Supporting Information

A Concise Route to Highly-Functionalized Azetidine Precursor: Enantioselective Synthesis of Penaresidin B

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General Techniques

Unless otherwise specified, all reactions were carried out in oven-dried (>120 ˚C) glassware equipped with a magnetic stir bar and a rubber septum under a positive pressure of nitrogen or argon. Air- or moisture-sensitive reagents were transferred to the reaction vessel under positive pressure of nitrogen or argon via syringe or stainless steel cannula.Reactions were run at room temperature (20-25 °C) unless otherwise noted in the experimental procedure, and reported reaction temperatures refer to the external temperatures measured for the bath in which the reaction vessel was immersed. Heating was obtained through the use of a silicone oil bath. For reactions run below room temperature, the term "-78˚C" refers to a bath of acetone and dry ice, and "0 ˚C" refers to an ice-water bath. Intermediate temperatures were obtained by the careful addition of dry ice toan acetone bath at periodic intervals to maintain the desired temperature. "Concentration" refers to the removal of solvent using a Buchi rotary evaporator equipped with a portable vacuum pump. Removal of residual solvents was accomplished by evacuation of the container for a period of 12-20 hours using a high vacuum line maintained at 0.1-1.0 Torr.

Reagents and Solvents

Unless otherwise specified, all commercial reagents, solvents, and solutions were used without further purification with the following exceptions. Tetrahydrofuran and diethyl ether were purified *via* distillation from sodium benzophenoneketyl. Dichloromethane and toluene was purified via distillation from calcium hydride. Dichloroethane, pyridine, and triethylamine were distilled from calcium hydride under a positive pressure of nitrogen.

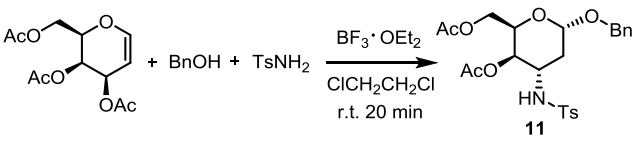
Chromatography

Analytical thin-layer chromatography (TLC) was performed using Merck 0.25 mm silica gel plates with a 254nM fluorescent indicator. Plates were developed in a covered chamber visualized with ultraviolet light, followed by staining of the plate with either p-anisaldehyde solution, ceric ammonium molybdate solution, or potassium permanganate solution, and heating. The term "flash chromatography" refers to column chromatography using Merck silica gel 60 (230-400 mesh), with a description of the eluent used noted in parenthesis following the description of purification.

Physical and Spectroscopic Data

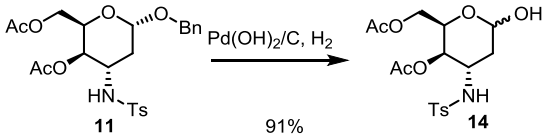
Proton and Carbon NMR spectra were measured on a Bruker ACF-300, Bruker DPX-400, Bruker AMX-500, and JEOL ECA-400nuclear magnetic resonance spectrometers. ^{1}H NMR spectra are reported as chemical shifts in parts per million (ppm) as referenced from a residual solvent peak (chloroform: δ 7.26 unless otherwise noted; methanol: δ 3.31) and coupling constants (*J*) are reported in Hertz. The reported chemical shifts are tabulated in one of the following format: multiplicity, coupling constant (s), number of protons. Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, td = triplet ofdoublets, qd = quartet of doublets, m = multiplet. Proton-decoupled ^{13}C NMR spectra are reported as chemical shifts in parts per million (ppm) as referenced to residual solvent peaks (chloroform: δ 77.0; methanol: δ49.0).Infrared spectra were measured on a Restige-21 (Shimadzu) Fourier Transform Spectrometer (FT-IR) using material applied as a thin film on a NaCl plate and are reported as wave numbers (cm^{-1}). Optical rotations were measured at 589 nm (Na-D line) on a Jasco P-2000 digital polarimeter using solutions of dichloromethane, chloroform, or methanol. All values are reported in the following format: $[\alpha]_D$ = specific rotation (concentration of the solution reported in units of 10 mg sample per 1 mL solvent, solvent used). High-resolution mass spectroscopy (HRMS) services were recorded on a Waters Q-Tofpremier™ mass spectrometer.

Procedures



Benzyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-glacopyranoside(11)[1]

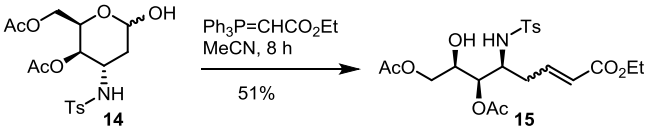
To a solution of 3,4,6-tri-*O*-acetyl-D-galactal (500 mg, 1.8 mmol) and *p*-toluenesulfonamide (340 mg, 2.0mmol, 1.1 equiv) in DCE (20 mL) was added benzyl alcohol (210 μL, 2.0 mmol, 1.1 equiv) under N_2 atmosphere. $BF_3{\cdot}OEt_2$ (500 μL, 4.0 mmol, 2.2 equiv) was then added to thismixture. The reaction mixture was stirred for 20 min at room temperature, quenched with saturated $NaHCO_3$ (30mL) and subsequently extracted with CH_2Cl_2 (3 × 50 mL). The extract was washed with water, brine, dried and concentrated, which residue was subjected to column chromatography (silica gel, hexane-EtOAc) to obtain the title compound **11** as a colourless oil (688mg, 78%): $[\alpha]^D_{20}$ = +41.6 (c = 0.5 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.28-7.42 (m, 7H), 6.06 (d, *J* = 8.0 Hz, 1H), 4.94 (d, *J* = 7.2 Hz, 1H), 4.78 (d, *J* = 2.8 Hz, 1H), 4.75 (d, *J* = 12.0Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.28 (t, *J* = 6.0 Hz, 1H), 3.99-4.10 (m, 2H), 3.63 (q, *J* = 2.8 Hz, 1H), 2.42 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.01 (dt, *J* = 19.2, 4.8 Hz, 1H), 1.45 (d, *J* = 14.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.5, 169.5, 143.5, 137.8, 136.5, 129.8, 128.7, 128.3, 128.1, 127.1, 95.7, 69.4, 67.9, 63.4, 62.9, 47.6, 28.6, 21.6, 20.8, 20.7; IR ($CHCl_3$): 3417, 1643, 1214, 1175, 1042, 665 cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{24}H_{29}NO_8SNa$ 514.1512, found 514.1516.



3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-glacopyranoside (14)

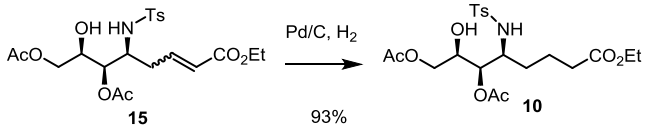
To a solution of **11** (600 mg, 1.2 mmol) in MeOH (12 mL) was added 10% $Pd(OH)_2/C$ (90 mg) under an Ar atmosphere. The resulting reaction mixture was stirred at room temperature under a H_2 atmosphere for 12 h and then filtrated through a Celite® pad and washed with EtOAc (2 × 50 mL). On removing the solvent, the residue was purified by flash column chromatography on silica gel (eluent:

n-hexane: EtOAc = 10: 1 to 2:1) to give the title compound **14** as a colourless gum (437mg, 91%): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, *J* =8.4 Hz, 2H), 7.32 (d, *J* =8.0 Hz, 2H), 6.16 (d, *J* = 8.4Hz, 1H), 5.37 (d, *J* = 15.2 Hz, 1H), 4.80 (d, *J* = 2.8 Hz, 1H), 4.51 (t, *J* = 6.0 Hz, 1H), 4.04-4.06 (m, 2H), 3.63-3.66 (m, 1H), 3.02 (t, *J* = 2.8 Hz, 1H), 2.43(s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.95-2.00 (m, 1H), 1.49 (d, *J* = 13.6 Hz, 1H); ^{13}C NMR ($CDCl_3$,100 MHz): δ 170.6, 169.5, 143.5, 137.8, 129.8, 127.1, 92.0, 67.9, 63.2, 62.9, 47.6, 28.4, 21.6, 20.8, 20.7; IR ($CHCl_3$): 3382, 1668, 1233, 1156, 653 cm^{-1}; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{23}NO_8SNa$ 424.1042, found 424.1045.



(*2R,3R,4S*)-8-ethoxy-2-hydroxy-4-((4-methylphenyl)sulfonamido)-8-oxooct-6-ene-1,3-diyl diacetate (15)[2]

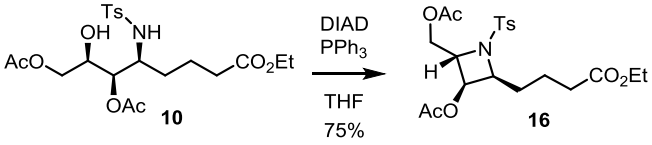
The mixture of compound **14** (400 mg, 1.0 mmol) and $EtO_2CCH{=}PPh_3$ (382mg, 1.1 mmol, 1.1 equiv.) in MeCN (10 mL) was stirred at room temperature for 7 h. After reaction was completed, the reaction mixture was loaded to column chromatography (*n*-hexane: EtOAc = 10: 1 to 2:1) to give the product as a mixture of *Z*/*E* isomers with ratio of 1/2 (240 mg, 0.51 mmol, 51%), which was used for next step directly.



(2R,3R,4S)-8-ethoxy-2-hydroxy-4-((4-methylphenyl)sulfonamido)-8-oxooctane-1,3-diyl diacetate (10)

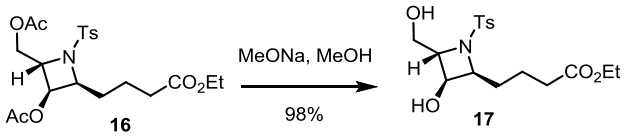
To a solution of compound **15** (471 mg, 1.0 mmol) in MeOH (10 mL) was added 10% Pd/C (60 mg) under a H_2 atmosphere. After stirring at room temperature for 12 h, the reaction mixture was filtrated through a Celite® pad. On removing the solvent, the residue was purified by flash column chromatography on silica gel (eluent, *n*-hexane: EtOAc = 10: 1 to 2:1) to give the title compound **14** as

a colourless gum (440 mg, 93%): $[\alpha]^{D}_{20}$ = +11.4 (c = 0.5 in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ7.78 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.32 (d, *J* = 8.4 Hz, 1H), 4.87-4.91(m, 1H), 4.34 (d, *J* = 3.6Hz, 1H), 4.06-4.13 (m, 3H),3.67-3.69 (m, 2H),3.31-3.37 (m, 1H), 2.43(s, 3H), 2.19-2.21 (m, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 1.38-1.43 (m, 2H), 1.22-1.27 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.2, 171.7, 170.2, 143.5, 129.6, 127.3, 127.1, 71.5,71.0, 62.9, 60.4, 55.0, 33.4, 27.6, 21.5, 21.0, 20.8, 20.7, 14.2; IR ($CHCl_3$): 3300, 1743, 1678, 1123cm^{-1}; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{21}H_{31}NO_9SNa$ 496.1617, found 496.1613.



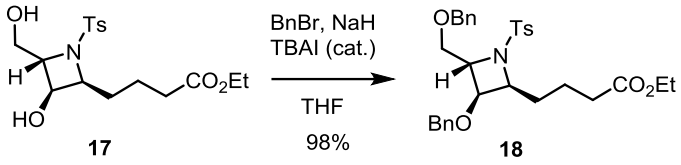
ethyl 4-((2S,3R,4S)-3-acetoxy-4-(acetoxymethyl)-1-tosylazetidin-2-yl)butanoate (16)[3]

To a solution of PPh_3 (668 mg, 2.55 mmol, 3.0 equiv.) in dry THF (8 mL), diethylazodicarboxylate (0.5 mL, 2.55 mmol, 3.0 equiv.) was added dropwise at 0 ^{o}C and the mixture was stirred for 0.5 h. A solution of the compound **10** (400 mg, 0.85 mmol, 3.0 equiv.) in dry THF (8 mL) was added slowly. The reaction mixture was warmed to room temperature over 12 h and removal of solvent was followed by flash column chromatography (eluent, *n*-hexane: EtOAc = 10: 1 to 4:1) to afford the title compound **16** as a colorless oil (290 mg, 75%):$[\alpha]^{D}_{20}$ = +35.5 (c 0.5 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 4.73-4.78 (m, 1H), 4.20 (dd, *J* = 12.0, 2.8 Hz, 1H), 4.08-4.13 (m, 2H), 3.80 (dd, *J* = 12.0, 5.2 Hz, 1H), 3.00 (dd, *J* = 12.0, 7.2 Hz, 1H), 2.84-2.89 (m, 1H), 2.45 (s, 3H), 2.24-2.28 (m, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 1.52-1.58 (m, 3H), 1.38-1.45 (m, 1H), 1.24 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.8, 170.3, 169.6, 145.1, 134.3, 129.7, 128.1, 127.1, 67.8, 63.7, 60.3, 44.2, 41.8, 33.4, 26.2, 22.6, 21.6, 20.7, 14.2; IR ($CHCl_3$): 2922, 1676, 11135, 678cm^{-1}; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{21}H_{29}NO_8SNa$ 478.1512, found 478.1510.



ethyl 4-((2S,3R,4S)-3-hydroxy-4-(hydroxymethyl)-1-tosylazetidin-2-yl)butanoate (17)

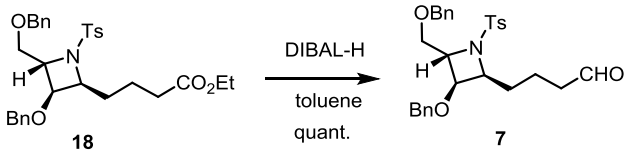
MeONa (6 mg, 0.1 mmol) was added to a solution of compound **16** (250 mg, 0.55 mmol) in MeOH (6 mL) and the mixture was stirred at room temperature for 8h. The solvent was evaporated in vacuo and the residue was purified by flashing chromatography (eluent, *n*-hexane: EtOAc = 5: 1 to 1:1) to afford the title compound **17** as a clear colourless oil (200 mg, 98%): $[\alpha]^{D}_{20}$ = +22.8 (c 0.5 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ7.67 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H),4.71 (d, *J* = 8.8 Hz, 1H), 3.99-4.05 (m, 2H), 3.76 (d, *J* = 12.4 Hz, 1H), 3.44-3.69 (m, 2H), 2.96(d, *J* = 2.0 Hz, 2H), 2.35 (s, 3H), 2.11-2.13 (m, 2H), 1.41-1.52 (m, 4H), 1.20 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.1, 143.6, 138.0, 129.7, 127.0, 60.6, 60.5, 56.7, 55.9, 52.2, 33.6, 33.3, 21.5, 20.6, 14.2; IR ($CHCl_3$): 3345, 2907, 1655, 1183, 731cm^{-1}; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{25}NO_6SNa$ 394.1300, found 394.1305.



ethyl 4-((2S,3R,4S)-3-(benzyloxy)-4-((benzyloxy)methyl)-1-tosylazetidin-2-yl)butanoate (18)

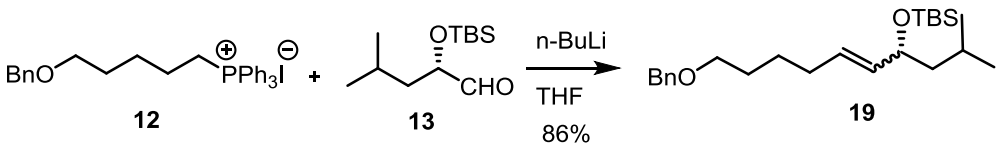
To the solution of compound **17** (160 mg, 0.43 mmol) in THF (5 mL) was added NaH (52 mg, 1.3 mmol) and TBAI (16 mg, 0.043 mmol) at 0 ^{o}C under N_2. After 10min of stirring, BnBr (153 µL, 1.3 mmol) was added slowly. The reaction was stirred for 30 min at 0°C and then allowed to warm to room temperature. After 8h, the reaction was quenched by saturated aqueous ammonium chloride and extracted with EtOAc (3 × 10 mL). The extracts were washed with aq. $NaHCO_3$ solution (40 mL), dried over Na_2SO_4 and concentrated under reduced pressure to give the residue, which was purified by column chromatography (eluent, *n*-hexane: EtOAc = 10: 1 to 4:1) to afford the title compound **18** as a colourless oil (232 mg, 98%): $[\alpha]^{D}_{20}$ = +63.1 (c 0.6 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.20-7.35 (m, 12H), 4.33-4.52 (m, 4H), 4.05-4.11 (m, 2H), 3.79-3.81 (m, 1H), 3.27 (dd, *J* = 11.6, 2.4 Hz, 1H), 3.11 (dd, *J* = 11.6, 2.4 Hz, 1H), 2.81-2.85 (m, 2H), 2.41(s, 3H), 2.06-2.09 (m, 2H), 1.34-1.39 (m, 4H), 1.25 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.0, 143.3, 137.8, 137.6, 129.6, 128.6, 128.5, 128.4, 127.8, 127.7, 127.6, 127.5, 127.4, 73.3, 69.5, 60.3, 59.1, 56.2, 55.7, 48.5,

33.6, 28.1, 21.5, 21.4, 14.2; IR ($CHCl_3$): 2875, 1705, 1068, 718 cm^{-1}; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{31}H_{37}NO_6SNa$ 574.2239, found 574.2243.



4-((2S,3R,4S)-3-(benzyloxy)-4-((benzyloxy)methyl)-1-tosylazetidin-2-yl)butanal (7)

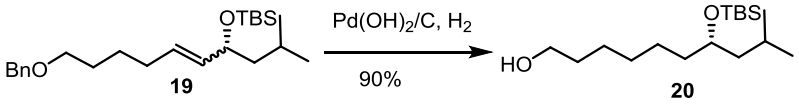
To a solution of ethyl ester **18** (200 mg, 0.36 mmol) in anhydrous toluene (5 mL) was added dropwise DIBAL-H (0.43 mL, 0.43 mmol, 1M in toluene, 1.2 equiv.) at –78 °C under Ar atmosphere. After 2 h, MeOH (1 mL) was added dropwise followed by EtOAc (5 mL) and sodium potassium tartrate (20%-H_2O, 5 mL) at –78 °C. The mixture was stirred for 1 h at room temperature before extracting with EtOAc (3 × 10 mL). The organic layers were washed with brine and dried over Na_2SO_4. Filtration and evaporation of the solvent under reduced pressure *in vacuo* gave the azetidine core **7**, which was used for next step directly without any purification. $[\alpha]^D_{20}$ = +53.2 (c = 0.44, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 9.56 (t, *J* = 1.6 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.21-7.32 (m, 12H), 4.38-4.49 (m, 4H), 3.78-3.81 (m, 1H), 3.29 (dd, *J* = 11.2, 2.4 Hz, 1H), 3.15 (dd, *J* = 11.2, 2.4 Hz, 1H), 2.81-2.85 (m, 2H), 2.41 (s, 3H), 2.17-2.19 (m, 2H), 1.31-1.45 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 201.7, 143.4, 137.8, 137.7, 137.6, 129.7, 128.6, 128.4, 127.9, 127.8, 127.7, 127.6, 127.4, 73.3, 69.4, 59.1, 56.1, 48.5, 43.1, 28.1, 21.5, 18.6, 14.2; IR ($CHCl_3$): 3087, 2966, 2868, 1599, 1497, 1455, 1335, 1207, 1154, 1093, 1043, 914, 815, 738, 699, 680 cm^{-1}; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{29}H_{33}NO_5SNa$ 530.1977, found 530.2001.



((10-(benzyloxy)-2-methyldec-5-en-4-yl)oxy)(tert-butyl)dimethylsilane(19)

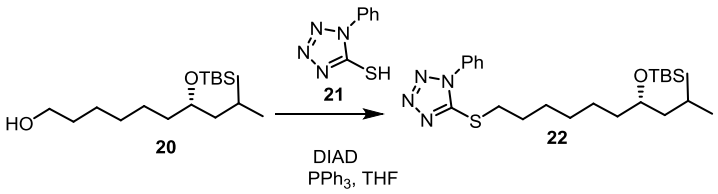
To a solution of Wittig salt **12** (prepared from pentane-l,5-diol *via* 3 steps)[4] (800mg, 1.4 mmol, 1.1 equiv.) in THF (5 mL) at 0°C was added nBuLi (1.7 M in THF, 0.82 mL, 1.4 mmol, 1.1 equiv.). The reaction was warmed up to room temperature and stirred for 0.5h, then cooled to -78 °C and a solution

of the aldehyde **13** (prepared from L-leucine *via* 4 steps)[5] (300 mg, 1.28 mmol, 1.0 equiv.) in THF (2 mL) was added slowly and stirred for 0.5 h. The reaction mixture was warmed to room temperature over 12 h, then the reaction mixture was quenched with satd. aq. NH_4Cl (20 mL) and extracted with EtOAc (3 × 20 mL). The combined extracts were washed with water, brine, dried over Na_2SO_4 and concentrated *in vacuo* to give the crude product. The residue was purified by column chromatography (eluent, *n*-hexane: EtOAc = 50: 1 to 10:1) to give the title compound **19** as colourless liquid (430 mg, 86%): ^{1}H NMR ($CDCl_3$, 400 MHz): δ7.28-7.35 (m, 5H), 5.27-5.36 (m, 2H), 4.50 (s, 2H), 4.44-4.49 (m, 1H), 3.48 (t, *J* = 6.4 Hz, 2H), 2.03-2.09 (m, 2H), 1.60-1.70 (m, 3H), 1.43-1.50 (m, 3H), 1.11-1.17 (m, 1H), 0.84-0.95 (m, 15H), 0.03 (d, *J* = 8.0 Hz, 6H); ^{13}C NMR($CDCl_3$, 100 MHz): δ138.6, 134.8, 128.4, 128.3, 127.6, 127.5, 72.9, 70.3, 67.0, 47.8, 29.5, 27.6, 26.3, 25.9, 25.8, 24.1, 23.4, 22.3, 18.2, -4.1, -4.8; IR ($CHCl_3$): 2974, 2865, 1460, 1125, 729cm^{-1};HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{24}H_{42}O_2SiNa$ 413.2852, found 413.2854.



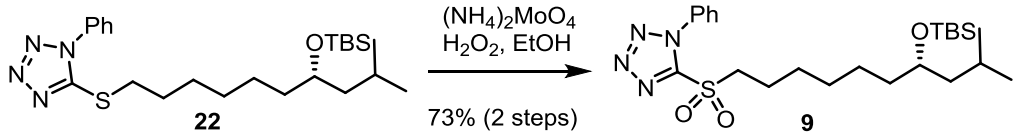
(S)-7-((tert-butyldimethylsilyl)oxy)-9-methyldecan-1-ol (20)

To a solution of compound **19** (390 mg, 1.0 mmol) in MeOH (10 mL) was added10% $Pd(OH)_2/C$ (80 mg) under a H_2 atmosphere. After stirring at room temperature for 18 h, the reaction mixture was filtrated through a Celite® pad. On removing the solvent, the residue was purified by flash column chromatography on silica gel (eluent, *n*-hexane: EtOAc = 10: 1 to 2:1) to give the title compound **20** as a colourless gum (272 mg, 90%): $[\alpha]^D_{20}$ = -55.6 (c 1.0 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.67-3.70 (m, 1H), 3.63 (t, *J* = 6.8 Hz, 2H), 1.63-1.70 (m, 1H), 1.53-1.59 (m, 2H), 1.20-1.41 (m, 11H), 0.86-0.88 (m, 15H), 0.05 (s, 6H); ^{13}C NMR($CDCl_3$, 100 MHz): δ70.5, 63.0, 46.6, 37.5, 32.8, 29.7, 26.0, 25.8, 25.1, 24.4, 23.2, 22.8, 18.1, -4.2, -4.4;IR ($CHCl_3$): 3405, 2976, 1485, 1055, 744, 693 cm^{-1}; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{17}H_{38}O_2SiNa$ 325.2539, found 325.2540.



(S)-5-((7-((tert-butyldimethylsilyl)oxy)-9-methyldecyl)thio)-1-phenyl-1H-tetrazole(22)[6]

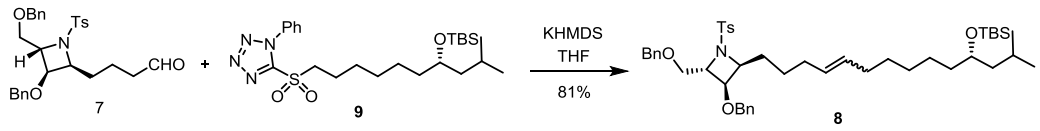
To a stirred solution of alcohol **20** (250 mg, 0.83mmol) in anhydrous THF (5 mL) were added N-phenyltetrazolethiol **21** (667 mg, 0.91 mmol, 1.1 equiv.) and triphenylphosphine (981 mg, 0.91 mmol, 1.1 equiv.). The resulting mixture was cooled at 0 °C and diethylazodicarboxylate (0.58 mL, 3.74 mmol) was added dropwise under an atmosphere of nitrogen. The reaction mixture was allowed to warm to room temperature gradually and stirred further for 4 h. Evaporation of the solvent under reduced pressure afforded a crude product that was purified by columnchromatography with use of 10% EtOAc/hexane (v/v) as the eluent to afford the sulfide **22** (310mg, 0.67 mmol) in 81% yield as a gum liquid. TLC: Rf = 0.6 (25% EtOAc/hexane). $[\alpha]^{D}_{20}$ = -48.4 (c 1.5 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51-7.59 (m, 5H), 3.66-3.69 (m, 1H), 3.39 (t, *J* = 7.2 Hz, 2H), 1.78-1.85 (m, 2H), 1.62-1.69 (m, 1H), 1.24-1.45 (m, 10H), 0.86-0.91 (m, 15H), 0.04 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.5, 133.8, 130.1, 129.8, 123.9, 70.4, 46.6, 37.4, 33.4, 29.3, 29.1, 28.7, 26.0, 24.9, 24.4, 23.2, 22.8, 18.1, -4.2, -4.4; IR ($CHCl_3$): 3044, 2953, 2867, 1483, 1106, 759 cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{24}H_{42}N_4OSSiNa$ 485.2746, found 485.2749.



(S)-5-((7-((tert-butyldimethylsilyl)oxy)-9-methyldecyl)thio)-1-phenyl-1H-tetrazole (9) [6]

A solution of sulfide (300 mg, 0.65 mmol, 1.0 equiv) and $(NH_4)_2MoO_4$ (161 mg, 0.13 mmol, 0.2 equiv) in EtOH (13 mL) was cooled to 0°C and H_2O_2 (35 mass%) (6.5 ml, 6.5 mmol, 10 equiv) was added dropwise within 10 min. The resulting mixture was stirred at 0°C for additional 30 min before it was allowed to warm to room temperature. After 12 h at room temperature, water (20 mL) was added and the resulting layers were separated. The aqueous layer was extracted with EtOAc (3 x 50 mL) and the combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, filtered and the

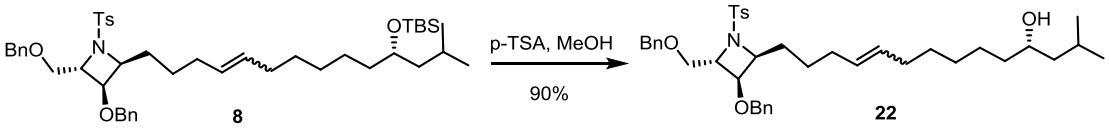
solvents were evaporated under reduced pressure. The residue was purified by flash column chromatography (eluent, *n*-hexane: EtOAc = 10: 1 to 5:1) yielding the desired sulfone (273mg, 0.6 mmol, 91 % yield) as a colorless viscose oil. TLC: R_f = 0.55 (25% EtOAc/hexane). $[\alpha]^{D}_{20}$ = -23.4 (c 0.9 $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ7.58-7.70 (m, 5H), 3.68-3.75 (m, 3H), 1.92-1.99 (m, 2H), 1.63-1.69 (m, 1H), 1.20-1.50 (m, 10H), 0.86-0.90 (m, 15H), 0.04 (s, 6H); ^{13}C NMR($CDCl_3$, 100 MHz): δ153.5, 133.1, 131.5, 129.7, 125.1, 70.4, 56.0, 46.5, 37.3, 29.3, 28.2, 26.0, 24.7, 24.5, 23.2, 22.8, 22.0, 18.1, -4.2, -4.4; IR ($CHCl_3$): 3018, 2956, 2860, 1635, 1494, 1143, 768 cm^{-1}; HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{24}H_{42}N_4O_3SSiNa$ 517.2645, found 517.2647.



(2S,3R,4S)-3-(benzyloxy)-2-((benzyloxy)methyl)-4-((S)-11-((tert-butyldimethylsilyl)oxy)-13-methyltetradec-4-en-1-yl)-1-tosylazetidine (8)[6]

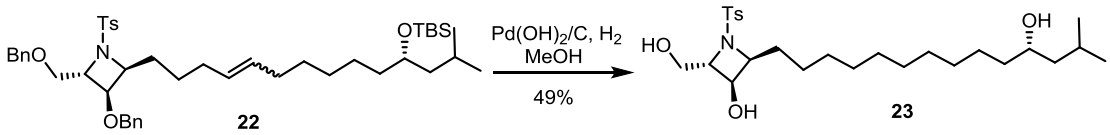
To a stirred solution of sulfone **9** (468 mg, 1.24 mmol, 1.5 equiv.) in anhydrous THF (3 mL) cooled at -78 ^{o}C was added KHMDS (1 M in toluene, 0.4 mL, 0.4 mmol, 2.4 equiv.) under nitrogen atmosphere and the reaction mixture was stirred at the same temperature for 1 h. A solution of aldehyde **7** (0.16 mmol) in anhydrous THF (1 mL) was added dropwise *via* a syringe over a period of 10 min. The reaction mixture was stirred for 2 h at -78 ^{o}C and then water (10 mL) was added. The clear layers were separated and the aqueous phase was extracted once with EtOAc (3 × 10 mL). The combined organic extracts were successively washed with water and brine and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a crude product that was purified by flash column chromatography (eluent, *n*-hexane: EtOAc = 10: 1 to 5:1) yielding the desired alkene (100mg, 0.6 mmol, 81 % yield) as a colorless viscose oil. TLC: R_f = 0.5 (25% EtOAc/hexane).^{1}H NMR ($CDCl_3$, 400 MHz): δ7.73 (d, *J* = 8.0Hz, 2H), 7.20-7.34 (m, 12H), 5.25-5.30 (m, 1H), 5.10-5.13 (m, 1H), 4.39-4.51 (m, 3H), 4.26-4.28 (m, 1H), 3.76-3.81 (m, 1H), 3.66-3.72 (m, 1H), 3.27 (dd, *J* = 11.6, 2.0 Hz, 1H), 3.12 (dd, *J* = 11.6, 1.6 Hz, 1H), 2.81 (d, *J* = 5.2 Hz, 2H), 2.41 (s, 3H), 1.91-1.93 (m, 2H), 1.67-1.77 (m, 3H), 1.30-1.41 (m, 12H), 1.22-1.24 (m, 2H), 0.86-0.88 (m, 15H), 0.04 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ143.2, 138.0, 137.8, 137.7, 131.0, 129.5, 129.2, 128.7, 128.5, 128.4, 128.3, 127.8,

127.7, 127.4, 73.3, 70.6, 69.6, 59.4, 56.2, 55.9, 48.5, 46.6, 37.6, 32.6, 32.1, 29.8, 29.7, 29.6, 28.2, 26.0, 25.0, 24.5, 23.3, 22.8, 21.5, 18.2, -4.2, -4.4; IR ($CHCl_3$): 2944, 2823, 1446, 1235, 1178, 1082, 690 cm^{-1}; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{46}H_{69}NO_5SSiNa$ 798.4563, found 798.4566.



(S)-14-((2S,3R,4S)-3-(benzyloxy)-4-((benzyloxy)methyl)-1-tosylazetidin-2-yl)-2-methyltetradec-10-en-4-ol (22)[7]

To a stirred solution of compound **8** (80 mg, 0.1mmol) in MeOH (2 mL) cooled at 0 ^oC was added *p*-TSA (2 mg, 0.01 mmol, 0.1 equiv.). The reaction mixture was allowed to warm to room temperature gradually and stirred further until no remaining starting material could be detected by TLC (ca. 10 h). The reaction mixture was diluted with EtOAc (2mL) and an excess of aqueous saturated $NaHCO_3$ solution was added dropwise. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic extracts were successively washed with brine and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a crude product that was that was purified by flash column chromatography (eluent: *n*-hexane: EtOAc = 10: 1 to 5:1) to obtain the desired product **22** (58 mg, 0.09 mmol, 90 % yield) as a colorless viscose oil. TLC: R_f = 0.3 (30% EtOAc/hexane).^{1}H NMR ($CDCl_3$, 400 MHz): δ7.73 (d, *J* = 7.6Hz, 2H), 7.20-7.36 (m, 12H), 5.08-5.28 (m, 2H), 4.27-4.50 (m, 4H), 3.75-3.78 (m, 1H), 3.58-3.63 (m, 1H), 3.29 (dd, *J* = 11.2, 1.6Hz, 1H), 3.15(dd, *J* = 11.6, 2.0 Hz, 1H), 2.81-2.83 (m, 2H), 2.41 (s, 3H), 1.93-1.94 (m, 2H), 1.74-1.80 (m, 3H), 1.11-1.58 (m, 15H), 0.91 (dd, *J* = 12.0, 5.6Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.2, 138.0, 137.8, 137.6, 131.0, 129.5, 129.3, 128.5, 128.4, 128.3, 127.8, 127.7, 127.4, 73.3, 69.9, 69.6, 59.4, 56.2, 55.9, 48.5, 46.8, 38.1, 32.5, 32.1, 29.6, 29.3, 28.2, 26.0, 25.5, 24.7, 23.5, 22.1, 21.5; IR ($CHCl_3$): 3463, 3006, 2879, 1457, 1368, 1099, 698 cm^{-1}; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{40}H_{55}NO_5SNa$ 684.3699, found 684.3703.



(2S,3R,4S)-2-((S)-11-hydroxy-13-methyltetradecyl)-4-(hydroxymethyl)-1-tosylazetidin-3-ol (23) [7]

To a solution of compound **22** (45 mg, 0.07 mmol) in MeOH (4 mL) was added 10% $Pd(OH)_2/C$ (10 mg) under a H_2 atmosphere. After stirring at room temperature for 36 h, the reaction mixture was filtrated through a Celite® pad. On removing the solvent, the residue was purified by flash column chromatography on silica gel (eluent, *n*-hexane: EtOAc = 4: 1 to 1:1) to give the title compound **23** as a colourless gum (16mg,49%). TLC: R_f = 0.2 (60% EtOAc/hexane). $[\alpha]^D_{20}$ = +43.7 (c 0.35 $CHCl_3$);^{1}H NMR ($CDCl_3$, 400 MHz): δ7.81 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.75 (d, *J* = 9.6Hz, 1H), 4.09 (dd, *J* = 12.0, 1.6 Hz, 1H), 3.97-4.07 (m, 1H),3.91 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.80 (d, *J* = 7.6 Hz, 1H), 3.67-3.73 (m, 2H), 3.27 (br, 1H), 2.46(s, 3H), 1.76-1.83 (m, 2H), 1.30-1.45 (m, 22H), 0.96 (d, *J* = 5.2 Hz, 3H), 0.94(d, *J* = 4.8 Hz, 3H); ^{13}C NMR($CDCl_3$, 100 MHz): δ 143.4, 138.2, 129.7, 127.1, 73.4, 70.1, 64.5, 60.9, 54.4, 46.9, 38.1, 33.1, 29.7, 29.5, 29.4, 29.2, 29.1, 28.9, 25.6, 25.5, 24.7, 23.5, 22.1, 21.5;IR ($CHCl_3$): 3488, 2905, 1449, 1366, 1156, 723 cm^{-1}; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{26}H_{43}NO_5SNa$ 504.2760, found 504.2761.

Literature

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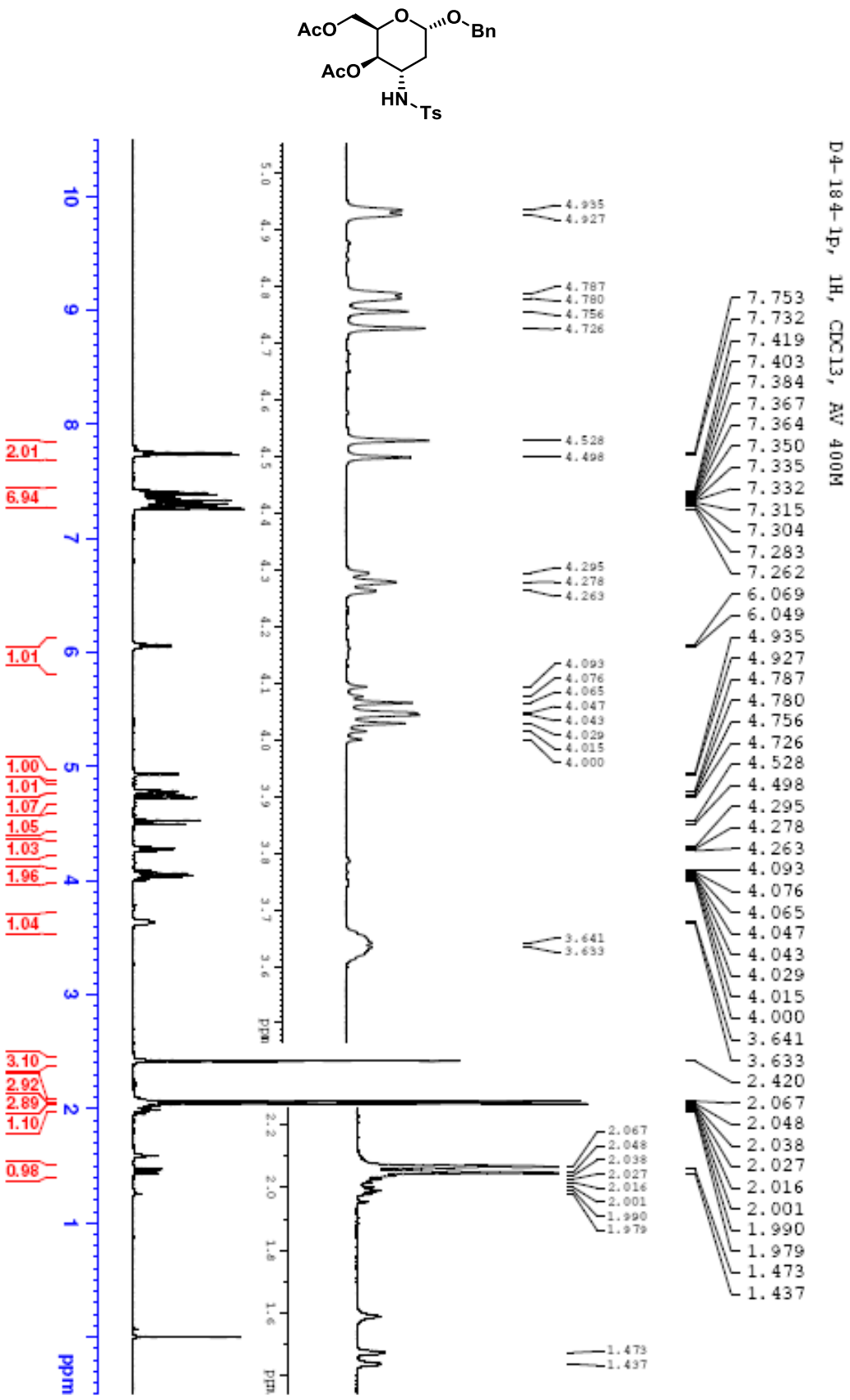
NMR Spectra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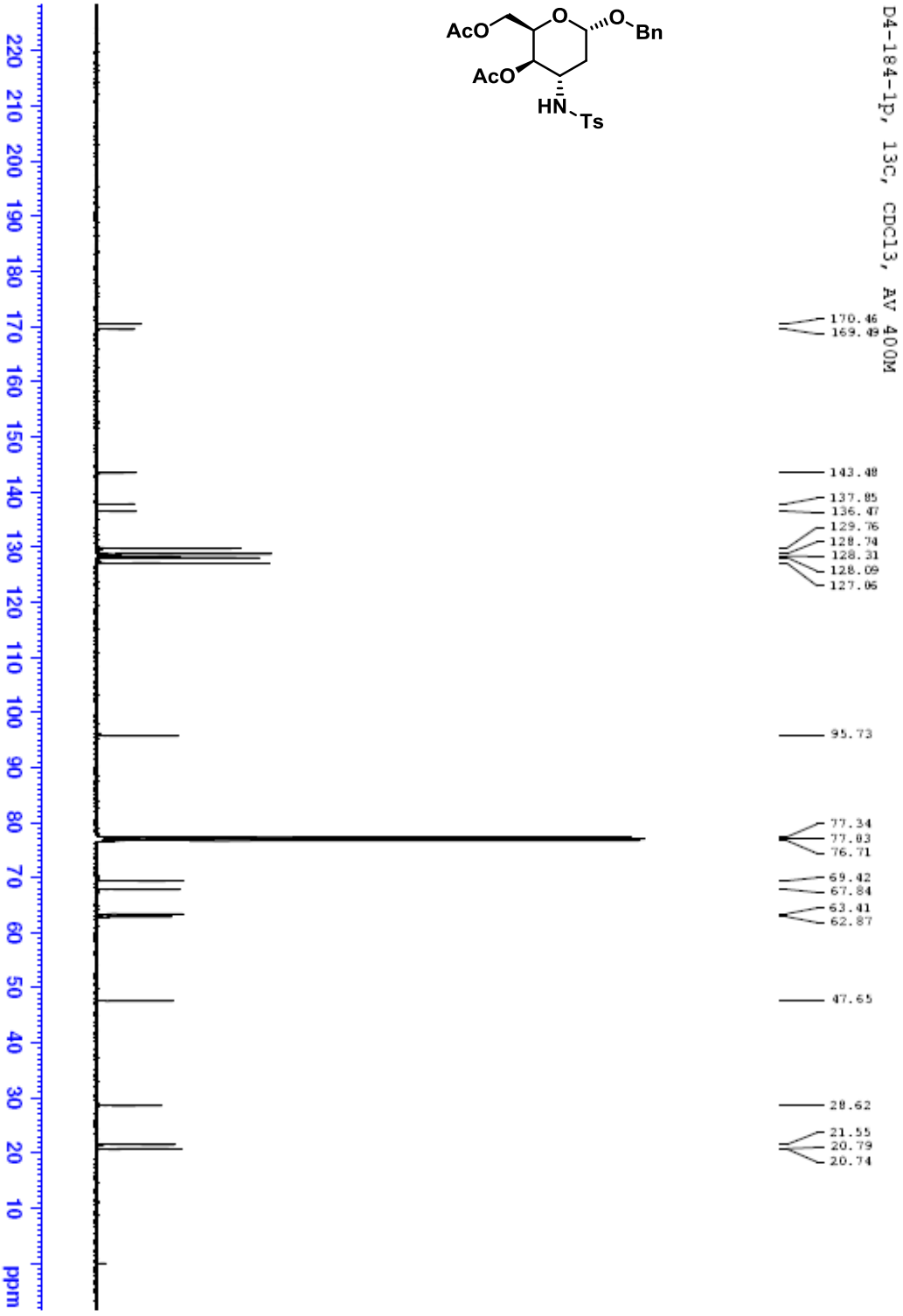
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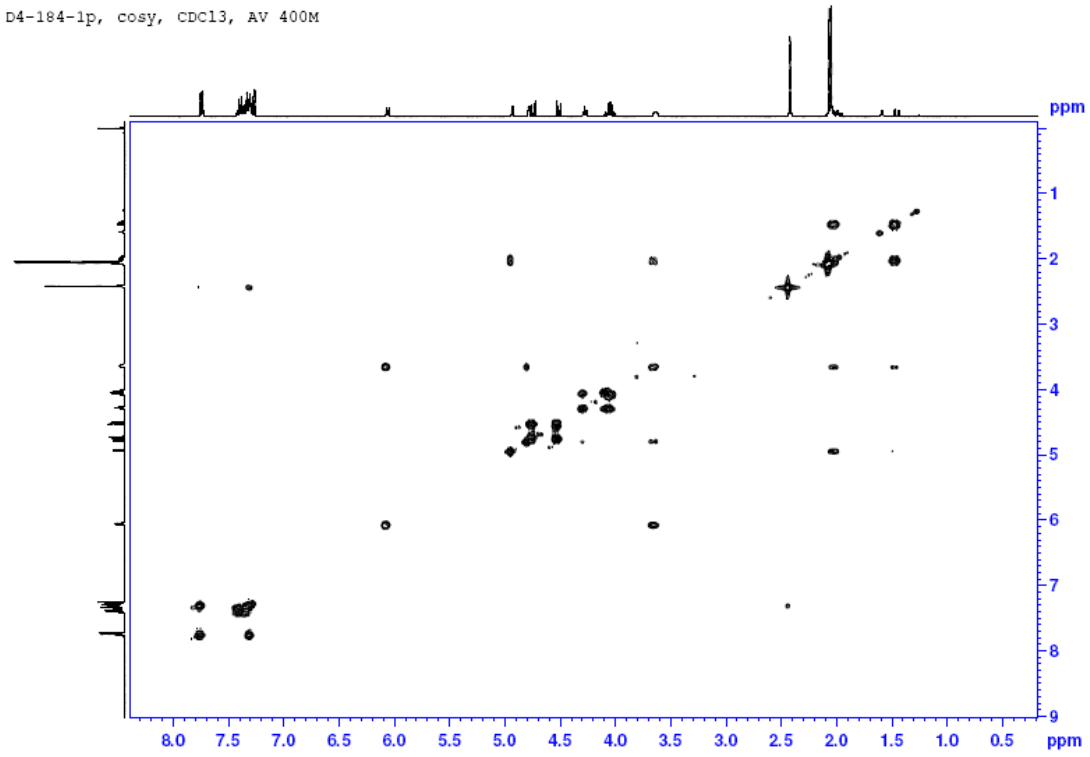
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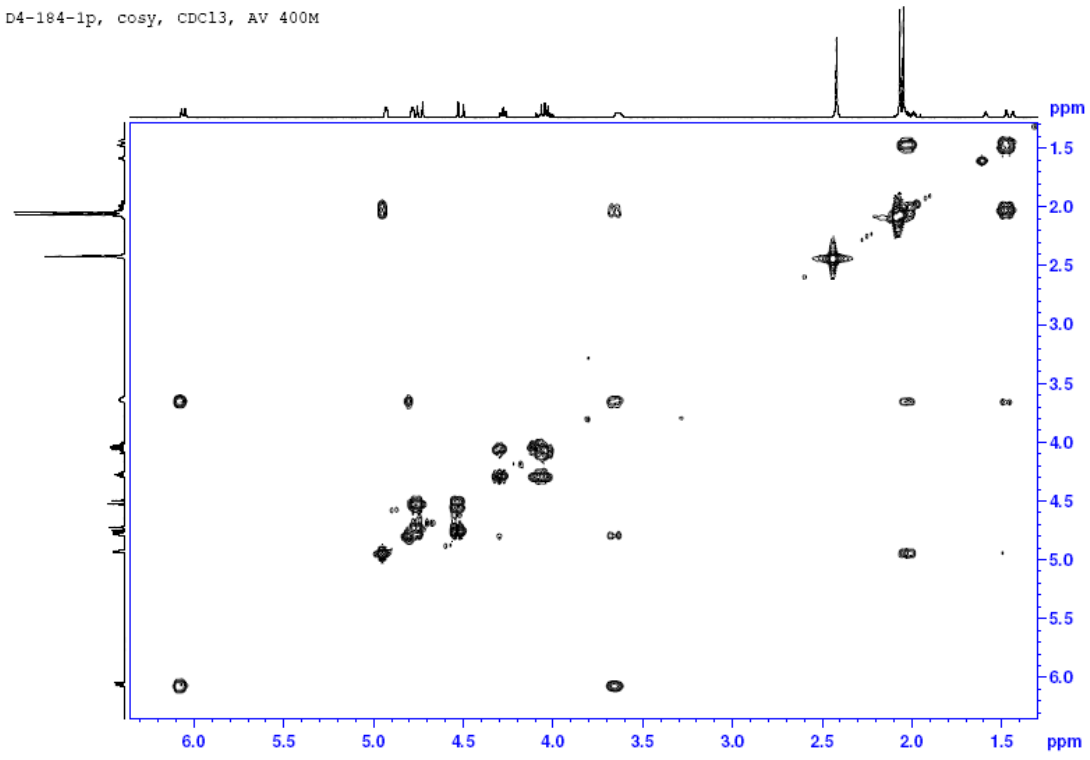
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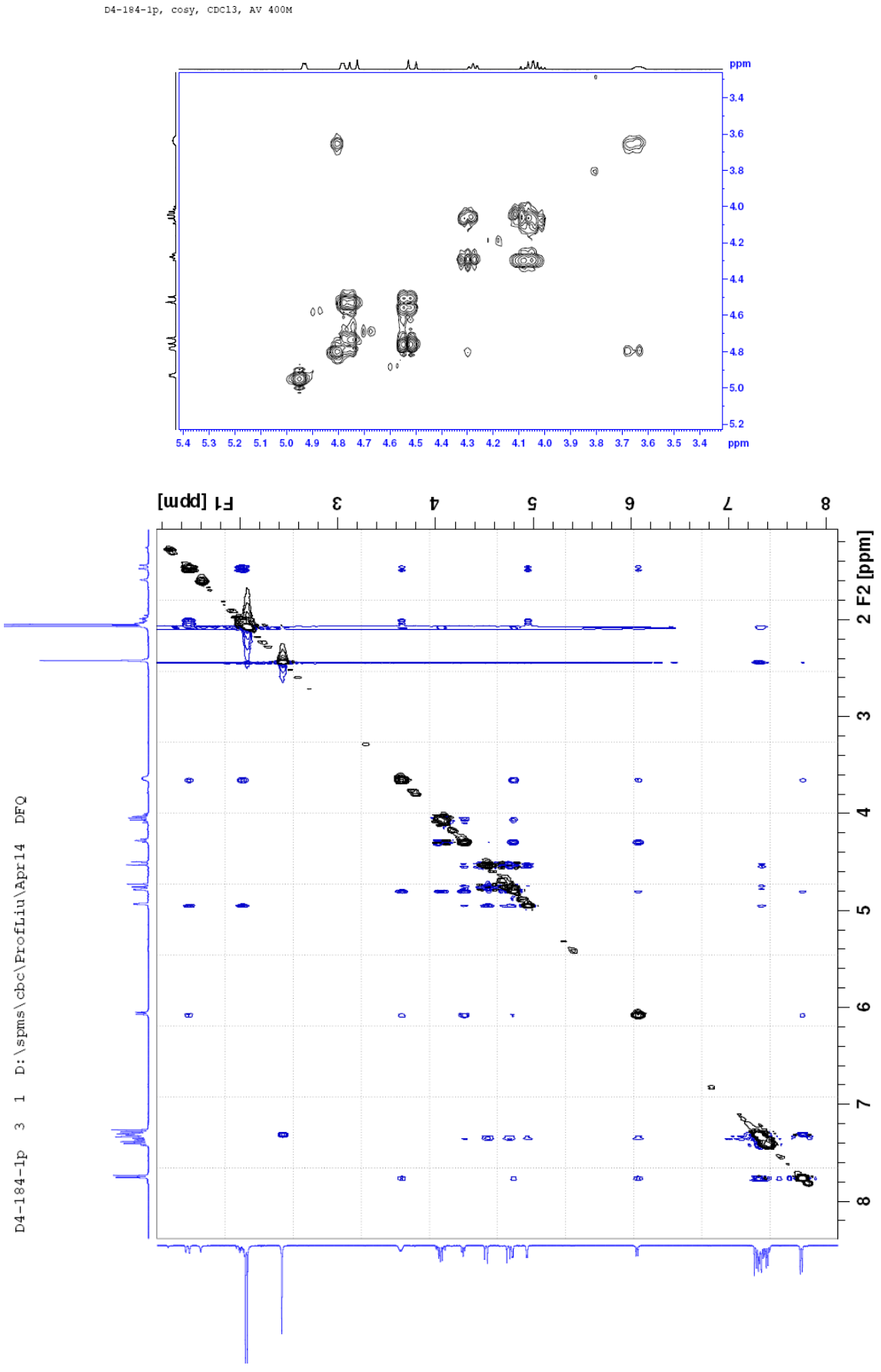
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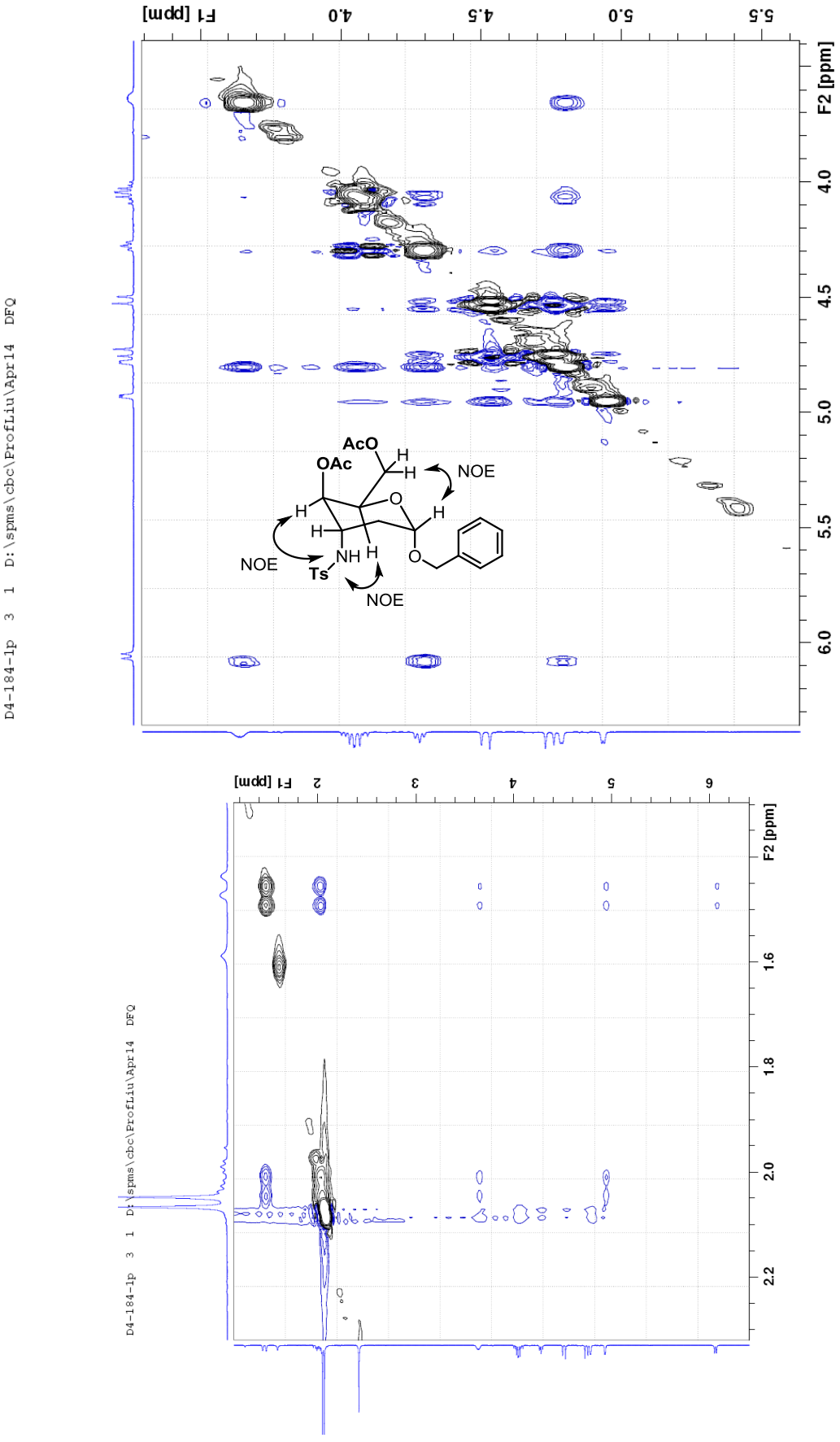
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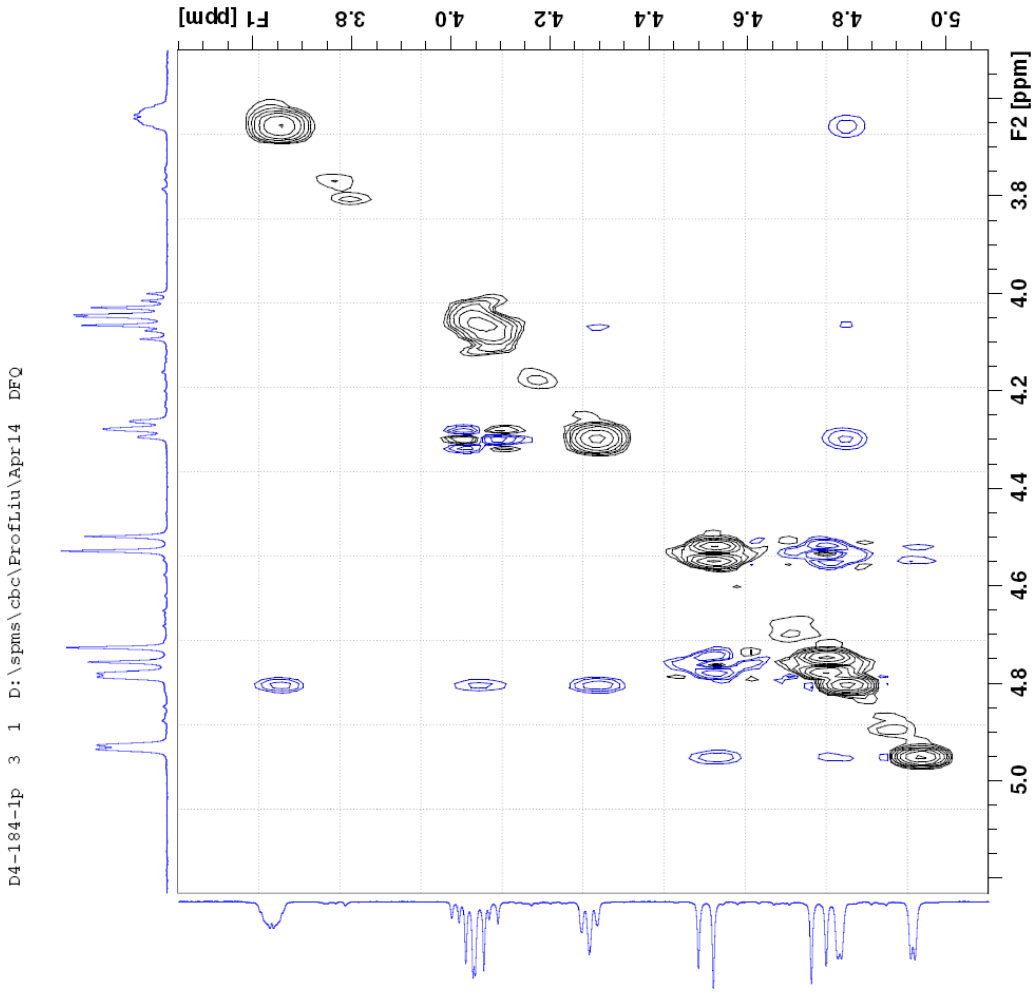
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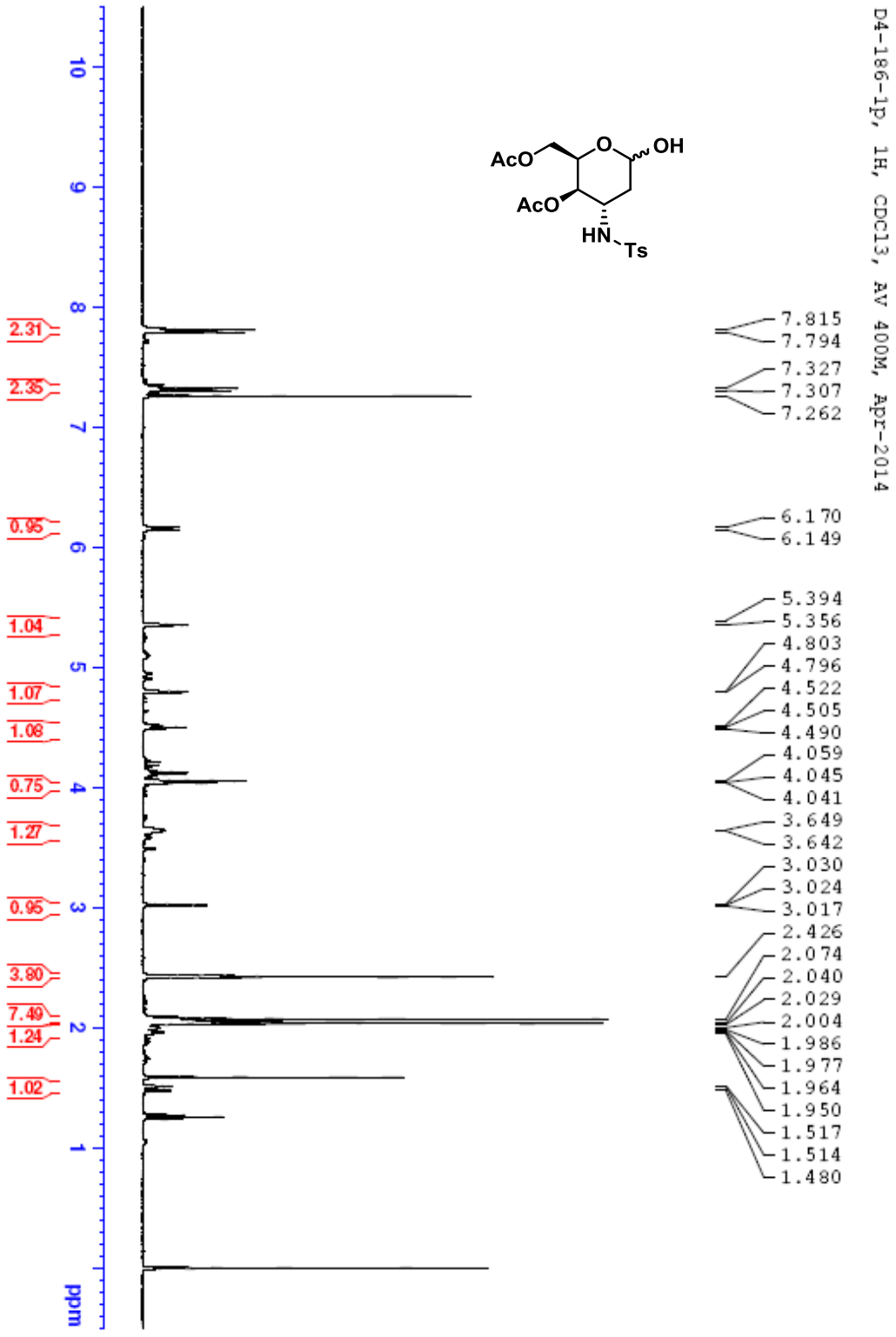
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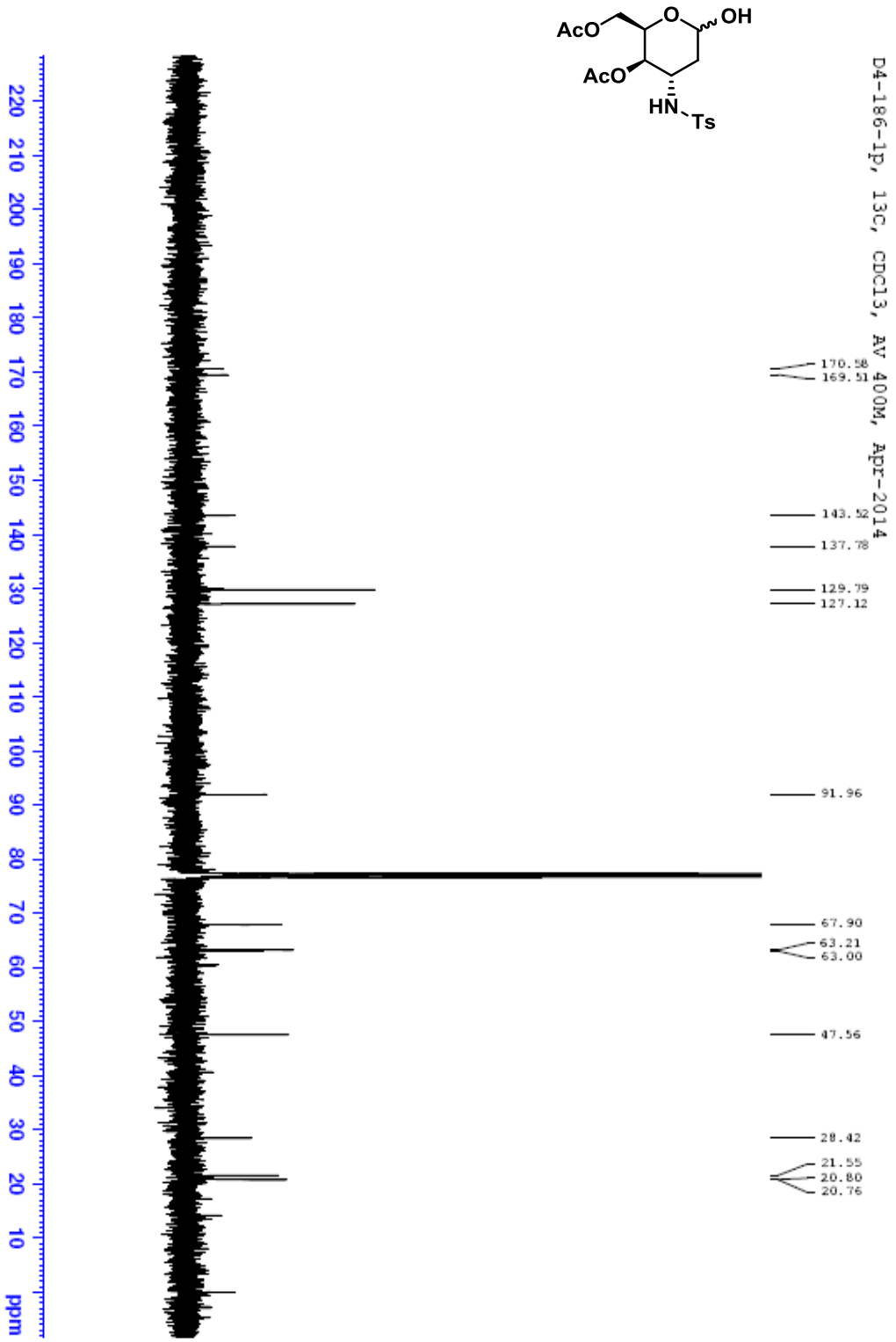
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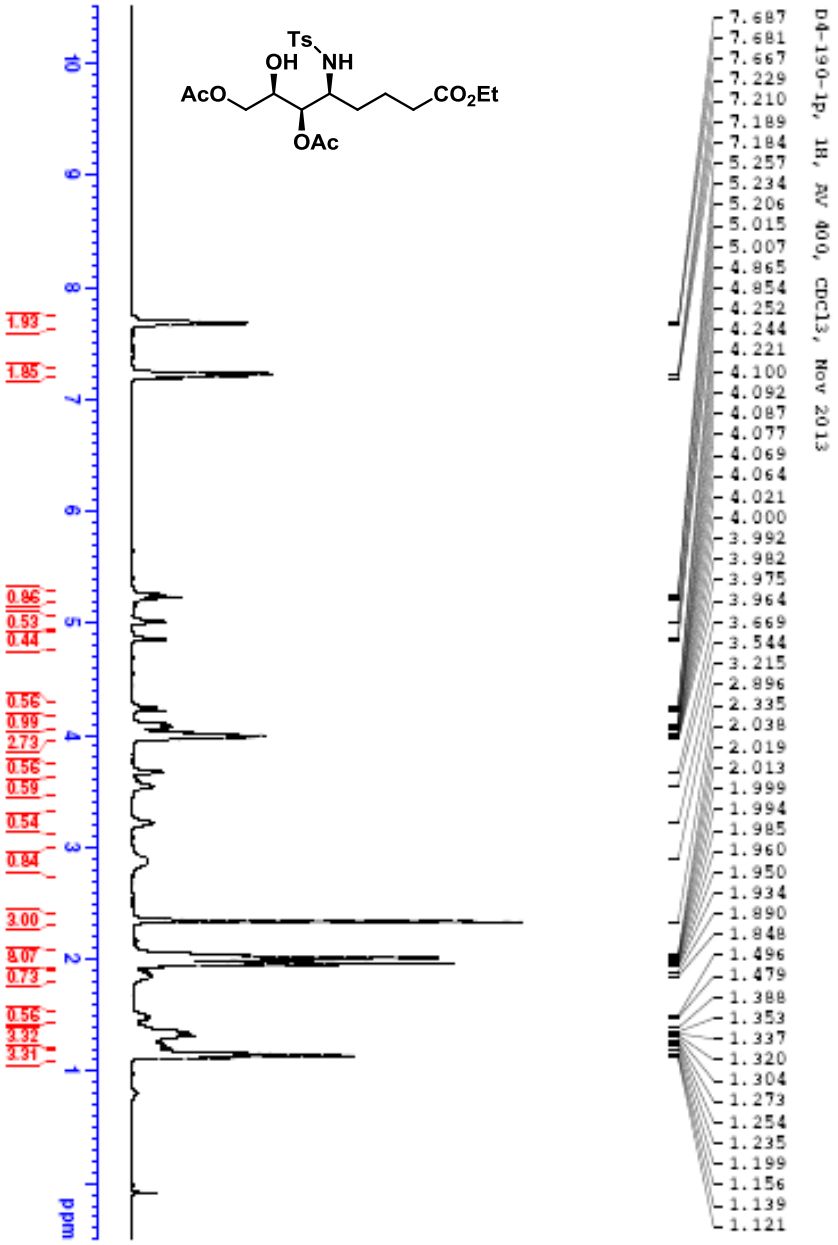
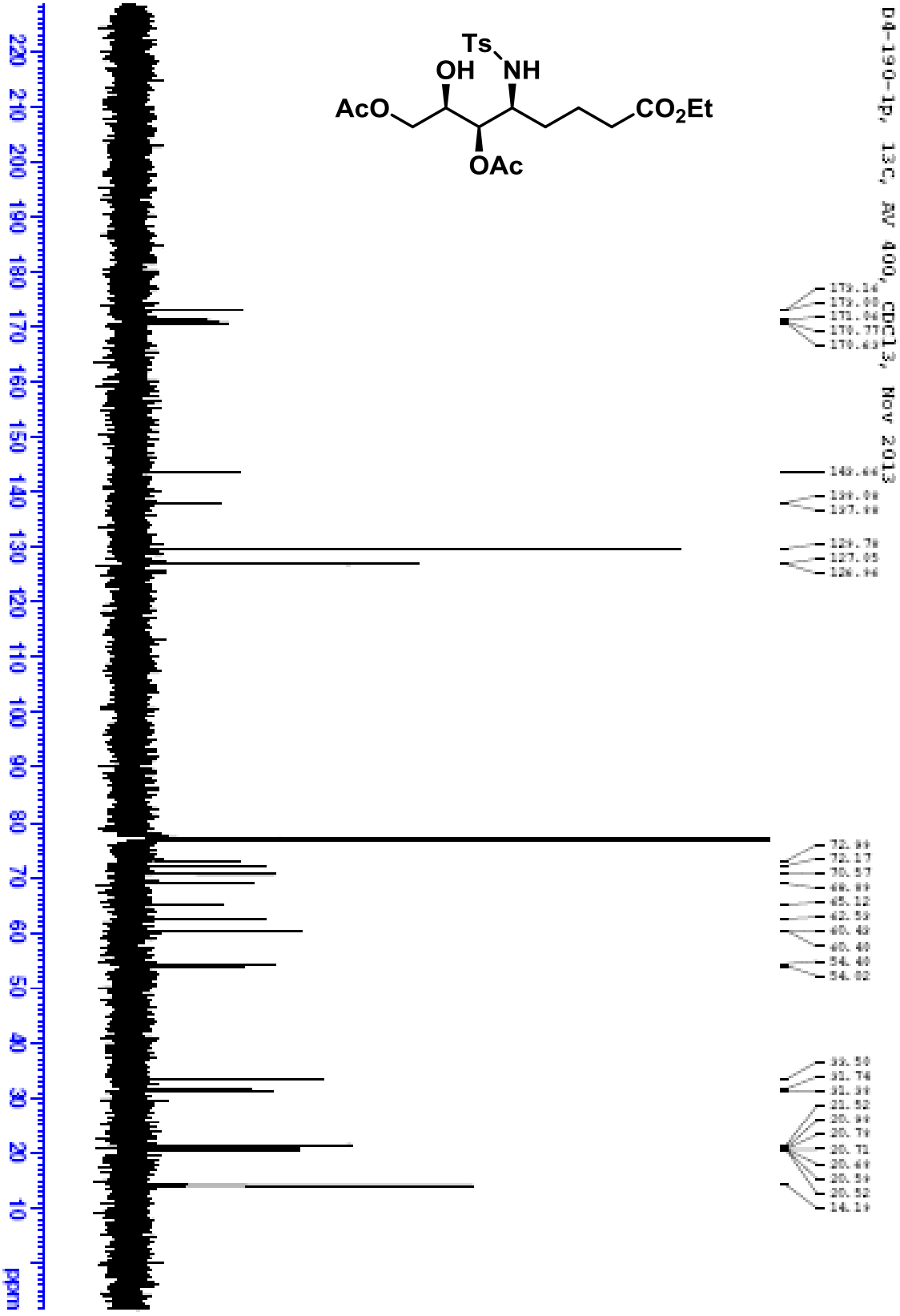
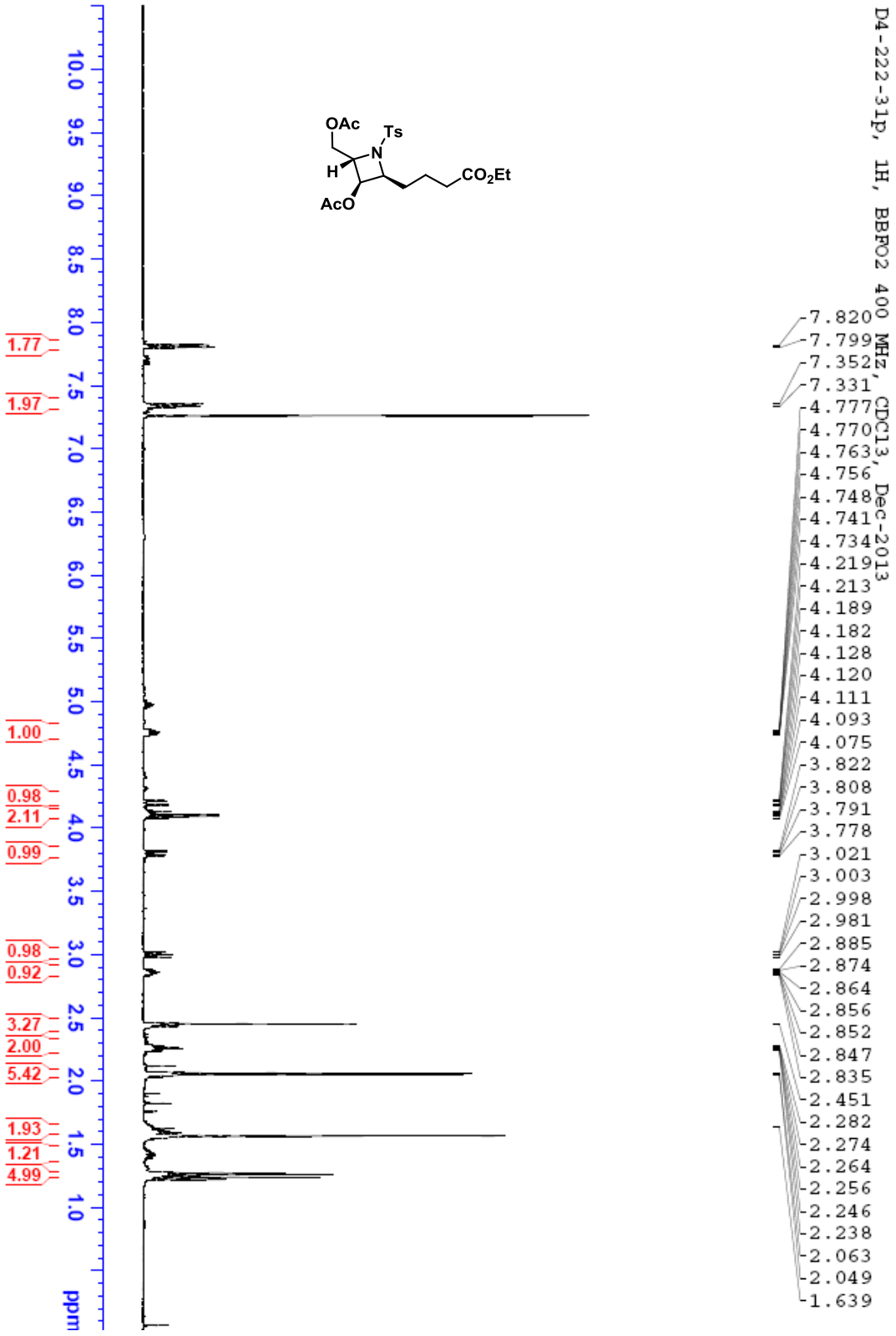
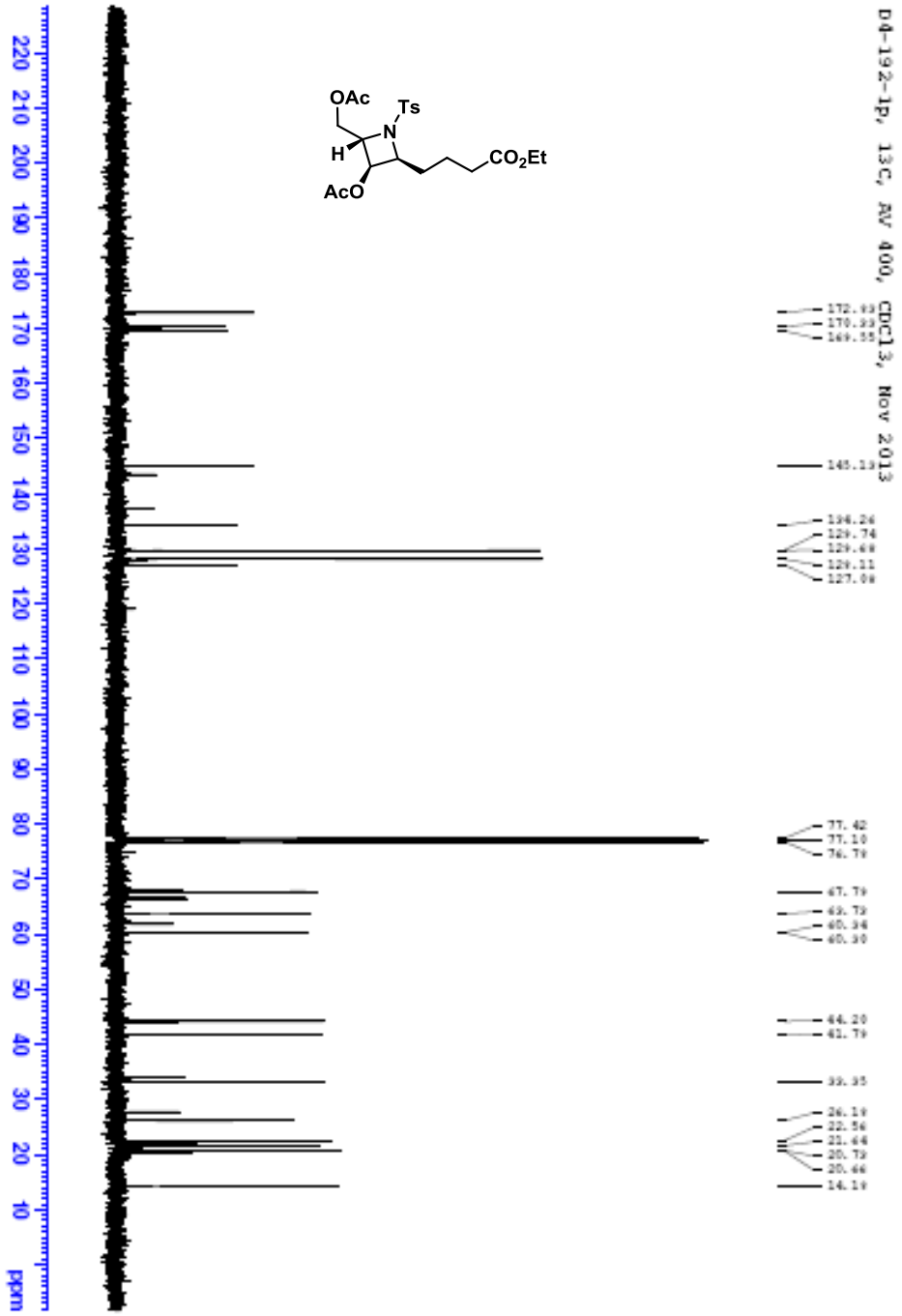
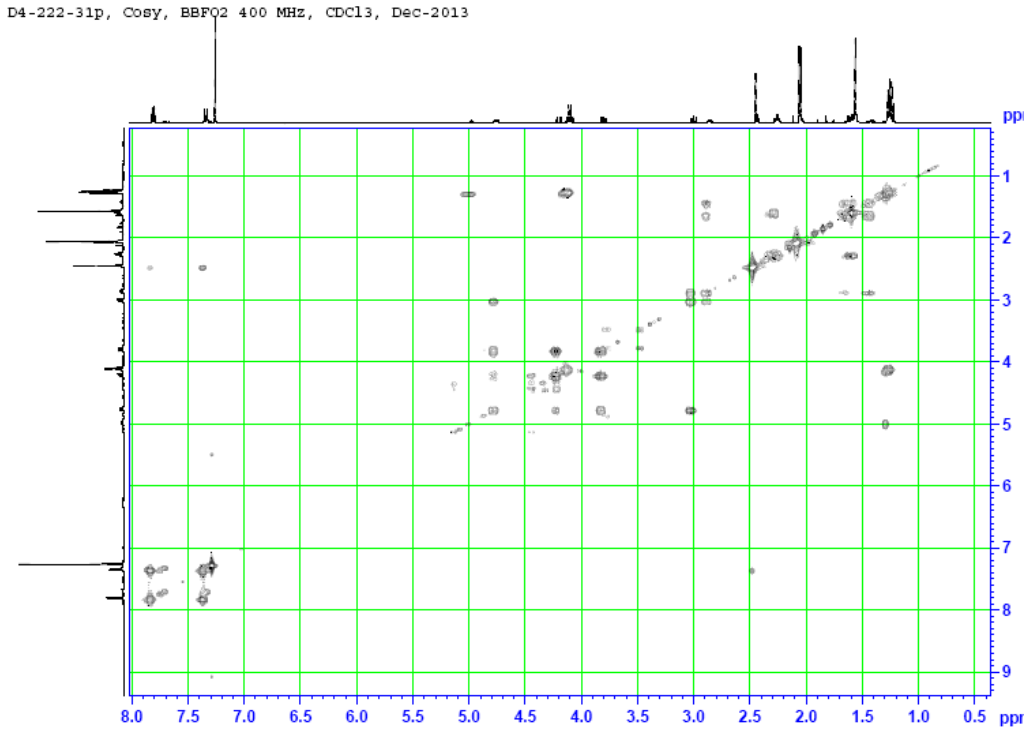
D4-186-1p, 13C, CDCl3, AV 400M, Apr-2014
170.58
169.51
143.52
137.78
129.79
127.12
91.96
67.90
63.21
63.00
47.56
28.42
21.55
20.80
20.76
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

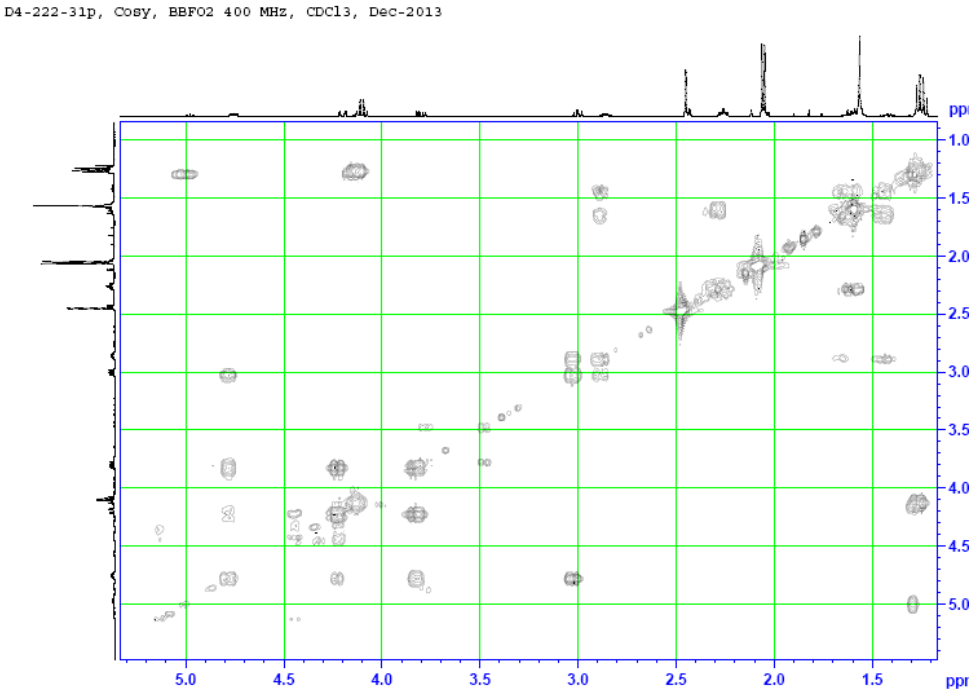

Ts
NH
OH
AcO
CO2Et
OAc
ppm
1.93
1.85
0.86
0.53
0.44
0.56
0.99
2.73
0.56
0.59
0.54
0.84
3.00
8.07
0.73
0.56
3.32
3.31
D4-190-1p, 1H, AV 400, CDCl3, Nov 2013
7.687
7.681
7.667
7.229
7.210
7.189
7.184
5.257
5.234
5.206
5.015
5.007
4.865
4.854
4.252
4.244
4.221
4.100
4.092
4.087
4.077
4.069
4.064
4.021
4.000
3.992
3.982
3.975
3.964
3.669
3.544
3.215
2.896
2.335
2.038
2.019
2.013
1.999
1.994
1.985
1.960
1.950
1.934
1.890
1.848
1.496
1.479
1.388
1.353
1.337
1.320
1.304
1.273
1.254
1.235
1.199
1.156
1.139
1.121

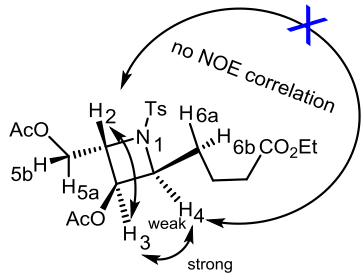

Ts
OH
NH
AcO
CO2Et
OAc
04-196-1p, 13C, AV 400, CDCl3, Nov 2013
ppm

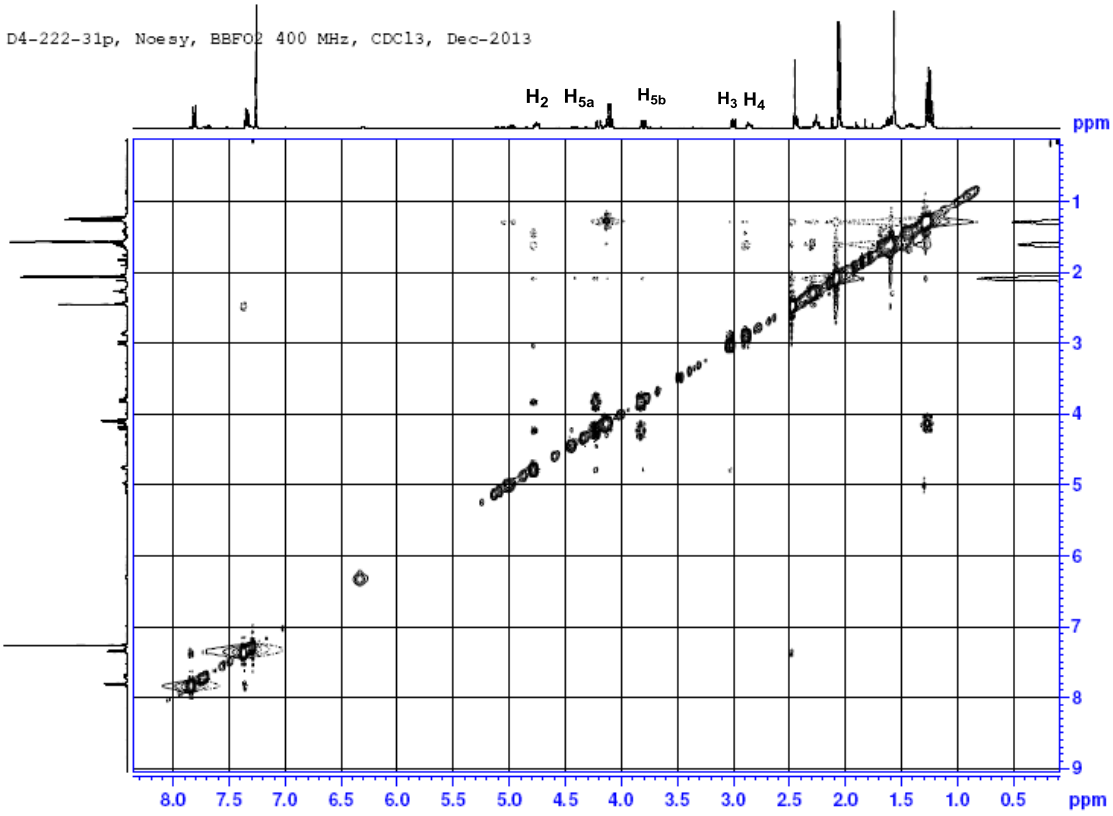

OAc
Ts
N
H
AcO
CO2Et
D4-222-31p, 1H, BBFO2 400 MHz, CDCl3, Dec-2013
7.820
7.799
7.352
7.331
4.777
4.770
4.763
4.756
4.748
4.741
4.734
4.219
4.213
4.189
4.182
4.128
4.120
4.111
4.093
4.075
3.822
3.808
3.791
3.778
3.021
3.003
2.998
2.981
2.885
2.874
2.864
2.856
2.852
2.847
2.835
2.451
2.282
2.274
2.264
2.256
2.246
2.238
2.063
2.049
1.639
1.77
1.97
1.00
0.98
2.11
0.99
0.98
0.92
3.27
2.00
5.42
1.93
1.21
4.99
10.0
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
ppm

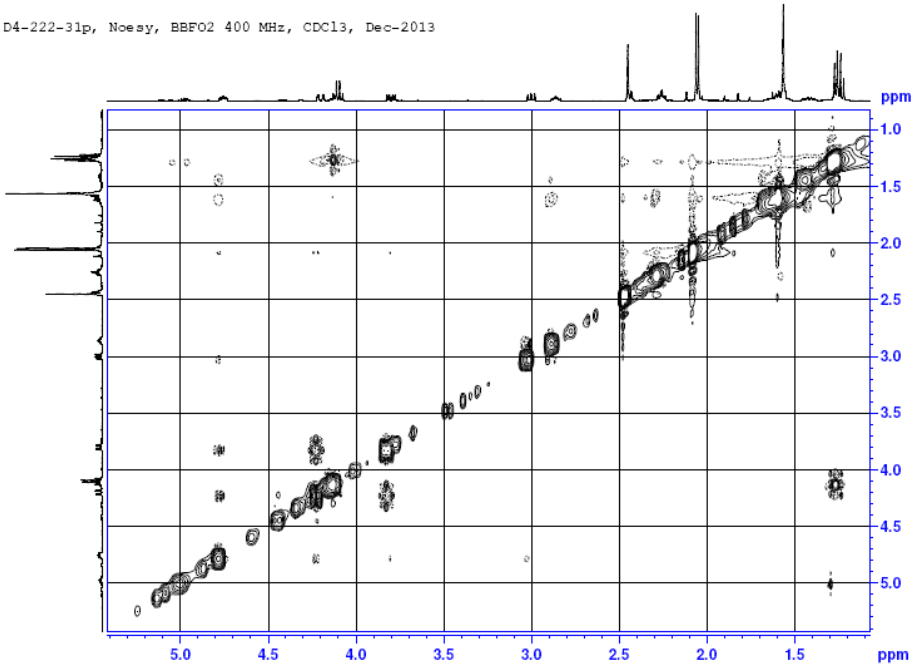

OAc
Ts
N
H
AcO
CO2Et
D4-192-1p, 13C, AV 400, cdcl3, Nov 2013
172.93
170.33
169.55
145.13
136.26
129.74
129.68
129.11
127.09
77.42
77.10
76.79
67.79
63.73
60.34
60.30
44.20
41.79
33.35
26.19
22.56
21.64
20.73
20.66
14.19
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

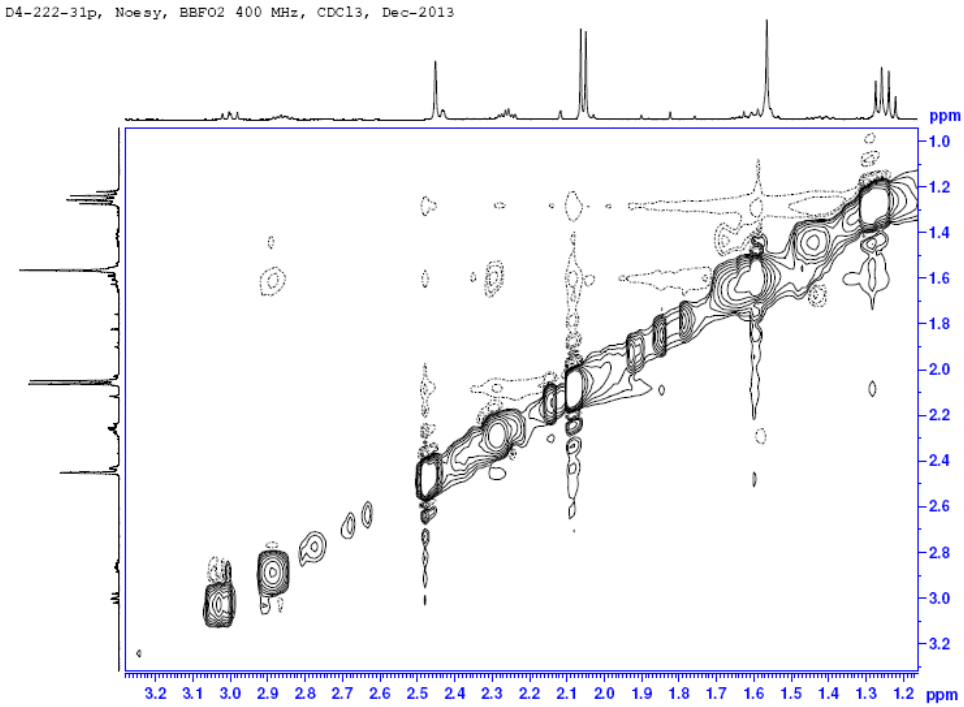

D4-222-31p, Cosy, BBF02 400 MHz, CDCl3, Dec-2013
ppm
1
2
3
4
5
6
7
8
9
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

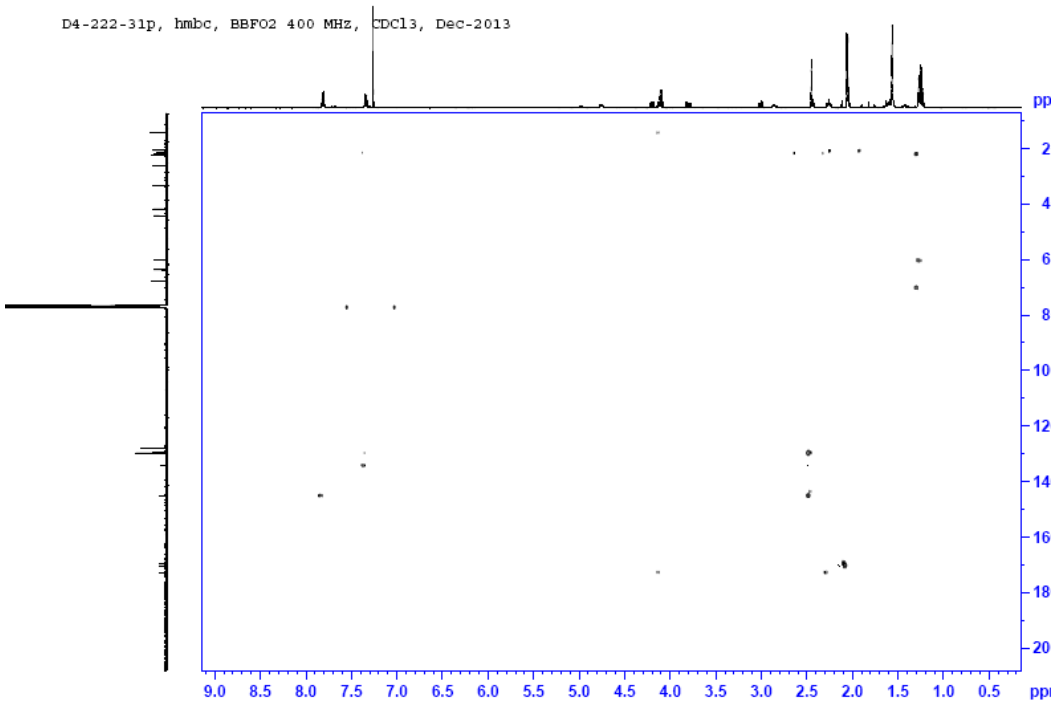

D4-222-31p, Cosy, BBF02 400 MHz, CDCl3, Dec-2013
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm

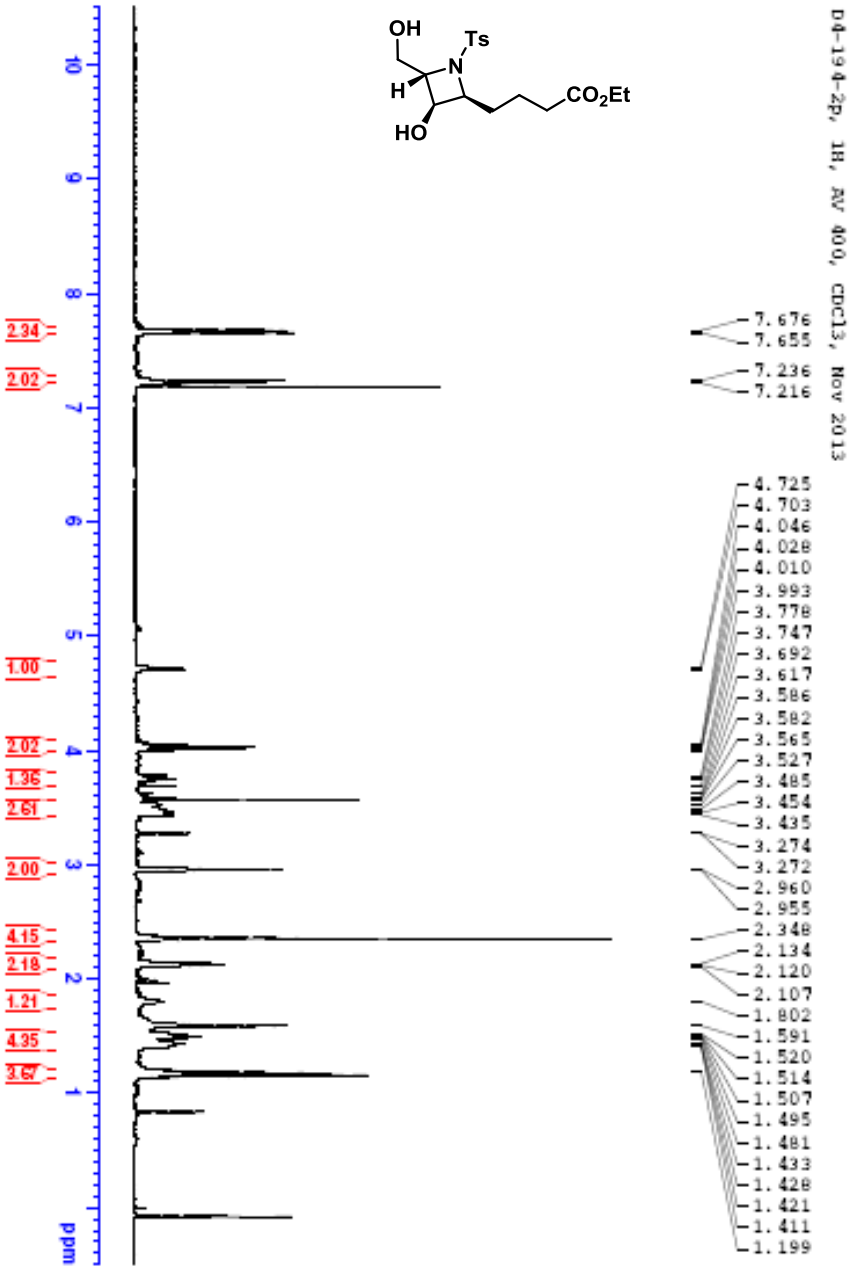

no NOE correlation
AcO
H2
Ts
H6a
N1
H
6b
CO2Et
5b
H
H5a
AcO
H4
H3
weak
strong

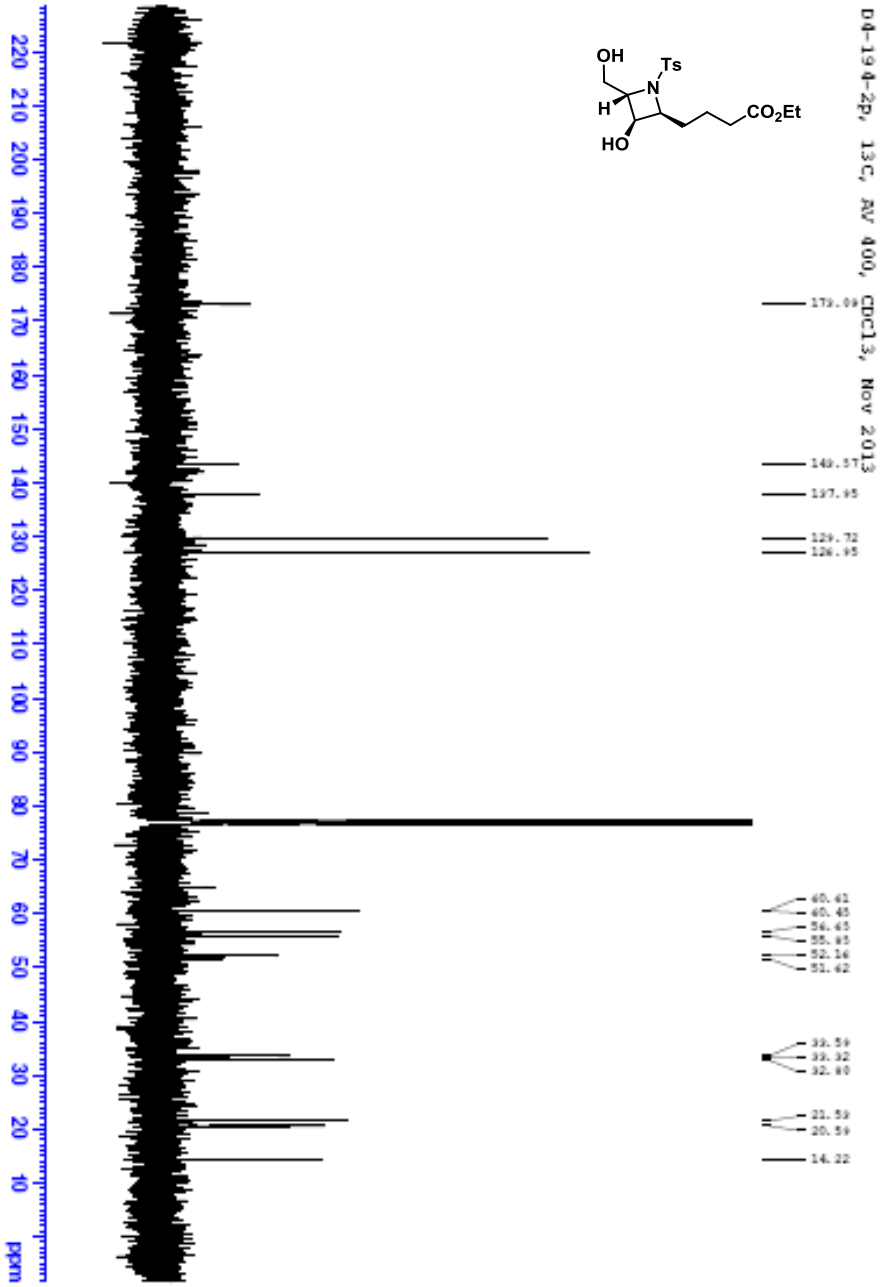

D4-222-31p, Noesy, BBFO2 400 MHz, CDCl3, Dec-2013
H2
H5a
H5b
H3 H4
ppm
1
2
3
4
5
6
7
8
9
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

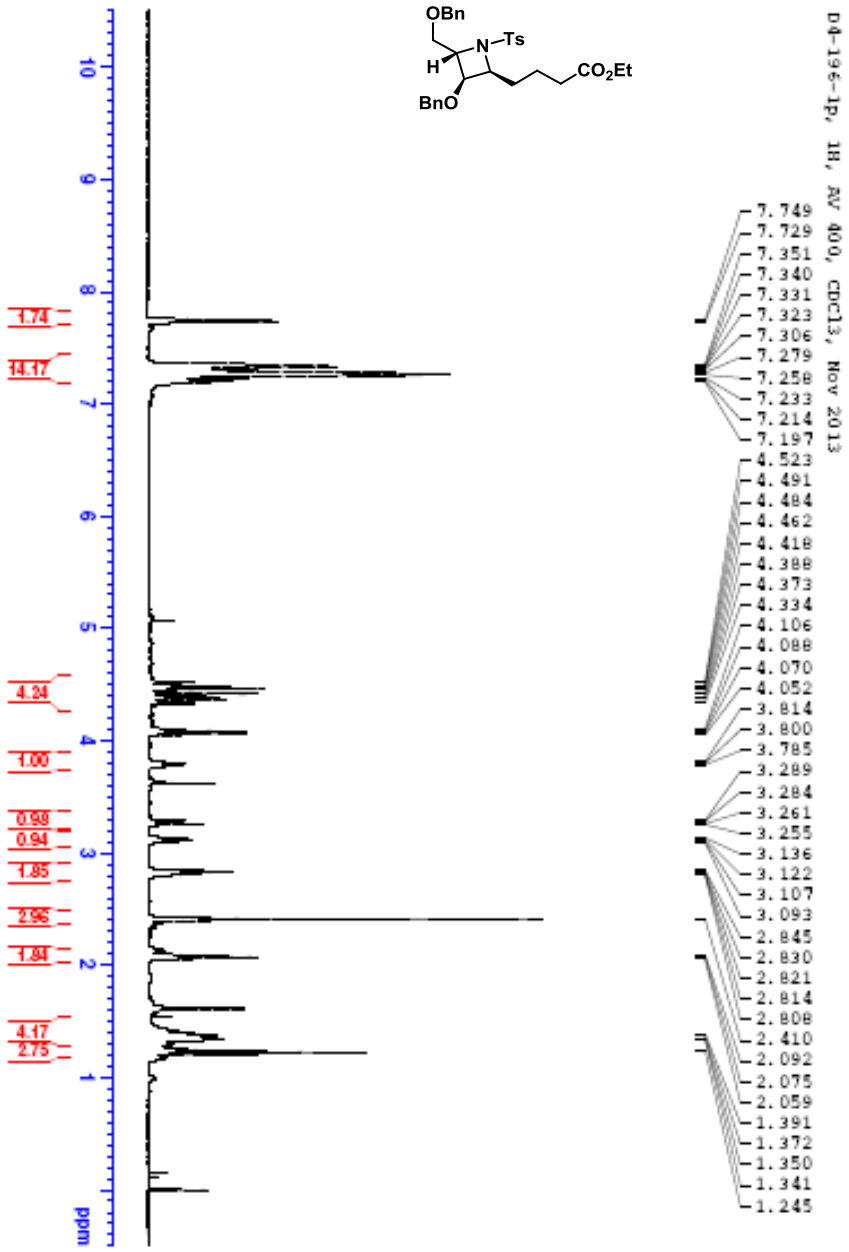

D4-222-31p, Noesy, BBFO2 400 MHz, CDCl3, Dec-2013
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm

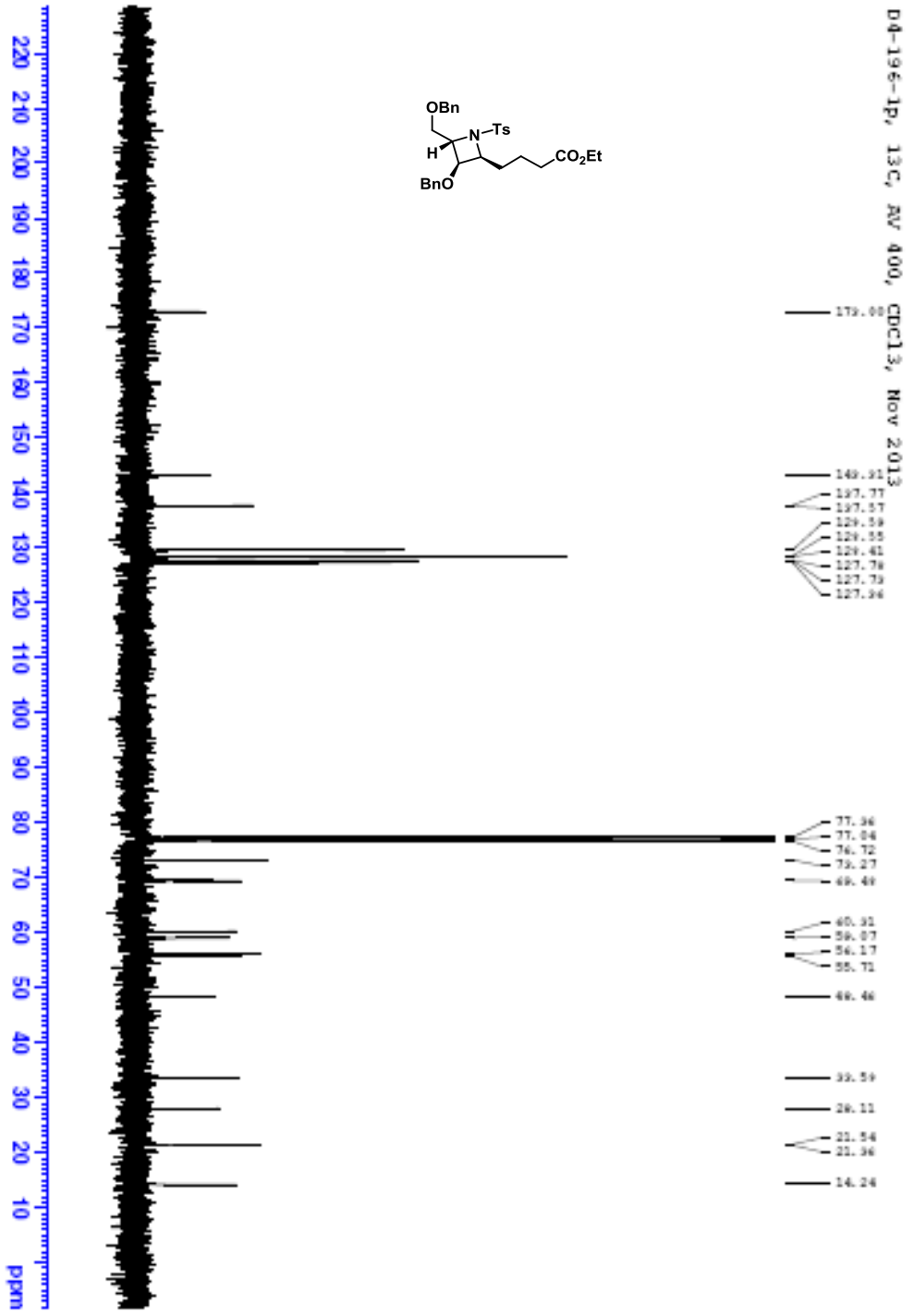

D4-222-31p, Noesy, BBFO2 400 MHz, CDCl3, Dec-2013
ppm
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 ppm

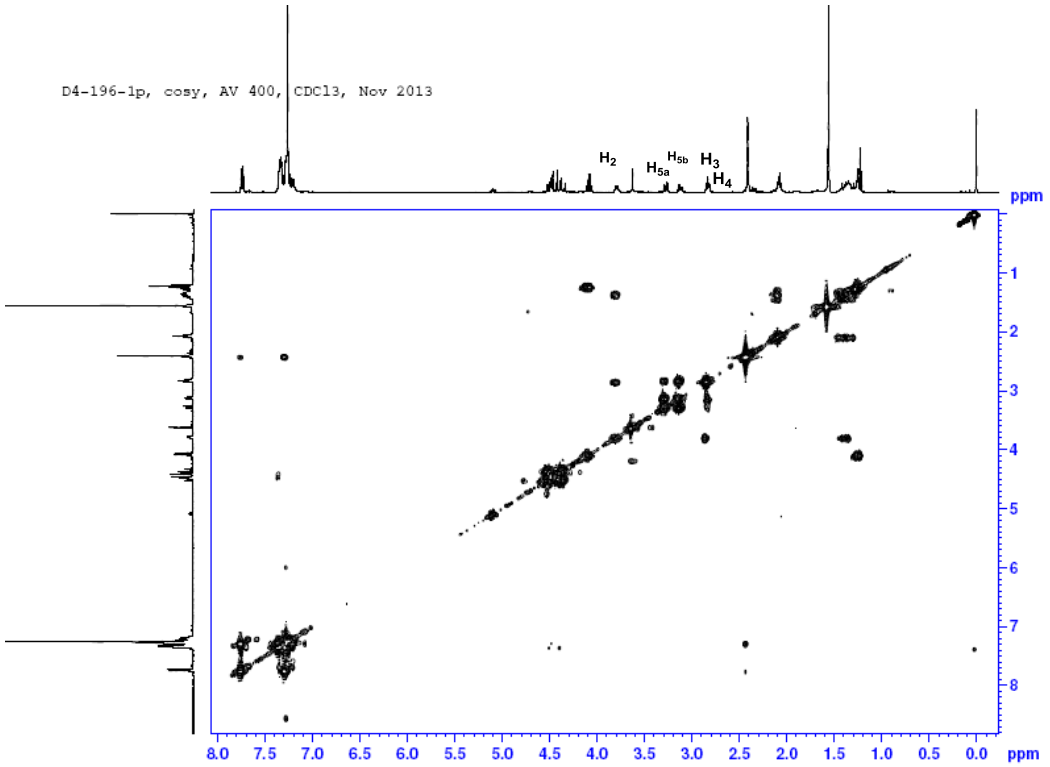

D4-222-31p, hmbc, BBF02 400 MHz, CDCl3, Dec-2013
ppm
2
4
6
8
10
12
14
16
18
20
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

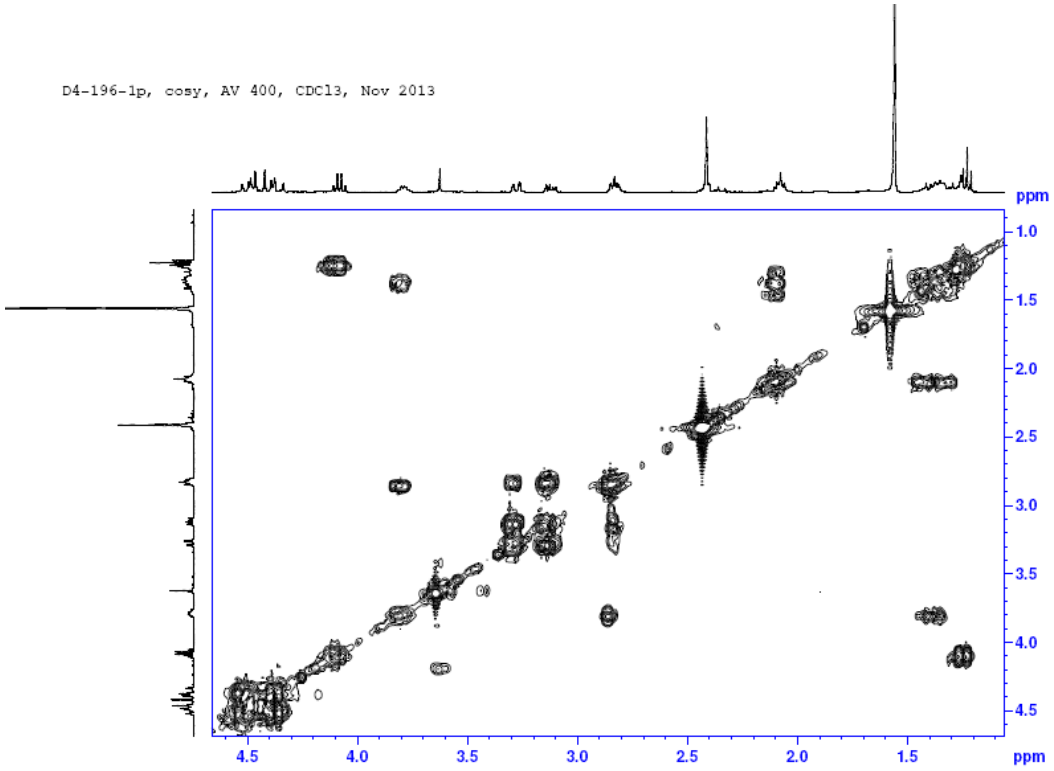

OH
Ts
N
H
HO
CO2Et
D4-194-2p, 1H, AV 400, CDCl3, Nov 2013
7.676
7.655
7.236
7.216
4.725
4.703
4.046
4.028
4.010
3.993
3.778
3.747
3.692
3.617
3.586
3.582
3.565
3.527
3.485
3.454
3.435
3.274
3.272
2.960
2.955
2.348
2.134
2.120
2.107
1.802
1.591
1.520
1.514
1.507
1.495
1.481
1.433
1.428
1.421
1.411
1.199
2.34
2.02
1.00
2.02
1.36
2.61
2.00
4.15
2.18
1.21
4.35
3.67
ppm

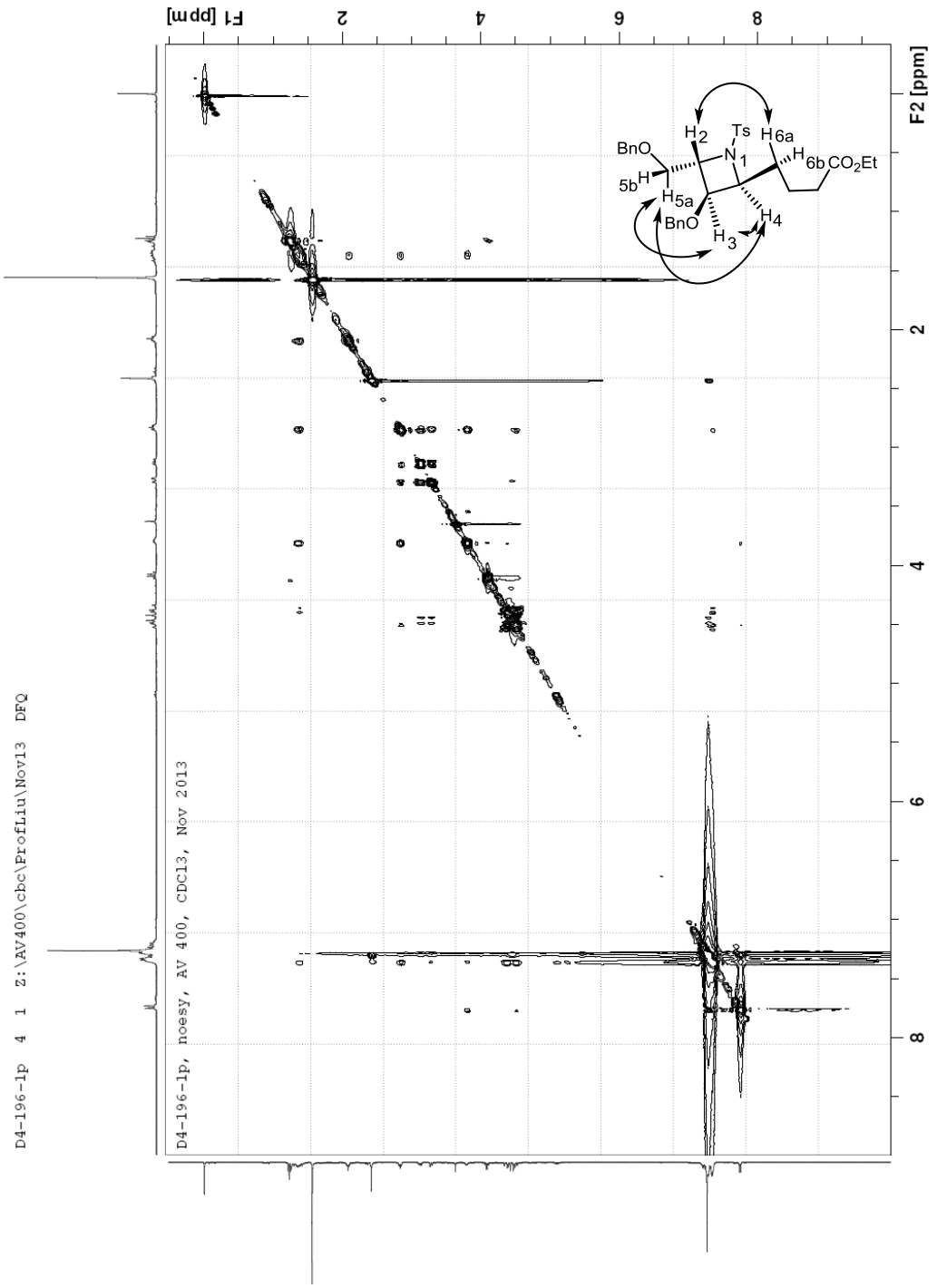

D4-194-2p, 13C, AV 400, CDCl3, Nov 2013
OH
Ts
N
H
HO
CO2Et
179.09
149.57
137.95
129.72
126.95
60.61
60.48
56.45
55.65
52.14
51.42
33.59
33.32
32.80
21.59
20.59
14.22
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

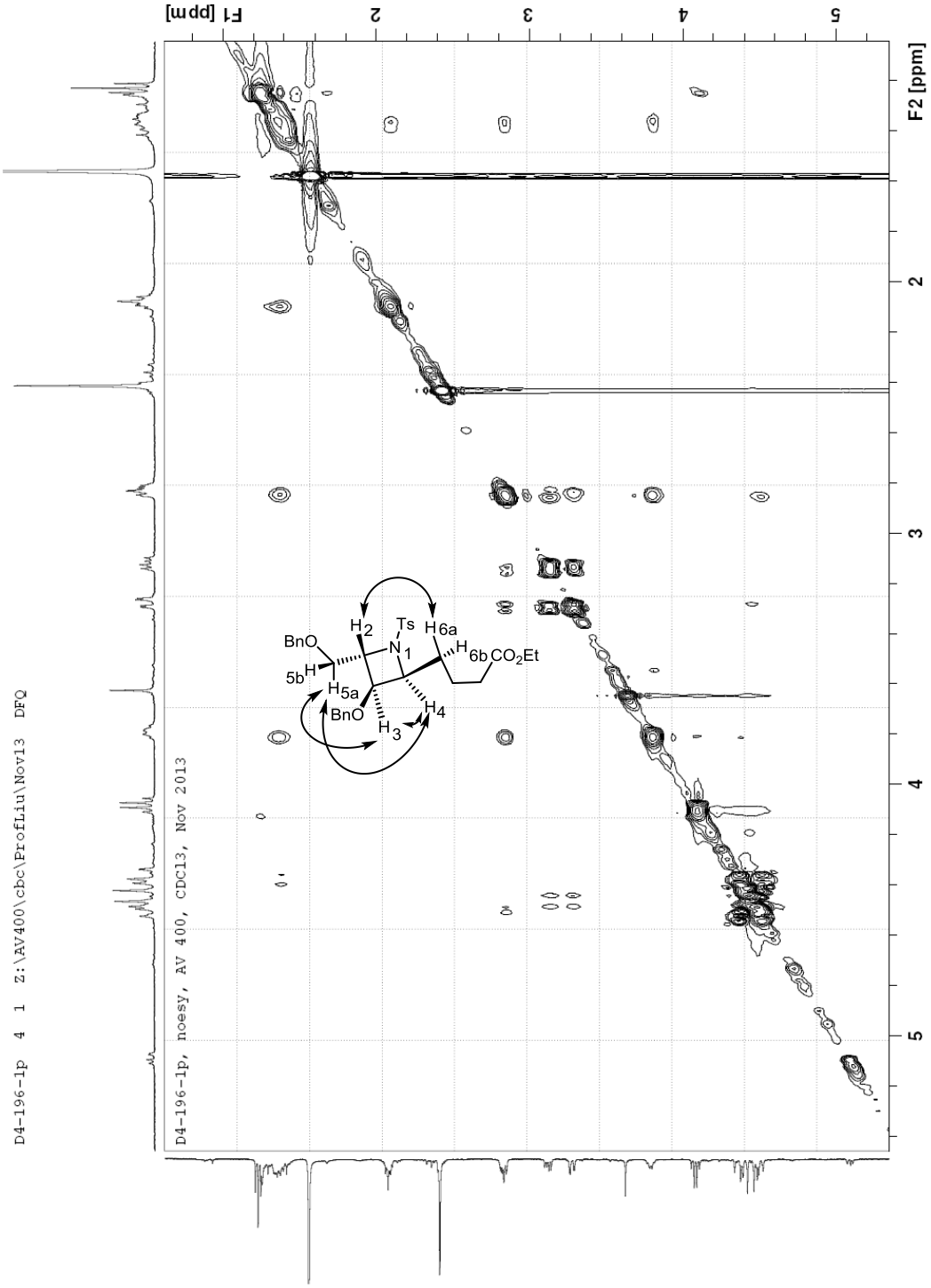

OBn
N
Ts
H
BnO
CO2Et
D4-196-1p, 1H, AV 400, CDCl3, Nov 2013
7.749
7.729
7.351
7.340
7.331
7.323
7.306
7.279
7.258
7.233
7.214
7.197
4.523
4.491
4.484
4.462
4.418
4.388
4.373
4.334
4.106
4.088
4.070
4.052
3.814
3.800
3.785
3.289
3.284
3.261
3.255
3.136
3.122
3.107
3.093
2.845
2.830
2.821
2.814
2.808
2.410
2.092
2.075
2.059
1.391
1.372
1.350
1.341
1.245
1.74
14.17
4.24
1.00
0.98
0.94
1.85
2.96
1.84
4.17
2.75
ppm

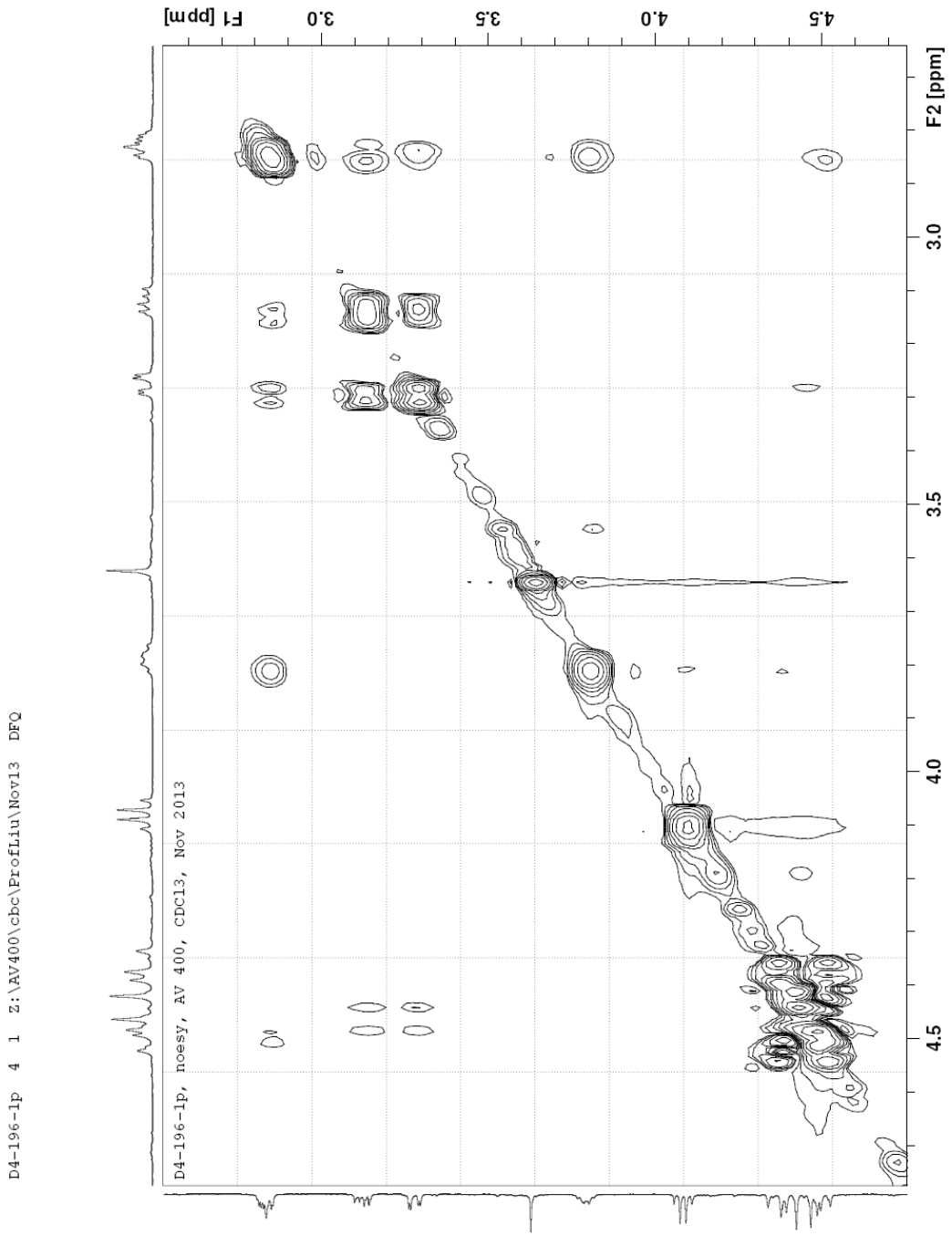

D4-196-1p, 13C, AV 400, CDCl3, Nov 2013
OBn
N
Ts
H
BnO
CO2Et
179.00
149.91
137.77
137.57
129.59
129.55
129.41
127.78
127.73
127.36
77.36
77.04
76.72
73.27
69.49
60.31
59.07
56.17
55.71
48.46
33.59
28.11
21.54
21.36
14.24
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

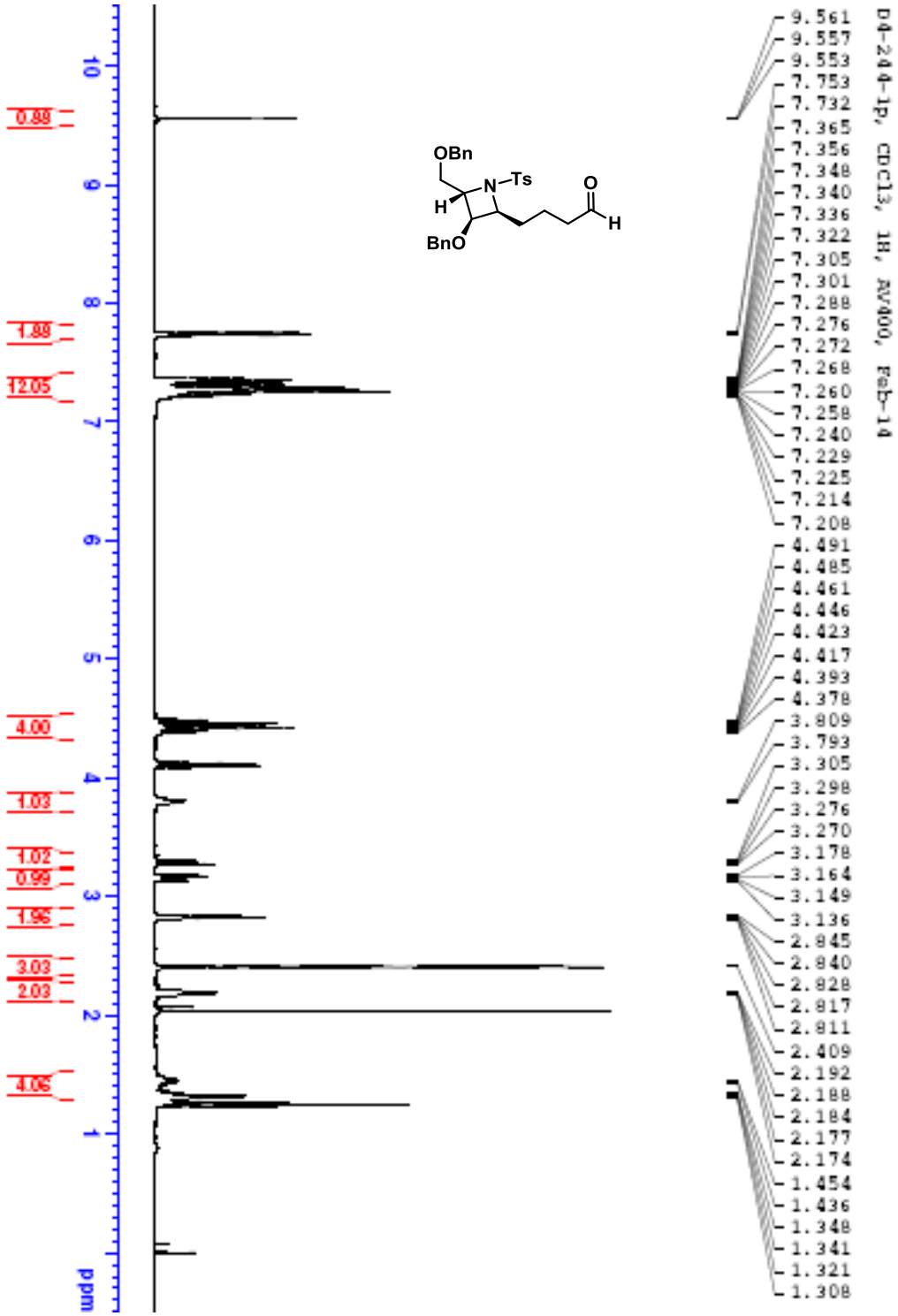

D4-196-1p, cosy, AV 400, CDCl3, Nov 2013
H2
H5a
H5b
H3
H4
ppm
1
2
3
4
5
6
7
8
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

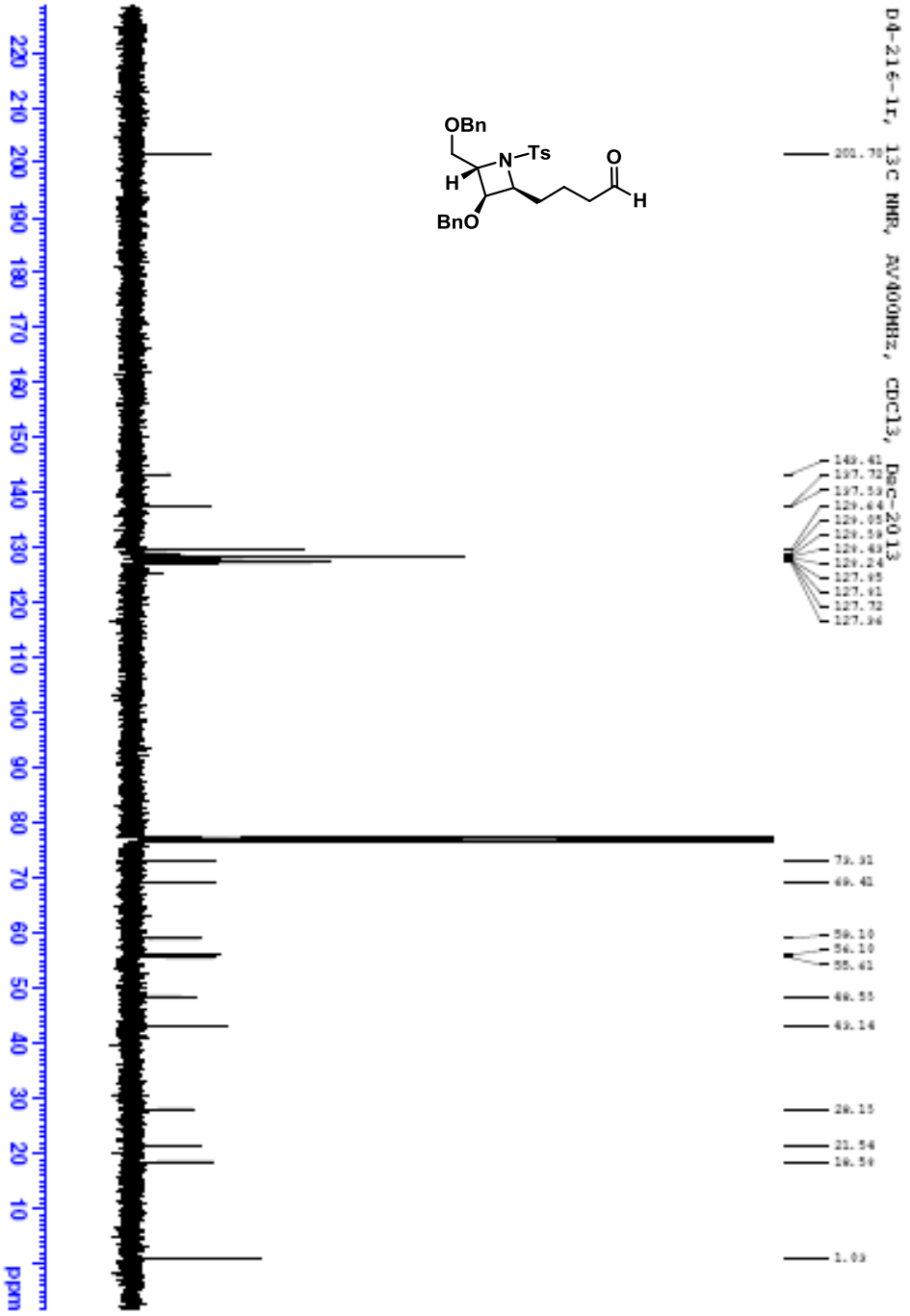

D4-196-1p, cosy, AV 400, CDCl3, Nov 2013
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm

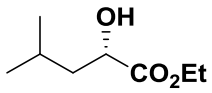

F1 [ppm]
F2 [ppm]
D4-196-1p, noesy, AV 400, CDCl3, Nov 2013
D4-196-1p 4 1 z:\AV400\cbc\Profliu\Nov13 DFQ
BnO
5b
H
H2
Ts
N1
H6a
H6b
CO2Et
H5a
BnO
H3
H4

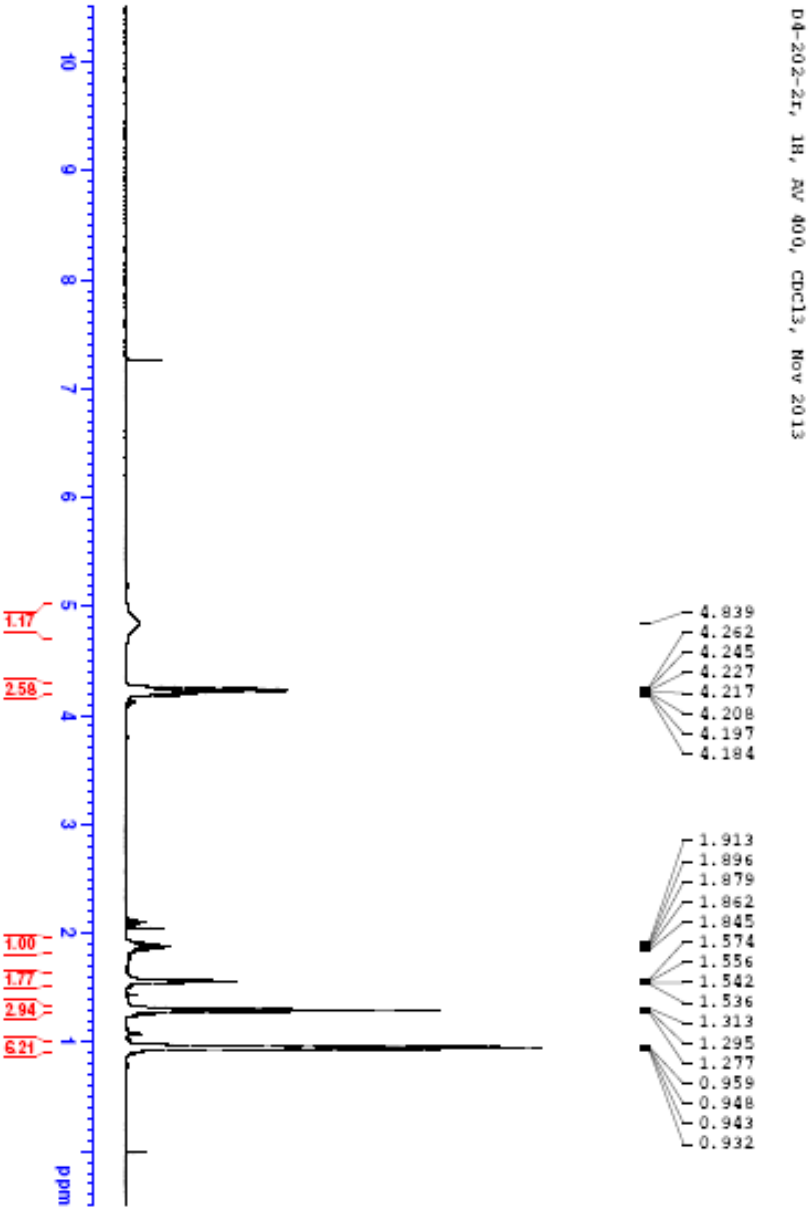

F1 [ppm]
F2 [ppm]
D4-196-1p, noesy, AV 400, CDCl3, Nov 2013
D4-196-1p 4 1 Z:\AV400\cbc\ProfLiu\Nov13 DFQ
BnO
H2
Ts
N1
H6a
H6b
CO2Et
5b
H5a
BnO
H3
H4

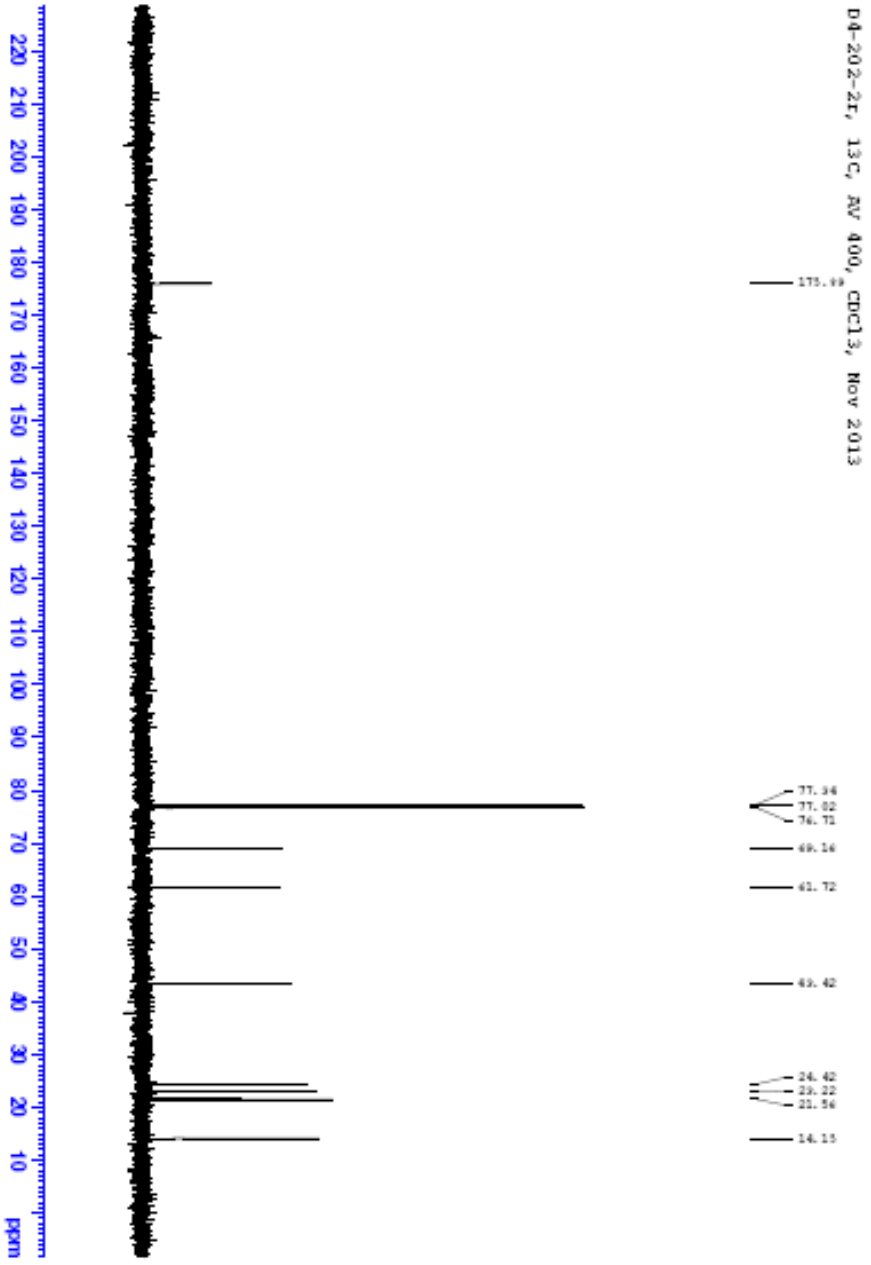

D4-196-1p 4 1 Z:\AV400\cbc\Profliu\Nov13 DFQ
D4-196-1p, noesy, AV 400, CDCl3, Nov 2013
F1 [ppm]
F2 [ppm]
4.5
4.0
3.5
3.0

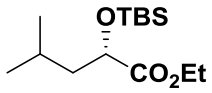

OBn
N
Ts
O
H
H
BnO
0.88
1.88
12.05
4.00
1.03
1.02
0.99
1.96
3.03
2.03
4.06
10
9
8
7
6
5
4
3
2
1
ppm
D4-244-1p, CDCl3, 1H, AV400, Feb-14
9.561
9.557
9.553
7.753
7.732
7.365
7.356
7.348
7.340
7.336
7.322
7.305
7.301
7.288
7.276
7.272
7.268
7.260
7.258
7.240
7.229
7.225
7.214
7.208
4.491
4.485
4.461
4.446
4.423
4.417
4.393
4.378
3.809
3.793
3.305
3.298
3.276
3.270
3.178
3.164
3.149
3.136
2.845
2.840
2.828
2.817
2.811
2.409
2.192
2.188
2.184
2.177
2.174
1.454
1.436
1.348
1.341
1.321
1.308

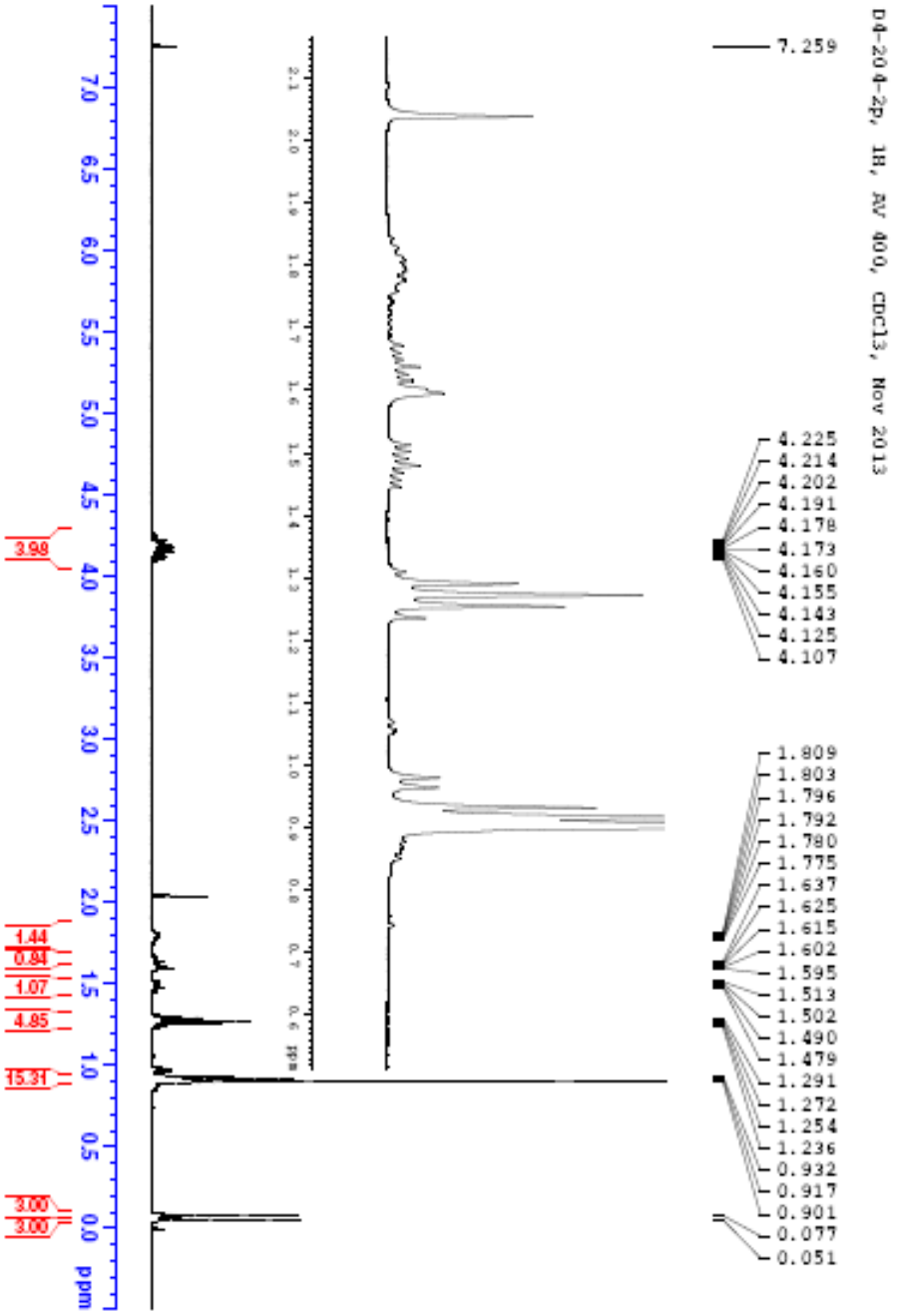

D4-216-1r, 13C NMR, AV400MHz, CDCl3, Dec-2013
OBn
N
Ts
O
H
H
BnO
201.70
149.41
137.72
137.53
129.64
129.05
129.59
129.43
129.24
127.95
127.91
127.72
127.36
79.31
69.41
59.10
56.10
55.61
46.55
43.14
28.15
21.54
18.59
1.03
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

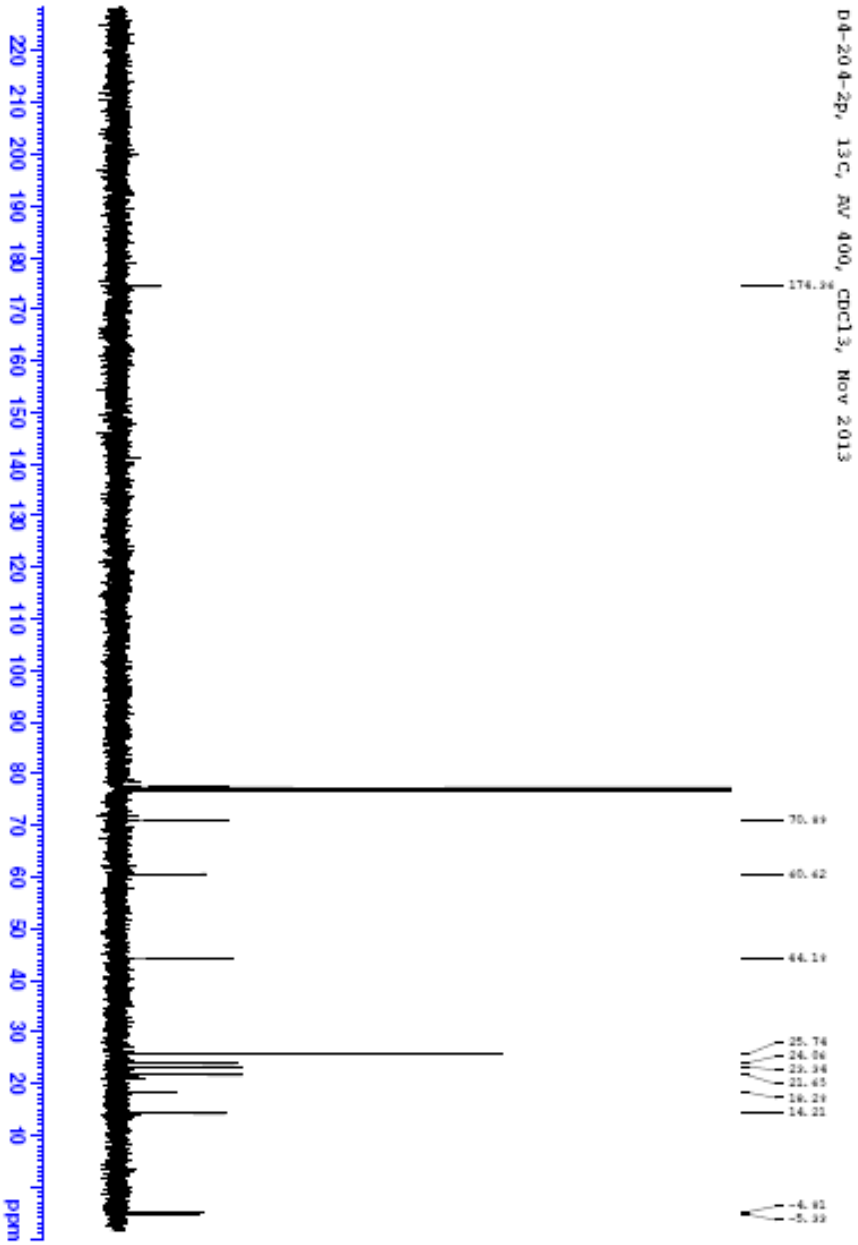

OH
CO2Et

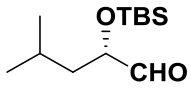

D4-202-2r, 1H, AV 400, CDCl3, Nov 2013
4.839
4.262
4.245
4.227
4.217
4.208
4.197
4.184
1.913
1.896
1.879
1.862
1.845
1.574
1.556
1.542
1.536
1.313
1.295
1.277
0.959
0.948
0.943
0.932
1.17
2.58
1.00
1.77
2.94
6.21
ppm

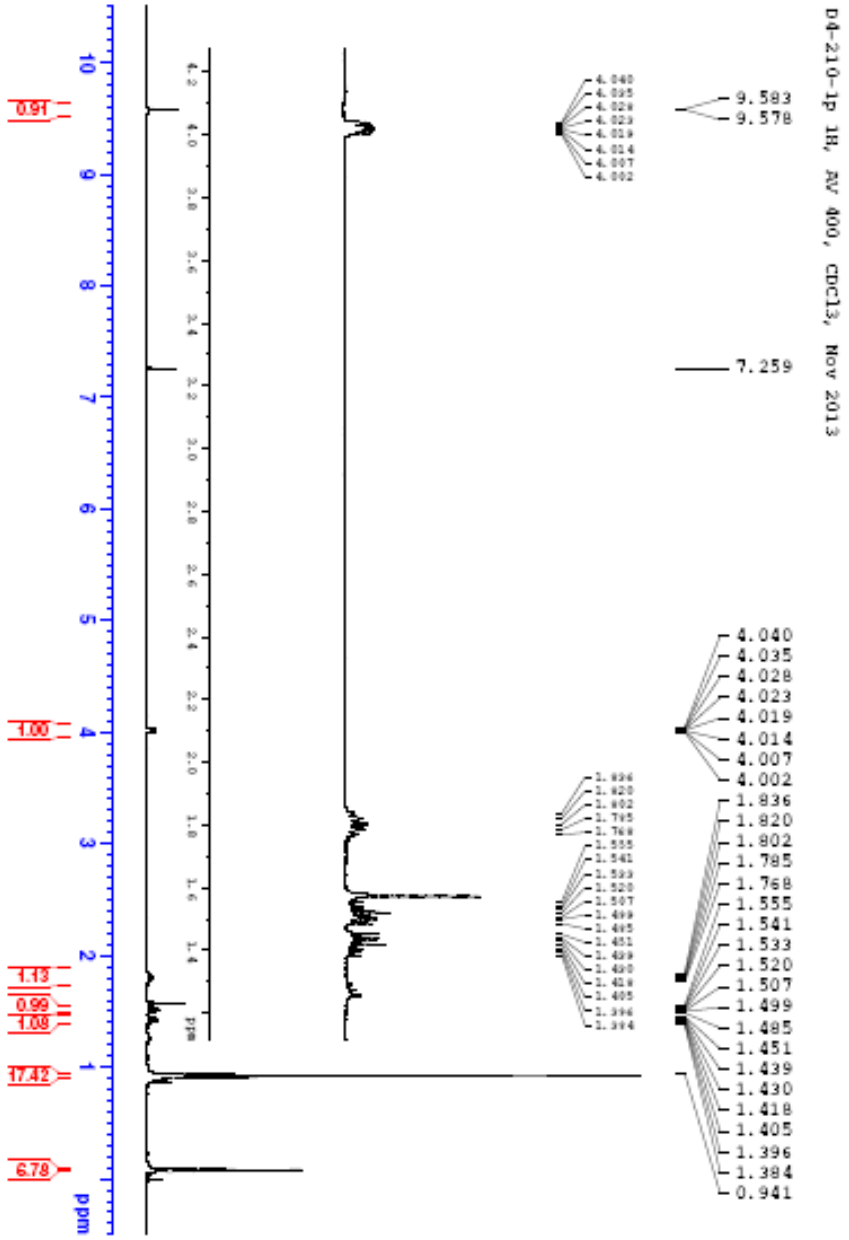

D4-202-2r, 13C, AV 400, CDCl3, Nov 2013
175.99
77.34
77.02
76.71
69.16
61.72
49.42
24.42
23.22
21.56
14.15
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

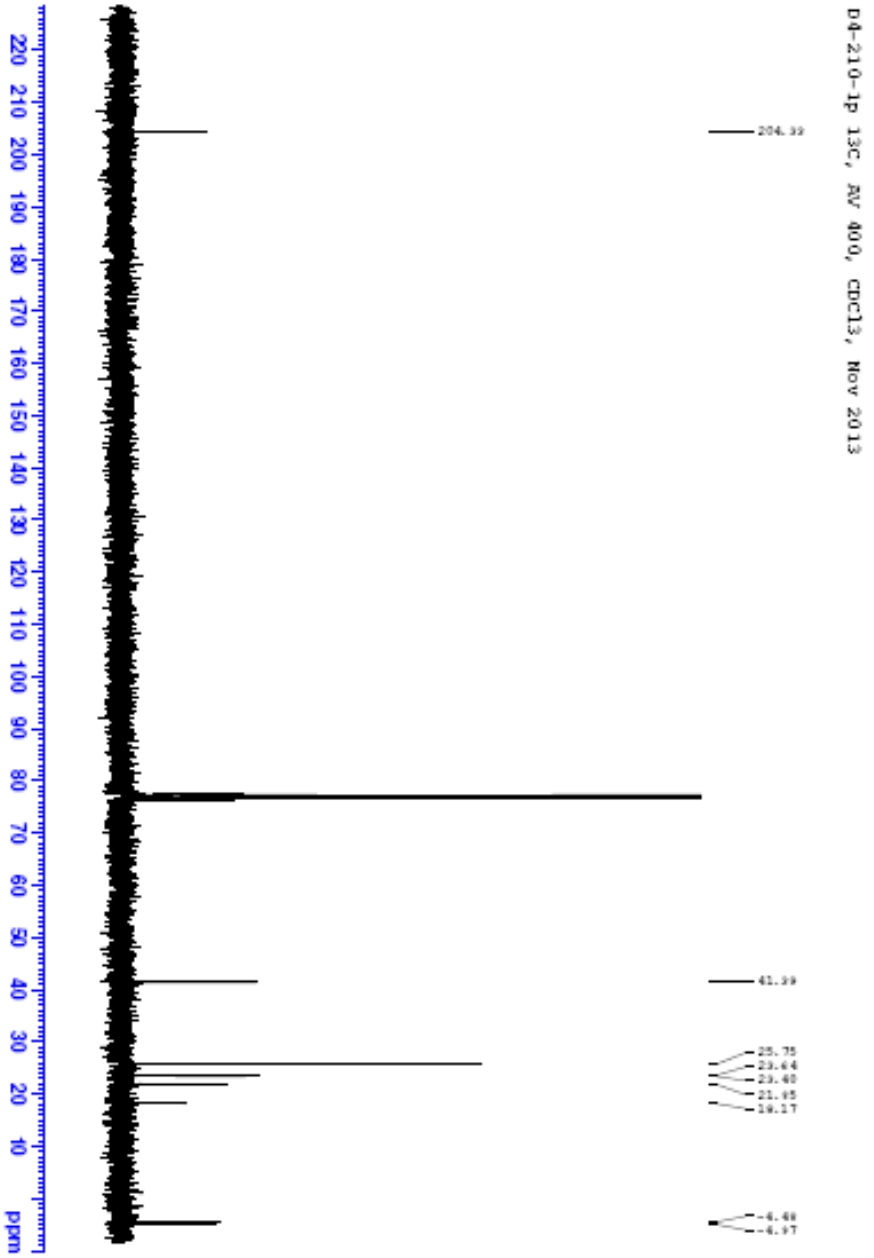

OTBS
CO2Et

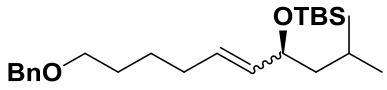

D4-204-2p, 1H, AV 400, CDCl3, Nov 2013
7.259
4.225
4.214
4.202
4.191
4.178
4.173
4.160
4.155
4.143
4.125
4.107
1.809
1.803
1.796
1.792
1.780
1.775
1.637
1.625
1.615
1.602
1.595
1.513
1.502
1.490
1.479
1.291
1.272
1.254
1.236
0.932
0.917
0.901
0.077
0.051
3.98
1.44
0.84
1.07
4.85
15.31
3.00
3.00
ppm

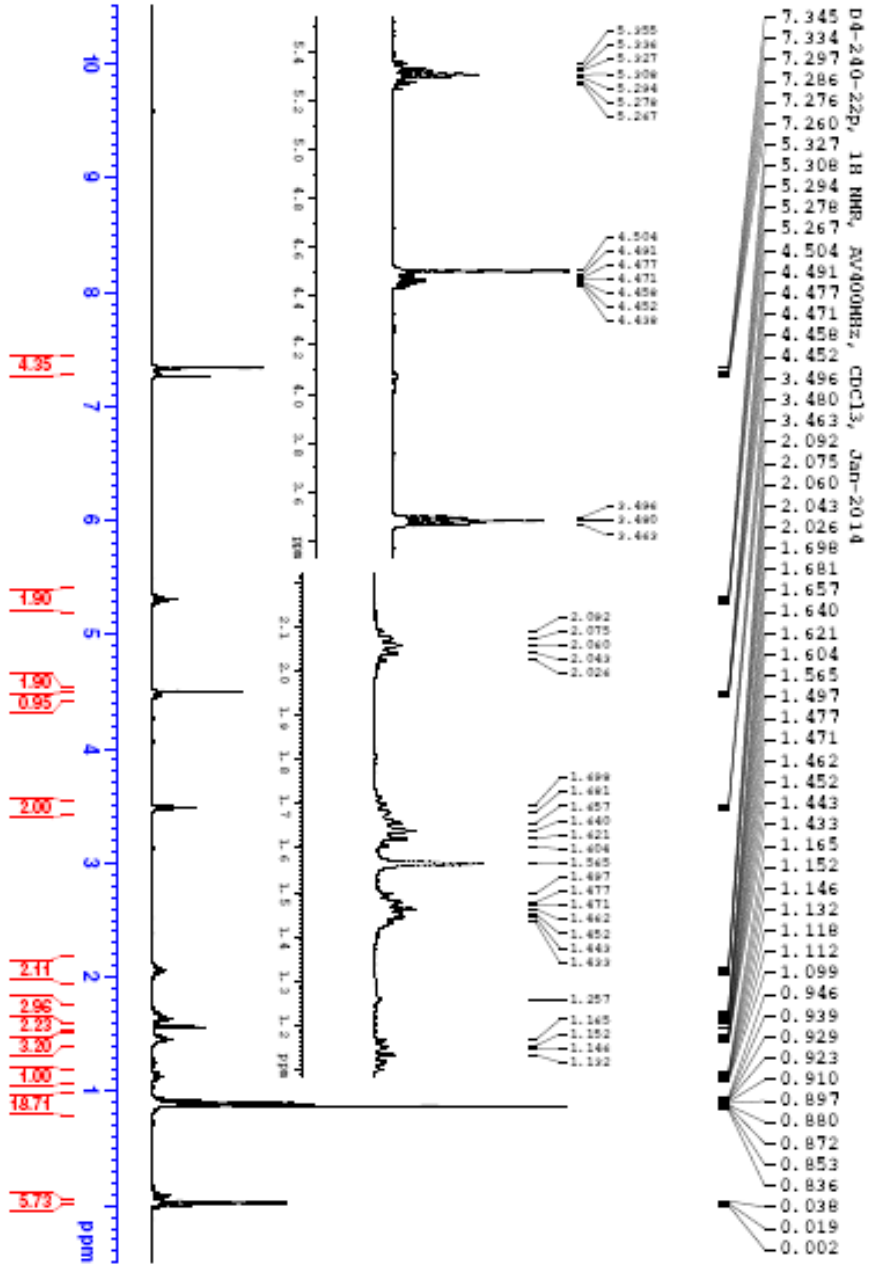

D4-204-2p, 13C, AV 400, CDCl3, Nov 2013
176.36
70.89
60.62
44.19
25.74
24.06
23.34
21.65
18.29
14.21
-4.91
-5.33
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

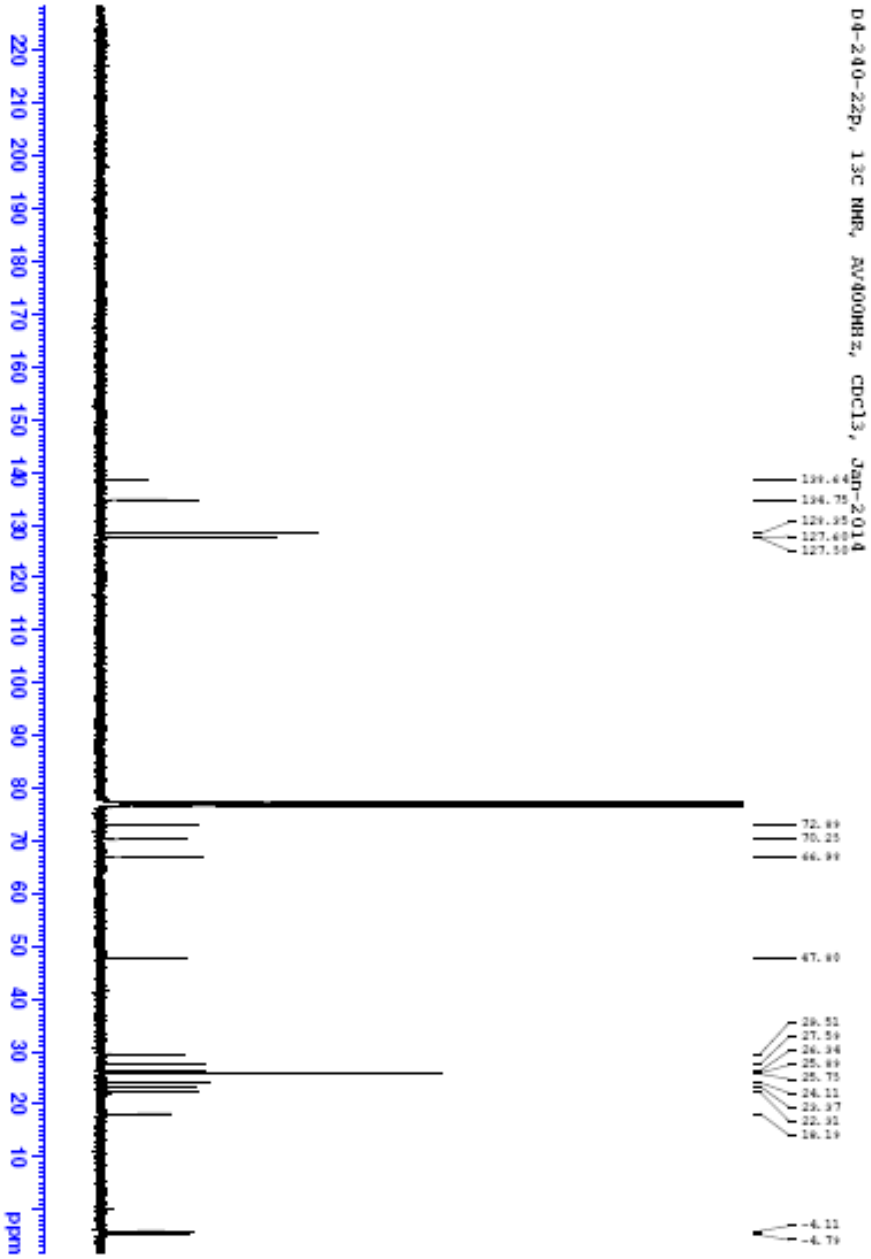

OTBS
CHO

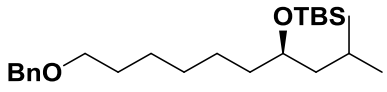

D4-210-1p 1H, AV 400, CDCl3, Nov 2013
9.583
9.578
7.259
4.040
4.035
4.028
4.023
4.019
4.014
4.007
4.002
1.836
1.820
1.802
1.785
1.768
1.555
1.541
1.533
1.520
1.507
1.499
1.485
1.451
1.439
1.430
1.418
1.405
1.396
1.384
0.941
0.91
1.00
1.13
0.99
1.08
17.42
6.78
ppm

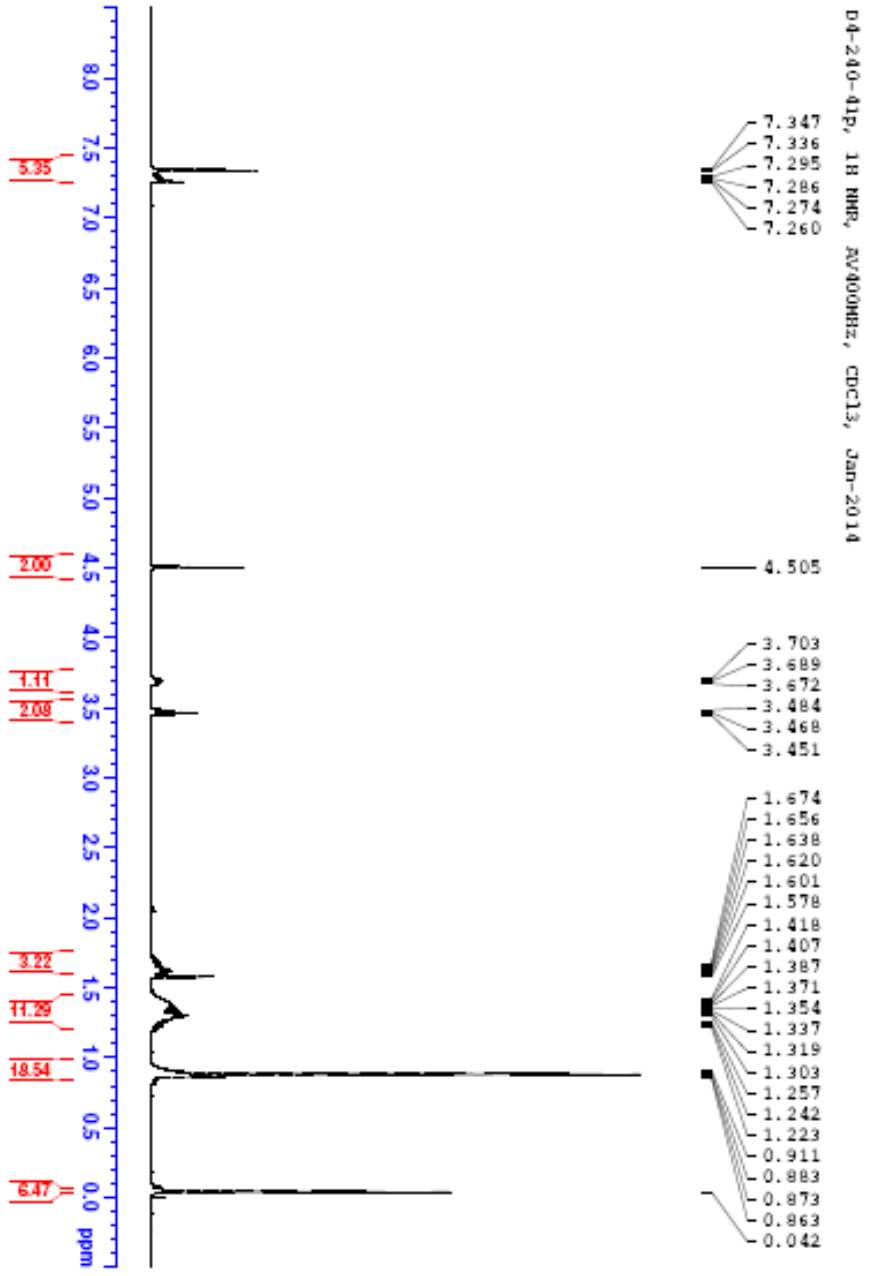

D4-210-1p 13C, AV 400, CDCl3, Nov 2013
204.33
41.39
25.75
23.64
23.40
21.95
19.17
-4.48
-4.97
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

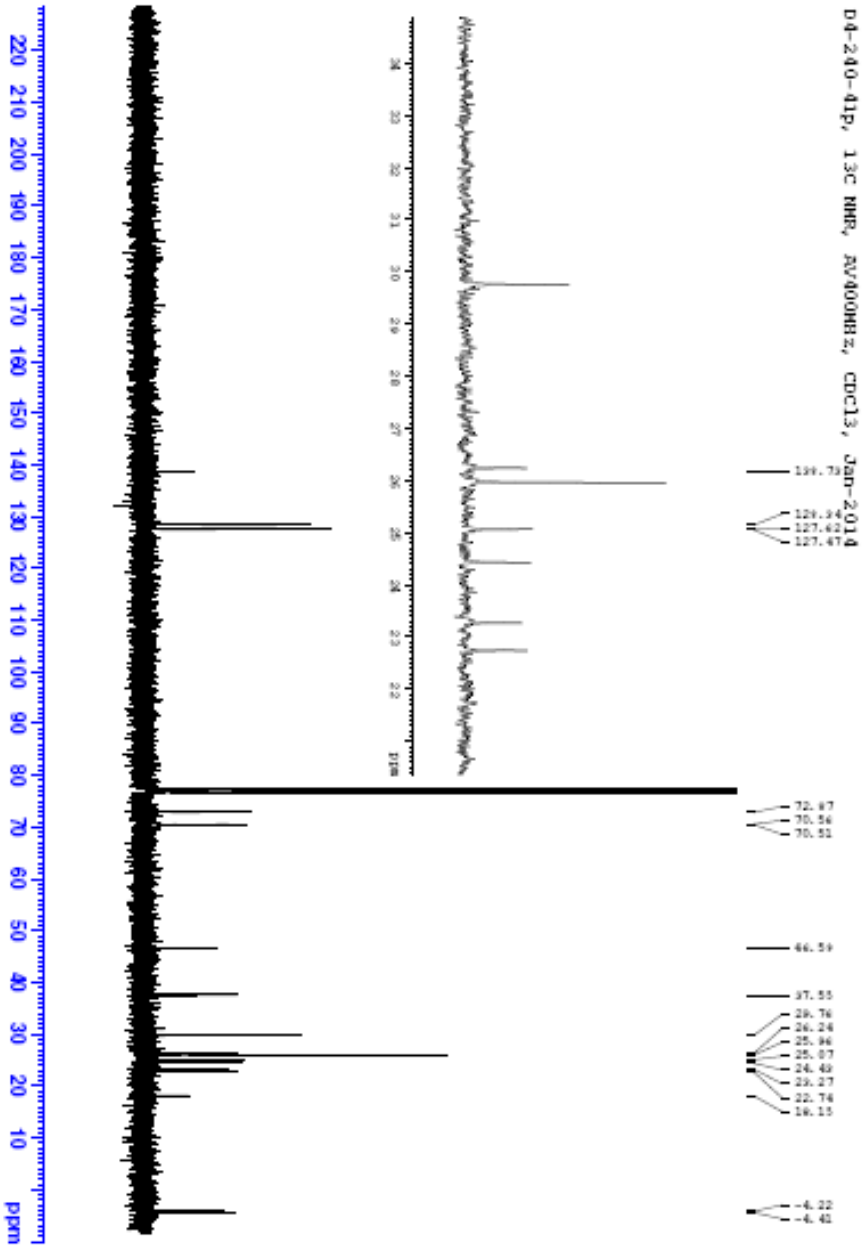

OTBS
BnO

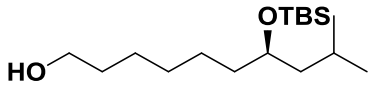

D4-240-22p, 1H NMR, AV400MHz, CDCl3, Jan-2014
7.345
7.334
7.297
7.286
7.276
7.260
5.327
5.308
5.294
5.278
5.267
4.504
4.491
4.477
4.471
4.458
4.452
3.496
3.480
3.463
2.092
2.075
2.060
2.043
2.026
1.698
1.681
1.657
1.640
1.621
1.604
1.565
1.497
1.477
1.471
1.462
1.452
1.443
1.433
1.165
1.152
1.146
1.132
1.118
1.112
1.099
0.946
0.939
0.929
0.923
0.910
0.897
0.880
0.872
0.853
0.836
0.038
0.019
0.002
4.35
1.90
1.90
0.95
2.00
2.11
2.96
2.23
3.20
1.00
18.71
5.73
ppm

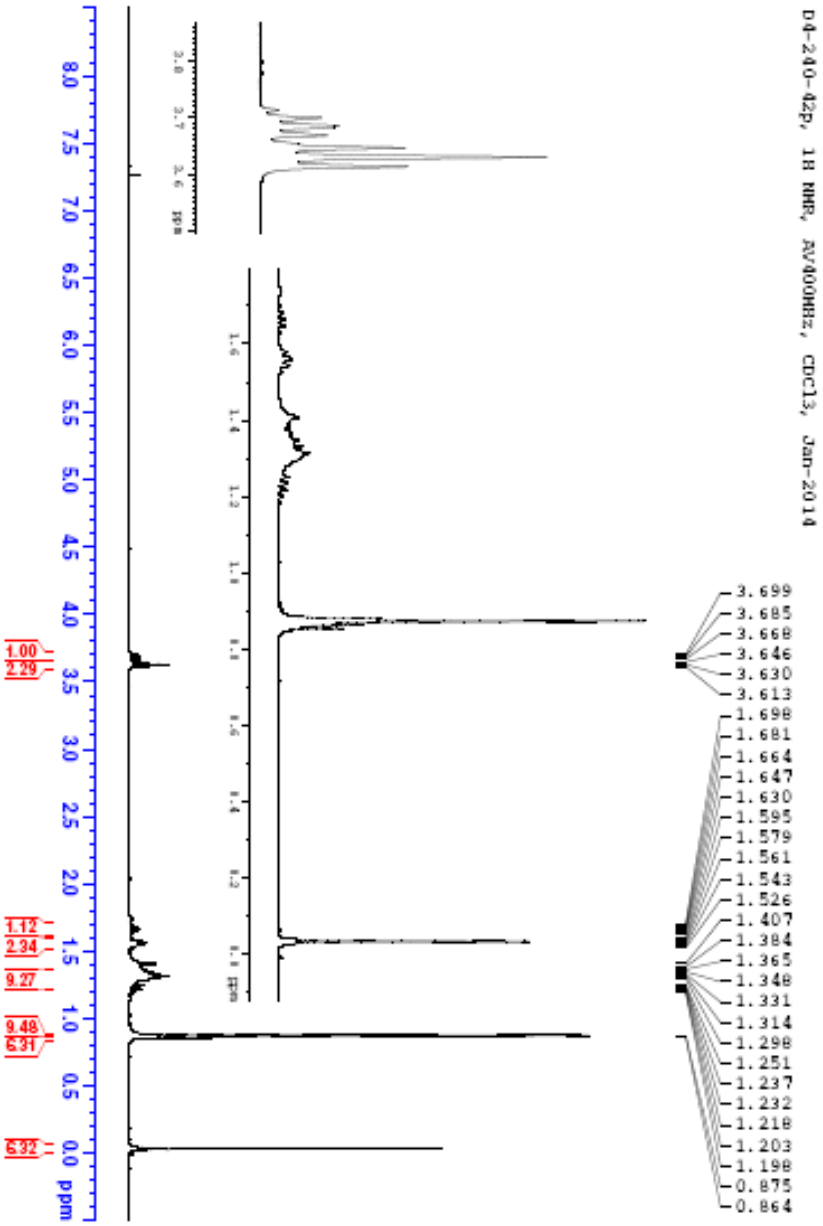

D4-240-22P, 13C NMR, AV600MHz, CDCl3, Jan-2014
139.64
136.75
129.35
127.60
127.50
72.89
70.25
66.99
47.80
29.51
27.59
26.34
25.89
25.75
24.11
23.37
22.31
18.19
-4.11
-4.79
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

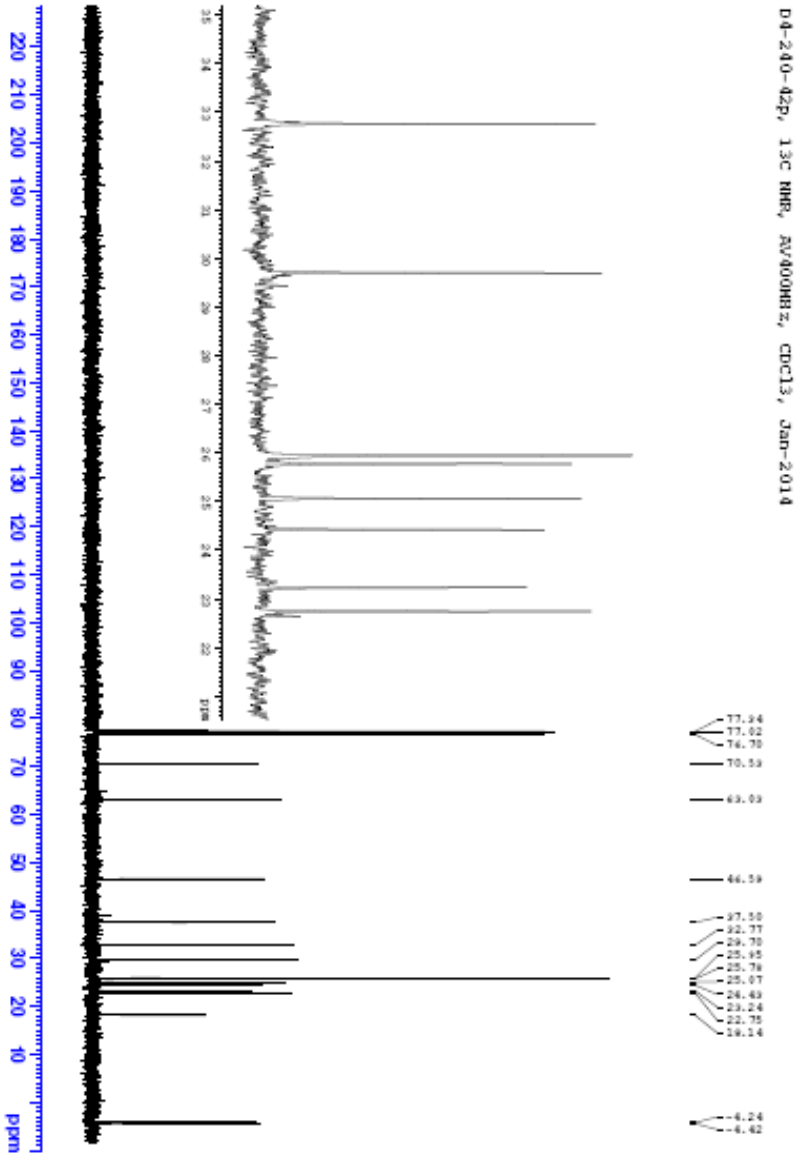

OTBS
BnO

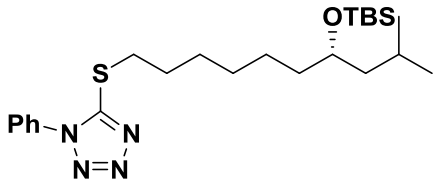

D4-240-41p, 1H NMR, AV400MHz, CDCl3, Jan-2014
7.347
7.336
7.295
7.286
7.274
7.260
4.505
3.703
3.689
3.672
3.484
3.468
3.451
1.674
1.656
1.638
1.620
1.601
1.578
1.418
1.407
1.387
1.371
1.354
1.337
1.319
1.303
1.257
1.242
1.223
0.911
0.883
0.873
0.863
0.042
5.35
2.00
1.11
2.08
3.22
11.29
18.54
6.47
ppm

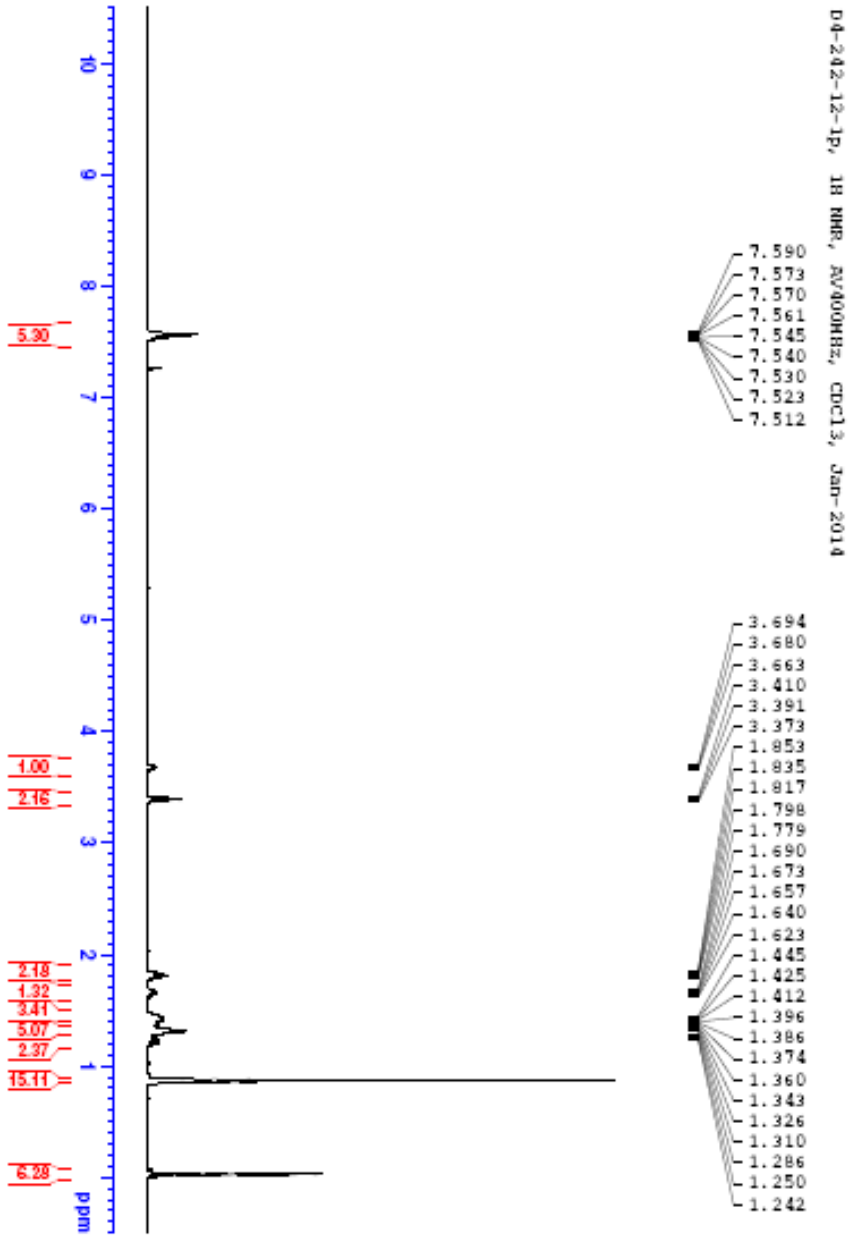

D4-240-41p, 13C NMR, AV400MHz, CDCl3, Jan-2014
139.79
129.34
127.62
127.47
72.87
70.56
70.51
66.59
37.55
29.76
26.24
25.96
25.87
24.49
23.27
22.74
14.15
-4.22
-4.41
ppm

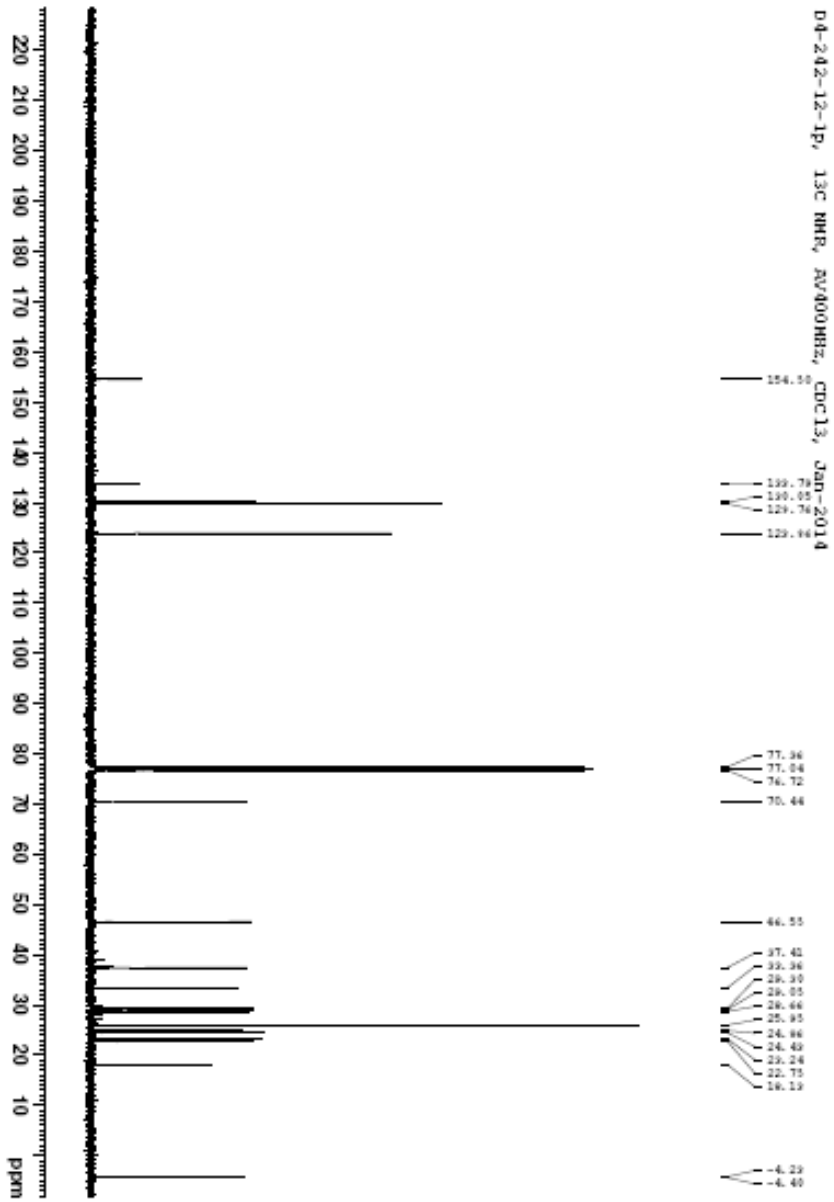

OTBS
HO

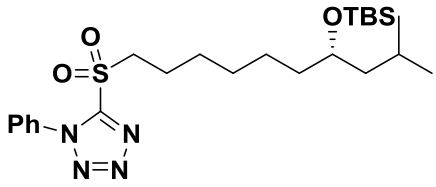

D4-240-42p, 1H NMR, AV400MHz, CDCl3, Jan-2014
3.699
3.685
3.668
3.646
3.630
3.613
1.698
1.681
1.664
1.647
1.630
1.595
1.579
1.561
1.543
1.526
1.407
1.384
1.365
1.348
1.331
1.314
1.298
1.251
1.237
1.232
1.218
1.203
1.198
0.875
0.864
1.00
2.29
1.12
2.34
9.27
9.48
6.31
6.32
ppm

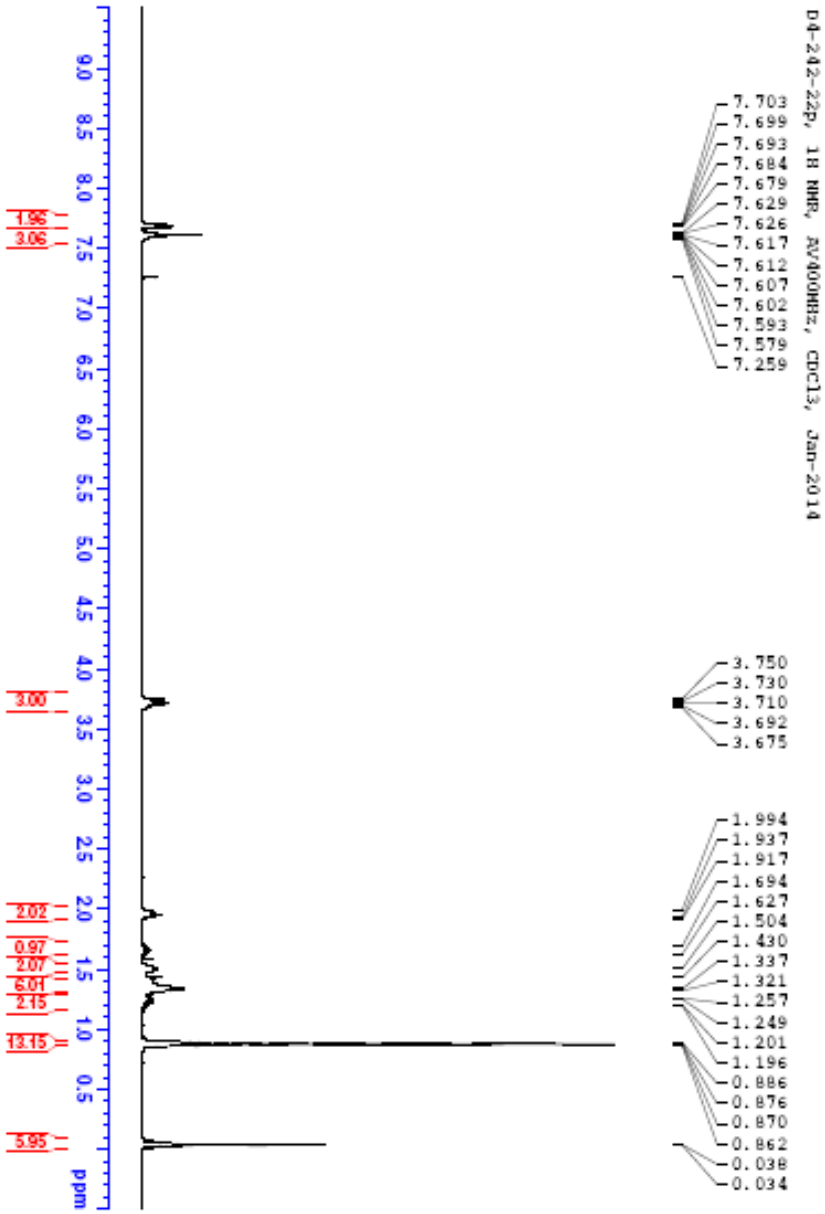

D4-240-42p, 13C NMR, AV400MHz, CDCl3, Jan-2014
77.34
77.02
76.70
70.59
63.03
46.59
37.50
32.77
29.70
25.95
25.78
25.07
24.63
23.24
22.75
19.14
-4.24
-4.42
ppm

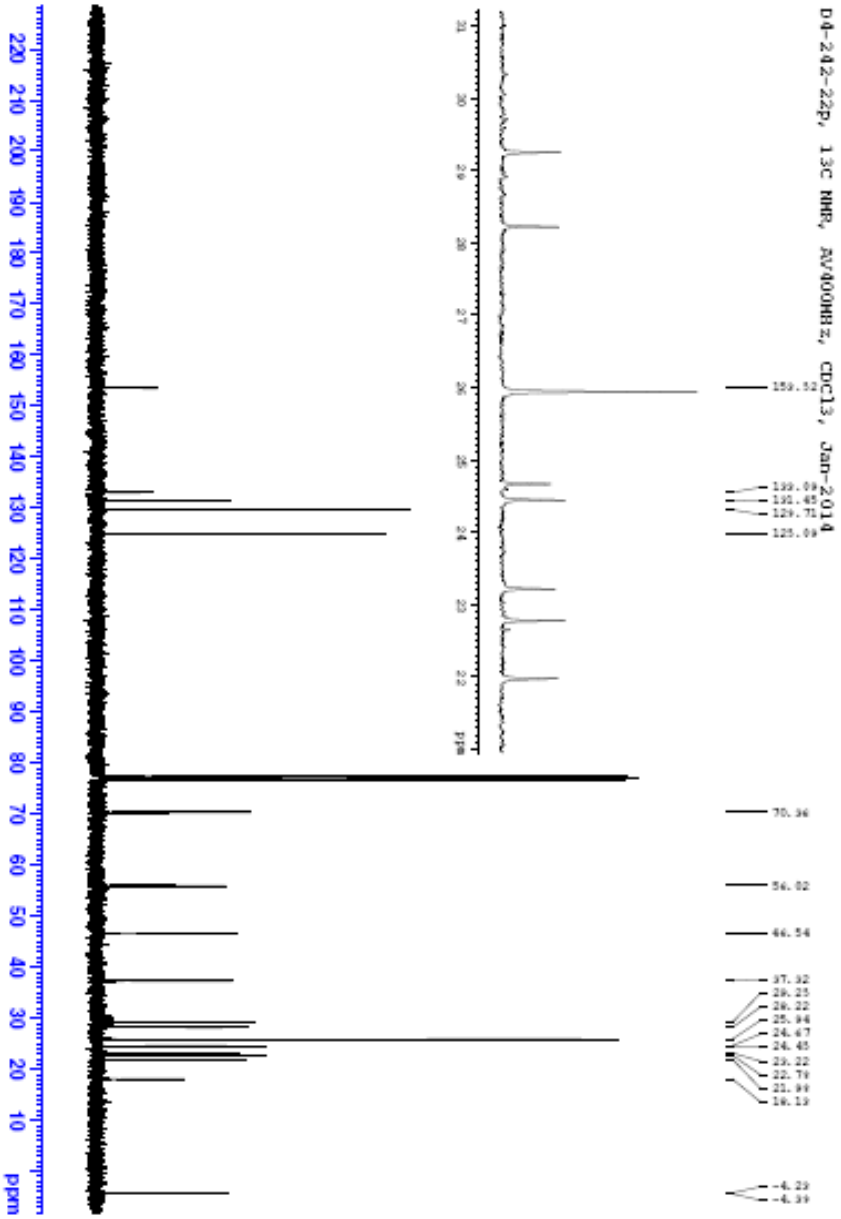

OTBS
S
Ph
N
N
N
N

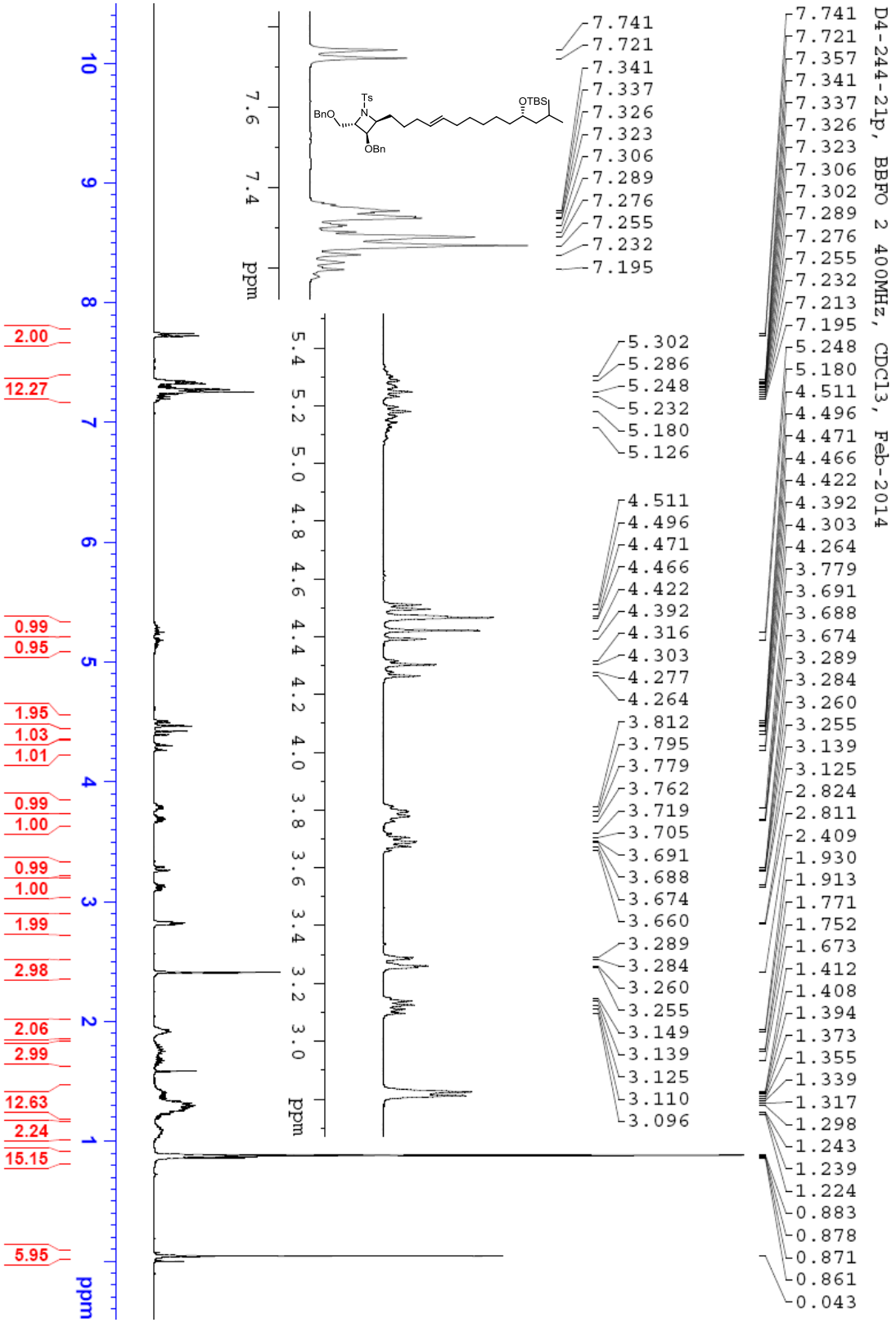

D4-242-12-1p, 1H NMR, AV400MHz, CDCl3, Jan-2014
7.590
7.573
7.570
7.561
7.545
7.540
7.530
7.523
7.512
3.694
3.680
3.663
3.410
3.391
3.373
1.853
1.835
1.817
1.798
1.779
1.690
1.673
1.657
1.640
1.623
1.445
1.425
1.412
1.396
1.386
1.374
1.360
1.343
1.326
1.310
1.286
1.250
1.242
5.30
1.00
2.16
2.18
1.32
3.41
5.07
2.37
15.11
6.28
ppm

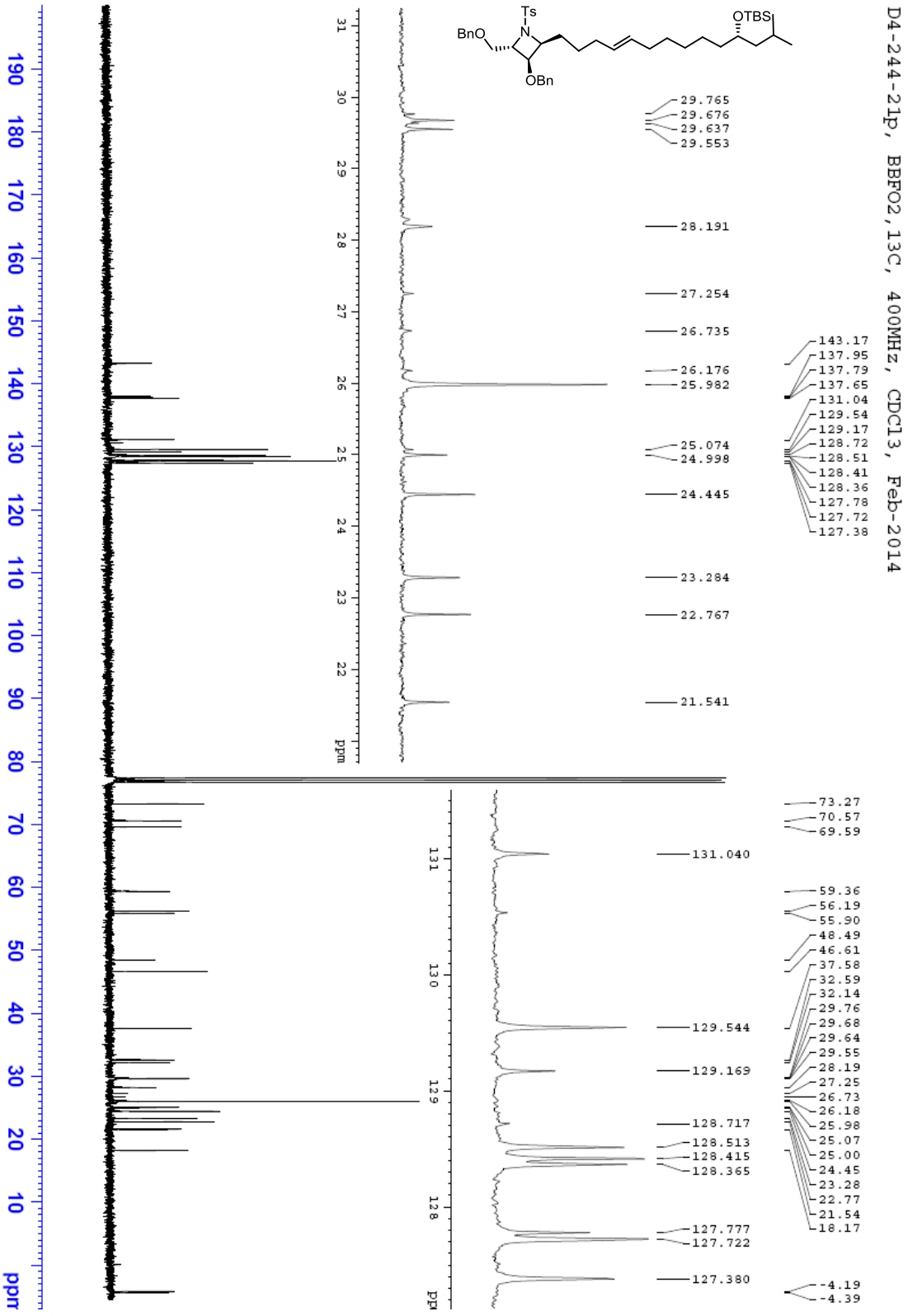

D4-242-12-1p, 13C NMR, AV400MHz, CDCl3, Jan-2014
154.50
133.78
130.05
129.76
129.44
77.36
77.04
76.72
70.44
66.55
37.41
33.36
29.30
29.05
28.66
25.95
24.86
24.43
23.24
22.75
18.13
-4.23
-4.40
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

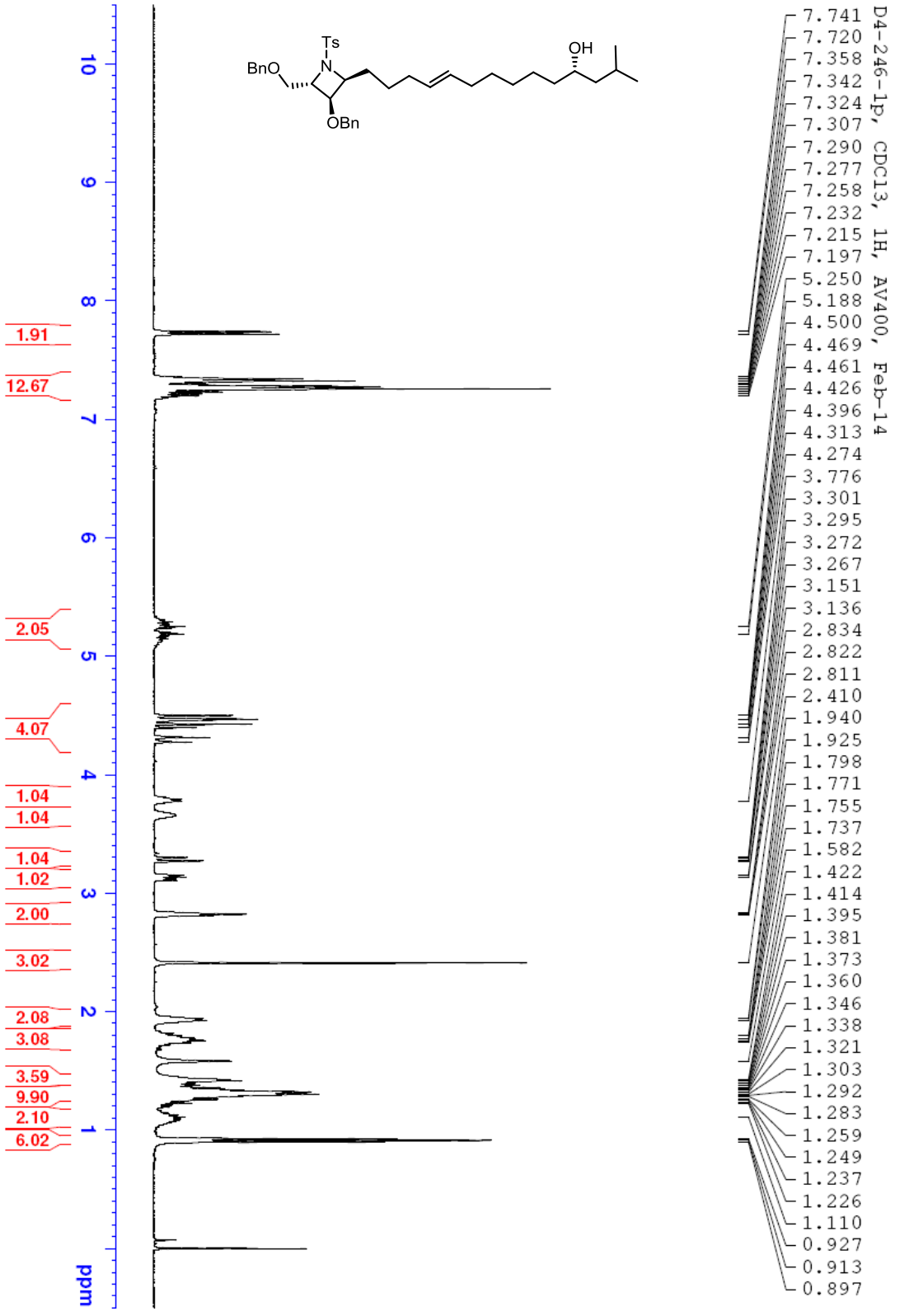

OTBS
O
O=S
Ph
N
N
N=N

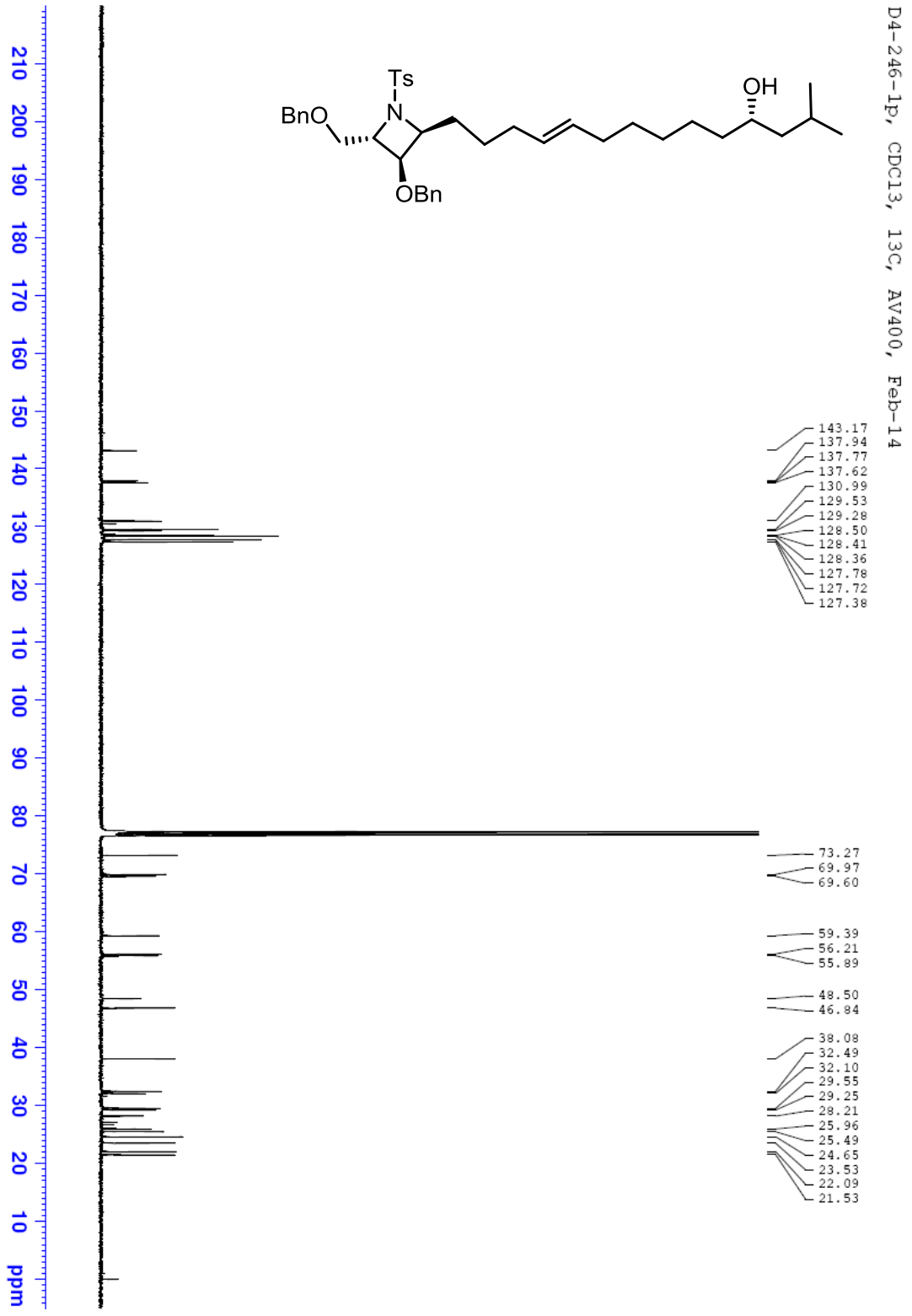

D4-242-22p, 1H NMR, AV400MHz, CDCl3, Jan-2014
7.703
7.699
7.693
7.684
7.679
7.629
7.626
7.617
7.612
7.607
7.602
7.593
7.579
7.259
3.750
3.730
3.710
3.692
3.675
1.994
1.937
1.917
1.694
1.627
1.504
1.430
1.337
1.321
1.257
1.249
1.201
1.196
0.886
0.876
0.870
0.862
0.038
0.034
1.96
3.06
3.00
2.02
0.97
2.07
6.01
2.15
13.15
5.95
ppm

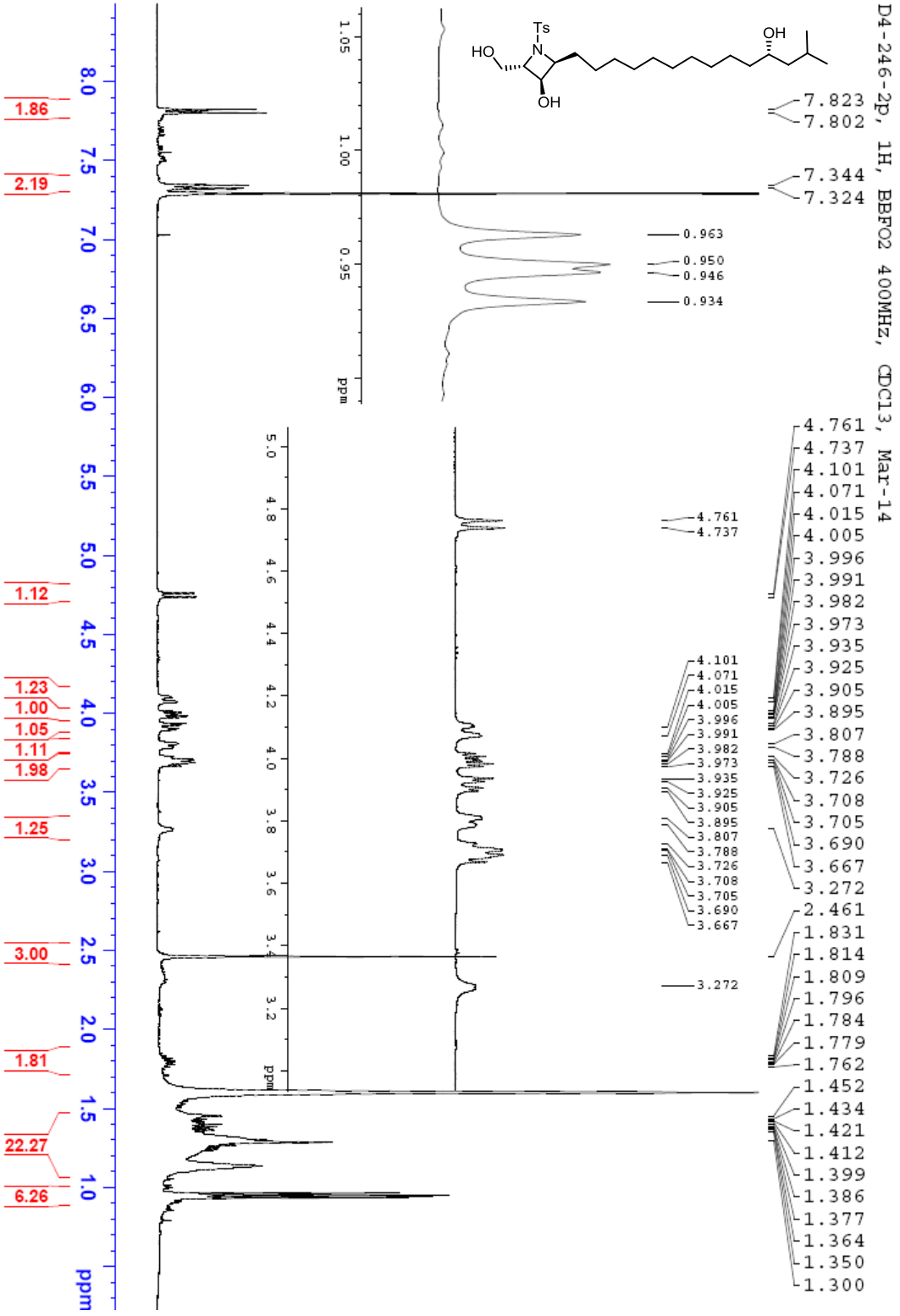

D4-242-22p, 13C NMR, AV400MHz, CDCl3, Jan-2014
159.52
133.09
131.45
129.71
125.09
70.36
56.02
46.54
37.32
29.25
28.22
25.94
24.47
24.45
23.22
22.79
21.99
10.19
-4.29
-4.39
ppm

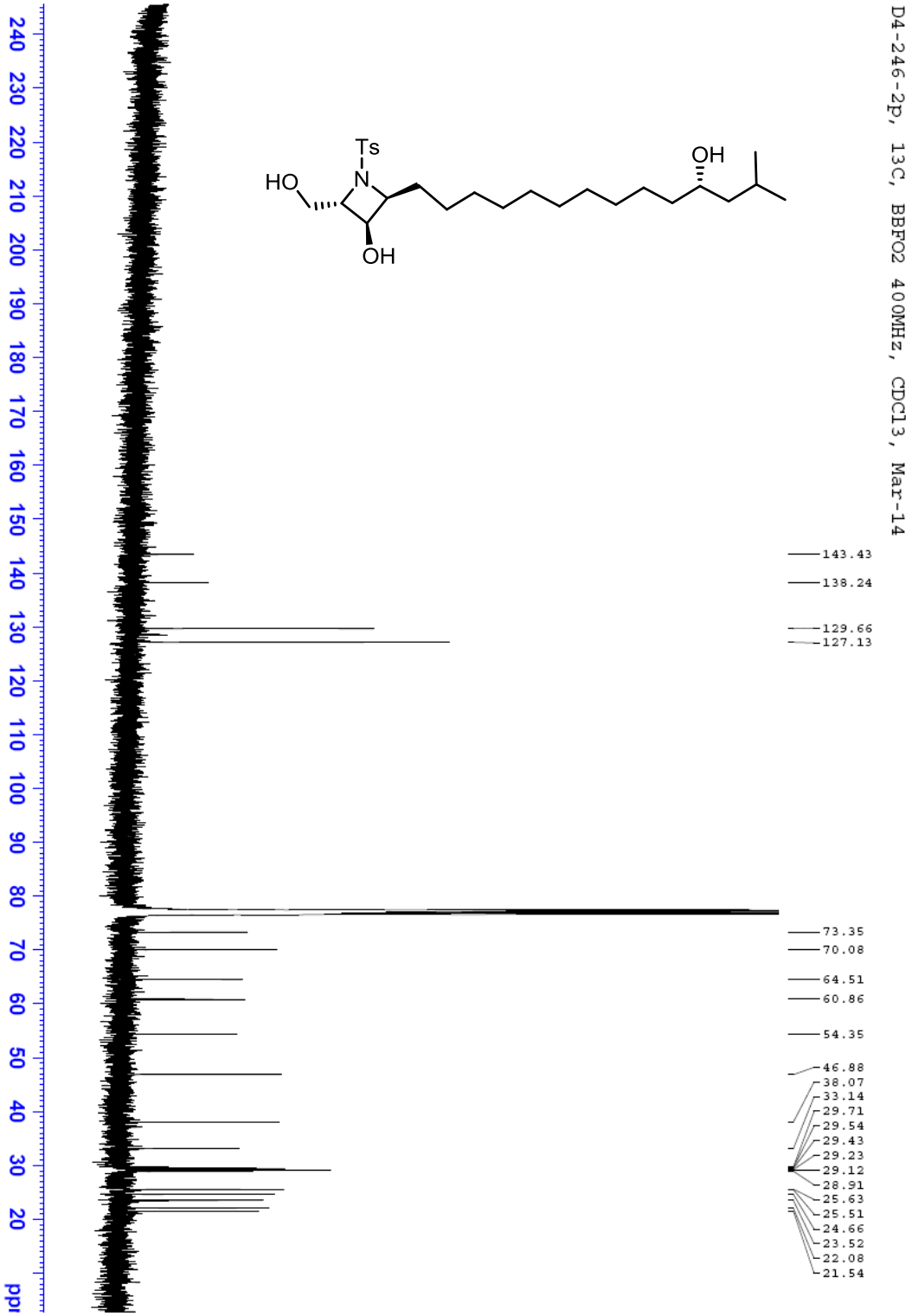

D4-244-21p, BBFO 2 400MHz, CDCl3, Feb-2014
Ts
N
BnO
OBn
OTBS
7.741
7.721
7.357
7.341
7.337
7.326
7.323
7.306
7.302
7.289
7.276
7.255
7.232
7.213
7.195
5.248
5.180
4.511
4.496
4.471
4.466
4.422
4.392
4.303
4.264
3.779
3.691
3.688
3.674
3.289
3.284
3.260
3.255
3.139
3.125
2.824
2.811
2.409
1.930
1.913
1.771
1.752
1.673
1.412
1.408
1.394
1.373
1.355
1.339
1.317
1.298
1.243
1.239
1.224
0.883
0.878
0.871
0.861
0.043
5.302
5.286
5.248
5.232
5.180
5.126
4.511
4.496
4.471
4.466
4.422
4.392
4.316
4.303
4.277
4.264
3.812
3.795
3.779
3.762
3.719
3.705
3.691
3.688
3.674
3.660
3.289
3.284
3.260
3.255
3.149
3.139
3.125
3.110
3.096
2.00
12.27
0.99
0.95
1.95
1.03
1.01
0.99
1.00
0.99
1.00
1.99
2.98
2.06
2.99
12.63
2.24
15.15
5.95
ppm


D4-244-21p, BBFO2,13C, 400MHz, CDCl3, Feb-2014
Ts
N
BnO
OBn
OTBS
29.765
29.676
29.637
29.553
28.191
27.254
26.735
26.176
25.982
25.074
24.998
24.445
23.284
22.767
21.541
143.17
137.95
137.79
137.65
131.04
129.54
129.17
128.72
128.51
128.41
128.36
127.78
127.72
127.38
73.27
70.57
69.59
131.040
59.36
56.19
55.90
48.49
46.61
37.58
32.59
32.14
29.76
29.68
29.64
29.55
28.19
27.25
26.73
26.18
25.98
25.07
25.00
24.45
23.28
22.77
21.54
18.17
129.544
129.169
128.717
128.513
128.415
128.365
127.777
127.722
127.380
-4.19
-4.39
ppm


Ts
N
BnO
OBn
OH
10
9
8
7
6
5
4
3
2
1
ppm
1.91
12.67
2.05
4.07
1.04
1.04
1.04
1.02
2.00
3.02
2.08
3.08
3.59
9.90
2.10
6.02
D4-246-1p, CDCl3, 1H, AV400, Feb-14
7.741
7.720
7.358
7.342
7.324
7.307
7.290
7.277
7.258
7.232
7.215
7.197
5.250
5.188
4.500
4.469
4.461
4.426
4.396
4.313
4.274
3.776
3.301
3.295
3.272
3.267
3.151
3.136
2.834
2.822
2.811
2.410
1.940
1.925
1.798
1.771
1.755
1.737
1.582
1.422
1.414
1.395
1.381
1.373
1.360
1.346
1.338
1.321
1.303
1.292
1.283
1.259
1.249
1.237
1.226
1.110
0.927
0.913
0.897


D4-246-1p, CDCl3, 13C, AV400, Feb-14
Ts
N
BnO
OBn
OH
143.17
137.94
137.77
137.62
130.99
129.53
129.28
128.50
128.41
128.36
127.78
127.72
127.38
73.27
69.97
69.60
59.39
56.21
55.89
48.50
46.84
38.08
32.49
32.10
29.55
29.25
28.21
25.96
25.49
24.65
23.53
22.09
21.53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


D4-246-2p, 1H, BBFO2 400MHz, CDCl3, Mar-14
Ts
N
HO
OH
OH
7.823
7.802
7.344
7.324
0.963
0.950
0.946
0.934
4.761
4.737
4.101
4.071
4.015
4.005
3.996
3.991
3.982
3.973
3.935
3.925
3.905
3.895
3.807
3.788
3.726
3.708
3.705
3.690
3.667
3.272
2.461
1.831
1.814
1.809
1.796
1.784
1.779
1.762
1.452
1.434
1.421
1.412
1.399
1.386
1.377
1.364
1.350
1.300
1.86
2.19
1.12
1.23
1.00
1.05
1.11
1.98
1.25
3.00
1.81
22.27
6.26
ppm


D4-246-2p, 13C, BBFO2 400MHz, CDCl3, Mar-14
Ts
N
HO
OH
OH
143.43
138.24
129.66
127.13
73.35
70.08
64.51
60.86
54.35
46.88
38.07
33.14
29.71
29.54
29.43
29.23
29.12
28.91
25.63
25.51
24.66
23.52
22.08
21.54
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm