Enantioselective syntheses of (*R*)-pipecolic, (2*R*,3*R*)-3-hydroxypipecolic acid, *β*-(+)-conhydrine and (-)-swainsonine using aziridine derived common chiral synthon

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Supporting Information

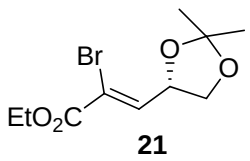
Contents:

General information:

All reagents and solvents were used as received from the manufacturer. HRMS (ESI) were recorded on ORBITRAP mass analyser (Thermo Scientific, Q Exactive). Mass spectra were measured with ESI ionization in MSQ LCMS mass spectrometer. IR spectra were recorded on a Perkin-Elmer Infrared Spectrophotometer Model 68B or on a Perkin-Elmer 1615 FT Infrared spectrophotometer. Melting points of solids were measured in Buchi melting point apparatus and are uncorrected. Optical rotation values were recorded on P-2000 polarimeter at 589 nm. ^{1}H (200 and 400 MHz) and ^{13}C (50 and 100 MHz) NMR spectra were recorded on Bruker and Bruker Advance 400 spectrometers, using a 1:1 mixture of $CDCl_3$ and CCl_4 as solvent. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion with reference to chloroform, δ 7.27 (for ^{1}H) or the central line (77.0 ppm) of $CDCl_3$ (for ^{13}C). In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2, or CH_3) was determined by recording the DEPT-135 spectra. The following abbreviations were used to explain the multiplicities: br = broad, s = singlet, d = doublet, t = triplet, q = quartet. The reaction progress was monitored by the TLC analysis using thin layer plates precoated with silica gel 60 F_{254} (Merck) and visualized by fluorescence quenching or iodine or by charring after treatment with ethanolic solution of ninhydrin or anisaldehyde. Merck's flash silica gel (230-400 mesh) was used for column chromatography.

Experimental:

(*S*)-Ethyl 2-bromo-3-(2,2-dimethyl-1,3-dioxolan-4-yl)acrylate (21):[1] Freshly prepared (*R*)-glyceraldehyde acetonide **20** (5.24 g, 0.020 mol) from Di-*O*-isopropylidene (D)-mannitol **19** was taken in CH_2Cl_2 (75 mL). To this was added a solution of ethyl 2-bromo-2-(triphenylphosphoranylidene)acetate[2] **(**18.8 g, 0.044 mol) in CH_2Cl_2 (150 mL) and stirred for 2 h at room temperature. Organic layer was separated and aqueous layer was extracted with CH_2Cl_2. Combined organic layer was dried over anhydrous Na_2SO_4, filtered and solvent was evaporated under reduced pressure. Residue was purified by column chromatography using pet. ether: ethyl acetate (95:5) to give bromoester **21** (*E/Z* = 7:93). R_f: 0.5 (pet. ether-ethyl acetate, 9:1); Yield: 10.5 g, 84% over two steps; IR ($CHCl_3$, cm^{-1}): νmax 2980, 1720, 1620; ^{1}H NMR (200 MHz, $CDCl_3$+CCl_4): *δ* 1.36 (t, *J* = 8.0 Hz, 3H), 1.41 (s, 3H), 1.46 (s, 3H), 3.70 (dd, *J* = 6.6 & 8.3 Hz, 1H), 4.27 (q, *J* = 8.0 Hz, 3H), 4.95 (dd, *J* = 6.7 & 13.3 Hz, 1H), 7.36 (d, *J* = 6.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$+CCl_4): *δ* 14.1, 25.5, 26.4, 62.6, 68.0, 75.5, 110.2, 116.7, 144.0, 161.4. MS (ESI): *m/z*: 279 $(M+H)^+$.



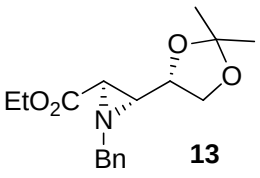
21

E/Z = 7: 93

(2*R*,3*R*)-Ethyl 1-benzyl-3-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)aziridine-2-carboxylate (13): 8.37 g (0.030 mol) of bromoacrylate **3** was dissolved in dry toluene (100 mL) and the solution was stirred. To stirred solution was added 3.21 g (0.030 mol) of benzylamine and 3.03 g (0.030 mol) of triethylamine at −5 °C. The reaction mixture was stirred for 24 h at room temperature. Solvent was filtered on simple filter paper, residue was again washed with toluene (20 mL) and concentrated under reduced pressure to yield yellow oil of *trans* aziridine **13** as major isomer and *cis* aziridine **33** as minor isomer in ratio of 9:1

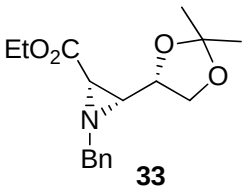
which were separated using flash chromatography (pet. ether-ethyl acetate, 9:1). Yield: 75%; For **13**- Yield: 68%; For **33**- Yield: 7%

(2*R*,3*R*)-Ethyl 1-benzyl-3-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)aziridine-2-carboxylate (13): R_f: 0.5 (pet. ether-ethyl acetate, 8:2); IR ($CHCl_3$, cm^{-1}): νmax 2984, 1728, 1599, 1107. $[\alpha]_D^{25}$ +52.41 (*c* 1, $CHCl_3$), {Lit.[1] $[\alpha]_D^{25}$ +52.8 (*c* 1, $CHCl_3$)}.^{1}H NMR (200 MHz, $CDCl_3$+CCl_4): δ 1.19 (t, *J* = 8 Hz, 3H), 1.34 (s, 3 H), 1.42 (s, 3 H), 2.48 (t, *J* = 2.4 Hz, 1H), 2.63 (d, *J* = 2.4 Hz, 1H), 3.63-3.68 (m, 1H), 3.86-3.97 (m, 3H), 4.07-4.17 (m, 3H), 7.27-7.32 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$+CCl_4): δ 14.0, 25.5, 26.6, 37.2, 47.4, 54.8, 60.1, 66.4, 75.9, 109.5, 126.9, 128.1, 138.8, 168.5; MS (ESI): *m/z*: 306.71 $[M+H]^+$; HRMS: Calculated for $C_{17}H_{24}NO_4$-306.1700, found-306.1694.



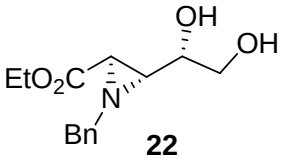
13
trans

(2*S*,3*R*)-Ethyl 1-benzyl-3-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)aziridine-2-carboxylate (33): R_f: 0.4 (pet. ether-ethyl acetate, 8:2); IR ($CHCl_3$, cm^{-1}): νmax 2986, 1728, 1600, 1107; $[\alpha]_D^{25}$ −9.7 (*c* 1, $CHCl_3$), {Lit.[1] $[\alpha]_D^{25}$ −9.9 (*c* 1, $CHCl_3$)}; ^{1}H NMR (200 MHz, $CDCl_3$+CCl_4): δ 1.18 (t, 3H), 1.27 (s, 3 H), 1.37 (s, 3H), 2.08 (t, *J* = 6.7 Hz, 1H), 2.23 (d, *J* = 6.7 Hz, 1H), 3.42 (d, *J* = 13.0 Hz, 1H), 3.66 (dd, *J* = 6.0 & 8.0 Hz, 1H), 3.89-3.97 (m, 2H), 4.11-4.22 (m, 3H), 7.27-7.35 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$+CCl_4): δ 14.1, 25.3, 26.8, 40.4, 47.8, 61.0, 63.2, 66.9, 75.2, 109.6, 127.2, 127.9, 128.2, 137.2 , 168.9; MS (ESI): *m/z*: 306.18 $[M+H]^+$; HRMS: Calculated for $C_{17}H_{24}NO_4$-306.1700, found-306.1698.



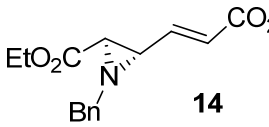
33

(2*R*,3*R*)-Ethyl -1-benzyl-3-((*S*)-1,2-dihydroxyethyl)aziridine-2-carboxylate (22): To a stirred, ice-cold solution of the aziridine acetonide **13** (0.163 g, 0.53 mmol) in anhydrous CH_2Cl_2 (2 mL) under an inert atmosphere, was added TMSOTf (0.24 mL, 1.3 mmol) through a syringe. The resulting solution was stirred at the same temperature for 1h, followed by quenching the reaction by addition of a saturated aqueous $NaHCO_3$ solution. After stirring the mixture for 5 min, the organic layer was separated and the aqueous layer was saturated with solid NaCl and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered. Concentration of the solvent under reduced pressure and column chromatographic purification (pet. ether-ethyl acetate, 7:3) of the residue provided the pure acetonide-cleaved product **22** as a thick liquid (0.127 g). R_f: 0.4 (pet. ether-ethyl acetate, 1:1); Yield: 90%; $[\alpha]_D^{25}$ +20.22 (*c* 2.1, $CHCl_3$), {Lit[3] $[\alpha]_D^{25}$ +19.6 (*c* 0.56, $CHCl_3$)}; IR ($CHCl_3$, cm^{-1}): νmax 3588, 3369, 2927, 1727, 1603, 1454, 1371, 1193; ^{1}H NMR (200 MHz, $CDCl_3$+CCl_4): δ 1.23 (t, *J* = 7.2 Hz, 3H), 2.52 (t, *J* = 2.9 Hz, 1H), 2.75 (d, *J* = 2.9 Hz, 1H), 3.26-3.32 (m, 1H), 3.44-3.50 (m, 1H), 3.61 (br s, 1H), 3.96 (s, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 7.27-7.31 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$+CCl_4): δ 14.1, 37.4, 46.4, 54.4, 61.3, 65.2, 69.1, 127.5, 128.5, 128.6, 138.4, 168.5; MS (ESI): *m/z*: 266.13 $(M+H)^+$, 288.10 $(M+Na)^+$; HRMS: Calculated for $C_{14}H_{20}O_4N$-266.1387, found-266.1385.



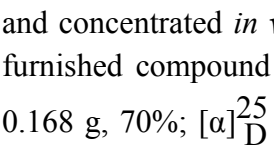
22

(2*R*,3*S*)-Ethyl 1-benzyl-3-((E)-3-ethoxy-3-oxoprop-1-en-1-yl)aziridine-2-carboxylate (14): Diol **22** (0.21 g, 0.79 mmol) was dissolved in acetone–water (3 mL, 2:1) at 0 ℃, treated with sodium metaperiodate (0.203 g, 0.95 mmol) and stirred at 15 ℃ for 15 min. The reaction was quenched using ethylene glycol (0.01 mL), extracted with CH_2Cl_2 (3 × 15 mL), washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated to afford crude aldehyde which was used as such for next reaction. To a stirred solution of NaH (0.038 g, 1.58 mmol, prewashed with *n*-hexane) dissolved in THF (2 mL), was added triethyl phosphonoacetate (0.31 mL, 1.58 mmol) slowly at 0 °C and stirred for 10 minutes. The aldehyde from above reaction dissolved in dry THF (3 mL) was added and stirring continued for another 2 h at same temperature until completion of reaction. The reaction was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were then washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Purification on flash column chromatography (pet. ether-ethyl acetate, 9:1) furnished compound **14** (0.168 g) as thick colorless oil. R_f: 0.5 (pet. ether-ethyl acetate, 8:2); Yield: 0.168 g, 70%; $[\alpha]_D^{25}$ −36 (*c* 1, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): νmax 2926, 2850, 1720, 1651, 1456, 1368, 1265, 1180, 1030; ^1H NMR (200 MHz, $CDCl_3$+CCl_4): δ 1.22-1.32 (m, 6H), 2.55-2.73 (m, 1H), 2.46-3.17 (m, 1H), 3.84-4.20 (m, 8H), 6.05-6.25 (m,1H), 6.60-6.89 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$+CCl_4): δ 14.0, 14.1, 42.9, 45.9, 54.4, 60.2, 61.1, 123.3, 127.6, 127.9, 128,2, 138.4, 145.3, 165.4, 167.8; doubling of peaks in ^1H and ^{13}C is attributed to invertomerism; MS (ESI): *m/z*: 303.28 $(M)^+$, 326.21 $(M+Na)^+$; HRMS: Calculated for $C_{17}H_{21}NO_4Na$-326.1363, found-326.1358.

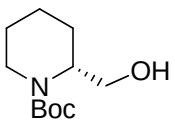


14

(*R*)-Ethyl 6-oxopiperidine-2-carboxylate (7): To a stirred solution of compound **14** (0.15 g, 0.49 mmol) in ethanol (5 mL) was added ammonium formate (0.27 g, 4.9 mmol) and 10% Pd/C (0.05 g) and refluxed for 1 h under nitrogen atmosphere. Reaction mass was filtered through celite, dried and column purified (pet. ether: ethyl acetate, 10:90) to yield 0.071 g of amide-ester **7** as colourless liquid. R_f: 0.3 (ethyl acetate); Yield: 85%; $[\alpha]_D^{25}$ +13.4 (*c* 1.4, $CHCl_3$) {Lit.[4] for *ent*-**7**, $[\alpha]_D^{25}$ −13.7 (*c* 0.3, $CHCl_3$)}; IR ($CHCl_3$, cm^{-1}): νmax 2958, 1739, 1666, 1468, 1198; ^1H NMR (200 MHz, $CDCl_3$+CCl_4): δ 1.30 (t, *J* = 7.3 Hz, 3H), 1.78-1.98 (m, 3H), 2.20-2.22 (m, 1H), 2.36-2.47 (m, 2H), 4.1 (dd, *J* = 5.5 & 7.0 Hz, 1H), 4.24 (qd, *J* = 1.2 & 7.3 Hz, 2H), 6.65 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$+CCl_4): δ 14.1, 19.2, 25.2, 30.7, 54.7, 61.9, 170.7, 171.9; MS (ESI): *m/z*: 194.08 $(M+Na)^+$; HRMS: Calculated for $C_8H_{14}O_3N$-172.0968, found-172.0966.



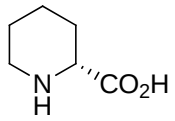
(*R*)-*tert*-Butyl 2-(hydroxymethyl)piperidine-1-carboxylate (15): To a stirred suspension of LAH (0.22g, 5.85 mmol) in dry THF (5 mL) was added amide **7** (0.2 g, 1.17 mmol) dissolved in dry THF (5 mL) slowly at 0 °C *via* syringe under inert atmosphere (N_2 gas). After stirring for 24 h at room temperature, the reaction mixture was cooled to 0 °C, quenched carefully with minimum amount of water followed by 15% NaOH (0.25 mL). Again water (1 mL) was added and stirred for 0.5 h at room temperature. Anhydrous Na_2SO_4 was added and stirring continued for another 0.5 h. Filtration through Celite and concentration under



15

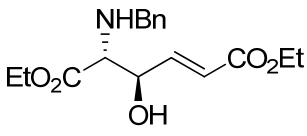
vacuum gave crude amine which was used as such for next reaction. To a solution of amine in THF:water (5 mL, 1:1) was added solid $NaHCO_3$ (0.2 g, 2.34 mmol) and $(Boc)_2O$ (0.536 mL, 2.34 mmol) and then the mixture was vigorously stirred at room temperature for 6 h. The reaction mixture was extracted with ethyl acetate (3 × 10 mL), washed with brine, dried over anhydrous Na_2SO_4, filtered, concentrated *in vacuo* and purified by column chromatography (pet. ether–ethyl acetate, 8:2) to afford **15** as a white solid. R_f: 0.5 (pet. ether-ethyl acetate, 8:2); Yield: 0.176 g, 70% over two steps; MP: 81-84 °C, lit[5] 81-84 °C; $[\alpha]_D^{25}$ +38.5 (*c* 1, $CHCl_3$) {For *ent*-**15** Lit[5] $[\alpha]_D^{25}$ −40.5 (*c* 1, $CHCl_3$)}; IR ($CHCl_3$, cm^{-1}): νmax 3443, 2940, 2890, 1655, 1280; ^1H NMR (200 MHz, $CDCl_3$+CCl_4): δ 1.46 (s, 9H), 1.60-1.65 (m, 6H), 2.11 (br s, 1H), 2.87 (t, *J* = 13.0 Hz, 1H), 3.59 (dd, *J* = 5.9 & 11.0 Hz, 1H), 3.79 (dd, *J* = 9.0 & 11.0 Hz, 1H), 3.93 (br d, *J* = 13.5 Hz, 1H), 4.25-4.29 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$+CCl_4): δ 19.3, 24.8, 25.1, 28.3, 39.7, 52.0, 60.6, 79.4, 155.8; MS (ESI): *m/z*: 238 $(M+Na)^+$; HRMS: Calculated for $C_{11}H_{22}O_3N$-216.1600, found-216.1954; HPLC detail for racemic hydroxy compound (**15**): HPLC Kromacil 5-Amycoat column (250×4.6 mm). Isopropanol/n-Hexane = 4:96; flow rate 0.5 ml/min, λ = 210 nm) retention time (min): rt1 = 22.18; rt2 = 24.05 (1:1). Enantiomerically pure hydroxy compound (**15**) HPLC Kromacil 5-Amycoat column (250 × 4.6 mm) isopropanol/n-Hexane = 4:96; flow rate 0.5 ml/min, λ = 210 nm) retention time (min): rt1 = 22.07 (major); rt2 = 24.02 (>97% *ee*).

(*R*)-Piperidine-2-carboxylic acid (*ent*-1): To a solution of alcohol **15** (0.1 g, 0.465 mmol) in CH_2Cl_2 (5 mL) at 0 °C, was slowly added TFA (0.1 mL, 1.3 mmol) and the reaction mixture was stirred at same temperature for 0.5 h, concentrated and resulting salt was used as such for next step. To a solution of salt from above step in 3N H_2SO_4 (4.5 mL) at 10 °C, was slowly added $KMnO_4$ (0.12 g, 0.744 mmol) and the reaction mixture was stirred at room temperature for 3 h, filtered through a pad of Celite and concentrated. (*R*)-Pipecolic acid *ent*-**1** was isolated after elution on Dowex 50W-X4 ion-exchange column (NH_4OH, 1 N). Yield: 0.044 g, 73%; R_f: 0.4 (CH_2Cl_2-MeOH-NH_4OH, 9:1:1%); MP: 271-273 °C; lit.[6] 271-274 °C; $[\alpha]_D^{25}$ +24.9 (*c* 1.15, H_2O) {Lit.[5] $[\alpha]_D^{25}$ +25.8 (*c* 1, H_2O)}; ^1H NMR (400 MHz, D_2O): δ 1.46-1.64 (m, 3H), 1.73-1.80 (m, 2H), 2.14-2.18 (m, 1H), 2.87-2.94 (m, 1H), 3.31-3.54 (m, 1H), 3.78 (dd, *J* = 8.0 Hz & 10.0 Hz, 1H); ^{13}C NMR (100 MHz, D_2O): δ 21.5, 21.6, 26.0, 44.0, 57.2, 172.2; MS (ESI): *m/z*: 152.28 $(M+Na)^+$.



ent-**1**

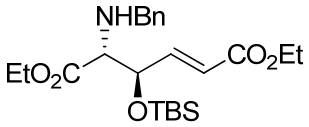
(4*R*,5*R*,*E*)-Diethyl 5-(benzylamino)-4-hydroxyhex-2-enedioate (16): To a stirred solution of ester **14** (1.18 g, 3.89 mmol) in CH_3CN:water (9:1, 20 mL) was added TFA (0.45 mL, 7.79 mmol) drop wise at 0 ºC. The reaction mixture was slowly warmed to room temperature and stirred until complete disappearance of starting material (~ 5-6 h). Reaction was quenched by excess $NaHCO_3$, water (10 mL) was added and organic mass was extracted with ethyl acetate (3 × 15 mL). Combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure followed by column chromatographic purification using ethyl acetate:pet ether (15:85) to yield 0.95 g of amino-alcohol **16** as thick liquid. R_f: 0.5 (pet ether-ethyl



16

acetate, 7:3); Yield: 76% over two steps; $[\alpha]_D^{25}$ +20 (*c* 0.5, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): νmax 3554, 3359, 2980, 1720, 1620; ^1H NMR (200 MHz, $CDCl_3$+CCl_4): 1.26-1.34 (m, 6H), 3.53 (d, *J* = 5Hz, 1H), 3.68 (d, *J* = 13 Hz, 1H), 3.94 (d, *J* = 13 Hz, 1H), 4.13-4.28 (m, 4H), 4.52-4.56 (m, 1H), 6.08 (dd, *J* = 2 & 15.5 Hz, 1H), 6.75 (dd, *J* = 4.0 & 15.5 Hz, 1H), 7.27-7.30 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$+CCl_4): 14.2, 52.6, 60.3, 61.3, 64.1, 70.1, 122.7, 127.5, 128.2, 128.4, 138.9, 145.2, 165.7, 171.6; MS (ESI):*m/z*: 344.18 $(M+Na)^+$; HRMS: Calculated for $C_{17}H_{24}O_5N$-322.1649, found-322.1640.

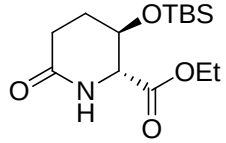
(4*R*,5*R*,*E*)-Diethyl 5-(benzylamino)-4-((*tert*-butyldimethylsilyl)oxy)hex-2-enedioate (23): To a stirred solution of hydroxyl amino ester **16** (0.7 g, 2.18 mmol), imidazole (0.3 g, 4.36 mmol) and DMAP (0.027 g, 0.22 mmol) in CH_2Cl_2 (20 mL) was added TBSCl (0.6 g, 4.36 mmol) dissolved in CH_2Cl_2 (5 mL) slowly at 0 ºC after which reaction was heated to reflux for 6 h until completion of reaction. Reaction mass was concentrated under reduced pressure followed by column chromatography using ethyl acetate-pet ether (5:95) to yield 0.8 g of TBS ether **23** as thick colorless liquid.



23

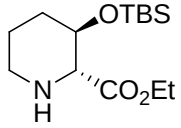
R_f: 0.5 (pet. ether-ethyl acetate, 8:2); Yield: 85% over two steps. $[\alpha]_D^{25}$ −7.69 (*c* 1, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): νmax 2980, 1720, 1620; ^1H NMR (500 MHz, $CDCl_3$+CCl_4): 0.01 (s, 3H), 0.03 (s, 3H), 0.87 (s, 9H), 1.24-1.31 (m, 6H), 2.17 (br s, 1H), 3.28 (d, *J* = 5.5 Hz, 1H), 3.65 (d, *J* = 13 Hz, 1H), 3.84 (d, *J* = 13.0 Hz, 1H), 4.12-4.20 (m, 5H), 4.47-4.48 (m, 1H), 5.95 (dd, *J* = 1.5 & 15.5 Hz, 1H), 6.95 (dd, *J* = 5.2 & 15.5 Hz, 1H), 7.21-7.28 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$+CCl_4): −4.6, −4.4, 14.3, 18.1, 25.7, 52.2, 60.3, 60.7, 65.7, 73.7, 121.7, 127.1, 128.2, 128.3, 139.4, 147.5, 166.0, 172.0; MS (ESI): *m/z*: 436.68 $(M+H)^+$; HRMS: Calculated for $C_{23}H_{38}ON_5Si$-436.2514, found-436.2505.

(2*R*,3*R*)-Methyl 3-((*tert*-butyldimethylsilyl)oxy)-6-oxopiperidine-2-carboxylate (24): The amino ester **23** (0.8 g, 2.2 mmol) was dissolved in ethanol (10 mL) and to that was added catalytic amount of palladium hydroxide over carbon (10%, 20 mg). The resulting reaction mixture was stirred under hydrogen atmosphere using balloon for 2 h. The reaction mixture was filtered through Celite and the filtrate was concentrated *in vacuo*. The crude product was purified by flash chromatography using silica gel (pet ether-ethyl acetate, 7:3) to provide amide **24** (0.52 g) as a colorless thick oil. R_f: 0.4 (pet. ether-ethyl acetate, 8:2); Yield: 85%; $[\alpha]_D^{25}$ −26 (*c* 1.5, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): νmax 3399, 2955, 2857, 1732, 1643, 1215; ^1H NMR (200 MHz, $CDCl_3$): δ 0.12 (s, 6H), 0.90 (s, 9H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.68 (br s, 1H), 1.79-1.88 (m, 2H), 2.26-2.40 (m, 1H), 2.54-2.72 (m, 1H), 3.99-4.02 (m, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 4.35-4.39 (m, 1H), 5.96 (br s, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ –5.1, –4.9, 14.1, 17.9, 25.6, 26.4, 26.5, 61.8, 62.3, 65.4, 170.1, 171.4. MS (ESI): *m/z*: 302.2 $(M+H)^+$; HRMS: Calculated for $C_{14}H_{28}O_4NSi$-302.1782, found-302.1777.



24

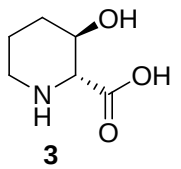
(2*R*,3*R*)-Ethyl 3-((*tert*-butyldimethylsilyl)oxy)piperidine-2-carboxylate (25): To the amide **24** (0.2 g, 0.7 mmol) in anhydrous THF (5 mL) was added BH_3·DMS (0.2 mL, 2 mmol) dropwise at 0 ºC. The resulting reaction mixture was further stirred at 5 ºC for 20 h. Methanol (excess) was added to the reaction mixture, stirred for 4 h and concentrated under reduced pressure. Water (10 mL) was added



25

and the reaction mixture was extracted using dichloromethane (3 × 10 mL). The collected organics were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to give the crude product which was purified using flash chromatography over silica gel (70:30, EtOAc: pet ether) to furnish amine **25** (0.147 g, 78%) as a colorless dense liquid. R_f: 0.5 (pet. ether-ethyl acetate, 2:8); Yield: 78%; $[\alpha]_D^{25}$ –27 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$, cm^{-1}): νmax 3436, 3020, 2931, 2400, 1731, 1215 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$+CCl_4): δ 0.00 (s, 3H), 0.06 (s, 3H), 0.86 (s, 9H), 1.36 (t, *J* = 7.3 Hz, 3H), 1.41-1.51 (m, 2H), 1.58-1.68 (m, 2H), 1.84-1.87 (m, 1H), 2.01-2.05 (m, 1H), 2.53-2.64 (m, 1H), 3.11 (dd, *J* = 1.1 & 10.1 Hz, 1H), 3.32 (d, *J* = 13.5 Hz, 1H), 3.78 (dt, *J* = 5.4 & 10.5 Hz, 1H), 3.98 (m, 1H), 4.10-4.18 (m, 1H), 4.31-4.39 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$+CCl_4): δ –5.3, –4.2, 13.9, 17.8, 23.1, 25.5, 32.2, 52.2, 61.8, 70.2, 70.5, 170.8; MS (ESI): *m/z*: 288.23 $(M+H)^+$, 310.14 $(M+Na)^+$; HRMS: Calculated for $C_{14}H_{30}O_3NSi$- 288.1989, found- 288.1979.

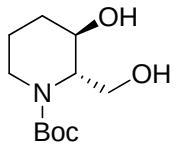
(2*R*,3*R*)-3-Hydroxypiperidine-2-carboxylic acid (3): A mixture of amine **25** (100 mg, 0.35 mmol) and



3

6 N HCl (10 mL) was kept at 120 ºC for 3 h. The solvent was removed under reduced pressure and the residue was dissolved in H_2O (50 mL). The mixture was loaded on an ion-exchange column (DOWEX 50W X8) and eluted with H_2O and then with aq. NH_3 solution. The eluate of aq. NH_3 was concentrated to dryness under reduced pressure to give **3** (46 mg, 91%) as a crystalline solid. R_f: 0.3 (CH_2Cl_2-MeOH-NH_4OH, 9:1:1%); Yield: 91%; MP: 238–243 ºC (dec.), lit.[7] 230-238 °C; $[\alpha]_D^{25}$ –13.8 (*c* 1.0, aq. HCl 10%), {lit.[7] $[\alpha]_D^{20}$ –14 (*c* 0.5, aq. HC1 10%)}; IR ($CHCl_3$, cm^{-1}): νmax 3287, 2920, 1625, 1405 cm^{-1}; ^1H NMR (400 MHz, D_2O): δ 1.64-1.80 (m, 2H), 2.02-2.08 (m, 2H), 2.22 (s, 1H), 3.07-3.12 (m, 1H), 3.40-3.36 (m, 1H), 3.83 (d, *J* = 7.8 Hz, 1H), 4.17-4.13 (m, 1H); ^{13}C-NMR (100 MHz, D_2O): δ 18.5, 28.7, 42.5, 60.8, 65.5, 170.0; MS (ESI): *m/z*: 146 $(M+H)^+$.

(2*S*,3*R*)-*tert*-Butyl 3-hydroxy-2-(hydroxymethyl)piperidine-1-carboxylate (26): To stirred

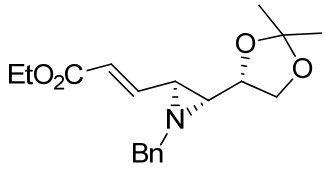


26

suspension of LAH (0.152 g, 4 mmol) in anhydrous THF (3 mL) was added the lactam **24** (240 mg, 0.8 mmol) dissolved in anhydrous THF (3 mL) and the reaction mixture was stirred for 8 h at room temperature. Water (10 mL) was added to the reaction mixture and extracted with ethyl acetate (3 × 25 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue thus obtained was purified by flash chromatography (pet ether–ethyl acetate 10:90) to afford diol **26** (138 mg) as a white crystalline solid. . R_f: 0.5 (pet. ether-ethyl acetate, 2:8); Yield: 75%; MP: 126-128 ºC, lit.[8] 124-126 °C; $[\alpha]_D^{25}$ +27 (c 1.0, MeOH), {lit.[8] $[\alpha]_D^{25}$ +29.8 (*c* 0.99, MeOH)}; IR ($CHCl_3$, cm^{-1}) : υmax 3448, 3025, 2945, 1674, 1215, 1120, 838 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$+CCl_4+DMSO-d_6): δ 1.15-1.29 (m, 1H), 1.39 (s, 9H), 1.61-1.82 (m, 3H), 2.69-2.82 (m, 1H), 3.45-3.61 (m, 2H), 3.89-3.92 (m, 2H), 4.08-4.16 (m, 1H); ^{13}C (125 MHz, $CDCl_3$+CCl_4+DMSO-d_6): δ 18.8, 26.3, 28.0, 39.6, 59.1, 59.8, 63.8, 79.1, 155.9; MS(ESI): *m/z*: 232 $(M+H)^+$, 254 $(M+Na)^+$; HRMS: Calculated for $C_{11}H_{21}NNaO_4$-254.1368, found-254.1369. HPLC detail for racemic dihydroxy compound (**26**) HPLC

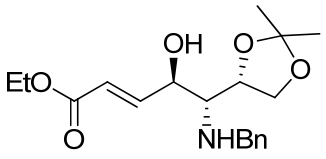
chiracel OJ-H column (250×4.6 mm). Isopropanol/pet ether = 5:95 flow rate 0.5 ml/min, λ = 210 nm) retention time (min): rt1 = 13.39; rt2 = 14.98 (1:1). Enantiomerically pure dihydroxy compound (**26**) HPLC chiracel OJ-H column (250 × 4.6 mm) isopropanol/pet ether = 5:95 flow rate 0.5 ml/min, λ = 210 nm) retention time (min): rt1 = 13.18 (major); rt2 = 15.05 (>97% *ee*).

(*E*)-Ethyl 3-((2*S*,3*R*)-1-benzyl-3-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)aziridin-2-yl)acrylate (17): To a stirred solution of *trans* aziridine-2-carboxylate **13** (1 g, 3.27 mmol) in dry CH_2Cl_2 (30 mL) was added DIBAL-H (3.6 mL, 3.6 mmol, 1 M solution in toluene) at −78 °C slowly over period of 15 min and stirred for another 15 min. TLC showed complete convertion of ester to aldehyde. Reaction was quenched by addition of MeOH (0.3 mL) and allowed to warm to 0 °C. Saturated aqueous NH_4Cl (10 mL) was added and stirred for 0.25 h after which organic layer was separated and aqueous layer was washed with CH_2Cl_2 (3 × 20 mL). Combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, concentrated *in vacuo* and used as such for next reaction. To a stirred solution NaH (0.09 g, 3.6 mmol, prewashed with dry *n*-hexane) dissolved in THF (10 mL) was added triethyl phosphonoacetate (0.71 mL, 3.6 mmol) slowly at 0 °C and stirred for 10 minutes. The aldehyde from above reaction dissolved in 5 ml of dry THF was added and stirring continued for another 2 h at same temperature until completion of reaction. The reaction was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were then washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Purification on flash column chromatography (pet. ether: ethyl acetate, 1:9) furnished compound **17** (0.75 g) as thick colorless oil. . R_f: 0.5 (pet ether-ethyl acetate, 8:2); Yield: 75%, over two steps; IR ($CHCl_3$, cm^{-1}): νmax 2984, 2932, 1716, 1644, 1370, 1265; $[\alpha]_D^{25}$ −34 (*c* 1, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$+CCl_4): δ 1.30 (t, *J* = 7.0 Hz, 3H), 1.33 (s, 3H), 1.40 (s, 3H), 2.12 (dd, *J* = 2.6 & 4.9 Hz, 1H), 2.72 (dd, *J* = 2.4 & 9.9 Hz, 1H), 3.61 (dd, *J* = 5.5 & 7.9 Hz, 1H), 3.72-3.85 (m, 2H), 3.91-4.09 (m, 2H), 4.20 (q, *J* = 7.0 Hz, 2H), 6.13 (d, *J* = 15.2 Hz, 1H), 6.89 (dd, *J* = 9.9 & 15.2 Hz, 1H), 7.26-7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$+CCl_4): δ 14.2, 25.5, 26.7, 40.1, 49.6, 57.0, 60.3, 66.24, 76.1, 109.5, 125.1, 127.1, 127.9, 128.2, 138.6, 142.9, 165.3; MS (ESI): *m/z*: 354.15 $[M+Na]^+$; HRMS: Calculated for $C_{19}H_{26}O_4N$-332.1862, found-332.1858.



17

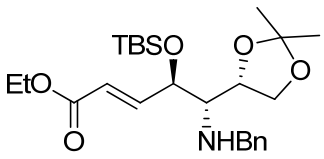
(4*R*,5*R*,*E*)-Ethyl 5-(benzylamino)-5-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-hydroxypent-2-enoate (27): To a stirred solution of ester **17** (1.4 g, 4.2 mmol) in CH_3CN: water (9:1, 25 mL) was added TFA (0.64 mL, 8.4 mmol) dropwise at 0 ºC. The reaction mixture was slowly warmed to room temperature and stirred until complete disappearance of starting material (~ 5-6 h). Reaction was quenched by addition of excess $NaHCO_3$, water (10 mL) was added and organic mass was extracted with ethyl acetate (3 × 20 mL). Combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure followed by column chromatographic purification using ethyl acetate-pet. ether (15:85) to yield 1.11 g of amino-alcohol **27** as thick liquid. . R_f: 0.5 (pet. ether-ethyl acetate, 7:3); Yield: 80%; IR ($CHCl_3$, cm^-



27

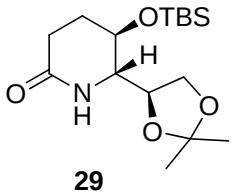
[1]): νmax 3453, 2985, 1717, 1656, 1455, 1370, 1263, 1175; $[\alpha]_D^{25}$−50 (*c* 1.8, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$+CCl_4): δ 1.29 (t, *J* = 7.0 Hz, 3H), 1.32 (s, 3H), 1.39 (s,3H), 2.74 (dd, *J* = 3.6 & 5.4 Hz, 1H), 3.77-4.03 (m, 4H), 4.1-4.26 (m, 3H), 4.55 (dd, *J* = 3.6 & 5.4Hz, 1H), 6.2 (dd, *J* = 2 & 15.6 Hz, 1H), 6.9 (dd, *J* = 3.7 & 15.6 Hz, 1H), 7.26-7.34 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.1, 25.1, 26.3, 51.0, 60.3, 61.3, 67.3, 69.0, 74.9, 109.0, 121.3, 127.1, 128.1, 128.4, 139.5, 147.0, 166.1; MS (ESI):*m/z*: 372.14 $[M+Na]^+$. HRMS: Calculated for $C_{19}H_{28}O_5N$-350. 1967, found 350. 1962.

(4*R*,5*S*,*E*)-Ethyl 5-(benzylamino)-4-((tert-butyldimethylsilyl)oxy)-5-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)pent-2-enoate (28): To a stirred solution of hydroxyl amino ester **27** (1 g, 2.86 mmol), imidazole (0.4 g, 6 mmol) and DMAP (0.0.24 g, 0.2 mmol) in CH_2Cl_2 (20 mL) was added TBSCl (1.27 g, 8.44 mmol) dissolved in CH_2Cl_2 (5 mL) slowly at ^oC after which reaction was heated to reflux for 6 h until completion of reaction. Reaction mass was concentrated under reduced pressure followed by column chromatography using ethyl acetate: pet ether (5:95) to yield 1.18 g of -OTBS protected amino-alcohol **28** as thick colourless liquid. . R_f: 0.5 (pet. ether-ethyl acetate, 8:2); Yield: 90 %; IR ($CHCl_3$, cm^{-1}): νmax 2984, 2931, 1721, 1657, 1472, 1369, 1260, 1160, 1059. $[\alpha]_D^{25}$+11.11 (*c* 2.7, $CHCl_3$); ^{1}HNMR (200 MHz, $CDCl_3$+CCl_4): δ 0.04 (s, 3H), 0.09 (s, 3H), 0.91 (s, 9H), 1.31 (t, 3H), 1.35 (s, 3H), 1.40 (s, 3H), 2.72 (br s, 1H), 3.70 (t, *J* = 7.7 Hz, 1H), 3.84-4.04 (m, 1H), 4.22 (q, 2H), 4.29-4.46 (m, 2H), 6.08 (dd, *J* = 1.4 & 15.6 Hz, 1H), 7.1 (dd, *J* = 5.2 & 15.6 Hz, 1H), 7.25-7.36 (m, 5H); ^{13}C NMR(50 MHz, $CDCl_3$): δ −4.9, −4.5, 14.1, 18.1, 25.2, 25.8, 26.8, 53.1, 60.3, 63.7, 66.9, 73.3, 75.5, 108.8, 121.4, 126.9, 128.2, 149.0, 166.2; MS (ESI): *m/z*: 486.27 $[M+Na]^+$; HRMS: Calculated for $C_{25}H_{42}O_5NSi$-464.2832, found-464.2827.



28

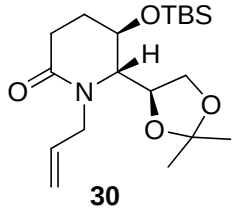
(5*R*,6*S*)-5-((*tert*-Butyldimethylsilyl)oxy)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)piperidin-2-one (29): A suspension of **28** (0.9 g, 1.94 mmol) and 10% $Pd(OH)_2$/C (60 mg) in MeOH (20 mL) was stirred under a H_2 atmosphere at room temperature for 2.5 h, filtered through Celite and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (EtOAc/pet. ether = 1:3) to afford **29** (0.59 g) as a colorless thick liquid. . R_f: 0.5 (pet. ether-ethyl acetate, 1:1); Yield: 92 %; IR ($CHCl_3$, cm^{-1}): νmax 3408, 2927, 1670, 1457, 1380, 1216; $[\alpha]_D^{25}$–22.9 (*c* 1.15, $CHCl_3$). ^{1}HNMR (400 MHz, $CDCl_3$+CCl_4): δ 0.1 (s, 3H), 0.11 (s, 3H), 0.91 (s, 9H), 1.34 (s, 3H), 1.41 (s, 3H), 1.78-1.87 (m, 1H), 1.94-2.01 (m, 1H), 2.29-2.38 (m, 1H), 2.47-2.85 (m, 1H), 3.20 (t, *J* = 7 Hz, 1H), 3.72-3.77 (m, 1H), 3.84 (dd, *J* = 5 & 8 Hz, 1H), 4.00-4.1 (m, 2H), 6.02 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$+CCl_4): δ –4.5, –4.1, 17.9, 25.2, 25.8, 26.6, 28.5, 29.1, 61.7, 67.2, 68.1, 76.3, 109.3, 170.6; MS (ESI): *m/z*: 352.18 $[M+Na]^+$; HRMS: Calculated for $C_{16}H_{32}O_4NSi$-330.2101, found-330.2095.



29

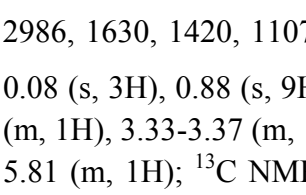
(5*R*,6*S*)-1-Allyl-5-((*tert*-butyldimethylsilyl)oxy)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)piperidin-2-one (30): To the NaH (0.044 g, 1.8 mmol, prewashed with dry *n*-hexane) in DMF (2 mL) was added amide **29** (0.4 gm, 1.21 mmol) in DMF (2 mL) dropwise at 0 ºC and stirred for 1 h at room temperature.

Allyl bromide (0.154 mL, 1.8 mmol) was added dropwise at 0 ºC. The resulting reaction mixture stirred for 3-4 h at room temperature. Reaction mixture was then quenched using water (20 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organics washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was column purified on flash chromatography (pet. ether-ethyl acetate, 7:3) to afford the allylated product **30** as colorless liquid. . R_f: 0.5 (pet. ether-ethyl acetate, 2:1); Yield: 0.357 g, 85%; IR ($CHCl_3$, cm^{-1}): νmax 2986, 1630, 1420, 1107. $[\alpha]_D^{25}$ –83.4 (*c* 1, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$+CCl_4): δ 0.07 (s, 3H), 0.08 (s, 3H), 0.88 (s, 9H), 1.35 (s, 3H), 1.43 (s, 3H), 1.88-1.92 (m, 4H), 2.33-2.44 (m, 1H),), 2.53-2.67 (m, 1H), 3.33-3.37 (m, 1H), 3.54-3.75 (m, 3H), 4.03-4.05 (m, 2H), 4.9 (m, 1H), 5.11-5.24 (m, 2H), 5.61-5.81 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$+CCl_4):δ –4.9, 17.8, 25.4, 25.5, 25.6, 26.3, 26.5, 48.4, 64.4, 65.4, 66.7, 78.5, 109.6, 117.1, 133.4, 168.8; MS (ESI): *m/z*: 356.41 $[M+H]^+$.



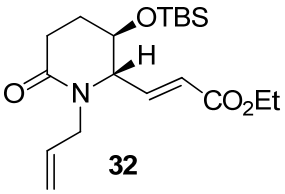
30

((5*R*,6*S*)-1-Allyl-5-((*tert*-butyldimethylsilyl)oxy)-6-((*S*)-1,2-dihydroxyethyl)piperidin-2-one (31): Protected lactam **30** (0.2 g, 0.56 mmol) was treated with 80% aqueous acetic acid (2 mL), and the resulting mixture was allowed to react at 80 °C. The reaction was monitored by TLC and was judged to be complete after 3 h. The solution was then diluted with H_2O (8 mL) and extracted with EtOAc (3 × 10 mL). The extracts were treated with saturated $NaHCO_3$ solution, and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated to give a crude residue that was purified by flash chromatography (pet. ether-ethyl acetate, 1:9). Pure terminal diol **31** (0.14 g) was obtained as a thick gummy liquid. R_f: 0.4 (ethyl acetate); Yield: 75 %; IR ($CHCl_3$, cm^{-1}): νmax 3554, 3340, 2986, 1627, 1423, 1107; $[\alpha]_D^{25}$ –34.9 (*c* 1, $CHCl_3$); ^{1}HNMR (200 MHz, $CDCl_3$+CCl_4): δ 0.06 (s, 3H), 0.07 (s, 3H), 0.88 (s, 9H), 1.99-2.11 (m, 2H), 2.14-2.33 (m, 1H), 2.53-2.63 (m, 1H), 3.35-3.37 (m, 1H), 3.54-3.69 (m, 4H), 3.94 (s, 1H), 4.71-4.77 (m, 2H), 5.26-5.58 (m, 2H), 5.72-5.88 (m, 1H); ^{13}C NMR(100 MHz, $CDCl_3$+CCl_4): –4.8, –4.7, 18.0, 25.3, 25.8, 26.9, 50.3, 64.1, 64.7, 66.1, 73.6, 117.5, 132.8, 171.0; MS (ESI): *m/z*: 352.23 $[M+Na]^+$.



31

(*E*)-Ethyl 3-((2*S*,3*R*)-1-allyl-3-((tert-butyldimethylsilyl)oxy)-6-oxopiperidin-2-yl)acrylate (32): Diol **31** (0.2 g, 0.607 mmol) was dissolved in acetone–water (3 mL, 2:1) at 0 ºC, treated with sodium metaperiodate (0.2 g, 0.9 mmol) and stirred at 15 ºC for 15 min. The reaction was quenched using ethylene glycol (0.01 mL), extracted with CH_2Cl_2 (3 ×10 mL), washed with brine, dried over anhydrous Na_2SO_4 and filtered. The combined organics were concentrated under reduced pressure to afford crude aldehyde which was used as such for next reaction.

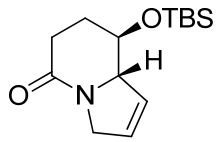


32

To a solution of aldehyde from above reaction in CH_2Cl_2 (15 mL) was added (carboethoxymethylene) triphenylphosphorane (0.4 g, 1.2 mmol) and the reaction mixture was stirred for 6 h. Solvent was evaporated and the reaction mixture was adsorbed on silica. Purification by column chromatography (pet. ether–ethyl acetate, 8:2) gave **32** as a thick liquid (0.167 g). R_f: 0.5 (pet. ether-ethyl acetate, 1:1);

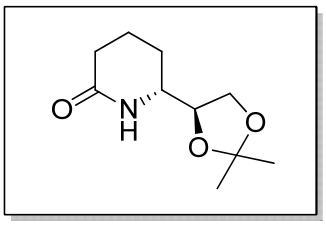
Yield: 75% over two steps; IR ($CHCl_3$, cm^{-1}): νmax 2986, 1723, 1656, 1630, 1107; $[\alpha]_D^{25}$ –45 (*c* 1, $CHCl_3$) ^{1}HNMR (200 MHz, $CDCl_3$+CCl_4): δ 0.06 (s, 3H), 0.08 (s, 3H), 0.87 (s, 9H), 1.30 (t, *J* = *7* Hz, 3H), 1.73-1.75 (m, 1H), 1.86-1.93 (m, 1H),), 2.35 (m, 1H), 2.59-2.68 (m, 1H), 2.99 (dd, *J* = 7 & 16 Hz, 1H), 3.99 (m, 1H), 4.19 (q, *J* = *7* Hz, 2H), 5.84 (dt, *J* = 2 & 16 Hz, 1H), 5.11-5.18 (m, 1H), 5.62-5.72 (m, 1H), 5.88 (dd, *J* = 1 & 16 Hz, 1H), 6.73 (dd, *J* = 6 & 16 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$+CCl_4): δ -4.8, 14.2, 24.8, 25.6, 26.7, 47.3, 60.7, 64.3, 67.0, 117.3, 123.9, 132.3, 144.5, 165.4, 169.1; MS (ESI) *m/z*: 390.12 $[M+Na]^+$; HRMS: Calculated for $C_{19}H_{34}O_4NSi$-368.2252, found-368.2247.

(8*R*,8a*S*)-8-((*tert*-Butyldimethylsilyl)oxy)-6,7,8,8a-tetrahydroindolizin-5(3H)-one (18): The olefinic compound **32** (0.075 g, 0.2 mmol) and Grubbs' 2nd generation catalyst (5 mg, 2 mol %) in anhydrous CH_2Cl_2 (50 mL) was refluxed for 5 h. The reaction mixture was filtered through Celite and concentrated *in vacuo* to provide crude **18**. The crude product was purified using column chromatography (pet. ether-ethyl acetate, 1:1) to provide the ring closed product **18** (0.044 g, 80%) as a colorless sticky liquid. R_f: 0.3 (pet. ether-ethyl acetate, 1:1); Yield: 80 %; IR ($CHCl_3$, cm^{-1}): νmax 1640, 1620; $[\alpha]_D^{25}$ +53 (*c* 1, $CHCl_3$); lit[9] {for *ent*-$[\alpha]_D^{25}$ –53.73 (*c* 1.10, $CHCl_3$)}; ^{1}HNMR (400 MHz, $CDCl_3$+CCl_4): δ 0.08 (s, 6H), 0.90 (s, 9H), 1.79-1.81 (m, 1H), 2.02-2.03 (m, 1H), 2.39-2.46 (m, 1H), 2.60-2.62 (m, 1H), 3.53-3.55 (m, 1H), 4.02-4.06 (m, 1H), 4.15-4.16 (m, 1H), 4.45-4.50 (m, 1H), 5.92-5.94 (m, 2H); ^{13}C NMR(100 MHz, $CDCl_3$+CCl_4): δ −4.6, −4.1, 18.0, 25.7, 29.7,30.2, 53.3, 69.1, 71.1, 126.8, 128.5, 168.2. MS (ESI): *m/z*: 268.02 $[M+H]^+$. HRMS: Calculated for $C_{14}H_{26}NO_2Si$-268.1733; found-268.1741.

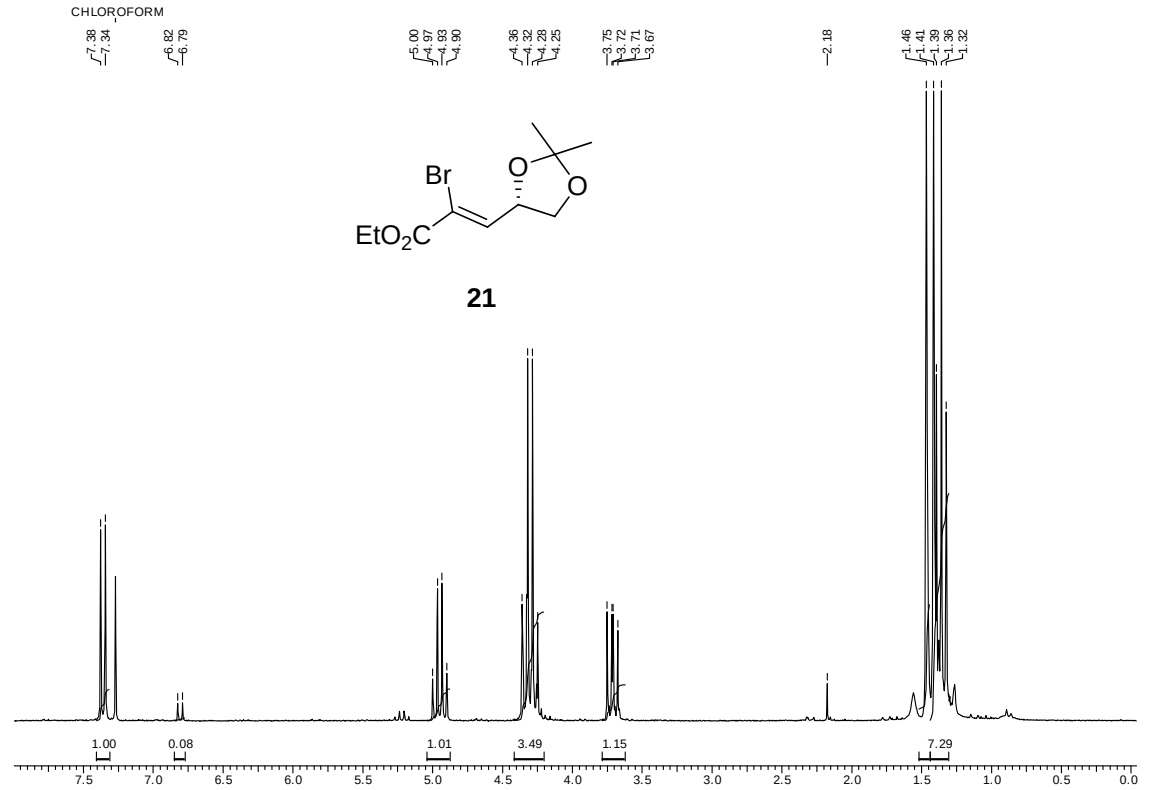


18

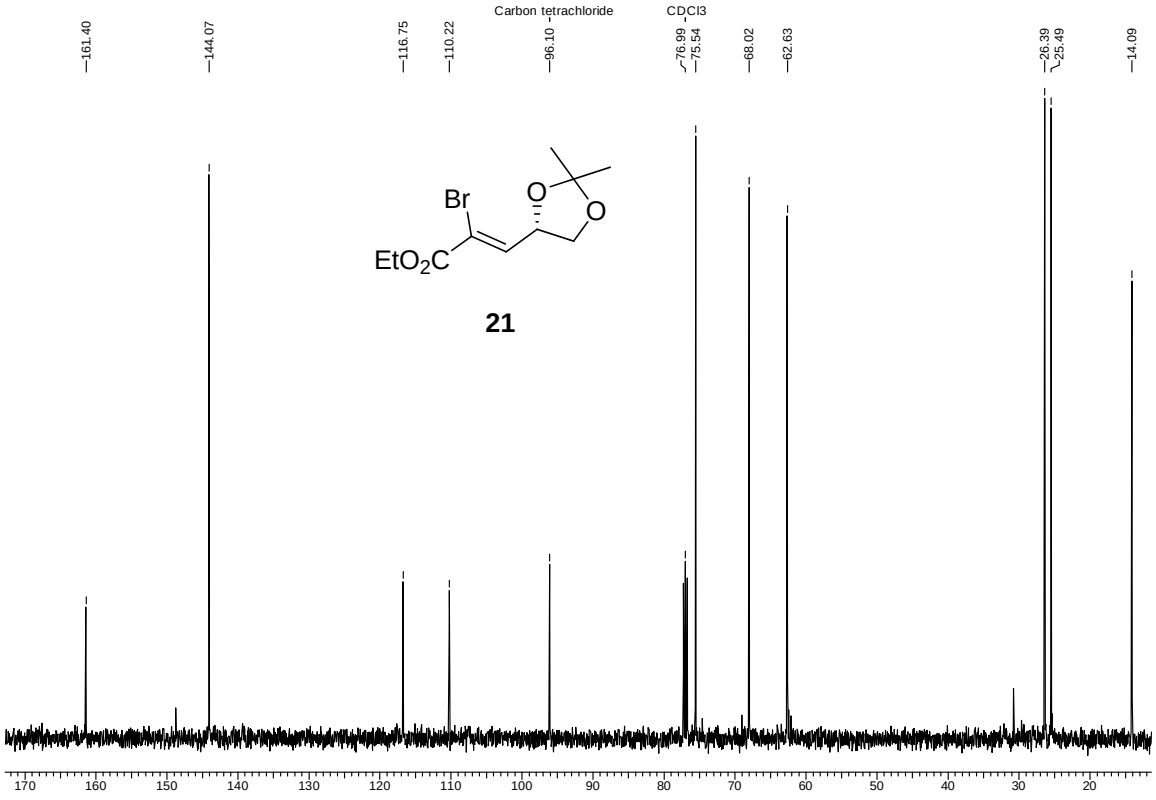
***R*)-6-((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)piperidin-2-one (33):** To a stirred solution of aziridine ester **17** (0.66 g, 1.99 mmol) in methanol (10 mL) was added ammonium formate (1.24 g, 19.9 mmol) and 10% Pd/C (100 mg), and the mixture was refluxed for 3 h. The reaction mixture was filtered through Celite, concentrated and purified by column chromatography (pet ether-ethyl acetate, 2:8) to afford **33** as a thick yellowish liquid. R_f: 0.4 (Ethyl acetate); Yield: 0.37 g, 95%; $[\alpha]_D^{25}$ −17.5 (*c* 1.1, $CHCl_3$); {lit.[10] $[\alpha]_D^{25}$ –14.4, (*c* 0.5, $CHCl_3$)}; IR ($CHCl_3$, cm^{-1}): νmax 3402, 2985, 2936, 1664, 1457, 1371, 1072; ^{1}H NMR (400 MHz, $CDCl_3$+CCl_4): δ 1.20-1.28 (m, 1H), 1.33 (s, 3H), 1.40 (s, 3H), 1.63-1.83 (m, 2H), 1.85-2.01 (m, 1H), 2.17-2.49 (m, 2H), 3.31 (td, *J* = 5.4 & 8.7 Hz, 1H), 3.66 (dd, *J* = 5.4 & 8.2 Hz, 1H), 3.86-3.88 (m, 1H), 4.03 (dd, *J* = 6.0 & 8.2 Hz, 1H), 6.21 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$+CCl_4): δ 19.7, 24.8, 25.3, 26.8, 31.3, 56.2, 66.2, 79.1, 109.79, 171.2; MS (ESI): *m/z*: 200.11 $(M+H)^+$, 222.10 $(M+Na)^+$; HRMS: Calculated for $C_7H_{18}NO_3$-200.1281, found-200.1277.



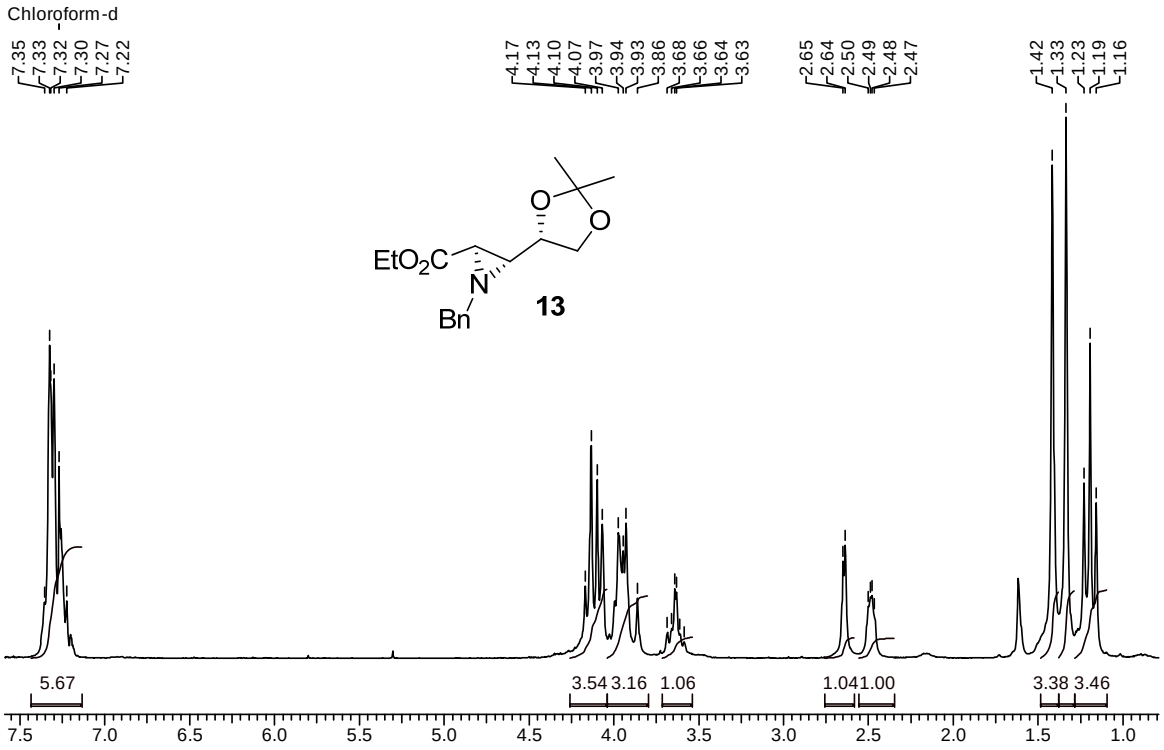
^{1}H NMR, ^{13}C NMR Spectra for all New Compounds



21



21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7.33
7.32
7.30
7.27
7.22
4.17
4.13
4.10
4.07
3.97
3.94
3.93
3.86
3.68
3.66
3.64
3.63
2.65
2.64
2.50
2.49
2.48
2.47
1.42
1.33
1.23
1.19
1.16
EtO2C
N
Bn
O
O
13
5.67
3.54
3.16
1.06
1.04
1.00
3.38
3.46
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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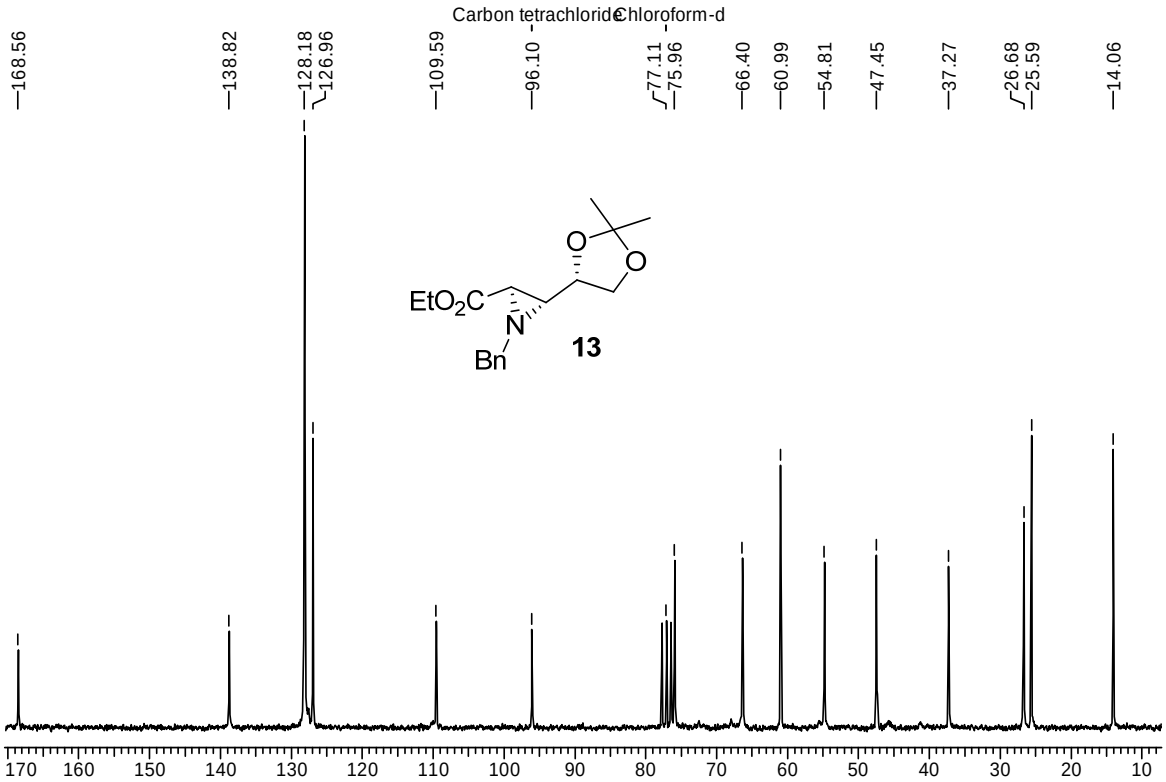
1.5
1.0


Carbon tetrachloride
Chloroform-d
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138.82
128.18
126.96
109.59
96.10
77.11
75.96
66.40
60.99
54.81
47.45
37.27
26.68
25.59
14.06
EtO2C
N
Bn
O
O
13
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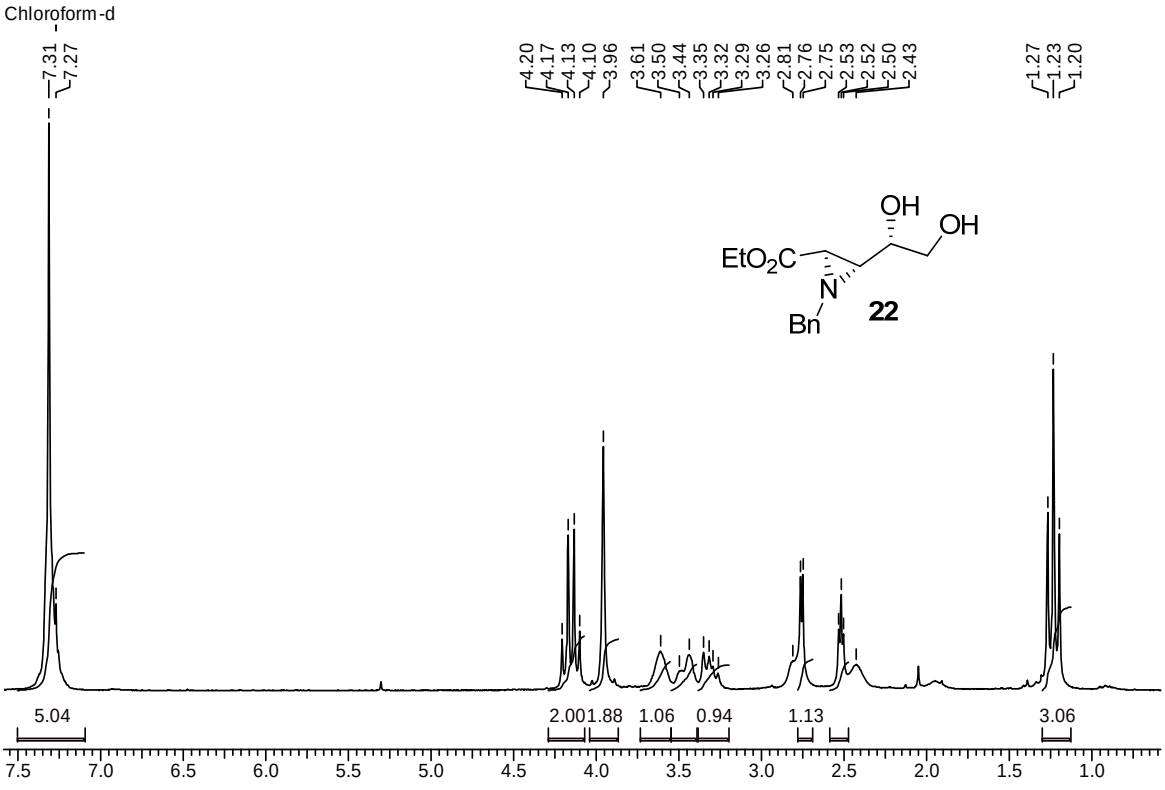
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


Chloroform-d
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4.17
4.13
4.10
3.96
3.61
3.50
3.44
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3.32
3.29
3.26
2.81
2.76
2.75
2.53
2.52
2.50
2.43
1.27
1.23
1.20
OH
OH
EtO2C
N
Bn
22
5.04
2.00
1.88
1.06
0.94
1.13
3.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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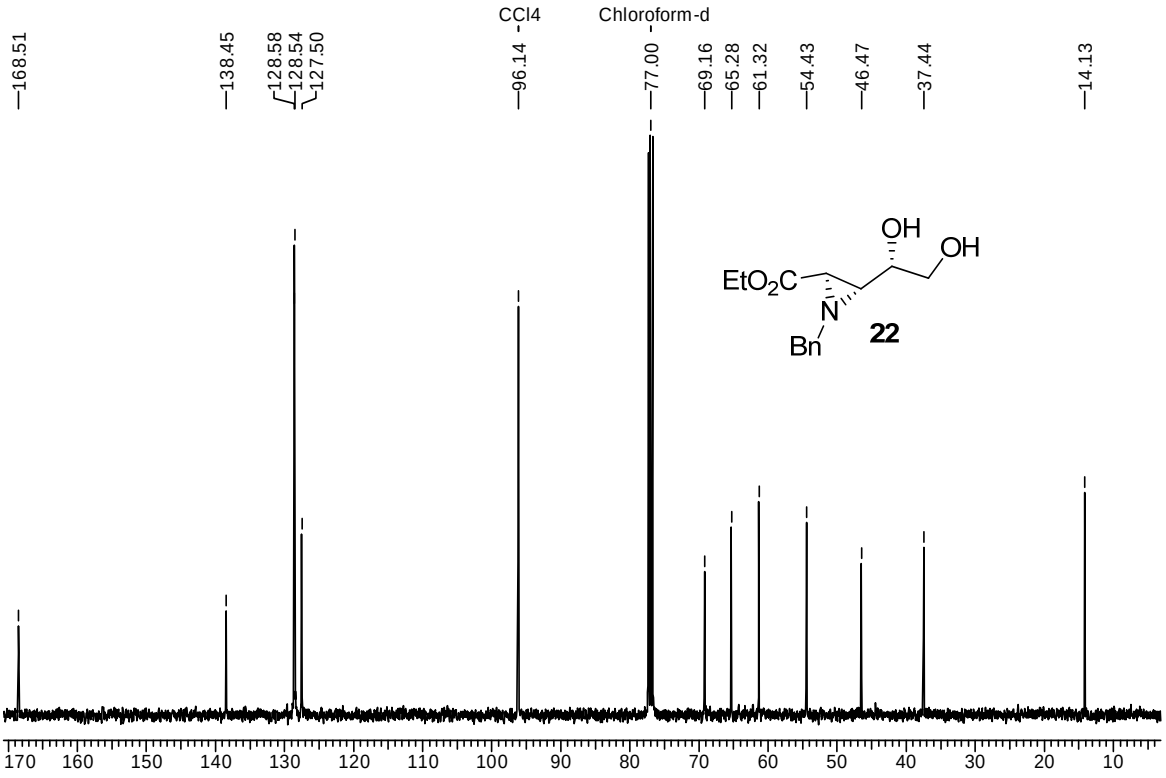
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Chloroform-d
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128.58
128.54
127.50
96.14
77.00
69.16
65.28
61.32
54.43
46.47
37.44
14.13
OH
OH
EtO2C
N
Bn
22
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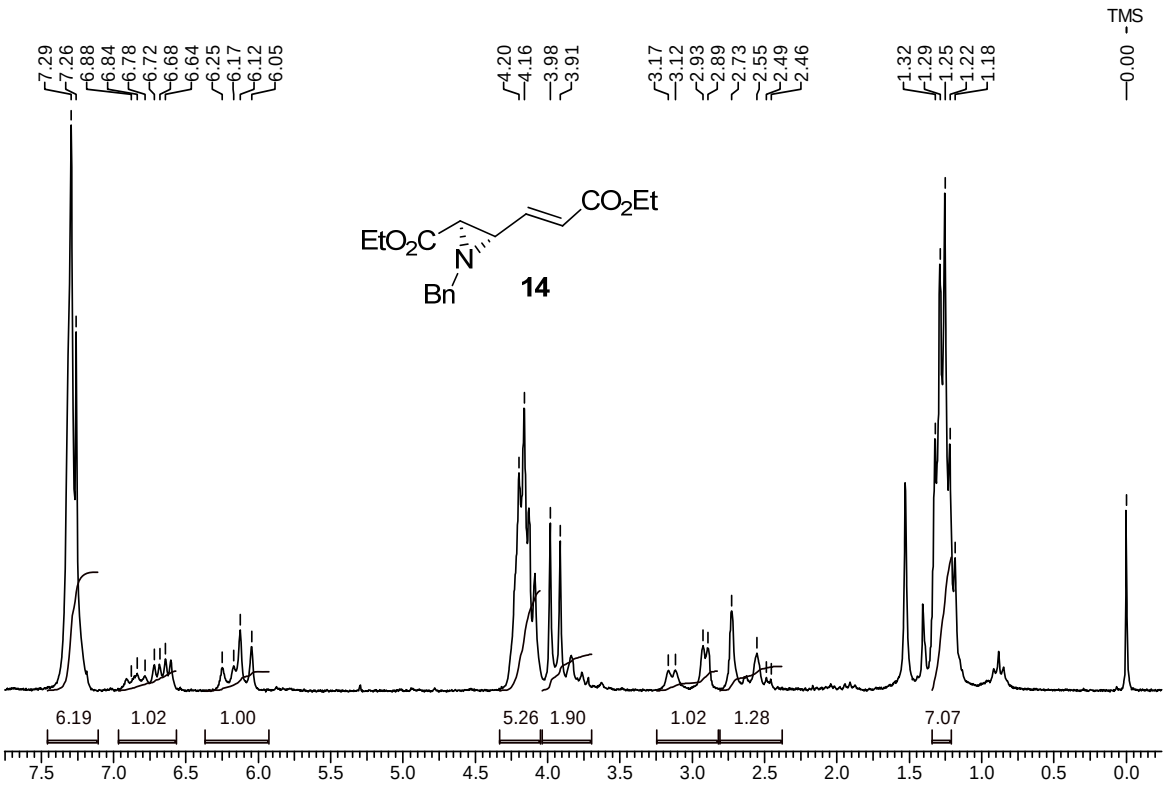
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


TMS
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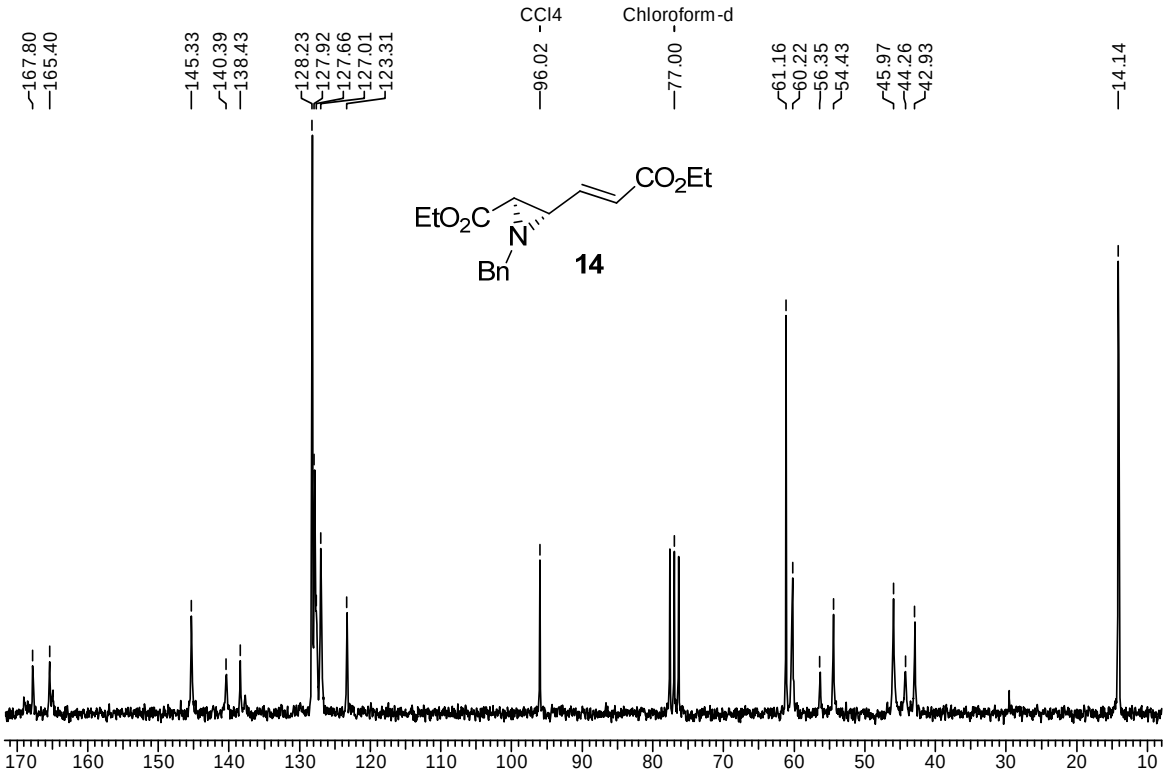
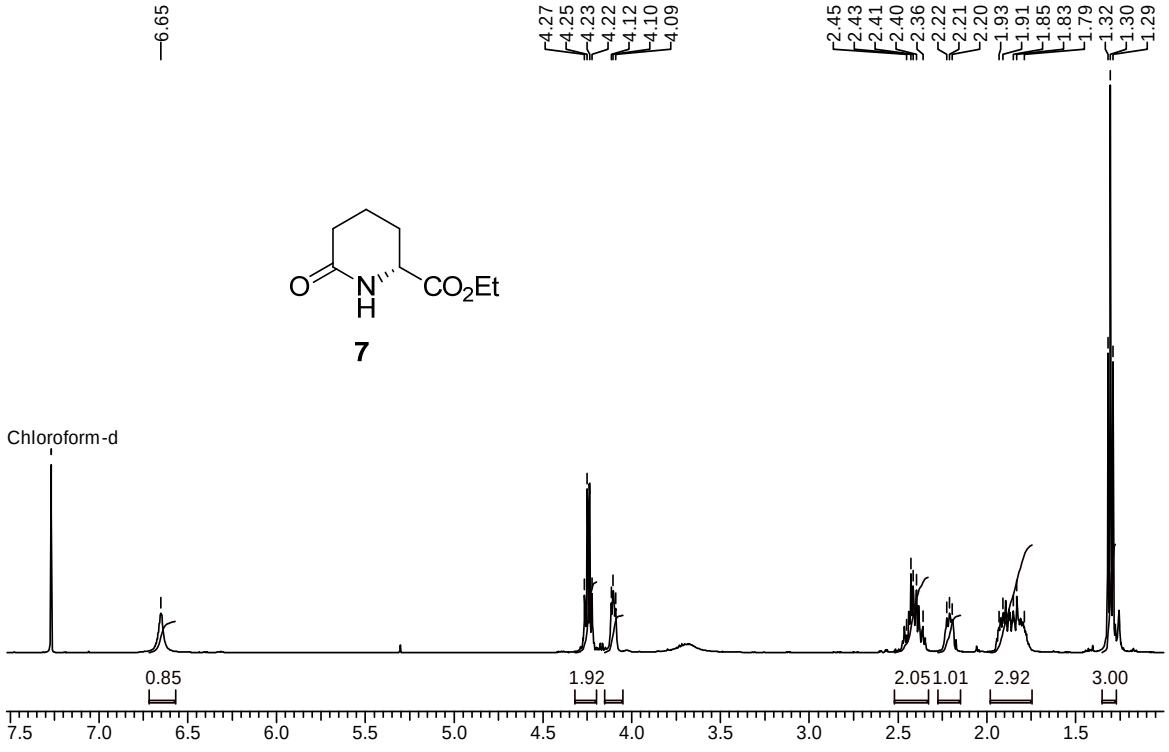
6.84
6.78
6.72
6.68
6.64
6.25
6.17
6.12
6.05
4.20
4.16
3.98
3.91
3.17
3.12
2.93
2.89
2.73
2.55
2.49
2.46
1.32
1.29
1.25
1.22
1.18
0.00
CO2Et
EtO2C
N
Bn
14
6.19
1.02
1.00
5.26
1.90
1.02
1.28
7.07


CCl4
Chloroform-d
167.80
165.40
145.33
140.39
138.43
128.23
127.92
127.66
127.01
123.31
96.02
77.00
61.16
60.22
56.35
54.43
45.97
44.26
42.93
14.14
CO2Et
EtO2C
N
Bn
14


6.65
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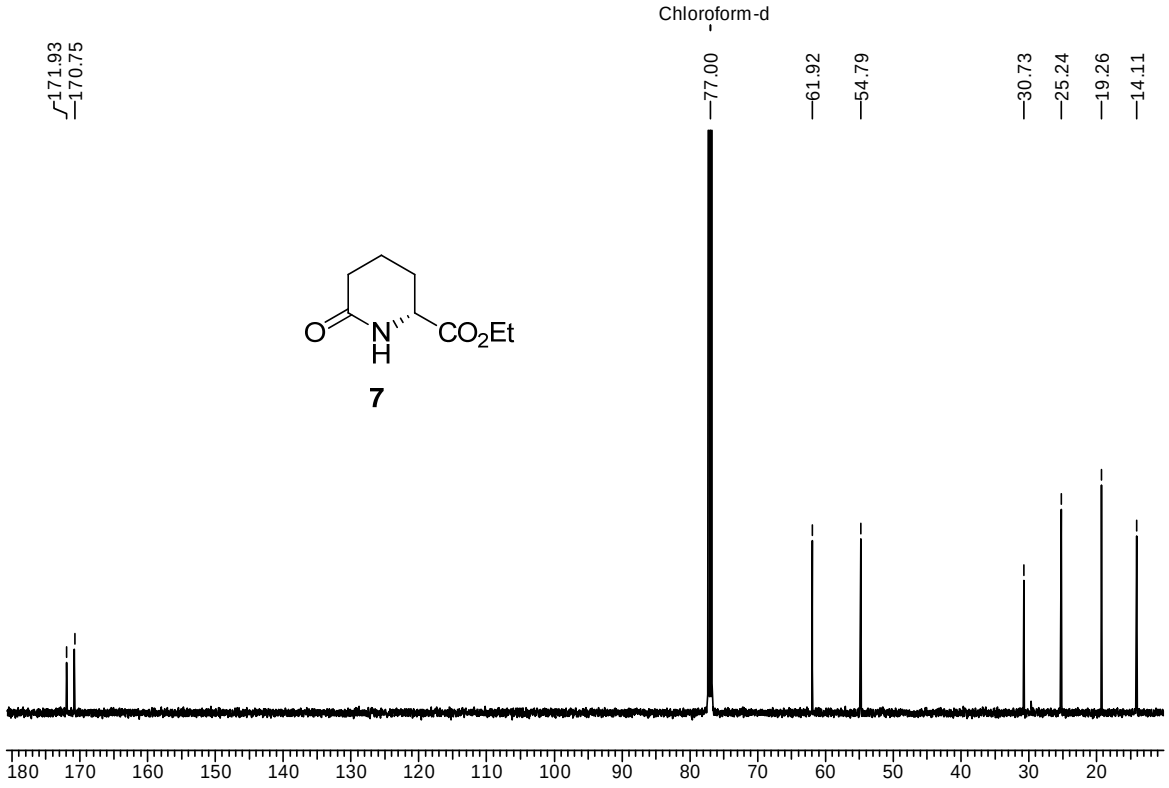
4.25
4.23
4.22
4.12
4.10
4.09
2.45
2.43
2.41
2.40
2.36
2.22
2.21
2.20
1.93
1.91
1.85
1.83
1.79
1.32
1.30
1.29
O
N
H
CO2Et
7
Chloroform-d
0.85
1.92
2.05
1.01
2.92
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5


171.93
170.75
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77.00
61.92
54.79
30.73
25.24
19.26
14.11
O
N
H
CO2Et
7
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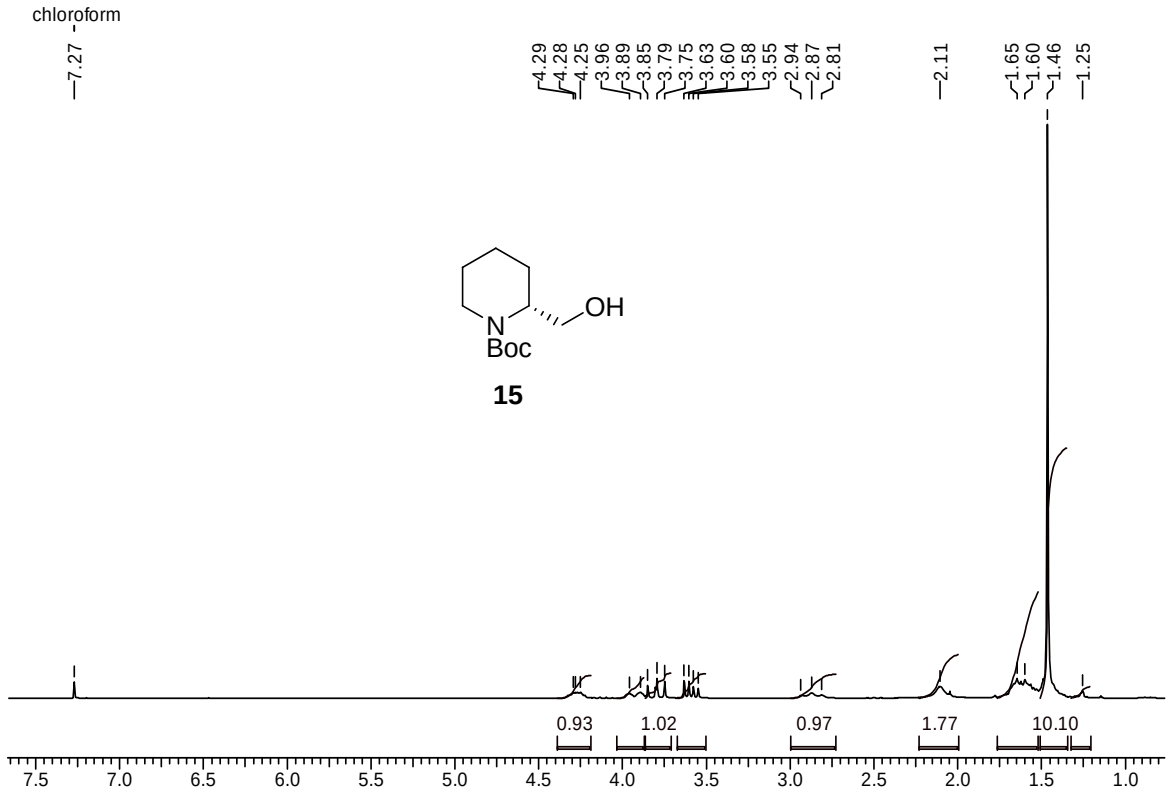
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20


chloroform
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4.25
3.96
3.89
3.85
3.79
3.75
3.63
3.60
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3.55
2.94
2.87
2.81
2.11
1.65
1.60
1.46
1.25
OH
N
Boc
15
0.93
1.02
0.97
1.77
10.10
7.5
7.0
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5.5
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4.5
4.0
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3.0
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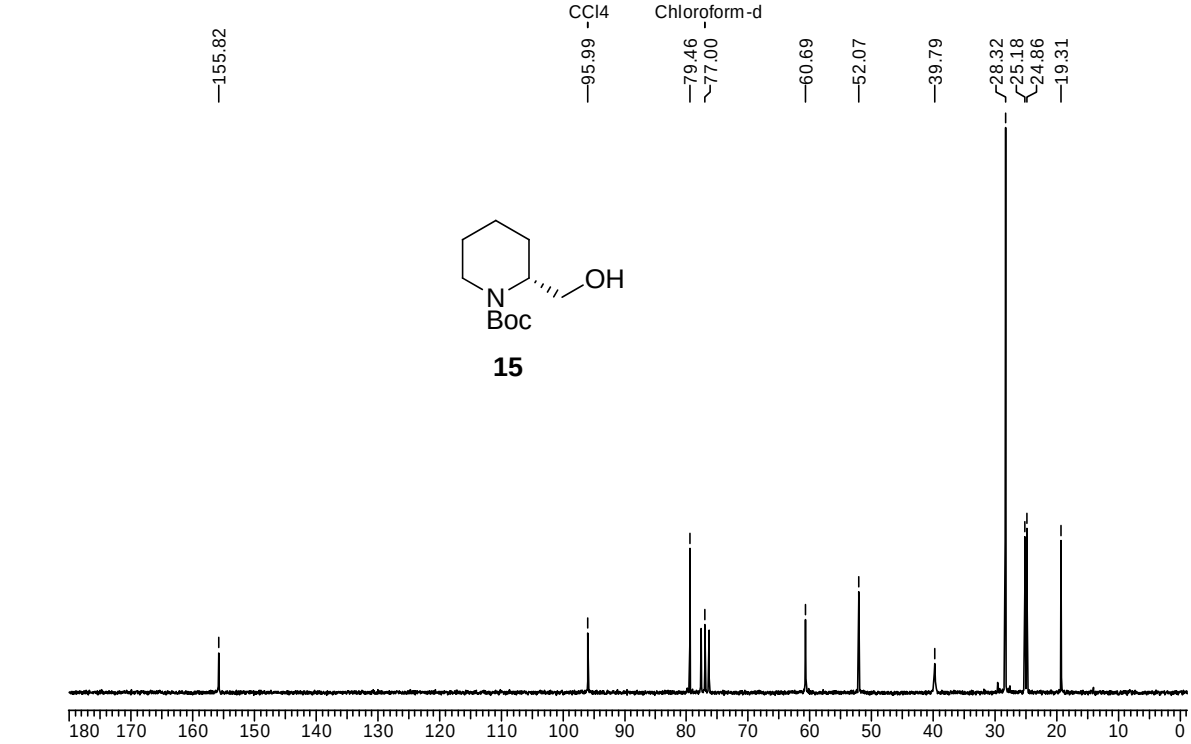
1.0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60.69
52.07
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28.32
25.18
24.86
19.31
OH
N
Boc
15
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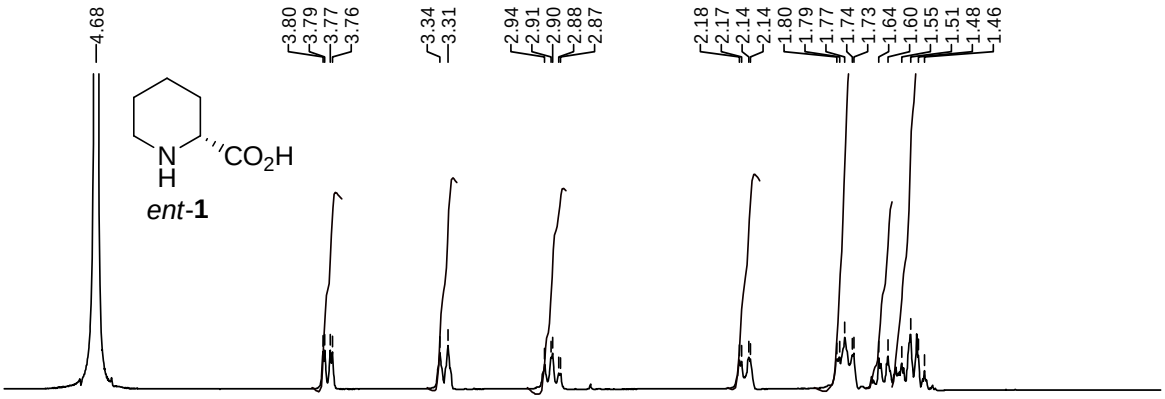
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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3.77
3.76
3.34
3.31
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2.90
2.88
2.87
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1.48
1.46
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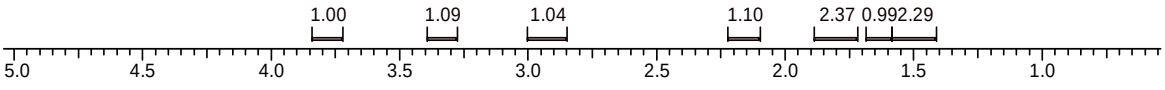
H
CO2H
ent-1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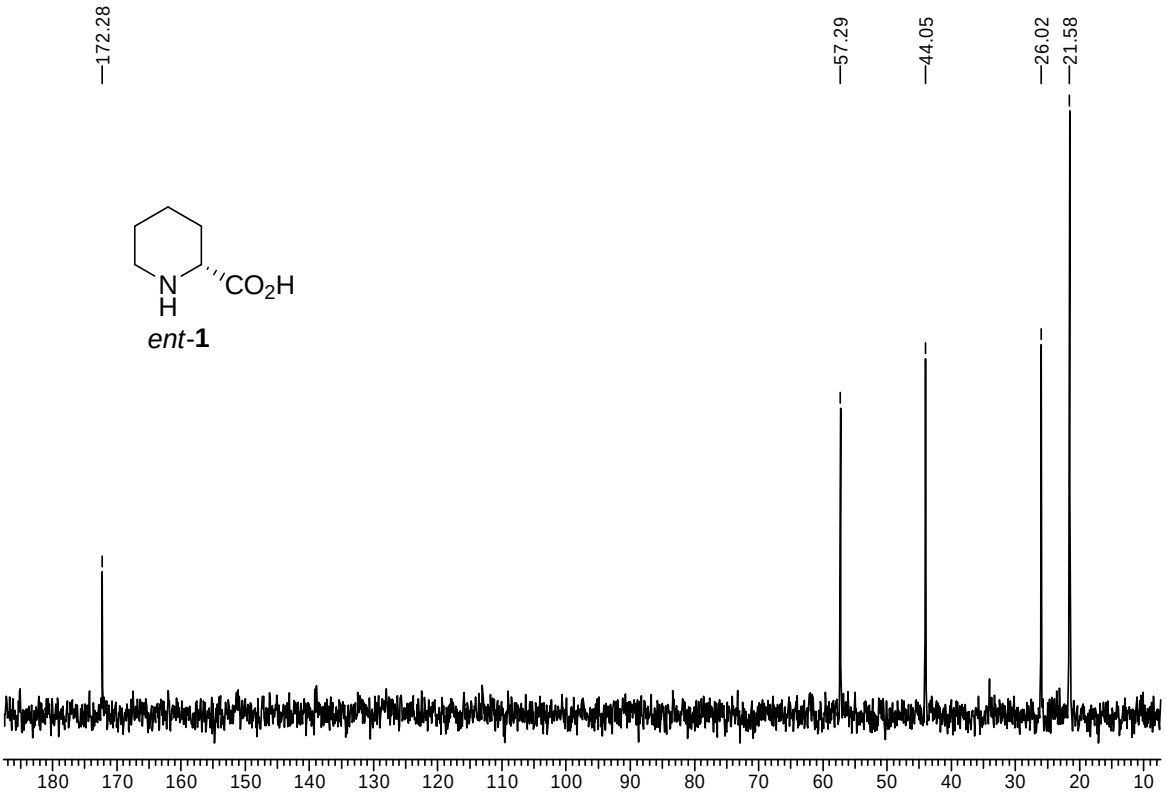
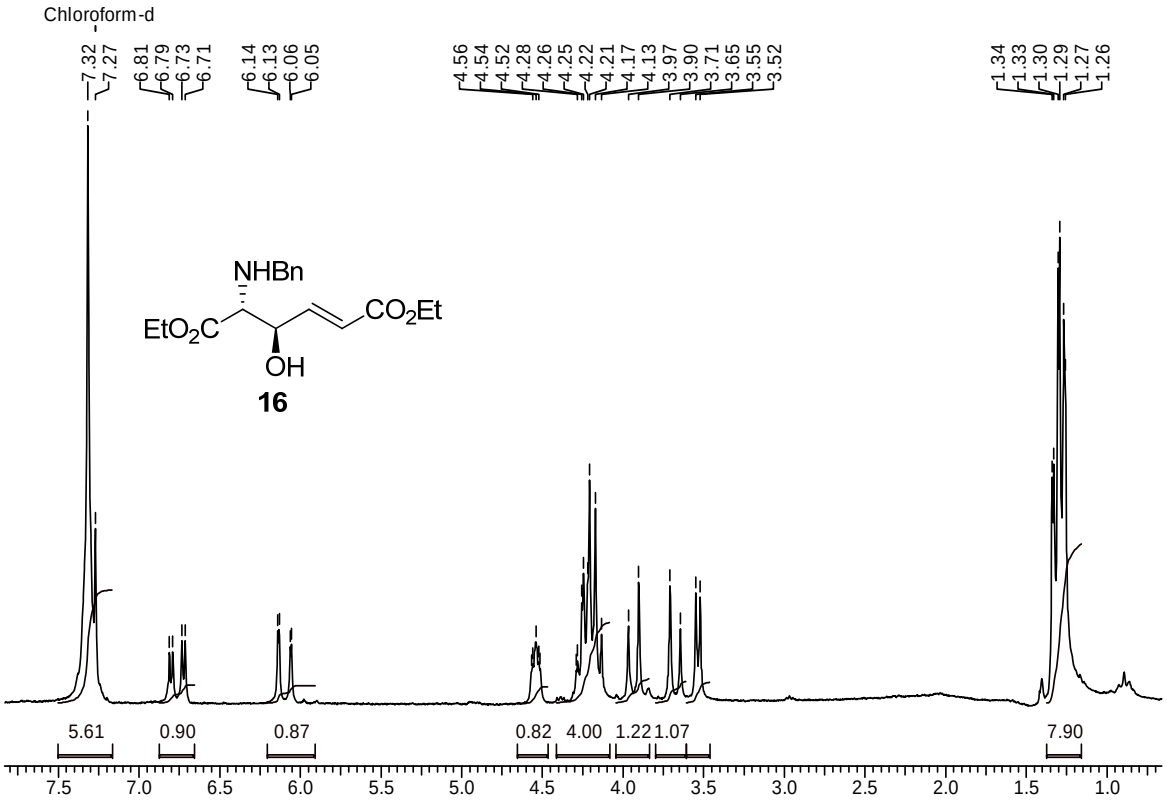

172.28
57.29
44.05
26.02
21.58
N
H
CO2H
ent-1
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


Chloroform-d
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7.27
6.81
6.79
6.73
6.71
6.14
6.13
6.06
6.05
4.56
4.54
4.52
4.28
4.26
4.25
4.22
4.21
4.17
4.13
3.97
3.90
3.71
3.65
3.55
3.52
1.34
1.33
1.30
1.29
1.27
1.26
NHBn
EtO2C
CO2Et
OH
16
5.61
0.90
0.87
0.82
4.00
1.22
1.07
7.90
7.5
7.0
6.5
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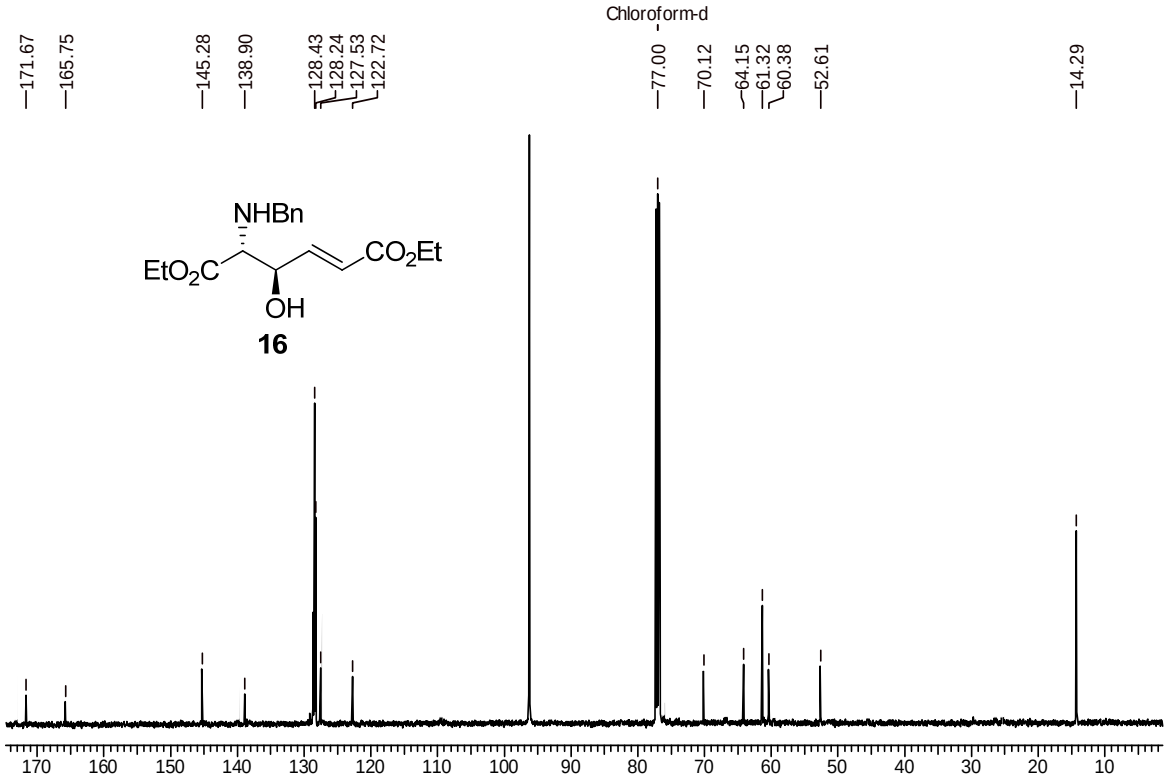
Chloroform-d
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128.43
128.24
127.53
122.72
77.00
70.12
64.15
61.32
60.38
52.61
14.29
NHBn
EtO2C
CO2Et
OH
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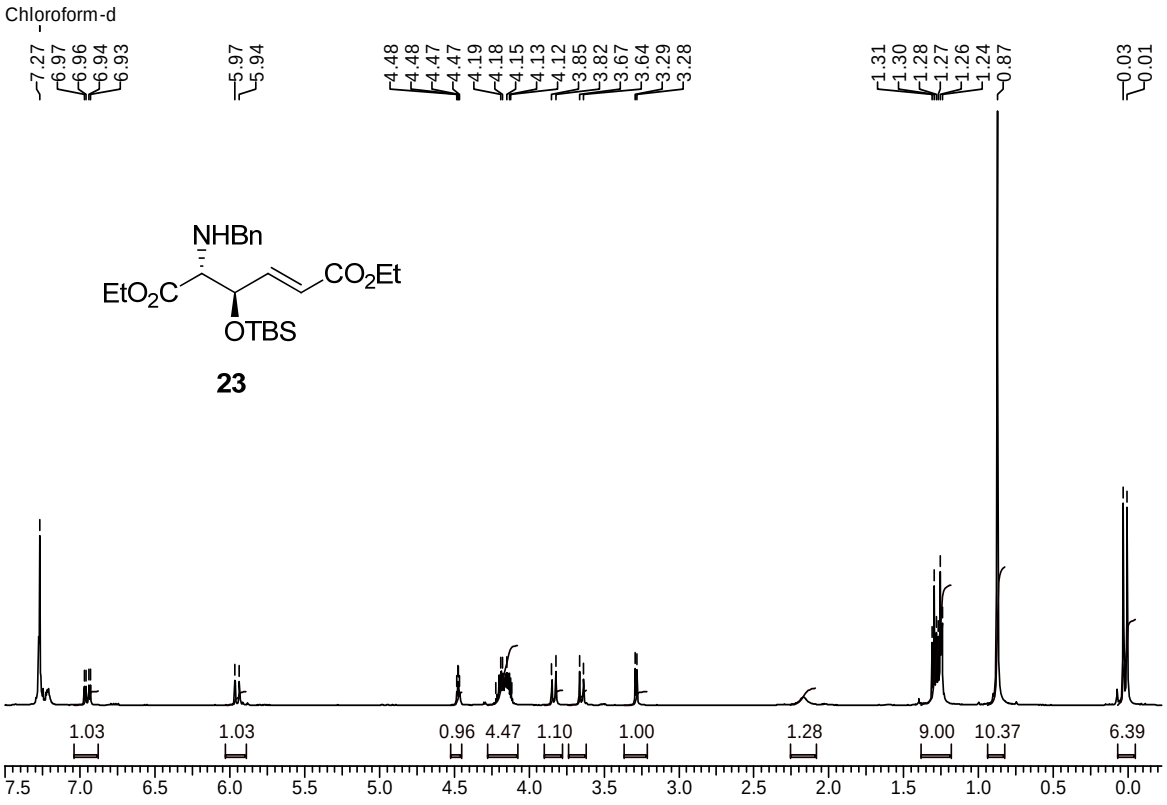
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


Chloroform-d
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5.97
5.94
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4.48
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3.85
3.82
3.67
3.64
3.29
3.28
1.31
1.30
1.28
1.27
1.26
1.24
0.87
0.03
0.01
NHBn
EtO2C
CO2Et
OTBS
23
1.03
1.03
0.96
4.47
1.10
1.00
1.28
9.00
10.37
6.39
7.5
7.0
6.5
6.0
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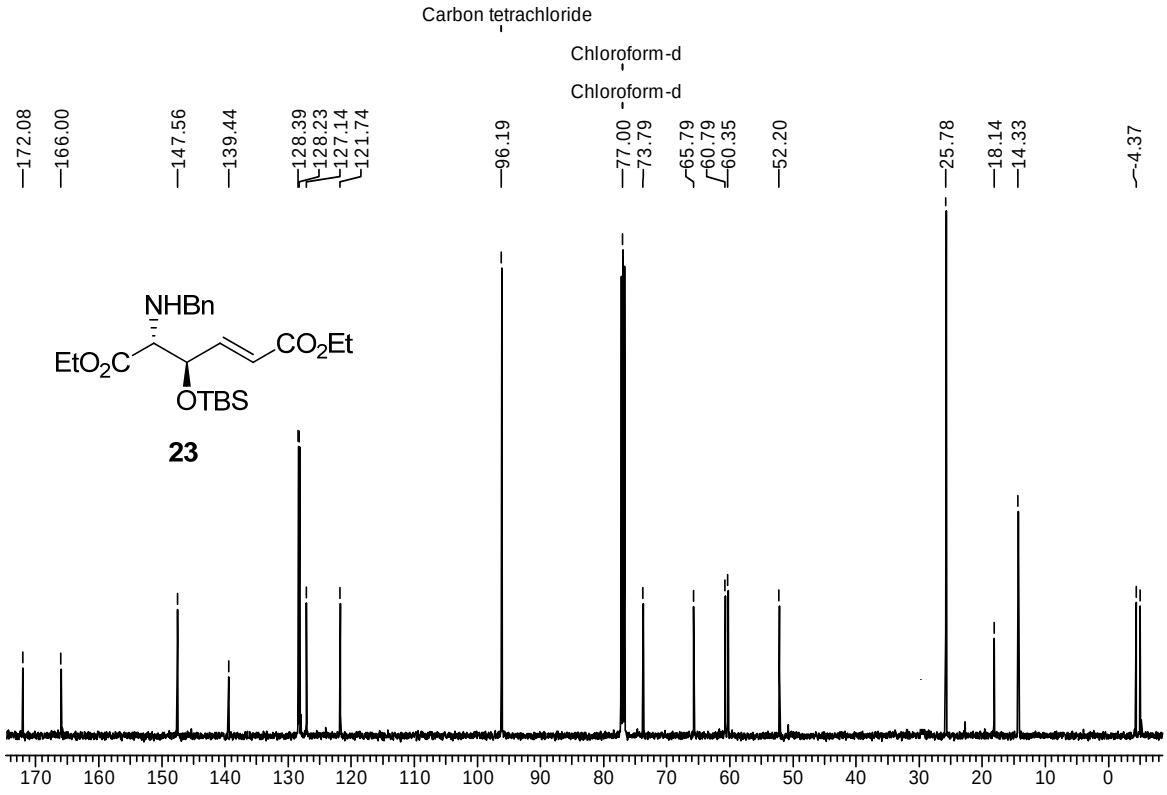
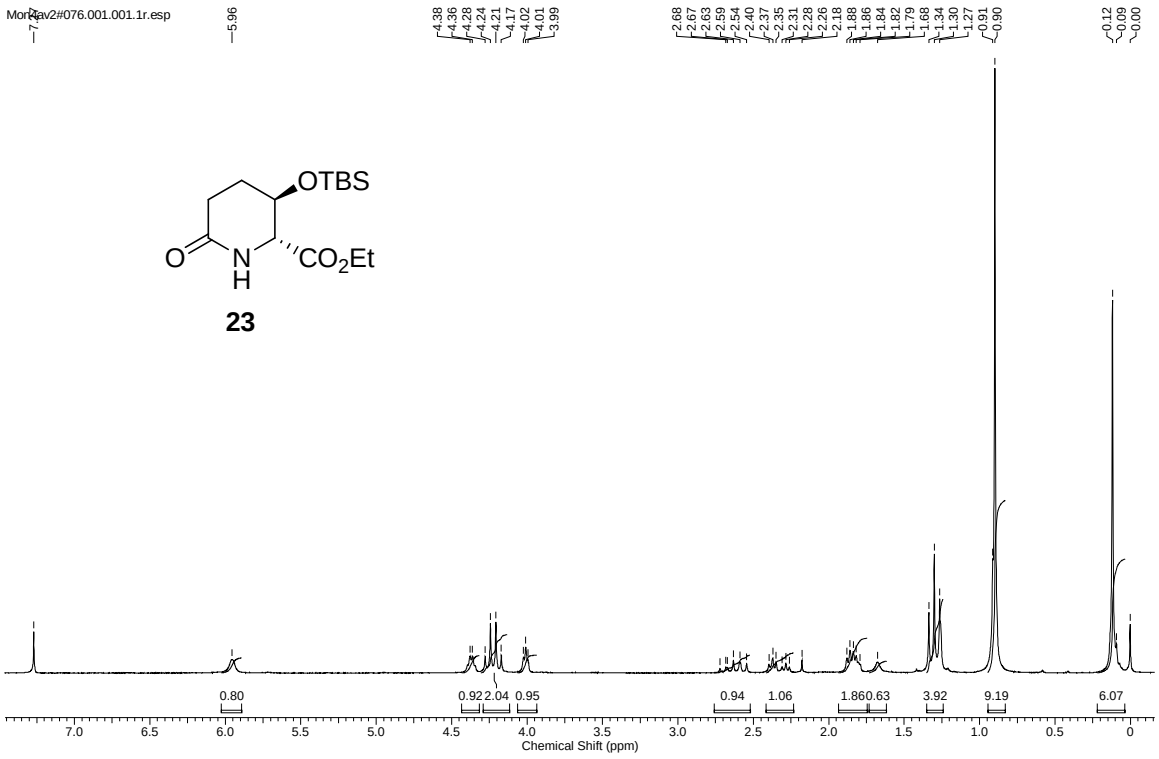
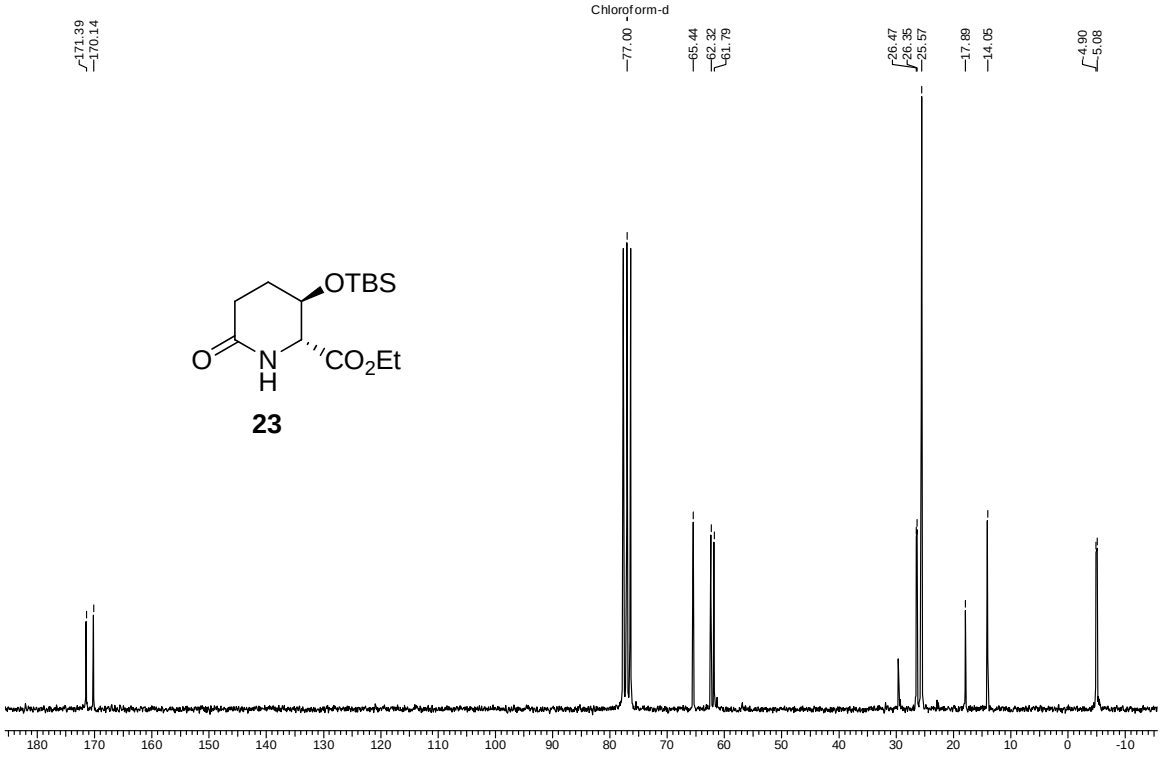
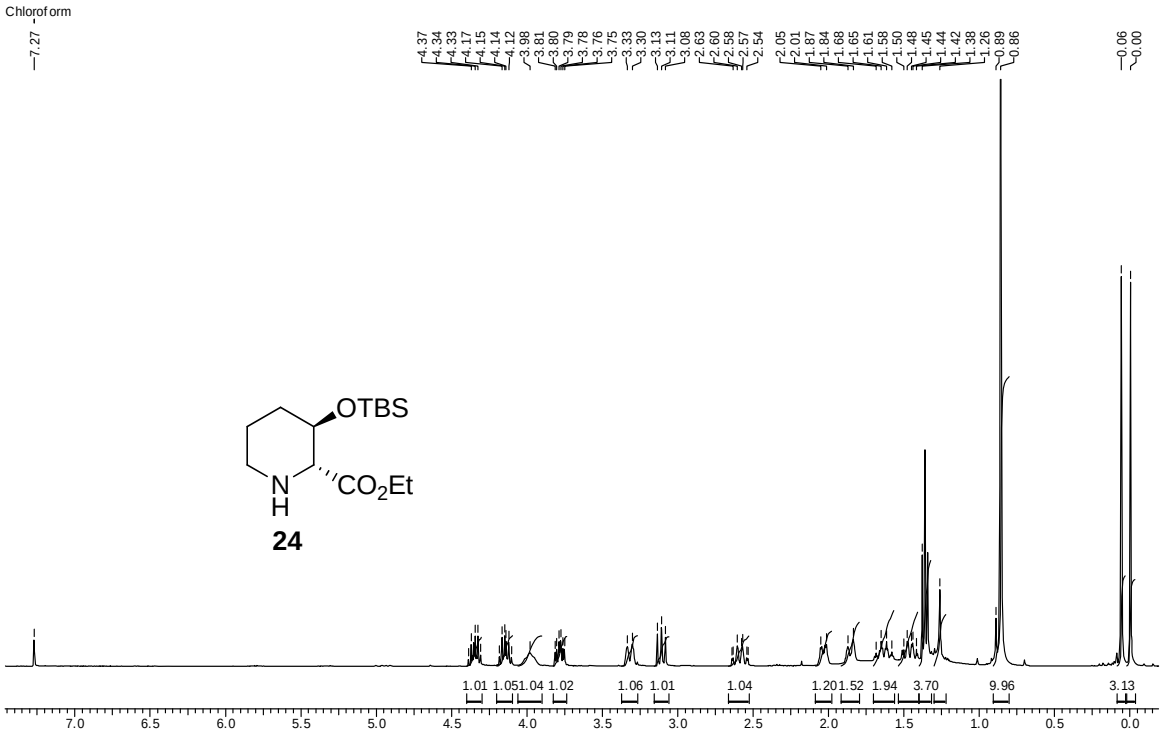
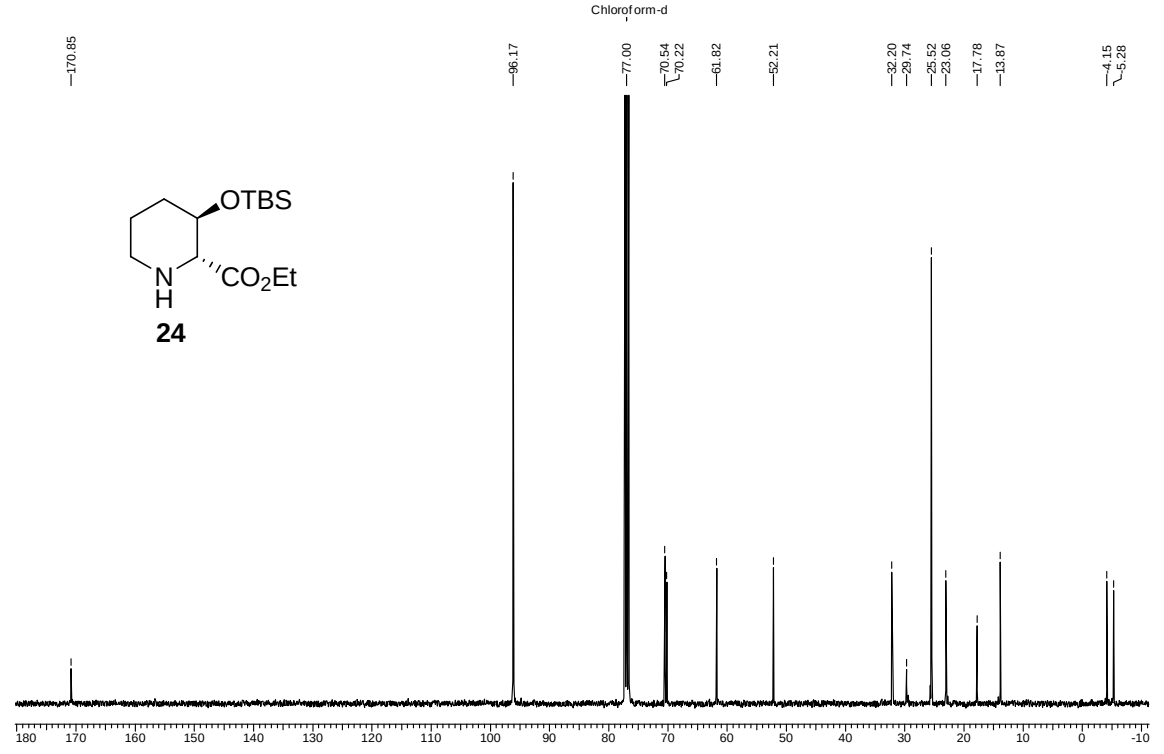
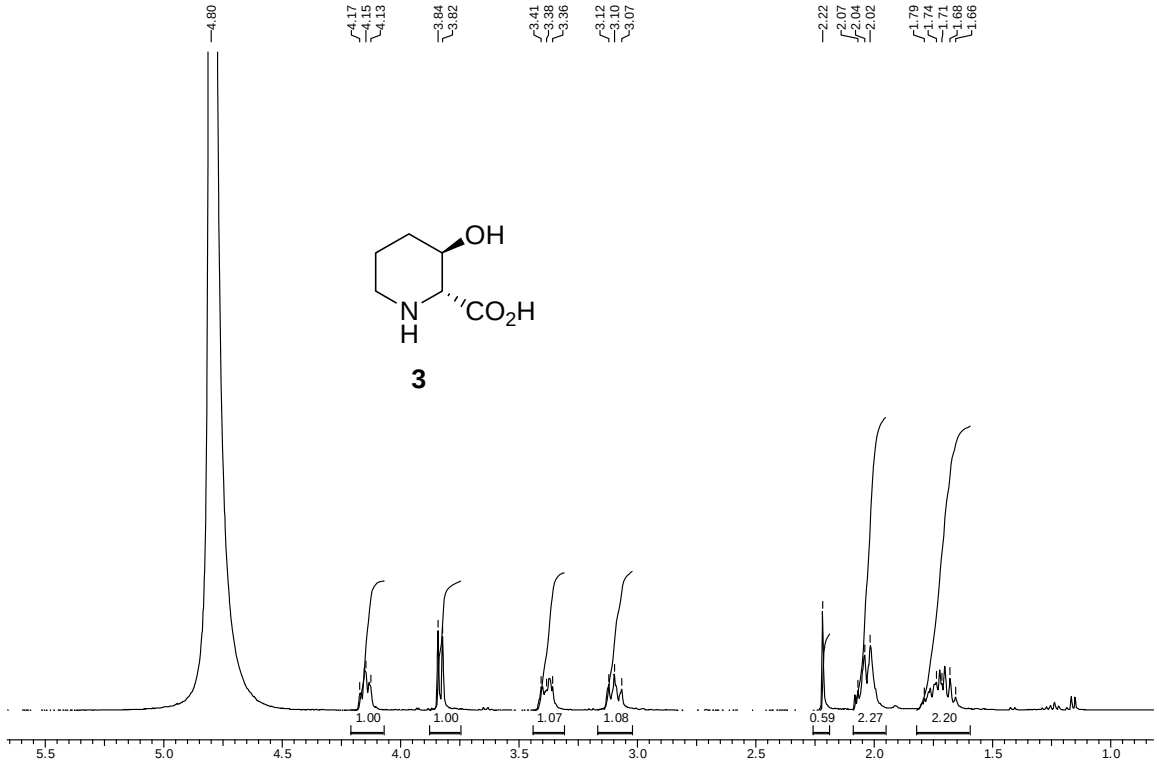

Carbon tetrachloride
Chloroform-d
Chloroform-d
172.08
166.00
147.56
139.44
128.39
128.23
127.14
121.74
96.19
77.00
73.79
65.79
60.79
60.35
52.20
25.78
18.14
14.33
-4.37
NHBn
EtO2C
CO2Et
OTBS
23
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

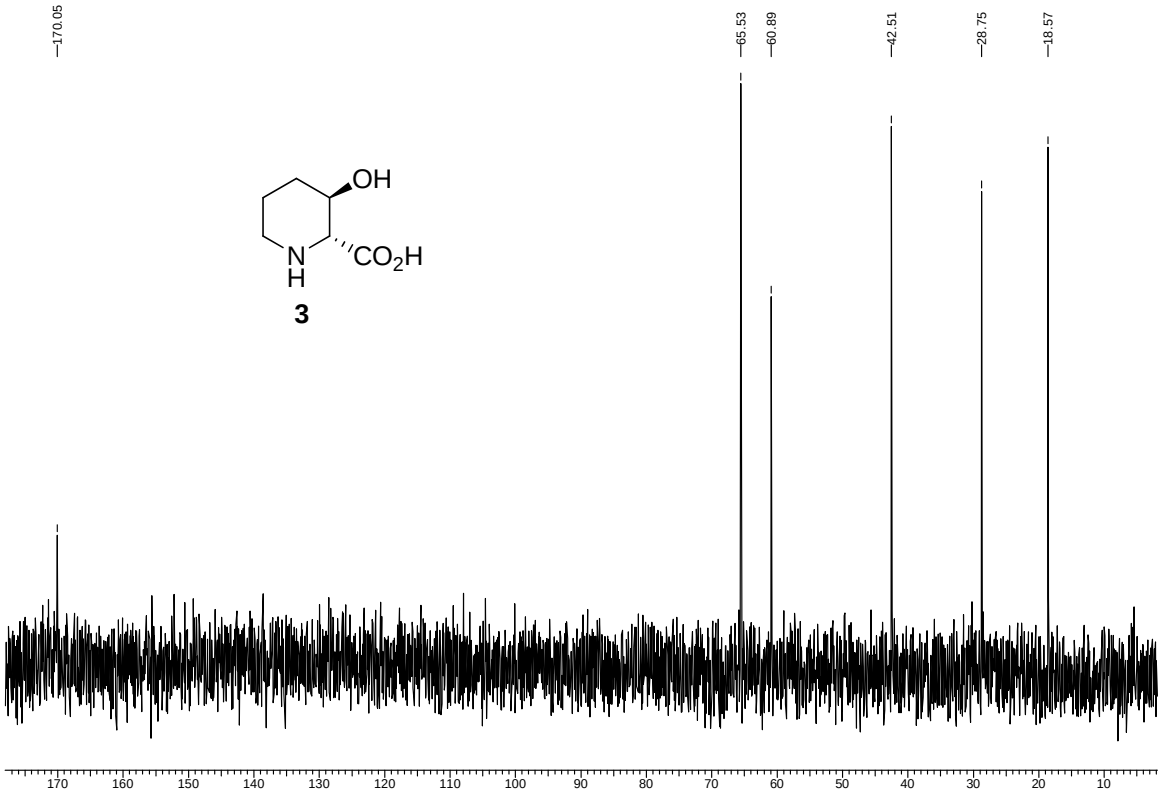

OTBS
O
N
H
CO2Et
23
Chemical Shift (ppm)

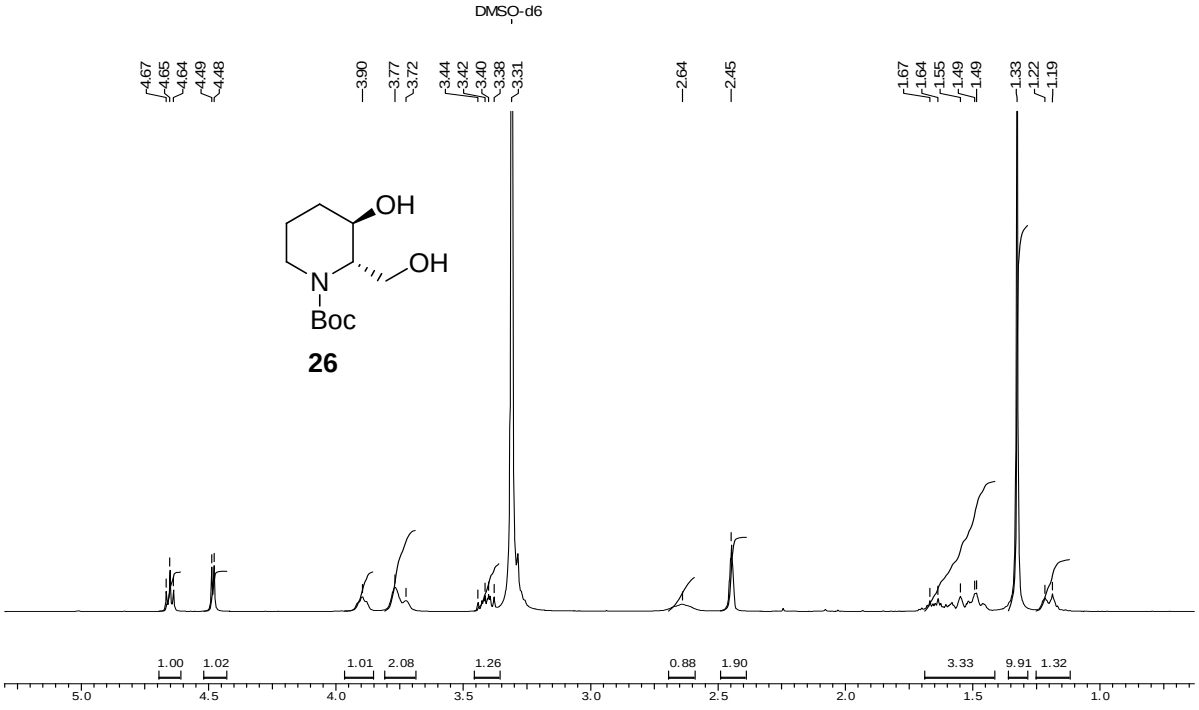

Chloroform-d
OTBS
O
N
H
CO2Et
23

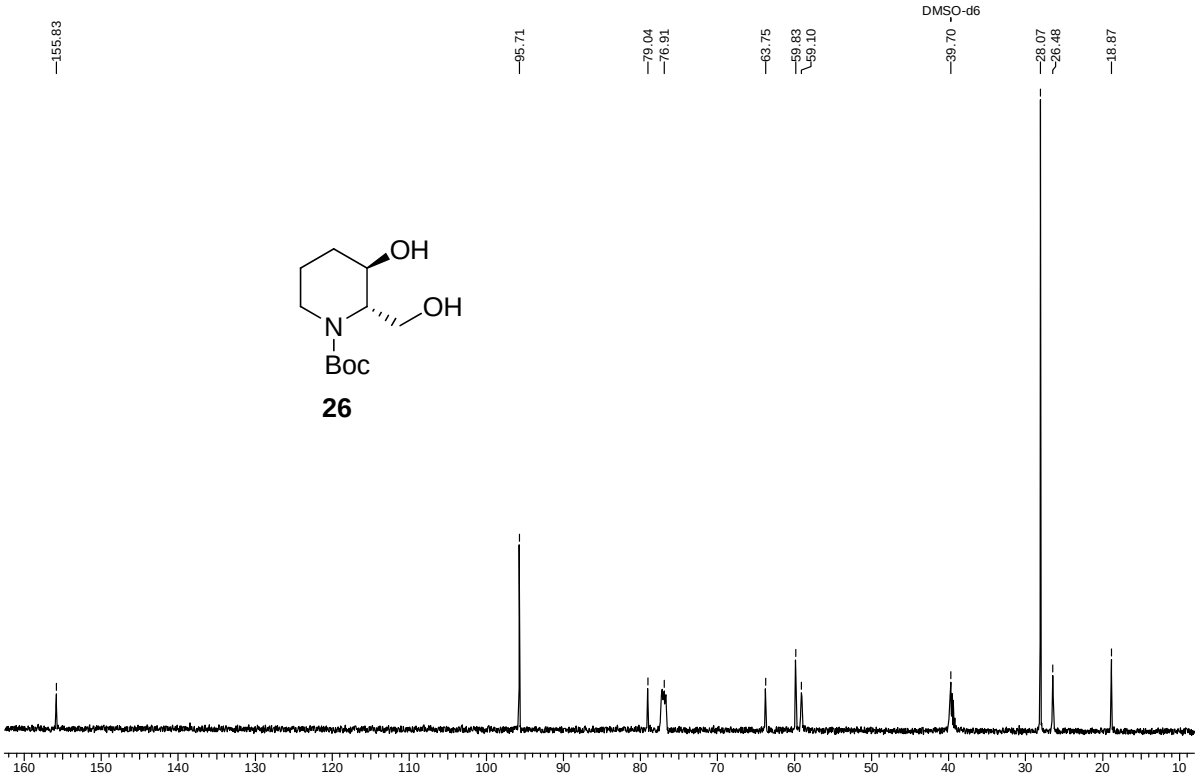

Chloroform
7.27
4.37
4.34
4.33
4.17
4.15
4.14
4.12
3.98
3.81
3.80
3.79
3.78
3.76
3.75
3.33
3.30
3.13
3.11
3.08
2.63
2.60
2.58
2.57
2.54
2.05
2.01
1.87
1.84
1.68
1.65
1.61
1.58
1.50
1.48
1.45
1.44
1.42
1.38
1.26
0.89
0.86
0.06
0.00
OTBS
N
H
CO2Et
24
1.01 1.05 1.04 1.02 1.06 1.01 1.04 1.20 1.52 1.94 3.70 9.96 3.13
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

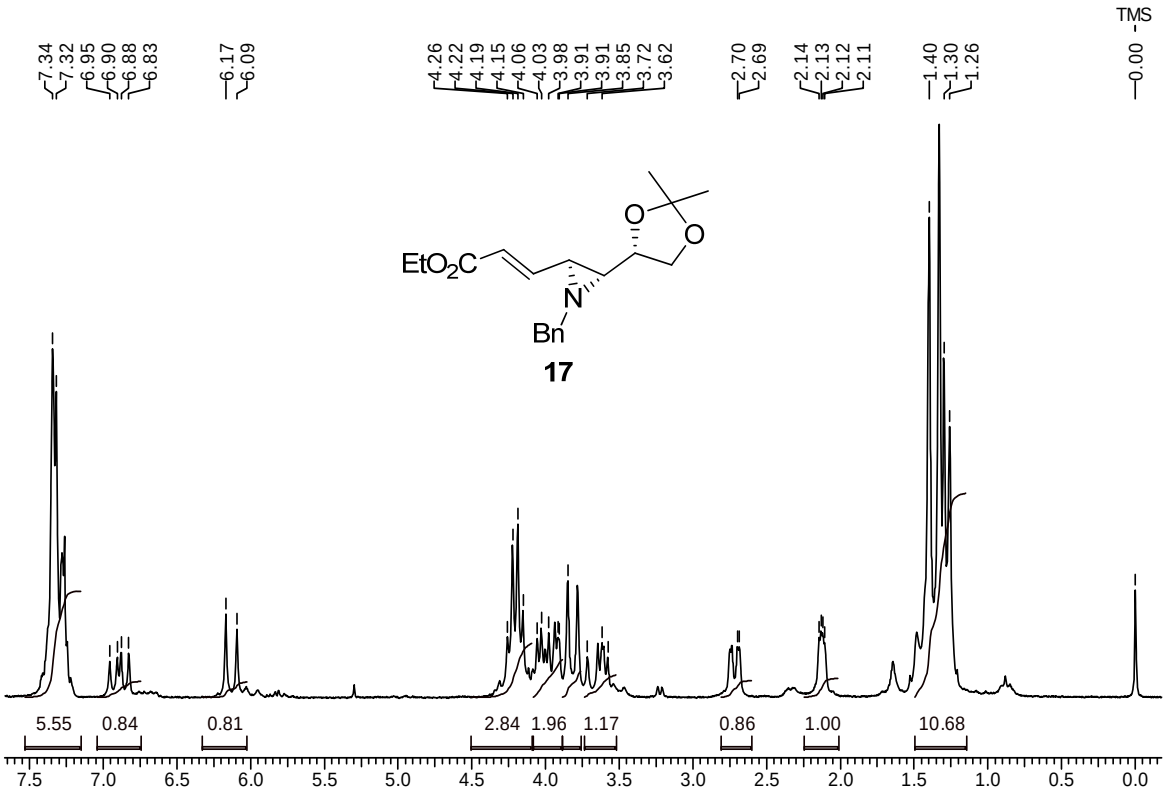

Chloroform-d
170.85
96.17
77.00
70.54
70.22
61.82
52.21
32.20
29.74
25.52
23.06
17.78
13.87
4.15
5.28
OTBS
N
H
CO2Et
24
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

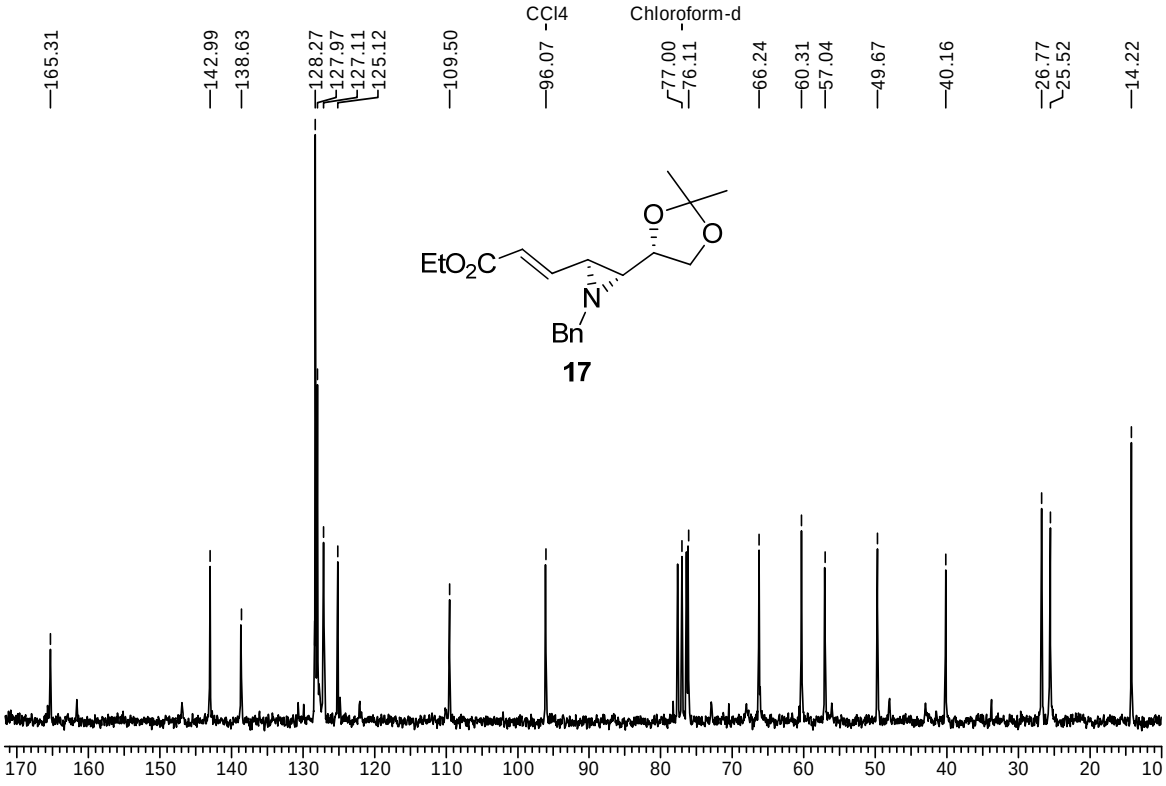

4.80
4.17
4.15
4.13
3.84
3.82
3.41
3.38
3.36
3.12
3.10
3.07
2.22
2.07
2.04
2.02
1.79
1.74
1.71
1.68
1.66
OH
N
H
CO2H
3
1.00
1.00
1.07
1.08
0.59
2.27
2.20
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

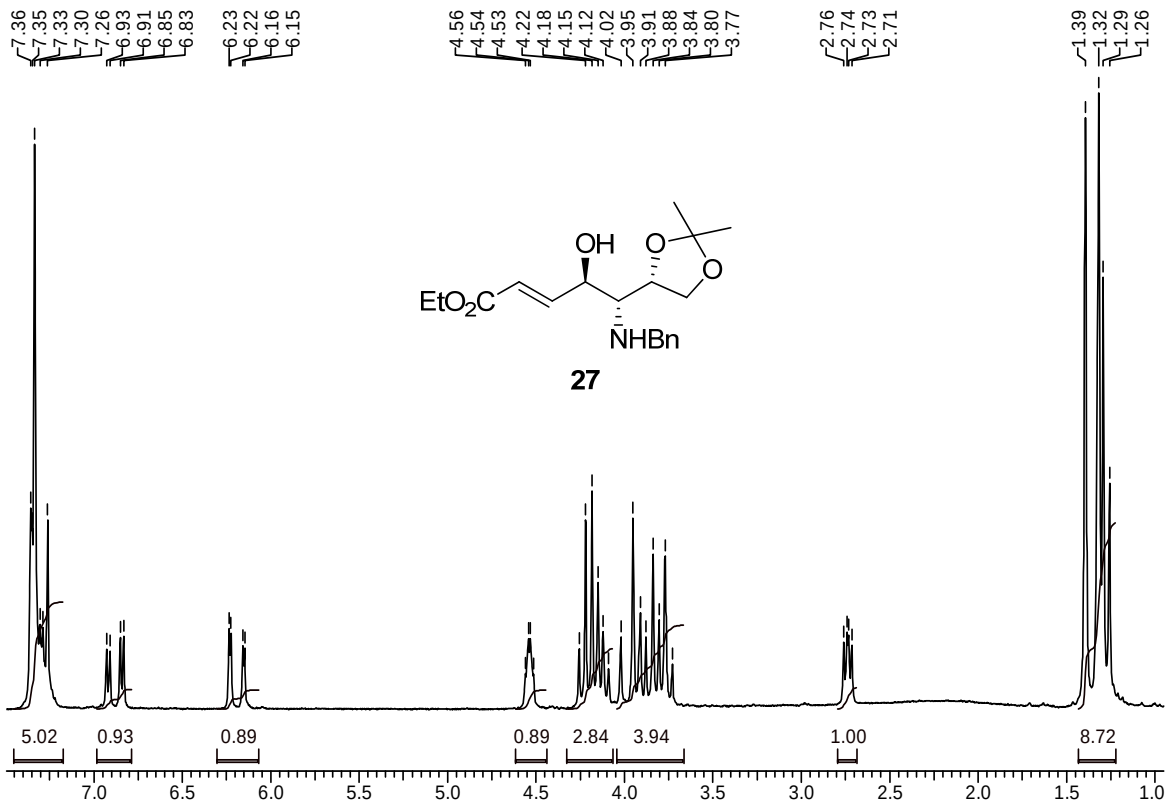

170.05
65.53
60.89
42.51
28.75
18.57
OH
N
H
CO2H
3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

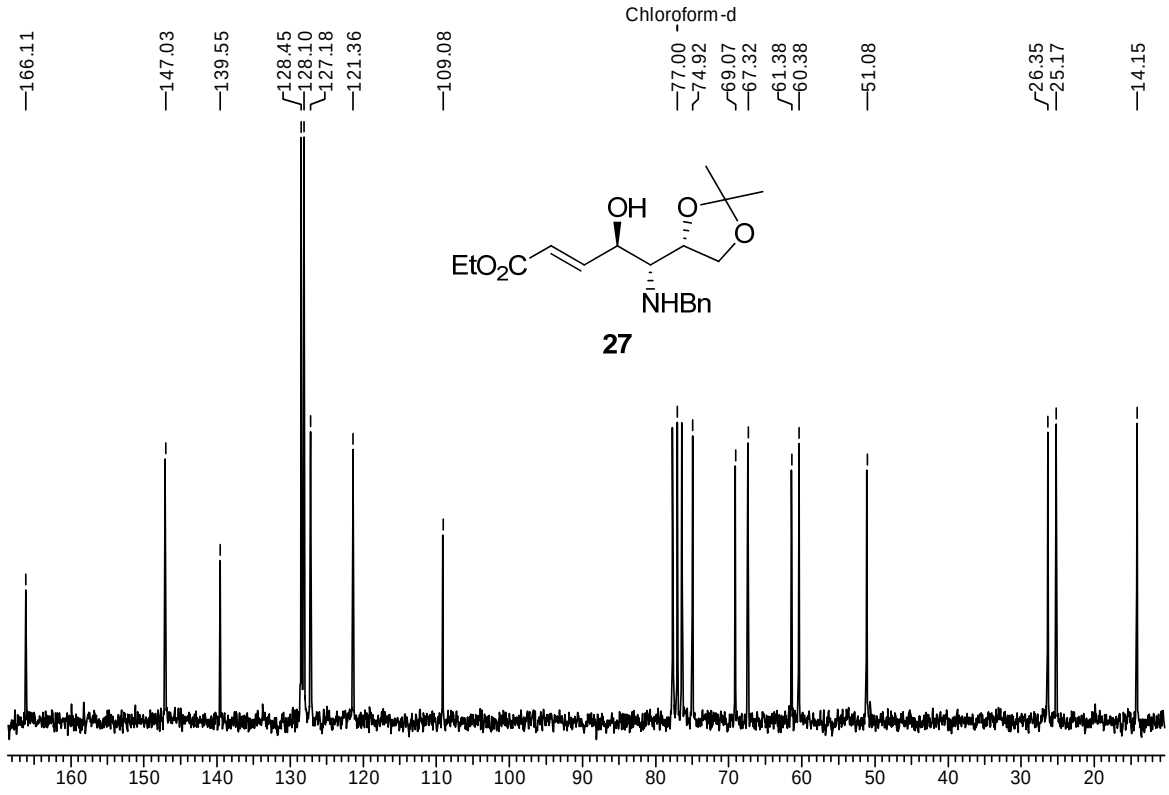

DMSO-d6
4.67
4.65
4.64
4.49
4.48
3.90
3.77
3.72
3.44
3.42
3.40
3.38
3.31
2.64
2.45
1.67
1.64
1.55
1.49
1.49
1.33
1.22
1.19
OH
OH
N
Boc
26
1.00
1.02
1.01
2.08
1.26
0.88
1.90
3.33
9.91
1.32

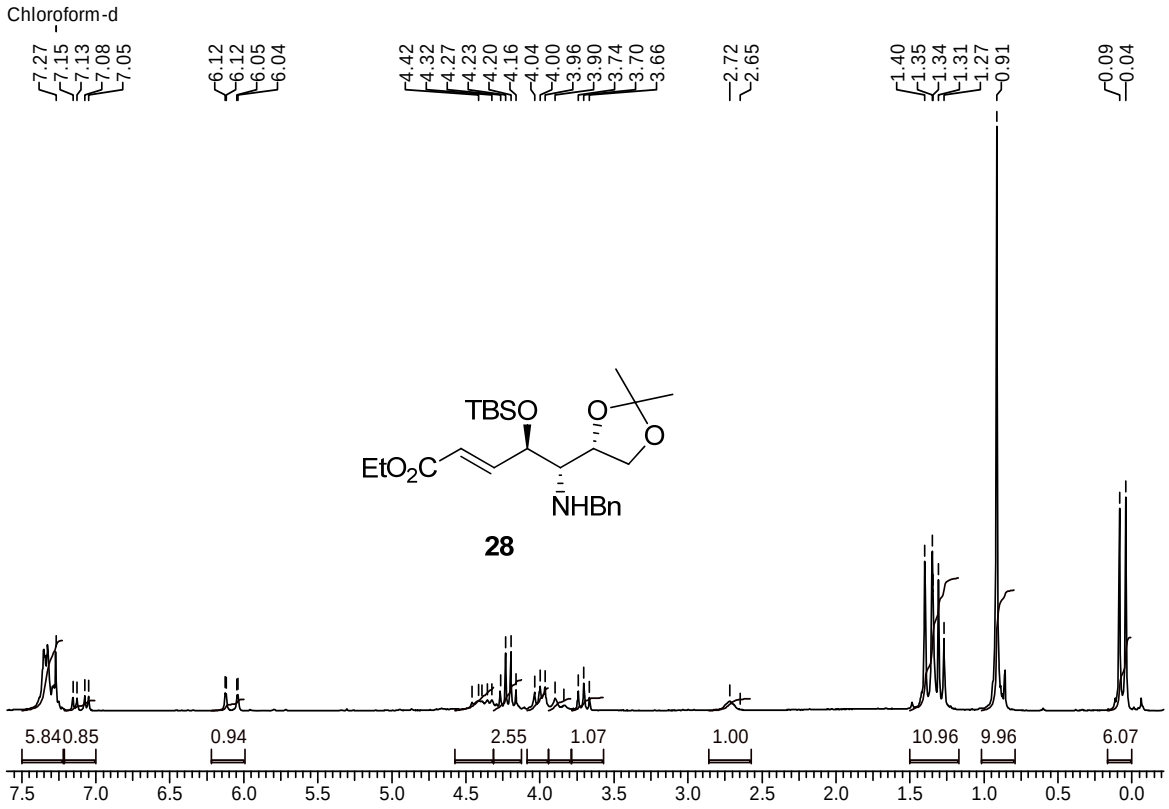

DMSO-d6
155.83
95.71
79.04
76.91
63.75
59.83
59.10
39.70
28.07
26.48
18.87
OH
OH
N
Boc
26

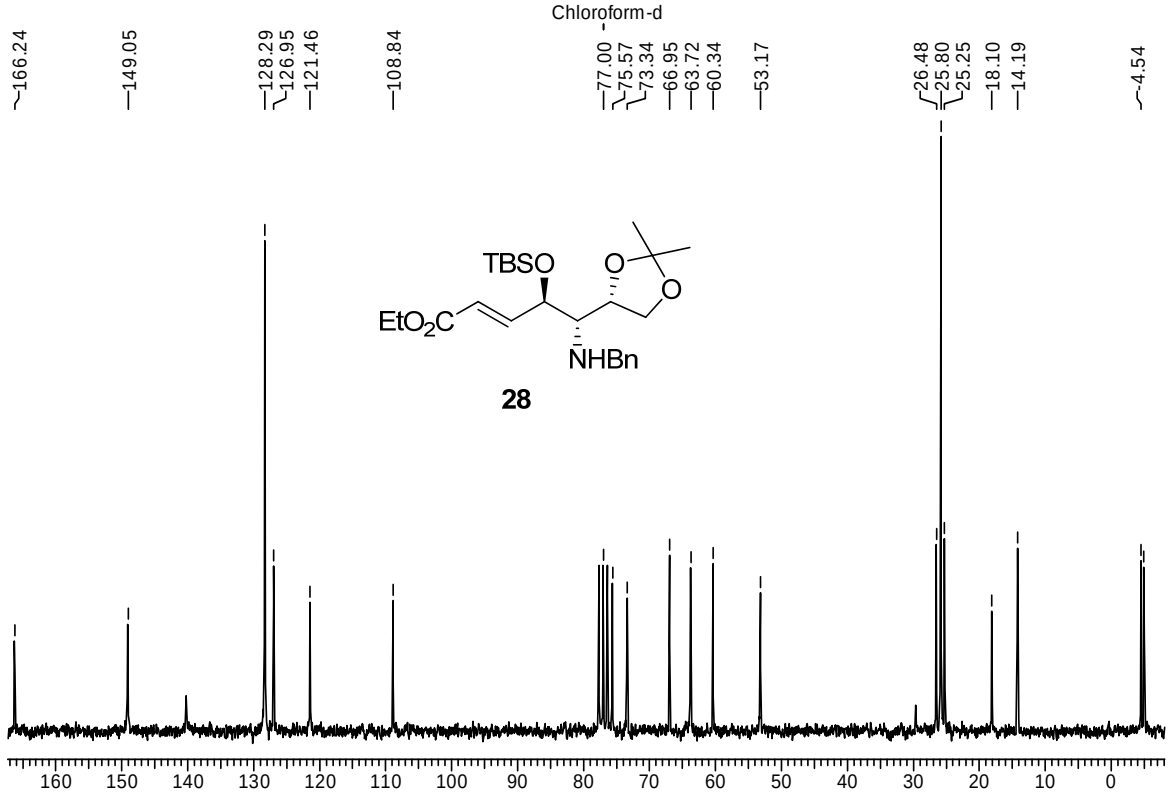

TMS
7.34
7.32
6.95
6.90
6.88
6.83
6.17
6.09
4.26
4.22
4.19
4.15
4.06
4.03
3.98
3.91
3.91
3.85
3.72
3.62
2.70
2.69
2.14
2.13
2.12
2.11
1.40
1.30
1.26
0.00
EtO2C
O
O
N
Bn
17
5.55
0.84
0.81
2.84
1.96
1.17
0.86
1.00
10.68
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

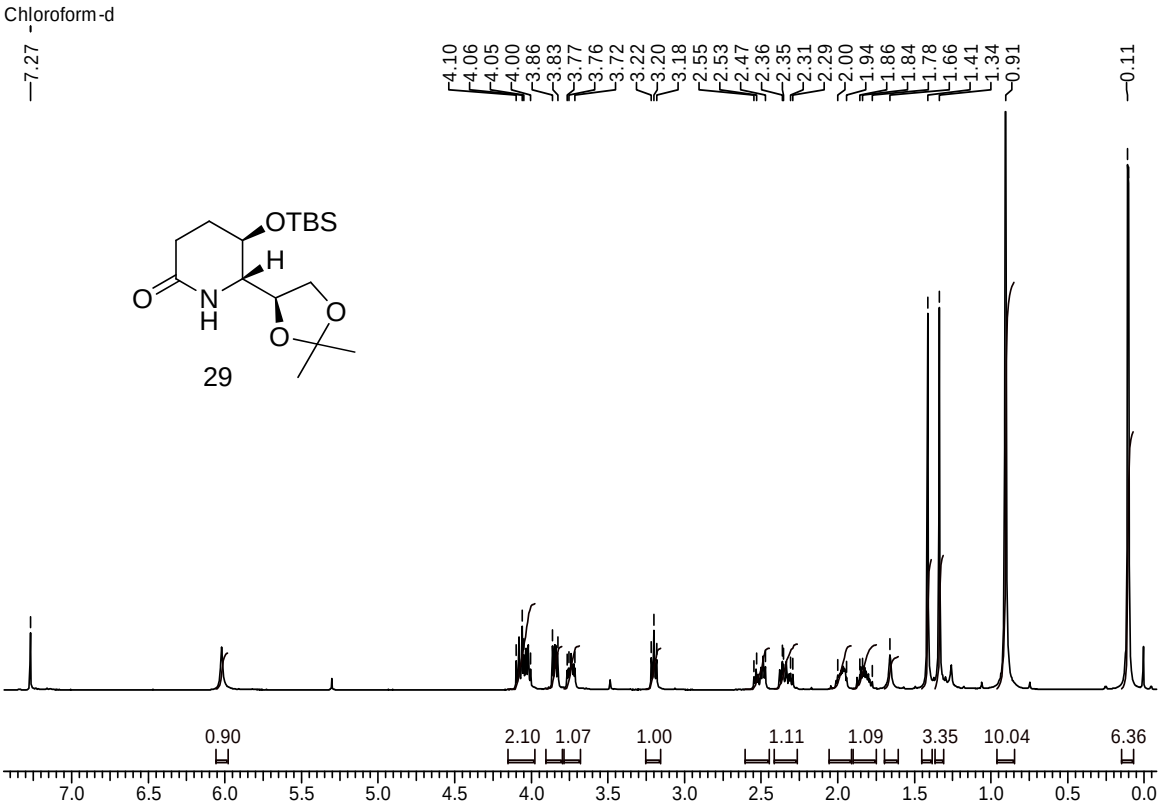

CCl4
Chloroform-d
165.31
142.99
138.63
128.27
127.97
127.11
125.12
109.50
96.07
77.00
76.11
66.24
60.31
57.04
49.67
40.16
26.77
25.52
14.22
EtO2C
O
O
N
Bn
17
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

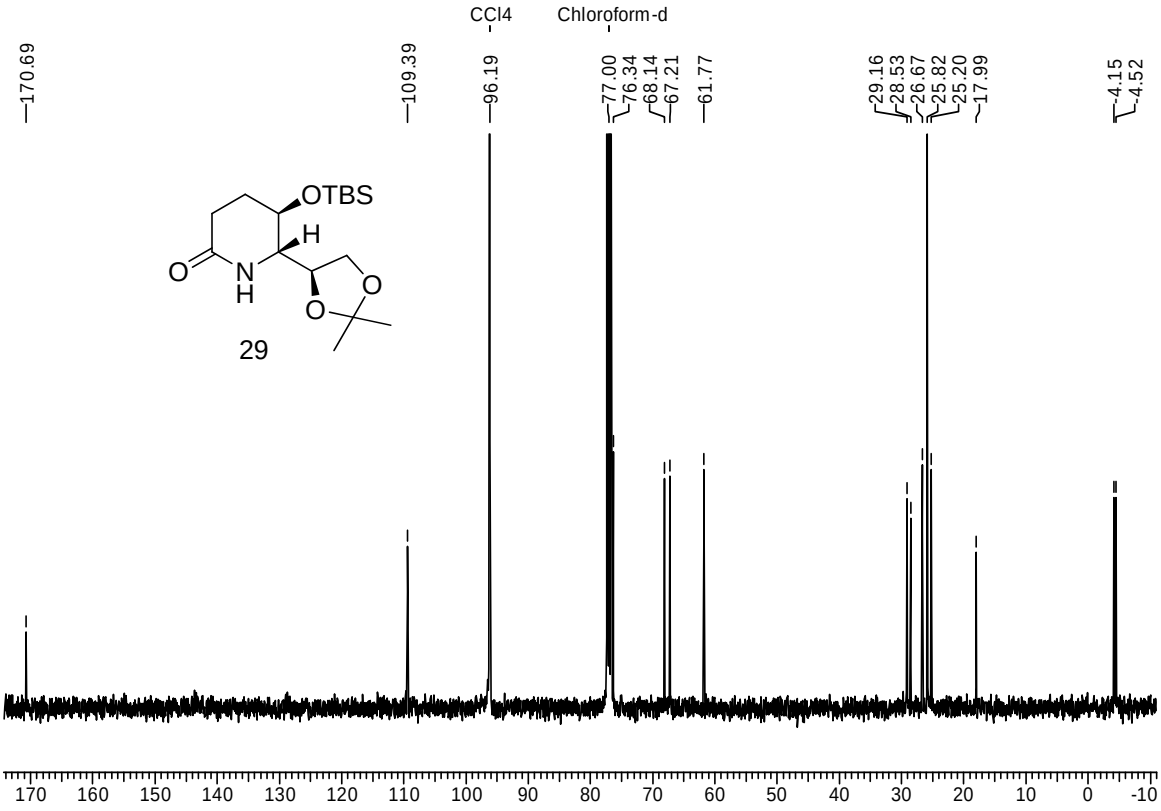

7.36
7.35
7.33
7.30
7.26
6.93
6.91
6.85
6.83
6.23
6.22
6.16
6.15
4.56
4.54
4.53
4.22
4.18
4.15
4.12
4.02
3.95
3.91
3.88
3.84
3.80
3.77
2.76
2.74
2.73
2.71
1.39
1.32
1.29
1.26
OH
O
O
EtO2C
NHBn
27
5.02
0.93
0.89
0.89
2.84
3.94
1.00
8.72
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

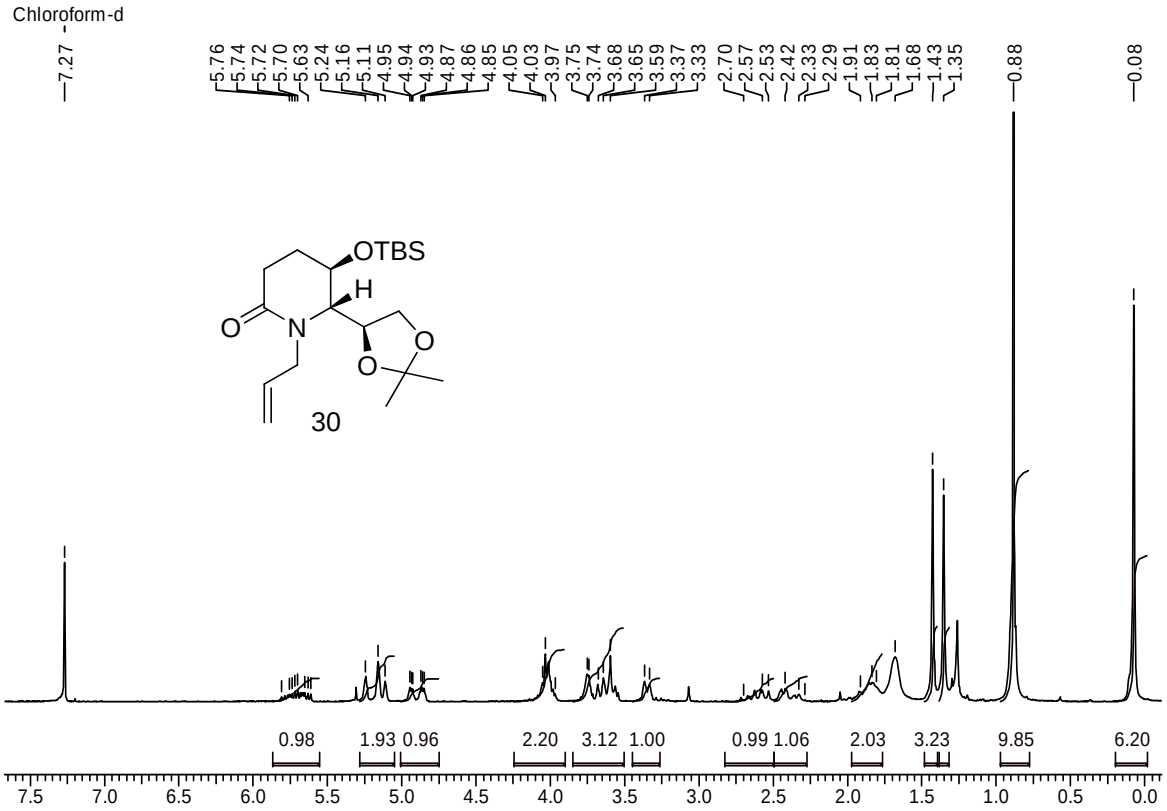

Chloroform-d
166.11
147.03
139.55
128.45
128.10
127.18
121.36
109.08
77.00
74.92
69.07
67.32
61.38
60.38
51.08
26.35
25.17
14.15
OH
O
O
EtO2C
NHBn
27
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

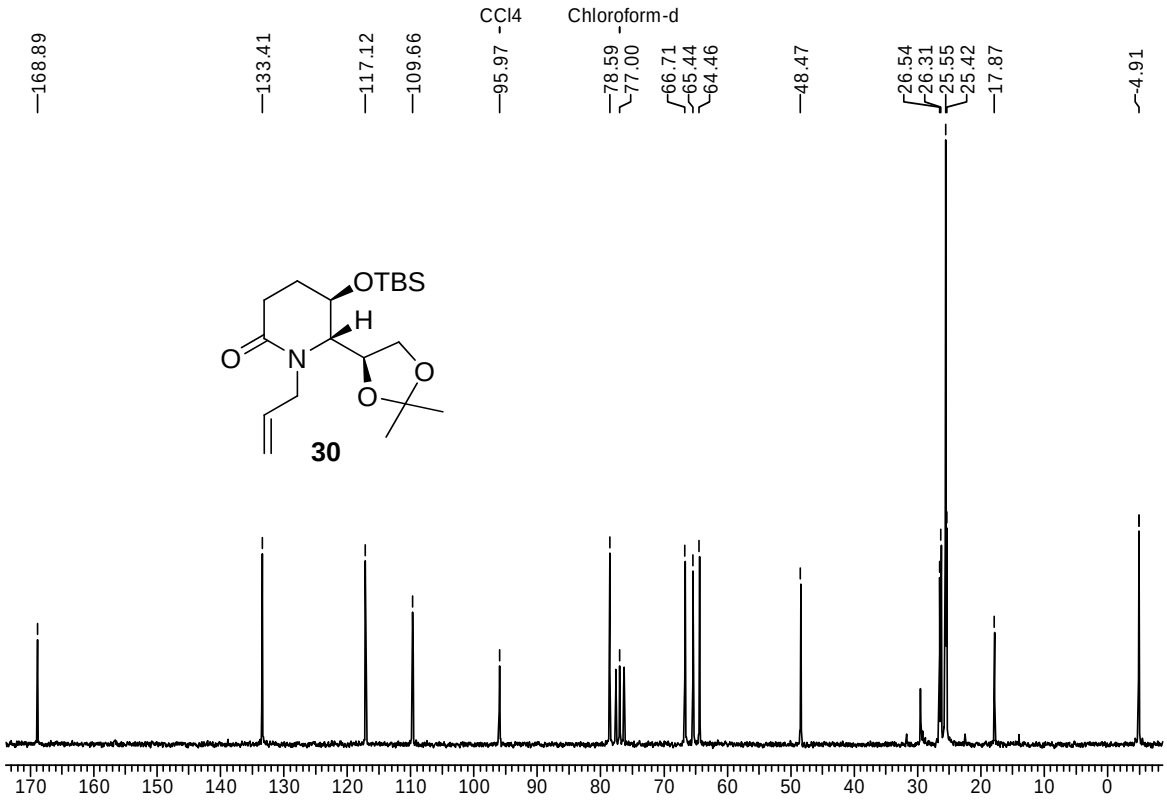

Chloroform-d
7.27
7.15
7.13
7.08
7.05
6.12
6.12
6.05
6.04
4.42
4.32
4.27
4.23
4.20
4.16
4.04
4.00
3.96
3.90
3.74
3.70
3.66
2.72
2.65
1.40
1.35
1.34
1.31
1.27
0.91
0.09
0.04
TBSO
O
O
EtO2C
NHBn
28
5.84
0.85
0.94
2.55
1.07
1.00
10.96
9.96
6.07
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

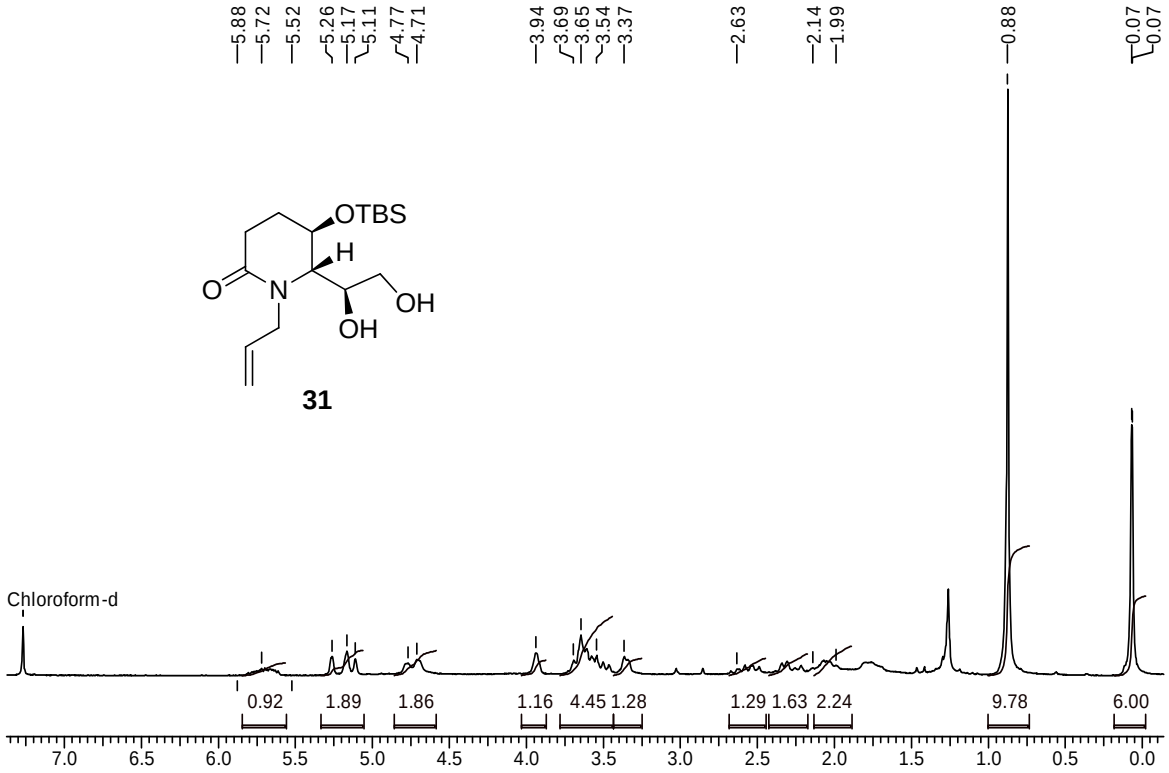

Chloroform-d
166.24
149.05
128.29
126.95
121.46
108.84
77.00
75.57
73.34
66.95
63.72
60.34
53.17
26.48
25.80
25.25
18.10
14.19
-4.54
TBSO
O
O
EtO2C
NHBn
28
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

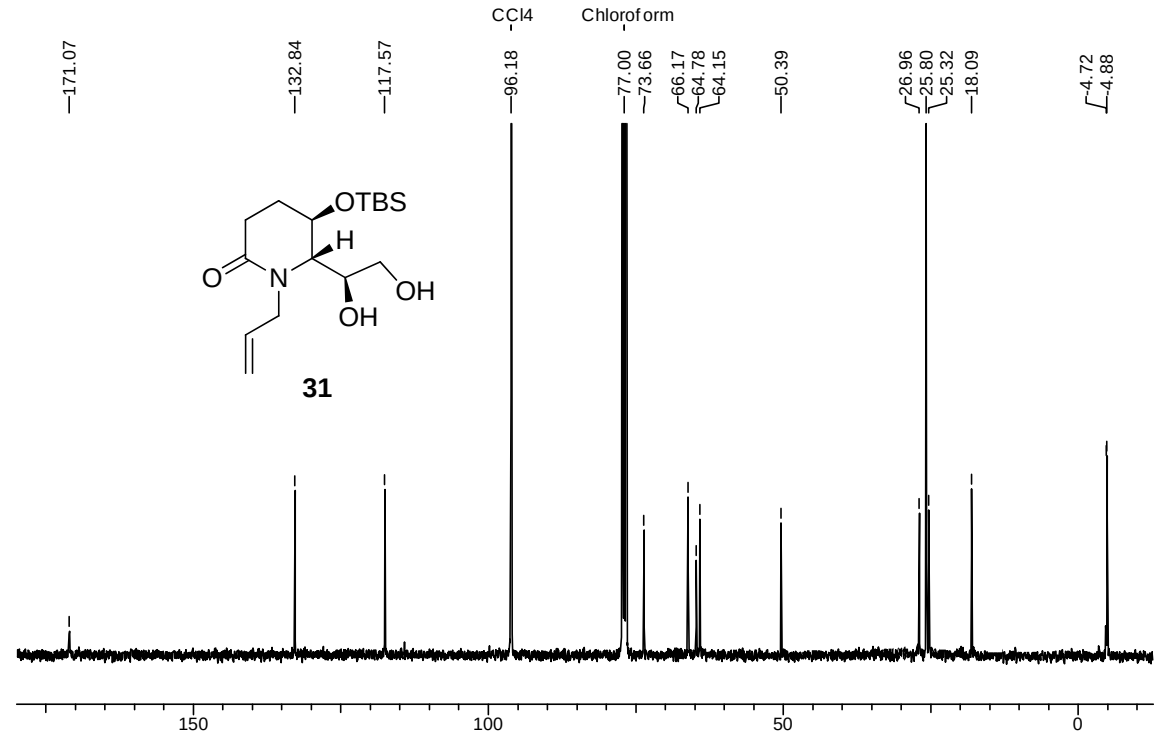

Chloroform-d
7.27
4.10
4.06
4.05
4.00
3.86
3.83
3.77
3.76
3.72
3.22
3.20
3.18
2.55
2.53
2.47
2.36
2.35
2.31
2.29
2.00
1.94
1.86
1.84
1.78
1.66
1.41
1.34
0.91
0.11
OTBS
H
O
N
H
O
O
29
0.90
2.10
1.07
1.00
1.11
1.09
3.35
10.04
6.36
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

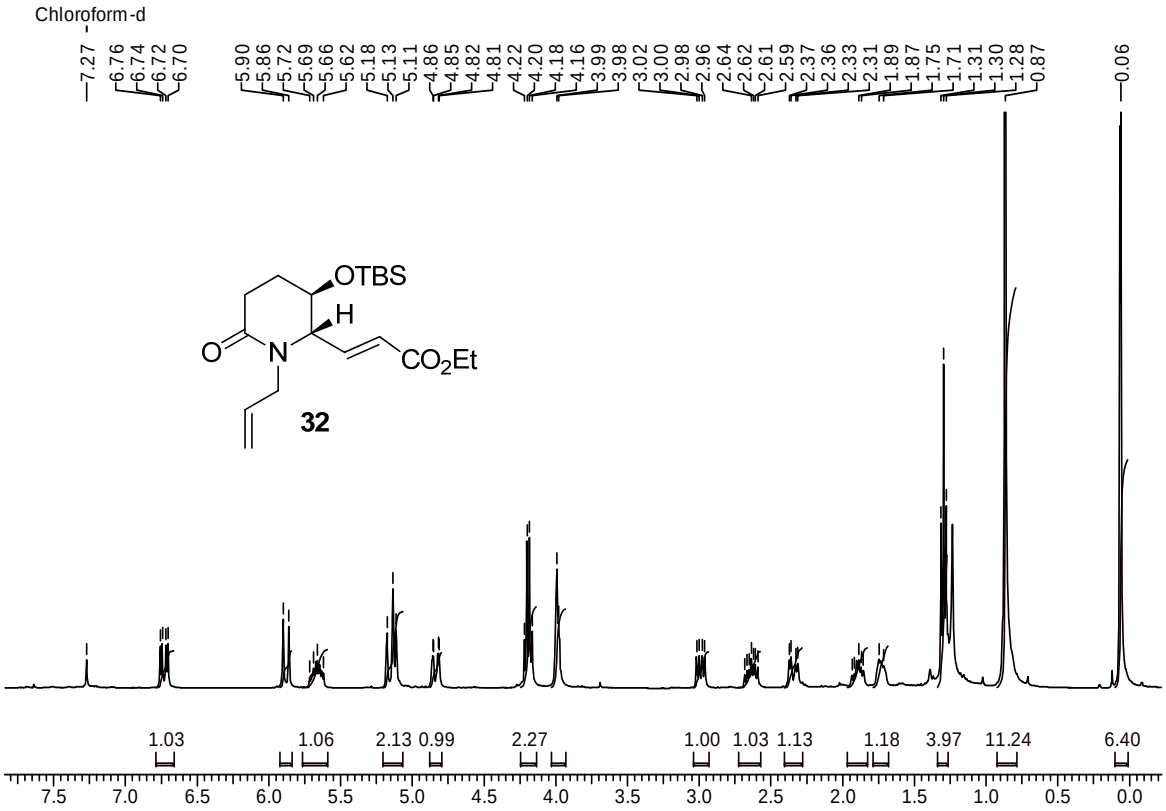

CCl4
Chloroform-d
170.69
109.39
96.19
77.00
76.34
68.14
67.21
61.77
29.16
28.53
26.67
25.82
25.20
17.99
4.15
4.52
OTBS
H
O
N
H
O
O
29
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

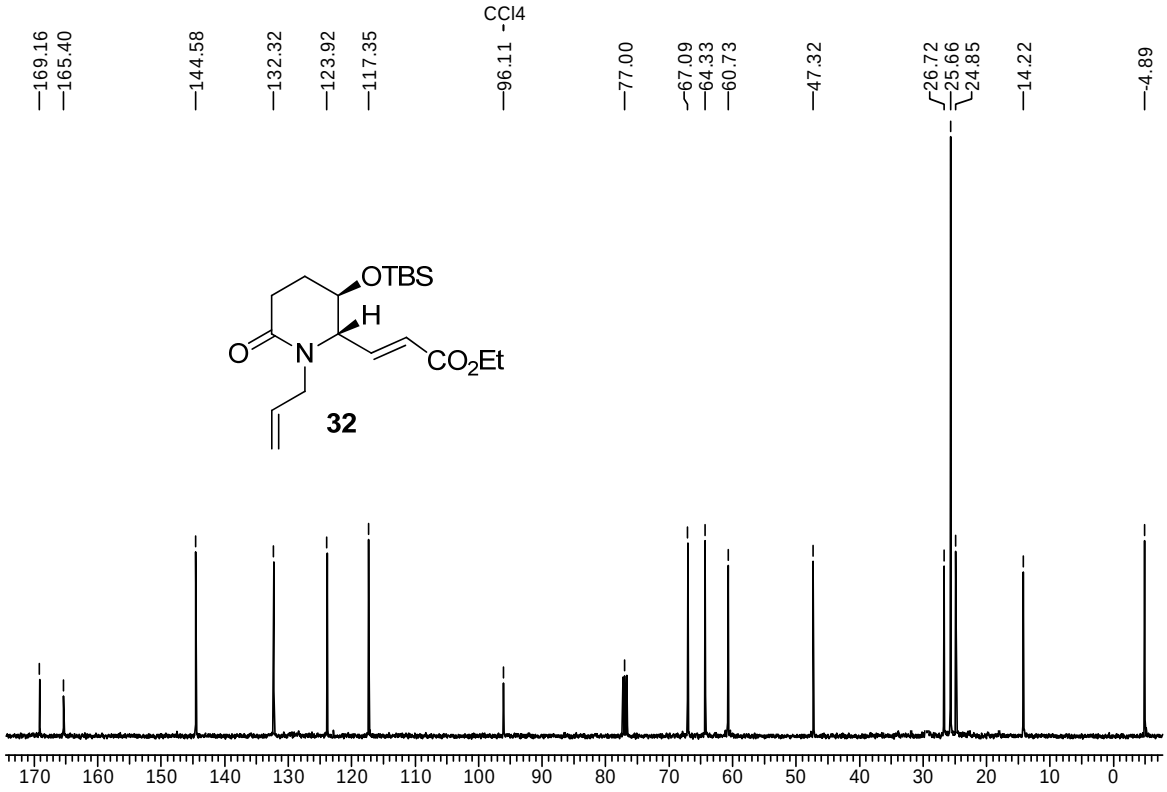

Chloroform-d
7.27
5.76
5.74
5.72
5.70
5.63
5.24
5.16
5.11
4.95
4.94
4.93
4.87
4.86
4.85
4.05
4.03
3.97
3.75
3.74
3.68
3.65
3.59
3.37
3.33
2.70
2.57
2.53
2.42
2.33
2.29
1.91
1.83
1.81
1.68
1.43
1.35
0.88
0.08
OTBS
H
O
N
O
O
30
0.98
1.93
0.96
2.20
3.12
1.00
0.99
1.06
2.03
3.23
9.85
6.20
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

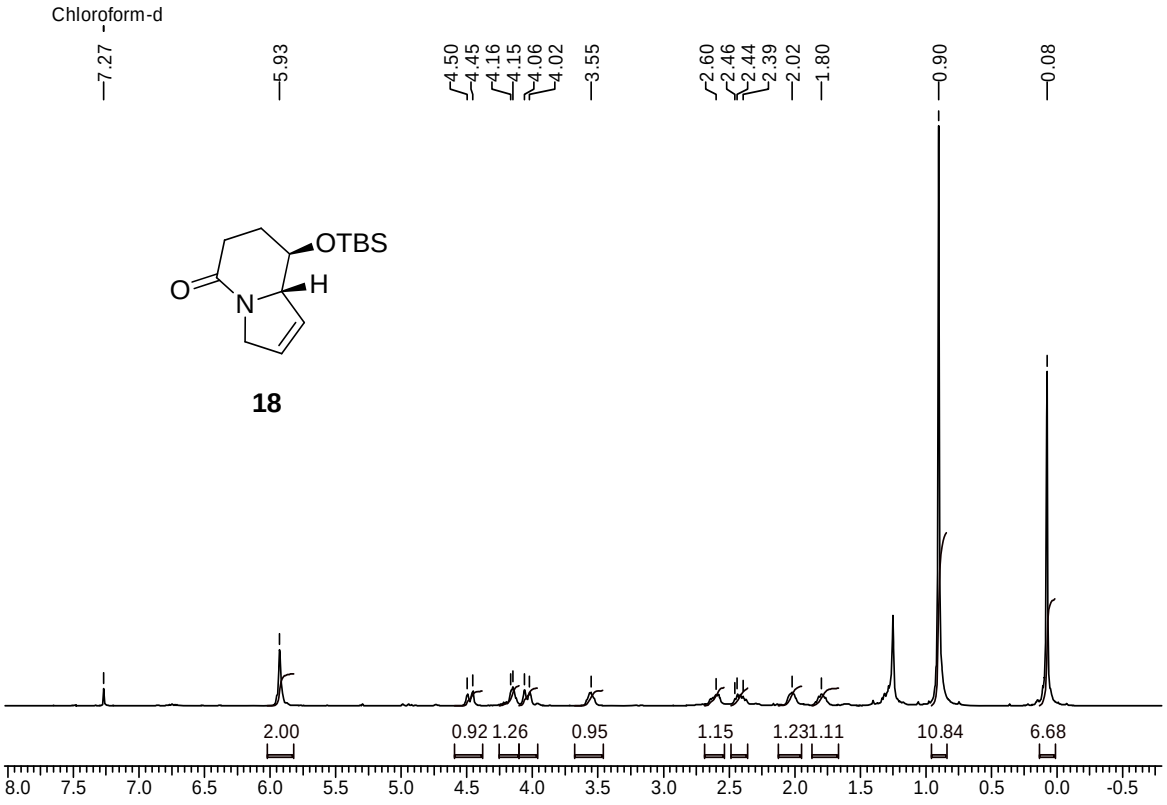

CCl4
Chloroform-d
168.89
133.41
117.12
109.66
95.97
78.59
77.00
66.71
65.44
64.46
48.47
26.54
26.31
25.55
25.42
17.87
4.91
OTBS
H
O
N
O
O
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


5.88
5.72
5.52
5.26
5.17
5.11
4.77
4.71
3.94
3.69
3.65
3.54
3.37
2.63
2.14
1.99
0.88
0.07
0.07
OTBS
H
O
N
OH
OH
31
Chloroform-d
0.92
1.89
1.86
1.16
4.45
1.28
1.29
1.63
2.24
9.78
6.00
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

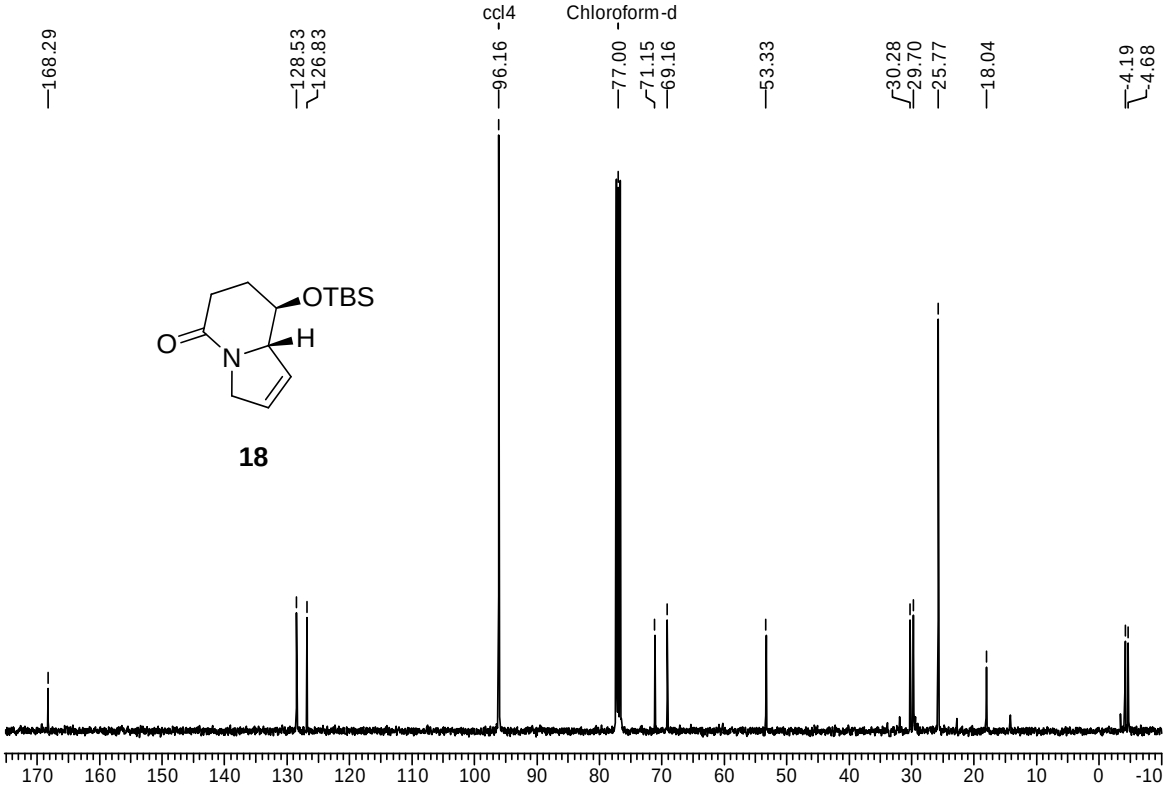

CCl4
Chloroform
171.07
132.84
117.57
96.18
77.00
73.66
66.17
64.78
64.15
50.39
26.96
25.80
25.32
18.09
4.72
4.88
OTBS
H
O
N
OH
OH
31
150
100
50
0


Chloroform-d
7.27
6.76
6.74
6.72
6.70
5.90
5.86
5.72
5.69
5.66
5.62
5.18
5.13
5.11
4.86
4.85
4.82
4.81
4.22
4.20
4.18
4.16
3.99
3.98
3.02
3.00
2.98
2.96
2.64
2.62
2.61
2.59
2.37
2.36
2.33
2.31
1.89
1.87
1.75
1.71
1.31
1.30
1.28
0.87
0.06
OTBS
H
O
N
CO2Et
32
1.03
1.06
2.13
0.99
2.27
1.00
1.03
1.13
1.18
3.97
11.24
6.40
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

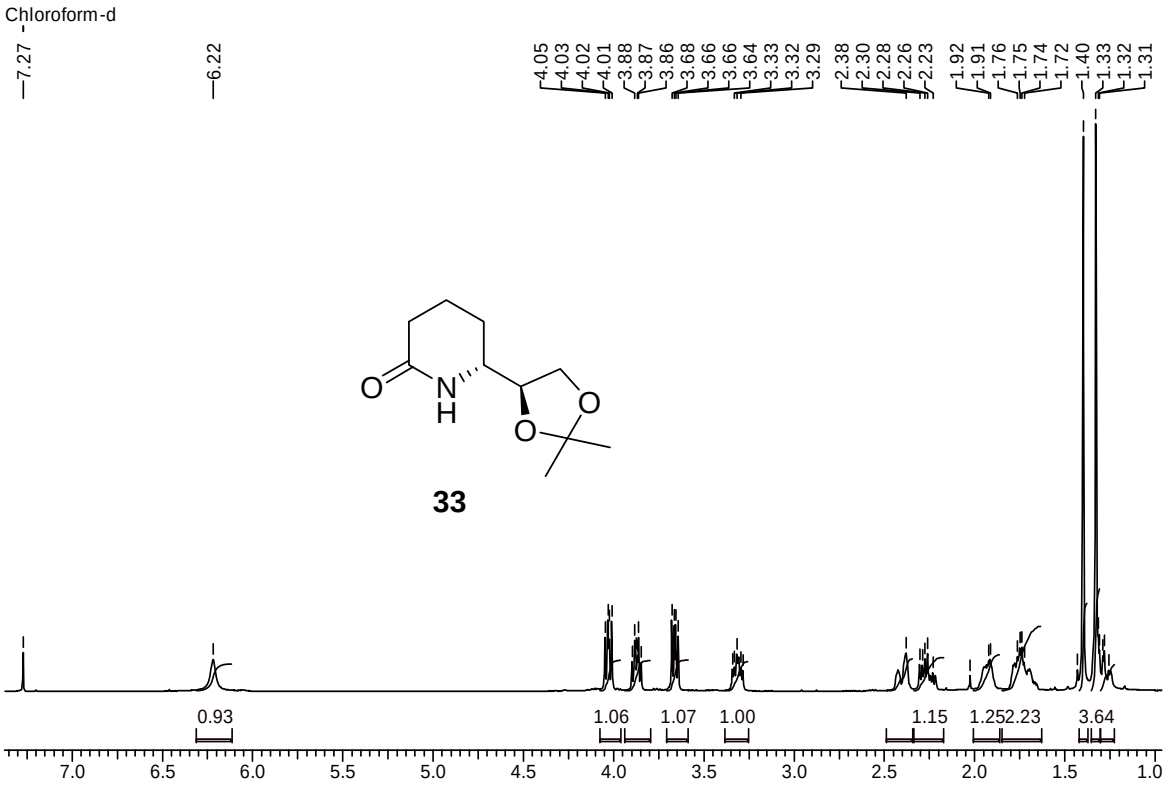

169.16
165.40
144.58
132.32
123.92
117.35
CCl4
96.11
77.00
67.09
64.33
60.73
47.32
26.72
25.66
24.85
14.22
4.89
OTBS
H
O
N
CO2Et
32
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

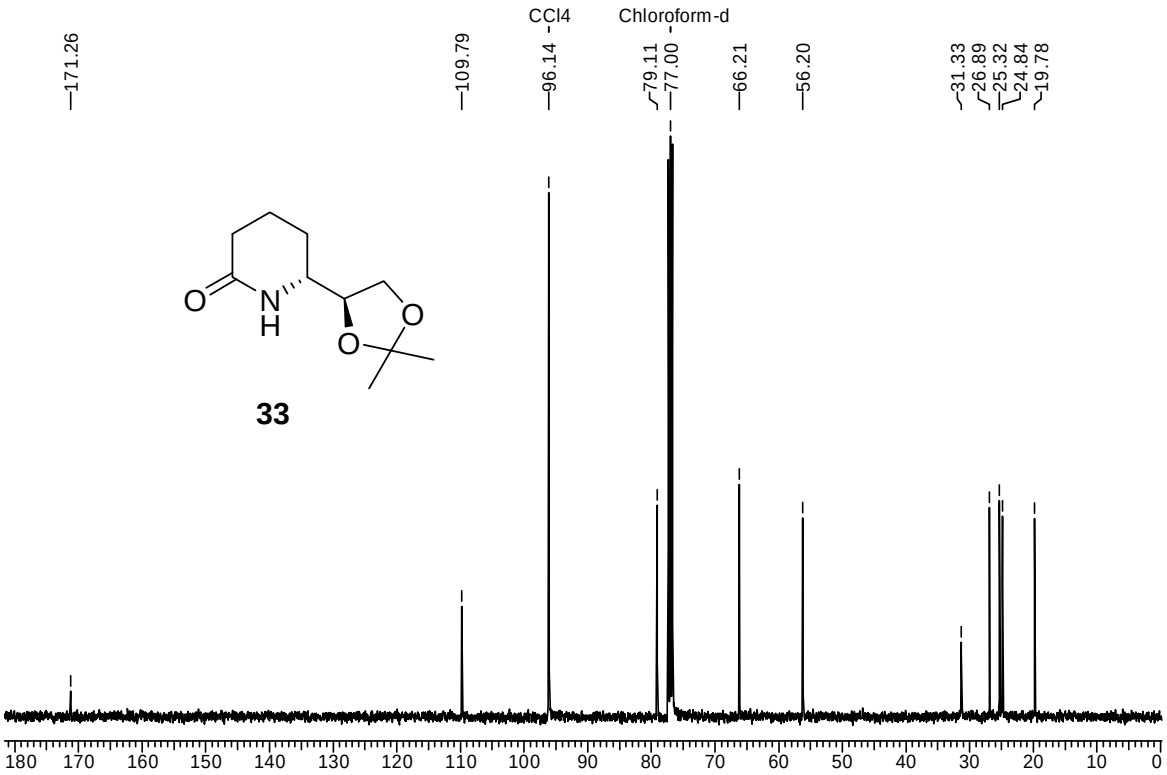

Chloroform-d
7.27
5.93
4.50
4.45
4.16
4.15
4.06
4.02
3.55
2.60
2.46
2.44
2.39
2.02
1.80
0.90
0.08
OTBS
O
N
H
2.00
0.92
1.26
0.95
1.15
1.23
1.11
10.84
6.68

18


ccl4
Chloroform-d
168.29
128.53
126.83
96.16
77.00
71.15
69.16
53.33
30.28
29.70
25.77
18.04
4.19
4.68
OTBS
O
N
H

18


Chloroform-d
7.27
6.22
4.05
4.03
4.02
4.01
3.88
3.87
3.86
3.68
3.66
3.66
3.64
3.33
3.32
3.29
2.38
2.30
2.28
2.26
2.23
1.92
1.91
1.76
1.75
1.74
1.72
1.40
1.33
1.32
1.31
O
N
H
O
O
33
0.93
1.06
1.07
1.00
1.15
1.25
2.23
3.64
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


CCl4
Chloroform-d
171.26
109.79
96.14
79.11
77.00
66.21
56.20
31.33
26.89
25.32
24.84
19.78
O
N
H
O
O
33
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Shimadzu CLASS-VP V6.12 SP5
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Data Name: C:\CLASS-VP\Data\Dr. CHAVAN S. P\Lk1031
User: System
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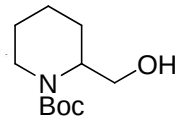
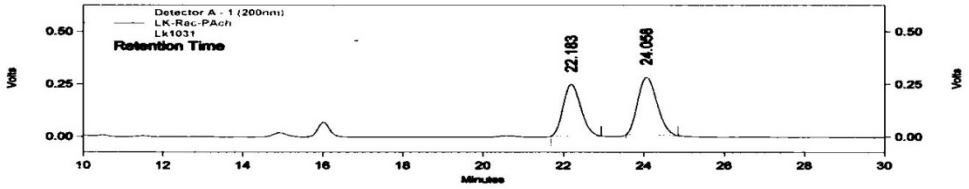
Printed: 5/4/12 4:27:24 PM
Sample Name LK-Rac-PAch



Racemic-**15**

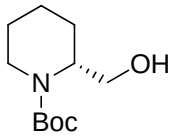


Detector A - 1 (200nm)

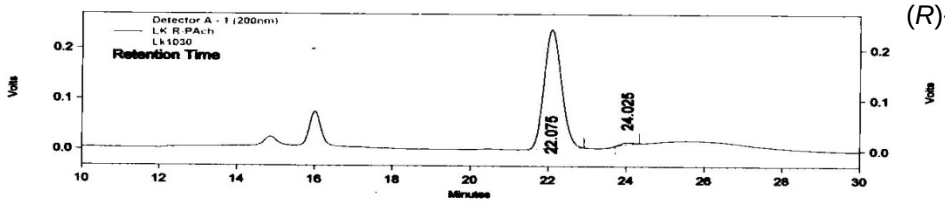
Retention Time	C Area	Area %
22.183	7539900	45.080
24.058	9185600	54.920
Totals	**16725500**	**100.000**

Project Leader : Dr. S. P. Chavan
Column :Kromacil 5-Amycoat (250x4.6 mm)
Mobile Phase :IPA : n-Hexane (4:96)
Wavelength : 200nm
Flow Rate :0.5ml/min (312 psi)
conc. : X mg/1.5 mL
Inj vol- :5 ul

Shimadzu CLASS-VP V6.12 SP5
Method Name: C:\CLASS-VP\Method ch 2.met
Data Name: C:\CLASS-VP\Data\Dr. CHAVAN S. P\Lk1030
User: System
Acquired: 5/4/12 3:09:49 PM
Printed: 5/4/12 3:44:10 PM
Sample Name LK-R-PAch



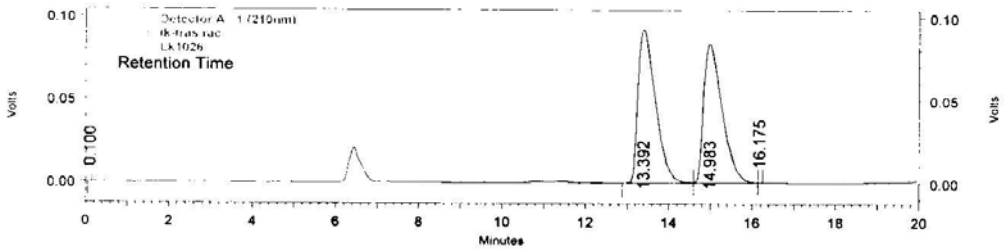
(*R*)-**15**



Detector A - 1 (200nm)

Retention Time	C Area	Area %
22.075	7297559	98.762
24.025	91497	1.238
Totals	**7389056**	**100.000**

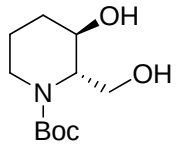
Project Leader : Dr. S. P. Chavan
Column :Kromacil 5-Amycoat (250x4.6 mm)
Mobile Phase :IPA : n-Hexane (4:96)
Wavelength : 200nm
Flow Rate :0.5ml/min (312 psi)
conc. : X mg/1.5 mL
Inj vol- :5 ul



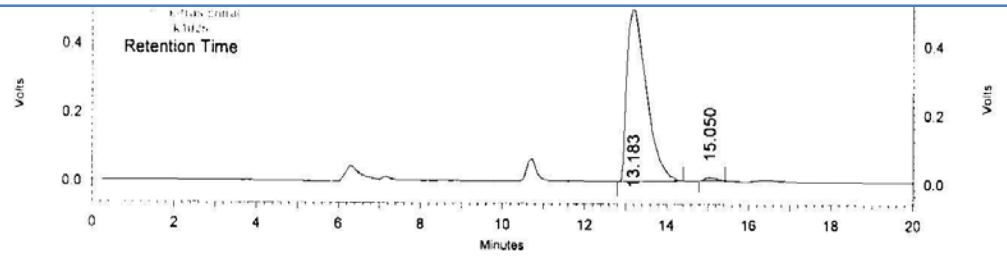
Detector A - 1 (210nm)

Retention Time	C Area	Area %
0.100	335	0.006
13.392	2694263	50.984
14.983	2589648	49.004
16.175	303	0.006
Totals	5284549	100.000

Project Leader : Dr. S P Chavan
Column :Chiracel OJ-H (250x4.6 mm)
Mobile Phase :Pet Ether:IPA (95:05)
Wavelength : 210 nm
Flow Rate :0.5ml/min (23Kgf)
conc. :1mg/1.0mL
Inj vol- :10 ul



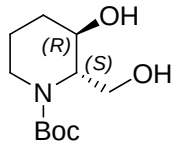
recemic **26**



Detector A - 1 (210nm)

Retention Time	C Area	Area %
13.183	16582875	98.896
15.050	185057	1.104
Totals	16767932	100.000

Project Leader : Dr. S P Chavan
Column :Chiracel OJ-H (250x4.6 mm)
Mobile Phase :Pet Ether:IPA (95:05)
Wavelength : 210 nm
Flow Rate :0.5ml/min (23Kgf)
conc. :1mg/1.0mL
Inj vol- :10 ul



(2*S*,3*R*)-**26**

1) Purity of chiral -13

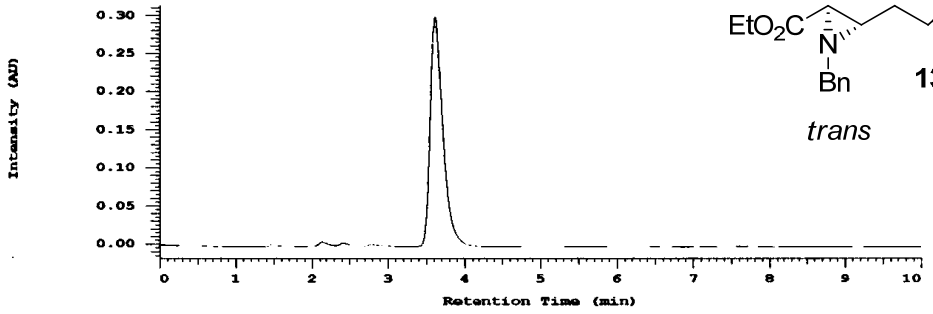
D-7000 HPLC System Manager Report

Analyzed: 05/20/15 02:09 PM
Reported: 05/20/15 02:21 PM
Processed: 05/20/15 02:21 PM

Data Path: C:\WIN32APP\HSM\HPLC\DATA\8000\
Processing Method: SANTOSHH

System(acquisition): Sys 1
Series:8000
Application: HPLC
Volume: 10.0 ul
Sample Name: SK-4-C
Injection from this vial: 1 of 1
Sample Description: MEOH:H2O(80:20)

Chrom Type: HPLC Channel : 1



trans

No.	RT	Height	Area	Area %
1	1.48	859	3513	0.204
2	2.13	2109	13040	0.756
3	2.42	899	4412	0.256
4	2.79	736	4315	0.250
5	3.61	149395	1700365	98.535
		153998	1725645	100.000

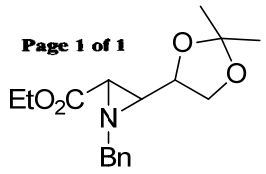
Peak rejection level: 0

```
Group Leader   :- DR.Subhash Chavan
COLUMN         :- kromasil RP-18 (150 X 4.6mm)
MOBILE PHASE   :-MEOH:H20(80:20)
WAVELENGTH     :- 230nm
FLOW RATE      :- 1.0 ml/min (1840psi)
SAMPLE CONC    :- 1 mg/1ml Injection vol:2ul
```

2) Racemic -13

Area % Report

Page 1 of 1



sk-3-R
Method Name: C:\CLASS-VP\Data\Dr. Patil N. T\VSS
Data Name: C:\CLASS-VP\Data\Dr. CHAVAN S. P\Sk1001
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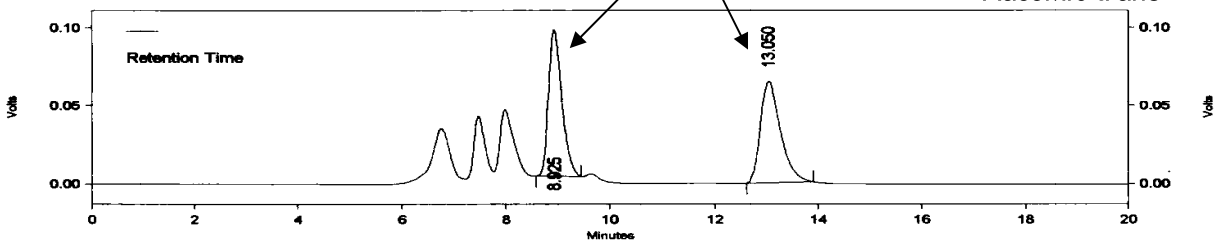
Racemic trans **13**

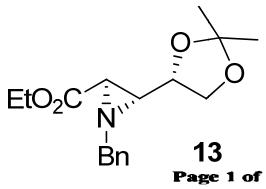
Racemic-trans **13**



Detector A - 1 (230nm)

Pk #	Retention Time	Area	Area %
1	8.925	1674225	49.119
2	13.050	1734307	50.881
Totals		3408532	100.000

Project Leader :Dr.S P Chavan
Column :Kromasil 5- AmyCoat (250mm x 4.6mm)
Mobile Phase :IPA:Pet Ethar (20:80)
Wavelength : 230 nm
Flow Rate : 0.5mL/min
Inj vol- : 05 uL



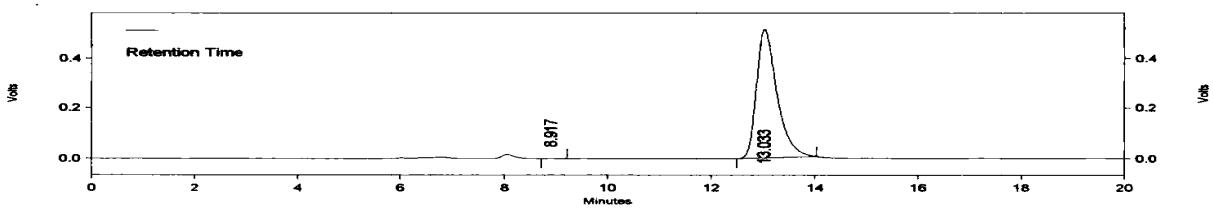
13

trans

Area % Report

Page 1 of 1

sk-4-C
Method Name: C:\CLASS-VP\Data\Dr. Patil N. T\VSS
Data Name: C:\CLASS-VP\Data\Dr. CHAVAN S. P\SK1002
User: System
Acquired: 5/20/15 4:22:23 PM
Printed: 5/20/15 4:48:19 PM



Detector A - 1 (230nm)

Pk #	Retention Time	Area	Area %
1	8.917	10535	0.075
2	13.033	14073412	99.925
Totals		14083947	100.000

Project Leader :Dr.S P Chavan
Column :Kromasil 5- AmyCoat (250mm x 4.6mm)
Mobile Phase :IPA:Pet Ethar (20:80)
Wavelength : 230 nm
Flow Rate : 0.5mL/min
Inj vol- : 05 uL

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10. Deshmukh, S. C.; Roy, A.; Talukdar, P. *Org. Biomol. Chem*. **2012**, *10*, 7536.