Gold Catalyzed Alkyne-Diol Bicycloketalization Enables Enantioselective Divergent Total Syntheses of Attenols.

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Supporting Information

1. General information

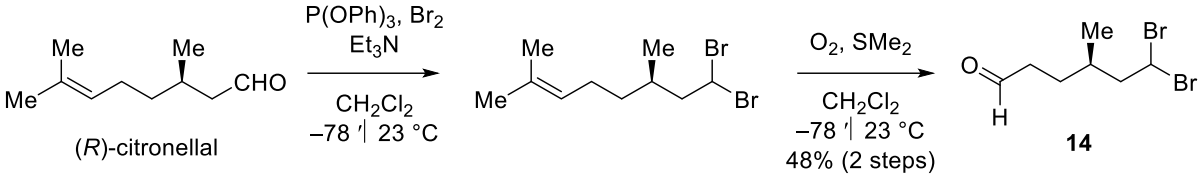
All reactions were performed in oven-dried or flame-dried flasks. Unless otherwise noted, the flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon. Stainless steel syringes or cannula were used to transfer air- and moisture-sensitive liquids. Flash column chromatography was performed as described by Still et al. using silica gel g silica gel (60-Å pore size, 40–63 μm, 4-6% H_2O content, Merck).[1] Analytical thin–layer chromatography (TLC) was performed using glass plates pre-coated with 0.25 mm silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light, exposure to iodine vapor, or treatment with acidic anisaldehyde or an aqueous ammonium cerium nitrate/ammonium molybdate (Seebach's staining). [2]

2. Materials and Instrumentations

Unless otherwise stated, all commercial reagents and solvents were used without additional purification with the following exceptions: Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from sodiumbenzophenone ketyl under nitrogen; dichloromethane (CH_2Cl_2) was distilled from P_2O_5; benzene and toluene were washed with concentrated sulfuric acid and water, and distilled from sodium.

^1H and ^{13}C nuclear magnetic resonance spectra were recorded with Bruker Avance III HD (9.4 T) 400 (400 MHz), Bruker Avance III HD Nanobay 400 (400 MHz), Bruker Avance NEO Nanobay 400 (400 MHz), Bruker Avance Neo (11.74 T) 500 (500 MHz) and calibrated by using the undeuterated chloroform (δ_H= 7.24 ppm) and $CDCl_3$ (δ_C= 77.00 ppm), undeuterated methanol-*d*$_4$ (δ_H= 3.31 ppm) and methanol-*d*$_4$ (δ_C= 49.00 ppm) or undeuterated benzene (δ_H 7.16 ppm) and C_6D_6 (δ_C= 128.06 ppm) as internal references. Data are reported in the following manners: chemical shift in ppm [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, br = broad), coupling constant(s) in Hertz, integration]. The NMR solvent $CDCl_3$ was taken from a stock containing anhydrous K_2CO_3 to remove residual DCl. High resolution mass spectra were recorded on Bruker Daltonik micrOTOF-Q II (ESI ionization) from KAIST Research Analysis Center (Daejeon). Specific rotation $[\alpha]_D$ was obtained by JASCO P2000 polarimeter.

3. Experimental Procedures and Physical Data for Compounds

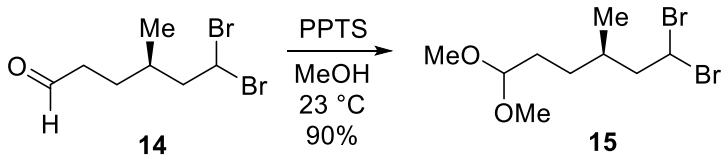


(−)-Aldehyde 14[1]

To a stirred solution of triphenylphosphite (5.9 mL, 22.47 mmol) in dry CH_2Cl_2 (65 mL) at −78 °C was added bromine (1.15 mL, 22.48 mmol) dropwise. Trimethylamine (7.83 mL, 56.19 mmol) and *(R)*-(+)-citronellal (2.9 g, 18.73 mmol) were added dropwise to the stirring mixture at the same temperature. The mixture was slowly warmed to 23 °C and let stirred for 1 hr. The solvent was concentrated under reduced pressure and crude residue was purified by flash column chromatography on silica gel (Hexane). To a stirred solution of the resulting gem-dibromide compound in dry CH_2Cl_2 in two neck RBF at −78 °C, ozone was purged for 40 minutes. Then, dimethylsulfide (5.3 mL, 72.15 mmol) was added to the mixture and heated to 23 °C. After stirring for 1 hr, the reaction mixture was quenched with saturated NH_4Cl (aq.) and extracted three times with CH_2Cl_2. The combined organic layer was drived over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:20) to give the known aldehyde **14**. (2.14 g, 2 step 48%, pale yellowish oil).

^{1}H NMR (400 MHz, Benzene-d_6) δ 9.19 (s, 1H), 5.23 (dd, J = 8.5, 5.7 Hz, 1H), 1.99 (ddd, J = 14.2, 8.5, 5.5 Hz, 1H), 1.77 (dd, J = 8.2, 5.9 Hz, 1H), 1.63 – 1.51 (m, 2H), 1.41 – 1.30 (m, 1H), 1.13 – 1.01 (m, 1H), 0.87 (dddd, J = 14.0, 9.1, 7.9, 6.3 Hz, 1H), 0.33 (d, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Benzene-d_6) δ 199.9, 52.3, 44.9, 40.9, 32.1, 27.7, 17.8.



(−)-Dimethyl-acetal 15

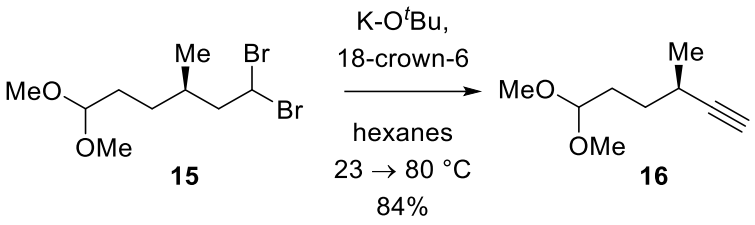
To a stirred solution of aldehyde **14 (**3.19 g, 11.73 mmol) in MeOH was added PPTS (295 mg, 1.17 mmol, 0.1 eq.) at 23°C and let stirred for 2.5 hr. The reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:20 → 1:10) to give acetal **15** (3.40 g, 90%, pale yellowish oil).

^{1}H NMR (400 MHz, Benzene-d_6) δ 5.35 (dd, J = 8.4, 5.9 Hz, 1H), 4.17 (t, J = 5.6 Hz, 1H), 3.11 (d, J = 1.6 Hz, 6H), 2.17 (ddd, J = 14.2, 8.4, 5.6 Hz, 1H), 1.90 (ddd, J = 14.5, 8.0, 5.9 Hz, 1H), 1.59 – 1.53 (m, 1H), 1.50 – 1.36 (m, 2H), 1.19 – 1.06 (m, 1H), 1.05 – 0.88 (m, 1H), 0.50 (d, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Benzene-d_6) δ 104.5, 52.8, 52.3, 52.3, 45.3, 32.5, 30.9, 29.9, 18.2.

HRMS (EI) m/z: Calculated for $C_9H_{17}Br_2O_2$ [M−H]· : 314.9595, Found: 314.9595

$[\alpha]_D^{25}$ −8.42 (c 1.03, $CHCl_3$)



(+)-Alkyne 16

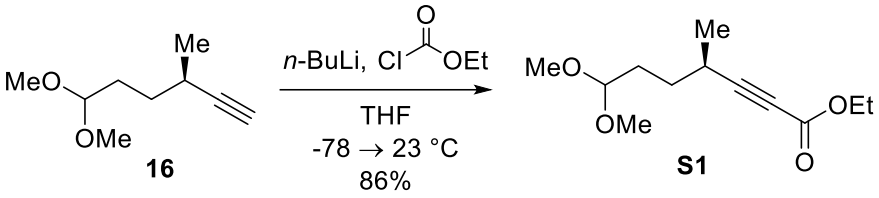
To a stirred solution of gem-dibromide **15** (2.14 g, 6.73 mmol) in two-neck RBF, in hexane at 23 °C were added K-O^{t}Bu (2.27 g, 20.20 mmol) and 18-crown-6 (89.1 mg, 0.337 mmol) in one portion and heated to 80 °C. After heating for overnight, the reaction mixture was cooled to 23 °C, and quenched with saturated NH_4Cl (aq.) and extracted three times with Et_2O. The combined organic layer was drived over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Et_2O: pentane = 1:20) to give alkyne **16** (0.88 g, 84%, pale yellowish oil). *Caution when handling the product as it has low b.p.*

^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.36 (t, *J* = 5.7 Hz, 1H), 3.39 – 3.17 (m, 6H), 2.53 – 2.29 (m, 1H), 2.03 (t, *J* = 1.6 Hz, 1H), 1.81 (ddd, *J* = 10.2, 6.6, 4.3 Hz, 1H), 1.68 (ddd, *J* = 10.4, 8.2, 5.2 Hz, 1H), 1.54 – 1.44 (m, 2H), 1.17 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 104.3, 88.5, 68.6, 52.8, 52.6, 31.5, 30.1, 25.5, 21.0.

HRMS (ESI): Calculated for $C_9H_{16}NaO_2$ $[M+Na]^+$: 179.1043, Found: 179.1054

$[\alpha]_D^{25}$ +4.3 (c 0.62, $CHCl_3$)



(−)-Ester S1

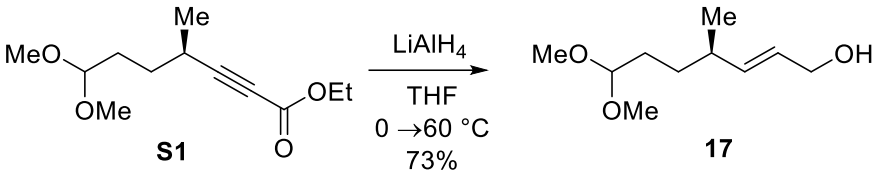
To a stirred solution of alkyne **16** (852 mg, 5.45 mmol) in THF at −78 °C was added *n*-BuLi (2.5 M solution in hexanes) (2.62 mL, 6.54 mmol). The mixture was stirred for 0.5 hr, and $ClCO_2Et$ (0.78 mL, 8.18 mmol) was added dropwise at −78 °C and heated to 23 °C. After stirring for 1 hr at 23 °C, the mixture was quenched with saturated NH_4Cl (aq.) and extracted three times with Et_2O. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:20 → 1:10) to give Ester **S1** (1.07 g, 86%, transparent oil).

^{1}H NMR (400 MHz, Benzene-d_6) δ 4.16 (t, J = 5.6 Hz, 1H), 3.90 (q, J = 7.1 Hz, 2H), 3.09 (d, J = 1.3 Hz, 6H), 2.35 – 2.10 (m, 1H), 1.83 – 1.69 (m, 1H), 1.60 (ddt, J = 13.7, 9.9, 5.9 Hz, 1H), 1.46 – 1.24 (m, 2H), 0.90 – 0.83 (m, 6H).

^{13}C NMR (101 MHz, Benzene-d_6) δ 153.8, 104.2, 92.2, 74.7 61.5, 52.5, 52.2, 31.1, 30.4, 25.9, 19.9, 13.9.

HRMS (ESI): Calculated for $C_{12}H_{20}NaO_4$ $[M+Na]^+$: 251.1254, Found: 251.1261

$[\alpha]_D^{25}$ −24.7 (c 0.52, $CHCl_3$)



(−)-Allylic alcohol 17

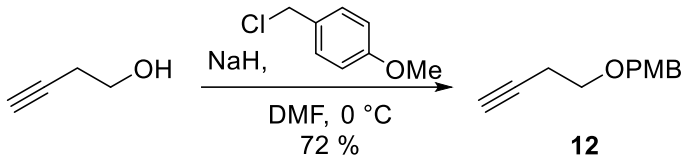
To a stirred suspension of $LiAlH_4$ (341 mg, 8.98 mmol) in THF (15 mL) at 0 °C in two-neck RBF, prepared for reflux, was added alkynyl ester **S1** (957.7 mg, 4.270 mmol) in THF (5 mL) dropwise. The mixture was slowly heated to 23 °C, then to reflux (60 °C) and let stirred for 1.5 hrs. The mixture was cooled to 0 °C, and H_2O (1mL) and saturated aq. Na_2SO_4 (1 mL) were added. After stirring the mixture for 10 mins at 0 °C, the crude mixture was filtered through celite and washed with Et_2O. Crude mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:2) to give allylic alcohol **17** (587 mg, 73%, transparent oil).

^{1}H NMR (400 MHz, Benzene-d_6) δ 5.70 – 5.25 (m, 2H), 4.28 (t, J = 5.7 Hz, 1H), 3.93 (d, J = 5.2 Hz, 2H), 3.15 (d, J = 0.7 Hz, 6H), 2.19 – 1.87 (m, 1H), 1.79 (s, 1H), 1.72 – 1.52 (m, 2H), 1.34 (dtd, J = 9.4, 6.8, 2.0 Hz, 2H), 0.93 (d, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Benzene-d_6) δ 137.2, 128.9, 104.8, 63.4, 52.3, 36.6, 32.0, 30.7, 20.8.

HRMS (ESI): Calculated for $C_{10}H_{20}NaO_3$ $[M+Na]^+$: 211.1305, Found: 211.1313

$[\alpha]_D^{25}$ −10.8 (c 1.03, $CHCl_3$)



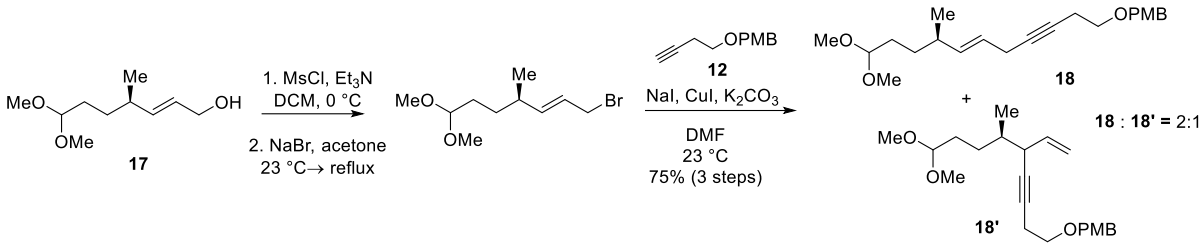
PMB-butyn-1-ol 12

To a stirred solution of 4-PMBCl (2.15 mL, 15.85 mmol) in DMF (15 mL) was added 3-butyn-1-ol at 0 °C. NaH was added portionwise over 5 mins and stirred for 1h. The reaction mixture was quenched with saturated NH_4Cl (aq.) and extracted with Et_2O. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The organic residue was purified by flash column chromatography on silica gel (EtOAc: Hexane= 1:20 → 1:10) to give PMB protected butyn-1-ol **12** (2.18 g, 72%) following the procedure by Ogawa et al.[3]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.47 (s, 2H), 3.79 (s, 3H), 3.55 (t, *J* = 7.0 Hz, 2H), 2.47 (td, *J* = 7.0, 2.7 Hz, 2H), 1.97 (t, *J* = 2.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.2, 130.1, 129.3, 113.8, 81.3, 72.6, 69.3, 67.8, 55.3, 19.9.

HRMS (ESI): Calculated for $C_{12}H_{14}NaO_2$ $[M+Na]^+$: 213.0886, Found: 213.0884

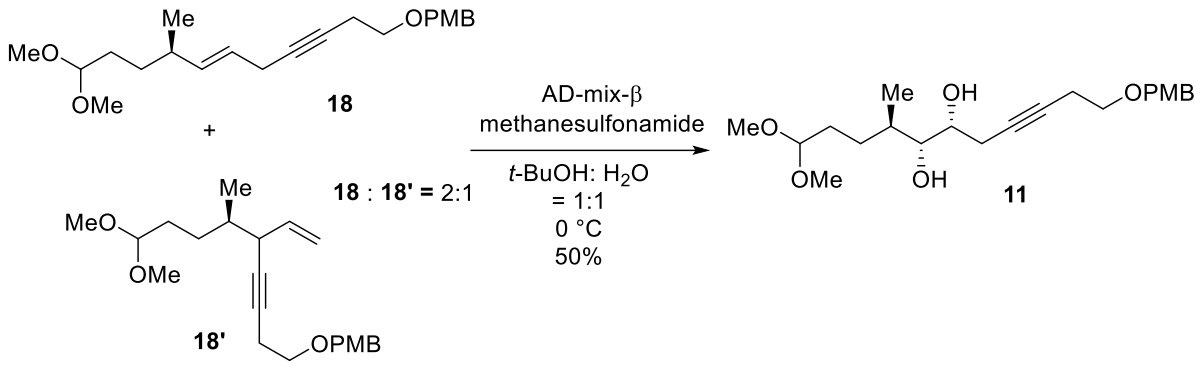


Enyne-18 and 18'

To a stirred solution of allylic alcohol **17** (362.9 mg, 1.93 mmol) in dry CH_2Cl_2 (7mL) was added Et_3N (0.30 mL, 2.12 mmol), and methanesulfonyl chloride (0.16 mL, 2.02 mmol) at 0 °C. The mixture was let stirred for 30 minutes and heated to 23°C and quenched with saturated $NaHCO_3$ (aq.) and extracted three times with CH_2Cl_2. Combined organic layer was evaporated under reduced pressure to give crude product which was used for next step without purification.

To the crude mixture of mesylated allylic alcohol in acetone (10 mL) at 23 °C was added NaBr (298 mg, 2.89 mmol) at 23 °C. The mixture was heated to reflux and after stirring for 6hrs, the mixture was cooled to 23°C and quenched with saturated $NaHCO_3$ (aq.) and extracted three times with Et_2O. After evaporating the solvent under reduced pressure, allylic bromide was dissolved in DMF (10mL). To the stirring solution of the allylic bromide, NaI (580 mg, 3.86 mmol), CuI (735 mg, 3.86 mmol) and K_2CO_3 (400 mg, 2.88 mmol) were added sequentially at 23°C. Then alkyne **12** (0.4 mL, 2.3 mmol) was added to the mixture dropwise. The mixture was stirred for 5 hrs and quenched with saturated NH_4Cl (aq.) and extracted three times with Et_2O. The combined organic layer was drived over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:10) to give mixture of enynes **18** and **18'** as 2:1 ratio (524 mg, 75%, yellowish transparent oil). Even after extensive tries to separate the two compounds, we could not isolate **18** as a clean product. Thus, the mixture was submitted to the next step.

HRMS (ESI): Calculated for $C_{22}H_{32}NaO_4$ $[M+Na]^+$: 383.2193, Found: 383.2204



(+)-Diol 11

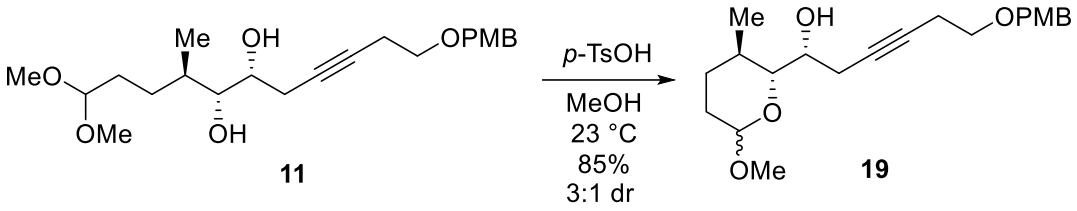
To a stirred solution of mixture of enynes **18** and **18'** (500 mg, 1.39 mmol) in *t*-BuOH and water (1:1 ratio, 5 mL each), were added AD-mix- β (2.14 g, 2.78 mmol) and methanesulfonamide (297 mg, 3.12 mmol) at 0 °C. The mixture was let stirred for 17 hrs and saturated $Na_2S_2O_5$ (aq.) was added slowly and stirred for 10 minutes. The mixture heated to 23 °C and quenched with water and extracted three times with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:1) to give **11** as single product. (273 mg, 50%, transparent oil).

^{1}H NMR (400 MHz, Benzene-d_6) δ 7.21 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 4.31 (t, J = 5.0 Hz, 1H), 4.29 (s, 2H), 3.69 (dd, J = 6.0, 2.6 Hz, 1H), 3.35 (t, J = 6.6 Hz, 2H), 3.32 (s, 3H), 3.24 (td, J = 6.6, 2.6 Hz, 1H), 3.16 (s, 6H), 2.44 – 2.29 (m, 5H), 2.23 (d, J = 6.6 Hz, 1H), 1.84 – 1.73 (m, 2H), 1.73 – 1.64 (m, 1H), 1.62 – 1.50 (m, 1H), 1.40 – 1.24 (m, 1H), 0.86 (d, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Benzene-d_6) δ 159.9, 130.8, 129.6, 114.1, 105.0, 80.3, 78.3, 76.8, 72.7, 69.8, 68.6, 54.8, 52.4, 52.1, 36.0, 30.2, 27.4, 25.7, 20.6, 16.3.

HRMS (ESI): Calculated for $C_{22}H_{34}NaO_6$ $[M+Na]^+$: 417.2248, Found: 417.2252

$[\alpha]_D^{25}$ 10.6 (c 0.115, $CHCl_3$)



Acetal 19

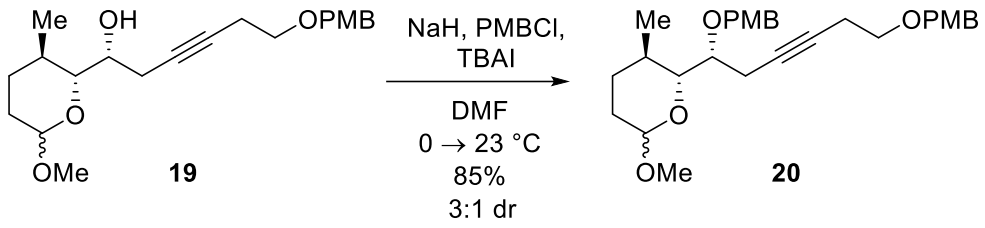
To a stirred solution of diol **11** (370 mg, 0.94 mmol) in MeOH (5mL) was added *p*-toluenesulfonic acid (181.5 mg, 0.94 mmol) at 23 °C and let stirred for 30 mins. The reaction mixture was quenched with saturated $NaHCO_3$ (aq.) and extracted three times with Et_2O. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:5→ 1:2) to give methyl-acetal **19** (290 mg, 85%, transparent oil) as a mixture of diastereomer.

^{1}H NMR (400 MHz, Benzene-d_6) δ 7.19 (d, J = 8.6 Hz, 2H), 6.86 – 6.73 (m, 2H), 4.55 (d, J = 3.4 Hz, 1H), 4.29 (s, 2H), 3.94 (d, J = 7.2 Hz, 1H), 3.63 (d, J = 10.2 Hz, 1H), 3.43 (t, J = 7.0 Hz, 2H), 3.31 (s, 3H), 3.25 (s, 3H), 2.60 (d, J = 2.8 Hz, 2H), 2.41 (m, 2H), 2.08 (s, 1H), 1.80 (dtd, J = 11.6, 6.5, 3.2 Hz, 1H), 1.66 – 1.53 (m, 2H), 1.44 (tdd, J = 13.9, 5.9, 3.1 Hz, 1H), 1.30 (ddt, J = 9.7, 4.1, 1.7 Hz, 1H), 0.77 (d, J = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, Benzene-d_6) δ 159.8, 131.0, 129.4, 114.1, 98.6, 79.3, 78.6, 74.3, 72.7, 69.7, 68.9, 54.8, 54.4, 30.7, 30.5, 27.1, 25.0, 20.7, 17.6.

*NMR data of the major diasteromer have been collected and reported here. The diastereomeric mixture was submitted to the next three steps.

HRMS (ESI): Calculated for $C_{21}H_{30}NaO_5$ $[M+Na]^+$: 385.1985, Found: 385.1990



PMB-alcohol 20

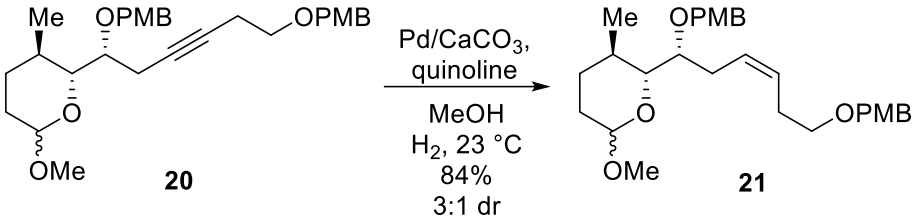
To a stirred solution of acetal **19** (as mixed diastereomer) (290 mg, 0.8 mmol) in DMF (5mL) was added sodium hydride (35 mg, 0.88 mmol) at 0°C and let stirred for 30 mins. Then, PMBCl (0.12 mL, 0.88 mmol) and TBAI (30 mg, 0.08 mmol) were added at same temperature and heated to 23 °C and let stirred for 15 hrs. The reaction mixture was quenched with water and extracted three times with Et_2O. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:10) to give PMB protected alcohol acetal **20** (328.0 mg, 85%, transparent oil) as 3:1 diastereomeric mixture.

^{1}H NMR (500 MHz, Benzene-d_6) δ 7.22 (dd, J = 19.1, 8.6 Hz, 4H), 6.86 – 6.76 (m, 4H), 4.75 – 4.67 (m, 1H), 4.59 (d, J = 11.4 Hz, 1H), 4.39 – 4.24 (m, 3H), 3.85 – 3.70 (m, 2H), 3.50 – 3.41 (m, 3H), 3.37 (s, 3H), 3.30 (d, J = 6.9 Hz, 7H), 3.00 – 2.86 (m, 1H), 2.73 (ddt, J = 16.1, 5.1, 2.4 Hz, 1H), 2.51 – 2.36 (m, 2H), 1.99 (dddd, J = 11.9, 10.4, 6.6, 3.9 Hz, 1H), 1.72 – 1.53 (m, 3H), 1.42 – 1.27 (m, 1H), 0.72 (d, J = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, Benzene-d_6) δ 159.8, 131.4, 131.0, 129.7, 129.4, 114.1, 114.0, 98.7, 79.3, 79.0, 77.4, 74.2, 72.7, 71.8, 68.9, 54.8, 54.5, 30.7, 30.6, 27.5, 20.7, 20.1, 17.8.

*2 Diastereomers could not be separated even after extensive purifications, thus NMR data of the mixed diastereomers are attached. ^{1}H NMR and ^{13}C NMR data of the major diastereomer in the mixture are listed above.

HRMS (ESI): Calculated for $C_{29}H_{38}NaO_6$ $[M+Na]^+$: 505.2561, Found: 505.2586



Olefin 21

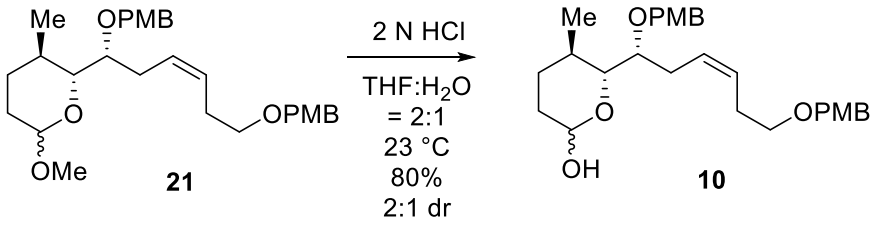
To a stirred solution of PMB-alcohol **20** (328 mg, 0.68 mmol) in MeOH (5 mL) at 23°C was added quinolone (0.045 mL, 0.34 mmol) and $Pd/CaCO_3$ (70 mg, 0.034 mmol) and stirred under hydrogen balloon. After stirring for 30 mins the mixture was filtered through celite and concentrated under reduced pressure, which was dissolved in Et_2O and washed with 1N HCl, then with saturated aq. $NaHCO_3$. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:10) to give olefin **21** as mixed diastereomer (275 mg, 84%, pale yellow oil) of 3:1 ratio.

^{1}H NMR (500 MHz, Benzene-d_6) δ 7.26 (dd, J = 28.0, 8.6 Hz, 4H), 6.80 (d, J = 8.5 Hz, 4H), 5.78 – 5.71 (m, 1H), 5.70 – 5.61 (m, 1H), 4.68 (d, J = 3.2 Hz, 1H), 4.61 (d, J = 11.3 Hz, 1H), 4.41 (d, J = 11.3 Hz, 1H), 4.34 (s, 2H), 3.63 (td, J = 6.8, 2.2 Hz, 1H), 3.56 (dd, J = 10.1, 2.1 Hz, 1H), 3.40 (t, J = 6.8 Hz, 2H), 3.30 (d, J = 1.2 Hz, 6H), 3.23 (s, 3H), 2.80 – 2.72 (m, 1H), 2.71 – 2.63 (m, 1H), 2.56 – 2.45 (m, 2H), 1.95 (tdd, J = 10.2, 6.5, 3.7 Hz, 1H), 1.71 – 1.51 (m, 3H), 1.36 (ddd, J = 14.4, 5.7, 2.2 Hz, 1H), 0.81 (d, J = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, Benzene-d_6) δ 159.6, 131.7, 131.3, 129.5, 129.3, 128.8, 128.3, 114.0, 114.0, 98.6, 79.0, 74.8, 72.7, 71.7, 69.8, 54.7, 54.4, 30.9, 30.5, 28.8, 28.4, 27.6, 18.0.

* NMR data of the major diastereomer is reported. The mixture of two diastereomers were used for the next step of the synthesis.

HRMS (ESI): Calculated for $C_{29}H_{40}NaO_6$ $[M+Na]^+$: 507.2717, Found: 507.2741



Lactol 10

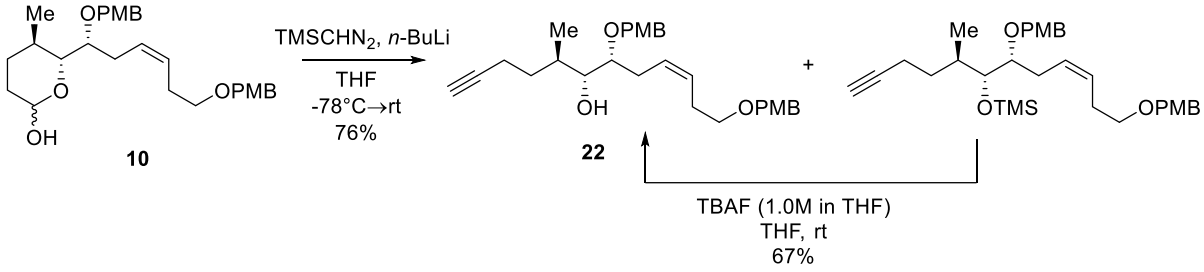
To a stirred solution of acetal **21** (275 mg, 0.57 mmol) in THF/H_2O = 2:1 (8 mL/4 mL) at 23°C was added 2N HCl (3.2 mL, 5.7 mmol). After stirring for overnight, 2N HCl (1.6 mL, 2.9 mmol) more was added. After the completion of reaction, the mixture was quenched slowly using saturated $NaHCO_3$ (aq.) and extracted three times with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:2) to give lactol **10** as mixed diastereomer (215 mg, 80% , transparent oil) of ~2:1 ratio.

^{1}H NMR (500 MHz, Benzene-d_6) δ 7.40 – 7.19 (m, 4H), 6.92 – 6.72 (m, 4H), 5.46 (d, J = 3.3 Hz, 2H), 4.60 (d, J = 11.3 Hz, 1H), 4.42 – 4.27 (m, 2H), 3.84 (dd, J = 10.1, 2.3 Hz, 1H), 3.63 (ddd, J = 10.0, 5.2, 2.2 Hz, 1H), 3.30 (s, 6H), 3.05 – 2.88 (m, 2H), 2.86 – 2.66 (m, 1H), 2.54 – 2.25 (m, 2H), 2.17 – 2.01 (m, 2H), 1.86 – 1.65 (m, 4H), 1.52 – 1.34 (m, 2H), 0.79 (d, J = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, Benzene-d_6) δ 159.9, 159.6, 131.8, 130.3, 129.9, 129.5, 129.5, 128.1, 127.9, 114.1, 114.0, 91.8, 81.3, 77.8, 77.6, 73.9, 72.8, 71.1, 69.4, 54.7, 31.0, 30.9, 28.4, 28.1, 27.2, 17.8.

*Diastereomers could not be separated even after extensive purifications, thus NMRs of the mixed diastereomers are attached. ^{1}HNMR and ^{13}CNMR of the major diastereomer in the mixture are listed above.

HRMS (ESI): Calculated for $C_{28}H_{38}NaO_6$ $[M+Na]^+$: 493.2561, Found: 493.2566



(−)-Alkyne 22

To a stirred solution of lactol **10** (139.4 mg, 0.296 mmol) in THF (2 mL) at −78°C was added *n*-BuLi (2.5 M in Hx, 0.12 mL, 0.296 mmol) dropwise and stirred for 30 minutes. In another RBF, TMS-diazomethane (0.28 mL, 0.563 mmol) was dissolved in THF (1 mL) and *n*-BuLi (2.5 M in Hx, 0.24mL, 0.59 mmol) was added dropwise and stirred for 30 minutes at −78°C. Then to the stirring solution of lactol **10**, lithiated TMS-diazomethane was cannulated at −78°C and the mixture was heated to 23°C and stirred further for 30 minutes. The reaction mixture was quenched using saturated NH_4Cl (aq.) and extracted three times with EtOAc. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:5) **22** (62 mg, 45%, transparent oil) along with side product (49.5 mg, 31%, transparent oil).

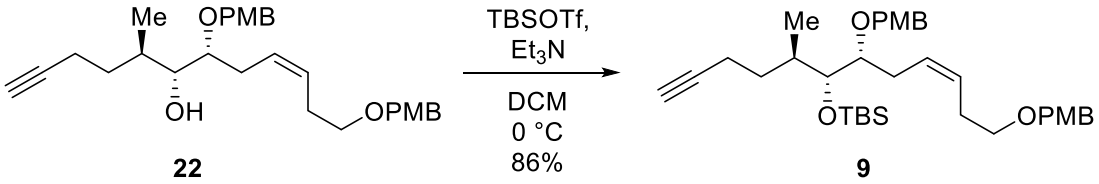
TMS-protected alcohol was obtained as side product (49.5 mg, 0.092 mmol), which was deprotected with TBAF (1.0 M in THF, 0.12 mL, 0.11 mmol) at 23°C. The reaction mixture was quenched with water after stirring for 1 hr, and extracted three times with EtOAc. . The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:5) **22** (30.9 mg, 72%, total, 92.9 mg).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 2.8 Hz, 4H), 6.85 (d, *J* = 8.5 Hz, 4H), 5.49 (q, *J* = 5.7 Hz, 2H), 4.61 (d, *J* = 11.0 Hz, 1H), 4.42 (s, 2H), 4.37 (d, *J* = 11.1 Hz, 1H), 3.78 (d, *J* = 1.4 Hz, 6H), 3.52 – 3.45 (m, 1H), 3.43 (dt, *J* = 6.8, 3.6 Hz, 2H), 3.20 (td, *J* = 6.6, 3.9 Hz, 1H), 2.47 (dt, *J* = 11.6, 6.5 Hz, 1H), 2.41 (dd, *J* = 6.8, 3.3 Hz, 2H), 2.38 – 2.21 (m, 2H), 2.20 – 2.07 (m, 1H), 1.91 (t, *J* = 2.6 Hz, 1H), 1.86 – 1.72 (m, 2H), 1.35 (dq, *J* = 13.3, 5.0 Hz, 1H), 0.82 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.3, 159.2, 130.4, 130.4, 129.5, 129.3, 128.6, 126.7, 113.8, 113.8, 84.8, 78.3, 76.2, 72.6, 71.5, 69.3, 68.3, 55.3, 55.3, 34.2, 30.5, 28.4, 28.2, 16.2, 16.1.

HRMS (ESI): Calculated for $C_{29}H_{38}NaO_5$ $[M+Na]^+$: 489.2611, Found: 489.2608

$[\alpha]_D^{25}$ −18.3 (c 0.145, $CHCl_3$)



22 **9**

(+)-TBS-protected alcohol 9

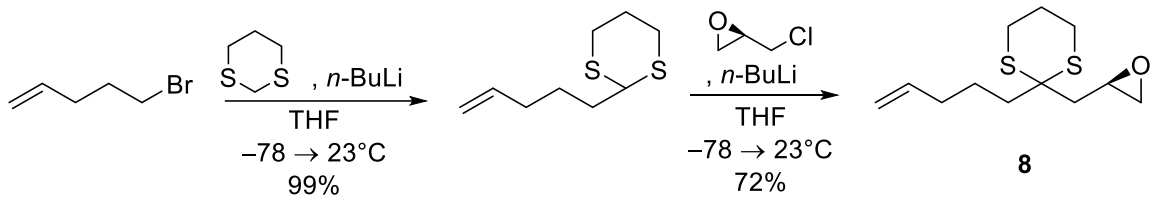
To a stirred solution of alcohol **22** (92.9 mg, 0.20 mmol) in CH_2Cl_2 (3 mL) at 0 °C was added trimethylamine (0.08 mL, 0.6 mmol) and TBSOTf (0.09 mL, 0.40 mmol) and let stirred for 1.5 hrs. The resulting mixture was quenched with saturated $NaHCO_3$ (aq.) and extracted three times with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:10) to give **9** (100 mg, 86%, transparent oil).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 8.0 Hz, 4H), 6.87 (t, *J* = 9.0 Hz, 4H), 5.68 – 5.55 (m, 1H), 5.53 – 5.45 (m, 1H), 4.49 (s, 2H), 4.44 (s, 2H), 3.81 (d, *J* = 1.7 Hz, 6H), 3.56 (t, *J* = 5.1 Hz, 1H), 3.44 (t, *J* = 7.1 Hz, 2H), 3.42 – 3.39 (m, 1H), 2.41 (s, 1H), 2.39 (d, *J* = 7.3 Hz, 2H), 2.34 – 2.23 (m, 2H), 2.14 (dtd, *J* = 16.6, 8.1, 2.6 Hz, 1H), 1.95 (t, *J* = 2.8 Hz, 1H), 1.88 – 1.74 (m, 2H), 1.35 (dtd, *J* = 13.7, 8.4, 5.0 Hz, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.90 (s, 9H), 0.02 (d, *J* = 20.1 Hz, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.1, 158.9, 131.1, 130.6, 129.2, 129.1, 128.2, 127.1, 113.7, 113.6, 84.8, 81.8, 76.9, 72.5, 71.6, 69.6, 68.3, 55.2, 34.0, 30.7, 28.2, 27.8, 26.1, 18.3, 17.1, 16.2, -4.0, -4.5.

HRMS (ESI): Calculated for $C_{35}H_{52}NaO_5Si$ $[M+Na]^+$: 603.3476, Found: 603.3448

$[\alpha]_D^{25}$ 11.97 (c 0.175, $CHCl_3$)



(+)-Epoxide 8

To a stirred solution of 1,3-dithiane (1.3 g, 11.03 mmol) in dry THF (22 mL) cooled to −20 °C was added *n*-BuLi (2.5 M in hexane, 5.3 mL, 13.25 mmol). The reaction mixture was stirred for 1h and cooled to −78 °C and solution of 5-bromo-1-pentene (1.57 mL) was added dropwise and the mixture was warmed to 23 °C. After 30 mins, the mixture was diluted by Et_2O, and quenched with saturated NH_4Cl solution. The layers were separated and the aqueous phase was extracted with Et_2O and the combined layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The organic residue was purified by flash column chromatography on silica gel (EtOAc: Hexane = 1:10) to give dithiane product following the procedure by Araki et al.[2]

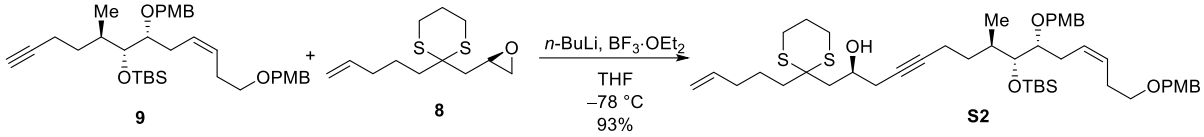
Then to a solution of dithiane (4.7 g, 24.9 mmol) in THF (83 mL) was added *n*-BuLi (2.5M in hexane, 10.5 mL, 26.2 mmol) slowly at 0 °C. The reaction mixture was stirred for 1h, and after cooling to −78 °C, (*R*)-epichlorohydrin (2.2 mL, 27.3 mmol) was added. The reaction mixture was heated to and stirred at 23°C for 18 hrs, then quenched with saturated NH_4Cl (aq.) solution. The layers were separated and the aqueous phase was extracted with Et_2O and the combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The organic residue was purified by flash column chromatography on silica gel (EtOAc: Hexane= 1:20) to give epoxide **8** (4.4 g, 72%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.77 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 1H), 5.21 – 4.79 (m, 2H), 3.15 (dtd, *J* = 6.4, 4.4, 2.7 Hz, 1H), 2.95 – 2.72 (m, 5H), 2.49 (dd, *J* = 5.1, 2.7 Hz, 1H), 2.16 (dd, *J* = 14.9, 4.9 Hz, 1H), 2.11 – 2.02 (m, 3H), 1.99 – 1.85 (m, 4H), 1.68 – 1.48 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.2, 115.0, 52.0, 48.9, 46.7, 41.4, 38.8, 33.6, 26.1, 26.1, 25.1, 23.4.

HRMS (ESI): Calculated for $C_{12}H_{20}NaOS_2$ $[M+Na]^+$: 267.0848, Found: 267.0841

$[\alpha]_D^{25}$ +3.40 (c 2.05, $CHCl_3$)



(+)-dithiane S2

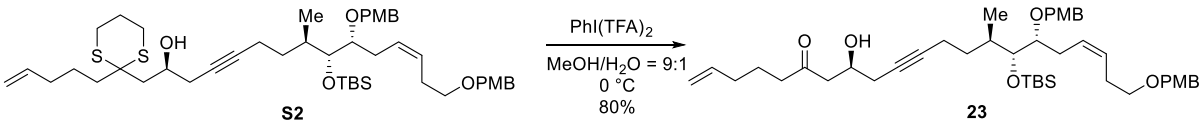
To a stirred solution of alkyne **9** (68.5 mg, 0.12 mmol) in THF (1mL) was added *n*-BuLi (2.5 M in Hx, 0.05 mL, 0.12 mmol) at −78 °C and stirred for 30 minutes. Then, $BF_3.OEt_2$ (0.04 mL, 0.106 mmol) was added dropwise at the same temperature and stirred for further 30 minutes. Then epoxide **8** (18 mg, 0.073 mmol) in THF (1mL) was cannulated to the stirring mixture. The reaction mixture was stirred further at same temperature for 1 hr. The reaction mixture was quenched using saturated $NaHCO_3$ (aq.) and extracted three times with EtOAc. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:5 → 1:3) to give dithiane **S2** (56.0 mg, 93%, transparent oil).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.1 Hz, 4H), 6.88 (t, *J* = 8.4 Hz, 4H), 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.66 – 5.55 (m, 1H), 5.55 – 5.43 (m, 1H), 5.12 – 4.91 (m, 2H), 4.49 (s, 2H), 4.44 (s, 2H), 4.11 – 3.96 (m, 1H), 3.81 (d, *J* = 1.6 Hz, 6H), 3.55 (t, *J* = 5.0 Hz, 1H), 3.48 – 3.42 (m, 3H), 3.43 – 3.38 (m, 1H), 2.98 (dddd, *J* = 30.6, 13.6, 10.2, 2.9 Hz, 2H), 2.76 (ddd, *J* = 14.7, 6.6, 3.0 Hz, 2H), 2.51 – 2.19 (m, 9H), 2.15 – 2.01 (m, 5H), 1.99 – 1.86 (m, 2H), 1.81 (ddt, *J* = 9.2, 6.1, 2.8 Hz, 1H), 1.77 – 1.61 (m, 2H), 1.39 – 1.24 (m, 2H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.90 (s, 9H), 0.02 (d, *J* = 17.0 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.1, 158.9, 138.1, 131.1, 129.2, 129.1, 128.2, 127.1, 115.1, 113.7, 113.6, 82.9, 81.7, 77.2, 76.9, 76.2, 72.5, 71.6, 69.6, 67.7, 55.3, 52.0, 43.1, 39.1, 34.2, 33.7, 31.2, 28.2, 28.1, 27.9, 26.4, 26.1, 26.0, 25.0, 23.0, 18.3, 17.2, 16.7, -4.0, -4.5.

HRMS (ESI): Calculated for $C_{47}H_{72}NaO_6S_2Si$ $[M+Na]^+$: 847.4432, Found: 847.4423

$[\alpha]_D^{25}$ 19.8 (c 0.137, $CHCl_3$)



(+)-ketone 23

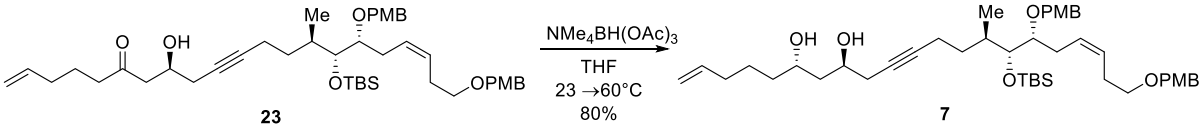
To a stirred solution of dithiane **S2** (48.7 mg, 0.059 mmol) in MeOH:H_2O = 9:1 (0.9 mL/0.1mL) at 0 °C was added PIFA(35 mg, 0.082 mmol) and let stirred for 1 hr. The reaction mixture was quenched with saturated $Na_2S_2O_3$ (aq.) and stirred for few minutes, and saturated $NaHCO_3$ (aq.) was added and extracted three times with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:3) to give ketone **23** (34.2 mg, 80%, transparent oil).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 9.8 Hz, 4H), 6.88 (t, *J* = 8.6 Hz, 4H), 5.84 – 5.71 (m, 1H), 5.63 – 5.53 (m, 1H), 5.53 – 5.43 (m, 1H), 5.08 – 4.95 (m, 2H), 4.49 (s, 2H), 4.44 (s, 2H), 4.19 – 4.08 (m, 1H), 3.81 (s, 6H), 3.55 (d, *J* = 5.0 Hz, 1H), 3.45 (t, *J* = 7.1 Hz, 2H), 3.41 (t, *J* = 4.3 Hz, 1H), 3.15 (d, *J* = 4.1 Hz, 1H), 2.73 (dd, *J* = 17.3, 3.3 Hz, 1H), 2.60 (dd, *J* = 17.3, 8.5 Hz, 1H), 2.45 (t, *J* = 7.5 Hz, 2H), 2.39 (d, *J* = 7.0 Hz, 4H), 2.28 (ddd, *J* = 26.0, 13.9, 6.7 Hz, 2H), 2.13 (t, *J* = 8.1 Hz, 1H), 2.07 (q, *J* = 7.3 Hz, 2H), 1.89 – 1.78 (m, 1H), 1.70 (td, *J* = 18.0, 16.6, 9.3 Hz, 4H), 1.30 (ddt, *J* = 18.5, 14.0, 6.3 Hz, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.90 (s, 9H), 0.02 (d, *J* = 19.2 Hz, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 211.3, 159.1, 158.9, 137.8, 131.0, 130.5, 129.2, 129.1, 128.2, 127.1, 115.3, 113.7, 113.6, 83.2, 81.8, 76.8, 75.7, 72.5, 71.7, 69.6, 66.6, 55.2, 47.9, 42.7, 34.0, 33.0, 31.2, 28.2, 27.8, 26.7, 26.0, 22.5, 18.2, 17.2, 16.6, -4.0, -4.5.

HRMS (ESI): Calculated for $C_{44}H_{66}NaO_7Si$ $[M+Na]^+$: 757.4470, Found: 775.4453

$[\alpha]_D^{25}$ 14.2 (c 0.308, $CHCl_3$)



23 7

(+)-diol 7

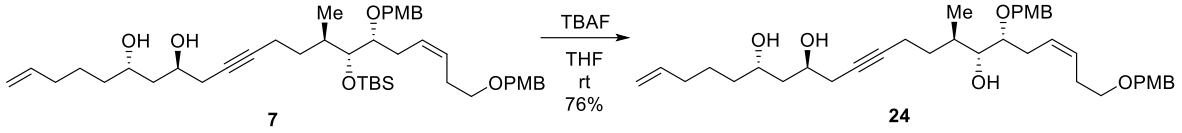
To a stirred solution of ketone **23** (32.1 mg, 0.044 mmol) in THF (1.5mL) at 23 °C was added triacetoxytetramethylammoniumborohydride (115 mg, 0.44 mmol) and heated to 60 °C. The mixture was let stirred for 5 hrs. The reaction mixture was quenched saturated NH_4Cl (aq.) was added and extracted three times with EtOAc. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:1) to give diol **7** (26.0 mg, 80%, transparent oil).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.18 (m, 4H), 6.84 (dd, *J* = 8.6, 6.7 Hz, 4H), 5.78 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.53 (m, 1H), 5.44 (m, 1H), 5.04 – 4.90 (m, 2H), 4.45 (s, 2H), 4.40 (s, 2H), 3.96 (d, *J* = 6.8 Hz, 1H), 3.85 (s, 1H), 3.77 (d, *J* = 1.1 Hz, 6H), 3.52 (dd, *J* = 5.4, 4.2 Hz, 1H), 3.41 (t, *J* = 7.1 Hz, 2H), 3.37 (td, *J* = 5.0, 2.6 Hz, 1H), 2.84 (s, 1H), 2.48 – 2.39 (m, 1H), 2.39 – 2.17 (m, 6H), 2.14 – 1.92 (m, 3H), 1.84 (ddd, *J* = 10.0, 6.8, 3.8 Hz, 1H), 1.79 – 1.63 (m, 2H), 1.60 – 1.34 (m, 5H), 1.24 (dddd, *J* = 14.5, 9.3, 7.2, 4.9 Hz, 1H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.86 (s, 9H), -0.03 (d, *J* = 15.4 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.2, 159.0, 138.7, 131.0, 130.5, 129.3, 129.2, 128.4, 127.0, 114.6, 113.8, 113.6, 83.1, 82.0, 76.8, 76.4, 72.6, 71.8, 69.6, 69.0, 67.8, 55.3, 41.6, 36.8, 33.7, 33.6, 31.0, 28.2, 27.9, 27.9, 26.1, 25.1, 18.3, 17.5, 16.6, -4.0, -4.5.

HRMS (ESI): Calculated for $C_{44}H_{68}NaO_7Si$ $[M+Na]^+$: 759.4627, Found: 759.4600

$[\alpha]_D^{25}$ 14.3 (c 0.1, $CHCl_3$)



7 24

(−)-Triol 24

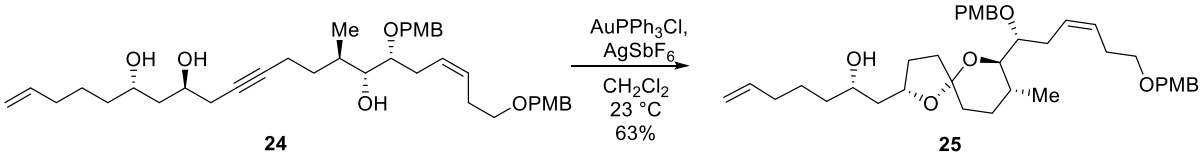
To a stirred solution of TBS protected alcohol **7** (7.2 mg, 0.01 mmol) in THF (1 mL) was added TBAF (1.0 M in THF, 0.012 mL) and stirred for 2 hours. The reaction mixture was quenched with H_2O and extracted three times with EtOAc. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 2:1) to give triol **24** (3.8 mg, 76%, transparent oil).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 2.6 Hz, 4H), 6.85 (d, *J* = 8.6 Hz, 4H), 5.87 – 5.68 (m, 1H), 5.56 – 5.33 (m, 2H), 5.02 – 4.89 (m, 2H), 4.61 (d, *J* = 10.9 Hz, 1H), 4.42 (s, 2H), 4.36 (d, *J* = 11.0 Hz, 1H), 3.95 (s, 1H), 3.78 (d, *J* = 1.2 Hz, 6H), 3.46 (dd, *J* = 6.1, 2.7 Hz, 1H), 3.45 – 3.36 (m, 2H), 3.21 (dd, *J* = 8.7, 5.1 Hz, 1H), 2.74 (d, *J* = 4.3 Hz, 1H), 2.56 (d, *J* = 7.1 Hz, 1H), 2.52 – 2.37 (m, 3H), 2.36 – 2.18 (m, 4H), 2.12 (q, *J* = 8.5 Hz, 1H), 2.07 – 1.99 (m, 2H), 1.87 – 1.71 (m, 2H), 1.69 – 1.55 (m, 2H), 1.51 – 1.28 (m, 5H), 0.80 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.3, 159.2, 138.7, 130.4, 130.3, 129.5, 129.5, 129.4, 128.5, 126.8, 114.6, 113.8, 113.8, 83.3, 78.2, 76.0, 72.6, 71.5, 69.3, 69.0, 67.9, 55.3, 55.3, 41.6, 36.7, 34.2, 33.7, 31.1, 28.4, 28.2, 27.9, 25.0, 16.3, 16.0.

HRMS (ESI): Calculated for $C_{38}H_{54}NaO_7$ $[M+Na]^+$: 645.3762, Found: 645.3751

$[\alpha]_D^{25}$ −11.4 (c 0.25, $CHCl_3$)



24 **25**

(−)-PMB-protected attenol A (25)

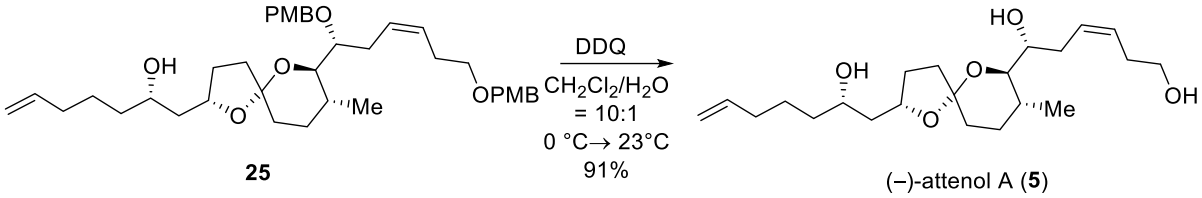
To a stirred solution of triol **24** (4.7 mg, 0.0076 mmol) in CH_2Cl_2 (0.8 mL) at 23 °C was added $AgSbF_6$ (0.3 mg, 0.1 eq.), $AuPPh_3Cl$ (0.4 mg, 0.1 eq.) and let stirred for 5 minutes. The reaction mixture was quenched with saturated $NaHCO_3$ (aq.) and extracted three times with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:4 → 1:2) to give PMB-protected attenol A **25** (3.0 mg, 63%, transparent oil).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 (s, 1H), 7.23 (s, 3H), 6.83 (dd, *J* = 13.7, 8.6 Hz, 4H), 5.78 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H), 5.54 (q, *J* = 8.5, 7.4 Hz, 1H), 5.50 – 5.41 (m, 1H), 5.01 – 4.89 (m, 2H), 4.59 (d, *J* = 11.6 Hz, 1H), 4.43 (s, 2H), 4.38 (d, *J* = 11.6 Hz, 1H), 4.32 – 4.19 (m, 1H), 3.78 (m, 1H), 3.77 (s, 6H), 3.49 – 3.44 (m, 1H), 3.44 (t, *J* = 6.9 Hz, 2H), 3.37 (dd, *J* = 10.1, 2.0 Hz, 1H), 2.50 (p, *J* = 7.4 Hz, 2H), 2.37 (q, *J* = 7.3 Hz, 2H), 2.34 – 2.28 (m, 1H), 2.08 (d, *J* = 7.1 Hz, 1H), 2.07 – 2.00 (m, 2H), 1.96 – 1.85 (m, 1H), 1.86 – 1.69 (m, 4H), 1.69 – 1.54 (m, 4H), 1.51 – 1.33 (m, 4H), 0.62 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.1, 138.8, 130.9, 130.6, 129.7, 129.2, 128.5, 127.2, 125.2, 114.6, 113.8, 113.6, 106.3, 77.7, 72.6, 71.3, 69.7, 69.5, 55.3, 43.3, 38.4, 36.6, 34.1, 33.7, 31.1, 30.0, 29.4, 28.2, 28.1, 25.2, 17.2.

HRMS (ESI): Calculated for $C_{38}H_{54}NaO_7$ $[M+Na]^+$: 645.3762, Found: 645.3751

$[\alpha]_D^{25}$ −24.3 (c 0.1, $CHCl_3$)



25 (–)-attenol A (**5**)

(−)-attenol A (5)

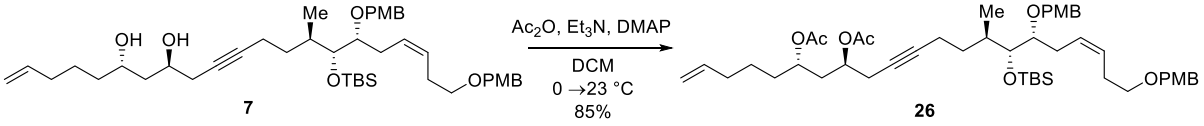
To a stirred solution of **25** (1.8 mg, 0.003 mmol) in CH_2Cl_2/H_2O = 10:1 (0.9 mL, 0.1mL each) at 0 °C was added DDQ (3.3 mg, 0.015 mmol) portionwise. The mixture was heated to 23 °C and let stirred for 1.5 hrs. The reaction mixture was quenched with saturated $NaHCO_3$ (aq.) until pH becomes 7, and extracted three times with CH_2Cl. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:1 → 2:1 → EtOAc) to give (−)-attenol A (**5**) (1.7 mg, 91%, transparent colourless oil).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.75 – 5.62 (m, 1H), 5.54 (td, *J* = 10.2, 9.4, 6.9 Hz, 1H), 5.01 (dd, *J* = 17.1, 1.9 Hz, 1H), 4.96 (d, *J* = 10.2 Hz, 1H), 4.43 – 4.13 (m, 1H), 3.83 (s, 1H), 3.67 (ddd, *J* = 20.2, 9.0, 5.5 Hz, 3H), 3.32 (dd, *J* = 10.2, 1.4 Hz, 1H), 2.56 (d, *J* = 7.6 Hz, 1H), 2.55 – 2.47 (m, 1H), 2.42 (dt, *J* = 14.2, 7.0 Hz, 1H), 2.29 (dt, *J* = 14.0, 6.6 Hz, 1H), 2.11 (s, 1H), 2.11 – 2.07 (m, 3H), 2.05 – 1.96 (m, 2H), 1.84 (tdd, *J* = 11.6, 9.4, 6.9 Hz, 1H), 1.75 (dd, *J* = 8.4, 4.1 Hz, 2H), 1.73 – 1.68 (m, 2H), 1.65 (dt, *J* = 9.7, 2.8 Hz, 2H), 1.61 – 1.56 (m, 2H), 1.53 – 1.38 (m, 4H), 0.88 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.7, 129.7, 128.0, 114.6, 106.4, 78.0, 78.0, 70.1, 69.7, 62.0, 43.6, 38.5, 36.6, 33.9, 33.7, 33.0, 30.9, 30.8, 30.4, 29.0, 25.1, 17.3.

HRMS (ESI): Calculated for $C_{22}H_{38}NaO_5$ $[M+Na]^+$: 405.2611, Found: 405.2595

$[\alpha]_D^{25}$ −10.7 (c 0.1, $CHCl_3$)



(+)-Diacetate 26

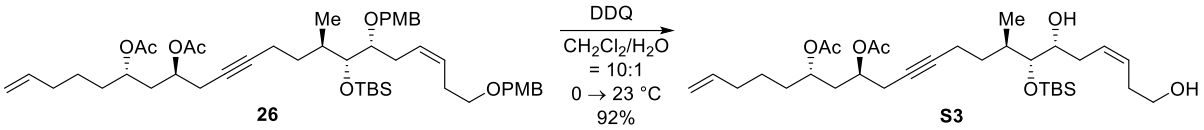
To a stirred solution of diol **7** (14.4 mg, 0.0195 mmol) in CH_2Cl_2 (1 mL) at 0 °C was added DMAP (7.3 mg, 0.06 mmol) and Et_3N (0.03 mL, 0.2 mmol). Then acetic anhydride (0.01 mL, 0.098 mmol) was added to the mixture and was heated to 23°C and let stirred for 30 mins. The reaction mixture was quenched saturated NH_4Cl (aq.) was added and extracted three times with CH_2Cl_2 combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:10 → 1:5) to give diacetate **26** (13.7 mg, 85%, transparent oil).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 – 7.20 (m, 4H), 6.84 (t, *J* = 9.1 Hz, 4H), 5.75 (ddt, *J* = 17.1, 10.5, 6.7 Hz, 1H), 5.59 – 5.49 (m, 1H), 5.49 – 5.34 (m, 1H), 5.10 – 4.83 (m, 4H), 4.45 (s, 2H), 4.40 (s, 2H), 3.77 (d, *J* = 2.1 Hz, 6H), 3.51 (t, *J* = 5.0 Hz, 1H), 3.41 (t, *J* = 7.0 Hz, 2H), 3.39 – 3.31 (m, 1H), 2.45 – 2.41 (m, 1H), 2.40 (s, 2H), 2.39 – 2.31 (m, 2H), 2.31 – 2.14 (m, 2H), 2.03 (s, 2H), 2.02 – 1.99 (m, 6H), 1.86 (dd, *J* = 7.6, 5.7 Hz, 2H), 1.77 – 1.65 (m, 2H), 1.57 – 1.43 (m, 3H), 1.41 – 1.34 (m, 2H), 1.26 (ddd, *J* = 16.8, 8.1, 3.7 Hz, 1H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.86 (s, 9H), -0.01 (d, *J* = 21.1 Hz, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.7, 170.4, 159.1, 158.9, 138.3, 131.1, 130.6, 129.2, 129.1, 128.3, 127.1, 114.9, 113.7, 113.6, 83.0, 81.9, 74.7, 72.5, 71.7, 71.0, 69.8, 69.6, 68.3, 55.2, 37.5, 37.0, 34.4, 34.2, 33.5, 31.4, 28.2, 27.9, 26.1, 24.7, 24.4, 21.1, 21.0, 18.3, 17.1, 16.6, -4.0, -4.5.

HRMS (ESI): Calculated for $C_{48}H_{72}NaO_9$ $[M+Na]^+$: 843.4838, Found: 843.4826

$[\alpha]_D^{25}$ +26.9 (c 0.074, $CHCl_3$)



(+)-Diol S3

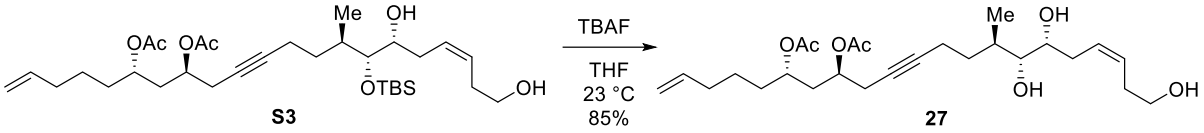
To a stirred solution of **26** (12.9 mg, 0.016 mmol) in CH_2Cl_2/H_2O = 10:1 (0.9 mL, 0.1 mL each) at 0°C was added DDQ (21.4 mg, 0.094 mmol) portionwise. The mixture was heated to 23°C and let stirred for 40 mins. The reaction mixture was quenched with saturated $NaHCO_3$ (aq.) until pH becomes 7, and extracted three times with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:2) to give diol **S3** (8.4 mg, 92%, transparent oil).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.75 (ddt, *J* = 16.9, 10.3, 6.7 Hz, 1H), 5.66 – 5.57 (m, 1H), 5.57 – 5.48 (m, 1H), 5.08 – 4.76 (m, 4H), 3.69 – 3.60 (m, 2H), 3.59 – 3.55 (m, 1H), 3.45 (t, *J* = 3.5 Hz, 1H), 2.57 (s, 1H), 2.42 (m, 3H), 2.34 – 2.16 (m, 4H), 2.15 – 2.07 (m, 2H), 2.01 (d, *J* = 6.4 Hz, 6H), 1.86 (dd, *J* = 7.6, 5.8 Hz, 2H), 1.78 (td, *J* = 7.1, 3.6 Hz, 1H), 1.55 – 1.47 (m, 4H), 1.38 (ddd, *J* = 7.2, 4.8, 1.9 Hz, 2H), 1.34 – 1.24 (m, 1H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.91 (s, 9H), 0.10 (s, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.7, 170.5, 138.3, 128.9, 128.3, 114.9, 82.4, 77.9, 75.2, 70.6, 69.8, 68.3, 62.0, 37.6, 36.5, 34.2, 33.5, 33.4, 31.2, 30.9, 26.0, 24.7, 24.4, 21.1, 21.1, 18.3, 16.9, 15.3, -4.0, -4.3.

HRMS (ESI): Calculated for $C_{32}H_{56}NaO_7Si$ $[M+Na]^+$: 603.3688, Found: 603.3671

$[\alpha]_D^{25}$ +24.2 (c 0.03, $CHCl_3$)



(+)-Triol 27

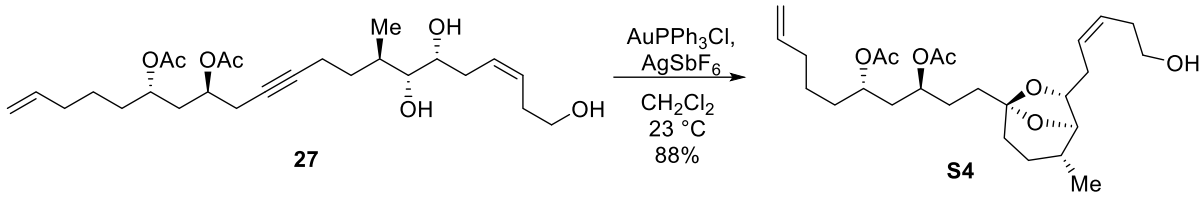
To a stirred solution of TBS protected alcohol **S3** (5.5 mg, 0.01 mmol) in THF (1 mL) was added TBAF (1.0M in THF, 0.012 mL) and stirred for 2 hours. The reaction mixture was quenched with H_2O and extracted three times with EtOAc. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 2:1 → EtOAc) to give triol **27** (3.8 mg, 85%, transparent oil).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.80 – 5.70 (m, 1H), 5.58 (dd, *J* = 8.7, 5.3 Hz, 2H), 5.09
– 4.86 (m, 4H), 3.70 (td, *J* = 9.5, 7.8, 3.2 Hz, 3H), 3.27 – 3.08 (m, 1H), 2.56 – 2.19 (m, 8H), 2.04 (s, 2H), 2.02 (d, *J* = 11.3 Hz, 6H), 1.96 – 1.71 (m, 4H), 1.54 (m, 1H) 1.38 (q, *J* = 7.4 Hz, 2H), 1.34 – 1.27 (m, 1H), 1.24 (t, *J* = 5.2 Hz, 2H), 0.90 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.9, 170.8, 138.3, 129.3, 128.4, 114.9, 82.7, 77.4, 70.5, 70.0, 68.5, 61.8, 37.7, 34.6, 34.1, 33.5, 32.3, 31.2, 30.3, 24.9, 24.4, 21.1, 21.1, 16.4, 15.8, 15.7.

HRMS (ESI): Calculated for $C_{26}H_{42}NaO_7$ $[M+Na]^+$: 489.2823, Found: 489.2821

$[\alpha]_D^{25}$ +27.1 (c 0.14, $CHCl_3$)



(+)-Acetyl protected attenol B (S4)

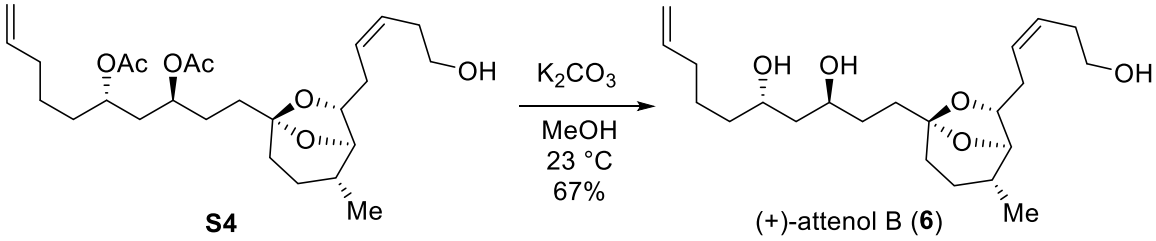
To a stirred solution of triol **27** (3.8 mg, 0.0081 mmol) in CH_2Cl_2 (0.8mL) at 23 °C was added $AgSbF_6$ (0.3 mg, 0.1 eq.), $AuPPh_3Cl$ (0.4 mg, 0.1 eq.) and let stirred for 5 minutes. The reaction mixture was quenched with saturated $NaHCO_3$ (aq.) and extracted three times with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 1:1) to give acetyl-protected attenol B (**S4**, 3.3 mg, 88%, transparent oil).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.77 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.59 – 5.45 (m, 2H), 5.09 – 4.88 (m, 4H), 4.00 (t, *J* = 6.8 Hz, 1H), 3.87 (s, 1H), 3.65 (t, *J* = 6.5 Hz, 2H), 2.42 – 2.29 (m, 2H), 2.31 – 2.20 (m, 2H), 2.05 (s, 1H), 2.04 – 1.99 (m, 6H), 2.00 – 1.94 (m, 1H), 1.88 (td, *J* = 18.9, 16.5, 9.4 Hz, 1H), 1.79 – 1.74 (m, 2H), 1.73 – 1.59 (m, 6H), 1.53 (q, *J* = 7.6, 7.1 Hz, 2H), 1.46 – 1.35 (m, 3H), 1.31 (dd, *J* = 13.8, 5.5 Hz, 1H), 1.10 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.8, 170.8, 138.3, 128.1, 127.9, 114.8, 109.2, 82.9, 80.0, 71.2, 70.1, 70.0, 62.1, 38.4, 34.2, 33.6, 33.5, 32.9, 31.2, 31.1, 30.4, 28.1, 24.4, 23.2, 21.1, 17.0.

HRMS (ESI): Calculated for $C_{26}H_{42}NaO_7$ $[M+Na]^+$: 489.2823, Found: 489.2821

$[\alpha]_D^{25}$ +69.2 (c 0.076, $CHCl_3$)



(+)-attenol B (6)

To a stirred solution of acetyl protected (+)-attenol B (**S4**, 2.2 mg, 0.005 mmol) in MeOH (0.5 mL) at 23 °C was added K_2CO_3 (6.4 mg, 0.047 mmol) and let stirred for overnight. The reaction mixture was quenched with saturated NH_4Cl (aq.) and extracted three times with EtOAc. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: Hexane = 2:1 → EtOAc) to give (+)-attenol B (**6**) (1.2 mg, 67%, transparent oil).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.81 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.60 – 5.45 (m, 2H), 5.01 (dd, *J* = 17.1, 1.9 Hz, 1H), 4.94 (d, *J* = 10.2 Hz, 1H), 4.08 (t, *J* = 6.7 Hz, 1H), 4.01 – 3.94 (m, 1H), 3.93 (s, 1H), 3.77 – 3.49 (m, 2H), 3.40 (s, 1H), 1.61 (br, 1H) 2.50 – 2.34 (m, 2H), 2.34 – 2.25 (m, 2H), 2.17 – 2.02 (m, 2H), 2.06 – 1.97 (m, 1H), 1.94 – 1.76 (m, 3H), 1.73 – 1.63 (m, 2H), 1.63 – 1.58 (m, 2H), 1.54 – 1.48 (m, 4H), 1.48 – 1.39 (m, 2H), 1.34 (dd, *J* = 14.2, 5.4 Hz, 1H), 1.12 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.8, 128.45, 127.9, 114.5, 109.6, 83.1, 80.1, 70.3, 69.2, 61.9, 42.5, 36.9, 34.5, 33.7, 33.7, 31.3, 31.2, 30.3, 30.3, 25.0, 23.1, 16.9.

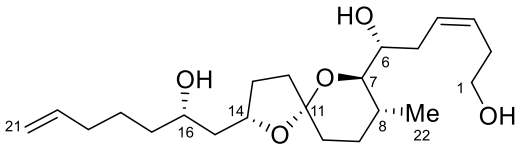
HRMS (ESI): Calculated for $C_{22}H_{38}NaO_5$ $[M+Na]^+$: 405.2611, Found: 405.2595

$[\alpha]_D^{25}$ +32.0 (c 0.05, $CHCl_3$)

4. Comparison of Spectroscopic Data of Natural and Synthetic Compounds

4.1 NMR Data Natural and Synthetic (−)-attenol A (5)

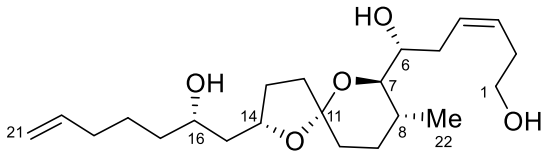
Table S1. Comparison of ^{1}H NMR spectroscopic data between synthetic and isolated (−)-attenol A (5)



(–)-attenol A (**5**)

position	Natural (–)-attenol A (Uemura, 1999)[4] ^{1}H NMR (400 MHz, $CDCl_3$)	Synthetic (–)-attenol A (Yadav, 2013)[5] ^{1}H NMR (500 MHz, $CDCl_3$)	Synthetic (–)-attenol A this report ^{1}H NMR (500 MHz, $CDCl_3$)
1	3.65 (2H, m)	3.66 (2H, m)	3.67 (2H, m)
2	2.29 (m), 2.41 (m)	2.29 (m), 2.42 (m)	2.29 (dt), 2.42 (dt)
3	5.54 (m)	5.56 (m)	5.53 (m)
4	5.68 (m)	5.68 (m)	5.69 (m)
5	2.12 (m), 2.51 (br dt, 13.8, 8.8)	2.11 (m), 2.52 (m)	2.11 (m), 2.51 (m)
6	3.72 (m)	3.66 (m)	3.67 (m)
7	3.31 (dd, 10.4, 1.2)	3.31 (dd, 10.1, 1.4)	3.32 (dd, 10.2, 1.4)
8	1.74 (m)	1.70 (m)	1.74 (m)
9	1.50 (m), 1.65 (m)	1.49 (m), 1.70 (m)	1.49 (m), 1.65 (m)
10	1.64 (m), 1.75 (m)	1.70 (2H, m)	1.65 (m), 1.75 (m)
12	1.70 (m), 2.02 (m)	1.70 (m), 2.01 (m)	1.70 (m), 2.02 (m)
13	1.84 (m), 2.02 (m)	1.84 (m), 2.01 (m)	1.84 (m), 2.02 (m)
14	4.31 (m)	4.32 (m)	4.32 (m)
15	1.72 (2H, m)	1.70 (2H, m)	1.72 (2H, m)
16	3.83 (m)	3.83 (m)	3.83 (m)
17	1.50 (2H, m)	1.49 (2H, m)	1.49 (2H, m)
18	1.43 (m), 1.56 (m)	1.49 (2H, m)	1.49 (2H, m)
19	2.09 (2H, m)	2.11 (2H, m)	2.09 (2H, m)
20	5.81 (ddt, 17.2, 10.2, 6.8)	5.81 (ddt, 16.9, 10.2, 6.7)	5.81 (ddt, 16.9, 10.2, 6.6)
21	4.95 (br d, 10.2), 5.01 (br d, 17.2)	4.95 (d, 10.1), 5.01 (dd, 17.2, 1.8)	4.95 (br d, 10.2), 5.01 (dd, 17.1, 1.9)
22	0.87 (3H, d, 6.4)	0.88 (3H, d, 6.6)	0.88 (3H, d, 6.5)

Table S2. Comparison of ^{13}C NMR spectroscopic data between synthetic and isolated (−)-attenol A (5)

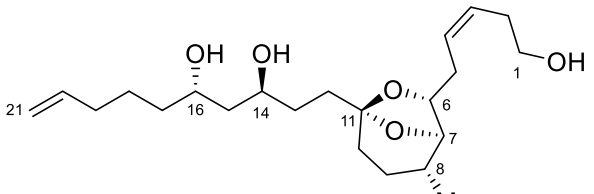


(–)-attenol A (**5**)

position	Natural (–)-attenol A (Uemura, 1999)[4] ^{13}C NMR (100 MHz, $CDCl_3$)	Synthetic (–)-attenol A (Yadav, 2013)[5] ^{1}H NMR (75 MHz, $CDCl_3$)	Synthetic (–)-attenol A this report ^{13}C NMR (125MHz, $CDCl_3$)
1	61.9	61.8	61.9
2	30.9	30.8	30.9
3	128.0	128.0	128.0
4	129.6	129.4	129.6
5	33.0	32.8	33.0
6	70.1	70.0	70.1
7	78.0	77.9	78.0
8	30.4	30.8	30.4
9	29.0	29.0	29.0
10	33.9	33.8	33.9
11	106.4	106.3	106.4
12	38.5	38.5	38.5
13	30.8	30.8	30.8
14	78.0	77.9	78.0
15	43.6	43.7	43.6
16	69.6	69.5	69.6
17	36.6	36.6	36.6
18	25.1	25.0	25.1
19	33.7	33.6	33.7
20	138.7	138.6	138.7
21	114.6	114.5	114.6
22	17.3	17.2	17.3

4.2 NMR Data Natural and Synthetic (+)-attenol B (6)

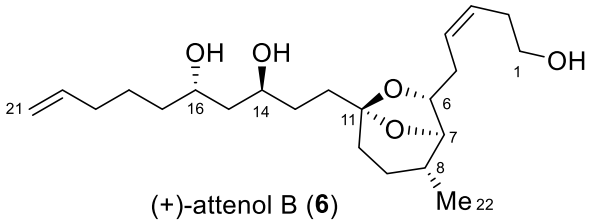
Table S3. Comparison of ^{1}H NMR spectroscopic data between synthetic and isolated (+)-attenol B (6)



(+)-attenol B (**6**)

position	Natural (+)-attenol B (Uemura, 1999)[4] ^{1}H NMR (400 MHz, $CDCl_3$)	Synthetic (+)-attenol B (Tong, 2015)[6] ^{1}H NMR (400 MHz, $CDCl_3$)	Synthetic (+)-attenol B this report ^{1}H NMR (400 MHz, $CDCl_3$)
1	3.63 (2H, m)	3.63 (2H, m)	3.63 (2H, m)
2	2.31 (m), 2.39 (m)	2.29 (m), 2.40 (m)	2.31 (m), 2.30 (m)
3	5.53 (m)	5.54 (m)	5.54 (m)
4	5.54 (m)	5.54 (m)	5.54 (m)
5	2.31 (m), 2.39 (m)	2.29 (m), 2.40 (m)	2.31 (m), 2.40 (m)
6	4.09 (t, 6.7)	4.09 (t, 6.8)	4.08 (t, 6.7)
7	3.92 (s)	3.93 (s)	3.93 (s)
8	1.67 (m)	1.63 (m)	1.68 (m)
9	1.34 (dd, 15.2, 5.7) 2.02 (m)	1.34 (dd, 13.9, 5.0) 2.00 (m)	1.34 (dd, 14.2, 5.4) 2.02 (m)
10	1.51 (m), 1.68 (m)	1.53 (m), 1.63 (m)	1.52 (m), 1.68 (m)
12	1.85 (m), 1.90 (m)	1.82 (2H, m)	1.84 (m), 1.90 (m)
13	1.61 (m), 1.81 (m)	1.63 (m), 1.84 (m)	1.61 (m), 1.79 (m)
14	3.95 (m)	3.96 (m)	3.95 (m)
15	1.58 (m), 1.65 (m)	1.63 (2H, m)	1.51 (m), 1.61 (m)
16	3.93 (m)	3.96 (m)	3.95 (m)
17	1.43 (m), 1.54 (m)	1.45 (m), 1.63 (m)	1.43 (m), 1.52(m)
18	1.40 (m), 1.53 (m)	1.45 (m), 1.63 (m)	1.43 (m), 1.52(m)
19	2.08 (2H, m)	2.08 (2H, m)	2.08 (2H, m)
20	5.81 (ddt, 17.2, 10.2, 6.8)	5.81 (m)	5.81 (ddt, 17.0, 10.2, 6.7)
21	4.95 (br d, 10.1), 5.01 (br d, 17.2)	4.95 (d, 10.0), 5.01 (d, 17.3)	4.94 (d, 10.2), 5.01 (d, 17.3)
22	1.12 (3H, d, 7.0)	1.12 (3H, d, 7.1)	1.12 (3H, d, 7.1)

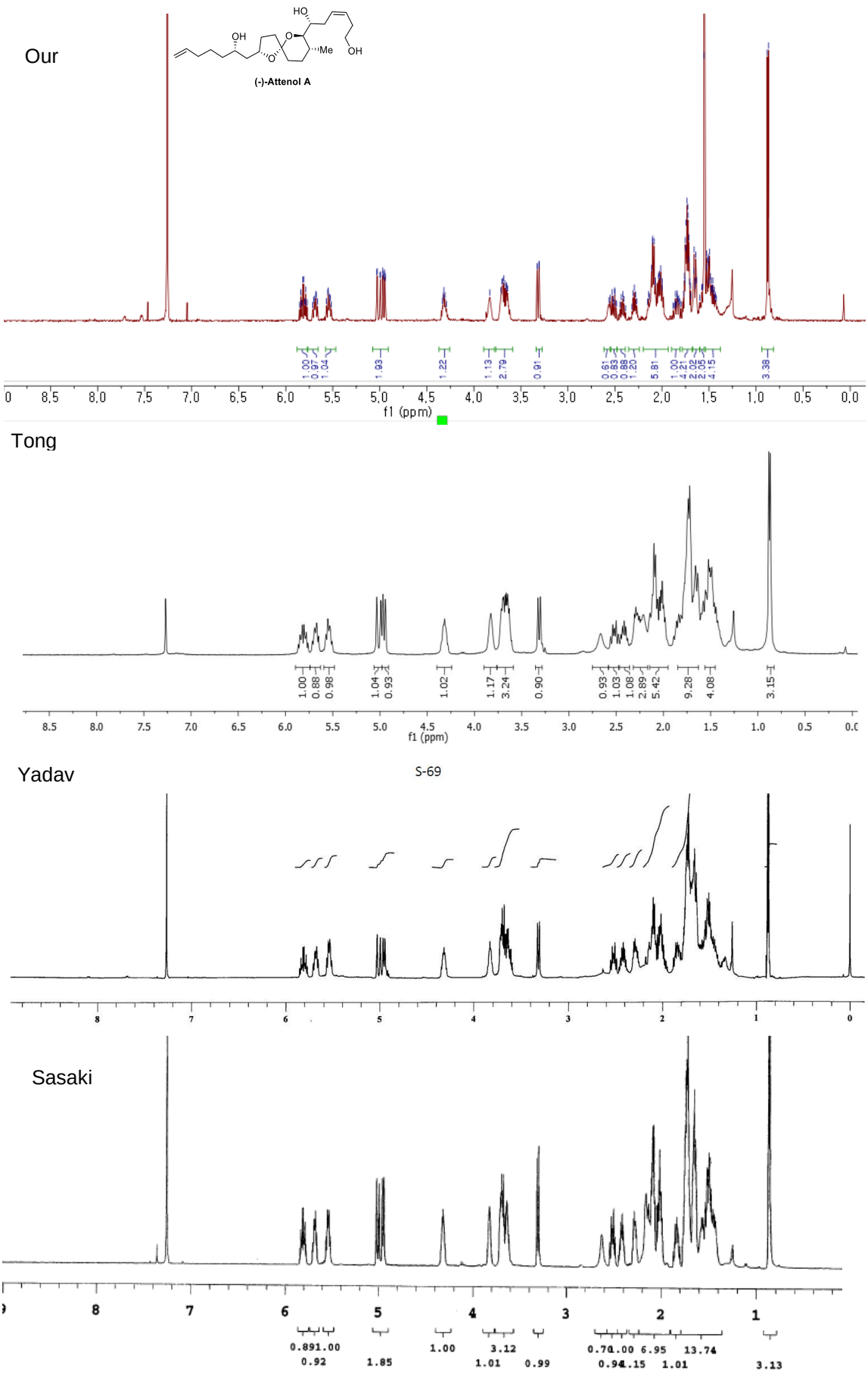
Table S4. Comparison of ^{13}C NMR spectroscopic data between synthetic and isolated (+)-attenol B (6)



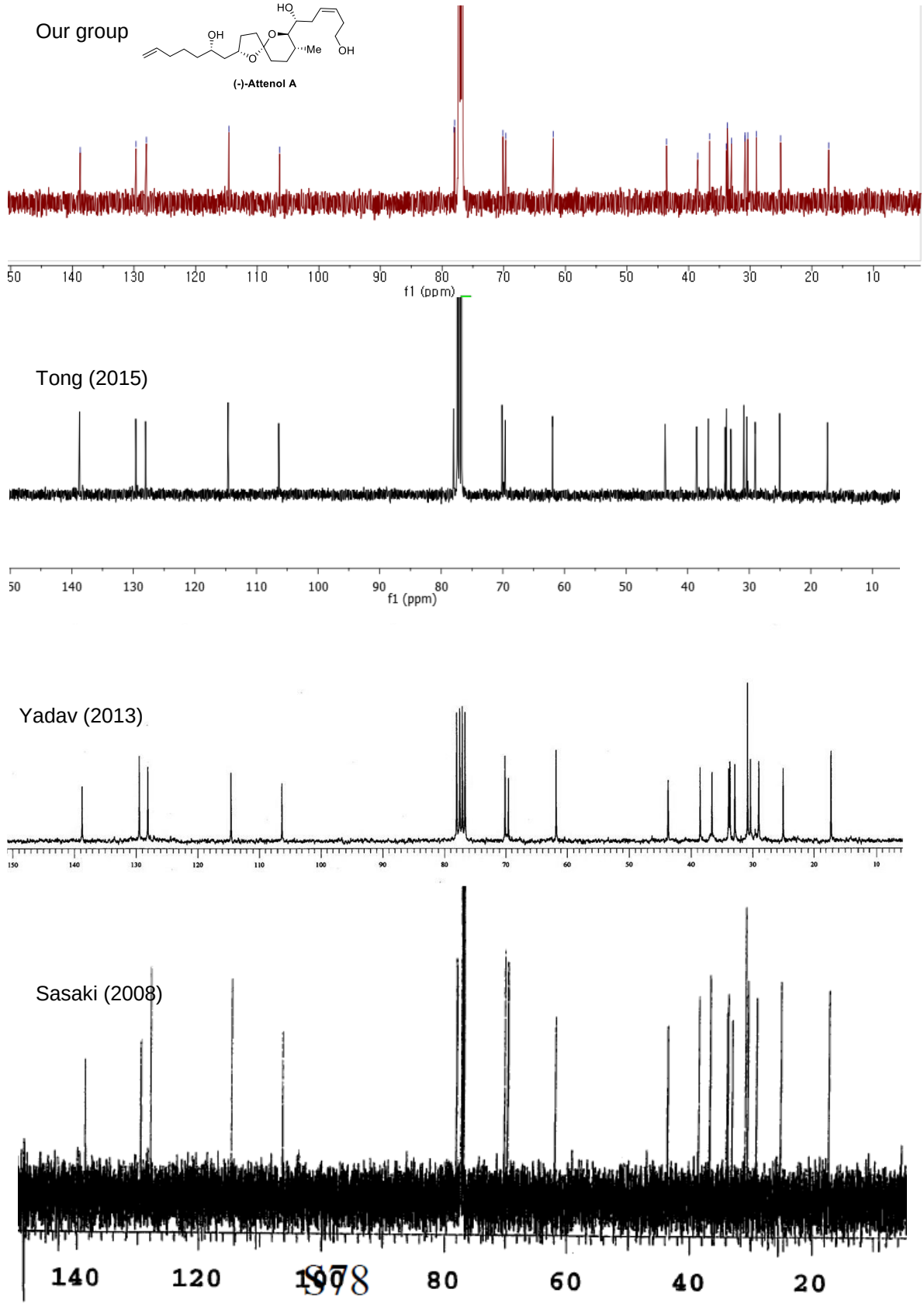
(+)-attenol B (**6**)

position	Natural (+)-attenol B (Uemura, 1999)[4] ^{13}C NMR (100 MHz, $CDCl_3$)	Synthetic (+)-attenol B (Tong, 2015)[6] ^{13}C NMR (100 MHz, $CDCl_3$)	Synthetic (+)-attenol B this report ^{13}C NMR (125 MHz, $CDCl_3$)
1	61.9	61.9	61.9
2	31.3	31.3	31.3
3	128.5	128.5	128.5
4	127.9	127.9	127.9
5	33.7	33.7	33.7
6	80.1	80.1	80.1
7	83.1	83.1	83.1
8	31.2	31.2	31.2
9	23.1	23.1	23.1
10	30.3	30.3	30.3
11	109.6	109.6	109.6
12	34.5	34.5	34.5
13	30.3	30.2	30.3
14	70.2	70.2	70.2
15	42.5	42.5	42.5
16	69.2	69.2	69.2
17	36.9	36.9	36.9
18	25.0	25.1	25.0
19	33.7	33.7	33.7
20	138.8	138.8	138.8
21	114.5	114.5	114.5
22	16.9	16.9	16.9

4.3 Comparison of ^{1}HNMR spectrum of Synthetic (−)-attenol A (5) (500 MHz)

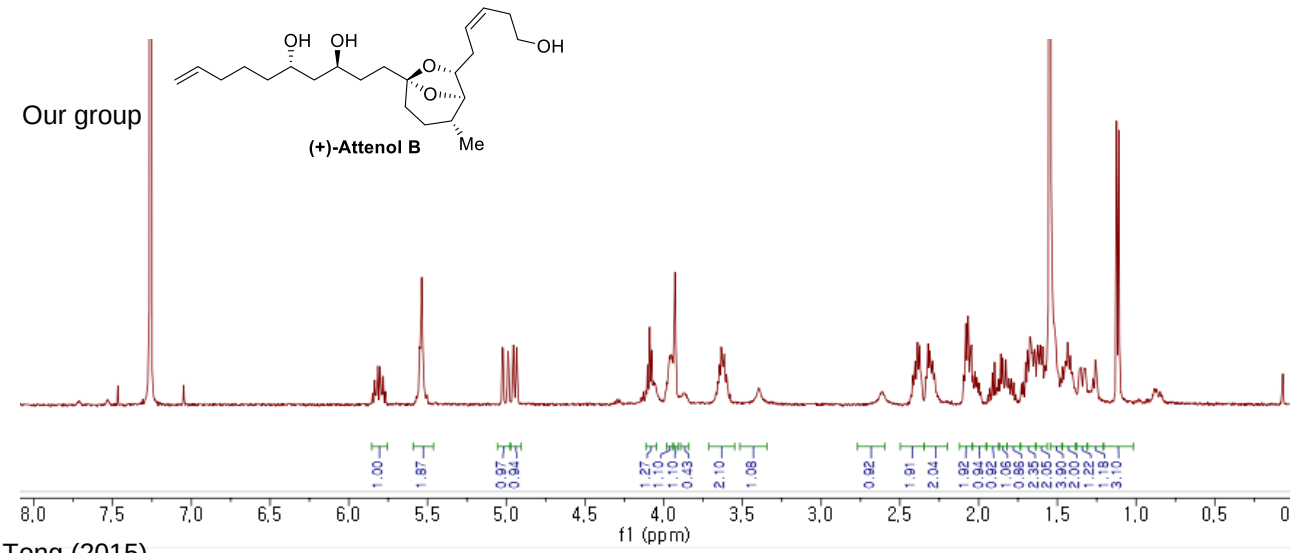


4.4 Comparison of ^{13}CNMR spectrum of Synthetic (−)-attenol A (5) (500 MHz)

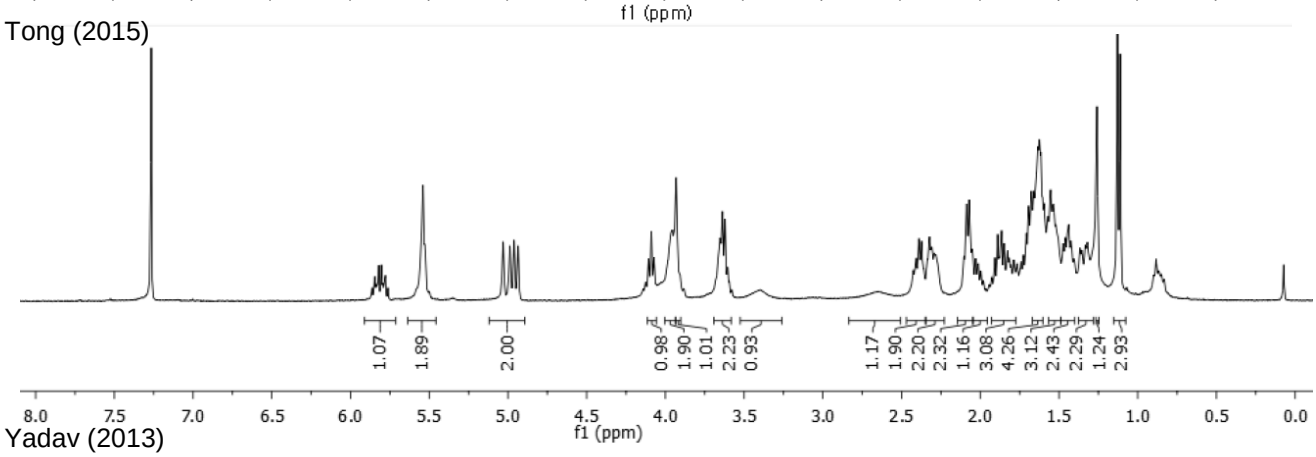


4.5 Comparison of ^{1}HNMR spectrum of Synthetic (+)-attenol B (6) (500 MHz)

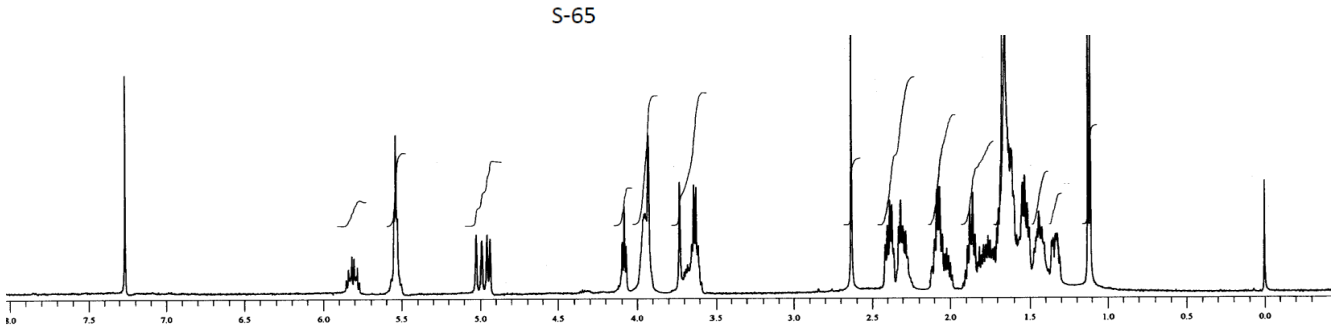
Our group



Tong (2015)

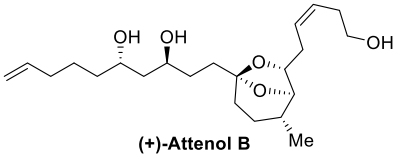


Yadav (2013)



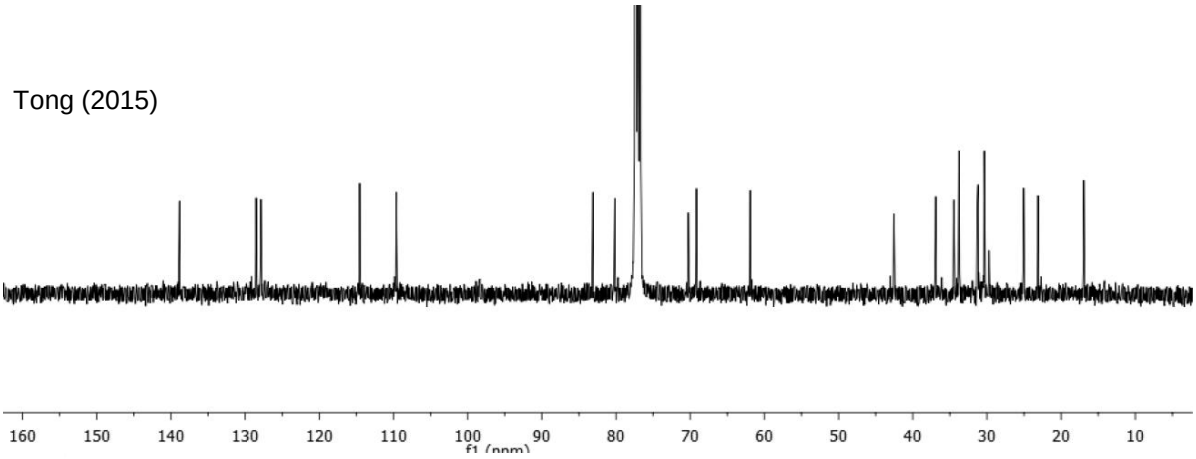
4.6 Comparison of ^{13}CNMR spectrum of Synthetic (+)-attenol B (6) (500 MHz)

Our group

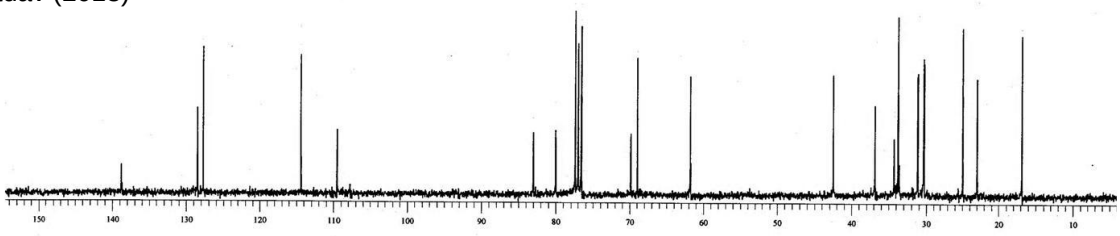


(+)-Attenol B

Tong (2015)



Yadav (2013)



5. References

1. Y.-J. Kim, Y. Yoon and H.-Y. Lee, An asymmetric total synthesis of (+)-pentalenene, *Tetrahedron*, 2013, **69**, 7810–7816.

2. K. Araki, K. Suenaga, T. Sengoku and D. Uemura, Total synthesis of attenols A and B, *Tetrahedron*, 2002, **58**, 1983–1995.

3. N. Ogawa, T. Amano and Y. Kobayashi, Synthesis of Optically Active Maresin 2 and Maresin $2_{n\text{-}3\ DPA}$, *Synlett*, 2021, **32**, 295–298.

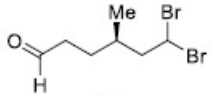
4. N. Takada, K.Suenaga, K. Yamada, S.-Z. Zheng, H.-S. Chen and D. Uemura, Isolation and Structures of Attenols A and B. Novel Bicyclic Triols from the Chinese Bivalve Pinna attenuata, *Chem. Lett.*, 1999, **1999**, 1025–1026

5. J. S. Yadav, P. A. N. Reddy, Y. J. Reddy, S. Meraj and A. R. Prasad, Stereoselective Total Synthesis of Attenols A and B, *European J. Org. Chem.*, 2013, **2013**, 6317–6324.

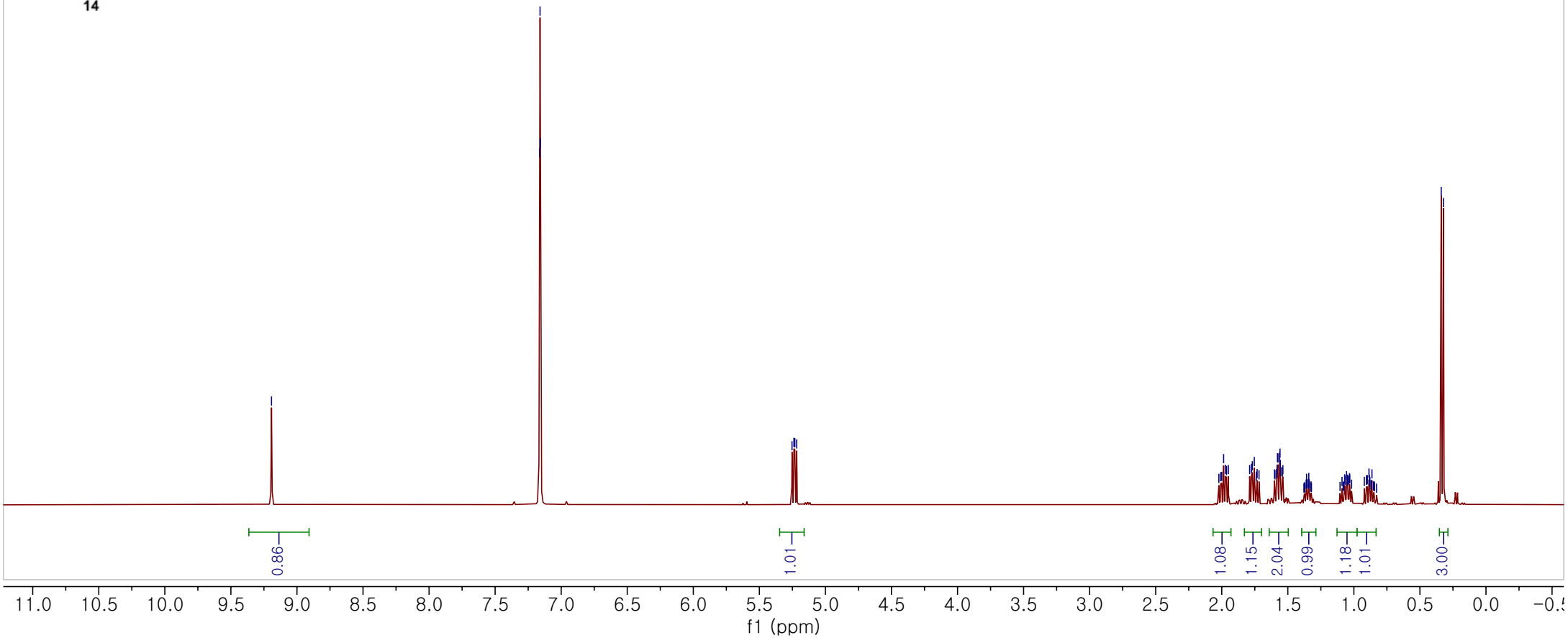
6. J. Ren, J. Wang and R. Tong, Asymmetric Total Synthesis of (+)-Attenol B, *Org. Lett.*, 2015, **17**, 744–747.

6. Copies of ^{1}H and ^{13}C NMR spectra

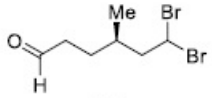
Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	spect
4 Solvent	C6D6
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z8246_0041 (PH DUL 400SB C-H-D-05 Z)
8 Spectrometer Frequency	400.12
9 Nucleus	1H



14

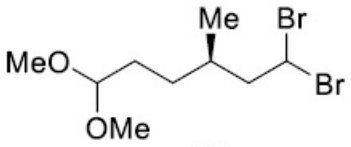


Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	spect
4 Solvent	C6D6
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z8246_0041 (PH DUL 400SB C-H-D-05 Z)
8 Spectrometer Frequency	100.62
9 Nucleus	13C



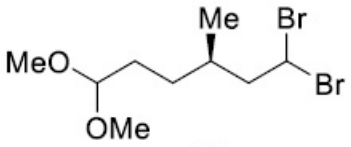
14

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	spect
4 Solvent	C6D6
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z8246_0041 (PH DUL 400SB C-H-D-05 Z)
8 Spectrometer Frequency	400.12
9 Nucleus	1H



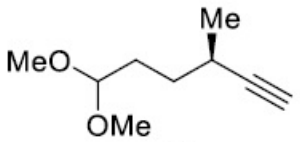
15

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	spect
4 Solvent	C6D6
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z8246_0041 (PH DUL 400SB C-H-D-05 Z)
8 Spectrometer Frequency	100.62
9 Nucleus	13C



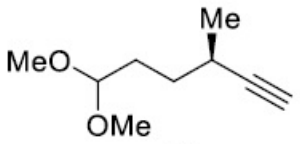
15

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	500.23
9 Nucleus	1H



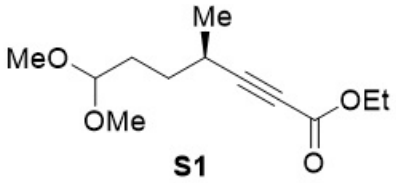
16

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.2
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	125.80
9 Nucleus	13C



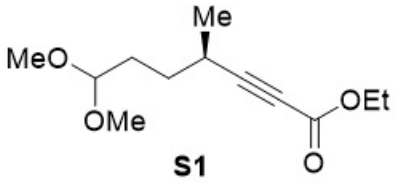
16

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	spect
4 Solvent	C6D6
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z116098_0402 (PA BBO 400S1 BBF-H-D-05 Z SP)
8 Spectrometer Frequency	400.12
9 Nucleus	1H



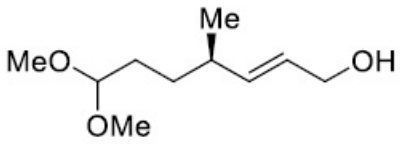
S1

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	spect
3 Solvent	C6D6
4 Temperature	298.0
5 Experiment	1D
6 Probe	Z116098_0402 (PA BBO 400S1 BBF-H-D-05 Z SP)
7 Number of Scans	500
8 Spectrometer Frequency	100.62
9 Nucleus	13C



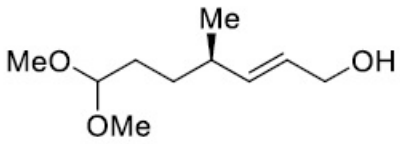
S1

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	spect
4 Solvent	C6D6
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z163739_0458 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	400.12
9 Nucleus	1H



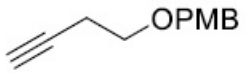
17

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	spect
4 Solvent	C6D6
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z163739_0458 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	100.62
9 Nucleus	13C



17

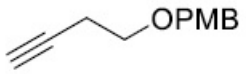
Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	500.23
9 Nucleus	1H



12

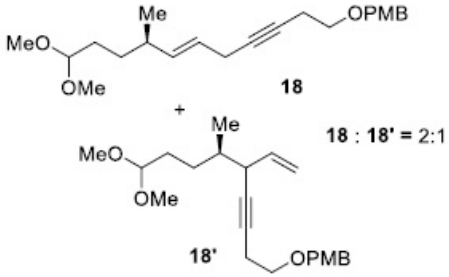
Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.3
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	125.80
9 Nucleus	13C

159.24
130.07
129.32
113.79
81.32
72.63
69.25
67.81
55.25
19.85

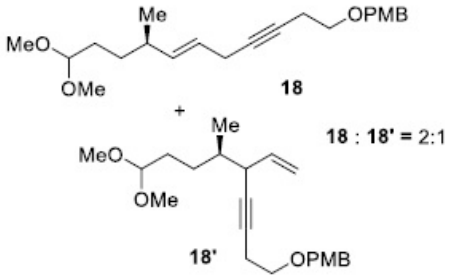


12

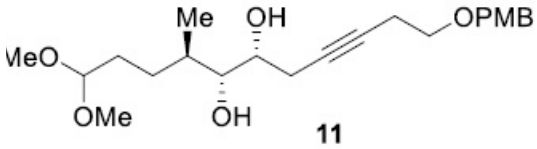
Parameter	Value
1 Title	
2 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
3 Instrument	spect
4 Solvent	C6D6
5 Temperature	295.2
6 Experiment	1D
7 Probe	5 mm Dual 13C/ 1H Z8246/ 0025
8 Spectrometer Frequency	400.13
9 Nucleus	1H



Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	C6D6
5 Temperature	298.2
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	125.80
9 Nucleus	13C

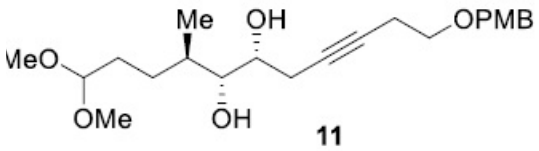


Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	C6D6
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z163739_0458 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	400.23
9 Nucleus	1H



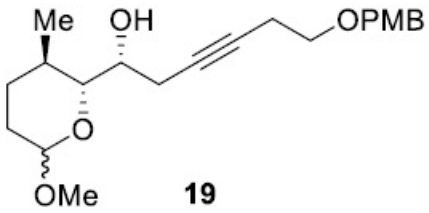
11

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	C6D6
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z163739_0458 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	100.65
9 Nucleus	13C



11

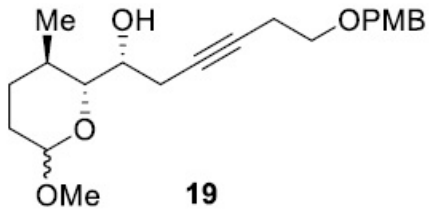
Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	spect
4 Solvent	C6D6
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z8246_0041 (PH DUL 400SB C-H-D-05 Z)
8 Spectrometer Frequency	400.12
9 Nucleus	1H



19

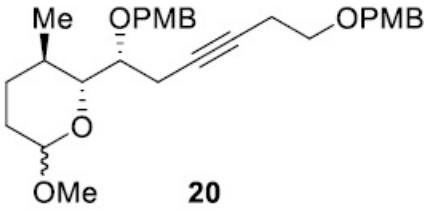
Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	spect
4 Solvent	C6D6
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z8246_0041 (PH DUL 400SB C-H-D-05 Z)
8 Spectrometer Frequency	100.62
9 Nucleus	13C

159.75
130.97
129.42
114.09
98.57
79.30
78.62
74.26
72.68
69.72
68.91
54.79
54.40
30.69
30.51
27.06
25.02
20.65
17.58



19

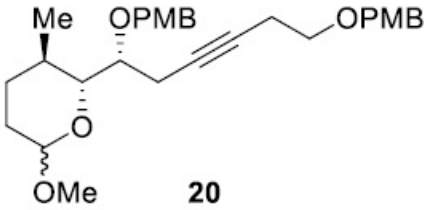
Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	C6D6
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	500.23
9 Nucleus	1H



20

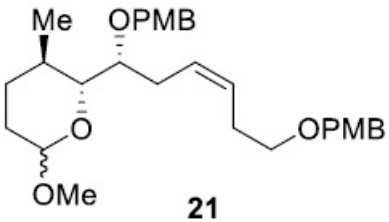
Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	C6D6
5 Temperature	298.3
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	125.80
9 Nucleus	13C

159.75
139.36
139.05
129.74
129.42
114.08
114.05
114.03
98.67
79.27
79.03
77.38
74.23
72.73
72.70
71.83
68.90
54.78
54.53
30.65
30.56
27.51
20.74
20.14
17.78



20

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	C6D6
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	500.23
9 Nucleus	1H



21

13220707

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	C6D6
5 Temperature	298.3
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	125.80
9 Nucleus	13C

159.63
131.66
131.30
129.54
129.32
128.61
128.29
114.02
113.97
98.61
79.03
74.76
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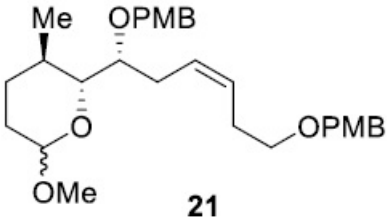
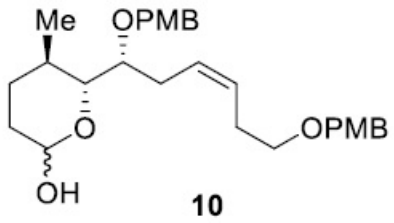
30.91
30.47
28.82
28.39
27.56
18.00



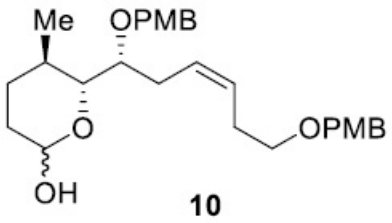
21

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	C6D6
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	500.23
9 Nucleus	1H



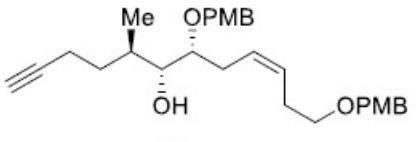
10

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	spect
4 Solvent	C6D6
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z116098_0402 (PA BBO 400S1 BBF-H-D-05 Z SP)
8 Spectrometer Frequency	100.62
9 Nucleus	13C



10

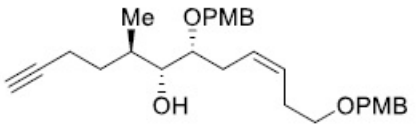
Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z163739_0458 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	400.23
9 Nucleus	1H



22

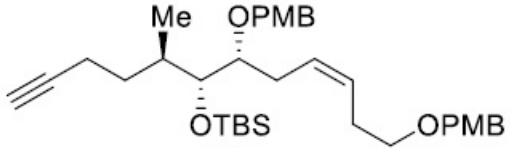
159.28
159.16
130.42
130.36
129.51
129.31
128.57
126.68
113.81
113.76
84.76
78.25
78.24
72.58
71.50
69.29
68.25
55.28
55.26
34.22
30.52
28.39
28.19
16.18
16.05

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	125.80
9 Nucleus	13C



22

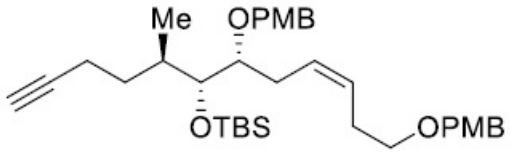
Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	500.23
9 Nucleus	1H



9

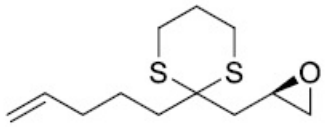
159.09
158.92
131.11
130.60
129.20
129.06
128.15
127.11
113.72
113.57
84.76
81.77
76.91
72.49
71.63
69.58
68.26
55.24
33.98
30.66
28.21
27.80
26.05
18.25
17.14
16.24
-3.96
-4.50

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.2
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	125.80
9 Nucleus	13C



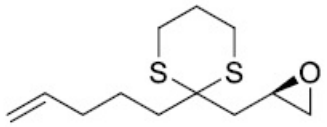
9

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	500.23
9 Nucleus	1H



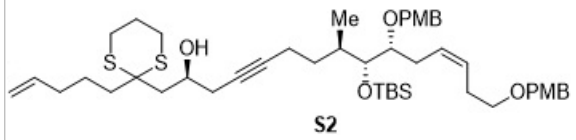
8

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.1
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	125.80
9 Nucleus	13C



8

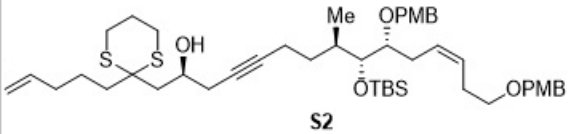
Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z163739_0458 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	400.23
9 Nucleus	1H



S2

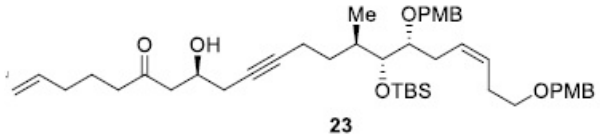
159.09
158.92
138.14
131.12
129.21
129.08
128.19
127.10
115.10
113.73
113.57
82.94
81.76
77.20
76.93
76.22
72.51
71.64
69.59
67.72
55.25
51.96
43.07
39.06
34.21
33.71
31.16
28.20
28.10
27.89
26.41
26.07
25.97
25.03
22.92
18.27
17.23
16.66
-3.96
-4.47

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.1
6 Experiment	1D
7 Probe	Z163739_0458 (PI HR-BBO400S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	100.65
9 Nucleus	13C



S2

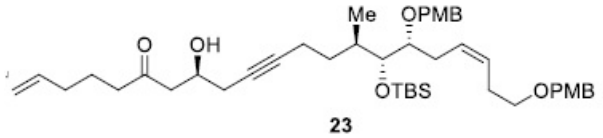
Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	500.23
9 Nucleus	1H



23

211.25
159.09
158.94
137.81
131.04
130.52
129.22
129.09
128.24
127.08
115.32
113.72
113.57
83.20
81.82
76.81
75.66
72.51
71.67
69.57
66.56
55.23
47.88
42.68
34.02
32.96
31.17
28.19
27.83
26.72
26.03
22.47
18.24
17.24
16.60
-3.99
-4.51

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.3
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	125.80
9 Nucleus	13C



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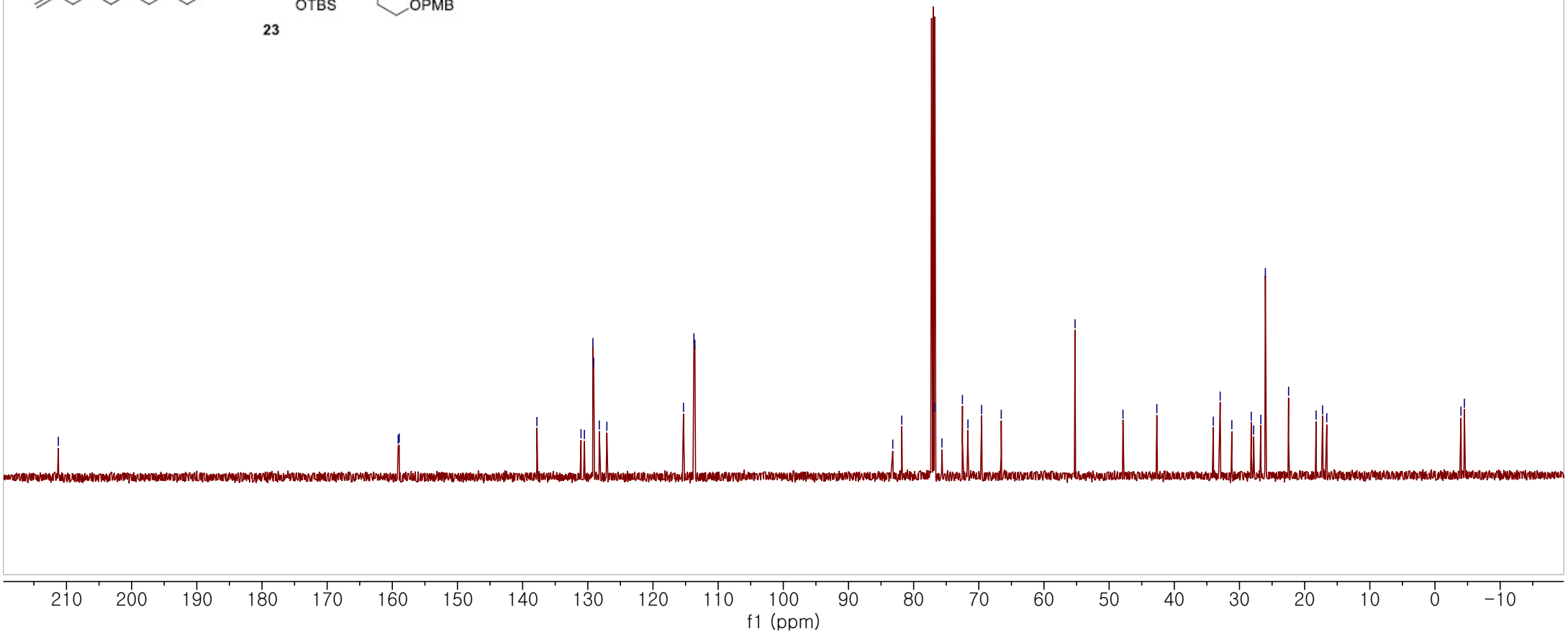
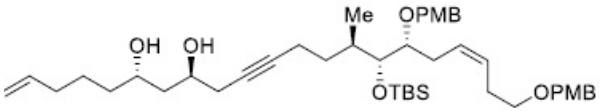
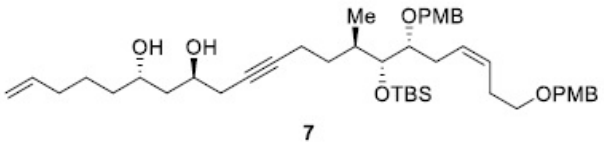


Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	spect
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z116098_0402 (PA BBO 400S1 BBF-H-D-05 Z SP)
8 Spectrometer Frequency	400.12
9 Nucleus	1H



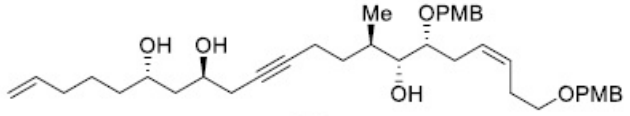
7

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	spect
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z116098_0402 (PA BBO 400S1 BBF-H-D-05 Z SP)
8 Spectrometer Frequency	100.62
9 Nucleus	13C

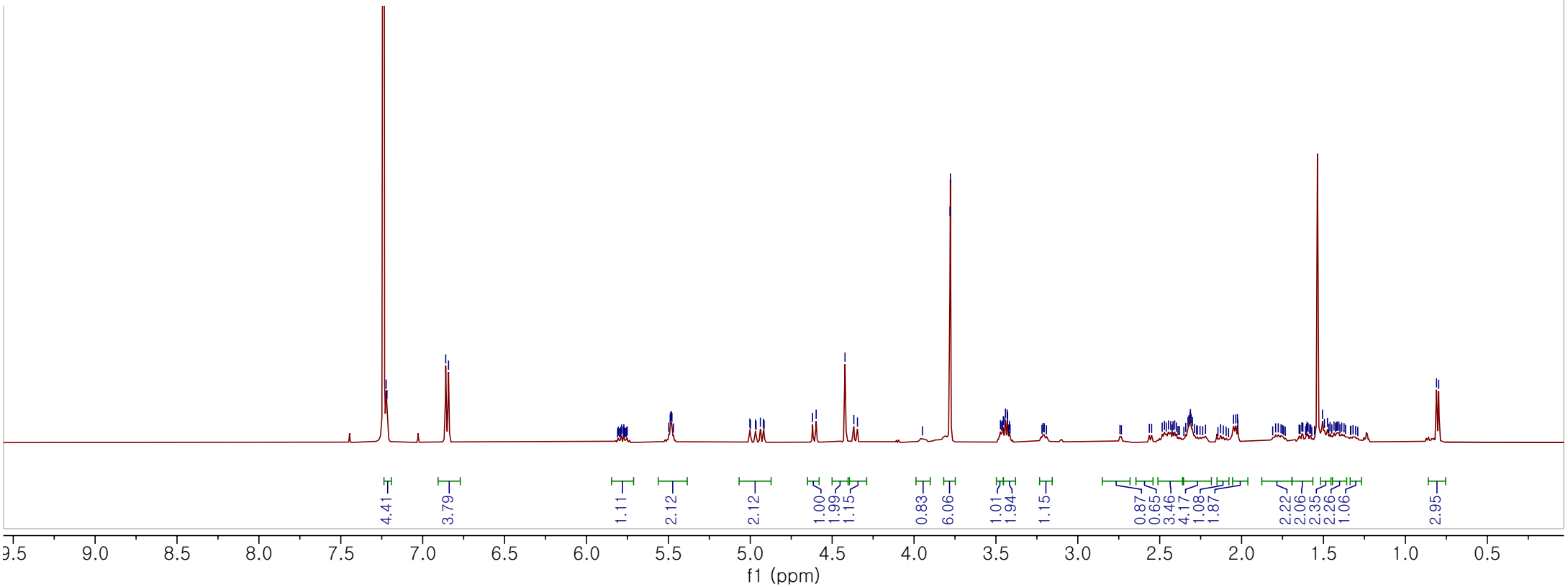


7

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	500.23
9 Nucleus	1H

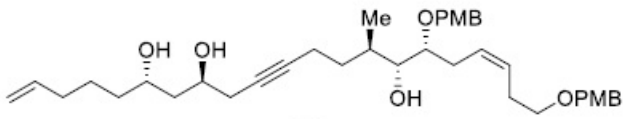


24



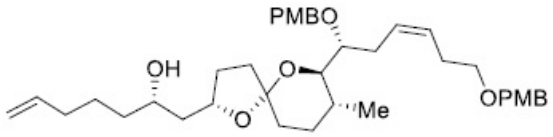
Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.3
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	125.80
9 Nucleus	13C

159.28
159.19
138.69
130.37
130.29
129.52
129.49
129.37
128.50
126.79
114.61
113.81
113.78
83.25
78.24
77.00
76.03
72.63
71.47
69.31
68.95
67.86
55.28
55.26
41.60
36.72
34.23
33.67
31.09
28.35
28.19
27.88
25.04
16.33
15.97



24

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	500.23
9 Nucleus	1H



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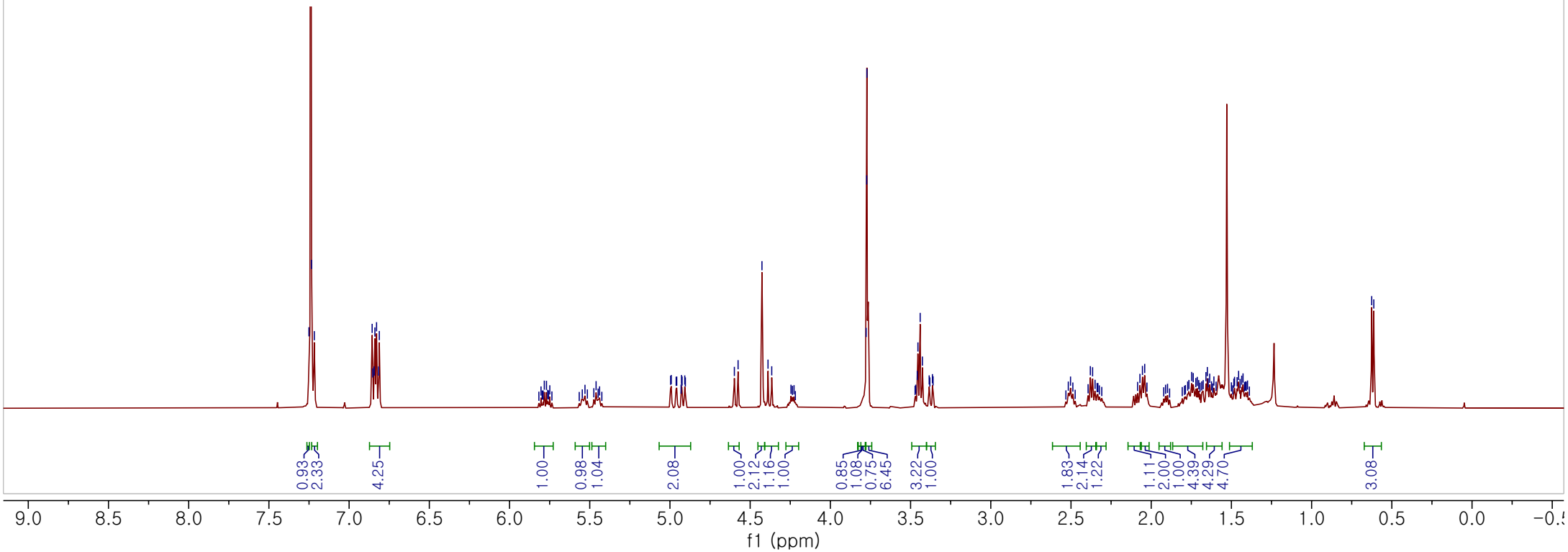
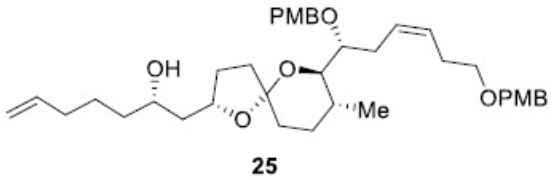


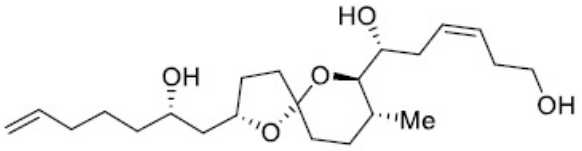
Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.3
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	125.80
9 Nucleus	13C

159.12
130.89
130.46
129.73
129.44
128.46
127.40
125.20
114.55
113.75
113.60
106.33
77.70
72.55
71.32
69.73
69.52
55.25
43.34
38.39
36.64
34.07
33.74
31.09
30.04
29.44
28.23
28.06
25.15
17.23

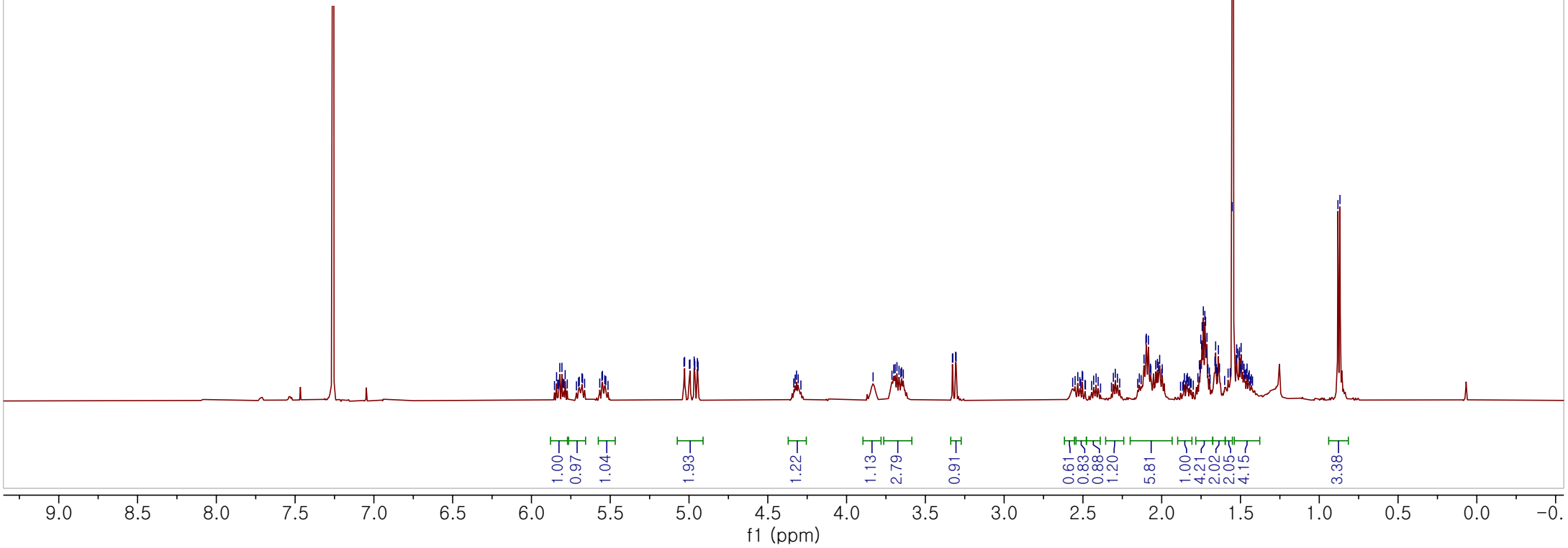


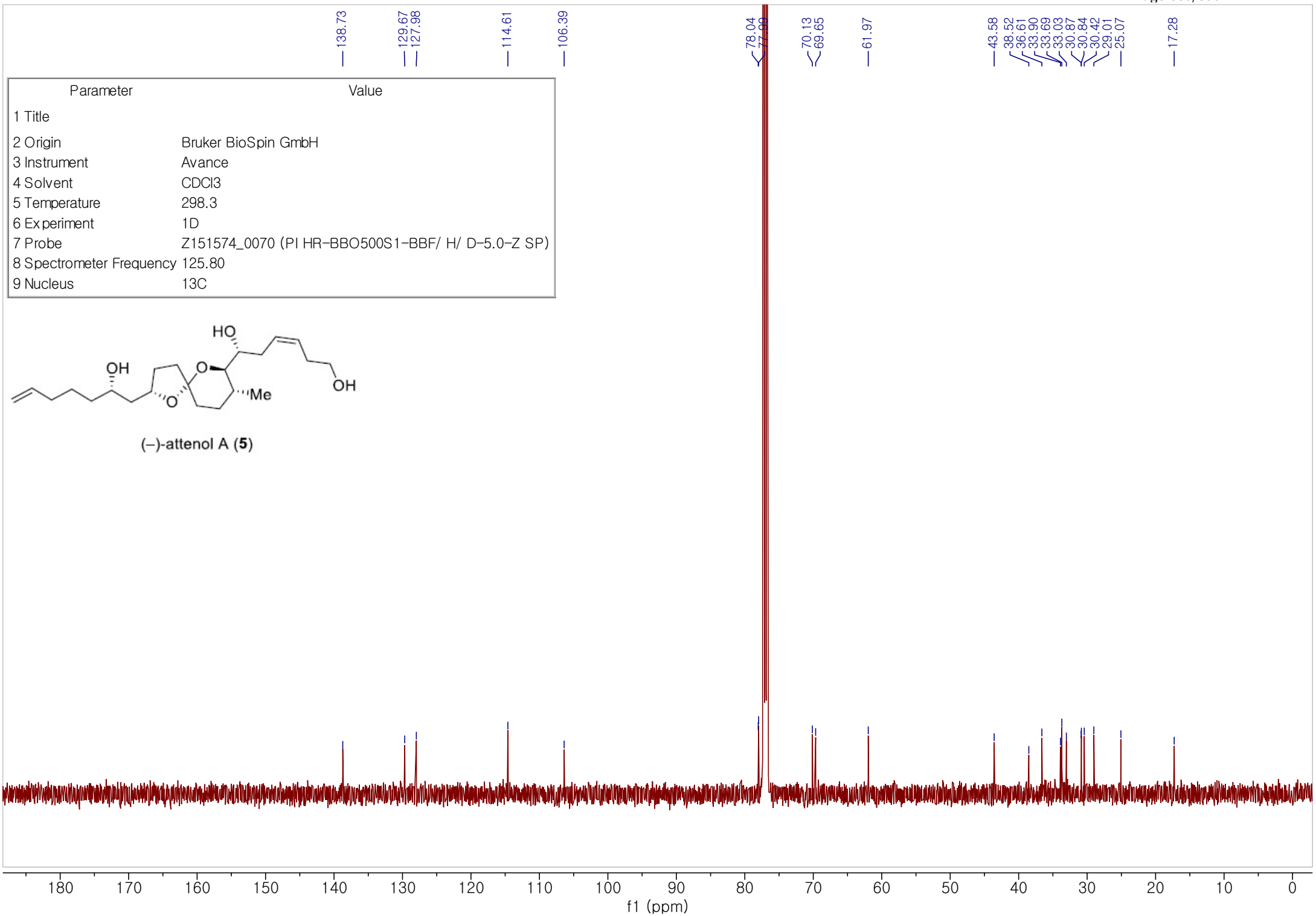
25

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	500.23
9 Nucleus	1H

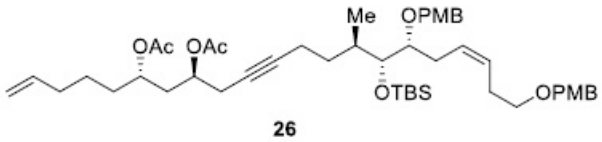


(–)-attenol A (**5**)




138.73
129.67
127.98
114.61
106.39
78.04
77.99
70.13
69.65
61.97
43.58
38.52
36.61
33.90
33.69
33.03
30.87
30.84
30.42
29.01
25.07
17.28
Parameter
Value
1 Title
2 Origin
Bruker BioSpin GmbH
3 Instrument
Avance
4 Solvent
CDCl3
5 Temperature
298.3
6 Experiment
1D
7 Probe
Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency
125.80
9 Nucleus
13C
HO
OH
O
O
Me
OH
(–)-attenol A (5)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

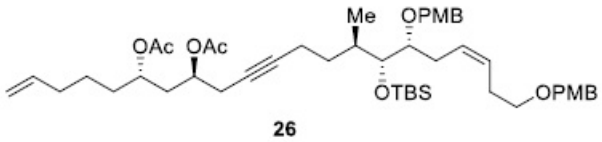
Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	500.23
9 Nucleus	1H



26

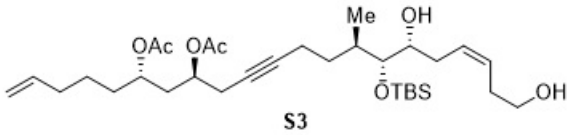
Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.4
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	125.80
9 Nucleus	13C

170.66
170.24
159.09
158.93
138.29
131.10
130.59
129.19
129.05
128.46
127.14
114.85
113.72
113.57
83.02
81.90
77.25
77.00
76.75
74.69
72.51
71.66
71.00
69.82
69.58
68.28
55.24
37.50
37.03
34.43
34.23
33.49
31.40
28.19
27.85
26.05
24.70
24.44
21.08
21.04
18.25
17.05
16.64
-3.99
-4.46



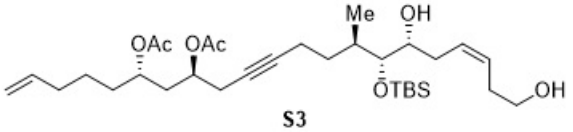
26

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	500.23
9 Nucleus	1H



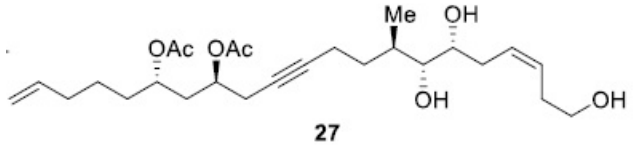
S3

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.3
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	125.80
9 Nucleus	13C

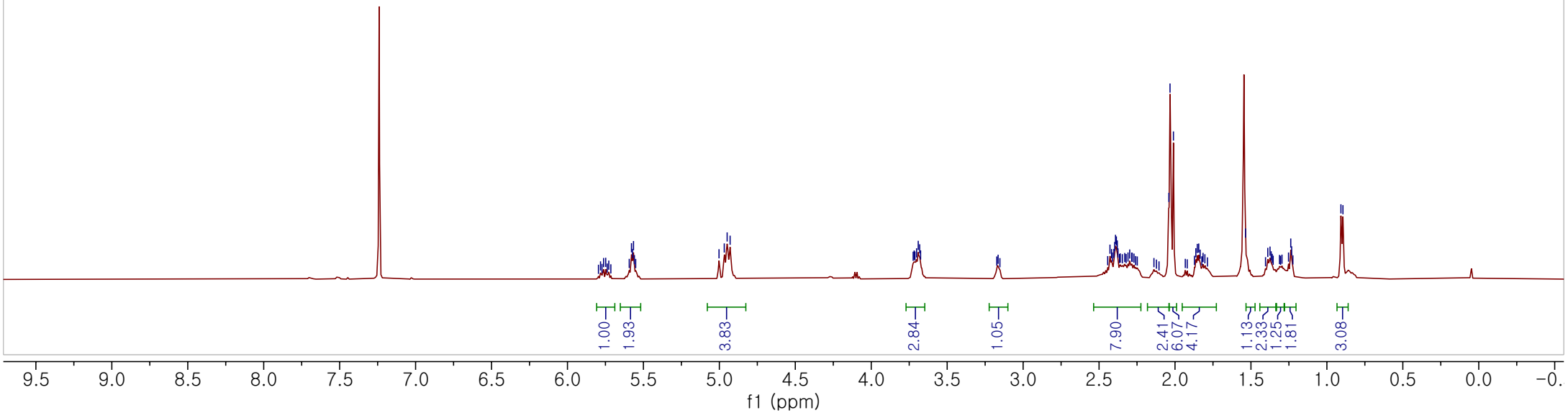


S3

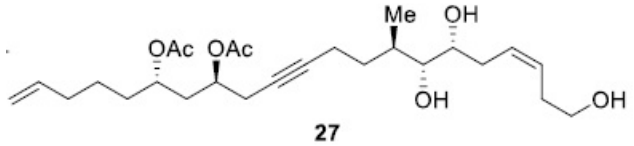
Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	500.23
9 Nucleus	1H



27

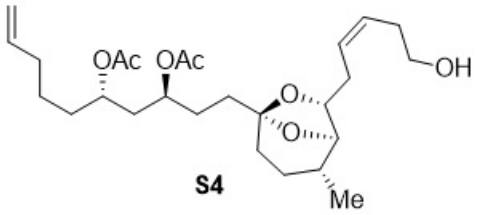


Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.1
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	125.80
9 Nucleus	13C

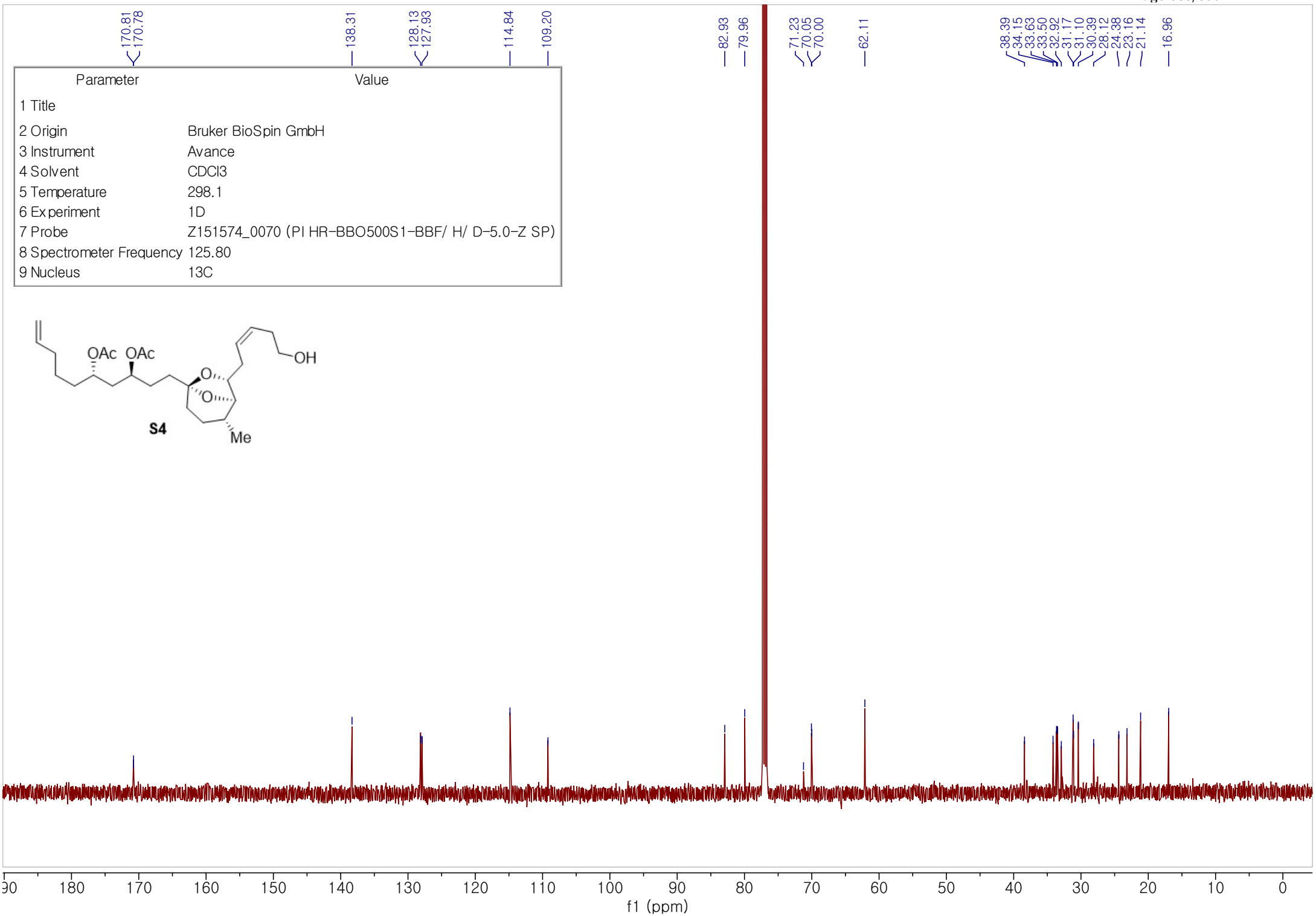


27

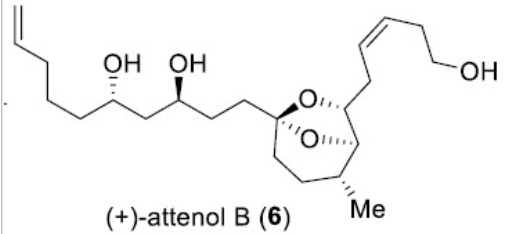
Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	500.23
9 Nucleus	1H



S4

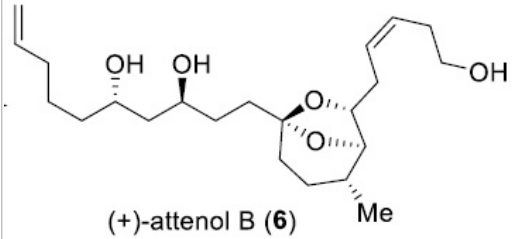

170.81
170.78
138.31
128.13
127.93
114.84
109.20
82.93
79.96
71.23
70.05
70.00
62.11
38.39
34.15
33.63
33.50
32.92
31.17
31.10
30.39
28.12
24.38
23.16
21.14
16.96
Parameter
Value
1 Title
2 Origin
Bruker BioSpin GmbH
3 Instrument
Avance
4 Solvent
CDCl3
5 Temperature
298.1
6 Experiment
1D
7 Probe
Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency
125.80
9 Nucleus
13C
OAc
OAc
OH
O
O
Me
S4
f1 (ppm)

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.0
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	500.23
9 Nucleus	1H



(+)-attenol B (**6**)

Parameter	Value
1 Title	
2 Origin	Bruker BioSpin GmbH
3 Instrument	Avance
4 Solvent	CDCl3
5 Temperature	298.2
6 Experiment	1D
7 Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
8 Spectrometer Frequency	125.80
9 Nucleus	13C



(+)-attenol B (**6**)