Catalytic Asymmetric Transformations of Racemic α-Borylmethyl-(*E*)-crotylboronate via Kinetic Resolution or Enantioconvergent Reaction Pathways

*Shang Gao, Jiaming Liu, and Ming Chen**

Department of Chemistry and Biochemistry, Auburn University, Auburn, AL 36849

E-mail: mzc0102@auburn.edu

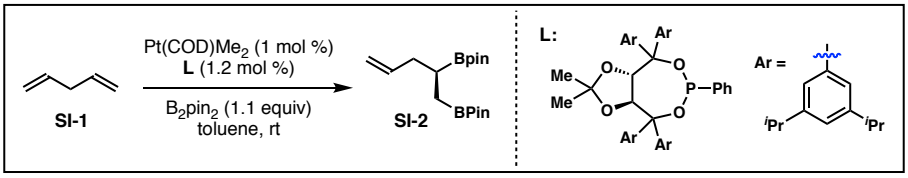
Supporting Information: Experimental Procedures, Tabulated Spectroscopic Data,

^{1}H and ^{13}C Spectra of New Compounds

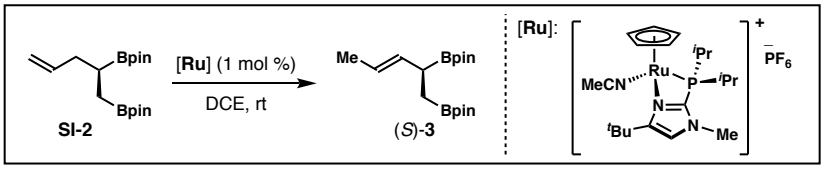
General Experimental Details. All reaction solvents were purified before use. Tetrahydrofuran, diethyl ether and toluene were purified by passing through a solvent column composed of activated A-1 alumina. Unless indicated otherwise, all reactions were conducted under an atmosphere of argon using flame-dried or oven-dried (120 ˚C) glassware. The term "concentrated under reduced pressure" refers to the removal of solvents and other volatile materials using a rotary evaporator with the water bath temperature below 30 ˚C, followed by the removal of residual solvents at high vacuum (< 0.2 mbar).

Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired on commercial instruments (400 and 600 MHz) at Auburn University NMR facility. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were acquired at 101 and 151 MHz. The proton signal for the residual non-deuterated solvent (δ 7.26 for $CHCl_3$) was used as an internal reference for ^{1}H NMR spectra. For ^{13}C NMR spectra, chemical shifts are reported relative to the δ 77.36 resonance of $CHCl_3$. Coupling constants are reported in Hz. High-resolution mass spectra were recorded on a commercial high-resolution mass spectrometer via the Micro Mass/Analytical Facility operated by the College of Chemistry and Biochemistry, Auburn University.

Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F254 glass plates precoated with a 0.25 mm thickness of silica gel. The TLC plates were visualized with UV light and/or by staining with Hanessian solution (ceric sulfate and ammonium molybdate in aqueous sulfuric acid) or $KMnO_4$. Column chromatography was generally performed using Kieselgel 60 (230-400 mesh) silica gel, typically using a 50-100:1 weight ratio of silica gel to crude product.

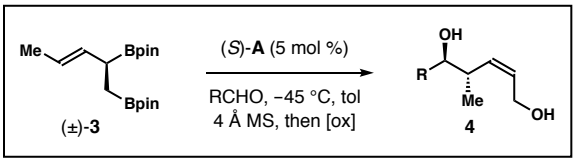


(*S*)-2,2'-(Pent-4-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (SI-2) To a reaction vial containing a Teflon-coated magnetic stirring bar were sequentially added $Pt(COD)Me_2$ (0.01 mmol, 1 mol %), **L** (0.012 mmol, 1.2 mol %) and B_2Pin_2 (280 mg, 1.1 mmol, 1.1 equiv), followed by addition of toluene (1 mL) in an argon-filled glove box. The vial was sealed with a cap containing a PTFE-lined silicone septum, removed from the glove box and stirred at 100 °C for 2 h. The reaction mixture was cooled to ambient temperature and brought into the glove box. Penta-2,4-diene **SI-1** (1.0 mmol, 1.0 equiv) in hexane (v:v = 1:1) was added to the vial and resulting mixture was kept stirring at ambient temperature for 3~7 days. After complete consumption of diene **SI-1**, the reaction mixture was directly purified by flash column chromatography (gradient elution with hexane and ethyl acetate) to provide product **SI-2** in 78% yield (251 mg) as a colorless oil. The enantiopurity (94% ee) was determined from a diol derivative by HPLC analysis. $[\alpha]_D^{20}$ = –0.20 (c 1.70, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.77 (ddt, *J* = 16.8, 9.9, 7.0 Hz, 1H), 4.97 (d, *J* = 17.1 Hz, 1H), 4.91 (d, *J* = 10.1 Hz, 1H), 2.20 (dt, *J* = 13.6, 6.8 Hz, 1H), 2.07 (dt, *J* = 14.0, 7.2 Hz, 1H), 1.21 (*app.* s, 25H), 0.85 (dd, *J* = 15.9, 9.8 Hz, 1H), 0.80 (dd, *J* = 16.0, 6.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.9, 115.4, 83.25, 83.17, 38.2, 25.18, 25.14, 25.08, 25.05, 18.3, 12.4. HRMS (ESI^+): *m*/*z* for $C_{17}H_{33}B_2O_4$ $[M+H]^+$ calcd. 323.2565, found 323.2570. The enantiomer *ent*-**SI-2** was synthesized using the same procedure with *ent*-**L** as the ligand.

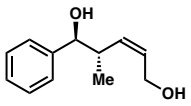


(*S*,*E*)-2,2'-(Pent-3-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) [(*S*)-3] In an argon-filled glove box, [Ru] complex (6 mg, 0.01 mmol, 1.0 mol %) was added to an oven-dried 4 mL vial equipped with a Teflon-coated magnetic stirring bar. The vial was capped with a rubber septum and removed from the glove box. A solution of boronate **SI-2** (322 mg, 1.0 mmol, 1.0 equiv) in DCE (3.0 mL) was added to the vial and the solution was kept stirring at ambient temperature. After complete consumption of

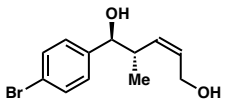
boronate **SI-2**, the solvent was removed under reduced pressure. The *E*/*Z* ratio (>20:1) was determined by ^{1}H NMR analysis of the crude reaction mixture. Purification of the crude product by flash column chromatography (gradient elution with hexane and ethyl acetate) gave product (*S*)-**3** in 97 % yield (312 mg) as a colorless oil. $[\alpha]_D^{20}$ = +0.18 (c 5.35, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.50 (dd, *J* = 14.8, 7.3 Hz, 1H), 5.37 (dq, *J* = 14.9, 6.1 Hz, 1H), 1.89 – 1.93 (m, 1H), 1.62 (*app.* s, 3H), 1.21 – 1.22 (m, 24H), 0.99 (dd, *J* = 15.9, 9.4 Hz, 1H), 0.88 (dd, *J* = 15.9, 6.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 133.8, 123.0, 83.3, 83.2, 25.2, 25.04 (two overlapping carbon signals), 24.95, 23.5, 18.5, 12.7. HRMS (ESI^+): *m*/*z* for $C_{17}H_{33}B_2O_4$ $[M+H]^+$ calcd. 323.2565, found 323.2574.



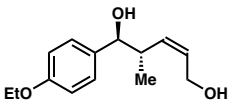
General procedure for the syntheses of homoallylic alcohols 4: To a reaction flask containing a Teflon-coated magnetic stir bar and freshly activated 4 Å molecular sieves (50 mg) was added phosphoric acid (*S*)-**A** (4 mg, 0.005 mmol, 5 mol %). Toluene (0.2 mL) was added to the flask followed by dropwise addition of freshly distilled aldehyde (0.1 mmol, if it is a liquid). The reaction flask was placed in a −45 °C cold bath and stirred for 5 min. Then boron reagent (±)-**3**[1] (97 mg, 0.3 mmol) in toluene (0.1 mL) was added slowly to the reaction mixture *via* a microliter syringe. The mixture was kept stirring at −45 °C for 24 h. After complete consumption of the aldehyde, 3N NaOH (0.5 mL) was added to the reaction mixture followed by slow addition of 30% H_2O_2 (0.5 mL) at 0 °C. The reaction was vigorously stirred at 0 °C for 3 h. Then ethyl acetate (1 mL) and brine (1 mL) were added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 mL x 3). The combined organic extracts were concentrated under reduced pressure. The crude reaction product was dissolved in Et_2O (1.0 mL); water (1.0 mL) and $NaIO_4$ (107 mg, 0.5 mmol) were added. The resulting mixture was stirred at ambient temperature for 2 h. Then Brine (1 mL) and ethyl acetate (1.0 mL) were added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (1 mL x 3). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography to give diol **4**.



(4*S*,5*S*,*Z*)-4-Methyl-5-phenylpent-2-ene-1,5-diol (4a) Prepared according to the general procedure, the crude mixture was purified by flash column chromatography to give the title compound as a colorless oil in 83% yield (16 mg, *Z*:*E* = 10:1). A 1 mmol scale reaction was also conducted and **4a** was isolated in 86% yield (166 mg, *Z*:*E* = 9:1). Enantiomeric excess was determined by HPLC analysis to be 99% ee (254 nm, 25 ˚C); t_1 = 8.57 min, t_2 = 10.5 min [(Chiralpak IA) hexane/i-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{20}$ = −37 (c 0.55, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.38 (m, 4H), 7.29 – 7.32 (m, 1H), 5.89 (dt, *J* = 10.6, 7.1 Hz, 1H), 5.53 (dd, *J* = 10.6, 10.4 Hz, 1H), 4.31 (d, *J* = 8.3 Hz, 1H), 4.22 (dd, *J* = 11.5, 7.8 Hz, 1H), 4.02 (dd, *J* = 12.2, 6.6 Hz, 1H), 2.84 – 2.90 (m, 1H), 2.29 (brs, 1H), 2.13 (brs, 1H), 0.82 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.0, 136.5, 130.5, 128.8, 128.3, 127.2, 78.5, 58.4, 40.4, 17.9. HRMS (ESI^+): *m*/*z* for $C_{12}H_{16}O_2Na$ $[M+Na]^+$ calcd. 215.1048, found 215.1044.

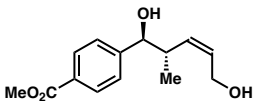


(4*S*,5*S*,*Z*)-5-(4-Bromophenyl)-4-methylpent-2-ene-1,5-diol (4b) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as a colorless oil in 81% yield (22 mg, *Z*:*E* = 8:1). Enantiomeric excess was determined by HPLC analysis to be 99% ee (254 nm, 25 ˚C); t_1 = 8.72 min, t_2 = 10.5 min [(Chiralpak IE) hexane/i-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{20}$ = −79 (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.49 (m, 2H), 7.21 – 7.23 (m, 2H), 5.88 (dt, *J* = 11.3, 7.1 Hz, 1H), 5.49 (dd, *J* = 10.6, 10.3 Hz, 1H), 4.25 (d, *J* = 8.5 Hz, 1H), 4.22 (ddd, *J* = 12.3, 7.4, 1.4 Hz, 1H), 4.05 (dd, *J* = 12.3, 6.7 Hz, 1H), 2.76 – 2.84 (m, 1H), 1.96 (brs, 2H), 0.80 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.9, 136.2, 131.9, 130.8, 128.9, 122.1, 77.8, 58.4, 40.5, 17.8. HRMS (ESI^+): *m*/*z* for $C_{12}H_{15}O_2BrNa$ $[M+Na]^+$ calcd. 293.0153, found 293.0140.

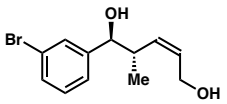


(4*S*,5*S*,*Z*)-5-(4-Ethoxyphenyl)-4-methylpent-2-ene-1,5-diol (4c) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as a colorless oil in 89% yield (21 mg *Z*:*E* = 12:1). Enantiomeric excess was determined by HPLC analysis to be 98% ee (254 nm, 25 ˚C); t_1 = 6.51 min, t_2 = 8.01 min [(Chiralpak ID) hexane/i-PrOH, 80:20, 1.0 mL/min]; $[\alpha]_D^{20}$ = −69 (c 0.35, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.1 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 5.90 (dt, *J* = 10.7, 7.1 Hz, 1H), 5.52 (dd, *J* = 10.5, 10.4 Hz, 1H), 4.23 – 4.28 (m, 2H), 4.02 – 4.05 (m, 3H), 2.82 – 2.88 (m, 1H), 2.25 (brs, 1H), 1.41 (t, *J* = 7.0 Hz, 3H), 0.78 (d, *J* = 6.7 Hz, 3H). ^{13}C

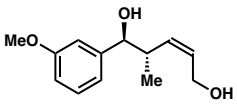
NMR (151 MHz, $CDCl_3$) δ 159.1, 136.9, 134.9, 130.4, 128.3, 114.7, 78.0, 63.8, 58.4, 40.3, 17.9, 15.2. HRMS (ESI^+): *m/z* for $C_{14}H_{20}O_3Na$ $[M+Na]^+$ calcd. 259.1310, found 259.1307.



Methyl 4-((1*S*,2*S*,*Z*)-1,5-dihydroxy-2-methylpent-3-en-1-yl) benzoate (4d) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as a colorless oil in 80% yield (20 mg, *Z*:*E* = 8:1. Enantiomeric excess was determined by HPLC analysis to be 99% ee (254 nm, 25 ˚C); t_1 = 8.49 min, t_2 = 11.5 min [(Chiralpak ID) hexane/i-PrOH, 80:20, 1.0 mL/min]; $[\alpha]_D^{20}$ = −83 (c 0.25, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 5.88 (dt, *J* = 10.8, 6.9 Hz, 1H), 5.50 (dd, *J* = 10.5, 10.4 Hz, 1H), 4.36 (d, *J* = 8.3 Hz, 1H), 4.20 (dd, *J* = 11.8, 7.7 Hz, 1H), 4.06 (dd, *J* = 12.3, 6.7 Hz, 1H), 3.92 (s, 3H), 2.81 – 2.88 (m, 1H), 2.02 (brs, 2H), 0.82 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 148.1, 136.0, 130.9, 130.09, 130.06, 127.2, 78.0, 58.4, 52.5, 40.5, 17.8. HRMS (ESI^+): *m/z* for $C_{14}H_{18}O_4Na$ $[M+Na]^+$ calcd. 273.1103, found 273.1102.

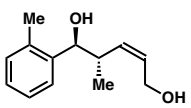


(4*S*,5*S*,*Z*)-5-(3-Bromophenyl)-4-methylpent-2-ene-1,5-diol (4e) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as a colorless oil in 77% yield (21 mg, *Z*:*E* = 6:1). Enantiomeric excess was determined by HPLC analysis to be 99% ee (254 nm, 25 ˚C); t_1 = 8.40 min, t_2 = 10.9 min [(Chiralpak ID) hexane/i-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{20}$ = −67 (c 1.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 1.9, 1.6 Hz, 1H), 7.43 (ddd, *J* = 7.7, 1.9, 1.3 Hz, 1H), 7.26 – 7.27 (m, 1H), 7.22 (dd, *J* = 7.7, 7.7 Hz, 1H), 5.89 (dt, *J* = 10.9, 7.0 Hz, 1H), 5.49 (dd, *J* = 10.7, 10.4 Hz, 1H), 4.26 (d, *J* = 8.3 Hz, 1H), 4.23 (ddd, *J* = 12.4, 7.3, 1.5 Hz, 1H), 4.07 (dd, *J* = 12.3, 6.7 Hz, 1H), 2.79 – 2.85 (m, 1H), 2.42 (brs, 1H), 2.04 (brs, 1H), 0.83 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3, 136.1, 131.4, 130.9, 130.3, 130.2, 126.0, 122.9, 77.8, 58.4, 40.5, 17.8. HRMS (ESI^+): *m/z* for $C_{12}H_{15}O_2BrNa$ $[M+Na]^+$ calcd. 293.0153, found 293.0147.

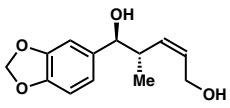


(4*S*,5*S*,*Z*)-5-(3-Methoxyphenyl)-4-methylpent-2-ene-1,5-diol (4f) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as a colorless oil in 81% yield (18 mg, *Z*:*E* = 8:1). Enantiomeric excess was determined by HPLC analysis to be 99% ee (254 nm, 25 ˚C); t_1 = 7.06 min, t_2 = 10.9 min [(Chiralpak

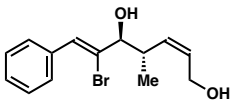
IE) hexane/i-PrOH, 80:20, 1.0 mL/min]; $[\alpha]_D^{20}$ = –105 (c 0.95, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 7.9, 7.8 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.90 (dd, *J* = 2.6, 1.7 Hz, 1H), 6.84 (ddd, *J* = 8.2, 2.7, 1.1 Hz, 1H), 5.88 (dt, *J* = 10.8, 7.3 Hz, 1H), 5.51 (dd, *J* = 10.4, 10.4 Hz, 1H), 4.27 (d, *J* = 8.4 Hz, 1H), 4.23 (ddd, *J* = 12.2, 7.6, 1.4 Hz, 1H), 4.02 (dd, *J* = 12.4, 6.9 Hz, 1H), 3.82 (s, 3H), 2.81 – 2.89 (m, 1H), 2.02 (brs, 2H), 0.82 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 144.6, 136.6, 130.5, 129.8, 119.6, 113.6, 112.8, 78.4, 58.4, 55.6, 40.3, 17.9. HRMS (ESI^+): *m*/*z* for $C_{13}H_{18}O_3Na$ $[M+Na]^+$ calcd. 245.1154, found 245.1143.



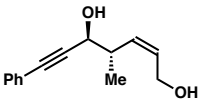
(4*S*,5*S*,*Z*)-4-Methyl-5-(*o*-tolyl)pent-2-ene-1,5-diol (4g) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as a colorless oil in 78% yield (16 mg, *Z*:*E* = 6:1). Enantiomeric excess was determined by HPLC analysis to be 95% ee (254 nm, 25 ˚C); t_1 = 8.56 min, t_2 = 10.3 min [(Chiralpak ID) hexane/i-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{20}$ = –120 (c 0.90, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.7 Hz, 1H), 7.23 (dd, *J* = 7.6, 7.3 Hz, 1H), 7.19 (ddd, *J* = 7.5, 7.2, 1.3 Hz, 1H), 7.15 (d, *J* = 7.3 Hz, 1H), 5.85 – 5.89 (m, 1H), 5.55 (dd, *J* = 10.7, 10.3 Hz, 1H), 4.67 (d, *J* = 8.0 Hz, 1H), 4.13 (ddd, *J* = 12.3, 7.7, 1.5 Hz, 1H), 3.96 (dd, *J* = 12.3, 6.6 Hz, 1H), 2.91 – 2.98 (m, 1H), 2.38 (s, 3H), 1.95 (brs, 2H), 0.88 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 136.3, 135.6, 130.8, 130.6, 127.9, 126.8, 126.6, 74.1, 58.5, 39.7, 19.8, 17.7. HRMS (ESI^+): *m*/*z* for $C_{13}H_{18}O_2Na$ $[M+Na]^+$ calcd. 229.1204, found 229.1197.



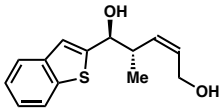
(4*S*,5*S*,*Z*)-5-(Benzo[*d*][1,3]dioxol-5-yl)-4-methylpent-2-ene-1,5-diol (4h) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 76% yield (18 mg, *Z*:*E* = 6:1). Enantiomeric excess was determined by HPLC analysis to be 99% ee (254 nm, 25 ˚C); t_1 = 9.60 min, t_2 = 17.7 min [(Chiralpak ID) hexane/i-PrOH, 80:20, 1.0 mL/min]; $[\alpha]_D^{20}$ = –9.3 (c 0.90, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 6.87 (dd, *J* = 1.2, 1.1 Hz, 1H), 6.76 – 6.80 (m, 2H), 5.96 (s, 2H), 5.90 (ddd, *J* = 10.8, 7.6, 6.7 Hz, 1H), 5.48 – 5.52 (m, 1H), 4.27 (ddd, *J* = 12.4, 7.6, 1.4 Hz, 1H), 4.19 (d, *J* = 8.7 Hz, 1H), 4.05 (ddd, *J* = 12.2, 6.7, 0.8 Hz, 1H), 2.77 – 2.85 (m, 1H), 1.86 (brs, 2H), 0.79 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2, 147.6, 136.9, 136.7, 130.5, 120.9, 108.3, 107.3, 101.4, 78.3, 58.4, 40.4, 17.9. HRMS (ESI^+): *m*/*z* for $C_{13}H_{16}O_4Na$ $[M+Na]^+$ calcd. 259.0946, found 259.0941.



(2*Z*,4*S*,5*S*,6*Z*)-6-Bromo-4-methyl-7-phenylhepta-2,6-diene-1,5-diol (4i) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as a colorless oil in 81% yield (24 mg, *Z*:*E* = 11:1). Enantiomeric excess was determined by HPLC analysis to be 99% ee (254 nm, 25 ˚C); t_1 = 11.4 min, t_2 = 16.4 min [(Chiralpak IE) hexane/i-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{20}$ = −6.2 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.5 Hz, 2H), 7.37 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.32 (dd, *J* = 7.4, 7.3 Hz, 1H), 7.02 (s, 1H), 5.90 (dt, *J* = 10.7, 7.0 Hz, 1H), 5.52 (dd, *J* = 10.7, 10.2 Hz, 1H), 4.33 (ddd, *J* = 12.2, 7.4, 1.3 Hz, 1H), 4.11 (dd, *J* = 12.2, 6.7 Hz, 1H), 3.88 (d, *J* = 8.7 Hz, 1H), 3.03 – 3.09 (m, 1H), 1.99 (brs, 2H), 1.00 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.7, 135.2, 130.8, 130.7, 129.5, 128.9, 128.7, 128.6, 81.3, 58.4, 37.2, 17.9. HRMS (ESI^+): *m*/*z* for $C_{14}H_{17}O_2BrNa$ $[M+Na]^+$ calcd. 319.0310, found 319.0310.

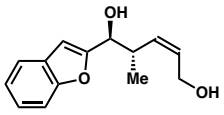


(4*S*,5*S*,*Z*)-4-Methyl-7-phenylhept-2-en-6-yne-1,5-diol (4j) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give the title compound as a colorless oil in 74% yield (16 mg, *Z*:*E* = 11:1). Enantiomeric excess was determined by HPLC analysis to be 98% ee (254 nm, 25 ˚C); t_1 = 9.96 min, t_2 = 11.2 min [(Chiralpak IE) hexane/i-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{20}$ = −27 (c 0.80, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.47 (m, 2H), 7.29 – 7.35 (m, 3H), 5.86 (dt, *J* = 10.9, 7.0 Hz, 1H), 5.47 (dd, *J* = 10.6, 10.5 Hz, 1H), 4.32 (d, *J* = 7.8 Hz, 1H), 4.28 (ddd, *J* = 12.4, 7.3, 1.4 Hz, 1H), 4.13 (dd, *J* = 12.4, 6.7 Hz, 1H), 2.87 – 2.93 (m, 1H), 2.06 (brs, 2H), 1.18 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.1, 132.1, 131.0, 128.9, 128.7, 122.7, 88.8, 86.3, 66.9, 58.6, 39.5, 17.5. HRMS (ESI^+): *m*/*z* for $C_{14}H_{16}O_2Na$ $[M+Na]^+$ calcd. 239.1048, found 239.1039.

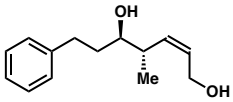


(4*S*,5*S*,*Z*)-5-(Benzo[*b*]thiophen-2-yl)-4-methylpent-2-ene-1,5-diol (4k) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as a colorless oil in 81% yield (20 mg, *Z*:*E* = 8:1). Enantiomeric excess was determined by HPLC analysis to be 99% ee (254 nm, 25 ˚C); t_1 = 14.3 min, t_2 = 18.1 min [(Chiralpak ID) hexane/i-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{20}$ = −87 (c 0.90, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.30 – 7.36 (m, 2H), 7.22 (s, 1H), 5.92 (dt, *J* = 10.9, 6.9 Hz, 1H), 5.53 (dd, *J* = 10.4, 10.4 Hz, 1H), 4.63 (d, *J* = 8.6 Hz, 1H), 4.29 – 4.33 (m, 1H), 4.10 (dd, *J* = 12.3, 6.6 Hz, 1H), 2.93 – 2.99 (m, 1H), 2.11 (brs, 2H), 0.92 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.3, 139.8, 139.5, 135.9,

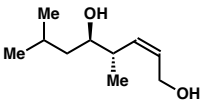
131.0, 124.70, 124.68, 123.8, 122.9, 122.2, 74.7, 58.5, 40.7, 18.0. HRMS (ESI^+): *m*/*z* for $C_{14}H_{16}O_2SNa$ $[M+Na]^+$ calcd. 271.0769, found 271.0760.



(4*S*,5*S*,*Z*)-5-(Benzofuran-2-yl)-4-methylpent-2-ene-1,5-diol (4l) Prepared according to the general procedure. The crude mixture was purified by c flash column chromatography to give the title compound as a colorless oil in 77% yield (18 mg, *Z*:*E* = 7:1). Enantiomeric excess was determined by HPLC analysis to be 98% ee (254 nm, 25 ˚C); t_1 = 8.80 min, t_2 = 10.6 min [(Chiralpak IC) hexane/i-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{20}$ = –169 (c 0.95, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.28 (dd, *J* = 7.1, 6.6 Hz, 1H), 7.22 (dd, *J* = 7.4, 7.2 Hz, 1H), 6.67 (s, 1H), 5.89 (dt, *J* = 10.9, 7.0 Hz, 1H), 5.52 (dd, *J* = 10.6, 10.5 Hz, 1H), 4.48 (d, *J* = 8.5 Hz, 1H), 4.30 (dd, *J* = 12.1, 7.3 Hz, 1H), 4.12 (dd, *J* = 12.1, 6.7 Hz, 1H), 3.16 – 3.23 (m, 1H), 2.69 (brs, 1H), 1.98 (brs, 1H), 0.93 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.9, 155.2, 135.8, 130.8, 128.3, 124.6, 123.2, 121.4, 111.7, 104.7, 72.1, 58.4, 37.9, 17.7. HRMS (ESI^+): *m*/*z* for $C_{14}H_{16}O_3Na$ $[M+Na]^+$ calcd. 255.0997, found 255.0999.

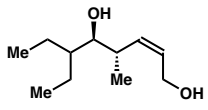


(4*S*,5*R*,*Z*)-4-Methyl-7-phenylhept-2-ene-1,5-diol (4m) Prepared according to the general procedure with 10 mol % of catalyst (*S*)-**A**. The crude mixture was purified by flash column chromatography to give the title compound as a colorless oil in 82% yield (18 mg, *Z*:*E* = 12:1). Enantiomeric excess was determined by HPLC analysis to be 95% ee (254 nm, 25 ˚C); t_1 = 7.99 min, t_2 = 10.3 min [(Chiralpak IA) hexane/i-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{20}$ = +21 (c 0.95, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.30 (m, 2H), 7.18 – 7.21 (m, 3H), 5.80 (dt, *J* = 10.6, 7.0 Hz, 1H), 5.41 (dd, *J* = 10.6, 10.5 Hz, 1H), 4.21 (dd, *J* = 12.2, 7.2 Hz, 1H), 4.10 (dd, *J* = 12.2, 6.8 Hz, 1H), 3.32 – 3.34 (m, 1H), 2.85 (ddd, *J* = 14.1, 10.4, 5.0 Hz, 1H), 2.65 – 2.70 (m, 1H), 2.53 – 2.60 (m, 1H), 1.86 – 1.92 (m, 1H), 1.72 (brs, 2H), 0.98 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.4, 136.2, 130.3, 128.80, 128.78, 126.2, 74.4, 58.6, 38.8, 36.4, 32.3, 17.6. HRMS (ESI^+): *m*/*z* for $C_{14}H_{20}O_2Na$ $[M+Na]^+$ calcd. 243.1361, found 243.1354.

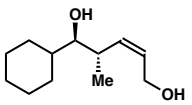


(4*S*,5*R*,*Z*)-4,7-Dimethyloct-2-ene-1,5-diol (4n) Prepared according to the general procedure with 10 mol % (*S*)-**A**. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 81% yield (14 mg, *Z*:*E* = 18:1). Enantiomeric excess was determined by HPLC analysis of the corresponding mono-OBz (primary) to be 93% ee (254 nm, 25 ˚C);

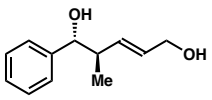
t_1 = 5.15 min, t_2 = 6.28 min [(Chiralpak IA) hexane/i-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{20}$ = +36.6 (c 0.65, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (dt, *J* = 11.0, 7.0 Hz, 1H), 5.43 (dd, *J* = 10.6, 10.6 Hz, 1H), 4.22 (ddd, *J* = 12.4, 7.2, 1.5 Hz, 1H), 4.11 (ddd, *J* = 12.4, 6.9, 1.0 Hz, 1H), 3.38 (ddd, *J* = 9.9, 7.2, 3.1 Hz, 1H), 2.46 – 2.54 (m, 1H), 1.76 – 1.87 (m, 1H), 1.64 (brs, 2H), 1.25 – 1.39 (m, 2H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.2, 130.2, 73.1, 58.7, 44.0, 39.3, 24.9, 24.3, 21.9, 17.7. HRMS (ESI^+): *m*/*z* for $C_{10}H_{20}O_2Na$ $[M+Na]^+$ calcd. 195.1361, found 195.1355.



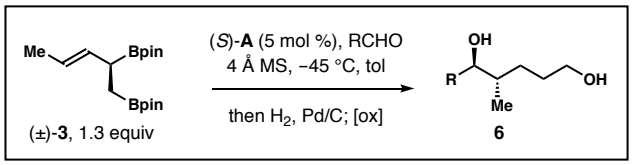
(4*S*,5*R*,*Z*)-6-Ethyl-4-methyloct-2-ene-1,5-diol (4o) Prepared according to the general procedure with 10 mol % catalyst (*S*)-**A**. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 75% yield (14 mg, *Z*:*E* > 20:1). Enantiomeric excess was determined by HPLC analysis of the corresponding mono-OBz (primary) to be 90% ee (254 nm, 25 ˚C); t_1 = 6.46 min, t_2 = 7.39 min [(Chiralpak IB) hexane/i-PrOH, 95:5, 1.0 mL/min]; $[\alpha]_D^{20}$ = +13.7 (c 0.60, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.83 (dt, *J* = 10.9, 7.3 Hz, 1H), 5.45 (dd, *J* = 10.6, 10.4 Hz, 1H), 4.25 (ddd, *J* = 12.3, 7.3, 1.5 Hz, 1H), 4.06 (ddd, *J* = 12.3, 6.7, 0.8 Hz, 1H), 3.32 (dd, *J* = 8.6, 2.8 Hz, 1H), 2.74 – 2.80 (m, 1H), 1.82 (brs, 2H), 1.48 – 1.58 (m, 2H), 1.29 – 1.40 (m, 2H), 1.22 – 1.29 (m, 1H), 0.91– 0.95 (m, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4, 129.8, 75.6, 58.5, 43.0, 35.7, 23.3, 20.5, 17.7, 12.5, 12.1. HRMS (ESI^+): *m*/*z* for $C_{11}H_{22}O_2Na$ $[M+Na]^+$ calcd. 209.1517, found 209.1512.



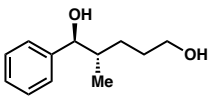
(4*S*,5*R*,*Z*)-5-Cyclohexyl-4-methylpent-2-ene-1,5-diol (4p) Prepared according to the general procedure with 10 mol % of catalyst (*S*)-**A**. The crude mixture was purified by flash column chromatography to give the title compound as a colorless oil in 86% yield (17 mg, *Z*:*E* > 20:1). Enantiomeric excess was determined by HPLC analysis of the corresponding mono-OBz (primary) to be 94% ee (254 nm, 25 ˚C); t_1 = 6.71 min, t_2 = 7.22 min [(Chiralpak ID) hexane/i-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{20}$ = +5.0 (c 0.40, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (dt, *J* = 10.4, 6.9 Hz, 1H), 5.45 (dd, *J* = 10.5, 10.5 Hz, 1H), 4.23 (dd, *J* = 12.6, 7.1 Hz, 1H), 4.05 (dd, *J* = 12.4, 6.7 Hz, 1H), 3.09 – 3.11 (m, 1H), 2.68 – 2.78 (m, 1H), 1.95 (brs, 2H), 1.68 – 1.77 (m, 4H), 1.44 – 1.58 (m, 2H), 1.10 – 1.32 (m, 5H), 0.96 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.0, 129.7, 78.8, 58.5, 40.1, 35.2, 31.0, 27.0, 26.9, 26.5, 25.7, 17.7. HRMS (ESI^+): *m*/*z* for $C_{12}H_{22}O_2Na$ $[M+Na]^+$ calcd. 221.1517, found 221.1510.



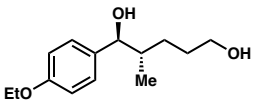
(4*R*,5*R*,*E*)-4-Methyl-5-phenylpent-2-ene-1,5-diol (5a) Enantiomeric excess was determined by HPLC analysis to be 99% ee (254 nm, 25 ˚C); t_1 = 10.1 min, t_2 = 11.0 min [(Chiralpak IA) hexane/i-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{20}$ = +114.9 (c 0.75, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.35 (m, 6H), 5.78 (dt, *J* = 15.4, 5.6 Hz, 1H), 5.68 (dd, *J* = 15.5, 8.1 Hz, 1H), 4.34 (d, *J* = 8.0 Hz, 1H), 4.12 (d, *J* = 5.5 Hz, 2H), 2.46 – 2.52 (m, 1H), 2.34 (brs, 1H), 1.95 (brs, 1H), 0.85 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.9, 134.8, 131.4, 128.6, 128.1, 127.1, 78.7, 63.8, 45.0, 17.3. HRMS (ESI^+): *m*/*z* for $C_{12}H_{16}O_2Na$ $[M+Na]^+$ calcd. 215.1048, found 215.1039.



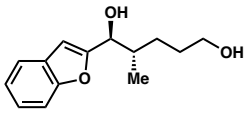
General procedure for the syntheses of diol 6: To an oven-dried reaction flask containing a magnetic stir bar and freshly activated 4 Å molecular sieves (50 mg) were added chiral phosphoric acid (*S*)-**A** (4 mg, 0.005 mmol, 5 mol %), toluene (0.2 mL) and freshly distilled aldehyde (0.1 mmol, if it is a liquid). The reaction flask was placed in a −45 °C cold bath and stirred for 5 min. Then a solution of boronate (±)-**3** (42 mg, 0.13 mmol, 1.3 equiv) in toluene (0.1 mL) was added slowly to the reaction mixture *via* a microliter syringe. The resulting mixture was kept stirring at −45 °C. After complete consumption of the aldehyde, ethyl acetate (0.5 mL) and Pd/C (10 mg) were added to the reaction flask. The reaction mixture was stirred at ambient temperature under hydrogen atmosphere for 24 h (equipped with a hydrogen balloon). Then a solution of 3N NaOH (0.5 mL) was added to the flask followed by slow addition of 30% H_2O_2 (0.5 mL) at 0 °C. The resulting mixture was stirred vigorously for 3 h at 0 °C. Then diethyl ether (1 mL) and brine (1 mL) were added to the flask. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 mL x 3). The combined organic extracts were concentrated under reduced pressure. The crude product was dissolved in Et_2O (1 mL). Then water (1 mL) and $NaIO_4$ (214 mg, 1.0 mmol) were added to the reaction flaks. The resulting mixture was stirred at ambient temperature for 2 h. Brine (1 mL) and ethyl acetate (0.5 mL) were added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 x 1 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by flash chromatography to give diol **6**.



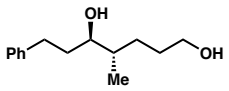
(1*S*,2*S*)-2-Methyl-1-phenylpentane-1,5-diol (6a) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 88% yield (17 mg). Enantiomeric excess was determined by HPLC analysis to be 98% ee (254 nm, 25 ˚C); t_1 = 10.8 min, t_2 = 12.8 min [(Chiralpak IA) hexane/i-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{20}$ = –25.6˚ (c 0.75, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.36 (m, 5H), 4.43 (d, *J* = 7.3 Hz, 1H), 3.62 – 3.69 (m, 2H), 1.83 – 1.89 (m, 1H), 1.67 – 1.78 (m, 2H), 1.67 (brs, 2H), 1.49 – 1.58 (m, 1H), 1.21 – 1.28 (m, 1H), 0.77 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 128.6, 127.9, 127.0, 79.4, 63.5, 40.2, 30.4, 28.7, 16.3. HRMS (ESI^+): *m*/*z* for $C_{12}H_{18}O_2Na$ $[M+Na]^+$ calcd. 217.1204, found 217.1194.



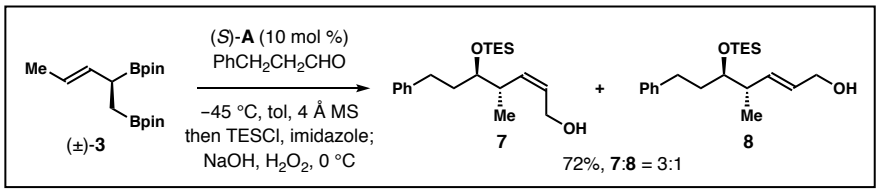
(1*S*,2*S*)-1-(4-Ethoxyphenyl)-2-methylpentane-1,5-diol (6b) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 88% yield (21 mg). Enantiomeric excess was determined by HPLC analysis to be 99% ee (254 nm, 25 ˚C); t_1 = 7.15 min, t_2 = 9.87 min [(Chiralpak ID) hexane/i-PrOH, 80:20, 1.0 mL/min]; $[\alpha]_D^{20}$ = –28.2 (c 0.95, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 4.37 (d, *J* = 7.5 Hz, 1H), 4.03 (q, *J* = 7.0 Hz, 2H), 3.66 (t, *J* = 5.8 Hz, 2H), 1.68 – 1.87 (m, 3H), 1.50 – 1.59 (m, 1H), 1.55 (brs, 2H), 1.41 (t, *J* = 7.0 Hz, 3H), 1.20 – 1.27 (m, 1H), 0.74 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 135.9, 128.1, 114.6, 79.1, 63.8, 63.6, 40.2, 30.4, 28.9, 16.2, 15.2. HRMS (ESI^+): *m*/*z* for $C_{14}H_{22}O_3Na$ $[M+Na]^+$ calcd. 261.1467, found 261.1474.



(1*S*,2*S*)-1-(Benzofuran-2-yl)-2-methylpentane-1,5-diol (6c) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 94% yield (22 mg). Enantiomeric excess was determined by HPLC analysis to be 99% ee (254 nm, 25 ˚C); t_1 = 6.33 min, t_2 = 7.11 min [(Chiralpak ID) hexane/i-PrOH, 80:20, 1.0 mL/min]; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.55 (m, 1H), 7.45 – 7.46 (m, 1H), 7.25 – 7.28 (m, 1H), 7.22 (ddd, *J* = 7.5, 7.3, 1.1 Hz, 1H), 6.63 (s, 1H), 4.62 (d, *J* = 7.0 Hz, 1H), 3.64 – 3.70 (m, 2H), 2.09 – 2.15 (m, 1H), 1.70 – 1.78 (m, 2H), 1.53 – 1.62 (m, 1H), 1.53 (brs, 2H), 1.28 – 1.35 (m, 1H), 0.93 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 155.0, 128.4, 124.4, 123.1, 121.3, 111.6, 104.0, 73.3, 63.5, 38.2, 30.3, 28.5, 16.1. HRMS (ESI^+): *m*/*z* for $C_{14}H_{18}O_3Na$ $[M+Na]^+$ calcd. 257.1154, found 257.1144.

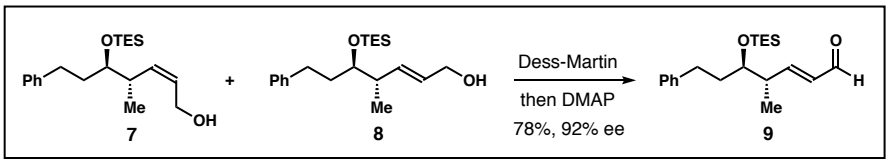


(4*S*,5*R*)-4-Methyl-7-phenylheptane-1,5-diol (6d) Prepared according to the general procedure with 10 mol % catalyst (*S*)-**A**. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 81% yield (18 mg). Enantiomeric excess was determined by HPLC analysis to be 90% ee (254 nm, 25 ˚C); t_1 = 7.43 min, t_2 = 8.77 min [(Chiralpak IC) hexane/i-PrOH, 80:20, 1.0 mL/min]; $[\alpha]_D^{20}$ = +4.2 (c 0.85, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.30 (m, 2H), 7.17 – 7.22 (m, 3H), 3.64 (t, *J* = 6.2 Hz, 2H), 3.52 – 3.43 (m, 1H), 2.86 (ddd, *J* = 15.0, 10.0, 5.3 Hz, 1H), 2.65 (ddd, *J* = 13.7, 9.7, 6.7 Hz, 1H), 1.80 (dddd, *J* = 14.0, 9.9, 6.7, 2.9 Hz, 1H), 1.62 – 1.74 (m, 2H), 1.44 – 1.61 (m, 3H), 1.44 (brs, 1H), 1.31 (brs, 1H), 1.16 – 1.22 (m, 1H), 0.92 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 128.79, 128.77, 126.2, 75.7, 63.5, 39.2, 35.8, 32.8, 30.6, 28.4, 15.7. HRMS (ESI^+): *m*/*z* for $C_{14}H_{18}O_3Na$ $[M+Na]^+$ calcd. 245.1517, found 245.1508.

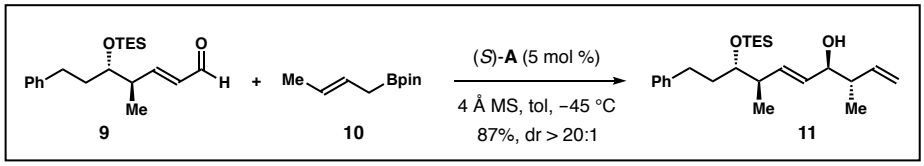


(4*S*,5*R*)-4-Methyl-7-phenyl-5-((triethylsilyl)oxy)hept-2-en-1-ol (a mixture of *Z* and *E* isomers) To an oven-dried reaction flask containing a magnetic stir bar and freshly activated 4 Å molecular sieves (250 mg) were added chiral phosphoric acid (*S*)-**A** (75 mg, 0.1 mmol, 0.01 equiv), toluene (4 mL) and hydrocinnamic aldehyde (134 mg, 1 mmol, 1.0 equiv). The reaction flask was placed in a −45 °C cold bath and stirred for 5 min. Then a solution of boronate (±)-**3** (419 mg, 1.3 mmol, 1.3 equiv) in toluene (1 mL) was added slowly to the reaction mixture *via* a microliter syringe. The resulting mixture was kept stirring at −45 °C. After complete consumption of hydrocinnamic aldehyde, imidazole (204 mg, 3 mmol, 3.0 equiv), TESCl (377 mg, 2.5 mmol, 2.5 equiv) and DMF (5 mL) were sequentially added to the reaction flask. The resulting mixture was allowed to warm to ambient temperature, and the reaction process was monitored by TLC analysis. After completion of the reaction, a solution of 3N NaOH (5 mL) was added to the flask followed by slow addition of 30% H_2O_2 (5 mL) at 0 °C. The resulting mixture was stirred vigorously at 0 °C for 3 h. Then diethyl ether (10 mL) was added. The organic layer was separated and the aqueous layer was extracted with diethyl ether (10 mL x 3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product by flash column

chromatography (gradient elution with hexane and ethyl acetate) gave a 3:1 mixture of allylic alcohols **7** and **8** as a colorless oil (241 mg, 72%).

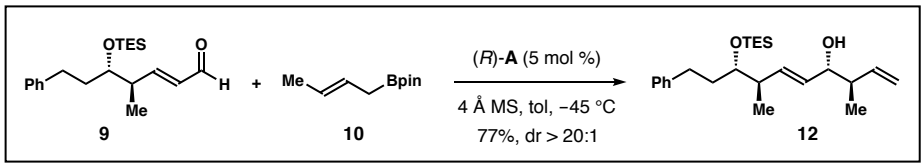


(4*S*,5*R*,*E*)-4-Methyl-7-phenyl-5-((triethylsilyl)oxy)hept-2-enal (9) To a reaction flask containing allylic alcohols **7** and **8** (234 mg, 0.7 mmol, 1.0 equiv) were sequentially added a Teflon-coated magnetic stirring bar and dichloromethane (5 mL). The reaction was stirred at ambient temperature for 5 min. Then Dess-Martin periodinane (445 mg, 1.05 mmol, 1.5 equiv) and water (0.1 mL) were added. The reaction mixture was kept stirring at ambient temperature, and the reaction process was monitored by TLC analysis. After complete consumption of the allylic alcohols, hexane and diethyl ether (10 mL, v:v = 9:1) was added to the flask and the resulting mixture was filtered through a pad of silica gel. The filtrate was concentrated under reduced pressure to give a mixture of two aldehydes. The resulting crude aldehydes were dissolved in CH_3CN (2 mL), and DMAP (30 mg, 0.35 mmol, 0.5 equiv) was added. The reaction mixture was stirred at ambient temperature for 48 h. The *E*/*Z* ratio was determined to be >50:1 by ^{1}H NMR analysis of the crude reaction mixture. The solvent was removed under reduced pressure. Purification of the crude product was performed by flash chromatography (gradient elution with hexane and ethyl acetate) to give aldehyde **9** as a colorless oil (78%, 182 mg, *E*:*Z* > 50:1, 92% ee). $[\alpha]_D^{20} = -2.4$ (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.52 (d, *J* = 7.8 Hz, 1H), 7.27 (dd, *J* = 7.6, 7.4 Hz, 2H), 7.19 (dd, *J* = 7.4, 7.3 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 2H), 6.88 (dd, *J* = 15.8, 7.8 Hz, 1H), 6.12 (ddd, *J* = 15.8, 7.8, 0.8 Hz, 1H), 3.73 – 3.76 (m, 1H), 2.58 – 2.68 (m, 3H), 1.76 – 1.80 (m, 1H), 1.66 – 1.71 (m, 1H), 1.13 (d, *J* = 6.8 Hz, 3H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.63 (q, *J* = 7.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.5, 160.8, 142.2, 133.2, 128.8, 128.6, 126.3, 75.4, 42.7, 37.1, 32.1, 15.9, 7.3, 5.5. HRMS (ESI$^+$): *m*/*z* for $C_{20}H_{33}O_2Si$ $[M+H]^+$ calcd. 333.2250, found 333.2256.



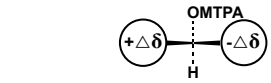
(3*S*,4*R*,7*R*,8*S*,*E*)-3,7-dimethyl-10-phenyl-8-((triethylsilyl)oxy)deca-1,5-dien-4-ol (11) To an oven-dried reaction flask containing a magnetic stir bar and freshly activated 4 Å

molecular sieves (50 mg) were added chiral phosphoric acid (*S*)-**A** (4 mg, 0.005 mmol, 0.005 equiv), aldehyde **9** (33 mg, 0.1 mmol, 1.0 equiv) and toluene (0.2 mL). The reaction flask was placed in a −45 °C cold bath and stirred for 5 min. Then a solution of allylboronate **10** (25 mg, 0.15 mmol, 1.5 equiv) in toluene (0.1 mL) was added slowly to the reaction mixture *via* a microliter syringe. The resulting mixture was kept stirring at −45 °C for 24 h. After complete consumption of the aldehyde, diethyl ether (5 mL) was added and the resulting mixture was filtered through a pad of silica gel. The filtrate was concentrated under reduced pressure. Purification of the crude product by flash column chromatography (gradient elution with hexane and ethyl acetate) gave product **11** as a colorless oil (dr > 20:1, 34 mg, 87%). $[\alpha]_D^{20}$ = – 1.0 (c 0.95, $CHCl_3$);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.28 (d, *J* = 4.6 Hz, 2H), 7.15 – 7.19 (m, 3H), 5.72 – 5.79 (m, 1H), 5.65 (dd, *J* = 15.6, 7.7 Hz, 1H), 5.44 (dd, *J* = 15.6, 7.2 Hz, 1H), 5.11 – 5.14 (m, 2H), 3.83 (dd, *J* = 7.1, 7.1 Hz, 1H), 3.62 – 3.65 (m, 1H), 2.66 – 2.72 (m, 1H), 2.50 – 2.56 (m, 1H), 2.35 – 2.42 (m, 1H), 2.21 – 2.28 (m, 1H), 1.67 – 1.71 (m, 2H), 1.65 (brs, 1H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.96 – 1.00 (m, 12H), 0.62 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 140.8, 135.7, 131.2, 128.68, 128.65, 126.1, 116.7, 76.6, 76.1, 44.9, 42.3, 36.1, 32.7, 16.5, 15.9, 7.4, 5.6. HRMS (ESI$^+$): *m*/*z* for $C_{24}H_{41}O_2Si$ $[M+H]^+$ calcd. 389.2876, found 389.2871.

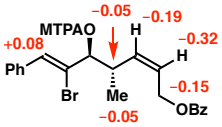


(3*R*,4*S*,7*R*,8*S*,*E*)-3,7-dimethyl-10-phenyl-8-((triethylsilyl)oxy)deca-1,5-dien-4-ol (12)
The procedure for the synthesis of compound **11** was adopted with (*R*)-**A** as the catalyst. Purification of the crude product by flash column chromatography (gradient elution with hexane and ethyl acetate) gave product **12** as a colorless oil (dr > 20:1, 30 mg, 77%). $[\alpha]_D^{20}$ = + 0.7 (c 0.95, $CHCl_3$);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.28 (m, 2H), 7.16 – 7.19 (m, 3H), 5.72 – 5.79 (m, 1H), 5.66 (dd, *J* = 15.6, 7.3 Hz, 1H), 5.44 (dd, *J* = 15.6, 7.3 Hz, 1H), 5.11 – 5.15 (m, 2H), 3.82 (dd, *J* = 7.2, 7.3 Hz, 1H), 3.64 – 3.67 (m, 1H), 2.68 – 2.74 (m, 1H), 2.51 – 2.57 (m, 1H), 2.37 – 2.43 (m, 1H), 2.20 – 2.27 (m, 1H), 1.67 – 1.71 (m, 2H), 1.66 (brs, 1H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.96 – 0.99 (m, 12H), 0.62 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 140.9, 135.6, 131.1, 128.7 (two overlapping carbon signals), 126.0, 116.7, 76.7, 75.8, 44.9, 42.3, 35.9, 32.8, 16.5, 15.4, 7.4, 5.6. HRMS (ESI$^+$): *m*/*z* for $C_{24}H_{41}O_2Si$ $[M+H]^+$ calcd. 389.2876, found 389.2878.

Assignment of the absolute configuration of the secondary alcohol using modified Mosher ester analysis:[2]

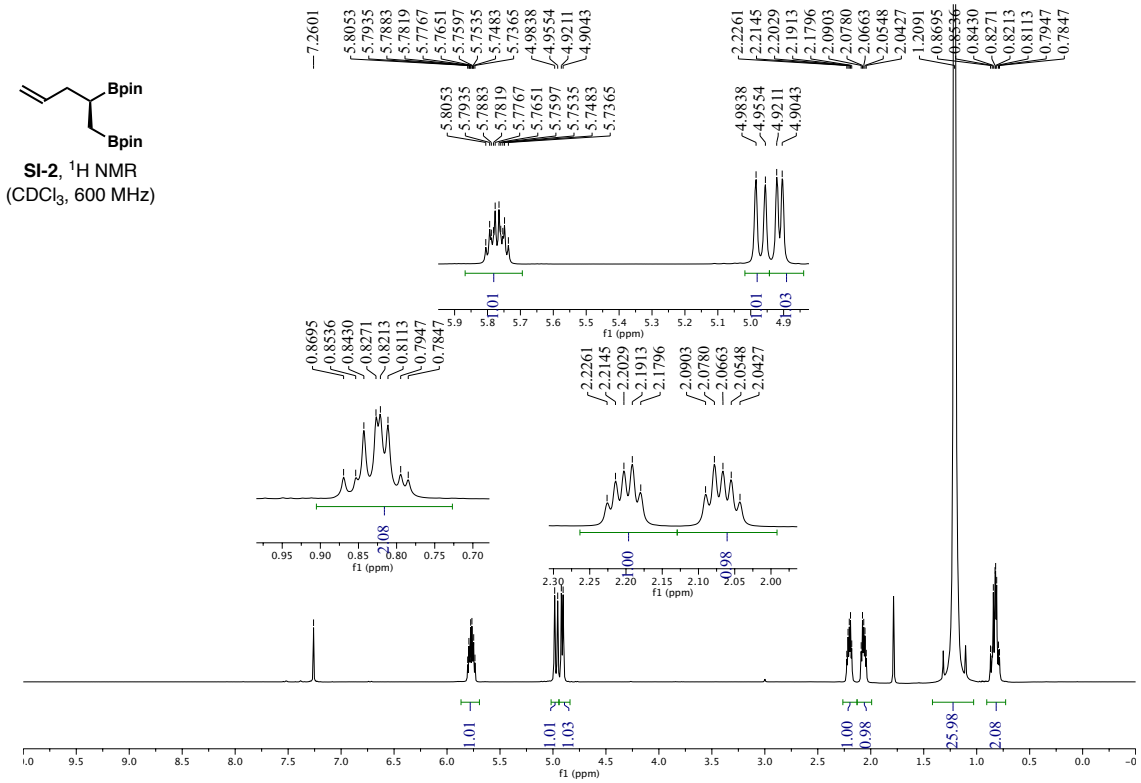


$\triangle\delta = \delta_{S\text{-ester}} - \delta_{R\text{-ester}}$

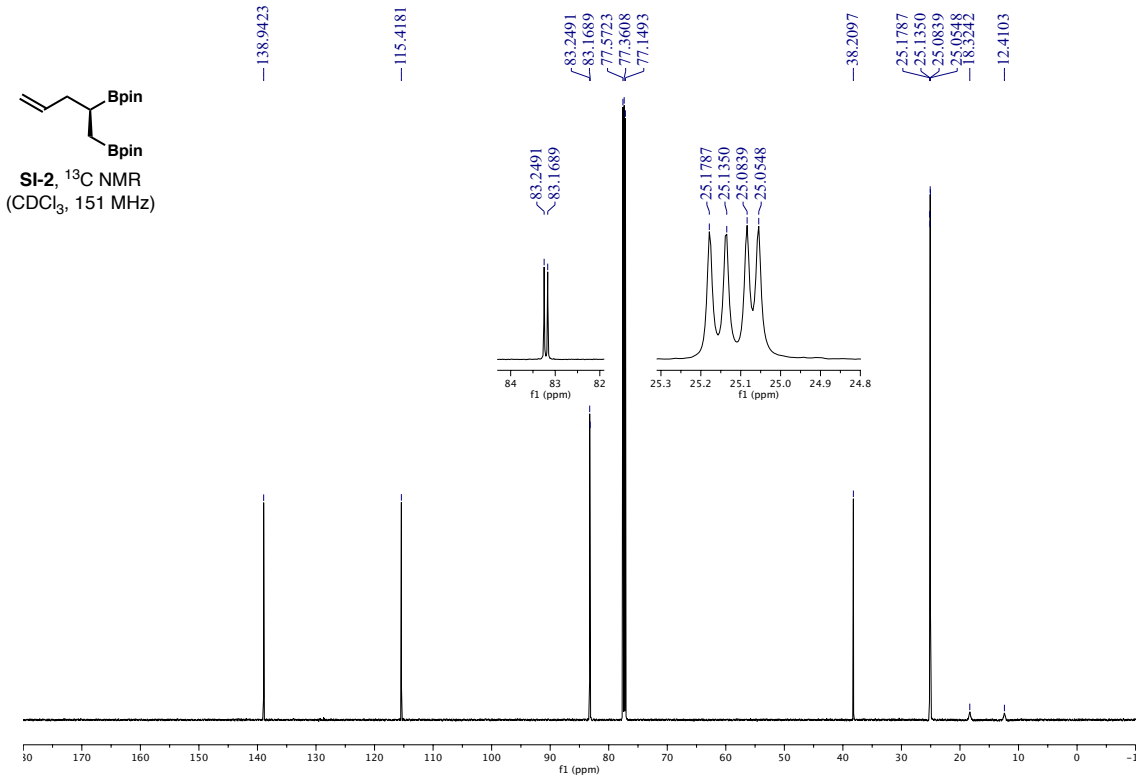


Reference:

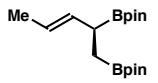
1. (a) Ishiyama, T.; Yamamoto, M.; Miyaura, N. *Chem. Commun*. **1997**, 689. (b) Davenport, E.; Fernández, E. *Chem. Commun.* **2018**, *54*, 10104. (c) R. J. Maza, R. Davenport, N. Miralles, J. J. Carbó, E. Fernández, *Org. Lett.* **2019**, *21*, 2251.
2. (a) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512. (b) Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc*. **1991**, *113*, 4092.



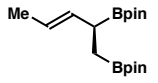
SI-2, ^{1}H NMR
($CDCl_3$, 600 MHz)



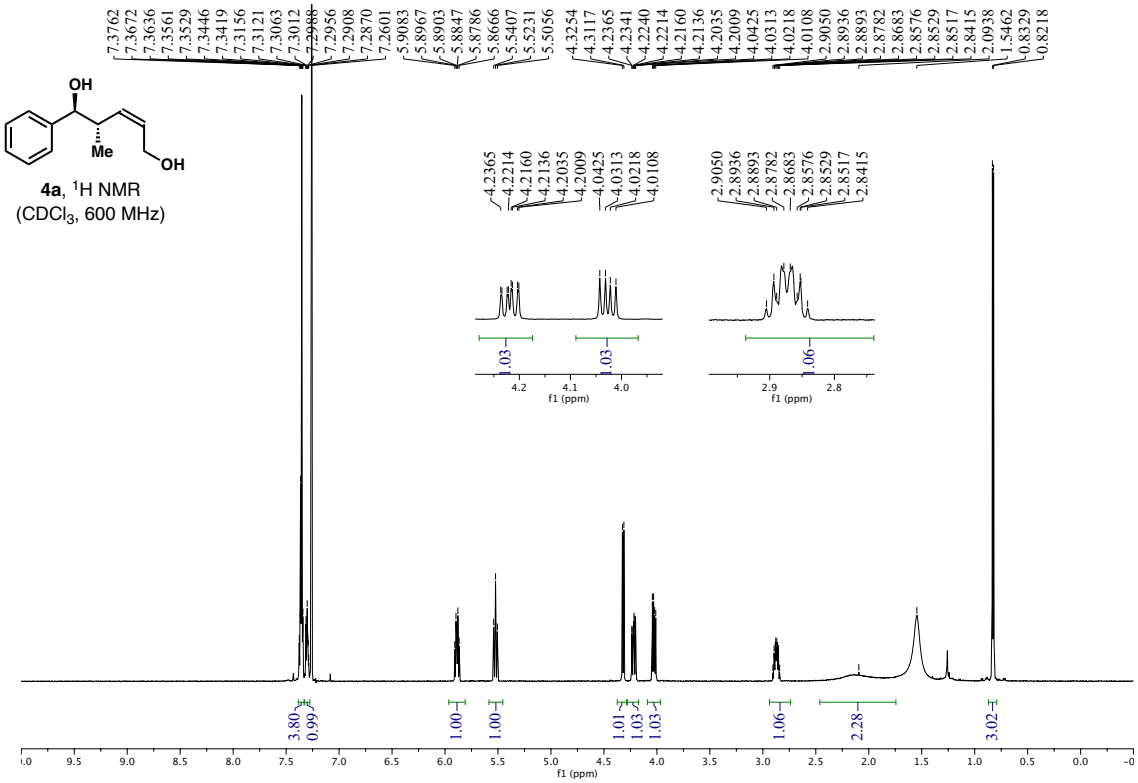
SI-2, ^{13}C NMR
($CDCl_3$, 151 MHz)



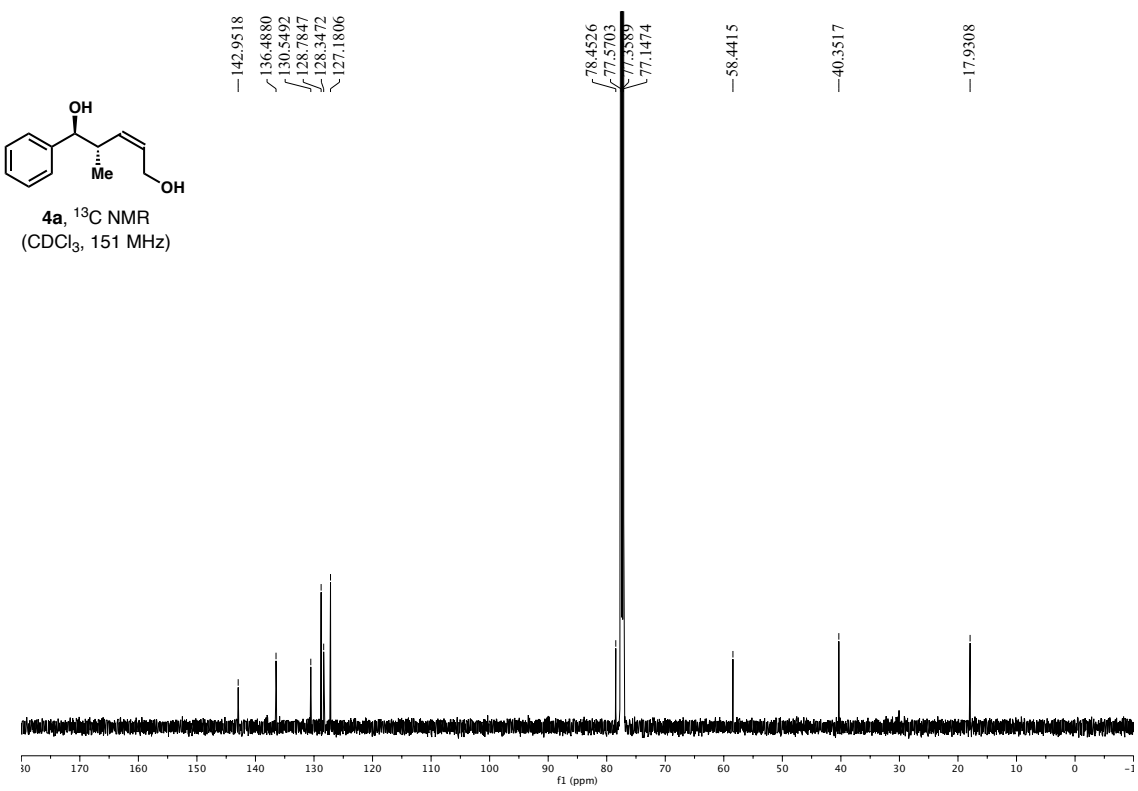
(±)-**3**, ^{1}H NMR
($CDCl_3$, 600 MHz)



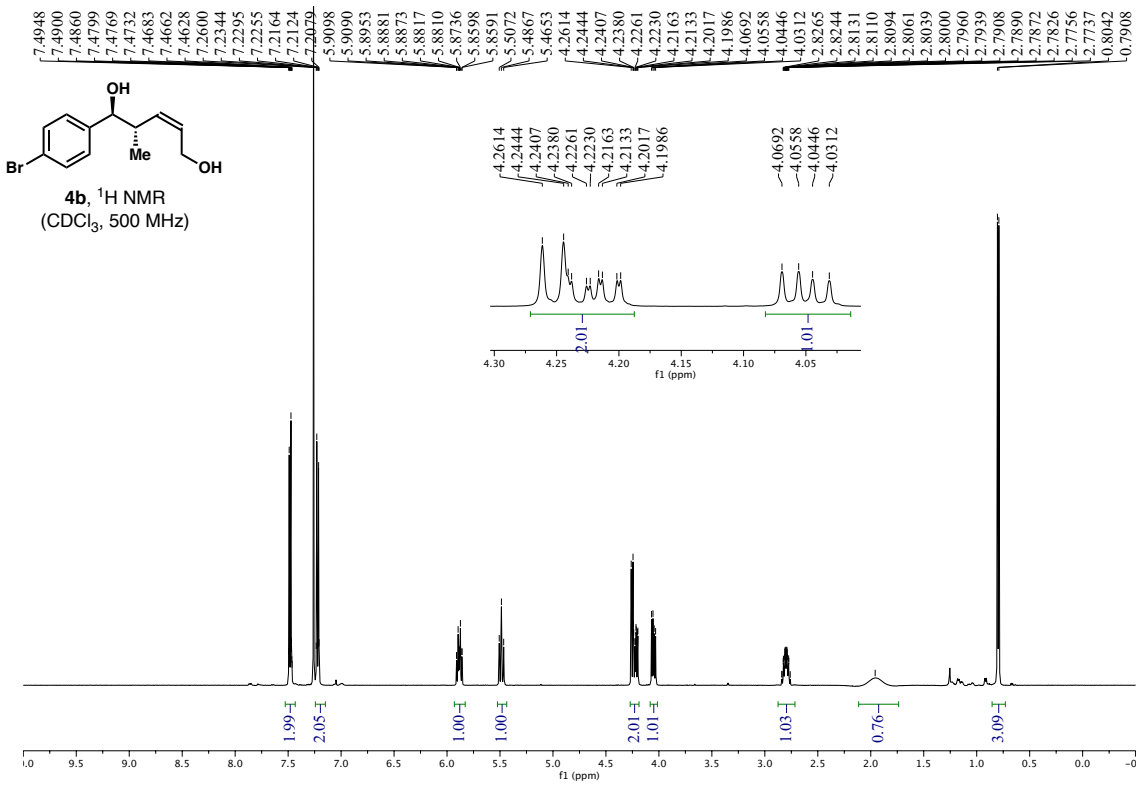
(±)-**3**, ^{13}C NMR
($CDCl_3$, 151 MHz)

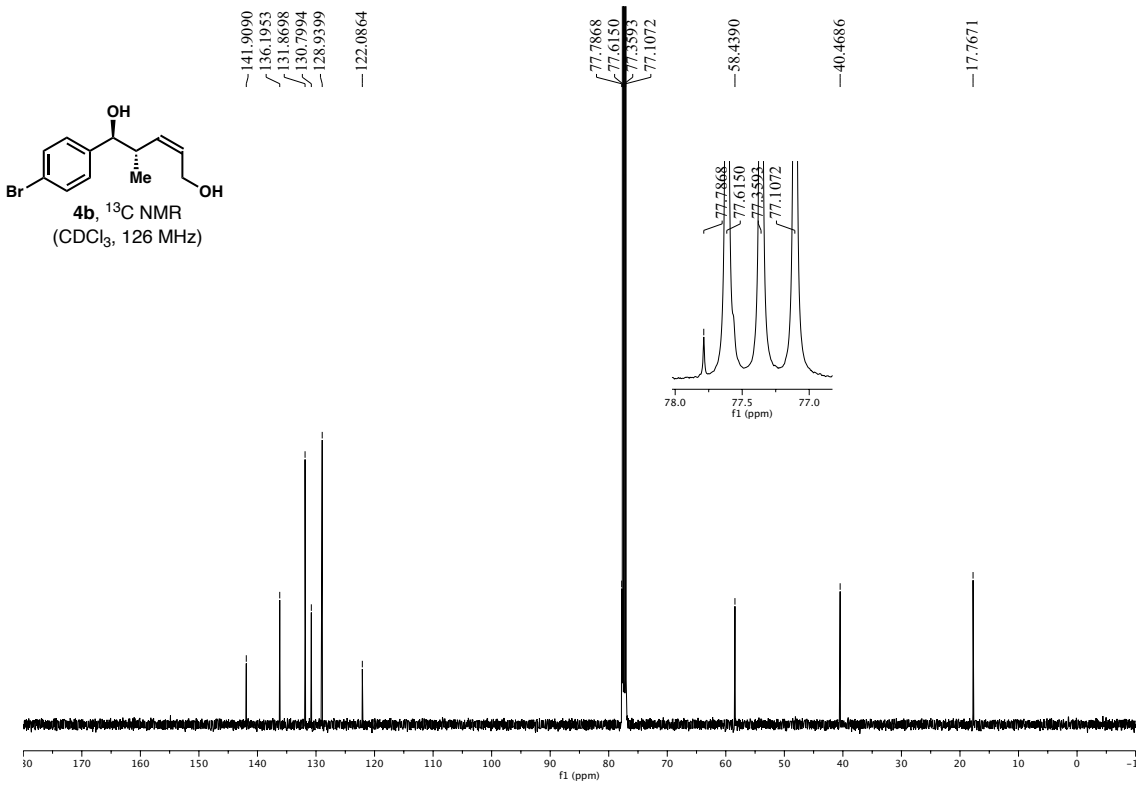


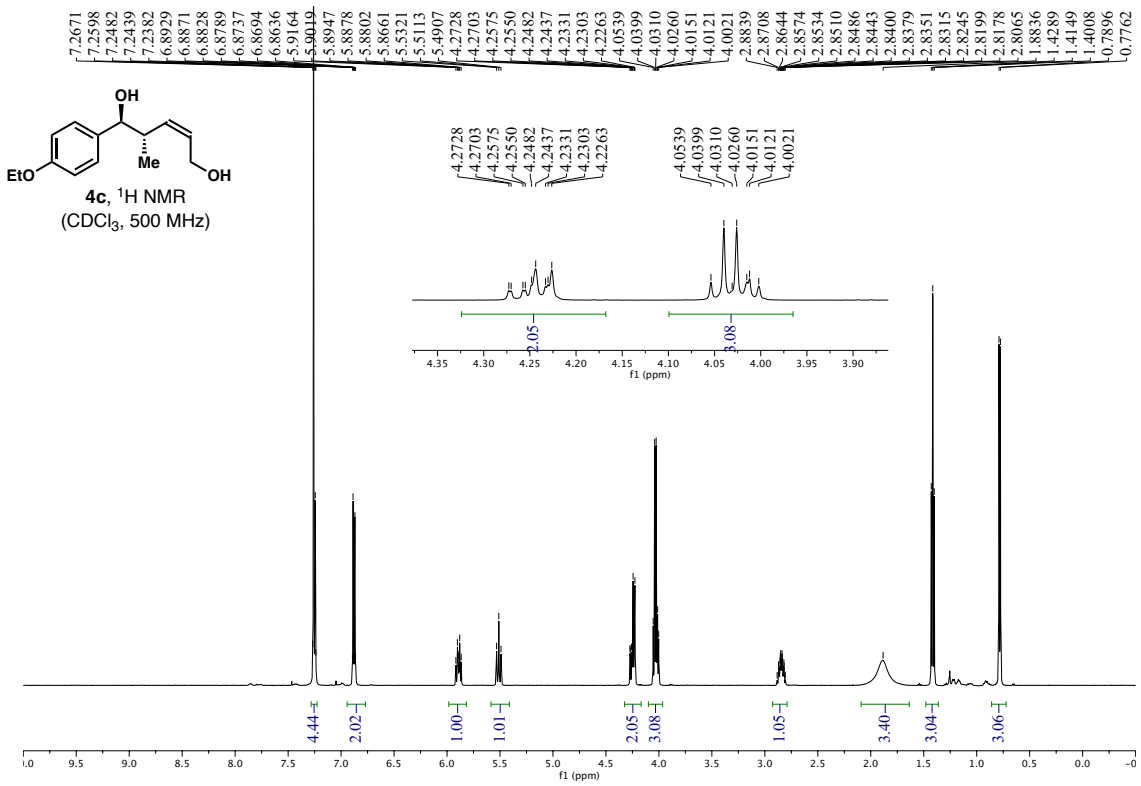
4a, ^{1}H NMR
($CDCl_3$, 600 MHz)

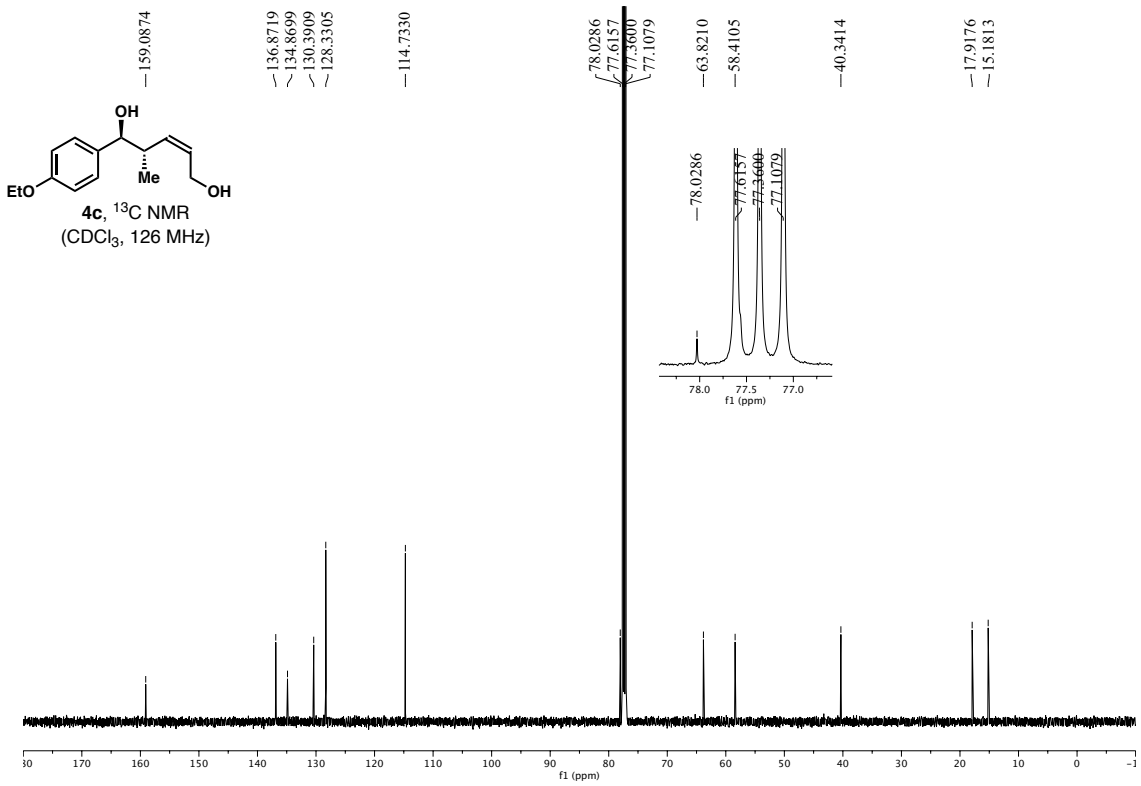


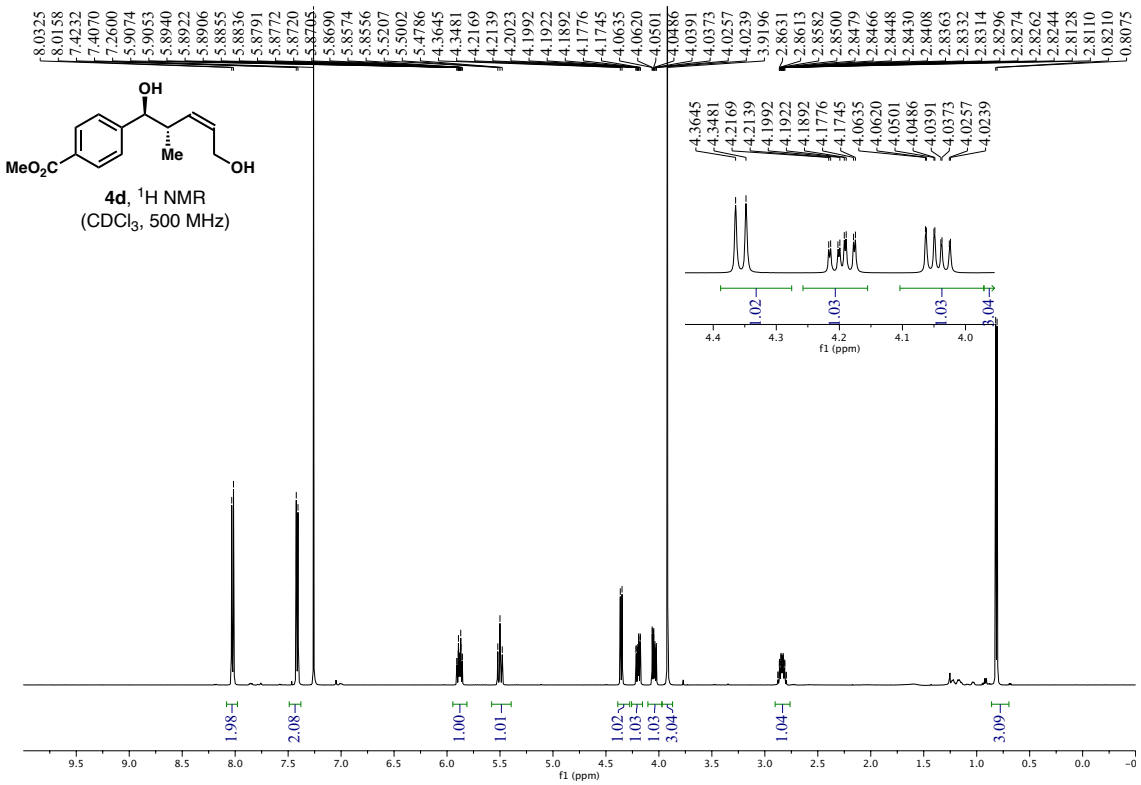
4a, ^{13}C NMR
($CDCl_3$, 151 MHz)

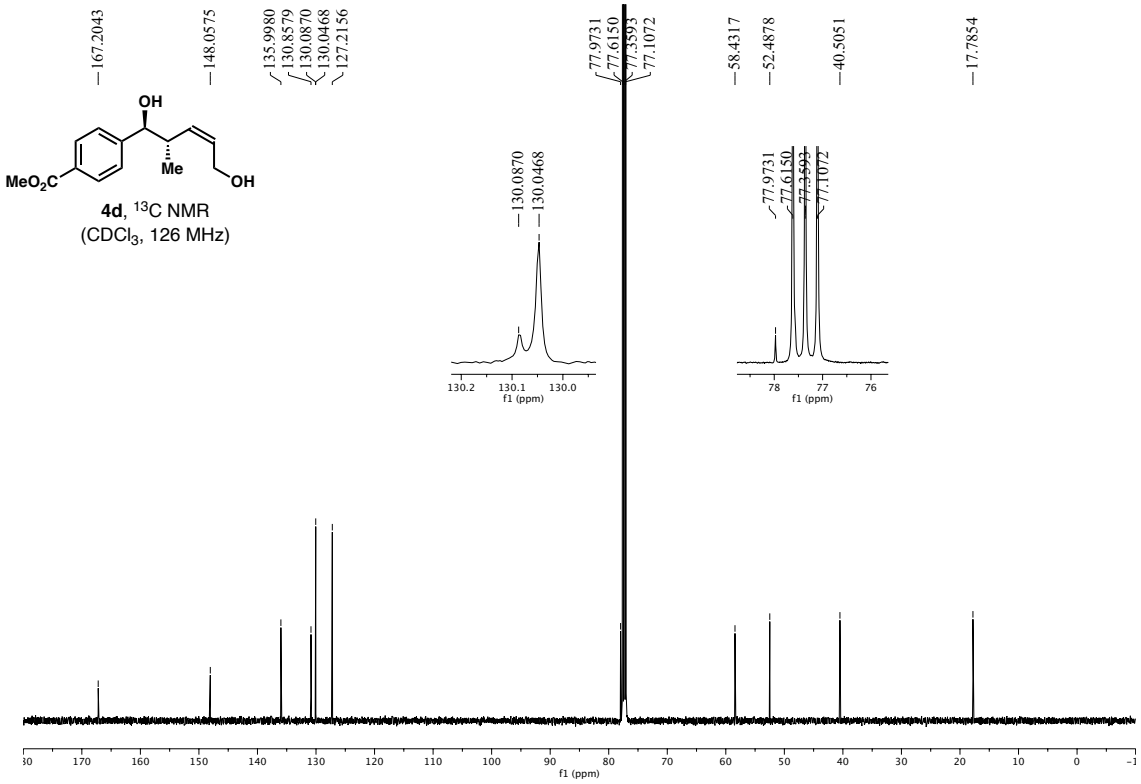

OH
Br
Me
OH
4b, 1H NMR
(CDCl3, 500 MHz)
f1 (ppm)

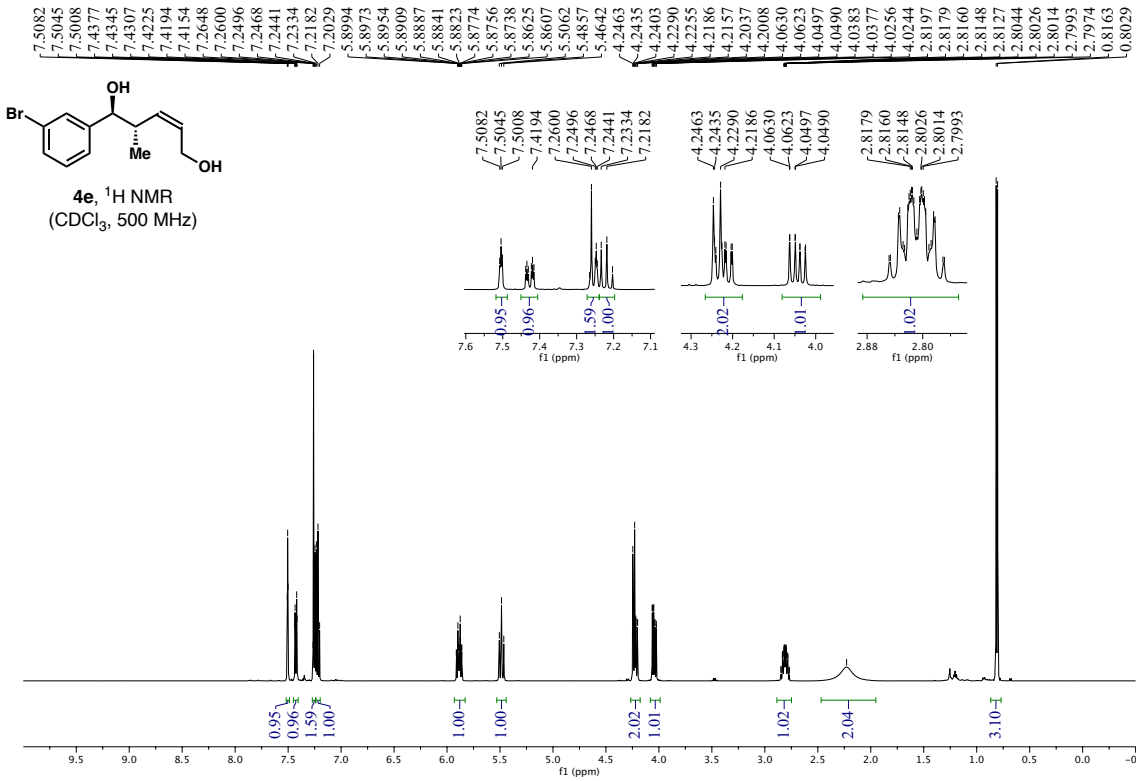

OH
Br
Me
OH
4b, 13C NMR
(CDCl3, 126 MHz)
f1 (ppm)


OH
Me
EtO
OH
4c, 1H NMR
(CDCl3, 500 MHz)
f1 (ppm)

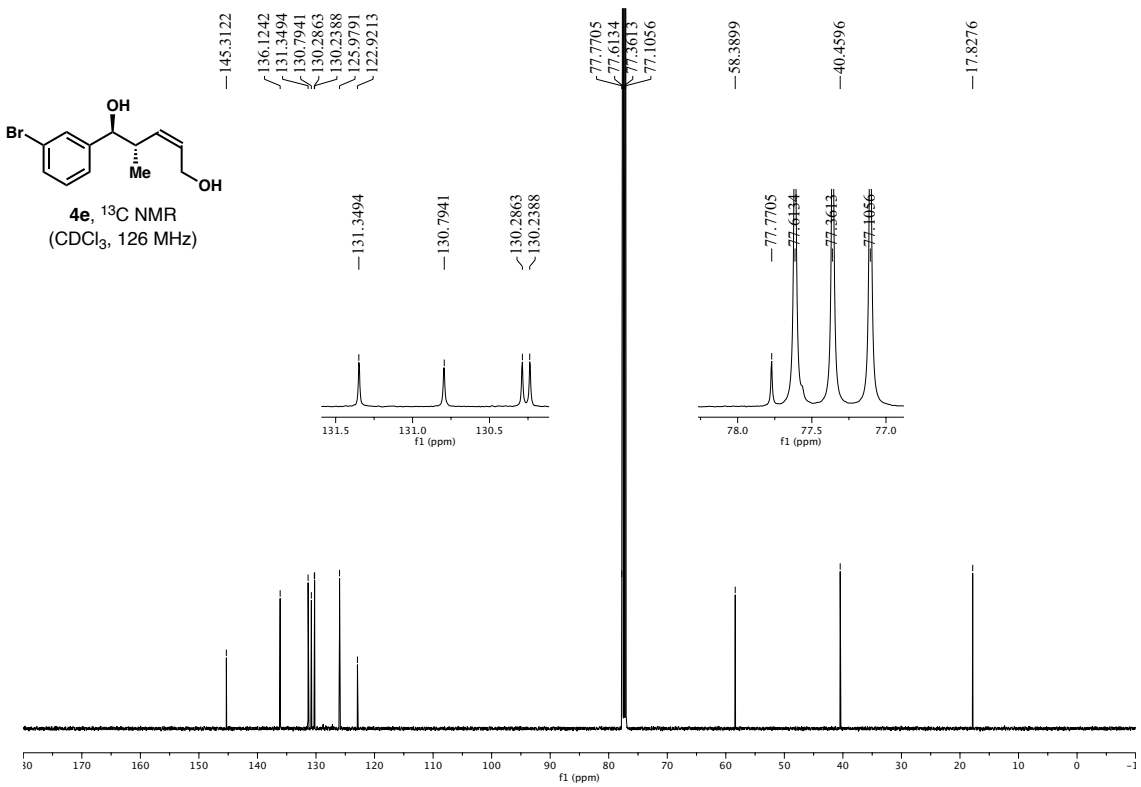

OH
Me
EtO
OH
4c, 13C NMR
(CDCl3, 126 MHz)
f1 (ppm)


OH
Me
MeO2C
OH
4d, 1H NMR
(CDCl3, 500 MHz)
f1 (ppm)

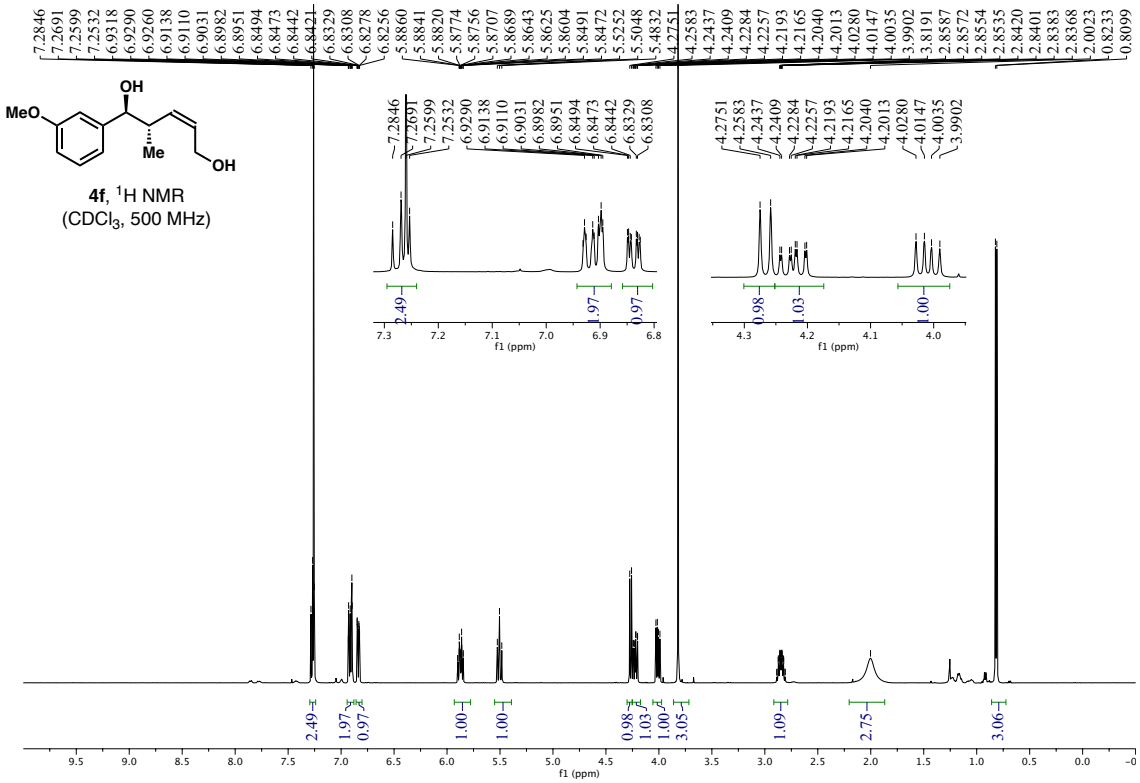

OH
Me
MeO2C
OH
4d, 13C NMR
(CDCl3, 126 MHz)
f1 (ppm)



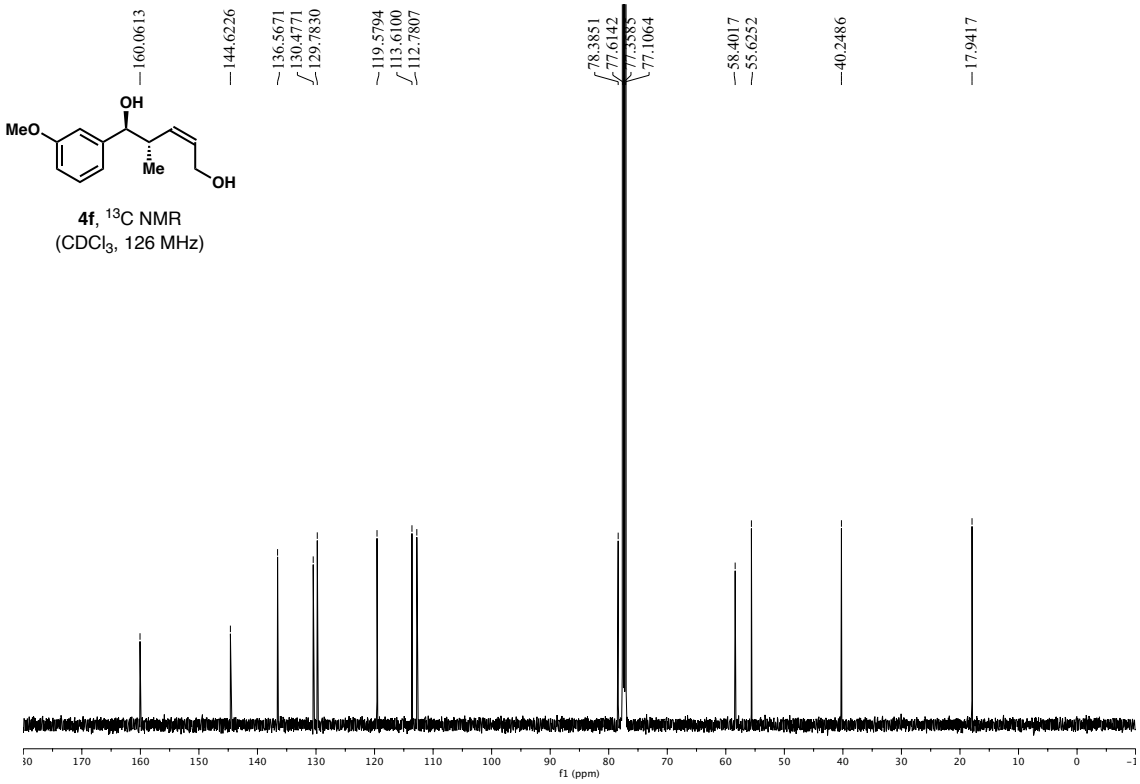
4e, ^{1}H NMR
($CDCl_3$, 500 MHz)



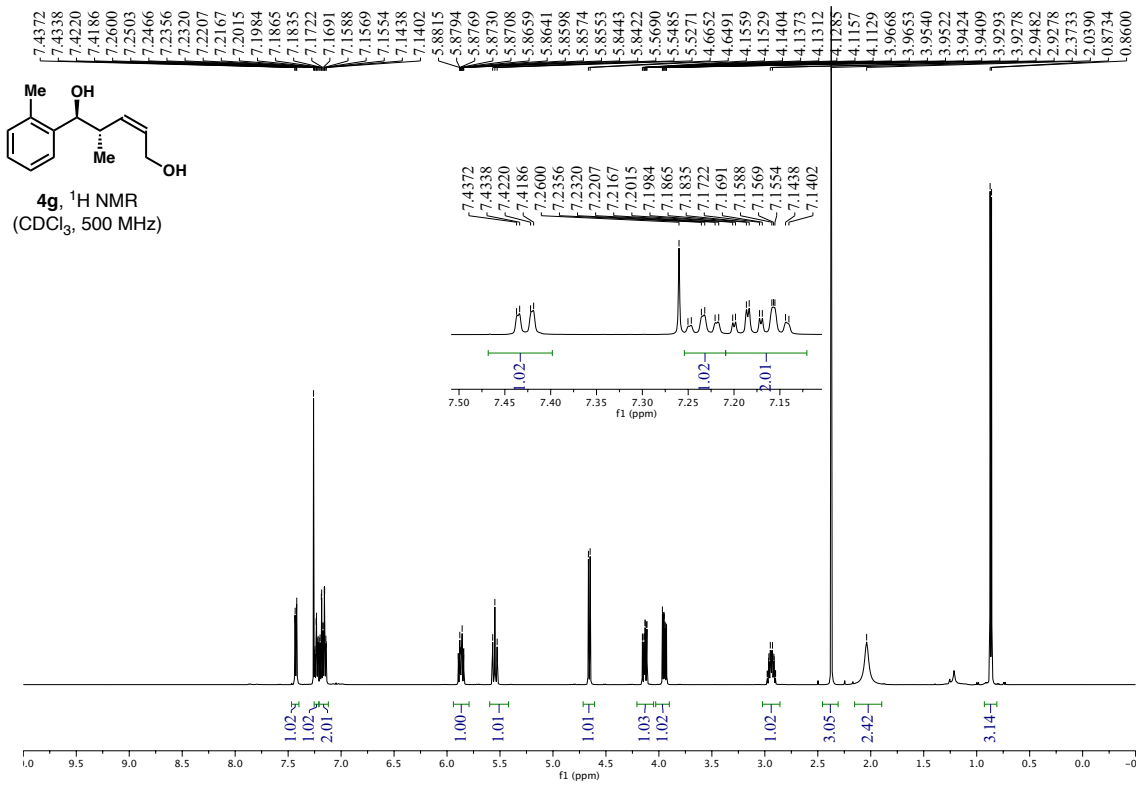
4e, ^{13}C NMR
($CDCl_3$, 126 MHz)



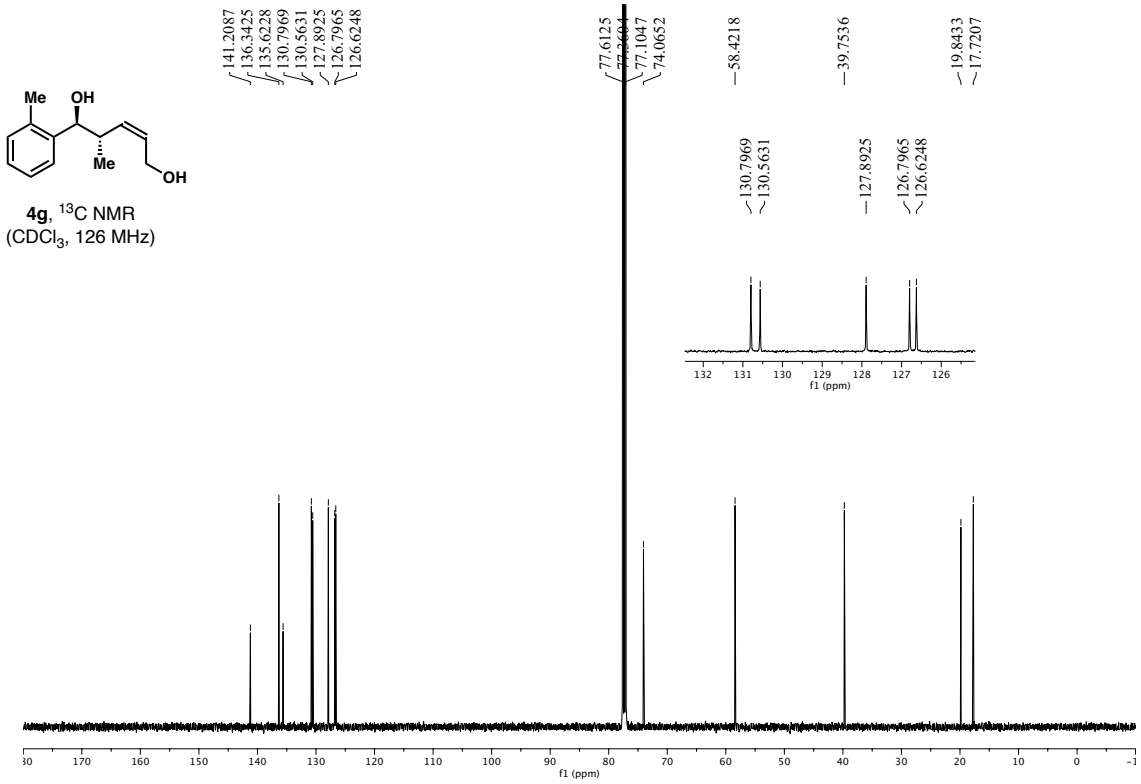
4f, ^{1}H NMR
($CDCl_3$, 500 MHz)



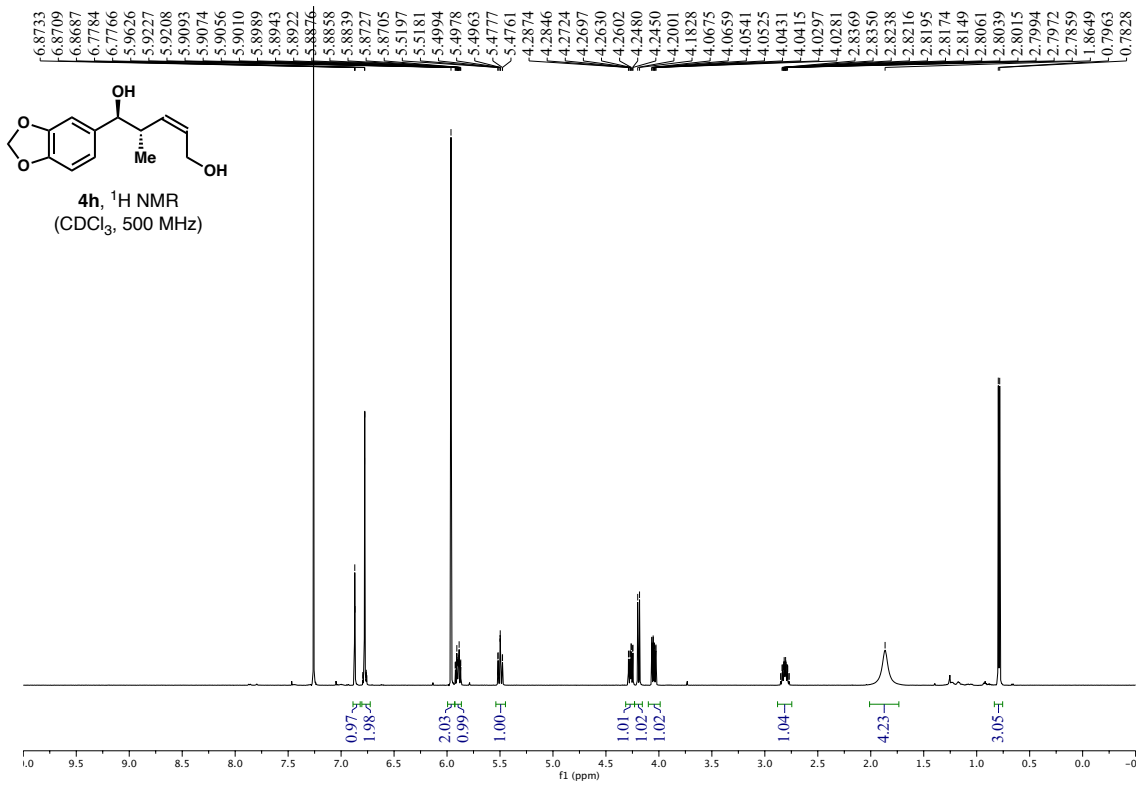
4f, ^{13}C NMR
($CDCl_3$, 126 MHz)



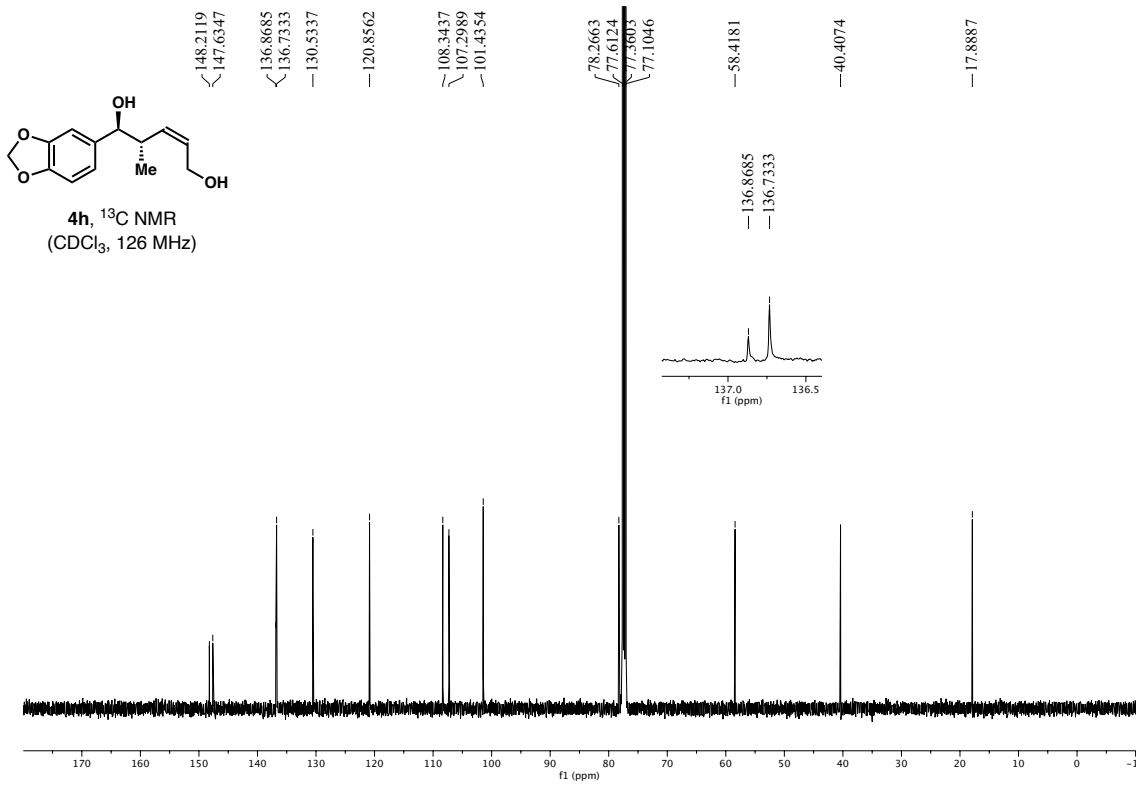
4g, ^{1}H NMR
($CDCl_3$, 500 MHz)



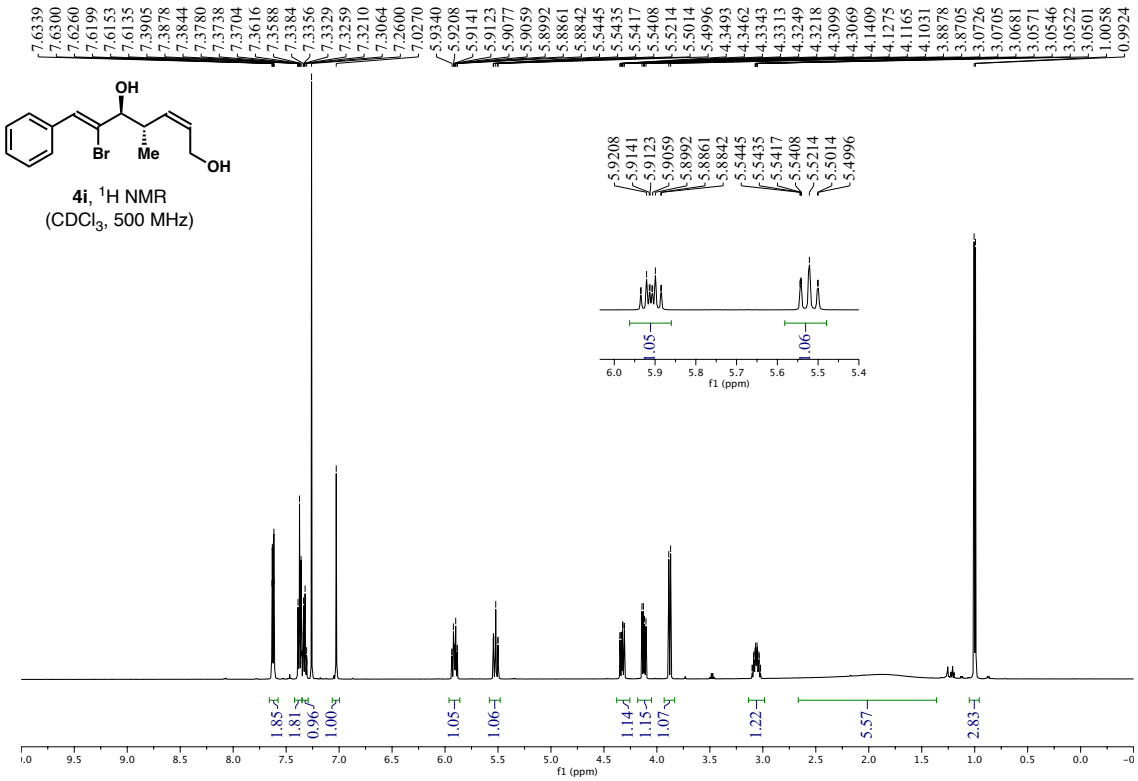
4g, ^{13}C NMR
($CDCl_3$, 126 MHz)

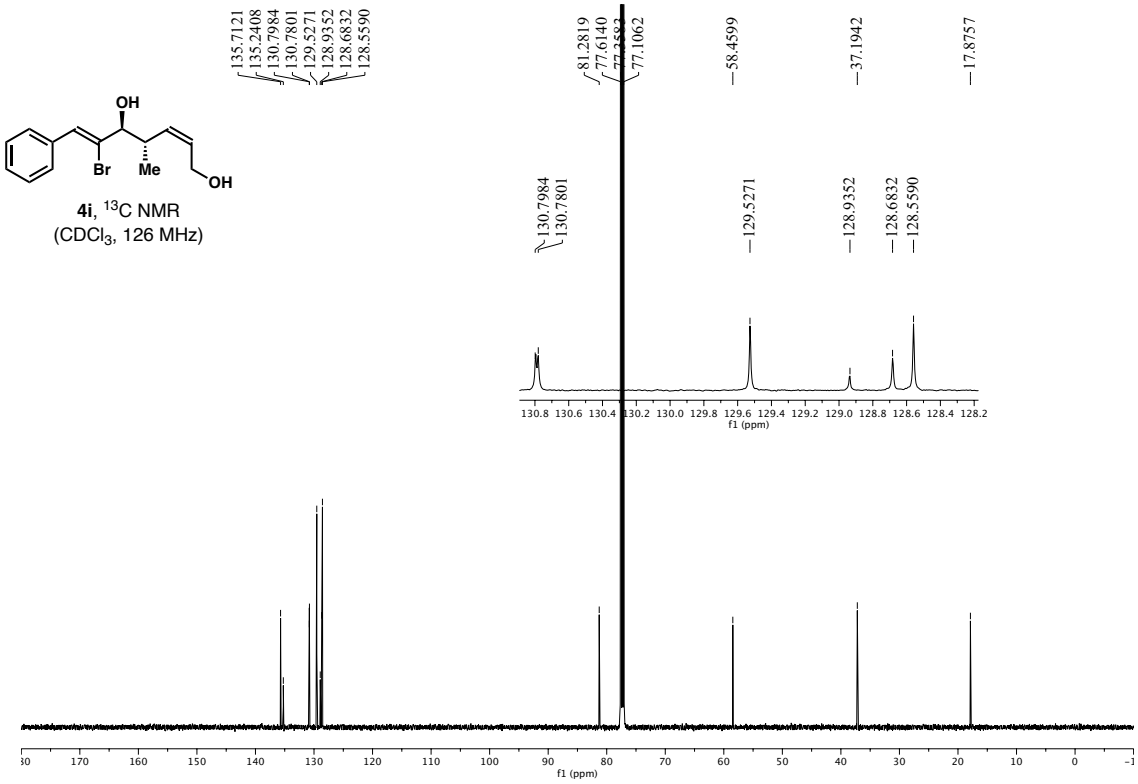


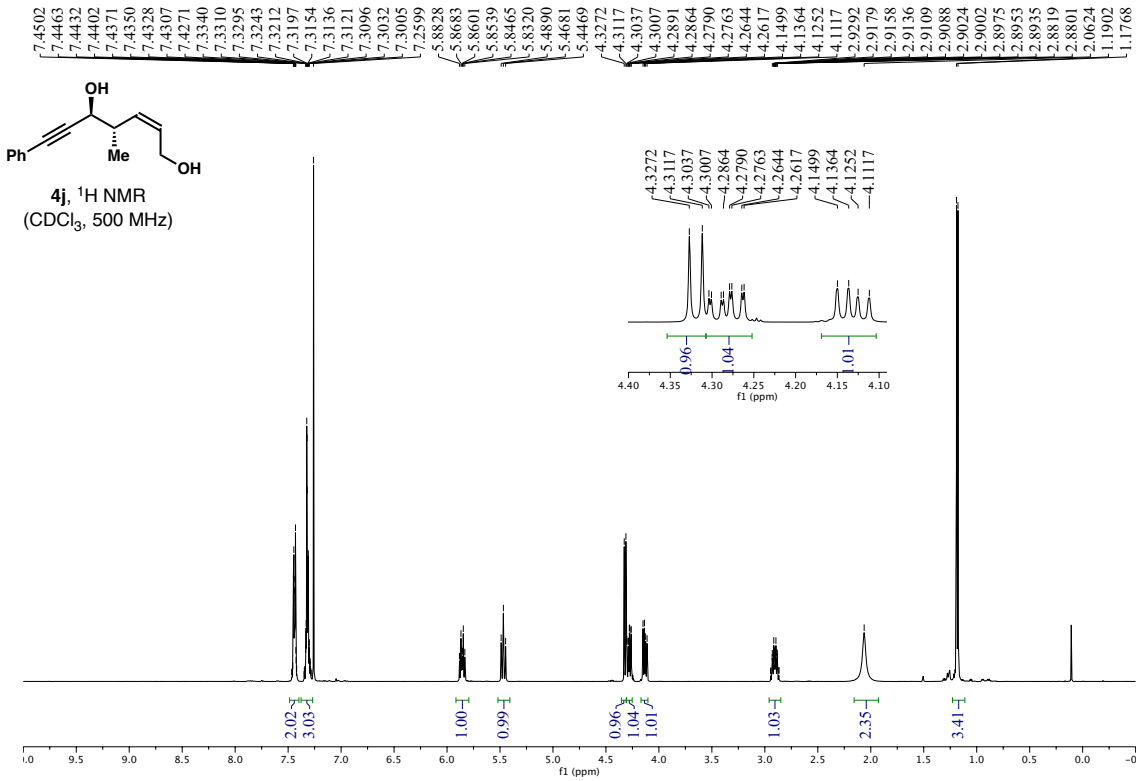
4h, ^{1}H NMR
($CDCl_3$, 500 MHz)



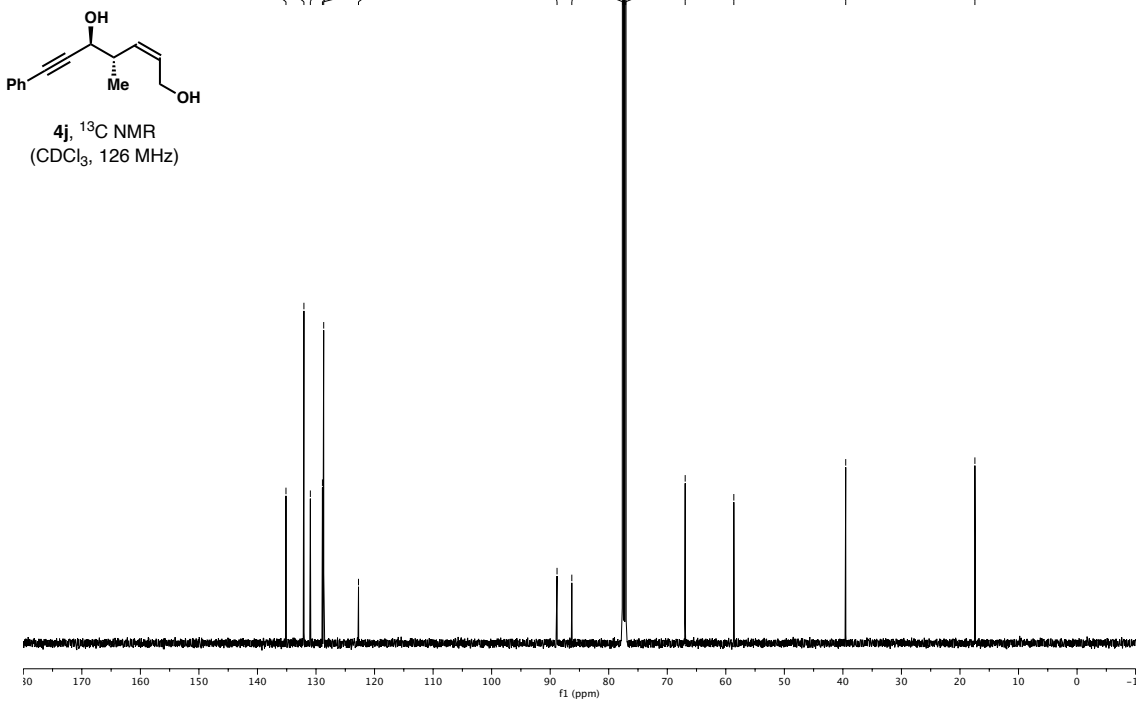
4h, ^{13}C NMR
($CDCl_3$, 126 MHz)


OH
Br
Me
OH
4i, 1H NMR
(CDCl3, 500 MHz)
f1 (ppm)

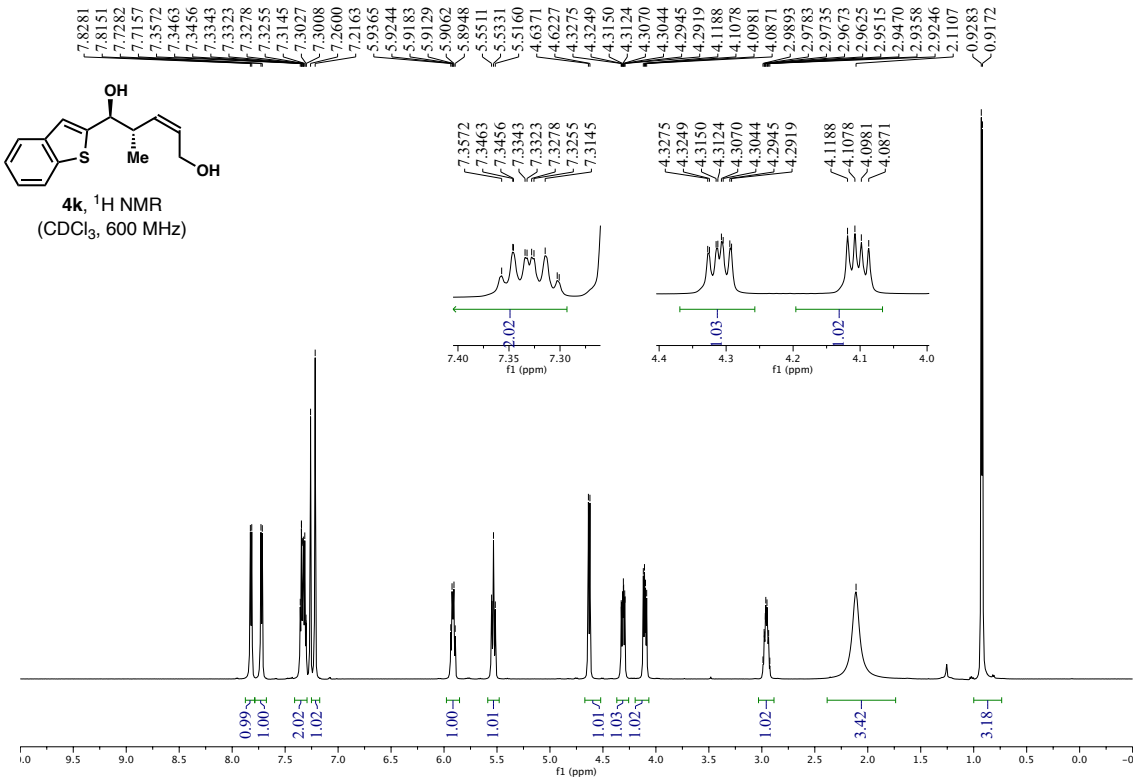

OH
Br
Me
OH
4i, 13C NMR
(CDCl3, 126 MHz)
f1 (ppm)

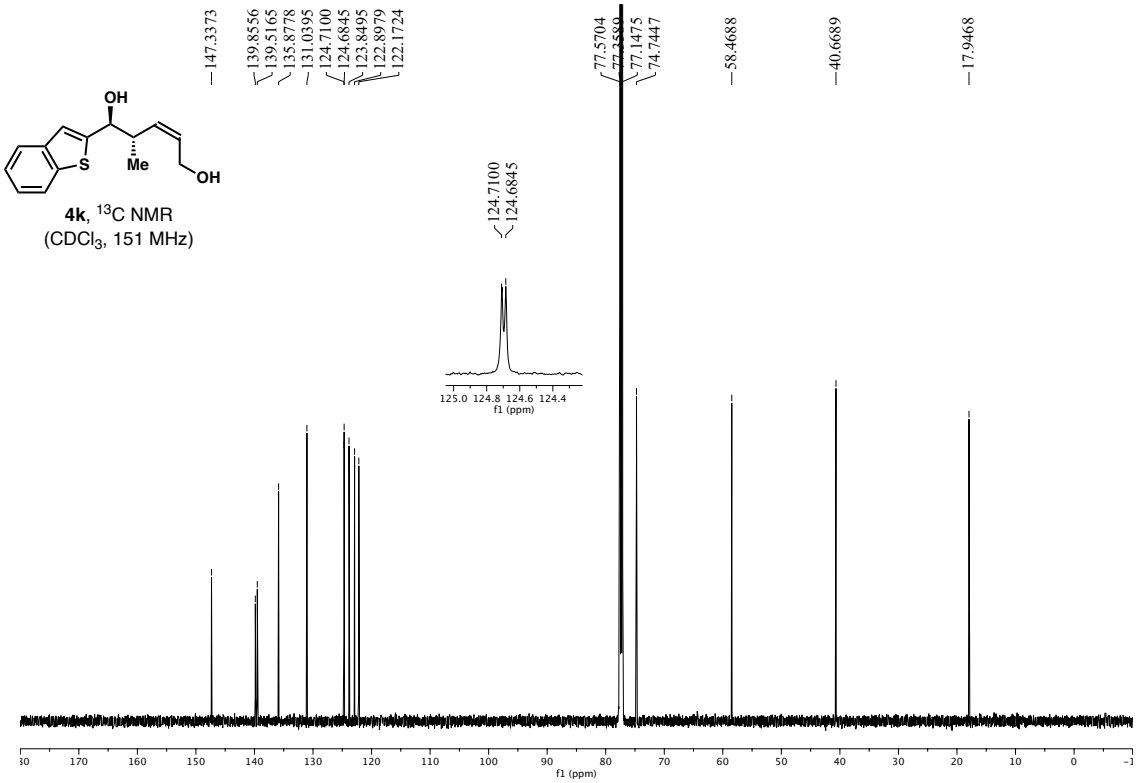


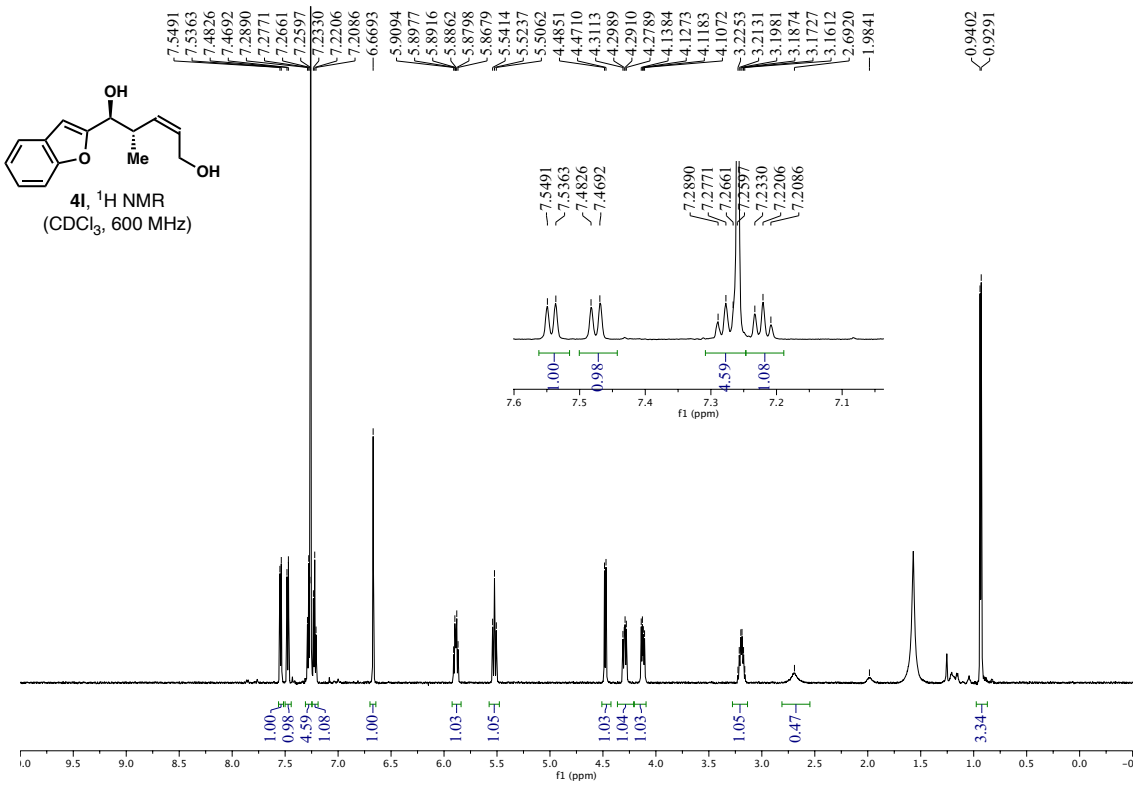
4j, ^{1}H NMR
($CDCl_3$, 500 MHz)



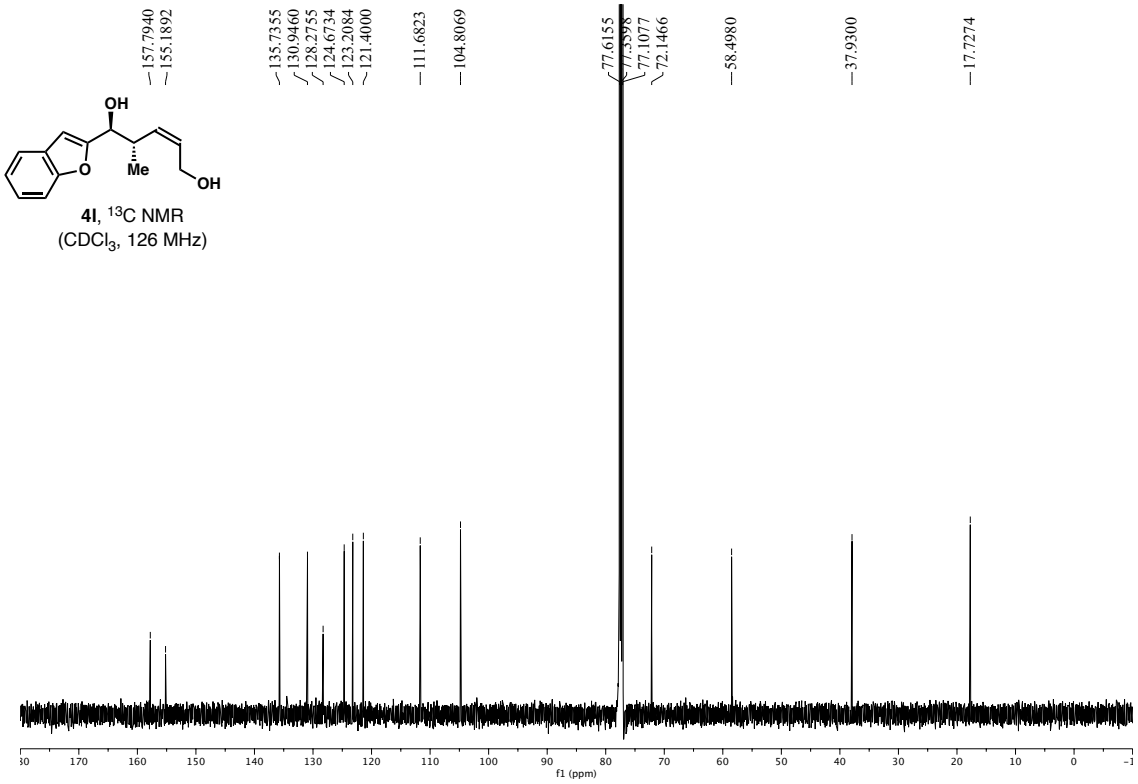
4j, ^{13}C NMR
($CDCl_3$, 126 MHz)


OH
S
Me
OH
4k, 1H NMR
(CDCl3, 600 MHz)
f1 (ppm)

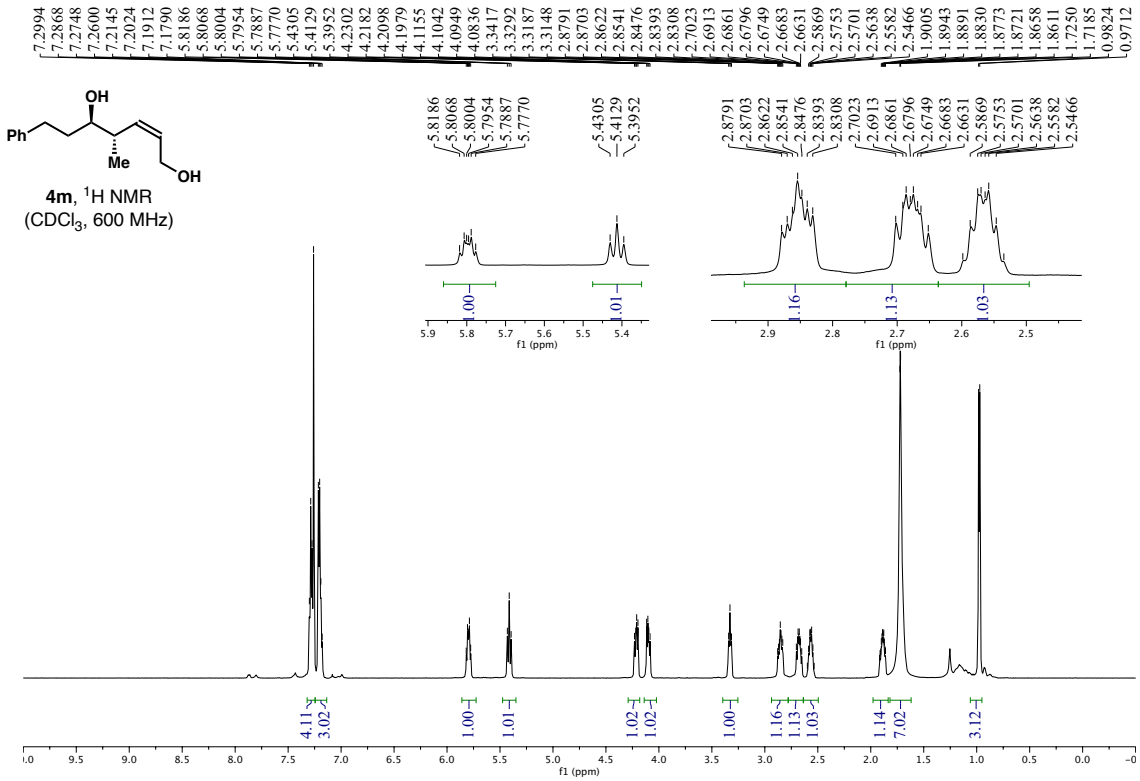

OH
S
Me
OH
4k, 13C NMR
(CDCl3, 151 MHz)
f1 (ppm)



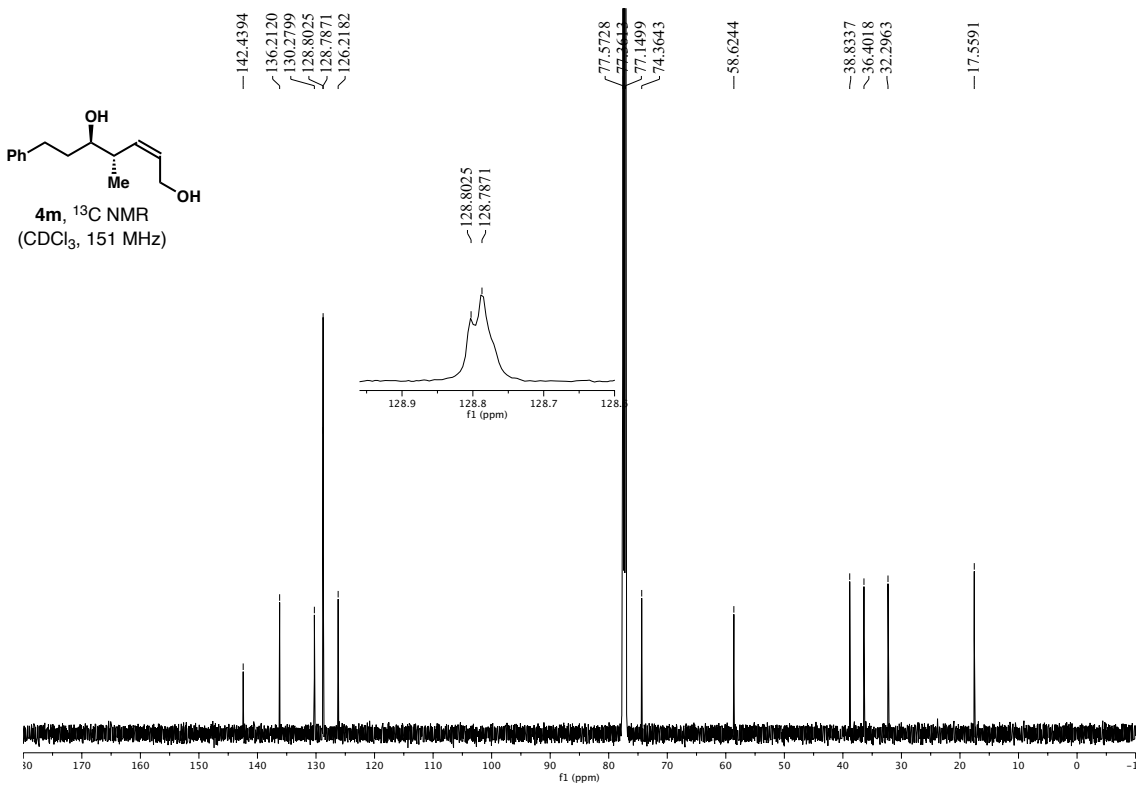
4l, ^{1}H NMR
($CDCl_3$, 600 MHz)



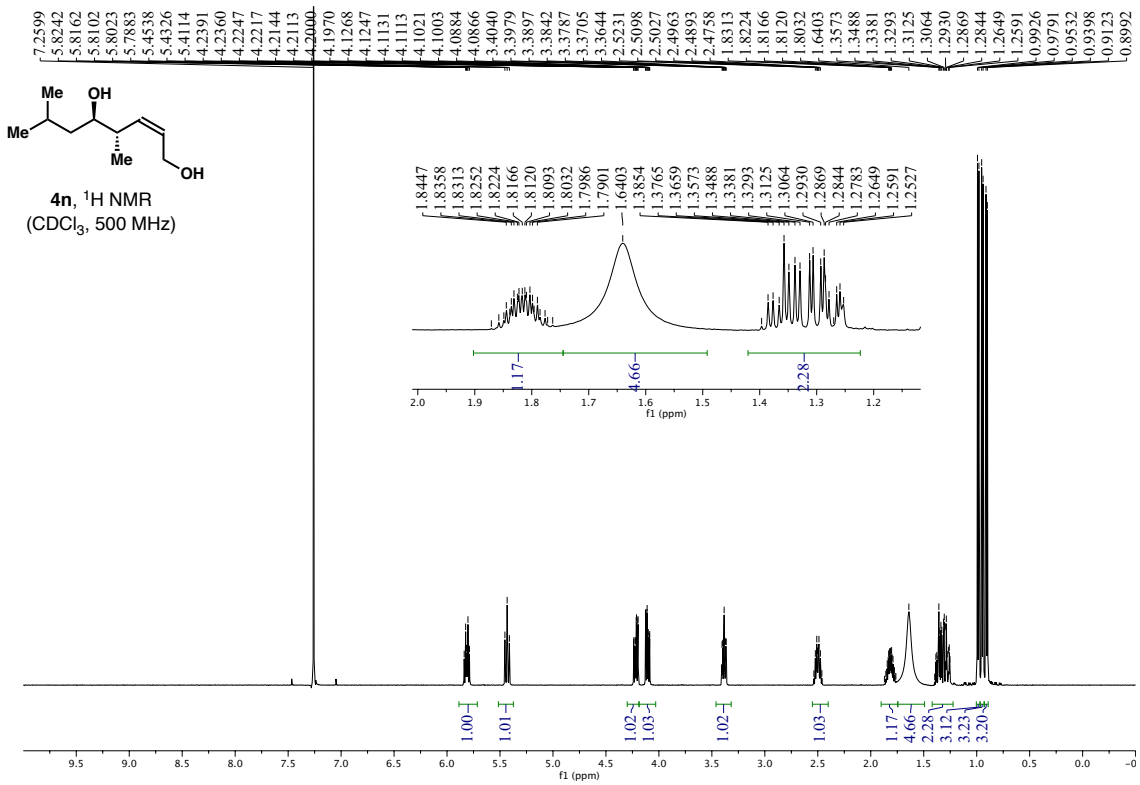
4l, ^{13}C NMR
($CDCl_3$, 126 MHz)



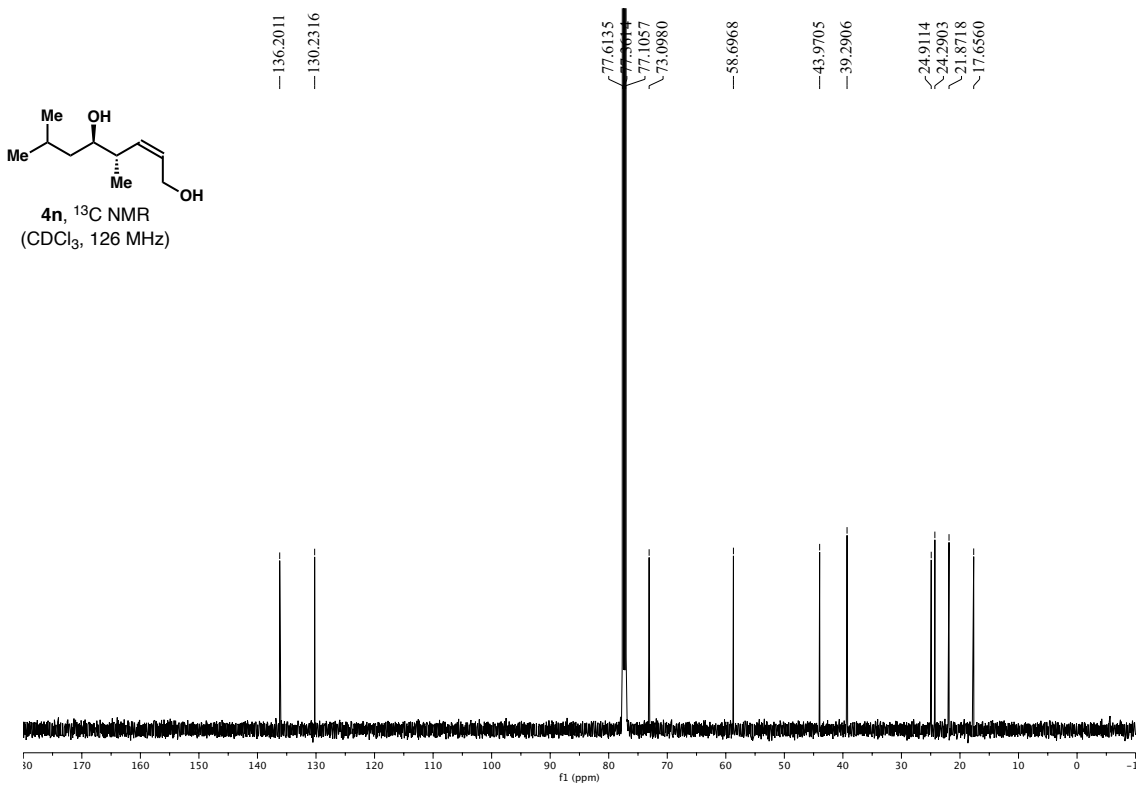
4m, ^{1}H NMR
($CDCl_3$, 600 MHz)



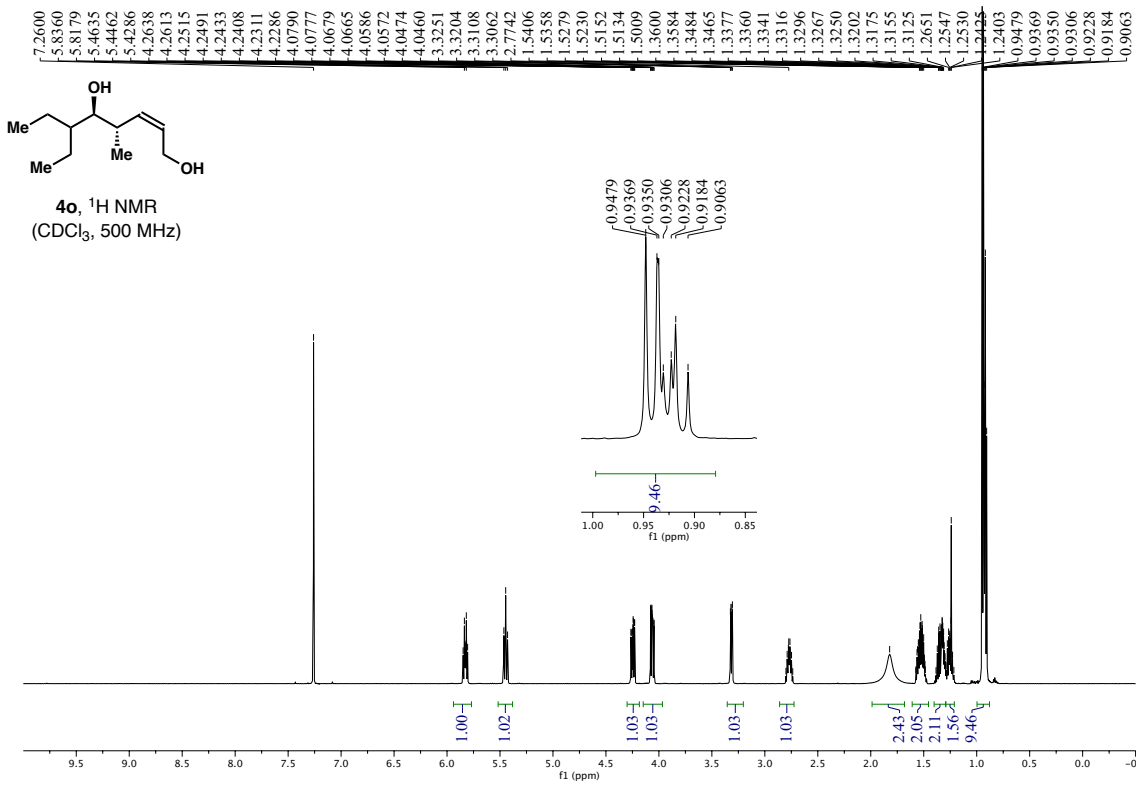
4m, ^{13}C NMR
($CDCl_3$, 151 MHz)



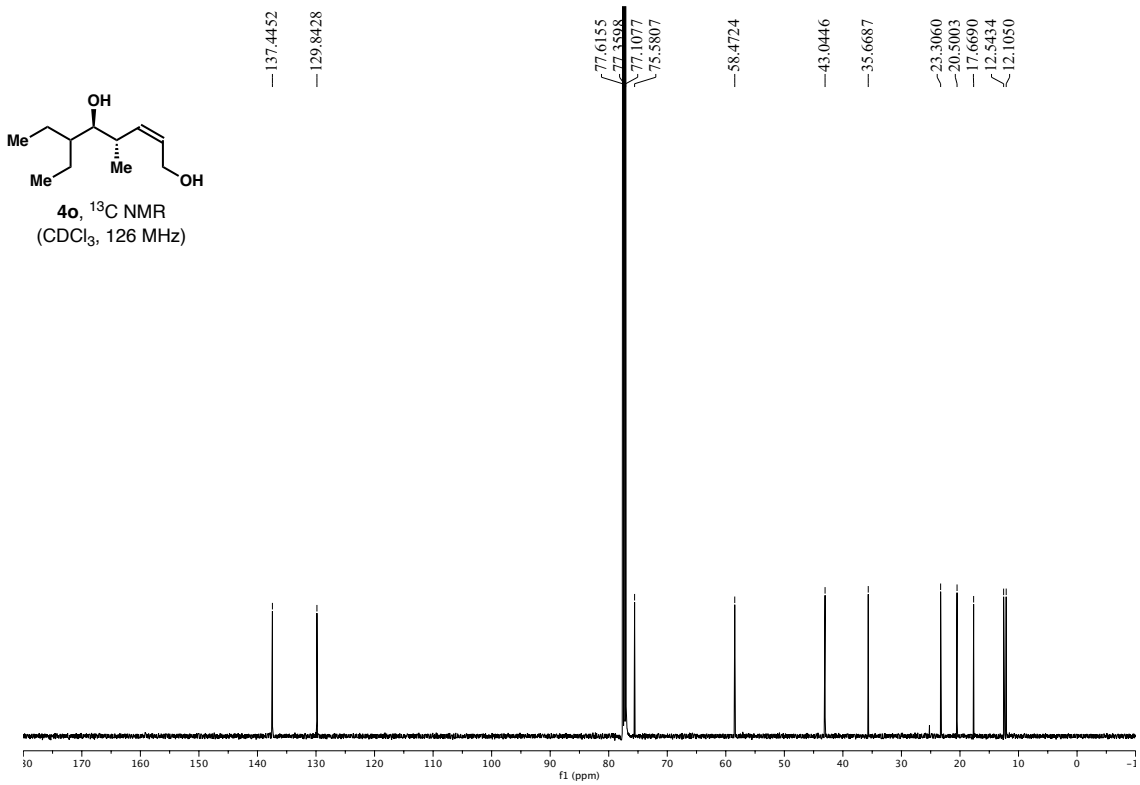
4n, ^{1}H NMR
($CDCl_3$, 500 MHz)



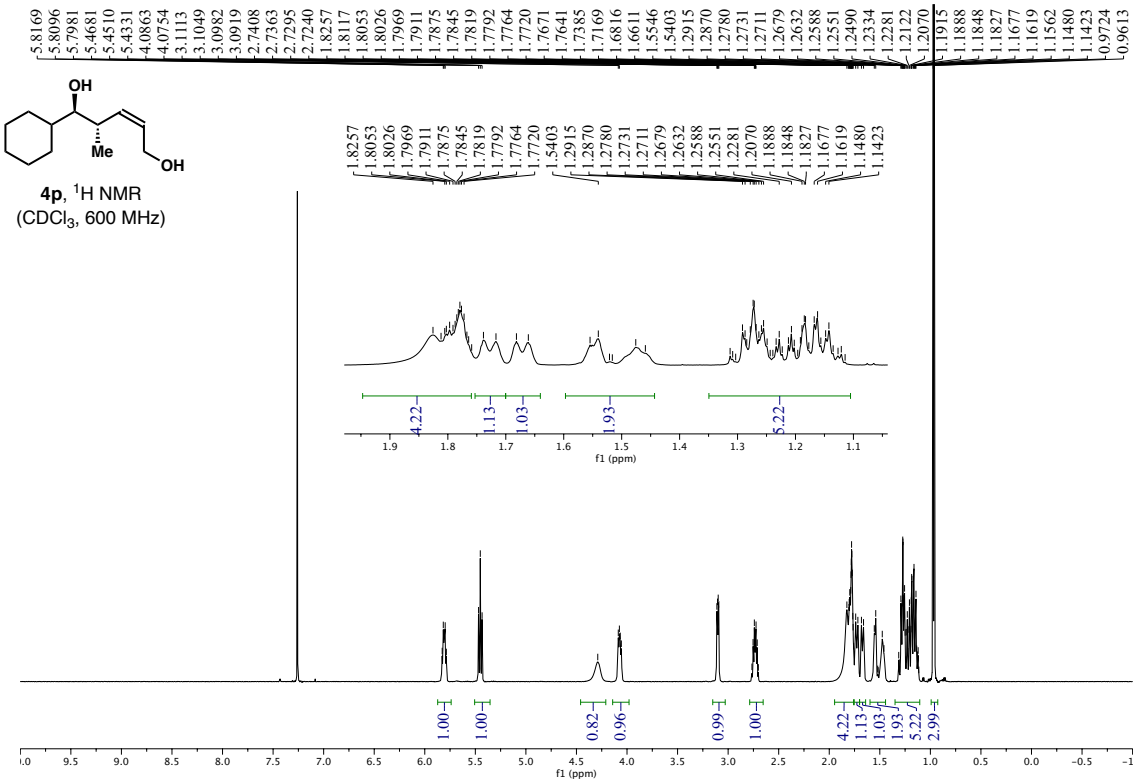
4n, ^{13}C NMR
($CDCl_3$, 126 MHz)

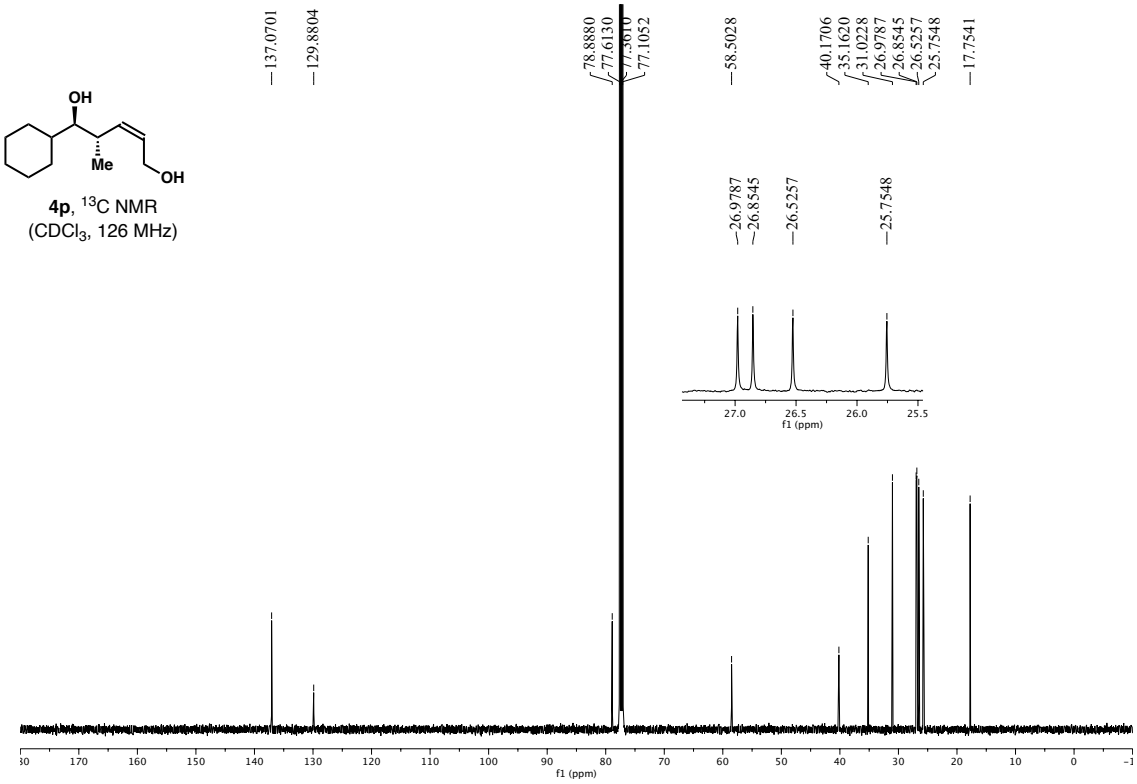


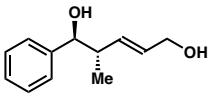
4o, ^{1}H NMR
($CDCl_3$, 500 MHz)



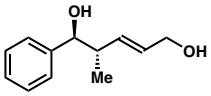
4o, ^{13}C NMR
($CDCl_3$, 126 MHz)


OH
Me
OH
4p, 1H NMR
(CDCl3, 600 MHz)
f1 (ppm)

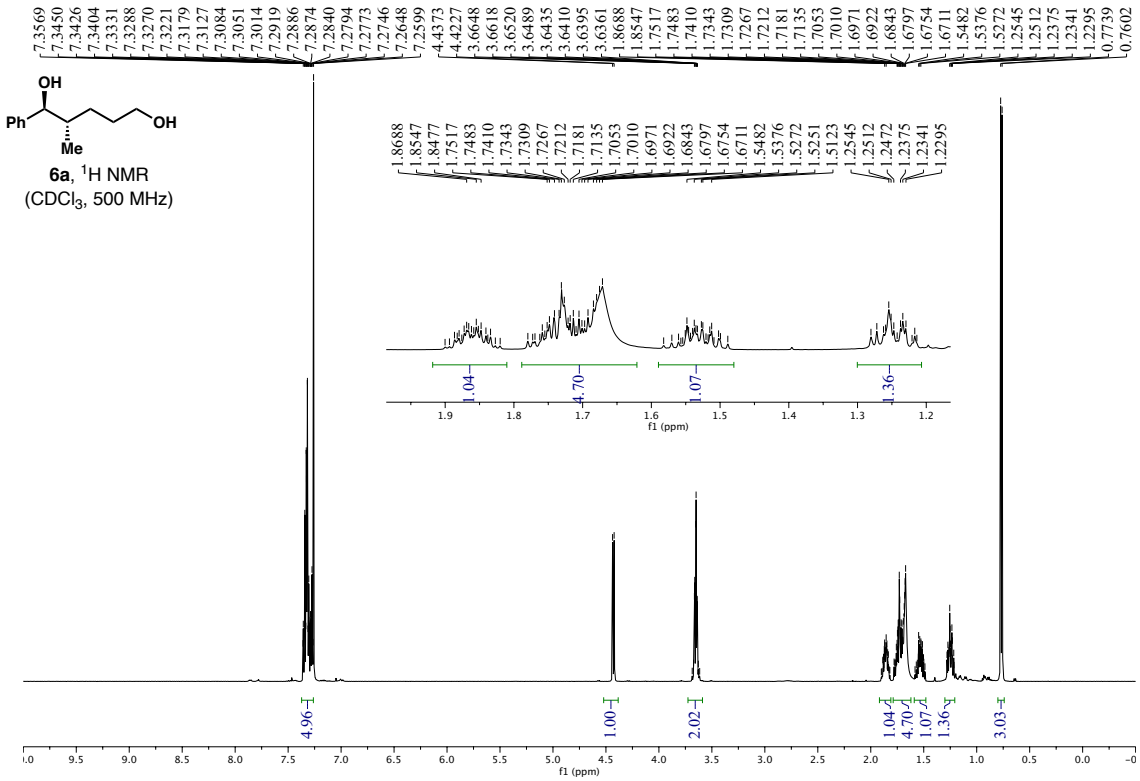

OH
Me
OH
4p, 13C NMR
(CDCl3, 126 MHz)
f1 (ppm)



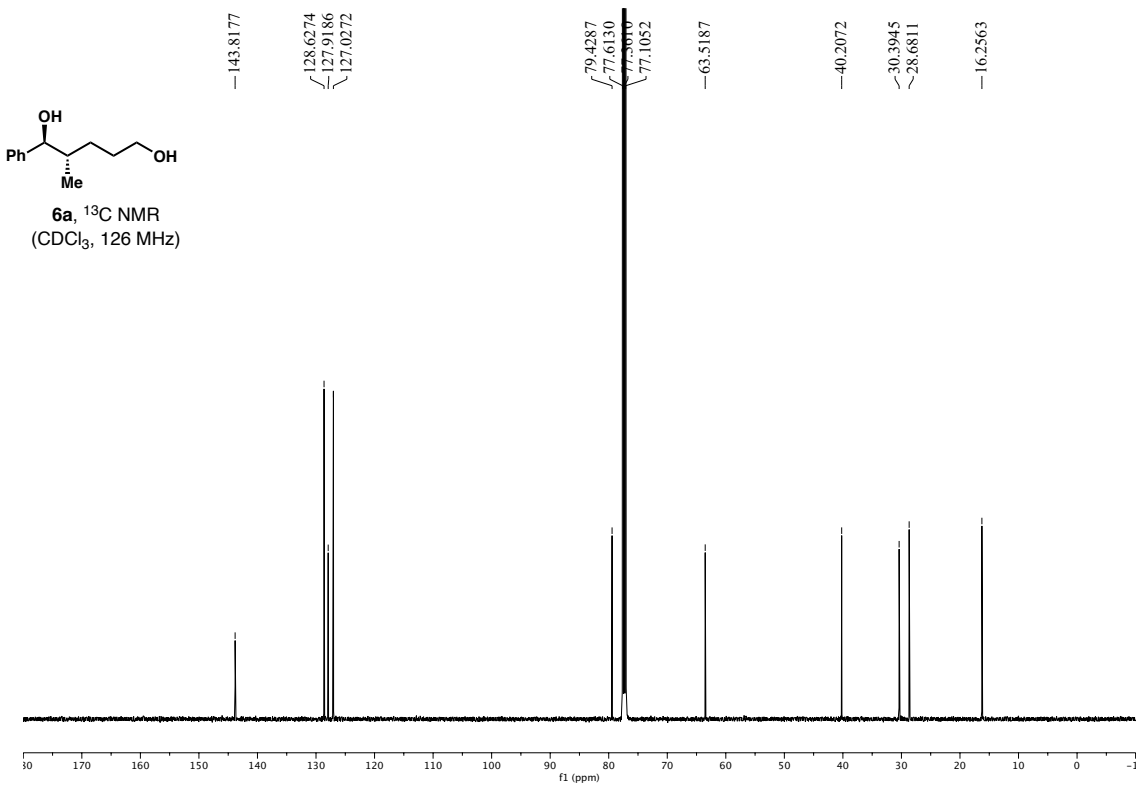
5a, ^{1}H NMR
($CDCl_3$, 600 MHz)



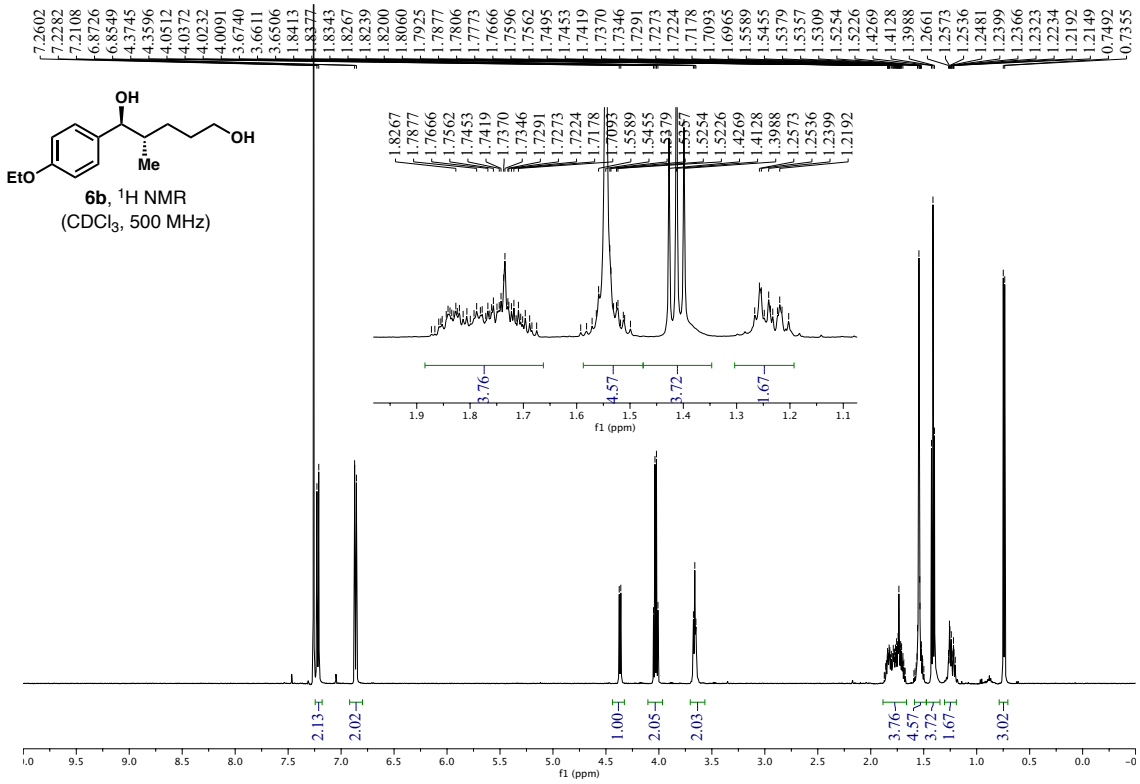
5a, ^{13}C NMR
($CDCl_3$, 151 MHz)



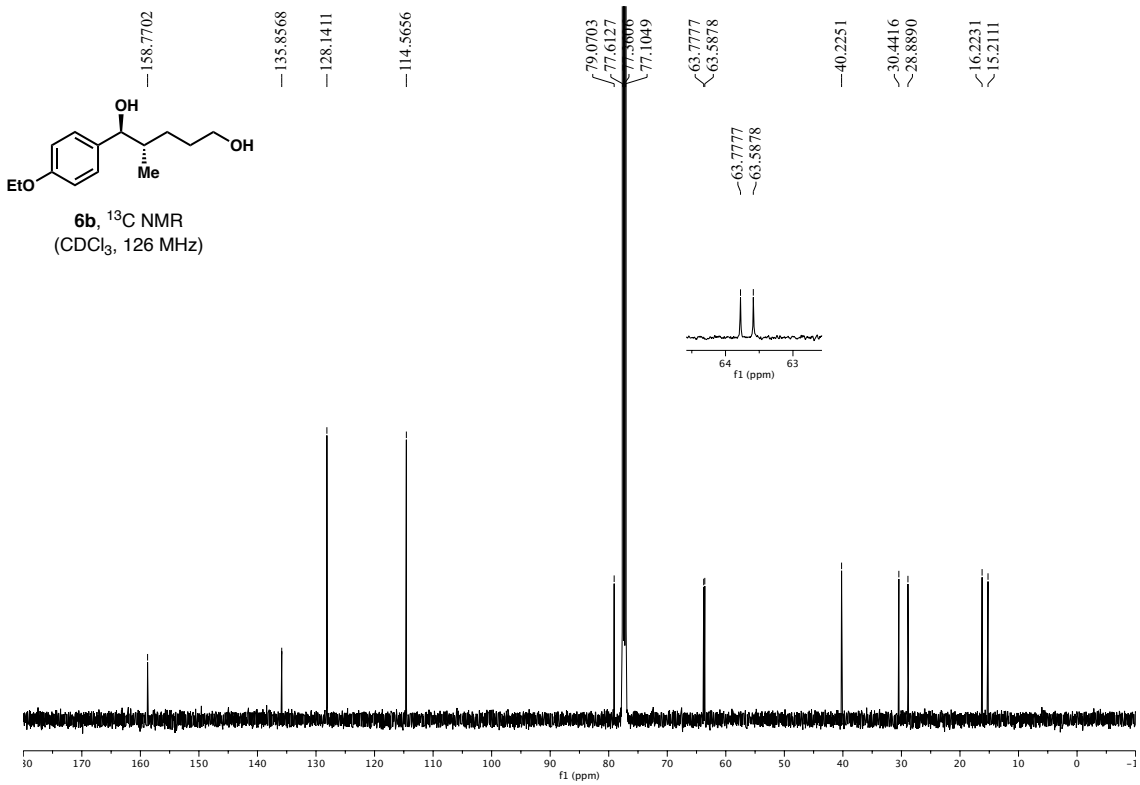
6a, ^{1}H NMR
($CDCl_3$, 500 MHz)



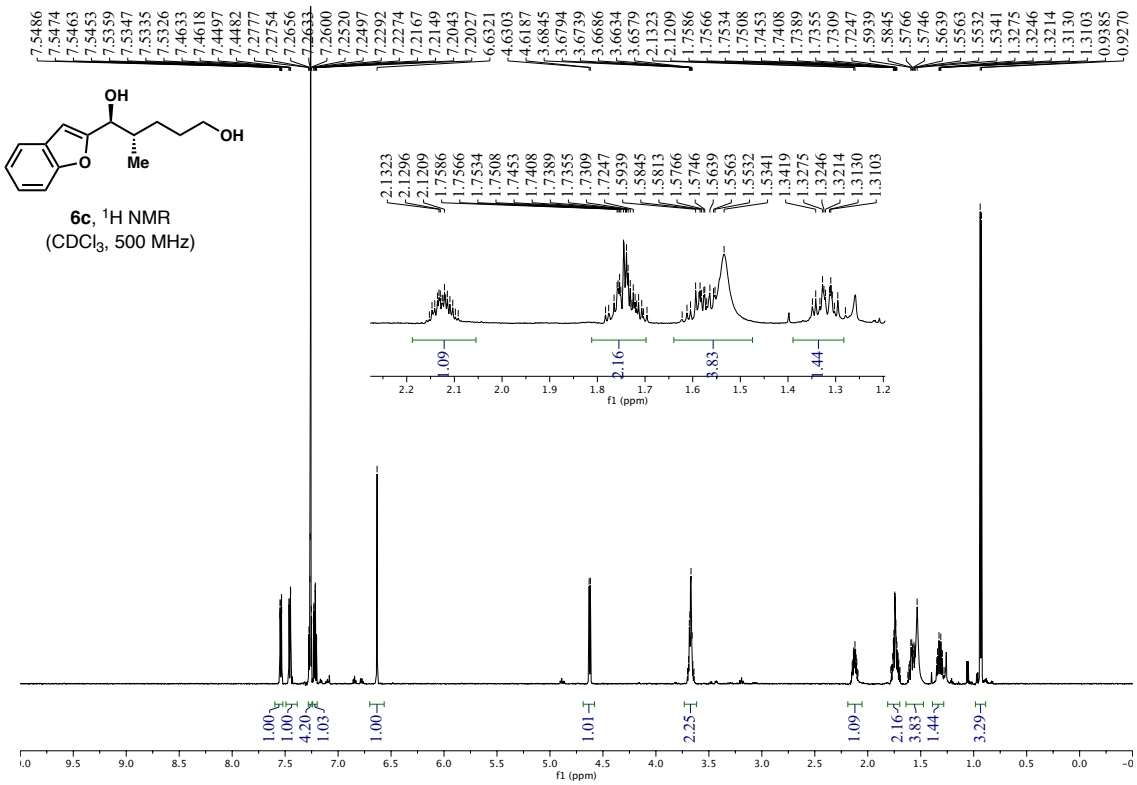
6a, ^{13}C NMR
($CDCl_3$, 126 MHz)



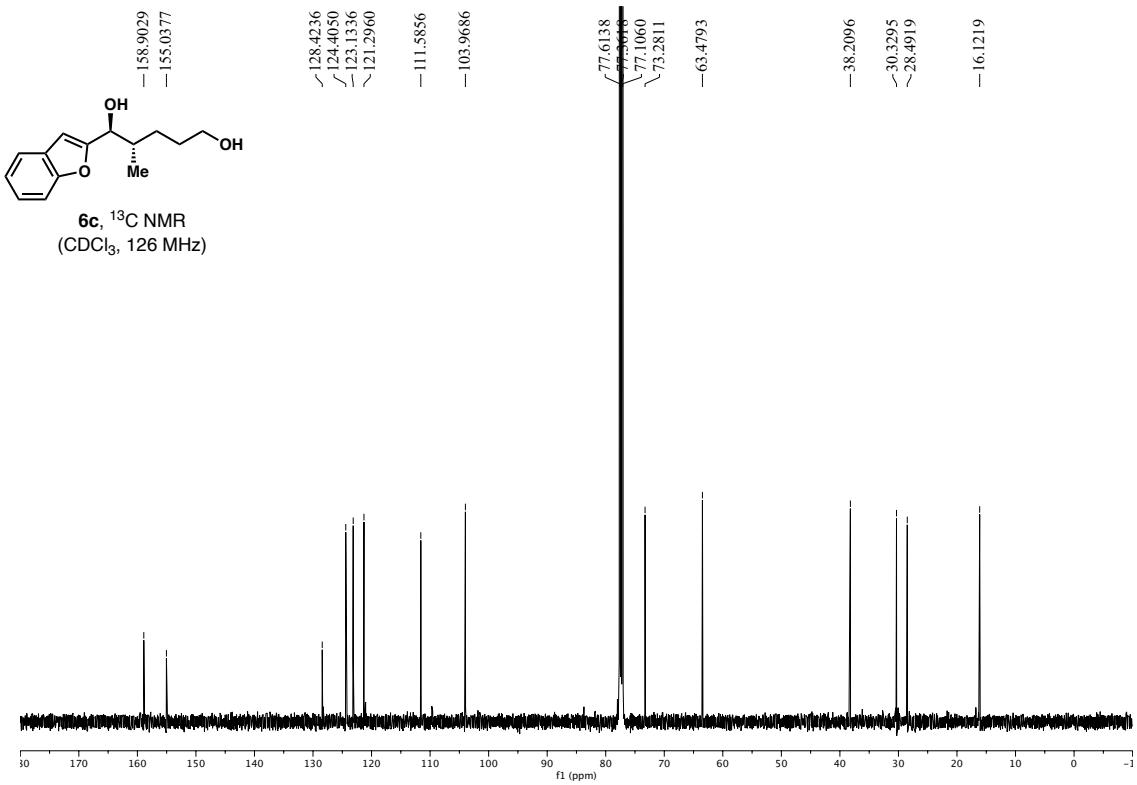
6b, ^{1}H NMR
($CDCl_3$, 500 MHz)



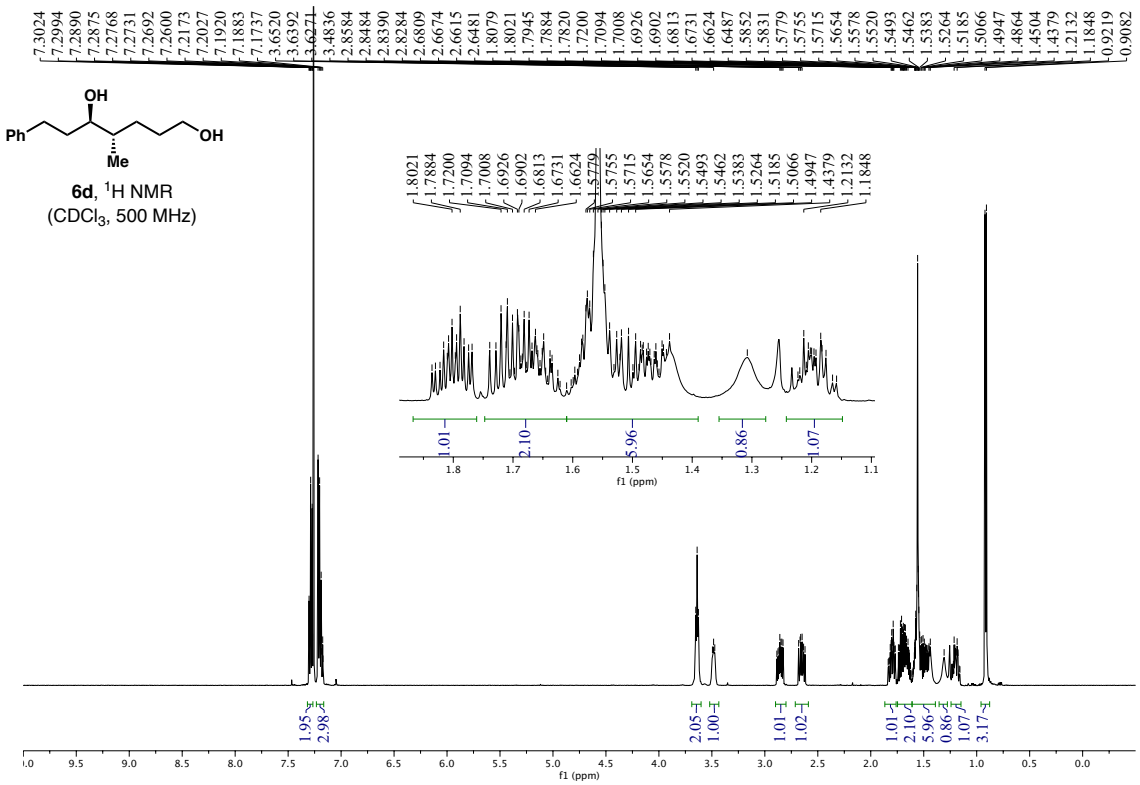
6b, ^{13}C NMR
($CDCl_3$, 126 MHz)

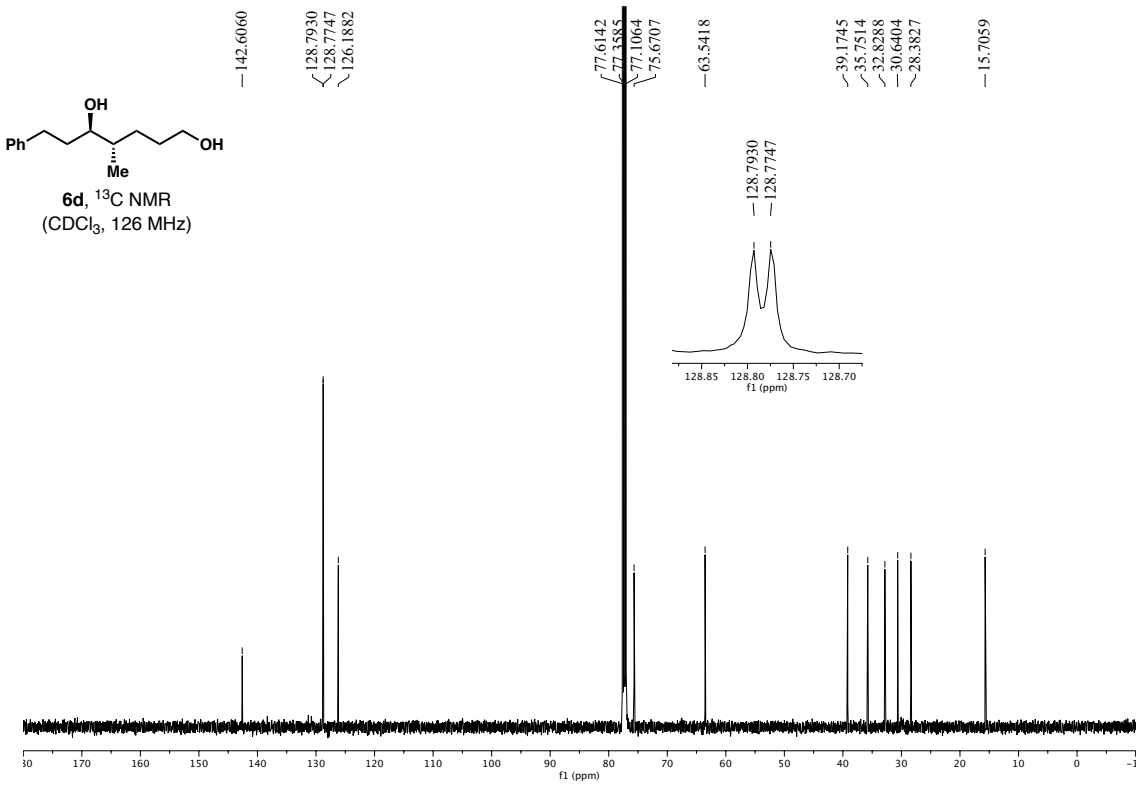


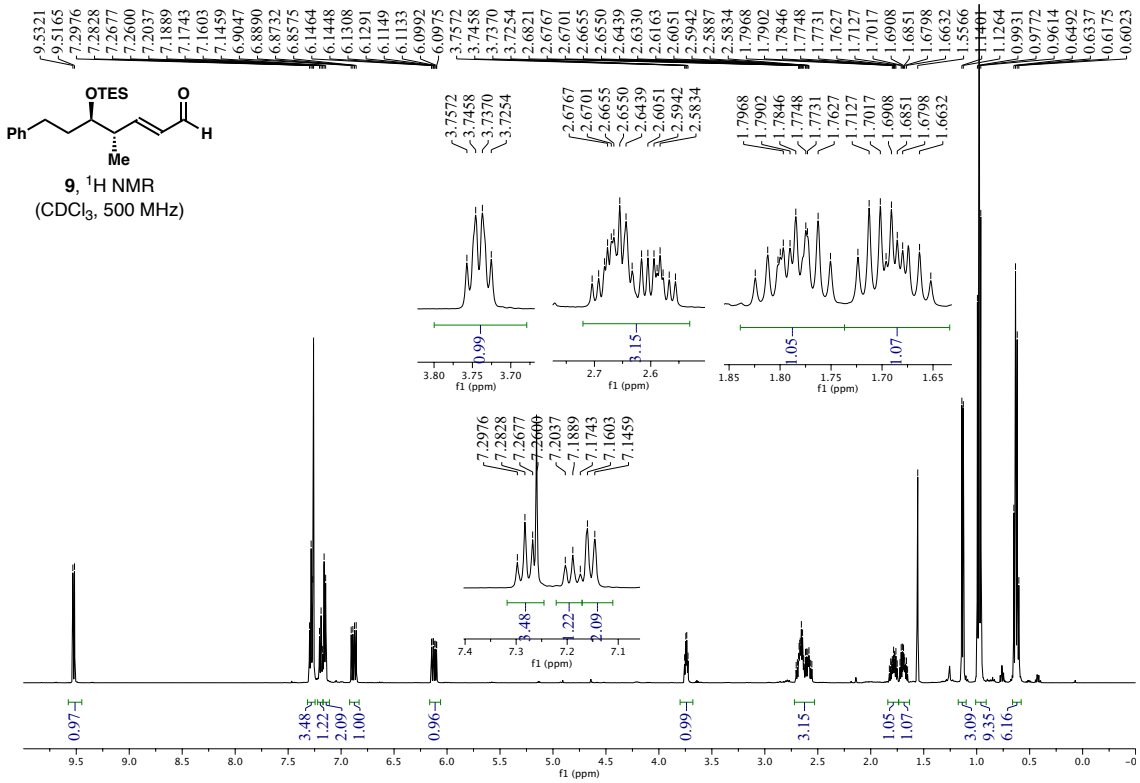
6c, ^{1}H NMR
($CDCl_3$, 500 MHz)



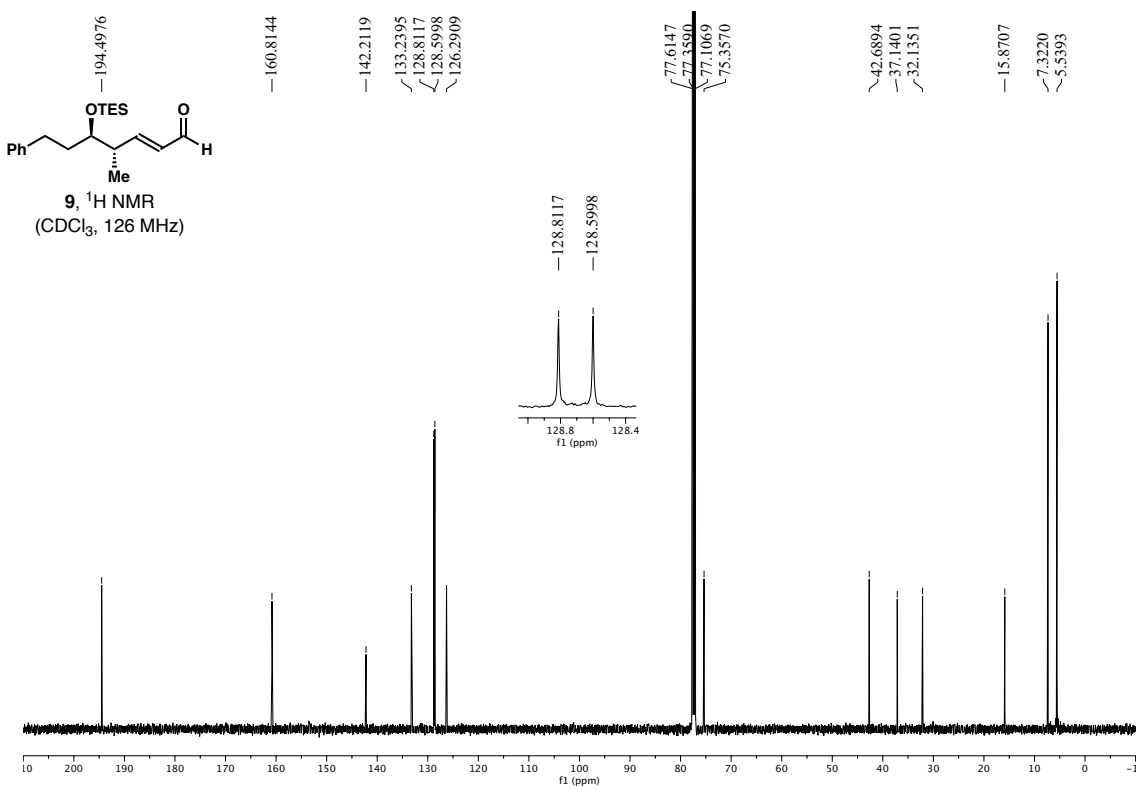
6c, ^{13}C NMR
($CDCl_3$, 126 MHz)


OH
Ph
OH
Me
6d, 1H NMR
(CDCl3, 500 MHz)
f1 (ppm)

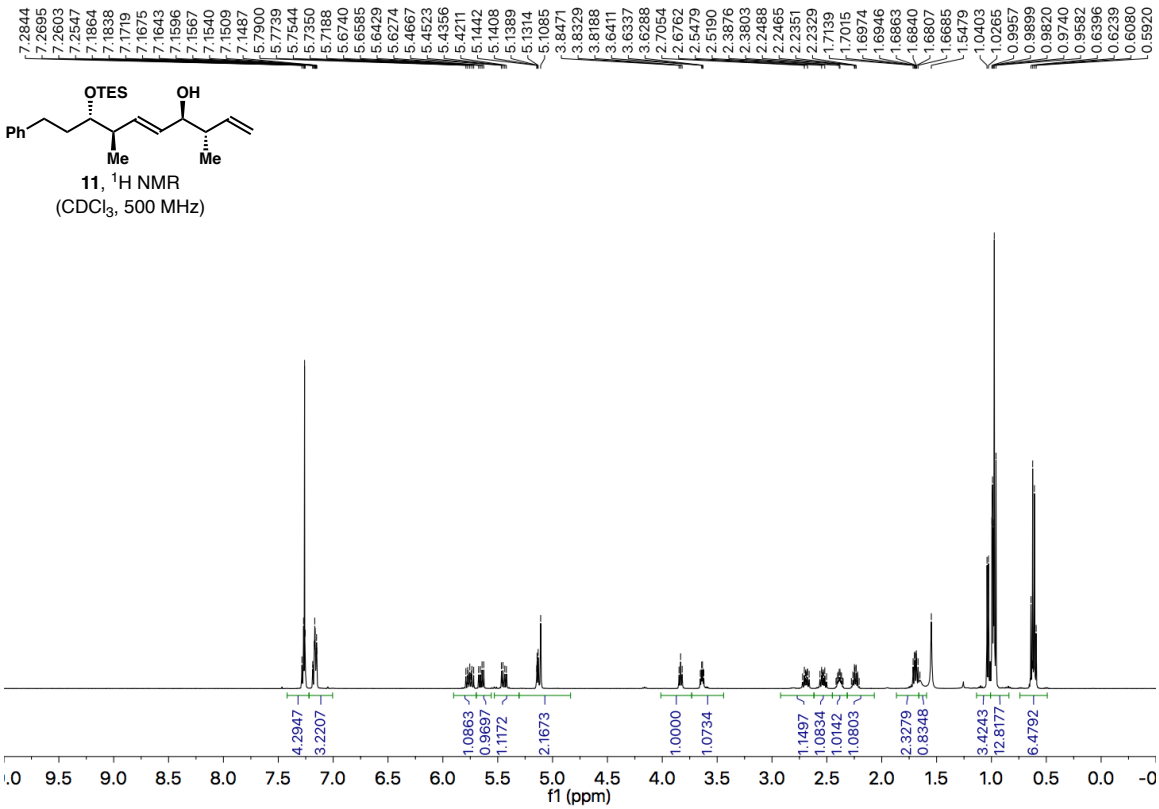

OH
Ph
OH
Me
6d, 13C NMR
(CDCl3, 126 MHz)
f1 (ppm)

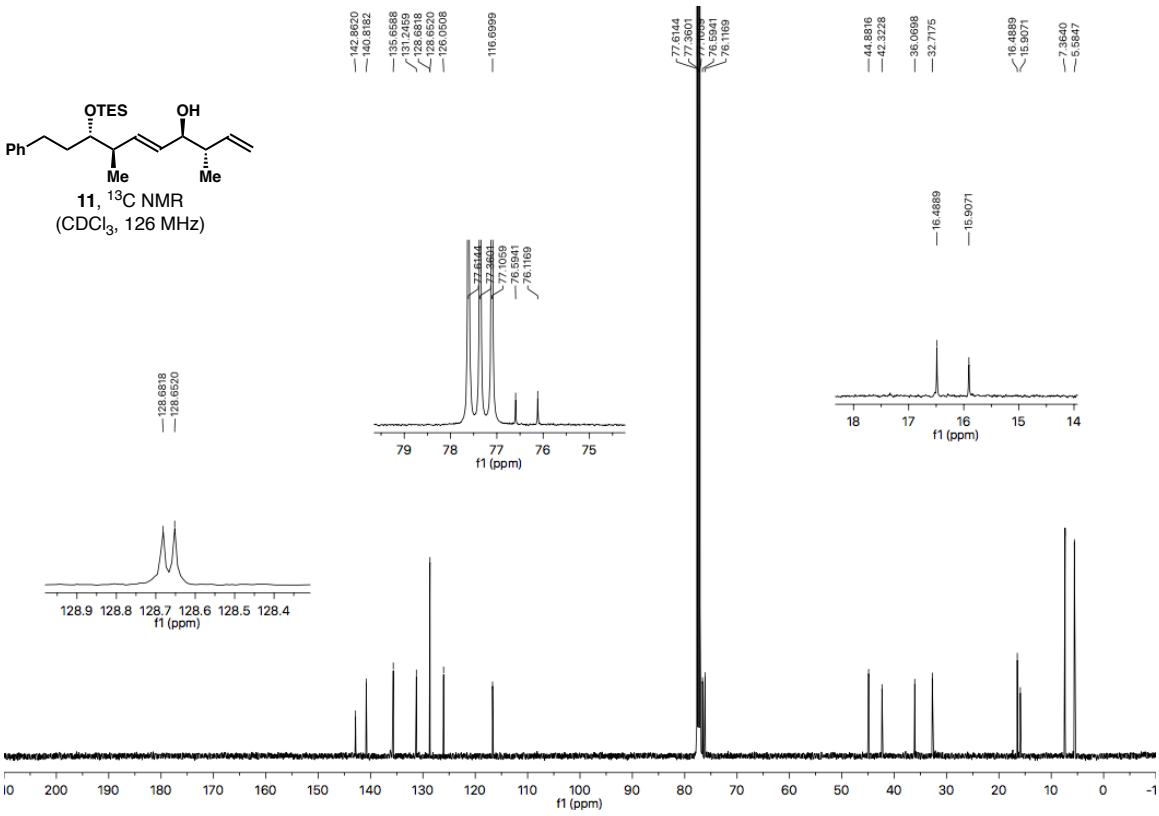


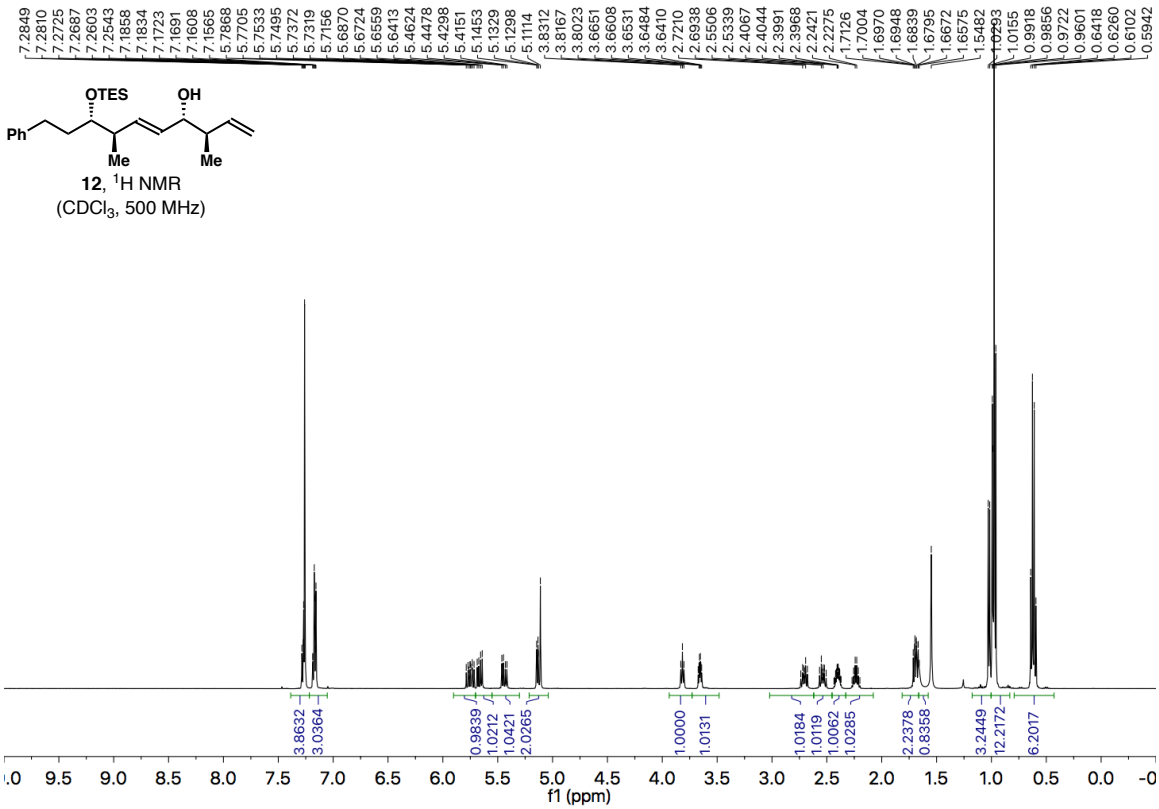
9, ^{1}H NMR
($CDCl_3$, 500 MHz)

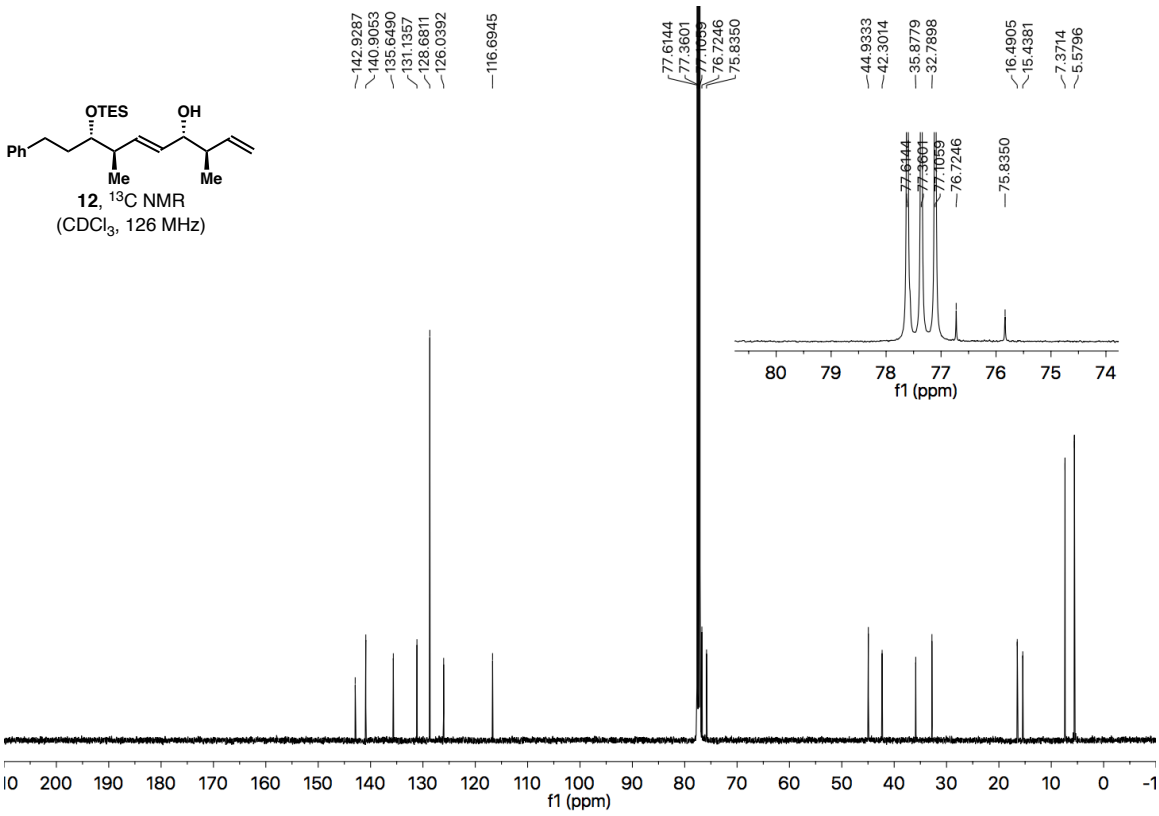


9, ^{1}H NMR
($CDCl_3$, 126 MHz)


OTES
OH
Ph
Me
Me
11, 1H NMR
(CDCl3, 500 MHz)
f1 (ppm)


OTES
OH
Ph
Me
Me
11, 13C NMR
(CDCl3, 126 MHz)
f1 (ppm)


OTES
OH
Ph
Me
Me
12, ^{1}H NMR
($CDCl_3$, 500 MHz)
f1 (ppm)


OTES
OH
Ph
Me
Me
12, ^{13}C NMR
($CDCl_3$, 126 MHz)
f1 (ppm)