

# Supporting Information for

## Rhenium-Catalyzed Didehydroxylation of Vicinal Diols to Alkenes Using a Simple Alcohol as a Reducing Agent

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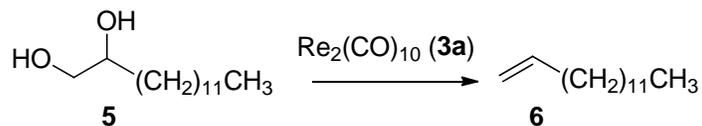
### Table of Contents

1. General information	S-2
2. <b>TABLE S1.</b> Reaction of 1,2-tetradecanediol ( <b>5</b> ) with $\text{Re}_2(\text{CO})_{10}$ ( <b>3a</b> ) in solvent free conditions under air: effect of reaction temperature	S-3
3. <b>TABLE S2</b> Effect of bases as additives in the reaction of diol <b>5</b> with $\text{Re}_2(\text{CO})_{10}$ ( <b>3a</b> ) in the presence of an alcohol ( <b>7a</b> , <b>7b</b> ) as a reductant.	S-4
4. Experimental procedures and associated Figures F1-F7 ( $^1\text{H}$ and $^{13}\text{C}$ NMR, GC-MS)	S-5

## GENERAL INFORMATION:

Unless otherwise specified, all commercial materials were used without further purification. 1,2-tetradecanediol, *cis*-1,2-cyclohexanediol, *trans*-1,2-cyclohexanediol, *meso*-erythritol, *trans*-4-octene, 3-octanol, 1,3,5-trimethoxybenzene and *para*-toluenesulfonic acid were purchased from Aldrich. *Trans*-3-decene was purchased from ChemSampCo. 5-Nonanol was purchased from Alfa Aesar. Dirhenium decacarbonyl and rhenium pentacarbonyl bromide were purchased from Strem Chemicals. Nuclear magnetic resonance (NMR) spectra were recorded with Bruker AVB-400, AVQ-400 and AV-300 spectrometers.  $^1\text{H}$  and  $^{13}\text{C}$  NMR shifts are reported in ppm downfield of tetramethylsilane and referenced to the residual solvent peak. GC-MS analysis was carried out using an Agilent Technologies 6890 network GC system coupled with an Agilent technologies 5973 network mass selective detector.

**TABLE S1.** Reaction of 1,2-tetradecanediol (**5**) with  $\text{Re}_2(\text{CO})_{10}$  (**3a**) in solvent free conditions under air: effect of reaction temperature.<sup>a</sup>



	$\text{Re}_2(\text{CO})_{10}$	Temperature (°C)	Time	Conversion (%)	Olefin 6 Yield (%) <sup>b</sup>
<b>1</b>	2.5 mol%	<b>100</b>	7 h <sup>c</sup>	0	0
<b>2</b>	2.5 mol%	<b>150</b>	5 h <sup>c</sup>	0	0
<b>3</b>	2.5 mol%	<b>150</b>	50 h	>90	0
<b>4</b>	2.5 mol%	<b>130</b>	60 h	>90	0
<b>5</b>	2.5 mol%	<b>170</b>	2.25 h	<b>1/2</b> 1 / 7	n.d. <sup>d</sup>
<b>6</b>	2.5 mol%	<b>170</b>	15.5 h	50	n.d. <sup>d</sup>
<b>7</b>	2.5 mol%	<b>180</b>	3.5 h	100	48-52
<b>8</b>	5 mol%	<b>180</b>	2 h	100	47

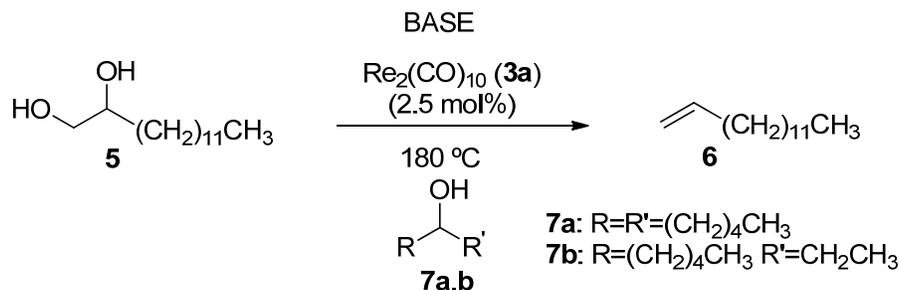
<sup>a</sup> Reactions were performed at a 5 mmol (**5**) scale in a 25 mL round bottom flask connected to a reflux condenser open to air. The mixture was stirred for the indicated time and heated using a silicon oil bath. The temperature in the mixture was monitored by an immersed thermometer.

<sup>b</sup>The yield and conversion was calculated by <sup>1</sup>H NMR spectroscopy using an internal standard (1,3,5-trimethoxybenzene)

<sup>c</sup>After that time, the mixture was heated to 180 °C and the reaction proceeded like entry 7

<sup>d</sup>n.d.= non determined

**TABLE S2.** Effect of bases as additives in the reaction of diol **5** with  $\text{Re}_2(\text{CO})_{10}$  (**3a**) in the presence of an alcohol (**7a**, **7b**) as a reductant.<sup>a</sup>

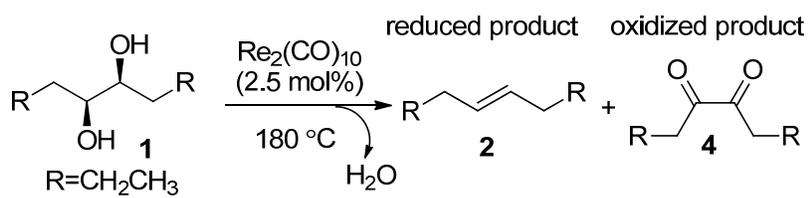


	diol <b>5</b> (mmol)	Reductant (mL)	Base	Temp. (°C)	Time (h)	Conv. <sup>b</sup> (%)	<b>6</b> <sup>b</sup> (%)
<b>1</b>	2.5	<b>7a</b> (3.5)	(Hex) <sub>3</sub> N (1 equiv)	180	10 (stops)	64	44
<b>2</b>	2.5	-- (0)	(Hex) <sub>3</sub> N (1.7 mL, 5 mmol)	180-195	8.5 (stops)	30	25
<b>3</b>	2.5	<b>7b</b> (5)	(Hex) <sub>3</sub> N (0.21 mL, 25 mol%)	170	13	90	55
<b>4</b>	5	<b>7a</b> (3.5)	K <sub>2</sub> CO <sub>3</sub> (1 equiv)	180	6	1	traces
<b>5</b>	2.5	<b>7b</b> (2.5)	<b>2,2,6,6-tetramethylpiperidine</b> (0.05mL, 25mol%)	170	9.5	100	56

<sup>a</sup> Reactions were performed at a 2.5 mmol (**5**) scale in a 25 mL round bottom flask connected to a reflux condenser open to air. The mixture was stirred for the indicated time and heated using a silicon oil bath. The temperature in the mixture was monitored by an immersed thermometer.

<sup>b</sup>The yield and conversion was calculated by <sup>1</sup>H NMR spectroscopy using an internal standard (1,3,5-trimethoxybenzene)

Figure F1:



$^1\text{H}$  NMR spectrum of an aliquot (at 2h at  $180^\circ\text{C}$ ) from the reaction mixture:

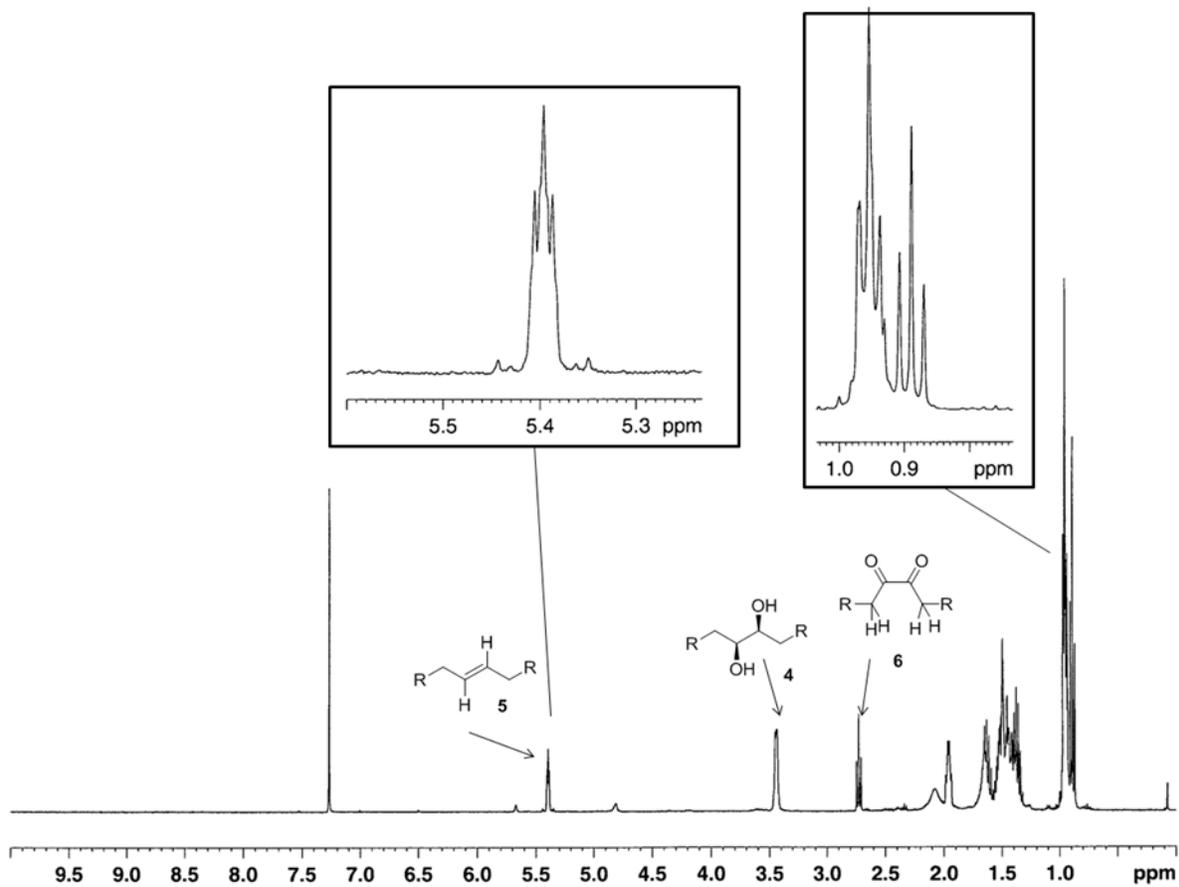
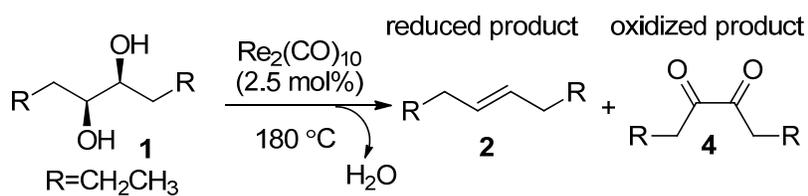


Figure F2



$^{13}\text{C}$  NMR spectrum of a distillate obtained by high vacuum, room temperature distillation from the crude mixture after a 2 h reaction time. Product **4** distilled to the collection flask with the olefin **2**, and the starting material **1** remained in the distillation flask. Further attempts to isolate pure **4** by fractional distillation or chromatography were unsuccessful due to decomposition.

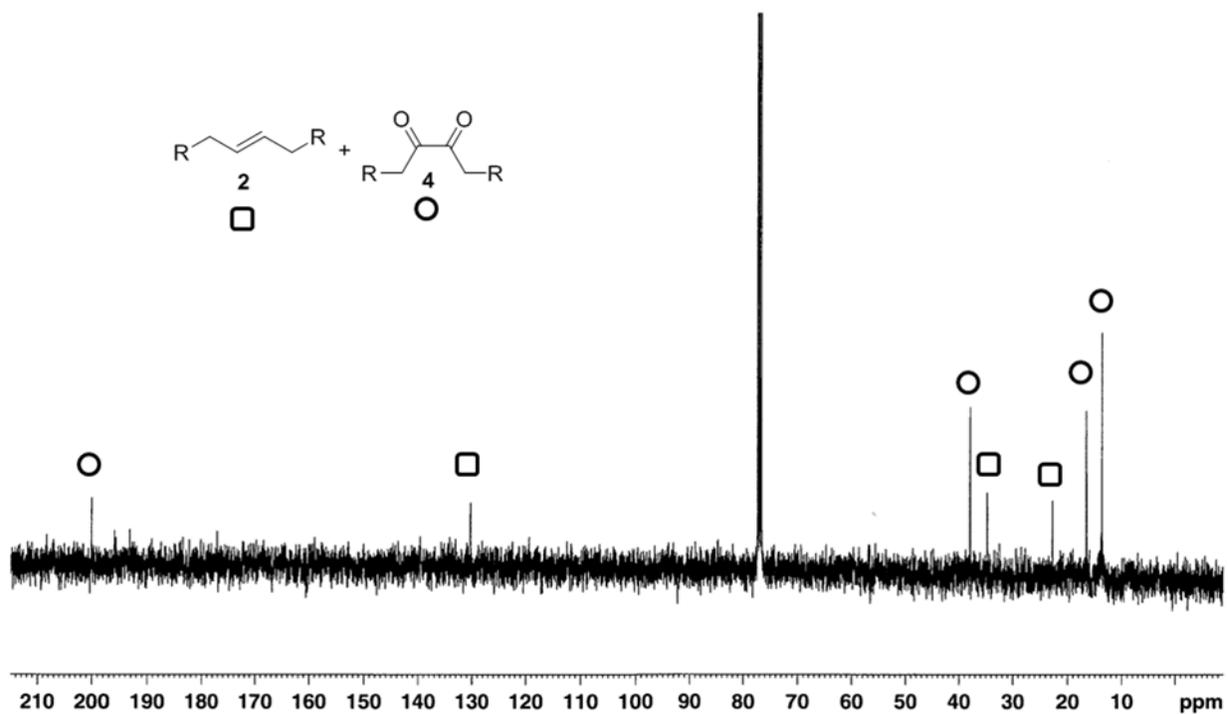
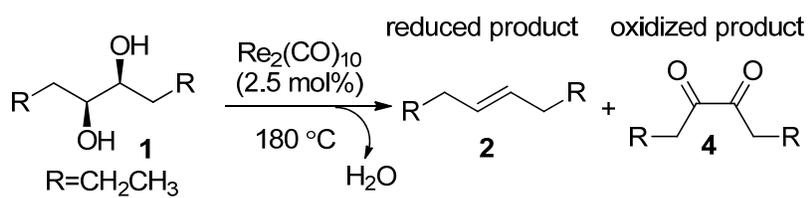
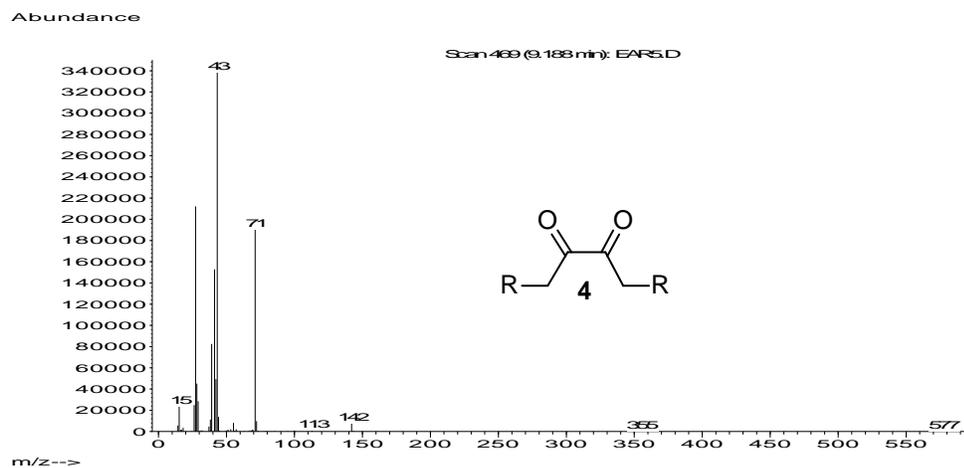
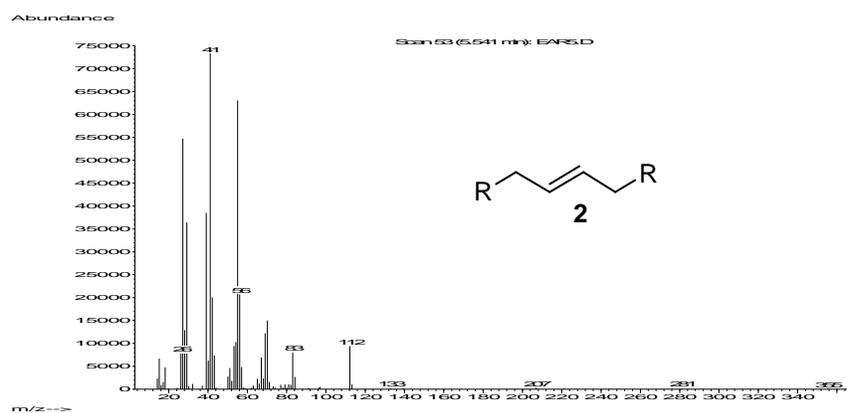
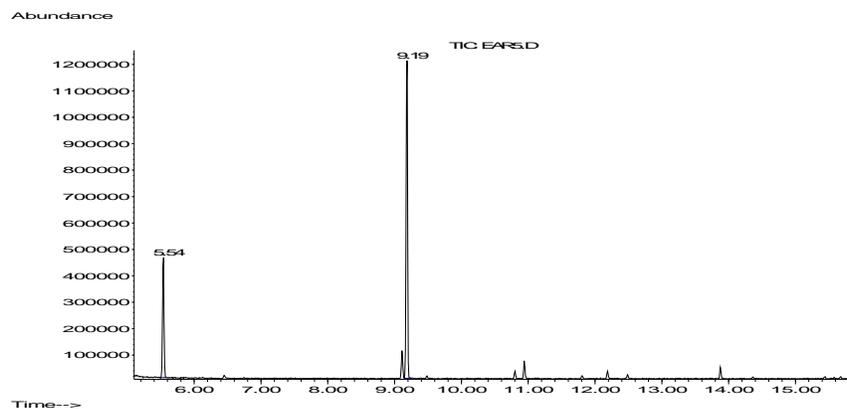


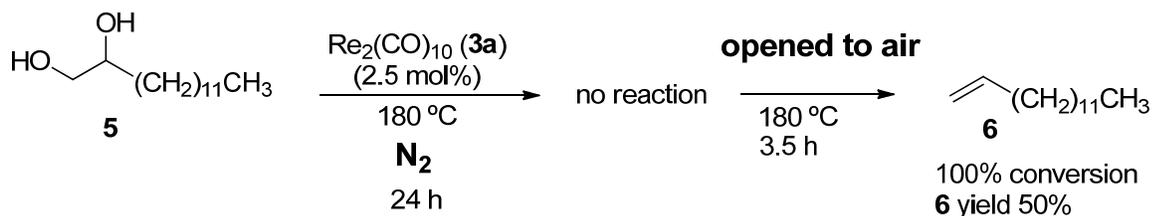
Figure F3:



Aliquot from reaction mixture, GC-MS analysis



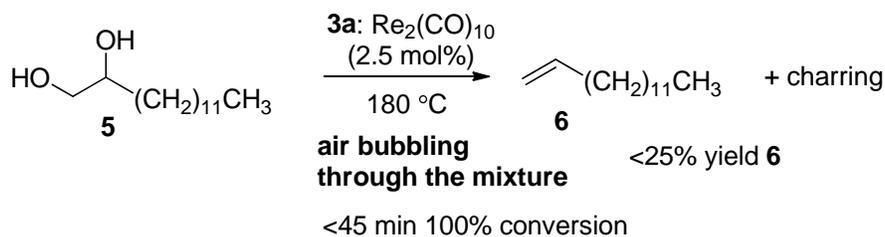
### Reaction performed in a nitrogen atmosphere



The reaction was performed at a 5 mmol (**5**) scale in a 25 mL round bottom flask connected to a reflux condenser under a nitrogen atmosphere. After heating the mixture at 180 °C for 24 h, analysis of an aliquot by NMR spectroscopy showed only starting material. After that, when the same mixture was heated to 180 °C in air, it performed in the same way as entry 7, Table S1.

### Reaction performed at 180 °C with air bubbling

The reaction was performed at a 5 mmol (**5**) scale in a three necked 25 mL round bottom flask connected to a reflux condenser under air. Additionally to contact with atmospheric air, a stream of air was bubbled through the reaction mixture using a perforated tube immersed in the solution. The temperature in the reaction mixture was measured by an immersed thermometer.

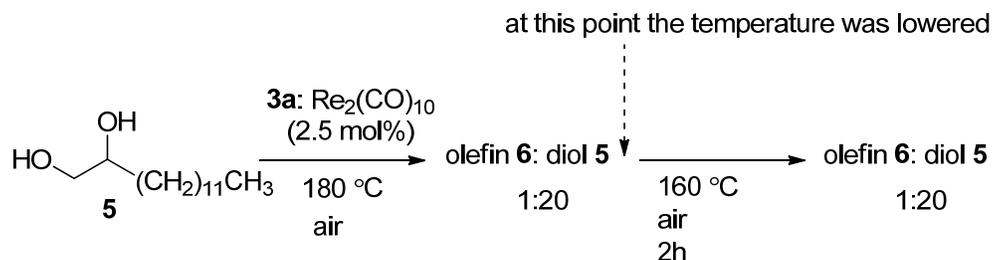


The reaction was performed while applying a stream of air through the reaction mixture while heating the mixture to 180 °C. Very rapid disappearance of the starting material took place and charring was observed, along with a complicated mixture of products with less than 25% yield of olefin **6**. The yield and conversion was calculated by <sup>1</sup>H NMR spectroscopy using an internal standard (1,3,5-trimethoxybenzene).

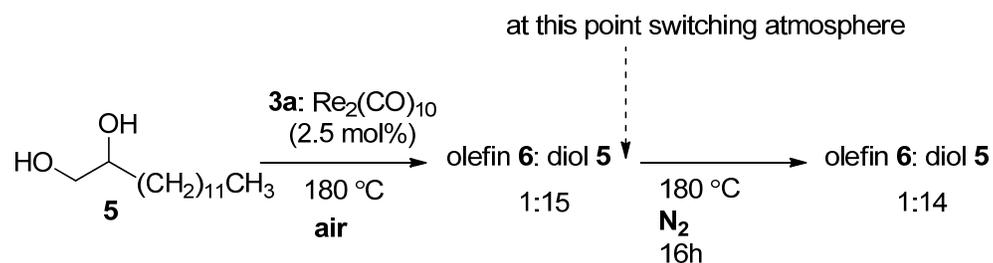
### Attempts to pre-activate the catalyst

A) In an effort to pre-activate the catalyst, the rhenium carbonyl was heated to 180 °C under air in the presence of the diol until transformation of the diol **5** to the olefin **6** commenced. The

temperature was then decreased from 180 °C to a temperature below 170 °C, at which time conversion of diol **5** to olefin **6** ceased.



**B)** In a separate experiment, replacement of the ambient atmospheric by nitrogen after initiation of the reaction (as described above) resulted in no further conversion even at 180 °C.



**C)** In addition, the reaction proceeded identically in the absence of light, and all attempts of photo-initiation by means of irradiation using a mercury lamp were unsuccessful.

### Thermal stability of vicinal diketones

Compounds such as diketones or alpha-keto aldehydes are highly sensitive compounds that would be expected to decompose under the reaction conditions. In fact, when heating the commercially available 1,2-cyclohexanedione and 3,4-hexanedione at or above 100 °C in the presence of  $\text{Re}_2(\text{CO})_{10}$ , complete decomposition was observed within minutes. Indeed, even in the absence of the rhenium complex, these diketones promptly decomposed when heated to 180 °C.

### Experimental procedure for the dirhenium decacarbonyl mediated deoxygenation of diol **5** in solvent free conditions and under air

The diol **5** (1.15g, 5 mmol) and  $\text{Re}_2(\text{CO})_{10}$  **3a** (0.081 g, 0.125 mmol, 2.5 mol%) were first mixed at room temperature in a flask fitted with a reflux condenser open to air. The temperature was monitored by a thermometer immersed in the reaction mixture. The reaction was performed by heating the mixture at 180 °C over a preheated silicone oil bath. Under these conditions, the reaction could be monitored by cooling down the mixture to room temperature and taking an aliquot for its analysis by  $^1\text{H}$  NMR spectroscopy (see spectrum for example aliquot at 2 h in Figure F4). Heating was continued until no more starting diol was observed (3.5 h). See  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the crude mixture in Figures F5 and F6. The yield of olefin **6** (50%) was calculated by adding an internal standard to the reaction mixture (1,3,5-trimethoxybenzene). Olefin **6** was also isolated (49% yield) by column chromatography. **6**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.81 (m, 1H,  $\text{HC}=\text{C}$ ), 5.00 (d, 1H,  $\text{HCH}=\text{CH}$ ,  $J=17.1$  Hz), 4.93 (d, 1H,  $\text{HCH}=\text{CH}$ ,  $J=10.2$  Hz), 2.07 (m, 2H,  $\text{CH}_2$ ), 1.48-1.20 (m, 20H,  $\text{CH}_2$ ), 0.89 (m, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  139.3, 114.0, 33.8, 31.9, 29.6, 29.5, 29.3, 29.1, 29.0, 28.9, 22.7, 14.1.

Figure F4:

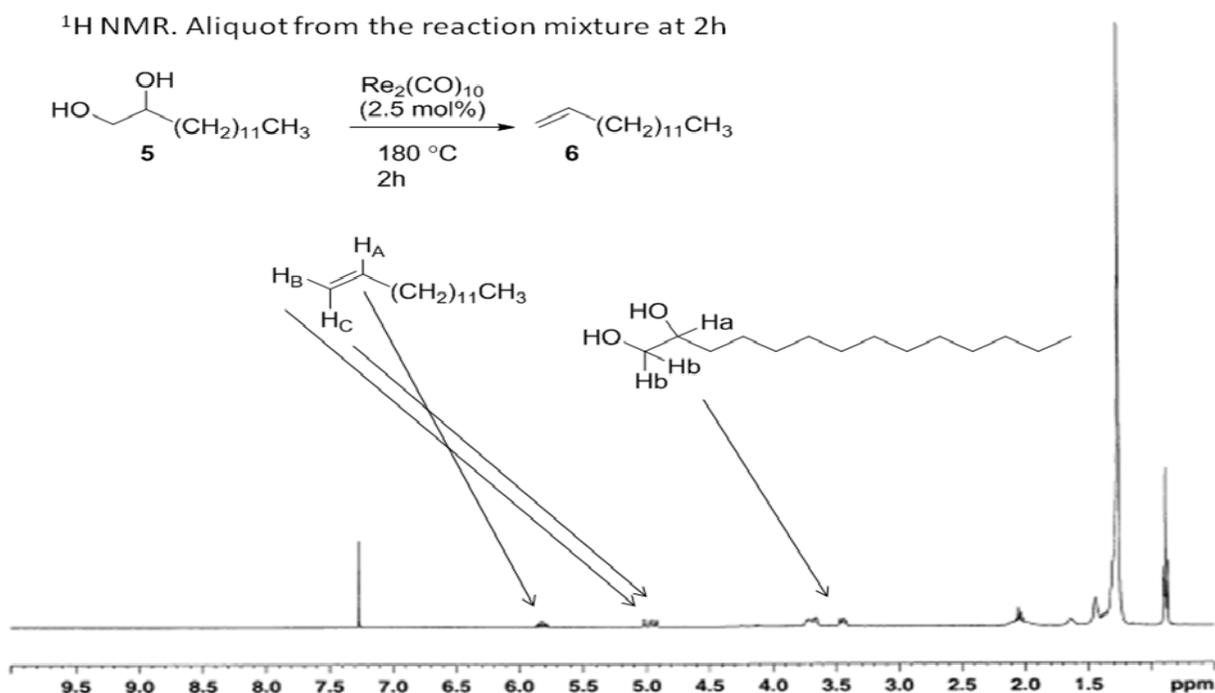


Figure F5:

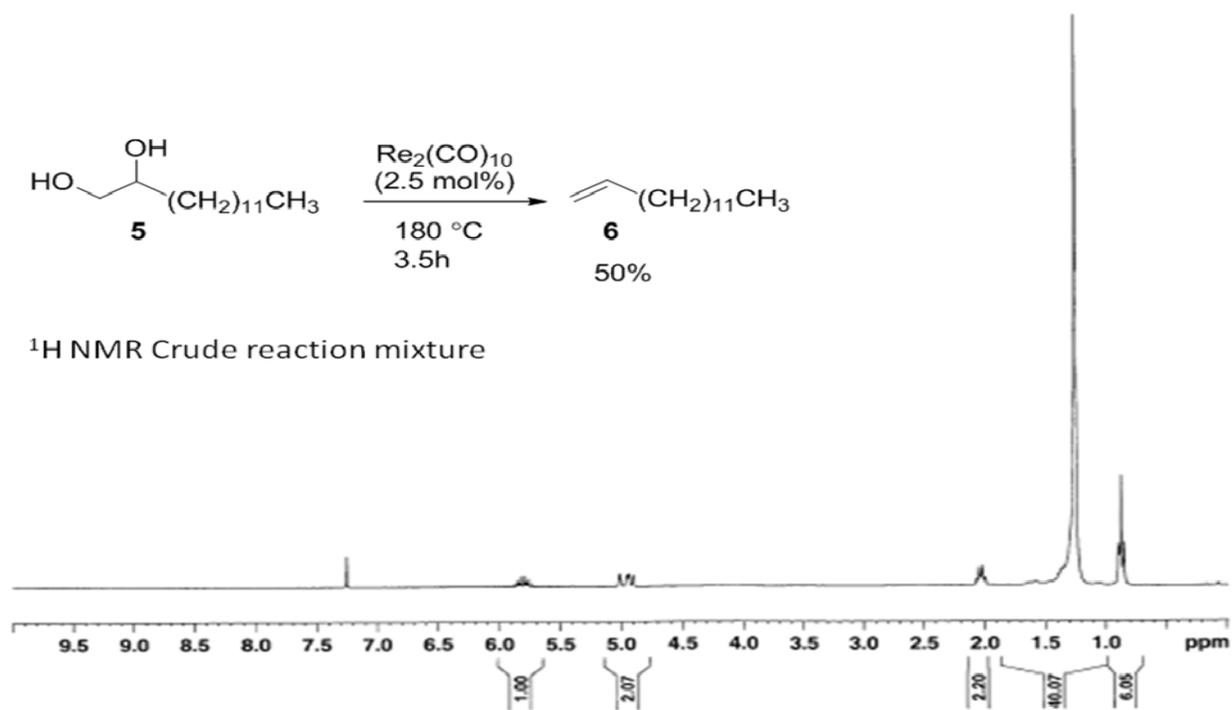
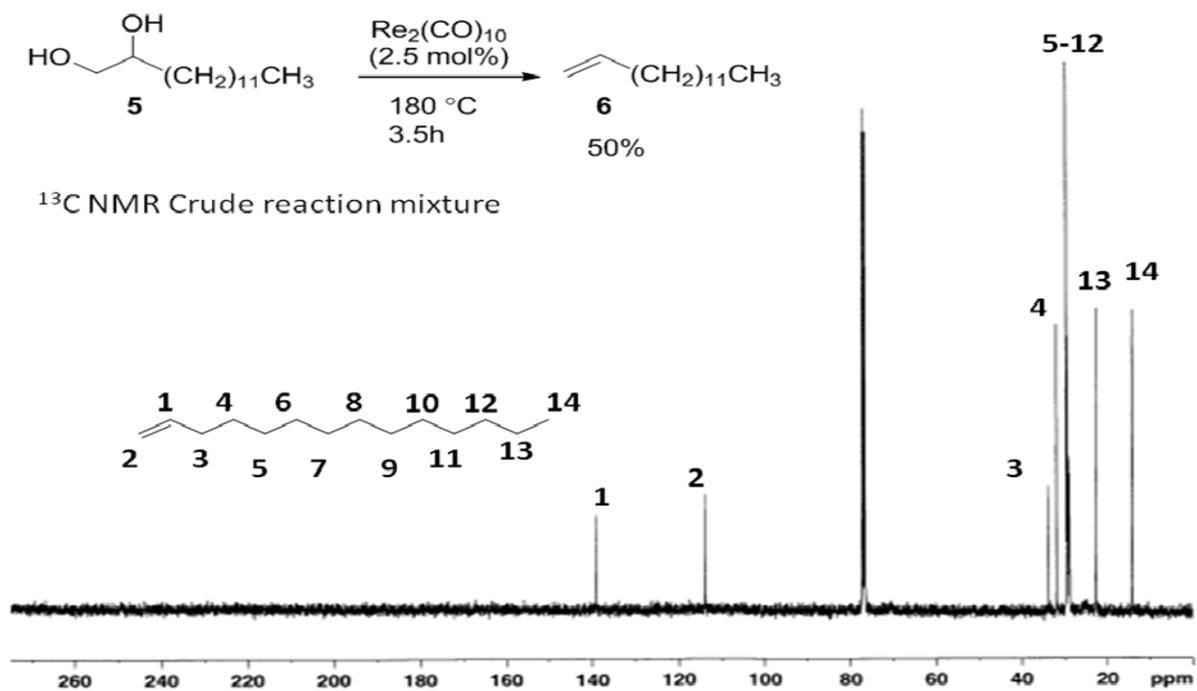
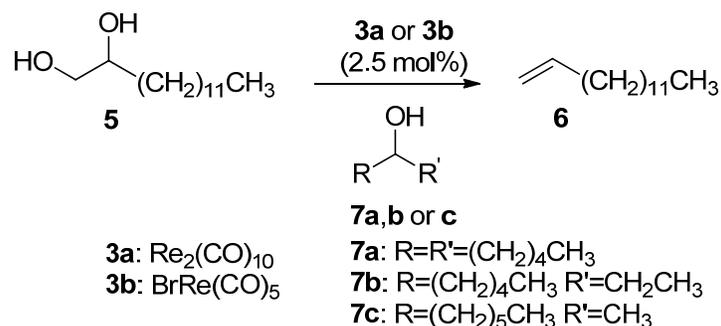


Figure F6:



**General experimental procedure for the rhenium mediated deoxygenation of diol 5 under air using alcohols 7a,b or c as reductants**

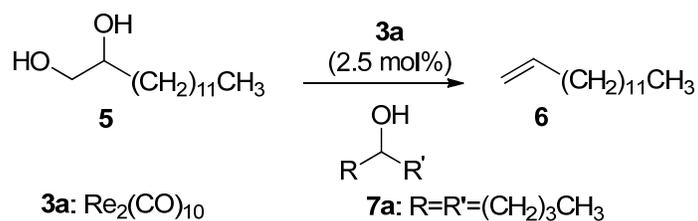


The diol **5**, the alcohol 5-nonanol (**7a**) or 3-octanol (**7b**) and Re<sub>2</sub>(CO)<sub>10</sub> **3a** or Re(CO)<sub>5</sub>Br **3b** (2.5 mol%) were first mixed at room temperature in a flask fitted with a reflux condenser open to air. The temperature was monitored by a thermometer immersed in the reaction mixture. The reaction was performed by heating the mixture at 170-180 °C using a preheated silicone oil bath. Under these conditions, the reaction could be monitored by cooling down the mixture to room temperature and taking an aliquot for its analysis by <sup>1</sup>H NMR spectroscopy. Heating was continued until no more starting diol was observed (reaction time, amount of reductant, temperature and yield are specified in Table 1 in the manuscript). The yield of olefin was calculated by adding an internal standard to the reaction mixture (1,3,5-trimethoxybenzene). All reaction mixtures were also analyzed by GC-MS.

For a representative example, see Figure F7 with the <sup>1</sup>H NMR spectrum of the crude mixture with internal standard added (1,3,5-trimethoxybenzene: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.1 (s, 3H, arom), 3.8 (s, 9H, OCH<sub>3</sub>))

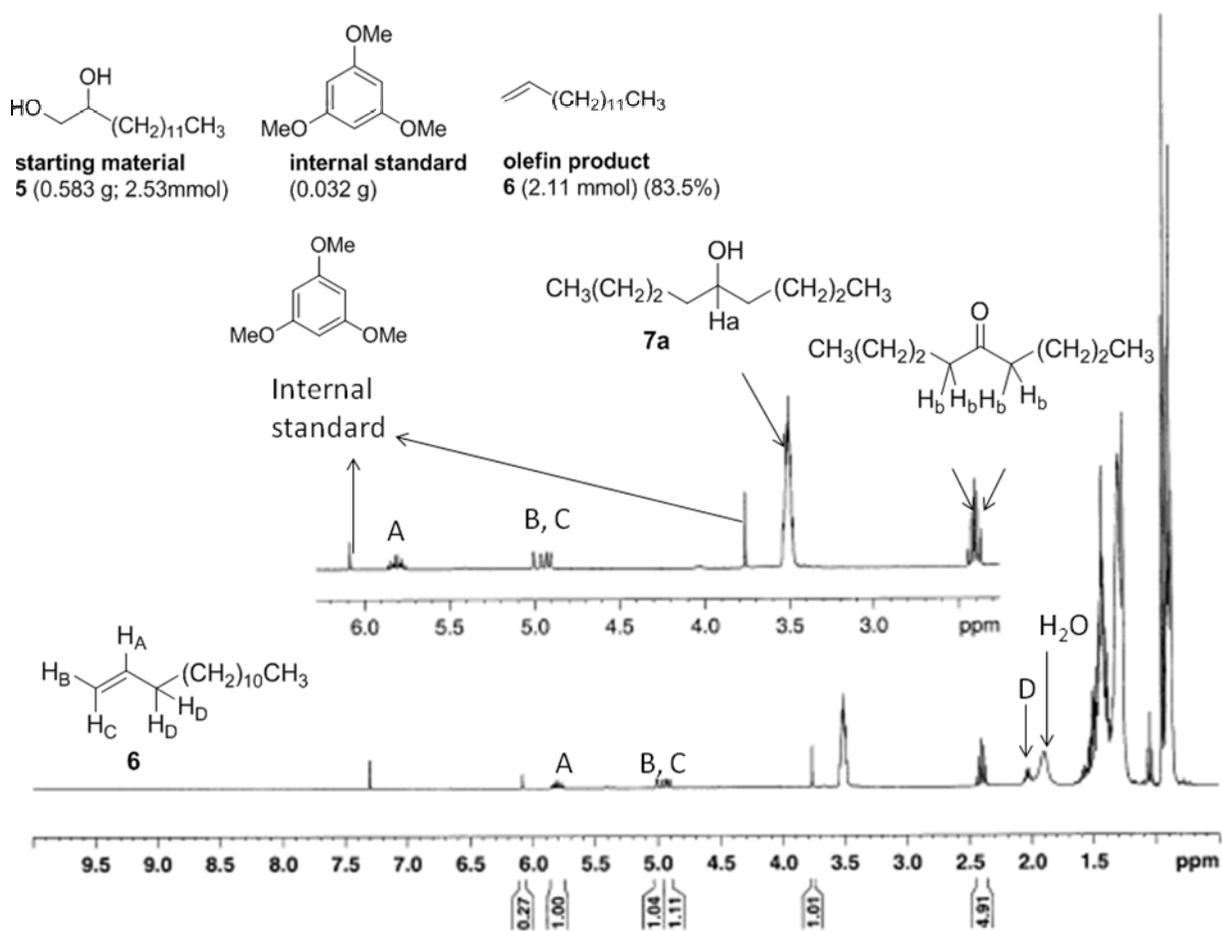
Separation of olefin **6** from the crude reaction mixture was carried out by the following procedure: first the crude reaction mixture was passed through a short plug of silica gel (washed with pentane, 5-10 mL) in order to remove most of the 3-octanol. After removing the pentane under vacuum, the resulting crude was purified by flash column chromatography (silica gel, hexane: ethyl acetate 40:1). Isolated yields of the olefin **6** for representative examples are reported in Table 1 in the manuscript.

Figure F7

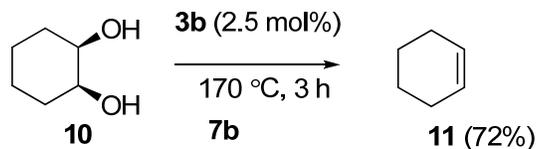


catalyst	reductant (mL)	temperature (°C)	time (h)	yield <b>6</b> (%)
<b>3a</b>	<b>7a</b> (4)	180	3.5	83

$^1\text{H}$  NMR spectrum of the crude reaction mixture (in  $\text{CDCl}_3$ ) from the reaction depicted above, with added internal standard:

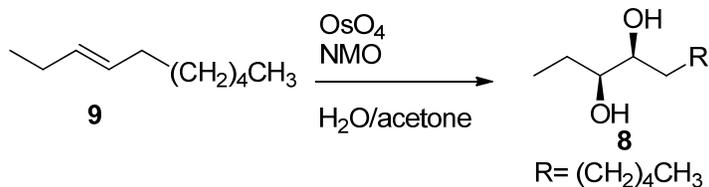


### Experimental procedure for the rhenium mediated deoxygenation of diol **10** under air using alcohol **7b** as reductant



The diol **10** (0.290 g, 2.5 mmol) the alcohol 3-octanol (**7b**) (4 mL, 25.2 mmol, 10 equiv) and  $\text{Re}(\text{CO})_5\text{Br}$  (0.025 g, 0.06 mmol, 2.5 mol%) were first mixed at room temperature in a flask fitted with a reflux condenser open to air. The temperature was monitored by a thermometer immersed in the reaction mixture. The reaction was performed by heating the mixture at 170 °C using a preheated silicone oil bath. Under these conditions, the reaction could be monitored by cooling down the mixture to room temperature and taking an aliquot for its analysis by  $^1\text{H}$  NMR spectroscopy. Heating was continued for 3 h until no more starting diol was observed. The yield of the olefin **11** (72%) was determined by  $^1\text{H}$  NMR spectroscopy of the crude mixture using 1,3,5-trimethoxybenzene as internal standard, by integrating the olefinic protons at 5.63 ppm. GC-MS analysis of the reaction mixture further confirmed the identity of product **11**. The authors believe that the reported yield is the lower limit of the actual value due to potential loss of final product during the course of the reaction because of its high volatility. Cyclohexene (**11**),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.63 (m, 2H,  $\text{HC}=\text{CH}$ ), 1.99 (m, 4H,  $\text{CH}_2$ ), 1.62 (m, 4H,  $\text{CH}_2$ ).

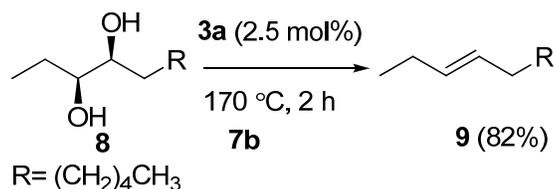
### Synthesis of (3*R*\*, 4*R*\*)-decane-3,4-diol (**8**)



A mixture of commercially available *trans*-3-decene **9** (2.8 g, 20 mmol), 4-methylmorpholine *N*-oxide hydrate (NMO) (60% wt in  $\text{H}_2\text{O}$ ) (6.8 mL, 40 mmol),  $\text{OsO}_4$  (100 mg, 0.4 mmol) in a  $\text{H}_2\text{O}$  solution (1 mL) and acetone (8 mL) were mixed at room temperature and stirred for 24 h. The reaction was quenched with a saturated aqueous solution of  $\text{Na}_2\text{SO}_3$ , and the resulting mixture was extracted three times with ethyl acetate. The combined organic phases were washed with saturated  $\text{Na}_2\text{SO}_3$  and brine, dried over  $\text{MgSO}_4$ , filtered and concentrated under reduced pressure

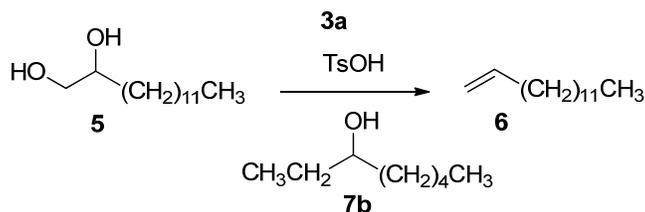
to give the crude diol, which was purified by silica gel flash column chromatography (hexanes/ethyl acetate 10:1) to give 2.79 g (80% yield) of the pure diol **8**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.42 (m, 1H, *H*COH), 3.33 (m, 1H, *H*COH), 2.27 (bs, 2H, OH), 1.64-1.22 (m, 12H,  $\text{CH}_2$ ), 0.98 (t, 3H,  $\text{CH}_3$ ,  $J=7.5$  Hz), 0.88 (m, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  75.8, 74.1, 33.6, 31.8, 29.3, 26.4, 25.6, 22.6, 14.0, 10.0.

**Experimental procedure for the rhenium mediated deoxygenation of diol **8** under air using alcohol **7b** as reductant**



The diol **8** (0.365 g, 2.5 mmol), 3-octanol (**7b**) (4.5 mL, 28.4 mmol, 11.4 equiv) and  $\text{Re}_2(\text{CO})_{10}$  (0.040 g, 0.06 mmol, 2.5 mol%) were first mixed at room temperature in a flask fitted with a reflux condenser open to air. The temperature was monitored by a thermometer immersed in the reaction mixture. The reaction was performed by heating the mixture at 170 °C using a preheated silicone oil bath. Under these conditions, the reaction could be monitored by cooling down the mixture to room temperature and taking an aliquot for its analysis by  $^1\text{H}$  NMR spectroscopy. Heating was continued for 2 h until no more starting diol was observed. The yield of the olefin **9** (80%) was determined by  $^1\text{H}$  NMR spectroscopy of the crude mixture using 1,3,5-trimethoxybenzene as internal standard. GC-MS analysis of the reaction mixture further confirmed the identity of product **9**.

**Experimental procedure for the rhenium mediated deoxygenation of diol 5 under air using an alcohol as reductant with *para*-toluenesulfonic acid as additive**



The diol **5**, 3-octanol (**7b**), Re<sub>2</sub>(CO)<sub>10</sub> **3a** (2.5 mol%) and *para*-toluenesulfonic acid monohydrate (TsOH) (2 to 5 mol%) were first mixed at room temperature in a flask fitted with a reflux condenser open to air. The temperature was monitored by a thermometer immersed in the reaction mixture. The reaction was performed by heating the mixture to 155 °C over a preheated silicone oil bath. The reaction could be monitored by cooling down the mixture to room temperature and taking an aliquot for its analysis by <sup>1</sup>H NMR spectroscopy. Heating was continued until no more starting diol is observed. (Quantities of catalyst and TsOH, reaction time, temperature and yield are specified in Table 2 in the manuscript). The yield of olefin was calculated by adding an internal standard to the reaction mixture (1,3,5-trimethoxybenzene). All reaction mixtures were analyzed by GC-MS.

Separation of olefin **6** from the crude reaction mixture was carried out by the following procedure: first the crude reaction mixture was passed through a short plug of silica gel (washed with pentane, 5-10 mL) in order to remove most of the 3-octanol. After removing the pentane under vacuum, the resulting crude was purified by flash column chromatography (silica gel, hexane: ethyl acetate 40:1). Isolated yields of the olefin **6** for representative examples are reported in Table 2 in the manuscript.

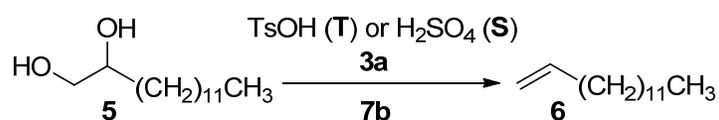
**Experimental procedure for the rhenium mediated deoxygenation of diol 5 under air using an alcohol as reductant with sulfuric acid as additive**

The diol **5**, 3-octanol (**7b**), Re<sub>2</sub>(CO)<sub>10</sub> **3a** (2.5 mol%) and sulfuric acid (2 to 5 mol%, from a solution of H<sub>2</sub>SO<sub>4</sub> in 3-octanol) were first mixed at room temperature in a flask fitted with a reflux condenser open to air. The temperature was monitored by a thermometer immersed in the reaction mixture. The reaction was performed by heating the mixture to 155 °C over a preheated silicone oil bath. The reaction could be monitored by cooling down the mixture to room temperature and taking an aliquot for its analysis by <sup>1</sup>H NMR spectroscopy. Heating was

continued until no more starting diol is observed. (Quantities of catalyst and H<sub>2</sub>SO<sub>4</sub>, reaction time, temperature and yield are specified in Table 2 in the manuscript). The yield of olefin was calculated by adding an internal standard to the reaction mixture (1,3,5-trimethoxybenzene). All reaction mixtures were analyzed by GC-MS.

Separation of olefin **6** from the crude reaction mixture was carried out by the following procedure: first the crude reaction mixture was passed through a short plug of silica gel (washed with pentane, 5-10 mL) in order to remove most of the 3-octanol. After removing the pentane under vacuum, the resulting crude was purified by flash column chromatography (silica gel, hexane: ethyl acetate 40:1). Isolated yields of the olefin **6** for a representative example reported in Table 2 in the manuscript.

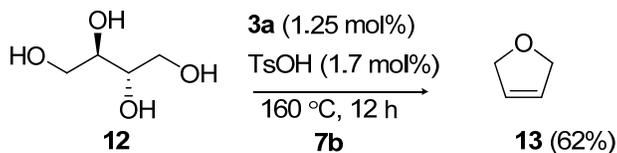
**Control experiments** *para*-toluenesulfonic acid (**T**) and sulfuric acid (**S**) in the absence of Re<sub>2</sub>(CO)<sub>10</sub>



entry <sup>a</sup>	<b>3a</b> (mol%)	<b>7b</b> (mL)	acid (mol%)	temp. (°C)	time (h)	conv <sup>b</sup> . (%)	yield <sup>b</sup> <b>6</b> (%)
1	--	4	<b>T</b> (5)	170	5h	0	0
2	--	5	<b>S</b> (2)	160	4h	1	0

<sup>a</sup>Reactions conducted at 2.5 mmol scale, under air. <sup>b</sup>Determined by <sup>1</sup>H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

**Experimental procedure for the rhenium mediated deoxygenation of *meso*-erythritol under air using an alcohol as reductant with *para*-toluenesulfonic acid as additive**



*Meso*-erythritol (**12**) (1.22 g, 10 mmol), 3-octanol (**7b**) (10 mL, 63 mmol),  $\text{Re}_2(\text{CO})_{10}$  **3a** (0.081 g, 1.25 mol%) and *para*-toluenesulfonic acid monohydrate (TsOH) (0.032 g, 1.7 mol%) were mixed at room temperature in a Parr reactor (125 mL volume). The reactor was sealed and heated at 160 °C for 12 h using a silicone oil bath. After cooling the reactor to room temperature, the yield of 2,5-dihydrofuran (62%, **13**) was determined by  $^1\text{H}$  NMR spectroscopy using an internal standard (1,3,5-trimethoxybenzene). The product 2,5-dihydrofuran was isolated by fractional distillation from the crude reaction mixture at atmospheric pressure (200 mm Vigreux column). The isolated yield of **13**, corrected for ca. 5.5 mol% 3-octanone impurity (NMR), was 0.381 g (55%). **13**:  $^1\text{H}$  NMR  $\delta$  ( $\text{CDCl}_3$ ) 5.80 (s, 2H), 4.55 (s, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  126.2, 75.4. The  $^1\text{H}$   $^{13}\text{C}$  NMR spectra of this product are provided below.

