**Supplementary data**

**First enantioselective strategy towards speciosins**

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**Experimental:**

All non-hydrolytic reactions were carried out in nitrogen atmosphere with standard techniques for the exclusion of air. All solvents were distilled prior to use. Melting points are uncorrected. Mass spectra were recorded using the electron impact mode (70 or 20 eV) in a GCMS QP2010 Shimadzu HP 5971 spectrometer. High resolution mass spectra were recorded in a Bruker Daltonics Q-TOF spectrometer using ESI mode. Infrared spectra were recorded on neat samples (NaCl disks) using a Shimadzu FT/IR-8101 Type A spectrometer. NMR spectra were obtained in a Bruker Advance DPX-400 instrument at 400 MHz for $^{1}$H NMR and 100 MHz for $^{13}$C NMR in $CDCl_3$ or MeOH-$D_4$. Proton chemical shifts are reported in ppm downfield from TMS as an internal reference, and carbon chemical shifts are reported in ppm relative to the center line of the $CDCl_3$ triplet (77.0 ppm). Optical rotations were measured in Kruss Optronic P8000 polarimeter using a 0.5 dm cell. $[\alpha]_D$ values are given in units of deg · $cm^2$ · $g^{-1}$ and concentration values are expressed in g/100mL. Analytical TLC was performed on plates pre-coated with silica gel 60F 254 and visualized with UV light (254 nm) and/or *p*-anisaldehyde in acidic ethanolic solution. Flash column chromatography was performed using silica gel (Kieselgel 60, EM reagent, 230 – 400 mesh).

**(1*S*,2*R*)1,2-isopropylidenedioxo-3-[(O-tosyl)-4-hydroxy-1-butynyl]-3,5-cyclohexadiene (3b)**
To a stirred mixture of $Pd(PPh_3)_4$ (250 mg; 0.22 mmol) and CuI (52 mg; 0.27 mmol), a solution of compound **1b** (830 mg; 3.60 mmol) in toluene (4.6 mL) was added, followed by neat $NEt_3$ (760 µL; 5.50 mmol) and a slow dropwise addition of a solution of the alkyne (1.2 g; 5.40 mmol) in toluene (1.6 mL).The reaction mixture was allowed to stir at room temperature until **1b** was consumed. Toluene was distilled, and the residue was dissolved in dichloromethane. The organic layer was washed with $NH_4Cl$(sat) (3x 5mL), $NaHCO_3$(sat)(2x 5mL) and NaCl(sat) (5 mL), it was dried over $Na_2SO_4$and concentrated under vacuum to afford a brown oil residue. The crude product was purified by flash column chromatography with 8:2 Hexanes:AcOEt to obtain **3b** as a yellow oil (807 mg, 60%).

$^{1}$H-RMN (400MHz, $CDCl_3$) δ (ppm): 1.41 (s, 3H), 1.41 (s, 3H), 2.45 (s, 3H), 2.76 (t, $J_1$=$J_2$=7.2 *Hz*, 2H), 4.13 (t, $J_1$=$J_2$=7.2 *Hz*, 2H), 4.50 (d, *J*=8.5 *Hz*, 1H), 4.70 (dd, $J_1$=3.6*Hz*; $J_2$=8.5*Hz*, 1H), 5.92 (dd, $J_1$=3.6*Hz*; $J_2$=9.7*Hz*, 1H), 6.00 (dd, $J_1$=5.8*Hz*; $J_2$=9.7*Hz*, 1H), 6.20 (d, *J*=5.8 *Hz*, 1H), 7.35 (d, *J*=8,3 *Hz*, 2H), 7.81 (d, *J*=8.3 *Hz*, 2H)

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ (ppm): 20.8, 21.8, 25.1, 26.9, 67.7, 71.1, 72.5, 82.1, 88.0, 105.8, 119.7, 123.5, 126.3, 128.1, 129.5, 130.0, 133.0, 145.1; EI MS *m/z* (70 eV): 144 (31); 116 (38); 115 (100); 43 (27)

HRMS $C_{20}H_{22}O_5S$+Na calc: 397.1080; exp: 397.1076

IR (NaCl): 2220; 1120; 815 $cm^{-1}$

$[\alpha]_{589\,nm}^{25.5}$= 109.7° (0.445g/100mL, MeCN)

**(1*S*,2*S*,3*S*,4*S*)-1,2-epoxy-2-[(*O*-tosyl)-4-hydroxy-1-butynyl]-3,4-isopropylidenedioxocyclo-5-hexene (4a)**

Compound **3b** (200 mg; 0.53 mmol) was dissolved in $CHCl_3$ (3 mL) and stirred under reflux. *m*-CPBA (189 mg; 1.20 mmol) was added in small amounts and after five minutes the reaction mixture was diluted with dichloromethane and allowed to cool. The organic layer was washed with $NaHCO_3$(sat) (3x 5mL) and NaCl(sat) (5 mL), dried over $Na_2SO_4$ and concentrated under vacuum to afford a brown oil residue. The crude material was purified by flash column chromatography with 95:5 Toluene:AcOEt to obtain **4a** as a colourless oil (107 mg, 52%).

$^1$H-RMN (400MHz, $CDCl_3$) δ (ppm): 1.40 (s, 3H), 1.41(s, 3H), 2.46 (s, 3H), 2.65 (t, $J_1$=$J_2$=7.2 *Hz*, 2H), 3.47 (dt, $J_1$=1.0 *Hz*, $J_2$=3.9 *Hz,* 1H), 4.11 (td, $J_1$=1.6 *Hz,* $J_2$=$J_3$=7.3 *Hz*, 2H), 4.48 (dt, $J_1$=1.9 *Hz*$J_2$=6.5 *Hz*, 1H), 4.64 (d, *J*=6.5 *Hz*, 1H), 5.77 (ddt, $J_1$=$J_2$=1.1 *Hz,* $J_3$=2.0 *Hz,* $J_4$=10.1 *Hz*; 1H), 5.98 (ddd, $J_1$=1.9 *Hz*; $J_2$=3.9 *Hz*; $J_3$=10.1 *Hz*; 1H), 7.36 (d, *J*=8.0 *Hz*, 2H), 7.81 (d, *J*=8,0*Hz*, 2H)

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ (ppm): 20.0, 21.8, 26.5, 28.1, 48.9, 54.4, 67.2, 72.1, 73.3, 79.1, 79.7, 111.0, 122.0, 128.1, 130.1, 132.9, 133.6, 145.1.

EI MS *m/z* (20 eV): 303(67); 293(99); 160(56); 131(96); 121(31); 110(50); 109(35); 100(100); 85(48); 82(34); 81(83); HRMS $C_{20}H_{22}O_6S$+Na calc: 413.1030; exp: 413.1029

IR (NaCl): 2250; 1363; 1236; 1161; 1060 $cm^{-1}$

$[\alpha]_{589\,nm}^{25.5}$= -16.9° (0.810g/100mL, MeOH)

**(1*R*,2*R*,3*R*,4*R*)-1,2-epoxy-5-[(*O*-tosyl)-4-hydroxy-1-butynyl]-3,4-isopropylidenedioxocyclo-5-hexene (4b)**

Compound **4b** was obtained as minor product (53mg, 26%) during the procedure to obtain **4a**

$^1$H-RMN (400MHz, $CDCl_3$) δ (ppm): 1.41 (s, 6H), 2.46 (s, 3H), 2.72 (t, $J_1$=$J_2$=7.1 *Hz*, 2H), 3.37 (t, $J_1$=$J_2$=3.8 *Hz*, 1H), 3.58 (dd, $J_1$=1.7 *Hz*; $J_2$=3.8 *Hz*; 1H), 4.11 (t, $J_1$=$J_2$=7.1 *Hz*, 2H), 4.29 (d, *J*=6.6 *Hz*, 1H), 4.75 (dd, $J_1$=1.7 *Hz*; $J_2$=6.6 *Hz*; 1H), 6.24 (d, *J*=3.8 *Hz*, 1H), 7.35 (d, *J*=8.2 *Hz*, 2H), 7.80 (d, *J*=8.2 *Hz*, 2H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ (ppm): 20.5, 21.7, 26.0, 27.6, 46.9, 50.0, 67.4, 71.3, 72.1, 80.3, 87.0, 111.1, 126.3, 128.0, 129.5, 129.9, 132.8, 145.0.

**(1*R*,2*S*,3*S*,4*S*)-2-(but-3-en-1-ynyl)-1,2-dihydroxy-3,4-isopropylydenedioxocyclo-5-hexene (5)**

Compound **4a** (40.0 mg; 0,10 mmol) was dissolved in THF (4 mL) and a 10% aqueous solution of KOH (4 mL) was added. The reaction mixture was refluxed for two hours and extra 2 mL of KOH 10% aqueous solution were added. After 3 more hours of reflux the reaction mixture was allowed to cool and HCl 5% was added dropwise to neutralize. The crude mixture was extracted with AcOEt (3x 5mL). The combined organic layers were dried over $Na_2SO_4$ and evaporated under vacuum to afford a colorless oil which was purified by flash column chromatography using 1:1 AcOEt:Hexanes to obtain **5** as a colorless oil (15.1 mg, 55%).

$^1$H-RMN (400MHz, $CDCl_3$) δ (ppm): 1.41 (s, 3H), 1.59 (s, 3H), 2.57 (d, *J*=9.3 *Hz*, 1H), 3.13 (s, 1H), 4.13 (d, *J* =7.4 *Hz*, 1H), 4.31 (d, *J* =6.8 *Hz*, 1H), 4.71 (dt, $J_1$=1.4*Hz*; $J_2$=6.8*Hz*;1H), 5.53 (dd, $J_1$=2.2*Hz*$J_2$=11.0*Hz*; 1H), 5.69 (dd, $J_1$=2.2*Hz*; $J_2$=17.6*Hz*; 1H), 5.83 (dd, $J_1$=11.0*Hz*, $J_2$=17.6 *Hz*; 1H), 5.87 (dt; $J_1$=$J_2$=1.5*Hz*, $J_3$=10.2*Hz*; 1H), 5.93 (dt, $J_1$=$J_2$=2.5 *Hz*,*J3*=10.2 *Hz*, 1H)

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ (ppm): 25.7, 26.8, 72.4, 72.7, 74.0, 79.9, 86.7, 87.8, 111.5, 116.5, 125.4, 128.4, 132.0

EI MS *m/z* (70 eV): 151 (30); 127 (48); 99 (32); 81 (38); 79 (100); 43 (47)

HRMS: $C_{13}H_{16}O_4$+Na calc:259.0941; exp: 259.0943

IR (NaCl): 3419; 2092; 1639; 1253; 1215 $cm^{-1}$

$[\alpha]_{589\,nm}^{25.5}$= 6.0° (0.665g/100mL, MeCN:AcOEt 4:1)

**(2*R*,3*S*,4*S*)-2-(but-3-en-1-ynyl)-2-hydroxy-3,4-isopropylydenedioxocyclo-5-hexenone (6)**

Compound **5** (40 mg; 0.17 mmol) was dissolved in *N*,*N*-dimethylformamide (2 mL) and IBX (*o*-iodoxybenzoic acid) (71.4 mg; 0.25 mmol) was added. The reaction mixture was stirred at room temperature for four hours and then diluted with $Et_2O$ and washed with $CuSO_4$(sat) (3x 5 mL) and NaCl(sat) (5 mL). The organic layer was dried over $Na_2SO_4$ and concentrated under vaccum to afford a white solid which was purified by flash column chromatography using 7:3 Hexanes:AcOEt to obtain **6** as a white solid (30.4 mg, 76%); ); mp=109-111°C.

$^1$H-RMN (400MHz, $CDCl_3$) δ (ppm): 1.46 (s, 3H), 1.64 (s, 3H), 3.77 (s, 1H), 4.49 (d, *J=6.6 Hz*, 1H), 4.88 (ddd, $J_1$=1.2 *Hz*$J_2$=3.7 *Hz*$J_3$=6.6 *Hz*, 1H), 5.54 (dd, $J_1$=2.3 *Hz*$J_2$=10.9 *Hz*; 1H), 5.69 (dd, $J_1$=2.3 *Hz*; $J_2$=17.6 *Hz*; 1H), 5.81 (dd, $J_1$=10.9 *Hz*, $J_2$=17.6*Hz*; 1H), 6.28 (dd; $J_1$=1.1*Hz*, $J_2$=10.2 *Hz*; 1H), 6.93 (dd, $J_1$=3.7 *Hz*; $J_2$=10.2*Hz*, 1H)

$^{13}$C-NMR (100 MHz, $CDCl_3$) δ (ppm): 25.8, 26.8, 71.4, 73.5, 80.4, 86.9, 87.9, 112.5, 116.4, 127.4, 128.9, 143.1, 193.2

EI MS *m/z* (70 eV): 147 (29); 131 (33); 97 (100); 79 (91); 43 (33)

HRMS $C_{13}H_{14}O_4$+Na calc:257.0784; exp: 257.0786

IR (NaCl): 3387; 2092; 1639 ); mp=109-111°C.

$[\alpha]_{589\,nm}^{25.5}$= 186.2° (0.145g/100mL, MeCN)

**(2*R*,3*S*,4*S*)-2-(but-3-en-1-ynyl)-2,3,4-trihydroxycyclo-5-hexenone (7)**

Compound **6** (30.0 mg; 0.13mmol) was dissolved in MeOH (1.2 mL). Acidic resin Dowex® 50W 8 50-100 mesh (120 mg) and water (240 µL) were added to the solution and the reaction mixture was allowed to stir at 50°C for 9 hours. The resin was filtered off and washed with MeOH. The crude mixture was evaporated under vacuum to afford a white solid which was purified by flash column chromatography with 7:3 AcOEt:Hexanes to obtain **7** as a white solid (22.5 mg, 91%); mp= 58-61°C.

$^1$H-RMN (400MHz, $CDCl_3$) δ (ppm): 2.72 (d, *J*=9.4 *Hz*; 1H), 3.19 (s, 1H), 3.92 (s; 1H), 4.00 (br s; 1H), 4.54 (br s; 1H), 5.61 (dd; $J_1$=3.0 *Hz*, $J_2$=10.1 *Hz*; 1H), 5.73 (dd, $J_1$=3.0*Hz*; $J_2$=17.6 *Hz*, 1H); 5.80 (dd, $J_1$=10.2 *Hz*; $J_2$=17.6 *Hz*, 1H); 6.30 (d, *J*=10.1*Hz;* 1H); 7.07 (dd, $J_1$=5.1*Hz*; $J_2$=10.1 *Hz*, 1H)

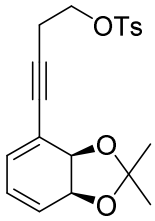
$^{13}$C-NMR (100 MHz, $CDCl_3$) δ (ppm): 66.2, 73.4, 73.7, 86.0, 88.6, 115.5, 127.2, 130.2, 147.0, 193.0

EI MS *m/z* (70 eV): 165 (22); 147 (42); 131 (32); 110 (84); 97 (41); 84 (100); 82 (25); 81 (58); 80 (30); 79 (49); 69 (42)

IR (NaCl): 3435; 2088; 1641 $cm^{-1}$

$[\alpha]_{589\,nm}^{22.0}$= 87.3° (0.440g/100mL, MeOH)

$^{1}$H-NMR and $^{13}$C-NMR spectra of compounds **3b**, **4a**, **5**, **6** and **7**




**3b**

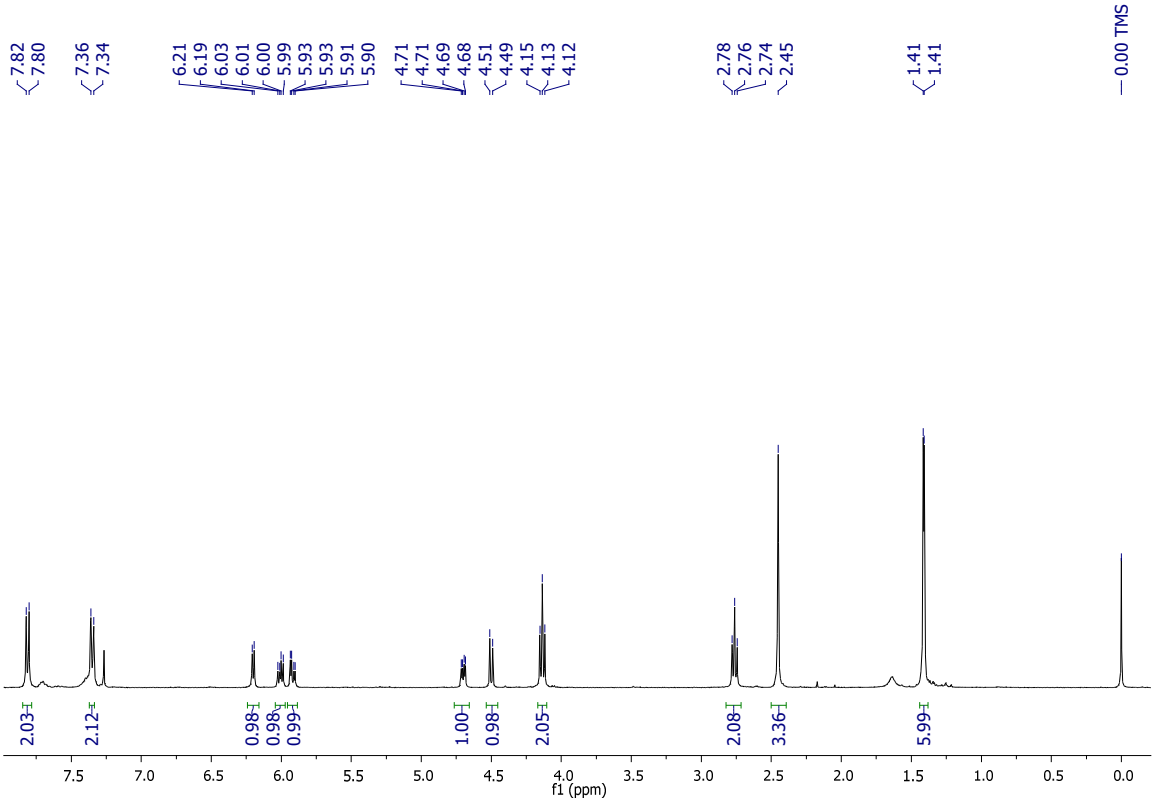



**Figure S1:** $^{1}$H-NMR spectrum of compound **3b**

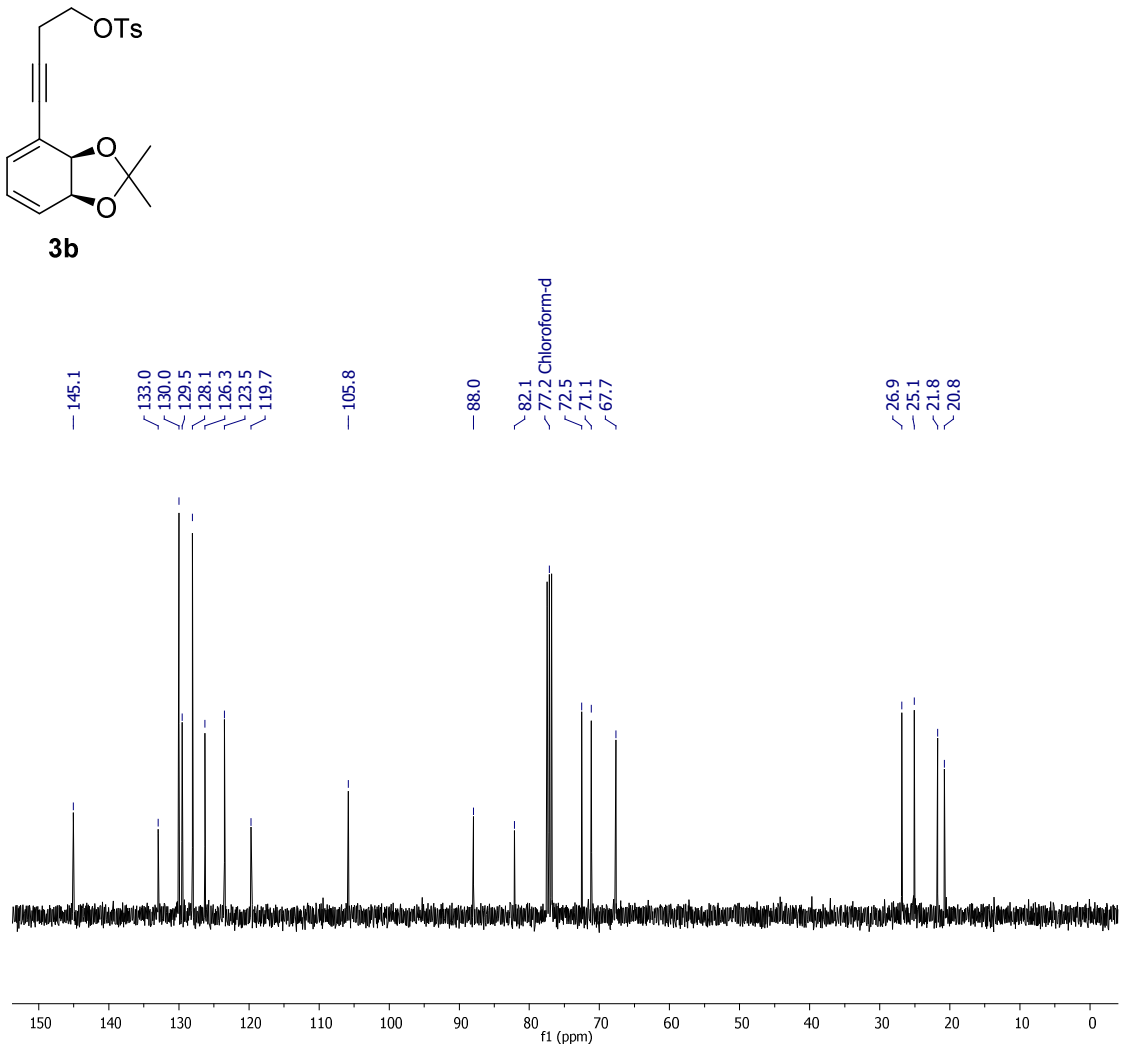
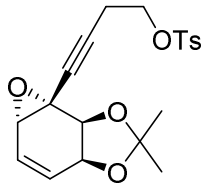



**Figure S2:** $^{13}$C-NMR spectrum of compound **3b**




**4a**

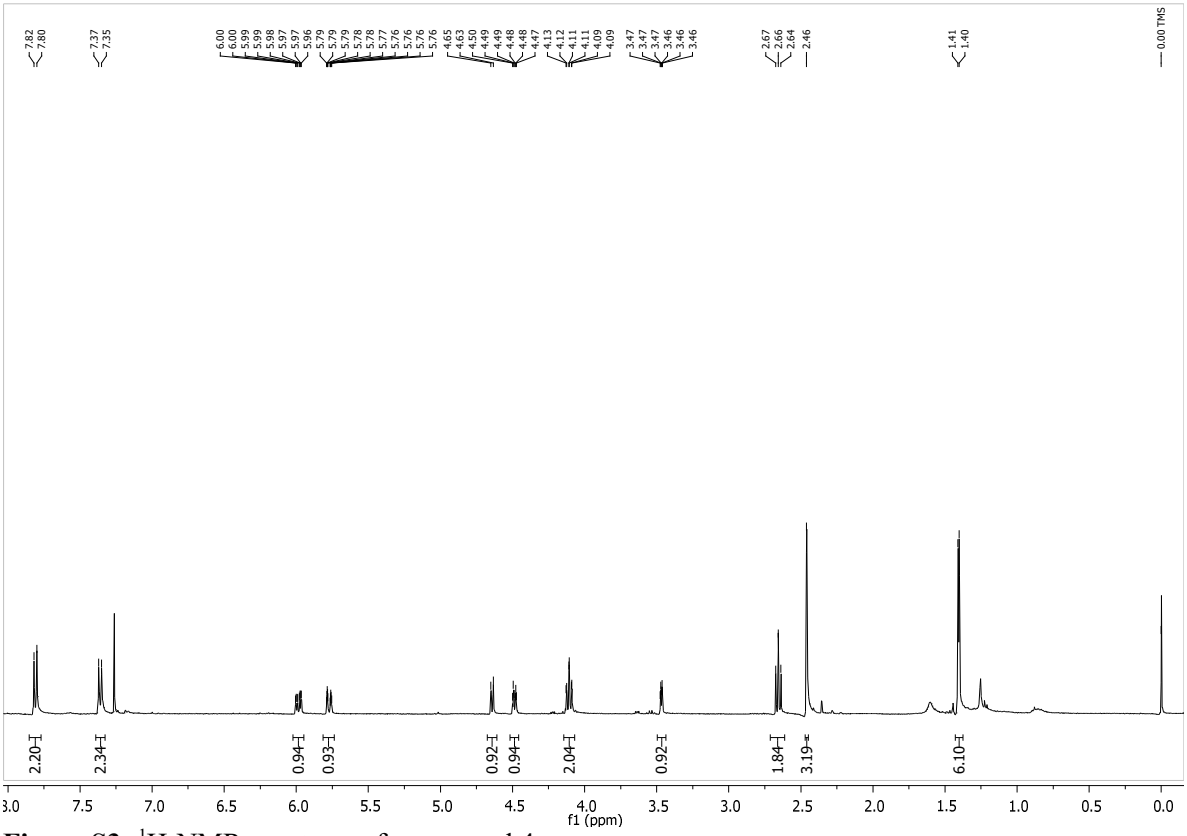



**Figure S3:** $^{1}$H-NMR spectrum of compound **4a**

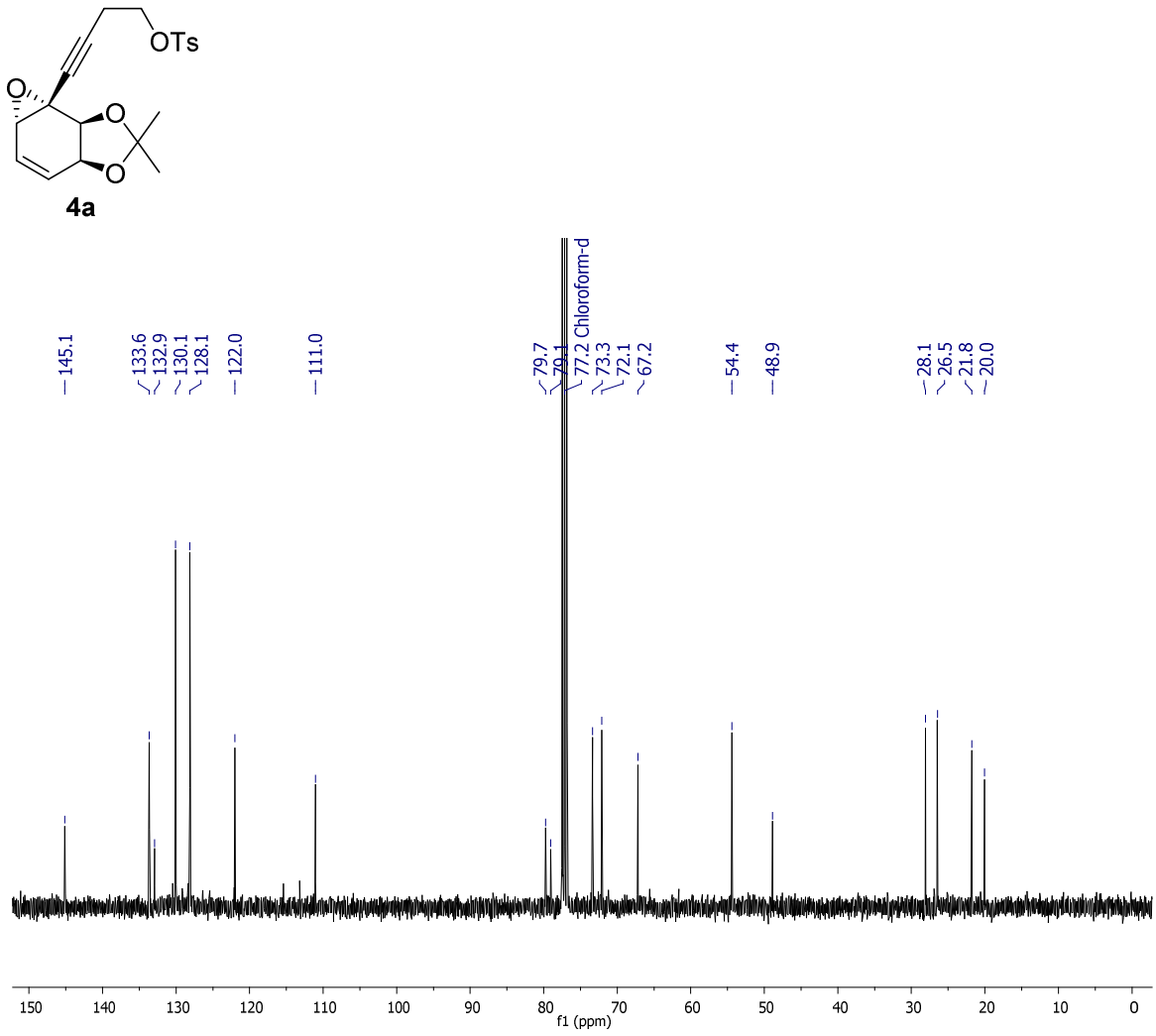
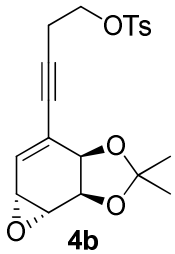



**Figure S4:** $^{13}$C-NMR spectrum of compound **4a**



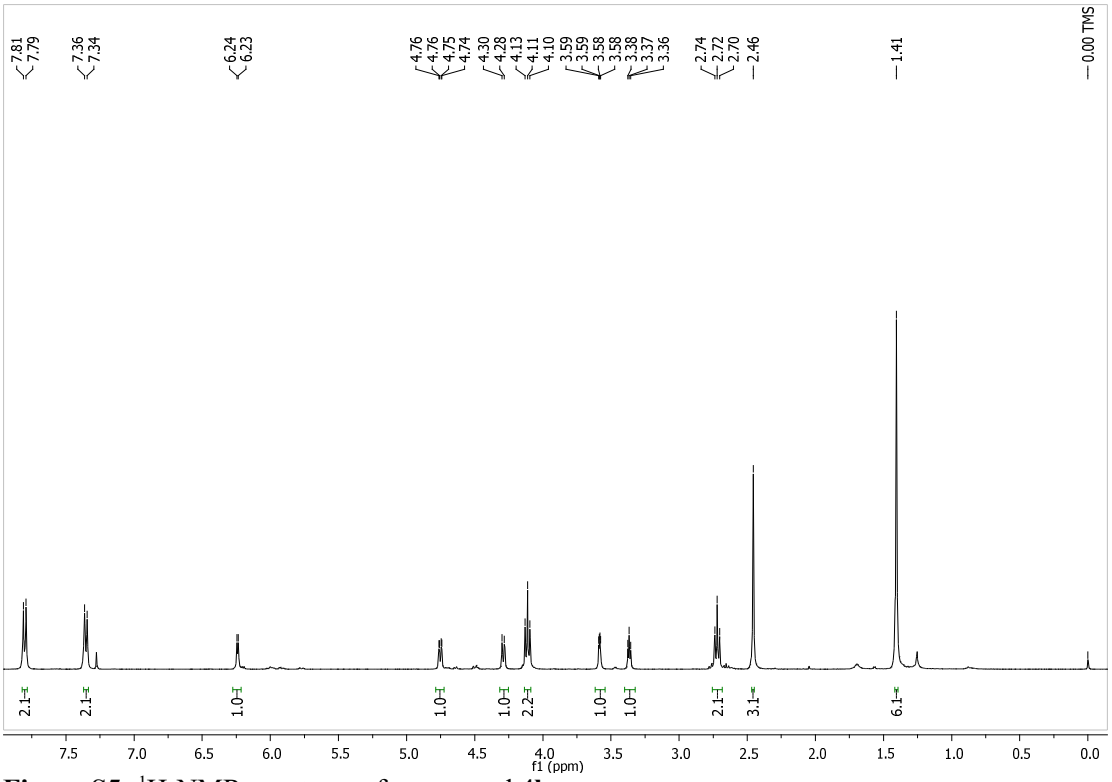




**Figure S5:** $^{1}$H-NMR spectrum of compound **4b**

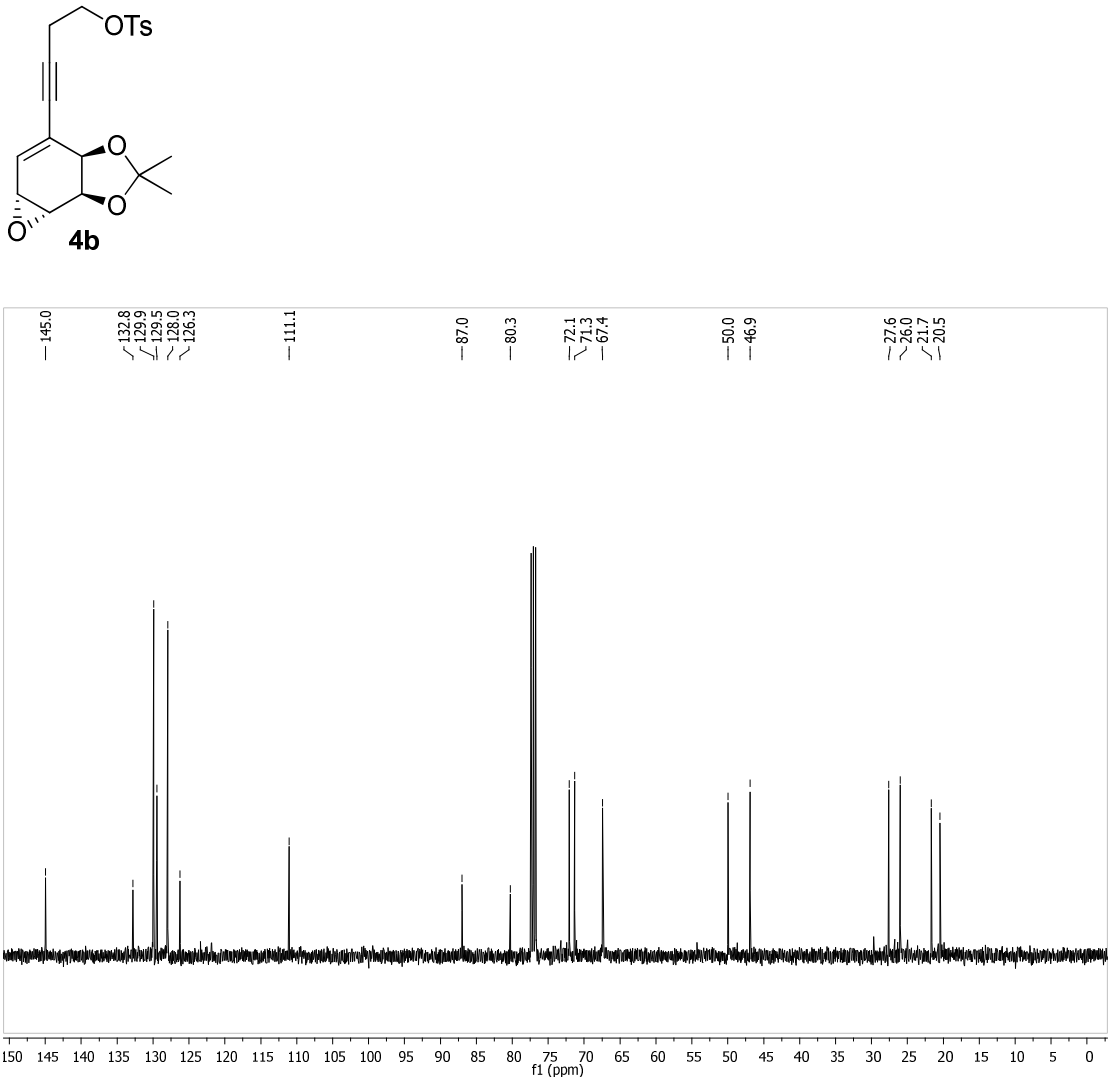



**Figure S6:** $^{13}$C-NMR spectrum of compound **4b**

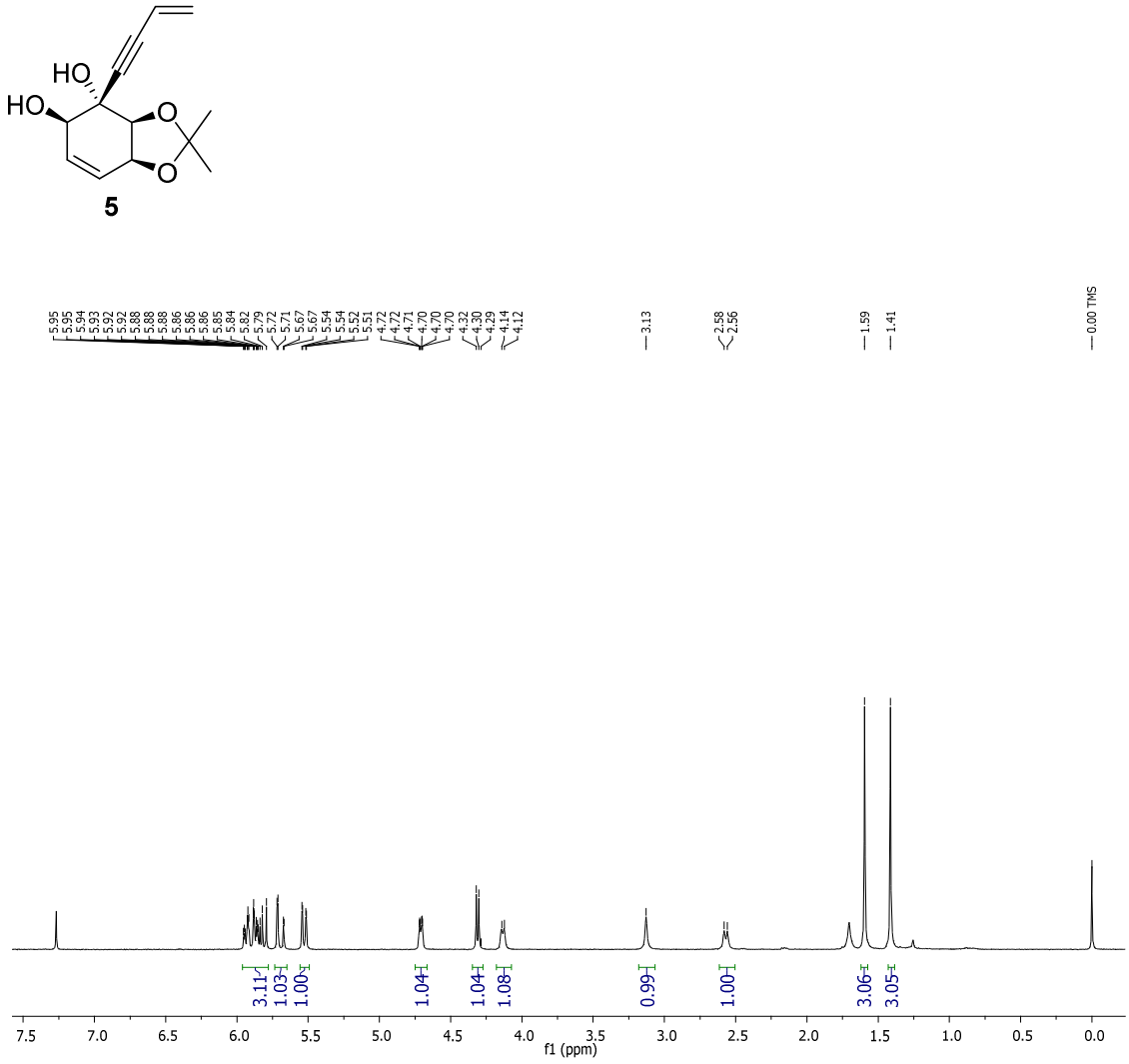



**Figure S7:** $^{1}$H-NMR spectrum of compound **5**

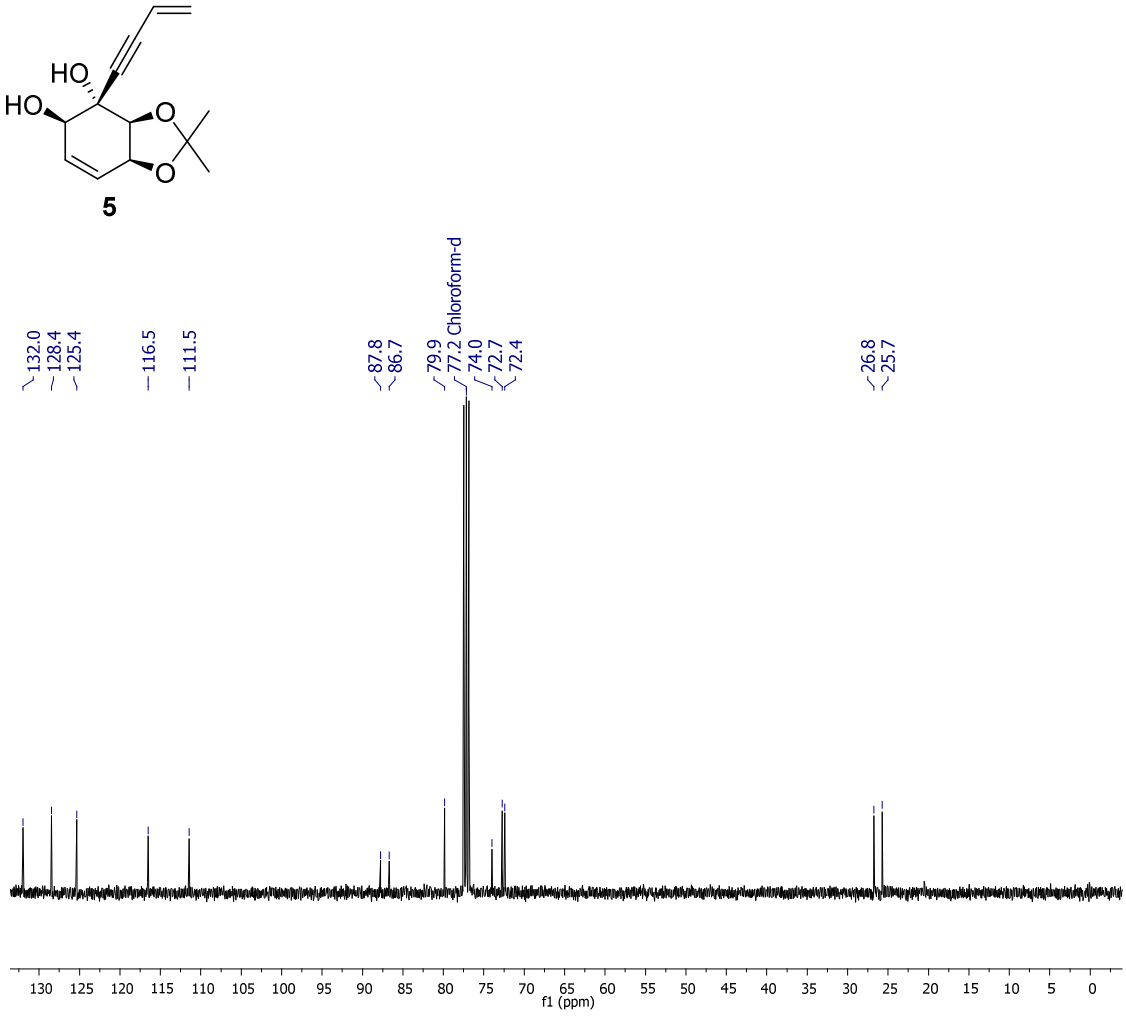



**Figure S8:** $^{13}$C-NMR spectrum of compound **5**

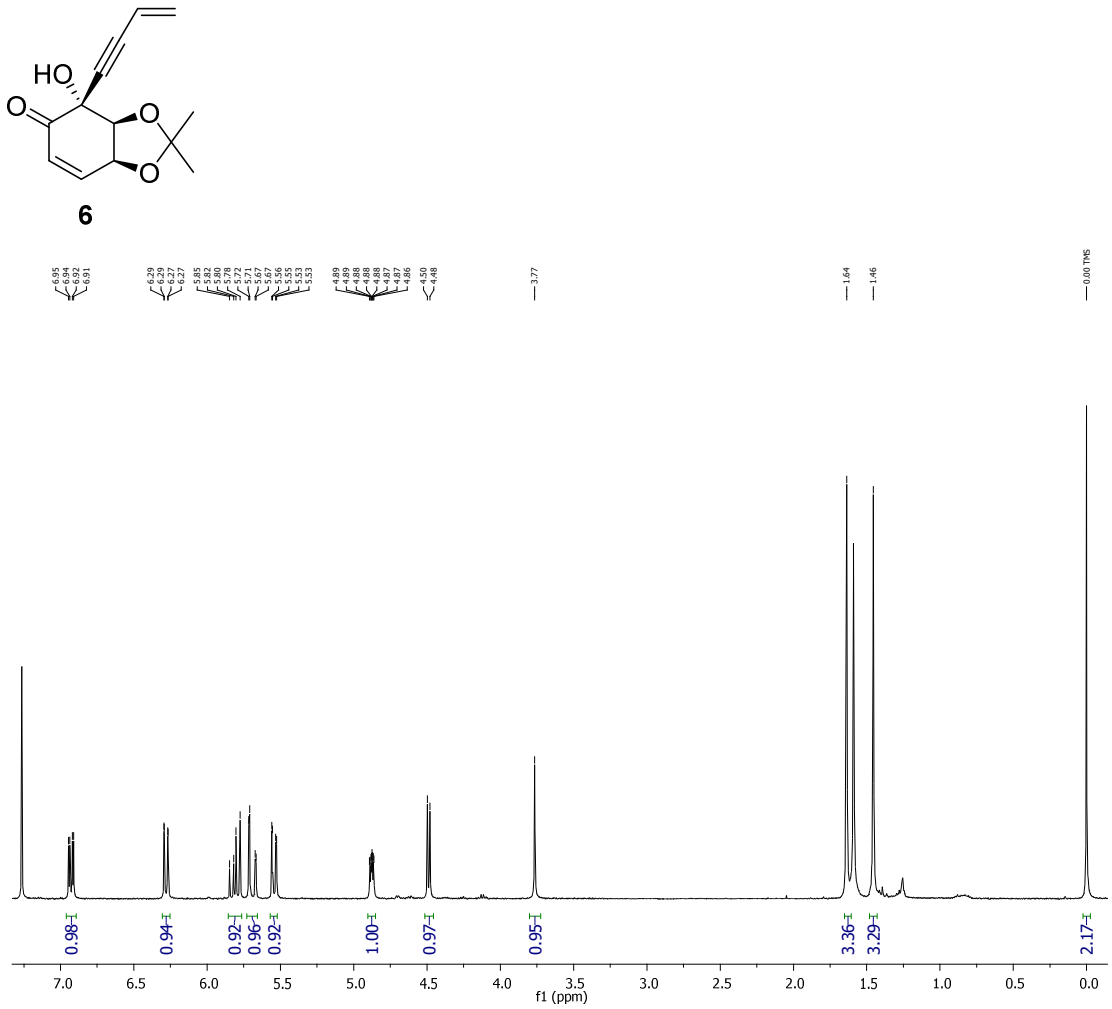



**Figure S9:** $^{1}$H-NMR spectrum of compound **6**

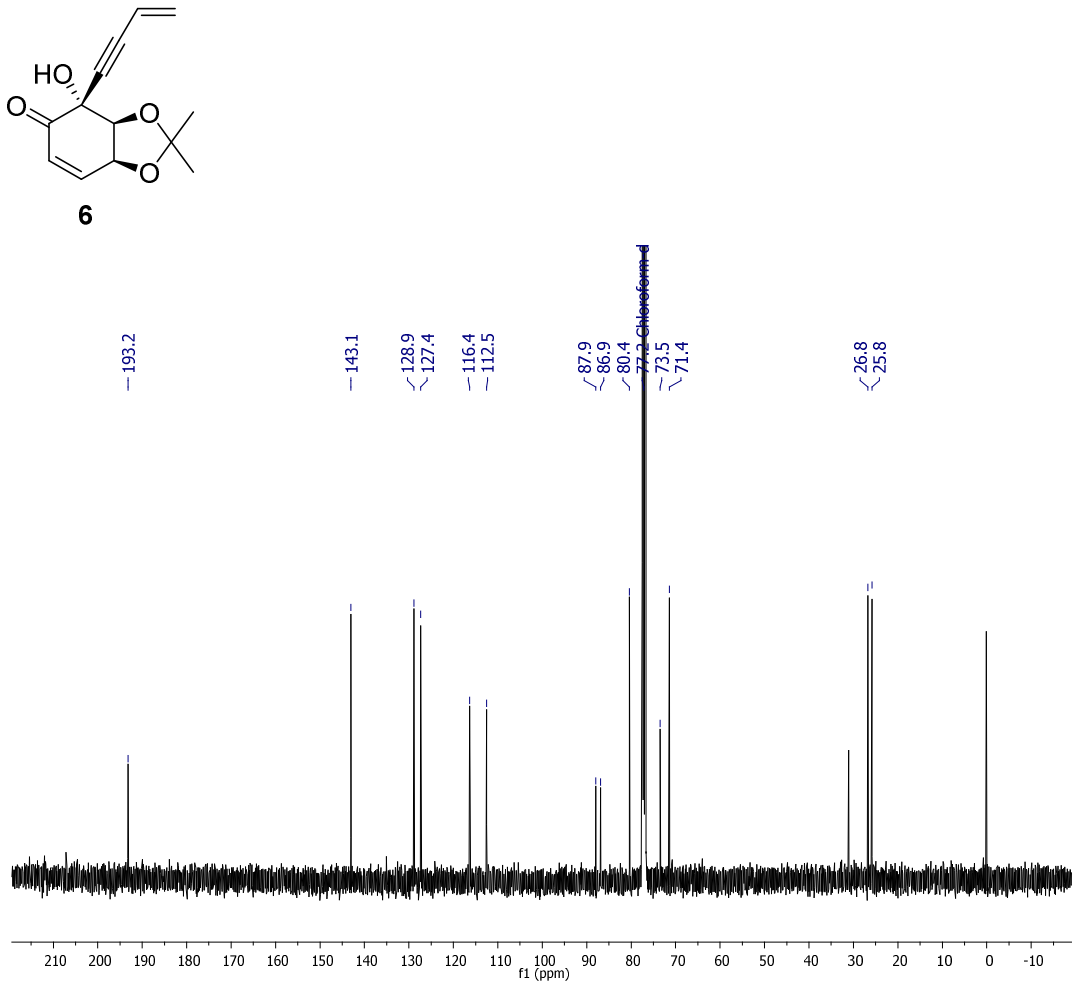



**Figure S10:** $^{13}$C-NMR spectrum of compound **6**

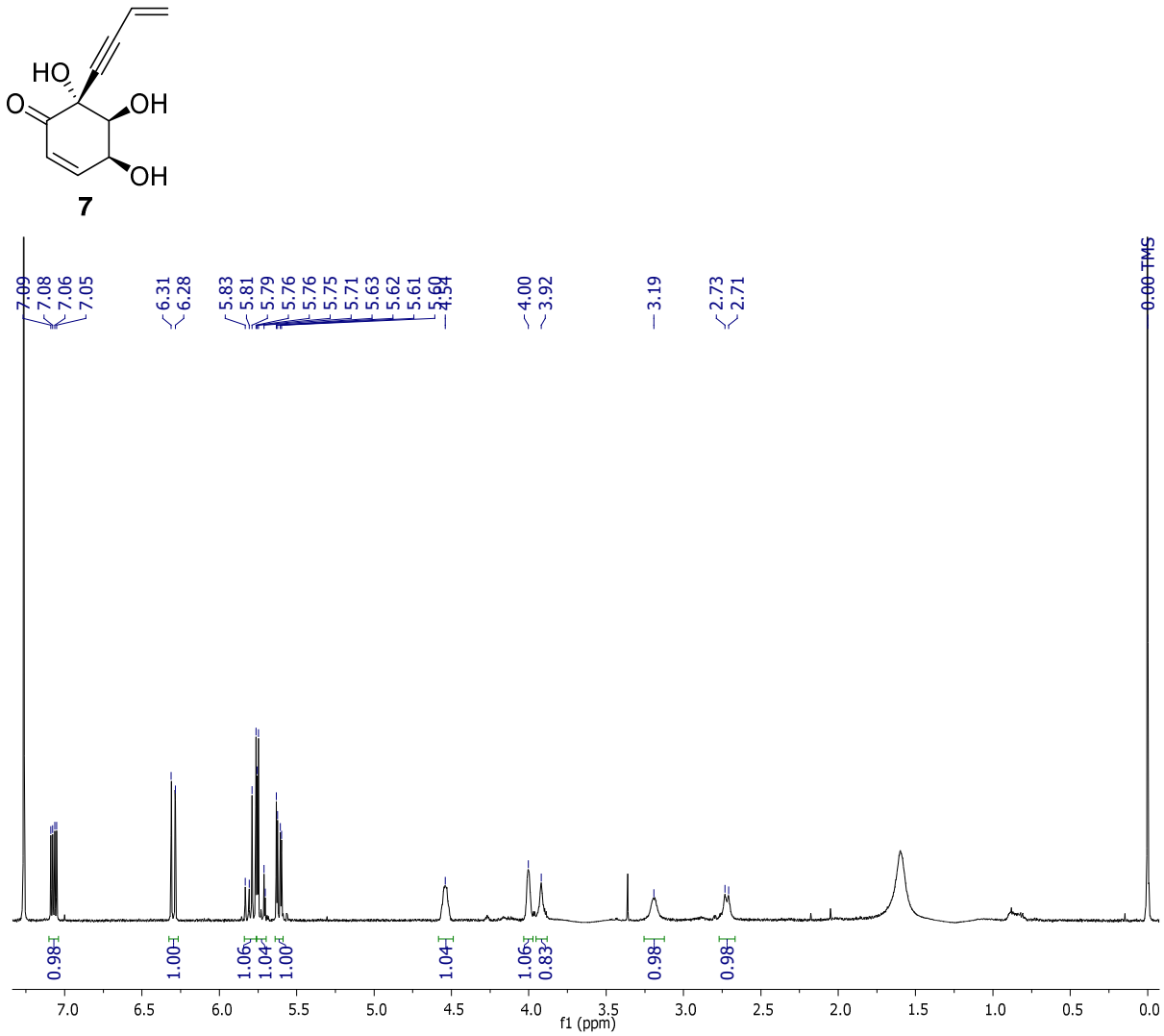
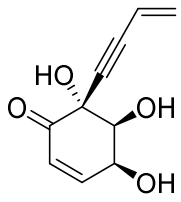



**Figure S11:** $^{1}$H-NMR spectrum of compound **7**




**7**

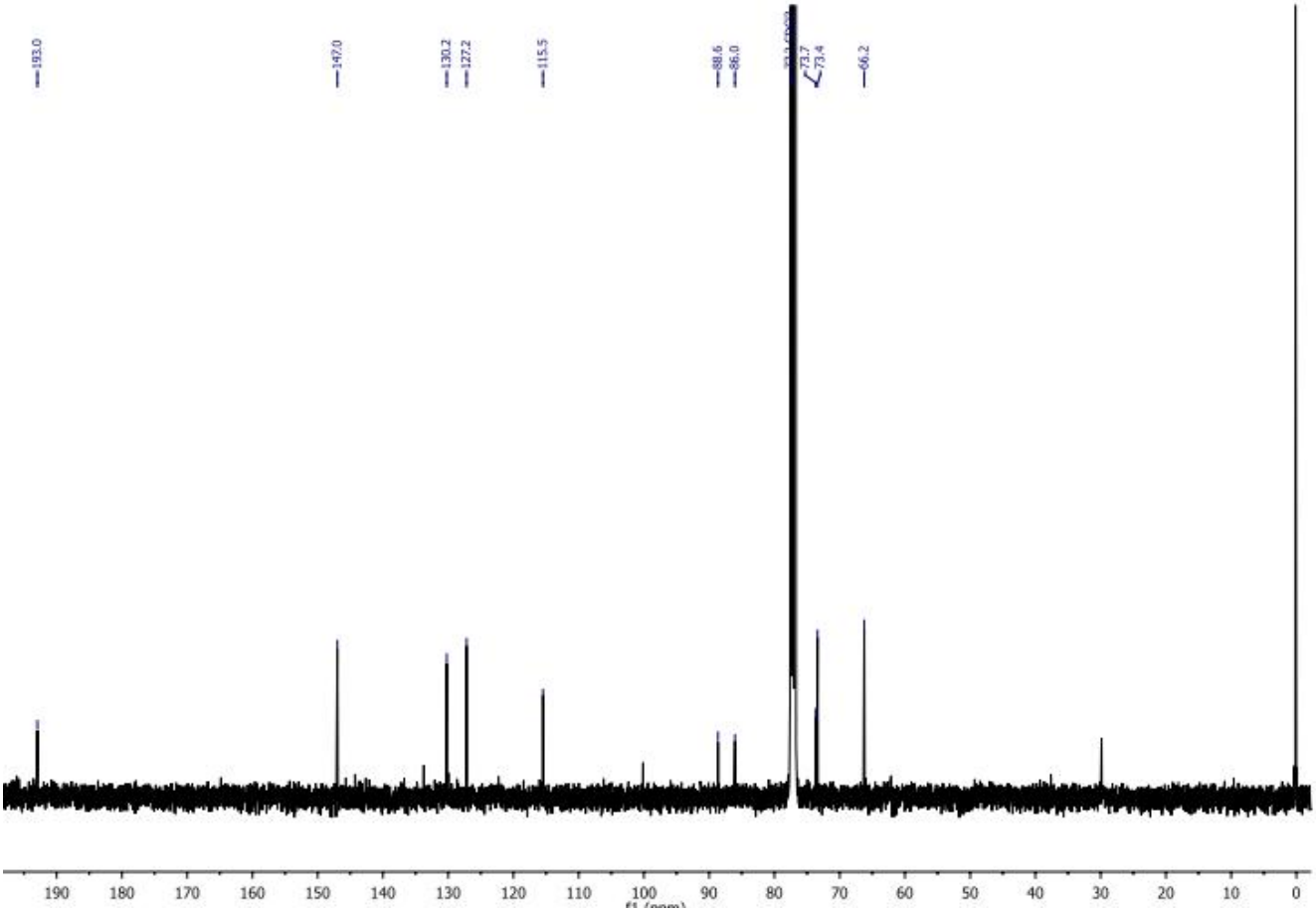



**Figure S12:** $^{13}$C-NMR spectrum of compound **7**

X-Ray Diffraction crystal structure for compound **6**

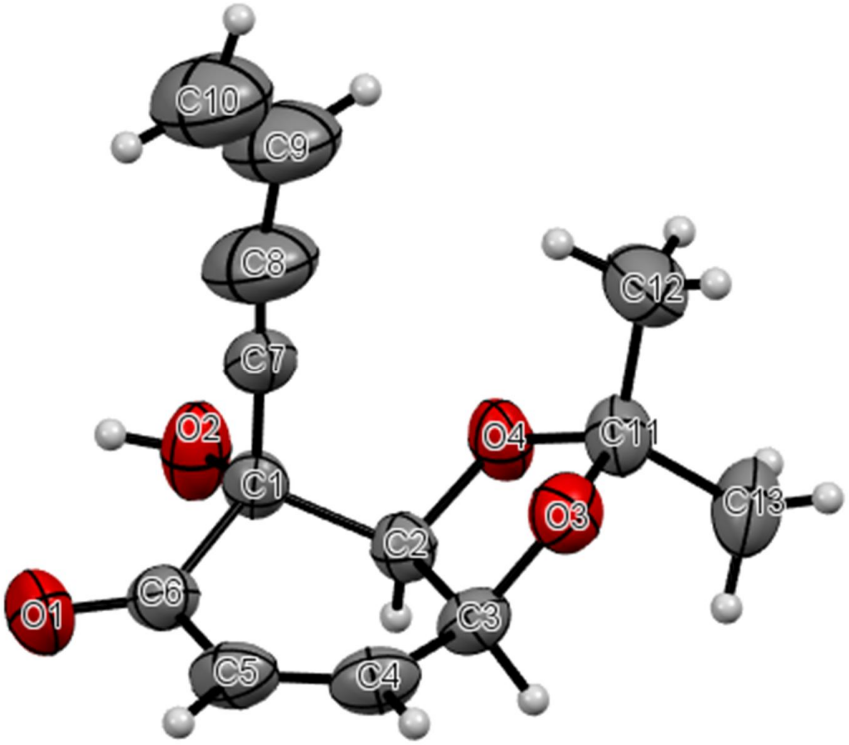



**Figure S13**: ORTEP plot of Compound **6** with atom labelling scheme

**Table S1:** Sample, crystal data, data collection and structure refinement for compound **6**.

| | | |
|---|---|---|
| **Empirical formula** | C13 H14 O4 | |
| **Formula weight** | 234.24 | |
| **Temperature** | 298(2) K | |
| **Wavelength** | 1.54178 Å | |
| **Crystal system** | Monoclinic | |
| **Space group** | $P2_1$ | |
| **Unit cell dimensions** | a = 8.9464(3) Å | □= 90°. |
| | b = 6.8743(2) Å | □= 90.100(2)°. |
| | c = 9.9114(3) Å | □ = 90°. |
| **Volume** | 609.55(3) $Å^3$ | |
| **Z** | 2 | |
| **Density (calculated)** | 1.276 $Mg/m^3$ | |
| **Absorption coefficient** | 0.785 $mm^{-1}$ | |
| **F(000)** | 248 | |
| **Crystal size** | 0.179 x 0.128 x 0.042 $mm^3$ | |
| **Theta range for data collection** | 4.461 to 72.659°. | |
| **Index ranges** | -11<=h<=11, -8<=k<=8, -12<=l<=12 | |
| **Reflections collected** | 22280 | |
| **Independent reflections** | 2418 [R(int) = 0.0626] | |
| **Completeness to theta = 67.679°** | 100.0 % | |
| **Absorption correction** | Semi-empirical from equivalents | |
| **Max. and min. transmission** | 0.968 and 0.871 | |
| **Refinement method** | Full-matrix least-squares on $F^2$ | |
| **Data / restraints / parameters** | 2418 / 35 / 180 | |
| **Goodness-of-fiton $F^2$** | 1.123 | |
| **Final R indices [I>2sigma(I)]** | R1 = 0.0471, wR2 = 0.1093 | |
| **R indices (all data)** | R1 = 0.0605, wR2 = 0.1167 | |
| **Absolute structure parameter** | -0.19(14) | |
| **Extinction coefficient** | 0.020(3) | |

| | | |
|---|---|---|
| **Largest diff. peak and hole** | 0.172 and -0.205 e.Å$^{-3}$ | |

**Table S2:** Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for compound **6**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(3) | 5463(3) | 6198(4) | 8052(2) | 53(1) |
| C(11) | 6033(4) | 8098(6) | 7809(4) | 52(1) |
| O(4) | 5058(3) | 8902(4) | 6782(3) | 54(1) |
| C(2) | 4252(4) | 7368(5) | 6169(3) | 42(1) |
| C(1) | 2566(4) | 7632(5) | 6351(4) | 44(1) |
| O(2) | 2138(3) | 9132(4) | 5466(3) | 65(1) |
| C(6) | 1763(4) | 5712(5) | 5989(4) | 50(1) |
| O(1) | 615(3) | 5774(5) | 5340(3) | 76(1) |
| C(5) | 2437(5) | 3933(6) | 6516(4) | 57(1) |
| C(4) | 3842(5) | 3879(6) | 6939(4) | 56(1) |
| C(3) | 4894(4) | 5531(5) | 6790(3) | 45(1) |
| C(7) | 2153(4) | 8043(6) | 7754(4) | 58(1) |
| C(8) | 1717(12) | 8260(30) | 8871(7) | 69(1) |
| C(9) | 1641(7) | 8782(11) | 10308(6) | 74(1) |
| C(10) | 479(8) | 8263(14) | 10986(7) | 98(2) |
| C(8B) | 1920(30) | 8360(70) | 8923(13) | 69(1) |
| C(9B) | 882(13) | 8390(30) | 10068(11) | 73(2) |
| C(10B) | 1424(19) | 8500(30) | 11272(10) | 79(3) |
| C(13) | 7605(4) | 8064(8) | 7269(4) | 70(1) |
| C(12) | 5875(6) | 9265(8) | 9080(5) | 82(2) |

**Table S3:** Bond lengths [Å] and angles [°] for compound **6**.

| | |
|---|---|
| O(3)-C(11) | 1.422(5) |
| O(3)-C(3) | 1.425(4) |
| C(11)-O(4) | 1.449(4) |
| C(11)-C(12) | 1.500(6) |
| C(11)-C(13) | 1.506(5) |
| O(4)-C(2) | 1.414(4) |
| C(2)-C(3) | 1.517(5) |
| C(2)-C(1) | 1.530(5) |
| C(2)-H(2) | 0.9800 |
| C(1)-O(2) | 1.407(4) |
| C(1)-C(7) | 1.467(5) |
| C(1)-C(6) | 1.545(5) |
| O(2)-H(2A) | 0.8200 |
| C(6)-O(1) | 1.212(4) |
| C(6)-C(5) | 1.460(6) |
| C(5)-C(4) | 1.324(6) |
| C(5)-H(5) | 0.9300 |
| C(4)-C(3) | 1.483(5) |
| C(4)-H(4) | 0.9300 |
| C(3)-H(3) | 0.9800 |
| C(7)-C(8) | 1.184(6) |
| C(7)-C(8B) | 1.197(8) |
| C(8)-C(9) | 1.470(7) |
| C(9)-C(10) | 1.289(8) |
| C(9)-H(9) | 0.9300 |
| C(10)-H(10A) | 0.9300 |
| C(10)-H(10B) | 0.9300 |
| C(8B)-C(9B) | 1.470(7) |
| C(9B)-C(10B) | 1.289(8) |
| C(9B)-H(9B) | 0.9300 |
| C(10B)-H(10C) | 0.9300 |
| C(10B)-H(10D) | 0.9300 |
| C(13)-H(13A) | 0.9600 |
| C(13)-H(13B) | 0.9600 |
| C(13)-H(13C) | 0.9600 |
| C(12)-H(12A) | 0.9600 |
| C(12)-H(12B) | 0.9600 |
| C(12)-H(12C) | 0.9600 |
| C(11)-O(3)-C(3) | 105.9(3) |
| O(3)-C(11)-O(4) | 104.7(3) |
| O(3)-C(11)-C(12) | 108.3(3) |
| O(4)-C(11)-C(12) | 109.2(3) |
| O(3)-C(11)-C(13) | 112.4(3) |
| O(4)-C(11)-C(13) | 108.5(3) |
| C(12)-C(11)-C(13) | 113.3(4) |
| C(2)-O(4)-C(11) | 108.9(3) |
| O(4)-C(2)-C(3) | 104.7(3) |
| O(4)-C(2)-C(1) | 111.3(3) |
| C(3)-C(2)-C(1) | 115.1(3) |
| O(4)-C(2)-H(2) | 108.5 |
| C(3)-C(2)-H(2) | 108.5 |
| C(1)-C(2)-H(2) | 108.5 |
| O(2)-C(1)-C(7) | 112.4(3) |
| O(2)-C(1)-C(2) | 106.3(3) |
| C(7)-C(1)-C(2) | 112.6(3) |
| O(2)-C(1)-C(6) | 110.9(3) |
| C(7)-C(1)-C(6) | 105.5(3) |
| C(2)-C(1)-C(6) | 109.3(3) |
| C(1)-O(2)-H(2A) | 109.5 |
| O(1)-C(6)-C(5) | 124.7(4) |
| O(1)-C(6)-C(1) | 119.1(4) |
| C(5)-C(6)-C(1) | 116.2(3) |
| C(4)-C(5)-C(6) | 121.9(4) |
| C(4)-C(5)-H(5) | 119.1 |
| C(6)-C(5)-H(5) | 119.1 |
| C(5)-C(4)-C(3) | 123.3(4) |
| C(5)-C(4)-H(4) | 118.3 |
| C(3)-C(4)- | 118.3 |

| | |
|---|---|
| H(4) | |
| O(3)-C(3)-C(4) | 112.6(3) |
| O(3)-C(3)-C(2) | 102.9(3) |
| C(4)-C(3)-C(2) | 116.0(3) |
| O(3)-C(3)-H(3) | 108.3 |
| C(4)-C(3)-H(3) | 108.3 |
| C(2)-C(3)-H(3) | 108.3 |
| C(8)-C(7)-C(1) | 174.2(7) |
| C(8B)-C(7)-C(1) | 175.2(15) |
| C(7)-C(8)-C(9) | 162.3(10) |
| C(10)-C(9)-C(8) | 118.5(7) |
| C(10)-C(9)-H(9) | 120.8 |
| C(8)-C(9)-H(9) | 120.8 |
| C(9)-C(10)-H(10A) | 120.0 |
| C(9)-C(10)-H(10B) | 120.0 |
| H(10A)-C(10)-H(10B) | 120.0 |
| C(7)-C(8B)-C(9B) | 149(2) |
| C(10B)-C(9B)-C(8B) | 118.6(7) |
| C(10B)-C(9B)-H(9B) | 120.7 |
| C(8B)-C(9B)-H(9B) | 120.7 |
| C(9B)-C(10B)-H(10C) | 120.0 |
| C(9B)-C(10B)-H(10D) | 120.0 |
| H(10C)-C(10B)-H(10D) | 120.0 |
| C(11)-C(13)-H(13A) | 109.5 |
| C(11)-C(13)-H(13B) | 109.5 |
| H(13A)-C(13)-H(13B) | 109.5 |
| C(11)-C(13)-H(13C) | 109.5 |
| H(13A)-C(13)-H(13C) | 109.5 |
| H(13B)-C(13)-H(13C) | 109.5 |
| C(11)-C(12)-H(12A) | 109.5 |
| C(11)-C(12)-H(12B) | 109.5 |
| H(12A)-C(12)-H(12B) | 109.5 |
| C(11)-C(12)-H(12C) | 109.5 |
| H(12A)-C(12)-H(12C) | 109.5 |
| H(12B)-C(12)-H(12C) | 109.5 |

Symmetry transformations used to generate equivalent atoms:

**Table S4:** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| O(3) | 54(2) | 58(2) | 46(1) | 6(1) | -4(1) | 3(1) |
| C(11) | 43(2) | 59(2) | 53(2) | 2(2) | -6(2) | 0(2) |
| O(4) | 46(1) | 40(1) | 77(2) | 2(1) | -14(1) | -6(1) |
| C(2) | 40(2) | 40(2) | 46(2) | 1(2) | -1(1) | -2(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(1) | 42(2) | 33(2) | 56(2) | 1(2) | -4(2) | 0(2) |
| O(2) | 49(2) | 52(2) | 94(2) | 18(2) | -19(2) | 0(1) |
| C(6) | 46(2) | 44(2) | 61(2) | -13(2) | 10(2) | -6(2) |
| O(1) | 52(2) | 71(2) | 104(2) | -24(2) | -13(2) | -10(2) |
| C(5) | 67(2) | 34(2) | 70(2) | -7(2) | 16(2) | -6(2) |
| C(4) | 72(3) | 37(2) | 60(2) | 4(2) | 10(2) | 9(2) |
| C(3) | 46(2) | 42(2) | 49(2) | -1(2) | 2(2) | 8(2) |
| C(7) | 50(2) | 54(2) | 69(2) | -20(2) | 4(2) | 5(2) |
| C(8) | 61(2) | 72(2) | 73(2) | -23(2) | 7(2) | 4(2) |
| C(9) | 63(3) | 87(3) | 72(3) | -27(3) | 9(2) | -3(3) |
| C(10) | 80(4) | 129(5) | 86(4) | -26(4) | 18(3) | -18(4) |
| C(8B) | 61(2) | 72(2) | 73(2) | -23(2) | 7(2) | 4(2) |
| C(9B) | 63(3) | 81(3) | 74(3) | -24(3) | 9(3) | 1(3) |
| C(10B) | 68(6) | 92(6) | 78(6) | -21(6) | 10(5) | -2(6) |
| C(13) | 45(2) | 93(3) | 73(3) | 8(3) | -3(2) | 0(2) |
| C(12) | 74(3) | 95(4) | 77(3) | -30(3) | -3(2) | -10(3) |

**Table S5:** Hydrogen coordinates (x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for compound **6**.

| | **x** | **y** | **z** | **U(eq)** |
|---|---|---|---|---|
| H(2) | 4474 | 7365 | 5202 | 50 |
| H(2A) | 1229 | 9108 | 5360 | 98 |
| H(5) | 1865 | 2805 | 6556 | 69 |
| H(4) | 4186 | 2748 | 7351 | 67 |
| H(3) | 5738 | 5102 | 6236 | 55 |
| H(9) | 2414 | 9469 | 10718 | 89 |
| H(10A) | -286 | 7577 | 10565 | 118 |
| H(10B) | 407 | 8576 | 11896 | 118 |
| H(9B) | -145 | 8339 | 9928 | 87 |
| H(10C) | 2453 | 8559 | 11401 | 95 |
| H(10D) | 786 | 8529 | 12012 | 95 |
| H(13A) | 7655 | 7201 | 6510 | 106 |
| H(13B) | 8275 | 7619 | 7961 | 106 |
| H(13C) | 7887 | 9351 | 6993 | 106 |
| H(12A) | 6198 | 10576 | 8918 | 123 |

| | | | | |
|---|---|---|---|---|
| H(12B) | 6479 | 8696 | 9778 | 123 |
| H(12C) | 4847 | 9269 | 9357 | 123 |

**Table S6:** Torsion angles [°] for compound **6**.

| | |
|---|---|
| C(3)-O(3)-C(11)-O(4) | 33.3(3) |
| C(3)-O(3)-C(11)-C(12) | 149.7(3) |
| C(3)-O(3)-C(11)-C(13) | -84.2(3) |
| O(3)-C(11)-O(4)-C(2) | -16.7(3) |
| C(12)-C(11)-O(4)-C(2) | -132.5(3) |
| C(13)-C(11)-O(4)-C(2) | 103.5(4) |
| C(11)-O(4)-C(2)-C(3) | -5.2(3) |
| C(11)-O(4)-C(2)-C(1) | 119.7(3) |
| O(4)-C(2)-C(1)-O(2) | 74.2(3) |
| C(3)-C(2)-C(1)-O(2) | -166.9(3) |
| O(4)-C(2)-C(1)-C(7) | -49.3(4) |
| C(3)-C(2)-C(1)-C(7) | 69.6(4) |
| O(4)-C(2)-C(1)-C(6) | -166.1(3) |
| C(3)-C(2)-C(1)-C(6) | -47.2(4) |
| O(2)-C(1)-C(6)-O(1) | -21.5(5) |
| C(7)-C(1)-C(6)-O(1) | 100.4(4) |
| C(2)-C(1)-C(6)-O(1) | -138.3(3) |
| O(2)-C(1)-C(6)-C(5) | 160.8(3) |

| | |
|---|---|
| C(7)-C(1)-C(6)-C(5) | -77.3(4) |
| C(2)-C(1)-C(6)-C(5) | 44.0(4) |
| O(1)-C(6)-C(5)-C(4) | 164.0(4) |
| C(1)-C(6)-C(5)-C(4) | -18.5(5) |
| C(6)-C(5)-C(4)-C(3) | -6.5(6) |
| C(11)-O(3)-C(3)-C(4) | -161.6(3) |
| C(11)-O(3)-C(3)-C(2) | -36.0(3) |
| C(5)-C(4)-C(3)-O(3) | 120.8(4) |
| C(5)-C(4)-C(3)-C(2) | 2.7(5) |
| O(4)-C(2)-C(3)-O(3) | 25.0(3) |
| C(1)-C(2)-C(3)-O(3) | -97.5(3) |
| O(4)-C(2)-C(3)-C(4) | 148.4(3) |
| C(1)-C(2)-C(3)-C(4) | 25.9(4) |
| C(8B)-C(7)-C(8)-C(9) | 4(14) |
| C(7)-C(8)-C(9)-C(10) | -173(5) |
| C(8)-C(7)-C(8B)-C(9B) | -2(12) |
| C(7)-C(8B)-C(9B)-C(10B) | 164(7) |

Symmetry transformations used to generate equivalent atoms:

**Table S7:** Hydrogen bonds for compound **6** [Å and °].

| **D-H...A** | **d(D-H)** | **d(H...A)** | **d(D...A)** | **<(DHA)** |
|---|---|---|---|---|
| O(2)-H(2A)...O(1)#1 | 0.82 | 2.12 | 2.823(4) | 143.2 |
| O(2)-H(2A)...O(1) | 0.82 | 2.36 | 2.684(4) | 104.6 |

Symmetry transformations used to generate equivalent atoms:

#1 -x,y+1/2,-z+1