Supplementary Information

Chemoselective Nozaki-Hiyama-Takai-Kishi and Grignard reaction:

Short synthesis of some carbahexopyranoses

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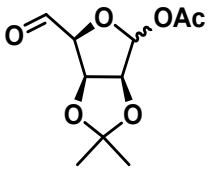
Experimental Section

General Information: Moisture- and oxygen-sensitive reactions were carried out under nitrogen. All solvents and reagents were purified by standard techniques. All other reagents were obtained from commercial sources and used without further purification. TLC was performed on Merck Kiesel gel 60, F254 plates (layer thickness: 0.25 mm). Column chromatography was performed on silica gel (Acme, 60–120 mesh) by using ethyl acetate, hexane, chloroform, and MeOH as eluents. Organic solutions were dried over anhydrous Na_2SO_4 and concentrated below 40 °C under reduced pressure. IR spectra were recorded on a Perkin–Elmer RX-1and JASCO FT/IR-5300 FTIR system. NMR spectra were recorded at 300, 400, 500 MHz (H) and 75, 100, 125 MHz (C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: δ = 7.26 and C: δ = 77.16 ppm) as internal standard, and coupling constants (*J*) are given in Hz. Optical rotations were measured on JASCO P-2000 polarimeter at 20 °C using 50 mm cell of 1 mL capacity. Accurate mass measurements were performed on a Q STAR mass spectrometer (Applied Biosystems, USA).

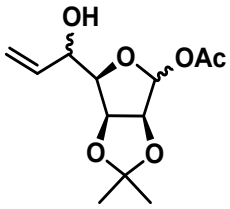
Experimental procedure:

Procedure for glycol cleavage for intermediate 2:



Vicinal diol **1** (1 g, 3.8 mmol) was dissolved in THF: H_2O (4:1) (15 mL) & silica gel-supported $NaIO_4$ reagent (2.43 g, 11.4 mmol) was added. After stirring 0.5 h at 0 °C temperature, the silica gel was filtered through a celite pad, and washed with EtOAc (3 × 30 mL), then dried over Na_2SO_4, and concentrated to afford the crude aldehyde **2**, which was taken to the next step without purification.

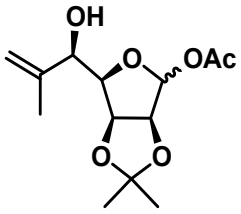
(3a*S*,6*R*,6a*S*)-6-(1-hydroxyallyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl acetate (3a & 3b):



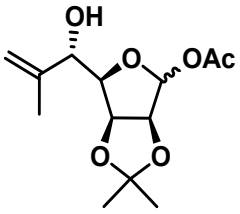
The crude aldehyde **2** (0.9 g) was dissolved in THF (45 mL), then added vinylmagnesium bromide 0.5 M in THF solution (15.0 mL, 7.5 mmol) dropwise at –78 °C under N_2 over 1.5h. After the addition, the mixture was quenched with saturated NH_4Cl (15 mL) solution at –78 °C and extraction with EtOAc (3 × 40 mL). The collected organic layers were combined, washed with water, brine, then dried (Na_2SO_4), concentrated & purified by column chromatography (hexane: EtOAc = 9: 1) to afford the corresponding alcohol **3a** & **3b** as colorless oil in the dr ratio of 1.5: 1 (*anti-syn*) (0.44 g, 51% for two steps) as an inseparable mixture.

$[\alpha]_D^{23}$: + 57.6 (*c* 0.95, $CHCl_3$); IR (neat) ν_{max} : 3497, 2988, 1742, 1209, 1110, 957, 768 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) : δ 6.19 (d, *J* = 3.9 Hz, 2.5H), 6.08 – 5.95 (m, 2.5H), 5.56 – 5.49 (m, 1H), 5.44 (dd, *J* = 17.3, 0.8 Hz, 1.5H), 5.31 – 5.24 (m, 2.5H), 4.94 – 4.89 (m, 1.5H), 4.78 – 4.73 (m, 1H), 4.73 – 4.66 (m, 2.5H), 4.58 – 4.51 (m, 1H), 4.46 (t, *J* = 5.8 Hz, 1.5H), 3.99 – 3.94 (m, 1.5H), 3.94 – 3.89 (m, 1H), 2.06 (s, 7.5H), 1.52 (s, 4.5H), 1.49 (s, 3H), 1.35 (s, 4.5H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ (169.41, 169.31)*, (137.19, 135.06)*, (117.06, 116.39)*, (113.29, 113.24)*, (100.65, 100.40)*, (85.37, 85.07)*, (84.81, 83.58)*, (79.70, 79.47)*, (70.71, 70.70)*, (25.99, 25.89)*, (24.70, 24.60)*, 21.0; ESI-MS (*m/z*) : 281 $[M+Na]^+$; HRMS calcd for $C_{12}H_{18}O_6Na$ 281.1001 found 281.0982.

(3a*S*,6*R*,6a*S*)-6-((*R*/*S*)-1-hydroxy-2-methylallyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl acetate (4a & 4b):



4a



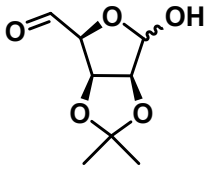
4b

The crude aldehyde **2** (0.9 g) was dissolved in THF (45 mL), to it 0.5 M THF solution of isopropenylmagnesium bromide (15.0 mL, 7.5 mmol) was added dropwise at –78 °C under N_2 over 1.5h. After the addition, the reaction was quenched with saturated NH_4Cl (15 mL)

solution at –78 °C and extracted with EtOAc (3 × 40 mL). The collected organic layers were combined, washed with water, brine, then dried (Na_2SO_4) concentrated and purified on column chromatography (hexane: EtOAc = 9:1) to afford the mixture of corresponding alcohols **4a** & **4b** as colorless oil in the dr ratio of 2.5: 1 (*anti-syn*) (0.68 g, 68% for two steps).

Data for major isomer 4a: $[\alpha]_D^{23}$: + 100.2 (*c* 0.6, $CHCl_3$); IR (neat) ν_{max} : 3494, 2922, 1743, 1375, 1210, 1090, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : δ 6.17 (s, 1H), 5.11 (s, 1H), 5.00 (s, 1H), 4.92 (dd, *J* = 5.4, 4.0 Hz, 1H), 4.70 (d, *J* = 6.0 Hz, 1H), 4.39 (d, *J* = 7.8 Hz, 1H), 4.08 (dd, *J* = 7.7, 3.5 Hz, 1H), 2.06 (s, 3H), 1.83 (s, 3H), 1.52 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 169.24, 144.15, 113.59, 113.10, 100.73, 84.73, 82.01, 79.72, 73.08, 25.85, 24.64, 20.88, 18.01; ESI-MS (*m/z*) : 295 $[M+Na]^+$; HRMS Calcd for $C_{13}H_{20}O_6Na$ 295.1158 found 295.1141.

Procedure for glycol cleavage intermediate 6 :

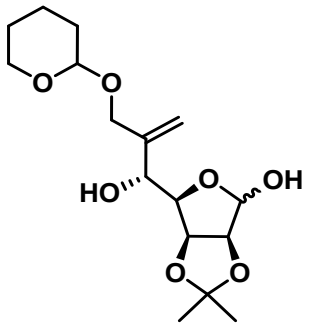


Vicinal diol **5** (1 g, 4.5 mmol) was dissolved in THF: H_2O (4:1) (15 mL) and silica gel-supported $NaIO_4$ reagent (2.90 g) was added. After stirring 0.5 h at temperature, the mixture was filtered through a celite pad, and the silica gel was thoroughly washed with EtOAc (3 × 10 mL), then dried over Na_2SO_4, concentrated under reduced pressure afford the crude aldehyde **6** (0.84 g).

Procedure for Nozaki-Hiyama-Kishi reaction:

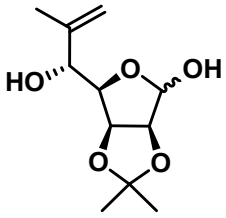
A mixture of $CrCl_2$ (2.70 g, 21.2 mmol) and a catalytic amount of $NiCl_2$ (0.068 g, 0.53 mmol) in dry DMF (10 mL) was stirred at 25 °C for 10 min under nitrogen atmosphere. To it a solution of aldehyde **6** (1.0 g, 5.31 mmol) in DMF (5 mL) and iodo compound **7** (5.61 g, 13.2 mmol) were added at 0 °C successively. After stirring at room temperature for 12 h, the reaction mixture was diluted with ether poured into water, and extracted with ether repeatedly. The combined extracts were dried (Na_2SO_4) and concentrated. Purification by silica gel column chromatography (hexane: ethyl acetate = 4:1) as eluents provided alcohol **8** as a yellow oil (1.0 g, 57%) and **9** also as a yellow oil (0.26 g, 15%) in the ratio of 4:1 (1.26 g, 72%).

Major isomer: (3a*S*,6*R*,6a*S*)-6-((1*R*)-1-hydroxy-2-(((tetrahydro-2*H*-pyran-2-yl)oxy)methyl)allyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-ol (8):

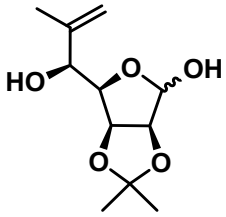


$[\alpha]_D^{23}$: –16.5 (*c* 1.4, $CHCl_3$); IR (neat) ν_{max} : 3529, 2956, 2173, 1643, 1034 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) : δ 5.39 (d, *J* = 2.6 Hz, 1H), 5.35 (s, 1H), 5.31 (d, *J* = 1.2 Hz, 1H), 4.93 – 4.87 (m, 1H), 4.68 (s, 1H), 4.63 – 4.59 (m, 1H), 4.49 (d, *J* = 6.5 Hz, 1H), 4.30 – 4.08 (m, 2H), 3.91 – 3.84 (m, 1H), 3.71 (t, *J* = 2.7 Hz, 1H), 3.58 – 3.47 (m, 1H), 1.86 – 1.68 (m, 2H), 1.66 – 1.51 (m, 4H), 1.50 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (144.65, 144.50) *, 130.78, 128.67, (115.71, 115.54)*, 112.50, 100.98, 98.04, 85.22, 80.22, (80.18, 80.08)*, (71.72, 71.60)*, (68.00, 67.93)*, (63.41, 62.17)*, (30.37, 30.27)*, 25.86, 25.18, (24.58, 24.55)*, (19.17, 19.11)*; ESI-MS (*m/z*) : 353 $[M+Na]^+$; HRMS calcd for calcd for $C_{17}H_{28}O_6Na$ 353.1570 found 353.1573..

(3a*S*,6*R*,6a*S*)-6-((*R*/*S*)-1-hydroxy-2-methylallyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-ol 10a & 10b:



10a



10b

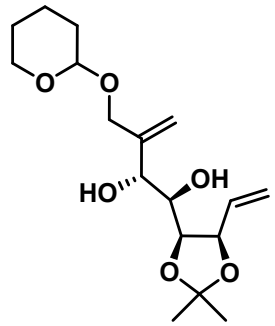
A mixture of $CrCl_2$ (5.44 g, 42.5 mmol) and a catalytic amount of $NiCl_2$ (0.137 g, 1.0 mmol) in dry DMF (20 mL) was stirred at 25 °C for 10 min under nitrogen atmosphere. To it a solution of aldehyde **6** (2.0 g, 10.6 mmol) in DMF (10 mL) and 2-bromopropene (2.36 mL, 26.5 mmol) were added at 0 °C successively. After stirring at room temperature for 12 h, the reaction mixture was diluted with ether, poured into water, and extracted with ether repeatedly. The combined extracts were dried (Na_2SO_4) and concentrated. Purification by silica gel column

chromatography (hexane: ethyl acetate = 4:1) as eluents provided alcohols **10a** and **10b** as yellow oils in the ratio of 4:1 (1.95 g, 80%).

Data for major isomer 10a:

$[\alpha]_D^{23}$: +17.67 (*c* 1.4, $CHCl_3$); IR (neat) ν_{max} : 3027, 2902, 2860, 1370, 1202, 1160, 1106, 739, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : δ 5.41 (s, 1H), 5.10 (d, *J* = 0.7 Hz, 1H), 5.03 – 4.98 (m, 1H), 4.88 (dd, *J* = 5.9, 3.7 Hz, 1H), 4.62 (d, *J* = 5.9 Hz, 1H), 4.37 (d, *J* = 7.7 Hz, 1H), 4.21 – 4.15 (m, 1H), 1.83 (s, 3H), 1.50 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 144.42, 113.66, 112.64, 101.95, 85.27, 80.20, 79.66, 73.67, 25.87, 24.57, 17.89; ESI-MS (*m/z*) : 253 $[M+Na]^+$; HRMS calcd for $C_{11}H_{18}O_5Na$ 253.1052 found 253.1040.

(1*R*,2*R*)-1-((4*S*,5*R*)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)-3-(((tetrahydro-2*H*-pyran-2-yl)oxy)methyl)but-3-ene-1,2-diol (11):

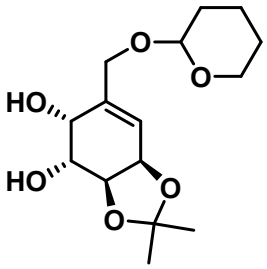


To a mixture of methyltriphenylphosphonium iodide (22.3 g, 54.5 mmol) and potassium *tert*-butoxide (5.1 g, 45.4 mmol) was added dry THF (80 mL) and stirred at room temperature under N_2 for 4 h. Stirring was stopped and solid was allowed to settle. The clear supernatant orange-yellow liquid was cannulated into the solution of compound **8** (3.0 g, 9.08 mmol) in dry THF (15 mL) at 0 °C. The reaction mixture was allowed to attain room temperature. After 3h, the reaction mixture was quenched with crushed ice and diluted with ethyl acetate. The organic portion was separated and dried over anhydrous Na_2SO_4, filtered and evaporated. The resulting syrup was purified by silica gel column chromatography (hexane: ethyl acetate = 10:1) to give **11** (2.26 g, 76%) as pale yellow syrup.

$[\alpha]_D^{23}$: –3.24 (*c* 0.69, $CHCl_3$); IR (neat) ν_{max} : 3562, 2929, 1465, 1063, 1009, 927 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) : δ 6.23 – 6.00 (m, 1H), 5.43 – 5.23 (m, 4H), 4.74 – 4.59 (m, 2H), 4.49 (td, *J* = 7.1, 1.9 Hz, 1H), 4.36 (dd, *J* = 11.7, 9.9 Hz, 1H), 4.22 (dd, *J* = 6.9, 4.4 Hz, 1H), 4.07 (dd, *J* = 12.0, 5.3 Hz, 1H), 3.95 – 3.80 (m, 1H), 3.79 – 3.65 (m, 1H), 3.58 – 3.47 (m, 1H), 1.86 – 1.66 (m, 2H), 1.87 – 1.36 (m, 12H).; ^{13}C NMR (125 MHz, $CDCl_3$) : δ (144.7, 144.6)*, 134.5, 119.5, (117.2,

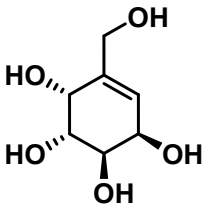
117.0)*, 108.7, (98.5, 98.3)*, 79.4, (76.7, 76.6)* (75.8, 75.7,)*, 70.2, (68.7, 68.6)*, 62.3, 30.4, 26.8, 25.2, 24.7, 19.3.; ESI-MS (*m/z*) : 351 $[M+Na]^+$; HRMS calcd for $C_{17}H_{28}O_6Na$ 351.1778 found 351.1780.

(3a*S*,4*R*,5*R*,7a*R*)-2,2-dimethyl-6-(((tetrahydro-2*H*-pyran-2-yl)oxy)methyl)-3a,4,5,7a-tetrahydrobenzo[*d*][1,3]dioxole-4,5-diol (12):



To the solution of diene **11** (0.5 g, 1.5 mmol) in toluene (60 mL), Grubbs' second-generation catalyst (0.13 g, 0.15 mmol) was added at room temperature. Refluxed the reaction mixture for 12 h. Toulene was removed under vacuum, applied for column chromatography (hexane: ethyl acetate = 2:3) to provide cyclohexenol **12** as an oily compound (0.38 g, 85%).
$[\alpha]_D^{23}$: +11.0 (*c* 2.2, $CHCl_3$).; IR (neat) ν_{max} : 3516, 2924, 2173, 1377, 1033 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) : δ 5.86 (dd, 1H, *J* = 2.8, 13 Hz), 4.73 – 4.51 (m, 2H), 4. 39 – 4.23 (m, 2H), 4. 20 – 4. 0 (m, 1.7H), 3.95 – 3.74 (m, 2H), 3.72 – 3.61 (m, 0.3H), 3.58 – 3.40 (m, 1H), 1.89 – 1.32 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (138.42, 138.36)*, (123.78, 123.42)*, (109.64, 109.57)*, (99.44, 98.84)*, 75.90, (72.32, 72.26)*, (71.44, 71.42)*, (69.73, 69.64)*, (68.08, 66.92)*, (63.41, 62.66)*, (30.80, 30.53)*, 28.08, (25.93, 25.89)*, (25.32, 25.26)*, (20.01, 19.55)*; ESI-MS (*m/z*) : 323 $[M+Na]^+$; HRMS calcd for $C_{15}H_{24}O_6Na$ 323.1465 found 323.1468.

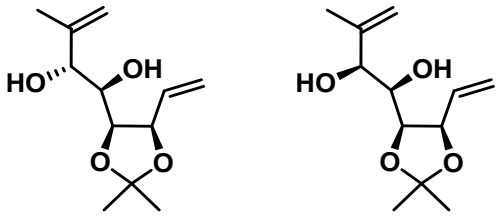
(1*R*,2*R*,3*R*,4*R*)-5-(hydroxymethyl)cyclohex-5-ene-1,2,3,4-tetraol (or) (–)-MK-7607:



To the solution of compound **12** (0.1 g, 0.33 mmol) in TFA (2 mL) and H_2O (1 mL) was stirred at room temperature for 3 h. The reaction mixture was concentrated under reduced pressure to give syrup which was purified by column chromatography (methylenechloride: methanol = 17:3) to give (–)-MK7607 in 70% yield (0.041 g) as a colourless oil.

$[\alpha]_D^{23}$: –189 (*c* 1.1, H_2O). [for enantiomer lit.[1a] $[\alpha]_D^{20}$ +198 (*c* 0.95, H_2O)]; IR (neat) ν_{max} : 3336, 2929,1732, 1373, 1239, 1043 cm^{-1}; ^1H NMR (400 MHz, D_2O) : δ 5.72 (d, 1H, *J* = 4.7 Hz), 4.18 (t, 2H, *J* = 4.1, 7.7 Hz), 4.11 (d, 1H, *J* = 3.0 Hz), 4.01 (s, 2H), 3.74 (t, 2H, *J* = 2.8, 6.0 Hz).; ^{13}C NMR (100 MHz, D_2O): δ 141.23, 125.03, 69.59, 69.26, 67.60, 67.01, 63.1.; ESI-MS (*m/z*) : 119 $[M+Na]^+$; HRMS calcd for $C_7H_{12}O_5Na$ 199.0582 found 199.0579. ^1H and ^{13}C values are similar to the reported data.[20b]

(1*R*,2*R/S)*-1-((4*S*,5*R*)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)-3-methylbut-3-ene-1,2-diol 13a & 13b:



13a **13b**

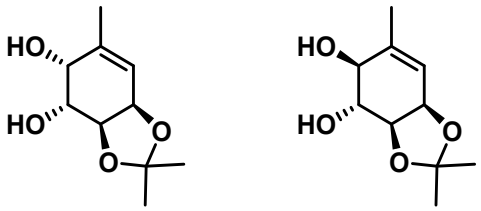
To a mixture of methyltriphenylphosphonium iodide (21.7 g, 52.1 mmol) and potassium *tert*-butoxide (4.87 g, 43.4 mmol) was added dry THF (70 mL) and stirred at room temperature under N_2 for 4 h. Stirring was stopped and solid was allowed to settle. The clear supernatant orange-yellow liquid was cannulated into the solution of compounds **10a** & **10b** (2.0 g, 8.69 mmol) in dry THF (10 mL) at 0 °C. The reaction mixture was allowed to attain room temperature. After the 3h reaction mixture was quenched with crushed ice and diluted with ethyl acetate. The organic portion was separated and dried over anhydrous Na_2SO_4, filtered and evaporated. The resulting syrup was purified by silica gel column chromatography (hexane: ethyl acetate = 10:1) to give **13a** & **13b** in the ratio of 4:1 (1.62 g, 82%) as pale yellow syrup.

Data for major isomer 13a:

$[\alpha]_D^{23}$: –54.12 (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} : 3463, 2924, 2854, 1453, 1212, 1061, 746, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : δ 6.13 (ddd, *J* = 17.3, 10.2, 8.0 Hz, 1H), 5.40 – 5.30 (m, 2H), 5.08 (d, *J* = 0.7 Hz, 1H), 5.00 (dd, *J* = 1.4, 0.9 Hz, 1H), 4.66 (t, *J* = 7.7 Hz, 1H), 4.39 (dd, *J* = 7.4, 1.8 Hz, 1H), 4.12 (d, *J* = 6.0 Hz, 1H), 3.66 – 3.57 (m, 1H), 1.76 (s, 3H), 1.55 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 144.70, 134.19, 119.79, 113.18, 108.77, 79.41, 77.14, 76.41,

69.28, 26.69, 24.62, 18.35; ESI-MS (*m/z*) : 251 $[M+Na]^+$; HRMS calcd for $C_{12}H_{20}O_4Na$ 251.1259 found 251.1244.

(3a*S*,4*R*,5*R*/*S*,7a*R*)-2,2,6-trimethyl-3a,4,5,7a-tetrahydrobenzo[*d*][1,3]dioxole-4,5-diol 14a & 14b:



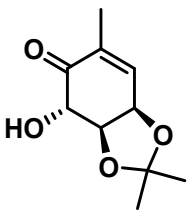
14a **14b**

To the solution of diene **13a** & **13b** (0.5 g, 1.5 mmol) in toluene (60 mL), Grubbs' second-generation catalyst (0.13 g, 0.15 mmol) was added at room temperature. Refluxed the reaction mixture for 12 h. Toulene was removed under vacuum, applied for column chromatography (hexane: ethyl acetate = 2:3) to provide cyclohexenol **14a** & **14b** in the ratio of 4:1 as an oily compound (0.44 g, 85%).

Data for major isomer 14a:

$[\alpha]_D^{23}$: –104 (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} : 3031, 2924, 2854, 1454, 1366, 1094, 1040, 738, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) : δ 5.65 (s, 1H), 4.64 (s, 1H), 4.30 (t, *J* = 7.0 Hz, 1H), 4.05 (s, 1H), 3.85 – 3.76 (m, 1H), 1.89 (s, 3H), 1.47 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 138.99, 120.88, 109.31, 75.45, 72.61, 71.80, 70.23, 27.95, 25.68, 21.04; ESI-MS (*m/z*) : 223 $[M+Na]^+$; HRMS calcd for $C_{10}H_{16}O_4Na$ 223.0946 found 223.0946.

(3a*S*,4*S*,7a*R*)-4-hydroxy-2,2,6-trimethyl-3a,7a-dihydrobenzo[*d*][1,3]dioxol-5(4*H*)-one (15):

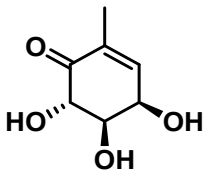


To the compounds **14a** & **14b** (0.4 g, 2 mmol) dissolved in DCM (30 mL) was added Dess-Martin periodinane (1 g, 2.4) and stirred at r.t. for 1 h. After completion of the reaction, it was quenched by the addition of a saturated hypo solution (10 mL) followed by the addition of a saturated bicarbonate solution (5mL). The organic fraction was extracted using DCM (3× 15 mL), all the fractions were collected and dried over Na_2SO_4, concentrated under reduced

pressure on rota vapor. The resulting syrup was purified by silica gel column chromatography (hexane: ethyl acetate = 1:1) to give **15** in the ratio of (0.277 g, 70%) as pale yellow syrup.

$[\alpha]_D^{23}$: –38.1 (*c* 1.5, $CHCl_3$); IR (neat) ν_{max} : 3394, 2924, 2853, 1692, 1216, 1061, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : δ 6.68 – 6.64 (m, 1H), 4.82 – 4.76 (m, 1H), 4.36 (d, *J* = 8.5 Hz, 1H), 4.29 (dd, *J* = 8.5, 6.3 Hz, 1H), 3.51 (s, 1H), 1.93 (t, *J* = 1.4 Hz, 3H), 1.60 (s, 3H), 1.45 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) : δ 198.42, 137.08, 135.95, 111.56, 79.19, 75.52, 70.98, 27.97, 25.99, 15.70; ESI-MS (*m/z*) : 221 $[M+Na]^+$; HRMS calcd for $C_{10}H_{14}O_4Na$ 221.0790 found 221.0797.

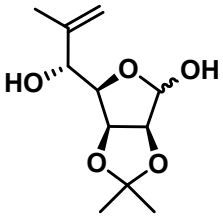
(4*R*,5*R*,6*S*)-4,5,6-trihydroxy-2-methylcyclohex-2-en-1-one (or) (–)-gabosine A:



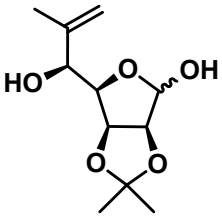
To the solution of compound **15** (0.05 g, 0.13 mmol) in TFA (2 mL) and H_2O (1 mL) was stirred at room temperature for 3 h. The reaction mixture was concentrated under reduced pressure to give syrup which was purified by column chromatography (methylenechloride: methanol = 24:1) to give (–)-gabosine A in 80% yield (0.029 g) as a colourless oil.

$[\alpha]_D^{23}$: −120.8 (*c* 0.19, MeOH). [lit.[2a] $[\alpha]_D^{26}$ −130.5 (c 0.20, MeOH)]; IR (neat) ν_{max} : 3349, 2923, 1682, 1382, 1221, 1093, 1029, 772 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) : δ 6.75 (dd, *J* = 5.6, 1.4 Hz, 1H), 4.39 (t, *J* = 4.5 Hz, 1H), 4.32 (d, *J* = 10.0 Hz, 1H), 3.73 (dd, *J* = 10.0, 3.9 Hz, 1H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) : δ 200.50, 143.08, 136.94, 75.15, 74.00, 67.49, 15.65; ESI-MS (*m/z*) : 181 $[M+Na]^+$; HRMS calcd for $C_7H_{10}O_4Na$ 181.0477 found 181.0471. ^1H and ^{13}C values are similar to the reported data.[1b]

(3a*S*,6*R*,6a*S*)-6-((*R*/*S*)-1-hydroxy-2-methylallyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-ol (10a & 10b):



10a



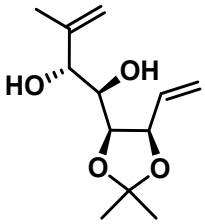
10b

To compound **4a** & **4b** (1.2 g, 4.4 mmol) in MeOH (15 mL) was added K_2CO_3 (1.82 g, 13.2 mmol) and the reaction mixture was stirred for 2 h at r.t. Then the MeOH (15 mL) was removed under *vacuo*. The reaction mixture was quenched with saturated $NaHCO_3$ solution (5 mL) & extracted with EtOAc (100 mL). The combined organic fractions were collected and washed with water, brine, dried ($MgSO_4$) & concentrated. Purification to column chromatography (hexane: EtOAc = 4:1) afforded the mixture of the corresponding alcohols **10a** & **10b** as colorless oil in the dr ratio of 2.5: 1 (*anti-syn*) (0.91 g, 91%).

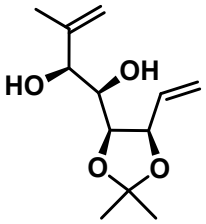
Data for major isomer 10a:

$[\alpha]_D^{23}$: +74.1 (*c* 0.47, $CHCl_3$); IR (neat) ν_{max} : 3420, 2941, 2860, 1377, 1213, 1066, 746 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) : δ 5.41 (s, 1H), 5.10 (d, *J* = 0.5 Hz, 1H), 4.99 (s, 1H), 4.88 (dd, *J* = 5.7, 3.8 Hz, 1H), 4.62 (d, *J* = 5.9 Hz, 1H), 4.37 (d, *J* = 7.5 Hz, 1H), 4.18 (dt, *J* = 8.5, 4.2 Hz, 1H), 1.83 (s, 3H), 1.50 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 144.43, 113.61, 112.62, 100.92, 85.29, 80.21, 79.63, 73.64, 25.87, 24.57, 17.90; ESI-MS (*m/z*) : 253 $[M+Na]^+$; HRMS calcd for $C_{11}H_{18}O_5Na$ 253.1052 found 253.1040.

(1*R*,2*R*/*S*)-1-((4*S*,5*R*)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)-3-methylbut-3-ene-1,2-diol (13a & 13b):



62a



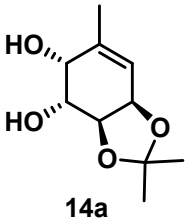
62b

To methyltriphenylphosphonium iodide (8.43 g, 20.8 mmol) & potassium *tert*-butoxide (1.95 g, 17.3 mmol) was added dry THF (80 mL) and stirred at r.t. under N_2 for 4h. Stirring was stopped & solid was allowed to settle. The clear supernatant orange-yellow liquid was cannulated into the solution of compounds **10a** & **10b** (0.8 g, 3.5 mmol) in dry THF (5 mL) at 0 °C. The mixture was allowed to attain r.t. After 3h, the mixture was quenched with crushed ice & diluted with EtOAc. The organic portion was dried (Na_2SO_4), filtered & evaporated. The resulting syrup was applied on column chromatography (hexane: EtOAc = 9: 1) to obtain the corresponding olefin **13a** & **13b** as colorless oils in the dr ratio of 2.5: 1 (*anti*:*syn*) (0.705 g, 89%).

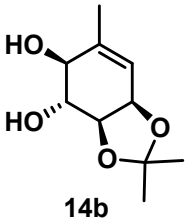
Data for major isomer 13a:

$[\alpha]_D^{23}$: –132.4 (*c* 0.28, $CHCl_3$); IR (neat) ν_{max} : 3463, 2924, 1431, 1214, 1043, 749 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) : δ 6.18 – 6.08 (m, 1H), 5.35 (dd, *J* = 18.8, 13.8 Hz, 2H), 5.08 (s, 1H), 5.00 (s, 1H), 4.66 (t, *J* = 7.7 Hz, 1H), 4.39 (dd, *J* = 7.4, 1.5 Hz, 1H), 4.13 (d, *J* = 6.0 Hz, 1H), 3.62 (d, *J* = 6.1 Hz, 1H), 1.76 (s, 3H), 1.55 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 144.70, 134.21, 119.78, 113.19, 108.81, 79.45, 77.21, 76.44, 69.30, 26.71, 24.64, 18.38; ESI-MS (*m/z*) : 251 $[M+Na]^+$; HRMS calcd for $C_{12}H_{20}O_4Na$ 251.1259, found 251.1244.

(3a*S*,4R,5*R*/*S*,7a*R*)-2,2,6-trimethyl-3a,4,5,7a-tetrahydrobenzo[*d*][1,3]dioxole-4,5-diol (14a & 14b):



14a



14b

To the solution of diene **13a** & **13b** (0.5 g, 1.5 mmol) in anhydrous toluene (60 mL) was degassed by purging argon for 15 min and then treated with Grubbs second-generation catalyst (0.186 g, 0.22 mmol, 10 mol %). The solution was refluxed under argon for 6 h. The dark brown solution was concentrated to give crude material, that was purified by column chromatography (hexane: ethyl acetate = 2:3) to provide cyclohexenols **14a** & **14b** in the ratio of 2.5:1 (*anti-syn*) as an oily compound (0.35 g, 80%).

Data for major isomer 14a:

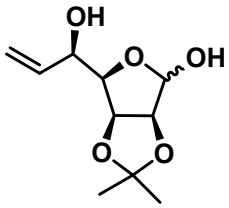
$[\alpha]_D^{23}$: –52.4 (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} : 3394, 2923, 1714, 1217, 1058, 772 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) : δ 5.68 (s, 1H), 4.65 (t, *J* = 3.9 Hz, 1H), 4.29 (dd, *J* = 7.8, 6.4 Hz, 1H), 4.08 (d, *J* = 2.6 Hz, 1H), 3.84 (dd, *J* = 8.0, 3.3 Hz, 1H), 1.90 (s, 3H), 1.47 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 138.93, 121.17, 109.50, 75.60, 72.61, 71.92, 70.29, 28.09, 25.80, 21.14; ESI-MS (*m/z*) : 223 $[M+Na]^+$; HRMS calcd for $C_{10}H_{16}O_4Na$ 223.0946 found 223.0946.

(3a*S*,6*R*,6a*S*)-6-((*R*)-1-hydroxyallyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-ol (16):

To the mixture of compounds **3a** & **3b** (2 g, 7.7 mmol) in MeOH (30 mL) was added K_2CO_3 (3.2 g, 23.2 mmol) and the reaction mixture was stirred for 2 h at r.t. Then the methanol (30 mL) was removed under *vacuo*. The reaction mixture was quenched with saturated $NaHCO_3$ solution (15 mL) & extracted with EtOAc (3 × 60 mL). The combined organic fractions were collected and washed with water, brine, dried ($MgSO_4$) & concentrated. The crude compound

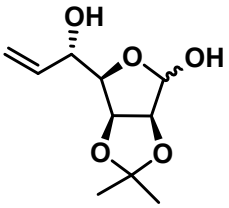
was passed through column (hexane: EtOAc = 4:1) to obtain lactols first **16** (0.875 g, 52.5 %) and followed by **17** (0.625 g, 37.5 %) as viscous liquids in 90% total yield.

Data of major isomer 16:



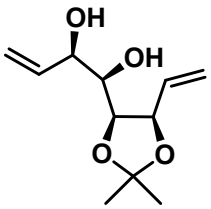
$[\alpha]_D^{23}$: +122.5 (*c* 0.32, $CHCl_3$); IR (neat) ν_{max} : 3395, 2938, 1378, 1211, 1068, 771 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) : δ 6.09 – 5.96 (m, 1H), 5.42 (d, *J* = 13.0 Hz, 2H), 5.26 (d, *J* = 10.4 Hz, 1H), 4.88 (s, 1H), 4.62 (d, *J* = 5.4 Hz, 1H), 4.44 (t, *J* = 5.6 Hz, 1H), 4.06 (s, 1H), 1.50 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 137.43, 116.52, 112.70, 100.88, 85.27, 81.32, 80.17, 71.18, 25.83, 24.43; ESI-MS (*m/z*) : 239 $[M+Na]^+$; HRMS Calcd for $C_{10}H_{16}O_5Na$ 239.0895, found 239.0878.

Data of minor isomer: (3a*S*,6*R*,6a*S*)-6-((*S*)-1-hydroxyallyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-ol (17):



$[\alpha]_D^{23}$: +28.8 (c 0.29, $CHCl_3$); IR (neat) ν_{max} : 3394, 2924, 1734, 1450, 1219, 772 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) : δ 6.01 (ddd, *J* = 17.2, 10.7, 5.0 Hz, 1H), 5.49 (dt, *J* = 17.3, 1.6 Hz, 1H), 5.45 (s, 1H), 5.27 (dt, *J* = 10.7, 1.5 Hz, 1H), 4.75 (dd, *J* = 5.9, 3.6 Hz, 1H), 4.63 (d, *J* = 5.9 Hz, 1H), 4.58 – 4.54 (m, 1H), 4.03 (dd, *J* = 6.6, 3.6 Hz, 1H), 1.49 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 135.94, 116.65, 112.74, 101.01, 85.77, 82.58, 80.25, 70.94, 25.95, 24.54; ESI-MS (*m/z*) : 239 $[M+Na]^+$; HRMS Calcd for $C_{10}H_{16}O_5Na$ 239.0895, found 239.0895.

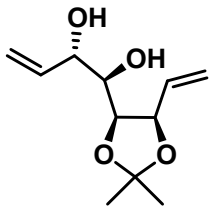
(1*R*,2*R*)-1-((4*S*,5*R*)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)but-3-ene-1,2-diol (18):



To methyltriphenylphosphonium iodide (5.61 g, 13.8 mmol) & potassium *tert*-butoxide (1.29 g, 11.5 mmol) was added dry THF (80 mL) and stirred at r.t under N_2 for 4h. Stirring was stopped and solid was allowed to settle. The clear supernatant orange-yellow liquid was cannulated into the compound **16** (0.5 g, 2.3 mmol) in dry THF (5 mL) at 0 °C. The reaction mixture was allowed to attain r.t. After 3h, the mixture was quenched with crushed ice & diluted with EtOAc. The organic portion was separated and dried (Na_2SO_4), filtered & concentrated. The syrup was purified on column chromatography (hexane: EtOAc = 9:1) to give **18** (0.445 g, 90%) as a pale yellow syrup.

$[\alpha]_D^{23}$: –22.8 (c 0.33, $CHCl_3$); IR (neat) ν_{max}: 3394, 2923, 1738, 1457, 1218, 1069, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : δ 6.18 – 6.01 (m, 1H), 5.98 – 5.89 (m, 1H), 5.40 (t, *J* = 1.4 Hz, 1H), 5.36 (t, *J* = 1.3 Hz, 1H), 5.33 (ddd, *J* = 10.2, 1.5, 0.7 Hz, 1H), 5.28 (dt, *J* = 10.6, 1.5 Hz, 1H), 4.64 (dd, *J* = 8.0, 7.3 Hz, 1H), 4.36 (dd, *J* = 7.2, 2.6 Hz, 1H), 4.19 (dt, *J* = 6.7, 5.4 Hz, 1H), 3.57 (ddd, *J* = 7.8, 5.3, 2.6 Hz, 1H), 1.54 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 137.24, 134.10, 119.88, 116.68, 108.87, 79.32, 76.67, 74.43, 71.35, 26.91, 24.73; ESI-MS (*m/z*) : 237 $[M+Na]^+$; HRMS Calcd for $C_{11}H_{18}O_6Na$ 237.1103, found 237.1104.

(1*R*,2*S*)-1-((4*S*,5*R*)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)but-3-ene-1,2-diol (19):

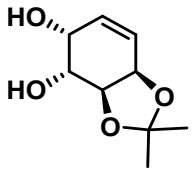


To a mixture of methyltriphenylphosphonium iodide (5.61 g, 13.8 mmol) & potassium *tert*-butoxide (1.29 g, 11.5 mmol) was added dry THF (80 mL) and stirred at r.t. under N_2 for 4h. Stirring was stopped & solid was allowed to settle. The clear supernatant orange-yellow liquid was cannulated into the solution of compound **17** (0.5 g, 2.3 mmol) in dry THF (5 mL) at 0 °C. The mixture was allowed to attain r.t. After 3h, the mixture was quenched with crushed ice & diluted with EtOAc. The organic portion was separated & dried (Na_2SO_4), filtered & concentrated. The syrup was purified on column chromatography (hexane: EtOAc = 9: 1) to give **19** (0.435 g, 78%) as a pale yellow syrup.

$[\alpha]_D^{23}$: +19.4 (*c* 0.55, $CHCl_3$).; IR (neat) ν_{max}: 3394, 2923, 1737, 1457, 1218, 1060, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : δ 6.11 – 5.99 (m,1H), 5.92 – 5.80 (m, 1H), 5.43 – 5.39 (m, 1H), 5.38 –

5.31 (m, 2H), 5.28 – 5.24 (m, 1H), 4.67 (dd, *J* = 7.9, 7.2 Hz, 1H), 4.29 (dd, *J* = 7.1, 3.3 Hz, 2H), 4.14 (dd, *J* = 6.1, 5.0 Hz, 2H), 3.48 (t, *J* = 3.5 Hz, 1H), 1.55 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 136.89, 133.75, 120.01, 117.54, 109.00, 79.25, 77.59, 73.90, 71.57, 26.99, 24.78; ESI-MS (*m/z*) : 237 $[M+Na]^+$; HRMS Calcd for $C_{11}H_{18}O_4Na$ 237.1103, found 237.1115.

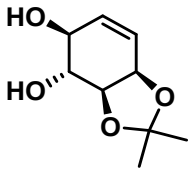
(3a*S*,4*R*,5*R*,7a*R*)-2,2-dimethyl-3a,4,5,7a-tetrahydrobenzo[*d*][1,3]dioxole-4,5-diol (20):



A solution of diene **18** (0.4 g, 1.8 mmol) in dry toluene (70 mL) was degassed by purging argon for 15 min and then treated with Grubbs second-generation catalyst (0.158 g, 0.18 mmol, 10 mol %). The solution was refluxed under argon for 3 h. The dark brown solution was concentrated to give crude compound, which was purified on column chromatography (hexane: EtOAc = 1:4) to provide cyclohexenol **20** as an oily compound (0.32 g, 80%).

$[\alpha]_D^{23}$: –132.6 (*c* 0.42, $CHCl_3$); IR (neat) ν_{max} : 3393, 2922, 1735, 1462, 1218, 1021, 771 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 5.98 – 5.88 (m, 2H), 4.70 – 4.63 (m, 1H), 4.37 (t, *J* = 6.3 Hz, 1H), 4.31 (dd, *J* = 3.3, 2.1 Hz, 1H), 3.98 (dd, *J* = 6.8, 3.7 Hz, 1H), 1.44 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 129.88, 127.40, 109.45, 75.73, 71.82, 71.08, 65.90, 27.86, 25.88; ESI-MS (*m/z*) : 209 $[M+Na]^+$; HRMS Calcd for $C_9H_{14}O_4Na$ 209.0790, found 209.0790.

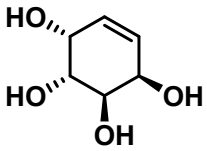
(3a*S*,4*R*,5*S*,7a*R*)-2,2-dimethyl-3a,4,5,7a-tetrahydrobenzo[*d*][1,3]dioxole-4,5-diol (21):



Prepared according to the procedure as described above (RCM reaction). Purification by column chromatography (hexane: EtOAc = 1:4) provided cyclohexenol **21** as a oil (0.29 g, 72%).

$[\alpha]_D^{23}$: +68.0 (*c* 0.15, $CHCl_3$); IR (neat) ν_{max} : 2916, 1610, 1510, 1099, 771cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) : δ 5.89 – 5.81 (m, 2H), 4.62 (dd, *J* = 6.5, 2.4 Hz, 1H), 4.11 – 4.04 (m, 2H), 3.58 (t, *J* = 8.6 Hz, 1H), 1.49 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 133.50, 123.55, 110.64, 77.64, 75.15, 72.65, 70.41, 28.21, 25.85; ESI-MS (*m/z*) : 209 $[M+Na]^+$; HRMS Calcd for $C_9H_{14}O_4Na$ 209.0790, found 209.0790.

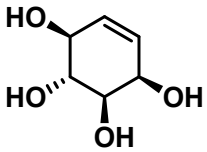
(1*R*,2*R*,3*R*,4*R*)-cyclohex-5-ene-1,2,3,4-tetraol (or) (–)-conduritol E:



To the solution of **20** (0.1 g, 0.53 mmol) in TFA (2 mL) and H_2O (1 mL) was stirred at r.t. for 3 h. The mixture was concentrated to give syrup that was purified by column chromatography (methylene chloride: methanol = 22:1) to give (–)-conduritol E in 96% yield (0.074 g) as a syrup.

$[\alpha]_D^{25}$: –300 (*c* 0.5, H_2O) {lit.[3] –247 (*c* 0.1, H_2O)); IR (neat) ν_{max} : 2915, 1610, 1511, 1105, 772 cm^{-1}; ^1H NMR (500 MHz, CD_3OD) : δ 5.76 (d, *J* = 1.5 Hz, 2H), 4.25 (s, 2H), 3.92 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (125 MHz, CD_3OD) : δ 130.93, 71.30, 67.84; ESI-MS (*m/z*) : 169 $[M+Na]^+$; HRMS Calcd for $C_6H_{10}O_4Na$ 169.0477, found 169.0470. ^1H and ^{13}C values are similar to the reported data.[3b]

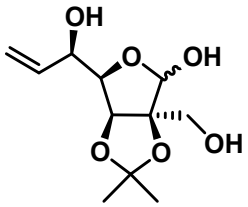
(1*R*,2*R*,3*R*,4*S*)-cyclohex-5-ene-1,2,3,4-tetraol (or) (–)-conduritol F:



To the solution of **21** (0.1 g, 0.53 mmol) in TFA (2 mL) and H_2O (1 mL) was stirred at r.t. for 3 h. The mixture was concentrated to give syrup that was purified on flash chromatography (DCM: MeOH = 20:1) to give (–)-conduritol F in 96% yield (0.074 g) as a syrup.

$[\alpha]_D^{25}$: –69.9 (*c* 0.72, MeOH) {lit.[3] –71.0 (*c* 0.75, MeOH); IR (neat) ν_{max} : 2929, 1612, 1512, 1213, 772 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) : δ 5.80 (ddd, *J* = 9.6, 4.7, 1.7 Hz, 1H), 5.72 (dd, *J* = 10.0, 1.4 Hz, 1H), 4.17 (t, *J* = 4.4 Hz, 1H), 3.94 (dt, *J* = 7.6 Hz, 1.7, 1H), 3.63 (dd, *J* = 10.3, 7.6 Hz, 1H), 3.43 (dd, *J* = 10.3, 4.2 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD) : δ 133.89, 128.10, 74.09, 73.94, 72.73, 68.09; ESI-MS (*m/z*) : 169 $[M+Na]^+$; HRMS Calcd for $C_6H_{10}O_4Na$ 169.0477, found 169.0483. ^1H and ^{13}C values are similar to the reported data.[3b]

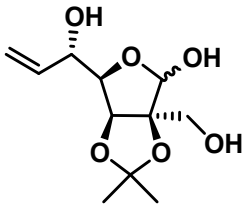
(3a*S*,6*R*,6a*S*)-6-((*R*)-1-hydroxyallyl)-3a-(hydroxymethyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-ol (22):



The vinyl lactol **16** (1.5 g, 6.9 mmol), and K_2CO_3 (1.43 g, 10.4 mmol) were taken in MeOH (30 mL) and 37 % aqueous solution of formaldehyde (15 mL) was added. The mixture was refluxed at 85 °C for 12 h. After completion of the reaction, the reaction mixture was neutralized with 5% aqueous HCl solution at 0 °C, MeOH was removed under vacuum, aqueous layer extracted with EtOAc (80 mL), dried (Na_2SO_4) & concentrated to give syrup. This syrup was purified on column chromatography (hexane: ethylacetate = 2:3) to give diol **22** as colorless oil (1.49 g, 85%).

$[\alpha]_D^{25}$: +60.0 (*c* 0.14, $CHCl_3$); IR (neat) ν_{max} : 3393, 2922, 1711, 1462, 1219, 772 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) : δ 6.03 (ddd, *J* = 7.4, 6.6, 3.3 Hz, 1H), 5.45 (d, *J* = 1.5 Hz,1H), 5.30 – 5.26 (m, 1H), 4.75 (d, *J* = 2.6 Hz, 1H), 4.47 (td, *J* = 7.1, 1.1 Hz, 1H), 4.09 (td, *J* = 7.1, 2.3 Hz, 1H), 3.99 (dd, *J* = 12.0, 1.0 Hz, 1H), 3.85 (dd, *J* = 12.0, 1.0 Hz, 1H), 3.78 (dd, *J* = 9.2, 0.8 Hz, 1H), 1.52 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 137.41, 116.70, 114.00, 103.64, 97.50, 83.31, 82.18, 77.19, 71.40, 63.47, 27.34, 27.34; ESI-MS (*m/z*) : 269 $[M+Na]^+$; HRMS Calcd for $C_{11}H_{18}O_6Na$ $[M+Na]^+$ 269.1001 found 269.1001.

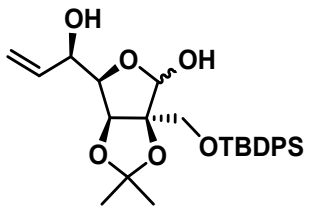
(3a*S*,6*R*,6a*S*)-6-((*S*)-1-hydroxyallyl)-3a-(hydroxymethyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-ol (23):



The vinyl lactol **17** (1.0 g, 4.6 mmol), K_2CO_3 (0.95 g, 6.9 mmol) were taken in MeOH (20 mL) and 37 % aqueous solution of formaldehyde (10 mL) was added. The mixture was refluxed at 85 °C for 12 h. After completion of the reaction, the reaction mixture was neutralized with 5% aqueous HCl solution at 0 °C, MeOH was removed under vacuum, Extracted with EtOAc (80 mL), dried (Na_2SO_4) & concentrated to give syrup. This syrup was purified on column chromatography (hexane: ethylacetate = 2:3) to give diol **23** as colorless oil (0.9 g, 80%).

$[\alpha]_D^{25}$: +22.5 (*c* 0.35, $CHCl_3$); IR (neat) ν_{max} : 3394, 2924, 1712, 1376, 1217, 1055, 771 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) : δ 6.08 – 5.90 (m, 1H), 5.50 (ddd, *J* = 17.3, 3.4, 1.6 Hz, 1H), 5.28 (ddd, *J* = 10.7, 3.1, 1.6 Hz, 1H), 4.60 (d, *J* = 2.9 Hz, 1H), 4.54 (d, *J* = 3.0 Hz, 1H), 4.05 (dd, *J* = 7.1, 2.8 Hz, 1H), 3.98 (d, *J* = 12.0 Hz, 1H), 3.82 (d, *J* = 12.1 Hz, 1H), 3.77 (d, *J* = 7.9 Hz, 1H), 1.50 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 135.62, 117.01, 113.89, 103.53, 97.21, 83.59, 83.24, 71.13, 63.45, 27.34, 27.28; ESI-MS (*m/z*) : 269 $[M+Na]^+$; HRMS Calcd for $C_{11}H_{18}O_6Na$ 269.1001 found 269.0985.

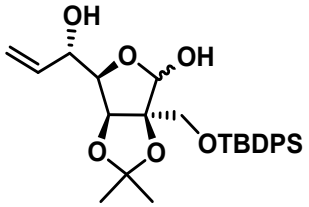
(3a*S*,6*R*,6a*S*)-3a-(((tert-butyldiphenylsilyl)oxy)methyl)-6-((*R*)-1-hydroxyallyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-ol (24):



To diol **22** (1.4 g, 5.6 mmol) in CH_2Cl_2 (15 mL) was added imidazole (0.58 g, 33.0 mmol) at r.t. After 15 min, TBDPS-Cl (1.74 mL, 6.8 mmol) was added dropwise followed by DMAP (0.68 g, 5.6 mmol). Stirring continued for 6 h at r.t. the mixture was taken in DCM, washed with water followed by brine, dried ($MgSO_4$) & concentrated. The crude applied on flash chromatography (hexane: EtOAc = 4: 1) to give silyl compound **24** as a syrup (2.36 g, 86%).

$[\alpha]_D^{25}$: +77.1 (*c* 0.46, $CHCl_3$); IR (neat) ν_{max} : 3469, 2932, 2858, 1426, 1217, 1105, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) : δ 7.70 – 7.62 (m, 4H), 7.46 – 7.38 (m, 6H), 6.05 (ddd, *J* = 17.2, 10.6, 5.6 Hz, 1H), 5.43 (dt, *J* = 17.3, 1.5 Hz, 1H), 5.27 (dd, *J* = 10.5, 1.3 Hz, 1H), 5.13 (d, *J* = 10.6 Hz, 1H), 4.73 (d, *J* = 3.0 Hz, 1H), 4.46 (dd, *J* = 7.3, 5.8 Hz, 1H), 3.78 (d, *J* = 10.6 Hz, 1H), 3.75 (d, *J* = 10.6 Hz, 1H), 3.51 (dd, *J* = 7.5, 3.0 Hz, 1H), 1.54 (s, 3H), 1.32 (s, 3H), 1.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 137.58, 135.53, 135.48, 132.39, 132.15, 130.01, 127.87, 116.31, 113.74, 97.32, 88.70, 82.67, 78.02, 70.69, 63.74, 26.87, 26.78, 26.58, 19.15; ESI-MS (*m/z*) : 507 $[M+Na]^+$; HRMS Calcd for $C_{27}H_{36}O_6Na$ 507.2179, found 507.2175.

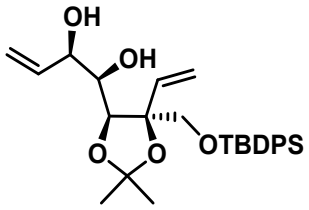
(3a*S*,6*R*,6a*S*)-3a-(((tert-butyldiphenylsilyl)oxy)methyl)-6-((*S*)-1-hydroxyallyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-ol (25):



Compound **25** prepared from **23** according to the procedure as described above. Purification by column chromatography (hexane: ethyl acetate = 4: 1) gave the product **25** as a syrup (1.55 g, 88%).

$[\alpha]_D^{25}$: -13.0 (*c* 0.91, $CHCl_3$); IR (neat) ν_{max} : 3462, 2931, 2857, 1427, 1217, 1107, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) : δ 7.63 (ddd, *J* = 8.3, 4.9, 1.5 Hz, 4H), 7.47 – 7.38 (m, 6H), 5.93 (ddd, *J* = 17.3, 10.7, 5.4 Hz, 1H), 5.50 (dt, *J* = 17.3, 1.6 Hz, 1H), 5.29 (dt, *J* = 10.7, 1.5 Hz, 1H), 5.14 (d, *J* = 11.4 Hz, 1H), 4.53 – 4.48 (m, 1H), 4.48 (d, *J* = 2.9 Hz, 1H), 3.78 (d, *J* = 10.6 Hz, 1H), 3.73 (d, *J* = 10.6 Hz, 1H), 3.46 (dd, *J* = 7.7, 2.9 Hz, 1H), 1.52 (s, 3H), 1.27 (s, 3H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 135.55, 135.52, 135.22, 132.49, 132.22, 130.06, 127.90, 117.19, 113.71, 97.16, 89.20, 82.45, 79.46, 70.90, 63.86, 26.86, 26.81, 26.45, 19.19; ESI-MS (*m/z*) : 507 $[M+Na]^+$; HRMS Calcd for $C_{27}H_{36}O_6NaSi$ 507.2179, found 507.2179.

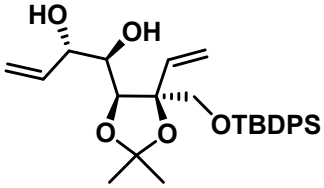
(1*R*,2*R*)-1-((4*S*,5*S*)-5-(((tert-butyldiphenylsilyl)oxy)methyl)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)but-3-ene-1,2-diol (26):



To methyltriphenylphosphonium iodide (11.0 g, 27.2 mmol) in toluene (55 ml) was added potassium *tert*-butoxide (2.54 g, 22.7 mmol) & the mixture was stirred at 105 °C for 1.5h, then cooled to 0 °C. Stirring was stopped and solid was allowed to settle. The clear supernatant orange-yellow liquid was cannulated into the solution of **24** (2.2 g, 4.5 mmol) in toluene (10 ml) at 0 °C & the resulting mixture was stirred at 105 °C for 2h, then cooled. the mixture was quenched with crushed ice & diluted with ethyl acetate. The organic portion was separated and dried (Na_2SO_4), filtered & evaporated. The crude syrup was purified on flash column chromatography (hexane: EtOAc = 9:1) to give **26** (1.92 g, 88%) as a pale yellow oil.

$[\alpha]_D^{25}$: +20.6 (*c* 0.8, $CHCl_3$); IR (neat) ν_{max} : 3497, 2930, 1427, 1218, 1108, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) : δ 7.70 – 7.63 (m, 4H), 7.47 – 7.35 (m, 6H), 6.08 (dd, *J* = 17.1, 10.8 Hz, 1H), 5.99 (ddd, *J* = 17.2, 10.6, 5.0 Hz, 1H), 5.49 – 5.37 (m, 2H), 5.29 – 5.20 (m, 2H), 4.59 (d, *J* = 1.5 Hz, 1H), 4.25 – 4.20 (m, 1H), 3.80 (d, *J* = 4.5 Hz, 1H), 3.64 (d, *J* = 10.5 Hz, 1H), 3.57 (d, *J* = 10.5 Hz, 1H), 1.54 (s, 3H), 1.44 (s, 3H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 137.28, 136.92, 135.70, 135.58, 132.79, 132.56, 129.86, 129.75, 127.72, 116.39, 115.83, 108.86, 84.27, 77.69, 74.97, 70.65, 67.73, 27.88, 27.01, 26.80, 19.16; ESI-MS (*m/z*) : 505 $[M+Na]^+$; HRMS Calcd for $C_{28}H_{38}O_5SiNa$ 505.2386, found 505.2384.

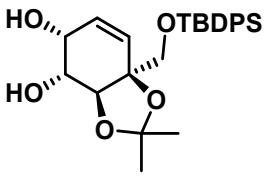
(1*R*,2*S*)-1-((4*S*,5*S*)-5-(((tert-butyldiphenylsilyl)oxy)methyl)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)but-3-ene-1,2-diol (27):



Compound **27** prepared from **25** according to the procedure as described above. Purification by column chromatography (hexane: EtOAc = 9:1) gave **27** (1.22 g, 82%) as a pale yellow syrup.

$[\alpha]_D^{25}$: +30.0 (*c* 0.89, $CHCl_3$); IR (neat) ν_{max} : 3395, 2928, 2856, 1732, 1377, 1109, 701 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) : δ 7.69 – 7.62 (m, 4H), 7.47 – 7.35 (m, 6H), 6.06 (dd, *J* = 17.1, 10.8 Hz, 1H), 5.88 (ddd, *J* = 17.2, 10.4, 6.7 Hz, 1H), 5.49 – 5.39 (m, 2H), 5.29 (dt, *J* = 10.4, 1.3 Hz, 1H), 5.23 (dd, *J* = 10.8, 1.9 Hz, 1H), 4.50 (d, *J* = 2.0 Hz, 1H), 4.15 (t, *J* = 6.3 Hz, 1H), 3.69 – 3.60 (m, 2H), 3.56 (d, *J* = 10.5 Hz, 1H), 1.53 (s, 3H), 1.43 (s, 3H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 136.76, 135.66, 135.58, 132.73, 132.55, 129.87, 129.77, 127.72, 118.23, 115.86, 108.81, 84.26, 78.56, 74.88, 71.20, 67.86, 27.91, 27.00, 26.80, 19.14; ESI-MS (*m/z*) : 505 $[M+Na]^+$; HRMS Calcd for $C_{28}H_{38}O_5SiNa$ 505.2386, found 505.2385.

(3a*S*,4*R*,5*R*,7a*S*)-7a-(((tert-butyldiphenylsilyl)oxy)methyl)-2,2-dimethyl-3a,4,5,7a-tetrahydrobenzo[*d*][1,3]dioxole-4,5-diol (28):

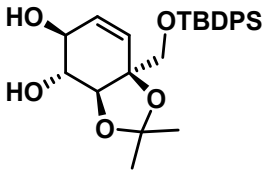


A diene **26** (1.0 g, 2.0 mmol) in anhydrous toluene (80 mL) was degassed by purging argon for 15 min & then treated with Grubbs second-generation catalyst (0.176 g, 0.20 mmol, 10 mol

%). The solution was refluxed under argon for 3 h. The dark brown solution was concentrated to give crude material, which was applied on column chromatography (hexane: EtOAc = 7:3) to provide cyclohexenol **28** as an oily compound (0.75 g, 80%).

$[\alpha]_D^{25}$: +16.4 (*c* 0.74, $CHCl_3$); IR (neat) ν_{max} : 3394, 2926, 1711, 1428, 1220, 1078, 703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) : δ 7.69 – 7.63 (m, 4H), 7.50 – 7.38 (m, 6H), 5.86 (dt, *J* = 10.5, 1.6 Hz, 1H), 5.42 (dt, *J* = 10.4, 1.9 Hz, 1H), 4.40 (dd, *J* = 3.7, 1.5 Hz, 1H), 4.31 (s, 1H), 4.28 – 4.22 (m, 1H), 4.05 (d, *J* = 10.2 Hz, 1H), 3.63 (q, *J* = 9.8 Hz, 2H), 1.31 (d, *J* = 5.4 Hz, 6H), 1.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 135.82, 135.53, 132.05, 131.76, 131.39, 130.25, 130.13, 128.26, 127.91, 109.11, 80.10, 78.70, 68.41, 67.96, 65.35, 27.63, 27.04, 26.70, 19.01; ESI-MS (*m/z*) : 477 $[M+Na]^+$; HRMS Calcd for $C_{26}H_{34}O_5SiNa$ 477.2073, found 477.2073.

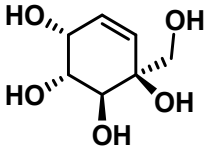
(3a*S*,4*R*,5*S*,7a*S*)-7a-(((tert-butyldiphenylsilyl)oxy)methyl)-2,2-dimethyl-3a,4,5,7a-tetrahydrobenzo[*d*][1,3]dioxole-4,5-diol (29):



Compound **29** was prepared from **27** according to the procedure as described above. Purification by chromatography (hexane: EtOAc = 7:3) provided cyclohexenol **29** as an oily compound (0.7 g, 75%).

$[\alpha]_D^{25}$: +30.2 (*c* 0.81, $CHCl_3$); IR (neat) ν_{max} : 3395, 2925, 1737, 1428, 1218, 1109, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) : δ 7.65 (dd, *J* = 8.0, 1.5 Hz, 4H), 7.47 – 7.37 (m, 6H), 6.10 (ddd, *J* = 10.3, 4.4, 0.9 Hz, 1H), 5.52 (dt, *J* = 10.3, 1.1 Hz, 2H), 4.40 (dt, *J* = 4.3, 1.2 Hz, 1H), 4.21 (t, *J* = 3.4 Hz, 1H), 4.08 (t, *J* = 3.4 Hz, 1H), 3.62 (q, *J* = 10.1 Hz, 2H), 1.41 (s, 3H), 1.32 (s, 3H), 1.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) : δ 135.84, 135.55, 131.93, 131.60, 130.20, 130.12, 130.07, 128.96, 127.88, 110.00, 80.39, 79.58, 69.39, 67.88, 67.51, 28.11, 27.17, 26.67, 19.02; ESI-MS (*m/z*) : 477 $[M+Na]^+$; HRMS Calcd for $C_{26}H_{34}O_5SiNa$ 477.2073, found 477.2098.

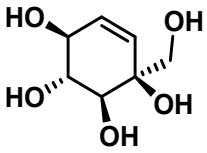
(1*S*,2*S*,3*R*,4*R*)-1-(hydroxymethyl)cyclohex-5-ene-1,2,3,4-tetraol (30):



The diol **28** (0.1 g, 0.2 mmol) in TFA (2 mL) and H_2O (1 mL) was stirred at rt. for 3 h. The mixture was concentrated to give syrup that was purified on column chromatography (DCM: MeOH = 9: 1) to give carbasugar **30** in 90% yield (0.032 g) as a syrup.

$[\alpha]_D^{25}$: −140.8 (*c* 0.3, MeOH) [for enantiomer lit.[4] $[\alpha]_D^{26}$ +161.5 (*c* 0.61, MeOH)]; IR (neat) v_{max} : 3368, 2925, 1676, 1200, 1140, 772 cm^{-1}; ^1H NMR (500 MHz, CD_3OD) : δ 5.92 (dd, *J* = 9.9, 5.3 Hz, 1H), 5.79 (d, *J* = 9.9 Hz, 1H), 4.20 – 4.17 (m, 1H),3.82 – 3.78 (m, 2H), 3.57 – 3.53 (m, 2H); ^{13}C NMR (125 MHz, CD_3OD) : δ 133.03, 131.15, 74.08, 71.02, 69.91, 68.05, 67.51; ESI-MS (*m/z*) : 199 $[M+Na]^+$; HRMS Calcd for $C_7H_{12}O_5Na$ 199.0582, found 199.0582. ^1H and ^{13}C values are similar to the reported data.[4]

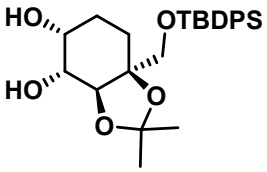
(1*S*,2*S*,3*R*,4*S*)-1-(hydroxymethyl)cyclohex-5-ene-1,2,3,4-tetraol (31):



To compound **29** (0.1 g, 0.2 mmol) in TFA (2 mL) and H_2O (1 mL) was stirred at rt. for 3 h. The mixture was concentrated to give syrup which was purified by column chromatography (methylene chloride: MeOH = 9: 1) to give carbasugar **31** in 92% yield (0.033 g) as a syrup.

$[\alpha]_D^{25}$: +19.7 (*c* 0.65, MeOH); IR (neat) v_{max} : 3365, 2925, 1676, 1200, 1142, 772 cm^{-1}; ^1H NMR (500 MHz, CD_3OD) : δ 5.75 (d, *J* = 10.1 Hz, 1H), 5.65 (dd, *J* = 10.1, 1.4 Hz, 1H), 3.97 (d, *J* = 7.6 Hz, 1H), 3.67 – 3.55 (m, 2H), 3.48 (m, 2H); ^{13}C NMR (125 MHz, CD_3OD) : δ 134.28, 130.30, 75.14, 73.96, 73.58, 71.98, 66.75; ESI-MS (*m/z*) : 199 $[M+Na]^+$; HRMS Calcd for $C_7H_{12}O_5Na$ 199.0582, found 199.0579.

(3a*S*,4*R*,5*R*,7a*S*)-7a-(((tert-butyldiphenylsilyl)oxy)methyl)-2,2-dimethylhexahydrobenzo[*d*][1,3]dioxole-4,5-diol (32):

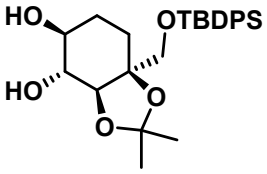


To compound **28** (0.3 g, 0.16 mmol) in ethyl acetate (2 mL) was added 5% Pd/C (cat.) under the H_2 atmosphere then the mixture was stirred for 3 h at rt. Next Pd-C was filtered through a short pad of celite and washed with ethyl acetate (3 × 5 mL) and the filtrate was evaporated.

The crude was purified on column chromatography (hexane: EtOAc = 7: 3) to provide cyclohexanol **32** as an oily compound (0.29 g, 98%).

$[\alpha]_D^{25}$: +18.4 (*c* 0.69, $CHCl_3$); IR (neat) ν_{max} : 3395, 2929, 1719, 1378, 1074, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : δ 7.71 (m, 4H), 7.48 – 7.35 (m, 6H), 4.35 (d, *J* = 2.7 Hz, 1H), 4.18 (s, 1H), 4.01 – 3.92 (m, 1H), 3.69 (q, *J* = 10.5 Hz, 2H), 3.00 (s, 1H), 1.88 – 1.78 (m, 1H), 1.69 (m, 3H), 1.46 (s, 3H), 1.34 (s, 3H), 1.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 135.77, 135.64, 132.50, 132.43, 129.90, 129.85, 127.79, 127.75, 108.22, 80.27, 79.41, 69.78, 68.22, 68.02, 30.65, 28.31, 26.82, 26.77, 26.01, 19.18; ESI-MS (*m/z*) : 479 $[M+Na]^+$; HRMS Calcd for $C_{26}H_{36}O_5SiNa$ 479.2230, found 479.2227.

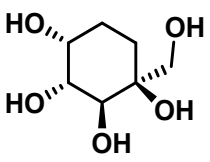
(3a*S*,4*R*,5*S*,7a*S*)-7a-(((tert-butyldiphenylsilyl)oxy)methyl)-2,2-dimethylhexahydrobenzo[*d*][1,3]dioxole-4,5-diol (33):



Compound **33** was prepared from **29** according to the procedure as described above. Purification by chromatography (hexane: EtOAc = 7: 3) provided cyclohexanol **33** as an oily compound (0.28 g, 98%).

$[\alpha]_D^{25}$: –30.2 (*c* 0.94, $CHCl_3$); IR (neat) ν_{max} : 3382, 2930, 1641, 1428, 1109, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) : δ 7.72 – 7.62 (m, 4H), 7.49 – 7.35 (m, 6H), 4.20 (d, *J* = 5.0 Hz, 1H), 3.97 (t, *J* = 5.1 Hz, 1H), 3.66 (d, *J* = 10.0 Hz, 2H), 3.53 (d, *J* = 10.0 Hz, 1H), 2.93 (s, 1H), 2.67 (s, 1H), 1.96 – 1.85 (m, 2H), 1.75 – 1.58 (m, 2H), 1.50 (s, 3H), 1.30 (s, 3H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 135.66, 135.60, 132.50, 129.93, 127.80, 109.04, 82.31, 80.91, 73.68, 70.48, 67.77, 28.71, 28.02, 26.83, 26.71, 26.00, 19.18; ESI-MS (*m/z*) : 479 $[M+Na]^+$; HRMS Calcd for $C_{26}H_{36}O_5SiNa$ 479.2230, found 479.2231.

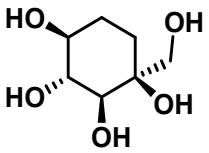
(1*S*,2*S*,3*R*,4*R*)-1-(hydroxymethyl)cyclohexane-1,2,3,4-tetraol (or) 6a-carba-β-D-fructopyranose (34):



The diol **32** (0.1 g, 0.22 mmol) in TFA (2 mL) and H_2O (1 mL) was stirred at rt. for 3 h. The mixture was concentrated to give syrup which was purified on column chromatography (methylene chloride: MeOH = 9: 1) to give 6a-carba-β-D-fructopyranose **34** in 95% yield (0.038 g) as a syrup.

$[\alpha]_D^{25}$: −49.8 (*c* 0.45, MeOH). [lit.[5] $[\alpha]_D^{26}$ −53.5 (*c* 0.5, MeOH)] [for enantiomer lit.[28] $[\alpha]_D^{25}$ +50.0 (*c* 0.5, MeOH)]; IR (neat) v_{max} : 3362, 2922, 2852, 1460, 1377, 1015, 772 cm^{-1}; ^1H NMR (400 MHz, D_2O) : δ 4.03 (m, 1H), 3.68 (dd, *J* = 9.9, 2.9 Hz, 1H), 3.62 (d, *J* = 9.9 Hz, 1H), 3.53 (d, *J* = 11.4 Hz, 1H), 3.44 (d, *J* = 11.4 Hz, 1H), 1.71 (m, 3H), 1.50 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD) : δ 75.57, 74.09, 72.52, 70.97, 68.39, 27.48, 26.73; ESI-MS (*m/z*) : 201 $[M+Na]^+$; HRMS Calcd for $C_7H_{14}O_5Na$ 201.0733, found 201.0730. ^1H and ^{13}C values are similar to the reported data.[5b]

(1*S*,2*S*,3*R*,4*S*)-1-(hydroxymethyl)cyclohexane-1,2,3,4-tetraol (35):



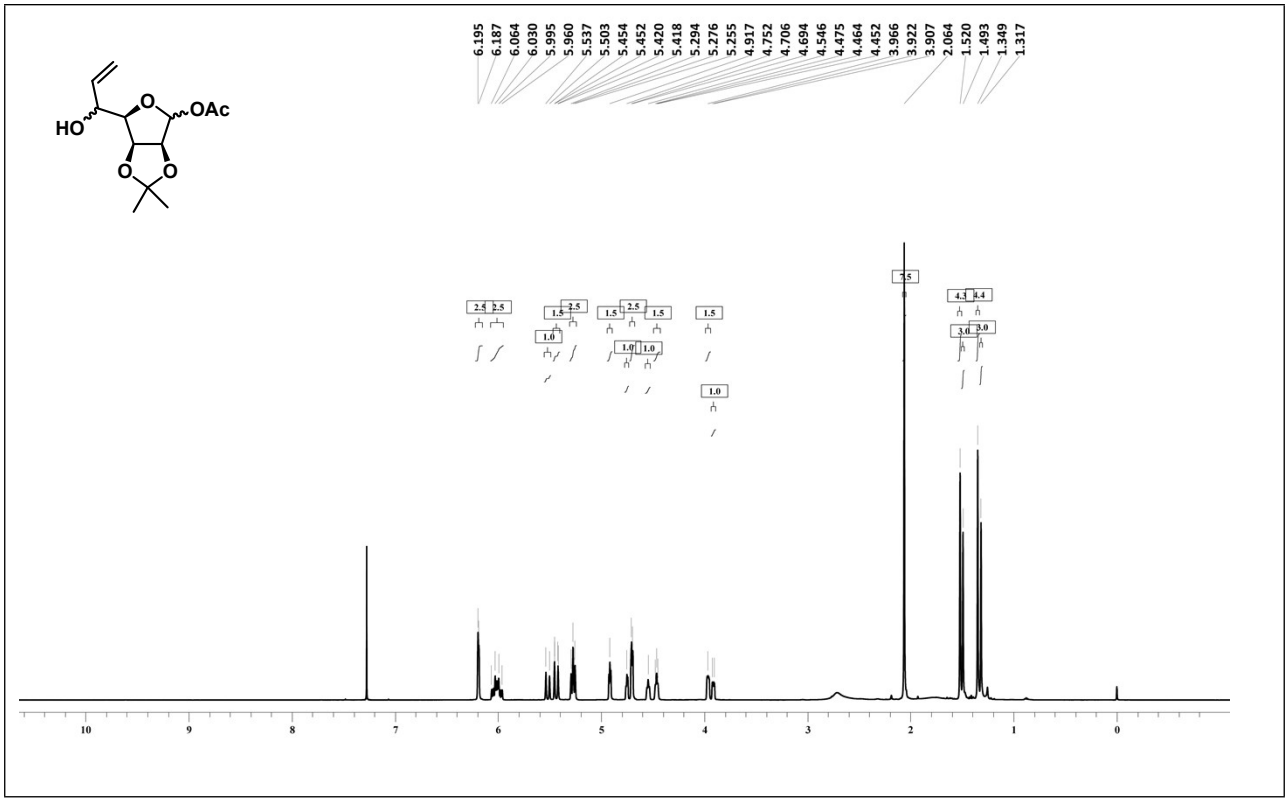
The diol **33** (0.1 g, 0.22 mmol) in TFA (2 mL) and H_2O (1 mL) was stirred at rt. for 3 h. The mixture was concentrated to give syrup which was purified by column chromatography (methylene chloride: MeOH = 9: 1) to give carbasugar **35** in 95% yield (0.037 g) as a syrup.

$[\alpha]_D^{25}$: +28.8 (*c* 0.47, MeOH); IR (neat) v_{max} : 3362, 2922, 2853, 1460, 1219 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) : δ 3.57 (d, *J* = 10.8 Hz, 1H), 3.48 (t, *J* = 9.2 Hz, 1H), 3.36 (m, 3H), 1.76 – 1.65 (m, 2H), 1.64 – 1.48 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) : δ 77.81, 75.13, 74.14, 67.84, 29.94, 28.26; ESI-MS (*m/z*) : 201 $[M+Na]^+$; HRMS Calcd for $C_7H_{14}O_5Na$ $[M+Na]^+$ 201.0733, found 201.0732.

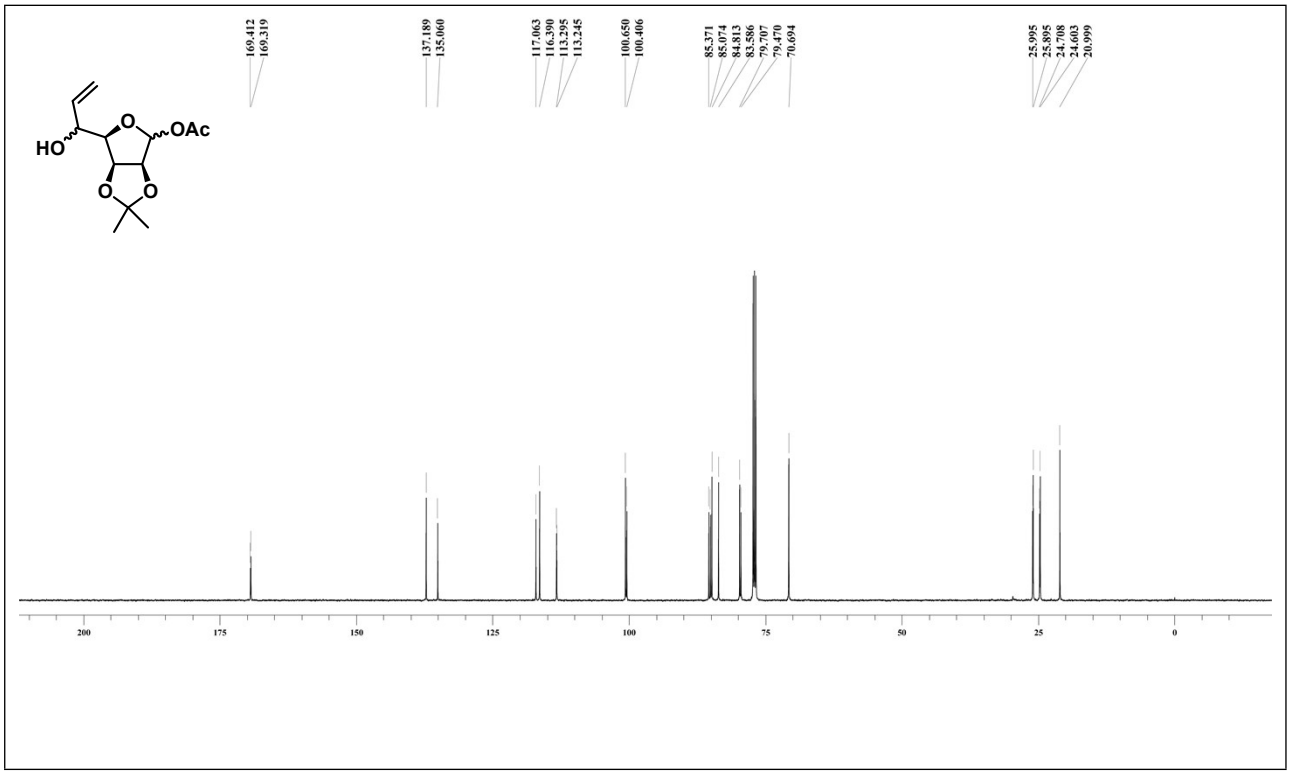
1. Experimental Section

3. NMR spectra of the products:

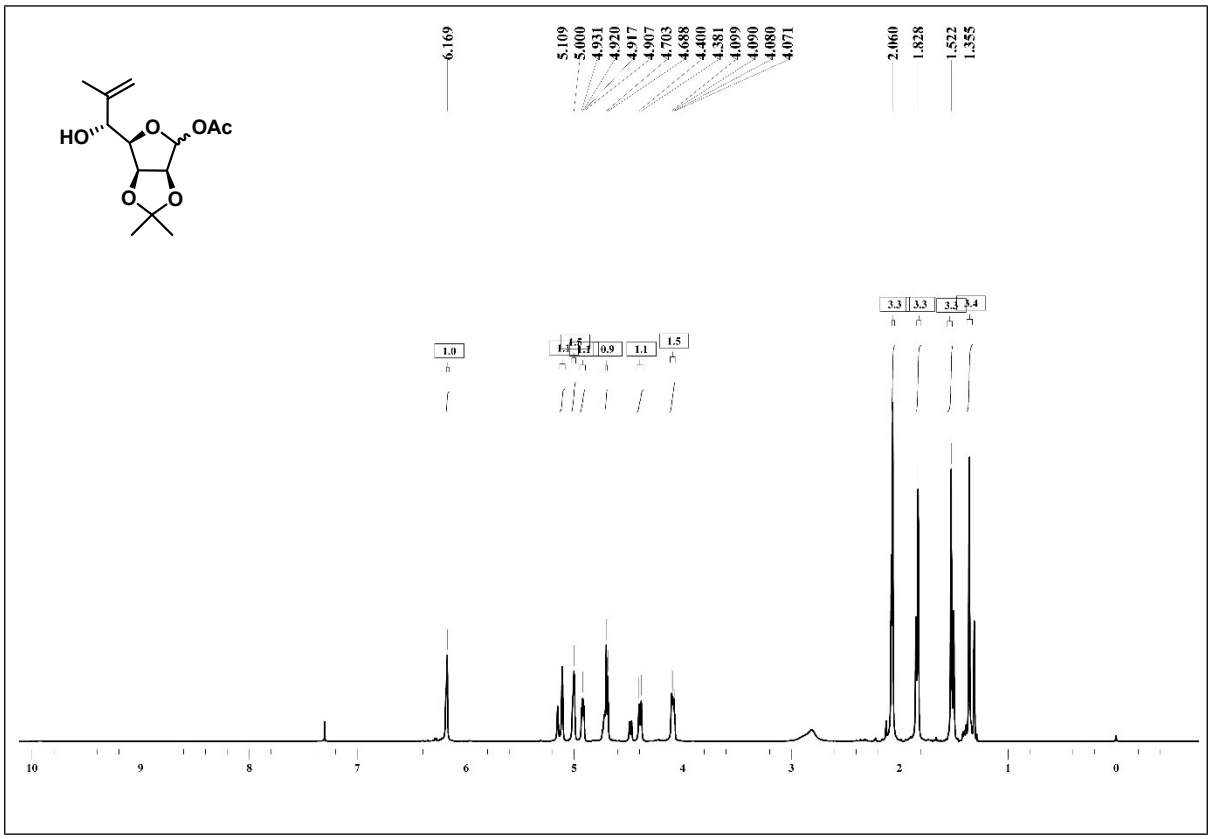
^{1}H NMR (500MHz, $CDCl_3$) spectrum of compound 3a & 3b:



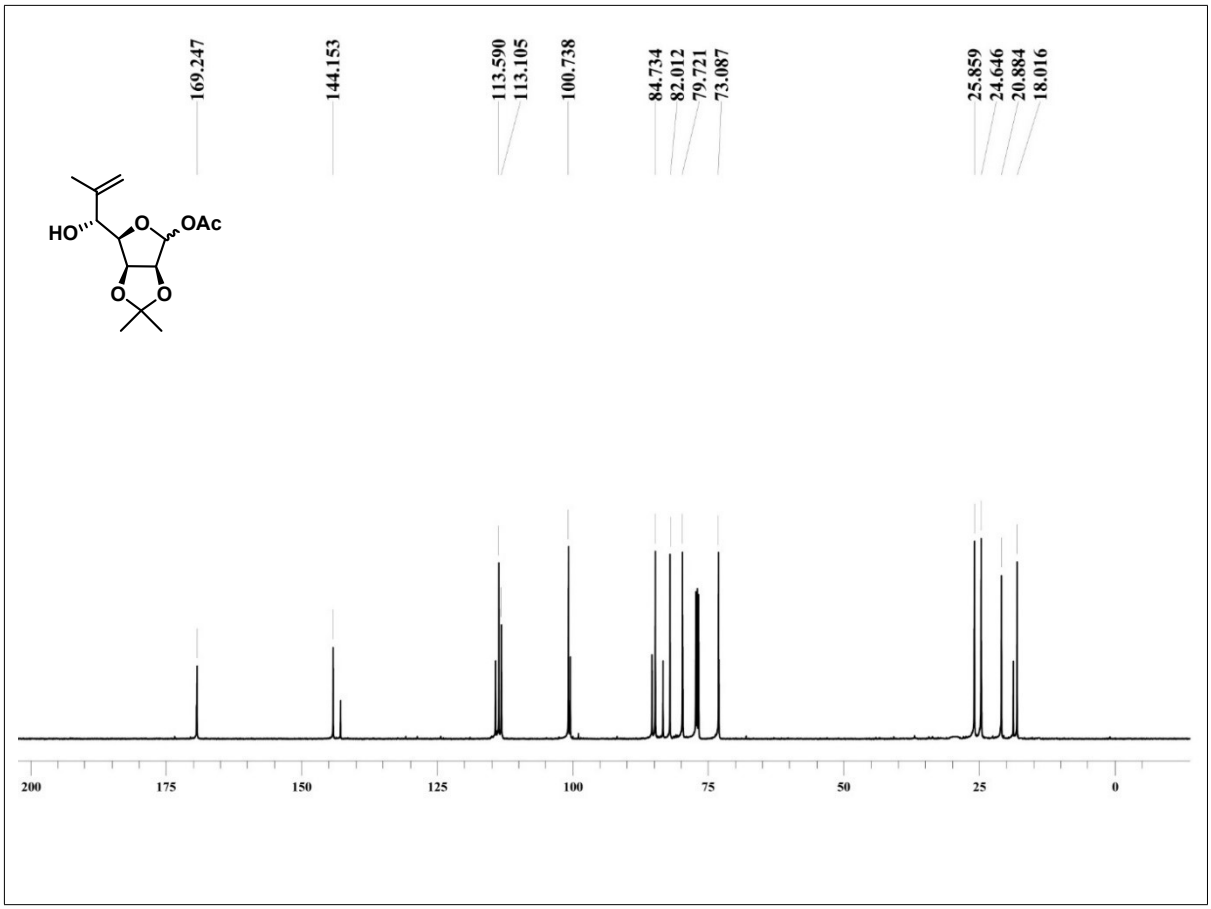
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 3a & 3b:



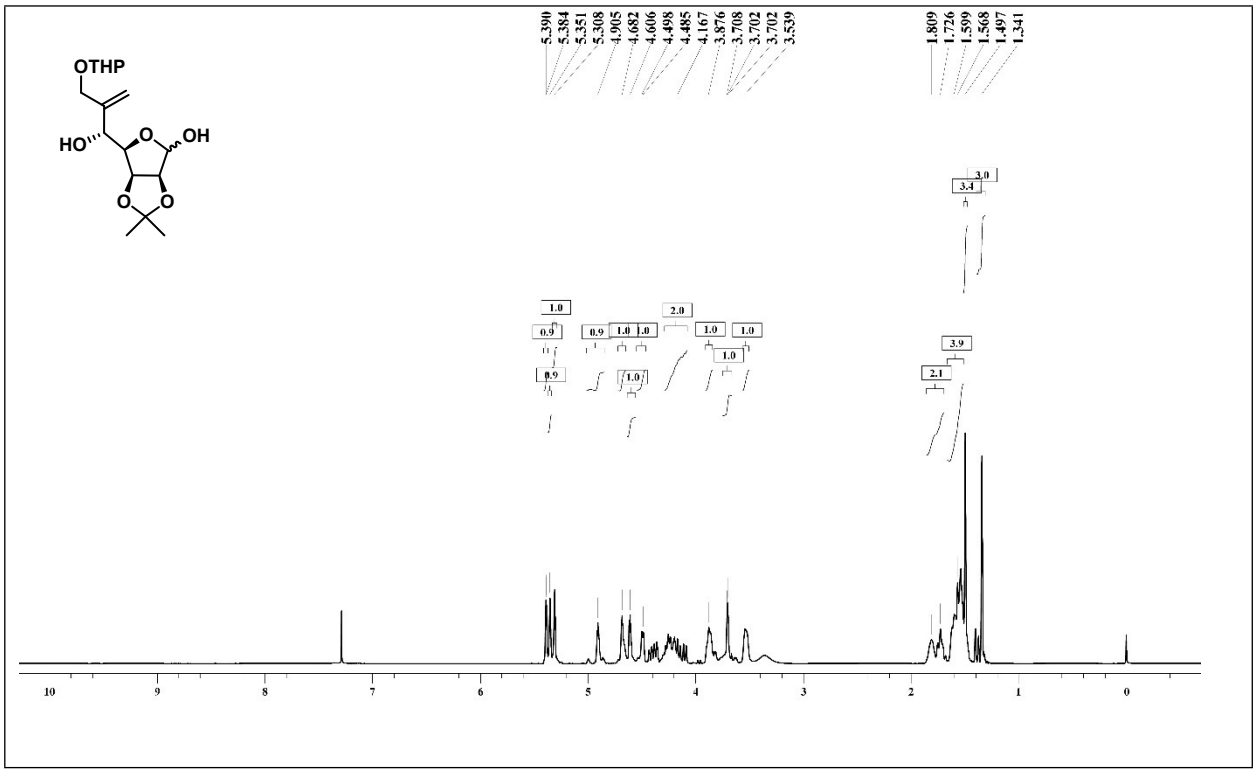
^{1}H NMR (500MHz, $CDCl_3$) spectrum of compound 4a & 4b:



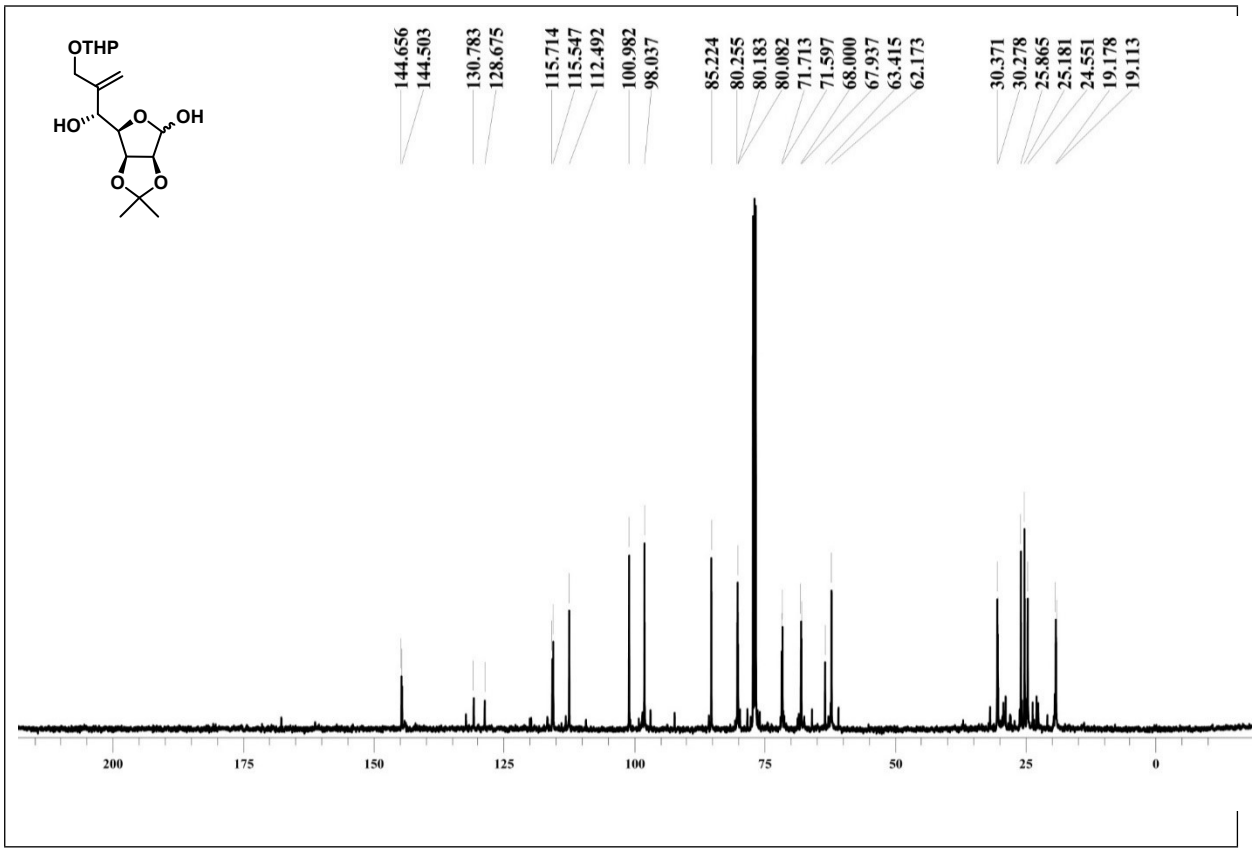
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 4a & 4b



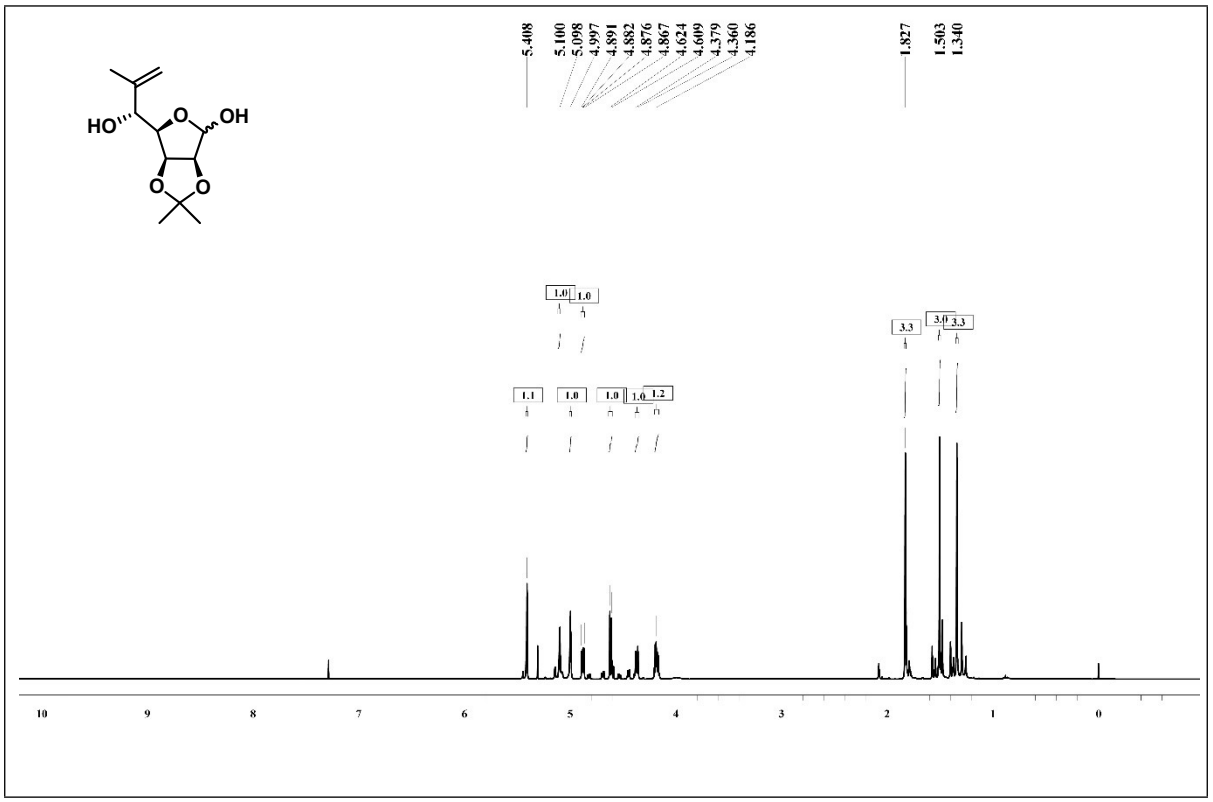
^{1}H NMR (500MHz, $CDCl_3$) spectrum of 8:



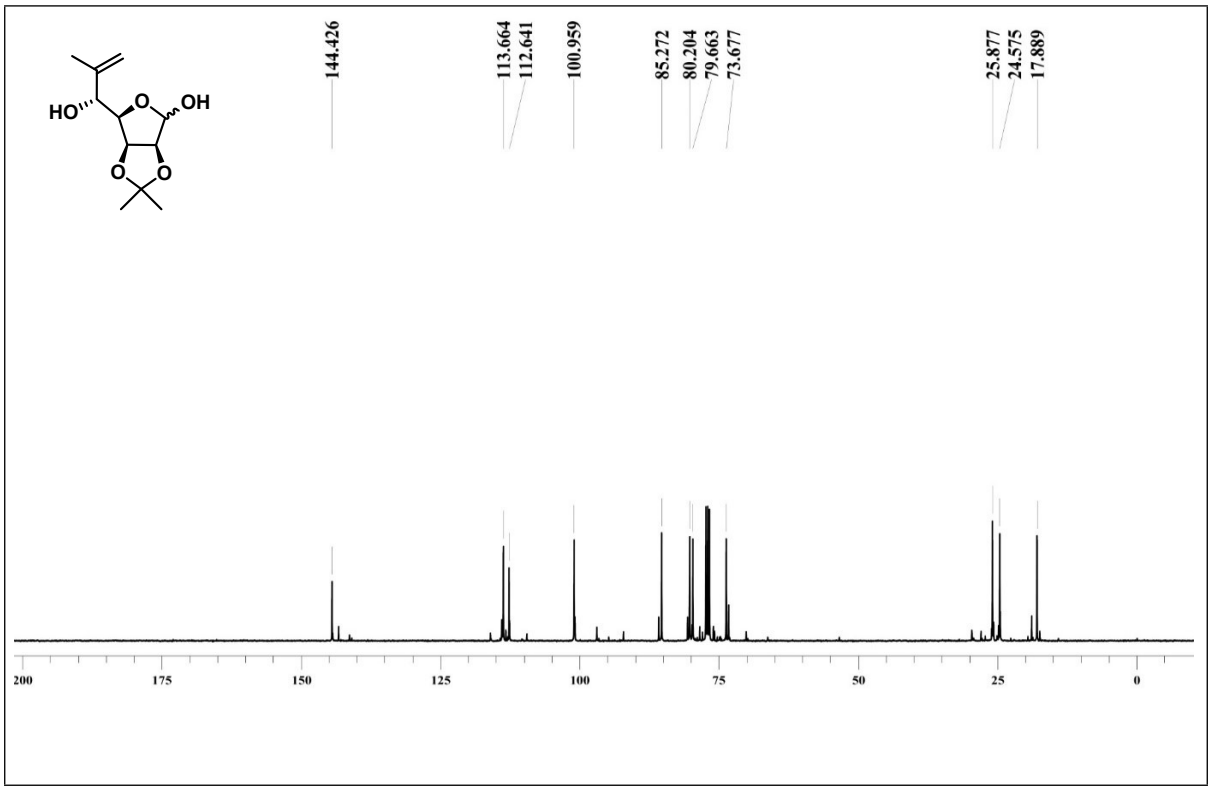
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 8:



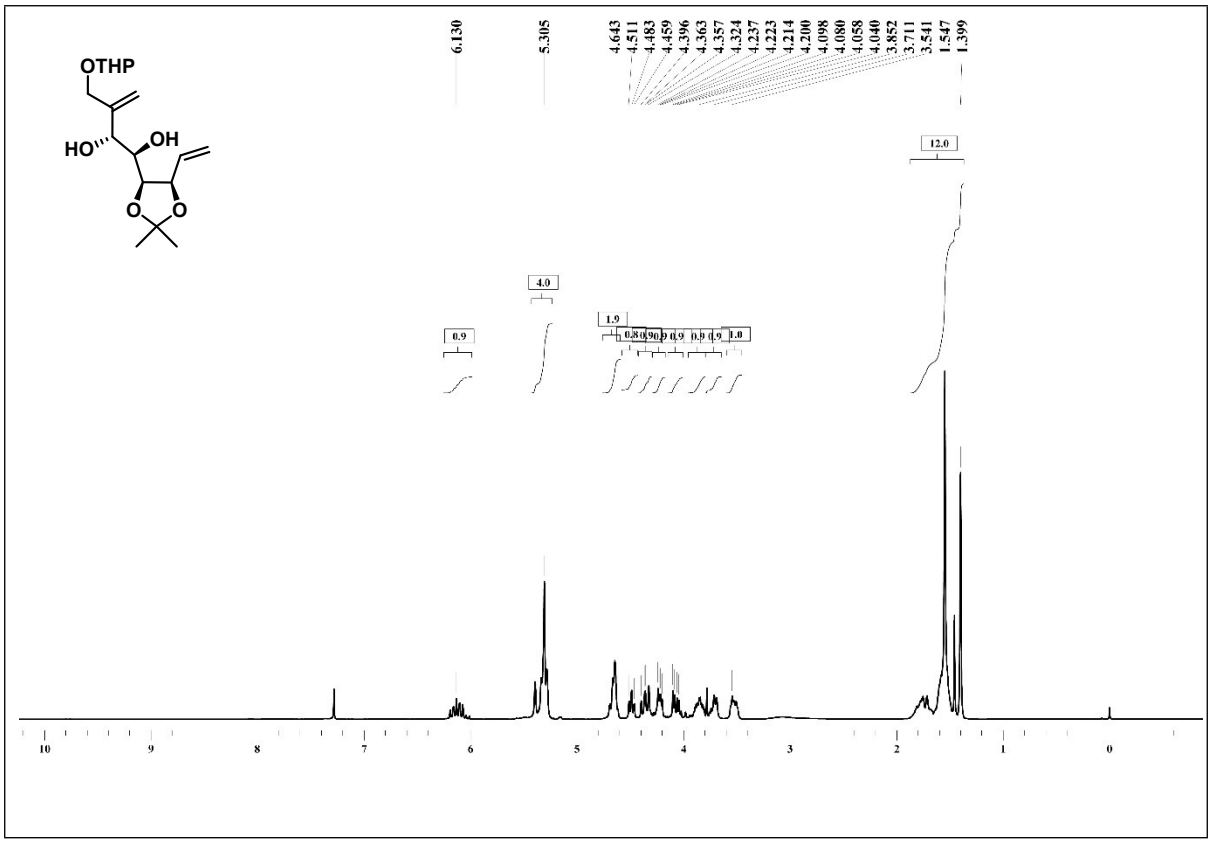
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound 10a & 10b:



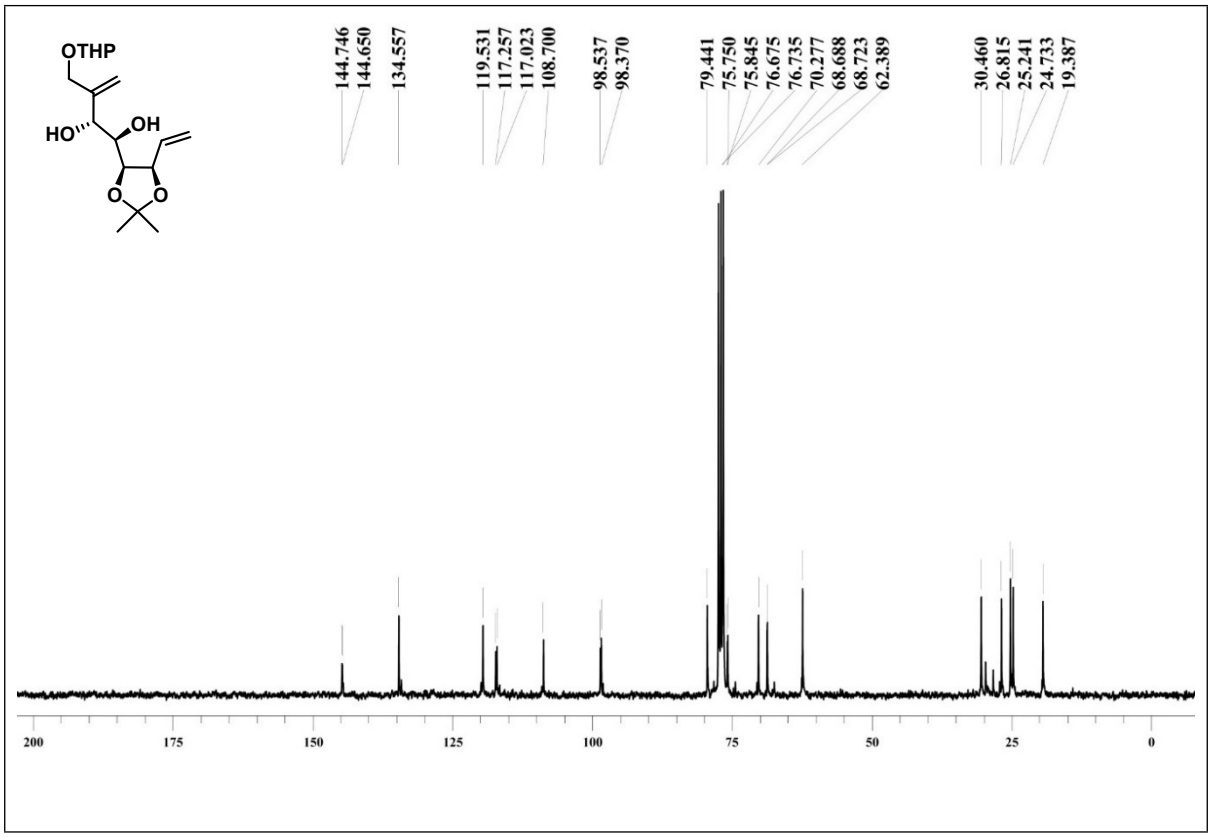
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 10a & 10b:



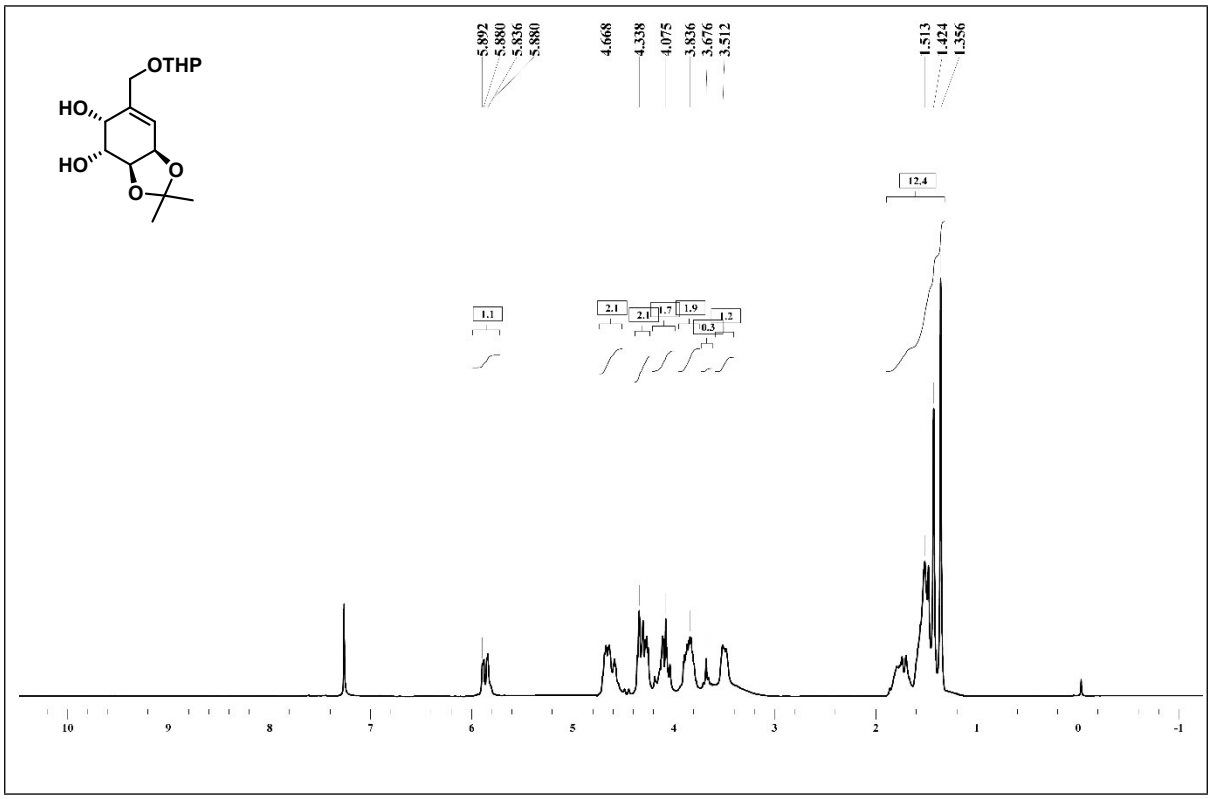
^{1}H NMR (300MHz, $CDCl_3$) spectrum of compound 11:



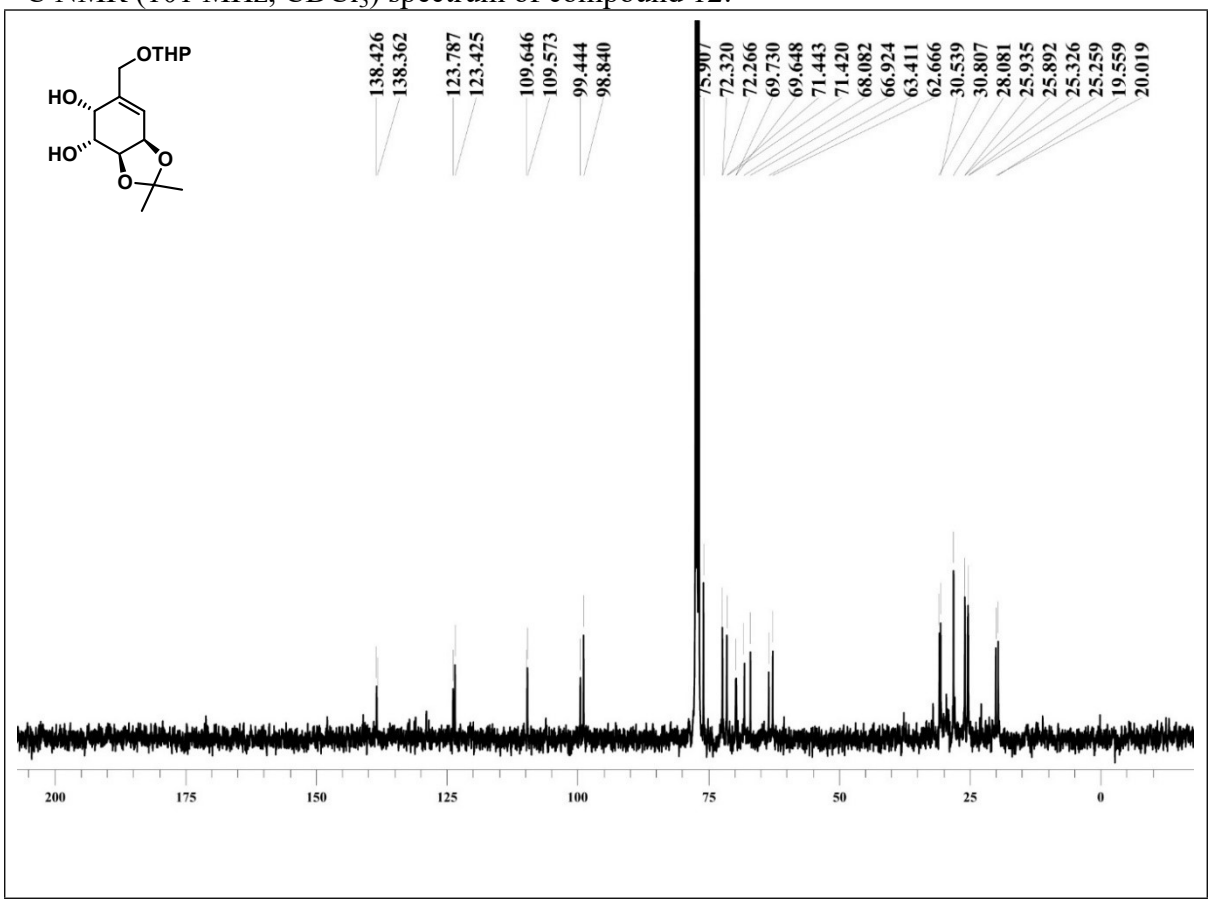
^{13}C NMR (126MHz, $CDCl_3$) spectrum of compound 11:



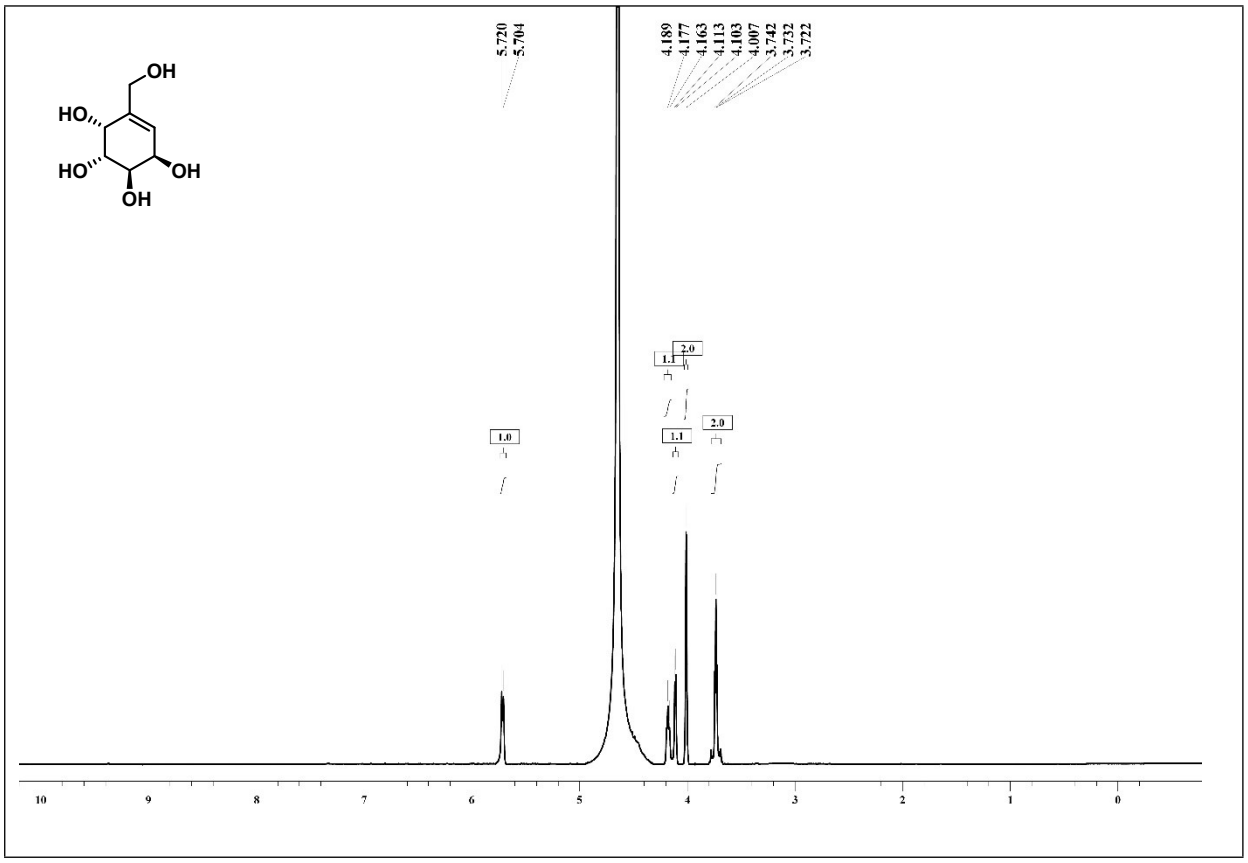
^{1}H NMR (300MHz, $CDCl_3$) spectrum of compound 12:



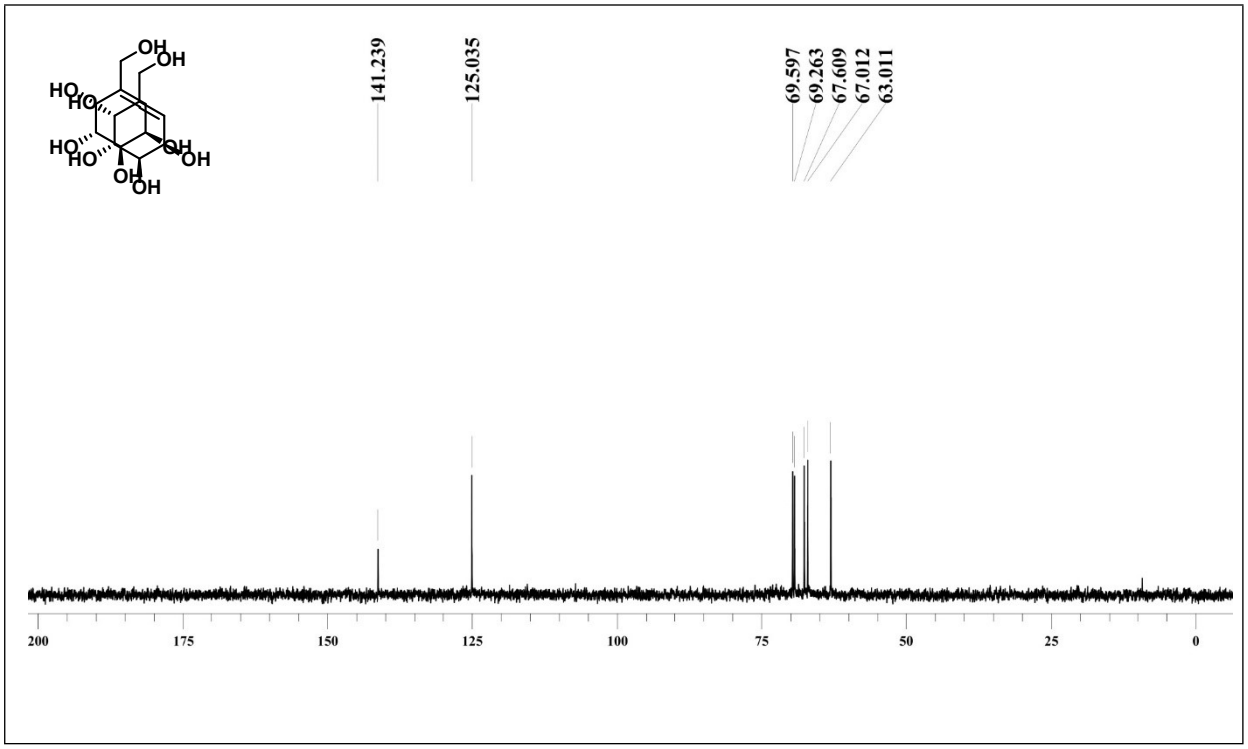
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 12:



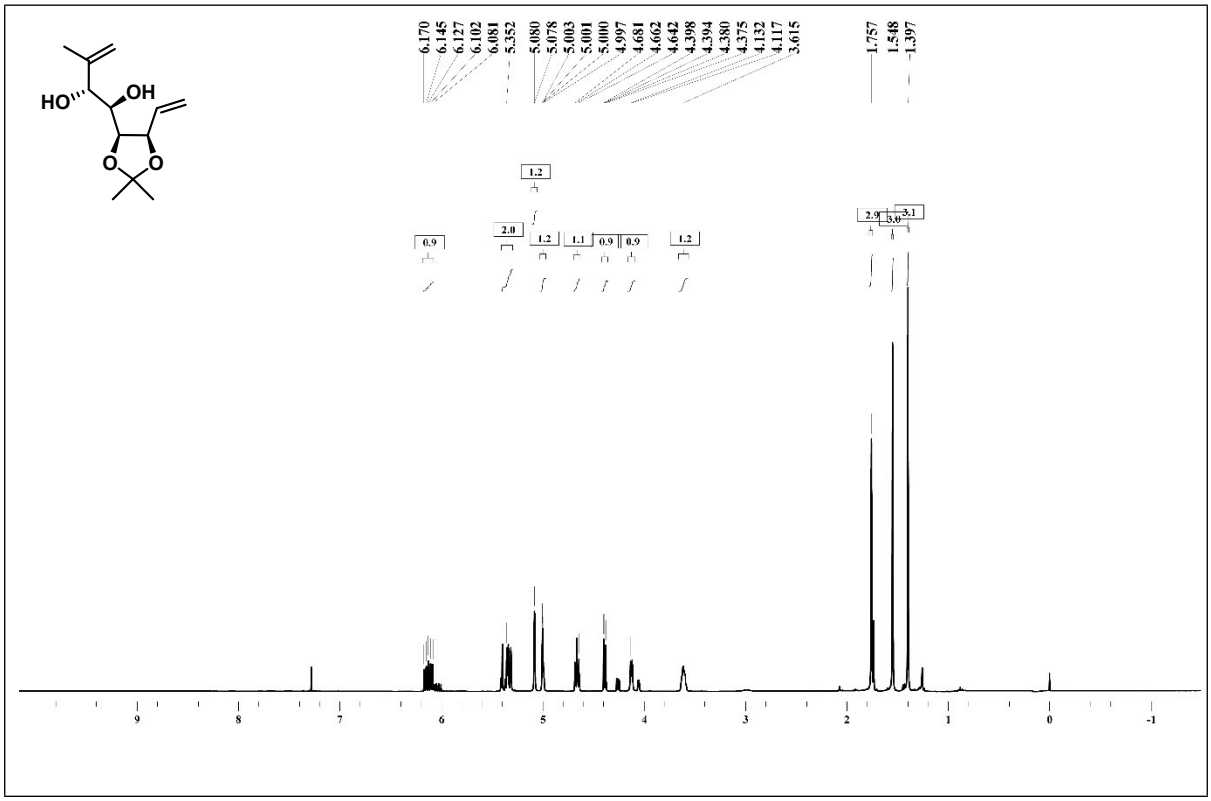
^{1}H NMR (400MHz, D_2O) spectrum of compound (–)-MK7607:



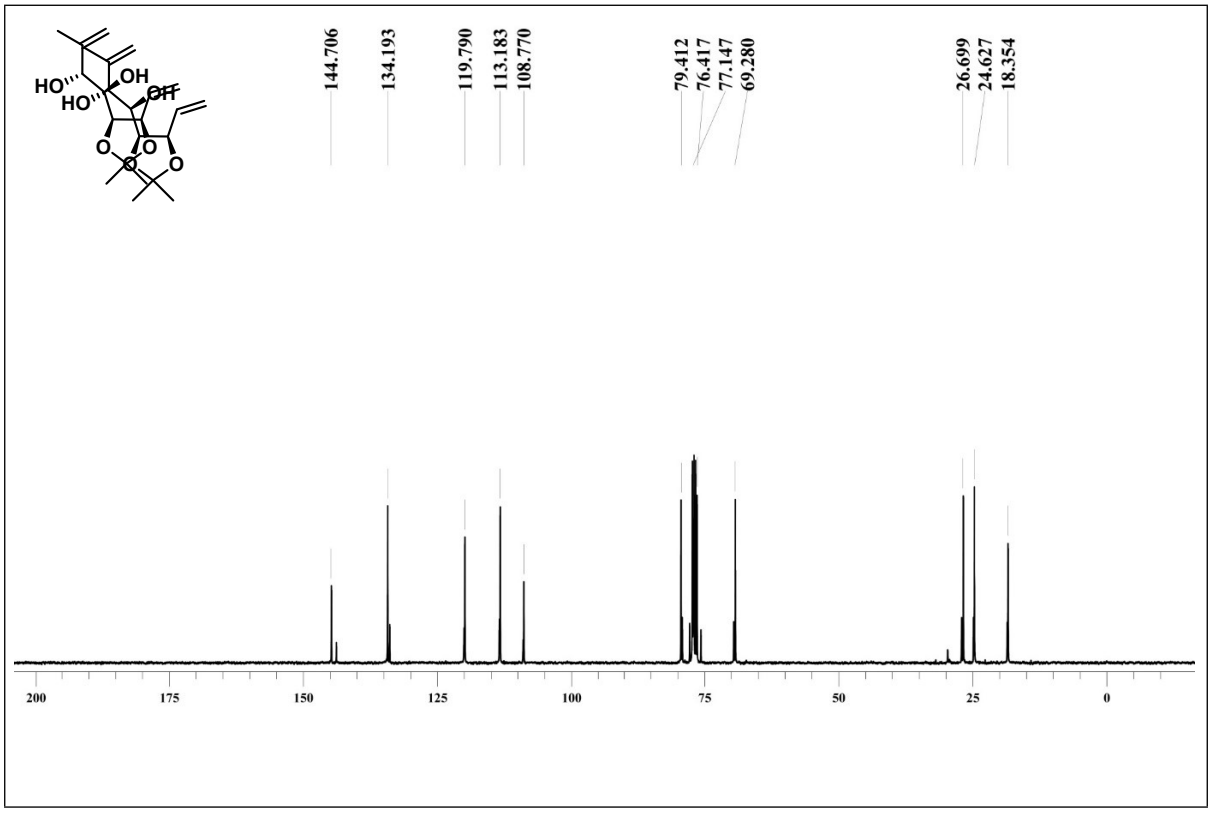
^{13}C NMR (101 MHz, D_2O) spectrum of compound (–)-MK7607:



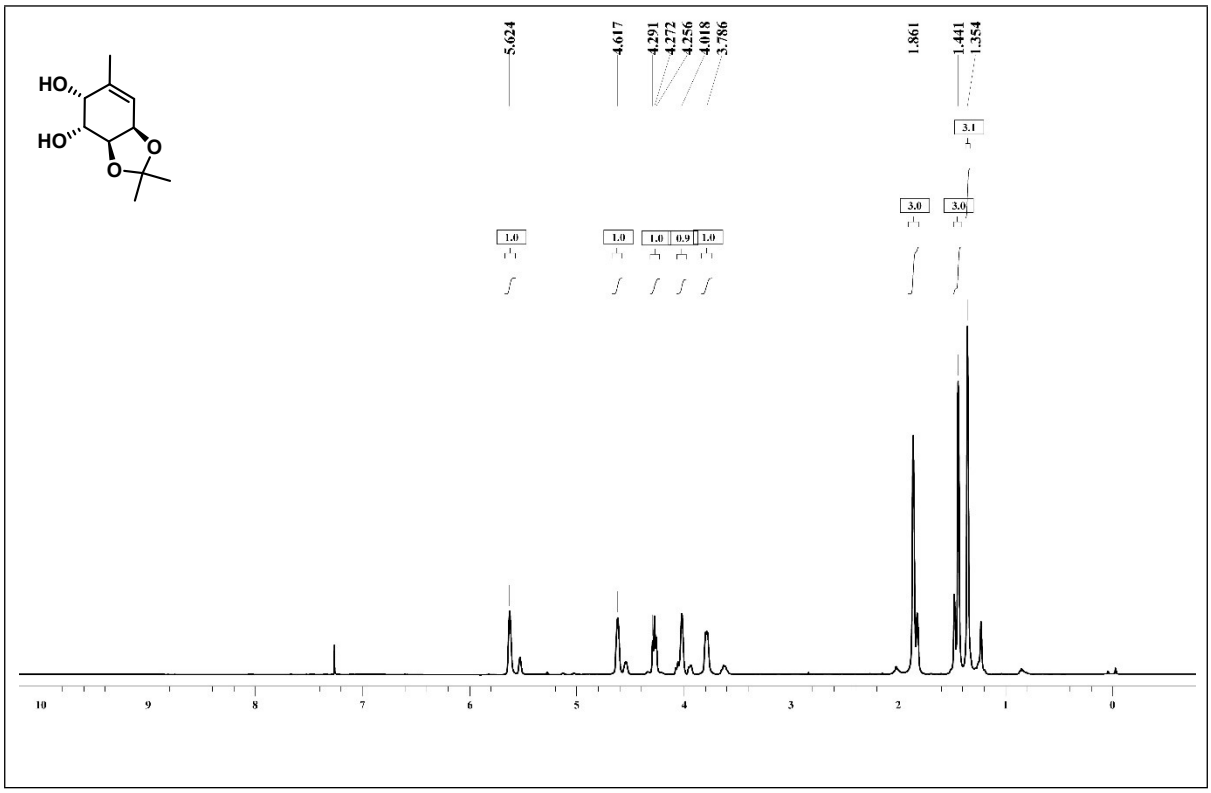
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound 13a & 13b:



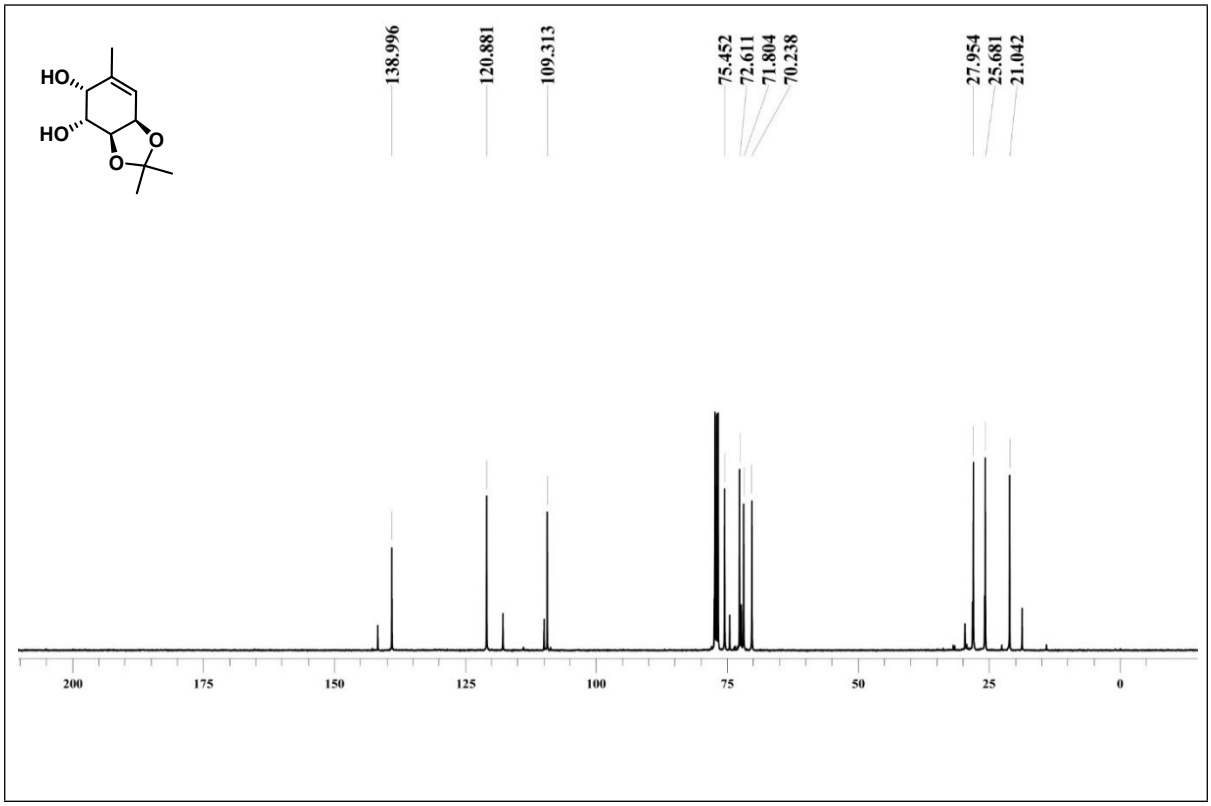
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 13a & 13b:



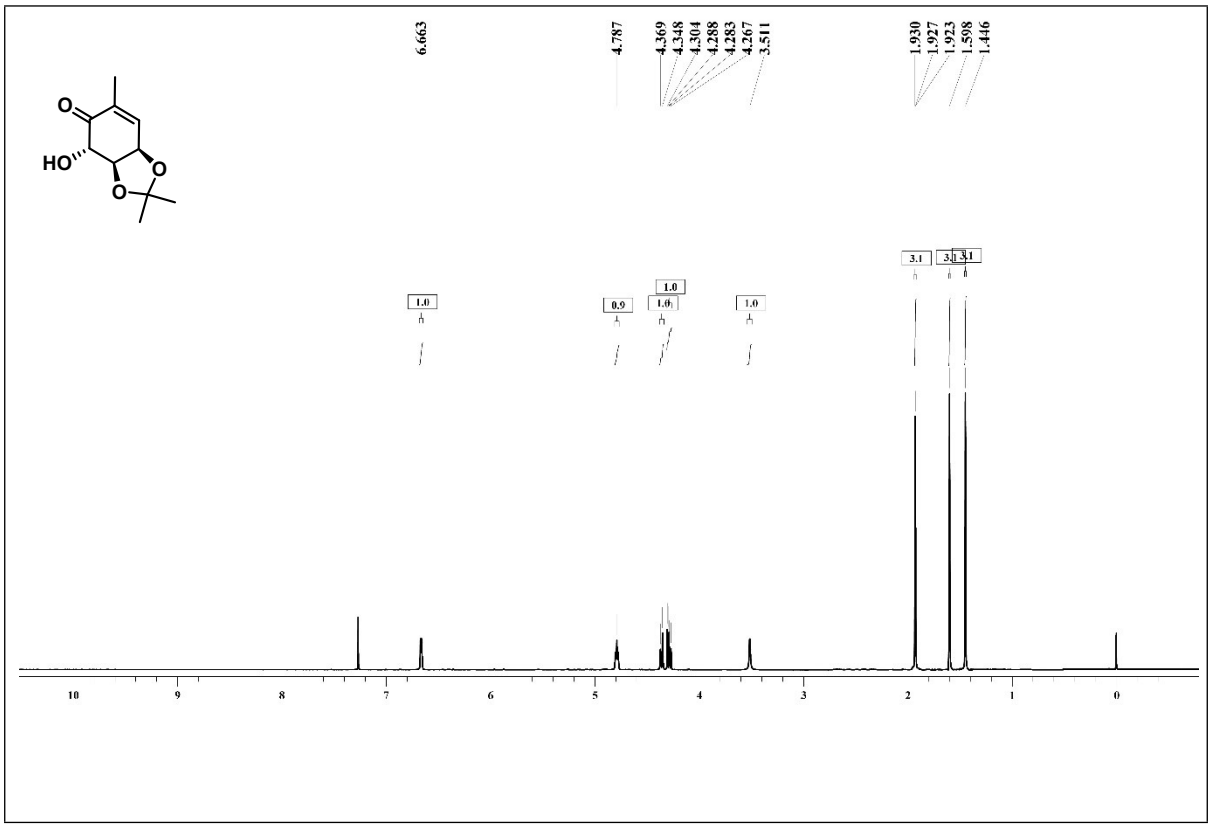
^{1}H NMR (300MHz, $CDCl_3$) spectrum of compound 14a & 14b:



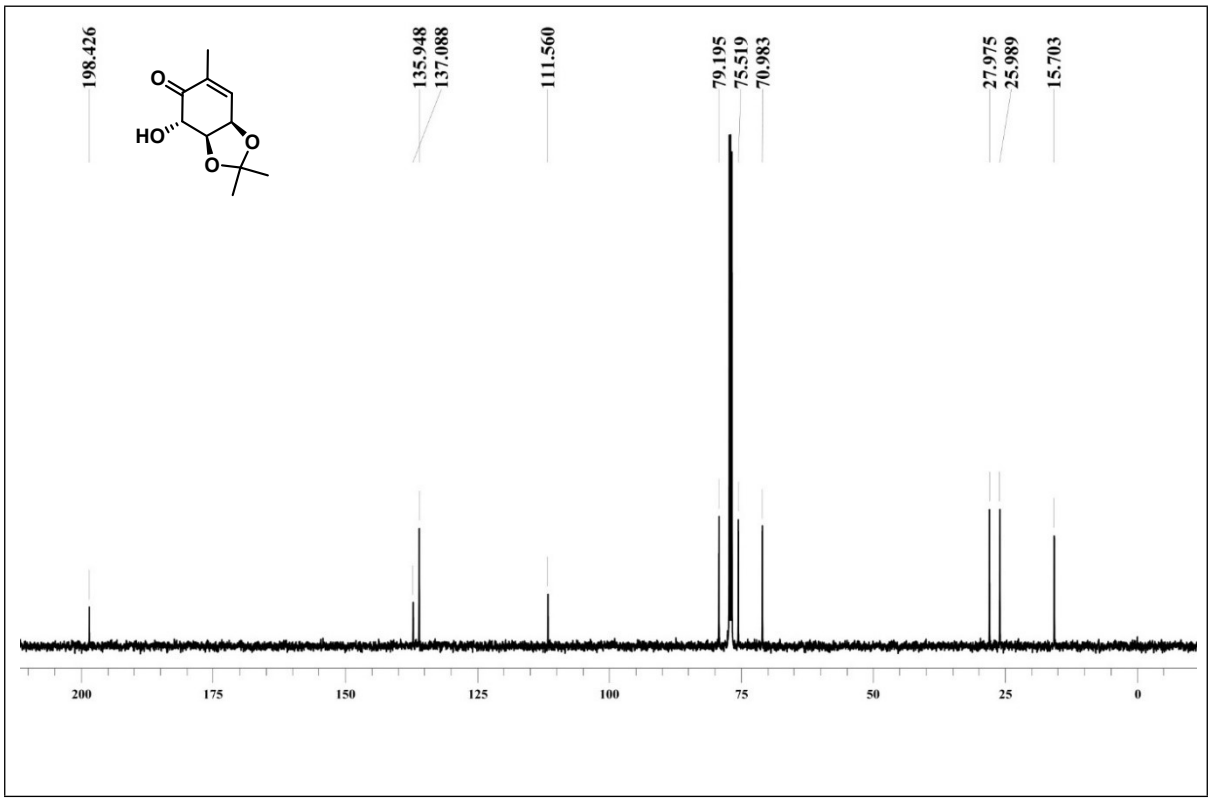
^{13}C NMR (126MHz, $CDCl_3$) spectrum of compound 14a & 14b:



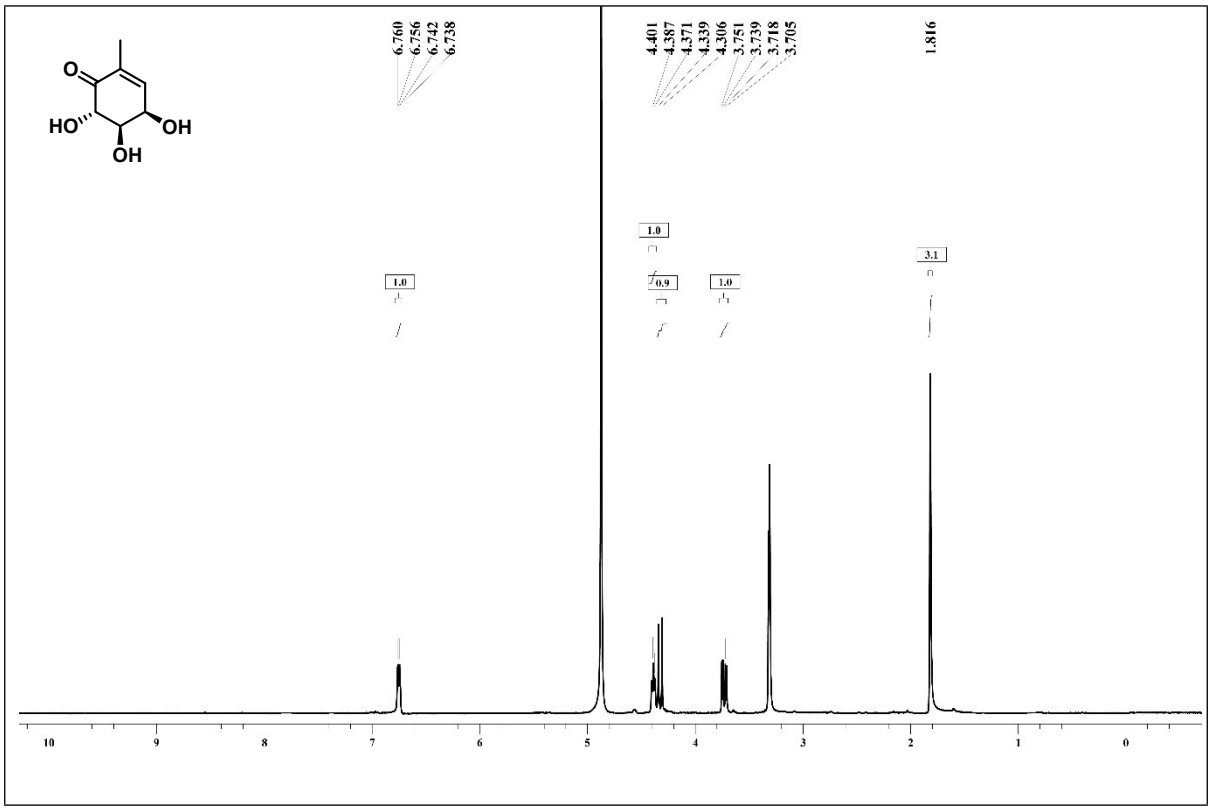
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound 15:



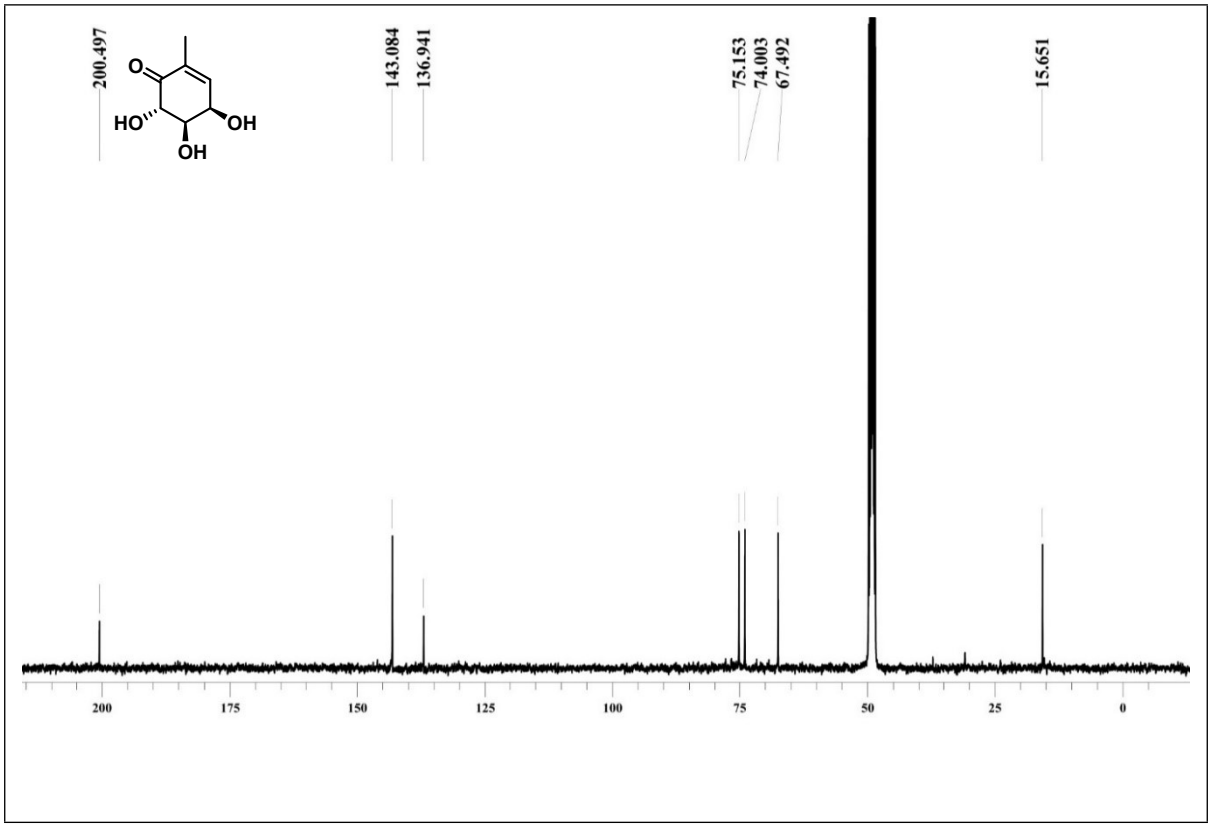
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 15:



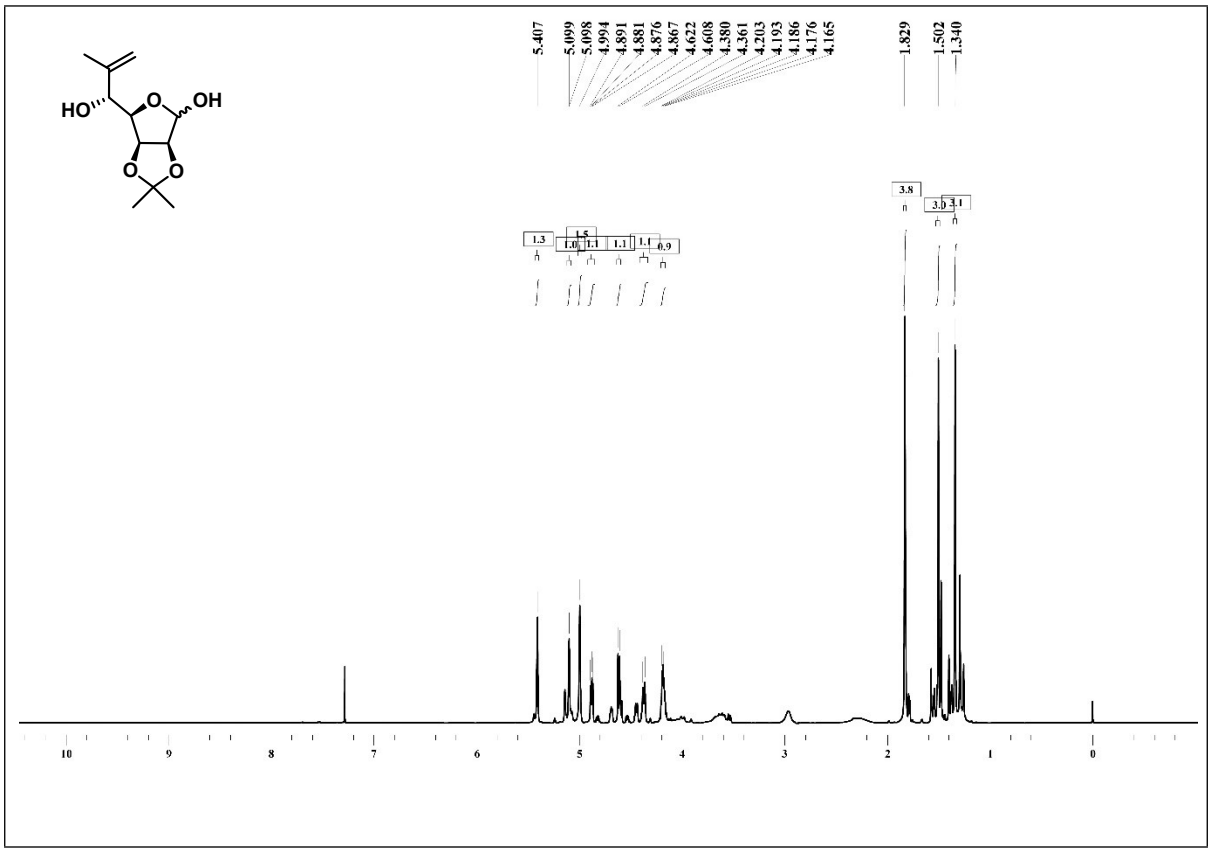
^{1}H NMR (300MHz, CD_3OD) spectrum of (–)-gabosine A:



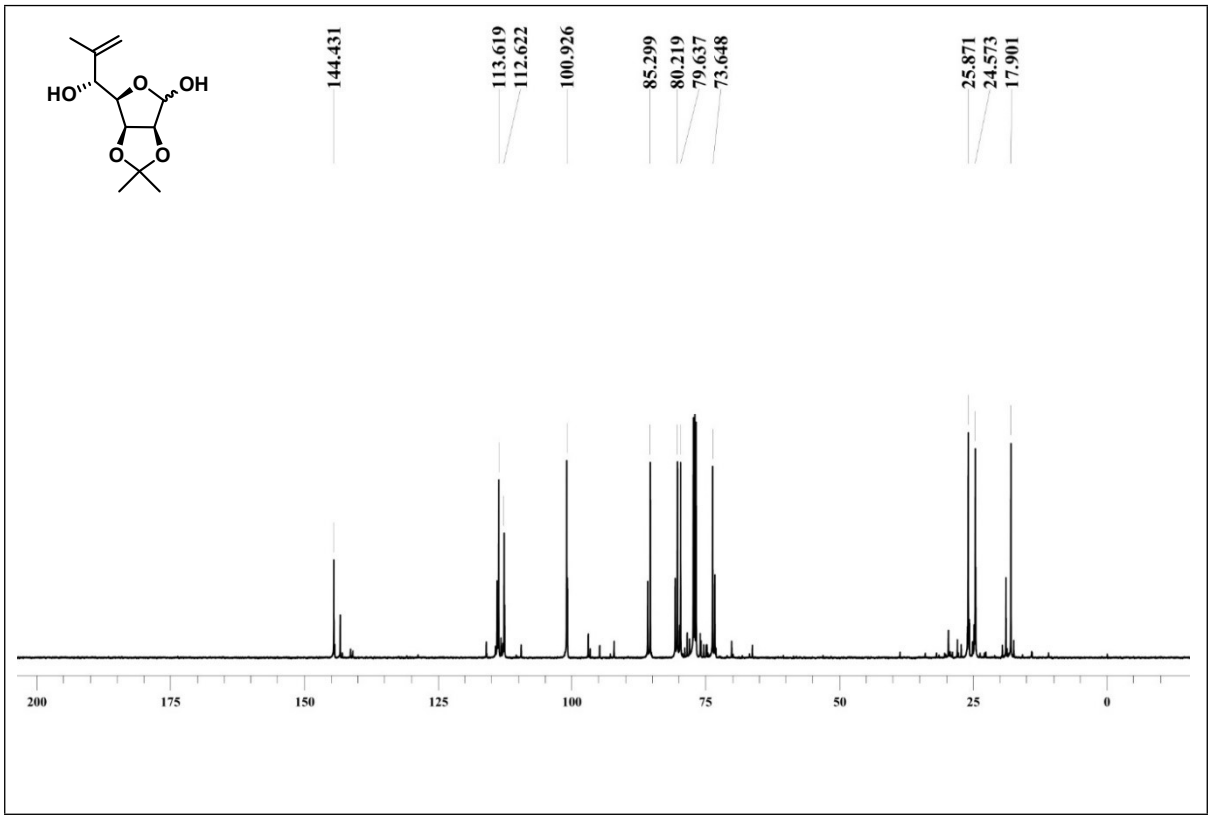
^{13}C NMR (101 MHz, CD_3OD) spectrum of (–)-gabosine A:



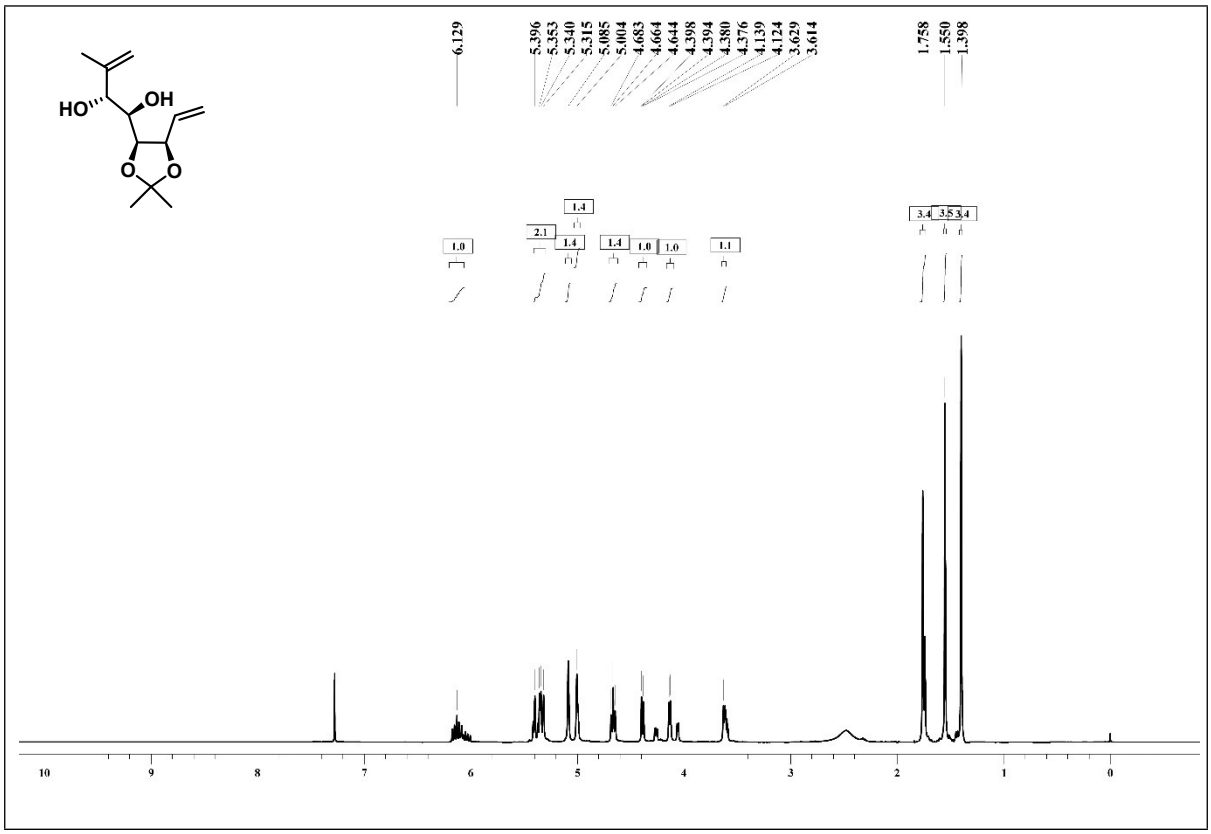
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound 10a & 10b**:**



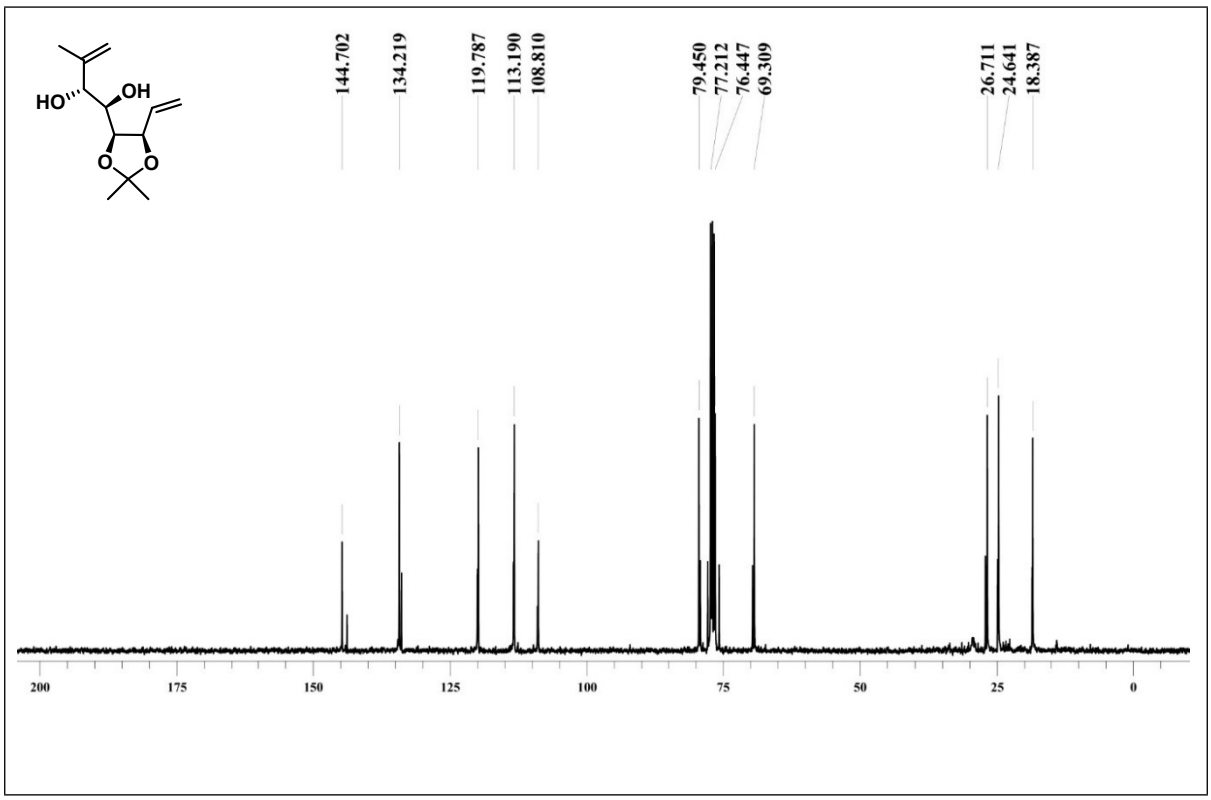
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 10a & 10b**:**



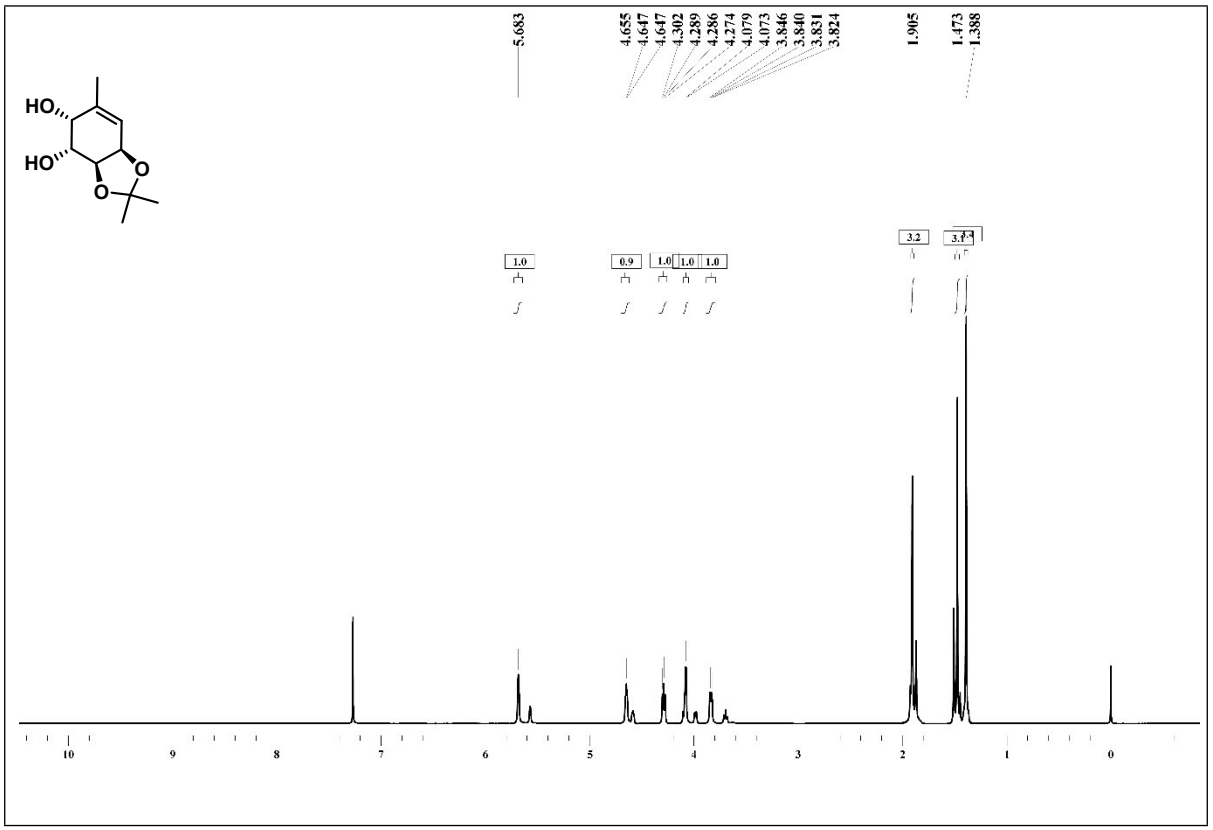
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound 13a & 13b:



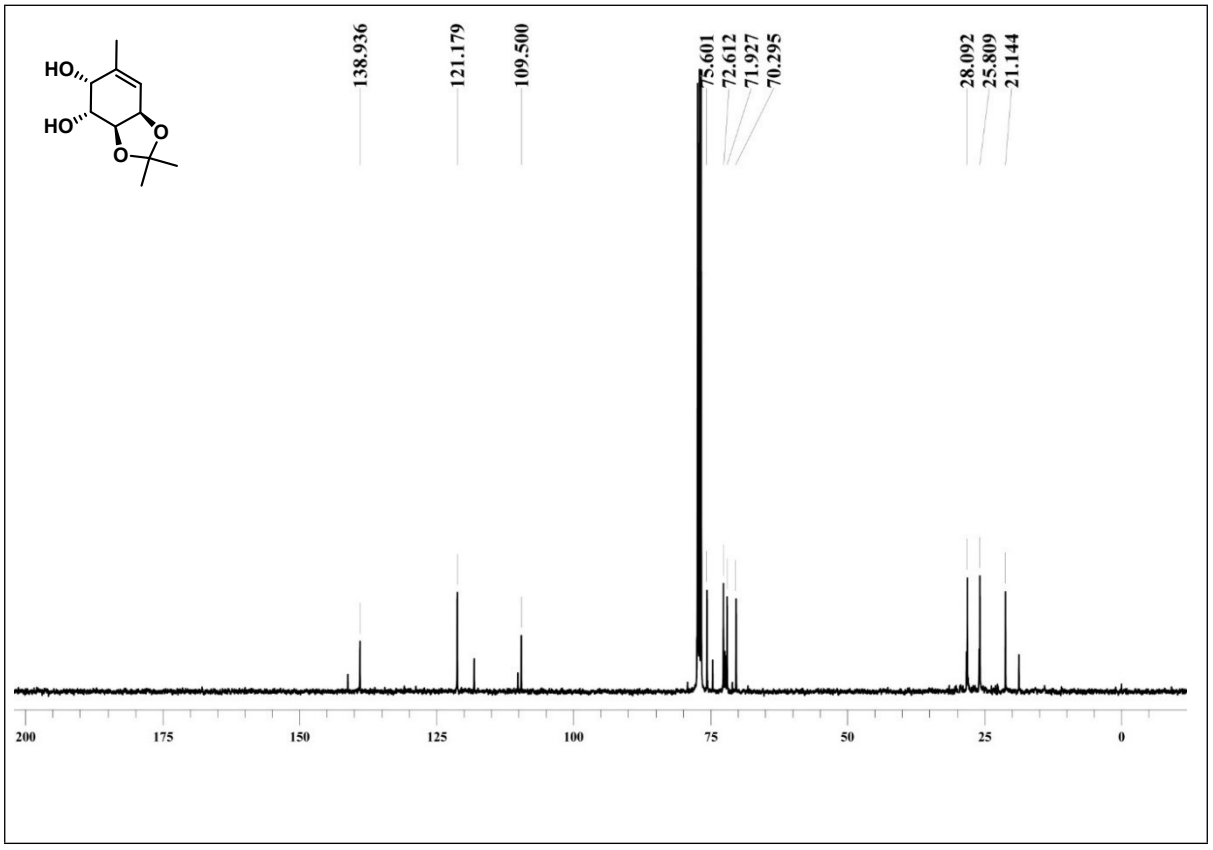
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 13a & 13b**:**



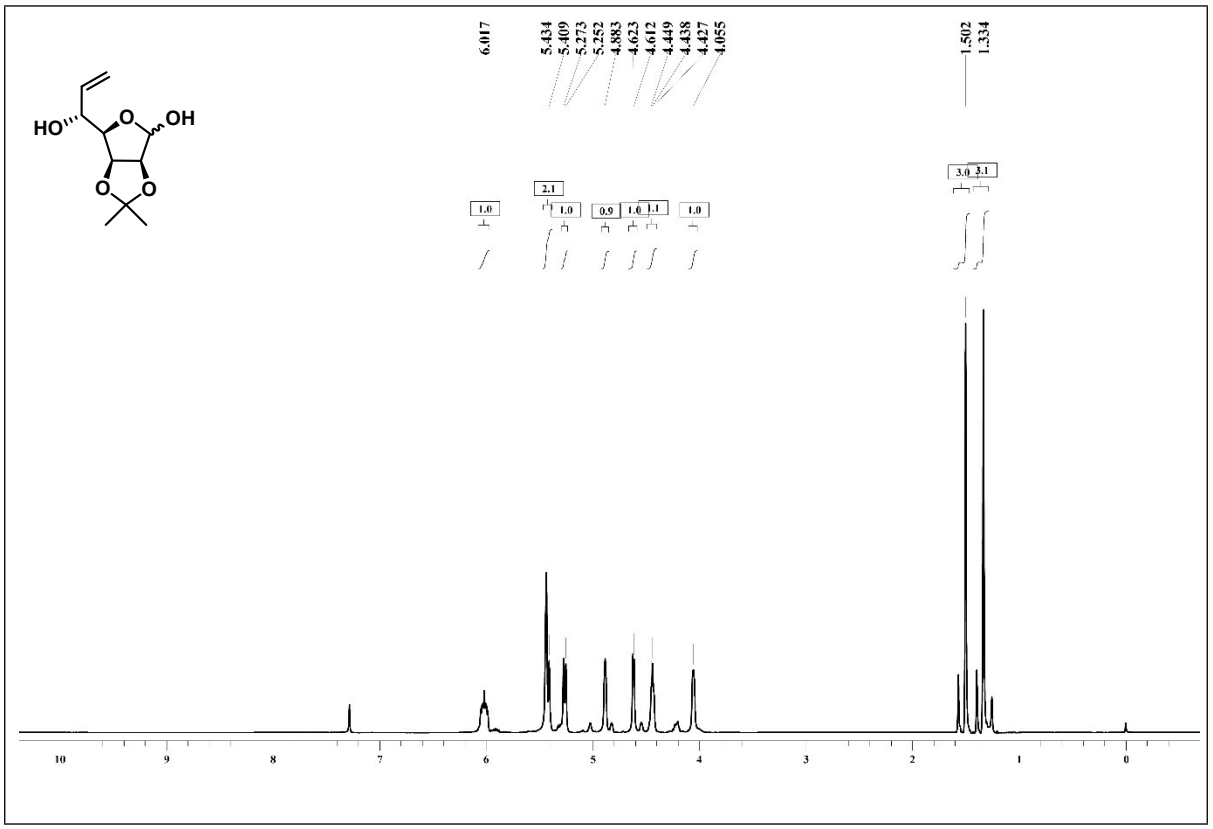
^{1}H NMR (500MHz, $CDCl_3$) spectrum of compound 14a & 14b**:**



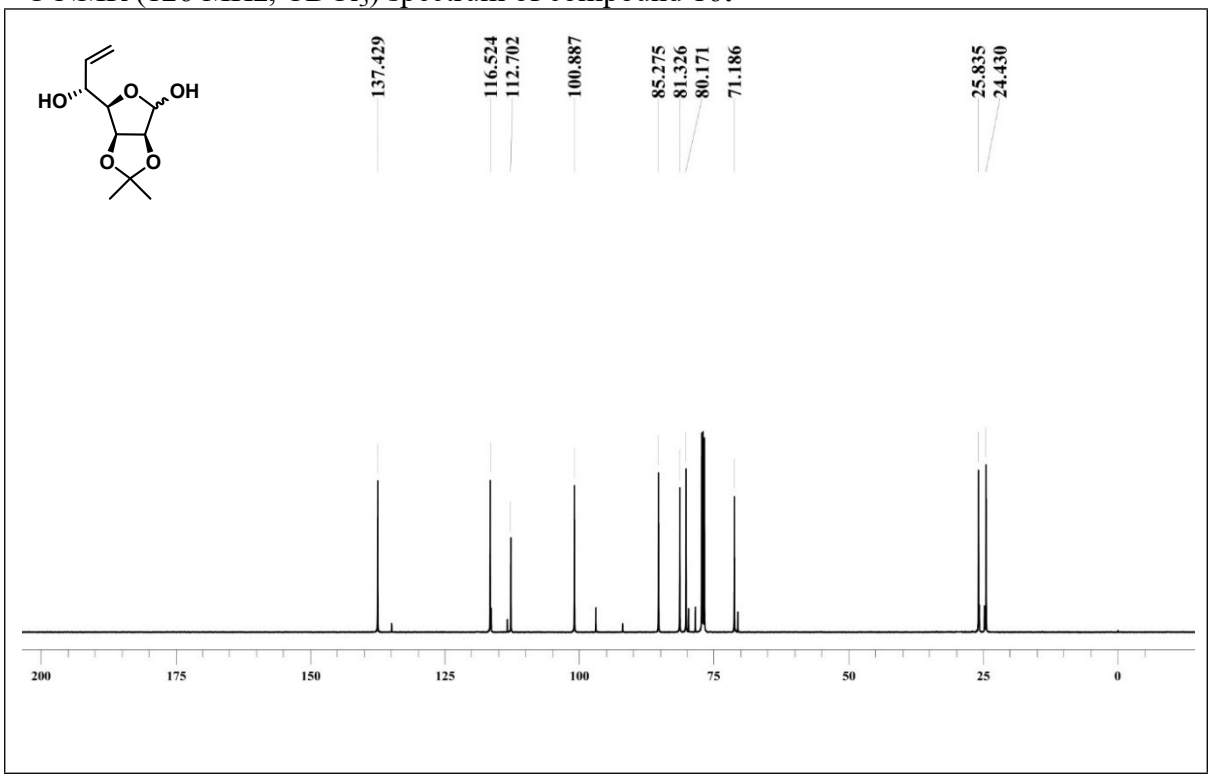
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 14a & 14b**:**



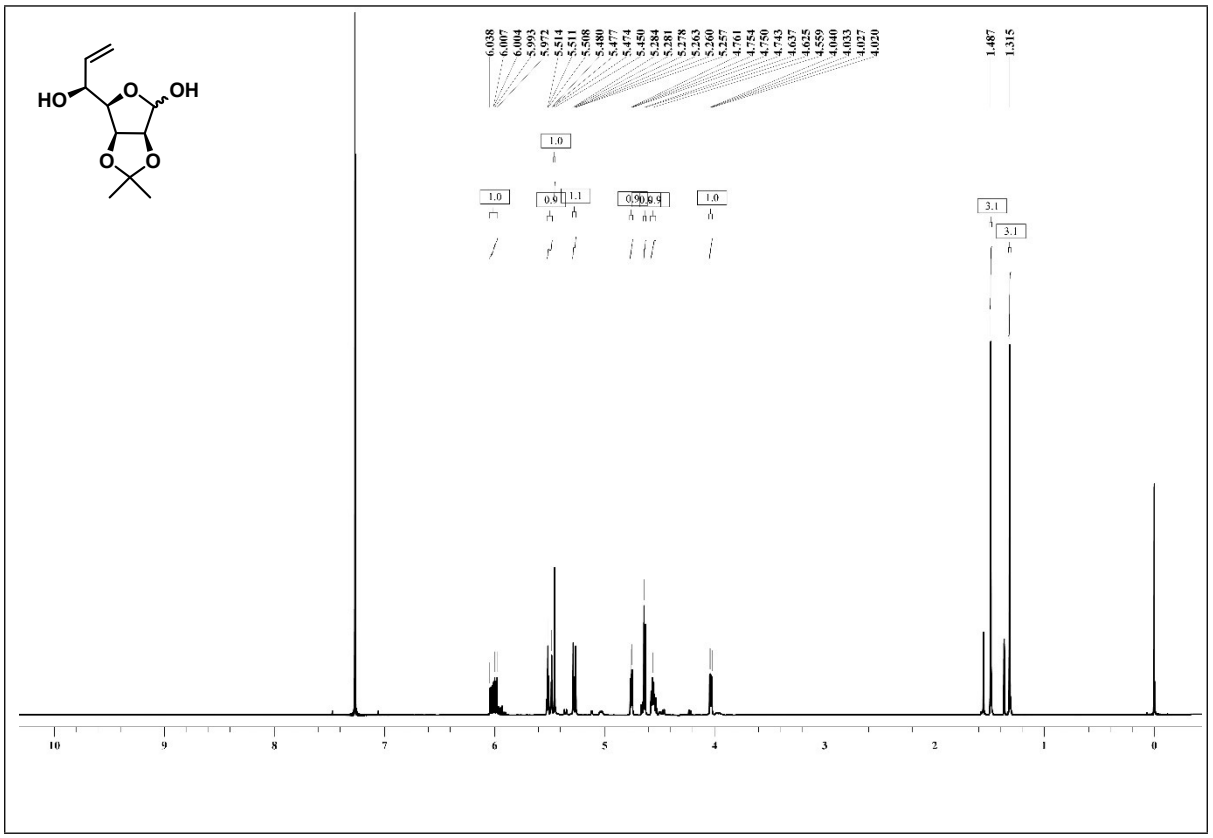
^{1}H NMR (500MHz, $CDCl_3$) spectrum of compound 16**:**



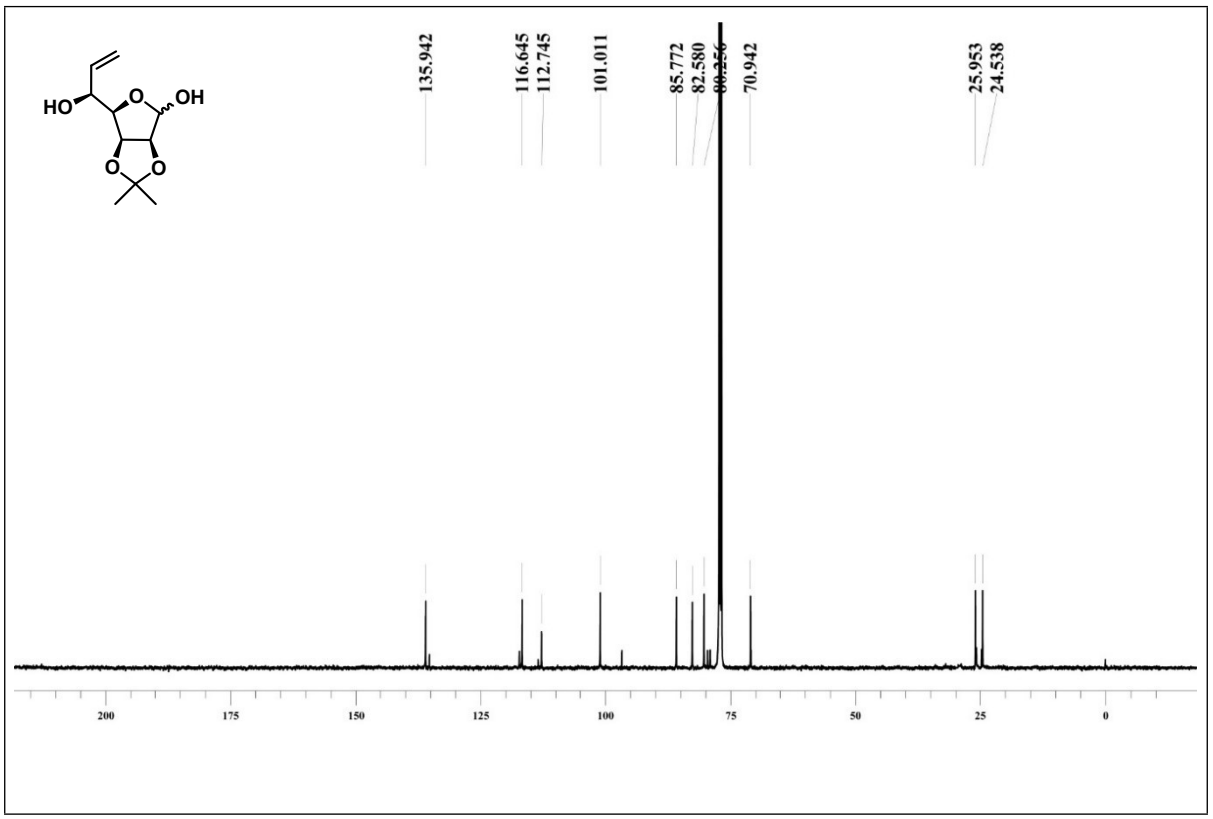
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 16**:**



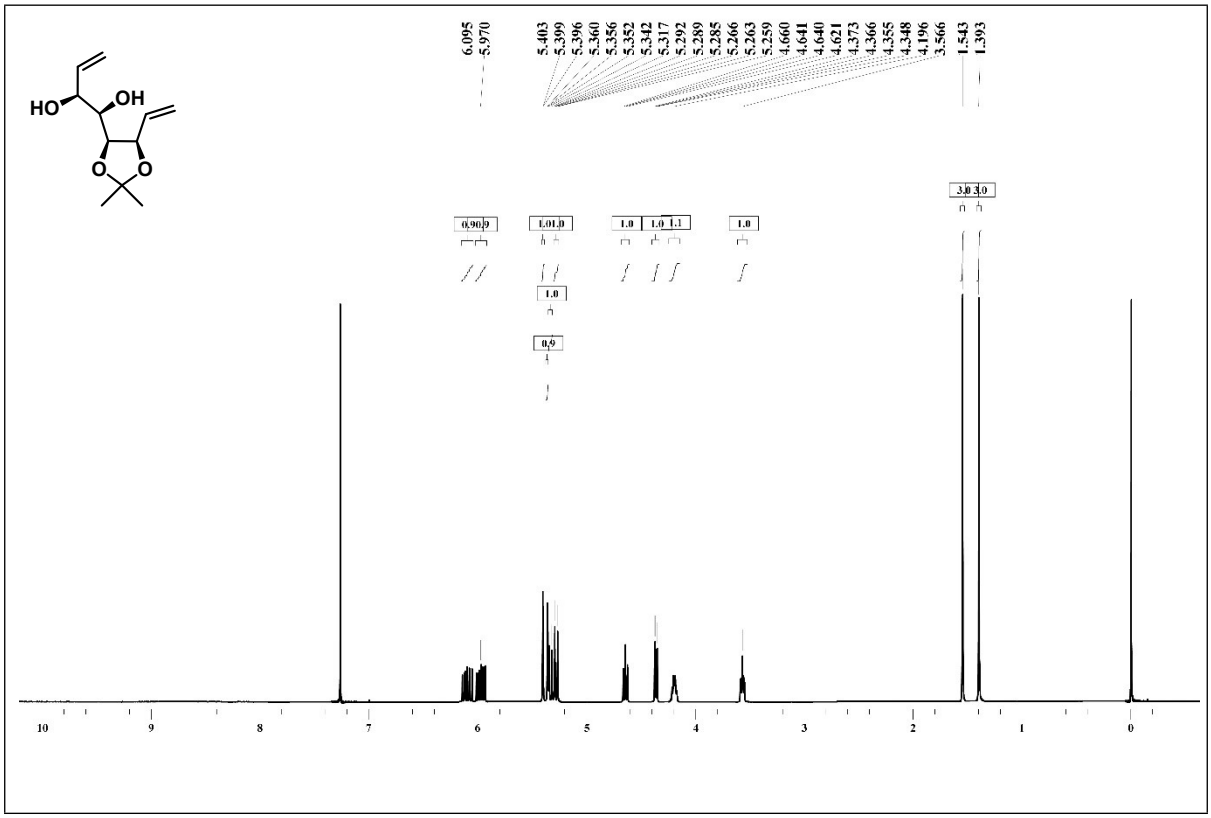
^{1}H NMR (500MHz, $CDCl_3$) spectrum of compound 17:



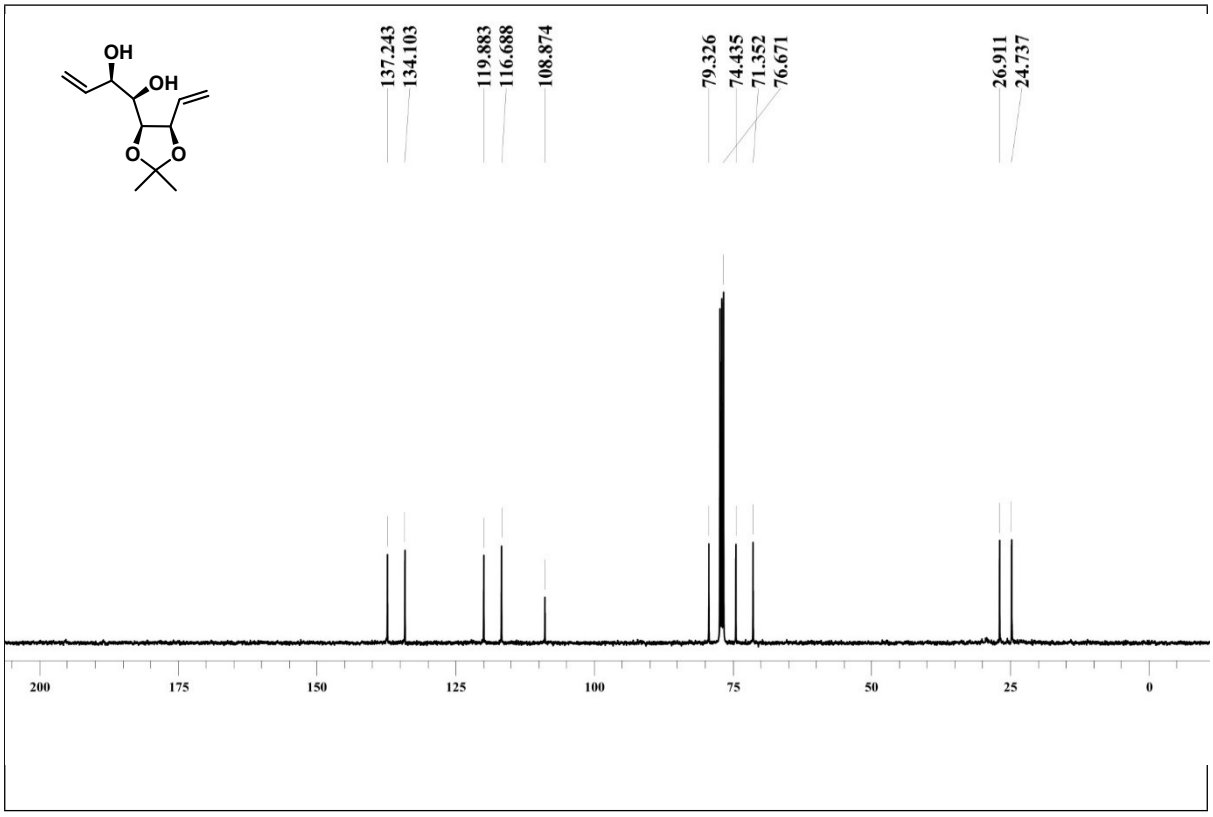
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 17**:**



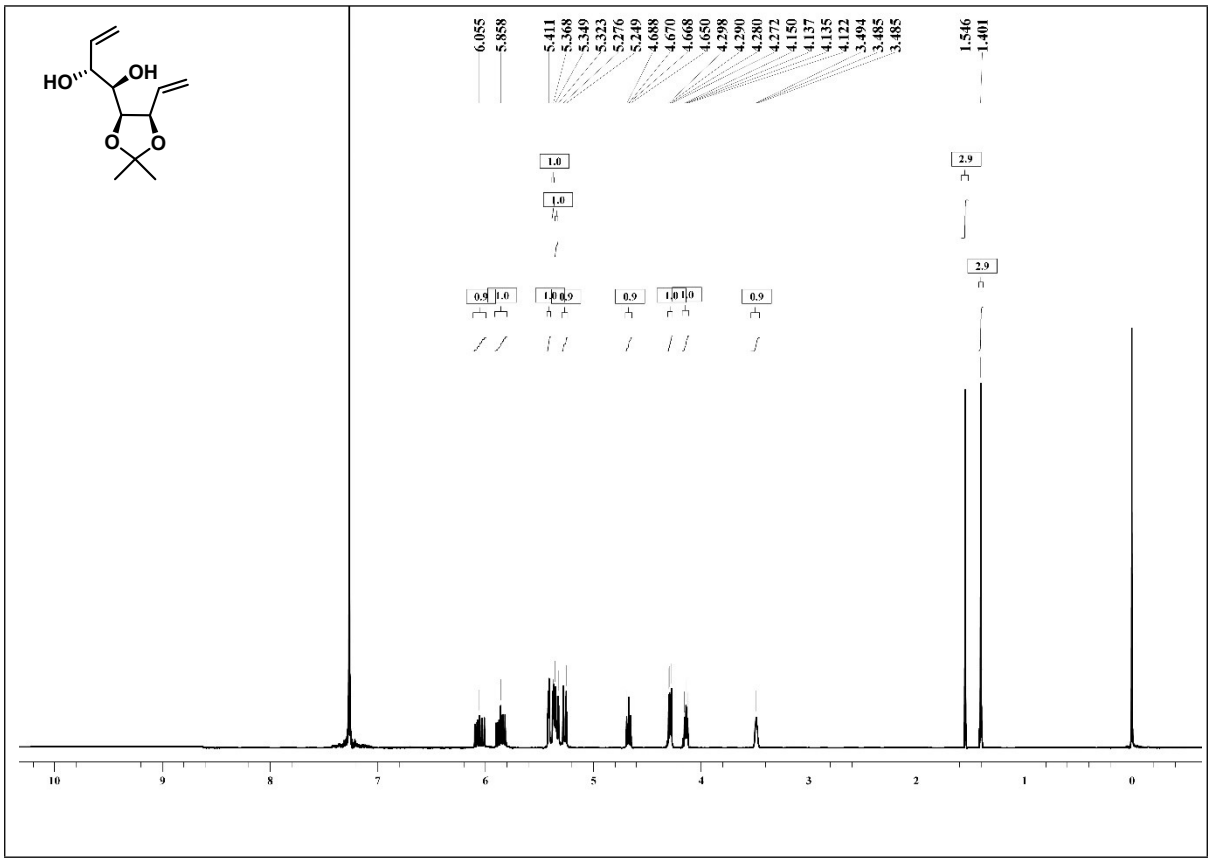
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound 18**:**



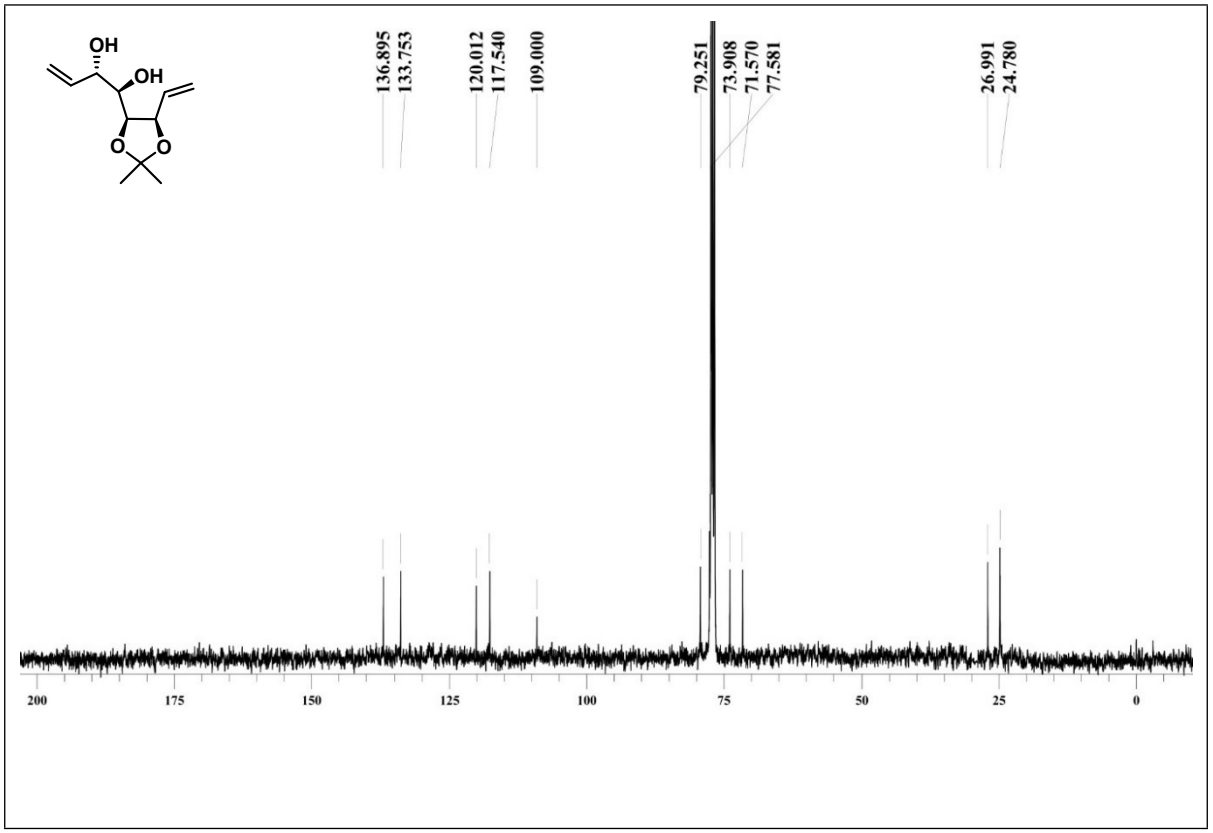
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 18**:**



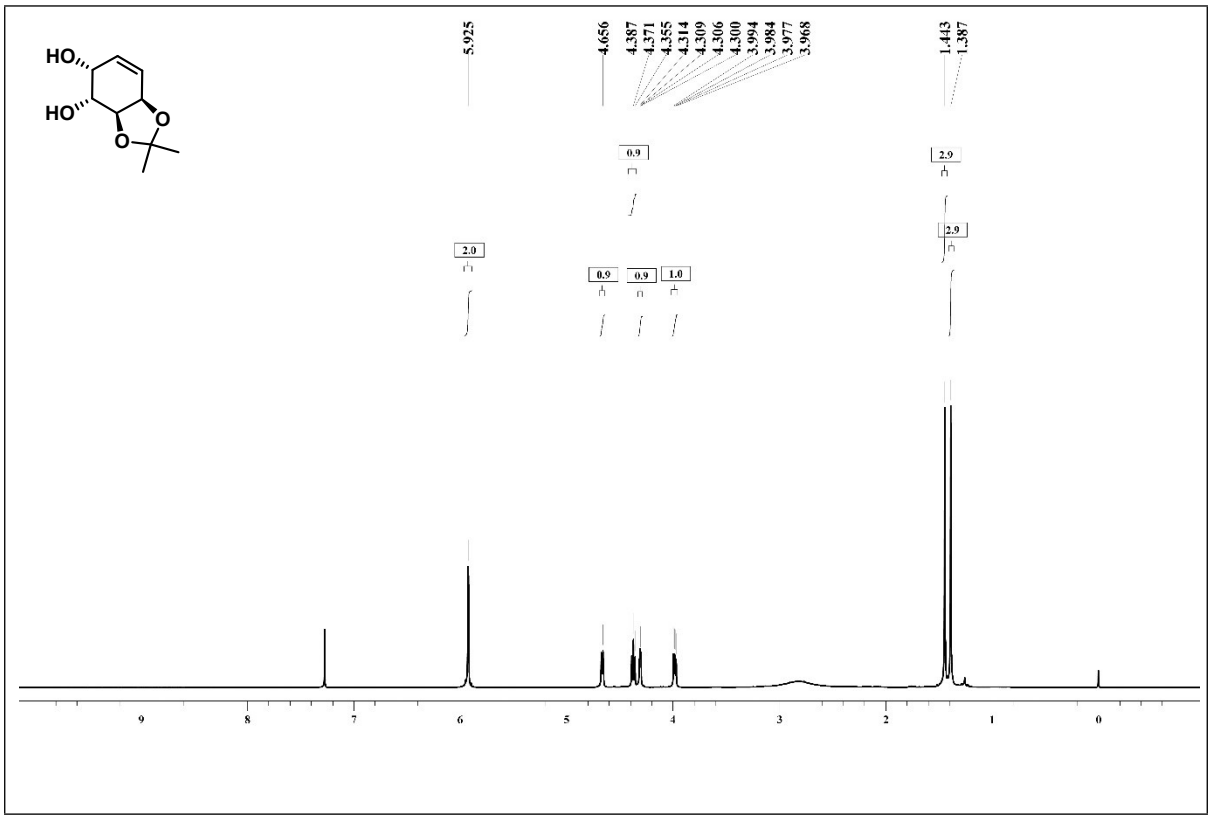
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound 19**:**



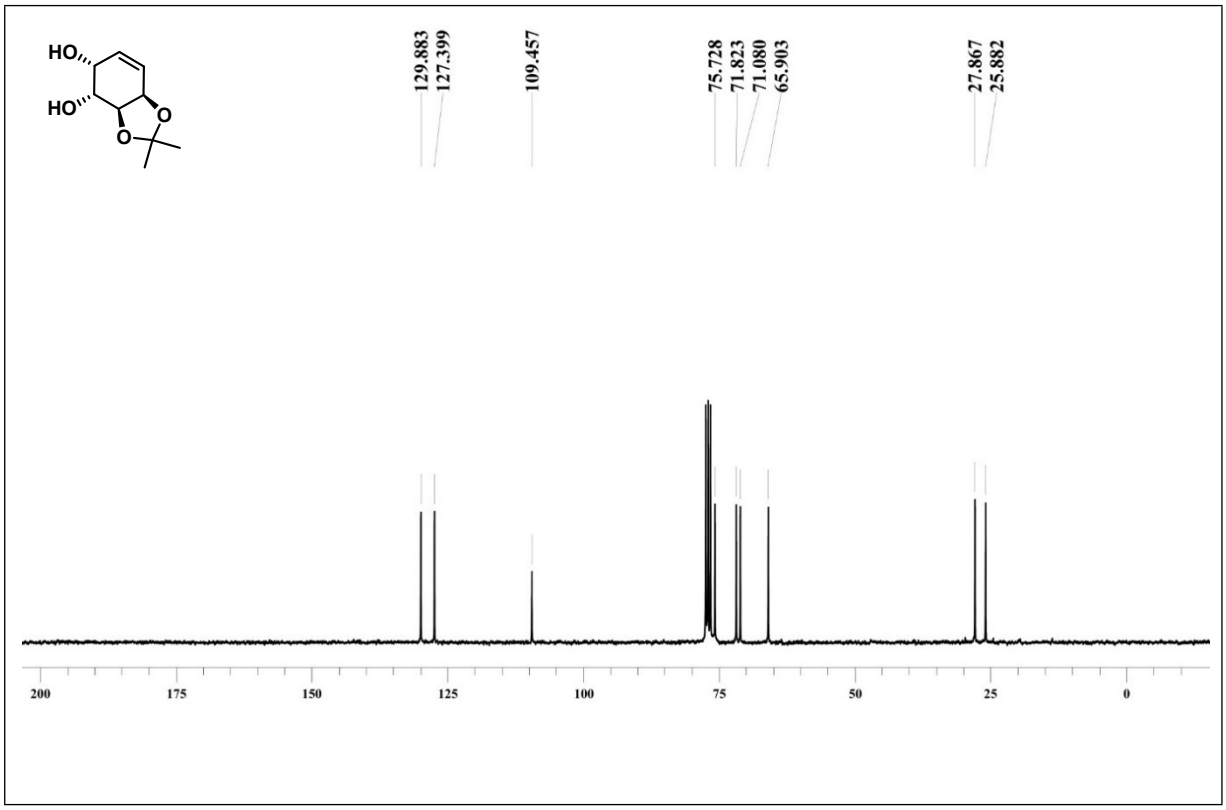
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 19**:**



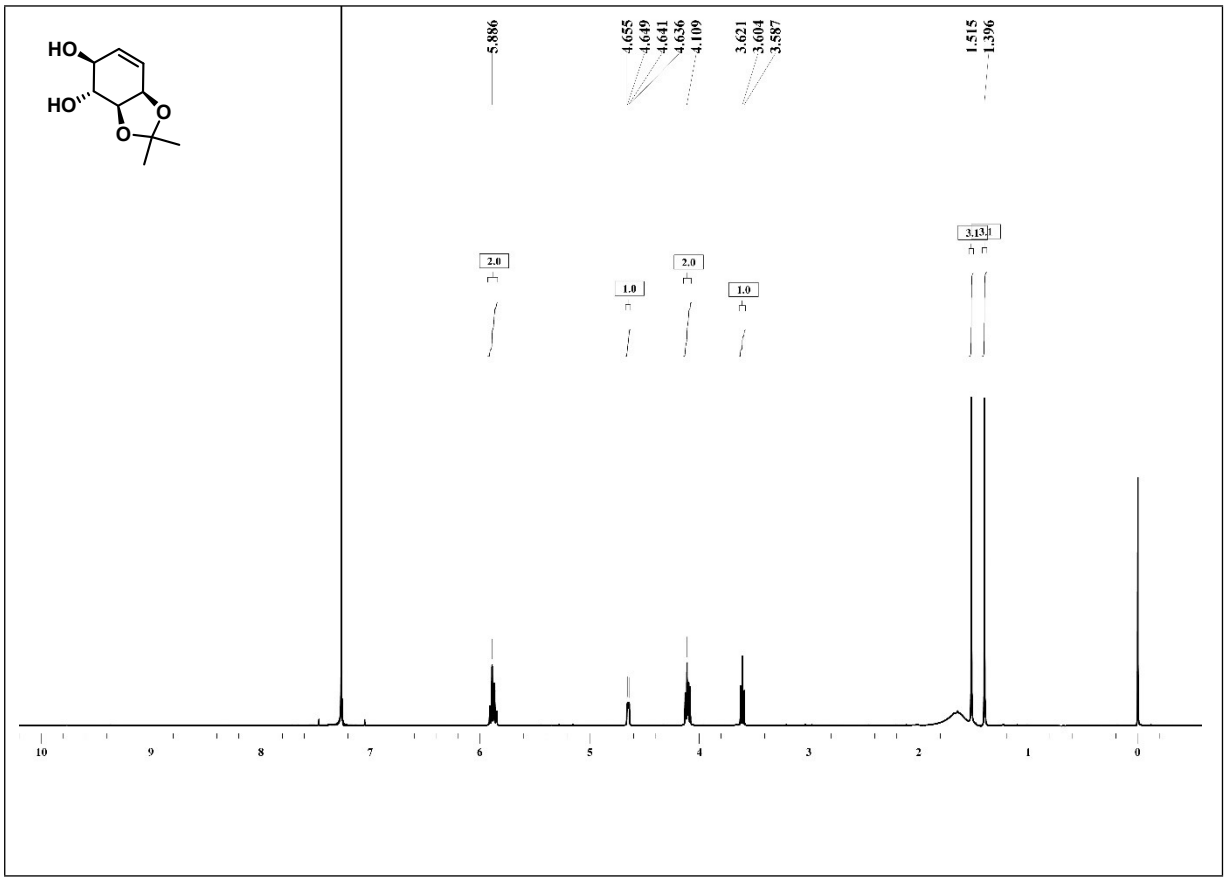
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound 20**:**



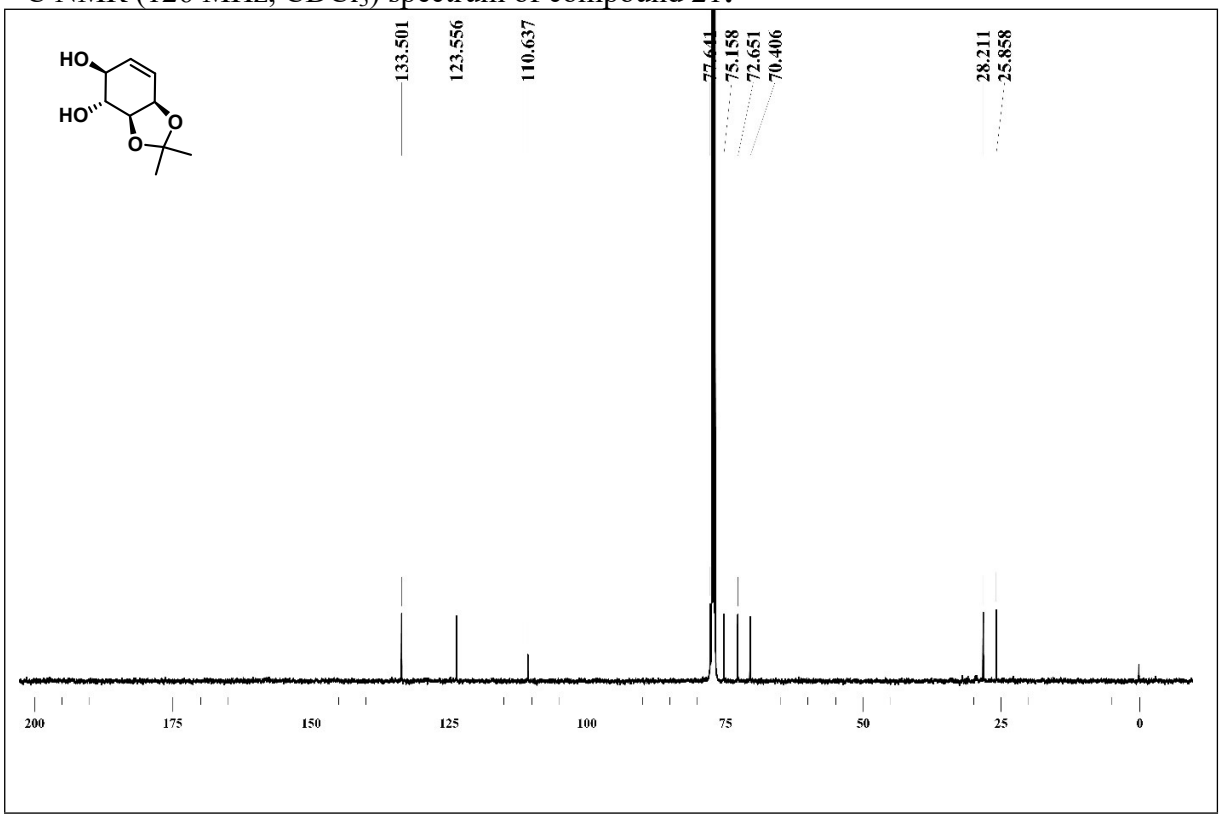
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound 20**:**



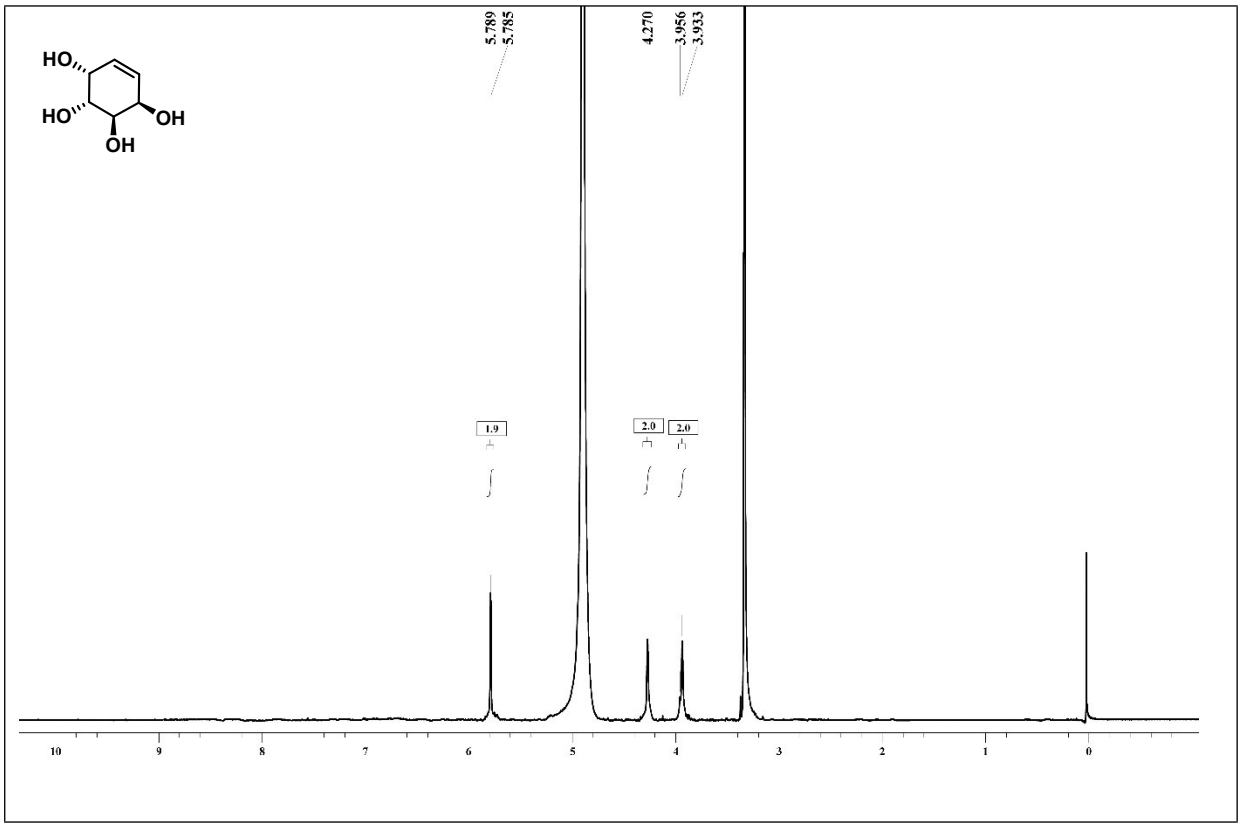
^{1}H NMR (500MHz, $CDCl_3$) spectrum of compound 21:



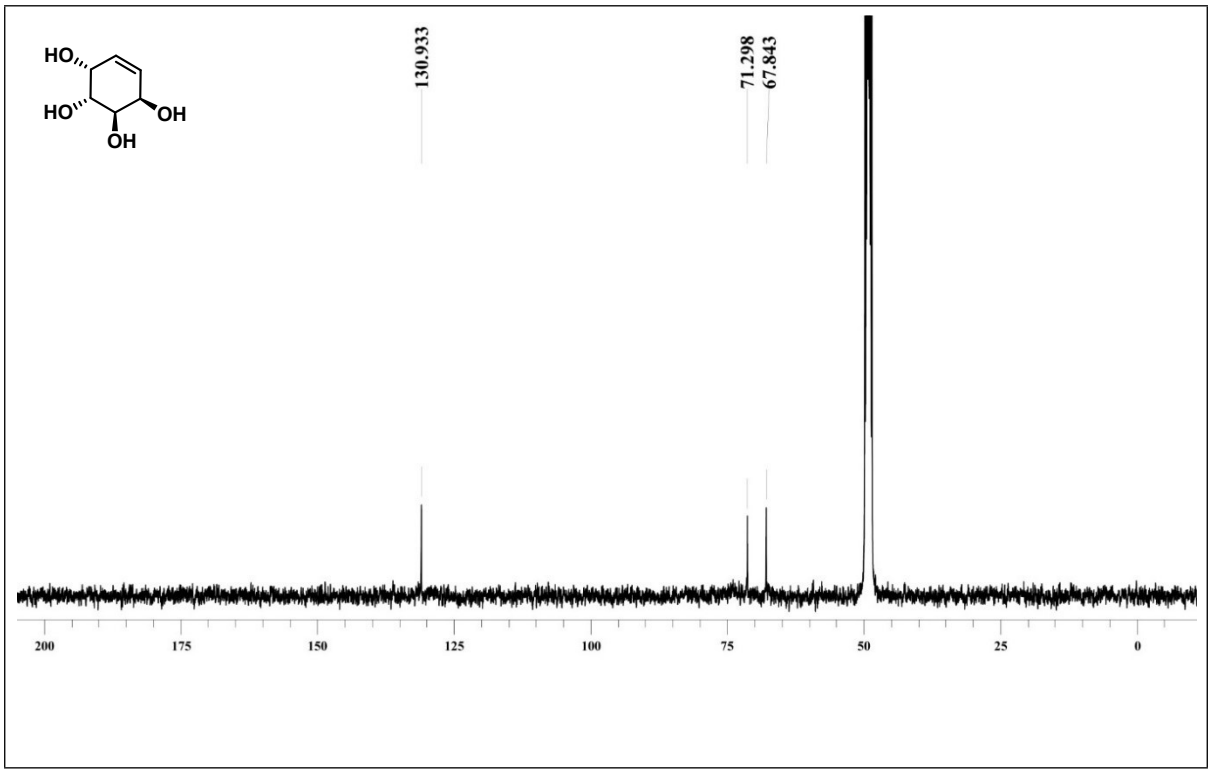
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 21:



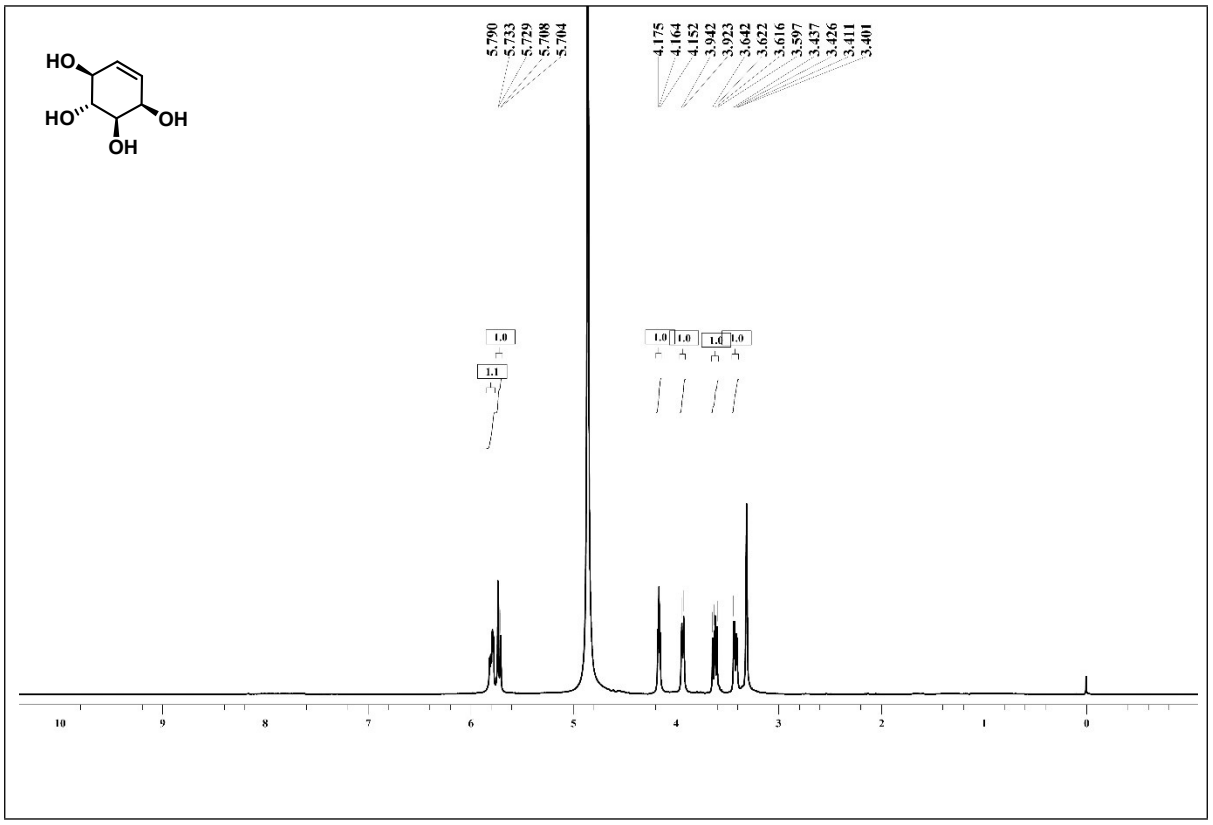
^{1}H NMR (400MHz, CD_3OD) spectrum of compound (–)-conduritol E**:**



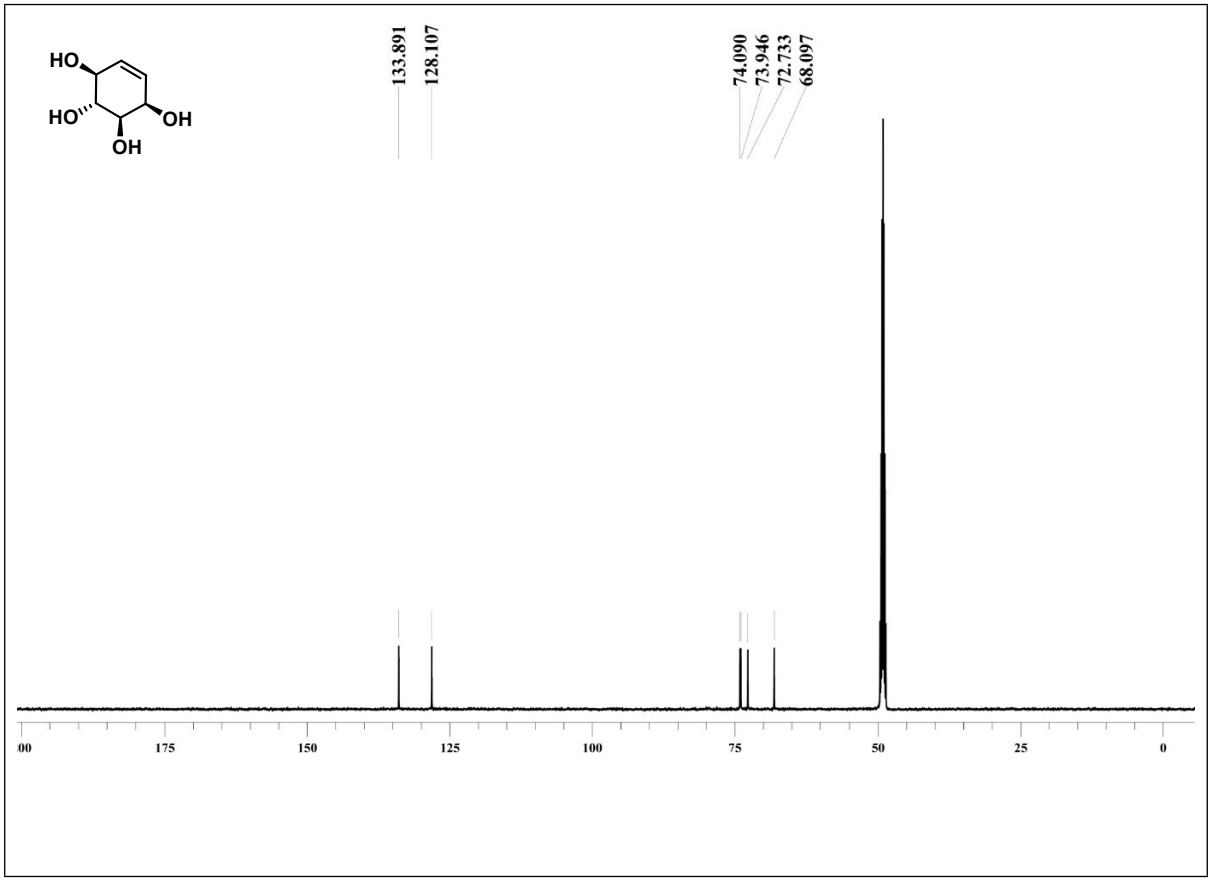
^{13}C NMR (101 MHz, CD_3OD) spectrum of compound (–)-conduritol E**:**



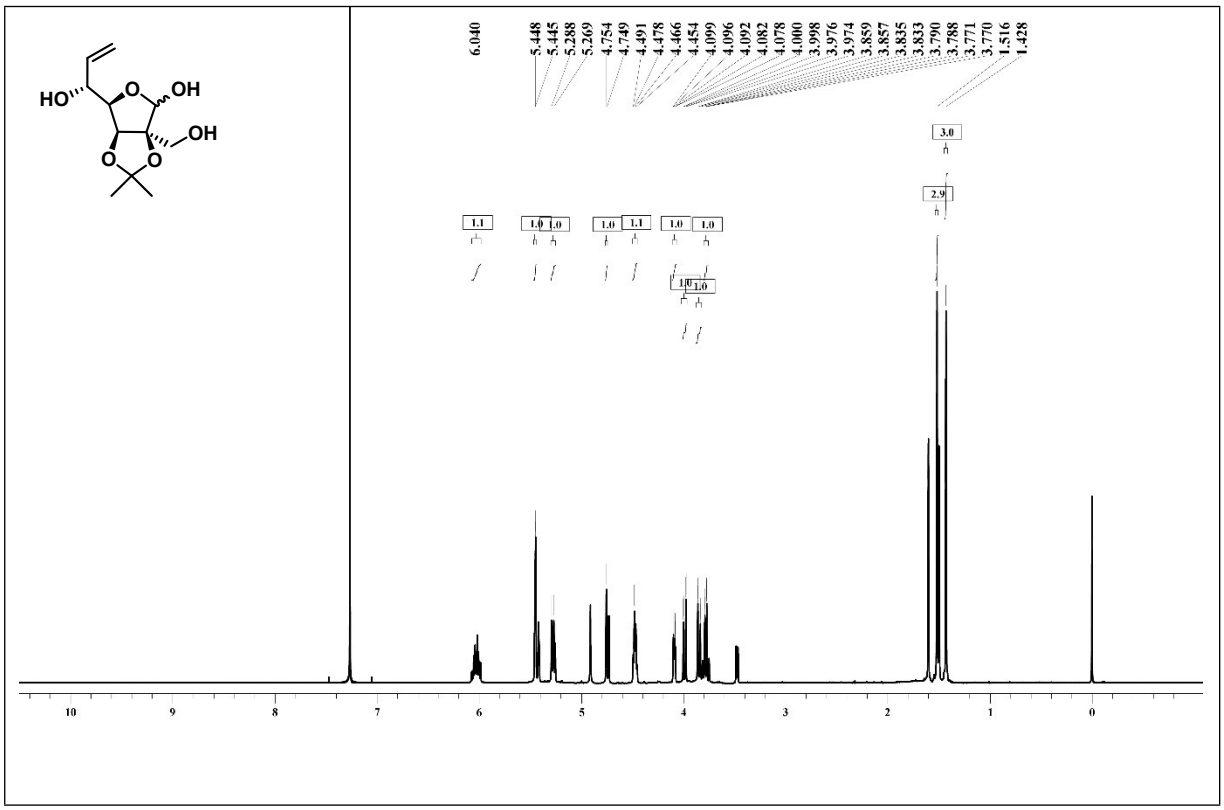
^{1}H NMR (400MHz, CD_3OD) spectrum of compound (–)-conduritol F**:**



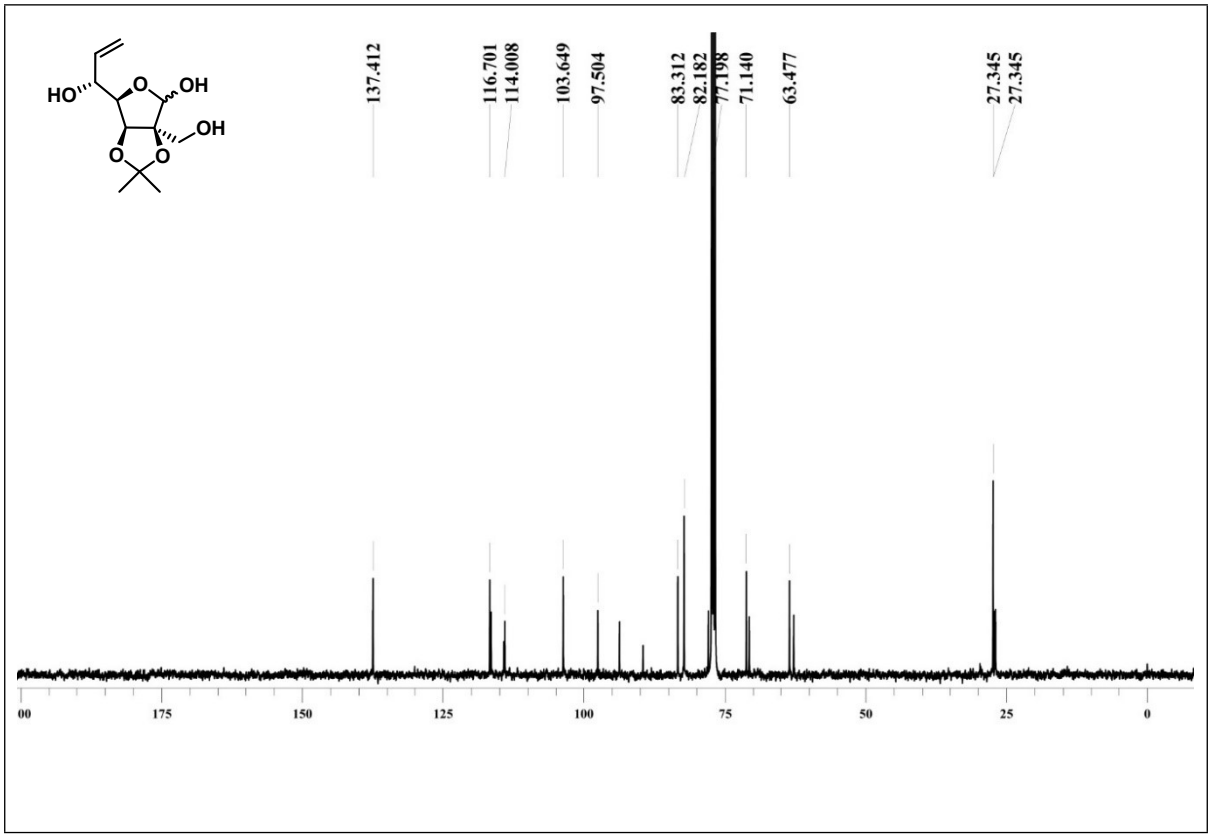
^{13}C NMR (126 MHz, CD_3OD) spectrum of compound (–)-conduritol F**:**



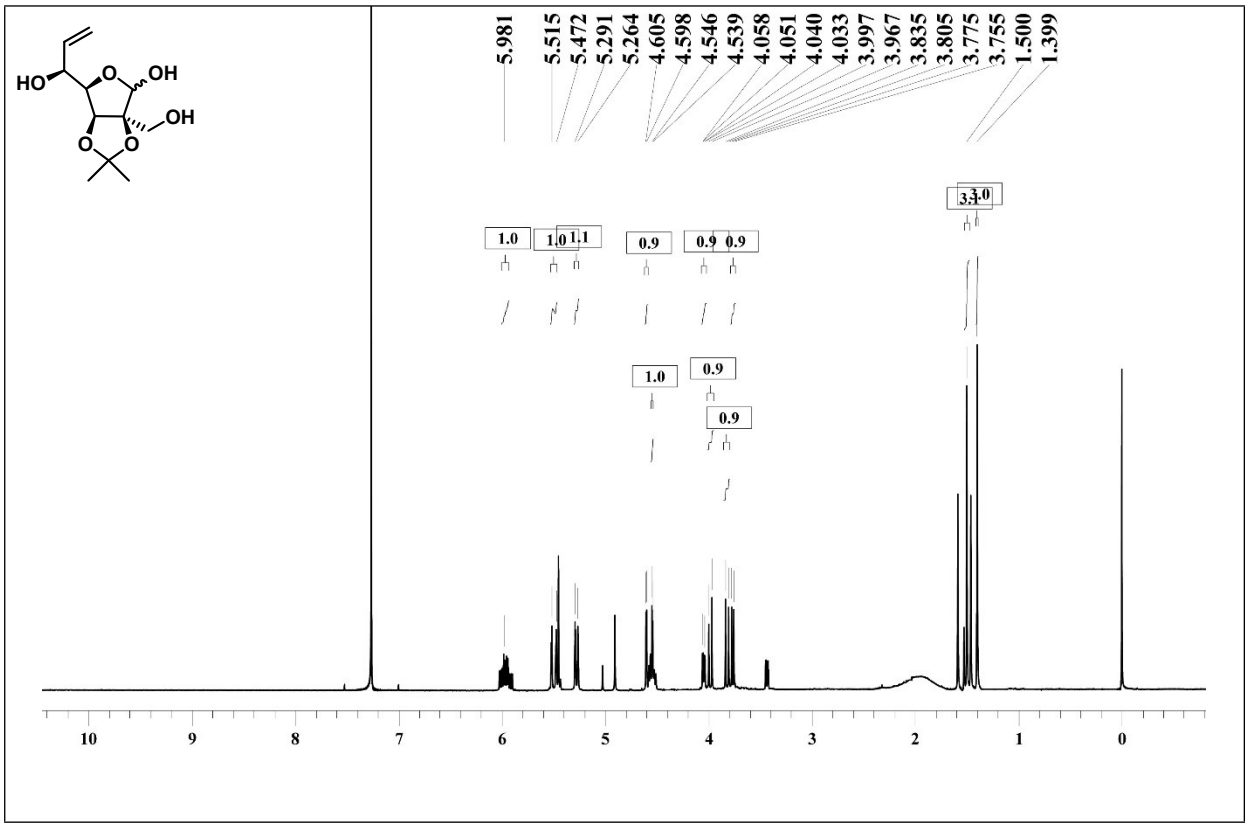
^{1}H NMR (500MHz, $CDCl_3$) spectrum of compound 22**:**



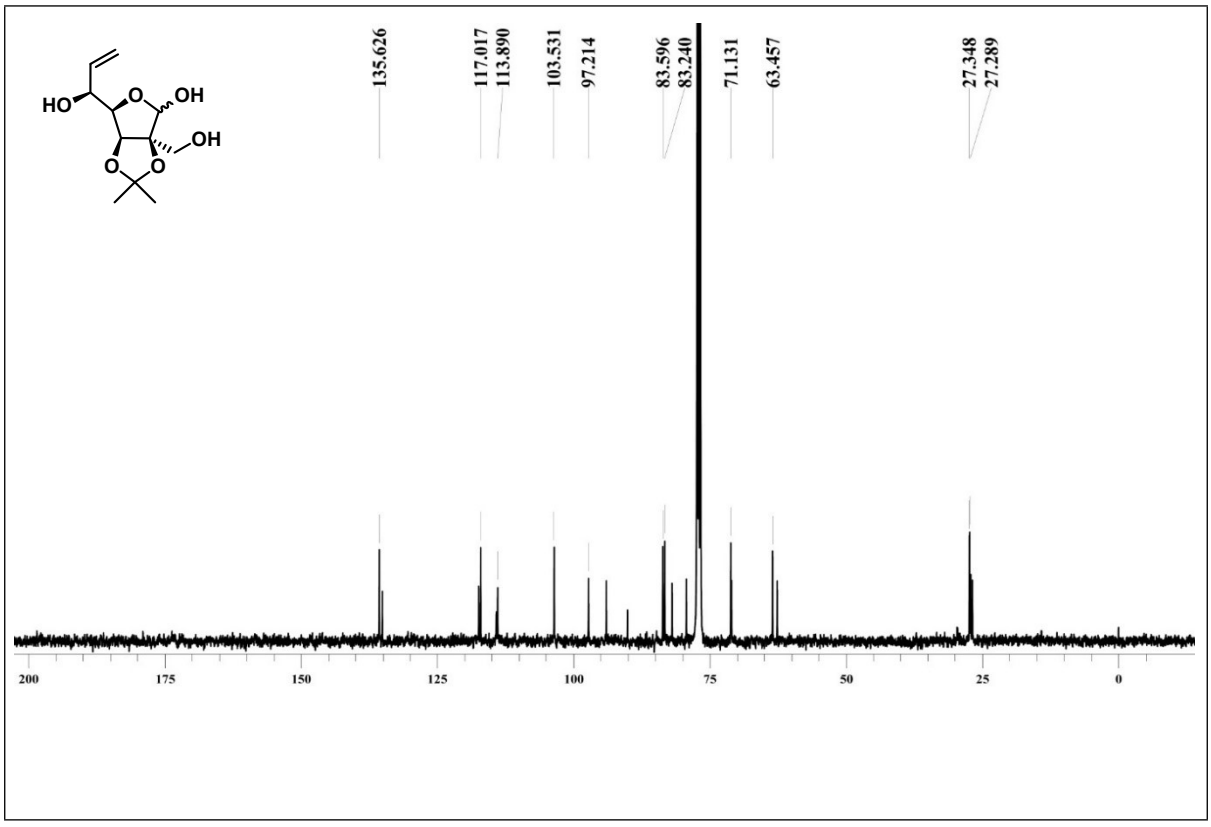
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 22**:**



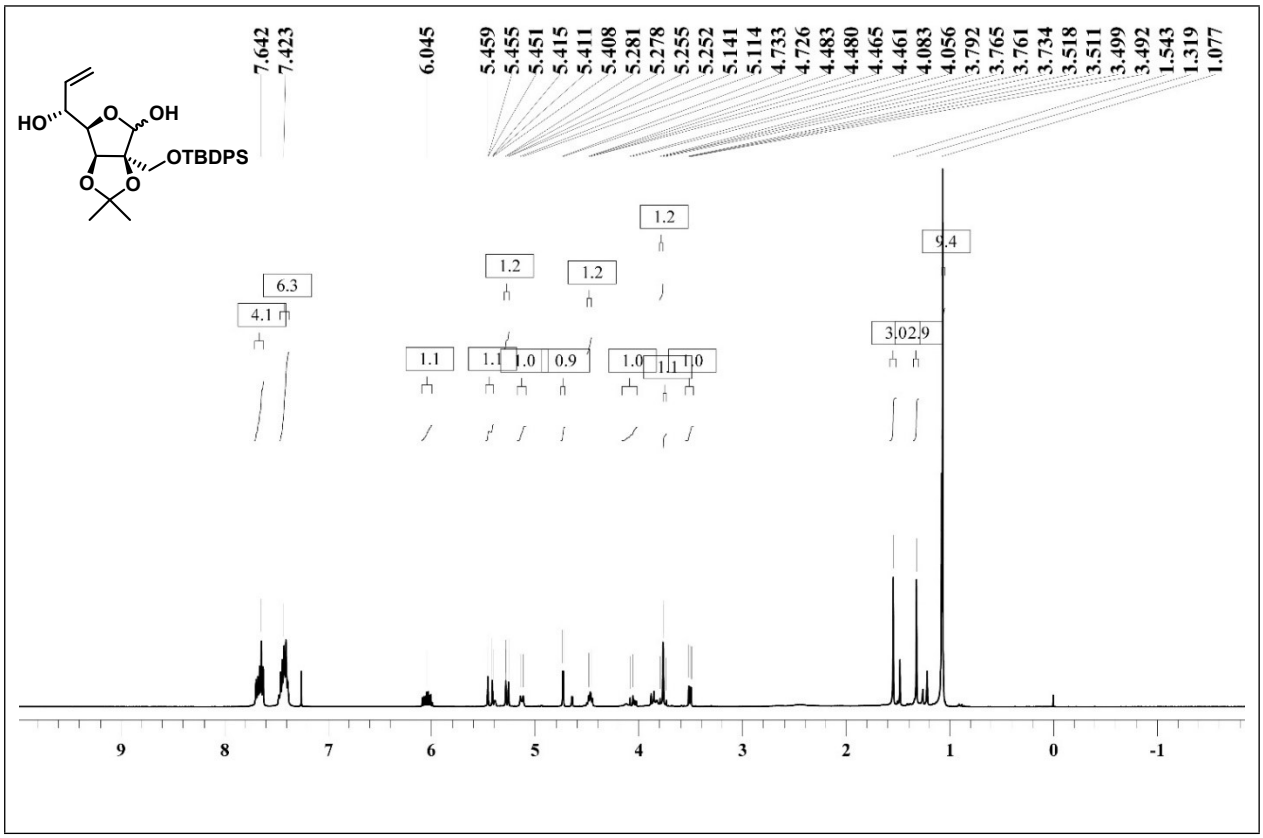
^{1}H NMR (500MHz, $CDCl_3$) spectrum of compound 23:



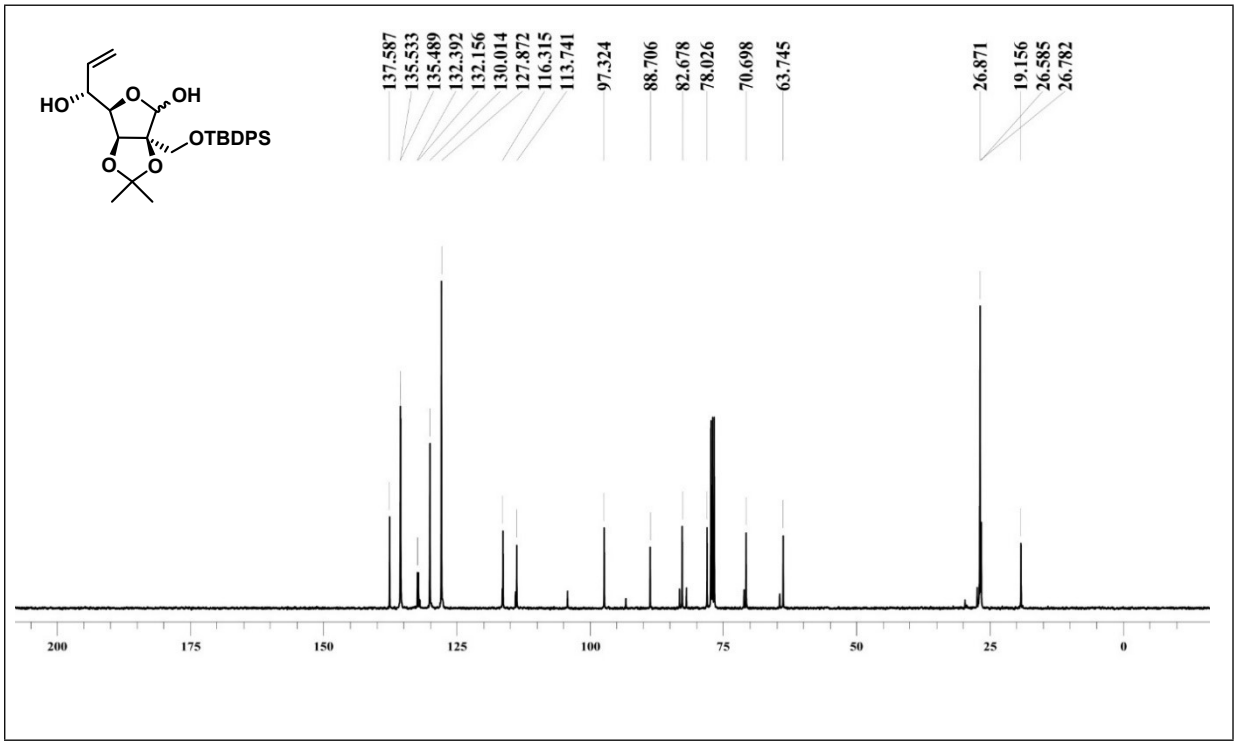
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 23:



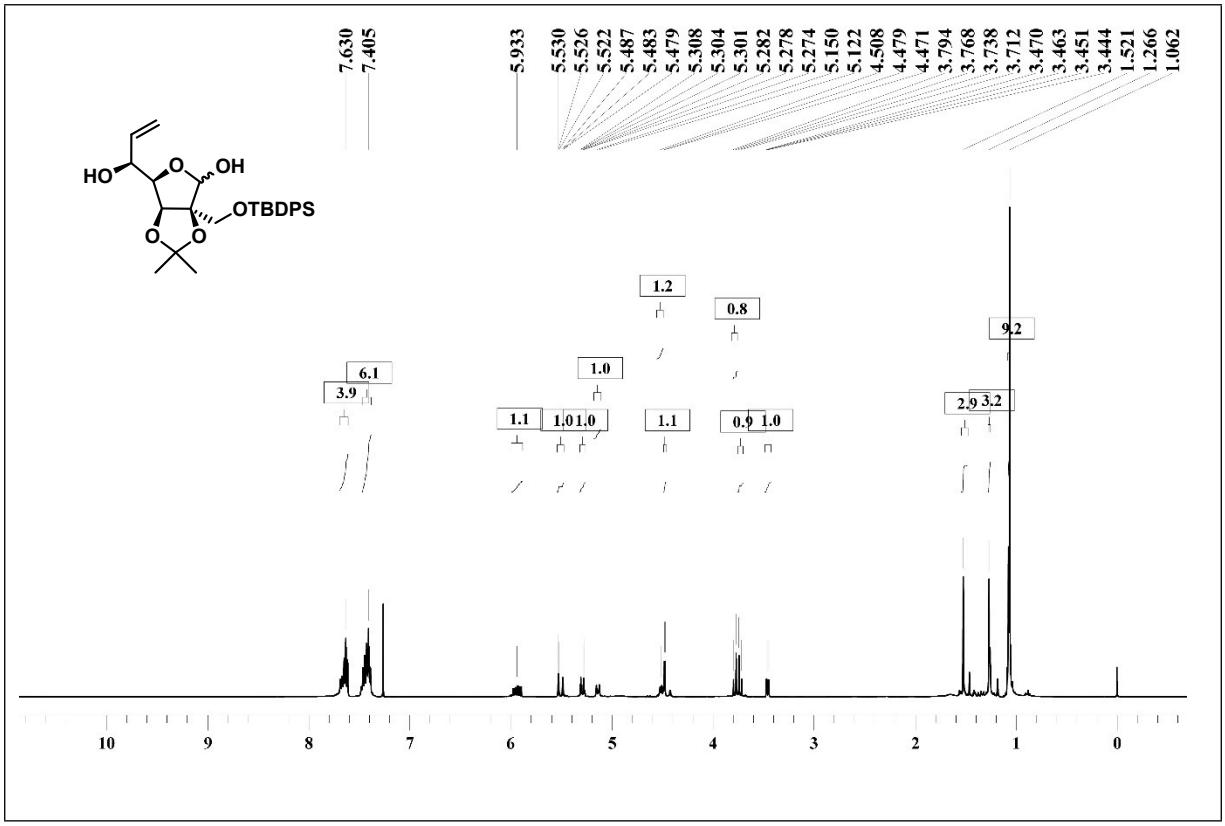
^{1}H NMR (500MHz, $CDCl_3$) spectrum of compound 24**:**



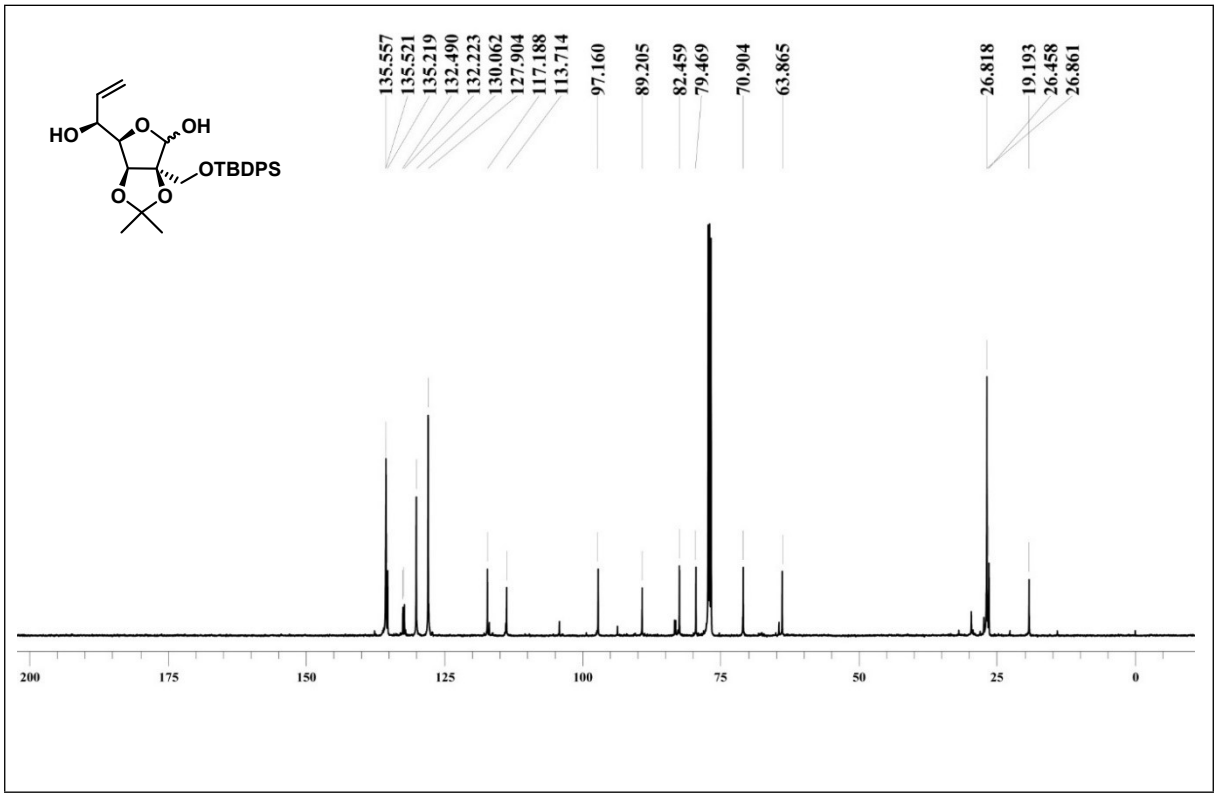
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 24**:**



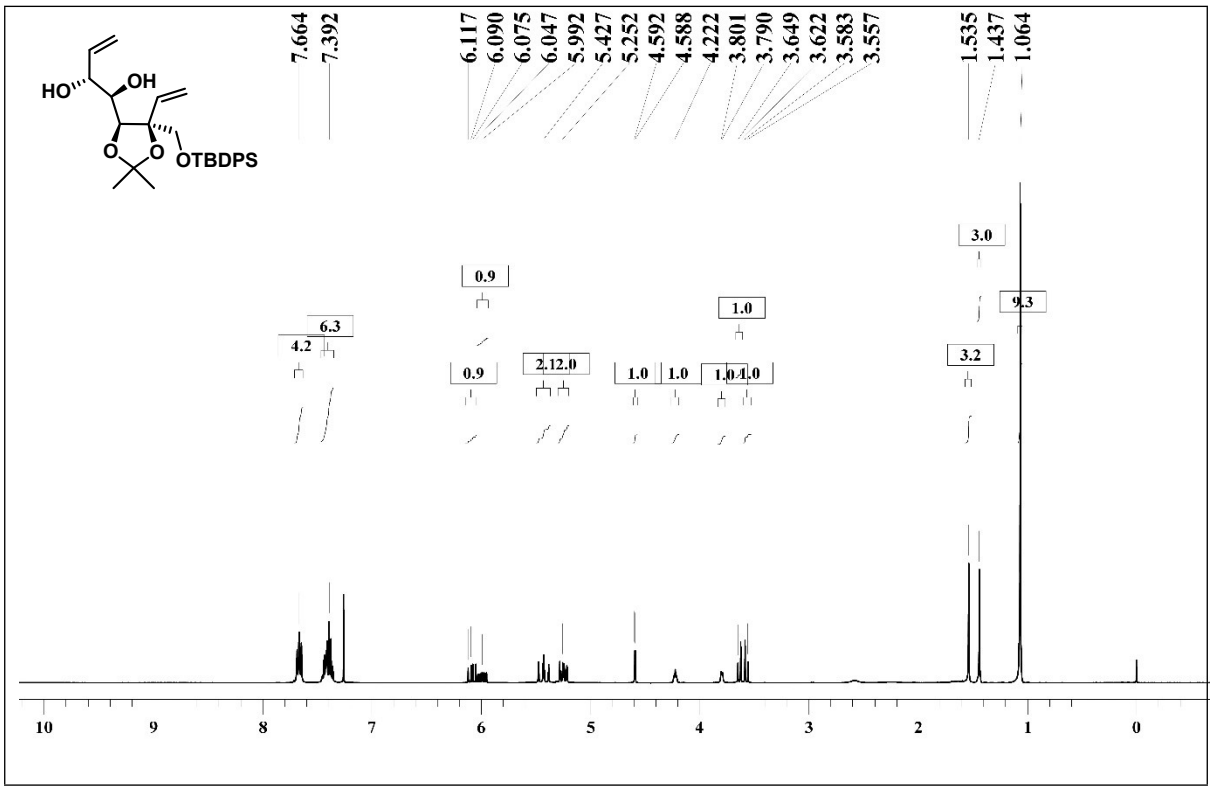
^{1}H NMR (500MHz, $CDCl_3$) spectrum of compound 25**:**



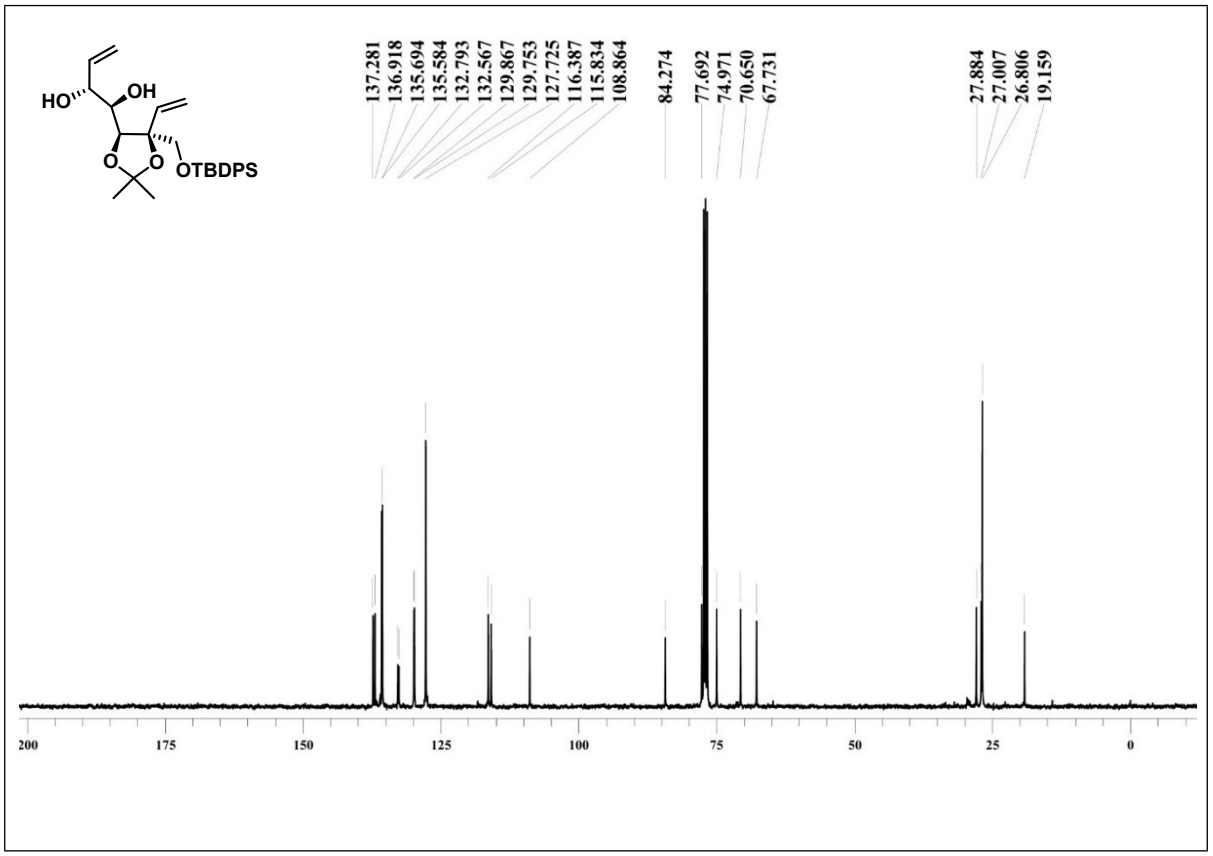
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 25:



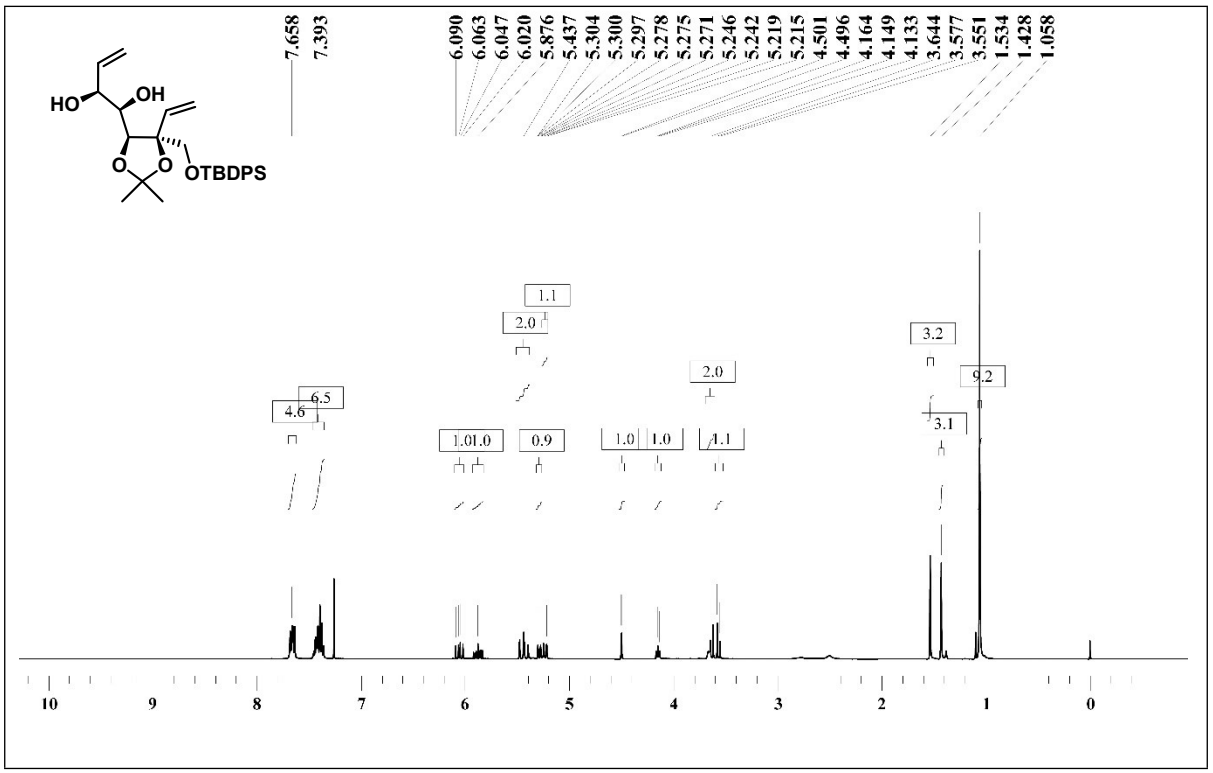
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 26**:**



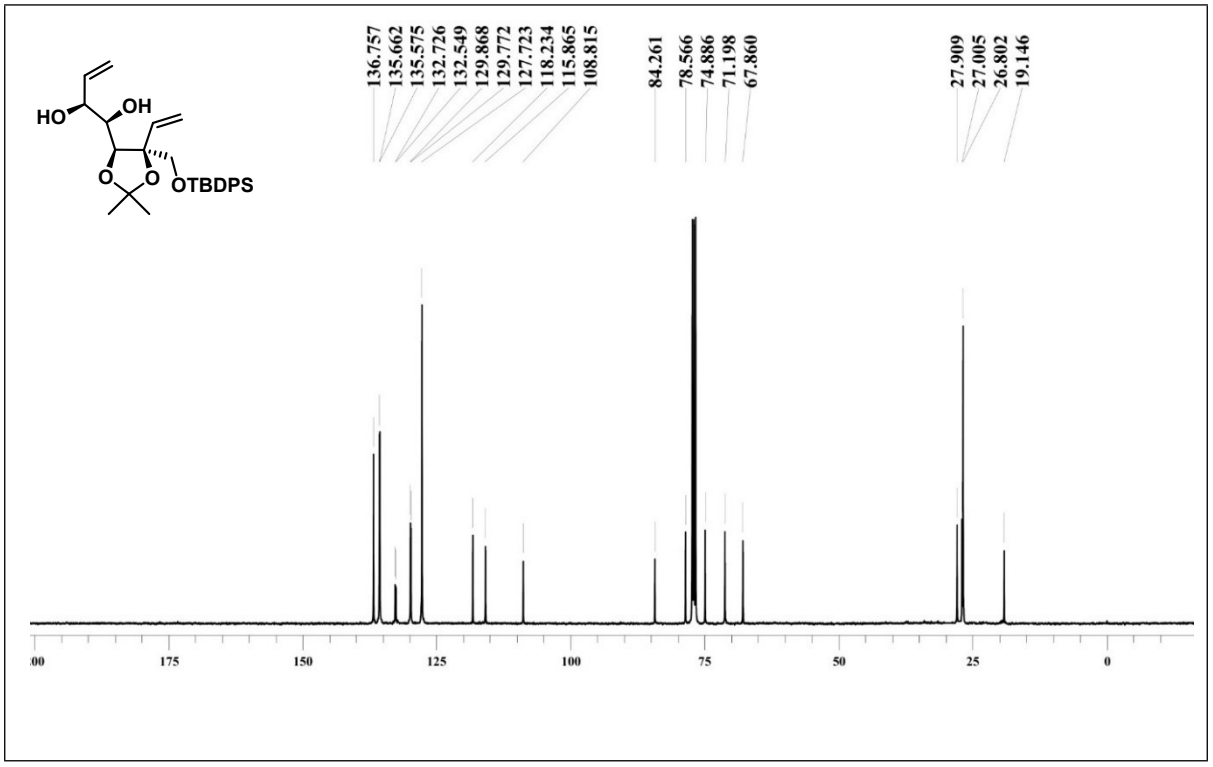
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 26:



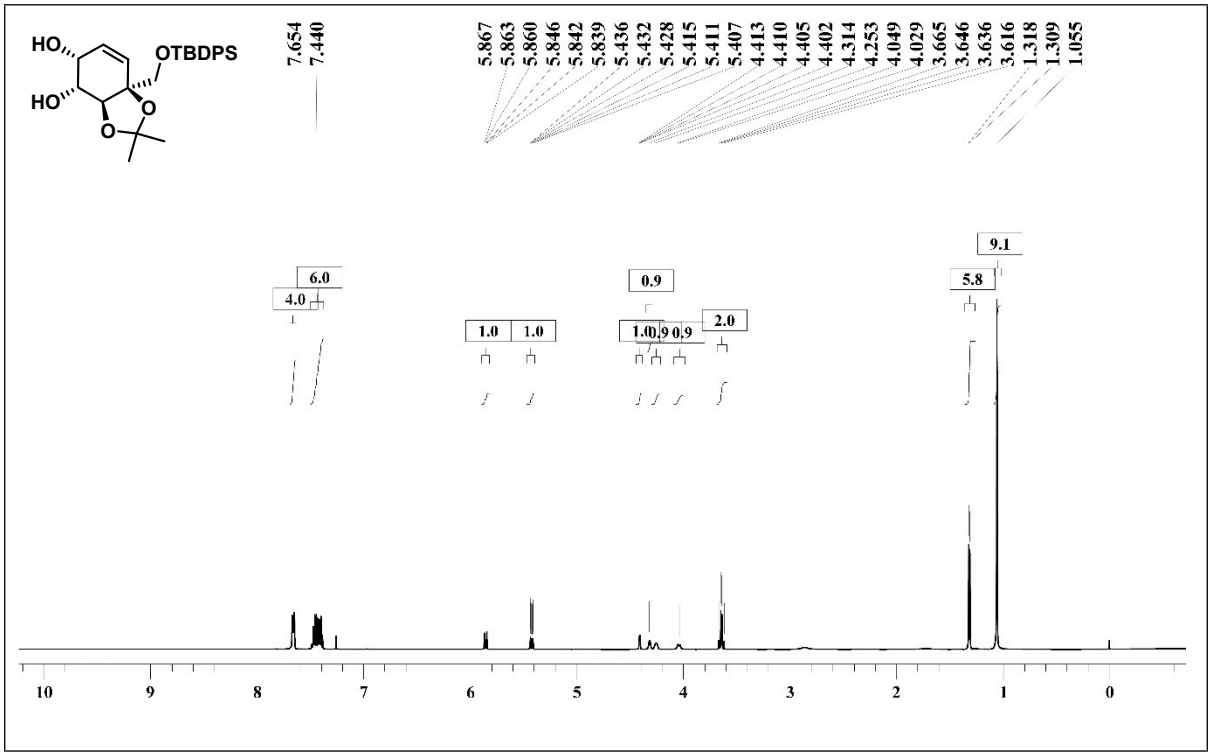
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound 27**:**



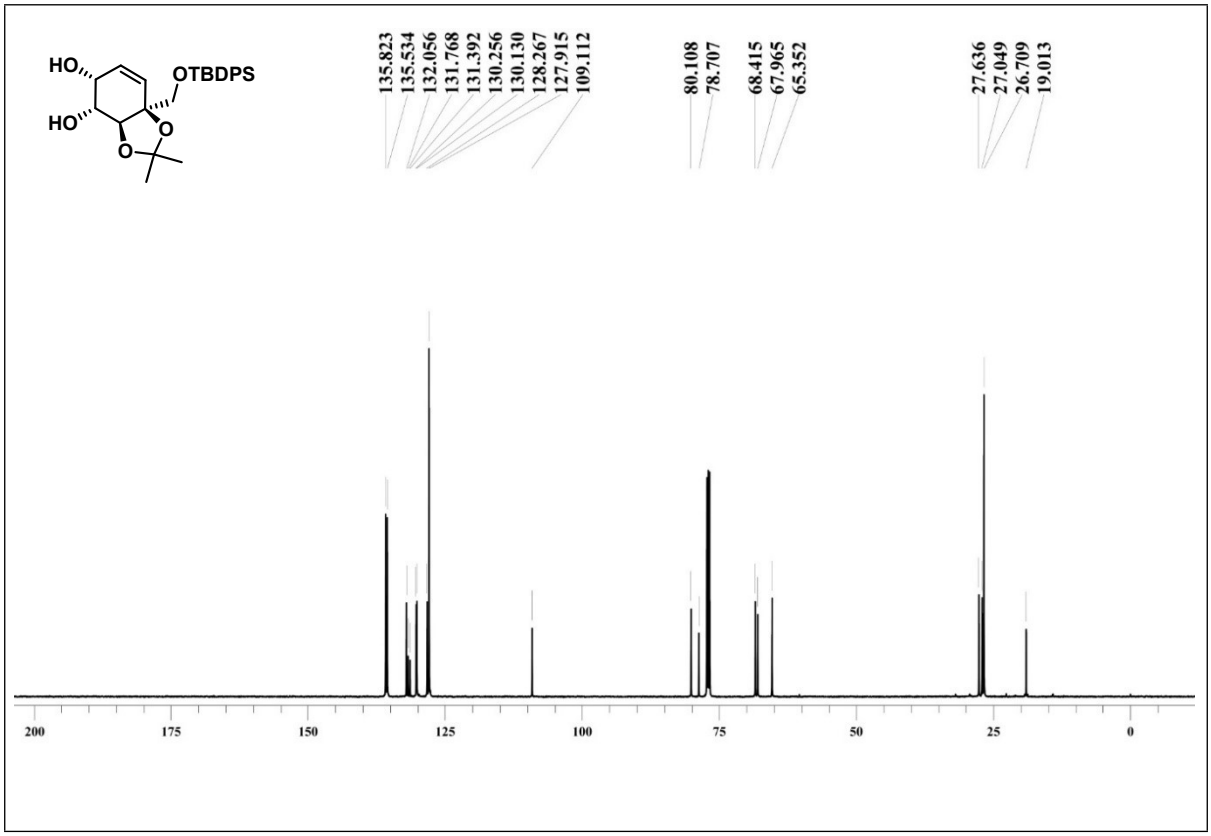
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 27:



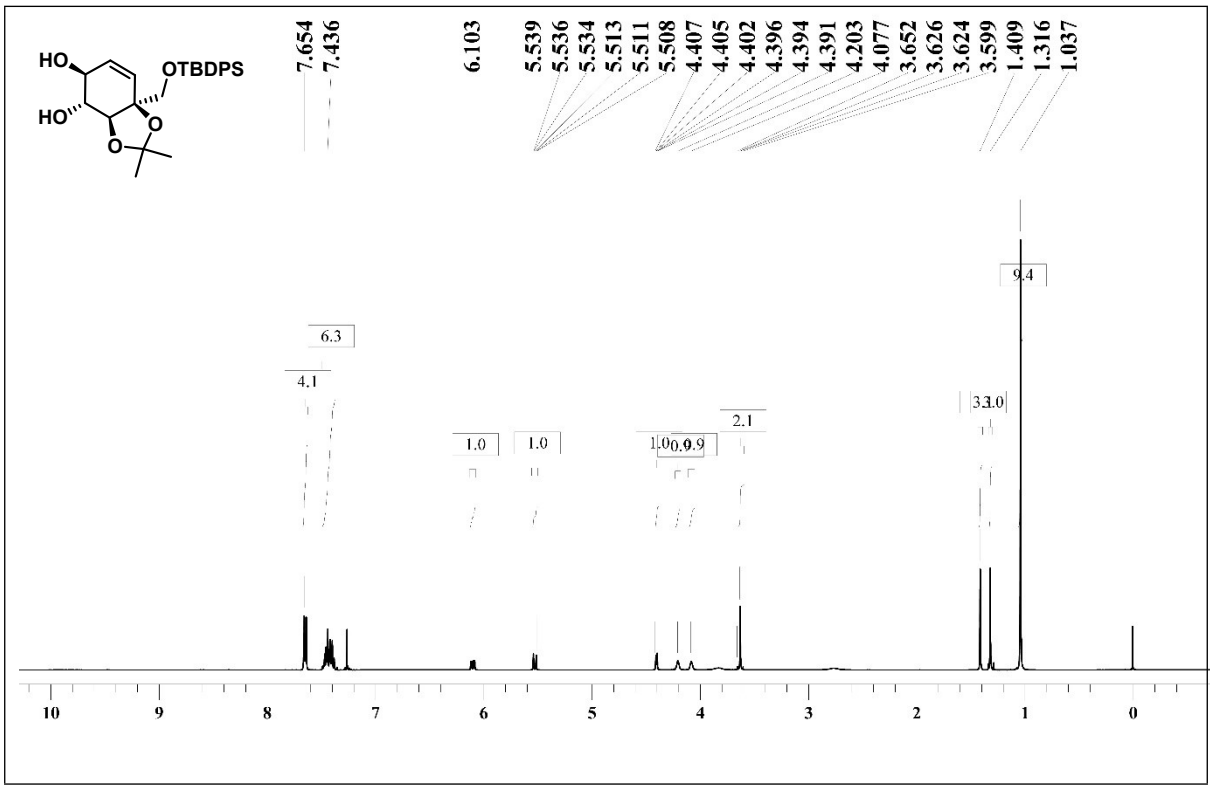
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 28:



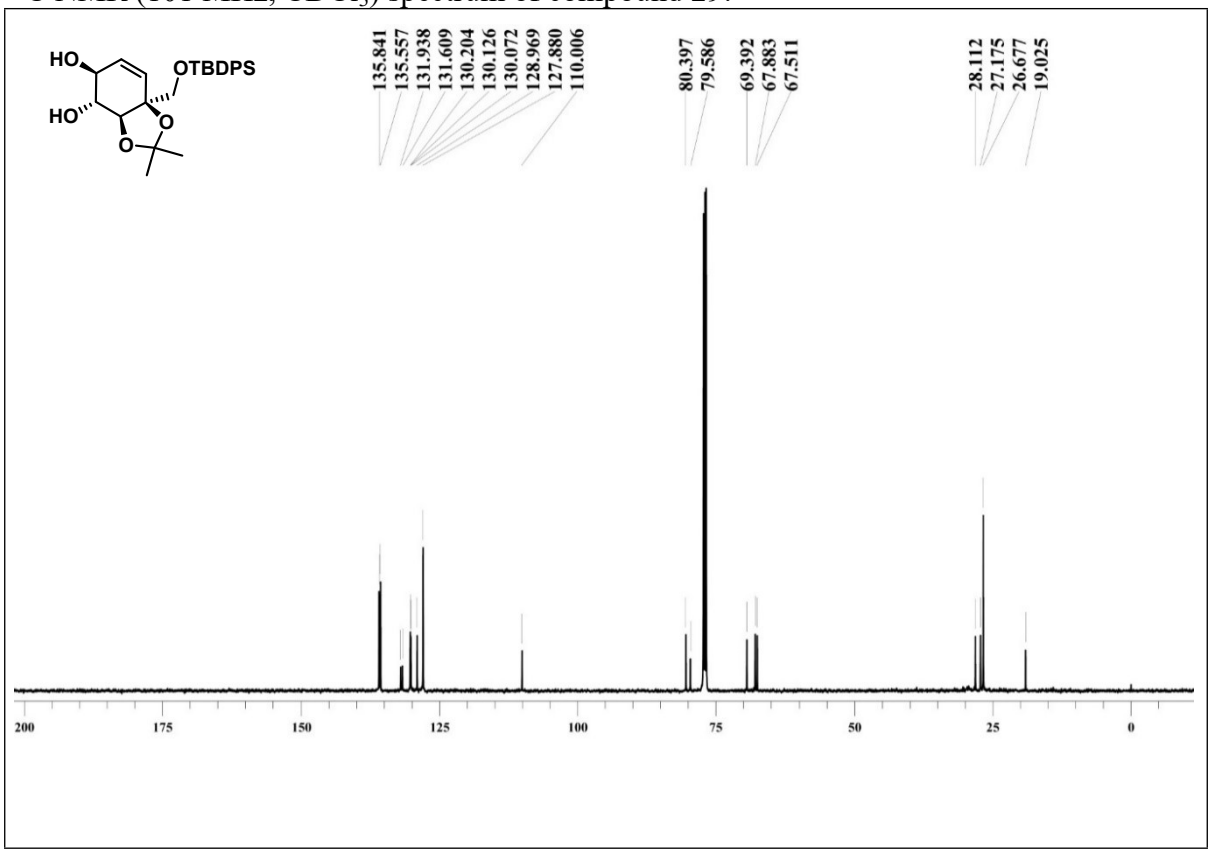
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 28:



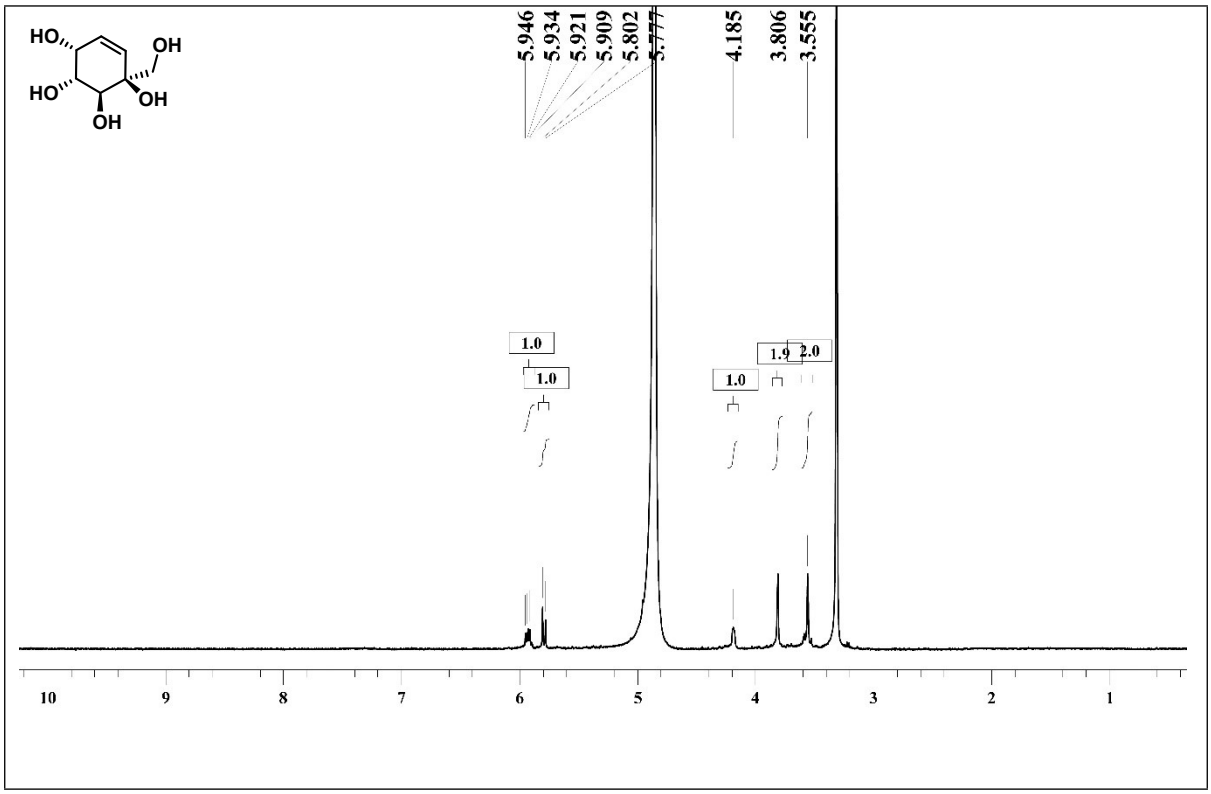
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 29:



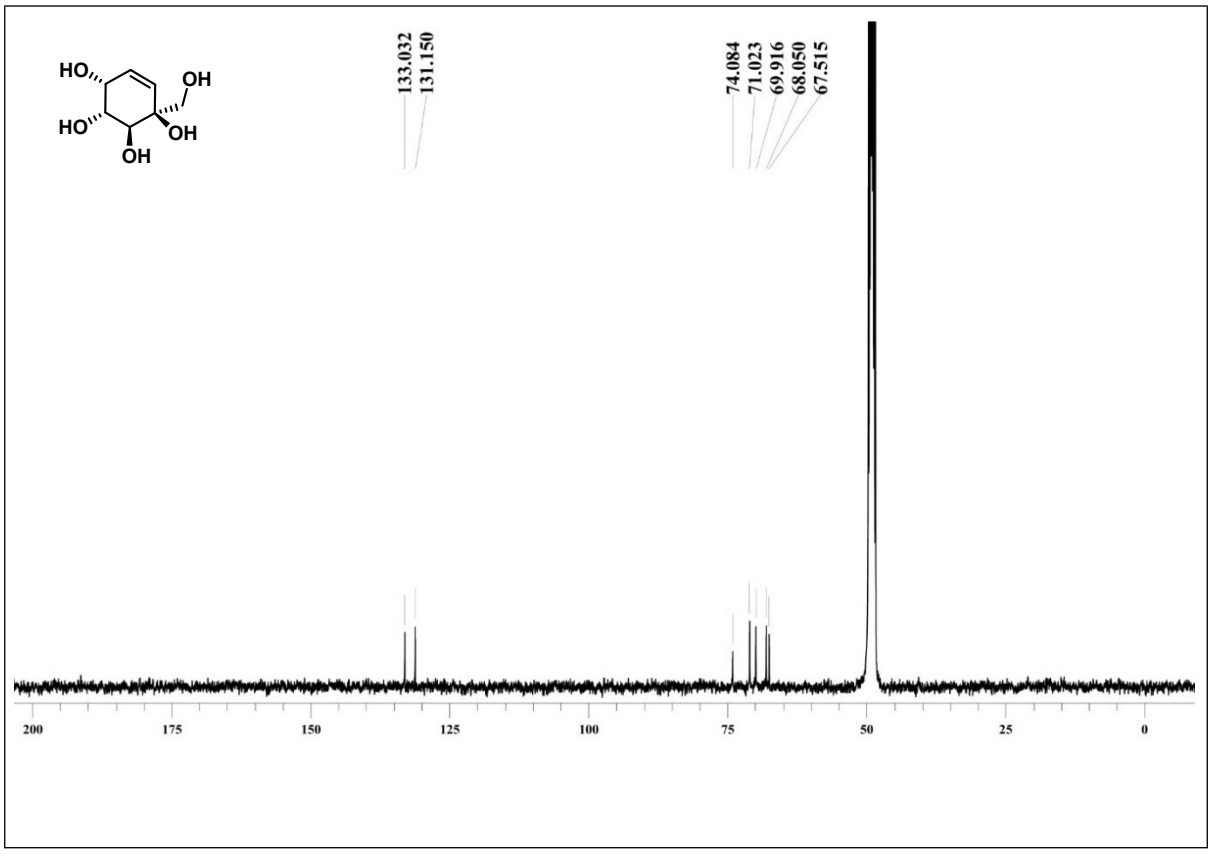
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 29:



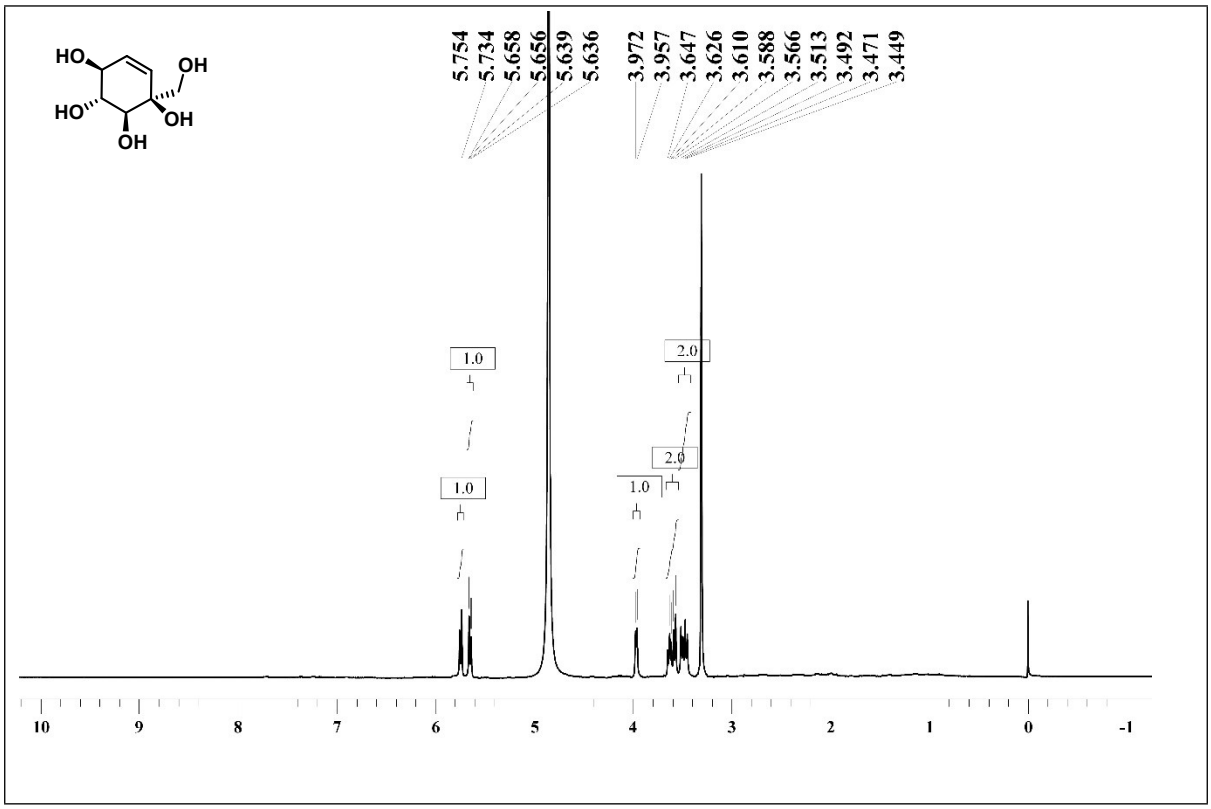
^{1}H NMR (500MHz, CD_3OD) spectrum of compound 30:



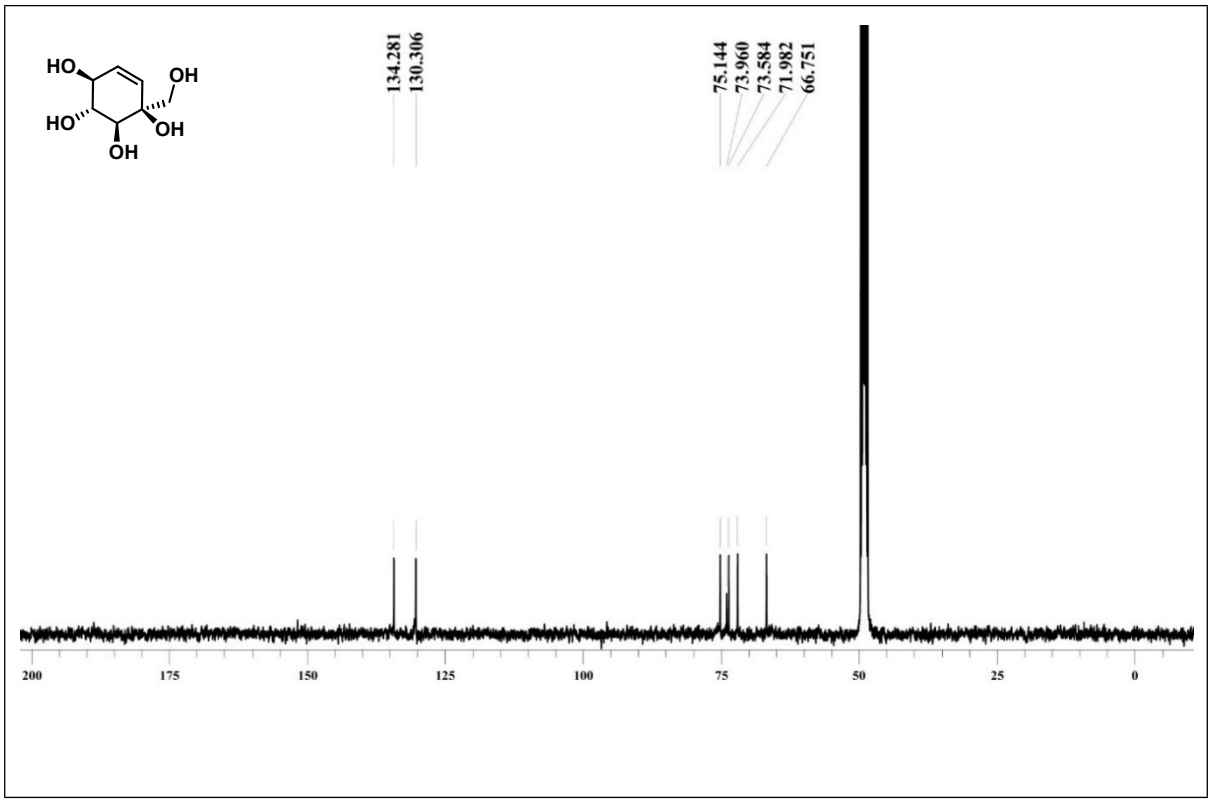
^{13}C NMR (101 MHz, CD_3OD) spectrum of compound 30:



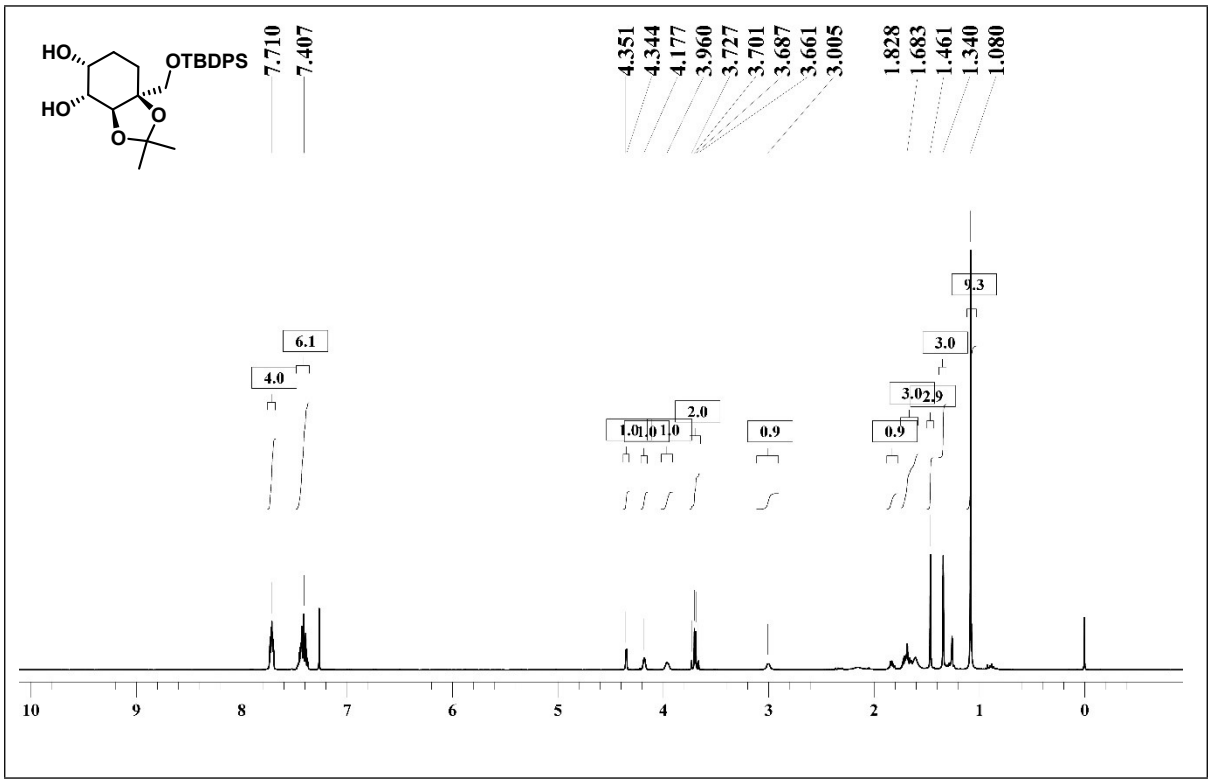
^{1}H NMR (500MHz, CD_3OD) spectrum of compound 31:



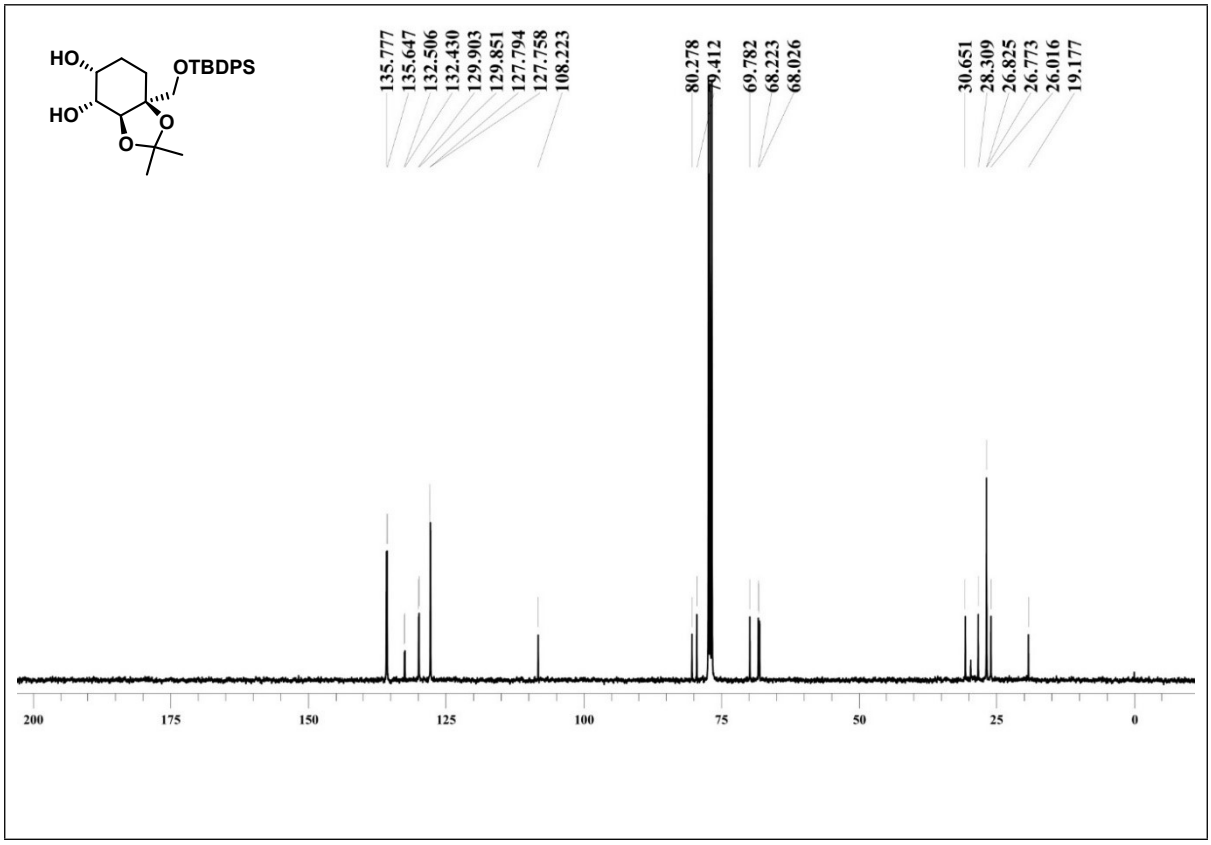
^{13}C NMR (101 MHz, CD_3OD) spectrum of compound 31:



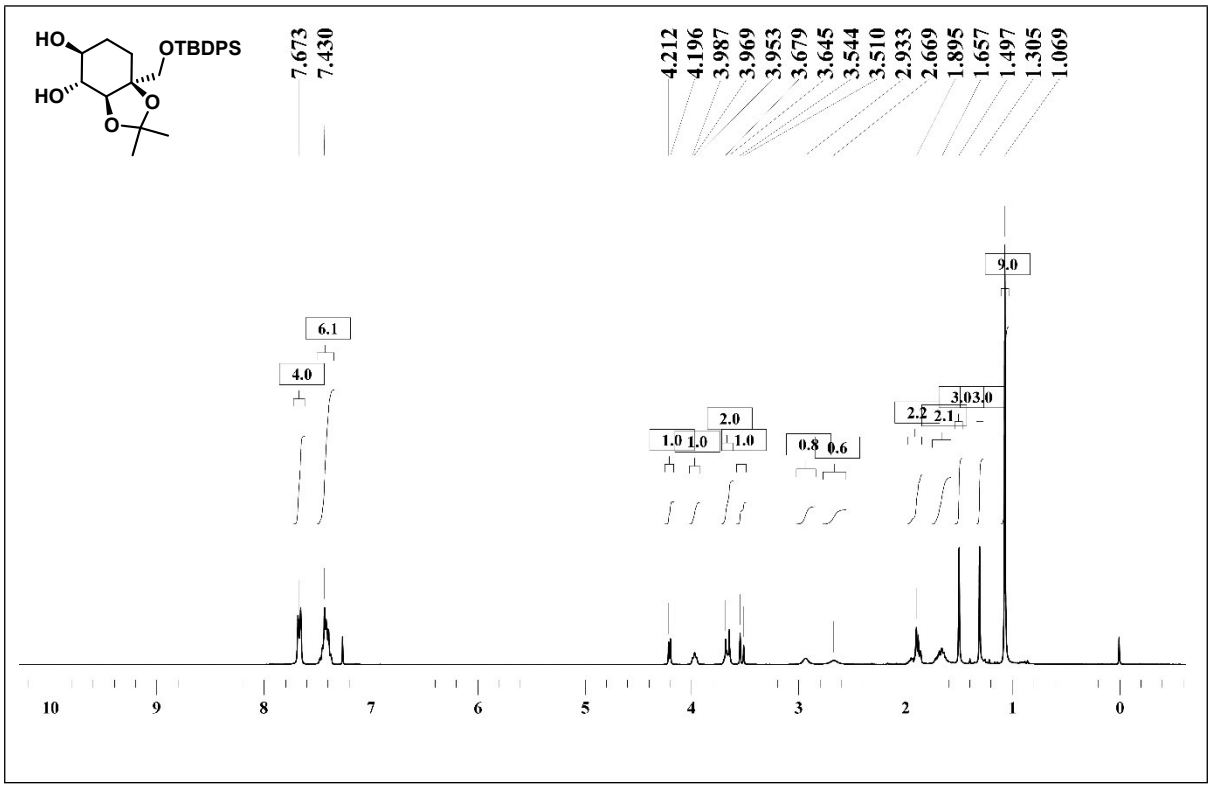
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound 32:



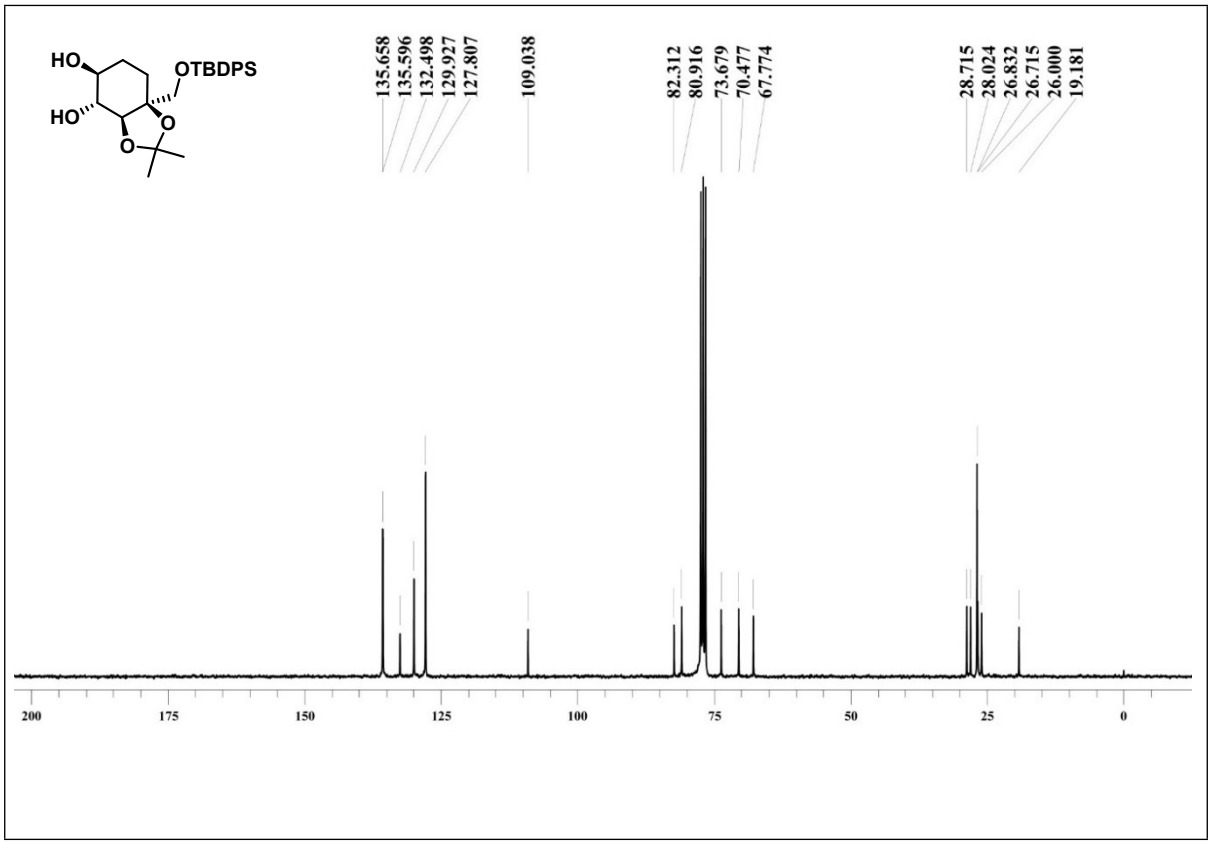
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 32:



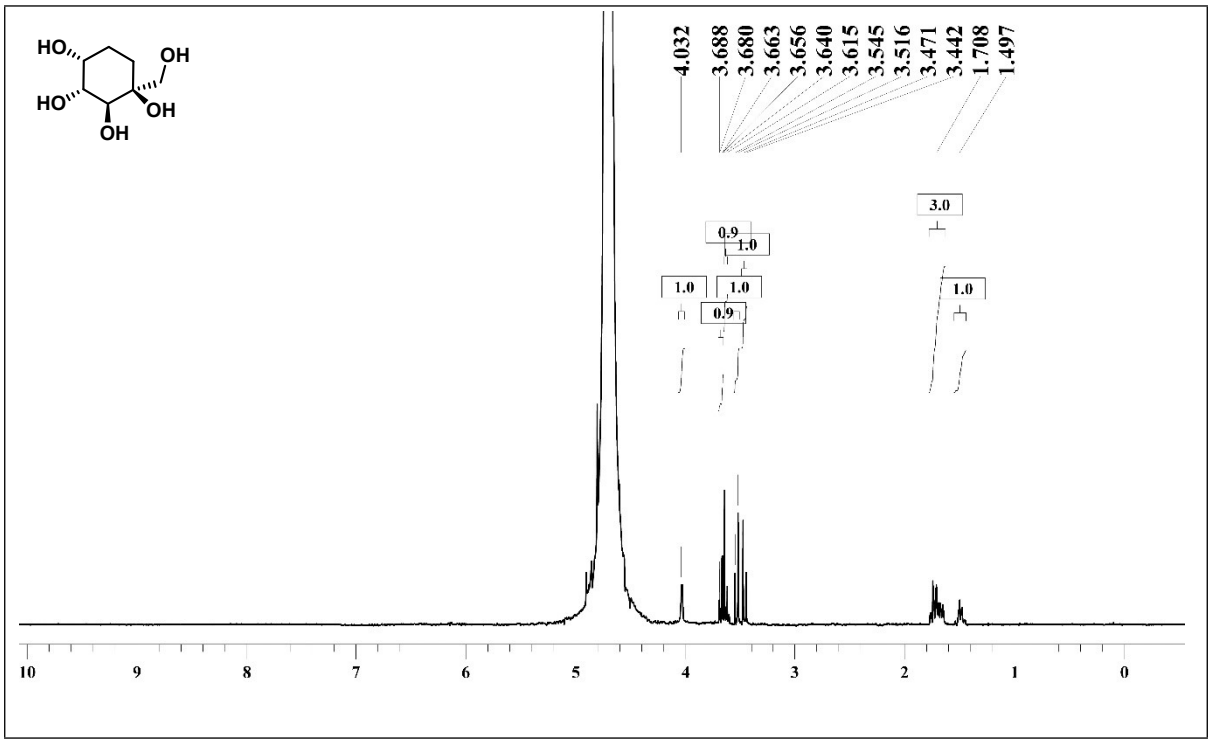
^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound 33:



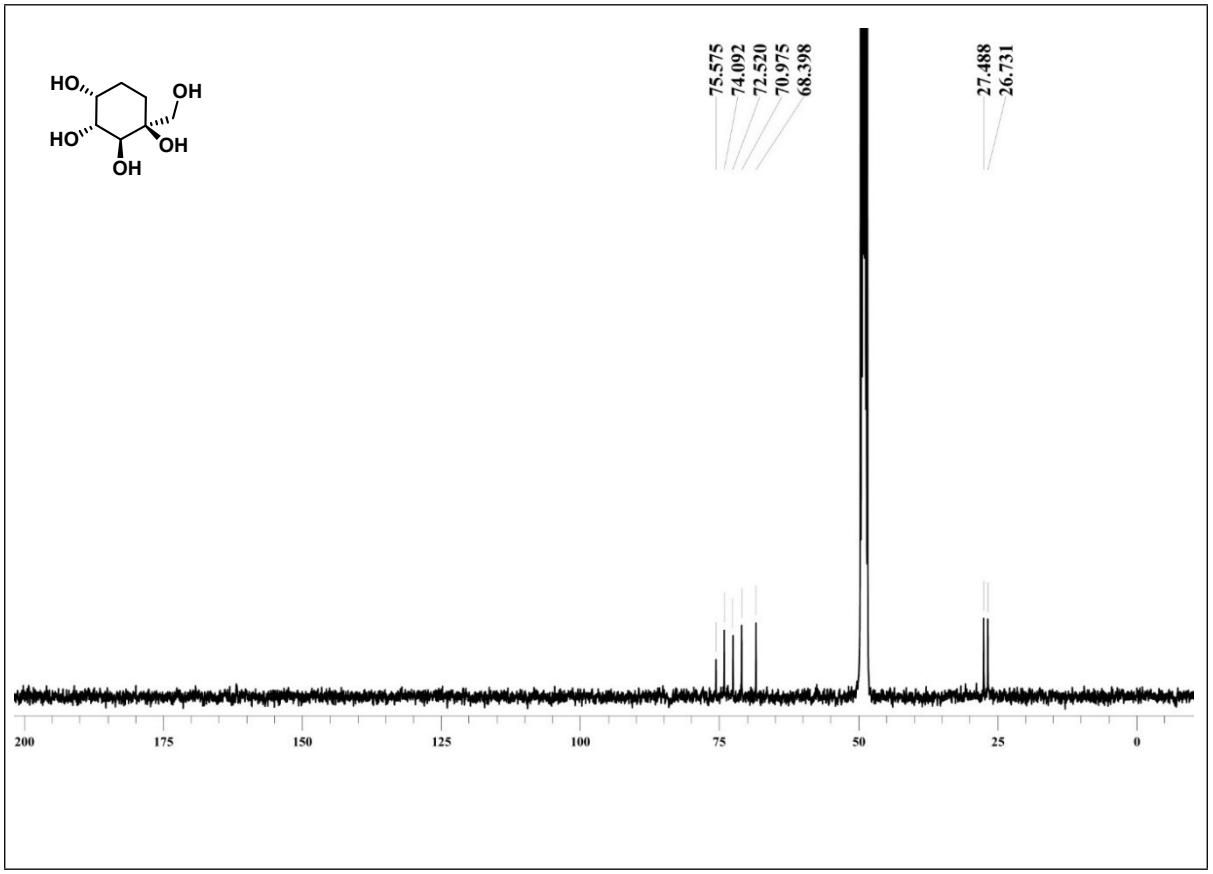
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of compound 33:



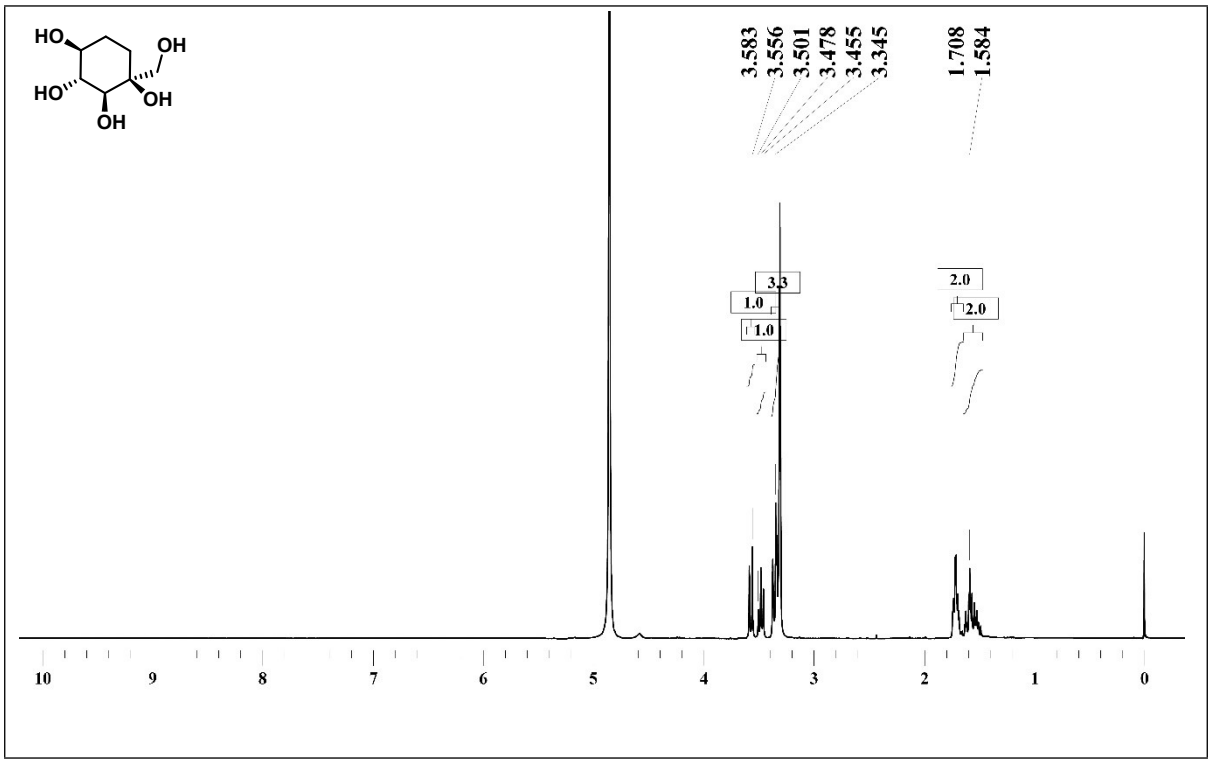
^{1}H NMR (400MHz, D_2O) spectrum of compound 6a-carba-β-D-fructopyranose 34:



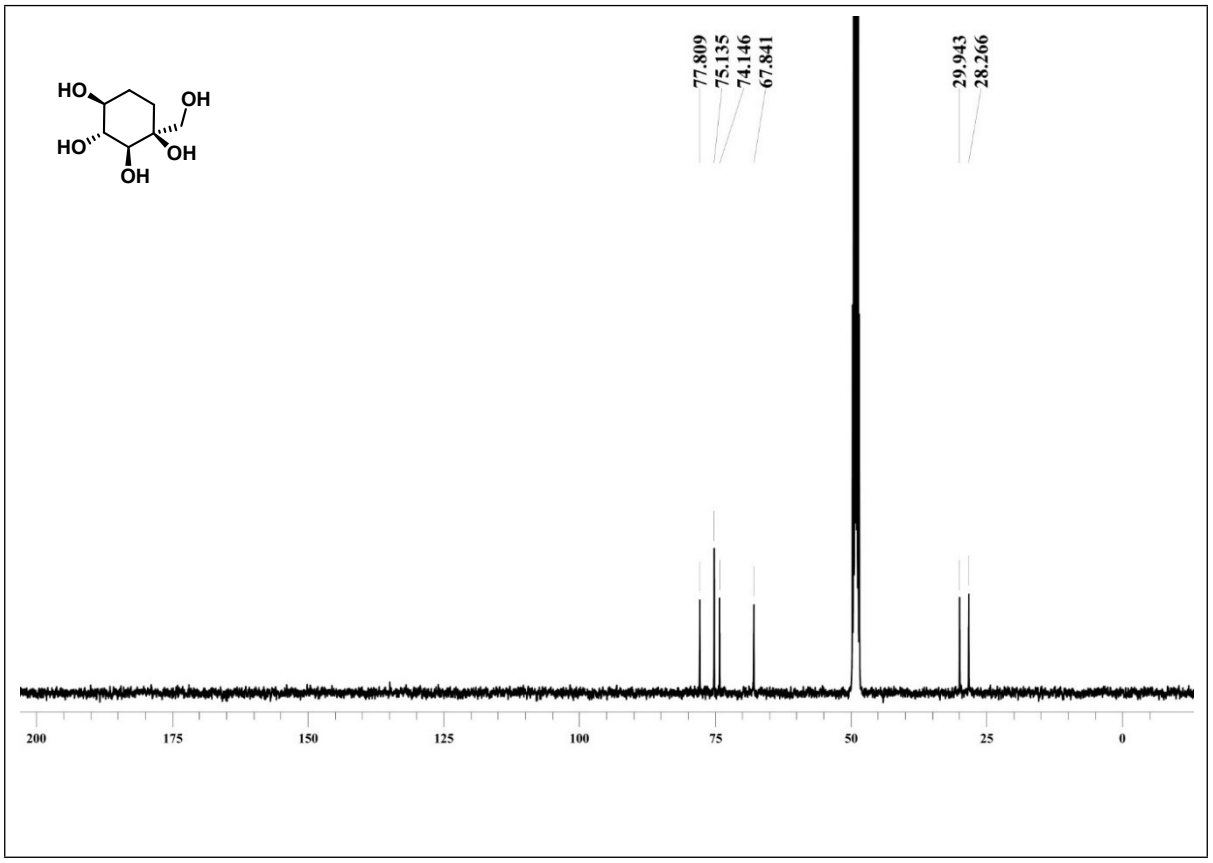
^{13}C NMR (101 MHz, CD_3OD) spectrum of compound 6a-carba-β-D-fructopyranose 34:



^{1}H NMR (400MHz, CD_3OD) spectrum of compound 35:



^{13}C NMR (101 MHz, CD_3OD) spectrum of compound 35:



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