

Supplementary Information for

An Efficient Didehydroxylation Method for the Biomass-Derived Polyols Glycerol and Erythritol. Mechanistic Studies of a Formic Acid-Mediated Deoxygenation

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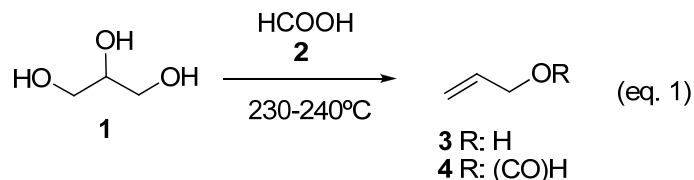
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Materials and methods

General Information:

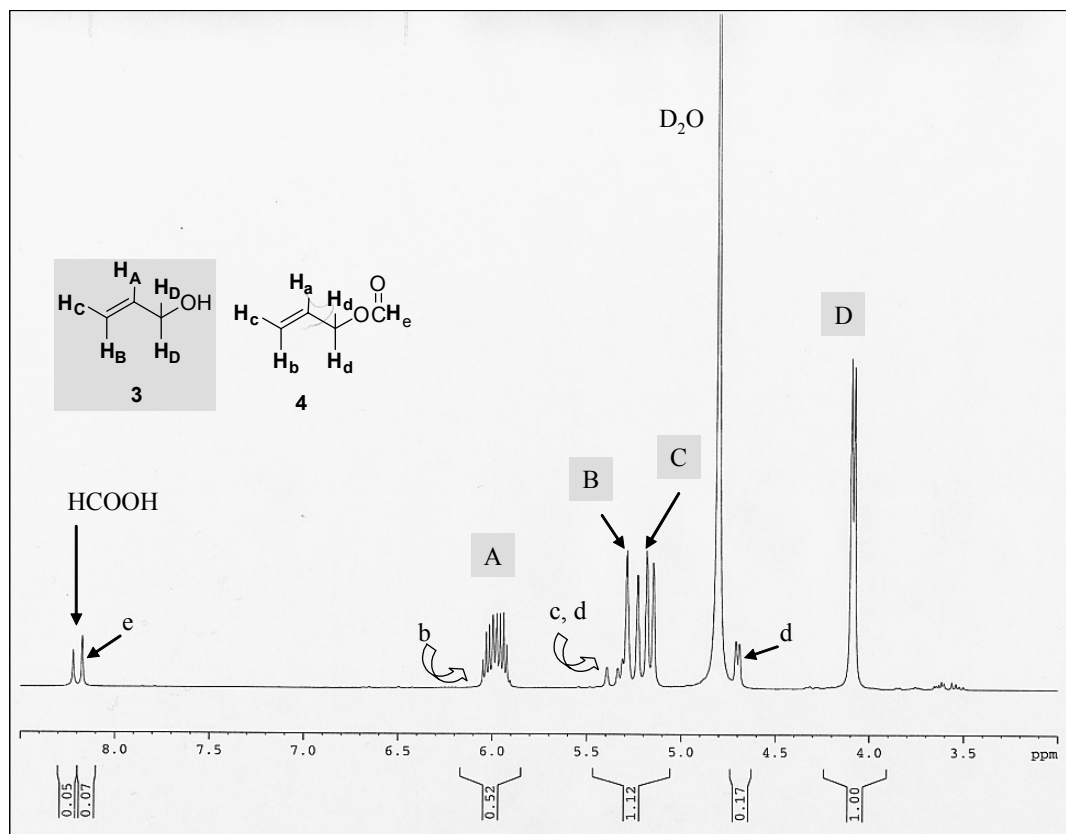
Unless otherwise specified, all commercial materials were used without further purification. Glycerol, [1,1,2,3,3-²H₅]glycerol, [²H₂]-formic acid, 1,2-octanediol, 1,2-decanediol, *cis* and *trans* 1,2-cyclopentanediol, *trans*-1,2-cyclopentanediol, *cis*-1,2-cyclohexanediol, *cis*-1,2-cyclooctanediol, 1,2,6-hexanetriol, *meso*-erythritol and diethoxymethyl acetate were purchased from Aldrich. 1,2,3-hexanetriol was purchased from Fluka and formic acid from Acros. *Trans* and *cis*-3-decene were purchased from ChemSampCo. Nuclear magnetic resonance (NMR) spectra were recorded with Bruker AVB-400, AVQ-400 and AV-300 spectrometers. ¹H and ¹³C NMR shifts are reported in ppm downfield of tetramethylsilane and referenced to the residual solvent peak.

Formic acid-mediated deoxygenation of glycerol (1)



In a 100 mL three neck round-bottomed flask were placed 150 mmol (13.8 g) of glycerol and 89 mmol of 99 per cent formic acid (3.36 mL). The flask was connected to a condenser set: fractioning column, reflux condenser and collecting flask. The temperature in the reaction mixture was measured by an immersed thermometer. A tube was run from the side arm of the distilling flask to a bubbler containing a NaOH solution. Nitrogen was bubbled through the reaction mixture using a perforated tube immersed in the solution for 20 minutes at room temperature. After that, the mixture was heated using a preheated sand bath with continuation of the nitrogen bubbling. A temperature of 235 °C was reached in 30 minutes and distillation occurred for about 45 minutes. Heating was continued until the temperature reached 240 °C and then the mixture was allowed to cool to room temperature. A second portion of formic acid (63.5 mmol, 2.40 mL) was added and the distillation was then repeated in the same manner as described above. Finally a third portion of formic acid was added. The combined three distillates contained allyl alcohol (**3**) with some formic acid, water and allyl formate (**4**) (**3:4**, 100:17) (Figure 1S). Potassium carbonate was added in order to salt out the allyl alcohol and neutralize the acid present. The olefin product was then separated through decantation from the aqueous phase. Allyl alcohol (**3**) was further purified by distillation (7.16 g) (Yield 82%). **3**: ¹H NMR (CDCl₃) δ 5.92 (m, 1H, CH=CH₂), 5.21 (ddd, 1H, HCH=CH, J=17.2 Hz, J'=1.8 Hz), 5.08 (ddd, 1H, HCH=CH, J=10.4 Hz, J=1.5 Hz), 4.05 (d, 2H, J=5.3 Hz), 3.78 (s, 1H, OH). ¹³C NMR (CDCl₃) δ 137.5, 115.2, 63.6.

Fig.1S ^1H NMR (D_2O) of the crude distillate obtained from the reaction of glycerol (**1**) and formic acid (**2**).



The reaction was carried out starting with different amounts of glycerol and using the exact same procedure in order to prove scalability. 10 mmol (0.9 g) of **1** yielded 0.46 g of **3** (79%), 20 mmol (1.8 g) of **1** yielded 0.98 g of **3** (84%), 50 mmol (4.6 g) of **1** yielded 2.58 g of **3** (89%) and 500 g of **1** (5.4 Mol) yielded 265 g of **1** (84%).^[1]

Isotopic labeling experiments (A, B, C)

A. Isotopic labeling experiment using d_5 -glycerol ($[1,1,2,3,3\text{-}^2\text{H}_5]\text{glycerol}$) (**1d₅**) with undeuterated formic acid (eq. 2). The incorporation of deuterium in the final product was monitored by ^2H -NMR. The allyl product was completely deuterated at all carbon positions (**3-d₅**, **4-d₅**). See figure 2S.

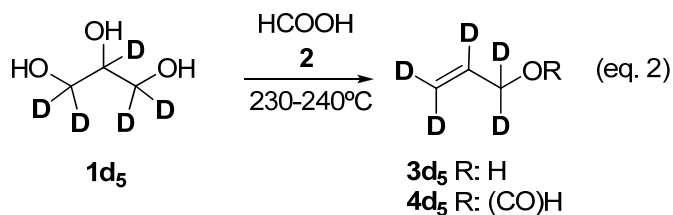
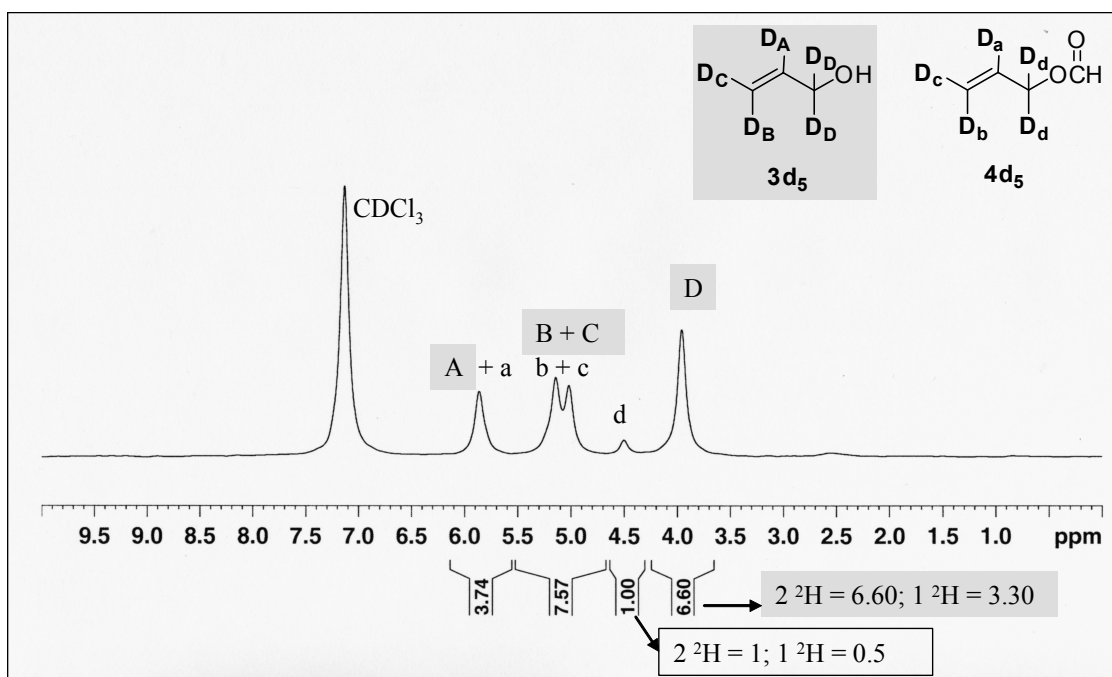


Fig. 2S ^2H NMR ($\text{CDCl}_3/\text{CHCl}_3$) of the distillate obtained from the reaction of d_5 -glycerol ($\mathbf{1d_5}$) and formic acid (**2**).



B. Isotopic labeling experiment using d_5 -glycerol ($[\text{1,1,2,3,3-}^2\text{H}_5]\text{glycerol}$) ($\mathbf{1d_5}$) (2 mmol) and undeuterated glycerol (**1**) (13 mmol) with undeuterated formic acid (**2**) (three consecutive portions of 9, 6.3 and 6.3 mmol as described above)(eq. 3). The ^1H -NMR of the distillate showed the usual spectrum obtained when using undeuterated materials. The ^2H -NMR showed that the allyl product was completely deuterated at all carbon positions ($\mathbf{3-d_5}$, $\mathbf{4-d_5}$). See figure 3S.

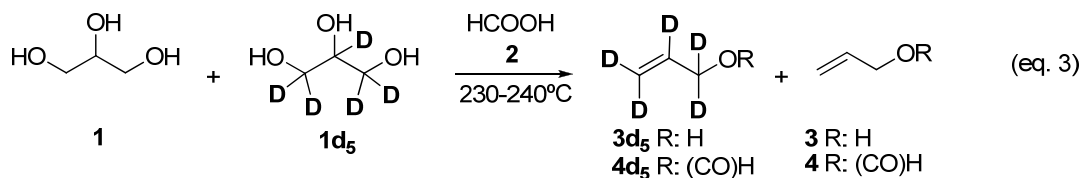
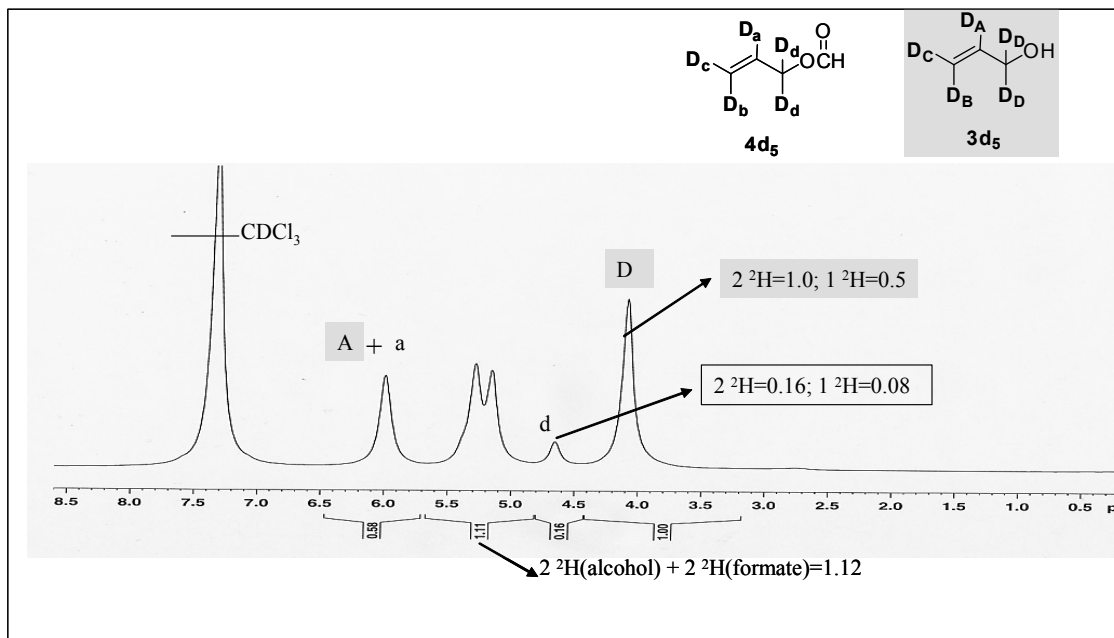


Fig. 3S ^2H NMR ($\text{CDCl}_3/\text{CHCl}_3$) of the distillate obtained from the reaction of d_5 -glycerol (**1d₅**), glycerol (**1**) and formic acid (**2**).



C. Isotopic labeling experiment employing perdeuterated formic acid ($[\text{D}_2]$ -formic acid) (**2d₂**) in the reaction with non-labeled glycerol (**1**) (eq. 4). No deuterium was incorporated in the final product (**3**), except for the exchange of deuterium into the hydroxyl group (**3-d₁**) and the formyl proton of the minor allyl ester **4-d₁**. (See figures 4S and 5S for NMR spectra)

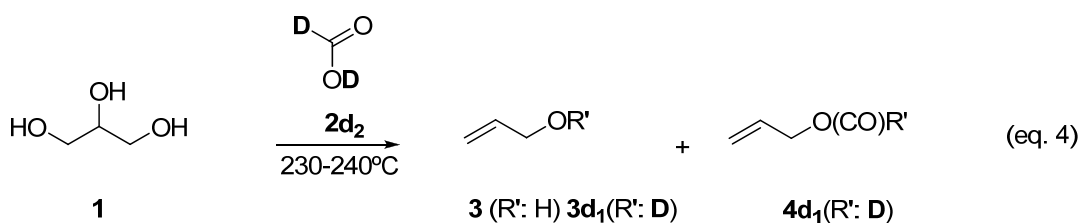


Fig. 4S ^2H NMR in 1) $\text{H}_2\text{O}/\text{D}_2\text{O}$ and in 2) $\text{CHCl}_3/\text{CDCl}_3$ of the distillate obtained from the reaction of glycerol **1** and perdeuterated formic acid (**2d₂**)

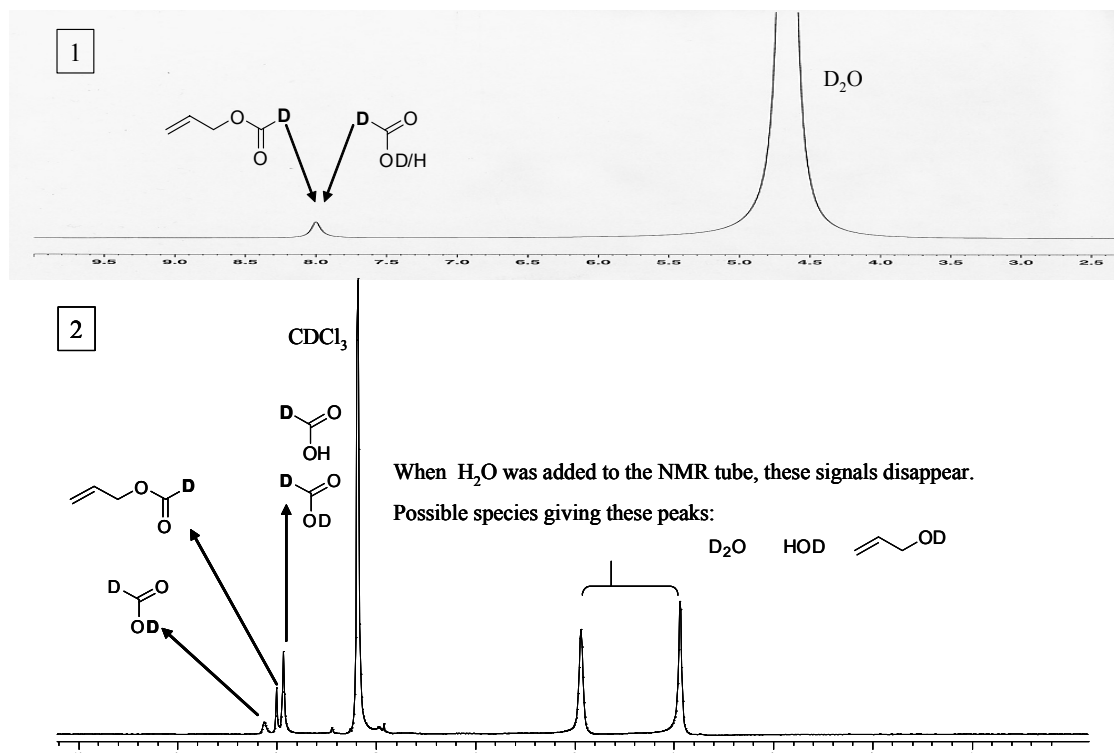
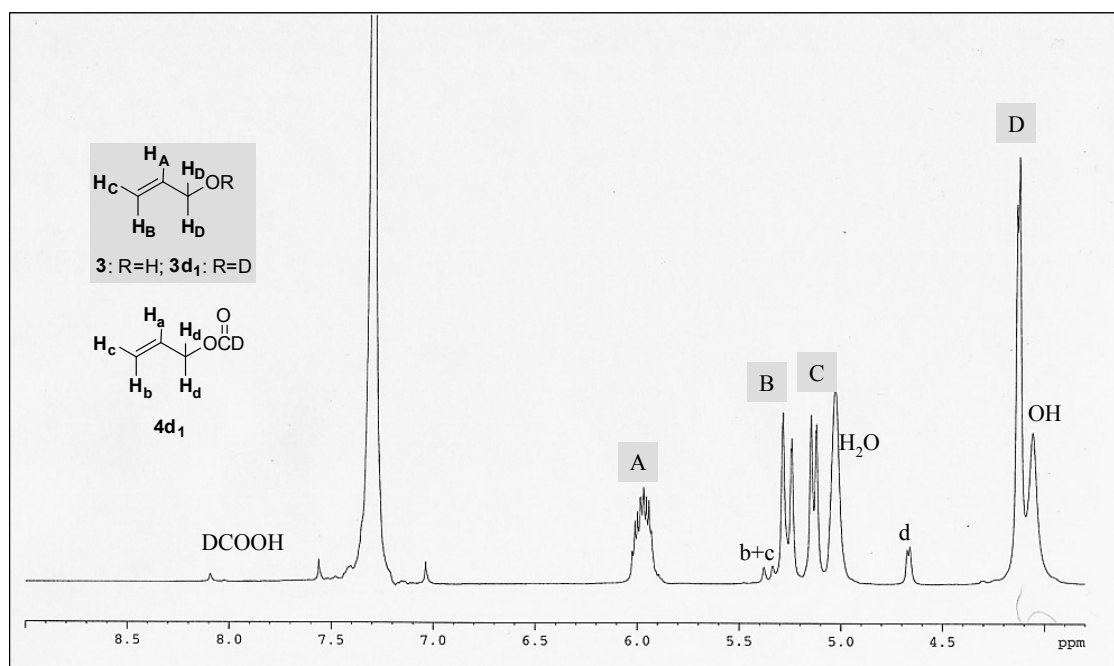


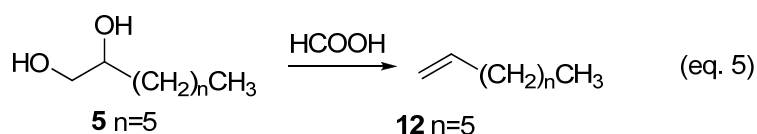
Fig. 5S ^1H NMR (CDCl_3) of the distillate obtained from the reaction of glycerol **1** and perdeuterated formic acid (**2d₂**).



General method for the formic acid-mediated deoxygenation of 1,2-diols

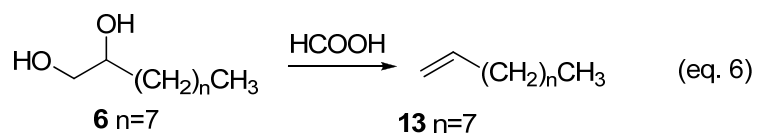
The diol and formic acid (**2**) (0.60 equivalents) are first mixed in a flask fitted with a distillation set: fractioning column, reflux condenser and collecting flask. The temperature is monitored by a thermometer immersed in the reaction mixture. Nitrogen is bubbled through the mixture using a perforated tube immersed in the solution for 20 minutes at room temperature or, when the starting material is a solid, at a temperature slightly over its melting point. The reaction is performed by heating the mixture to 230-240 °C using a preheated sand bath with continuation of the nitrogen bubbling. Under these conditions distillation of the product takes place. Heating is continued until no more distillate appears. This procedure is repeated in the same manner as described above, by making two more additions of formic acid (0.42 equivalents each). When all the starting material is consumed, potassium carbonate is added to the distillate and water is removed by decantation; the resulting product is the pure corresponding alkene. The final products were identified by ¹H and ¹³C NMR spectroscopy, in agreement with the literature data.

Deoxygenation of 1,2-octanediol (5**)**



1,2-octanediol (20 mmol) (2.92 g) was deoxygenated with formic acid following the general method to give 2.05 g of 1-octene (**12**) (Yield 91%). **12**: ¹H NMR (CDCl₃) δ 5.77 (m, 1H, HC=C), 4.97 (dd, 1H, HCH=CH, J= 17.0 Hz, J'= 2.1 Hz), 4.91 (d, 1H, HCH=CH, J=10.1 Hz), 2.02 (m, 2H, CH₂), 1.28-1.48 (m, 8H, CH₂), 0.87 (m, 3H, CH₃). ¹³C NMR (CDCl₃) δ 139.2, 114.1, 33.9, 31.8, 29.0, 28.9, 22.7, 14.0.

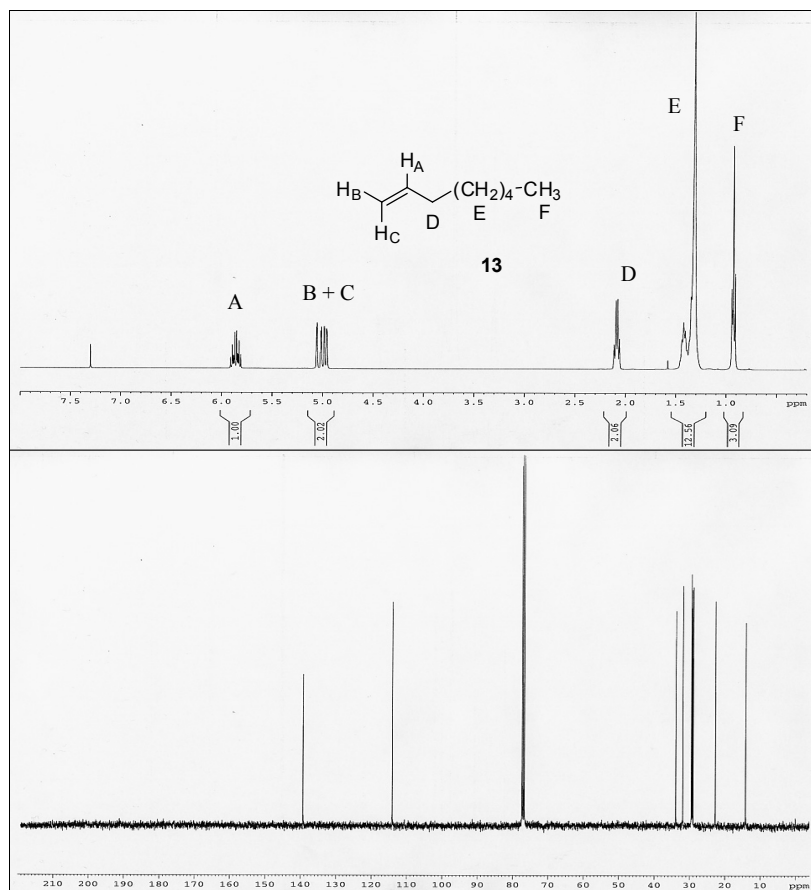
Deoxygenation of 1,2-decanediol (6**)**



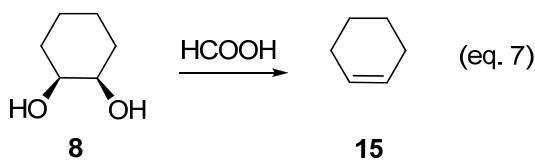
1,2-decanediol (20 mmol) (3.48 g) was deoxygenated with formic acid following the general method to give 2.60 g of 1-decene (**13**) (Yield 93%). **13**: ¹H NMR (CDCl₃) δ 5.86 (m, 1H, HC=C), 5.04 (d, 1H, HCH=CH, J= 17.0 Hz), 4.97 (dd, 1H, HCH=CH, J= 10.4

Hz, $J' = 2.02$ Hz), 2.09 (m, 2H, CH₂), 1.42 (m, 2H, CH₂), 1.31 (m, 10H, CH₂), 0.93 (m, 3H, CH₃). ¹³C NMR (CDCl₃) δ 139.3, 114.1, 33.9, 31.9, 29.5, 29.3, 29.2, 29.0, 22.7, 14.1. ¹H and ¹³C NMR spectra are provided in Figure 6S as an example of the purity of the alkene product obtained in these reactions without any further purification.

Fig. 6S ¹H NMR and ¹³C NMR (CDCl₃) of the distillate product obtained from the reaction of 1,2-decanediol **6** and formic acid (**2**) after separation of the aqueous phase.

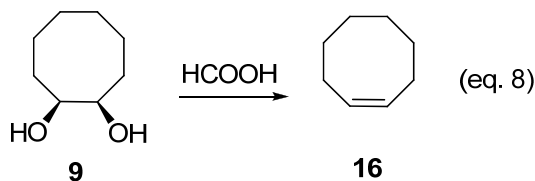


Deoxygenation of *cis*-1,2-cyclohexanediol (**8**)



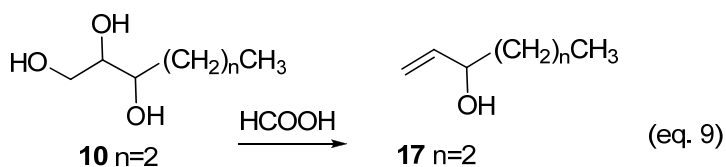
Cis-1,2-cyclohexanediol (20 mmol) (2.31 g) was deoxygenated with formic acid following the general method to give 1.28 g of cyclohexene (**15**) (Yield 78%). **15**: ¹H NMR (CDCl₃) δ 5.63 (m, 2H, HC=CH), 1.99 (m, 4H, CH₂), 1.62 (m, 4H, CH₂). ¹³C NMR (CDCl₃) δ 127.3, 25.1, 22.6.

Deoxygenation of *cis*-1,2-cyclooctanediol (**9**)



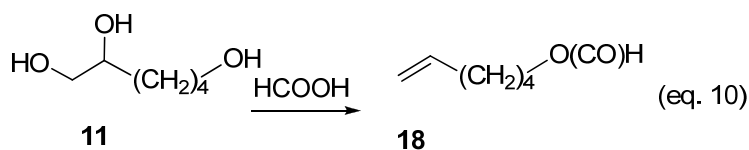
Cis-1,2-cyclooctanediol (25 mmol) (3.6 g) was deoxygenated with formic acid following the general method to give 2.64 g of cyclooctene (**16**) (Yield 96%). **16**: ^1H NMR (CDCl_3) δ 5.67 (m, 2H, $\text{HC}=\text{CH}$), 2.19 (m, 4H, CH_2), 1.54 (m, 8H, CH_2). ^{13}C NMR (CDCl_3) δ 130.2, 29.2, 26.2, 25.5.

Deoxygenation of 1,2,3-hexanetriol (**10**)



1,2,3-hexanetriol (15 mmol) (2.01 g) was deoxygenated with formic acid following the general method and subsequent distillation, to give 0.84 g of hex-1-en-3-ol (**17**) (Yield 56%). **17**: ^1H NMR (CDCl_3) δ 5.80 (m, 1H, $\text{HC}=\text{CH}_2$), 5.19 (d, 1H, $\text{CH}_2=\text{CH}$, $J=17.4$ Hz), 5.05 (d, 1H, $\text{CH}_2=\text{CH}$, $J=10.7$ Hz), 4.08 (m, 1H, HCOH), 2.06 (m, 1H, CHOH), 1.50-1.26 (m, 4H, CH_2), 0.90 (t, 3H, CH_3). ^{13}C NMR (CDCl_3) δ 141.0, 114.6, 73.0, 39.1, 18.4, 13.8.

Deoxygenation of 1,2,6-hexanetriol (**11**)



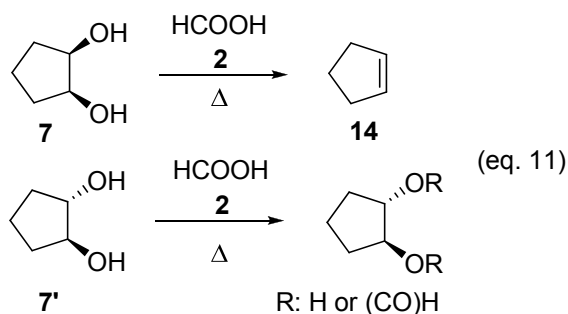
1,2,6-hexanetriol (50 mmol) (6.71 g) was deoxygenated with formic acid following the general method to give 5.36 g of hex-5-enyl formate (**18**) (Yield 84%). **18**: ^1H NMR (CDCl_3) δ 8.10 (s, 1H, $\text{O}(\text{C}=\text{O})\text{H}$), 5.84 (m, 1H, $\text{CH}=\text{CH}_2$), 5.05 (dd, 1H, $\text{HCH}=\text{CH}$, $J=17.2$ Hz, $J'=1.8$ Hz), 5.01 (d, 1H, $\text{HCH}=\text{CH}$, $J=10.1$ Hz), 4.21 (t, 2H, $\text{CH}_2\text{O}(\text{C}=\text{O})\text{H}$, $J=6.6$ Hz), 2.12 (m, 2H, $\text{CH}_2\text{C}=\text{C}$), 1.72 (m, 2H, CH_2), 1.51 (m, 2H, CH_2). ^{13}C NMR (CDCl_3) δ 161.2, 138.2, 114.6, 63.8, 33.2, 27.9, 25.0.

Stereochemistry of the formic acid-mediated deoxygenation reaction

Deoxygenation of *cis*-1,2-cyclopentanediol (**7**)

Cis-1,2-cyclopentanediol (**7**) reacted cleanly with formic acid to yield cyclopentene (**14**), while *trans*-1,2-cyclopentanediol (**7'**) did not form the olefin (eq. 11). The same behavior was observed with *cis* and *trans* 1,2-cyclohexanediol.

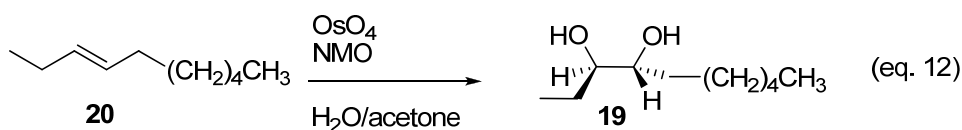
Cis-1,2-cyclopentanediol (20 mmol) (2.05 g) was deoxygenated with formic acid following the general method described above to give 1.17 g of cyclopentene (**14**) (Yield 86%). **14**: ^1H NMR (CDCl_3) δ 5.75 (m, 2H, $\text{HC}=\text{CH}$), 2.32 (m, 4H, CH_2), 1.83 (m, 2H, CH_2). ^{13}C NMR (CDCl_3) δ 130.6, 32.4, 22.7.



Reaction of *trans*-1,2-cyclopentanediol (**7'**)

Under equal conditions, the *trans* isomer **7'**, commercially available, only gave a mixture of the mono and diesters of formic acid and no olefin product was detected by NMR analysis.

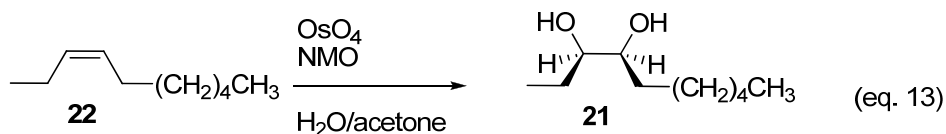
Synthesis of (3*R**, 4*R**)-decane-3,4-diol (**19**)



A mixture of commercially available *trans*-3-decene **20** (2.8 g, 20 mmol), 4-methylmorpholine N-oxide hydrate (NMO) (60% wt in H_2O) (6.8 mL, 40 mmol), OsO_4 (100 mg, 0.4 mmol) in a H_2O solution (1 mL) and acetone (8 mL) were mixed at room temperature and stirred for 24 hours ^[2]. The reaction was quenched with a saturated aqueous solution of Na_2SO_3 , and the resulting mixture was extracted three times with ethyl acetate. The combined organic phases were washed with saturated Na_2SO_3 and brine, dried over MgSO_4 , filtered and concentrated under reduced pressure to give the

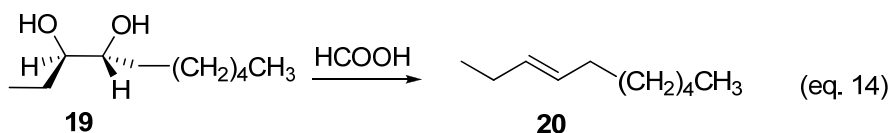
crude diol, which was purified by silica gel flash column chromatography (hexanes/ethyl acetate 10:1) to give 2.79 g (80% yield) of the pure diol **19**: ^1H NMR (CDCl_3) δ 3.42 (m, 1H, *H*COH), 3.33 (m, 1H, *H*COH), 2.27 (bs, 2H, OH), 1.64-1.22 (m, 12H, CH_2), 0.98 (t, 3H, CH_3 , $J = 7.5$ Hz), 0.88 (m, 3H, CH_3). ^{13}C NMR (CDCl_3) δ 75.8, 74.1, 33.6, 31.8, 29.3, 26.4, 25.6, 22.6, 14.0, 10.0.

Synthesis of (3*S**, 4*R**)-decane-3,4-diol (**21**)



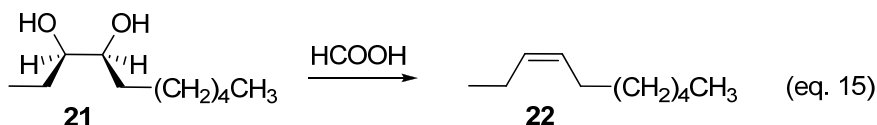
The procedure described above for the preparation of **19** was followed to prepare **21**, starting from the commercially available *cis*-3-decene **22** (2.8 g, 20 mmol). The crude diol was purified by silica gel flash column chromatography (hexanes/ethyl acetate 10:1) and subsequent precipitation in pentane to afford the pure diol **21** (1.91 g) (55% yield). **21**: mp 92°C. ^1H NMR (CDCl_3) δ 3.59 (m, 1H, *H*COH), 3.49 (m, 1H, *H*COH), 2.76 (d, 1H, OH), 2.74 (d, 1H, OH), 1.53-1.21 (m, 12H, CH_2), 0.97 (t, 3H, CH_3 , $J = 7.6$ Hz), 0.87 (m, 3H, CH_3). ^{13}C NMR (CDCl_3) δ 76.2, 74.5, 31.1, 29.3, 26.0, 24.0, 22.6, 14.0, 10.5.

Deoxygenation of (3*R**, 4*R**)-decane-3,4-diol (**19**)



The general method for the formic acid-mediated deoxygenation of 1,2-diols, described above, was followed [1.74 g (10 mmol) of the diol **19** yielded 1.16 g (83% yield) of *trans*-3-decene **20**]. The diastereomeric purity of **20** was determined to be >99% by ^{13}C NMR. By NMR analysis of the crude distillate no signals due to the alkene with the opposite stereochemistry were detected. By spiking a sample of crude distillate with 2% of *cis*-3-decene the distinguishing signals at 131.4, 27.1, 20.4 and 14.4 ppm were perfectly detectable by ^{13}C NMR. We therefore conservatively estimate that $\geq 1\%$ of this minor isomer would have been detectable in the original distillate. **20**: ^1H NMR (CDCl_3) δ 5.42 (m, 2H, $\text{HC}=\text{CH}$), 1.99 (m, 4H, $\text{CH}_2\text{C}=\text{C}$), 1.30 (m, 8H, CH_2), 0.97 (t, 3H, CH_3 , $J = 7.4$ Hz), 0.89 (m, 3H, CH_3). ^{13}C NMR (CDCl_3) δ 131.8, 129.4, 32.6, 31.7, 29.6, 28.8, 25.6, 22.6, 14.0, 13.9.

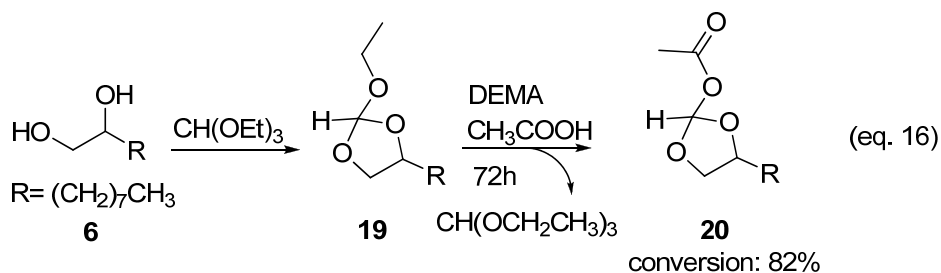
Deoxygenation of (3*S**, 4*R**)-decane-3,4-diol (**21**)



The general method for the formic acid-mediated deoxygenation of diols, described above, was followed [1.41 g (8.1 mmol) of the diol **21** yielded 0.83 g (74% yield) of *cis*-3-decene **22**]. The diastereomeric purity of **21** was determined to be >99% by ^{13}C NMR. By NMR analysis of the crude distillate no signals due to the alkene with the opposite stereochemistry were detected. By spiking the sample crude distillate with 2% of *trans*-3-decene the distinguishing signals at 131.8, 32.6, 25.6 ppm were perfectly detectable by ^{13}C NMR. We therefore conservatively estimate that $\geq 1\%$ of this minor isomer would have been detectable in the original distillate. **22**: ^1H NMR (CDCl_3) δ 5.36 (m, 2H, $\text{HC}=\text{CH}$), 2.06 (m, 4H, $\text{CH}_2\text{C}=\text{C}$), 1.33 (m, 8H, CH_2), 0.98 (t, 3H, CH_3 , $J = 7.6$ Hz), 0.91 (m, 3H, CH_3). ^{13}C NMR (CDCl_3) δ 131.4, 129.2, 31.8, 29.7, 29.0, 27.1, 22.6, 20.4, 14.4, 14.0.

Synthesis and thermal transformation of 2-acetoxy-1,3-dioxolane

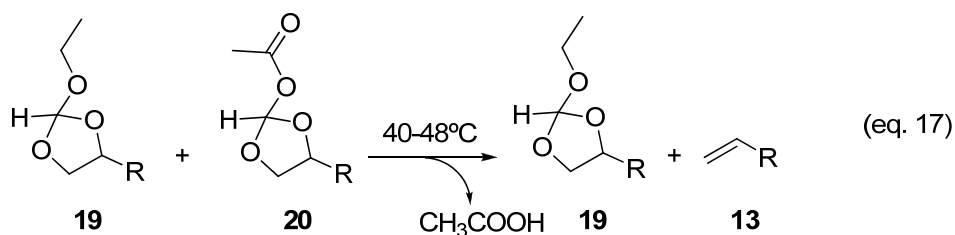
In order to demonstrate the thermal transformation of the cyclic orthoesters of type **d** in the proposed mechanism to generate a double bond (Figure 3A in the manuscript), the synthesis of a 2-acyloxy-1,3-dioxolane from a 2-alkyloxy-1,3-dioxolane was considered. 1,2-decanediol (**6**) was used as a model system for this study.



The 2-ethoxy-1,3-dioxolane derivative **19** of 1,2-decanediol (**6**) was simply prepared by combining equimolar quantities of the diol **6** (1.46 g, 10 mmol) and triethyl orthoformate (1.66 mL, 10 mmol), heating the mixture to 100 °C and removing ethanol from the mixture by distillation (eq. 16). The ^1H NMR spectrum showed two singlet peaks at 5.83

ppm and 5.81 ppm that were assigned to the proton in position 3, as the product consisted of a mixture of *cis* and *trans* dioxolane.

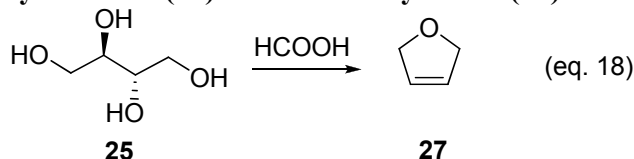
The 2-acetoxy-1,3-dioxolane **20** was prepared at room temperature from the 2-ethoxy-1,3-dioxolane **19** (0.40 g, 2 mmol) in the presence of 15 equivalents of diethoxymethyl acetate (DEMA) (5 g, 30 mmol) and a catalytic quantity of acetic acid (2 drops) ^[3]. The ¹H NMR spectrum showed two singlets at 6.87 and 6.85 ppm that were assigned to the two orthoformyl protons, revealing the product as a mixture of *cis* and *trans* dioxolane products. After 27 h at room temperature a conversion of 82% was observed by ¹H NMR.



Acetic acid, triethyl orthoformate and the remaining diethoxymethyl acetate were then removed under vacuum (<1 mmHg) at a temperature below 30 °C. When the remaining mixture of dioxolanes **19** and **20** was carefully heated, the 2-acetoxy-1,3-dioxolane **20** completely transformed into the olefin **13** at 40-48 °C, while compound **19** was unaffected as monitored by NMR analysis.

Deoxygenation of erythritol

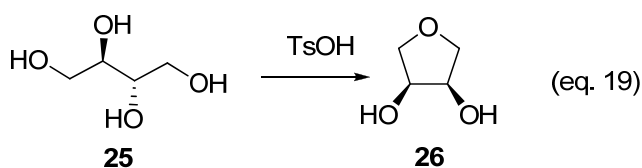
Synthesis of 2,5-dihydrofuran (**27**) from *meso*-erythritol (**25**)



In a 500 mL three neck round-bottomed flask, *meso*-erythritol (**25**) (36.6 g, 300 mmol) was placed along with 99% formic acid (**2**) (7.54 mL, 240 mmol). The flask was fitted with a distillation apparatus, thermometer for internal temperature monitoring and a nitrogen inlet to bubble nitrogen gas through the solution. The collecting flask was cooled using a cold bath (-78 °C). The mixture was slowly heated to 240 °C over an hour. After that, the mixture was heated and stirred for 12 h at an internal temperature of 210 °C and a distillate was collected in the cold flask. The mixture was then cooled to room

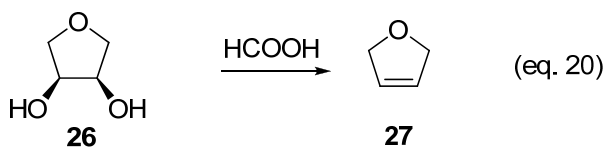
temperature and another portion of formic acid (6.8 mL, 180 mmol) was added. The solution was heated again to 210 °C for 9 hours with concomitant distillation of product and formic acid. The mixture was allowed to cool to room temperature and a final portion of formic acid (180 mmol) was added. The mixture was then slowly reheated to 210 °C for 9 hours. The distillate was then redistilled affording 39.8 g (117 mmol) of pure 2,5-dihydrofuran (**27**) in 39.3% yield. **27**: bp 65-67 °C. ¹H NMR (CD₃CN) δ 4.59 (d, 4H, J=1Hz), 5.91 (s, 2H). ¹³C NMR (CD₃CN) δ 74.8, 125.7.

Synthesis of *cis*-1,4-anhydroerythritol (26**) from *meso*-erythritol (**25**)**^[4]



meso-Erythritol (**25**) (122 g, 1.00 mol) and *para*-toluenesulfonic acid mono-hydrate (9.51 g, 50.0 mmol) were mixed in a round-bottomed flask with a stir bar. The reaction flask was fitted to a distillation apparatus: fractioning column, reflux condenser and collecting flask. The system was heated to 175 °C under reduced pressure (0.5 torr) for 4 hours. After that time, the collecting flask contained 91.5 g (880 mmol) of 1,4-anhydroerythritol (**26**) (88% yield). **26**: bp 110-112 °C at 0.5 torr. ¹H NMR: (CD₃CN) δ 3.54 (m, 2H), 3.62 (broad s, 2H), 3.81 (m, 2H), 4.13 (m, 2H); ¹³C NMR (CD₃CN) δ 69.1, 71.9.

Deoxygenation of *cis*-1,4-anhydroerythritol (26**) to 2,5-dihydrofuran (**27**)**



The general method described above for the formic acid-mediated deoxygenation of 1,2-diols was followed. 1.56 g (15 mmol) of *cis*-1,4-anhydroerythritol (**26**) yielded 0.914 g of 2,5-dihydrofuran (**27**) (87%). **27**: bp 65-67 °C. ¹H NMR δ (CD₃CN) 4.59 (d, 4H, J=1 Hz), 5.91 (s, 2H), ¹³C NMR (CD₃CN) δ 74.8, 125.7.

References and notes

- [1] Similar yields were obtained when the reaction of glycerol (20 mmol or 150 mmol) was carried out employing 85% formic acid (aqueous) instead of 99% formic acid.
- [2] Y. Kaburagi, Y. Kishi, *Org. Lett.* **2007**, *9*, 723.
- [3] J. W. Scheeren, Vanderve.Ap, W. Stevens, *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 195.
- [4] K. G. Childers, S. D. Dreher, J. Lee, J. M. Williams, *Org. Process Res. Dev.* **2006**, *10*, 934. The yield was improved by modifying the previously reported procedure: the reaction was carried out under reduced pressure (0.5 Torr) and the pure product was obtained via continuous distillation from the reaction flask.