Reference

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Use of Carbohydrates and Triglycerides for the Production of Fuels and Chemical feedstocks.

Pete Silks, Jin Kyung Kim, Weizong Chen, Ruilian Wu, John C. Gordon, Ryszard Michalczyk.

Los Alamos National Laboratory, Bioscience and Chemistry Divisions, MS 529, Los Alamos, New Mexico, 87545, USA.

LANL Bioenergy Catalysis Programs in Bioscience and Chemistry Divisions

LDRD DR
Biomass to Fuels
new start FY10
Gordon PI, Silks Co-PI

LDRD ER
Lignin Deconstruction
New start FY19
Silks PI, Hanson Co-PI

CRADA
Chemical Feedstocks from Biomass
Silks PI

LDRD ER
Developing a Mild Catalytic Route for the Reduction of N_2 to NH_3
Gordon, PI

EERE
Chemical Feedstocks from Biomass
Silks PI

NABC
Fuels from Biomass via Catalysis
Gordon, Silks PI

LANL-TT
New Biodegradable
Chemical Feedstocks from Biomass
Ruilian Wu

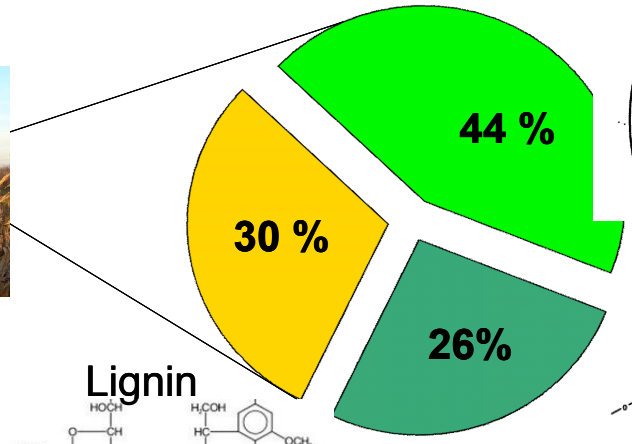
LANL-NAABB
Fuels-Chemical Conversion
Silks, Lodwig, Unkefer

Upgrading of Biorenewables into (High Energy Density) Fuels and Feedstocks

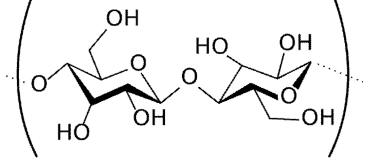
Non-food based sources:
agricultural residues (*e.g.* corn stover), dedicated energy crops, wood residues (paper mill discards), municipal paper waste

~ 200 x 10^9 tons
Lignocellulose/yr

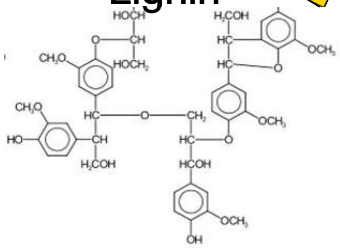
Ligno-cellulosic Biomass



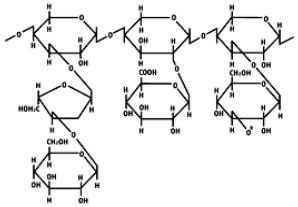
Cellulose



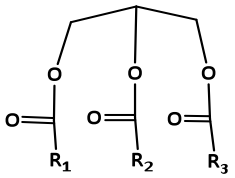
Lignin



Hemicellulose

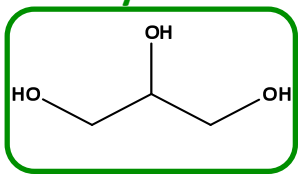


Other (Plentiful) Biomass Derived Molecules..

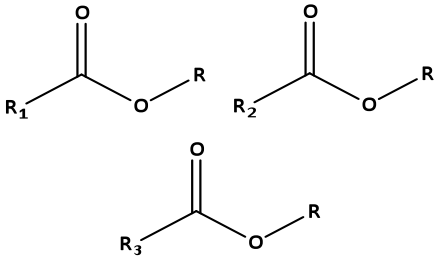


vegetable oils

ROH



Glycerol



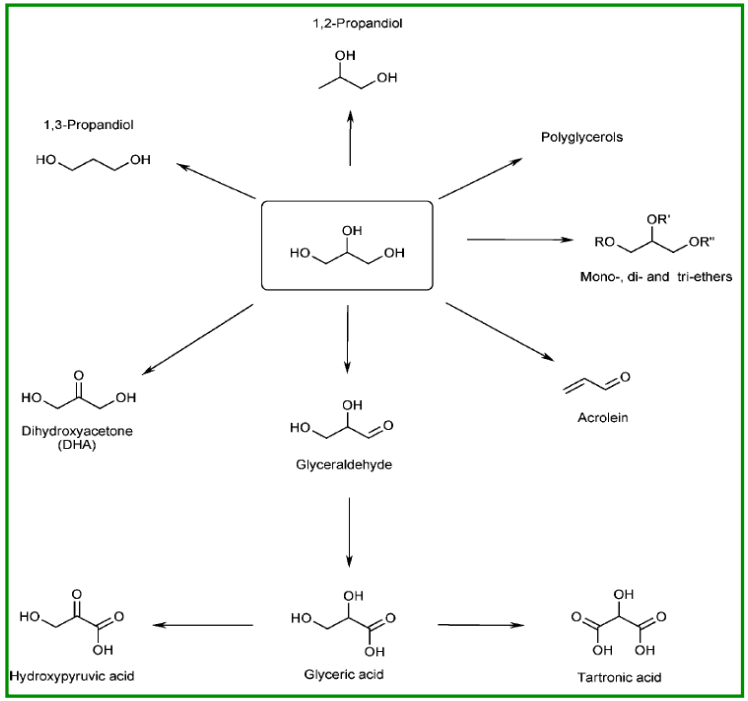
Biodiesel

> 1 million tons/ year!

- Low cost

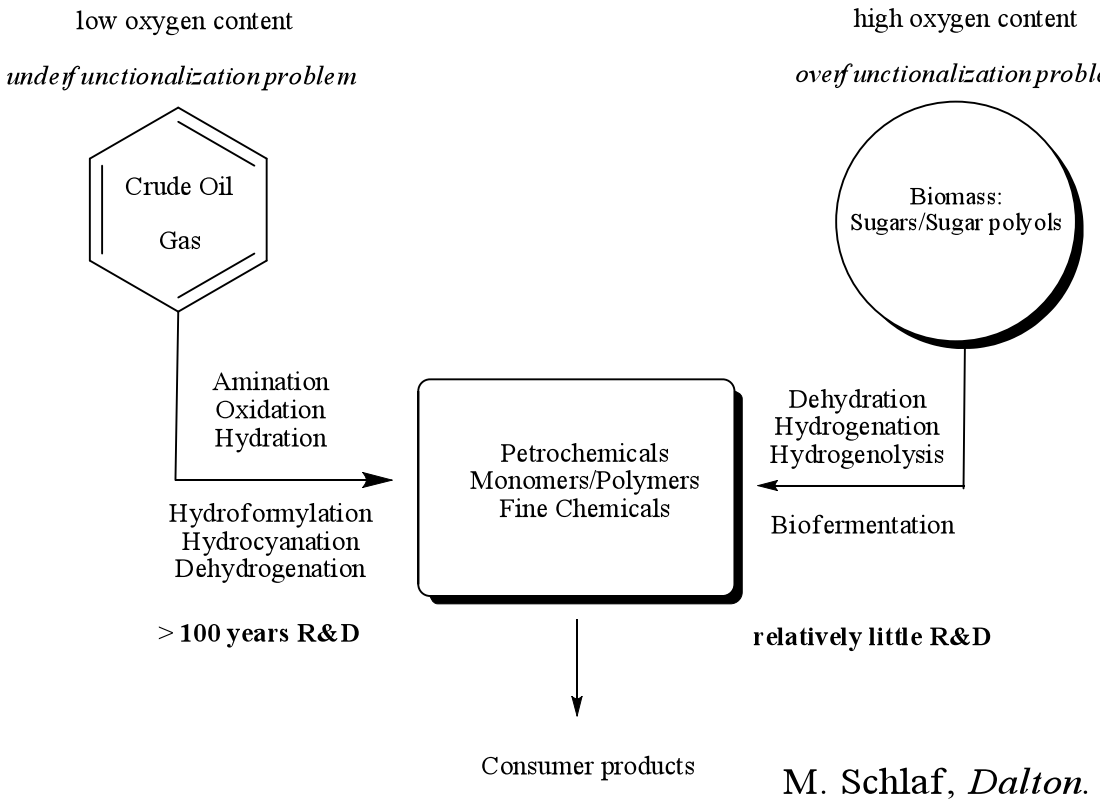
- Feedstock to valuable intermediates

-Low selectivity



Green Chem. **2010**, *12*, 2225

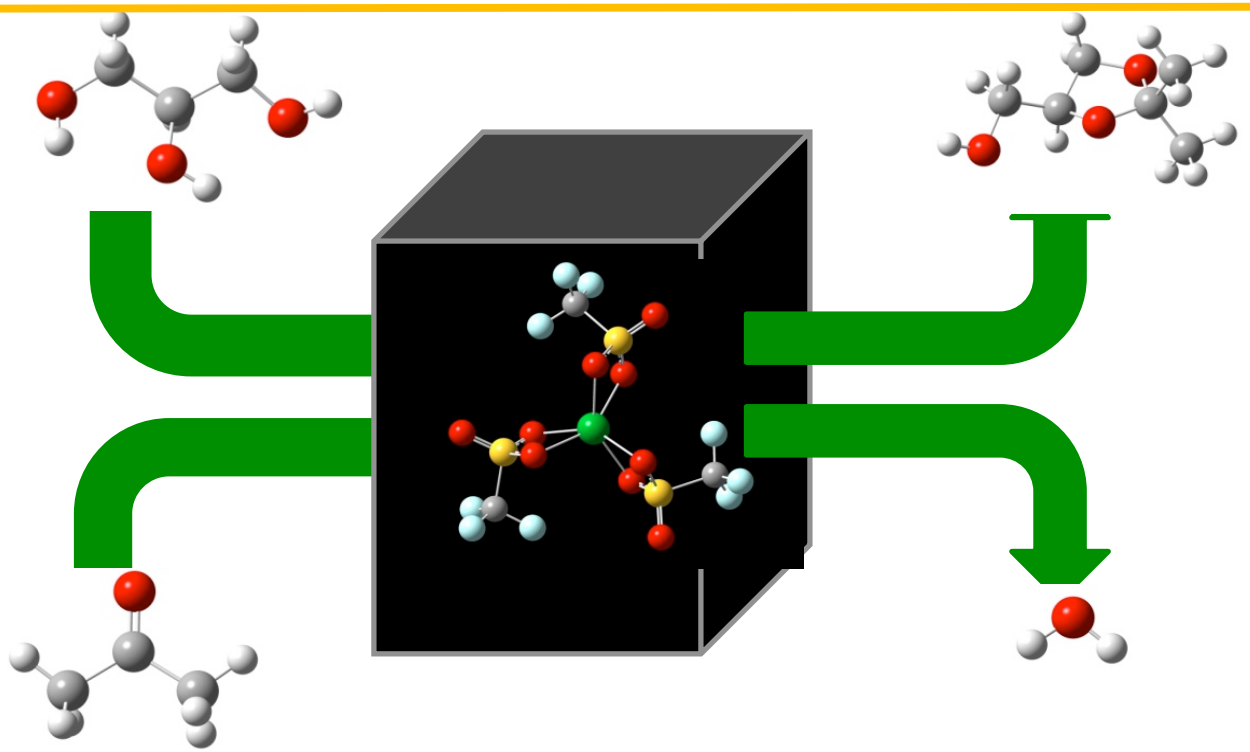
The Problem/Paradigm…



M. Schlaf, *Dalton. Trans.* **2006**, 4645

Development of effective biomass conversion technologies that integrates with existing fuel production and distribution infrastructure: shift away from our dependence on foreign petroleum imports

Overview of the Presentation



BACKGROUND (*as to how we stumbled into acetals…)*

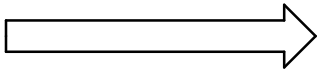
Upgrading of Cellulosics into (High Energy Density) Fuels

Smaller Bioderived Polyols and Lanthanide Catalyzed Dehydrations

Use of Simple Biomass Derived Polyols..?

Also require O-atom removal..

Want to avoid use of Brønsted Acids
(may want stereo - and chemo-selectivity….).

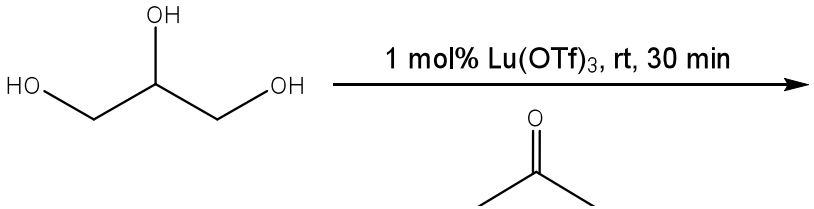


LA catalysis..

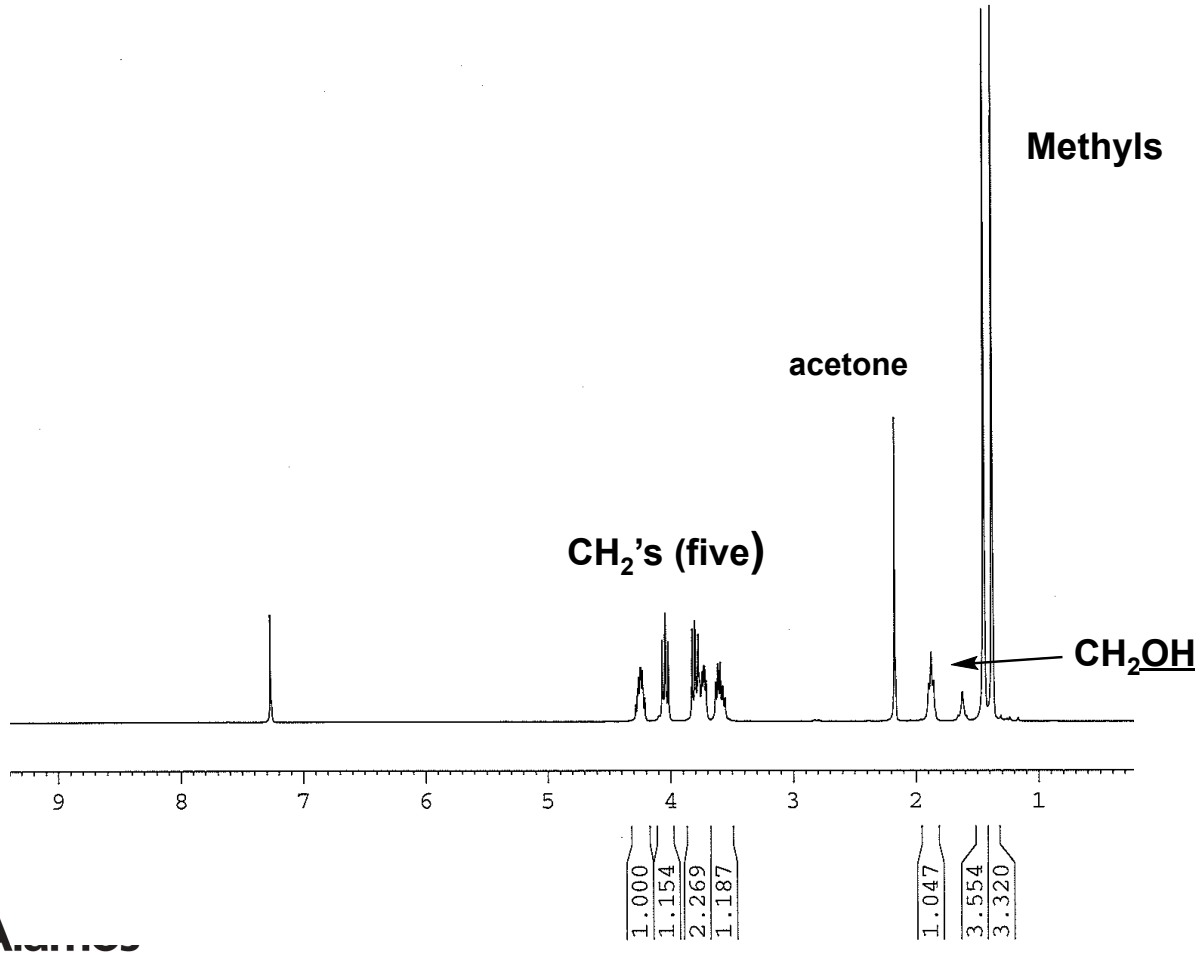
Also for dehydration chemistry, need water tolerant catalysts…….

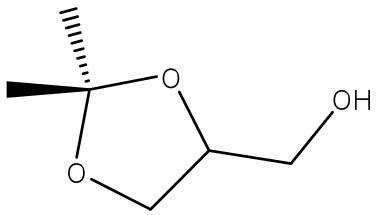
$Lu(OTf)_3$ (strongly Lewis Acidic and f^{14} system)

Glycerol + $Lu(OTf)_3$ (*in acetone……*)



1

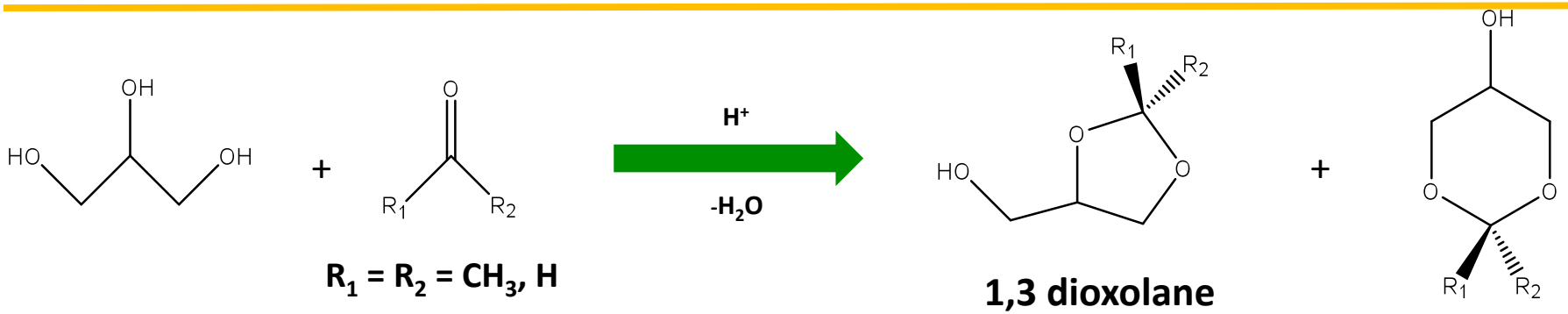




1

5-membered dioxolane

Glycerol Protection - Acetals/Ketals as Fuel Additives..



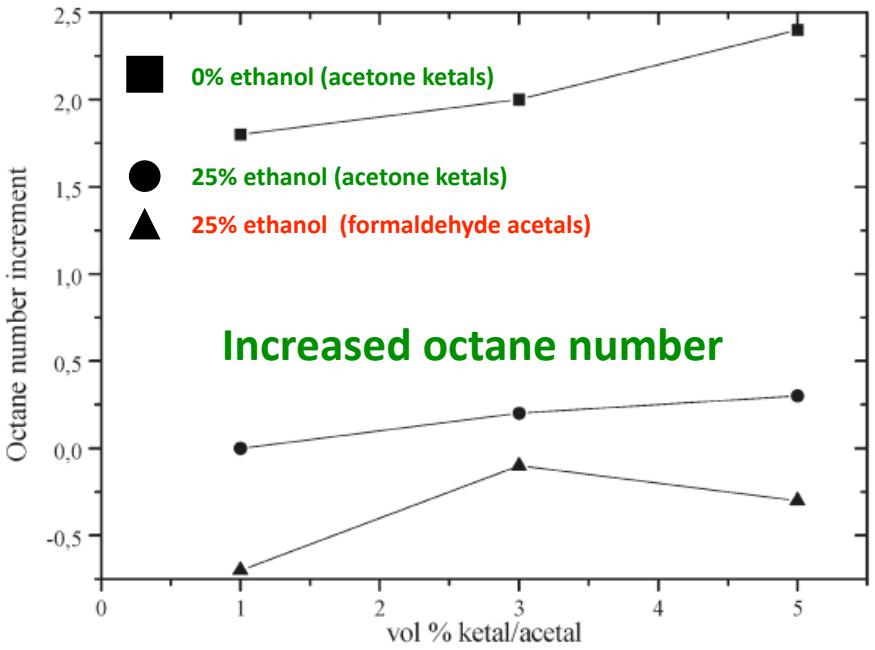
$R_1 = R_2 = CH_3$, H

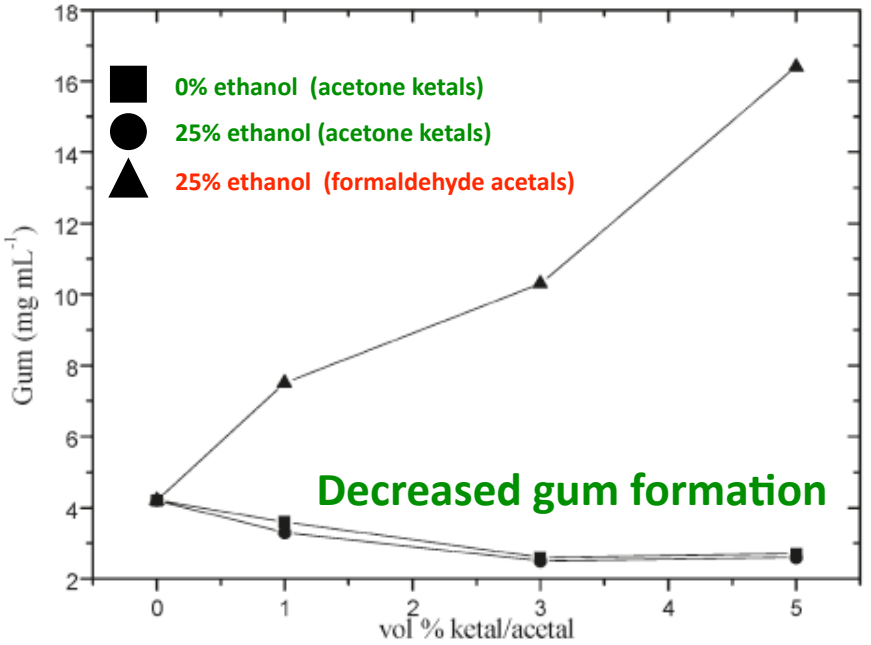
1,3 dioxolane

1,3 dioxane

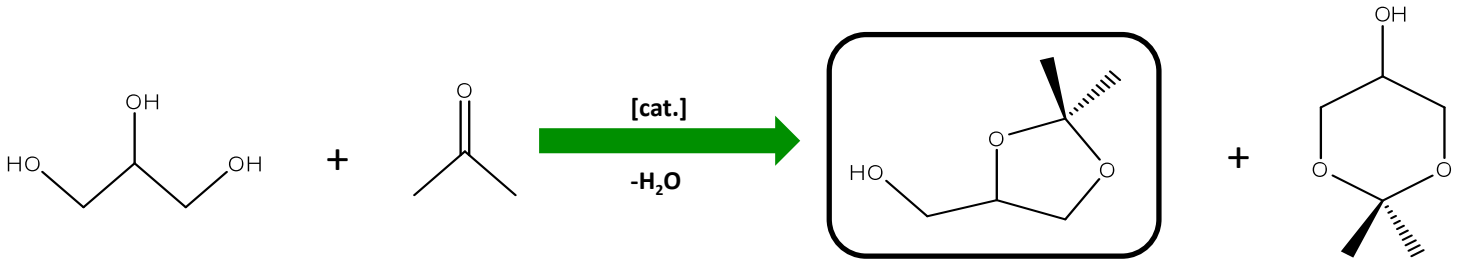
Energy Fuels **2010**, *24*, 2733

Acetals/Ketals as Fuel Additives



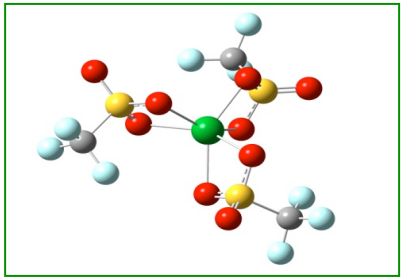


Experimental Comparisons



a b

Catalyst	T (°C)	RT(min.)	%conv	% Selectivity (a)	Ref.
Amberlyst-36	38.1-40.0	480	88	100	i
Amberlyst-15	70	15	95	100	ii
Zeolite beta	35	240	100	100	iii
$[Cp^*IrCl_2]_2$	40	60	86	98	iv
$Lu(OTf)_3$	**R.T.**	**60**	**100**	**100**	**present work**



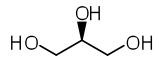
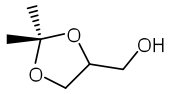
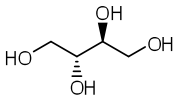
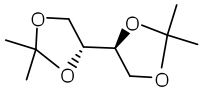
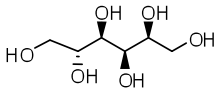
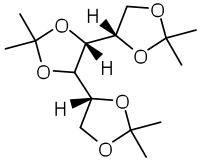
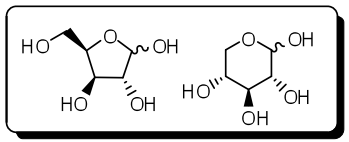
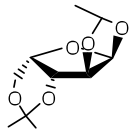
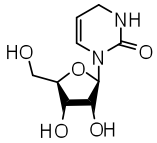
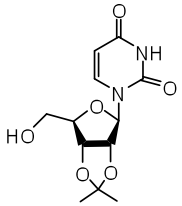
- Selectivity for 5-membered dioxolane *in all cases*

- $Lu(OTf)_3$:100% conversion after 1hr. at R.T., 1 mol% !

- Mechanistic explanations needed

i. *J. Catal.*, **2007**, *245*, 428
ii. *Green Chem.*, **2009**, *11*, 38
iii. *Pet. Chem.*, **2011**, *51*, 61
iv. *Green Chem.*, **2010**, *12*, 2225

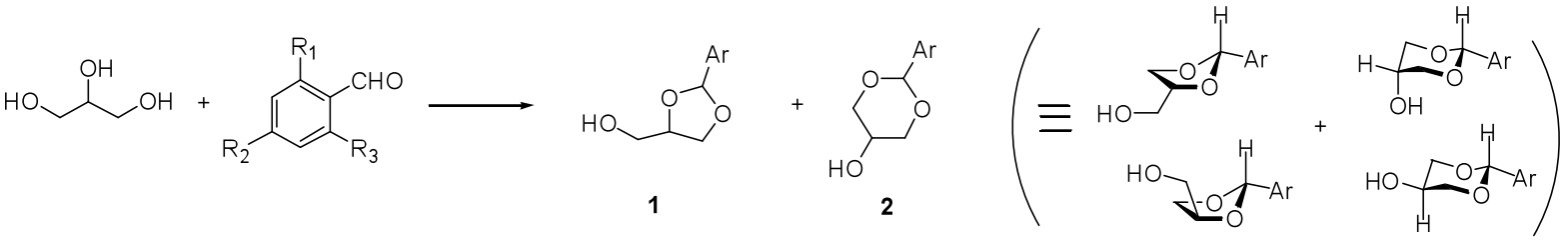
RT Polyol Reactivity with Acetone (Small Selection…)

	Polyol	Product	Reaction time (hr)	NMR conversion (%)	Isolated Yield (%)
Linear	 glycerol		1	99	83
Linear	 erythritol	 X-ray	3	94	88
Linear	 D-sorbitol		5	99	76
Cyclic	 D-xylose		20 *	90	90
Nucleosides	 uridine	 X-ray	48	99	81

Typical conditions: 0.01 mmol $Lu(OTf)_3$; 1 mmol polyol; 10mL acetone: RT

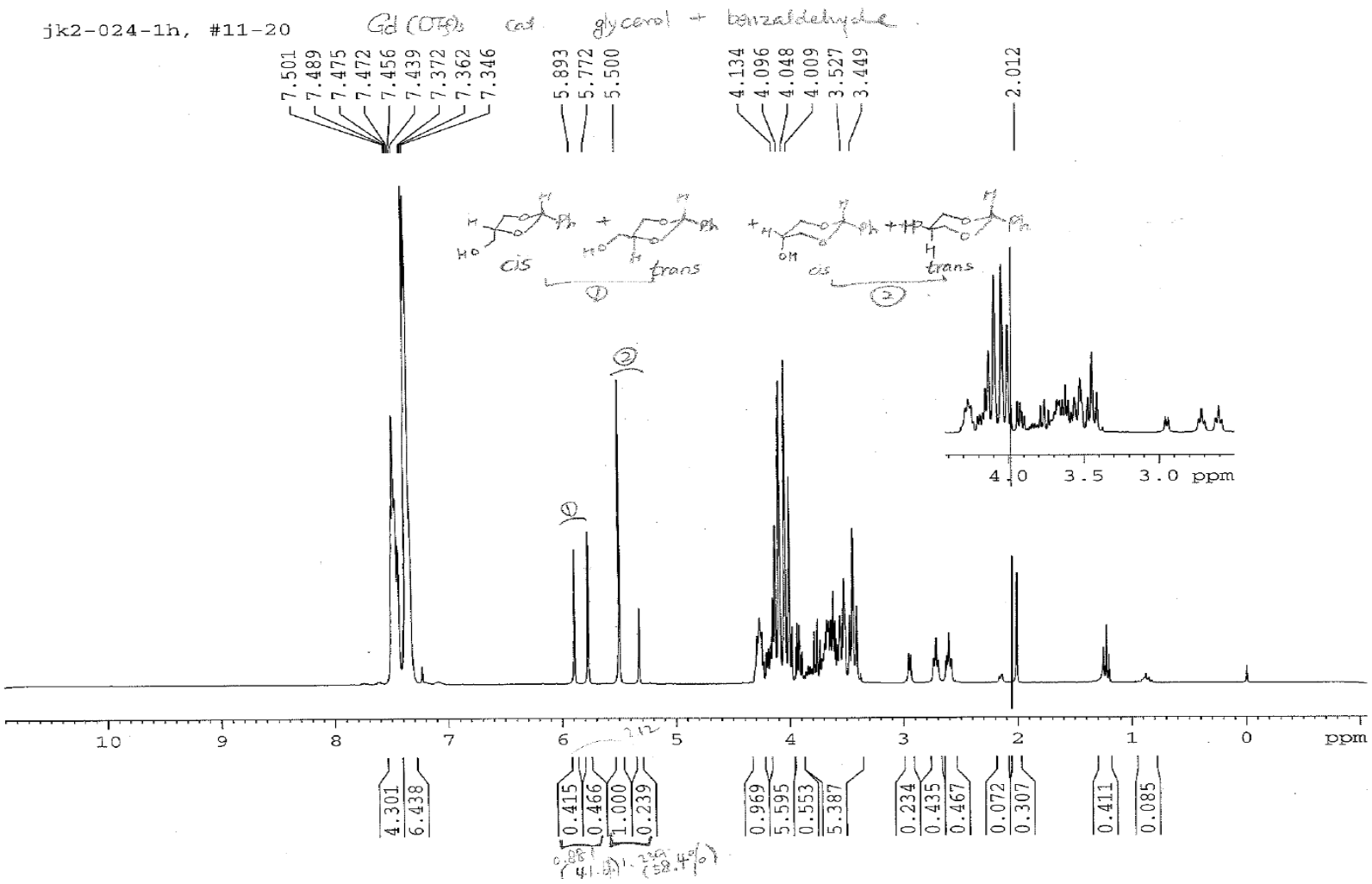
(* = 40°C)

RT Polyol Reactivity Evaluation (Small Selection…)



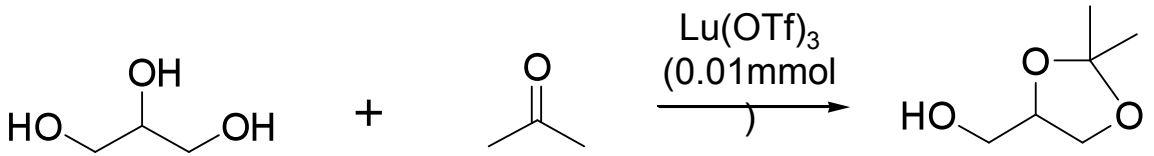
Entry	Aldehyde	Conditions	Glycerol conversion	**1** : **2** (in %)
1	Benzaldehyde (R_1=R_2=R_3=H)	$Lu(OTf)_3$ (0.01), CH_3CN, rt, 24h	74%	40 : 60
2		$Gd(OTf)_3$ (0.01), CH_3CN, rt, 2d	N/A	42 : 58 (27% isolated, combined)
3		$Lu(OTf)_3$ (0.01), CH_3CN, MS, rt, 24h	40%	83 : 17 (1h), 74 : 26 (6h)
4		$Lu(OTf)_3$ (0.01), CH_2Cl_2, reflux (39°C), 6h	75%	48 : 52
5		$Lu(OTf)_3$ (0.01), CH_3CN, reflux (81°C), 6h	70%	42 : 58
6		$Lu(OTf)_3$ (0.01), CH_3CN, MS, reflux (81°C), 6h	~100%	58 : 42 → 48 : 52 after cooling/standing
7	Tolualdehyde (R_1=R_3=H, R_2=CH_3)	$Lu(OTf)_3$ (0.01), CH_3CN, rt, 48h	52%	44 : 56 (36% combined, isolated)
8	Mesitaldehyde (R_1=R_2=R_3=CH_3)	$Lu(OTf)_3$ (0.01), CH_3CN, rt then 80°C, 3d	34%	33 : 67
9	*p*-Anisaldehyde (R_1=R_3=H, R_2=OCH_3)	$Lu(OTf)_3$ (0.01), CH_3CN, rt, 4d	29%	38 : 62
10	*o*-Anisaldehyde (R_1=R_3=H, R_2=OCH_3)	$Lu(OTf)_3$ (0.01), CH_3CN, rt, 4d	80 %	40 : 60
11	4-Fluorobenzaldehyde (R_1=R_3=H, R_2=F)	$Lu(OTf)_3$ (0.01), CH_3CN, rt, 18h	92 %	33 : 67
12	4-Hydroxybenzaldehyde (R_1=R_3=H, R_2=OH)	$Lu(OTf)_3$ (0.01), CH_3CN, rt, 18h	23 %	41 : 59

RT Polyol Reactivity Evaluation (Small Selection…)



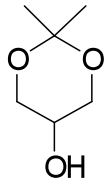
Peak assignment ref : *Journal of Catalysis* **2007**, *245*, 428

Water Sensitity Evaluation (Small Selection…)

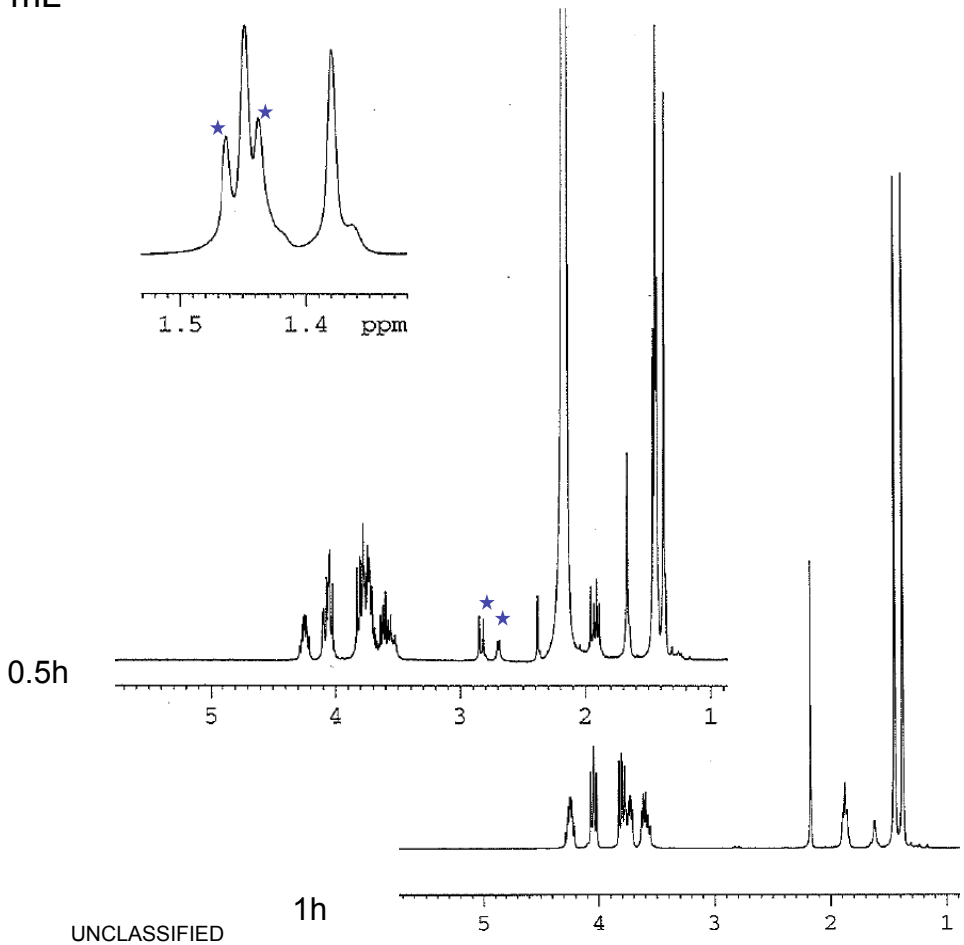


1.0 mmol 10.0 mL

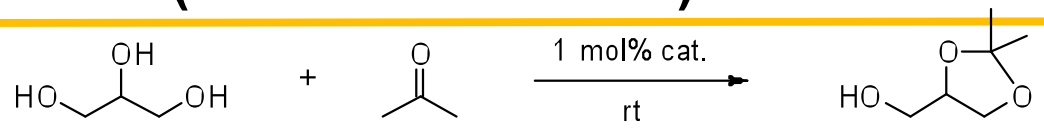
H_2O added /mL	Time to completion / h
0.00	1
0.020	1
0.050	2

★ = 

?

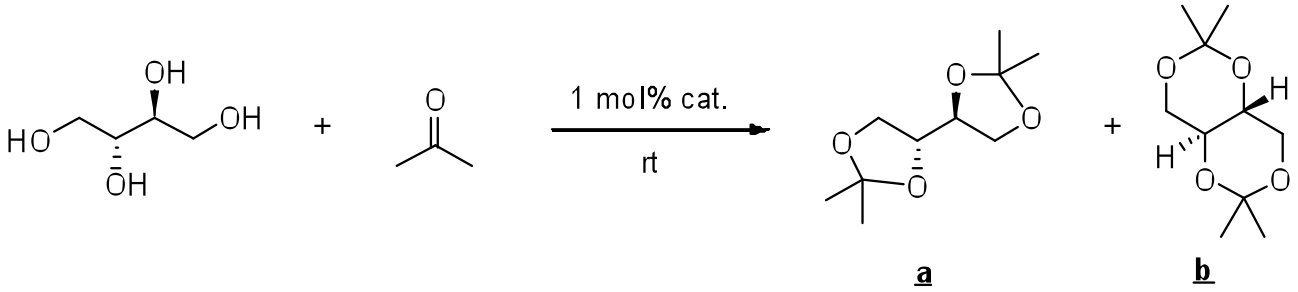


Comparison (Small Selection…)



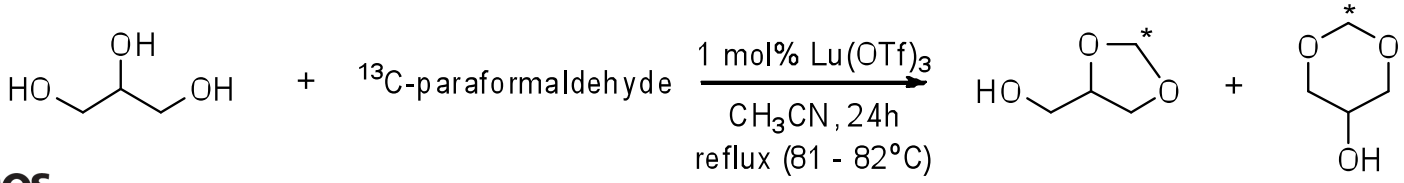
Catalyst	time	% conversion
p-TsOH	0.5 h	> 99 *
$Lu(OTf)_3$	1.0 h	> 99

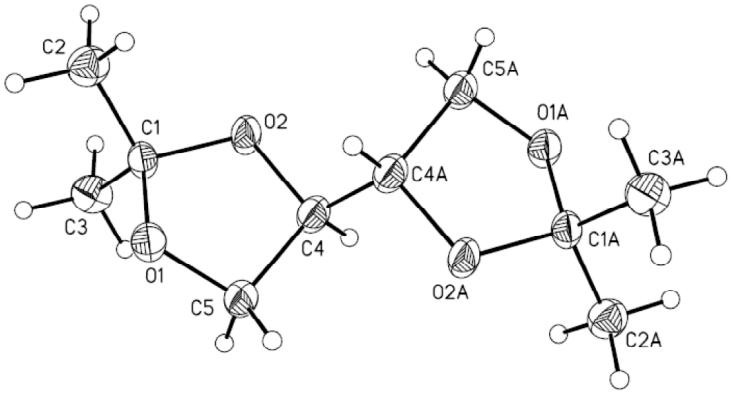
* Reverse reaction competes

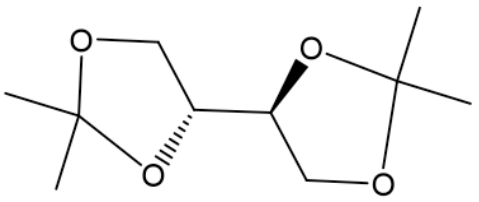


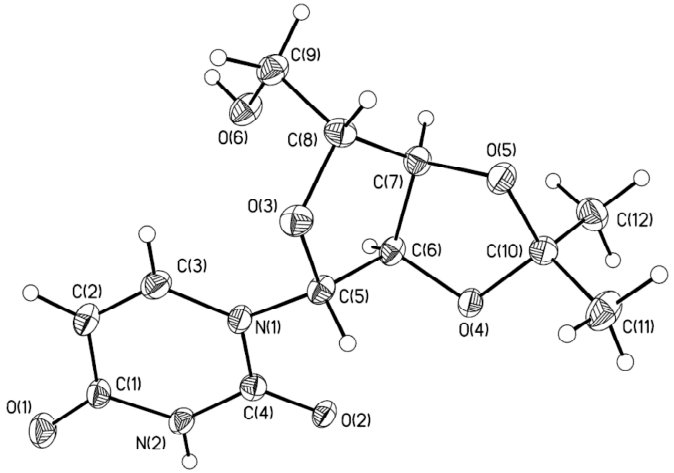
a **b**

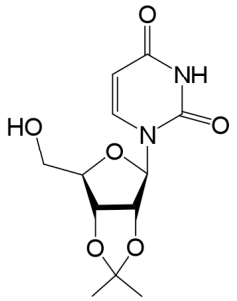
Catalyst	time	**a : b**
p-TsOH	1.5 h	86 : 14
$Lu(OTf)_3$	3.0 h	> 99 : 0

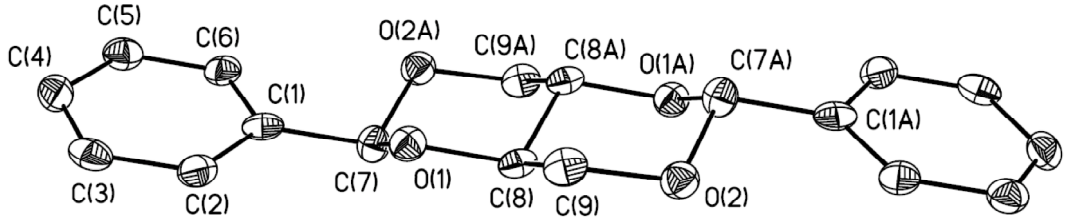


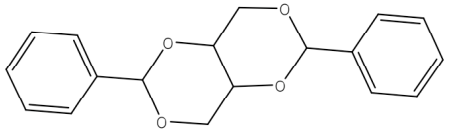

C2
C1
O2
C5A
O1A
C3A
C4A
C3
C4
C1A
O1
O2A
C5
C2A


O
O
O
O

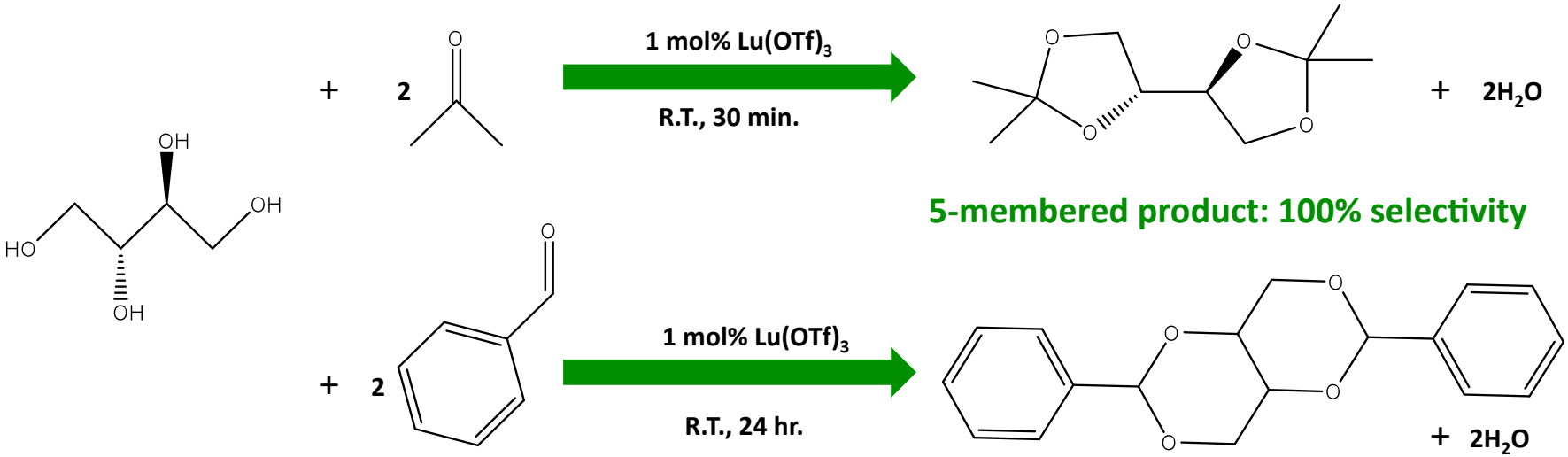

C(9)
O(6)
C(8)
O(5)
C(7)
O(3)
C(12)
C(6)
C(10)
C(3)
C(2)
C(5)
N(1)
O(4)
C(11)
C(1)
O(1)
C(4)
O(2)
N(2)


O
NH
HO
N
O
O
O
O


C(5)
C(6)
C(4)
C(1)
C(3)
C(2)
C(7)
O(1)
O(2A)
C(9A)
C(8A)
O(1A)
C(7A)
C(1A)
C(8)
C(9)
O(2)



Future Work

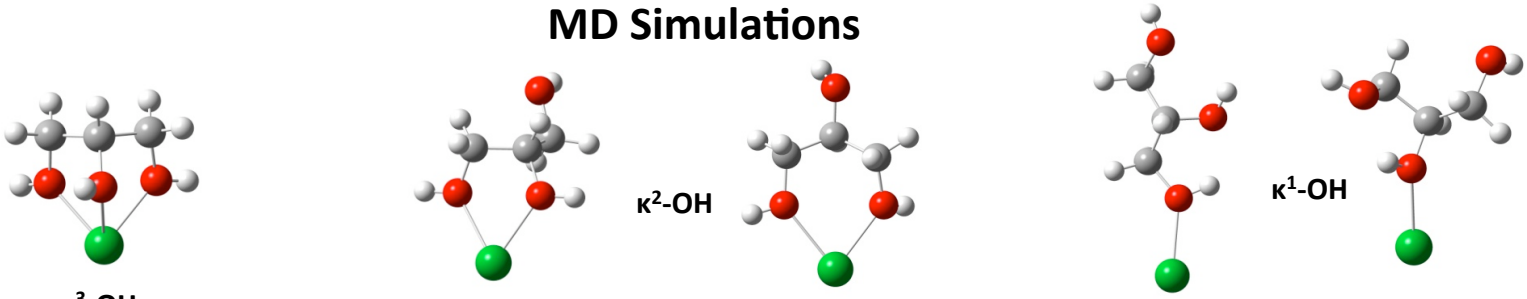


5-membered product: 100% selectivity

6-membered product: 100% selectivity

Why is stereoselectivity reversed with benzaldehyde?

MD Simulations



Glycerol/hemiketal/ketal binding modes?

H_2O/Acetone solvation?

Role of OTf^- counterions?

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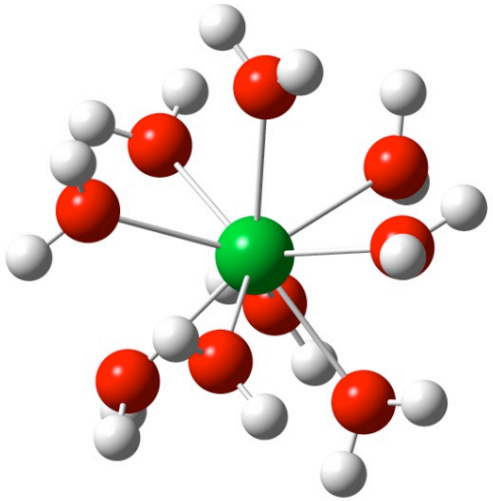
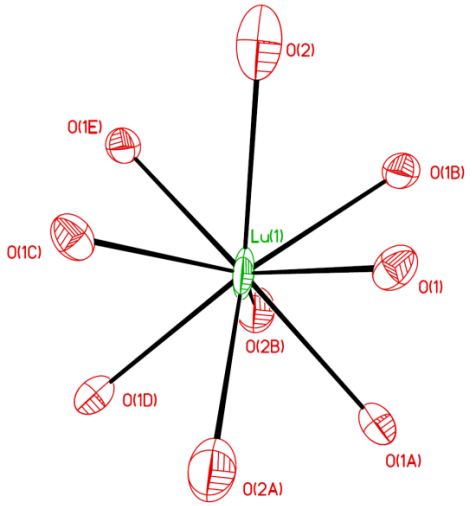
LDRD