CHEMISTRY
A European Journal

Supporting Information

Total Synthesis and Absolute Configuration Assignment of MRSA Active Garcinol and Isogarcinol

Cecilia Socolsky[a] and Bernd Plietker*[b]

chem_201406077_sm_miscellaneous_information.pdf

Supplementary Information

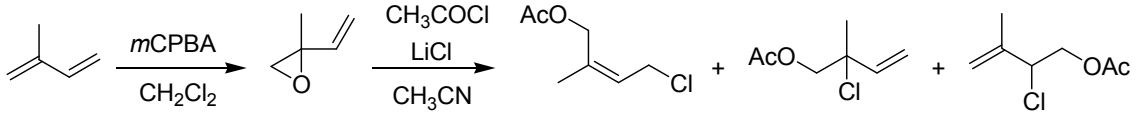
Total Synthesis and Absolute Configuration Assignment of MRSA-active Garcinol and Isogarcinol

Cecilia Socolsky and Bernd Plietker*

Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, DE-70569 Stuttgart, Germany. Fax: (+49) 711 685 642 69. E-mail: bernd.plietker@oc.uni-stuttgart.de. Homepage: www.plietker-group.de

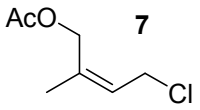
Experimental procedures

Preparation of compound 7: [1]

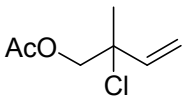


64 % (2.7 : 1.4 : 1)

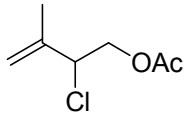
To a cold solution (0 ºC) of isoprene (4 mL, 40 mmol, 1 eq.) in 120 mL of CH_2Cl_2 *m*CPBA 75% (9.36 g, 40 mmol, 1 eq.) was added slowly. After the addition was complete, the reaction mixture was allowed to warm to room temperature and was further stirred for 8 h. Then, it was washed with 1N NaOH solution (120 mL), and dried over Na_2SO_4. The resulting solution was dissolved in 60 mL of CH_3CN. Then, LiCl (1.7 g, 40 mmol, 1eq.) and acetyl chloride (3.77 g, 48 mmol, 1.2 eq.) were added successively. The slurry mixture was stirred at room temperature for 48 h, diluted with water and extracted with Et_2O. The combined organic layers were washed with $NaHCO_3$ (sat.), dried over Na_2SO_4, and the solvent was removed. The residue was filtered through a plug of silica gel using *n*-pentane-Et_2O (10:1) to afford a slightly yellow liquid as a mixture of isomers (64 % yield; 2.7 : 1.4 : 1).



^{1}H NMR: ($CDCl_3$, 300 MHz) δ 5.64 (1H, brt, J = 8.1 Hz), 4.62 (2H, s), 4.13 (2H, d, J = 8.1 Hz), 2.07 (3H, s), 1.82 (3H, brs); **^{13}C NMR**: ($CDCl_3$, 75 MHz) δ 170.9, 136.3, 125.7, 62.3, 39.7, 21.6, 21.0; **HR-ESI-MS**: *m/z* calculated for $[C_7H_{11}O_2{}^{35}ClNa]^+$/$[C_7H_{11}O_2{}^{37}ClNa]^+$: 185.0345/187.0316, found: 185.0325/ 187.0291.



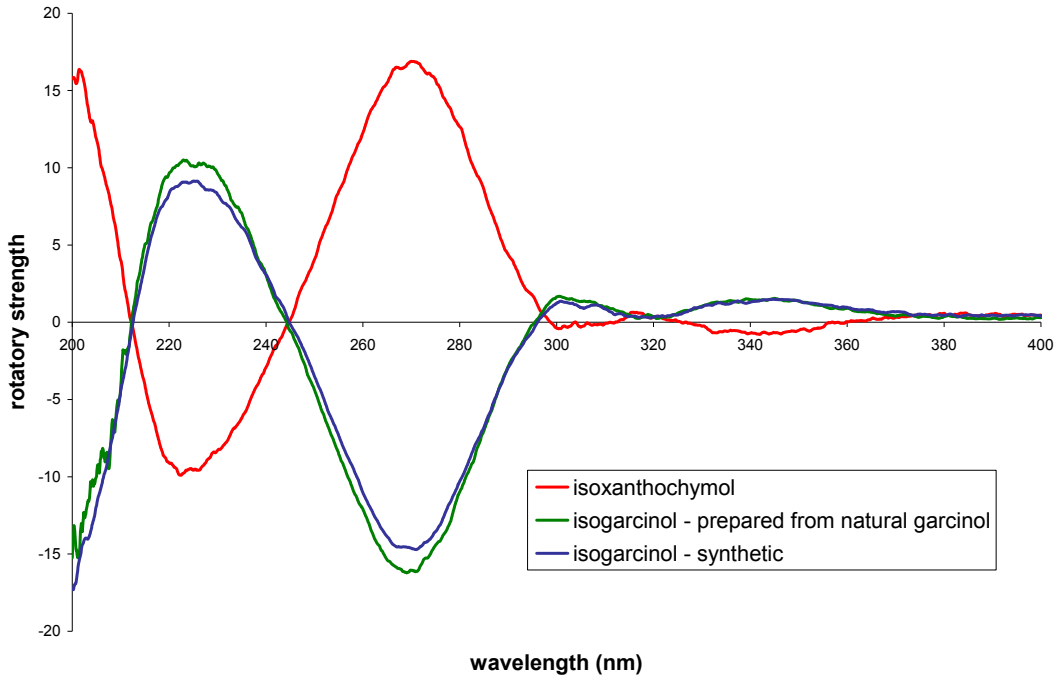
^{1}H NMR: ($CDCl_3$, 300 MHz) δ 5.99 (1H, dd, J = 17.2, 10.6 Hz), 5.36 (1H, d, J = 17.2 Hz), 5.21 (1H, d, J = 10.6 Hz), 4.25 (1H, d, J = 11.5 Hz), 4.20 (1H, d, J = 11.5 Hz), 2.10 (3H, s), 1.68 (3H, s); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 170.4, 139.4, 115.7, 70.6, 67.7, 26.1, 20.8; **HR-CI-MS**: *m/z* calculated for $[C_7H_{12}O_2{}^{35}Cl]^+$/ $[C_7H_{12}O_2{}^{37}Cl]^+$: 163.0526/165.0498, found: 163.0525/165.0492.



^{1}H NMR: ($CDCl_3$, 300 MHz) δ 5.10 (1H, br.s), 5.01 (1H, br. s), 4.57 (1H, t, J = 7.1 Hz), 4.29 (2H, d, J = 7.1 Hz), 2.07 (3H, s), 1.83 (3H, br.s); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 170.3, 141.0, 116.3, 65.4, 61.8, 20.7, 17.4.

[1] Yoo S.-H., Lee S.-H., Yi K.-Y., J. Nakcheol, *Tet. Lett.* **1990**, *31*, 6877-6880.

Figure S1. Comparison of the experimental ECD spectra of isoxanthochymol and isogarcinol.



Part II: NMR data

Figure S2. Comparison of the ^{1}H NMR spectra of synthetic (±)-garcinol (**A**) and natural garcinol (**B**) in $CDCl_3$ (500 MHz). Due to the presence of traces of water in the sample of (±)-garcinol, the signals arising from the aromatic protons are shifted.

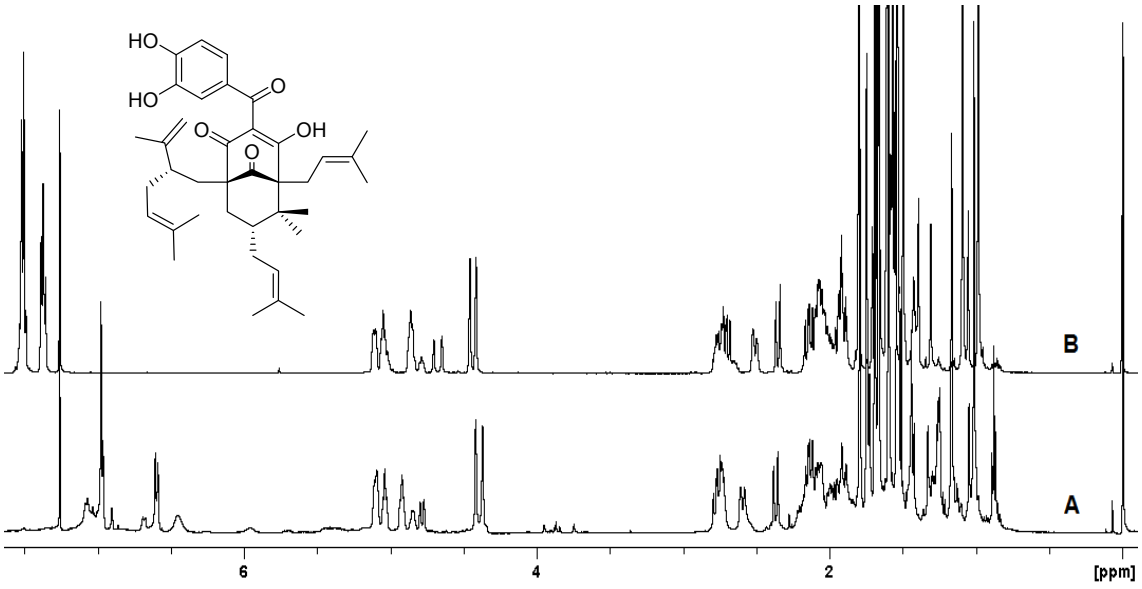


Figure S3. ^{13}C NMR spectrum of (±)-garcinol in $CDCl_3$ (125 MHz).

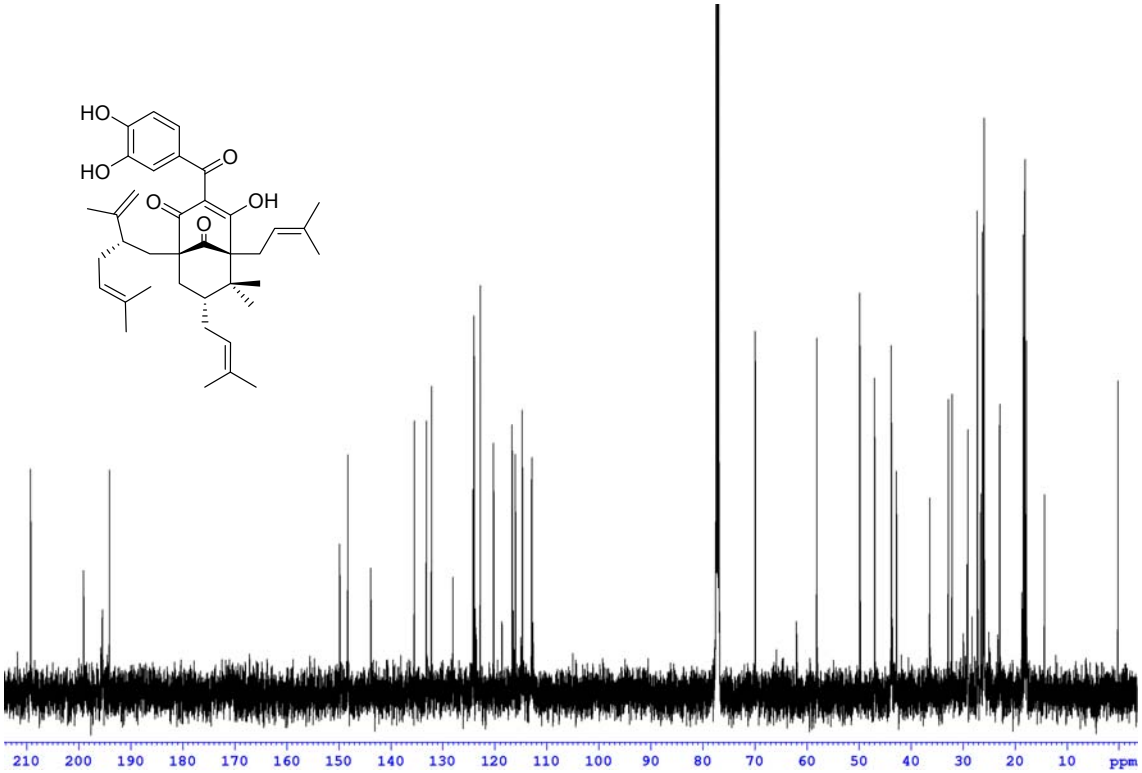
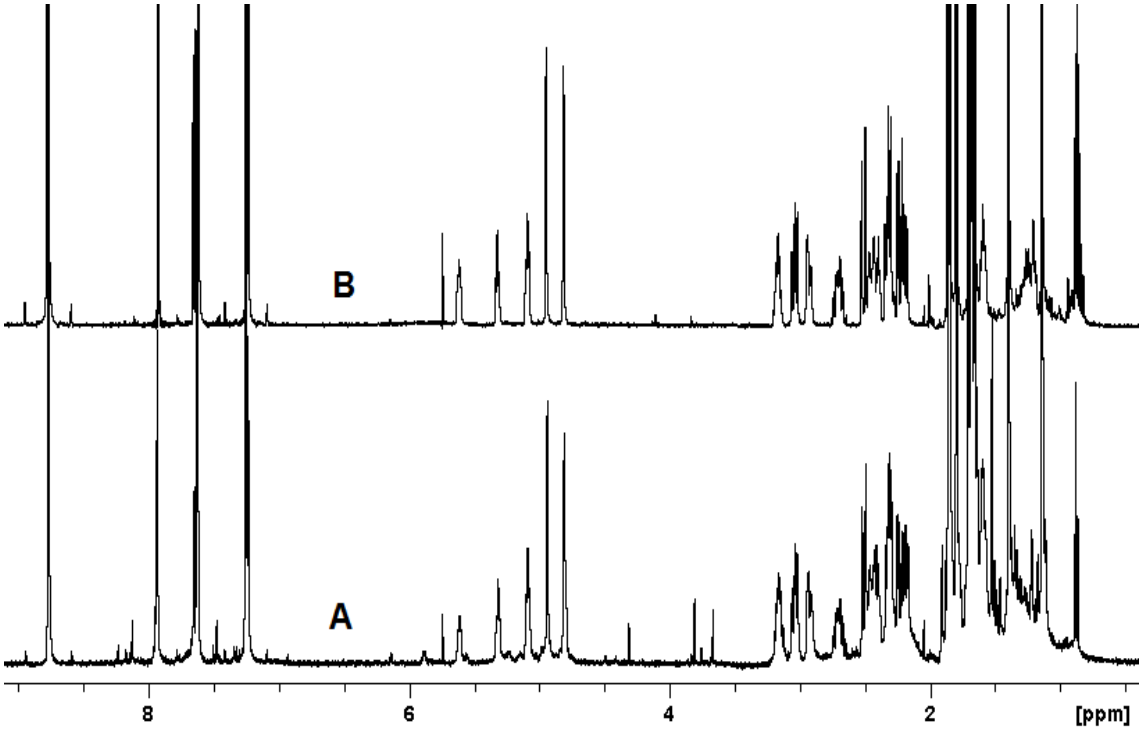


Figure S4. Comparison of the ^{1}H NMR spectra of synthetic (±)-garcinol (**A**) and natural garcinol (**B**) (pyridine-d_5, 500 MHz)*.



* water suppression was achieved via presaturation during the recycle delay.

Figure S5. ^{1}H NMR spectrum of (±)-garcinol in CD_3OD + 0.1 % TFA (500 MHz).

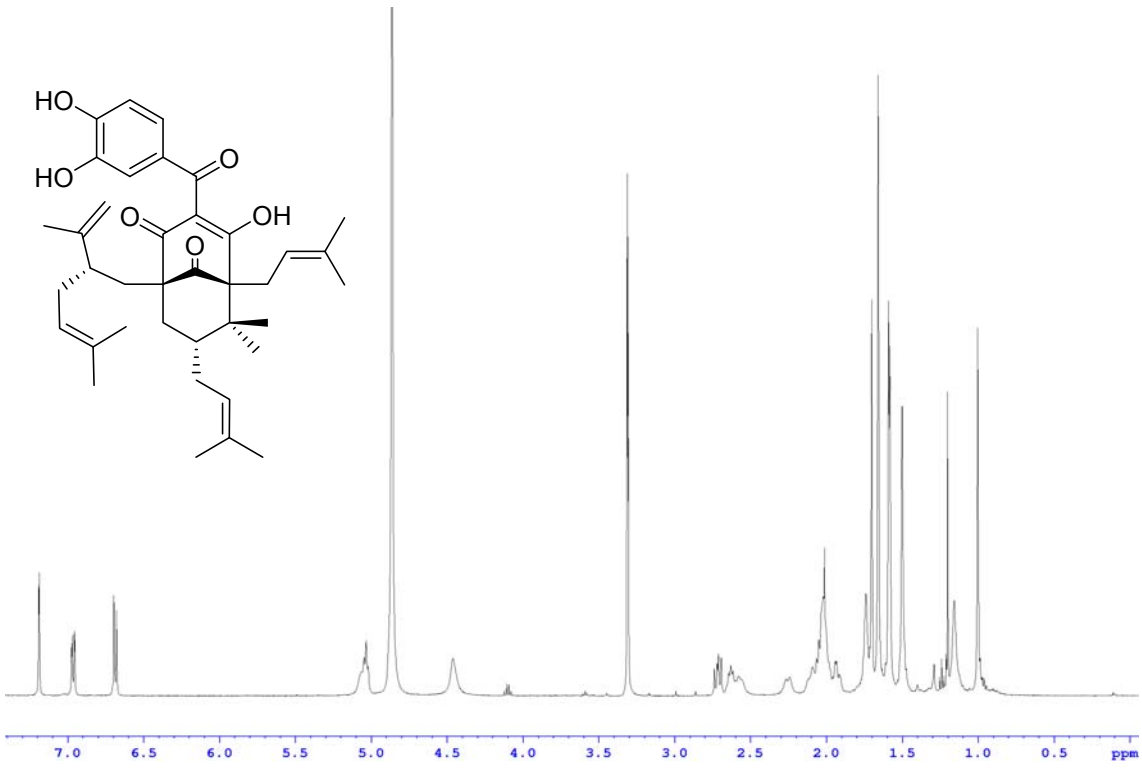


Figure S6. Comparison of the ^{1}H NMR spectra of isoxanthochymol (**A**), isogarcinol obtained from racemic garcinol and isolated via chiral HPLC (**B**) and isogarcinol obtained from commercial enantiomerically pure garcinol (**C**) ($CDCl_3$, 500MHz).

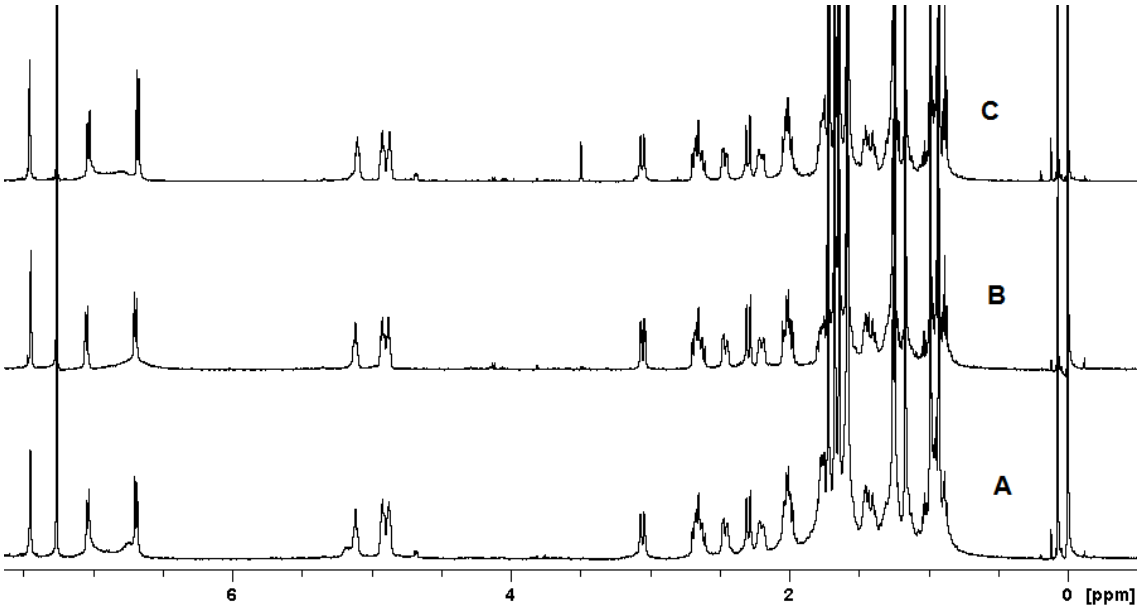


Figure S7. ^{1}H NMR spectrum of isogarcinol (**3**) obtained from commercial enantiomerically pure garcinol ($CDCl_3$, 500MHz).

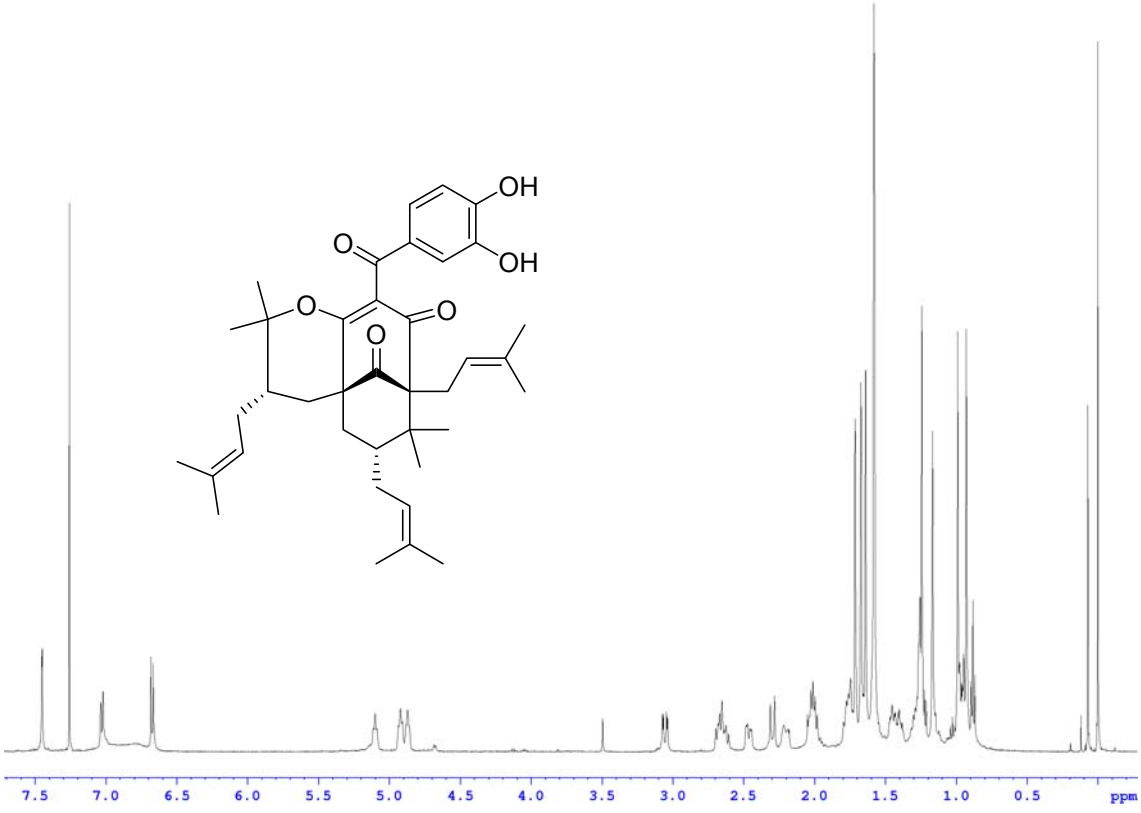


Figure S8. ^{13}C NMR spectrum of isogarcinol (**3**) obtained from commercial enantiomerically pure garcinol in ($CDCl_3$-CD_3OD 5:1, 125 MHz).

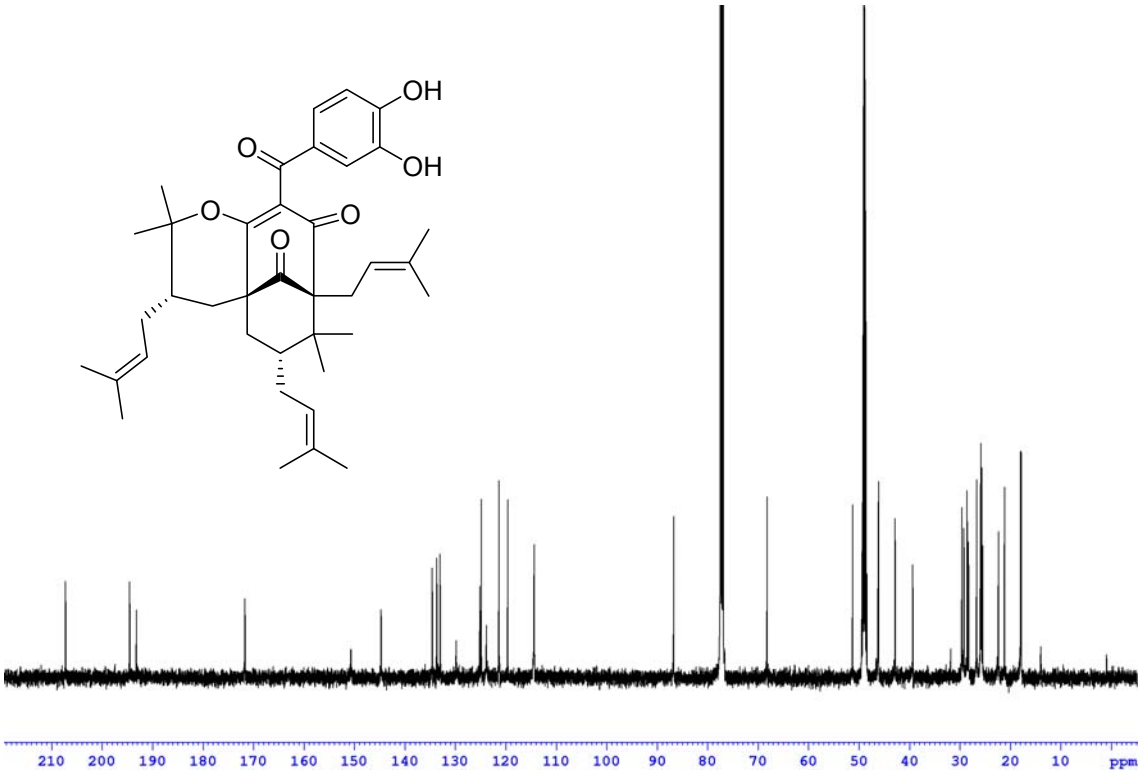


Figure S9. ^{1}H NMR spectrum of isogarcinol (**3**) obtained from (±)-garcinol and purified by chiral HPLC ($CDCl_3$, 500MHz).

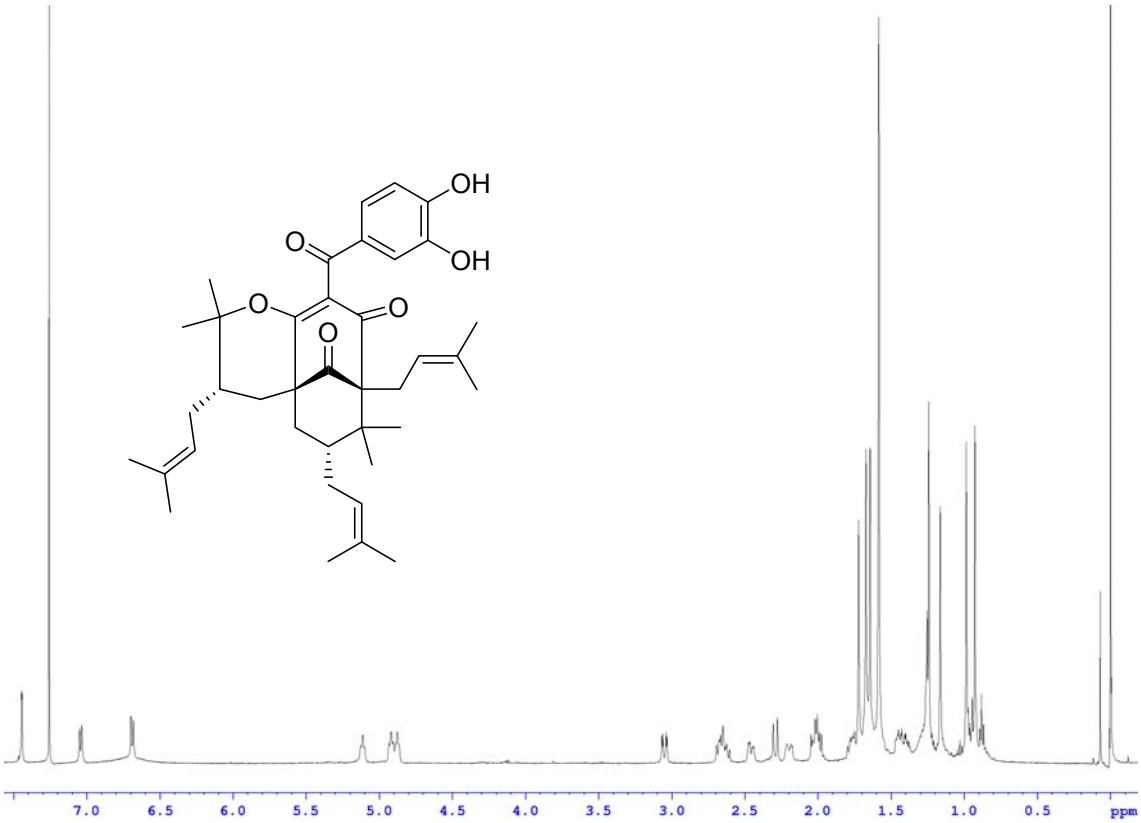


Figure S10. ^{1}H NMR spectrum of isogarcinol (**3**) obtained from commercial enantiomerically pure garcinol (acetone-d_6, 500MHz).

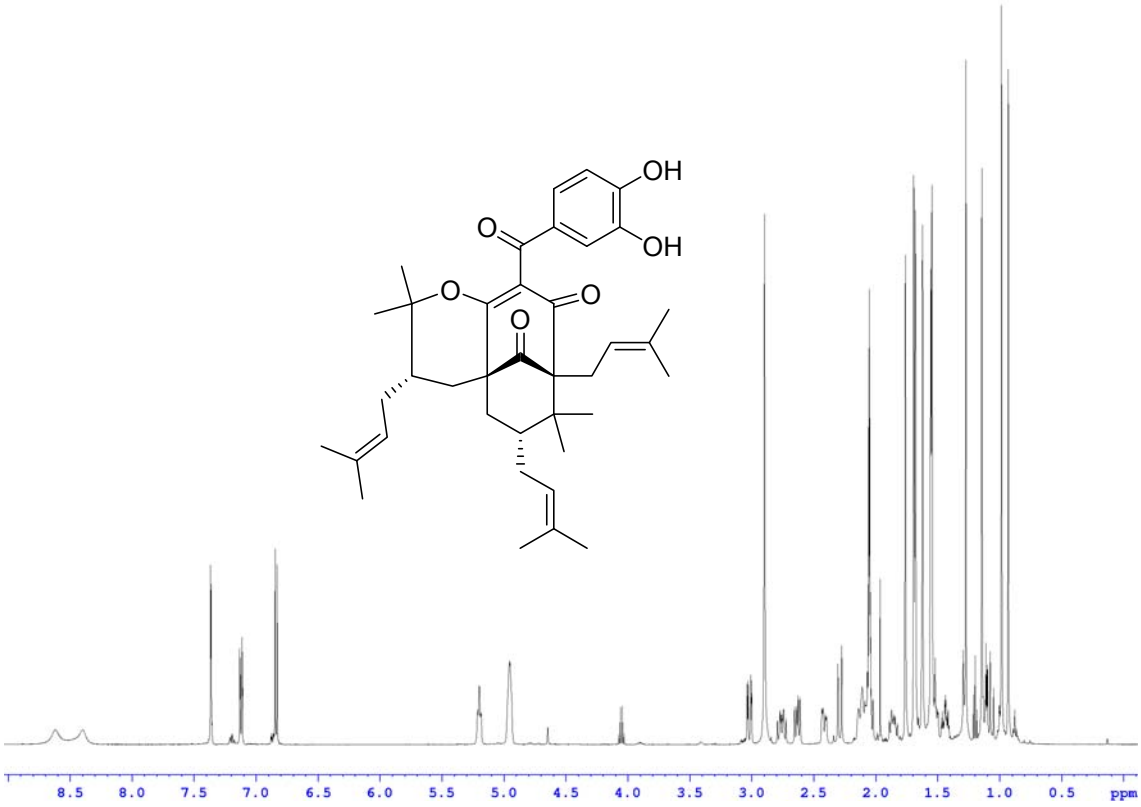


Figure S11. ^{1}H NMR spectrum of isoxanthochymol (**4**) ($CDCl_3$, 500MHz).

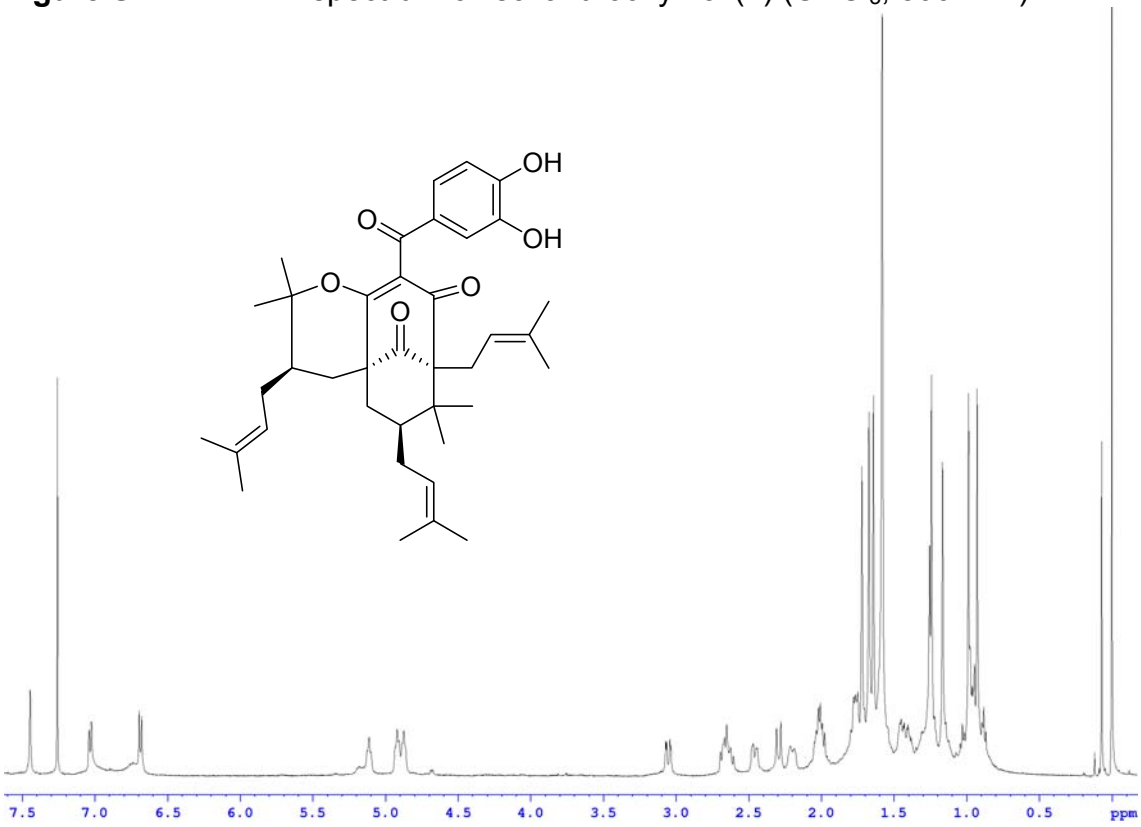


Figure S12. ^{13}C NMR spectrum of isoxanthochymol (**4**) ($CDCl_3$-CD_3OD 5:1, 125 MHz).

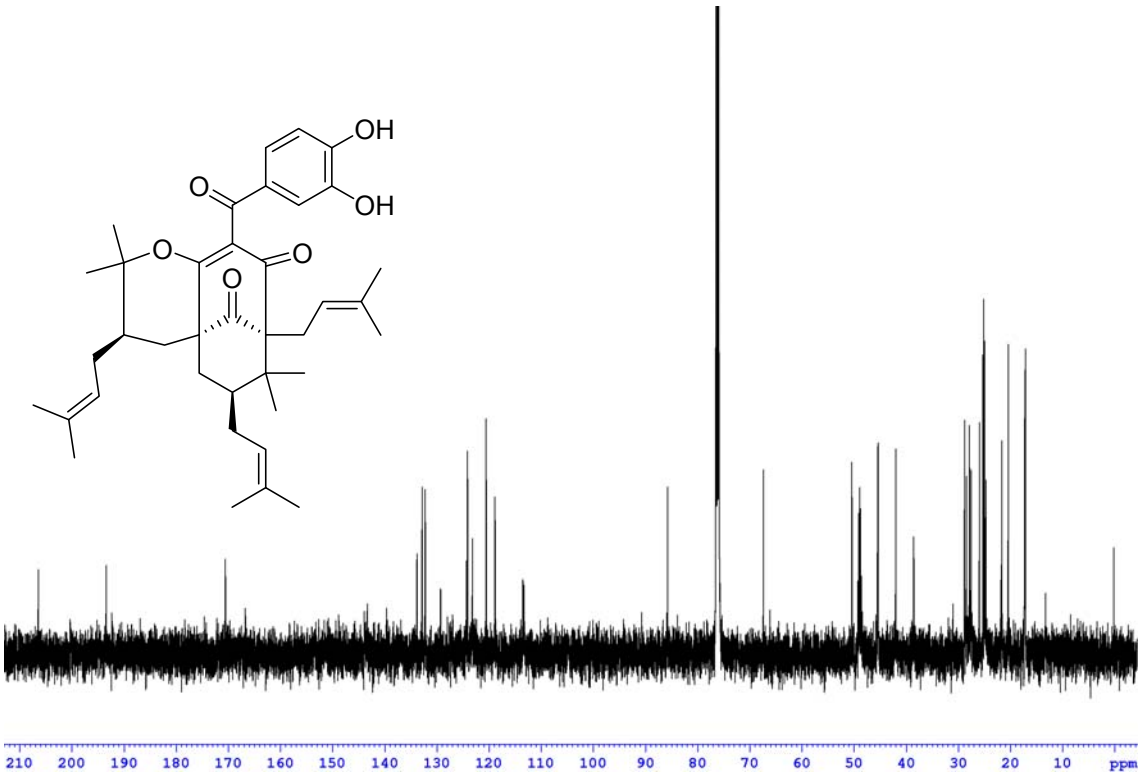


Figure S13. ^{1}H NMR spectrum of compound **7** ($CDCl_3$, 500 MHz).

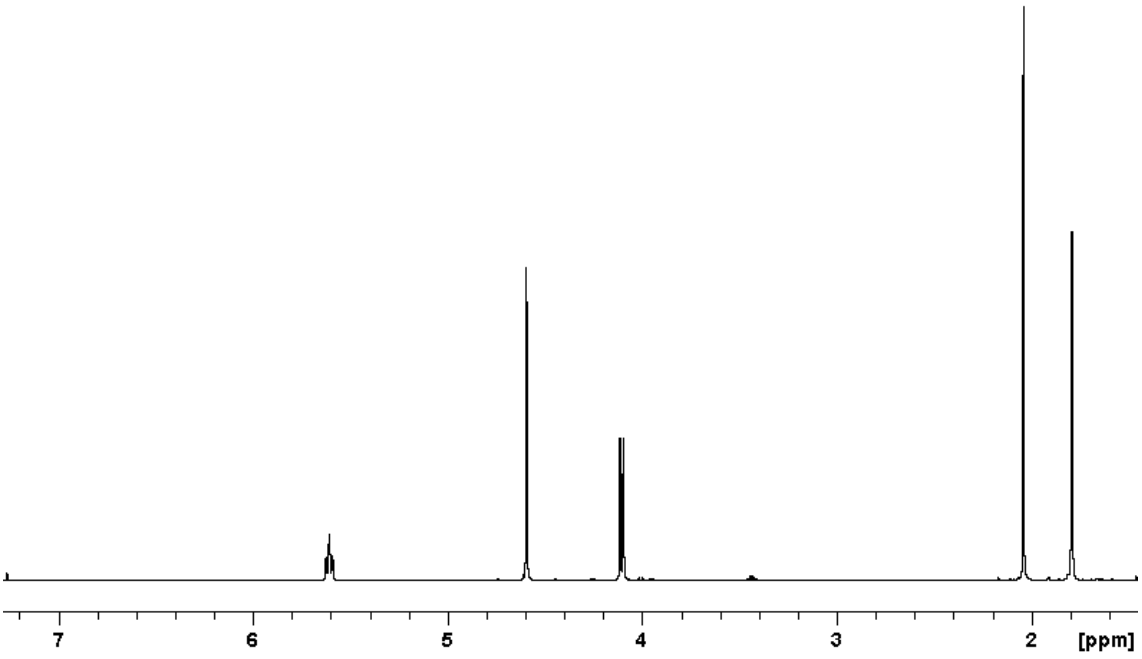


Figure S14. ^{1}H NMR spectrum of compound **8** ($CDCl_3$, 500 MHz).

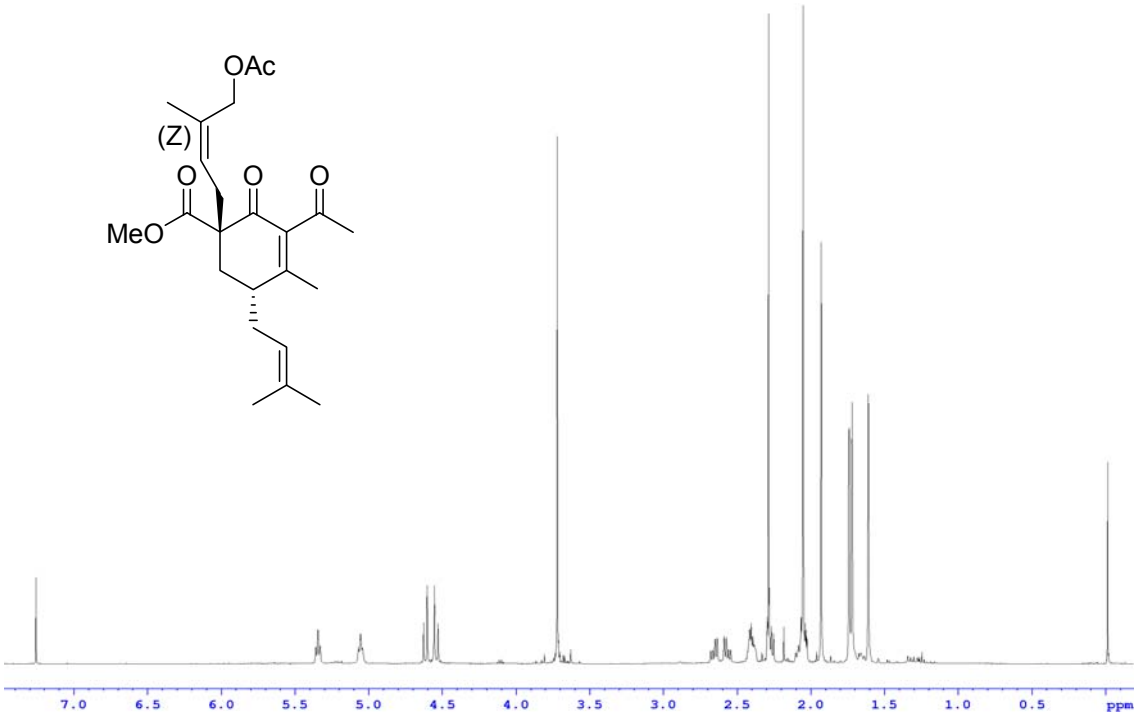


Figure S15. ^{1}H NMR spectrum of compound **9a** ($CDCl_3$, 500 MHz).

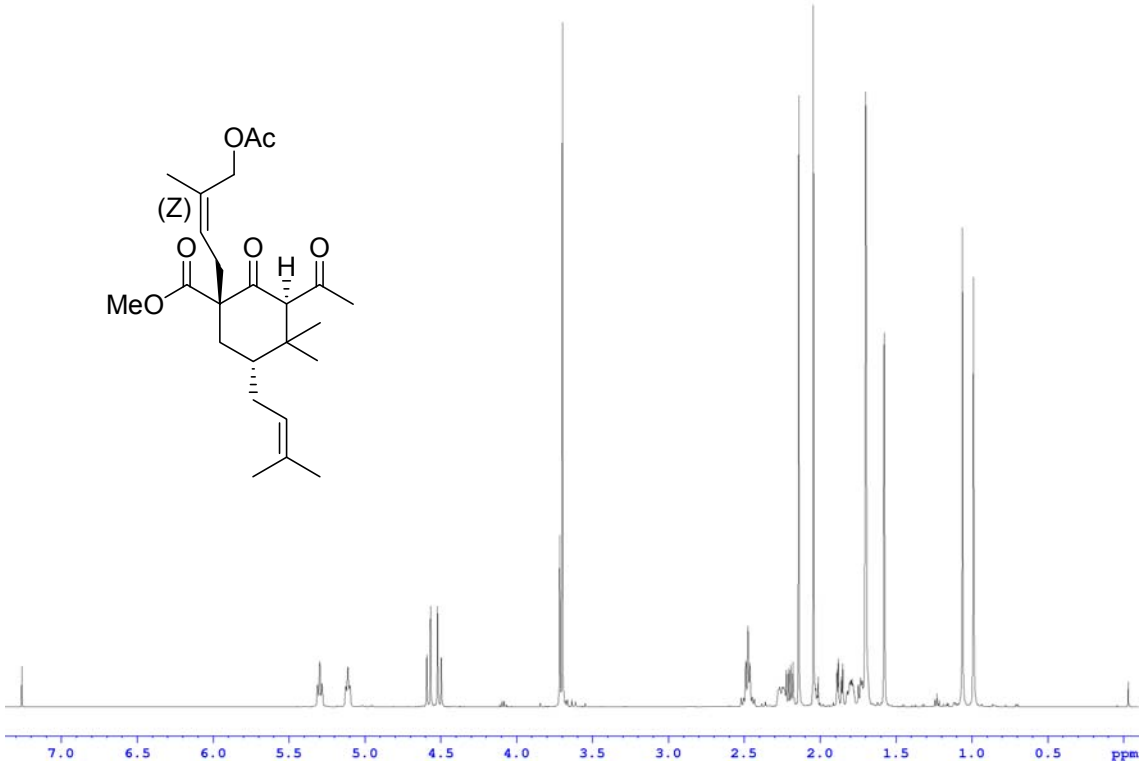


Figure S16. ^{1}H NMR spectrum of compound **9b** ($CDCl_3$, 500 MHz).

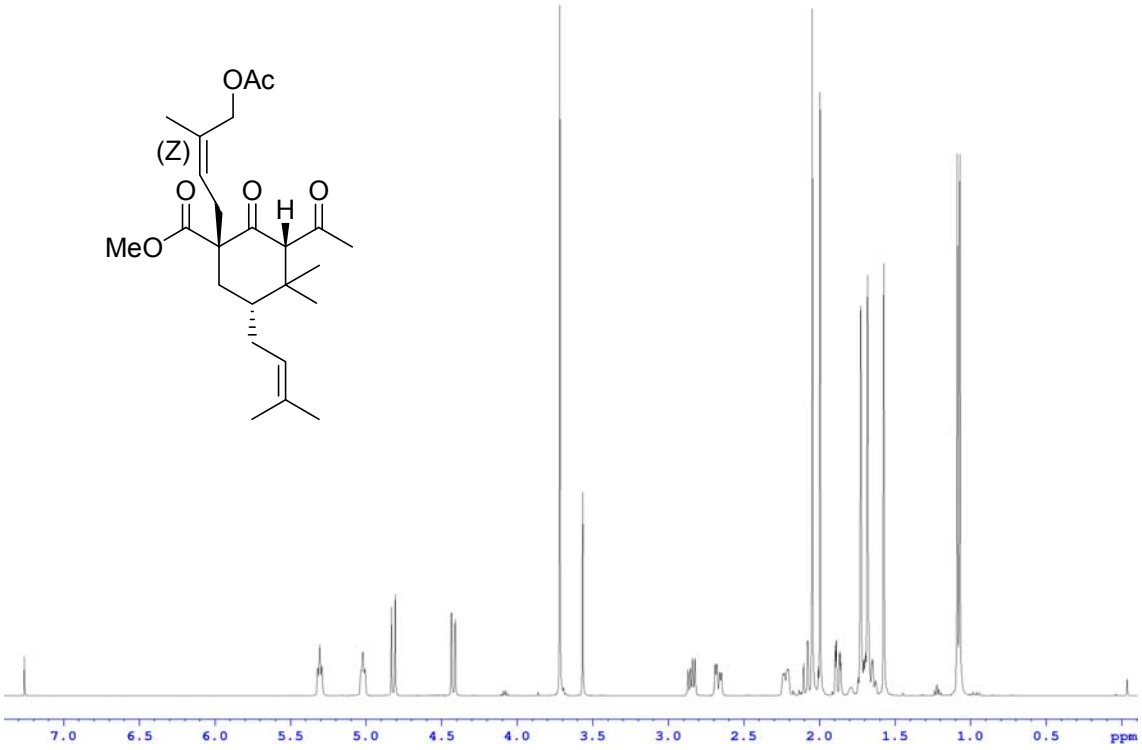


Figure S17. ^{1}H NMR spectrum of compound **10a** ($CDCl_3$, 500 MHz).

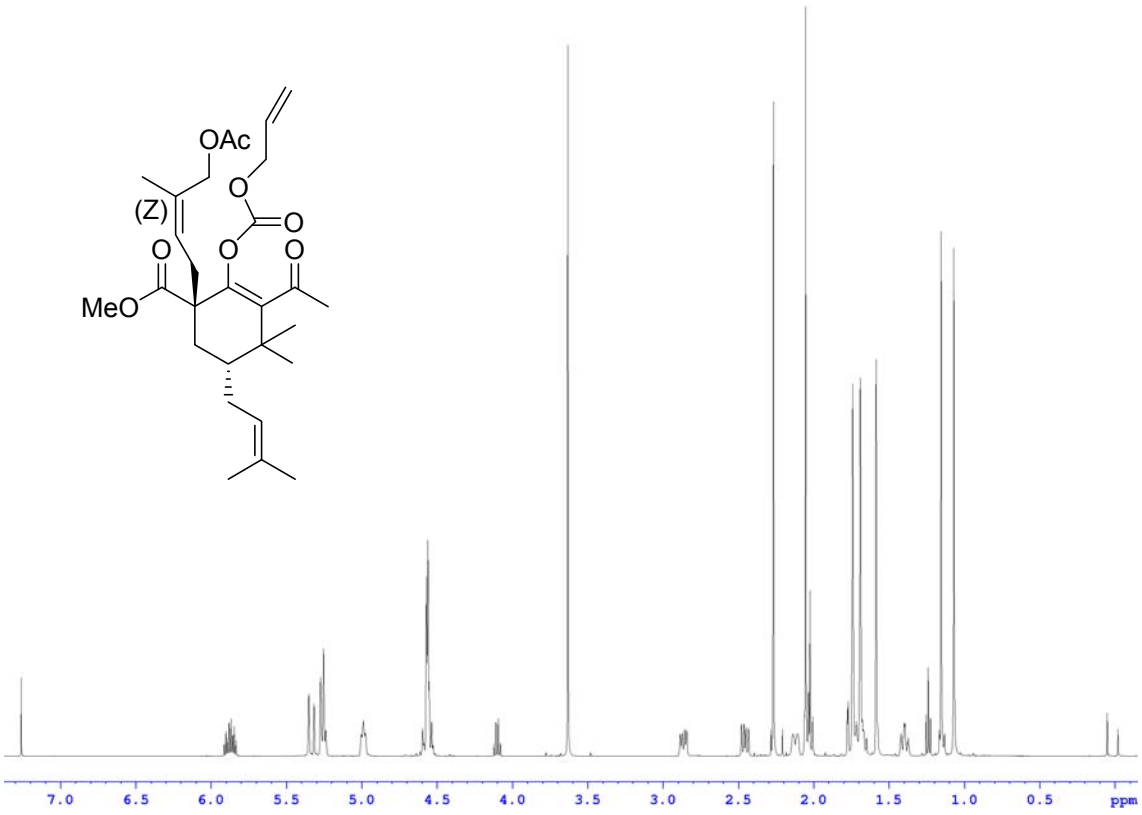


Figure S18. ^{1}H NMR spectrum of compound **10b** ($CDCl_3$, 500 MHz).

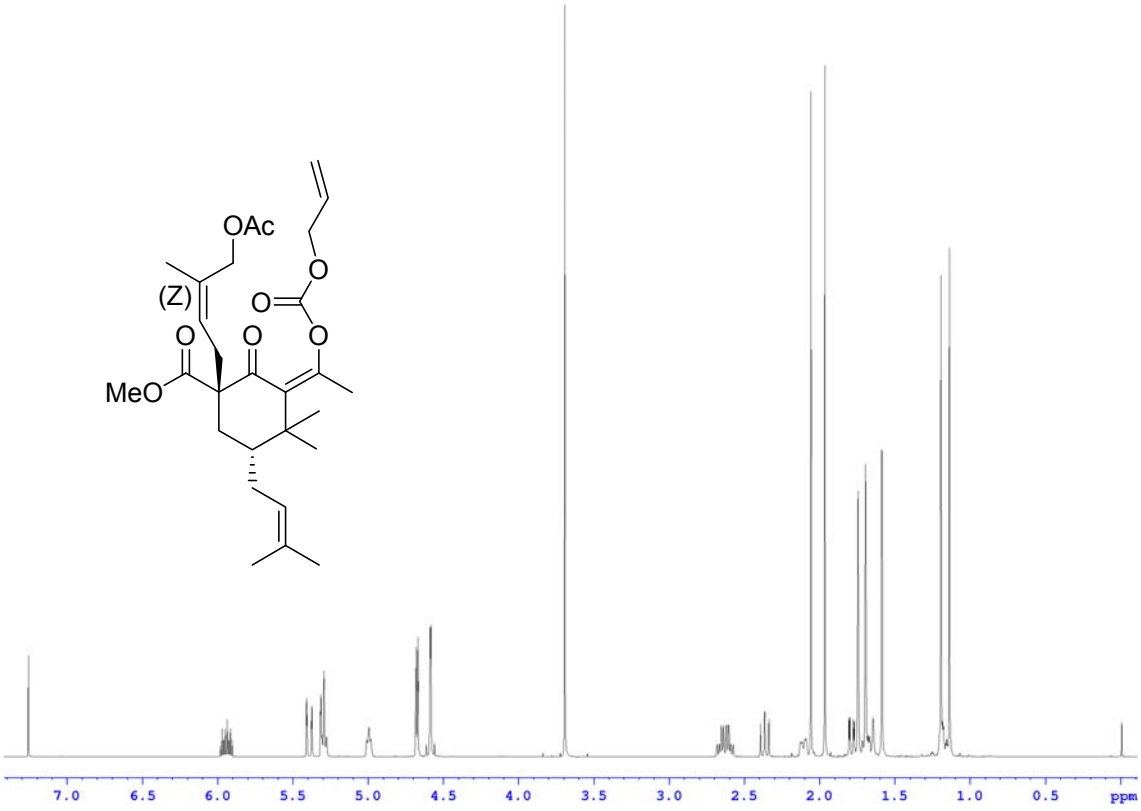


Figure S19. ^{1}H NMR spectrum of compound **12** ($CDCl_3$, 500 MHz).

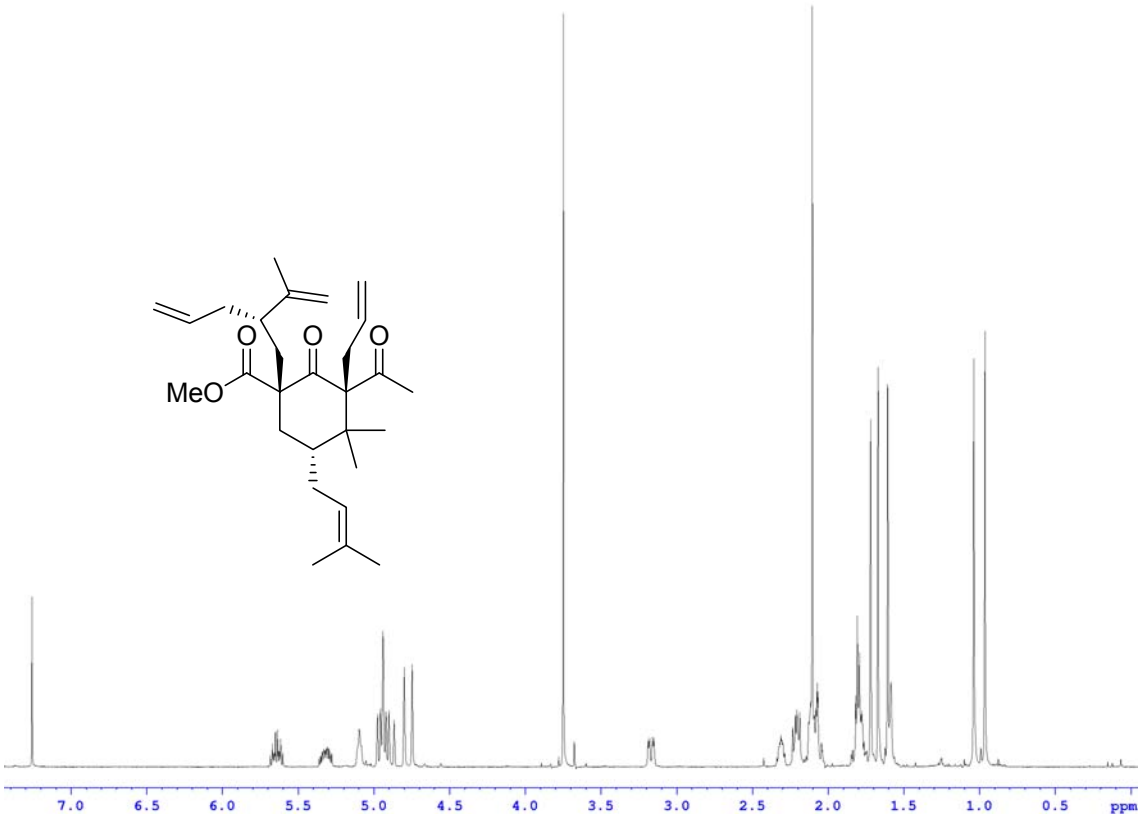


Figure S20. ^{1}H NMR spectrum (300 MHz) of compound **13** ($CDCl_3$, 300 MHz).

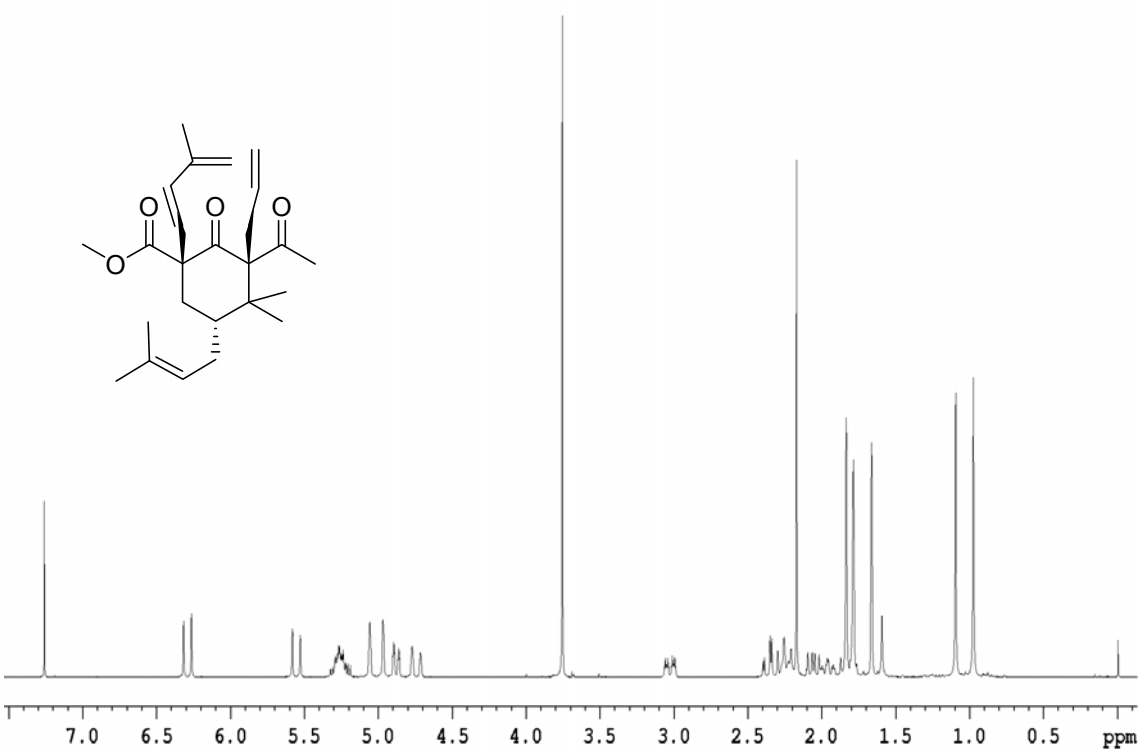


Figure S21. ^{1}H NMR spectrum of compound **14** ($CDCl_3$, 500 MHz).

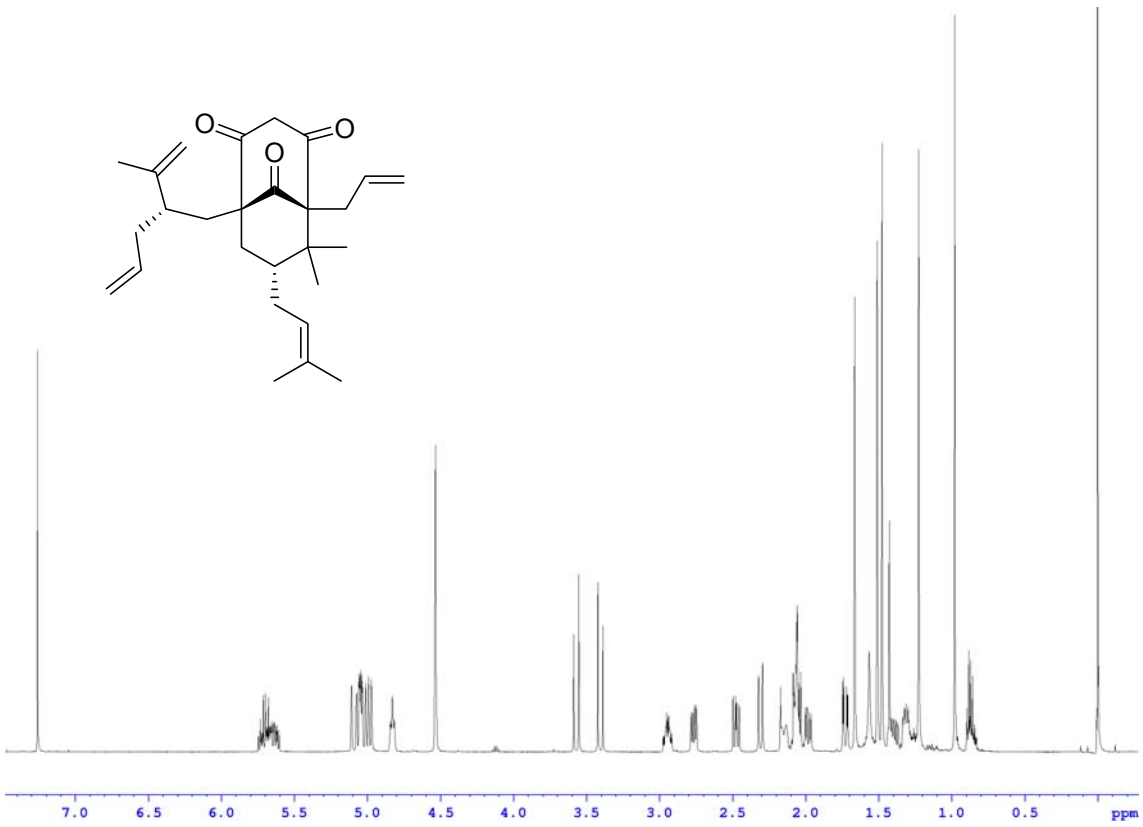
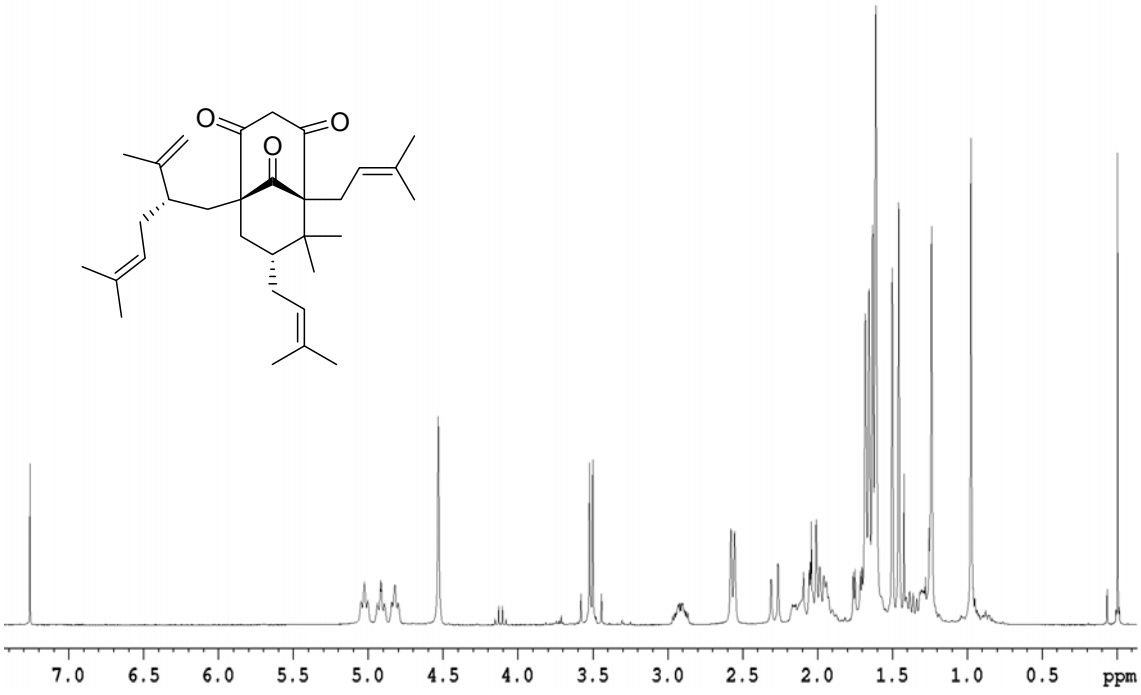


Figure S22. ^{1}H NMR spectrum of compound **15** ($CDCl_3$, 300 MHz).



Part III: X-ray data

Figure S23. X-ray structure of compound **11**

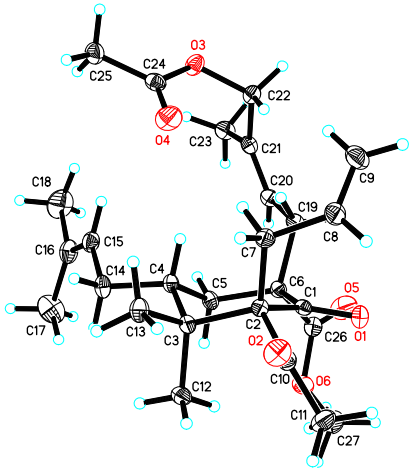


Table S1. Crystal data and structure refinement for **11**

Identification code	s2001lm
Empirical formula	C27 H40 O6
Formula weight	460.59
Temperature	110(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 16.4986(10) A alpha = 90 deg. b = 8.6788(5) A beta = 112.833(2) c = 19.4564(12) A gamma = 90 deg.
Volume	2567.6(3) A^3
Z, Calculated density	4, 1.191 Mg/m^3
Absorption coefficient	0.083 mm^-1
F(000)	1000
Crystal size	0.38 x 0.34 x 0.25 mm
Theta range for data collection	2.14 to 30.53 deg.
Limiting indices	-23<=h<=23, -12<=k<=12, -27<=l<=27
Reflections collected / unique	79903 / 7838 [R(int) = 0.0336]
Completeness to theta = 30.53	99.7 %
Absorption correction	Semi-empirical from equivalents

Max. and min. transmission	0.7461 and 0.7111
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7838 / 0 / 306
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.1104
R indices (all data)	R1 = 0.0540, wR2 = 0.1167
Largest diff. peak and hole	0.371 and -0.262 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s2001lm. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	7083(1)	3666(1)	6225(1)	19(1)
C(1)	7201(1)	4416(1)	6782(1)	13(1)
O(2)	5669(1)	7289(1)	5698(1)	24(1)
C(2)	6616(1)	5815(1)	6742(1)	13(1)
O(3)	6460(1)	1950(1)	9463(1)	21(1)
C(3)	7074(1)	7047(1)	7378(1)	14(1)
C(4)	7485(1)	6164(1)	8131(1)	14(1)
O(4)	6060(1)	4133(1)	8799(1)	30(1)
C(5)	8213(1)	5075(1)	8135(1)	15(1)
O(5)	8891(1)	1860(1)	7441(1)	33(1)
O(6)	9025(1)	4291(1)	7111(1)	24(1)
C(6)	7881(1)	3820(1)	7531(1)	14(1)
C(7)	5742(1)	5208(1)	6784(1)	16(1)
C(8)	5301(1)	3929(1)	6252(1)	21(1)
C(9)	5074(1)	2598(1)	6454(1)	28(1)
C(10)	6363(1)	6607(1)	5969(1)	17(1)
C(11)	6968(1)	6558(1)	5553(1)	24(1)
C(12)	7784(1)	7941(1)	7208(1)	19(1)
C(13)	6399(1)	8237(1)	7410(1)	19(1)
C(14)	7843(1)	7214(1)	8825(1)	20(1)
C(15)	8097(1)	6300(1)	9534(1)	20(1)
C(16)	8861(1)	6293(1)	10124(1)	24(1)
C(17)	9650(1)	7232(2)	10187(1)	37(1)
C(18)	8983(1)	5319(2)	10797(1)	39(1)
C(19)	7411(1)	2483(1)	7759(1)	17(1)
C(20)	7934(1)	1862(1)	8527(1)	17(1)
C(21)	7624(1)	1374(1)	9028(1)	17(1)
C(22)	6657(1)	1251(1)	8869(1)	18(1)
C(23)	8231(1)	833(1)	9792(1)	21(1)
C(24)	6199(1)	3435(1)	9368(1)	18(1)
C(25)	6132(1)	4063(1)	10061(1)	23(1)
C(26)	8646(1)	3176(1)	7361(1)	18(1)
C(27)	9756(1)	3821(2)	6925(1)	30(1)

Table S3. Bond lengths [A] and angles [deg] for s2001lm.

O(1)-C(1)	1.2138(11)
C(1)-C(2)	1.5345(12)
C(1)-C(6)	1.5418(12)
O(2)-C(10)	1.2133(12)
C(2)-C(10)	1.5570(13)
C(2)-C(7)	1.5660(12)
C(2)-C(3)	1.5872(12)
O(3)-C(24)	1.3488(12)
O(3)-C(22)	1.4492(11)
C(3)-C(13)	1.5386(12)
C(3)-C(12)	1.5433(13)
C(3)-C(4)	1.5566(13)
C(4)-C(5)	1.5265(12)
C(4)-C(14)	1.5430(13)
C(4)-H(4)	1.0000
O(4)-C(24)	1.2045(12)
C(5)-C(6)	1.5390(12)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
O(5)-C(26)	1.2012(13)
O(6)-C(26)	1.3413(12)
O(6)-C(27)	1.4463(12)
C(6)-C(26)	1.5288(12)
C(6)-C(19)	1.5539(13)
C(7)-C(8)	1.4996(13)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.3213(15)
C(8)-H(8)	0.9500
C(9)-H(9A)	0.9500
C(9)-H(9B)	0.9500
C(10)-C(11)	1.5092(14)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-C(15)	1.5031(14)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.3361(14)
C(15)-H(15)	0.9500
C(16)-C(17)	1.5016(16)
C(16)-C(18)	1.5050(17)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-C(20)	1.5060(13)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900

C(20)-C(21)	1.3351(13)
C(20)-H(20)	0.9500
C(21)-C(22)	1.5062(13)
C(21)-C(23)	1.5085(13)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-C(25)	1.4978(14)
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
O(1)-C(1)-C(2)	119.95(8)
O(1)-C(1)-C(6)	117.97(8)
C(2)-C(1)-C(6)	121.77(7)
C(1)-C(2)-C(10)	108.99(7)
C(1)-C(2)-C(7)	107.74(7)
C(10)-C(2)-C(7)	106.99(7)
C(1)-C(2)-C(3)	113.13(7)
C(10)-C(2)-C(3)	108.92(7)
C(7)-C(2)-C(3)	110.87(7)
C(24)-O(3)-C(22)	116.66(8)
C(13)-C(3)-C(12)	107.03(8)
C(13)-C(3)-C(4)	110.46(7)
C(12)-C(3)-C(4)	111.17(7)
C(13)-C(3)-C(2)	110.45(7)
C(12)-C(3)-C(2)	110.06(7)
C(4)-C(3)-C(2)	107.69(7)
C(5)-C(4)-C(14)	109.14(7)
C(5)-C(4)-C(3)	111.26(7)
C(14)-C(4)-C(3)	114.28(7)
C(5)-C(4)-H(4)	107.3
C(14)-C(4)-H(4)	107.3
C(3)-C(4)-H(4)	107.3
C(4)-C(5)-C(6)	112.88(7)
C(4)-C(5)-H(5A)	109.0
C(6)-C(5)-H(5A)	109.0
C(4)-C(5)-H(5B)	109.0
C(6)-C(5)-H(5B)	109.0
H(5A)-C(5)-H(5B)	107.8
C(26)-O(6)-C(27)	115.99(8)
C(26)-C(6)-C(5)	110.20(7)
C(26)-C(6)-C(1)	106.17(7)
C(5)-C(6)-C(1)	113.36(7)
C(26)-C(6)-C(19)	109.49(7)
C(5)-C(6)-C(19)	112.30(7)
C(1)-C(6)-C(19)	105.01(7)
C(8)-C(7)-C(2)	115.01(8)
C(8)-C(7)-H(7A)	108.5
C(2)-C(7)-H(7A)	108.5
C(8)-C(7)-H(7B)	108.5
C(2)-C(7)-H(7B)	108.5
H(7A)-C(7)-H(7B)	107.5
C(9)-C(8)-C(7)	123.97(10)
C(9)-C(8)-H(8)	118.0
C(7)-C(8)-H(8)	118.0
C(8)-C(9)-H(9A)	120.0

C(8)-C(9)-H(9B)	120.0
H(9A)-C(9)-H(9B)	120.0
O(2)-C(10)-C(11)	119.31(9)
O(2)-C(10)-C(2)	119.26(8)
C(11)-C(10)-C(2)	121.43(8)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(3)-C(12)-H(12A)	109.5
C(3)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(3)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(3)-C(13)-H(13A)	109.5
C(3)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(3)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(15)-C(14)-C(4)	111.48(8)
C(15)-C(14)-H(14A)	109.3
C(4)-C(14)-H(14A)	109.3
C(15)-C(14)-H(14B)	109.3
C(4)-C(14)-H(14B)	109.3
H(14A)-C(14)-H(14B)	108.0
C(16)-C(15)-C(14)	128.74(10)
C(16)-C(15)-H(15)	115.6
C(14)-C(15)-H(15)	115.6
C(15)-C(16)-C(17)	124.48(10)
C(15)-C(16)-C(18)	120.95(11)
C(17)-C(16)-C(18)	114.56(10)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(20)-C(19)-C(6)	113.15(7)
C(20)-C(19)-H(19A)	108.9
C(6)-C(19)-H(19A)	108.9
C(20)-C(19)-H(19B)	108.9
C(6)-C(19)-H(19B)	108.9
H(19A)-C(19)-H(19B)	107.8
C(21)-C(20)-C(19)	127.17(8)
C(21)-C(20)-H(20)	116.4
C(19)-C(20)-H(20)	116.4
C(20)-C(21)-C(22)	123.26(8)
C(20)-C(21)-C(23)	121.46(9)
C(22)-C(21)-C(23)	115.22(8)
O(3)-C(22)-C(21)	110.72(8)
O(3)-C(22)-H(22A)	109.5

C(21)-C(22)-H(22A)	109.5
O(3)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	108.1
C(21)-C(23)-H(23A)	109.5
C(21)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(21)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
O(4)-C(24)-O(3)	122.96(9)
O(4)-C(24)-C(25)	126.23(9)
O(3)-C(24)-C(25)	110.80(8)
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
O(5)-C(26)-O(6)	123.55(9)
O(5)-C(26)-C(6)	125.74(9)
O(6)-C(26)-C(6)	110.71(8)
O(6)-C(27)-H(27A)	109.5
O(6)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
O(6)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for s2001lm. The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	22(1)	19(1)	17(1)	-4(1)	6(1)	1(1)
C(1)	12(1)	13(1)	16(1)	0(1)	6(1)	-2(1)
O(2)	22(1)	27(1)	21(1)	6(1)	5(1)	7(1)
C(2)	12(1)	14(1)	13(1)	0(1)	4(1)	0(1)
O(3)	27(1)	18(1)	20(1)	2(1)	12(1)	6(1)
C(3)	14(1)	13(1)	15(1)	-1(1)	5(1)	0(1)
C(4)	14(1)	14(1)	13(1)	-2(1)	4(1)	0(1)
O(4)	40(1)	24(1)	31(1)	10(1)	18(1)	7(1)
C(5)	14(1)	14(1)	15(1)	-1(1)	3(1)	0(1)
O(5)	40(1)	24(1)	44(1)	9(1)	27(1)	15(1)
O(6)	20(1)	22(1)	37(1)	-5(1)	18(1)	-3(1)
C(6)	13(1)	12(1)	15(1)	0(1)	5(1)	1(1)
C(7)	12(1)	19(1)	17(1)	-1(1)	5(1)	-1(1)
C(8)	15(1)	27(1)	21(1)	-6(1)	6(1)	-4(1)
C(9)	22(1)	26(1)	36(1)	-8(1)	12(1)	-7(1)
C(10)	20(1)	15(1)	15(1)	0(1)	6(1)	-1(1)
C(11)	31(1)	25(1)	21(1)	5(1)	16(1)	4(1)
C(12)	19(1)	17(1)	21(1)	0(1)	8(1)	-4(1)
C(13)	20(1)	18(1)	20(1)	-2(1)	6(1)	4(1)
C(14)	22(1)	18(1)	16(1)	-5(1)	4(1)	0(1)

C(15)	20(1)	23(1)	16(1)	-5(1)	6(1)	-2(1)
C(16)	23(1)	26(1)	18(1)	-4(1)	4(1)	3(1)
C(17)	20(1)	38(1)	40(1)	-1(1)	-2(1)	-1(1)
C(18)	43(1)	48(1)	19(1)	4(1)	4(1)	5(1)
C(19)	16(1)	15(1)	17(1)	1(1)	5(1)	-2(1)
C(20)	15(1)	15(1)	19(1)	2(1)	5(1)	0(1)
C(21)	17(1)	13(1)	18(1)	-1(1)	5(1)	0(1)
C(22)	19(1)	19(1)	18(1)	-2(1)	9(1)	0(1)
C(23)	20(1)	22(1)	19(1)	3(1)	5(1)	-1(1)
C(24)	15(1)	16(1)	24(1)	1(1)	8(1)	0(1)
C(25)	23(1)	18(1)	27(1)	-3(1)	11(1)	1(1)
C(26)	15(1)	19(1)	17(1)	-1(1)	5(1)	2(1)
C(27)	20(1)	40(1)	37(1)	-11(1)	18(1)	-4(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for s2001lm.

	x	y	z	U(eq)
H(4)	7009	5516	8181	17
H(5A)	8479	4576	8630	18
H(5B)	8678	5682	8056	18
H(7A)	5872	4843	7298	19
H(7B)	5325	6079	6686	19
H(8)	5178	4086	5737	26
H(9A)	5189	2406	6964	33
H(9B)	4796	1832	6090	33
H(11A)	6792	5712	5191	37
H(11B)	7574	6395	5907	37
H(11C)	6930	7536	5290	37
H(12A)	7500	8598	6770	29
H(12B)	8177	7210	7107	29
H(12C)	8124	8583	7638	29
H(13A)	6707	9124	7708	29
H(13B)	6024	7766	7639	29
H(13C)	6034	8577	6903	29
H(14A)	8363	7782	8824	24
H(14B)	7388	7980	8802	24
H(15)	7654	5639	9566	24
H(17A)	9521	7818	9725	55
H(17B)	10151	6545	10267	55
H(17C)	9795	7946	10608	55
H(18A)	8452	4702	10702	59
H(18B)	9087	5987	11229	59
H(18C)	9488	4632	10899	59
H(19A)	6836	2854	7740	20
H(19B)	7297	1636	7392	20
H(20)	8554	1812	8670	20
H(22A)	6314	1772	8392	22
H(22B)	6482	152	8820	22
H(23A)	8843	964	9846	32
H(23B)	8119	-257	9852	32
H(23C)	8126	1442	10174	32
H(25A)	6723	4179	10450	34
H(25B)	5790	3352	10234	34

H(25C)	5840	5069	9953	34
H(27A)	10177	3236	7341	45
H(27B)	10045	4735	6830	45
H(27C)	9540	3173	6477	45

Table S6. Torsion angles [deg] for s2001lm.

O(1)-C(1)-C(2)-C(10)	-34.01(11)
C(6)-C(1)-C(2)-C(10)	152.47(8)
O(1)-C(1)-C(2)-C(7)	81.74(10)
C(6)-C(1)-C(2)-C(7)	-91.77(9)
O(1)-C(1)-C(2)-C(3)	-155.34(8)
C(6)-C(1)-C(2)-C(3)	31.15(11)
C(1)-C(2)-C(3)-C(13)	-168.19(7)
C(10)-C(2)-C(3)-C(13)	70.44(9)
C(7)-C(2)-C(3)-C(13)	-47.03(10)
C(1)-C(2)-C(3)-C(12)	73.84(9)
C(10)-C(2)-C(3)-C(12)	-47.52(9)
C(7)-C(2)-C(3)-C(12)	-164.99(7)
C(1)-C(2)-C(3)-C(4)	-47.49(9)
C(10)-C(2)-C(3)-C(4)	-168.86(7)
C(7)-C(2)-C(3)-C(4)	73.67(9)
C(13)-C(3)-C(4)-C(5)	-175.16(7)
C(12)-C(3)-C(4)-C(5)	-56.50(10)
C(2)-C(3)-C(4)-C(5)	64.14(9)
C(13)-C(3)-C(4)-C(14)	-51.00(10)
C(12)-C(3)-C(4)-C(14)	67.66(10)
C(2)-C(3)-C(4)-C(14)	-171.70(7)
C(14)-C(4)-C(5)-C(6)	171.33(8)
C(3)-C(4)-C(5)-C(6)	-61.65(10)
C(4)-C(5)-C(6)-C(26)	158.69(8)
C(4)-C(5)-C(6)-C(1)	39.87(10)
C(4)-C(5)-C(6)-C(19)	-78.95(9)
O(1)-C(1)-C(6)-C(26)	38.96(11)
C(2)-C(1)-C(6)-C(26)	-147.40(8)
O(1)-C(1)-C(6)-C(5)	160.08(8)
C(2)-C(1)-C(6)-C(5)	-26.28(11)
O(1)-C(1)-C(6)-C(19)	-76.98(10)
C(2)-C(1)-C(6)-C(19)	96.66(9)
C(1)-C(2)-C(7)-C(8)	-50.23(10)
C(10)-C(2)-C(7)-C(8)	66.83(10)
C(3)-C(2)-C(7)-C(8)	-174.52(8)
C(2)-C(7)-C(8)-C(9)	126.48(10)
C(1)-C(2)-C(10)-O(2)	150.60(9)
C(7)-C(2)-C(10)-O(2)	34.36(11)
C(3)-C(2)-C(10)-O(2)	-85.54(10)
C(1)-C(2)-C(10)-C(11)	-30.06(11)
C(7)-C(2)-C(10)-C(11)	-146.30(9)
C(3)-C(2)-C(10)-C(11)	93.80(10)
C(5)-C(4)-C(14)-C(15)	-63.73(10)
C(3)-C(4)-C(14)-C(15)	170.98(8)
C(4)-C(14)-C(15)-C(16)	126.65(11)
C(14)-C(15)-C(16)-C(17)	-0.80(18)
C(14)-C(15)-C(16)-C(18)	178.42(11)
C(26)-C(6)-C(19)-C(20)	73.13(10)
C(5)-C(6)-C(19)-C(20)	-49.63(10)
C(1)-C(6)-C(19)-C(20)	-173.25(7)

C(6)-C(19)-C(20)-C(21)	142.86(10)
C(19)-C(20)-C(21)-C(22)	5.23(16)
C(19)-C(20)-C(21)-C(23)	-177.65(9)
C(24)-O(3)-C(22)-C(21)	93.99(10)
C(20)-C(21)-C(22)-O(3)	-132.11(10)
C(23)-C(21)-C(22)-O(3)	50.60(11)
C(22)-O(3)-C(24)-O(4)	6.07(14)
C(22)-O(3)-C(24)-C(25)	-172.65(8)
C(27)-O(6)-C(26)-O(5)	0.93(15)
C(27)-O(6)-C(26)-C(6)	-179.54(8)
C(5)-C(6)-C(26)-O(5)	119.05(11)
C(1)-C(6)-C(26)-O(5)	-117.81(11)
C(19)-C(6)-C(26)-O(5)	-4.94(13)
C(5)-C(6)-C(26)-O(6)	-60.47(10)
C(1)-C(6)-C(26)-O(6)	62.67(9)
C(19)-C(6)-C(26)-O(6)	175.54(8)

Figure S24. X-ray structure of compound **12**

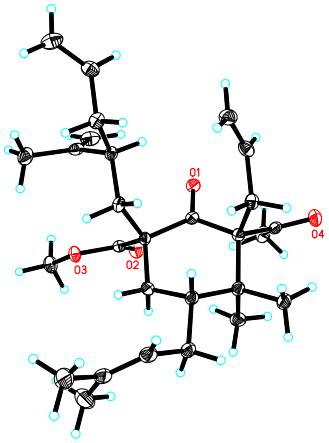


Table S7. Crystal data and structure refinement for compound **12**

Identification code	s2084lm
Empirical formula	C28 H42 O4
Formula weight	442.62
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 7.0512(4) A alpha = 87.953(3) b = 11.7101(7) A beta = 77.950(3) c = 16.0176(9) A gamma = 89.526(3)
Volume	1292.61(13) A^3
Z, Calculated density	2, 1.137 Mg/m^3
Absorption coefficient	0.074 mm^-1

F(000)	484
Crystal size	0.22 x 0.16 x 0.12 mm
Theta range for data collection	1.74 to 28.35 deg.
Limiting indices	-9<=h<=9, -15<=k<=15, -21<=l<=21
Reflections collected / unique	33377 / 6440 [R(int) = 0.0402]
Completeness to theta = 28.35	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7421 and 0.7251
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6440 / 0 / 296
Goodness-of-fit on F^2	1.068
Final R indices [I>2sigma(I)]	R1 = 0.0448, wR2 = 0.0795
R indices (all data)	R1 = 0.0777, wR2 = 0.0856
Largest diff. peak and hole	0.353 and -0.211 e.A^-3

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for s2084lm. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	4198(1)	3988(1)	7889(1)	16(1)
C(1)	5200(2)	3270(1)	7476(1)	13(1)
O(2)	1668(1)	2109(1)	7817(1)	21(1)
C(2)	6635(2)	3659(1)	6662(1)	13(1)
O(3)	2816(1)	705(1)	8565(1)	17(1)
C(3)	7240(2)	2686(1)	5996(1)	16(1)
O(4)	6662(1)	5433(1)	5859(1)	22(1)
C(4)	7790(2)	1611(1)	6494(1)	16(1)
C(5)	6046(2)	1159(1)	7151(1)	16(1)
C(6)	5116(2)	2031(1)	7826(1)	13(1)
C(7)	8464(2)	4145(1)	6932(1)	16(1)
C(8)	8118(2)	4943(1)	7661(1)	20(1)
C(9)	9128(2)	4905(1)	8269(1)	24(1)
C(10)	5666(2)	4661(1)	6241(1)	16(1)
C(11)	3512(2)	4675(1)	6277(1)	21(1)
C(12)	5566(2)	2416(1)	5548(1)	21(1)
C(13)	8985(2)	3076(1)	5297(1)	21(1)
C(14)	8655(2)	620(1)	5920(1)	21(1)
C(15)	9669(2)	-248(1)	6386(1)	23(1)
C(16)	9080(2)	-1289(1)	6676(1)	27(1)
C(17)	10310(3)	-2050(1)	7126(1)	41(1)
C(18)	7193(2)	-1814(1)	6596(1)	40(1)
C(19)	2992(2)	1674(1)	8079(1)	15(1)
C(20)	882(2)	242(1)	8788(1)	22(1)

C(21)	6199(2)	1962(1)	8580(1)	15(1)
C(22)	5518(2)	2736(1)	9342(1)	14(1)
C(23)	7113(2)	2762(1)	9868(1)	18(1)
C(24)	6650(2)	3531(1)	10610(1)	21(1)
C(25)	6719(2)	3249(1)	11404(1)	27(1)
C(26)	3577(2)	2407(1)	9906(1)	17(1)
C(27)	2030(2)	3063(1)	9931(1)	23(1)
C(28)	3484(2)	1331(1)	10457(1)	24(1)

Table S9. Bond lengths [A] and angles [deg] for s2084lm.

O(1)-C(1)	1.2163(14)
C(1)-C(2)	1.5316(17)
C(1)-C(6)	1.5327(16)
O(2)-C(19)	1.2033(14)
C(2)-C(10)	1.5566(16)
C(2)-C(7)	1.5604(17)
C(2)-C(3)	1.5846(17)
O(3)-C(19)	1.3444(15)
O(3)-C(20)	1.4401(15)
C(3)-C(13)	1.5404(18)
C(3)-C(12)	1.5432(17)
C(3)-C(4)	1.5561(17)
O(4)-C(10)	1.2148(15)
C(4)-C(5)	1.5261(17)
C(4)-C(14)	1.5474(17)
C(4)-H(4)	1.0000
C(5)-C(6)	1.5540(17)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(19)	1.5252(17)
C(6)-C(21)	1.5564(16)
C(7)-C(8)	1.5005(18)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.3196(19)
C(8)-H(8)	0.9500
C(9)-H(9A)	0.9500
C(9)-H(9B)	0.9500
C(10)-C(11)	1.5076(18)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-C(15)	1.5026(18)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.3283(19)
C(15)-H(15)	0.9500
C(16)-C(18)	1.501(2)
C(16)-C(17)	1.506(2)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800

C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(22)	1.5398(17)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-C(26)	1.5184(18)
C(22)-C(23)	1.5407(17)
C(22)-H(22)	1.0000
C(23)-C(24)	1.4964(18)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-C(25)	1.3123(19)
C(24)-H(24)	0.9500
C(25)-H(25A)	0.9500
C(25)-H(25B)	0.9500
C(26)-C(27)	1.3235(18)
C(26)-C(28)	1.5054(18)
C(27)-H(27A)	0.9500
C(27)-H(27B)	0.9500
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
O(1)-C(1)-C(2)	118.36(11)
O(1)-C(1)-C(6)	119.15(11)
C(2)-C(1)-C(6)	122.26(10)
C(1)-C(2)-C(10)	107.30(9)
C(1)-C(2)-C(7)	107.81(10)
C(10)-C(2)-C(7)	107.64(10)
C(1)-C(2)-C(3)	114.09(10)
C(10)-C(2)-C(3)	109.47(9)
C(7)-C(2)-C(3)	110.30(10)
C(19)-O(3)-C(20)	114.92(10)
C(13)-C(3)-C(12)	107.41(10)
C(13)-C(3)-C(4)	110.14(10)
C(12)-C(3)-C(4)	110.78(10)
C(13)-C(3)-C(2)	110.18(10)
C(12)-C(3)-C(2)	110.90(10)
C(4)-C(3)-C(2)	107.46(9)
C(5)-C(4)-C(14)	108.57(10)
C(5)-C(4)-C(3)	111.18(10)
C(14)-C(4)-C(3)	114.23(10)
C(5)-C(4)-H(4)	107.5
C(14)-C(4)-H(4)	107.5
C(3)-C(4)-H(4)	107.5
C(4)-C(5)-C(6)	114.77(10)
C(4)-C(5)-H(5A)	108.6
C(6)-C(5)-H(5A)	108.6
C(4)-C(5)-H(5B)	108.6
C(6)-C(5)-H(5B)	108.6
H(5A)-C(5)-H(5B)	107.6
C(19)-C(6)-C(1)	108.23(9)
C(19)-C(6)-C(5)	104.35(10)
C(1)-C(6)-C(5)	113.61(10)
C(19)-C(6)-C(21)	113.70(10)
C(1)-C(6)-C(21)	108.30(9)
C(5)-C(6)-C(21)	108.74(9)

C(8)-C(7)-C(2)	116.95(10)
C(8)-C(7)-H(7A)	108.1
C(2)-C(7)-H(7A)	108.1
C(8)-C(7)-H(7B)	108.1
C(2)-C(7)-H(7B)	108.1
H(7A)-C(7)-H(7B)	107.3
C(9)-C(8)-C(7)	123.11(12)
C(9)-C(8)-H(8)	118.4
C(7)-C(8)-H(8)	118.4
C(8)-C(9)-H(9A)	120.0
C(8)-C(9)-H(9B)	120.0
H(9A)-C(9)-H(9B)	120.0
O(4)-C(10)-C(11)	119.30(11)
O(4)-C(10)-C(2)	119.63(11)
C(11)-C(10)-C(2)	121.05(11)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(3)-C(12)-H(12A)	109.5
C(3)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(3)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(3)-C(13)-H(13A)	109.5
C(3)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(3)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(15)-C(14)-C(4)	112.14(11)
C(15)-C(14)-H(14A)	109.2
C(4)-C(14)-H(14A)	109.2
C(15)-C(14)-H(14B)	109.2
C(4)-C(14)-H(14B)	109.2
H(14A)-C(14)-H(14B)	107.9
C(16)-C(15)-C(14)	128.43(14)
C(16)-C(15)-H(15)	115.8
C(14)-C(15)-H(15)	115.8
C(15)-C(16)-C(18)	124.72(13)
C(15)-C(16)-C(17)	121.01(15)
C(18)-C(16)-C(17)	114.27(13)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(2)-C(19)-O(3)	123.36(11)
O(2)-C(19)-C(6)	125.96(11)
O(3)-C(19)-C(6)	110.24(10)
O(3)-C(20)-H(20A)	109.5

O(3)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
O(3)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(22)-C(21)-C(6)	118.67(10)
C(22)-C(21)-H(21A)	107.6
C(6)-C(21)-H(21A)	107.6
C(22)-C(21)-H(21B)	107.6
C(6)-C(21)-H(21B)	107.6
H(21A)-C(21)-H(21B)	107.1
C(26)-C(22)-C(21)	114.65(10)
C(26)-C(22)-C(23)	110.88(10)
C(21)-C(22)-C(23)	108.58(10)
C(26)-C(22)-H(22)	107.5
C(21)-C(22)-H(22)	107.5
C(23)-C(22)-H(22)	107.5
C(24)-C(23)-C(22)	113.50(10)
C(24)-C(23)-H(23A)	108.9
C(22)-C(23)-H(23A)	108.9
C(24)-C(23)-H(23B)	108.9
C(22)-C(23)-H(23B)	108.9
H(23A)-C(23)-H(23B)	107.7
C(25)-C(24)-C(23)	125.91(13)
C(25)-C(24)-H(24)	117.0
C(23)-C(24)-H(24)	117.0
C(24)-C(25)-H(25A)	120.0
C(24)-C(25)-H(25B)	120.0
H(25A)-C(25)-H(25B)	120.0
C(27)-C(26)-C(28)	121.10(12)
C(27)-C(26)-C(22)	120.97(12)
C(28)-C(26)-C(22)	117.90(11)
C(26)-C(27)-H(27A)	120.0
C(26)-C(27)-H(27B)	120.0
H(27A)-C(27)-H(27B)	120.0
C(26)-C(28)-H(28A)	109.5
C(26)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(26)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5

Table S10. Anisotropic displacement parameters (A^2 x 10^3) for s2084lm. The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	16(1)	16(1)	16(1)	-1(1)	-4(1)	3(1)
C(1)	12(1)	16(1)	14(1)	0(1)	-6(1)	0(1)
O(2)	17(1)	22(1)	27(1)	4(1)	-8(1)	0(1)
C(2)	13(1)	13(1)	14(1)	0(1)	-3(1)	1(1)
O(3)	15(1)	16(1)	20(1)	4(1)	-2(1)	-3(1)
C(3)	17(1)	15(1)	13(1)	1(1)	-3(1)	2(1)

O(4)	27(1)	17(1)	22(1)	5(1)	-4(1)	-1(1)
C(4)	17(1)	15(1)	14(1)	0(1)	-2(1)	2(1)
C(5)	19(1)	13(1)	16(1)	0(1)	-4(1)	1(1)
C(6)	14(1)	13(1)	13(1)	1(1)	-3(1)	1(1)
C(7)	12(1)	19(1)	18(1)	1(1)	-2(1)	-1(1)
C(8)	16(1)	17(1)	26(1)	-2(1)	-2(1)	-2(1)
C(9)	24(1)	26(1)	23(1)	-4(1)	-3(1)	-5(1)
C(10)	21(1)	15(1)	11(1)	-1(1)	-2(1)	2(1)
C(11)	21(1)	24(1)	20(1)	4(1)	-6(1)	6(1)
C(12)	28(1)	18(1)	19(1)	-2(1)	-10(1)	3(1)
C(13)	26(1)	19(1)	16(1)	1(1)	1(1)	3(1)
C(14)	27(1)	18(1)	15(1)	0(1)	0(1)	5(1)
C(15)	27(1)	21(1)	19(1)	-4(1)	-2(1)	7(1)
C(16)	39(1)	20(1)	18(1)	-4(1)	1(1)	9(1)
C(17)	70(1)	25(1)	28(1)	2(1)	-9(1)	19(1)
C(18)	50(1)	23(1)	42(1)	-3(1)	3(1)	-4(1)
C(19)	17(1)	14(1)	13(1)	-2(1)	-2(1)	0(1)
C(20)	17(1)	22(1)	25(1)	4(1)	-1(1)	-6(1)
C(21)	12(1)	17(1)	14(1)	3(1)	-3(1)	1(1)
C(22)	14(1)	15(1)	14(1)	1(1)	-4(1)	1(1)
C(23)	13(1)	23(1)	18(1)	1(1)	-4(1)	-1(1)
C(24)	17(1)	21(1)	27(1)	-3(1)	-9(1)	-1(1)
C(25)	23(1)	35(1)	23(1)	-9(1)	-6(1)	6(1)
C(26)	16(1)	21(1)	15(1)	-5(1)	-4(1)	-2(1)
C(27)	16(1)	30(1)	24(1)	-9(1)	-4(1)	0(1)
C(28)	22(1)	30(1)	19(1)	3(1)	0(1)	-6(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for s2084lm.

	x	y	z	U(eq)
H(4)	8792	1848	6812	19
H(5A)	6456	478	7452	19
H(5B)	5045	911	6845	19
H(7A)	9240	3491	7084	20
H(7B)	9261	4550	6429	20
H(8)	7126	5502	7686	24
H(9A)	10128	4353	8257	29
H(9B)	8855	5429	8717	29
H(11A)	2914	5299	6632	32
H(11B)	2947	3945	6525	32
H(11C)	3274	4788	5699	32
H(12A)	5364	3068	5175	32
H(12B)	4377	2272	5979	32
H(12C)	5895	1738	5206	32
H(13A)	9133	2569	4815	32
H(13B)	10165	3049	5531	32
H(13C)	8769	3860	5103	32
H(14A)	7602	239	5712	25
H(14B)	9587	935	5416	25
H(15)	10891	-22	6486	27
H(17A)	11530	-1661	7136	62
H(17B)	10588	-2764	6823	62
H(17C)	9612	-2220	7713	62
H(18A)	6497	-1281	6281	60

H(18B)	6401	-1978	7167	60
H(18C)	7449	-2526	6288	60
H(20A)	27	779	9144	33
H(20B)	903	-488	9105	33
H(20C)	402	121	8266	33
H(21A)	6127	1161	8804	18
H(21B)	7583	2132	8343	18
H(22)	5386	3528	9107	17
H(23A)	7318	1977	10082	21
H(23B)	8341	3019	9489	21
H(24)	6270	4291	10497	26
H(25A)	7091	2498	11547	32
H(25B)	6398	3797	11835	32
H(27A)	836	2858	10301	28
H(27B)	2114	3738	9579	28
H(28A)	2188	1256	10823	36
H(28B)	4453	1369	10814	36
H(28C)	3752	670	10093	36

Table S12. Torsion angles [deg] for s2084lm.

O(1)-C(1)-C(2)-C(10)	-35.64(14)
C(6)-C(1)-C(2)-C(10)	149.86(10)
O(1)-C(1)-C(2)-C(7)	80.05(13)
C(6)-C(1)-C(2)-C(7)	-94.46(12)
O(1)-C(1)-C(2)-C(3)	-157.08(10)
C(6)-C(1)-C(2)-C(3)	28.42(15)
C(1)-C(2)-C(3)-C(13)	-168.00(10)
C(10)-C(2)-C(3)-C(13)	71.77(12)
C(7)-C(2)-C(3)-C(13)	-46.49(13)
C(1)-C(2)-C(3)-C(12)	73.22(13)
C(10)-C(2)-C(3)-C(12)	-47.02(13)
C(7)-C(2)-C(3)-C(12)	-165.28(10)
C(1)-C(2)-C(3)-C(4)	-48.00(13)
C(10)-C(2)-C(3)-C(4)	-168.23(10)
C(7)-C(2)-C(3)-C(4)	73.51(12)
C(13)-C(3)-C(4)-C(5)	-176.27(10)
C(12)-C(3)-C(4)-C(5)	-57.59(13)
C(2)-C(3)-C(4)-C(5)	63.70(12)
C(13)-C(3)-C(4)-C(14)	-52.99(14)
C(12)-C(3)-C(4)-C(14)	65.70(14)
C(2)-C(3)-C(4)-C(14)	-173.02(10)
C(14)-C(4)-C(5)-C(6)	175.15(10)
C(3)-C(4)-C(5)-C(6)	-58.38(13)
O(1)-C(1)-C(6)-C(19)	50.24(14)
C(2)-C(1)-C(6)-C(19)	-135.30(11)
O(1)-C(1)-C(6)-C(5)	165.62(10)
C(2)-C(1)-C(6)-C(5)	-19.92(15)
O(1)-C(1)-C(6)-C(21)	-73.45(13)
C(2)-C(1)-C(6)-C(21)	101.01(12)
C(4)-C(5)-C(6)-C(19)	151.60(10)
C(4)-C(5)-C(6)-C(1)	33.94(14)
C(4)-C(5)-C(6)-C(21)	-86.74(12)
C(1)-C(2)-C(7)-C(8)	-45.56(14)
C(10)-C(2)-C(7)-C(8)	69.90(13)
C(3)-C(2)-C(7)-C(8)	-170.72(10)
C(2)-C(7)-C(8)-C(9)	138.49(13)
C(1)-C(2)-C(10)-O(4)	146.26(11)

C(7)-C(2)-C(10)-O(4)	30.46(15)
C(3)-C(2)-C(10)-O(4)	-89.44(13)
C(1)-C(2)-C(10)-C(11)	-35.41(15)
C(7)-C(2)-C(10)-C(11)	-151.21(11)
C(3)-C(2)-C(10)-C(11)	88.89(13)
C(5)-C(4)-C(14)-C(15)	-71.50(14)
C(3)-C(4)-C(14)-C(15)	163.81(11)
C(4)-C(14)-C(15)-C(16)	105.97(16)
C(14)-C(15)-C(16)-C(18)	-0.7(2)
C(14)-C(15)-C(16)-C(17)	179.47(13)
C(20)-O(3)-C(19)-O(2)	-2.83(17)
C(20)-O(3)-C(19)-C(6)	-175.58(10)
C(1)-C(6)-C(19)-O(2)	21.64(17)
C(5)-C(6)-C(19)-O(2)	-99.66(14)
C(21)-C(6)-C(19)-O(2)	142.02(12)
C(1)-C(6)-C(19)-O(3)	-165.84(9)
C(5)-C(6)-C(19)-O(3)	72.86(12)
C(21)-C(6)-C(19)-O(3)	-45.46(13)
C(19)-C(6)-C(21)-C(22)	-63.22(14)
C(1)-C(6)-C(21)-C(22)	57.12(14)
C(5)-C(6)-C(21)-C(22)	-178.98(10)
C(6)-C(21)-C(22)-C(26)	70.86(14)
C(6)-C(21)-C(22)-C(23)	-164.53(10)
C(26)-C(22)-C(23)-C(24)	-55.62(14)
C(21)-C(22)-C(23)-C(24)	177.57(11)
C(22)-C(23)-C(24)-C(25)	128.65(14)
C(21)-C(22)-C(26)-C(27)	-111.12(13)
C(23)-C(22)-C(26)-C(27)	125.49(12)
C(21)-C(22)-C(26)-C(28)	70.86(14)
C(23)-C(22)-C(26)-C(28)	-52.54(14)

Part IV: Computational details

Table S13. Cartesian coordinates of the lowest energy conformer of isogarcinol (optimized at PBE0/def2-SVPD)

Atom	x	y	z
C	0.279939	-1.246920	-0.505373
C	-0.397243	-0.741299	-1.814802
C	-0.980181	0.677841	-1.810228
C	0.025276	1.717766	-1.219995
C	0.625877	1.202942	0.172308
C	1.266140	-0.138936	-0.131918
C	-0.714720	-1.356631	0.622748
C	-0.507980	1.026145	1.190878
C	-1.062451	-0.292664	1.401784
O	2.462203	-0.299900	-0.171529
C	1.672558	2.166138	0.772631
C	2.159066	1.761592	2.134149
C	3.413681	1.460660	2.511169
C	3.716226	1.098855	3.937812
C	4.604702	1.452366	1.600618
C	-0.648778	3.081216	-1.059506
C	1.171856	1.896450	-2.229400
C	-2.441507	0.741875	-1.293435
C	-3.325697	1.632288	-2.115260
C	-4.216776	2.541837	-1.685781
C	-4.476492	2.861046	-0.242448
C	-5.036590	3.338512	-2.660225
C	-2.115170	-0.438729	2.467767
C	-1.689901	-0.905199	3.802027
O	-3.276322	-0.157279	2.215621
O	-0.897439	1.989778	1.842401
C	-2.662537	-1.084626	4.801777
C	-2.293996	-1.518925	6.061096
C	-0.935627	-1.778984	6.349320
C	0.030768	-1.598486	5.362629
C	-0.345192	-1.163563	4.096509
O	-3.145216	-1.728456	7.092938
O	-0.579289	-2.200234	7.573087
O	-1.331267	-2.501460	0.860806
C	-0.760913	-3.815916	0.545679
C	0.742721	-3.624376	0.313151
C	0.979528	-2.585941	-0.773236
C	-1.522089	-4.368270	-0.649600
C	-1.055789	-4.635820	1.792440
C	1.486117	-4.930050	-0.005910
C	2.973178	-4.761248	0.072716
C	3.871212	-4.814586	-0.925836
C	5.334325	-4.608548	-0.656630

Table S13. (Continued)

C	3.530562	-5.068481	-2.365055
H	-1.173698	-1.461848	-2.104297
H	0.381117	-0.812506	-2.587234
H	-1.047494	0.943537	-2.876696
H	1.206269	3.157020	0.846844
H	2.509940	2.249086	0.074893
H	1.391023	1.736774	2.912834
H	4.457992	1.790611	4.369837
H	4.161473	0.092187	3.996749
H	2.817547	1.117695	4.567761
H	5.086852	0.461720	1.617376
H	5.361365	2.171995	1.953228
H	4.357882	1.687364	0.560993
H	-1.087738	3.376828	-2.021136
H	0.078614	3.852112	-0.777882
H	-1.448085	3.078202	-0.312819
H	1.885853	2.658740	-1.896135
H	0.753706	2.237089	-3.185818
H	1.734218	0.974746	-2.422021
H	-2.501232	1.016583	-0.237622
H	-2.849593	-0.281790	-1.342346
H	-3.232758	1.498128	-3.200142
H	-4.274190	3.926481	-0.044193
H	-3.880096	2.260906	0.453507
H	-5.539435	2.699603	-0.000481
H	-6.114095	3.177417	-2.491963
H	-4.806184	3.078921	-3.701595
H	-4.860645	4.418485	-2.524327
H	-3.710368	-0.880568	4.573020
H	1.074332	-1.803411	5.603713
H	0.415172	-1.019051	3.329628
H	-4.057959	-1.539223	6.847375
H	-1.364553	-2.273084	8.134516
H	1.147698	-3.233756	1.264391
H	0.641422	-2.987746	-1.737786
H	2.055586	-2.400872	-0.869764
H	-1.199260	-5.395320	-0.860916
H	-1.373195	-3.768279	-1.554693
H	-2.595468	-4.390582	-0.423972
H	-0.499599	-4.248684	2.655913
H	-0.784765	-5.687100	1.638865
H	-2.128387	-4.591631	2.018839
H	1.178644	-5.289651	-0.997221
H	1.182557	-5.702805	0.716445
H	3.355328	-4.549033	1.078255
H	5.722049	-3.761378	-1.245566
H	5.916970	-5.492396	-0.964197
H	5.534049	-4.413210	0.404768

Table S13. (Continued)

H	3.856316	-4.219064	-2.987278
H	2.461112	-5.226752	-2.540463
H	4.074134	-5.950873	-2.739377

Table S14. TD-DFT results for isogarcinol (**3**)

Transition	Excitation energy (nm)	Rotatory strength[a] (*R* x 10^{40} cgs)	Oscillator strength *f*	Contributions	Weight^2*100
1	299.28	5.6675	0.0075	163 → 165	44.5
				162 → 165	32.7
				163 → 164	9.2
				158 → 164	2.8
				158 → 165	2.5
2	296.11	15.8597	0.2178	161 → 164	83.8
				157 → 164	7.3
3	292.64	-15.1239	0.0028	162 → 164	29.9
				158 → 164	20.6
				159 → 164	14.8
				156 → 164	12.3
				155 → 164	9.0
				163 → 164	6.6
4	288.94	17.0056	0.0089	162 → 165	51.4
				163 → 165	37.3
				162 → 164	2.4
5	271.01	-43.3838	0.0484	160 → 165	84.9
				159 → 165	5.9
6	266.86	-18.5630	0.0666	158 → 164	41.2
				157 → 164	20.1
				155 → 164	19.6
				156 → 164	4.8
				159 → 165	2.8
				161 → 167	2.6
7	266.28	-60.6100	0.1356	159 → 165	40.2
				157 → 164	18.6
				158 → 164	15.3
				160 → 165	7.5
				155 → 164	6.4
				155 → 165	2.5
8	246.95	-17.0178	0.0078	159 → 166	53.0
				162 → 166	15.9
				163 → 166	13.6
				160 → 166	9.9
9	242.18	27.2995	0.0701	155 → 165	74.9
				158 → 165	9.2
				159 → 165	3.1
				160 → 166	3.1
10	223.61	52.5435	0.0469	158 → 166	44.1
				156 → 166	41.7
				155 → 166	6.6

Table S14. (Continued)

11	223.21	22.3130	0.2260	161 → 167	78.2
				157 → 164	11.1
				157 → 176	2.0
12	204.75	-22.5088	0.0142	162 → 168	40.0
				163 → 168	34.1
				162 → 172	3.9
				162 → 171	3.6
				162 → 173	2.6
				163 → 172	2.2
				162 → 169	1.9
				163 → 144	1.7
13	202.88	-6.6850	0.0081	155 → 166	56.8
				154 → 165	16.4
				156 → 166	10.0
				153 → 165	9.8
14	200.62	-10.9817	0.0372	154 → 165	21.0
				155 → 166	19.1
				154 → 164	11.6
				153 → 165	11.3
				153 → 164	9.4
				163 → 173	4.9
				163 → 168	3.7
				162 → 168	3.2
				156 → 166	1.8
				163 → 174	1.5
				163 → 170	1.5
				162 → 173	1.2
15	200.42	43.4160	0.0454	163 → 173	20.5
				163 → 168	13.7
				162 → 168	12.4
				163 → 174	7.0
				154 → 164	6.7
				162 → 173	5.9
				153 → 164	4.8
				163 → 170	3.6
				154 → 165	3.2
				155 → 166	2.8
				162 → 174	2.5
				163 → 171	2.2
				153 → 165	1.9
				160 → 168	1.9
				163 → 179	1.3

[a] Excited states with $-5 < R < 5$ were not presented.

Table S15. Cartesian coordinates of the lowest energy conformer of isoxanthochymol (optimized at PBE0/def2-SVPD)

Atom	x	y	z
C	-0.378447	0.478406	2.719992
C	0.299420	-0.025696	4.029667
C	0.882164	-1.444899	4.026545
C	-0.123705	-2.485414	3.438095
C	-0.724986	-1.972179	2.045473
C	-1.364948	-0.629895	2.348488
C	0.615564	0.586606	1.591181
C	0.408478	-1.796894	1.026152
C	0.963021	-0.478330	0.813316
O	-2.560989	-0.468815	2.388693
C	-1.772147	-2.935869	1.446789
C	-2.259220	-2.532571	0.085108
C	-3.513899	-2.231564	-0.291666
C	-3.816892	-1.870869	-1.718499
C	-4.704530	-2.222026	0.619392
C	0.550106	-3.849133	3.278890
C	-1.269787	-2.662797	4.448297
C	2.343220	-1.509675	3.509106
C	3.227701	-2.399214	4.331552
C	4.118196	-3.309615	3.902687
C	4.376816	-3.630806	2.459590
C	4.938361	-4.105321	4.877629
C	2.015853	-0.333538	-0.252676
C	1.592611	0.140683	-1.584874
O	3.175592	-0.622208	-0.002149
O	0.797205	-2.761436	0.375621
C	2.566362	0.322479	-2.583088
C	2.199863	0.764532	-3.840307
C	0.842394	1.029637	-4.128099
C	-0.125170	0.846469	-3.143036
C	0.248783	0.404066	-1.878914
O	3.052423	0.977587	-4.870334
O	0.488004	1.458258	-5.349892
O	1.232290	1.731076	1.351733
C	0.661922	3.046035	1.664822
C	-0.841553	2.854879	1.898782
C	-1.077600	1.817876	2.986699
C	1.423911	3.600531	2.858585
C	0.955800	3.863776	0.416395
C	-1.584429	4.161111	2.216816
C	-3.071640	3.992470	2.140723
C	-3.968006	4.047602	3.140665
C	-5.431621	3.841583	2.874206
C	-3.624930	4.303591	4.578942

Table S15. (Continued).

H	1.076133	0.695091	4.317852
H	-0.478527	0.046599	4.802420
H	0.950165	-1.709092	5.093325
H	-1.306058	-3.926904	1.373397
H	-2.609192	-3.017891	2.145038
H	-1.491508	-2.508584	-0.693931
H	-4.559173	-2.562638	-2.149606
H	-4.261682	-0.864038	-1.778114
H	-2.918478	-1.890669	-2.348793
H	-5.185865	-1.230978	0.602565
H	-5.461890	-2.941206	0.267354
H	-4.457439	-2.456846	1.658997
H	0.989548	-4.143622	4.240646
H	-0.177548	-4.620282	2.998609
H	1.349031	-3.847101	2.531789
H	-1.983964	-3.425512	4.116396
H	-0.851127	-3.002157	5.404950
H	-1.832084	-1.740860	4.639974
H	2.402494	-1.785535	2.453561
H	2.751409	-0.485993	3.556763
H	3.135394	-2.263492	5.416284
H	4.173364	-4.696275	2.262694
H	3.780633	-3.030875	1.763268
H	5.439788	-3.470723	2.216856
H	6.015820	-3.944981	4.708346
H	4.708850	-3.844106	5.918796
H	4.761778	-5.185402	4.743387
H	3.613476	0.114371	-2.354694
H	-1.168055	1.055210	-3.383797
H	-0.512460	0.257532	-1.113292
H	3.964144	0.782042	-4.625931
H	1.273786	1.531539	-5.910539
H	-1.247389	2.463106	0.948382
H	-0.738622	2.220869	3.950450
H	-2.153605	1.633105	3.084383
H	1.101200	4.627931	3.068338
H	1.275701	3.002068	3.764812
H	2.497121	3.622519	2.632120
H	0.399314	3.474821	-0.446060
H	0.684405	4.915214	0.568229
H	2.028287	3.819590	0.189445
H	-1.275491	4.522174	3.207133
H	-1.281788	4.932717	1.492850
H	-3.455471	3.778837	1.136129
H	-5.818750	2.995729	3.465410
H	-6.013416	4.726270	3.180989

Table S15. (Continued).

H	-5.633108	3.644254	1.813506
H	-3.949328	3.454928	5.202900
H	-2.555231	4.462463	4.752297
H	-4.168155	5.186297	4.953017

Table S16. TD-DFT results for isoxanthochymol (**4**)

Transition	Excitation energy (nm)	Rotatory strength[a] (*R* x 10^{40} cgs)	Oscillator strength *f*	Contributions	Weight^2*100
1	296.18	-17.5915	0.2167	161 → 164	83.5
				157 → 164	7.1
2	292.67	16.7429	0.0034	162 → 164	28.6
				158 → 164	20.6
				159 → 164	15.0
				156 → 164	12.3
				155 → 164	9.0
				163 → 164	6.8
3	289.0	-16.8821	0.0089	162 → 165	50.9
				163 → 165	37.3
				162 → 164	2.6
4	271.02	42.9551	0.0478	160 → 165	84.5
				159 → 165	5.9
5	266.95	20.3689	0.0728	158 → 164	39.1
				157 → 164	21.9
				155 → 164	18.4
				156 → 164	4.5
				159 → 165	3.6
				161 → 167	2.8
6	266.27	57.3587	0.1291	159 → 165	39.7
				158 → 164	17.2
				157 → 164	16.8
				155 → 164	7.3
				160 → 165	7.1
				155 → 165	2.3
7	246.98	16.7465	0.0077	159 → 166	52.3
				162 → 166	16.4
				163 → 166	14.2
				160 → 166	9.6
8	242.22	-27.2971	0.0695	155 → 165	74.3
				158 → 165	9.1
				159 → 165	3.1
				160 → 166	3.1
				155 → 164	3.1
9	223.66	-52.6648	0.0458	158 → 166	44.2
				156 → 166	41.7
				155 → 166	6.6
10	223.24	-22.2292	0.2267	161 → 167	78.3
				157 → 164	11.1
				157 → 176	2.0

Table S16. (Continued)

11	204.94	22.5005	0.0139	162 → 168	40.4
				163 → 168	33.8
				162 → 171	3.7
				162 → 172	3.6
				162 → 173	2.7
				162 → 169	2.1
				163 → 172	2.1
				163 → 174	1.6
12	202.91	6.7889	0.0082	155 → 166	56.2
				154 → 165	16.8
				156 → 166	9.9
				153 → 165	9.3
13	200.57	-33.6874	0.0587	163 → 173	13.4
				154 → 164	11.7
				163 → 168	9.3
				154 → 165	8.8
				162 → 168	8.5
				153 → 164	8.2
				155 → 166	8.1
				163 → 174	5.4
				153 → 165	4.8
				162 → 173	3.9
				163 → 170	2.3
				160 → 168	2.1
				162 → 174	1.7
				163 → 171	1.6
				163 → 179	0.9
14	200.02	6.2107	0.0243	154 → 164	37.4
				153 → 164	22.8
				154 → 165	16.5
				153 → 165	9.6
				155 → 166	4.0

[a] Excited states with $-5 < R < 5$ were not presented.