Electronic Supporting Information

An Expedient Procedure for the Oxidative Cleavage of Olefinic Bonds with $PhI(OAc)_2$, NMO, and Catalytic OsO_4

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I) Experimental Procedures

General procedures. All reactions were carried out under an atmosphere of air unless otherwise mentioned, and methylene chloride, tetrahydrofuran, and acetone were not dried prior to use. No special precautions were taken to exclude moisture from the system, except for reactions from Scheme 3. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogenous material, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated.

Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as a visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate, an aqueous solution of potassium permanganate, or an ethanolic solution of 2,4-dinitrophenylhydrazide with heat as developing agents. E. Merck silica gel (60, particle size 0.040-0.063 mm) was used for flash column chromatography. NMR spectra were recorded on Bruker DRX-600, Bruker DRX-500, or AV-400 instruments and calibrated using residual undeuterated solvent ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.0 ppm and C_6D_6: δ_H = 7.16 ppm, δ_C = 128.0 ppm) as an internal reference. The following abbreviations were used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad, AB = A-B spin system.

Infrared (IR) spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a VG ZAB-ZSE mass spectrometer using ESI (electrospray ionization). Optical rotations were recorded on a Perkin−Elmer Model 343 polarimeter at 589 nm, and are reported in units of 10^{-1} (deg cm^2 g^{-1}).

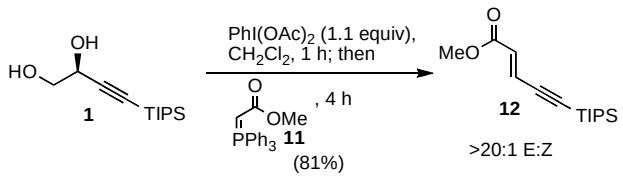
Chemical nomenclature was generated using ChemBioDraw Ultra, Version 11.0.1.

General procedure for $PhI(OAc)_2$ mediated diol cleavage. To a solution of a diol (100 mg) in methylene chloride (0.1 M) was added $PhI(OAc)_2$ (1.2 equiv). After the reaction was complete (as monitored by TLC), the mixture was concentrated without work-up and purified by flash column chromatography (silica gel, ethyl acetate or diethyl ether in hexanes) to give the pure products.

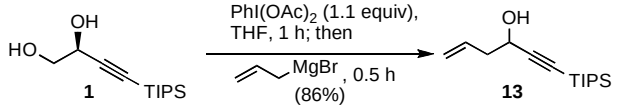
General procedure for OsO_4/$PhI(OAc)_2$/2,6-lutidine mediated oxidative cleavage of alkenes. To a solution of an alkene (100 mg) in THF (0.1 M) were added water (0.1 mL), 2,6-lutidine (2.5 equiv), osmium tetroxide (0.02 equiv), and $PhI(OAc)_2$ (2.3 equiv). After the reaction was complete (as monitored by TLC), the reaction was quenched with saturated aqueous sodium thiosulfate (10 mL). The mixture was extracted with ethyl acetate (3 × 10 mL), washed with saturated aqueous copper sulfate (2 × 20 mL), dried over sodium sulfate, and concentrated in vacuo. The crude residue was purified by flash column chromatography (silica gel, ethyl acetate or diethyl ether in hexanes) to give the product.

General procedure for OsO_4/NMO/$PhI(OAc)_2$/2,6-lutidine mediated oxidative cleavage of alkenes. To a solution of alkene (100 mg) in 10:1 acetone:water (0.1 M) were added 2,6-lutidine (2.0 equiv), 4-methylmorpholine *N*-oxide (1.5 equiv), and osmium tetroxide (0.02 equiv). When the starting material had been consumed as monitored by TLC, $PhI(OAc)_2$ (1.5 equiv) was added. After stirring for 2 h, the reaction was quenched with saturated aqueous sodium thiosulfate (10 mL). The mixture was extracted with ethyl acetate (3 × 10 mL), washed with saturated aqueous copper sulfate (2 × 20 mL), dried over sodium sulfate, and concentrated in vacuo. The crude residue was purified by flash column chromatography (silica gel, ethyl acetate or diethyl ether in hexanes) to give the product.

(*E*)-Methyl 5-(triisopropylsilyl)pent-2-en-4-ynoate (12): To a solution of the diol **1** (110 mg, 0.41 mmol) in anhydrous DCM (4 mL) was added $PhI(OAc)_2$ (1.1 equiv, 145 mg, 0.45 mmol) at room temperature under Argon atmosphere. After stirring for 1 h, the ylide (2.6 equiv, 394 mg, 1.18 mmol) was added, and the reaction was allowed to stir for 4 h until the intermediate aldehyde had disappeared by TLC. The reaction mixture was then concentrated. Purification via flash column chromatography (silica gel, 9:1 hexanes:ethyl acetate) gave the conjugated ester **12** (89 mg, 0.36 mmol, 81%).

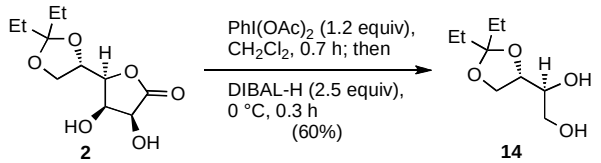


1-(Triisopropylsilyl)hex-5-en-1-yn-3-ol (13): To a solution of the diol **1** (50 mg, 0.20 mmol) in anhydrous THF (4 mL) was added $PhI(OAc)_2$ (1.1 equiv, 73 mg, 0.22 mmol mmol) at room temperature under Argon atmosphere. After stirring for 1 h, allyl magnesium bromide (3 equiv, 0.6 mL of 1 M solution) was added, and the reaction mixture was allowed to stir until TLC showed the complete disappearance of the intermediate aldehyde. The reaction was then quenched by adding 2 mL of saturated aqueous NH_4Cl. The mixture was diluted with water (3 mL) and ether (3 mL), and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 4 mL), and the combined organics were dried over sodium sulfate, filtered, and concentrated. Purification by flash column chromatography (silica gel, 1:5 ethyl acetate:hexanes yielded the propargyl alcohol **13** (45 mg, 0.17 mmol, 86%). The spectroscopic properties of this product exactly matched those reported in the literature.[1]



(*S*)-1-((*S*)-2,2-Diethyl-1,3-dioxolan-4-yl)ethane-1,2-diol (14): To a solution of diol **2** (100 mg, 0.41 mmol) in anhydrous DCM (10 mL) was added $PhI(OAc)_2$ (1.2 equiv, 158 mg, 0.49 mmol)

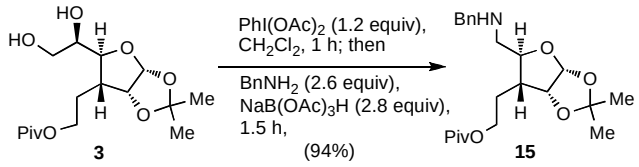
(1) a) Langille, N. F. *Org. Lett*. **2004**, *6*, 3203–3206. b) Robles, O. *Org. Lett*. **2009**, *11*, 5498–5501.



2 **14**

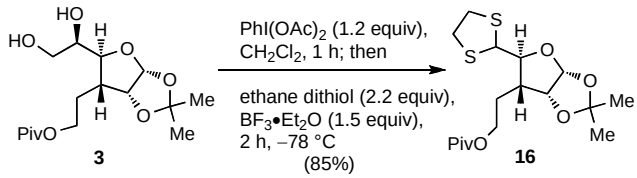
at room temperature under Argon atmosphere. After stirring for 40 min, the reaction mixture was cooled to 0 °C, and DIBAL-H (2.5 equiv, 2.5 mL of 1 M in DCM) was added. The reaction mixture was stirred for 20 min before being quenched by the cautious addition of 10 mL of saturated aqueous Rochelle's salt. The mixture was filtered through a plug of silica gel, and the layers were separated. The aqueous layer was extracted with DCM (3 × 10 mL), and the combined organics were dried over sodium sulfate and concentrated. The resulting product was purified via flash column chromatography (silica gel, 3:2 ethyl acetate:hexanes) to give diol **14** (47 mg, 0.25 mmol, 60%).

2-((3a*R*,5*S*,6*R*,6a*R*)-5-((Benzylamino)methyl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)ethyl pivalate (15): To a solution of diol **3** (100 mg, 0.30 mmol) in anhydrous DCM (3 mL) was added $PhI(OAc)_2$ (1.2 equiv, 156 mg, 0.36 mmol) at room temperature under Argon. After stirring for 1 h, benzyl amine (84 mg, 0.78 mmol, 2.6 equiv) was added. The reaction mixture was stirred for 15 min before sodium tri-acetoxyborohydride (178 mg, 0.84 mmol, 2.8 equiv) was added at room temperature. The reaction was allowed to stir for 1.5 h and then quenched by the addition of saturated aqueous sodium bicarbonate (3 mL). The layers were separated, and the aqueous layer was extracted with DCM (3 × 5 mL), and the combined organics were dried over sodium sulfate, filtered, and concentrated. Purification by flash column chromatography (silica gel, 1:5 ethyl acetate:hexanes) provided the amine **15** (110 mg, 0.28 mmol, 94%).



3 **15**

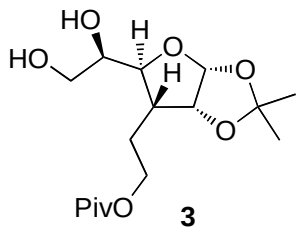
2-((3a*R*,5*S*,6*S*,6a*R*)-5-(1,3-Dithiolan-2-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)ethyl pivalate (16): To a solution of diol **3** (100 mg, 0.30 mmol) in anhydrous DCM (3 mL)



was added $PhI(OAc)_2$ (1.2 equiv, 156 mg, 0.36 mmol) at room temperature under Argon atmosphere. The reaction mixture was stirred for 1 h before ethane dithiol (0.062 mL, 0.66 mmol, 2.2 equiv) was added. The reaction mixture was cooled to –78 °C, and $BF_3•Et_2O$ (0.064 mL, 0.45 mmol, 1.5 equiv) was added dropwise. The reaction mixture was stirred at that temperature for 2 h, and then quenched by the addition of water (3 mL) and warmed to room temperature. The layers were separated, and the organic layer was washed sequentially with water (3 mL), 2 N aqueous NaOH (3 mL), and water (3 mL). The organics were dried over sodium sulfate, filtered, and concentrated. Purification by flash column chromatography (silica gel, 1:5 ethyl acetate:hexanes) provided dithiane **16** (98 mg, 0.26 mmol, 85%).

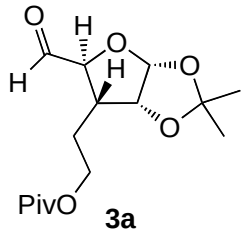
II) Physical Data for New Compounds

2-((3a*R*,5*S*,6*R*,6a*R*)-5-((*R*)-1,2-Dihydroxyethyl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)ethyl pivalate (3, *This substrate was prepared from diacetone-D-glucose as part of a total synthesis program.):* R_f = 0.3 (silica gel, acetone:hexanes, 3:7); $[\alpha]_D^{25}$ = +41.7 (*c* = 0.23 in $CHCl_3$); FT-IR (neat) ν_{max} = 3432, 2977, 2936, 1726, 1378, 1370, 1287, 1213, 1103, 1031, 1019, 872 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 5.78 (d, *J* = 3.5 Hz, 1 H), 4.66 (t, *J* = 4.0 Hz, 1 H), 4.24 – 4.20 (m, 1 H), 4.16 (quin, *J* = 5.5 Hz, 1 H), 3.91 (dd, *J* = 9.5, 4.5 Hz, 1 H), 3.73 – 3.72 (m, 3 H), 2.64 (d, *J* = 5.5 Hz, 1 H), 2.27 (t, *J* = 5 Hz, 1 H), 2.00 – 1.95 (m, 3 H), 1.50 (s, 3 H), 1.32 (s, 3 H), 1.2 (s, 9 H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 179.1, 112.4,



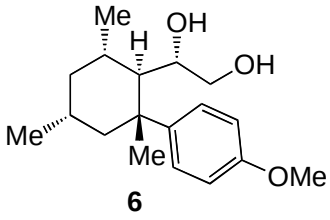
105.2, 82.8, 81.6, 73.3, 63.9, 63.3, 44.1, 27.6, 27.2, 26.8, 25.0 ppm; HRMS (ESI) calcd for $C_{16}H_{28}O_7Na^+$ [*M*+Na^+] 355.1727, found 355.1736.

2-((3a*R*,5*S*,6*R*,6a*R*)-5-Formyl-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)ethyl pivalate (3a): R_f = 0.6 (silica gel, acetone:hexanes, 3:7); $[\alpha]_D^{25}$ = –10.2 (*c* = 1.0 in CH_2Cl_2); FT-IR (neat) ν_{max} = 2978, 2936, 2911, 1725, 1481, 1460, 1372, 1284, 1216, 1159, 1022, 874, 771 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 9.65 (d, *J* = 2.4 Hz, 1 H), 5.94 (d, *J* = 3.2 Hz, 1 H), 4.70 (t, *J* = 3.6 Hz, 1 H), 4.23 (ddd, *J* = 11.3, 8.0, 6.2 Hz, 1 H), 4.21 – 4.08 (m, 2 H), 2.12 – 1.99 (m, 2 H), 1.91 – 1.86 (m, 1 H), 1.51 (s, 3 H), 1.34 (s, 3 H), 1.19 (s, 9 H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 200.2, 178.4, 112.7, 106.3, 84.5, 80.5, 62.3, 43.4, 38.7, 27.2, 26.9, 26.5, 23.7 ppm; HRMS (ESI) calcd for $C_{15}H_{24}O_6Na^+$ [*M*+Na^+] 323.1465, found 323.1465.



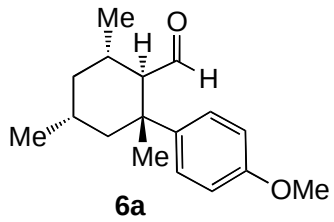
3a

(*S*)-1-((1*R*,2*R*,4*R*,6*S*)-2-(4-Methoxyphenyl)-2,4,6-trimethylcyclohexyl)ethane-1,2-diol (6, *This compound was prepared from (+)–pulegone as part of a total synthesis program.***):** R_f = 0.15 (silica gel, diethyl ether:hexanes, 2:8); $[\alpha]_D^{25}$ = +2.1 (*c* = 1.0 in CH_2Cl_2); FT-IR (neat) ν_{max} = 3401, 2947, 2906, 1608, 1510, 1457, 1185, 1028, 823 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz): δ = 7.26 – 7.25 (m, 2 H), 6.86 – 6.85 (m, 2 H), 3.67 (dt, *J* = 9.6, 2.0 Hz, 1 H), 3.42 (s, 3 H), 3.33 – 3.29 (m, 1 H), 3.20 (dd, *J* = 11.1, 2.5 Hz, 1 H), 2.28 (bs, 1 H), 1.79 (bs, 1 H), 1.75 – 1.72 (m, 1 H), 1.69 – 1.66 (m, 1 H), 1.58 (dq, *J* = 13.0, 3.4 Hz, 1 H), 1.52 – 1.47 (m, 1 H), 1.31 (dt, *J* = 13.3, 2.7 Hz, 1 H), 1.28 (s, 3 H), 1.22 – 1.17 (m, 1 H) 1.14 (d, *J* = 6.1 Hz, 3 H), 0.78 (d, *J* = 6.4 Hz, 3 H), 0.67 (q, *J* = 12.0 Hz, 1 H) ppm; ^{13}C NMR (C_6D_6, 125 MHz): δ = 158.1, 143.2, 127.2, 113.9, 73.9, 65.8, 54.8, 54.6, 54.0, 46.1, 41.7, 29.8, 28.1, 22.7, 22.6, 20.8 ppm; HRMS (ESI) calcd for $C_{18}H_{28}O_3Na^+$ [*M*+Na^+] 315.1931, found 315.1919.



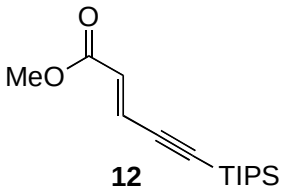
6

(1*R*,2*R*,4*R*,6*S*)-2-(4-Methoxyphenyl)-2,4,6-trimethylcyclohexanecarbaldehyde (6a): R_f = 0.75 (silica gel, diethyl ether:hexanes, 2:8); $[\alpha]_D^{25}$ = –54.4 (*c* = 1.1 in CH_2Cl_2); FT-IR (neat) ν_{max} = 2996, 2954, 2906, 2742, 1706, 1609, 1509, 1458, 1254, 1182, 1027, 820, 723 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz): δ = 9.35 (d, *J* = 2.9 Hz, 1 H), 7.19 – 7.17 (m, 2 H), 6.83 – 6.80 (m, 2 H), 3.37 (s, 3 H), 2.27 (dd, *J* = 11.0 , 2.9 Hz, 1 H), 1.93 – 1.87 (m, 1 H), 1.50 – 1.41 (m, 2 H), 1.32 – 1.28 (m, 1 H), 1.21 (s, 3 H), 1.21 – 1.16 (m, 1 H), 0.88 (d, *J* = 6.4 Hz, 3 H), 0.73 (d, *J* = 6.3 Hz, 3 H), 0.45 (q, *J* = 12.5 Hz, 1 H) ppm; ^{13}C NMR (C_6D_6, 125 MHz): δ = 204.2, 158.5, 140.5, 127.0, 114.0, 64.4, 54.8, 51.5, 43.5, 40.6, 28.1, 27.8, 22.6, 21.0, 19.6 ppm; HRMS (ESI) calcd for $C_{17}H_{24}O_2Na^+$ [*M*+Na^+] 283.1668, found 283.1665.



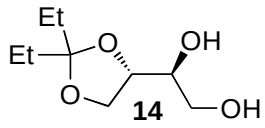
6a

(*E*)-methyl 5-(triisopropylsilyl)pent-2-en-4-ynoate (12): R_f = 0.70 (silica gel, ethyl acetate:hexanes, 1:9); FT-IR (neat) ν_{max} = 2944, 2866, 1726, 1726, 1616, 1463, 1434, 1303, 1268, 1170, 959, 882, 741, 676, 661 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 6.77 (d, *J* = 15.5 Hz, 1 H), 6.26 (d, *J* = 16.0 Hz, 1 H), 3.75 (s, 3 H), 1.11 (s, 21 H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 166.6, 130.6, 125.6, 103.4, 102.6, 52.0, 18.8, 11.3 ppm; HRMS (ESI) calcd for $C_{15}H_{26}O_2SiH^+$ [*M*+H^+] 267.1775, found 267.1772.



12

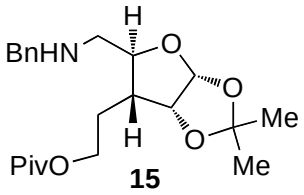
(*S*)-1-((*S*)-2,2-Diethyl-1,3-dioxolan-4-yl)ethane-1,2-diol (14): R_f = 0.45 (silica gel, ethyl acetate); $[\alpha]_D^{25}$ = –2.0 (*c* = 1.0 in CH_2Cl_2); FT-IR (neat) ν_{max} = 3409, 2972, 2940, 2883, 1462, 1199, 1172, 929 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 4.14 (dt, *J* = 7.3, 4.9 Hz, 1 H), 4.05 (dd, *J* = 8.1, 6.5 Hz, 1 H), 3.80 (t, *J* = 8 Hz, 1 H), 3.72 – 3.60 (m, 3 H), 1.67 (qd, *J* = 7.2, 2.3 Hz, 2 H), 1.63 (q, *J* = 7.5 Hz, 2 H), 0.91 (t, *J* = 7.5 Hz, 3 H), 0.89 (t, *J* = 7.0 Hz, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 113.5,



14

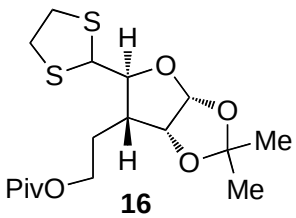
99.6, 71.6, 66.2, 64.3, 29.5, 29.0, 8.1, 8.0 ppm; HRMS (ESI) calcd for $C_9H_{18}O_4Na^+$ [*M*+Na^+] 213.1097, found 213.1101.

2-((3a*R*,5*S*,6*R*,6a*R*)-5-((Benzylamino)methyl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)ethyl pivalate (15): R_f = 0.45 (silica gel, ethyl acetate:hexanes 7:3); $[\alpha]_D^{25}$ = +38.8 (*c* = 1.0 in CH_2Cl_2); FT-IR (neat) ν_{max} = 2977, 1725, 1480, 1454, 1371, 1283, 1213, 1155, 1022, 875, 738, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.31 – 7.29 (m, 4 H), 7.24 – 7.20 (m, 1 H), 5.78 (d, *J* = 4.7 Hz, 1 H), 4.62 (dd, *J* = 5.1, 5.1 Hz, 1 H), 4.24 – 4.18 (m, 1 H), 4.15 – 4.09 (m, 1H), 3.97 (ddd, *J* = 12.7, 7.6, 3.2 Hz, 1H), 3.84 – 3.76 (AB, *J* = 16.6 Hz, 2 H), 2.90 (dd, *J* = 15.6, 3.3 Hz, 1 H), 2.61 (dd, *J* = 15.6, 7.9 Hz, 1 H), 2.00 – 1.85 (m, 2 H), 1.67 – 1.62 (m, 1 H), 1.48 (s, 3 H), 1.30 (s, 3 H), 1.19 (s, 9 H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 178.5, 140.2, 128.3, 128.0, 126.9, 111.5, 104.9, 81.0, 62.8, 54.0, 50.4, 43.2, 38.7, 27.2, 26.7, 26.4, 24.2 ppm; HRMS (ESI) calcd for $C_{22}H_{33}NO_5H^+$ [*M*+H^+] 392.2431, found 392.2437.



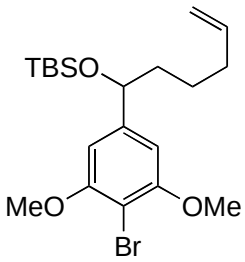
15

2-((3a*R*,5*S*,6*S*,6a*R*)-5-(1,3-Dithiolan-2-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)ethyl pivalate (16): R_f = 0.6 (silica gel, ethyl acetate:hexanes 1:9); $[\alpha]_D^{25}$ = +6.4 (*c* = 0.7 in CH_2Cl_2); FT-IR (neat) ν_{max} = 2973, 2932, 2870, 1724, 1480, 1371, 1283, 1158, 1033, 874, 770 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 5.79 (d, *J* = 3.6 Hz, 1 H), 4.66 (dd, *J* = 3.9, 3.9 Hz, 1 H), 4.62 (d, *J* = 3.7 Hz, 1 H), 4.24 – 4.14 (m, 2 H), 4.04 (dd, *J* = 9.6, 3.6 Hz, 1 H), 3.35 – 3.29 (m, 2 H), 3.28 – 3.14 (m, 2 H), 2.11 – 2.04 (m, 1 H), 1.98 – 1.94 (m, 2 H), 1.50 (s, 3 H), 3.32 (s, 3 H), 1.22 (s, 9 H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 178.5, 112.0, 104.8, 85.5, 81.4, 62.6, 54.6, 44.9, 38.7, 38.7, 27.2, 27.0, 26.6, 24.9 ppm; HRMS (ESI) calcd for $C_{17}H_{28}O_5S_2Na^+$ [*M*+Na^+] 399.1270, found 399.1270.



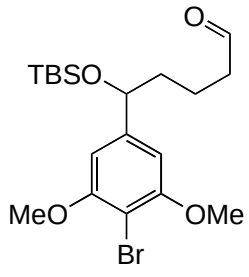
16

(1-(4-Bromo-3,5-dimethoxyphenyl)hex-5-enyloxy)(*tert*-butyl)dimethylsilane (20, *This substrate was prepared from 4-bromo-3,5-dimethoxybenzoic acid as part of a total synthesis program*)**:** R_f = 0.8 (silica gel, ethyl acetate:hexanes, 2:8); FT-IR (neat) ν_{max} = 3076, 2930, 2856, 1587, 1456, 1411, 1360, 1232, 1090, 1034, 832, 874 cm^{-1}; ^1H NMR (C_6D_6, 500 MHz): δ = 6.49 (s, 2 H), 5.76 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1 H), 5.06 – 5.02 (m, 1 H), 5.00 – 4.97 (m, 1 H), 4.57 (dd, *J* = 7.5, 4.1 Hz, 1 H), 3.39 (s, 6 H), 2.02 (q, *J* = 6.5 Hz, 2 H), 1.81 – 1.73 (m, 1 H), 1.68 – 1.54 (m, 2 H), 1.49 – 1.41 (m, 1 H), 0.99 (s, 9 H), 0.09 (s, 3 H), –0.07 (s, 3 H) ppm; ^{13}C NMR (C_6D_6, 125 MHz): δ = 157.7, 147.0, 138.8, 114.9, 102.3, 100.1, 75.3, 55.8, 40.8, 34.0, 26.0, 25.3, 18.4, –4.4, –4.8 ppm; HRMS (ESI) calcd for $C_{20}H_{33}BrO_3SiH^+$ [*M*+H^+] 429.1455, found 429.1440.



20

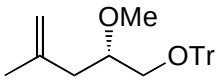
5-(4-Bromo-3,5-dimethoxyphenyl)-5-(*tert*-butyldimethylsilyloxy)pentanal (20a): R_f = 0.6 (silica gel, ethyl acetate:hexanes, 2:8); FT-IR (neat) ν_{max} = 2930, 2855, 1723, 1588, 1459, 1413, 1233, 1100, 835, 776 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 9.73 (t, *J* = 1.7 Hz, 1 H), 6.53 (s, 2 H), 4.64 (t, *J* = 6.4 Hz, 1 H), 3.88 (s, 6 H), 2.42 (td, *J* = 6.8, 1.7 Hz, 2 H), 1.73 – 1.60 (m, 4 H), 0.90 (s, 9 H), 0.05 (s, 3 H), –0.10 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 202.2, 156.8, 146.4, 102.1, 98.9, 74.5, 56.4, 43.7, 40.1, 25.8, 18.2, 18.1, –4.6, –5.0 ppm; HRMS (ESI) calcd for $C_{19}H_{31}BrO_4SiNa^+$ [*M*+Na^+] 453.1067, found 453.1072.



20a

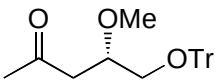
(*S*)-((2-Methoxy-4-methylpent-4-enyloxy)methanetriyl)tribenzene (22*, This compound was prepared from (R)-glycidol as of a total synthesis program.***)**: R_f = 0.8 (silica gel, ethyl acetate:hexanes, 2:8); $[\alpha]_D^{25}$ = –14.7 (*c* = 1.0 in CH_2Cl_2); FT-IR (neat) ν_{max} = 3060, 2885, 1646, 1597, 1490, 1448, 1220, 1077, 1036, 897, 763, 746, 704 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ =

7.38 – 7.36 (m, 6 H), 7.21 – 7.18 (m, 6 H), 7.14 – 7.11 (m, 3 H), 4.62 (bs, 1 H), 4.57 (bs, 1 H), 3.37 – 3.32 (m, 1 H), 3.31 (s, 3 H), 3.04 (m, 2 H), 2.13 (d, J = 6.7 Hz, 2 H), 1.70 (bs, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 144.2, 142.6, 128.8, 127.7, 126.9, 112.4, 99.6, 79.2, 65.4, 58.0, 40.4, 22.8 ppm; HRMS (ESI) calcd for $C_{26}H_{28}O_2Na^+$ [M+Na^+] 395.1981, found 395.1978.



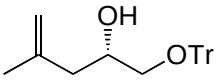
22

(*S*)-4-Methoxy-5-(trityloxy)pentan-2-one (22a): R_f = 0.4 (silica gel, ethyl acetate:hexanes, 2:8); $[\alpha]_D^{25}$ = –22.6 (c = 1.0 in CH_2Cl_2); FT-IR (neat) ν_{max} = 3058, 2930, 1717, 1596, 1490, 1448, 1357, 1221, 1159, 1075, 900, 764, 747 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.37 – 7.35 (m, 6 H), 7.19 – 7.15 (m, 6 H), 7.14 – 7.12 (m, 3 H), 3.76 – 3.72 (m, 1 H), 3.27 (s, 3 H), 3.05 (d, J = 4.9 Hz, 2 H), 2.62 (dd, J = 16.4, 8.35 Hz, 1 H), 2.49 (dd, J = 16.4, 4.2 Hz, 1 H), 2.05 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 207.1, 143.9, 128.6, 127.8, 127.0, 86.7, 76.5, 64.4, 58.0, 46.3, 31.0 ppm; HRMS (ESI) calcd for $C_{25}H_{26}O_3Na^+$ [M+Na^+] 397.1774, found 397.1780.



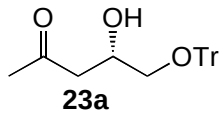
22a

(*S*)-4-Methyl-1-(trityloxy)pent-4-en-2-ol (23, *This compound was prepared from (R)-glycidol*
): R_f = 0.4 (silica gel, diethyl ether:hexanes, 3:7); $[\alpha]_D^{25}$ = –0.5 (c = 2.7 in $CHCl_3$); FT-IR (neat) ν_{max} = 3451, 3059, 3027, 2930, 2881, 1641, 1687, 1491, 1448, 1220, 1073, 898, 764, 746 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.35 – 7.33 (m, 6 H), 7.22 – 7.18 (m, 6 H), 7.15 – 7.12 (m, 3 H), 4.69 – 4.68 (m, 1 H), 4.62 – 4.61 (m, 1 H), 3.83 – 3.79 (m, 1 H), 3.07 (dd, J = 9.4, 4.0 Hz, 1 H), 3.01 (dd, J = 9.4, 6.8 Hz, 1 H), 2.13 (d, J = 3.3 Hz, 1 H), 2.09 – 2.04 (m, 2 H) 1.60 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 143.9, 142.1, 128.7, 127.8, 127.1, 113.1, 86.7, 68.7, 67.5, 42.1, 22.4 ppm; HRMS (ESI) calcd for $C_{25}H_{26}O_2Na^+$ [M+Na^+] 381.1825, found 381.1835.



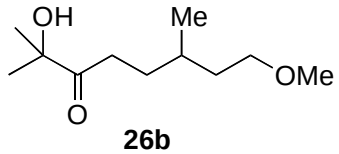
23

(*S*)-4-Hydroxy-5-(trityloxy)pentan-2-one (23a): R_f = 0.3 (silica gel, ethyl acetate:hexanes, 2:8); $[\alpha]_D^{25}$ = –0.8 (*c* = 1 in CH_2Cl_2); FT-IR (neat) ν_{max} = 3548, 3058, 2927, 1711, 1490, 1448, 1359, 1221, 1159, 1073, 985, 901, 765, 747 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.34 – 7.29 (m, 6 H), 7.22 – 7.19 (m, 6 H), 7.16 – 7.13 (m, 3 H), 4.18 – 4.12 (m, 1 H), 3.04 (d, *J* = 5.5 Hz, 2 H), 2.85 – 2.84 (m, 1 H), 2.52 – 2.51 (m, 2 H), 2.05 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 208.7, 143.8, 128.6, 127.9, 127.1, 86.7, 67.2, 66.7, 46.9, 30.8 ppm; HRMS (ESI) calcd for $C_{24}H_{24}O_3Na^+$ [*M*+Na^+] 383.1618, found 383.1613.



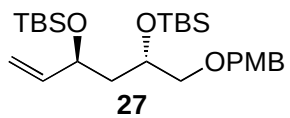
23a

(2-Hydroxy-8-methoxy-2,6-dimethyloctan-3-one (26b): R_f = 0.6 (silica gel, ethyl acetate:hexanes 1:1); FT-IR (neat) ν_{max} = 3434, 2962, 2930, 2865, 1706, 1462, 1377, 1185, 1165, 1115, 960 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.43 – 3.34 (m, 2 H), 3.30 (s, 3 H), 2.62 – 2.48 (m, 2 H), 1.67 – 1.50 (m, 3 H), 1.50 – 1.36 (m, 2 H), 1.35 (s, 6 H), 0.88 (d, *J* = 6.4 Hz, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 214.7, 76.2, 70.8, 58.6, 36.4, 33.1, 30.8, 29.6, 26.5, 19.4 ppm; HRMS (ESI) calcd for $C_{11}H_{22}O_3Na^+$ [*M*+Na^+] 225.1461, found 225.1455.



26b

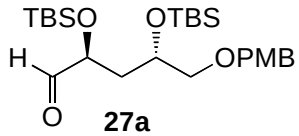
5*S*,7*S*)-5-((4-Methoxybenzyloxy)methyl)-2,2,3,3,9,9,10,10-octamethyl-7-vinyl-4,8-dioxa-3,9-disilaundecane (27, *This substrate was prepared from L–(–)–malic acid as part of a total synthesis program.***)**: R_f = 0.8 (silica gel, diethyl ether:hexanes 5:95); $[\alpha]_D^{25}$ = –0.1 (*c* = 0.9 in CH_2Cl_2); FT-IR (neat) ν_{max} = 2954, 2929, 2887, 2856, 1613, 1513, 1248, 1090, 1038, 774 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.16 (m, 2 H), 6.78 – 6.76 (m, 2 H), 5.70 (ddd, *J* = 17.25, 10.3, 7.1 Hz, 1 H), 5.01 (dd, *J* = 17.2, 0.6 Hz, 1 H), 4.91 (dd, *J* = 10.25, 0.7 Hz, 1 H), 4.35 (s, 2 H), 4.17 – 4.13 (m, 1 H), 3.88 – 3.86 (m, 1 H), 3.70 (s, 3 H), 3.31 – 3.25 (m, 2 H), 1.70 – 1.66 (m, 1 H), 1.51 – 1.46 (m, 1 H), 0.79 (s, 18 H), –0.03 (s, 3 H), –0.05 (s, 6 H), –0.07 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 159.1, 142.1,



27

130.6, 129.1, 128.3, 114.0, 113.7, 74.9, 72.8, 71.5, 69.0, 55.2, 44.0, 26.0, 25.9, 18.5, –3.0, –3.9, –4.0, –4.6 ppm; HRMS (ESI) calcd for $C_{26}H_{48}O_4Si_2Na^+$ [*M*+Na^+] 503.2983, found 503.2964.

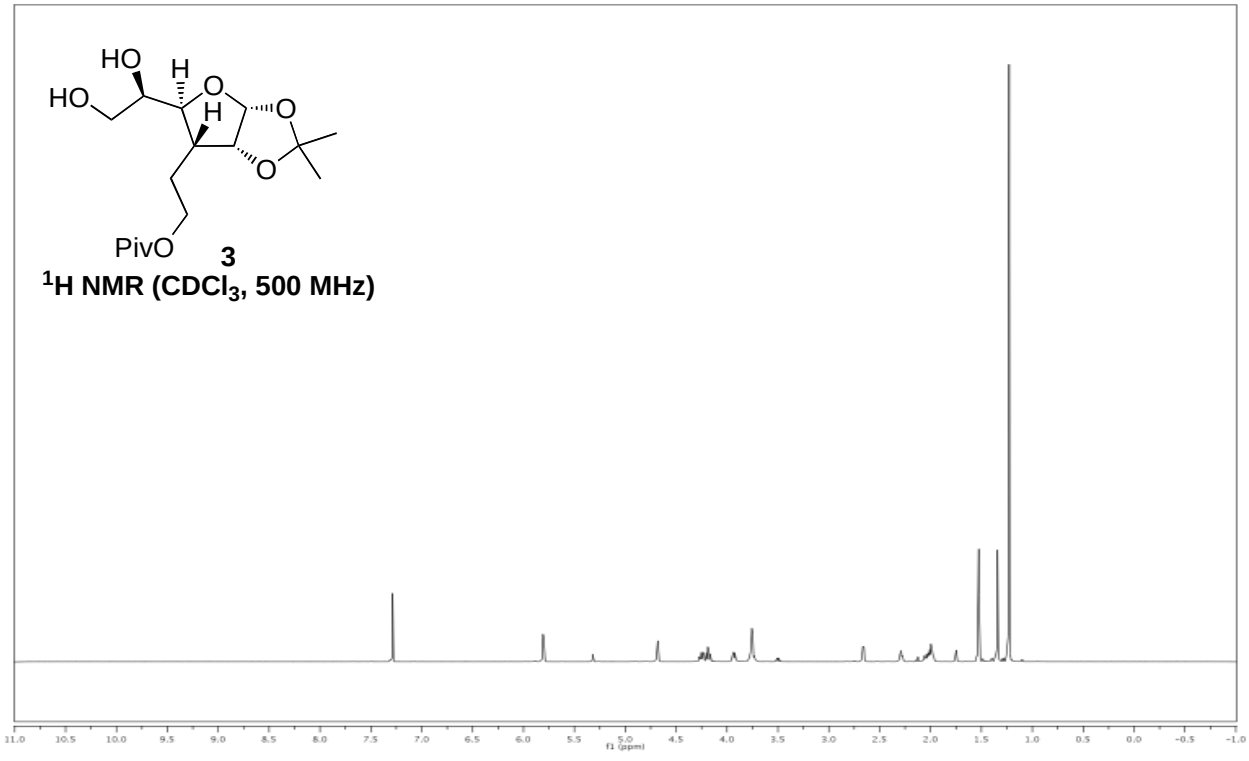
(2*S*,4*S*)-2,4-Bis(*tert*-butyldimethylsilyloxy)-5-(4-methoxybenzyloxy)pentanal (27a): R_f = 0.5 (silica gel, diethyl ether:hexanes 5:95); $[\alpha]_D^{25}$ = –5.9 (*c* = 1.0 in CH_2Cl_2); FT-IR (neat) ν_{max} =



27a

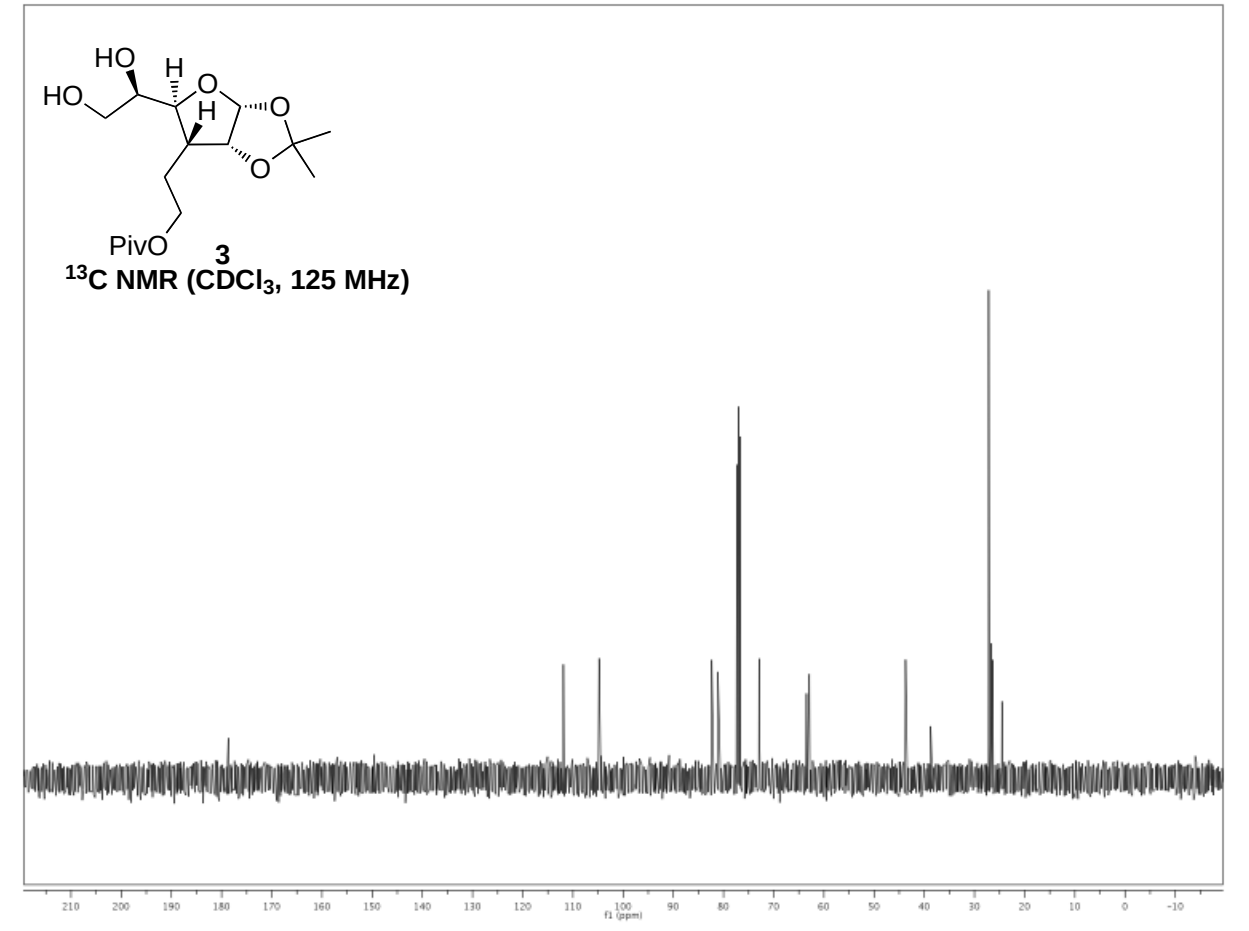
2954, 2929, 2886, 2857, 1736, 1613, 1514, 1471, 1249, 1101, 1038, 809, 777 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 9.56 (d, *J* = 1.5 Hz, 1 H), 7.25 – 7.23 (m, 2 H), 6.88 – 6.86 (m, 2 H), 4.40 (d, *J* = 11.6 Hz, 1 H), 4.41 (d, *J* = 11.6 Hz, 1 H), 4.19 (ddd, *J* = 6.5, 5.0, 1.0 Hz, 1 H), 4.04 (p, *J* = 5.2 Hz, 1 H), 3.80 (s, 3 H), 3.43 (dd, *J* = 9.8, 5.7 Hz, 1 H), 3.40 (dd, *J* = 9.8, 5.1 Hz, 1 H), 1.92 – 1.84 (m, 2 H), 0.91 (s, 9 H), 0.87 (s, 9 H), 0.09 (s, 3 H), 0.07 (s, 3 H), 0.06 (s, 6 H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 202.9, 159.1, 130.3, 129.2, 113.7, 75.5, 74.5, 72.8, 68.5, 55.2, 38.2, 25.9, 25.8, 18.2, –4.1, –4.4, –4.7, –4.8 ppm; HRMS (ESI) calcd for $C_{25}H_{46}O_5Si_2Na^+$ [*M*+Na^+] 505.2776, found 505.2754.

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



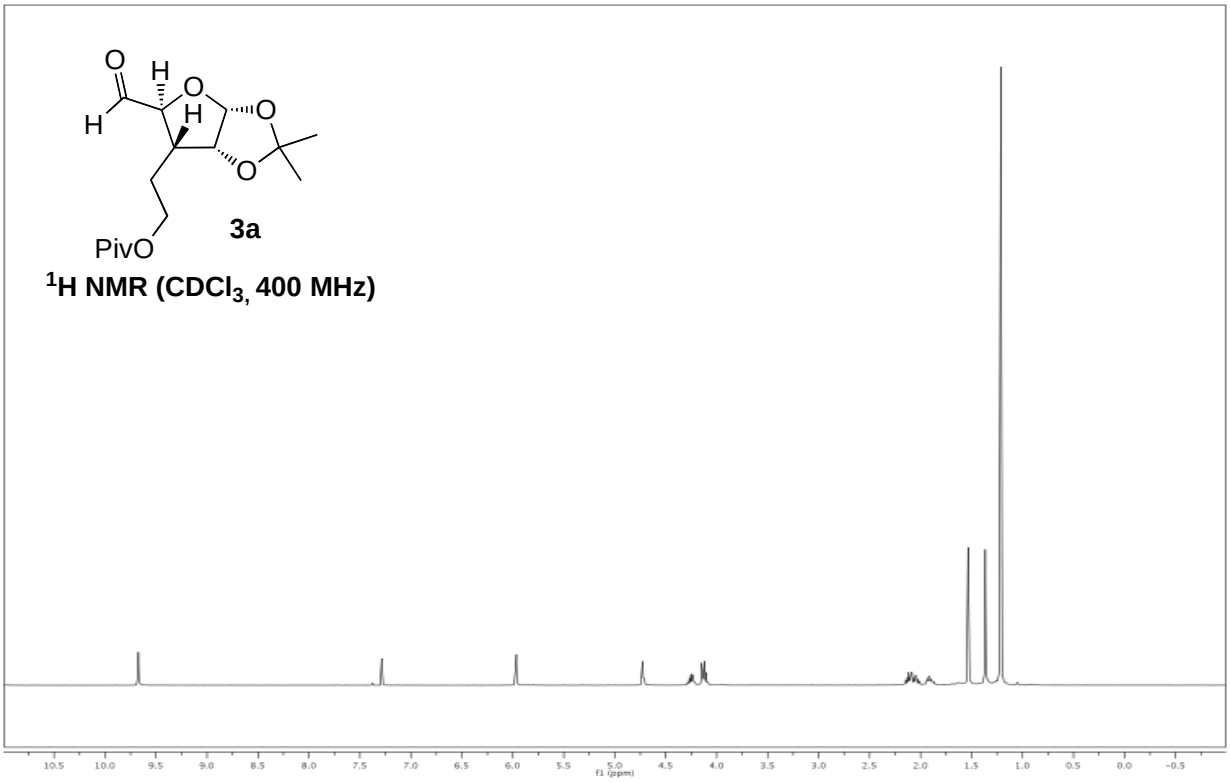
3

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



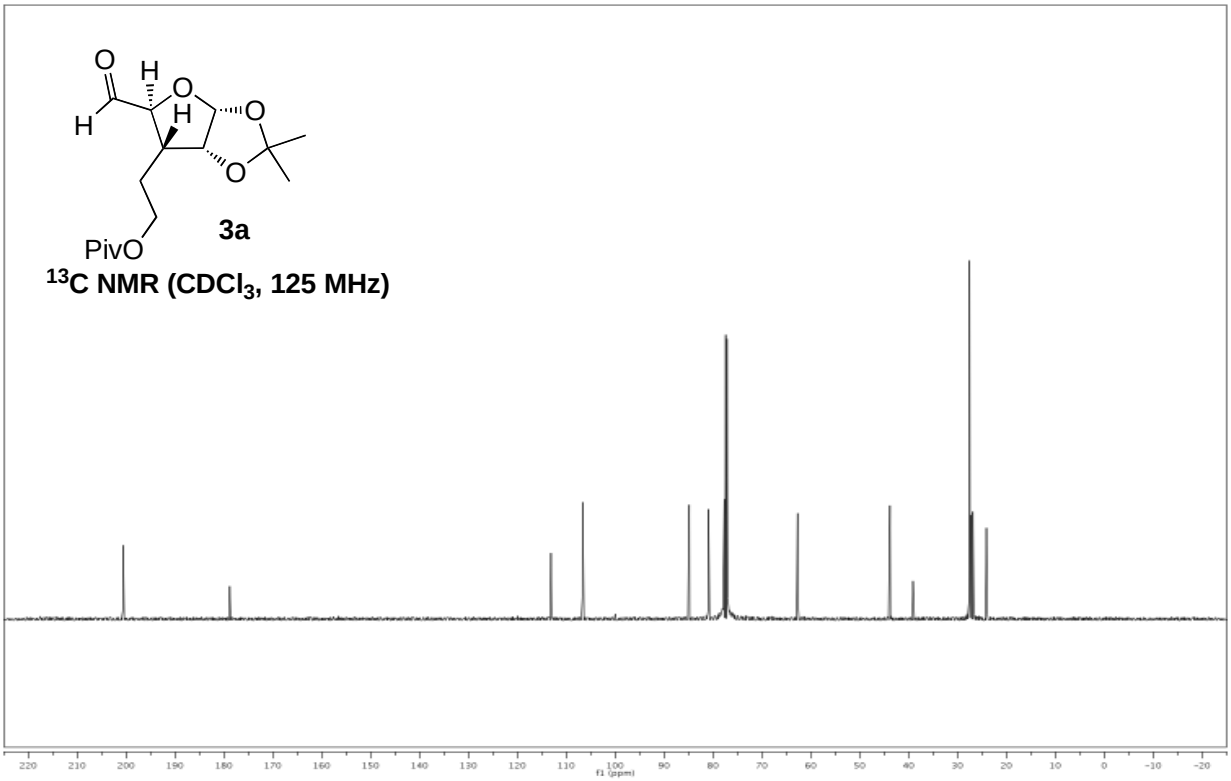
3

^{13}C NMR ($CDCl_3$, 125 MHz)



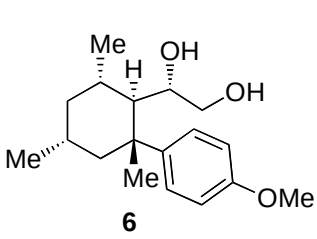
3a

^{1}H NMR ($CDCl_3$, 400 MHz)



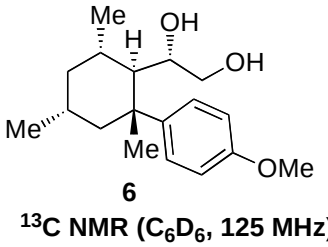
3a

^{13}C NMR ($CDCl_3$, 125 MHz)



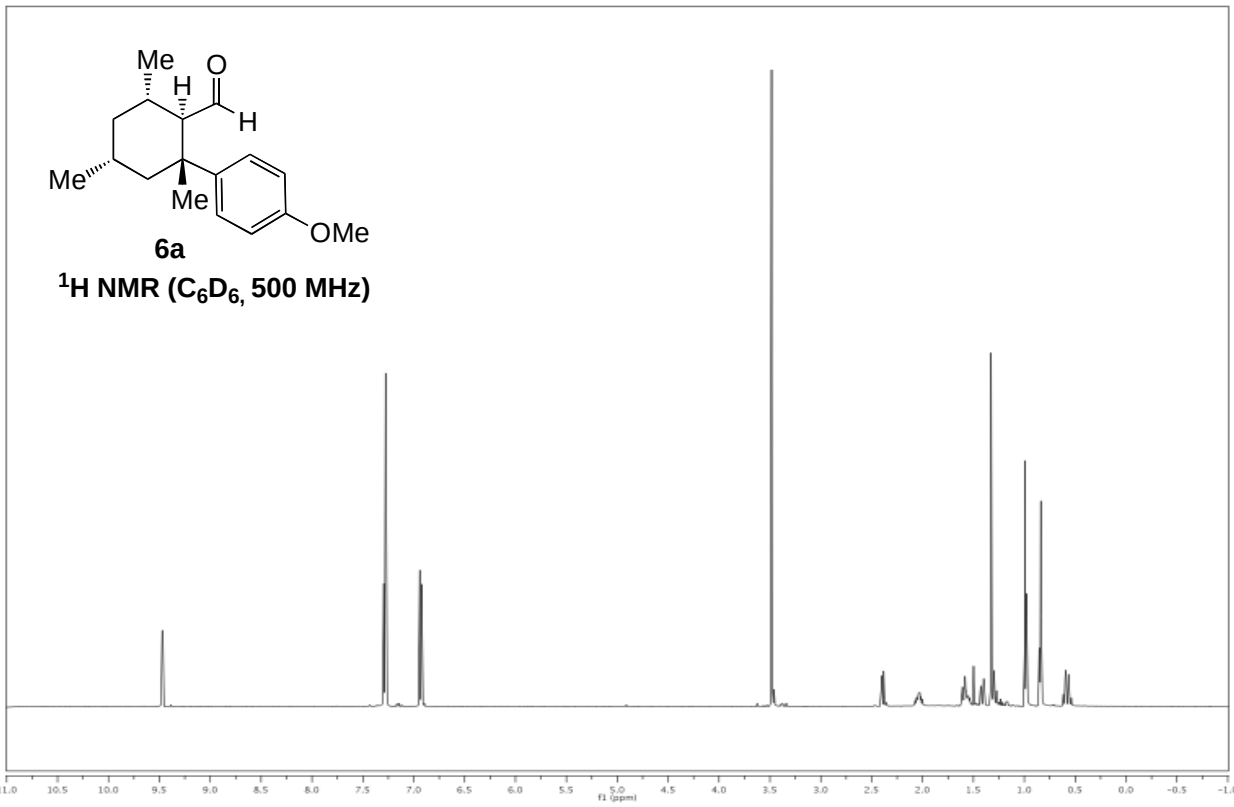
6

^{1}H NMR (C_6D_6, 500 MHz)



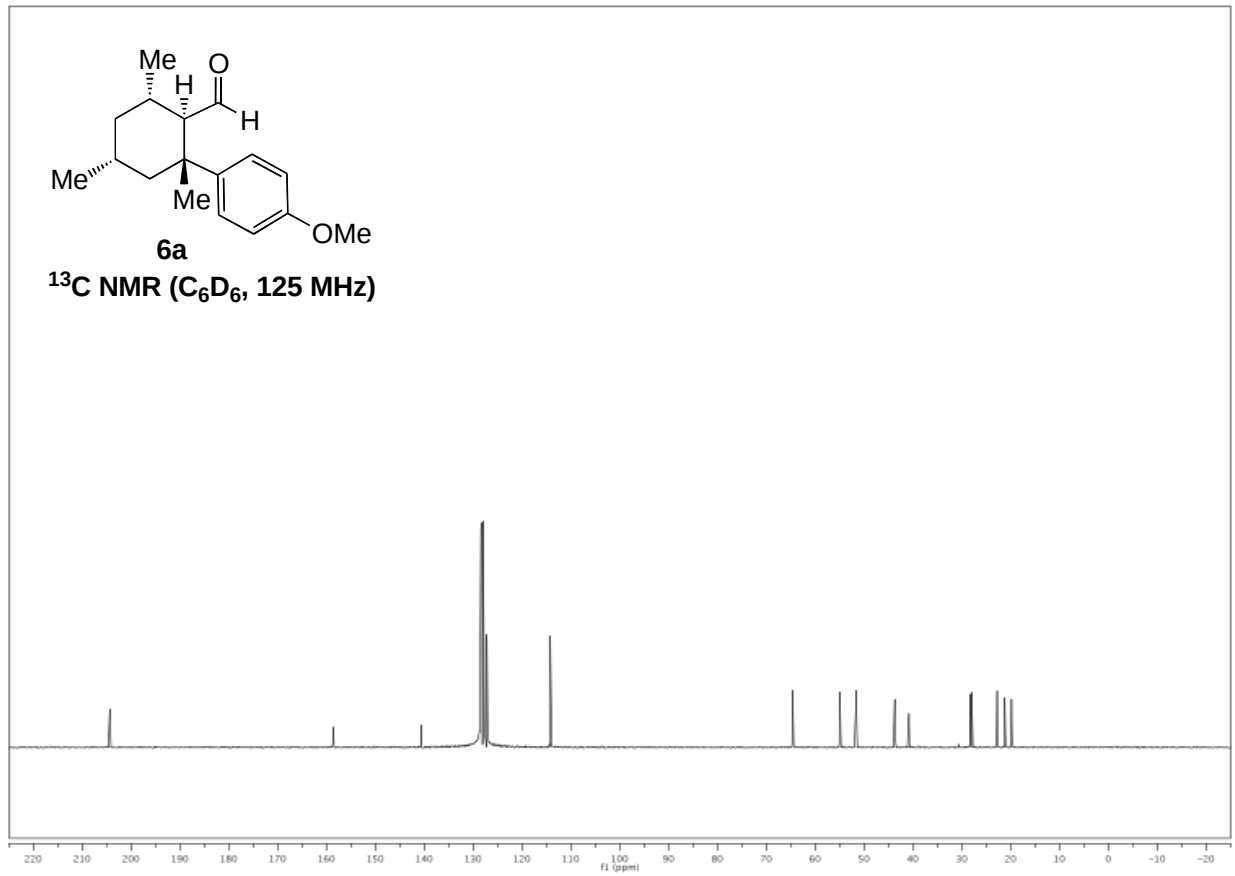
6

^{13}C NMR (C_6D_6, 125 MHz)



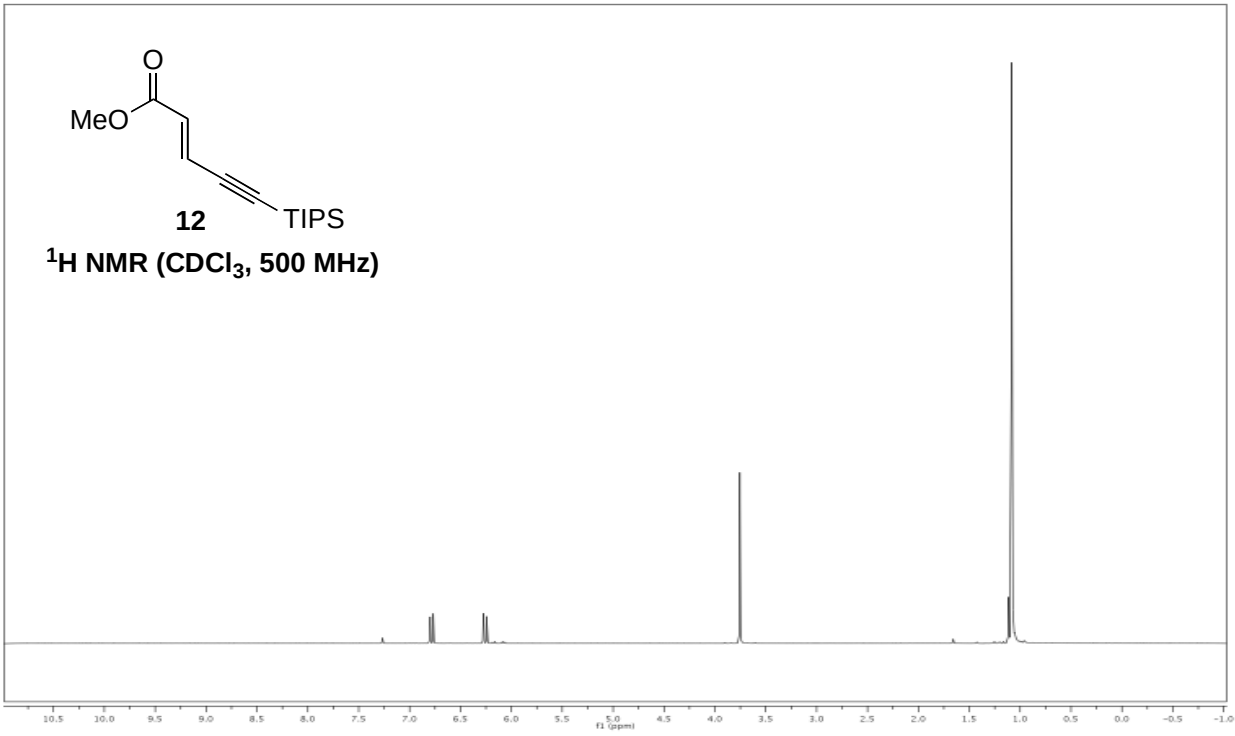
6a

^{1}H NMR (C_6D_6, 500 MHz)



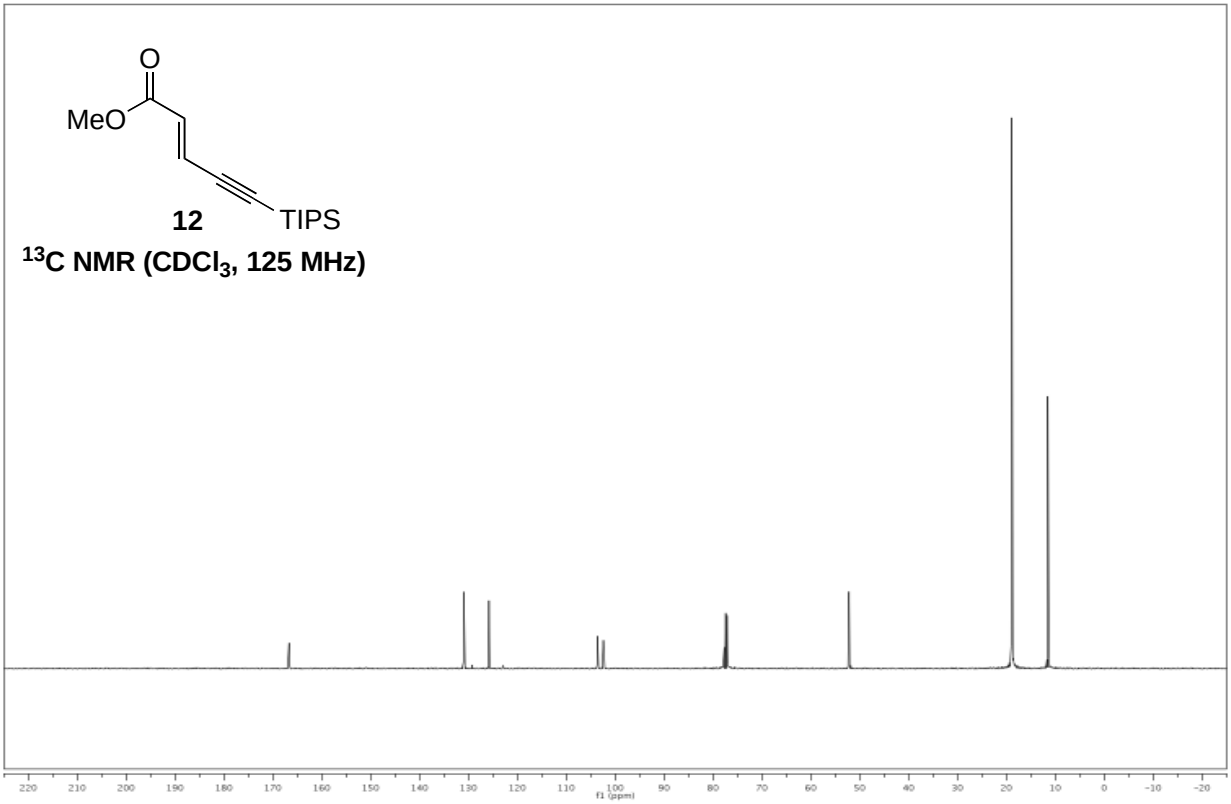
6a

^{13}C NMR (C_6D_6, 125 MHz)



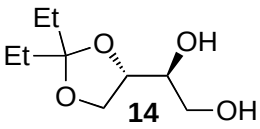
12

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



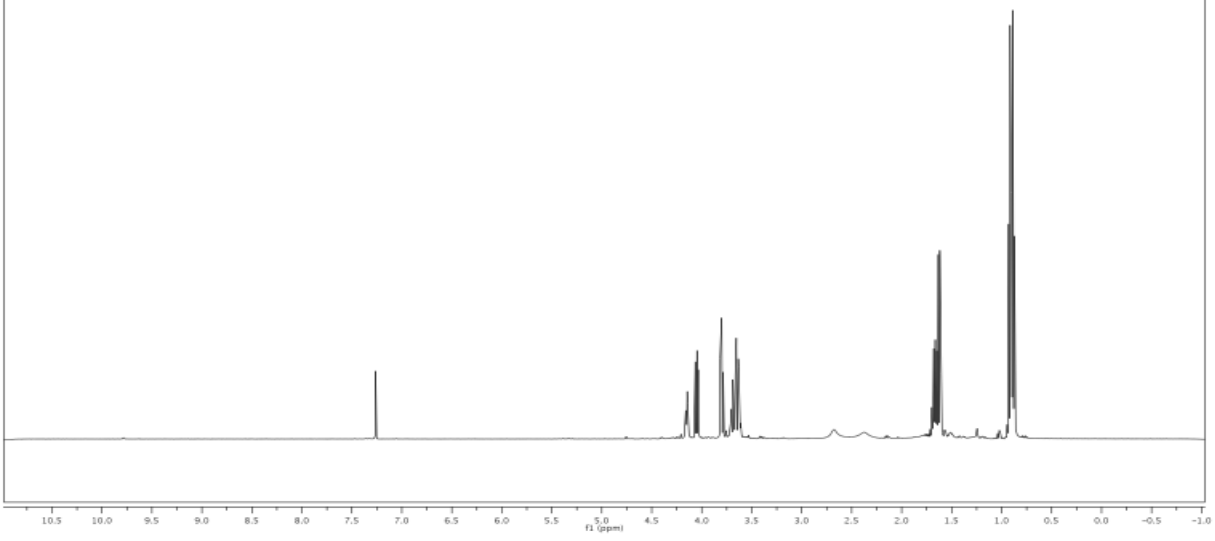
12

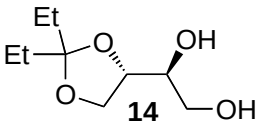
^{13}C NMR ($CDCl_3$, 125 MHz)



14

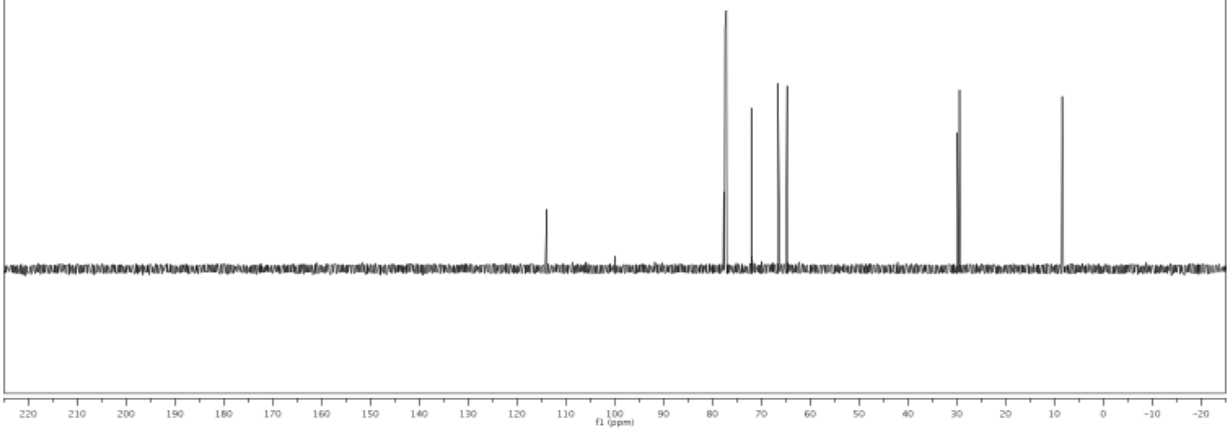
^{1}H NMR ($CDCl_3$, 500 MHz)

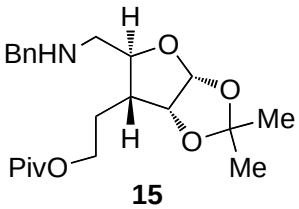




14

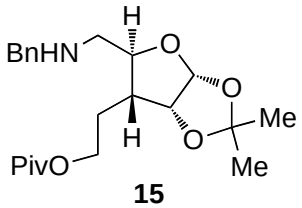
^{13}C NMR ($CDCl_3$, 125 MHz)





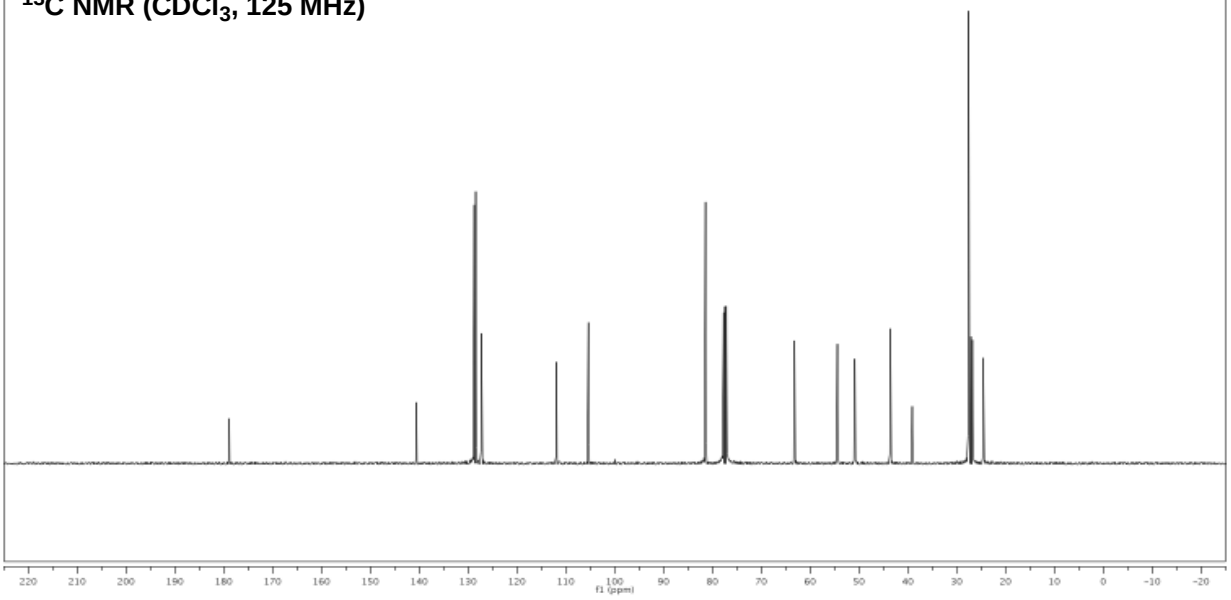
15

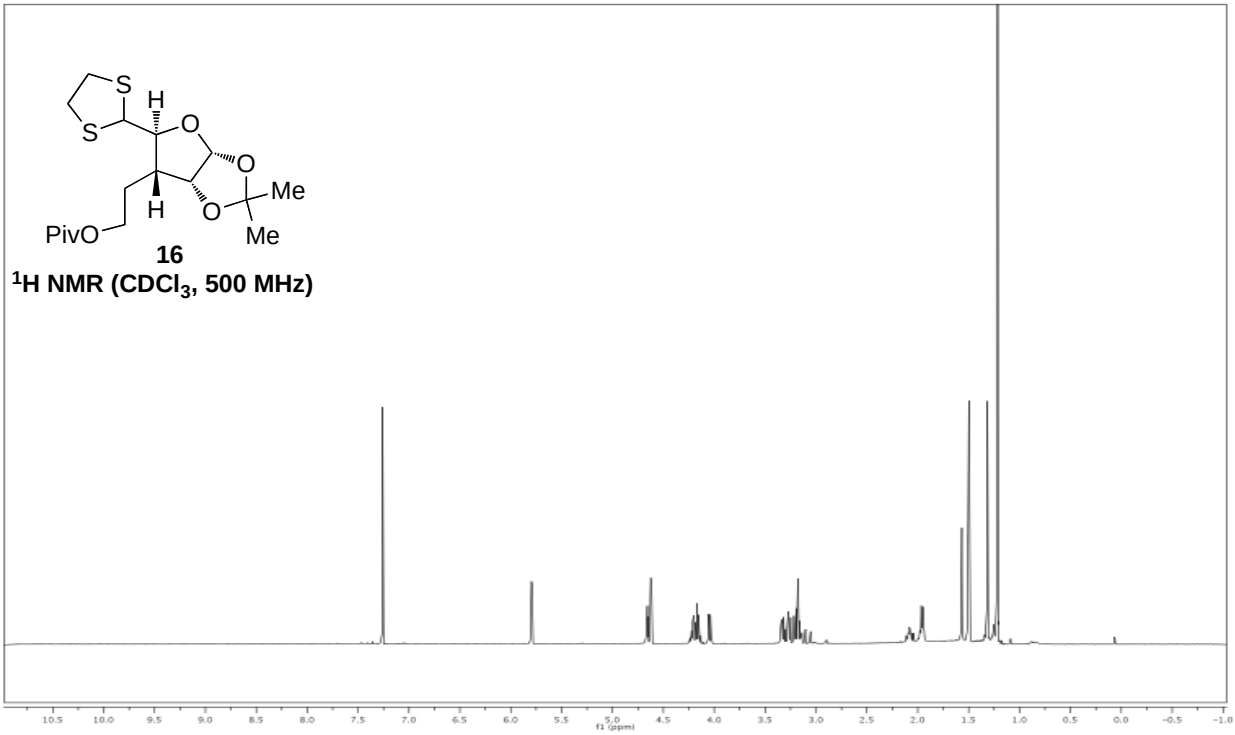
^{1}H NMR ($CDCl_3$, 500 MHz)



15

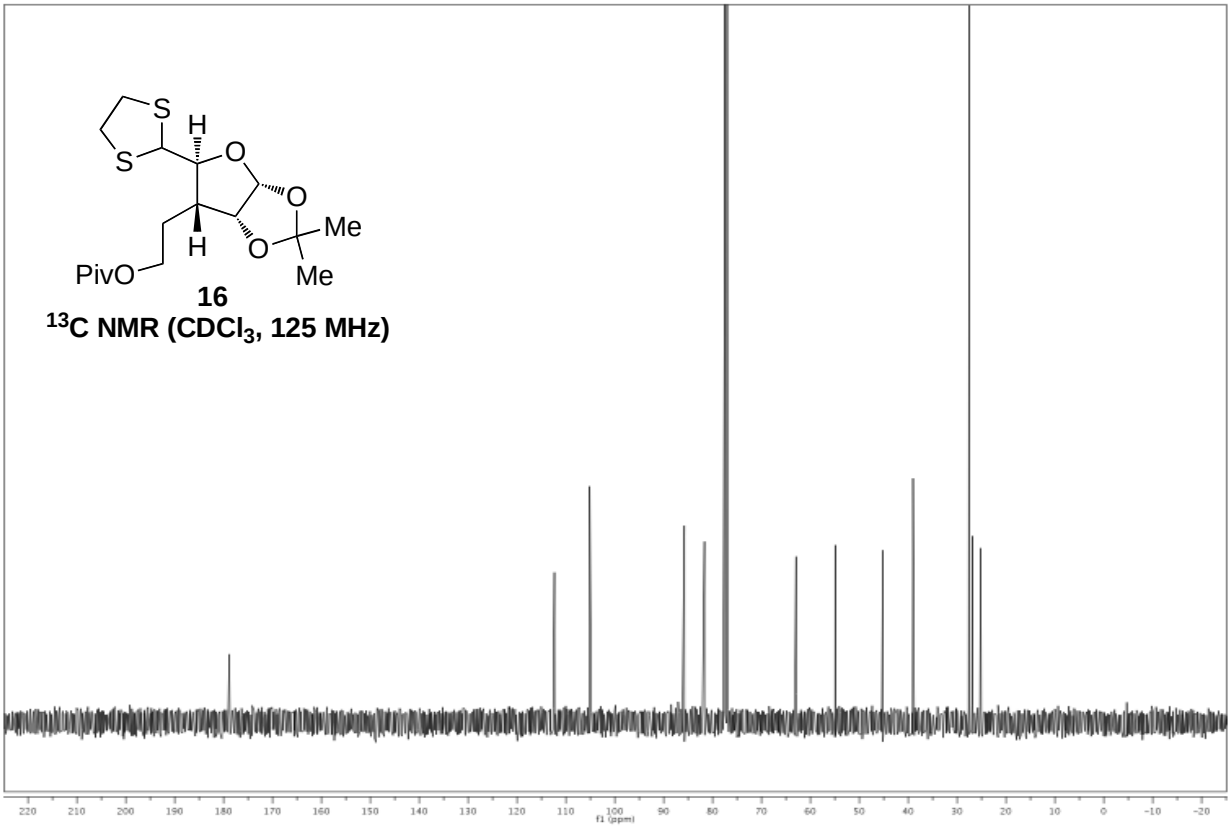
^{13}C NMR ($CDCl_3$, 125 MHz)





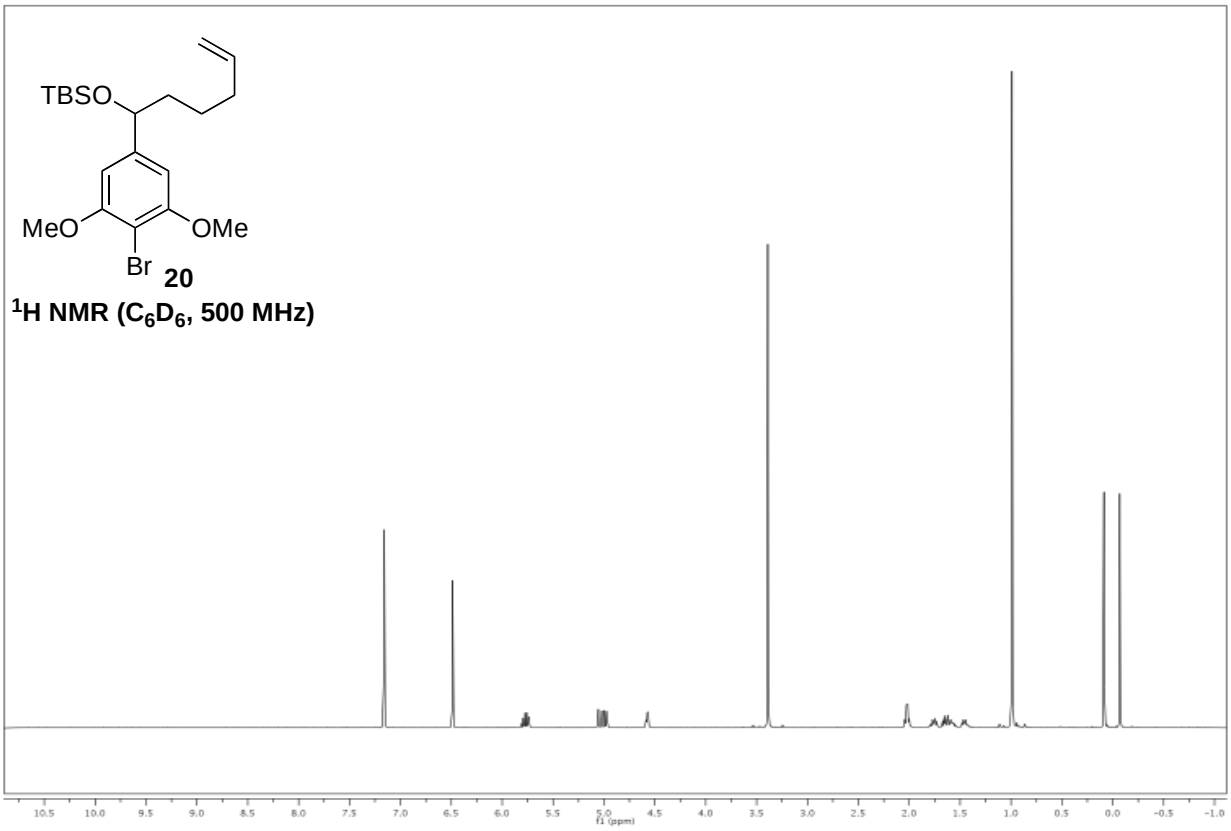
16

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



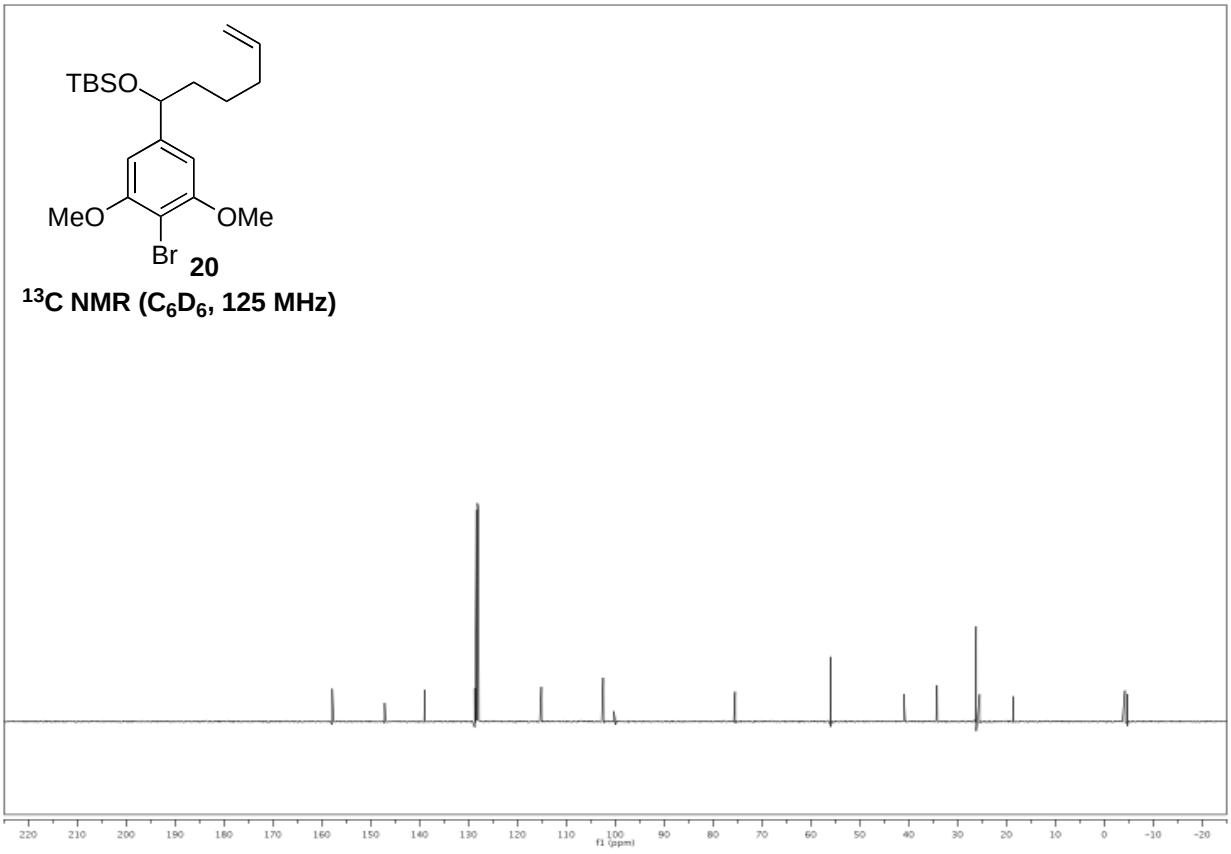
16

^{13}C NMR ($CDCl_3$, 125 MHz)



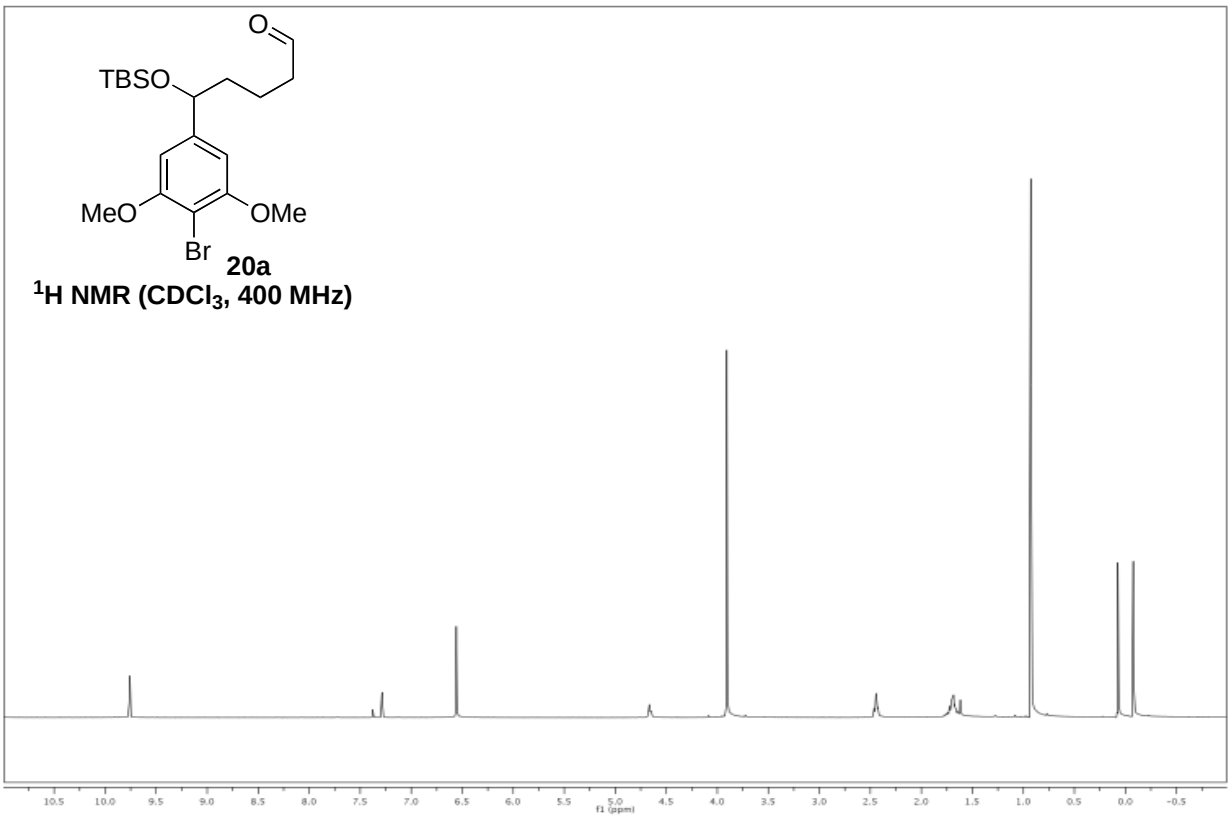
20

^{1}H NMR (C_6D_6, 500 MHz)



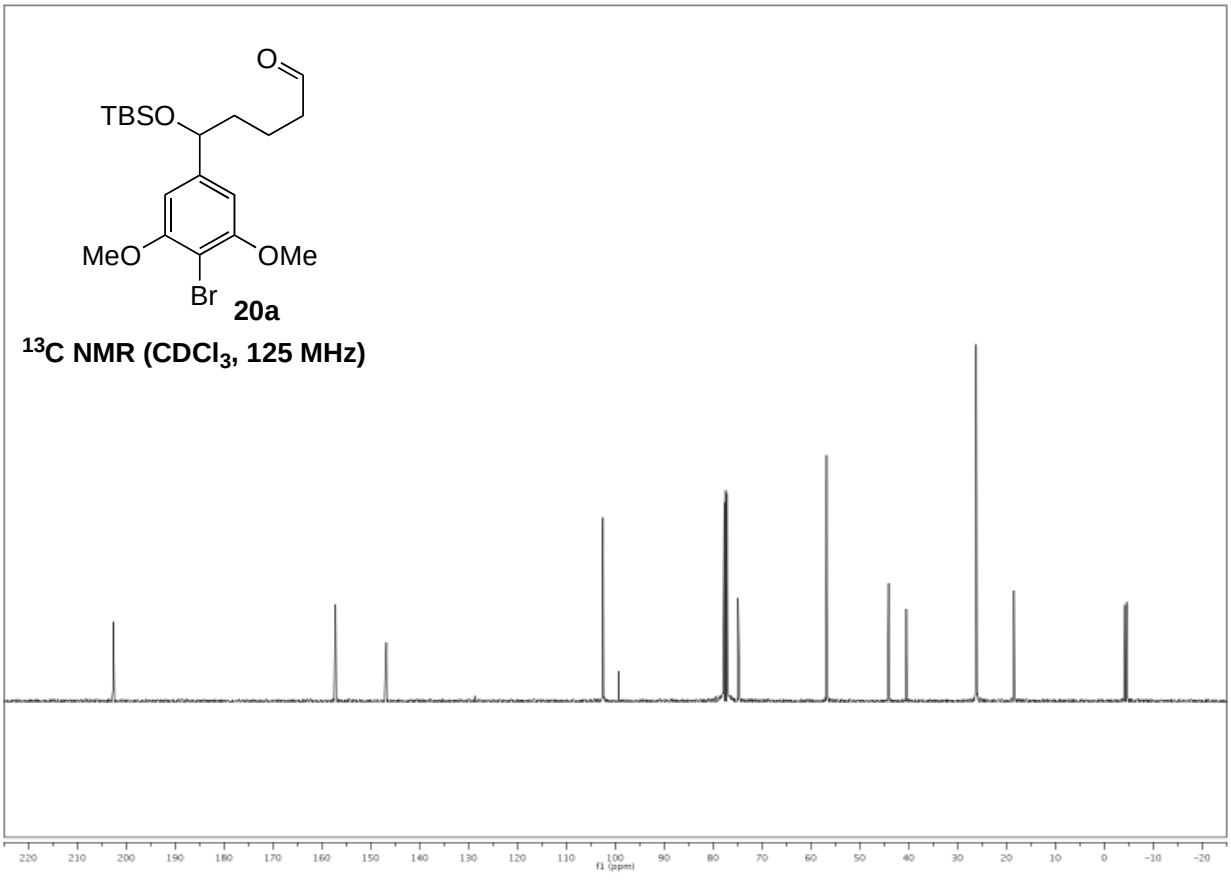
20

^{13}C NMR (C_6D_6, 125 MHz)



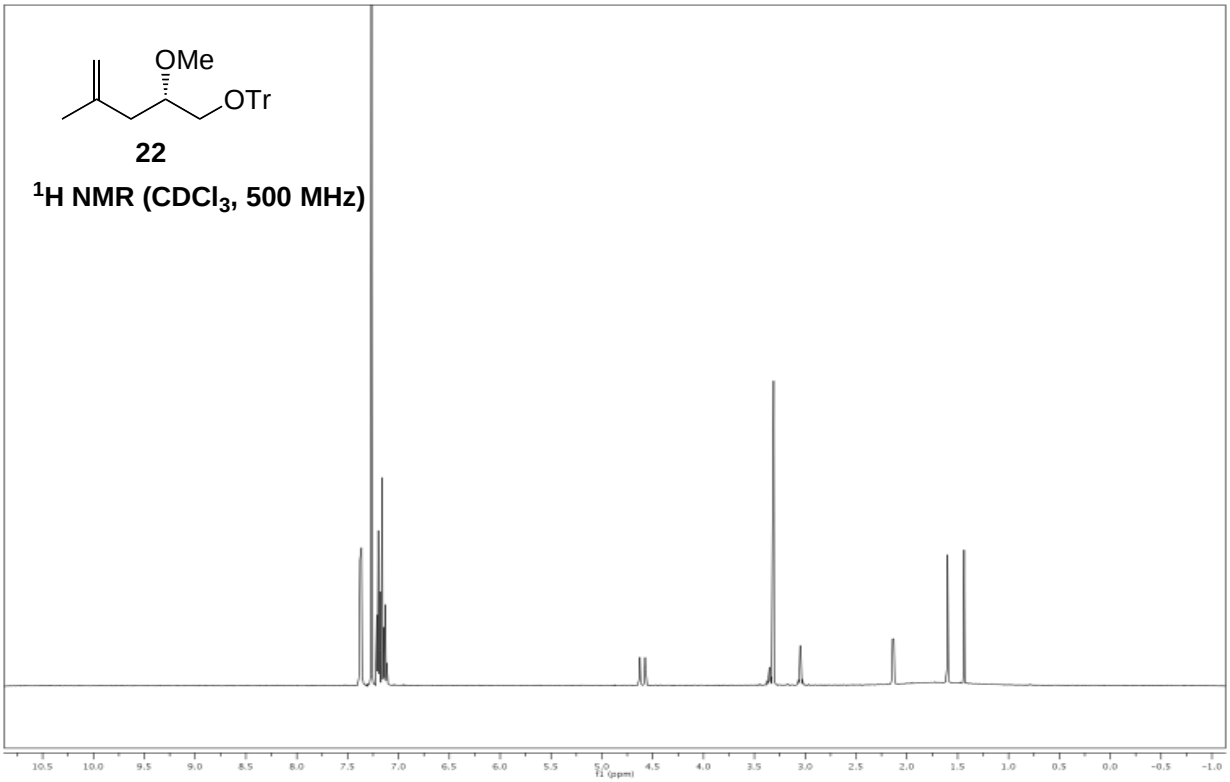
20a

^{1}H NMR ($CDCl_3$, 400 MHz)



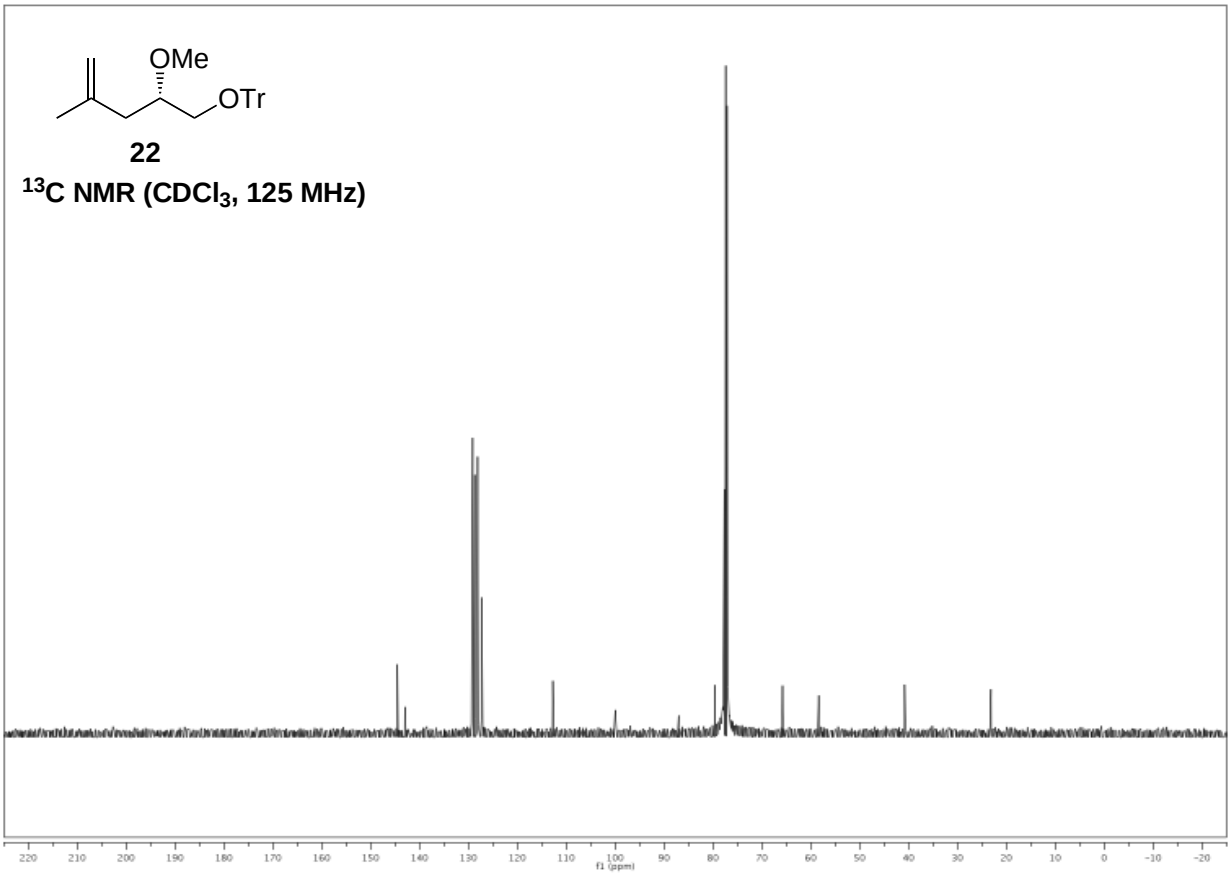
20a

^{13}C NMR ($CDCl_3$, 125 MHz)



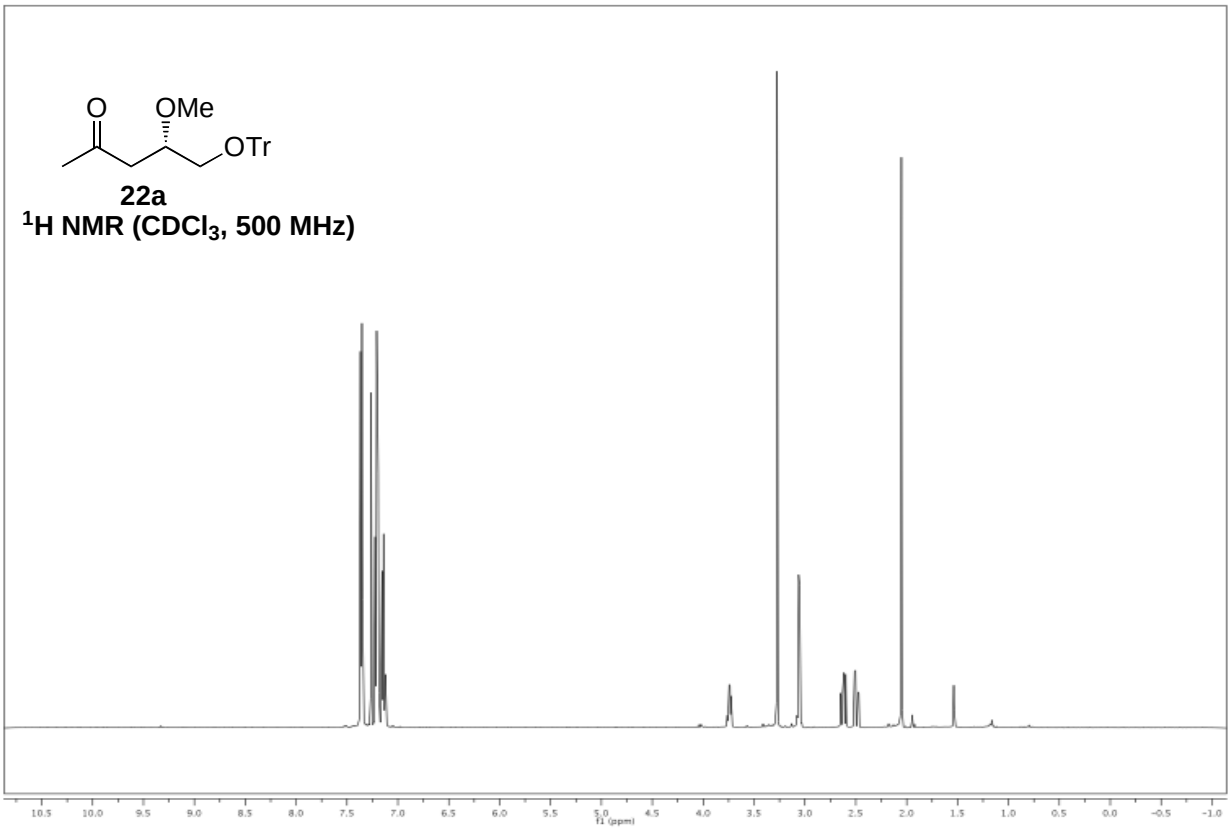
22

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



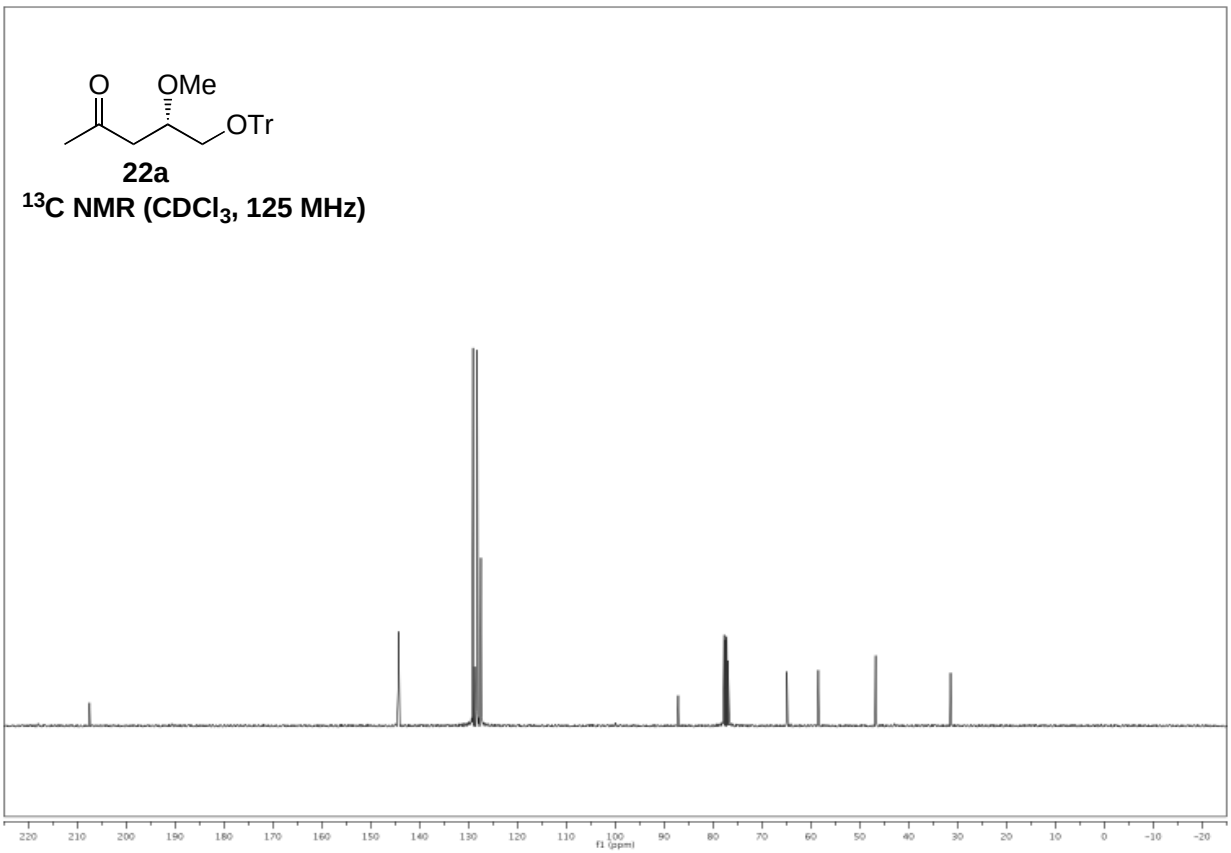
22

^{13}C NMR ($CDCl_3$, 125 MHz)



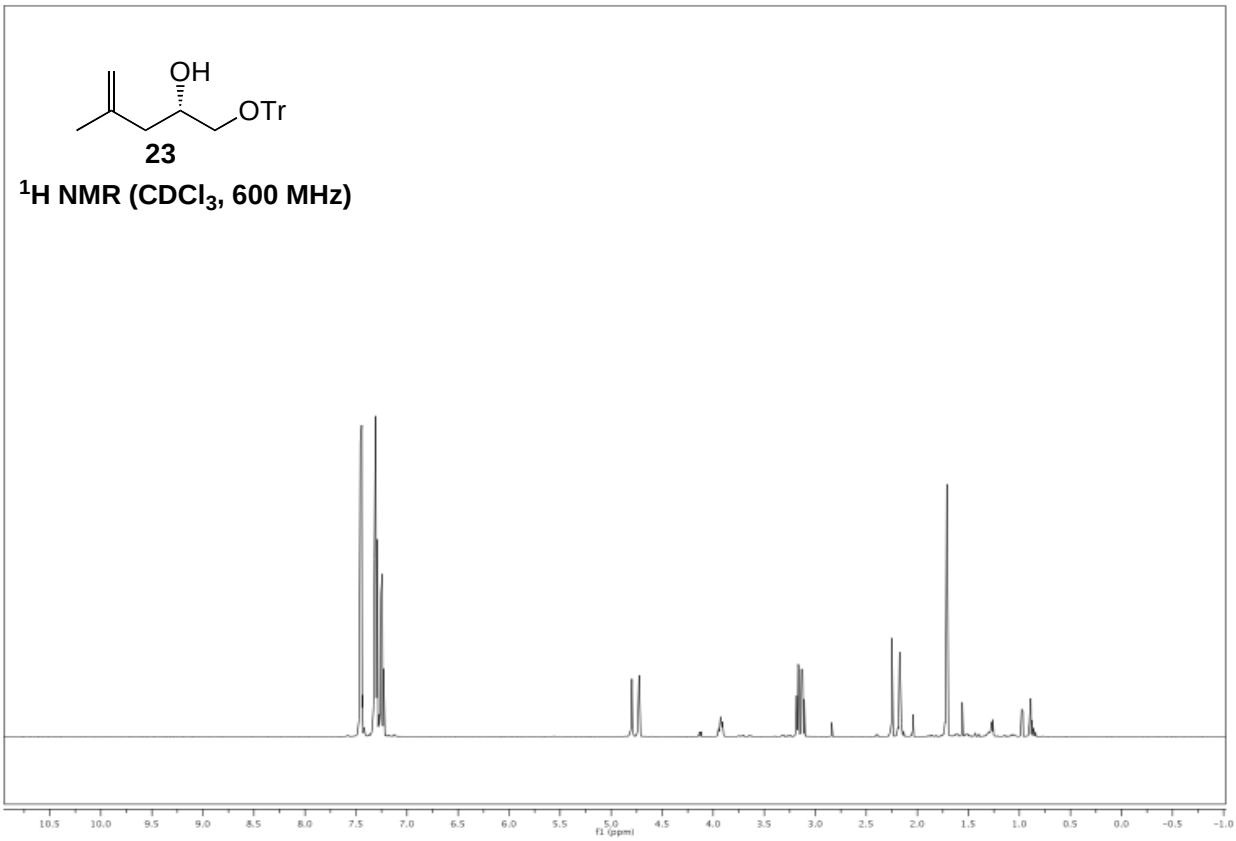
22a

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



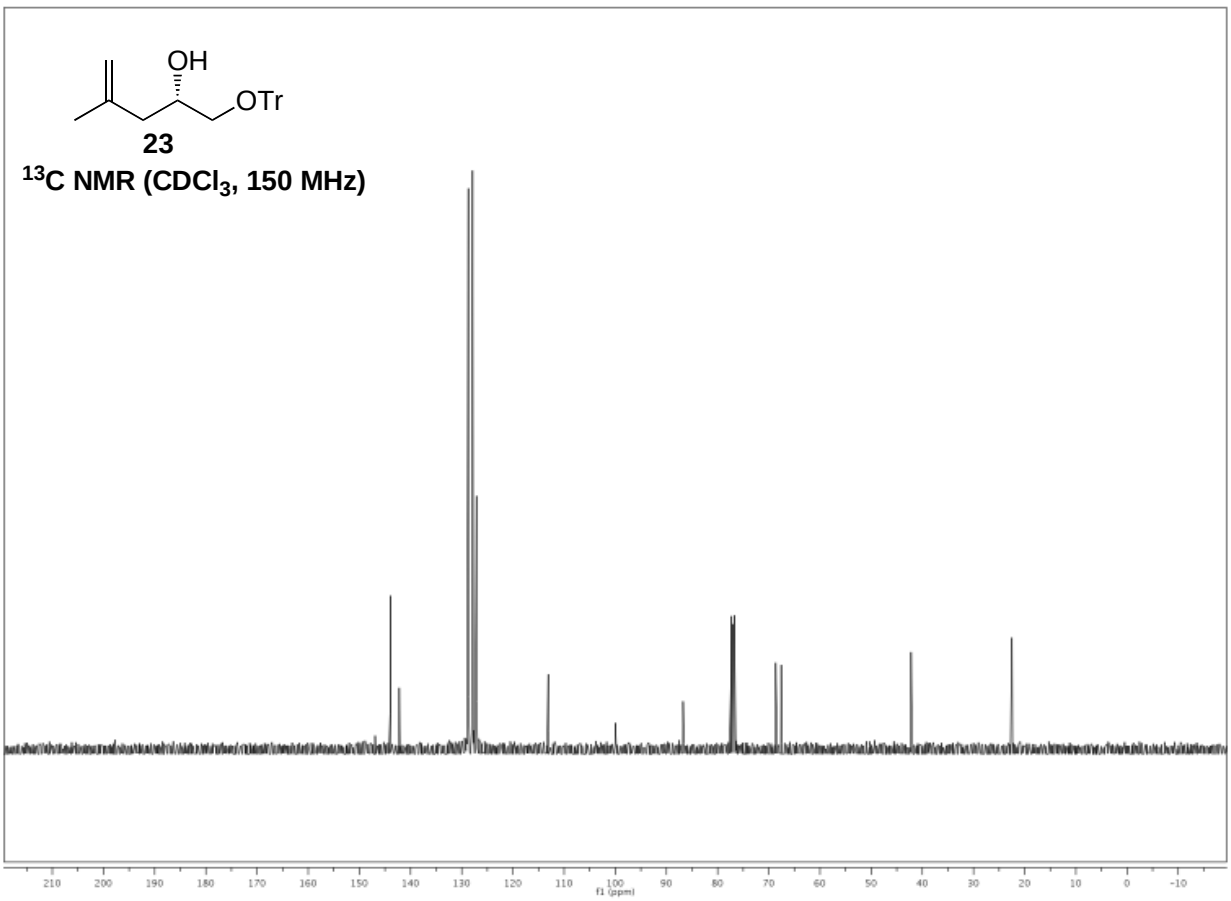
22a

^{13}C NMR ($CDCl_3$, 125 MHz)



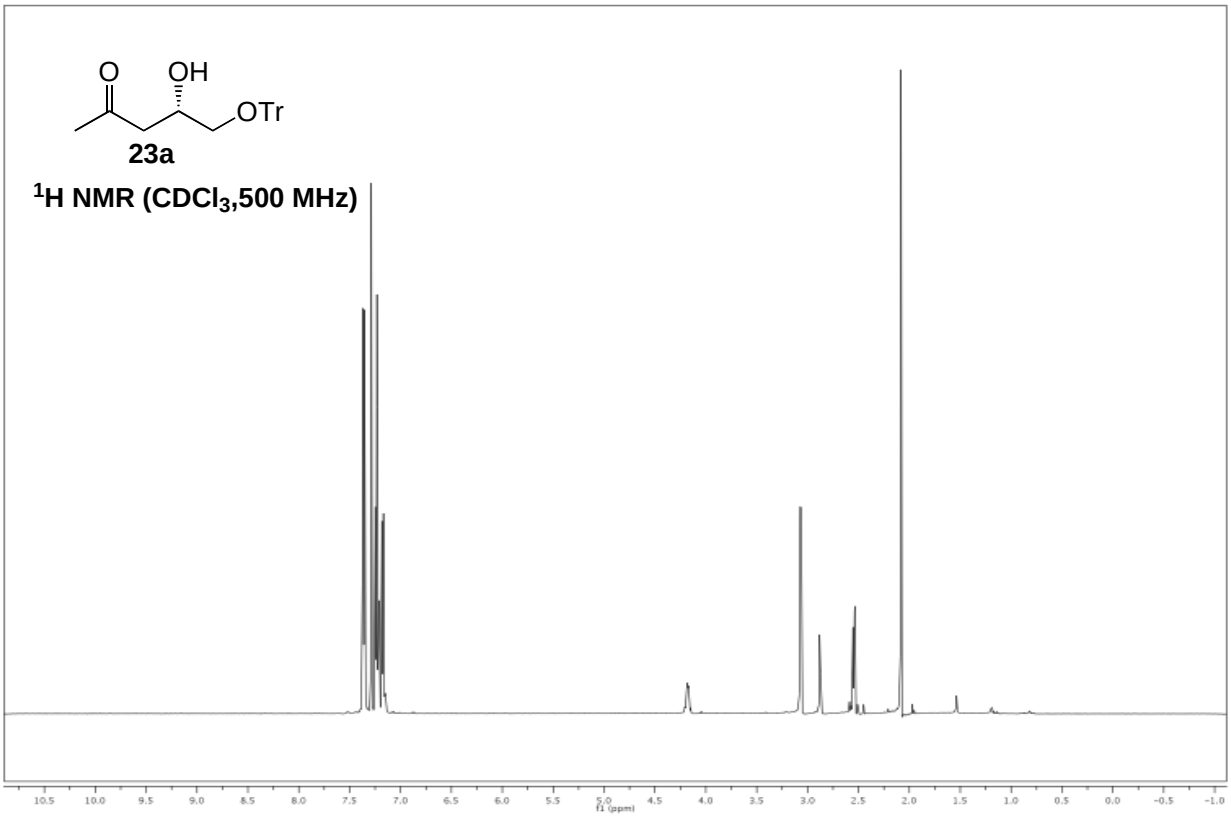
23

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



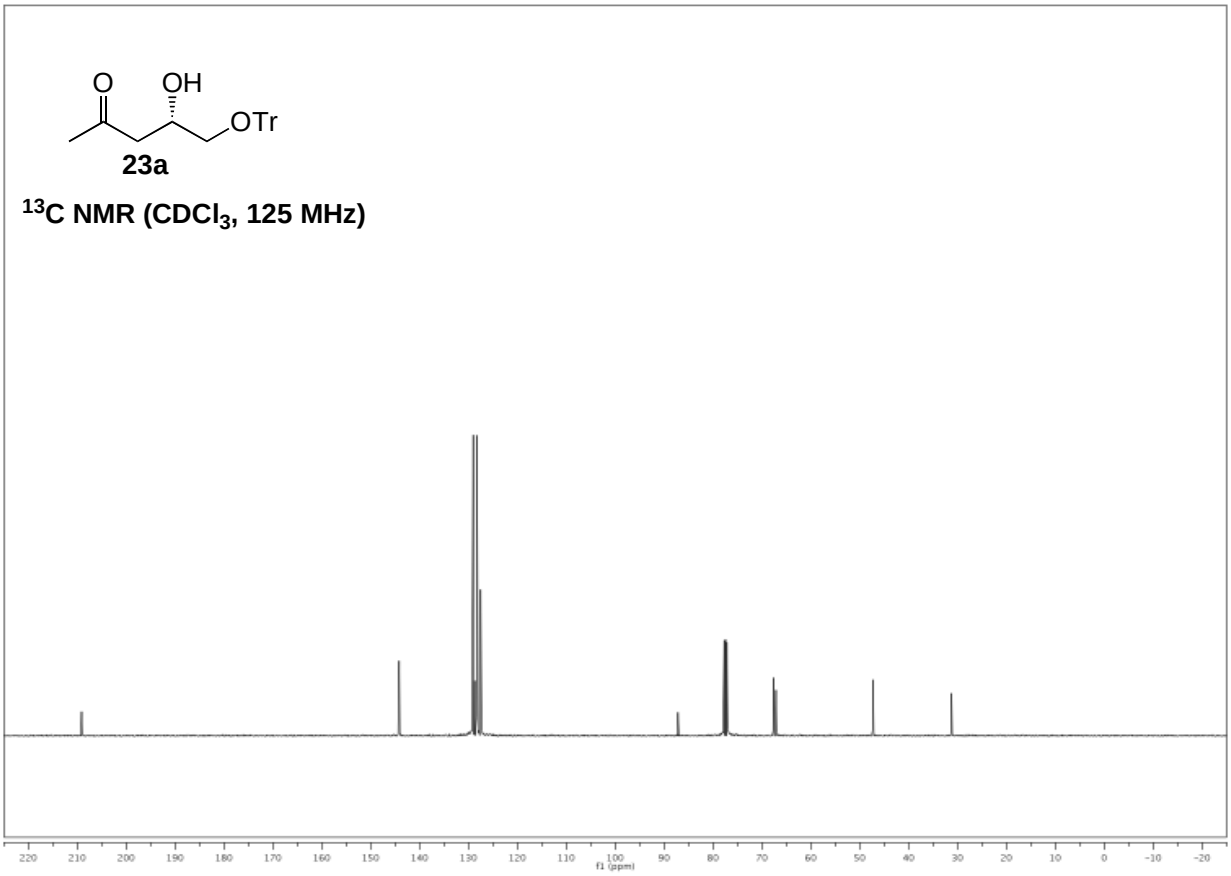
23

^{13}C NMR ($CDCl_3$, 150 MHz)



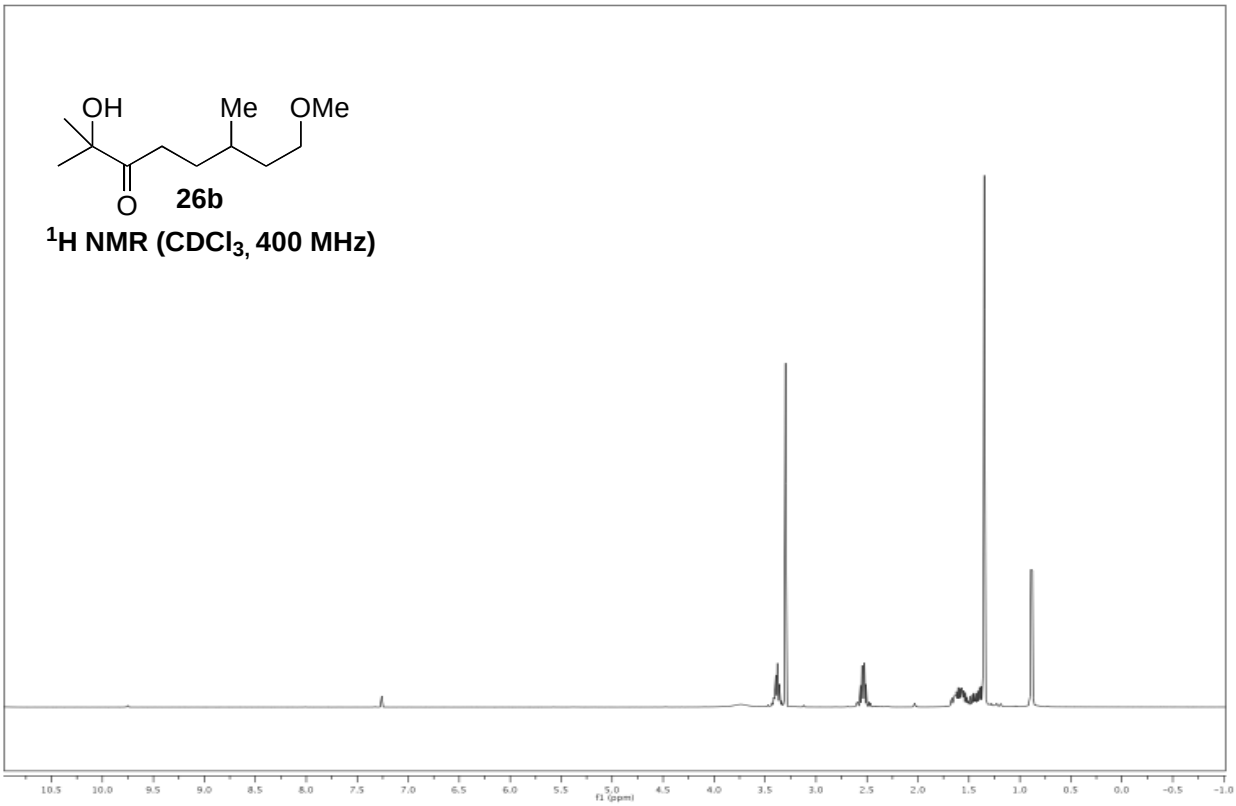
23a

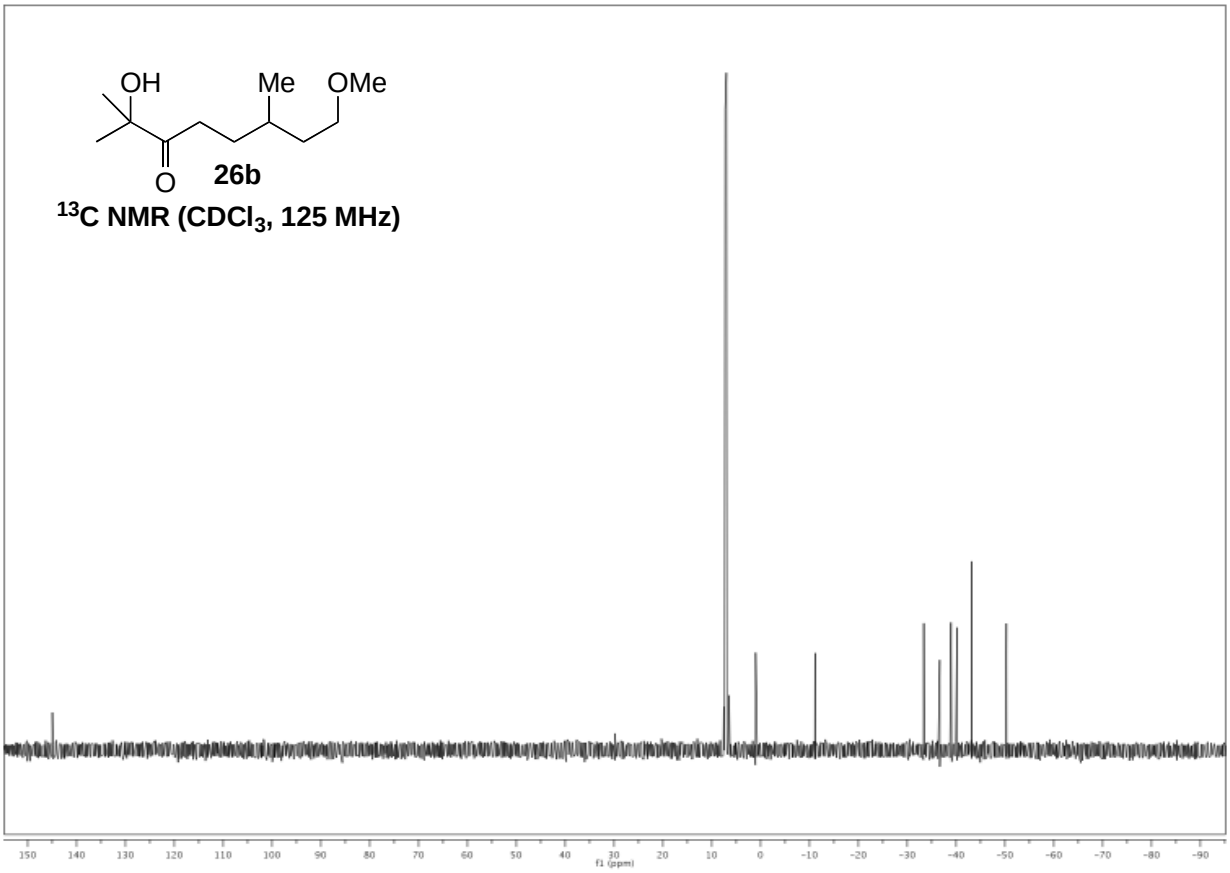
^{1}H NMR ($CDCl_3$,500 MHz)

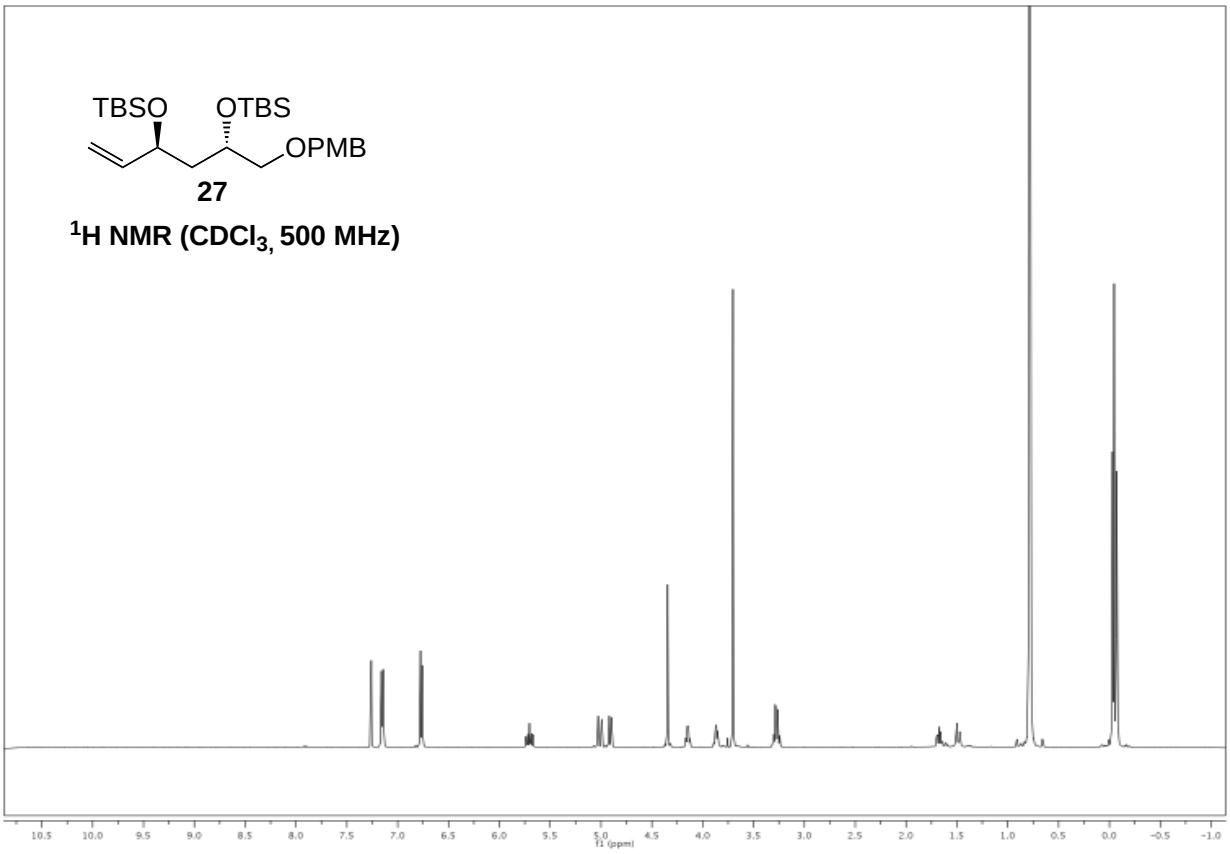


23a

^{13}C NMR ($CDCl_3$, 125 MHz)

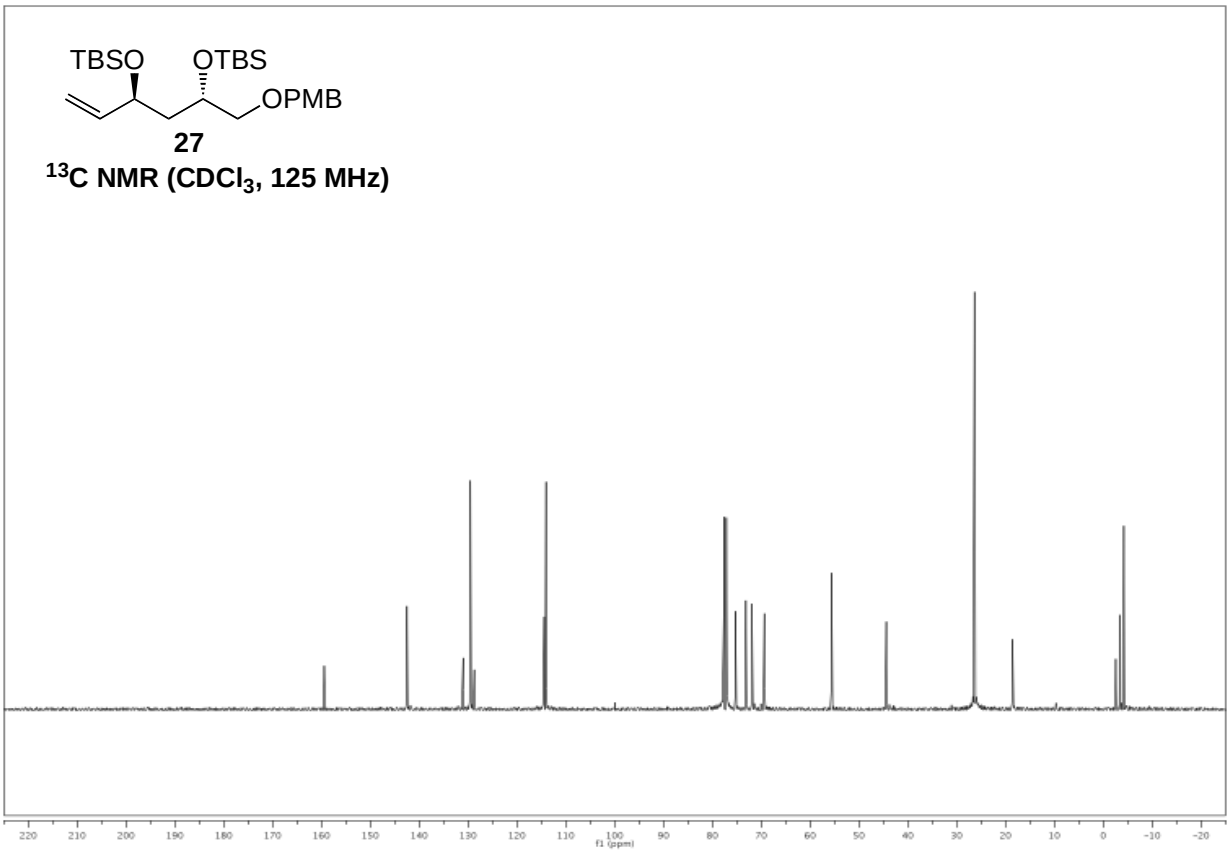

OH
Me
OMe
O
26b
^{1}H NMR (CDCl$_3$, 400 MHz)


OH
Me
OMe
O
26b
^{13}C NMR (CDCl$_3$, 125 MHz)



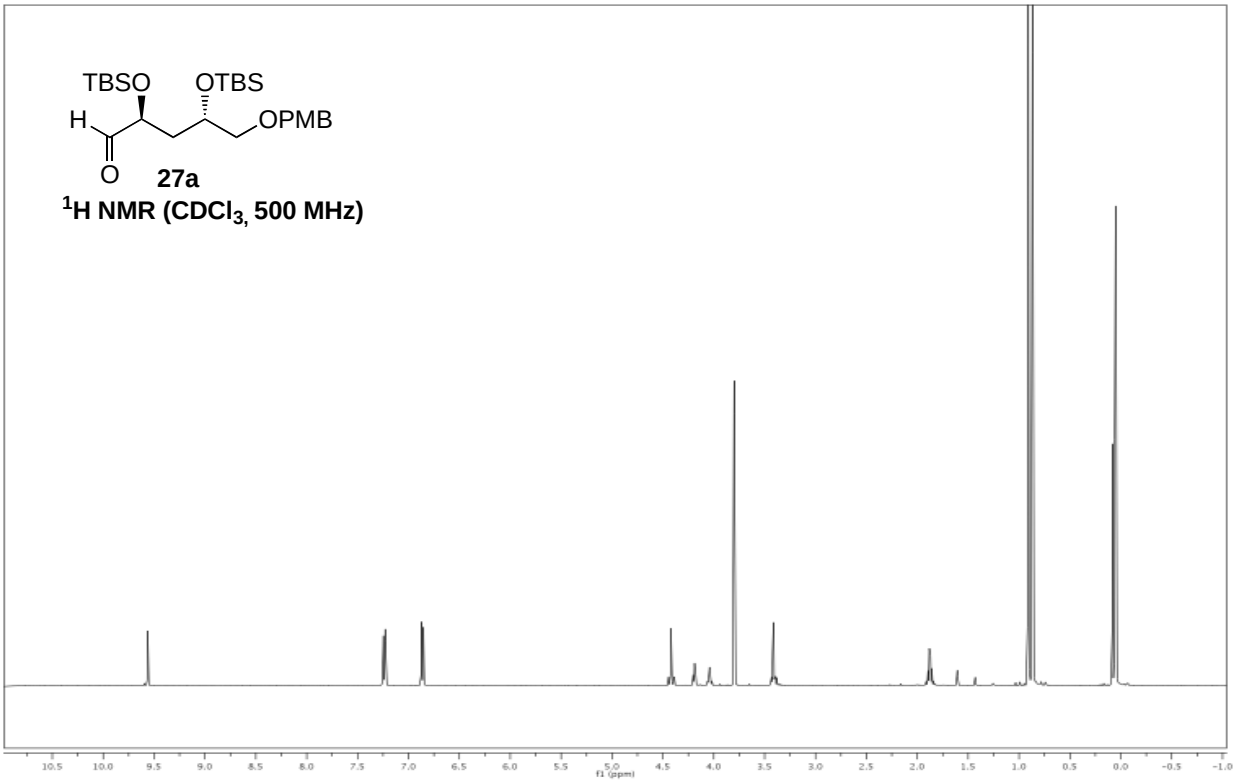
27

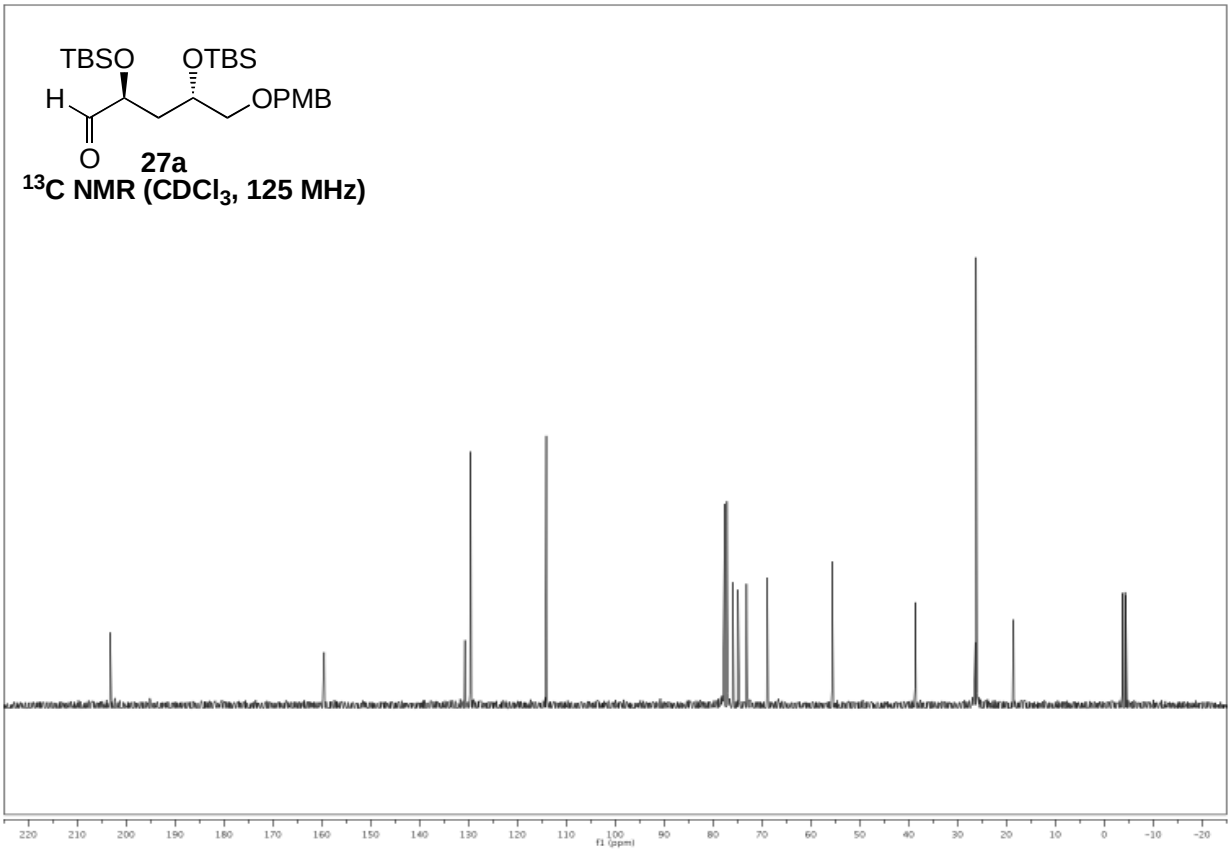
^{1}H NMR ($CDCl_3$, 500 MHz)



27

^{13}C NMR ($CDCl_3$, 125 MHz)


TBSO
OTBS
H
OPMB
O
27a
^{1}H NMR (CDCl$_3$, 500 MHz)


TBSO
OTBS
H
OPMB
O
27a
^{13}C NMR (CDCl$_3$, 125 MHz)