Stereoselective Syntheses of 2-Methyl-1,3-diol Acetals via Re-Catalyzed [1,3]-Allylic Alcohol Transposition

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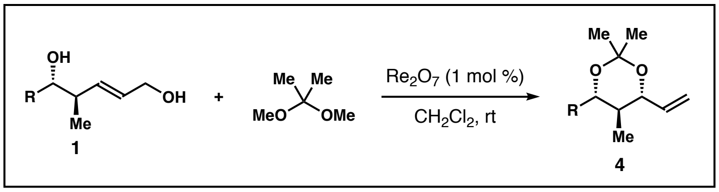
Supporting Information: Experimental Procedures, Tabulated Spectroscopic Data, ^{1}H and ^{13}C Spectra of New Compounds

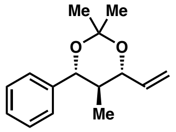
General Experimental Details. All reaction solvents were purified before use. Tetrahydrofuran, dichloromethane, diethyl ether and toluene were purified by passing through a solvent column composed of activated A-1 alumina. Unless indicated otherwise, all reactions were conducted under an atmosphere of 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 removal of residual solvent 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 126 and 151 MHz. The proton signal for residual nondeuterated solvent (δ 7.26 for $CHCl_3$) was used as an internal reference for the ^{1}H NMR spectra. For the ^{13}C NMR spectra, chemical shifts are reported relative to the δ 77.36 resonance of $CHCl_3$. Coupling constants are reported in Hz. Optical rotations were measured on a PerkinElmer 241 Automatic Polarimeter. 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.

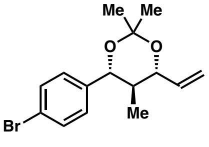
Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F254 glass plates precoated with a 0.25 mm thickness of silica gel. The TLC plates were visualized with UV light and/or by staining with Hanessian solution (ceric sulfate and ammonium molybdate in aqueous sulfuric acid) or $KMnO_4$. 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.



General procedure for the syntheses of acetonides 4 from diols 1: In an Ar-filled glove box, Re_2O_7 (0.5 mg, 0.001 mmol, 1 mol %) and a Teflon-coated magnetic stirring bar were added into a reaction vial. The vial was sealed with rubber septum and removed from the glove box. Then a solution of 2,2-dimethoxypropane (0.2 mmol, 21 mg, 2.0 equiv) and diol **1** (0.10 mmol, 1.0 equiv) in dichloromethane (1 mL) were added to the vial under an argon atmosphere. The vial was sealed with a cap containing a PTFE-lined silicone septum and kept stirring at ambient temperature for 12 h. Then saturated $NaHCO_3$ solution (1.0 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with Et_2O (2 mL x 3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution with hexane and ethyl acetate 100:1 to 50:1) to give product **4**.

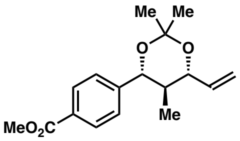


(4*R*,5*R*,6*R*)-2,2,5-trimethyl-4-phenyl-6-vinyl-1,3-dioxane (4a) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4a** in 95% yield (22 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.39 (m, 4H), 7.26 – 7.30 (m, 1H), 5.81 (ddd, *J* = 17.4, 10.3, 7.3 Hz, 1H), 5.33 (ddd, *J* = 17.1, 1.7, 0.9 Hz, 1H), 5.25 (dd, *J* = 10.3, 1.6 Hz, 1H), 4.47 (d, *J* = 10.3 Hz, 1H), 4.08 (dd, *J* = 10.2, 7.3 Hz, 1H), 1.58 – 1.66 (m, 1H), 1.60 (s, 3H), 1.52 (s, 3H), 0.63 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.8, 137.3, 128.7, 128.4, 128.0, 118.6, 99.2, 78.7, 77.7, 40.5, 30.6, 20.1, 12.6. HRMS (EI^+): m/z for $C_{15}H_{20}O_2$ $[M]^+$ calcd. 232.1463, found: 232.1450.

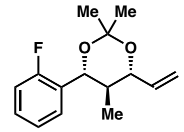


(4*R*,5*R*,6*R*)-4-(4-bromophenyl)-2,2,5-trimethyl-6-vinyl-1,3-dioxane (4b) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4b** in 84% yield (26 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 5.79 (ddd, *J* = 17.4, 10.3, 7.3 Hz, 1H), 5.33 (d, *J* = 17.2 Hz, 1H), 5.25 (dd, *J* = 10.3, 1.6 Hz, 1H), 4.44 (d, *J* = 10.3 Hz, 1H), 4.06 (dd, *J* = 10.2, 7.3 Hz, 1H), 1.58 (s, 3H), 1.53 – 1.57 (m, 1H), 1.50 (s, 3H), 0.62 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR

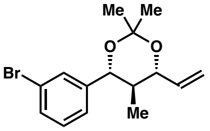
(126 MHz, $CDCl_3$) δ 139.9, 137.1, 131.8, 129.7, 122.2, 118.7, 99.3, 78.1, 77.5, 40.5, 30.5, 20.0, 12.5. HRMS (EI^+): m/z for $C_{15}H_{19}BrO_2$ $[M]^+$ calcd. 310.0568, found: 310.0578.



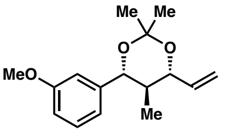
Methyl 4-((4*R*,5*R*,6*R*)-2,2,5-trimethyl-6-vinyl-1,3-dioxan-4-yl)benzoate (4c) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4c** in 96% yield (28 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 5.79 (ddd, *J* = 17.4, 10.3, 7.3 Hz, 1H), 5.33 (d, *J* = 17.2 Hz, 1H), 5.26 (dd, *J* = 10.2, 2.1 Hz, 1H), 4.54 (d, *J* = 10.4 Hz, 1H), 4.08 (dd, *J* = 10.1, 7.2 Hz, 1H), 3.91 (s, 3H), 1.56 – 1.62 (m, 1H), 1.60 (s, 3H), 1.52 (s, 3H), 0.62 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 145.8, 137.1, 130.2, 130.0, 128.0, 118.8, 99.3, 78.3, 77.5, 52.5, 40.5, 30.5, 20.0, 12.5. HRMS (ESI^+): m/z for $C_{17}H_{22}O_4Na$ $[M+Na]^+$ calcd. 313.1416, found: 313.1429.



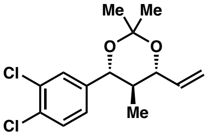
(4*R*,5*R*,6*R*)-4-(2-fluorophenyl)-2,2,5-trimethyl-6-vinyl-1,3-dioxane (4d) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4d** in 76% yield (19 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.23 – 7.28 (m, 1H), 7.18 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.02 (dd, *J* = 9.2, 9.2 Hz, 1H), 5.77 – 5.84 (m, 1H), 5.34 (d, *J* = 16.5 Hz, 1H), 5.26 (d, *J* = 9.6 Hz, 1H), 4.97 (d, *J* = 10.5 Hz, 1H), 4.11 (dd, *J* = 10.0, 7.6 Hz, 1H), 1.58 – 1.66 (m, 1H), 1.62 (s, 3H), 1.51 (s, 3H), 0.66 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6 (d, *J* = 245.9 Hz), 137.2, 129.6 (d, *J* = 8.7 Hz), 128.9 (d, *J* = 3.7 Hz), 128.2 (d, *J* = 13.3 Hz), 125.0 (d, *J* = 3.7 Hz), 118.7, 115.4 (d, *J* = 22.5 Hz), 99.4, 77.7 (via DEPT 135), 70.3, 40.6, 30.5, 20.0, 12.1. HRMS (EI^+): m/z for $C_{15}H_{19}FO_2$ $[M]^+$ calcd. 250.1369 found: 250.1376.



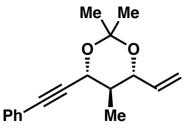
(4*R*,5*R*,6*R*)-4-(3-bromophenyl)-2,2,5-trimethyl-6-vinyl-1,3-dioxane (4e) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4e** in 77% yield (24 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 1.8, 1.8 Hz, 1H), 7.41 – 7.43 (m, 1H), 7.28 – 7.30 (m, 1H), 7.21 (dd, *J* = 7.8, 7.8 Hz, 1H), 5.79 (ddd, *J* = 17.4, 10.3, 7.3 Hz, 1H), 5.33 (ddd, *J* = 17.2, 1.7, 1.0 Hz, 1H), 5.26 (ddd, *J* = 10.3, 1.7, 0.6 Hz, 1H), 4.44 (d, *J* = 10.3 Hz, 1H), 4.06 (dd, *J* = 10.2, 7.3 Hz, 1H), 1.56 – 1.61 (m, 1H), 1.58 (s, 3H), 1.51 (s, 3H), 0.64 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 137.1, 131.5, 131.0, 130.2, 126.7, 122.9, 118.8, 99.3, 78.1, 77.5, 40.4, 30.5, 20.0, 12.6. HRMS (EI$^+$): m/z for $C_{15}H_{19}BrO_2$ [M]$^+$ calcd. 310.0568, found: 310.0561.



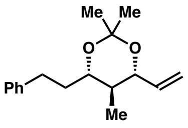
(4*R*,5*R*,6*R*)-4-(3-methoxyphenyl)-2,2,5-trimethyl-6-vinyl-1,3-dioxane (4f) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4f** in 72% yield (19 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.27 (m, 1H), 6.94 – 6.96 (m, 2H), 6.82 – 6.84 (m, 1H), 5.80 (ddd, *J* = 17.4, 10.2, 7.3 Hz, 1H), 5.33 (ddd, *J* = 17.2, 1.8, 0.9 Hz, 1H), 5.25 (dd, *J* = 10.3, 1.7 Hz, 1H), 4.45 (d, *J* = 10.2 Hz, 1H), 4.07 (dd, *J* = 10.2, 7.3 Hz, 1H), 3.82 (s, 3H), 1.57 – 1.65 (m, 1H), 1.60 (s, 3H), 1.51 (s, 3H), 0.64 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 142.3, 137.3, 129.6, 120.5, 118.6, 114.0, 113.4, 99.2, 78.6, 77.6 (via DEPT 135), 55.6, 40.4, 30.6, 20.1, 12.7. HRMS (ESI$^+$): m/z for $C_{16}H_{22}O_3Na$ [M+Na]$^+$ calcd. 285.1467, found: 285.1453.



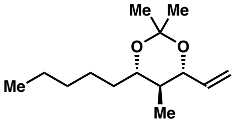
(4*R*,5*R*,6*R*)-4-(3,4-dichlorophenyl)-2,2,5-trimethyl-6-vinyl-1,3-dioxane (4g) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4g** in 80% yield (24 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 2.1 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.20 (dd, *J* = 8.2, 2.1 Hz, 1H), 5.79 (ddd, *J* = 17.4, 10.3, 7.2 Hz, 1H), 5.33 (d, *J* = 17.1 Hz, 1H), 5.26 (dd, *J* = 10.1, 1.8 Hz, 1H), 4.43 (d, *J* = 10.3 Hz, 1H), 4.06 (dd, *J* = 10.2, 7.2 Hz, 1H), 1.58 (s, 3H), 1.51 – 1.56 (m, 1H), 1.50 (s, 3H), 0.64 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 136.9, 132.9, 132.3, 130.6, 130.0, 127.4, 118.9, 99.4, 77.6 (via DEPT 135), 77.4 (via DEPT 135), 40.5, 30.5, 20.0, 12.5. HRMS (EI$^+$): m/z for $C_{15}H_{18}Cl_2O_2$ [M]$^+$ calcd. 300.0684, found: 300.0688.



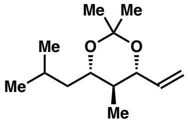
(4*R*,5*R*,6*R*)-2,2,5-trimethyl-4-(phenylethynyl)-6-vinyl-1,3-dioxane (4i) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4i** in 66% yield (17 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.47 (m, 2H), 7.28 – 7.32 (m, 3H), 5.75 – 5.82 (m, 1H), 5.32 (d, *J* = 17.2 Hz, 1H), 5.26 (d, *J* = 10.4 Hz, 1H), 4.55 (d, *J* = 10.5 Hz, 1H), 3.97 (dd, *J* = 9.9, 7.8 Hz, 1H), 1.71 – 1.80 (m, 1H), 1.55 (s, 3H), 1.51 (s, 3H), 0.99 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.9, 132.3, 128.8, 128.5, 122.9, 118.8, 99.5, 87.2, 85.6, 77.3, 67.4, 39.8, 30.4, 19.7, 13.2. HRMS (EI$^+$): m/z for $C_{17}H_{20}O_2$ [M]$^+$ calcd. 256.1463, found: 256.1471.



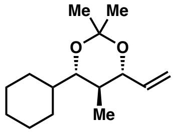
(4*S*,5*S*,6*R*)-2,2,5-trimethyl-4-phenethyl-6-vinyl-1,3-dioxane (4j) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4j** in 69% yield (18 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.29 (m, 2H), 7.16 – 7.20 (m, 3H), 5.74 (ddd, *J* = 17.4, 10.3, 7.4 Hz, 1H), 5.25 (d, *J* = 17.2 Hz, 1H), 5.21 (dd, *J* = 10.3, 1.9 Hz, 1H), 3.85 (dd, *J* = 10.2, 7.5 Hz, 1H), 3.45 (td, *J* = 9.6, 2.4 Hz, 1H), 2.80 – 2.85 (m, 1H), 2.60 – 2.66 (m, 1H), 1.90 – 1.97 (m, 1H), 1.65 – 1.73 (m, 1H), 1.455 (s, 3H), 1.447 (s, 3H), 1.29 – 1.37 (m, 1H), 0.73 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 137.7, 128.9, 128.6, 126.0, 118.5, 98.5, 77.4, 73.3, 38.6, 35.3, 31.4, 30.6, 20.1, 12.5. HRMS (EI$^+$): m/z for $C_{17}H_{24}O_2$ $[M]^+$ calcd. 260.1776, found: 260.1788.



(4*S*,5*S*,6*R*)-2,2,5-trimethyl-4-pentyl-6-vinyl-1,3-dioxane (4k) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4k** in 88% yield (20 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 (ddd, *J* = 17.5, 10.3, 7.5 Hz, 1H), 5.26 (ddd, *J* = 17.2, 1.7, 0.9 Hz, 1H), 5.21 (dd, *J* = 10.3, 1.8 Hz, 1H), 3.87 (dd, *J* = 10.2, 7.5 Hz, 1H), 3.48 (ddd, *J* = 10.4, 8.1, 2.5 Hz, 1H), 1.57 – 1.63 (m, 1H), 1.44 – 1.54 (m, 4H), 1.19 – 1.43 (m, 10H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.76 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 118.4, 98.4, 77.5 (via DEPT 135), 74.4, 38.4, 33.5, 32.2, 30.6, 25.0, 23.0, 20.1, 14.5, 12.6. HRMS (EI$^+$): m/z for $C_{14}H_{26}O_2$ $[M]^+$ calcd. 226.1933, found: 226.1951.

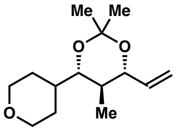


(4*S*,5*S*,6*R*)-4-isobutyl-2,2,5-trimethyl-6-vinyl-1,3-dioxane (4l) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4l** in 66% yield (14 mg) as white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.74 (ddd, *J* = 17.5, 10.3, 7.4 Hz, 1H), 5.26 (ddd, *J* = 17.2, 1.8, 0.9 Hz, 1H), 5.21 (dd, *J* = 10.3, 2.4 Hz, 1H), 3.88 (dd, *J* = 10.2, 7.4 Hz, 1H), 3.54 (td, *J* = 10.0, 3.3 Hz, 1H), 1.82 – 1.90 (m, 1H), 1.47 (s, 3H), 1.41 (s, 3H), 1.30 – 1.38 (m, 1H), 1.23 – 1.29 (m, 2H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.75 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 118.4, 98.3, 77.7, 72.4, 42.7, 39.1, 30.6, 24.2, 24.1, 21.7, 19.9, 12.7. HRMS (EI$^+$): m/z for $C_{13}H_{24}O_2$ $[M]^+$ calcd. 212.1776, found: 212.1785.

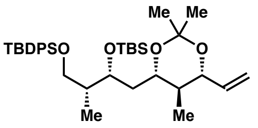


(4*S*,5*R*,6*R*)-4-cyclohexyl-2,2,5-trimethyl-6-vinyl-1,3-dioxane (4m) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4m** in 71%

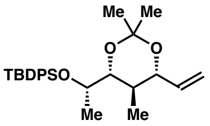
yield (17 mg) as colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.74 (ddd, *J* = 17.5, 10.3, 7.5 Hz, 1H), 5.26 (ddd, *J* = 17.2, 1.8, 0.9 Hz, 1H), 5.21 (dd, *J* = 10.3, 1.8 Hz, 1H), 3.86 (dd, *J* = 10.1, 7.5 Hz, 1H), 3.34 (dd, *J* = 10.3, 2.1 Hz, 1H), 1.72 – 1.77 (m, 2H), 1.61-1.66 (m, 1H), 1.56-1.61 (m, 1H), 1.46 – 1.54 (m, 3H), 1.40 – 1.45 (m, 4H), 1.38 (s, 3H), 1.19 – 1.30 (m, 2H), 1.10 – 1.18 (m, 2H), 0.73 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 138.0, 118.4, 98.3, 78.1, 77.8, 38.9, 34.9, 30.7, 30.5, 27.2, 26.93, 26.89, 25.2, 20.0, 12.2. HRMS (EI$^+$): m/z for $C_{15}H_{26}O_2$ [M]$^+$ calcd. 238.1933, found: 238.1941.



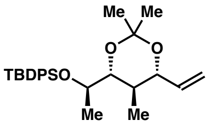
(4*S*,5*R*,6*R*)-2,2,5-trimethyl-4-(tetrahydro-2*H*-pyran-4-yl)-6-vinyl-1,3-dioxane (4n) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4n** in 75% yield (18 mg) as colorless oil. ^{1}H NMR (600 MHz, CDCl$_3$) δ 5.74 (ddd, *J* = 17.4, 10.3, 7.5 Hz, 1H), 5.27 (d, *J* = 17.1 Hz, 1H), 5.22 (dd, *J* = 10.3, 1.8 Hz, 1H), 3.98 – 4.02 (m, 2H), 3.88 (dd, *J* = 10.1, 7.4 Hz, 1H), 3.32 – 3.42 (m, 3H), 1.84 – 1.91 (m, 1H), 1.76 – 1.81 (m, 1H), 1.68 – 1.75 (m, 1H), 1.45 – 1.51 (m, 1H), 1.43 (s, 3H), 1.43 – 1.38 (m, 1H), 1.38 (s, 3H), 1.26 – 1.29 (m, 1H), 0.76 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 137.7, 118.6, 98.4, 77.5, 76.9, 68.7, 68.6, 36.3, 34.6, 30.4, 29.9, 25.5, 20.0, 12.2. HRMS (ESI$^+$): m/z for $C_{14}H_{24}O_3Na$ [M+Na]$^+$ calcd. 263.1623, found: 263.1633.



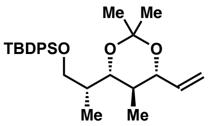
(5*R*,6*R*)-2,2,3,3,6,10,10-heptamethyl-9,9-diphenyl-5-(((4S,5S,6R)-2,2,5-trimethyl-6-vinyl-1,3-dioxan-4-yl)methyl)-4,8-dioxa-3,9-disilaundecane (4o) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4o** in 79% yield (48 mg) as colorless oil. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.65 – 7.68 (m, 4H), 7.39 – 7.43 (m, 2H), 7.35 – 7.38 (m, 4H), 5.73 (ddd, *J* = 17.4, 10.3, 7.4 Hz, 1H), 5.26 (d, *J* = 17.2 Hz, 1H), 5.21 (dd, *J* = 10.3, 2.1 Hz, 1H), 4.19 – 4.21 (m, 1H), 3.86 (dd, *J* = 10.2, 7.4 Hz, 1H), 3.62 (dd, *J* = 9.8, 7.7 Hz, 1H), 3.44 – 3.49 (m, 2H), 1.81 – 1.88 (m, 2H), 1.49 – 1.53 (m, 1H), 1.42 (s, 3H), 1.36 (s, 3H), 1.26 – 1.32 (m, 1H), 1.06 (s, 9H), 0.83 (s, 9H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.76 (d, *J* = 6.7 Hz, 3H), 0.05 (s, 3H), -0.02 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 137.7, 135.9 (two overlapping carbon signals), 134.6, 134.5, 129.83, 129.82, 127.91, 127.89, 118.4, 98.2, 77.4 (via DEPT 135), 71.8, 67.7, 67.0, 39.1, 39.0, 38.8, 30.4, 27.3, 26.3, 19.9, 19.6, 18.4, 12.7, 9.6, -3.7, -4.5. HRMS (ESI$^+$): m/z for $C_{36}H_{58}O_4Si_2Na$ [M+Na]$^+$ calcd. 633.3771, found: 633.3754.



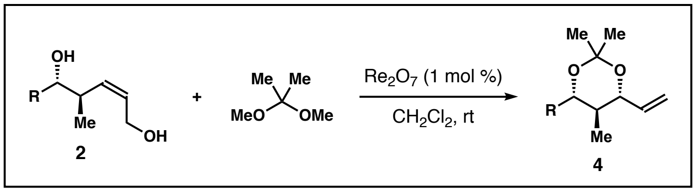
***tert*-Butyldiphenyl((*S*)-1-((4*R*,5*R*,6*R*)-2,2,5-trimethyl-6-vinyl-1,3-dioxan-4-yl)ethoxy)silane (4p)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4p** in 68% yield (30 mg) as colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.73 – 7.75 (m, 2H), 7.67 – 7.69 (m, 2H), 7.40 – 7.44 (m, 2H), 7.35 – 7.39 (m, 4H), 5.64 (ddd, *J* = 17.5, 10.3, 7.5 Hz, 1H), 5.17 – 5.20 (m, 1H), 5.15 – 5.17 (m, 1H), 3.97 – 4.01 (m, 1H), 3.66 (dd, *J* = 10.1, 7.5 Hz, 1H), 3.38 (dd, *J* = 10.6, 2.0 Hz, 1H), 1.45 (s, 3H), 1.36 (s, 3H), 1.15 – 1.23 (m, 1H), 1.16 (d, *J* = 6.4 Hz, 3H), 1.07 (s, 9H), 0.32 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 137.6, 136.4, 136.3, 134.84, 134.83, 129.9 (two overlapping carbon signals), 127.9, 127.8, 118.6, 98.5, 77.9, 77.2, 69.6, 34.8, 30.5, 27.4, 20.0, 19.6, 17.0 11.9. HRMS (ESI$^+$): m/z for $C_{27}H_{38}O_3SiNa$ [M+Na]$^+$ calcd. 461.2488, found: 461.2491.



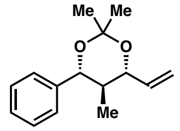
***tert*-Butyldiphenyl((*R*)-1-((4*R*,5*R*,6*R*)-2,2,5-trimethyl-6-vinyl-1,3-dioxan-4-yl)ethoxy)silane (4q)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4q** in 64% yield (28 mg) as colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.72 – 7.75 (m, 4H), 7.37 – 7.46 (m, 6H), 5.75 (ddd, *J* = 17.4, 10.2, 7.4 Hz, 1H), 5.23 – 5.29 (m, 2H), 4.00 – 4.01 (m, 1H), 3.84 (dd, *J* = 10.3, 7.4 Hz, 1H), 3.41 (dd, *J* = 10.2, 2.6 Hz, 1H), 1.66 – 1.71 (m, 1H), 1.40 (s, 3H), 1.32 (s, 3H), 1.11 (d, *J* = 6.4 Hz, 3H), 1.08 (s, 9H), 0.85 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 137.7, 136.3, 136.2, 134.8, 134.7, 130.0, 129.8, 128.0, 127.7, 118.6, 98.4, 77.5, 77.1, 71.1, 34.3, 30.4, 27.3, 19.8, 19.6, 18.6, 12.5. HRMS (ESI$^+$): m/z for $C_{27}H_{38}O_3SiNa$ [M+Na]$^+$ calcd. 461.2488, found: 461.2481.



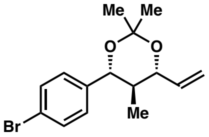
***tert*-Butyldiphenyl((*R*)-2-((4*S*,5*R*,6*R*)-2,2,5-trimethyl-6-vinyl-1,3-dioxan-4-yl)propoxy)silane (4r)** Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4r** in 82% yield (37 mg) as colorless oil. ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.66 – 7.69 (m, 4H), 7.41 – 7.43 (m, 2H), 7.36 – 7.39 (m, 4H), 5.77 (ddd, *J* = 17.5, 10.3, 7.4 Hz, 1H), 5.28 (d, *J* = 17.2 Hz, 1H), 5.22 (dd, *J* = 10.2, 1.8 Hz, 1H), 3.91 – 3.94 (m, 2H), 3.69 (dd, *J* = 9.4, 9.4 Hz, 1H), 3.46 (dd, *J* = 9.6, 5.7 Hz, 1H), 1.95 – 1.98 (m, 1H), 1.43 – 1.53 (m, 1H), 1.46 (s, 3H), 1.38 (s, 3H), 1.05 (s, 9H), 0.76 (d, *J* = 7.0 Hz, 3H), 0.74 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 137.9, 135.9 (two overlapping carbon signals), 134.40, 134.38, 129.88, 129.85, 128.0, 127.9, 118.4, 98.3, 77.7, 72.3, 65.8, 36.6, 34.9, 30.5, 27.2, 20.2, 19.6, 12.2, 9.4. HRMS (ESI$^+$): m/z for $C_{28}H_{40}O_3SiNa$ [M+Na]$^+$ calcd. 475.2644, found: 475.2627.



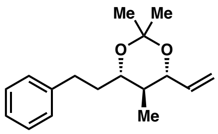
General procedure for the syntheses of acetonides 4 from diols 2: In an Ar-filled glove box, Re_2O_7 (0.5 mg, 0.001 mmol, 1 mol %) and a Teflon-coated magnetic stirring bar were added into a reaction vial. The vial was sealed with rubber septum and removed from the glove box. Then a solution of 2,2-dimethoxypropane (0.2 mmol, 21 mg, 2.0 equiv) and diol **2** (0.10 mmol, 1.0 equiv) in dichloromethane (1 mL) were added to the vial under an argon atmosphere. The vial was sealed with a cap containing a PTFE-lined silicone septum and kept stirring at ambient temperature for 12 h. Then saturated $NaHCO_3$ solution (1.0 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with Et_2O (2 mL x 3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution with hexane and ethyl acetate 100:1 to 50:1) to give product **4**.



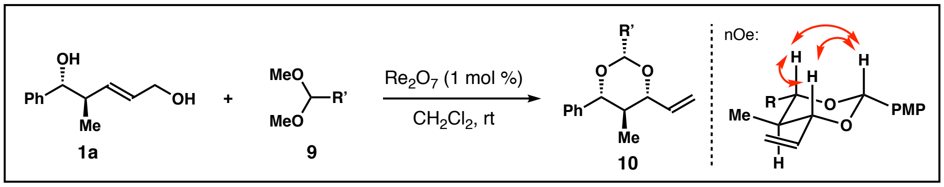
(4*R*,5*R*,6*R*)-2,2,5-trimethyl-4-phenyl-6-vinyl-1,3-dioxane (4a) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4a** in 73% yield (17 mg) as colorless oil.



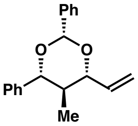
(4*R*,5*R*,6*R*)-4-(4-bromophenyl)-2,2,5-trimethyl-6-vinyl-1,3-dioxane (4b) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4b** in 77% yield (24 mg) as colorless oil.



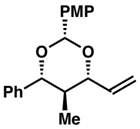
(4*S*,5*S*,6*R*)-2,2,5-trimethyl-4-phenethyl-6-vinyl-1,3-dioxane (4j) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **4j** in 65% yield (17 mg) as colorless oil.



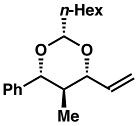
General procedure for the syntheses of acetals 10 from diol 1a: In an Ar-filled glove box, Re_2O_7 (0.5 mg, 0.001 mmol, 1 mol %) and a Teflon-coated magnetic stirring bar were added into a reaction vial. The vial was sealed with rubber septum and removed from the glove box. Then a solution of diol **1a** (0.10 mmol, 19 mg, 1.0 equiv) and acetal **9** (0.2 mmol, 2.0 equiv) in dichloromethane (1 mL) were added to the vial under an argon atmosphere. The vial was sealed with a cap containing a PTFE-lined silicone septum and kept stirring at ambient temperature for 12 h. Then saturated $NaHCO_3$ solution (1.0 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with Et_2O (2 mL x 3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution with hexane and ethyl acetate 100:1 to 50:1) to give product **10**.



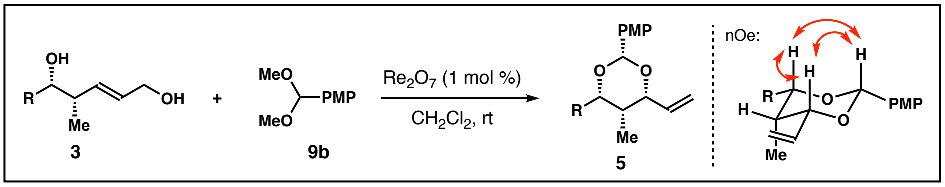
(2*R*,4*R*,5*R*,6*R*)-5-methyl-2,4-diphenyl-6-vinyl-1,3-dioxane (10a) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **10a** in 93% yield (26 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.57 (m, 2H), 7.41 – 7.44 (m, 2H), 7.29 – 7.37 (m, 6H), 5.90 – 5.97 (m, 1H), 5.80 (s, 1H), 5.41 (d, *J* = 17.1 Hz, 1H), 5.29 (d, *J* = 10.4 Hz, 1H), 4.44 (d, *J* = 10.0 Hz, 1H), 4.08 (dd, *J* = 10.0, 7.2 Hz, 1H), 1.83 – 1.91 (m, 1H), 0.69 (d, *J* = 6.8, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 138.8, 136.4, 129.1, 128.7, 128.5 (two overlapping carbon signals), 128.1, 126.8, 118.8, 101.4, 86.2, 84.8, 40.5, 12.6. HRMS (EI$^+$): m/z for $C_{19}H_{19}O_2$ $[M–H]^+$ calcd. 279.1385, found: 279.1380.



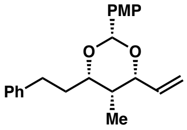
(2*R*,4*R*,5*R*,6*R*)-2-(4-methoxyphenyl)-5-methyl-4-phenyl-6-vinyl-1,3-dioxane (10b) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **10b** in 87% yield (27 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.50 (m, 2H), 7.40 – 7.43 (m, 2H), 7.33 – 7.37 (m, 2H), 7.28 – 7.32 (m, 1H), 6.86 – 6.88 (m, 2H), 5.93 (ddd, *J* = 17.4, 10.4, 7.2 Hz, 1H), 5.75 (s, 1H), 5.38 – 5.42 (m, 1H), 5.27 – 5.29 (m, 1H), 4.42 (d, *J* = 9.9 Hz, 1H), 4.06 (dd, *J* = 9.9, 7.2 Hz, 1H), 3.79 (s, 3H), 1.81 – 1.89 (m, 1H), 0.68 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 140.2, 136.5, 131.5, 128.7, 128.5, 128.1, 128.0, 118.7, 113.9, 101.3, 86.1, 84.8, 55.6, 40.4, 12.6. HRMS (EI$^+$): m/z for $C_{20}H_{22}O_3Na$ [M+Na]$^+$ calcd. 333.1467, found: 333.1457.



(2*R*,4*R*,5*R*,6*R*)-2-hexyl-5-methyl-4-phenyl-6-vinyl-1,3-dioxane (10c) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **10c** in 90% yield (26 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.37 (m, 4H), 7.28 – 7.32 (m, 1H), 5.87 (ddd, *J* = 17.4, 10.4, 7.1 Hz, 1H), 5.33-5.37 (m, 1H), 5.25 – 5.27 (m, 1H), 4.80 (t, *J* = 5.0 Hz, 1H), 4.19 (d, *J* = 10.0 Hz, 1H), 3.82 (dd, *J* = 9.9, 7.1 Hz, 1H), 1.66 – 1.74 (m, 3H), 1.40 – 1.47 (m, 2H), 1.22 – 1.32 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 1H), 0.61 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 136.7, 128.7, 128.4, 128.0, 118.5, 102.2, 85.7, 84.2, 40.4, 35.5, 32.1, 29.6, 24.3, 22.9, 14.4, 12.6. HRMS (EI$^+$): m/z for $C_{19}H_{27}O_2$ [M–H]$^+$ calcd. 287.2011, found: 287.2003.

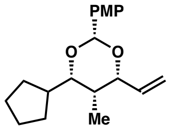


General procedure for the syntheses of acetals 5 from diols 3: In an Ar-filled glove box, Re_2O_7 (0.5 mg, 0.001 mmol, 1 mol %) and a Teflon-coated magnetic stirring bar were added into a reaction vial. The vial was sealed with rubber septum and removed from the glove box. Then a solution of diol **3** (0.10 mmol, 19 mg, 1.0 equiv) and acetal **9b** (0.2 mmol, 36 mg, 2.0 equiv) in dichloromethane (1 mL) were added to the vial under an argon atmosphere. The vial was sealed with a cap containing a PTFE-lined silicone septum and kept stirring at ambient temperature for 12 h. Then saturated $NaHCO_3$ solution (1.0 mL) was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with Et_2O (2 mL x 3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution with hexane and ethyl acetate 100:1 to 50:1) to give product **5**.

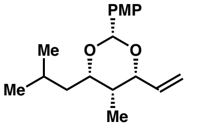


(2*S*,4*S*,5*R*,6*R*)-2-(4-methoxyphenyl)-5-methyl-4-phenethyl-6-vinyl-1,3-dioxane (5a) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound

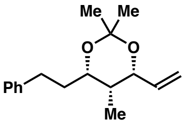
5a in 83% yield (28 mg) as colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.46 – 7.49 (m, 2H), 7.28 – 7.31 (m, 2H), 7.18 – 7.22 (m, 3H), 6.89 – 6.92 (m, 2H), 5.85 (ddd, *J* = 17.4, 10.8, 4.8 Hz, 1H), 5.54 (s, 1H), 5.30 – 5.34 (m, 1H), 5.18 – 5.21 (m, 1H), 4.40 – 4.42 (m, 1H), 3.86 – 3.89 (m, 1H), 3.81 (s, 3H), 2.78 – 2.84 (m, 1H), 2.66 – 2.72 (m, 1H), 2.01 – 2.09 (m, 1H), 1.68 – 1.75 (m, 1H), 1.55 – 1.60 (m, 1H), 0.99 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 160.2, 142.3, 137.1, 131.9, 128.9, 128.7, 127.9, 126.2, 115.6, 113.9, 101.6, 81.6, 80.0, 55.7, 36.2, 34.6, 32.0, 6.7. HRMS (ESI$^+$): m/z for $C_{22}H_{27}O_3$ [M+H]$^+$ calcd. 339.1960, found: 339.1953.



(2*R*,4*S*,5*S*,6*R*)-4-cyclopentyl-2-(4-methoxyphenyl)-5-methyl-6-vinyl-1,3-dioxane (5b) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **5b** in 86% yield (26 mg) as colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.45 – 7.48 (m, 2H), 6.86 – 6.90 (m, 2H), 5.87 (ddd, *J* = 17.4, 10.8, 4.8 Hz, 1H), 5.54 (s, 1H), 5.31 – 5.36 (m, 1H), 5.18 – 5.21 (m, 1H), 4.40 – 4.42 (m, 1H), 3.80 (s, 3H), 3.52 (dd, *J* = 10.0, 2.2 Hz, 1H), 2.04 – 2.13 (m, 1H), 1.89 – 1.95 (m, 1H), 1.60 – 1.73 (m, 4H), 1.50 – 1.59 (m, 2H), 1.36 – 1.43 (m, 1H), 1.08 – 1.16 (m, 1H), 0.98 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 160.1, 137.4, 132.0, 127.8, 115.4, 113.9, 101.4, 86.4, 81.7, 55.7, 41.8, 35.3, 31.0, 27.9, 25.7, 25.6, 6.9. HRMS (EI$^+$): m/z for $C_{19}H_{26}O_3$ [M]$^+$ calcd. 302.1882, found: 302.1871.

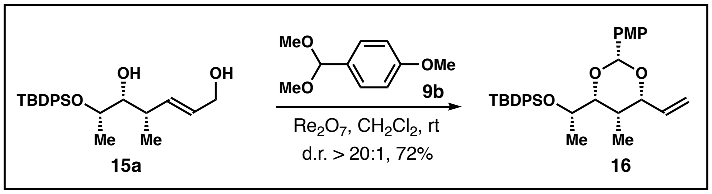


(2*S*,4*S*,5*R*,6*R*)-4-isobutyl-2-(4-methoxyphenyl)-5-methyl-6-vinyl-1,3-dioxane (5c) Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give compound **5c** in 83% yield (24 mg) as colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44 – 7.47 (m, 2H), 6.87 – 6.90 (m, 2H), 5.86 (ddd, *J* = 17.4, 10.8, 4.7 Hz, 1H), 5.56 (s, 1H), 5.31 – 5.35 (m, 1H), 5.19 – 5.21 (m, 1H), 4.44 – 4.46 (m, 1H), 3.96 – 3.99 (m, 1H), 3.80 (s, 3H), 1.74 – 1.82 (m, 1H), 1.59 – 1.64 (m, 1H), 1.52 – 1.57 (m, 1H), 1.23 – 1.28 (m, 1H), 0.94 – 0.97 (m, 9H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 160.2, 137.3, 132.0, 127.8, 115.5, 113.9, 101.5, 81.7, 79.2, 55.6, 41.9, 36.3, 24.6, 23.4, 23.0, 6.7. HRMS (EI$^+$): m/z for $C_{18}H_{26}O_3$ [M]$^+$ calcd. 290.1882, found: 290.1898.

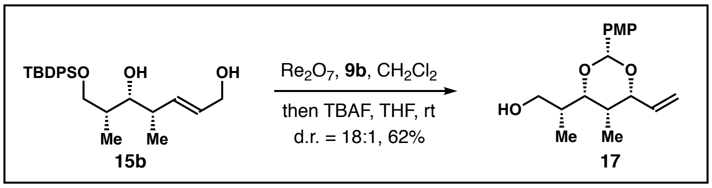


(4*S*,5*R*,6*R*)-2,2,5-trimethyl-4-phenethyl-6-vinyl-1,3-dioxane (13a) Prepared according to the general procedure with 2,2-dimethoxypropane. The crude mixture was purified by flash column chromatography to give compound **13a** in 73% yield (19 mg) as colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.26

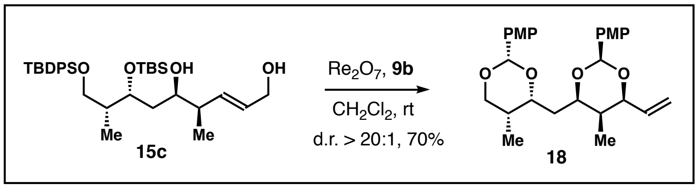
– 7.30 (m, 2H), 7.17 – 7.20 (m, 3H), 5.75 – 5.82 (m, 1H), 5.24 (d, *J* = 17.2 Hz, 1H), 5.15 (d, *J* = 10.8 Hz, 1H), 4.41 – 4.43 (m, 1H), 3.89 – 3.92 (m, 1H), 2.72 – 2.78 (m, 1H), 2.57 – 2.63 (m, 1H), 1.88 – 1.94 (m, 1H), 1.58 – 1.65 (m, 1H), 1.46 (s, 3H), 1.39 – 1.44 (m, 4H), 0.88 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 142.4, 137.9, 128.9, 128.7, 126.2, 115.4, 99.4, 74.6, 72.1, 36.4, 34.9, 31.9, 30.4, 20.1, 5.7. HRMS (EI$^+$): m/z for $C_{17}H_{24}O_2$ [M]$^+$ calcd. 260.1776, found: 260.1793.



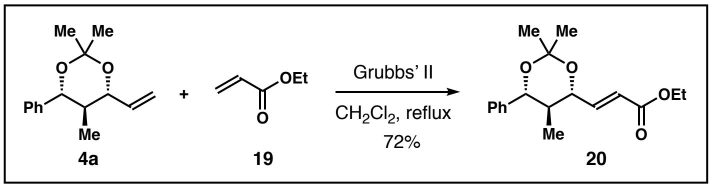
tert-Butyl((*S*)-1-((2*R*,4*R*,5*S*,6*R*)-2-(4-methoxyphenyl)-5-methyl-6-vinyl-1,3-dioxan-4-yl)ethoxy)diphenylsilane (16): Prepared according to the general procedure using diol **15a** and acetal **9b**. The crude mixture was purified by column chromatography to give the title compound as colorless oil in 72% yield (37 mg, dr > 20:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.68 – 7.72 (m, 4H), 7.34 – 7.44 (m, 8H), 6.83 – 6.86 (m, 2H), 5.89 (ddd, *J* = 17.4, 10.8, 4.6 Hz, 1H), 5.54 (s, 1H), 5.32 – 5.37 (m, 1H), 5.20 – 5.23 (m, 1H), 4.45 – 4.47 (m, 1H), 3.81 – 3.86 (m, 1H), 3.78 (s, 3H), 3.71 (dd, *J* = 8.7, 2.1 Hz, 1H), 2.06 – 2.11 (m, 1H), 1.10 (d, *J* = 6.0 Hz, 3H), 1.04 (s, 9H), 0.88 (d, *J* = 6.9 Hz, 4H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 160.2, 137.3, 136.29, 136.25, 135.2, 133.7, 131.7, 130.1, 129.8, 128.0, 127.8, 127.7, 115.5, 113.8, 101.5, 85.6, 81.6, 69.0, 55.6, 33.4, 27.3, 21.5, 19.6, 6.9. HRMS (ESI$^+$): m/z for $C_{30}H_{42}O_4SiNa$ [M+Na]$^+$ calcd. 517.2750, found: 517.2775.



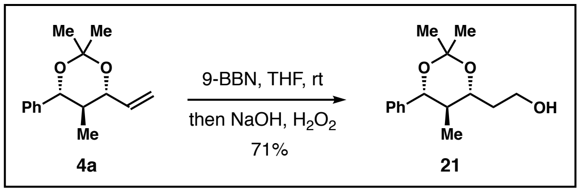
(*R*)-2-((2*R*,4*S*,5*S*,6*R*)-2-(4-methoxyphenyl)-5-methyl-6-vinyl-1,3-dioxan-4-yl)propan-1-ol (17): Prepared according to the general procedure using diol **15b** and acetal **9b** to give crude acetal product. The crude product was dissolved in THF (0.5 mL) and treated with TBAF•H$_2$O (65 mg, 0.25 mmol, 2.5 equiv). Then reaction mixture was kept stirring at ambient temperature for 12 h. Ethyl acetate (1 mL) and brine (1 mL) were added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (1 mL x 3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography to give compound **17** as colorless oil in 62% yield (18 mg, dr = 18:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.48 (m, 2H), 6.88 – 6.91 (m, 2H), 5.86 (ddd, *J* = 17.4, 10.8, 4.7 Hz, 1H), 5.56 (s, 1H), 5.32 – 5.36 (m, 1H), 5.19 – 5.22 (m, 1H), 4.42 – 4.44 (m, 1H), 3.81 (s, 3H), 3.74 (dd, *J* = 9.6, 2.1 Hz, 1H), 3.65 – 3.69 (m, 1H), 3.58 – 3.63 (m, 1H), 1.91 – 1.99 (m, 1H), 1.74 – 1.79 (m, 1H), 1.33 (t, *J* = 5.5 Hz, 1H), 1.13 (d, *J* = 6.7 Hz, 3H), 1.00 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 137.1, 131.9, 127.8, 115.6, 113.9, 101.7, 83.1, 81.5, 64.5, 55.7, 37.1, 34.6, 14.3, 7.1. HRMS (ESI$^+$): m/z for $C_{17}H_{24}O_4Na$ $[M+Na]^+$ calcd. 315.1572, found: 315.1569.



(2*R*,4*R*,5*S*,6*S*)-2-(4-methoxyphenyl)-4-(((2*S*,4*R*,5*R*)-2-(4-methoxyphenyl)-5-methyl-1,3-dioxan-4-yl)methyl)-5-methyl-6-vinyl-1,3-dioxane (18): Prepared according to the general procedure using diol **15c** and acetal **9b** (3 equiv) for 24 h. The crude mixture was purified by column chromatography to give compound **18** as colorless oil in 70% yield (32 mg, dr > 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.48 (m, 4H), 6.89 – 6.92 (m, 4H), 5.83 (ddd, *J* = 17.3, 10.8, 4.7 Hz, 1H), 5.57 (s, 1H), 5.49 (s, 1H), 5.28 – 5.32 (m, 1H), 5.17 – 5.20 (m, 1H), 4.43 – 4.45 (m, 1H), 4.15 – 4.20 (m, 2H), 4.07 (dd, *J* = 11.2, 2.6 Hz, 1H), 3.98 (dd, *J* = 11.1, 1.3 Hz, 1H), 3.81 (app. s, 6H), 1.63 – 1.72 (m, 2H), 1.51 – 1.57 (m, 2H), 1.19 (d, *J* = 6.9 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.28, 160.27, 137.1, 132.0, 131.9, 127.9, 127.7, 115.6, 114.01, 113.96, 102.0, 101.6, 81.5, 76.9, 76.2, 74.1, 55.7 (two overlapping carbon signals), 37.4, 36.7, 32.8, 11.7, 6.8. HRMS (ESI$^+$): m/z for $C_{27}H_{35}O_6$ $[M+H]^+$ calcd. 455.2434, found: 455.2425.

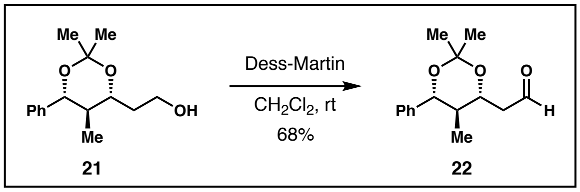


Ethyl (*E*)-3-((4*R*,5*R*,6*R*)-2,2,5-trimethyl-6-phenyl-1,3-dioxan-4-yl)acrylate (20): To an oven-dried 2-dram vial equipped with a magnetic stirring bar was added Grubbs 2nd generation catalyst (8 mg, 0.01 mmol, 10 mol %). Then acrylate **19** (50 mg, 0.5 mmol, 5 equiv) was added to the vial followed by the addition of a solution of acetal **4a** (23 mg, 0.10 mmol, 1.0 equiv) in dichloromethane (0.5 mL). The reaction mixture was kept stirring under argon in refluxing CH_2Cl_2 for 12 h. After complete consumption of acetal **4a**, the reaction mixture was diluted with diethyl ether (10 mL). The resulting mixture was filtered through a shot pad of silica gel, and the filtrate was concentrated under reduced pressure. The crude reaction product was purified by flash column chromatography (gradient elution with hexane and ethyl acetate, 30:1 to 10:1) to give product **20** as colorless oil (22 mg, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.37 (m, 4H), 7.28 – 7.32 (m, 1H), 6.96 (dd, *J* = 15.6, 5.7 Hz, 1H), 6.13 (dd, *J* = 15.6, 1.4 Hz, 1H), 4.48 (d, *J* = 10.2 Hz, 1H), 4.28 (dd, *J* = 10.3, 5.7 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.62 – 1.71 (m, 1H), 1.59 (s, 3H), 1.52 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 4H), 0.69 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 145.5, 140.3, 128.8, 128.6, 128.0, 122.9, 99.4, 78.6, 74.9, 60.8, 40.5, 30.4, 19.9, 14.6, 12.5. HRMS (ESI$^+$): m/z for $C_{18}H_{28}O_4N$ $[M+NH_4]^+$ calcd. 322.2018, found: 322.2002.

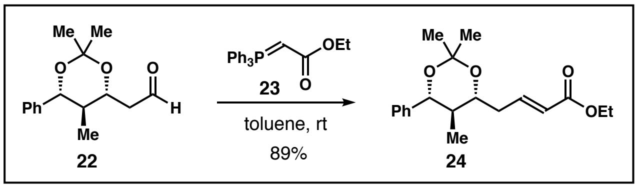


2-((4*R*,5*R*,6*R*)-2,2,5-trimethyl-6-phenyl-1,3-dioxan-4-yl)ethan-1-ol (21): In an Ar-filled glove box, **4a** (70 mg, 0.30 mmol, 1.0 equiv), THF (0.5 mL), 9-BBN (110 mg, 0.45 mmol, 1.5 equiv) and a Teflon-coated magnetic stirring bar were sequentially added to a 1-dram vial. And the mixture was kept stirring for 2 h at ambient temperature in the glove box. After complete consumption of **4a**, the vial was removed from the glove box. An aqueous solution of NaOH (3 N, 0.5 mL) was added to the reaction mixture, followed by slow addition a solution of 30% H_2O_2 (0.5 mL). The resulting mixture was kept stirring at ambient temperature for 1 h. Then diethyl ether (1 mL) and brine (1 mL) was added. The organic layer was separated and the aqueous layer was extracted with Et_2O (2 mL x 3). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution with hexane and ethyl acetate 20:1 to 10:1) to give alcohol **21** in 71% yield (53 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.38 (m, 4H), 7.27 – 7.31 (m, 1H), 4.44 (d, *J* = 10.3 Hz, 1H), 3.90 – 3.94 (m, 1H), 3.77 – 3.87 (m, 2H), 2.73 (dd, *J* = 7.1, 3.9 Hz, 1H), 1.94 – 2.00 (m, 1H), 1.66 –

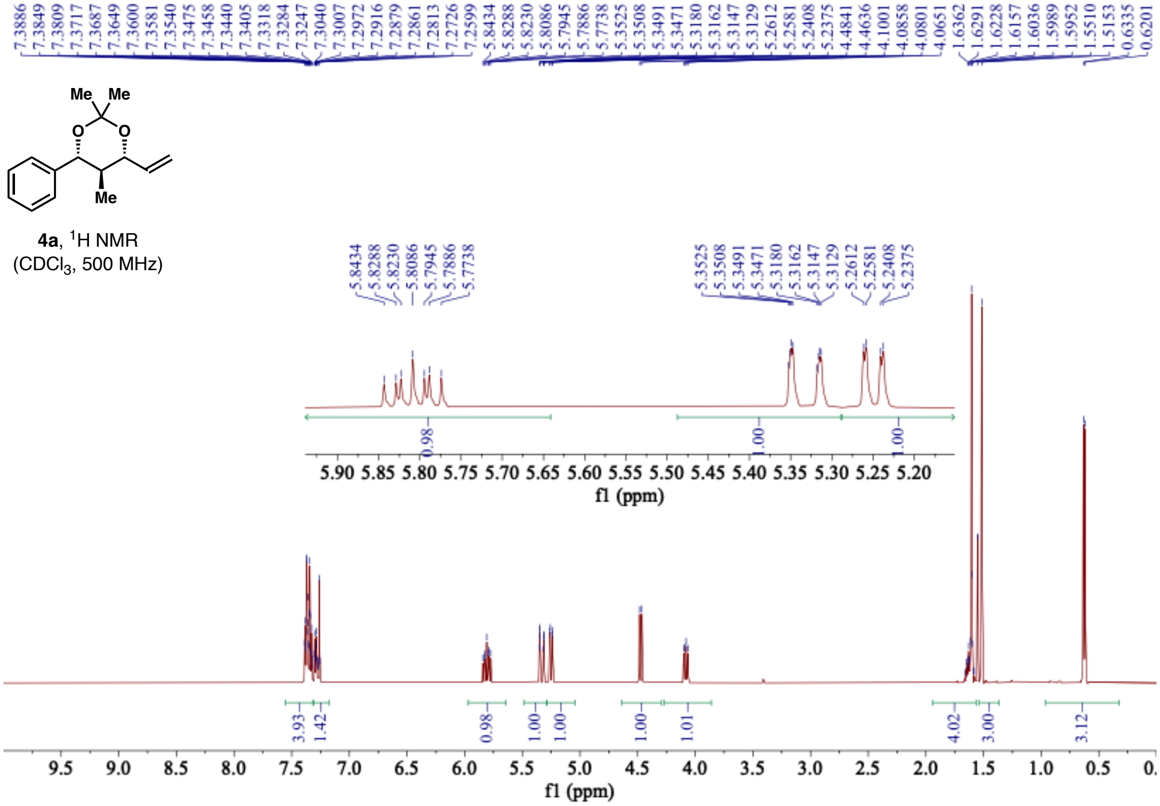
1.76 (m, 2H), 1.59 (s, 3H), 1.48 (s, 3H), 0.64 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 128.7, 128.5, 128.0, 99.1, 78.8, 76.0, 61.5, 40.6, 35.2, 30.6, 20.0, 12.5.

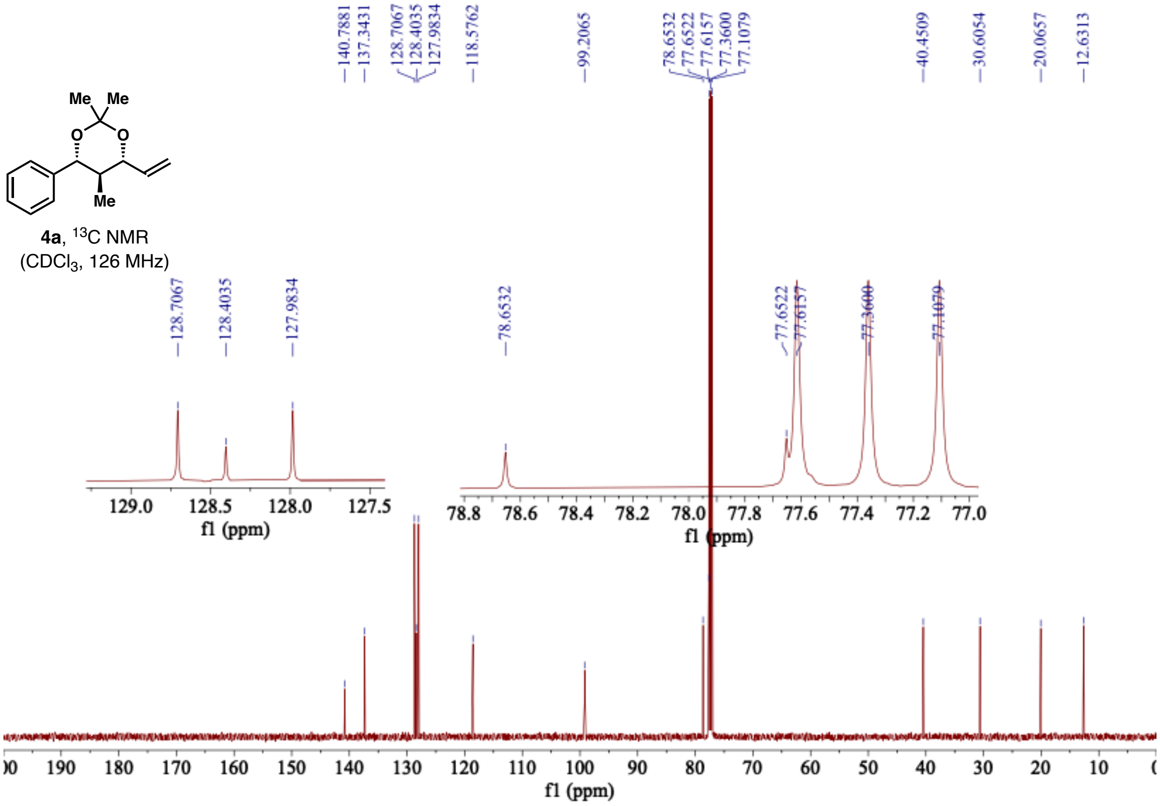


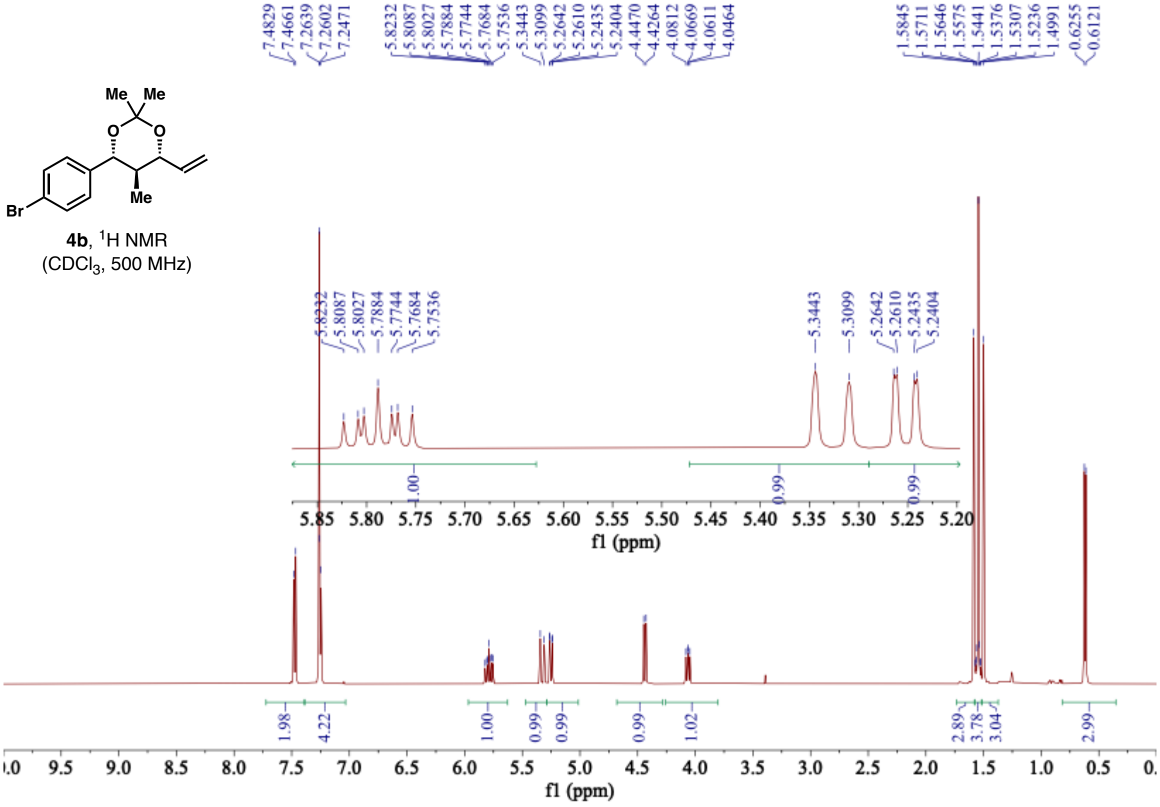
2-((4*R*,5*R*,6*R*)-2,2,5-trimethyl-6-phenyl-1,3-dioxan-4-yl)acetaldehyde (22): To a reaction vial containing a Teflon-coated magnetic stirring bar were added alcohol **21** (50 mg, 0.20 mmol, 1.0 equiv), Dess-Martin periodinane (127 mg, 0.30 mmol, 1.5 equiv) and dichloromethane (1.0 mL). The reaction mixture was allowed to stir at ambient temperature for 2 h. After complete consumption of alcohol **21**, the reaction mixture was diluted with diethyl ether (5 mL). The resulting suspension was filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution with hexane and ethyl acetate, 30:1 to 10:1) to give aldehyde **22** in 68% yield (34 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.84 (dd, *J* = 2.9, 1.6 Hz, 1H), 7.32 – 7.39 (m, 4H), 7.32 – 7.28 (m, 1H), 4.47 (d, *J* = 10.2 Hz, 1H), 4.21 – 4.26 (m, 1H), 2.63 – 2.67 (m, 1H), 2.54 – 2.60 (m, 1H), 1.62 – 1.71 (m, 1H), 1.59 (s, 3H), 1.46 (s, 3H), 0.65 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.9, 140.4, 128.8, 128.6, 128.0, 99.3, 78.7, 71.3, 47.5, 40.8, 30.4, 19.9, 12.5.



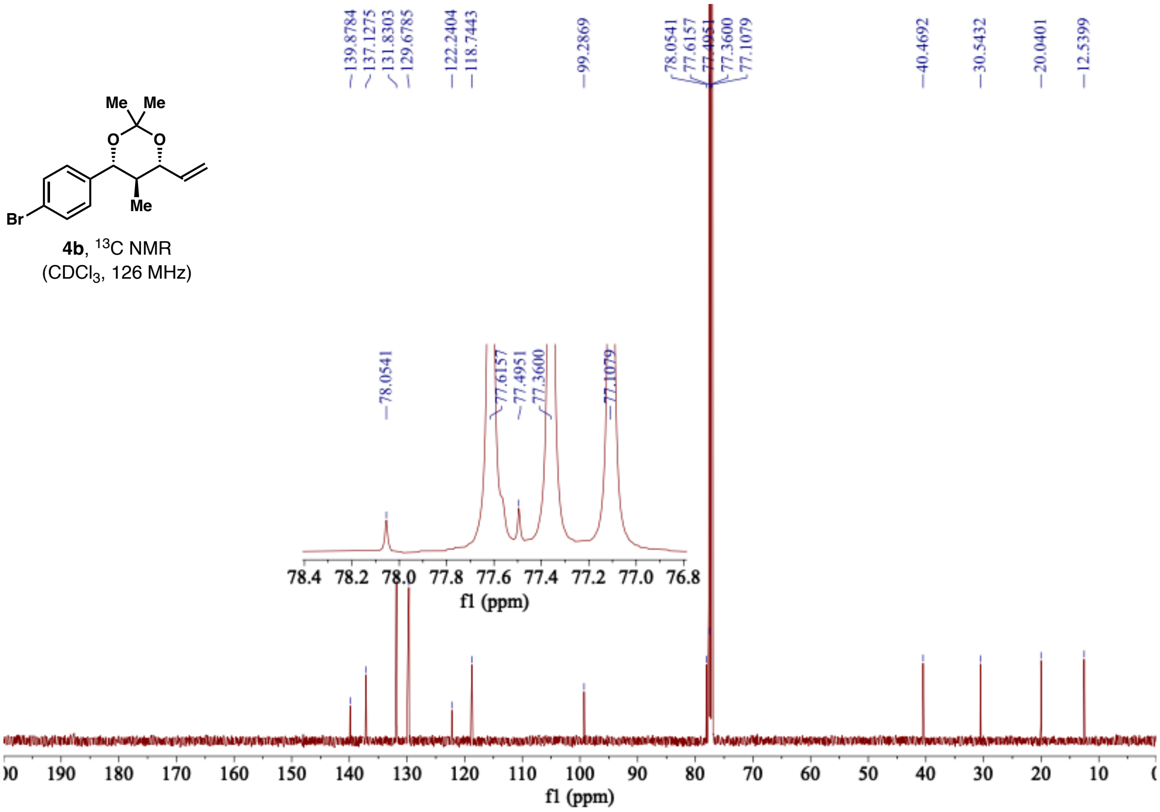
Ethyl (*E*)-4-((4*R*,5*R*,6*R*)-2,2,5-trimethyl-6-phenyl-1,3-dioxan-4-yl)but-2-enoate (24): To a 2-dram vial containing a Teflon-coated magnetic stirring bar was added aldehyde **22** (12 mg, 0.05 mmol, 1.0 equiv). Then ethyl (triphenylphosphoranylidene)acetate **23** (35 mg, 0.1 mmol, 2.0 equiv) and toluene (0.3 mL) were added to the vial. The reaction mixture was kept stirring for 48 h at ambient temperature. After complete consumption of **22**, the mixture was diluted with diethyl ether (10 mL). The resulting solution was filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution with hexane and ethyl acetate, 30:1 to 10:1) to give product **24** in 89% yield (14 mg, *E*:*Z* > 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.37 (m, 4H), 7.27 – 7.31 (m, 1H), 7.06 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.89 (d, *J* = 15.7 Hz, 1H), 4.42 (d, *J* = 10.3 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.77 – 3.81 (m, 1H), 2.53 – 2.59 (m, 1H), 2.34 – 2.41 (m, 1H), 1.57 – 1.65 (m, 1H), 1.55 (s, 3H), 1.47 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.64 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 145.7, 140.7, 128.7, 128.4, 128.1, 123.5, 99.2, 78.7, 74.0, 60.6, 40.4, 36.3, 30.5, 19.9, 14.6, 12.5. HRMS (ESI$^+$): m/z for $C_{19}H_{26}O_4Na$ $[M+Na]^+$ calcd. 341.1729, found: 341.1720.


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

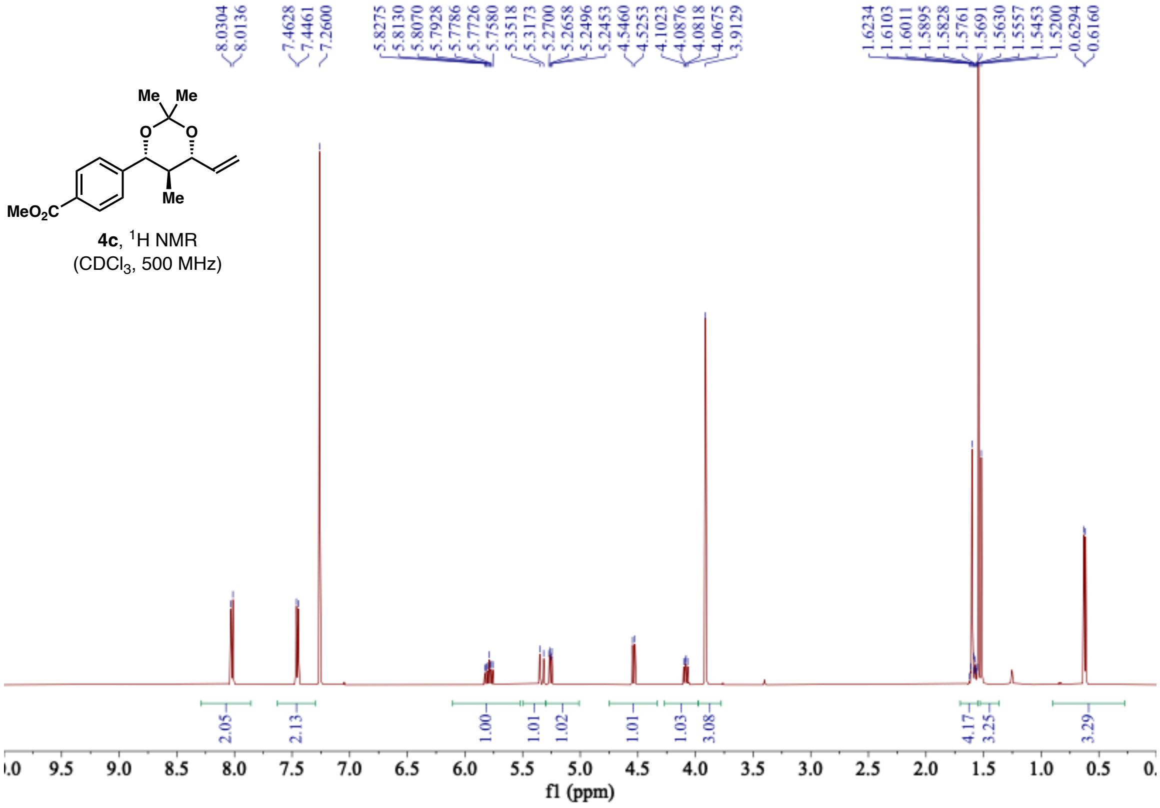

4a, ^{13}C NMR
($CDCl_3$, 126 MHz)

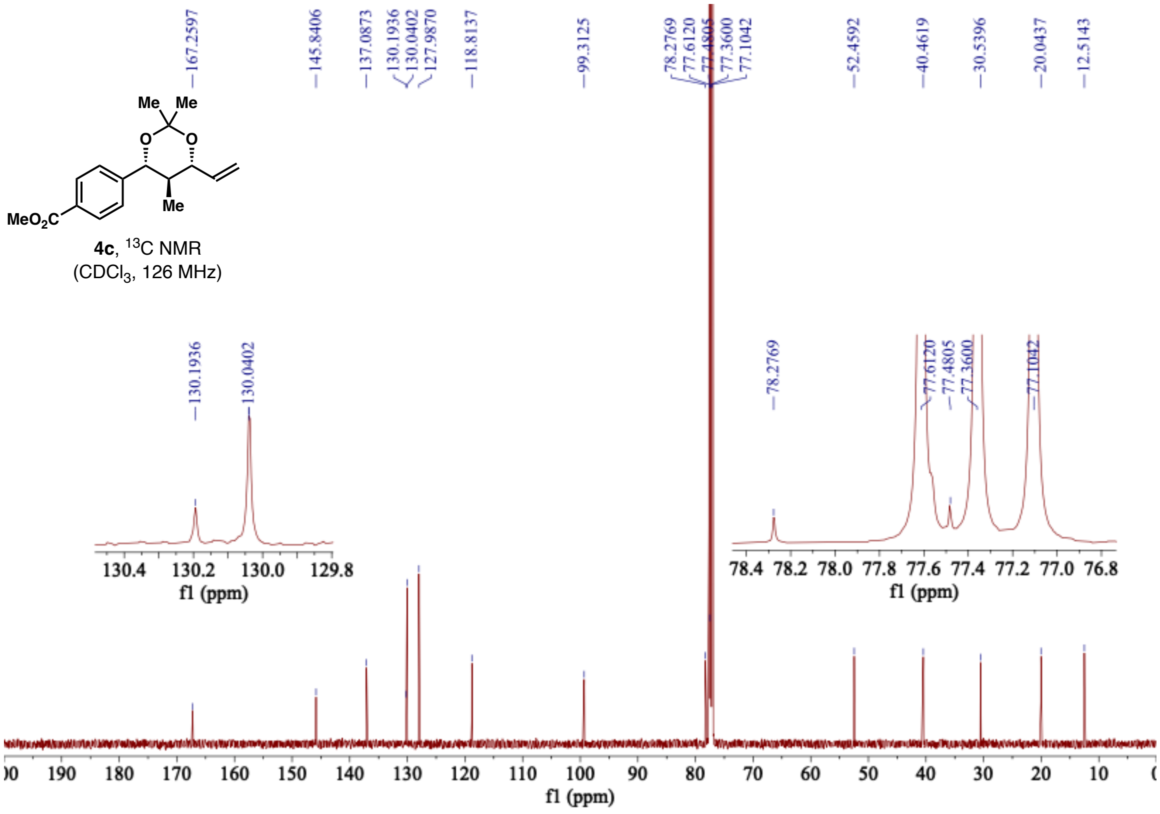


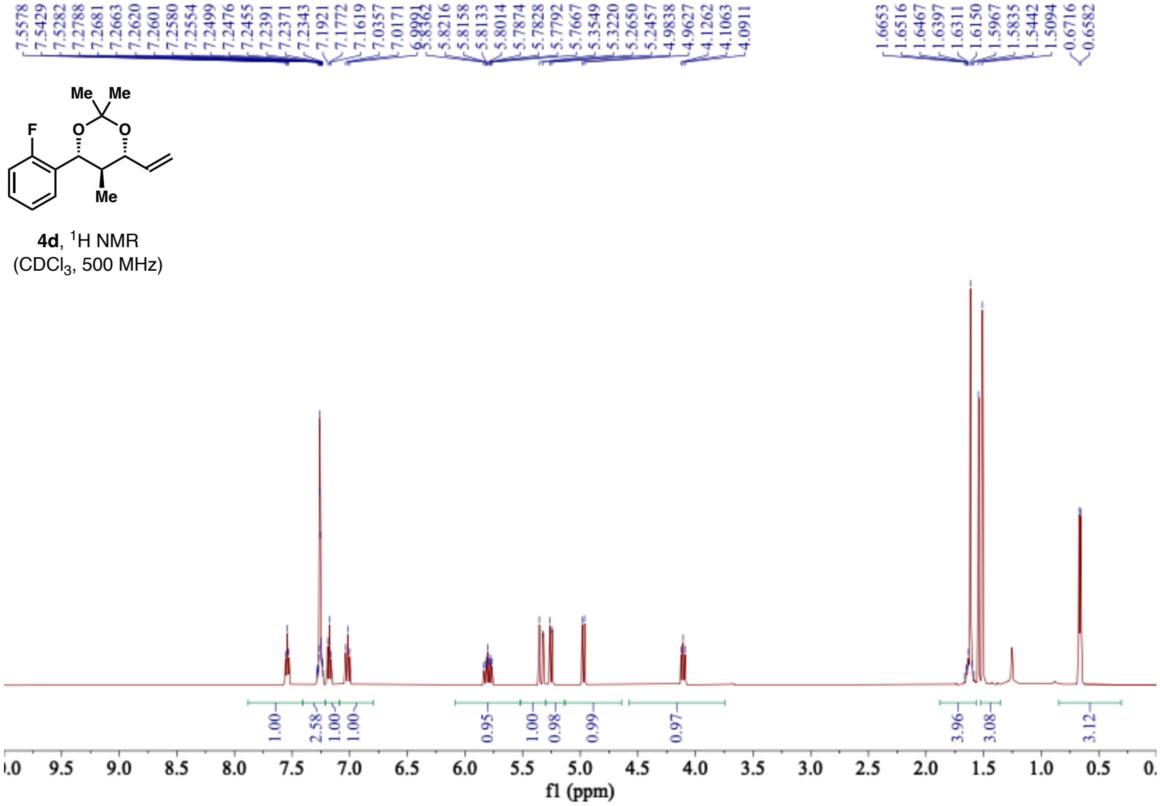
4b, ^{1}H NMR
(CDCl$_3$, 500 MHz)



4b, ^{13}C NMR
(CDCl$_3$, 126 MHz)


4c, ^{1}H NMR
(CDCl$_3$, 500 MHz)


4c, ^{13}C NMR
(CDCl$_3$, 126 MHz)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Me
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4d, ^{1}H NMR
(CDCl$_3$, 500 MHz)
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1.00
1.00
0.95
1.00
0.98
0.99
0.97
3.96
3.08
3.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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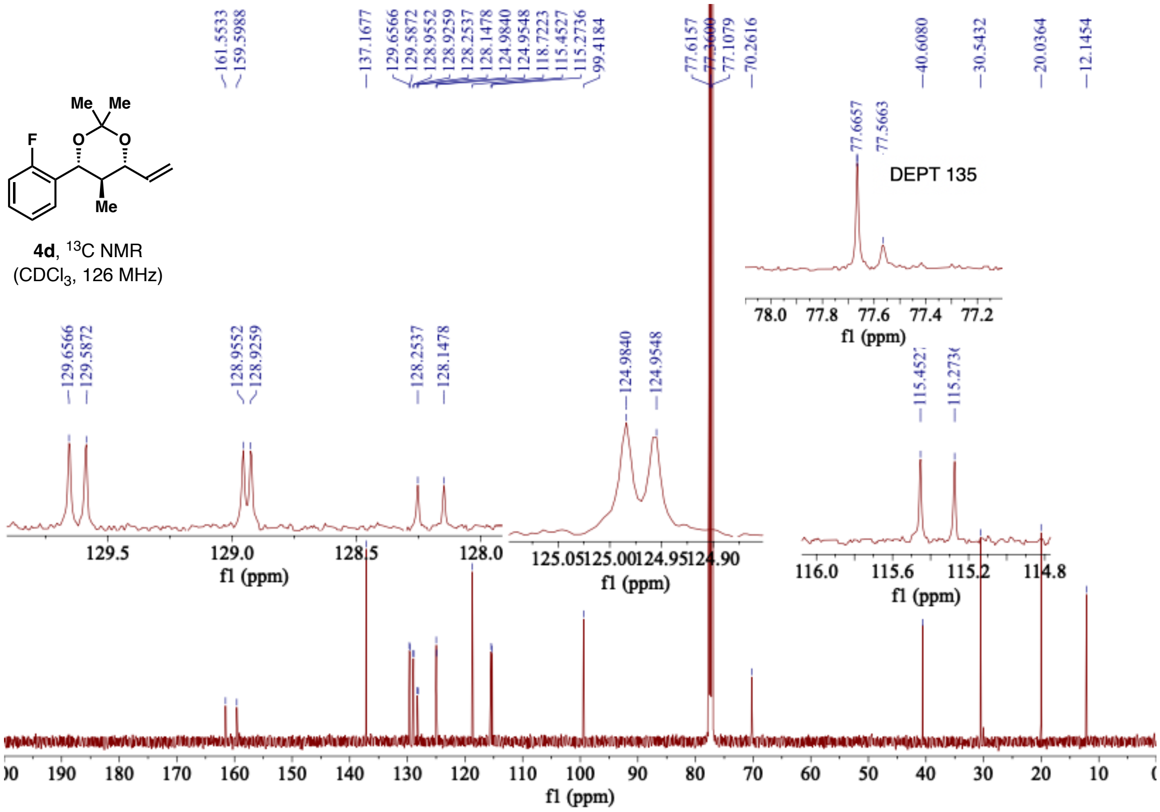
0.5
f1 (ppm)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(CDCl$_3$, 126 MHz)
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f1 (ppm)
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115.2
114.8
f1 (ppm)
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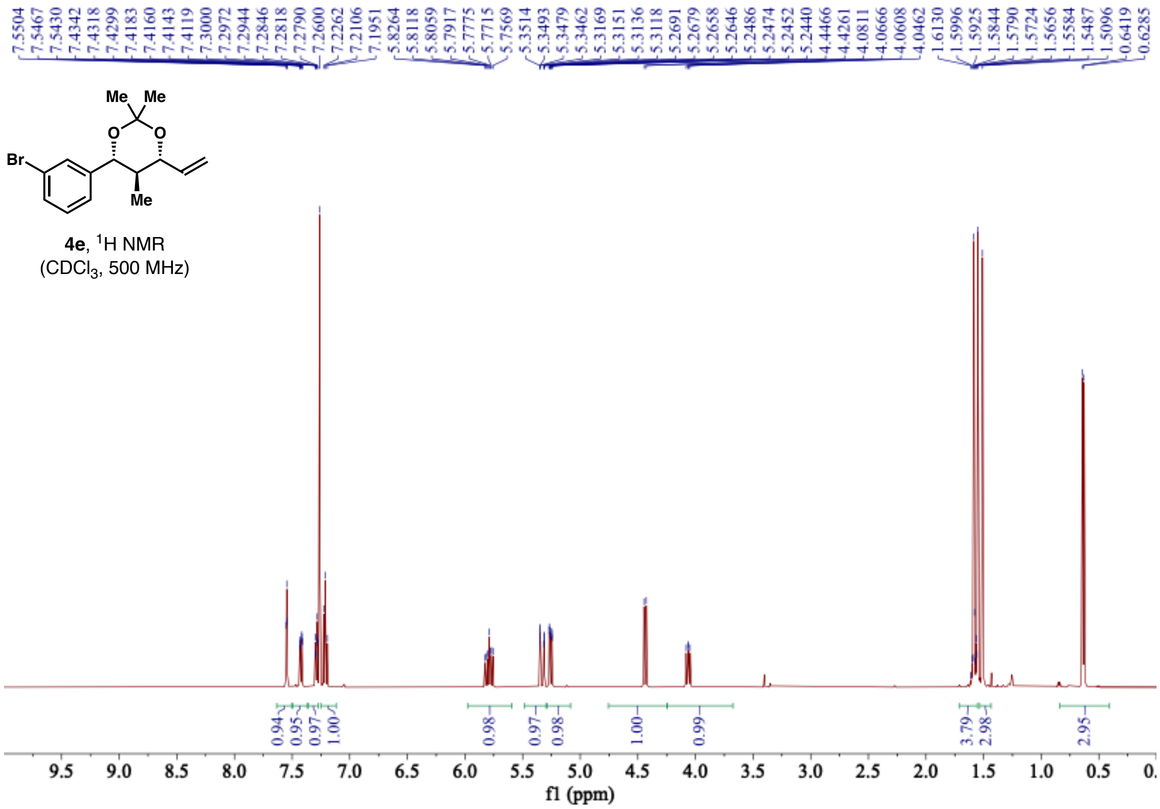
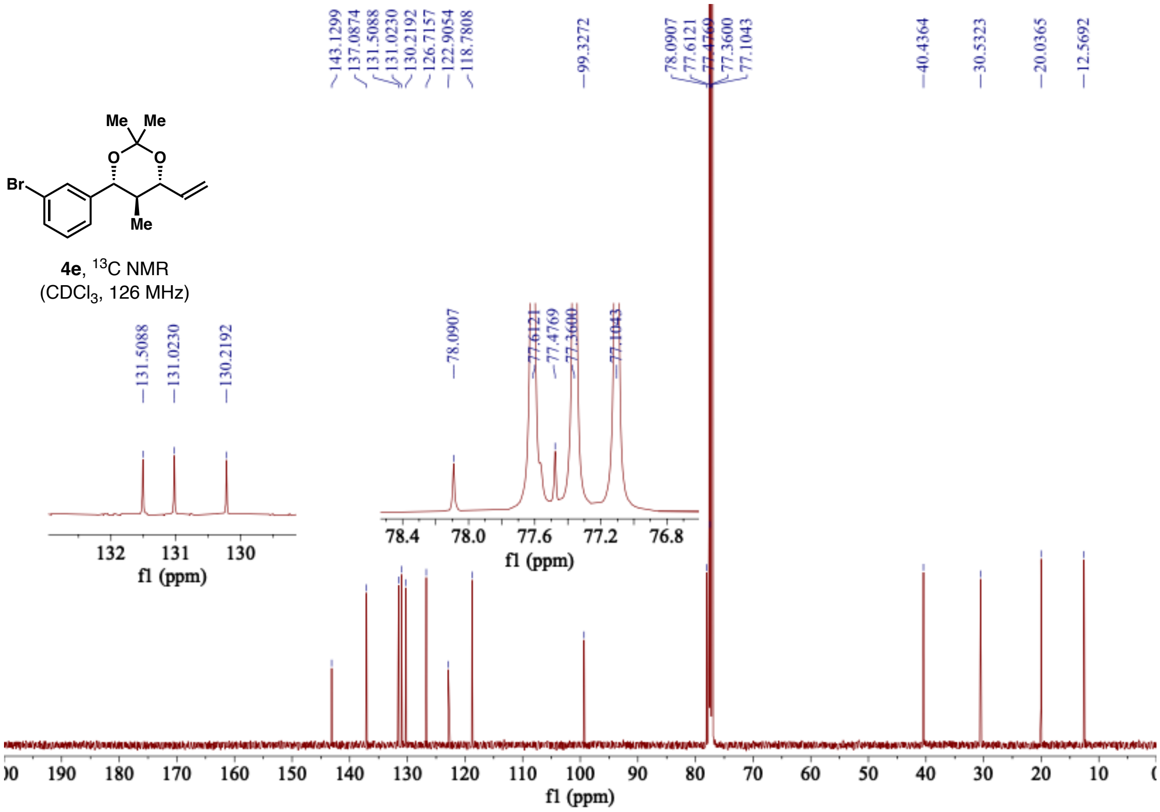
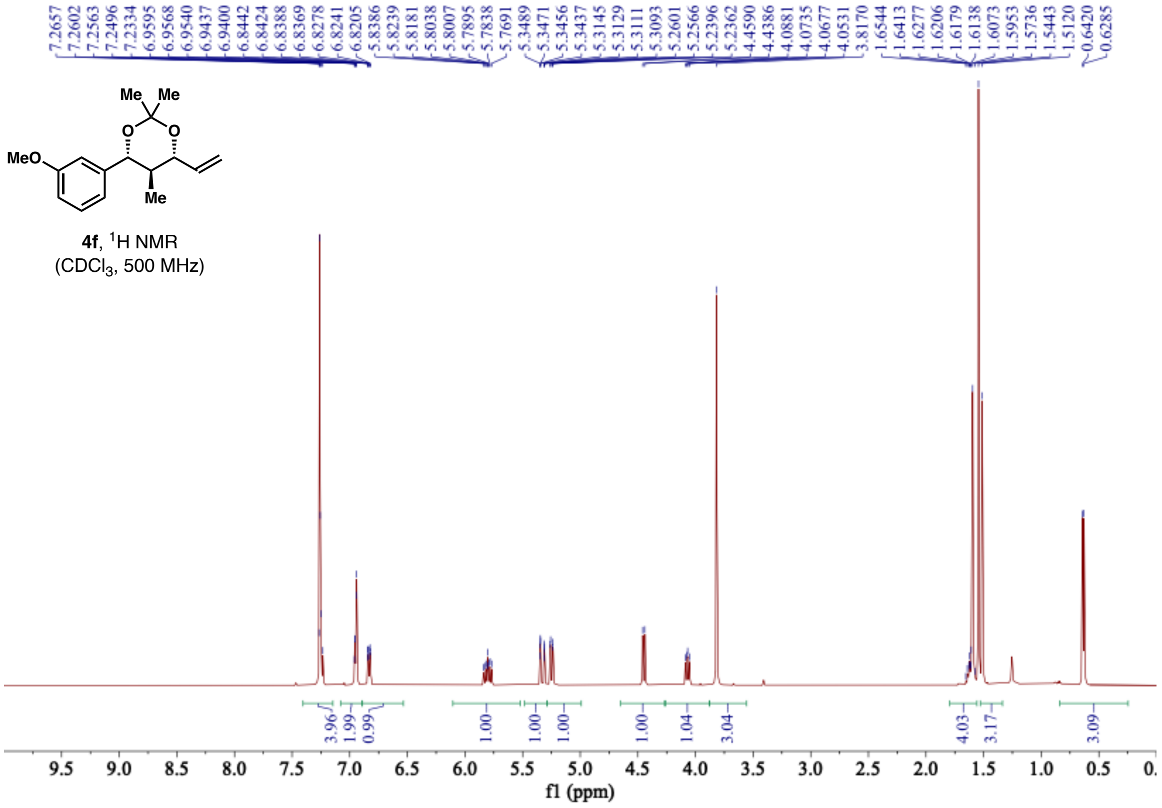
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



4e, ^{1}H NMR
(CDCl$_3$, 500 MHz)



4e, ^{13}C NMR
(CDCl$_3$, 126 MHz)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MeO
Me
4f, 1H NMR
(CDCl3, 500 MHz)
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1.00
1.00
1.00
1.00
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3.04
4.03
3.17
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9.0
8.5
8.0
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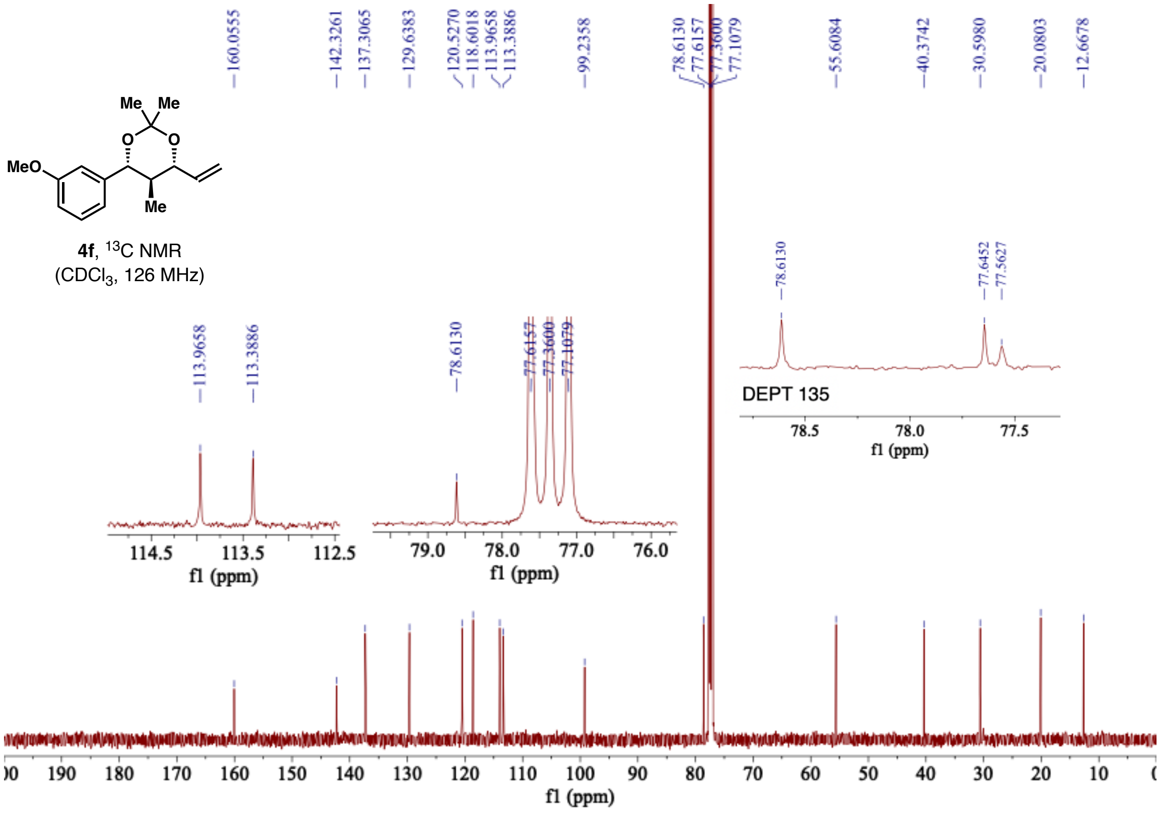
f1 (ppm)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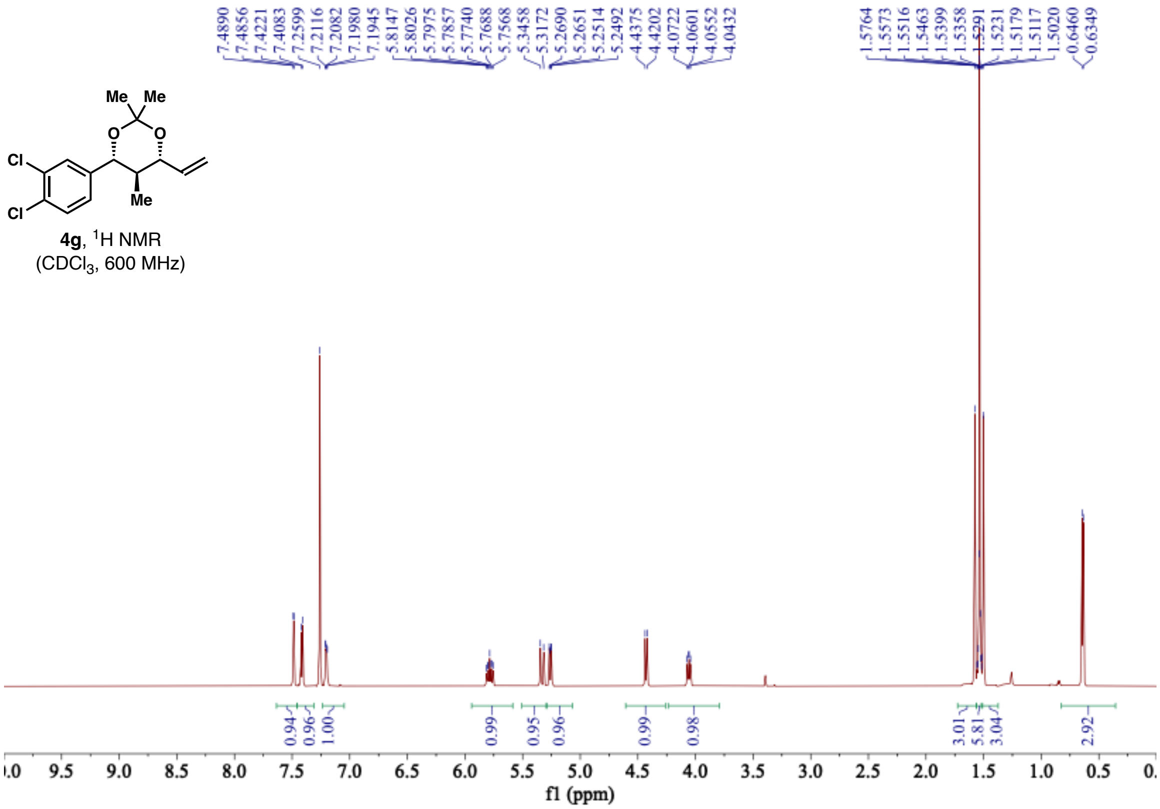
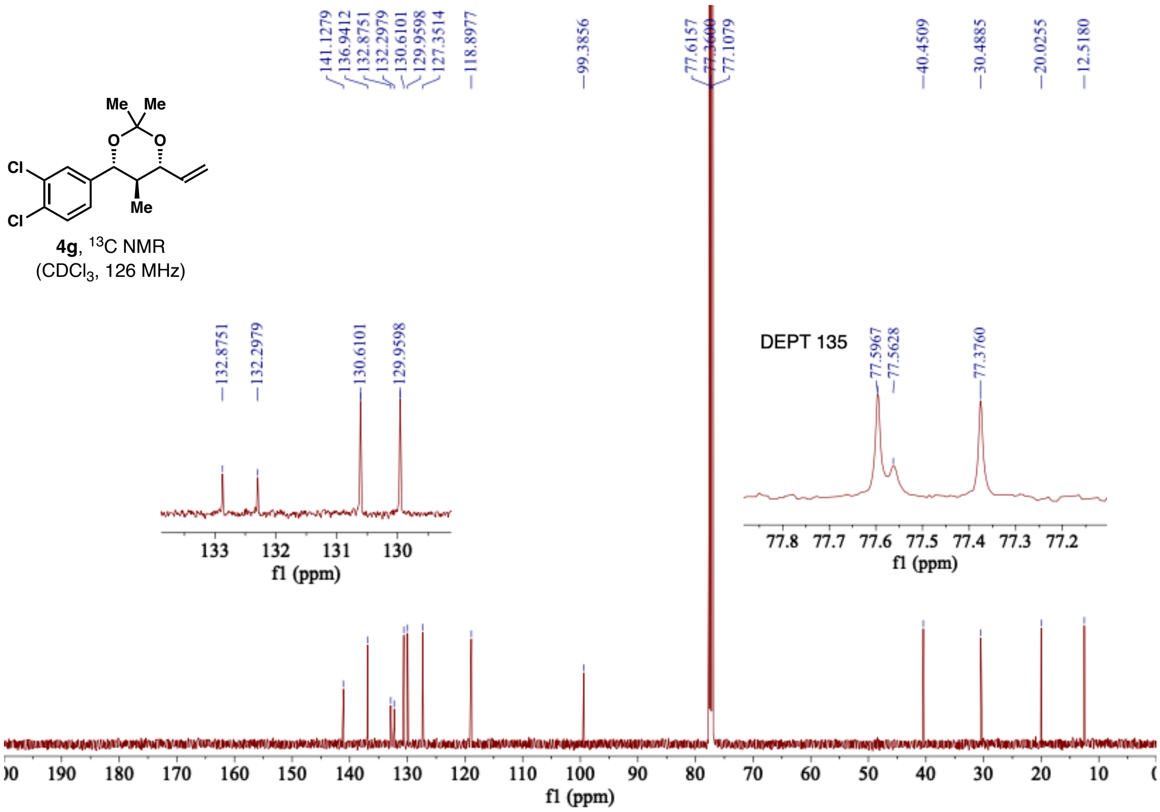
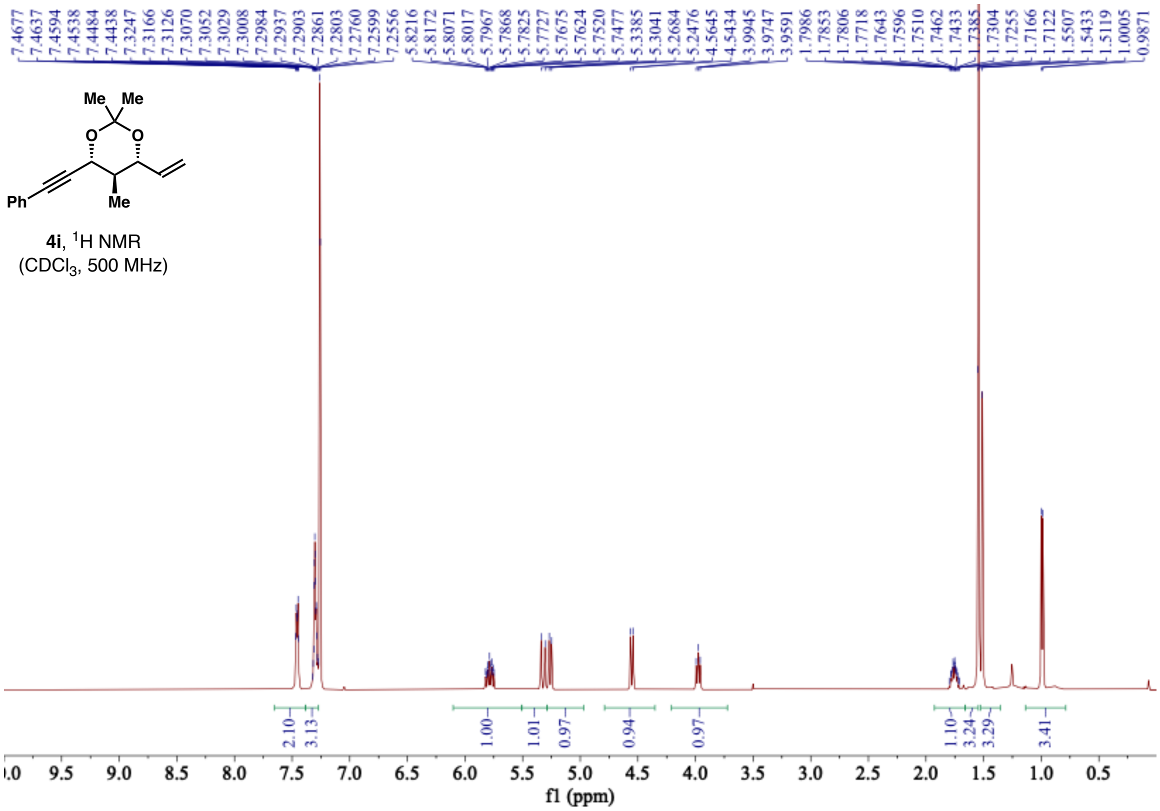
77.6157
77.3600
77.1079
55.6084
40.3742
30.5980
20.0803
12.6678
Me
Me
O
O
MeO
Me
4f, 13C NMR
(CDCl3, 126 MHz)
113.9658
113.3886
114.5
113.5
112.5
f1 (ppm)
78.6130
77.6157
77.3600
77.1079
79.0
78.0
77.0
76.0
f1 (ppm)
78.6130
77.6452
77.5627
DEPT 135
78.5
78.0
77.5
f1 (ppm)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

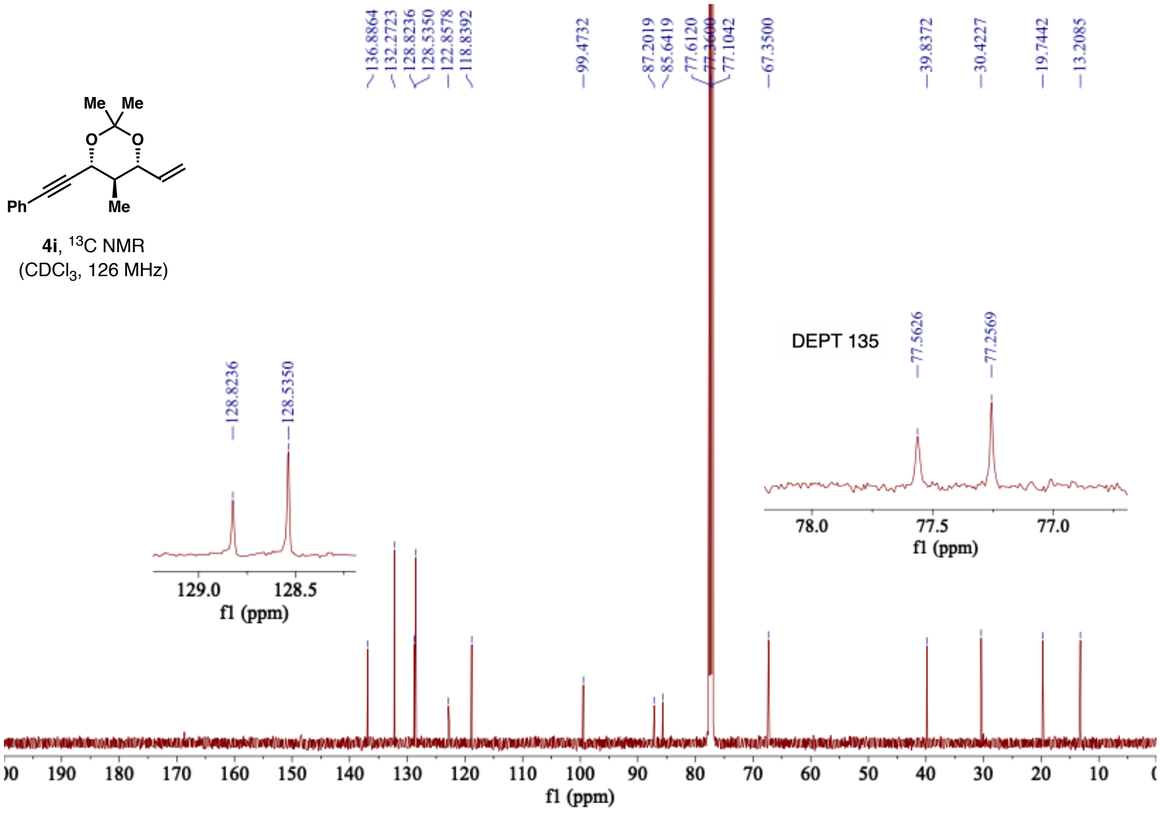


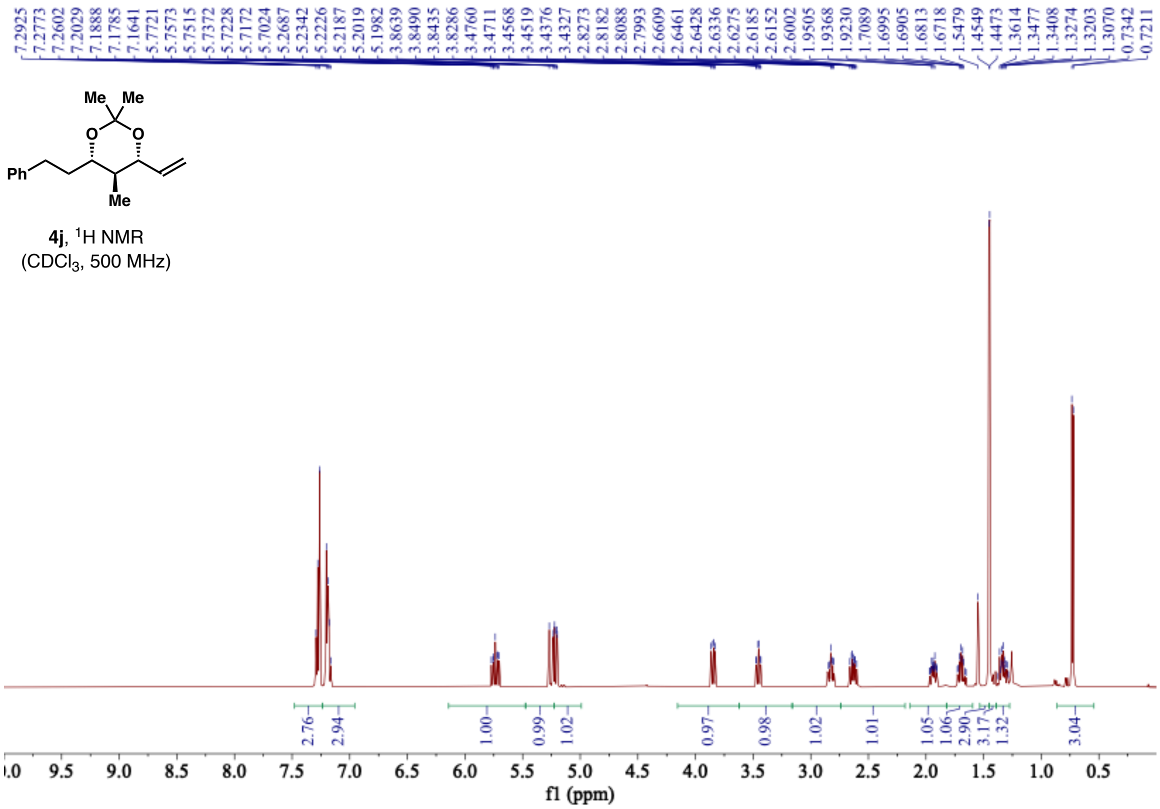
4g, ^{1}H NMR
($CDCl_3$, 600 MHz)



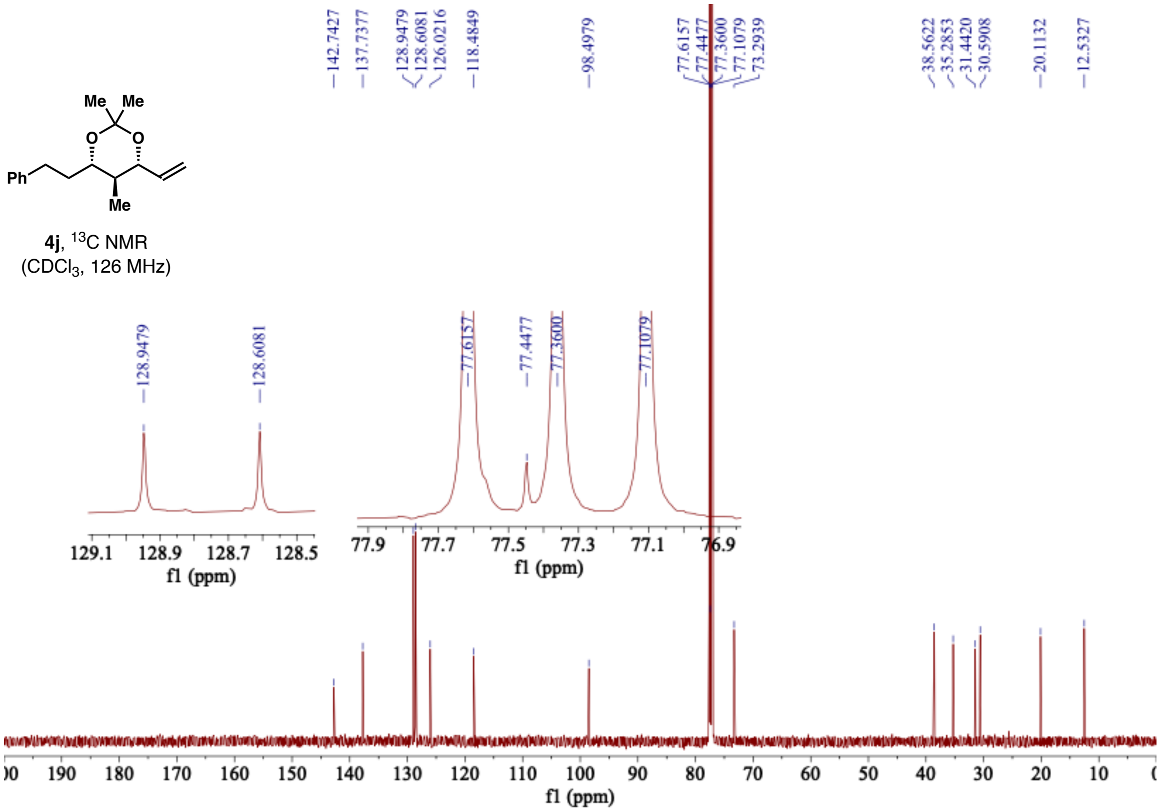
4g, ^{13}C NMR
($CDCl_3$, 126 MHz)


4i, ¹H NMR
($CDCl_3$, 500 MHz)

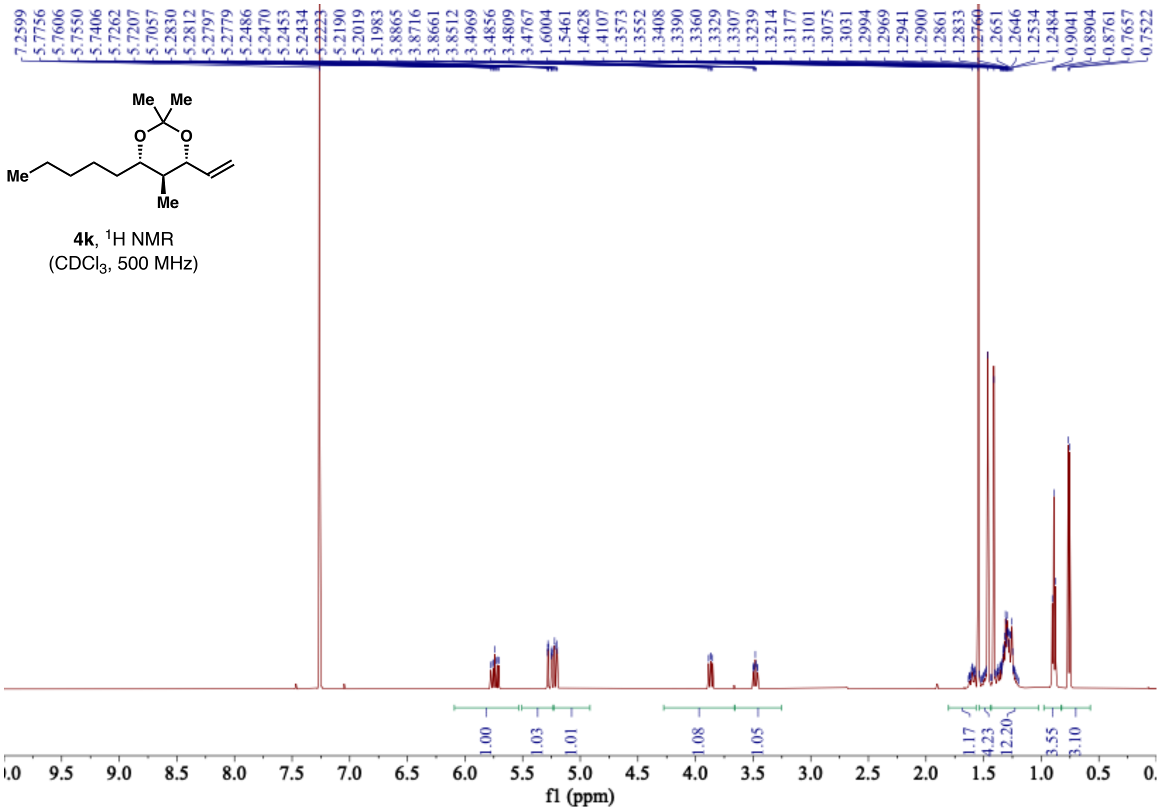

4i, ¹³C NMR
($CDCl_3$, 126 MHz)



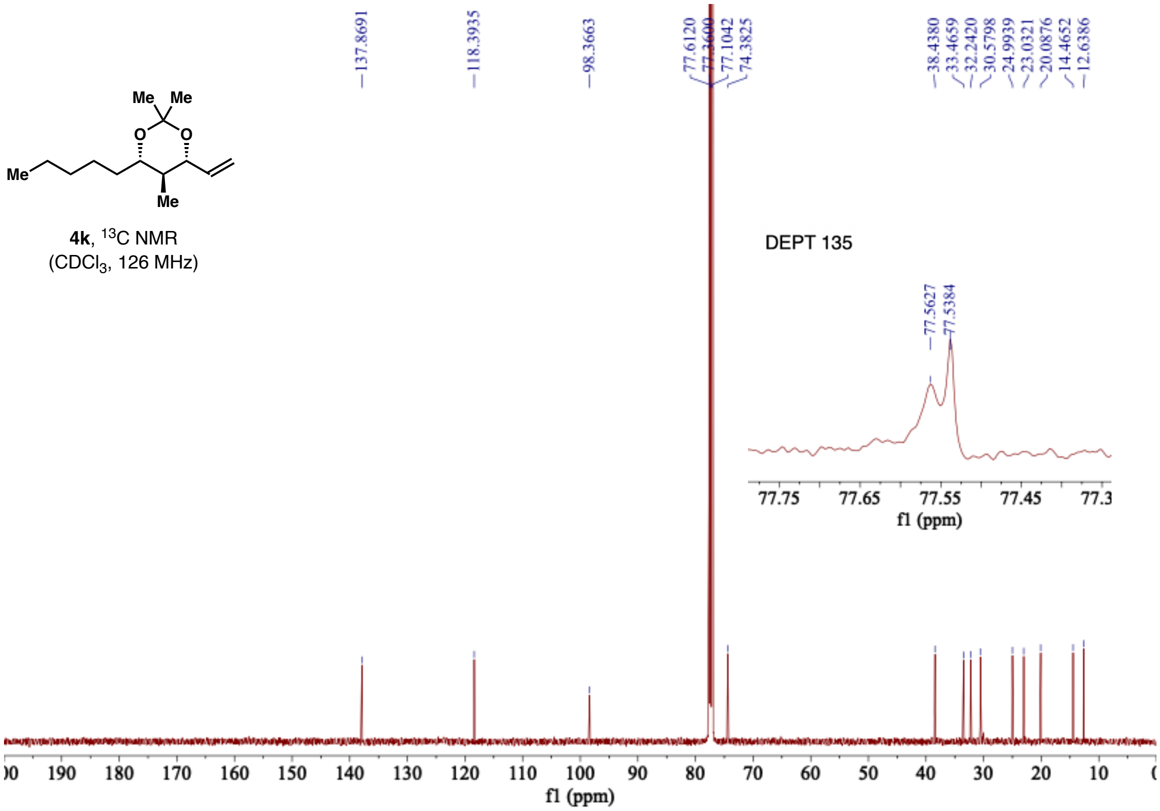
4j, ^{1}H NMR
(CDCl$_3$, 500 MHz)



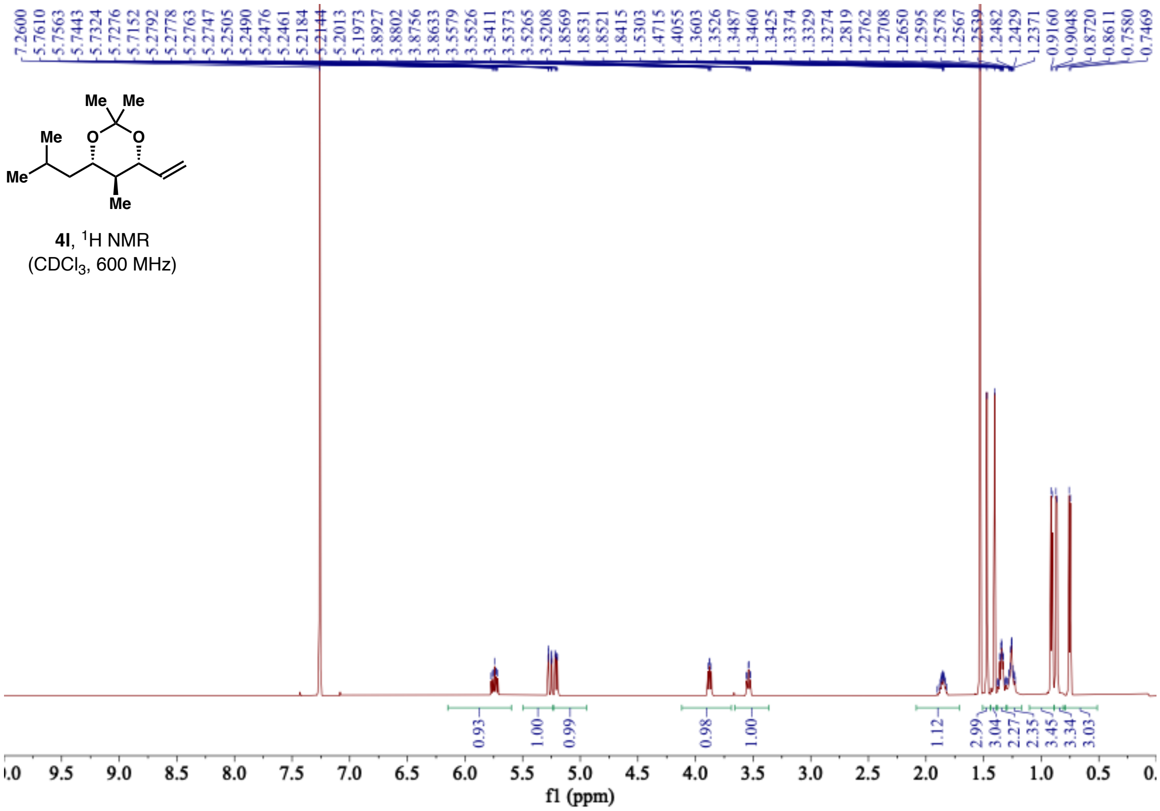
4j, ^{13}C NMR
(CDCl$_3$, 126 MHz)



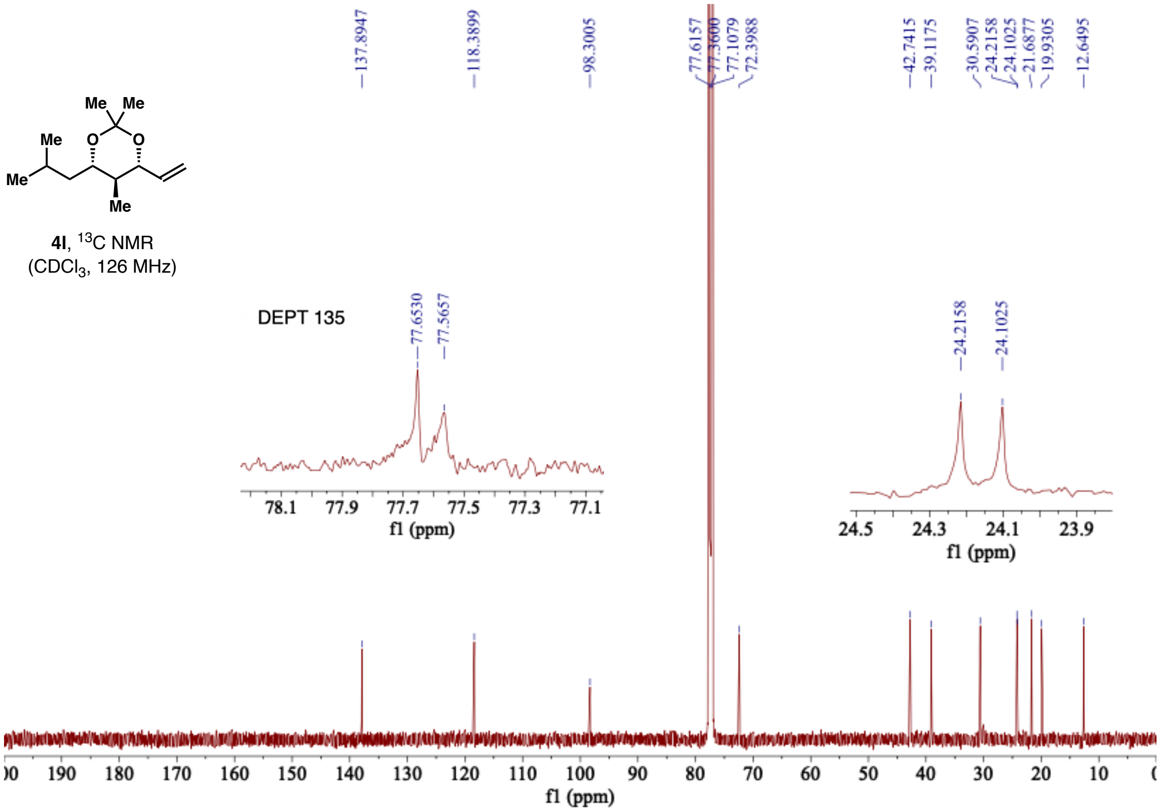
4k, ^{1}H NMR
($CDCl_3$, 500 MHz)



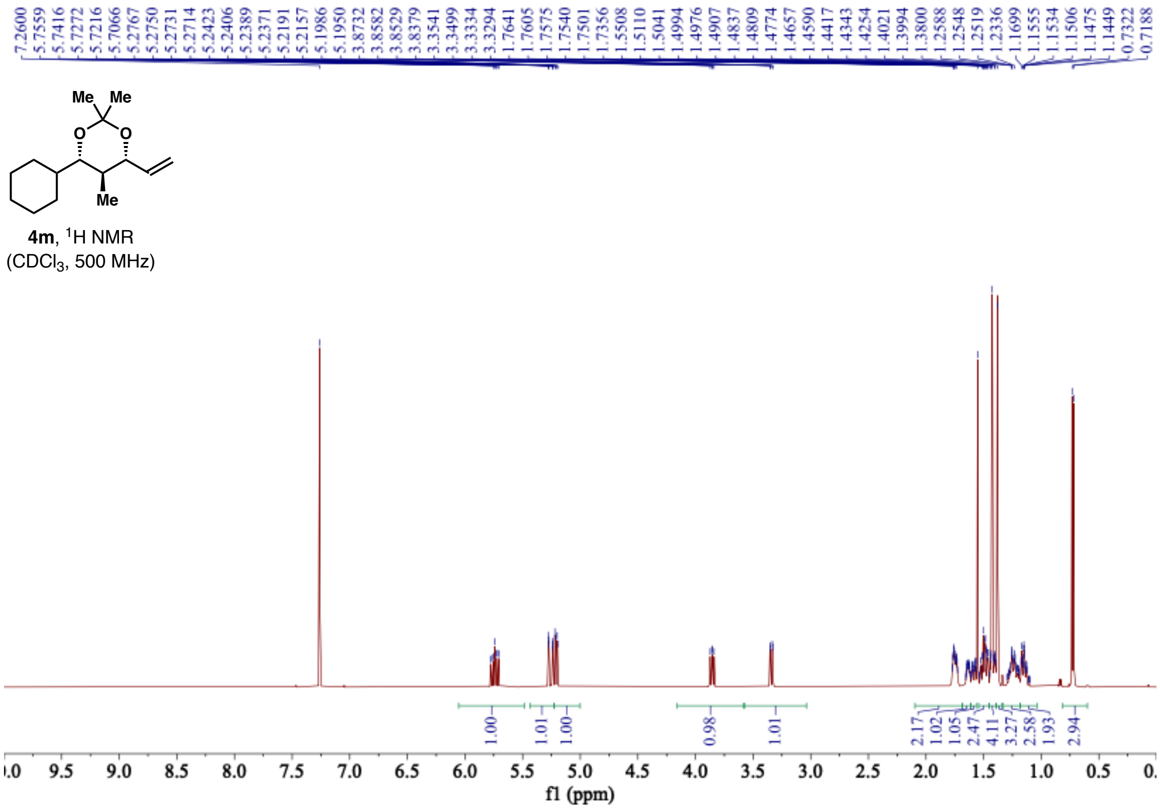
4k, ^{13}C NMR
($CDCl_3$, 126 MHz)



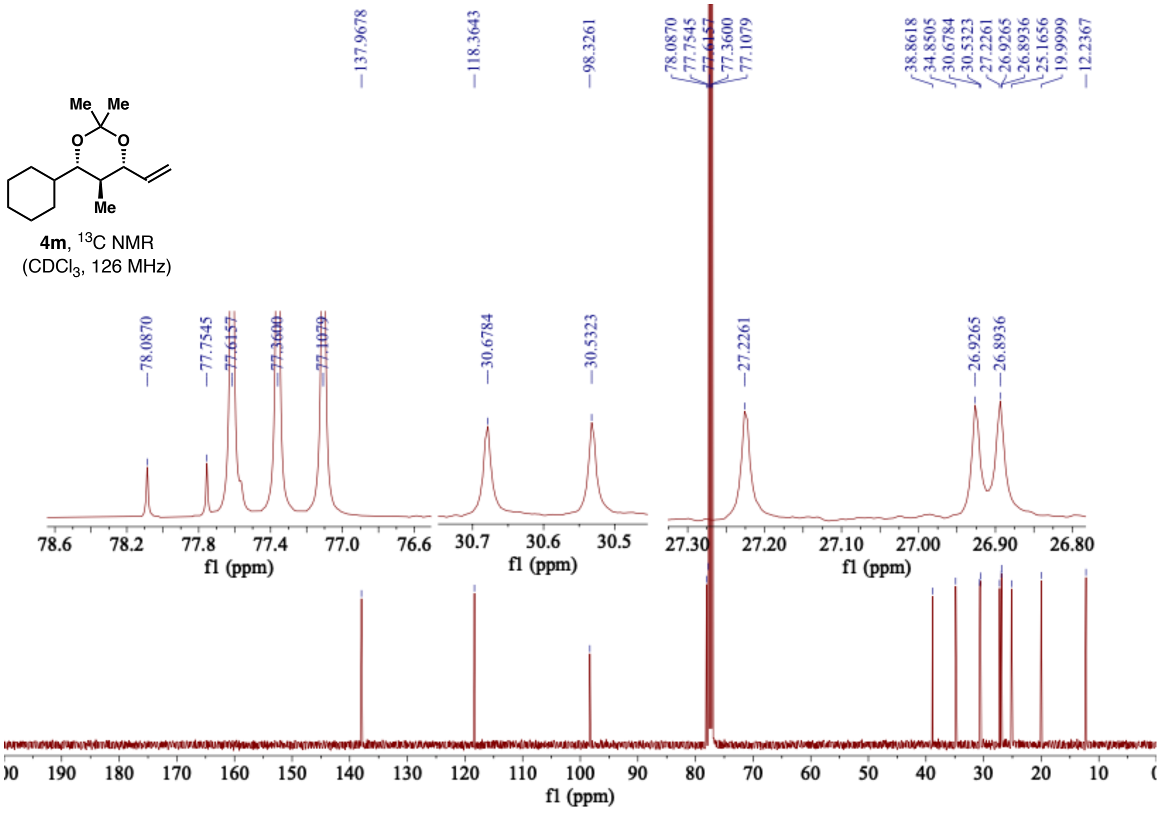
4l, ^{1}H NMR
($CDCl_3$, 600 MHz)



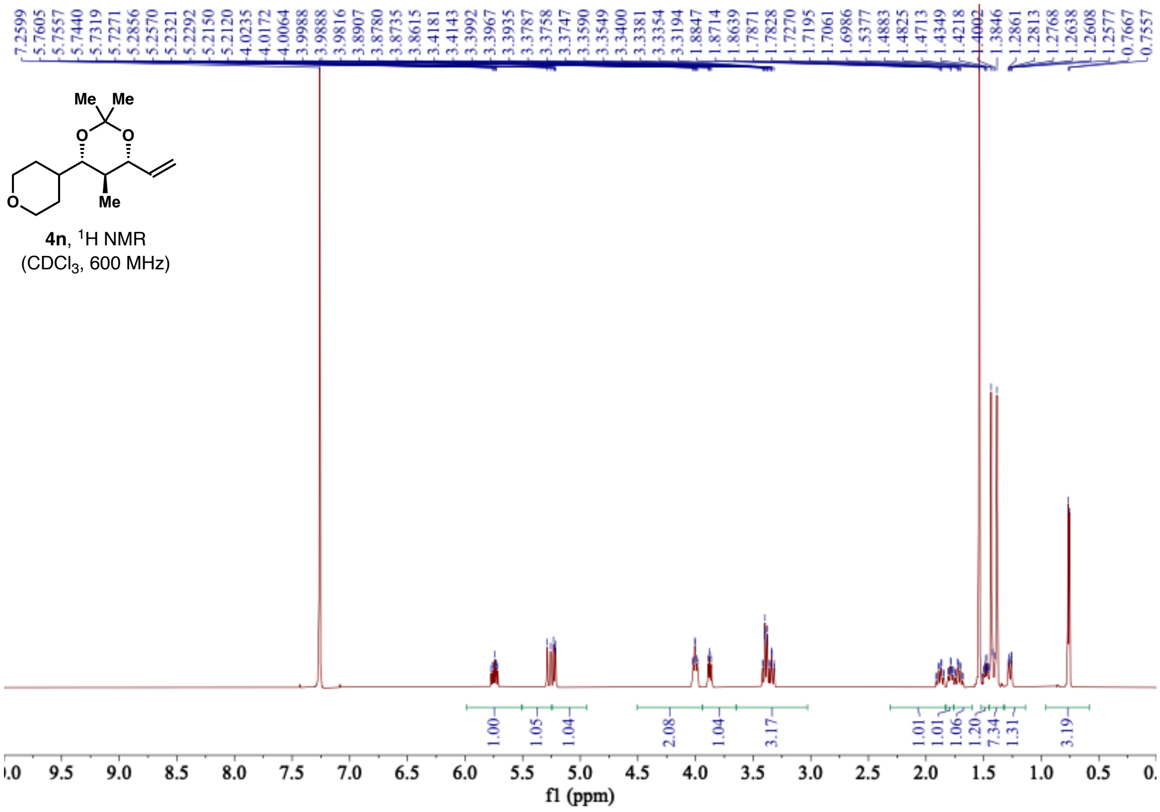
4l, ^{13}C NMR
($CDCl_3$, 126 MHz)

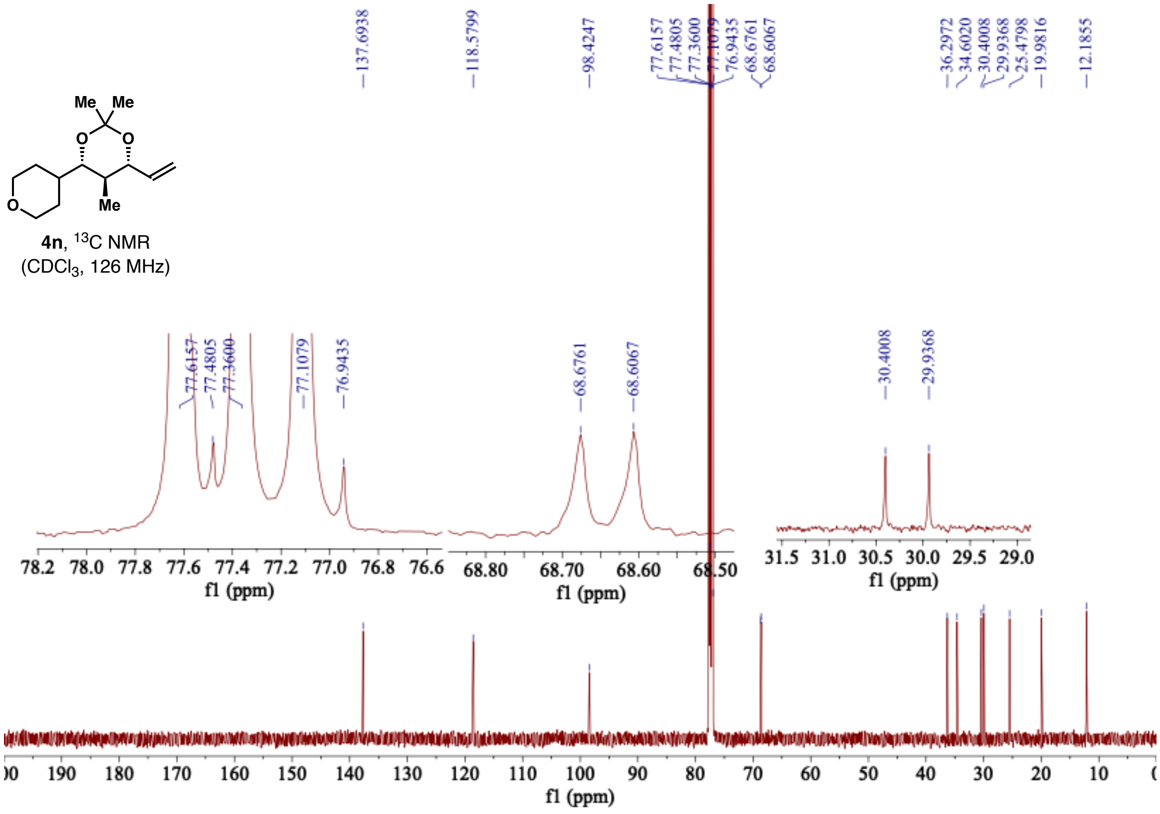


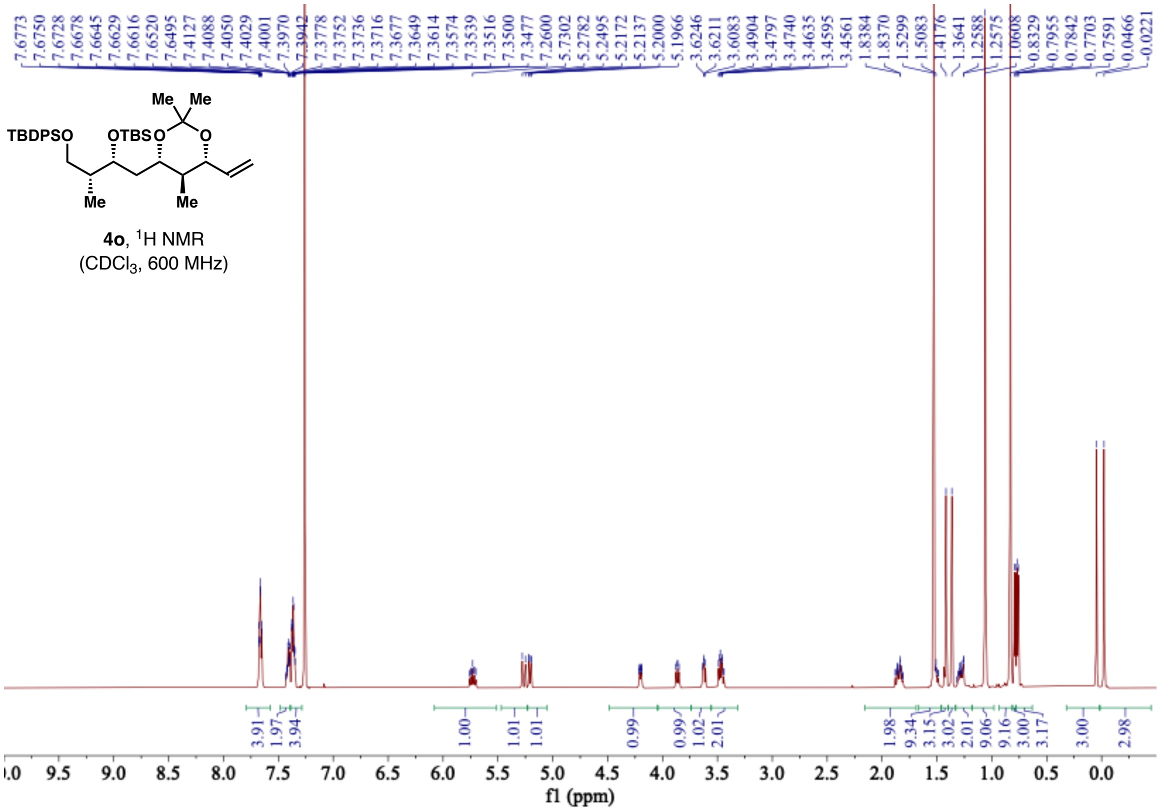
4m, ^{1}H NMR
($CDCl_3$, 500 MHz)



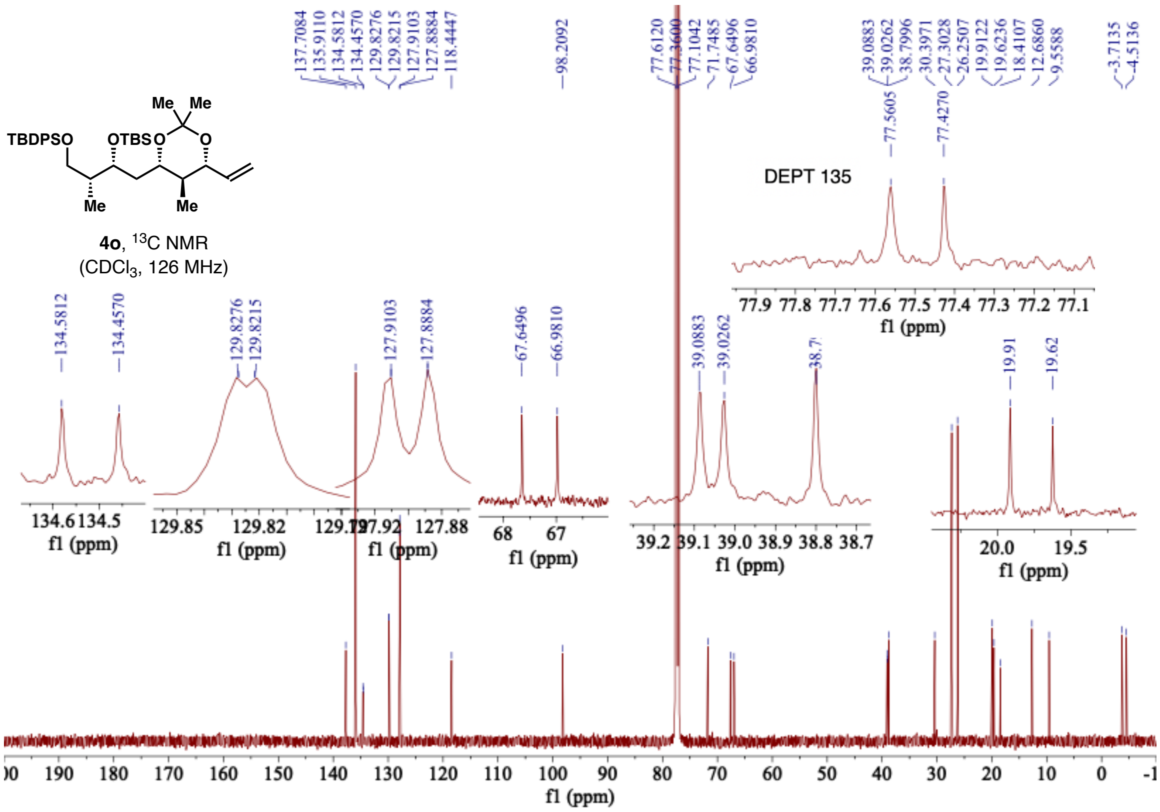
4m, ^{13}C NMR
($CDCl_3$, 126 MHz)


4n, ^{1}H NMR
(CDCl$_3$, 600 MHz)

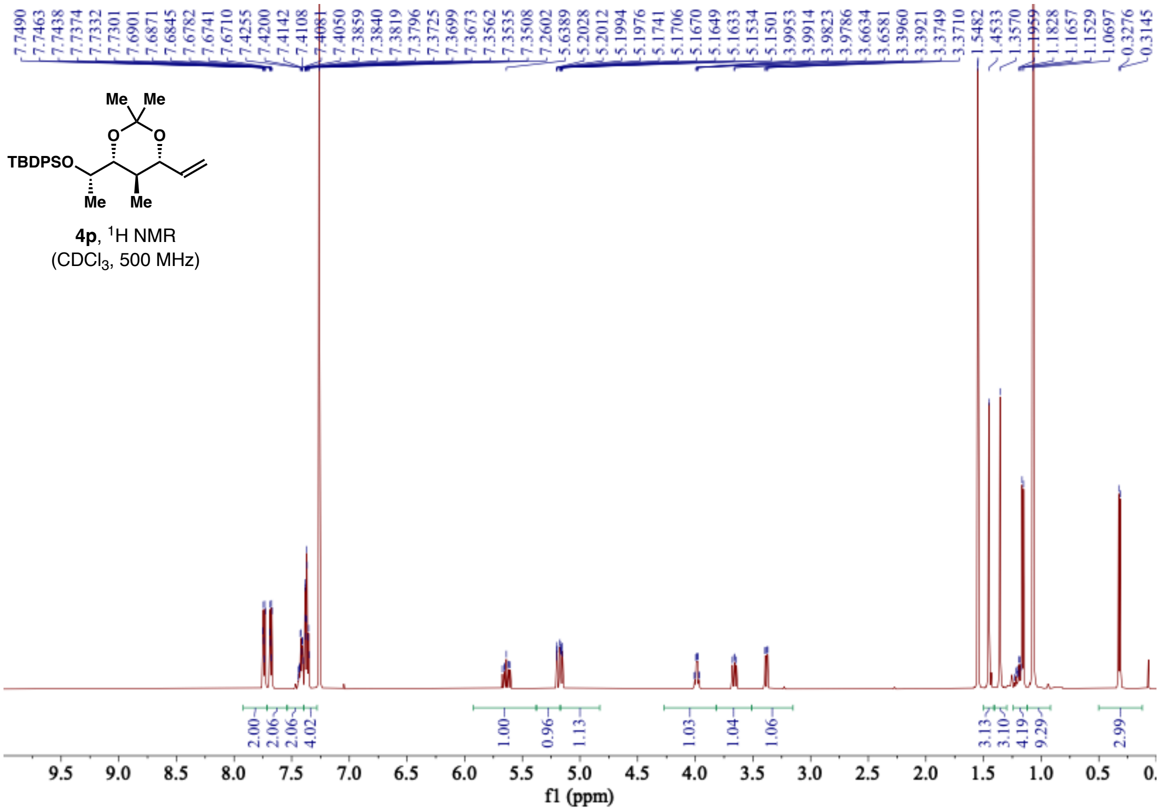

4n, ^{13}C NMR
(CDCl$_3$, 126 MHz)



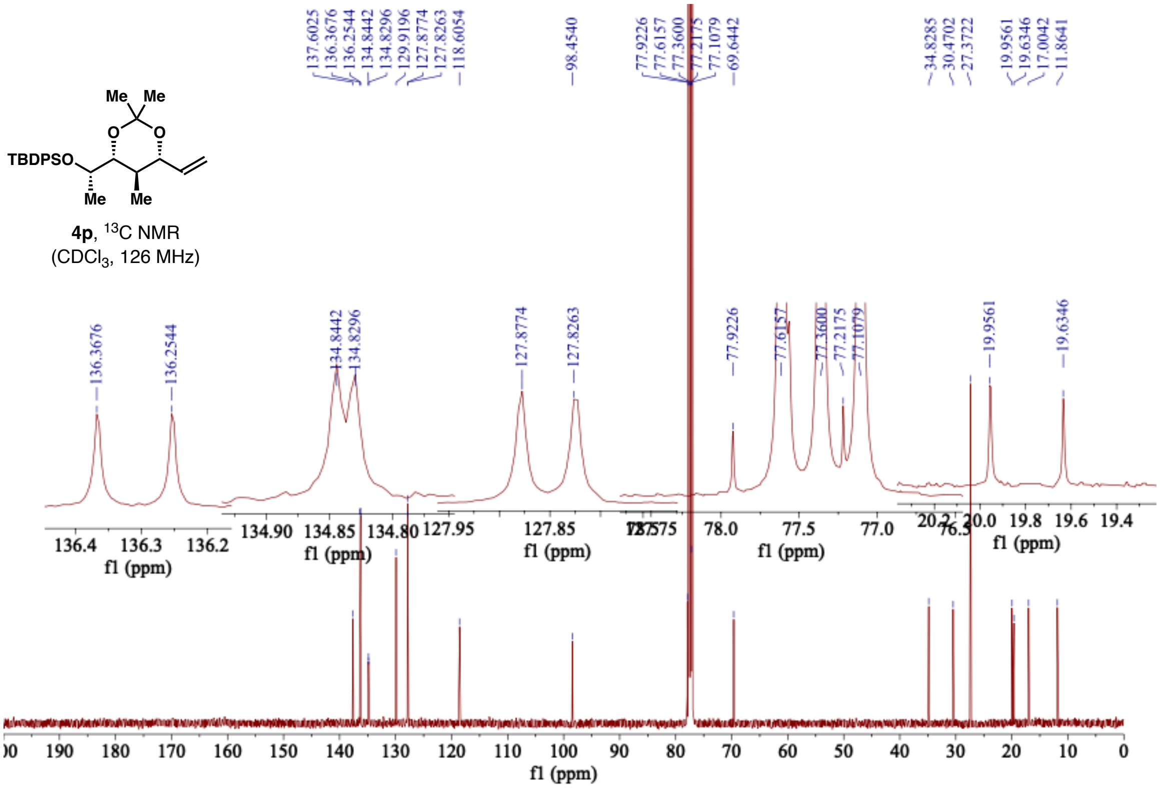
4o, ^{1}H NMR
(CDCl$_3$, 600 MHz)



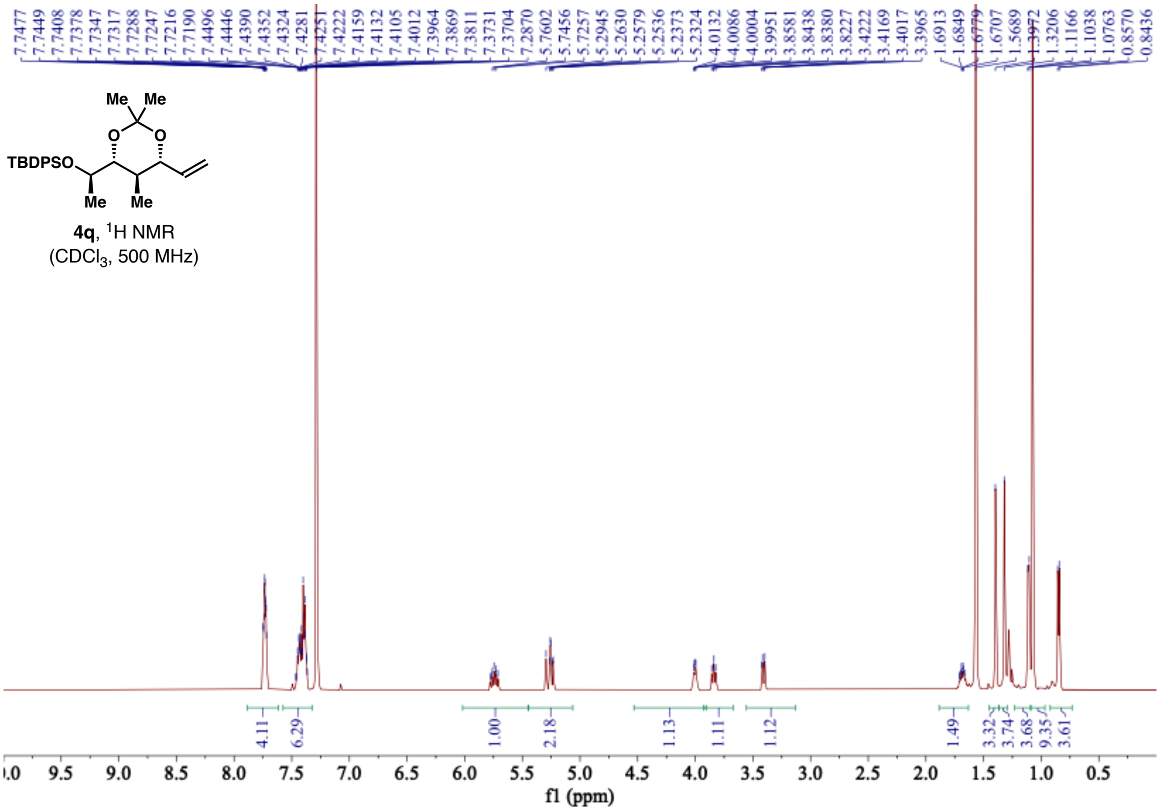
4o, ^{13}C NMR
(CDCl$_3$, 126 MHz)

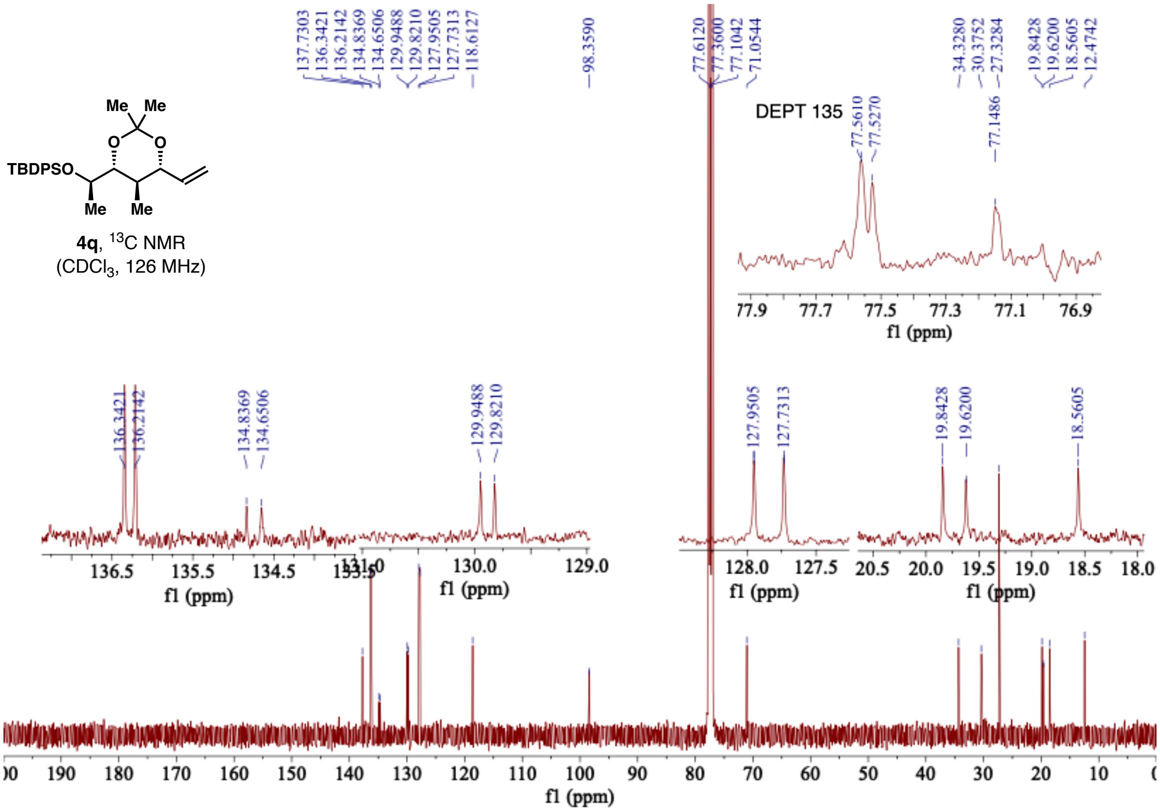


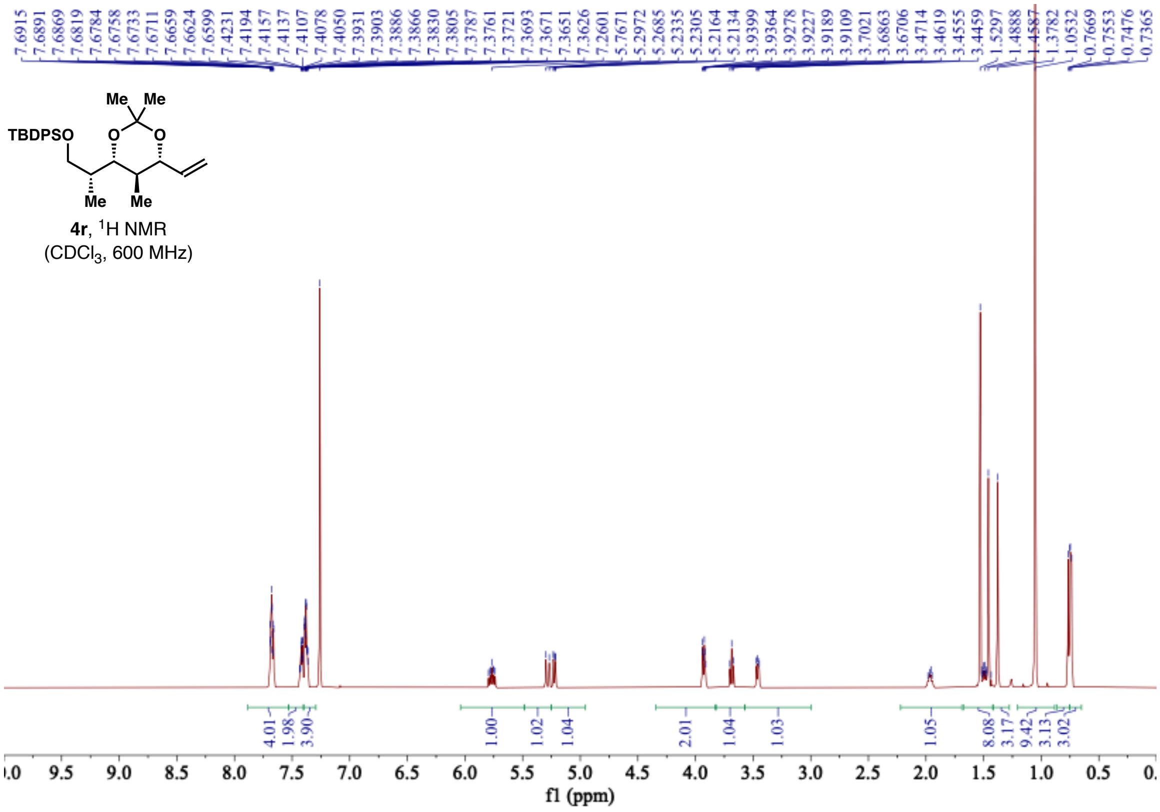
4p, ^{1}H NMR
(CDCl$_3$, 500 MHz)

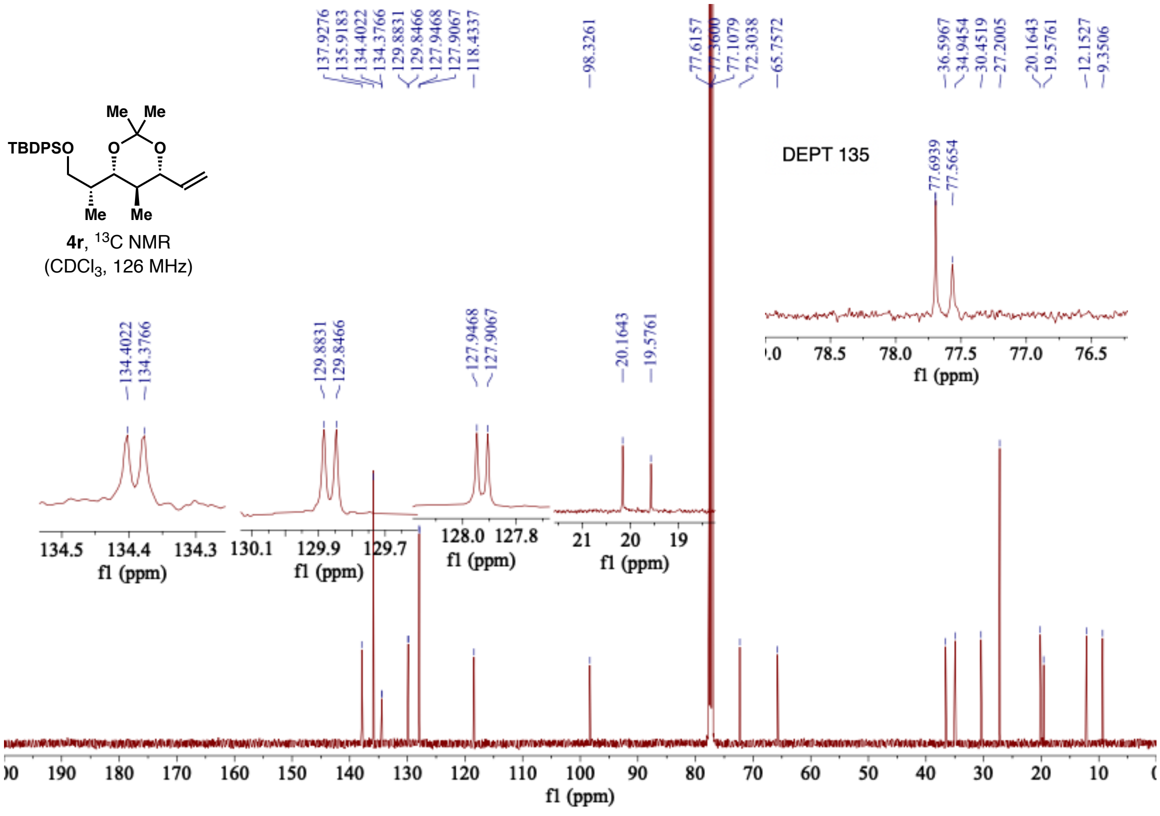


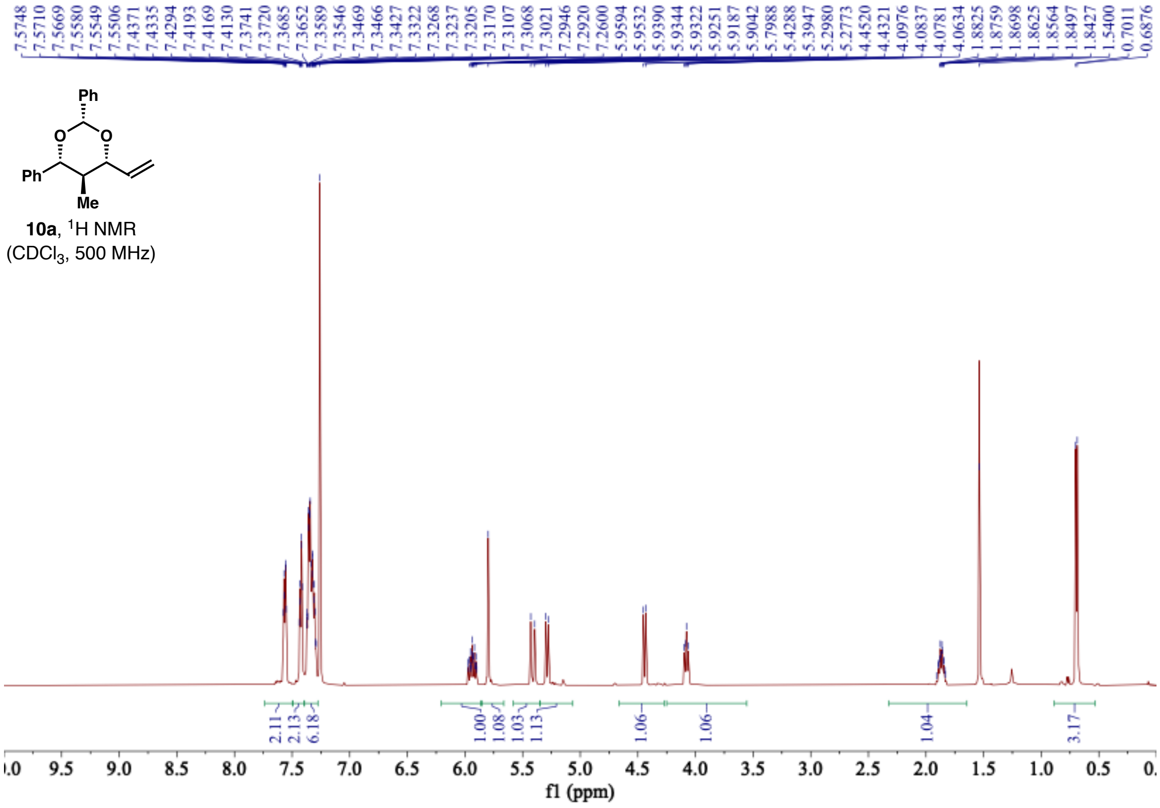
4p, ^{13}C NMR
(CDCl$_3$, 126 MHz)


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

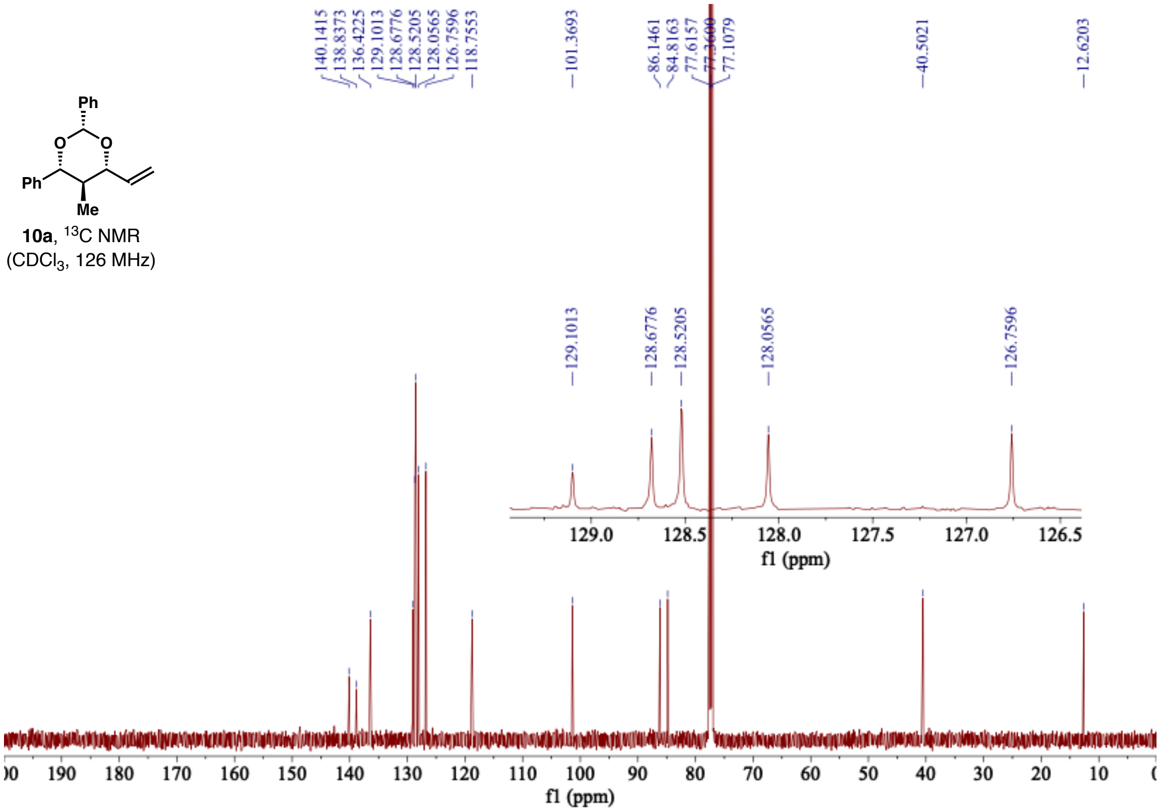

4q, ^{13}C NMR
($CDCl_3$, 126 MHz)


7.6915
7.6891
7.6869
7.6819
7.6784
7.6758
7.6733
7.6711
7.6659
7.6624
7.6599
7.4231
7.4194
7.4157
7.4137
7.4107
7.4078
7.4050
7.3931
7.3903
7.3886
7.3866
7.3830
7.3805
7.3787
7.3761
7.3721
7.3693
7.3671
7.3651
7.3626
7.2601
5.7671
5.2972
5.2685
5.2335
5.2305
5.2164
5.2134
3.9399
3.9364
3.9278
3.9227
3.9189
3.9109
3.7021
3.6863
3.6706
3.4714
3.4619
3.4555
3.4459
1.5297
1.4888
1.4587
1.3782
1.0532
0.7669
0.7553
0.7476
0.7365
Me
Me
TBDPSO
O
O
Me
Me
4r, ¹H NMR
(CDCl₃, 600 MHz)
4.01
1.98
3.90
1.00
1.02
1.04
2.01
1.04
1.03
1.05
8.08
3.17
9.42
3.13
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

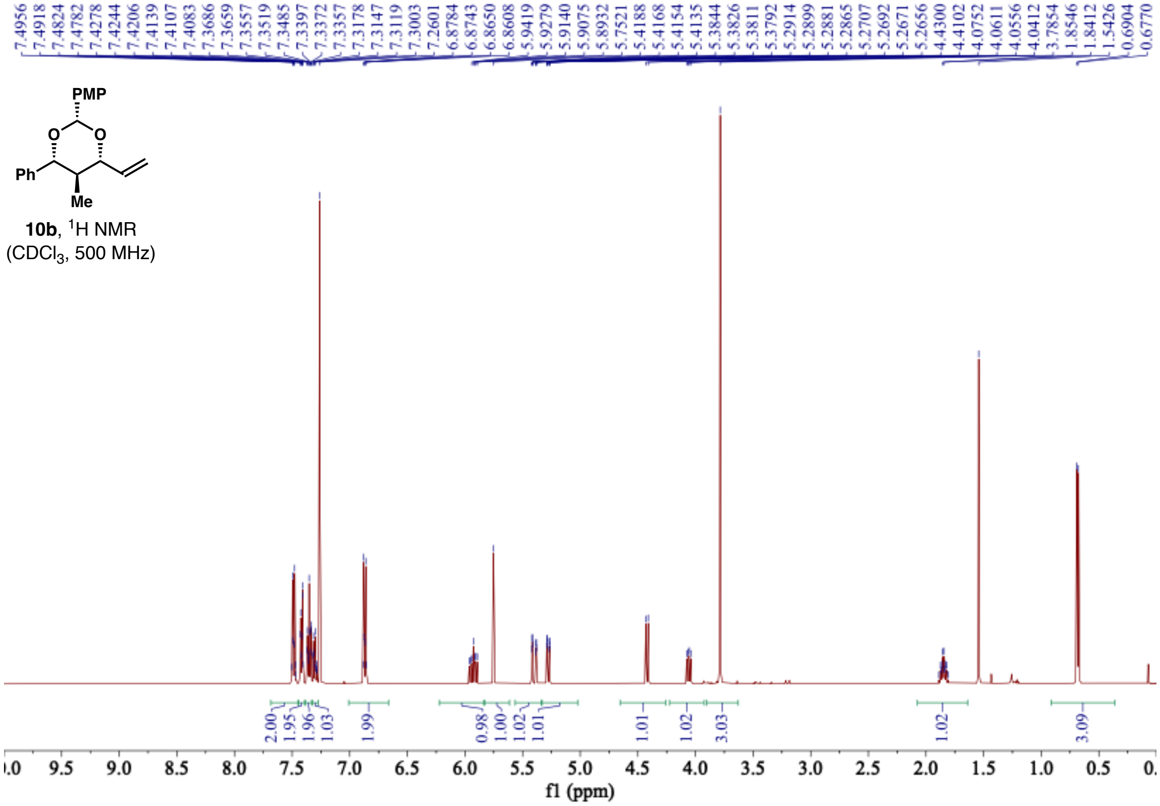

137.9276
135.9183
134.4022
134.3766
129.8831
129.8466
127.9468
127.9067
118.4337
98.3261
77.6157
77.3600
77.1079
72.3038
65.7572
36.5967
34.9454
30.4519
27.2005
20.1643
19.5761
12.1527
9.3506
Me
Me
TBDPSO
O
O
Me
Me
4r, ¹³C NMR
(CDCl₃, 126 MHz)
DEPT 135
77.6939
77.5654
78.5
78.0
77.5
77.0
76.5
f1 (ppm)
134.4022
134.3766
134.5
134.4
134.3
f1 (ppm)
129.8831
129.8466
130.1
129.9
129.7
f1 (ppm)
127.9468
127.9067
128.0
127.8
f1 (ppm)
20.1643
19.5761
21
20
19
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

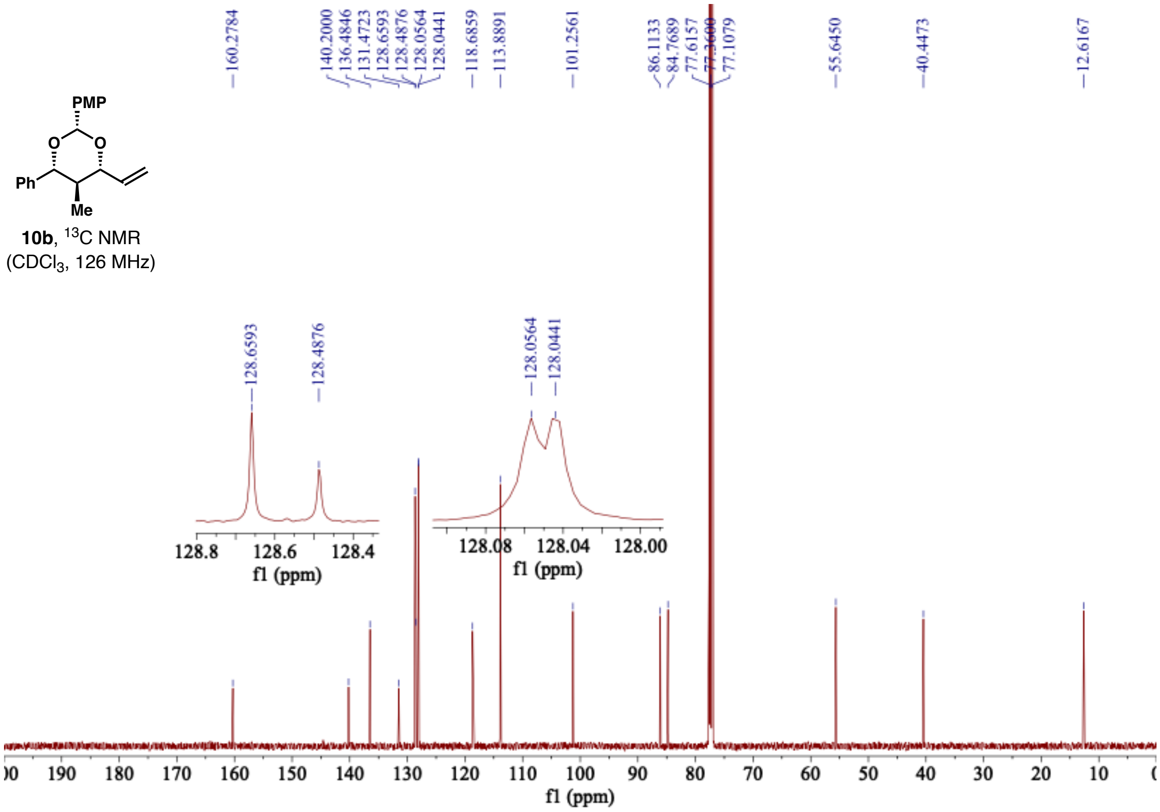


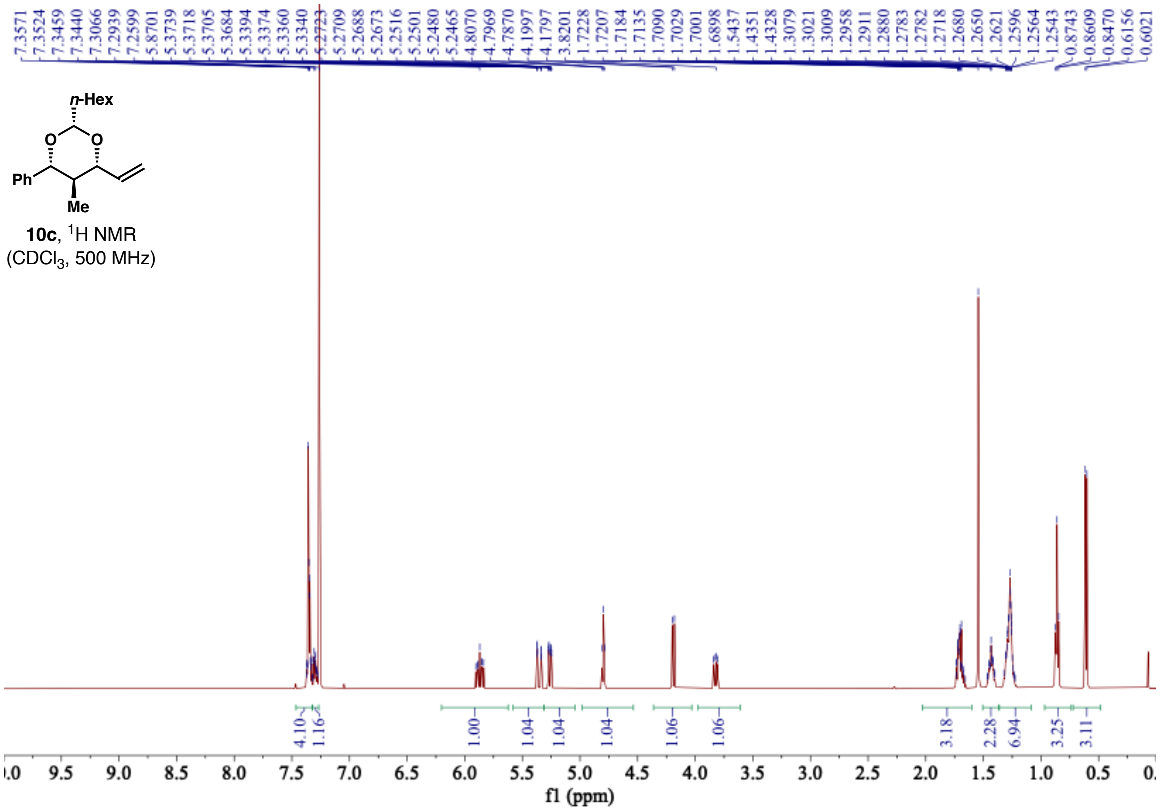
10a, ^{1}H NMR
($CDCl_3$, 500 MHz)



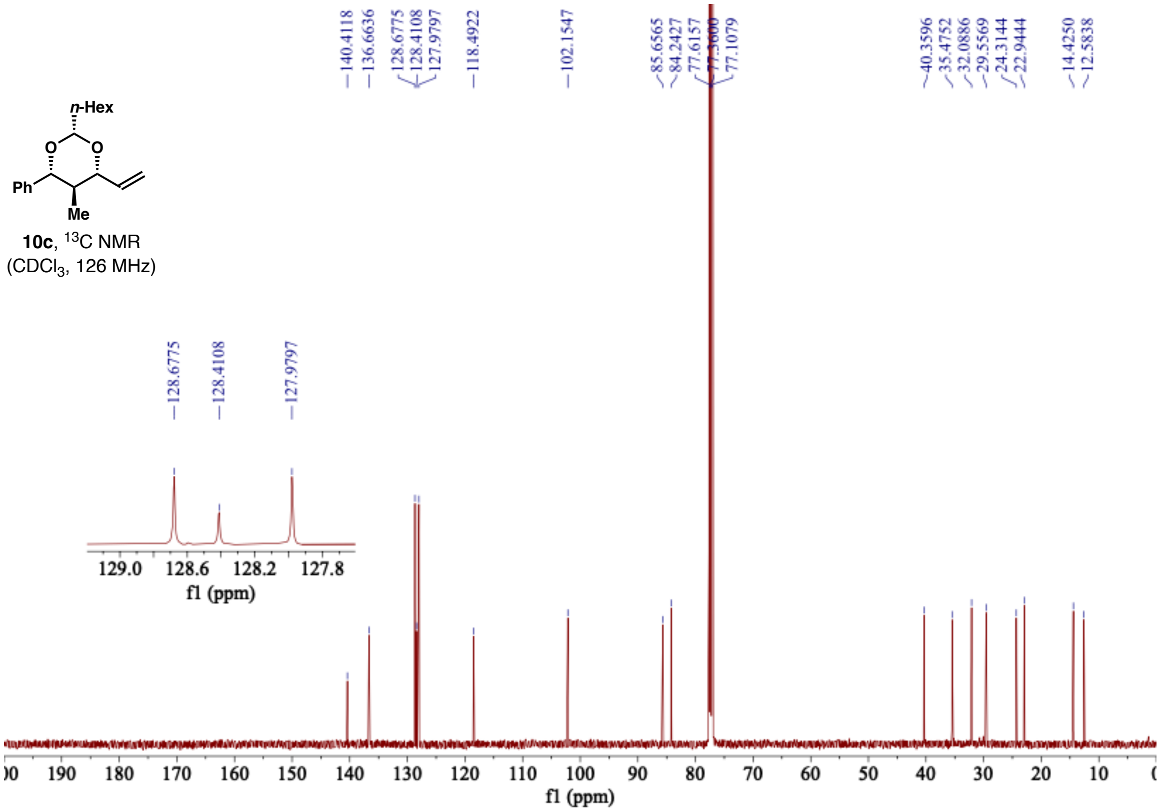
10a, ^{13}C NMR
($CDCl_3$, 126 MHz)


10b, ^{1}H NMR
(CDCl$_3$, 500 MHz)

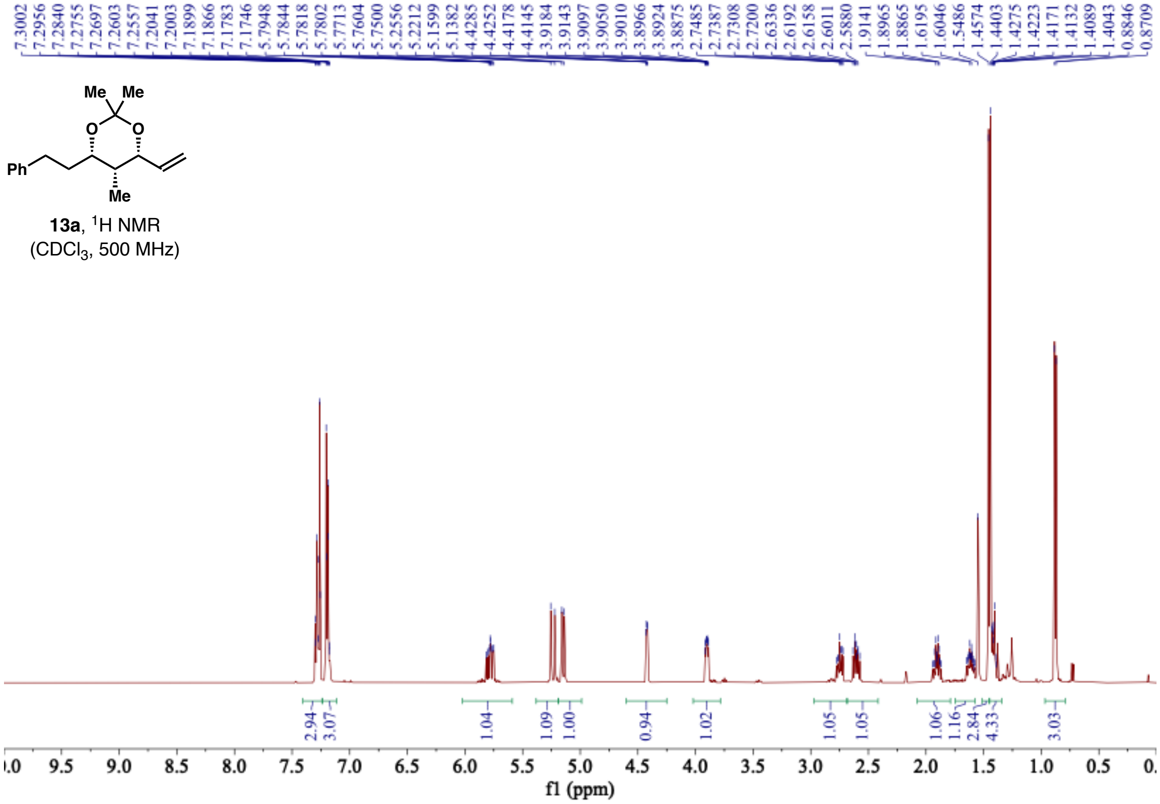

10b, ^{13}C NMR
(CDCl$_3$, 126 MHz)



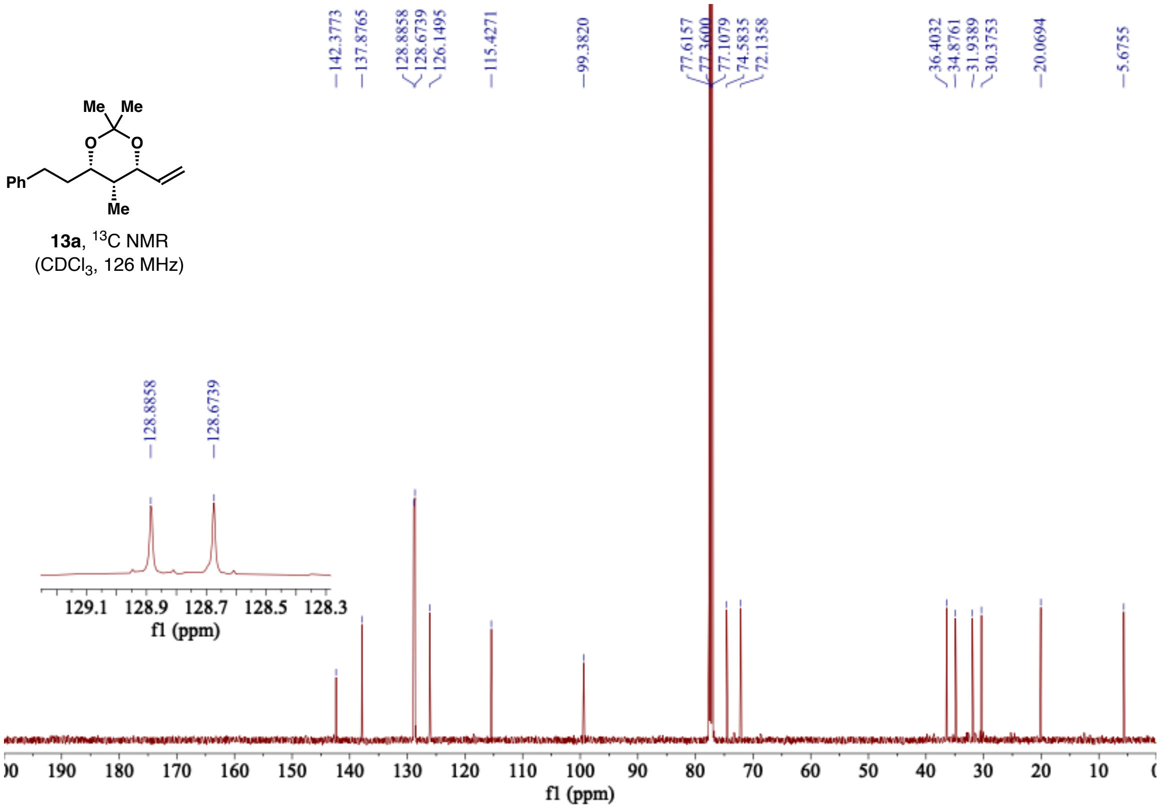
10c, ^1H NMR ($CDCl_3$, 500 MHz)



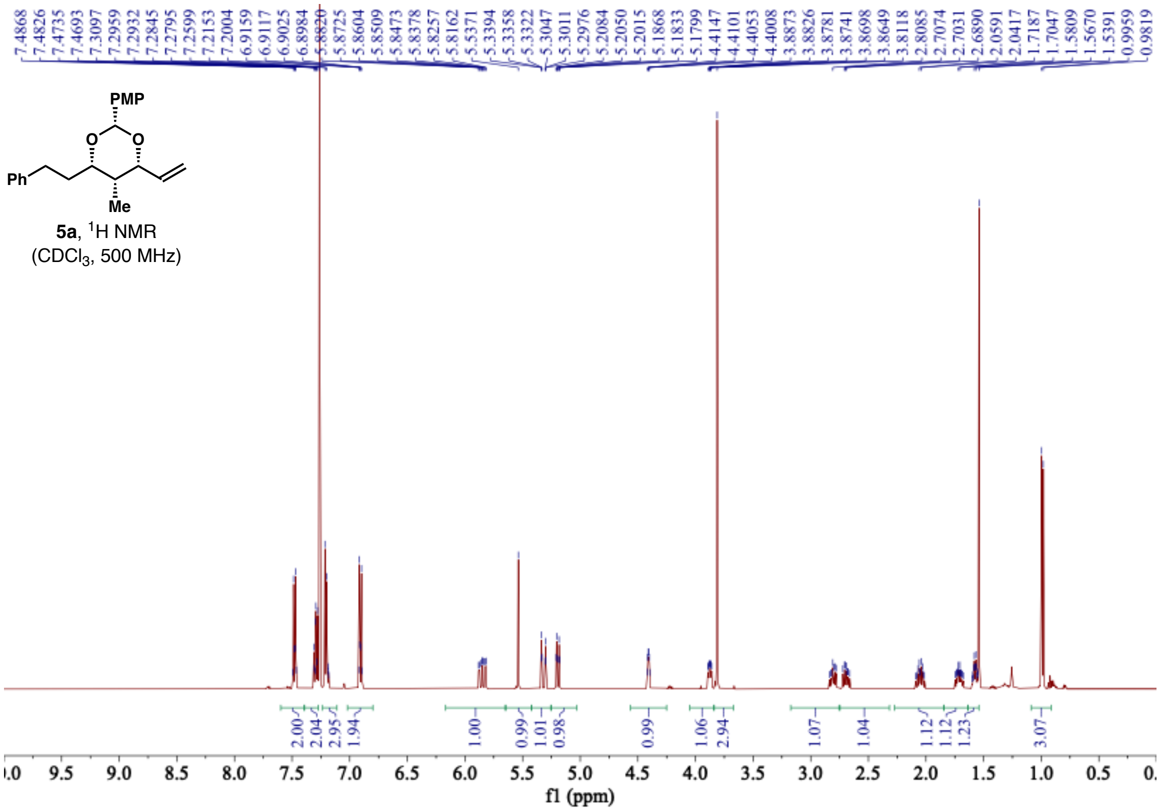
10c, ^{13}C NMR ($CDCl_3$, 126 MHz)



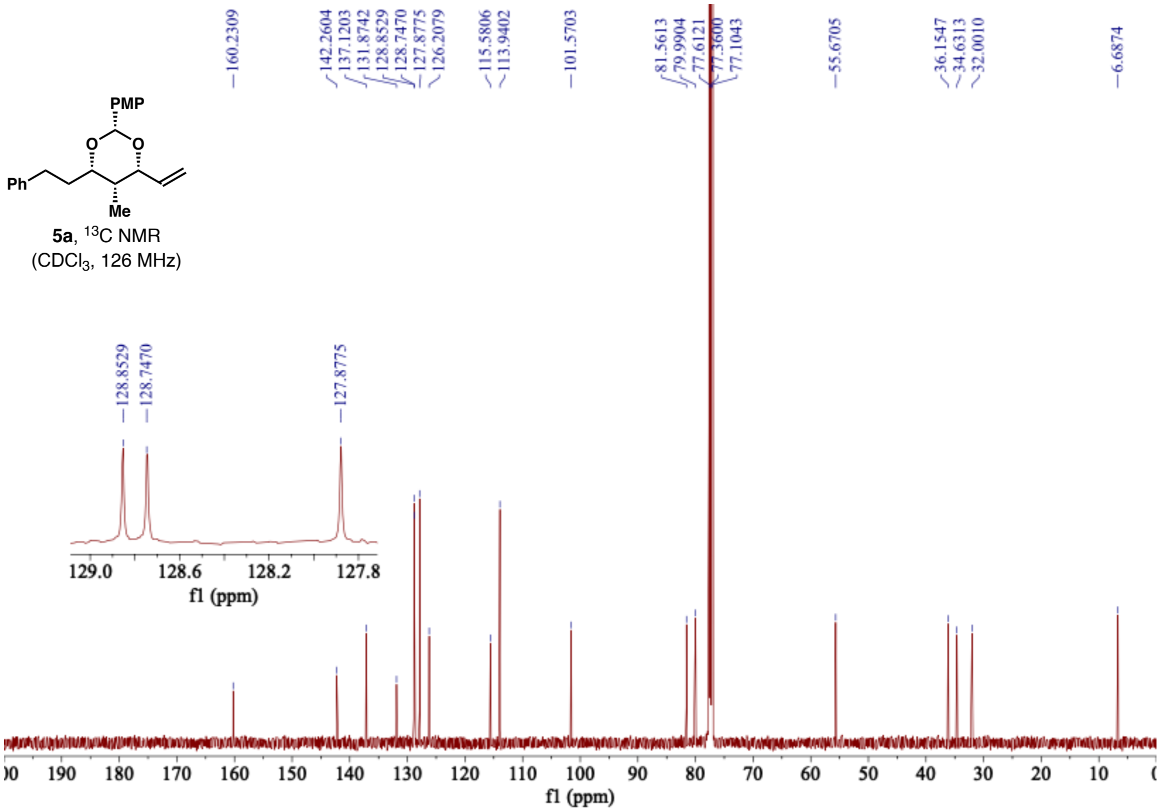
13a, ^{1}H NMR
($CDCl_3$, 500 MHz)



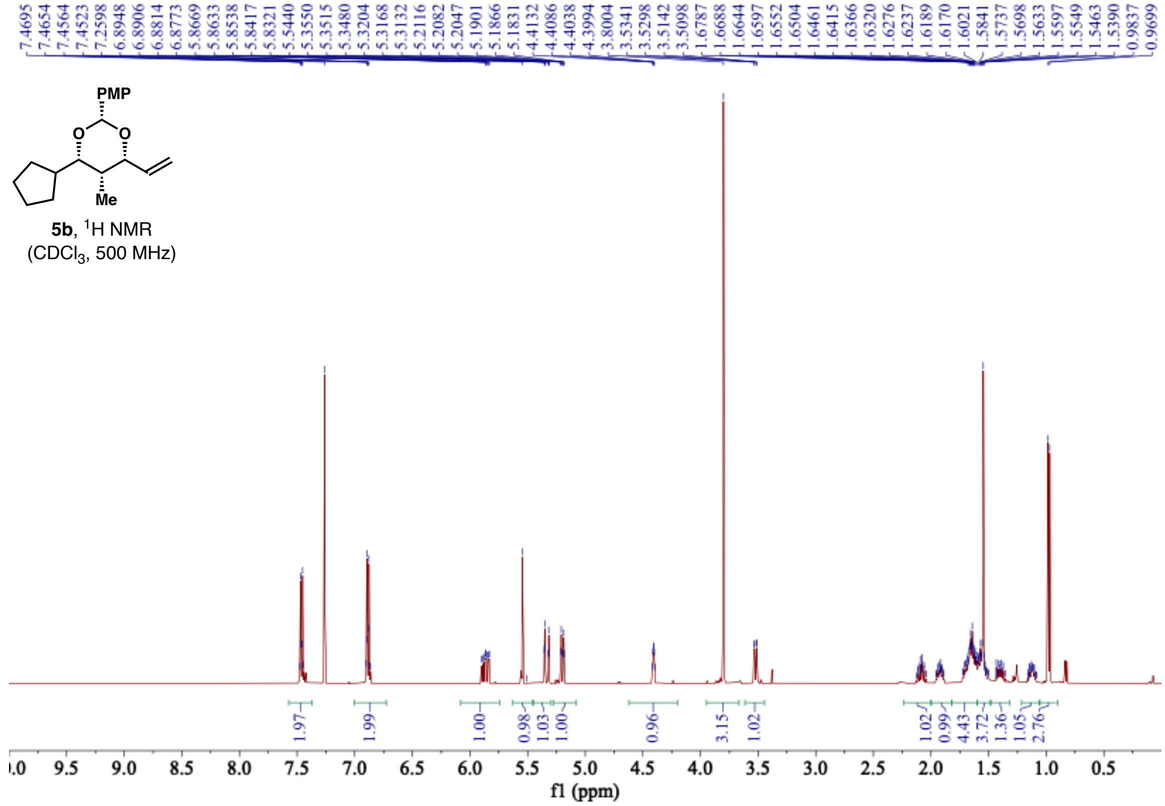
13a, ^{13}C NMR
($CDCl_3$, 126 MHz)



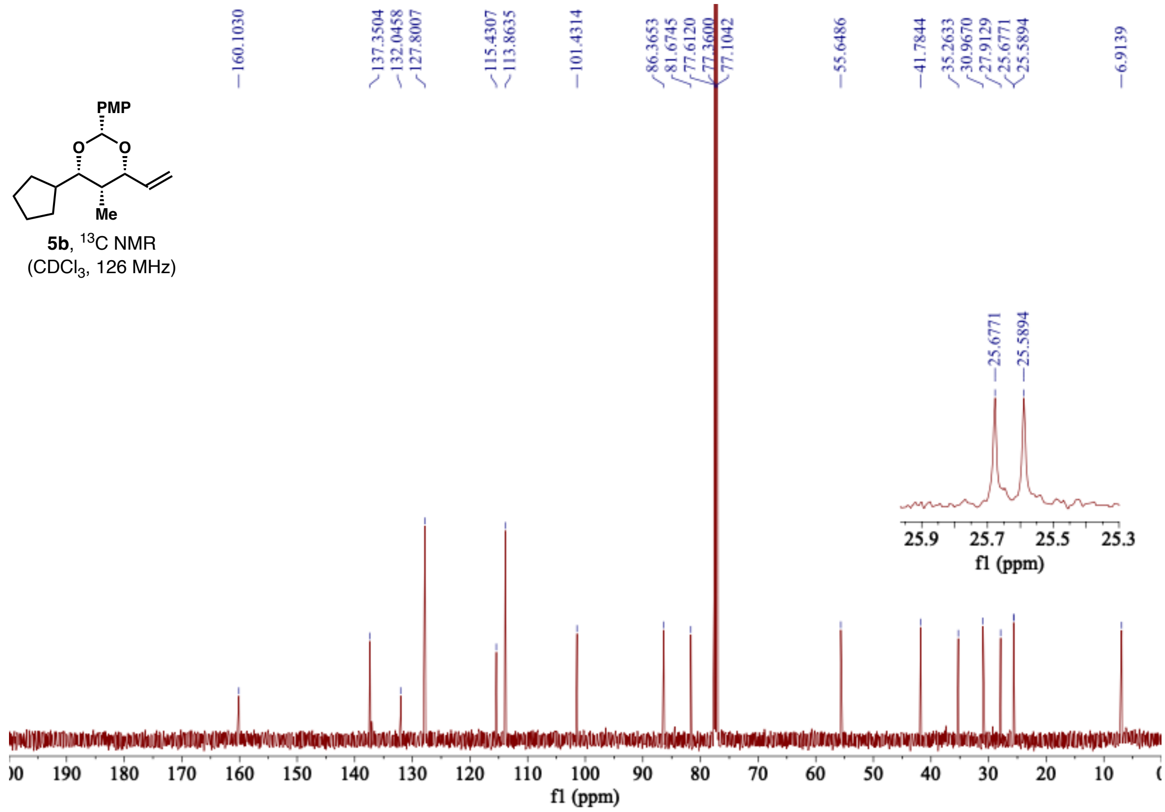
5a, ^{1}H NMR
($CDCl_3$, 500 MHz)



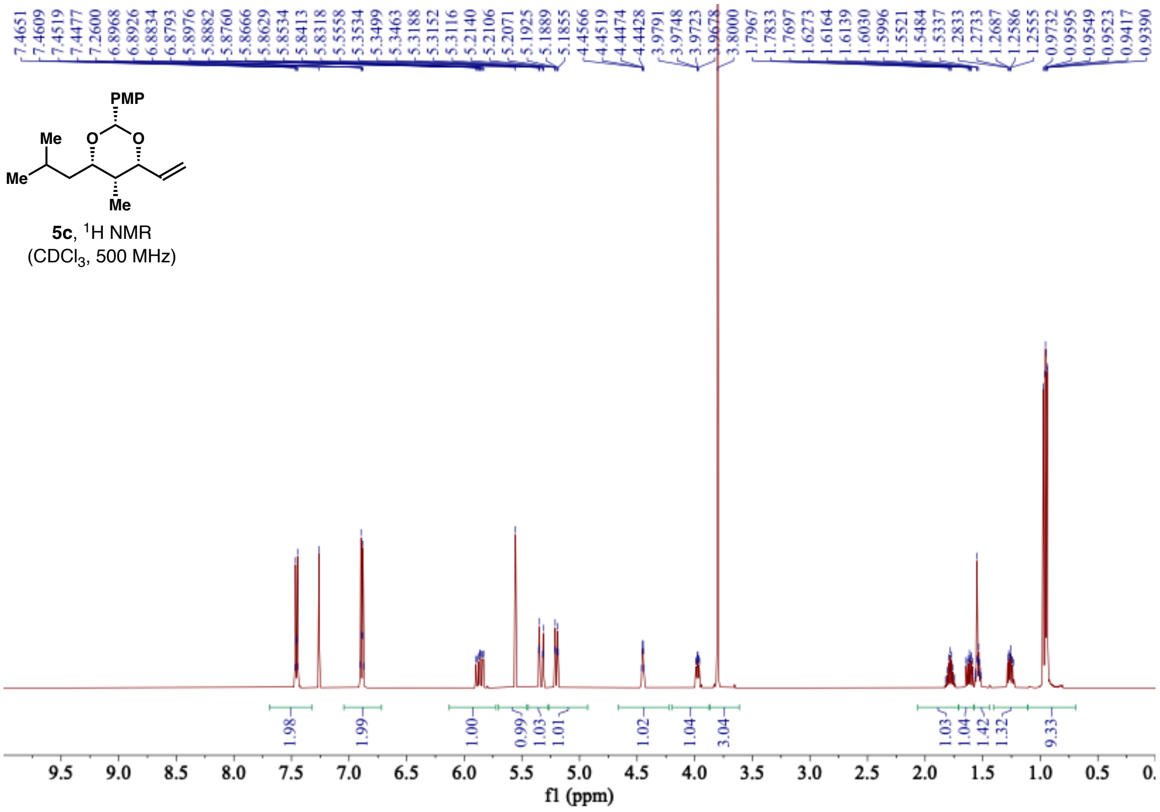
5a, ^{13}C NMR
($CDCl_3$, 126 MHz)

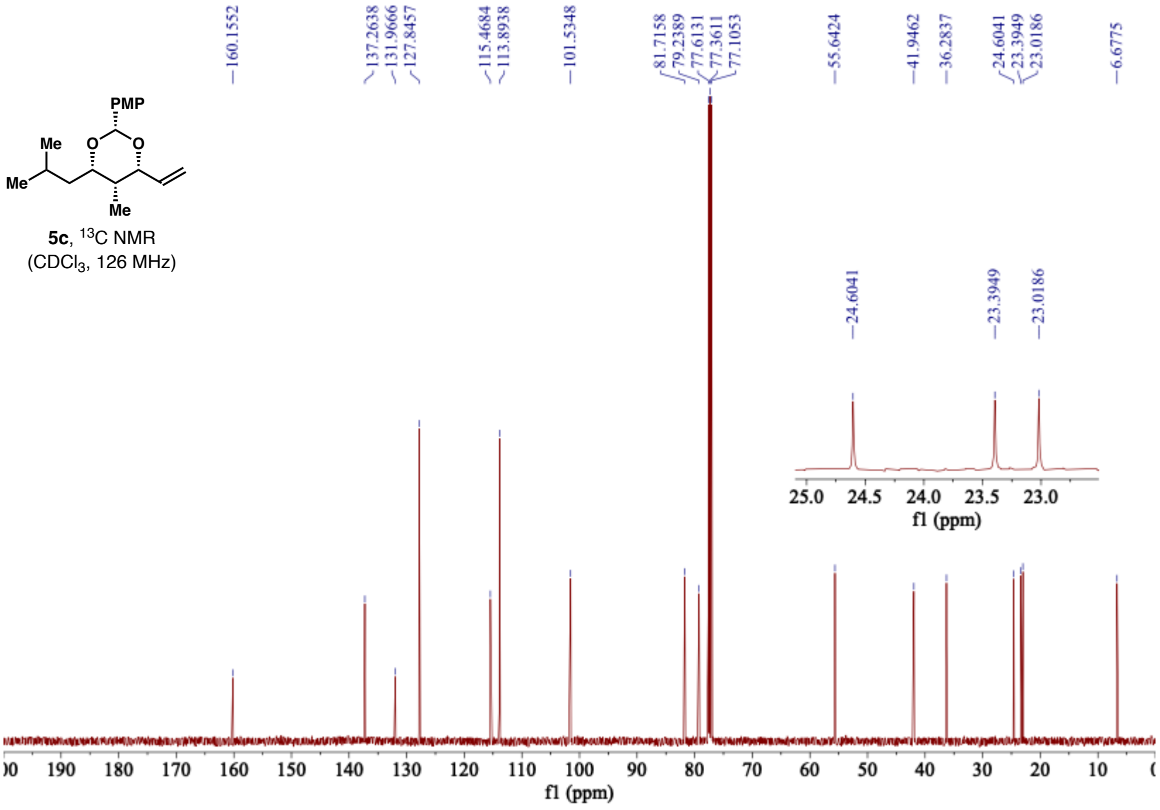


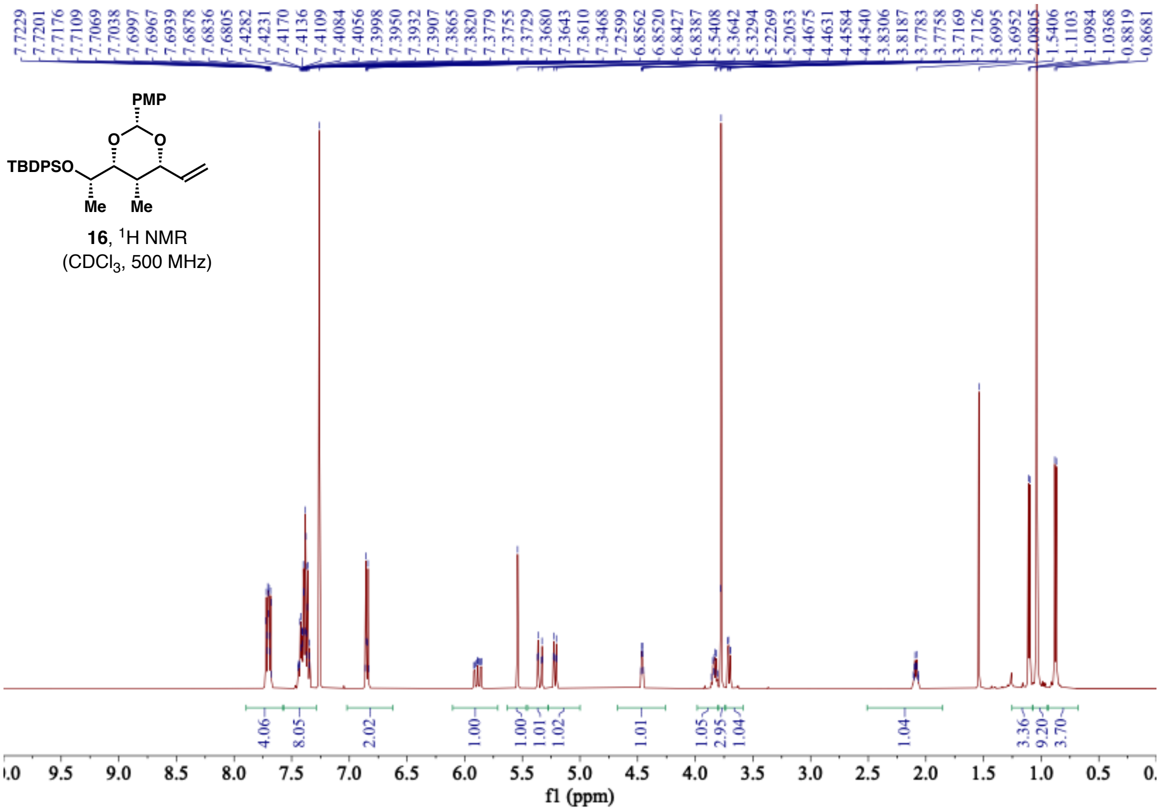
5b, ^{1}H NMR
($CDCl_3$, 500 MHz)



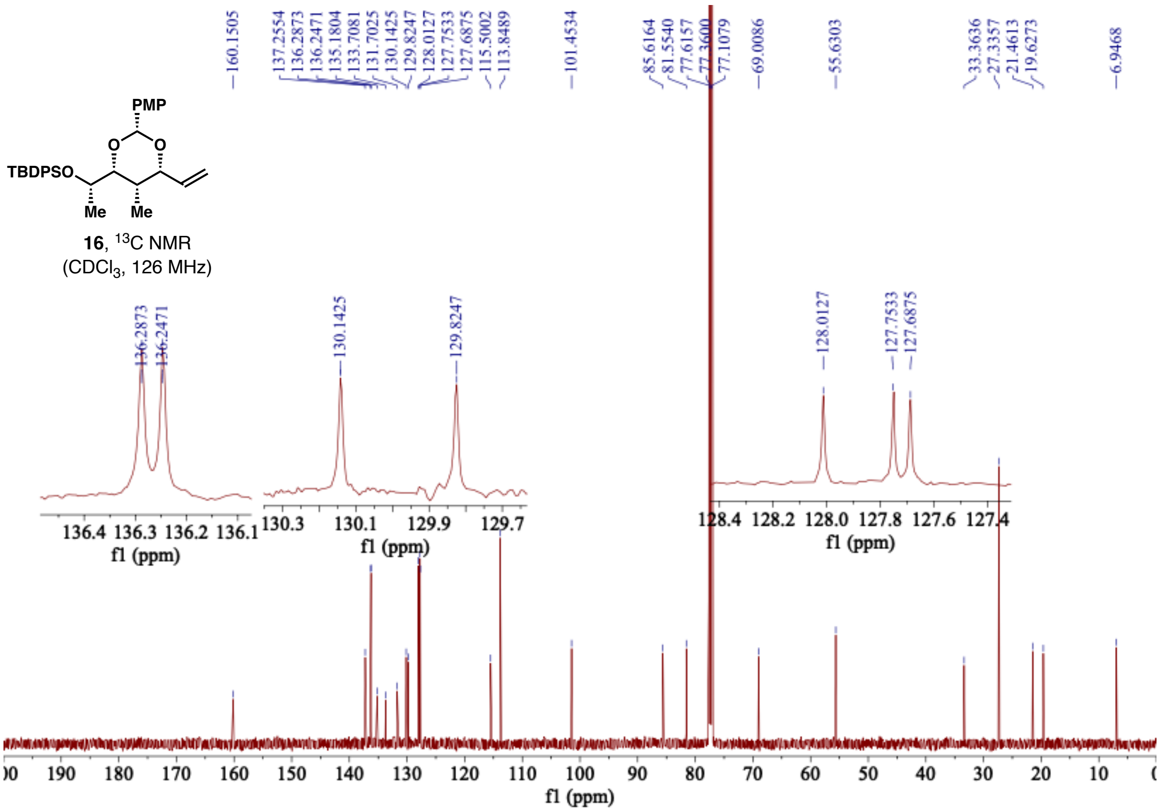
5b, ^{13}C NMR
($CDCl_3$, 126 MHz)


5c, ^{1}H NMR
($CDCl_3$, 500 MHz)

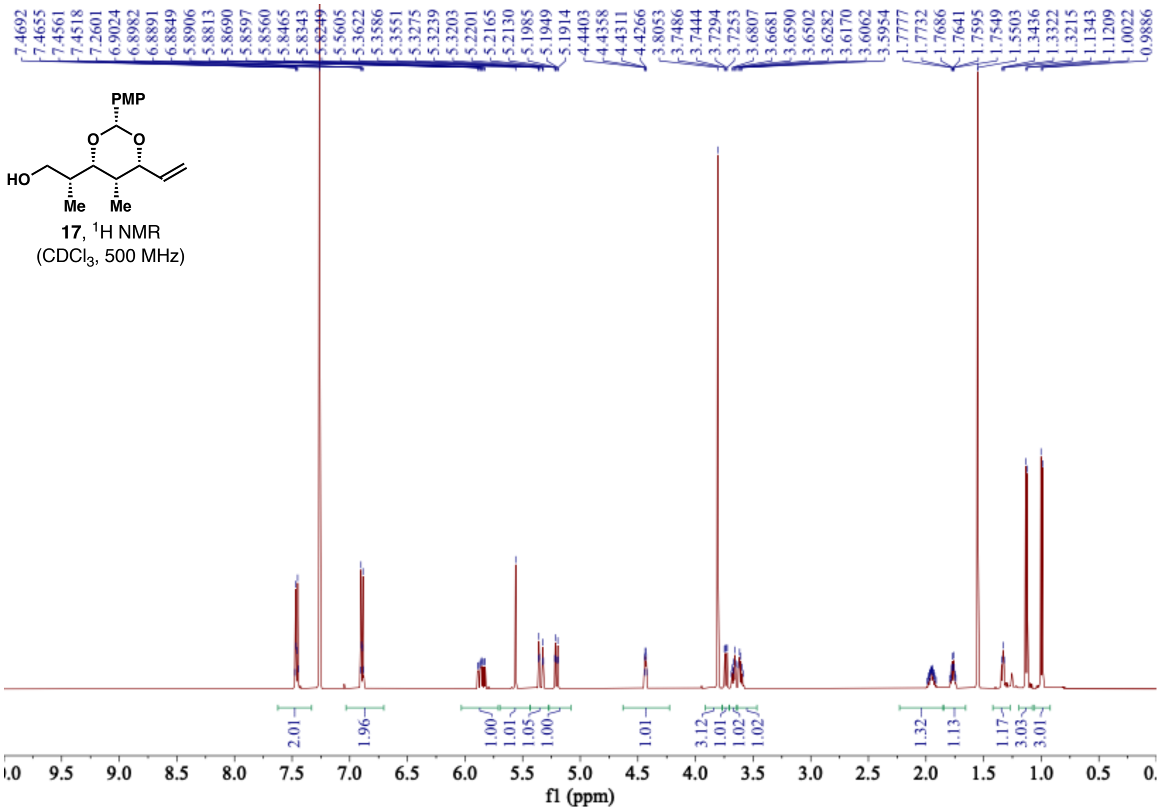

5c, ^{13}C NMR
($CDCl_3$, 126 MHz)



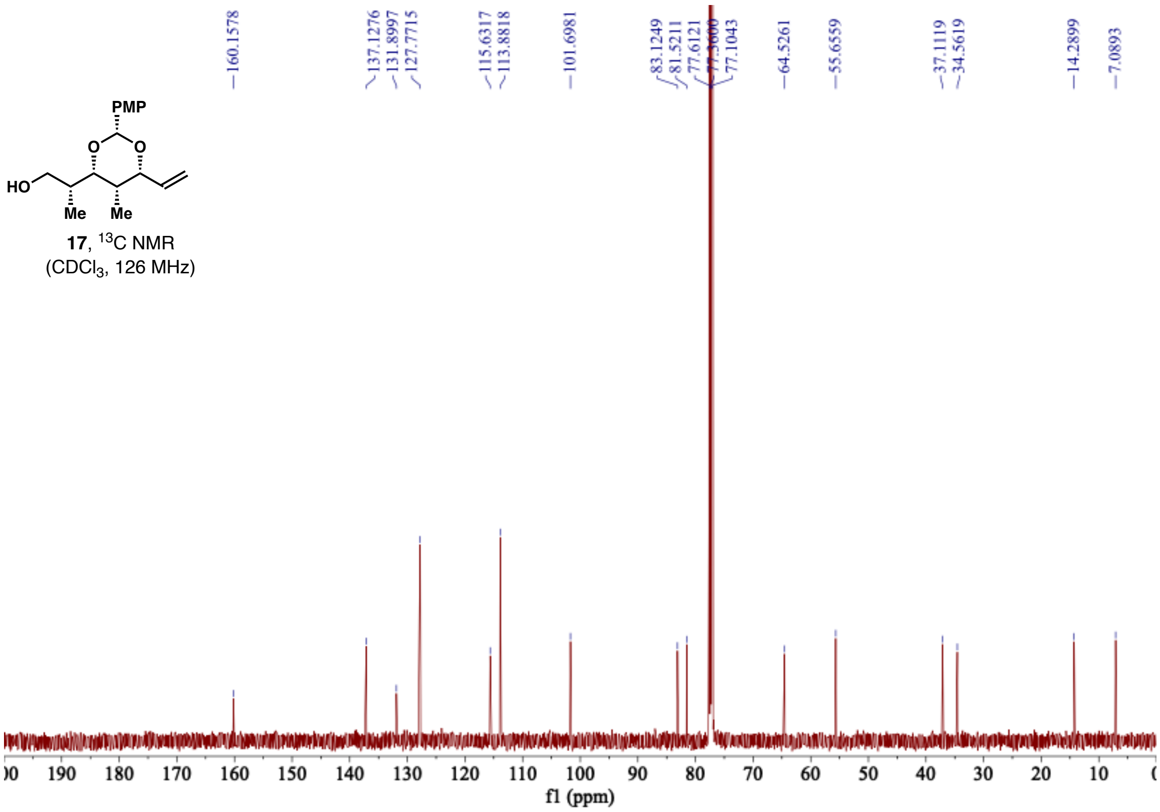
16, ^{1}H NMR
($CDCl_3$, 500 MHz)



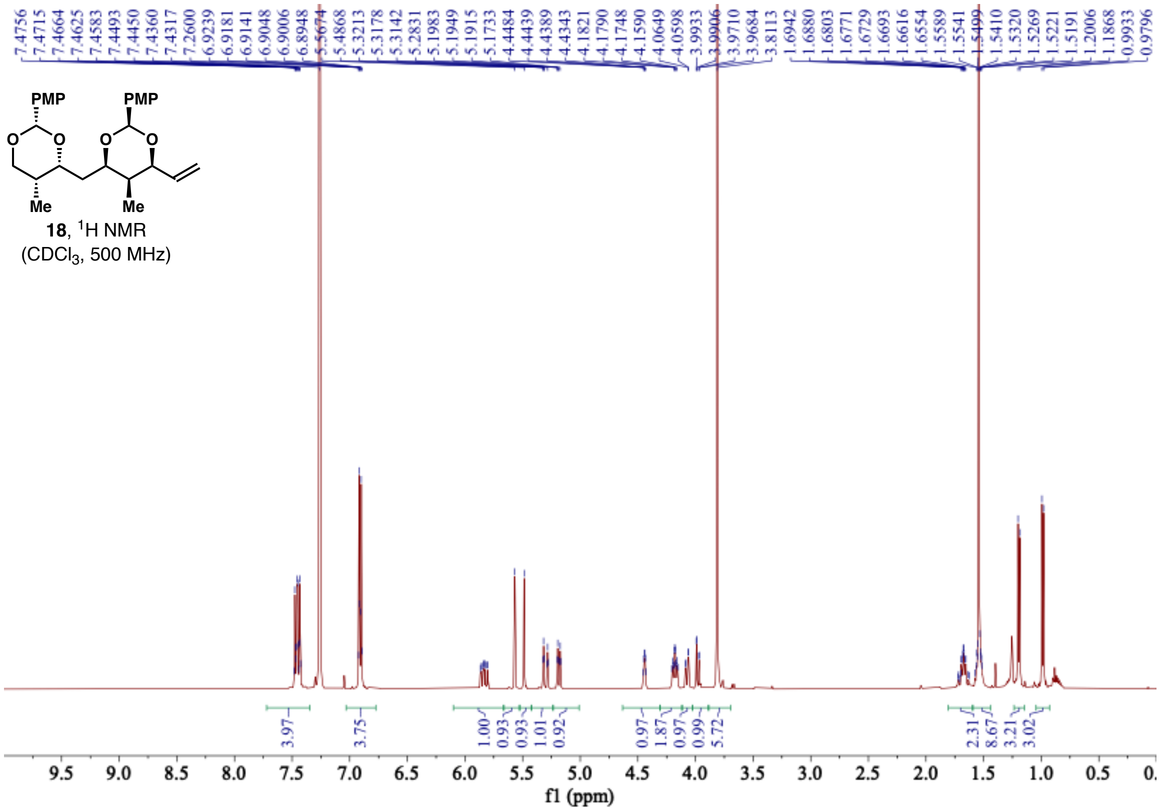
16, ^{13}C NMR
($CDCl_3$, 126 MHz)



17, ^{1}H NMR ($CDCl_3$, 500 MHz)



17, ^{13}C NMR ($CDCl_3$, 126 MHz)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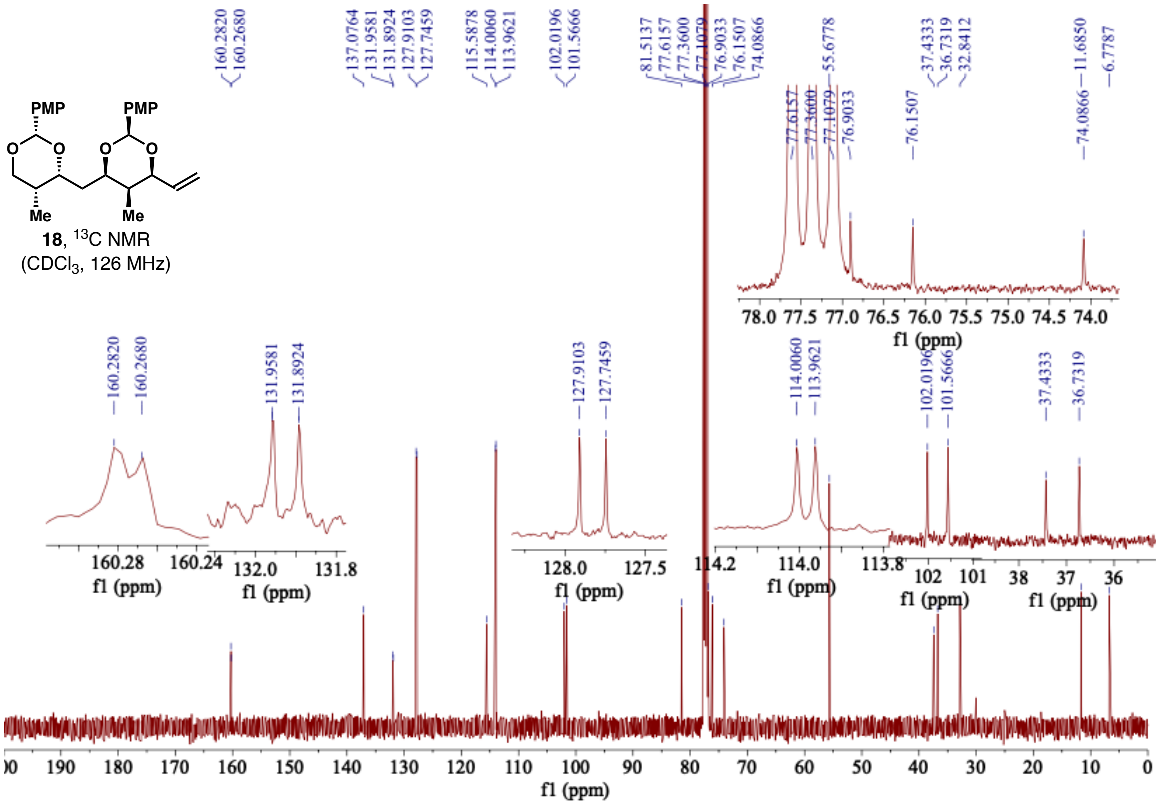
7.4317
7.2600
6.9239
6.9181
6.9141
6.9048
6.9006
6.8948
5.5674
5.4868
5.3213
5.3178
5.3142
5.2831
5.1983
5.1949
5.1915
5.1733
4.4484
4.4439
4.4389
4.4343
4.1821
4.1790
4.1748
4.1590
4.0649
4.0598
3.9933
3.9906
3.9710
3.9684
3.8113
1.6942
1.6880
1.6803
1.6771
1.6729
1.6693
1.6616
1.6554
1.5589
1.5541
1.5499
1.5410
1.5320
1.5269
1.5221
1.5191
1.2006
1.1868
0.9933
0.9796
PMP
PMP
O
O
O
O
Me
Me
18, ^{1}H NMR
(CDCl$_3$, 500 MHz)
3.97
3.75
1.00
0.93
0.93
1.01
0.92
0.97
1.87
0.97
0.99
5.72
2.31
8.67
3.21
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)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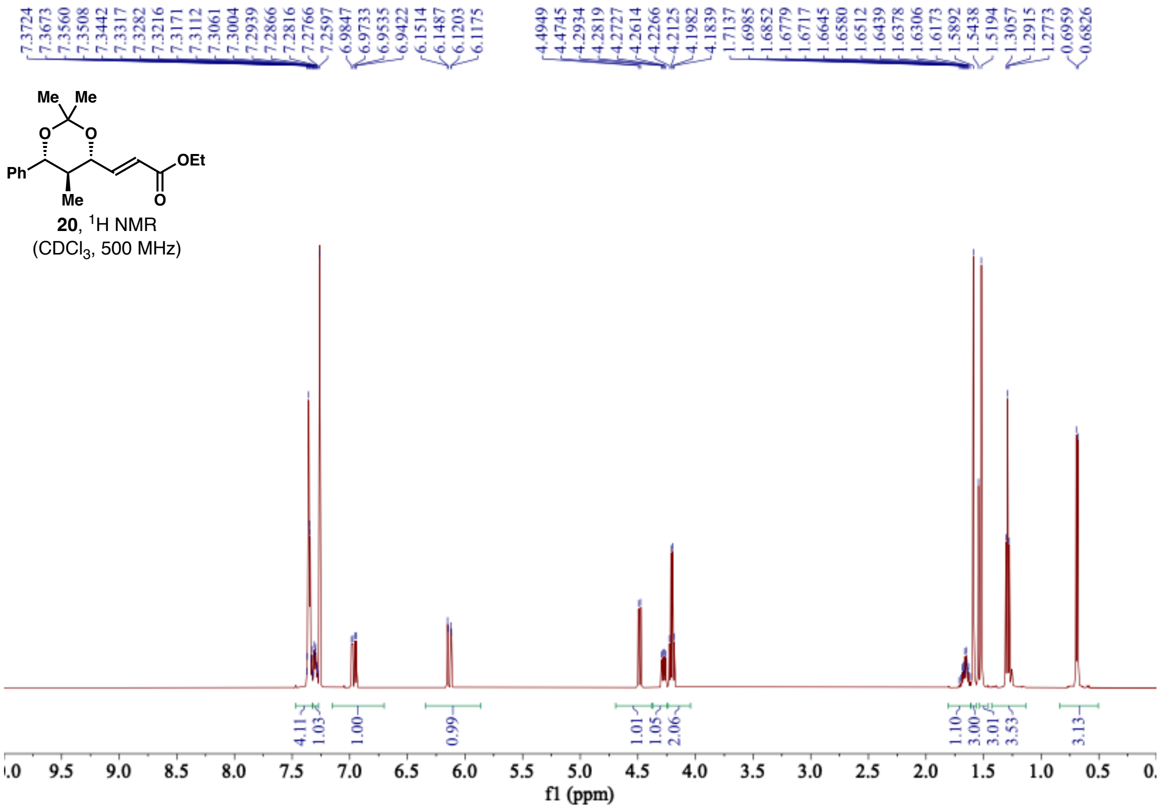
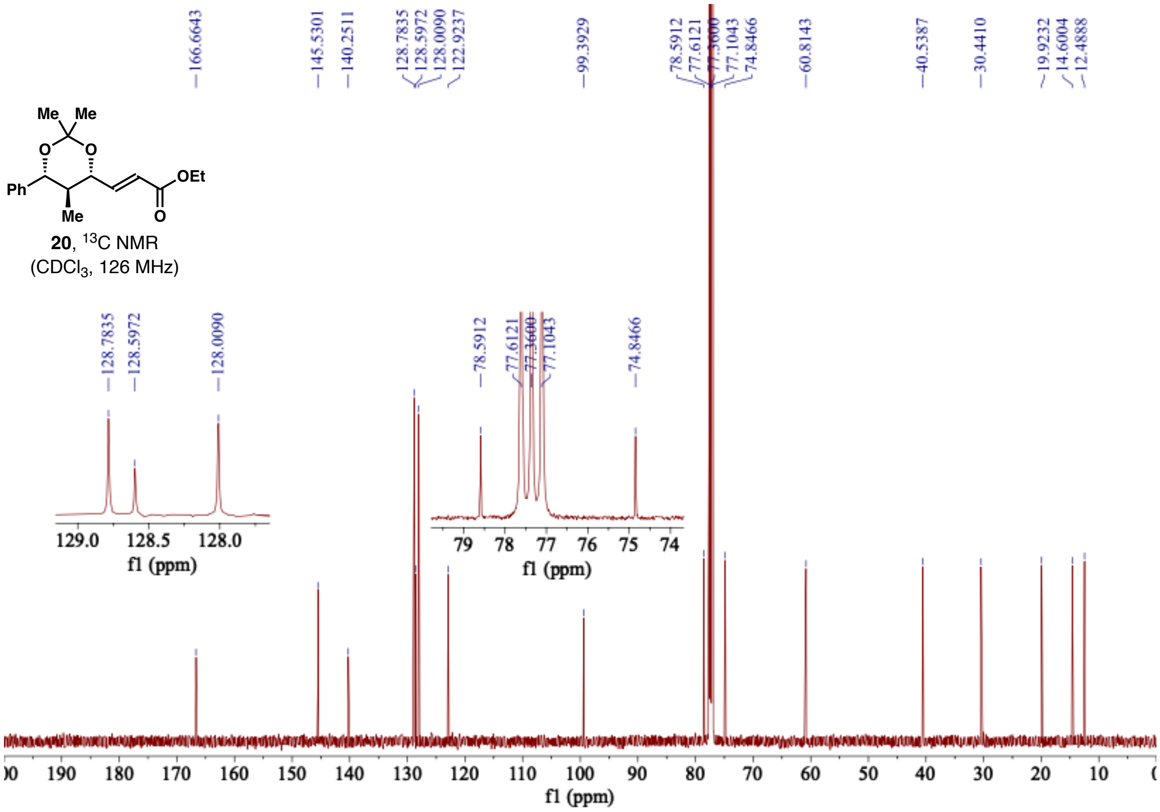
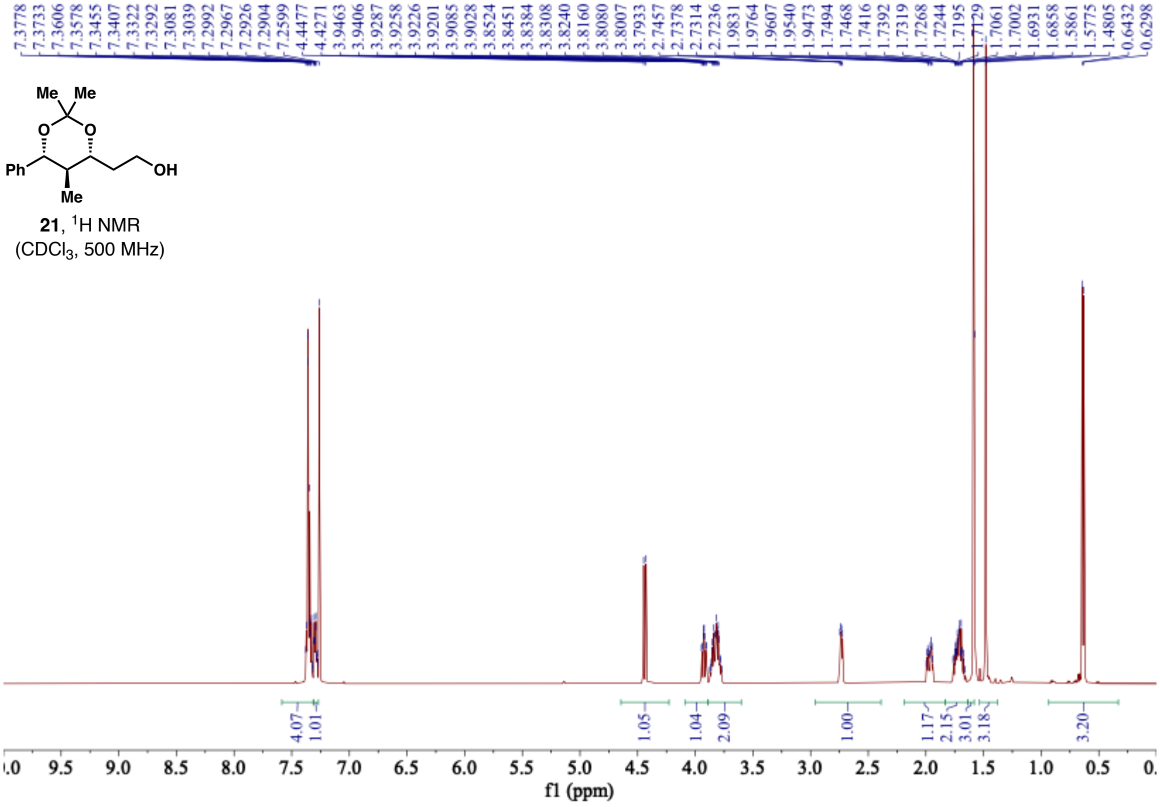
137.0764
131.9581
131.8924
127.9103
127.7459
115.5878
114.0060
113.9621
102.0196
101.5666
81.5137
77.6157
77.3600
77.1079
76.9033
76.1507
74.0866
55.6778
37.4333
36.7319
32.8412
11.6850
6.7787
PMP
PMP
O
O
O
O
Me
Me
18, ^{13}C NMR
(CDCl$_3$, 126 MHz)
77.6157
77.3600
77.1079
76.9033
76.1507
74.0866
78.0
77.5
77.0
76.5
76.0
75.5
75.0
74.5
74.0
f1 (ppm)
160.2820
160.2680
160.28
160.24
f1 (ppm)
131.9581
131.8924
132.0
131.8
f1 (ppm)
127.9103
127.7459
128.0
127.5
f1 (ppm)
114.0060
113.9621
114.2
114.0
113.8
f1 (ppm)
102.0196
101.5666
102
101
f1 (ppm)
37.4333
36.7319
38
37
36
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



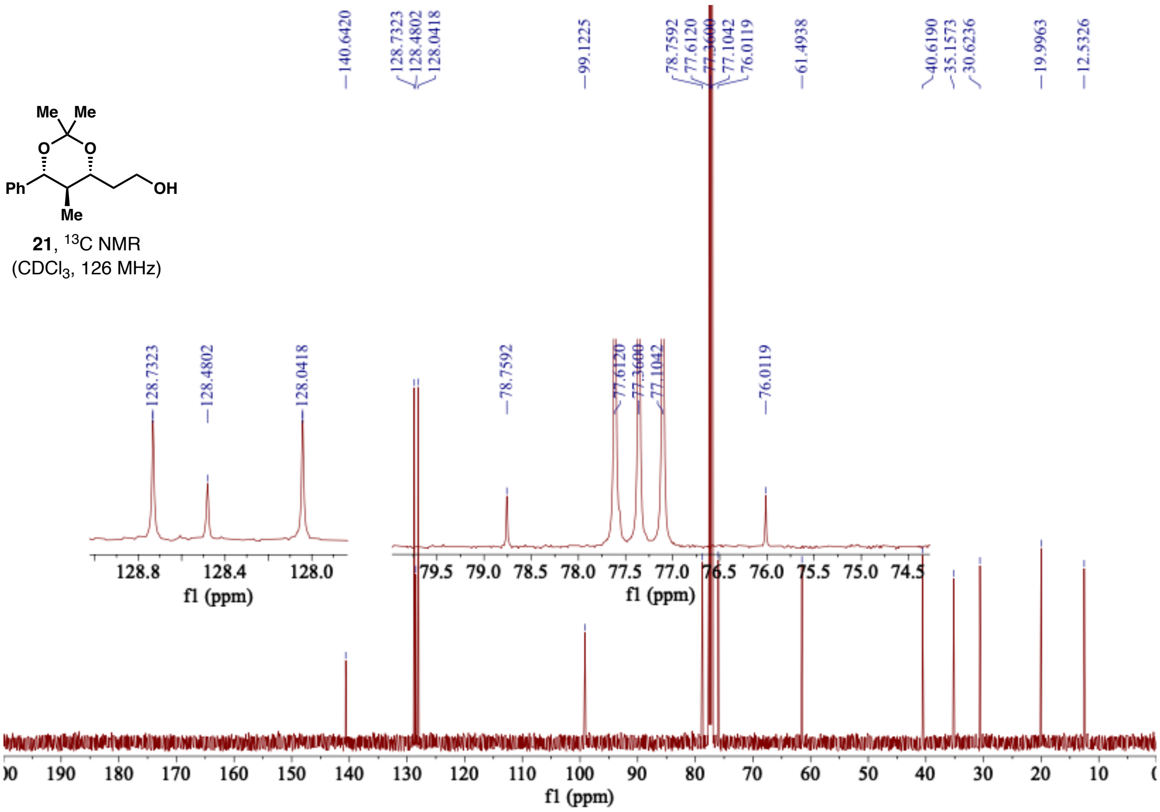
20, ^{1}H NMR
($CDCl_3$, 500 MHz)



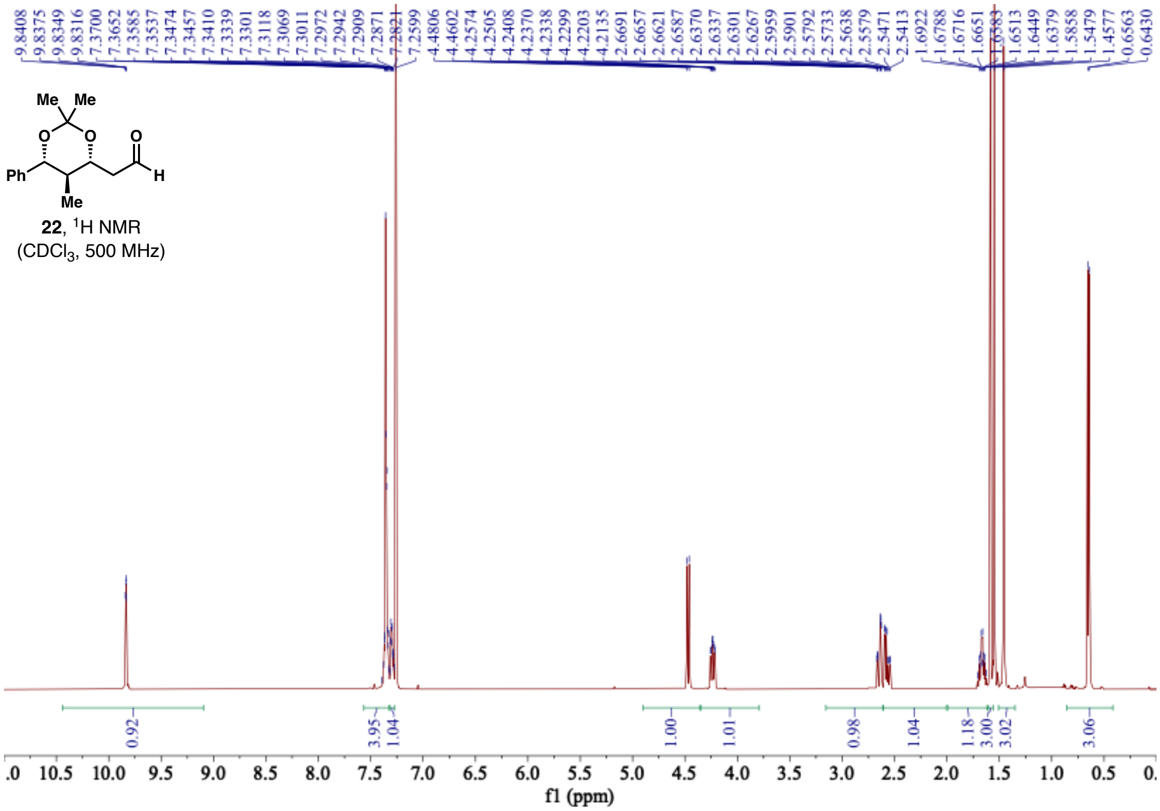
20, ^{13}C NMR
($CDCl_3$, 126 MHz)



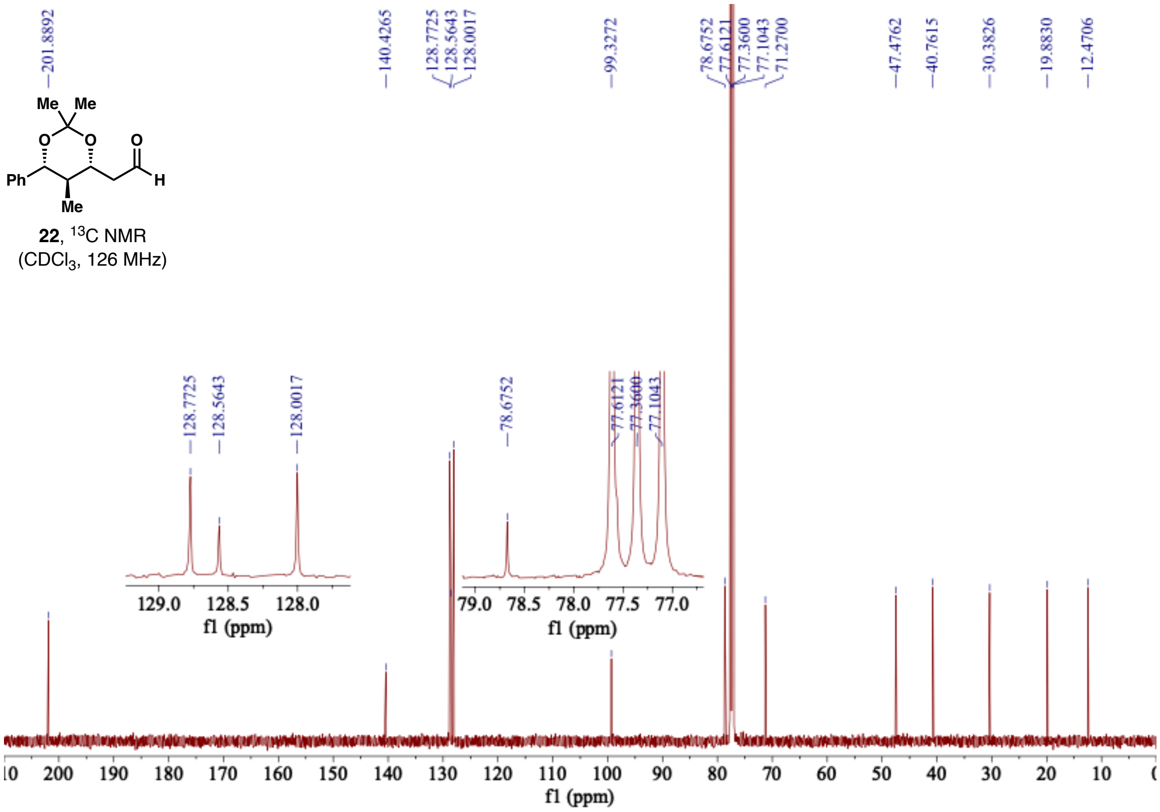
21, ^{1}H NMR
(CDCl$_3$, 500 MHz)



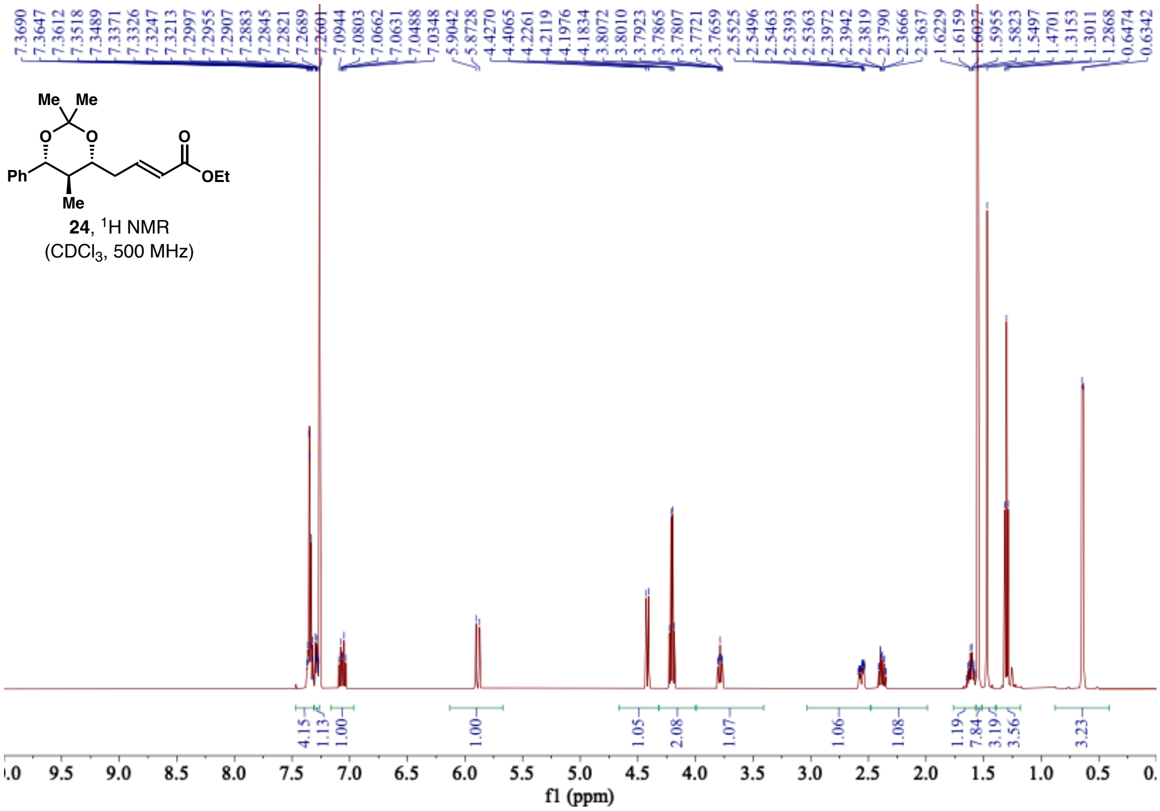
21, ^{13}C NMR
(CDCl$_3$, 126 MHz)



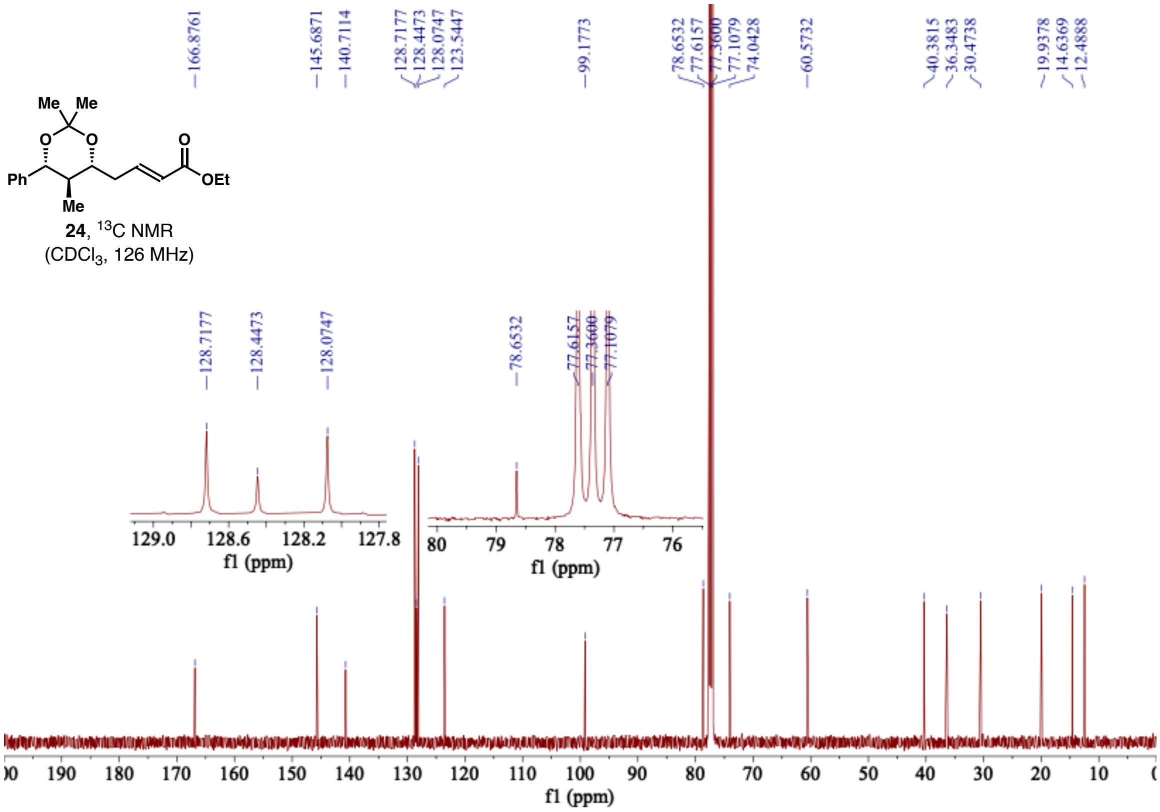
22, ^{1}H NMR
($CDCl_3$, 500 MHz)



22, ^{13}C NMR
($CDCl_3$, 126 MHz)



24, ^{1}H NMR
($CDCl_3$, 500 MHz)



24, ^{13}C NMR
($CDCl_3$, 126 MHz)