Supporting Information

Enantioselective Synthesis of Spliceostatin E and Evaluation of Biological Activity

Arun K. Ghosh, Anne M. Veitschegger, Venkata Reddy Sheri, Kerstin A. Effenberger, Beth E. Prichard and Melissa S. Jurica

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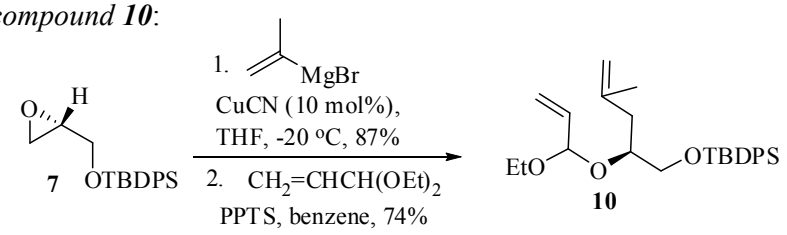
General Information: Those reactions which required anhydrous conditions were carried out under an argon atmosphere using oven-dried glassware (120 ^{o}C). All chemicals and reagents were purchased from commercial suppliers and used without further purification. Compound **7** was synthesized from the literature procedure (*J. Org. Chem.* **2014**, *79*, 599-607). Anhydrous solvents were obtained as follows: anhydrous tetrahydrofuran and diethyl ether were distilled from sodium metal under argon, anhydrous dichloromethane was dried via distillation from CaH_2 immediately prior to use under argon, and anhydrous methanol and ethanol were distilled from activated magnesium under argon. All other solvents were reagent grade. TLC analysis was conducted using glass-backed Thin-Layer Silica Gel Chromatography Plates (60 Å, 250 μm thickness, F-254 indicator). Flash chromatography was performed using 230-400 mesh, 60 Å pore diameter silica gel. ^{1}H NMR spectra were recorded at 400 or 500 MHz. ^{13}C NMR spectra were recorded at 100 or 125 MHz. Chemical shifts are reported in parts per million and are referenced to the deuterated residual solvent peak. NMR data is reported as: δ value (chemical shift, *J*-value (Hz), integration, where s = singlet, d = doublet, t = triplet, q = quartet, bs = broad singlet). IR spectra were recorded on a Varian 2000 Infrared spectrophotometer and are reported as cm^{-1}. LRMS spectra were recorded at the Purdue University Department of Chemistry Mass Spectrometry Center.

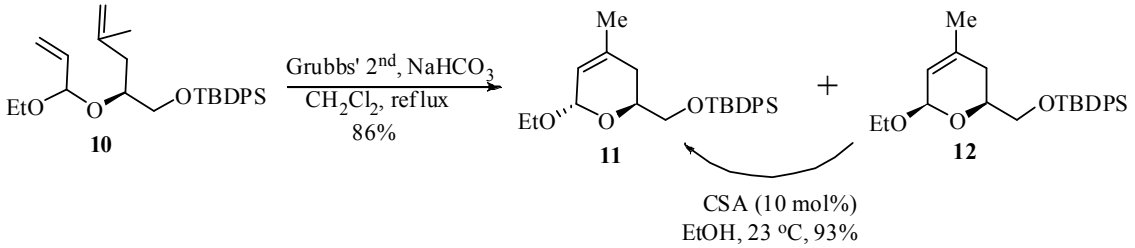
*Synthesis of compound **10***:



To a slurry of **7** (1.0 g, 3.2 mmol), CuCN (29.0 mg) in THF (20 mL) at -20 °C was added dropwise isopropenylmagnesium bromide (0.5 M in THF, 9.6 mL). The reaction mixture was stirred for 30 min. The reaction was quenched by addition of a saturated aqueous solution of NH_4Cl (5 mL), and the mixture was extracted into ethyl acetate (2 x 10 mL). The reaction mixture was washed with brine (10 mL), dried (Na_2SO_4) and evaporated. The products were purified by silica gel column chromatography (hexane/ethylacetate, 94:6) to afford homoallylic alcohol as colorless oil (987.0 mg, 87 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.65 (m, 4H), 7.47-7.37 (m, 6H), 4.80 (s, 1H), 4.74 (s, 1H), 3.92-3.85 (m, 1H), 3.69-3.64 (m, 1H), 3.59-3.49 (m, 1H), 2.43 (bs, 1H), 2.18 (d, J = 6.7 Hz, 2H), 1.73 (s, 3H), 1.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 135.5, 133.1, 129.7, 127.7, 112.8, 69.6, 67.6, 41.5, 26.8, 22.4, 19.2.

To a solution of homoallylic alcohol (950.0 mg, 2.68 mmol) in benzene (15 mL) was added acrolein diethyl acetal (0.62 mL, 4.02 mmol) and PPTS (34.0 mg, 0.134 mmol). The resulting mixture was stirred for 12 h. The mixture was concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (hexane/ethylacetate, 96:4) to yield as a colorless oil (870.0 mg, 74%). $[\alpha]_D^{20}$ -16.8 (*c* 0.23, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.64 (m, 8H), 7.48-7.32 (m, 12H), 5.92-5.74 (m, 2H), 5.42-5.20 (m, 4H), 5.12-5.07 (m, 1H), 4.98-4.93 (m, 1H), 4.83-4.72 (m, 4H), 3.98-3.89 (m, 1H), 3.88-3.76 (m, 2H), 3.73-3.39 (m, 9H), 2.49-2.21 (m, 3H), 1.82-1.67 (m, 5H), 1.28-1.01 (m, 28H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 135.8, 135.6, 133.6, 133.5, 129.7, 129.6, 127.7, 127.6, 117.8, 113.0, 112.9, 101.4, 75.1, 74.8, 66.0, 60.9, 60.3, 60.2, 40.7, 40.3, 26.8, 22.9, 22.7, 19.2, 15.1; IR (neat) 3071, 2930, 2858, 1648, 1472, 1428, 1113, 824, 702 cm^{-1}; LRMS (ESI), *m/z* 461.3 $(M+Na)^+$.

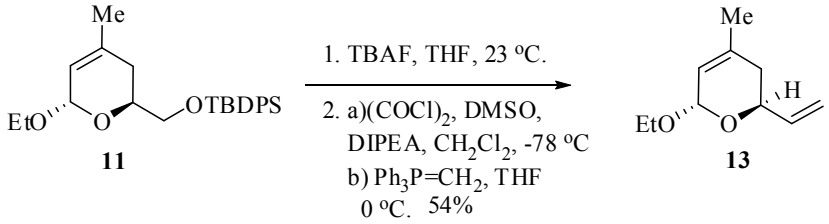
*Synthesis of compound **11***:



A solution of **10** (360.0 mg, 0.82 mmol) in 16 mL of dried CH_2Cl_2 was purged with argon for 15 min, and solid $NaHCO_3$ (138.0 mg, 1.64 mmol) followed by solution of Grubbs' catalyst II (70.0 mg, 0.08 mmol) in 4.0 mL of dried CH_2Cl_2 was added dropwise under a argon atmosphere. Then the reaction mixture was refluxed under a argon atmosphere for 8 h. After removal of the solvent under reduced pressure, the residue was dissolved in CH_2Cl_2 and filtered through a short plug of silica gel, evaporated to get **11** and **12** (330.0 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.65 (m, 8H), 7.46-7.34 (m, 12H), 5.49 (s, 1H), 5.38 (s, 0.74H), 5.05 (s, 0.74H), 5.0 (s, 1H), 4.13-4.05 (m, 1H), 3.93-3.63 (m, 8H), 3.56-3.46 (m, 2H), 2.13-1.92 (m, 2H), 1.83-1.67 (m, 7H), 1.27-1.15 (m, 7H), 1.07-1.06 (m, 16H).

The mixture of **11** and **12** (330.0 mg, 0.81 mmol) was dissolved in EtOH (5 mL), CSA (19 mg, 0.08 mmol) was added. The resulting mixture was stirred at 23 °C for 2 h. The mixture was quenched with Et_3N (100 μL) and the mixture was concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (hexane/ethylacetate, 95:5) to yield **11** as colorless oil (307.0 mg, 93%). $[\alpha]_D^{20}$ -32.0 (*c* 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.68 (m, 4H), 7.46-7.35 (m, 6H), 5.50 (s, 1H), 5.01 (s, 1H), 4.15-4.07 (m, 1H), 3.93-3.84 (m, 1H), 3.82-3.76 (m, 1H), 3.70-3.65 (m, 1H), 3.56-3.47 (m, 1H), 2.02-1.92 (m, 1H), 1.83-1.76 (m, 1H), 1.74 (s, 3H), 1.24 (t, *J* = 7.6 Hz, 3H), 1.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 135.6, 133.5, 129.5, 127.6, 119.8, 94.7, 67.4, 66.6, 62.8, 31.8, 26.7, 22.9, 19.1, 15.3; IR (neat) 3070, 2930, 2858, 1684, 1589, 1473, 1428, 1383, 1111, 1063, 1001, 824, 702, 505 cm^{-1}; LRMS (ESI), *m/z* 433.3 $(M+Na)^+$.

*Synthesis of compound **13***:



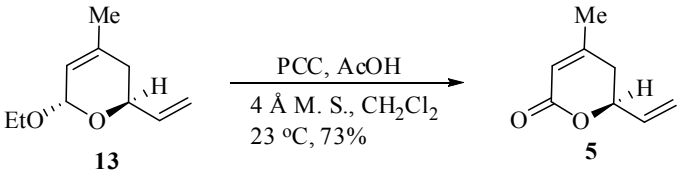
To a solution of **11** (300.0 mg, 0.73 mmol) in 2 mL of THF was added TBAF (0.8 mL, 1 M in THF) at 0 °C, the mixture was warmed to room temperature and kept stirring for 3 h. After removal of the solvent under reduced pressure, the residue was purified on a silica gel column (hexane/ethylacetate, 80:20) to afford alcohol as colorless syrup (110.0 mg, 90%). $[\alpha]_D^{20}$ -50.2 (*c* 1.82, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 (s, 1H), 4.98 (s, 1H), 4.07-3.99 (m, 1H), 3.85-3.76 (m, 1H), 3.75-3.68 (m, 1H), 3.63-3.55 (m, 1H), 3.54-3.45 (m, 1H),

2.21-2.12 (m, 1H), 2.13-2.03 (m, 1H), 1.73 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 119.5, 94.8, 66.9, 65.1, 63.1, 30.7, 22.8, 15.3; IR (neat) 3435, 2973, 2912, 2878, 1685, 1445, 1385, 1333, 1169, 1139, 997, 814, 754 cm^{-1}.

To a solution of oxalyl chloride (75 µL, 0.87 mmol) in dry CH_2Cl_2 (2 mL) at -78 ^{o}C, dry DMSO (124 µL, 1.74 mmol) was added dropwise and stirred for 30 min. A solution of alcohol (100 mg, 0.58 mmol) in dry CH_2Cl_2 (3 mL) was added and stirred at -78 ^{o}C for 30 min. It was quenched with DIPEA (620 µL, 3.5 mmol) and diluted with CH_2Cl_2 (10 mL). The reaction mixture was washed with water (5 mL), brine (5 mL), dried (Na_2SO_4) and evaporated to furnish the corresponding aldehyde as a pale yellow liquid.

To a stirred and cooled (0 ^{o}C) solution of (methyltriphenyl)phosphonium bromide (0.73 g, 2.03 mmol) in THF (3 mL) under argon, *n*-BuLi (1.1 mL, 1.74 mmol, 1.6 M solution of in hexanes) was added. After 30 min, a solution of aldehyde (0.1 g, 0.58 mmol) in THF (3 mL) was added and stirred for 8 h at 23 ^{o}C. The reaction mixture was quenched with saturated aq. NH_4Cl (3 mL) and extracted with ether (2 x 10 mL). The organic layers were washed with brine (10 mL), dried (Na_2SO_4), evaporated and purified the residue by column chromatography (hexane/ethylacetate, 99:1) to yield **13** as a colorless oil (58.0 mg, 60%). $[\alpha]_D^{20}$ -71.4 (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97-5.87 (m, 1H), 5.49 (s, 1H), 5.30 (d, J = 17.2 Hz, 1H), 5.16 (d, J = 10.4 Hz, 1H), 5.02 (s, 1H), 4.44-4.37 (m, 1H), 3.88-3.78 (m, 1H), 3.58-3.48 (m, 1H), 2.12-2.01 (m, 1H), 1.90-1.80 (m, 1H), 1.74 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 137.0, 119.7, 115.3, 95.0, 77.1, 67.0, 63.1, 35.0, 22.7, 15.3; IR (neat) 2973, 2915, 2879, 1670, 1607, 1440, 1383, 1328, 1130, 1062, 1011, 922, 760 cm^{-1}.

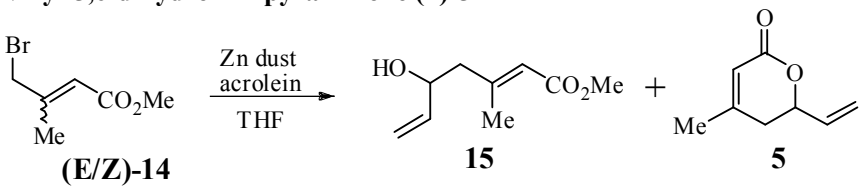
*Synthesis of compound **5***:



A solution of lactol **13** (50.0 mg, 0.30 mmol) in CH_2Cl_2 (6 mL) was treated with PCC (32.0 mg, 1.48 mmol), 4 Å molecular sieves (30 mg) and AcOH (0.17 mL, 2.97 mmol) at rt. After stirring at rt for 5 h, water (3 mL) was added and the reaction mixture was extracted with CH_2Cl_2 (2 x 5 mL) and the solvent was removed under reduced pressure at water bath temperature not exceed 10 °C. Purified the residue by column chromatography (hexane/ethylacetate, 80:20) furnished **5** as colorless oil (30.0 mg, 73%). $[\alpha]_D^{20}$ -162.8 (*c*

0.21, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98-5.87 (m, 1H), 5.82 (s, 1H), 5.42-5.24 (m, 2H), 4.91-4.83 (m, 1H), 2.46-2.28 (m, 2H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 156.5, 134.9, 117.6, 116.6, 77.1, 34.5, 22.9; IR (neat) 2916, 1720, 1651, 1435, 1384, 1248, 1012, 847 cm^{-1}; LRMS (ESI), *m/z* 139 $(M+H)^+$.

4-methyl-6-vinyl-5,6-dihydro-2*H*-pyran-2-one (±)-5

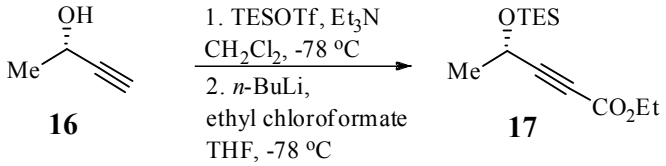


(E/Z)-14 **15** **5**

To a flask was added zinc dust (3 g, 46 mmol). Enough TMS-Cl was added to the flask to cover the zinc and the mixture stirred for 1 h. TMS-Cl was decanted and the zinc was washed with 0.5 M HCl, water, acetone and ether successively. The zinc was dried over night under vacuum at 80 °C and then cooled under argon. To a flask was added activated zinc (340 mg, 5.18 mmol), THF (0.5 mL) and a crystal of iodine. A solution of **14**[1] (100 mg, 0.518 mmol, 1:1 E/Z mixture) and THF (0.4 mL) and a solution of acrolein (35 μL, 0.52 mmol) and THF (1.8 mL) were added to the reaction flask via cannula. The reaction mixture set to stir under reflux for 2 h. The flask was then cooled and quenched in ice water. The aqueous phase was extracted with ethyl acetate three times and the combined organic extracts were washed once with brine. The organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography (1:19 to 1:4 ethyl acetate/hexanes) yielding **15** (22 mg, 25 %) and (±)-**5** (39 mg, 54%).[2]

Compound (±)-**5** was separated by chiral HPLC using an analytical column, Chiralpak IA (25 cm), 5:95 isopropanol/hexanes, 0.5 mL/min, wavelength 215 nm. (-)-**5** = 24.701 min; (+)-**5** = 25.918 min.

*Synthesis of compound **17***:



16 **17**

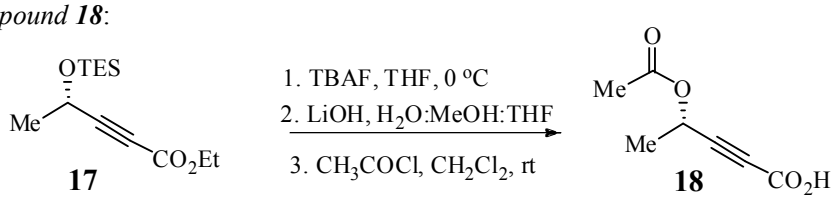
A solution of commercially available (*S*)-but-3-yn-2-ol **16** (200 mg, 2.85 mmol) in CH_2Cl_2 (35 mL), triethylamine (2 mL, 14.3 mmol) was added and cooled to -78 °C. Triethylsilyl trifluoromethanesulfonate (0.71 mL, 3.14 mmol) was then added and stirred at -78 °C for 0.5 h. The

[1] Lei, B.; Fallis, A. G.; *Can. J. Chem.* **1991**, 69, 1450.
[2] Ghosh, A. K.; Cheng, X. *Org. Lett.* **2011**, 13, 4108.

reaction mixture was quenched with $NaHCO_3$. Once warmed to room temperature, the aqueous phase was extracted three times with ethyl acetate. The organic layers were combined and washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel chromatography (1:9 to 1:4 ethyl acetate/hexane) yielding (*S*)-(but-3-yn-2-yloxy)triethylsilane (492 mg, 94%) as a colorless oil; $[\alpha]_D^{20}$ -3.7 (*c* 0.135, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.52 (q, *J* = 6.4, 4.5 Hz, 1H), 2.37 (s, 1H), 1.44 (d, *J* = 6.7 Hz, 3H), 0.99 (t, *J* = 8 Hz, 9H), 0.66 (q, *J* = 15.0, 7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 71.0, 58.3, 25.3, 6.6, 4.6; IR (neat) 2922, 2852, 2352, 1464 cm^{-1}.

To a solution of (*S*)-(but-3-yn-2-yloxy)triethylsilane (320 mg, 1.7 mmol) in THF (17 mL) at -78 °C was added *n*-butyllithium (1.3 mL, 2.1 mmol, 1.6 M solution in hexanes). After stirring for 0.5 h at -78 °C, freshly distilled ethyl chloroformate was added (0.2 mL, 2.1 mmol) dropwise and continued stirring at -78 °C. After 1 h, the reaction mixture was quenched with $NaHCO_3$. Once warmed to room temperature, the aqueous phase was extracted with ethyl acetate three times. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified via silica gel chromatography (1:19 to 1:9 ethyl acetate/hexane) to afford **17** (381 mg, 86%) as a pale yellow oil. $[\alpha]_D^{20}$ -61.8 (*c* 0.11, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.61 (q, *J* = 13.6, 6.8 Hz, 1H), 4.23 (q, *J* = 14.0, 7.2 Hz, 2H), 1.48 (d, *J* = 6.4 Hz, 3H), 1.30 (t, *J* = 6.8 Hz, 3H), 0.97 (t, *J* = 7.6 Hz, 9H), 0.66 (q, *J* = 8.4, 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 88.9, 75.1, 61.8, 58.2, 24.4, 13.9, 6.5, 4.5; IR (neat) 2957, 2346, 2236, 1718, 1458, 1246, 1102, 1074, 1018, 748 cm^{-1}; LRMS (ESI), *m/z* 280.2 $(M+Na)^+$.

*Synthesis of compound **18***:

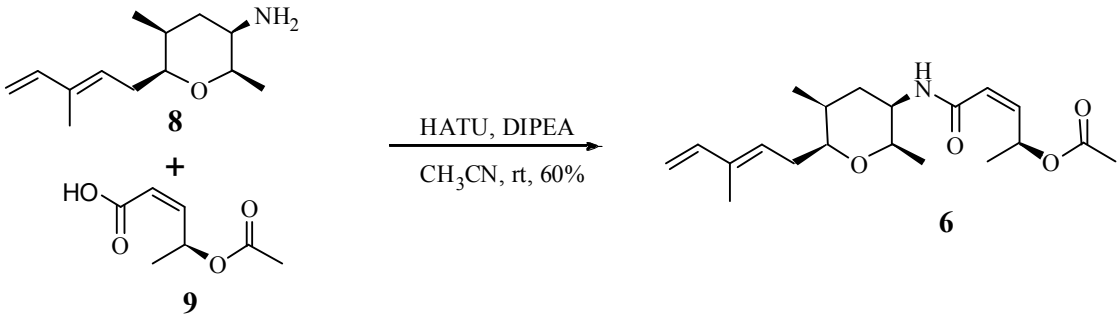


To a solution of **17** (377 mg, 1.5 mmol) in THF (15 mL) at 0 °C was added TBAF (1 M in THF, 1.6 mL, 1.6 mmol). The reaction mixture was quenched immediately with water. The aqueous phase was extracted with ethyl acetate three times. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel chromatography (1:4 to 1:1 ethyl acetate/hexane) to afford ethyl (*S*)-4-hydroxypent-2-ynoate (163 mg, 78%) as a colorless oil. $[\alpha]_D^{20}$ -24.7 (*c* 0.95, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.65 (q, *J* = 13.4, 6.6 Hz, 1H), 4.25 (q, *J* = 14.3, 7.3 Hz, 2H), 1.53 (d, *J* = 5.0 Hz, 3H), 1.31 (t, *J* = 5.8

Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 88.3, 75.7, 62.1, 57.9, 23.1, 13.9; IR (neat) 3403, 2987, 2245, 1714, 1369, 1249, 1124, 1063, 1020, 896, 752 cm^{-1}.

To ethyl (*S*)-4-hydroxypent-2-ynoate (147 mg, 1 mmol) was added LiOH (1 M aqueous solution, 3 mL), a few drops of THF and MeOH (1 mL) and was set to stir at room temperature. After 1 h, the reaction mixture was cooled to 0 ^{o}C and 1 N HCl was added to adjust the pH to 1-2. The aqueous phase was extracted with ethyl acetate four times and the combined organic extracts were washed with brine, filtered, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel chromatography (1:9 to 3:7 ethyl acetate/hexane) to afford (*S*)-4-hydroxypent-2-ynoic acid[2] (98 mg, 83%) as a colorless oil. (*S*)-4-hydroxypent-2-ynoic acid (98 mg, 0.86 mmol) was used to generate **18** (100 mg, 75%) by following the known procedure of Ghosh and co-workers.[3]

*Synthesis of amide **6***:

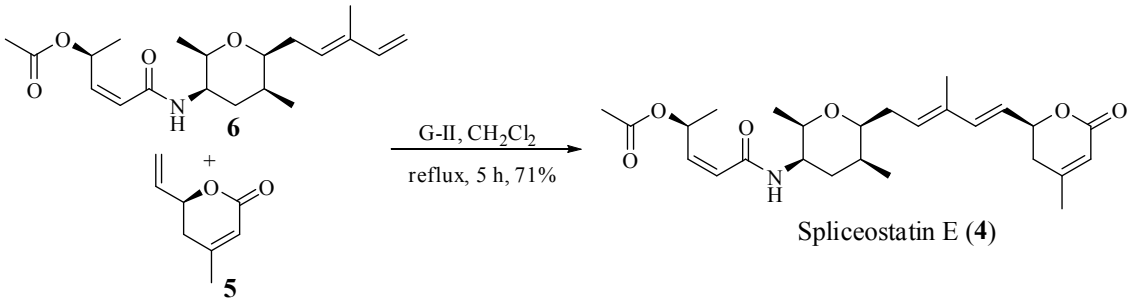


To a stirred solution of acid **9** (19.5 mg, 0.12 mmol) in anhydrous acetonitrile (2 mL) at room temperature under argon was added HATU (49 mg, 0.12 mmol) and DIPEA (68 μL, 0.38 mmol). The resulting mixture was then transferred via cannula to a stirred solution of amine **8** (20 mg, 0.09 mmol) in acetonitrile (2 mL) at room temperature and rinsed with additional acetonitrile (1 mL). After stirring for 24 h, the reaction was quenched by addition of saturated aqueous NH_4Cl (1 mL) and then diluted with ethyl acetate (5 mL). The aqueous layer was extracted with ethyl acetate (3 x 5 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated. The residue was purified via silica gel chromatography (hexane/ethyl acetate, 83:17) to afford amide **6** (20 mg, 60%) as colorless oil. $[\alpha]_D^{20}$ -58.6 (c 1.05, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (dd, *J* = 17.6, 10.8 Hz, 1H), 6.26 (dt, *J* = 13.6, 6.8 Hz, 1H), 6.00 (d, *J* = 8.8 Hz, 1H), 5.89 (dd, *J* = 11.6, 8.0 Hz, 1H), 5.70 (d, *J* = 11.6 Hz, 1H), 5.46 (t, *J* = 6.8 Hz, 1H), 5.10 (d, *J* = 17.6 Hz, 1H), 4.95 (d, *J* = 10.8 Hz, 1H), 3.94 (t, *J*

[3] Ghosh, A. K.; Chen, Z.; Effenberger, K. A.; Jurica, M. S. *J. Org. Chem.* **2014**, 79, 5697.

= 3.2 Hz, 1H), 3.67 (dd, *J* = 6.4, 2.0 Hz, 1H), 3.54 (dt, *J* = 7.6, 2.8 Hz, 1H), 2.45−2.32 (m, 1H), 2.30−2.17 (m, 1H), 2.04 (s, 3H), 2.00−1.86 (m, 2H), 1.84-1.75 (m, 1H), 1.75 (s, 3H), 1.39 (d, *J* = 6.4 Hz, 3H), 1.15 (d, *J* = 6.4 Hz, 3H), 1.02 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 164.8, 143.6, 141.3, 135.7, 128.1, 122.5, 111.1, 80.8, 76.0, 68.9, 47.1, 35.8, 31.9, 28.9, 21.2, 20.0, 17.8, 15.0, 11.9; IR (neat) 3358, 2977, 2934, 1739, 1668, 1634, 1520, 1369, 1243, 1049, 1011 cm^{-1}; HRMS (ESI), m/z $(M + Na)^+$ calcd for $C_{20}H_{31}NO_4Na$ 372.2151, found 372.2152.

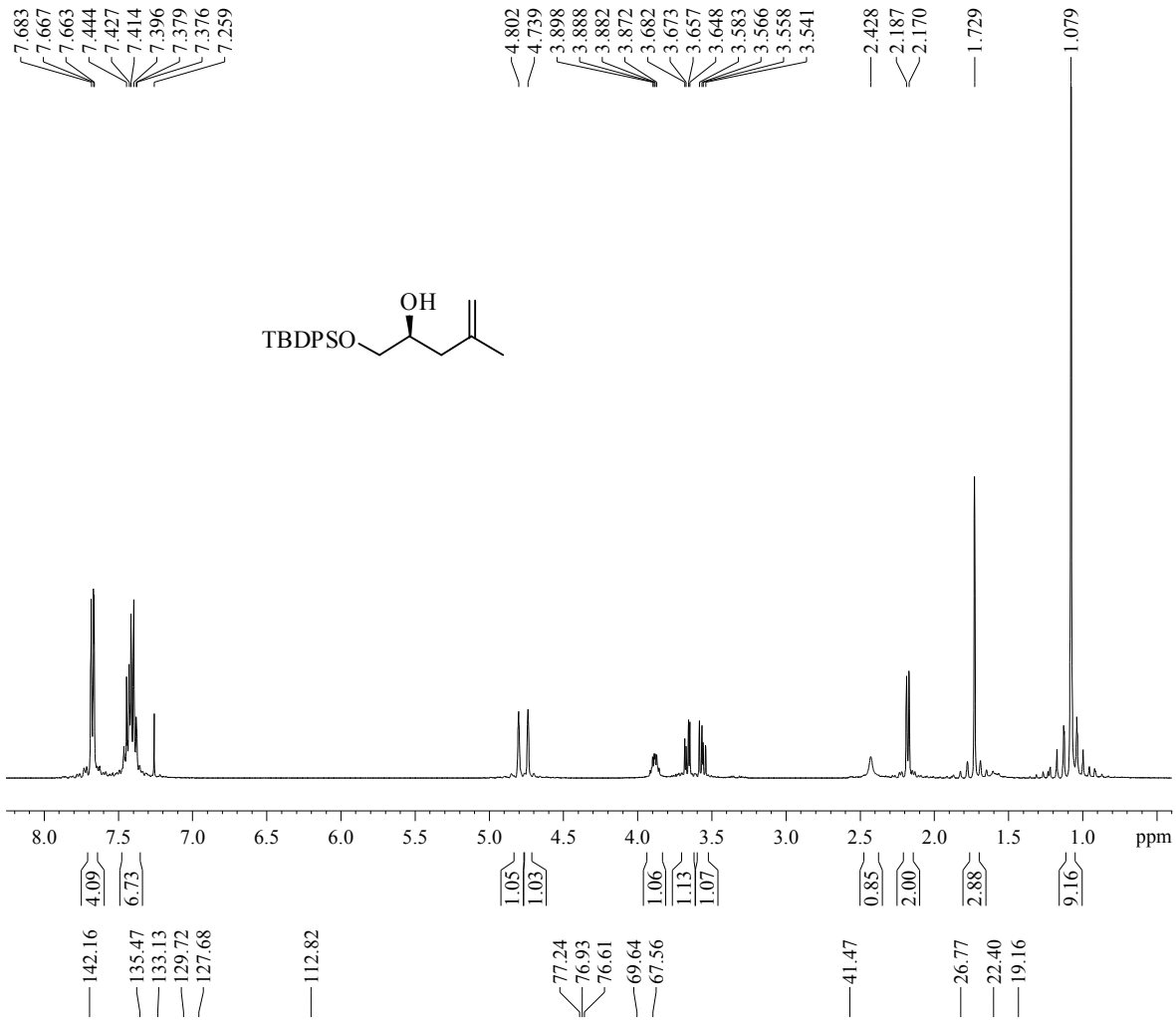
*Synthesis of (-) Spliceostatin E (**4**)*:



Spliceostatin E (**4**)

To a solution of **6** (7.5 mg, 0.021 mmol) in anhydrous dichloromethane (1 mL) at room temperature under argon was added a solution of **5** (4.5 mg, 0.032 mmol) in anhydrous dichloromethane (500 μL) and Grubbs' 2nd generation catalyst (2.0 mg, 0.002 mmol). The resulting mixture was heated to reflux for 5 h and then concentrated. The residue was purified by column chromatography (hexane/ethylacetate, 70:30) to afford spliceostatin E (**4**) (7.0 mg, 71%) as a white solid. $[\alpha]_D^{20}$ -70.0 (*c* 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, DMSO-*d6*) δ 7.79 (d, *J* = 7.9 Hz, 1H), 6.36-6.29 (m, 2H), 6.07 (dd, *J* = 11.6, 1.2 Hz, 1H), 5.83 (dd, *J* = 11.6, 7.5 Hz, 1H), 5.73 (s, 1H), 5.63 (dd, *J* = 15.8, 6.7 Hz, 1H), 5.57 (t, *J* = 6.9 Hz, 1H), 4.94-4.89 (m, 1H), 3.64-3.59 (m, 2H), 3.51-3.46 (m, 1H), 2.44-2.37 (m, 2H), 2.33-2.25 (m, 1H), 2.21-2.14 (m, 1H), 1.94 (s, 3H), 1.92 (s, 3H), 1.80-1.75 (m, 2H), 1.68 (s, 3H), 1.21 (d, *J* = 6.5 Hz, 3H), 1.03 (d, *J* = 6.3 Hz, 3H), 0.91 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-*d6*) δ 170.0, 164.9, 164.4, 159.0, 143.1, 137.5, 133.7, 131.1, 124.4, 123.1, 115.7, 80.2, 77.5, 75.2, 68.4, 46.7, 35.5, 34.6, 32.1, 29.1, 22.8, 21.4, 20.3, 18.1, 14.6, 12.7; IR (neat) 3352, 2923, 2853, 1723, 1717, 1698, 1677, 1517, 1451, 1383, 1243, 1045, 855 cm^{-1}; LRMS (ESI), *m/z* 482.5 $(M+Na)^+$.

.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7.379
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4.739
3.898
3.888
3.882
3.872
3.682
3.673
3.657
3.648
3.583
3.566
3.558
3.541
2.428
2.187
2.170
1.729
1.079
OH
TBDPSO
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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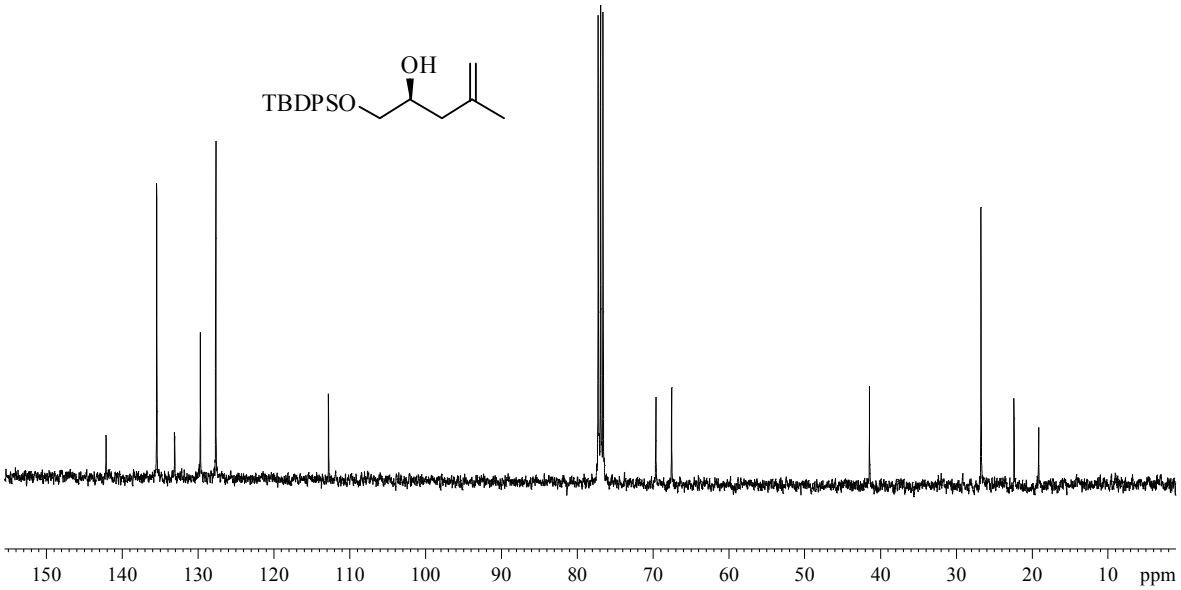
1.05
1.03
1.06
1.13
1.07
0.85
2.00
2.88
9.16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133.13
129.72
127.68
112.82
77.24
76.93
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69.64
67.56
41.47
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22.40
19.16
OH
TBDPSO
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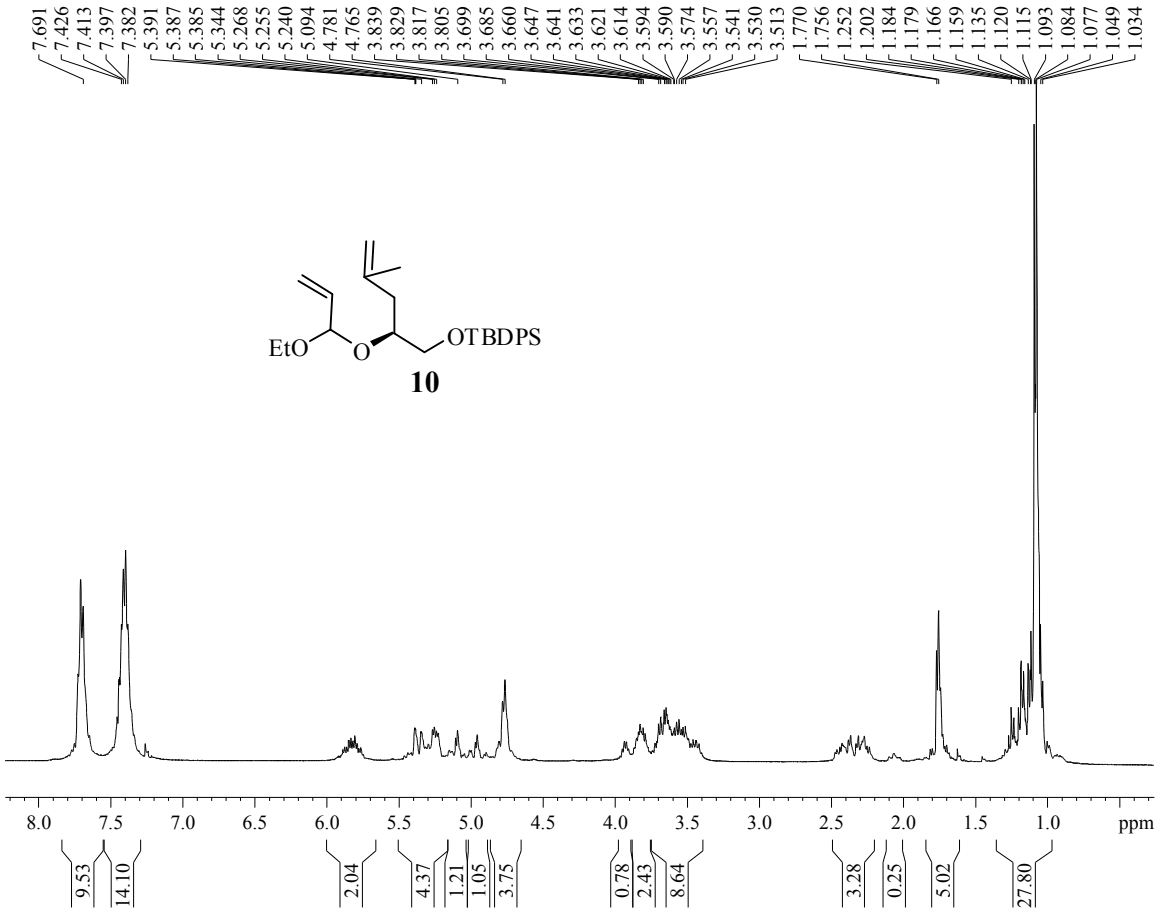
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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5.391
5.387
5.385
5.344
5.268
5.255
5.240
5.094
4.781
4.765
3.839
3.829
3.817
3.805
3.699
3.685
3.660
3.647
3.641
3.633
3.621
3.614
3.594
3.590
3.574
3.557
3.541
3.530
3.513
1.770
1.756
1.252
1.202
1.184
1.179
1.166
1.159
1.135
1.120
1.115
1.093
1.084
1.077
1.049
1.034
EtO
O
OTBDPS
10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
9.53
14.10
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1.21
1.05
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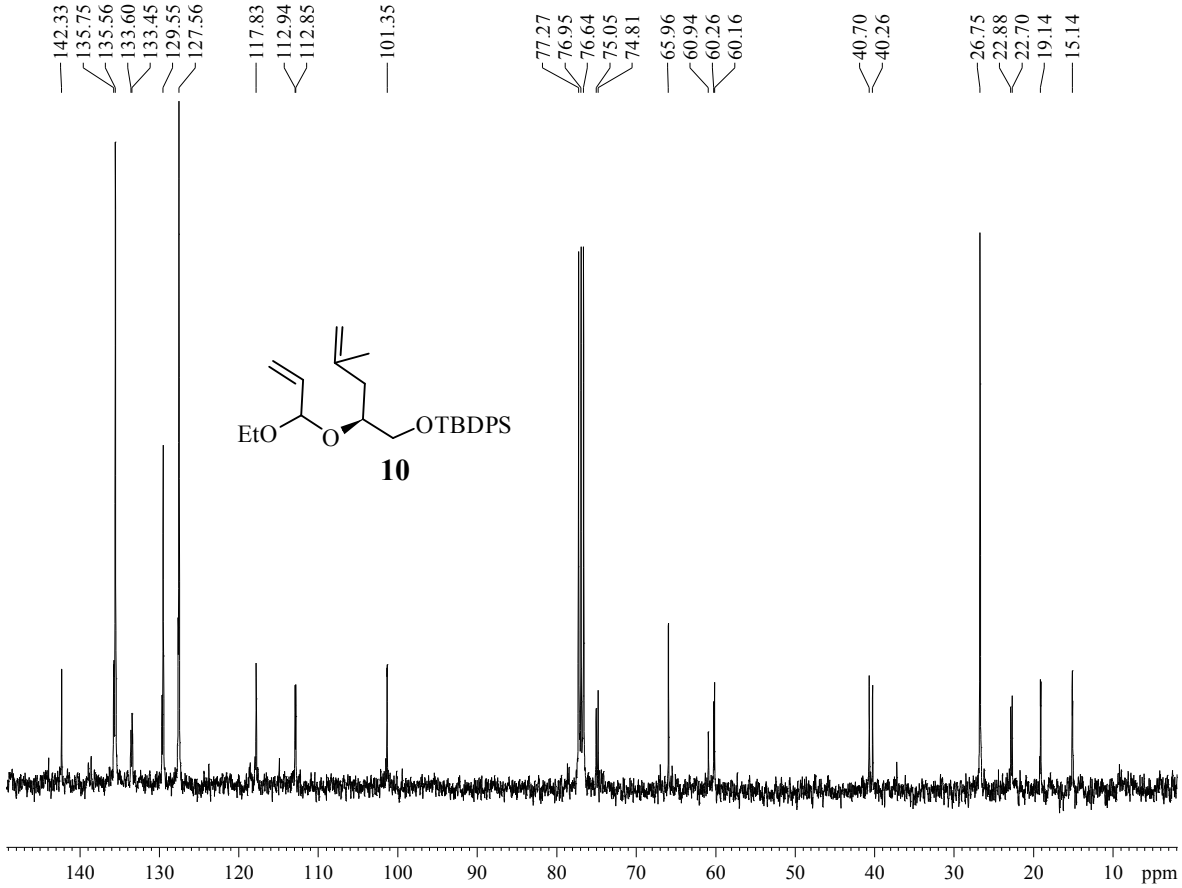
0.78
2.43
8.64
3.28
0.25
5.02
27.80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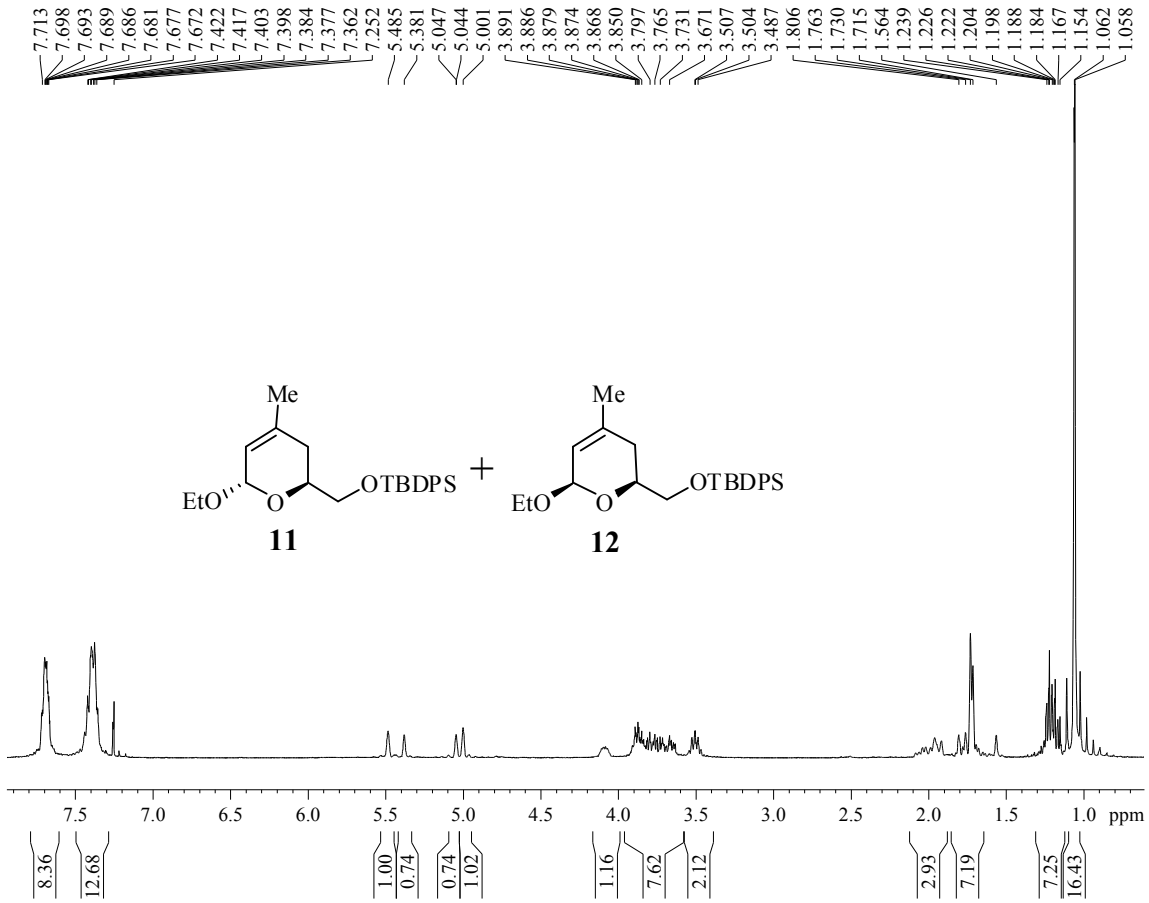
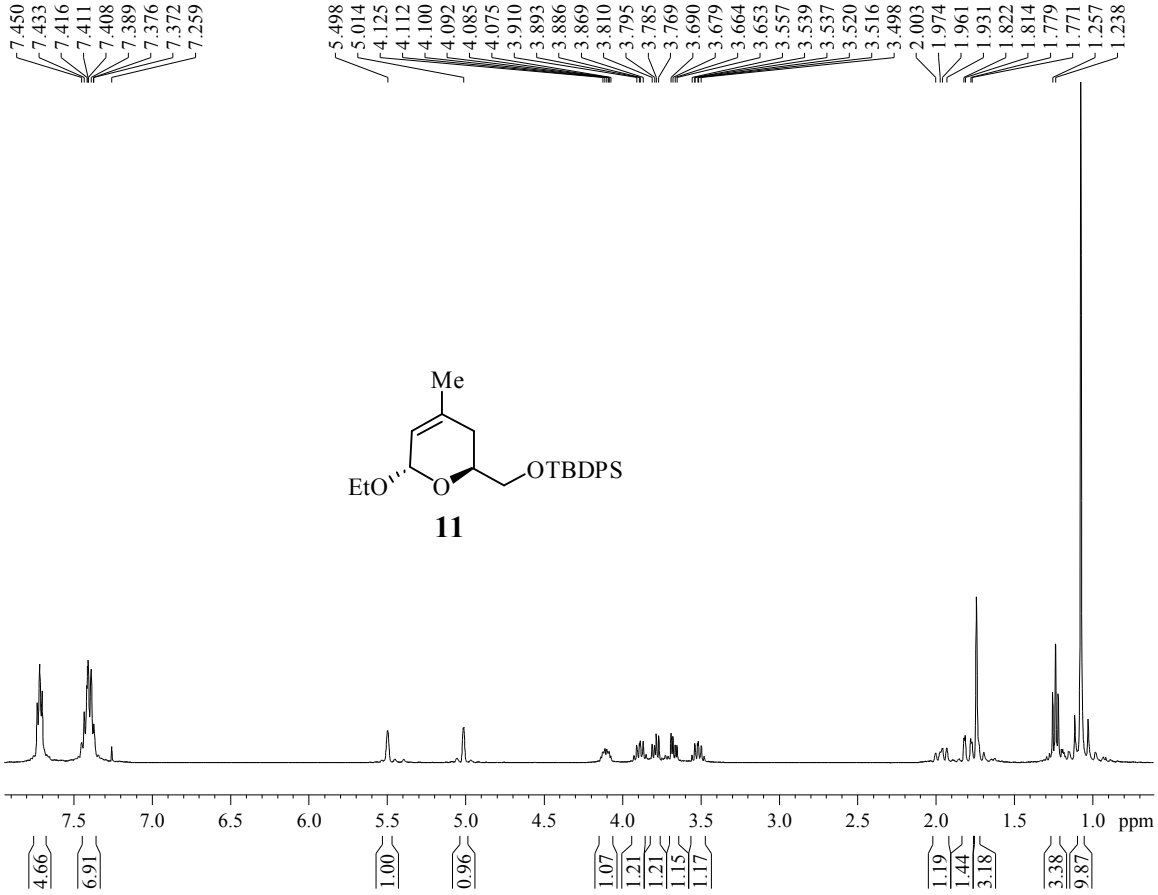
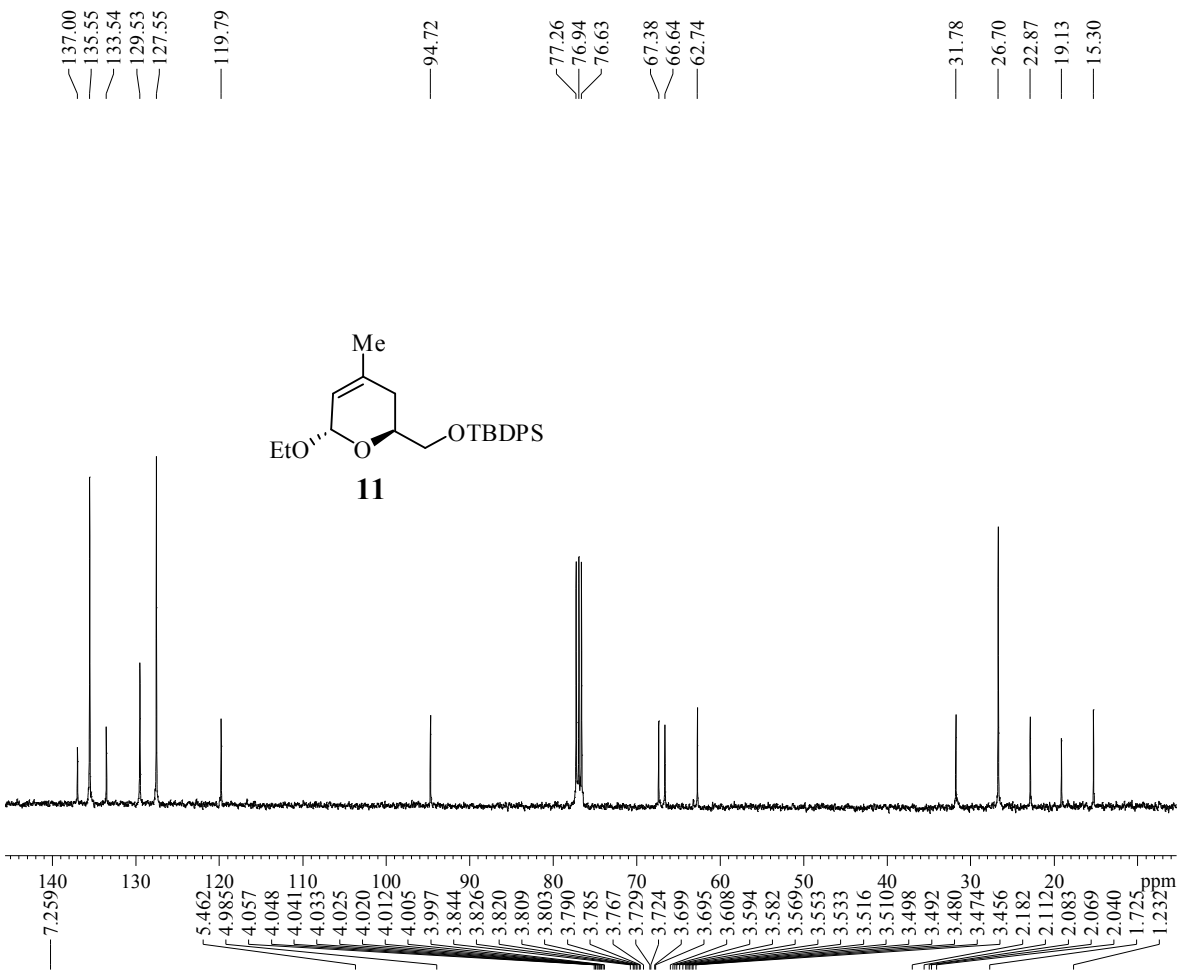
135.75
135.56
133.60
133.45
129.55
127.56
117.83
112.94
112.85
101.35
77.27
76.95
76.64
75.05
74.81
65.96
60.94
60.26
60.16
40.70
40.26
26.75
22.88
22.70
19.14
15.14
EtO
O
OTBDPS
10
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Me
EtO
O
OTBDPS
11
+
Me
EtO
O
OTBDPS
12
ppm


Me
EtO
O
OTBDPS
11
ppm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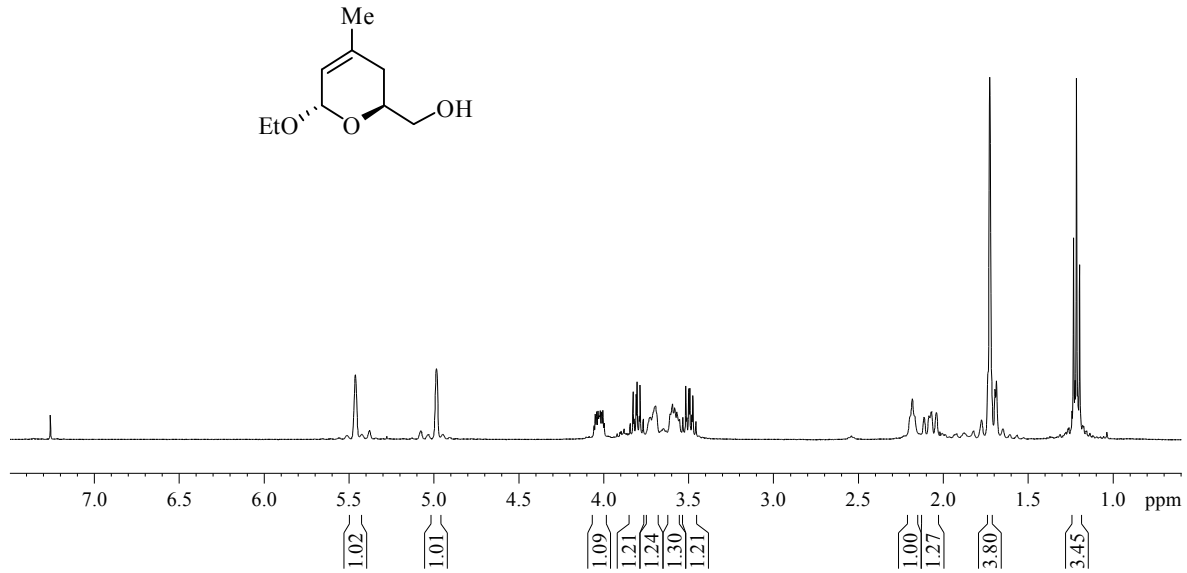
127.55
119.79
94.72
77.26
76.94
76.63
67.38
66.64
62.74
31.78
26.70
22.87
19.13
15.30
Me
EtO
O
OTBDPS
11
7.259
5.462
4.985
4.057
4.048
4.041
4.033
4.025
4.020
4.012
4.005
3.997
3.844
3.826
3.820
3.809
3.803
3.790
3.785
3.767
3.729
3.724
3.699
3.695
3.608
3.594
3.582
3.569
3.553
3.533
3.516
3.510
3.498
3.492
3.480
3.474
3.456
2.182
2.112
2.083
2.069
2.040
1.725
1.232
ppm


Me
EtO
O
OH
ppm
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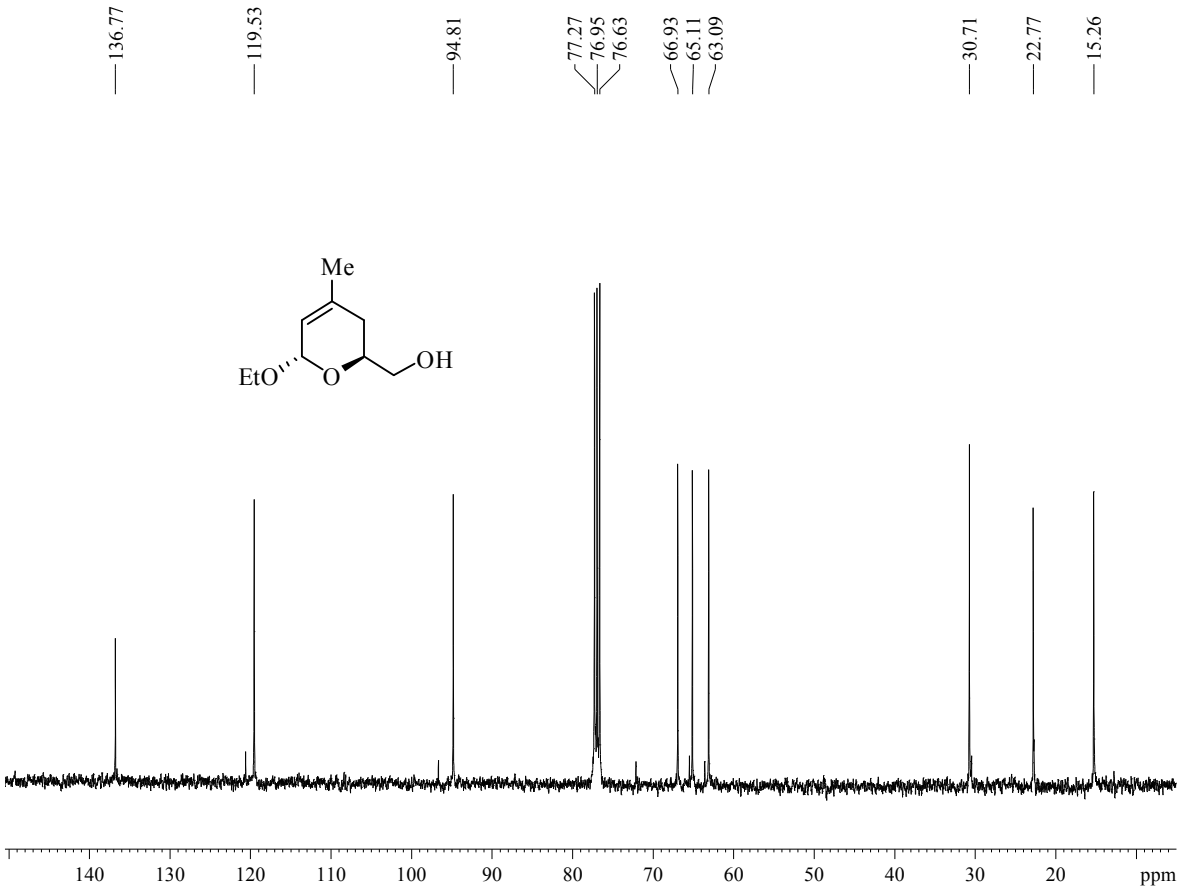
1.09
1.21
1.24
1.30
1.21
1.00
1.27
3.80
3.45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63.09
30.71
22.77
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O
OH
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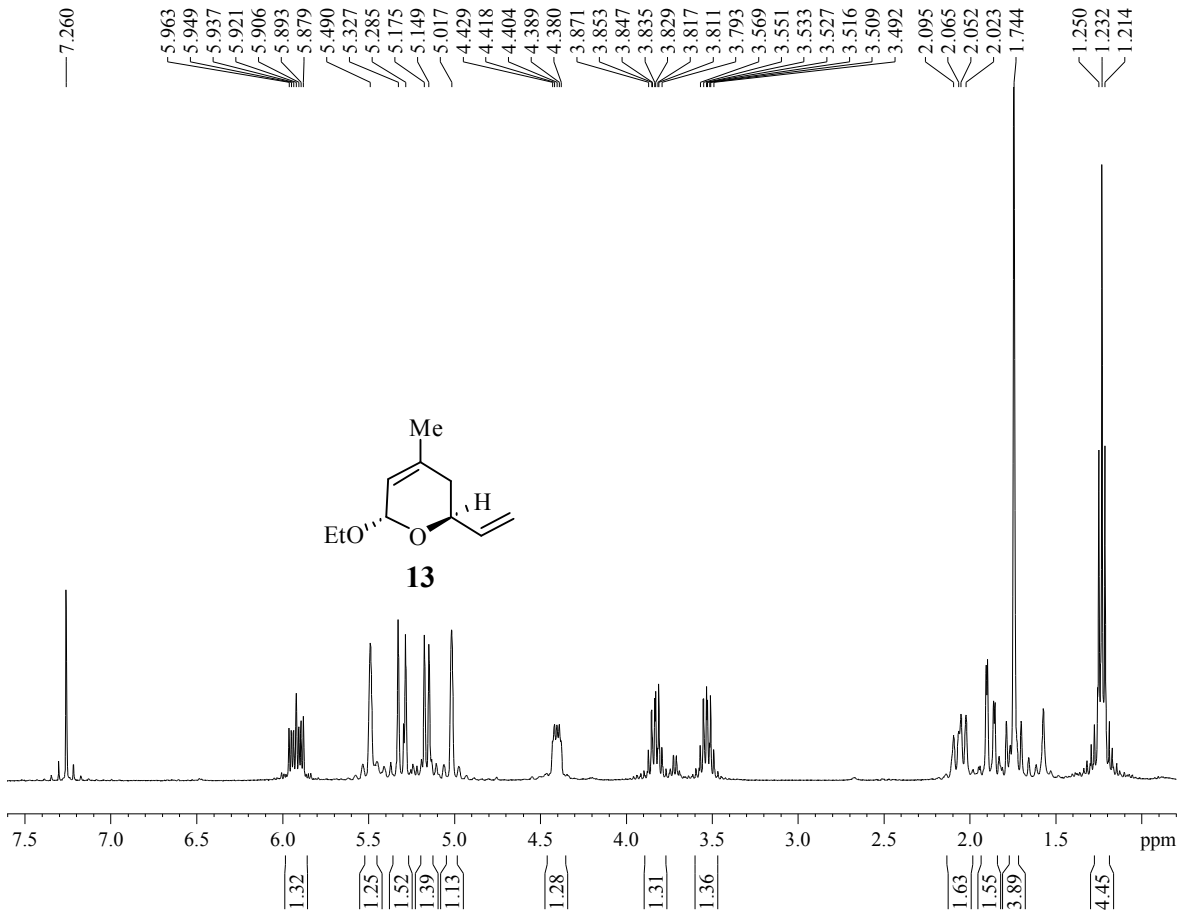
130
120
110
100
90
80
70
60
50
40
30
20
ppm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5.175
5.149
5.017
4.429
4.418
4.404
4.389
4.380
3.871
3.853
3.847
3.835
3.829
3.817
3.811
3.793
3.569
3.551
3.533
3.527
3.516
3.509
3.492
2.095
2.065
2.052
2.023
1.744
1.250
1.232
1.214
Me
H
EtO
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
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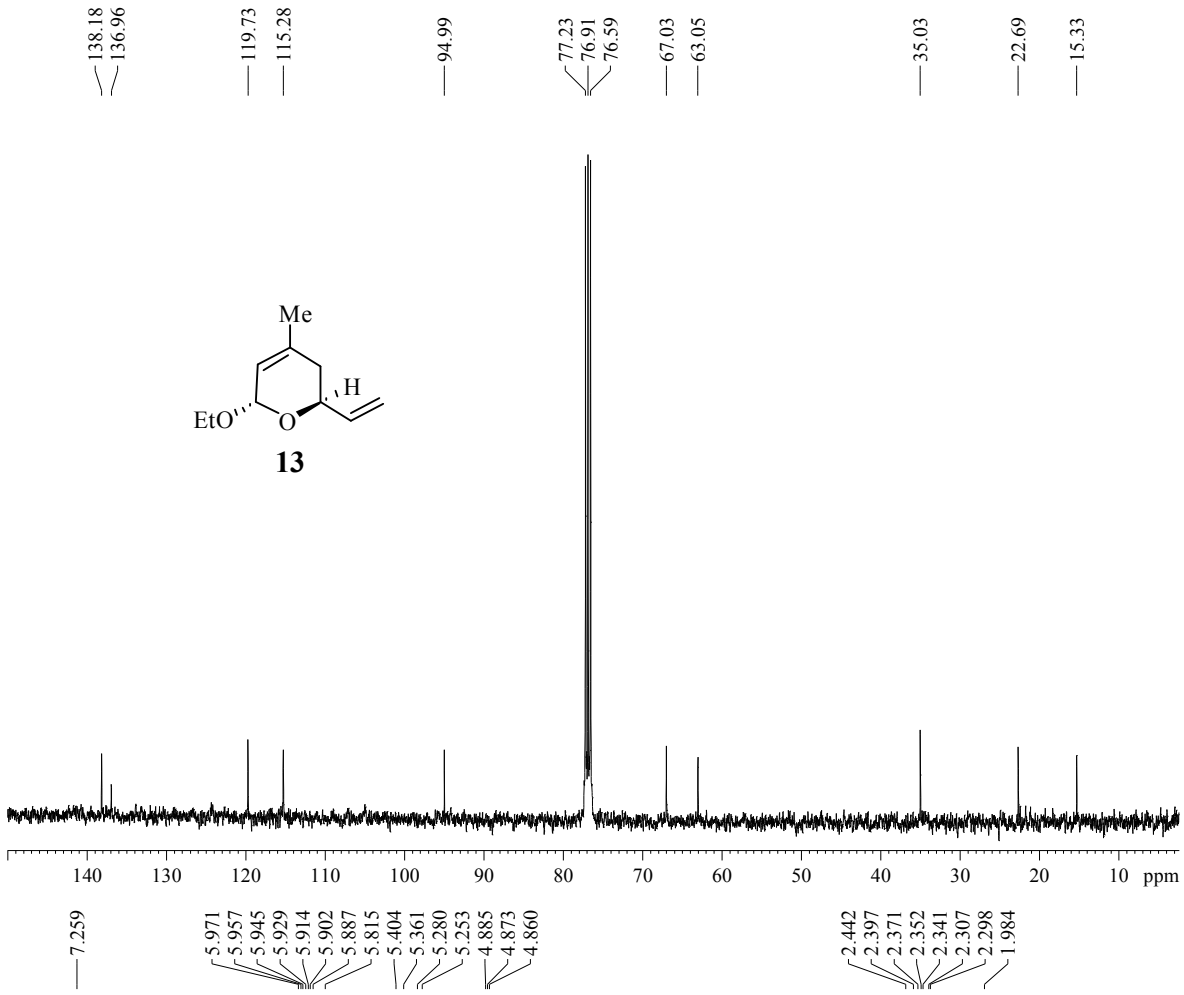
1.28
1.31
1.36
1.63
1.55
3.89
4.45

13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115.28
94.99
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76.91
76.59
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63.05
35.03
22.69
15.33
Me
H
EtO
O
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
7.259
5.971
5.957
5.945
5.929
5.914
5.902
5.887
5.815
5.404
5.361
5.280
5.253
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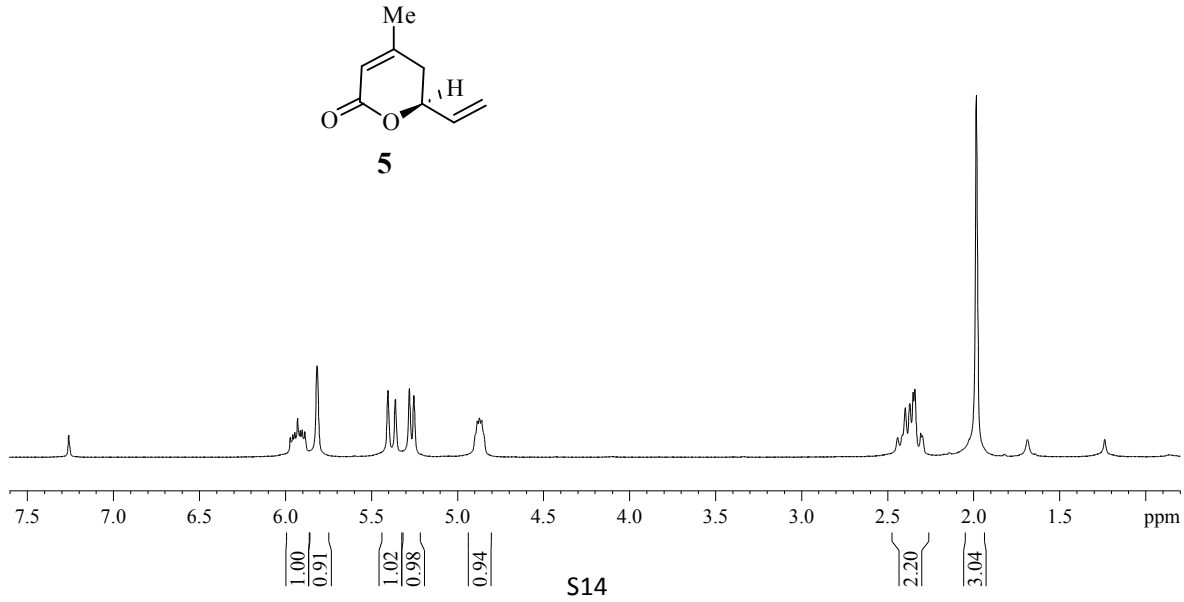
4.860
2.442
2.397
2.371
2.352
2.341
2.307
2.298
1.984

13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H
O
O
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5.0
4.5
4.0
3.5
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2.5
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1.5
ppm
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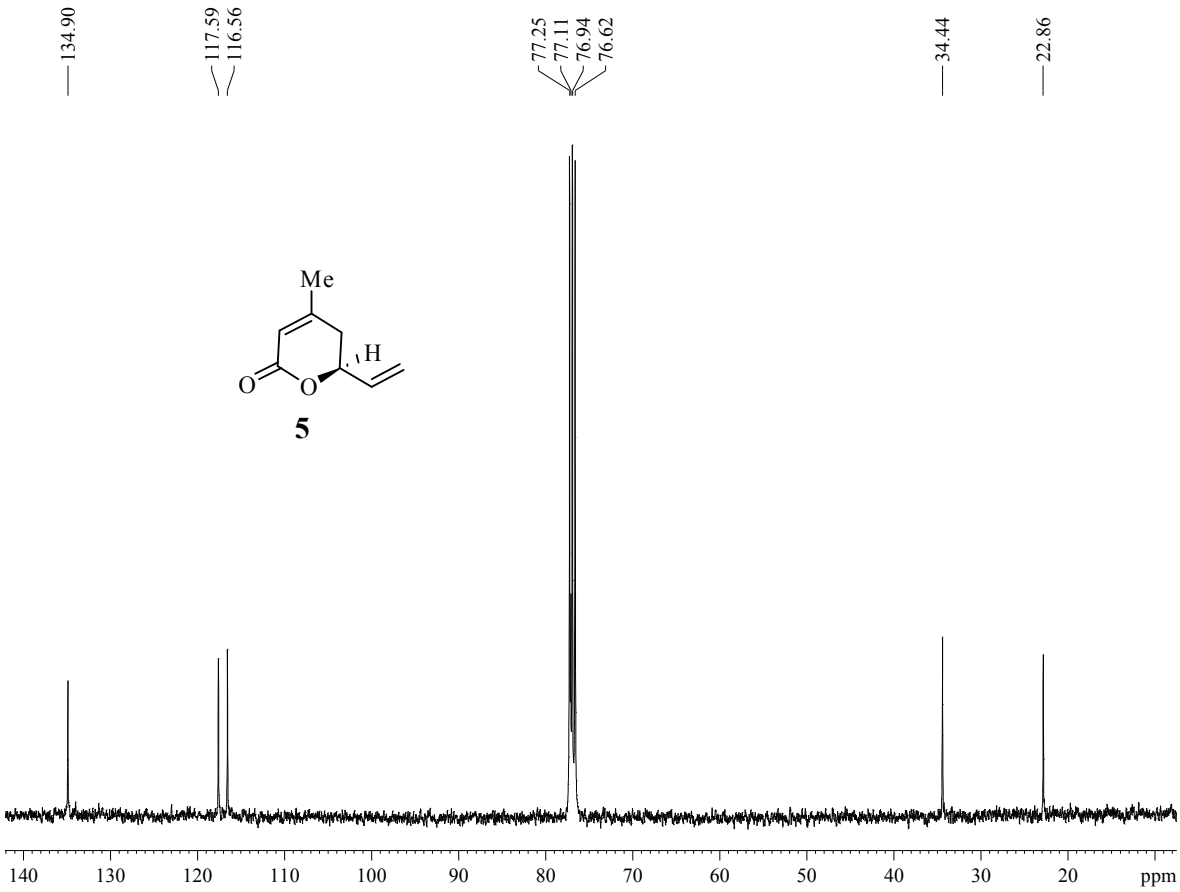
1.02
0.98
0.94
2.20
3.04

5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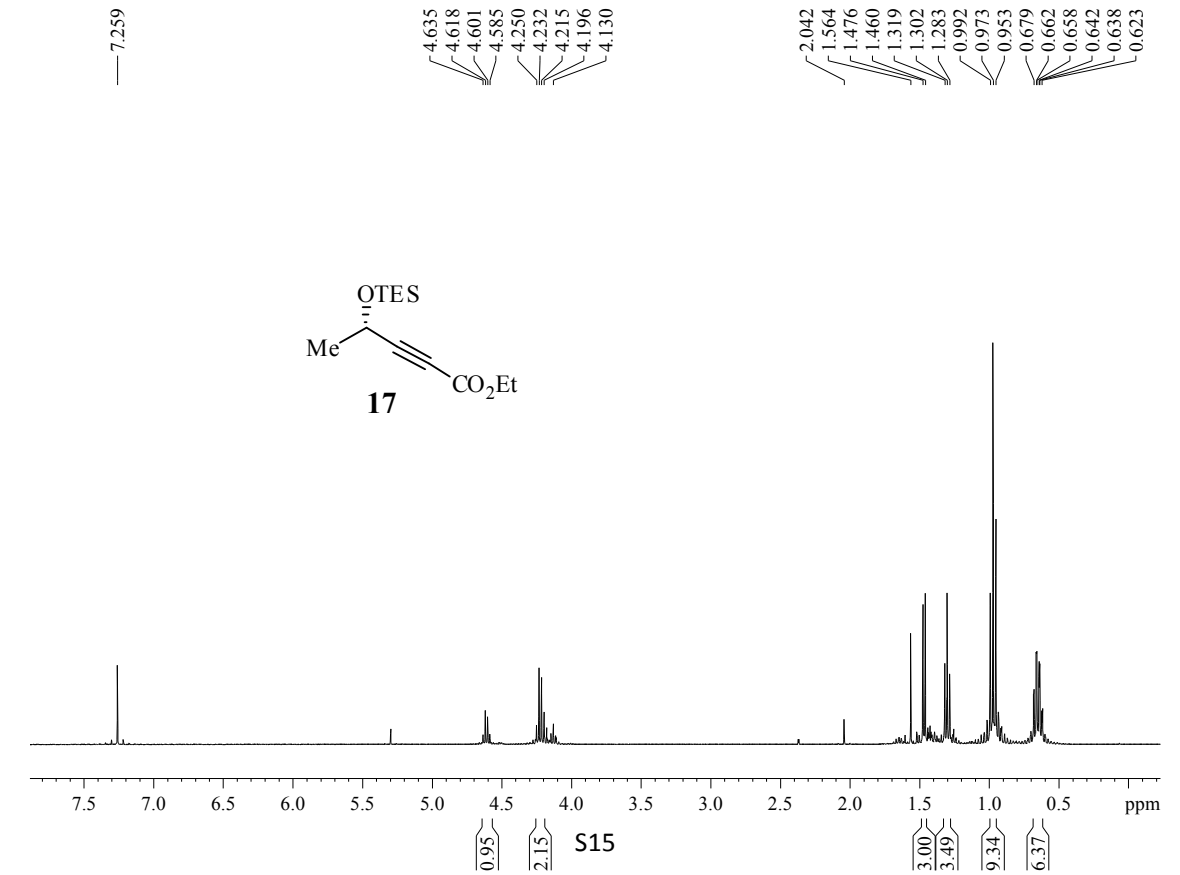
77.11
76.94
76.62
34.44
22.86
Me
H
O
O
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

5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4.130
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1.476
1.460
1.319
1.302
1.283
0.992
0.973
0.953
0.679
0.662
0.658
0.642
0.638
0.623
OTES
Me
CO2Et
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
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ppm
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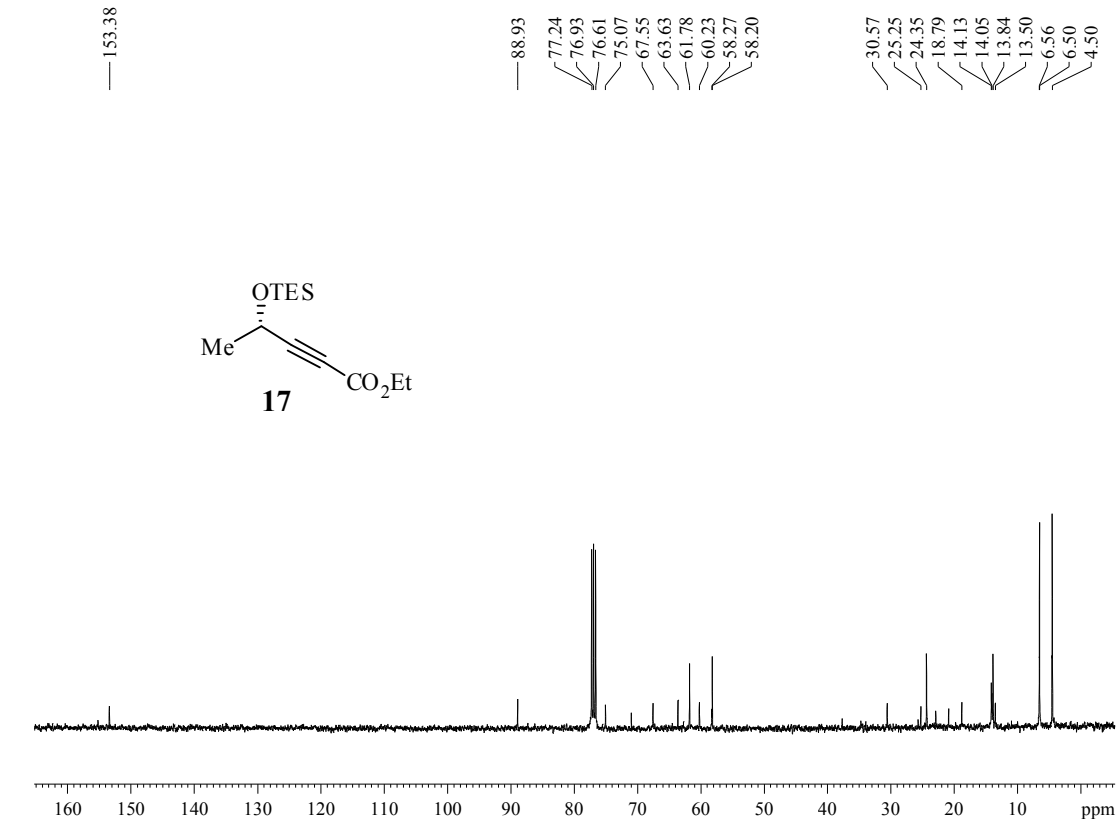
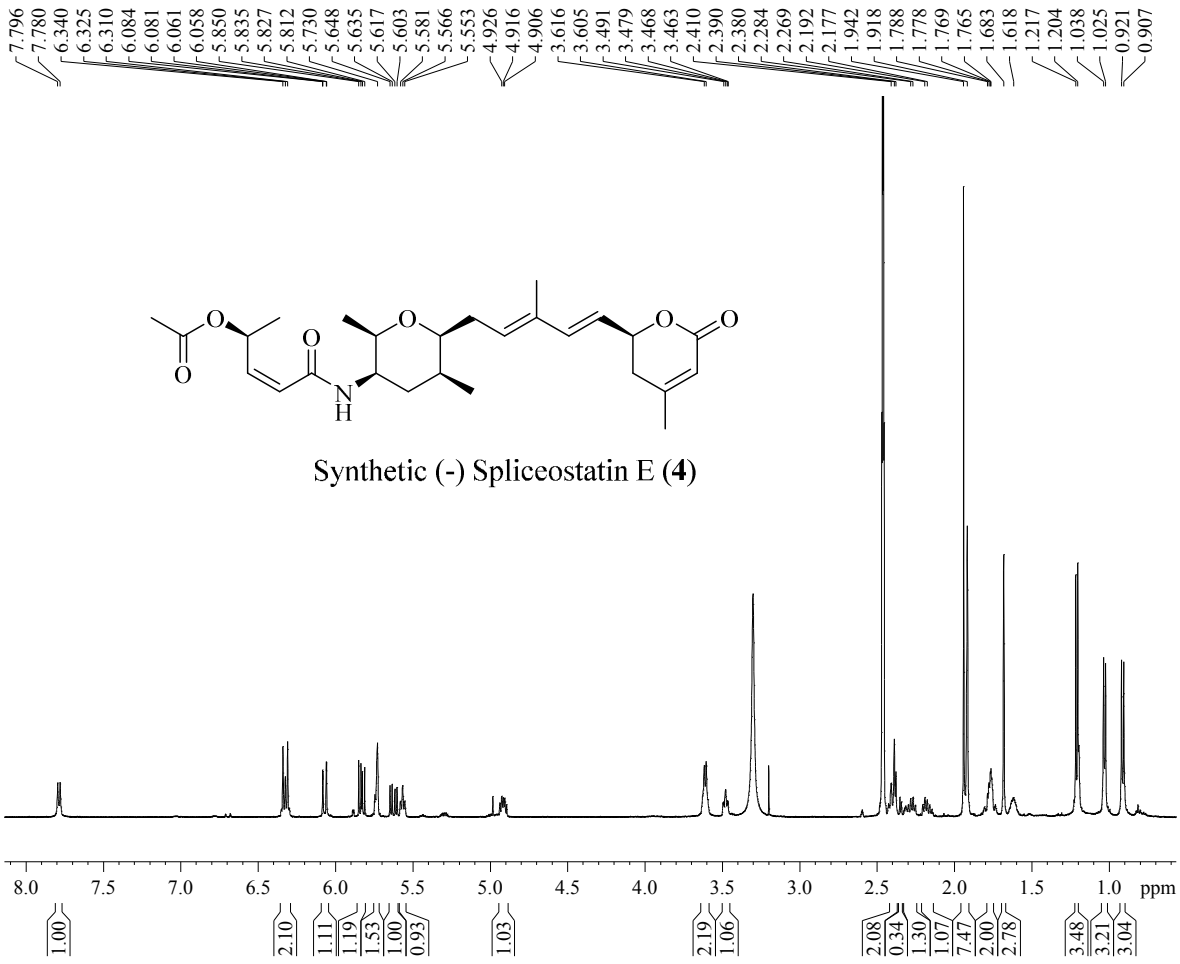
3.00
3.49
9.34
6.37

17

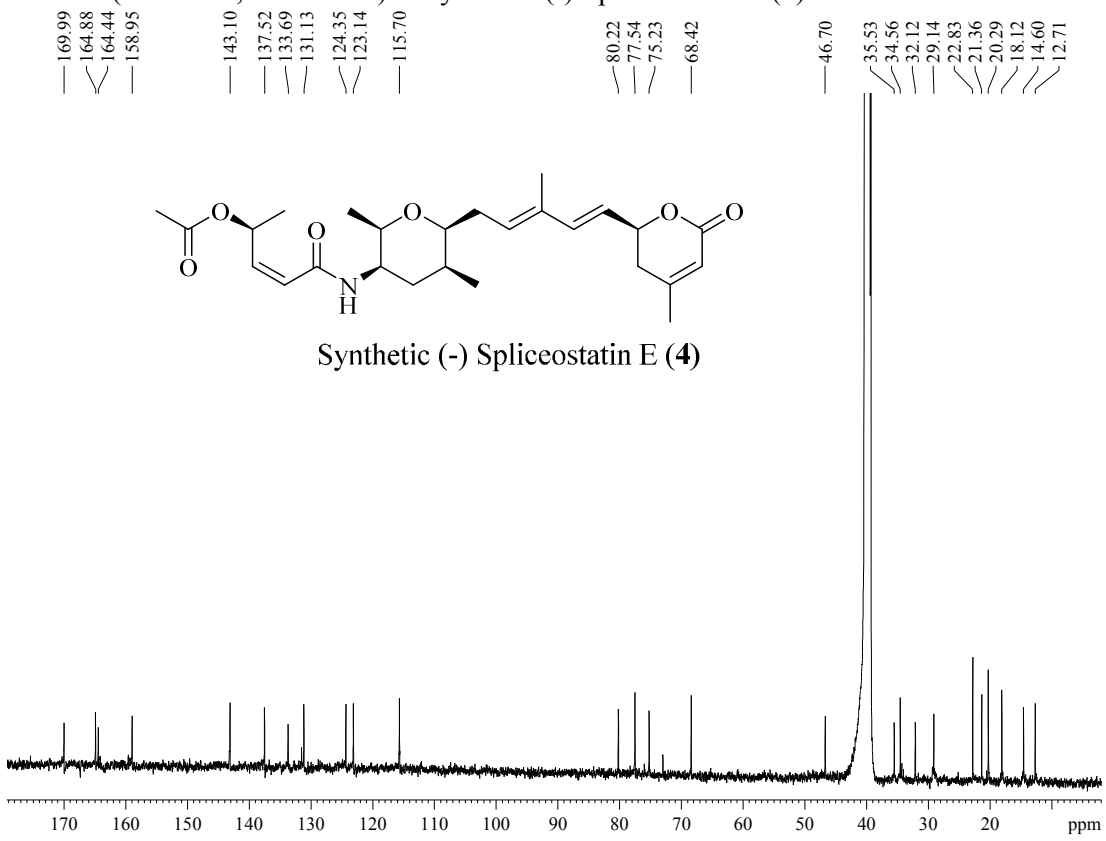


^{1}H NMR (500 MHz, DMSO-*d6*) of synthetic (-) Spliceostatin E

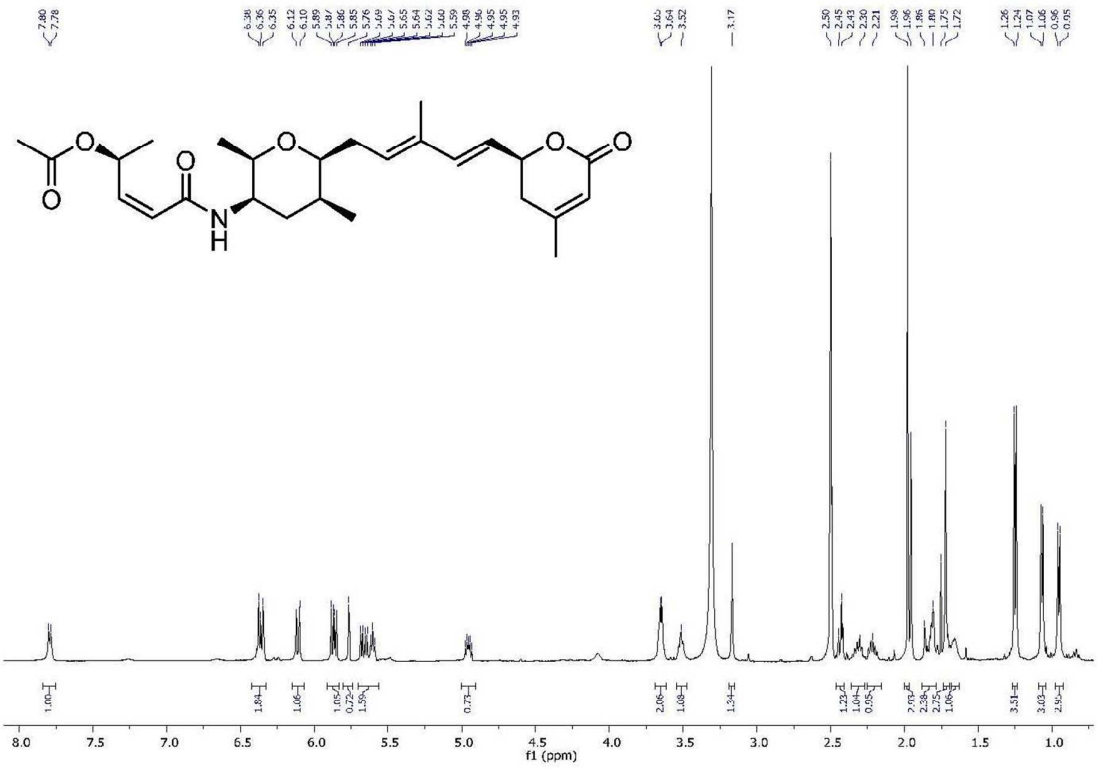


Synthetic (-) Spliceostatin E (**4**)

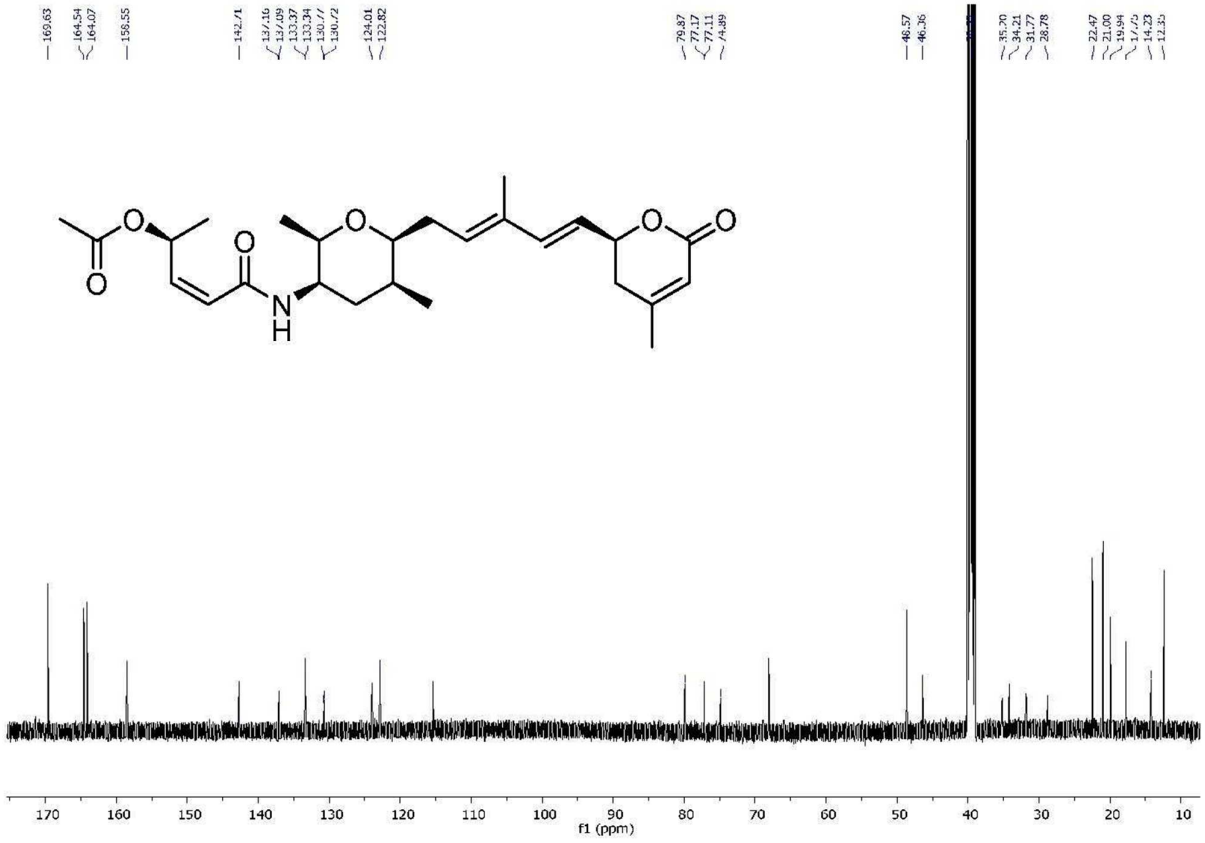
^{13}C NMR (125 MHz, DMSO-*d6*) of synthetic (-) Spliceostatin E (**4**)



^{1}H NMR (500 MHz, DMSO-*d6*) of Spliceostatin E (*J. Nat. Prod*. **2014**, *77*, 1864)



^{13}C NMR (125 MHz, DMSO-*d6*) of Spliceostatin E (*J. Nat. Prod*. **2014**, *77*, 1864)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164.07
158.55
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133.37
133.34
130.77
130.72
124.01
122.82
79.87
77.17
77.11
74.89
46.57
46.36
35.70
34.21
31.77
28.78
22.47
21.00
19.94
17.75
14.23
12.35
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)