

Supporting Information

Total Synthesis of Highly Oxygenated Phomopsol B via Acid-Induced Etherification to Construct Bridged Structure

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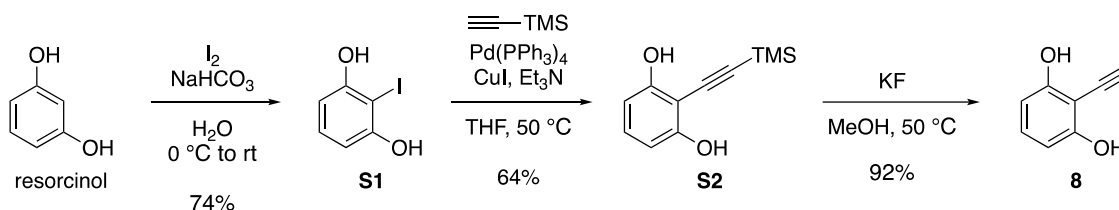
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General

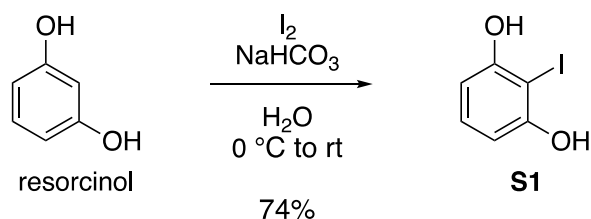
All reactions involving air- and moisture-sensitive reagents were carried out using standard syringe-septum cap techniques. Unless otherwise noted, all solvents and reagents were obtained from commercial suppliers and used without further purification. Routines monitoring of reactions were carried out Merck silica gel 60 F254 TLC plates. Column chromatography was performed on Kanto Chemical Silica Gel 60N (spherical, neutral 60–230 μm) with the solvents indicated. Melting points were taken on a Yanako MP-S3 micro melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were measured with a JASCO EZC 400S (400 MHz) spectrometer. Chemical shifts were expressed in ppm using CHCl_3 (7.26 ppm for ^1H NMR, 77.0 ppm for ^{13}C NMR) in CDCl_3 and CH_3OH (3.31 ppm for ^1H NMR, 49.0 ppm for ^{13}C NMR) in CD_3OD as internal standard. Infrared spectral measurements were carried out with a JASCO FT/IR-4700 and only noteworthy absorptions were listed. HRMS spectra measured on a Micromass LCT spectrometer. Oil bath was used in reactions that require heating and each temperature indicates oil bath temperature.

Experimental procedure

synthetic scheme of known compound **8**



2-iodobenzene-1,3-diol (**S1**)

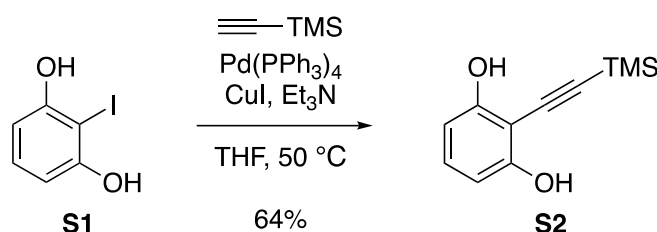


To a stirred solution of resorcinol (5.00 g, 45.5 mmol) in H_2O (50 mL) were added I_2 (17.3 g, 68.1

mmol) and NaHCO₃ (4.20 g, 50.0 mmol) at 0 °C under Ar atmosphere, and the mixture was stirred for 1 h at room temperature. The reaction mixture was extracted with AcOEt (twice). The combined organic layers were washed with brine, dried over MgSO₄ and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (AcOEt, 100%) to afford **S1** (7.94 g, 74%) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 5.28 (s, 2H), 6.56 (d, J = 8.2 Hz, 2H), 7.11 (t, J = 8.2 Hz, 1H).

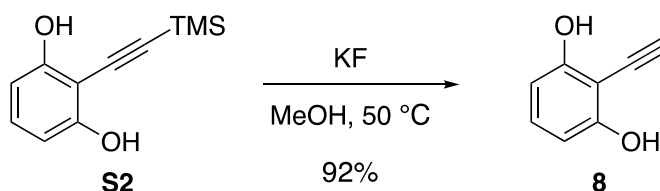
2-((trimethylsilyl)ethynyl)benzene-1,3-diol (**S2**)



To a stirred solution of **S1** (3.00 g, 12.7 mmol) in THF (90 mL) were added CuI (483 mg, 2.54 mmol), Pd(PPh₃)₄ (1.00 g, 0.865 mmol), trimethylsilylacetylene (3.80 mL, 26.9 mmol) and Et₃N (8.80 mL, 63.1 mmol) at room temperature under Ar atmosphere, and the mixture was stirred for 12 h at 50 °C. The reaction mixture was quenched with sat. NH₄Cl aq. and extracted with AcOEt (twice). The combined organic layers were washed with brine, dried over MgSO₄ and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (Hexane-AcOEt, 7:1) to afford **S2** (1.69 g, 64%) as a brown solid.

¹H NMR (400 MHz, CDCl₃) δ 0.30 (s, 9H), 5.58 (s, 2H), 6.51 (d, J = 8.2 Hz, 2H), 7.12 (t, J = 8.2 Hz, 1H).

2-ethynylbenzene-1,3-diol (**8**)

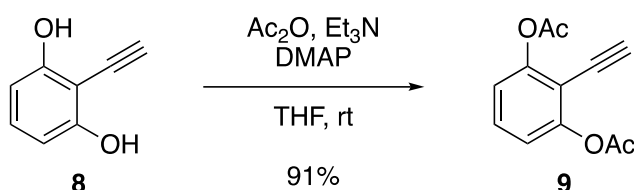


To a stirred solution of **S2** (1.32 g, 6.40 mmol) in MeOH (140 mL) was added KF (744 mg, 12.8 mmol) at room temperature, and the mixture was stirred for 0.5 h at 50 °C. The reaction mixture

was quenched with sat. NH_4Cl aq. and extracted with AcOEt (twice). The combined organic layers were washed with brine, dried over MgSO_4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (Hexane-AcOEt, 3:1) to afford **8** (790 mg, 92%) as a brown solid.

^1H NMR (400 MHz, CDCl_3) δ 3.81 (s, 1H), 5.61 (s, 2H), 6.52 (d, $J = 8.2$ Hz, 2H), 7.15 (t, $J = 8.2$ Hz, 1H).

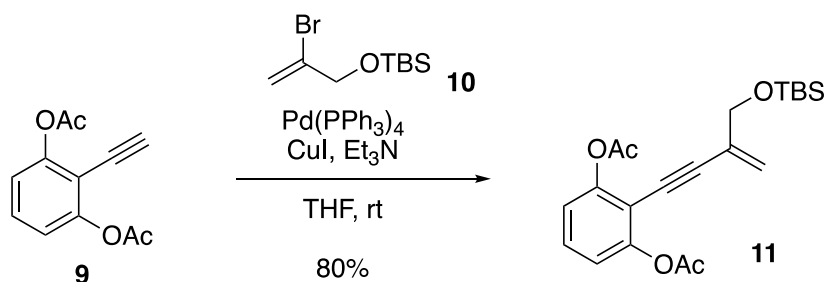
2-ethynyl-1,3-phenylene diacetate (**9**)



To a stirred solution of **8** (578 mg, 4.31 mmol) in THF (10 mL) were added DMAP (105 mg, 0.859 mmol), Ac_2O (1.60 mL, 16.9 mmol) and Et_3N (1.20 mL, 8.61 mmol) at room temperature under Ar atmosphere, and the mixture was stirred for 20 min at the same temperature. The reaction mixture was quenched with H_2O and extracted with AcOEt (twice). The combined organic layers were washed with brine, dried over MgSO_4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (Hexane-AcOEt, 3:1) to afford **9** (854 mg, 91%) as a white solid.

m.p. 105-108 $^\circ\text{C}$; IR (KBr) 3282, 1770, 1607, 1456, 1025, 903, 830, 745, 664 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.34 (s, 6H), 3.41 (s, 1H), 7.03 (d, $J = 8.2$ Hz, 2H), 7.37 (t, $J = 8.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.8(2C), 85.6(2C), 119.9(3C), 129.7(2C), 152.9(2C), 168.5(2C); HRMS (ESI-TOF) Calcd for $\text{C}_{12}\text{H}_{10}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ 241.0471. Found 241.0475.

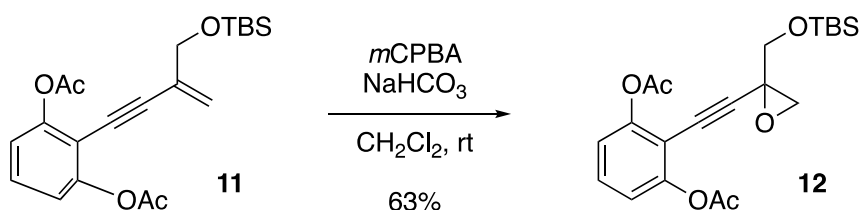
2-(3-(((*tert*-butyldimethylsilyl)oxy)methyl)but-3-en-1-yn-1-yl)-1,3-phenylene diacetate (**11**)



To a stirred solution of **9** (1.41 g, 6.46 mmol) in THF (30 mL) were added CuI (246 mg, 1.29 mmol), Pd(PPh₃)₄ (523 mg, 0.453 mmol), **10** (1.90 g, 7.76 mmol) and Et₃N (2.70 mL, 19.4 mmol) at room temperature under Ar atmosphere, and the mixture was stirred for 10 min at the same temperature. The reaction mixture was quenched with sat. NH₄Cl aq. and extracted with AcOEt (twice). The combined organic layers were washed with brine, dried over MgSO₄ and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (Hexane-AcOEt, 7:1) to afford **11** (2.03 g, 81%) as a yellow oil.

IR (neat) 2930, 2857, 1775, 1604, 1460, 1369, 1186, 1113, 1029, 838 779, cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.10 (s, 6H), 0.93 (s, 9H), 2.32 (s, 6H), 4.20 (s, 2H), 5.53 (s, 1H), 5.70 (s, 1H), 7.02 (d, J = 8.2 Hz, 2H), 7.34 (t, J = 8.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ -5.7 (2C), 18.1, 20.4 (2C), 25.5(3C), 64.3, 80.1, 96.3, 111.9, 119.5(2C), 119.9, 128.8, 130.1, 151.9(2C), 168.1 (2C); HRMS (ESI-TOF) Calcd for C₂₁H₂₈O₅NaSi [M+Na]⁺ 411.1598. Found 411.1597.

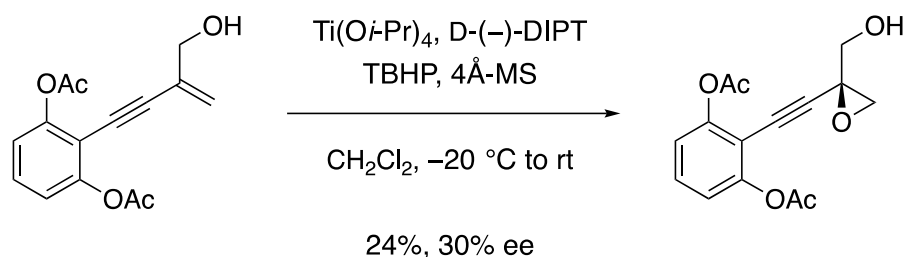
2-((2-(((*tert*-butyldimethylsilyl)oxy)methyl)oxiran-2-yl)ethynyl)-1,3-phenylene diacetate (**12**)



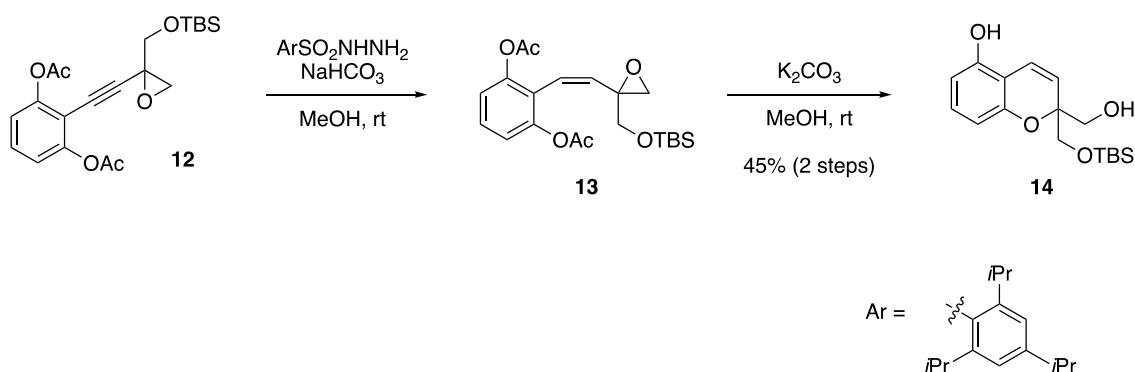
To a stirred solution of **11** (1.67 g, 4.29 mmol) in CH₂Cl₂ (25 mL) were added *m*CPBA (2.20 g, 12.7 mmol) and NaHCO₃ (2.20 g, 26.2 mmol) at room temperature under Ar atmosphere, and the mixture was stirred for 2 h at the same temperature. The reaction mixture was quenched with sat. NaHCO₃ aq. and filtrated with celite (CHCl₃), and then extracted with CHCl₃ (twice). The combined organic layers were washed with brine, dried over MgSO₄ and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (Hexane-AcOEt, 5:1) to afford **12** (1.08 g, 63%) as a yellow oil.

IR (KBr) 2930, 2857, 1777, 1608, 1461, 1370, 1117, 1030, 838, 781 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.08 (d, J = 4.6 Hz, 6H) 0.89 (s, 9H), 2.32 (s, 6H), 2.99 (d, J = 5.9 Hz, 1H), 3.12 (d, J = 6.4 Hz, 1H), 3.93 (dd, J = 21.5, 11.9 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 7.35 (t, J = 8.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ -5.45, -5.37, 18.3, 20.8(2C), 25.8(3C), 51.3, 63.5, 74.2, 95.5, 111.2, 119.8(2C), 129.6, 152.6(2C), 168.4(2C); HRMS (ESI-TOF) Calcd for C₂₁H₂₈O₆NaSi [M+Na]⁺ 427.1547. Found 427.1547.

Asymmetric epoxidation using the corresponding allyl alcohol (removed TBS group) was attempted, but it resulted in unsatisfactory yield and poor enantioselectivity.



2-(((*tert*-butyldimethylsilyl)oxy)methyl)-2-(hydroxymethyl)-2*H*-chromen-5-ol (**14**)

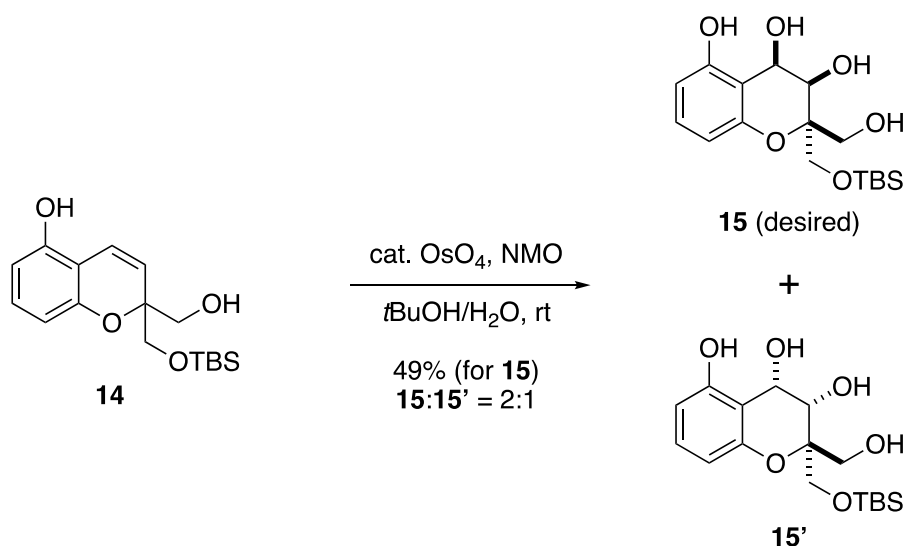


To a stirred solution of **12** (970 mg, 2.40 mmol) in MeOH (10 mL) were added $\text{ArSO}_2\text{NHNH}_2$ (2.15 g, 7.20 mmol) and NaHCO_3 (670 mg, 7.92 mmol) at room temperature under Ar atmosphere, and the mixture was stirred for 3 h at the same temperature. The reaction mixture was quenched with sat. NaHCO_3 aq. and extracted with AcOEt (twice). The combined organic layers were washed with brine, dried over MgSO_4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (Hexane-AcOEt, 5:1) to afford **13** (695 mg, including impurities) as a yellow oil.

To a stirred solution of **13** in MeOH (10 mL) was added K_2CO_3 (920 mg, 6.66 mmol) at room temperature under Ar atmosphere, and the mixture was stirred for 0.5 h at the same temperature. The reaction mixture was quenched with H_2O and extracted with AcOEt (twice). The combined organic layers were washed with brine, dried over MgSO_4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (Hexane-AcOEt, 3:1) to afford **14** (276 mg, 45% in 2 steps) as a yellow oil.

IR (neat) 3347, 2929, 2857, 1635 1586, 1462, 1257, 1085, 838, 755, 667 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.04 (d, $J = 10.1$ Hz, 6H), 0.88 (s, 9H), 2.57 (s, 1H), 3.73 (d, $J = 10.5$ Hz, 1H), 3.86-3.83 (m, 3H), 5.60 (d, $J = 10.1$ Hz, 1H), 6.31 (d, $J = 7.8$ Hz, 1H), 6.39 (d, $J = 8.2$ Hz, 1H), 6.83 (d, $J = 10.1$ Hz, 1H), 6.92 (t, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ -5.24, -5.20, 18.5, 26.1(3C), 65.5, 65.7, 80.6, 108.5, 109.1, 109.7, 120.2, 122.2, 129.6, 152.0, 153.7; HRMS (ESI-TOF) Calcd for $\text{C}_{17}\text{H}_{26}\text{O}_4\text{NaSi}$ $[\text{M}+\text{Na}]^+$ 345.1493. Found 345.1493.

(2*S*,3*R*,4*R*)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-2-(hydroxymethyl)chromane-3,4,5-triol
(**15**)



To a stirred solution of **14** (773 mg, 2.39 mmol) in *t*BuOH (15 mL)/ H_2O (5 mL) were added NMO (843 mg, 7.19 mmol) and OsO_4 (4% in H_2O , 0.300 mL, 0.0539 mmol) at room temperature under Ar atmosphere, and the mixture was stirred for 12 h at the same temperature. The reaction mixture was quenched with sat. $\text{Na}_2\text{S}_2\text{O}_3$ aq. and extracted with CHCl_3 (twice). The combined organic layers were washed with brine, dried over MgSO_4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (Hexane-AcOEt, 1:1) to afford **15** (420 mg, 49%) as a yellow oil and **15'** as a yellow oil.

Data for **15**

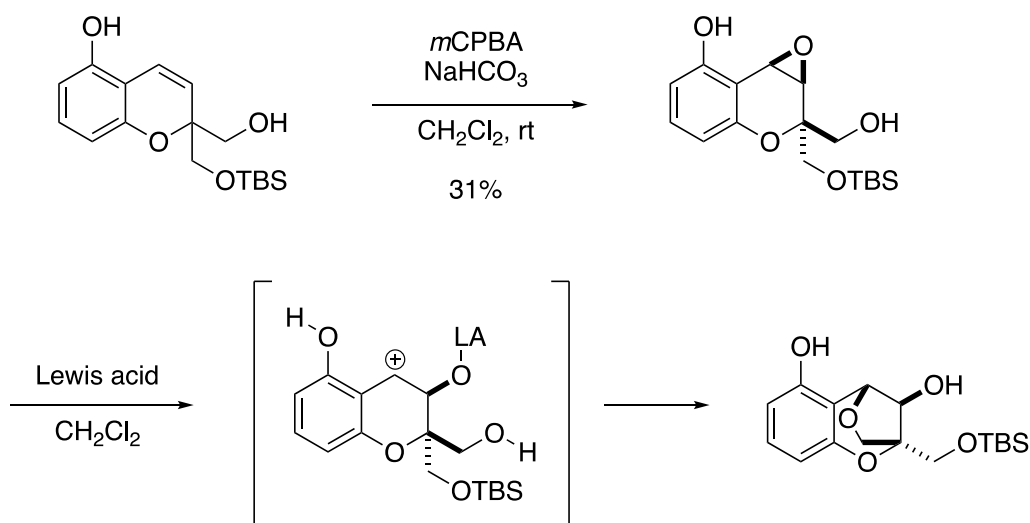
IR (neat) 3365, 2929, 2857, 1590, 1470, 1390, 1255, 1033, 837, 780, 667 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.03 (d, $J = 11.4$ Hz, 6H), 0.87 (s, 9H), 3.61 (d, $J = 10.5$ Hz, 1H), 3.71 (d, $J = 11.0$ Hz, 1H), 3.93 (d, $J = 12.3$ Hz, 1H), 4.11 (d, $J = 12.3$ Hz, 1H), 4.34 (d, $J = 4.6$ Hz, 1H), 5.02 (d, $J = 4.6$ Hz, 1H), 6.39 (d, $J = 8.2$ Hz, 1H), 6.50 (d, $J = 7.8$ Hz, 1H), 7.07 (t, $J = 8.2$ Hz, 1H); ^{13}C

NMR (100 MHz, CDCl₃) δ -5.69, -5.67, 18.0, 25.7(3C), 63.7, 64.6, 65.3, 67.0, 79.2, 107.9, 108.2, 109.4, 130.1, 152.6, 158.1; HRMS (ESI-TOF) Calcd for C₁₇H₂₈O₆NaSi [M+Na]⁺ 379.1547. Found 379.1544.

Data for **15'**

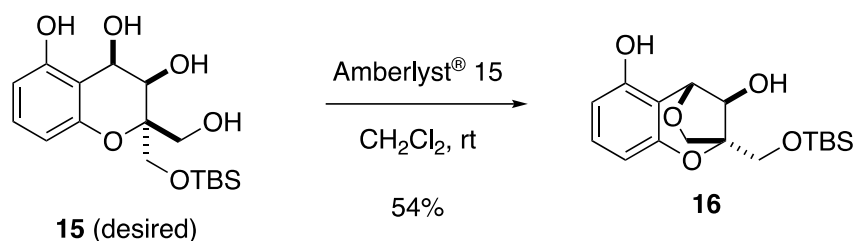
IR (neat) 3347, 2930, 2857, 1591, 1469, 1391, 1255, 1031, 836, 779, 667 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ -0.04 (s, 3H), 0.09 (s, 3H), 0.83 (s, 9H), 1.80 (d, J = 26.5 Hz, 1H), 2.40 (d, J = 23.3 Hz, 1H), 3.49-3.45 (m, 1H), 3.65 (d, J = 11.9 Hz, 1H), 3.77 (d, J = 11.9 Hz, 1H), 4.01 (s, 2H), 4.26 (s, 2H), 4.96 (s, 1H), 6.38 (d, J = 8.2 Hz, 1H), 6.48 (dd, J = 8.2, 1.8 Hz, 1H), 7.06 (td, J = 8.1, 2.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ -6.21, -6.16, 17.8 25.3(3C), 63.0, 64.0, 64.1, 66.5, 78.7, 108.0, 108.3, 108.6, 129.8, 152.7, 157.0; HRMS (ESI-TOF) Calcd for C₁₇H₂₈O₆NaSi [M+Na]⁺ 379.1547. Found 379.1547.

Hydroxyl group-directed epoxidation with compound **14** was also conducted, but low yield. In addition, exposure of the corresponding epoxide to some Lewis acids failed to construct the desired bridged structure.



entry	Lewis acid	temp.	result
1	BF ₃ ·OEt ₂	-78 °C	decomposition
2	TiCl ₄	-78 °C	decomposition
3	AlCl ₃	-78 °C to rt	no reaction
4	BCl ₃	-78 °C to rt	no reaction

(2*S*,5*R*,10*R*)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-2,3-dihydro-5*H*-2,5-methanobenzo[*e*][1,4]dioxepine-6,10-diol (**15**)

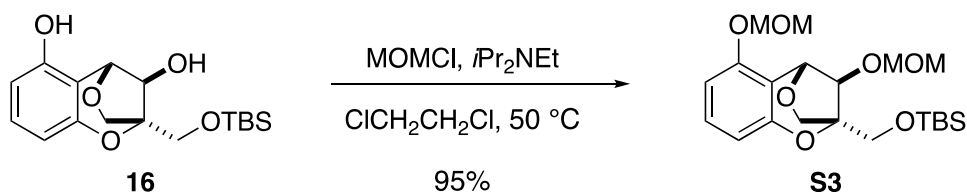


To a stirred solution of **15** (24.1 mg, 0.0670 mmol) in CH_2Cl_2 (2 mL) was added Amberlyst 15 (6.5 mg) at room temperature under Ar atmosphere, and the mixture was stirred for 19 h at the same temperature. The insoluble material was removed by filtration, and the filtrate was concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (Hexane-AcOEt, 2:1) to afford **16** (12.2 mg, 54%) as a white solid.

m.p. 155-160 °C; IR (KBr) 3400, 2928, 2858, 1472, 1248, 1214, 1100 1033, 838, 780, 669 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.14 (s, 6H), 0.92 (s, 9H), 3.22 (d, $J = 4.6$ Hz, 1H), 4.06 (d, $J = 11.4$ Hz, 1H), 4.23-4.13 (m, 3H), 4.49 (d, $J = 4.1$ Hz, 1H), 5.19 (s, 1H), 5.43 (s, 1H), 6.34 (q, $J = 8.4$ Hz, 2H), 7.01 (t, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ -5.43, -5.37, 18.3, 25.8(3C), 62.8, 73.6, 74.1(2C), 87.1, 108.0, 108.2, 111.4, 130.5, 152.9, 154.0; HRMS (ESI-TOF) Calcd for $\text{C}_{17}\text{H}_{26}\text{O}_5\text{NaSi}$ $[\text{M}+\text{Na}]^+$ 361.1442 Found 361.1441.

The structure of compound **16** was determined by X-ray crystallographic analysis (CCDC2298603, see page 34)

((*2R*,5*R*,10*R*)-6,10-bis(methoxymethoxy)-5*H*-2,5-methanobenzo[*e*][1,4]dioxepin-2(3*H*)-yl)methyl(*tert*-butyl)dimethylsilane (**S3**)

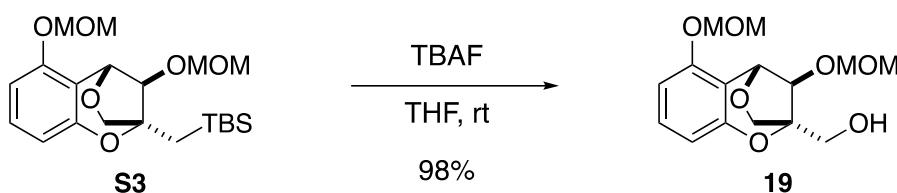


To a stirred solution of **16** (29.5 mg, 0.0870 mmol) in $\text{CICH}_2\text{CH}_2\text{Cl}$ (3 mL) were added MOMCl

(0.200 mL, 2.63 mmol) and *i*Pr₂NEt (0.400 mL, 2.35 mmol) at 50 °C under Ar atmosphere, and the mixture was stirred for 12 h at the same temperature. The reaction mixture was quenched with H₂O and extracted with CHCl₃ (twice). The combined organic layers were washed with brine, dried over MgSO₄ and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (Hexane-AcOEt, 3:1) to afford **14** (35.2 mg, 95%) as a yellow oil.

IR (neat) 2952, 2856, 1607, 1461, 1258, 1217, 1105, 1043, 838, 778, 675 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 0.12 (d, J = 3.4 Hz, 6H), 0.90 (s, 9H), 3.47 (d, J = 15.6 Hz, 6H), 4.00-3.95 (m, 2H), 4.11 (q, J = 10.8 Hz, 2H), 4.48 (s, 1H), 4.85 (s, 2H), 5.18 (dd, J = 10.5, 6.9 Hz, 2H), 5.33 (s, 1H), 6.46 (d, J = 8.2 Hz, 1H), 6.62 (d, J = 7.8 Hz, 1H), 7.09 (t, J = 8.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ -5.58 -5.34, 18.0, 25.5(3C), 55.4, 56.0, 61.5, 71.6, 74.2, 76.0, 88.5, 94.6, 94.9, 106.2, 109.1, 113.6, 130.1, 153.7, 153.9; HRMS (ESI-TOF) Calcd for C₂₁H₃₄O₇NaSi [M+Na]⁺ 449.1966. Found 449.1969.

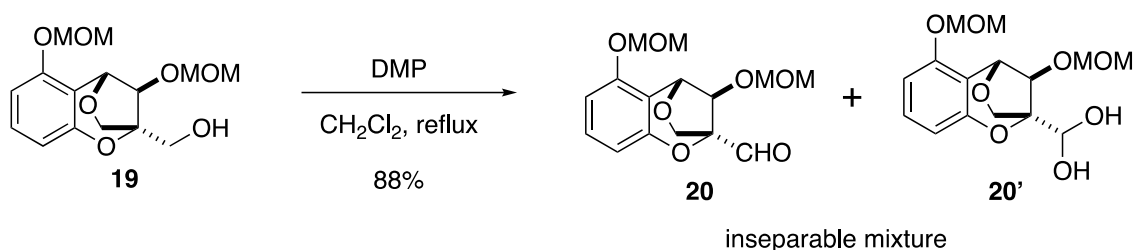
((2*R*,5*R*,10*R*)-6,10-bis(methoxymethoxy)-5*H*-2,5-methanobenzo[*e*][1,4]dioxepin-2(3*H*-yl)methanol (**19**))



To a stirred solution of **S3** (59.0 mg, 0.138 mmol) in THF (3 mL) was added TBAF (1.00 M in THF, 0.270 mL, 0.270 mmol) at room temperature under Ar atmosphere, and the mixture was stirred for 1 h at the same temperature. The reaction mixture was quenched with sat. NH₄Cl aq. and extracted with AcOEt (twice). The combined organic layers were washed with brine, dried over MgSO₄ and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (Hexane-AcOEt, 1:1) to afford **14** (42.0 mg, 98%) as a yellow oil.

IR (neat) 3453, 2949, 2827 1607, 1478, 1269, 1216, 1043, 854, 779, 673 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 2.43 (dd, J = 8.2, 5.5 Hz, 1H), 3.48 (d, J = 9.6 Hz, 6H), 4.07-3.93 (m, 3H), 4.16 (d, J = 10.5 Hz, 1H), 4.51 (s, 1H), 4.86 (dd, J = 22.0, 6.4 Hz, 2H), 5.18 (s, 2H), 5.38 (s, 1H), 6.49 (d, J = 8.2 Hz, 1H), 6.66 (d, J = 8.2 Hz, 1H), 7.11 (t, J = 8.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 55.8, 56.3, 61.0, 71.8, 74.1, 77.1, 88.4, 94.9, 95.5, 107.1, 109.5, 113.8, 130.6, 153.7, 154.1; HRMS (ESI-TOF) C₁₅H₂₀O₇Na [M+Na]⁺ 335.1101. Found 335.1102.

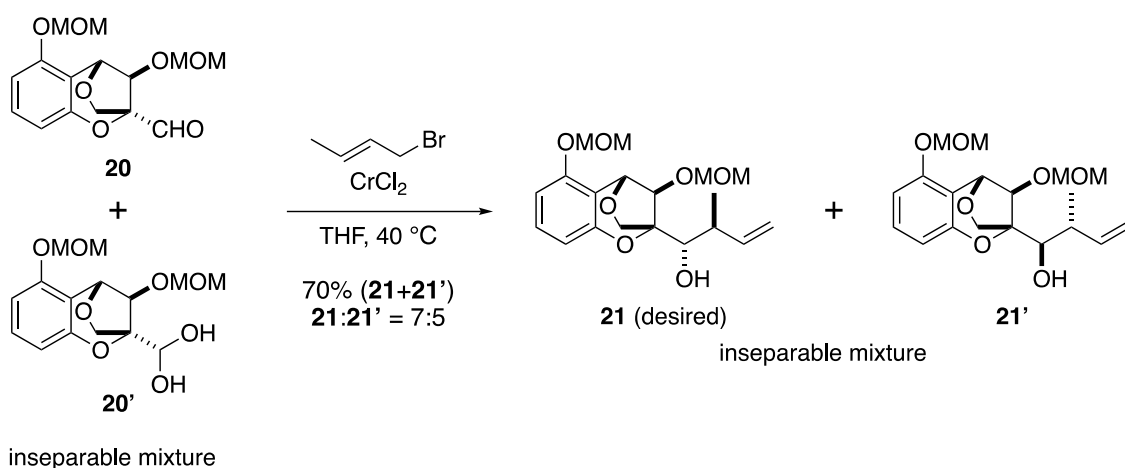
(2*R*,5*R*,10*R*)-6,10-bis(methoxymethoxy)-5*H*-2,5-methanobenzo[*e*][1,4]dioxepine-2(3*H*)-carbaldehyde (**20**)



To a stirred solution of **19** (16.0 mg, 0.0512 mmol) in CH₂Cl₂ (1 mL) was added Dess-Martin Periodinane (DMP) (10% in CH₂Cl₂, 0.600 ml, 0.0600 mmol) at 40 °C (reflux) under Ar atmosphere, and the mixture was stirred for 1 h at the same temperature. The reaction mixture was quenched with sat. Na₂S₂O₃ aq./sat. NaHCO₃ aq. (2:3) and extracted with CHCl₃ (twice). The combined organic layers were washed with brine, dried over MgSO₄ and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (Hexane-AcOEt, 1:1) to afford an inseparable mixture of **20** and hydrated product **20'** (13.6 mg, 88%) as a yellow oil.

IR (neat) 3433, 2951, 1737, 1592, 1479, 1257, 1217, 1039, 853, 776 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.50-3.41 (m, 6H), 4.31-3.97 (m, 2H), 4.92-4.45 (m, 3H), 5.48-5.17 (m, 3H), 6.72-6.43 (m, 2H), 7.18-7.08 (m, 1H), 9.92 (s, 0.3H); ¹³C NMR (100 MHz, CDCl₃) δ 55.9, 56.0, 56.3, 72.4, 73.2, 78.6, 88.3, 89.8, 94.9, 95.4, 106.9, 107.7, 109.6, 113.1, 130.6, 131.0, 152.5, 154.1, 154.2, 194.7; HRMS (ESI-TOF) C₁₅H₁₈O₇Na [M+Na]⁺ 333.0945. Found 333.0947.

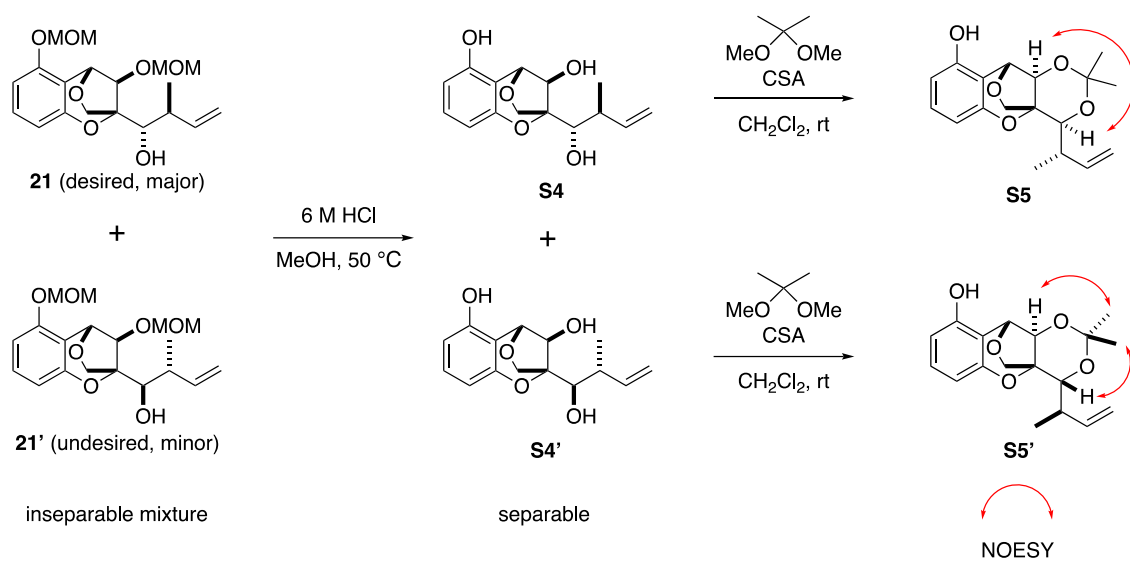
(1*S*,2*S*)-1-((2*S*,5*R*,10*R*)-6,10-bis(methoxymethoxy)-5*H*-2,5-methanobenzo[*e*][1,4]dioxepin-2(3*H*)-yl)-2-methylbut-3-en-1-ol (**21**)



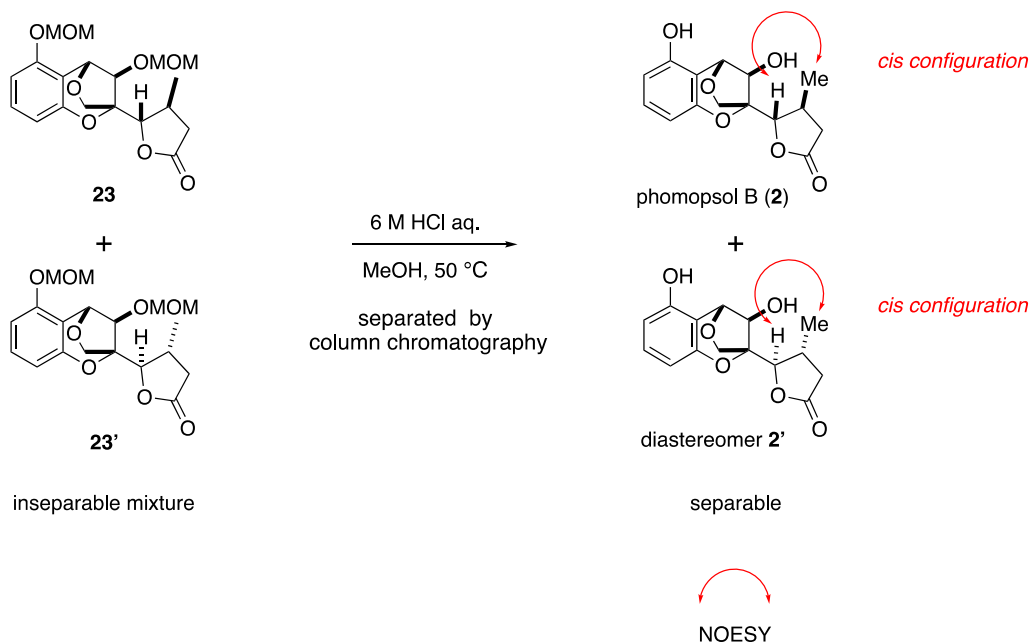
To a stirred solution of CrCl_2 (70.0 mg, 0.570 mmol) in THF (1 mL) were added the inseparable mixture of **20** and hydrated product **20'** (14.4 mg, 0.0464 mmol) and crotylbromide (30.0 μL , 0.230 mmol) at $0\text{ }^\circ\text{C}$ under Ar atmosphere, and the mixture was stirred at room temperature and then $40\text{ }^\circ\text{C}$ for 16 h. The reaction mixture was quenched with H_2O and extracted with AcOEt (twice). The combined organic layers were washed with brine, dried over MgSO_4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (Hexane-AcOEt, 3:1) to afford an inseparable mixture of **21** and **21'** (11.8 mg, 70%) as a yellow oil.

IR (neat) 3492, 2916, 1731, 1607, 1593, 1479, 1404, 1257, 1216, 1051, 756, 666 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.15 (d, $J = 6.9\text{ Hz}$, 3H), 1.21 (d, $J = 6.9\text{ Hz}$, 3H), 2.58-2.49 (m, 2H), 2.89-2.80 (m, 2H) 3.49 (d, $J = 4.6\text{ Hz}$, 12H), 3.92 (q, $J = 4.7\text{ Hz}$, 1H), 4.09 (d, $J = 10.1\text{ Hz}$, 1H), 4.20 (t, $J = 10.1\text{ Hz}$, 3H), 4.31 (d, $J = 10.5\text{ Hz}$, 1H), 4.45 (s, 1H), 4.55 (s, 1H), 4.78 (d, $J = 6.9\text{ Hz}$, 1H), 4.87 (s, 2H), 4.94 (d, $J = 6.9\text{ Hz}$, 1H), 5.18-5.06 (m, 8H), 5.36 (d, $J = 22.9\text{ Hz}$, 2H), 6.10-5.94 (m, 2H), 6.48 (d, $J = 7.8\text{ Hz}$, 2H), 6.65 (q, $J = 4.1\text{ Hz}$, 2H), 7.11 (q, $J = 7.3\text{ Hz}$, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.7, 18.1, 39.4, 40.1, 55.9(2C), 56.2(2C) 56.3(2C), 70.4, 71.4, 72.6, 74.4, 74.7, 75.1, 78.0, 80.4, 88.0, 89.9, 94.9, 95.7, 107.0(2C), 109.5, 109.6, 113.7(2C), 115.8, 116.1, 130.5, 130.6, 139.3, 139.7, 153.4, 153.6, 154.1, 154.2; HRMS (ESI-TOF) Calcd for $\text{C}_{19}\text{H}_{26}\text{O}_7\text{Na}$ $[\text{M}+\text{Na}]^+$ 389.1571. Found 389.1568.

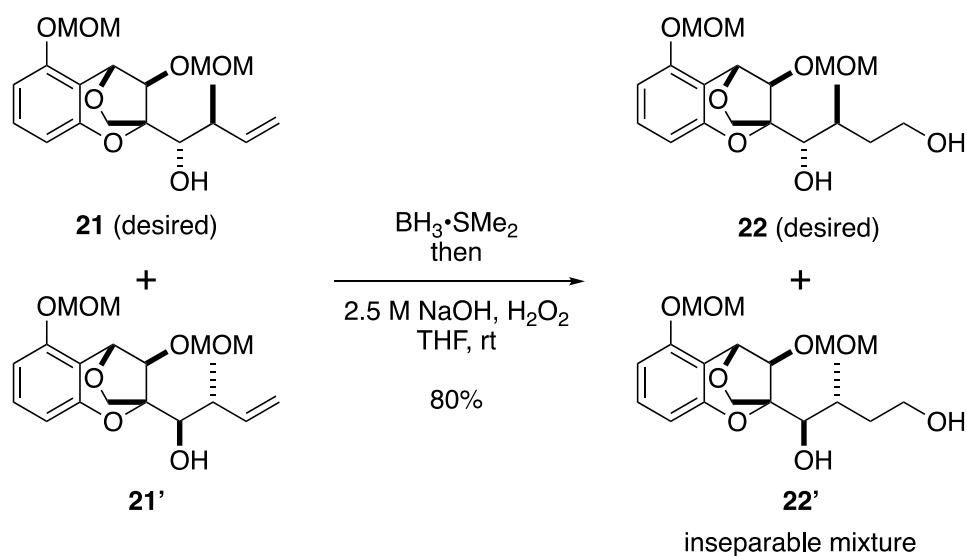
The relative stereochemistry of **21** (desired, major) and **21'** (undesired, minor) was determined by NOESY experiment of the corresponding acetonides **S5** and **S5'**. (see page 41)



The relative stereochemistry between the secondary alcohol and methyl group in **21** and **21'** was determined by NOESY experiment of phomopsol B (**2**) and its diastereomer **2'**. (see page 43)



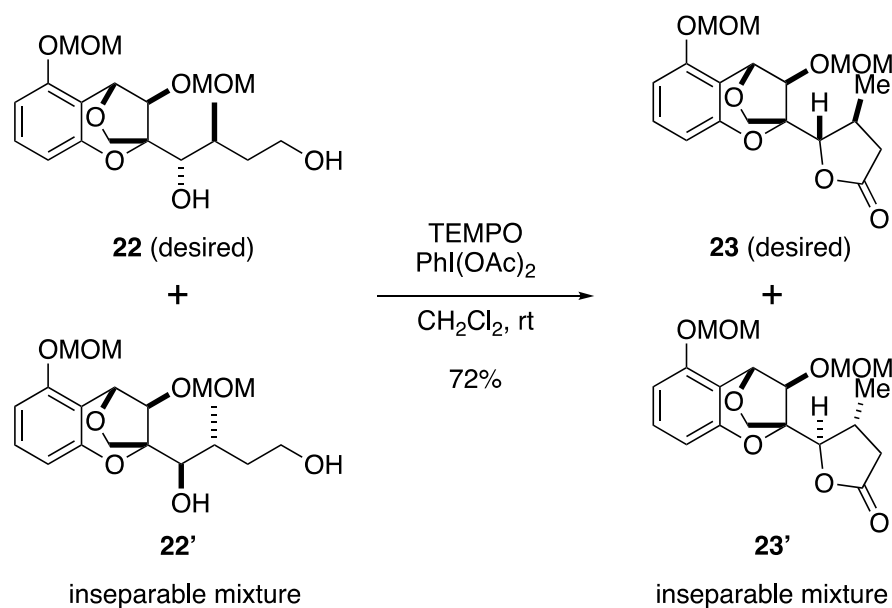
(1*S*,2*S*)-1-((2*S*,5*R*,10*R*)-6,10-bis(methoxymethoxy)-5*H*-2,5-methanobenzo[*e*][1,4]dioxepin-2(3*H*)-yl)-2-methylbutane-1,4-diol (**22**)



To a stirred solution of an inseparable mixture of **21** and **21'** (16.3 mg, 0.0445 mmol) in CH_2Cl_2 (3 mL) was added $\text{BH}_3 \cdot \text{SMe}_2$ (0.500 mL, 0.380 mmol) at 0°C under Ar atmosphere, and the mixture was stirred for 1 h at room temperature. To the mixture were added NaOH (2.5 M in H_2O , 3.50 mL) and H_2O_2 (30% in H_2O , 7.00 mL) at 0°C , and the mixture was stirred for 1 h at the same temperature. The reaction mixture was quenched with sat. $\text{Na}_2\text{S}_2\text{O}_3$ aq. and extracted with CHCl_3 (twice). The combined organic layers were washed with brine, dried over MgSO_4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (Hexane-AcOEt, 1:1) to afford an inseparable mixture of **22** and **22'** (13.7 mg, 80%) as a yellow oil.

IR (neat) 3433, 3016, 2933, 1607, 1463, 1407, 1216, 1051, 763, 666 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.05 (d, $J = 6.9$ Hz, 3H), 1.14 (d, $J = 7.3$ Hz, 3H), 1.84-1.70 (m, 2H), 2.02-1.97 (m, 2H), 2.41-2.24 (m, 6H), 3.48 (t, $J = 3.9$ Hz, 12H), 3.85-3.64 (m, 4H), 3.91 (d, $J = 5.0$ Hz, 1H), 4.04 (d, $J = 10.5$ Hz, 1H), 4.13 (d, $J = 4.1$ Hz, 1H), 4.24 (dd, $J = 25.6, 10.5$ Hz, 2H), 4.43-4.39 (m, 2H), 4.56 (s, 1H), 4.78 (d, $J = 6.9$ Hz, 1H), 4.88 (d, $J = 1.8$ Hz, 2H), 4.93 (d, $J = 6.9$ Hz, 1H), 5.18 (d, $J = 3.2$ Hz, 4H), 5.31 (s, 1H), 5.42 (s, 1H), 6.47 (q, $J = 3.8$ Hz, 2H), 6.66 (t, $J = 7.5$ Hz, 2H), 7.10 (td, $J = 8.2, 5.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.8, 17.3, 17.5, 22.3, 31.3, 32.1, 32.8, 33.7, 35.2, 55.6, 55.9, 60.2, 70.4, 70.9, 73.0, 74.1, 74.9, 75.4, 78.1, 79.6, 88.6(2C), 90.8, 94.6, 95.6, 106.8(2C), 109.1, 109.2, 113.2, 130.2, 130.3, 152.9, 153.2, 153.8, 153.9; HRMS (ESI-TOF) Calcd for $\text{C}_{19}\text{H}_{28}\text{O}_8\text{Na}$ $[\text{M}+\text{Na}]^+$ 407.1676. Found 407.1674.

(4*S*,5*S*)-5-((2*S*,5*R*,10*R*)-6,10-bis(methoxymethoxy)-5*H*-2,5-methanobenzo[*e*][1,4]dioxepin-2(3*H*)-yl)-4-methyldihydrofuran-2(3*H*)-one (**23**)

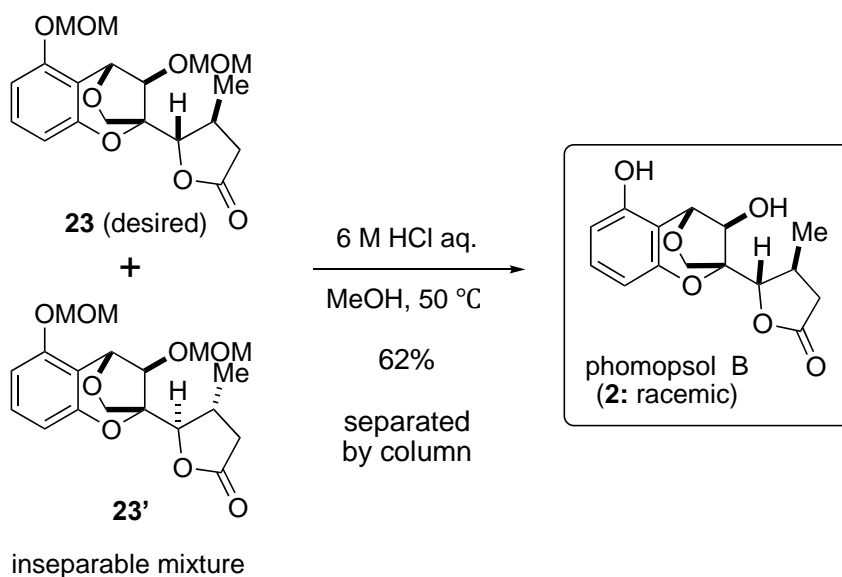


To a stirred solution of an inseparable mixture of **22** and **22'** (4.80 mg, 0.0124 mmol) in CH_2Cl_2 (0.5 mL) were added TEMPO (0.400 mg, 0.00256 mmol) and PhI(OAc)_2 (10.0 mg, 0.0299 mmol) at room temperature under Ar atmosphere, and the mixture was stirred for 13 h at the same temperature. The reaction mixture was quenched with sat. NaHCO_3 aq. and extracted with AcOEt (twice). The combined organic layers were washed with brine, dried over MgSO_4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (Hexane-AcOEt, 1:1) to afford an inseparable mixture of **23** and **23'** (3.40 mg, 72%) as a yellow oil.

IR (neat) 2955, 1781, 1593, 1462, 1258, 1219, 1154, 1115, 1052, 774 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.22 (d, $J = 6.9$ Hz, 3H), 1.26 (d, $J = 7.3$ Hz, 3H), 2.23-2.15 (m, 2H), 2.68 (dd, $J = 6.6, 4.3$ Hz, 1H), 3.05-2.98 (m, 2H), 2.68 (dd, $J = 6.6, 4.3$ Hz, 1H), 3.48 (d, $J = 9.6$ Hz, 12H), 4.05 (d, $J = 10.1$ Hz, 1H), 4.16 (d, $J = 10.1$ Hz, 1H), 4.25-4.34 (2H), 4.37-4.46 (1H), 4.54 (s, 1H), 4.64 (d, $J = 3.7$ Hz, 1H), 4.77-4.73 (m, 2H), 4.87 (q, $J = 7.3$ Hz, 2H), 4.93 (d, $J = 6.9$ Hz, 1H), 5.18 (s, 4H), 5.40 (s, 1H), 5.50 (s, 1H), 6.43 (t, $J = 8.9$ Hz, 2H), 6.67 (q, $J = 4.1$ Hz, 2H), 7.11 (dd, $J = 14.0, 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 20.2, 20.4, 30.3, 31.0, 36.8, 37.1, 56.1, 56.3, 56.4, 71.1, 71.8, 73.8(2C), 76.0(2C), 83.5(2C), 86.0(2C), 87.7, 88.0, 94.95, 94.99, 95.4, 107.36, 107.39, 109.7(2C), 113.3, 113.4, 130.8, 130.9, 153.1, 153.2, 154.2, 154.3, 176.7, 177.0; HRMS (ESI-TOF) Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_8\text{Na}$ $[\text{M}+\text{Na}]^+$ 403.1363. Found 403.1361.

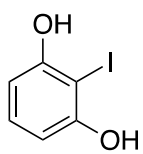
(4*S*,5*S*)-5-((2*R*,5*R*,10*R*)-6,10-dihydroxy-5*H*-2,5-methanobenzo[*e*][1,4]dioxepin-2(3*H*)-yl)-4-

methylidihydrofuran-2(3*H*)-one (**2**: phomopsol B)

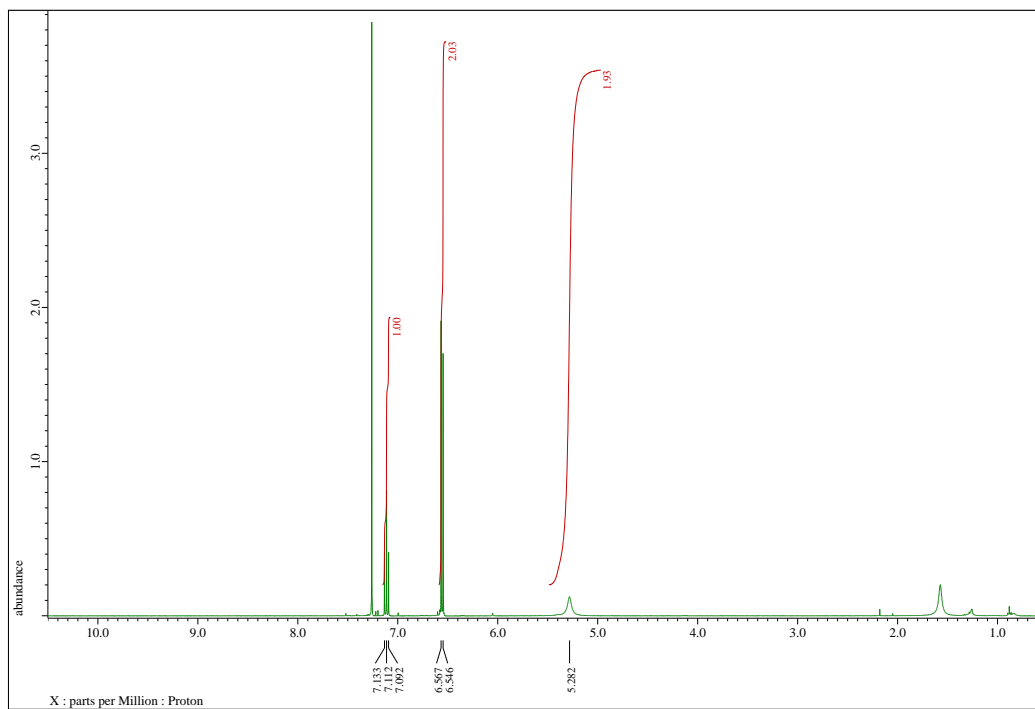


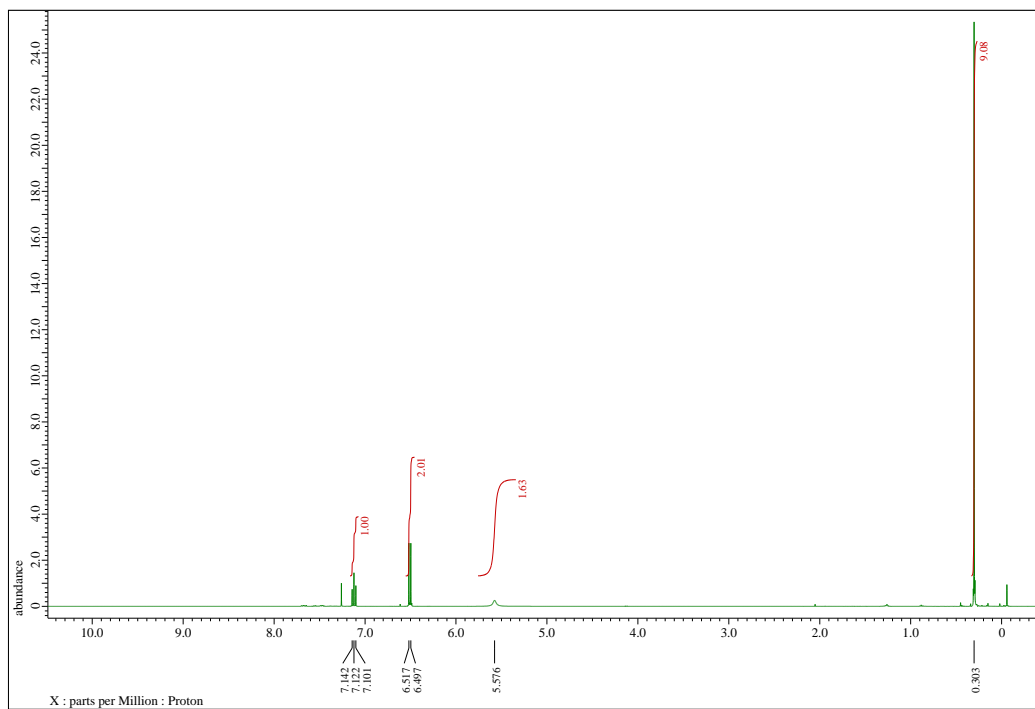
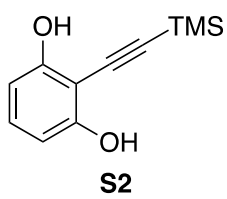
To a stirred solution of an inseparable mixture of **23** and **23'** (4.00 mg, 0.0105 mmol) in MeOH (1 mL) was added 6 M HCl (0.05 mL) at room temperature under Ar atmosphere, and the mixture was stirred for 24 h at 50 °C. The reaction mixture was quenched with sat. NaHCO₃ aq. and extracted with AcOEt (twice). The combined organic layers were washed with brine, dried over MgSO₄ and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (Hexane-AcOEt, 2:3) to afford **2** (1.9 mg, 62%) as a colorless oil.

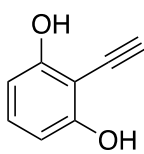
IR (neat) 3374, 2927, 1769, 1600, 1467, 1297, 1216, 1182, 1095, 1034, 897, 667 cm⁻¹; ¹H NMR (400 MHz, CD₃OD) δ 1.28 (d, J = 6.4 Hz, 3H), 2.28-2.16 (m, 1H), 2.98-2.92 (m, 2H), 4.15 (d, J = 10.5 Hz, 1H), 4.27 (d, J = 10.5 Hz, 1H), 4.42 (s, 1H), 4.76 (d, J = 3.7 Hz, 1H), 5.17 (s, 1H), 6.27 (d, J = 8.2 Hz, 1H), 6.35 (d, J = 7.8 Hz, 1H), 6.98 (t, J = 8.2 Hz, 1H); ¹³C NMR (100 MHz, CD₃OD) δ 19.9, 32.0, 37.6, 73.7, 75.9, 76.4, 88.3, 89.2, 107.7, 109.0, 112.8, 131.4, 154.8, 155.7, 179.4; HRMS (ESI-TOF) Calcd for C₁₅H₁₆O₆Na [M+Na]⁺ 315.0839. Found 315.0824.



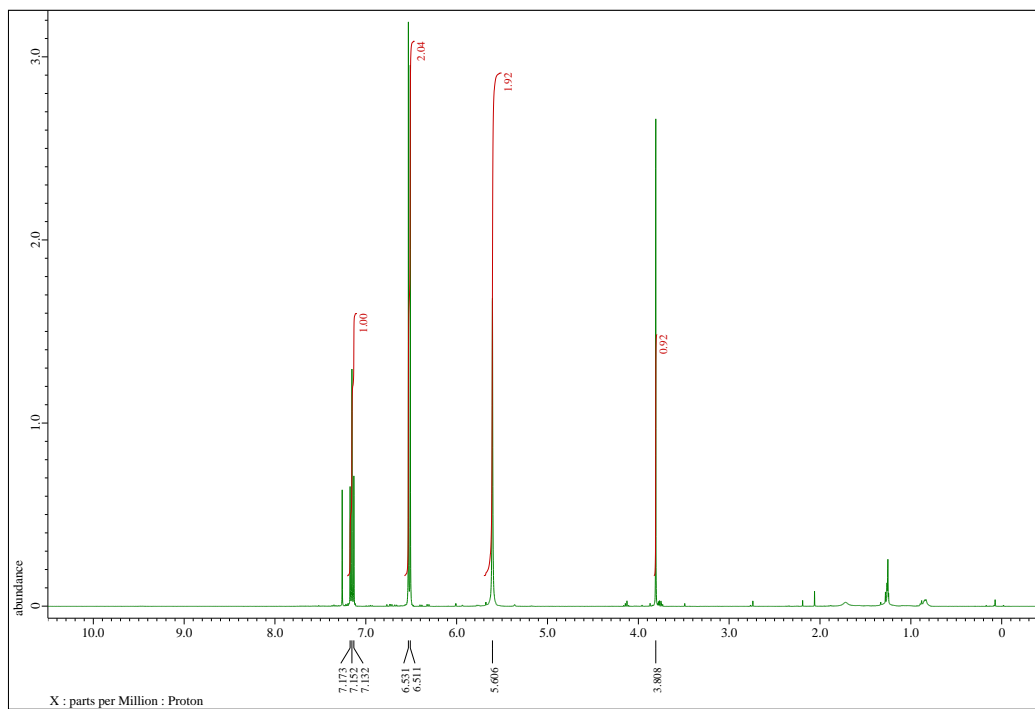
S1

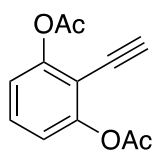




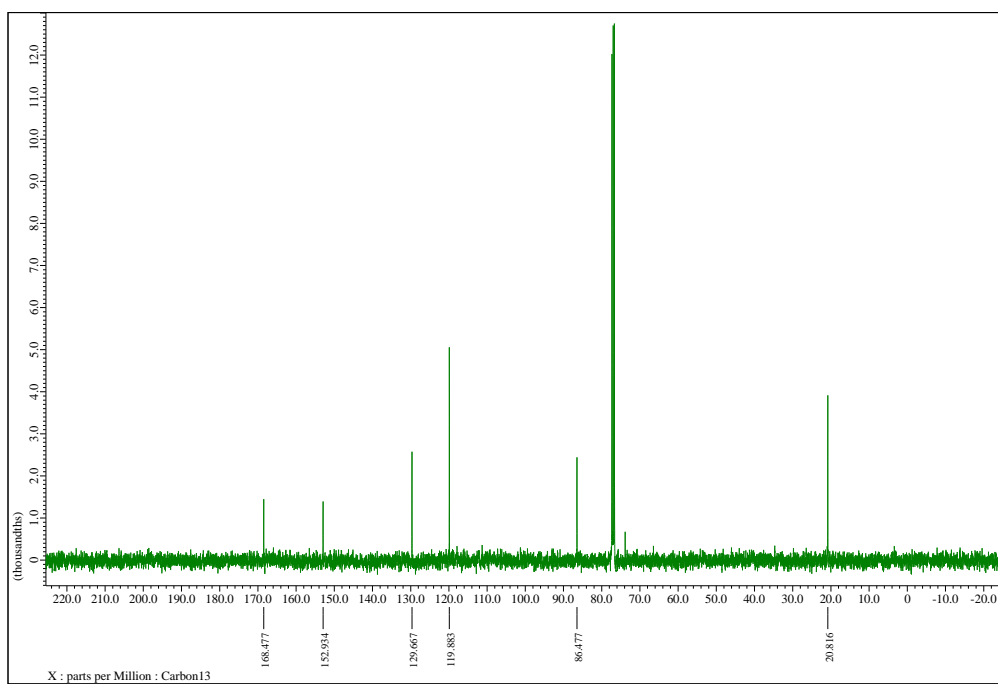
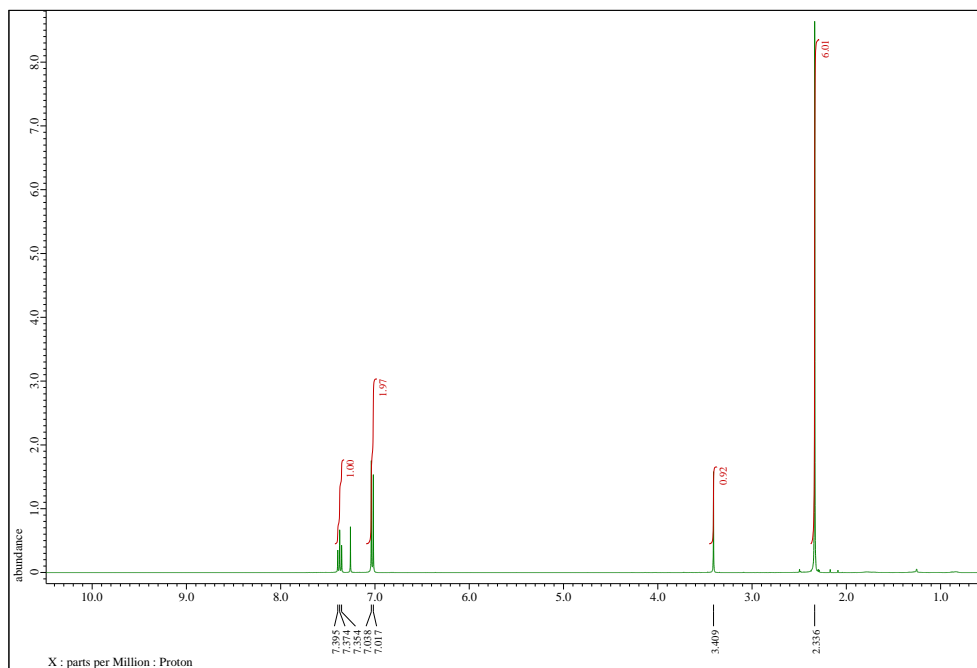


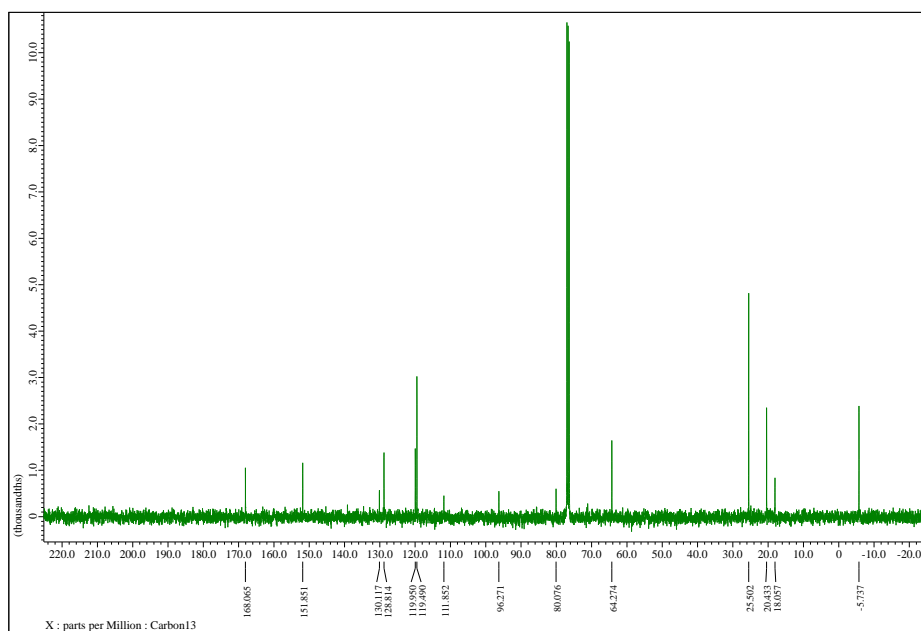
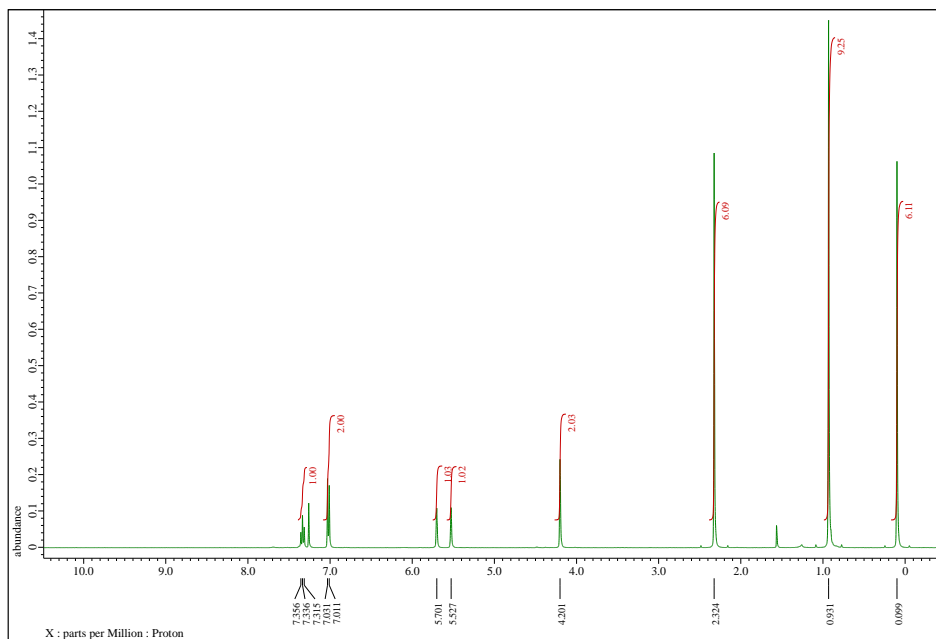
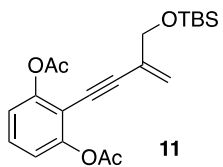
8

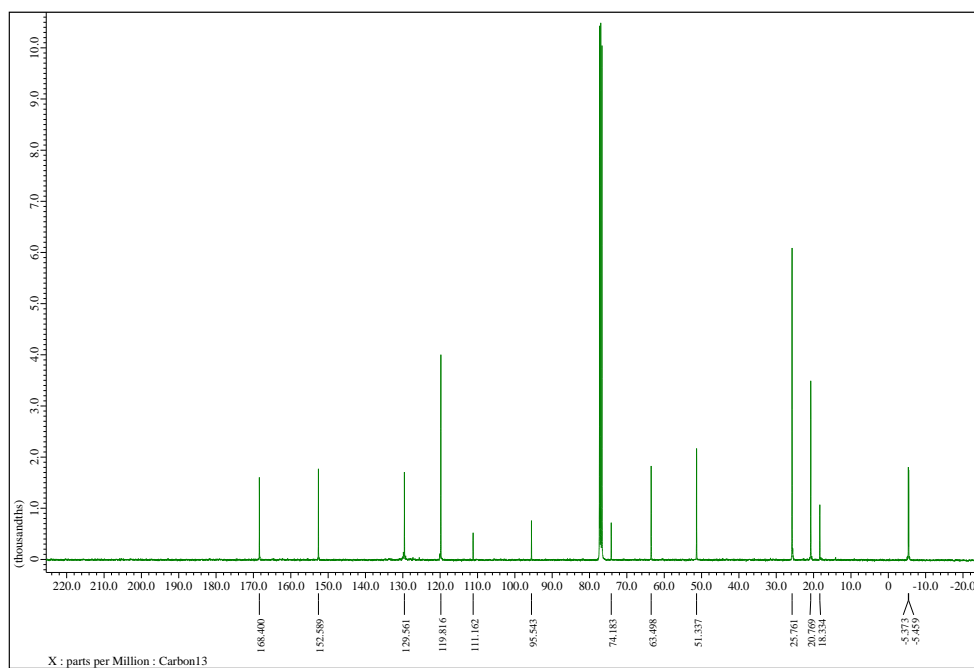
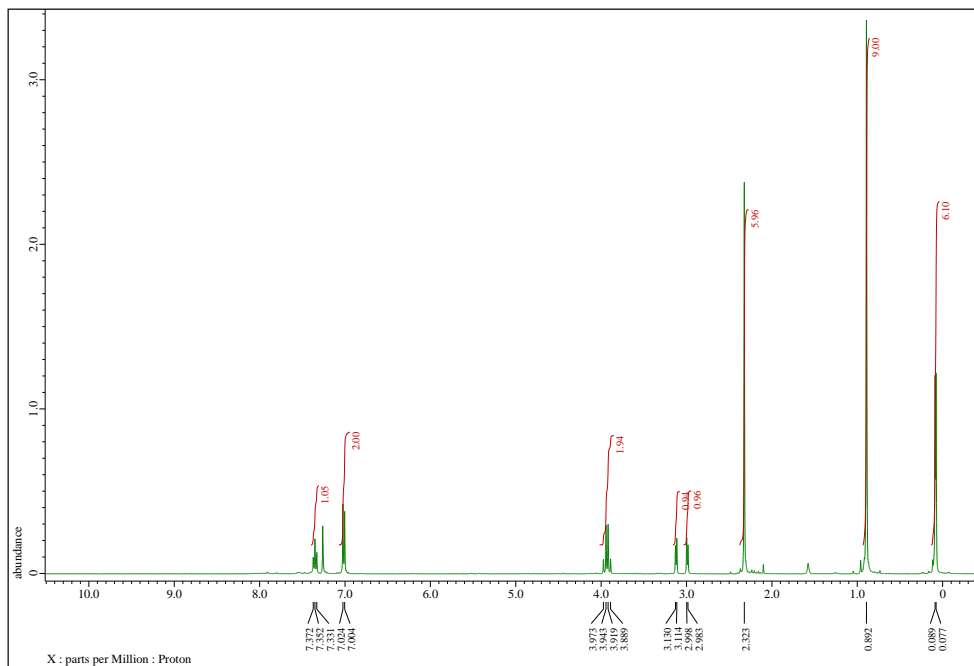
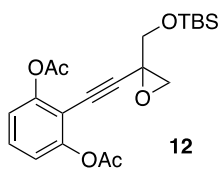


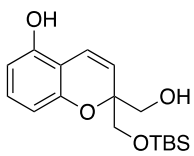


9

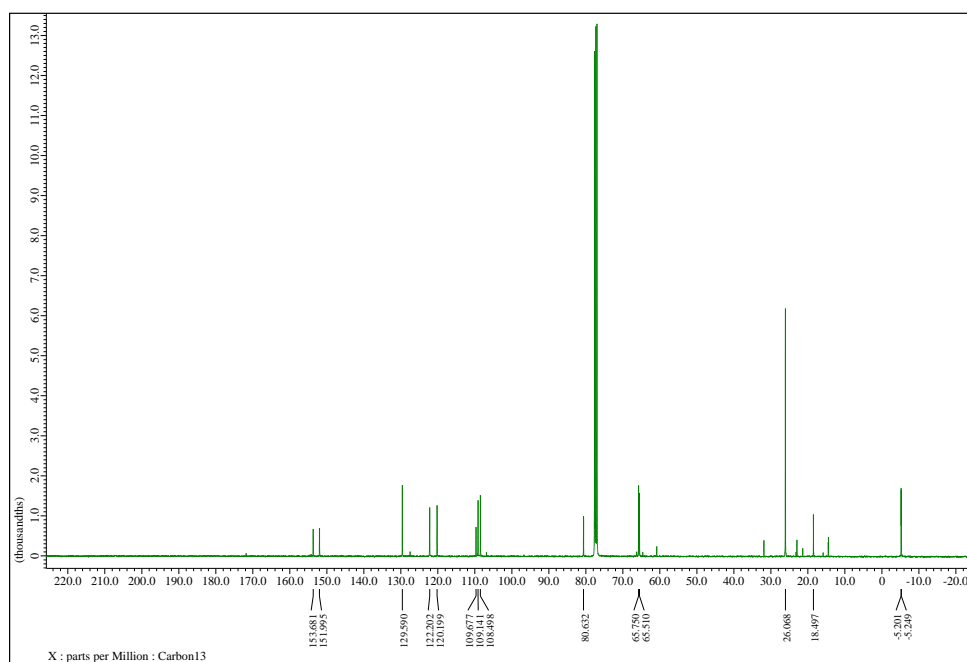
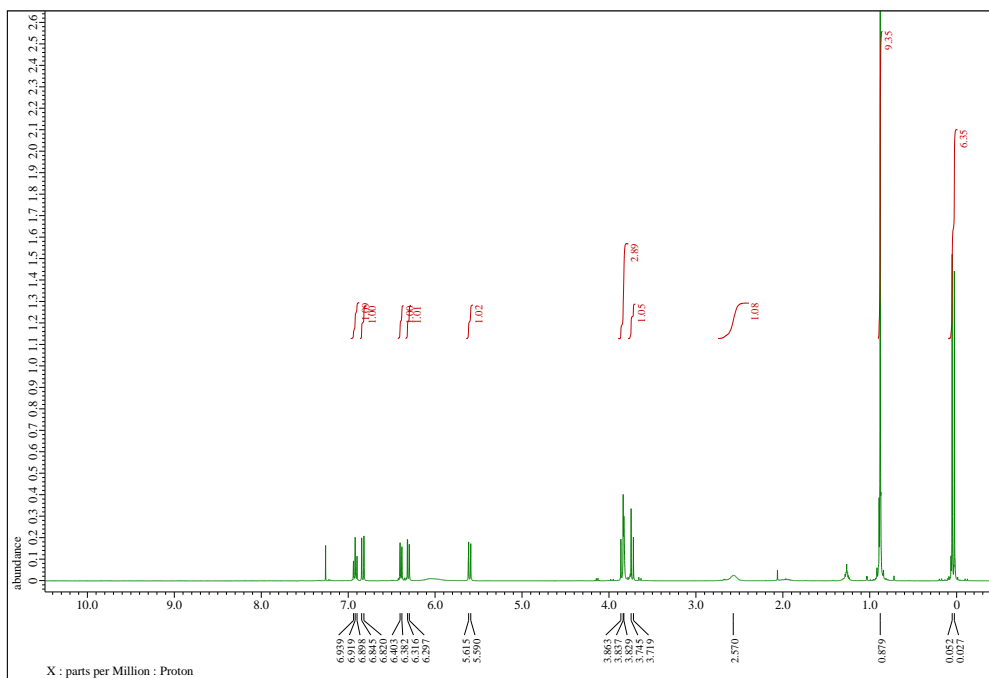


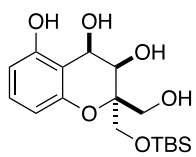




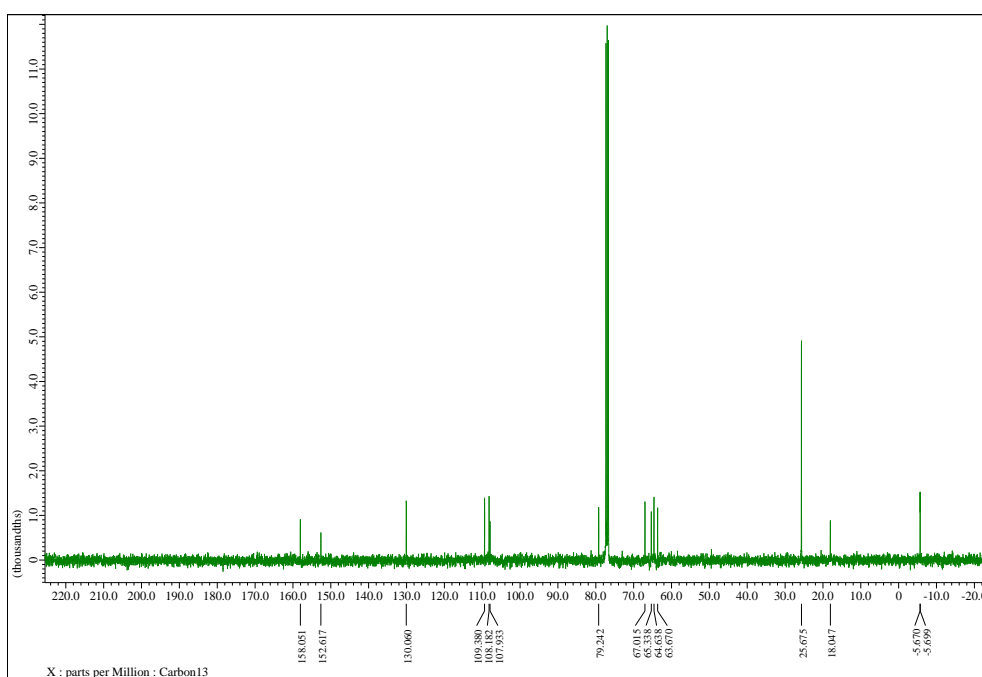
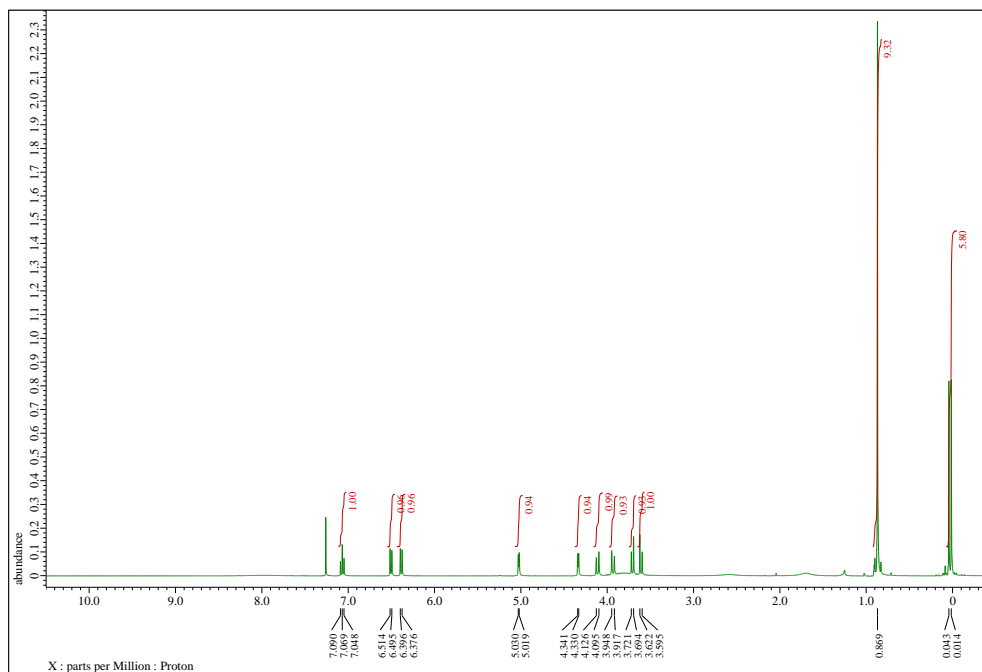


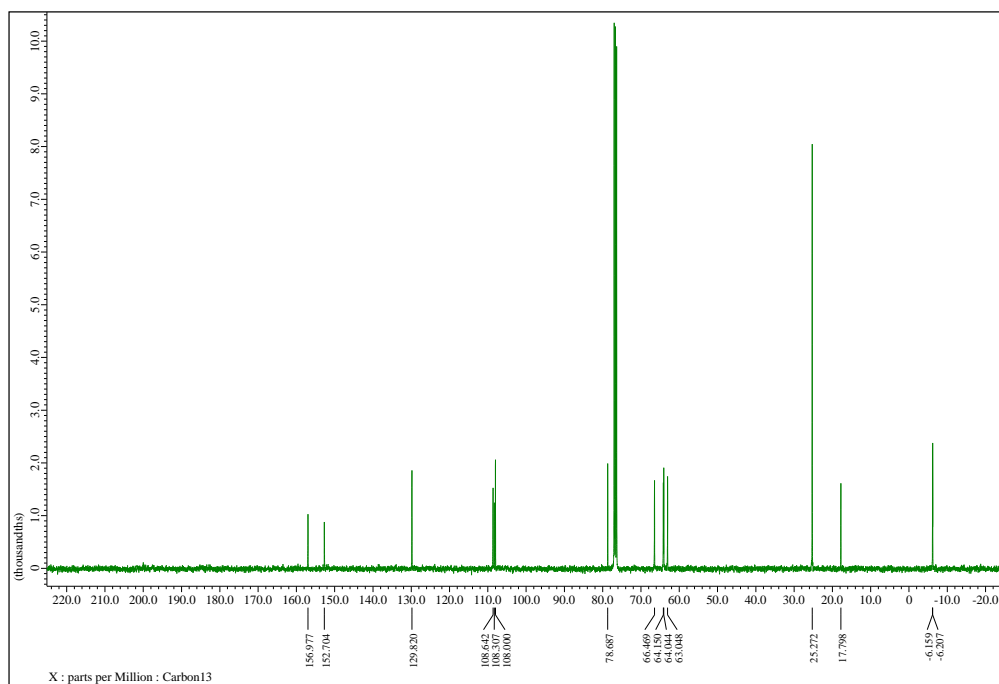
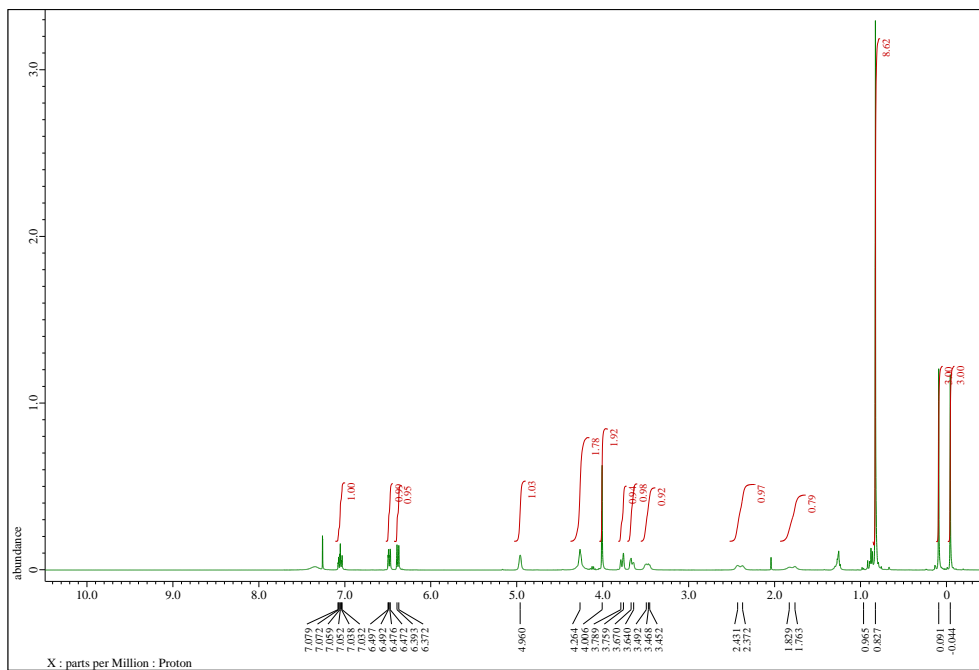
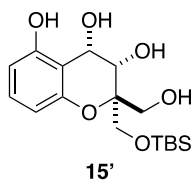
14

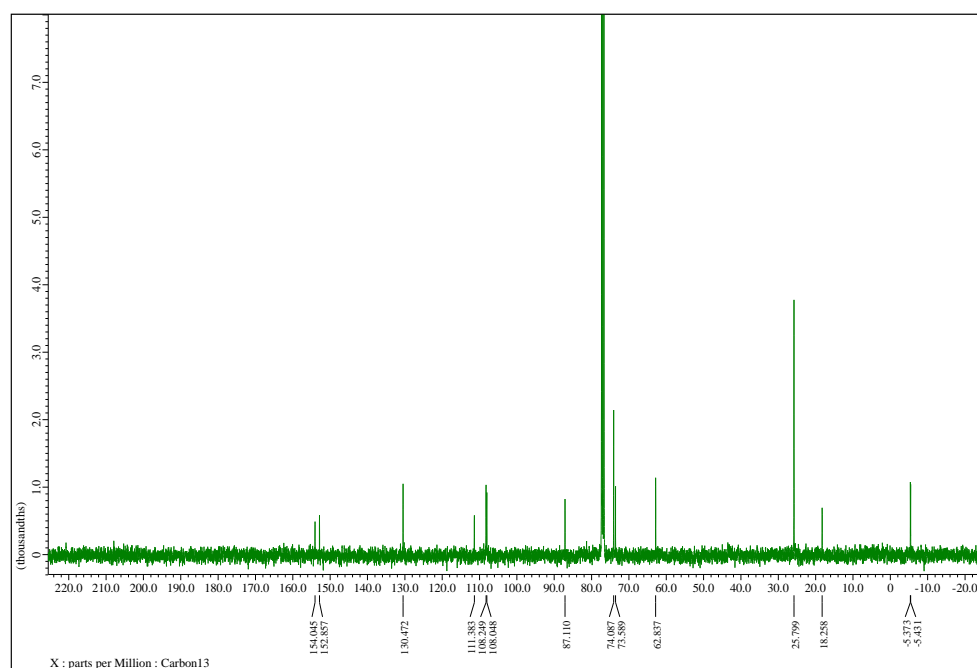
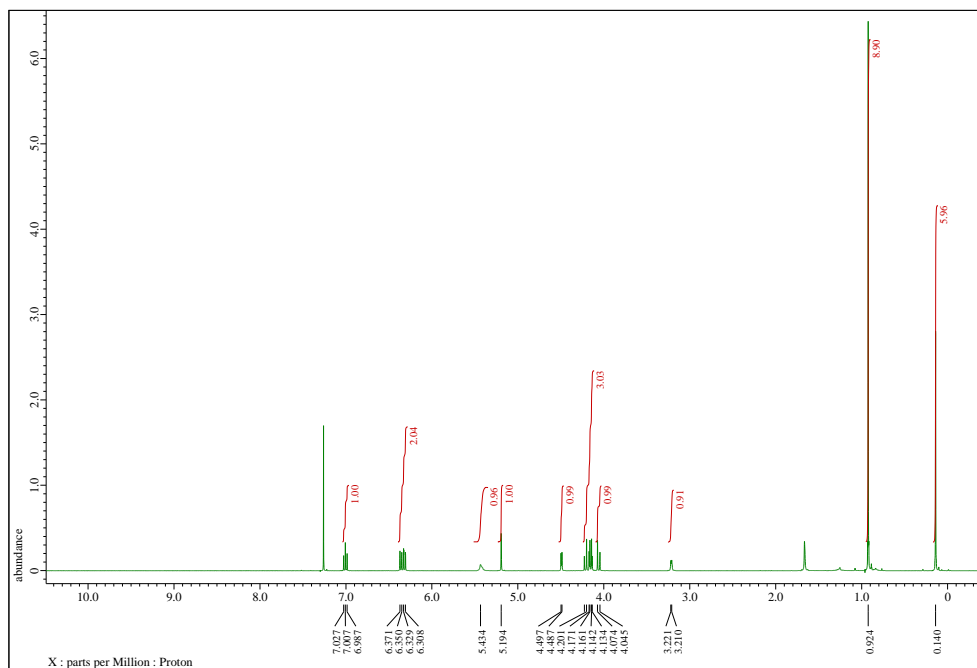
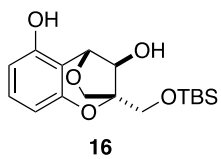


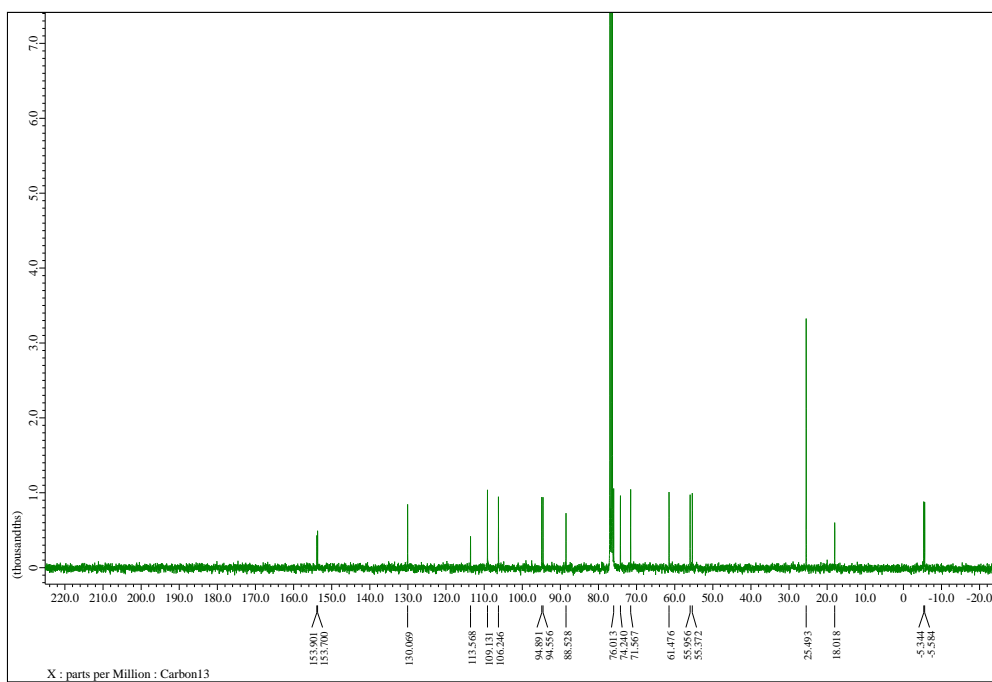
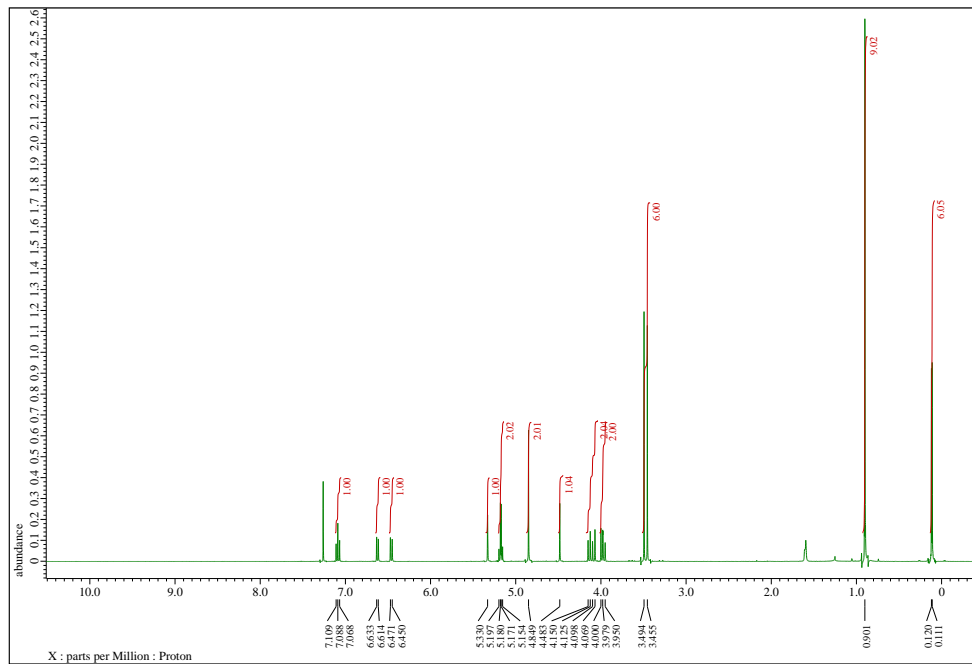
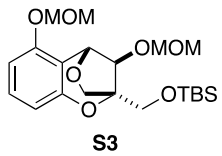


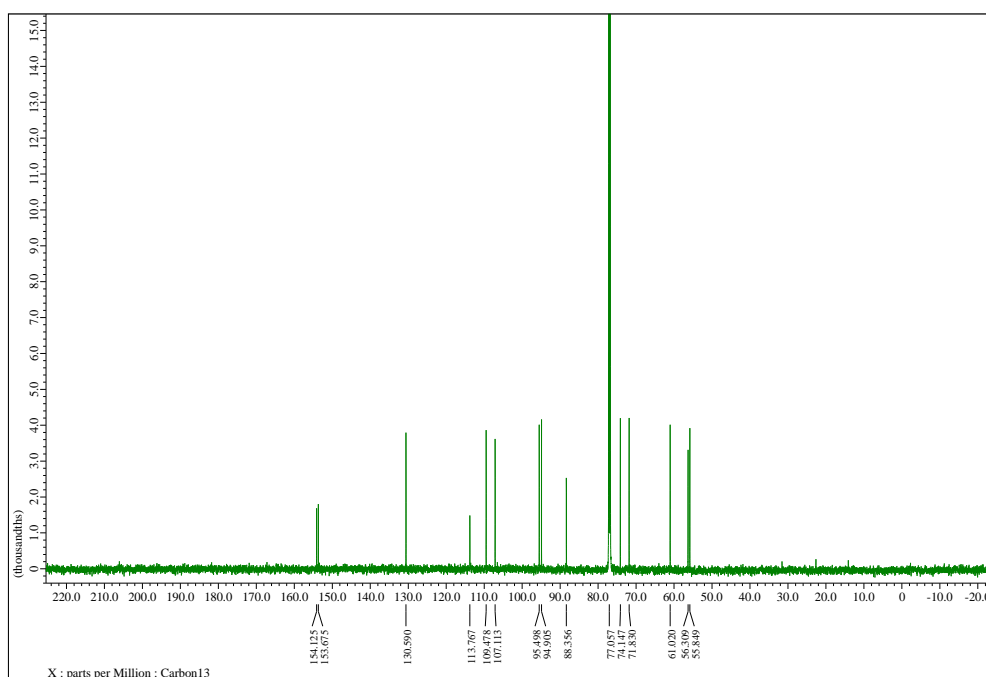
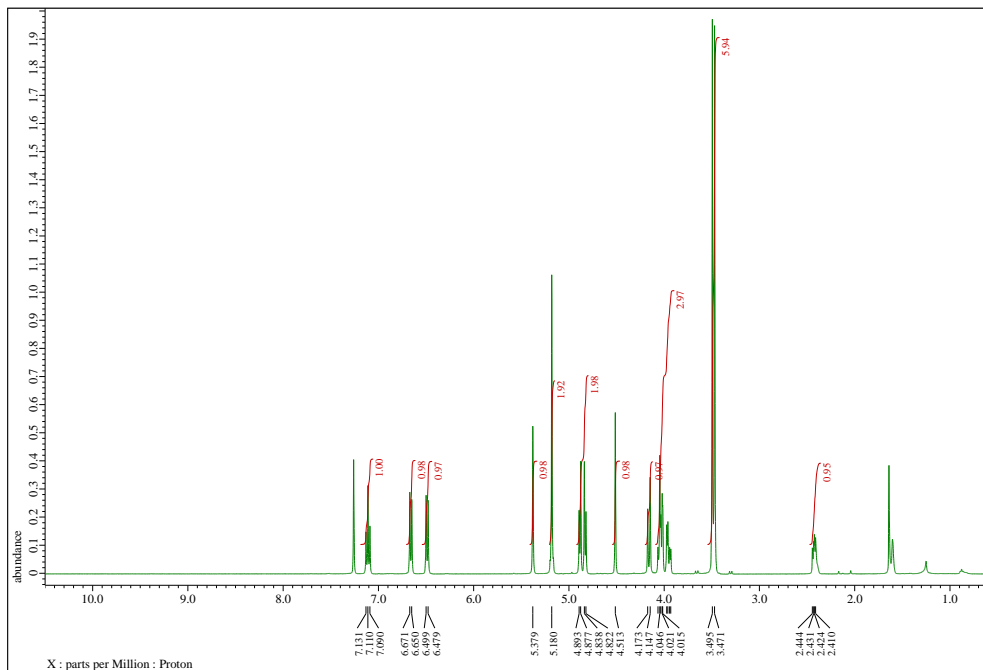
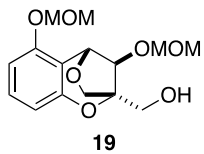
15 (desired)

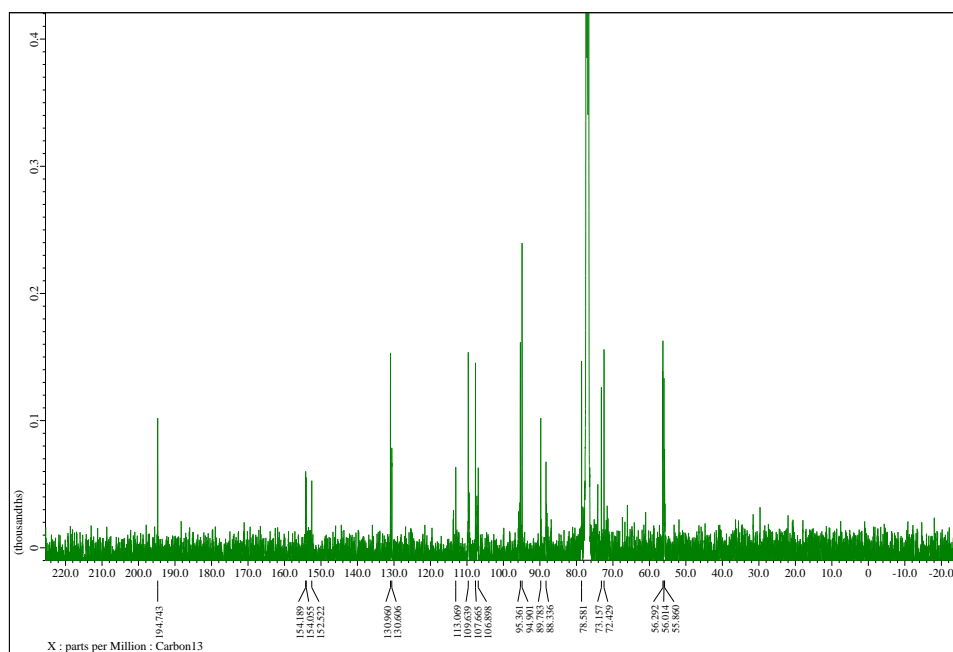
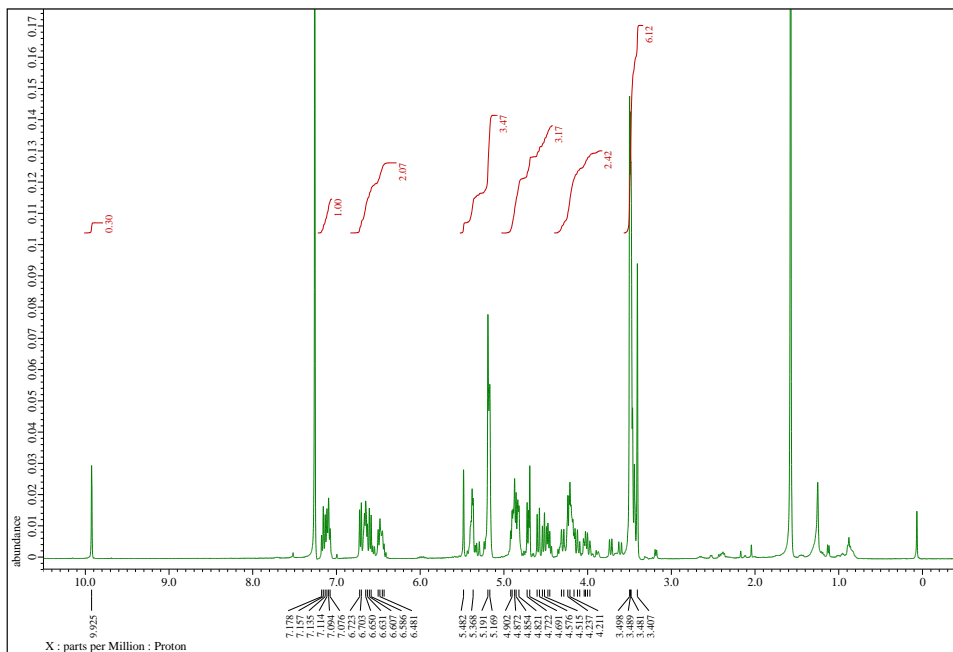
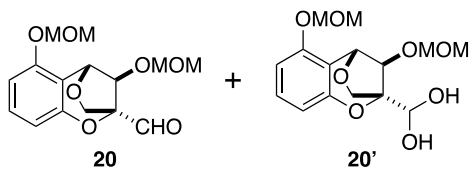


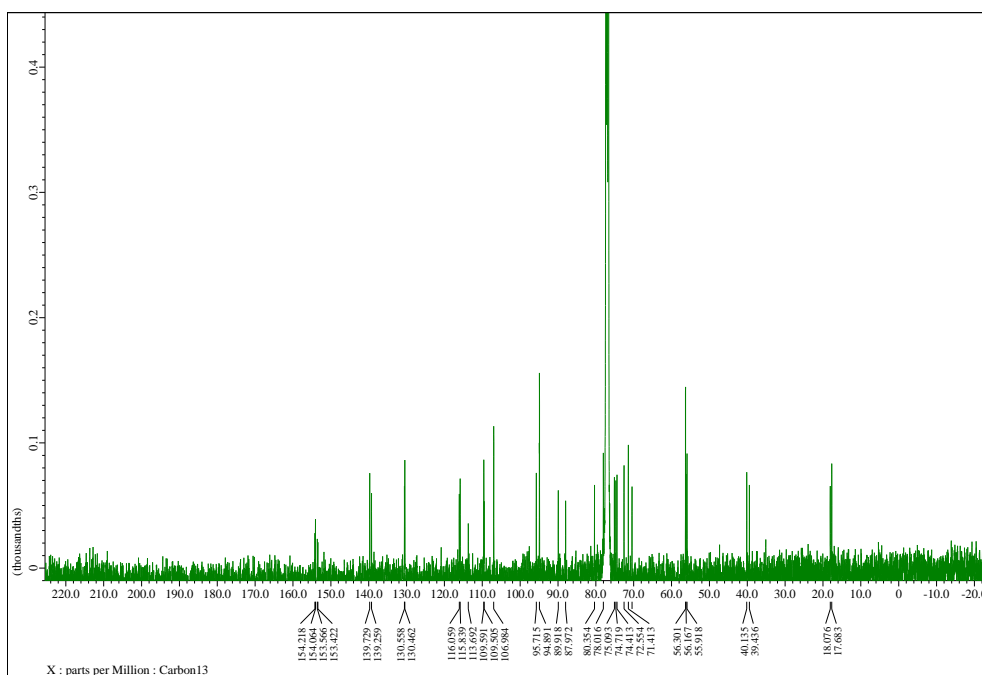
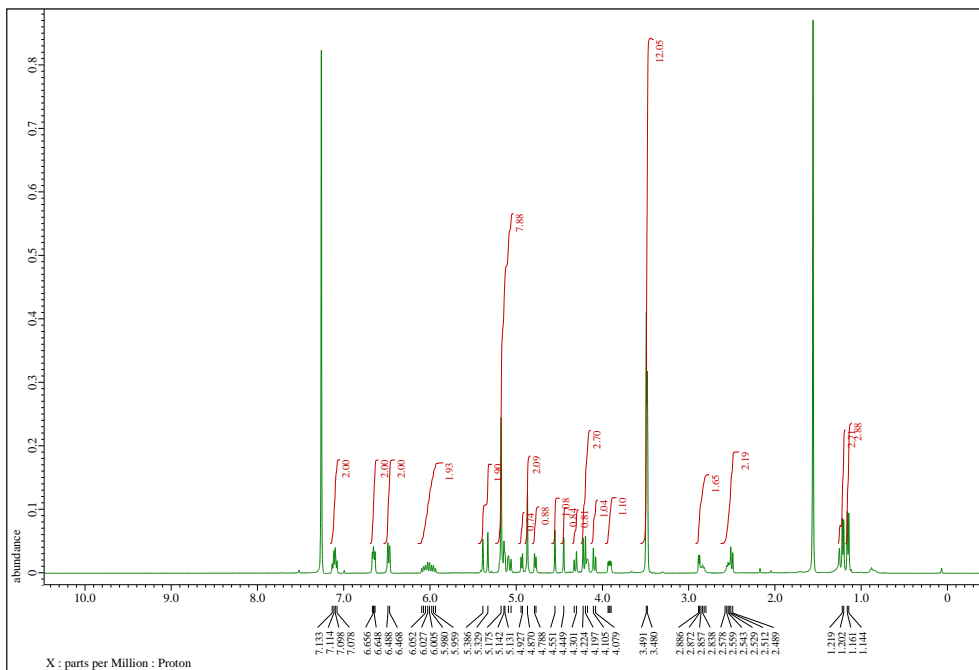
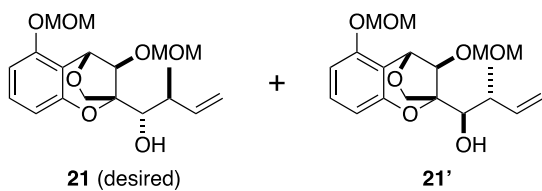


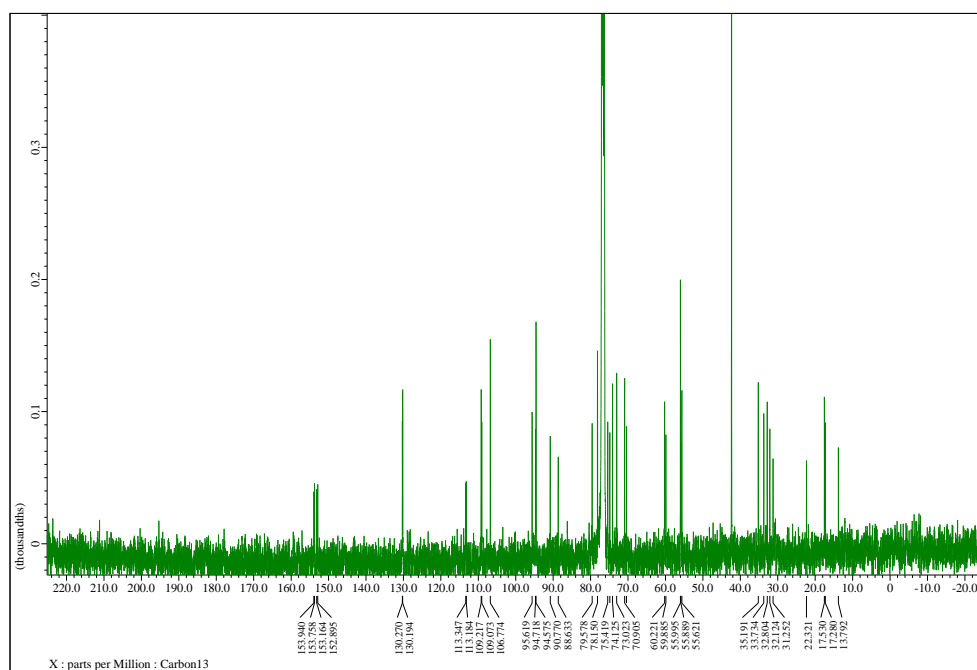
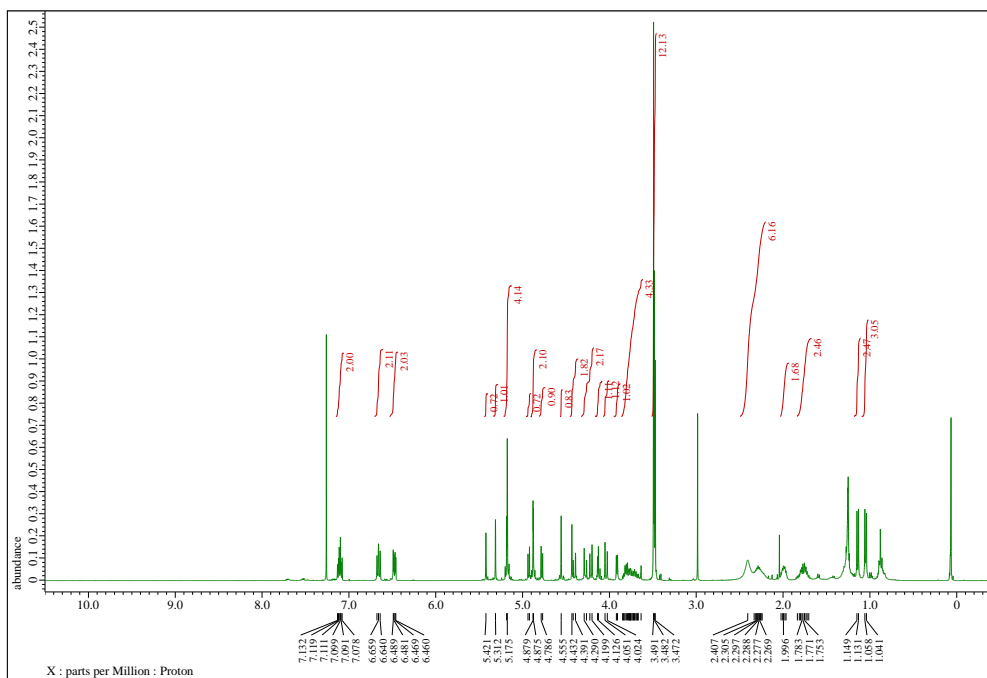
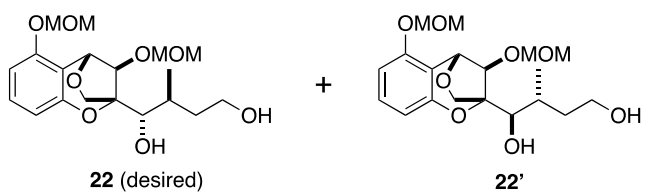


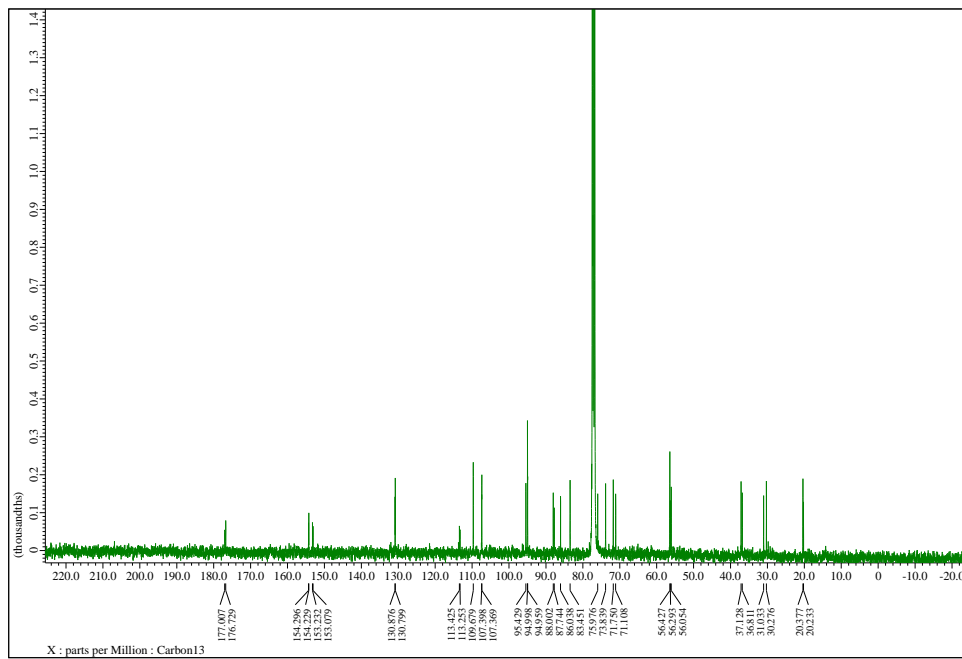
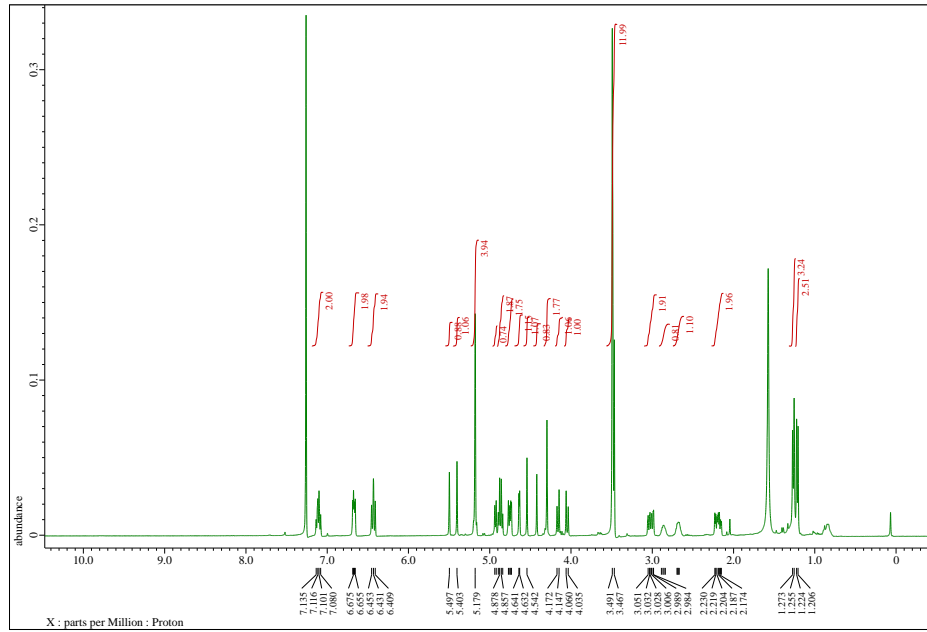
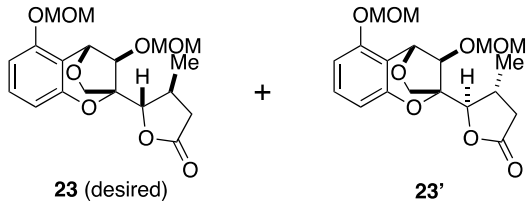


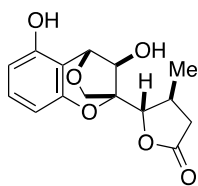






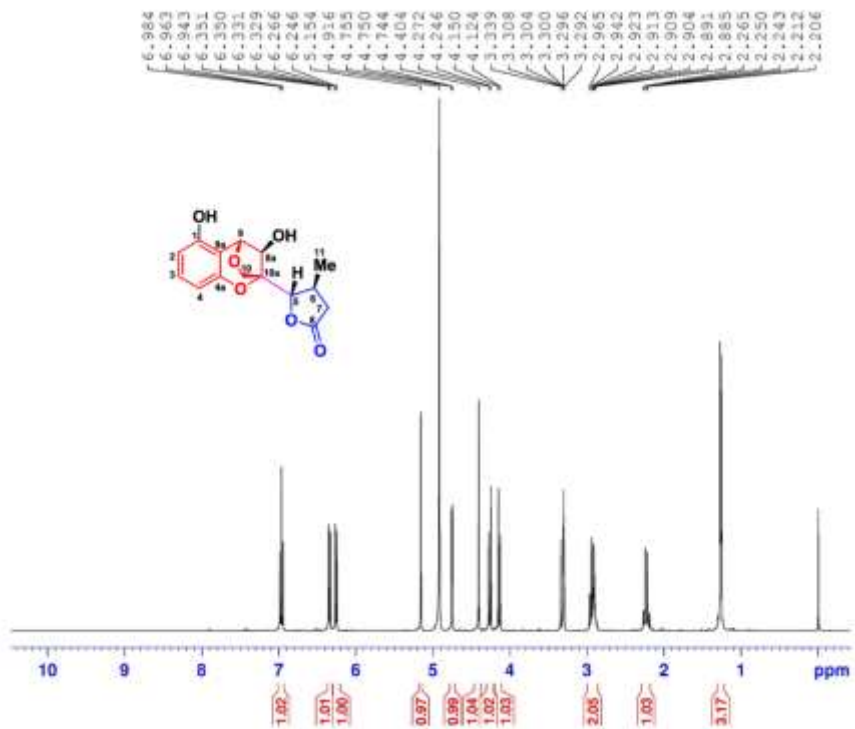
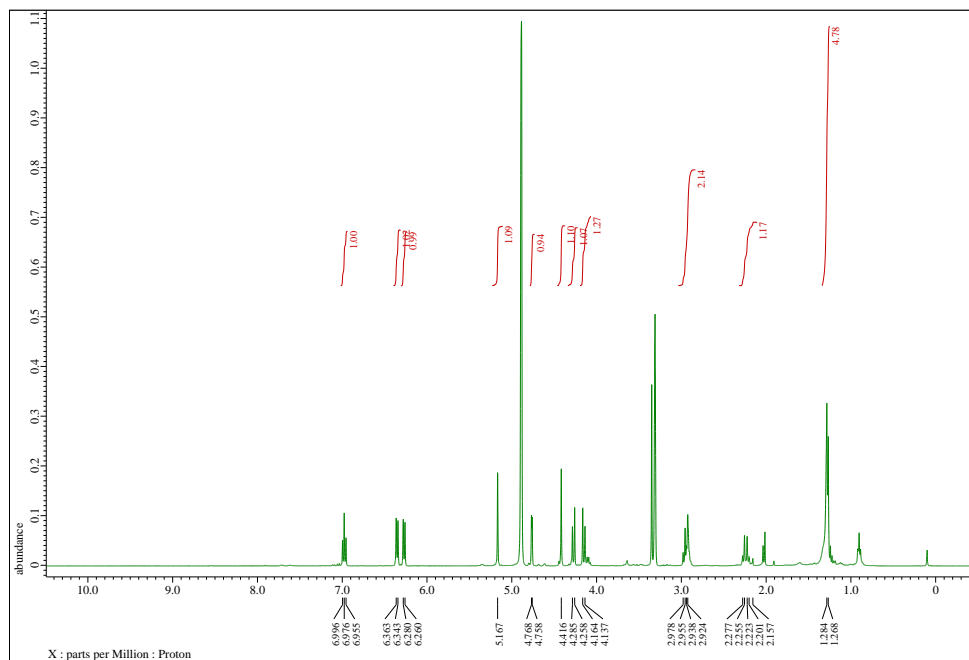




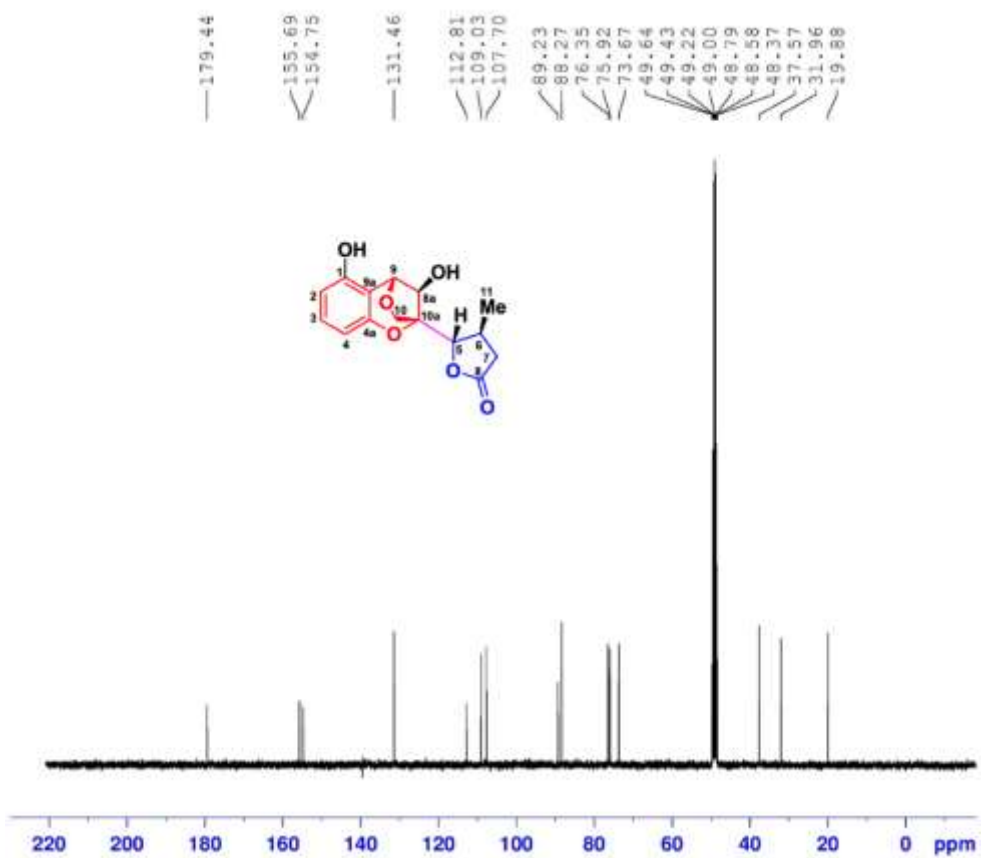
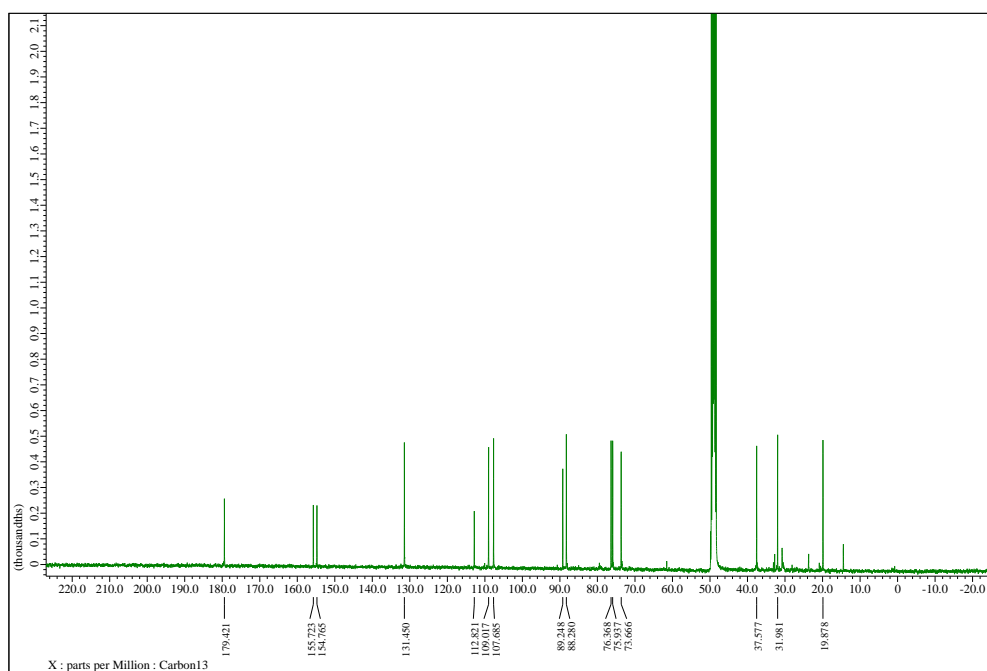


phomopsol B
(2: racemic)

upper: synthetic, bottom: literature for ^1H NMR



upper: synthetic, bottom: literature for ^{13}C NMR



X-ray crystallographic analysis of compound **16** (CCDC2298603)

NA-1-66-2

Single crystals of $C_{17}H_{26}O_5Si$ [NA-1-66-2] were grown from vapour diffusion of pentane in chloroform solvent at room temperature. A suitable crystal was selected and was mounted on a MiTeGEN MicroMounts in perfluoropolyether oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 90 K during data collection. Using Olex2 [1], the structure was solved with the XT [2] structure solution program using Intrinsic Phasing and refined with the XL [3] refinement package using Least Squares minimisation.

Table 1

Experimental details

Crystal data	
Chemical formula	$C_{17}H_{26}O_5Si$
M_r	338.47
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	90
a, b, c (Å)	7.9252 (8), 9.8381 (9), 12.6943 (12)
α, β, γ (°)	98.475 (1), 107.944 (1), 106.441 (1)
V (Å ³)	872.76 (14)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.16
Crystal size (mm)	0.29 × 0.24 × 0.22
Data collection	
Diffractometer	Bruker SMART APEX II CCD area detector
Absorption correction	Numerical SADABS2016/2 (Bruker,2016/2) was used for absorption correction. $wR_2(int)$ was 0.0712 before and 0.0345 after correction. The Ratio of minimum to maximum transmission is 0.9425. The $\lambda/2$ correction factor is Not present.
T_{min}, T_{max}	0.937, 0.995
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10735, 4301, 3963
R_{int}	0.024
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.686
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.037, 0.100, 1.04
No. of reflections	4301
No. of parameters	215
No. of restraints	191
H-atom treatment	H-atom parameters constrained
ρ_{max}, ρ_{min} (e Å ⁻³)	0.84, -0.22

Crystal structure determination of [NA-1-66-2]

Crystal Data for $C_{17}H_{26}O_5Si$ ($M = 338.47$ g/mol): triclinic, space group $P\bar{1}$ (no. 2), $a = 7.9252(8)$ Å, $b = 9.8381(9)$ Å, $c = 12.6943(12)$ Å, $\alpha = 98.4750(10)^\circ$, $\beta = 107.9440(10)^\circ$, $\gamma = 106.4410(10)^\circ$, $V = 872.76(14)$ Å³, $Z = 2$, $T = 90$ K, $\mu(MoK\alpha) = 0.157$ mm⁻¹, $D_{calc} = 1.288$ g/cm³, 10735 reflections measured ($3.49^\circ \leq 2\theta \leq 58.356^\circ$), 4301 unique ($R_{int} = 0.0236$, $R_{sigma} = 0.0273$) which were used in all calculations. The final R_1 was 0.0369 ($I > 2\sigma(I)$) and wR_2 was 0.0998 (all data).

References

- [1] Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* 42, 339-341.
- [2] Sheldrick, G. M. (2008). *Acta Cryst.* A64, 112-122.
- [3] Sheldrick, G. M. (2015). *Acta Cryst.* A71, 3-8.

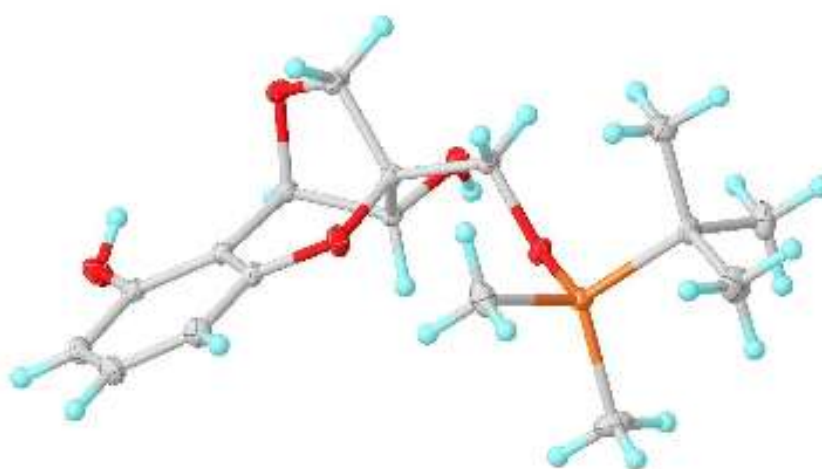


Fig. 1 ORTEP drawing of NA-1-66-2 with thermal ellipsoids at 50% probability level.

supporting information

NA-1-66-2

Computing details

Cell refinement: *SAINT* V8.40B (2016); data reduction: *SAINT* V8.40B (2016); program(s) used to solve structure: *SHELXT* 2018/2 (Sheldrick, 2018); program(s) used to refine structure: *XL* (Sheldrick, 2008); molecular graphics: *Olex2* 1.5 (Dolomanov *et al.*, 2009); software used to prepare material for publication: *Olex2* 1.5 (Dolomanov *et al.*, 2009).

Crystal data

$C_{17}H_{18}O_8Si$
 $M_r = 338.47$
 Triclinic, $P\bar{1}$
 $a = 7.9252$ (8) Å
 $b = 9.8381$ (9) Å
 $c = 12.6943$ (12) Å
 $\alpha = 98.475$ (1)°
 $\beta = 107.944$ (1)°
 $\gamma = 106.441$ (1)°
 $V = 872.76$ (14) Å³

Data collection

Bruker SMART APEX II CCD area detector diffractometer
 Radiation source: rotating-anode X-ray tube, Bruker TXS fine-focus Turbo X-ray Source
 Bruker Helios multilayered confocal mirror monochromator
 Detector resolution: 8.333 pixels mm⁻¹
 φ and ω scans

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.100$
 $S = 1.04$
 4301 reflections
 215 parameters
 191 restraints
 Primary atom site location: dual

$Z = 2$
 $F(000) = 364$
 $D_x = 1.288$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 6161 reflections
 $\theta = 2.2$ – 29.0°
 $\mu = 0.16$ mm⁻¹
 $T = 90$ K
 Block, colourless
 0.29 × 0.24 × 0.22 mm

Absorption correction: numerical
SADABS2016/2 (Bruker, 2016/2) was used for absorption correction. $wR2(\text{int})$ was 0.0712 before and 0.0345 after correction. The Ratio of minimum to maximum transmission is 0.9425. The $\lambda/2$ correction factor is Not present.
 $T_{\text{min}} = 0.937$, $T_{\text{max}} = 0.995$
 10735 measured reflections
 4301 independent reflections
 3963 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\text{max}} = 29.2^\circ$, $\theta_{\text{min}} = 1.8^\circ$
 $h = -10 \rightarrow 10$
 $k = -13 \rightarrow 13$
 $l = -16 \rightarrow 17$

Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 0.4171P]$ where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\rho_{\text{max}} = 0.84$ e Å⁻³
 $\rho_{\text{min}} = -0.22$ e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.41958 (16)	0.32816 (12)	0.65413 (10)	0.0114 (2)
C2	0.69958 (16)	0.31042 (13)	0.78648 (10)	0.0130 (2)
C3	0.82504 (18)	0.34150 (14)	0.89825 (11)	0.0166 (2)
H3	0.809448	0.397868	0.959736	0.020*
C4	0.97404 (18)	0.28846 (14)	0.91844 (11)	0.0181 (2)
H4	1.061917	0.310194	0.994439	0.022*
C5	0.99654 (17)	0.20413 (14)	0.82920 (11)	0.0168 (2)
H5	1.099961	0.169732	0.844064	0.020*
C6	0.86620 (16)	0.17039 (13)	0.71771 (10)	0.0134 (2)
C7	0.71769 (16)	0.22575 (12)	0.69440 (10)	0.0118 (2)
C8	0.57460 (16)	0.20017 (12)	0.57626 (10)	0.0114 (2)
H8	0.622469	0.172965	0.514915	0.014*
C9	0.52323 (16)	0.33838 (12)	0.57007 (10)	0.0112 (2)
H9	0.637304	0.429570	0.596546	0.013*
C10	0.30123 (17)	0.16412 (13)	0.61878 (11)	0.0150 (2)
H10A	0.294953	0.128626	0.686999	0.018*
H10B	0.170826	0.145882	0.566256	0.018*
C11	0.30010 (16)	0.42437 (12)	0.65398 (10)	0.0131 (2)
H11A	0.198369	0.396461	0.577600	0.016*
H11B	0.239966	0.408645	0.711063	0.016*
C12	0.47973 (19)	0.63829 (16)	0.92282 (11)	0.0213 (3)
H12A	0.594990	0.613737	0.937752	0.032*
H12B	0.373019	0.550953	0.912880	0.032*
H12C	0.497164	0.715557	0.987659	0.032*
C13	0.6338 (2)	0.86420 (15)	0.80210 (13)	0.0250 (3)
H13A	0.659060	0.944041	0.867357	0.038*
H13B	0.603761	0.897107	0.731591	0.038*
H13C	0.746001	0.835989	0.813595	0.038*
C14	0.20446 (17)	0.74743 (13)	0.75585 (10)	0.0138 (2)
C15	0.1543 (2)	0.78285 (16)	0.63796 (12)	0.0220 (3)
H15A	0.039293	0.808017	0.621188	0.033*
H15B	0.132691	0.697079	0.578616	0.033*
H15C	0.258919	0.865946	0.639248	0.033*
C16	0.2347 (2)	0.88192 (15)	0.84832 (12)	0.0232 (3)
H16A	0.338859	0.965790	0.850095	0.035*
H16B	0.265782	0.859808	0.923285	0.035*
H16C	0.118658	0.905669	0.830390	0.035*
C17	0.03720 (18)	0.61865 (15)	0.75205 (12)	0.0207 (3)
H17A	-0.075101	0.647132	0.737908	0.031*
H17B	0.068436	0.592504	0.825453	0.031*
H17C	0.011491	0.534116	0.690347	0.031*
O1	0.55758 (12)	0.36904 (9)	0.76998 (7)	0.01473 (18)
O2	0.89299 (12)	0.08436 (10)	0.63401 (8)	0.0186 (2)

supporting information

H2	0.788134	0.035962	0.581173	0.028*
O3	0.39157 (12)	0.32541 (10)	0.46122 (7)	0.01484 (18)
H3A	0.449871	0.354570	0.419017	0.022*
O4	0.39606 (12)	0.09006 (9)	0.56154 (7)	0.01302 (17)
O5	0.41267 (12)	0.57573 (9)	0.68070 (7)	0.01316 (17)
Si1	0.43041 (4)	0.70403 (3)	0.79027 (3)	0.01146 (9)

Atomic displacement parameters (\AA^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	0.0125 (5)	0.0105 (5)	0.0126 (5)	0.0052 (4)	0.0057 (4)	0.0031 (4)
C2	0.0135 (5)	0.0120 (5)	0.0171 (5)	0.0062 (4)	0.0075 (4)	0.0062 (4)
C3	0.0184 (6)	0.0178 (6)	0.0146 (5)	0.0075 (5)	0.0065 (4)	0.0040 (4)
C4	0.0167 (6)	0.0193 (6)	0.0162 (5)	0.0059 (5)	0.0031 (4)	0.0058 (5)
C5	0.0136 (5)	0.0173 (6)	0.0221 (6)	0.0081 (5)	0.0064 (4)	0.0076 (5)
C6	0.0121 (5)	0.0107 (5)	0.0191 (5)	0.0038 (4)	0.0079 (4)	0.0040 (4)
C7	0.0115 (5)	0.0102 (5)	0.0148 (5)	0.0038 (4)	0.0058 (4)	0.0041 (4)
C8	0.0106 (5)	0.0100 (5)	0.0145 (5)	0.0037 (4)	0.0062 (4)	0.0026 (4)
C9	0.0117 (5)	0.0106 (5)	0.0124 (5)	0.0044 (4)	0.0051 (4)	0.0037 (4)
C10	0.0174 (6)	0.0107 (5)	0.0221 (6)	0.0061 (4)	0.0132 (5)	0.0043 (4)
C11	0.0132 (5)	0.0103 (5)	0.0178 (5)	0.0056 (4)	0.0075 (4)	0.0028 (4)
C12	0.0227 (6)	0.0299 (7)	0.0159 (6)	0.0150 (6)	0.0071 (5)	0.0082 (5)
C13	0.0204 (6)	0.0167 (6)	0.0336 (8)	-0.0010 (5)	0.0143 (6)	-0.0009 (5)
C14	0.0158 (5)	0.0128 (5)	0.0165 (5)	0.0079 (4)	0.0074 (4)	0.0051 (4)
C15	0.0272 (7)	0.0251 (7)	0.0212 (6)	0.0165 (6)	0.0094 (5)	0.0119 (5)
C16	0.0264 (7)	0.0208 (6)	0.0258 (7)	0.0135 (5)	0.0117 (5)	0.0013 (5)
C17	0.0137 (6)	0.0208 (6)	0.0301 (7)	0.0068 (5)	0.0098 (5)	0.0091 (5)
O1	0.0179 (4)	0.0177 (4)	0.0125 (4)	0.0119 (3)	0.0058 (3)	0.0032 (3)
O2	0.0126 (4)	0.0201 (5)	0.0215 (5)	0.0081 (4)	0.0052 (3)	-0.0015 (4)
O3	0.0150 (4)	0.0185 (4)	0.0133 (4)	0.0072 (3)	0.0056 (3)	0.0071 (3)
O4	0.0123 (4)	0.0092 (4)	0.0189 (4)	0.0036 (3)	0.0084 (3)	0.0018 (3)
O5	0.0161 (4)	0.0101 (4)	0.0167 (4)	0.0062 (3)	0.0088 (3)	0.0044 (3)
Si1	0.01136 (16)	0.01067 (16)	0.01308 (16)	0.00427 (12)	0.00538 (12)	0.00245 (12)

Geometric parameters (\AA , $^\circ$)

C1—C9	1.5325 (16)	C11—O5	1.4286 (14)
C1—C10	1.5349 (16)	C12—H12A	0.9800
C1—C11	1.5164 (15)	C12—H12B	0.9800
C1—O1	1.4512 (14)	C12—H12C	0.9800
C2—C3	1.3878 (17)	C12—Si1	1.8603 (13)
C2—C7	1.4018 (16)	C13—H13A	0.9800
C2—O1	1.3786 (14)	C13—H13B	0.9800
C3—H3	0.9500	C13—H13C	0.9800
C3—C4	1.3908 (18)	C13—Si1	1.8568 (14)
C4—H4	0.9500	C14—C15	1.5443 (17)
C4—C5	1.3908 (18)	C14—C16	1.5413 (17)
C5—H5	0.9500	C14—C17	1.5350 (17)
C5—C6	1.3954 (17)	C14—Si1	1.8936 (12)
C6—C7	1.4018 (16)	C15—H15A	0.9800
C6—O2	1.3659 (14)	C15—H15B	0.9800
C7—C8	1.5092 (16)	C15—H15C	0.9800

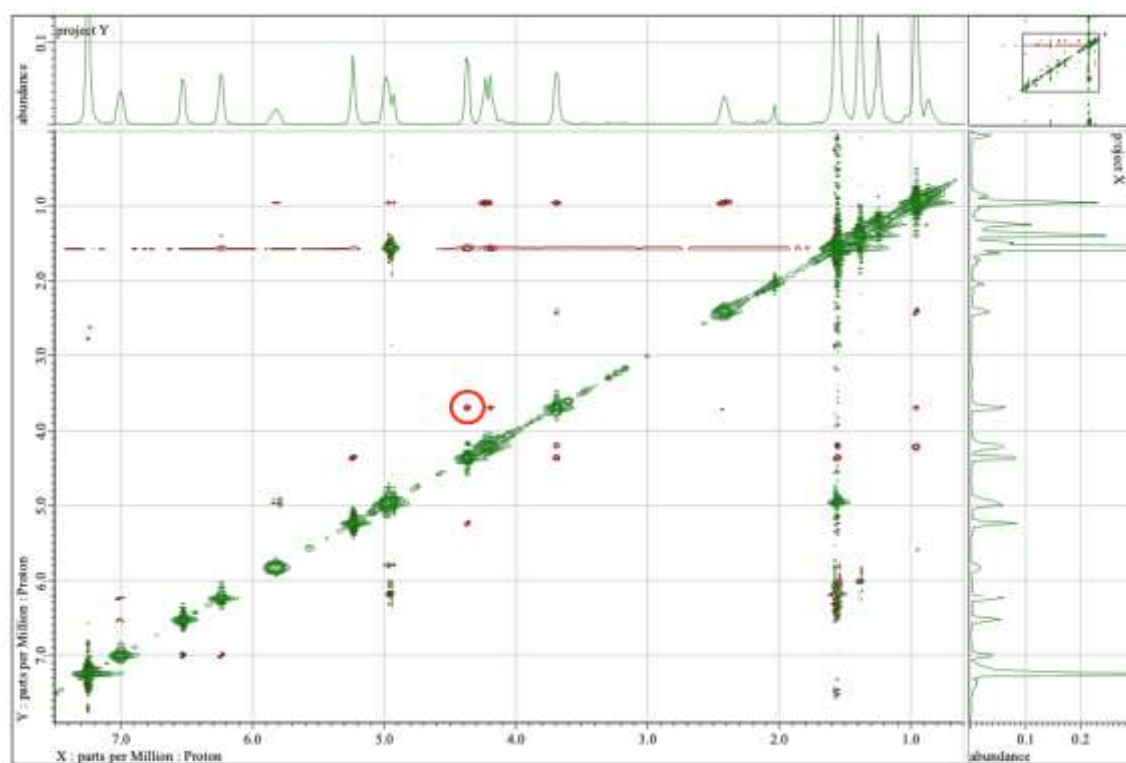
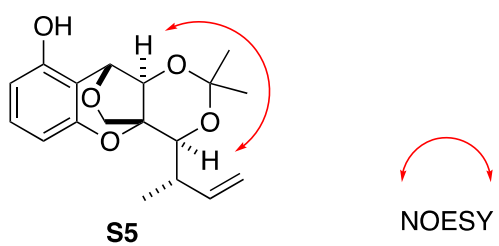
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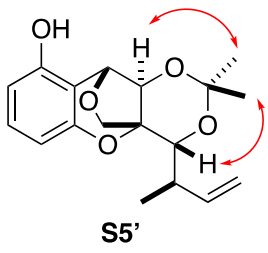
C8—H8	1.0000	C16—H16A	0.9800
C8—C9	1.5316 (16)	C16—H16B	0.9800
C8—O4	1.4562 (13)	C16—H16C	0.9800
C9—H9	1.0000	C17—H17A	0.9800
C9—O3	1.4137 (13)	C17—H17B	0.9800
C10—H10A	0.9900	C17—H17C	0.9800
C10—H10B	0.9900	O2—H2	0.8400
C10—O4	1.4540 (13)	O3—H3A	0.8400
C11—H11A	0.9900	O5—Si1	1.6761 (9)
C11—H11B	0.9900		
C9—C1—C10	102.12 (9)	H12A—C12—H12B	109.5
C11—C1—C9	116.46 (10)	H12A—C12—H12C	109.5
C11—C1—C10	112.46 (10)	H12B—C12—H12C	109.5
O1—C1—C9	109.06 (9)	Si1—C12—H12A	109.5
O1—C1—C10	110.39 (9)	Si1—C12—H12B	109.5
O1—C1—C11	106.32 (9)	Si1—C12—H12C	109.5
C3—C2—C7	121.84 (11)	H13A—C13—H13B	109.5
O1—C2—C3	116.70 (10)	H13A—C13—H13C	109.5
O1—C2—C7	121.44 (10)	H13B—C13—H13C	109.5
C2—C3—H3	120.7	Si1—C13—H13A	109.5
C2—C3—C4	118.66 (11)	Si1—C13—H13B	109.5
C4—C3—H3	120.7	Si1—C13—H13C	109.5
C3—C4—H4	119.4	C15—C14—Si1	109.53 (8)
C3—C4—C5	121.10 (12)	C16—C14—C15	109.12 (10)
C5—C4—H4	119.4	C16—C14—Si1	109.12 (9)
C4—C5—H5	120.2	C17—C14—C15	108.39 (10)
C4—C5—C6	119.56 (11)	C17—C14—C16	108.65 (11)
C6—C5—H5	120.2	C17—C14—Si1	111.99 (8)
C5—C6—C7	120.55 (11)	C14—C15—H15A	109.5
O2—C6—C5	116.95 (10)	C14—C15—H15B	109.5
O2—C6—C7	122.49 (11)	C14—C15—H15C	109.5
C2—C7—C6	118.23 (11)	H15A—C15—H15B	109.5
C2—C7—C8	117.39 (10)	H15A—C15—H15C	109.5
C6—C7—C8	124.38 (10)	H15B—C15—H15C	109.5
C7—C8—H8	111.8	C14—C16—H16A	109.5
C7—C8—C9	108.33 (9)	C14—C16—H16B	109.5
C9—C8—H8	111.8	C14—C16—H16C	109.5
O4—C8—C7	109.77 (9)	H16A—C16—H16B	109.5
O4—C8—H8	111.8	H16A—C16—H16C	109.5
O4—C8—C9	102.83 (9)	H16B—C16—H16C	109.5
C1—C9—H9	112.6	C14—C17—H17A	109.5
C8—C9—C1	97.77 (9)	C14—C17—H17B	109.5
C8—C9—H9	112.6	C14—C17—H17C	109.5
O3—C9—C1	108.04 (9)	H17A—C17—H17B	109.5
O3—C9—C8	112.36 (9)	H17A—C17—H17C	109.5
O3—C9—H9	112.6	H17B—C17—H17C	109.5
C1—C10—H10A	110.5	C2—O1—C1	116.40 (9)
C1—C10—H10B	110.5	C6—O2—H2	109.5
H10A—C10—H10B	108.7	C9—O3—H3A	109.5
O4—C10—C1	106.13 (9)	C10—O4—C8	106.73 (8)
O4—C10—H10A	110.5	C11—O5—Si1	123.83 (7)

supporting information

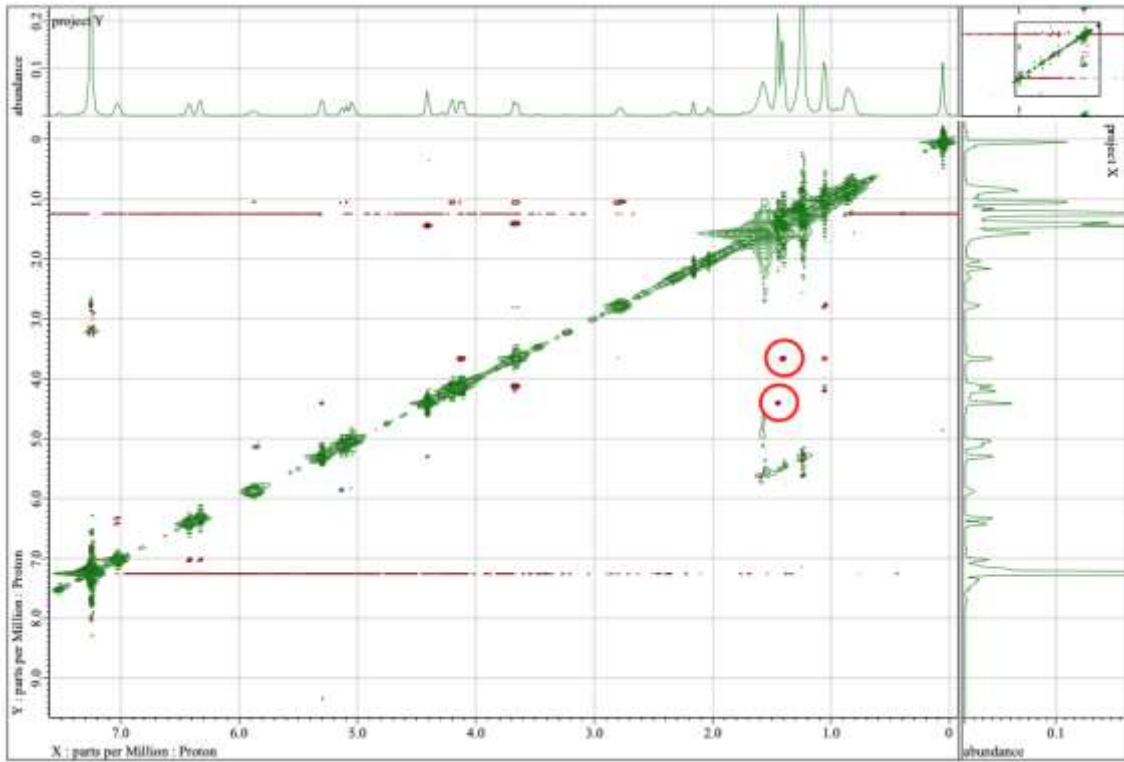
O4—C10—H10B	110.5	C12—Si1—C14	110.84 (6)
C1—C11—H11A	109.4	C13—Si1—C12	111.14 (7)
C1—C11—H11B	109.4	C13—Si1—C14	111.42 (6)
H11A—C11—H11B	108.0	O5—Si1—C12	109.57 (5)
O5—C11—C1	111.01 (9)	O5—Si1—C13	103.71 (6)
O5—C11—H11A	109.4	O5—Si1—C14	109.93 (5)
O5—C11—H11B	109.4		
C1—C10—O4—C8	7.58 (12)	C11—C1—C9—C8	-165.50 (10)
C1—C11—O5—Si1	-122.69 (9)	C11—C1—C9—O3	-48.87 (13)
C2—C3—C4—C5	-0.90 (19)	C11—C1—C10—O4	148.73 (10)
C2—C7—C8—C9	35.15 (13)	C11—C1—O1—C2	-170.88 (9)
C2—C7—C8—O4	-76.42 (12)	C11—O5—Si1—C12	48.40 (10)
C3—C2—C7—C6	0.77 (18)	C11—O5—Si1—C13	167.13 (9)
C3—C2—C7—C8	-179.33 (11)	C11—O5—Si1—C14	-73.64 (10)
C3—C2—O1—C1	-176.03 (10)	C15—C14—Si1—C12	-172.96 (9)
C3—C4—C5—C6	-0.86 (19)	C15—C14—Si1—C13	62.72 (10)
C4—C5—C6—C7	2.63 (18)	C15—C14—Si1—O5	-51.67 (10)
C4—C5—C6—O2	-178.50 (11)	C16—C14—Si1—C12	67.65 (10)
C5—C6—C7—C2	-2.57 (17)	C16—C14—Si1—C13	-56.67 (11)
C5—C6—C7—C8	177.55 (11)	C16—C14—Si1—O5	-171.07 (8)
C6—C7—C8—C9	-144.97 (11)	C17—C14—Si1—C12	-52.68 (11)
C6—C7—C8—O4	103.46 (12)	C17—C14—Si1—C13	-177.00 (9)
C7—C2—C3—C4	0.94 (18)	C17—C14—Si1—O5	68.60 (10)
C7—C2—O1—C1	5.01 (16)	O1—C1—C9—C8	74.23 (10)
C7—C8—C9—C1	-67.80 (10)	O1—C1—C9—O3	-169.14 (8)
C7—C8—C9—O3	178.99 (9)	O1—C1—C10—O4	-92.72 (11)
C7—C8—O4—C10	79.53 (11)	O1—C1—C11—O5	62.47 (12)
C9—C1—C10—O4	23.13 (11)	O1—C2—C3—C4	-178.01 (11)
C9—C1—C11—O5	-59.25 (13)	O1—C2—C7—C6	179.67 (10)
C9—C1—O1—C2	-44.55 (12)	O1—C2—C7—C8	-0.44 (16)
C9—C8—O4—C10	-35.60 (11)	O2—C6—C7—C2	178.62 (11)
C10—C1—C9—C8	-42.59 (10)	O2—C6—C7—C8	-1.26 (18)
C10—C1—C9—O3	74.04 (11)	O4—C8—C9—C1	48.37 (10)
C10—C1—C11—O5	-176.61 (9)	O4—C8—C9—O3	-64.85 (11)
C10—C1—O1—C2	66.88 (12)		

NOESY data of the corresponding acetonides **S5** and **S5'**.





NOESY



NOESY data of phomopsol B (2) and its diastereomer 2'

