Supplementary Information (SI) for Organic Chemistry Frontiers.

Convergent and Stereoselective Synthesis of Nonulosonic acids (NulOs) Scaffolds via Imine/Aldehyde Reductive Coupling

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Abstract: Nonulosonic acids (NulOs) represents an important class of monosaccharides, which has received increasing interest due to their biological roles and potential in vaccine development. As they are only sparsely found in nature, their chemical synthesis is key to exploit their full potential. In this work we describe a building block approach starting from the abundant natural products glucose and threonine. With a few simple modifications these can serve as coupling partners in a SmI_2 mediated reductive cross-coupling, where two new stereocenters are constructed together with the C9 backbone. The approach is easily modified to access the desired diastereomer and we demonstrate, by the synthesis of 7 NulOs, how both natural occurring as well as unknown NulOs can be synthesized in a few steps from the available building blocks. The stereochemistry of the newly established stereocenters are carefully studied by transforming the NulOs derivatives into their pyranosides followed by NMR studies. The assignment of stereochemistry is furthermore supported by a crystal structure and a model for the coupling reaction allowing us to propose rules for the stereochemical outcome making the stereochemical outcome of this approach predictable.

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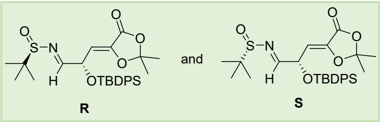
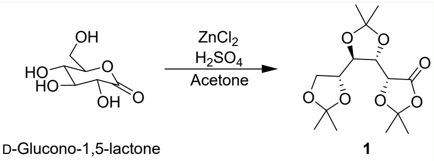
General Experimental

All chemicals and solvents were acquired from commercial providers and used without further purification unless specified differently. Synthesis of compounds **2**, **R**, **S**, **17** were done multiple times, but in the supporting are shown one example. Dry THF was obtained from an Innovative Technology PS-MD-05 solvent drying system or by drying over 4Å MS . Dry toluene, CH_2Cl_2, and MeOH were obtained by drying over 4Å MS. Reactions were monitored by thin-layer chromatography (TLC) carried out on VWR aluminum plates coated with silica F254 and visualized with UV light and/or stained with vanillin. Compounds were purified using Buchi Pure C-815 or C-810 Flash systems equipped with FlashPure EcoFlex Silica cartridges. NMR spectra were recorded on a Bruker 500 MHz Ultra Shield Plus spectrometer with a cryoprobe and a Bruker 500 MHz. The spectra were referenced using residual undeuterated solvent as an internal reference ($CDCl_3$: ^{1}H NMR δ = 7.26 ppm, ^{13}C NMR δ = 77.16 ppm; DMSO-d$_6$: ^{1}H NMR δ = 2.50 ppm, ^{13}C NMR δ = 39.52 ppm; D_2O ^{1}H NMR δ = 4.79 ppm; MeOD-d$_4$: ^{1}H NMR δ = 3.31 ppm, ^{13}C NMR δ = 49.00 ppm). The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad and their combinations. The peaks were assigned using ^{1}H, ^{13}C, COSY, HSQC, HMBC and APT NMR experiments data. High resolution mass spectra (HRMS) were recorded on a Bruker SolariX XR7T ESI/MALDI-FT-ICR-MS instrument.

Experimental Procedures



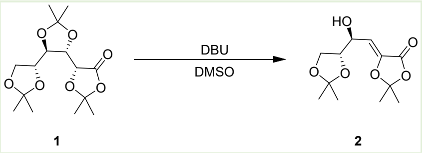
R **S**



D-Glucono-1,5-lactone **1**

Compound **1** was prepared following the procedure of Jarosz *et al.*[1] $ZnCl_2$ (219 g, 1.57 mol, 2.8 equiv.) was suspended in acetone (1.15 L, 15.5 mol, 27.6 equiv.) under N_2 atmosphere and H_2SO_4 (1.9 mL, 95%, 34 mmol, 0.06 equiv.) was added dropwise. After 15 min to a resulting clear solution D-glucono-1,5-lactone (100 g, 561 mmol, 1.0 equiv.) was added in one portion. And the reaction was stirred at room temperature under N_2 atmosphere for 24 h. Afterwards, the reaction mixture was poured into toluene/brine (600 mL/150 mL) and layers were separated. The organic layer was washed four times with brine (150 mL) until neutral pH. The first brine layer was back-extracted once with toluene (100 mL). The back extract was washed four times with brine (50 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated *in vacuo*, suspended in MeOH (400 mL) and kept in the freezer (- 25 ºC) overnight. The resulting precipitates were filtered and dried under a high vacuum to give isopropylidene **1** (100.8 g) as an off-white solid. The mother liquid was concentrated *in vacuo*, suspended in MeOH (200 mL) and kept in the freezer (- 25 ºC) for 3 days. The resulting precipitates were filtered and dried under a high vacuum to provide a second portion of **1** (4.5 g) as white solid. The mother liquid was concentrated *in vacuo* again, suspended in MeOH (100 mL) and kept in the freezer (- 25 ºC) for overnight. The precipitates were filtered and dried *in vacuo* to give third portion of compound **1** (2.0 g) as a white solid. Total yield of the desired product **1** (107 g, 61%). ^{1}H, ^{13}C NMR was consistent with the literature.[1][2]

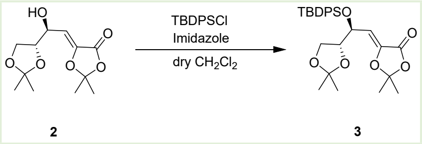
Data for **1**: Off-white solid; R_f=0.49 (Heptane/EtOAc 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.61 (d, $J_{2,3}$ = 1.6 Hz, 1H; H2), 4.27 (dd, J = 8.3, 1.5 Hz, 1H; H3), 4.14 (dd, J = 8.4, 6.0 Hz, 1H; H6), 4.11 – 4.07 (m, 1H; H5), 3.98 (dd, J = 8.4, 3.9 Hz, 1H; H6'), 3.94 (t, J = 8.5 Hz, 1H; H4), 1.64 (s, 3H; CH_3), 1.56 (s, 3H; CH_3), 1.41 (s, 3H; CH_3), 1.39 (s, 3H; CH_3), 1.38 (s, 3H; CH_3), 1.33 (s, 3H; CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8 (C1), 111.6 (CMe_2), 110.5 ($C'Me_2$), 109.9 ($C''Me_2$), 78.8 (C3), 77.3 (C5), 76.5 (C4), 73.9 (C2), 68.0 (C6), 27.3 (CH_3), 27.1 (CH_3), 27.1 (CH_3), 26.8 (CH_3), 26.7 (CH_3), 25.3 (CH_3).



1 **2**

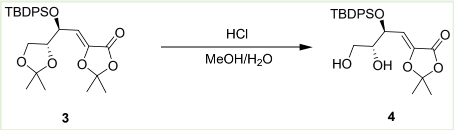
1,2:3,4:5,6-tri-*O*-isopropylidene-D-gluconate (**1**) (10.0 g, 31.6 mmol, 1.0 equiv.) was suspended in DMSO (60 mL) under N_2 atmosphere and DBU (0.97 mL, 6.4 mmol, 0.2 equiv.) was added dropwise. The reaction was stirred at 70 ºC for 7h. Afterwards, the mixture was cooled to room temperature, poured into H_2O/EtOAc (60 mL : 60 mL), layers were separated, and the organic layer was additionally washed twice with H_2O (30 mL). The combined water layers were back-extracted once with EtOAC (20 mL). The combined organic layers were washed once with brine (15 mL), dried over Na_2SO_4, filtered, concentrated on silica gel, and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 25 g column, eluent: 15% : 85% EtOAc/Heptane → 100% EtOAc) to yield (Z)-3-deoxy-1,2:5,6-di-*O*-isopropylidene-D-*erythro*-hex-3-enolactone (**2**) (2.92 g, 36%) as an yellowish oil and to recover starting material **1** (3.88 g, 39%) as a white solid. Yield based on recovered starting material: 59%. ^{1}H NMR was consistent with the literature.[2]

Data for **2**: Yellowish oil; R_f=0.39 (Heptane/EtOAc 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.60 (d, *J* = 7.9 Hz, 1H; H3), 4.63 (ddd, *J* = 7.9, 4.8, 3.9 Hz, 1H; H4), 4.18 (td, *J* = 6.2, 4.7 Hz, 1H; H5), 4.02 (dd, *J* = 8.5, 6.6 Hz, 1H; H6), 3.93 (dd, *J* = 8.4, 5.9 Hz, 1H; H6'), 2.31 (d, *J* = 3.9 Hz, 1H; OH), 1.64 (s, 6H; 2 x CH_3), 1.44 (s, 3H; CH_3), 1.36 (s, 3H; CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2 (C1), 130.0 (C2), 112.0 (CMe_2), 109.8 ($C'Me_2$), 107.1 (C3), 77.7 (C4), 67.2 (C5), 65.3 (C6), 26.9 (CH_3), 26.9 (CH_3), 26.6 (CH_3), 25.2 (CH_3).



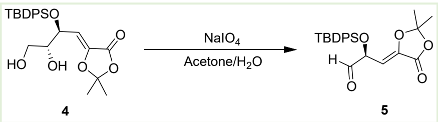
TBDPSCl (5.0 mL, 18.7 mmol, 1.05 equiv.) was added dropwise over 10 min to a stirred solution of 1,2:5,6-di-*O*-isopropylidene-D-*erythro*-hex-3-enolactone (**2**) (4.57 g, 17.7 mmol, 1.0 equiv.) and imidazole (2.43 g, 35.4 mmol, 2.0 equiv.) in dry CH_2Cl_2 (50 mL) under N_2 atmosphere at 0 ºC. After 10 min, the ice bath was removed, and the reaction was stirred at room temperature for 3.5h. Afterwards, the mixture was poured into CH_2Cl_2/H_2O (150 mL : 50 mL), layers were separated. The organic layer was washed twice with H_2O (50 mL), once with brine (20 mL), dried over Na_2SO_4, filtered and concentrated under high vacuum to yield crude (Z)-5-((S)-2-((tert-butyldiphenylsilyl)oxy)-2-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)ethylidene)-2,2-dimethyl-1,3-dioxolan-4-one (**3**) (9.76 g) as a colorless oil, which was used in the next step without further purification. A small amount of the crude oil was purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 11% : 89% EtOAc/Heptane → 100% EtOAc) for the analysis.

Data for **3**: Colorless oil; R_f=0.49 (Heptane/EtOAc 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H; TBDPS), 7.64 – 7.59 (m, 2H; TBDPS), 7.45 – 7.40 (m, 1H; TBDPS), 7.40 – 7.35 (m, 3H; TBDPS), 7.35 – 7.31 (m, 2H; TBDPS), 5.44 (d, *J* = 9.3 Hz, 1H; H3), 4.60 (dd, *J* = 9.2, 5.9 Hz, 1H; H4), 4.10 – 4.04 (m, 1H; H5), 4.01 (dd, *J* = 8.3, 6.2 Hz, 1H; H6), 3.93 (dd, *J* = 8.3, 5.6 Hz, 1H; H6'), 1.46 (s, 3H; CH_3), 1.33 (s, 3H; CH_3), 1.32 (s, 3H; CH_3), 1.28 (s, 3H; CH_3), 1.06 (s, 9H; TBDPS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2 (C=O), 138.9 (C2), 136.1 (TBDPS), 136.1 (TBDPS), 133.7 (TBDPS), 133.4 (TBDPS), 130.0 (TBDPS), 129.9 (TBDPS), 127.7 (TBDPS), 127.6 (TBDPS), 111.4 (CMe_2) , 109.6 ($C'Me_2$), 108.9 (C3), 78.8 (C5), 68.9 (C4), 66.2 (C6), 27.1 (TBDPS), 26.7 ($C(CH_3)_2$), 26.6 ($C(CH_3)_2$), 26.4 ($C(CH_3)_2$), 25.5 ($C(CH_3)_2$), 19.5 (TBDPS). HRMS (ESI+): *m/z* calcd for $C_{28}H_{36}O_6SiNa^+$: 519.21734 $[M+Na]^+$; found: 519.21833.



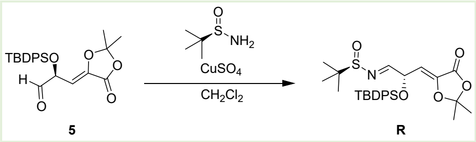
The crude (Z)-5-((S)-2-((tert-butyldiphenylsilyl)oxy)-2-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)ethylidene)-2,2-dimethyl-1,3-dioxolan-4-one (**3**) (9.44 g) was dissolved in $MeOH/H_2O$ (90 mL; 13 : 2) and HCl (0.15 mL, 37%, 1.8 mmol, 0.1 equiv.) was added dropwise. The reaction was stirred at room temperature for 3 days. Afterwards, the mixture was concentrated, dissolved in EtOAc, concentrated on silica gel and purified using Büchi Pure C-810 Flash system (FlashPure EcoFlex Silica 40 g column, eluent: 37% : 63% EtOAc/Heptane → 100% EtOAc) to yield (Z)-5-((2S,3R)-2-((tert-butyldiphenylsilyl)oxy)-3,4-dihydroxybutylidene)-2,2-dimethyl-1,3-dioxolan-4-one (**4**) (6.93 g, 89% over two steps) as a colorless oil.

Data for **4**: Colorless oil; R_f=0.36 (Heptane/EtOAc 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.67 (m, 2H; TBDPS), 7.63 – 7.60 (m, 2H; TBDPS), 7.47 – 7.42 (m, 1H; TBDPS), 7.42 – 7.38 (m, 3H; TBDPS), 7.36 – 7.32 (m, 2H; TBDPS), 5.57 (d, *J* = 9.0 Hz, 1H; H3), 4.66 (dd, *J* = 8.9, 4.2 Hz, 1H; H4), 3.73 (dt, *J* = 6.0, 3.9 Hz, 1H; H5), 3.69 (dd, *J* = 11.3, 6.1 Hz, 1H; H6), 3.61 (dd, *J* = 11.3, 3.6 Hz, 1H; H6'), 2.05 (br, 2H; 2 x OH), 1.48 (s, 3H; CH_3), 1.29 (s, 3H; CH_3), 1.08 (s, 9H; TBDPS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0 (C=O), 138.8 (C2), 136.1 (TBDPS), 136.0 (TBDPS), 133.1 (TBDPS), 132.9 (TBDPS), 130.2 (TBDPS), 130.2 (TBDPS), 128.0 (TBDPS), 127.8 (TBDPS), 111.6 (CMe_2), 108.1 (C3), 74.8 (C5), 70.4 (C4), 63.2 (C6), 27.1 (TBDPS), 26.7 ($C(CH_3)_2$), 26.5 ($C(CH_3)_2$), 19.4 (TBDPS). HRMS (ESI+): *m/z* calcd for $C_{25}H_{32}O_6SiNa^+$: 479.18604 $[M+Na]^+$; found: 479.18495.



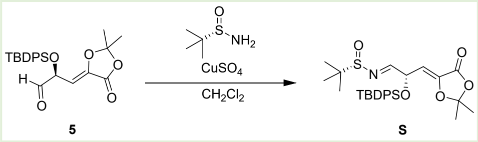
(Z)-5-((2S,3R)-2-((tert-butyldiphenylsilyl)oxy)-3,4-dihydroxybutylidene)-2,2-dimethyl-1,3-dioxolan-4-one (**4**) (6.78 g, 14.9 mmol, 1.0 equiv.) was dissolved in acetone/H_2O (100 mL, 3 : 2) and $NaIO_4$ (3.81 g, 17.8 mmol, 1.2 equiv.) was added in one portion. The reaction was stirred at room temperature for 4h. Afterwards, the mixture was poured into EtOAc/brine (100 mL : 75 mL) and the water layer was additionally extracted twice with EtOAc (50 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated under high vacuum to give a cloudy oil. The oil was dissolved in $CHCl_3$, filtered and concentrated *in vacuo* to give the crude (S,Z)-2-((tert-butyldiphenylsilyl)oxy)-3-(2,2-dimethyl-5-oxo-1,3-dioxolan-4-ylidene)propanal (**5**) (6.09 g) as a slightly yellow oil, which was used in the next step without additional purification. A small amount of the crude oil was purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 14% : 86% EtOAc/Heptane → 100% EtOAc) for the analysis.

Data for **5**: Colorless oil; R_f=0.55 (Heptane/EtOAc 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.54 (d, *J* = 1.1 Hz, 1H; H5), 7.67 – 7.62 (m, 4H; TBDPS), 7.47 – 7.41 (m, 2H; TBDPS), 7.40 – 7.34 (m, 4H; TBDPS), 5.54 (d, *J* = 8.4 Hz, 1H; H3), 4.88 (dd, *J* = 8.4, 1.1 Hz, 1H; H4), 1.54 (s, 3H; CH_3), 1.41 (s, 3H; CH_3), 1.11 (s, 9H; TBDPS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.7 (C5), 161.8 (C1), 140.5 (C2), 135.9 (TBDPS), 135.9 (TBDPS), 132.8 (TBDPS), 132.6 (TBDPS), 130.3 (TBDPS), 130.2 (TBDPS), 128.0 (TBDPS), 127.9 (TBDPS), 112.2 (CMe_2), 104.1 (C3), 74.4 (C4), 26.9 (TBDPS), 26.7 ($C(CH_3)_2$), 26.6 ($C(CH_3)_2$), 19.4 (TBDPS). HRMS (ESI+): *m*/*z* calcd for $C_{24}H_{28}O_5SiNa^+$: 447.15982 $[M+Na]^+$; found: 447.16282



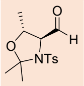
Crude (S,Z)-2-((tert-butyldiphenylsilyl)oxy)-3-(2,2-dimethyl-5-oxo-1,3-dioxolan-4-ylidene)propanal (**5**) (1.00 g, 2.4 mmol, 1.0 equiv.), (R)-2-methylpropane-2-sulfinamide (0.58 g, 4.7 mmol, 2.0 equiv.) and $CuSO_4$ (0.83 g, 5.2 mmol, 2.2 equiv.) were suspended in dry CH_2Cl_2 (20 mL) under N_2 atmosphere. The reaction was stirred at room temperature in a vial with a cap for 5 days. Afterwards, the mixture was filtered through celite layer and the pad rinsed with CH_2Cl_2. The filtrate was concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 25 g column, eluent: 17% : 83% EtOAc/Heptane → 100% EtOAc) to yield sulfinimine **R** (1.05 g, 84% over two steps) as a yellow oil.

Data for **R**: Yellow oil; R_f=0.30 (Heptane/EtOAc 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 4.1 Hz, 1H; H5), 7.67 – 7.62 (m, 4H; TBDPS), 7.45 – 7.39 (m, 2H; TBDPS), 7.39 – 7.32 (m, 4H; TBDPS), 5.64 (d, *J* = 8.4 Hz, 1H; H3), 5.33 (dd, *J* = 8.4, 4.2 Hz, 1H; H4), 1.49 (s, 3H; CH_3), 1.38 (s, 3H; CH_3), 1.12 (s, 9H; *t*BuS(O)N), 1.08 (s, 9H; TBDPS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7 (C5), 161.9 (C4), 139.1 (C2), 135.9 (TBDPS), 135.9 (TBDPS), 133.0 (TBDPS), 132.7 (TBDPS), 130.2 (TBDPS), 130.1 (TBDPS), 127.9 (TBDPS), 127.8 (TBDPS) 112.0 (CMe_2), 106.9 (C3), 70.7 (C4), 57.4 $(CH_3)_3CS(O)N)$, 26.9 (TBDPS), 26.7 ($C(CH_3)_2$), 26.6 ($C(CH_3)_2$), 22.5 $(CH_3)_3CS(O)N)$, 19.4 (TBDPS). HRMS (ESI+): *m*/*z* calcd for $C_{28}H_{37}NO_5SSiNa^+$: 550.20539 $[M+Na]^+$; found: 550.20604



Crude (S,Z)-2-((tert-butyldiphenylsilyl)oxy)-3-(2,2-dimethyl-5-oxo-1,3-dioxolan-4-ylidene)propanal (**5**) (1.00 g, 2.4 mmol, 1.0 equiv.), (S)-2-methylpropane-2-sulfinamide (0.59 g, 4.7 mmol, 2.0 equiv.) and $CuSO_4$ (0.83 g, 5.2 mmol, 2.2 equiv.) were suspended in dry CH_2Cl_2 (20 mL) under N_2 atmosphere. The reaction was stirred at room temperature in a vial with a cap for 5 days. Afterwards, the mixture was filtered through celite layer and the pad rinsed with CH_2Cl_2. The filtrate was concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 25 g column, eluent: 17% : 83% EtOAc/Heptane → 100% EtOAc) to yield sulfinimine **S** (1.05 g, 84% over two steps) as a yellow oil.

Data for **S**: Yellow oil; R_f=0.31 (Heptane/EtOAc 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 3.5 Hz, 1H; H5), 7.69 – 7.62 (m, 4H; TBDPS), 7.45 – 7.39 (m, 2H; TBDPS), 7.38 – 7.32 (m, 4H; TBDPS), 5.61 (d, *J* = 8.4 Hz, 1H; H3), 5.31 (dd, *J* = 8.4, 3.5 Hz, 1H; H4), 1.50 (s, 3H; CH_3), 1.38 (s, 3H; CH_3), 1.16 (s, 9H; *t*BuS(O)N), 1.07 (s, 9H; TBDPS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5 (C5), 162.1 (C1), 139.3 (C2), 136.0 (TBDPS), 135.9 (TBDPS), 133.1 (TBDPS), 132.9 (TBDPS), 130.1 (TBDPS), 130.1 (TBDPS), 127.9 (TBDPS), 127.8 (TBDPS), 112.0 ($z(CH_3)_2$), 106.7 (C3), 70.5 (C4), 57.2 $(CH_3)_3CS(O)N)$, 26.9 (TBDPS), 26.7 ($C(CH_3)_2$), 26.6 ($C(CH_3)_2$), 22.5 $(CH_3)_3CS(O)N)$, 19.4 (TBDPS). HRMS (ESI+): *m*/*z* calcd for $C_{28}H_{37}NO_5SSiH^+$: 528.22345 $[M+H]^+$; found: 528.22616



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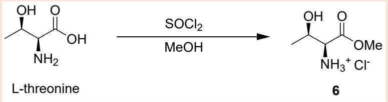
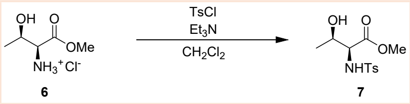


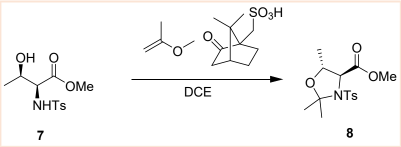
MeOH (100 mL) was cooled in an ice bath and $SOCl_2$ (7.0 mL, 96 mmol, 1.0. equiv.) was added dropwise under N_2 atmosphere. To the resultant solution of HCl in MeOH, L-threonine (12.0 g, 97.7 mmol, 1.0 equiv.) was added in one portion and the reaction was refluxed for 4h. Afterwards, the mixture was cooled to room temperature and concentrated under reduced pressure to yield crude L-threonine methyl ester hydrochloride (**6**) (16.8 g) as a colorless oil, which was used in next steps without additional purification. Note: some of MeOH is still remaining after high vacuum drying.[3] NMR was consistent with the literature.[4]

^{1}H NMR (500 MHz, D_2O) δ 4.49 – 4.42 (m, 1H; H3), 4.13 (d, *J* = 3.8 Hz, 1H; H2), 3.89 (s, 3H; OMe), 1.36 (d, *J* = 6.6 Hz, 3H; CH_3). ^{13}C NMR (126 MHz, D_2O) δ 169.2 (C=O), 65.2 (C3), 58.4 (C2), 53.7 (OMe), 18.7 (CH_3). HRMS (ESI+): *m*/*z* calcd for $C_5H_{12}NO_3^+$: 134.08117 $[M+H]^+$; found: 134.08127.



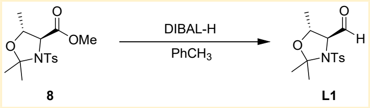
Compound **7** was prepared following slightly modified procedure of Minakata *et al*.[5] To a suspension of crude L-threonine methyl ester hydrochloride (**6**) (1.85 g, 10.9 mmol, 1.0 equiv.) in dry CH_2Cl_2 (40 mL) cooled in an ice bath under N_2 atmosphere was added Et_3N (3.1 mL, 22 mmol, 2.0 equiv.) followed by addition of TsCl (2.23 g, 11.5 mmol, 1.05 equiv.) in two portions. The reaction was stirred at 1 ºC for 22h. Afterwards, the solids were filtered off and the filtrate was concentrated *in vacuo*, dissolved in EtOAc (50 mL), washed with sat. $NaHCO_3$ (20 mL), aqueous HCl (20 mL, 0.1 M), H_2O (20 mL), dried over Na_2SO_4, filtered, concentrated under reduced pressure to yield crude product as a colorless oil. The crude oil was dissolved in EtOAc/Hexane (20 mL, 1:1) and cooled in an ice bath. The formed precipitates were filtered and dried under high vacuum to yield *N*-tosyl-L-threonine methyl ester (**7**) (1.96 g, 63%) as a white solid. The mother liquid was concentrated, dissolved in EtOAc/Hexane (10 mL, 1:1) and kept in the freezer (-25 ºC) overnight. The formed solids were filtered and dried under high vacuum to yield a second portion of desired product **7** (0.55 g, 17%) as a white solid. Total yield: 80% (2.51 g). ^{1}H NMR was consistent with the literature.[6]

Data for **7**: White solid; R_f=0.20 (Heptane/EtOAc 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.7 Hz, 2H; Ts), 7.29 (d, *J* = 8.5 Hz, 2H; Ts), 5.48 (d, *J* = 9.6 Hz, 1H; NH), 4.18 – 4.10 (m, 1H; H3), 3.82 (ddd, *J* = 9.6, 3.0, 0.9 Hz, 1H; H2), 3.52 (s, 3H; OMe), 2.42 (s, 3H; Ts), 2.12 (br, 1H; OH), 1.27 (dd, *J* = 6.4, 0.9 Hz, 3H; H4). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8 (C=O), 143.9 (Ts), 136.8 (Ts), 129.8 (Ts), 127.4 (Ts), 68.5 (C3), 61.1 (C2), 52.8 (OMe), 21.7 (Ts), 20.0 (C4). HRMS (ESI+): *m*/*z* calcd for $C_{12}H_{18}NO_5S^+$: 288.09002 [*M*+H]$^+$; found: 288.09010.



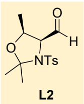
Compound **8** was prepared following slightly modified procedure of Koide *et al*.[7] *N*-tosyl-L-threonine methyl ester (**7**) (2.50 g, 8.70 mmol, 1.0 equiv.) and (+)-10-Camphorsulfonic acid (40 mg, 0.17 mmol, 2 mol%) were dissolved in DCE (15 mL) under N_2 atmosphere and 2-methoxypropene (1.7 mL, 17 mmol, 2.0 equiv.) was added dropwise. The reaction was refluxed for 2.5h, cooled to room temperature, concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 25 g column, eluent: 21% : 79% EtOAc/Heptane → 100% EtOAc) to yield methyl (4S,5R)-2,2,5-trimethyl-3-tosyloxazolidine-4-carboxylate (**8**) (2.76 g, 97%) as a yellow oil. NMR was consistent with the literature.[7]

Data for **8**: Yellow oil; R_f=0.53 (Heptane/EtOAc 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 2H; Ts), 7.32 – 7.28 (m, 2H; Ts), 4.30 (dq, *J* = 7.6, 6.1 Hz, 1H; H3), 3.92 (d, *J* = 7.4 Hz, 1H; H2), 3.79 (s, 3H; OMe), 2.42 (s, 3H; Ts), 1.60 (s, 3H; $C(CH_3)_2$), 1.53 (s, 3H; $C(CH_3)_2$), 1.32 (d, *J* = 6.0 Hz, 3H; H4). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8 (C=O), 143.7 (Ts), 137.7 (Ts), 129.6 (Ts), 127.7 (Ts), 98.1 ($C(CH_3)_2$), 74.5 (C3), 67.3 (C2), 52.8 (OMe), 27.9 ($C(CH_3)_2$), 26.2 ($C(CH_3)_2$), 21.5 (Ts), 18.5 (C4). HRMS (ESI+): *m*/*z* calcd for $C_{15}H_{21}NO_5SNa^+$: 350.10326 [*M*+Na]$^+$; found: 350.10343.

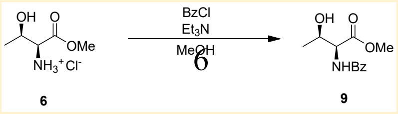


A solution of methyl (4S,5R)-2,2,5-trimethyl-3-tosyloxazolidine-4-carboxylate (**8**) (2.66 g, 8.12 mmol, 1.0 equiv.) in dry $PhCH_3$ (55 mL) was cooled to -78 ºC under N_2 atmosphere and DIBAL-H (9.5 mL, 25%, 14 mmol, 1.7 equiv.) in $PhCH_3$ was added dropwise over 10 min. The reaction was stirred at -78 ºC for 3h and subsequently quenched with MeOH (1.5 mL). The quenched reaction mixture was diluted with Et_2O (50 mL), sat. Rochelle's salt (50 mL) and H_2O (100 mL). The water layer was extracted three times with EtOAc (50 mL). The combined organic layers were washed once with H_2O (30 mL), once with brine (30 mL), dried over Na_2SO_4, filtered and concentrated. The resulting solid was dissolved in Et_2O/Heptane (20 mL, 1:1) and left overnight in the freezer (-25 ºC). The formed precipitates were filtered, dried under high vacuum to yield (4S,5R)-2,2,5-trimethyl-3-tosyloxazolidine-4-carbaldehyde (**L1**) (2.0 g, 82%) as white crystals. The mother liquid was concentrated, dissolved in Et_2O/Heptane (10 mL, 1:1) and left in the freezer (-25 ºC) overnight. The resulting solids were filtered, dried *in vacuo* to yield a second portion of the aldehyde **L1** (0.13 g, 5%) as white crystals. Total yield 87% (2.1 g).

Data for **L1**: White crystals; R_f=0.39 (Heptane/EtOAc 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.58 (d, *J* = 4.6 Hz, 1H; H1), 7.70 – 7.63 (m, 2H; Ts), 7.32 (d, *J* = 7.9 Hz, 2H; Ts), 4.22 (dq, *J* = 8.4, 6.1 Hz, 1H; H3), 3.50 (dd, *J* = 8.3, 4.5 Hz, 1H; H2), 2.43 (s, 3H; Ts), 1.67 (s, 3H; $C(CH_3)_2$), 1.49 (s, 3H; $C(CH_3)_2$), 1.27 (d, *J* = 6.0 Hz, 3H; H4). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2 (C1), 144.2 (Ts), 136.8 (Ts), 130.0 (Ts), 127.7 (Ts), 98.3 ($C(CH_3)_2$), 72.4 (C2), 70.5 (C3), 29.0 ($C(CH_3)_2$), 25.7 ($C(CH_3)_2$), 21.7 (Ts), 17.4 (C4). HRMS (ESI+): *m*/*z* calcd for $C_{14}H_{19}NO_4SNa^+$: 320.09270 [*M*+Na]$^+$; found: 320.09232

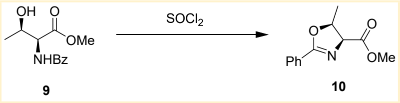


L2



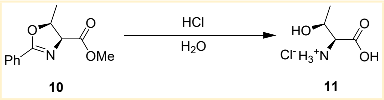
Compound **9** was prepared following slightly modified procedure of Tanner *et al.*[8] The crude L-threonine methyl ester hydrochloride (**6**) (13.2 g, 21.8 mmol, 1.0 equiv.) was dissolved in dry MeOH (50 mL) under N_2 atmosphere and Et_3N (32.0 mL, 230 mmol, 3.0 equiv.) was added dropwise. After 15 min, the reaction mixture was cooled in an ice bath and BzCl (9.6 mL, 83 mmol, 1.1 equiv.) was added dropwise. The reaction was stirred at 0 ºC for 3h. Afterwards, the mixture was concentrated, diluted with H_2O (50 mL) and extracted three times with EtOAc (50 mL). The combined organic layers were washed once with H_2O (25 mL), once with brine (25 mL). The combined water layers were back-extracted once with EtOAc (25 mL).The combined organic layers were dried over Na_2SO_4, filtered and concentrated to give yellowish oil. The oil was dissolved in Et_2O (30 mL) and kept in the freezer (-25 ºC) overnight. The formed solids were filtered and dried under high vacuum to yield *N*-benzoyl-L-threonine methyl ester (**9**) (14.6 g, 79% over two steps) as off-white solids. NMR was consistent with the literature.[8]

Data for **9**: Off-white solid; R_f=0.44 (Heptane/EtOAc 1:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 2H; Bz), 7.54 – 7.49 (m, 1H; Bz), 7.43 (ddd, *J* = 8.0, 6.5, 1.3 Hz, 2H; Bz), 7.00 (d, *J* = 9.0 Hz, 1H; NH), 4.82 (dd, *J* = 8.7, 2.4 Hz, 1H; H2), 4.45 (qd, *J* = 6.5, 2.5 Hz, 1H; H3), 3.78 (s, 3H; OMe), 2.63 (s, 1H; OH), 1.28 (d, *J* = 6.3 Hz, 3H; CH_3; H4). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8 (C1), 168.1 (Bz), 133.8 (Bz), 132.1 (Bz), 128.8 (Bz), 127.3 (Bz), 68.4 (C3), 57.8 (C2), 52.8 (OMe), 20.2 (C4). HRMS (ESI+): *m*/*z* calcd for $C_{12}H_{16}NO_4^+$: 238.10738 $[M+H]^+$; found: 238.10740.



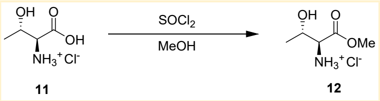
Compound **10** was prepared following the modified procedure of Sulikowski *et al.*[9] To $SOCl_2$ (45.0 mL, 620 mmol, 10.5 equiv.) at 0 ºC under N_2 atmosphere, *N*-benzoyl-L-threonine methyl ester (**9**) (14.0 g, 59.0 mmol, 1.0 equiv.) was added in three portions. The reaction was stirred at 1 ºC for 5 days. Afterwards, the mixture was concentrated, dissolved in CH_2Cl_2, slowly poured into sat. $NaHCO_3$ (100 mL) and extracted three times with CH_2Cl_2 (50 mL). The combined organic layers were washed once with H_2O (50 mL), once with brine (20 mL), dried over Na_2SO_4, filtered, concentrated and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 40 g column, eluent: 32% : 68% EtOAc/Heptane → 100% EtOAc) to yield methyl (4*S*,5*S*)-5-methyl-2-phenyl-4,5-dihydrooxazole-4-carboxylate (**10**) (12.4 g, 96 %) as a yellowish oil. NMR was consistent with the literature.[10]

Data for **10**: Yellowish oil; R_f=0.45 (Heptane/EtOAc 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H; Ph), 7.51 – 7.47 (m, 1H; Ph), 7.43 – 7.39 (m, 2H; Ph), 5.10 – 5.03 (m, 1H; H3), 4.98 (d, *J* = 10.1 Hz, 1H; H2), 3.77 (s, 3H; OMe), 1.38 (d, *J* = 6.3 Hz, 3H; H4). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5 (C1), 166.3 (Ph*C*(O)N), 131.9 (Ph), 128.7 (Ph), 128.4 (Ph), 127.4 (Ph), 77.8 (C3), 71.9 (C2), 52.2 (OMe), 16.4 (C4). HRMS (ESI+): *m*/*z* calcd for $C_{12}H_{14}NO_3^+$: 220.09682 $[M+H]^+$; found: 220.09685.



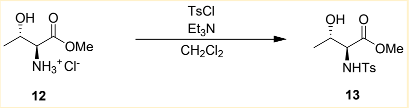
Compound **11** was prepared following slightly modified procedure of Sulikowski *et al.*[9] Methyl (4*S*,5*S*)-5-methyl-2-phenyl-4,5-dihydrooxazole-4-carboxylate (**10**) (12.4 g, 56.6 mmol, 1.0 equiv.) was suspended in H_2O (75 mL) and HCl (65 mL, 37%, 0.78 mol, 14 equiv.) was added via syringe. The reaction mixture was refluxed for 5h. Afterwards, the mixture was cooled to room temperature and washed three times with Et_2O (75 mL). The aqueous layer was concentrated *in vacuo* to give L-*allo*-threonine hydrochloride (**11**) (9.0 g) as a yellowish oil, which was used in next steps without additional purifications. NMR was consistent with the literature.[11]

Data for **11**: Yellowish oil; ^{1}H NMR (500 MHz, D_2O) δ 4.37 (qd, *J* = 6.6, 3.5 Hz, 1H; H3), 4.11 (d, *J* = 3.7 Hz, 1H; H2), 1.30 (d, *J* = 6.7 Hz, 3H; H4). ^{13}C NMR (126 MHz, D_2O) δ 169.7 (C1), 65.3 (C3), 58.1 (C2), 17.2 (C4). HRMS (ESI+): *m*/*z* calcd for $C_4H_{10}NO_3^+$: 120.06552 $[M+H]^+$; found: 120.06591.



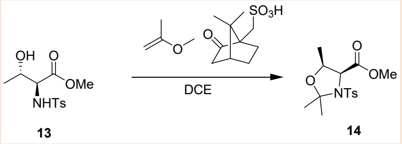
MeOH (45 mL) was cooled in an ice bath and $SOCl_2$ (3.2 mL, 44 mmol, 1.0. equiv.) was added dropwise under N_2 atmosphere. The resultant solution of HCl in MeOH was added to the crude L-*allo*-threonine hydrochloride (**11**) (6.76 g, 44 mmol, 1.0 equiv.) and the reaction was refluxed for 4h. Afterwards, the mixture was cooled to room temperature and concentrated under reduced pressure to yield crude L-*allo*-threonine methyl ester hydrochloride (**12**) (7.5 g) as a colorless oil, which was used in next steps without additional purification. Note: some of MeOH is still remaining after high vacuum drying.[3] NMR was consistent with the literature.[4]

Data for **12**: Yellowish oil; ^{1}H NMR (500 MHz, D_2O) δ 4.39 – 4.34 (m, 1H; H3), 4.23 (d, *J* = 3.5 Hz, 1H; H2), 3.89 (s, 3H; OMe), 1.32 (d, *J* = 6.6 Hz, 3H; H4). ^{13}C NMR (126 MHz, D_2O) δ 168.3 (C1), 65.6 (C3), 58.0 (C2), 53.5 (OMe), 17.7 (Ch). HRMS (ESI+): *m*/*z* calcd for $C_5H_{12}NO_3^+$: 134.08117 $[M+H]^+$; found: 134.08136.



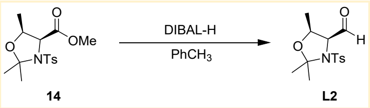
Compound **13** was prepared following slightly modified procedure of Minakata *et al.*[5] To a suspension of crude L-*allo*-threonine methyl ester hydrochloride (**12**) (1.95 g, 11.5 mmol, 1.0 equiv.) in dry CH_2Cl_2 (40 mL) cooled in an ice bath under N_2 atmosphere was added Et_3N (3.3 mL, 24 mmol, 2.1 equiv.) followed by addition of TsCl (2.35 g, 12.1 mmol, 1.05 equiv.) in two portions. The reaction was stirred at 1 ºC for 22h. Afterwards, the solids were filtered off and the filtrate was concentrated *in vacuo*, dissolved in EtOAc (50 mL), washed with sat. $NaHCO_3$ (20 mL), aqueous HCl (20 mL, 0.1 M), H_2O (20 mL), dried over Na_2SO_4, filtered, concentrated under reduced pressure to yield crude product as a colorless oil. The crude oil was dissolved in EtOAc/Hexane (25 mL, 2:3) and cooled in an ice bath. The formed precipitates were filtered and dried under high vacuum to yield *N*-tosyl-L-*allo*-threonine methyl ester (**13**) (1.5 g, 46%) as a white solid. The mother liquid was concentrated, dissolved in EtOAc/Hexane (10 mL, 1:1) and kept in the freezer (-25 ºC) for 3 days. The formed solids were filtered and dried under high vacuum to yield a second portion of desired product **13** (0.72 g, 22%) as a white solid. The mother liquid was concentrated and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 46% : 54% EtOAc/Heptane → 100% EtOAc) to yield third portion of the compound **13** (0.40 g, 12%) Total yield: 80% (2.6 g) over three steps.

Data for **13**: White solid; R_f=0.50 (Heptane/EtOAc 1:3); ^1H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H; Ts), 7.32 – 7.27 (m, 2H; Ts), 5.57 (d, *J* = 9.0 Hz, 1H; NH), 4.09 – 4.03 (m, 1H; H3), 3.94 (dd, *J* = 8.9, 4.0 Hz, 1H; H2), 3.53 (s, 3H; OMe), 2.44 (br, 1H; OH), 2.42 (s, 3H; Ts), 1.17 (d, *J* = 6.5 Hz, 3H; H4.). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1 (C1), 144.1 (Ts), 136.4 (Ts), 129.9 (Ts), 127.5 (Ts), 68.7 (C3), 61.0 (C2), 52.8 (OMe), 21.7 (Ts), 19.1 (C4). HRMS (ESI+): *m/z* calcd for $C_{12}H_{18}NO_5S^+$: 288.09002 [*M*+H]+; found: 288.09013.



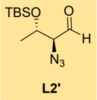
Compound **14** was prepared following slightly modified procedure of Koide *et al.*[7] *N*-tosyl-L-*allo*-threonine methyl ester (**13**) (2.50 g, 8.70 mmol, 1.0 equiv.) and (+)-10-Camphorsulfonic acid (40 mg, 0.17 mmol, 2 mol%) were dissolved in DCE (15 mL) under N_2 atmosphere and 2-methoxypropene (1.7 mL, 17 mmol, 2.0 equiv.) was added dropwise. The reaction was refluxed for 2.5h, cooled to room temperature, concentrated on silica gel and purified using Büchi Pure C-810 Flash system (FlashPure EcoFlex Silica 40 g column, eluent: 19% : 81% EtOAc/Heptane → 100% EtOAc) to yield methyl (4*S*,5*S*)-2,2,5-trimethyl-3-tosyloxazolidine-4-carboxylate (**14**) (2.63 g, 92%) as a yellowish solid.

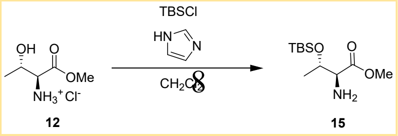
Data for **14**: Yellowish solid; R_f=0.37 (Heptane/EtOAc 3:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H; Ts), 7.31 – 7.26 (m, 2H; Ts), 4.34 (p, *J* = 6.1 Hz, 1H; H3), 4.27 (d, *J* = 6.3 Hz, 1H; H2), 3.52 (s, 3H; OMe), 2.41 (s, 3H; Ts), 1.79 (s, 3H; $C(CH_3)_2$), 1.63 (s, 3H; $C(CH_3)_2$), 1.18 (d, *J* = 6.3 Hz, 3H; H4). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6 (C1), 143.8 (Ts), 137.6 (Ts), 129.6 (Ts), 127.7 (Ts), 98.7 ($\mathit{C}(CH_3)_2$), 72.8 (C3), 64.0 (C2), 52.0 (OMe), 27.9 ($C(\mathit{C}H_3)_2$), 26.3 ($C(\mathit{C}H_3)_2$), 21.6 (Ts), 15.1 (C4). HRMS (ESI+): *m/z* calcd for $C_{15}H_{22}NO_5S^+$: 328.12132 [*M*+H]+; found: 328.12150.



A solution of methyl (4*S*,5*S*)-2,2,5-trimethyl-3-tosyloxazolidine-4-carboxylate (**14**) (2.52 g, 7.70 mmol, 1.0 equiv.) in dry $PhCH_3$ (50 mL) was cooled to -78 ºC under N_2 atmosphere and DIBAL-H (8.8 mL, 25%, 13 mmol, 1.7 equiv.) in $PhCH_3$ was added dropwise over 20 min. The reaction was stirred at -78 ºC for 3h and subsequently quenched with MeOH (1.5 mL). The quenched reaction mixture was diluted with Et_2O (30 mL), sat. Rochelle's salt (50 mL) and H_2O (100 mL). The water layer was extracted three times with EtOAc (50 mL). The combined organic layers were washed once with H_2O (30 mL), once with brine (30 mL), dried over Na_2SO_4, filtered, concentrated and purified using Büchi Pure C-810 Flash system (FlashPure EcoFlex Silica 40 g column, eluent: 21% : 79% EtOAc/Heptane → 100% EtOAc) to yield aldehyde **L2** (1.97 g, 86%) as an off-white solid.

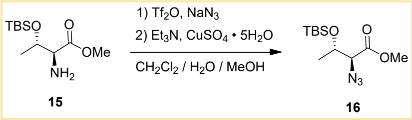
Data for **L2**: Off-white solid; R_f=0.34 (Heptane/EtOAc 3:1); ^1H NMR (500 MHz, $CDCl_3$) δ 9.43 (d, *J* = 4.5 Hz, 1H; H1), 7.75 – 7.66 (m, 2H; Ts), 7.30 (d, *J* = 8.2 Hz, 2H; Ts), 4.29 (p, *J* = 6.3 Hz, 1H; H3), 3.83 (dd, *J* = 6.6, 4.6 Hz, 1H; H2), 2.42 (s, 3H; Ts), 1.84 (s, 3H; $C(CH_3)_2$), 1.60 (s, 3H; $C(CH_3)_2$), 1.22 (d, *J* = 6.6 Hz, 3H; H4). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.5 (C1), 144.3 (Ts), 137.2 (Ts), 130.0 (Ts), 127.7 (Ts), 98.6 ($\mathit{C}(CH_3)_2$), 73.6 (C3), 68.3 (C2), 29.5 ($C(\mathit{C}H_3)_2$), 25.4 ($C(\mathit{C}H_3)_2$), 21.7 (Ts), 15.1 (C4). HRMS (ESI+): *m/z* calcd for $C_{14}H_{20}NO_4S^+$: 298.11076 [*M*+H]+; found: 298.11093





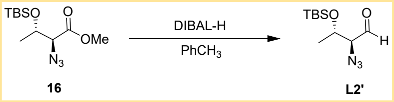
Crude *L*-allo-threonine methyl ester hydrochloride (**12**) (1.04 g, 6.11 mmol, 1.0 equiv.) was dispersed in CH_2Cl_2 and evaporated. The procedure was repeated once more. Then, Ester **12** was suspended in dry CH_2Cl_2 (20 mL) under N_2 atmosphere and imidazole (1.25 g, 18.3 mmol, 3.0 equiv.) was added. After 1h, TBSCl (1.0 g, 6.7 mmol, 1.1 equiv.) was added in one portion and the reaction was stirred at room temperature for 22h. Afterwards, the mixture was concentrated under reduced pressure and the residue was dissolved in H_2O/EtOAc (60 mL; 1:1). The water layer was additionally extracted twice with EtOAc (30 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 25 g column, eluent: 29% : 71% EtOAc/Heptane → 100% EtOAc). Fractions with the product were concentrated, co-evaporated twice with $CHCl_3$ and dried each time for 0.5h at 40 ºC, 50 mbar to yield methyl *O*-(*tert*-butyldimethylsilyl)-*L*-*allo*-threoninate (**15**) (1.05 g, 70% over three steps) as a yellowish liquid oil.

Data for **15**: Yellowish liquid oil; R_f=0.55 (EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 4.03 (qd, *J* = 6.2, 4.7 Hz, 1H; H3), 3.71 (s, 3H; OMe), 3.48 (d, *J* = 4.9 Hz, 1H; H2), 1.57 (br, 2H; NH_2), 1.13 (d, *J* = 6.1 Hz, 3H; H4), 0.87 (s, 9H; TBS), 0.07 (s, 3H; TBS), 0.06 (s, 3H; TBS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0 (C1), 70.5 (C3), 61.1 (C2), 51.9 (OMe), 25.8 (TBS), 18.9 (C4), 18.1 (TBS), -4.3 (TBS), -4.9 (TBS). HRMS (ESI+): *m*/*z* calcd for $C_{11}H_{26}NO_3Si^+$: 248.16765 [*M*+H]$^+$; found: 248.16783.



Compound **16** was prepared following adopted procedure from Nicolaou *et al*.[12] Tf_2O (1.6 mL, 9.4 mmol, 3.0 equiv.) was added dropwise to a solution of NaN_3 (1.23 g, 18.6 mmol, 6.0 equiv.) in CH_2Cl_2/H_2O (6 mL, 1:1) at 0 ºC. The reaction was stirred at 0 ºC for 2h and sat. $NaHCO_3$ (3 mL) was added. The layers were separated, and the water layer was additionally extracted twice with CH_2Cl_2 (3 mL). The combined organic layers were washed once with sat. $NaHCO_3$ (3 mL). Formed solution of TfN_3 solution in CH_2Cl_2 was added to a solution of methyl *O*-(*tert*-butyldimethylsilyl)-*L*-*allo*-threoninate (**15**) (0.769 g, 3.11 mmol, 1.0 equiv.) in MeOH (25 mL) and H_2O (8 mL), followed by addition of Et_3N (1.3 mL, 9.3 mmol, 3.0 equiv.) and $CuSO_4{\cdot}5H_2O$ (39 mg, 0.16 mmol, 5 mol%) at room temperature. The mixture was stirred at room temperature for 1.5h and volatiles were removed *in vacuo*. The residual aqueous layer was extracted three times with EtOAc (10 mL). The combined organic layers were washed once with brine (10 mL), dried over Na_2SO_4, filtered, concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 3% : 97% EtOAc/Heptane → 100% EtOAc). Fractions with the product were concentrated, co-evaporated twice with $CHCl_3$ and dried each time for 20 min at 40 ºC, 50 mbar to yield methyl (2*S*,3*S*)-2-azido-3-((*tert*-butyldimethylsilyl)oxy)butanoate (**16**) (0.67 g, 79%) as a colorless oil.

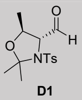
Data for **16**: Colorless oil; R_f=0.51 (Heptane/EtOAc 10:1); ^1H NMR (500 MHz, $CDCl_3$) δ 4.23 (qd, *J* = 6.1, 5.4 Hz, 1H; H3), 3.85 (d, *J* = 5.5 Hz, 1H; H2), 3.77 (s, 3H; OMe), 1.24 (d, *J* = 6.1 Hz, 3H; H4), 0.88 (s, 9H; TBS), 0.09 (s, 3H; TBS), 0.08 (s, 3H; TBS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2 (C1), 69.8 (C3), 68.1 (C2), 52.6 (OMe), 25.7 (TBS), 19.9 (C4), 18.0 (TBS), -4.3 (TBS), -5.0 (TBS). HRMS (ESI+): *m*/*z* calcd for $C_{11}H_{23}N_3O_3SiNa^+$: 296.14009 [*M*+H]$^+$; found: 296.14088



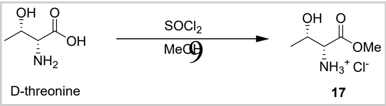
A solution of methyl (2S,3S)-2-azido-3-((*tert*-butyldimethylsilyl)oxy)butanoate (**16**) (0.562 g, 2.06 mmol, 1.0 equiv.) in dry $PhCH_3$ (8 mL) was cooled to -78 ºC under N_2 atmosphere and DIBAL-H (1.9 mL, 25%, 13 mmol, 1.1 equiv.) in $PhCH_3$ was added dropwise over 10 min. The reaction was stirred at -78 ºC for 2h and subsequently quenched with MeOH (1.5 mL). The quenched reaction mixture was diluted with EtOAc (30 mL) and sat. Rochelle's salt (30 mL). The water layer was additionally extracted twice with EtOAc (50 mL). The combined organic layers were washed once with H_2O (30 mL), once with brine (30 mL), dried over Na_2SO_4, filtered, concentrated *in vacuo*, co-evaporated twice with $CHCl_3$ and dried each time for 20 min at 40 ºC, 50 mbar to yield crude (2S,3S)-2-azido-3-((tert-butyldimethylsilyl)oxy)butanal (**L2'**) (0.50 g, quantitively) as a yellowish oil, which was used in next steps without additional purification.

Note: Due to stability issues of the aldehyde **L2'**, it was not possible to obtain HRMS, and it should be used in the next step as soon as possible.

Data for **L2'**: Yellowish oil; R_f=0.34 (Heptane/EtOAc 10:1); ^1H NMR (500 MHz, $CDCl_3$) δ 9.59 (d, *J* = 1.3 Hz, 1H; H1), 4.22 (qd, *J* = 6.3, 4.6 Hz, 1H; H3), 3.86 (dd, *J* = 4.6, 1.3 Hz, 1H; H2), 1.28 (d, *J* = 6.3 Hz, 3H; H4), 0.89 (s, 9H; TBS), 0.10 (s, 6H; TBS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.9 (C1), 73.0 (C2), 69.8 (C3), 25.8 (TBS), 20.4 (C4), 18.0 (TBS), -4.3 (TBS), -4.9 (TBS).

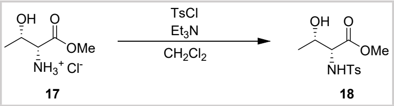


D1



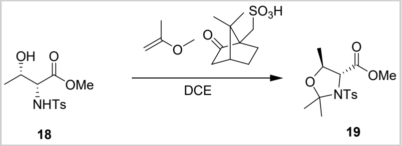
MeOH (85 mL) was cooled in an ice bath and $SOCl_2$ (6.0 mL, 82 mmol, 1.0. equiv.) was added dropwise under N_2 atmosphere. To the resultant solution of HCl in MeOH, D-threonine (10.0 g, 84.0 mmol, 1.0 equiv.) was added in one portion and the reaction was refluxed for 4h. Afterwards, the mixture was cooled to room temperature and concentrated under reduced pressure to yield crude D-threonine methyl ester hydrochloride (**17**) (14.8 g) as a colorless oil, which was used in next steps without additional purification. Note: some of MeOH is still remaining after high vacuum drying.[3]

^{1}H NMR (500 MHz, D_2O) δ 4.49 – 4.42 (m, 1H; H3), 4.14 (d, J = 2.6 Hz, 1H; H2), 3.89 (s, 3H; OMe), 1.36 (d, J = 6.7 Hz, 3H; H4). ^{13}C NMR (126 MHz, D_2O) δ 169.2 (C1), 65.2 (C3), 58.4 (C2), 53.7 (OMe), 18.8 (C4). HRMS (ESI+): m/z calcd for $C_5H_{12}NO_3^+$: 134.08117 [M+H]$^+$; found: 134.08134.



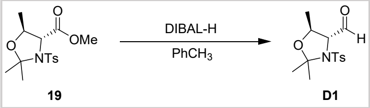
Compound **18** was prepared following adopted procedure from Minakata *et al*.[5] To a suspension of crude D-threonine methyl ester hydrochloride (**17**) (3.35 g, 25.2 mmol, 1.0 equiv.) in dry CH_2Cl_2 (50 mL) cooled in an ice bath under N_2 atmosphere was added Et_3N (7.0 mL, 50 mmol, 2.0 equiv.) followed by addition of TsCl (5.04 g, 26.4 mmol, 1.05 equiv.). The reaction was stirred at 0 ºC for 16h. Afterwards, the solids were filtered off and the filtrate was concentrated *in vacuo*, dissolved in EtOAc, washed with sat. $NaHCO_3$, brine, dried over $MgSO_4$, filtered, concentrated under reduced pressure to yield crude product as an off-white solid. The crude was recrystallized from EtOAc/Heptane (1:1) to give *N*-tosyl-D-threonine methyl ester (**18**) (5.72 g, 79%) as a white solid.

Data for **18**: White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 2H; Ts), 7.34 – 7.27 (m, 2H; Ts), 5.39 (d, J = 9.5 Hz, 1H; NH), 4.19 – 4.08 (m, 1H; H3), 3.82 (dd, J = 9.6, 3.2 Hz, 1H; H2), 3.52 (s, 3H; OMe), 2.42 (s, 3H; Ts), 1.91 (br, 1H; OH), 1.27 (d, J = 6.5 Hz, 3H; H4). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8 (C1), 143.9 (Ts), 136.8 (Ts), 129.8 (Ts), 127.4 (Ts), 68.5 (C3), 61.0 (C2), 52.8 (OMe), 21.7 (Ts), 20.0 (C4). HRMS (ESI+): m/z calcd for $C_{12}H_{18}NO_5S^+$: 288.09002 [M+H]$^+$; found: 288.09005.



Compound **19** was prepared following adopted procedure from Koide *et al*.[7] *N*-tosyl-D-threonine methyl ester (**18**) (2.00 g, 6.96 mmol, 1.0 equiv.) and (+)-10-camphorsulfonic acid (32 mg, 0.13 mmol, 2 mol%) were dissolved in DCE (15 mL) under N_2 atmosphere and 2-methoxypropene (1.3 mL, 14 mmol, 2.0 equiv.) was added dropwise. The reaction was refluxed for 2h, cooled to room temperature, concentrated and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 25 g column, eluent: 5% : 95% EtOAc/Heptane → 100% EtOAc) to yield methyl (4R,5S)-2,2,5-trimethyl-3-tosyloxazolidine-4-carboxylate (**19**) (2.10 g, 92%) as a yellow oil.

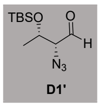
Data for **19**: Yellow oil; R_f=0.35 (Heptane/EtOAc 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 2H; Ts), 7.35 – 7.27 (m, 2H; Ts), 4.30 (dq, J = 7.6, 6.1 Hz, 1H; H3), 3.92 (d, J = 7.6 Hz, 1H; H2), 3.79 (s, 3H; OMe), 2.42 (s, 3H; Ts), 1.60 (s, 3H; $C(CH_3)_2$), 1.53 (s, 3H; $C(CH_3)_2$), 1.32 (d, J = 6.0 Hz, 3H; H4). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9 (C1), 143.8 (Ts), 137.8 (Ts), 129.7 (Ts), 127.8 (Ts), 98.2 ($C(CH_3)_2$), 74.7 (C3), 67.4 (C2), 53.0 (OMe), 28.1 ($C(CH_3)_2$), 26.4 ($C(CH_3)_2$), 21.7 (Ts), 18.7 (C4). HRMS (ESI+): m/z calcd for $C_{15}H_{22}NO_5S^+$: 328.12132 [M+H]$^+$; found: 328.12160.



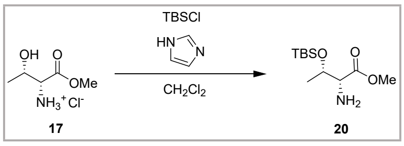
A solution of methyl (4R,5S)-2,2,5-trimethyl-3-tosyloxazolidine-4-carboxylate (**19**) (1.06 g, 3.25 mmol, 1.0 equiv.) in dry $PhCH_3$ (20 mL) was cooled to -78 ºC under N_2 atmosphere and DIBAL-H (4.6 mL, 1.2 M, 5.5 mmol, 1.7 equiv.) in $PhCH_3$ was added dropwise over 10 min. The reaction was stirred at -78 ºC for 3h and subsequently quenched with MeOH (1.0 mL). The quenched reaction mixture was diluted with Et_2O (15 mL), sat. Rochelle's salt (25 mL) and H_2O (50 mL). The water layer was extracted three times with EtOAc (25 mL). The combined organic layers were washed once with H_2O (15 mL), once with brine (15 mL), dried over Na_2SO_4, filtered and concentrated. The resulting solid was dissolved in Et_2O/Heptane (30 mL, 5:1) and left overnight in the freezer (-25 ºC). The formed precipitates were filtered, dried under high vacuum to yield (4R,5S)-2,2,5-trimethyl-3-tosyloxazolidine-4-carbaldehyde (**D1**) (0.75 g, 78%) as white crystals.

Data for **D1**: White solid; R_f=0.42 (Heptane/EtOAc 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.58 (d, J = 4.6 Hz, 1H; H1), 7.70 – 7.62 (m, 2H; Ts), 7.32 (d, J = 8.2 Hz, 2H; Ts), 4.22 (dq, J = 8.4, 6.1 Hz, 1H; H3), 3.50 (dd, J = 8.3, 4.5 Hz, 1H; H2), 2.44 (s, 3H; Ts), 1.67 (s, 3H; $C(CH_3)_2$), 1.50 (s, 3H; $C(CH_3)_2$), 1.27 (d, J = 6.0 Hz, 3H; H4). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2 (C1), 144.2 (Ts), 136.9 (Ts), 130.0

(Ts), 127.7 (Ts), 98.3 ($C(CH_3)_2$), 72.4 (C2), 70.5 (C3), 29.0 ($C(CH_3)_2$), 25.7 ($C(CH_3)_2$), 21.7 (Ts), 17.4 (C4). HRMS (ESI+): *m*/*z* calcd for $C_{14}H_{19}NO_4SNa^+$: 320.09270 [*M*+Na]+; found: 320.09313

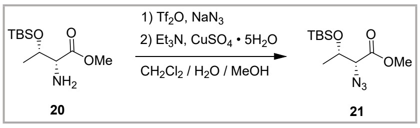


D1'



Crude D-threonine methyl ester hydrochloride (**17**) (7.12 g, 42.0 mmol, 1.0 equiv.) was dispersed in CH_2Cl_2 and evaporated. The procedure was repeated once more. Then, Ester **17** was suspended in dry CH_2Cl_2 (140 mL) under N_2 atmosphere and imidazole (8.57 g, 126 mmol, 3.0 equiv.) was added. After 1h, TBSCl (7.2 g, 46 mmol, 1.1 equiv.) was added in one portion and the reaction was stirred at room temperature for 22h. Afterwards, the mixture was concentrated under reduced pressure and the residue was dissolved in H_2O/EtOAc (200 mL; 1:1). The water layer was additionally extracted twice with EtOAc (100 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 40 g column, eluent: 62% : 38% EtOAc/Heptane → 100% EtOAc). Fractions with the product were concentrated, co-evaporated twice with $CHCl_3$ and dried each time for 0.5h at 40 °C, 50 mbar to yield methyl *O*-(*tert*-butyldimethylsilyl)-D-threoninate (**20**) (7.28 g, 70% over two steps) as a colorless oil. NMR was consistent with the literature.[13]

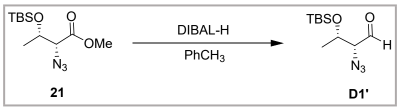
Data for **20**: Colorless oil; R_f=0.38 (Heptane/EtOAc 1:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.29 (qd, *J* = 6.3, 2.7 Hz, 1H; H3), 3.71 (s, 3H; OMe), 3.28 (d, *J* = 2.7 Hz, 1H; 2), 1.61 (s, 2H; NH_2), 1.24 (d, *J* = 6.3 Hz, 3H; H4), 0.84 (s, 9H; TBS), 0.04 (s, 3H; TBS), -0.02 (s, 3H; TBS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.1 (C1), 69.6 (C3), 60.9 (C2), 52.0 (OMe), 25.8 (TBS), 21.0 (C4), 18.0 (TBS), -4.2 (TBS), -5.1 (TBS). HRMS (ESI+): *m*/*z* calcd for $C_{11}H_{26}NO_3Si^+$: 248.16765 [*M*+H]+; found: 248.16787.



Compound **21** was prepared following adopted procedure from Nicolaou *et al.*[12] Tf_2O (2.10 mL, 12.4 mmol, 3.0 equiv.) was added dropwise to a solution of NaN_3 (1.58 g, 24.3 mmol, 6.0 equiv.) in CH_2Cl_2/H_2O (8 mL, 1:1) at 0 °C. The reaction was stirred at 0 °C for 2h and sat. $NaHCO_3$ (5 mL) was added. The layers were separated, and the water layer was additionally extracted twice with CH_2Cl_2 (3 mL). The combined organic layers were washed once with sat. $NaHCO_3$ (3 mL). Formed solution of TfN_3 solution in CH_2Cl_2 was added to a solution of methyl *O*-(*tert*-butyldimethylsilyl)-*D*-threoninate (**20**) (1.00 g, 4.04 mmol, 1.0 equiv.) in MeOH (33 mL) and H_2O (10 mL), followed by addition of Et_3N (1.7 mL, 12 mmol, 3.0 equiv.) and $CuSO_4{\cdot}5H_2O$ (50 mg, 0.20 mmol, 5 mol%) at room temperature. The mixture was stirred at room temperature for 1.5h and volatiles were removed *in vacuo*. The residual aqueous layer was extracted three times with EtOAc (15 mL). The combined organic layers were washed once with brine (10 mL), dried over Na_2SO_4, filtered, concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 25 g column, eluent: 3% : 97% EtOAc/Heptane → 100% EtOAc). Fractions with the product were concentrated, co-evaporated twice with $CHCl_3$ and dried each time for 0.5h at 40 °C, 50 mbar to yield methyl (2*R*,3*S*)-2-azido-3-((*tert*-butyldimethylsilyl)oxy)butanoate (**21**) (0.75 g, 67%) as a colorless oil. NMR was consistent with the literature.[14]

Note: Due to the sensitivity of the compound **21,** it was not possible to obtain HRMS.

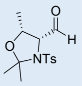
Data for **21**: Colorless oil; R_f=0.39 (Heptane/EtOAc 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.46 (qd, *J* = 6.3, 2.8 Hz, 1H; H3), 3.80 (s, 3H; OMe), 3.39 (d, *J* = 2.8 Hz, 1H; H2)), 1.32 (d, *J* = 6.3 Hz, 3H; H4), 0.87 (s, 9H; TBS), 0.08 (s, 3H; TBS), 0.03 (s, 3H; TBS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0 (C1), 70.8 (C3), 67.2 (C2), 52.6 (OMe), 25.6 (TBS), 21.2 (C4), 17.9 (TBS), -4.3 (TBS), -5.2 (TBS).



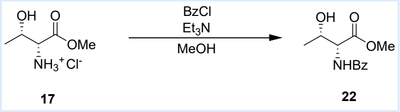
A solution of methyl (2*R*,3*S*)-2-azido-3-((*tert*-butyldimethylsilyl)oxy)butanoate (**21**) (0.406 g, 1.49 mmol, 1.0 equiv.) in dry $PhCH_3$ (6 mL) was cooled to -78 °C under N_2 atmosphere and DIBAL-H (1.4 mL, 1.2 M, 1.7 mmol, 1.1 equiv.) in $PhCH_3$ was added dropwise over 10 min. The reaction was stirred at -78 °C for 2h and subsequently quenched with MeOH (1.5 mL). The quenched reaction mixture was diluted with EtOAc (20 mL) and sat. Rochelle's salt (20 mL). The water layer was additionally extracted twice with EtOAc (20 mL). The combined organic layers were washed once with H_2O (20 mL), once with brine (20 mL), dried over Na_2SO_4, filtered, concentrated *in vacuo*, co-evaporated twice with $CHCl_3$ and dried each time for 20 min at 40 °C, 50 mbar to yield crude (2*R*,3*S*)-2-azido-3-((*tert*-butyldimethylsilyl)oxy)butanal (**D1'**) (0.35 g, 95%) as a yellowish oil, which was used in next steps without additional purification.

Note: Due to stability issues of the aldehyde **D1'**, it was not possible to obtain HRMS, and it should be used in the next step as soon as possible.

Data for **D1'**: Yellowish oil; R_f=0.33 (Heptane/EtOAc 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.70 (s, 1H; H1), 4.46 (qd, *J* = 6.3, 3.4 Hz, 1H; H3), 3.53 (d, *J* = 3.5 Hz, 1H; H2), 1.33 (d, *J* = 6.3 Hz, 3H; H4), 0.87 (s, 9H; TBS), 0.10 (s, 3H; TBS), 0.07 (s, 3H; TBS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.7 (C1), 72.6 (C2), 68.9 (C3), 25.7 (TBS), 20.8 (C4), 18.0 (TBS), -4.2 (TBS), -5.0 (TBS).

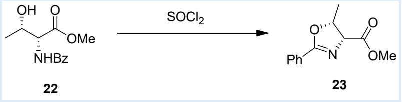


D2



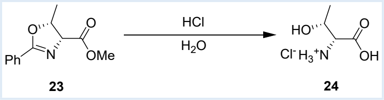
Compound **22** was prepared following adopted procedure from Tanner *et al.*[8] The crude *D*-threonine methyl ester hydrochloride (**17**) (11.2 g, 66.3 mmol, 1.0 equiv.) was dissolved in dry MeOH (40 mL) under N_2 atmosphere and Et_3N (28.0 mL, 200 mmol, 3.0 equiv.) was added dropwise. After 15 min, the reaction mixture was cooled in an ice bath and BzCl (8.5 mL, 72 mmol, 1.1 equiv.) was added dropwise. The reaction was stirred at 0 ºC for 3h. Afterwards, the mixture was concentrated, diluted with H_2O (50 mL) and extracted three times with EtOAc (40 mL). The combined organic layers were washed once with H_2O (20 mL), once with brine (10 mL), dried over Na_2SO_4, filtered and concentrated to give yellowish oil. The oil was dissolved in Et_2O (30 mL) and kept in the freezer (-25 ºC) overnight. The formed solids were filtered and dried under high vacuum to yield *N*-benzoyl-D-threonine methyl ester (**22**) (12.9 g, 82% over two steps) as off-white solid.

Data for **22**: Off-white solid; R_f=0.45 (Heptane/EtOAc 1:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 2H; Bz), 7.55 – 7.48 (m, 1H; Bz), 7.47 – 7.40 (m, 2H; Bz), 7.00 (d, *J* = 8.7 Hz, 1H; NH), 4.82 (dd, *J* = 8.8, 2.5 Hz, 1H; H2), 4.45 (qd, *J* = 6.4, 2.5 Hz, 1H; H3), 3.78 (s, 3H; OMe), 2.57 (br, 1H; OH), 1.28 (d, *J* = 6.4 Hz, 3H; H4). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8 (C1), 168.1 (Bz), 133.8 (Bz), 132.1 (Bz), 128.8 (Bz), 127.3 (Bz), 68.4 (C3), 57.7 (C2), 52.8 (OMe), 20.2 (C4). HRMS (ESI+): *m*/*z* calcd for $C_{12}H_{16}NO_4^+$: 238.10738 $[M+H]^+$; found: 238.10817.



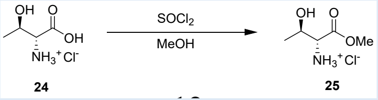
Compound **23** was prepared following adopted procedure from Sulikowski *et al.*[9] To $SOCl_2$ (38.0 mL, 522 mmol, 10.5 equiv.) at 0 ºC under N_2 atmosphere, *N*-benzoyl-D-threonine methyl ester (**22**) (11.8 g, 49.7 mmol, 1.0 equiv.) was added in three portions. The reaction was stirred at 1 ºC for 5 days. Afterwards, the mixture was concentrated, dissolved in CH_2Cl_2, slowly poured into sat. $NaHCO_3$ (100 mL) and extracted three times with CH_2Cl_2 (50 mL). The combined organic layers were washed once with H_2O (50 mL), once with brine (20 mL), dried over Na_2SO_4, filtered, concentrated and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 40 g column, eluent: 32% : 68% EtOAc/Heptane → 100% EtOAc) to yield methyl (4*R*,5*R*)-5-methyl-2-phenyl-4,5-dihydrooxazole-4-carboxylate (**23**) (9.07 g, 83 %) as a yellowish oil.

Data for **23**: Yellowish oil; R_f=0.52 (Heptane/EtOAc 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.91 (m, 2H; Ph), 7.51 – 7.45 (m, 1H; Ph), 7.42 – 7.35 (m, 2H; Ph), 5.05 (dq, *J* = 10.1, 6.4 Hz, 1H; H3), 4.97 (d, *J* = 10.2 Hz, 1H; H2), 3.76 (s, 3H; OMe), 1.37 (d, *J* = 6.5 Hz, 3H; H4). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5 (C1), 166.2 (Ph*C*(O)N), 131.9 (Ph), 128.6 (Ph), 128.4 (Ph), 127.3 (Ph), 77.7 (C3), 71.8 (C2), 52.2 (OMe), 16.3 (C4). HRMS (ESI+): *m*/*z* calcd for $C_{12}H_{14}NO_3^+$: 220.09682 $[M+H]^+$; found: 220.09685.



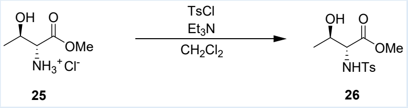
Compound **24** was prepared following adopted procedure from Sulikowski *et al.*[9] Methyl (4*R*,5*R*)-5-methyl-2-phenyl-4,5-dihydrooxazole-4-carboxylate (**23**) (8.11 g, 37.0 mmol, 1.0 equiv.) was suspended in H_2O (50 mL) and HCl (42 mL, 37%, 0.51 mol, 14 equiv.) was added via syringe. The reaction mixture was refluxed for 5h. Afterwards, the mixture was cooled to room temperature and washed three times with Et_2O (50 mL). The aqueous layer was concentrated *in vacuo* to give D-*allo*-threonine hydrochloride (**24**) (5.8 g, quantitively) as a yellowish foam, which was used in the next steps without additional purifications.

Data for **24**: Yellowish foam; ^{1}H NMR (500 MHz, D_2O) δ 4.36 (qd, *J* = 6.6, 3.5 Hz, 1H; H3), 4.13 (d, *J* = 3.5 Hz, 1H; H2), 1.30 (d, *J* = 6.6 Hz, 3H; H4). ^{13}C NMR (126 MHz, D_2O) δ 169.5 (C1), 65.3 (C3), 57.9 (C2), 17.3 (C4). HRMS (ESI+): *m*/*z* calcd for $C_4H_{10}NO_3^+$: 120.06552 $[M+H]^+$; found: 120.06596.



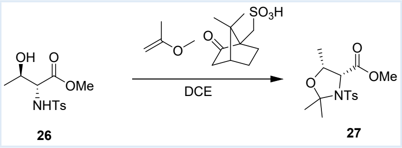
MeOH (35 mL) was cooled in an ice bath and $SOCl_2$ (2.5 mL, 34 mmol, 1.0. equiv.) was added dropwise under N_2 atmosphere. The resultant solution of HCl in MeOH was added to the crude D-*allo*-threonine hydrochloride (**24**) (5.2 g, 33.7 mmol, 1.0 equiv.) and the reaction was refluxed for 4h. Afterwards, the mixture was cooled to room temperature and concentrated under reduced pressure to yield crude D-*allo*-threonine methyl ester hydrochloride (**25**) (5.6 g, quantitively) as a yellowish oil, which was used in next steps without additional purification. NMR was consistent with the literature.[15]

Data for **25**: Yellowish oil; ^{1}H NMR (500 MHz, D_2O) δ 4.40 – 4.32 (m, 1H; H3), 4.26 – 4.18 (m, 1H; H2), 3.88 (s, 3H; OMe), 1.32 (d, *J* = 6.7 Hz, 3H; H4). ^{13}C NMR (126 MHz, D_2O) δ 168.3 (C1), 65.5 (C3), 58.0 (C2), 53.5 (OMe), 17.7 (C4). HRMS (ESI+): *m*/*z* calcd for $C_5H_{12}NO_3^+$: 134.08117 [*M*+H]$^+$; found: 134.08167.



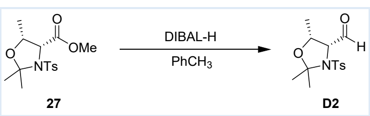
Compound **26** was prepared following adopted procedure from Minakata *et al*.[5] To a suspension of crude D-*allo*-threonine methyl ester hydrochloride (**25**) (2.45 g, 18.4 mmol, 1.0 equiv.) in dry CH_2Cl_2 (25 mL) cooled in an ice bath under N_2 atmosphere was added Et_3N (5.2 mL, 37 mmol, 2.0 equiv.) followed by addition of TsCl (3.68 g, 19.3 mmol, 1.05 equiv.) in one portion. The reaction was stirred at 0 ºC for 23h. Afterwards, the solids were filtered off and the filtrate was concentrated *in vacuo*, suspended in sat. NH_4Cl (50 mL) and extracted three times with EtOAc (25 mL). The combined organic layers were brine (20 mL), dried over Na_2SO_4, filtered, concentrated on silica gel and using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 40 g column, eluent: 39% : 61% EtOAc/Heptane → 100% EtOAc) to yield *N*-tosyl-D-*allo*-threonine methyl ester (**26**) (3.10 g, 59%) as an off-white solid.

Data for **26**: White solid; R_f=0.00 (Heptane/EtOAc 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.66 (m, 2H; Ts), 7.30 (d, *J* = 8.2 Hz, 2H; Ts), 5.59 (d, *J* = 9.0 Hz, 1H; NH), 4.06 (qd, *J* = 6.5, 4.0 Hz, 1H; H3), 3.94 (dd, *J* = 8.9, 4.0 Hz, 1H; H2), 3.53 (s, 3H; OMe), 2.42 (s, 3H; Ts), 2.35 (br, 1H; OH), 1.17 (d, *J* = 6.4 Hz, 3H; H4). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1 (C1), 144.1 (Ts), 136.4 (Ts), 129.9 (Ts), 127.5 (Ts), 68.7 (C3), 61.0 (C2), 52.8 (OMe), 21.7 (Ts), 19.1 (C4). HRMS (ESI+): *m*/*z* calcd for $C_{12}H_{17}NO_5SNa^+$: 310.07196 [*M*+Na]$^+$; found: 310.07219.



Compound **27** was prepared following adopted procedure from Koide *et al*.[7] *N*-tosyl-D-*allo*-threonine methyl ester (**26**) (0.50 g, 1.7 mmol, 1.0 equiv.) and (+)-10-Camphorsulfonic acid (8.8 mg, 0.038 mmol, 2 mol%) were dissolved in DCE (5 mL) under N_2 atmosphere and 2-methoxypropene (0.34 mL, 3.4 mmol, 2.0 equiv.) was added dropwise. The reaction was refluxed for 2.5h, cooled to room temperature, concentrated on silica gel and purified using Büchi Pure C-810 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 19% : 81% EtOAc/Heptane → 100% EtOAc) to yield methyl (4*R*,5*R*)-2,2,5-trimethyl-3-tosyloxazolidine-4-carboxylate (**27**) (0.54 g, 95%) as a white solid.

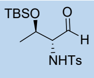
Data for **27**: White solid; R_f=0.30 (Heptane/EtOAc 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 2H; Ts), 7.31 – 7.26 (m, 2H; Ts), 4.34 (p, *J* = 6.3 Hz, 1H; H3), 4.27 (d, *J* = 6.3 Hz, 1H; H2), 3.52 (s, 3H; OMe), 2.41 (s, 3H; Ts), 1.79 (s, 3H; $C(CH_3)_2$), 1.63 (s, 3H; $C(CH_3)_2$), 1.18 (d, *J* = 6.1 Hz, 3H; H4). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6 (C1), 143.8 (Ts), 137.6 (Ts), 129.6 (Ts), 127.8 (Ts), 98.7 ($\mathit{C}(CH_3)_2$), 72.8 (C3), 64.0 (C2), 52.0 (OMe), 27.9 ($C(\mathit{CH}_3)_2$), 26.3 ($C(\mathit{CH}_3)_2$), 21.7 (Ts), 15.1 (C4). HRMS (ESI+): *m*/*z* calcd for $C_{15}H_{22}NO_5S^+$: 328.12132 [*M*+H]$^+$; found: 328.12175.



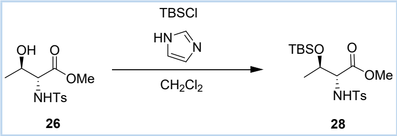
A solution of methyl (4*R*,5*R*)-2,2,5-trimethyl-3-tosyloxazolidine-4-carboxylate (**27**) (0.464 g, 1.42 mmol, 1.0 equiv.) in dry $PhCH_3$ (10 mL) was cooled to -78 ºC under N_2 atmosphere and DIBAL-H (2.0 mL, 1.2 M, 2.4 mmol, 1.7 equiv.) in $PhCH_3$ was added dropwise over 5 min. The reaction was stirred at -78 ºC for 3h and subsequently quenched with MeOH (0.5 mL). The quenched reaction mixture was diluted with Et_2O (10 mL), sat. Rochelle's salt (10 mL) and H_2O (20 mL). The water layer was extracted three times with EtOAc (20 mL). The combined organic layers were washed once with H_2O (10 mL), once with brine (10 mL), dried over Na_2SO_4, filtered, concentrated and purified using Büchi Pure C-810 Flash system (FlashPure EcoFlex Silica 25 g column, eluent: 21% : 79% EtOAc/Heptane → 100% EtOAc) to yield aldehyde **D2** (0.34 g, 81%) as a white solid.

Data for **D2**: White solid; R_f=0.34 (Heptane/EtOAc 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.43 (dd, *J* = 4.6, 0.9 Hz, 1H; H1), 7.75 – 7.68 (m, 2H; Ts), 7.32 – 7.26 (m, 2H; Ts), 4.29 (pd, *J* = 6.5, 0.9 Hz, 1H; H3), 3.83 (dd, *J* = 6.8, 4.6 Hz, 1H; H2), 2.42 (s, 3H; Ts), 1.84 (s, 3H; $C(CH_3)_2$), 1.60 (s, 3H; $C(CH_3)_2$), 1.22 (d, *J* = 6.6 Hz, 3H; H4). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.5 (C1), 144.3 (Ts), 137.2 (Ts), 130.0

(Ts), 127.7 (Ts), 98.6 (*C*(CH$_3$)$_2$), 73.6 (C3), 68.3 (C2), 29.5 (C(*C*H$_3$)$_2$), 25.4 (C(*C*H$_3$)$_2$), 21.7 (Ts), 15.1 (C4). HRMS (ESI+): *m*/*z* calcd for $C_{14}H_{19}NO_4SNa^+$: 320.09270 [*M*+Na]$^+$; found: 320.09310.

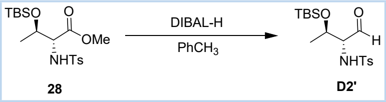


D2'



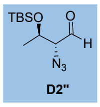
N-tosyl-D-*allo*-threonine methyl ester (**26**) (0.801 g, 2.79 mmol, 1.0 equiv.) and imidazole (0.385 g, 5.61 mmol, 2.0 equiv.) were dissolved in dry CH_2Cl_2 (10 mL) under N_2 atmosphere, cooled in an ice bath and TBSCl (0.450 g, 1.04 mmol, 1.04 equiv.) was added in two portions. After 10 min, the ice bath was removed and the reaction was stirred at room temperature for 22h. Afterwards, the mixture was poured into DCM/H_2O (70 mL, 5:2) and layers were separated. The organic layers was washed twice with H_2O (20 mL), once with brine (10 mL), dried over Na_2SO_4, filtered, concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 25 g column, eluent: 18% : 82% EtOAc/Heptane → 100% EtOAc) to yield methyl *O*-(*tert*-butyldimethylsilyl)-*N*-tosyl-D-*allo*-threoninate (**28**) (0.890 g, 80%) as a white solid. NMR was consistent with the literature.[16]

Data for **28**: White solid; R_f=0.39 (Heptane/EtOAc 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.61 (m, 2H; Ts), 7.28 (d, *J* = 8.2 Hz, 2H; Ts), 5.18 (d, *J* = 9.6 Hz, 1H; NH), 3.99 (qd, *J* = 6.3, 5.0 Hz, 1H; H3), 3.77 (dd, *J* = 9.6, 4.9 Hz, 1H; H2), 3.43 (s, 3H; OMe), 2.41 (s, 3H; Ts), 1.23 (d, *J* = 6.3 Hz, 3H; H4), 0.82 (s, 9H; TBS), 0.02 (s, 3H; TBS), 0.01 (s, 3H; TBS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3 (C1), 143.8 (Ts), 136.9 (Ts), 129.7 (Ts), 127.4 (Ts), 70.7 (C3), 62.0 (C2), 52.2 (OMe), 25.7 (TBS), 21.6 (Ts), 20.8 (C4), 18.0 (TBS), -4.3 (TBS), -5.0 (TBS). HRMS (ESI+): *m*/*z* calcd for $C_{18}H_{32}NO_5SSi^+$: 402.17650 [*M*+H]$^+$; found: 402.17835.

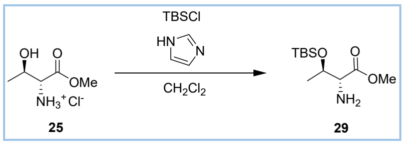


A solution of methyl *O*-(*tert*-butyldimethylsilyl)-*N*-tosyl-D-*allo*-threoninate (**28**) (0.724 g, 1.80 mmol, 1.0 equiv.) in dry $PhCH_3$ (15 mL) was cooled to -78 ºC under N_2 atmosphere and DIBAL-H (4.6 mL, 1.2 M, 5.5 mmol, 3.0 equiv.) in $PhCH_3$ was added dropwise over 45 min. The reaction was stirred at -78 ºC for 3h and subsequently quenched with MeOH (2.0 mL). The quenched reaction mixture was diluted with Et_2O (10 mL), sat. Rochelle's salt (25 mL) and H_2O (50 mL). The water layer was extracted three times with EtOAc (25 mL). The combined organic layers were washed once with H_2O (15 mL), once with brine (15 mL), dried over Na_2SO_4, filtered, concentrated and purified using Büchi Pure C-810 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 18% : 82% EtOAc/Heptane → 100% EtOAc) to yield aldehyde **D2'** (0.544 g, 81%) as a colourless oil.

Data for **D2'**: White solid; R_f=0.44 (Heptane/EtOAc 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (d, *J* = 0.9 Hz, 1H; 1), 7.74 – 7.65 (m, 2H; Ts), 7.28 (d, *J* = 8.2 Hz, 2H; Ts), 5.41 (d, *J* = 5.6 Hz, 1H; NH), 4.10 (qd, *J* = 6.4, 4.0 Hz, 1H; H3), 3.67 – 3.61 (m, 1H; H2), 2.40 (s, 3H; Ts), 1.35 (d, *J* = 6.4 Hz, 3H; H4), 0.79 (s, 9H; TBS), 0.01 (s, 3H; TBS), -0.03 (s, 3H; TBS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.5 (C1), 144.1 (Ts), 136.3 (Ts), 130.0 (Ts), 127.3 (Ts), 70.8 (C3), 66.7 (C2), 25.7 (TBS), 21.6 (Ts), 20.9 (C4), 18.0 (TBS), -4.5 (TBS), -5.0 (TBS). HRMS (ESI+): *m*/*z* calcd for $C_{17}H_{30}NO_4SSi^+$: 372.16593 [*M*+H]$^+$; found: 372.16660.

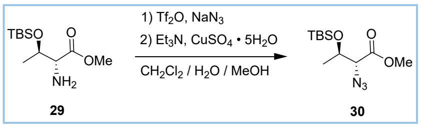


D2''



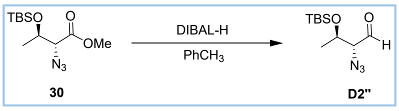
Crude D-*allo*-threonine methyl ester hydrochloride (**25**) (0.692 g, 4.08 mmol, 1.0 equiv.) was dispersed in CH_2Cl_2 and evaporated. The procedure was repeated once more. Then, Ester **25** was suspended in dry CH_2Cl_2 (14 mL) under N_2 atmosphere and imidazole (0.834 g, 12.3 mmol, 3.0 equiv.) was added. After 1h, TBSCl (0.698 g, 4.49 mmol, 1.1 equiv.) was added in one portion and the reaction was stirred at room temperature for 21h. Afterwards, the mixture was concentrated under reduced pressure and the residue was dissolved in H_2O/EtOAc (40 mL; 1:1). The water layer was additionally extracted twice with EtOAc (20 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 62% : 38% EtOAc/Heptane → 100% EtOAc). Fractions with the product were concentrated, co-evaporated twice with $CHCl_3$ and dried each time for 0.5h at 40 ºC, 50 mbar to yield methyl *O*-(*tert*-butyldimethylsilyl)-D-*allo*-threoninate (**29**) (0.786 g, 78% over three steps) as a colorless oil.

Data for **29**: Colorless oil; R_f=0.46 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.03 (qd, *J* = 6.3, 4.7 Hz, 1H; H3), 3.71 (s, 3H; OMe), 3.49 (d, *J* = 4.7 Hz, 1H; H2), 1.70 (s, 2H; NH_2), 1.13 (d, *J* = 6.3 Hz, 3H; H4), 0.87 (s, 9H; TBS), 0.07 (s, 3H; TBS), 0.06 (s, 3H; TBS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9 (C1), 70.5 (C3), 61.0 (C2), 52.0 (OMe), 25.8 (TBS), 18.9 (C4), 18.1 (TBS), -4.3 (TBS), -4.9 (TBS). HRMS (ESI+): *m*/*z* calcd for $C_{11}H_{26}NO_3Si^+$: 248.16765 [*M*+H]$^+$; found: 248.16770.



Compound **30** was prepared following adopted procedure from Nicolaou *et al.*[12] Tf_2O (1.6 mL, 9.4 mmol, 3.0 equiv.) was added dropwise to a solution of NaN_3 (1.23 g, 19.9 mmol, 6.0 equiv.) in CH_2Cl_2/H_2O (6 mL, 1:1) at 0 ºC. The reaction was stirred at 0 ºC for 2h and sat. $NaHCO_3$ (3 mL) was added. The layers were separated, and the water layer was additionally extracted twice with CH_2Cl_2 (3 mL). The combined organic layers were washed once with sat. $NaHCO_3$ (3 mL). Formed solution of TfN_3 solution in CH_2Cl_2 was added to a solution of methyl *O*-(*tert*-butyldimethylsilyl)-D-*allo*-threoninate (**29**) (0.778 g, 3.14 mmol, 1.0 equiv.) in MeOH (25 mL) and H_2O (8 mL), followed by addition of Et_3N (1.3 mL, 9.3 mmol, 3.0 equiv.) and $CuSO_4·5H_2O$ (39 mg, 0.16 mmol, 5 mol%) at room temperature. The mixture was stirred at room temperature for 1.5h and volatiles were removed *in vacuo*. The residual aqueous layer was extracted three times with EtOAc (10 mL). The combined organic layers were washed once with brine (10 mL), dried over Na_2SO_4, filtered, concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 3% : 97% EtOAc/Heptane → 100% EtOAc). Fractions with the product were concentrated, co-evaporated twice with $CHCl_3$ and dried each time for 0.5h at 40 ºC, 50 mbar to yield methyl (2*R*,3*R*)-2-azido-3-((*tert*-butyldimethylsilyl)oxy)butanoate (**30**) (0.78 g, 90%) as a colorless oil.

Data for **30**: Colorless oil; R_f=0.54 (Heptane/EtOAc 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.25 – 4.19 (m, 1H; H3), 3.84 (d, *J* = 5.5 Hz, 1H; H2), 3.77 (s, 3H; OMe), 1.24 (d, *J* = 6.1 Hz, 3H; H4), 0.87 (s, 9H; TBS), 0.09 (s, 3H; TBS), 0.08 (s, 3H; TBS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2 (C1), 69.8 (C3), 68.1 (C2), 52.6 (OMe), 25.7 (TBS), 19.9 (C4), 18.0 (TBS), -4.3 (TBS), -5.0 (TBS). HRMS (ESI+): *m*/*z* calcd for $C_{11}H_{24}N_3O_3Si^+$: 274.15814 [*M*+H]$^+$; found: 274.15855.



A solution of methyl (2*R*,3*R*)-2-azido-3-((*tert*-butyldimethylsilyl)oxy)butanoate (**30**) (0.764 g, 2.79 mmol, 1.0 equiv.) in dry $PhCH_3$ (10 mL) was cooled to -78 ºC under N_2 atmosphere and DIBAL-H (2.6 mL, 1.2 M, 3.1 mmol, 1.1 equiv.) in $PhCH_3$ was added dropwise over 10 min. The reaction was stirred at -78 ºC for 2h and subsequently quenched with MeOH (1.5 mL). The quenched reaction mixture was diluted with EtOAc (30 mL) and sat. Rochelle's salt (30 mL). The water layer was additionally extracted twice with EtOAc (30 mL). The combined organic layers were washed once with H_2O (30 mL), once with brine (30 mL), dried over Na_2SO_4, filtered, concentrated *in vacuo*, co-evaporated twice with $CHCl_3$ and dried each time for 20 min at 40 ºC, 50 mbar to yield crude (2*R*,3*R*)-2-azido-3-((*tert*-butyldimethylsilyl)oxy)butanal (**D2''**) (0.68 g, quantitively) as a yellowish oil, which was used in next steps without additional purification.

Note: Due to stability issues of the aldehyde **D2''**, it was not possible to obtain HRMS, and it should be used in the next step as soon as possible.

Data for **D2''**: Yellowish oil; R_f=0.33 (Heptane/EtOAc 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.59 (d, *J* = 1.1 Hz, 1H; H1), 4.22 (qd, *J* = 6.2, 4.5 Hz, 1H; H3), 3.86 (dd, *J* = 4.6, 1.3 Hz, 1H; H2), 1.28 (d, *J* = 6.3 Hz, 3H; H4), 0.89 (s, 9H; TBS), 0.10 (s, 6H; TBS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.9 (C1), 73.0 (C2), 69.8 (C3), 25.8 (TBS), 20.4 (C4), 18.0 (TBS), -4.3 (TBS), -4.9 (TBS).

SmI_2 Preparation

Typical Purification of 1,2-Diiodoethane

1,2-Diiodoethane was purified following procedure of Procter *et al.*[17] 1,2-Diiodoethane (1.0 g) was dissolved in Et_2O (20 mL), washed five times with sat. $Na_2S_2O_3$ (5 mL), once with H_2O (5 mL), dried over Na_2SO_4, filtered, concentrated, wrapped in aluminum foil and dried under high vacuum for 10-15 min to give a white solid.

Typical Preparation of SmI_2

SmI_2 was prepared following procedure of Procter *et al.*[17] A 50 mL round-bottom flask flame-dried under vacuum was equipped with a magnetic stir bar and evacuated/backfilled with N_2 three times using Schlenk line. The flask was removed from the Schlenk line, equipped with a septum, a N_2 balloon and Sm (0.60 g, 4.0 mmol) was added followed by addition of freshly purified 1,2-diiodoethane (0.56 g, 2.0 mmol). The mixture was evacuated/backfilled with N_2 three times, started to stir and dry THF (20 mL) was added via syringe. The flask with the mixture was evacuated/backfilled with N_2 three times. The N_2 balloon was then removed, the flask was sealed with parafilm, and the reaction mixture was stirred at room temperature for 1-3 days prior to use.

Imine/Aldehyde Reductive Cross-Couplings using SmI_2

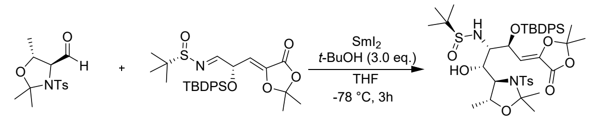
General Procedure **A** for the Cross-Coupling using SmI_2

The sulfimine (1.0 equiv.) and aldehyde (1.5 equiv.) were placed in a flame-dried 25 mL round-bottom flask equipped with a magnetic stir bar under N_2 atmosphere. The flask was subjected to three evacuation/backfilling cycles and dissolved in degassed dry THF. To this, a solution of *t*-BuOH (1.0 M, 3.0 eq) in degassed dry THF was added dropwise. The solution was cooled to -78 ºC and freshly prepared SmI_2 (0.1 M) solution in THF was added dropwise over 15-20 min. The reaction was stirred at -78 ºC for 3h. Afterwards, the reaction was quenched with sat. $Na_2S_2O_3$, warmed to r.t. and poured into sat. $Na_2S_2O_3$/EtOAc (2 : 3). Layers were separated and the water layer was extracted twice with EtOAc. The combined org. layers were dried over Na_2SO_4, filtered, concentrated on silica gel and purified using Büchi Pure C-815 Flash system.

General Procedure **B** for the Cross-Coupling using SmI_2

The sulfinimine (1.0 equiv.) was placed in a flame-dried 25 mL round-bottom flask equipped with a magnetic stir bar under N_2 atmosphere. The flask was subjected to three evacuation/backfilling cycles and dissolved in degassed dry THF. The solution was cooled to -78 ºC and freshly prepared SmI_2 (0.1 M, 3.0 eq) solution in THF was added dropwise over 15 min. To this, a solution of aldehyde (3.0 eq) and *t*-BuOH (3.0 eq) in degassed dry THF was added over 1h. Afterwards, the reaction was quenched with sat. $Na_2S_2O_3$, warmed to room temperature and poured into sat. $Na_2S_2O_3$/EtOAc (2 : 3). Layers were separated and the water layer was extracted twice with EtOAc. The combined org. layers were dried over Na_2SO_4, filtered, concentrated on silica gel and purified using Büchi Pure C-815 Flash system.

Optimization #1



L1 **S** **L1S**

The sulfinimine **S** (133 mg, 0.25 mmol, 1.5 equiv. or 88.5 mg, 0.17 mmol, 1.0 equiv.) and aldehyde **L1** (50.0 mg, 0.17 mmol, 1.0 equiv. or 74.8 mg, 0.25 mmol, 1.5 equiv.) were placed in a flame-dried 25 mL round-bottom flask equipped with a magnetic stir bar under N_2 atmosphere. The flask was subjected to three evacuation/backfilling cycles and dissolved in degassed dry THF (3 mL). To this, a solution of t-BuOH (0.50 mL, 1.0 M, 3.0 eq) in degassed dry THF was added dropwise followed by dropwise addition of additive. The solution was cooled to -78 ºC and freshly prepared SmI_2 (0.1 M) solution in THF was added dropwise over 15 min. The reaction was stirred at -78 ºC for 3h. Afterwards, the reaction mixture was quenched with sat. $Na_2S_2O_3$ (5 mL), warmed to r.t. and poured into sat. $Na_2S_2O_3$/EtOAc (25 mL, 2 : 3). Layers were separated and the water layer was extracted twice with EtOAc (20 mL). The combined org. layers were dried over Na_2SO_4, filtered, concentrated and ^1H NMR was performed. Afterwards, the crude was concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 33% : 67% EtOAc/Heptane → 100% EtOAc). Results are shown in Table S1.

Table S1. Optimization #1

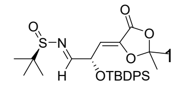
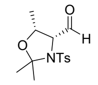
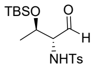
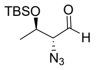
Entry	**L1** equiv.	**S** equiv.	SmI_2 equiv.	Additives	Conversion, % [a]	Yield of **L1S**, % [b]	dr[c]
1	1.0	1.5	2.0		70	49	8:1
2			3.0		81	69	50:1
3			2.0	H_2O (50 eq)	traces	0	
4			3.0	HMPA (12 eq)	Full	0	
5[d]					80	68	25:1
6		1.0			72	58	33:1
7	1.5				75	73	33:1

[a] Based on crude ^1H NMR and isolated yield of **L1S**. [b] Isolated yield. [c] Based on crude ^1H NMR. [d] **L1**, **S** and *t*-BuOH were added to the cooled solution of SmI_2 in THF.

Comparison of differently protected D-*allo*-threonine derived aldehydes in cross-coupling with sulfinimine **R**

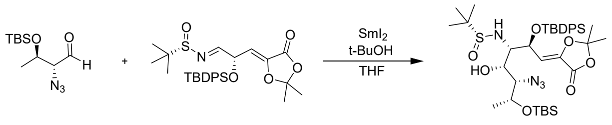
Table S2. Cross-Coupling between sulfimine **R** and various D-allothreonine derived aldehydes

Entry[a]	Sulfinimine		Aldehyde		Deviations from General Procedure **A**	Yield, %[b]
	Structure	equiv.	Structure	equiv.		

1	 **R**	1.0	 **D2**	1.5	-78 ºC, 5h and slowly warmed to room temperature overnight	<2
2			 **D2'**		-78 ºC, 5h and slowly warmed to room temperature overnight	<9
3			 **D2''**		-	32[c]

[a] Followed General Procedure **A**. [b] Based on crude ^{1}H NMR. [c] Isolated yield.

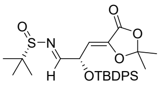
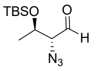
Optimization #2



D2'' **S** **D2''S**

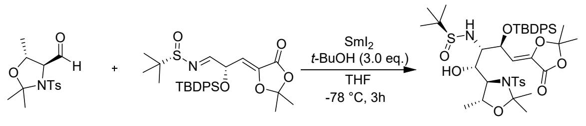
Cross-couplings were performed following general procedure **A** or **B** on a 0.17 mmol scale. The exact conditions and the results are summarized in table **S3**.

Table S3. Optimization #2

Entry	Sulfimine Structure	Sulfimine equiv.	Aldehyde Structure	Aldehyde equiv.	Procedure	Yield, %[a]
1	 **S**	1.0	 **D2''**	1.5	**A**	5
2				3.0		16
3				1.5	**B**	14
4				3.0		18

[a] Isolated yields.

Imine/Aldehyde Reductive Cross-Couplings using SmI$_2$

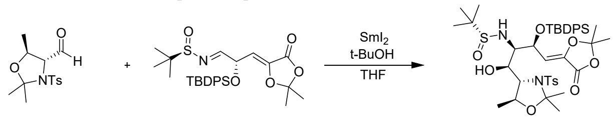


L1 **S** **L1S**

Compound **L1S** was prepared following general procedure **A**. The sulfinimine **S** (141 mg, 0.268 mol, 1.0 equiv.) and aldehyde **L1** (120 mg, 0.402 mmol, 1.5 equiv.) were placed in a flame-dried 25 mL round-bottom flask equipped with a magnetic stir bar under N$_2$

atmosphere. The flask was subjected to three evacuation/backfilling cycles and dissolved in degassed dry THF (4.5 mL). To this, a solution of *t*-BuOH (0.80 mL, 1.0 M, 3.0 eq) in degassed dry THF was added dropwise. The solution was cooled to -78 ºC and freshly prepared SmI_2 (8.0 mL, 0.1 M, 0.80 mmol, 3.0 equiv.) solution in THF was added dropwise over 15 min. The reaction was stirred at -78 ºC for 3h. Afterwards, the reaction was quenched with sat. $Na_2S_2O_3$ (5 mL), warmed to r.t. and poured into sat. $Na_2S_2O_3$/EtOAc (35 mL, 2 : 3). Layers were separated and the water layer was extracted twice with EtOAc (20 mL). The combined org. layers were dried over Na_2SO_4, filtered, concentrated on silica gel and purified using Büchi Pure C-810 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 33% : 67% EtOAc/Heptane → 100% EtOAc) to yield desired product **L1S** (0.169 g, 76%) as a colorless oil.

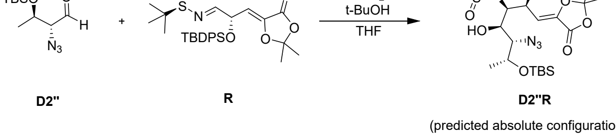
Data for **L1S**: Colorless oil; R_f=0.37 (Heptane/EtOAc 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H; TBDPS), 7.74 – 7.68 (m, 2H; Ts), 7.65 – 7.58 (m, 2H; TBDPS), 7.54 – 7.49 (m, 3H; TBDPS), 7.42 – 7.38 (m, 1H; TBDPS), 7.36 – 7.31 (m, 2H; TBDPS), 7.28 – 7.25 (m, 2H; Ts), 6.30 (d, *J* = 9.6 Hz, 1H; H3), 5.07 (dd, *J* = 9.6, 0.9 Hz, 1H; H4), 4.43 (d, *J* = 9.1 Hz, 1H; NH), 4.25 (qd, *J* = 6.3, 4.6 Hz, 1H; H8), 4.12 (ddd, *J* = 10.7, 6.1, 1.9 Hz, 1H; H6), 3.72 (dd, *J* = 4.7, 1.7 Hz, 1H; H7), 2.93 – 2.82 (m, 1H; H5), 2.43 (s, 3H; Ts), 1.54 (s, 3H; $C(CH_3)_2$), 1.53 (s, 3H; $C(CH_3)_2$), 1.48 (s, 3H; $C(CH_3)_2$), 1.39 (br, 1H; OH), 1.22 (s, 9H; *t*BuS(O)N), 1.14 (d, 3H; H9), 1.13 (s, 9H; TBDPS), 1.09 (s, 3H; $C(CH_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2 (C1), 143.6 (Ts), 138.6 (C2), 138.5 (Ts), 136.6 (TBDPS), 136.3 (TBDPS), 132.8 (TBDPS), 132.6 (TBDPS), 130.7 (TBDPS), 130.1 (TBDPS), 129.7 (Ts), 128.4 (TBDPS), 127.6 (TBDPS)), 127.5 (Ts), 111.3 (*C*$(CH_3)_2$), 108.5 (C3), 97.7 (*C*$(CH_3)_2$), 71.0 (C6 and C8), 66.8 (C7), 65.6 (C4), 61.8 (C5), 56.7 ($(CH_3)_3$*C*S(O)N), 29.5 (C(*C*$H_3)_2$), 28.1 (C(*C*$H_3)_2$), 27.3 (TBDPS), 27.0 (C(*C*$H_3)_2$), 26.3 (C(*C*$H_3)_2$), 23.1 ((*C*$H_3)_3$CS(O)N), 22.3 (C9), 21.6 (Ts), 19.3 (TBDPS). HRMS (ESI+): *m/z* calcd for $C_{42}H_{58}N_2O_9S_2SiNa^+$: 849.32452 [*M*+Na]$^+$; found: 849.32927.



D1 **R** **D1R**

Compound **D1R** was prepared following general procedure **A**. The sulfinimine **R** (88.5 mg, 0.168 mol, 1.0 equiv.) and aldehyde **L1** (74.8 mg, 0.252 mmol, 1.5 equiv.) were placed in a flame-dried 25 mL round-bottom flask equipped with a magnetic stir bar under N_2 atmosphere. The flask was subjected to three evacuation/backfilling cycles and dissolved in degassed dry THF (3.0 mL). To this, a solution of *t*-BuOH (0.50 mL, 1.0 M, 0.50 mmol, 3.0 eq) in degassed dry THF was added dropwise. The solution was cooled to -78 ºC and freshly prepared SmI_2 (5.0 mL, 0.1 M, 0.50 mmol, 3.0 equiv.) solution in THF was added dropwise over 15 min. The reaction was stirred at -78 ºC for 3h. Afterwards, the reaction was quenched with sat. $Na_2S_2O_3$ (3 mL), warmed to r.t. and poured into sat. $Na_2S_2O_3$/EtOAc (25 mL, 2 : 3). Layers were separated and the water layer was extracted twice with EtOAc (15 mL). The combined org. layers were dried over Na_2SO_4, filtered, concentrated on silica gel and purified using Büchi Pure C-810 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 33% : 67% EtOAc/Heptane → 100% EtOAc) to yield a mixture of two diastereomers (0.114 g, 82%), where desired product **D1R** is a major diastereomer (dr 10:1).

Data for **D1R** (major diastereomer): Colorless oil; R_f=0.50 (Heptane/EtOAc 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 6H; TBDPS and Ts), 7.43 – 7.36 (m, 6H; TBDPS), 7.26 – 7.24 (m, 2H; Ts), 5.79 (d, *J* = 8.5 Hz, 1H; H3), 5.24 (dd, *J* = 8.5, 2.2 Hz, 1H; H4), 4.29 (ddd, *J* = 10.4, 5.0, 1.9 Hz, 1H; H6), 4.24 (p, *J* = 6.1 Hz, 1H; H8), 3.68 (dd, *J* = 5.7, 1.9 Hz, 1H; H7), 3.59 (d, *J* = 9.1 Hz, 1H; NH), 3.21 (ddd, *J* = 11.0, 9.1, 2.2 Hz, 1H; H5), 2.63 (d, *J* = 5.0 Hz, 1H; OH), 2.41 (s, 3H; Ts), 1.63 (s, 3H; $C(CH_3)_2$), 1.62 (s, 3H; $C(CH_3)_2$), 1.53 (s, 3H; $C(CH_3)_2$), 1.33 (s, 3H; $C(CH_3)_2$), 1.15 (d, *J* = 6.3 Hz, 3H; H9), 1.11 (s, 18H; TBDPS and *t*BuS(O)N). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1 (C1), 143.8 (Ts), 137.9 (Ts), 137.3 (C2), 136.2 (TBDPS), 136.1 (TBDPS), 133.3 (TBDPS), 133.1 (TBDPS), 130.1 (TBDPS), 130.0 (TBDPS), 129.8 (Ts), 127.9 (TBDPS), 127.8 (TBDPS), 127.6 (Ts), 111.7 (*C*$(CH_3)_2$), 109.6 (C3), 97.8 (*C*$(CH_3)_2$), 71.2 (C4), 71.0 (C8), 70.8 (C6), 66.7 (C7), 62.1 (C5), 56.6 ($(CH_3)_3$*C*S(O)N), 29.3 (C(*C*$H_3)_2$), 28.0 (C(*C*$H_3)_2$), 27.2 (TBDPS), 26.7 (C(*C*$H_3)_2$), 26.6 (C(*C*$H_3)_2$), 22.8 ((*C*$H_3)_3$CS(O)N), 22.0 (C9), 21.6 (Ts), 19.5 (TBDPS). HRMS (ESI+): *m/z* calcd for $C_{42}H_{58}N_2O_9S_2SiNa^+$: 849.32452 [*M*+Na]$^+$; found: 849.32814.

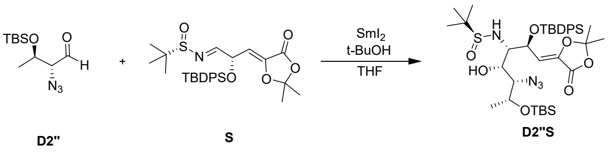


D2" **R** **D2"R**

(predicted absolute configuration)

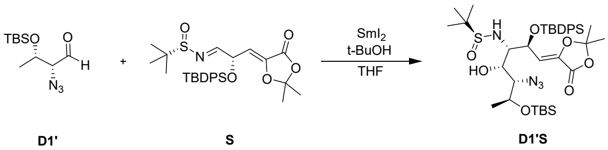
Compound **D2"R** was prepared following slightly modified general procedure **A**. The sulfinimine **R** (88.5 mg, 0.168 mol, 1.0 equiv.) was placed in a flame-dried 25 mL round-bottom flask equipped with a magnetic stir bar under N_2 atmosphere. The flask was subjected to three evacuation/backfilling cycles and dissolved in degassed dry THF (2.0 mL). To this, a solution of aldehyde **D2"** (1.0 mL, 0.25 M, 0.252 mmol, 1.5 equiv.) in degassed dry THF was added followed by a solution of *t*-BuOH (0.50 mL, 1.0 M, 0.50 mmol, 3.0 eq) in degassed dry THF addition. The solution was cooled to -78 ºC and freshly prepared SmI_2 (5.0 mL, 0.1 M, 0.50 mmol, 3.0 equiv.) solution in THF was added dropwise over 20 min. The reaction was stirred at -78 ºC for 3h. Afterwards, the reaction was quenched with sat. $Na_2S_2O_3$ (3 mL), warmed to r.t. and poured into sat. $Na_2S_2O_3$/EtOAc (25 mL, 2 : 3). Layers were separated and the water layer was extracted twice with EtOAc (15 mL). The combined org. layers were dried over Na_2SO_4, filtered, concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 34% : 66% EtOAc/Heptane → 100% EtOAc) to yield desired product **D2"R** (41.4 mg, 32%) as a yellowish foam. Note: Product contains ~6% of an impurity, which forms during flash chromatography.

Data for **D2''R**: Yellowish foam; R_f=0.24 (Heptane/EtOAc 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, 2H; TBDPS), 7.67 – 7.63 (m, 2H; TBDPS), 7.46 – 7.34 (m, 6H; TBDPS), 5.64 (d, *J* = 9.0 Hz, 1H; H3), 5.02 (dd, *J* = 9.0, 4.3 Hz, 1H; H4), 4.32 – 4.25 (m, 1H; H8), 4.10 (d, *J* = 6.1 Hz, 1H; NH), 3.74 (ddd, *J* = 6.0, 4.3, 3.2 Hz, 1H; H5), 3.62 (ddd, *J* = 9.9, 5.3, 3.3 Hz, 1H; H6), 3.56 (dd, *J* = 9.9, 3.1 Hz, 1H; H7), 3.19 (d, *J* = 5.2 Hz, 1H; OH), 1.48 (s, 3H; $C(CH_3)_2$), 1.24 (s, 9H; *t*BuS(O)N), 1.21 (s, 3H; $C(CH_3)_2$), 1.14 (d, *J* = 6.3 Hz, 3H), 1.08 (s, 9H; TBDPS), 0.88 (s, 9H; TBS), 0.08 (s, 3H; TBS), 0.06 (s, 3H; TBS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9 (C1), 138.4 (C2), 136.1 (TBDPS), 136.1 (TBDPS), 132.9 (TBDPS), 132.1 (TBDPS), 130.3 (TBDPS), 130.1 (TBDPS), 128.0 (TBDPS), 127.8 (TBDPS), 111.8 ($\mathit{C}(CH_3)_2$), 108.2 (C3), 71.4 (C6), 70.0 (C8), 69.7 (C4), 67.9 (C7), 61.2 (C5), 56.6 ($(CH_3)_3\mathit{C}S(O)N$), 27.1 (TBDPS), 26.9 ($C(\mathit{C}H_3)_2$), 26.4 ($C(\mathit{C}H_3)_2$), 25.9 (TBS), 22.9 ($(\mathit{C}H_3)_3CS(O)N$), 19.4 (TBDPS), 18.0 (C9), 17.5 (TBS), -4.3 (TBS), -4.6 (TBS). HRMS (ESI+): *m*/*z* calcd for $C_{38}H_{61}N_4O_7SSi_2^+$: 773.37940 [*M*+H]$^+$; found: 773.38203.



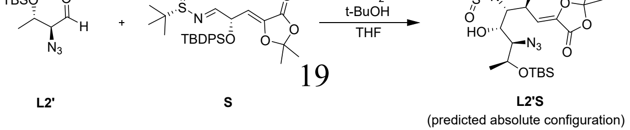
Compound **D2''S** was prepared following general procedure **B**. The sulfinimine **S** (88.5 mg, 0.168 mol, 1.0 equiv.) was placed in a flame-dried 25 mL round-bottom flask equipped with a magnetic stir bar under N_2 atmosphere. The flask was subjected to three evacuation/backfilling cycles and dissolved in degassed dry THF (2.0 mL). The solution was cooled to -78 ºC and freshly prepared SmI_2 (5.0 mL, 0.1 M, 0.50 mmol, 3.0 eq) solution in THF was added dropwise over 15 min. To this, a solution of aldehyde **D2''** (122 mg, 0.50 mmol, 3.0 equiv.) and *t*-BuOH (37 mg, 0.50 mmol, 3.0 equiv.) in degassed dry THF (2.0 mL) was added dropwise over 1h. The reaction was stirred at -78 ºC for 3h. Afterwards, the reaction was quenched with sat. $Na_2S_2O_3$ (3 mL), warmed to r.t. and poured into sat. $Na_2S_2O_3$/EtOAc (25 mL, 2 : 3). Layers were separated and the water layer was extracted twice with EtOAc (15 mL). The combined org. layers were dried over Na_2SO_4, filtered, concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 25 g column, eluent: 29% : 71% EtOAc/Heptane → 100% EtOAc) to yield desired product **D2''S** (24.1 mg, 18%) as a yellowish oil.

Data for **D2''S**: Yellowish oil; R_f=0.34 (Heptane/EtOAc 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H; TBDPS), 7.63 – 7.59 (m, 2H; TBDPS), 7.46 – 7.41 (m, 1H; TBDPS), 7.40 – 7.35 (m, 3H; TBDPS), 7.35 – 7.30 (m, 2H; TBDPS), 6.06 (d, *J* = 9.3 Hz, 1H; H3), 5.25 (dd, *J* = 9.3, 1.3 Hz, 1H; H4), 4.27 – 4.15 (m, 2H; H8 and NH), 3.91 (ddd, *J* = 9.9, 3.5, 1.3 Hz, 1H; H6), 3.34 – 3.24 (m, 2H; H5 and H7), 3.11 (d, *J* = 3.5 Hz, 1H; OH), 1.48 (s, 3H; $C(CH_3)_2$), 1.26 (s, 9H; *t*BuS(O)N), 1.21 (d, *J* = 6.3 Hz, 3H; H9), 1.17 (s, 3H; $C(CH_3)_2$), 1.08 (s, 9H; TBDPS), 0.90 (s, 9H; TBS), 0.14 (s, 3H; TBS), 0.12 (s, 3H; TBS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1 (C1), 138.3 (C2), 136.2 (TBDPS), 136.1 (TBDPS), 133.0 (TBDPS), 132.7 (TBDPS), 130.2 (TBDPS), 130.1 (TBDPS), 127.9 (TBDPS), 127.6 (TBDPS), 111.4 ($\mathit{C}(CH_3)_2$), 108.5 (C3), 70.8 (C8), 70.4 (C6), 66.4 (C4), 65.1 (C7), 61.7 (C5), 56.5 ($(CH_3)_3\mathit{C}S(O)N$), 27.2 (TBDPS), 26.9 ($C(\mathit{C}H_3)_2$), 26.4 ($C(\mathit{C}H_3)_2$), 25.9 (TBS), 23.1 ($(\mathit{C}H_3)_3CS(O)N$), 21.3 (C9), 19.5 (TBDPS), 17.9 (TBS), -4.3 (TBS), -4.9 (TBS). HRMS (ESI+): *m*/*z* calcd for $C_{38}H_{61}N_4O_7SSi_2^+$: 773.37940 [*M*+H]$^+$; found: 773.38086.



Compound **D1'S** was prepared following general procedure **B**. The sulfinimine **S** (88.5 mg, 0.168 mol, 1.0 equiv.) was placed in a flame-dried 25 mL round-bottom flask equipped with a magnetic stir bar under N_2 atmosphere. The flask was subjected to three evacuation/backfilling cycles and dissolved in degassed dry THF (2.0 mL). The solution was cooled to -78 ºC and freshly prepared SmI_2 (5.0 mL, 0.1 M, 0.50 mmol, 3.0 eq) solution in THF was added dropwise over 15 min. To this, a solution of aldehyde **D1'** (122 mg, 0.50 mmol, 3.0 equiv.) and *t*-BuOH (37 mg, 0.50 mmol, 3.0 equiv.) in degassed dry THF (2.5 mL) was added dropwise over 1h. The reaction was stirred at -78 ºC for 3h. Afterwards, the reaction was quenched with sat. $Na_2S_2O_3$ (3 mL), warmed to r.t. and poured into sat. $Na_2S_2O_3$/EtOAc (25 mL, 2 : 3). Layers were separated and the water layer was extracted twice with EtOAc (15 mL). The combined org. layers were dried over Na_2SO_4, filtered, concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 25 g column, eluent: 20% : 80% EtOAc/Heptane → 100% EtOAc) to yield desired product **D1'S** (44.3 mg, 34%) as a yellowish oil.

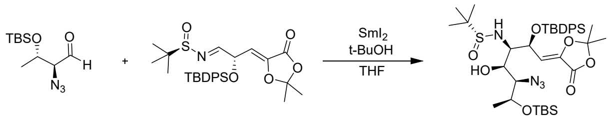
Data for **D1'S**: Yellowish oil; R_f=0.34 (Heptane/EtOAc 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H; TBDPS), 7.63 – 7.57 (m, 2H; TBDPS), 7.48 – 7.44 (m, 1H; TBDPS), 7.42 – 7.37 (m, 3H; TBDPS), 7.36 – 7.31 (m, 2H; TBDPS), 6.09 (d, *J* = 9.3 Hz, 1H; H3), 5.17 (dd, *J* = 9.5, 1.4 Hz, 1H; H4), 4.25 (d, *J* = 8.4 Hz, 1H; NH), 4.02 (p, *J* = 6.2 Hz, 1H; H8), 3.59 (dd, *J* = 9.8, 6.8 Hz, 1H; H6), 3.34 (dd, *J* = 7.1, 1.3 Hz, 1H; H7), 3.30 (ddd, *J* = 9.6, 8.3, 1.3 Hz, 1H; H5), 2.07 (d, *J* = 7.1 Hz, 1H; OH), 1.48 (s, 3H; $C(CH_3)_2$), 1.28 (s, 9H; *t*BuS(O)N), 1.18 – 1.14 (m, 6H; H9 and $C(CH_3)_2$), 1.07 (s, 9H; TBDPS), 0.90 (s, 9H; TBS), 0.12 (s, 3H; TBS), 0.11 (s, 3H; TBS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0 (C1), 138.4 (C2), 136.1 (TBDPS), 136.1 (TBDPS), 132.7 (TBDPS), 132.7 (TBDPS), 130.4 (TBDPS),



130.2 (TBDPS), 128.0 (TBDPS), 127.7 (TBDPS), 111.4 (*C*(CH$_3$)$_2$), 108.3 (C3), 71.8 (C6), 71.2 (C8), 68.0 (C7), 66.3 (C4), 62.2 (C5), 56.5 ((CH$_3$)$_3$*C*S(O)N), 27.1 (TBDPS), 26.8 (C(*C*H$_3$)$_2$), 26.4 (C(*C*H$_3$)$_2$), 25.9 (TBS), 23.1 ((*C*H$_3$)$_3$CS(O)N), 21.2 (C9), 19.5 (TBDPS), 18.0 (TBS), -4.3 (TBS), -4.8 (TBS). HRMS (ESI+): *m/z* calcd for $C_{38}H_{61}N_4O_7SSi_2^+$: 773.37940 [*M*+H]$^+$; found: 773.38066.

Compound **L2'S** was prepared following general procedure **B**. The sulfinimine **S** (125 mg, 0.236 mol, 1.0 equiv.) was placed in a flame-dried 25 mL round-bottom flask equipped with a magnetic stir bar under N$_2$ atmosphere. The flask was subjected to three evacuation/backfilling cycles and dissolved in degassed dry THF (3.0 mL). The solution was cooled to -78 ºC and freshly prepared SmI$_2$ (7.0 mL, 0.1 M, 0.70 mmol, 3.0 eq) solution in THF was added dropwise over 15 min. To this, a solution of aldehyde **L2'** (176 mg, 0.72 mmol, 3.0 equiv.) and *t*-BuOH (53 mg, 0.71 mmol, 3.0 equiv.) in degassed dry THF (3 mL) was added dropwise over 1h. The reaction was stirred at -78 ºC for 3h. Afterwards, the reaction was quenched with sat. Na$_2$S$_2$O$_3$ (5 mL), warmed to r.t. and poured into sat. Na$_2$S$_2$O$_3$/EtOAc (35 mL, 3 : 4). Layers were separated and the water layer was extracted twice with EtOAc (20 mL). The combined org. layers were dried over Na$_2$SO$_4$, filtered, concentrated and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 25 g column, eluent: 31% : 69% EtOAc/Heptane → 100% EtOAc) to yield desired product **L2'S** (54.8 mg, 30%) as a yellowish oil.

Data for **L2'S**: Yellowish oil; *R$_f$*=0.37 (Heptane/EtOAc 2:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.75 – 7.71 (m, 2H; TBDPS), 7.65 – 7.61 (m, 2H; TBDPS), 7.48 – 7.45 (m, 1H; TBDPS), 7.44 – 7.39 (m, 3H; TBDPS), 7.38 – 7.34 (m, 2H; TBDPS), 5.94 (d, *J* = 9.3 Hz, 1H; H3), 5.11 (dd, *J* = 9.3, 2.0 Hz, 1H; H4), 4.31 (d, *J* = 7.6 Hz, 1H; NH), 4.26 (qd, *J* = 6.1, 3.3 Hz, 1H; H8), 3.50 (dd, *J* = 7.6, 3.5 Hz, 1H; H7), 3.46 (t, *J* = 6.5 Hz, 1H; H6), 3.42 (ddd, *J* = 7.4, 5.2, 2.2 Hz, 1H; H5), 2.72 (br, 1H; OH), 1.48 (s, 3H; C(CH$_3$)$_2$), 1.27 (s, 9H; *t*BuS(O)N), 1.20 – 1.15 (m, 6H; H9 and C(CH$_3$)$_2$), 1.08 (s, 9H; TBDPS), 0.90 (s, 9H; TBS), 0.09 (s, 3H; TBS), 0.06 (s, 3H; TBS). ^{13}C NMR (126 MHz, CDCl$_3$) δ 161.7 (C1), 138.3 (C2), 136.2 (TBDPS), 136.1 (TBDPS), 132.7 (TBDPS), 132.4 (TBDPS), 130.5 (TBDPS), 130.3 (TBDPS), 128.1 (TBDPS), 127.8 (TBDPS), 111.5 (*C*(CH$_3$)$_2$), 108.5 (C3), 73.6 (C6), 69.7 (C8), 68.4 (C7), 67.5 (C4), 61.2 (C5), 56.5 ((CH$_3$)$_3$*C*S(O)N), 27.1 (TBDPS), 26.8 (C(*C*H$_3$)$_2$), 26.4 (C(*C*H$_3$)$_2$), 25.9 (TBS), 22.9 ((*C*H$_3$)$_3$CS(O)N), 19.4 (TBDPS), 18.6 (C9), 18.0 (TBS), -4.2 (TBS), -4.6 (TBS). HRMS (ESI+): *m/z* calcd for $C_{38}H_{60}N_4O_7SSi_2Na^+$: 795.36135 [*M*+Na]$^+$; found: 795.36344.



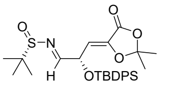
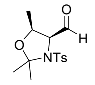
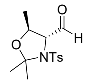
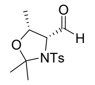
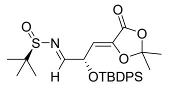
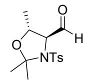
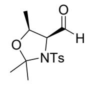
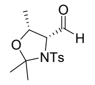
L2' R L2'R

Compound **L2'R** was prepared following general procedure **B**. The sulfinimine **R** (125 mg, 0.236 mol, 1.0 equiv.) was placed in a flame-dried 25 mL round-bottom flask equipped with a magnetic stir bar under N$_2$ atmosphere. The flask was subjected to three evacuation/backfilling cycles and dissolved in degassed dry THF (3.0 mL). The solution was cooled to -78 ºC and freshly prepared SmI$_2$ (7.0 mL, 0.1 M, 0.70 mmol, 3.0 eq) solution in THF was added dropwise over 15 min. To this, a solution of aldehyde **L2'** (176 mg, 0.72 mmol, 3.0 equiv.) and *t*-BuOH (53 mg, 0.71 mmol, 3.0 equiv.) in degassed dry THF (3 mL) was added dropwise over 1h. The reaction was stirred at -78 ºC for 3h. Afterwards, the reaction was quenched with sat. Na$_2$S$_2$O$_3$ (5 mL), warmed to r.t. and poured into sat. Na$_2$S$_2$O$_3$/EtOAc (35 mL, 3 : 4). Layers were separated and the water layer was extracted twice with EtOAc (20 mL). The combined org. layers were dried over Na$_2$SO$_4$, filtered, concentrated and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 25 g column, eluent: 26% : 74% EtOAc/Heptane → 100% EtOAc) to yield a mixture of three diastereomers (32.8 mg, 18%), where desired product **L2'R** is a major diastereomer (dr 10:1:2).

Data for **L2'R** (major diastereomer): Yellowish oil; *R$_f$*=0.40 (Heptane/EtOAc 2:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.72 – 7.67 (m, 4H; TBDPS), 7.43 – 7.33 (m, 6H; TBDPS), 5.70 (d, *J* = 8.7 Hz, 1H; H3), 5.16 (dd, *J* = 8.7, 3.0 Hz, 1H; H4), 4.16 – 4.08 (m, 2H; H6 and H8), 4.01 (d, *J* = 8.2 Hz, 1H; NH), 3.51 (td, *J* = 8.2, 3.0 Hz, 1H; H5), 3.41 (dd, *J* = 6.3, 1.3 Hz, 1H; H7), 2.70 (d, *J* = 6.6 Hz, 1H; OH), 1.49 (s, 3H; C(CH$_3$)$_2$), 1.29 (d, *J* = 6.3 Hz, 3H; H9), 1.24 (s, 3H; C(CH$_3$)$_2$), 1.21 (s, 9H; ; *t*BuS(O)N), 1.09 (s, 9H; TBDPS), 0.88 (s, 9H; TBS), 0.11 (s, 3H; TBS), 0.10 (s, 3H; TBS). ^{13}C NMR (126 MHz, CDCl$_3$) δ 162.2 (C1), 137.7 (C2), 136.2 (TBDPS), 136.1 (TBDPS), 133.2 (TBDPS), 132.8 (TBDPS), 130.1 (TBDPS), 130.0 (TBDPS), 127.9 (TBDPS), 127.7 (TBDPS), 111.6 (*C*(CH$_3$)$_2$), 109.0 (C3), 71.1 (C4), 70.0 (C6), 69.4 (C8), 67.1 (C7), 62.6 (C5), 56.6 ((CH$_3$)$_3$*C*S(O)N), 27.2 (TBDPS), 26.6 (C(*C*H$_3$)$_2$), 26.5 (C(*C*H$_3$)$_2$), 25.9 (TBS), 22.9 ((*C*H$_3$)$_3$CS(O)N), 21.4 (C9), 19.5 (TBDPS), 18.0 (TBS), -4.2 (TBS), -4.9 (TBS). HRMS (ESI+): *m/z* calcd for $C_{38}H_{60}N_4O_7SSi_2Na^+$: 795.36135 [*M*+Na]$^+$; found: 795.36352.

Table S4. Unsuccessfully utilized aldehydes

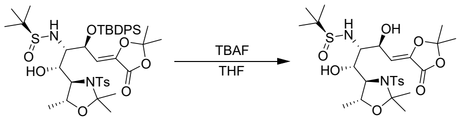
Entry[a]	Sulfinimine		Aldehyde		Deviations from General Procedure **A**	Yield, %[b]
	Structure	equiv.	Structure	equiv.		

1	 **S**	1.5	 **L2**	1.0	SmI_2 (2.0 equiv.), -78 ºC, 5h	<3
2		1.0	 **D1**	1.5	-78 ºC, 5h and slowly warmed to room temperature overnight	<5
3		1.0	 **D2**	1.5	-78 ºC, 5h and slowly warmed to room temperature overnight	<5
4	 **R**	1.0	 **L1**	1.5	-	<13
5		1.5	 **L2**	1.0	SmI_2 (2.0 equiv.), -78 ºC, 5h	<4
6		1.0	 **D2**	1.5	-78 ºC, 5h and slowly warmed to room temperature overnight	<2

[a] Followed General Procedure **A**. [b] Based on crude ^{1}H NMR.

Determination of Absolute Configuration

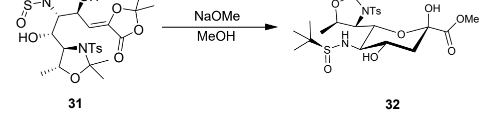
8-*epi*-Acinetaminic acids derivative



L1S **31**

Compound **L1S** (10.1 mg, 12.2 µmol, 1.0 equiv.) was dissolved in dry THF (1.0 mL) under N_2 atmosphere and a solution of TBAF (20 µL, 1.0 M, 20 µmol, 1.6 equiv.) was added dropwise. The reaction was stirred at room temperature for 45 min. Afterwards, the mixture was concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 63% : 37% EtOAc/Heptane → 100% EtOAc) to yield desired product **31** (7.2 mg, quantitively) as a yellowish oil.

Data for **31**: Yellowish oil; R_f=0.12 (Heptane/EtOAc 1:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H; Ts), 7.26 – 7.23 (m, 2H; Ts), 5.98 (d, *J* = 8.0 Hz, 1H; H3), 5.09 (dd, *J* = 8.0, 2.3 Hz, 1H; H4), 4.47 (p, *J* = 6.1 Hz, 1H; H8), 4.35 (d, *J* = 9.6 Hz, 1H; H6), 3.99 (d, *J* = 10.7 Hz, 1H; NH), 3.86 (br, 2H; OH), 3.69 (dd, *J* = 5.4, 2.7 Hz, 1H; H7), 3.41 (td, *J* = 9.8, 2.3 Hz, 1H; H5), 2.41 (s, 3H; Ts), 1.65 (s, 9H; 3 x $C(CH_3)_2$), 1.61 (s, 3H; $C(CH_3)_2$), 1.22 – 1.18 (m, 12H; H9 and *t*BuS(O)N). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6 (C1), 143.9 (Ts), 139.4 (C2), 137.7 (Ts), 129.8 (Ts), 127.7 (Ts), 112.1 ($\mathit{C}(CH_3)_2$), 108.8 (C3), 98.0 ($\mathit{C}(CH_3)_2$), 72.5 (C6), 71.4 (C8), 67.5 (C4), 67.1 (C7), 61.1 (C5), 56.8 ($(CH_3)_3\mathit{C}S(O)N$), 29.8 ($C(CH_3)_2$), 27.5 ($C(\mathit{C}H_3)_2$), 26.9 ($C(\mathit{C}H_3)_2$), 26.9 ($C(\mathit{C}H_3)_2$), 22.9 ($(\mathit{C}H_3)_3CS(O)N$), 21.9 (C9), 21.7 (Ts). HRMS (ESI+): *m*/*z* calcd for $C_{26}H_{40}N_2O_9S_2Na^+$: 611.20674 $[M+Na]^+$; found: 611.21274.



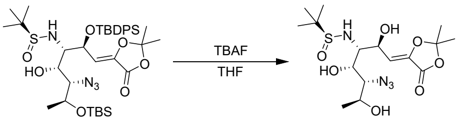
31 **32**

Compound **31** (7.2 mg, 12 µmol, 1.0 equiv.) was dissolved in dry MeOH (1.0 mL) under N_2 atmosphere and a solution of NaOMe (20 µL, 0.3 M, 6.0 µmol, 0.5 equiv.) was added dropwise. The reaction was stirred at room temperature for 3h. Afterwards, the mixture was quenched with sat. NH_4Cl (20 µL), concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 100% EtOAc → 10% : 90% MeOH/EtOAc) to yield desired product **32** (4.4 mg, 64%) as a yellowish oil.

Data for **32**: Yellowish oil; R_f=0.34 (Heptane/EtOAc 1:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.69 (m, 2H; Ts), 7.30 – 7.27 (m, 2H; Ts), 4.52 (dd, *J* = 11.2, 1.7 Hz, 1H; H6$_{ax}$), 4.45 (p, *J* = 6.1 Hz, 1H; H8), 4.05 (dd, *J* = 5.7, 1.7 Hz, 1H; H7), 3.88 – 3.83 (m, 1H; H4$_{ax}$), 3.82

(s, 3H; OMe), 3.21 (d, *J* = 11.2 Hz, 1H; NH), 2.83 (td, *J* = 11.1, 8.5 Hz, 1H; H5$_{ax}$), 2.43 (s, 3H; Ts), 2.28 (dd, *J* = 13.2, 5.2 Hz, 1H; H3$_{eq}$), 2.06 (dd, *J* = 13.2, 11.3 Hz, 1H; H3$_{ax}$), 1.63 (br, 2H, 2 x OH), 1.56 (s, 3H; C(CH$_3$)$_2$), 1.44 (s, 3H; C(CH$_3$)$_2$), 1.28 (s, 9H; *t*BuS(O)N), 1.24 (d, *J* = 6.1 Hz, 3H; H9). ^{13}C NMR (126 MHz, CDCl$_3$) δ 169.9 (C1), 143.7 (Ts), 138.8 (Ts), 129.7 (Ts), 127.5 (Ts), 97.6 (*C*(CH$_3$)$_2$), 94.9 (C2), 71.8 (C6), 70.4 (C8), 69.3 (C4), 65.0 (C7), 63.2 (C5), 56.7 ((CH$_3$)$_3$*C*S(O)N), 53.4 (OMe), 37.4 (C3), 28.4 (C(*C*H$_3$)$_2$), 27.7 (C(*C*H$_3$)$_2$), 22.9 ((*C*H$_3$)$_3$CS(O)N), 22.3 (C9), 21.7 (Ts). HRMS (ESI+): *m*/*z* calcd for $C_{24}H_{38}N_2O_9S_2Na^+$: 585.19109 [*M*+Na]$^+$; found: 585.19363.

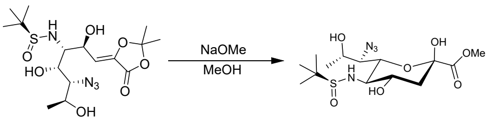
8-*epi*-Legionaminic acids derivative



D1'S **33**

Compound **D1'S** (15.7 mg, 20.3 µmol, 1.0 equiv.) was dissolved in dry THF (1.0 mL) under N$_2$ atmosphere and a solution of TBAF (60 µL, 1.0 M, 60 µmol, 3.0 equiv.) was added dropwise. The reaction was stirred at room temperature for 45 min. Afterwards, the mixture was concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: EtOAc) to yield desired product **33** (7.8 mg, 91%) as a yellowish oil.

Data for **33**: Yellowish oil; *R$_f$*=0.46 (EtOAc/MeOH 9:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.90 (d, *J* = 8.5 Hz, 1H; H3), 4.93 (dd, *J* = 8.4, 3.5 Hz, 1H; H4), 4.24 – 4.17 (m, 1H; H8), 4.00 (d, *J* = 9.8 Hz, 1H; NH), 3.93 (d, *J* = 8.4 Hz, 1H; H6), 3.65 (br, 1H; OH), 3.57 (ddd, *J* = 9.6, 8.0, 3.5 Hz, 1H; H5), 3.50 (br, 1H; OH), 3.34 (dd, *J* = 4.3, 1.9 Hz, 1H; H7), 2.54 (br, 1H; OH), 1.67 (s, 3H; C(CH$_3$)$_2$), 1.66 (s, 3H; C(CH$_3$)$_2$), 1.36 (d, *J* = 6.5 Hz, 3H; H9), 1.27 (s, 9H; *t*BuS(O)N). ^{13}C NMR (126 MHz, CDCl$_3$) δ 162.2 (C1), 139.7 (C2), 112.2 (*C*(CH$_3$)$_2$), 108.2 (C3), 74.4 (C6), 71.4 (C8), 66.7 (C4), 66.2 (C7), 62.7 (C5), 56.8 ((CH$_3$)$_3$*C*S(O)N), 27.0 (C(*C*H$_3$)$_2$), 27.0 (C(*C*H$_3$)$_2$), 23.0 ((*C*H$_3$)$_3$CS(O)N), 21.2 (C9). HRMS (ESI+): *m*/*z* calcd for $C_{16}H_{28}N_4O_7SNa^+$: 443.15709 [*M*+Na]$^+$; found: 443.15939.

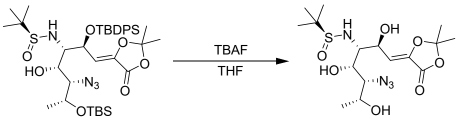


33 **34**

Compound **33** (6.8 mg, 16 µmol, 1.0 equiv.) was dissolved in dry MeOH (1.0 mL) under N$_2$ atmosphere and a solution of NaOMe (50 µL, 0.15 M, 7.5 µmol, 0.5 equiv.) was added dropwise. The reaction was stirred at room temperature for 0.5h. Afterwards, the mixture was quenched with sat. NH$_4$Cl (20 µL), concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 100% EtOAc → 4% : 96% MeOH/EtOAc) to yield desired product **34** (3.5 mg, 55%) as a colorless oil.

Data for **34**: Colorless oil; *R$_f$*=0.56 (EtOAc/MeOH 9:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.15 – 4.05 (m, 2H; H8 and OH), 3.96 (dd, *J* = 10.1, 2.1 Hz, 1H; H6$_{ax}$), 3.88 – 3.82 (m, 4H; H4$_{ax}$ and OMe), 3.40 – 3.34 (m, 2H; H5$_{ax}$ and H7), 2.99 (d, *J* = 10.7 Hz, 1H; NH), 2.24 (dd, *J* = 13.2, 5.1 Hz, 1H; H3$_{eq}$), 2.14 (dd, *J* = 13.2, 11.2 Hz, 1H; H3$_{ax}$), 1.29 (s, 9H; *t*BuS(O)N), 1.26 (d, *J* = 6.4 Hz, 3H; H9). ^{13}C NMR (126 MHz, CDCl$_3$) δ 170.3 (C1), 94.9 (C2), 73.5 (C6), 69.2 (C8), 68.5 (C4), 66.0 (C7), 62.5 (C5), 56.5 ((CH$_3$)$_3$*C*S(O)N), 54.0 (OMe), 37.7 (C3), 22.9 ((*C*H$_3$)$_3$CS(O)N), 20.1 (C9). HRMS (ESI+): *m*/*z* calcd for $C_{14}H_{27}N_4O_7S^+$: 395.15950 [*M*+H]$^+$; found: 395.16072.

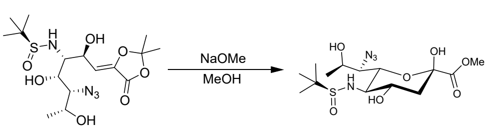
Legionaminic acids derivative



D2''S **35**

Compound **D2''S** (17.5 mg, 22.6 µmol, 1.0 equiv.) was dissolved in dry THF (1.0 mL) under N$_2$ atmosphere and a solution of TBAF (70 µL, 1.0 M, 70 µmol, 3.1 equiv.) was added dropwise. The reaction was stirred at room temperature for 1h. Afterwards, the mixture was concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: eluent: 100% EtOAc → 4% : 96% MeOH/EtOAc) to yield desired product **35** (5.5 mg, 58%) as a white solid.

Data for **35**: White solid; *R$_f$*=0.54 (EtOAc/MeOH 9:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.91 (d, *J* = 8.2 Hz, 1H; H3), 5.00 (dd, *J* = 8.2, 3.0 Hz, 1H; H4), 4.20 – 4.13 (m, 2H; H6 and H8), 4.09 – 3.93 (m, 2H; NH and OH), 3.82 (br, 1H; OH), 3.60 (td, *J* = 9.3, 2.9 Hz, 1H; H5), 3.34 – 3.04 (m, 2H; H7 and OH), 1.66 (s, 3H; C(CH$_3$)$_2$), 1.66 (s, 3H; C(CH$_3$)$_2$), 1.37 (d, *J* = 6.3 Hz, 3H; H9), 1.26 (s, 9H; *t*BuS(O)N). ^{13}C NMR (126 MHz, CDCl$_3$) δ 162.5 (C1), 139.4 (C2), 112.3 (*C*(CH$_3$)$_2$), 108.7 (C3), 70.7 (C6), 67.6 (C8), 66.7 (C4), 66.5 (C7), 62.5 (C5), 57.0 ((CH$_3$)$_3$*C*S(O)N), 26.9 (C(*C*H$_3$)$_2$), 26.9 (C(*C*H$_3$)$_2$), 23.0 ((*C*H$_3$)$_3$CS(O)N), 21.1 (C9). HRMS (ESI+): *m*/*z* calcd for $C_{16}H_{28}N_4O_7SNa^+$: 443.15709 [*M*+Na]$^+$; found: 443.15941.

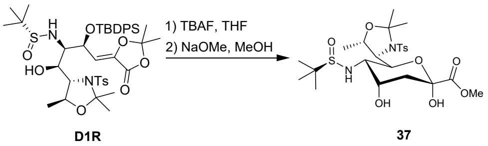


35 **36**

Compound **35** (4.9 mg, 11.7 µmol, 1.0 equiv.) was dissolved in dry MeOH (1.0 mL) under N_2 atmosphere and a solution of NaOMe (40 µL, 0.15 M, 6.0 µmol, 0.5 equiv.) was added dropwise. The reaction was stirred at room temperature for 20 min. Afterwards, the mixture was quenched with sat. NH_4Cl (20 µL), concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 100% EtOAc → 4% : 96% MeOH/EtOAc) to yield desired product **36** (4.2 mg, 91%) as a colorless oil.

Data for **35**: Colorless oil; R_f=0.54 (EtOAc/MeOH 9:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.28 (dd, *J* = 10.3, 1.9 Hz, 1H; H6$_{ax}$), 4.11 – 4.02 (m, 1H; H8), 3.91 (ddd, *J* = 11.3, 9.1, 5.0 Hz, 1H; H4$_{ax}$), 3.84 (s, 3H; OMe), 3.34 (q, *J* = 10.2 Hz, 1H; H5$_{ax}$), 3.27 – 3.10 (m, 2H; H7 and NH), 2.27 (dd, *J* = 13.1, 5.0 Hz, 1H; H3$_{eq}$), 2.12 (dd, *J* = 13.3, 11.3 Hz, 1H; H3$_{ax}$), 1.37 (d, *J* = 6.3 Hz, 3H; H9), 1.28 (s, 9H; *t*BuS(O)N). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6 (C1), 95.2 (C2), 71.3 (C6), 68.5 (C4), 66.0 (C8), 65.0 (C7), 62.3 (C5), 56.6 ($(CH_3)_3$*C*S(O)N), 53.7 (OMe), 37.8 (C3), 22.9 ((CH$_3$)$_3$CS(O)N), 21.5 (C9). HRMS (ESI+): *m/z* calcd for $C_{14}H_{26}N_4O_7SNa^+$: 417.14144 [*M*+Na]$^+$; found: 417.14188.

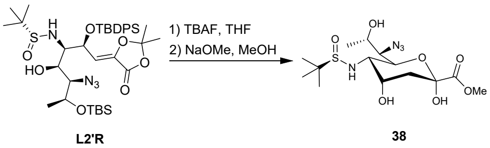
6,7-*epi*-Pseudaminic acids derivative



Compound **D1R** (dr 10:1) (15.5 mg, 18.7 µmol, 1.0 equiv.) was dissolved in dry THF (1.0 mL) under N_2 atmosphere, cooled in an ice bath and a solution of TBAF (20 µL, 1.0 M, 20 µmol, 1.1 equiv.) was added dropwise. After 35 min, the reaction mixture was diluted with MeOH (1.0 mL) and a solution of NaOMe (30 µL, 0.3 M, 9.0 µmol, 0.5 equiv.) was added dropwise. The reaction was stirred at room temperature for 4h. Afterwards, the mixture was poured into sat. NH_4Cl/EtOAc (15 mL; 1:2) and the water layer was additionally extracted twice with EtOAc (10 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified using Büchi Pure C-810 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 36% : 64% Heptane/EtOAc → 100% EtOAc) to yield a mixture of two diastereomers (7.8 mg, 74%), where desired product **37** is a major diastereomer (dr 10:1).

Data for **37** (major diastereomer): Colorless oil; R_f=0.37 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 2H; Ts), 7.31 – 7.25 (m, 2H; Ts), 4.79 (br, 1H; OH), 4.67 (dd, *J* = 11.3, 1.7 Hz, 1H; H6$_{ax}$), 4.47 (p, *J* = 6.2 Hz, 1H; H8), 4.35 (q, *J* = 3.3 Hz, 1H; H4$_{eq}$), 4.17 (d, *J* = 10.2 Hz, 1H; NH), 3.99 (dd, *J* = 5.4, 1.7 Hz, 1H; H7), 3.80 (s, 3H; OMe), 3.12 (ddd, *J* = 11.2, 10.2, 3.3 Hz, 1H; H5$_{ax}$), 2.43 (s, 3H; Ts), 2.30 (dd, *J* = 14.6, 3.2 Hz, 1H; H3), 2.26 (dd, *J* = 14.7, 3.3 Hz, 1H; H3'), 1.73 (br, 1H; OH), 1.59 (s, 3H; $C(CH_3)_2$), 1.45 (s, 3H; $C(CH_3)_2$), 1.26 – 1.23 (m, 12H; H9 and *t*BuS(O)N). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0 (C1), 143.7 (Ts), 138.3 (Ts), 129.7 (Ts), 127.8 (Ts), 97.6 (*C*$(CH_3)_2$), 95.1 (C2), 70.4 (C8), 68.3 (C6), 67.6 (C4), 65.0 (C7), 56.7 ($(CH_3)_3$*C*S(O)N), 56.3 (C5), 53.2 (OMe), 35.5 (C3), 28.4 (C(*C*H$_3$)$_2$), 27.9 (C(*C*H$_3$)$_2$), 22.8 ((*C*H$_3$)$_3$CS(O)N), 22.3 (C9), 21.7 (Ts). HRMS (ESI+): *m/z* calcd for $C_{24}H_{38}N_2O_9S_2Na^+$: 585.19109 [*M*+Na]$^+$; found: 585.19304.

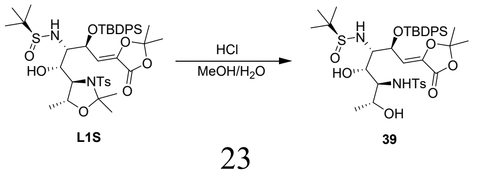
6-*epi*-Pseudaminic acids derivative



Compound **L2'R** (dr 10:1:2) (12.1 mg, 15.6 µmol, 1.0 equiv.) was dissolved in dry THF (1.0 mL) under N_2 atmosphere, cooled in an ice bath and a solution of TBAF (40 µL, 1.0 M, 40 µmol, 2.5 equiv.) was added dropwise. After 3.5h, the reaction mixture was concentrated *in vacuo*, dissolved in MeOH (1.0 mL) under N_2 atmosphere and a solution of NaOMe (30 µL, 0.3 M, 9.0 µmol, 0.6 equiv.) was added dropwise. The reaction was stirred at room temperature for 6 days. Afterwards, the mixture was quenched with sat. NH_4Cl (30 µL), concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 4 g column, eluent: 100% EtOAc → 4% : 96% MeOH/EtOAc) to yield a mixture of two diastereomers (3.4 mg, 55%), where desired product **38** is a major diastereomer (dr 10:1).

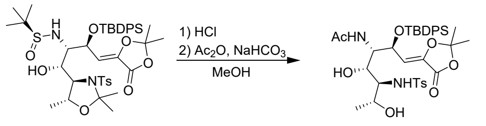
Data for **38** (major diastereomer): Yellowish oil; R_f=0.55 (EtOAc/MeOH 9:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.46 (dd, *J* = 10.5, 2.1 Hz, 1H; H6$_{ax}$), 4.43 (q, *J* = 3.4 Hz, 1H; H4$_{eq}$), 4.15 – 4.06 (m, 1H; H8), 3.81 (s, 3H; OMe), 3.61 (td, *J* = 10.4, 3.1 Hz, 1H; H5$_{ax}$), 3.21 (dd, *J* = 8.5, 2.1 Hz, 1H; H7), 2.34 (dd, *J* = 14.6, 3.1 Hz, 1H; H3), 2.25 (dd, *J* = 14.6, 3.3 Hz, 1H; H3'), 1.39 (d, *J* = 6.3 Hz, 3H; H9), 1.26 (s, 9H; *t*BuS(O)N). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3 (C1), 95.2 (C2), 67.7 (C4), 67.5 (C6), 66.1 (C8), 65.4 (C7), 56.9 ($(CH_3)_3$*C*S(O)N), 56.2 (C5), 53.4 (OMe), 35.9 (C3), 22.9 ((*C*H$_3$)$_3$CS(O)N), 21.3 (C9). HRMS (ESI+): *m/z* calcd for $C_{14}H_{26}N_4O_7SNa^+$: 417.14144 [*M*+Na]$^+$; found: 417.14259.

Selective Deprotection and Reactivity



Compound **L1S** (32.9 mg, 39.8 µmol, 1.0 equiv.) was dissolved in MeOH (0.8 mL) and a solution of HCl (40 µL, 0.1 M, 4 µmol, 0.1 equiv.) in H_2O was added dropwise. The reaction was stirred at room temperature for 4 days. Afterwards, the mixture was concentrated *in vacuo* and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 62% : 38% EtOAc/Heptane → 100% EtOAc) to yield desired product **39** (29.3 mg, 94%) as a colorless oil.

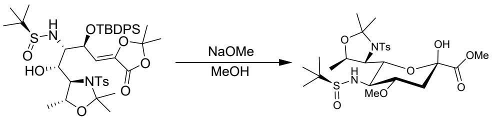
Data for **39**: Colorless oil; R_f=0.45 (EtOAc/Heptane 3:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 2H; Ts), 7.73 – 7.69 (m, 2H; TBDPS), 7.58 – 7.54 (m, 2H; TBDPS), 7.54 – 7.51 (m, 1H; TBDPS), 7.50 – 7.46 (m, 2H; TBDPS), 7.42 – 7.38 (m, 1H; TBDPS), 7.35 – 7.30 (m, 2H; TBDPS), 7.27 – 7.23 (m, 2H; Ts), 6.07 (d, *J* = 9.5 Hz, 1H; H3), 5.35 (d, *J* = 8.5 Hz, 1H; TsN*H*), 5.00 (dd, *J* = 9.3, 1.4 Hz, 1H; H4), 4.19 (d, *J* = 8.8 Hz, 1H; *t*BuS(O)N*H*), 4.07 (q, *J* = 6.2 Hz, 1H; H8), 3.71 (ddd, *J* = 10.7, 6.2, 2.3 Hz, 1H; H6), 3.38 (dd, *J* = 8.4, 3.2 Hz, 1H; H7), 3.10 (ddd, *J* = 10.4, 8.8, 1.5 Hz, 1H; H5), 2.94 (s, 1H; OH), 2.39 (s, 3H; Ts), 2.26 (br, 1H; NH), 1.48 (s, 3H; $C(CH_3)_2$), 1.24 (s, 9H; *t*BuS(O)N), 1.14 (s, 3H; $C(CH_3)_2$), 1.07 (s, 9H; TBDPS), 0.77 (d, *J* = 6.3 Hz, 3H; H9). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9 (C1), 143.6 (Ts), 138.9 (C2), 138.2 (Ts), 136.4 (TBDPS), 136.1 (TBDPS), 132.6 (TBDPS), 132.4 (TBDPS), 130.7 (TBDPS), 130.2 (TBDPS), 129.8 (Ts), 128.3 (TBDPS), 127.7 (TBDPS), 127.0 (Ts), 111.5 ($\mathit{C}(CH_3)_2$), 107.6 (C3), 76.1 (C6), 66.4 (C4), 65.7 (C8), 61.4 (C5), 56.6 ($(CH_3)_3\mathit{C}S(O)N$), 56.1 (C7), 27.2 (TBDPS), 26.9 ($C(\mathit{C}H_3)_2$), 26.3 ($C(\mathit{C}H_3)_2$), 23.0 ($(\mathit{C}H_3)_3CS(O)N$), 21.7 (Ts), 19.7 (C9), 19.2 (TBDPS). HRMS (ESI+): *m*/*z* calcd for $C_{39}H_{54}N_2O_9S_2SiNa^+$: 809.29322 [*M*+Na]$^+$; found: 809.29502.



L1S **40**

Compound **L1S** (32.6 mg, 39.4 µmol, 1.0 equiv.) was dissolved in MeOH (0.3 mL) and a solution of HCl (1.0 mL, 0.2 M, 0.20 mmol, 5.0 equiv.) in MeOH was added dropwise. The reaction was stirred at room temperature for 24h followed by concentration *in vacuo*. To the crude, $NaHCO_3$ (26.6 mg, 0.315 mmol, 8.0 equiv.) was added. The mixture was suspended in MeOH (0.5 mL) and a solution of Ac_2O (0.50 mL, 0.1 M, 50 µmol, 1.25 equiv.) in MeOH was added dropwise. The reaction was stirred at room temperature for 3h. Afterwards, the reaction mixture was concentrated on silica gel and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 63% : 37% EtOAc/Heptane → 100% EtOAc) to yield desired product **40** (23.7 mg, 83%) as a yellowish oil.

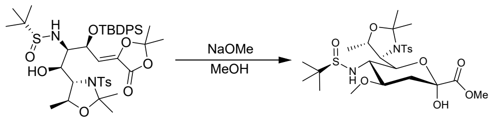
Data for **40**: Yellowish oil; R_f=0.34 (EtOAc/Heptane 3:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 2H; TBDPS), 7.71 – 7.66 (m, 2H; Ts), 7.60 – 7.56 (m, 2H; TBDPS), 7.54 – 7.46 (m, 3H; TBDPS), 7.45 – 7.41 (m, 1H TBDPS), 7.37 – 7.33 (m, 2H; TBDPS), 7.28 – 7.26 (m, 2H; Ts), 5.99 (d, *J* = 9.0 Hz, 1H; AcN*H*), 5.58 (d, *J* = 9.0 Hz, 1H; H3), 5.41 (d, *J* = 7.6 Hz, 1H; TsN*H*), 4.99 (dd, *J* = 9.1, 1.5 Hz, 1H; H4), 4.23 – 4.16 (m, 1H; H8), 3.90 – 3.80 (m, 2H; H5 and H6), 2.91 (d, *J* = 7.6 Hz, 1H; H7), 2.87 (d, *J* = 2.2 Hz, 1H; OH), 2.39 (s, 3H; Ts), 2.23 (d, *J* = 5.4 Hz, 1H; OH), 2.07 (s, 3H, Ac), 1.51 (s, 3H; $C(CH_3)_2$), 1.21 (s, 3H; $C(CH_3)_2$), 1.10 (s, 9H; TBDPS), 0.62 (d, *J* = 6.3 Hz, 3H; H9). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1 (Ac), 162.2 (C1), 143.7 (Ts), 138.7 (C2), 137.5 (Ts), 136.2 (TBDPS), 136.1 (TBDPS), 132.6 (TBDPS), 132.6 (TBDPS), 130.8 (TBDPS), 130.3 (TBDPS), 129.8 (Ts), 128.4 (TBDPS), 127.8 (TBDPS), 127.1 (Ts), 112.0 ($\mathit{C}(CH_3)_2$), 107.5 (C3), 76.1 (C6), 66.2 (C4), 65.7 (C8), 56.9 (C7), 54.6 (C5), 27.3 (TBDPS), 26.8 ($C(\mathit{C}H_3)_2$), 26.4 ($C(\mathit{C}H_3)_2$), 23.5 (Ac), 21.6 (Ts), 19.6 (C9), 19.3 (TBDPS). HRMS (ESI+): *m*/*z* calcd for $C_{37}H_{48}N_2O_9SSiNa^+$: 747.27420 [*M*+Na]$^+$; found: 747.27518.



L1S **41**

Compound **L1S** (101 mg, 0.122 mmol, 1.0 equiv.) was dissolved in dry MeOH (0.28 mL) and a solution of NaOMe (0.20 mL, 0.3 M, 60 µmol, 0.5 equiv.) was added dropwise. The reaction was stirred at room temperature for 3h. Afterwards, the mixture was quenched with sat. NH_4Cl (50 µL), poured into H_2O/EtOAc (25 mL, 2:3) and the water layer was additionally extracted twice with EtOAc (15 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 79% : 21% EtOAc/Heptane → 100% EtOAc) to yield product **41** (48.6 mg, 69%) as an off-white solid.

Data for **41**: Off-white solid; R_f=0.30 (EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 2H; Ts), 7.29 – 7.26 (m, 2H; Ts), 4.48 (dd, *J* = 11.0, 1.7 Hz, 1H; $H6_{ax}$), 4.42 (qd, *J* = 6.3, 4.8 Hz, 1H; H8), 4.10 (dd, *J* = 4.9, 1.6 Hz, 1H; H7), 4.01 (br, 1H; OH), 3.79 (s, 3H; COOMe), 3.58 (ddd, *J* = 11.2, 8.9, 5.0 Hz, 1H; $H4_{ax}$), 3.42 (s, 3H; OMe), 3.25 (d, *J* = 9.3 Hz, 1H; NH), 2.90 (dt, *J* = 10.9, 9.1 Hz, 1H; $H5_{ax}$), 2.42 – 2.38 (m, 4H; $H3_{eq}$ and Ts), 1.87 (dd, *J* = 13.1, 11.2 Hz, 1H; $H3_{ax}$), 1.53 (s, 3H; $C(CH_3)_2$), 1.47 (s, 3H; $C(CH_3)_2$), 1.20 (s, 9H; *t*BuS(O)N), 1.19 (d, *J* = 6.3 Hz, 3H; H9). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7 (C1), 143.6 (Ts), 138.8 (Ts), 129.7 (Ts), 127.5 (Ts), 97.7 ($\mathit{C}(CH_3)_2$), 94.9 (C2), 78.2 (C4), 72.9 (C6), 70.8 (C8), 65.0 (C7), 58.5 (C5), 56.7 (OMe), 56.7 ($(CH_3)_3\mathit{C}S(O)N$), 53.3 (COO*Me*), 34.7 (C3), 28.7 ($C(\mathit{C}H_3)_2$), 27.9 ($C(\mathit{C}H_3)_2$), 22.8 ($(\mathit{C}H_3)_3CS(O)N$), 22.4 (C9), 21.6 (Ts). HRMS (ESI+): *m*/*z* calcd for $C_{25}H_{40}N_2O_9S_2Na^+$: 599.20674 [*M*+Na]$^+$; found: 599.20620.



D1R **42**

Compound **D1R** (dr 10:1) (28.2 mg, 31.1 µmol, 1.0 equiv.) was dissolved in dry MeOH (0.42 mL) and a solution of NaOMe (60 µL, 0.3 M, 18 µmol, 0.5 equiv.) was added dropwise. The reaction was stirred at room temperature for 27h. Afterwards, the mixture was quenched with sat. NH$_4$Cl (50 µL), poured into H$_2$O/EtOAc (25 mL, 2:3) and the water layer was additionally extracted twice with EtOAc (15 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered, concentrated and purified using Büchi Pure C-815 Flash system (FlashPure EcoFlex Silica 12 g column, eluent: 79% : 21% EtOAc/Heptane → 100% EtOAc) to yield a mixture of two diastereomers (9.1 mg, 46%), where product **42** is a major diastereomer (dr 14:1).

Data for **42** (major diastereomer): White solid; R_f=0.32 (EtOAc); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.79 – 7.73 (m, 2H; Ts), 7.30 – 7.27 (m, 2H; Ts), 4.49 (dd, *J* = 11.0, 1.7 Hz, 1H; H6$_{\mathrm{ax}}$), 4.47 – 4.41 (m, 1H; H8), 4.12 (dd, *J* = 4.9, 1.7 Hz, 1H; H7), 3.82 (s, 3H; COOMe), 3.57 (ddd, *J* = 11.3, 8.9, 5.0 Hz, 1H; H4), 3.43 (s, 3H; OMe), 3.15 (d, *J* = 9.3 Hz, 1H; NH), 2.92 (dt, *J* = 11.0, 9.1 Hz, 1H; H5$_{\mathrm{ax}}$), 2.43 (s, 3H; Ts), 2.40 (dd, *J* = 13.0, 4.9 Hz, 1H; H3$_{\mathrm{eq}}$), 1.90 (t, *J* = 12.1 Hz, 1H; H3$_{\mathrm{ax}}$), 1.55 (s, 3H; C(CH$_3$)$_2$), 1.48 (s, 3H; C(CH$_3$)$_2$), 1.24 – 1.19 (m, 12H; H9 and *t*BuS(O)N). ^{13}C NMR (126 MHz, CDCl$_3$) δ 169.7 (C1), 143.7 (Ts), 138.9 (Ts), 129.7 (Ts), 127.5 (Ts), 97.7 (*C*(CH$_3$)$_2$), 94.9 (C2), 78.3 (C4), 72.9 (C6), 70.8 (C8), 65.1 (C7), 58.4 (C5), 56.8 (OMe), 56.7 ((CH$_3$)$_3$*C*S(O)N), 53.4 (COO*Me*), 34.7 (C3), 28.7 (C(*C*H$_3$)$_2$), 28.0 (C(*C*H$_3$)$_2$), 22.8 ((*C*H$_3$)$_3$CS(O)N), 22.4 (C9), 21.7 (Ts). HRMS (ESI+): *m/z* calcd for $C_{25}H_{41}N_2O_9S_2^+$: 577.22480 [*M*+H]$^+$; found: 577.22794.

XRD Data of Compound 41

mo_D8V6585

Datablock mo_d8v6585 - ellipsoid plot

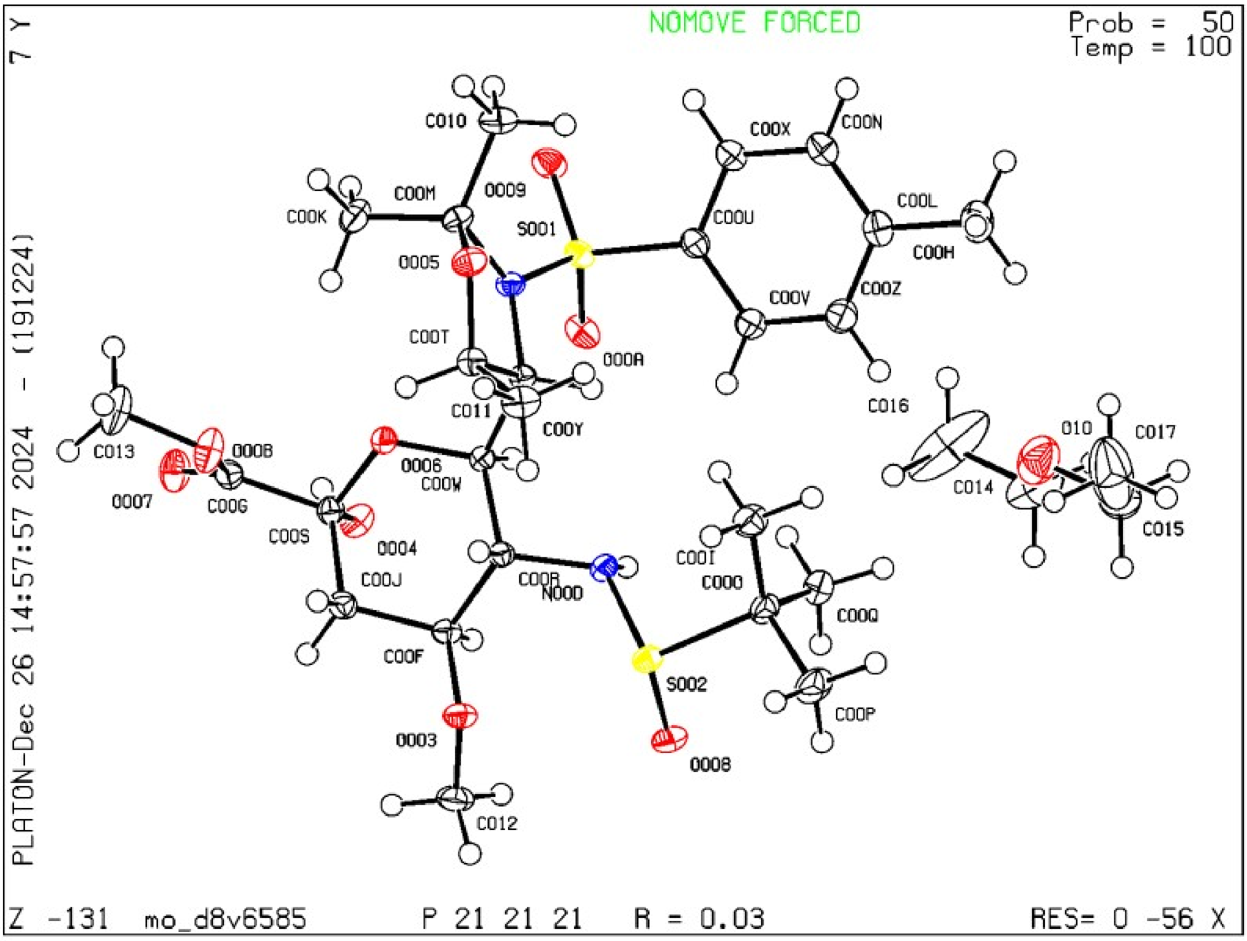


Table 1 Crystal data and structure refinement for mo_D8V6585.

Identification code	mo_D8V6585
Empirical formula	$C_{29}H_{50}N_2O_{10}S_2$
Formula weight	650.83
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	12.0149(4)
b/Å	16.4908(5)
c/Å	17.1438(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3396.79(18)
Z	4
ρ_{calc}g/cm^3	1.273
μ/mm^{-1}	0.211
F(000)	1400.0
Crystal size/mm^3	0.27 × 0.11 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.482 to 64.062
Index ranges	-17 ≤ h ≤ 17, -23 ≤ k ≤ 24, -24 ≤ l ≤ 25
Reflections collected	148871
Independent reflections	11815 [R_{int} = 0.0350, R_{sigma} = 0.0170]
Data/restraints/parameters	11815/0/403

Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0268, wR_2 = 0.0733
Final R indexes [all data]	R_1 = 0.0279, wR_2 = 0.0742
Largest diff. peak/hole / e $Å^{-3}$	0.66/-0.28
Flack parameter	0.018(6)

Table 2 Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times10^3$) for mo_D8V6585. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
S001	6141.7(3)	6347.1(2)	7248.7(2)	16.01(6)
S002	2259.6(2)	8948.4(2)	6810.0(2)	15.89(6)
O003	3104.3(8)	9318.0(6)	5260.4(6)	18.47(17)
O004	5355.9(8)	7493.1(6)	4575.4(6)	19.94(17)
O005	7244.5(8)	8418.0(6)	7693.1(6)	19.30(17)
O006	6063.5(8)	8110.8(6)	5694.5(5)	16.31(16)
O007	7247.2(10)	8140.0(7)	3932.7(6)	25.6(2)
O008	1289.0(8)	8718.8(6)	6307.5(6)	19.80(17)
O009	7136.0(9)	5868.5(6)	7300.0(6)	22.42(19)
O00A	5336.9(9)	6169.3(6)	6653.5(6)	21.21(18)
O00B	7381.0(9)	9045.2(7)	4900.2(6)	26.6(2)
O10	851.5(12)	5984.6(9)	9152.2(10)	45.5(3)
N00D	3325.7(9)	8313.1(7)	6660.5(6)	15.43(18)
N00E	6517.9(9)	7284.4(6)	7129.1(6)	15.25(18)
C00F	3883.6(10)	8672.1(7)	5288.1(7)	15.59(19)
C00G	6890.3(11)	8450.6(8)	4518.3(7)	17.2(2)
C00H	3605.1(14)	6078.2(11)	10293.1(9)	30.7(3)
C00I	2829.9(12)	8735.8(10)	8346.2(8)	25.0(3)
C00J	4912.7(11)	8870.2(8)	4801.1(7)	17.6(2)
C00K	8359.5(11)	7749.9(9)	6695.3(8)	23.2(3)
C00L	4244.9(12)	6139.8(8)	9541.6(8)	22.3(2)
C00M	7597.6(10)	7656.9(8)	7396.5(7)	17.5(2)
C00N	5369.8(12)	5937.7(8)	9504.1(8)	21.8(2)
C00O	1854.5(11)	8592.3(9)	7792.9(7)	20.1(2)
C00P	871.2(13)	9135.9(11)	8012.9(9)	30.0(3)
C00Q	1507.3(12)	7705.0(9)	7767.3(9)	24.7(3)
C00R	4227.0(10)	8578.4(7)	6141.7(7)	14.10(19)
C00S	5780.5(10)	8202.0(8)	4894.0(7)	15.8(2)
C00T	6316.7(10)	8698.0(7)	7245.2(7)	16.46(19)
C00U	5418.6(10)	6266.9(7)	8141.4(7)	17.3(2)
C00V	4287.0(11)	6457.6(8)	8162.6(8)	20.7(2)
C00W	5161.6(10)	7942.5(7)	6210.1(7)	13.87(19)
C00X	5961.5(11)	5996.2(8)	8809.6(8)	20.2(2)
C00Y	5701.9(12)	9306.3(8)	7746.0(9)	23.1(2)
C00Z	3711.5(12)	6397.9(9)	8861.5(8)	23.3(2)
C010	8176.8(12)	7239.2(9)	8071.8(9)	25.0(3)
C011	5662.8(10)	7921.9(7)	7033.8(7)	14.07(19)
C012	2324.8(12)	9243.5(9)	4639.5(8)	24.1(3)
C013	8470.0(14)	9283.5(11)	4612.5(11)	33.8(3)
C014	508.2(19)	5415.5(14)	8589.4(19)	54.5(6)
C015	-37(2)	6223.1(16)	9675.5(16)	56.3(7)
C016	1476(2)	5232.5(18)	8083(3)	88.0(14)
C017	386(3)	6877.7(17)	10193.3(19)	77.5(11)

Table 3 Anisotropic Displacement Parameters ($Å^2\times10^3$) for mo_D8V6585. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S001	20.03(13)	13.16(11)	14.84(11)	0.30(9)	-0.90(10)	1.30(10)
S002	14.21(11)	17.02(12)	16.44(12)	-3.15(10)	-1.14(9)	1.86(10)
O003	18.1(4)	19.4(4)	17.9(4)	-1.0(3)	-3.2(3)	5.9(3)
O004	17.6(4)	19.5(4)	22.7(4)	-7.0(3)	1.1(3)	0.2(3)
O005	17.6(4)	19.7(4)	20.6(4)	-4.6(3)	-4.5(3)	0.5(3)
O006	13.8(4)	21.4(4)	13.7(3)	1.3(3)	0.8(3)	0.6(3)
O007	29.3(5)	23.4(5)	24.1(5)	-5.3(4)	10.0(4)	-1.3(4)

O008	15.2(4)	23.0(4)	21.3(4)	-4.6(3)	-4.7(3)	3.0(3)
O009	26.7(5)	19.8(4)	20.7(4)	1.4(3)	1.8(4)	8.8(4)
O00A	28.8(5)	16.9(4)	17.9(4)	-0.3(3)	-4.9(3)	-4.0(3)
O00B	23.7(5)	30.4(5)	25.8(5)	-8.5(4)	8.3(4)	-9.8(4)
O10	36.0(7)	34.4(7)	66.1(10)	6.2(7)	9.5(7)	-3.2(6)
N00D	13.2(4)	16.0(4)	17.1(4)	-0.6(3)	1.3(3)	1.2(3)
N00E	13.8(4)	13.7(4)	18.3(4)	1.4(3)	-2.0(3)	0.8(3)
C00F	15.6(5)	15.7(5)	15.5(4)	-0.8(4)	-1.7(4)	2.8(4)
C00G	18.2(5)	16.3(5)	17.1(5)	0.8(4)	1.7(4)	1.2(4)
C00H	32.3(7)	37.2(8)	22.7(6)	-0.8(6)	7.2(5)	-0.4(6)
C00I	21.3(5)	36.3(7)	17.3(5)	-3.9(5)	-2.2(4)	1.4(5)
C00J	18.9(5)	18.5(5)	15.5(5)	0.8(4)	0.8(4)	2.7(4)
C00K	15.3(5)	30.7(7)	23.6(6)	-2.6(5)	1.8(4)	-1.9(5)
C00L	26.0(6)	20.1(6)	20.7(5)	-0.7(4)	2.8(5)	-1.7(5)
C00M	13.7(5)	19.1(5)	19.5(5)	-2.2(4)	-2.4(4)	0.1(4)
C00N	26.3(6)	21.1(6)	17.9(5)	1.1(4)	0.3(5)	0.3(5)
C00O	15.8(5)	27.5(6)	17.1(5)	-2.3(5)	1.9(4)	2.3(4)
C00P	22.6(6)	42.1(9)	25.3(6)	-6.0(6)	4.4(5)	9.6(6)
C00Q	19.8(6)	29.1(6)	25.2(6)	2.6(5)	2.8(5)	-1.9(5)
C00R	13.7(4)	15.2(5)	13.4(4)	-0.2(4)	-0.2(4)	1.3(4)
C00S	16.0(5)	17.1(5)	14.4(5)	-0.9(4)	1.0(4)	0.7(4)
C00T	16.6(5)	14.8(4)	18.0(5)	-1.1(4)	-1.8(4)	-0.6(4)
C00U	19.8(5)	14.5(5)	17.5(5)	0.8(4)	0.1(4)	-0.8(4)
C00V	19.7(5)	21.2(6)	21.2(5)	2.3(4)	-1.1(4)	-0.9(4)
C00W	13.0(4)	14.8(5)	13.9(4)	0.1(4)	0.2(4)	0.4(4)
C00X	23.0(6)	19.3(5)	18.2(5)	1.8(4)	-0.4(4)	1.1(4)
C00Y	25.0(6)	19.3(5)	25.0(6)	-7.1(5)	-4.0(5)	3.1(5)
C00Z	21.3(6)	23.9(6)	24.8(6)	0.7(5)	1.7(5)	-0.4(5)
C010	21.5(6)	28.5(7)	24.9(6)	0.1(5)	-8.1(5)	3.5(5)
C011	13.5(4)	13.9(5)	14.8(4)	0.0(4)	-0.9(4)	0.1(4)
C012	22.7(6)	30.0(7)	19.7(5)	1.9(5)	-6.5(5)	6.3(5)
C013	26.6(7)	35.1(8)	39.7(9)	-6.0(7)	13.0(6)	-12.0(6)
C014	32.5(9)	37.0(10)	94.2(19)	-0.7(11)	-8.7(11)	1.0(8)
C015	44.0(11)	60.2(15)	64.8(14)	28.8(12)	14.8(11)	20.5(10)
C016	34.5(10)	55.5(14)	174(4)	-74(2)	-0.4(16)	-2.0(10)
C017	110(3)	47.4(14)	75.3(18)	12.5(13)	55.7(19)	21.6(15)

Table 4 Bond Lengths for mo_D8V6585.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
S001	O009	1.4346(10)	C00F	C00J	1.5273(17)
S001	O00A	1.4361(10)	C00F	C00R	1.5282(16)
S001	N00E	1.6234(11)	C00G	C00S	1.5366(17)
S001	C00U	1.7648(13)	C00H	C00L	1.504(2)
S002	O008	1.4986(10)	C00I	C00O	1.5263(19)
S002	N00D	1.6744(11)	C00J	C00S	1.5253(17)
S002	C00O	1.8496(13)	C00K	C00M	1.5188(19)
O003	C00F	1.4190(14)	C00L	C00N	1.393(2)
O003	C012	1.4232(16)	C00L	C00Z	1.397(2)
O004	C00S	1.3874(15)	C00M	C010	1.5162(19)
O005	C00M	1.4192(15)	C00N	C00X	1.3900(18)
O005	C00T	1.4302(15)	C00O	C00P	1.530(2)
O006	C00S	1.4218(14)	C00O	C00Q	1.522(2)
O006	C00W	1.4256(14)	C00R	C00W	1.5409(16)
O007	C00G	1.2059(16)	C00T	C00Y	1.5130(18)
O00B	C00G	1.3182(16)	C00T	C011	1.5450(17)
O00B	C013	1.4526(18)	C00U	C00V	1.3960(18)
O10	C014	1.408(3)	C00U	C00X	1.3918(17)
O10	C015	1.449(3)	C00V	C00Z	1.3868(19)
N00D	C00R	1.4681(15)	C00W	C011	1.5355(16)
N00E	C00M	1.5067(16)	C014	C016	1.481(4)
N00E	C011	1.4790(15)	C015	C017	1.487(5)

Table 5 Bond Angles for mo_D8V6585.

Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**

O009	S001	O00A	119.47(6)	C00X	C00N	C00L	121.27(13)
O009	S001	N00E	107.44(6)	C00I	C00O	S002	108.35(9)
O009	S001	C00U	108.39(6)	C00I	C00O	C00P	110.41(12)
O00A	S001	N00E	106.99(6)	C00P	C00O	S002	103.99(10)
O00A	S001	C00U	105.63(6)	C00Q	C00O	S002	110.56(9)
N00E	S001	C00U	108.54(6)	C00Q	C00O	C00I	112.17(12)
O008	S002	N00D	110.44(6)	C00Q	C00O	C00P	111.02(12)
O008	S002	C00O	103.81(6)	N00D	C00R	C00F	114.28(10)
N00D	S002	C00O	98.17(6)	N00D	C00R	C00W	106.78(9)
C00F	O003	C012	113.23(10)	C00F	C00R	C00W	109.78(9)
C00M	O005	C00T	109.03(9)	O004	C00S	O006	112.26(10)
C00S	O006	C00W	115.93(9)	O004	C00S	C00G	112.26(10)
C00G	O00B	C013	115.81(12)	O004	C00S	C00J	108.43(10)
C014	O10	C015	112.90(19)	O006	C00S	C00G	103.02(10)
C00R	N00D	S002	118.07(8)	O006	C00S	C00J	109.92(10)
C00M	N00E	S001	126.12(8)	C00J	C00S	C00G	110.90(10)
C011	N00E	S001	119.81(8)	O005	C00T	C00Y	106.85(10)
C011	N00E	C00M	110.00(9)	O005	C00T	C011	104.77(9)
O003	C00F	C00J	110.82(10)	C00Y	C00T	C011	115.73(11)
O003	C00F	C00R	106.62(9)	C00V	C00U	S001	119.03(10)
C00J	C00F	C00R	109.06(9)	C00X	C00U	S001	120.48(10)
O007	C00G	O00B	124.79(13)	C00X	C00U	C00V	120.47(12)
O007	C00G	C00S	122.97(12)	C00Z	C00V	C00U	119.48(13)
O00B	C00G	C00S	112.23(11)	O006	C00W	C00R	111.98(9)
C00S	C00J	C00F	109.99(10)	O006	C00W	C011	106.05(9)
C00N	C00L	C00H	121.29(14)	C011	C00W	C00R	111.77(9)
C00N	C00L	C00Z	118.64(13)	C00N	C00X	C00U	119.18(13)
C00Z	C00L	C00H	120.07(13)	C00V	C00Z	C00L	120.93(13)
O005	C00M	N00E	102.25(9)	N00E	C011	C00T	102.10(9)
O005	C00M	C00K	111.99(11)	N00E	C011	C00W	112.94(9)
O005	C00M	C010	105.39(10)	C00W	C011	C00T	113.38(10)
N00E	C00M	C00K	108.61(10)	O10	C014	C016	107.89(18)
N00E	C00M	C010	116.25(11)	O10	C015	C017	108.3(2)
C010	C00M	C00K	111.94(11)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for mo_D8V6585.

Atom	***x***	***y***	***z***	**U(eq)**
H004	5869	7237	4351	30
H00D	3081(17)	7841(12)	6537(11)	19
H00F	3531	8160	5096	19
H00A	3906	5633	10608	46
H00B	2819	5973	10179	46
H00C	3673	6588	10583	46
H00E	3451	8381	8200	37
H00G	2599	8615	8882	37
H00H	3067	9303	8311	37
H00I	4701	8920	4245	21
H00J	5230	9395	4973	21
H00K	7968	8046	6282	35
H00L	8574	7212	6503	35
H00M	9028	8051	6848	35
H00N	5739	5756	9962	26
H00O	1099	9706	7982	45
H00P	632	9011	8546	45
H00Q	254	9039	7651	45
H00R	934	7630	7367	37
H00S	1209	7545	8277	37
H00T	2155	7368	7642	37
H00U	4516	9111	6333	17
H00V	6588	8968	6758	20
H00W	3914	6627	7702	25
H00X	4851	7396	6084	17

H00Y	6727	5853	8791	24
H00Z	5487	9051	8240	35
H	5033	9491	7471	35
HA	6187	9771	7852	35
H00	2944	6534	8878	28
H01A	8816	7565	8239	37
H01B	8434	6702	7906	37
H01C	7655	7180	8507	37
H011	5055	7836	7424	17
H01D	2717	9277	4139	36
H01E	1777	9683	4674	36
H01F	1943	8720	4678	36
H01G	8430	9377	4049	51
H01H	9008	8851	4721	51
H01I	8707	9783	4874	51
H01J	-109	5641	8274	65
H01K	243	4914	8848	65
H01L	-280	5753	9991	68
H01M	-684	6421	9372	68
H01N	1282	4793	7723	132
H01O	2108	5066	8407	132
H01P	1677	5718	7785	132
H01Q	612	7344	9876	116
H01R	1027	6677	10489	116
H01S	-203	7043	10556	116

Experimental

Single crystals of $C_{29}H_{50}N_2O_{10}S_2$ [mo_D8V6585] were [From dietylether]. A suitable crystal was selected and [silicone grease on kapton loop] on a Bruker D8Venture Photon3 microsource APEX5 diffractometer. The crystal was kept at 100.0 K during data collection. Using Olex2 [1], the structure was solved with the XT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [mo_D8V6585]

Crystal Data for $C_{29}H_{50}N_2O_{10}S_2$ (M =650.83 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 12.0149(4) Å, b = 16.4908(5) Å, c = 17.1438(5) Å, V = 3396.79(18) Å^3, Z = 4, T = 100.0 K, μ(MoKα) = 0.211 mm^{-1}, *Dcalc* = 1.273 g/cm^3, 148871 reflections measured (5.482° ≤ 2Θ ≤ 64.062°), 11815 unique (R_{int} = 0.0350, R_{sigma} = 0.0170) which were used in all calculations. The final R_1 was 0.0268 (I > 2σ(I)) and wR_2 was 0.0742 (all data).

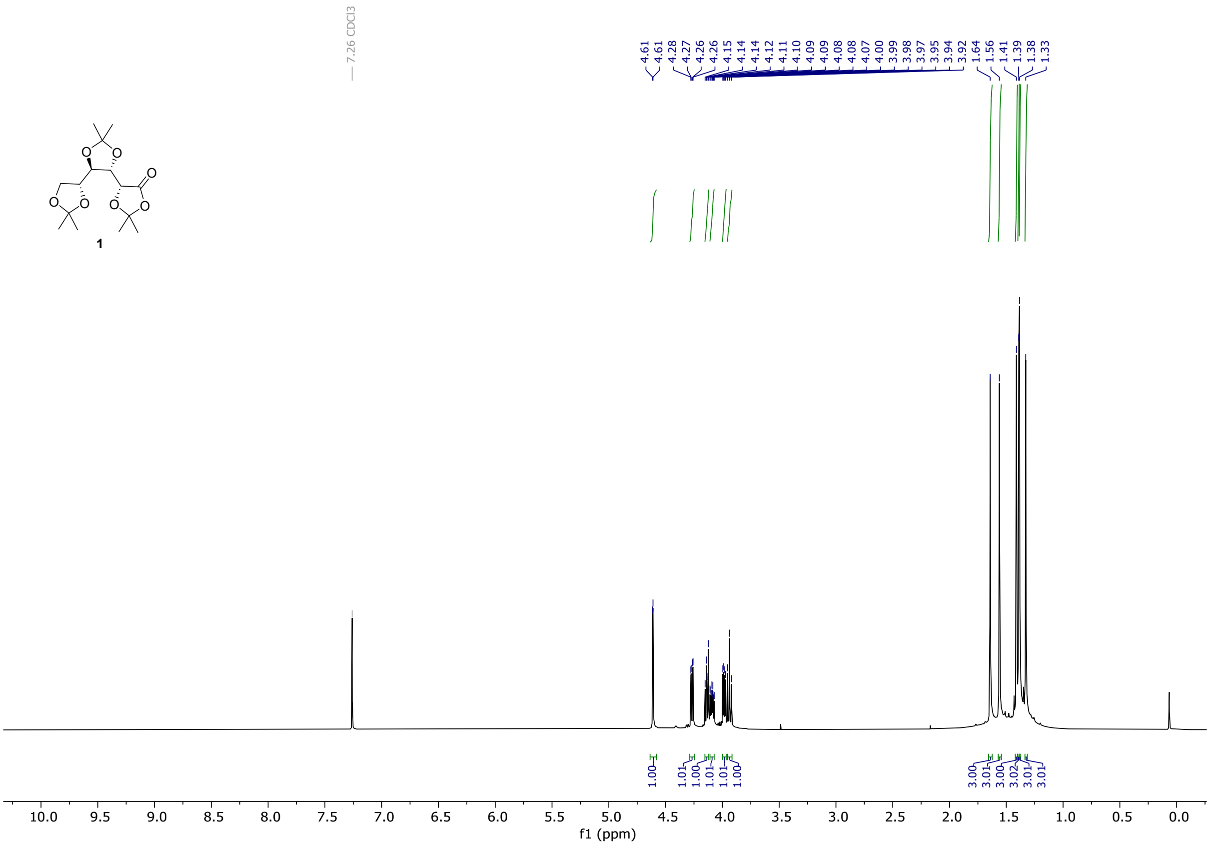
Refinement model description

Number of restraints - 0, number of constraints - unknown.
Details:
1. Fixed Uiso
   At 1.2 times of:
   All C(H) groups, All C(H,H) groups, All N(H) groups
   At 1.5 times of:
   All C(H,H,H) groups, All O(H) groups
2.a Ternary CH refined with riding coordinates:
   C00F(H00F), C00R(H00U), C00T(H00V), C00W(H00X), C011(H011)
2.b Secondary CH2 refined with riding coordinates:
   C00J(H00I,H00J), C014(H01J,H01K), C015(H01L,H01M)
2.c Aromatic/amide H refined with riding coordinates:
   C00N(H00N), C00V(H00W), C00X(H00Y), C00Z(H00)
2.d Idealised Me refined as rotating group:
   C00H(H00A,H00B,H00C), C00I(H00E,H00G,H00H), C00K(H00K,H00L,H00M), C00P(H00O, H00P,H00Q), C00Q(H00R,H00S,H00T), C00Y(H00Z,H,HA), C010(H01A,H01B,H01C), C012(H01D,H01E,H01F), C013(H01G,H01H,H01I), C016(H01N,H01O,H01P), C017(H01Q, H01R,H01S)

2.e Idealised tetrahedral OH refined as rotating group:
O004(H004)

This report has been created with Olex2, compiled on 2018.05.29 svn.r3508 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

NMR Spectra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4.10
4.09
4.09
4.08
4.08
4.07
4.00
3.99
3.98
3.97
3.95
3.94
3.92
1.64
1.56
1.41
1.39
1.38
1.33
O
O
O
O
O
O
O
1
1.00
1.01
1.00
1.01
1.01
1.00
3.00
3.01
3.00
3.02
3.01
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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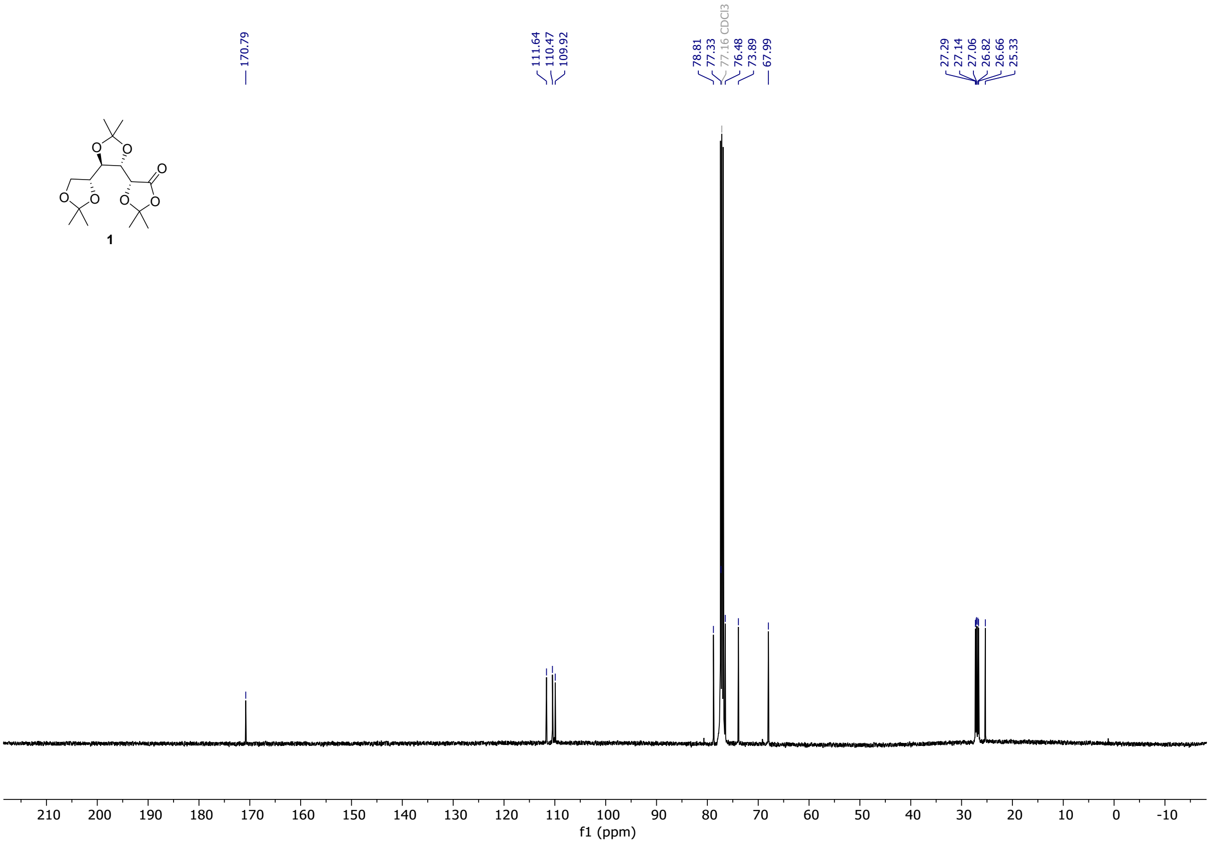
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27.14
27.06
26.82
26.66
25.33
O
O
O
O
O
O
O
1
210
200
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180
170
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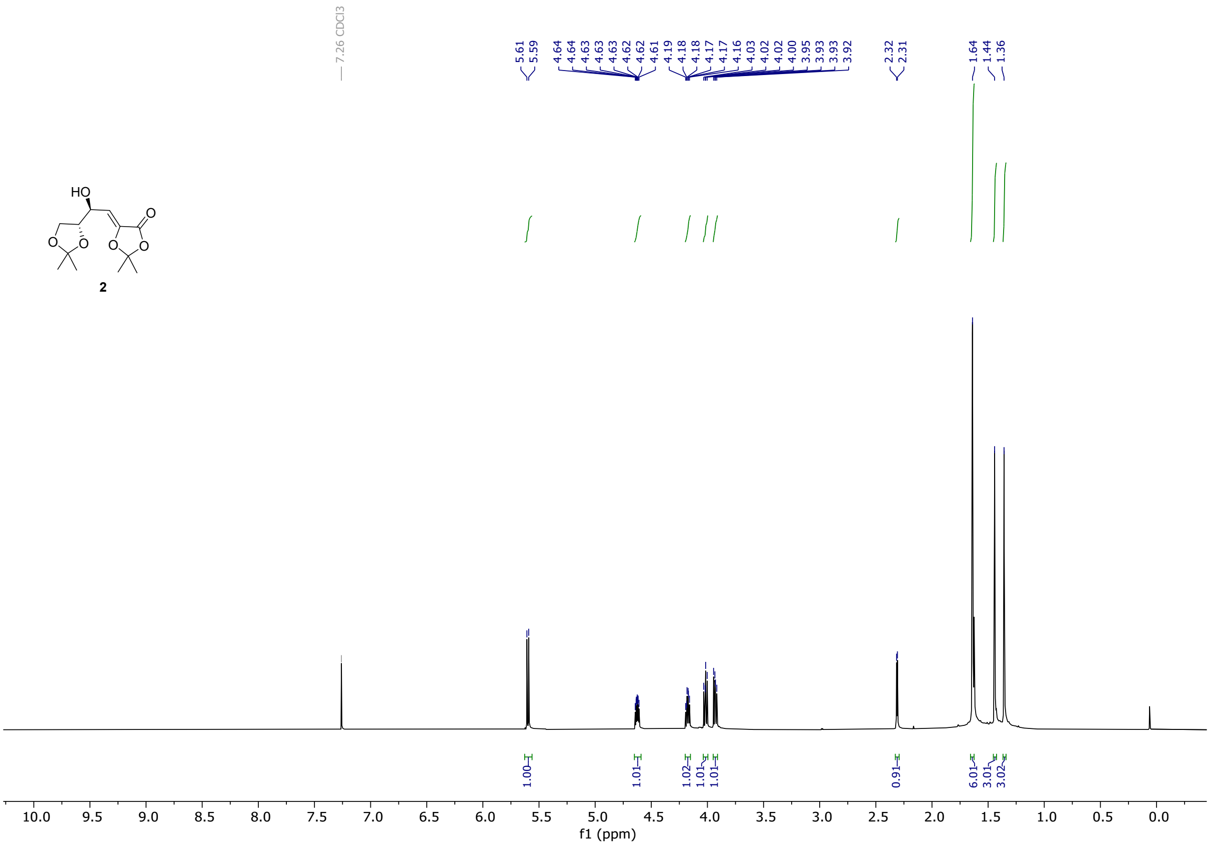
f1 (ppm)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4.17
4.16
4.03
4.02
4.02
4.00
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3.93
3.92
2.32
2.31
1.64
1.44
1.36
HO
O
O
O
O
O
2
1.00
1.01
1.02
1.01
1.01
0.91
6.01
3.01
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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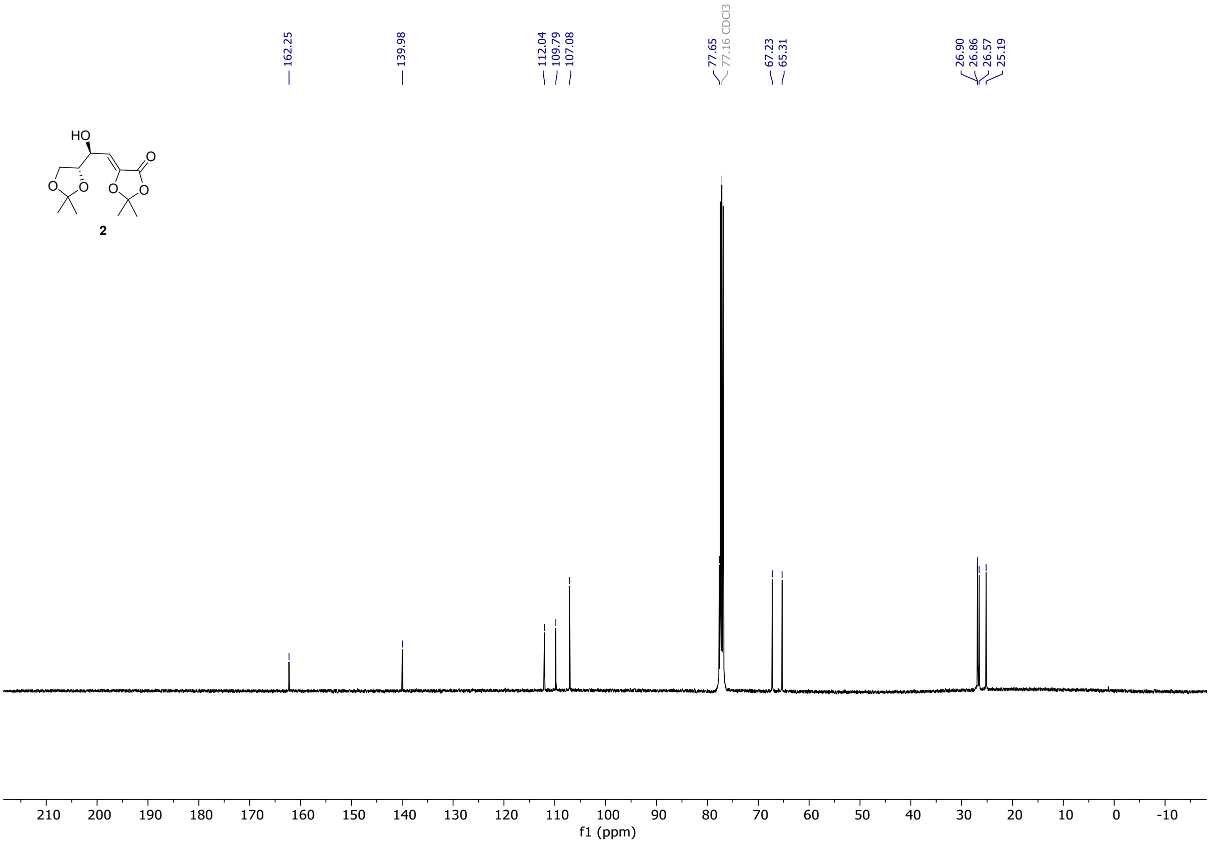
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80
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20
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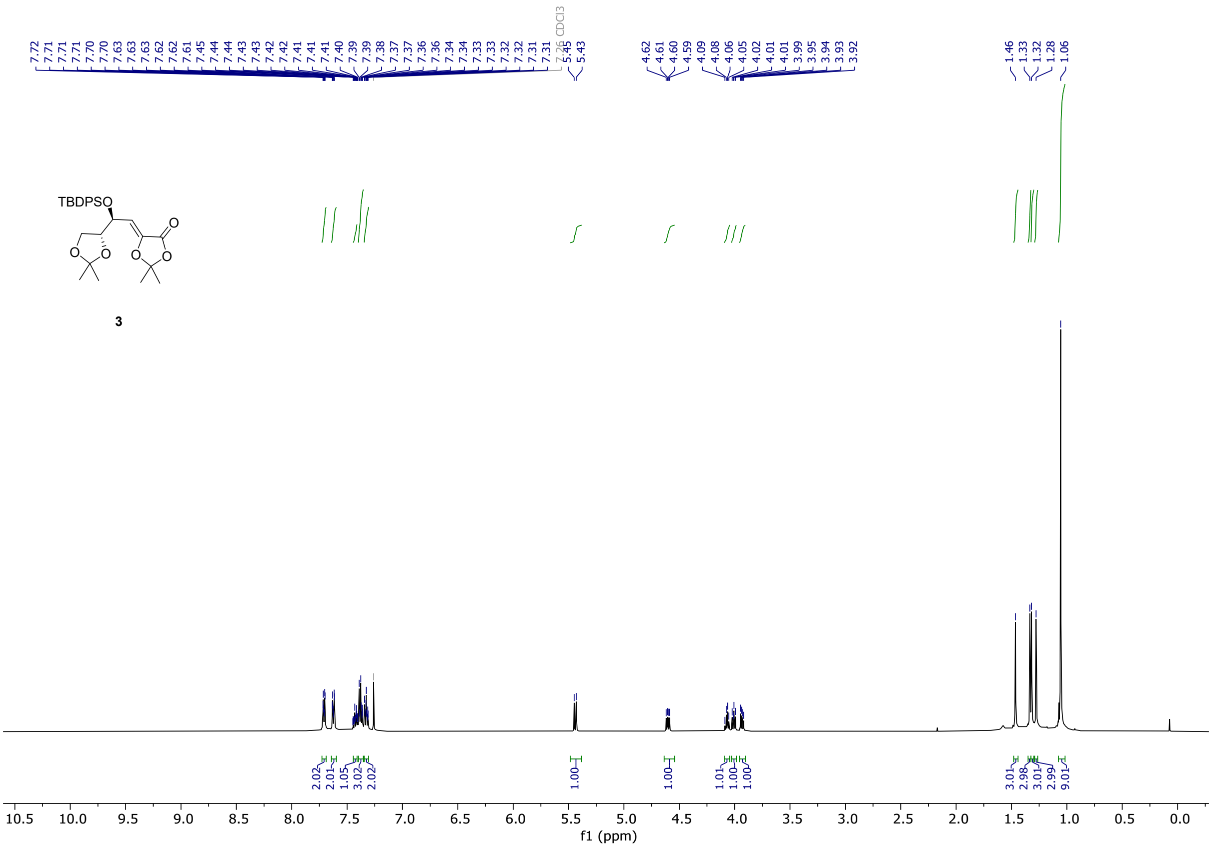
f1 (ppm)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7.43
7.43
7.42
7.42
7.41
7.41
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7.39
7.39
7.38
7.37
7.37
7.36
7.36
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7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.26 CDCl3
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5.43
4.62
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4.60
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4.09
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4.01
3.99
3.95
3.94
3.93
3.92
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1.33
1.32
1.28
1.06
TBDPSO
O
O
O
O
O
3
2.02
2.01
1.05
3.02
2.02
1.00
1.00
1.01
1.00
1.00
3.01
2.98
3.01
2.99
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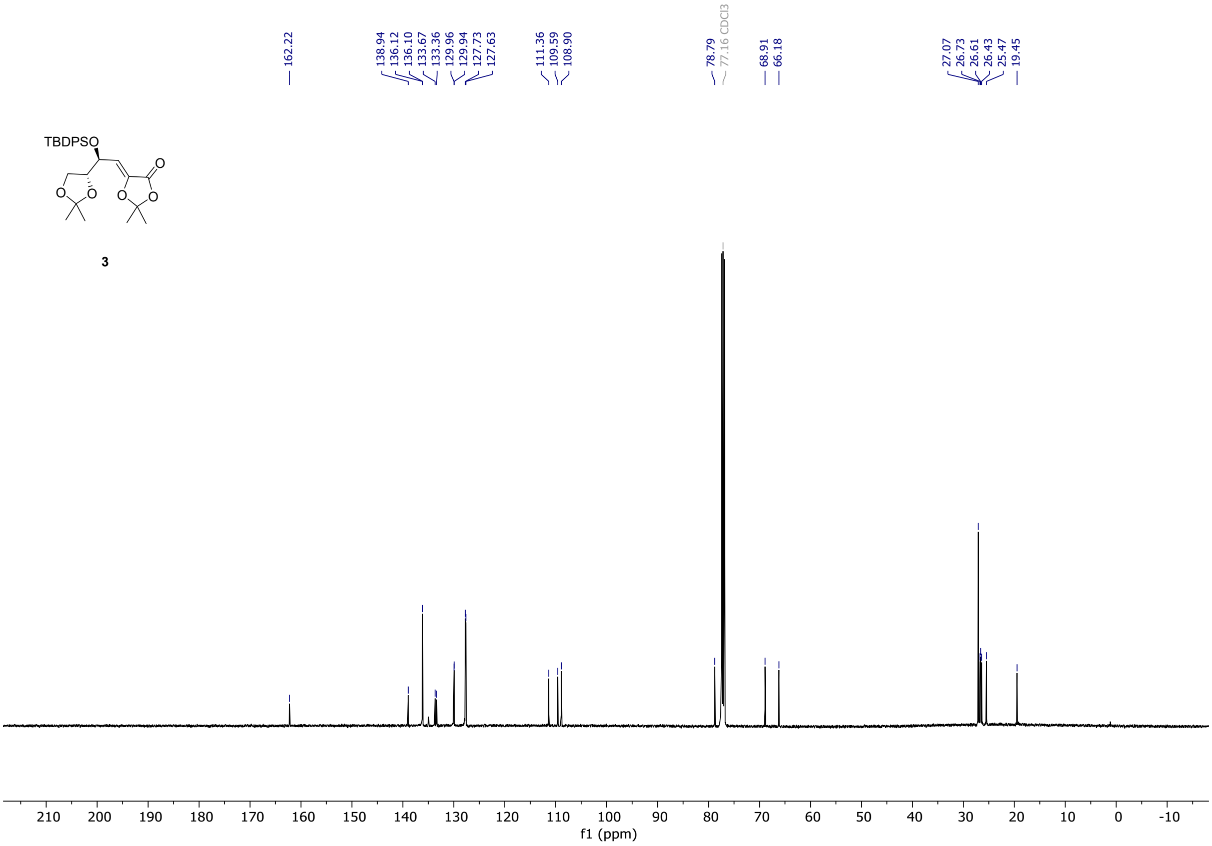
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78.79
77.16 CDCl3
68.91
66.18
27.07
26.73
26.61
26.43
25.47
19.45
TBDPSO
O
O
O
O
O
3
210
200
190
180
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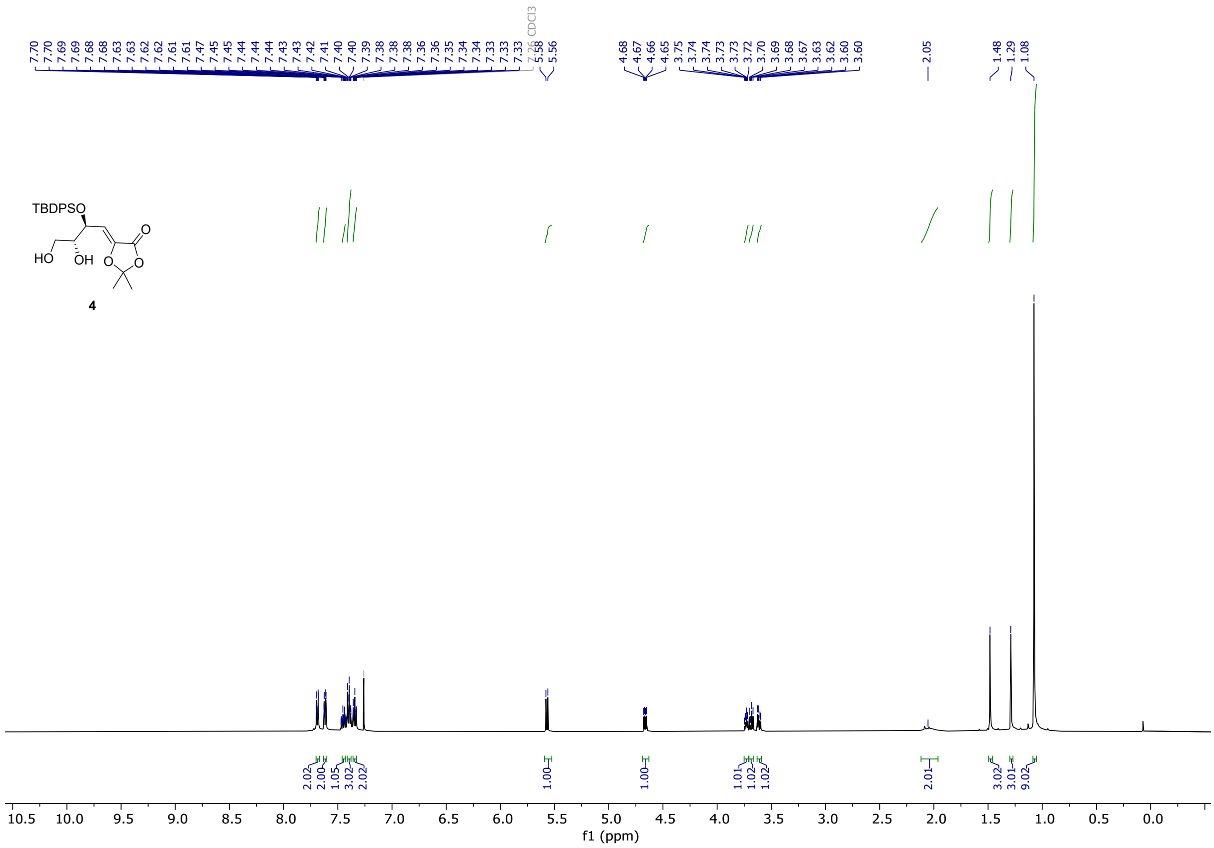

4

TBDPSO
HO
OH
O
O
O
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7.26 CDCl3
5.58 5.56
4.68 4.67 4.66 4.65
3.75 3.74 3.74 3.73 3.73 3.72 3.70 3.69 3.68 3.67 3.63 3.62 3.60 3.60
2.05
1.48
1.29
1.08
2.02 2.00 1.05 3.02 2.02
1.00
1.00
1.01 1.02 1.02
2.01
3.02 3.01 9.02
10.5 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 0.5 0.0
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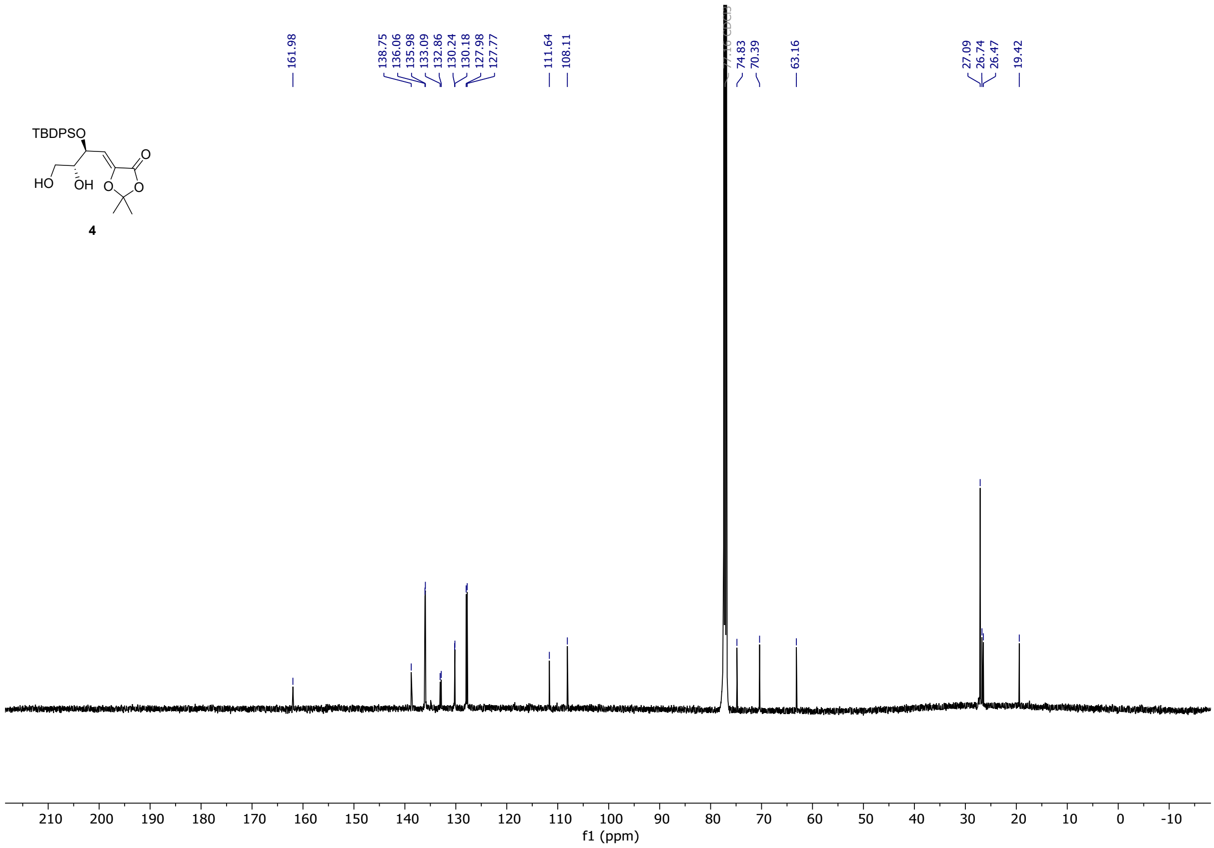

4

TBDPSO
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OH
O
O
O
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111.64
108.11
77.16 CDCl3
74.83
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19.42
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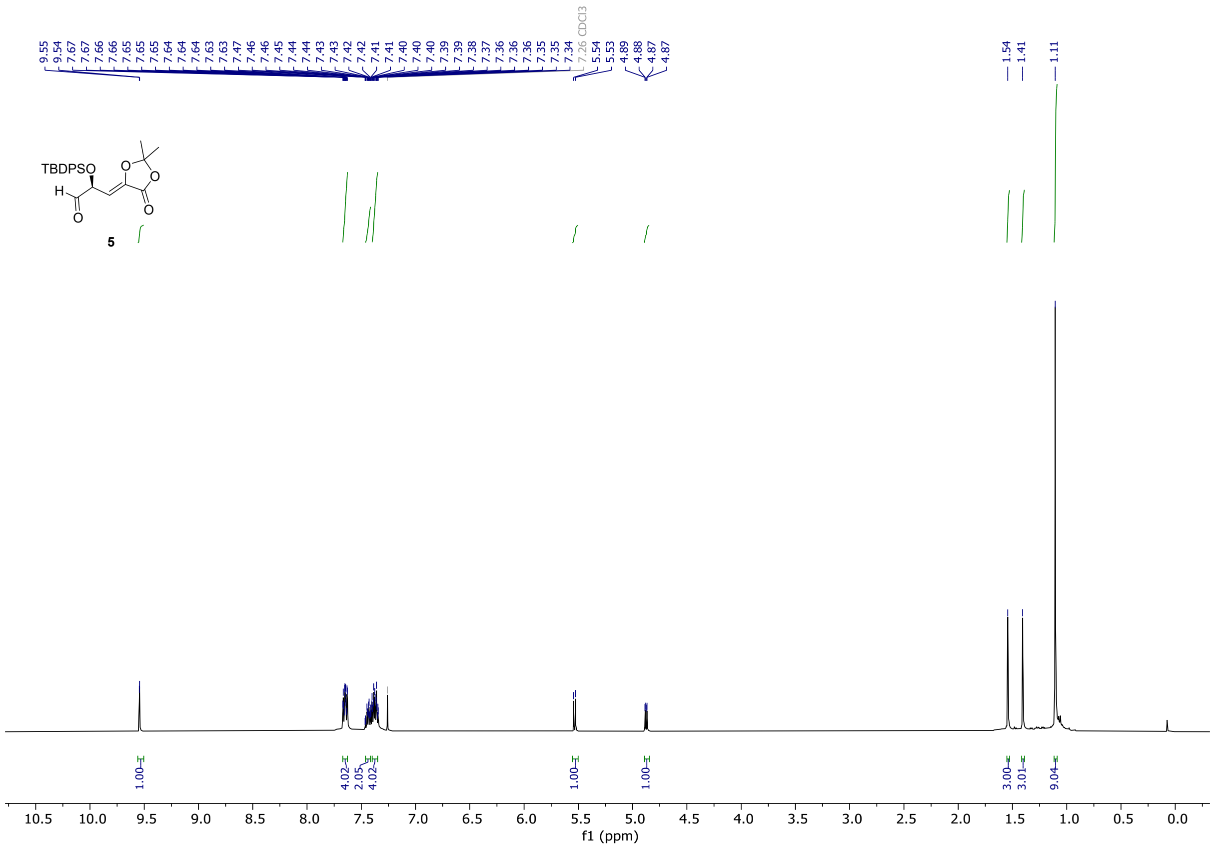
f1 (ppm)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7.43
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7.40
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7.34
7.26 CDCl3
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5.53
4.89
4.88
4.87
4.87
1.54
1.41
1.11
TBDPSO
H
O
O
O
O
5
1.00
4.02
2.05
4.02
1.00
1.00
3.00
3.01
9.04
10.5
10.0
9.5
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7.0
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3.0
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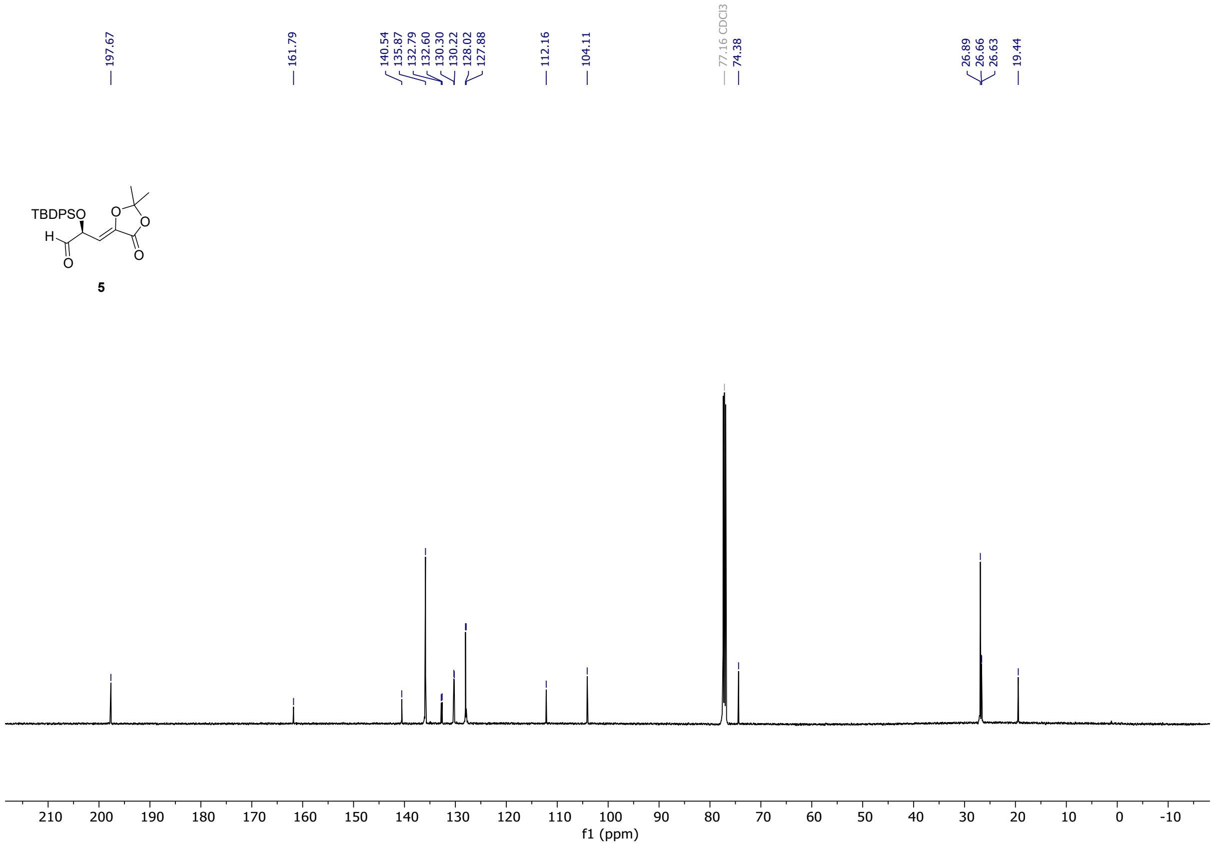
f1 (ppm)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74.38
26.89
26.66
26.63
19.44
TBDPSO
H
O
O
O
O
5
210
200
190
180
170
160
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140
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120
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100
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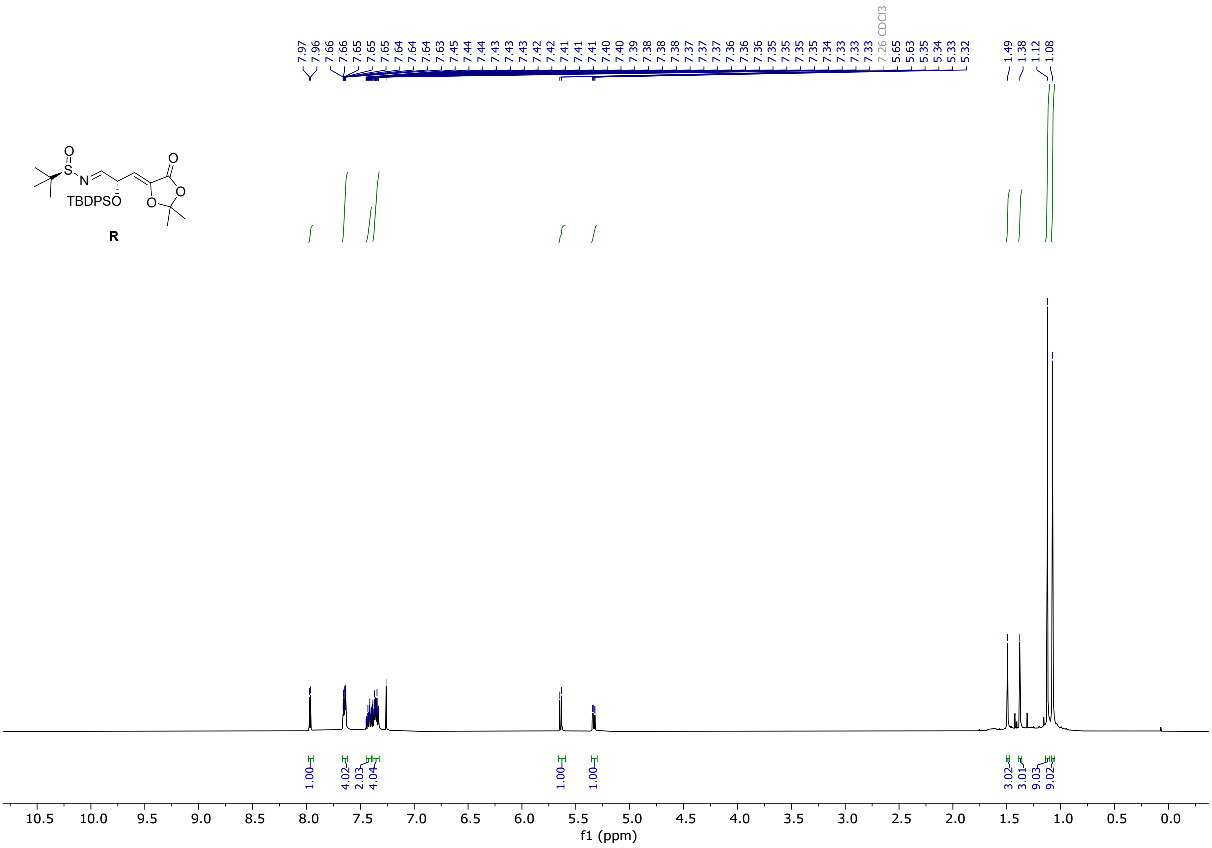
f1 (ppm)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7.37
7.36
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7.36
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7.33
7.33
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S
N
O
O
O
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R
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2.03
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1.00
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3.01
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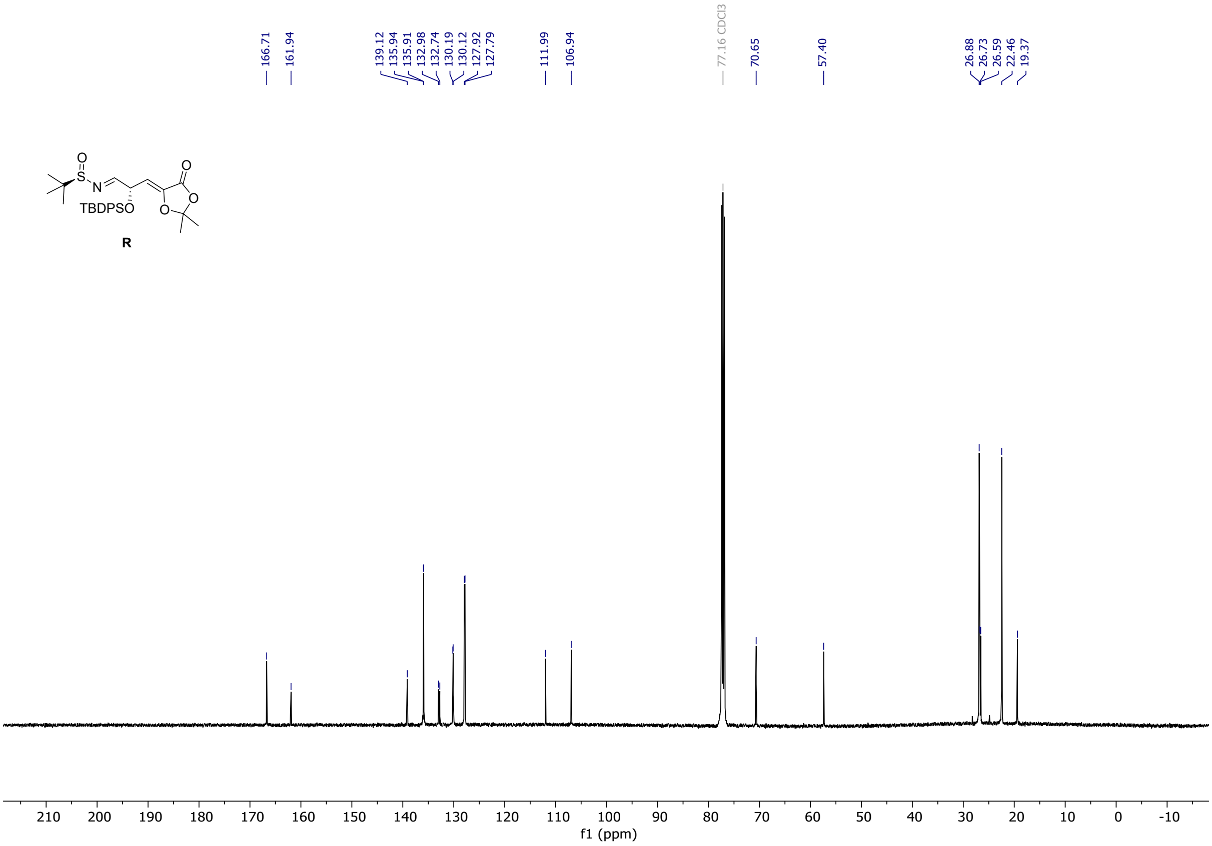
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26.73
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22.46
19.37
O
S
N
O
O
O
TBDPSO
R
210
200
190
180
170
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100
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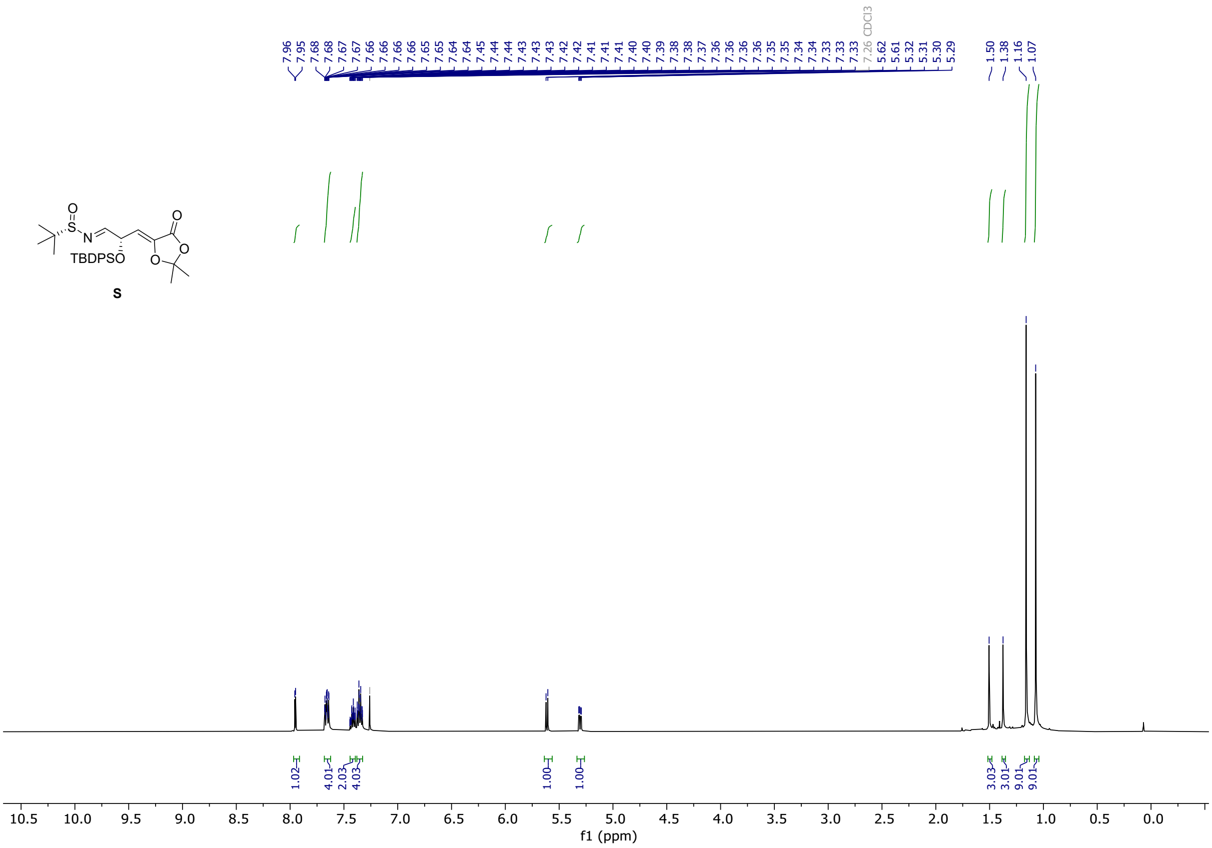
f1 (ppm)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7.38
7.37
7.36
7.36
7.36
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7.35
7.34
7.34
7.33
7.33
7.33
7.26 CDCl3
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1.07
TBDPSO
S
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4.03
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1.00
3.03
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9.01
10.5
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9.5
9.0
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8.0
7.5
7.0
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6.0
5.5
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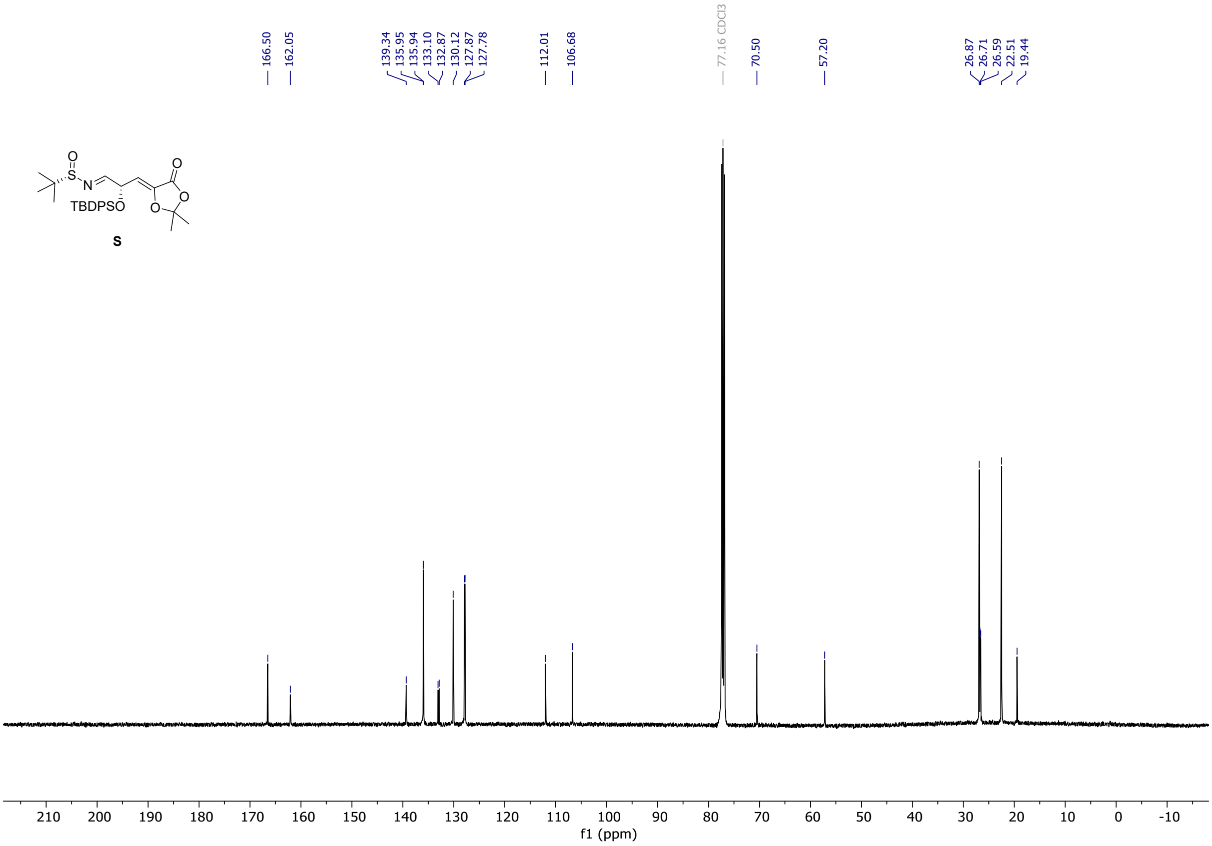
f1 (ppm)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77.16 CDCl3
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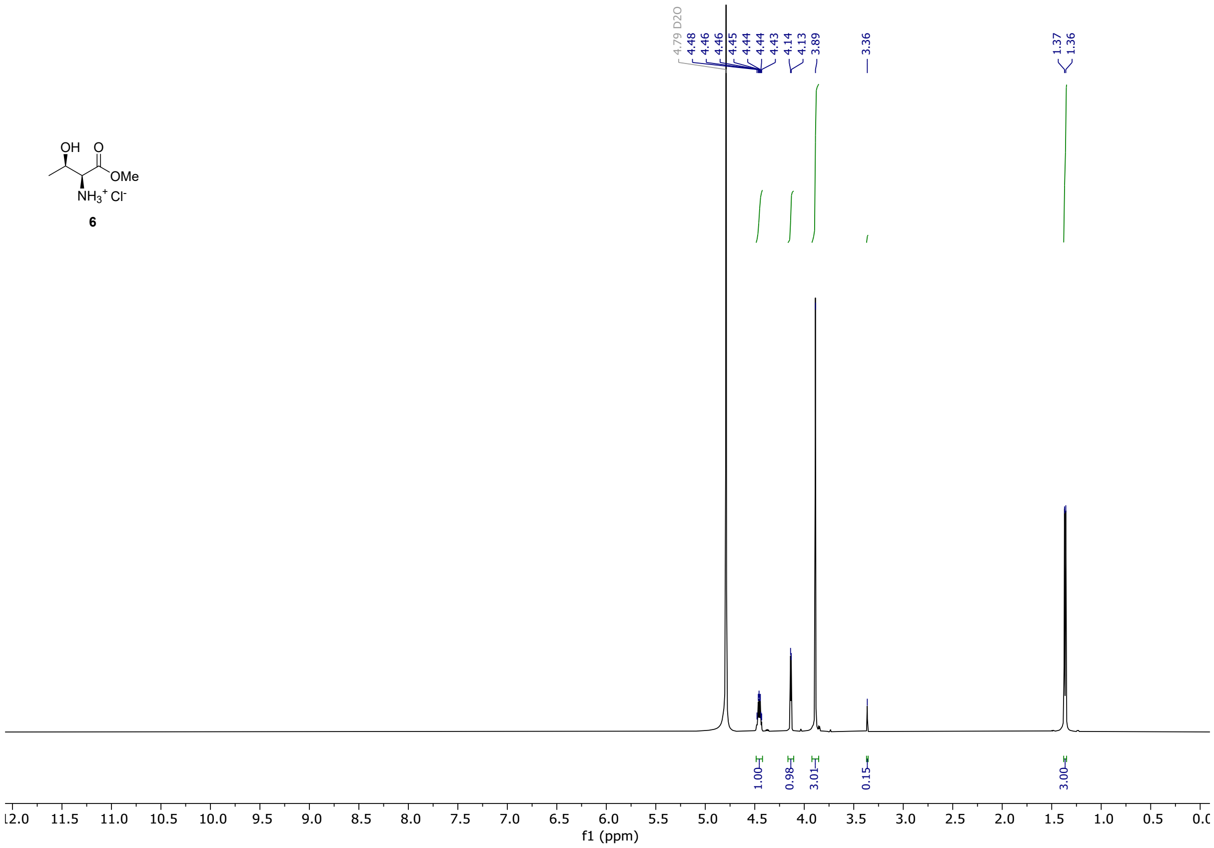
57.20
26.87
26.71
26.59
22.51
19.44
TBDPSO
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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OMe
NH3+ Cl-
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2.0
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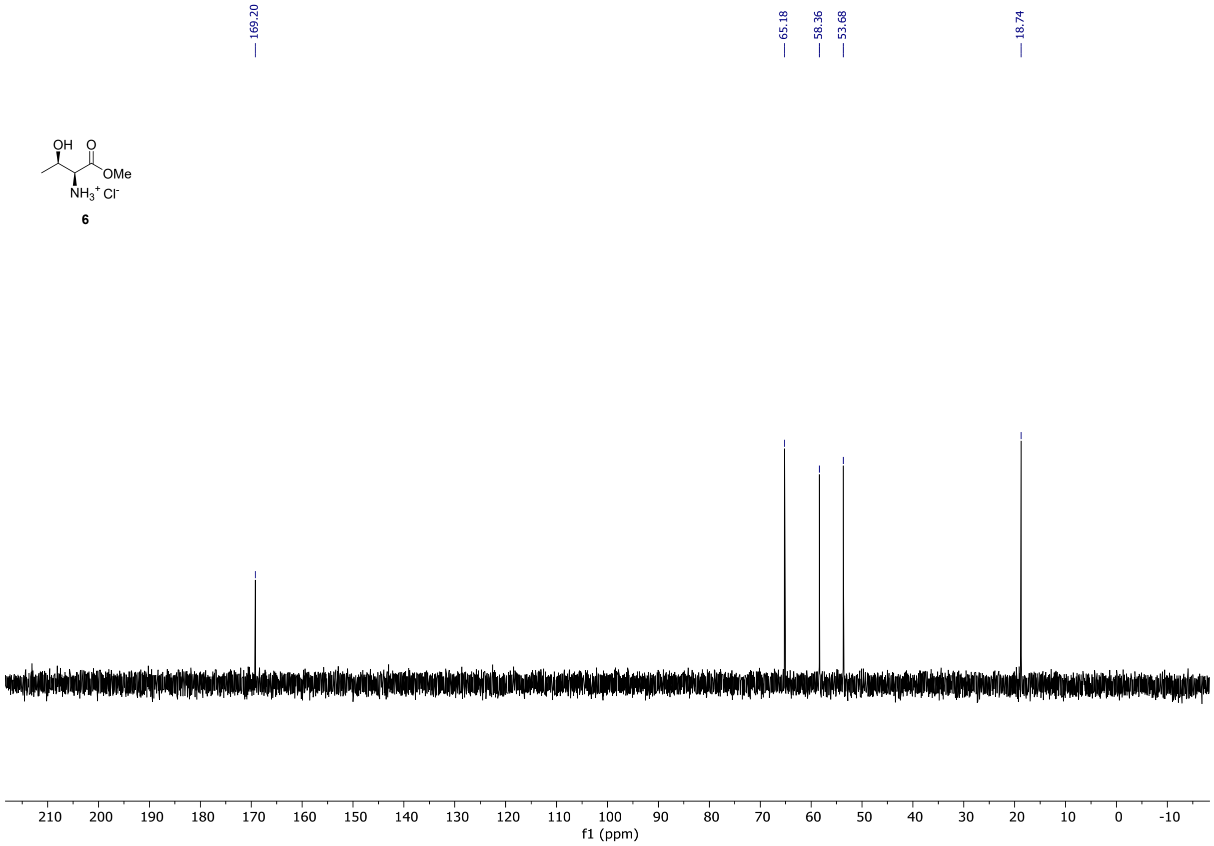
f1 (ppm)

6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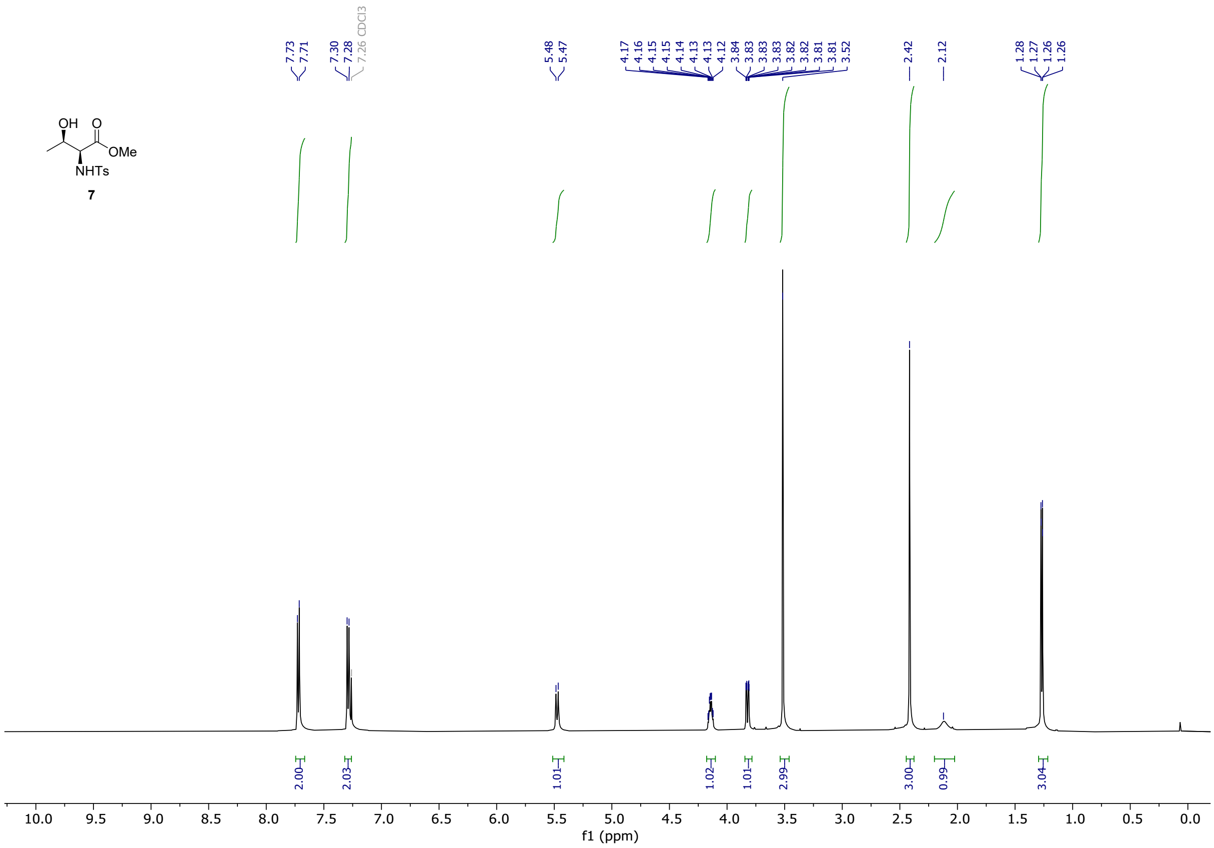
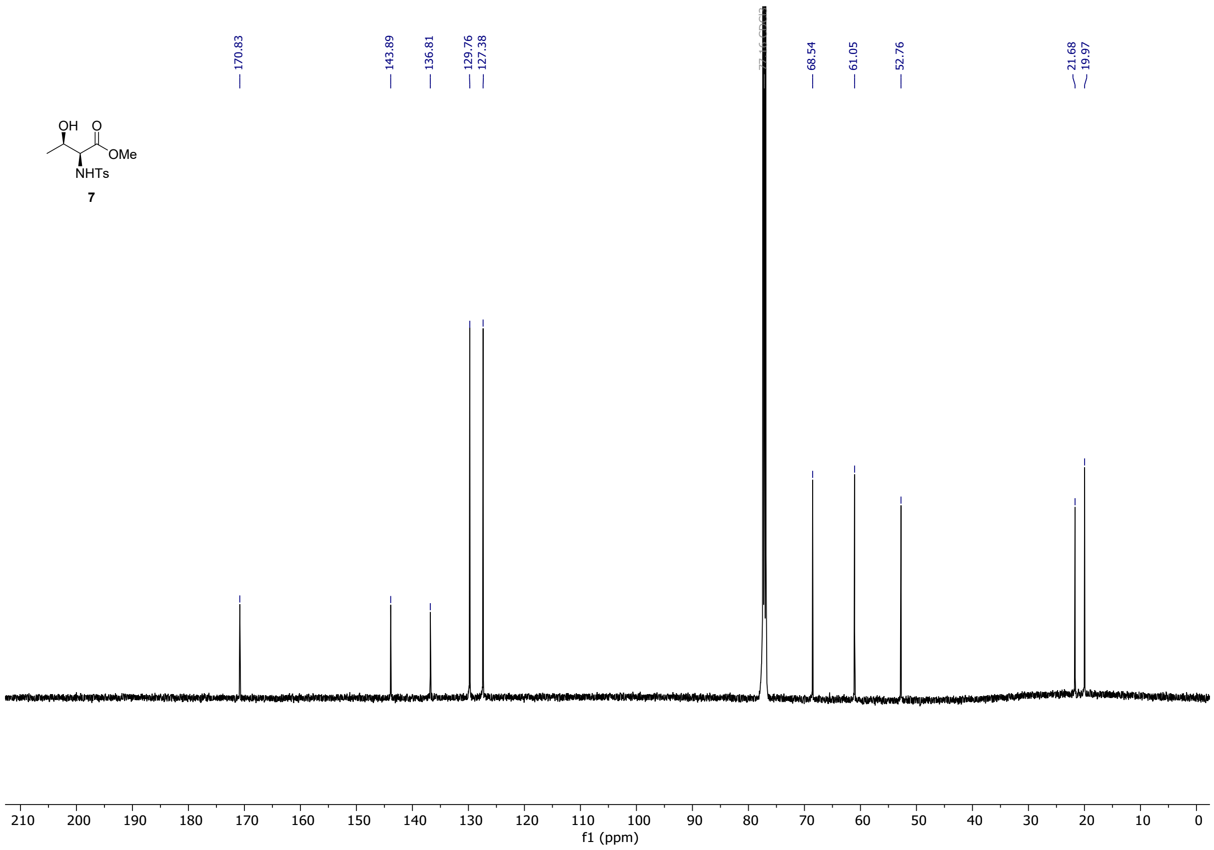
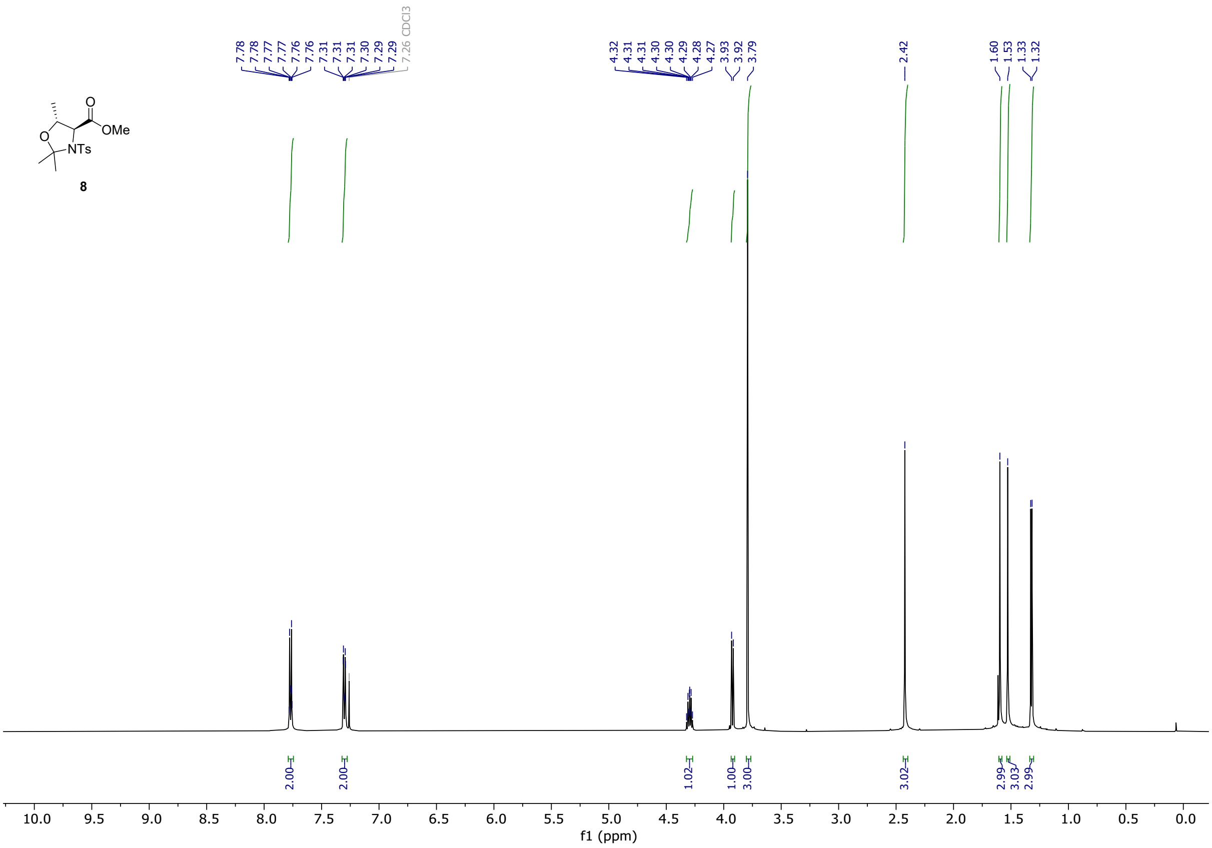
65.18
58.36
53.68
18.74
OH
O
OMe
NH3+ Cl-
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

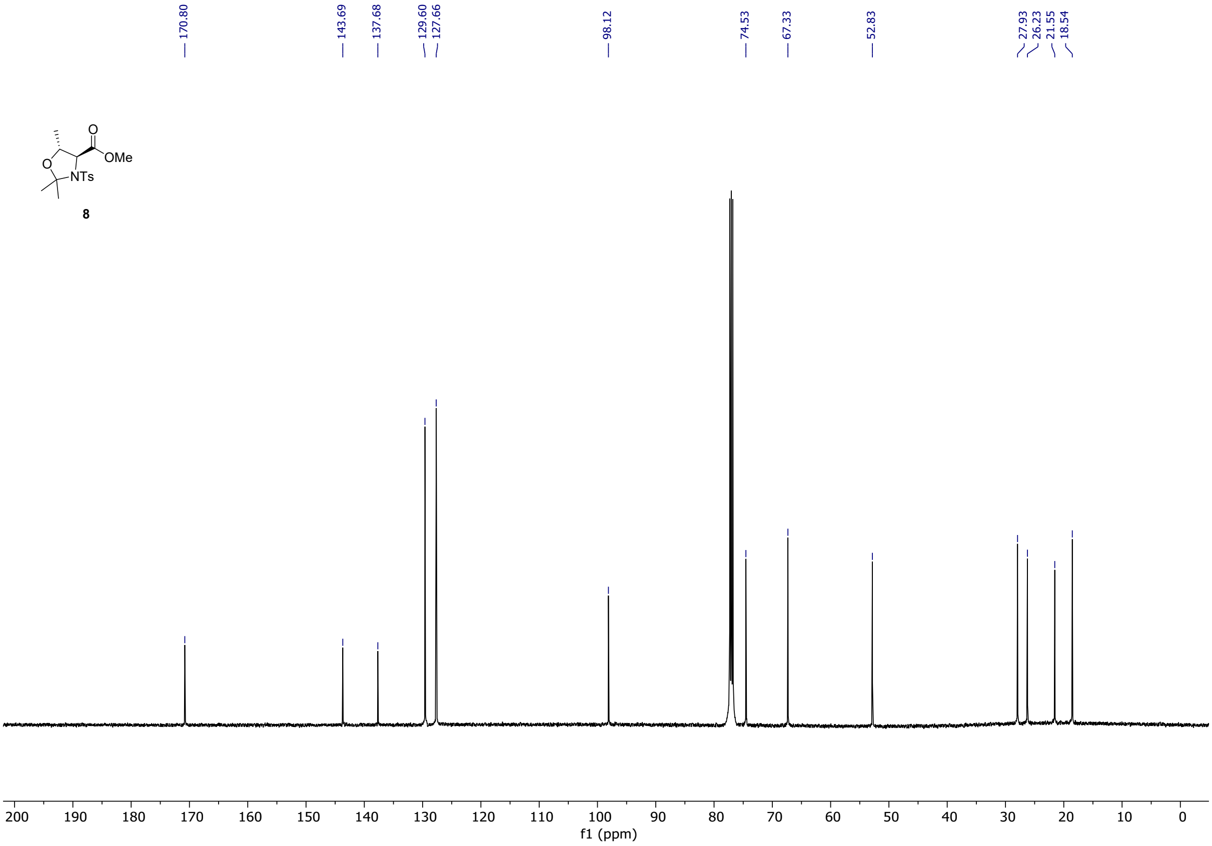
6


7.73
7.71
7.30
7.28
7.26 CDCl3
5.48
5.47
4.17
4.16
4.15
4.15
4.14
4.13
4.13
4.12
3.84
3.83
3.83
3.83
3.82
3.82
3.81
3.81
3.52
2.42
2.12
1.28
1.27
1.26
1.26
OH
O
OMe
NHTs
7
2.00
2.03
1.01
1.02
1.01
2.99
3.00
0.99
3.04
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
0.5
0.0
f1 (ppm)

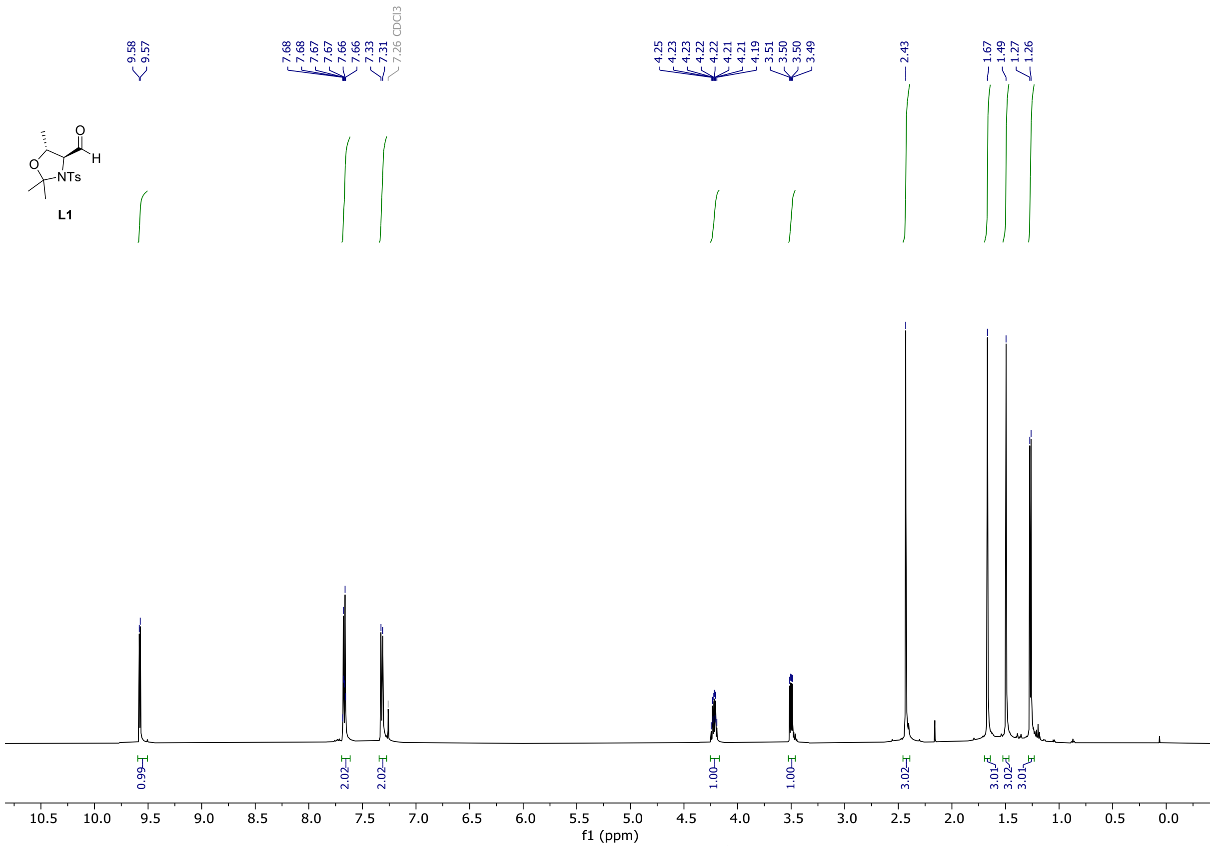

170.83
143.89
136.81
129.76
127.38
68.54
61.05
52.76
21.68
19.97
OH
O
OMe
NHTs
7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

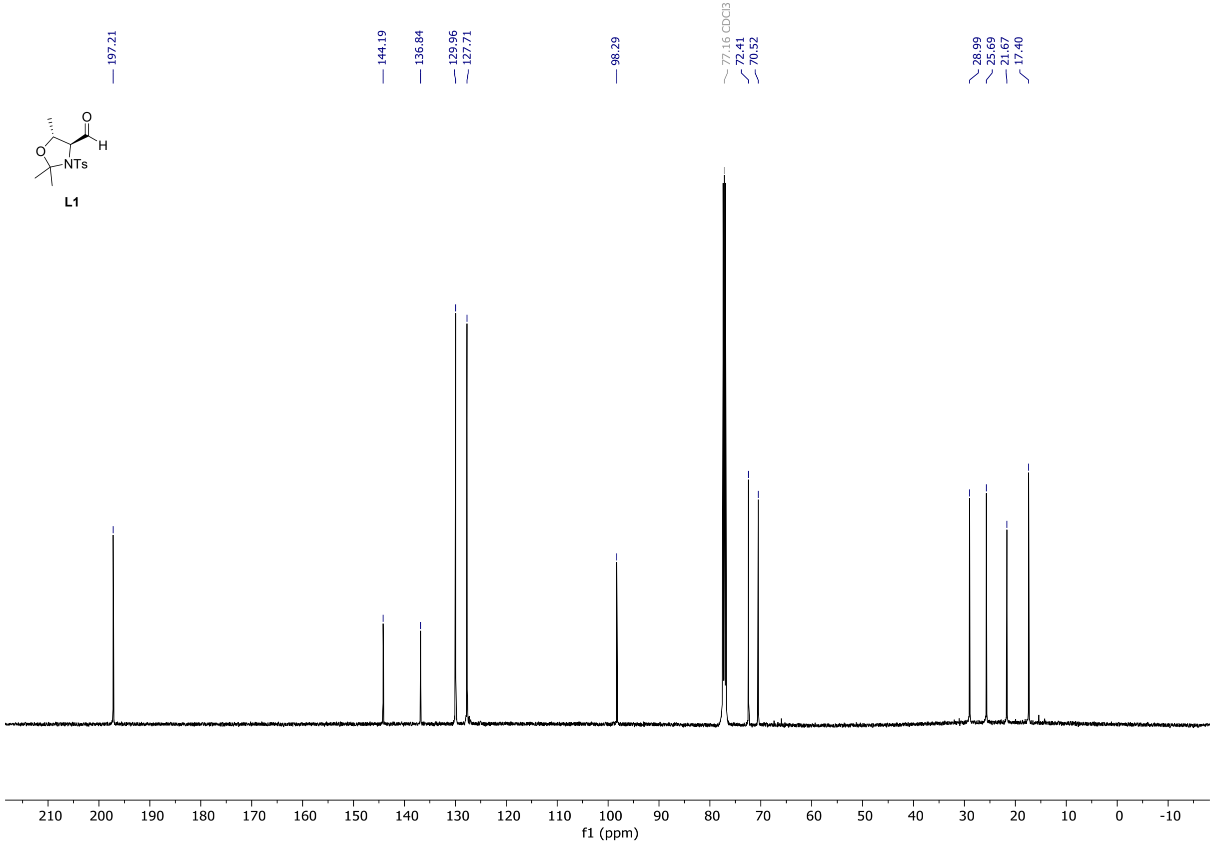

7.78
7.78
7.77
7.77
7.76
7.76
7.31
7.31
7.31
7.30
7.29
7.29
7.26 CDCl3
4.32
4.31
4.31
4.30
4.30
4.29
4.29
4.28
4.27
3.93
3.92
3.79
2.42
1.60
1.53
1.33
1.32
O
OMe
O
NTs
2.00
2.00
1.02
1.00
3.00
3.02
2.99
3.03
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

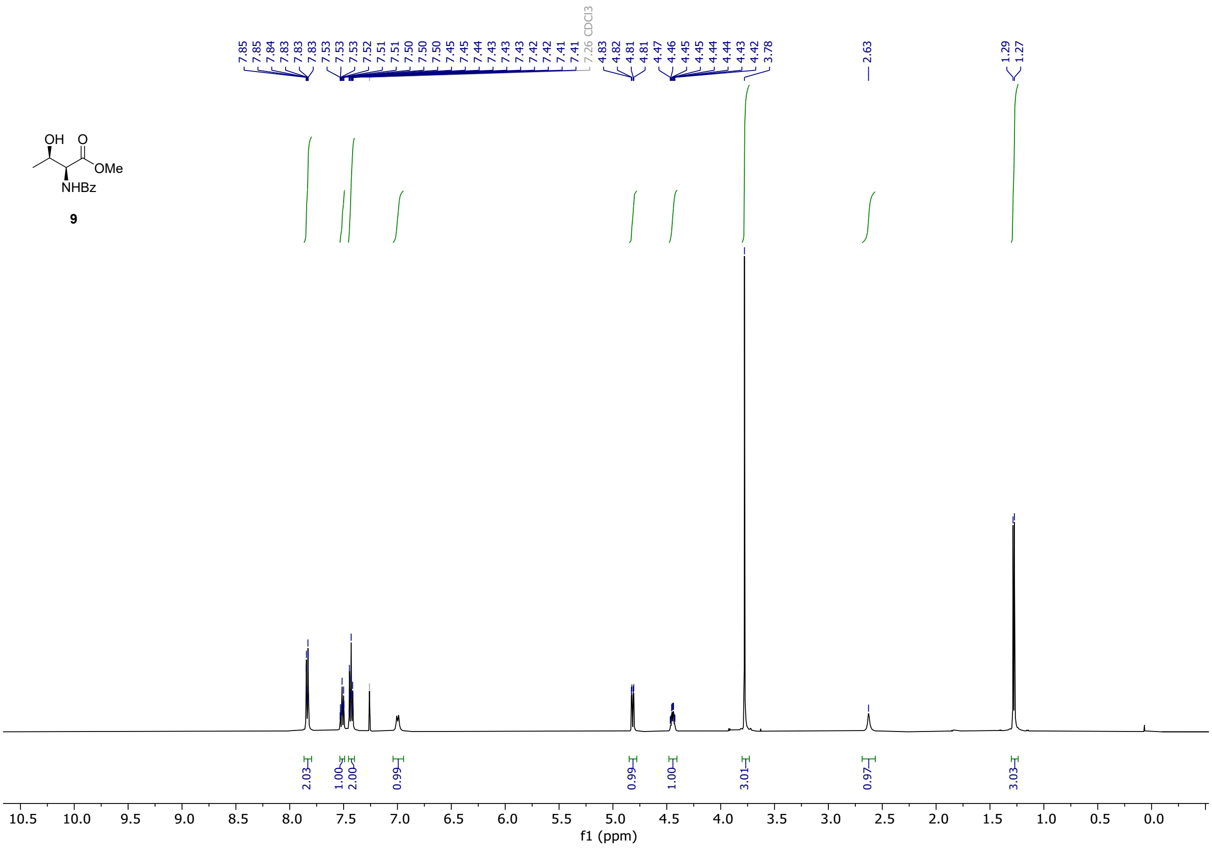
8

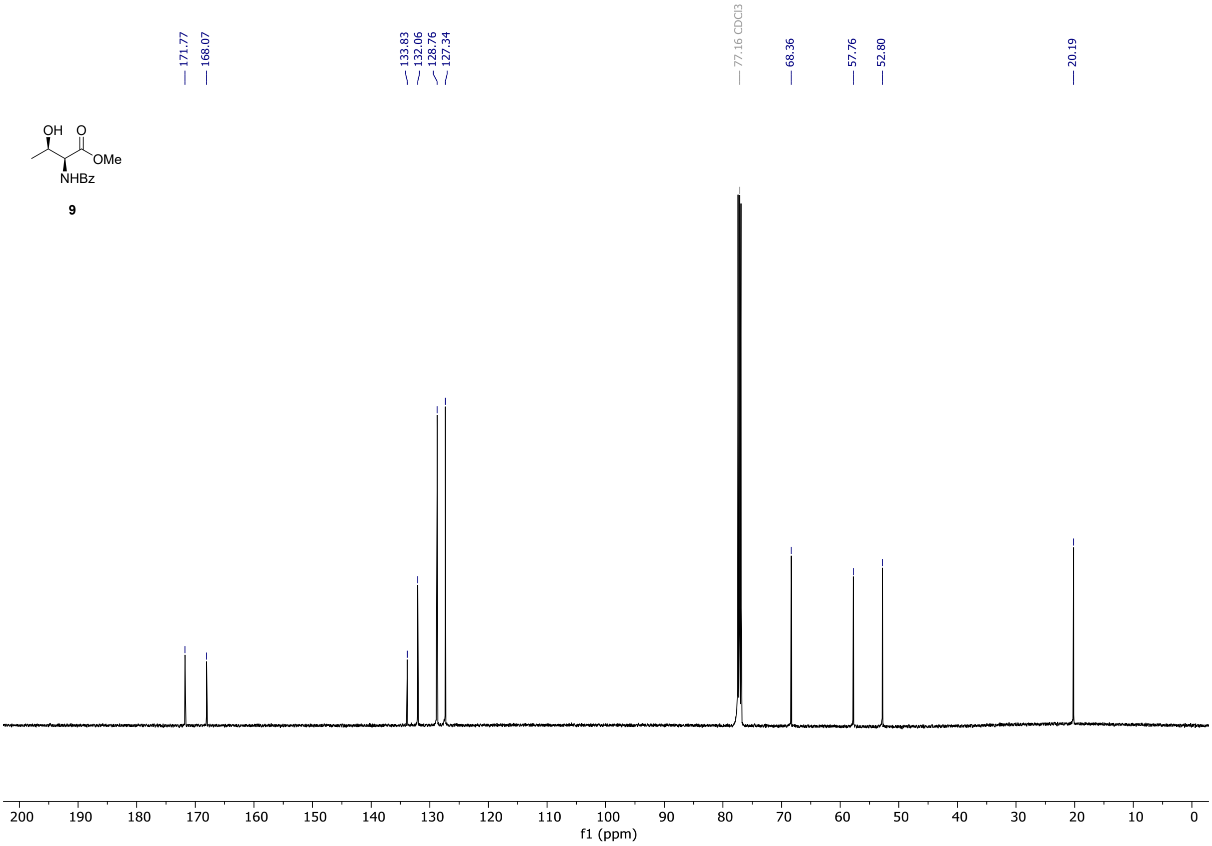

170.80
143.69
137.68
129.60
127.66
98.12
74.53
67.33
52.83
27.93
26.23
21.55
18.54
O
OMe
O
NTs
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

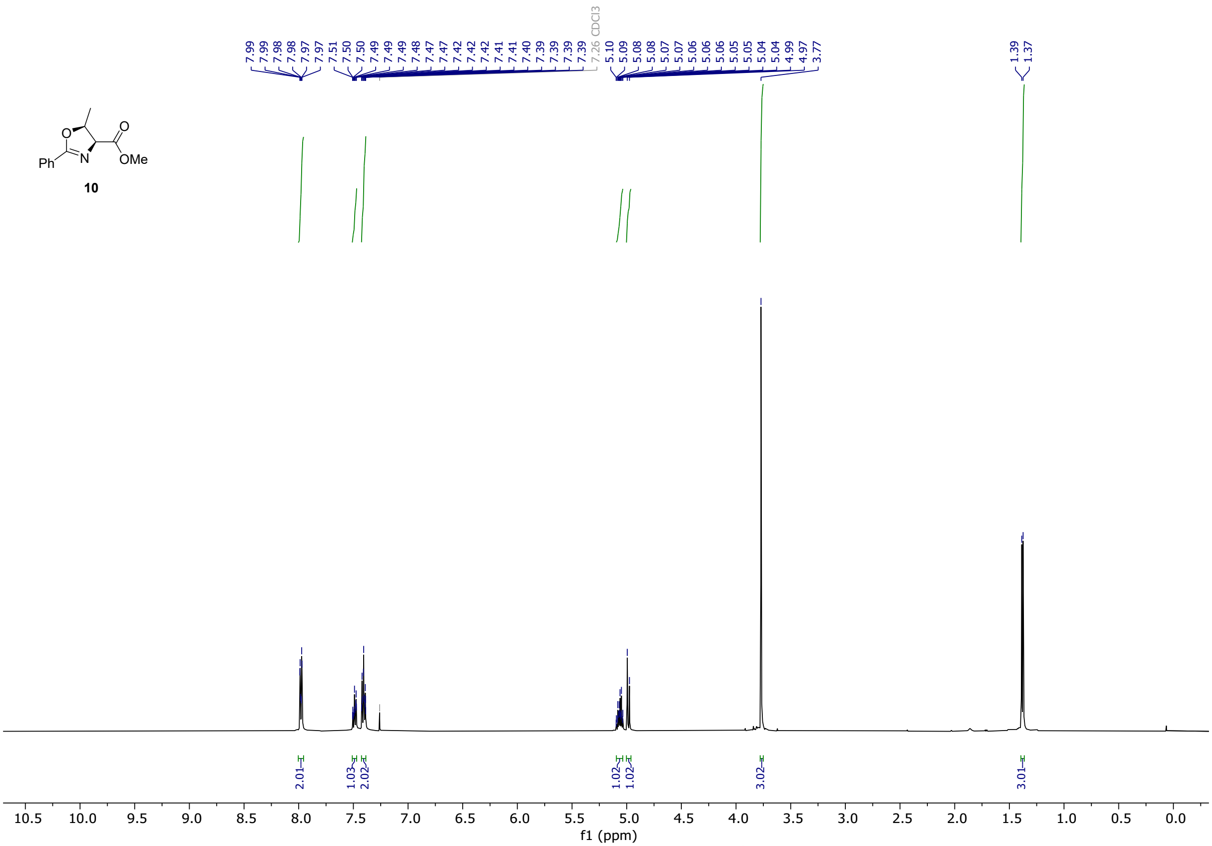
8

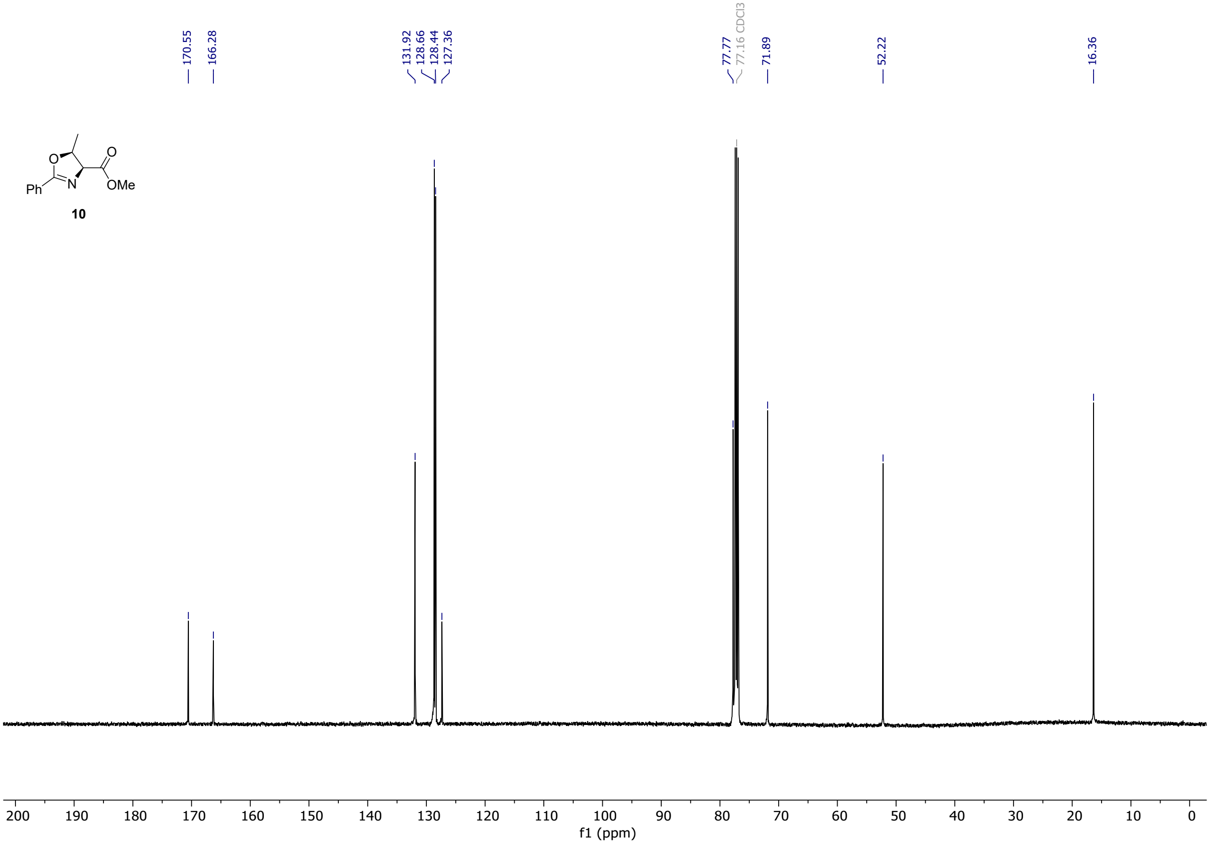

9.58
9.57
7.68
7.68
7.67
7.67
7.66
7.66
7.33
7.31
7.26 CDCl3
4.25
4.23
4.23
4.22
4.22
4.21
4.21
4.19
3.51
3.50
3.50
3.49
2.43
1.67
1.49
1.27
1.26
O
H
O
NTs
L1
0.99
2.02
2.02
1.00
1.00
3.02
3.01
3.02
3.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

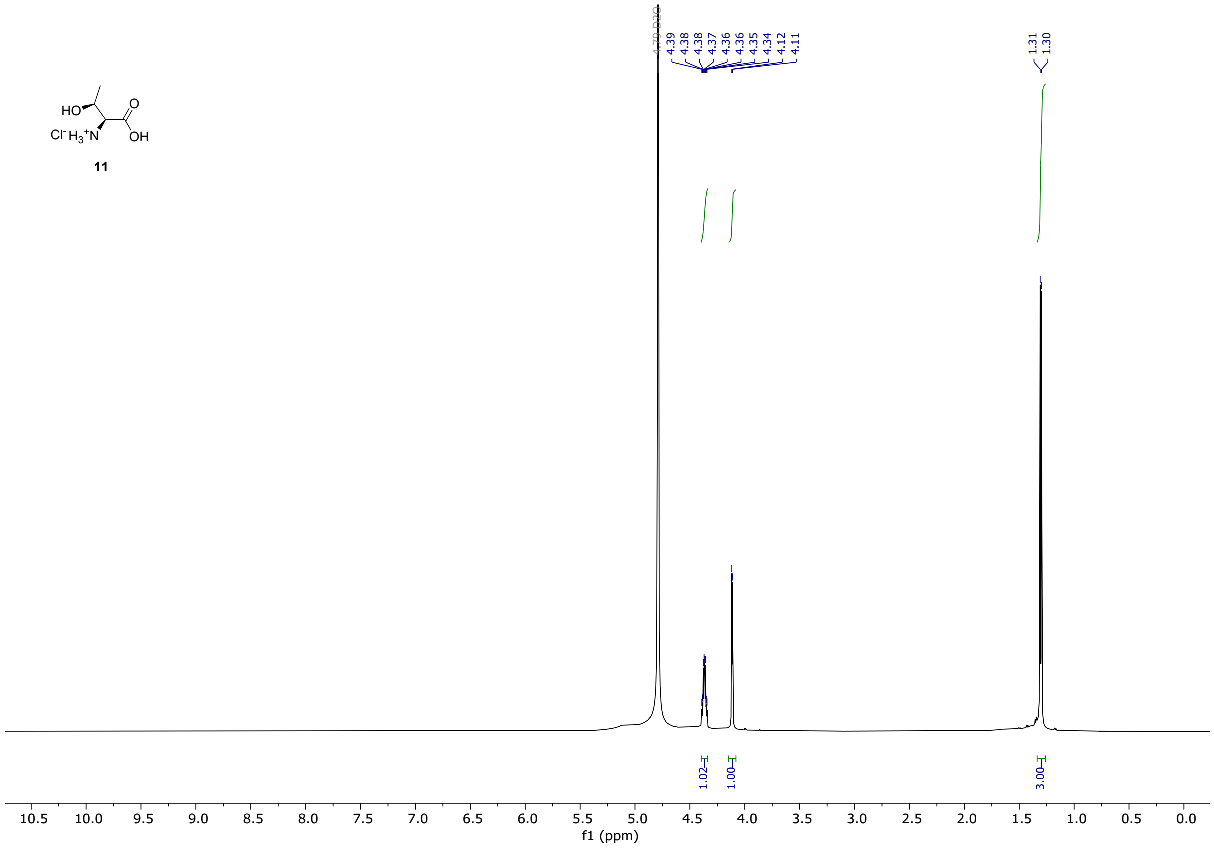

197.21
144.19
136.84
129.96
127.71
98.29
77.16 CDCl3
72.41
70.52
28.99
25.69
21.67
17.40
O
H
O
NTs
L1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

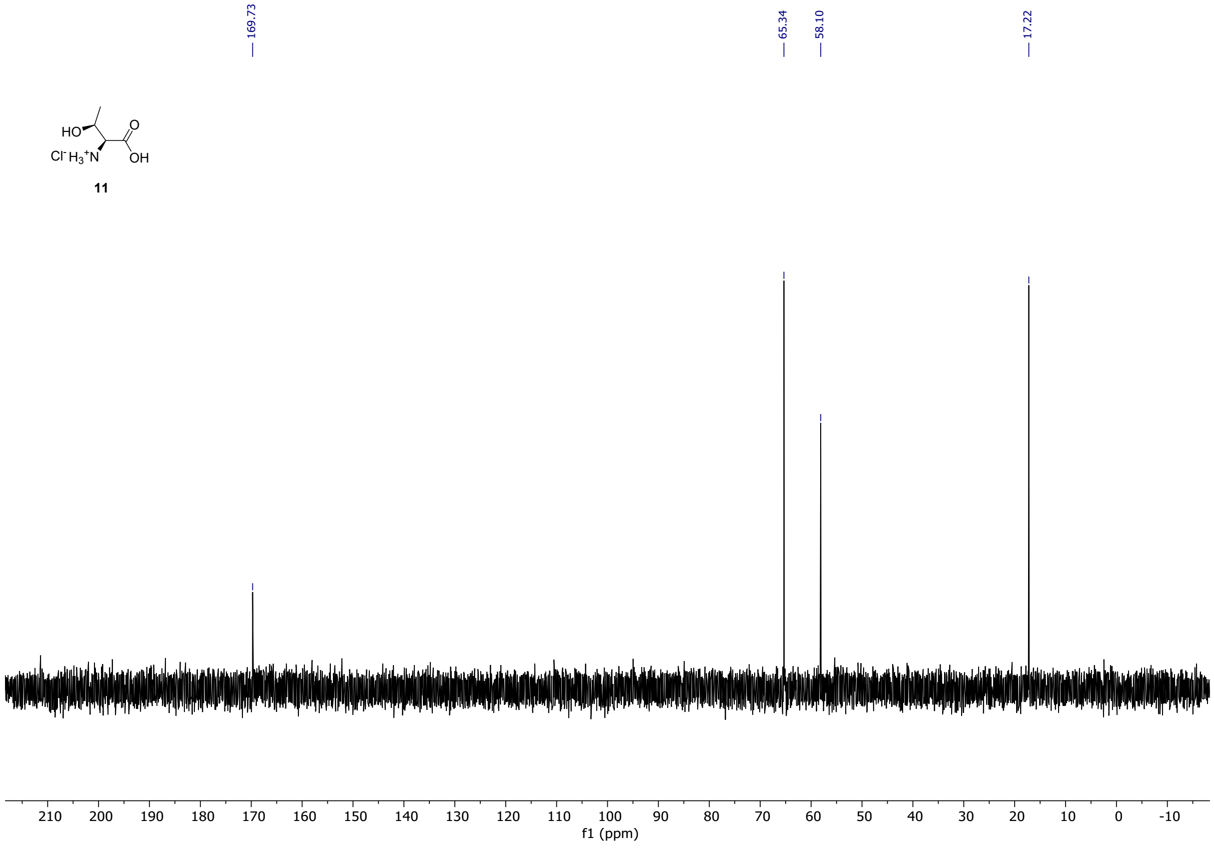

7.85
7.85
7.84
7.83
7.83
7.83
7.53
7.53
7.53
7.52
7.51
7.51
7.50
7.50
7.50
7.45
7.45
7.44
7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.26 CDCl3
4.83
4.82
4.81
4.81
4.47
4.46
4.45
4.45
4.44
4.44
4.43
4.42
3.78
2.63
1.29
1.27
OH O
OMe
NHBz
9
2.03
1.00
2.00
0.99
0.99
1.00
3.01
0.97
3.03
10.5 10.0 9.5 9.0 8.5 8.0 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 0.5 0.0
f1 (ppm)

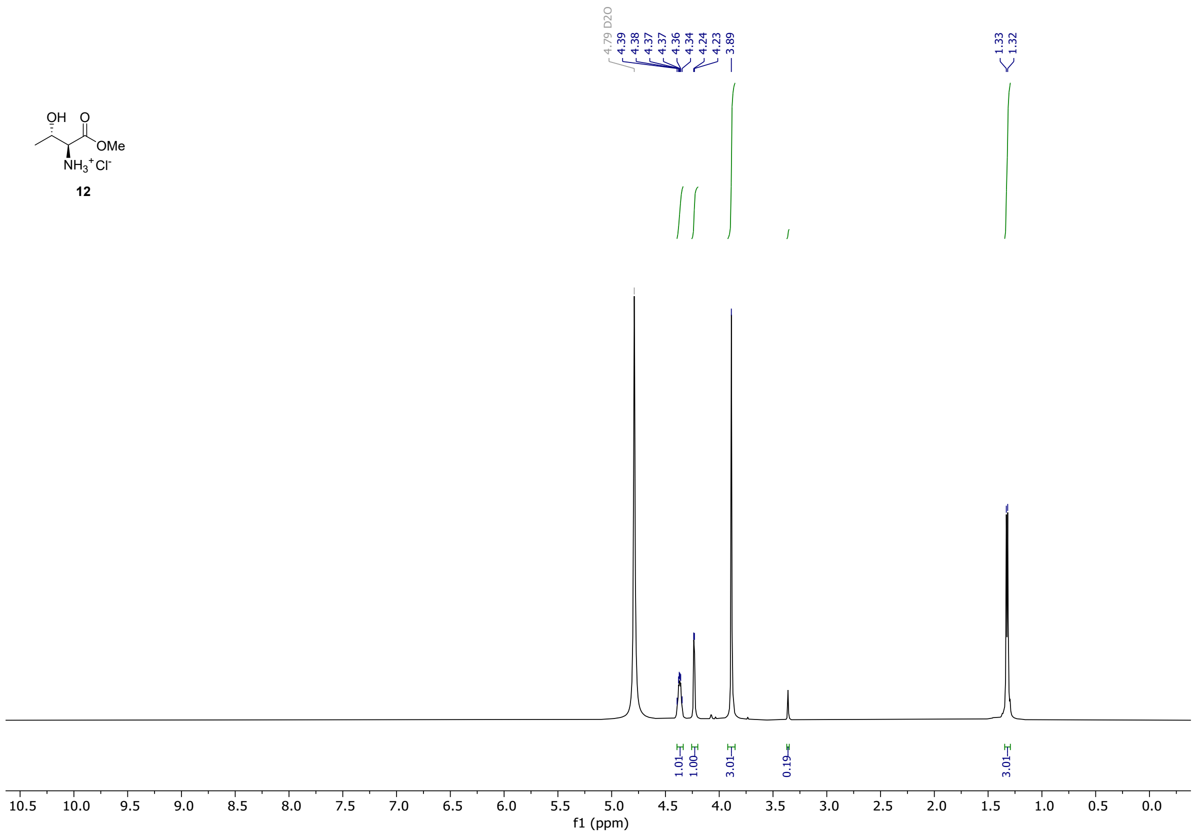

171.77
168.07
133.83
132.06
128.76
127.34
77.16 CDCl3
68.36
57.76
52.80
20.19
OH O
OMe
NHBz
9
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

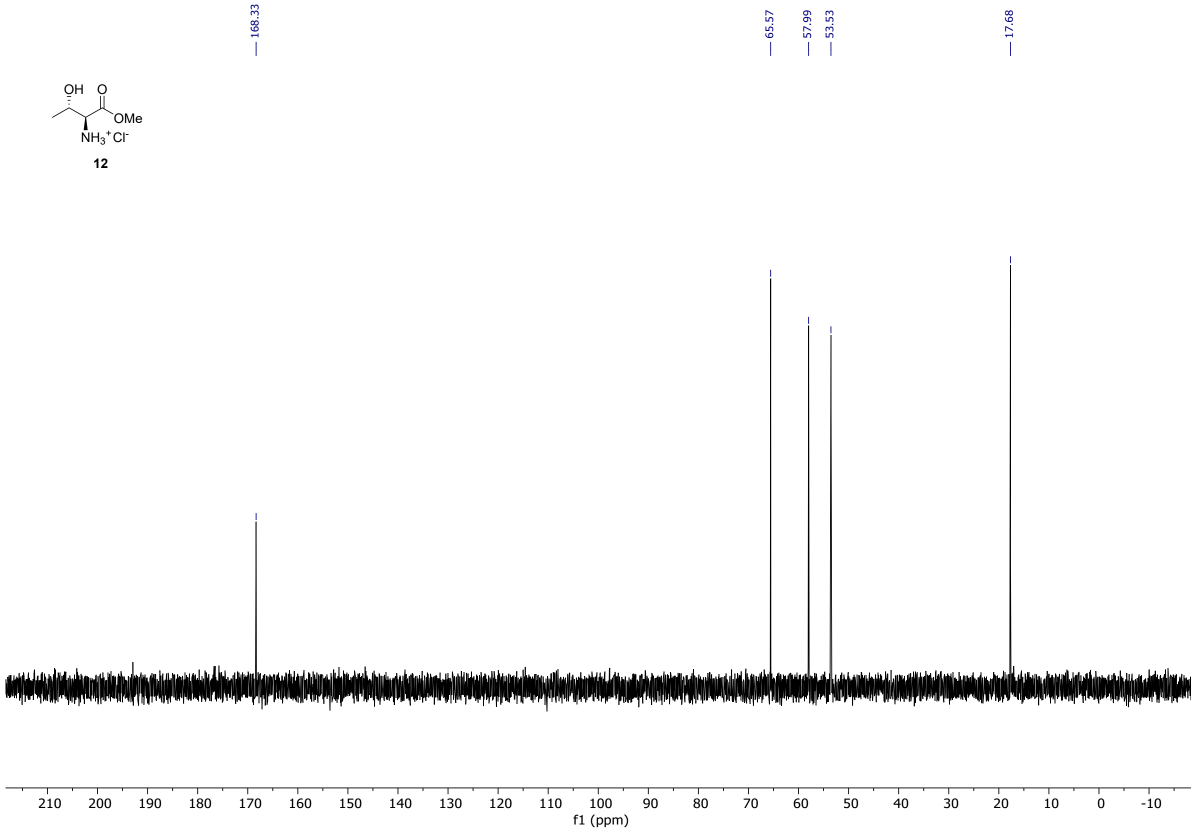

7.99
7.99
7.98
7.98
7.97
7.97
7.51
7.50
7.50
7.49
7.49
7.49
7.48
7.47
7.47
7.42
7.42
7.42
7.41
7.41
7.40
7.39
7.39
7.39
7.39
7.26 CDCl3
5.10
5.09
5.08
5.08
5.07
5.07
5.06
5.06
5.05
5.05
5.04
5.04
4.99
4.97
3.77
1.39
1.37
O
O
N
Ph
OMe
10
2.01
1.03
2.02
1.02
1.02
3.02
3.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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
0.5
0.0
f1 (ppm)

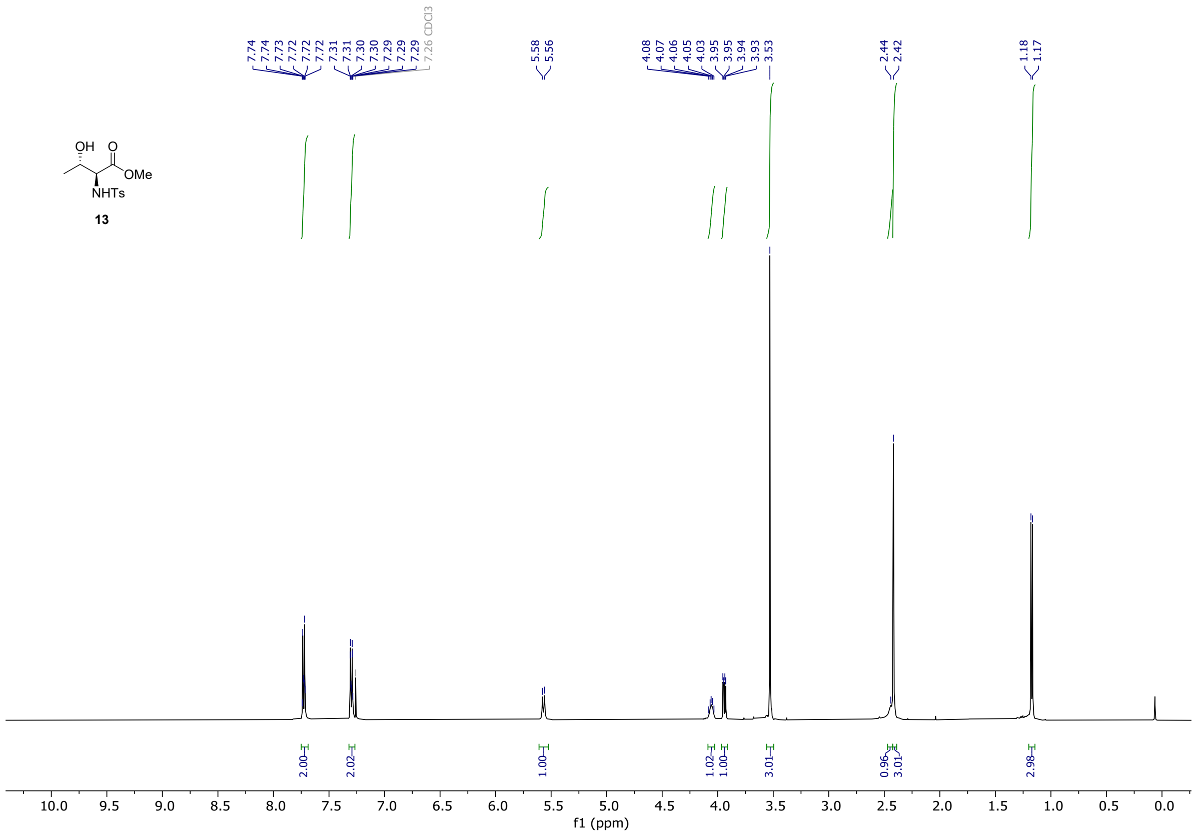

170.55
166.28
131.92
128.66
128.44
127.36
77.77
77.16 CDCl3
71.89
52.22
16.36
O
O
N
Ph
OMe
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

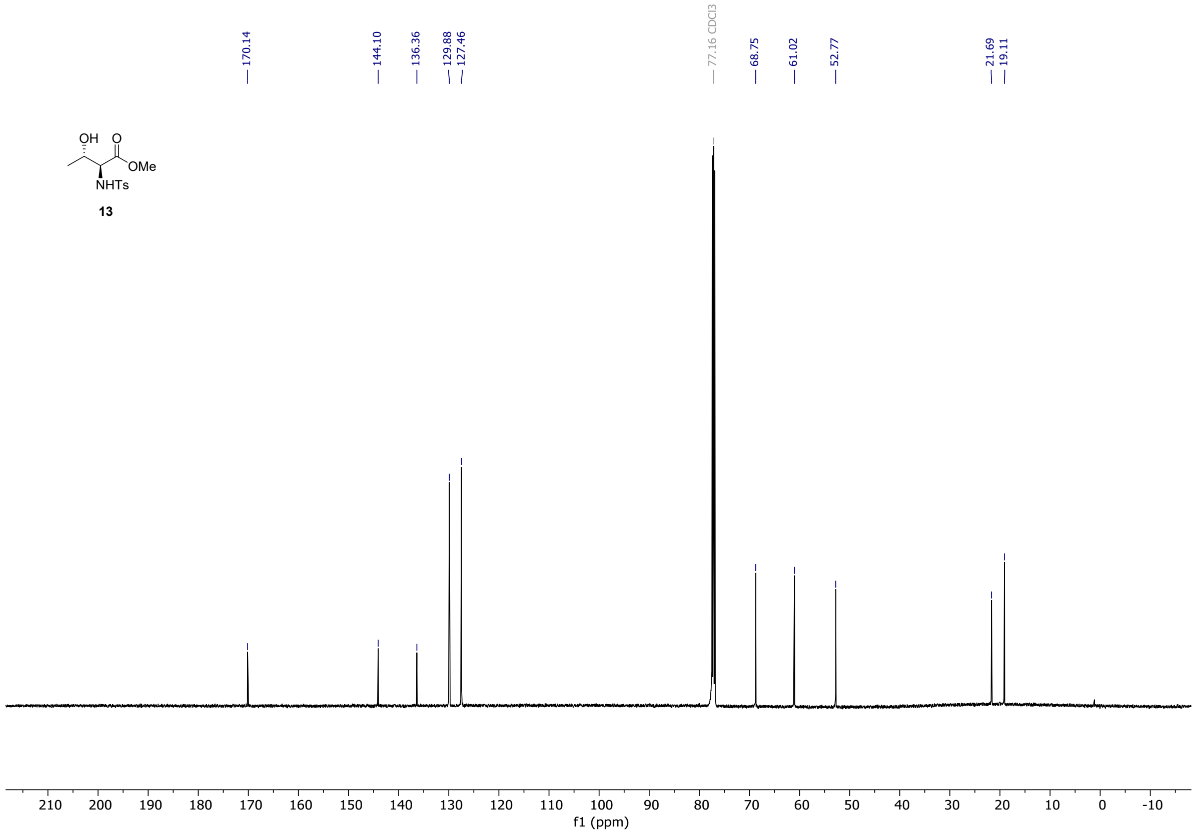

4.79 D2O
4.39
4.38
4.38
4.37
4.36
4.36
4.35
4.34
4.12
4.11
1.31
1.30
HO
O
OH
Cl⁻ H3⁺N
11
1.02
1.00
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

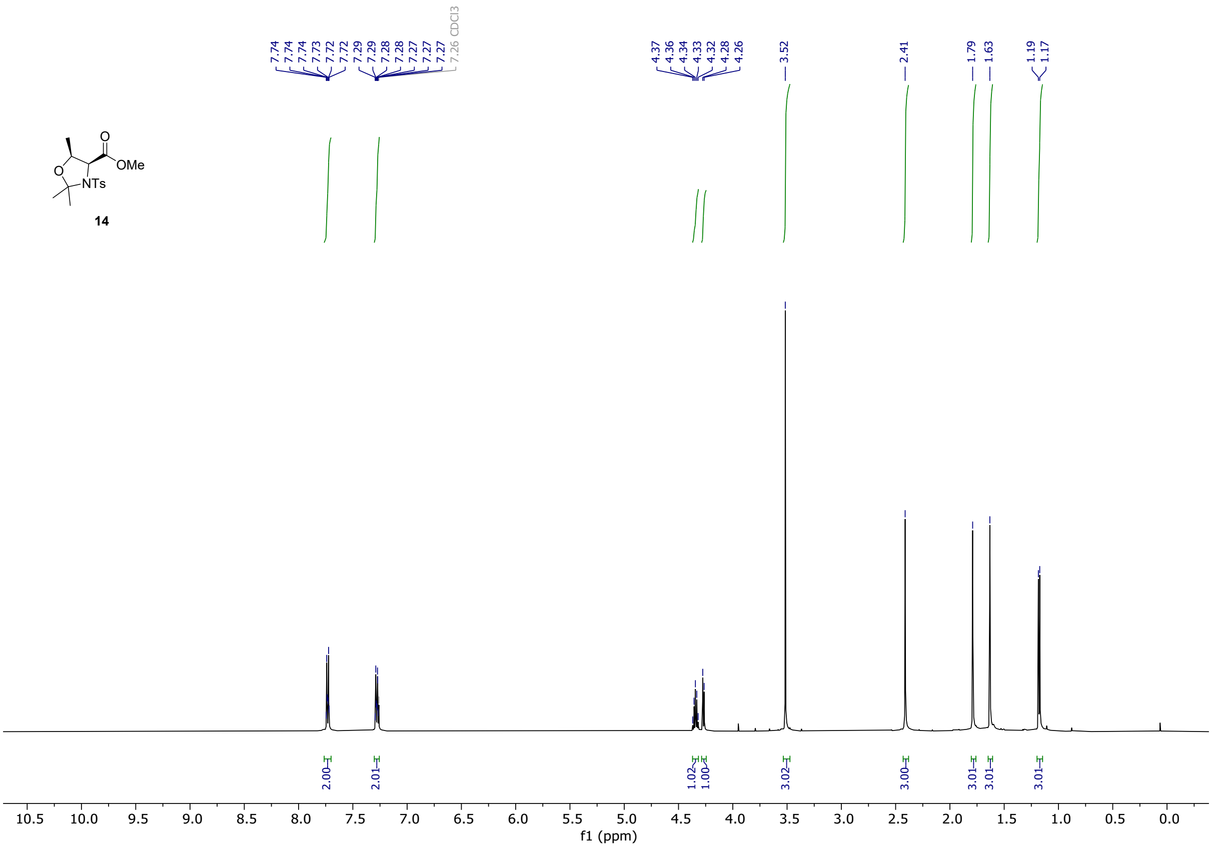

169.73
65.34
58.10
17.22
HO
O
OH
Cl⁻ H3⁺N
11
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


12
4.79 D2O
4.39
4.38
4.37
4.37
4.36
4.34
4.24
4.24
4.23
3.89
1.33
1.32
OH
O
OMe
NH3+ Cl-
1.01
1.00
3.01
0.19
3.01
10.5
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
0.5
0.0
f1 (ppm)

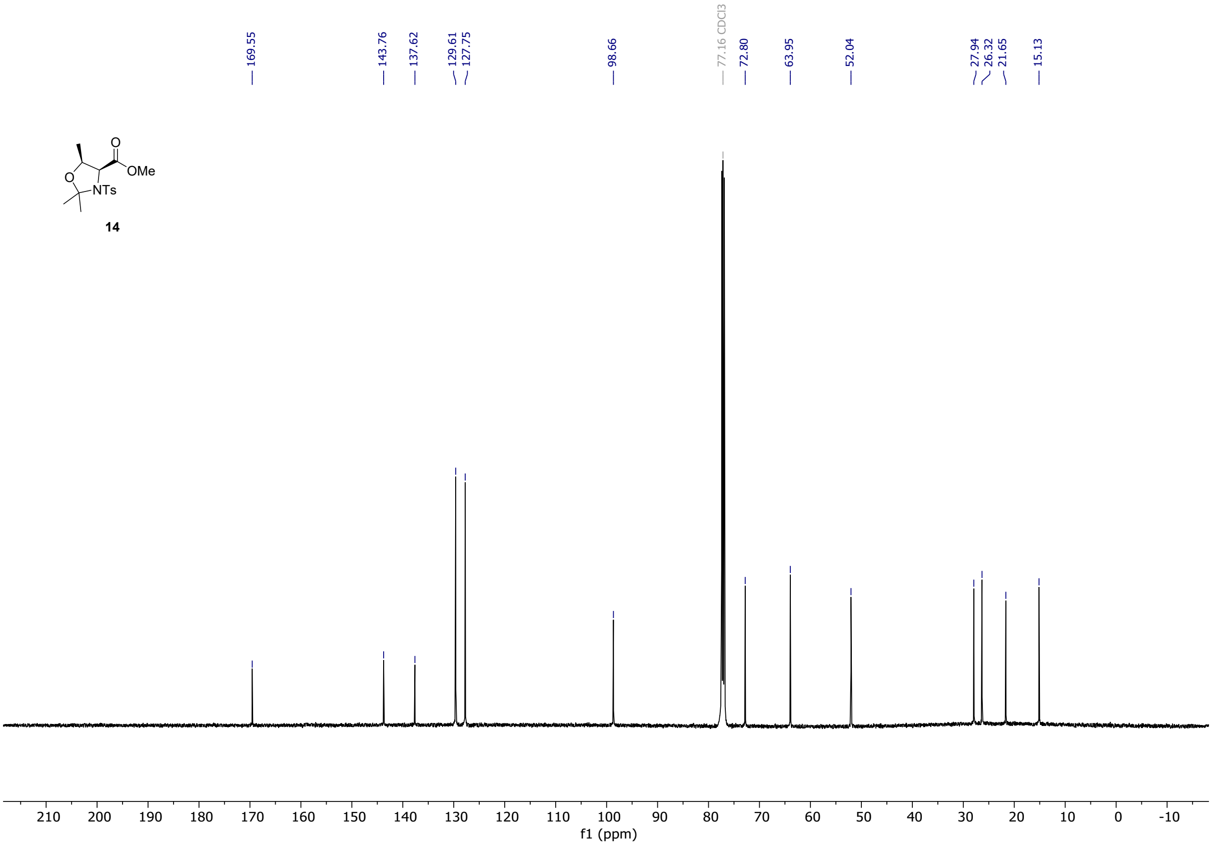

12
168.33
65.57
57.99
53.53
17.68
OH
O
OMe
NH3+ Cl-
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.74
7.74
7.73
7.72
7.72
7.72
7.31
7.31
7.30
7.30
7.29
7.29
7.29
7.26 CDCl3
5.58
5.56
4.08
4.07
4.06
4.05
4.03
3.95
3.95
3.94
3.93
3.53
2.44
2.42
1.18
1.17
OH
O
OMe
NHTs
13
2.00
2.02
1.00
1.02
1.00
3.01
0.96
3.01
2.98
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
0.5
0.0
f1 (ppm)

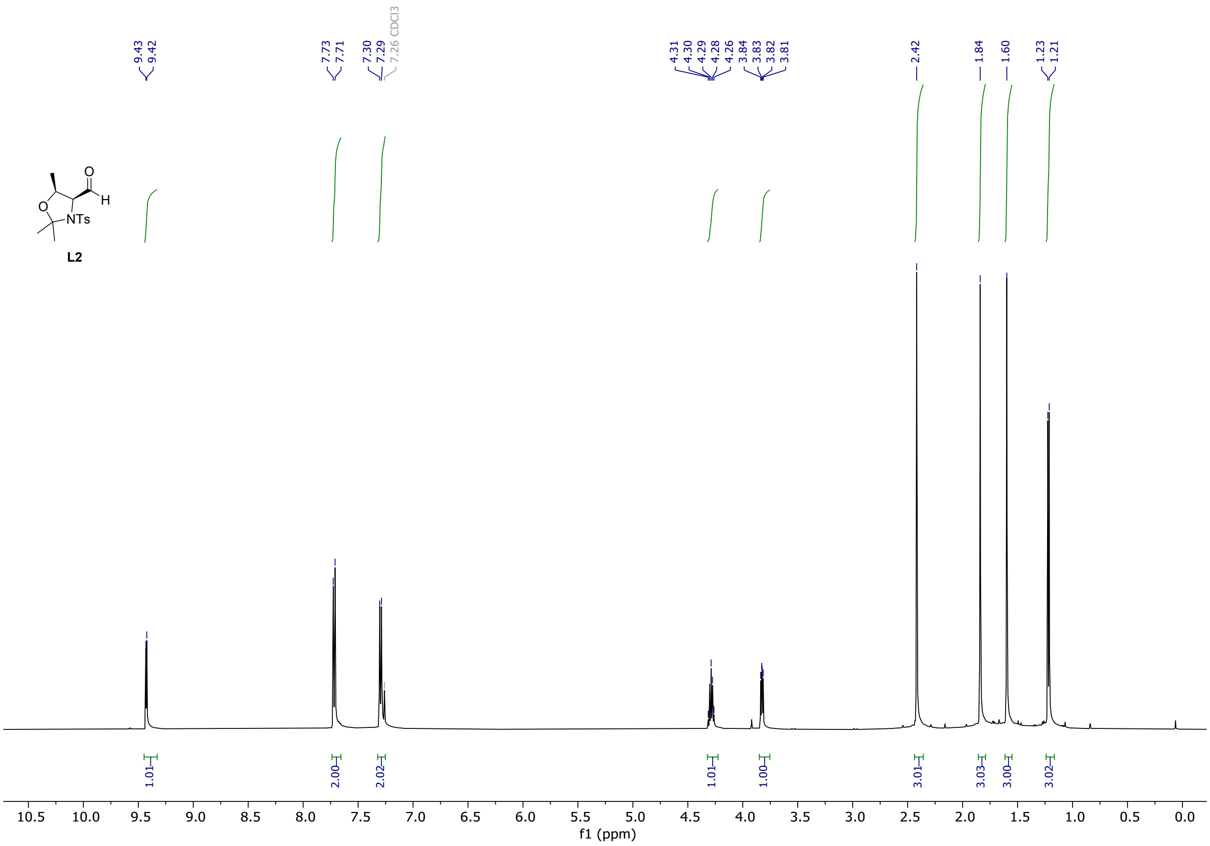

170.14
144.10
136.36
129.88
127.46
77.16 CDCl3
68.75
61.02
52.77
21.69
19.11
OH
O
OMe
NHTs
13
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

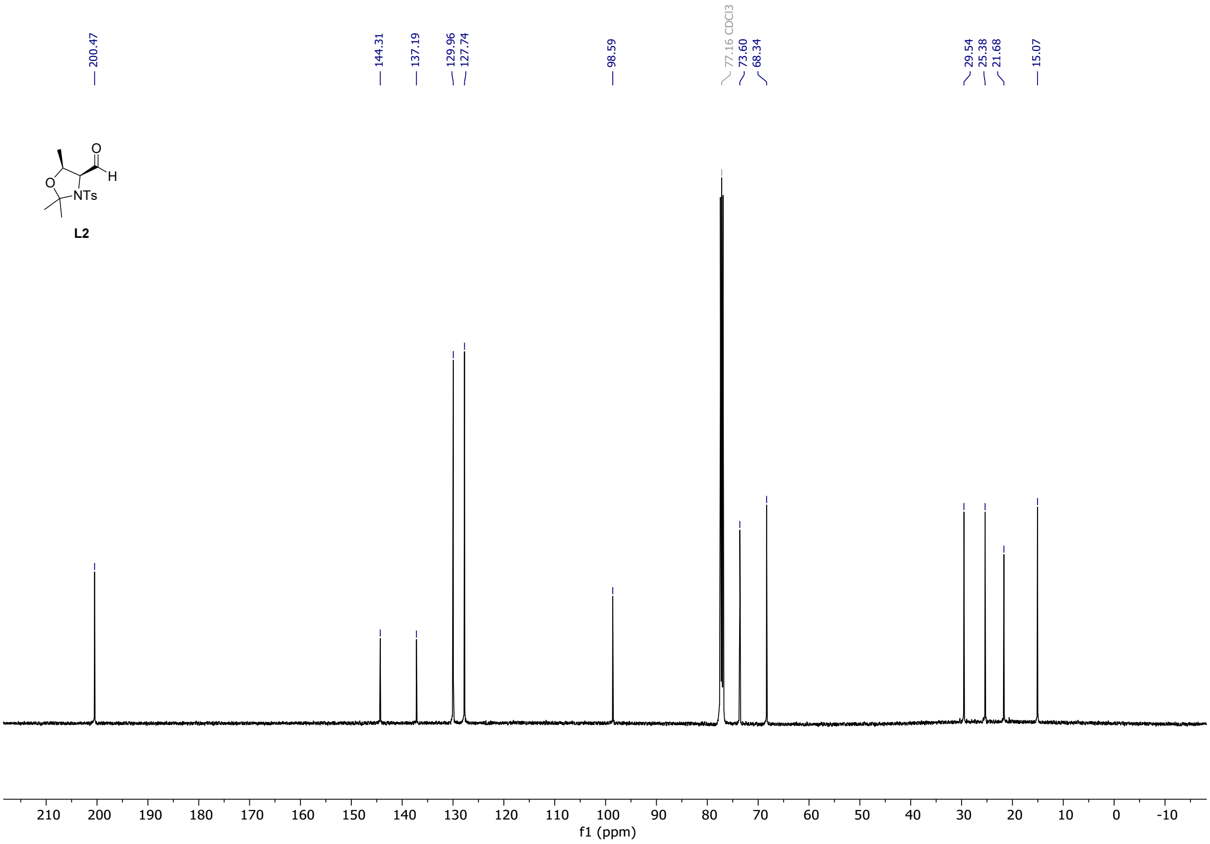

O
OMe
O
NTs
7.74
7.74
7.74
7.73
7.72
7.72
7.29
7.29
7.28
7.28
7.27
7.27
7.27
7.26 CDCl3
4.37
4.36
4.34
4.33
4.32
4.28
4.26
3.52
2.41
1.79
1.63
1.19
1.17
2.00
2.01
1.02
1.00
3.02
3.00
3.01
3.01
3.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

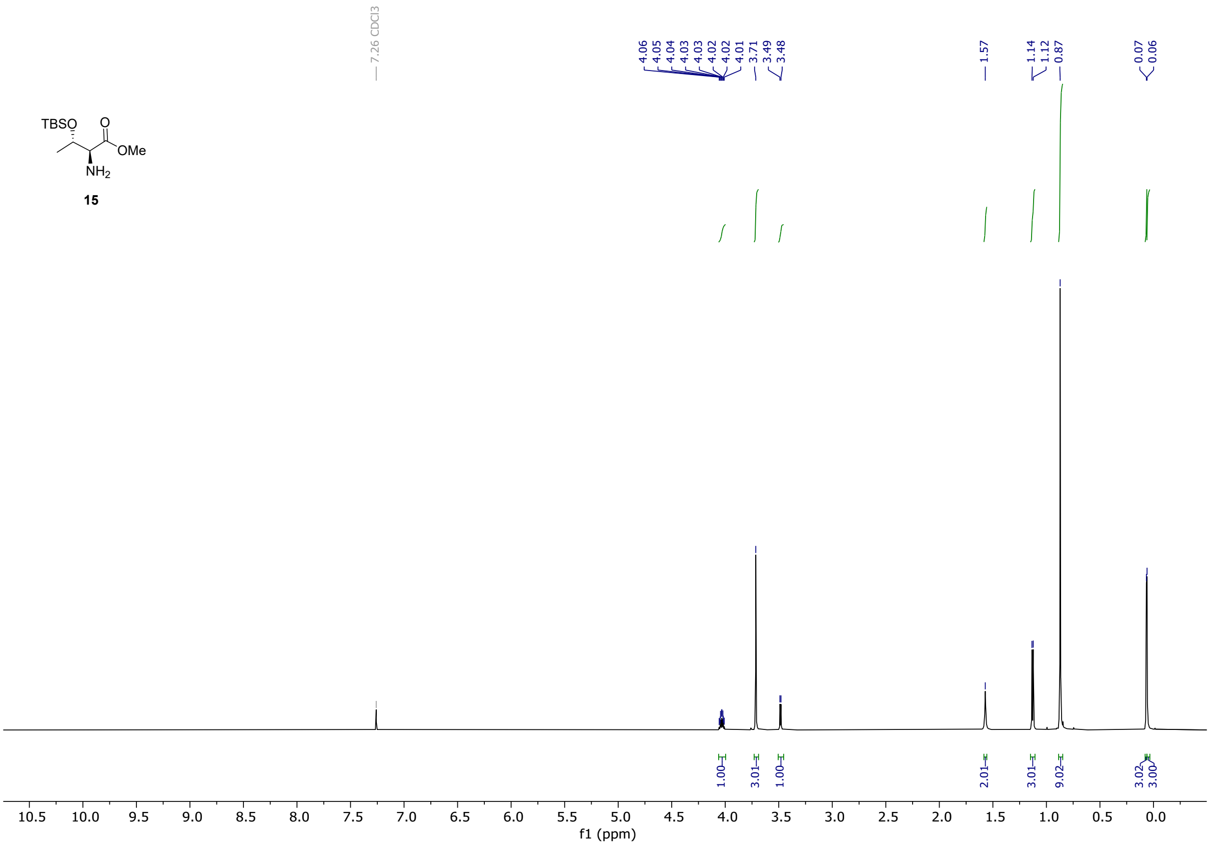
14

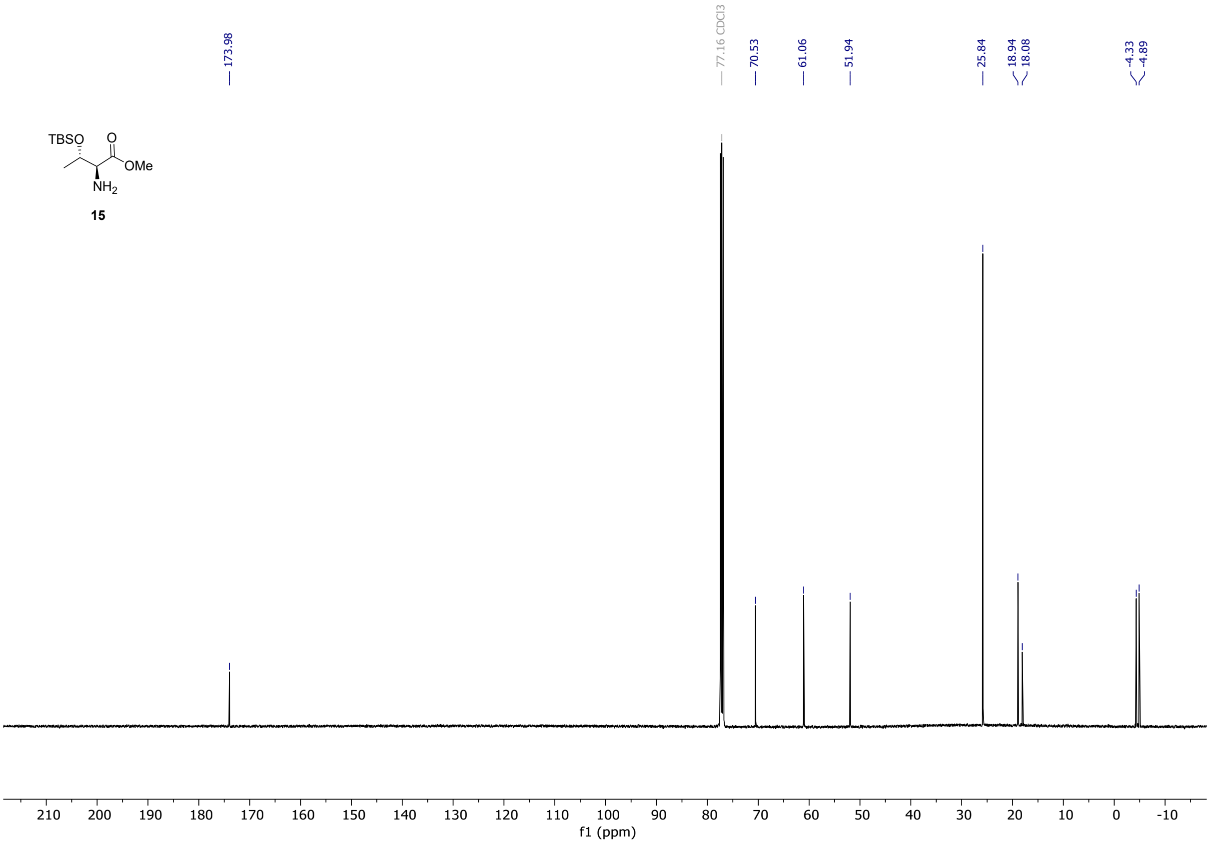

O
OMe
O
NTs
169.55
143.76
137.62
129.61
127.75
98.66
77.16 CDCl3
72.80
63.95
52.04
27.94
26.32
21.65
15.13
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

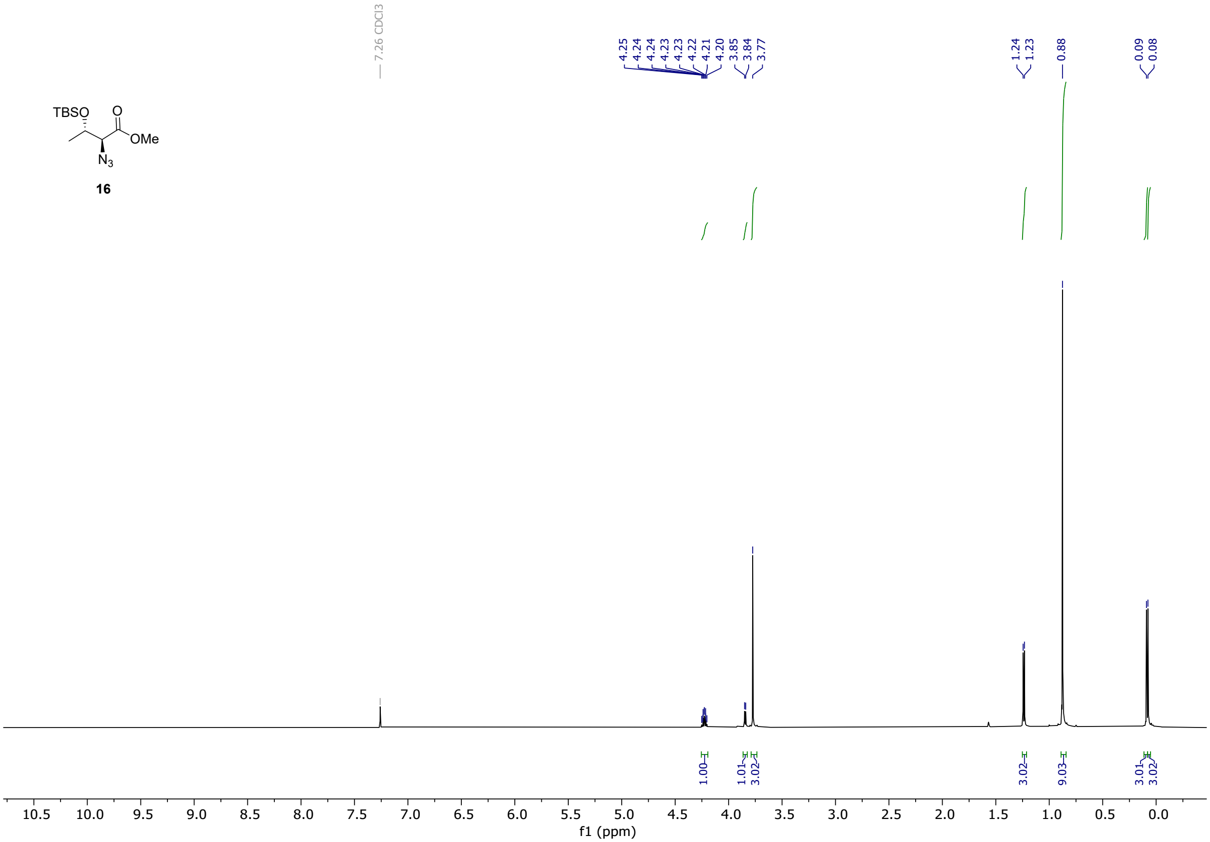
14

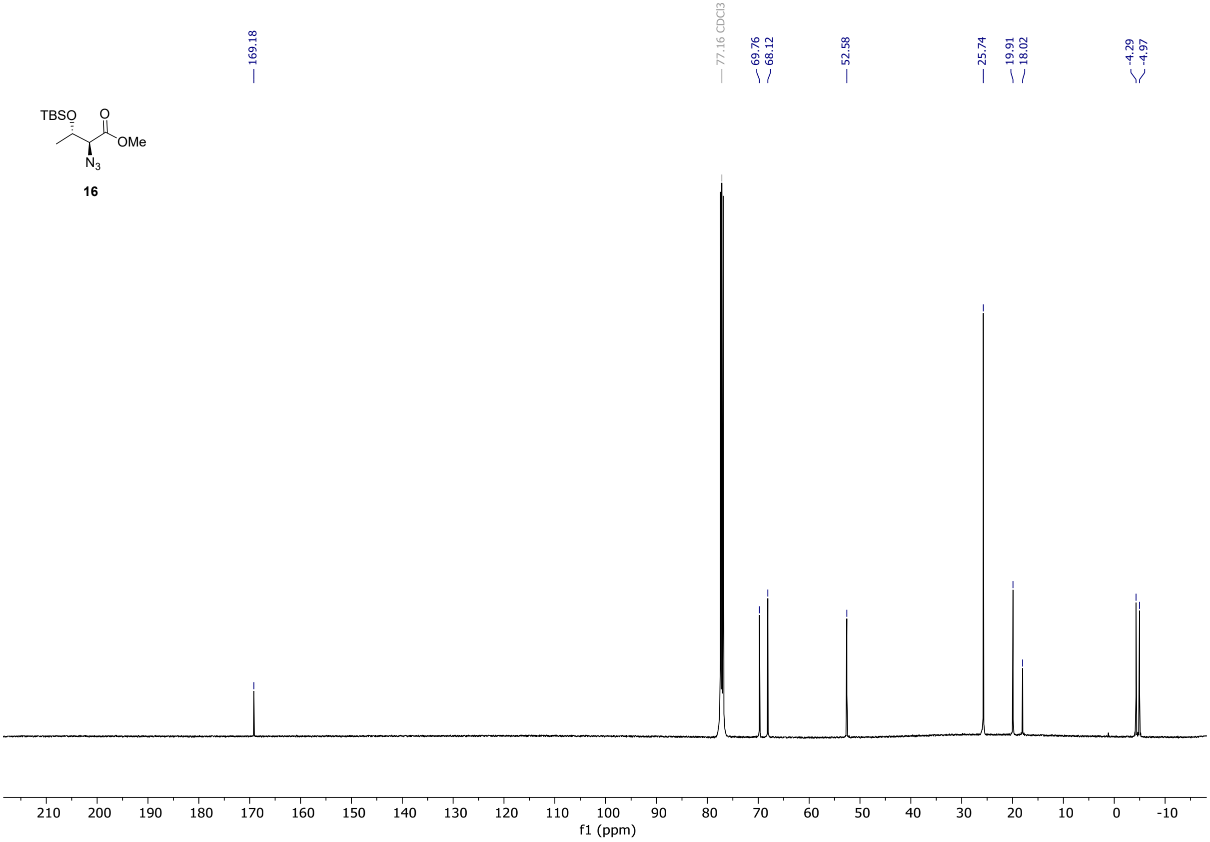

9.43
9.42
7.73
7.71
7.30
7.29
7.26 CDCl3
4.31
4.30
4.29
4.28
4.26
3.84
3.83
3.82
3.81
2.42
1.84
1.60
1.23
1.21
O
H
O
NTs
L2
1.01
2.00
2.02
1.01
1.00
3.01
3.03
3.00
3.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

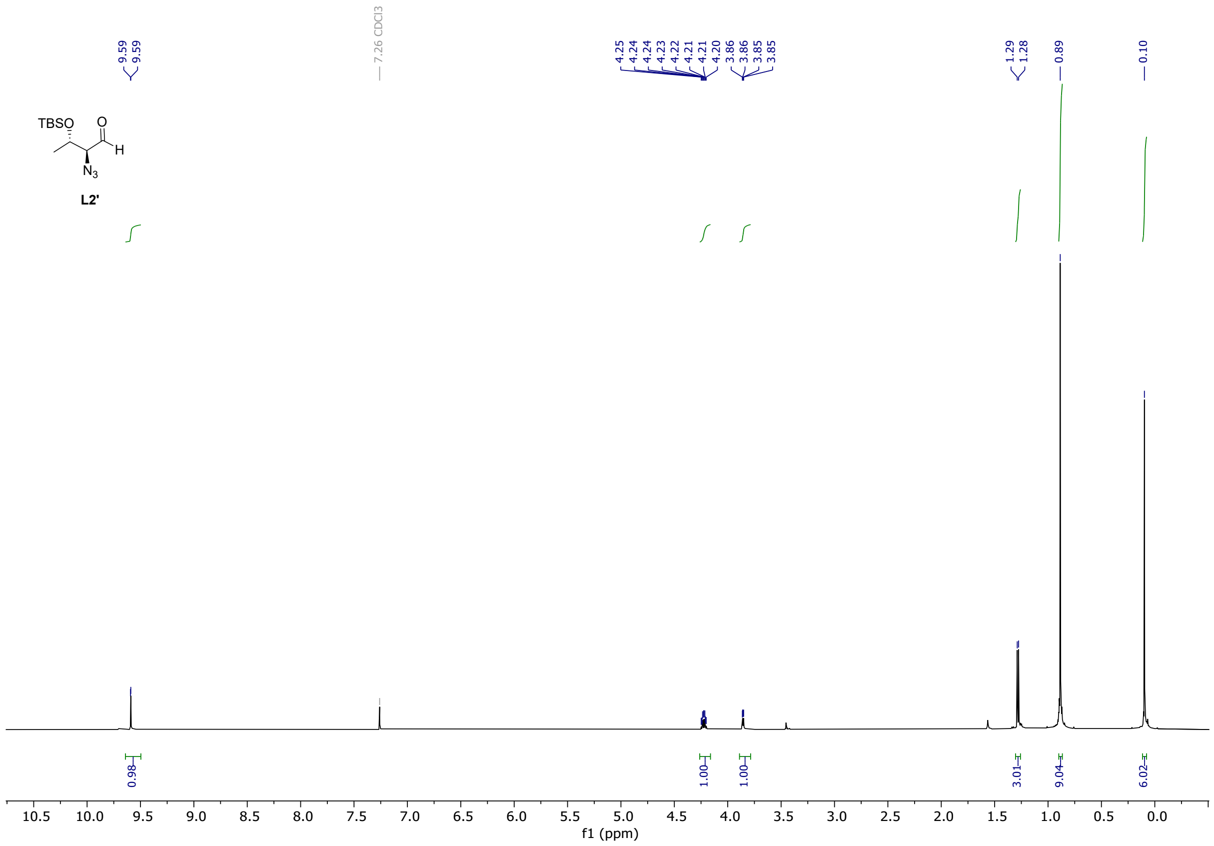

200.47
144.31
137.19
129.96
127.74
98.59
77.16 CDCl3
73.60
68.34
29.54
25.38
21.68
15.07
O
H
O
NTs
L2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

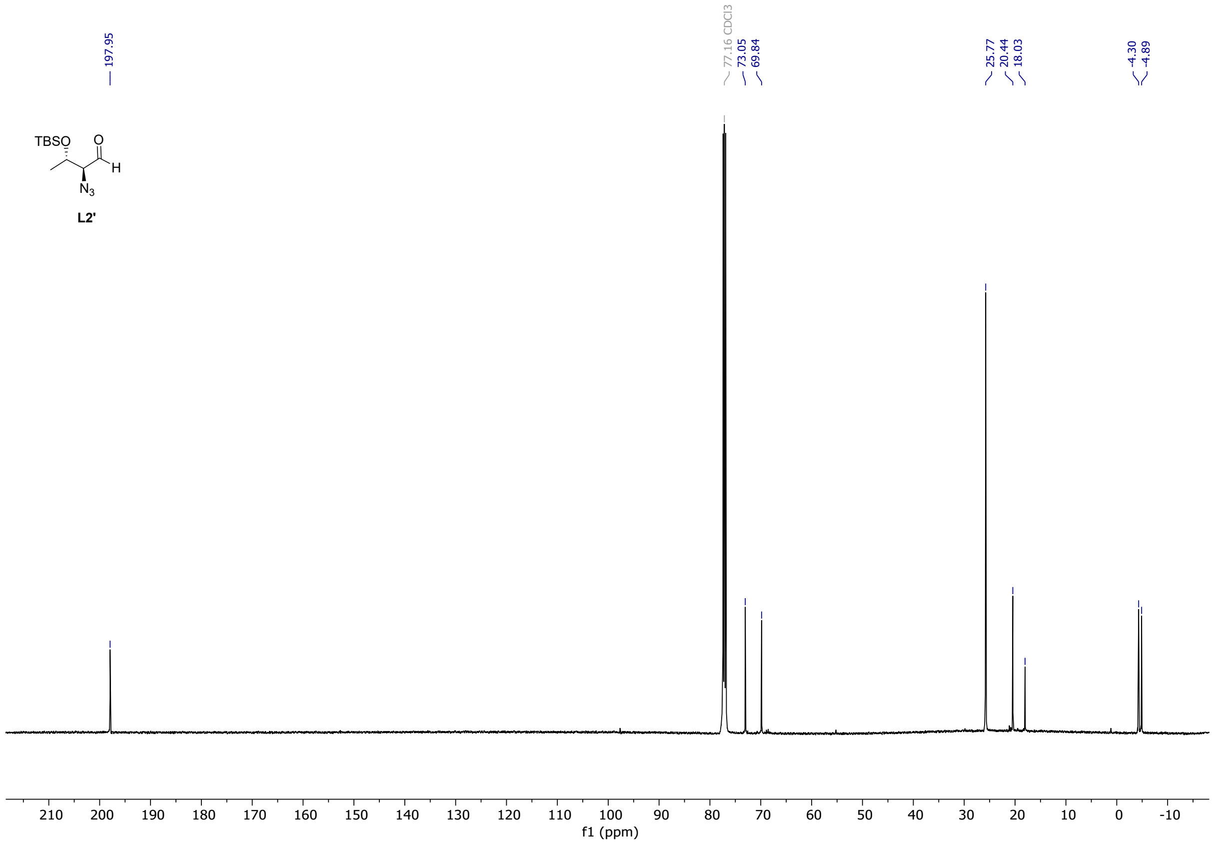

TBSO
O
OMe
NH2
15
7.26 CDCl3
4.06
4.05
4.04
4.03
4.03
4.02
4.02
4.01
3.71
3.49
3.48
1.57
1.14
1.12
0.87
0.07
0.06
1.00
3.01
1.00
2.01
3.01
9.02
3.02
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

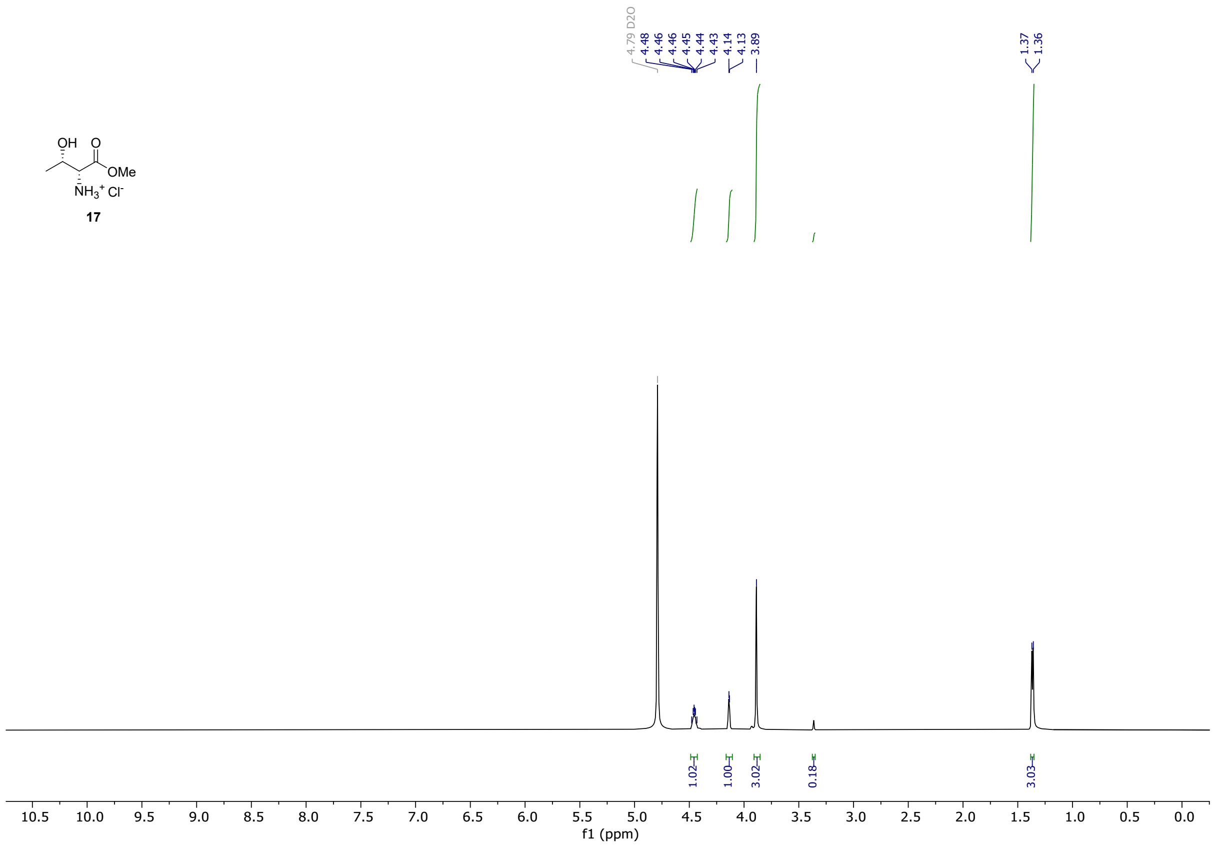

TBSO
O
OMe
NH2
15
173.98
77.16 CDCl3
70.53
61.06
51.94
25.84
18.94
18.08
-4.33
-4.89
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TBSO
O
OMe
N3
16
7.26 CDCl3
4.25
4.24
4.24
4.23
4.23
4.22
4.21
4.20
3.85
3.84
3.77
1.24
1.23
0.88
0.09
0.08
1.00
1.01
3.02
3.02
9.03
3.01
3.02
10.5
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
0.5
0.0
f1 (ppm)

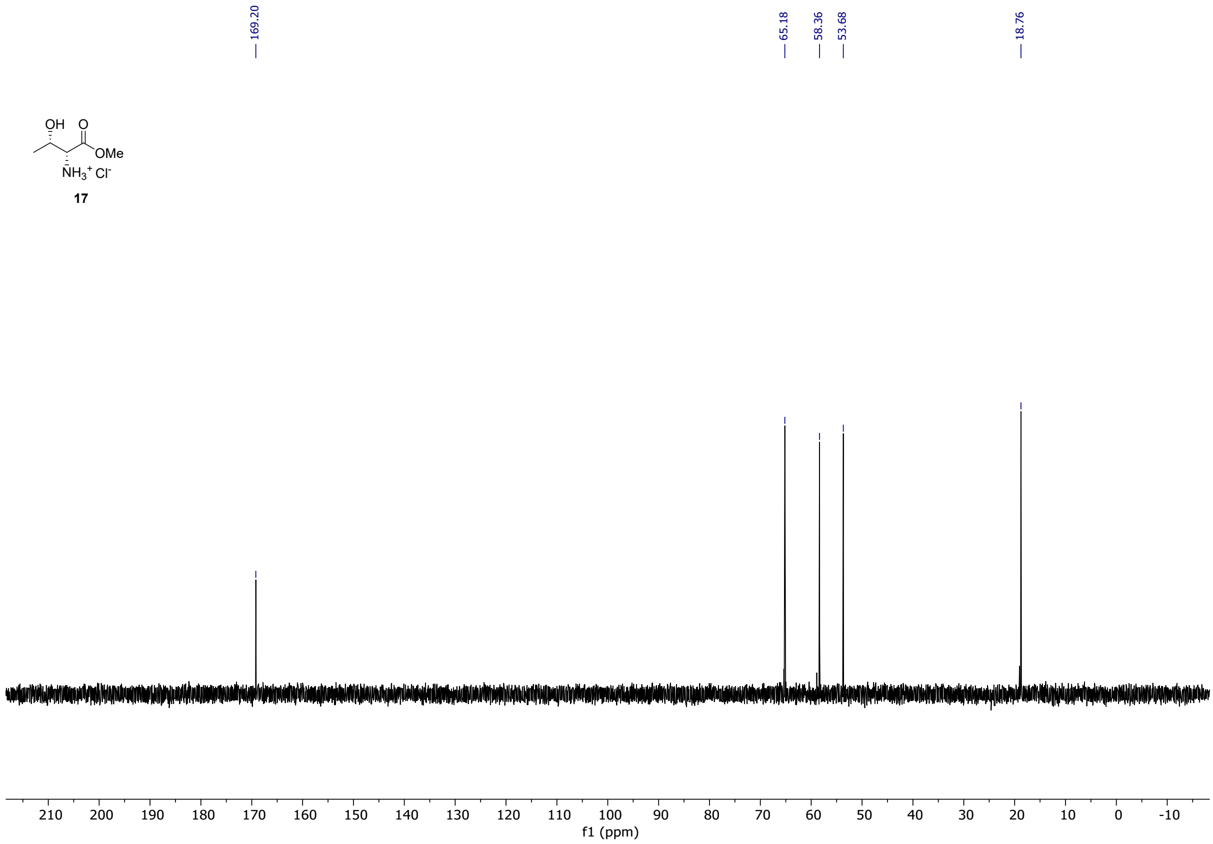

TBSO
O
OMe
N3
16
169.18
77.16 CDCl3
69.76
68.12
52.58
25.74
19.91
18.02
-4.29
-4.97
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


9.59
9.59
7.26 CDCl3
4.25
4.24
4.24
4.23
4.22
4.21
4.21
4.20
3.86
3.86
3.85
3.85
1.29
1.28
0.89
0.10
TBSO
O
H
N3
L2'
0.98
1.00
1.00
3.01
9.04
6.02
10.5 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 0.5 0.0
f1 (ppm)

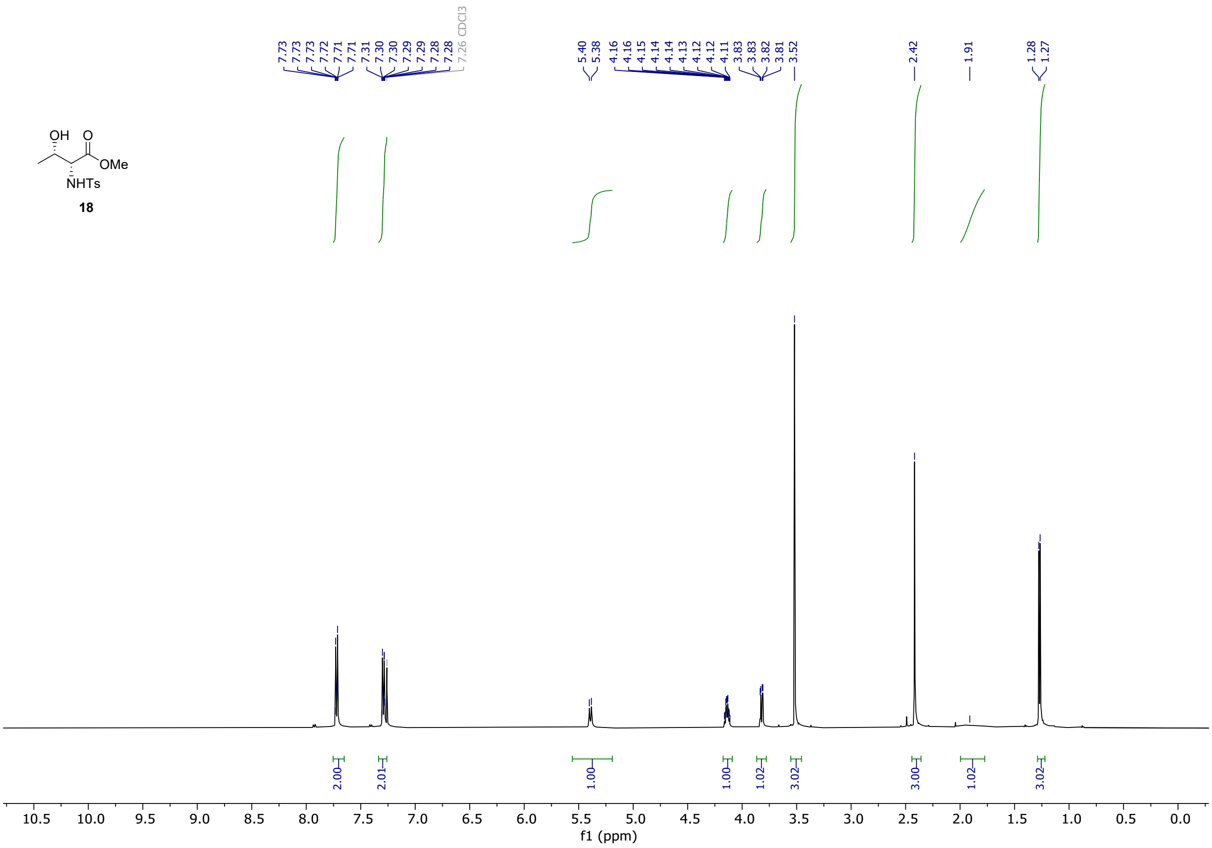

197.95
77.16 CDCl3
73.05
69.84
25.77
20.44
18.03
-4.30
-4.89
TBSO
O
H
N3
L2'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

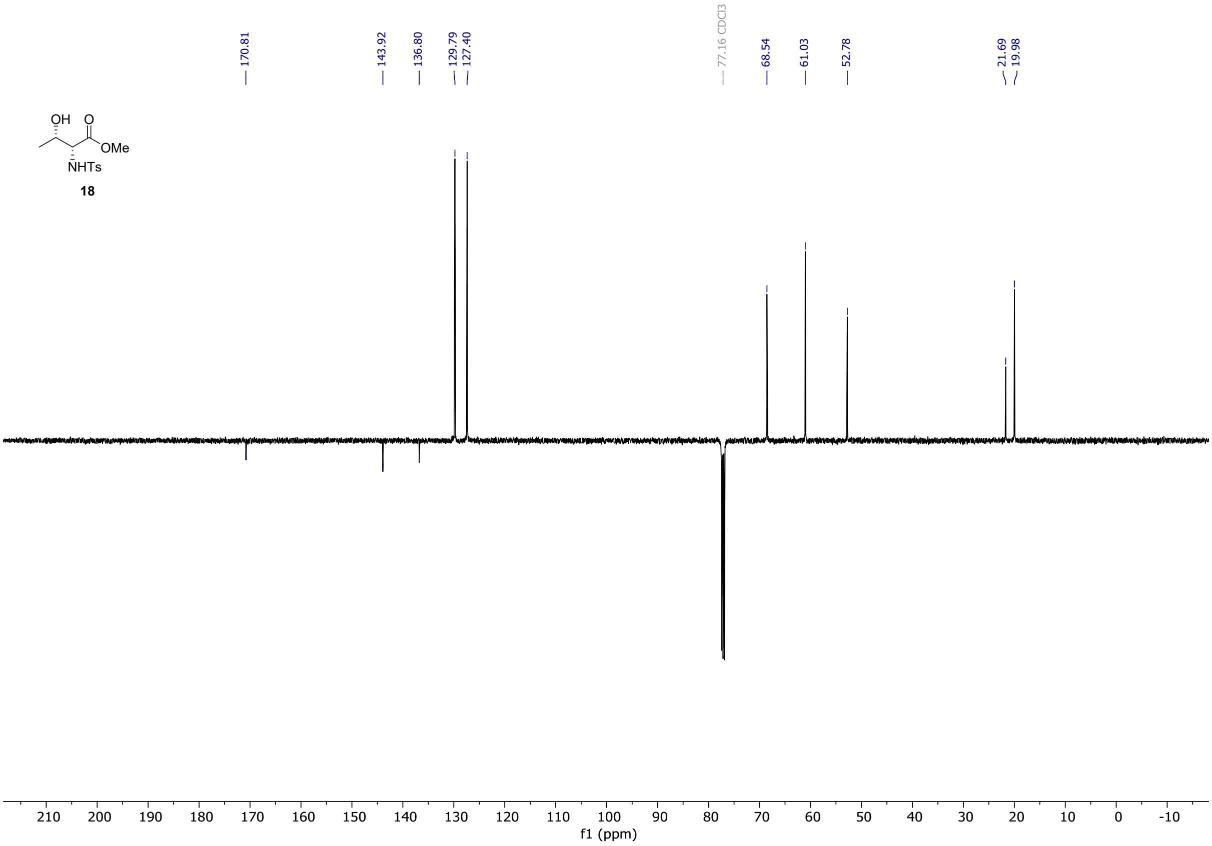


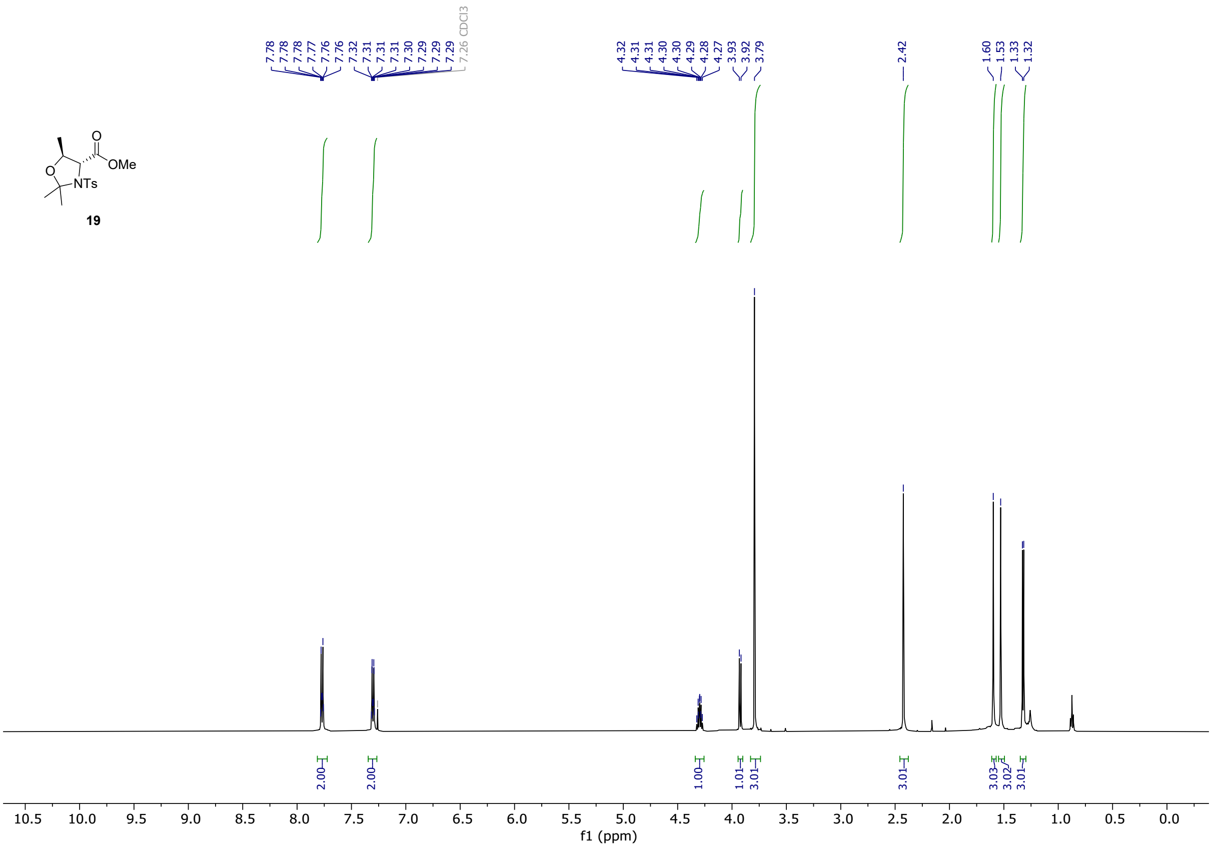
OH
O
OMe
NH3+ Cl-
17
4.79 D2O
4.48
4.46
4.46
4.45
4.44
4.43
4.14
4.13
3.89
1.37
1.36
1.02
1.00
3.02
0.18
3.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

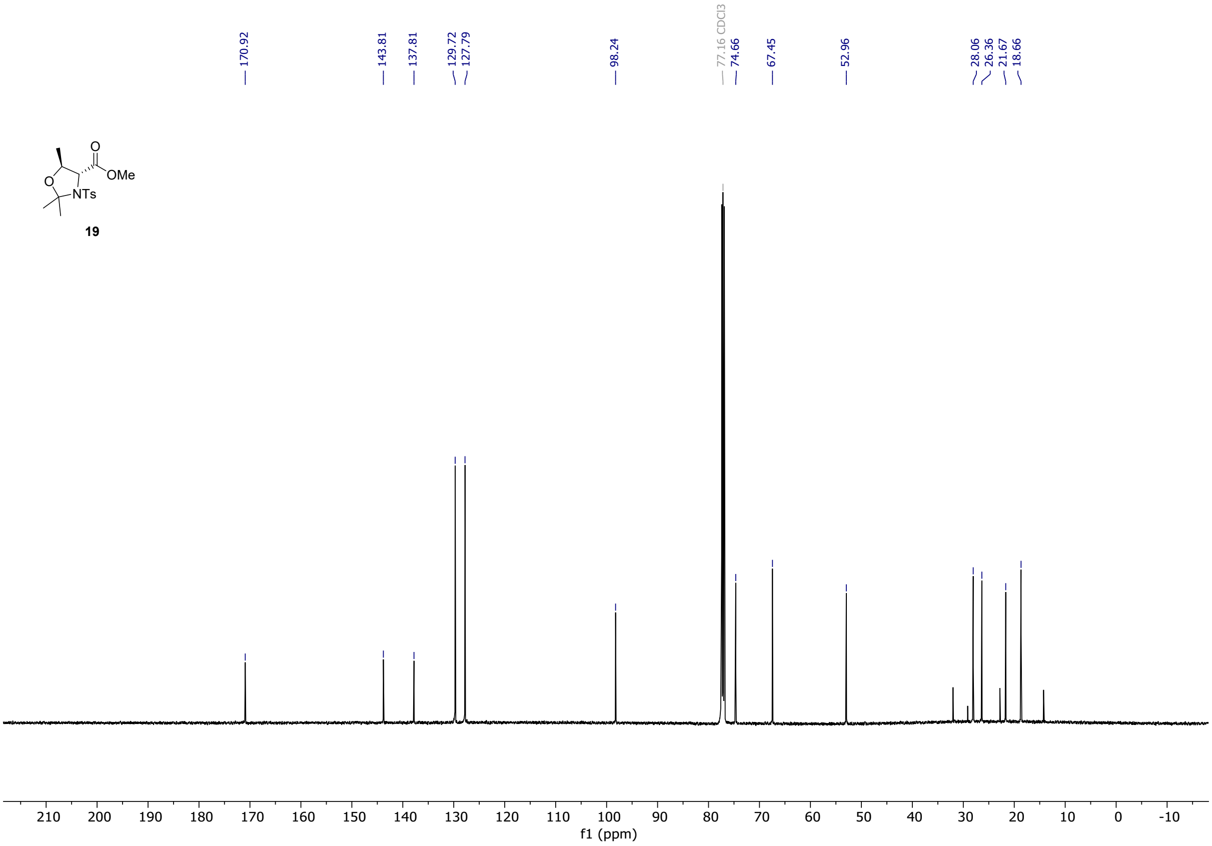


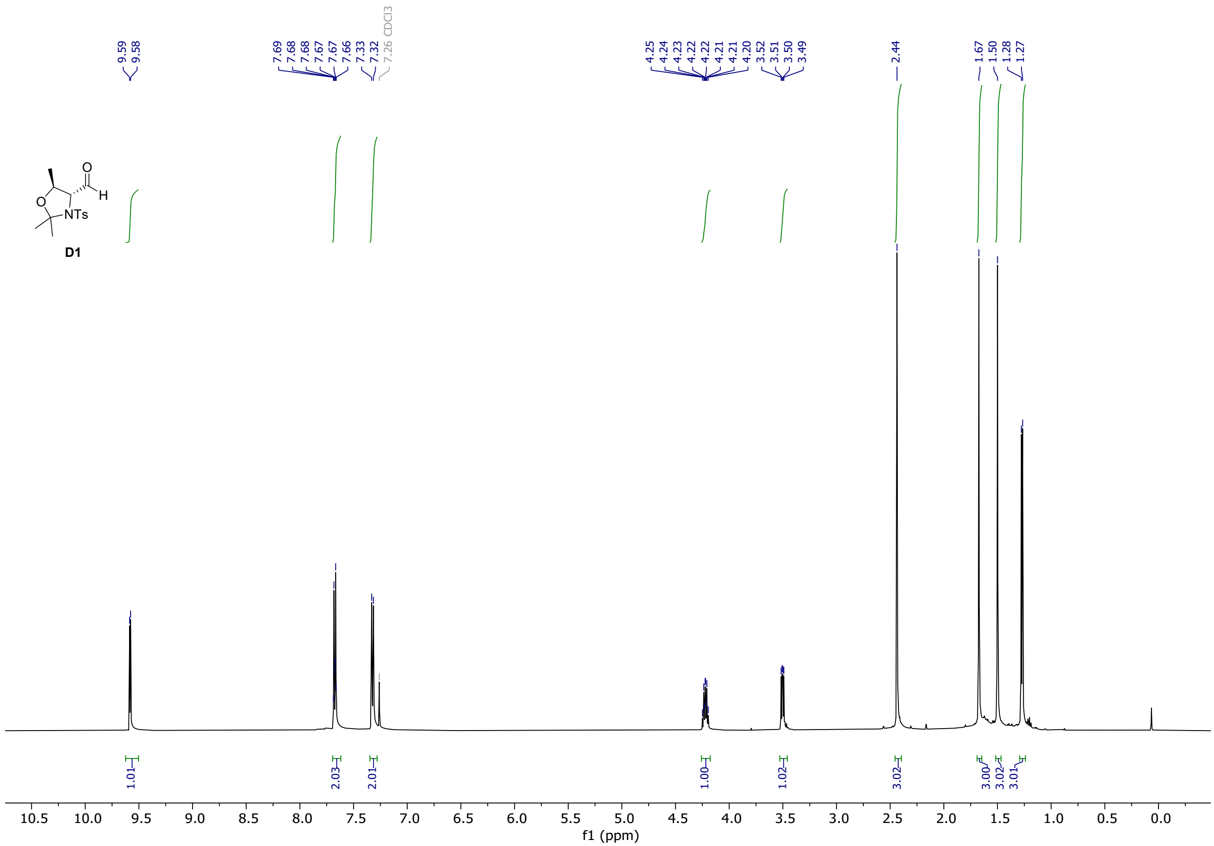
OH
O
OMe
NH3+ Cl-
17
169.20
65.18
58.36
53.68
18.76
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

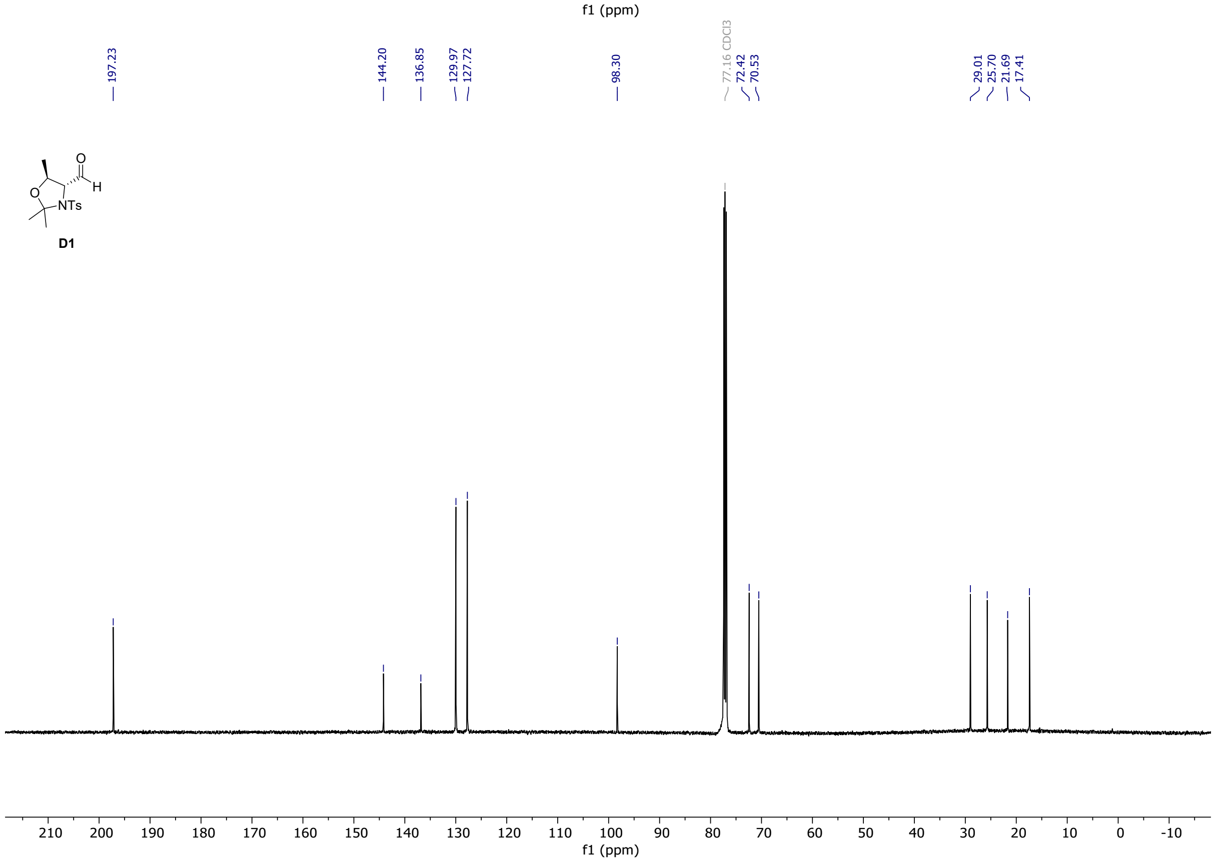

7.73
7.73
7.73
7.72
7.71
7.71
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.26 CDCl3
5.40
5.38
4.16
4.16
4.15
4.14
4.14
4.13
4.12
4.12
4.11
3.83
3.83
3.82
3.81
3.52
2.42
1.91
1.28
1.27
OH
O
OMe
NHTs
18
2.00
2.01
1.00
1.00
1.02
3.02
3.00
1.02
3.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

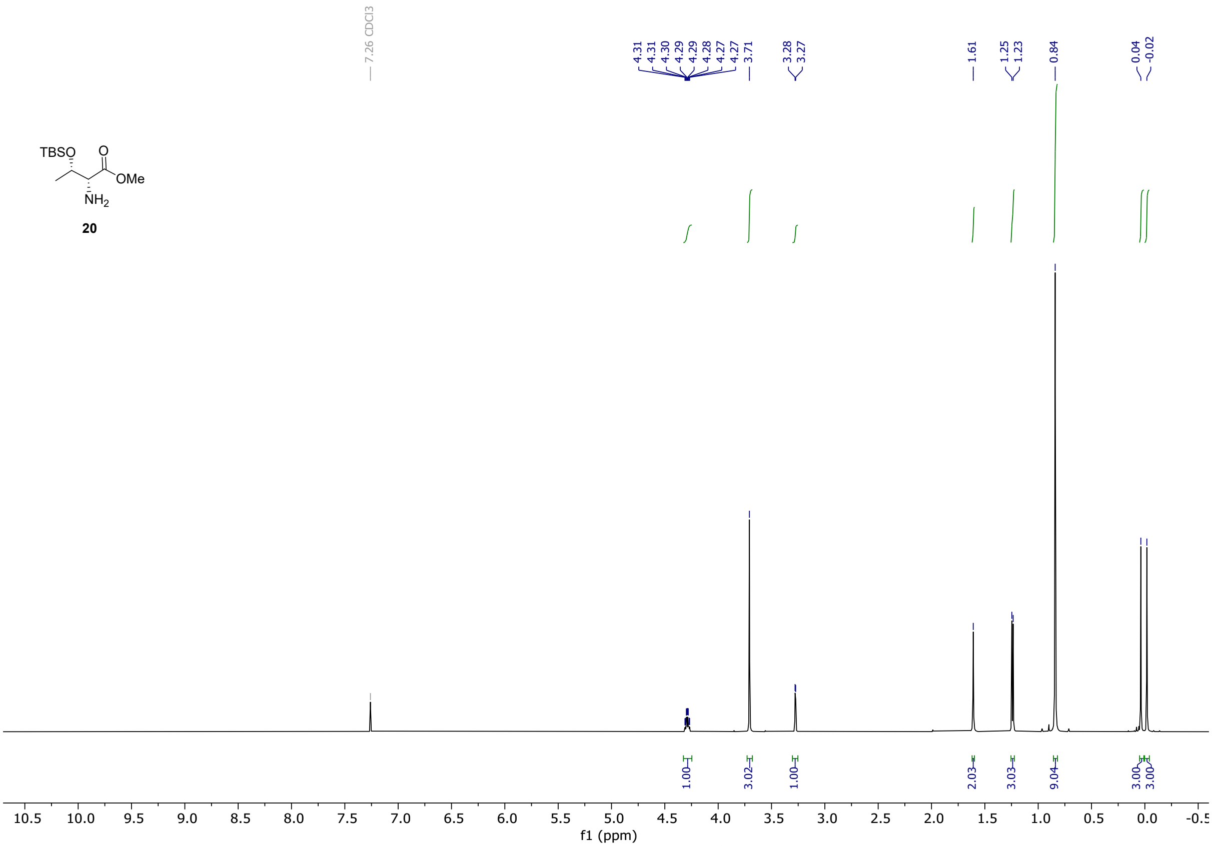

170.81
143.92
136.80
129.79
127.40
77.16 CDCl3
68.54
61.03
52.78
21.69
19.98
OH
O
OMe
NHTs
18
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

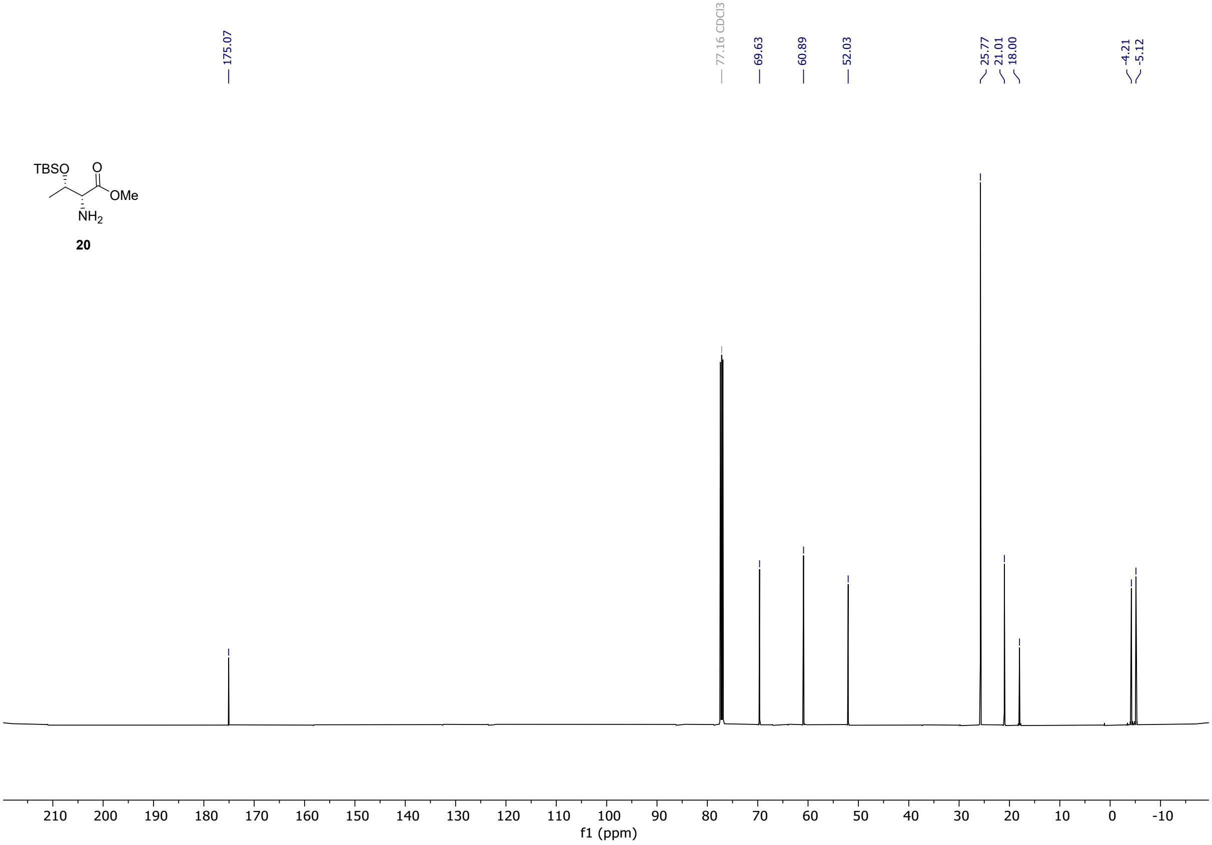

7.78
7.78
7.78
7.77
7.76
7.76
7.32
7.31
7.31
7.31
7.30
7.29
7.29
7.29
7.26 CDCl3
4.32
4.31
4.31
4.30
4.30
4.29
4.28
4.27
3.93
3.92
3.79
2.42
1.60
1.53
1.33
1.32
O
OMe
O
NTs
19
2.00
2.00
1.00
1.01
3.01
3.01
3.03
3.02
3.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

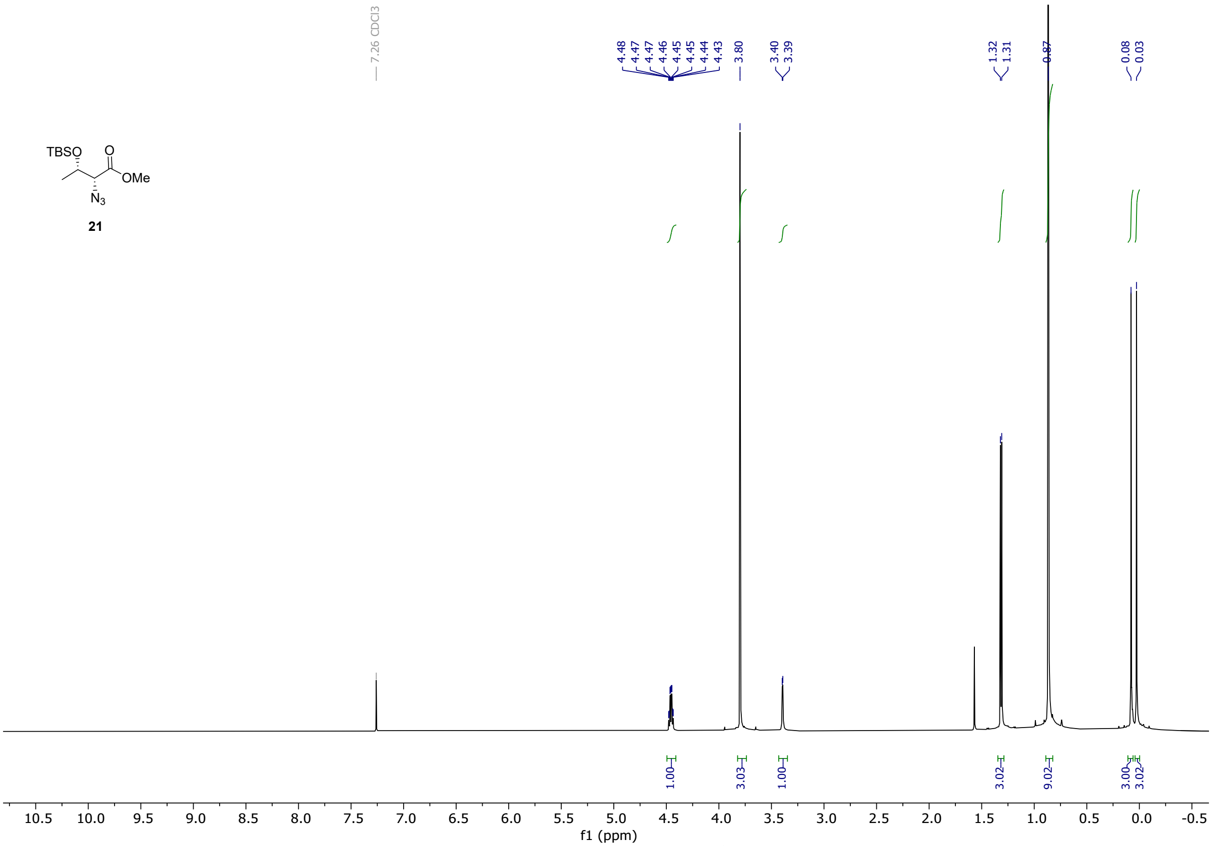

170.92
143.81
137.81
129.72
127.79
98.24
77.16 CDCl3
74.66
67.45
52.96
28.06
26.36
21.67
18.66
O
OMe
O
NTs
19
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

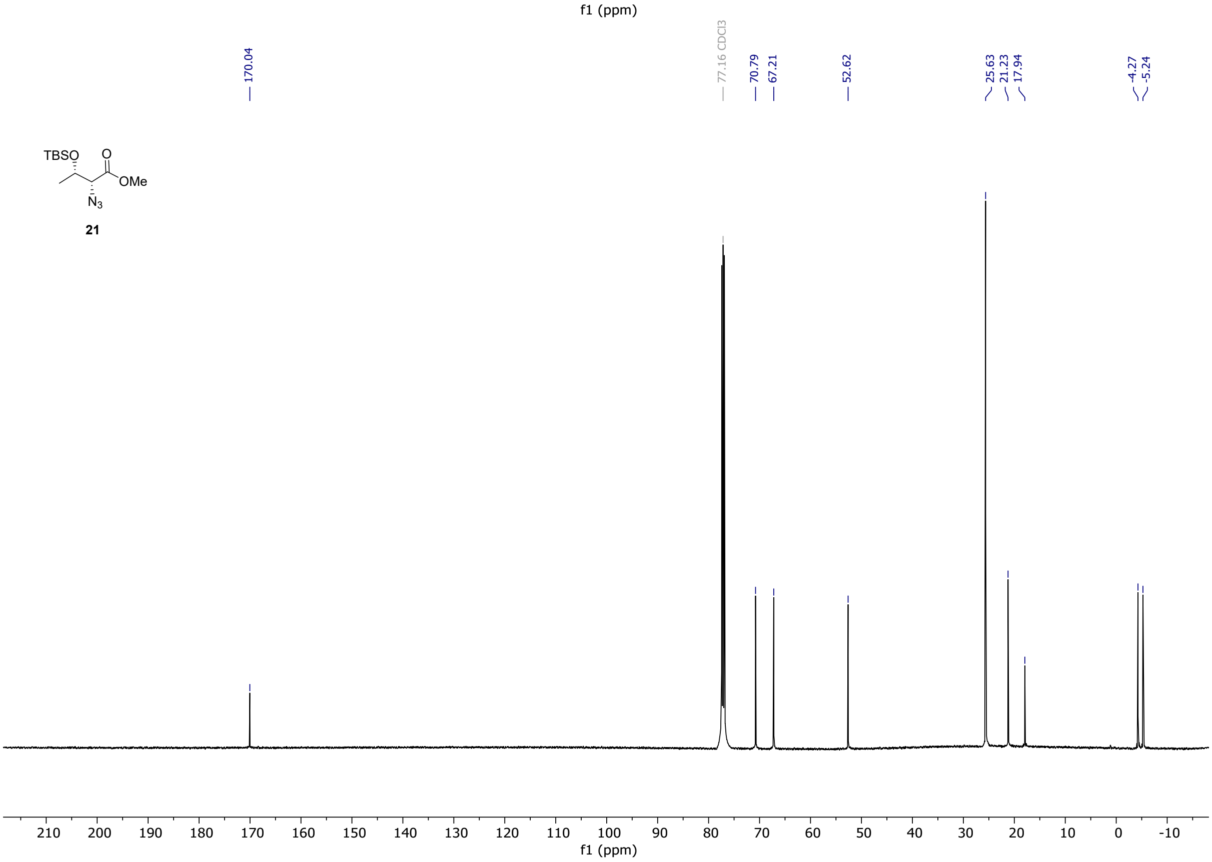

9.59
9.58
7.69
7.68
7.68
7.67
7.67
7.66
7.33
7.32
7.26 CDCl3
4.25
4.24
4.23
4.22
4.22
4.22
4.21
4.21
4.20
3.52
3.51
3.50
3.49
2.44
1.67
1.50
1.28
1.27
O
H
O
NTs
D1
1.01
2.03
2.01
1.00
1.02
3.02
3.00
3.02
3.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

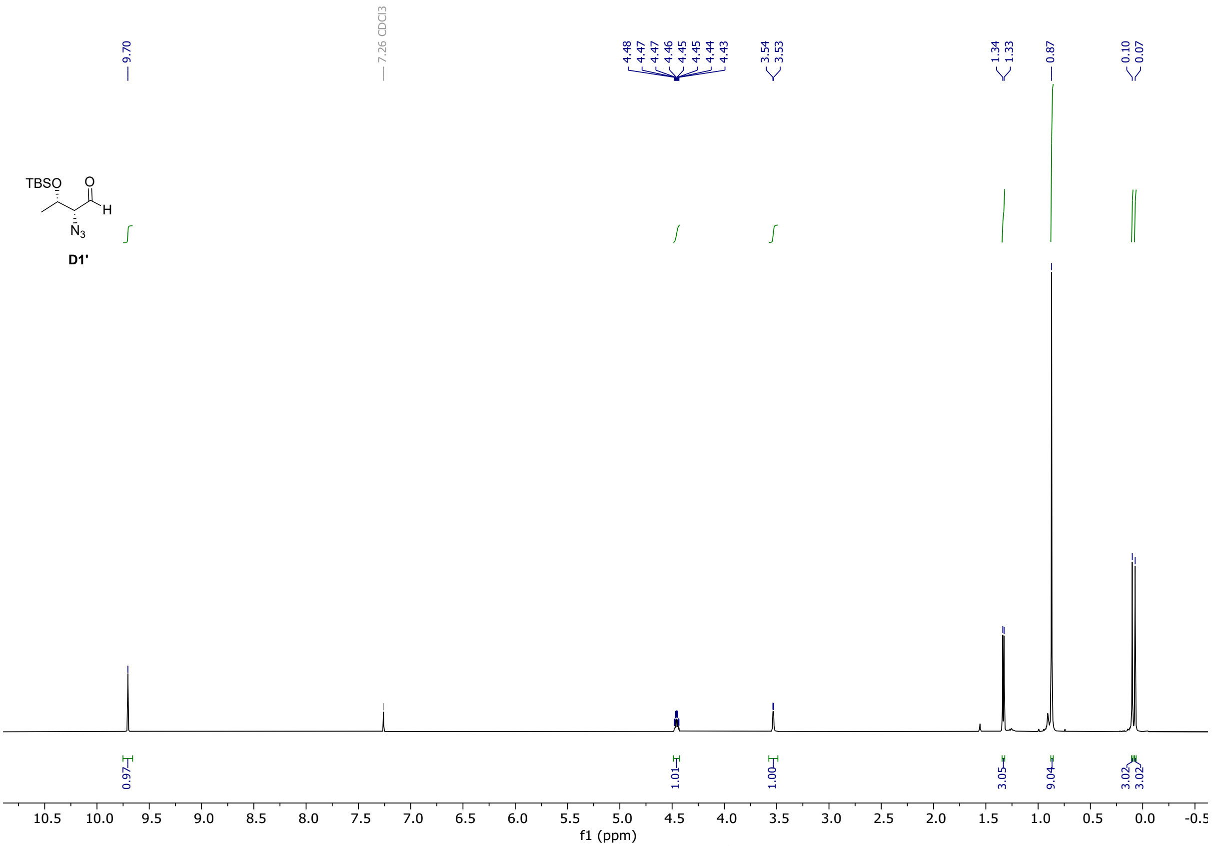

197.23
144.20
136.85
129.97
127.72
98.30
77.16 CDCl3
72.42
70.53
29.01
25.70
21.69
17.41
O
H
O
NTs
D1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

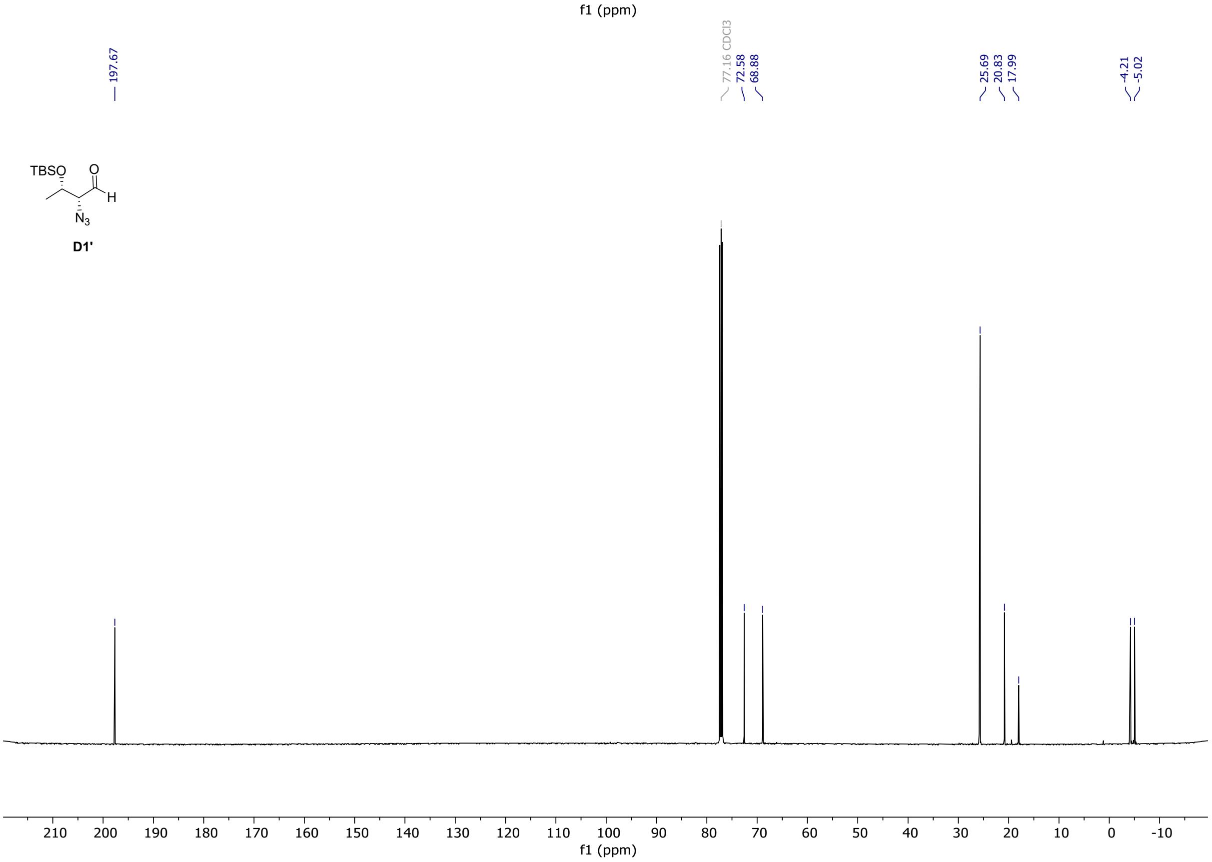

TBSO
O
OMe
NH2
20
7.26 CDCl3
4.31
4.31
4.30
4.29
4.29
4.29
4.28
4.27
4.27
3.71
3.28
3.27
1.61
1.25
1.23
0.84
0.04
-0.02
1.00
3.02
1.00
2.03
3.03
9.04
3.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

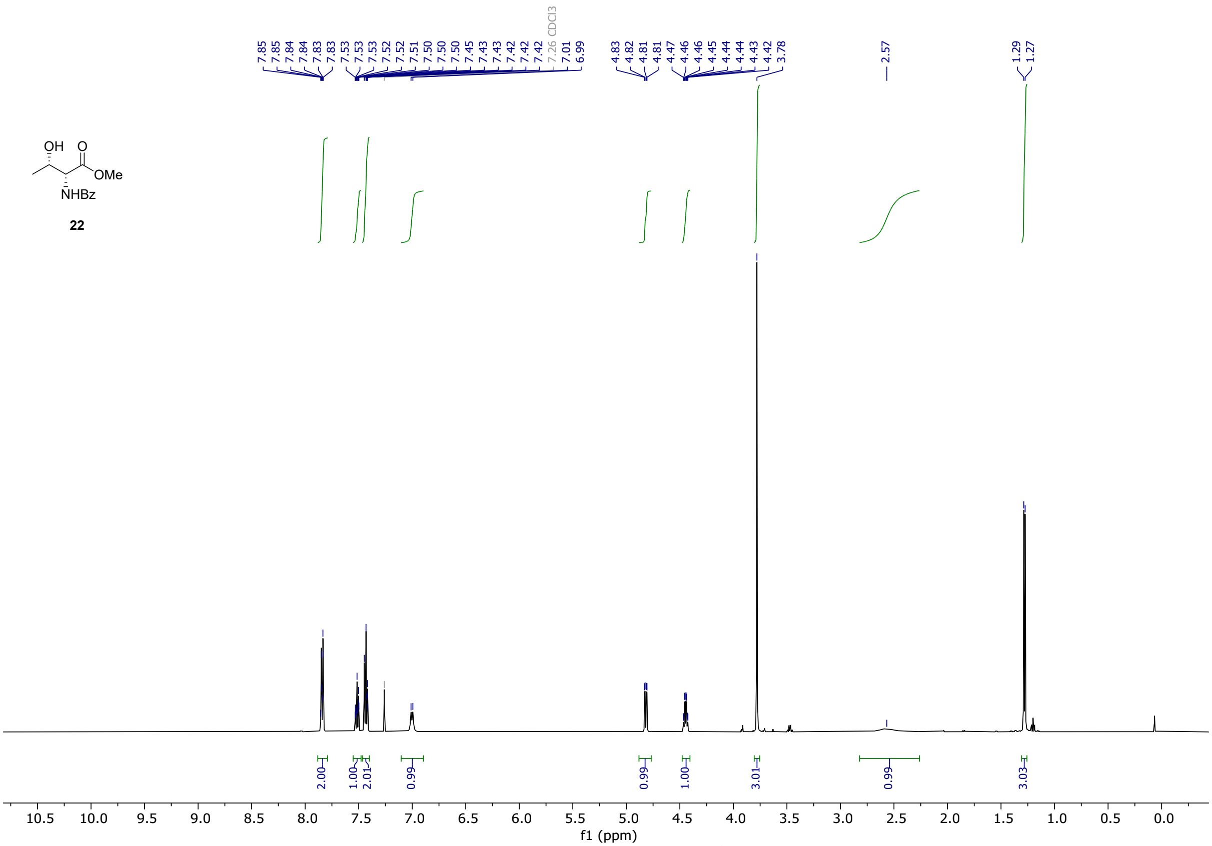

175.07
77.16 CDCl3
69.63
60.89
52.03
25.77
21.01
18.00
-4.21
-5.12
TBSO
O
OMe
NH2
20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

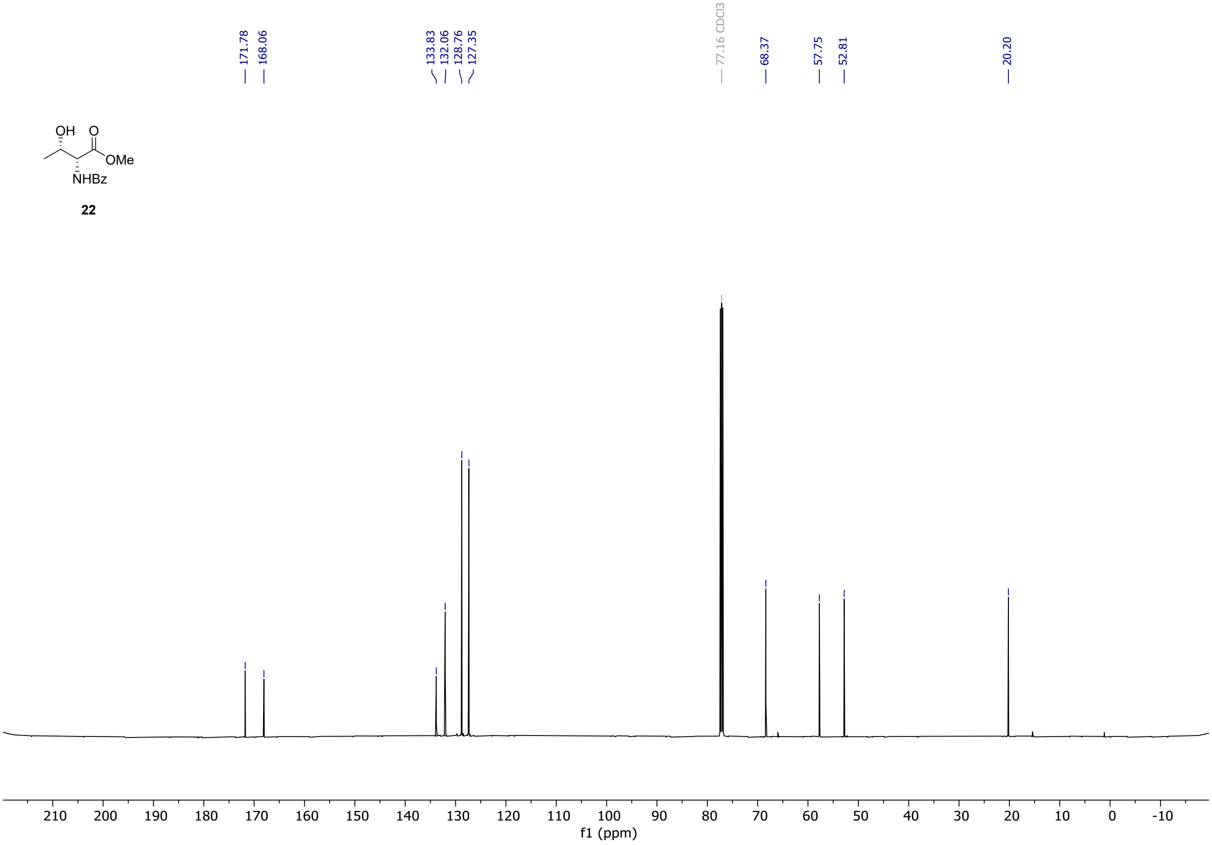

TBSO
O
OMe
N3
21
7.26 CDCl3
4.48
4.47
4.47
4.46
4.45
4.45
4.44
4.43
3.80
3.40
3.39
1.32
1.31
0.87
0.08
0.03
1.00
3.03
1.00
3.02
9.02
3.00
3.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

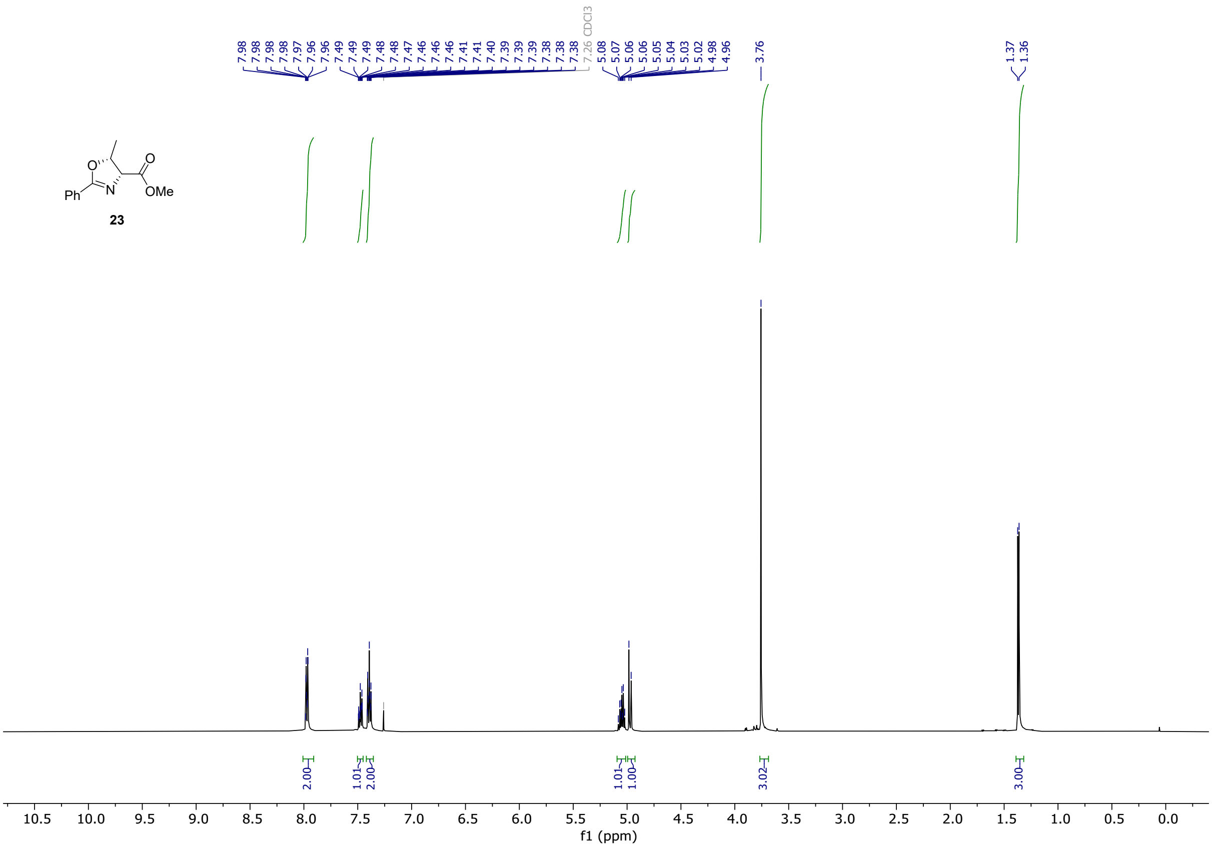

TBSO
O
OMe
N3
21
170.04
77.16 CDCl3
70.79
67.21
52.62
25.63
21.23
17.94
-4.27
-5.24
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

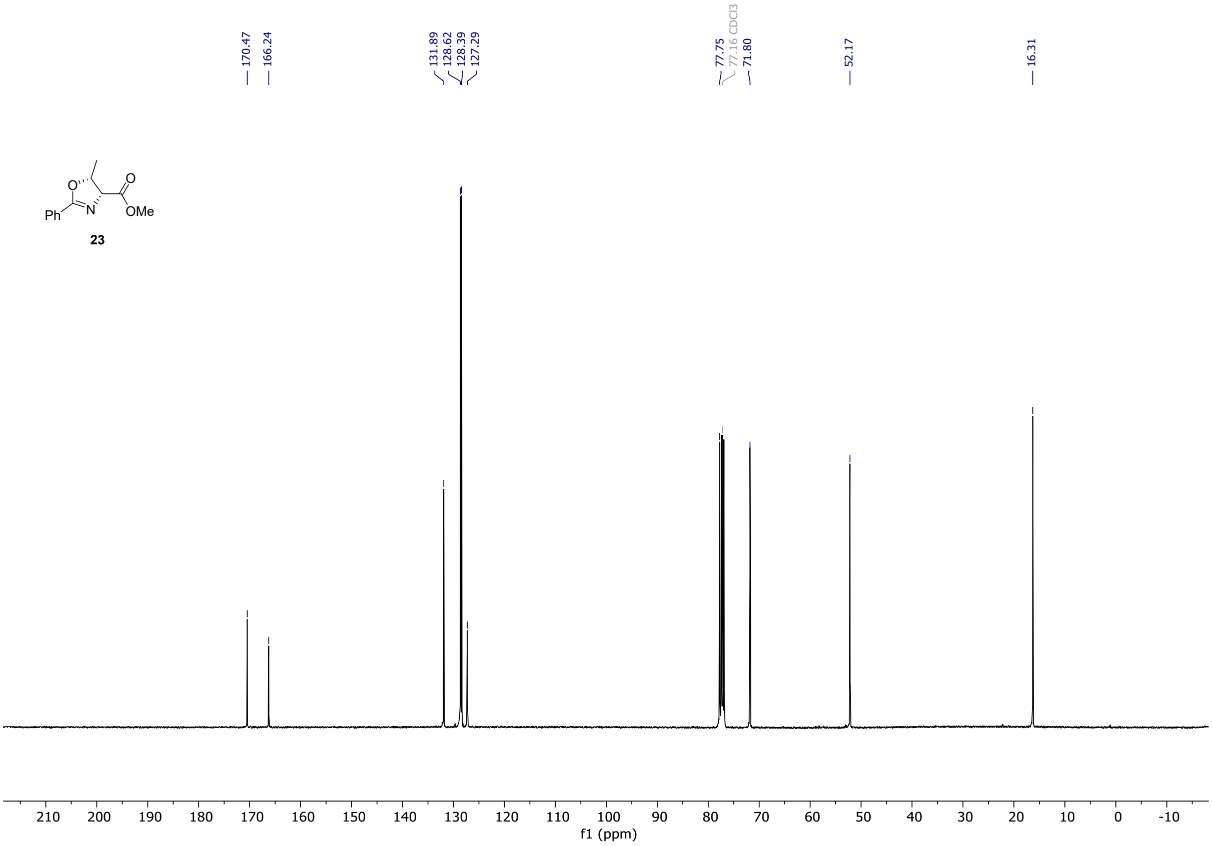

9.70
7.26 CDCl3
4.48
4.47
4.47
4.46
4.45
4.45
4.44
4.43
3.54
3.53
1.34
1.33
0.87
0.10
0.07
TBSO
O
H
N3
D1'
0.97
1.01
1.00
3.05
9.04
3.02
3.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

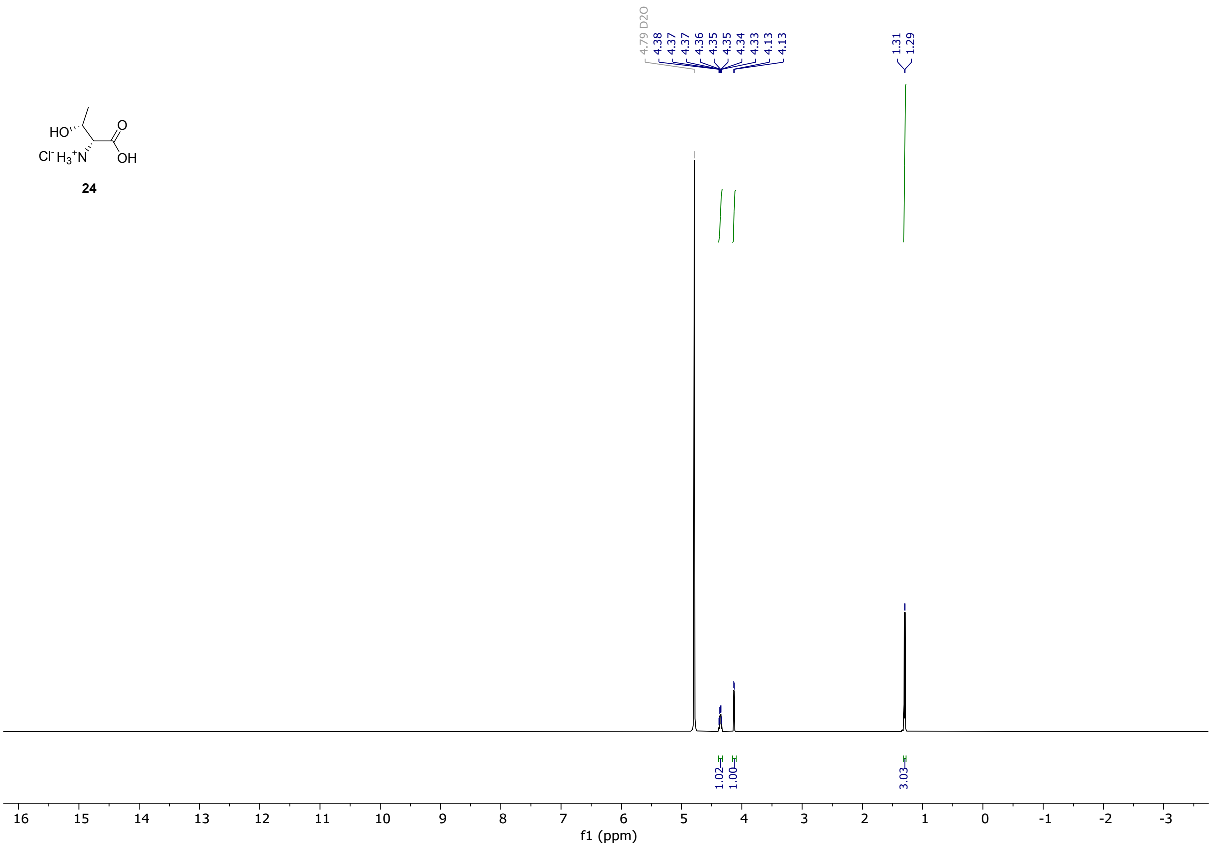

197.67
77.16 CDCl3
72.58
68.88
25.69
20.83
17.99
-4.21
-5.02
TBSO
O
H
N3
D1'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.85
7.85
7.84
7.84
7.83
7.83
7.53
7.53
7.53
7.52
7.52
7.51
7.50
7.50
7.50
7.45
7.43
7.43
7.42
7.42
7.42
7.26 CDCl3
7.01
6.99
4.83
4.82
4.81
4.81
4.47
4.46
4.45
4.44
4.44
4.43
4.42
3.78
2.57
1.29
1.27
OH
O
OMe
NHBz
22
2.00
1.00
2.01
0.99
0.99
1.00
3.01
0.99
3.03
10.5
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
0.5
0.0
f1 (ppm)


171.78
168.06
133.83
132.06
128.76
127.35
77.16 CDCl3
68.37
57.75
52.81
20.20
OH
O
OMe
NHBz
22
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

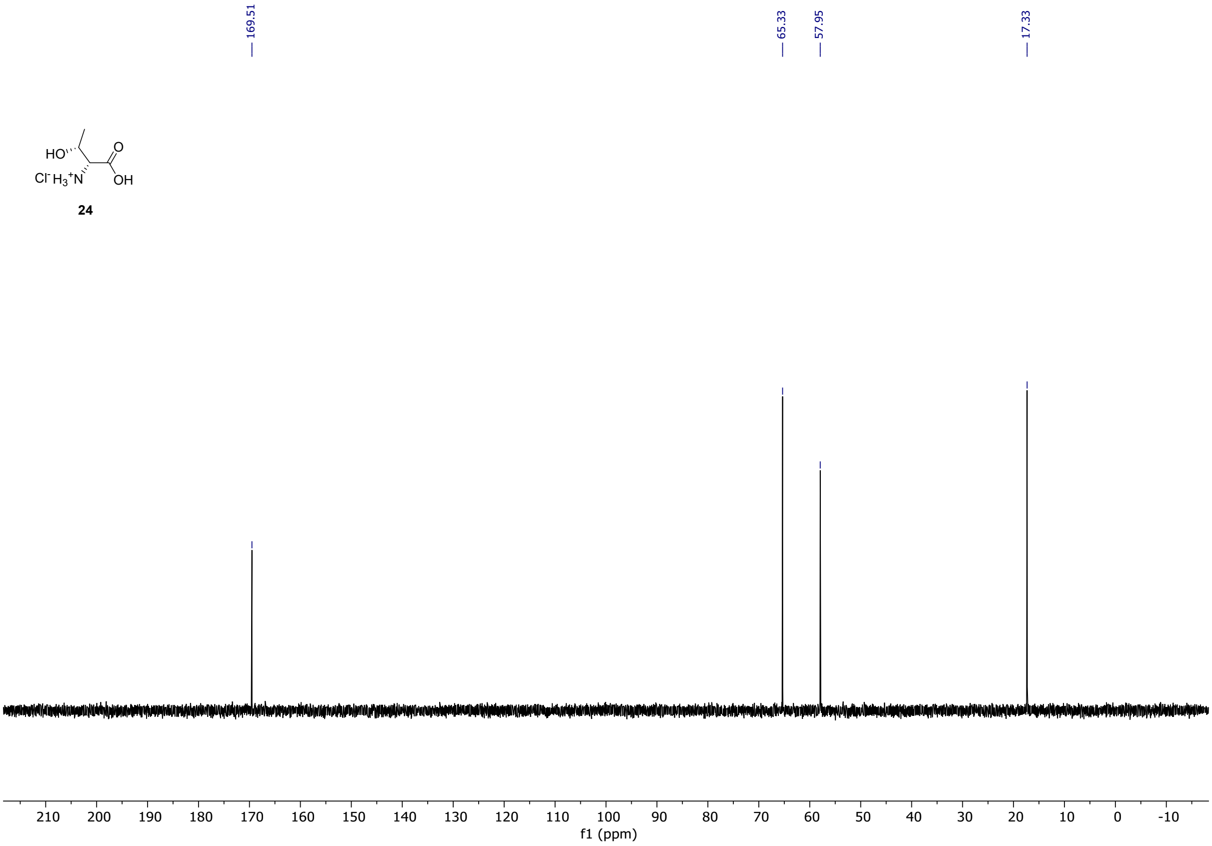

7.98
7.98
7.98
7.98
7.97
7.96
7.96
7.49
7.49
7.49
7.48
7.48
7.47
7.46
7.46
7.46
7.41
7.41
7.40
7.39
7.39
7.39
7.38
7.38
7.38
7.26 CDCl3
5.08
5.07
5.06
5.06
5.05
5.04
5.03
5.02
4.98
4.96
3.76
1.37
1.36
O
N
O
OMe
Ph
23
2.00
1.01
2.00
1.01
1.00
3.02
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


170.47
166.24
131.89
128.62
128.39
127.29
77.75
77.16 CDCl3
71.80
52.17
16.31
O
N
O
OMe
Ph
23
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



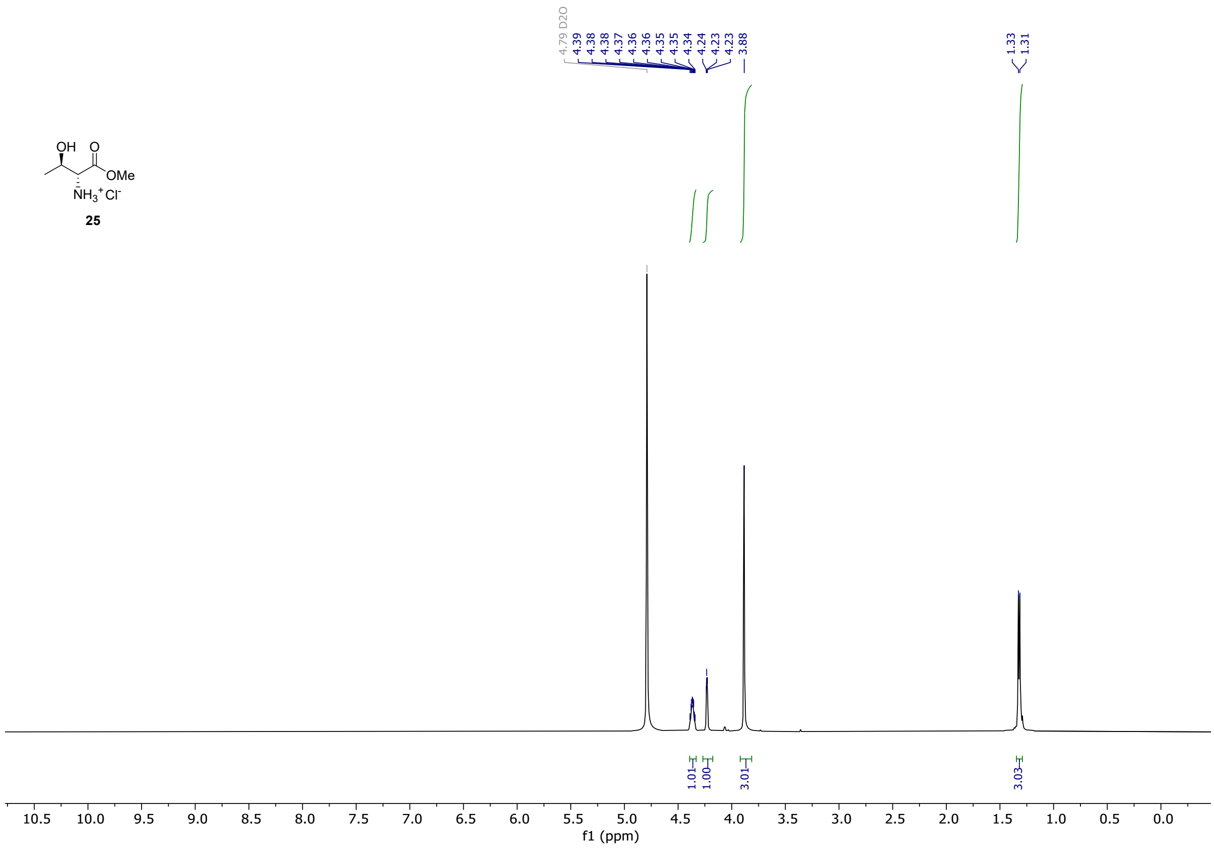
24

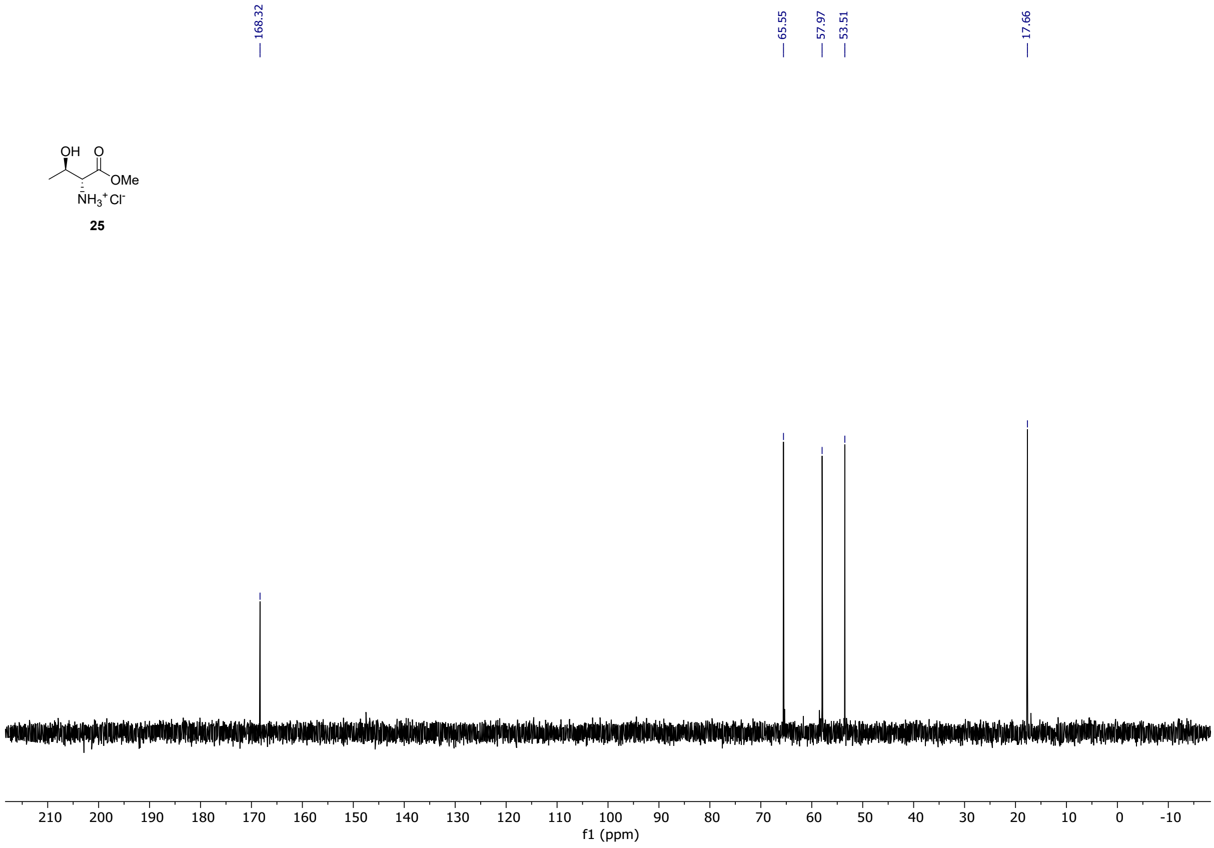
HO
O
Cl⁻ H3⁺N
OH
4.79 D2O
4.38
4.37
4.37
4.36
4.35
4.35
4.34
4.33
4.13
4.13
1.31
1.29
1.02
1.00
3.03
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

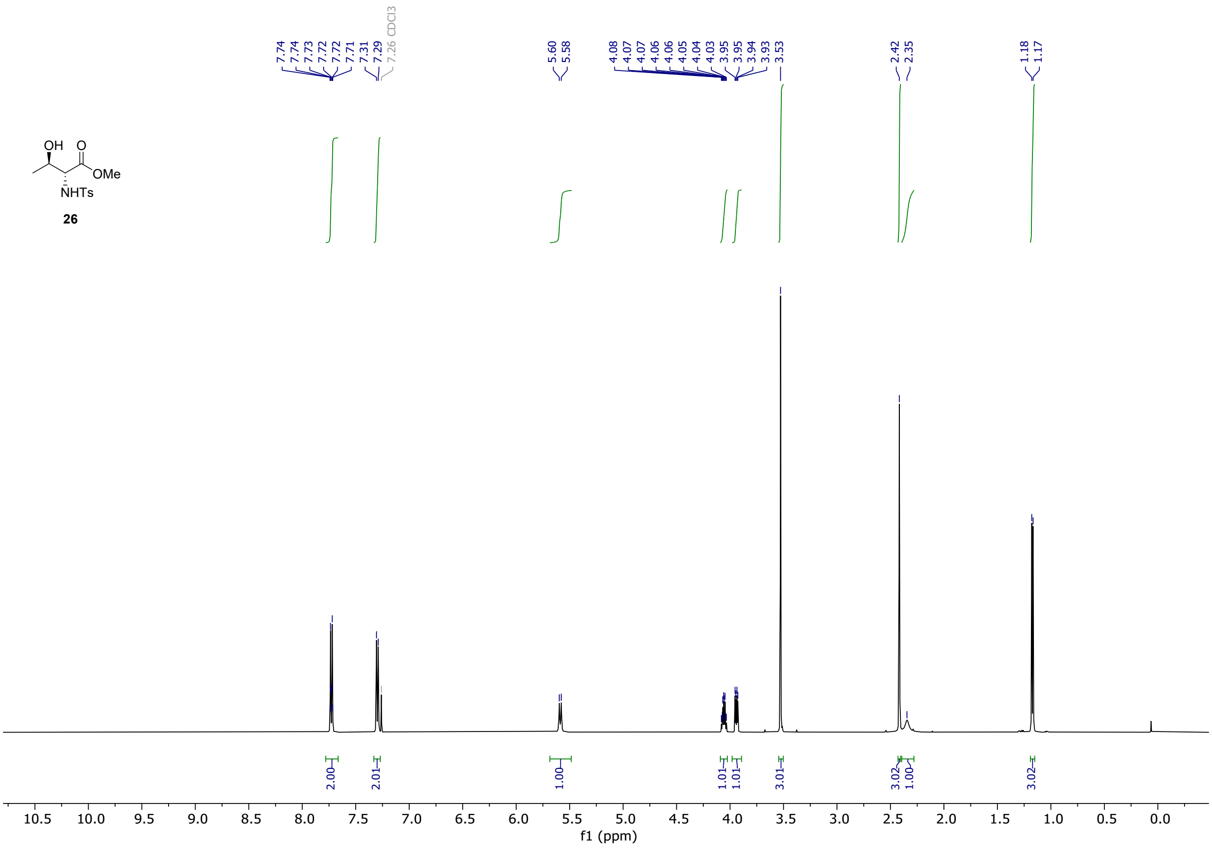


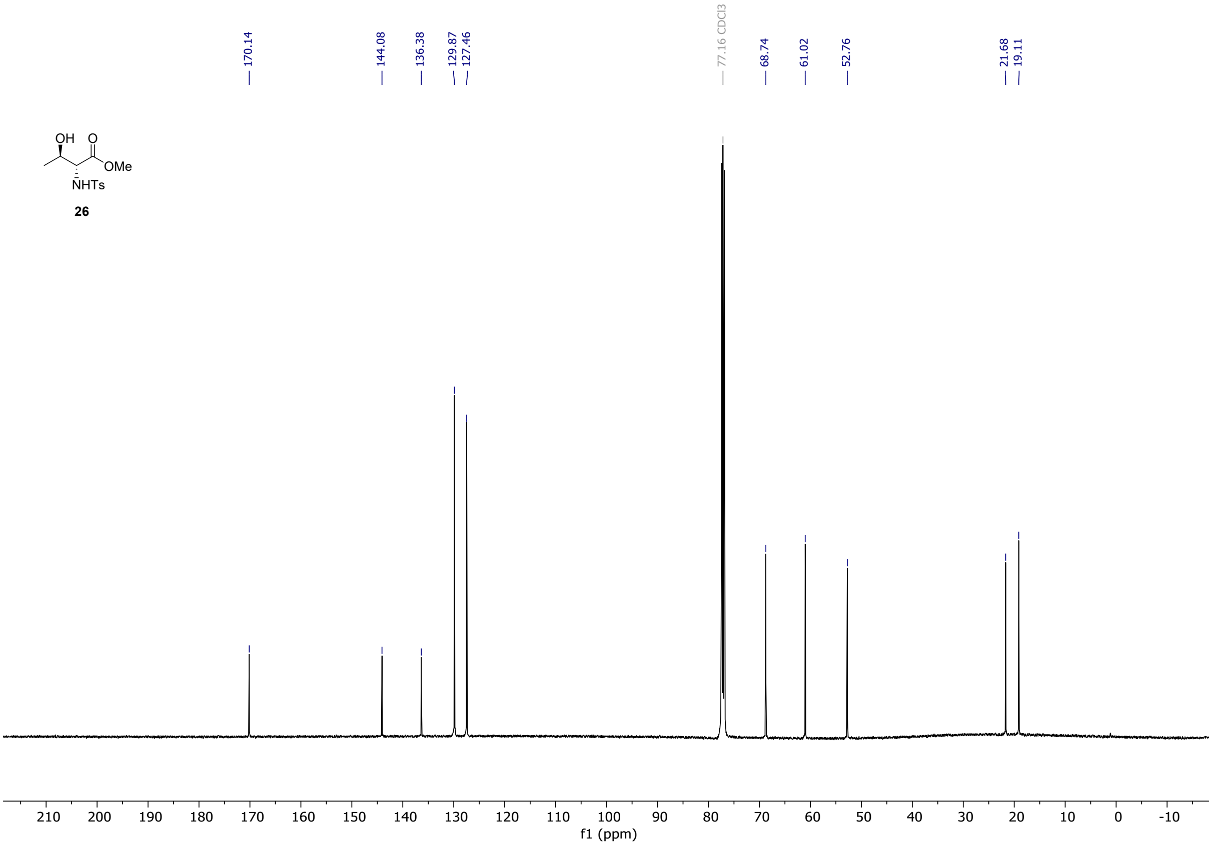
24

HO
O
Cl⁻ H3⁺N
OH
169.51
65.33
57.95
17.33
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


4.79 D2O
4.39
4.38
4.38
4.37
4.36
4.36
4.35
4.35
4.34
4.24
4.23
4.23
3.88
1.33
1.31
OH
O
OMe
NH_3^+ Cl^-
25
1.01
1.00
3.01
3.03
10.5
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
0.5
0.0
f1 (ppm)


168.32
65.55
57.97
53.51
17.66
OH
O
OMe
NH_3^+ Cl^-
25
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.74
7.74
7.73
7.72
7.72
7.71
7.31
7.29
7.26 CDCl3
5.60
5.58
4.08
4.07
4.07
4.06
4.06
4.05
4.04
4.03
3.95
3.95
3.94
3.93
3.53
2.42
2.35
1.18
1.17
OH
O
OMe
NHTs
26
2.00
2.01
1.00
1.01
1.01
3.01
3.02
1.00
3.02
10.5
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
0.5
0.0
f1 (ppm)


170.14
144.08
136.38
129.87
127.46
77.16 CDCl3
68.74
61.02
52.76
21.68
19.11
OH
O
OMe
NHTs
26
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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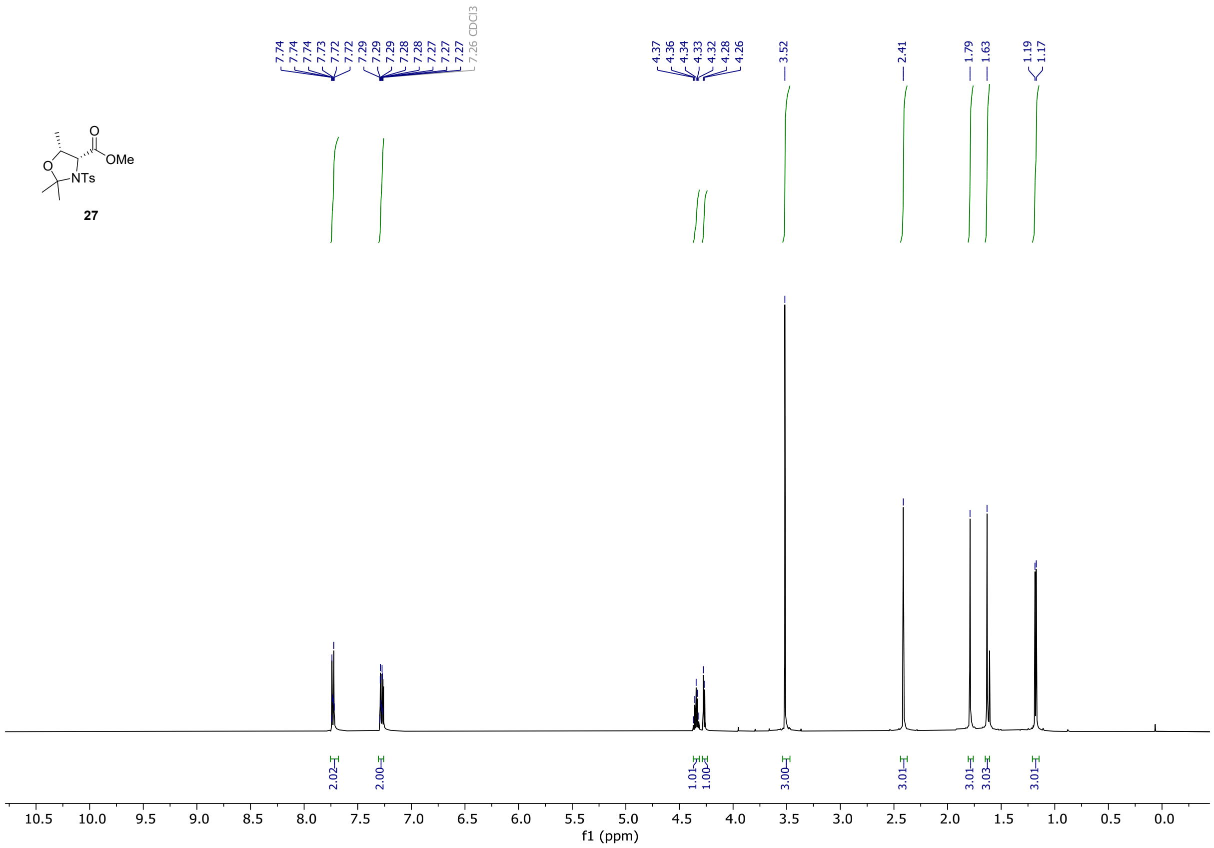
f1 (ppm)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7.28
7.28
7.27
7.27
7.27
7.26 CDCl3
4.37
4.36
4.34
4.33
4.32
4.28
4.26
3.52
2.41
1.79
1.63
1.19
1.17
OMe
O
NTs
2.02
2.00
1.01
1.00
3.00
3.01
3.01
3.03
3.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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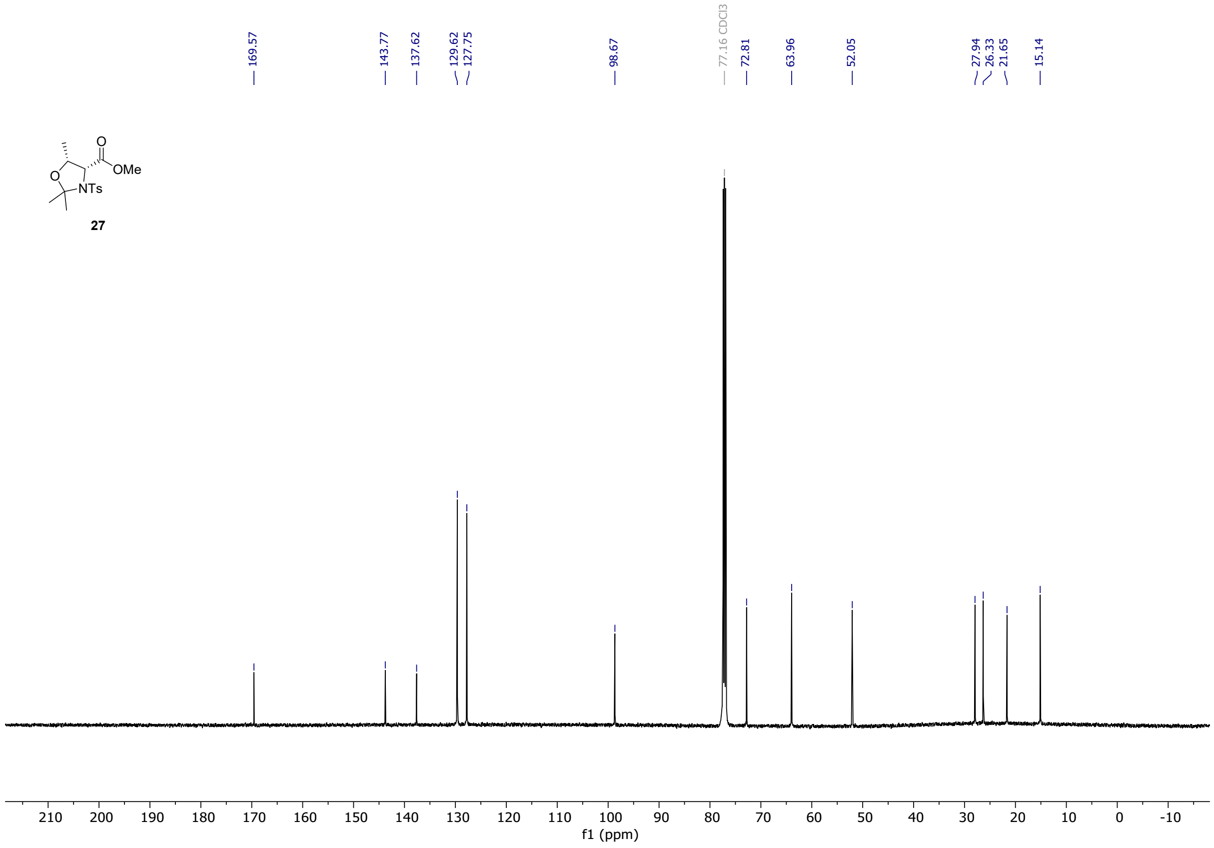
0.0
f1 (ppm)

27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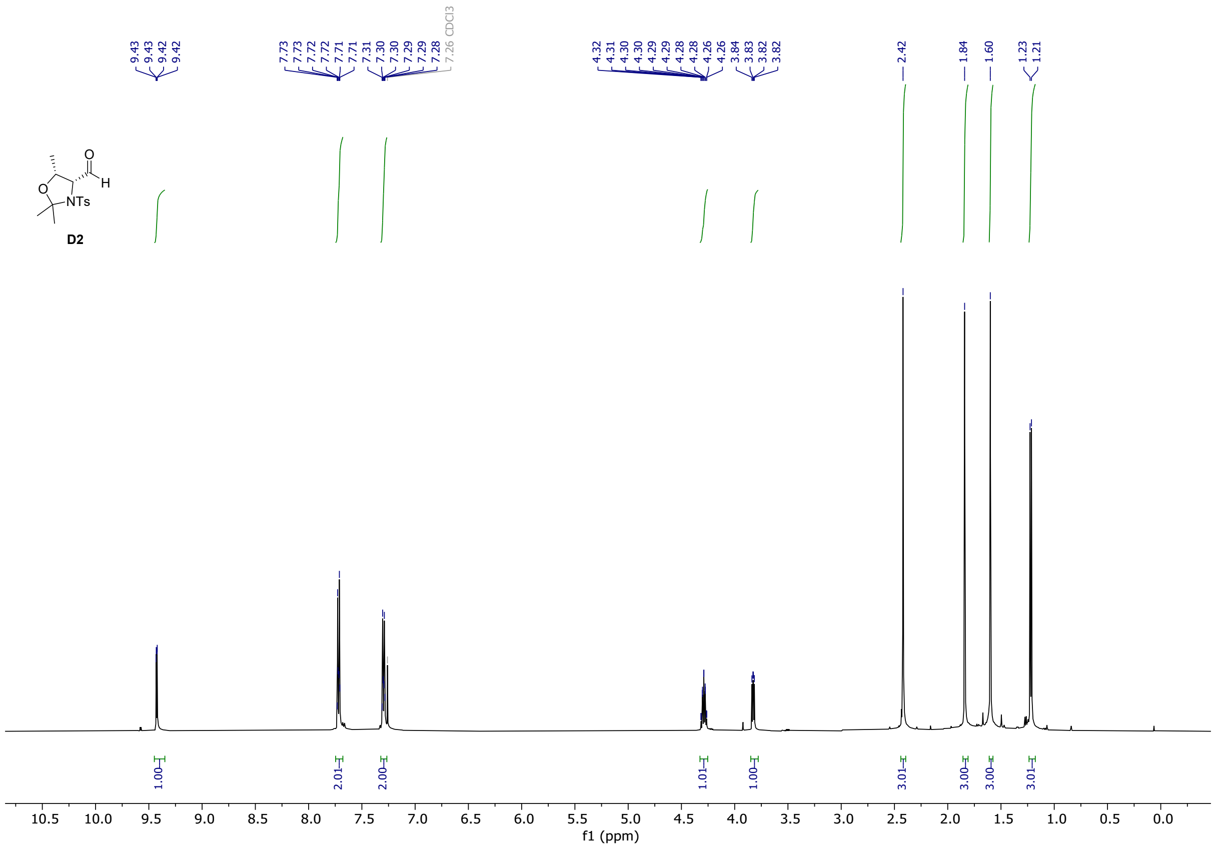
127.75
98.67
77.16 CDCl3
72.81
63.96
52.05
27.94
26.33
21.65
15.14
O
OMe
O
NTs
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

27



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7.30
7.30
7.29
7.29
7.28
7.26 CDCl3
4.32
4.31
4.30
4.30
4.29
4.29
4.28
4.28
4.26
4.26
3.84
3.83
3.82
3.82
2.42
1.84
1.60
1.23
1.21
O
H
O
NTs
D2
1.00
2.01
2.00
1.01
1.00
3.01
3.00
3.00
3.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
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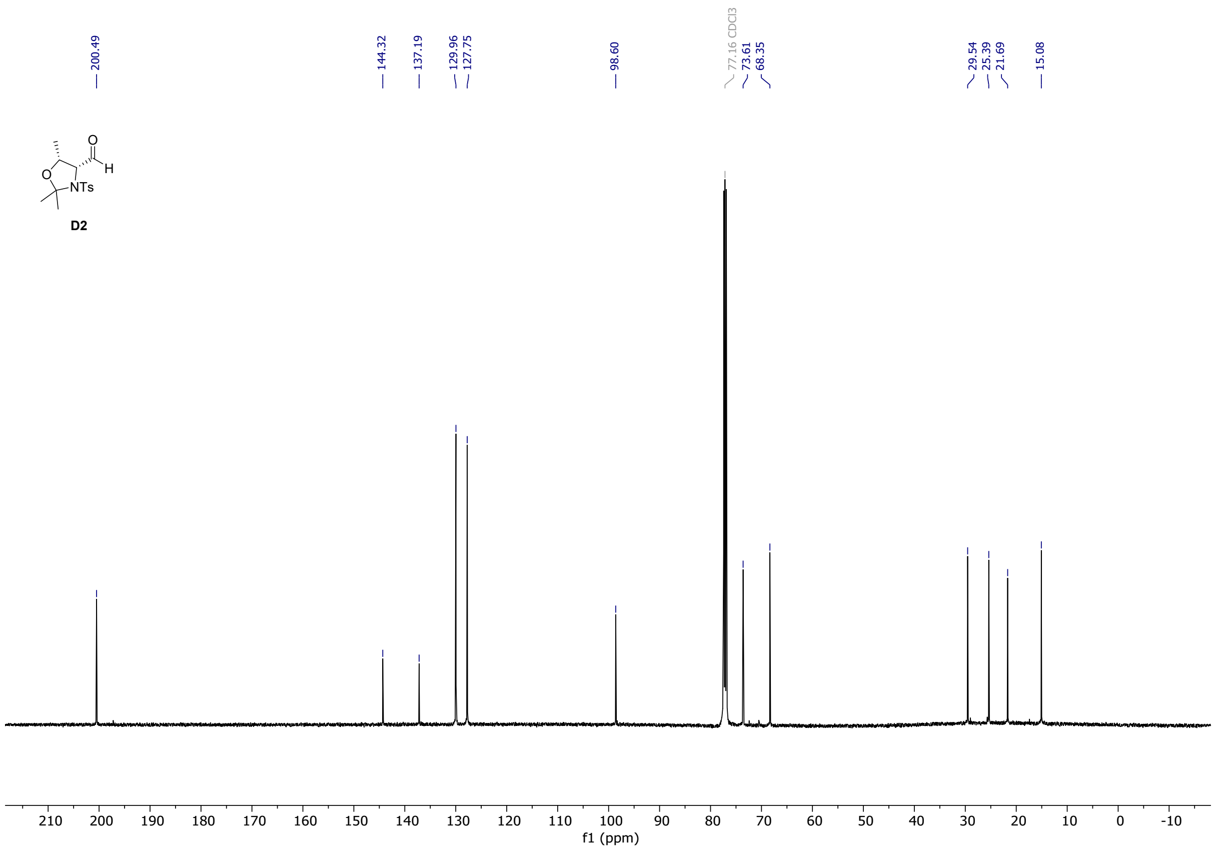
f1 (ppm)



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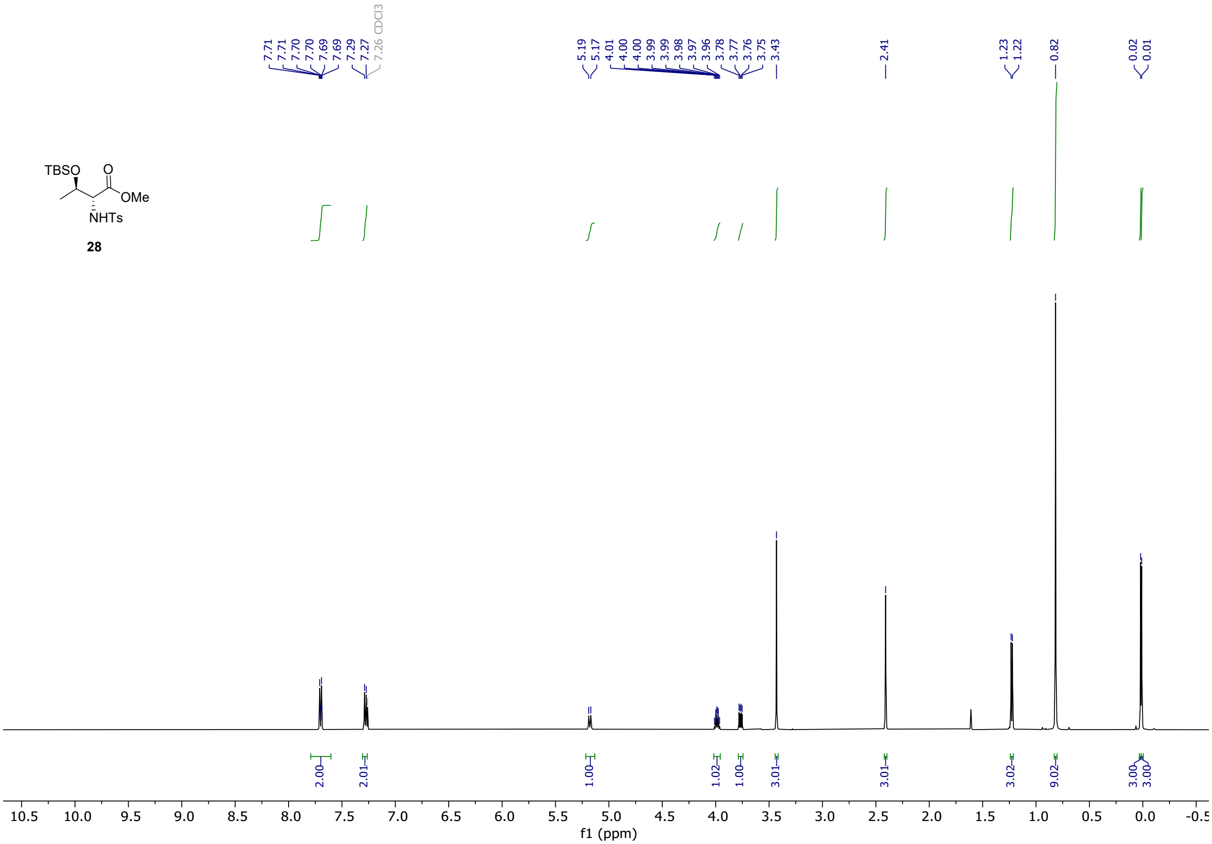
137.19
129.96
127.75
98.60
77.16 CDCl3
73.61
68.35
29.54
25.39
21.69
15.08
O
H
O
NTs
D2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.71
7.70
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7.69
7.69
7.29
7.27
7.26 CDCl3
5.19
5.17
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4.00
4.00
3.99
3.99
3.99
3.98
3.97
3.96
3.78
3.77
3.76
3.75
3.43
2.41
1.23
1.22
0.82
0.02
0.01
TBSO
O
OMe
NHTs
28
2.00
2.01
1.00
1.02
1.00
3.01
3.01
3.02
9.02
3.00
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
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2.0
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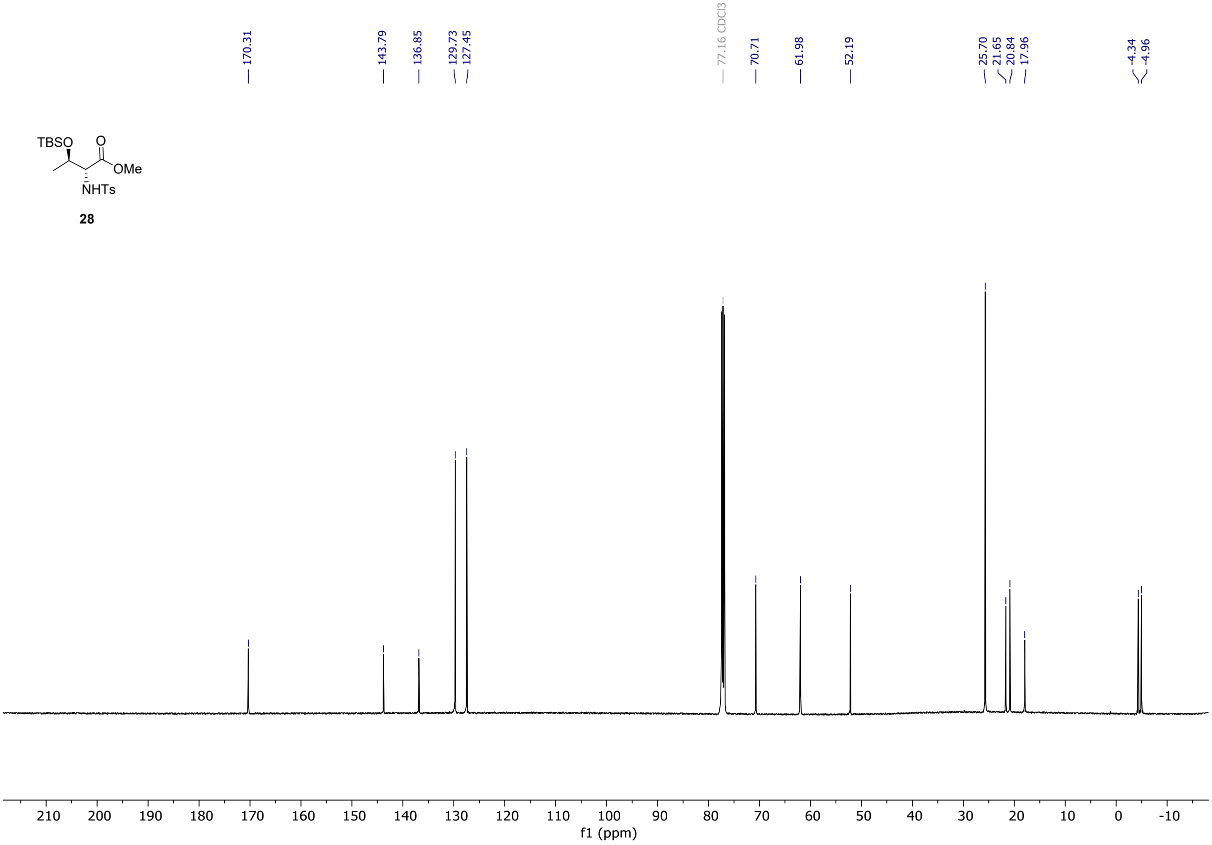
-0.5
f1 (ppm)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61.98
52.19
25.70
21.65
20.84
17.96
-4.34
-4.96
TBSO
O
OMe
NHTs
28
210
200
190
180
170
160
150
140
130
120
110
100
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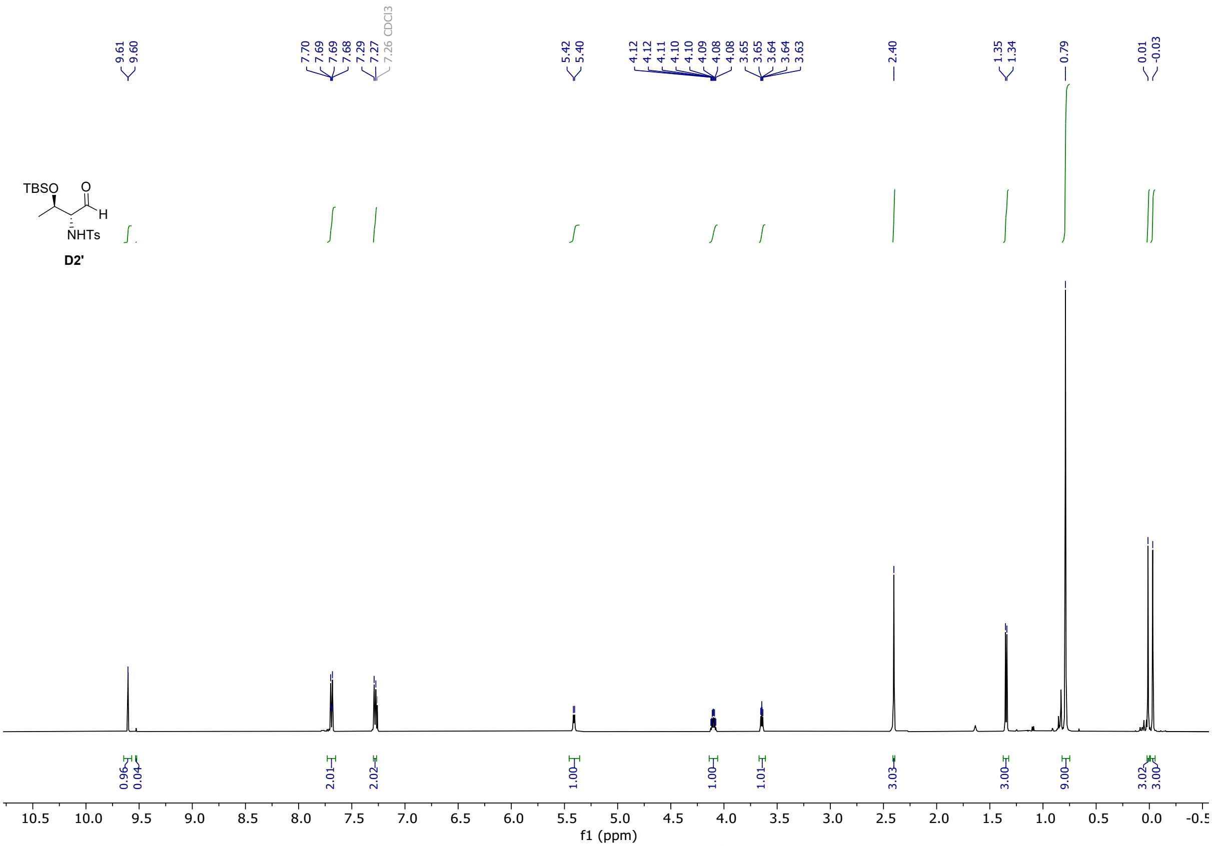
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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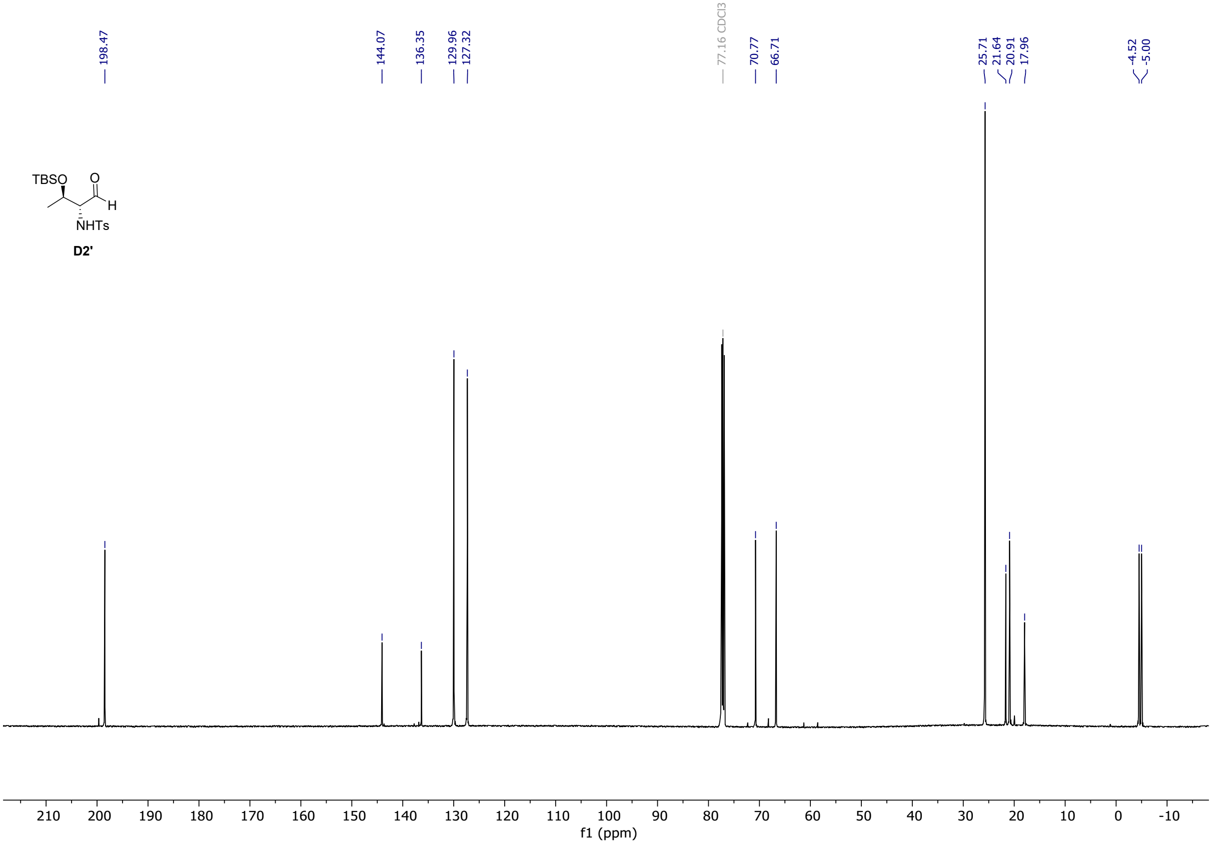
7.70
7.69
7.69
7.68
7.29
7.27
7.26 CDCl3
5.42
5.40
4.12
4.12
4.11
4.10
4.10
4.09
4.09
4.08
4.08
3.65
3.65
3.64
3.64
3.63
2.40
1.35
1.34
0.79
0.01
-0.03
TBSO
O
H
NHTs
D2'
0.96
0.04
2.01
2.02
1.00
1.00
1.01
3.03
3.00
9.00
3.02
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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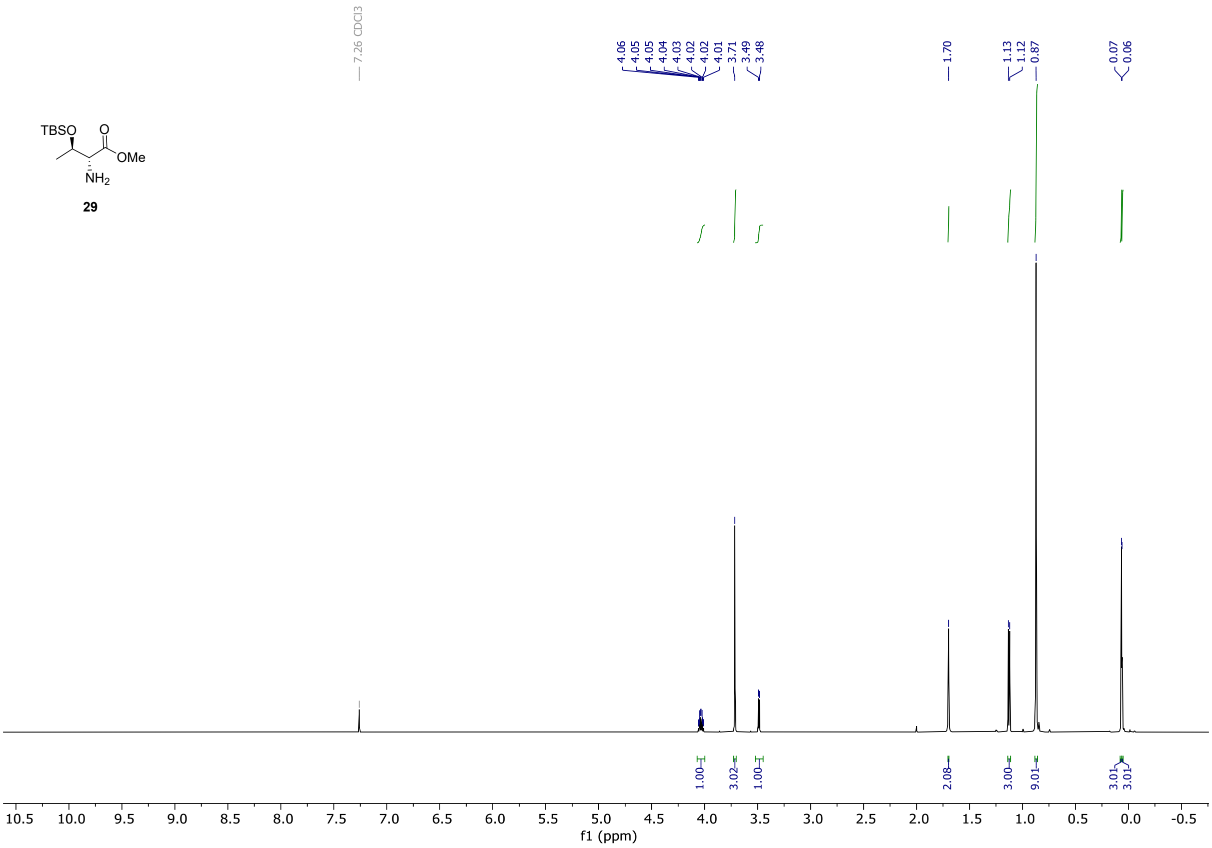
136.35
129.96
127.32
77.16 CDCl3
70.77
66.71
25.71
21.64
20.91
17.96
-4.52
-5.00
TBSO
O
H
NHTs
D2'
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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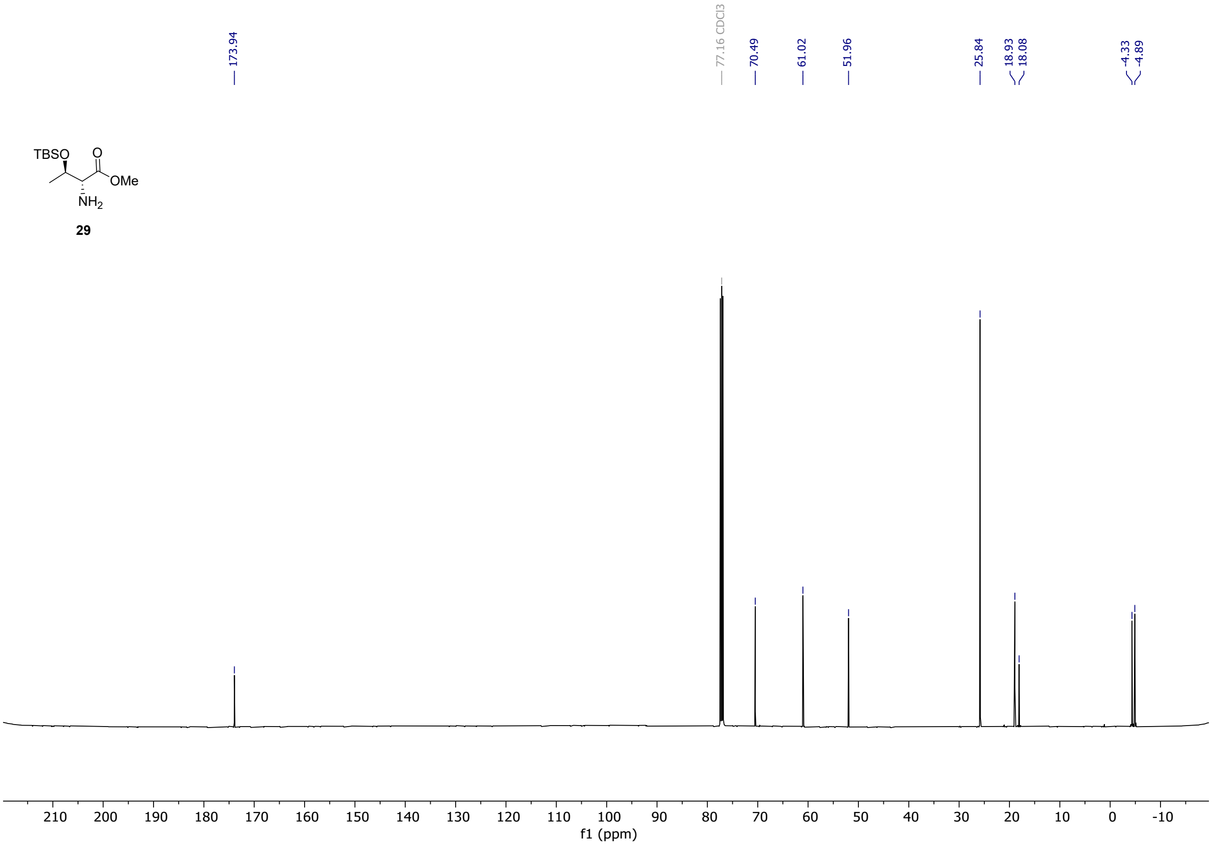
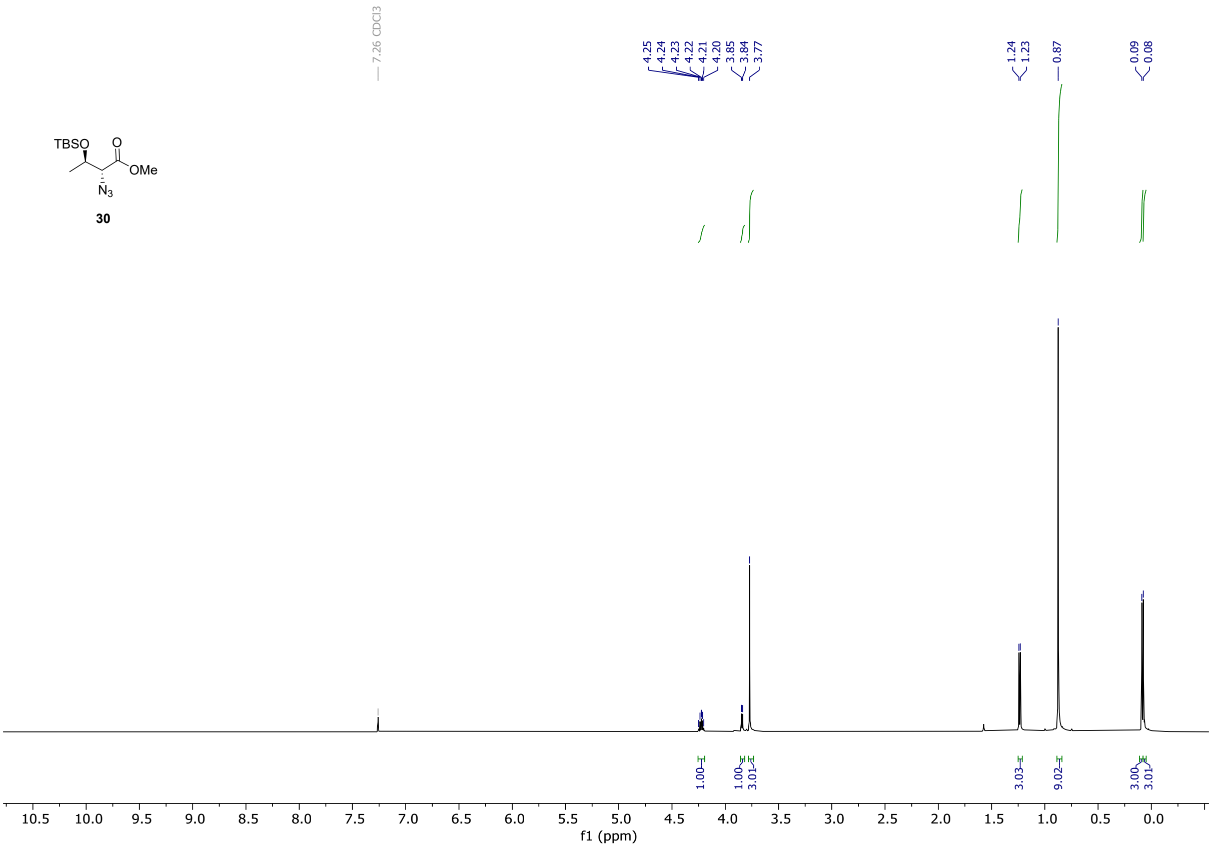
4.06
4.05
4.05
4.04
4.03
4.02
4.02
4.01
3.71
3.49
3.48
1.70
1.13
1.12
0.87
0.07
0.06
TBSO
O
OMe
NH2
1.00
3.02
1.00
2.08
3.00
9.01
3.01
3.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

29


173.94
77.16 CDCl3
70.49
61.02
51.96
25.84
18.93
18.08
-4.33
-4.89
TBSO
O
OMe
NH2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

29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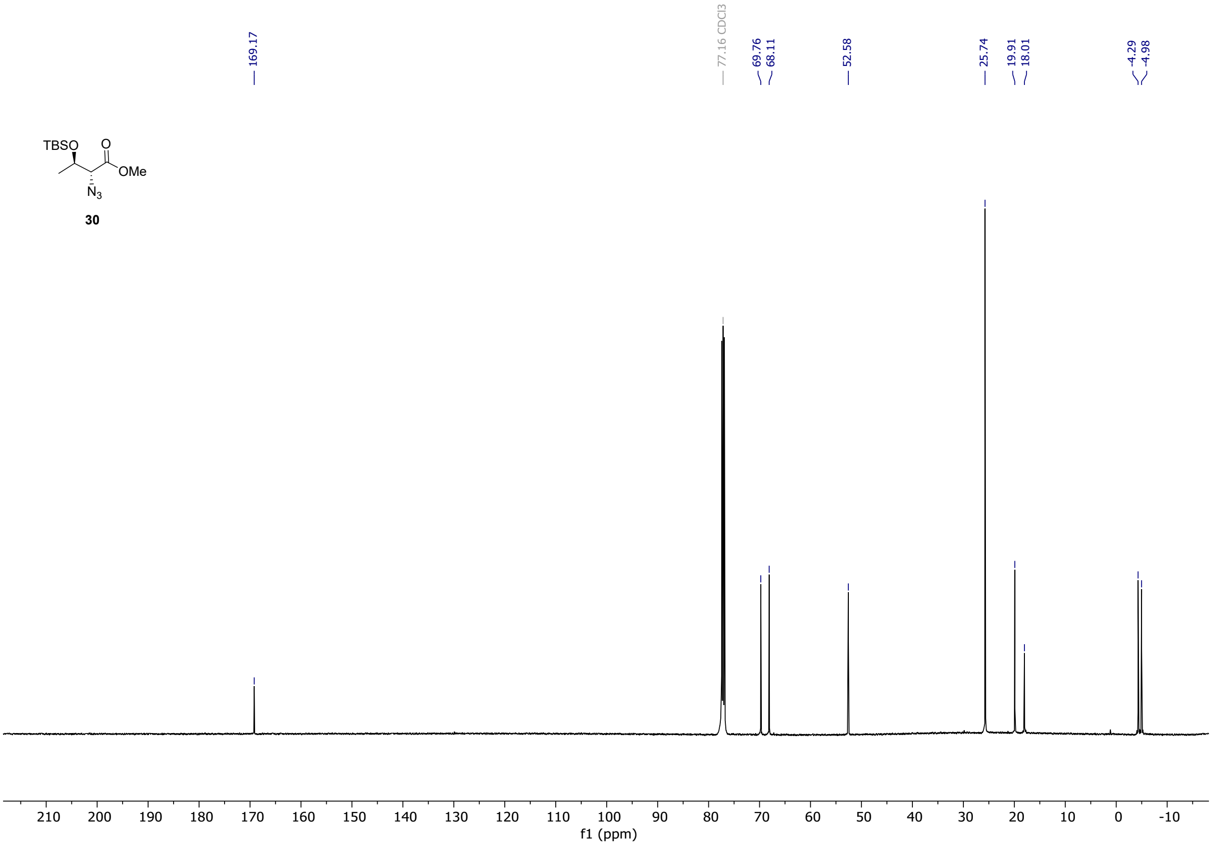
4.25
4.24
4.23
4.22
4.21
4.20
3.85
3.84
3.77
1.24
1.23
0.87
0.09
0.08
TBSO
O
OMe
N3
30
1.00
1.00
3.01
3.03
9.02
3.00
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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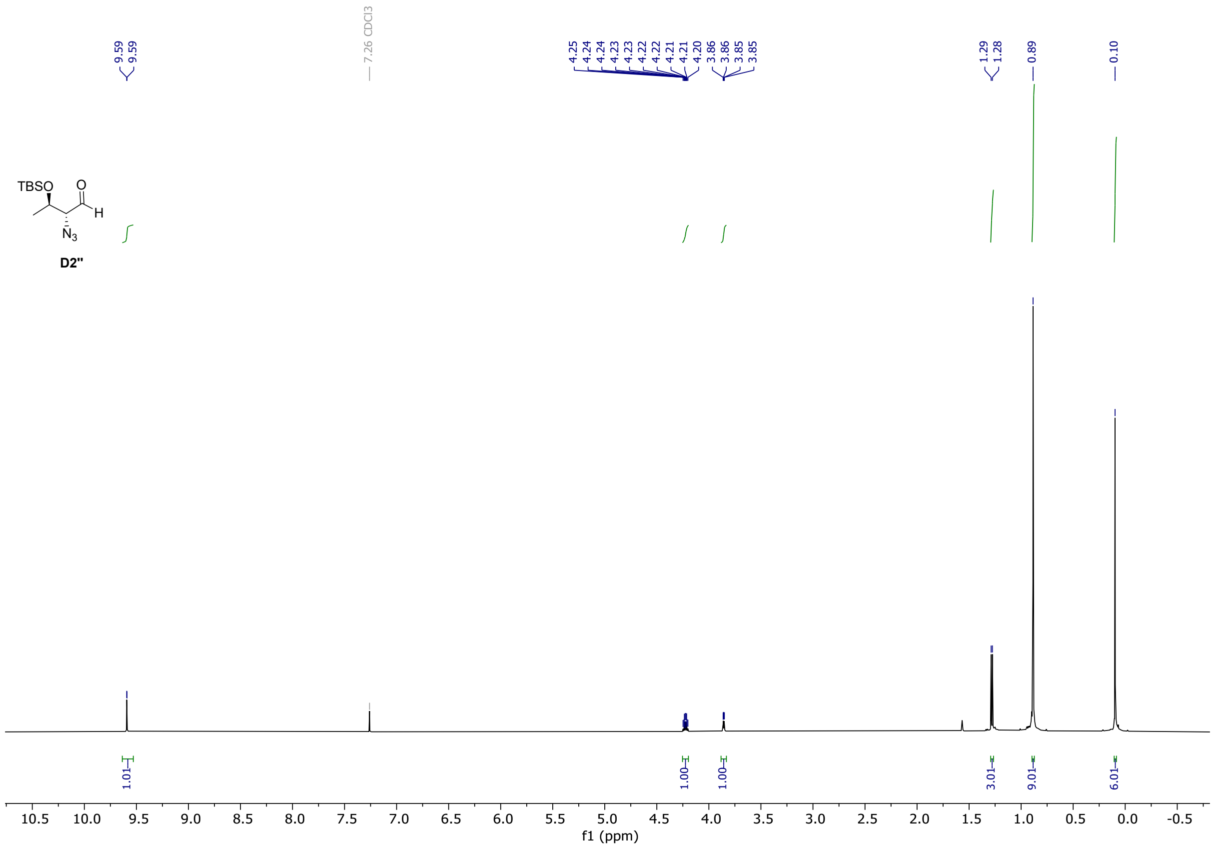
77.16 CDCl3
69.76
68.11
52.58
25.74
19.91
18.01
-4.29
-4.98
TBSO
O
OMe
N3
30
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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9.59
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4.23
4.23
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4.22
4.21
4.21
4.20
3.86
3.86
3.85
3.85
1.29
1.28
0.89
0.10
TBSO
O
H
N3
D2''
1.01
1.00
1.00
3.01
9.01
6.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
2.0
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0.5
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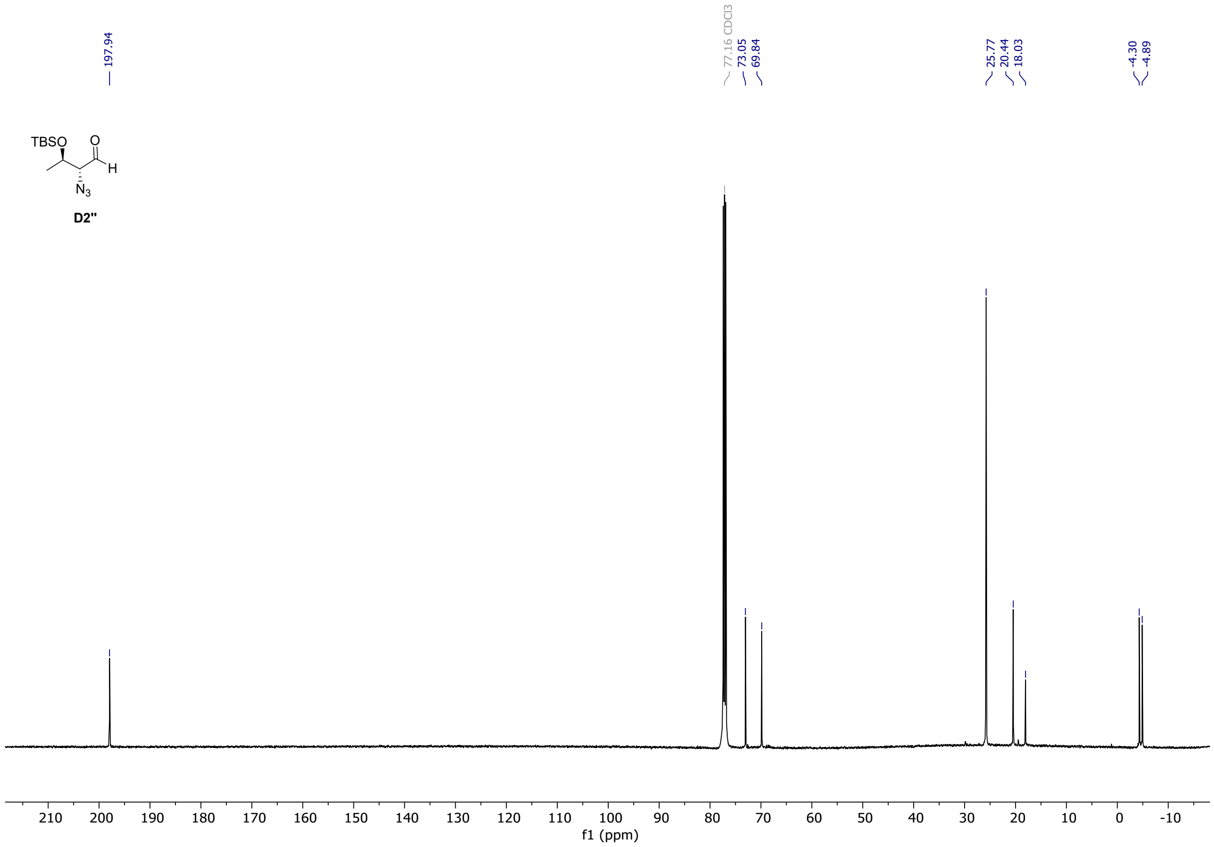
-0.5
f1 (ppm)


197.94
77.16 CDCl3
73.05
69.84
25.77
20.44
18.03
-4.30
-4.89
TBSO
O
H
N3
D2''
210
200
190
180
170
160
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140
130
120
110
100
90
80
70
60
50
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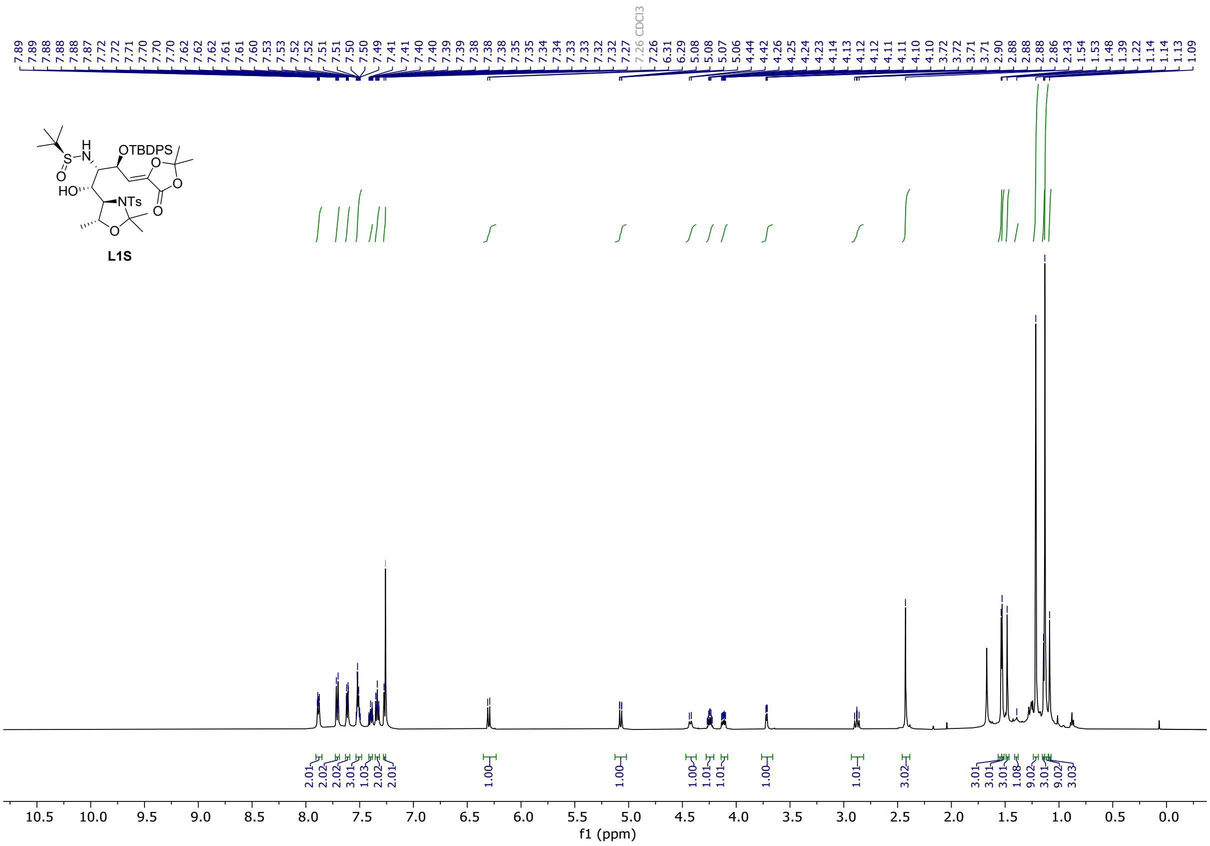
30
20
10
0
-10
f1 (ppm)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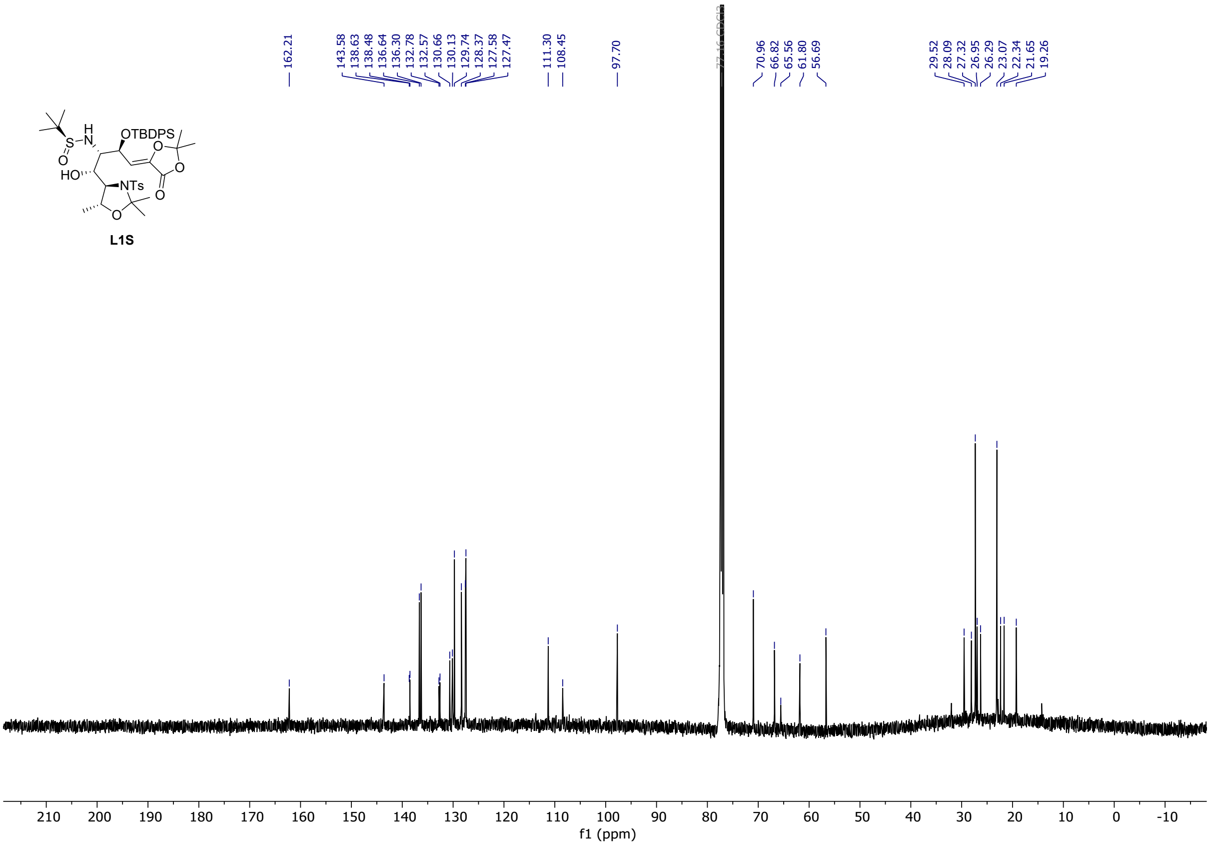
H
S
N
O
OTBDPS
O
O
O
HO
NTs
O
L1S
2.01 2.02 2.02 3.01 1.03 2.02 2.01 1.00 1.00 1.00 1.01 1.01 1.00 1.01 3.02 3.01 3.01 3.01 1.08 9.02 3.01 9.02 3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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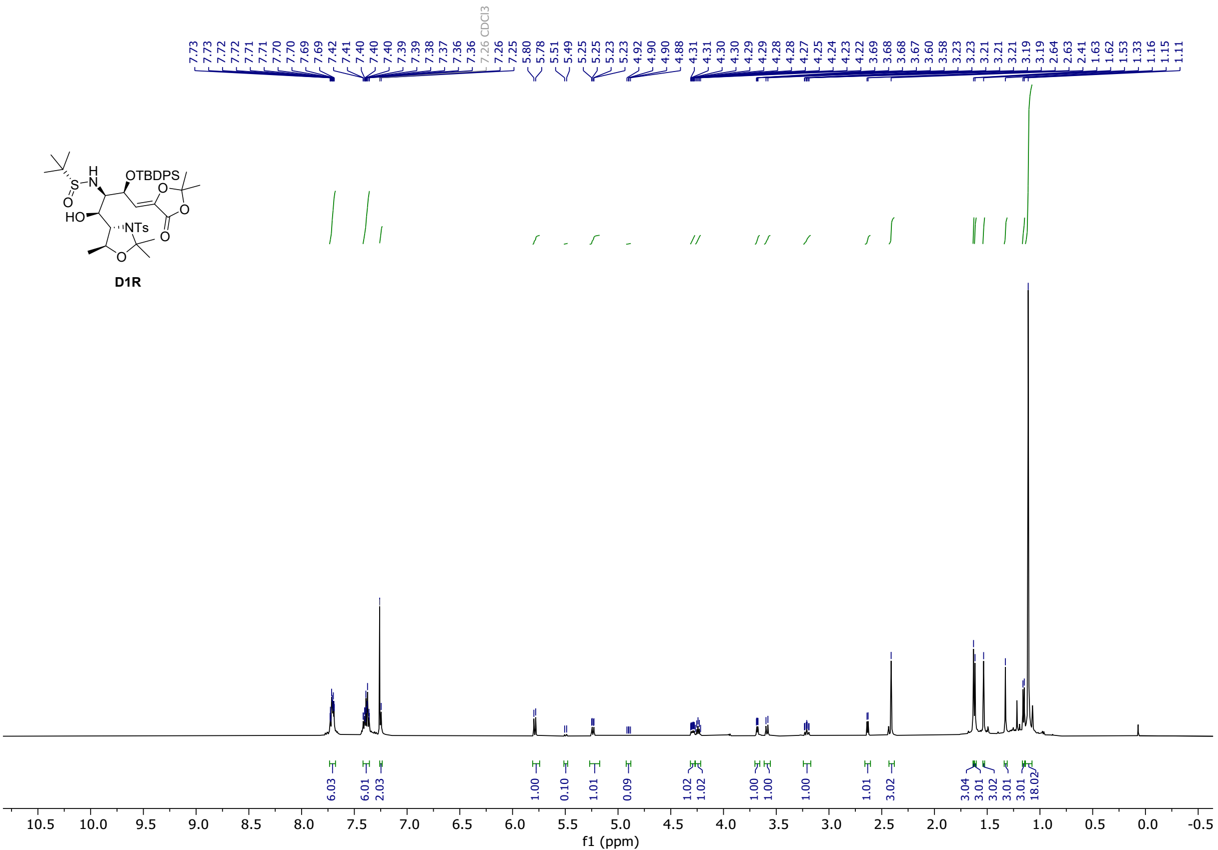
111.30 108.45
97.70
77.16 CDCl3
70.96 66.82 65.56 61.80 56.69
29.52 28.09 27.32 26.95 26.29 23.07 22.34 21.65 19.26
H
S
N
O
OTBDPS
O
O
O
HO
NTs
O
L1S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.40
7.39
7.39
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7.37
7.36
7.36
7.26 CDCl3
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7.25
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5.51
5.49
5.25
5.25
5.23
5.23
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4.90
4.90
4.88
4.31
4.31
4.30
4.30
4.29
4.29
4.28
4.28
4.27
4.25
4.24
4.23
4.22
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3.68
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3.21
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3.19
3.19
2.64
2.63
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1.63
1.62
1.53
1.33
1.16
1.15
1.11
H
S
N
O
OTBDPS
O
O
O
HO
NTs
O
6.03
6.01
2.03
1.00
0.10
1.01
0.09
1.02
1.02
1.00
1.00
1.00
1.01
3.02
3.04
3.01
3.02
3.01
3.01
18.02
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7.0
6.5
6.0
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5.0
4.5
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0.0
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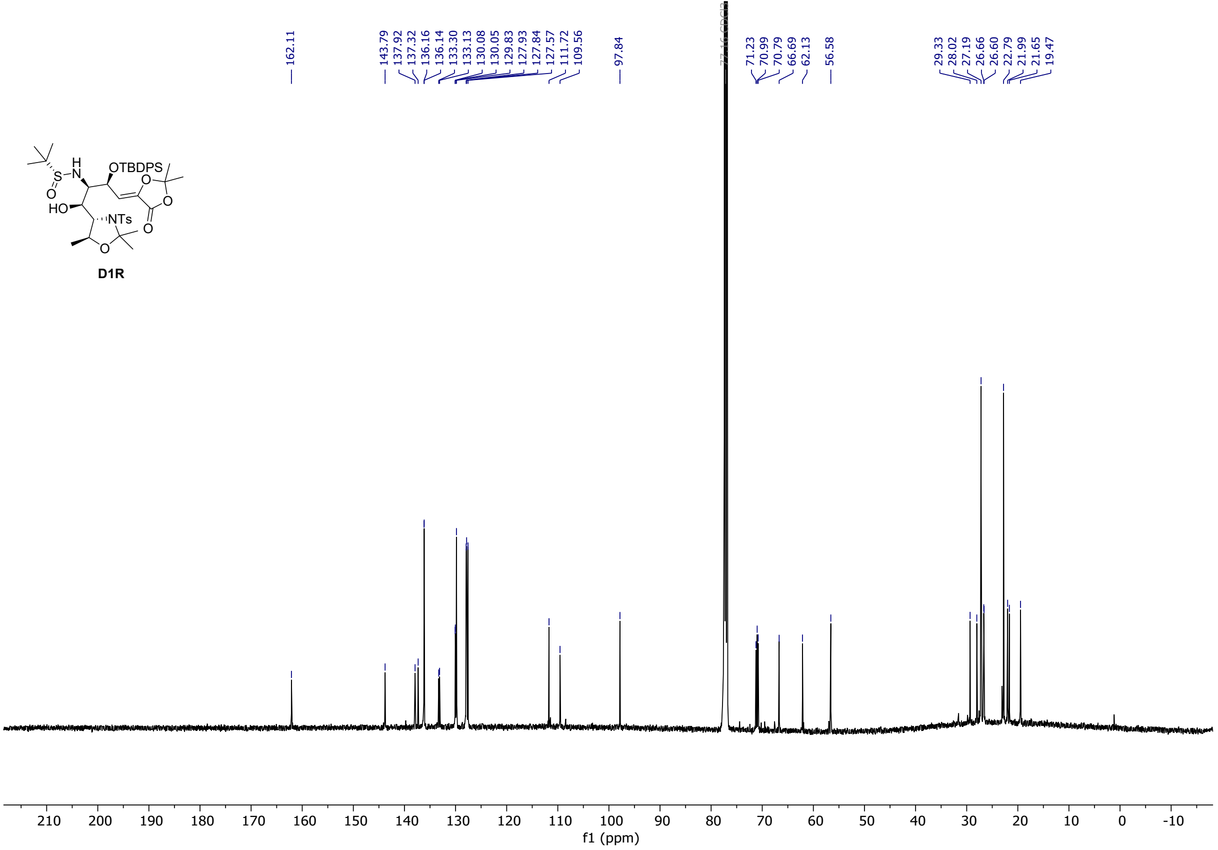
f1 (ppm)

D1R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129.83
127.93
127.84
127.57
111.72
109.56
97.84
77.16 CDCl3
71.23
70.99
70.79
66.69
62.13
56.58
29.33
28.02
27.19
26.66
26.60
22.79
21.99
21.65
19.47
H
S
N
O
OTBDPS
O
O
O
HO
NTs
O
210
200
190
180
170
160
150
140
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120
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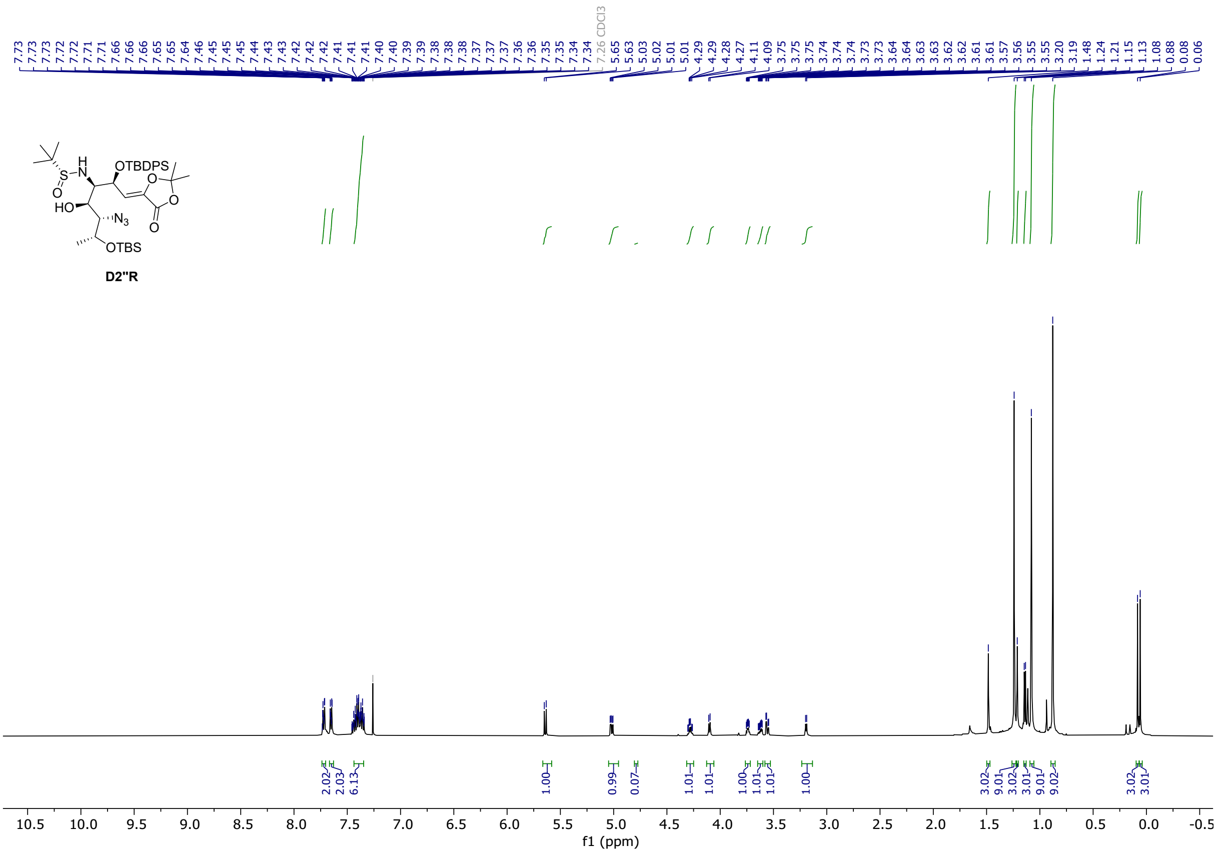
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

D1R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7.71
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7.66
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7.64
7.46
7.45
7.45
7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.41
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7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.26 CDCl3
5.65
5.63
5.03
5.02
5.01
5.01
4.29
4.29
4.28
4.27
4.11
4.09
3.75
3.75
3.75
3.74
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3.73
3.73
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3.63
3.63
3.62
3.61
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3.56
3.55
3.55
3.20
3.19
1.48
1.24
1.21
1.15
1.13
1.08
0.88
0.08
0.06
OTBDPS
OTBS
HO
N3
O
S
H
N
O
O
O
D2''R
2.02
2.03
6.13
1.00
0.99
0.07
1.01
1.01
1.00
1.01
1.01
1.00
3.02
9.01
3.02
3.01
9.01
9.02
3.02
3.01
10.5
10.0
9.5
9.0
8.5
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7.5
7.0
6.5
6.0
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5.0
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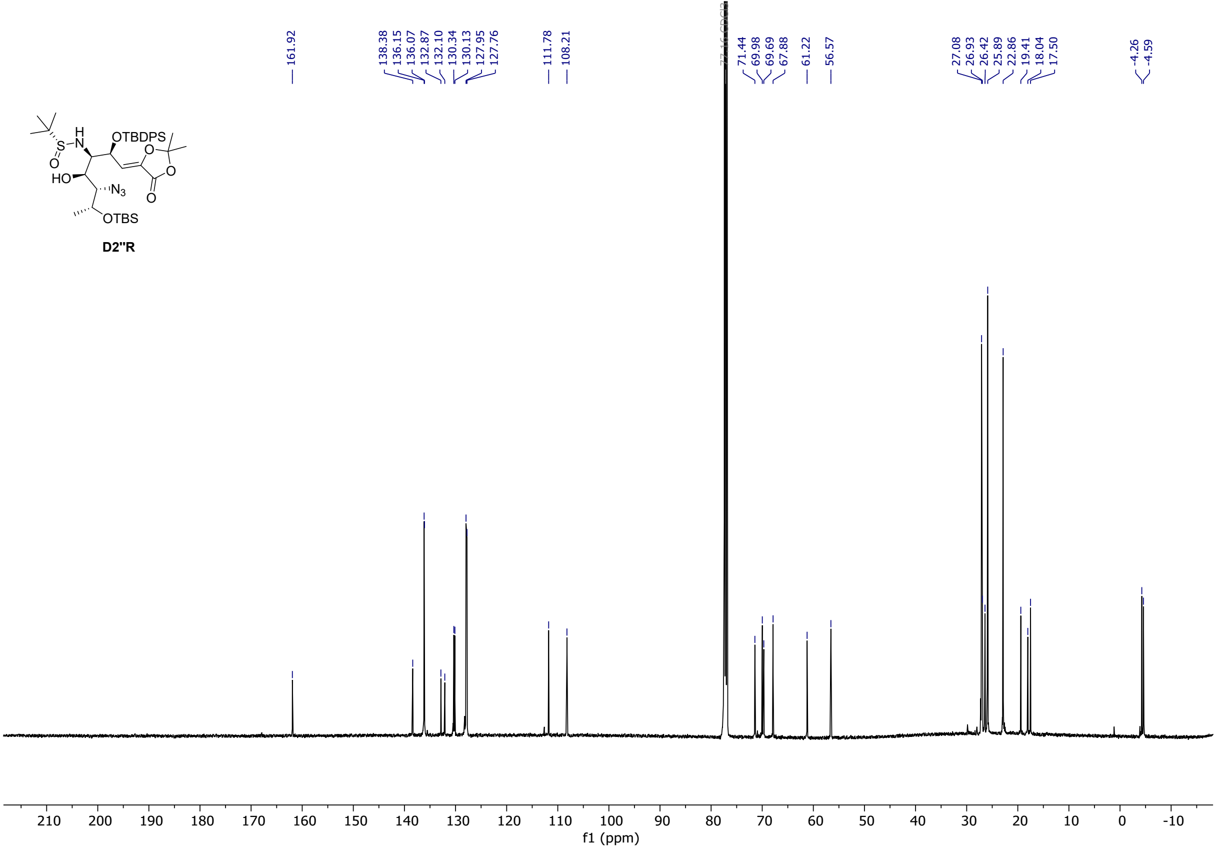
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


161.92
138.38
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136.07
132.87
132.10
130.34
130.13
127.95
127.76
111.78
108.21
77.16 CDCl3
71.44
69.98
69.69
67.88
61.22
56.57
27.08
26.93
26.42
25.89
22.86
19.41
18.04
17.50
-4.26
-4.59
OTBDPS
OTBS
HO
N3
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S
H
N
O
O
O
D2''R
210
200
190
180
170
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140
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100
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80
70
60
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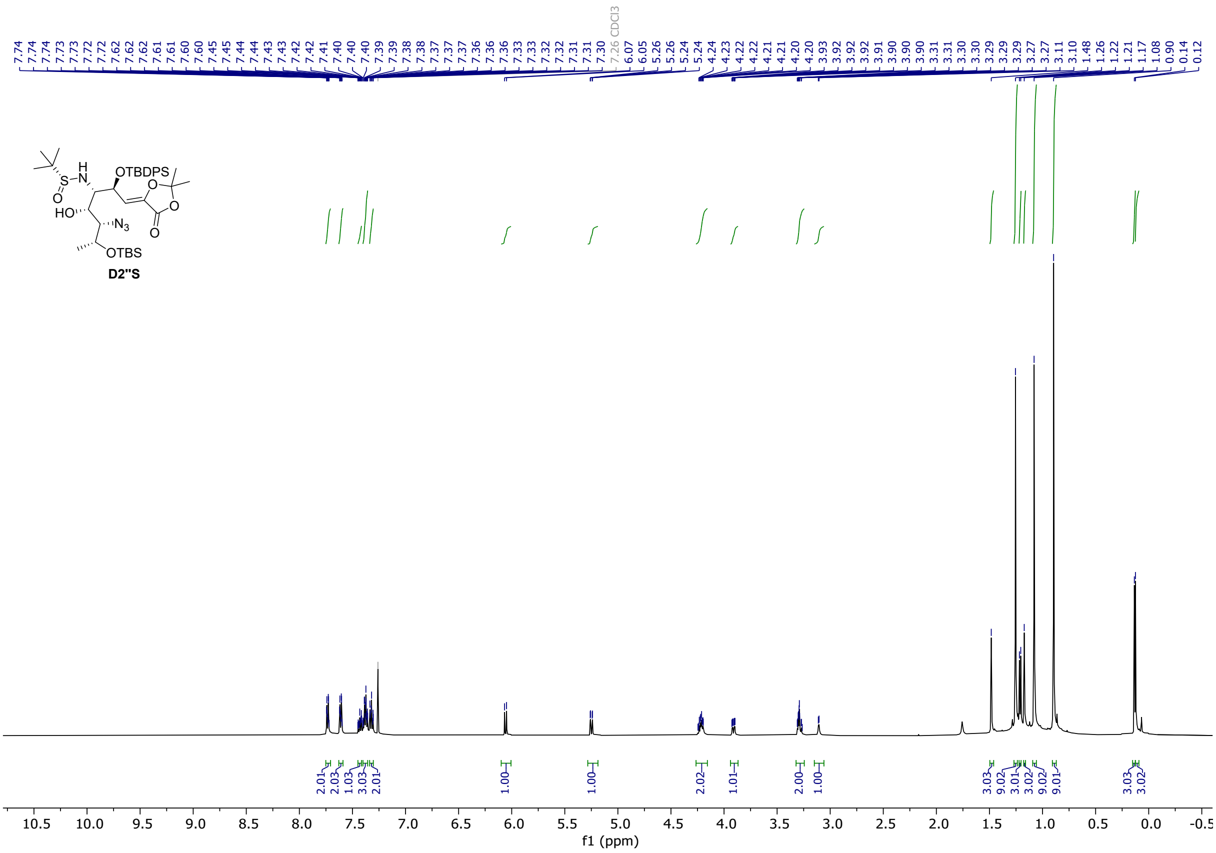
30
20
10
0
-10
f1 (ppm)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7.36
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7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.26 CDCl3
6.07
6.05
5.26
5.24
4.24
4.23
4.22
4.22
4.21
4.21
4.20
4.20
3.93
3.92
3.92
3.91
3.91
3.90
3.90
3.31
3.31
3.30
3.29
3.29
3.29
3.27
3.27
3.11
3.10
1.48
1.26
1.22
1.21
1.17
1.08
0.90
0.14
0.12
H
N
S
O
OTBDPS
O
O
O
HO
N3
OTBS
D2''S
2.01
2.03
1.03
3.03
2.01
1.00
1.00
2.02
1.01
2.00
1.00
3.03
9.02
3.01
3.02
9.01
3.03
3.02
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9.0
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6.0
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5.0
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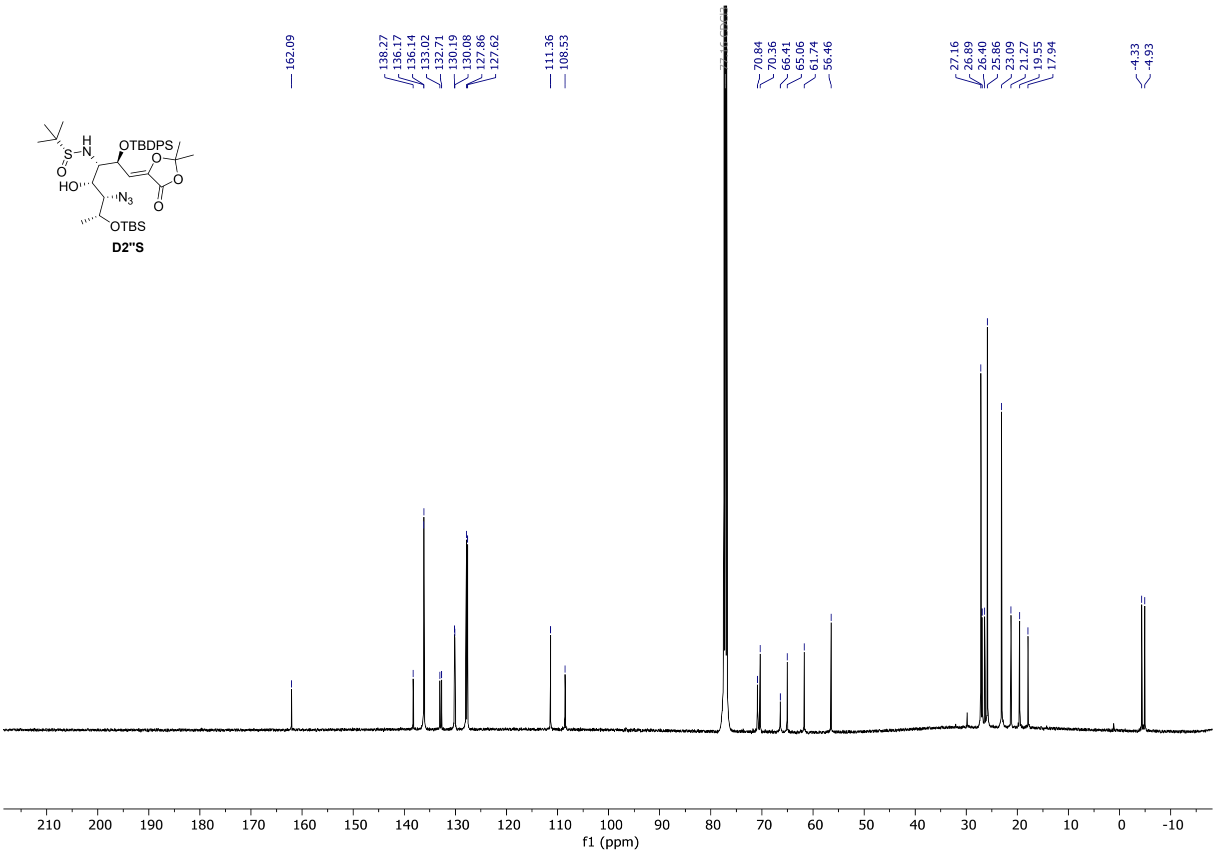
f1 (ppm)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130.08
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127.62
111.36
108.53
77.16 CDCl3
70.84
70.36
66.41
65.06
61.74
56.46
27.16
26.89
26.40
25.86
23.09
21.27
19.55
17.94
-4.33
-4.93
H
N
S
O
OTBDPS
O
O
O
HO
N3
OTBS
D2''S
210
200
190
180
170
160
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140
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120
110
100
90
80
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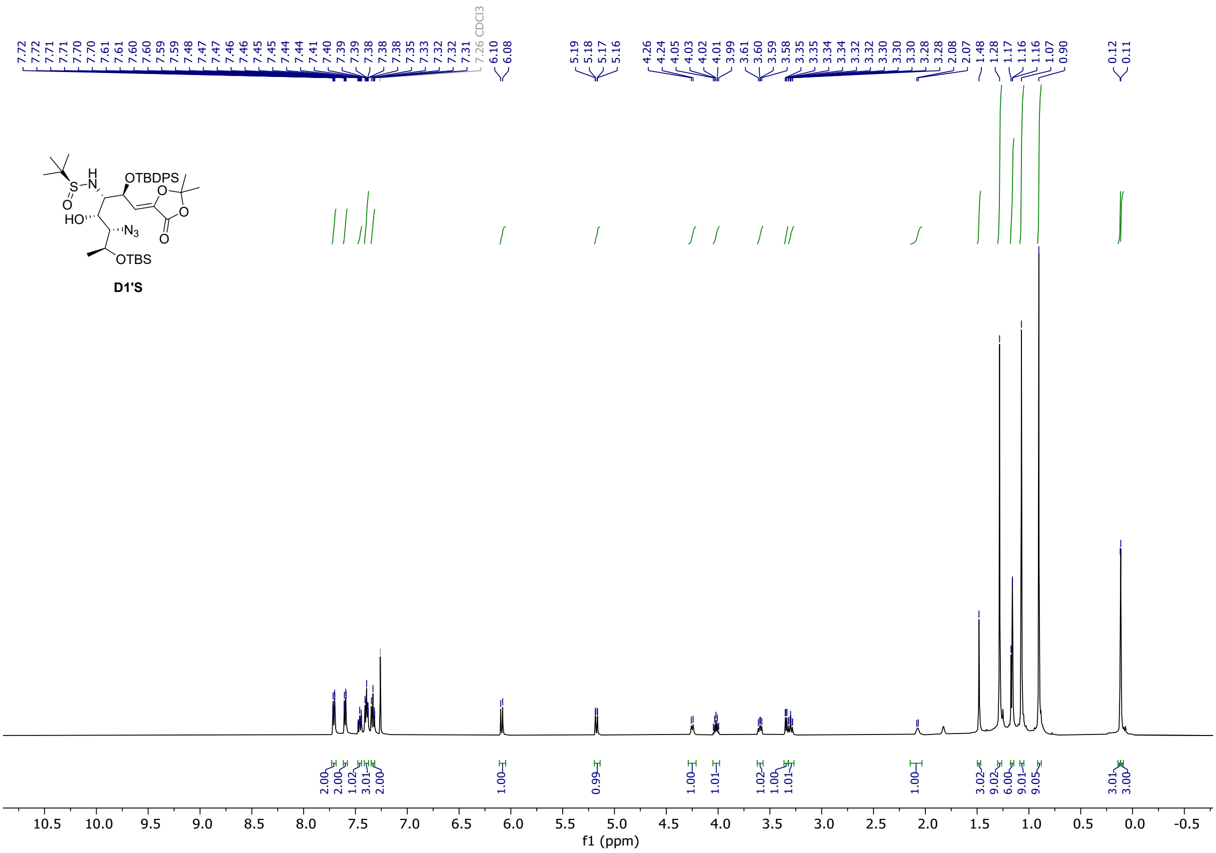
60
50
40
30
20
10
0
-10
f1 (ppm)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7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.41
7.40
7.39
7.39
7.38
7.38
7.38
7.35
7.33
7.32
7.32
7.31
7.26 CDCl3
6.10
6.08
5.19
5.18
5.17
5.16
4.26
4.24
4.05
4.03
4.02
4.01
3.99
3.61
3.60
3.59
3.58
3.35
3.35
3.34
3.32
3.32
3.30
3.30
3.30
3.28
3.28
2.08
2.07
1.48
1.28
1.17
1.16
1.16
1.07
0.90
0.12
0.11
H
N
S
O
OTBDPS
O
O
O
HO
N3
OTBS
D1'S
2.00
2.00
1.02
3.01
2.00
1.00
0.99
1.00
1.01
1.02
1.00
1.01
1.00
3.02
9.02
6.00
9.01
9.05
3.01
3.00
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10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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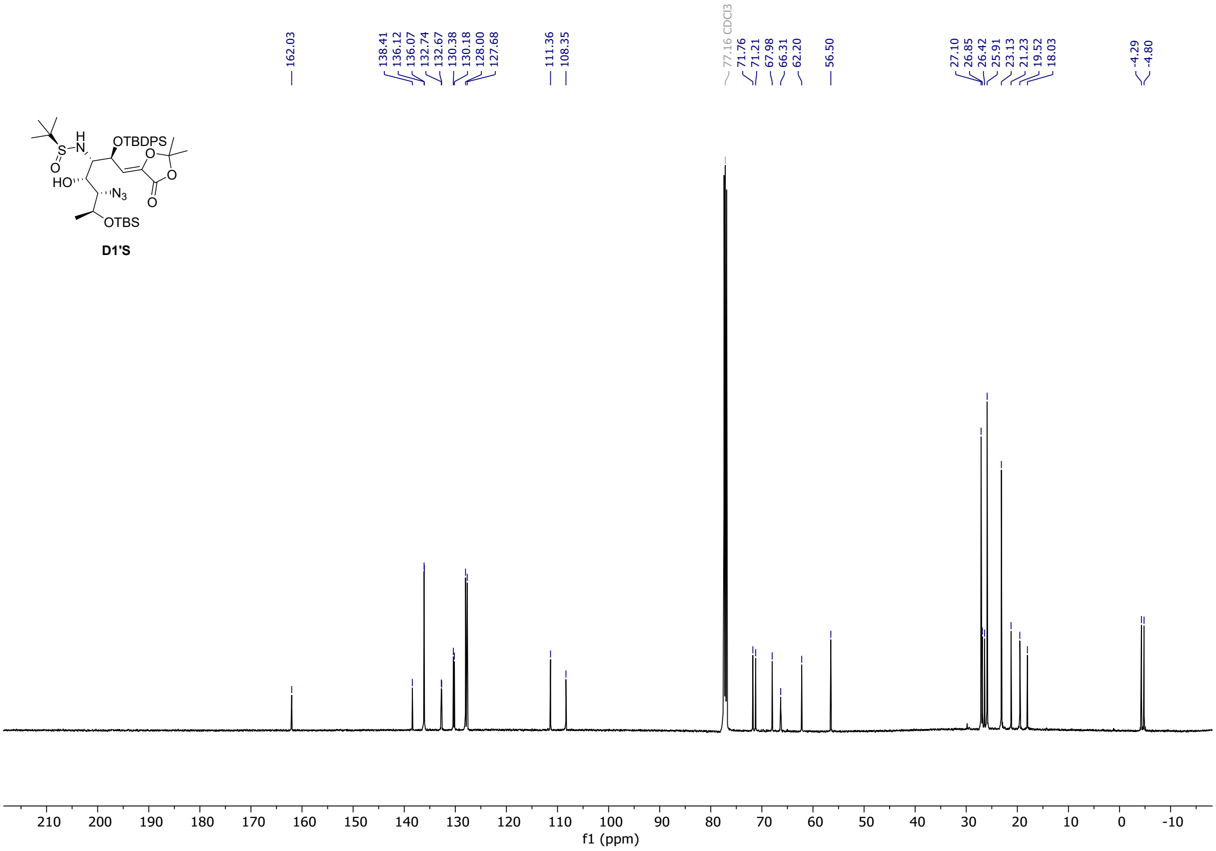
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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127.68
111.36
108.35
77.16 CDCl3
71.76
71.21
67.98
66.31
62.20
56.50
27.10
26.85
26.42
25.91
23.13
21.23
19.52
18.03
-4.29
-4.80
H
N
S
O
OTBDPS
O
O
O
HO
N3
OTBS
D1'S
210
200
190
180
170
160
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140
130
120
110
100
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80
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60
50
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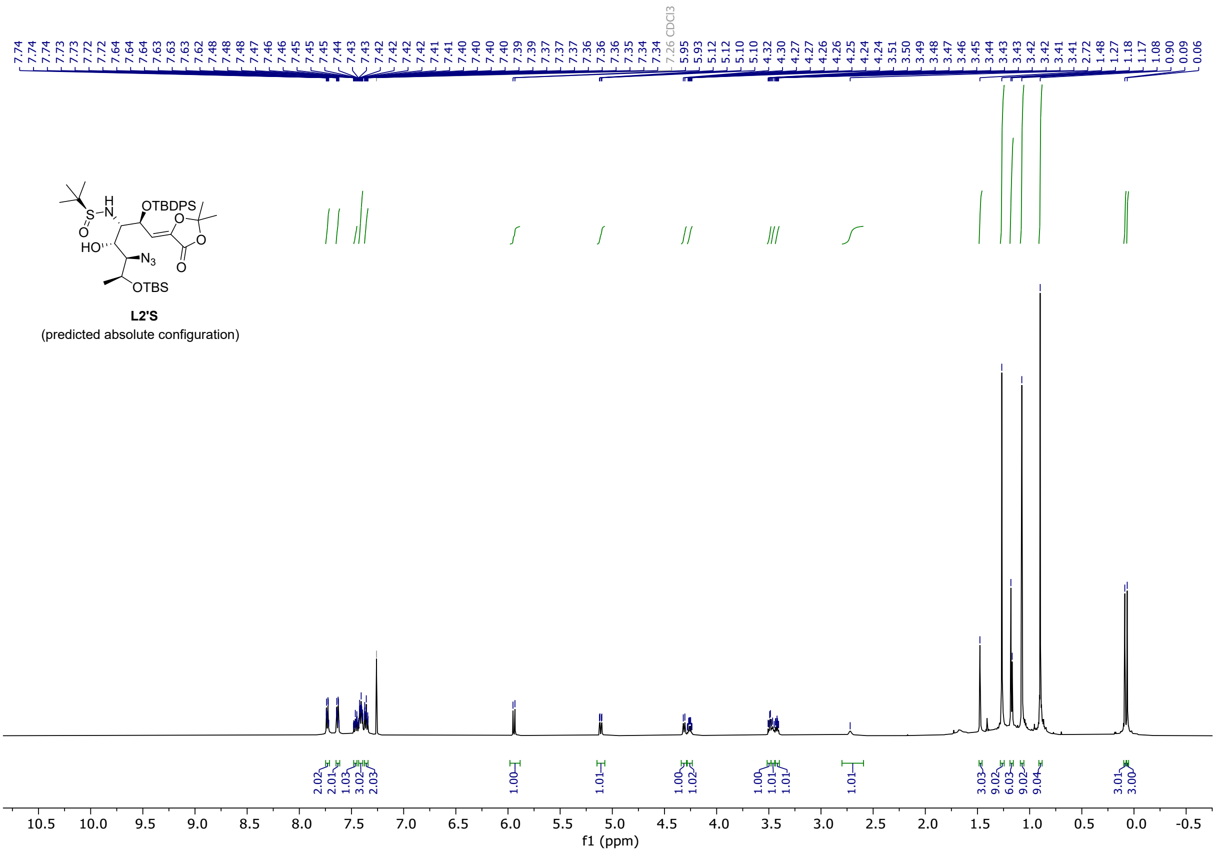
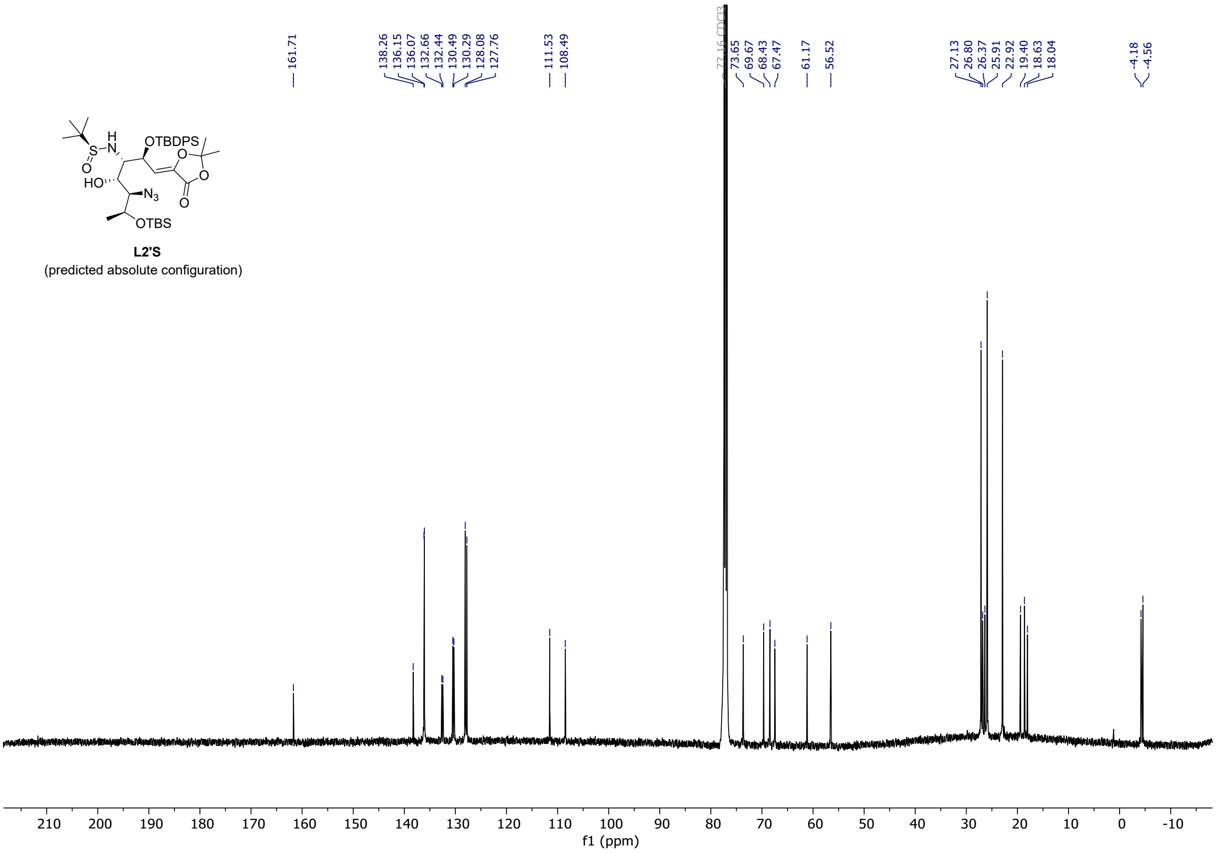
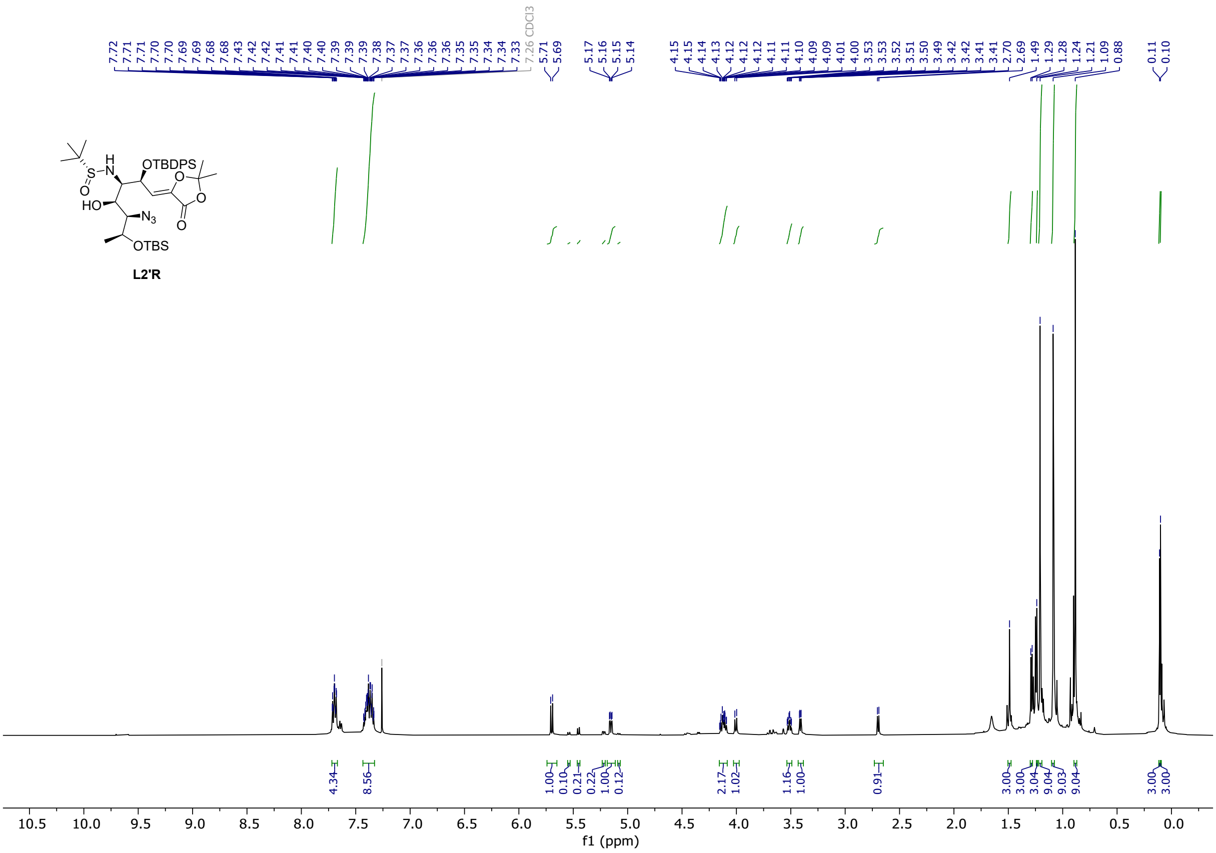
20
10
0
-10
f1 (ppm)



L2'S
(predicted absolute configuration)



L2'S
(predicted absolute configuration)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7.69
7.68
7.43
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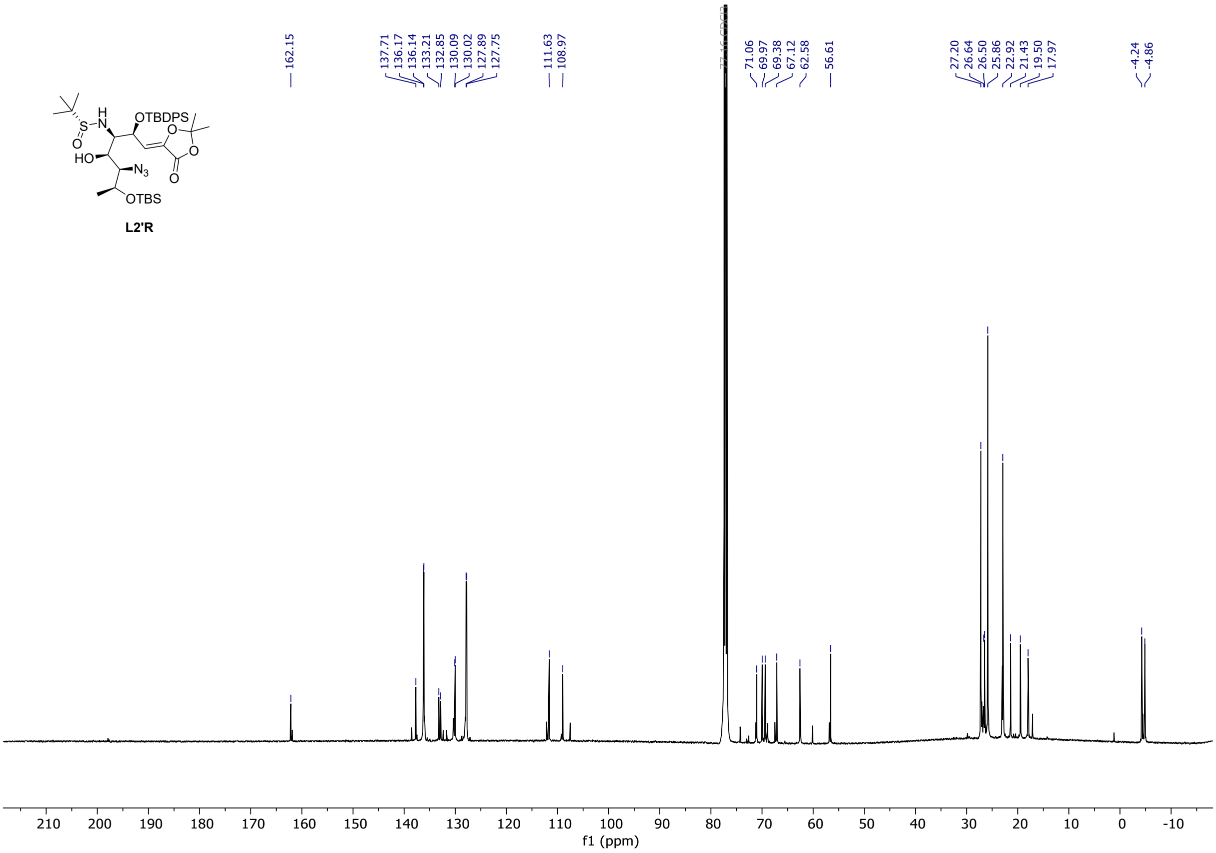
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.26 CDCl3
5.71
5.69
5.17
5.16
5.15
5.14
4.15
4.15
4.14
4.13
4.12
4.12
4.12
4.11
4.11
4.10
4.09
4.09
4.01
4.00
3.53
3.53
3.52
3.51
3.50
3.49
3.42
3.42
3.41
2.70
2.69
1.49
1.29
1.28
1.24
1.21
1.09
0.88
0.11
0.10
OTBDPS
HO
N3
OTBS
L2'R
4.34
8.56
1.00
0.10
0.21
0.22
1.00
0.12
2.17
1.02
1.16
1.00
0.91
3.00
3.00
3.04
9.04
9.03
9.04
3.00
3.00
10.5
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
0.5
0.0
f1 (ppm)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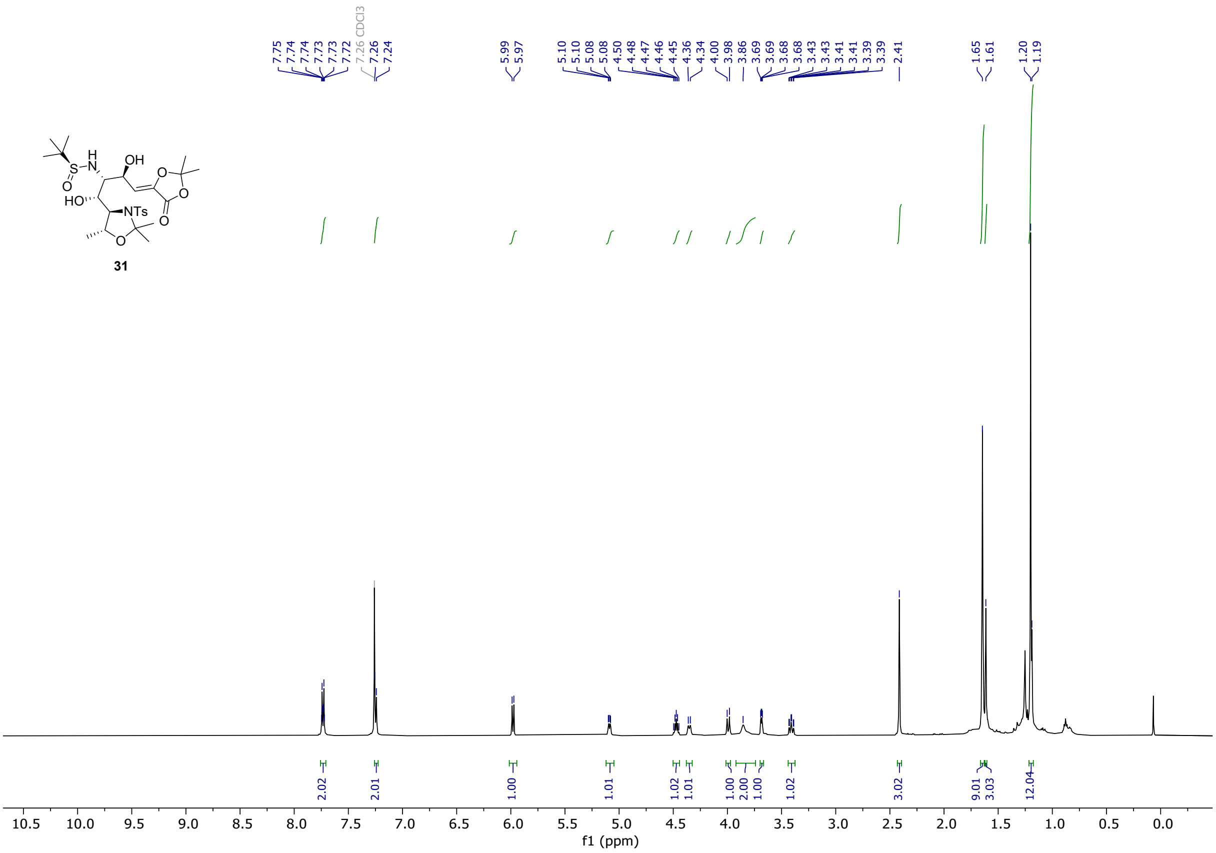
136.17
136.14
133.21
132.85
130.09
130.02
127.89
127.75
111.63
108.97
77.16 CDCl3
71.06
69.97
69.38
67.12
62.58
56.61
27.20
26.64
26.50
25.86
22.92
21.43
19.50
17.97
-4.24
-4.86
OTBDPS
HO
N3
OTBS
L2'R
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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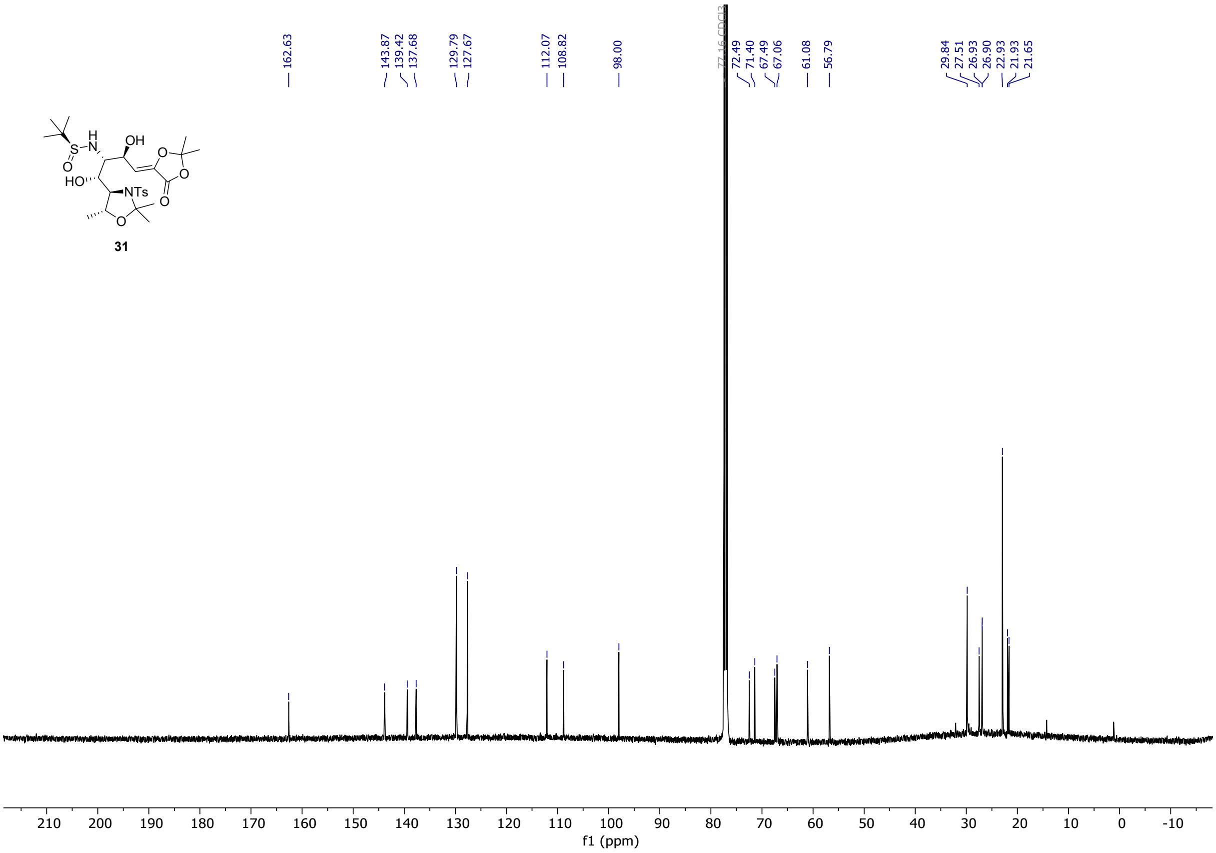
7.74
7.74
7.73
7.73
7.72
7.26 CDCl3
7.26
7.24
5.99
5.97
5.10
5.10
5.08
5.08
4.50
4.48
4.47
4.46
4.45
4.36
4.34
4.00
3.98
3.86
3.69
3.69
3.68
3.68
3.43
3.43
3.41
3.41
3.39
3.39
2.41
1.65
1.61
1.20
1.19
H
S
N
O
OH
O
O
O
HO
NTs
O
31
2.02
2.01
1.00
1.01
1.02
1.01
1.00
2.00
1.00
1.02
3.02
9.01
3.03
12.04
10.5
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
0.5
0.0
f1 (ppm)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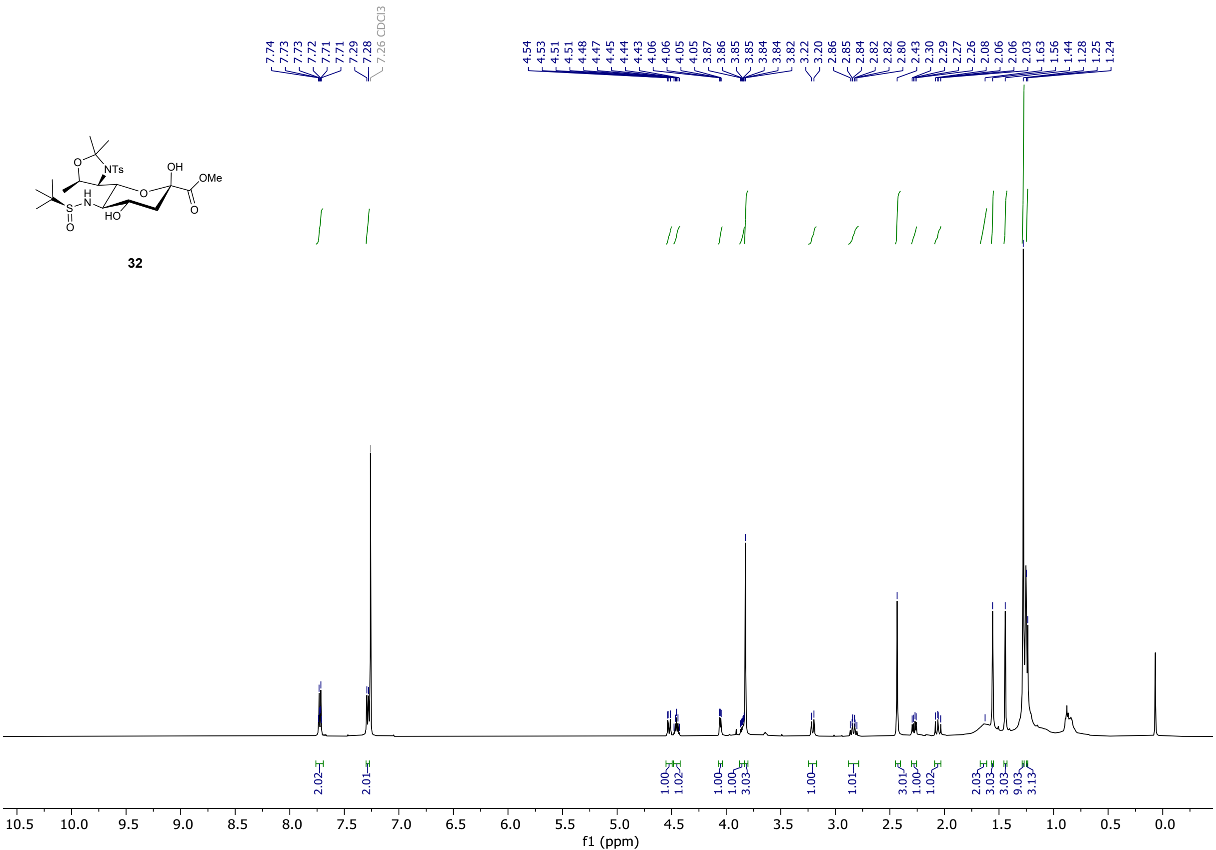
143.87
139.42
137.68
129.79
127.67
112.07
108.82
98.00
77.16 CDCl3
72.49
71.40
67.49
67.06
61.08
56.79
29.84
27.51
26.93
26.90
22.93
21.93
21.65
H
S
N
O
OH
O
O
O
HO
NTs
O
31
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.73
7.72
7.71
7.71
7.29
7.28
7.26 CDCl3
4.54
4.53
4.51
4.51
4.48
4.47
4.45
4.44
4.43
4.06
4.06
4.05
4.05
3.87
3.86
3.85
3.85
3.84
3.84
3.82
3.22
3.20
2.86
2.85
2.84
2.82
2.82
2.80
2.43
2.30
2.29
2.27
2.26
2.08
2.06
2.06
2.03
1.63
1.56
1.44
1.28
1.25
1.24
OH
OMe
NTs
O
O
H
N
S
O
HO
O
32
2.02
2.01
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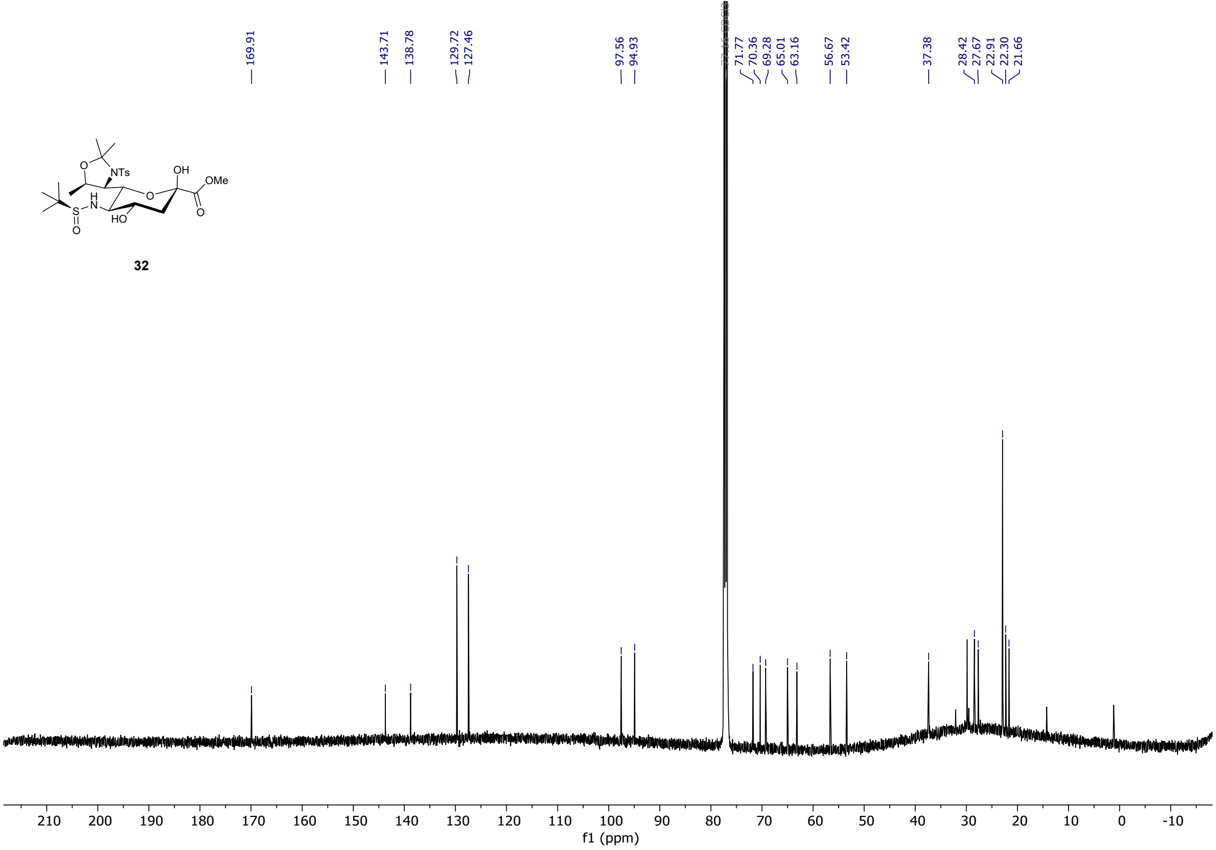
1.02
1.00
1.00
3.03
1.00
1.01
3.01
1.00
1.02
2.03
3.03
3.03
9.03
3.13
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.72
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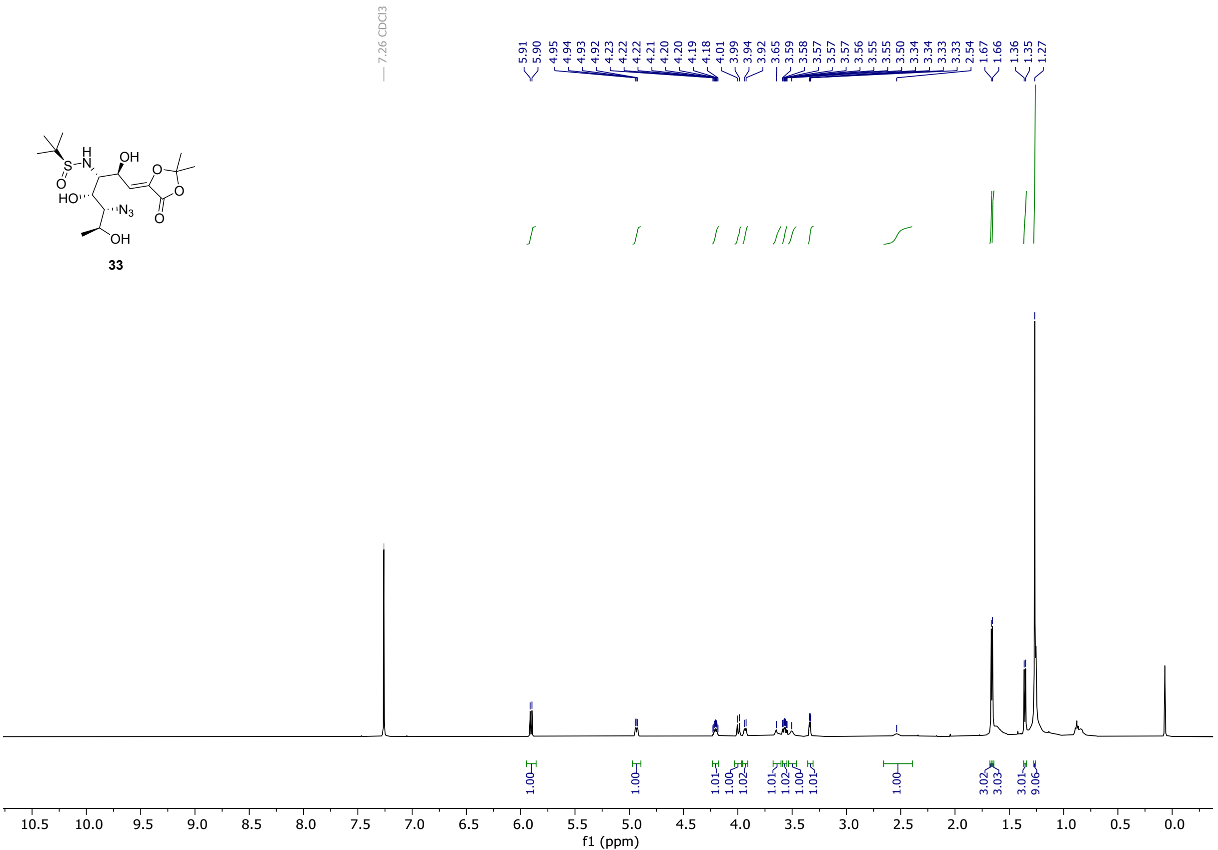
97.56
94.93
71.77
70.36
69.28
65.01
63.16
56.67
53.42
37.38
28.42
27.67
22.91
22.30
21.66
OH
OMe
NTs
O
O
H
N
S
O
HO
O
32
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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5.90
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4.94
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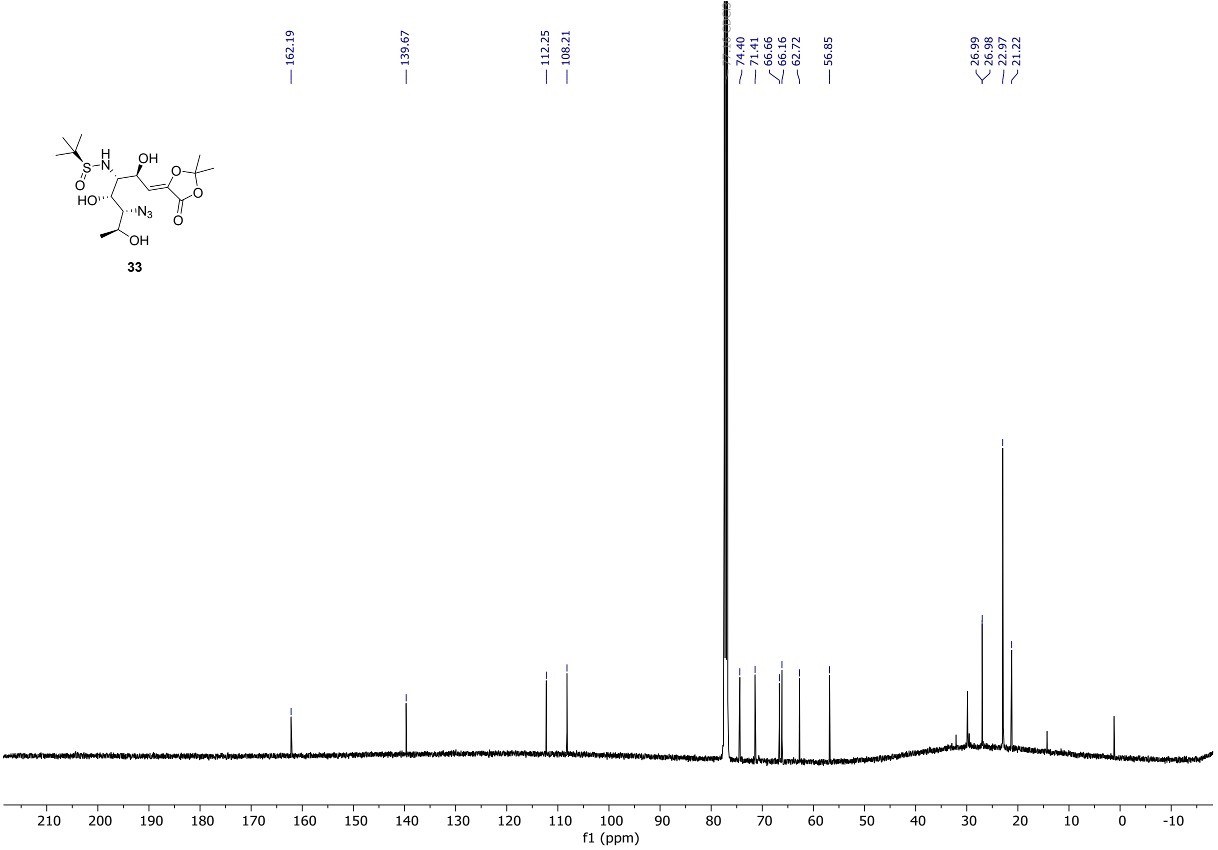
4.92
4.23
4.22
4.22
4.21
4.20
4.20
4.19
4.18
4.01
3.99
3.94
3.92
3.65
3.59
3.58
3.57
3.57
3.57
3.56
3.55
3.55
3.50
3.34
3.34
3.33
3.33
2.54
1.67
1.66
1.36
1.35
1.27
H
N
S
O
OH
O
O
O
HO
N3
OH
1.00
1.00
1.01
1.00
1.02
1.01
1.02
1.00
1.01
1.00
3.02
3.03
3.01
9.06
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

33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71.41
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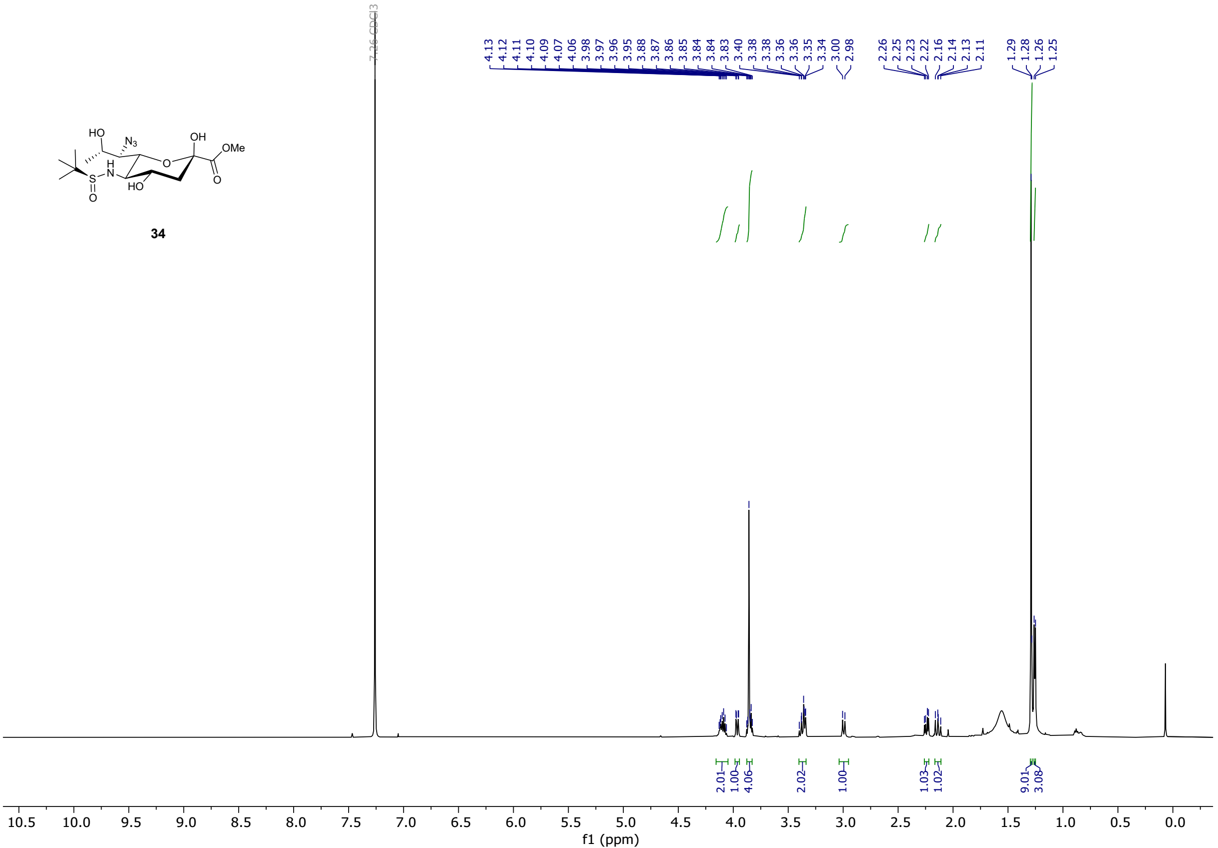
66.16
62.72
56.85
26.99
26.98
22.97
21.22
H
N
S
O
OH
O
O
O
HO
N3
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

33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4.07
4.06
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3.97
3.96
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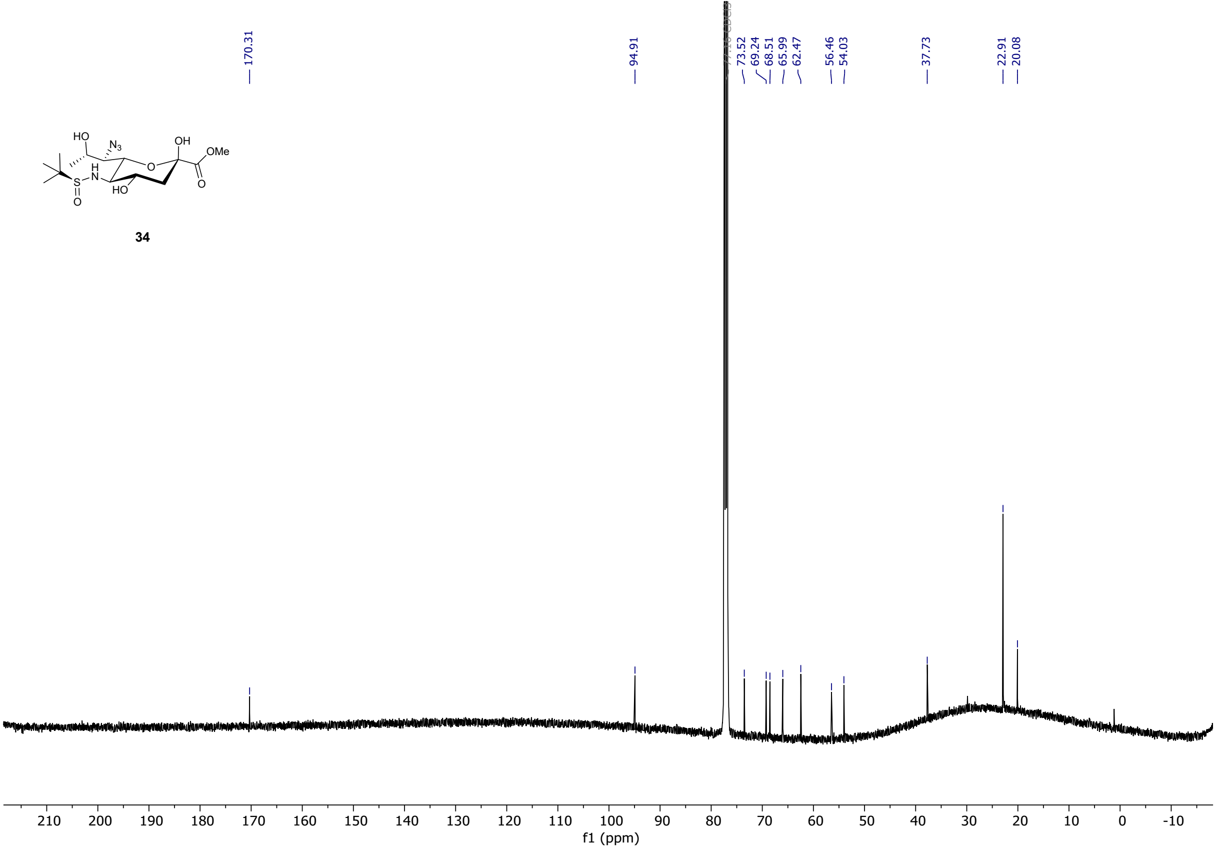
3.88
3.87
3.86
3.85
3.84
3.84
3.83
3.40
3.38
3.38
3.36
3.36
3.35
3.34
3.00
2.98
2.26
2.25
2.23
2.22
2.16
2.14
2.13
2.11
1.29
1.28
1.26
1.25
HO
N3
OH
OMe
H
N
S
O
HO
O
O
34
2.01
1.00
4.06
2.02
1.00
1.03
1.02
9.01
3.08
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


170.31
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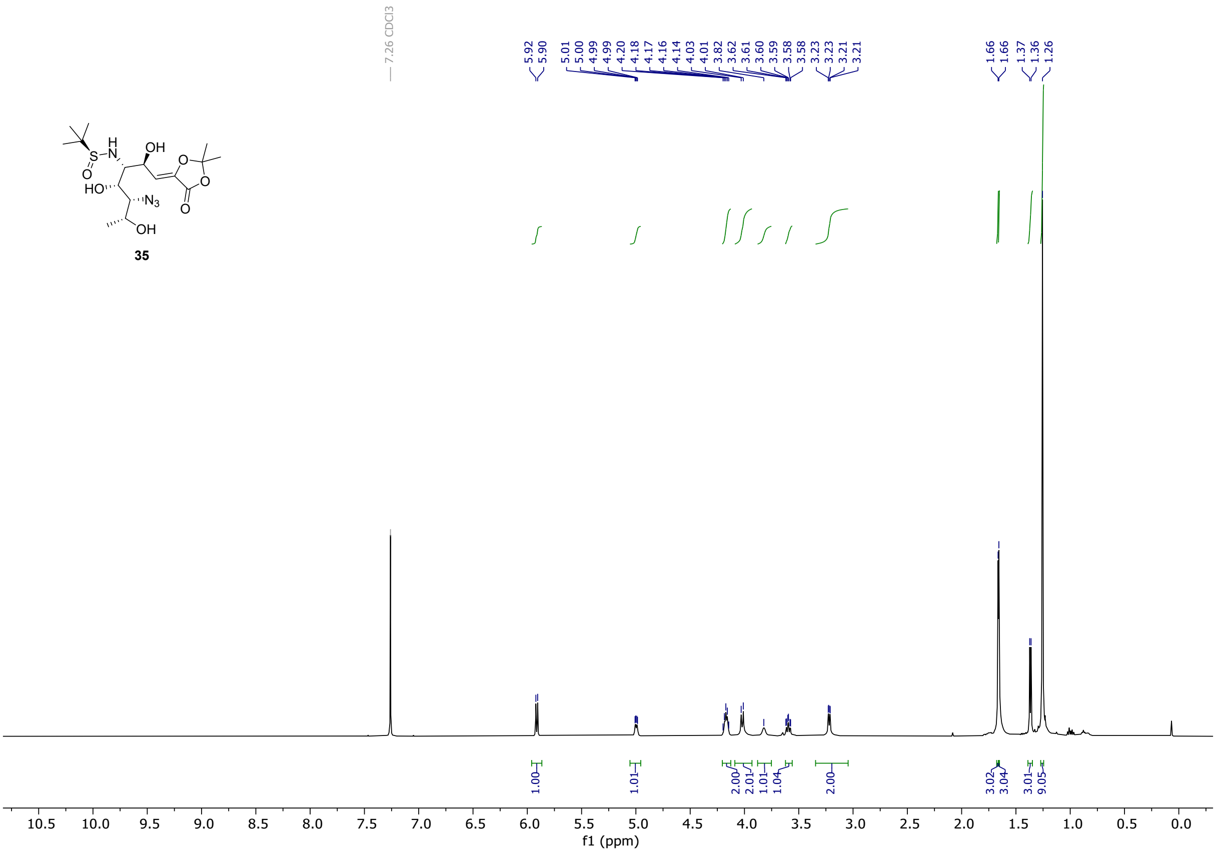
69.24
68.51
65.99
62.47
56.46
54.03
37.73
22.91
20.08
HO
N3
OH
OMe
H
N
S
O
HO
O
O
34
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



7.26 CDCl3
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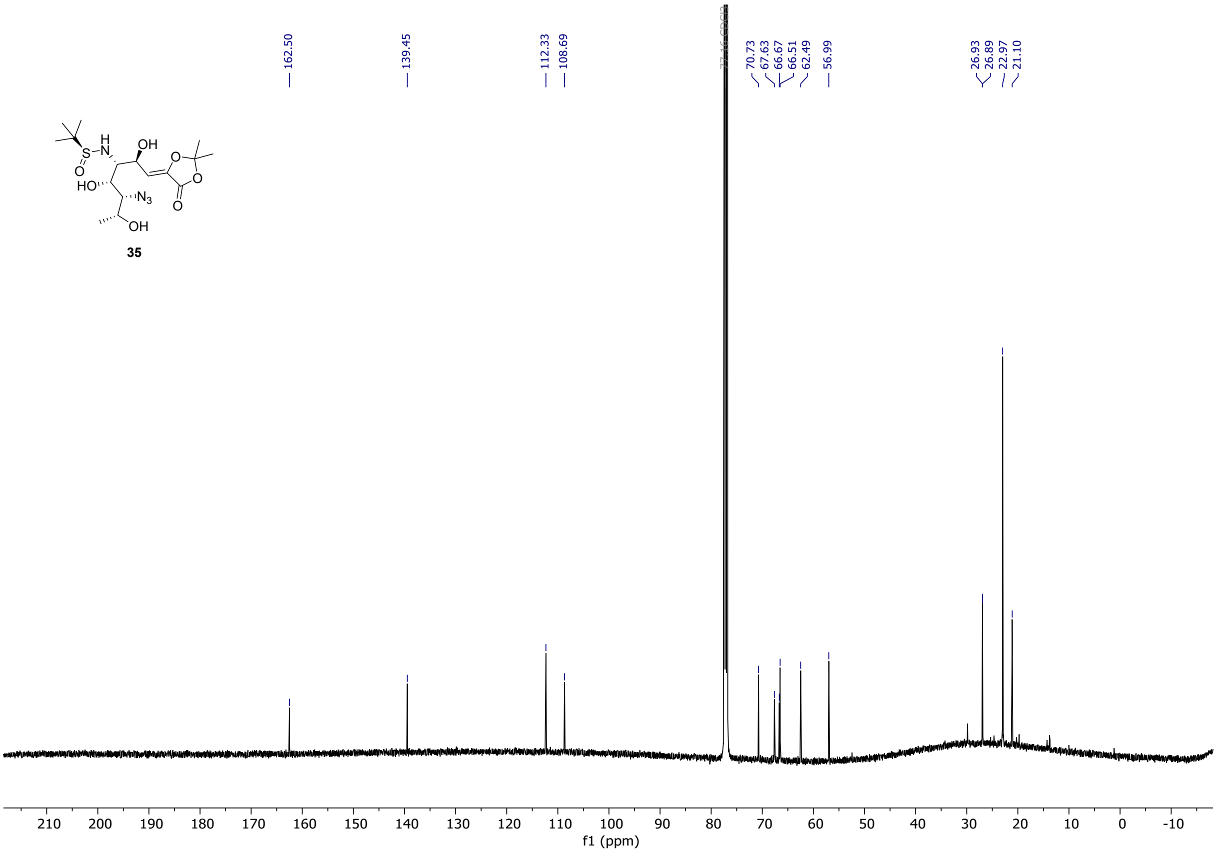
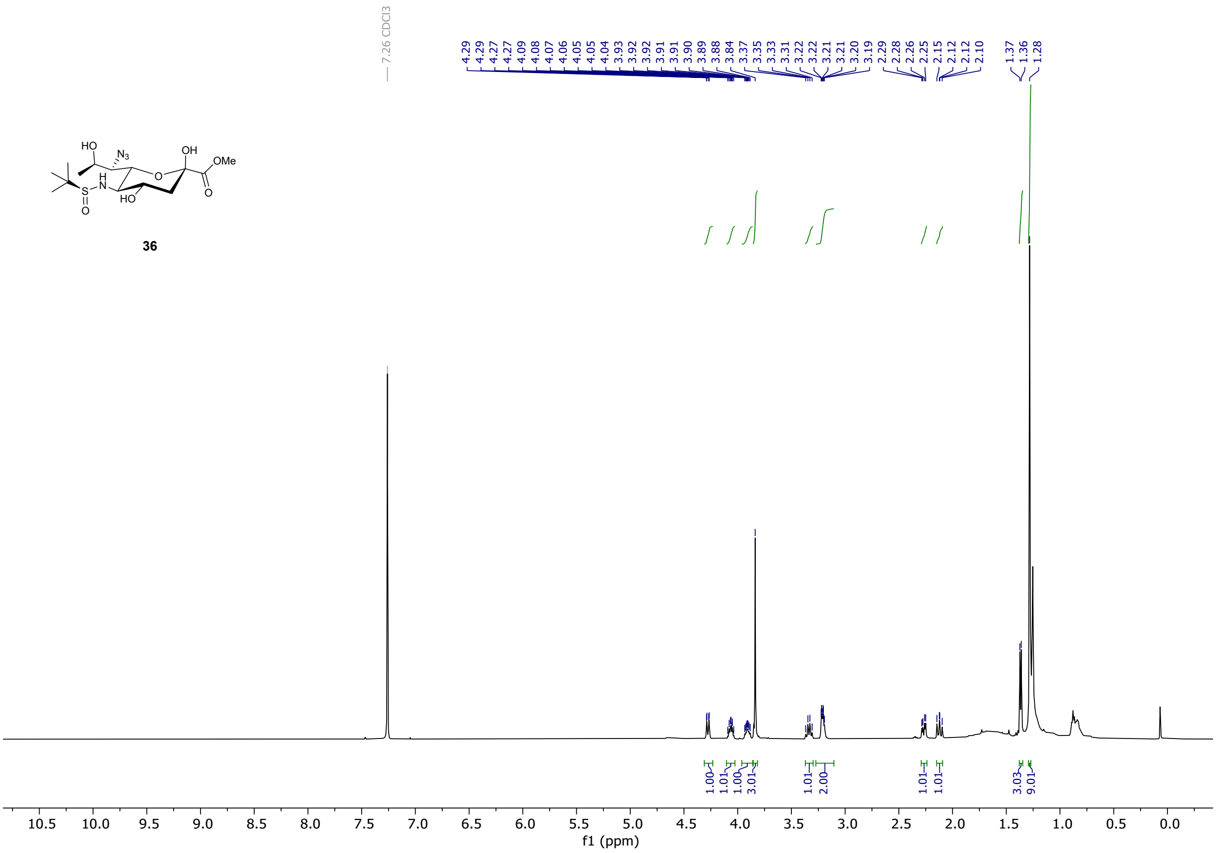
4.99
4.20
4.18
4.17
4.16
4.14
4.03
4.01
3.82
3.62
3.61
3.60
3.59
3.58
3.23
3.23
3.21
3.21
1.66
1.66
1.37
1.36
1.26
H
N
S
O
OH
O
O
HO
N3
O
OH
35
1.00
1.01
2.00
2.01
1.01
1.04
2.00
3.02
3.04
3.01
9.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



162.50
139.45
112.33
108.69
77.16 CDCl3
70.73
67.63
66.67
66.51
62.49
56.99
26.93
26.89
22.97
21.10
H
N
S
O
OH
O
O
HO
N3
O
OH
35
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.26 CDCl3
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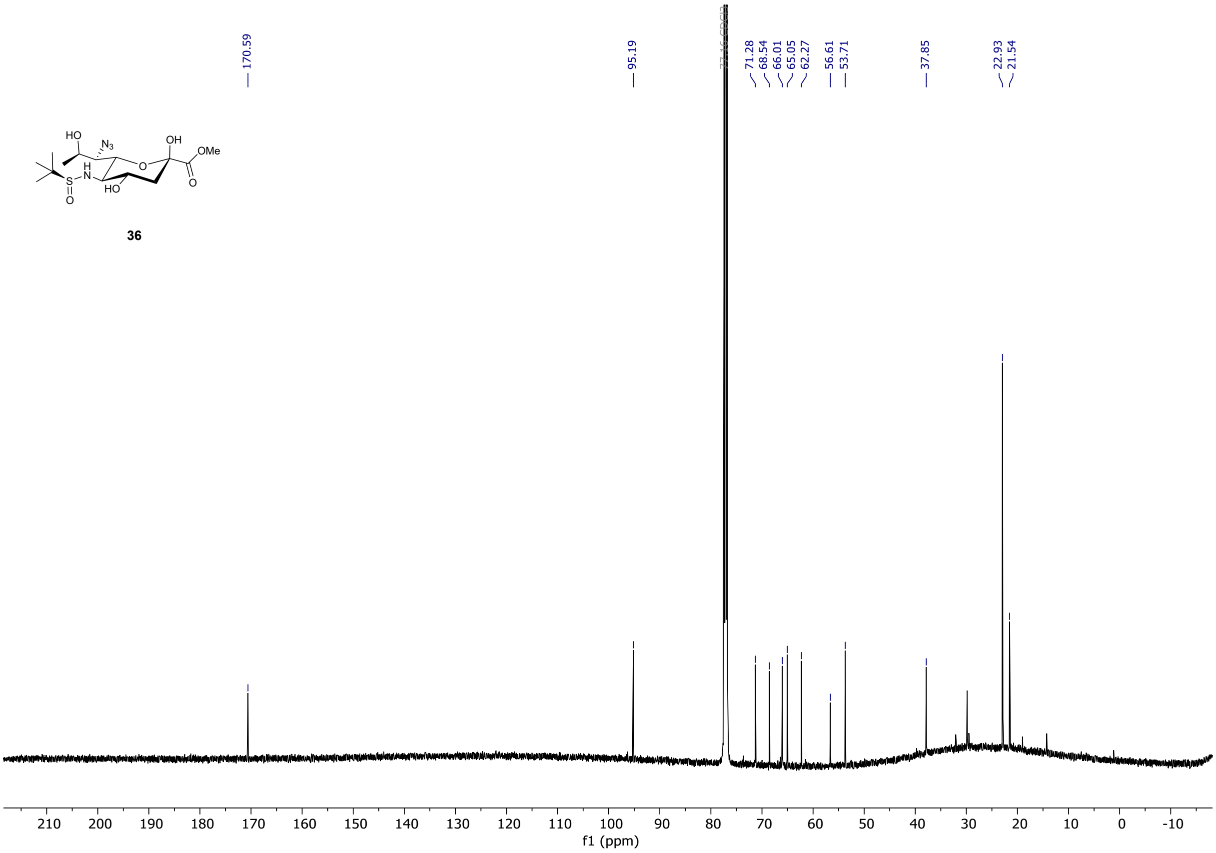
4.29
4.27
4.27
4.09
4.08
4.07
4.06
4.05
4.05
4.04
3.93
3.92
3.92
3.91
3.91
3.90
3.89
3.88
3.84
3.37
3.35
3.33
3.31
3.22
3.22
3.21
3.21
3.20
3.19
2.29
2.28
2.26
2.25
2.15
2.12
2.12
2.10
1.37
1.36
1.28
HO
N3
OH
OMe
H
N
O
S
O
HO
O
36
1.00
1.01
1.00
3.01
1.01
2.00
1.01
1.01
3.03
9.01
10.5
10.0
9.5
9.0
8.5
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
0.5
0.0
f1 (ppm)


170.59
95.19
77.16 CDCl3
71.28
68.54
66.01
65.05
62.27
56.61
53.71
37.85
22.93
21.54
HO
N3
OH
OMe
H
N
O
S
O
HO
O
36
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
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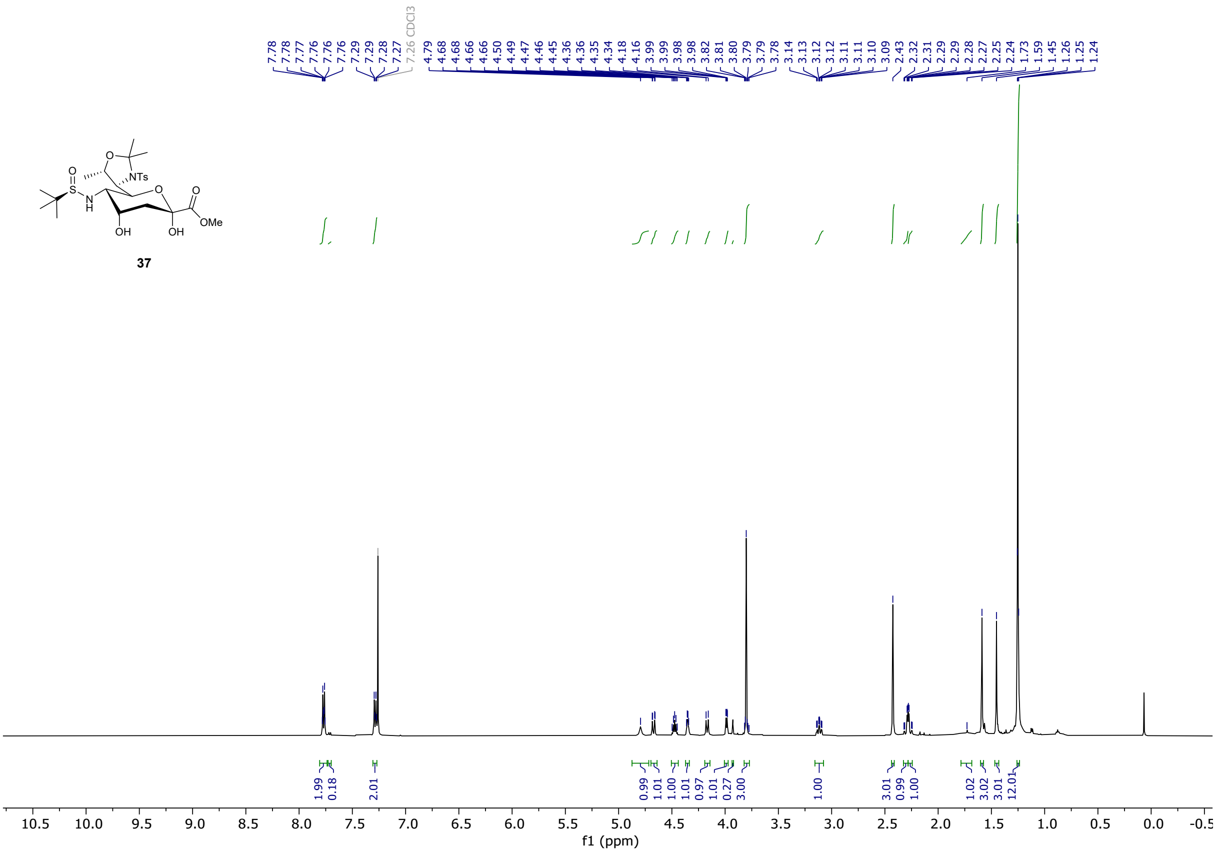
f1 (ppm)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4.68
4.66
4.66
4.50
4.49
4.47
4.46
4.45
4.36
4.36
4.35
4.34
4.18
4.16
3.99
3.99
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3.82
3.81
3.80
3.79
3.79
3.78
3.14
3.13
3.12
3.12
3.11
3.11
3.10
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H
O
O
OMe
OH
OH
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0.99
1.01
1.00
1.01
0.97
1.01
0.27
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1.00
3.01
0.99
1.00
1.02
3.02
3.01
12.01
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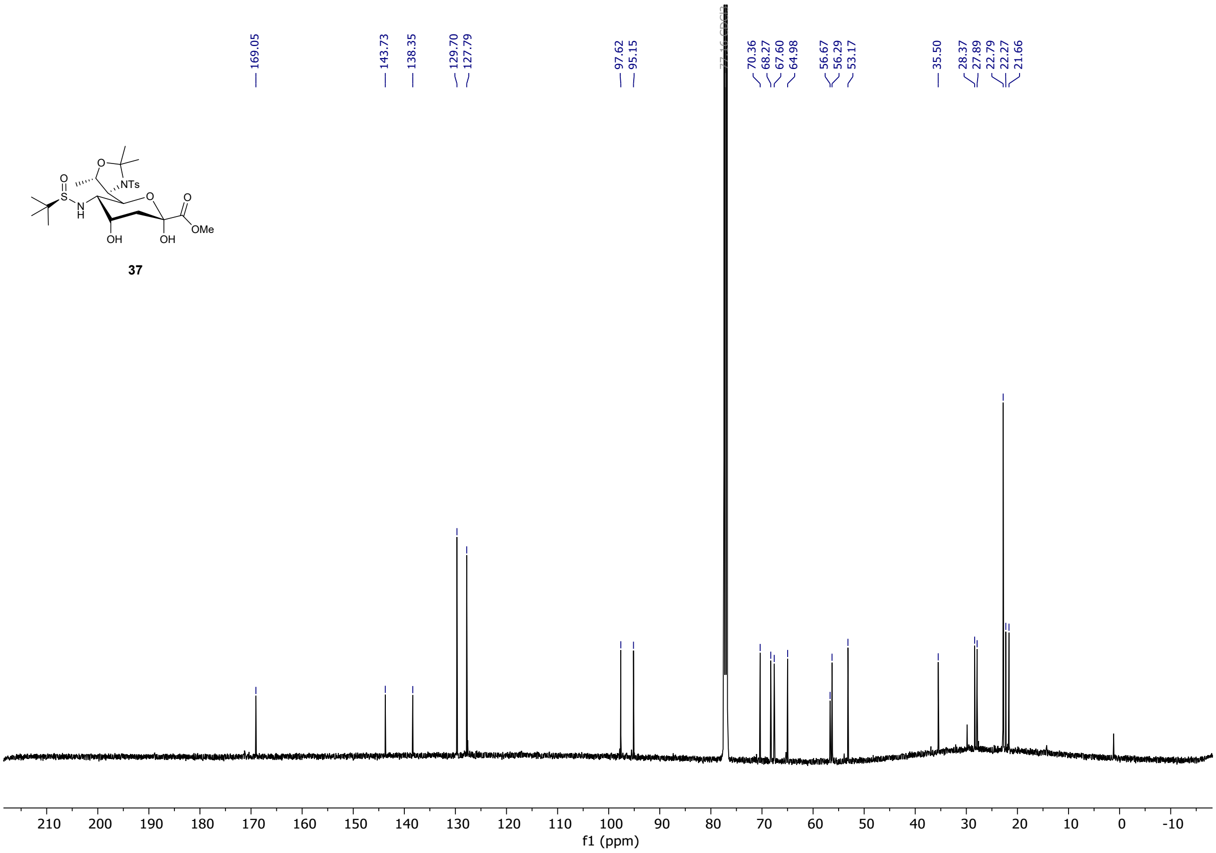
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64.98
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56.29
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35.50
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27.89
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22.27
21.66
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NTs
O
S
N
H
O
O
OMe
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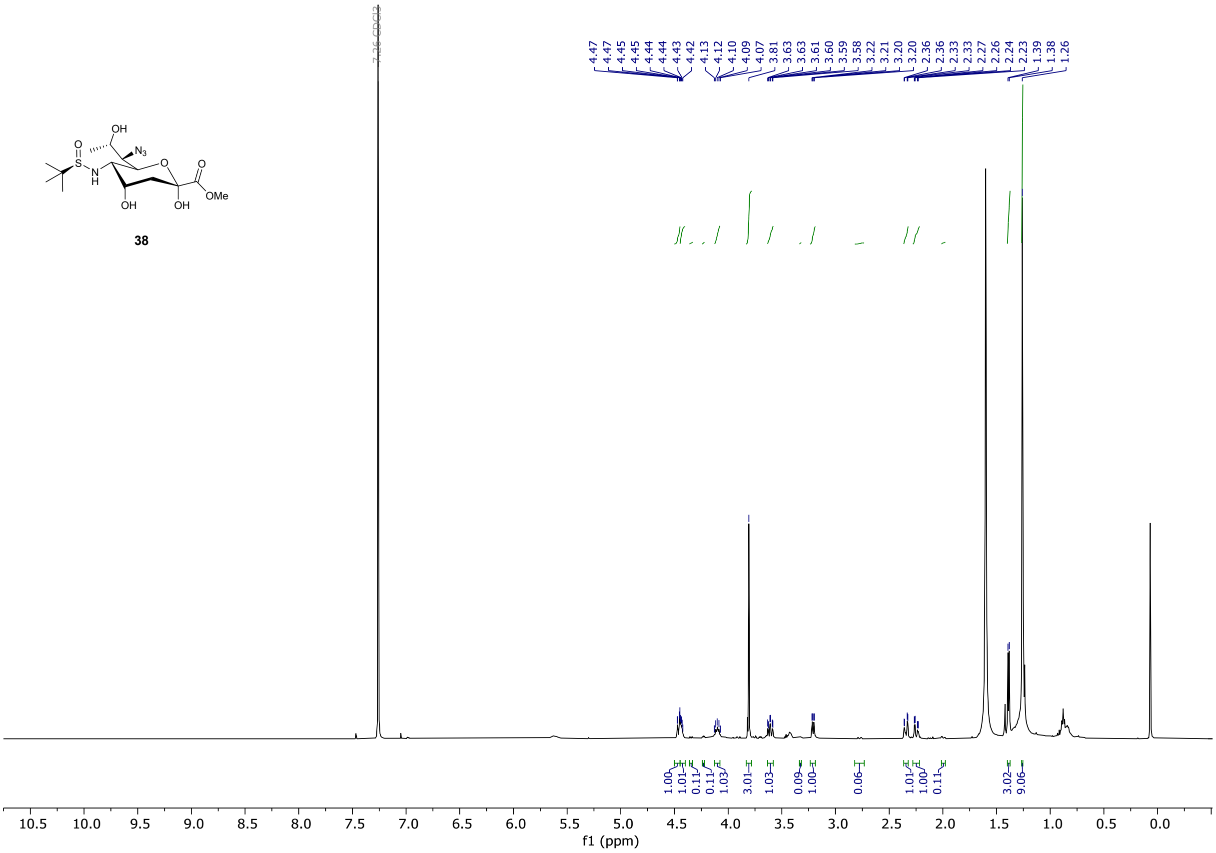
-10
f1 (ppm)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4.43
4.42
4.13
4.12
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4.09
4.07
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3.63
3.61
3.60
3.59
3.58
3.22
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3.20
2.36
2.36
2.33
2.33
2.27
2.26
2.24
2.23
1.39
1.38
1.26
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1.01
0.11
0.11
1.03
3.01
1.03
0.09
1.00
0.06
1.01
1.00
0.11
3.02
9.06
10.5 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 0.5 0.0
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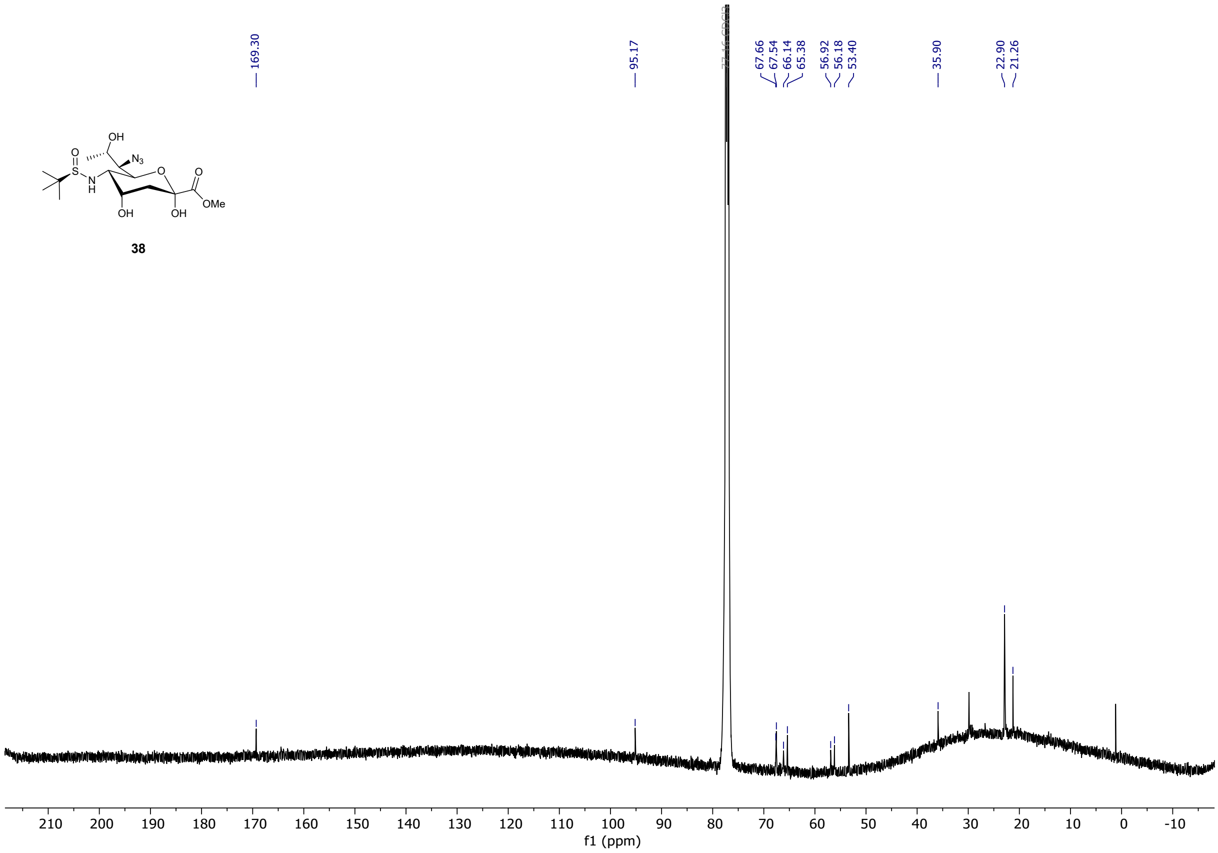
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OH
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66.14
65.38
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21.26
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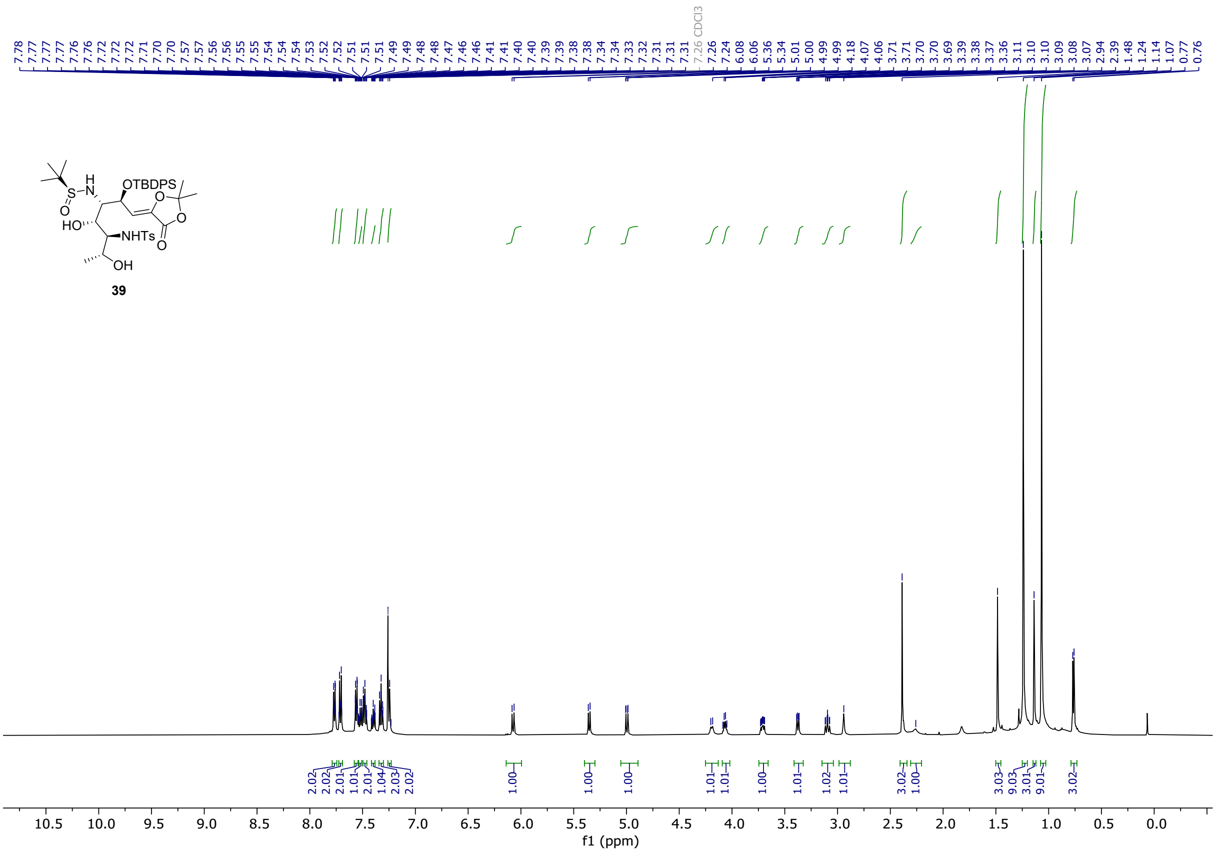
f1 (ppm)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7.34
7.33
7.32
7.31
7.31
7.31
7.26 CDCl3
7.24
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5.36
5.34
5.01
5.00
4.99
4.99
4.18
4.07
4.06
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3.70
3.70
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3.38
3.37
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3.10
3.10
3.09
3.08
3.07
2.94
2.39
1.48
1.24
1.14
1.07
0.77
0.76
OTBDPS
H
N
S
O
HO
NHTs
OH
O
O
O
39
2.02
2.02
2.01
1.01
2.01
1.04
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2.02
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1.00
1.00
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1.00
1.01
1.02
1.01
3.02
1.00
3.03
9.03
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9.01
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10.0
9.5
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8.0
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6.0
5.5
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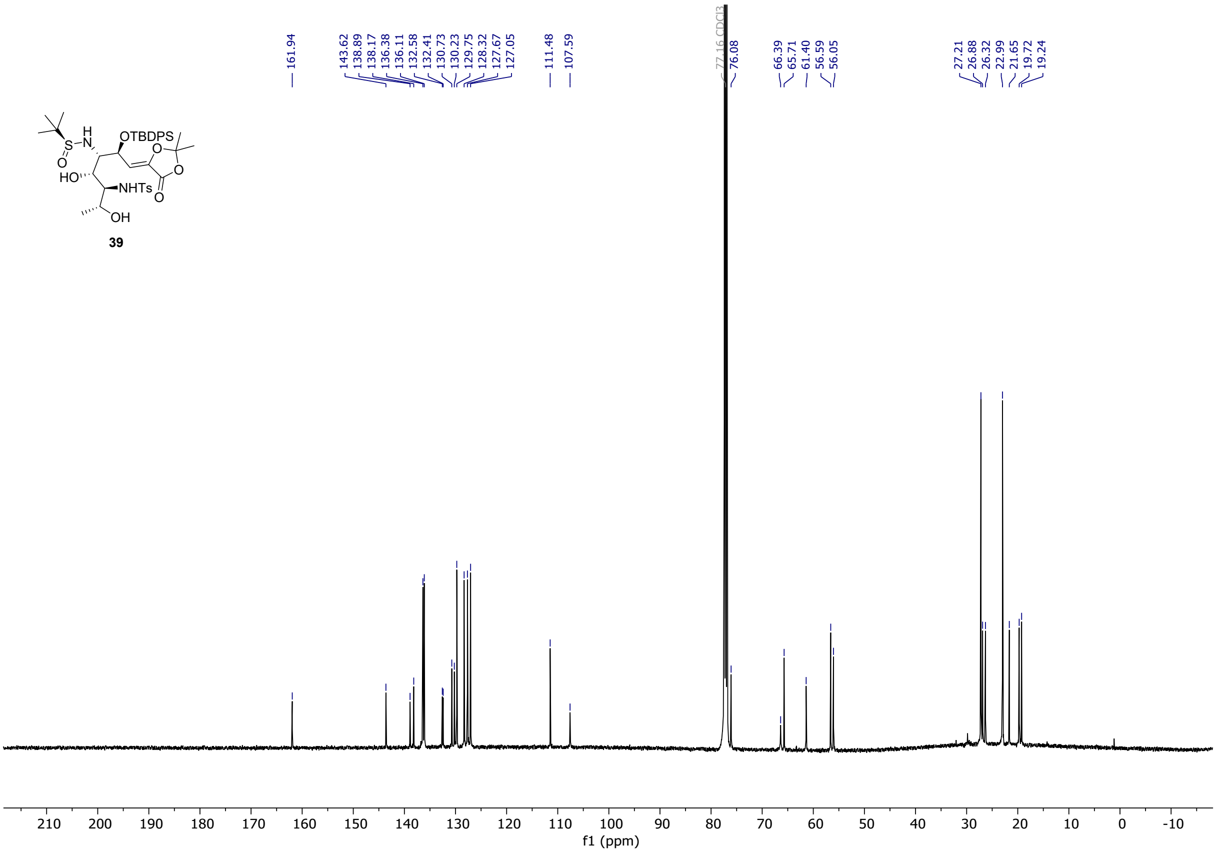
f1 (ppm)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127.67
127.05
111.48
107.59
77.16 CDCl3
76.08
66.39
65.71
61.40
56.59
56.05
27.21
26.88
26.32
22.99
21.65
19.72
19.24
OTBDPS
H
N
S
O
HO
NHTs
OH
O
O
O
39
210
200
190
180
170
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110
100
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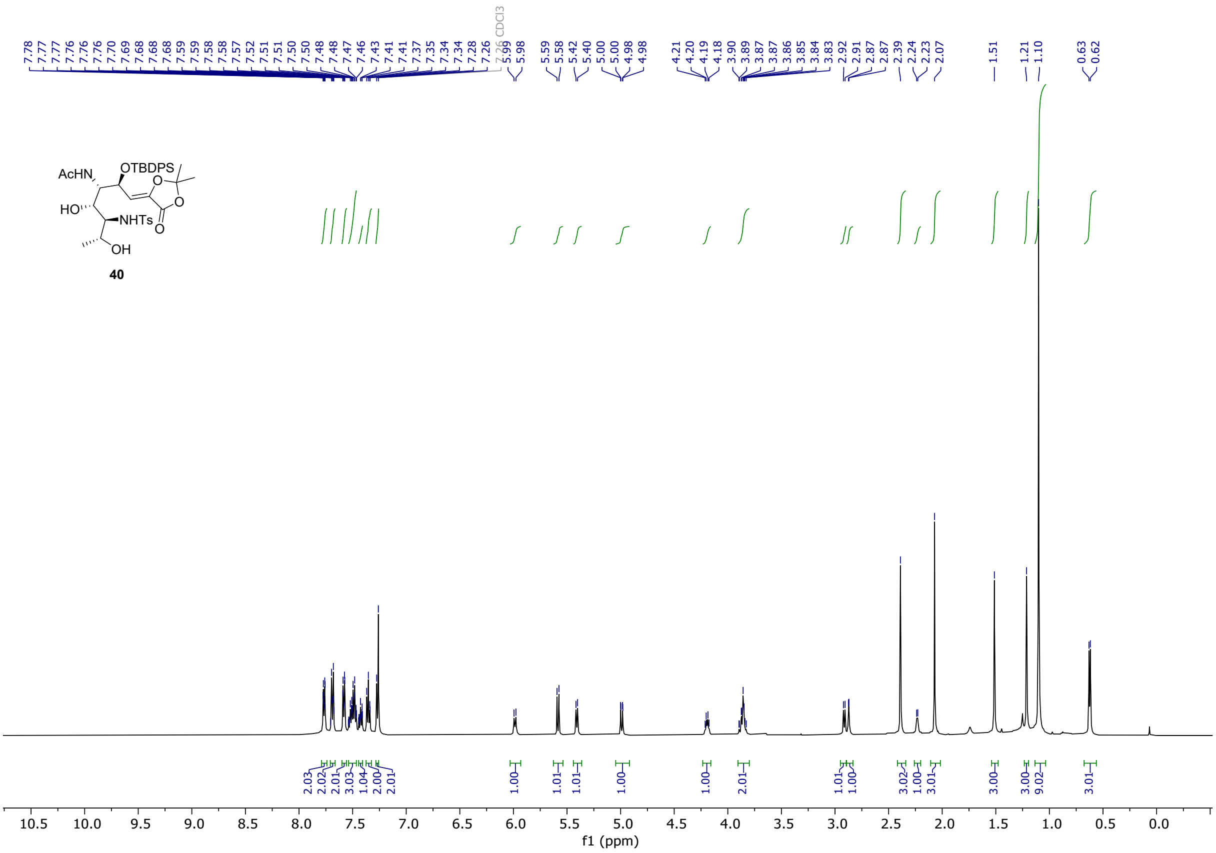
40
30
20
10
0
-10
f1 (ppm)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7.52
7.51
7.51
7.50
7.50
7.48
7.48
7.47
7.46
7.43
7.41
7.41
7.37
7.35
7.34
7.34
7.28
7.26
7.26 CDCl3
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5.98
5.59
5.58
5.42
5.40
5.00
5.00
4.98
4.98
4.21
4.20
4.19
4.18
3.90
3.89
3.87
3.87
3.86
3.85
3.84
3.83
2.92
2.91
2.87
2.87
2.39
2.24
2.23
2.07
1.51
1.21
1.10
0.63
0.62
AcHN
OTBDPS
O
O
HO
NHTs
O
OH
40
2.03
2.02
2.01
3.03
1.04
2.00
2.01
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1.00
2.01
1.01
1.00
3.02
1.00
3.01
3.00
3.00
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3.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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1.0
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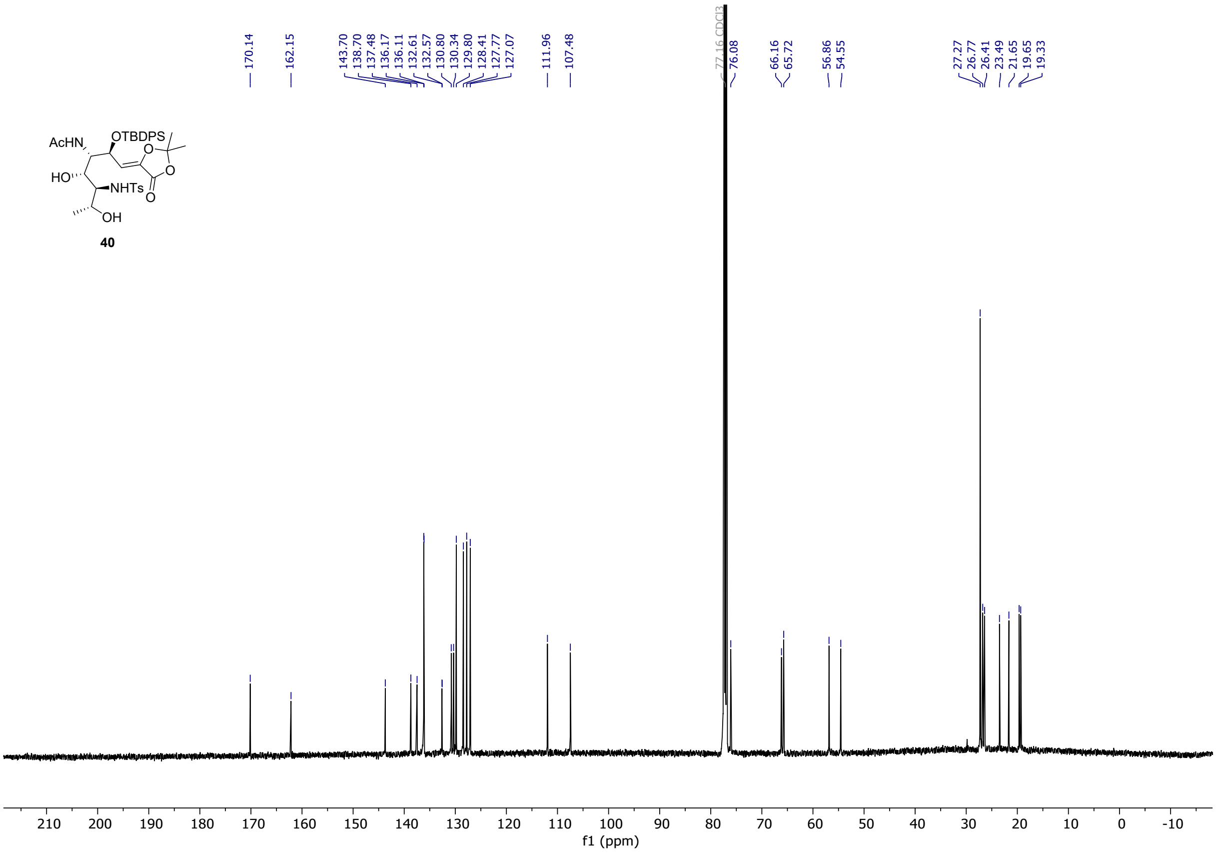
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66.16
65.72
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54.55
27.27
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AcHN
OTBDPS
O
O
HO
NHTs
O
OH
40
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200
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180
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30
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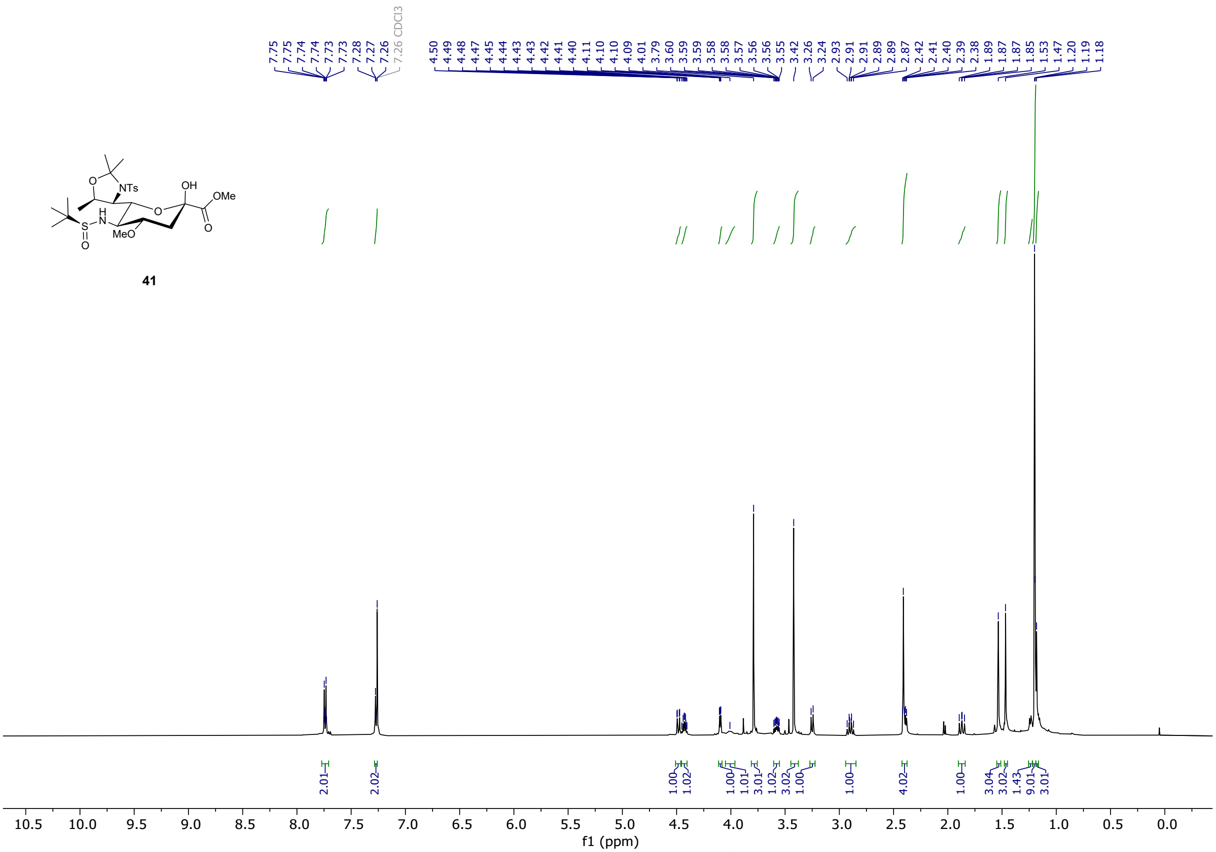
-10
f1 (ppm)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4.48
4.47
4.45
4.44
4.43
4.43
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4.41
4.40
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4.10
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3.58
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2.87
2.42
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1.85
1.53
1.47
1.20
1.19
1.18
OH
OMe
O
NTs
O
S
O
H
N
MeO
O
2.01
2.02
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1.02
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1.02
3.02
1.00
1.00
4.02
1.00
3.04
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6.0
5.5
5.0
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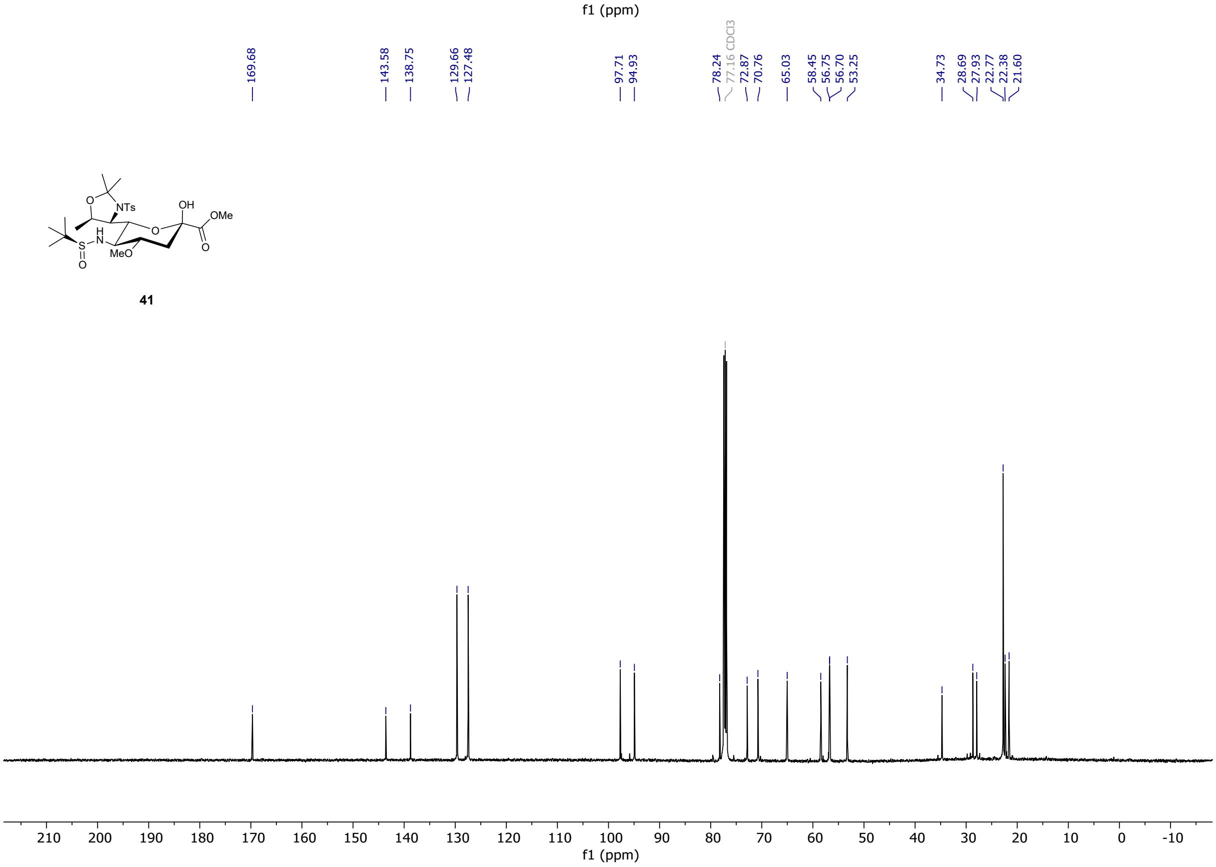
f1 (ppm)

41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56.75
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53.25
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28.69
27.93
22.77
22.38
21.60
OH
OMe
O
NTs
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S
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H
N
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180
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160
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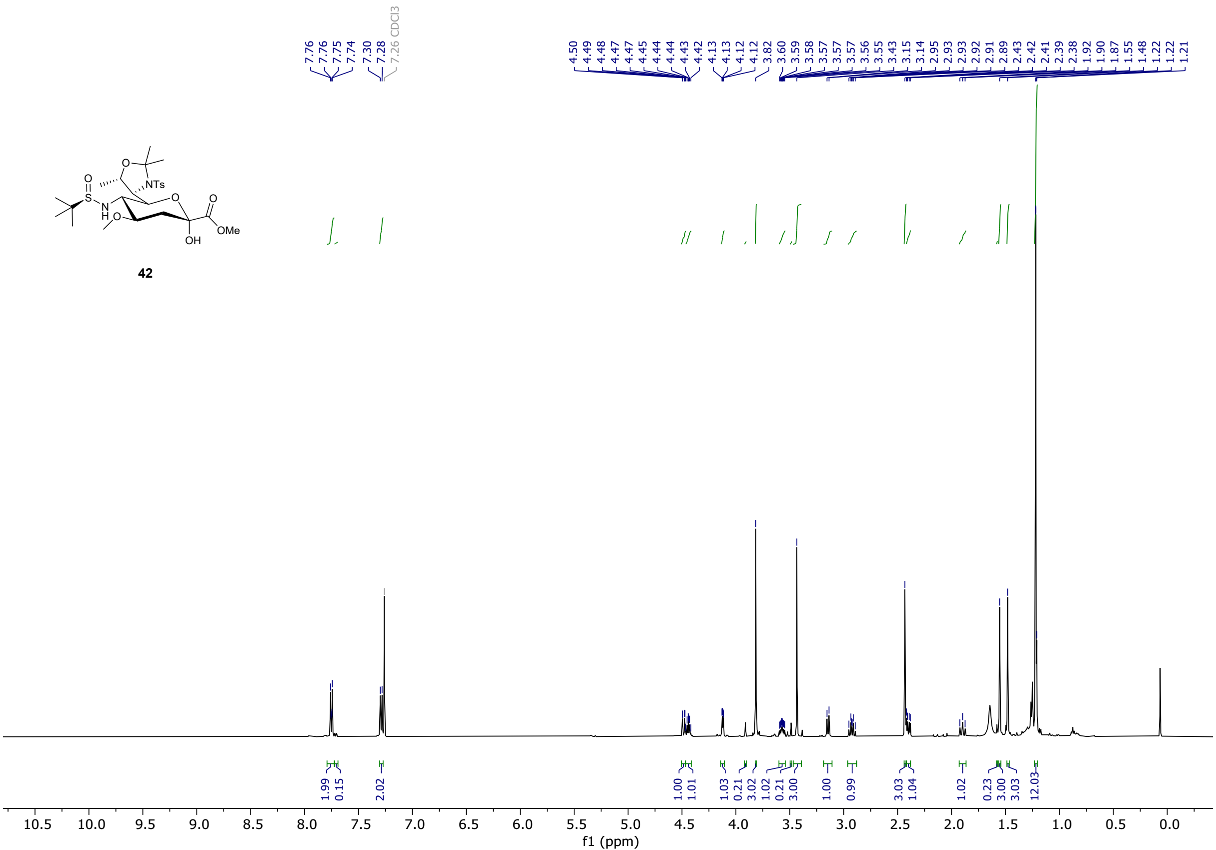
f1 (ppm)

41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4.45
4.44
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4.42
4.13
4.13
4.12
4.12
3.82
3.60
3.59
3.58
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3.57
3.57
3.56
3.55
3.43
3.15
3.14
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2.93
2.92
2.91
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2.43
2.42
2.41
2.39
2.38
1.92
1.90
1.87
1.55
1.48
1.22
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1.21
O
NTs
S
N
H
O
OH
O
OMe
O
42
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0.15
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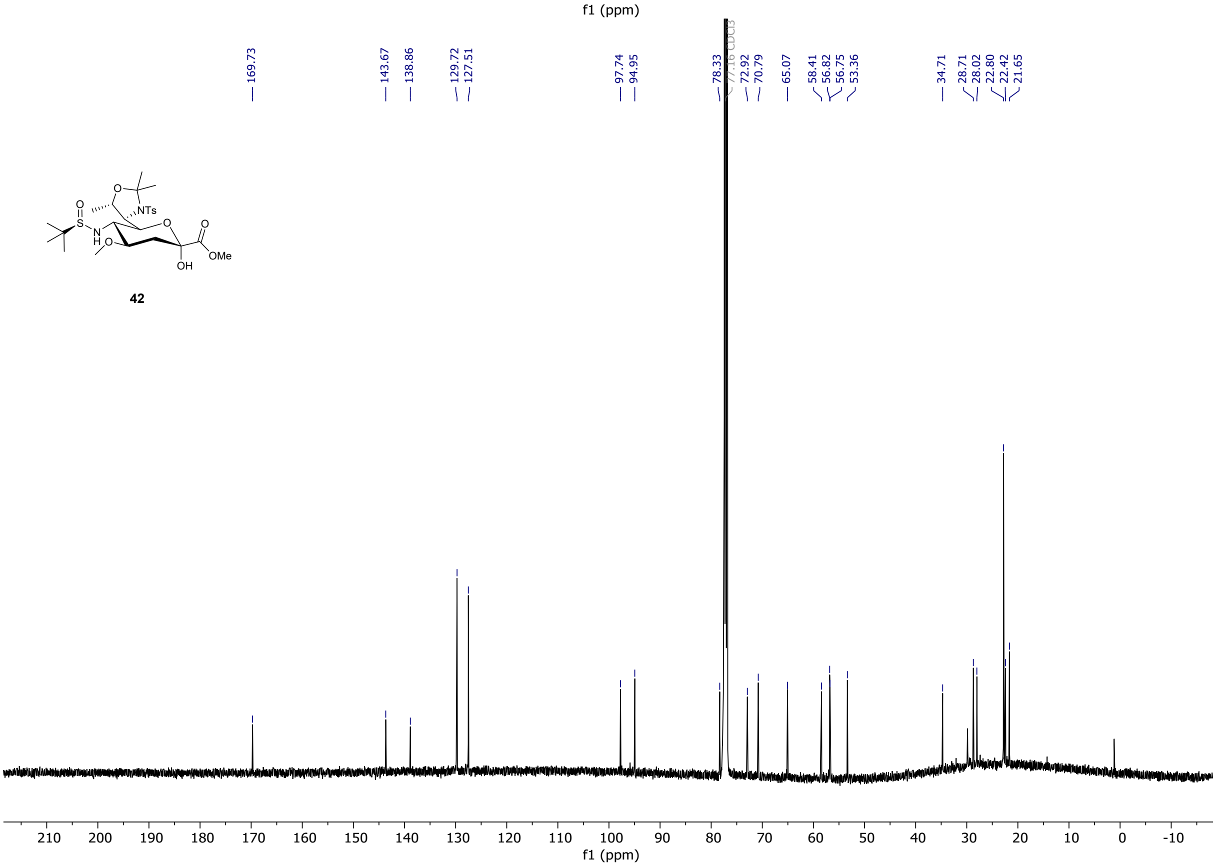
f1 (ppm)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58.41
56.82
56.75
53.36
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28.02
22.80
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21.65
O
NTs
S
N
H
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OH
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OMe
O
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210
200
190
180
170
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150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Author Contributions

Conceptualization (A.J. and C.M.P.), data curation, visualization, methodology (A.J.), formal analysis, investigation and writing original draft (A.J.), resources, supervision (C.M.P.), funding acquisition, validation, writing–review and editing (C.M.P.)

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