Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Electronic Supporting Information (ESI) for: Dioxirane Mediated Asymmetric Epoxidations. Stereochemical Studies via Isotopic Labeling

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Contents:

1.- X-Ray Analysis of the methanolysis product of 3

In order to establish if nucleophilic displacement onto **3** was possible, the methanolysis of **3** at room temperature and in the absence of acidic or basic catalyst was investigated. Compound **3** (16 mg, 0.05 mmol) was dissolved in methanol (1 mL) and the solution was allowed to stand, while allowing slow solvent evaporation. Single-crystals of the methanolate of **3** separated out from the solution. The structure of this newly isolated material could be unambiguously proven by single-crystal X-ray structure analysis, which revealed that methanol could stereoselectively displace the pro-*S* hydroxy group in **3**.

CCDC 640610 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

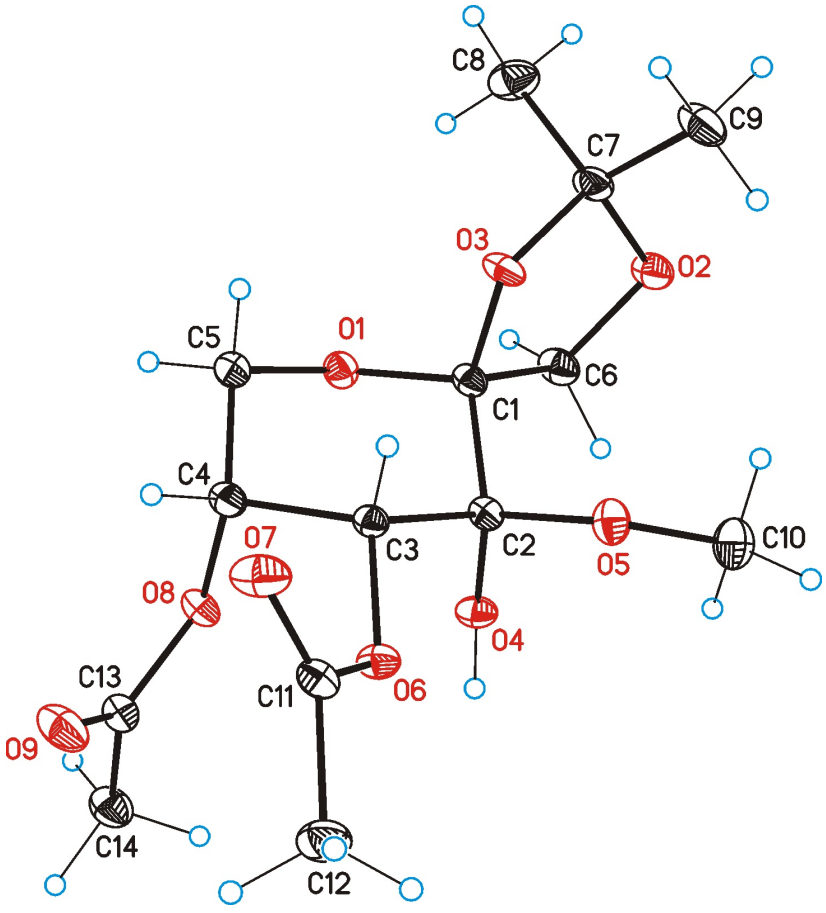

Figure I: ORTEP plot (thermal ellipsoids shown at 50 % probability level) of the methanolate of **3**.

Table I. Crystal data and structure refinement for the methanolate of **3**

Identification code	Methanolate of **3**	
Empirical formula	C14 H22 O9	
Formula weight	334.32	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 6.8203(8) Å	α= 90°.
	b = 5.5939(7) Å	ß= 97.914(3)°.
	c = 20.585(3) Å	γ = 90°.
Volume	777.89(17) $Å^3$	
Z	2	
Density (calculated)	1.427 Mg/m^3	
Absorption coefficient	0.120 mm^{-1}	
F(000)	356	
Crystal size	0.30 x 0.01 x 0.01 mm^3	
Theta range for data collection	3.00 to 39.71°.	
Index ranges (merged data)	$-11 \le h \le 11$, $0 \le k \le 9$, $0 \le l \le 37$	
Reflections collected	13917	
Independent reflections after merging	4265 [R(int) = 0.0649]	
Reflections number get (Fo > 4σ(Fo))	2978	
Completeness to theta = 39.71°	83.9 %	
Absorption correction	SADABS (Bruker-Nonius)	
Max. and min. transmission	1.0000 and 0.9595	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4265 / 1 / 214	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0500, wR2 = 0.1052	
R indices (all data)	R1 = 0.0939, wR2 = 0.1244	
Largest diff. peak and hole	0.543 and -0.297 $e.Å^{-3}$	

Table II. Bond lengths [Å] and angles [°] for the methanolate of **3**.

C(1)-O(3)	1.413(2)
C(1)-O(1)	1.417(2)
C(1)-C(6)	1.536(3)
C(1)-C(2)	1.558(2)
O(1)-C(5)	1.434(2)
C(2)-O(4)	1.400(2)
C(2)-O(5)	1.406(2)
C(2)-C(3)	1.532(3)
O(2)-C(7)	1.426(2)
O(2)-C(6)	1.427(3)
C(3)-O(6)	1.452(2)
C(3)-C(4)	1.527(3)
O(3)-C(7)	1.444(2)
C(4)-O(8)	1.444(2)
C(4)-C(5)	1.517(2)
O(5)-C(10)	1.451(3)
O(6)-C(11)	1.348(2)
C(7)-C(9)	1.498(3)
C(7)-C(8)	1.525(3)
O(7)-C(11)	1.210(2)
O(8)-C(13)	1.347(2)
O(9)-C(13)	1.213(3)
C(11)-C(12)	1.494(3)
C(13)-C(14)	1.500(3)

O(3)-C(1)-O(1)	112.25(14)
O(3)-C(1)-C(6)	104.60(16)
O(1)-C(1)-C(6)	105.54(15)
O(3)-C(1)-C(2)	108.10(14)
O(1)-C(1)-C(2)	110.53(16)
C(6)-C(1)-C(2)	115.77(15)

C(1)-O(1)-C(5)	114.96(14)
O(4)-C(2)-O(5)	112.41(15)
O(4)-C(2)-C(3)	113.81(17)
O(5)-C(2)-C(3)	104.04(14)
O(4)-C(2)-C(1)	105.19(14)
O(5)-C(2)-C(1)	113.36(17)
C(3)-C(2)-C(1)	108.18(14)
C(7)-O(2)-C(6)	106.70(16)
O(6)-C(3)-C(4)	109.93(16)
O(6)-C(3)-C(2)	107.43(13)
C(4)-C(3)-C(2)	113.17(14)
C(1)-O(3)-C(7)	109.24(14)
O(8)-C(4)-C(5)	108.07(15)
O(8)-C(4)-C(3)	110.10(14)
C(5)-C(4)-C(3)	108.55(17)
O(1)-C(5)-C(4)	112.13(15)
C(2)-O(5)-C(10)	117.59(15)
O(2)-C(6)-C(1)	104.54(16)
C(11)-O(6)-C(3)	116.35(14)
O(2)-C(7)-O(3)	104.42(16)
O(2)-C(7)-C(9)	109.10(19)
O(3)-C(7)-C(9)	108.40(16)
O(2)-C(7)-C(8)	110.87(17)
O(3)-C(7)-C(8)	110.26(18)
C(9)-C(7)-C(8)	113.37(18)
C(13)-O(8)-C(4)	118.66(15)
O(7)-C(11)-O(6)	123.64(17)
O(7)-C(11)-C(12)	123.88(18)
O(6)-C(11)-C(12)	112.48(16)
O(9)-C(13)-O(8)	124.1(2)
O(9)-C(13)-C(14)	125.9(2)
O(8)-C(13)-C(14)	110.03(17)

Table III. Torsion angles [°] for the methanolate of **3**.

O(3)-C(1)-O(1)-C(5)	-61.95(19)
C(6)-C(1)-O(1)-C(5)	-175.30(15)
C(2)-C(1)-O(1)-C(5)	58.83(19)
O(3)-C(1)-C(2)-O(4)	-168.90(15)
O(1)-C(1)-C(2)-O(4)	67.89(18)
C(6)-C(1)-C(2)-O(4)	-52.0(2)
O(3)-C(1)-C(2)-O(5)	-45.7(2)
O(1)-C(1)-C(2)-O(5)	-168.91(14)
C(6)-C(1)-C(2)-O(5)	71.2(2)
O(3)-C(1)-C(2)-C(3)	69.1(2)
O(1)-C(1)-C(2)-C(3)	-54.08(19)
C(6)-C(1)-C(2)-C(3)	-173.97(17)
O(4)-C(2)-C(3)-O(6)	58.51(19)
O(5)-C(2)-C(3)-O(6)	-64.16(18)
C(1)-C(2)-C(3)-O(6)	175.02(15)
O(4)-C(2)-C(3)-C(4)	-63.02(19)
O(5)-C(2)-C(3)-C(4)	174.31(15)
C(1)-C(2)-C(3)-C(4)	53.5(2)
O(1)-C(1)-O(3)-C(7)	-105.29(17)
C(6)-C(1)-O(3)-C(7)	8.64(19)
C(2)-C(1)-O(3)-C(7)	132.54(16)
O(6)-C(3)-C(4)-O(8)	-55.24(17)
C(2)-C(3)-C(4)-O(8)	64.88(19)
O(6)-C(3)-C(4)-C(5)	-173.35(15)
C(2)-C(3)-C(4)-C(5)	-53.23(19)
C(1)-O(1)-C(5)-C(4)	-59.2(2)
O(8)-C(4)-C(5)-O(1)	-66.0(2)
C(3)-C(4)-C(5)-O(1)	53.4(2)
O(4)-C(2)-O(5)-C(10)	44.7(2)
C(3)-C(2)-O(5)-C(10)	168.30(16)
C(1)-C(2)-O(5)-C(10)	-74.4(2)

C(7)-O(2)-C(6)-C(1)	-27.8(2)
O(3)-C(1)-C(6)-O(2)	11.64(19)
O(1)-C(1)-C(6)-O(2)	130.23(16)
C(2)-C(1)-C(6)-O(2)	-107.20(18)
C(4)-C(3)-O(6)-C(11)	-80.41(19)
C(2)-C(3)-O(6)-C(11)	156.05(17)
C(6)-O(2)-C(7)-O(3)	33.3(2)
C(6)-O(2)-C(7)-C(9)	149.05(15)
C(6)-O(2)-C(7)-C(8)	-85.4(2)
C(1)-O(3)-C(7)-O(2)	-25.8(2)
C(1)-O(3)-C(7)-C(9)	-142.05(16)
C(1)-O(3)-C(7)-C(8)	93.31(19)
C(5)-C(4)-O(8)-C(13)	-143.83(17)
C(3)-C(4)-O(8)-C(13)	97.76(19)
C(3)-O(6)-C(11)-O(7)	-2.0(3)
C(3)-O(6)-C(11)-C(12)	177.24(18)
C(4)-O(8)-C(13)-O(9)	0.8(3)
C(4)-O(8)-C(13)-C(14)	-178.87(16)