Synthesis of the bis(cyclohexenone) core of (–)-lomaiviticin A.

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Supporting Information

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General experimental procedures. All reactions were performed in single-neck, flame-dried, round-bottomed flasks fitted with rubber septa under a positive pressure of argon, unless otherwise noted. Air- and moisture-sensitive liquids were transferred via syringe or stainless steel cannula, or were handled in a nitrogen-filled drybox (working oxygen level <10 ppm). Organic solutions were concentrated by rotary evaporation at 28–32 °C. Flash-column chromatography was performed as described by Still et al.,[1] employing silica gel (SiliaFlash® P60, 60 Å, 40–63 μm particle size) purchased from SiliCycle (Québec, Canada). Analytical thin-layered chromatography (TLC) was performed using glass plates pre-coated with silica gel (250 μm, 60 Å pore size) impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light (UV) and/or submersion in aqueous ceric ammonium molybdate solution (CAM) or aqueous potassium permanganate solution ($KMnO_4$), followed by brief heating on a hot plate (120 °C, 10–15 s).

Materials. Commercial solvents and reagents were used as received with the following exceptions. Dess–Martin periodinane was purchased from Alfa Aesar and used as received. Dichloromethane, ether, *N,N*-dimethylformamide, tetrahydrofuran, and toluene were purified according to the method of Pangborn et al.[2] Degassed solvents were prepared via freeze-pump-thaw cycling. Pyridine was distilled from calcium hydride under an atmosphere of nitrogen immediately prior to use. Triethylamine was distilled from calcium hydride under an atmosphere of nitrogen immediately prior to use. *N*-Methylmorpholine was distilled from calcium hydride under an atmosphere of argon, and stored under argon at 23 °C. Concentrations of organolithium reagents were determined by titration against a standard solution of salicylaldehyde phenylhydrazone.[3] Concentrations of Grignard reagents were determined by titration against a standard solution of iodine and lithium chloride in tetrahydrofuran.[4] Trimethylsilyl trifluoromethanesulfonate was purified by vacuum transfer distillation and stored under argon at –20 °C. 2-Nitrobenzenesulfonylhydrazide (NBSH) was prepared according to the method of Myers et al.[5] Tris(dibenzylideneacetone)dipalladium chloroform complex, JohnPhos, copper (I) thiophene-2-carboxylate, chromium trioxide, methanesulfonic anhydride, lithium chloride, and sodium methanesulfonate were stored and handled in a nitrogen-filled drybox. The ketone **7** was prepared according to a published procedure.[6] Dimethyldioxirane (DMDO) was prepared and titrated according to the method of Taber et al.[7]

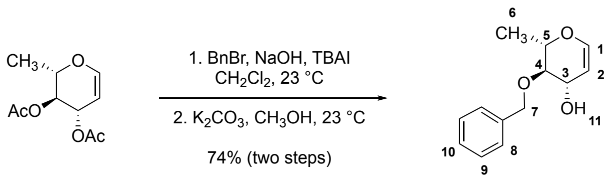
Instrumentation. Proton nuclear magnetic resonance spectra (^1H NMR) were recorded at 400, 500, or 600 MHz at 24 °C, unless otherwise stated. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$, δ 7.26; C_6D_5H, δ 7.16). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q= quartet, p = pentet, m = multiplet and/or multiple resonances, br = broad), integration, coupling constants in Hertz, and assignment. Proton-decoupled carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 100, 125, or 150 MHz at 24 °C, unless otherwise stated. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the NMR solvent ($CDCl_3$, δ 77.0, C_6D_6, δ 128.0). Two dimensional nuclear Overhauser effect spectroscopy (2D NOESY) experiments were performed at 500 MHz at 23 °C, unless otherwise noted.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were obtained using a Thermo Electron Corporation Nicolet 6700 FTIR spectrometer referenced to a polystyrene standard. Data are represented as follows: frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad). High-resolution mass spectrometry (HRMS) were obtained on a Waters UPLC/HRMS instrument equipped with a dual API/ESI high-resolution mass spectrometry detector and photodiode array detector. Unless otherwise noted samples were eluted over a reverse-phase C18 column (1.7 µm particle size, 2.1 × 50 mm) with a linear gradient of 5% acetonitrile–water containing 0.1% formic acid→95% acetonitrile–water containing 0.1% formic acid for 12 min, at a flow rate of 600 µL/min. Optical rotations were measured on a Rudolph Research Analytical Autopol IV polarimeter equipped with a sodium (589 nm, D) lamp. Optical rotation data are represented as follows: specific rotation ($[\alpha]_{D}^{\mathrm{T}}$,), concentration (g/mL), and solvent.

Synthetic procedures.

*Note: Synthetic intermediates appearing in the Supporting Information only are numbered consecutively beginning with **S1**.*

*Synthesis of 4-O-benzyl-3-hydroxy-L-rhamnal (**9**):*



8 **9**

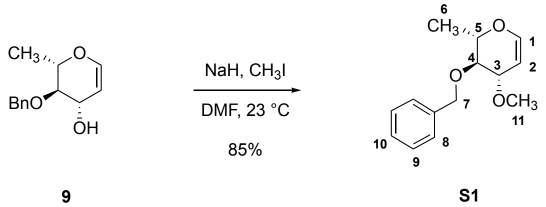
Benzyl bromide (24.9 mL, 209 mmol, 2.00 equiv), a solution of sodium hydroxide (41.9 g, 1.05 mol, 10.0 equiv) in water (42 mL), and tetrabutylammonium iodide (7.75 g, 21.0 mmol, 0.200 equiv) were added in sequence to a solution of 3,4-di-*O*-acetyl-6-deoxy-L-glucal (**8**, 22.4 g, 105 mmol, 1 equiv) in dichloromethane (52 mL) at 23 °C. The reaction mixture was stirred for 2.5 d at 23 °C. The product mixture was diluted with saturated aqueous ammonium chloride solution (300 mL). The diluted solution was extracted with dichloromethane (3 × 200 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

Potassium carbonate (3.10 g, 22.0 mmol, nominally 0.20 equiv) was added to a solution of the unpurified residue obtained in the preceding step in methanol (210 mL) at 23 °C. The reaction mixture was stirred for 3 h at 23 °C. The product mixture was diluted with saturated aqueous ammonium chloride solution (400 mL). The diluted solution was extracted with dichloromethane (3 × 300 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 10% ethyl acetate–hexanes) to provide 4-*O*-benzyl-3-hydroxy-L-rhamnal (**9**) as a white solid (16.7 g, 74% over two steps).

Spectroscopic data for 4-*O*-benzyl-3-hydroxy-L-rhamnal (**9**) obtained in this way were in agreement with literature values.[8]

R_f = 0.20 (30% ethyl acetate–hexanes, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 – 7.35 (m, 4H, H_8, H_9), 7.32 (td, J = 5.9, 2.6 Hz, 1H, H_{10}), 6.32 (dd, J = 6.0, 1.7 Hz, 1H, H_1), 4.85 (d, J = 11.5 Hz, 1H, H_7), 4.79 (d, J = 11.5 Hz, 1H, H_7), 4.69 (dd, J = 6.0, 2.4 Hz, 1H, H_2), 4.35 (d, J = 6.9 Hz, 1H, H_3), 3.91 (dq, J = 9.8, 6.5 Hz, 1H, H_5), 3.28 (dd, J = 9.6, 6.9 Hz, 1H, H_4), 2.00 (s, 1H, H_{11}), 1.41 (d, J = 6.5 Hz, 3H, H_6). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.6, 138.3, 128.6, 128.0, 127.9, 103.2, 82.4, 74.2, 74.1, 69.9, 17.6. IR (ATR-FTIR), cm^{-1}: 3272 (br), 1645 (s), 1248 (s), 1099 (s), 742 (s). $[\alpha]_D^{21}$ = –4.9° (c = 2.0, $CHCl_3$).

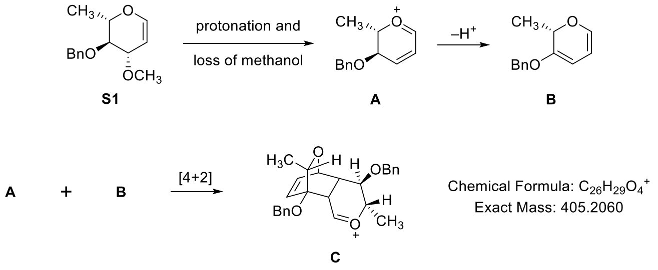
*Synthesis of 4-O-benzyl-3-methoxy-L-rhamnal (**S1**):*



Sodium hydride (60% dispersion in mineral oil, 4.48 g, 112 mmol, 1.30 equiv) was added to a solution of 4-*O*-benzyl-3-methoxy-L-rhamnal (**9**, 19.0 g, 86.0 mmol, 1 equiv) in *N,N*-dimethylformamide (220 mL) at 0 °C. The reaction mixture was stirred for 15 min at 0 °C. Methyl iodide (6.40 mL, 104 mmol, 1.20 equiv) was then added dropwise via syringe. The reaction mixture was stirred for 1 h at 0 °C. The product mixture was diluted with ethyl acetate (600 mL). The diluted product mixture was washed sequentially with water (2 × 500 mL) and saturated aqueous sodium chloride solution (500 mL). The washed organic layer was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 10% ethyl acetate–hexanes) to provide 4-*O*-benzyl-3-methoxy-L-rhamnal **S1** as a pale oil (17.1 g, 85%).

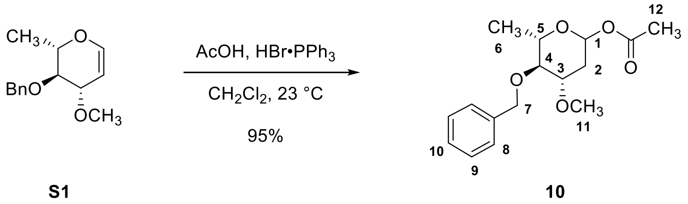
R_f = 0.40 (20% ethyl acetate–hexanes, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.34 (m, 4H, H_8, H_9), 7.33 – 7.29 (m, 1H, H_{10}), 6.38 (dd, J = 6.1, 1.4 Hz, 1H, H_1), 4.89 (d, J = 11.5 Hz, 1H, H_7), 4.86 (dd, J = 6.1, 2.5 Hz, 1H, H_2), 4.72 (d, J = 11.4 Hz, 1H, H_7), 4.01 (ddd, J = 6.5, 2.5, 1.5 Hz, 1H, H_3), 3.95 (dd, J = 9.0, 6.4 Hz, 1H, H_5), 3.41 (m, 4H, H_4, H_{11}), 1.39 (d, J = 6.4 Hz, 3H, H_6). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 138.4, 128.4, 127.9, 127.7, 99.8, 79.1, 78.3, 73.9, 73.8, 55.8, 17.5. IR (ATR-FTIR), cm^{-1}: 2882 (m), 1647 (m), 1104 (s), 1055 (s), 737 (m). HRMS-ESI (*m/z*):* $[2\times M - CH_3OH - CH_3O]^+$ calcd for $C_{26}H_{29}O_4$, 405.2060; found, 405.2092. $[\alpha]_D^{21}$ = –5.9 (c = 2.0, $CHCl_3$).

* The parent ion is believed to derived from ionization and dimerization of **S1**, as shown:



* other isomers of **C** equally plausible

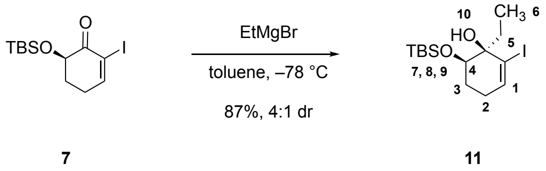
*Synthesis of the glycosyl acetate **10**:*



Triphenylphosphine hydrogen bromide (1.77 g, 5.00 mmol, 0.06 equiv) was added to a solution of 4-*O*-benzyl-3-methoxy-L-rhamnal (**S1**, 17.1 g, 73.0 mmol, 1 equiv) in dichloromethane (430 mL) at 23 °C. The resulting solution was stirred for 15 min at 23 °C. Acetic acid (7.90 mL, 138 mmol, 1.60 equiv) was then added. The reaction mixture was then stirred for 5 h at 23 °C. The product mixture was diluted with saturated aqueous sodium bicarbonate solution (400 mL). The diluted solution was extracted with dichloromethane (2 × 200 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 10% ethyl acetate–hexanes initially, grading to 30% ethyl acetate–hexanes, two steps) to provide the glycosyl acetate **10** as a pale oil (20.4 g, 95%).

R_f = 0.20 (20% ethyl acetate–hexanes, CAM). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.40 – 7.32 (m, 4H, H$_8$, H$_9$), 7.30 (d, J = 6.3 Hz, 1H, H$_{10}$), 6.16 (dd, J = 3.7, 1.6 Hz, 1H, H$_1$), 4.92 (d, J = 11.0 Hz, 1H, H$_7$), 4.66 (d, J = 11.0 Hz, 1H, H$_7$), 3.80 (dq, J = 9.5, 6.2 Hz, 1H, H$_5$), 3.66 (ddd, J = 11.4, 8.7, 5.0 Hz, 1H, H$_3$), 3.46 (s, 3H, H$_{11}$), 3.09 (t, J = 9.2 Hz, 1H, H$_4$), 2.28 (ddd, J = 13.6, 5.0, 1.7 Hz, 1H, H$_2$), 2.07 (s, 3H, H$_{12}$), 1.68 (ddd, J = 13.6, 11.4, 3.6 Hz, 1H, H$_2$), 1.28 (d, J = 6.3 Hz, 3H, H$_6$) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 169.5, 138.4, 128.4, 128.0, 127.7, 91.8, 83.5, 78.5, 75.2, 69.6, 57.3, 33.9, 21.1, 18.2 ppm. IR (ATR-FTIR), cm^{-1}: 2934 (w), 1750 (s), 1194 (m), 1101 (s), 965 (m). HRMS-ESI (*m/z*): [M + Na]$^+$ calcd for $C_{16}H_{22}O_5Na$, 317.1365; found, 317.1377. $[\alpha]_D^{21}$ = –79.9° (c = 2.0, CHCl$_3$).

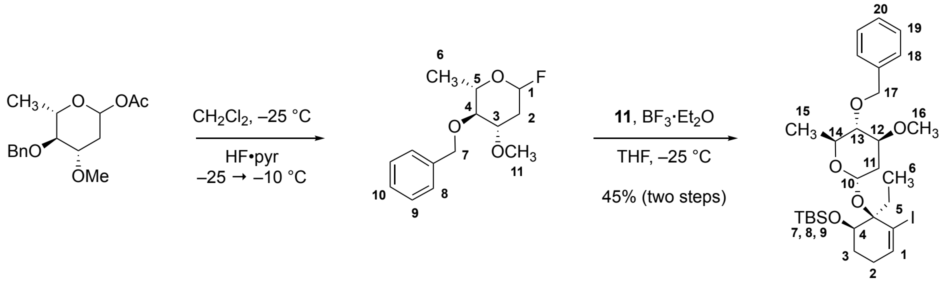
*Synthesis of the tertiary alcohol **11**:*



A solution of ethylmagnesium bromide in ether (3.0 M, 1.86 mL, 5.58 mmol, 1.50 equiv) was added dropwise via syringe to a solution of the ketone **7** (1.31 g, 3.72 mmol, 1 equiv) in toluene (40 mL) at –78 ºC. The reaction mixture was stirred for 10 min at –78 ºC. The product mixture was diluted with saturated aqueous ammonium chloride solution (100 mL). The diluted solution was extracted with ether (3 × 100 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with hexanes initially, grading to 2% ethyl acetate–hexanes, one step) to provide the tertiary alcohol **11** as a colorless oil (986 mg, 70%).

R_f = 0.40 (5% ethyl acetate–hexanes, CAM). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.50 (t, J = 4.1 Hz, 1H, H_1), 4.02 (dd, J = 7.7, 2.6 Hz, 1H, H_4), 2.93 (s, 1H, H_{10}), 2.23 – 2.13 (m, 1H, H_2), 2.00 – 1.91 (m, 1H, H_2), 1.88 – 1.73 (m, 3H, H_3, H_5), 1.62 (dq, J = 14.7, 7.4 Hz, 1H, H_3), 0.90 (s, 9H, H_9), 0.85 (t, J = 7.5 Hz, 3H, H_6), 0.11 (s, 3H, H_7), 0.11 (s, 3H, H_8). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 109.7, 74.7, 69.3, 31.7, 26.7, 26.2, 25.7, 18.0, 8.0, –4.3, –5.1. IR (ATR-FTIR), cm^{-1}: 3549 (br, w), 2930 (m), 1254 (m), 1085 (m), 836 (s). HRMS-ESI (*m/z*): [M + Na]$^+$ calcd for $C_{14}H_{27}IO_2SiNa$, 405.0723; found, 405.0743. $[\alpha]_D^{21}$ = –22.6 (c = 1.0, $CHCl_3$).

*Synthesis of the glycoside **12**:*



10 **6** **12**

A solution of hydrogen fluoride in pyridine (0.8 M, 6.50 mL, 5.23 mmol, 1.06 equiv) was added dropwise via syringe to a solution of the glycosyl acetate **10** (1.45 g, 4.93 mmol, 1 equiv) in dichloromethane (37 mL) in a high density polyethylene bottle at –25 ºC. The reaction mixture was stirred for 25 min at –25 ºC then was warmed to –10 ºC for 10 min. The product mixture was diluted with ice-cold water (80 mL). The mixture was transferred to a separatory funnel and the aqueous layer was extracted with dichloromethane (3 × 150 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated to provide the glycosyl fluoride **6** as a pale oil. The glycosyl fluoride **6** was unstable toward purification and was used directly in the following step.

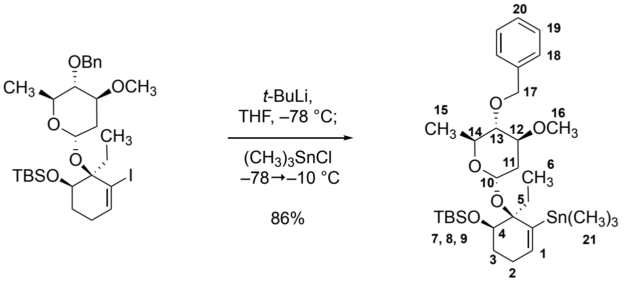
Partial characterization data for **6**: ^{1}H NMR (400 MHz, C_6D_6): δ 7.25 (d, *J* = 7.1 Hz, 2H, H_8), 7.17-7.11 (m, 2H, H_9), 7.09-7.02 (m, 1H, H_{10}), 5.37 (d, *J* = 52.4, 1 H, H_1), 4.84 (d, *J* = 11.5 Hz, 1H, H_7), 4.48 (d, *J* = 11.5 Hz, 1H, H_7), 4.01 (dq, *J* = 9.6, 6.2 Hz, 1 H, H_5), 3.58 (ddd, *J* = 11.3, 8.8, 5.1 Hz, 1H, H_3), 3.01 (s, 3H, H_{11}), 2.95 (t, *J* = 9.2 Hz, 1H, H_4), 2.05 (dtd, *J* = 13.7, 4.9, 1.6 Hz, 1H, H_2), 1.22 (d, *J* = 6.2 Hz, 3H, H_6), 1.20 (dddd, *J* = 52.4, 13.7, 11.4, 3.6 Hz, 1H, H_2).

Boron trifluoride diethyl etherate complex (640 µL, 5.18 mmol, 1.05 equiv) was added dropwise via syringe over 25 min to a solution of the unpurified glycosyl fluoride **6** obtained in the preceding step (nominally 4.93 mmol, 1 equiv) and the tertiary alcohol **11** (3.77 g, 9.87 mmol, 2.00 equiv) in tetrahydrofuran (52 mL) at –25 ºC. The reaction mixture was stirred for 1.5 h at –25 ºC. The product mixture was diluted with saturated aqueous sodium bicarbonate solution (75 mL). The diluted solution was extracted with dichloromethane (2 × 125 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 2% ethyl acetate–hexanes initially, grading to 6% ethyl acetate–hexanes, two steps) to provide the glycoside **12** as a colorless oil (1.37 g, 45% over two steps).

R_f = 0.40 (10% ethyl acetate–hexanes, CAM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 – 7.32 (m, 4H, H_{19}, H_{20}), 7.28 – 7.26 (m, 1H, H_{21}), 6.51 (d, *J* = 5.4 Hz, 1H, H_5), 5.49 (d, *J* = 3.3 Hz, 1H, H_{11}), 4.89 (d, *J* = 11.2 Hz, 1H, H_{11}), 4.65 (d, *J* = 11.2 Hz, 1H, H_{11}), 4.30 (dq, *J* =

9.6, 6.3 Hz, 1H, H_{15}), 3.92 – 3.86 (m, 1H, H_4), 3.75 (ddd, *J* = 11.5, 8.7, 4.9 Hz, 1H, H_{13}), 3.44 (s, 1H, H_{17}), 3.01 (t, *J* = 9.2 Hz, 1H, H_{14}), 2.29 (dd, *J* = 12.5, 5.0 Hz, 1H, H_{12}), 2.15 (dq, *J* = 14.6, 7.4 Hz, 1H, H_5), 2.08 – 2.01 (m, 3H, H_2, H_3), 1.88 (dq, *J* = 14.7, 7.5 Hz, 1H, H_5), 1.61 – 1.58 (m, 1H, H_3), 1.51 (td, *J* = 12.0, 3.9 Hz, 1H, H_{12}), 1.26 (d, *J* = 6.3 Hz, 3H, H_{16}), 0.90 (s, 9H, H_{10}), 0.82 (t, *J* = 7.4 Hz, 3H, H_6), 0.09 (s, 3H, H_8), 0.08 (s, 3H, H_9) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 142.6, 139.2, 128.4, 128.0, 127.6, 106.9, 92.8, 84.9, 82.5, 79.1, 74.8, 70.7, 67.4, 57.3, 36.5, 29.1, 27.5, 26.5, 25.9, 18.2, 18.1, 8.9, –4.0, –4.8 ppm. IR (ATR-FTIR), cm^{-1}: 2930 (m), 1102 (s), 1035 (m), 994 (s). HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{28}H_{45}INaO_5Si$, 639.1973; found, 639.1988.$[\alpha]_D^{21}$ = +40.7 (*c* = 1.0, $CHCl_3$).

*Synthesis of the vinyl stannane **13**:*

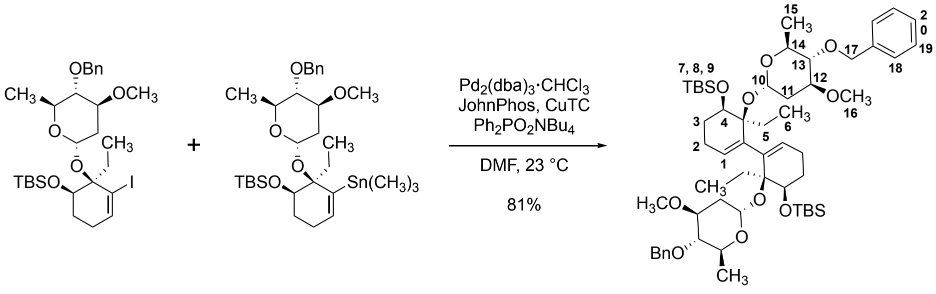


12 **13**

A solution of *tert*-butyllithium in pentane (1.7 M, 11.0 mL, 18.8 mmol, 2.20 equiv) was added dropwise via syringe to a solution of the glycoside **12** (5.26 g, 8.53 mmol, 1 equiv) in tetrahydrofuran (120 mL) at –78 ºC. The reaction mixture was stirred for 30 min at –78 ºC. A solution of trimethyltin chloride in tetrahydrofuran (1.0 M, 23.5 mL, 23.5 mmol, 2.75 equiv) was then added dropwise via syringe. The reaction mixture was warmed to –10 °C over 2.5 h. The product mixture was diluted sequentially with water (250 mL) and ether (400 mL). The resulting mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with ether (3 × 500 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with hexanes buffered with 2% triethylamine initially, grading to 3% ethyl acetate–hexanes buffered with 2% triethylamine, three steps) to provide the vinyl stannane **13** as a colorless oil (4.79 g, 86%).

R$_f$ = 0.55 (10% ethyl acetate–hexanes; CAM). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.37 – 7.25 (m, 5H, H$_{19}$, H$_{20}$, H$_{21}$), 5.89 (d, *J* = 3.2 Hz, 1H, H$_1$), 5.60 (d, *J* = 2.4 Hz, 1H, H$_{11}$), 4.90 (d, *J* = 11.4 Hz, 1H, H$_{18}$), 4.65 (d, *J* = 11.4 Hz, 1H, H$_{18}$), 3.97 – 3.90 (m, 1H, H$_{15}$), 3.81 (dd, *J* = 11.5, 3.3 Hz, 1H, H$_4$), 3.73 (ddd, *J* = 11.0, 8.6, 4.8 Hz, 1H, H$_{13}$), 3.41 (s, 3H, H$_{17}$), 2.98 (t, *J* = 9.0 Hz, 1H, H$_{14}$), 2.32 – 2.19 (m, 3H. H$_2$, H$_5$, H$_{12}$), 2.14 – 2.07 (m, 1H, H$_2$), 2.00 (qd, *J* = 11.5, 5.7 Hz, 1H, H$_3$), 1.60 – 1.46 (m, 3H, H$_3$, H$_5$, H$_{12}$), 1.22 (d, *J* = 6.2, 3H, H$_{16}$), 0.90 (s, 9H, H$_{110}$), 0.77 (t, *J* = 7.5 Hz, 3H, H$_6$), 0.16 (s, 9H, H$_{22}$, H$_{23}$, H$_{24}$), 0.09 (s, 3H, H$_8$), 0.08 (s, 3H, H$_9$) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 146.6, 140.4, 139.4, 128.3, 127.8, 127.4, 92.4, 84.9, 82.3, 79.2, 74.6, 72.7, 67.2, 57.0, 36.6, 28.5, 27.3, 26.8, 26.0, 18.6, 18.3, 9.5, –3.7, –4.8, –7.1 ppm. IR (ATR-FTIR), cm^{-1}: 2930 (m), 1099 (s), 1077 (m), 986 (s), 771 (s). $[\alpha]_D^{21}$ = +56.1° (*c* = 1.0, CHCl$_3$).

Synthesis of the diene ***4****:*

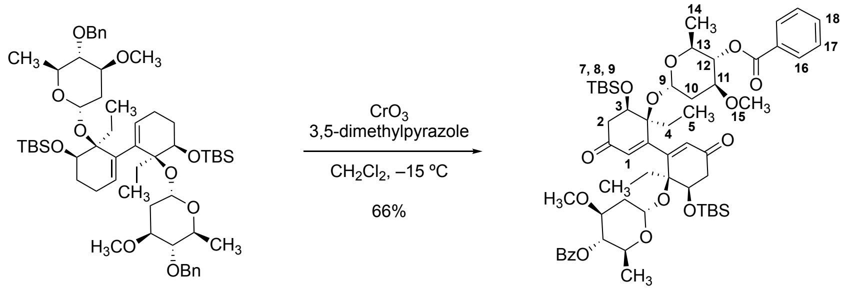


12 **13** **4**

JohnPhos (2.11 g, 7.06 mmol, 1.00 equiv), tris(dibenzylideneacetone)dipalladium chloroform complex (1.83 g, 1.77 mmol, 0.25 equiv), copper (I) thiophene-2-carboxylate (2.02 g, 10.6 mmol, 1.50 equiv) and tetra-*n*-butylammonium diphenylphosphinate (13.0 g, 28.3 mmol, 4.00 equiv) were added to a round-bottomed flask charged with the vinyl stannane **13** (4.62 g, 7.06 mmol, 1 equiv) and the vinyl iodide **12** (4.89 g, 7.93 mmol, 1.12 equiv) under argon. Degassed *N,N*-dimethylformamide (36 mL) was added, and the resulting mixture was sonicated for 10 min, with vigorous stirring. The reaction mixture was stirred for 15 h at 23 ºC. The product mixture was diluted with ethyl acetate (500 mL). The diluted mixture was transferred to a separatory funnel. The mixture was washed with saturated aqueous sodium chloride solution (3 × 150 mL). The aqueous layers were combined, and the combined aqueous layers were extracted with ethyl acetate (2 × 100 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 4% ethyl acetate–hexanes initially, grading to 16% ethyl acetate–hexanes, three steps) to provide the diene **4** as a pale yellow oil (5.62 g, 81%).

R_f = 0.40 (15% ethyl acetate–hexanes; CAM). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.38 – 7.27 (m, 5H, H$_{18}$, H$_{19}$, H$_{20}$), 6.35 (s, 1H, H$_1$), 5.62 (d, *J* = 3.7 Hz, 1H, H$_{10}$), 4.91 (d, *J* = 11.0 Hz, 1H, H$_{17}$), 4.63 (d, *J* = 11.0 Hz, 1H, H$_{17}$), 3.91 (dq, *J* = 9.3, 6.2 Hz, 1H, H$_{15}$), 3.83 (ddd, *J* = 11.3, 8.6, 4.7 Hz, 1H, H$_{12}$), 3.74 (dd, *J* = 12.0, 3.4 Hz, 1H, H$_4$), 3.47 (s, 3H, H$_{16}$), 3.00 (t, *J* = 9.0 Hz, 1H, H$_{13}$), 2.36 (dd, *J* = 12.8, 4.8 Hz, 1H, H$_{11}$), 2.24 – 2.00 (m, 5H, H$_2$, H$_3$, H$_5$), 1.56 – 1.51 (m, 2H, H$_3$, H$_{11}$), 1.22 (d, *J* = 6.4 Hz, 3H, H$_{15}$), 0.90 (s, 9H, H$_9$), 0.76 (t, *J* = 7.4 Hz, 3H, H$_6$), 0.11 (s, 3H, H$_7$), 0.09 (s, 3H, H$_8$). ^{13}C NMR (125 MHz, CDCl$_3$): δ 139.0, 134.5, 130.8, 128.4, 128.2, 127.6, 92.6, 84.8, 82.5, 79.2, 75.0, 74.6, 67.5, 57.2, 36.6, 26.0, 25.9, 25.2, 21.9, 18.3 (2C), 10.3, –3.4, –5.0. IR (ATR-FTIR), cm^{-1}: 2930 (m), 1100 (s), 984 (m), 835 (m). HRMS-ESI (*m/z*): [M + Na]$^+$ calcd for C$_{56}$H$_{90}$O$_{10}$Si$_2$Na, 1029.5550; found, 1029.5578. $[\alpha]_D^{21}$ = +3.6 (*c* = 1.0, CHCl$_3$).

Synthesis of the bis(enone) ***S2***:

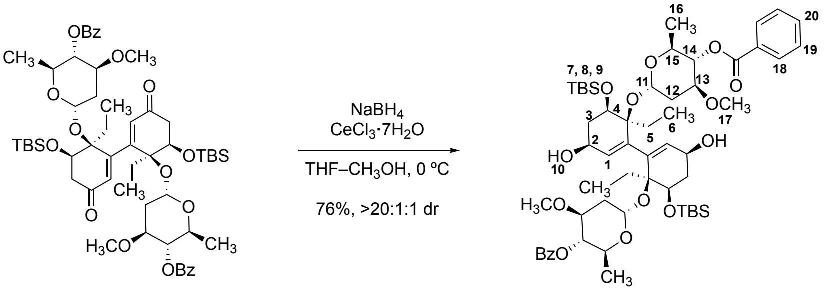


4 **S2**

3,5-Dimethylpyrazole (1.03 g, 10.7 mmol, 35.0 equiv) was added to a stirred suspension of chromium trioxide (1.07 g, 10.7 mmol, 35.0 equiv) in dichloromethane (7.0 mL) at –15 ºC. The resulting mixture was stirred for 15 min at –15 ºC. A solution of the diene **4** (300 mg, 306 µmol, 1 equiv) in dichloromethane (7.0 mL) was then added via cannula. The reaction mixture was stirred for 20 h at –15 °C. The product mixture was diluted sequentially with aqueous sodium hydroxide solution (3 M, 35 mL) and ether (100 mL). The diluted solution was washed with aqueous sodium hydroxide solution (3 M, 2 × 35 mL). The aqueous layers were combined, and the combined aqueous layers were extracted with ether (3 × 50 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was triturated with 10% ether–hexanes (~100 mL). The supernatant was filtered, and the filtrate was collected and concentrated. This process was repeated once. The residue obtained was purified by flash-column chromatography (eluting with 6% ethyl acetate–hexanes initially, grading to 24% ethyl acetate–hexanes, three steps) to provide the bis(enone) **S2** as a colorless oil (208.9 mg, 66%).

R_f = 0.30 (20% ethyl acetate–hexanes; CAM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.06 (d, J = 7.5 Hz, 2H, H_{16}), 7.56 (t, J = 7.4 Hz, 1H, H_{18}), 7.44 (t, J = 7.7 Hz, 2H, H_{17}), 6.71 (s, 1H, H_1), 5.68 (s, 1H, H_9), 4.95 (t, J = 9.0 Hz, 1H, H_{12}), 4.26 (dd, J = 11.0, 4.6 Hz, 1H, H_3), 4.11 (dq, J = 12.4, 6.4 Hz, 1H, H_{13}), 3.78 – 3.74 (m, 1H, H_{11}), 3.34 (s, 3H, H_{15}), 3.03 (dd, J = 16.9, 10.7 Hz, 1H, H_2), 2.67 (dd, J = 16.9, 4.5 Hz, 1H, H_2), 2.48 (dq, J = 15.0, 7.6 Hz, 1H, H_4), 2.36 – 2.34 (m, 1H, H_{10}), 2.16 (dd, J = 14.5, 7.5 Hz, 1H, H_4), 1.82 (ddd, J = 13.2, 10.8, 4.0 Hz, 1H, H_{10}), 1.29 (d, J = 6.2 Hz, 3H, H_{14}), 0.95 (t, J = 7.6 Hz, 3H, H_5), 0.94 (s, 9H, H_8), 0.15 (s, 3H, H_6), 0.14 (s, 3H, H_7). ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.7, 166.0, 153.0, 133.2, 132.8, 130.1, 129.9, 128.5, 93.1, 81.9, 76.8, 76.0, 71.2, 67.4, 57.4, 43.0, 35.4, 30.5, 25.9, 18.2, 17.7, 10.2, –3.6, –4.8. IR (ATR-FTIR), cm^{-1}: 2932 (m), 1726 (s), 1676 (m), 1262 (s), 1096 (s). HRMS-ESI (m/z): [M + Na]$^+$ calcd for $C_{56}H_{82}O_{14}Si_2Na$, 1057.5135; found, 1057.5184. $[\alpha]_D^{21}$ = –38.1° (c = 1.0, $CHCl_3$).

*Synthesis of the dienyl diol **14**:*

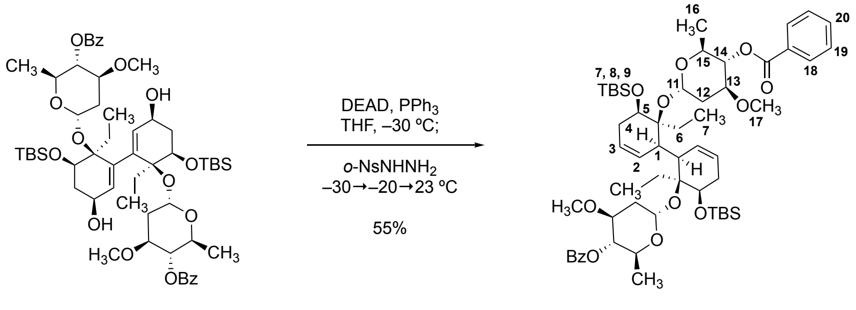


S2 **14**

Cerium (III) trichloride heptahydrate (2.57 g, 6.89 mmol, 8.00 equiv) was added to a solution of the bis(enone) **S2** (892 mg, 862 µmol, 1 equiv) in 50% tetrahydrofuran–methanol (v/v, 180 mL) at 23 ºC. The resulting solution was cooled to 0 ºC and stirred for 15 min at 0 ºC. Sodium borohydride (1.30 g, 34.46 mmol, 40.0 equiv) was then added. The reaction mixture was stirred for 1.5 h at 0 °C. The product mixture was diluted with saturated aqueous sodium chloride solution (200 mL). The diluted solution was extracted with ethyl acetate (4 × 200 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 15% ethyl acetate–hexanes initially, grading to 45% ethyl acetate–hexanes, two steps) to provide the dienyl diol **14** as a colorless oil (684 mg, 76%).

R_f = 0.60 (40% ethyl acetate–hexanes; CAM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 – 8.07 (m, 2H, H_{18}), 7.57 (t, J = 7.4 Hz, 1H, H_{20}), 7.45 (t, J = 7.8 Hz, 2H, H_{19}), 6.55 (s, 1H, H_1), 5.50 (s, 1H, H_{11}), 4.94 (t, J = 9.2 Hz, 1H, H_{14}), 4.35 – 4.29 (m, 2H, H_2, H_{15}), 3.89 (ddd, J = 11.1, 8.7, 4.6 Hz, 1H, H_{13}), 3.66 (dd, J = 12.3, 3.5 Hz, 1H, H_4), 3.34 (s, 3H, H_{17}), 2.45 (ddd, J = 12.9, 4.7, 1.9 Hz, 1H, H_{12}), 2.30 – 2.19 (m, 2H, H_3, H_5), 2.10 (ddd, J = 11.2, 6.9, 3.6 Hz, 1H, H_3), 2.02 (dq, J = 14.5, 7.4 Hz, 1H, H_5), 1.80 – 1.74 (m, 2H, H_{10}, H_{12}), 1.21 (d, J = 6.2 Hz, 3H, H_{16}), 0.95 (s, 9H, H_9), 0.84 (t, J = 7.5 Hz, 3H, H_6), 0.14 (s, 3H, H_8), 0.13 (s, 3H, H_7). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.1, 137.7, 133.9, 133.2, 130.3, 129.9, 128.5, 92.9, 82.6, 77.2, 76.1, 71.8, 66.8, 57.1, 36.2, 36.0, 26.0, 25.1, 18.2, 17.9, 10.3, –3.5, –5.0. IR (ATR-FTIR), cm^{-1}: 3503 (br, w), 2932 (m), 1727 (s), 1271 (s), 1098 (s). HRMS-ESI (*m/z*): [M + Na]$^+$ calcd for $C_{56}H_{86}O_{14}Si_2Na$, 1061.5448; found, 1061.5491. $[\alpha]_D^{21}$ = –36.9° (c = 1.0, $CHCl_3$).

Synthesis of the transposed diene ***15****:*

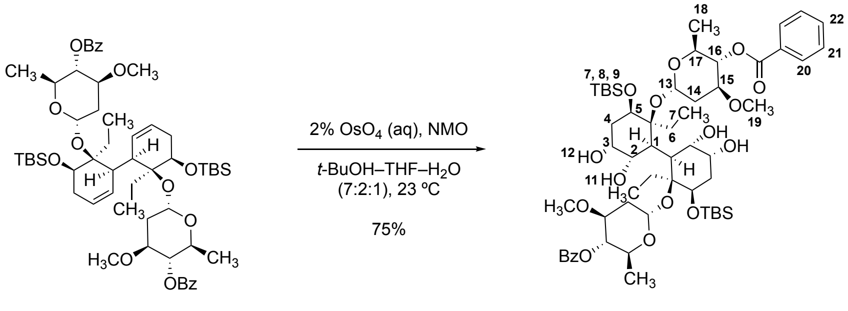


14 **15**

Diethyl azodicarboxylate (917 mg, 830 µL, 5.26 mmol, 8.00 equiv) was added dropwise via syringe to a solution of triphenylphosphine (1.52 g, 5.79 mmol, 8.80 equiv) in *N*-methylmorpholine (12 mL) at –30 ºC. The reaction mixture was stirred for 12 min at –30 °C. A solution of the dienyl diol **9** (684 mg, 658 µmol, 1 equiv) in tetrahydrofuran (12 mL) was then added dropwise via cannula. The resulting mixture was stirred for 20 min at –30 ºC. 2-Nitrobenzenesulfonyl hydrazine (1.14 g, 5.26 mmol, 8.0 equiv) was then added in one portion. The reaction mixture was stirred for 2 h at –30 ºC. The reaction mixture was warmed to –20 ºC. The reaction mixture was stirred for 5 h at –20 ºC and was then allowed to warm to 23 ºC. The reaction mixture was stirred for 16 h at 23 ºC. The product mixture was diluted with water (75 mL). The diluted product mixture was extracted with dichloromethane (3 × 50 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 5% ethyl acetate–hexanes initially, grading to 15% ethyl acetate–hexanes, two steps) to provide the transposed diene **15** as a colorless solid (366 mg, 55%).

R$_f$ = 0.50 (15% ethyl acetate–hexanes; CAM). ^{1}H NMR (600 MHz, CDCl$_3$): δ 8.07 – 8.05 (m, 2H, H$_{18}$), 7.60 – 7.57 (m, 1H, H$_{20}$), 7.47 (t, *J* = 7.8 Hz, 2H, H$_{19}$), 6.02 (d, *J* = 2.3 Hz, 1H, H$_3$), 5.73 (d, *J* = 10.3 Hz, 1H, H$_2$), 5.69 – 5.66 (m, 1H, H$_{11}$), 4.90 (t, *J* = 9.3 Hz, 1H, H$_{14}$), 3.97 – 3.93 (m, 2H, H$_5$, H$_{15}$), 3.79 (ddd, *J* = 11.6, 8.9, 4.9 Hz, 1H, H$_{13}$), 3.33 (s, 3H, H$_{17}$), 2.80 (s, 3H, H$_1$), 2.48 (dq, *J* = 14.7, 7.3 Hz, 1H, H$_6$), 2.32 – 2.21 (m, 3H, H$_4$, H$_{12}$), 1.74 (ddd, *J* = 12.7, 11.6, 3.8 Hz, 1H, H$_4$), 1.61 (dq, *J* = 14.6, 7.2 Hz, 1H, H$_6$), 1.16 (d, *J* = 6.3 Hz, 3H, H$_{16}$), 0.94 (t, *J* = 7.4 Hz, 3H, H$_7$), 0.91 (s, 9H, H$_{10}$), 0.12 (s, 3H, H$_9$), 0.09 (s, 3H, H$_8$). ^{13}C NMR (150 MHz, CDCl$_3$): δ 165.9, 133.2, 130.6, 130.5, 129.9, 128.5, 122.3, 92.6, 83.5, 77.2, 76.3, 72.7, 66.2, 57.1, 40.4, 35.8, 32.0, 26.0, 22.6, 18.2, 18.0, 9.2, –3.3, –5.0. IR (ATR-FTIR), cm^{-1}: 2930 (m), 1727 (s), 1267 (s), 1104 (s), 978 (s). HRMS-ESI (*m/z*): [M + Na]$^+$ calcd for $C_{56}H_{86}O_{12}Si_2Na$, 1029.5550; found, 1029.5594. $[\alpha]_D^{21}$ = –20.5 (*c* = 1.0, CHCl$_3$).

Synthesis of the tetraol ***16****:*

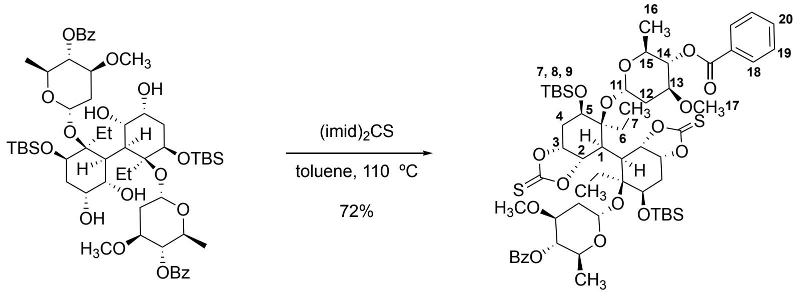


15 **16**

N-Methylmorpholine-*N*-oxide (25.2 mg, 215 µmol, 6.00 equiv) and a solution of osmium (IV) tetroxide in water (2% w/v, 107 µL, 7.17 µmol, 0.200 equiv) were added in sequence to a solution of the transposed diene **15** (36.1 mg, 35.8 µmol, 1 equiv) in *tert*-butanol–tetrahydrofuran–water (7:2:1 v/v, 1.4 mL) at 23 °C. The reaction mixture was stirred for 42 h at 23 ºC. The product mixture was diluted sequentially with saturated aqueous sodium sulfite solution (10 mL) and ethyl acetate (20 mL). The biphasic mixture was stirred vigorously for 60 min at 23 ºC. The biphasic mixture was transferred to a separatory funnel, and the aqueous layer was extracted with ethyl acetate (4 × 20 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 15% ethyl acetate–hexanes initially, grading to 45% ethyl acetate–hexanes, two steps) to provide the tetraol **16** as a colorless oil (29.0 mg, 75%).

R_f = 0.30 (40% ethyl acetate in hexanes; CAM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 – 8.05 (m, 2H), 7.59 – 7.56 (m, 1H), 7.48 – 7.45 (m, 2H), 6.21 (t, *J* = 4.3 Hz, 1H, H_{13}), 5.99 (s, 1H, H, H_2), 4.89 (dd, *J* = 8.2, 6.6 Hz, 1H, H_{16}), 4.37 (dd, *J* = 12.1, 4.2 Hz, 1H, H_5), 4.25 (dq, *J* = 8.2, 6.4 Hz, 1H, H_{17}), 4.15 – 4.09 (m, 2H, H_3, H_{11}), 3.79 (ddd, *J* = 8.7, 6.6, 4.6 Hz, 1H, H_{15}), 3.36 (s, 3H, H_{19}), 2.75 (s, 1H, H_1), 2.45 – 2.39 (m, 2H, H_6, H_{12}), 2.19 (dt, *J* = 13.7, 4.4 Hz, 1H, H_{14}), 2.08 (dt, *J* = 13.1, 3.9 Hz, 1H, H_4), 1.92 – 1.83 (m, 2H, H_4, H_{14}), 1.70 – 1.65 (m, 1H, H_6), 1.27 (d, *J* = 6.5 Hz, 3H, H_{17}), 0.97 (t, *J* = 7.3 Hz, 3H, H_7), 0.91 (s, 9H, H_{10}), 0.15 (s, 6H, H_8, H_9). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.9, 133.3, 130.0, 129.9, 128.6, 92.7, 86.2, 76.0, 75.4, 69.5, 68.8, 68.7, 67.8, 57.6, 41.9, 34.1, 33.2, 26.0, 23.6, 18.2, 17.8, 9.6, –3.2, –4.8. IR (ATR-FTIR), cm^{-1}: 3342 (br), 2933 (w), 1726 (s), 1261 (s), 1097 (s). HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{56}H_{90}O_{16}Si_2Na$, 1097.5660; found, 1097.5705. $[\alpha]_D^{21}$ = –73.6 (*c* = 1.0, $CHCl_3$)

*Synthesis of the thiocarbonate **17**:*



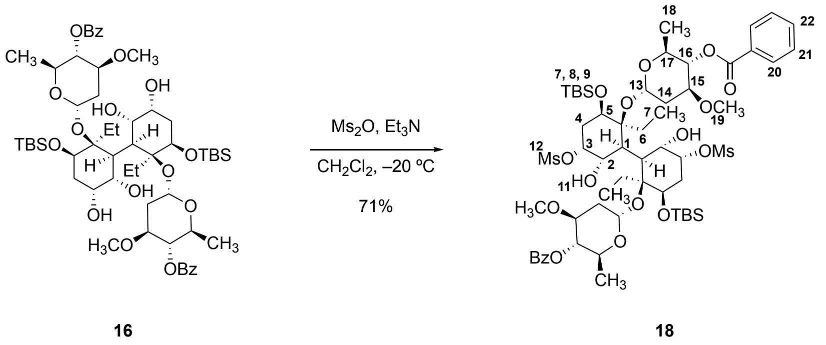
16 **17**

Thiocarbonyldiimidazole (90% purity, 12.1 mg, 61.0 μmol, 8.00 equiv) was added to a solution of the tetraol **16** (8.2 mg, 7.6 μmol, 1 equiv) in toluene (500 μL) at 23 °C. The reaction vessel was placed in an oil bath that had been preheated to 110 °C. The reaction mixture was stirred and heated for 24 h at 110 °C. The product mixture was cooled to 23 °C. The cooled product mixture was purified (without concentration) by flash-column chromatography (eluting with 10% ethyl acetate–hexanes initially, grading to 30% ethyl acetate–hexanes, two steps) to provide the cyclic thiocarbonate **17** as a white solid (6.4 mg, 72%).

Single crystals of **17** suitable for X-ray analysis were grown by the slow evaporation (4 °C) of solutions of **17** in 5% dichloromethane–hexanes.

R_f = 0.55 (30% ethyl acetate–hexanes; CAM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.28 (d, *J* = 7.4 Hz, 2H, H_{18}), 7.57 (t, *J* = 7.4 Hz, 1H, H_{20}), 7.45 (t, *J* = 7.8 Hz, 2H, H_{19}), 6.01 (dd, *J* = 4.9, 2.6 Hz, 1H, H_{11}), 5.06 (t, *J* = 7.2 Hz, 1H, H_3), 4.91 (dd, *J* = 9.4, 7.5 Hz, 1H, H_{11}), 4.69 (d, *J* = 7.6 Hz, 1H, H_2), 4.21 (dq, *J* = 9.5, 6.3 Hz, 1H, H_{15}), 4.13 (dd, *J* = 12.4, 3.8 Hz, 1H, H_5), 3.81 (ddd, *J* = 10.0, 7.5, 4.6 Hz, 1H, H_{13}), 3.39 (s, 3H, H_{17}), 3.22 (s, 1H, H_1), 2.50 (dq, *J* = 14.6, 7.3 Hz, 1H, H_6), 2.36 (ddd, *J* = 15.1, 12.4, 6.9 Hz, 1H, H_4), 2.16 (ddd, *J* = 13.6, 4.7, 2.6 Hz, 1H, H_{12}), 2.02 (dd, *J* = 15.2, 3.8 Hz, 1H, H_4), 1.90 (ddd, *J* = 13.5, 10.1, 4.9 Hz, 1H, H_{12}), 1.59 – 1.53 (m, 1H, H_6), 1.21 (d, *J* = 6.3 Hz, 3H, H_{15}), 1.01 (t, *J* = 7.4 Hz, 3H, H_7), 0.91 (s, 9H, H_{10}), 0.17 (s, 3H, H_9), 0.15 (s, 3H, H_8). ^{13}C NMR (150 MHz, $CDCl_3$): δ 189.3, 166.3, 133.3, 130.6, 129.9, 128.4, 93.7, 82.6, 81.8, 79.1, 76.0, 68.3, 67.1, 58.7, 40.6, 35.5, 32.7, 30.5, 25.8, 25.4, 18.1, 17.9, 8.9, –4.1, –4.8. IR (ATR-FTIR), cm^{-1}: 2955 (m), 1724 (s), 1287 (s), 976 (m). 3342, 2933, 2857, 1726, 1452, 1261, 1097, 1067, 1026, 978, 886, 711 cm^{-1}. HRMS-ESI (*m/z*): [M + Na]$^+$ calcd for $C_{58}H_{86}O_{16}S_2Si_2Na$, 1181.4788; found, 1181.4825. $[\alpha]_D^{21}$ = –20.2 (*c* = 0.5, $CHCl_3$).

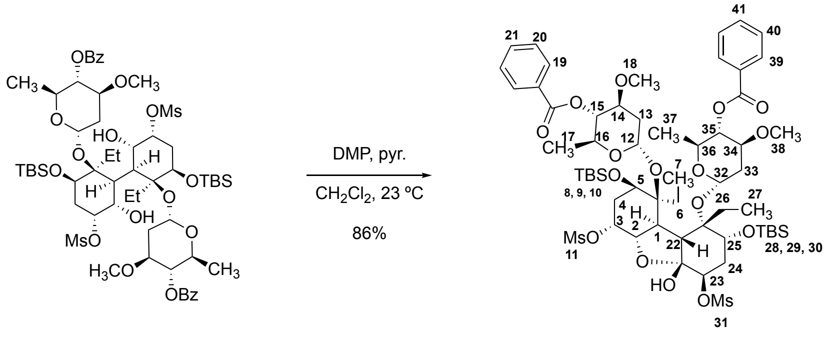
Synthesis of the bis(mesylate) ***18****:*



Triethylamine (62.9 mg, 87.0 µL, 621 µmol, 8.00 equiv) and a solution of methanesulfonic anhydride (54.1 mg, 311 µmol, 4.00 equiv) in dichloromethane (1.6 mL) were added in sequence to a solution of the tetraol **16** (83.5 mg, 77.6 µmol, 1 equiv) in dichloromethane (3.0 mL) at –20 ºC. The reaction mixture was stirred for 3 h at –20 ºC. The product mixture was diluted with saturated aqueous sodium bicarbonate solution (15 mL). The diluted solution was extracted with dichloromethane (3 × 30 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 20% ethyl acetate–hexanes initially, grading to 80% ethyl acetate–hexanes, three steps) to provide the bis(mesylate) **18** as a colorless oil (68.0 mg, 71%).

R_f = 0.40 (60% ethyl acetate–hexanes; CAM). ^{1}H NMR (600 MHz, CDCl$_3$): δ 8.01 (d, J = 7.3 Hz, 2H, H$_{20}$), 7.59 (t, J = 7.4 Hz, 1H, H$_{22}$), 7.47 (t, J = 7.8 Hz, 2H, H$_{21}$), 6.15 (t, J = 4.6 Hz, 1H, H$_{13}$), 5.58 (bs, 1H, H$_{11}$), 4.91 – 4.89 (m, 2H, H$_3$, H$_{16}$), 4.33 – 4.29 (m, 2H, H$_2$, H$_5$), 4.22 (p, J = 6.5 Hz, 1H, H$_{17}$), 3.67 (ddd, J = 7.4, 5.8, 4.1 Hz, 1H, H$_{15}$), 3.36 (s, 3H, H$_{19}$), 2.92 (s, 3H, H$_{12}$), 2.46 – 2.40 (m, 2H, H$_1$, H$_6$), 2.35 (dt, J = 13.6, 4.7 Hz, 1H, H$_4$), 2.10 (dt, J = 13.6, 4.7 Hz, 1H, H$_{14}$), 2.01 – 1.93 (m, 2H, H$_4$, H$_{14}$), 1.70 (dq, J = 14.3, 7.0 Hz, 1H, H$_6$), 1.35 (d, J = 6.5 Hz, 3H, H$_{18}$), 0.99 (t, J = 7.3 Hz, 3H, H$_7$), 0.91 (s, 9H, H$_{10}$), 0.17 (s, 3H, H$_8$), 0.15 (s, 3H, H$_9$). ^{13}C NMR (150 MHz, CDCl$_3$): δ 166.1, 133.5, 130.0, 129.8, 128.7, 91.9, 85.9, 81.0, 76.5, 73.9, 69.4, 67.5, 57.4, 43.0, 37.5, 34.2, 33.4, 30.5, 25.9, 23.4, 18.2, 17.7, 9.5, –3.3, –5.0. IR (ATR-FTIR), cm^{-1}: 3407 (br), 2955 (m), 1728 (s), 1271 (s), 1095 (s). HRMS-ESI (*m/z*): [M + Na]$^+$ calcd for C$_{58}$H$_{94}$O$_{20}$S$_2$Si$_2$Na, 1253.5211; found, 1253.5258. $[\alpha]_D^{21}$ = –55° (c = 0.1, CHCl$_3$).

Synthesis of the hemiketal ***19****:*

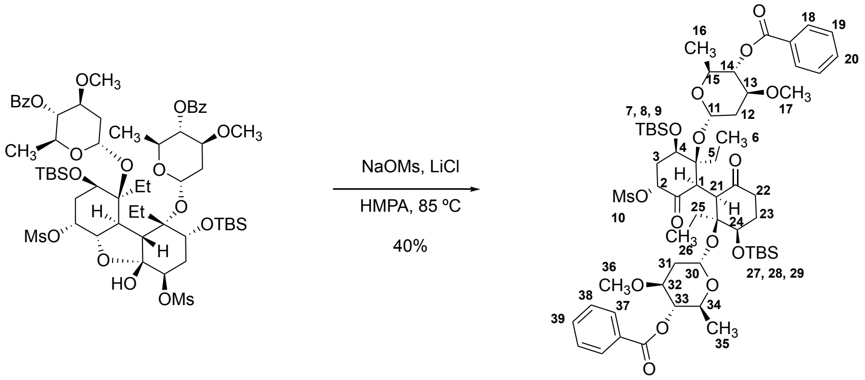


18 **19**

Pyridine (46.0 µL, 568 µmol, 20.0 equiv) and the Dess–Martin periodinane (120 mg, 284 µmol, 10.0 equiv) were added in sequence to a solution of the bis(mesylate) **18** (35.0 mg, 28.4 µmol, 1 equiv) in dichloromethane (2.0 mL) at 23 °C. The reaction mixture was stirred for 48 h at 23 °C. The product mixture was diluted with saturated aqueous sodium bicarbonate solution (15 mL). The diluted solution was extracted with dichloromethane (3 × 20 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 20% ethyl acetate–hexanes initially, grading to 60% ethyl acetate–hexanes, two steps) to provide the hemiketal **19** as a colorless oil (30.2 mg, 86%).

R_f = 0.55 (50% ethyl acetate–hexanes; CAM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13 – 8.08 (m, 4H, H_{19}, H_{39}), 7.62 – 7.57 (m, 2H, H_{21}, H_{41}), 7.50 – 7.43 (m, 4H, H_{20}, H_{40}), 5.92 (d, J = 2.3 Hz, 1H, H_{32}), 5.83 (bs, 1H, H_{12}), 5.43 (t, J = 9.2 Hz, 1H, H_{23}), 5.27 (d, J = 2.9 Hz, 1H, H_3), 4.95 – 4.91 (m, 2H, H_{15}, H_{35}), 4.66 (dd, J = 11.1, 2.1 Hz, 1H, H_2), 4.22 (dq, J = 9.9, 6.3 Hz, 1H, H_{36}), 4.11 – 4.05 (m, 3H, H_3, $H_{16,}$ H_{23}), 3.83 – 3.79 (m, 2H, H_{14}, H_{34}), 3.38 (s, 3H, H_{38}), 3.32 (s, 3H, H_{18}), 3.17 (s, 3H, H_{31}), 3.09 (s, 1H, H_{42}), 3.06 (s, 3H, H_{11}), 2.67 (dd, J = 11.0, 9.2 Hz, 1H, H_1), 2.56 (d, J = 9.5 Hz, 1H, H_{22}), 2.51 – 2.41 (m, 3H, $H_{6,}$ H_{26}, H_{33}), 2.37 – 2.28 (m, 2H, H_{13}, H_{24}), 2.23 (dt, J = 14.1, 4.3 Hz, 1H, H_4), 2.11 (ddd, J = 13.6, 9.4, 7.0 Hz, 1H, H_{24}), 1.98 – 1.94 (m, 1H, H_4), 1.80 – 1.73 (m, 2H, H_{13}, H_{33}), 1.64 – 1.56 (m, 2H, H_6, H_{26}), 1.18 (d, J = 6.1 Hz, 3H, H_{37}), 1.17 (d, J = 6.1 Hz, 1H, H_{17}), 1.04 (t, J = 7.3 Hz, 3H, H_{27}), 0.97 (t, J = 7.3 Hz, 1H, H_7), 0.91 (s, 9H, H_{30}), 0.90 (s, 9H, H_{10}), 0.14 (s, 3H, H_{29}), 0.13 (s, 6H, H_{28}, H_9), 0.10 (s, 3H, H_8). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.2, 166.0, 133.3, 133.2, 130.4, 130.2, 130.0, 129.9, 128.6 (2C), 105.0, 92.4, 91.7, 83.7, 82.9, 80.6, 76.1, 76.0, 75.9, 75.5, 70.8, 70.1, 67.0, 66.8, 57.6, 57.3, 52.0, 43.2, 39.3, 39.0, 36.0, 35.7, 35.4, 34.4, 29.9, 25.9 (2C), 23.0, 22.6, 18.2, 18.1, 18.0, 17.8, 10.2, 9.9, –3.3, –3.7, –4.9, –5.1 ppm. IR (ATR-FTIR), cm^{-1}: 2931 (m), 1728 (s), 1269 (s), 1112 (s). HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{58}H_{92}O_{20}S_2Si_2Na$, 1251.5054; found, 1251.5100. $[\alpha]_D^{21}$ = –22.5° (c = 1.0, $CHCl_3$).

*Synthesis of the C_1-symmetric diketone **20**:*

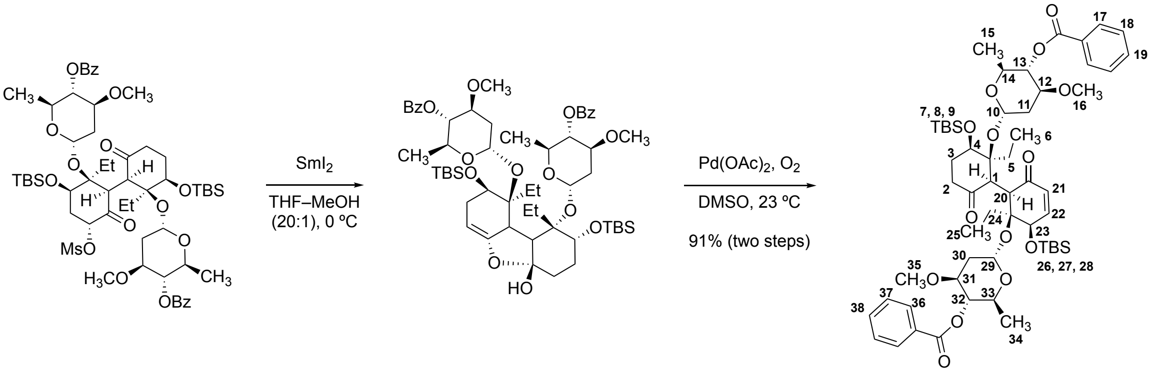


19 **20**

Lithium chloride (42.2 mg, 996 μmol, 25.0 equiv) and sodium methanesulfonate (235 mg, 1.99 mmol, 50.0 equiv) were added in sequence to a stirred solution of the hemiketal **19** (49.0 mg, 39.8 μmol, 1 equiv) in hexamethylphosphoramide (3.7 mL) at 23 °C. The reaction vessel was placed in an oil bath that had been preheated to 85 ºC. The reaction mixture was stirred and heated for 2 h 40 min at 85 ºC. The product mixture cooled to 23 °C over 5 min. The cooled product mixture was diluted with ethyl acetate (20 mL). The diluted solution was transferred to a separatory funnel. The solution was washed sequentially with water (2 × 20 mL) and saturated aqueous sodium chloride solution (20 mL). The washed organic layer was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 8% ethyl acetate–hexanes initially, grading to 30% ethyl acetate–hexanes, four steps) to provide separately the starting hemiketal **19** (24.5 mg, 50%, colorless oil) and the C_1-symmetric diketone **20** (18.1 mg, 40%, colorless oil).

R_f = 0.45 (30% ethyl acetate–hexanes; CAM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.26 – 8.18 (m, 2H, H_{19}), 8.07 – 7.98 (m, 2H, H_{37}), 7.63 – 7.57 (m, 2H, H_{20}, H_{39}), 7.54 (t, J = 7.3 Hz, 2H, H_{19}), 7.47 (t, J = 7.6 Hz, 2H, H_{38}), 6.16 (dd, J = 3.9, 1.8 Hz, 1H, H_2), 6.16 (bs, 1H, H_{11}), 6.02 (bs, 1H, H_{30}) 4.96 – 4.87 (m, 3H, H_{14}, H_{15}, H_{33}), 4.25 (dd, J = 11.5, 4.6 Hz, 1H, H_{24}), 3.98 (t, J = 9.0 Hz, 1H, H_4), 3.88 – 3.76 (m, 2H, H_{13}, H_{34}), 3.54 (ddd, J = 11.1, 8.9, 4.6 Hz, 1H, H_{32}), 3.36 (s, 3H, H_{17}), 3.25 (s, 3H, H_{36}), 3.19 (s, 4H, H_{10}, H_1), 2.71 (dq, J = 15.2, 7.5 Hz, 1H, H_5), 2.62 (s, 1H, H_{21}) 2.57 – 2.45 (m, 4H, H_3, H_{22}, H_{23}), 2.43 – 2.30 (m, 2H, H_3, H_{31}), 2.21 – 2.14 (m, 1H, H_{23}), 2.11 – 1.99 (m, 2H, H_5, H_{12}), 1.82 – 1.60 (m, 2H, H_{31}, H_{12}), 1.50 – 1.40 (m, 1H, H_5), 1.28 – 1.24 (m, 6H, H_{16}, H_{35}), 0.98 (t, J = 7.4 Hz 3H, H_6) 0.93 (s, 9H, H_9), 0.92 (s, 9H, H_{29}), 0.86 (t, J = 7.4 Hz, 3H, H_{26}) 0.18 (s, 3H, H_7), 0.16 (s, 3H, H_{27}), 0.15 (s, 3H, H_8), 0.11 (s, 3H, H_{28}). ^{13}C NMR (150 MHz, $CDCl_3$): δ 207.1, 202.3, 166.1, 165.6, 133.20, 133.17, 130.3, 130.1, 129.7, 129.6, 128.8, 128.5, 93.1, 92.5, 88.1, 85.5, 79.4, 76.4, 75.6, 75.2, 74.9, 70.5, 67.0, 65.8, 57.7, 57.4, 56.4, 47.2, 38.8, 38.6, 36.8, 35.4, 34.8, 30.6, 29.7, 25.8, 25.8, 24.4, 18.2, 18.0, 17.9, 9.4, 8.6, –3.1, –3.5, –5.0, –5.3 ppm. IR (ATR-FTIR), cm^{-1}: 2934 (m), 1724 (s), 1271 (m), 1095 (s). HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{57}H_{88}O_{17}SSi_2Na$, 1155.5173; found, 1155.5223. $[\alpha]_D^{21}$ = –35.5 (c = 0.2, $CHCl_3$).

*Synthesis of the enone **22**:*



20 **21** **22**

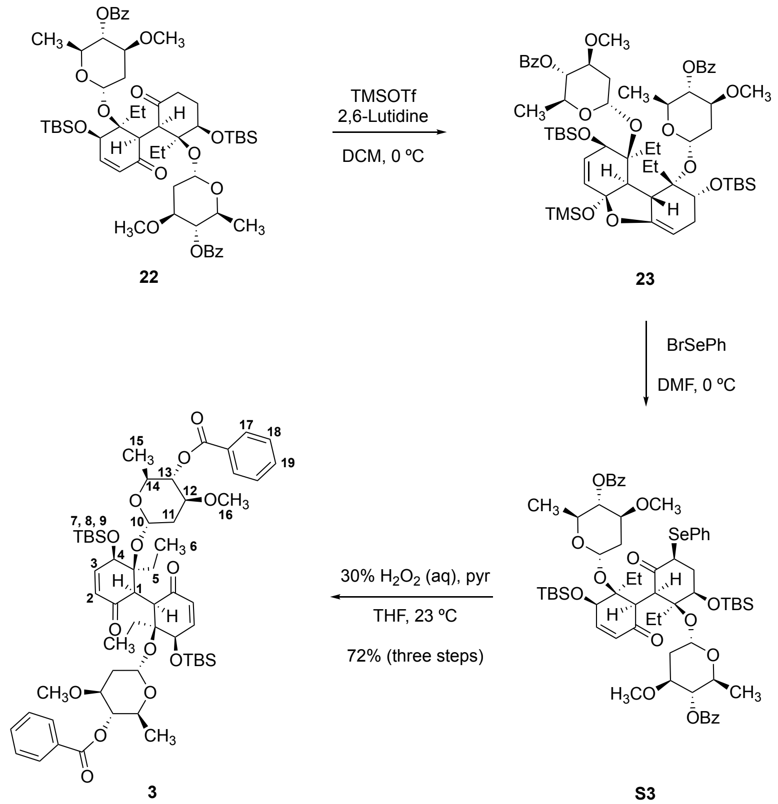
A solution of samarium (II) iodide in tetrahydrofuran (0.1 M, 1.8 mL, 180 µmol, 8.00 equiv) was added to a solution of the C_1-symmetric diketone **20** (25.7 mg, 22.7 µmol, 1 equiv) in degassed tetrahydrofuran–methanol (v/v, 20:1, 4.0 mL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C. The product mixture was diluted sequentially with saturated aqueous sodium bicarbonate solution (10 mL), saturated aqueous sodium thiosulfate solution (10 mL), and ethyl acetate (40 mL). The diluted solution was washed with saturated aqueous sodium chloride solution (10 mL). The washed organic layer was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 10% ethyl acetate–hexanes buffered with 4% triethylamine initially, grading to 30% ethyl acetate–hexanes buffered with 4% triethylamine, two steps) to provide the cyclic enol ether **21** as colorless oil. The enol ether **21** was unstable toward storage and was used directly in the following step.

Palladium (II) acetate (19.1 mg, 85.1 µmol, 5.00 equiv) was added to a solution of the unpurified cyclic enol ether **21** obtained in the preceding step (nominally 17.0 µmol, 1 equiv) in dimethyl sulfoxide (2.4 mL) at 23 °C. The headspace was purged with oxygen gas and the vessel was fitted with an oxygen-filled balloon. The reaction mixture was stirred for 16 h at 23 ºC. The product mixture was diluted sequentially with water (10 mL), saturated aqueous sodium bicarbonate solution (5 mL), and ethyl acetate (40 mL). The mixture was transferred to a separatory funnel and the layers that formed were separated. The organic layer was washed sequentially with water (10 mL), saturated aqueous sodium chloride solution (10 mL), and saturated aqueous ammonium chloride solution (10 mL). The washed organic layer was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 6% ethyl acetate–hexanes initially, grading to 25% ethyl acetate–hexanes, four steps) to provide the enone **22** as a colorless oil (16.0 mg, 91%).

R_f = 0.50 (20% ethyl acetate–hexanes; CAM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11 (d, J = 7.8 Hz, 2H, H_{17}), 8.06 (dd, J = 7.1, 1.4 Hz, 2H, H_{36}), 7.59-7.55 (m, 2H, H_{19}, H_{38}), 7.48 – 7.43 (m, 4H, H_{18}, H_{37}), 6.55 (ddd, J = 10.2, 3.3, 1.0 Hz, 1H, H_{22}), 6.25 (d, J = 10.2 Hz, 1H, H_{21}), 5.97 (d, J = 3.6 Hz, 1H, H_{10}), 5.70 (bs, 1H, H_{29}), 4.90 – 4.83 (m, 2H, H_{13}, H_{32}), 4.56

(s, 1H, H$_{23}$), 4.14 (dt, *J* = 9.5, 6.1 Hz, 2H, H$_{14}$), 4.10 – 4.05 (m, 1H, H$_{4}$), 3.84 (ddd, *J* = 11.0, 9.0, 4.9 Hz, 1H, H$_{12}$), 3.74 (ddd, *J* = 11.0, 8.8, 4.8 Hz, 1H, H$_{31}$), 3.32 (s, 4H, H$_{16,}$ H$_{1}$), 3.30 (3, 3H, H$_{35}$), 3.05 (s, 1H, H$_{20}$) 2.54 (tt, *J* = 15.4, 7.8 Hz, 1H, H$_{2}$), 2.34 (ddd, *J* = 14.9, 12.2, 7.1 Hz, 1H, H$_{3}$), 2.26 – 2.18 (m, 3H, H$_{2}$ H$_{11}$, H$_{30}$), 2.02 – 1.92 (m, 1H, H$_{2}$), 1.88 – 1.79 (m, 1H, H$_{5}$), 1.67 – 1.60 (m, 3H, H$_{3}$ H$_{11}$, H$_{30}$), 1.16 (m, 7H, H$_{15}$, H$_{34,}$), 1.07 (m, 3H, H$_{5}$, H$_{24)}$ 0.93 (m, 24H, H$_{6,}$ H$_{9,}$ H$_{24,}$ H$_{28}$), 0.17 – 0.11 (m, 12H, H$_{7}$, H$_{8}$, H$_{26}$, H$_{27}$), ppm□□^{13}C NMR (150 MHz, CDCl$_3$): δ 207.2 (2C), 166.0, 165.8, 133.0, 132.9, 130.4, 130.2, 129.8, 129.7, 129.7, 128.4, 128.3, 125.5, 92.6, 92.2, 85.1, 77.5, 75.8, 75.51, 75.47, 73.9, 66.8, 66.4, 66.2, 57.5, 57.3, 39.2, 38.8, 35.8, 35.4, 30.3, 29.7, 28.0, 26.0, 25.8, 24.0, 23.9, 18.0, 17.8, 17.7, 9.0, –3.7, –5.0 ppm. IR (ATR-FTIR), cm^{-1}: 2932 (s), 1727 (s), 1271 (s), 1111 (s). HRMS-ESI (*m/z*): [M + Na]$^+$ calcd for $C_{56}H_{84}O_{14}Si_2Na$, 1059.5292; found, 1059.5343. $[\alpha]_D^{21}$ = –45.0 (*c* = 0.2, CHCl$_3$).

Synthesis of the bis(enone) ***3****:*



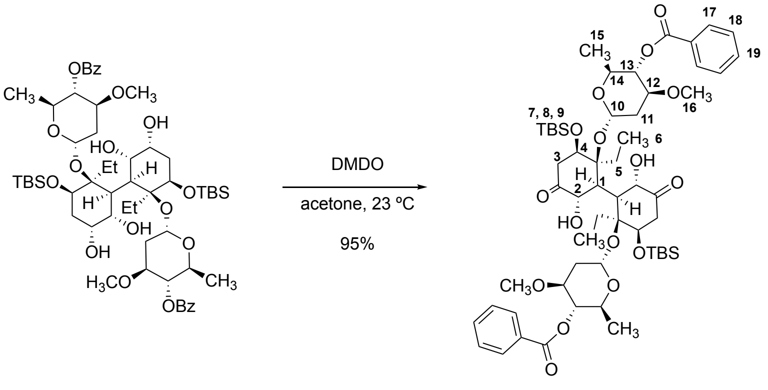
2,6-Lutidine (22.2 µL, 191 µmol, 15.0 equiv) and a solution of trimethylsilyl trifluoromethanesulfonate (16.1 µL, 89.1 µmol, 7.00 equiv) in dichloromethane (1.0 mL) were added in sequence to a solution of the enone **22** (13.2 mg, 12.7 µmol, 1 equiv) in dichloromethane (1.0 mL) at 0 ºC. The reaction mixture was stirred for 3 h at 0 ºC. The product mixture was diluted with water (20 mL). The diluted solution was extracted with dichloromethane (3 × 20 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated to provide cyclic enol ether **23** as a colorless oil. The cyclic enol ether **23** was unstable toward purification and was used directly in the following step.

A solution of phenylselenyl bromide (13.2 mg, 55.9 µmol, 5.00 equiv) in *N,N*-dimethylformamide (2.0 mL) was added dropwise via syringe to a solution of the unpurified enol ether **19** obtained in the preceding step (nominally 12.7 µmol) in *N,N*-dimethylformamide (500 µL) at 0 ºC. The reaction mixture was allowed to slowly warm to 23 ºC over 5 h. The product mixture was diluted sequentially with ethyl acetate (20 mL) and saturated aqueous sodium bicarbonate solution (15 mL). The layers that formed were separated, and the organic layer was washed sequentially with water (15 mL) and saturated aqueous sodium chloride solution (15 mL). The washed organic layer was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated to provide the selenide **S3** as a colorless oil.

Pyridine (30.4 µL, 370 µmol, 40.0 equiv) and a solution of hydrogen peroxide in water (30%, 21.5 µL, 188 µmol, 20.0 equiv) were added in sequence to a solution of the selenide **S3** (nominally 12.7 µmol) in tetrahydrofuran (1.9 mL) at 23 ºC. The reaction mixture was stirred for 2.5 h at 23 °C. The product mixture was diluted sequentially with ethyl acetate (20 mL), saturated aqueous sodium thiosulfate solution (15 mL), and saturated aqueous sodium bicarbonate solution (15 mL). The diluted solution was extracted with ethyl acetate (2 × 20 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 8% ethyl acetate–hexanes initially, grading to 24% ethyl acetate–hexanes, two steps) to provide the bis(enone) **3** as a colorless oil (9.5 mg, 72% from **22**).

R$_f$ = 0.50 (20% ethyl acetate–hexanes; CAM). ^{1}H NMR (600 MHz, CD$_2$Cl$_2$): δ 8.08 – 8.06 (m, 2H, H$_{17}$), 7.61 – 7.58 (m, 1H, H$_{19}$), 7.49 – 7.46 (m, 2H, H$_{18}$), 6.57 (dd, *J* = 10.2, 2.6 Hz, 1H, H$_3$), 6.15 (d, *J* = 10.0 Hz, 1H, H$_2$), 5.81 (s, 1H, H$_{10}$), 4.78 (t, *J* = 9.4 Hz, 1H, H$_{13}$), 4.69 (s, 1H, H$_4$), 4.24 (bs, 1H, H$_{14}$), 3.75 (ddd, *J* = 11.4, 9.1, 4.8 Hz, 1H, H$_{12}$), 3.26 (s, 3H, H$_{16}$), 3.20 (bs, 1H, H$_1$), 2.36 – 2.26 (m, 1H, H$_5$), 2.20 (dd, *J* = 12.6, 4.3 Hz, 1H, H$_{11}$), 1.86 (dt, *J* = 14.8, 7.0 Hz, 1H, H$_5$), 1.54 (td, *J* = 12.8, 3.8 Hz, 1H, H$_{11}$), 1.11 (d, *J* = 6.3 Hz, 3H, H$_{15}$), 1.08 (t, *J* = 7.2 Hz, 3H, H$_6$), 0.95 (s, 9H, H$_9$), 0.19 (s, 3H, H$_7$), 0.18 (s, 3H, H$_8$) □□ ^{13}C NMR (150 MHz, CD$_2$Cl$_2$): δ 196.7, 166.3, 143.7, 133.5, 131.1, 130.9, 130.1, 128.9, 92.9, 77.8, 76.2, 72.9, 67.0, 57.5, 57.4, 35.9, 30.6, 26.2, 18.6, 18.1, 9.4, –3.4, –3.5. IR (ATR-FTIR), cm^{-1}: 2929 (s), 1725 (s), 1684 (m), 1270 (s), 1101 (s). HRMS-ESI (*m/z*): [M + Na]$^+$ calcd for $C_{56}H_{84}O_{14}Si_2Na$, 1057.5141; found, 1057.5185. $[\alpha]_D^{21}$ = –45.0 (*c* = 0.5, CHCl$_3$).

*Synthesis of the hydroxy ketone **24**:*



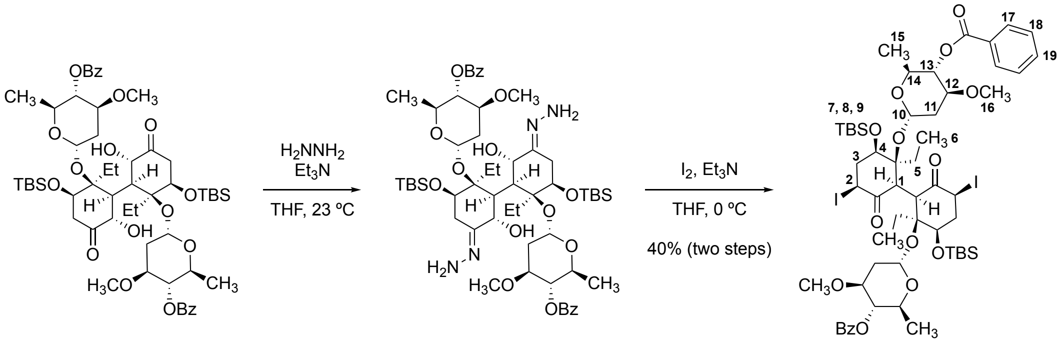
16

24

A solution of dimethlydioxirane in acetone (73.0 mM, 6.20 mL, 46.0 µmol, 7.00 equiv) was added to a round-bottomed flask charged with the tetraol **16** (70.0 mg, 65.0 µmol, 1 equiv) at 23 ºC. The reaction mixture was stirred for 24 h at 23 ºC. The product mixture was concentrated and the residue obtained was purified by flash-column chromatography (eluting with 30% ethyl acetate–hexanes initially, grading to 40% ethyl acetate–hexanes, one step) to provide the hydroxy ketone **24** as a pale oil (66.0 mg, 95%).

R_f = 0.50 (50% ethyl acetate–hexanes; CAM). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.7 Hz, 2H, H_{17}), 7.58 (t, *J* = 7.2 Hz, 1H, H_{19}), 7.47 (t, *J* = 7.6 Hz, 2H, H_{18}), 5.98 (t, *J* = 3.6 Hz, 1H, H_{18}), 4.84 (t, *J* = 7.3 Hz, 1H, H_{13}), 4.47 (d, *J* = 4.8 Hz, 1H, H_2), 4.39 (dd, *J* = 10.9, 6.1 Hz, 1H, H_4), 4.24 (p, *J* = 6.7 Hz, 1H, H_{14}), 4.01 (d, *J* = 4.2 Hz, 1H, H_{20}), 3.86 (td, *J* = 8.2, 4.5 Hz, 1H, H_{12}), 3.39 (s, 1H, H_{16}), 2.83 (dd, *J* = 15.1, 6.0 Hz, 1H, H_3), 2.67 (dd, *J* = 15.1, 10.9 Hz, 1H, H_3), 2.42-2.53 (m, 2H, H_1, H_5), 2.21 (dt, *J* = 13.3, 4.1 Hz, 1H, H_{11}), 1.84 (ddd, *J* = 12.9, 8.8, 3.6 Hz, 1H, H_{11}), 1.73 (dt, *J* = 14.2, 7.2 Hz, 1H, H_5), 1.25 (d, *J* = 6.4 Hz, 3H, H_{15}), 0.97 (t, *J* = 7.3 Hz, 3H, H_6), 0.91 (s, 9H, H_9), 0.12 (s, 3H, H_7), 0.11 (s, 3H, H_8); ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.9, 165.9, 133.2, 129.91, 129.86, 128.5, 128.3, 92.0, 84.6, 75.7, 75.2, 71.3, 68.1, 57.4, 45.2, 43.4, 34.2, 25.7, 23.0, 17.9, 17.4, 9.0, –3.7, –5.1. IR (ATR-FTIR), cm^{-1}: 3458 (br), 2931 (m), 1724 (s), 1259 (s), 1096 (s), 984 (s). HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{56}H_{86}O_{16}Si_2Na$, 1093.5347; found, 1093.5381$[\alpha]_D^{21}$ = –84.5 (*c* = 1.0, $CHCl_3$).

*Synthesis of the α-iodoketone **27**:*



24 **25** **30**

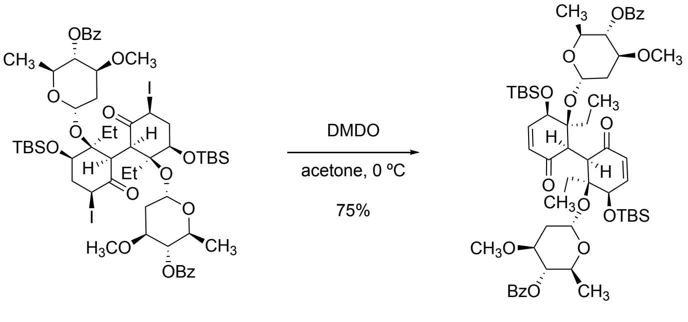
Triethylamine (130 µL, 930 µmol, 15.0 equiv) was added to a solution of the hydroxy ketone **24** (66 mg, 61.0 µmol, 1 equiv) in tetrahydrofuran (5.7 mL) at 23 °C. The resulting solution was cooled to 0 °C. A solution of hydrazine in tetrahydrofuran (1.0 M, 1.25 mL, 620 µmol, 10.0 equiv) was then added. The reaction mixture was warmed to 23 °C and was stirred for 16 h at 23 °C. The product mixture was concentrated to provide the bis(hydrazone) **25** as a pale brown oil. The bis(hydrazone) **25** was unstable toward purification and was used directly in the following step.

Triethylamine (346 µL, 2.48 mmol, 40.0 equiv) and a solution of iodine in tetrahydrofuran (1.9 M, 640 µL, 20.0 equiv) were added in sequence to a solution of the unpurified hydrazone **25** obtained in the preceding step (nominally 61.0 µmol, 1 equiv) in tetrahydrofuran (11 mL) at 0 °C. The reaction mixture was stirred for 20 min at 0 °C. The product mixture was diluted with saturated aqueous sodium thiosulfate solution (60 mL). The diluted product mixture was extracted with ethyl acetate (3 × 60 mL). The organic layers were combined, and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 1% methanol–dichloromethane initially, grading to 3% methanol–dichloromethane, two steps) to provide the α-iodoketone **30** as a pale yellow oil (31.2 mg, 40%).

R_f = 0.70 (30% ethyl acetate–hexanes; CAM). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 2H, H_{17}), 7.55 (t, *J* = 7.5 Hz, 1H, H_{19}), 7.42 (t, *J* = 7.4 Hz, 2H, H_{18}), 5.99 (d, *J* = 3.3 Hz, 1H, H_{10}), 4.94 (dd, *J* = 4.3, 2.3 Hz, 1H, H_2), 4.87 (t, *J* = 9.3 Hz, 1H, H_{13}), 4.57 (dd, *J* = 11.2, 2.7 Hz, 1H, H_4), 4.11 – 4.03 (m, 1H, H_{14}), 3.85 (ddd, *J* = 11.2, 9.0, 4.6 Hz, 1H, H_{12}), 3.37 (s, 3H, H_{16}), 3.29 (s, 1H, H_1), 2.64 (ddd, *J* = 15.1, 11.3, 4.4 Hz, 1H, H_3), 2.51 (dt, *J* = 14.6, 7.2 Hz, 1H, H_5), 2.35 (t, *J* = 7.5 Hz, 1H), 2.30 (dd, *J* = 12.8, 4.7 Hz, 1H, H_{11}), 2.01–1.94 (m, 1H, H_3), 1.72 (td, *J* = 12.2, 4.0 Hz, 1H, H_{11}), 1.41 (dd, *J* = 14.6, 7.4 Hz, 1H, H_5), 1.18 (d, *J* = 6.3 Hz, 3H, H_{15}), 1.08 (t, *J* = 7.3 Hz, 3H, H_6), 0.92 (s, 9H, H_9), 0.20 (s, 3H, H_8), 0.18 (s, 3H, H_7); ^{13}C NMR (150 MHz, $CDCl_3$) δ 203.2, 166.0, 133.0, 130.1, 128.3, 92.6, 82.9, 77.5, 75.5, 71.8, 66.9, 57.7, 50.0, 36.3, 35.2, 28.7, 25.7, 25.7, 23.2, 18.0, 17.8, 9.5, –3.4, –4.5. IR (ATR-FTIR), cm^{-1}: 2930 (m), 1724 (s), 1264 (s), 1101 (s), 980 (s).

HRMS-ESI (*m/z*): $[M + Na]^+$ calcd for $C_{56}H_{84}I_2O_{14}Si_2Na$, 1313.3381; found, 1313.3437.
$[\alpha]_D^{21}$ = –135 (c = 1.0, $CHCl_3$).

Synthesis of the bis(enone) ***3****:*



30 **3**

A solution of dimethlydioxirane in acetone (73.0 mM, 1.50 mL, 460 µmol, 15.0 equiv) was added to a solution of the α-iodoketone **30** (10.1 mg, 7.70 µmol, 1 equiv) in acetone (300 µL) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C. The product mixture was concentrated and the residue obtained was purified by flash-column chromatography (eluting with 25% ethyl acetate–hexanes) to provide the bis(enone) **3** as a pale oil (6.0 mg, 75%).

Spectroscopic data for the bis(enone) **3** obtained in this way were in agreement with those obtained by the alternative procedure above.

Crystallographic analysis of thiocarbonate 17.

Experimental

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) for the structure of 007-16115. The diffraction images were processed and scaled using the Rigaku CrystalClear software (CrystalClear and CrystalStructure; Rigaku/MSC: The Woodlands, TX, 2005). The data was collected and refined as a 2-component twin. The fractional volume contributions of the second twin component to the reflections list refined to 0.181(3). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The full numbering scheme of compound 007-16115 can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 2001251 (007-16115) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

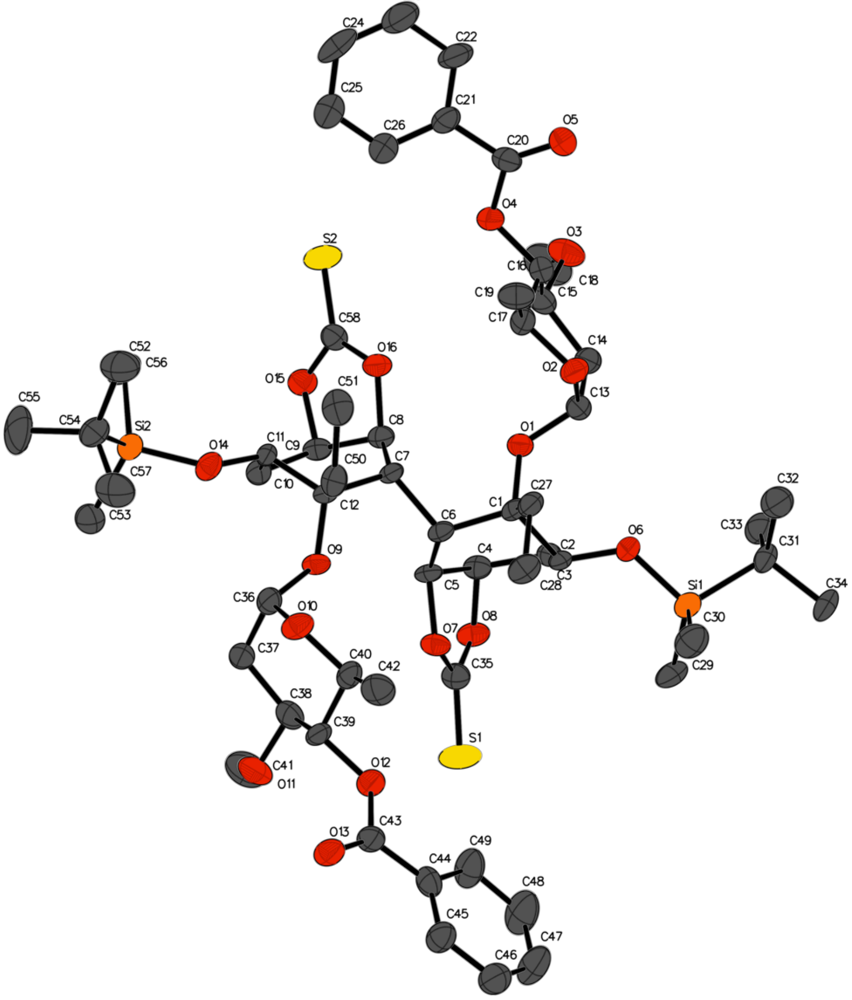


Figure S1. The complete numbering scheme of 007-16115 with 50% thermal ellipsoid probability levels. The hydrogen atoms have been removed for clarity.

Table S1. Crystal data and structure refinement for 007-16115.

Identification code	007-16115	
Empirical formula	C58 H86 O16 S2 Si2	
Formula weight	1159.56	
Temperature	93(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 17.8150(12) Å	□= 90°.
	b = 18.8153(13) Å	□= 90°.
	c = 19.2663(13) Å	□ = 90°.
Volume	6458.0(8) Å^3	
Z	4	
Density (calculated)	1.193 Mg/m^3	
Absorption coefficient	1.611 mm^{-1}	
F(000)	2488	
Crystal size	0.200 x 0.200 x 0.020 mm^3	
Theta range for data collection	3.283 to 68.094°.	
Index ranges	-21<=h<=21, 0<=k<=22, 0<=l<=23	
Reflections collected	11690	
Independent reflections	11690 [R(int) = 0.157]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.695	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11690 / 0 / 720	
Goodness-of-fit on F^2	1.086	
Final R indices [I>2sigma(I)]	R1 = 0.0711, wR2 = 0.2108	
R indices (all data)	R1 = 0.0823, wR2 = 0.2205	
Absolute structure parameter	0.032(8)	
Largest diff. peak and hole	0.552 and -0.375 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)
for 007-16115. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	9085(1)	4684(1)	3326(1)	44(1)
S(2)	3348(1)	5363(1)	2530(1)	46(1)
Si(1)	8602(1)	7638(1)	2446(1)	28(1)
Si(2)	4203(1)	4089(1)	5306(1)	31(1)
O(1)	6166(2)	6757(2)	2694(2)	25(1)
O(2)	5626(3)	7887(2)	2736(3)	33(1)
O(3)	4522(3)	7148(3)	1014(3)	42(1)
O(4)	3713(3)	7416(2)	2277(3)	33(1)
O(5)	3264(3)	8492(3)	1955(3)	46(1)
O(6)	7742(2)	7326(2)	2543(2)	28(1)
O(7)	7783(3)	5264(2)	3598(2)	26(1)
O(8)	7947(3)	4934(2)	2513(2)	29(1)
O(9)	6316(2)	5090(2)	4607(2)	25(1)
O(10)	6782(3)	5360(3)	5711(2)	35(1)
O(11)	8136(3)	3656(3)	5278(3)	44(1)
O(12)	8767(3)	5038(3)	5358(2)	34(1)
O(13)	9205(3)	4982(3)	6454(2)	38(1)
O(14)	4783(3)	4718(3)	5050(2)	31(1)
O(15)	4533(3)	4597(2)	2802(2)	30(1)
O(16)	4670(3)	5747(2)	2998(2)	29(1)
C(1)	6767(4)	6703(3)	3199(3)	24(1)
C(2)	7534(3)	6660(3)	2822(3)	25(1)
C(3)	7481(4)	6113(3)	2248(3)	27(1)
C(4)	7267(4)	5377(3)	2503(3)	26(1)
C(5)	7042(3)	5346(3)	3267(3)	24(1)
C(6)	6636(3)	5987(3)	3584(3)	22(1)

C(7)	5791(3)	5832(3)	3707(3)	22(1)
C(8)	5425(4)	5444(3)	3095(3)	24(1)
C(9)	5268(4)	4649(3)	3147(3)	25(1)
C(10)	5176(4)	4374(4)	3882(4)	30(1)
C(11)	4980(3)	4965(3)	4381(3)	24(1)
C(12)	5641(3)	5488(3)	4442(3)	23(1)
C(13)	6063(4)	7410(3)	2333(3)	28(1)
C(14)	5689(4)	7263(4)	1645(4)	34(2)
C(15)	4850(4)	7089(4)	1678(4)	34(2)
C(16)	4481(4)	7627(4)	2150(4)	31(2)
C(17)	4870(4)	7645(4)	2850(4)	31(2)
C(18)	4587(8)	6539(6)	608(6)	70(3)
C(19)	4525(4)	8129(4)	3375(4)	39(2)
C(20)	3172(4)	7920(4)	2224(4)	34(2)
C(21)	2464(4)	7686(4)	2562(4)	33(2)
C(22)	1840(4)	8115(4)	2477(5)	45(2)
C(23)	1171(5)	7951(5)	2836(6)	59(2)
C(24)	1144(5)	7373(6)	3277(6)	63(3)
C(25)	1777(5)	6945(5)	3358(5)	56(2)
C(26)	2441(5)	7109(4)	2994(4)	40(2)
C(27)	6733(4)	7333(4)	3711(4)	30(1)
C(28)	7326(5)	7324(4)	4291(4)	36(2)
C(29)	9268(4)	6899(5)	2271(5)	43(2)
C(30)	8915(5)	8103(5)	3250(4)	46(2)
C(31)	8522(4)	8269(4)	1691(4)	32(2)
C(32)	7981(5)	8872(4)	1870(5)	46(2)
C(33)	8244(5)	7872(4)	1048(4)	41(2)
C(34)	9302(5)	8591(5)	1534(5)	49(2)
C(35)	8251(4)	4973(4)	3143(4)	29(1)
C(36)	6429(4)	4849(4)	5296(3)	32(2)
C(37)	6883(4)	4163(4)	5262(4)	34(2)
C(38)	7726(4)	4277(4)	5116(4)	34(2)
C(39)	8013(4)	4865(4)	5573(4)	31(2)
C(40)	7533(4)	5531(4)	5500(4)	31(2)
C(41)	8131(7)	3146(5)	4749(6)	66(3)

C(42)	7781(5)	6136(4)	5945(4)	43(2)
C(43)	9310(4)	5088(4)	5842(4)	32(2)
C(44)	10045(4)	5298(4)	5537(4)	33(2)
C(45)	10629(4)	5462(4)	5983(4)	37(2)
C(46)	11325(5)	5657(5)	5717(4)	45(2)
C(47)	11436(5)	5655(5)	5018(5)	52(2)
C(48)	10858(6)	5488(6)	4572(5)	61(3)
C(49)	10156(5)	5310(5)	4831(4)	48(2)
C(50)	5495(4)	6080(4)	4971(3)	30(2)
C(51)	4763(5)	6481(4)	4872(4)	41(2)
C(52)	3425(4)	3972(5)	4663(5)	47(2)
C(53)	4762(5)	3259(4)	5408(4)	41(2)
C(54)	3816(4)	4412(4)	6166(4)	40(2)
C(55)	3414(7)	3799(6)	6535(6)	74(3)
C(56)	3262(5)	5011(5)	6036(5)	54(2)
C(57)	4458(5)	4684(6)	6624(4)	53(2)
C(58)	4202(4)	5230(3)	2788(4)	29(1)

Table 3. Bond lengths [Å] and angles [°] for 007-16115.

S(1)-C(35)	1.622(7)
S(2)-C(58)	1.619(7)
Si(1)-O(6)	1.651(4)
Si(1)-C(29)	1.860(8)
Si(1)-C(30)	1.864(8)
Si(1)-C(31)	1.882(7)
Si(2)-O(14)	1.647(5)
Si(2)-C(53)	1.863(8)
Si(2)-C(52)	1.873(8)
Si(2)-C(54)	1.894(8)
O(1)-C(13)	1.423(7)
O(1)-C(1)	1.451(8)
O(2)-C(13)	1.419(8)
O(2)-C(17)	1.439(8)
O(3)-C(18)	1.393(12)
O(3)-C(15)	1.412(9)
O(4)-C(20)	1.356(8)
O(4)-C(16)	1.446(8)
O(5)-C(20)	1.206(9)
O(6)-C(2)	1.412(8)
O(7)-C(35)	1.329(8)
O(7)-C(5)	1.474(7)
O(8)-C(35)	1.331(8)
O(8)-C(4)	1.471(7)
O(9)-C(36)	1.416(8)
O(9)-C(12)	1.452(7)
O(10)-C(36)	1.400(9)
O(10)-C(40)	1.435(8)
O(11)-C(41)	1.401(12)
O(11)-C(38)	1.412(9)
O(12)-C(43)	1.347(8)
O(12)-C(39)	1.443(8)
O(13)-C(43)	1.210(9)

O(14)-C(11)	1.413(8)
O(15)-C(58)	1.329(8)
O(15)-C(9)	1.472(8)
O(16)-C(58)	1.345(8)
O(16)-C(8)	1.472(7)
C(1)-C(27)	1.542(9)
C(1)-C(2)	1.549(9)
C(1)-C(6)	1.556(9)
C(2)-C(3)	1.514(10)
C(2)-H(2)	1.0000
C(3)-C(4)	1.517(9)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.527(9)
C(4)-H(4)	1.0000
C(5)-C(6)	1.533(9)
C(5)-H(5)	1.0000
C(6)-C(7)	1.552(8)
C(6)-H(6)	1.0000
C(7)-C(8)	1.532(9)
C(7)-C(12)	1.580(9)
C(7)-H(7)	1.0000
C(8)-C(9)	1.526(9)
C(8)-H(8)	1.0000
C(9)-C(10)	1.516(9)
C(9)-H(9)	1.0000
C(10)-C(11)	1.511(10)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(12)	1.539(9)
C(11)-H(11)	1.0000
C(12)-C(50)	1.532(9)
C(13)-C(14)	1.509(11)
C(13)-H(13)	1.0000
C(14)-C(15)	1.531(10)

C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.512(11)
C(15)-H(15)	1.0000
C(16)-C(17)	1.516(10)
C(16)-H(16)	1.0000
C(17)-C(19)	1.495(10)
C(17)-H(17)	1.0000
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-C(21)	1.486(10)
C(21)-C(26)	1.368(11)
C(21)-C(22)	1.384(10)
C(22)-C(23)	1.410(12)
C(22)-H(22)	0.9500
C(23)-C(24)	1.381(15)
C(23)-H(23)	0.9500
C(24)-C(25)	1.394(15)
C(24)-H(24)	0.9500
C(25)-C(26)	1.408(12)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500
C(27)-C(28)	1.538(10)
C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800

C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-C(32)	1.529(11)
C(31)-C(33)	1.530(11)
C(31)-C(34)	1.545(9)
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
C(36)-C(37)	1.525(11)
C(36)-H(36)	1.0000
C(37)-C(38)	1.542(10)
C(37)-H(37A)	0.9900
C(37)-H(37B)	0.9900
C(38)-C(39)	1.504(10)
C(38)-H(38)	1.0000
C(39)-C(40)	1.522(10)
C(39)-H(39)	1.0000
C(40)-C(42)	1.493(11)
C(40)-H(40)	1.0000
C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800
C(41)-H(41C)	0.9800
C(42)-H(42A)	0.9800
C(42)-H(42B)	0.9800
C(42)-H(42C)	0.9800
C(43)-C(44)	1.488(10)
C(44)-C(49)	1.375(11)
C(44)-C(45)	1.384(11)

C(45)-C(46)	1.392(12)
C(45)-H(45)	0.9500
C(46)-C(47)	1.361(13)
C(46)-H(46)	0.9500
C(47)-C(48)	1.379(13)
C(47)-H(47)	0.9500
C(48)-C(49)	1.387(13)
C(48)-H(48)	0.9500
C(49)-H(49)	0.9500
C(50)-C(51)	1.519(11)
C(50)-H(50A)	0.9900
C(50)-H(50B)	0.9900
C(51)-H(51A)	0.9800
C(51)-H(51B)	0.9800
C(51)-H(51C)	0.9800
C(52)-H(52A)	0.9800
C(52)-H(52B)	0.9800
C(52)-H(52C)	0.9800
C(53)-H(53A)	0.9800
C(53)-H(53B)	0.9800
C(53)-H(53C)	0.9800
C(54)-C(56)	1.519(12)
C(54)-C(57)	1.531(13)
C(54)-C(55)	1.533(12)
C(55)-H(55A)	0.9800
C(55)-H(55B)	0.9800
C(55)-H(55C)	0.9800
C(56)-H(56A)	0.9800
C(56)-H(56B)	0.9800
C(56)-H(56C)	0.9800
C(57)-H(57A)	0.9800
C(57)-H(57B)	0.9800
C(57)-H(57C)	0.9800

O(6)-Si(1)-C(29)	110.2(3)

O(6)-Si(1)-C(30)	110.5(3)
C(29)-Si(1)-C(30)	108.1(4)
O(6)-Si(1)-C(31)	104.0(3)
C(29)-Si(1)-C(31)	112.3(4)
C(30)-Si(1)-C(31)	111.7(4)
O(14)-Si(2)-C(53)	107.3(3)
O(14)-Si(2)-C(52)	110.5(3)
C(53)-Si(2)-C(52)	111.6(4)
O(14)-Si(2)-C(54)	105.0(3)
C(53)-Si(2)-C(54)	111.8(4)
C(52)-Si(2)-C(54)	110.4(4)
C(13)-O(1)-C(1)	119.0(5)
C(13)-O(2)-C(17)	113.3(5)
C(18)-O(3)-C(15)	114.2(6)
C(20)-O(4)-C(16)	117.8(5)
C(2)-O(6)-Si(1)	127.0(4)
C(35)-O(7)-C(5)	108.6(5)
C(35)-O(8)-C(4)	108.4(5)
C(36)-O(9)-C(12)	119.3(5)
C(36)-O(10)-C(40)	114.2(5)
C(41)-O(11)-C(38)	113.7(6)
C(43)-O(12)-C(39)	119.1(5)
C(11)-O(14)-Si(2)	131.7(4)
C(58)-O(15)-C(9)	110.2(5)
C(58)-O(16)-C(8)	108.9(5)
O(1)-C(1)-C(27)	110.2(5)
O(1)-C(1)-C(2)	109.9(5)
C(27)-C(1)-C(2)	112.0(5)
O(1)-C(1)-C(6)	105.6(5)
C(27)-C(1)-C(6)	110.8(5)
C(2)-C(1)-C(6)	108.1(5)
O(6)-C(2)-C(3)	110.0(5)
O(6)-C(2)-C(1)	111.3(5)
C(3)-C(2)-C(1)	108.8(5)
O(6)-C(2)-H(2)	108.9

C(3)-C(2)-H(2)	108.9
C(1)-C(2)-H(2)	108.9
C(2)-C(3)-C(4)	113.6(5)
C(2)-C(3)-H(3A)	108.8
C(4)-C(3)-H(3A)	108.8
C(2)-C(3)-H(3B)	108.8
C(4)-C(3)-H(3B)	108.8
H(3A)-C(3)-H(3B)	107.7
O(8)-C(4)-C(3)	108.4(5)
O(8)-C(4)-C(5)	100.5(5)
C(3)-C(4)-C(5)	114.3(5)
O(8)-C(4)-H(4)	111.1
C(3)-C(4)-H(4)	111.1
C(5)-C(4)-H(4)	111.1
O(7)-C(5)-C(4)	100.8(5)
O(7)-C(5)-C(6)	109.4(5)
C(4)-C(5)-C(6)	118.6(5)
O(7)-C(5)-H(5)	109.2
C(4)-C(5)-H(5)	109.2
C(6)-C(5)-H(5)	109.2
C(5)-C(6)-C(7)	111.8(5)
C(5)-C(6)-C(1)	114.9(5)
C(7)-C(6)-C(1)	112.4(5)
C(5)-C(6)-H(6)	105.6
C(7)-C(6)-H(6)	105.6
C(1)-C(6)-H(6)	105.6
C(8)-C(7)-C(6)	112.6(5)
C(8)-C(7)-C(12)	115.0(5)
C(6)-C(7)-C(12)	112.2(5)
C(8)-C(7)-H(7)	105.3
C(6)-C(7)-H(7)	105.3
C(12)-C(7)-H(7)	105.3
O(16)-C(8)-C(9)	102.8(5)
O(16)-C(8)-C(7)	107.6(5)
C(9)-C(8)-C(7)	119.6(5)

O(16)-C(8)-H(8)	108.8
C(9)-C(8)-H(8)	108.8
C(7)-C(8)-H(8)	108.8
O(15)-C(9)-C(10)	107.6(5)
O(15)-C(9)-C(8)	101.4(5)
C(10)-C(9)-C(8)	114.6(5)
O(15)-C(9)-H(9)	110.9
C(10)-C(9)-H(9)	110.9
C(8)-C(9)-H(9)	110.9
C(11)-C(10)-C(9)	111.6(5)
C(11)-C(10)-H(10A)	109.3
C(9)-C(10)-H(10A)	109.3
C(11)-C(10)-H(10B)	109.3
C(9)-C(10)-H(10B)	109.3
H(10A)-C(10)-H(10B)	108.0
O(14)-C(11)-C(10)	113.3(5)
O(14)-C(11)-C(12)	109.4(5)
C(10)-C(11)-C(12)	110.0(5)
O(14)-C(11)-H(11)	108.0
C(10)-C(11)-H(11)	108.0
C(12)-C(11)-H(11)	108.0
O(9)-C(12)-C(50)	111.6(5)
O(9)-C(12)-C(11)	108.7(5)
C(50)-C(12)-C(11)	112.7(5)
O(9)-C(12)-C(7)	105.6(5)
C(50)-C(12)-C(7)	109.1(5)
C(11)-C(12)-C(7)	108.9(5)
O(2)-C(13)-O(1)	110.5(5)
O(2)-C(13)-C(14)	110.8(5)
O(1)-C(13)-C(14)	109.2(5)
O(2)-C(13)-H(13)	108.8
O(1)-C(13)-H(13)	108.8
C(14)-C(13)-H(13)	108.8
C(13)-C(14)-C(15)	115.6(6)
C(13)-C(14)-H(14A)	108.4

C(15)-C(14)-H(14A)	108.4
C(13)-C(14)-H(14B)	108.4
C(15)-C(14)-H(14B)	108.4
H(14A)-C(14)-H(14B)	107.4
O(3)-C(15)-C(16)	108.2(6)
O(3)-C(15)-C(14)	110.5(6)
C(16)-C(15)-C(14)	107.9(6)
O(3)-C(15)-H(15)	110.1
C(16)-C(15)-H(15)	110.1
C(14)-C(15)-H(15)	110.1
O(4)-C(16)-C(15)	109.2(6)
O(4)-C(16)-C(17)	106.8(6)
C(15)-C(16)-C(17)	110.5(6)
O(4)-C(16)-H(16)	110.1
C(15)-C(16)-H(16)	110.1
C(17)-C(16)-H(16)	110.1
O(2)-C(17)-C(19)	107.2(6)
O(2)-C(17)-C(16)	107.5(6)
C(19)-C(17)-C(16)	115.3(6)
O(2)-C(17)-H(17)	108.9
C(19)-C(17)-H(17)	108.9
C(16)-C(17)-H(17)	108.9
O(3)-C(18)-H(18A)	109.5
O(3)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
O(3)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(17)-C(19)-H(19A)	109.5
C(17)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(17)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(5)-C(20)-O(4)	124.1(7)

O(5)-C(20)-C(21)	124.6(6)
O(4)-C(20)-C(21)	111.3(6)
C(26)-C(21)-C(22)	120.6(7)
C(26)-C(21)-C(20)	121.8(6)
C(22)-C(21)-C(20)	117.2(7)
C(21)-C(22)-C(23)	119.6(8)
C(21)-C(22)-H(22)	120.2
C(23)-C(22)-H(22)	120.2
C(24)-C(23)-C(22)	120.2(8)
C(24)-C(23)-H(23)	119.9
C(22)-C(23)-H(23)	119.9
C(23)-C(24)-C(25)	119.7(8)
C(23)-C(24)-H(24)	120.2
C(25)-C(24)-H(24)	120.2
C(24)-C(25)-C(26)	119.8(9)
C(24)-C(25)-H(25)	120.1
C(26)-C(25)-H(25)	120.1
C(21)-C(26)-C(25)	120.1(8)
C(21)-C(26)-H(26)	119.9
C(25)-C(26)-H(26)	119.9
C(28)-C(27)-C(1)	115.4(6)
C(28)-C(27)-H(27A)	108.4
C(1)-C(27)-H(27A)	108.4
C(28)-C(27)-H(27B)	108.4
C(1)-C(27)-H(27B)	108.4
H(27A)-C(27)-H(27B)	107.5
C(27)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
Si(1)-C(29)-H(29A)	109.5
Si(1)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5

Si(1)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
Si(1)-C(30)-H(30A)	109.5
Si(1)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
Si(1)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(32)-C(31)-C(33)	109.9(7)
C(32)-C(31)-C(34)	108.6(6)
C(33)-C(31)-C(34)	108.9(6)
C(32)-C(31)-Si(1)	110.0(5)
C(33)-C(31)-Si(1)	110.1(5)
C(34)-C(31)-Si(1)	109.3(5)
C(31)-C(32)-H(32A)	109.5
C(31)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(31)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(31)-C(33)-H(33A)	109.5
C(31)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
C(31)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
C(31)-C(34)-H(34A)	109.5
C(31)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(31)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
O(7)-C(35)-O(8)	111.7(6)
O(7)-C(35)-S(1)	124.8(5)

O(8)-C(35)-S(1)	123.5(5)
O(10)-C(36)-O(9)	112.3(5)
O(10)-C(36)-C(37)	111.6(6)
O(9)-C(36)-C(37)	107.8(6)
O(10)-C(36)-H(36)	108.4
O(9)-C(36)-H(36)	108.4
C(37)-C(36)-H(36)	108.4
C(36)-C(37)-C(38)	114.0(6)
C(36)-C(37)-H(37A)	108.7
C(38)-C(37)-H(37A)	108.7
C(36)-C(37)-H(37B)	108.7
C(38)-C(37)-H(37B)	108.7
H(37A)-C(37)-H(37B)	107.6
O(11)-C(38)-C(39)	107.7(6)
O(11)-C(38)-C(37)	110.4(6)
C(39)-C(38)-C(37)	109.1(6)
O(11)-C(38)-H(38)	109.9
C(39)-C(38)-H(38)	109.9
C(37)-C(38)-H(38)	109.9
O(12)-C(39)-C(38)	108.3(6)
O(12)-C(39)-C(40)	108.1(5)
C(38)-C(39)-C(40)	111.1(6)
O(12)-C(39)-H(39)	109.7
C(38)-C(39)-H(39)	109.7
C(40)-C(39)-H(39)	109.7
O(10)-C(40)-C(42)	106.5(6)
O(10)-C(40)-C(39)	108.3(5)
C(42)-C(40)-C(39)	114.1(6)
O(10)-C(40)-H(40)	109.3
C(42)-C(40)-H(40)	109.3
C(39)-C(40)-H(40)	109.3
O(11)-C(41)-H(41A)	109.5
O(11)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
O(11)-C(41)-H(41C)	109.5

H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
C(40)-C(42)-H(42A)	109.5
C(40)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
C(40)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
O(13)-C(43)-O(12)	123.5(7)
O(13)-C(43)-C(44)	124.3(6)
O(12)-C(43)-C(44)	112.2(6)
C(49)-C(44)-C(45)	120.2(7)
C(49)-C(44)-C(43)	121.4(7)
C(45)-C(44)-C(43)	118.4(6)
C(44)-C(45)-C(46)	119.9(7)
C(44)-C(45)-H(45)	120.0
C(46)-C(45)-H(45)	120.0
C(47)-C(46)-C(45)	119.6(8)
C(47)-C(46)-H(46)	120.2
C(45)-C(46)-H(46)	120.2
C(46)-C(47)-C(48)	120.6(8)
C(46)-C(47)-H(47)	119.7
C(48)-C(47)-H(47)	119.7
C(47)-C(48)-C(49)	120.3(8)
C(47)-C(48)-H(48)	119.8
C(49)-C(48)-H(48)	119.8
C(44)-C(49)-C(48)	119.3(8)
C(44)-C(49)-H(49)	120.4
C(48)-C(49)-H(49)	120.4
C(51)-C(50)-C(12)	115.0(6)
C(51)-C(50)-H(50A)	108.5
C(12)-C(50)-H(50A)	108.5
C(51)-C(50)-H(50B)	108.5
C(12)-C(50)-H(50B)	108.5
H(50A)-C(50)-H(50B)	107.5

C(50)-C(51)-H(51A)	109.5
C(50)-C(51)-H(51B)	109.5
H(51A)-C(51)-H(51B)	109.5
C(50)-C(51)-H(51C)	109.5
H(51A)-C(51)-H(51C)	109.5
H(51B)-C(51)-H(51C)	109.5
Si(2)-C(52)-H(52A)	109.5
Si(2)-C(52)-H(52B)	109.5
H(52A)-C(52)-H(52B)	109.5
Si(2)-C(52)-H(52C)	109.5
H(52A)-C(52)-H(52C)	109.5
H(52B)-C(52)-H(52C)	109.5
Si(2)-C(53)-H(53A)	109.5
Si(2)-C(53)-H(53B)	109.5
H(53A)-C(53)-H(53B)	109.5
Si(2)-C(53)-H(53C)	109.5
H(53A)-C(53)-H(53C)	109.5
H(53B)-C(53)-H(53C)	109.5
C(56)-C(54)-C(57)	109.4(8)
C(56)-C(54)-C(55)	109.3(8)
C(57)-C(54)-C(55)	109.4(8)
C(56)-C(54)-Si(2)	109.3(6)
C(57)-C(54)-Si(2)	109.9(5)
C(55)-C(54)-Si(2)	109.5(6)
C(54)-C(55)-H(55A)	109.5
C(54)-C(55)-H(55B)	109.5
H(55A)-C(55)-H(55B)	109.5
C(54)-C(55)-H(55C)	109.5
H(55A)-C(55)-H(55C)	109.5
H(55B)-C(55)-H(55C)	109.5
C(54)-C(56)-H(56A)	109.5
C(54)-C(56)-H(56B)	109.5
H(56A)-C(56)-H(56B)	109.5
C(54)-C(56)-H(56C)	109.5
H(56A)-C(56)-H(56C)	109.5

H(56B)-C(56)-H(56C)	109.5
C(54)-C(57)-H(57A)	109.5
C(54)-C(57)-H(57B)	109.5
H(57A)-C(57)-H(57B)	109.5
C(54)-C(57)-H(57C)	109.5
H(57A)-C(57)-H(57C)	109.5
H(57B)-C(57)-H(57C)	109.5
O(15)-C(58)-O(16)	111.5(6)
O(15)-C(58)-S(2)	124.2(5)
O(16)-C(58)-S(2)	124.3(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for 007-16115. The anisotropic
displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	29(1)	58(1)	44(1)	-15(1)	-9(1)	15(1)
S(2)	28(1)	48(1)	61(1)	-5(1)	-16(1)	1(1)
Si(1)	22(1)	36(1)	28(1)	1(1)	1(1)	-2(1)
Si(2)	26(1)	36(1)	31(1)	6(1)	2(1)	-2(1)
O(1)	22(2)	29(2)	23(2)	3(2)	0(2)	3(2)
O(2)	25(2)	27(2)	47(3)	0(2)	-1(2)	1(2)
O(3)	46(3)	52(3)	28(3)	2(2)	-11(2)	10(2)
O(4)	23(2)	29(2)	47(3)	7(2)	-1(2)	4(2)
O(5)	28(3)	36(3)	73(4)	21(3)	0(3)	2(2)
O(6)	22(2)	28(2)	32(2)	5(2)	2(2)	-2(2)
O(7)	24(2)	35(2)	21(2)	-3(2)	-4(2)	4(2)
O(8)	26(2)	36(2)	26(2)	-7(2)	-1(2)	8(2)
O(9)	22(2)	35(2)	19(2)	1(2)	-5(2)	1(2)
O(10)	30(3)	52(3)	22(2)	-3(2)	-3(2)	-5(2)
O(11)	45(3)	41(3)	45(3)	8(2)	-9(3)	9(2)
O(12)	29(3)	51(3)	22(2)	6(2)	-4(2)	-4(2)
O(13)	26(2)	64(3)	24(3)	8(2)	-2(2)	-3(2)
O(14)	30(2)	42(3)	20(2)	0(2)	3(2)	-7(2)
O(15)	31(2)	30(2)	29(2)	-4(2)	-7(2)	-1(2)
O(16)	24(2)	30(2)	33(3)	-1(2)	-5(2)	3(2)
C(1)	22(3)	31(3)	21(3)	-3(3)	1(2)	-1(3)
C(2)	20(3)	32(3)	24(3)	7(3)	2(2)	2(2)
C(3)	25(3)	34(3)	21(3)	5(3)	4(2)	4(3)
C(4)	24(3)	31(3)	21(3)	-5(3)	3(3)	7(2)
C(5)	19(3)	32(3)	20(3)	-2(3)	-5(2)	0(2)
C(6)	15(3)	31(3)	19(3)	-2(3)	1(2)	2(2)
C(7)	19(3)	27(3)	19(3)	0(2)	0(2)	0(2)

C(8)	21(3)	29(3)	24(3)	-1(3)	-2(2)	2(2)
C(9)	22(3)	30(3)	23(3)	-5(3)	-2(2)	3(3)
C(10)	35(4)	30(3)	26(3)	4(3)	-4(3)	-4(3)
C(11)	21(3)	31(3)	21(3)	7(3)	0(2)	-3(3)
C(12)	20(3)	26(3)	23(3)	2(3)	-1(2)	0(2)
C(13)	28(3)	29(3)	29(3)	9(3)	5(3)	5(3)
C(14)	29(4)	44(4)	29(4)	11(3)	9(3)	6(3)
C(15)	35(4)	39(4)	26(3)	8(3)	-5(3)	3(3)
C(16)	29(4)	27(3)	37(4)	9(3)	0(3)	1(3)
C(17)	28(3)	28(3)	37(4)	5(3)	6(3)	-1(3)
C(18)	90(8)	72(6)	48(5)	-6(5)	-22(5)	11(6)
C(19)	34(4)	42(4)	41(4)	-9(3)	-2(3)	11(3)
C(20)	27(3)	30(3)	44(4)	6(3)	-6(3)	5(3)
C(21)	22(3)	36(3)	41(4)	0(3)	-4(3)	-5(3)
C(22)	22(3)	43(4)	69(6)	1(4)	-5(4)	1(3)
C(23)	32(4)	61(5)	84(7)	6(5)	12(4)	3(4)
C(24)	27(4)	82(6)	79(7)	-3(6)	21(4)	-7(4)
C(25)	41(5)	65(5)	64(6)	19(5)	6(4)	-10(4)
C(26)	32(4)	43(4)	45(4)	6(4)	-1(3)	0(3)
C(27)	29(3)	30(3)	30(3)	-2(3)	4(3)	-3(3)
C(28)	42(4)	37(4)	27(3)	-11(3)	-3(3)	-8(3)
C(29)	21(3)	57(5)	52(5)	10(4)	7(3)	2(3)
C(30)	40(4)	59(5)	38(4)	-4(4)	-3(4)	-8(4)
C(31)	30(4)	32(3)	33(4)	4(3)	8(3)	-6(3)
C(32)	51(5)	40(4)	46(5)	2(4)	0(4)	-4(4)
C(33)	39(4)	50(4)	33(4)	7(4)	3(3)	-2(3)
C(34)	29(4)	59(5)	58(5)	16(4)	6(4)	-17(4)
C(35)	26(3)	31(3)	30(4)	-2(3)	-1(3)	4(3)
C(36)	31(3)	46(4)	19(3)	6(3)	-5(3)	-7(3)
C(37)	32(4)	40(4)	31(4)	13(3)	-8(3)	-4(3)
C(38)	38(4)	38(4)	27(4)	9(3)	-6(3)	-1(3)
C(39)	19(3)	47(4)	27(3)	8(3)	-3(3)	-5(3)
C(40)	29(3)	44(4)	21(3)	7(3)	-1(3)	-6(3)
C(41)	83(8)	45(5)	68(6)	-3(5)	-6(6)	21(5)
C(42)	43(5)	46(4)	39(4)	2(4)	-8(4)	-3(3)

C(43)	32(4)	39(4)	24(4)	2(3)	-5(3)	-1(3)
C(44)	39(4)	34(3)	26(3)	7(3)	2(3)	0(3)
C(45)	34(4)	48(4)	31(4)	2(3)	3(3)	-1(3)
C(46)	36(4)	57(5)	42(4)	1(4)	-2(4)	-1(4)
C(47)	36(4)	70(6)	50(5)	3(4)	8(4)	-17(4)
C(48)	59(6)	93(7)	32(4)	-2(5)	7(4)	-28(5)
C(49)	48(5)	68(5)	29(4)	-1(4)	-1(3)	-21(4)
C(50)	36(4)	35(3)	20(3)	-4(3)	9(3)	-4(3)
C(51)	47(5)	39(4)	37(4)	-5(3)	15(4)	7(3)
C(52)	28(4)	59(5)	54(5)	0(4)	-2(4)	-9(3)
C(53)	41(4)	43(4)	39(4)	5(3)	2(3)	3(3)
C(54)	35(4)	46(4)	40(4)	5(4)	13(3)	3(3)
C(55)	85(8)	68(6)	70(7)	17(6)	51(6)	-6(6)
C(56)	44(5)	66(5)	52(5)	-1(5)	2(4)	17(4)
C(57)	58(5)	74(6)	27(4)	-3(4)	-1(4)	13(5)
C(58)	31(4)	29(3)	25(3)	3(3)	-3(3)	0(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3})
for 007-16115.

	x	y	z	U(eq)
H(2)	7926	6506	3162	30
H(3A)	7971	6084	2008	32
H(3B)	7103	6273	1905	32
H(4)	6871	5162	2201	31
H(5)	6738	4908	3350	28
H(6)	6859	6051	4056	26
H(7)	5543	6309	3723	26
H(8)	5728	5536	2667	29
H(9)	5656	4369	2890	30
H(10A)	4775	4010	3891	37
H(10B)	5649	4144	4033	37
H(11)	4540	5229	4188	29
H(13)	6565	7629	2245	34
H(14A)	5951	6859	1421	41
H(14B)	5757	7684	1343	41
H(15)	4775	6598	1865	40
H(16)	4494	8109	1932	37
H(17)	4886	7152	3043	37
H(18A)	4349	6620	157	105
H(18B)	4340	6140	842	105
H(18C)	5120	6427	540	105
H(19A)	4838	8139	3793	59
H(19B)	4022	7956	3495	59
H(19C)	4487	8610	3183	59
H(22)	1861	8517	2180	54
H(23)	739	8239	2774	71

H(24)	696	7267	3523	75
H(25)	1761	6544	3657	68
H(26)	2873	6818	3049	48
H(27A)	6791	7780	3444	36
H(27B)	6230	7341	3927	36
H(28A)	7828	7298	4085	53
H(28B)	7244	6909	4589	53
H(28C)	7283	7759	4568	53
H(29A)	9252	6559	2657	65
H(29B)	9777	7089	2226	65
H(29C)	9125	6658	1840	65
H(30A)	8489	8355	3457	69
H(30B)	9312	8444	3134	69
H(30C)	9110	7753	3582	69
H(32A)	7484	8675	1972	69
H(32B)	7945	9199	1475	69
H(32C)	8168	9130	2277	69
H(33A)	8234	8197	651	61
H(33B)	7737	7689	1133	61
H(33C)	8583	7474	947	61
H(34A)	9492	8832	1949	73
H(34B)	9258	8933	1153	73
H(34C)	9649	8211	1401	73
H(36)	5928	4738	5504	38
H(37A)	6671	3857	4893	41
H(37B)	6828	3907	5708	41
H(38)	7802	4404	4617	41
H(39)	8015	4705	6068	37
H(40)	7530	5685	5003	38
H(41A)	8377	3340	4336	98
H(41B)	7612	3020	4636	98
H(41C)	8401	2721	4905	98
H(42A)	7416	6524	5911	64
H(42B)	8274	6303	5789	64
H(42C)	7816	5978	6429	64

H(45)	10554	5441	6471	45
H(46)	11721	5790	6021	54
H(47)	11917	5771	4836	63
H(48)	10940	5493	4085	74
H(49)	9756	5198	4523	58
H(50A)	5497	5869	5442	36
H(50B)	5914	6424	4948	36
H(51A)	4724	6643	4390	61
H(51B)	4751	6893	5184	61
H(51C)	4340	6166	4979	61
H(52A)	3224	4438	4534	70
H(52B)	3025	3684	4869	70
H(52C)	3619	3733	4248	70
H(53A)	4964	3115	4956	62
H(53B)	4440	2881	5592	62
H(53C)	5178	3345	5731	62
H(55A)	3004	3624	6241	112
H(55B)	3210	3968	6977	112
H(55C)	3771	3413	6621	112
H(56A)	3507	5388	5767	81
H(56B)	3091	5204	6481	81
H(56C)	2830	4828	5776	81
H(57A)	4801	4291	6728	80
H(57B)	4252	4873	7058	80
H(57C)	4731	5060	6379	80

Table 6. Torsion angles [°] for 007-16115.

C(29)-Si(1)-O(6)-C(2)	31.9(6)
C(30)-Si(1)-O(6)-C(2)	-87.5(6)
C(31)-Si(1)-O(6)-C(2)	152.5(5)
C(53)-Si(2)-O(14)-C(11)	93.2(6)
C(52)-Si(2)-O(14)-C(11)	-28.6(7)
C(54)-Si(2)-O(14)-C(11)	-147.6(6)
C(13)-O(1)-C(1)-C(27)	50.5(7)
C(13)-O(1)-C(1)-C(2)	-73.4(6)
C(13)-O(1)-C(1)-C(6)	170.2(5)
Si(1)-O(6)-C(2)-C(3)	-90.9(6)
Si(1)-O(6)-C(2)-C(1)	148.4(4)
O(1)-C(1)-C(2)-O(6)	73.6(6)
C(27)-C(1)-C(2)-O(6)	-49.3(7)
C(6)-C(1)-C(2)-O(6)	-171.6(5)
O(1)-C(1)-C(2)-C(3)	-47.7(6)
C(27)-C(1)-C(2)-C(3)	-170.6(5)
C(6)-C(1)-C(2)-C(3)	67.0(6)
O(6)-C(2)-C(3)-C(4)	179.4(5)
C(1)-C(2)-C(3)-C(4)	-58.5(7)
C(35)-O(8)-C(4)-C(3)	92.7(6)
C(35)-O(8)-C(4)-C(5)	-27.5(6)
C(2)-C(3)-C(4)-O(8)	-103.1(6)
C(2)-C(3)-C(4)-C(5)	8.0(8)
C(35)-O(7)-C(5)-C(4)	-24.8(6)
C(35)-O(7)-C(5)-C(6)	-150.5(5)
O(8)-C(4)-C(5)-O(7)	30.0(5)
C(3)-C(4)-C(5)-O(7)	-85.8(6)
O(8)-C(4)-C(5)-C(6)	149.3(5)
C(3)-C(4)-C(5)-C(6)	33.4(8)
O(7)-C(5)-C(6)-C(7)	-138.8(5)
C(4)-C(5)-C(6)-C(7)	106.5(6)
O(7)-C(5)-C(6)-C(1)	91.5(6)
C(4)-C(5)-C(6)-C(1)	-23.1(8)

O(1)-C(1)-C(6)-C(5)	91.5(6)
C(27)-C(1)-C(6)-C(5)	-149.1(5)
C(2)-C(1)-C(6)-C(5)	-26.1(7)
O(1)-C(1)-C(6)-C(7)	-37.8(6)
C(27)-C(1)-C(6)-C(7)	81.5(6)
C(2)-C(1)-C(6)-C(7)	-155.4(5)
C(5)-C(6)-C(7)-C(8)	-43.4(7)
C(1)-C(6)-C(7)-C(8)	87.5(6)
C(5)-C(6)-C(7)-C(12)	88.3(6)
C(1)-C(6)-C(7)-C(12)	-140.8(5)
C(58)-O(16)-C(8)-C(9)	-18.4(6)
C(58)-O(16)-C(8)-C(7)	-145.4(5)
C(6)-C(7)-C(8)-O(16)	-140.4(5)
C(12)-C(7)-C(8)-O(16)	89.3(6)
C(6)-C(7)-C(8)-C(9)	103.1(6)
C(12)-C(7)-C(8)-C(9)	-27.2(8)
C(58)-O(15)-C(9)-C(10)	101.1(6)
C(58)-O(15)-C(9)-C(8)	-19.5(7)
O(16)-C(8)-C(9)-O(15)	21.8(6)
C(7)-C(8)-C(9)-O(15)	140.8(5)
O(16)-C(8)-C(9)-C(10)	-93.8(6)
C(7)-C(8)-C(9)-C(10)	25.2(8)
O(15)-C(9)-C(10)-C(11)	-91.2(6)
C(8)-C(9)-C(10)-C(11)	20.7(8)
Si(2)-O(14)-C(11)-C(10)	-48.3(8)
Si(2)-O(14)-C(11)-C(12)	-171.4(4)
C(9)-C(10)-C(11)-O(14)	171.3(5)
C(9)-C(10)-C(11)-C(12)	-65.9(7)
C(36)-O(9)-C(12)-C(50)	47.6(7)
C(36)-O(9)-C(12)-C(11)	-77.3(7)
C(36)-O(9)-C(12)-C(7)	166.0(5)
O(14)-C(11)-C(12)-O(9)	72.4(6)
C(10)-C(11)-C(12)-O(9)	-52.7(6)
O(14)-C(11)-C(12)-C(50)	-51.8(7)
C(10)-C(11)-C(12)-C(50)	-176.9(5)

O(14)-C(11)-C(12)-C(7)	-173.0(5)
C(10)-C(11)-C(12)-C(7)	61.9(6)
C(8)-C(7)-C(12)-O(9)	100.8(6)
C(6)-C(7)-C(12)-O(9)	-29.7(6)
C(8)-C(7)-C(12)-C(50)	-139.2(6)
C(6)-C(7)-C(12)-C(50)	90.4(6)
C(8)-C(7)-C(12)-C(11)	-15.8(7)
C(6)-C(7)-C(12)-C(11)	-146.2(5)
C(17)-O(2)-C(13)-O(1)	-65.0(7)
C(17)-O(2)-C(13)-C(14)	56.2(7)
C(1)-O(1)-C(13)-O(2)	-83.9(6)
C(1)-O(1)-C(13)-C(14)	154.0(5)
O(2)-C(13)-C(14)-C(15)	-46.9(8)
O(1)-C(13)-C(14)-C(15)	75.0(7)
C(18)-O(3)-C(15)-C(16)	-157.0(8)
C(18)-O(3)-C(15)-C(14)	85.1(9)
C(13)-C(14)-C(15)-O(3)	164.4(6)
C(13)-C(14)-C(15)-C(16)	46.4(8)
C(20)-O(4)-C(16)-C(15)	-133.9(6)
C(20)-O(4)-C(16)-C(17)	106.6(7)
O(3)-C(15)-C(16)-O(4)	69.1(7)
C(14)-C(15)-C(16)-O(4)	-171.4(5)
O(3)-C(15)-C(16)-C(17)	-173.7(6)
C(14)-C(15)-C(16)-C(17)	-54.2(7)
C(13)-O(2)-C(17)-C(19)	170.4(6)
C(13)-O(2)-C(17)-C(16)	-65.1(7)
O(4)-C(16)-C(17)-O(2)	-177.4(5)
C(15)-C(16)-C(17)-O(2)	63.9(7)
O(4)-C(16)-C(17)-C(19)	-57.9(7)
C(15)-C(16)-C(17)-C(19)	-176.6(6)
C(16)-O(4)-C(20)-O(5)	14.5(11)
C(16)-O(4)-C(20)-C(21)	-163.3(6)
O(5)-C(20)-C(21)-C(26)	-164.6(8)
O(4)-C(20)-C(21)-C(26)	13.2(10)
O(5)-C(20)-C(21)-C(22)	9.5(12)

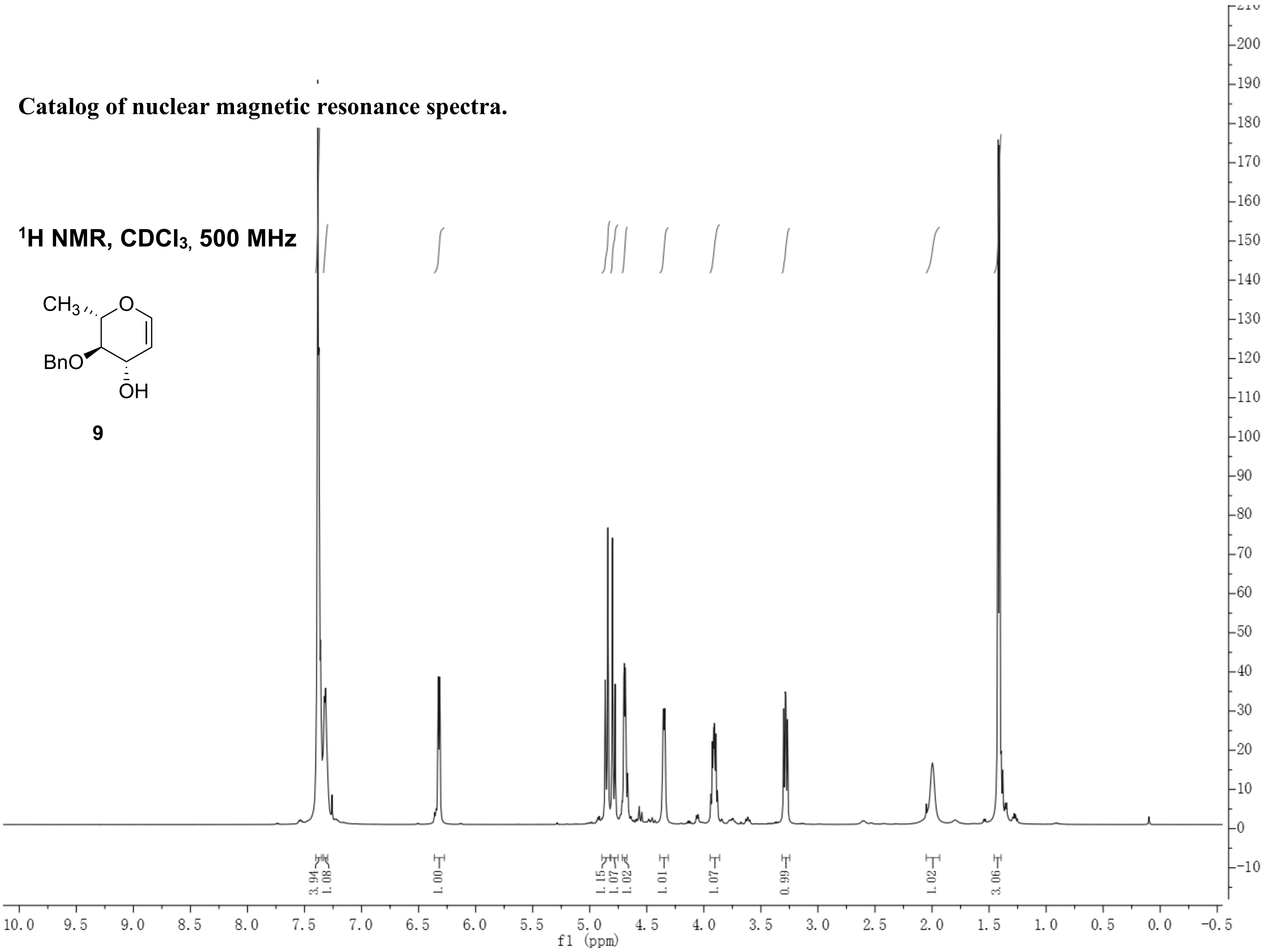
O(4)-C(20)-C(21)-C(22)	-172.7(7)
C(26)-C(21)-C(22)-C(23)	-0.4(13)
C(20)-C(21)-C(22)-C(23)	-174.6(8)
C(21)-C(22)-C(23)-C(24)	0.9(15)
C(22)-C(23)-C(24)-C(25)	-1.0(16)
C(23)-C(24)-C(25)-C(26)	0.5(16)
C(22)-C(21)-C(26)-C(25)	0.0(12)
C(20)-C(21)-C(26)-C(25)	173.9(8)
C(24)-C(25)-C(26)-C(21)	0.0(15)
O(1)-C(1)-C(27)-C(28)	177.9(6)
C(2)-C(1)-C(27)-C(28)	-59.4(7)
C(6)-C(1)-C(27)-C(28)	61.4(7)
O(6)-Si(1)-C(31)-C(32)	62.0(6)
C(29)-Si(1)-C(31)-C(32)	-178.8(5)
C(30)-Si(1)-C(31)-C(32)	-57.2(6)
O(6)-Si(1)-C(31)-C(33)	-59.3(5)
C(29)-Si(1)-C(31)-C(33)	59.9(6)
C(30)-Si(1)-C(31)-C(33)	-178.5(5)
O(6)-Si(1)-C(31)-C(34)	-178.9(5)
C(29)-Si(1)-C(31)-C(34)	-59.7(6)
C(30)-Si(1)-C(31)-C(34)	61.9(7)
C(5)-O(7)-C(35)-O(8)	8.4(7)
C(5)-O(7)-C(35)-S(1)	-170.6(5)
C(4)-O(8)-C(35)-O(7)	13.1(7)
C(4)-O(8)-C(35)-S(1)	-167.9(5)
C(40)-O(10)-C(36)-O(9)	-64.7(7)
C(40)-O(10)-C(36)-C(37)	56.4(7)
C(12)-O(9)-C(36)-O(10)	-87.0(7)
C(12)-O(9)-C(36)-C(37)	149.7(5)
O(10)-C(36)-C(37)-C(38)	-47.1(8)
O(9)-C(36)-C(37)-C(38)	76.6(7)
C(41)-O(11)-C(38)-C(39)	-158.3(7)
C(41)-O(11)-C(38)-C(37)	82.7(9)
C(36)-C(37)-C(38)-O(11)	164.0(6)
C(36)-C(37)-C(38)-C(39)	45.9(8)

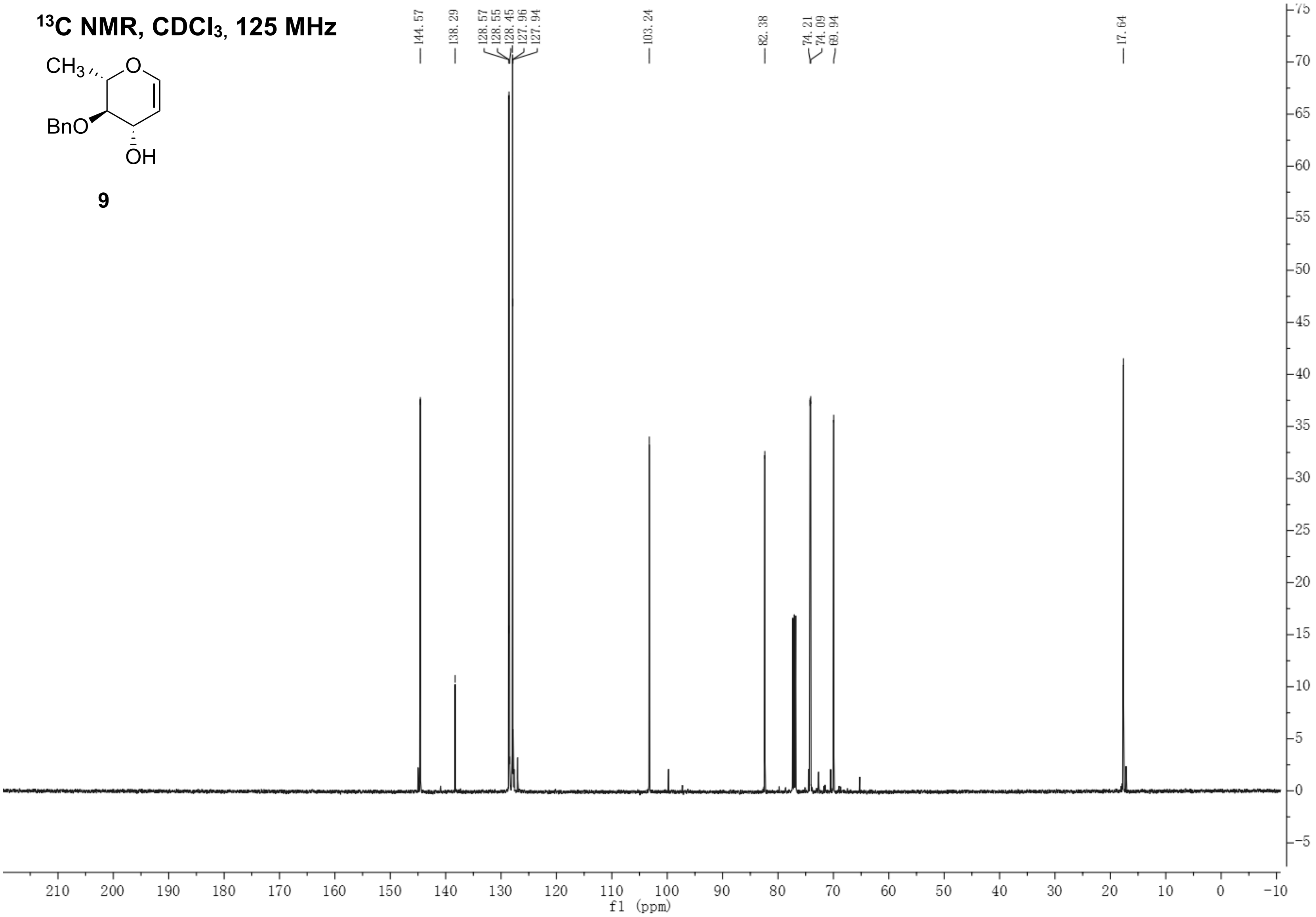
C(43)-O(12)-C(39)-C(38)	-131.2(6)
C(43)-O(12)-C(39)-C(40)	108.2(7)
O(11)-C(38)-C(39)-O(12)	68.8(7)
C(37)-C(38)-C(39)-O(12)	-171.4(5)
O(11)-C(38)-C(39)-C(40)	-172.6(6)
C(37)-C(38)-C(39)-C(40)	-52.8(7)
C(36)-O(10)-C(40)-C(42)	173.6(6)
C(36)-O(10)-C(40)-C(39)	-63.3(7)
O(12)-C(39)-C(40)-O(10)	179.8(5)
C(38)-C(39)-C(40)-O(10)	61.0(7)
O(12)-C(39)-C(40)-C(42)	-61.9(8)
C(38)-C(39)-C(40)-C(42)	179.4(6)
C(39)-O(12)-C(43)-O(13)	1.3(11)
C(39)-O(12)-C(43)-C(44)	-177.7(6)
O(13)-C(43)-C(44)-C(49)	170.5(8)
O(12)-C(43)-C(44)-C(49)	-10.5(11)
O(13)-C(43)-C(44)-C(45)	-7.6(11)
O(12)-C(43)-C(44)-C(45)	171.4(6)
C(49)-C(44)-C(45)-C(46)	1.6(12)
C(43)-C(44)-C(45)-C(46)	179.7(7)
C(44)-C(45)-C(46)-C(47)	-2.8(13)
C(45)-C(46)-C(47)-C(48)	2.3(15)
C(46)-C(47)-C(48)-C(49)	-0.7(17)
C(45)-C(44)-C(49)-C(48)	0.0(14)
C(43)-C(44)-C(49)-C(48)	-178.0(9)
C(47)-C(48)-C(49)-C(44)	-0.5(17)
O(9)-C(12)-C(50)-C(51)	-174.9(5)
C(11)-C(12)-C(50)-C(51)	-52.3(8)
C(7)-C(12)-C(50)-C(51)	68.8(7)
O(14)-Si(2)-C(54)-C(56)	73.4(7)
C(53)-Si(2)-C(54)-C(56)	-170.5(6)
C(52)-Si(2)-C(54)-C(56)	-45.7(7)
O(14)-Si(2)-C(54)-C(57)	-46.7(6)
C(53)-Si(2)-C(54)-C(57)	69.4(7)
C(52)-Si(2)-C(54)-C(57)	-165.8(6)

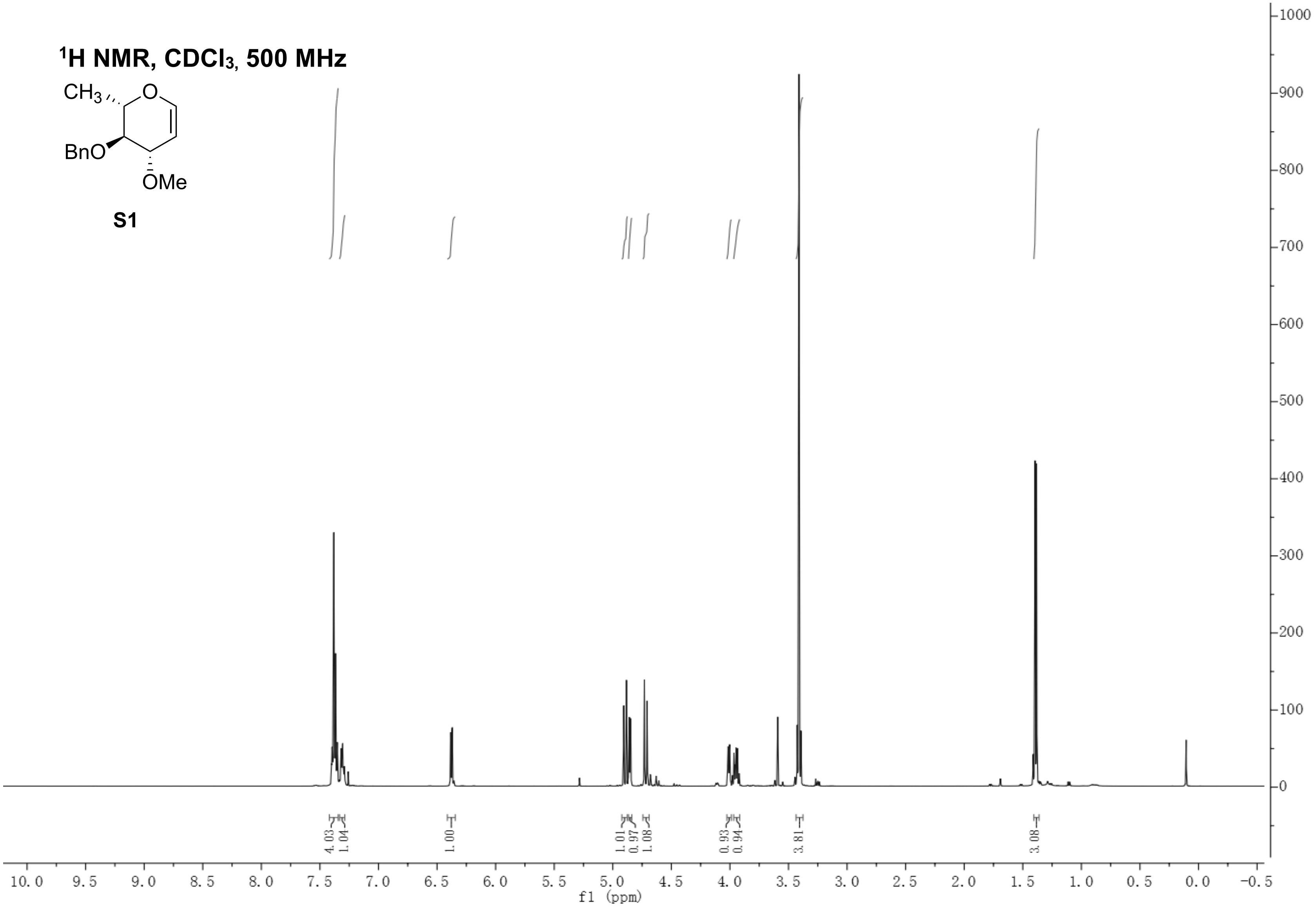
O(14)-Si(2)-C(54)-C(55)	-166.9(7)
C(53)-Si(2)-C(54)-C(55)	-50.8(8)
C(52)-Si(2)-C(54)-C(55)	74.0(8)
C(9)-O(15)-C(58)-O(16)	8.9(7)
C(9)-O(15)-C(58)-S(2)	-172.7(5)
C(8)-O(16)-C(58)-O(15)	6.7(7)
C(8)-O(16)-C(58)-S(2)	-171.8(5)

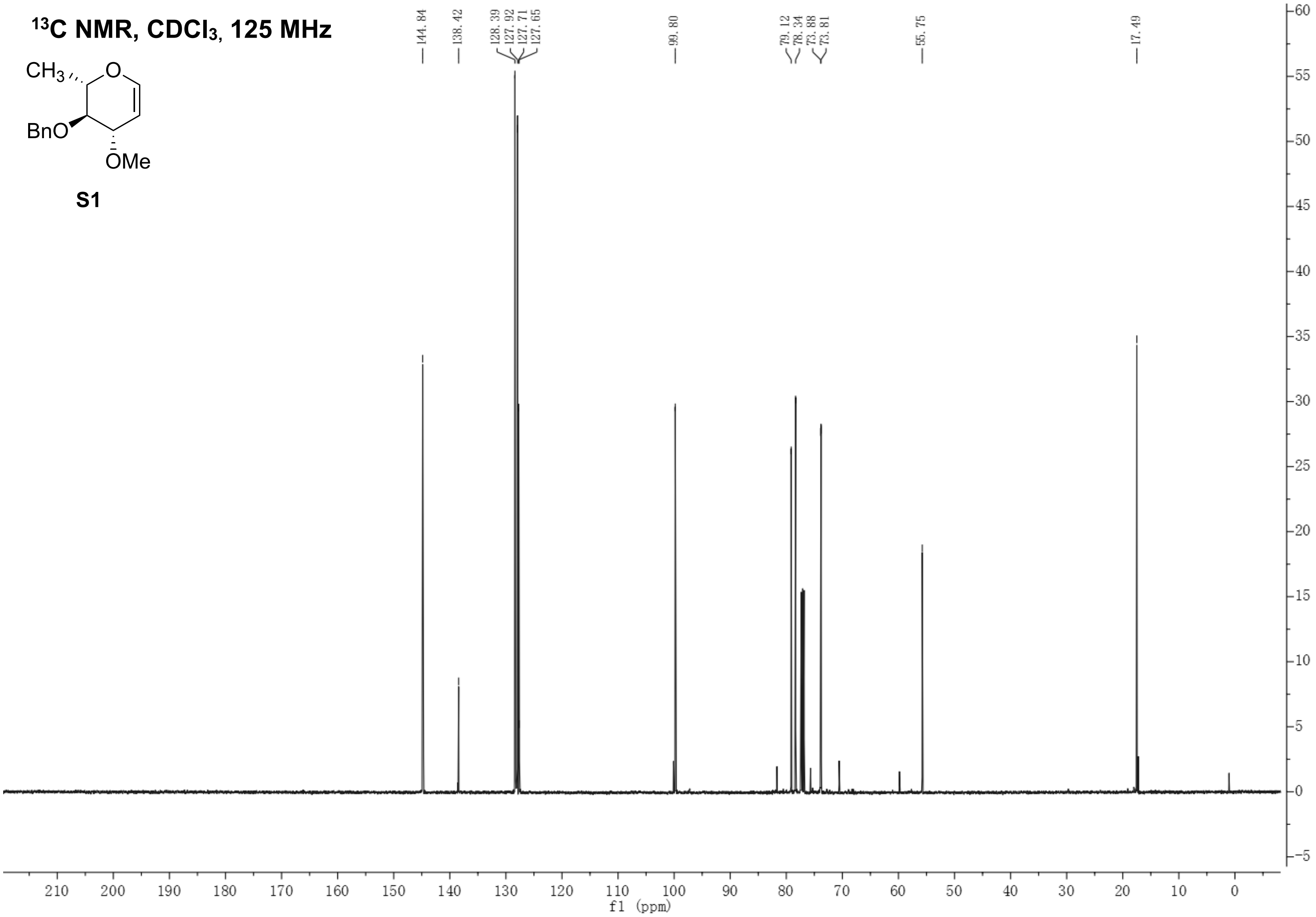
Symmetry transformations used to generate equivalent atoms:

Catalog of nuclear magnetic resonance spectra.



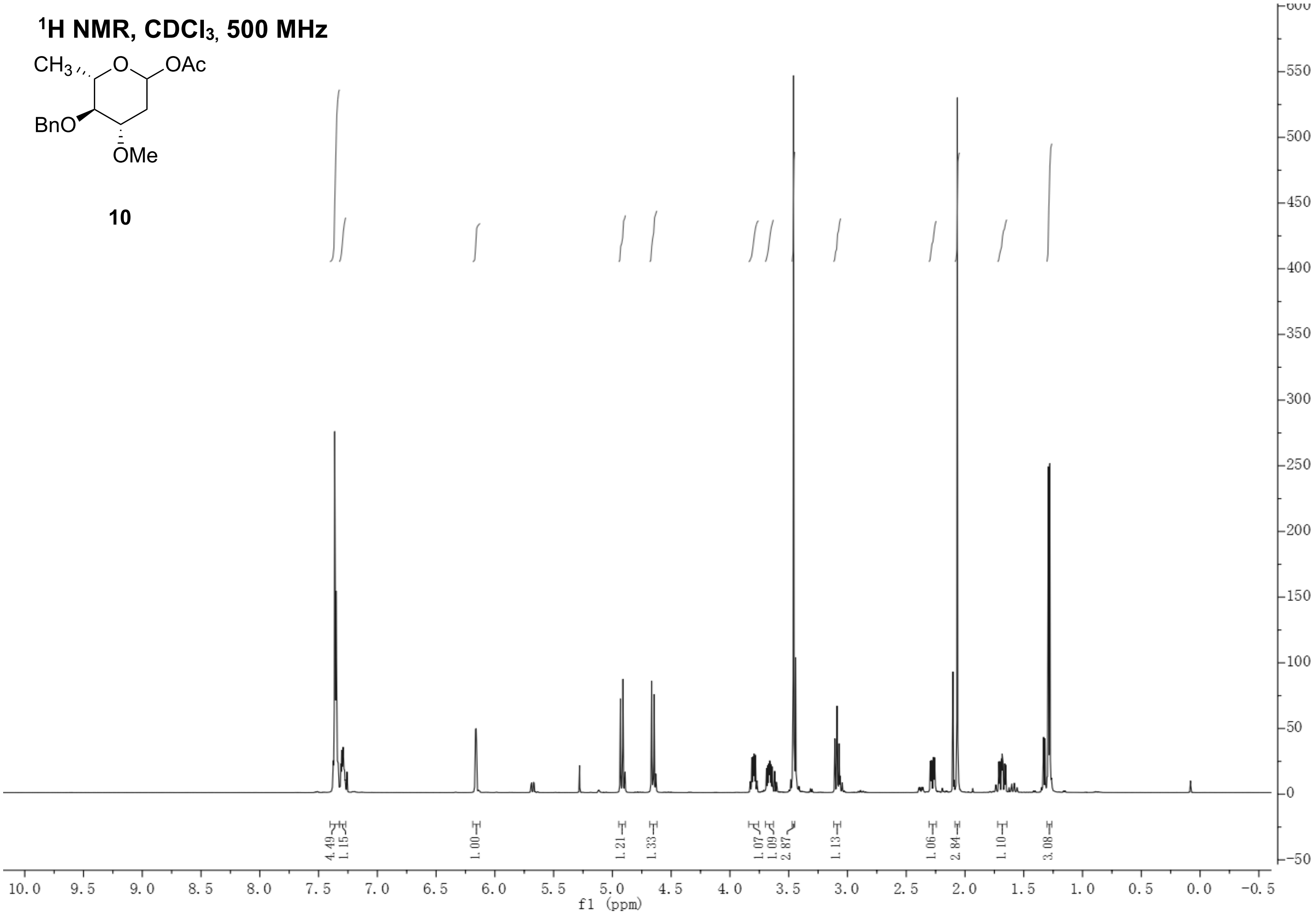

^{13}C NMR, CDCl$_3$, 125 MHz
CH$_3$
O
BnO
OH
9
144.57
138.29
128.57
128.55
128.45
127.96
127.94
103.24
82.38
74.21
74.09
69.94
17.64
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5


^{1}H NMR, CDCl$_3$, 500 MHz
CH$_3$
O
BnO
OMe
S1
4.03
1.04
1.00
1.01
0.97
1.08
0.93
0.94
3.81
3.08
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)
1000 900 800 700 600 500 400 300 200 100 0

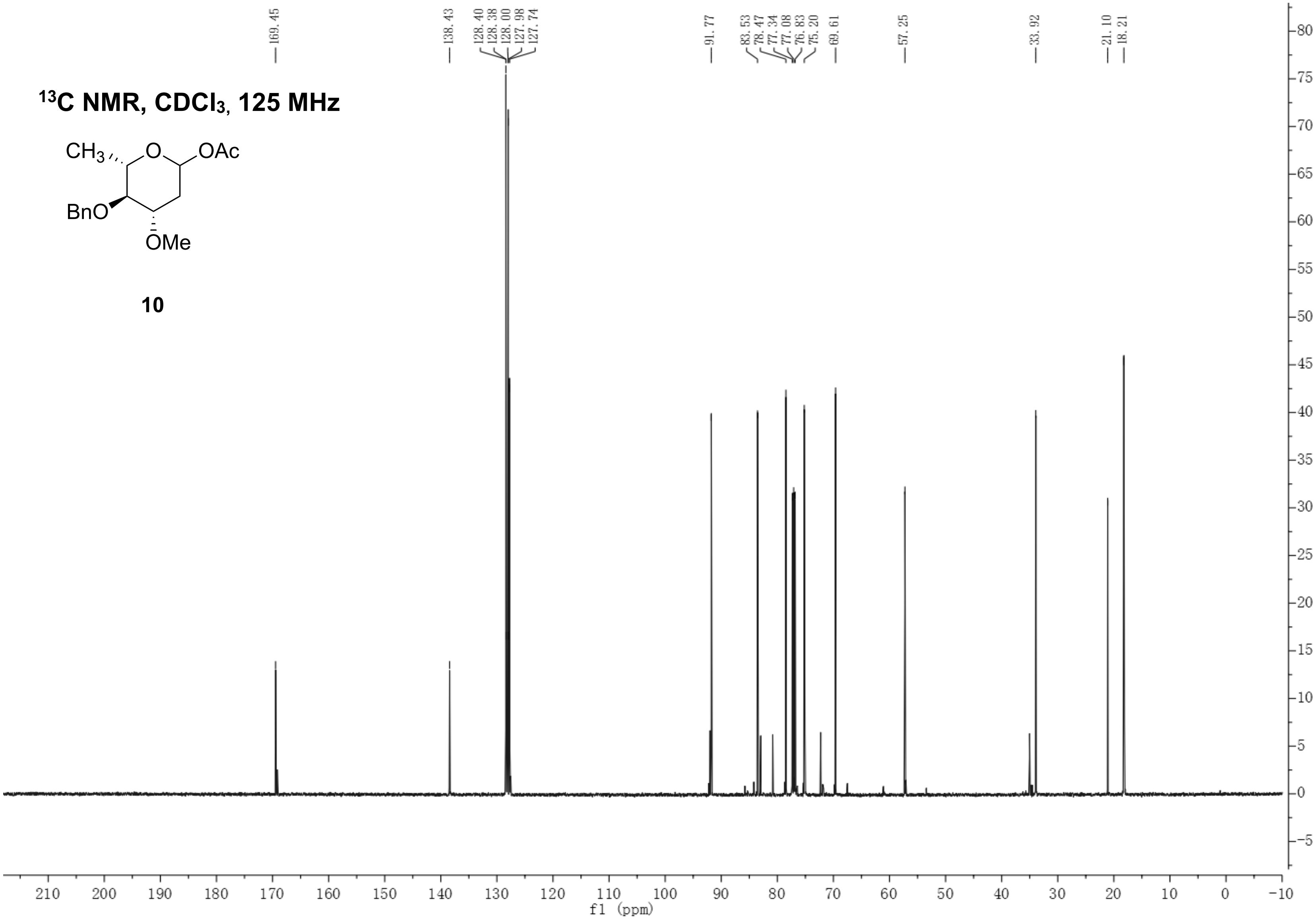


¹³C NMR, CDCl₃, 125 MHz
CH3
O
BnO
OMe
144.84
138.42
128.39
127.92
127.71
127.65
99.80
79.12
78.34
73.88
73.81
55.75
17.49
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

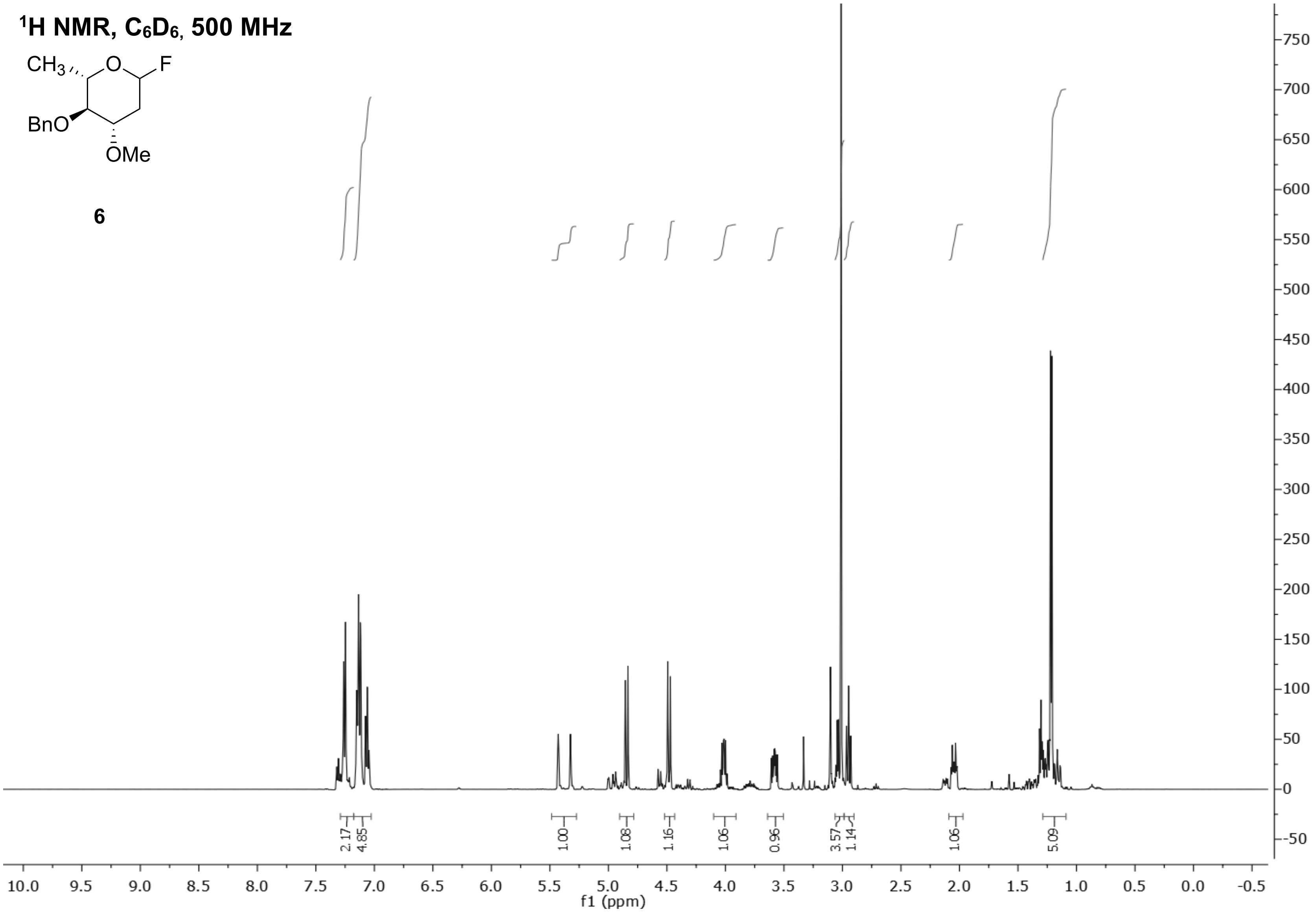
S1

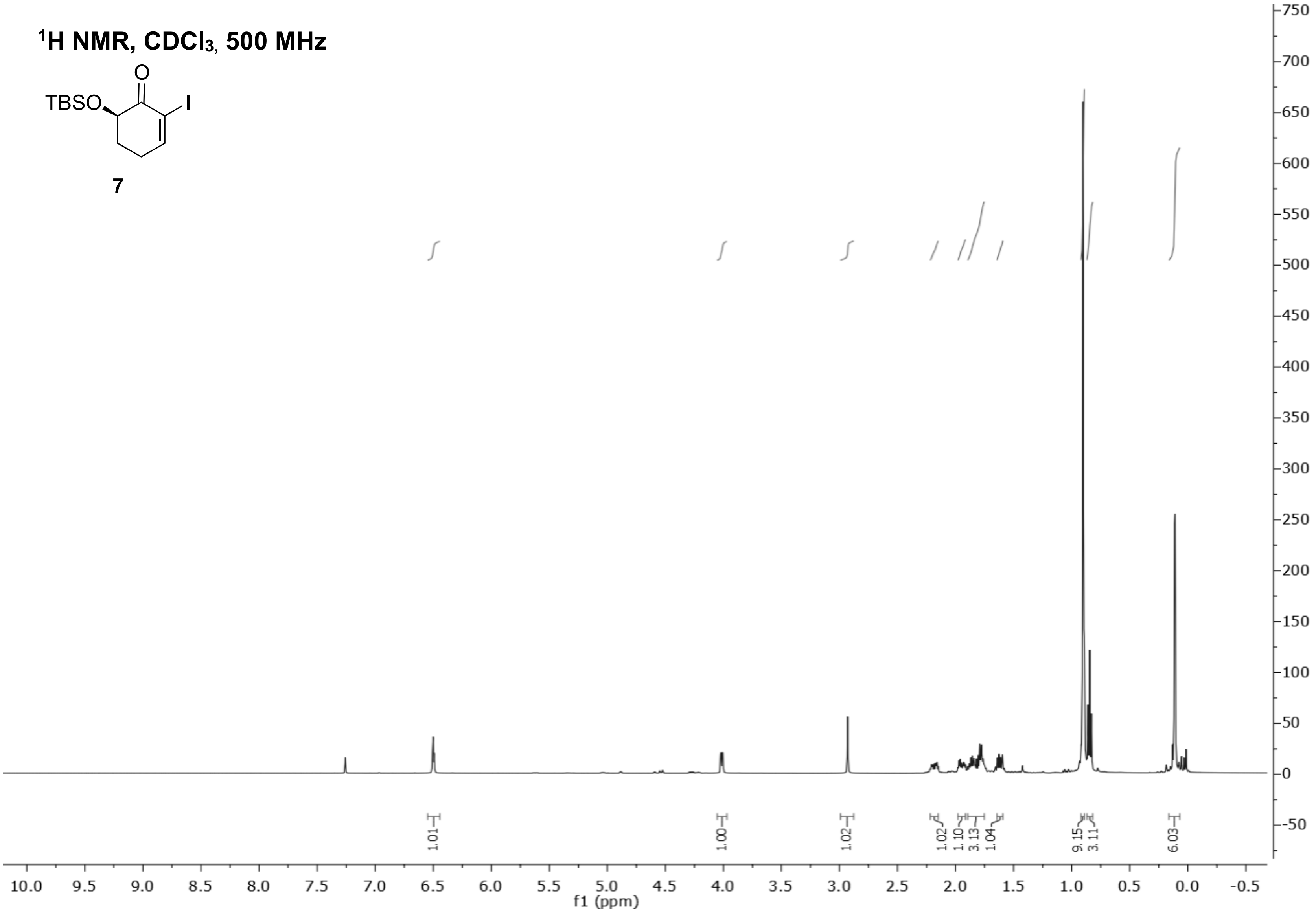


^{1}H NMR, CDCl$_3$, 500 MHz
CH3
O
OAc
BnO
OMe
10
4.49
1.15
1.00
1.21
1.33
1.07
1.09
2.87
1.13
1.06
2.84
1.10
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
600
550
500
450
400
350
300
250
200
150
100
50
0
-50



Rose et al. "Synthesis of the bis(cyclohexenone) core of (–)-lomaiviticin A." *Chem. Sci.*

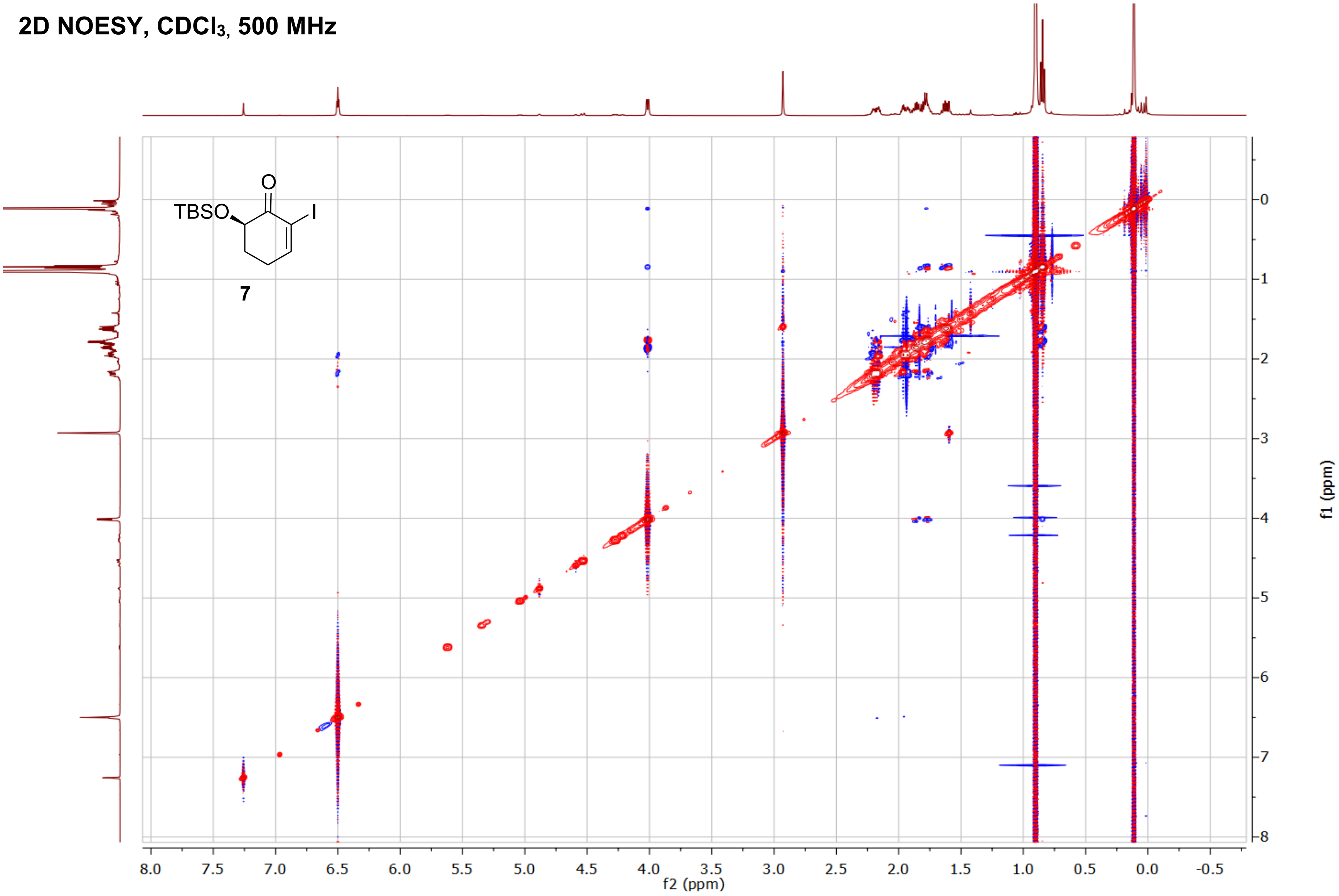

^{1}H NMR, C_6D_6, 500 MHz
CH3
O
F
BnO
OMe
6
2.17
4.85
1.00
1.08
1.16
1.06
0.96
3.57
1.14
1.06
5.09
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



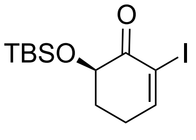
^{1}H NMR, $CDCl_3$, 500 MHz

7

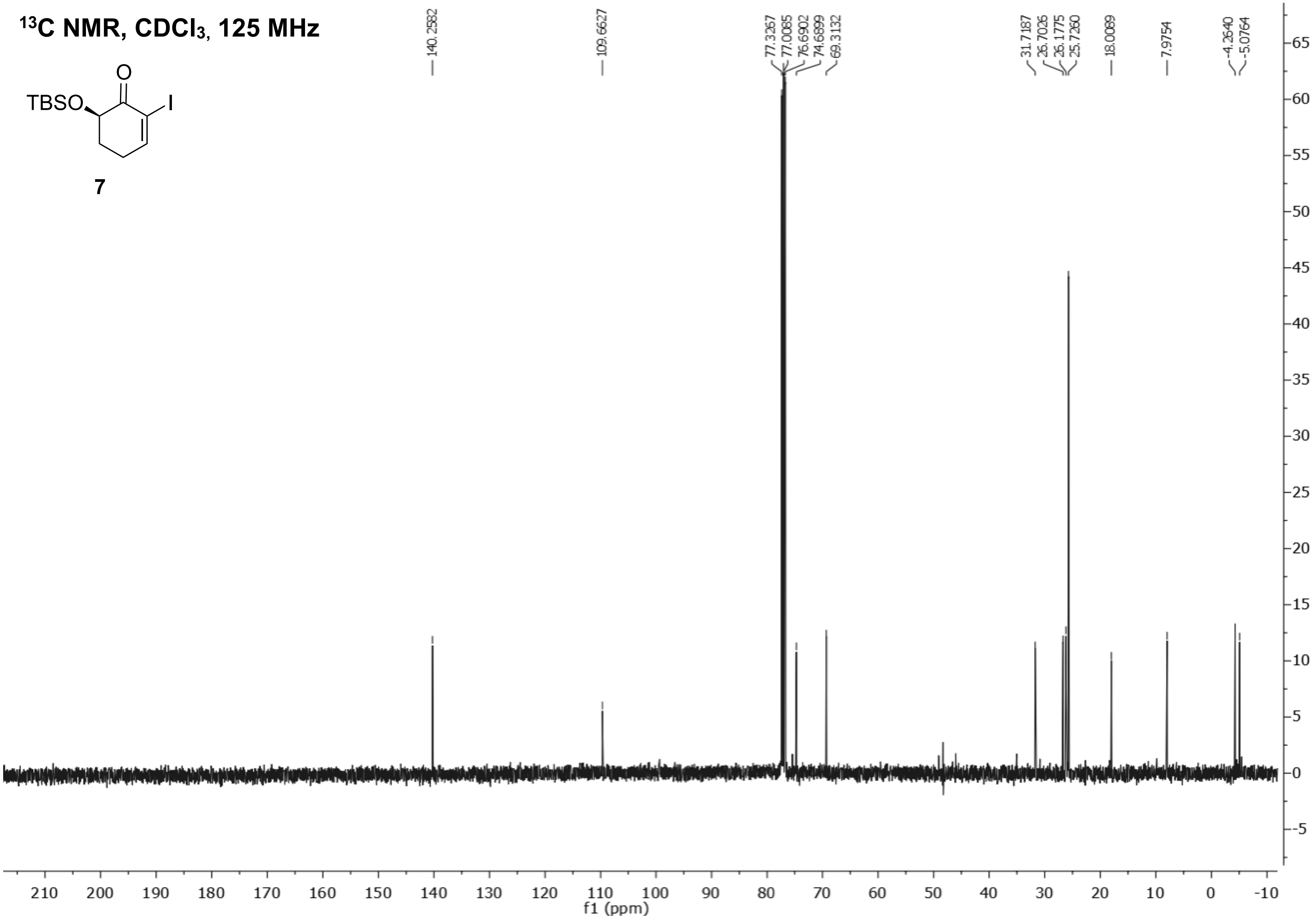
2D NOESY, $CDCl_3$, 500 MHz



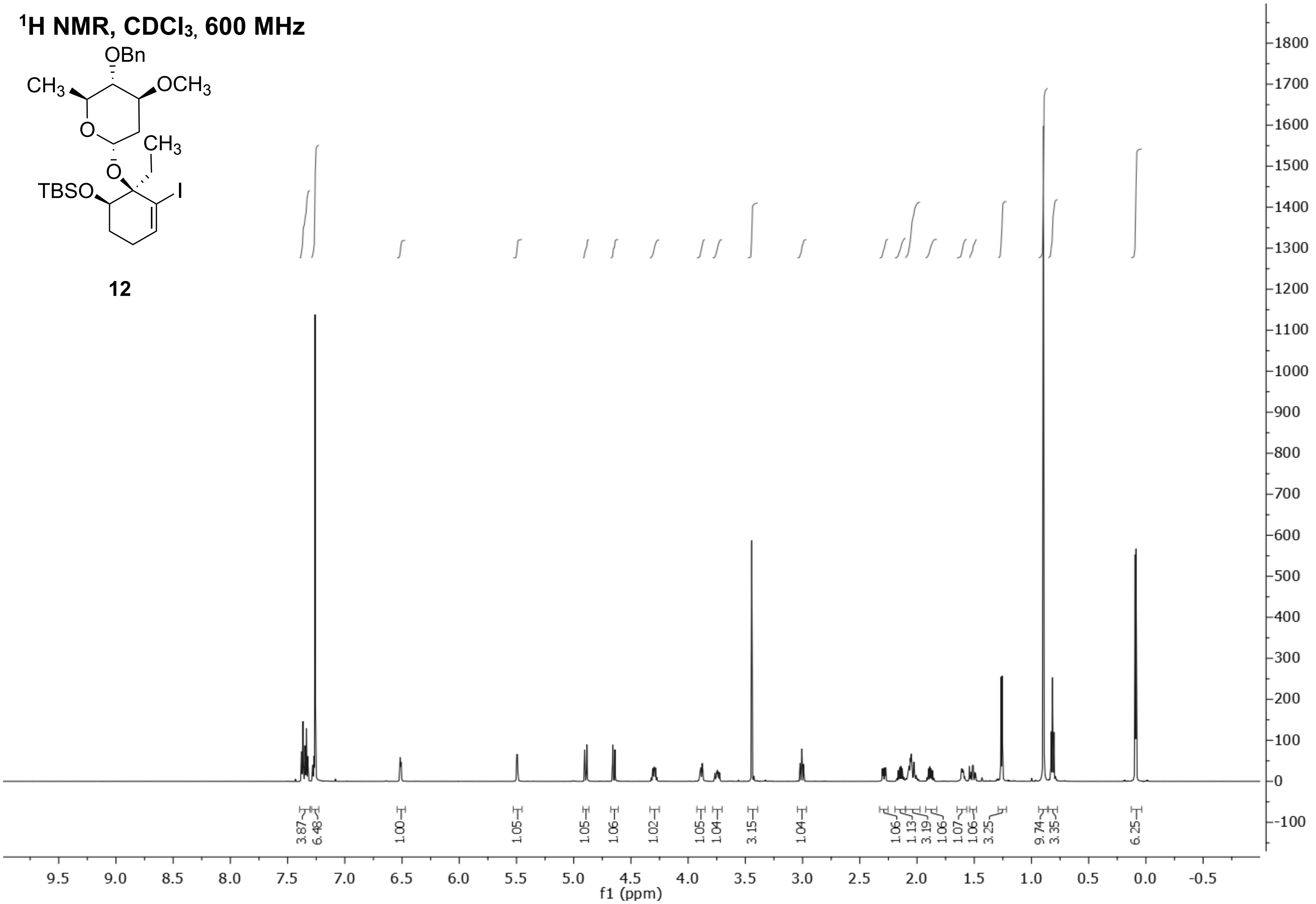
^{13}C NMR, CDCl$_3$, 125 MHz



7

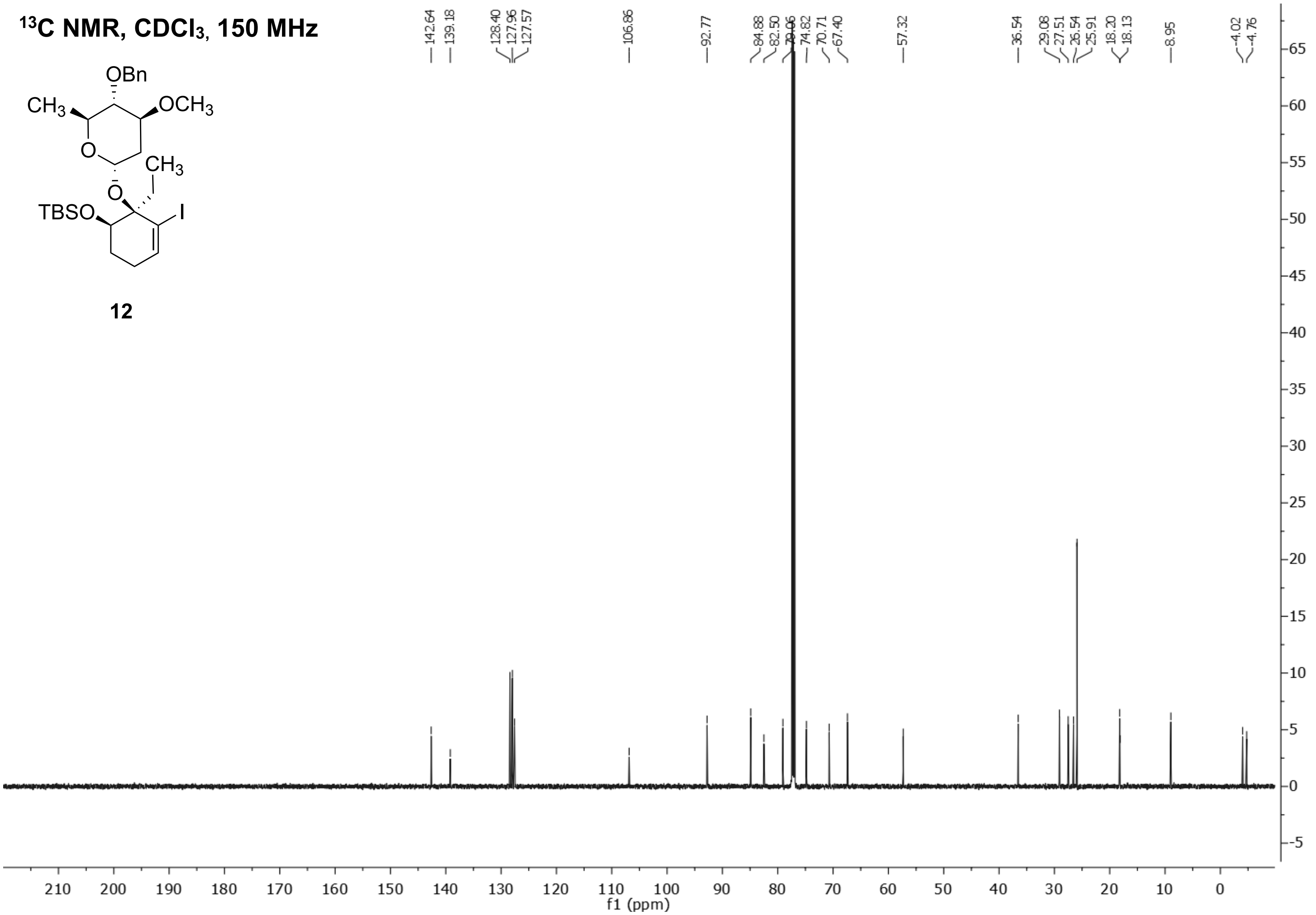


Rose et al. "Synthesis of the bis(cyclohexenone) core of (–)-lomaiviticin A." *Chem. Sci.*

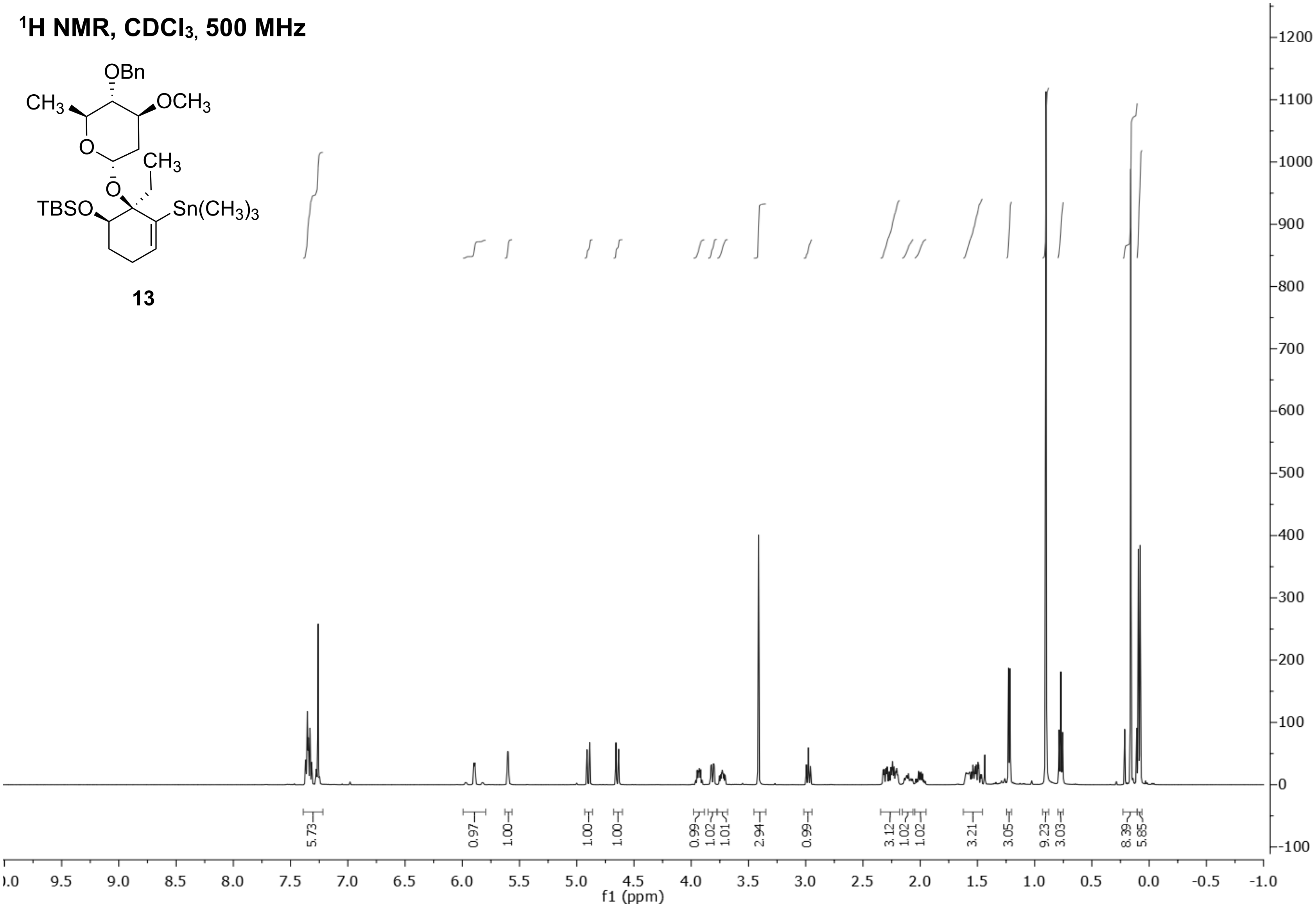


1H NMR, CDCl3, 600 MHz
OBn
CH3
OCH3
O
CH3
O
TBSO
I
12
3.87
6.48
1.00
1.05
1.05
1.06
1.02
1.05
1.04
3.15
1.04
1.06
1.13
3.19
1.06
1.07
1.06
3.25
9.74
3.35
6.25
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100

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



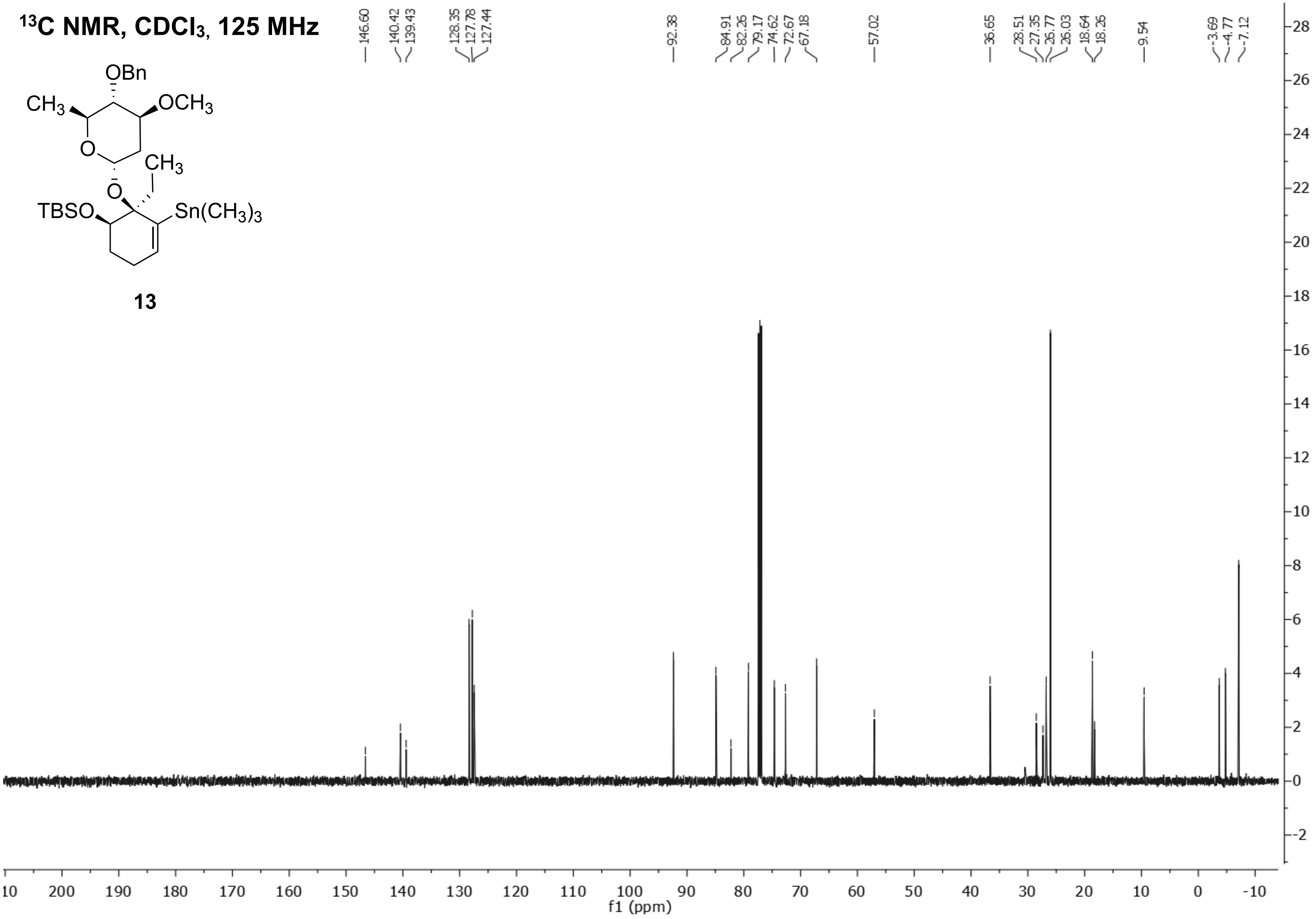
12



¹H NMR, CDCl₃, 500 MHz
OBn
CH3
OCH3
O
CH3
O
TBSO
Sn(CH3)3
5.73
0.97
1.00
1.00
1.00
0.99
1.02
1.01
2.94
0.99
3.12
1.02
1.02
3.21
3.05
9.23
3.03
8.39
5.85
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
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
-1.0
f1 (ppm)

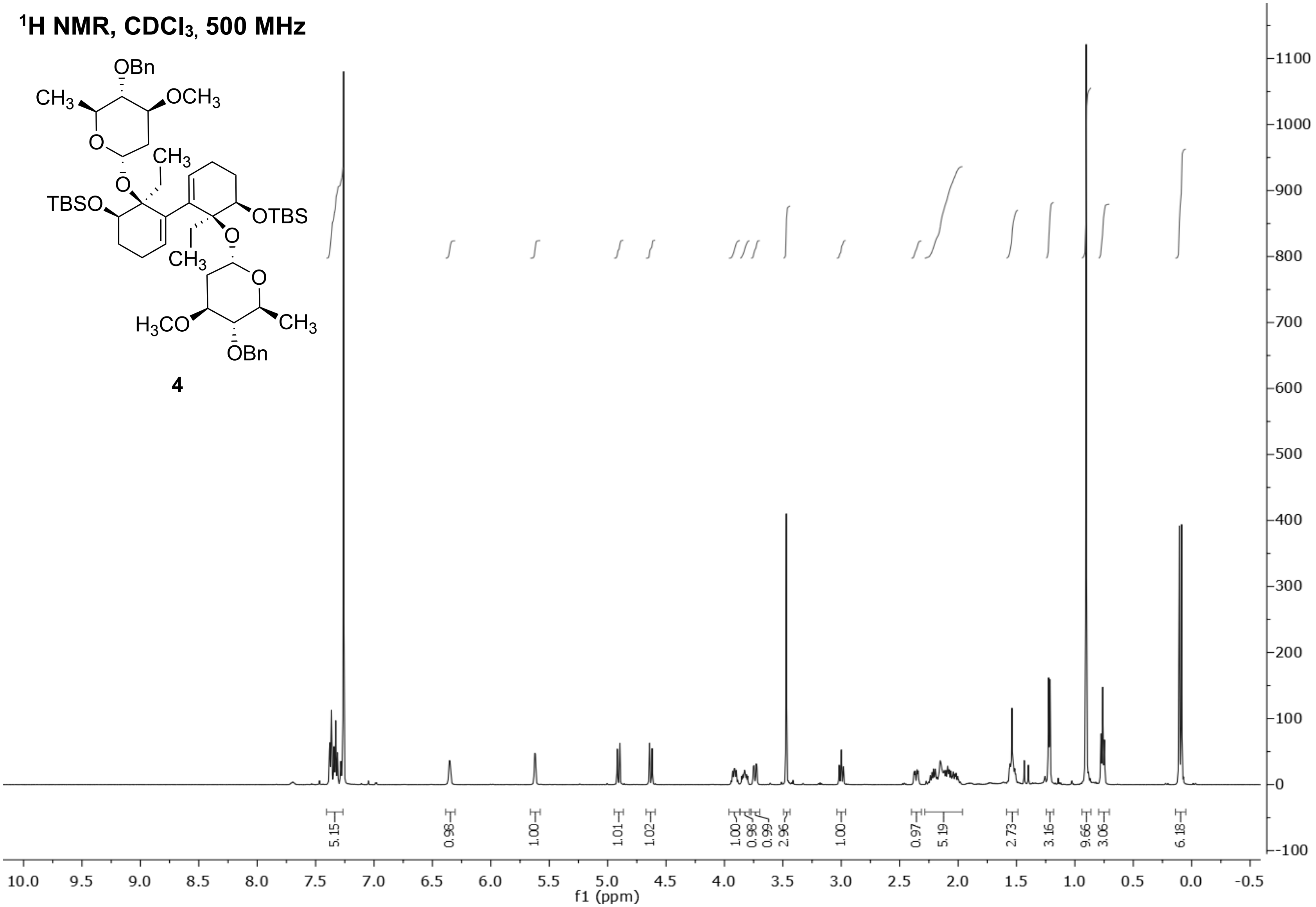
13

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



13

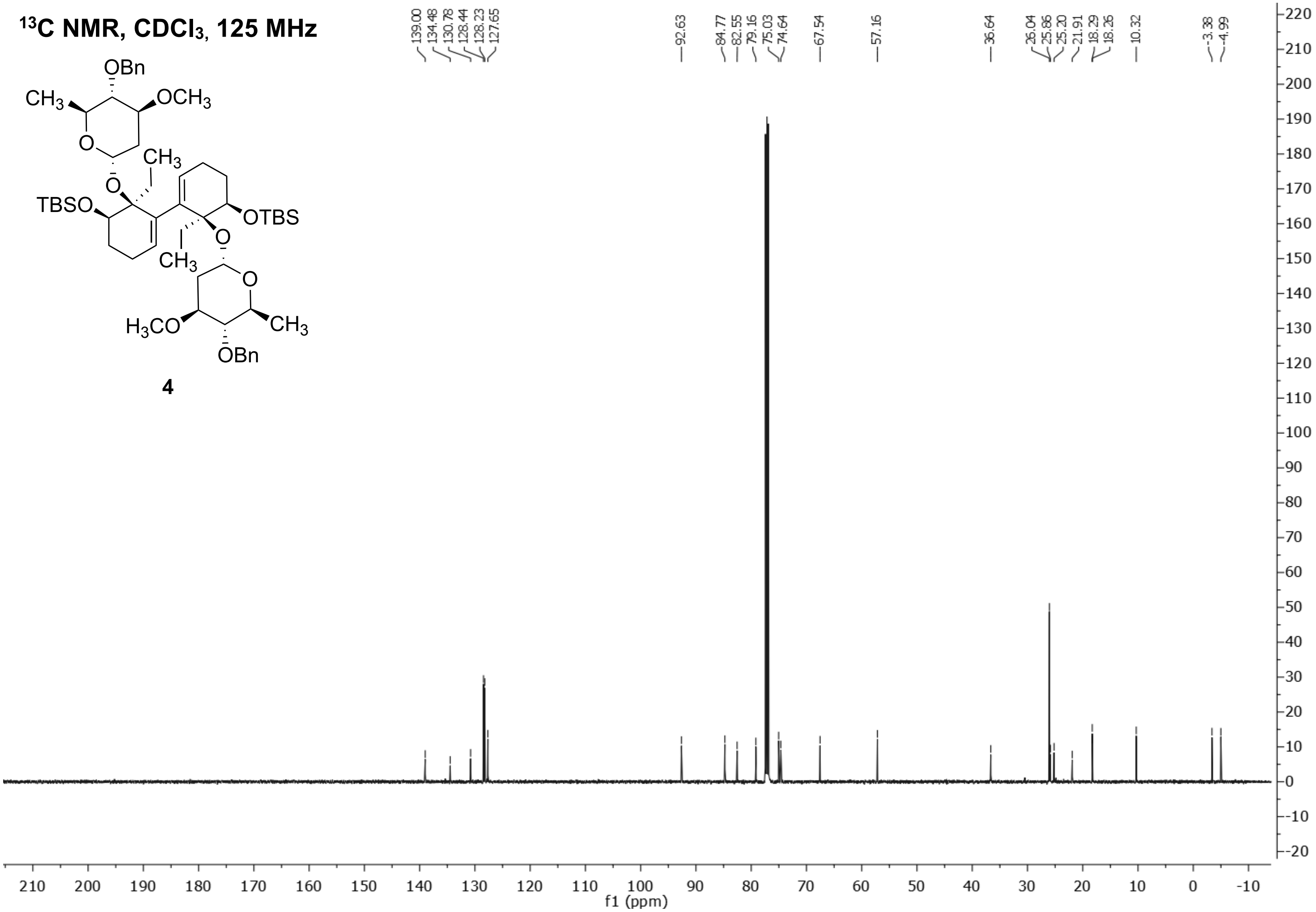
Rose et al. "Synthesis of the bis(cyclohexenone) core of (–)-lomaiviticin A." *Chem. Sci.*



^{1}H NMR, CDCl$_3$, 500 MHz
OBn
CH$_3$
OCH$_3$
O
CH$_3$
O
TBSO
OTBS
CH$_3$
O
O
H$_3$CO
CH$_3$
OBn
5.15
0.98
1.00
1.01
1.02
1.00
0.98
0.99
2.96
1.00
0.97
5.19
2.73
3.16
9.66
3.06
6.18
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)
1100 1000 900 800 700 600 500 400 300 200 100 0 -100

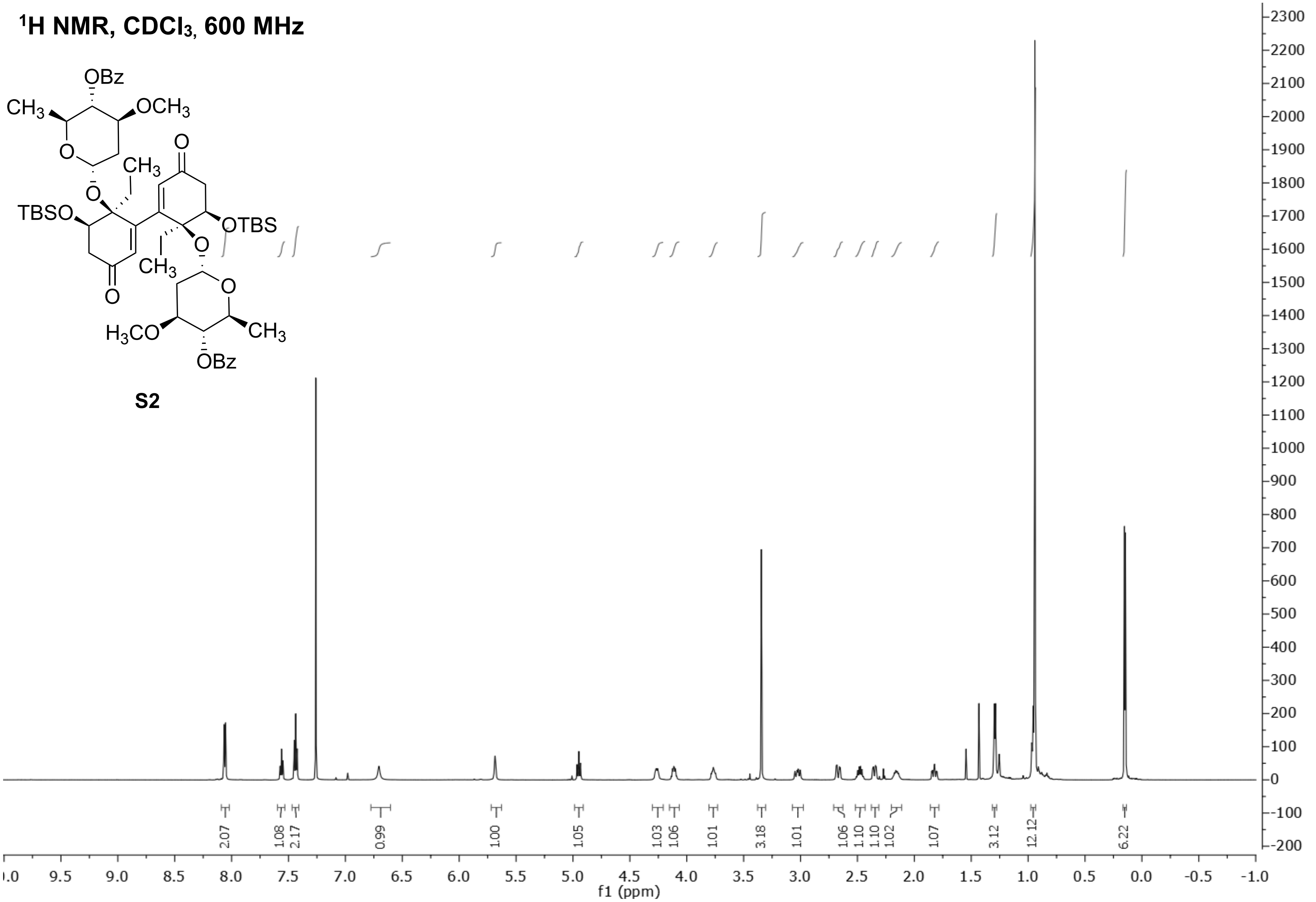
4

^{13}C NMR, CDCl$_3$, 125 MHz

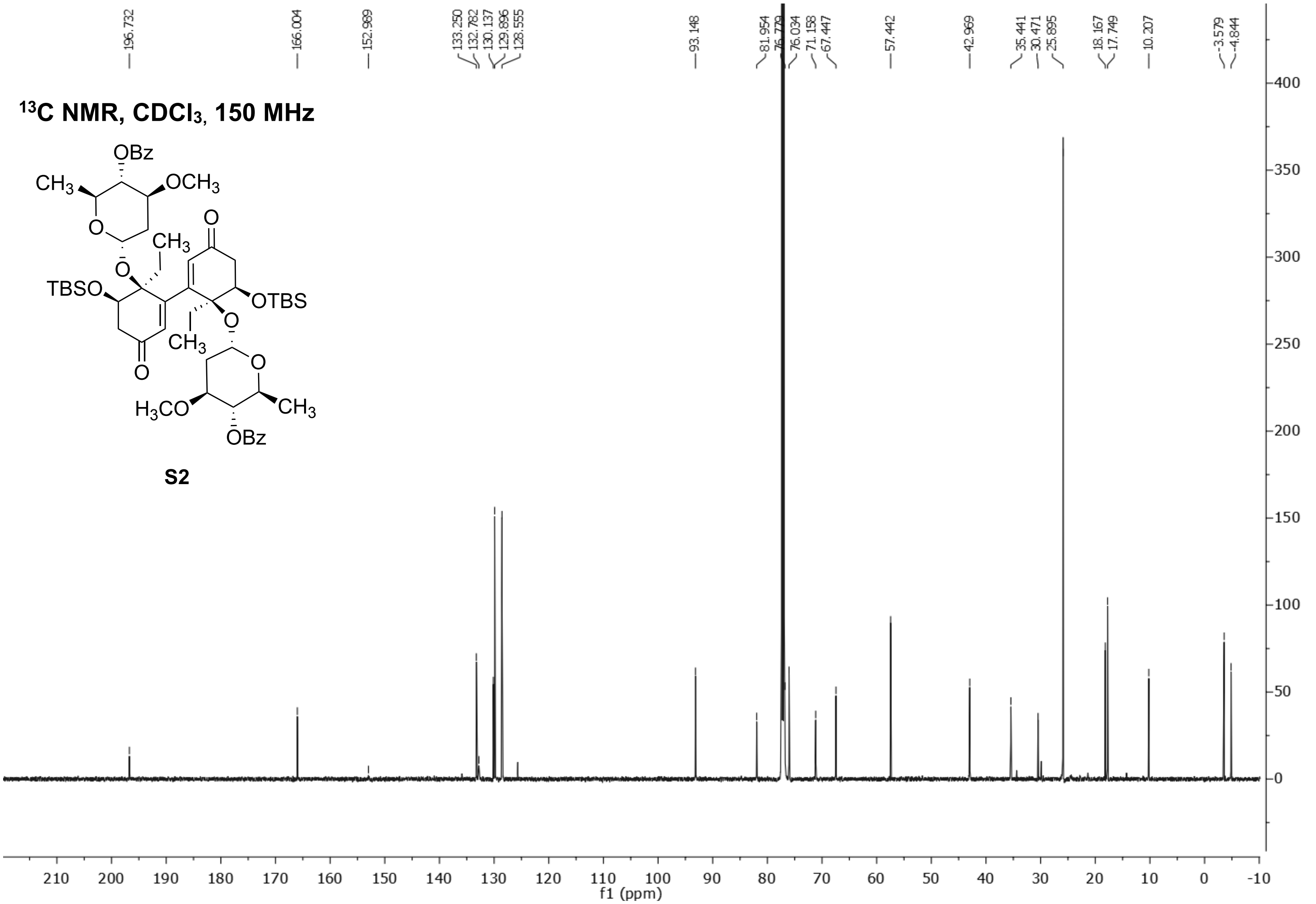


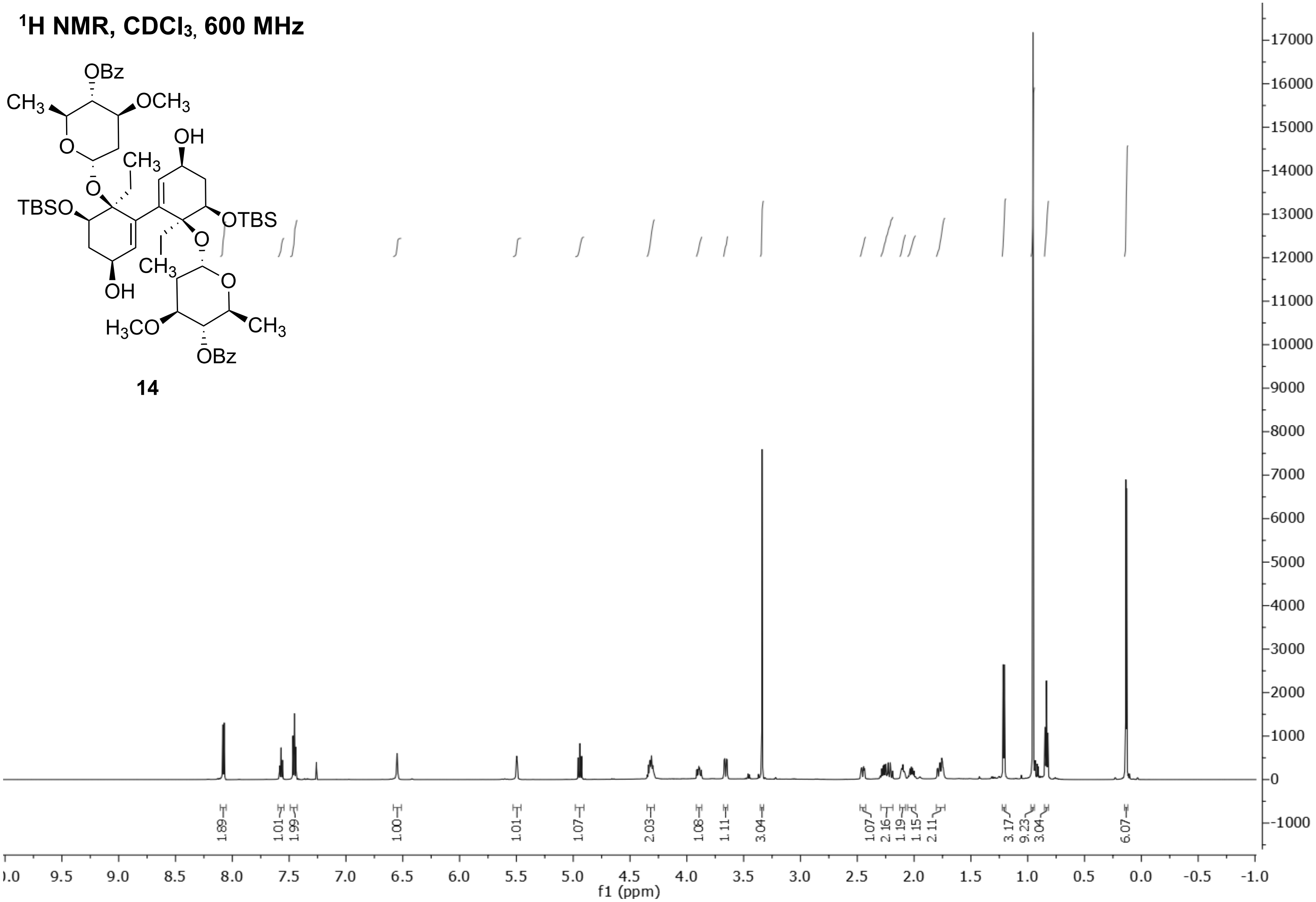
4

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

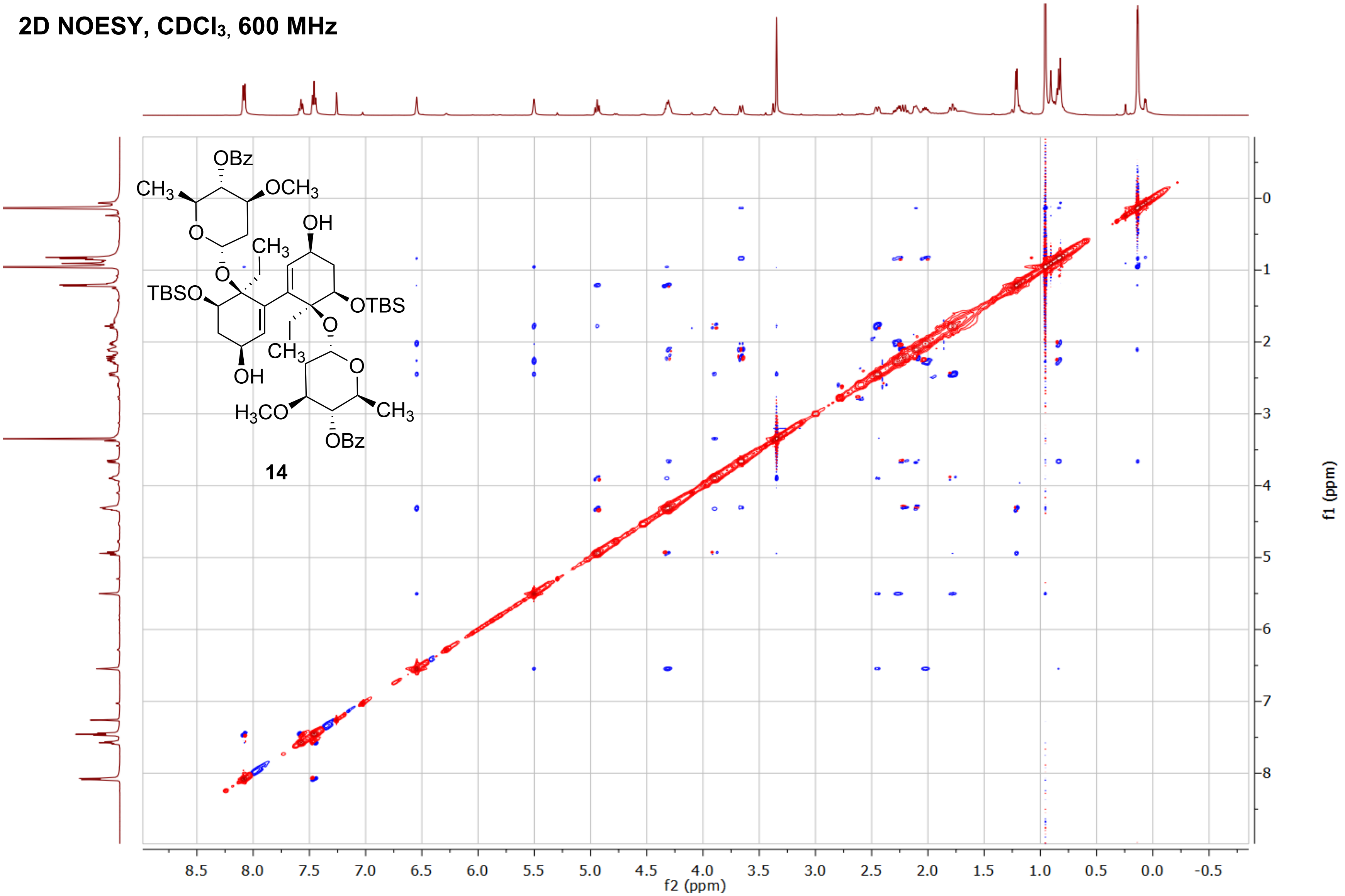


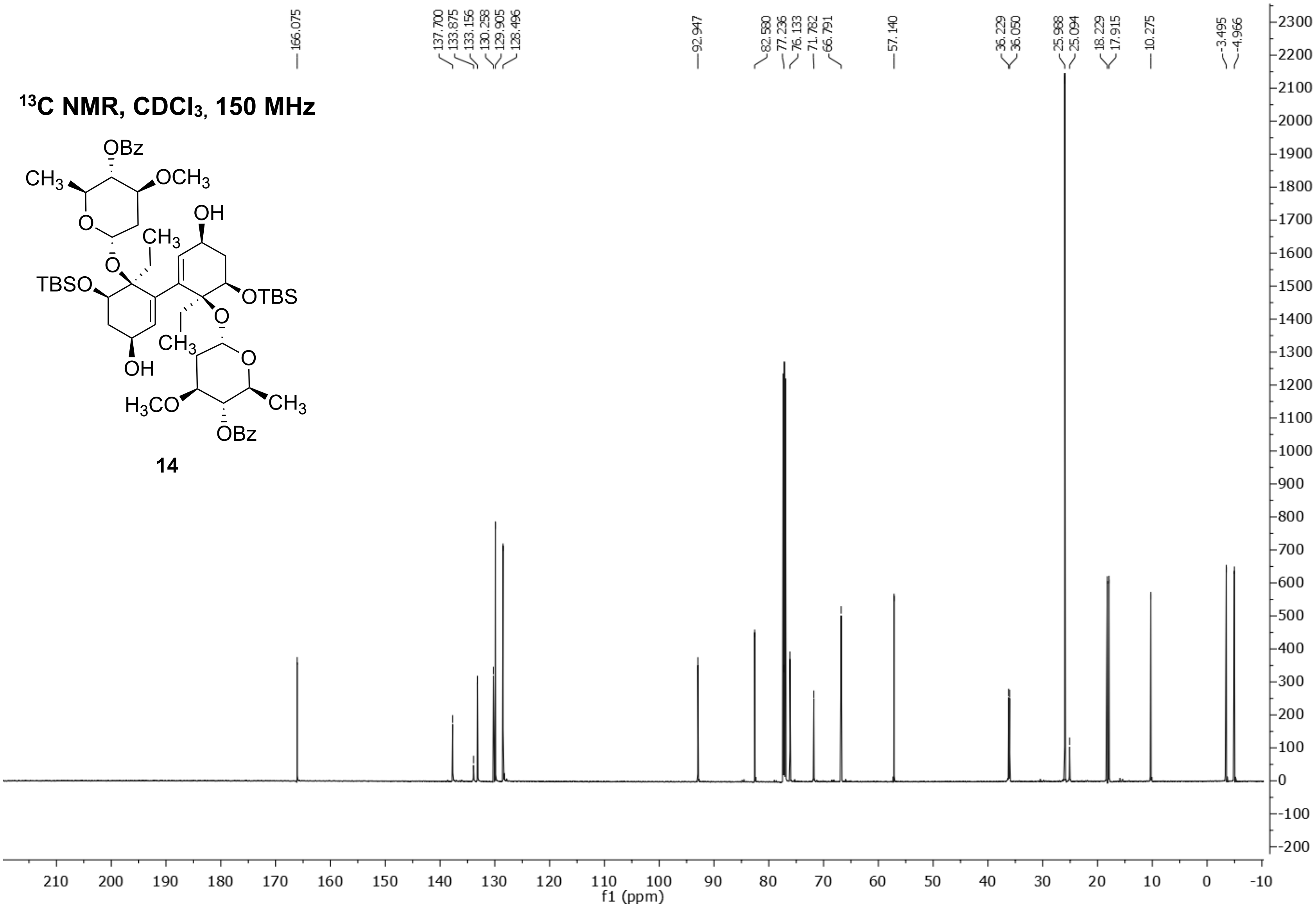
S2


^{13}C NMR, CDCl$_3$, 150 MHz
OBz
CH$_3$
OCH$_3$
O
CH$_3$
O
O
TBSO
OTBS
O
CH$_3$
O
O
H$_3$CO
CH$_3$
OBz
S2
196.732
166.004
152.969
133.250
132.782
130.137
129.896
128.555
93.148
81.954
76.779
76.034
71.158
67.447
57.442
42.969
35.441
30.471
25.895
18.167
17.749
10.207
-3.579
-4.844
400
350
300
250
200
150
100
50
0
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)


^{1}H NMR, CDCl$_3$, 600 MHz
OBz
CH$_3$
OCH$_3$
O
OH
CH$_3$
O
TBSO
OTBS
O
CH$_3$
OH
O
H$_3$CO
CH$_3$
OBz
14
1.89
1.01
1.99
1.00
1.01
1.07
2.03
1.08
1.11
3.04
1.07
2.16
1.19
1.15
2.11
3.17
9.23
3.04
6.07
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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
-1.0
f1 (ppm)

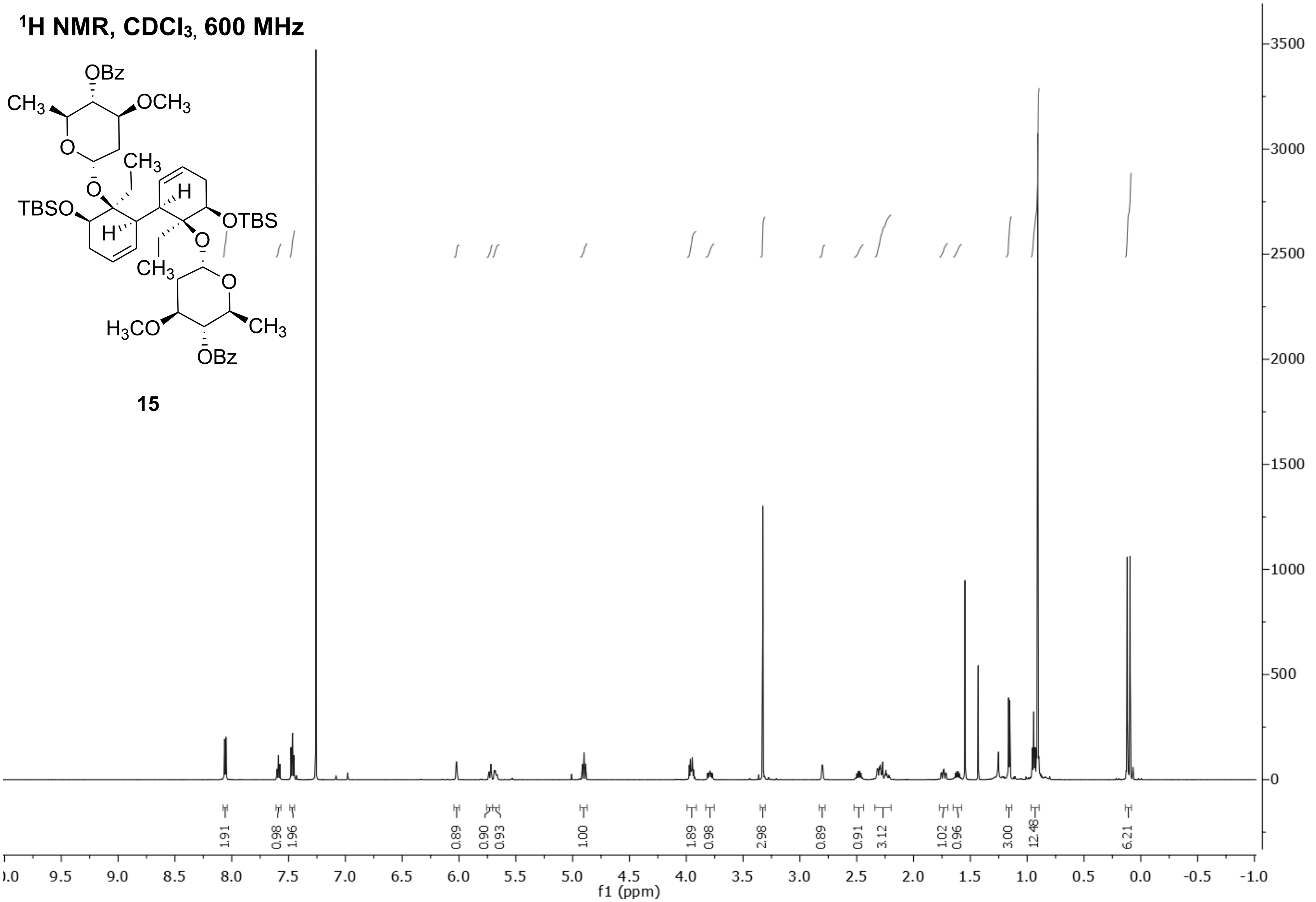
2D NOESY, $CDCl_3$, 600 MHz





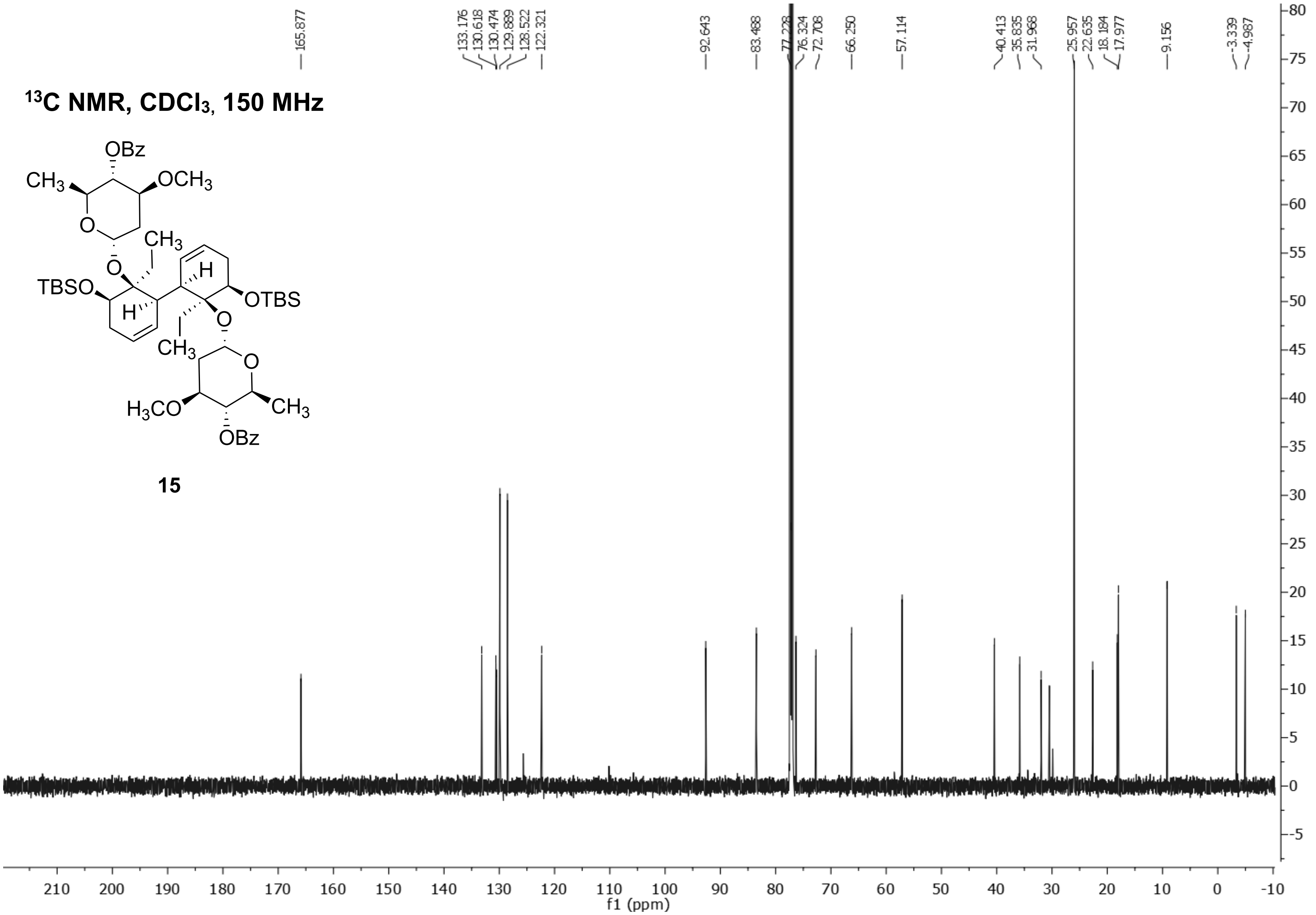
13C NMR, CDCl3, 150 MHz
OBz
CH3
OCH3
O
OH
CH3
O
TBSO
OTBS
O
CH3
O
OH
H3CO
CH3
OBz
166.075
137.700
133.875
133.156
130.258
129.905
128.496
92.947
82.580
77.236
76.133
71.782
66.791
57.140
36.229
36.050
25.988
25.094
18.229
17.915
10.275
-3.495
-4.966
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
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



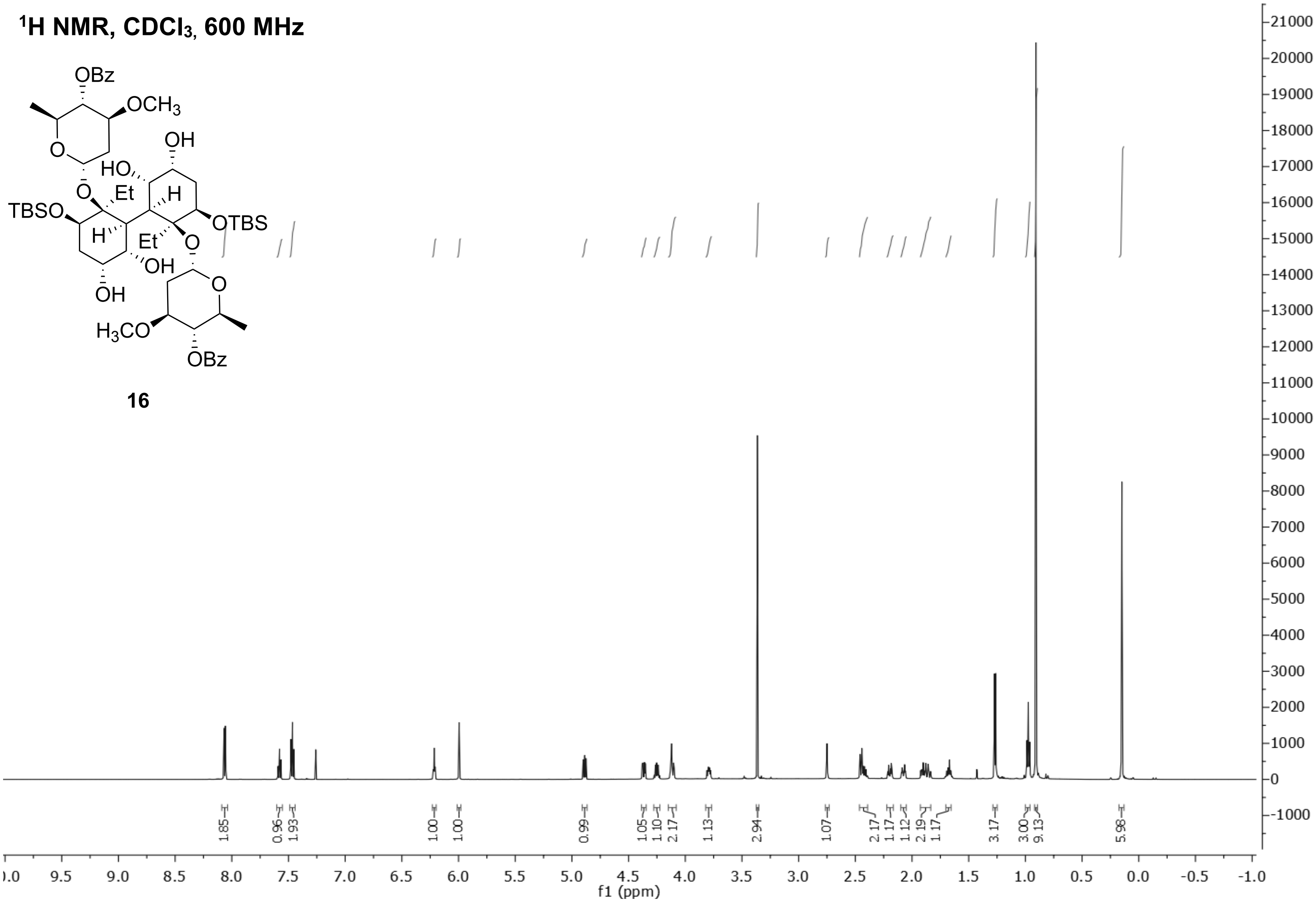
^{1}H NMR, CDCl$_3$, 600 MHz
OBz
CH$_3$
OCH$_3$
O
CH$_3$
O
TBSO
H
H
OTBS
O
CH$_3$
O
H$_3$CO
CH$_3$
OBz
1.91
0.98
1.96
0.89
0.90
0.93
1.00
1.89
0.98
2.98
0.89
0.91
3.12
1.02
0.96
3.00
12.48
6.21
3500
3000
2500
2000
1500
1000
500
0
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

15



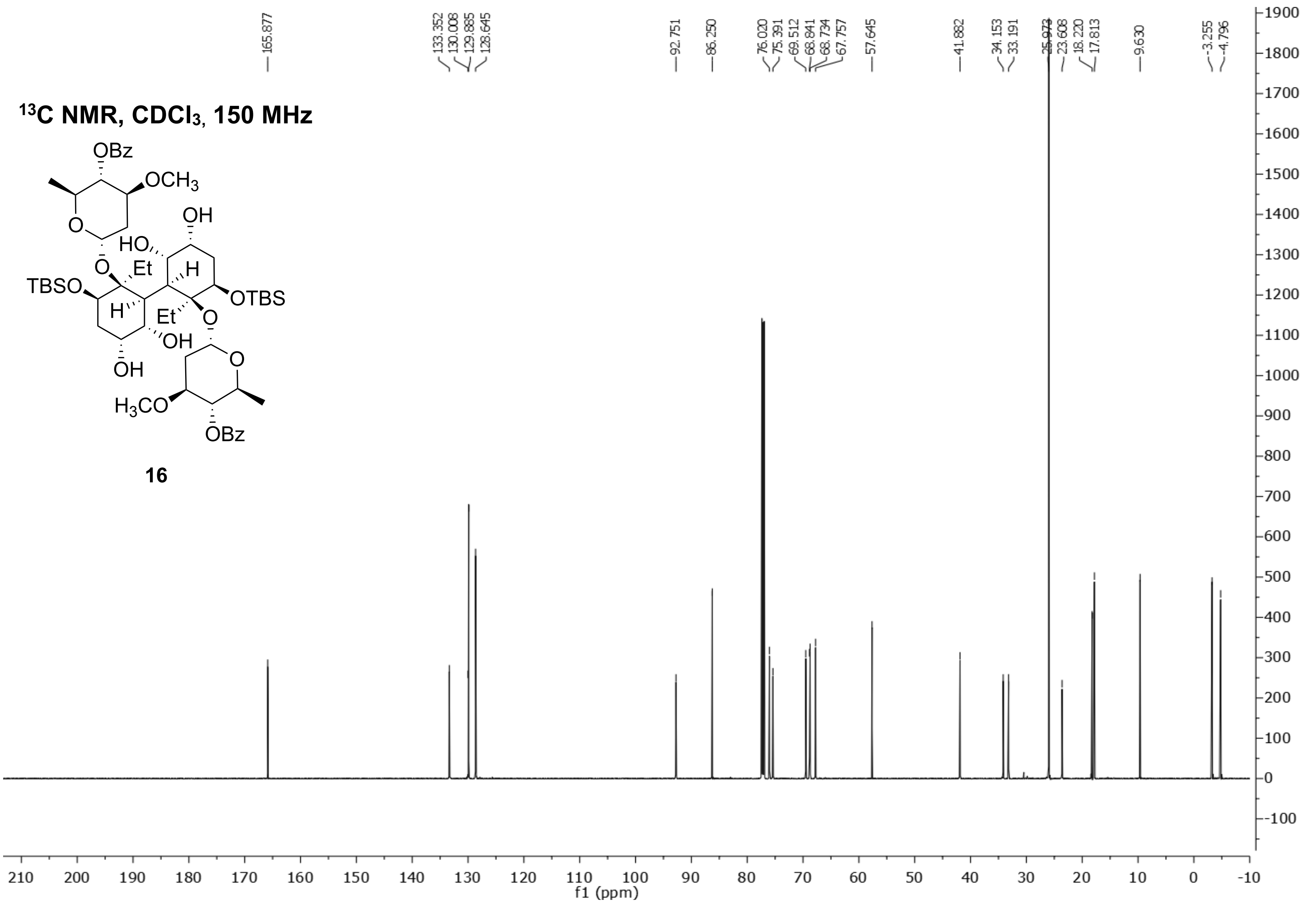
^{13}C NMR, CDCl$_3$, 150 MHz

15



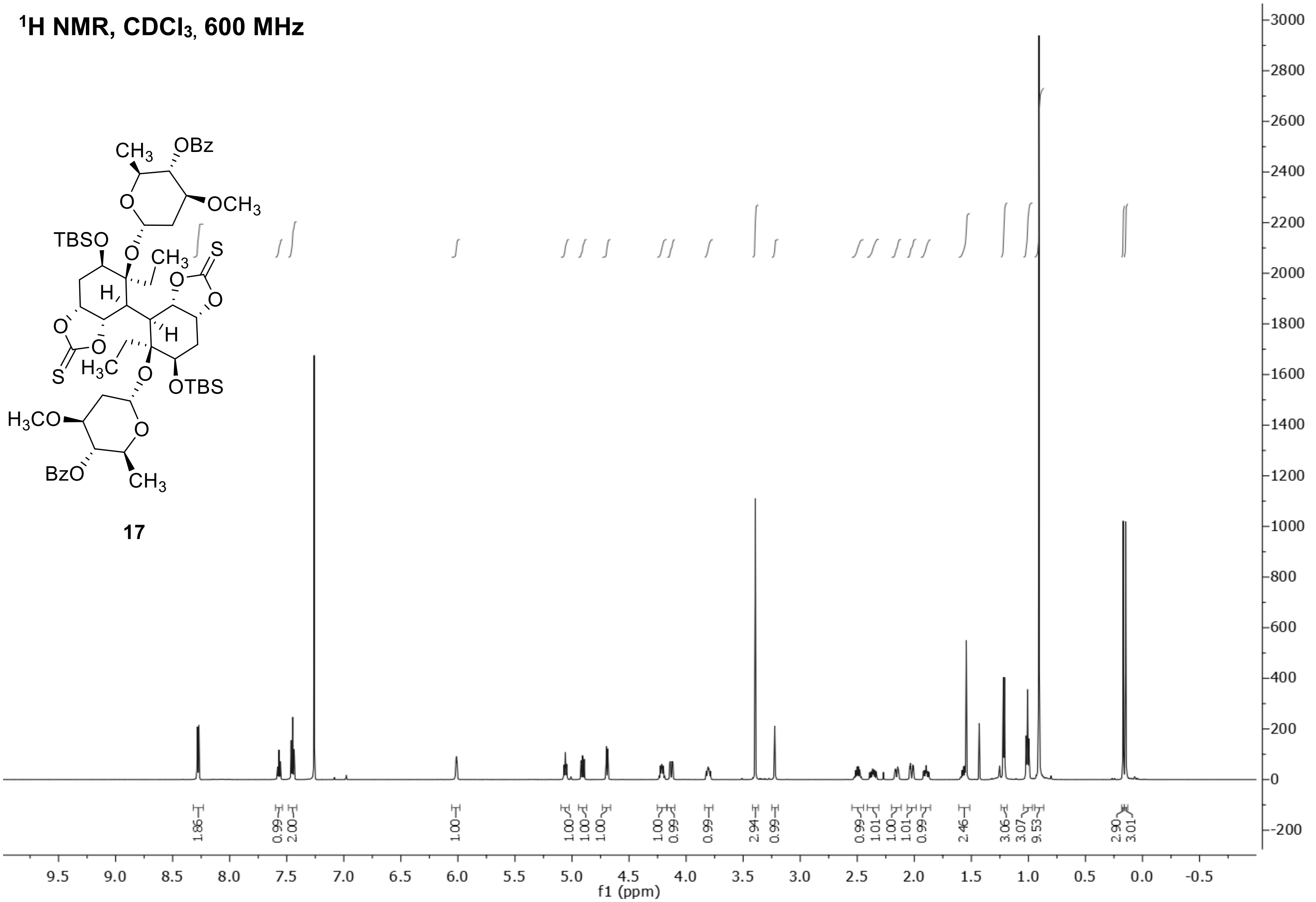
^{1}H NMR, $CDCl_3$, 600 MHz

16



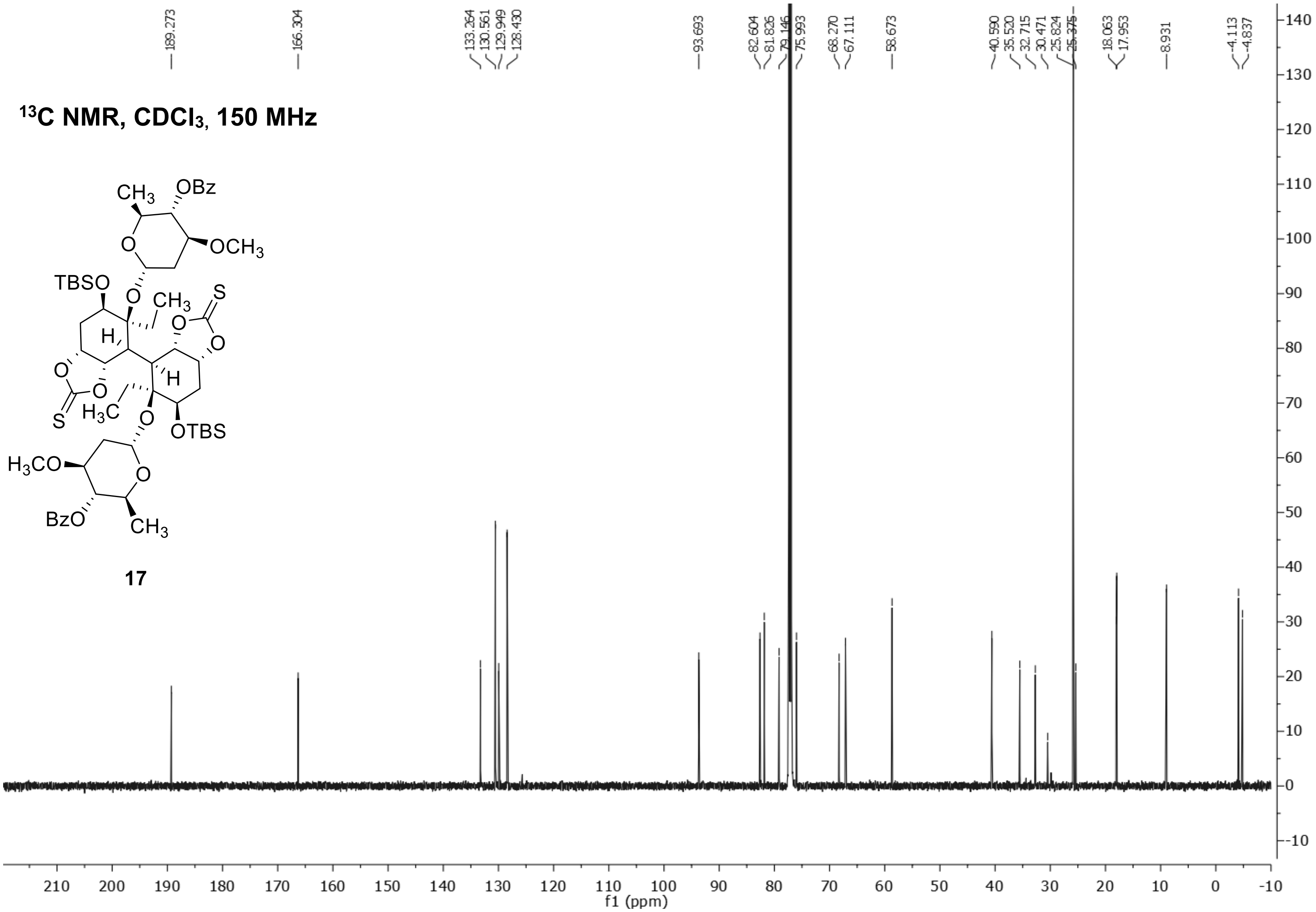
16

Rose et al. “Synthesis of the bis(cyclohexenone) core of (–)-lomaiviticin A.” *Chem. Sci.*



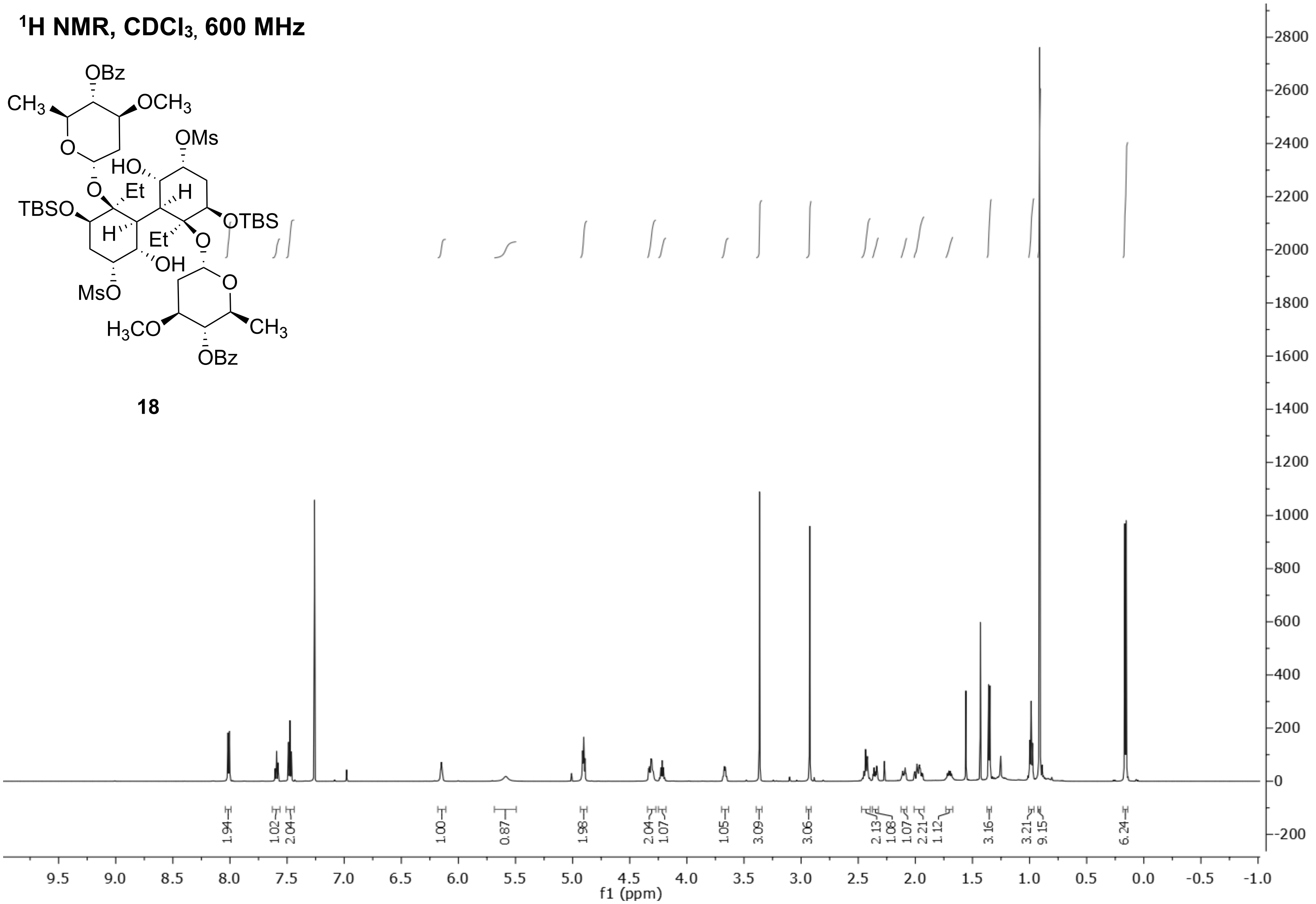
17

Rose et al. "Synthesis of the bis(cyclohexenone) core of (–)-lomaiviticin A." *Chem. Sci.*



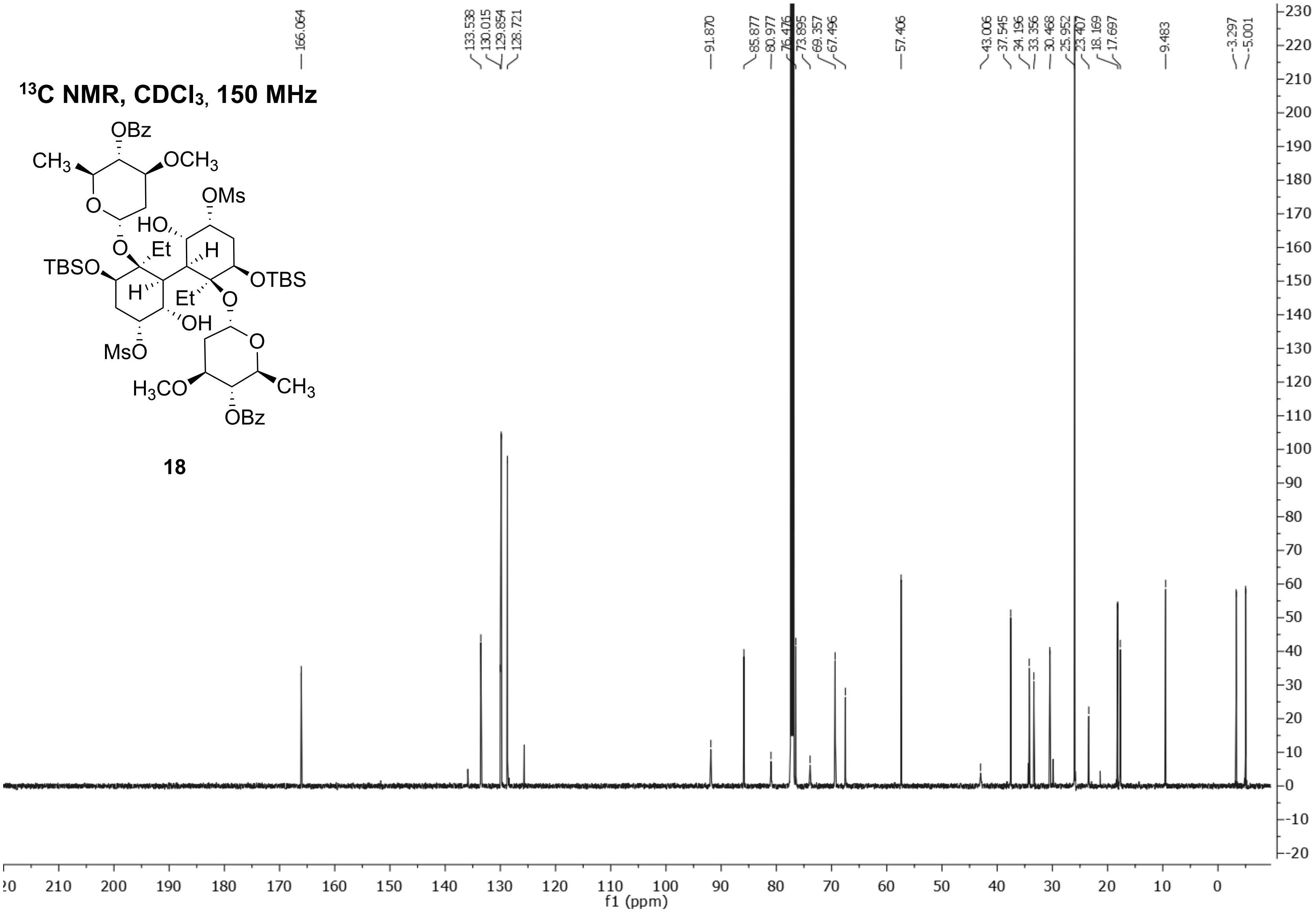
^{13}C NMR, CDCl$_3$, 150 MHz

17



^{1}H NMR, CDCl$_3$, 600 MHz
OBz
CH$_3$
OCH$_3$
O
OMs
HO
O
Et
H
TBSO
OTBS
H
Et
O
OH
O
MsO
H$_3$CO
CH$_3$
OBz
1.94
1.02
2.04
1.00
0.87
1.98
2.04
1.07
1.05
3.09
3.06
2.13
1.08
1.07
2.21
1.12
3.16
3.21
9.15
6.24
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
-1.0
f1 (ppm)
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

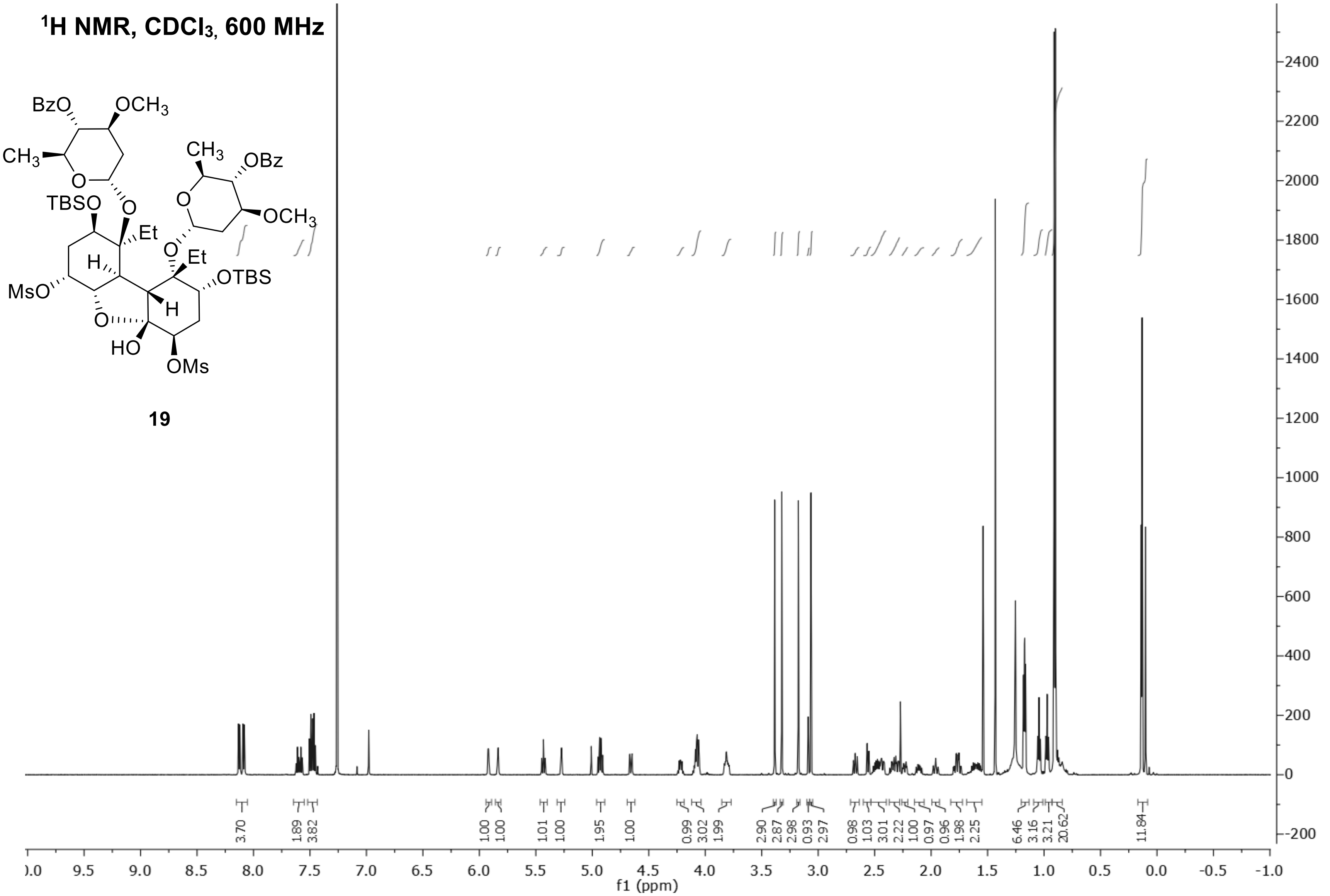
18



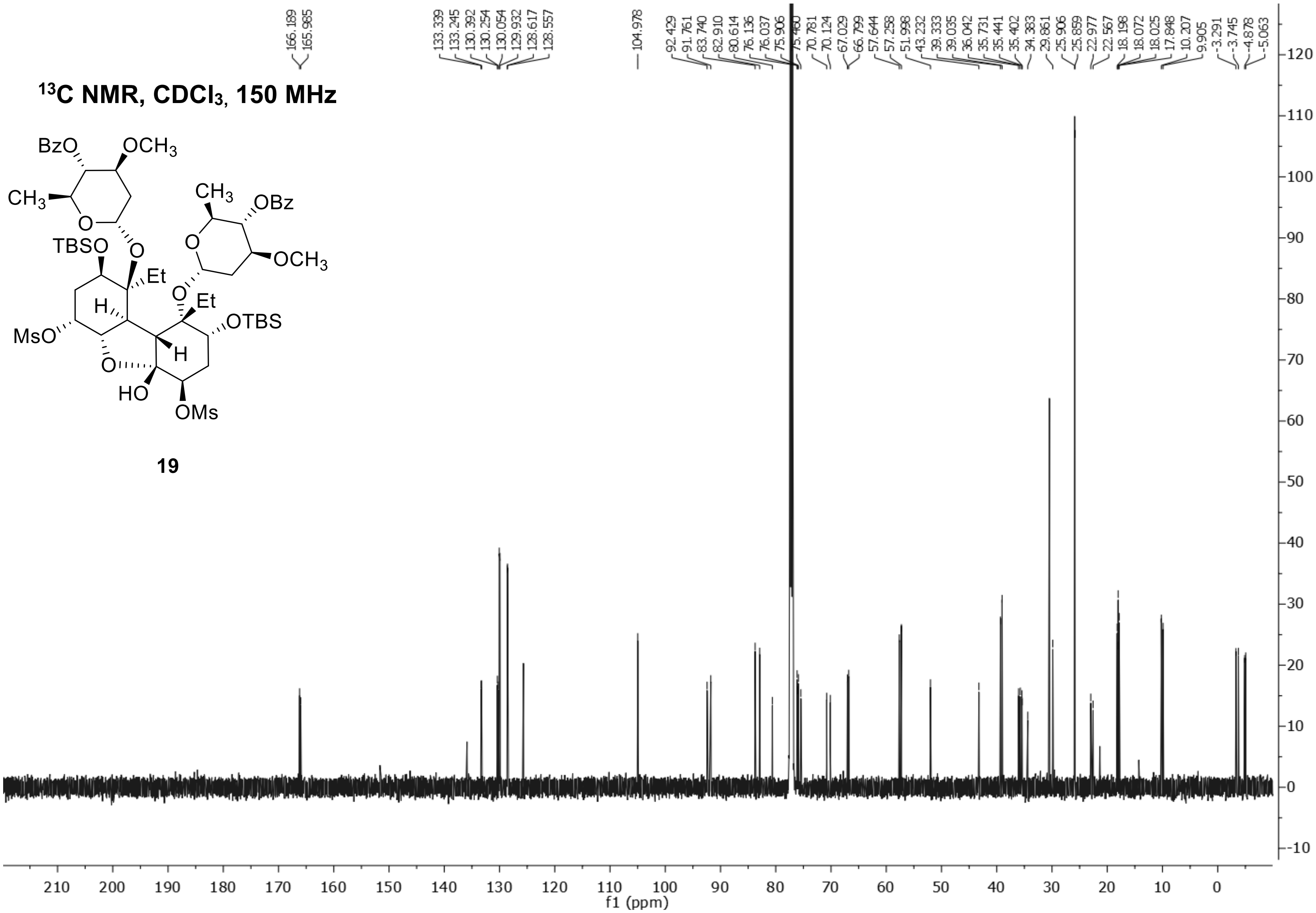
^{13}C NMR, CDCl$_3$, 150 MHz

18

Rose et al. “Synthesis of the bis(cyclohexenone) core of (–)-lomaiviticin A.” *Chem. Sci.*

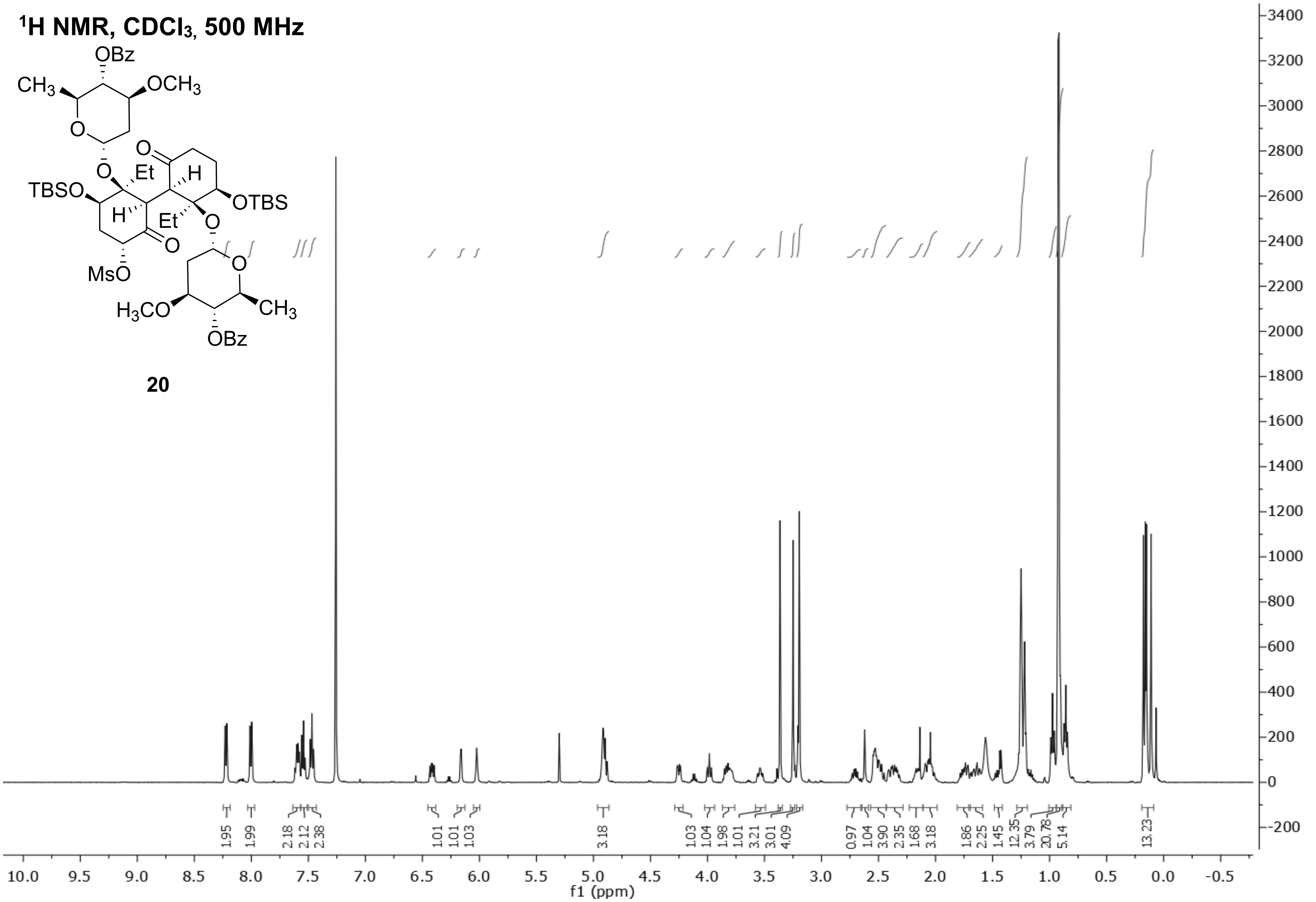


^{1}H NMR, CDCl$_3$, 600 MHz
BzO
OCH$_3$
CH$_3$
O
TBSO
O
Et
H
MsO
O
HO
OMs
CH$_3$
OBz
O
OCH$_3$
O
Et
OTBS
H
19
3.70
1.89
3.82
1.00
1.00
1.01
1.00
1.95
1.00
0.99
3.02
1.99
2.90
2.87
2.98
0.93
2.97
0.98
1.03
3.01
2.22
1.00
0.97
0.96
1.98
2.25
6.46
3.16
3.21
20.62
11.84
-2400
-2200
-2000
-1800
-1600
-1400
-1200
-1000
-800
-600
-400
-200
-0
--200
).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
-1.0
f1 (ppm)

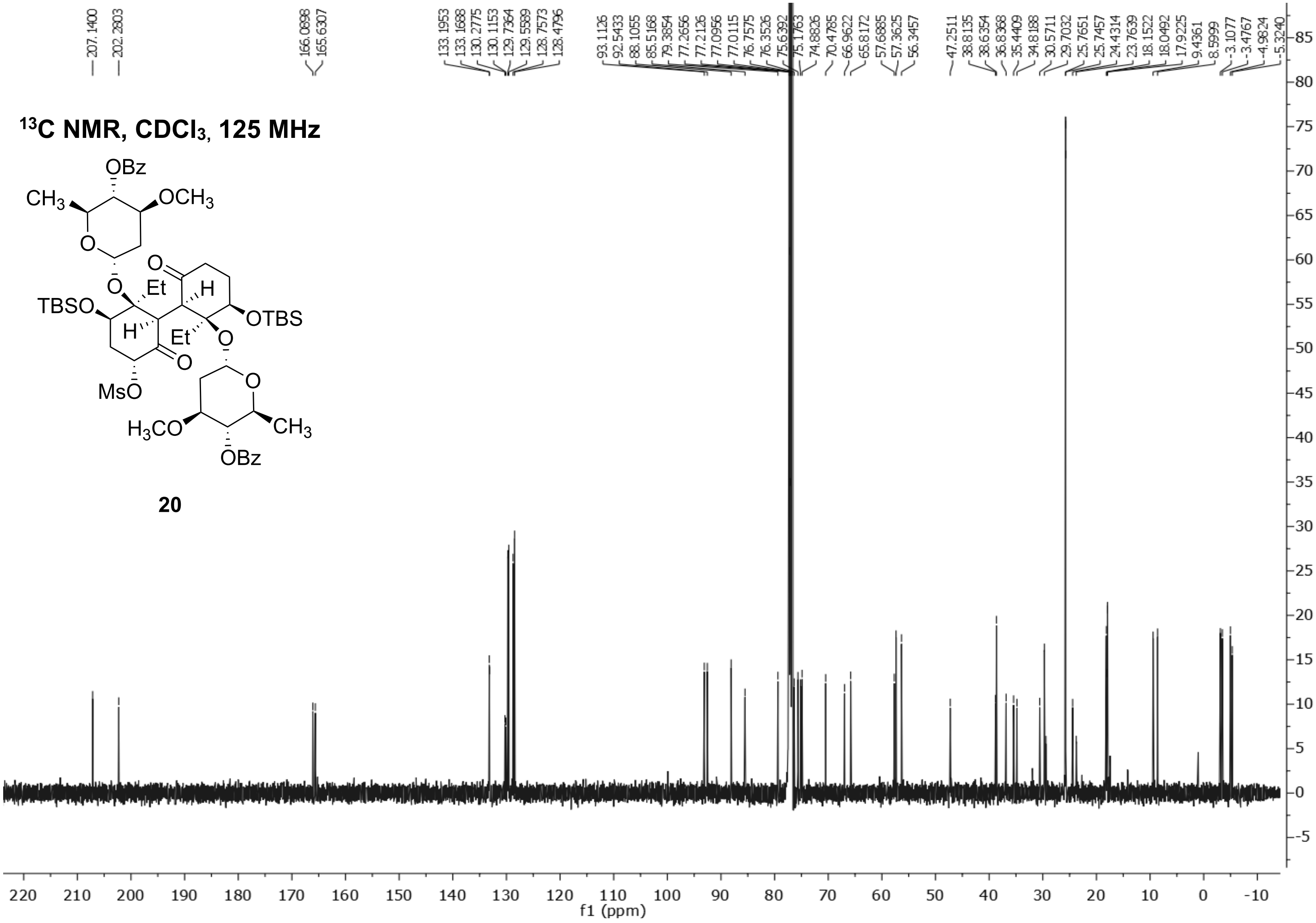


^{13}C NMR, $CDCl_3$, 150 MHz

19

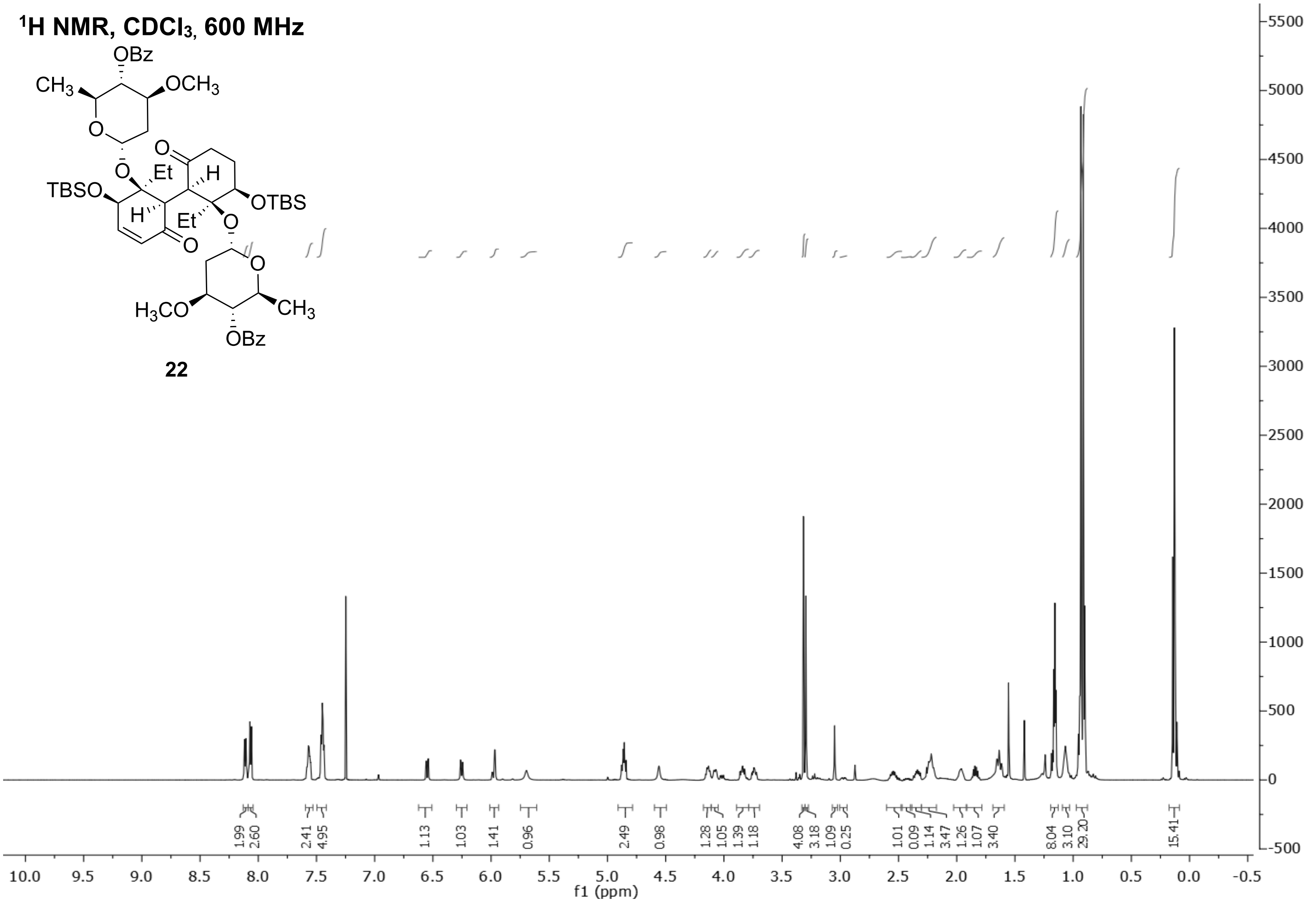

¹H NMR, CDCl₃, 500 MHz
OBz
CH₃
OCH₃
O
O
Et
H
TBSO
OTBS
H
Et
O
O
MsO
O
H₃CO
CH₃
OBz
1.95
1.99
2.18
2.12
2.38
1.01
1.01
1.03
3.18
1.03
1.04
1.98
1.01
3.21
3.01
4.09
0.97
1.04
3.90
2.35
1.68
3.18
1.86
2.25
1.45
12.35
3.79
20.78
5.14
13.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

20

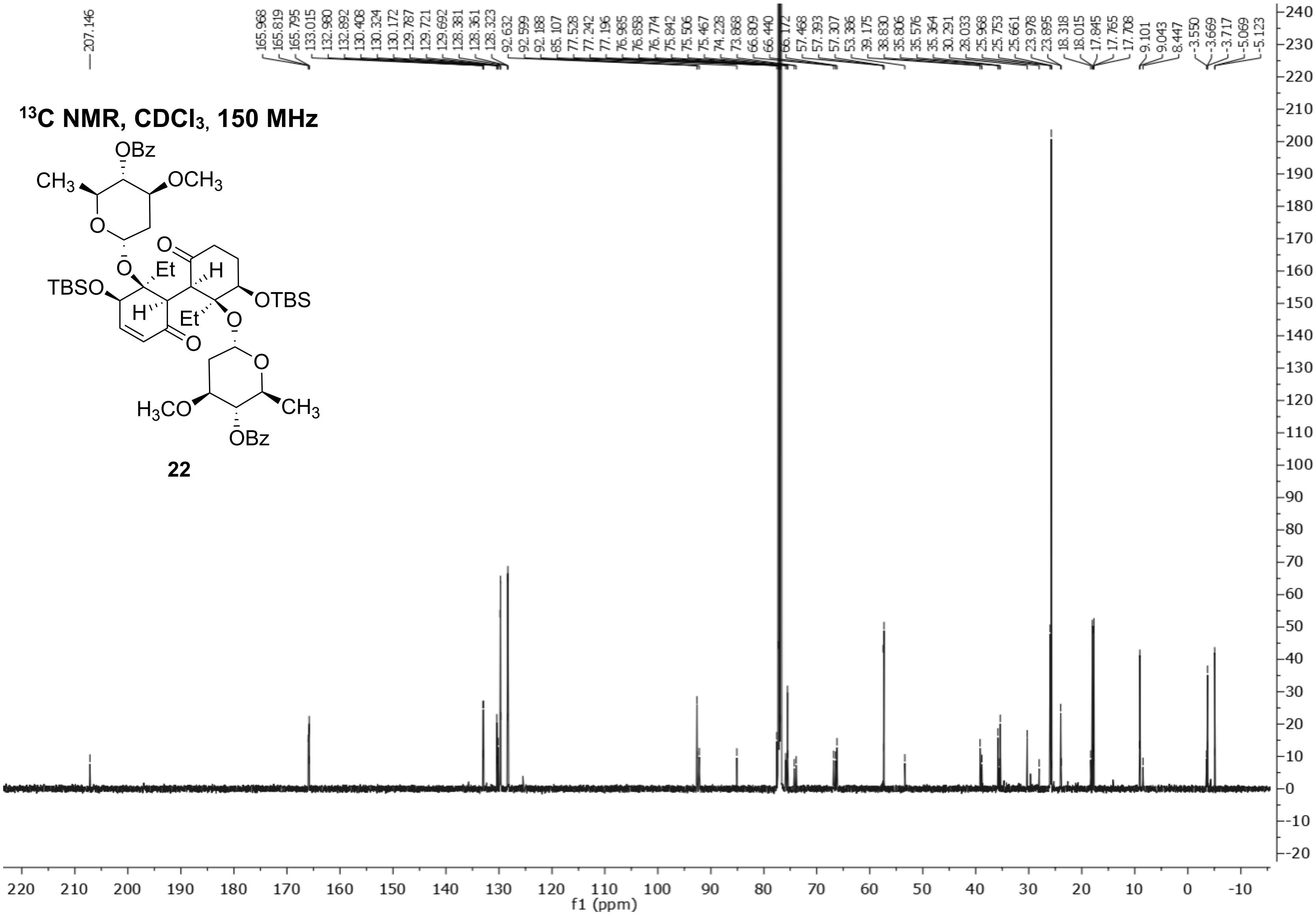


20

Rose et al. "Synthesis of the bis(cyclohexenone) core of (–)-lomaiviticin A." *Chem. Sci.*



¹H NMR, CDCl₃, 600 MHz
OBz
CH3
OCH3
O
O
Et
H
TBSO
OTBS
H
Et
O
O
O
H3CO
CH3
OBz
22
1.99
2.60
2.41
4.95
1.13
1.03
1.41
0.96
2.49
0.98
1.28
1.05
1.39
1.18
4.08
3.18
1.09
0.25
1.01
0.09
1.14
3.47
1.26
1.07
3.40
8.04
3.10
29.20
15.41
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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)

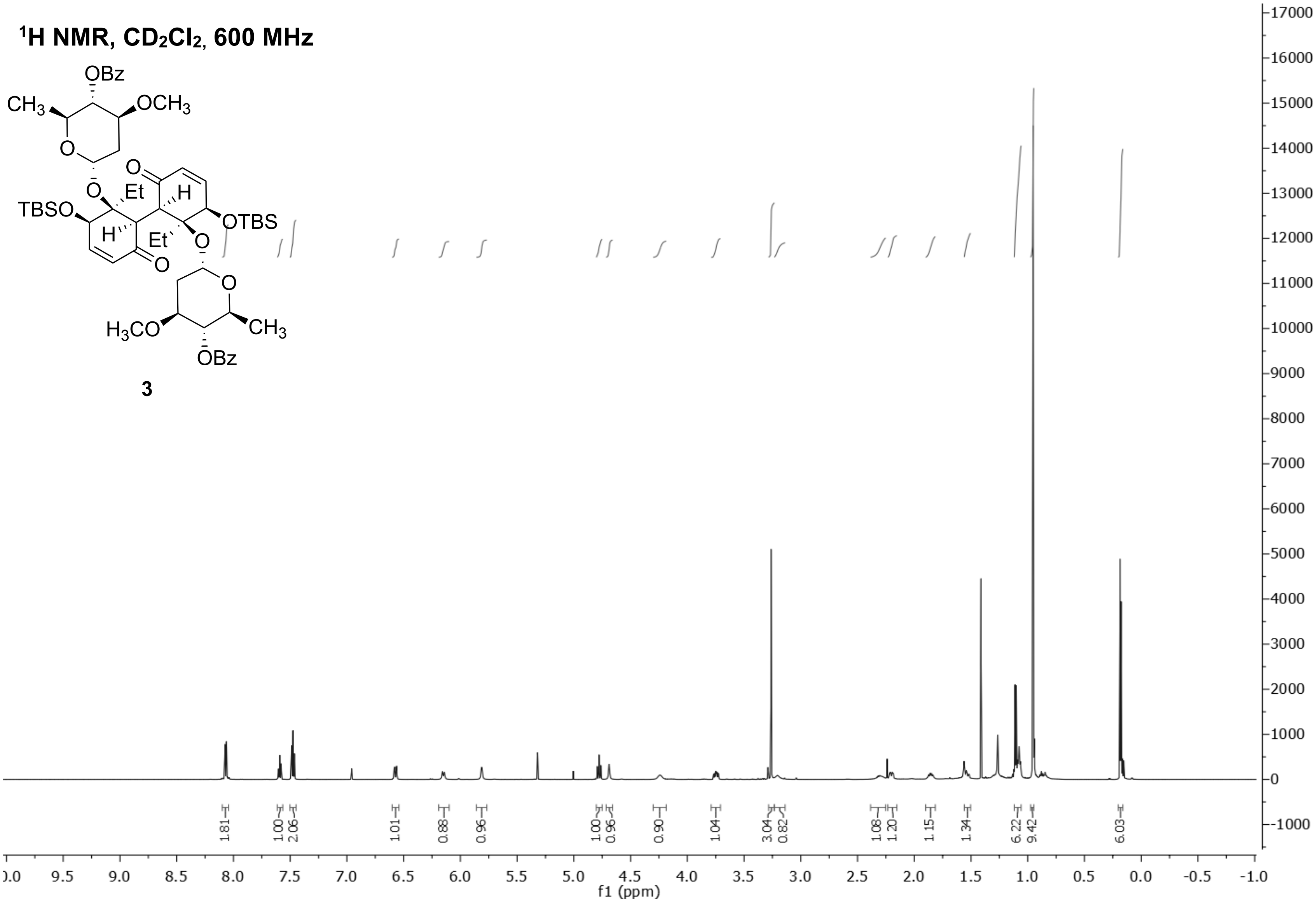


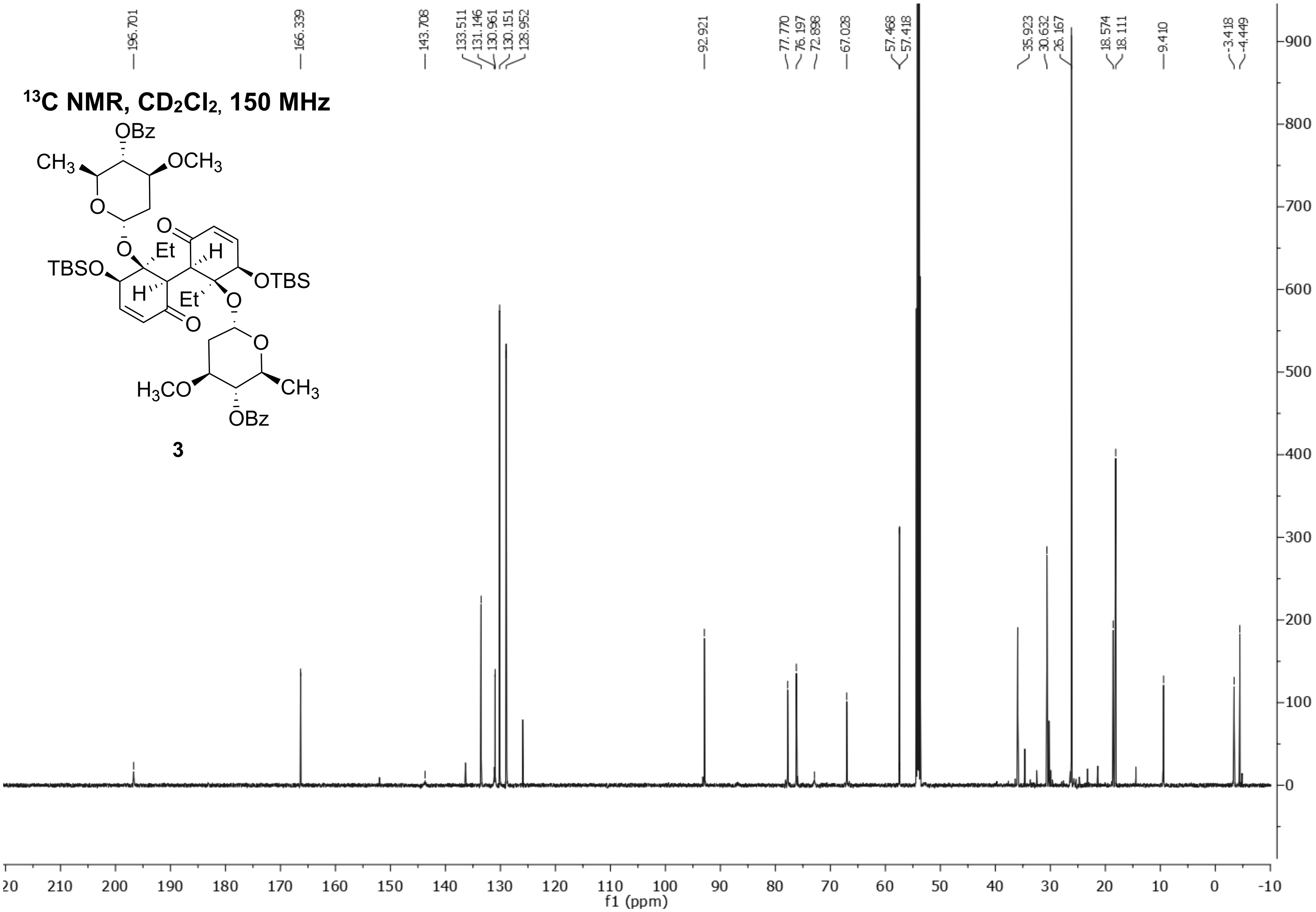
^{13}C NMR, $CDCl_3$, 150 MHz

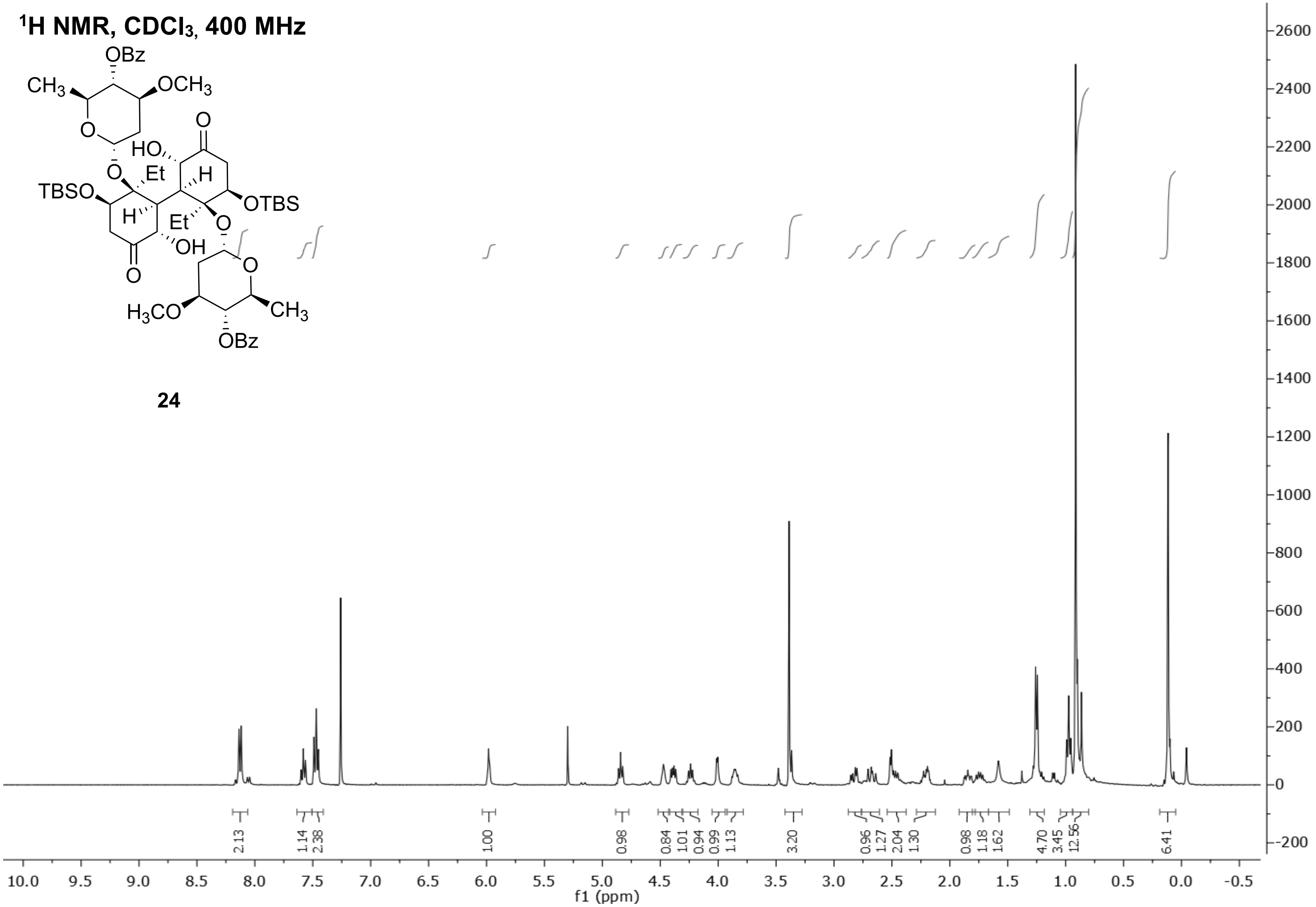
22

Rose et al. "Synthesis of the bis(cyclohexenone) core of (–)-lomaiviticin A." *Chem. Sci.*

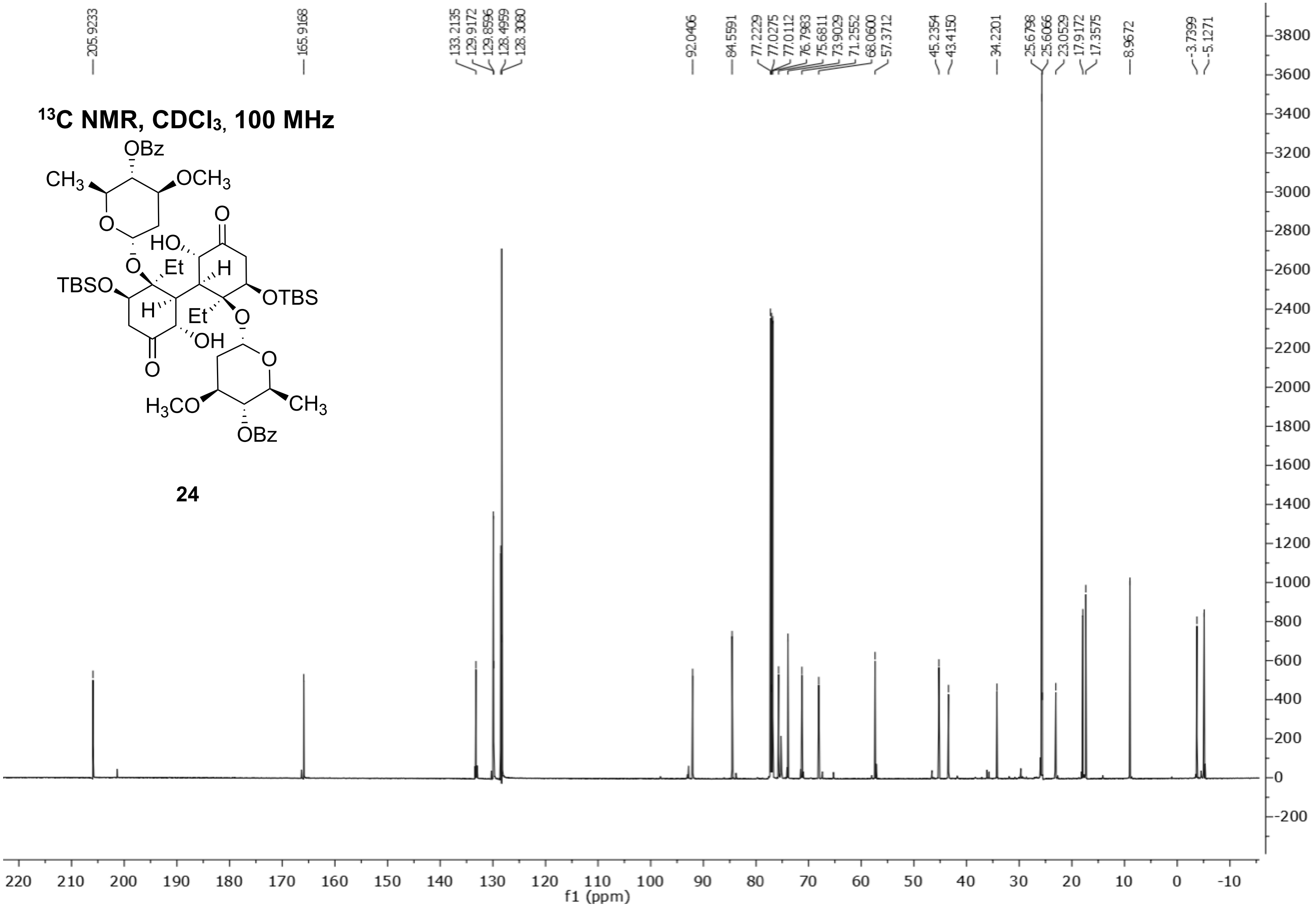
^{1}H NMR, CD_2Cl_2, 600 MHz

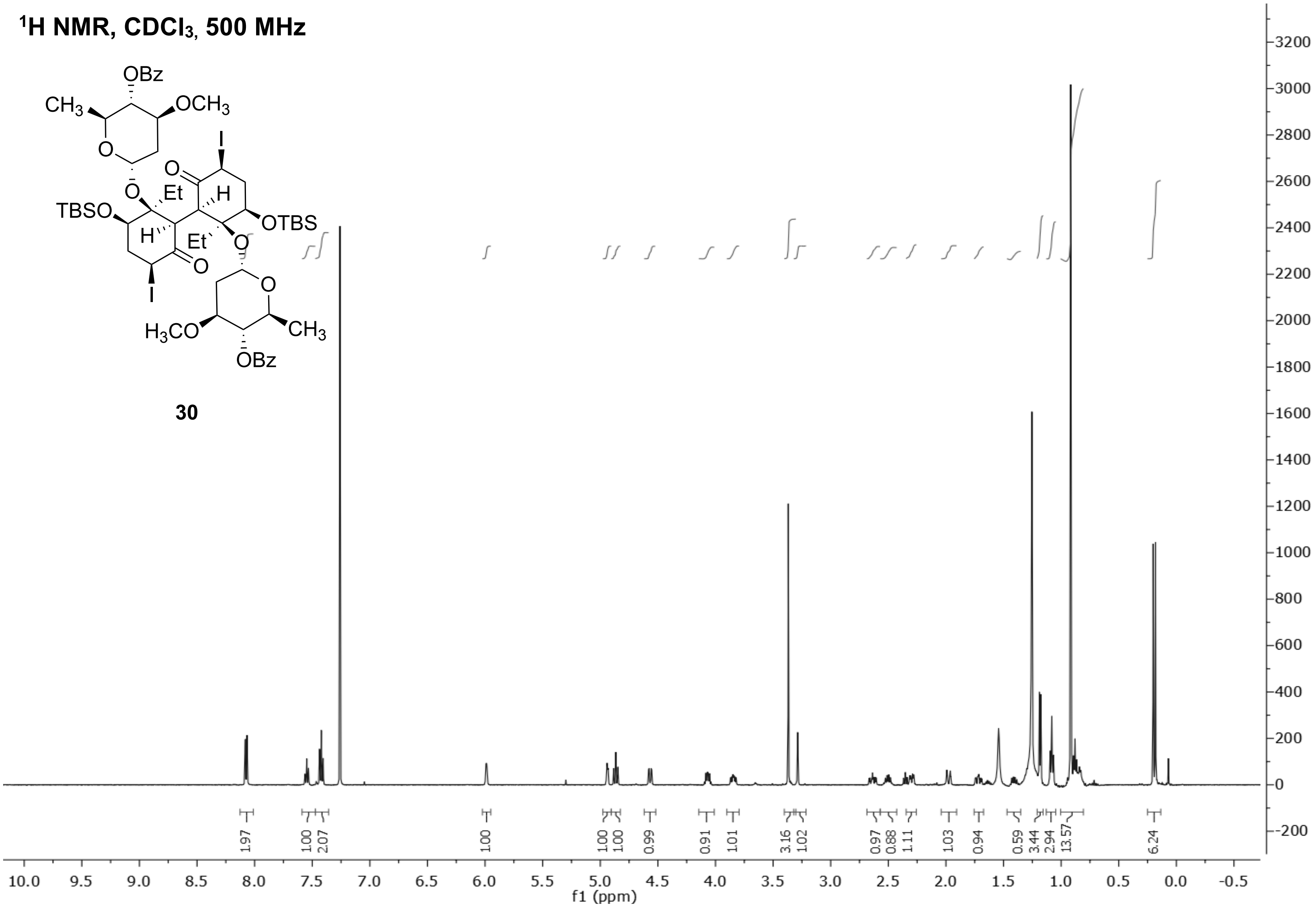


^{13}C NMR, CD$_2$Cl$_2$, 150 MHz
196.701
166.339
143.708
133.511
131.146
130.961
130.151
128.952
92.921
77.770
76.197
72.898
67.028
57.468
57.418
35.923
30.632
26.167
18.574
18.111
9.410
-3.418
-4.449
OBz
CH3
OCH3
O
Et
H
TBSO
OTBS
H3CO
3
900
800
700
600
500
400
300
200
100
0
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

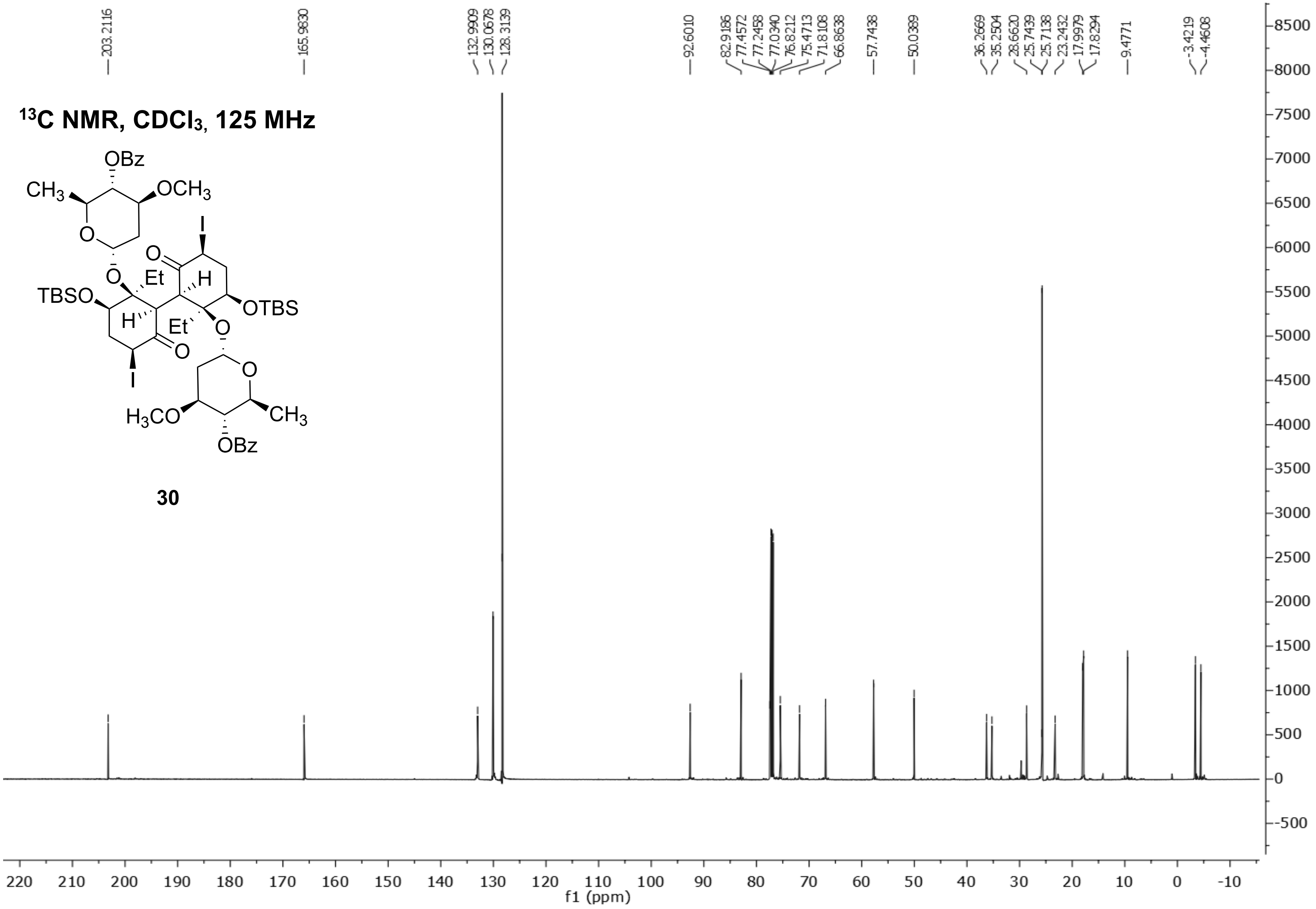

1H NMR, CDCl3, 400 MHz
OBz
CH3
OCH3
O
HO
Et
H
TBSO
OTBS
H
Et
OH
O
H3CO
CH3
OBz
2.13
1.14
2.38
1.00
0.98
0.84
1.01
0.94
0.99
1.13
3.20
0.96
1.27
2.04
1.30
0.98
1.18
1.62
4.70
3.45
12.56
6.41
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

24

^{13}C NMR, CDCl$_3$, 100 MHz
24
205.9233
165.9168
133.2135
129.9172
129.8596
128.4959
128.3080
92.0406
84.5591
77.2229
77.0275
77.0112
76.7983
75.6811
73.9029
71.2552
68.0600
57.3712
45.2354
43.4150
34.2201
25.6798
25.6066
23.0529
17.9172
17.3575
8.9672
-3.7399
-5.1271
OBz
CH3
OCH3
O
HO
Et
H
TBSO
OTBS
H
Et
OH
H3CO
CH3
OBz
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200



Rose et al. “Synthesis of the bis(cyclohexenone) core of (–)-lomaiviticin A.” *Chem. Sci.*



203.2116
165.9830
132.9909
130.0678
128.3139
92.6010
82.9186
77.4572
77.2458
77.0340
76.8212
75.4713
71.8108
66.8638
57.7438
50.0389
36.2669
35.2504
28.6620
25.7439
25.7138
23.2432
17.9979
17.8294
9.4771
-3.4219
-4.4608
^{13}C NMR, CDCl$_3$, 125 MHz
OBz
CH$_3$
OCH$_3$
O
I
O
O
Et
H
TBSO
OTBS
H
Et
O
O
I
O
H$_3$CO
CH$_3$
OBz
30
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220
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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