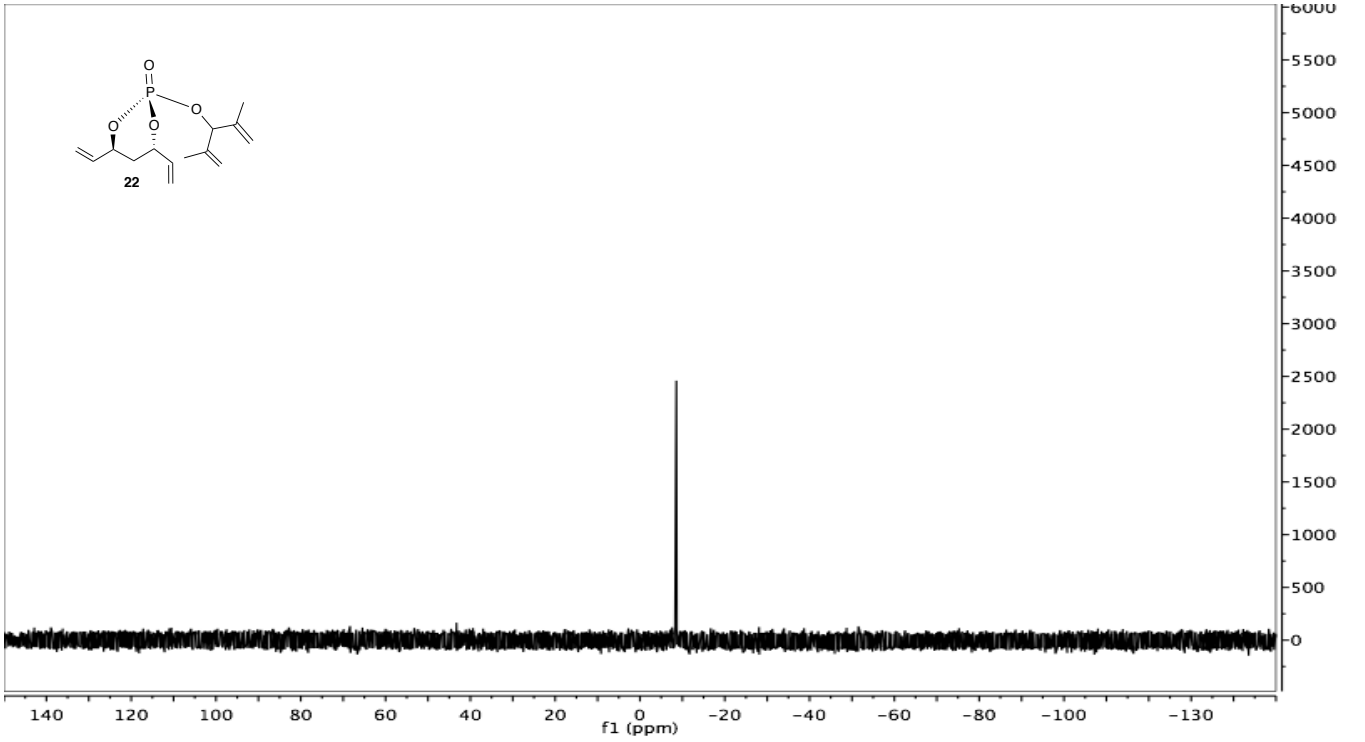




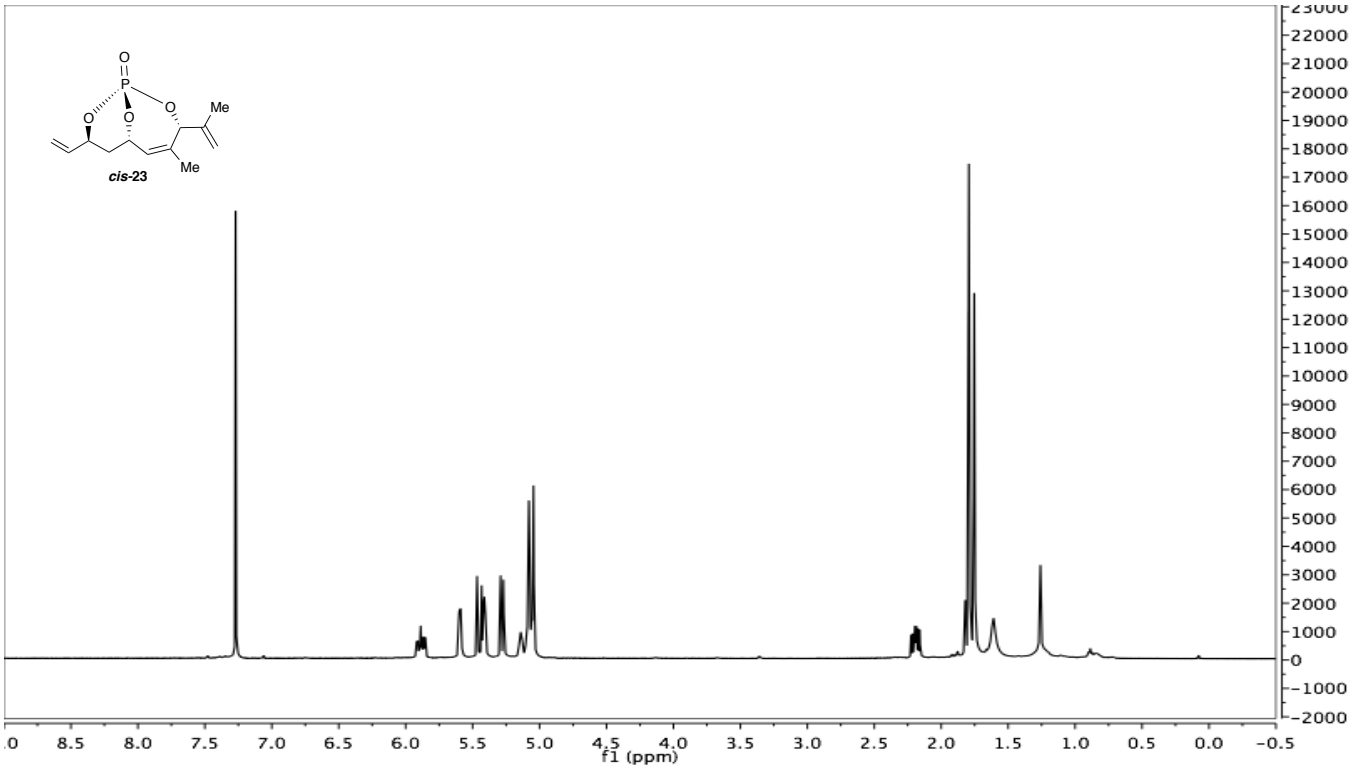
(4*S*,6*S*)-2-((2,4-dimethylpenta-1,4-dien-3-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (22):

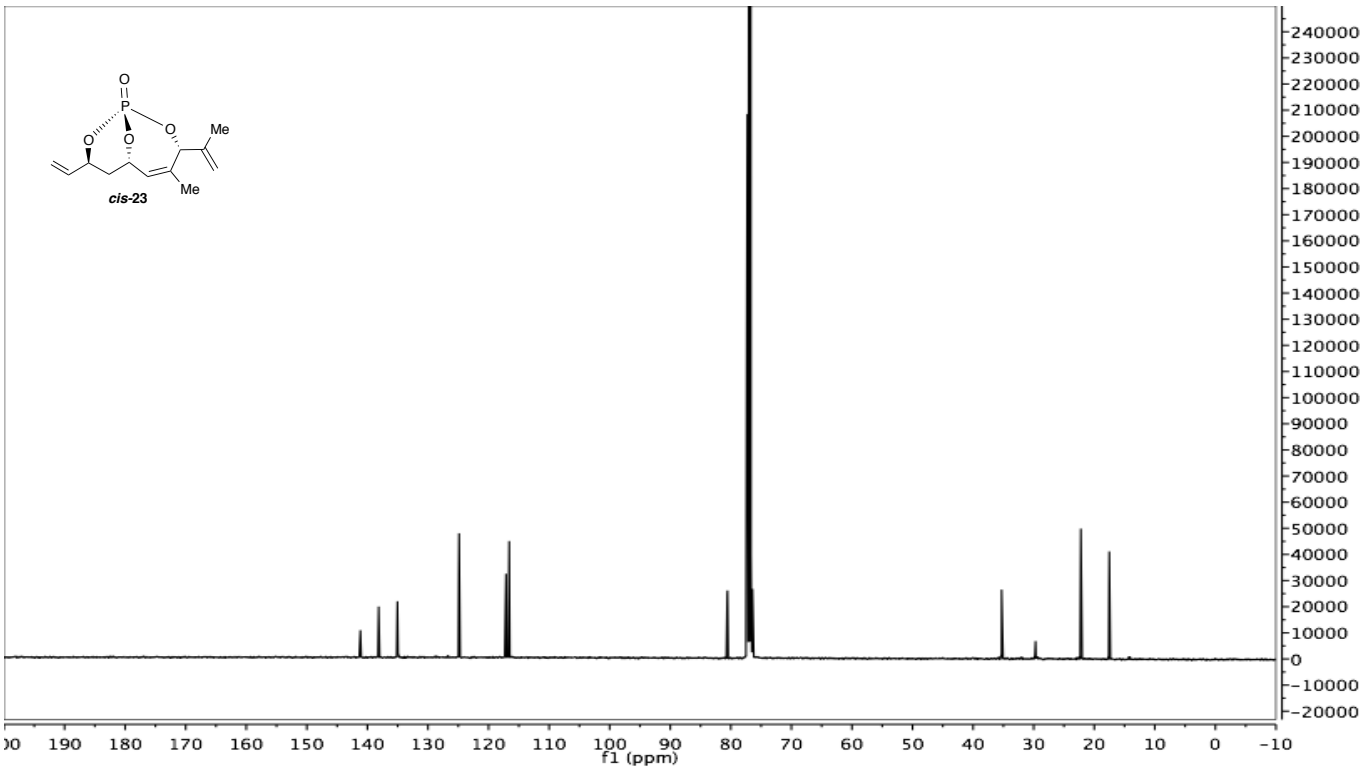


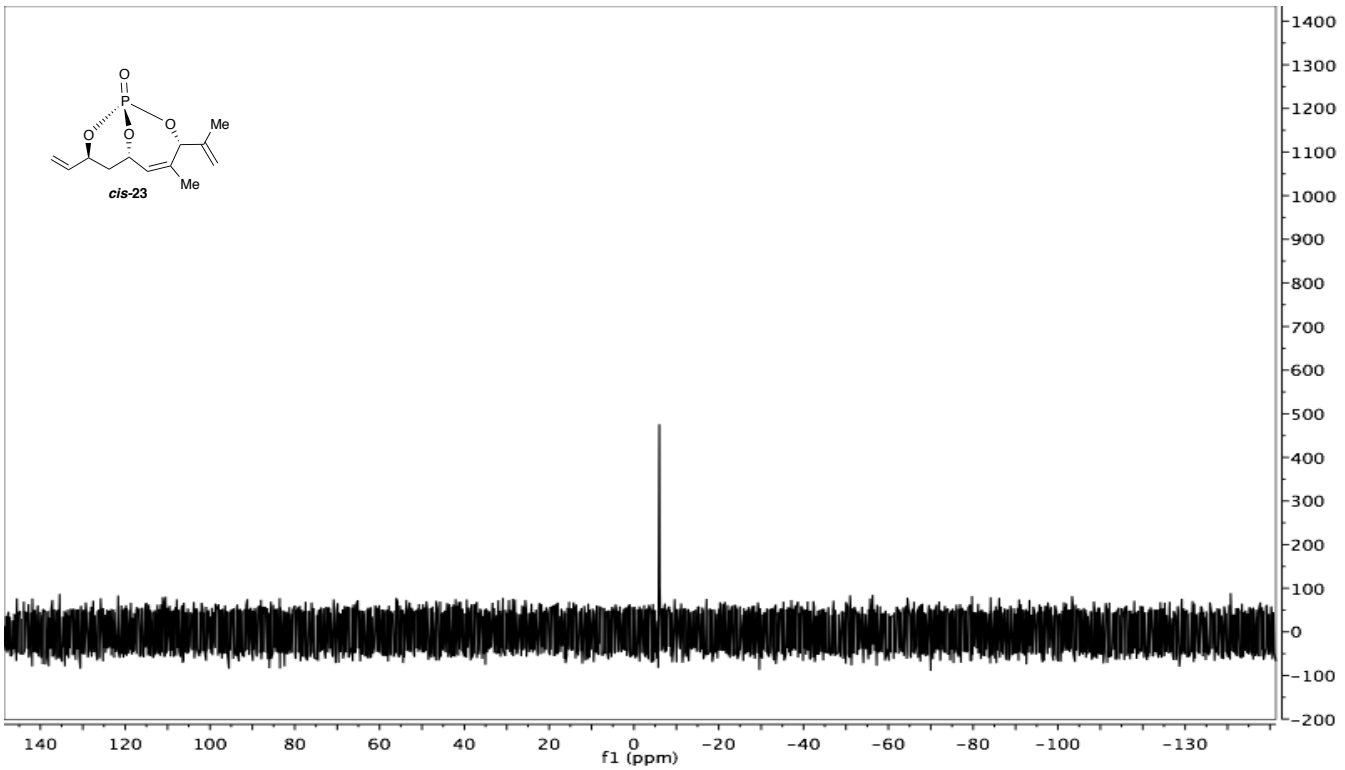

22
f1 (ppm)


22
f1 (ppm)

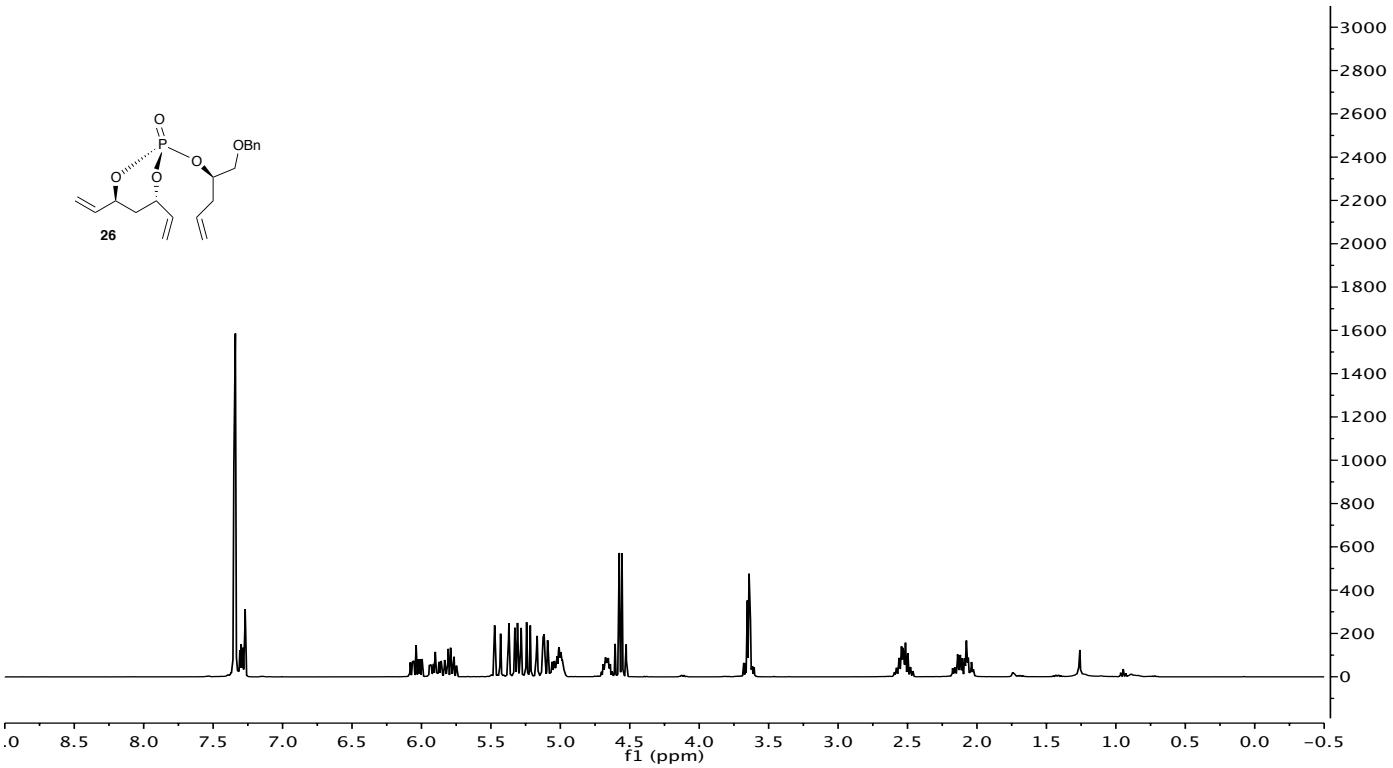
(1*S*,3*R*,6*S*,8*S*)-4-methyl-3-(prop-1-en-2-yl)-8-vinyl-2,9,10-trioxa-1-phosphabicyclo[4.3.1]dec-4-ene 1-oxide (*cis*-23):

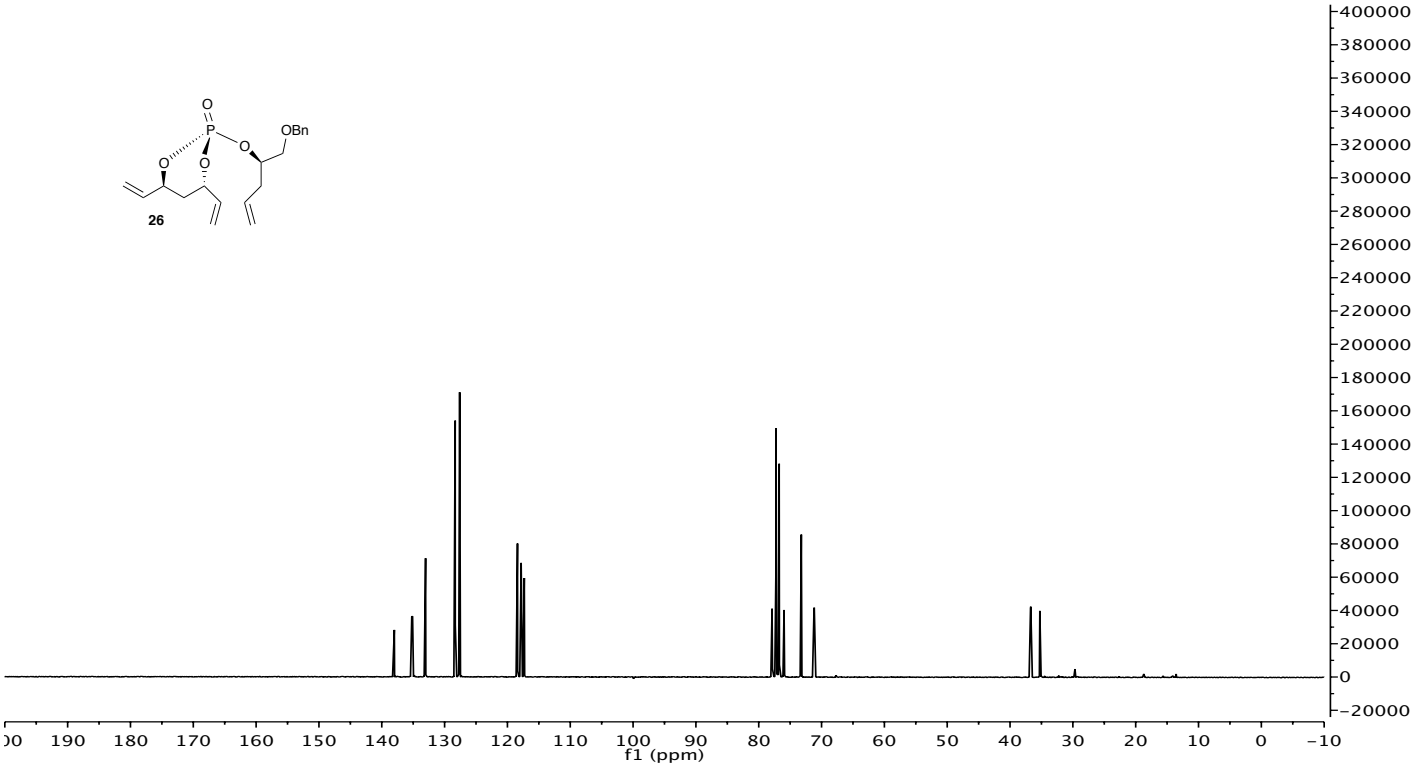


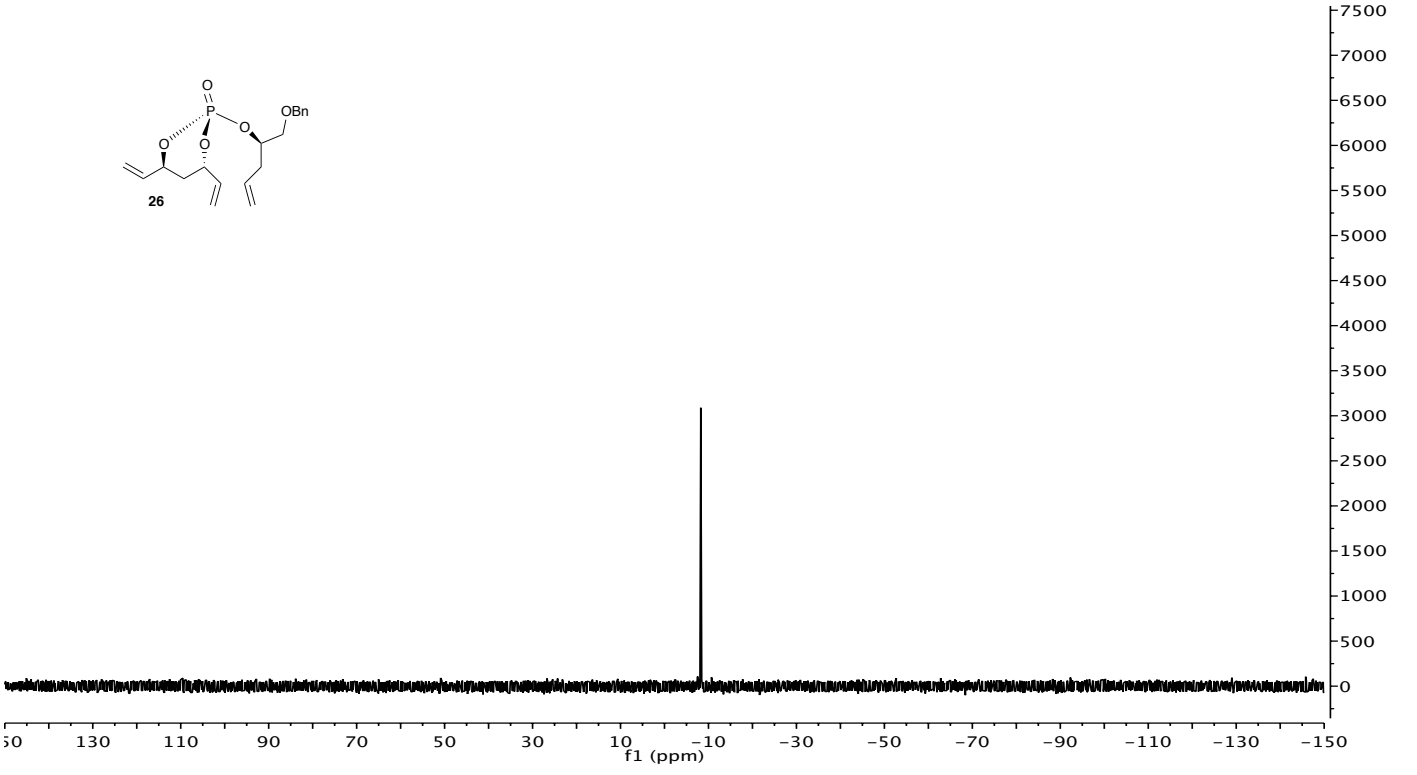




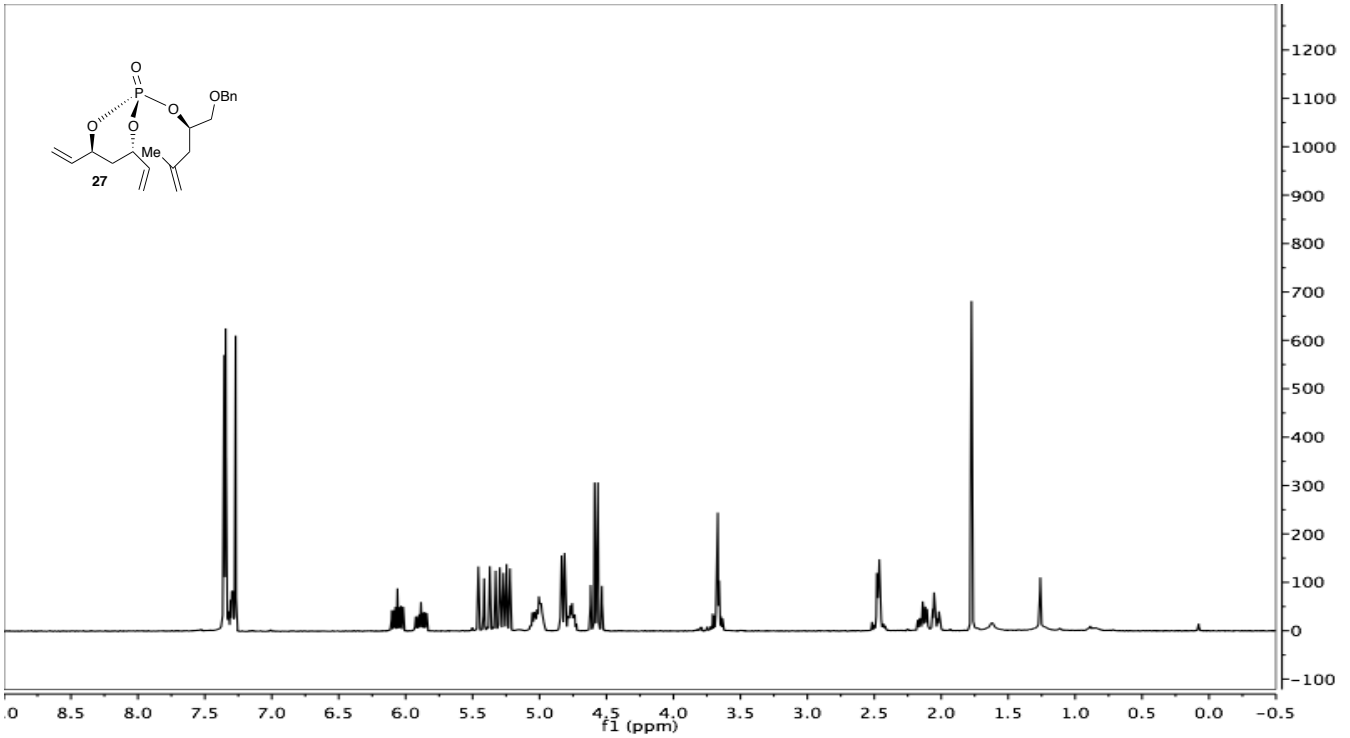
(4*S*,6*S*)-2-(((*R*)-1-(benzyloxy)pent-4-en-2-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (26):

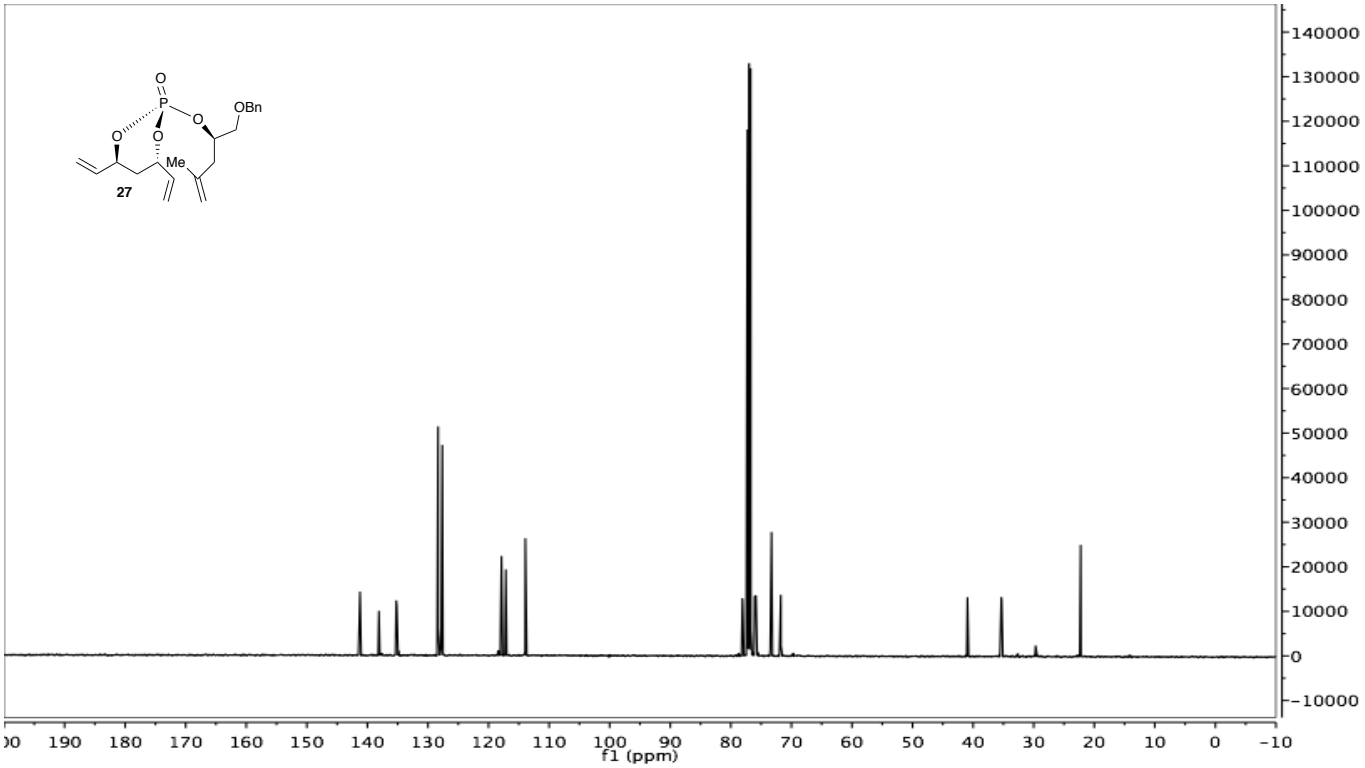


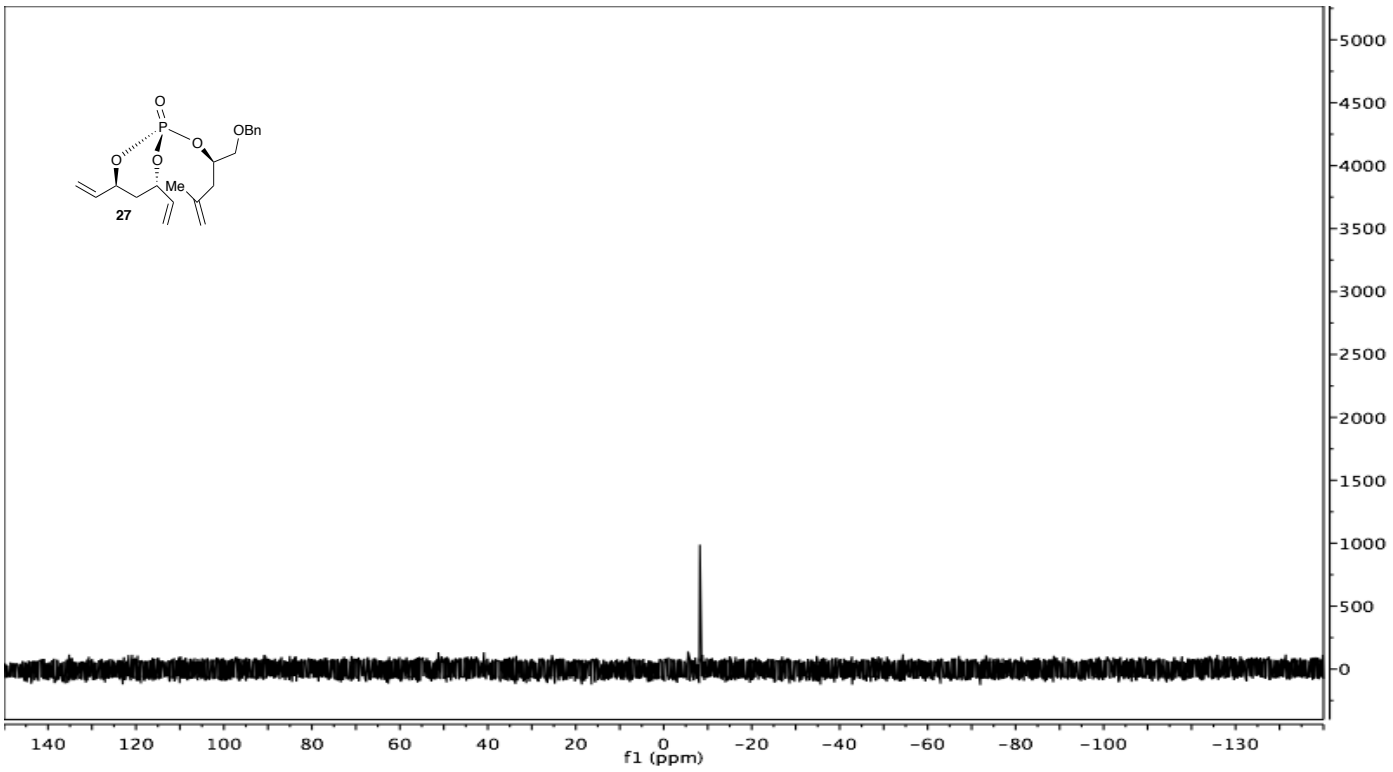

O
P
O
OBn
O
O
26
400000
380000
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
−20000
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


O
P
O
OBn
O
O
26
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150
f1 (ppm)

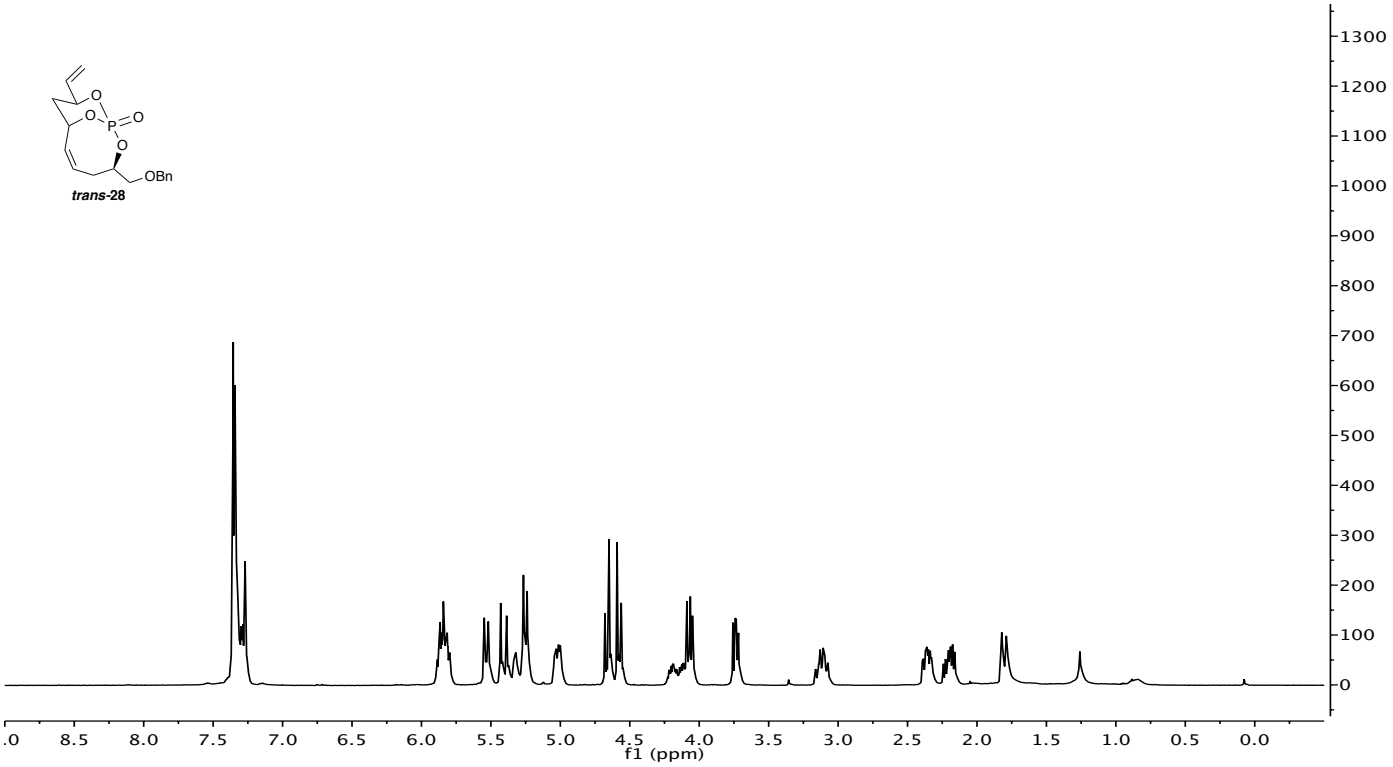
(4*S*,6*S*)-2-(((*R*)-1-(benzyloxy)-4-methylpent-4-en-2-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (27):

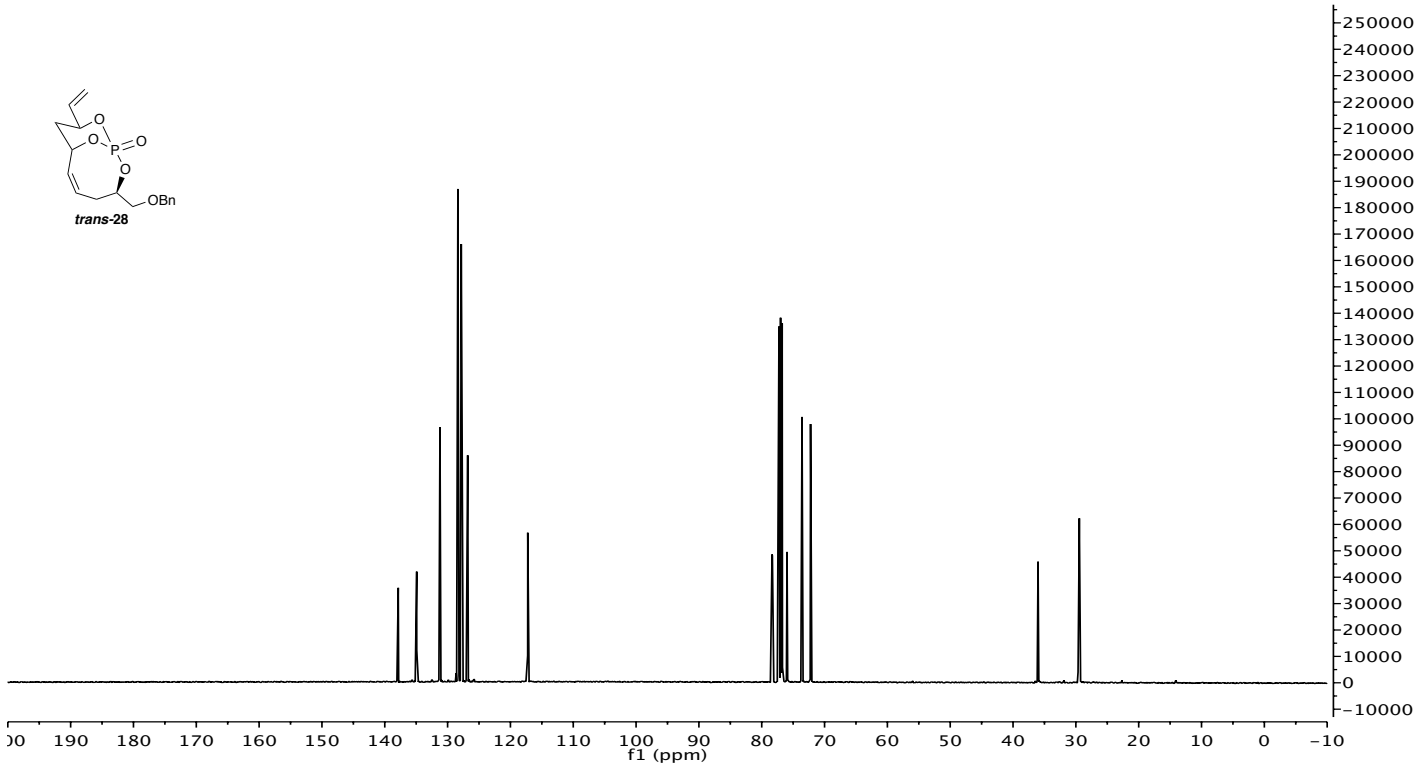


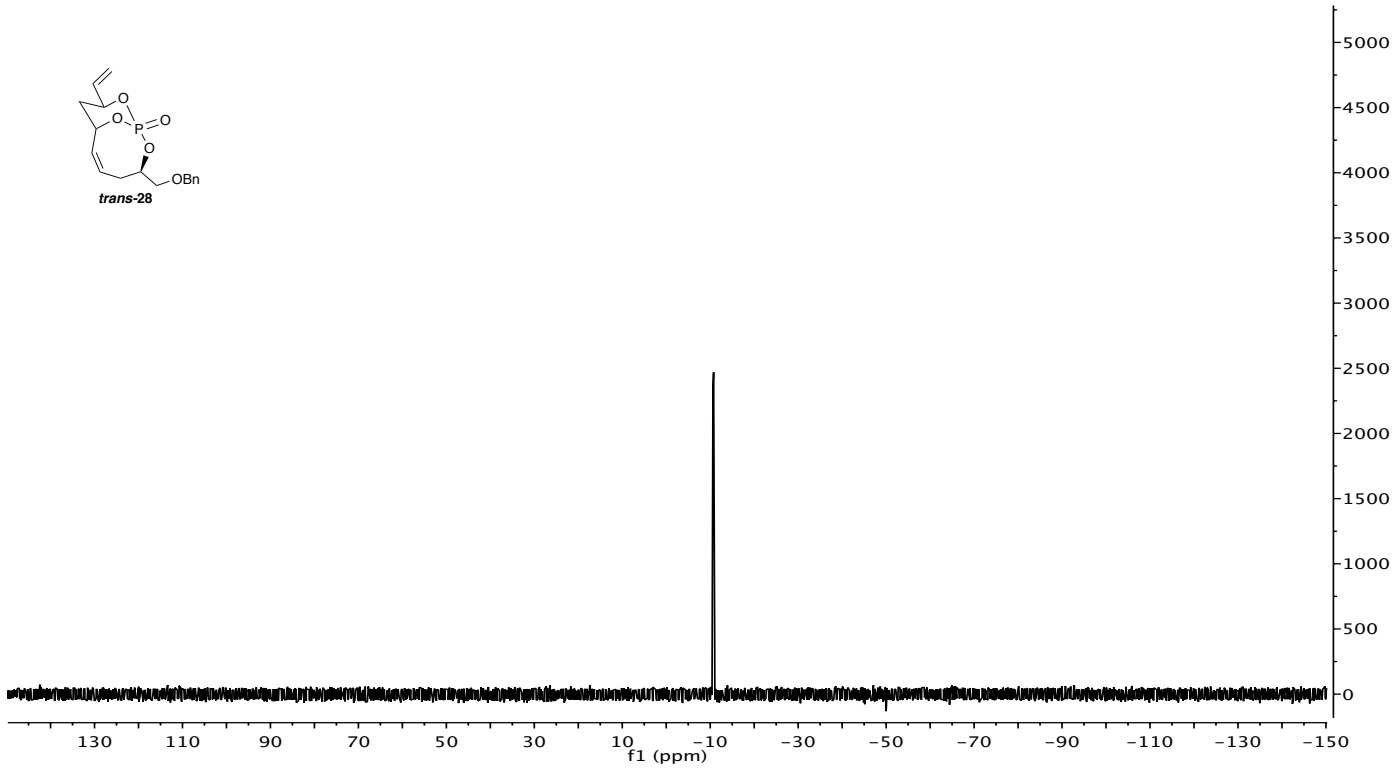




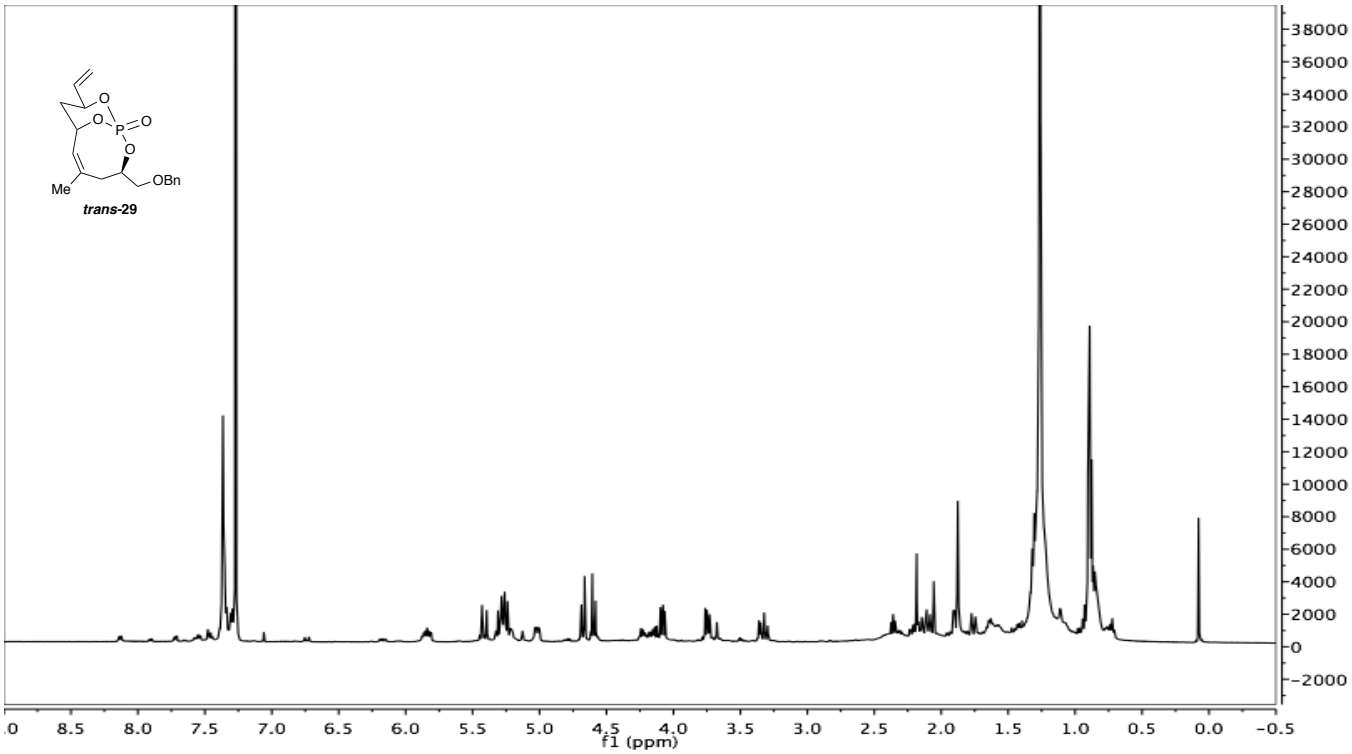
(1*S*,3*R*,7*S*,9*S*,*Z*)-3-((benzyloxy)methyl)-9-vinyl-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-5-ene 1-oxide (*trans*-28):

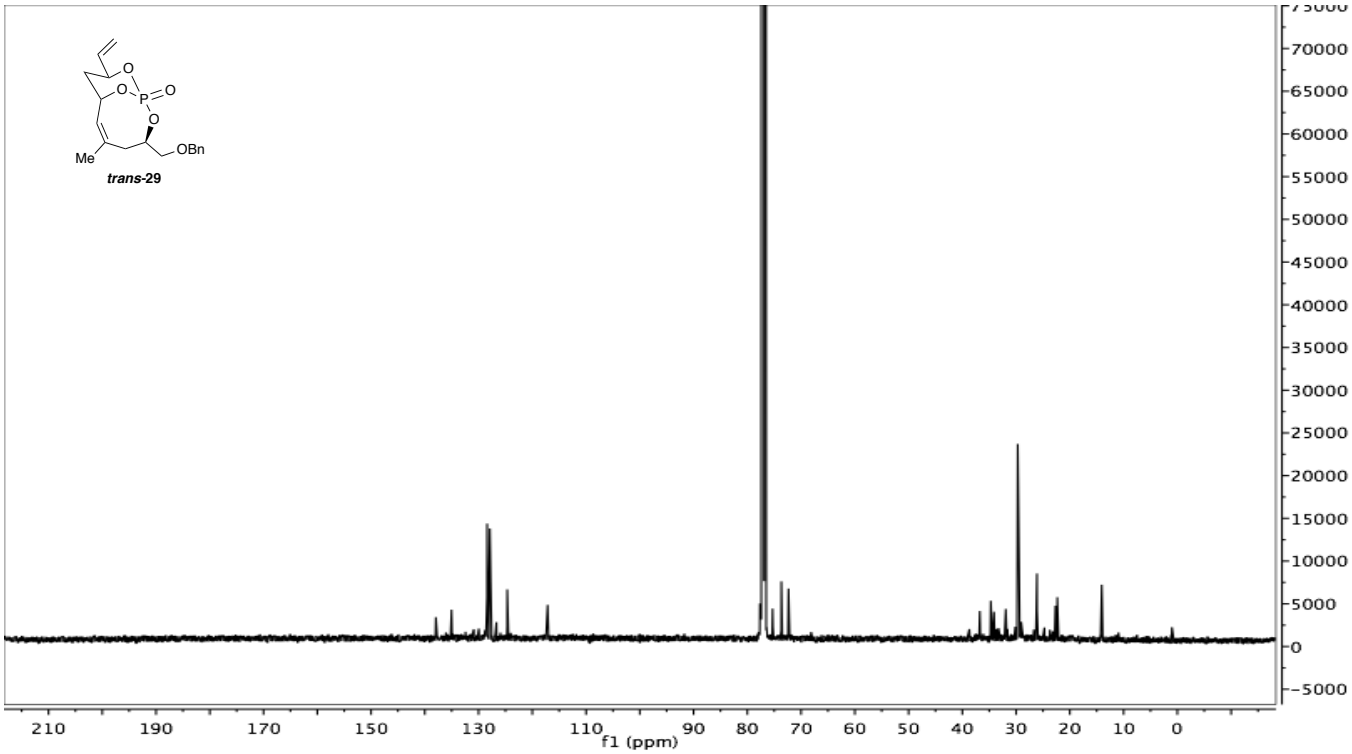


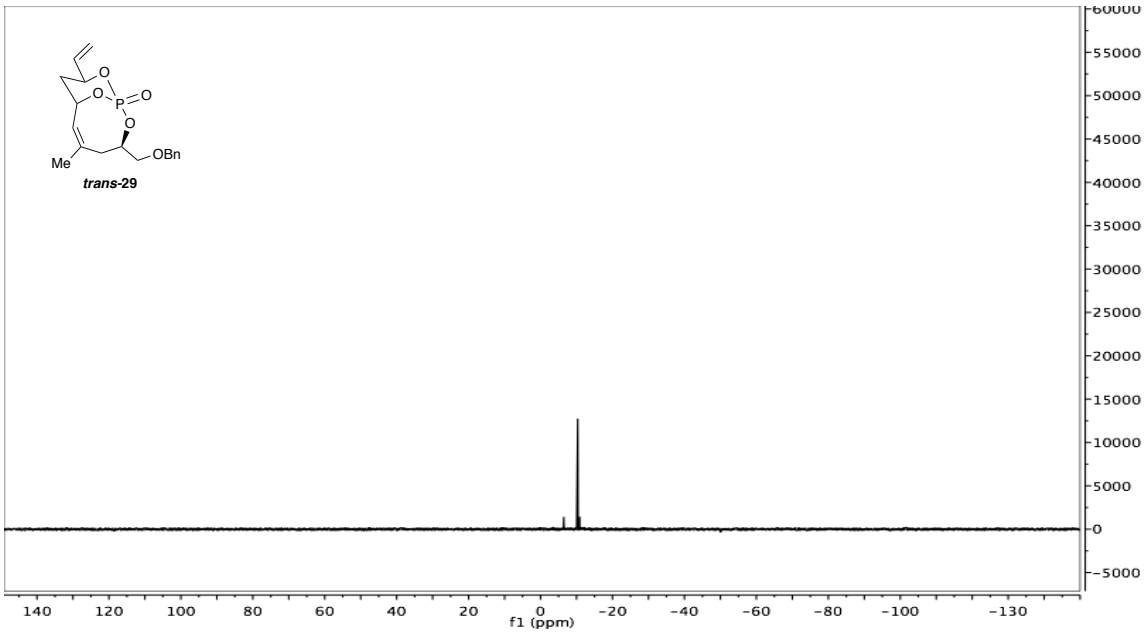

trans-28
f1 (ppm)


trans-28
f1 (ppm)

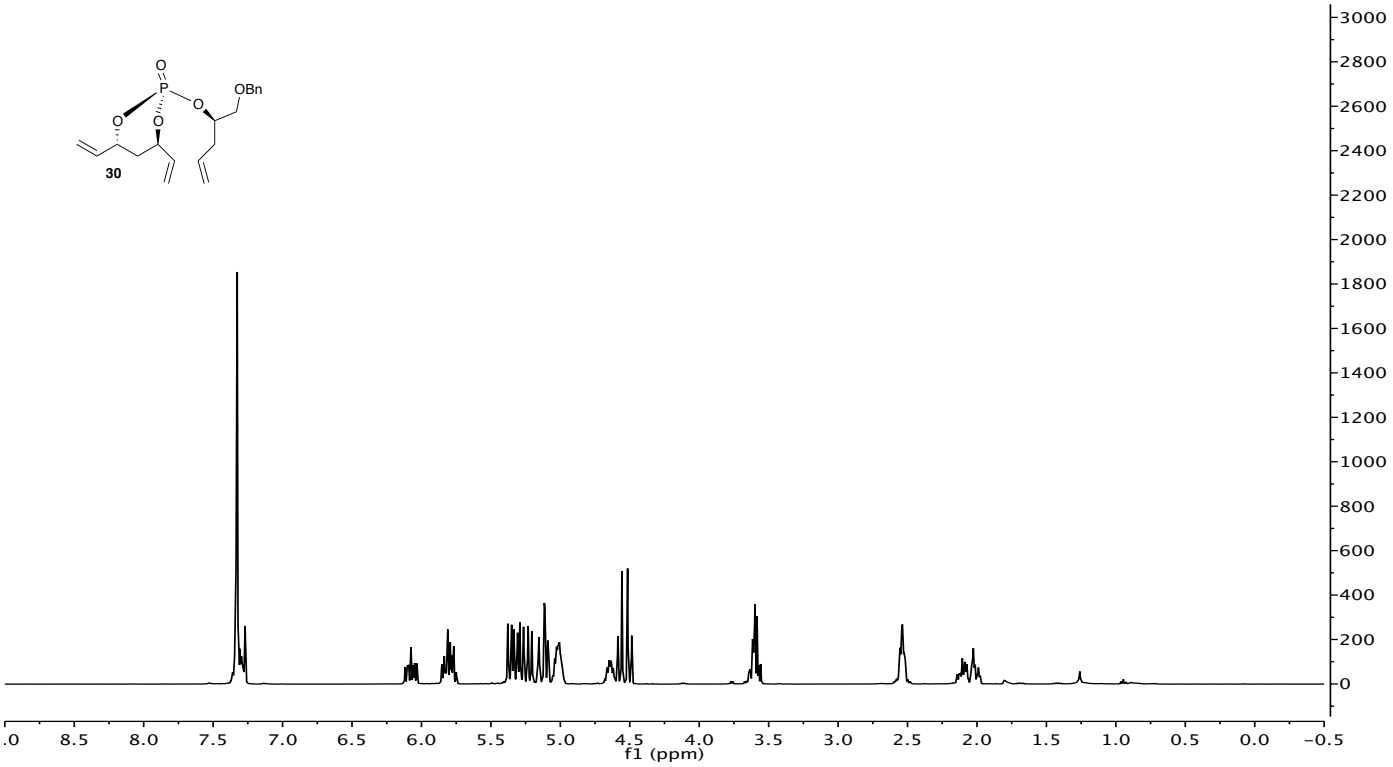
(1*S*,3*R*,7*S*,9*S*,*Z*)-3-((benzyloxy)methyl)-5-methyl-9-vinyl-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-5-ene 1-oxide (*trans*-29):

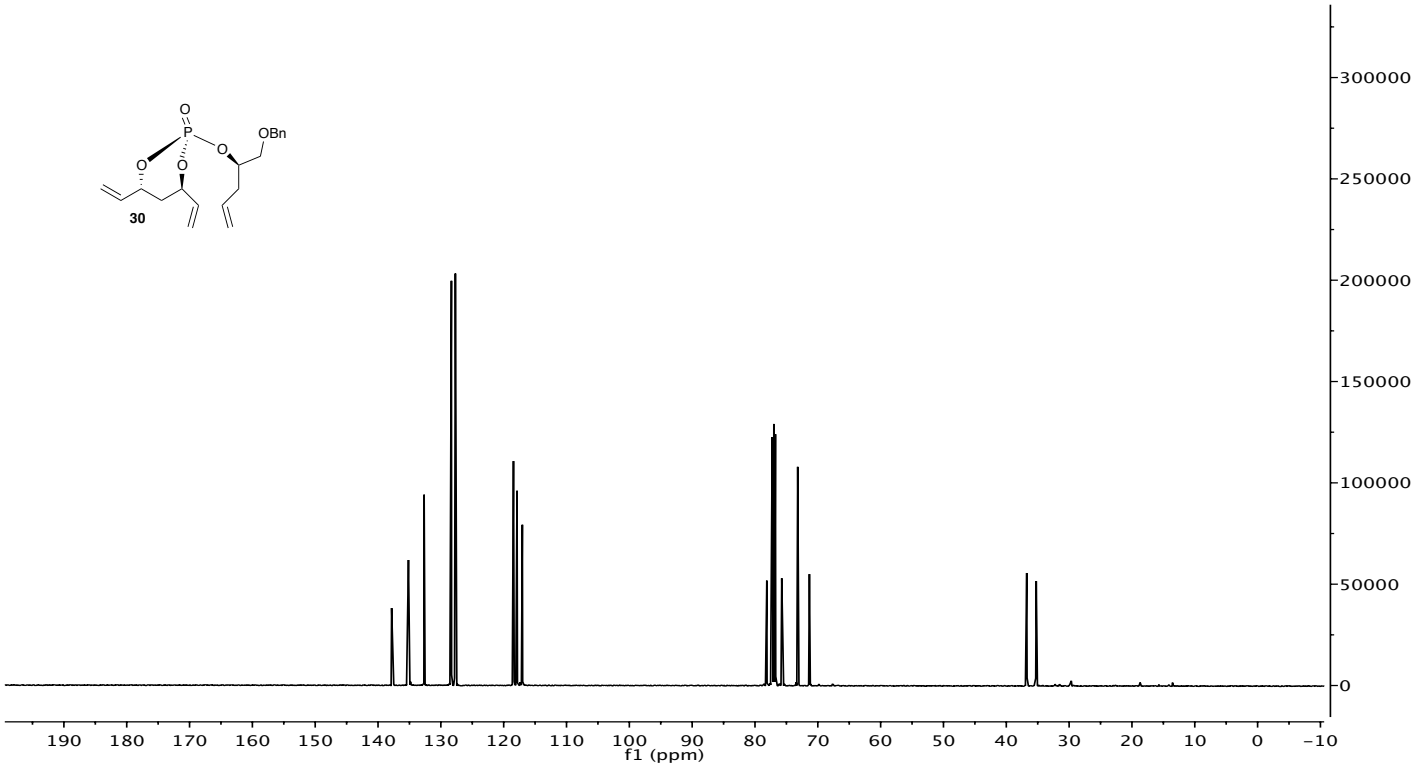


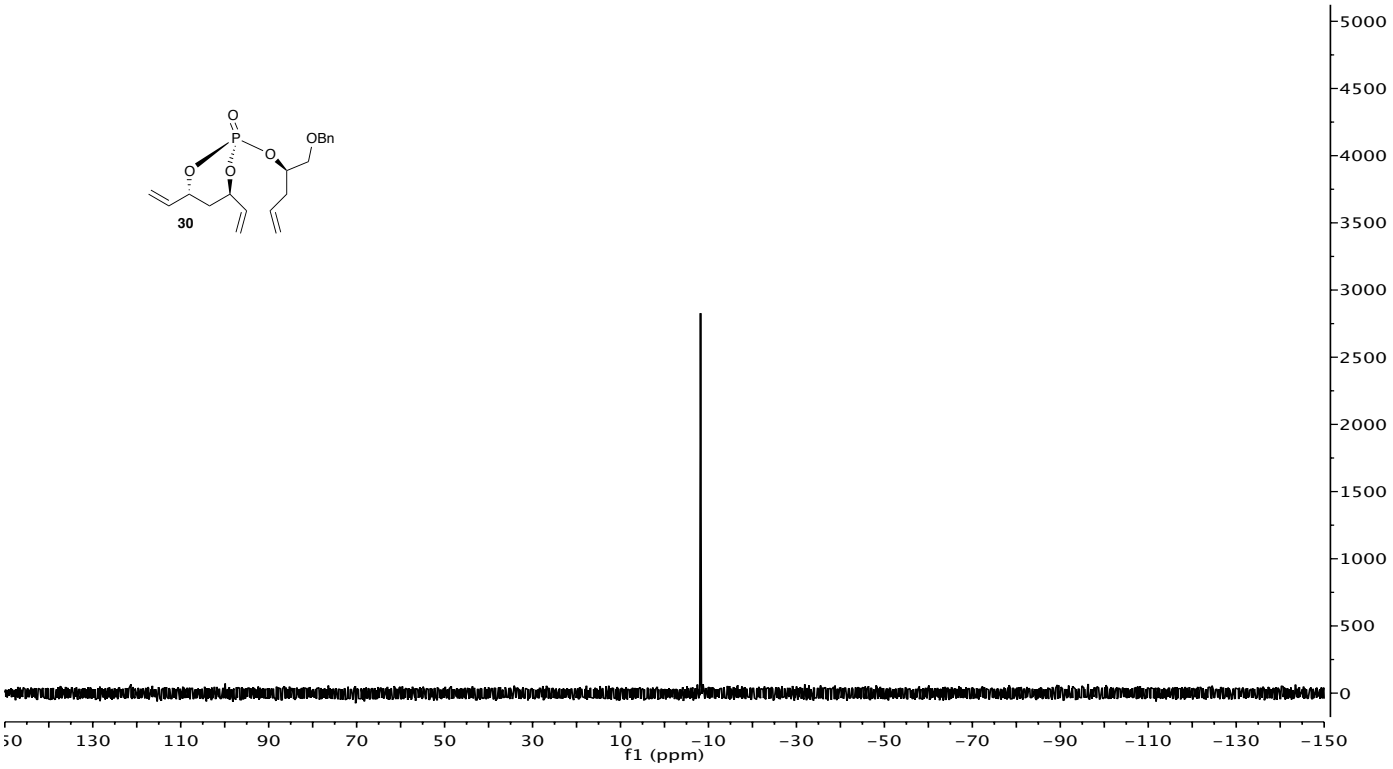




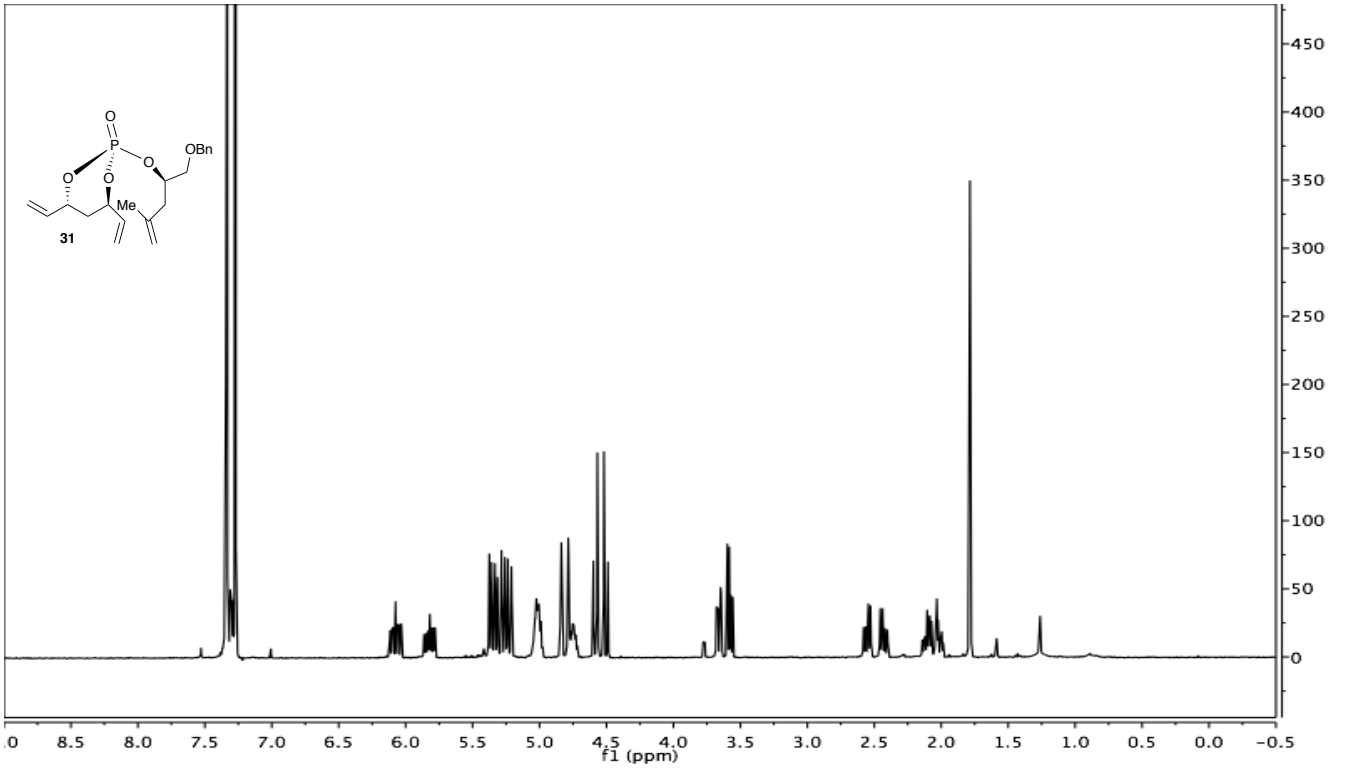
(4*R*,6*R*)-2-(((*R*)-1-(benzyloxy)but-3-en-2-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (30):

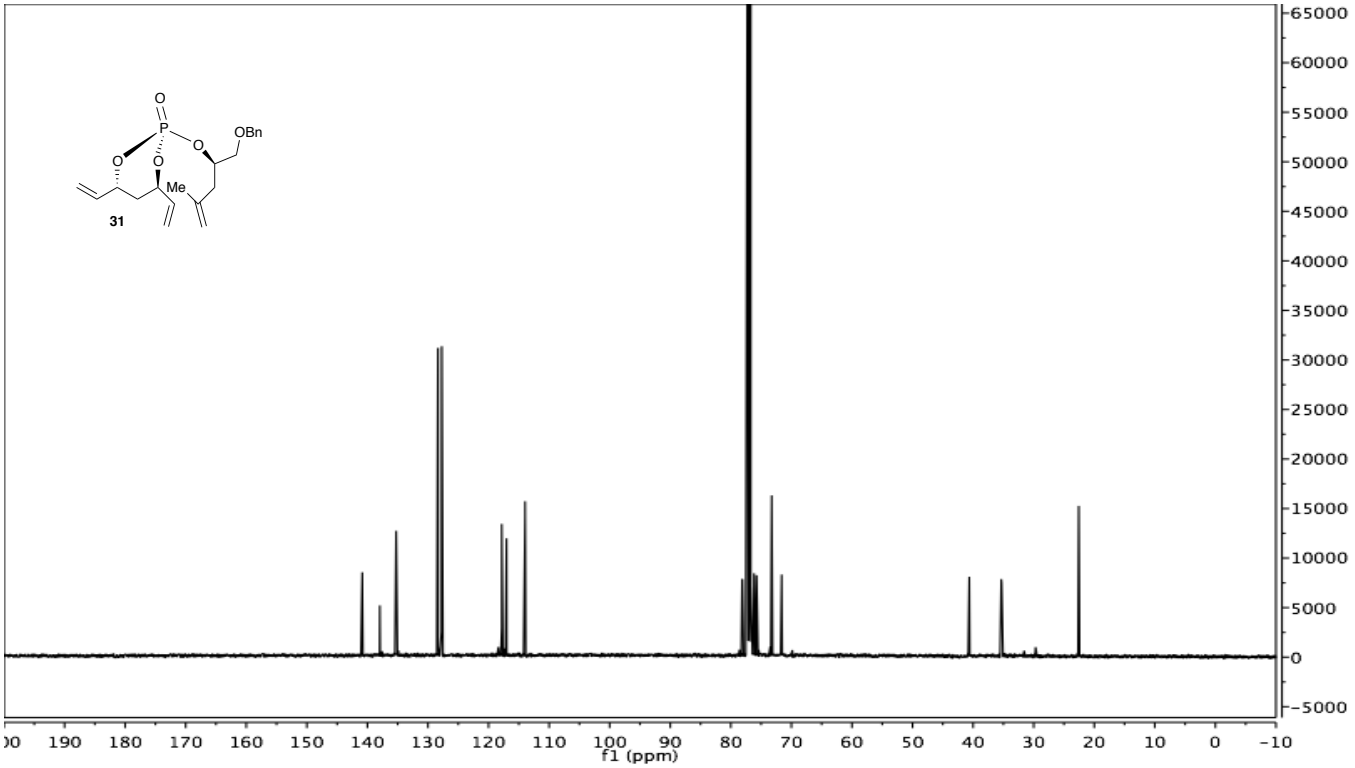


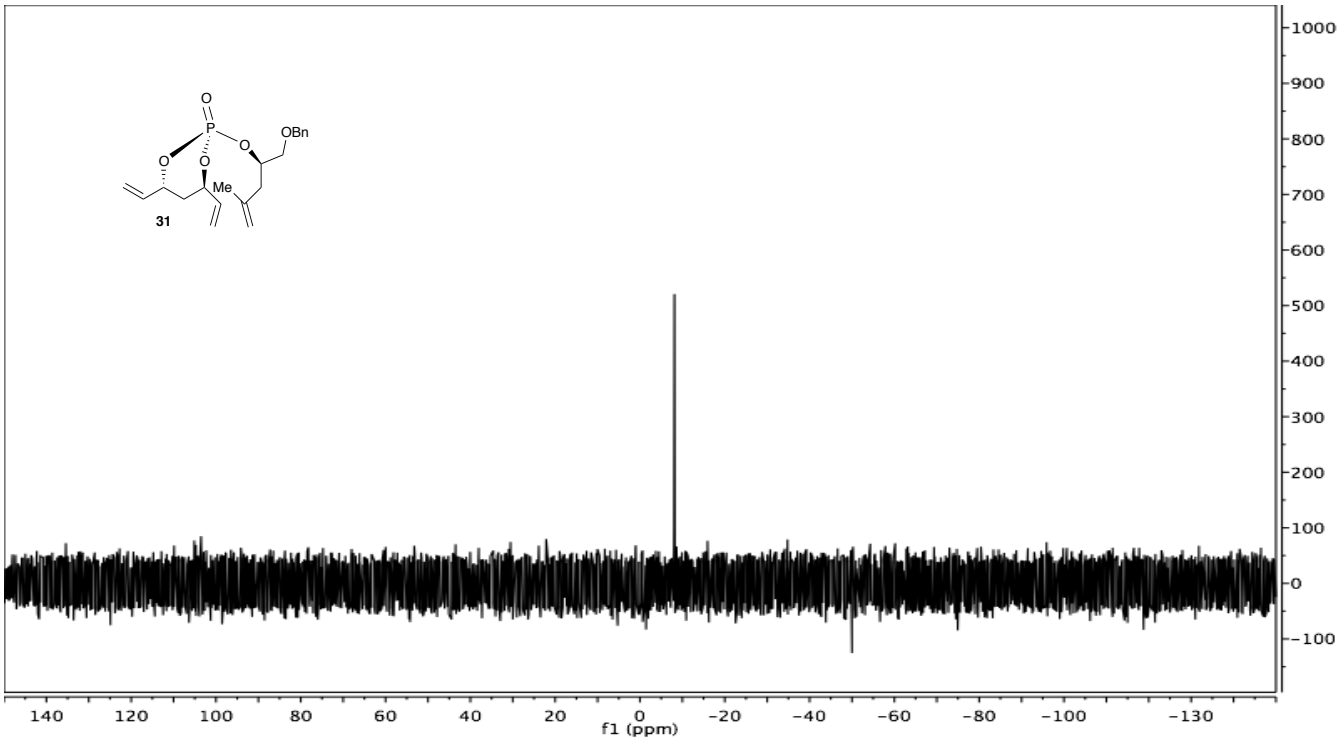

O
P
O
O
O
OBn
30
300000
250000
200000
150000
100000
50000
0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


O
P
O
O
O
OBn
30
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
50 130 110 90 70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150
f1 (ppm)

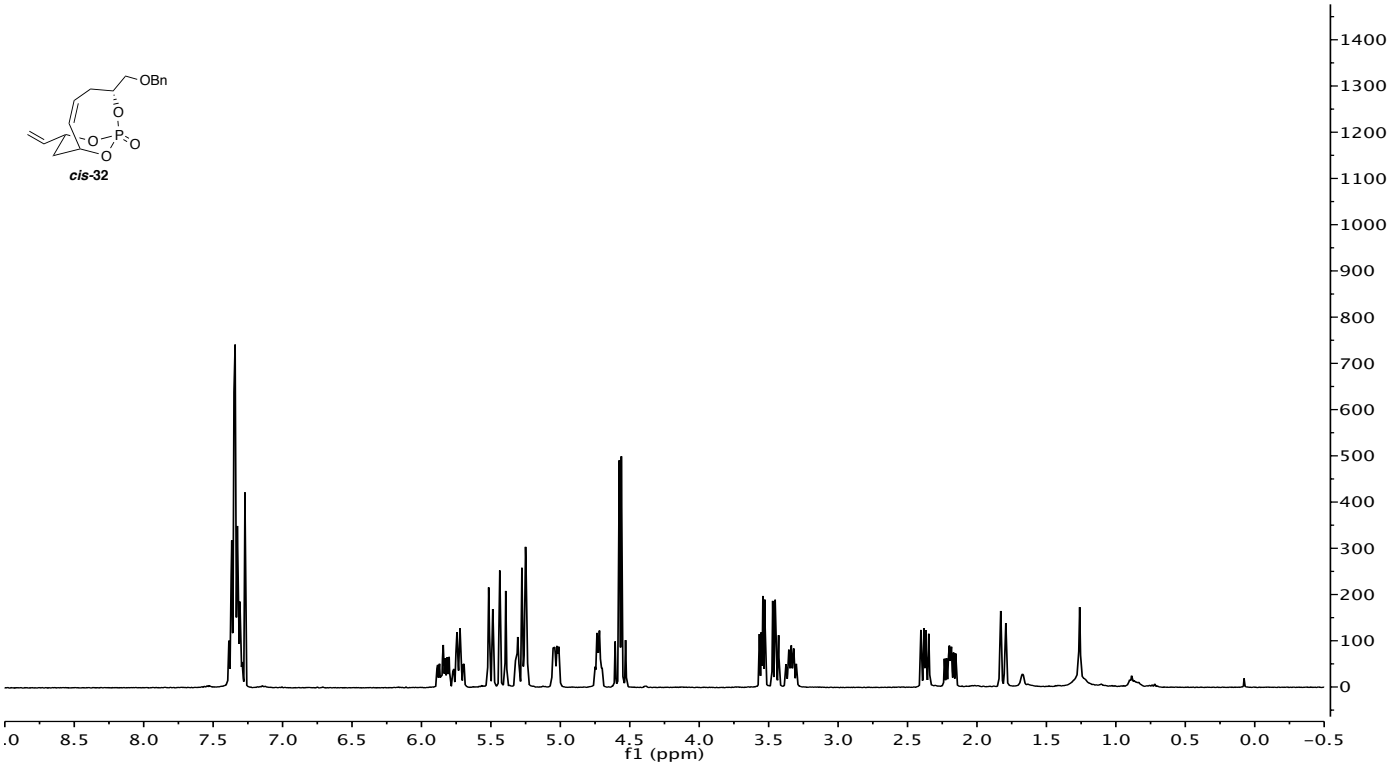
(4*R*,6*R*)-2-(((*R*)-1-(benzyloxy)-4-methylpent-4-en-2-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (31):

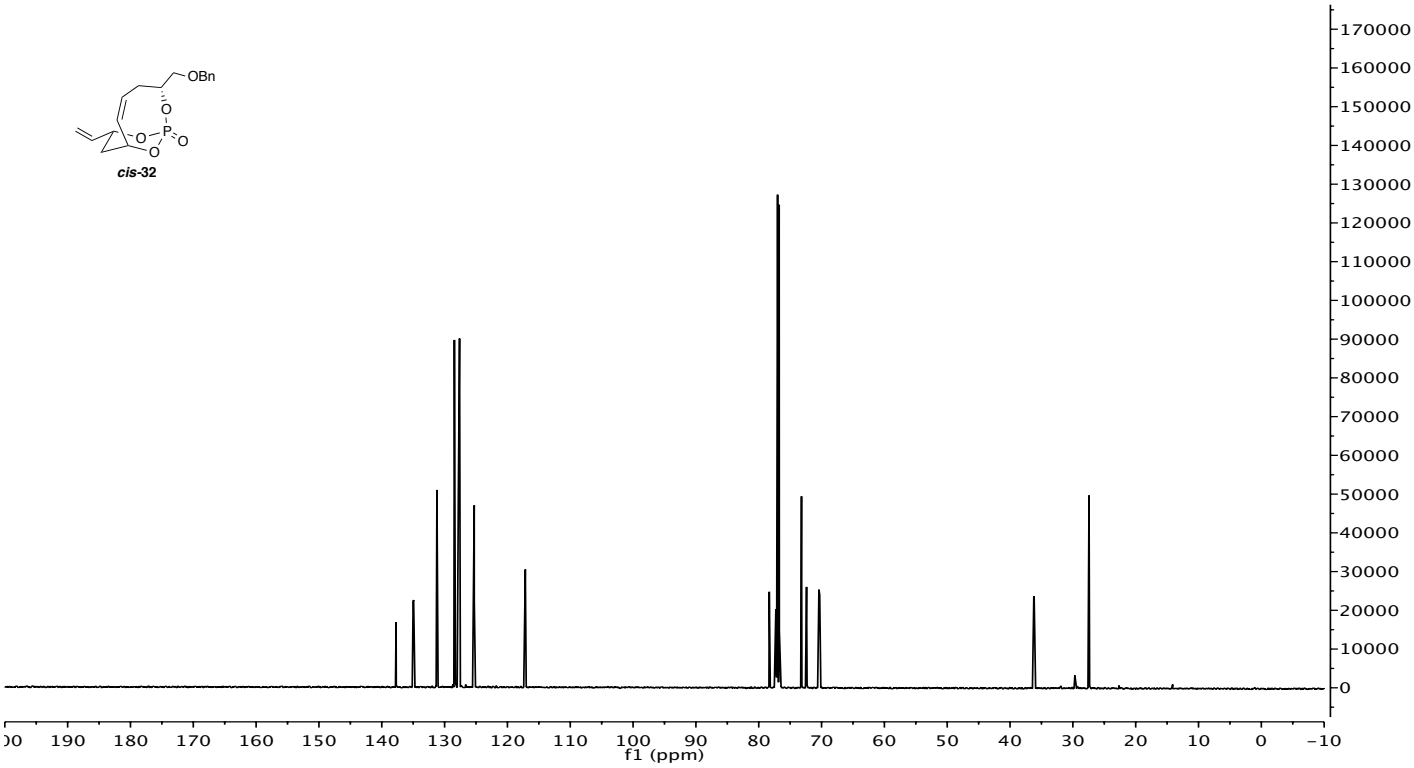


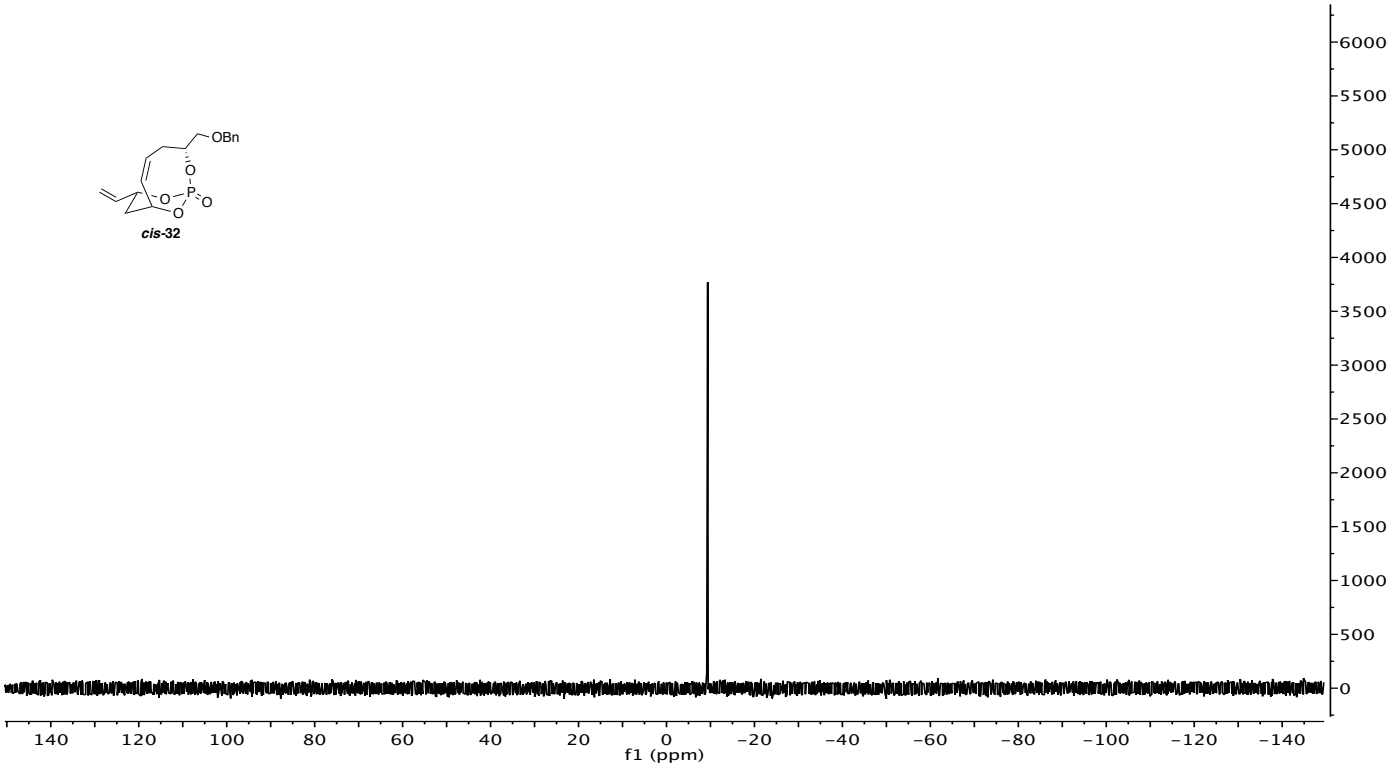




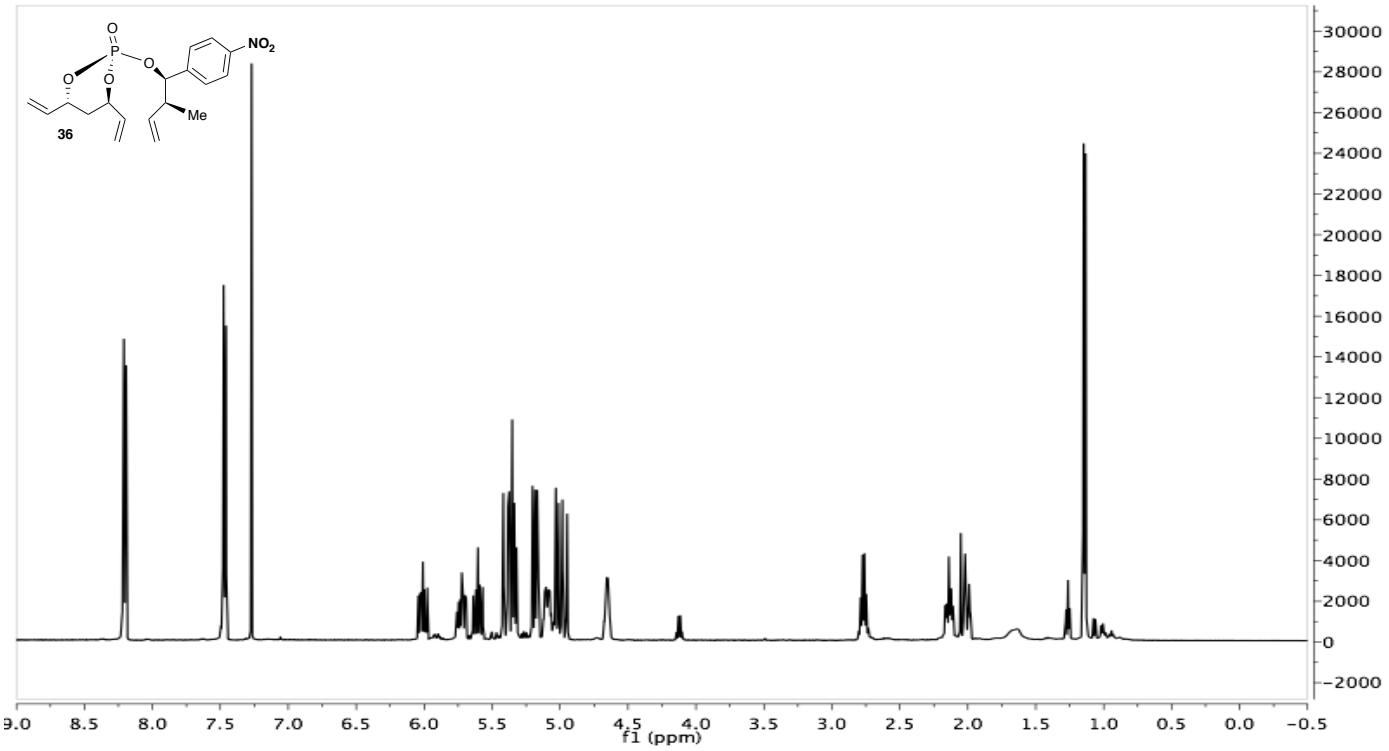
(1*R*,3*R*,7*R*,9*R*,*Z*)-3-((benzyloxy)methyl)-9-vinyl-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-5-ene 1-oxide (*cis*-32):

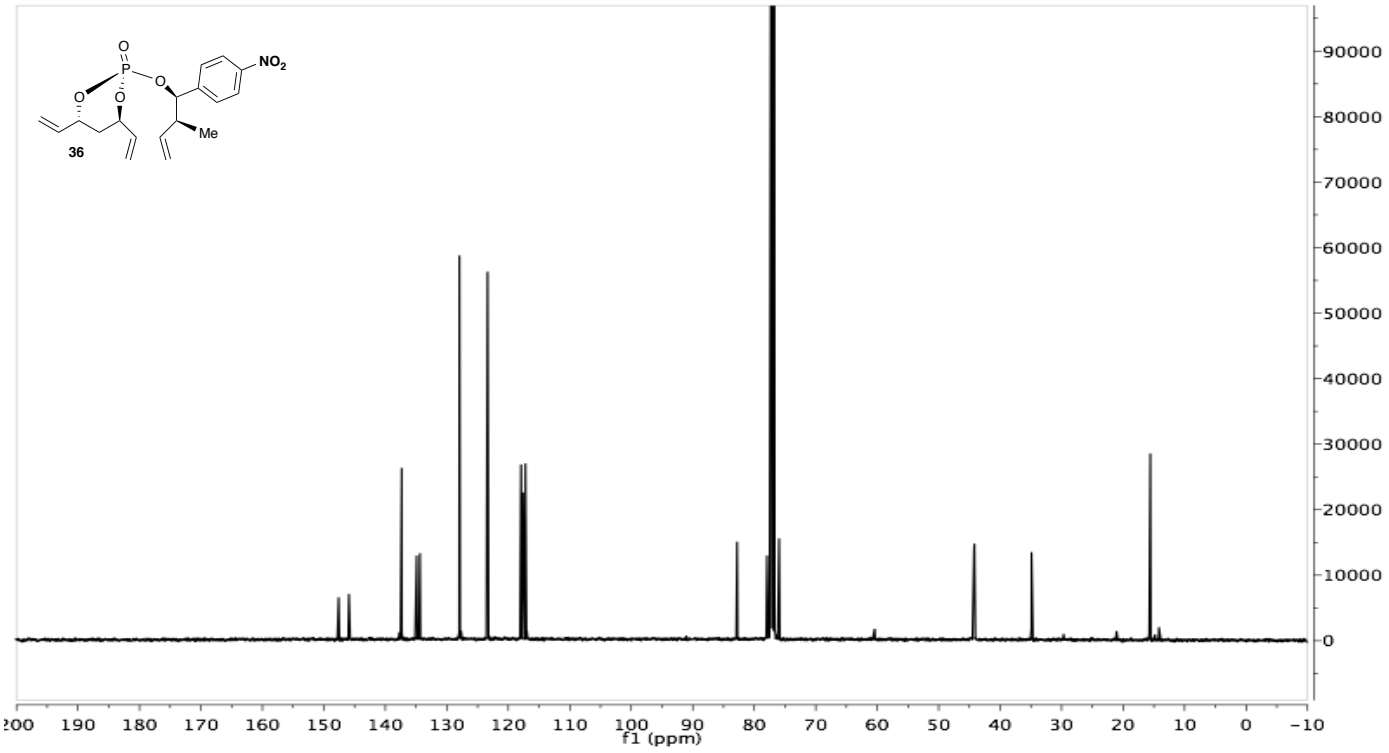


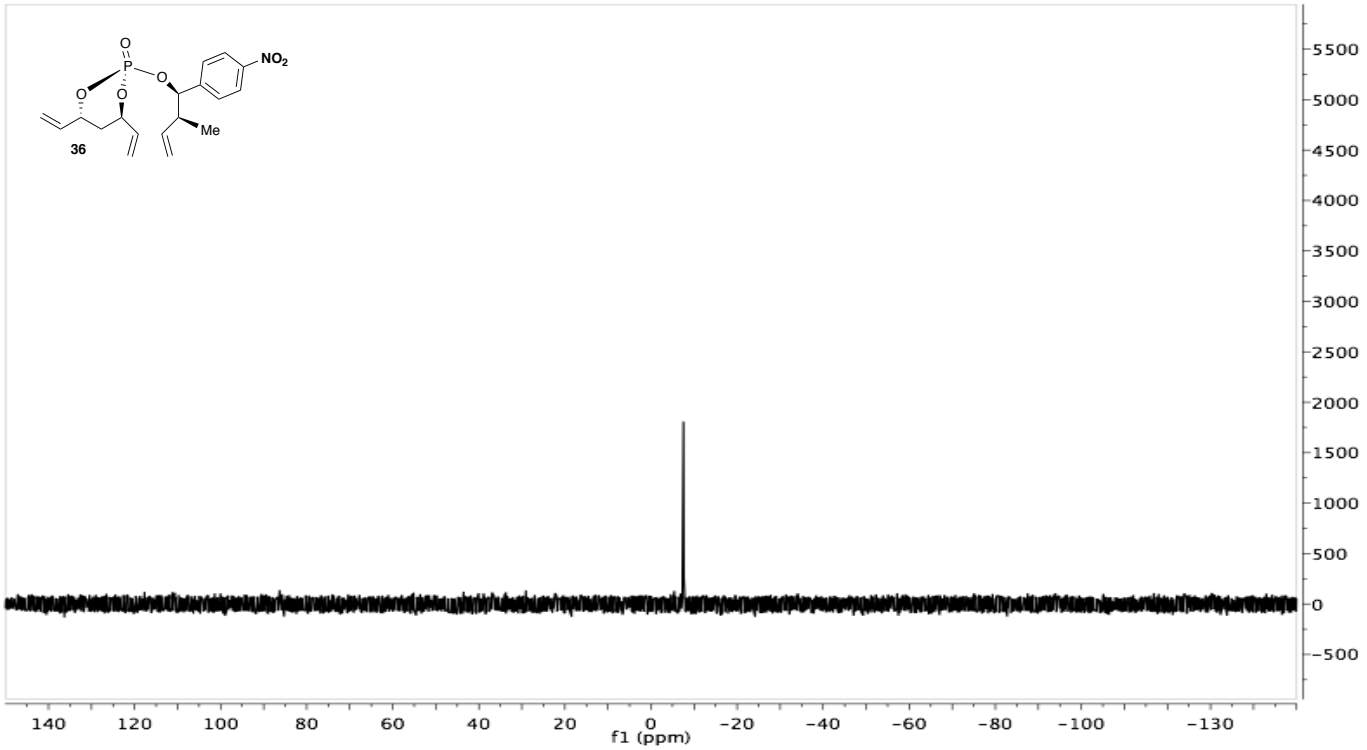

OBn
O
O
P
O
O
cis-32
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


OBn
O
O
P
O
O
cis-32
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140
f1 (ppm)

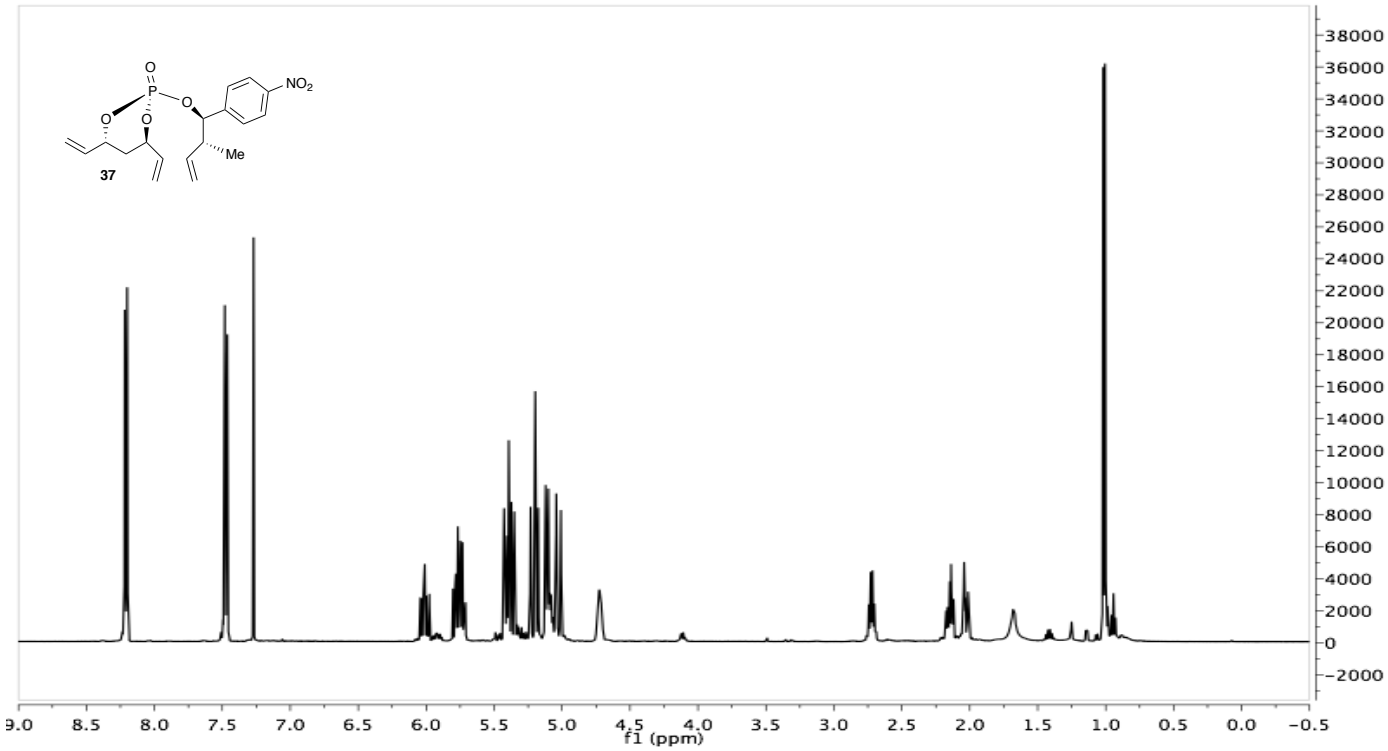
(4*R*,6*R*)-2-(((1*R*,2*S*)-2-methyl-1-(4-nitrophenyl)but-3-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (36):

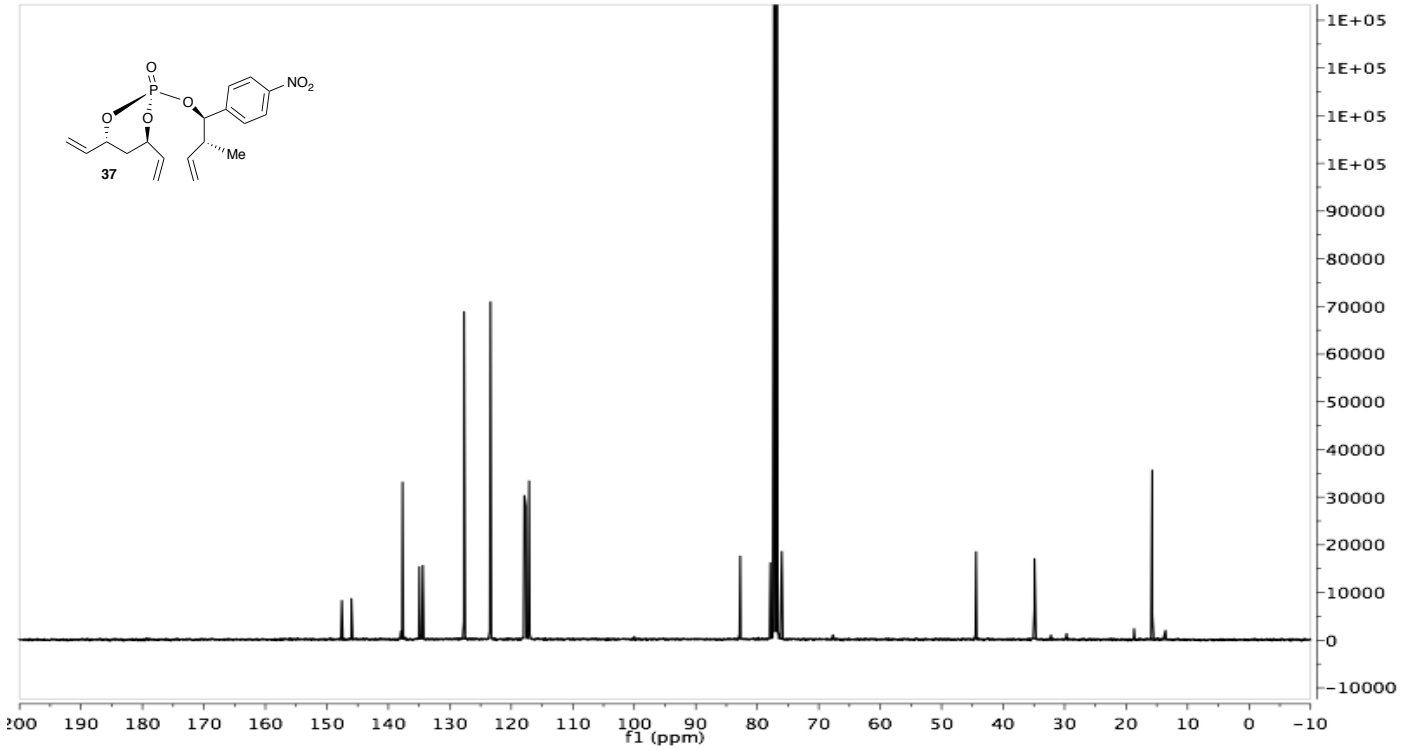


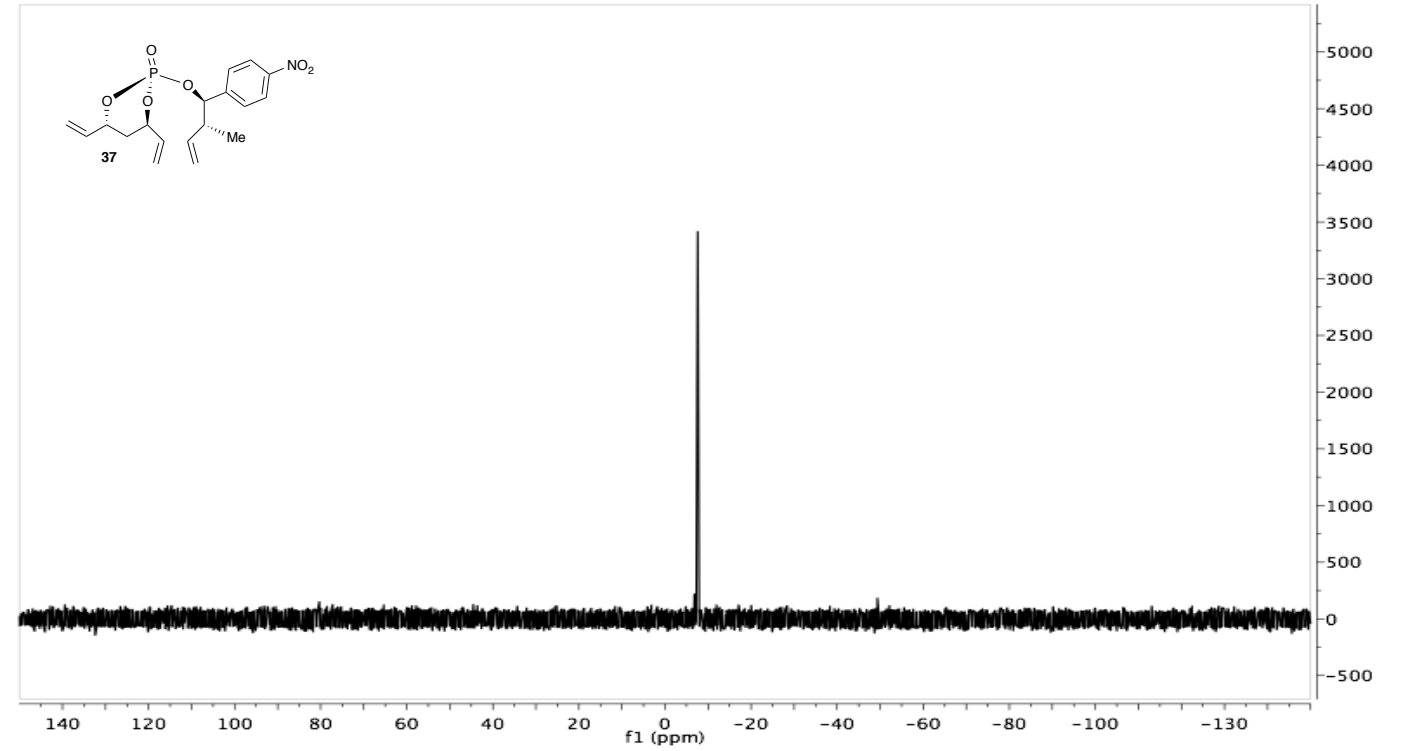




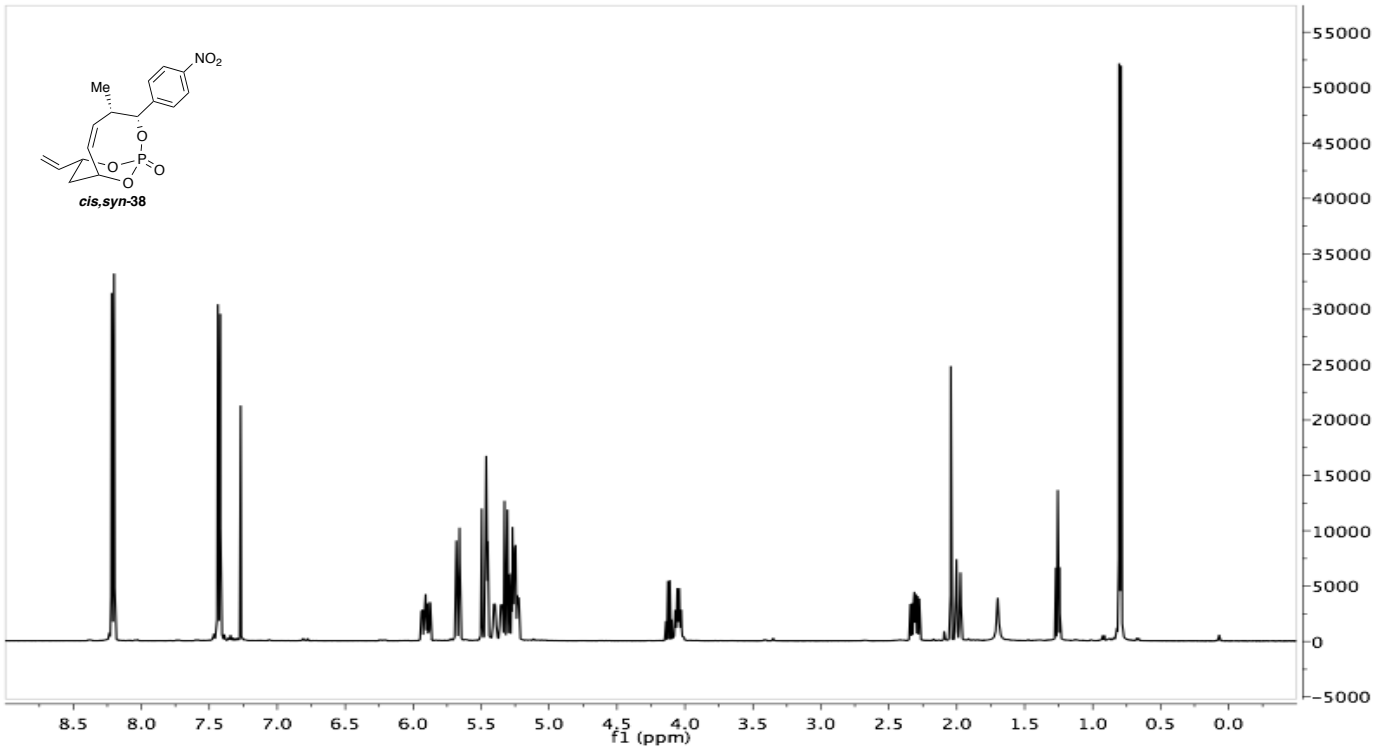
(4*R*,6*R*)-2-(((1*R*,2*R*)-2-methyl-1-(4-nitrophenyl)but-3-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (37):

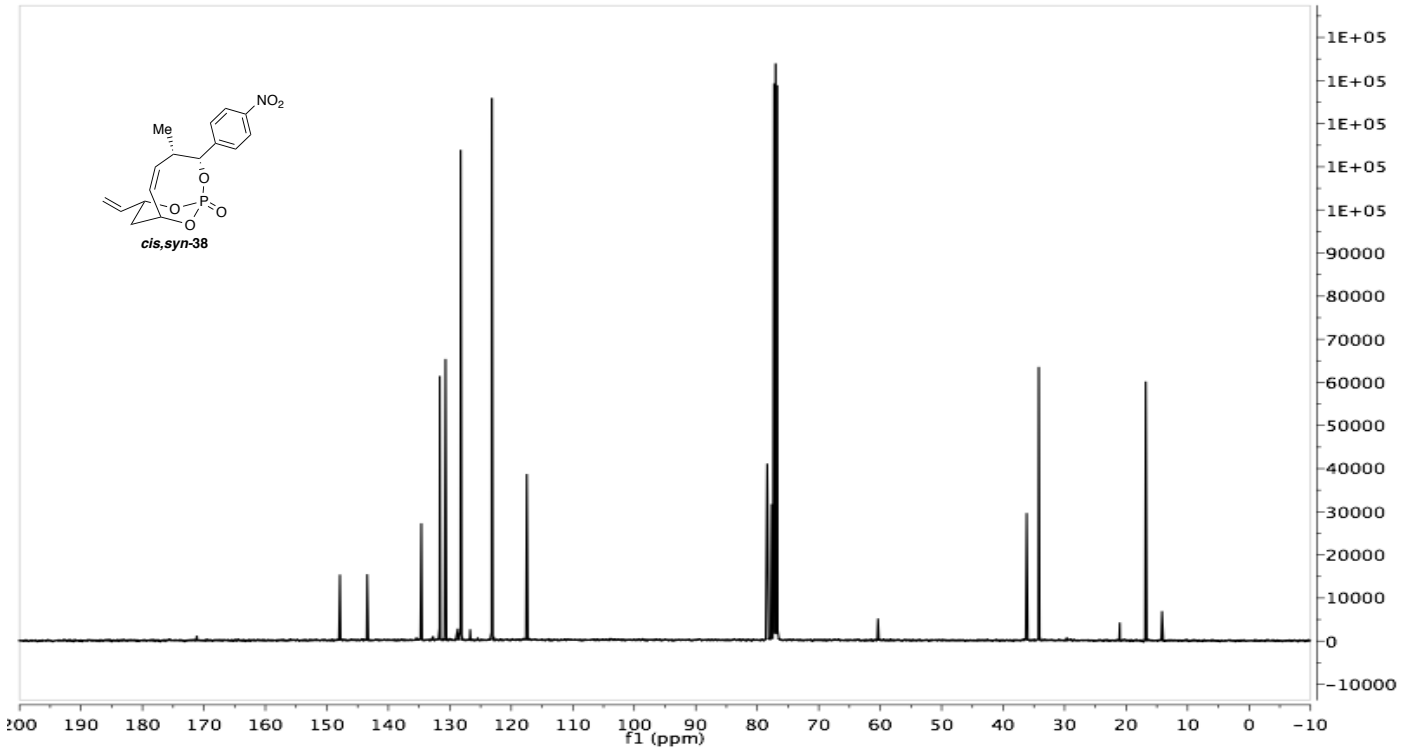


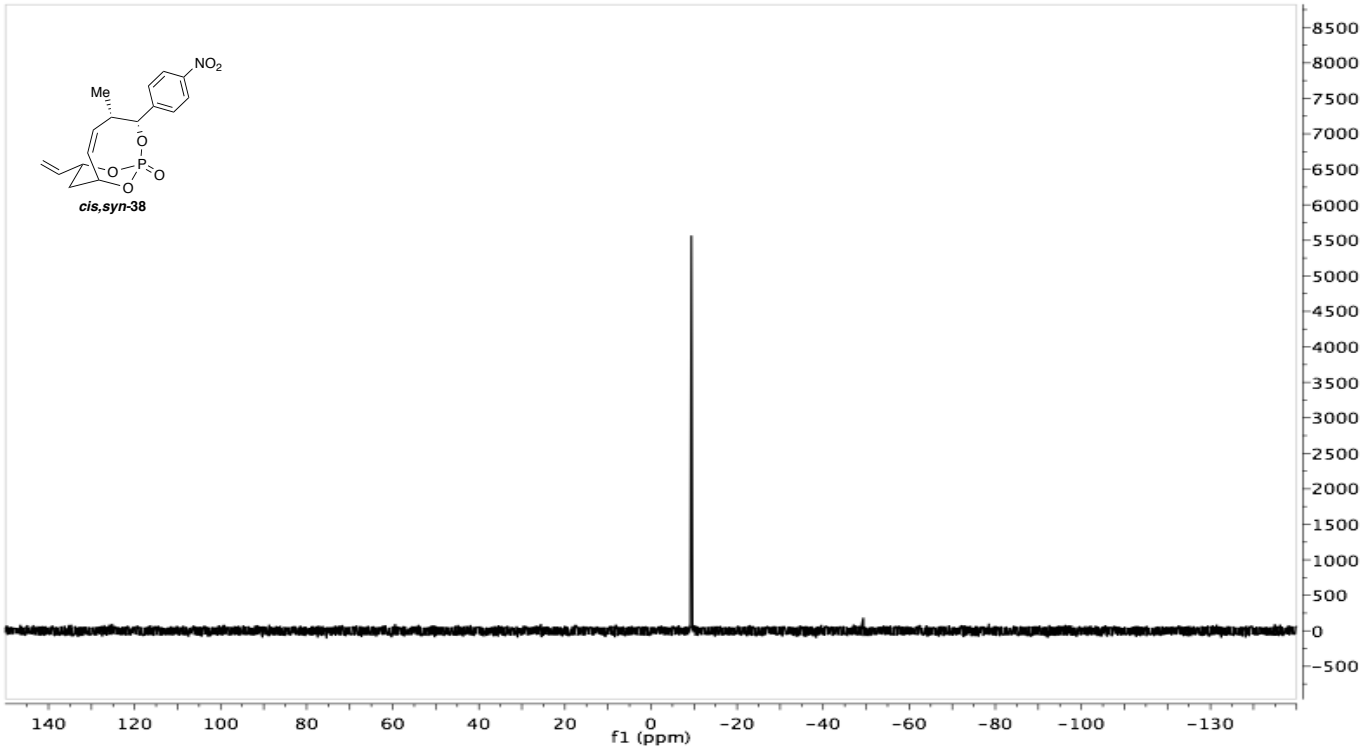

37
NO2
Me
f1 (ppm)


37
NO2
Me
f1 (ppm)

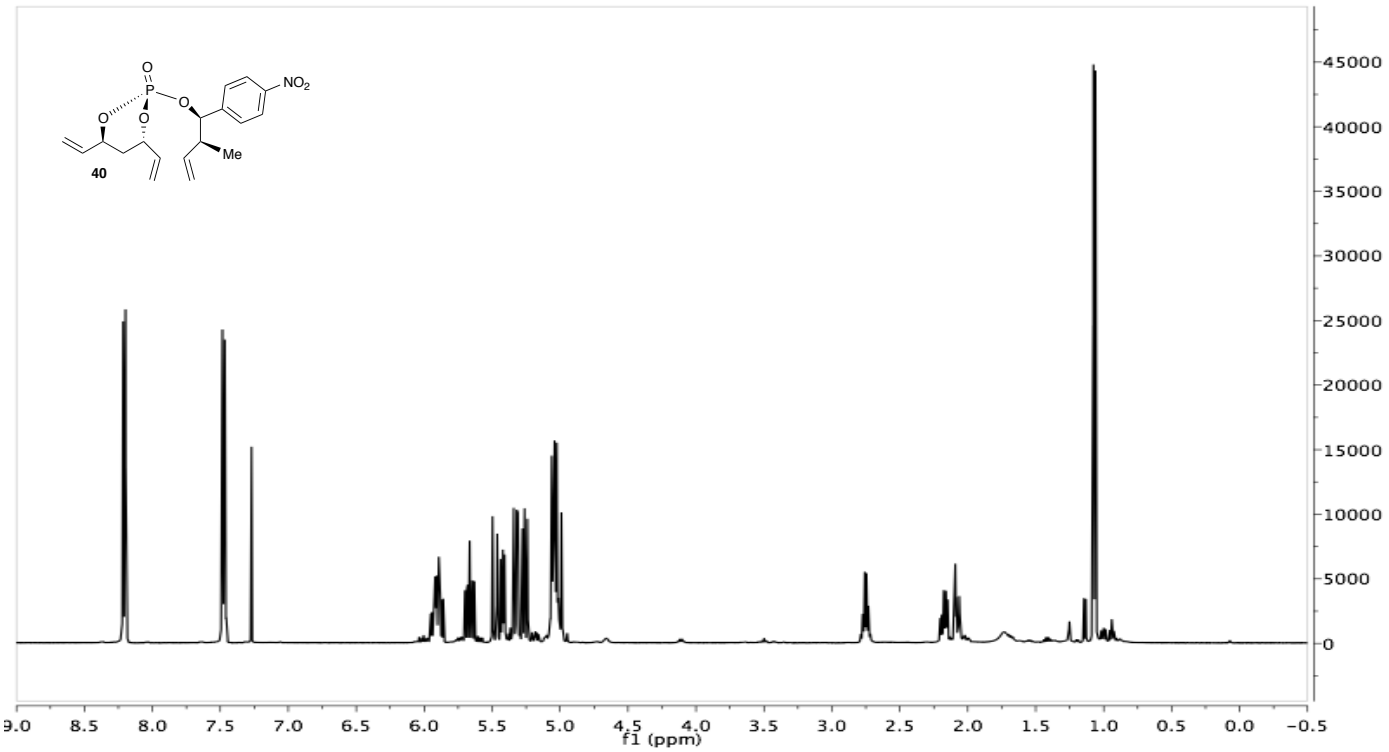
(1*R*,3*R*,4*S*,7*R*,9*R*,*Z*)-4-methyl-3-(4-nitrophenyl)-9-vinyl-2,10,11-trioxa-1 phosphabicyclo[5.3.1]undec-5-ene 1-oxide (*cis*,*syn*-38):

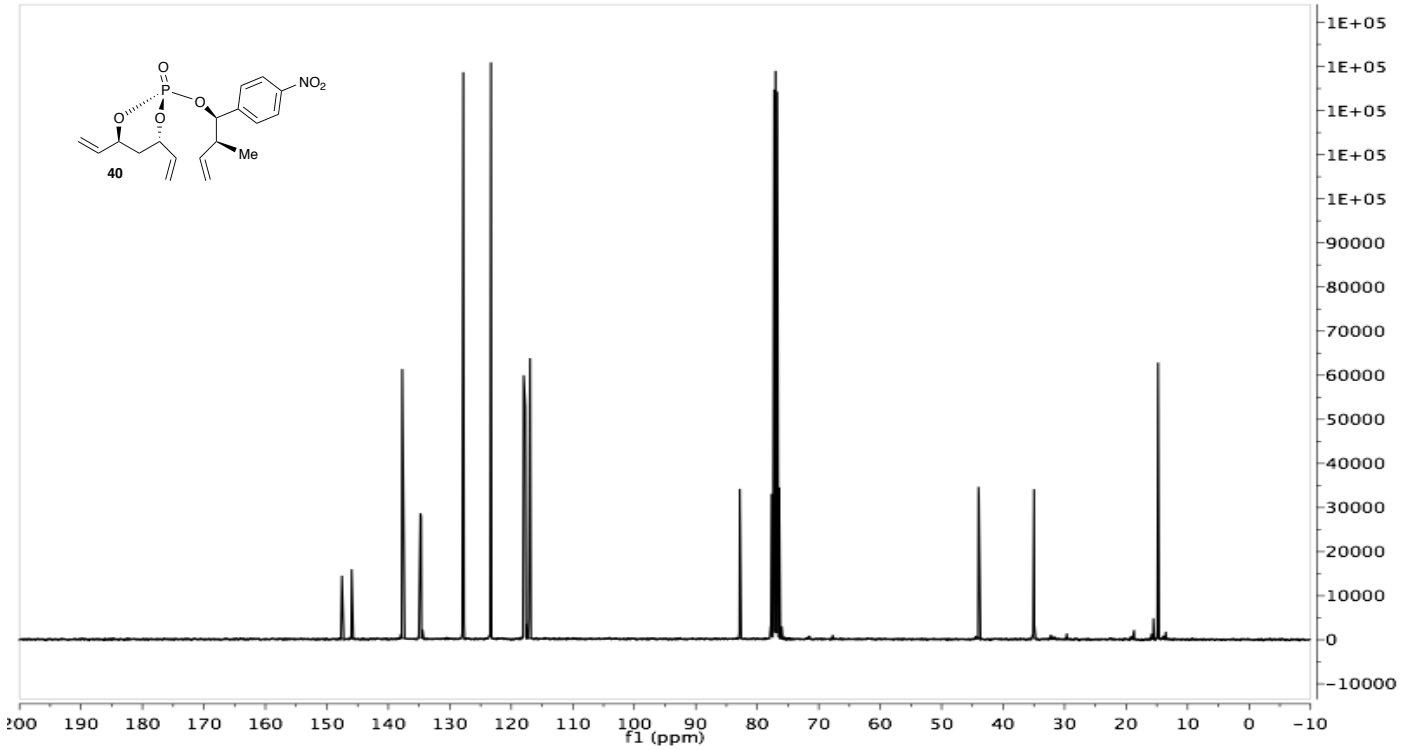


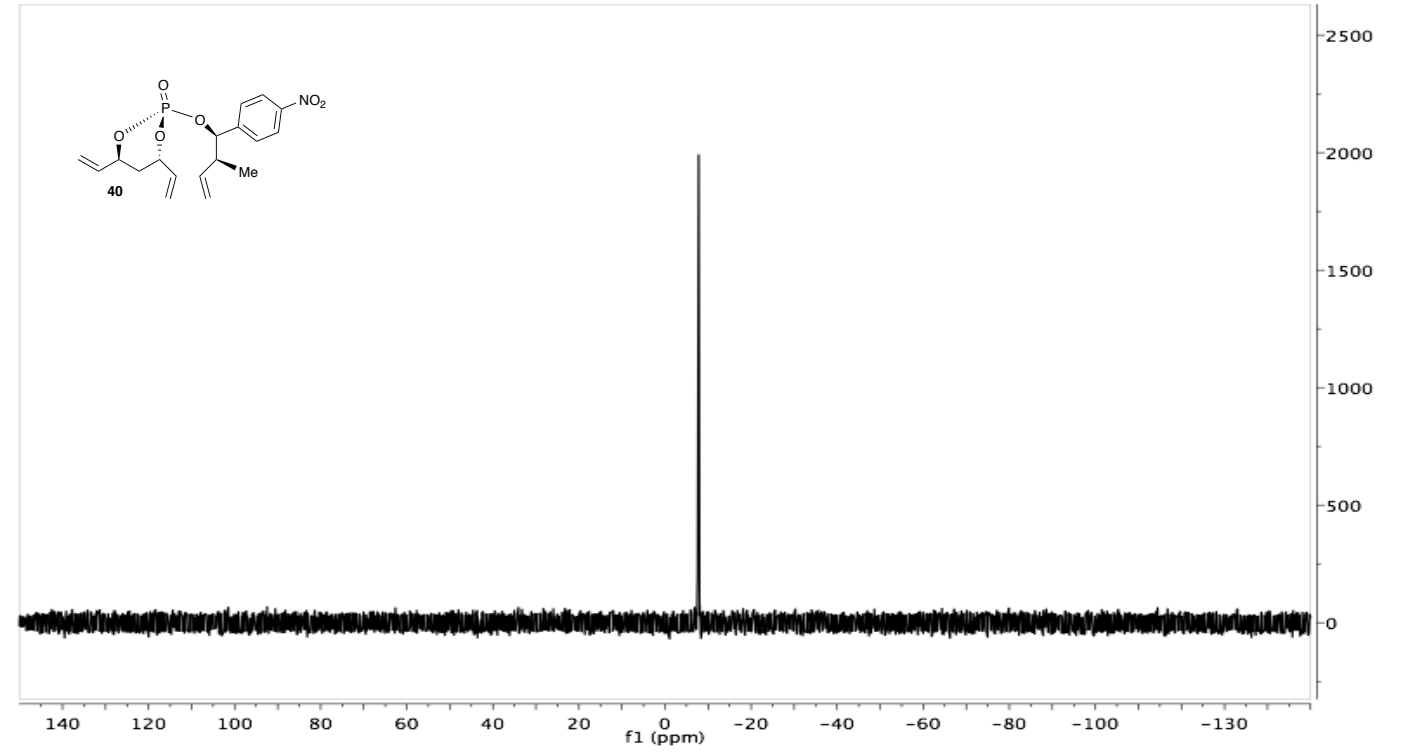




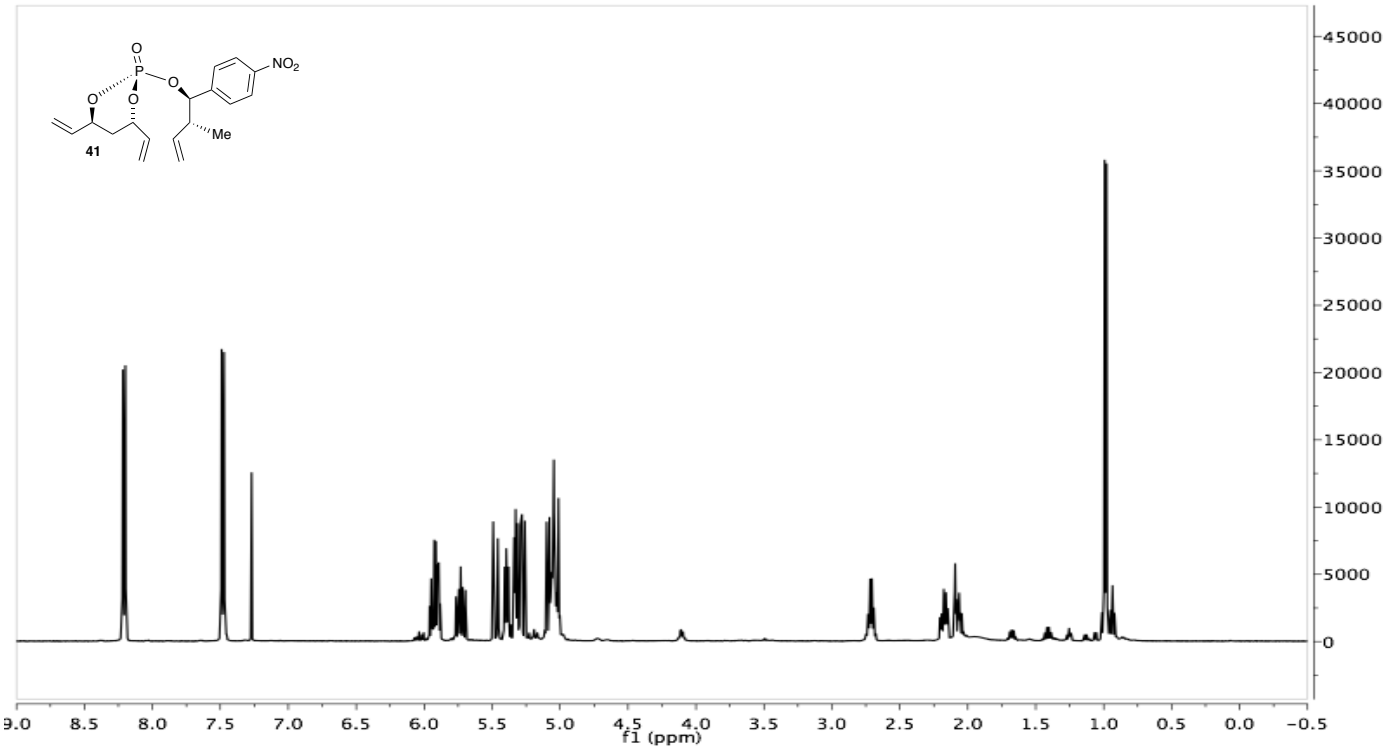
(4*S*,6*S*)-2-(((1*R*,2*S*)-2-methyl-1-(4-nitrophenyl)but-3-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (40):

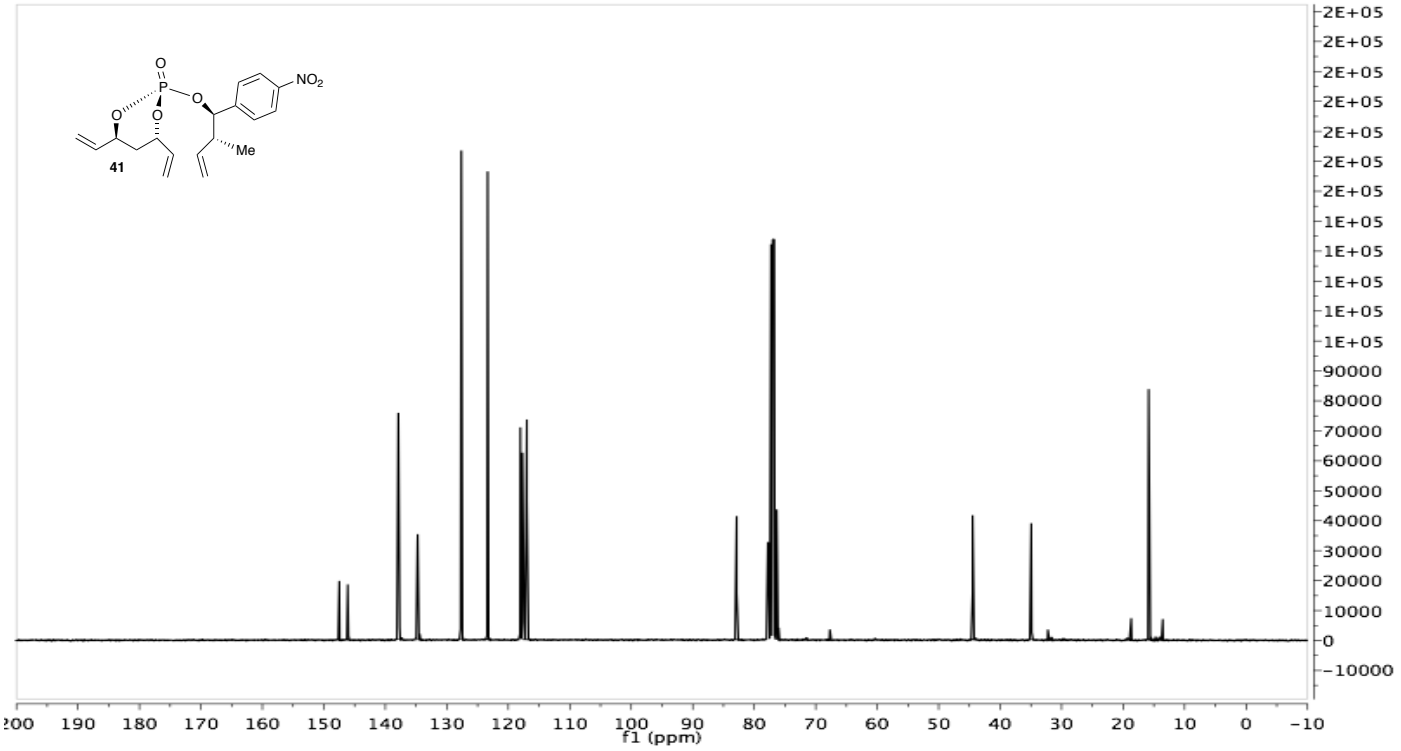


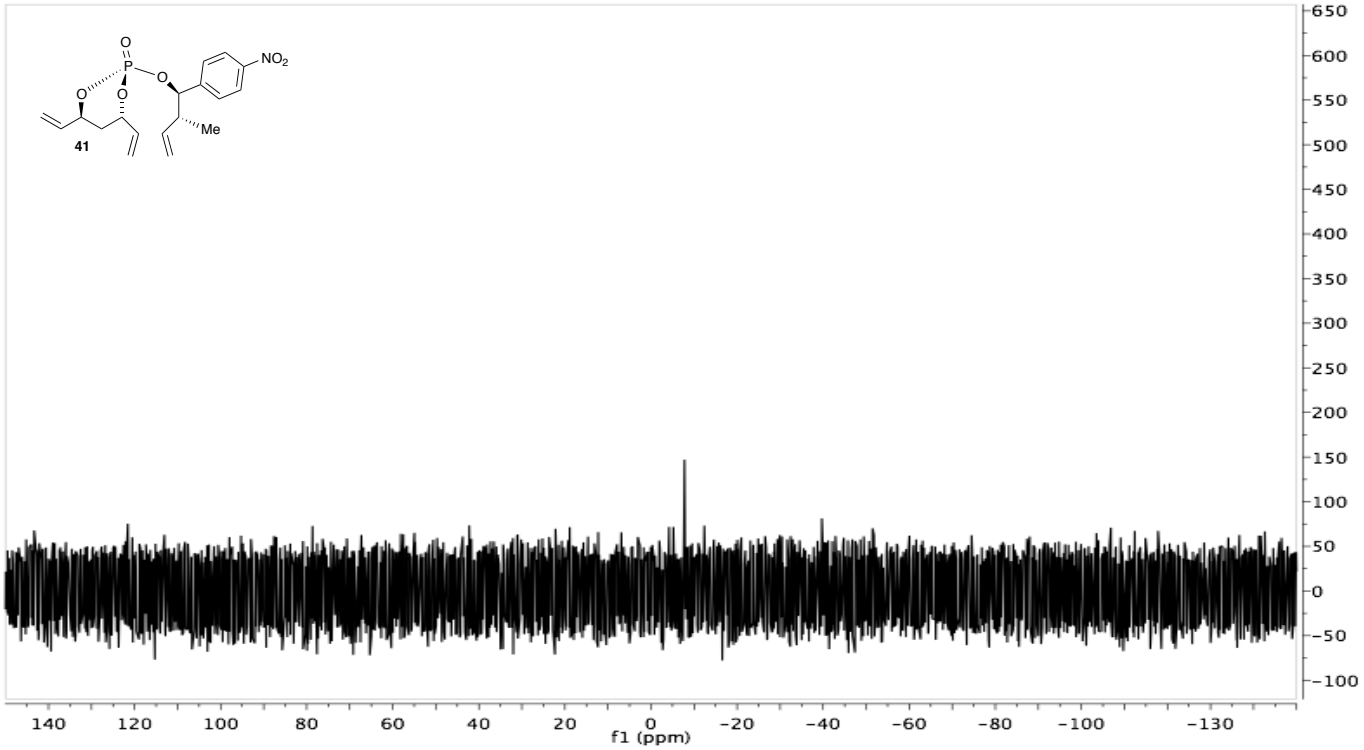

40
NO2
Me
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
−10000
f1 (ppm)


40
NO2
Me
2500
2000
1500
1000
500
0
f1 (ppm)

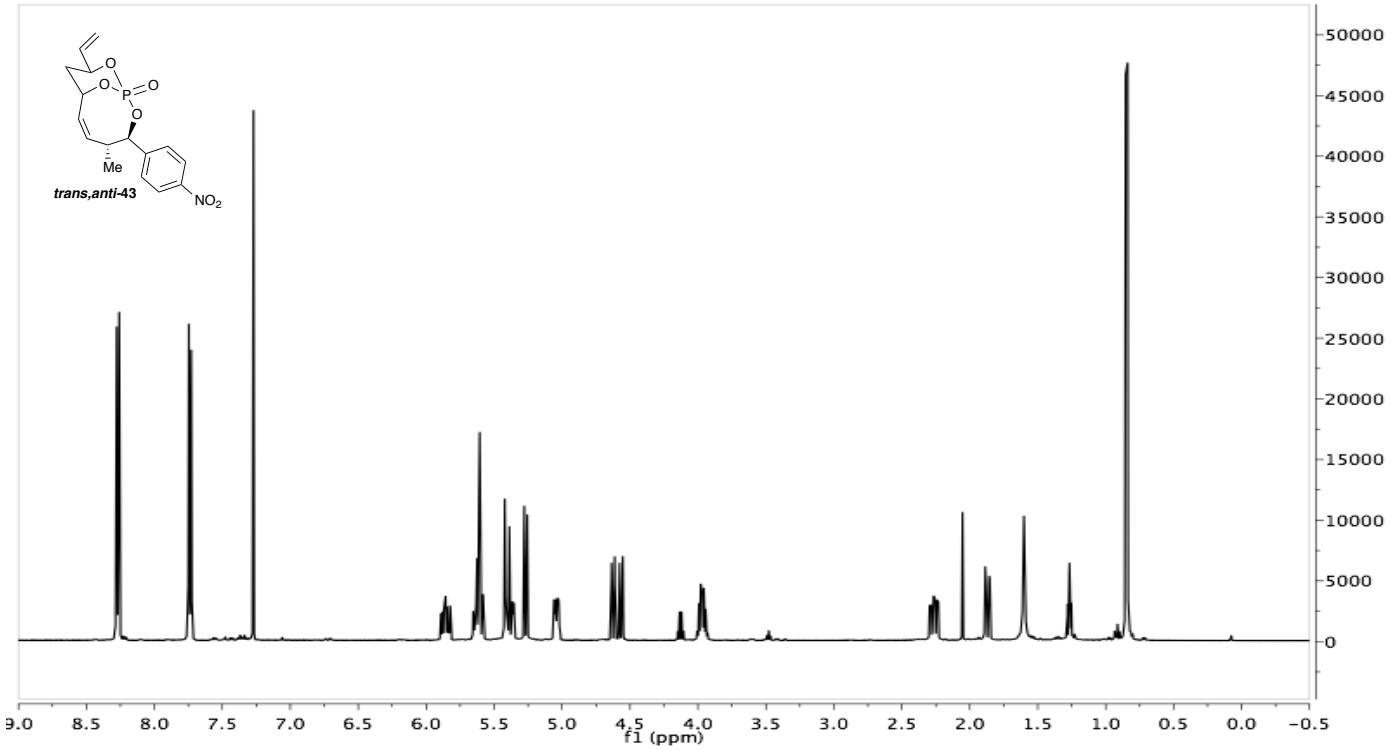
(4*S*,6*S*)-2-(((1*R*,2*R*)-2-methyl-1-(4-nitrophenyl)but-3-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (41):

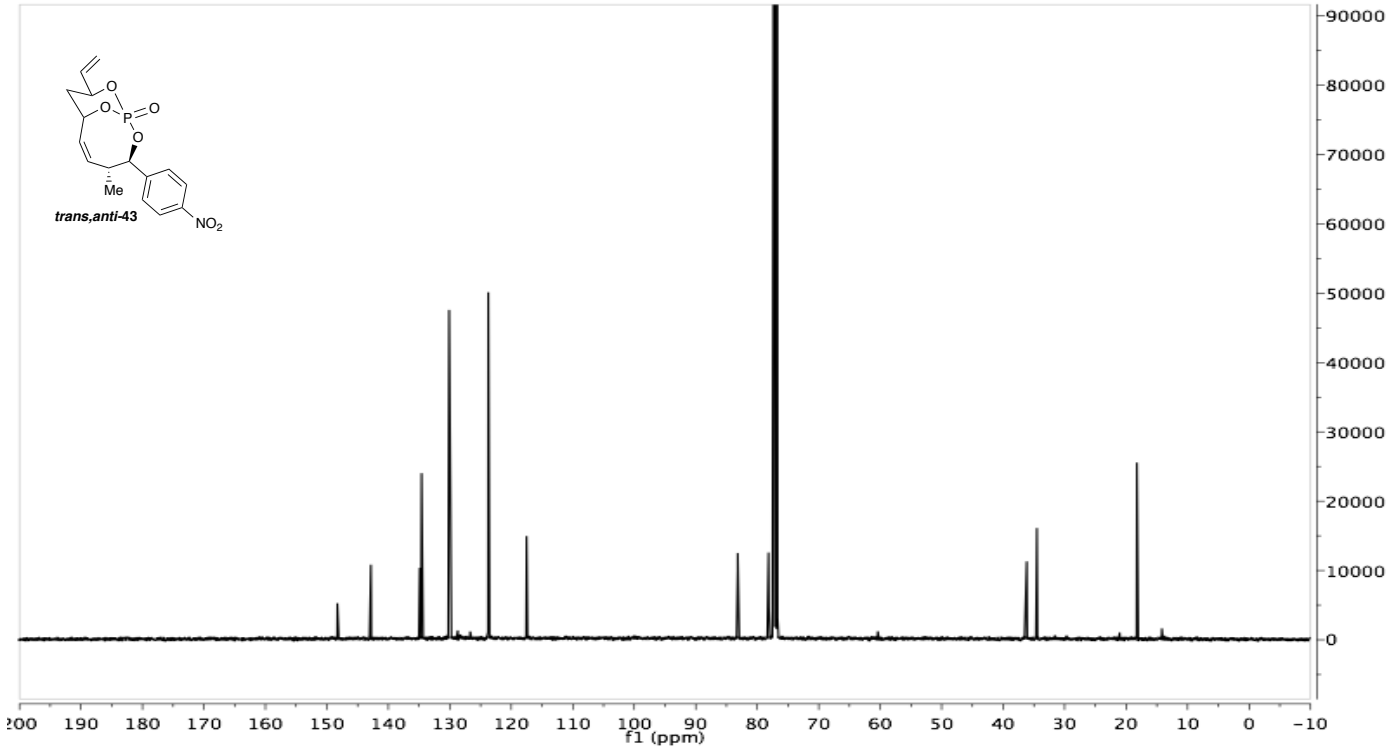


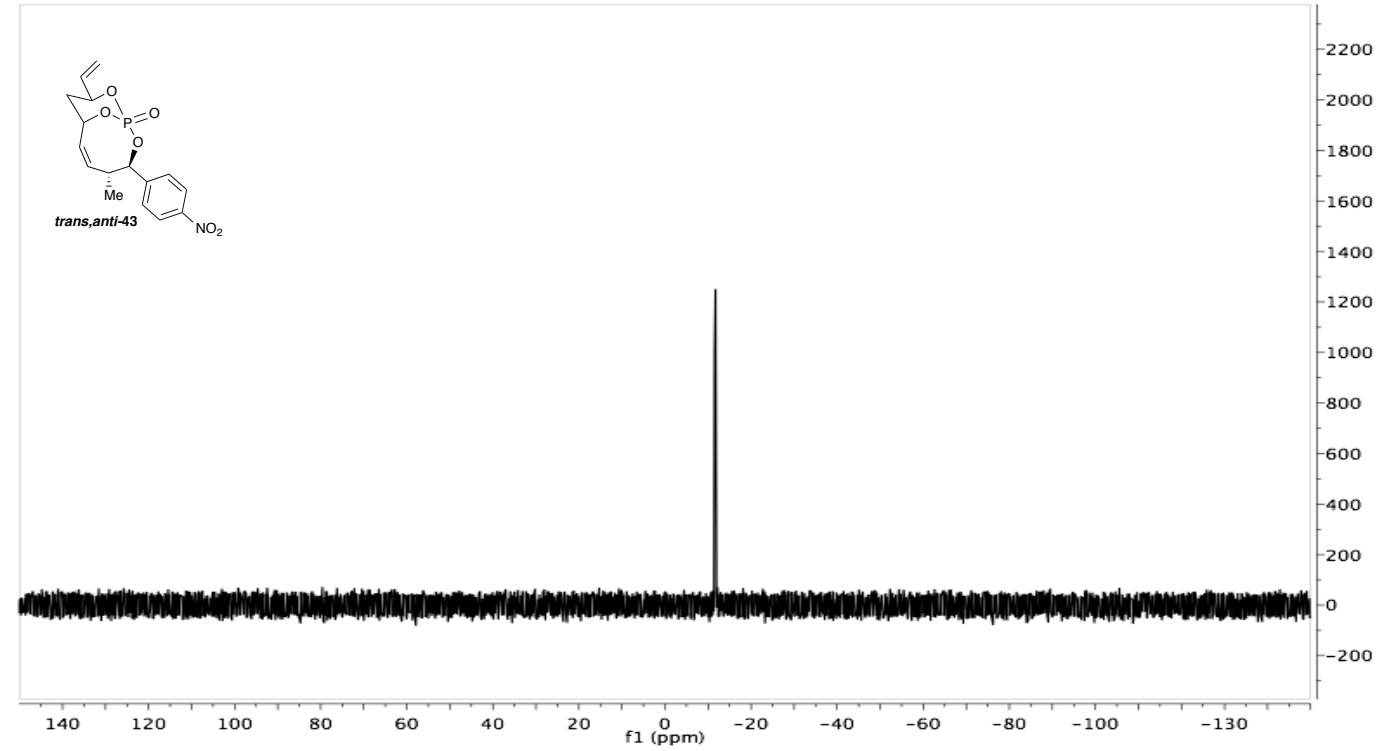




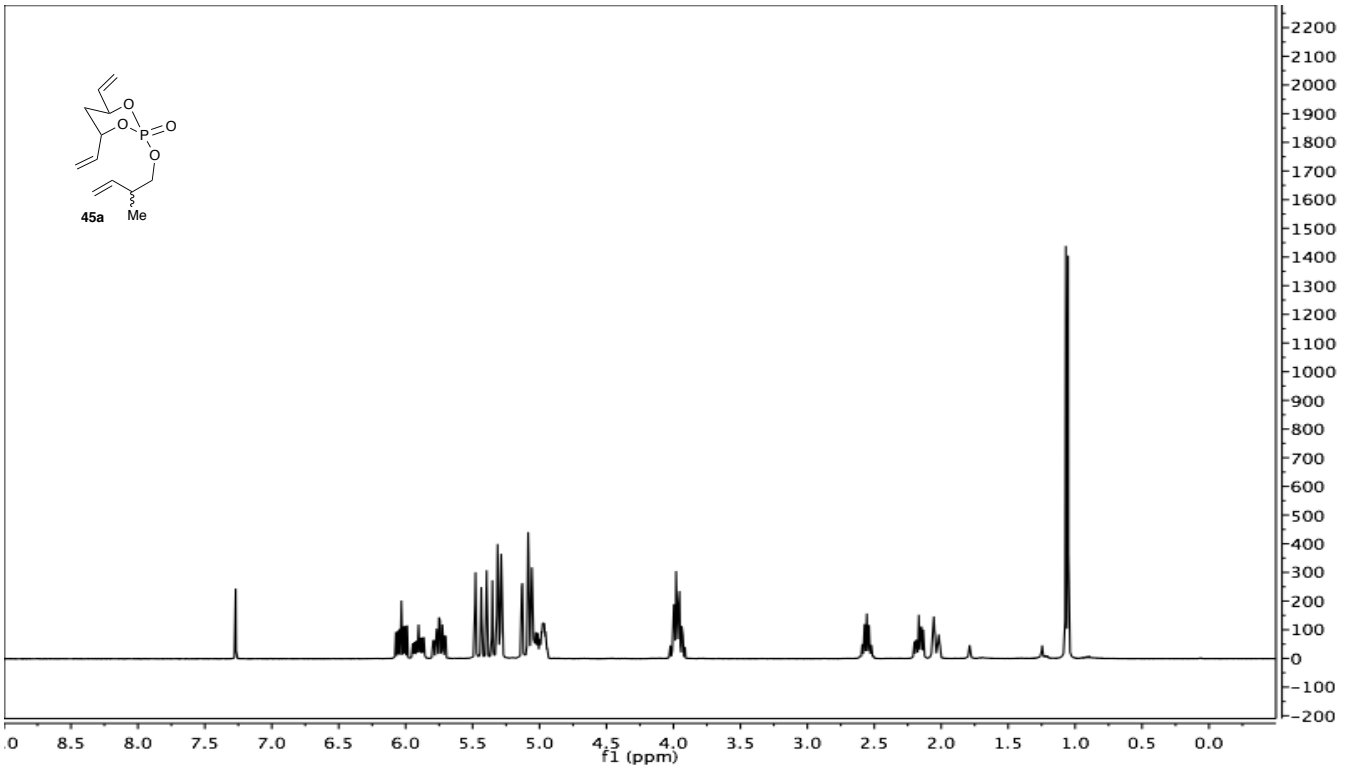
(1*S*,3*R*,4*R*,7*S*,9*S*,*Z*)-4-methyl-3-(4-nitrophenyl)-9-vinyl-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-5-ene 1-oxide (*trans*,*anti*-43):

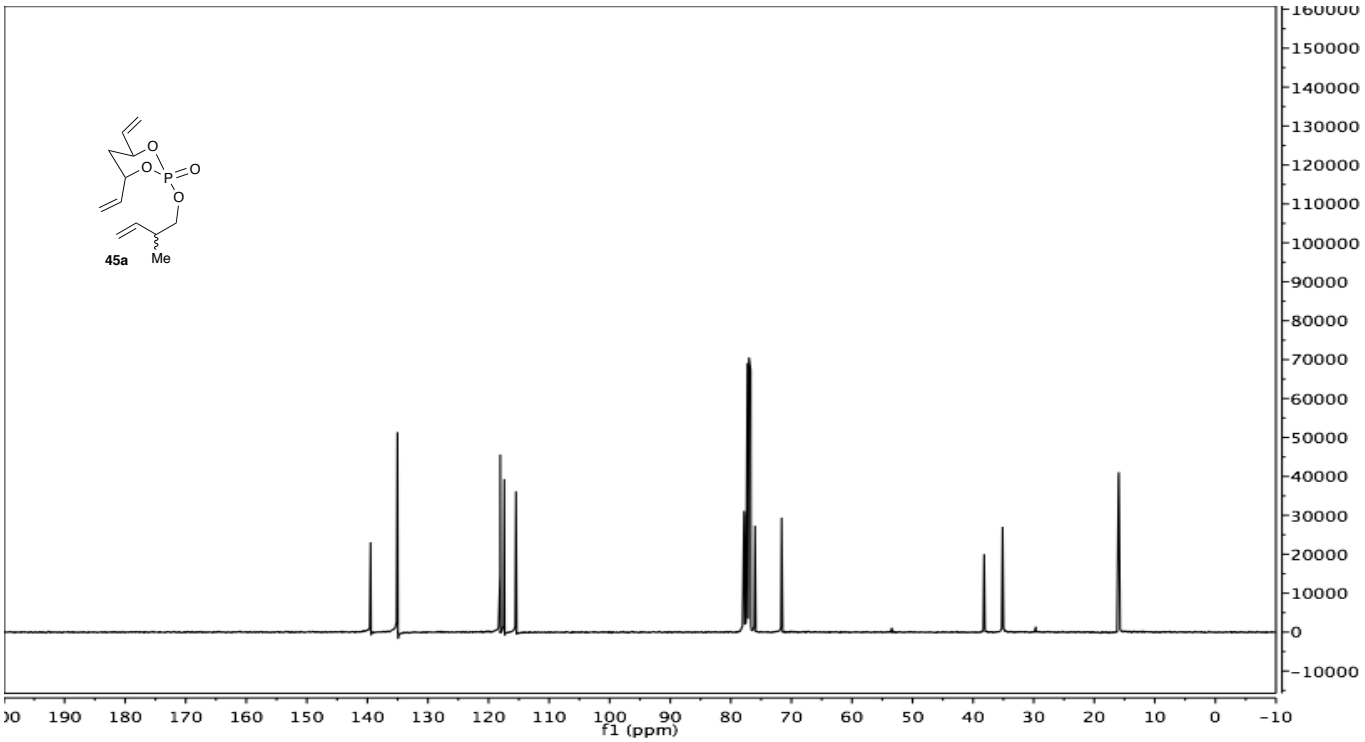


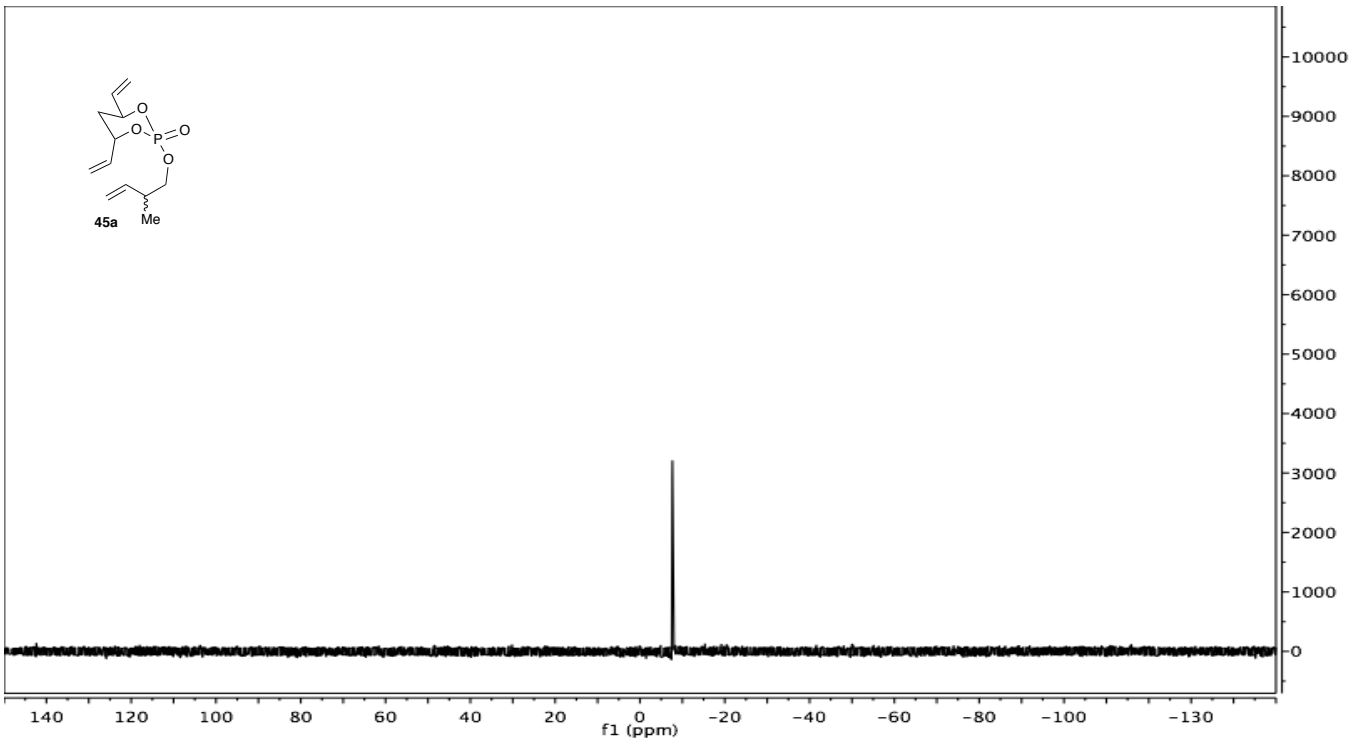

trans,anti-43
Me
NO2
f1 (ppm)


trans,anti-43
Me
NO2
f1 (ppm)

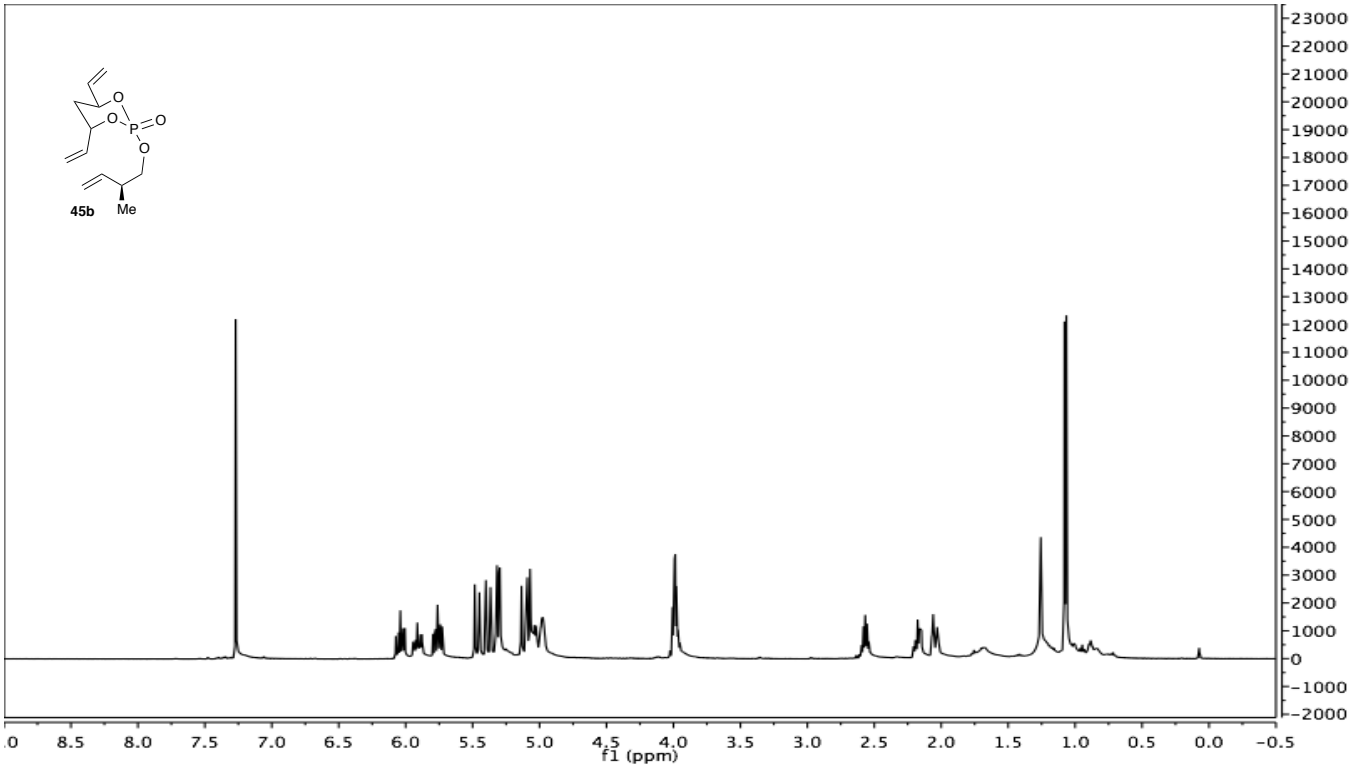
(4*S*,6*S*)-2-((2-methylbut-3-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (45a):

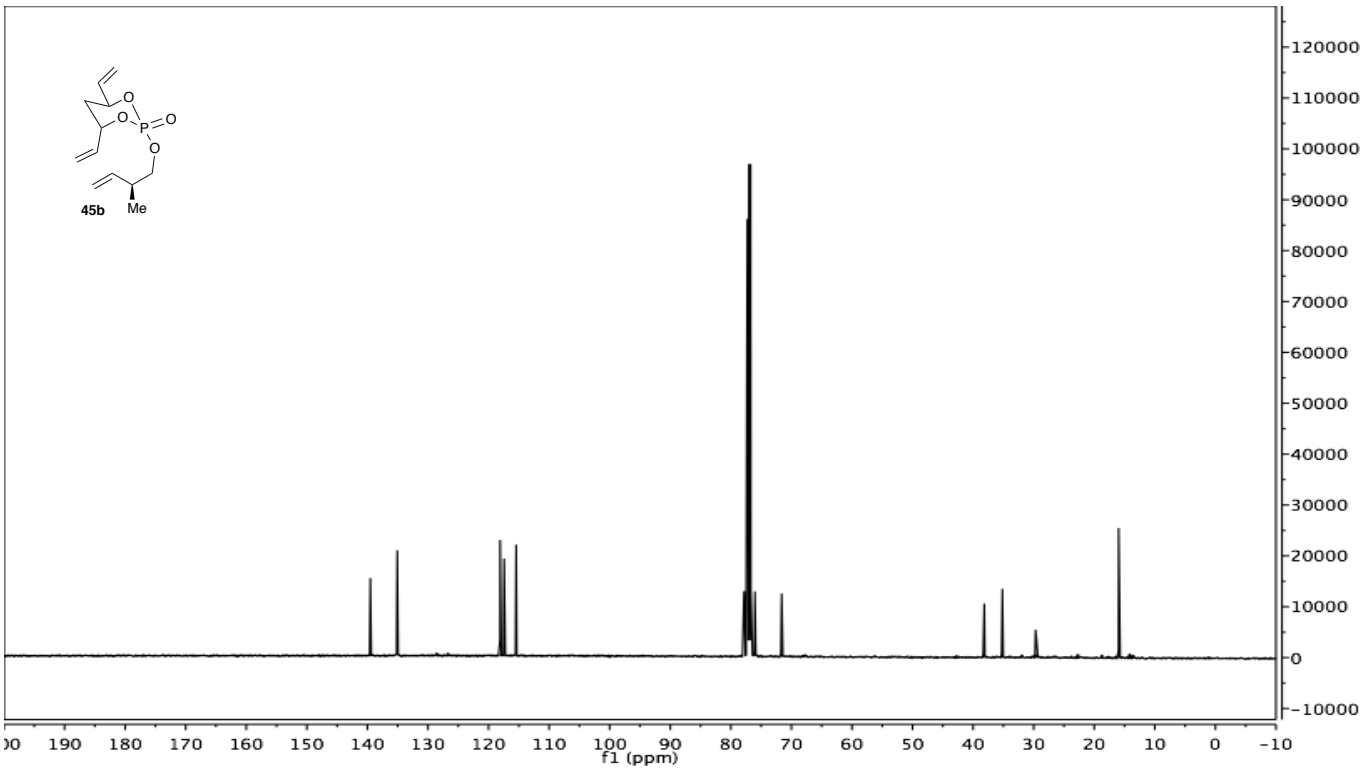


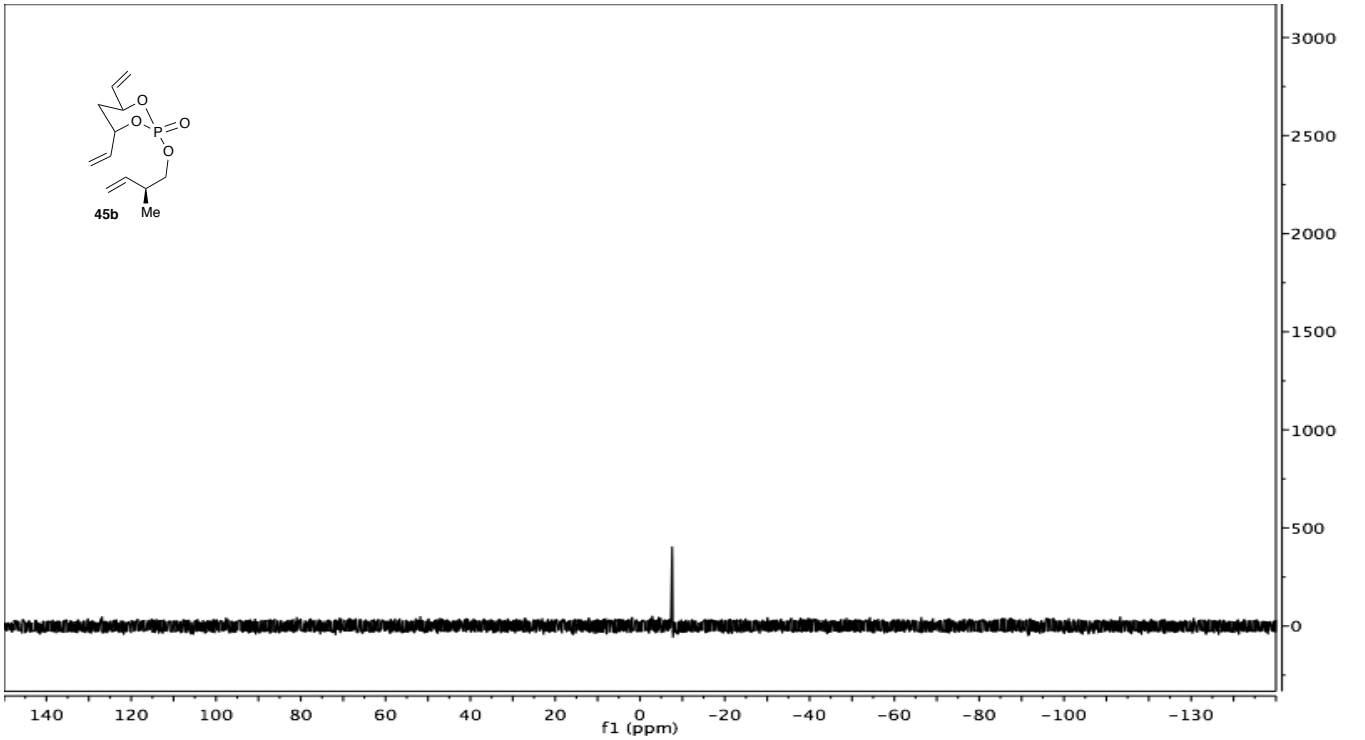




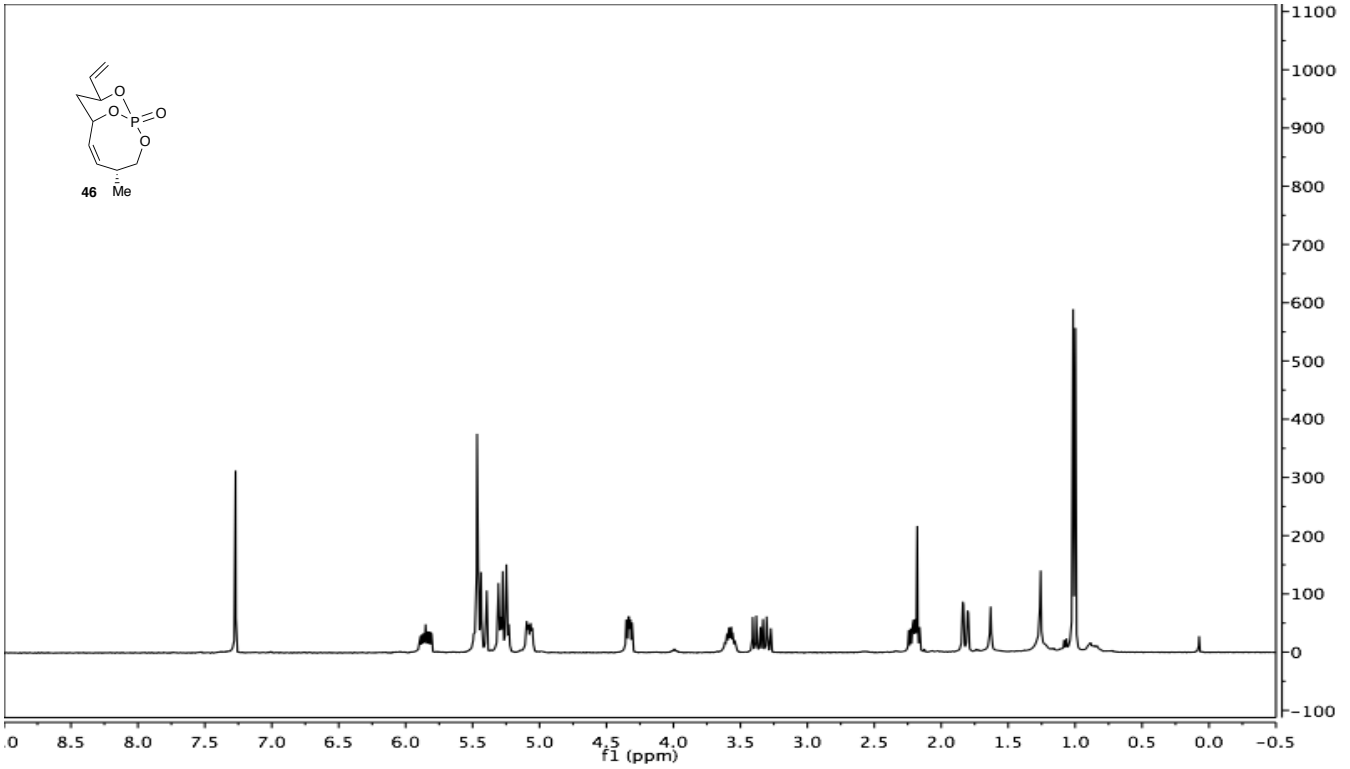
(4*S*,6*S*)-2-(((*S*)-2-methylbut-3-en-1-yl)oxy)-4,6-divinyl-1,3,2-dioxaphosphinane 2-oxide (45b):

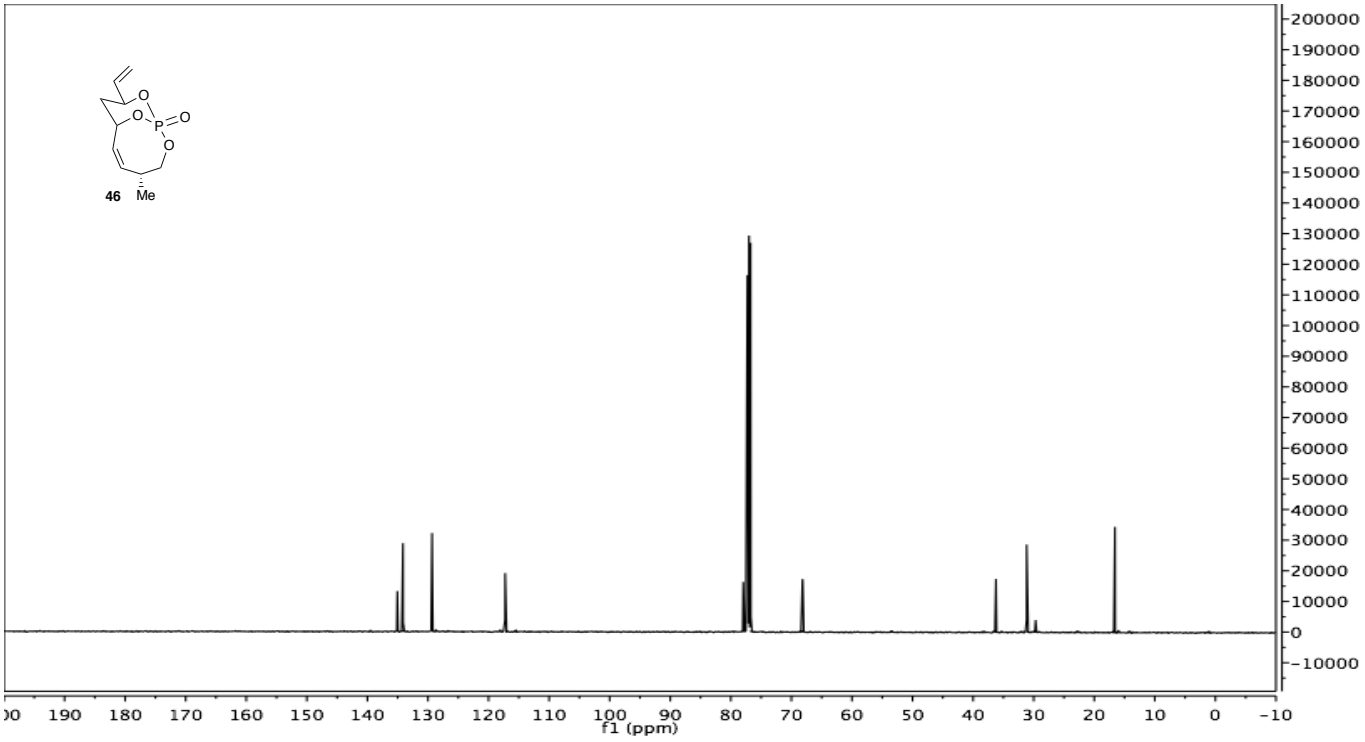


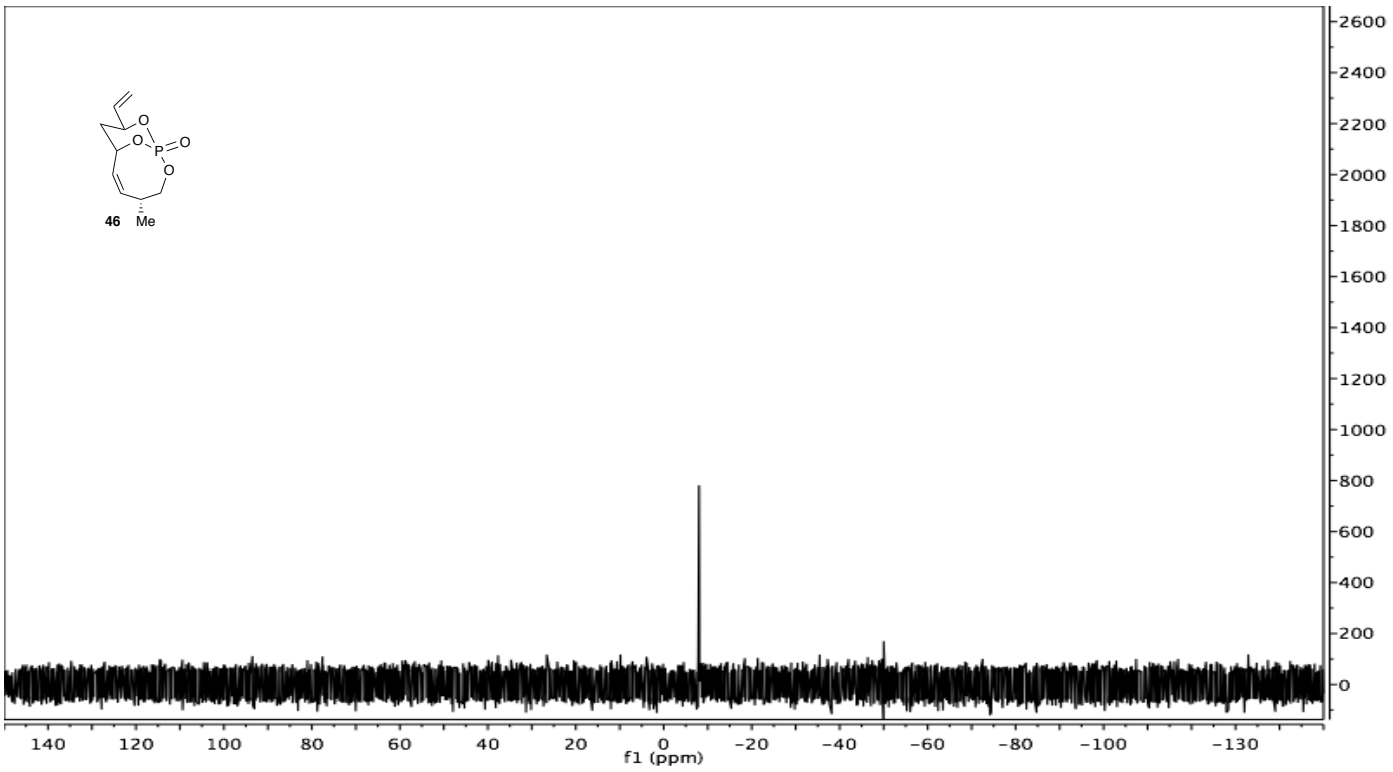

45b
Me
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
−10000
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


45b
Me
3000
2500
2000
1500
1000
500
0
140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −130
f1 (ppm)

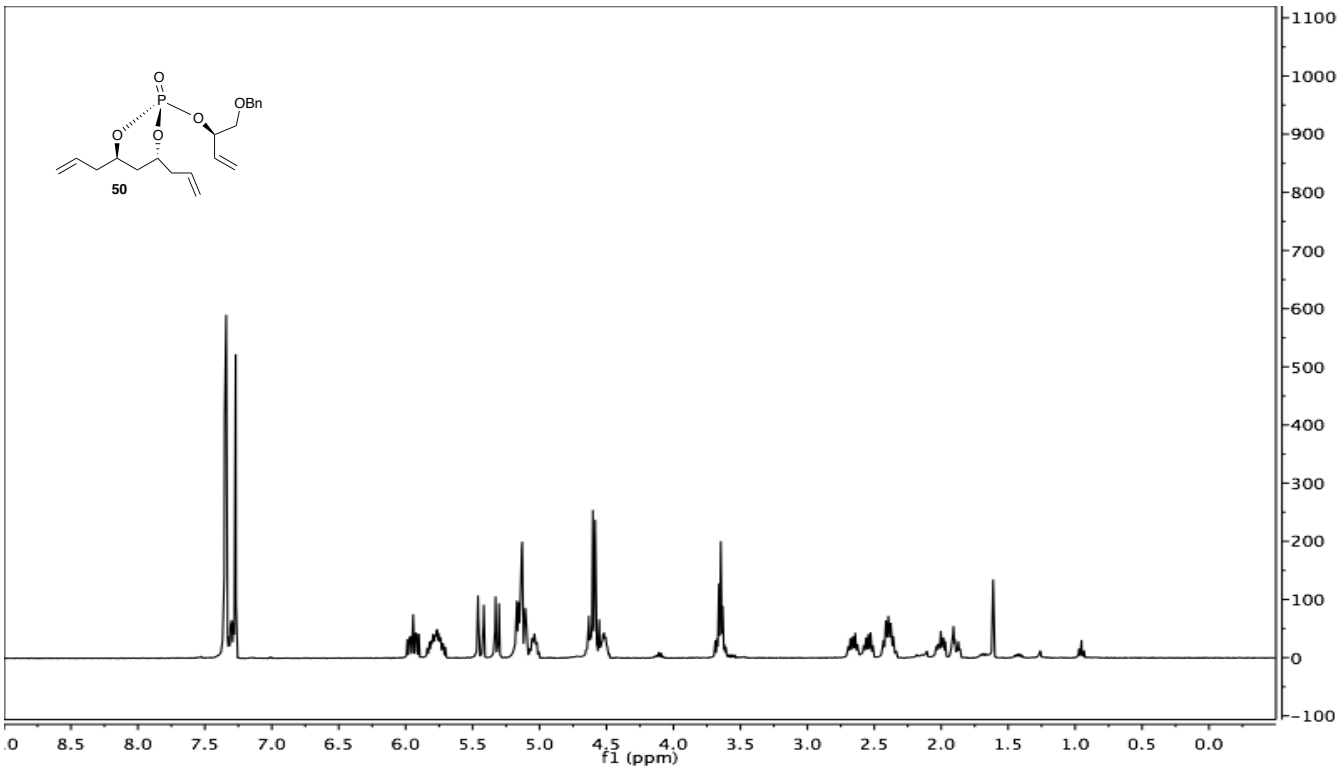
(1*S*,4*R*,7*S*,9*S*,*Z*)-4-methyl-9-vinyl-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-5-ene 1-oxide (46):

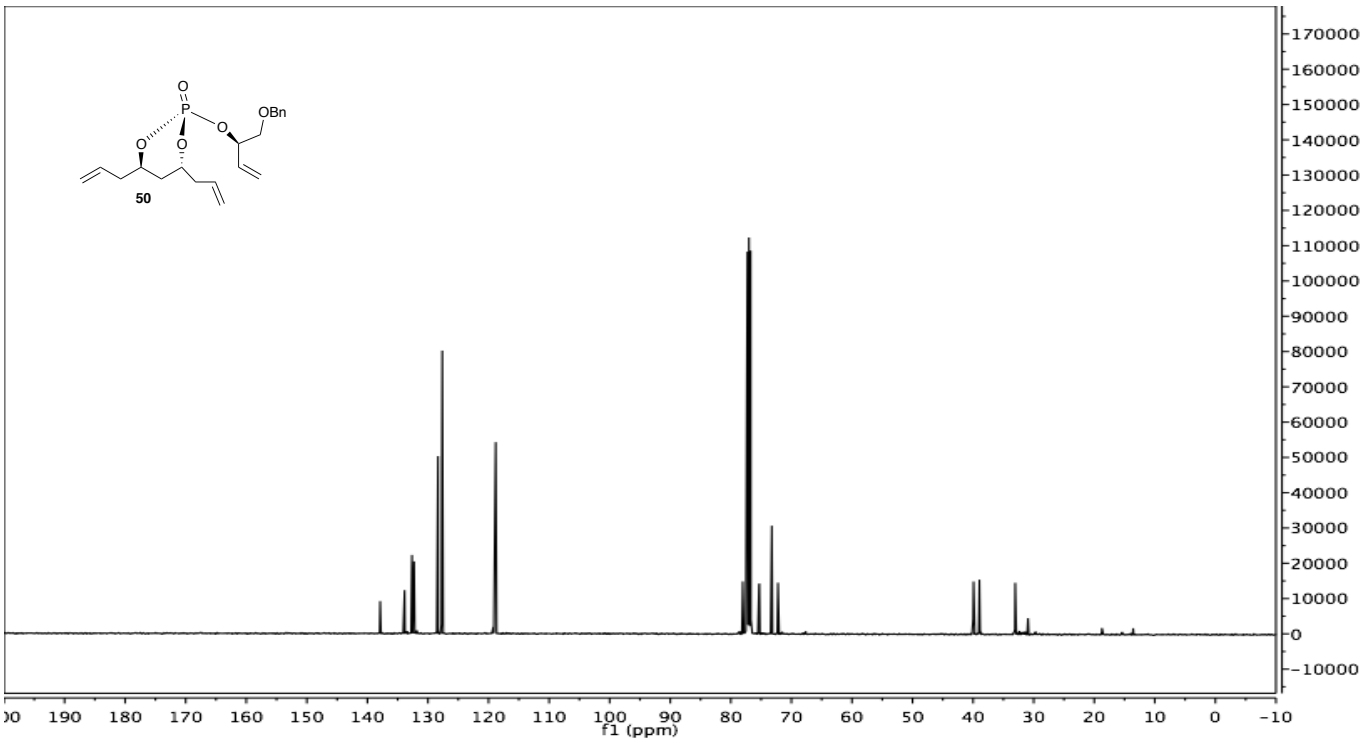


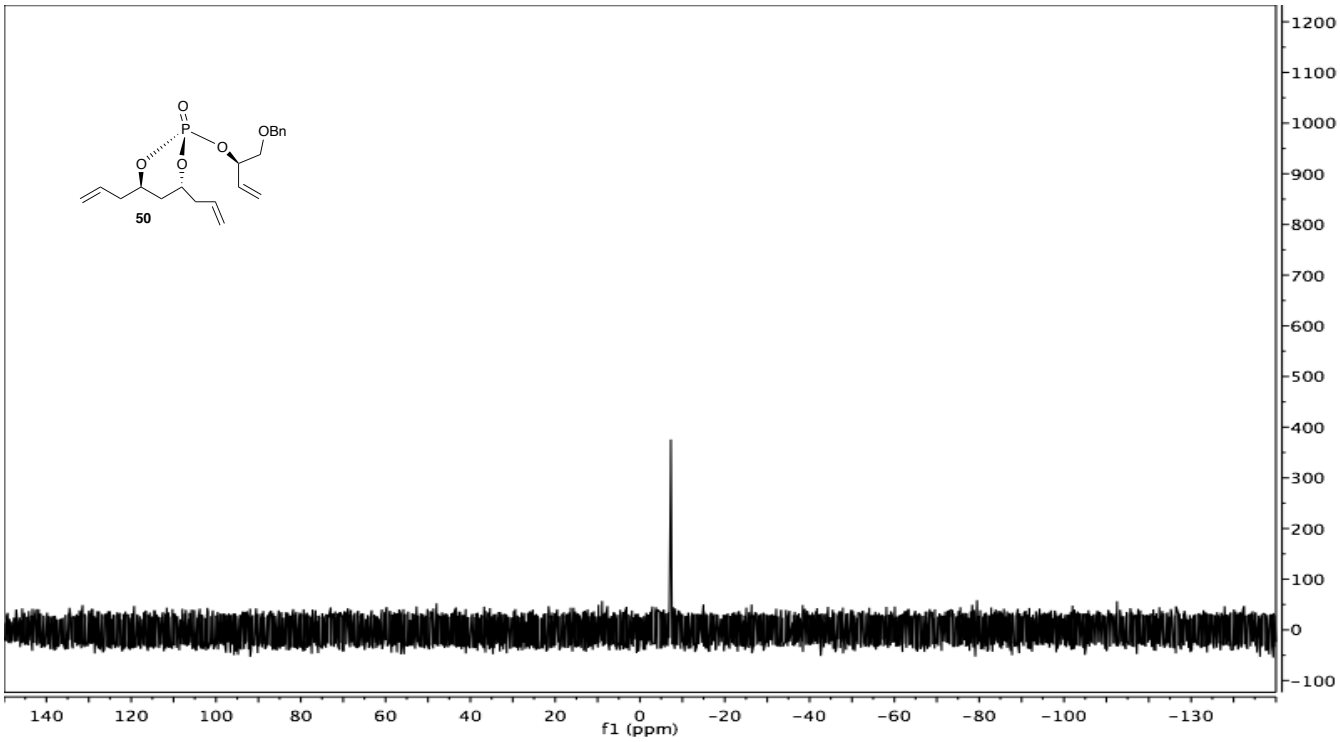




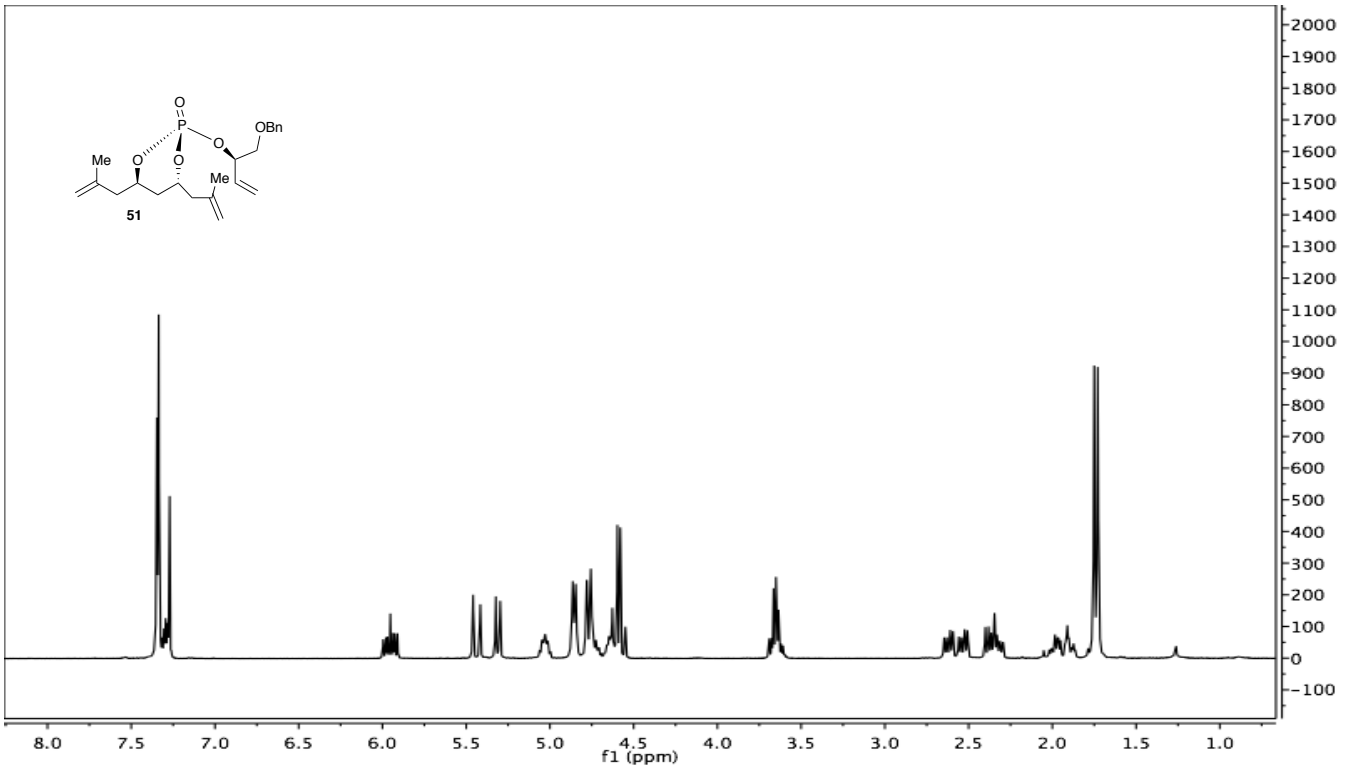
(4*R*,6*R*)-4,6-diallyl-2-(((*R*)-1-(benzyloxy)but-3-en-2-yl)oxy)-1,3,2-dioxaphosphinane 2-oxide (50):

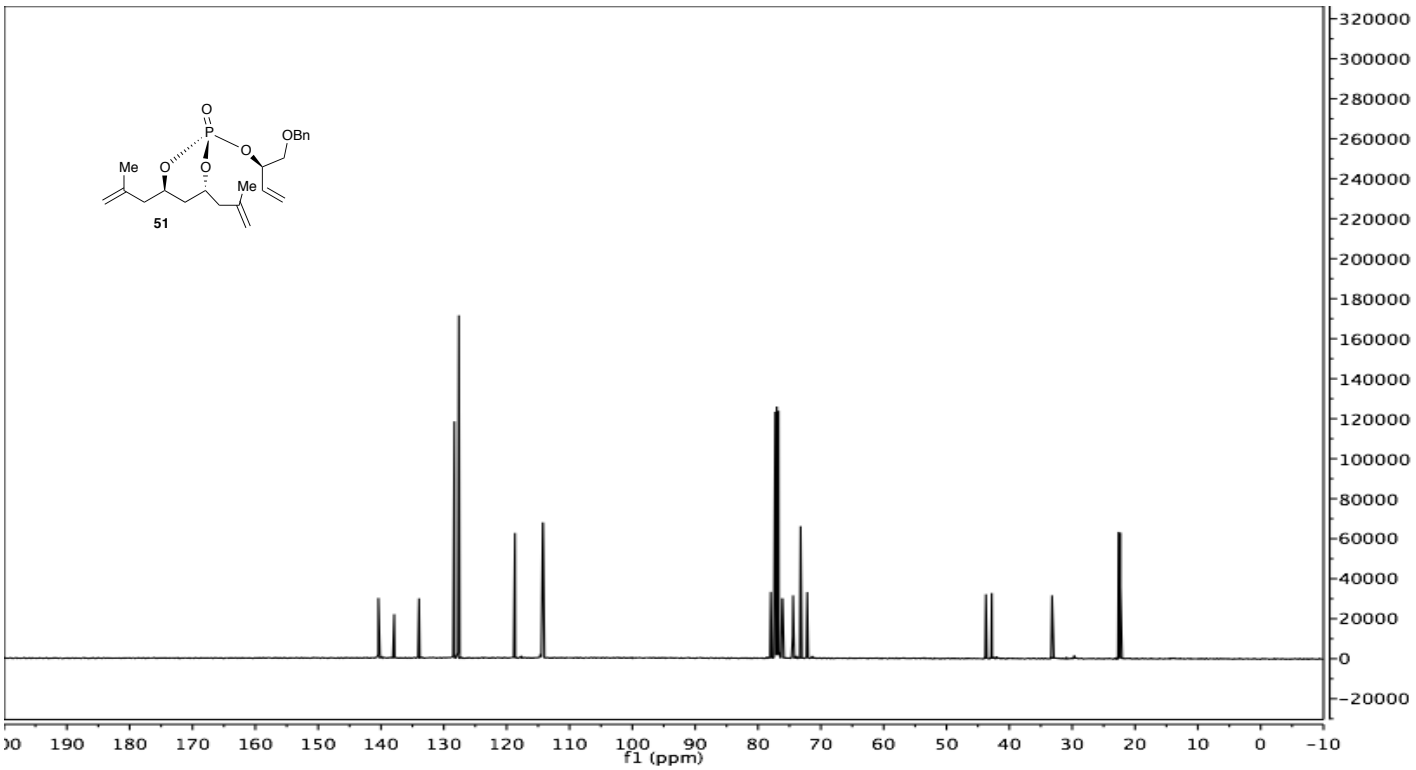


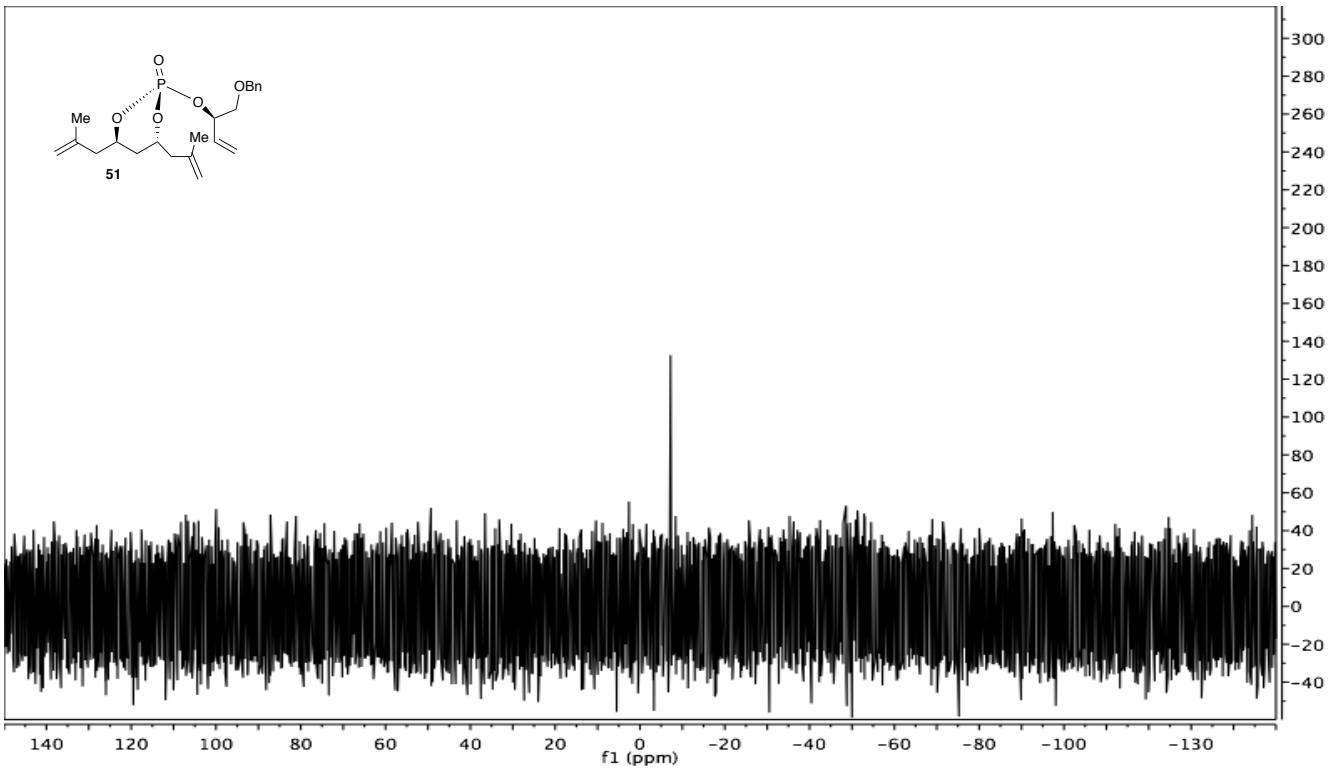

OBn
50
f1 (ppm)


OBn
50
f1 (ppm)

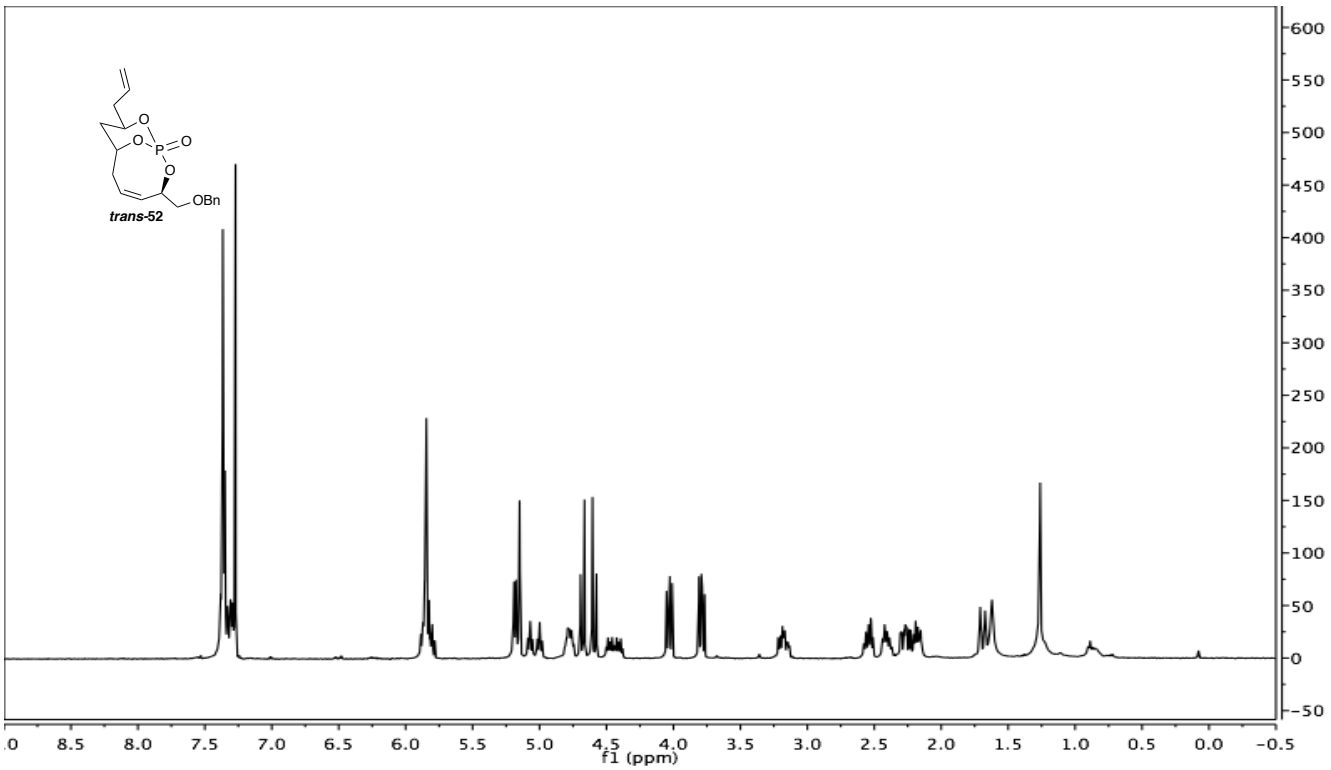
(4*R*,6*R*)-2-(((*R*)-1-(benzyloxy)but-3-en-2-yl)oxy)-4,6-bis(2-methylallyl)-1,3,2-dioxaphosphinane 2-oxide (51):

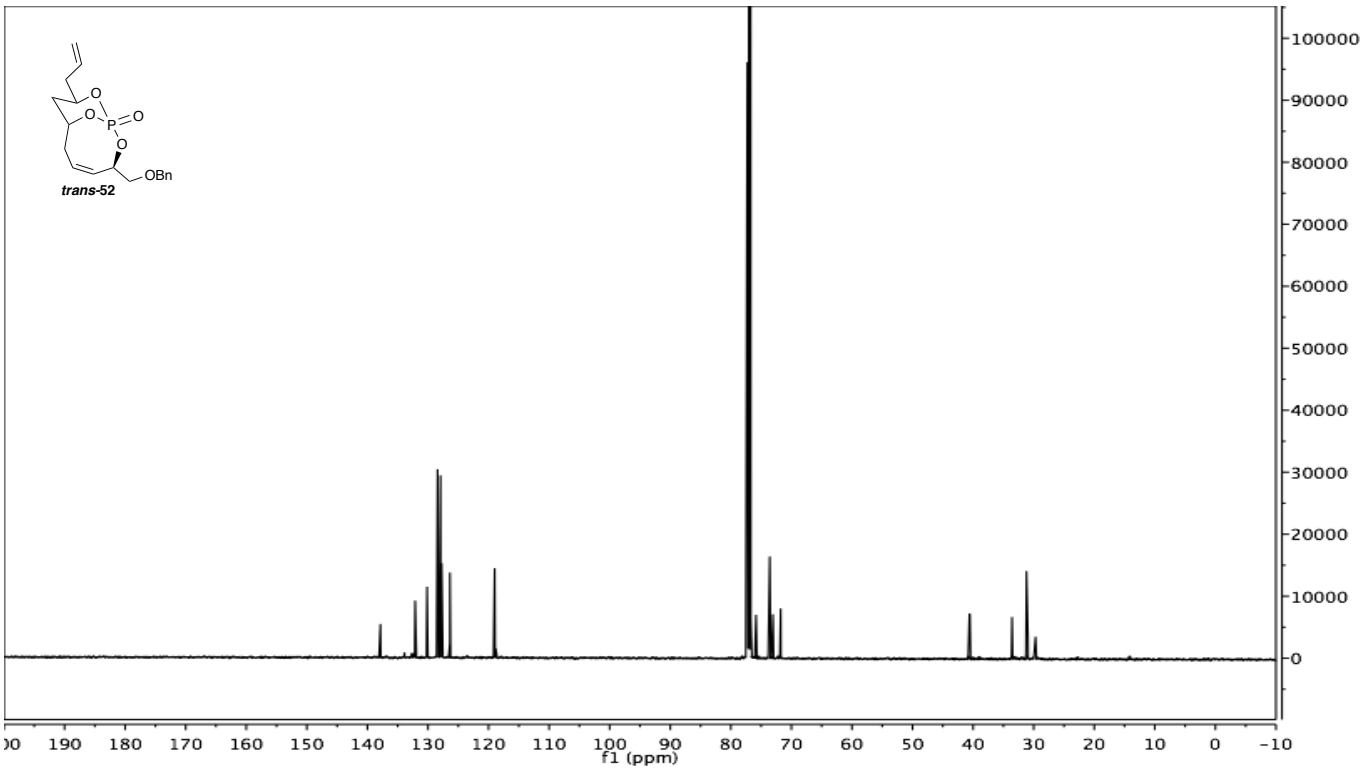


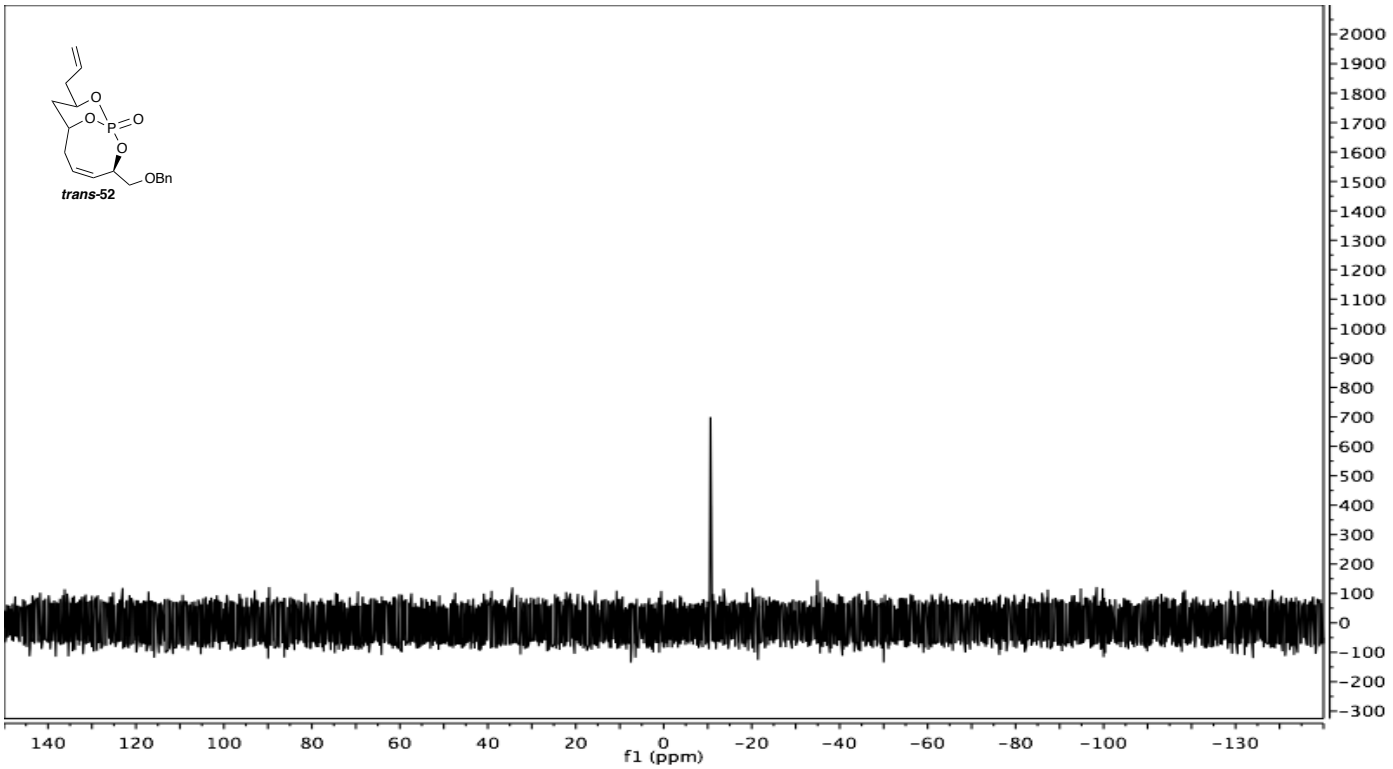




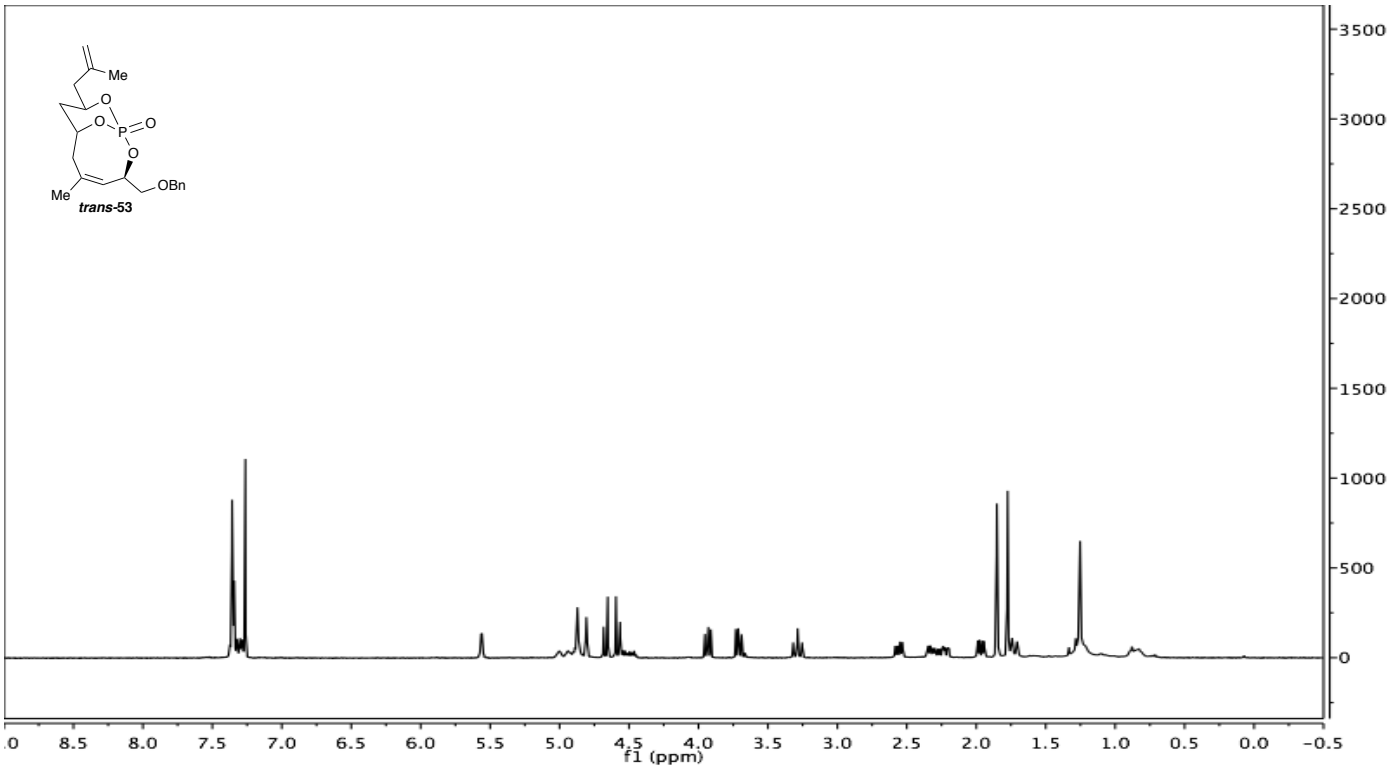
(1*S*,3*R*,7*R*,9*R*,*Z*)-9-allyl-3-((benzyloxy)methyl)-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-4-ene 1-oxide (*trans*-52):

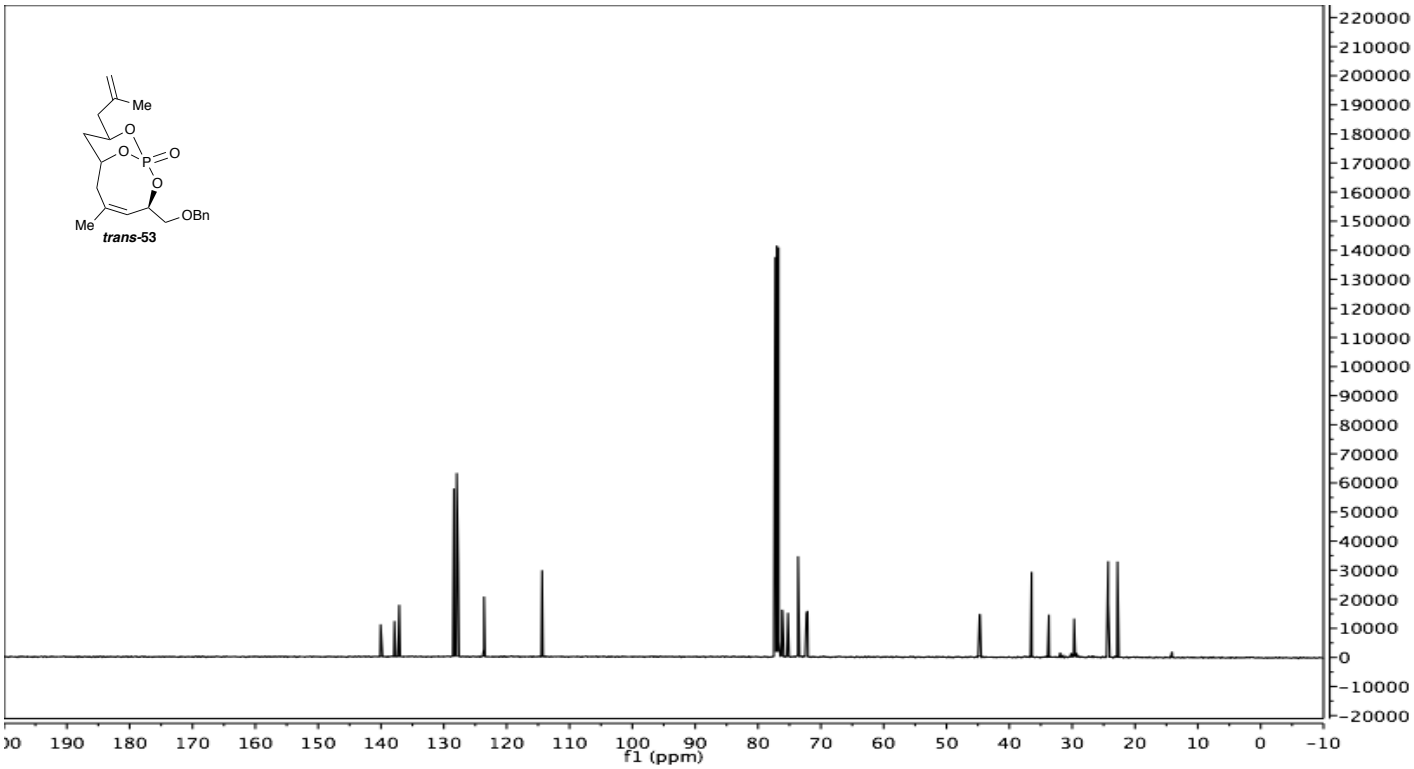


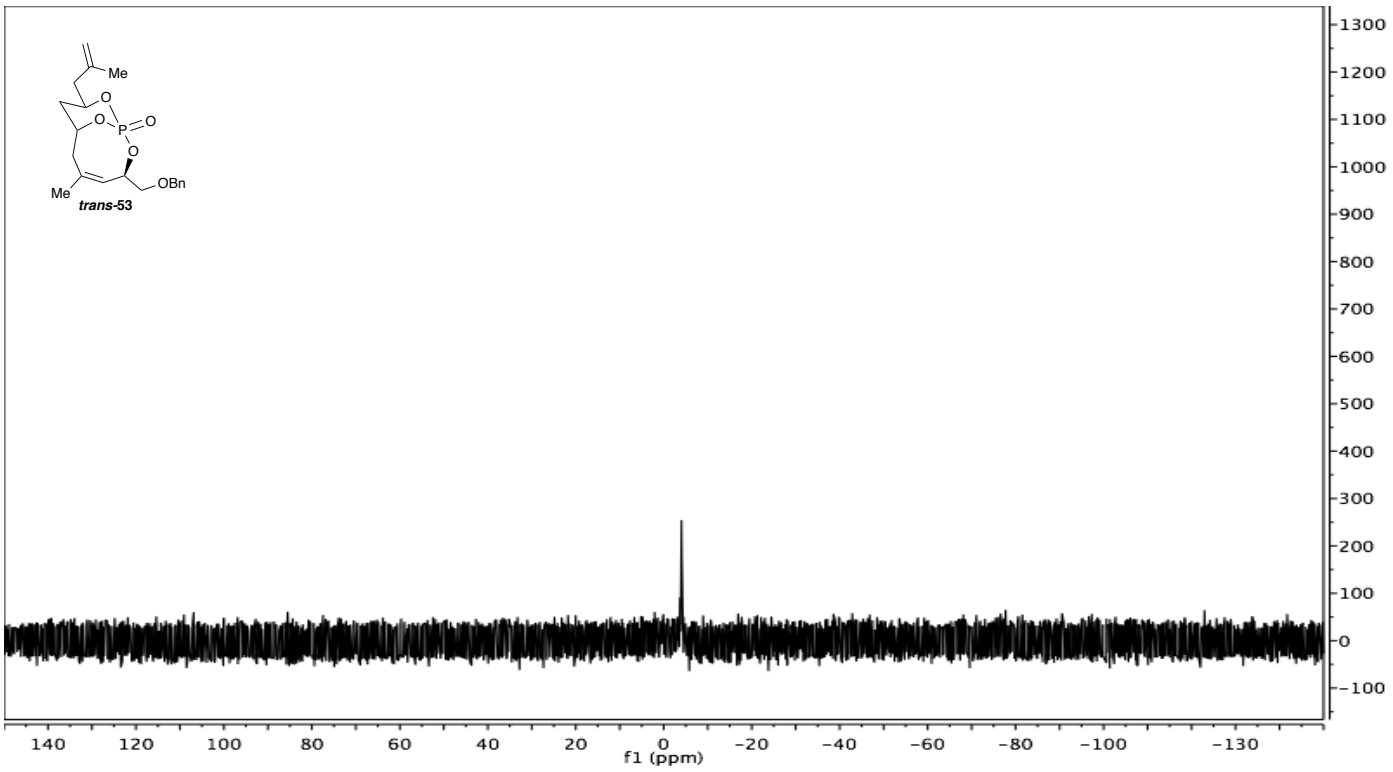

trans-52
OBn
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


trans-52
OBn
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
−300
140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −130
f1 (ppm)

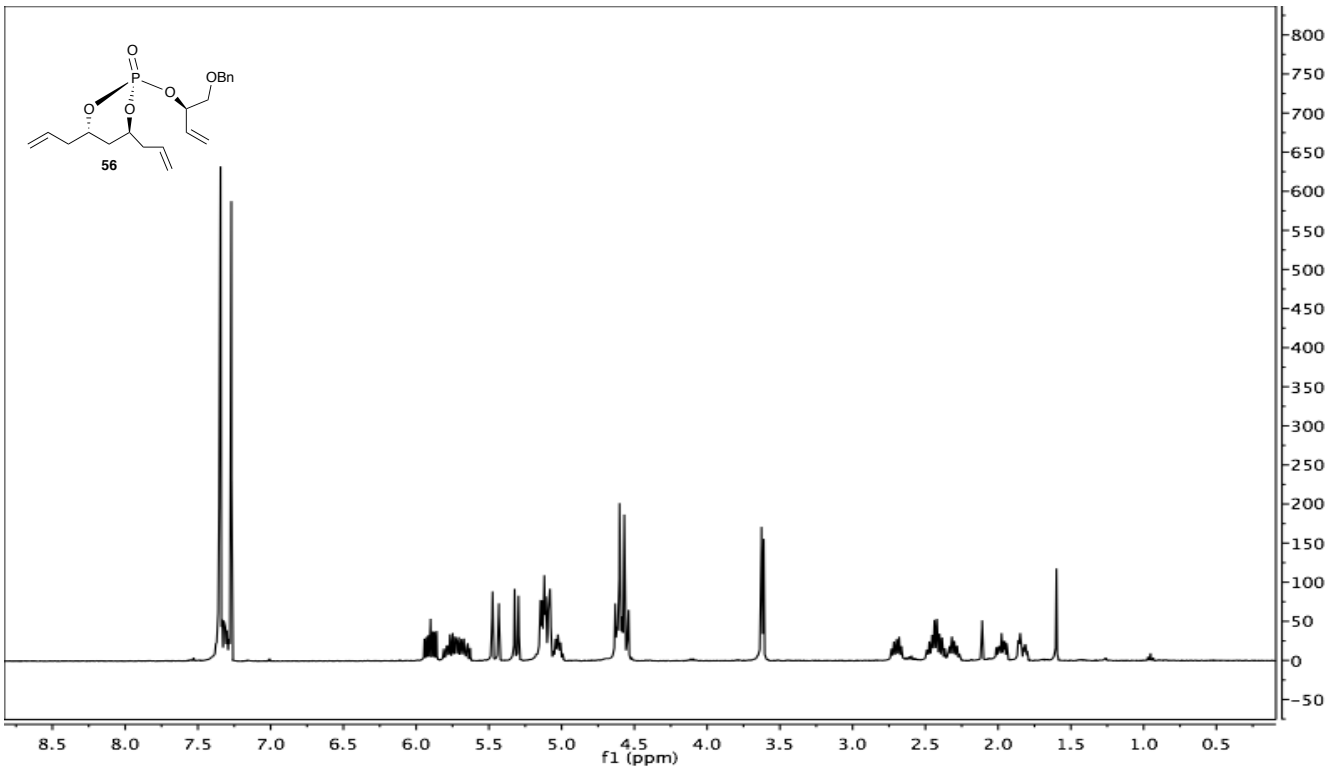
(1*S*,3*R*,7*R*,9*R*,*Z*)-3-((benzyloxy)methyl)-5-methyl-9-(2-methylallyl)-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-4-ene 1-oxide (*trans*-53):

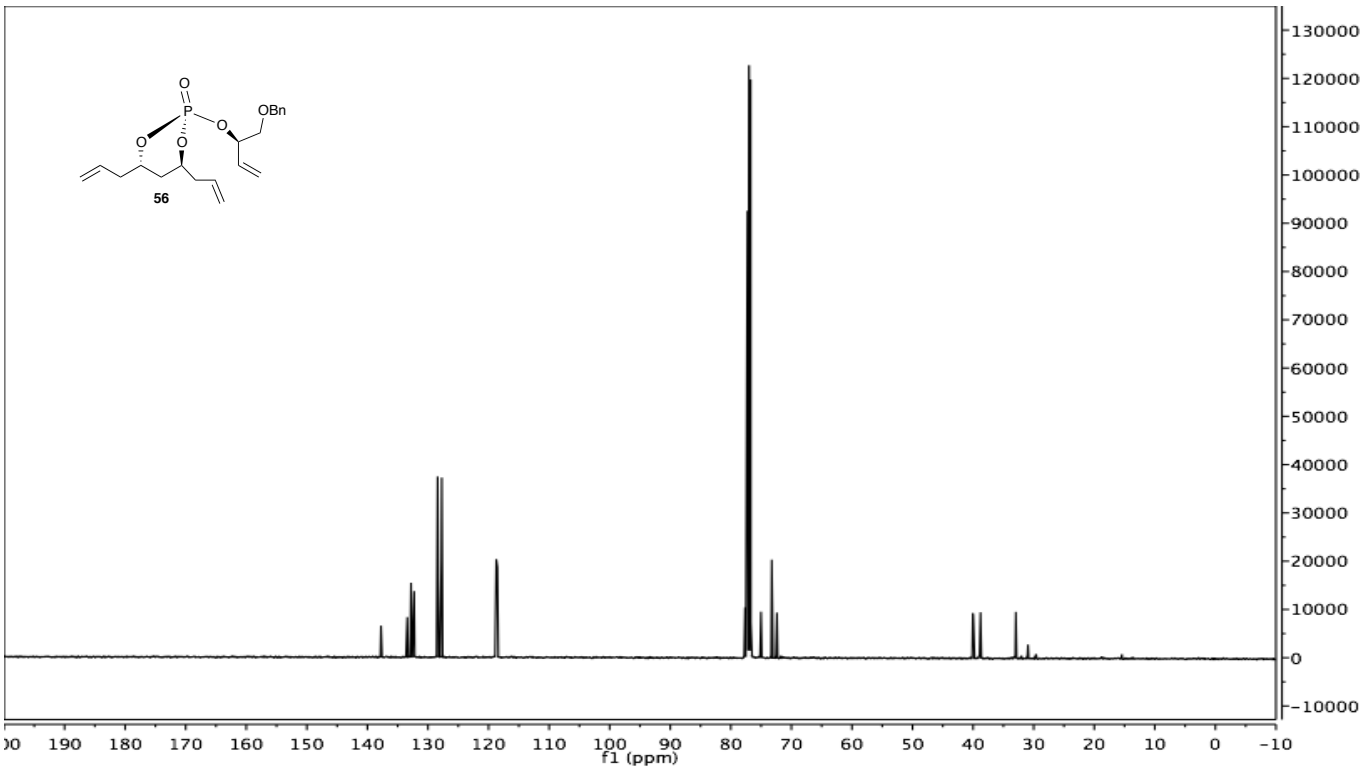


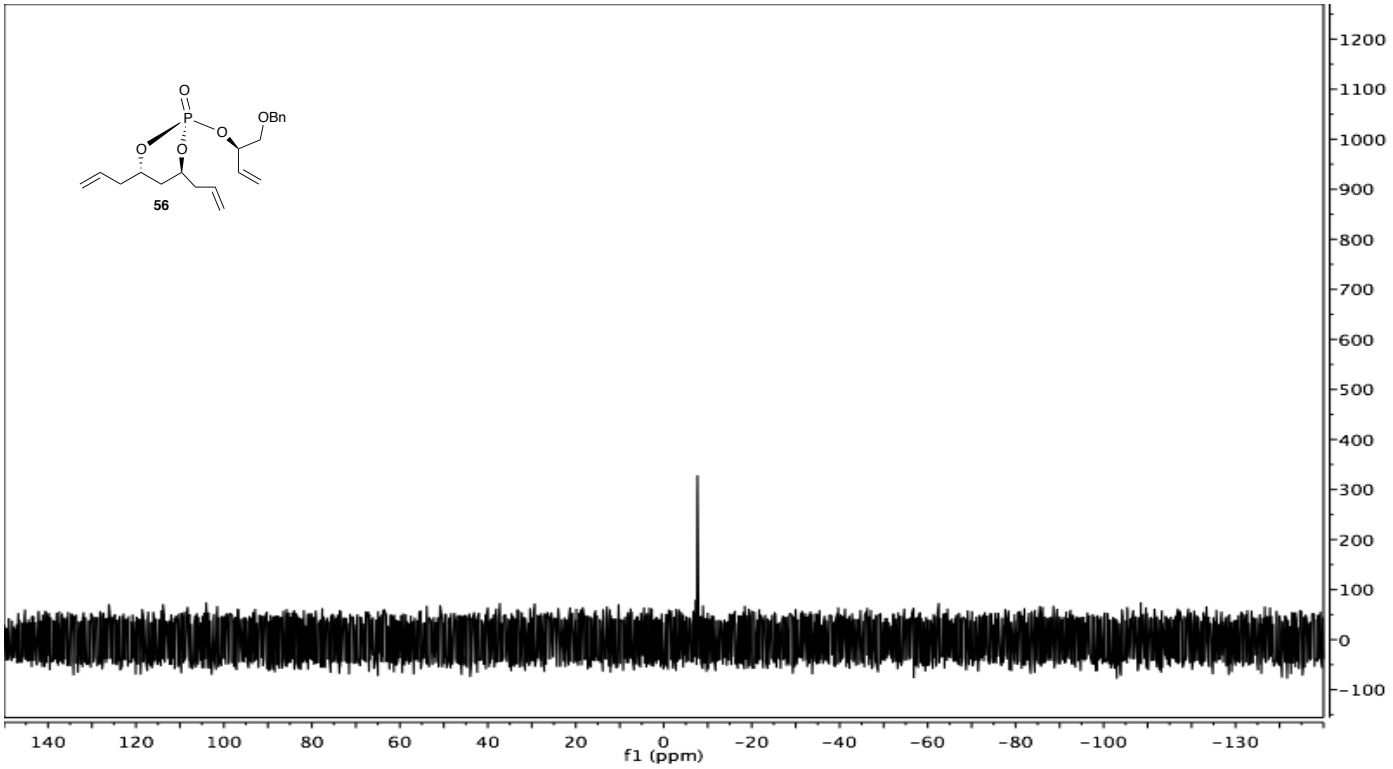




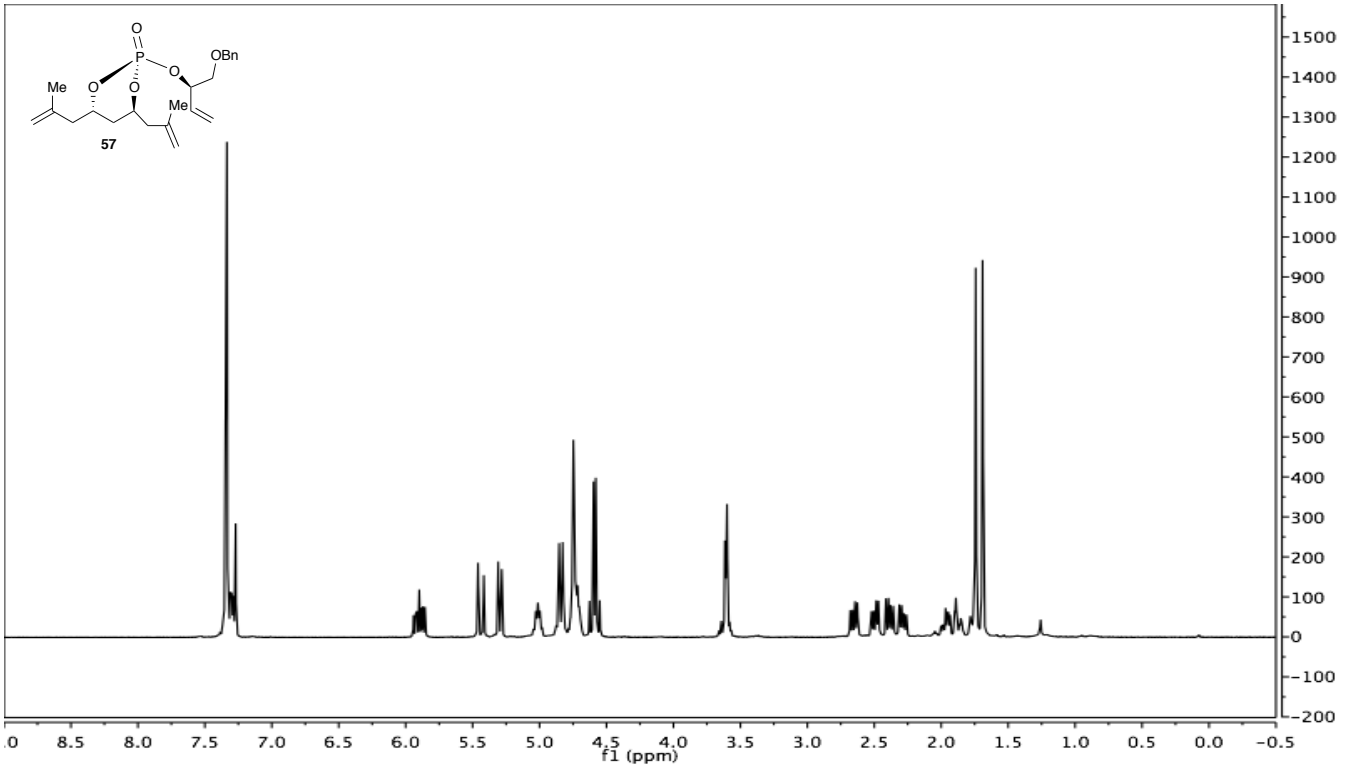
(4*S*,6*S*)-4,6-diallyl-2-(((*R*)-1-(benzyloxy)but-3-en-2-yl)oxy)-1,3,2-dioxaphosphinane 2-oxide (56):

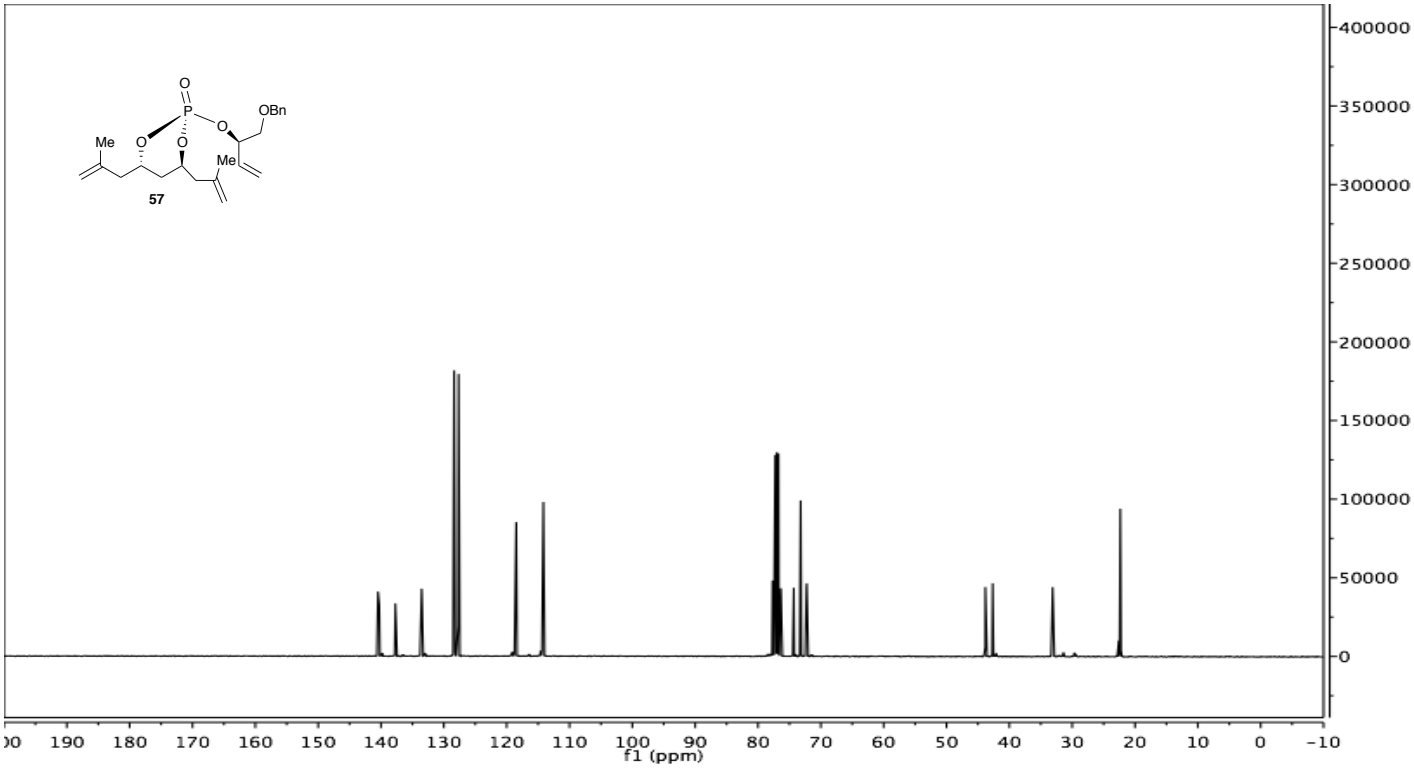


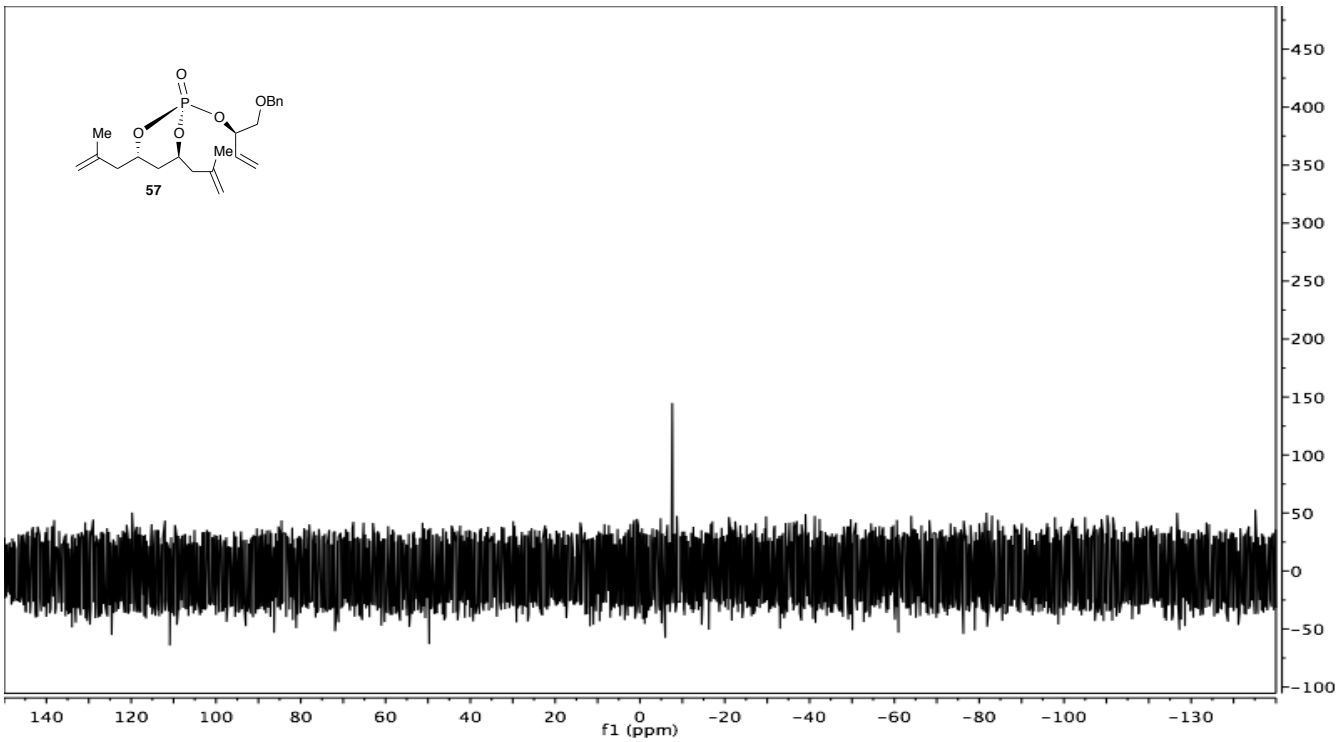

OBn
56
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
−10000
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


OBn
56
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −130
f1 (ppm)

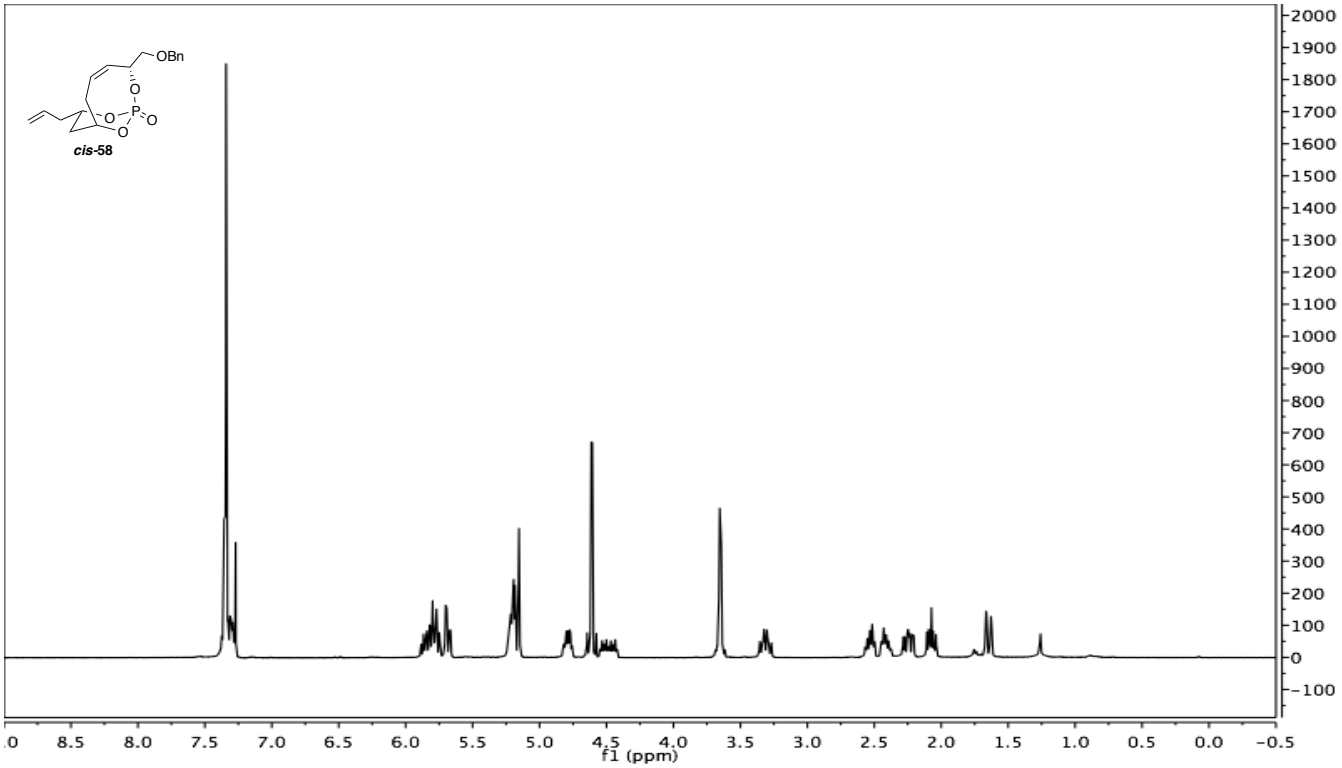
(4*S*,6*S*)-2-(((*R*)-1-(benzyloxy)but-3-en-2-yl)oxy)-4,6-bis(2-methylallyl)-1,3,2-dioxaphosphinane 2-oxide (57):

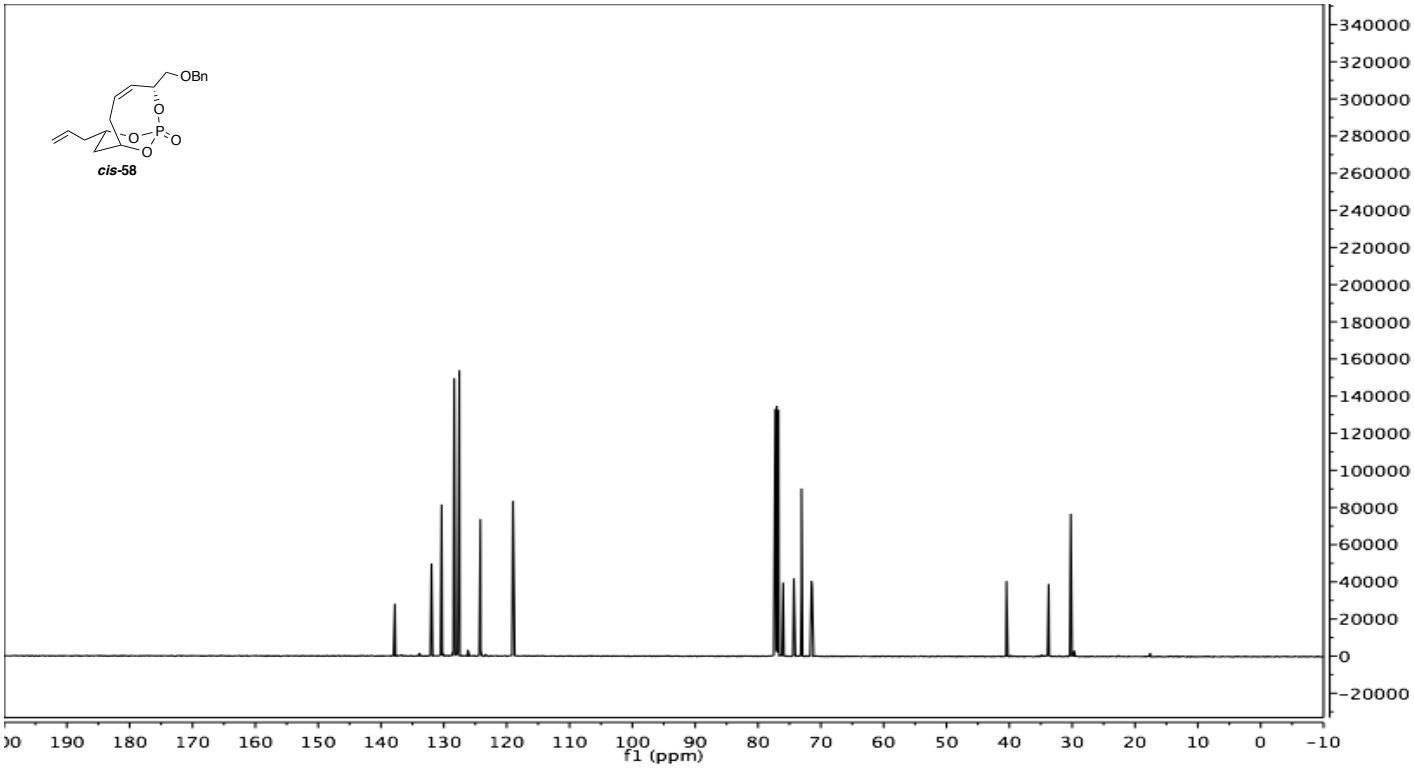


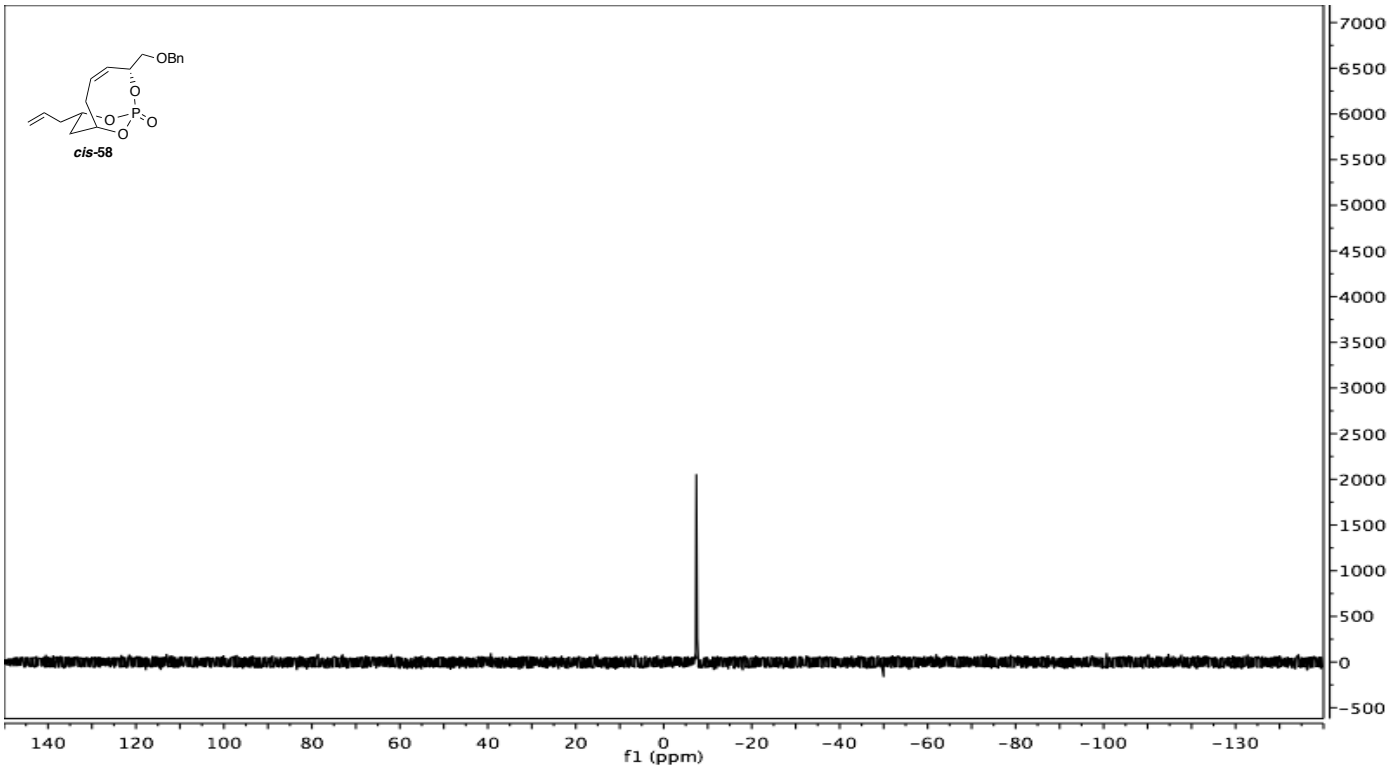




(1*R*,3*R*,7*S*,9*S*,*Z*)-9-allyl-3-((benzyloxy)methyl)-2,10,11-trioxa-1-phosphabicyclo[5.3.1]undec-4-ene 1-oxide (*cis*-58):




OBn
O
O
P
O
O
cis-58
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
−20000
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


OBn
O
O
P
O
O
cis-58
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −130
f1 (ppm)