Supporting Information

Tetrahydropyran Formation by Rearrangement of an Epoxy Ester:
A Model for the Biosynthesis of Marine Polyether Toxins

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Contents

Rearrangement kinetics S2

\(^1\)H NMR spectra of compounds 10-17 S3-11

\(^{13}\)C-NMR spectra of \(^{18}\)O-labeled compounds S12-15
Rearrangement of Epoxy Acetates in 50 mM TFA/CDCl3 at 30 C

-\ln(\% epoxide) vs. minutes

(S)-epoxide
(R)-epoxide

y = 0.0726x  
R² = 0.9994

y = 0.0246x  
R² = 0.9992
7.0 7.5 ppm

AcO

10
$^{18}$O-10
+ ca. 25% R-isomer $[^{18}\text{O}]-15$

$[^{18}\text{O}]-16$

$[^{18}\text{O}]-15$

$R$-isomer