

Electronic Supplementary Information for Catalytic Asymmetric Hydrophosphonylation of Ynones

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General Information: Infrared spectra were recorded on a JASCO FT/IR-300E spectrometer. ¹H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane (0.0 ppm) resonance as the internal standard. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sept = septet, m = multiplet, br = broad) and coupling constants (Hz). ¹³C NMR spectra were recorded on a JEOL JNM-ECS400 (101 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance (CDCl₃: 77.16 ppm). ³¹P NMR spectra were recorded on a JEOL JNM-ECS400 (162 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from H₃PO₄ (0.0 ppm) resonance as the external standard. Optical rotations were measured on a JASCO DIP-1000 polarimeter. The high resolution mass spectra were conducted on JEOL JMS-700 (MStation) (FAB) and a BRUKER DALTONICS microTOF focus-KR spectrometer (ESI-TOF). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF₂₅₄, 0.25 mm). Flash column chromatography was performed on silica gel 60 (spherical, 40-50 μm; Kanto Chemical Co., Inc.). Enantiomeric excesses were determined by HPLC analysis using chiral columns [ϕ 4.6 mm x 250 mm, DAICEL CHIRALPAK AD-H (ADH), CHIRALCEL OD-H (ODH), CHIRALPAK IA (IA), CHIRALPAK AS-H (ASH), or CHIRALCEL OJ-H (OJH)].

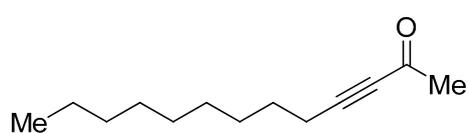
All reactions were carried out under an Argon (Ar) atmosphere in dried glassware. All substrates were purified by column chromatography, recrystallization, or distillation prior to use. Tetrahydrofuran (THF) was supplied from Kanto Chemical Co., Inc. as “Dehydrated solvent system”. Chiral aminophosphonium salts **1**¹ and ynones **3**² were prepared by following the literature procedure. Other simple chemicals were purchased and used as such.

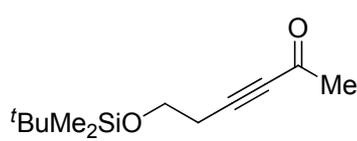
¹ D. Uraguchi, S. Sakaki and T. Ooi, *J. Am. Chem. Soc.*, 2007, **129**, 12392; D. Uraguchi, S. Sakaki, Y. Ueki, T. Ito and T. Ooi, *Heterocycles*, 2008, **76**, 1081.

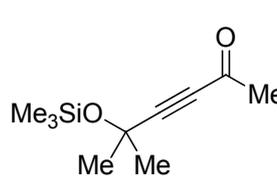
² L. Cao, J. Ding, M. Gao, Z. Wang, J. Li and A. Wu, *Org. Lett.*, 2009, **11**, 3810.

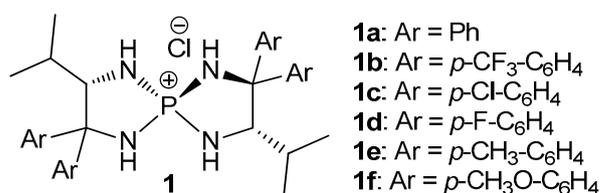
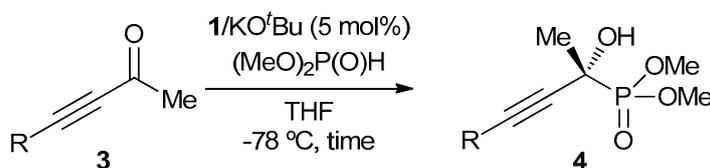
Experimental Section:

Characterization of Ynone:

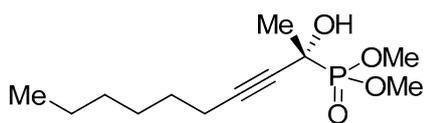
 **3c:** ^1H NMR (400 MHz, CDCl_3) δ 2.35 (2H, t, $J = 7.3$ Hz), 2.32 (3H, s), 1.57 (2H, quin, $J = 7.3$ Hz), 1.39 (2H, quin, $J = 7.3$ Hz), 1.27 (10H, br), 0.88 (3H, t, $J = 6.9$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 185.2, 94.4, 81.5, 32.9, 32.0, 29.5, 29.4, 29.2, 29.0, 27.8, 22.8, 19.1, 14.3; IR (liquid film) 2925, 2855, 2209, 1679, 1466, 1421, 1358, 1227, 960, 722 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{13}\text{H}_{23}\text{O}_1^+$ ($[\text{M}+\text{H}]^+$) 195.1749, Found 195.1752.

 **3g:** ^1H NMR (400 MHz, CDCl_3) δ 3.78 (2H, t, $J = 6.9$ Hz), 2.58 (2H, t, $J = 6.9$ Hz), 2.32 (3H, s), 0.90 (9H, s), 0.09 (6H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 184.9, 91.1, 82.2, 60.9, 32.9, 26.0, 23.5, 18.4, -5.2; IR (liquid film) 2929, 2857, 2213, 1681, 1471, 1360, 1227, 1110, 838, 778 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{12}\text{H}_{23}\text{O}_2\text{Si}_1^+$ ($[\text{M}+\text{H}]^+$) 227.1467, Found 227.1477.

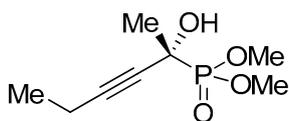
 **3h:** ^1H NMR (400 MHz, CDCl_3) δ 2.35 (3H, s), 1.53 (6H, s), 0.21 (9H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 184.4, 96.0, 82.6, 66.5, 32.6, 32.3, 1.9; IR (liquid film) 2987, 2213, 1683, 1418, 1361, 1250, 1167, 1038, 843, 756 cm^{-1} ; HRMS (ESI-TOF) Calcd for $\text{C}_{10}\text{H}_{18}\text{Na}_1\text{O}_2\text{Si}_1^+$ ($[\text{M}-\text{X}]^+$) 221.0974, Found 221.0982.



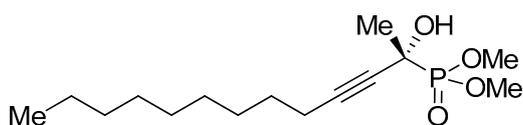
General Procedure for Chiral Tetraaminophosphonium Salt-Mediated Asymmetric Hydrophosphonylation of Ynones: To a dried test tube was weighted phosphonium salt **1** (0.055 equiv, 11 μmol) under Ar atmosphere and THF (2 mL) was introduced. Then, a 1.0 M THF solution of potassium *tert*-butoxide (10 μL , 0.050 equiv, 10 μmol) was added to the suspension at -78 $^\circ\text{C}$ and the resulting mixture was stirred for 30 min. Ynone **3** (1.0 equiv, 0.2 mmol) and dimethyl phosphite (36.7 μL , 2.0 equiv, 0.4 mmol) were introduced dropwise slowly and the stirring was continued for the reaction time given in the Tables of the manuscript. A solution of trifluoroacetic acid in toluene (0.5 M, 100 μL) was added to the reaction mixture and it was poured into ice-cooled water. The aqueous phase was extracted with ethyl acetate three times. The combined organic extracts were dried over Na_2SO_4 and filtered. All volatiles were removed by evaporation and the purification of the residue by column chromatography on silica gel gave the corresponding α -tetrasubstituted α -hydroxy phosphonate **4**, whose enantiomeric excess was determined by HPLC analysis.



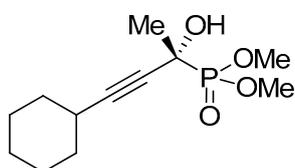
4a: HPLC ODH, hexane (H)/2-propanol (IPA) = 100:1, flow rate = 0.5 mL/min, $\lambda = 210$ nm, 30.2 min (major isomer), 33.2 min (minor isomer); ^1H NMR (400 MHz, CDCl_3) δ 3.89 (3H, d, $J_{P-H} = 10.1$ Hz), 3.88 (3H, d, $J_{P-H} = 10.5$ Hz), 3.5 (1H, br), 2.24 (1H, t, $J = 7.3$ Hz), 2.23 (1H, t, $J = 7.3$ Hz), 1.66 (3H, d, $J_{P-H} = 15.6$ Hz), 1.52 (2H, quin, $J = 7.3$ Hz), 1.41-1.34 (2H, m), 1.33-1.24 (4H, m), 0.89 (3H, t, $J = 7.1$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 88.2 (d, $J_{P-C} = 8.7$ Hz), 78.5, 65.9 (d, $J_{P-C} = 176.1$ Hz), 54.7₃ (d, $J_{P-C} = 6.8$ Hz), 54.6₆ (d, $J_{P-C} = 6.8$ Hz), 31.4, 28.6, 28.4 (d, $J_{P-C} = 2.9$ Hz), 25.4, 22.6, 19.0 (d, $J_{P-C} = 1.9$ Hz), 14.1; ^{31}P NMR (162 MHz, CDCl_3) δ 23.3; IR (liquid film): 3284, 2932, 2857, 2242, 1455, 1365, 1238, 1185, 1034, 834 cm^{-1} ; HRMS (ESI-TOF) Calcd for $\text{C}_{12}\text{H}_{23}\text{Na}_1\text{O}_4\text{P}_1^+$ ($[\text{M}+\text{Na}]^+$) 285.1226, Found 285.1240; $[\alpha]_D^{25}$ 25.0° ($c = 0.58$, MeOH).



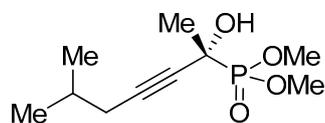
4b: HPLC OJH, H/IPA = 50:1, flow rate = 0.5 mL/min, $\lambda = 210$ nm, 20.2 min (major isomer), 23.2 min (minor isomer); ^1H NMR (400 MHz, CDCl_3) δ 3.89 (6H, d, $J_{P-H} = 10.1$ Hz), 3.23 (1H, br), 2.27 (1H, q, $J = 7.5$ Hz), 2.26 (1H, q, $J = 7.5$ Hz), 1.65 (3H, d, $J_{P-H} = 15.6$ Hz), 1.15 (3H, t, $J = 7.5$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 89.6 (d, $J_{P-C} = 8.7$ Hz), 77.8, 65.9 (d, $J_{P-C} = 176.1$ Hz), 54.8 (d, $J_{P-C} = 7.7$ Hz), 54.7 (d, $J_{P-C} = 6.8$ Hz), 25.3, 13.6, 12.7; ^{31}P NMR (162 MHz, CDCl_3) δ 23.3; IR (liquid film) 3290, 2958, 2243, 1645, 1456, 1366, 1237, 1031, 835, 754 cm^{-1} ; HRMS (ESI-TOF) Calcd for $\text{C}_8\text{H}_{15}\text{Na}_1\text{O}_4\text{P}_1^+$ ($[\text{M}+\text{Na}]^+$) 229.0600, Found 229.0595; $[\alpha]_D^{25}$ 26.2° ($c = 0.75$, MeOH).



4c: HPLC ODH, H/IPA = 100:1, flow rate = 0.5 mL/min, $\lambda = 210$ nm, 26.5 min (major isomer), 30.8 min (minor isomer); ^1H NMR (400 MHz, CDCl_3) δ 3.89 (3H, d, $J_{P-H} = 10.1$ Hz), 3.88 (3H, d, $J_{P-H} = 10.5$ Hz), 2.51 (1H, d, $J_{P-H} = 4.1$ Hz), 2.25 (1H, d, $J = 7.3$ Hz), 2.24 (1H, d, $J = 7.1$ Hz), 1.65 (3H, d, $J_{P-H} = 15.6$ Hz), 1.53 (1H, q, $J = 7.3$ Hz), 1.51 (1H, q, $J = 7.3$ Hz), 1.37 (2H, quin, $J = 7.3$ Hz), 1.32-1.23 (10H, br), 0.88 (3H, t, $J = 6.9$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 88.0 (d, $J_{P-C} = 9.7$ Hz), 78.6, 65.8 (d, $J_{P-C} = 175.1$ Hz), 54.7 (d, $J_{P-C} = 7.7$ Hz), 54.6 (d, $J_{P-C} = 6.8$ Hz), 31.9, 29.5, 29.3, 29.2, 28.9, 28.5, 25.4, 22.7, 18.9, 14.2; ^{31}P NMR (162 MHz, CDCl_3) δ 23.2; IR (liquid film) 3282, 2926, 2854, 2242, 1462, 1238, 1185, 1033, 834, 764 cm^{-1} ; HRMS (ESI-TOF) Calcd for $\text{C}_{15}\text{H}_{29}\text{Na}_1\text{O}_4\text{P}_1^+$ ($[\text{M}+\text{Na}]^+$) 327.1696, Found 327.1683; $[\alpha]_D^{25}$ 21.1° ($c = 1.79$, MeOH).

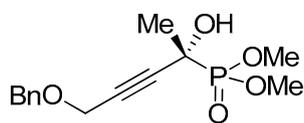


4d: HPLC IA, H/IPA = 100:1, flow rate = 0.5 mL/min, $\lambda = 210$ nm, 58.0 min (minor isomer), 61.2 min (major isomer); ^1H NMR (400 MHz, CDCl_3) δ 3.89 (3H, d, $J_{P-H} = 10.0$ Hz), 3.88 (3H, d, $J_{P-H} = 10.1$ Hz), 3.55 (1H, br), 2.48-2.38 (1H, m), 1.84-1.75 (2H, m), 1.74-1.65 (2H, m), 1.65 (3H, d, $J = 15.1$ Hz), 1.56-1.38 (3H, m), 1.37-1.24 (3H, m); ^{13}C NMR (101 MHz, CDCl_3) δ 92.0 (d, $J_{P-C} = 9.7$ Hz), 78.6, 65.9 (d, $J = 174.6$ Hz), 54.8 (d, $J_{P-C} = 8.7$ Hz), 54.7 (d, $J_{P-C} = 7.7$ Hz), 32.4, 29.1, 25.9, 25.5, 24.8, two carbons were not found due to overlapping; ^{31}P NMR (162 MHz, CDCl_3) δ 23.3; IR (liquid film) 3283, 2931, 2853, 2233, 1448, 1237, 1185, 1033, 835, 757 cm^{-1} ; HRMS (ESI-TOF) Calcd for $\text{C}_{12}\text{H}_{21}\text{Na}_1\text{O}_4\text{P}_1^+$ ($[\text{M}+\text{Na}]^+$) 283.1070, Found 283.1083; $[\alpha]_D^{25}$ 20.0° ($c = 3.28$, MeOH).

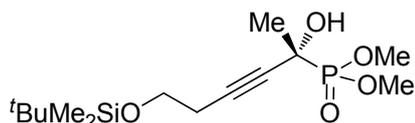


4e: HPLC ADH, H/IPA = 20:1, flow rate = 0.5 mL/min, $\lambda = 210$ nm, 15.1 min (minor isomer), 16.0 min (major isomer); ^1H NMR (400 MHz, CDCl_3) δ 3.89 (3H, d, $J_{P-H} = 10.5$ Hz), 3.88 (3H, d, $J_{P-H} = 10.1$ Hz), 2.55 (1H, br), 2.15 (1H, d, $J = 6.6$ Hz),

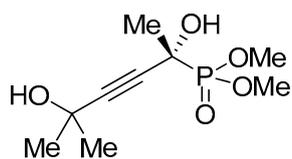
2.14 (1H, d, $J = 6.6$ Hz), 1.83 (1H, sept, $J = 6.6$ Hz), 1.66 (3H, d, $J_{P-H} = 15.6$ Hz), 0.98 (6H, d, $J = 6.6$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 87.1 (d, $J_{P-C} = 8.7$ Hz), 79.5, 66.0 (d, $J_{P-C} = 176.1$ Hz), 54.7 (d, $J_{P-C} = 6.8$ Hz), 54.6 (d, $J_{P-C} = 6.8$ Hz), 28.0, 25.4, 22.0, two carbons were not found probably due to overlapping; ^{31}P NMR (162 MHz, CDCl_3) δ 23.2; IR (liquid film) 3288, 2958, 2242, 1464, 1368, 1238, 1186, 1034, 832, 762 cm^{-1} ; HRMS (ESI-TOF) Calcd for $\text{C}_{10}\text{H}_{19}\text{Na}_1\text{O}_4\text{P}_1^+$ ($[\text{M}+\text{Na}]^+$) 257.0913, Found 257.0910; $[\alpha]_D^{25}$ 23.6° ($c = 1.98$, MeOH).



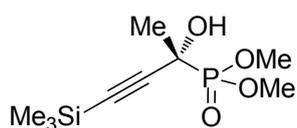
4f: HPLC OJH, H/IPA = 10:1, flow rate = 0.5 mL/min, $\lambda = 210$ nm, 31.4 min (major isomer), 33.2 min (minor isomer); ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.33 (4H, m), 7.33-7.27 (1H, m), 4.60 (2H, s), 4.22 (2H, d, $J_{P-H} = 4.1$ Hz), 3.89 (3H, d, $J_{P-H} = 10.5$ Hz), 3.88 (3H, d, $J_{P-H} = 10.6$ Hz), 1.70 (3H, d, $J_{P-H} = 15.6$ Hz), O-H proton was not found probably due to broadening; ^{13}C NMR (101 MHz, CDCl_3) δ 137.3, 128.6, 128.3, 128.1, 84.9, 83.2 (d, $J_{P-C} = 9.7$ Hz), 71.6, 65.8 (d, $J_{P-C} = 176.1$ Hz), 57.4, 54.9 (d, $J_{P-C} = 7.7$ Hz), 54.8 (d, $J_{P-C} = 7.7$ Hz), 25.1; ^{31}P NMR (162 MHz, CDCl_3) δ 22.9; IR (liquid film) 3270, 2957, 2855, 1714, 1454, 1355, 1235, 1034, 838, 753 cm^{-1} ; HRMS (ESI-TOF) Calcd for $\text{C}_{14}\text{H}_{19}\text{Na}_1\text{O}_5\text{P}_1^+$ ($[\text{M}+\text{Na}]^+$) 321.0862, Found 321.0856; $[\alpha]_D^{25}$ 20.3° ($c = 1.04$, MeOH).



4g: HPLC ASH, H/IPA = 10:1, flow rate = 0.5 mL/min, $\lambda = 210$ nm, 9.1 min (minor isomer), 11.3 min (major isomer); ^1H NMR (400 MHz, CDCl_3) δ 3.88 (3H, d, $J_{P-H} = 10.5$ Hz), 3.87 (3H, d, $J_{P-H} = 10.1$ Hz), 3.72 (2H, t, $J = 7.1$ Hz), 2.46 (2H, td, $J = 7.1$ Hz, $J_{P-H} = 4.6$ Hz), 1.65 (3H, d, $J_{P-H} = 15.6$ Hz), 0.89 (9H, s), 0.07 (6H, s), O-H proton was not found probably due to broadening; ^{13}C NMR (101 MHz, CDCl_3) δ 84.9 (d, $J_{P-C} = 9.7$ Hz), 79.6, 65.8 (d, $J_{P-C} = 175.1$ Hz), 61.6, 54.8 (d, $J_{P-C} = 7.7$ Hz), 54.7 (d, $J_{P-C} = 7.7$ Hz), 25.9, 25.4, 23.3, 18.4, -5.2; ^{31}P NMR (162 MHz, CDCl_3) δ 23.2; IR (KBr) 3278, 2957, 2240, 1471, 1360, 1240, 1101, 1028, 836, 773 cm^{-1} ; HRMS (ESI-TOF) Calcd for $\text{C}_{14}\text{H}_{29}\text{Na}_1\text{O}_5\text{P}_1\text{Si}_1^+$ ($[\text{M}+\text{Na}]^+$) 359.1414, Found 359.1413; $[\alpha]_D^{25}$ 19.8° ($c = 1.23$, MeOH).



4h: HPLC ASH, H/IPA = 10:1, flow rate = 0.5 mL/min, $\lambda = 210$ nm, 10.3 min (minor isomer), 11.3 min (major isomer); ^1H NMR (400 MHz, CDCl_3) δ 5.09 (1H, brd, $J_{P-H} = 1.4$ Hz), 4.62 (1H, br), 3.90 (6H, d, $J_{P-H} = 10.1$ Hz), 1.61 (3H, d, $J_{P-H} = 15.1$ Hz), 1.53 (3H, s), 1.50 (3H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 92.7 (d, $J_{P-C} = 9.7$ Hz), 80.2, 65.3 (d, $J_{P-C} = 176.1$ Hz), 64.7, 54.9₉ (d, $J_{P-C} = 7.7$ Hz), 54.9₆ (d, $J_{P-C} = 7.7$ Hz), 31.3, 30.8, 24.7; ^{31}P NMR (162 MHz, CDCl_3) δ 23.5; IR (liquid film) 3305, 2983, 2243, 1647, 1455, 1365, 1236, 1171, 1035, 787 cm^{-1} ; HRMS (ESI-TOF) Calcd for $\text{C}_9\text{H}_{17}\text{Na}_1\text{O}_5\text{P}_1^+$ ($[\text{M}+\text{Na}]^+$) 259.0706, Found 259.0696; $[\alpha]_D^{25}$ 21.0° ($c = 1.73$, MeOH).



4i: HPLC ADH, H/IPA = 50:1, flow rate = 0.5 mL/min, $\lambda = 210$ nm, 15.3 min (minor isomer), 16.6 min (major isomer); ^1H NMR (400 MHz, CDCl_3) δ 3.90 (3H, d, $J_{P-H} = 10.6$ Hz), 3.88 (3H, d, $J_{P-H} = 10.5$ Hz), 3.62 (1H, br), 1.67 (3H, d, $J = 15.6$ Hz), 0.18 (9H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 103.4, 92.2 (d, $J_{P-C} = 7.7$ Hz), 66.1 (d, $J_{P-C} = 174.2$ Hz), 55.1 (d, $J_{P-C} = 7.7$ Hz), 54.9 (d, $J_{P-C} = 7.7$ Hz), 25.2, -0.2; ^{31}P NMR (162 MHz, CDCl_3) δ 22.3; IR (KBr) 3287, 2963, 2160, 1252, 1238, 1160, 1054, 1028, 841, 783 cm^{-1} ; HRMS (ESI-TOF) Calcd for $\text{C}_9\text{H}_{19}\text{Na}_1\text{O}_4\text{P}_1\text{Si}_1^+$ ($[\text{M}+\text{Na}]^+$) 273.0682, Found 273.0688; $[\alpha]_D^{25}$ 21.4° ($c = 1.03$, MeOH).

Crystallographic Structure Determination:

Recrystallization of 4i: 4i was recrystallized from hexane at $-15\text{ }^{\circ}\text{C}$.

The single crystal thus obtained was mounted on CryoLoop. Data of X-ray diffraction were collected at 153 K on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073\text{ \AA}$). An absorption correction was made using SADABS. The structure was solved by direct methods and Fourier syntheses, and refined by full-matrix least squares on F^2 by using SHELXTL.³ All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in calculated positions and isotropic thermal parameters refined. The crystallographic data were summarized in the following table.

Table S1. Crystal Data and Structure Refinement for 4i.

Empirical formula	C ₉ H ₁₉ O ₄ P ₁ Si ₁	
Formula weight	250.30	
Temperature	153(2) K	
Wavelength	0.71073 \AA	
Crystal system	Monoclinic	
Space group	P2 ₁	
Unit cell dimensions	a = 9.5228(13) \AA	$\alpha = 90^{\circ}$.
	b = 7.4316(11) \AA	$\beta = 103.092(3)^{\circ}$.
	c = 9.7945(14) \AA	$\gamma = 90^{\circ}$.
Volume	675.14(17) \AA^3	
Z	2	
Density (calculated)	1.231 Mg/m ³	
Absorption coefficient	0.286 mm ⁻¹	
F(000)	268	
Crystal size	0.50 x 0.10 x 0.10 mm ³	
Theta range for data collection	2.13 to 28.29 $^{\circ}$.	
Index ranges	-7 \leq h \leq 12, -8 \leq k \leq 9, -13 \leq l \leq 11	
Reflections collected	5057	
Independent reflections	3033 [R _{int} = 0.0248]	
Completeness to theta = 28.29 $^{\circ}$	99.8%	
Absorption correction	Empirical	
Max. and min. transmission	0.9720 and 0.8702	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3033 / 1 / 143	
Goodness-of-fit on F^2	1.070	
Final R indices [$I > 2\sigma(I)$]	R ₁ = 0.0388, wR ₂ = 0.0968	
R indices (all data)	R ₁ = 0.0412, wR ₂ = 0.0990	
Absolute structure parameter	0.17(10)	
Largest diff. peak and hole	0.605 and -0.326 e. \AA^{-3}	

³ Sheldrick, G. M. SHELXTL 5.1, Bruker AXS Inc., Madison, Wisconsin, 1997.

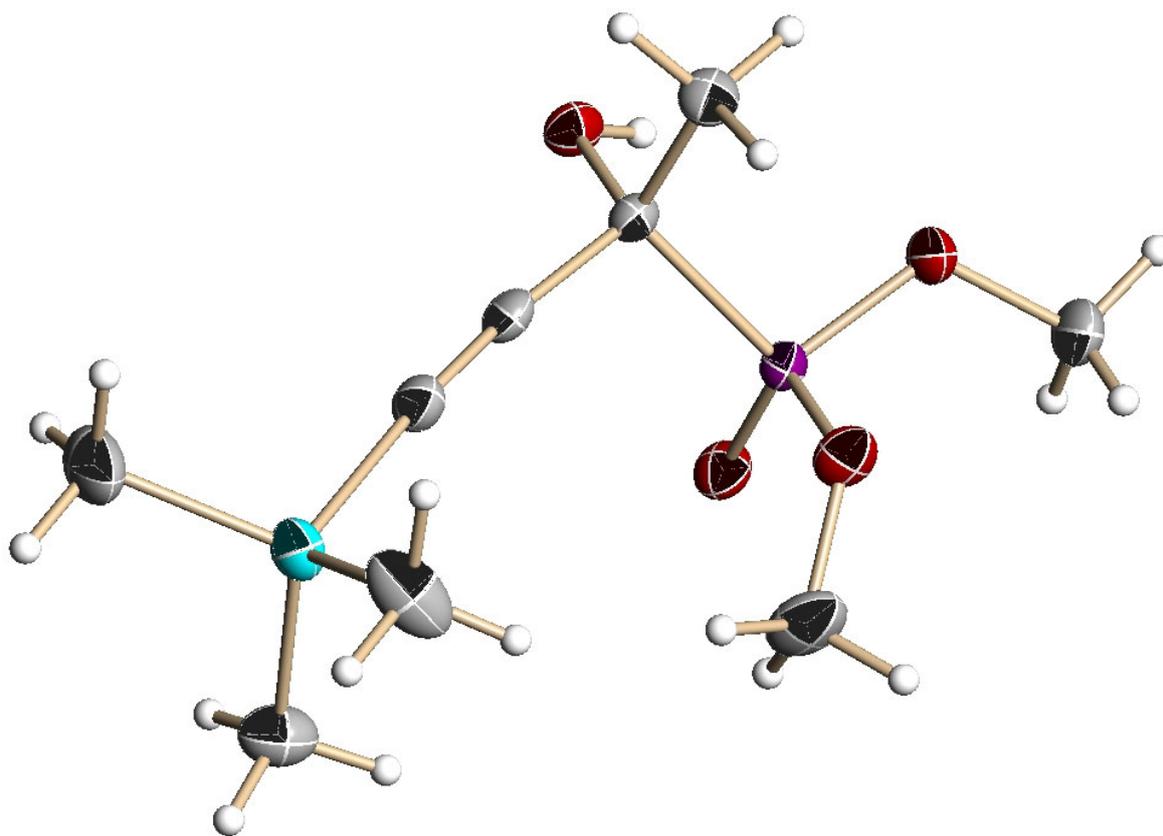
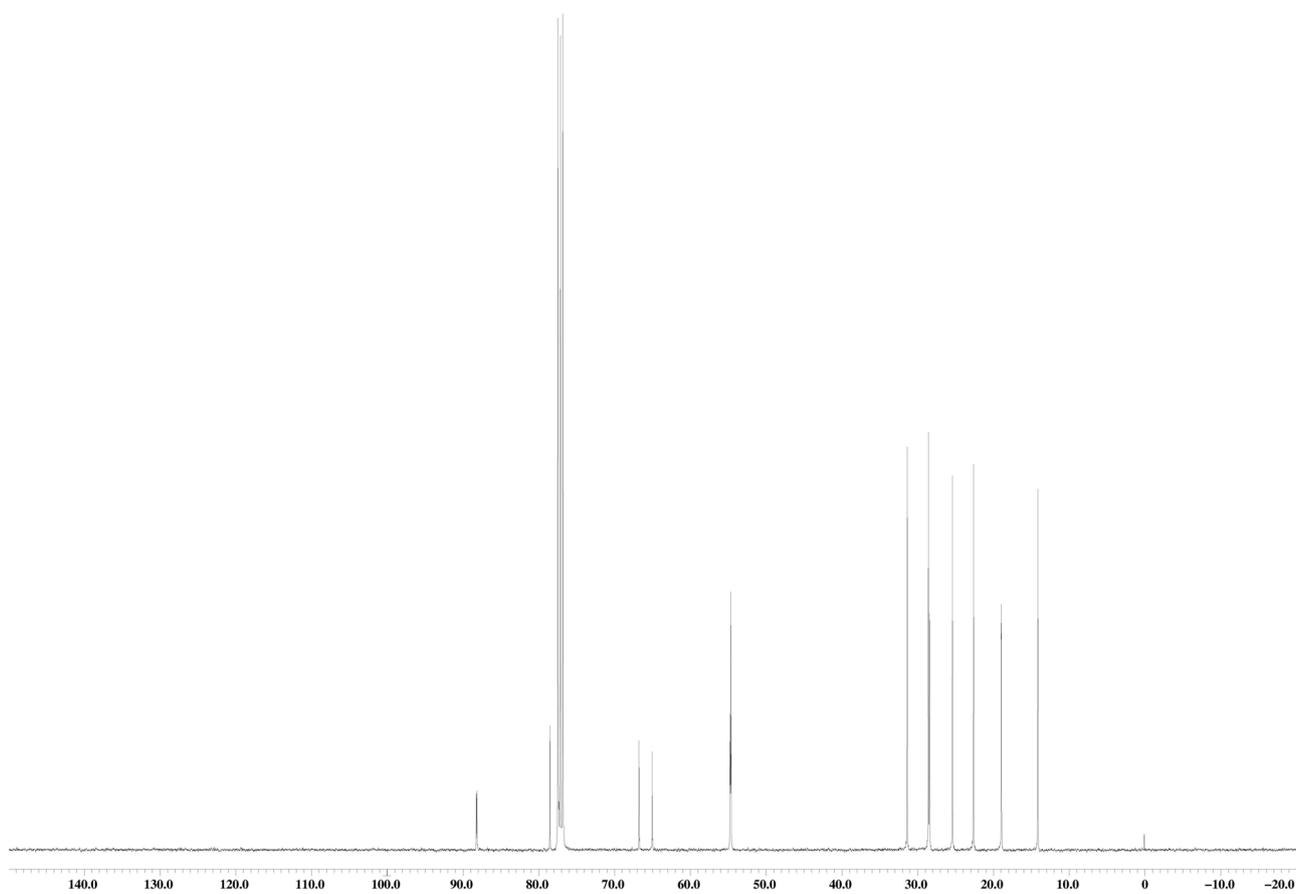
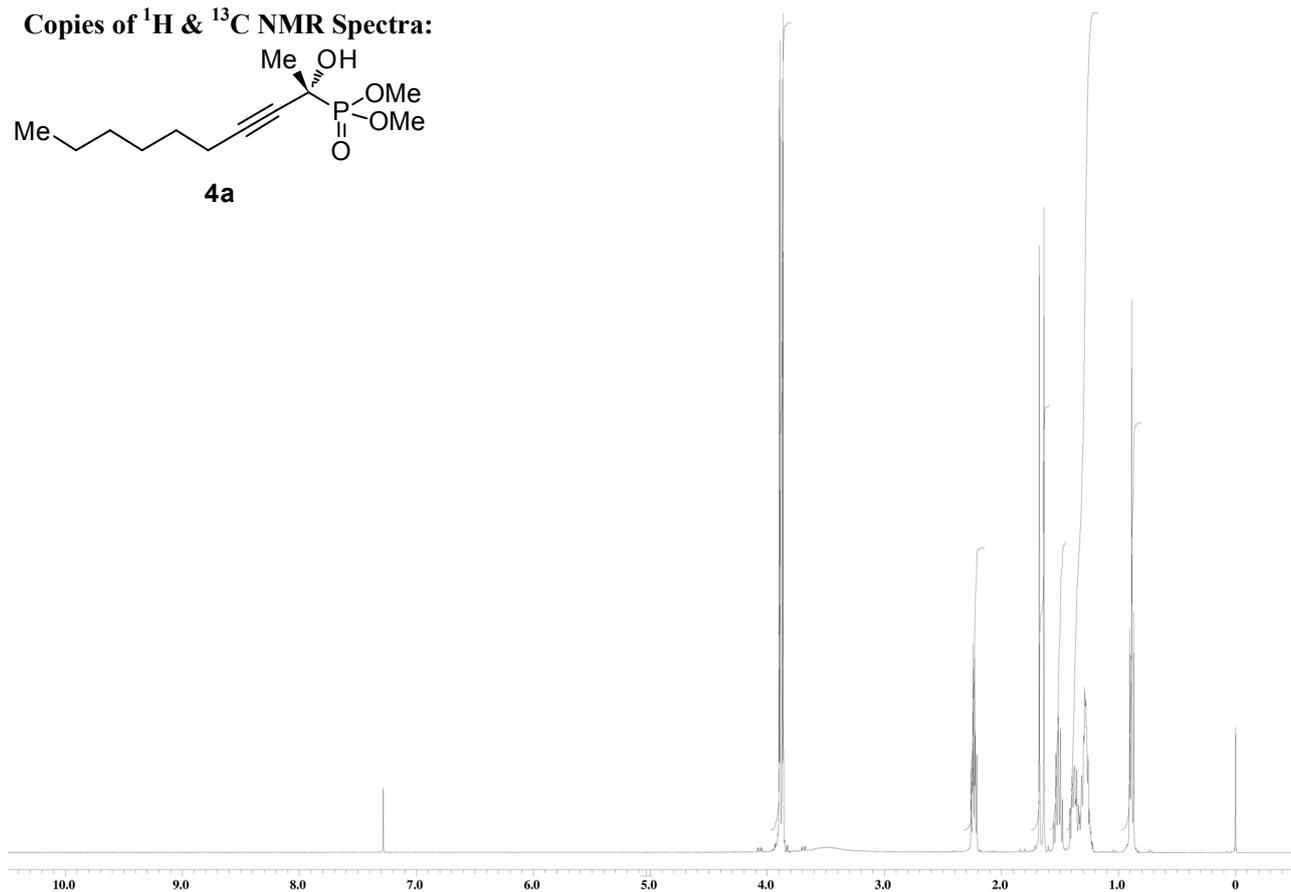
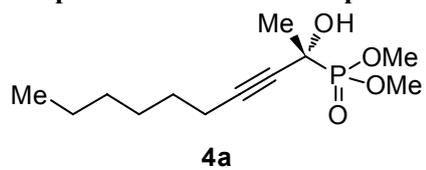
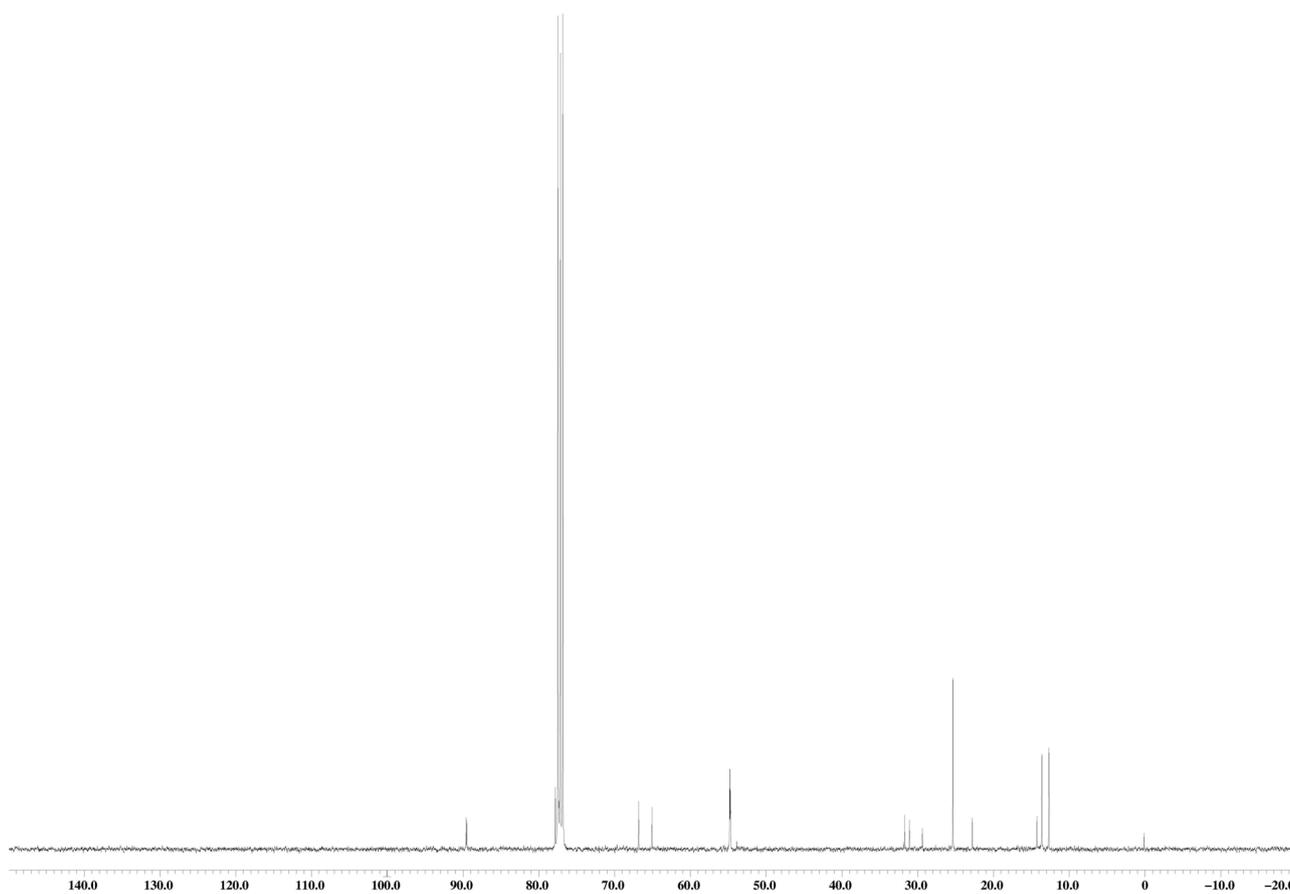
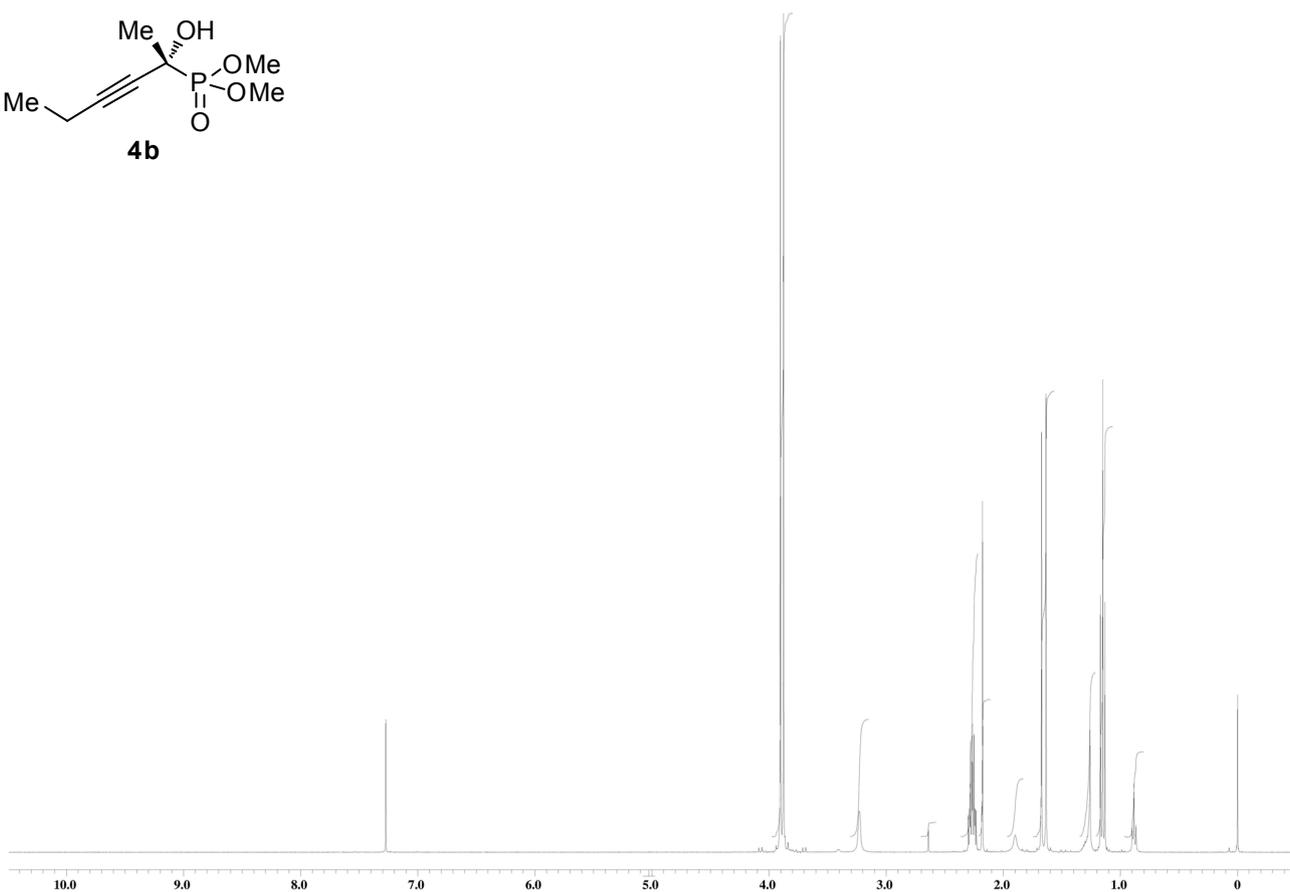
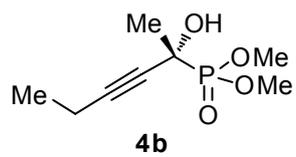
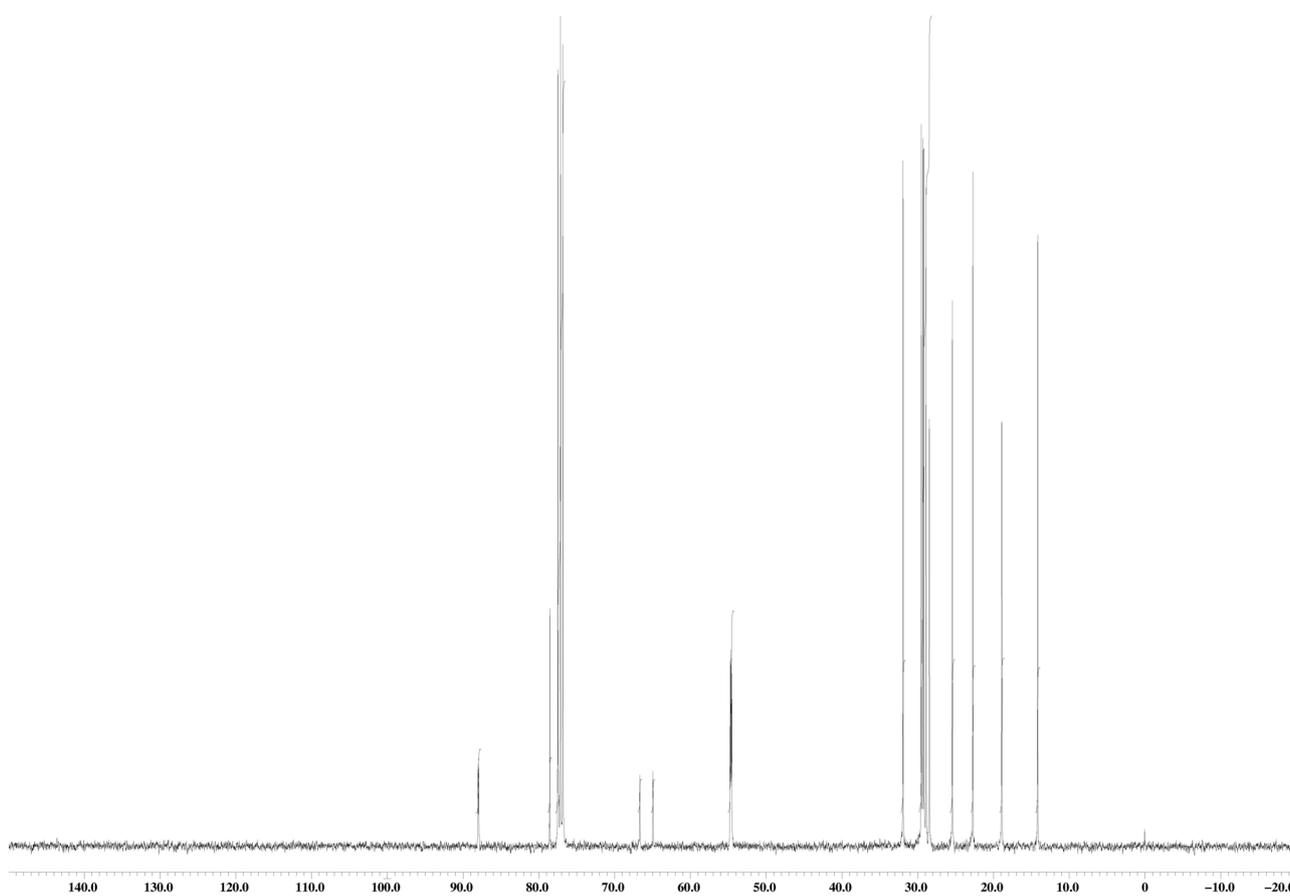
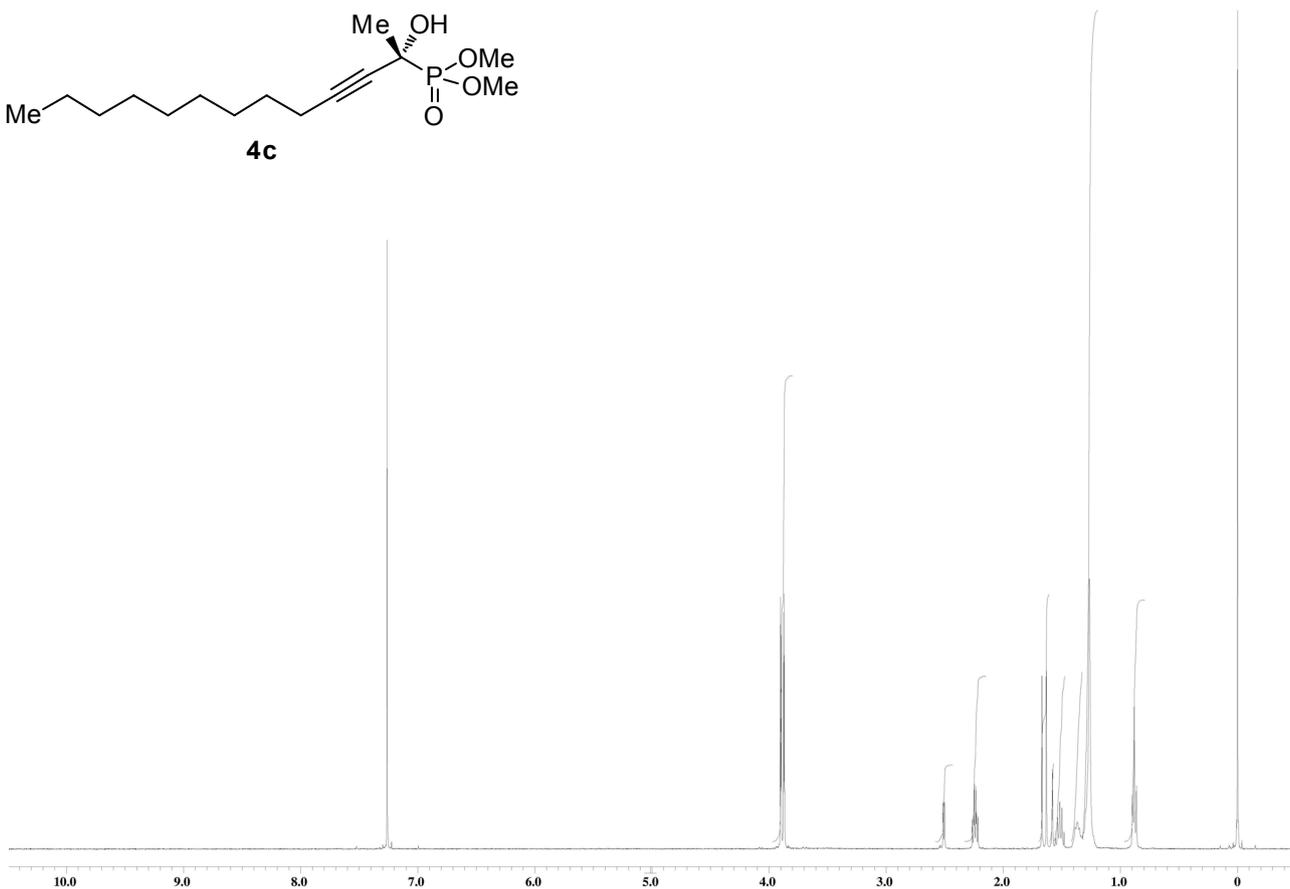
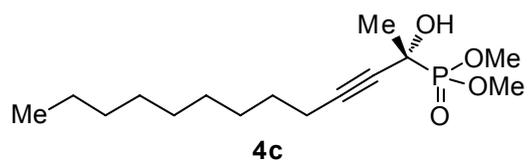


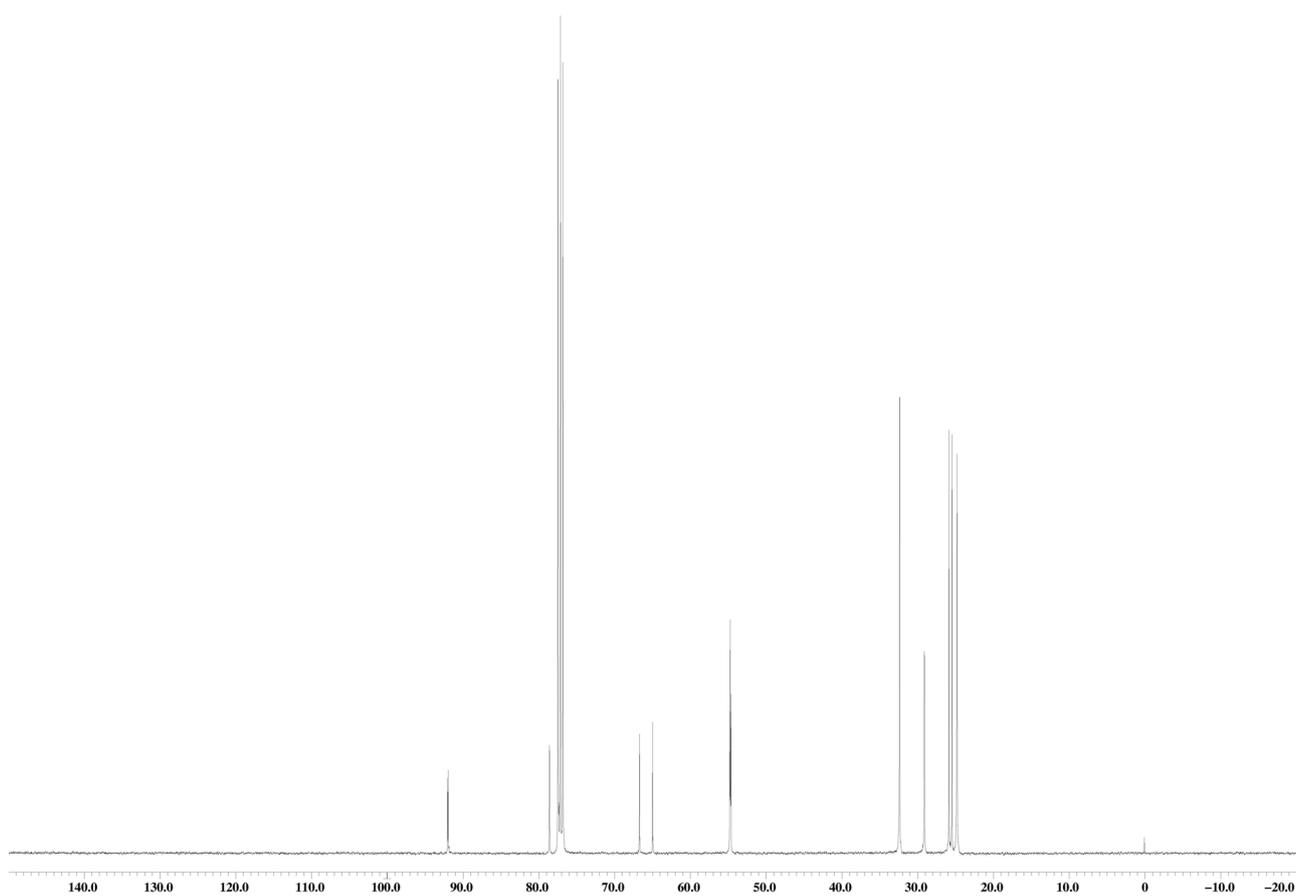
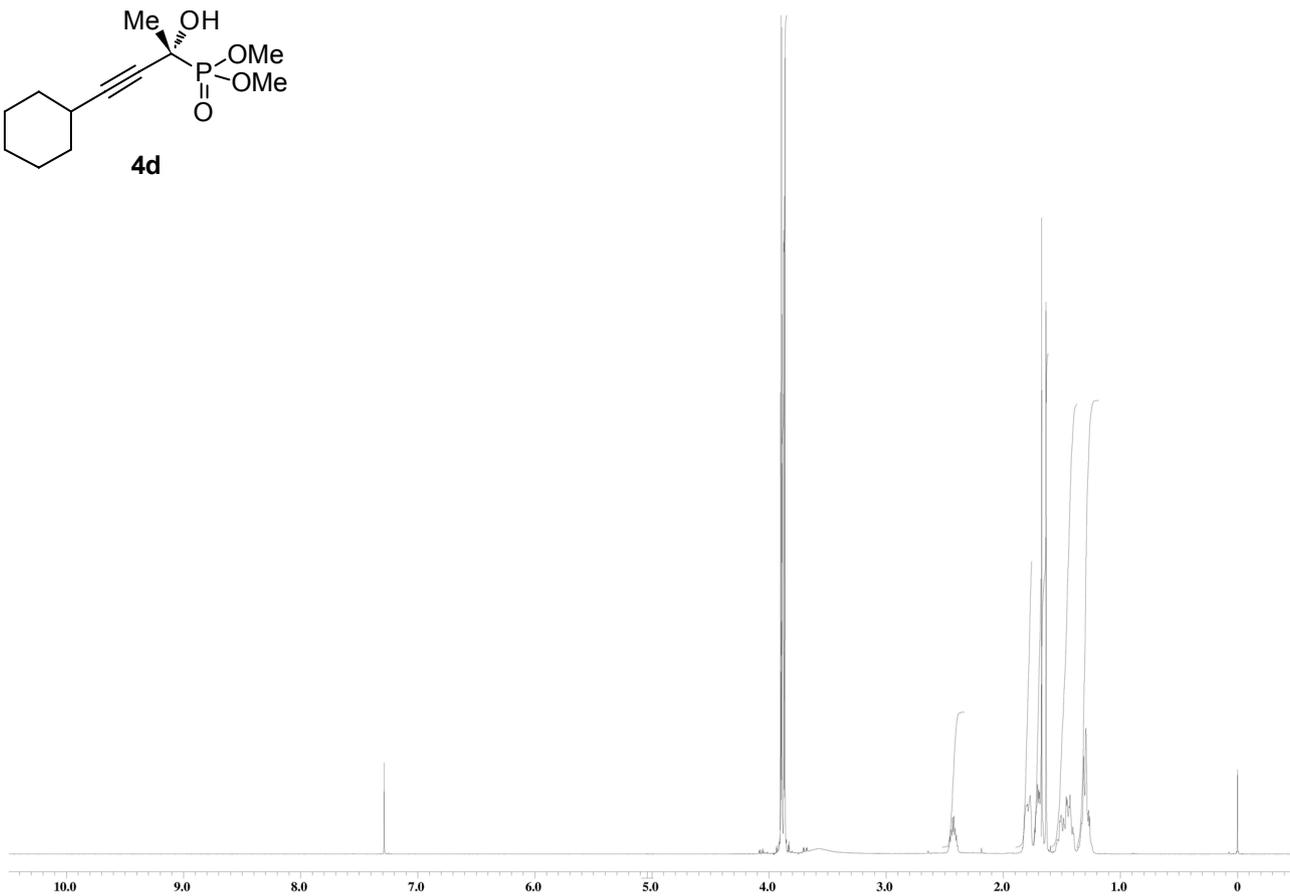
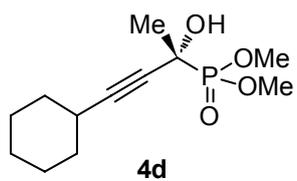
Figure S1. Molecular structure of **4i**. Purple = phosphorus, red = oxygen, light blue = silicon, black = carbon. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level.

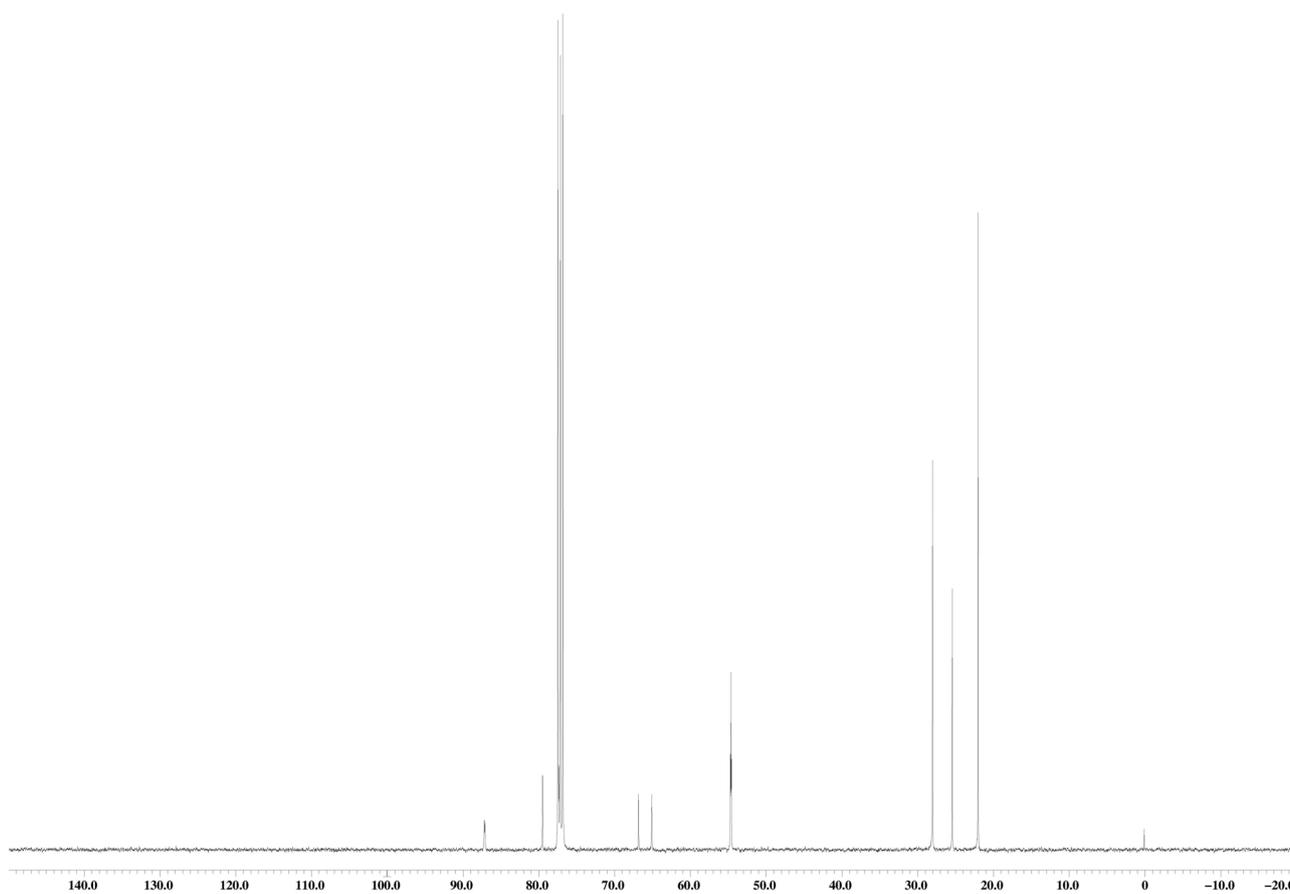
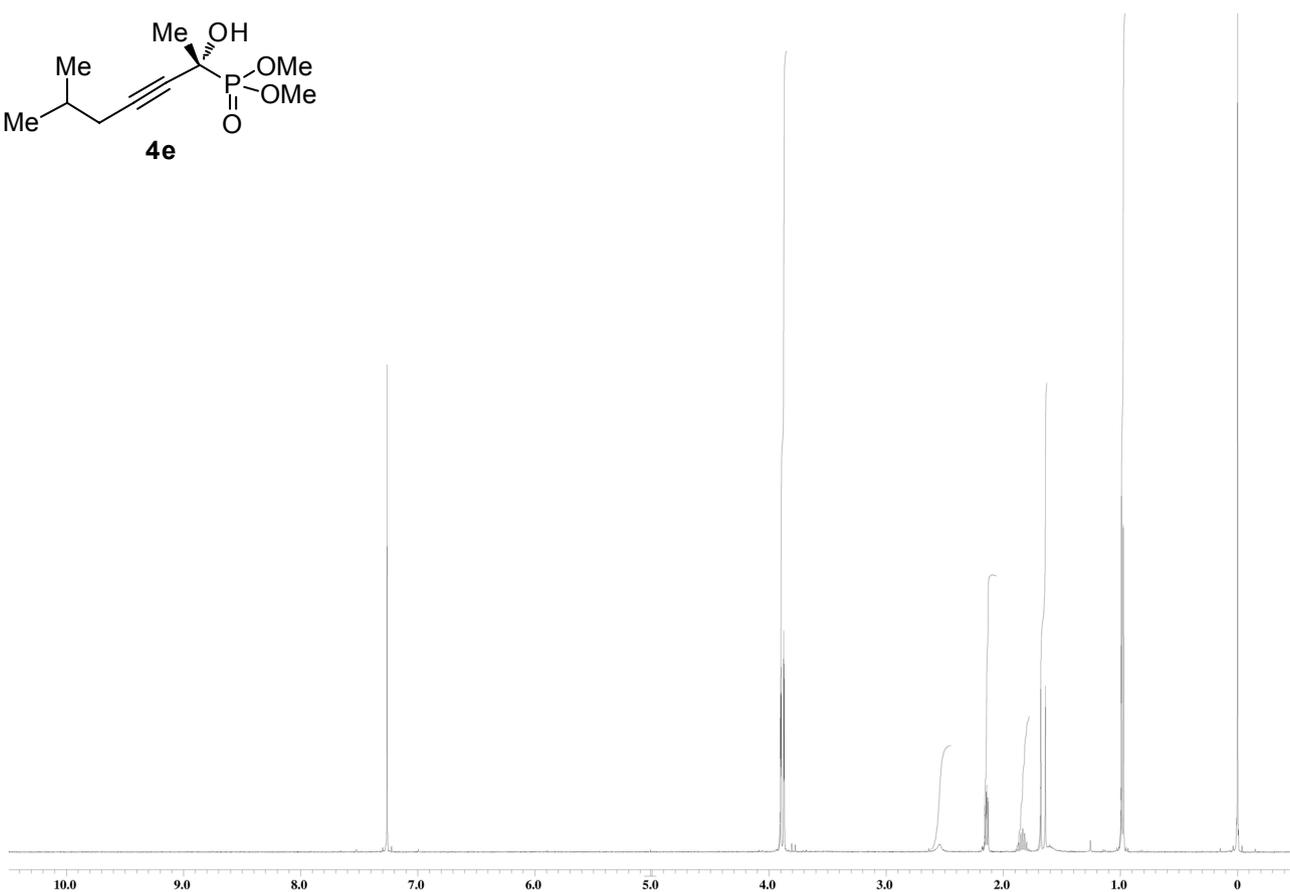
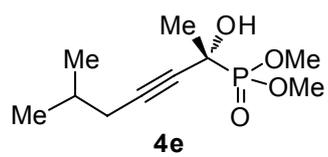
Copies of ^1H & ^{13}C NMR Spectra:

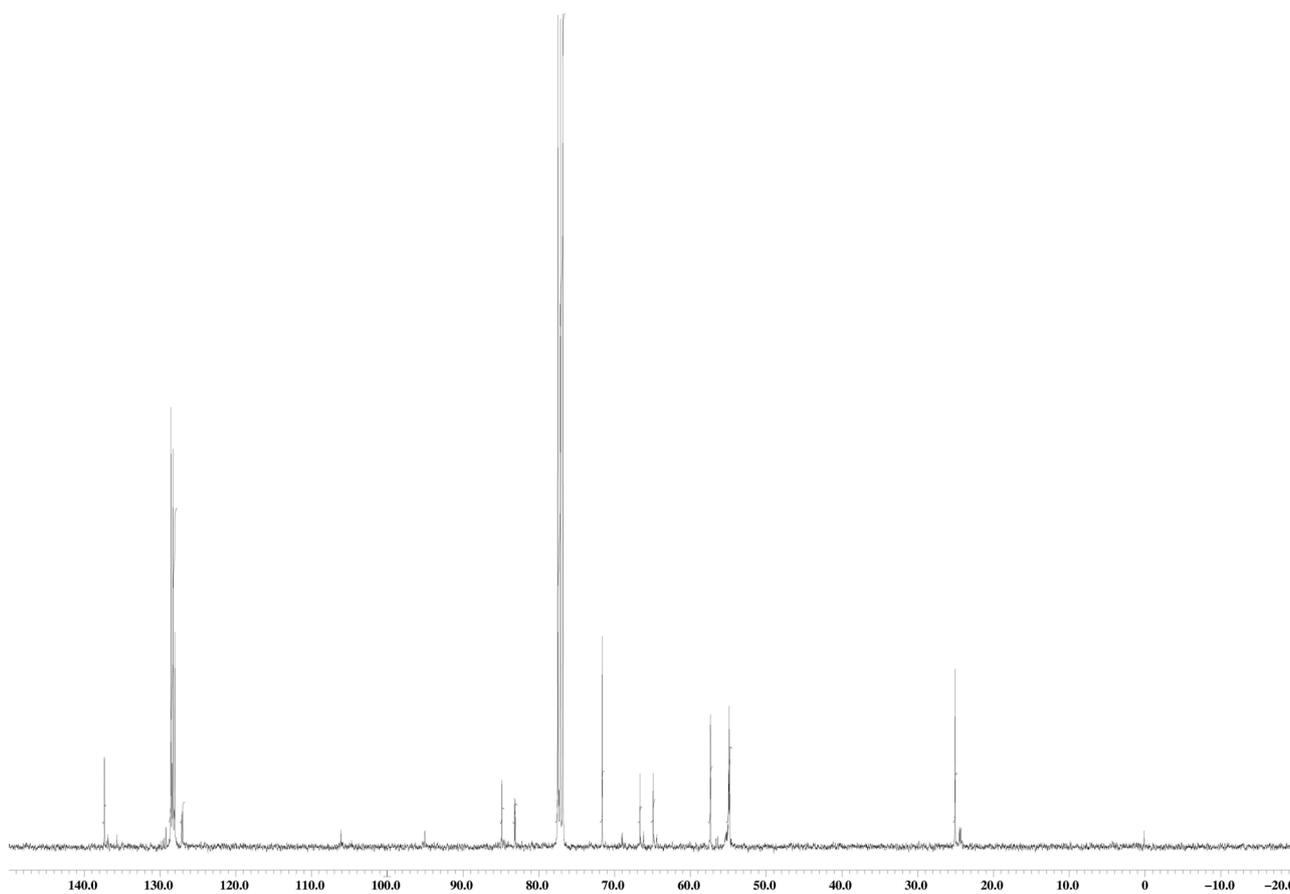
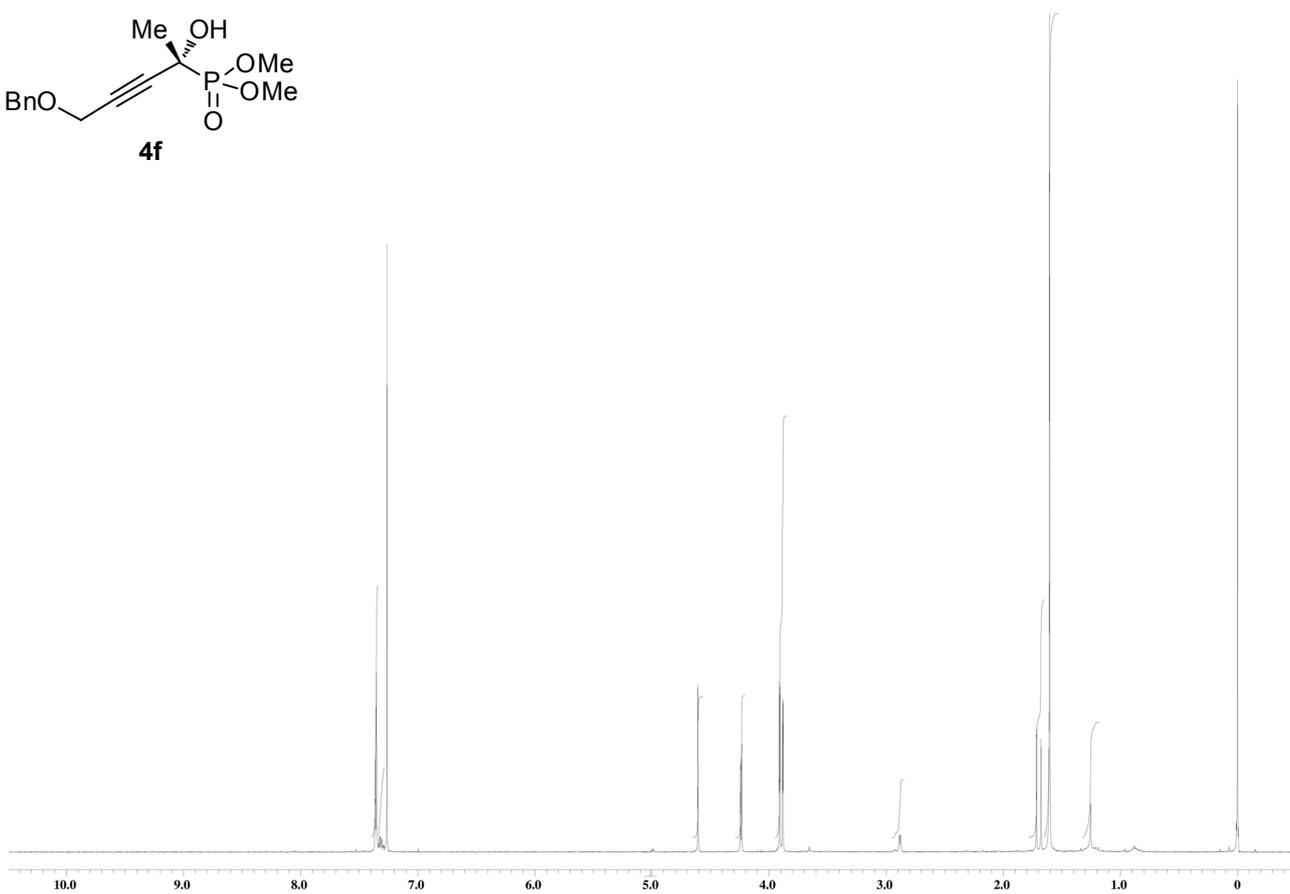
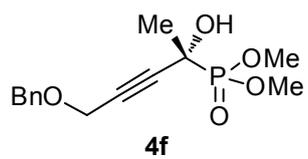


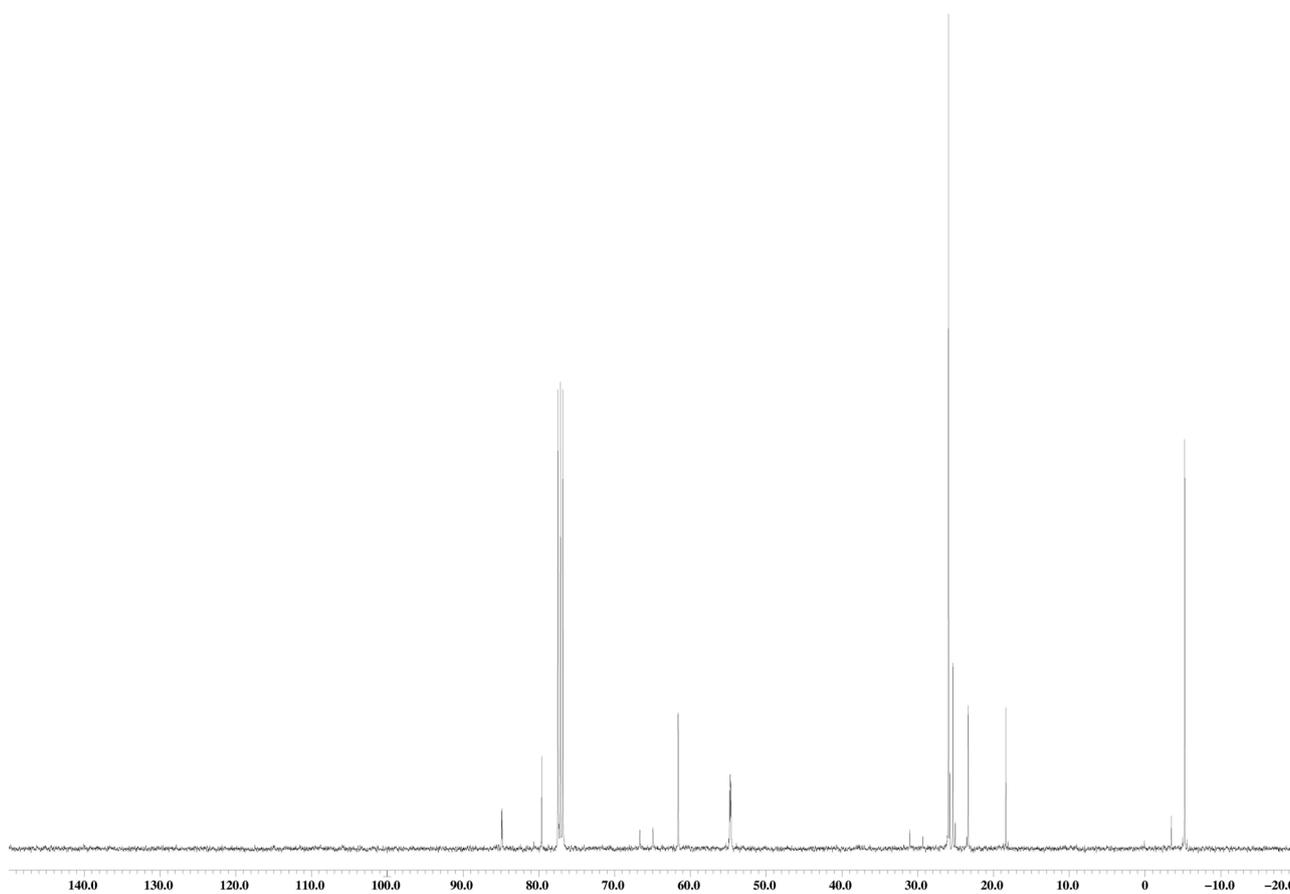
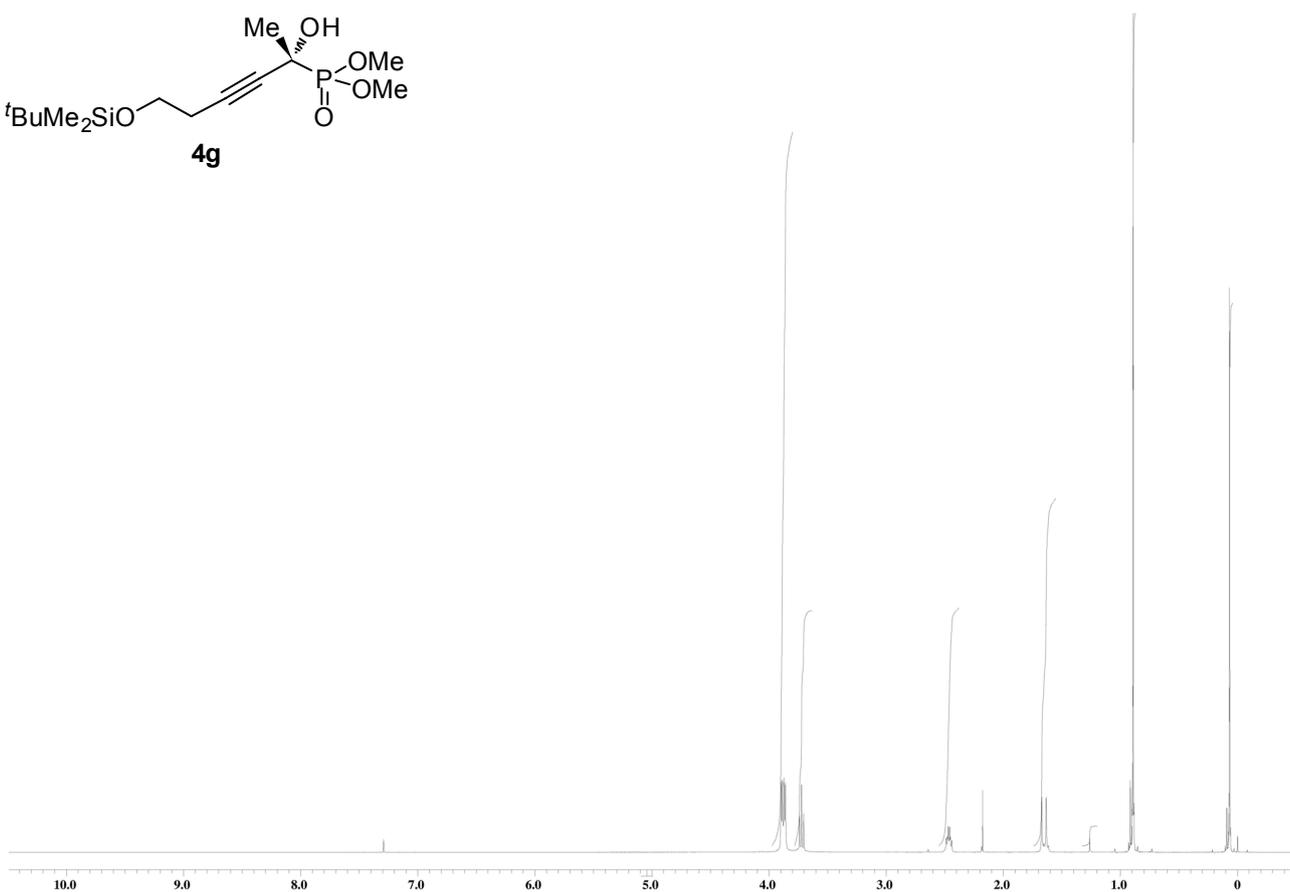
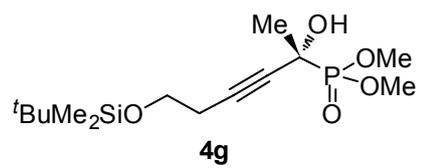


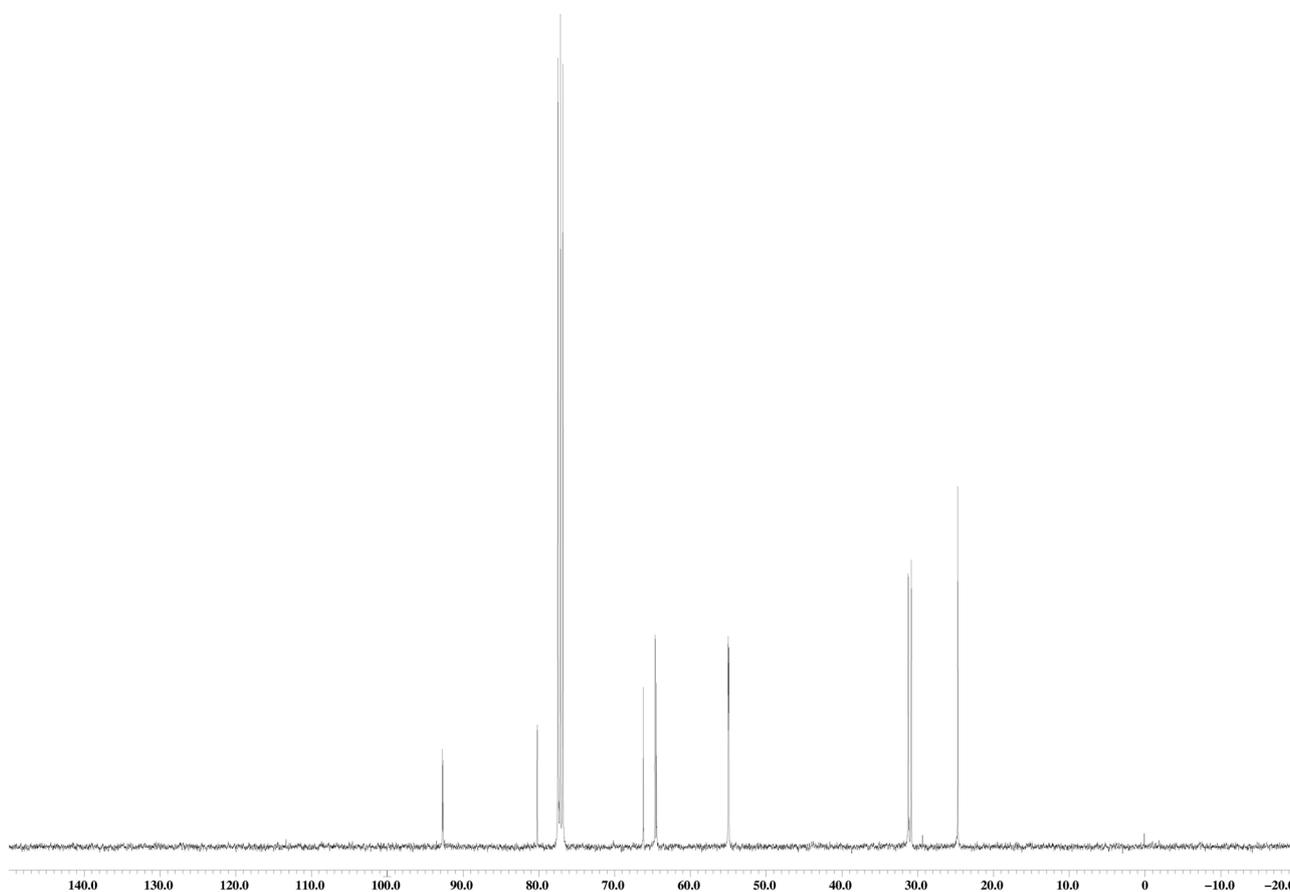
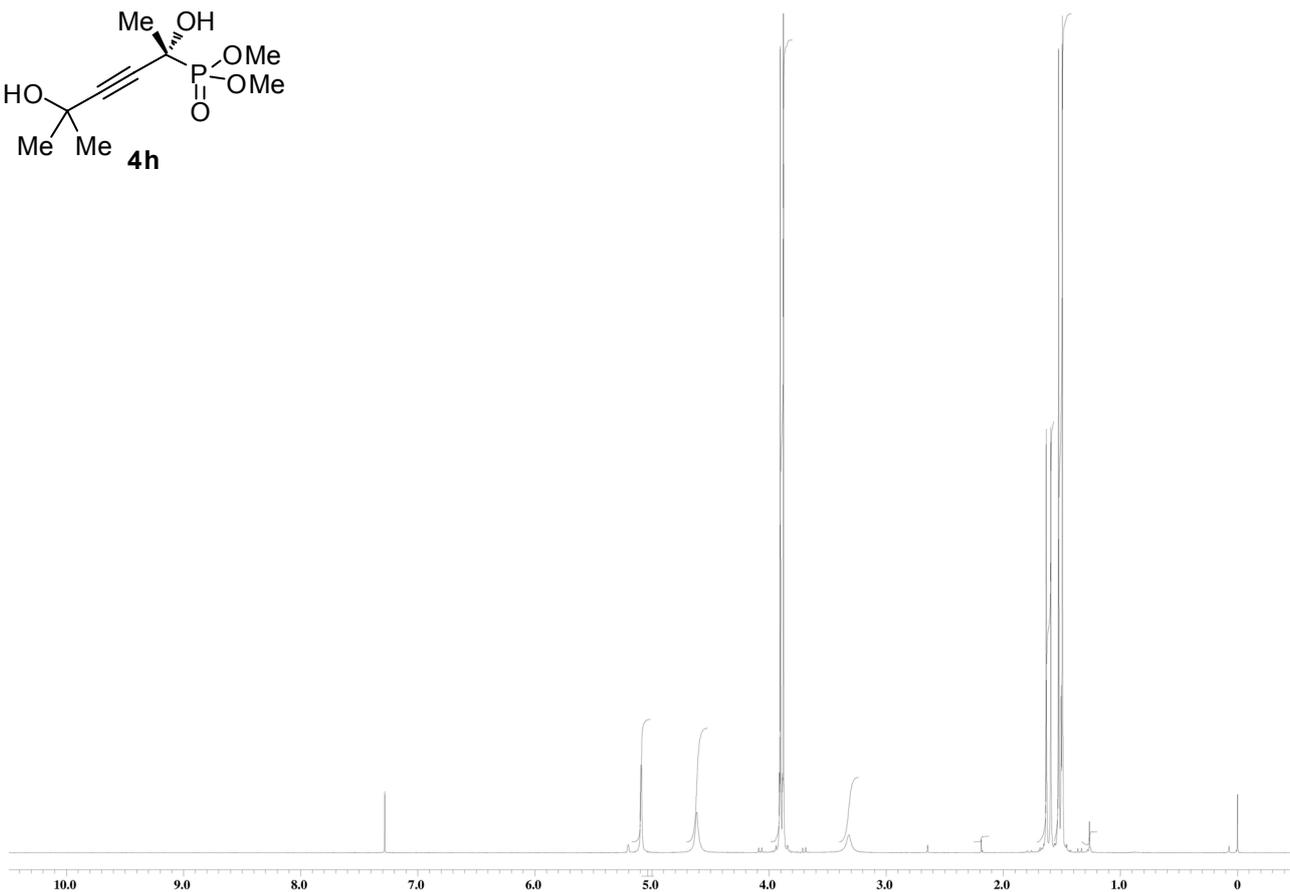
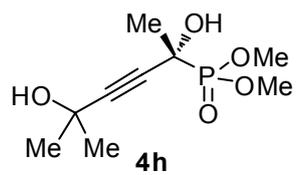


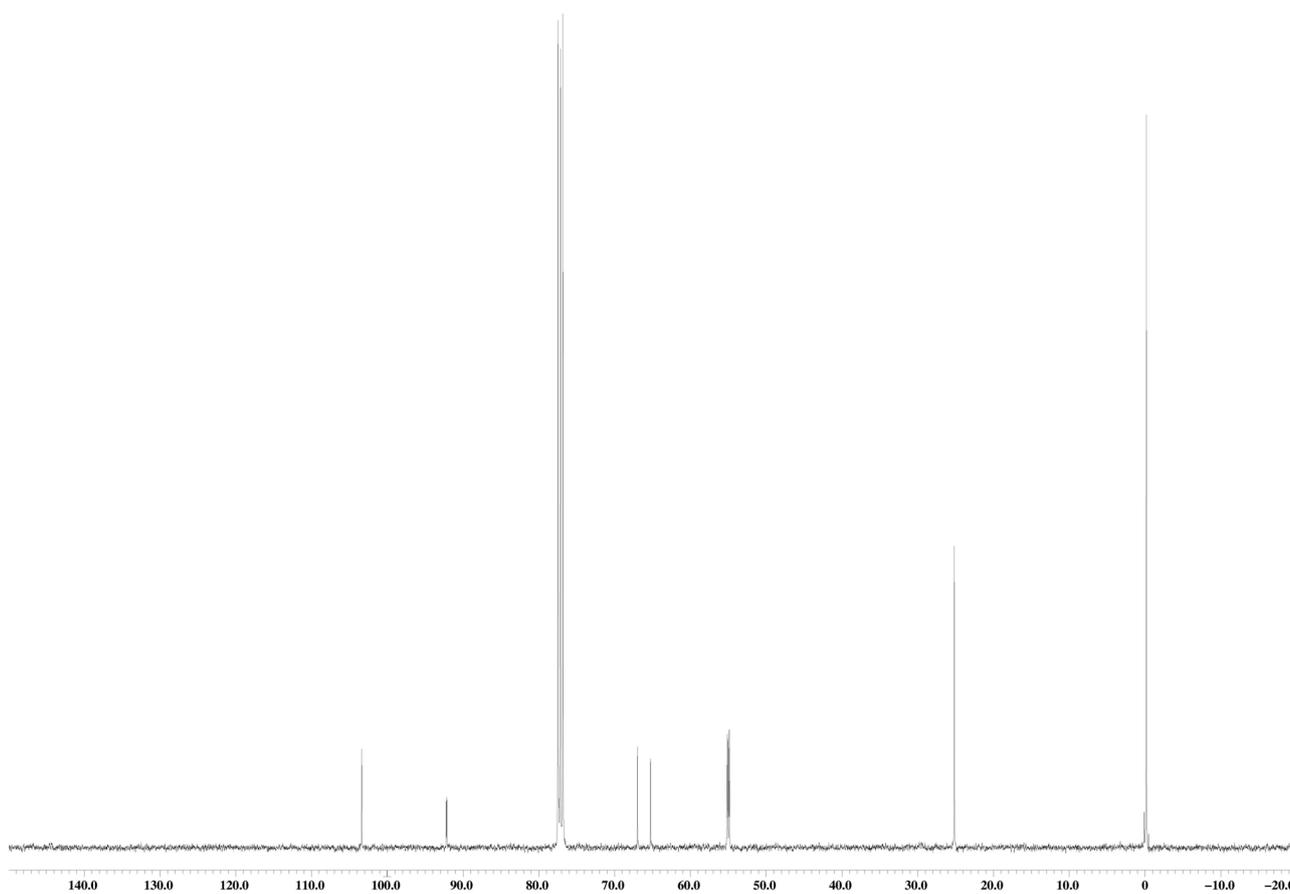
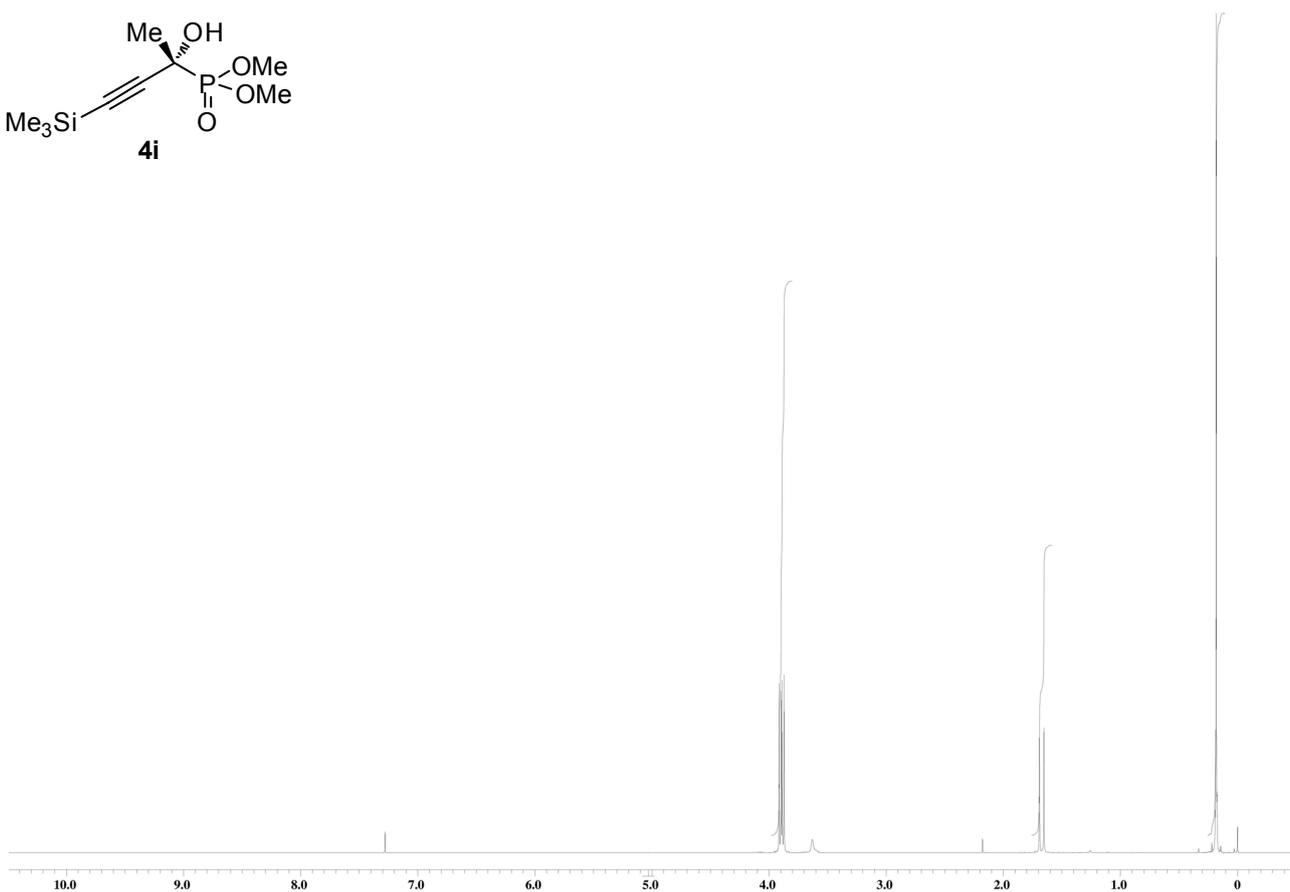
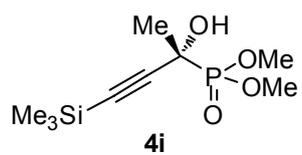






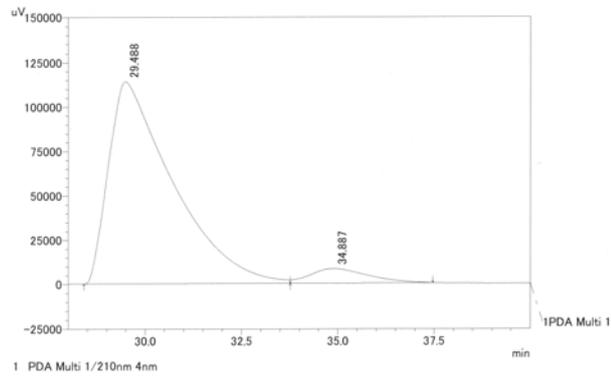
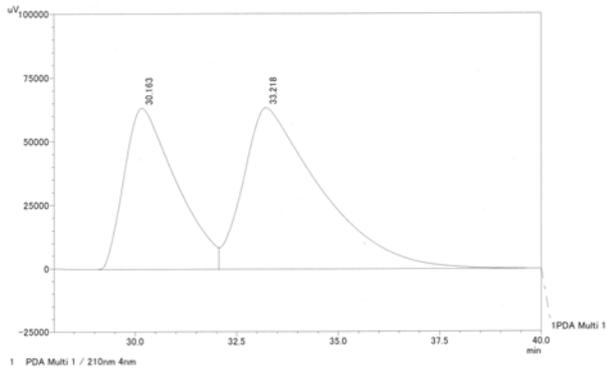






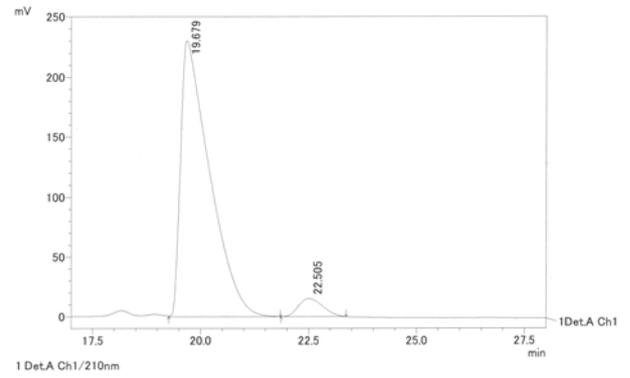
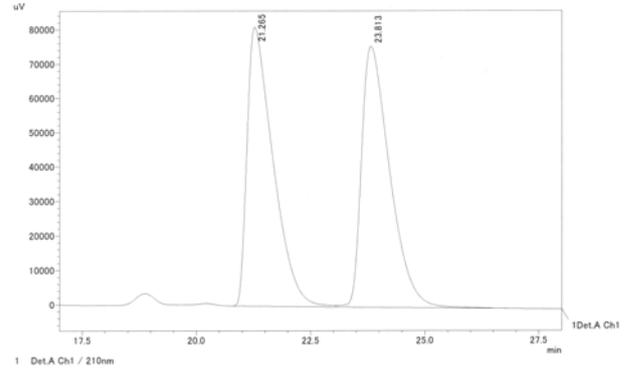
HPLC Chromatograms:

4a



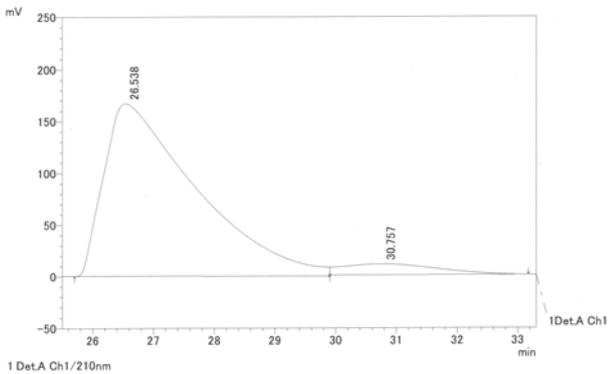
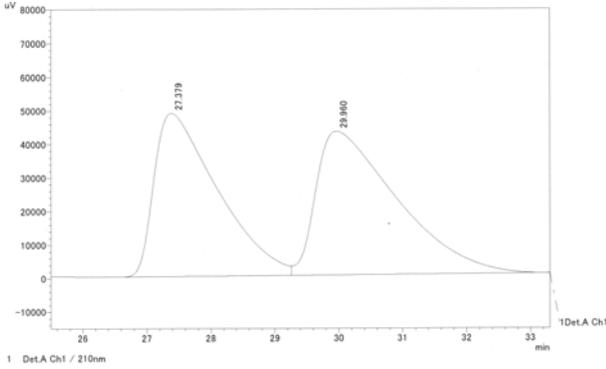
ピーク#	保持時間	面積%
1	29.488	93.931
2	34.887	6.069
合計		100.000

4b



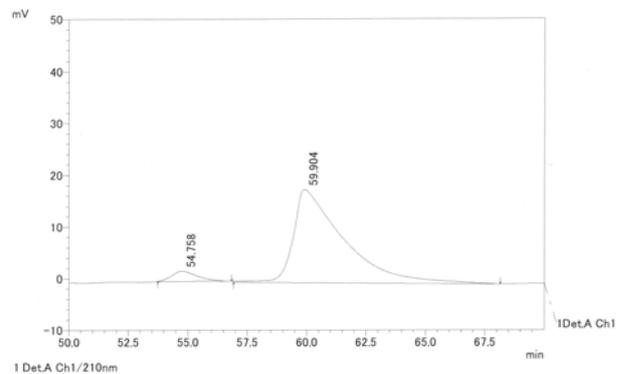
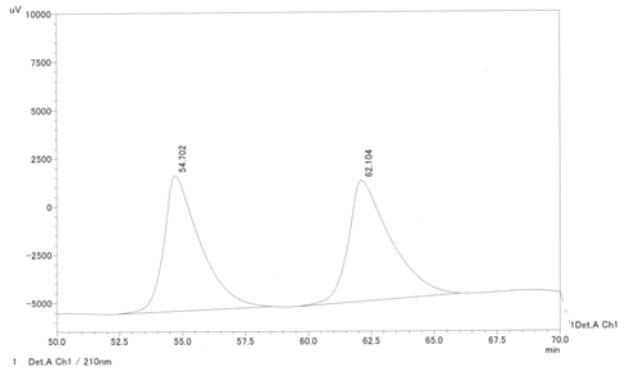
検出器A Ch1 210nm ピーク#	保持時間	面積%
1	19.679	94.810
2	22.505	5.190
合計		100.000

4c



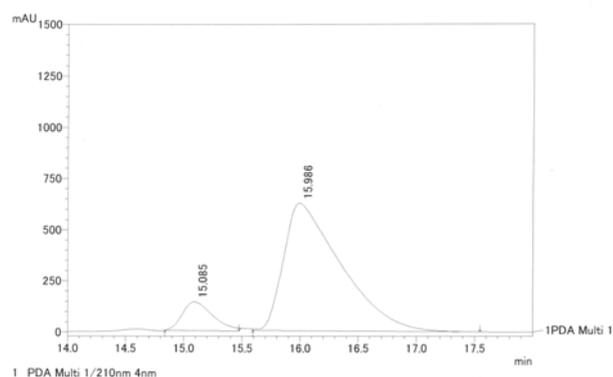
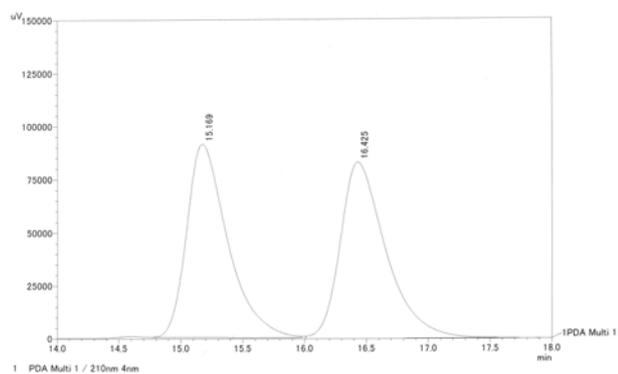
検出器A Ch1 210nm ピーク#	保持時間	面積%
1	26.538	93.896
2	30.757	6.104
合計		100.000

4d



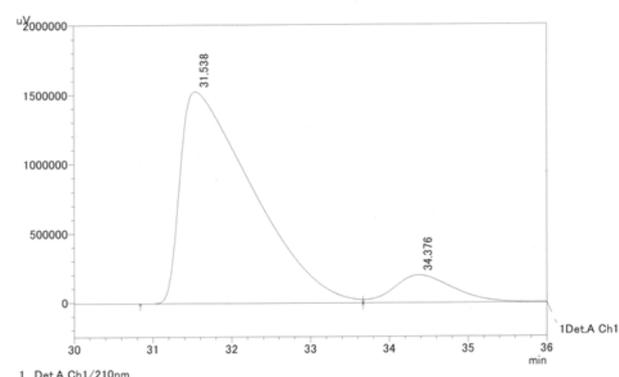
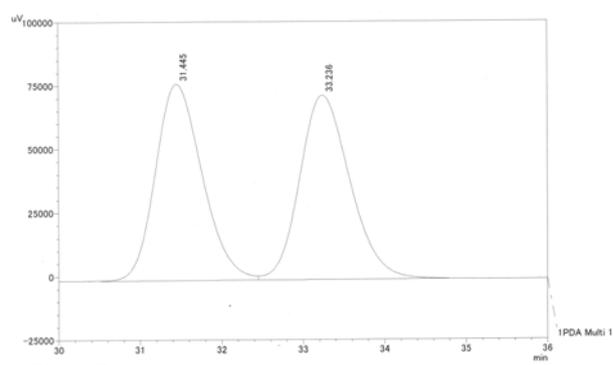
検出器A Ch1 210nm ピーク#	保持時間	面積%
1	54.758	5.235
2	59.904	94.765
合計		100.000

4e



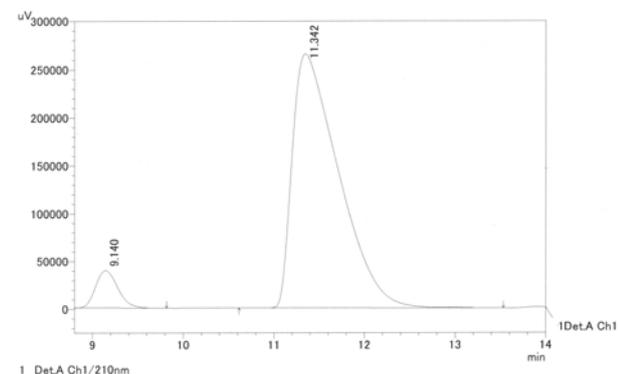
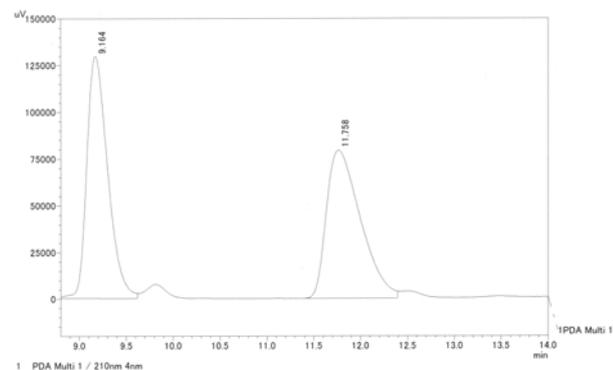
ピーク#	保持時間	面積%
1	15.085	10.703
2	15.986	89.297
合計		100.000

4f



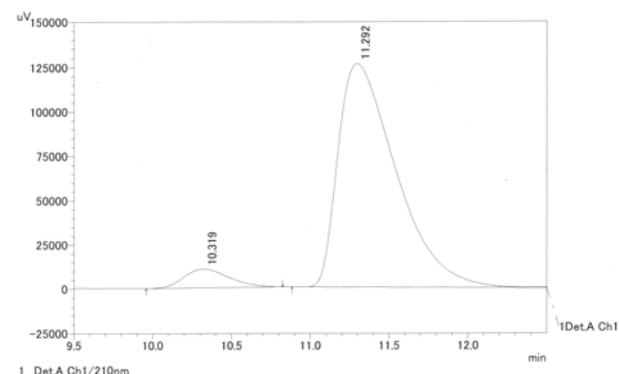
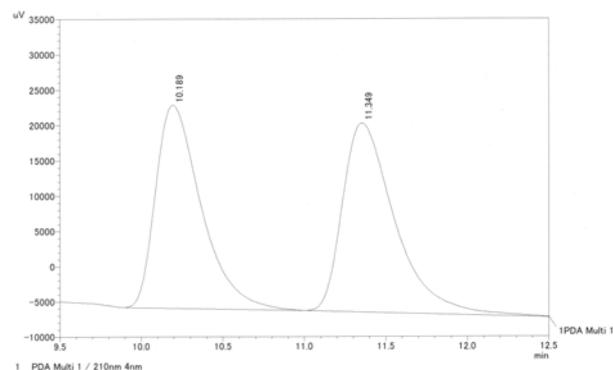
検出器A Ch1 210nm ピーク#	保持時間	面積%
1	31.538	90.374
2	34.376	9.626
合計		100.000

4g



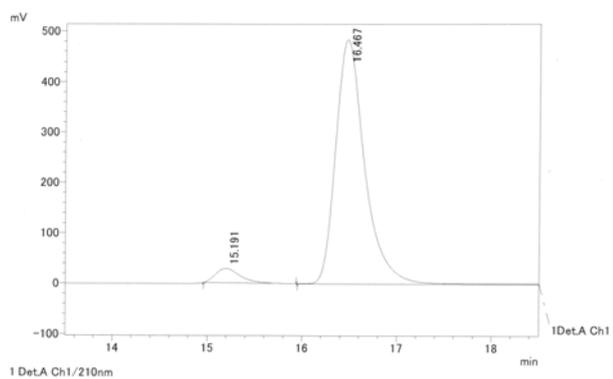
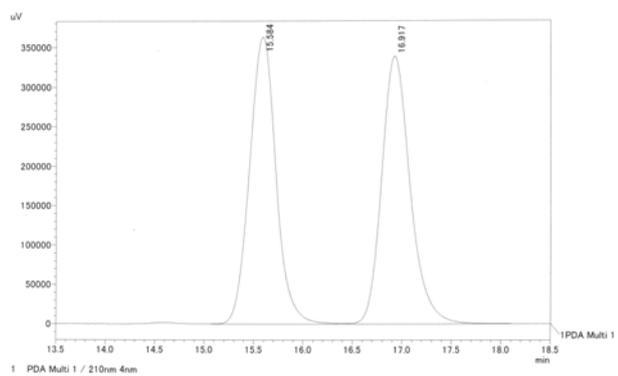
検出器A Ch1 210nm ピーク#	保持時間	面積%
1	9.140	6.603
2	11.342	93.397
合計		100.000

4h



検出器A Ch1 210nm ピーク#	保持時間	面積%
1	10.319	6.172
2	11.292	93.828
合計		100.000

4i



検出器A Ch1 210nm

ピーク#	保持時間	面積%
1	15.191	4.744
2	16.467	95.256
合計		100.000