SUPPORTING INFORMATION

Total Synthesis of Cristatic Acid

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General. All reactions were carried out under Ar in pre-dried glassware using Schlenk techniques. The solvents were dried by distillation over the drying agents indicated and were stored and transferred under Ar: CH_2Cl_2 (P_4O_{10}), toluene (Na/K), Et_2O, THF (magnesium/anthracene), MeOH (Mg), HMPA (CaH_2), pyridine, Et_3N (KOH). Flash chromatography: Merck silica gel (230-400 mesh). Mp: Gallenkamp apparatus (uncorrected). NMR: Spectra were recorded on a Bruker AC 200, DPX 300, AMX 400 or DMX 600 spectrometer in the solvent indicated. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. IR: Nicolet FT-7199, wavenumbers in cm^{-1}. MS: Finnigan MAT 8200 (70 eV) or Finnigan MAT SSQ 7000 (70 eV). HRMS: MAT 95 (70 eV). Elemental analyses: Dornis & Kolbe, Mülheim. Commercially available reagents (Aldrich, Fluka) were used as received.

X-Ray Structure Analysis of Compound 6

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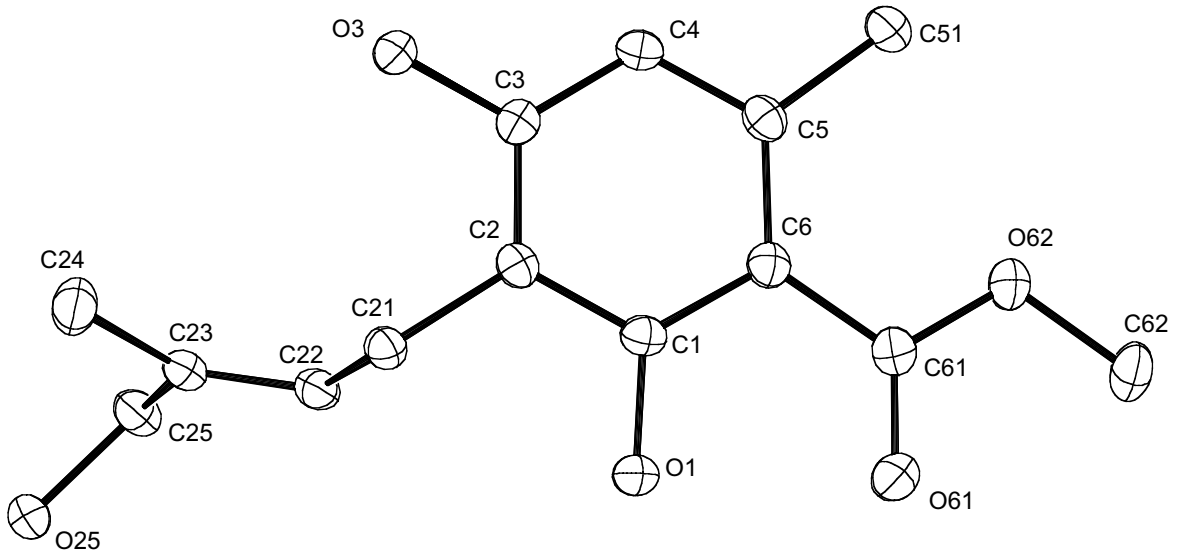

The complete lists of atomic coordinates, bond length and angles have been deposited with the Cambridge Crystallographic Data Center, Cambridge, U.K., under the deposition number **CCDC 144789** and may be obtained free of charge by applying to: „The Director, Cambridge Crystallographic Data Center, 12 Union Road, CB2 1EZ Cambridge, UK.“

Table 1. Crystal data and structure refinement.

Empirical formula	$C_{14} H_{18} O_5$	
Color	white	
Formula weight	266.28 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$, (no. 14)	
Unit cell dimensions	a = 7.5835(15) Å	α= 90°.
	b = 23.966(5) Å	β= 117.21(3)°.
	c = 8.1572(16) Å	γ = 90°.
Volume	1318.5(5) $Å^3$	
Z	4	
Density (calculated)	1.341 $Mg·m^{-3}$	
Absorption coefficient	0.102 mm^{-1}	
F(000)	568 e	
Crystal size	0.54 x 0.40 x 0.06 mm^3	
θ range for data collection	1.70 to 26.42°.	
Index ranges	$-9 \le h \le 9$, $-29 \le k \le 27$, $-10 \le l \le 10$	
Reflections collected	21722	
Independent reflections	2684 [R_{int} = 0.0584]	
Reflections with I>2σ(I)	2305	
Completeness to θ = 26.42°	96.3 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2684 / 0 / 244	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2σ(I)]	R_1 = 0.0378	wR^2 = 0.0949
R indices (all data)	R_1 = 0.0462	wR^2 = 0.0998
Largest diff. peak and hole	0.242 and -0.217 e·$Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2).
U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O(1)	0.3261(1)	0.0804(1)	0.3830(1)	0.024(1)
C(1)	0.2273(2)	0.0879(1)	0.1985(2)	0.019(1)
C(2)	0.1280(2)	0.1390(1)	0.1435(2)	0.018(1)
O(3)	-0.0756(1)	0.1990(1)	-0.0991(1)	0.021(1)
C(3)	0.0220(2)	0.1491(1)	-0.0442(2)	0.018(1)
C(4)	0.0137(2)	0.1097(1)	-0.1735(2)	0.019(1)
C(5)	0.1085(2)	0.0587(1)	-0.1210(2)	0.019(1)
C(6)	0.2205(2)	0.0469(1)	0.0698(2)	0.019(1)
C(21)	0.1296(2)	0.1791(1)	0.2879(2)	0.019(1)
C(22)	-0.0380(2)	0.1666(1)	0.3332(2)	0.020(1)
C(23)	-0.1717(2)	0.2023(1)	0.3352(2)	0.020(1)
C(24)	-0.1769(2)	0.2638(1)	0.2977(2)	0.028(1)
O(25)	-0.3302(1)	0.2069(1)	0.5377(1)	0.023(1)
C(25)	-0.3353(2)	0.1811(1)	0.3753(2)	0.023(1)
C(51)	0.0854(2)	0.0192(1)	-0.2742(2)	0.024(1)
O(61)	0.4284(1)	-0.0139(1)	0.3105(1)	0.040(1)
C(61)	0.3301(1)	-0.0054(1)	0.1458(2)	0.022(1)
O(62)	0.3173(1)	-0.0439(1)	0.0239(1)	0.026(1)
C(62)	0.4217(2)	-0.0959(1)	0.1014(2)	0.027(1)

Table 3. Bond lengths [Å] and angles [°].

O(1)-C(1)	1.3519(16)	O(1)-H(1)	0.93(2)
C(1)-C(2)	1.4002(18)	C(1)-C(6)	1.4203(18)
C(2)-C(3)	1.3871(18)	C(2)-C(21)	1.5160(17)
O(3)-C(3)	1.3687(16)	O(3)-H(3)	0.85(2)
C(3)-C(4)	1.3962(18)	C(4)-C(5)	1.3830(19)
C(4)-H(4)	0.939(16)	C(5)-C(6)	1.4199(19)
C(5)-C(51)	1.5117(18)	C(6)-C(61)	1.4744(19)
C(21)-C(22)	1.5077(18)	C(21)-H(21A)	1.000(15)
C(21)-H(21B)	0.962(16)	C(22)-C(23)	1.3332(19)
C(22)-H(22)	0.983(15)	C(23)-C(24)	1.503(2)
C(23)-C(25)	1.5083(18)	C(24)-H(24A)	0.99(2)
C(24)-H(24B)	1.00(2)	C(24)-H(24C)	1.01(2)
O(25)-C(25)	1.4464(16)	O(25)-H(25)	0.85(2)
C(25)-H(25A)	0.994(17)	C(25)-H(25B)	1.000(15)
C(51)-H(51A)	0.954(19)	C(51)-H(51B)	0.974(16)
C(51)-H(51C)	0.972(17)	O(61)-C(61)	1.2188(18)
C(61)-O(62)	1.3278(16)	O(62)-C(62)	1.4557(17)
C(62)-H(62A)	0.94(2)	C(62)-H(62B)	0.98(2)
C(62)-H(62C)	0.96(2)		
C(1)-O(1)-H(1)	106.9(12)	O(1)-C(1)-C(2)	114.56(11)
O(1)-C(1)-C(6)	123.01(12)	C(2)-C(1)-C(6)	122.41(12)
C(3)-C(2)-C(1)	117.48(11)	C(3)-C(2)-C(21)	122.77(12)
C(1)-C(2)-C(21)	119.64(11)	C(3)-O(3)-H(3)	109.4(13)
O(3)-C(3)-C(2)	117.87(11)	O(3)-C(3)-C(4)	120.86(12)
C(2)-C(3)-C(4)	121.28(12)	C(5)-C(4)-C(3)	121.79(12)
C(5)-C(4)-H(4)	119.8(9)	C(3)-C(4)-H(4)	118.4(9)
C(4)-C(5)-C(6)	118.72(12)	C(4)-C(5)-C(51)	116.73(12)
C(6)-C(5)-C(51)	124.55(12)	C(5)-C(6)-C(1)	118.31(12)
C(5)-C(6)-C(61)	124.69(12)	C(1)-C(6)-C(61)	116.99(12)
C(22)-C(21)-C(2)	110.83(11)	C(22)-C(21)-H(21A)	109.1(8)
C(2)-C(21)-H(21A)	109.6(8)	C(22)-C(21)-H(21B)	110.2(8)
C(2)-C(21)-H(21B)	110.1(9)	H(21A)-C(21)-H(21B)	106.9(12)
C(23)-C(22)-C(21)	127.30(12)	C(23)-C(22)-H(22)	116.4(8)
C(21)-C(22)-H(22)	116.3(8)	C(22)-C(23)-C(24)	125.23(13)
C(22)-C(23)-C(25)	119.43(12)	C(24)-C(23)-C(25)	115.34(12)

H(24A)-C(24)-H(24B)	109.2(16)	C(23)-C(24)-H(24C)	112.2(11)
H(24A)-C(24)-H(24C)	104.2(16)	H(24B)-C(24)-H(24C)	106.0(16)
C(25)-O(25)-H(25)	108.5(12)	O(25)-C(25)-C(23)	111.98(11)
O(25)-C(25)-H(25A)	107.6(9)	C(23)-C(25)-H(25A)	109.1(9)
O(25)-C(25)-H(25B)	107.2(8)	C(23)-C(25)-H(25B)	111.0(8)
H(25A)-C(25)-H(25B)	109.8(12)	C(5)-C(51)-H(51A)	108.9(10)
C(5)-C(51)-H(51B)	112.3(9)	H(51A)-C(51)-H(51B)	109.3(14)
C(5)-C(51)-H(51C)	112.3(10)	H(51A)-C(51)-H(51C)	107.3(14)
H(51B)-C(51)-H(51C)	106.6(13)	O(61)-C(61)-O(62)	120.52(12)
O(61)-C(61)-C(6)	123.23(12)	O(62)-C(61)-C(6)	116.25(12)
C(61)-O(62)-C(62)	115.51(11)	O(62)-C(62)-H(62A)	103.4(13)
O(62)-C(62)-H(62B)	110.2(11)	H(62A)-C(62)-H(62B)	108.6(16)
O(62)-C(62)-H(62C)	111.2(12)	H(62A)-C(62)-H(62C)	111.9(17)
H(62B)-C(62)-H(62C)	111.3(16)		

Table 4. Anisotropic displacement parameters (Å^2).

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(1)	0.031(1)	0.022(1)	0.016(1)	0.001(1)	0.008(1)	0.005(1)
C(1)	0.019(1)	0.022(1)	0.016(1)	0.001(1)	0.009(1)	-0.001(1)
C(2)	0.018(1)	0.018(1)	0.020(1)	-0.001(1)	0.010(1)	-0.002(1)
O(3)	0.023(1)	0.018(1)	0.019(1)	0.001(1)	0.008(1)	0.003(1)
C(3)	0.017(1)	0.017(1)	0.021(1)	0.002(1)	0.010(1)	-0.001(1)
C(4)	0.021(1)	0.022(1)	0.016(1)	0.001(1)	0.009(1)	0.000(1)
C(5)	0.020(1)	0.021(1)	0.020(1)	-0.002(1)	0.012(1)	-0.002(1)
C(6)	0.020(1)	0.019(1)	0.021(1)	0.001(1)	0.011(1)	0.000(1)
C(21)	0.022(1)	0.017(1)	0.018(1)	-0.001(1)	0.009(1)	0.000(1)
C(22)	0.024(1)	0.018(1)	0.016(1)	-0.001(1)	0.010(1)	-0.002(1)
C(23)	0.022(1)	0.021(1)	0.015(1)	-0.002(1)	0.008(1)	0.000(1)
C(24)	0.034(1)	0.023(1)	0.035(1)	0.004(1)	0.021(1)	0.007(1)
O(25)	0.026(1)	0.026(1)	0.019(1)	0.000(1)	0.011(1)	0.007(1)
C(25)	0.023(1)	0.027(1)	0.019(1)	-0.004(1)	0.010(1)	-0.001(1)
C(51)	0.031(1)	0.022(1)	0.019(1)	-0.002(1)	0.011(1)	0.002(1)
O(61)	0.056(1)	0.030(1)	0.022(1)	0.000(1)	0.008(1)	0.019(1)
C(61)	0.022(1)	0.021(1)	0.023(1)	-0.001(1)	0.011(1)	0.001(1)
O(62)	0.032(1)	0.020(1)	0.025(1)	-0.002(1)	0.012(1)	0.006(1)
C(62)	0.028(1)	0.019(1)	0.034(1)	-0.002(1)	0.013(1)	0.004(1)

X-Ray Structure Analysis of Compound 15

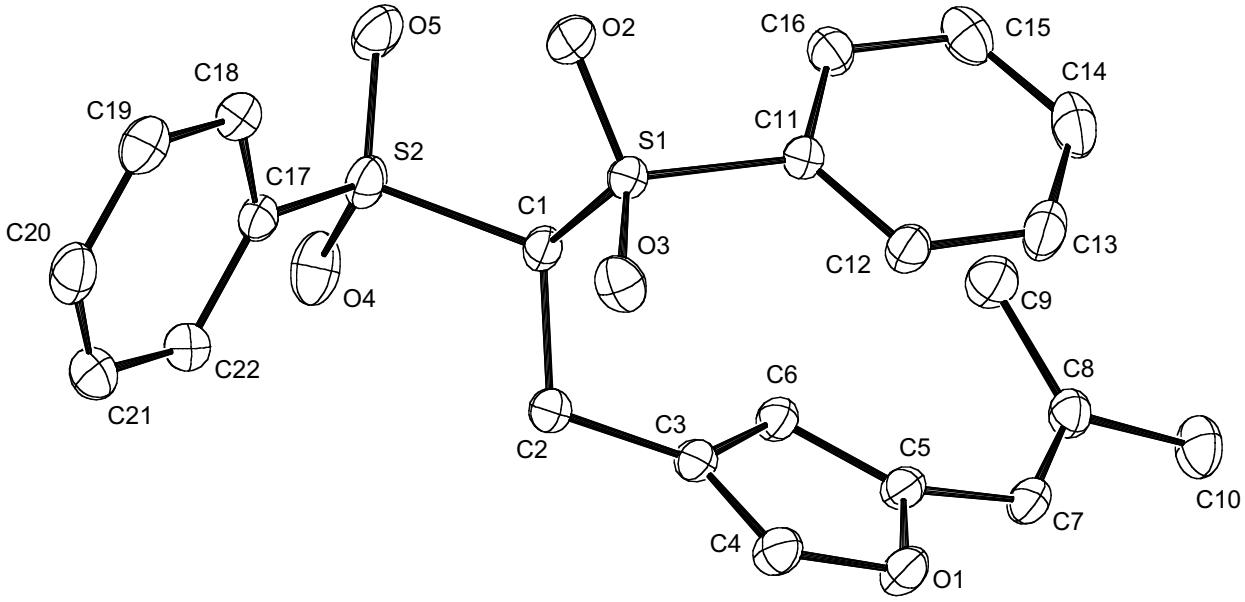

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Table 5. Crystal data and structure refinement.

Empirical formula	$C_{22}H_{22}O_5S_2$	
Color	colorless	
Formula weight	430.52 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	**P1, (no. 2)**	
Unit cell dimensions	a = 8.8917(4) Å	α= 77.317(2)°.
	b = 10.4269(5) Å	β= 73.545(2)°.
	c = 11.7085(5) Å	γ = 85.735(2)°.
Volume	1015.58(8) $Å^3$	
Z	2	
Density (calculated)	1.408 Mg · m^{-3}	
Absorption coefficient	0.294 mm^{-1}	
F(000)	452 e	
Crystal size	0.40 x 0.35 x 0.24 mm^3	
θ range for data collection	1.85 to 33.98°.	
Index ranges	$-11 \le h \le 13$, $-6 \le k \le 16$, $-18 \le l \le 18$	
Reflections collected	11435	
Independent reflections	6819 [R_{int} = 0.0214]	
Reflections with I>2σ(I)	5759	
Completeness to θ = 33.98°	82.4 %	
Absorption correction	SADABS	
Max. and min. transmission	1.00 and 0.86	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6819 / 0 / 262	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2σ(I)]	R_1 = 0.0469	wR^2 = 0.1336
R indices (all data)	R_1 = 0.0545	wR^2 = 0.1390
Extinction coefficient	0.007(2)	
Largest diff. peak and hole	0.942 and -0.706 e · $Å^{-3}$	

Table 6. Atomic coordinates and equivalent isotropic displacement parameters (Å^2).
U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
S(1)	0.3281(1)	0.4182(1)	0.3395(1)	0.018(1)
S(2)	0.6260(1)	0.3763(1)	0.1387(1)	0.022(1)
O(1)	0.3720(1)	0.8829(1)	0.3446(1)	0.024(1)
O(2)	0.2887(1)	0.2974(1)	0.3149(1)	0.028(1)
O(3)	0.3610(1)	0.4152(1)	0.4532(1)	0.025(1)
O(4)	0.7583(1)	0.4548(1)	0.0613(1)	0.033(1)
O(5)	0.5357(1)	0.3126(1)	0.0840(1)	0.034(1)
C(1)	0.4961(1)	0.4917(1)	0.2168(1)	0.018(1)
C(2)	0.5844(1)	0.5848(1)	0.2598(1)	0.020(1)
C(3)	0.4960(1)	0.7119(1)	0.2703(1)	0.019(1)
C(4)	0.4518(2)	0.7675(1)	0.3692(1)	0.023(1)
C(5)	0.3638(2)	0.9003(1)	0.2263(1)	0.019(1)
C(6)	0.4392(1)	0.7981(1)	0.1770(1)	0.019(1)
C(7)	0.2874(2)	1.0221(1)	0.1838(1)	0.021(1)
C(8)	0.2340(2)	1.0520(1)	0.0845(1)	0.021(1)
C(9)	0.2404(2)	0.9594(2)	0.0016(1)	0.027(1)
C(10)	0.1666(2)	1.1864(1)	0.0489(2)	0.029(1)
C(11)	0.1786(1)	0.5348(1)	0.3206(1)	0.018(1)
C(12)	0.1226(2)	0.6168(1)	0.4027(1)	0.022(1)
C(13)	0.0073(2)	0.7096(1)	0.3814(2)	0.029(1)
C(14)	-0.0481(2)	0.7204(2)	0.2800(2)	0.031(1)
C(15)	0.0105(2)	0.6378(2)	0.1986(1)	0.028(1)
C(16)	0.1241(2)	0.5437(1)	0.2187(1)	0.022(1)
C(17)	0.6949(1)	0.2592(1)	0.2463(1)	0.020(1)
C(18)	0.6199(1)	0.1392(1)	0.2980(1)	0.025(1)
C(19)	0.6850(1)	0.0454(1)	0.3758(1)	0.029(1)
C(20)	0.8215(2)	0.0725(2)	0.4008(1)	0.030(1)
C(21)	0.8951(2)	0.1922(2)	0.3487(2)	0.030(1)
C(22)	0.8320(2)	0.2871(1)	0.2712(1)	0.025(1)

Table 7. Bond lengths [Å] and angles [°].

S(1)-O(3)	1.4350(10)	S(1)-O(2)	1.4400(10)
S(1)-C(11)	1.7616(12)	S(1)-C(1)	1.8313(13)
S(2)-O(5)	1.4326(11)	S(2)-O(4)	1.4453(12)
S(2)-C(17)	1.7613(13)	S(2)-C(1)	1.8161(12)
O(1)-C(4)	1.3679(16)	O(1)-C(5)	1.3785(15)
C(1)-C(2)	1.5369(17)	C(1)-H(1)	1.0000
C(2)-C(3)	1.5004(17)	C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900	C(3)-C(4)	1.3536(18)
C(3)-C(6)	1.4385(17)	C(4)-H(4)	0.9500
C(5)-C(6)	1.3649(17)	C(5)-C(7)	1.4517(18)
C(6)-H(6)	0.9500	C(7)-C(8)	1.3438(18)
C(7)-H(7)	0.9500	C(8)-C(9)	1.4997(19)
C(8)-C(10)	1.5020(19)	C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800	C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800	C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800	C(11)-C(12)	1.3889(17)
C(11)-C(16)	1.3917(17)	C(12)-C(13)	1.392(2)
C(12)-H(12)	0.9500	C(13)-C(14)	1.389(2)
C(13)-H(13)	0.9500	C(14)-C(15)	1.391(2)
C(14)-H(14)	0.9500	C(15)-C(16)	1.3871(19)
C(15)-H(15)	0.9500	C(16)-H(16)	0.9500
C(17)-C(18)	1.3935(17)	C(17)-C(22)	1.3950(18)
C(18)-C(19)	1.3948	C(18)-H(18)	0.9500
C(19)-C(20)	1.3884(19)	C(19)-H(19)	0.9500
C(20)-C(21)	1.385(2)	C(20)-H(20)	0.9500
C(21)-C(22)	1.389(2)	C(21)-H(21)	0.9500
C(22)-H(22)	0.9500		
O(3)-S(1)-O(2)	118.74(7)	O(3)-S(1)-C(11)	109.78(6)
O(2)-S(1)-C(11)	108.26(6)	O(3)-S(1)-C(1)	107.88(6)
O(2)-S(1)-C(1)	109.19(6)	C(11)-S(1)-C(1)	101.65(6)
O(5)-S(2)-O(4)	119.03(8)	O(5)-S(2)-C(17)	109.83(7)
O(4)-S(2)-C(17)	107.31(7)	O(5)-S(2)-C(1)	107.30(6)
O(4)-S(2)-C(1)	104.15(6)	C(17)-S(2)-C(1)	108.77(6)
C(4)-O(1)-C(5)	107.27(10)	C(2)-C(1)-S(2)	112.68(8)
C(2)-C(1)-S(1)	111.24(8)	S(2)-C(1)-S(1)	115.22(7)

S(1)-C(1)-H(1)	105.6	C(3)-C(2)-C(1)	111.38(10)
C(3)-C(2)-H(2A)	109.4	C(1)-C(2)-H(2A)	109.4
C(3)-C(2)-H(2B)	109.4	C(1)-C(2)-H(2B)	109.4
H(2A)-C(2)-H(2B)	108.0	C(4)-C(3)-C(6)	106.35(11)
C(4)-C(3)-C(2)	127.19(12)	C(6)-C(3)-C(2)	126.46(11)
C(3)-C(4)-O(1)	110.40(11)	C(3)-C(4)-H(4)	124.8
O(1)-C(4)-H(4)	124.8	C(6)-C(5)-O(1)	109.28(11)
C(6)-C(5)-C(7)	136.29(12)	O(1)-C(5)-C(7)	114.32(10)
C(5)-C(6)-C(3)	106.69(11)	C(5)-C(6)-H(6)	126.7
C(3)-C(6)-H(6)	126.7	C(8)-C(7)-C(5)	126.82(12)
C(8)-C(7)-H(7)	116.6	C(5)-C(7)-H(7)	116.6
C(7)-C(8)-C(9)	124.00(12)	C(7)-C(8)-C(10)	120.05(12)
C(9)-C(8)-C(10)	115.93(12)	C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5	H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5	H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5	C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5	H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5	H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5	C(12)-C(11)-C(16)	122.12(12)
C(12)-C(11)-S(1)	120.54(10)	C(16)-C(11)-S(1)	117.30(9)
C(11)-C(12)-C(13)	118.09(13)	C(11)-C(12)-H(12)	121.0
C(13)-C(12)-H(12)	121.0	C(14)-C(13)-C(12)	120.63(13)
C(14)-C(13)-H(13)	119.7	C(12)-C(13)-H(13)	119.7
C(13)-C(14)-C(15)	120.28(13)	C(13)-C(14)-H(14)	119.9
C(15)-C(14)-H(14)	119.9	C(16)-C(15)-C(14)	120.00(14)
C(16)-C(15)-H(15)	120.0	C(14)-C(15)-H(15)	120.0
C(15)-C(16)-C(11)	118.87(13)	C(15)-C(16)-H(16)	120.6
C(11)-C(16)-H(16)	120.6	C(18)-C(17)-C(22)	121.52(12)
C(18)-C(17)-S(2)	120.44(9)	C(22)-C(17)-S(2)	117.90(11)
C(17)-C(18)-C(19)	118.64(7)	C(17)-C(18)-H(18)	120.7
C(19)-C(18)-H(18)	120.7	C(20)-C(19)-C(18)	120.08(8)
C(20)-C(19)-H(19)	120.0	C(18)-C(19)-H(19)	120.0
C(21)-C(20)-C(19)	120.73(13)	C(21)-C(20)-H(20)	119.6
C(19)-C(20)-H(20)	119.6	C(20)-C(21)-C(22)	120.11(13)
C(20)-C(21)-H(21)	119.9	C(22)-C(21)-H(21)	119.9
C(21)-C(22)-C(17)	118.93(13)	C(21)-C(22)-H(22)	120.5
C(17)-C(22)-H(22)	120.5		

Table 8. Anisotropic displacement parameters (Å^2).

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}
S(1)	0.019(1)	0.015(1)	0.021(1)	-0.004(1)	-0.007(1)	0.002(1)
S(2)	0.026(1)	0.023(1)	0.019(1)	-0.009(1)	-0.007(1)	0.008(1)
O(1)	0.033(1)	0.019(1)	0.023(1)	-0.008(1)	-0.012(1)	0.005(1)
O(2)	0.026(1)	0.017(1)	0.043(1)	-0.011(1)	-0.010(1)	0.001(1)
O(3)	0.025(1)	0.031(1)	0.020(1)	-0.002(1)	-0.008(1)	0.002(1)
O(4)	0.033(1)	0.032(1)	0.024(1)	-0.003(1)	0.003(1)	0.007(1)
O(5)	0.042(1)	0.036(1)	0.035(1)	-0.023(1)	-0.022(1)	0.016(1)
C(1)	0.019(1)	0.016(1)	0.019(1)	-0.005(1)	-0.006(1)	0.003(1)
C(2)	0.020(1)	0.017(1)	0.025(1)	-0.005(1)	-0.009(1)	0.002(1)
C(3)	0.020(1)	0.015(1)	0.023(1)	-0.004(1)	-0.008(1)	0.001(1)
C(4)	0.030(1)	0.018(1)	0.024(1)	-0.004(1)	-0.013(1)	0.003(1)
C(5)	0.023(1)	0.017(1)	0.021(1)	-0.006(1)	-0.009(1)	0.001(1)
C(6)	0.021(1)	0.016(1)	0.021(1)	-0.005(1)	-0.007(1)	0.002(1)
C(7)	0.024(1)	0.015(1)	0.025(1)	-0.007(1)	-0.008(1)	0.003(1)
C(8)	0.020(1)	0.018(1)	0.024(1)	-0.003(1)	-0.006(1)	0.002(1)
C(9)	0.032(1)	0.027(1)	0.026(1)	-0.008(1)	-0.013(1)	0.004(1)
C(10)	0.029(1)	0.021(1)	0.035(1)	-0.001(1)	-0.010(1)	0.007(1)
C(11)	0.018(1)	0.017(1)	0.021(1)	-0.005(1)	-0.006(1)	0.001(1)
C(12)	0.022(1)	0.021(1)	0.024(1)	-0.008(1)	-0.004(1)	0.001(1)
C(13)	0.026(1)	0.023(1)	0.036(1)	-0.010(1)	-0.002(1)	0.005(1)
C(14)	0.022(1)	0.028(1)	0.040(1)	-0.002(1)	-0.008(1)	0.007(1)
C(15)	0.023(1)	0.030(1)	0.029(1)	0.001(1)	-0.011(1)	0.002(1)
C(16)	0.020(1)	0.025(1)	0.023(1)	-0.005(1)	-0.007(1)	0.001(1)
C(17)	0.020(1)	0.021(1)	0.021(1)	-0.009(1)	-0.006(1)	0.004(1)
C(18)	0.024(1)	0.020(1)	0.033(1)	-0.010(1)	-0.010(1)	0.002(1)
C(19)	0.033(1)	0.020(1)	0.033(1)	-0.006(1)	-0.008(1)	0.004(1)
C(20)	0.034(1)	0.028(1)	0.029(1)	-0.009(1)	-0.014(1)	0.012(1)
C(21)	0.027(1)	0.032(1)	0.036(1)	-0.013(1)	-0.017(1)	0.008(1)
C(22)	0.022(1)	0.023(1)	0.032(1)	-0.009(1)	-0.010(1)	0.002(1)

Methyl 2,4-Dihydroxy-6-methyl-benzoate (2). Methyl acetoacetate (20 mL, 185.3 mmol) is slowly added to a stirred suspension of NaH (6.20 g, 258.3 mmol) in THF (100 mL) at 0°C. After the evolution of gas has ceased, the reaction mixture is cooled to –78°C and n-BuLi (1.6 M in hexane, 109.2 mL, 174.7 mmol) is added dropwise. The mixture is allowed to warm to ambient temperature overnight and is then refluxed for 24 h. The resulting dark red suspension is treated with aq. HCl (2 M) until pH ≈ 2 is reached and stirring is continued at ambient temperature for 14 h. A standard extractive work-up with EtOAc followed by flash chromatography of the crude product (hexane/EtOAc, 10/1→4/1) provides ester **2** as a colorless solid (10.13 g, 60%). Mp = 134-136°C (ref.[5]: 136-138°C). ^{1}H NMR (200 MHz, $CDCl_3$): _ 11.75 (s, 1H), 6.32-6.20 (m, 2H), 3.92 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): _ 172.1, 165.3, 160.3, 144.0, 139.1, 111.3, 101.3, 51.9, 24.2. MS: *m/z* (rel. intensity): 182 ([M^+], 45), 151 (24), 150 (100), 122 (39), 94 (11). IR (film): 3369, 3312, 3044, 2984, 2958, 1640, 1582, 1503, 1446, 1391, 1380, 1313, 1267, 1201, 1160, 1112, 1062, 1033, 995, 953, 854, 838, 800, 753, 703, 642, 624, 576, 524 cm^{-1}.

Methyl 2,4-Dihydroxy-6-methyl-3-(3-methyl-but-2-enyl)-benzoate (3). NaH (264 mg, 11.0 mmol) is added in portions to a suspension of ester **2** (2.00 g, 10.98 mmol) in toluene and the resulting mixture is stirred at 50°C for 4 h. The voluminous suspension formed is cooled to 35°C prior to the addition of 1-bromo-3-methyl-2-butene (1.67 mL, 14.34 mmmol) and stirring is continued at that temperature for 15 h. An aqueous work-up, extraction of the aqueous layer with EtOAc, evaporation of the solvent, and flash chromatography (hexane/EtOAc, 20/1→10/1) affords the title compound as colorless crystals (1.20 g, 73% based on recovered starting material [0.80 g]). Mp = 69-70°C. ^{1}H NMR (300 MHz, $CDCl_3$): _ 12.07 (s, 1H), 6.20 (s, 1H), 5.81 (s, 1H), 5.28-5.19 (m, 1H), 3.89 (s, 3H), 3.39 (d, J = 7.1 Hz, 1H), 2.43 (s, 3H), 1.79 (s, 3H), 1.72 (d, J = 1.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): _ 172.7, 162.6, 159.2, 140.8, 135.1, 121.5, 111.5, 111.3, 105.2, 51.8, 25.8, 24.1, 22.1, 17.9. MS: *m/z* (rel. intensity): 251 (13), 250 ([M^+], 85), 219 (19), 218 (96), 217 (11), 203 (40), 195 (14), 191 (14), 190 (100), 175 (74), 164 (11), 163 (100), 162 (19), 77 (11). IR (film): 3459, 3074, 3042, 2981, 2962, 2936, 2912, 1637, 1616, 1592, 1505, 1453, 1441, 1417, 1377, 1328, 1298, 1278, 1229, 1199, 1161, 1086, 1057, 1024, 999, 976, 912, 863, 822, 801, 778, 753, 657, 622, 579, 548, 452 cm^{-1}. HRMS ($C_{14}H_{18}O_4$): *calcd.*: 250.12051; *found*: 250.11975. $C_{14}H_{18}O_4$: *calcd.*: C, 67.18; H, 7.25; *found*: C, 67.04; H, 7.27.

Methyl 6-Methyl-3-(3-methyl-but-2-enyl)-2,4-bis-(2-trimethylsilanyl-ethoxymethoxy)benzoate (4). Diol **3** (850 mg, 3.40 mmol) is added to a suspension of KH (292 mg, 7.28 mmol) and 18-crown-6 (45 mg, 0.17 mmol) in THF (40 mL) at 0°C and the mixture is stirred for 5 min at that temperature. SEMCl (1.284 mL, 7.28 mmol) is introduced and stirring is continued for 5 h at ambient temperature. A standard extractive work-up followed by flash chromatography (hexane/ EtOAc, 20/1) affords product **4** as a colorless syrup (1.46 g, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): _ 6.72 (s, 1H), 5.20 (s, 2H), 5.17-5.08 (m, 1H), 4.98 (s, 2H), 3.85 (s, 3H), 3.79-3.67 (m, 4H), 3.33 (d,

0.00 (s, 9H), -0.03 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): _ 168.8, 156.9, 153.6, 135.1, 131.2, 122.9, 122.1, 111.6, 99.0, 92.4, 67.4, 66.2, 51.9, 25.7, 23.3, 19.9, 18.1, 18.0, 17.9, -1.5. MS: *m/z* (rel. intensity): 380 (22), 379 (70), 362 (10), 319 (15), 235 (10), 73 (100). IR (film): 2953, 2925, 2897, 2739, 1730, 1602, 1578, 1480, 1436, 1395, 1379, 1272, 1249, 1220, 1191, 1151, 1100, 1058, 1003, 940, 920, 860, 836, 758, 694, 663, 611 cm^{-1}. HRMS ($C_{26}H_{46}O_6Si_2$+Na): *calcd*.: 533.27307; *found*: 533.27499.

Methyl 3-((*E*)-4-Hydroxy-3-methyl-but-2-enyl)-6-methyl-2,4-bis-(2-trimethylsilanyl-ethoxy methoxy) benzoate (5). *tert*-BuOOH (70% w/w in water, 360 µL, 2.62 mmol) is added to a suspension of SeO_2 (120 mg, 1.08 mmol) in CH_2Cl_2 (20 mL) and the resulting mixture is stirred for 15 min. A solution of compound **4** (1.00 g, 1.96 mmol) in CH_2Cl_2 (5 mL) is added dropwise and the suspension is stirred for 6 h at ambient temperature. Water and CH_2Cl_2 are added, the organic layer is dried (Na_2SO_4) and evaporated, and the residue is purified by flash chromatography (hexane/EtOAc, 10/1) to afford product **5** as a colorless syrup (630 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$): _ 6.73 (s, 1H), 5.47-5.38 (m, 1H), 5.20 (s, 2H), 4.97 (s, 2H), 3.93 (s, 2H), 3.85 (s, 3H), 3.79-3.67 (m, 4H), 3.39 (d, *J* = 6.8 Hz, 2H), 2.25 (s, 3H), 1.79 (d, *J* = 0.9 Hz, 3H), 1.40 (bs, 1H), 1.01-0.88 (m, 4H), 0.00 (s, 9H), -0.03 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): _ 168.68, 156.96, 153.73, 135.50, 134.67, 124.75, 122.07, 121.31, 111.71, 99.02, 92.61, 69.01, 67.56, 66.35, 51.99, 22.89, 19.97, 18.09, 17.97, 13.82, -1.45. MS: *m/z* (rel. intensity): 379 (10), 378 (21), 377 (24), 320 (14), 306 (11), 305 (48), 289 (14), 288 (14), 273 (10), 73 (100). IR (film): 3444, 2952, 2897, 1729, 1603, 1576, 1481, 1436, 1395, 1380, 1274, 1250, 1222, 1191, 1153, 1099, 1058, 1011, 940, 920, 860, 837, 759, 694, 665, 611 cm^{-1}. HRMS ($C_{26}H_{46}O_7Si_2$+Na): *calcd*.: 549.26798; *found*: 549.26866. $C_{26}H_{46}O_7Si_2$: *calcd*.: C, 59.28; H, 8.80; *found*: C, 59.18; H, 8.72.

3-((*E*)-4-Brom-3-methyl-but-2-enyl)-6-methyl-2,4-bis-(2-trimethylsilanyl-ethoxymethoxy)-benzoic acid methyl ester (7). To a solution of alcohol **5** (100 mg, 0.19 mmol) in CH_2Cl_2 (10 mL) at 0°C are successively added Et_3N (30 µL, 0.22 mmol) and mesyl chloride (15 µL, 0.19 mmol). After stirring for 1 h, THF (2 mL) and LiBr (250 mg, 2.88 mmol) are introduced and stirring is continued for 2 h at ambient temperature. A standard extractive work-up followed by flash chromatography (hexane/EtOAc, 30/1) afford product **7** as a colorless syrup (85 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): _ 6.74 (s, 1H), 5.61 (t, *J* = 6.9 Hz, 1H), 5.20 (s, 2H), 4.97 (s, 2H), 3.91 (s, 2H), 3.86 (s, 3H), 3.79-3.67 (m, 4H), 3.38 (d, *J* = 6.9 Hz, 2H), 2.26 (s, 3H), 1.88 (d, *J* = 0.9 Hz, 3H), 1.00-0.89 (m, 4H), 0.00 (s, 9H), -0.02 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): _ 168.63, 157.04, 153.87, 135.84, 131.60, 129.72, 122.04, 120.44, 111.76, 99.17, 92.69, 67.56, 66.41, 52.04, 41.77, 23.62, 20.03, 18.08, 17.98, 14.80, -1.41. MS: *m/z* (rel. intensity): 451 (11), 393 (14), 361 (11), 320 (14), 305 (30), 290 (11), 289 (47), 73 (100). IR (film): 2952, 2899, 1729, 1653, 1603, 1576, 1481, 1436, 1394, 1380, 1272, 1249, 1225, 1204, 1190, 1153, 1100, 1056, 1012, 997, 940, 919, 860, 836, 758, 694, 668, 609 cm^{-1}. HRMS ($C_{26}H_{45}BrO_6Si_2$): *calcd*.: 611.18359; *found*: 611.18342.

***tert*-Butyl-{2-[3-(4-methoxy-benzyloxymethyl)-oxiranyl]-allyloxy}-dimethylsilane (10)**. To a stirred solution of sulfonium salt **8** (325 mg, 0.90 mmol)[12,13] in THF (15 mL) is slowly added *tert*-BuLi (1.7 M in hexane, 0.53 mL, 0.90 mmol) at –78°C. After stirring for 15 min at that temperature, aldehyde **9** (162 mg, 0.90 mmol)[14] is introduced and the reaction mixture is allowed to warm to ambient temperature. An aqueous extractive work-up followed by flash chromatography (hexane/EtOAc, 30/1) affords epoxide **10** as a colorless syrup (204 mg, 62%, mixture of diastereoisomers). ^{1}H NMR (300 MHz, $CDCl_3$): _ 7.24-7.18 (m, 2H), 6.85-6.78 (m, 2H), 5.21-5.12 (m), 5.04-4.98 (m) [2H], 4.50-4.33 (m, 2H), 4.13-3.98 (m, 2H), 3.743 (s), 3.741 (s) [3H], 3.71 (d, *J* = 2.9 Hz), 3.67 (d, *J* = 2.9 Hz), 3.54-3.23 (m), 3.13-3.08 (m) [4H], 0.84 (s, 9H), 0.00 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): _ 159.24, 143.94, 141.82, 130.04, 129.92, 129.40, 113.79, 113.76, 112.92, 111.50, 72.92, 72.86, 69.75, 67.34, 64.20, 62.45, 58.19, 56.54, 55.60, 55.25, 55.04, 25.85, 18.31, 18.28, -5.39, -5.43. MS: *m/z* (rel. intensity): 121 (100). IR (film): 2997, 2955, 2930, 2885, 2857, 1654, 1613, 1586, 1514, 1471, 1464, 1443, 1389, 1362, 1302, 1250, 1173, 1095, 1038, 1007, 912, 838, 778, 707, 669, 579 cm^{-1}. HRMS ($C_{20}H_{32}O_4Si$+Na): *calcd*.: 387.19676; *found*: 387.19700. $C_{20}H_{32}O_4Si$: *calcd*.: C, 65.819; H, 8.85; *found*: C, 65.81; H, 8.92.

6,6-Bis-phenylsulfonyl-4-(*tert*-butyldimethylsilanyloxymethyl)-1-(4-methoxy-benzyloxy)-hex-3-en-2-ol (11). To a solution of $Pd(PPh_3)_4$ (280 mg, 0.24 mmol), dppe (182 mg, 4.6 mmol) and bis(phenylsulfonyl)methane (1.007 g, 3.40 mmol) in THF (100 mL) is added epoxide **10** (1.25 g, 3.43 mmol) and the resulting mixture is stirred for 14 h at ambient temperature. An aqueous extractive work-up followed by flash chromatography of the crude material (hexane/EtOAc, 10/1→4/1) affords product **11** as a colorless syrup (2.20 g, 98%, mixture of diastereoisomers). ^{1}H NMR (300 MHz, $CDCl_3$): _ 7.98-7.83 (m, 4H), 7.73-7.46 (m, 6H), 7.28-7.21 (m, 2H), 6.90-6.83 (m, 2H), 5.53 (d, *J* = 8.9 Hz), 5.25 (d, *J* = 8.0 Hz) [1H], 5.39 (t, *J* = 6.4 Hz), 5.03 (dd, *J* = 6.0, 7.1 Hz) [1H], 4.57-4.39 (m, 3H), 4.19 (s), 4.09 (d, *J* = 1.0 Hz) [2H], 3.78 (s, 3H), 3.50-2.88 (m, 4H), 2.24 (bs, 1H), 0.86 (s, 9H), 0.031 (s), 0.027 (s), 0.015 (s) [6H]. ^{13}C NMR (75 MHz, $CDCl_3$): _ 159.35, 159.25, 138.16, 137.99, 137.67, 137.43, 136.60, 134.80, 134.52, 134.44, 134.38, 129.92, 129.74, 129.68, 129.64, 129.47, 129.43, 129.34, 129.21, 128.98, 128.91, 128.84, 128.05, 113.86, 113.79, 81.63, 81.59, 77.20, 74.47, 73.25, 73.10, 73.01, 72.95, 67.18, 66.80, 66.30, 60.47, 55.24, 31.51, 25.90, 25.87, 24.93, 18.32, 18.25, -5.32, -5.34, -5.40, -5.46. MS: *m/z* (rel. intensity): 125 (16), 122 (17), 121 (100). IR (film): 3532, 3065, 3003, 2953, 2929, 2856, 1681, 1612, 1585, 1513, 1464, 1448, 1390, 1331, 1250, 1156, 1079, 1035, 1000, 938, 837, 780, 753, 732, 687, 608, 569, 550 cm^{-1}. HRMS ($C_{33}H_{44}O_8S_2Si$+Na): *calcd*.: 683.21446; *found*: 683.21393. $C_{33}H_{44}O_8S_2Si$: *calcd*.: C, 59.97; H, 6.71; *found*: C, 60.08; H, 6.63.

[2-(2,2-Bis-phenylsulfonyl-ethyl)-5-(4-methoxy-benzyloxy)-4-(tetrahydro-pyran-2-yloxy)-pent-2-enyloxy]-*tert*-butyldimethylsilane. Pyridinium tosylate (30 mg, 0.12 mmol) is added to a

16.5 mmol) in CH_2Cl_2 (100 mL) at 0°C. The reaction mixture is then stirred for 4 h at ambient temperature and quenched by addition of aq. sat. $NaHCO_3$. Repeated extraction of the aqueous layer with CH_2Cl_2, drying of the combined organic phases (Na_2SO_4), evaporation of the solvent and flash chromatography of the crude product (hexane/EtOAc, 10/1) affords the title compound as a colorless syrup (2.05 g, 91%, mixture of diastereoisomers). ^{1}H NMR (300 MHz, $CDCl_3$): _ 8.00-7.83 (m, 4H), 7.70-7.42 (m, 6H), 7.29-7.19 (m, 2H), 6.92-6.80 (m, 2H), 5.62-4.07 (m, 6H), 3.78 (s), 3.77 (s) [3H], 3.95-2.80 (m, 8H), 1.90-1.38 (m, 6H), 0.86 (s), 0.85 (s) [9H], 0.02 (s), 0.01 (s) [6H]. MS: *m/z* (rel. intensity): 377 (12), 159 (13), 135 (10), 125 (25), 122 (12), 121 (100), 85 (42). IR (film): 3065, 3002, 2930, 2856, 1612, 1585, 1513, 1464, 1448, 1389, 1332, 1250, 1201, 1157, 1079, 1034, 933, 904, 836, 780, 754, 732, 688, 611, 567 cm^{-1}. HRMS ($C_{38}H_{52}O_9S_2Si$+Na): *calcd.*: 767.27198; *found*: 767.27364. $C_{38}H_{52}O_9S_2Si$: *calcd.*: C, 61.26; H, 7.03; *found*: C, 61.08; H, 6.93.

2-(2,2-Bis-phenylsulfonyl-ethyl)-5-(4-methoxy-benzyloxy)-4-(tetrahydro-pyran-2-yloxy)-pent-2-en-1-ol (12). A mixture of the silylether described above (1.90 g, 2.55 mmol) and n-$Bu_4NF{\cdot}3H_2O$ (1.61 g, 5.10 mmol) in THF (100 mL) is stirred for 16 h at 50°C. For work-up, the solvent is evaporated and the residue is purified by flash chromatography (hexane/EtOAc, 4/1→2/1) to afford product **12** as a colorless syrup (1.53 g, 95%, mixture of diastereoisomers). ^{1}H NMR (300 MHz, $CDCl_3$): _ 7.93-7.79 (m, 4H), 7.63-7.39 (m, 6H), 7.22-7.14 (m, 2H), 6.84-6.75 (m, 2H), 5.60-5.03 (m, 2H), 4.75-3.91 (m, 3H), 3.729 (s), 3.727 (s), 3.722 (s), 3.713 (s) [3H], 3.87-2.80 (m, 9H), 1.84-1.25 (m, 6H). MS (ESI pos): *m/z* (rel. intensity): 653 ([M+Na$^+$], 100). MS: *m/z* (rel. intensity): 377 (19), 235 (13), 137 (12), 125 (28), 122 (13), 121 (81), 85 (100), 77 (12), 67 (11), 57 (10). IR (film): 3527, 3451, 3064, 3001, 2939, 2864, 1612, 1585, 1513, 1465, 1448, 1331, 1249, 1201, 1157, 1079, 1034, 1001, 976, 903, 870, 817, 788, 754, 733, 688, 611, 567 cm^{-1}. HRMS ($C_{32}H_{38}O_9S_2$+Na): *calcd.*.: 653.18550; *found*: 653.18601. $C_{32}H_{38}O_9S_2$: *calcd.*: C, 60.93; H, 6.07; *found*: C, 60.94; H, 6.15.

4-(2,2-Bis-phenylsulfonyl-ethyl)-2-(4-methoxy-benzyloxymethyl)-furan (13). To a suspension of MnO_2 (1.39 g, 16.0 mmol) in CH_2Cl_2 (60 mL) is added alcohol **12** (1.00 g, 1.59 mmol) and the resulting mixture is stirred for 3 h at ambient temperature. Insoluble residues are filtered off through a pad of silica and are carefully rinsed with EtOAc (80 mL in several portions). All volatiles are removed in vacuo and the residue is dissolved in EtOAc (50 mL). Aq. HCl (2M, 300 μL) is added and the resulting solution is stirred for 12 h at ambient temperature. Extraction of the mixture with aq. $NaHCO_3$ and CH_2Cl_2, drying of the combined organic layers (Na_2SO_4), evaporation of all volatiles, and flash chromatography of the crude material (hexane/EtOAc, 4/1→2/1) provides furan **13** as a colorless solid (730 mg, 87%). Mp = 94-96°C. ^{1}H NMR (300 MHz, $CDCl_3$): _ 7.86-7.77 (m, 4H), 7.63-7.54 (m, 2H), 7.52-7.41 (m, 4H), 7.22-7.14 (m, 2H), 6.93 (d, *J* = 0.7 Hz, 1H), 6.85-6.78 (m, 2H), 5.96 (s, 1H), 4.47 (t, *J* = 5.3 Hz, 1H), 4.36 (s, 2H), 4.22 (s, 2H), 3.72 (s, 3H), 3.25 (d, *J* = 5.3 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): _ 159.22, 152.52, 140.62, 137.88, 134.57, 129.66,

m/z (rel. intensity): 549 ([M+Na^+], 100). MS: *m/z* (rel. intensity): 390 (22), 389 (15), 249 (28), 248 (77), 247 (29), 221 (10), 185 (12), 150 (11), 137 (14), 136 (17), 135 (10), 125 (16), 122 (25), 121 (100), 107 (79), 106 (15), 79 (17), 78 (13), 77 (44). IR (film): 3160, 3096, 3069, 3003, 2932, 2840, 1614, 1583, 1546, 1515, 1462, 1447, 1390, 1344, 1330, 1309, 1247, 1217, 1165, 1080, 1067, 1032, 928, 826, 784, 763, 736, 726, 689, 633, 598, 556, 525, 500 cm^{-1}. HRMS ($C_{27}H_{26}O_7S_2S$+Na): *calcd*.: 549.10177; *found*: 549.10189. $C_{27}H_{26}O_7S_2$: *calcd*.: C, 61.58; H, 4.98; *found*: C, 61.65; H, 4.99.

4-(2,2-Bis-phenylsulfonyl-ethyl)-2-(2-methyl-propenyl)-furan (15). DDQ (345 mg, 1.52 mmol) is added to a solution of furan **13** (600 mg, 1.14 mmol) in CH_2Cl_2 (50 mL) and water (2.5 mL) at 0°C. The mixture is stirred for 7 h prior to extraction with H_2O/CH_2Cl_2. The combined organic layers are dried (Na_2SO_4), the solvent is evaporated and the residue purified by flash chromatography (hexane/EtOAc, 2/1). Product **14** thus obtained (containing traces of DDQ) is dissolved in CH_2Cl_2 (50 mL) and reacted with MnO_2 (2.0 g, 23 mmol) for 3 h at room temperature. Insoluble residues are filtered off through a short pad of silica and are carefully rinsed with EtOAc (30 mL) in several portions. The combined filtrates are evaporated and the crude aldehyde thus formed is added to a freshly prepared solution of $Ph_3P{=}C(CH_3)_2$ [formed from isopropyltriphenylphosphonium bromide (2.47 g, 5.7 mmol) and n-BuLi (1.6 M in hexane, 3.56 mL, 5.70 mmol) in THF (40 mL) at 0°C for 1h]. After stirring for 14 h at 0°C, the reaction is quenced upon addition of water and EtOAc, the organic layer is dried (Na_2SO_4) and evaporated, and the residue is purified by flash chromatography (hexane/EtOAc, 10/1). This provides furan **15** as colorless crystals (280 mg, 57%). Mp = 106-108°C. ^{1}H NMR (300 MHz, $CDCl_3$): _ 7.92-7.85 (m, 4H), 7.69-7.62 (m, 2H), 7.57-7.49 (m, 4H), 6.89 (s, 1H), 6.87 (m, 1H), 5.75 (s, 1H), 4.55 (t, *J* = 5.3 Hz, 1H), 3.31 (d, *J* = 5.3 Hz, 2H), 1.85 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): _ 154.2, 138.3, 138.1, 136.1, 134.6, 129.5, 129.1, 121.0, 114.0, 107.4, 84.2, 26.9, 21.7, 20.1. MS: *m/z* (rel. intensity) 431 (14), 430 ([M^+], 55), 289 (13), 288 (34), 226 (18), 225 (100), 223 (12), 209 (31), 181 (21), 148 (63), 147 (10), 146 (19), 142 (15), 141 (11), 133 (16), 129 (14), 125 (13), 119 (11), 117 (10), 105 (23), 96 (15), 91 (30), 83 (46), 79 (11), 77 (46), 51 (11). HRMS ($C_{22}H_{22}O_5S_2$): *calcd*.: 430.09087; *found*: 430.09028. $C_{22}H_{22}O_5S_2$: *calcd*.: C, 61.38; H, 5.15; *found*: C, 61.51; H, 5.08.

4-(2-Phenylsulfonyl-ethyl)-2-(2-methyl-propenyl)-furan (16). Aluminum foil (400 mg) is immersed in an aq. solution of $HgCl_2$ (2 % w/w) for 30 sec and is then carefully rinsed with dry Et_2O. The activated Al is added to a solution of furan **15** (96 mg, 0.22 mmol) in THF (15 mL) and H_2O (0.75 mL). The reaction mixture is directly added on top of a silica gel column and purified by flash chromatography (EtOAc). This provides furan **16** as a colorless solid (62 mg, 96%). ^{1}H NMR (300 MHz, CD_2Cl_2): _ 7.98-7.88 (m, 2H), 7.75-7.55 (m, 3H), 7.10 (s, 1H), 6.00 (s, 1H), 5.97 (m, 1H), 3.39-3.28 (m, 2H), 2.88-2.77 (m, 2H), 1.92 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 154.3, 139.1, 137.2, 136.1, 133.8, 129.4, 128.1, 122.5, 114.0, 107.8, 56.3, 26.7, 19.8, 18.8. MS:

(14), 77 (16). IR (film): 3147, 3129, 2966, 2915, 1653, 1603, 1584, 1525, 1480, 1446, 1406, 1375, 1329, 1307, 1278, 1240, 1217, 1166, 1151, 1137, 1124, 1088, 1052, 1027, 992, 952, 928, 842, 799, 758, 704, 690, 663, 602, 554, 534, 501 cm^{-1}. HRMS ($C_{16}H_{18}O_3S$): *calcd*.: 290.09767; *found*: 290.09722.

6-Methyl-3-{3-methyl-6-[5-(2-methyl-propenyl)-furan-3-yl]-(*E*)-2-hexenyl}-2,4-bis-(2-trimethylsilanyl-ethoxymethoxy)-benzoic acid methylester (18). To a solution of furan **16** (21 mg, 0.14 mmol) in THF (2 mL) is added n-BuLi (1.6 M in hexane, 88 μL, 0.14 mmol) at 0°C. After stirring for 5 min, the mixture is cooled to –78°C, HMPA (0.5 mL) is introduced, and a solution of allyl bromide **7** (40 mg, 0.07 mmol) in THF (1 mL) is added. After the mixture has been allowed to warm to ambient temperature, the reaction is quenched with H_2O/EtOAc, the organic layer is dried (Na_2SO_4) and evaporated, and the residue is purified by flash chromatography (hexane/ EtOAc, 10/1) to afford product **17** as a colorless syrup.

This material is dissolved without further characterization in MeOH (10 mL) and the solution is treated with Na_2HPO_4 (32 mg, 0.23 mmol) and Na(Hg) (6% w/w) for 5 h at ambient temperature. Standard extractive work-up and flash chromatography (hexane/EtOAc, 30/1) delivers product **18** as a colorless syrup (26 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$): _ 7.06 (d, *J* = 0.5 Hz, 1H), 6.75 (s, 1H), 6.04 (s, 1H), 5.98 (m, 1H), 5.22 (s, 2H), 5.16 (m, 1H), 4.96 (s, 2H), 3.84 (s, 3H), 3.79-3.69 (m, 4H), 3.35 (d, *J* = 6.7 Hz, 2H), 2.33 (t, *J* = 7.5 Hz, 2H), 2.25 (s, 3H), 1.99 (t, *J* = 7.6 Hz, 2H), 1.94 (s, 3H), 1.87 (s, 3H), 1.75 (d, *J* = 1.0 Hz, 3H), 1.68-1.53 (m, 2H), 1.01-0.89 (m, 4H), 0.02 (s, 9H), -0.01 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): _ 168.56, 157.05, 153.62, 153.57, 136.78, 135.12, 134.87, 134.80, 126.73, 123.11, 122.28, 122.22, 114.46, 111.69, 108.83, 99.03, 92.77, 67.51, 66.41, 51.90, 39.30, 28.40, 26.71, 24.48, 23.20, 19.85, 19.69, 18.09, 17.97, 15.93, -1.72. MS: *m/z* (rel. intensity) 658 ([M^+], 3), 235 (13), 203 (14), 189 (11), 149 (13), 136 (26), 73 (100).

2,4-Dihydroxy-6-methyl-3-{3-methyl-6-[5-(2-methyl-propenyl)-furan-3-yl]-(*E*)-2-hexenyl}-benzoic acid methylester (19). A solution of furan **18** (15.5 mg, 0.024 mmol) and n-$Bu_4NF{\cdot}3H_2O$ (90 mg, 0.285 mmol) in HMPA (1 mL) is stirred for 12 h at 50°C. Water and EtOAc are added, the organic layer is dried over Na_2SO_4 and evaporated and the crude product is purified by flash chromatography (hexane/EtOAc, 10/1) to afford cristatic acid methyl ester **19** as a colorless syrup (5.6 mg, 60%). ^{1}H NMR (600 MHz, $CDCl_3$): _ 12.05 (s, 1H), 7.08 (d, *J* = 0.6 Hz, 1H) 6.22 (s, 1H), 6.05 (s, 1H), 5.99 (m, 1H), 5.69 (s, 1H), 5.24 (m, 1H), 3.91 (s, 3H), 3.39 (d, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 2.34 (t, *J* = 7.6 Hz, 2H), 2.05 (t, *J* = 7.6 Hz, 2H), 1.95 (s, 3H) 1.88 (s, 3H) 1.80 (d, *J* = 1.0 Hz, 3H), 1.65 (vp, *J* = 7.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): _ 173.1, 163.0, 159.4, 154.0, 141.3, 138.3, 137.1, 135.2, 127.0, 122.1, 114.8, 112.1, 111.4, 109.1, 105.6, 52.1, 39.5, 28.6, 27.0, 24.7, 24.2, 22.2, 20.2, 16.3. MS: *m/z* (rel. intensity): 398 ([M^+], 22), 204 (10), 203 (55), 189 (12), 163 (25), 149 (49), 137 (11), 136 (100). HRMS ($C_{24}H_{30}O_5$): *calcd*.: 398.20884; *found*: 398.20932.