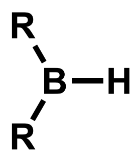
Catalysis Based on Reversible Covalent Interactions of Organoboron Compounds

2021/07/17 Ayumu Watanabe

Contents

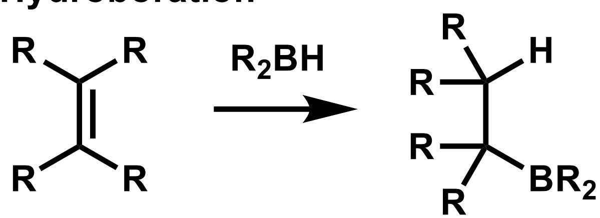
Contents

Organoborone Compounds

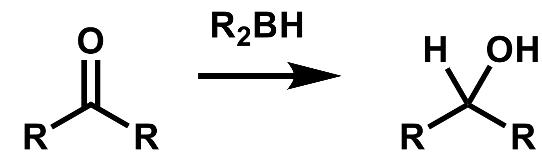


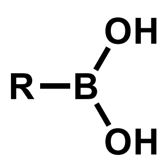
borane

・Hydroboration



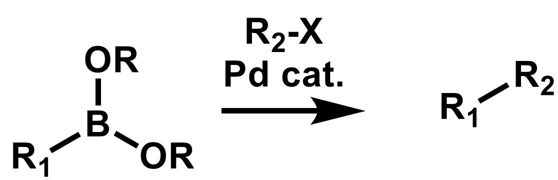
・Reduction



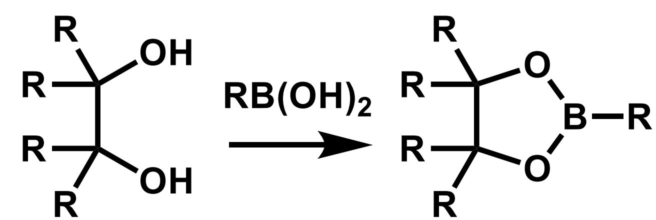


boronic acid

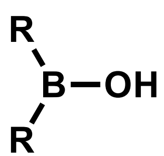
・Suzuki-Miyaura coupling



・Protecting group of diol



Lewis acid, CBS reduction, Et_3B...

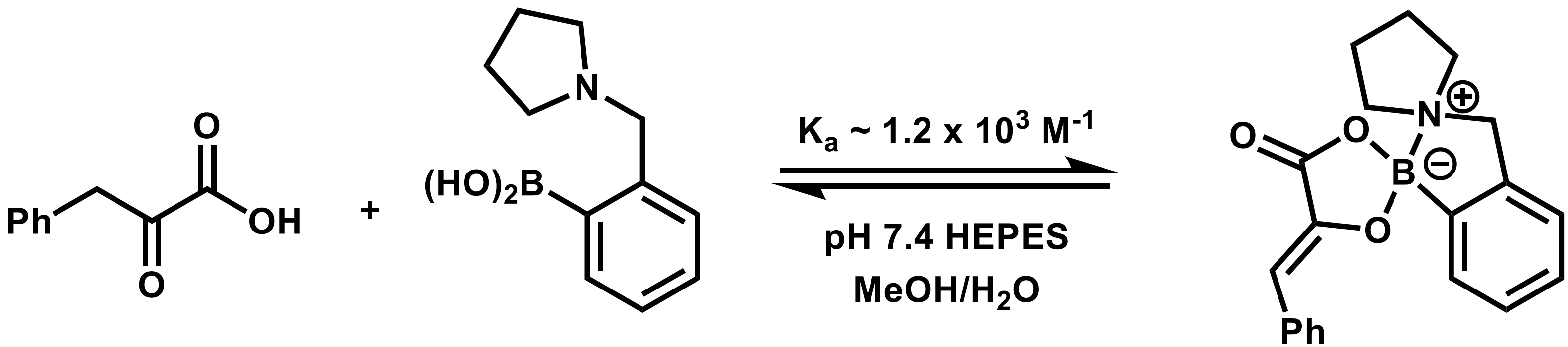


borinic acid

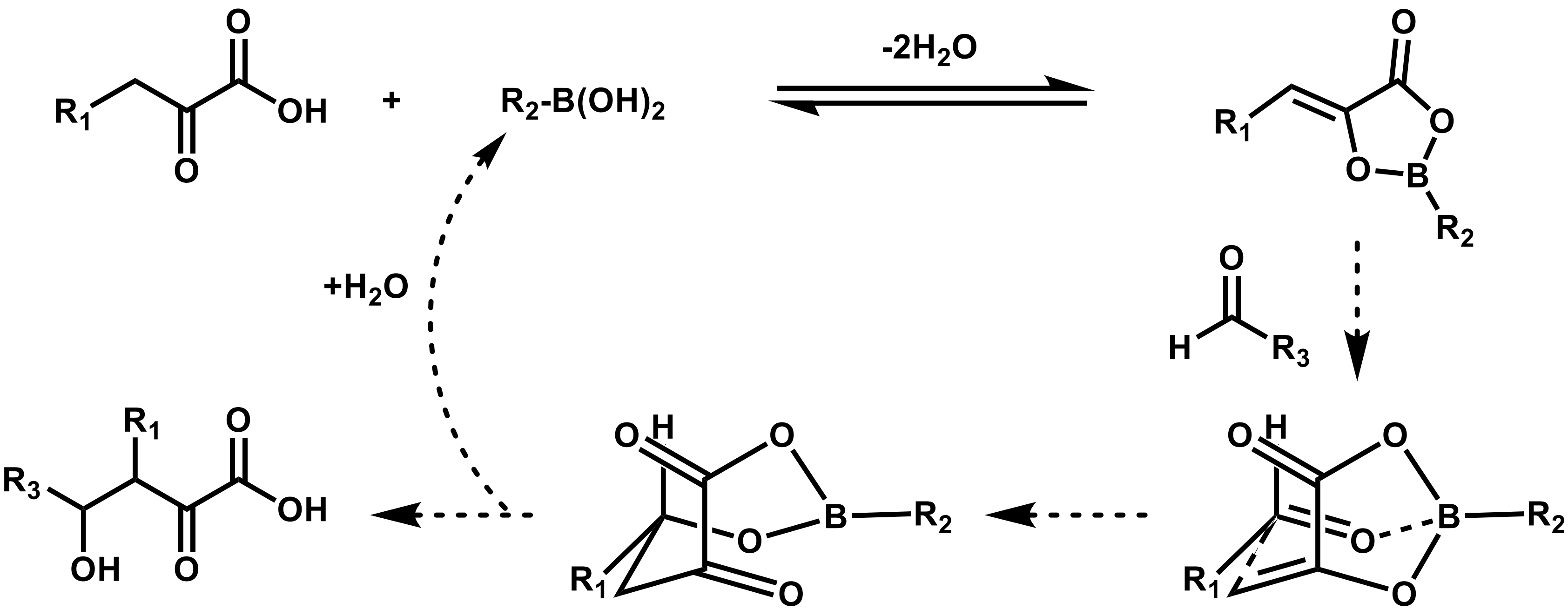
a few reacitons

Boronic Acid-catalyzed Aldol reaction

Observation of Pyruvate Enol-Boronic Acid Complexation[1)]

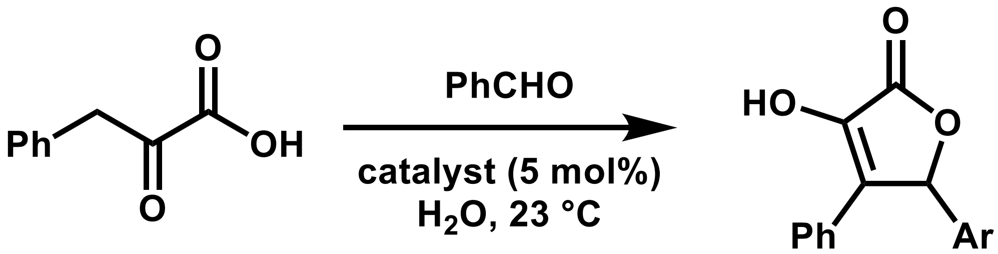


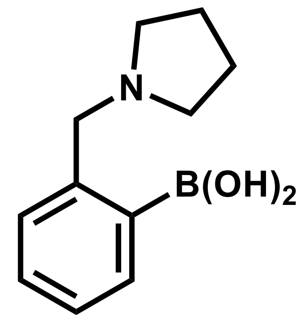
Envisioned Boronic Acid-catalyzed Aldol Reaction of Pyruvic Acids[2)]



1) Zhu, L.; Zhong, Z.; Anslyn, E. V., *J. Am. Chem. Soc.* **2005**, *127*, 4260.
2) Lee, D.; Newman, S. G.; Taylor, M. S., *Org. Lett.* **2009**, *11*, 5486.

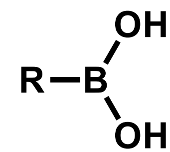
Screening of Boron Catalyst (1)



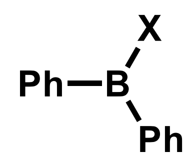


1a

entry	catalyst	yield[a] (%)
1	1a	<10
2	1b	19
3	1c	40
4	1d	8
5	2a	90
6	2b	83



1b: R = Ph
1c: R = 3,5-$(CF_3)_2C_6H_3$
1d: R = OH

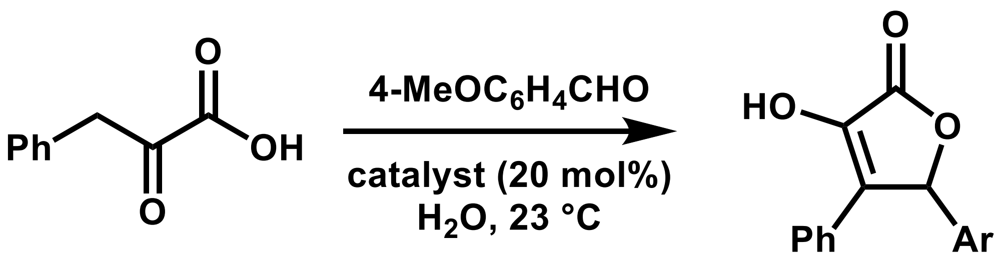


2a: X = OH
2b: X = $OCH_2CH_2NH_2$*
*commercially available
1g: 3,300 yen (Aldrich)

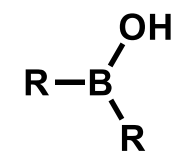
[a]Yield (0.2 mmol scale) as determined by NMR with 4,4′-di-tertbutylbiphenyl as a quantitative internal standard.

1) Lee, D.; Newman, S. G.; Taylor, M. S., *Org. Lett.* **2009**, *11*, 5486.

Screening of Boron Catalyst (2)



entry	catalyst	yield[a] (%)
1	2a	68
2	2b	42
3	2c	22
4	2d	66



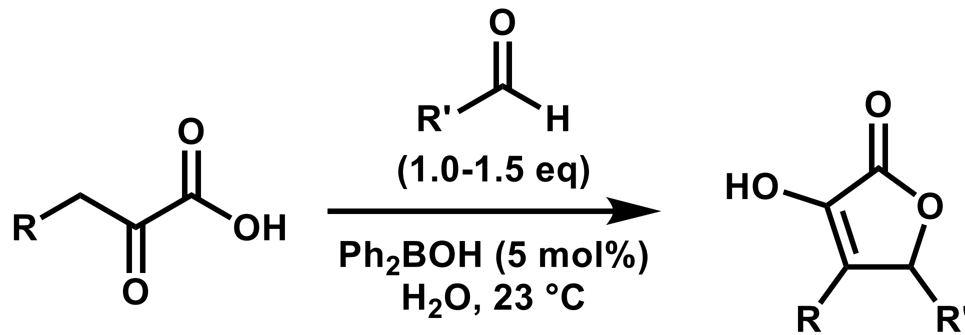
2a: R = Ph
2b: R = 3,5-$(CF_3)_2$-C_6H_3
2c: R = 4-$MeOC_6H_4$
2d: R = 3-$MeOC_6H_4$

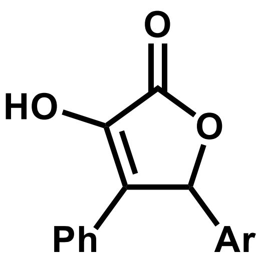
[a]Yield (0.2 mmol scale) as determined by NMR with 4,4′-di-tertbutylbiphenyl as a quantitative internal standard.

In addition, Brønsted acids and Lewis acidic metal salts did not efficiently catalyze the reaction under these conditions.

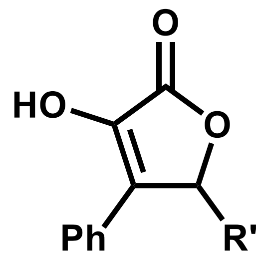
1) Lee, D.; Newman, S. G.; Taylor, M. S., *Org. Lett.* **2009**, *11*, 5486.

Substrate Scope (1)

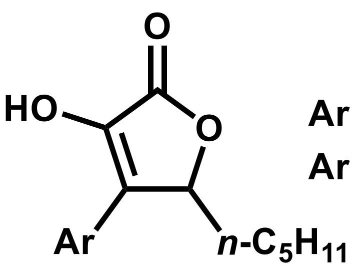




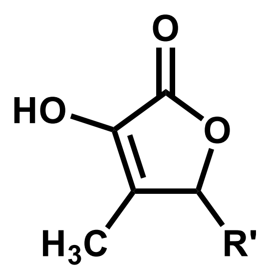
Ar = Ph: 90% (0.5 mol%)
Ar = 4-$MeOC_6H_4$: 70% (20 mol%)
Ar = 4-$F_3CC_6H_4$: 81%
Ar = 2-thienyl: 82%
Ar = 2-furyl: 89%



R' = n-C_5H_{11}: 90%[a] (1 mol%)
R' = cyclohexyl: 84%
R' = CH_3: 55% (5 eq of R'CHO)[a]



Ar = 4-HOC_6H_4: 80%
Ar = 2-$O_2NC_6H_4$: 89%



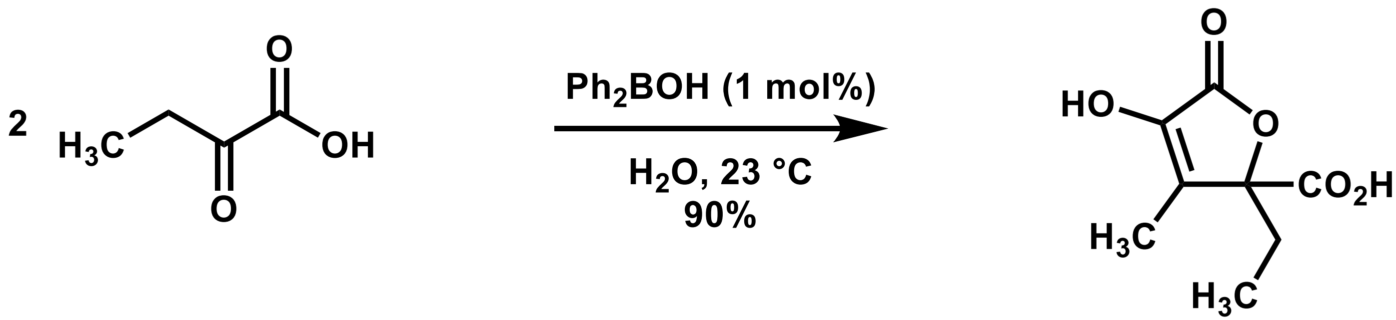
R' = Ph: 71% (3 eq of R'CHO)
R' = n-C_5H_{11}: 56% (3 eq of R'CHO)

[a]Isolated yield of O-silylated isotetronic acid, purified by column chromatography.

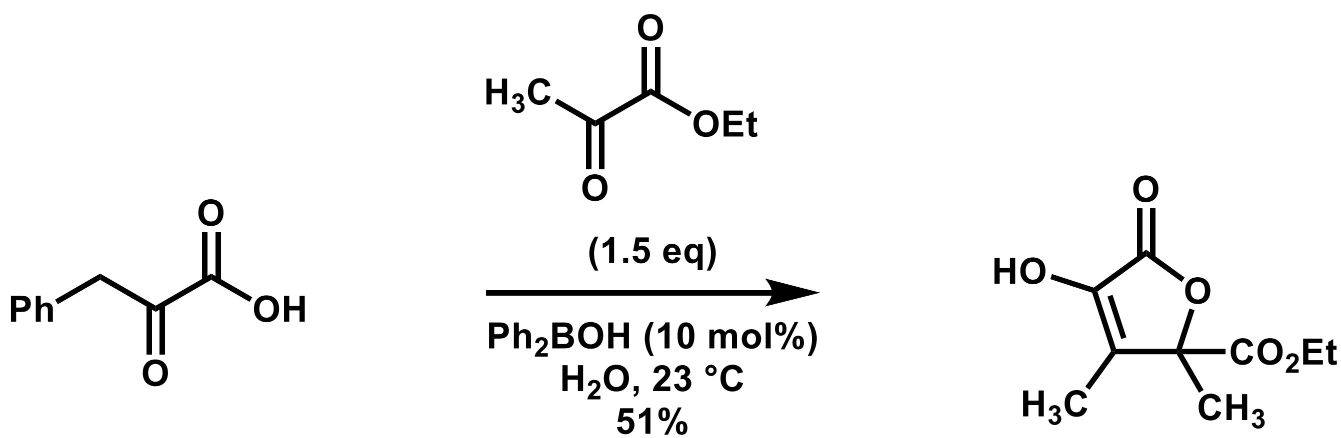
1) Lee, D.; Newman, S. G.; Taylor, M. S., *Org. Lett.* **2009**, *11*, 5486.

Substrate Scope (2)

Homo-Aldol Reaction of Pyruvates



Cross-Aldol Reaction of Pyruvates



1) Lee, D.; Newman, S. G.; Taylor, M. S., *Org. Lett.* **2009**, *11*, 5486.

Contents

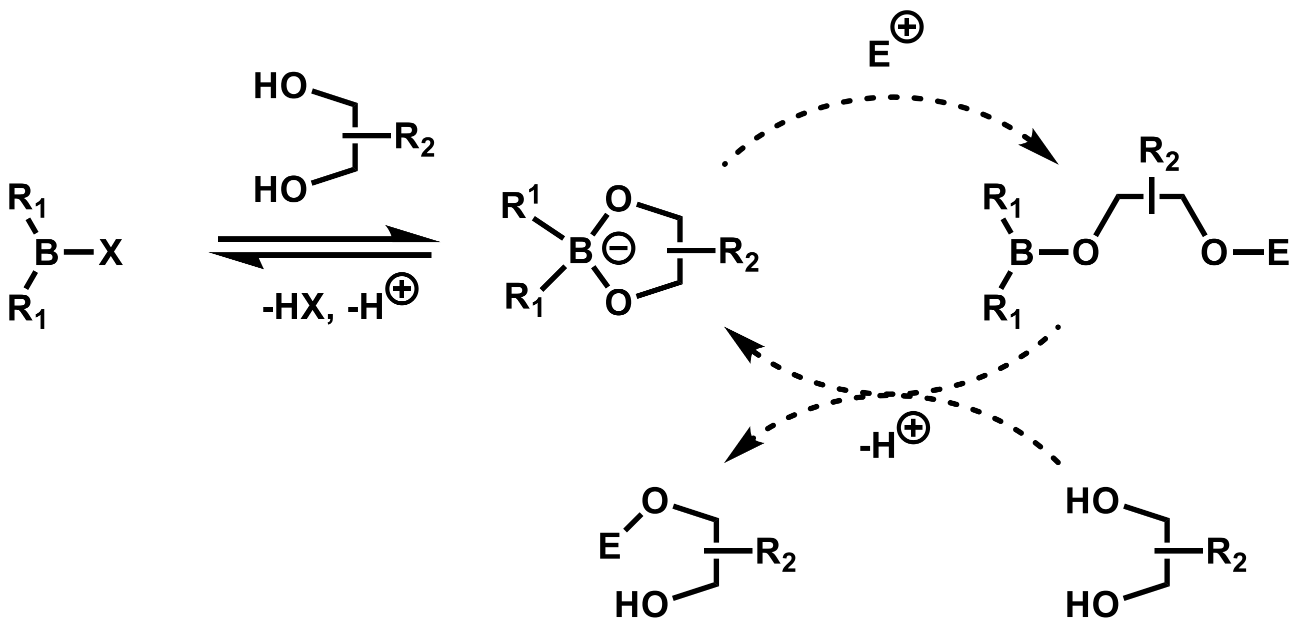
Prof. Mark S. Taylor

1999	B.S. @ University of Toronto
2005	Ph.D @ Harvard University (Prof. Eric N. Jacobsen)
2005-	Postdoctral fellow @ MIT (Timothy M. Swager)
2007-	Assistant Professor @ University of Toronto
2012-	Associate Professor
2017-	Professor of Chemistry
2012-	Canada Research Chair

Research topic: Catalysis (organoboron catalyst)
Molecular Recognition
(halogen bonding and chalcogen bonding)

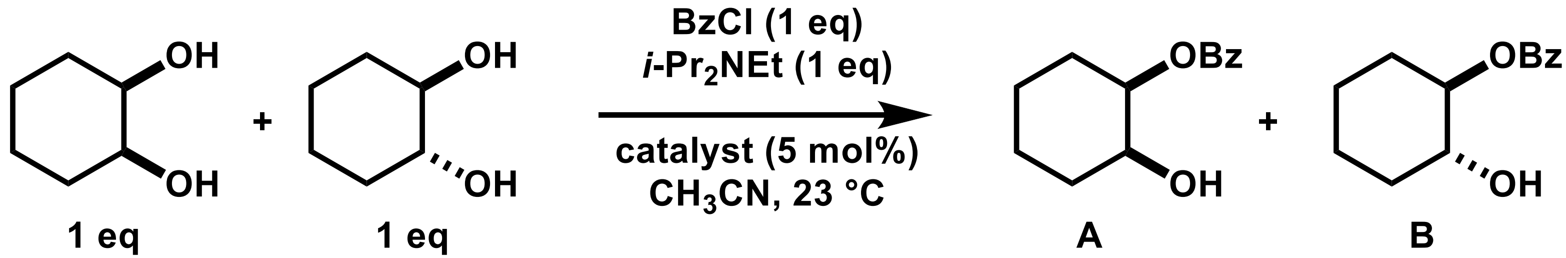
Borinic Acid Catalyzed Monofunctionalization of Diol

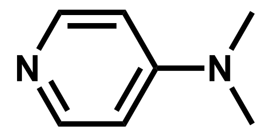
Envisioned Borinic Acid Catalyzed Monofunctionalization of Diols

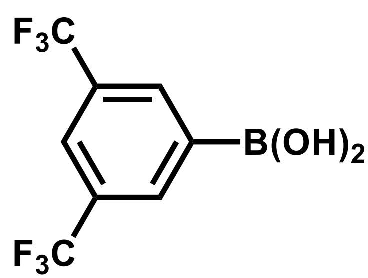
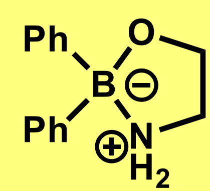


1) Lee, D.; Taylor, M. S., *J. Am. Chem. Soc.* **2011**, *133*, 3724.

Evaluation of Catalysts for Selective Acylation of *cis*-Cycloalkanediols



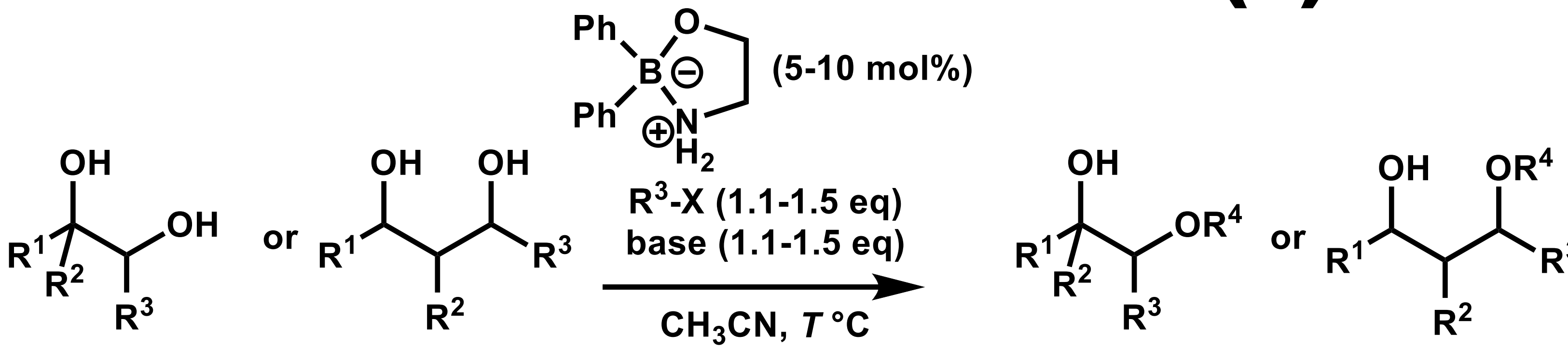
	None		Me_2SnCl_2
% conv.[a]	<5%	30%	96%
Ratio A : B[a]	-	1 : 1	1 : 1

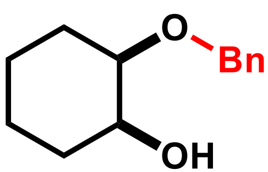
	$PhB(OH)_2$		Ph_2BOH	
% conv.[a]	35%	90%	70%	70%
Ratio A : B[a]	3 : 1	2 : 1	11 : 1	11 : 1

[a]Determined by ^{1}H NMR

1) Lee, D.; Taylor, M. S., *J. Am. Chem. Soc.* **2011**, *133*, 3724.

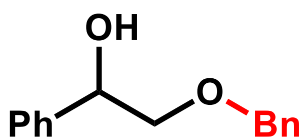
Monofunctionalization (1)





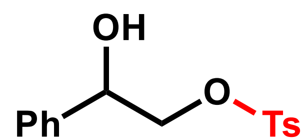
>99%[a](15%)[b]

BnBr, K_2CO_3, KI, 60 °C



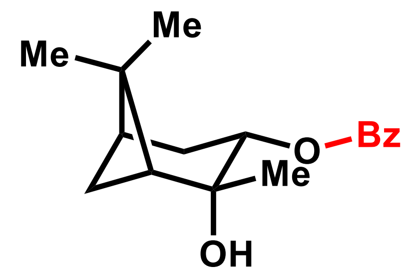
88%[a]

BnBr, K_2CO_3, KI, 60 °C



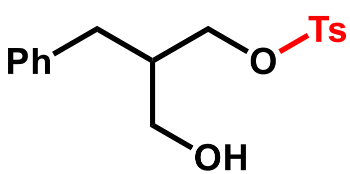
90%[a]

TsCl, *i*-Pr_2NEt, 23 °C



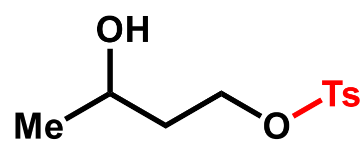
78%[a]

BzCl, *i*-Pr_2NEt, 23 °C



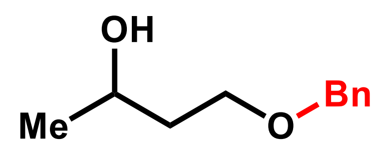
72%[a]

TsCl, *i*-Pr_2NEt, 23 °C



80%[a]

BzCl, *i*-Pr_2NEt, 23 °C



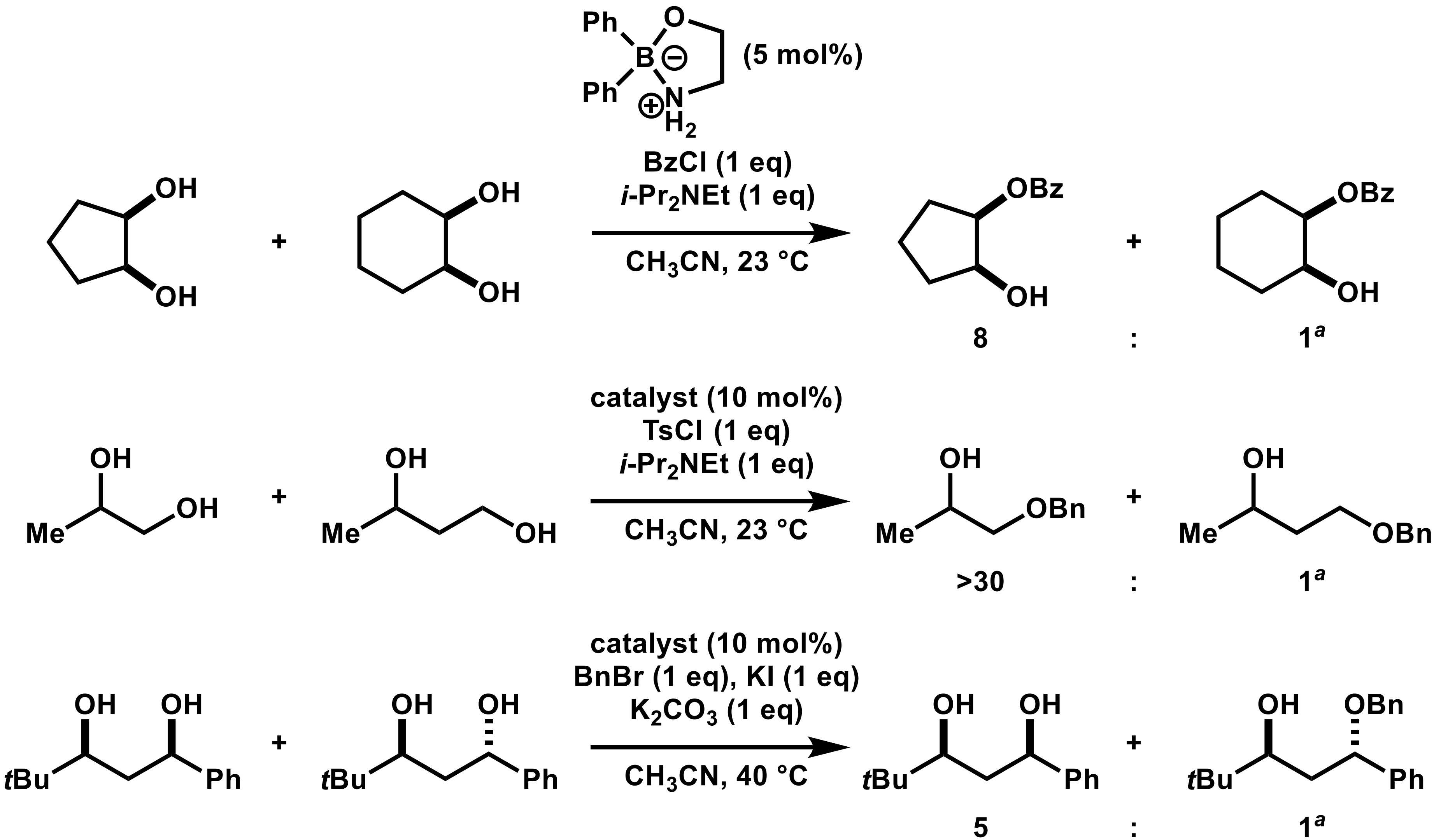
95%[a]

BnBr, K_2CO_3, KI, 60 °C

[a]Isolated yield. [b]Without catalyst. NMR yield with mesitylene as a quantitative internal standard.

1) Lee, D.; Taylor, M. S., *J. Am. Chem. Soc.* **2011**, *133*, 3724. 2) Chan, L.; Taylor, M. S., *Org. Lett.* **2011**, *13*, 3090. 3) Lee, D.; Williamson, C. L.; Chan, L.; Taylor, M. S., *J. Am. Chem. Soc.* **2012**, *134*, 8260.

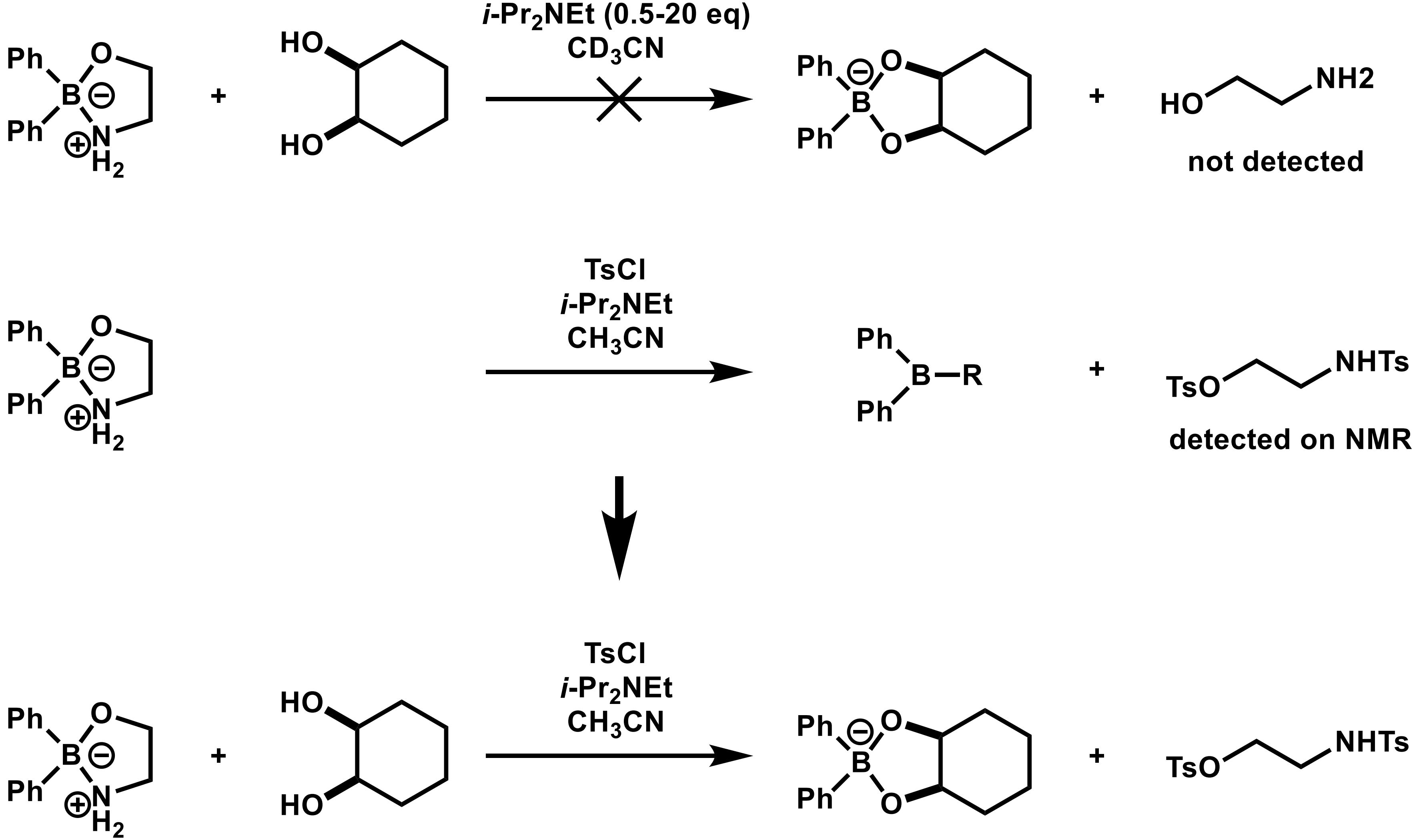
Monofunctionalization (2)



[a]Determined by ^{1}H NMR.

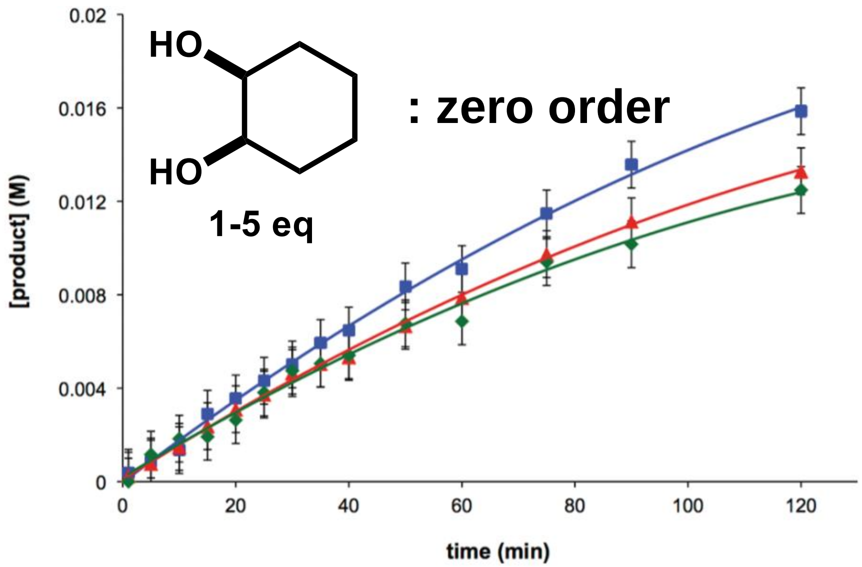
1) Lee, D.; Taylor, M. S., *J. Am. Chem. Soc.* **2011**, *133*, 3724. 2) Chan, L.; Taylor, M. S., *Org. Lett.* **2011**, *13*, 3090. 3) Lee, D.; Williamson, C. L.; Chan, L.; Taylor, M. S., *J. Am. Chem. Soc.* **2012**, *134*, 8260.

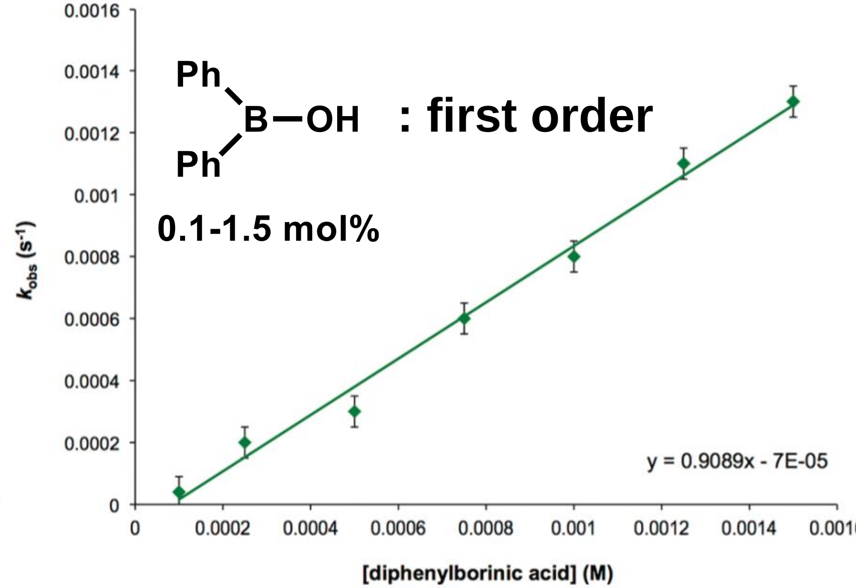
Investigation for Mechanism (1)

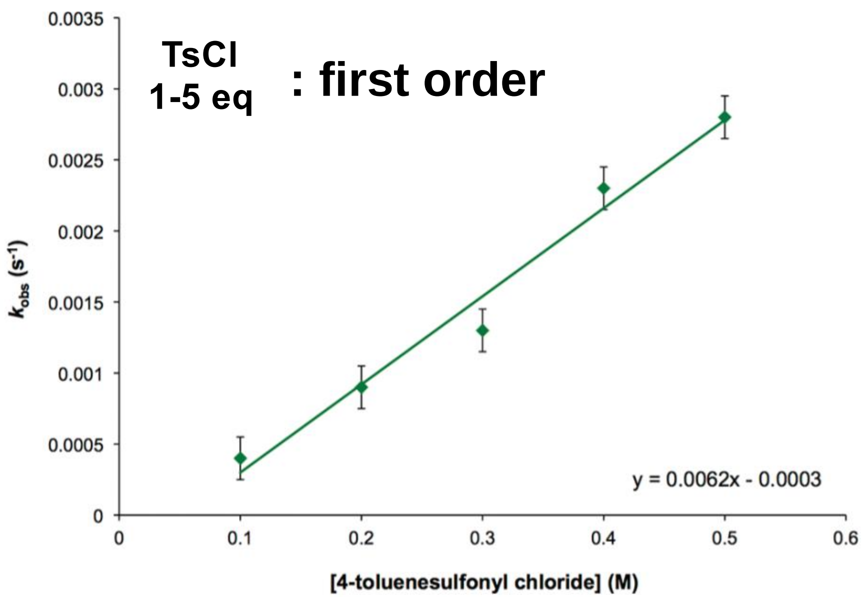


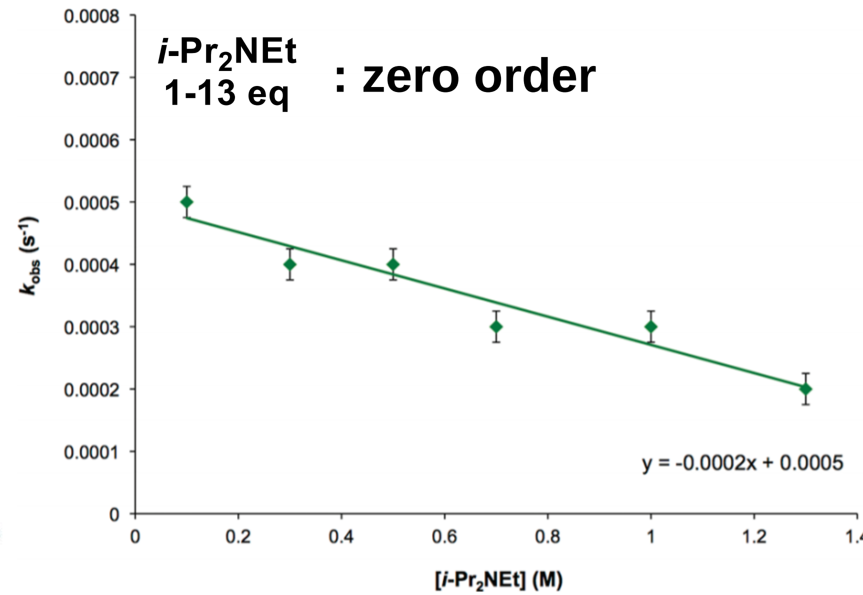
1) Lee, D.; Taylor, M. S., *J. Am. Chem. Soc.* **2011**, *133*, 3724. 2) Chan, L.; Taylor, M. S., *Org. Lett.* **2011**, *13*, 3090. 3) Lee, D.; Williamson, C. L.; Chan, L.; Taylor, M. S., *J. Am. Chem. Soc.* **2012**, *134*, 8260.

Investigation for Mechanism (2)



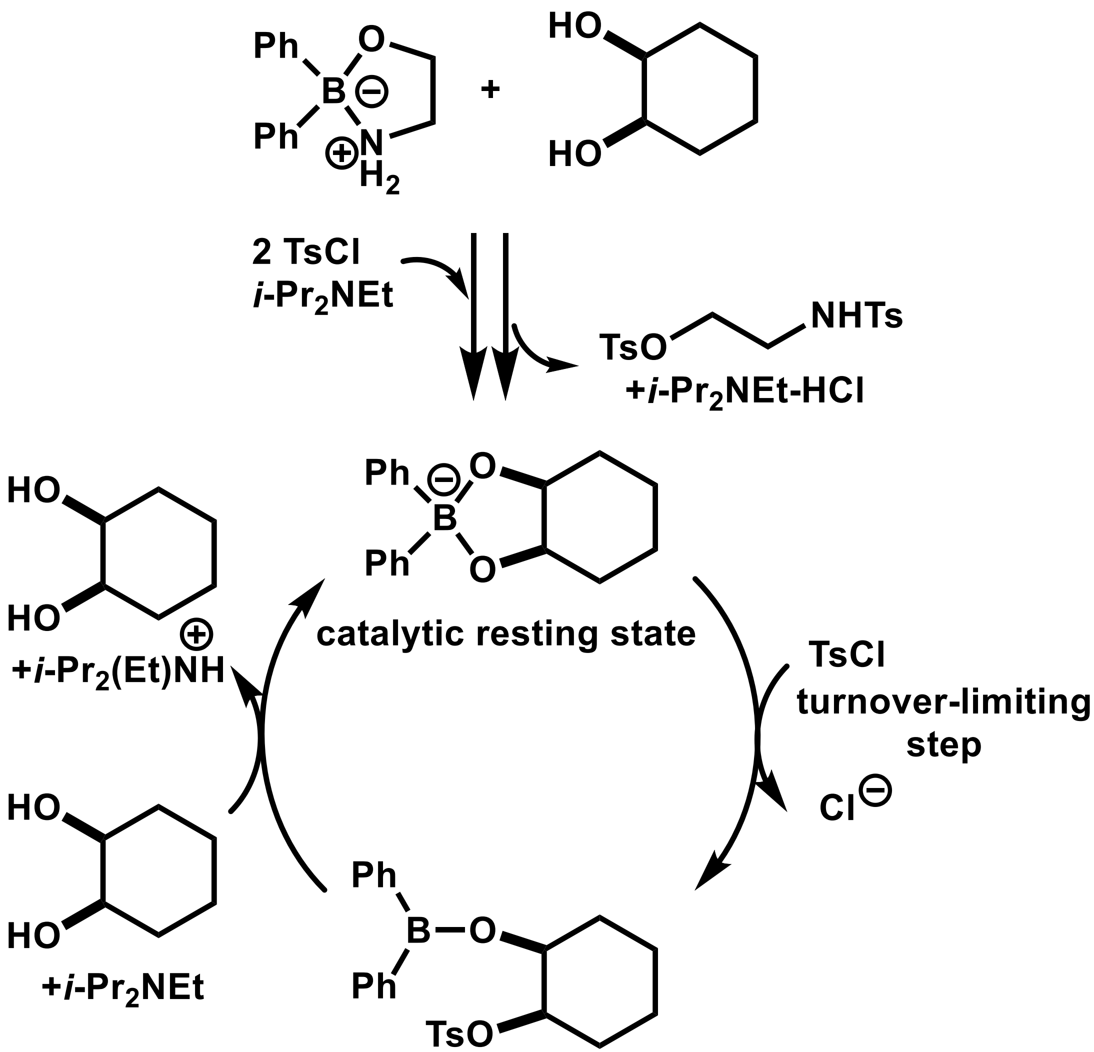




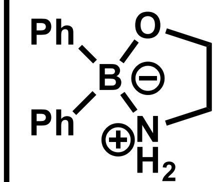
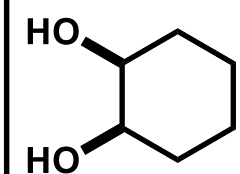


1) Lee, D.; Taylor, M. S., *J. Am. Chem. Soc.* **2011**, *133*, 3724. 2) Chan, L.; Taylor, M. S., *Org. Lett.* **2011**, *13*, 3090. 3) Lee, D.; Williamson, C. L.; Chan, L.; Taylor, M. S., *J. Am. Chem. Soc.* **2012**, *134*, 8260.

Proposed Catalytic Cycle of Sulfonylation

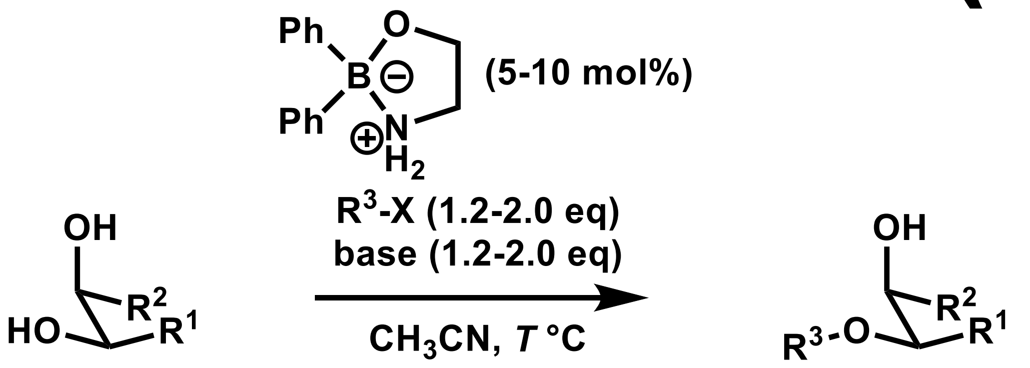


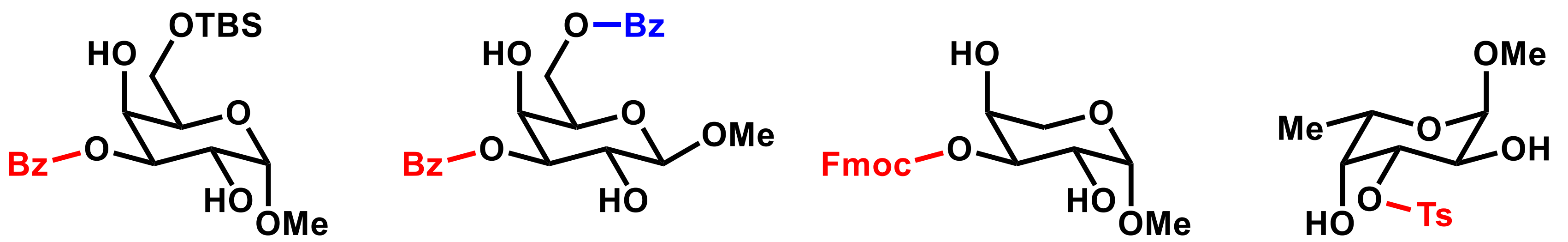
Kinetic orders:

	first order
	zero order (saturation)
TsCl	first order
i-Pr_2NEt	zero order

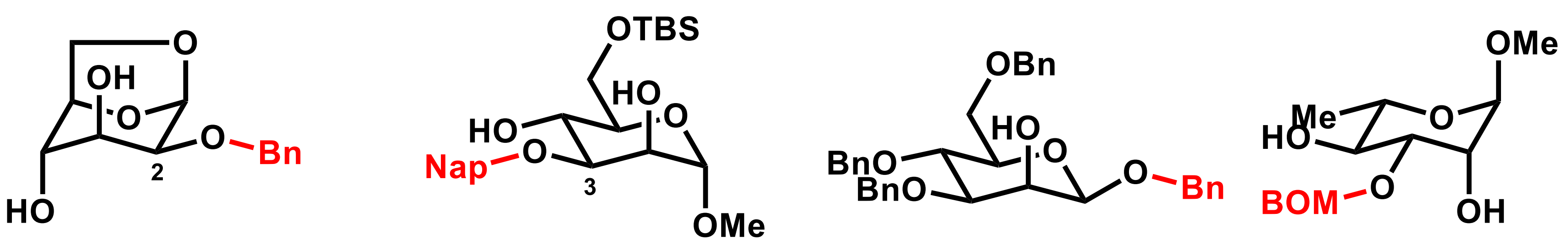
1) Lee, D.; Williamson, C. L.; Chan, L.; Taylor, M. S., *J. Am. Chem. Soc.* **2012**, *134*, 8260.

Monofunctionalization (3)





95%[a](11%)[b]	88%[a](20%)[b]	73%[a](5%)[b]	97%[a]
BzCl, *i*-Pr_2NEt, 23 °C	BzCl[c], *i*-Pr_2NEt[c], 23 °C	FmocCl, *i*-Pr_2NEt, 23 °C	TsCl, *i*-Pr_2NEt, 23 °C

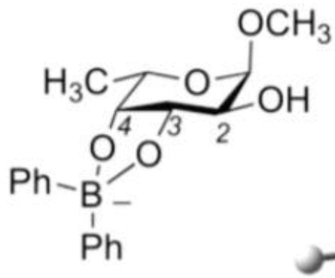


73%[a]	89%[a]	72%[a]	72%[a]
BnBr, Ag_2O, 40 °C	NapBr, Ag_2O, 40 °C	BnBr, Ag_2O, 40 °C	BOMCl, Ag_2O, 40 °C

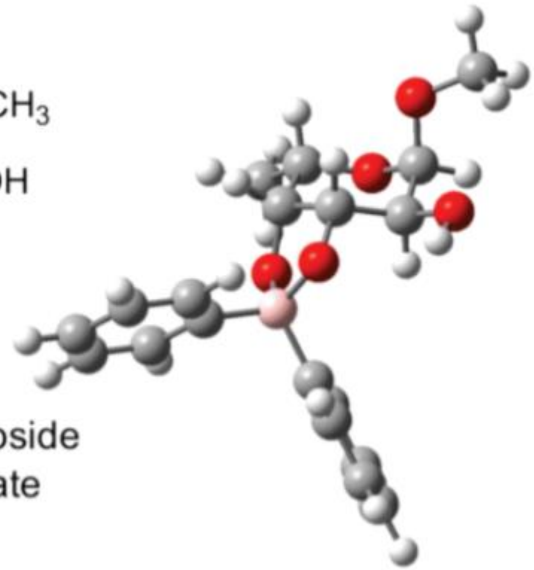
[a]Isolated yield. [b]RCOCl (1.2 eq) in pyridine, -30 to 23 °C. [c]4.0 eq

1) Lee, D.; Taylor, M. S., *J. Am. Chem. Soc.* **2011**, *133*, 3724. 2) Chan, L.; Taylor, M. S., *Org. Lett.* **2011**, *13*, 3090. 3) Lee, D.; Williamson, C. L.; Chan, L.; Taylor, M. S., *J. Am. Chem. Soc.* **2012**, *134*, 8260.

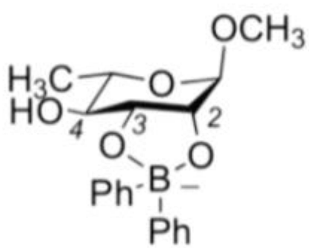
DFT-calculation



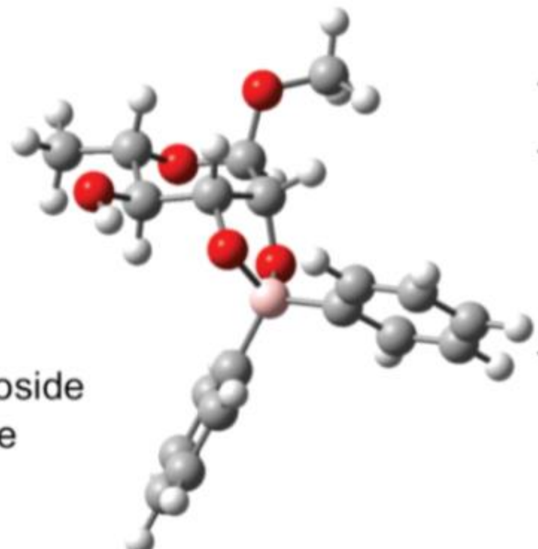
methyl α-fucopyranoside
3,4-diphenylborinate



atom	f^-_k	proton affinity
O-2	0.039	–
O-3	0.177	328 kcal/mol
O-4	0.132	318 kcal/mol



methyl α-rhamnopyranoside
2,3-diphenylborinate

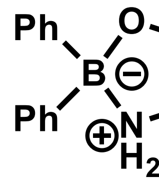


atom	f^-_k	proton affinity
O-2	0.138	321 kcal/mol
O-3	0.180	327 kcal/mol
O-4	0.038	–

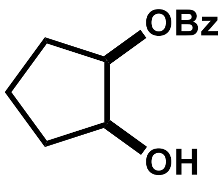
DFT-calculated (B3LYP/6-311+G**) condensed Fukui index f^-_k (a measure of relative nucleophilic reactivity)

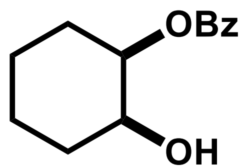
1) Lee, D.; Williamson, C. L.; Chan, L.; Taylor, M. S., *J. Am. Chem. Soc.* **2012**, *134*, 8260.

Short Summary



Highselectivity of diols





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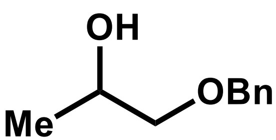
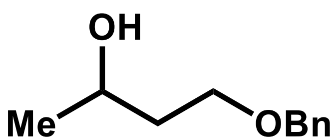
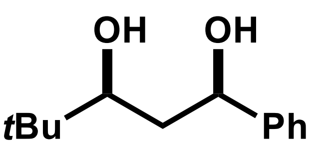
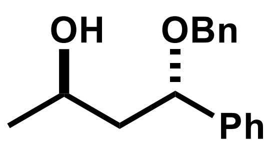




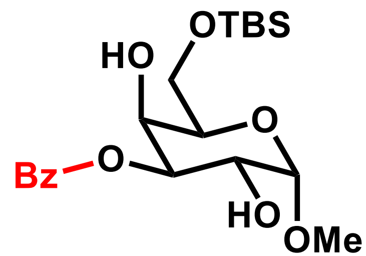
>30 : 1



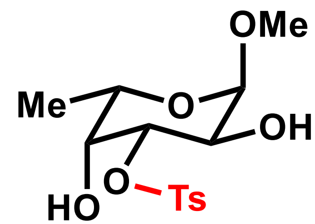


5 : 1

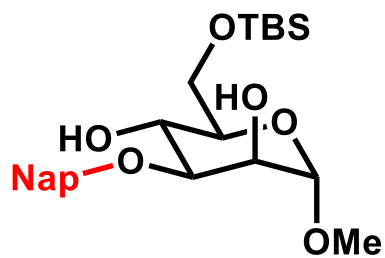
Acylation, sulfonylation and alkylation of carbohydrates



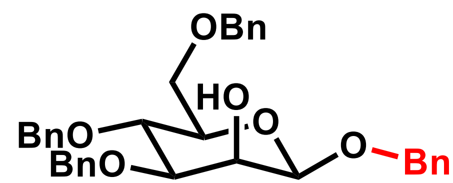
95%



97%



89%



72%

Contents

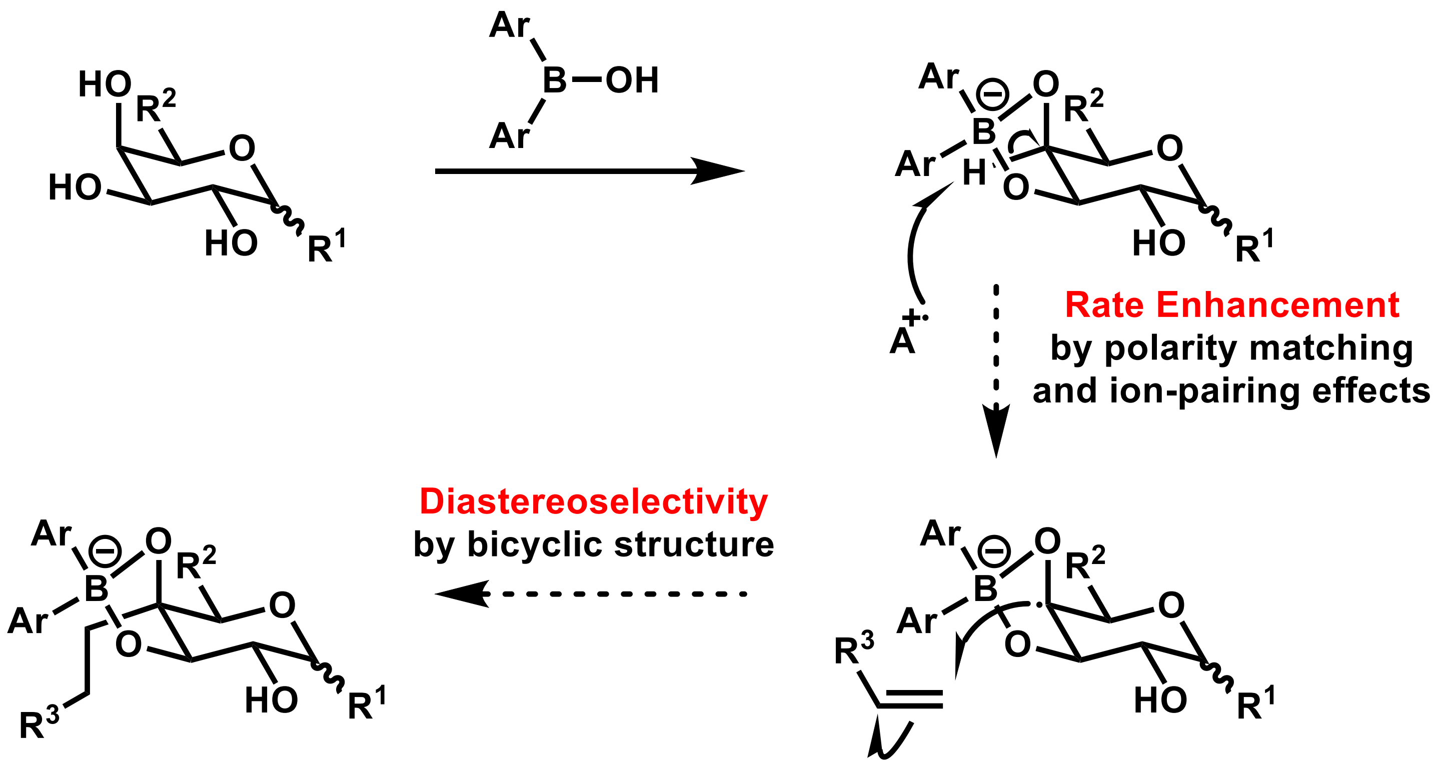
1. Introduction (Boronic acid and Boric acid)

2. Borinic Acid Catalyzed Monofunctionalization of Diols
(*J. Am. Chem. Soc.* **2012**, *134*, 8260.)

3. C-H alkylations of Carbohydrate via Combined Borinic Acid and Photoredox Catalysis
(*J. Am. Chem. Soc.* **2019**, *141*, 5149.)

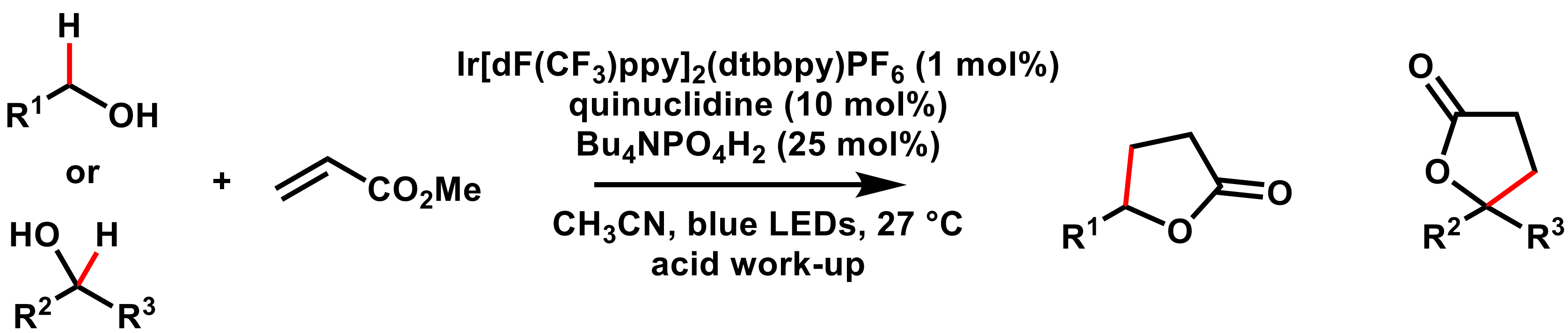
C-H Functionalization of Carbohydrates

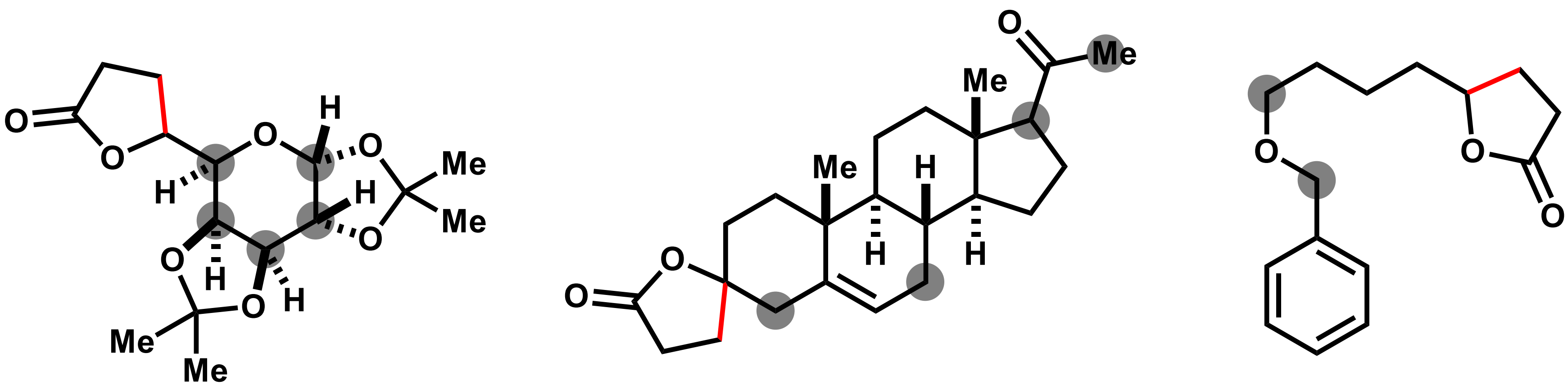
Envisioned C-H Functionalization of Carbohydrates



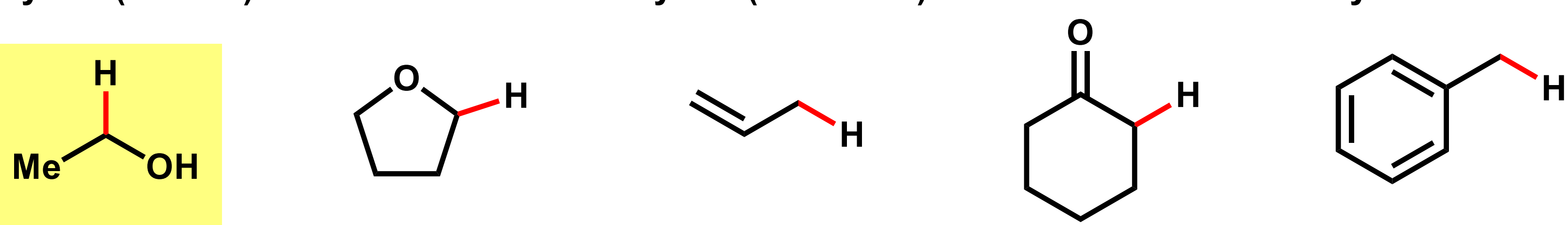
1) Dimakos, V.; Su, H. Y.; Garrett, G. E.; Taylor, M. S. *J., Am. Chem. Soc.* **2019**, *141*, 5149.

Selective C-Alkylation of Alocohols





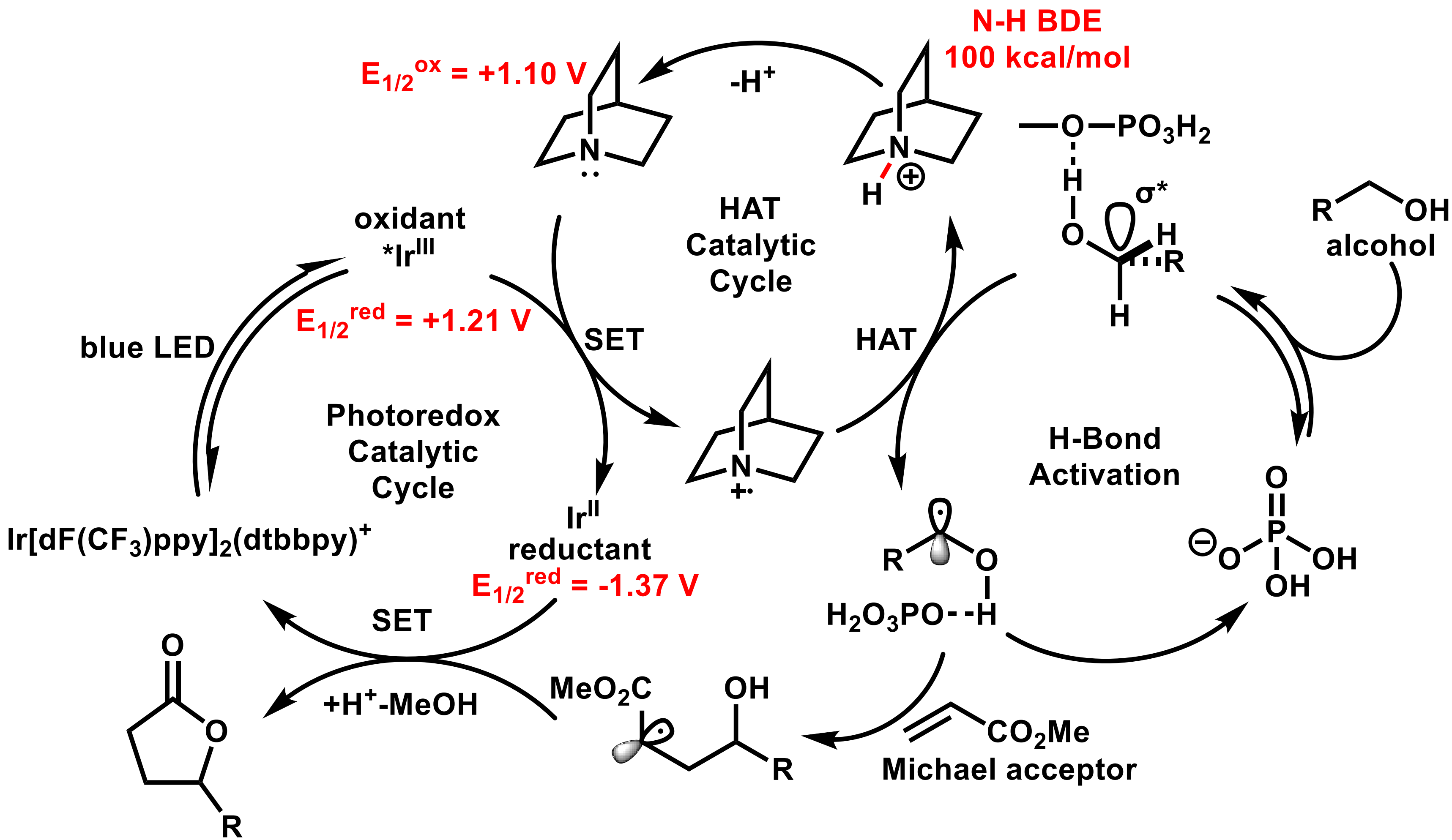
85% yield (1:1 d.r.) 70% yield (>20:1 d.r.) 75% yield



BDE values 92.0 kcal/mol 92.0 kcal/mol 88.8 kcal/mol 88.0 kcal/mol 89.8 kcal/mol

1) Jeffrey, J. L.; Terrett, J. A.; MacMillan, D. W. C. *Science* **2015**, *349*, 1532.

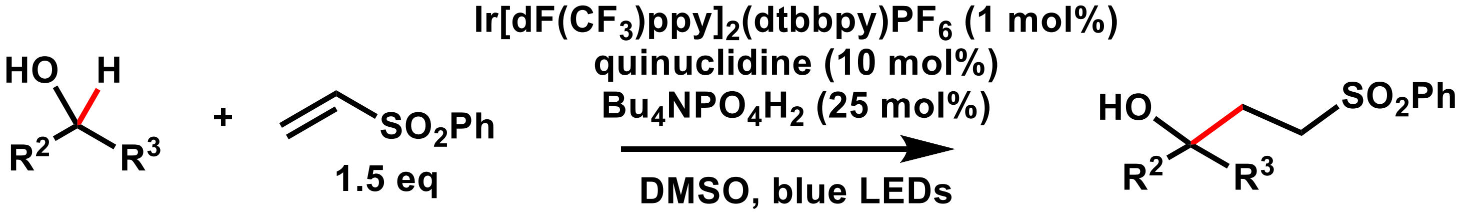
Proposed Mechanism

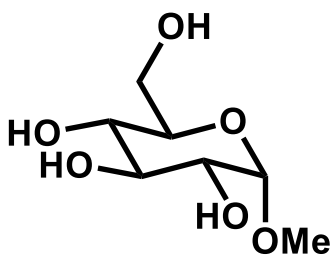
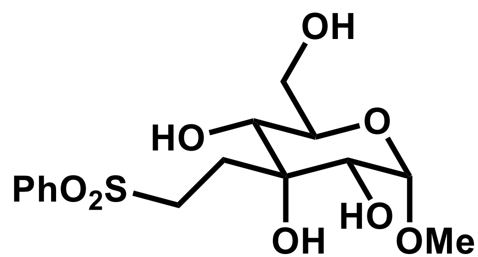
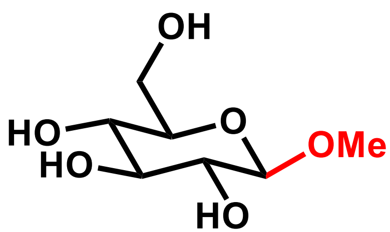
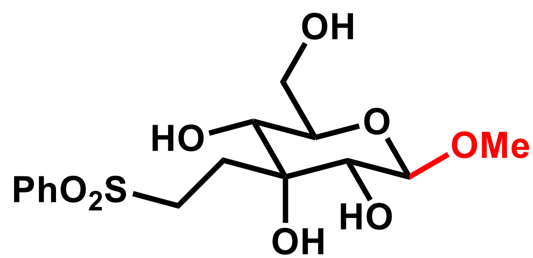
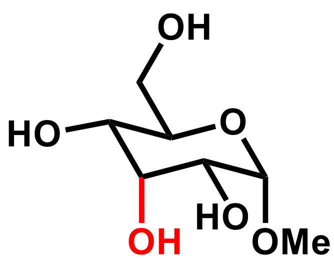
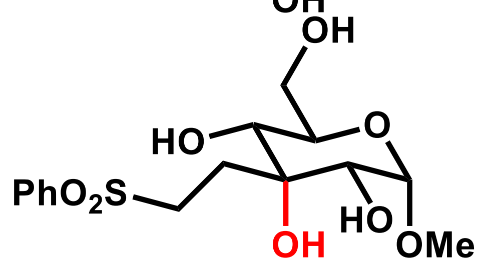


the hydroxyalkyl C–H bond is selectively polarized and weakened via O–H hydrogen bonding

1) Jeffrey, J. L.; Terrett, J. A.; MacMillan, D. W. C. *Science* **2015**, *349*, 1532.

Site-Selective Alkylation of Carbohydrates

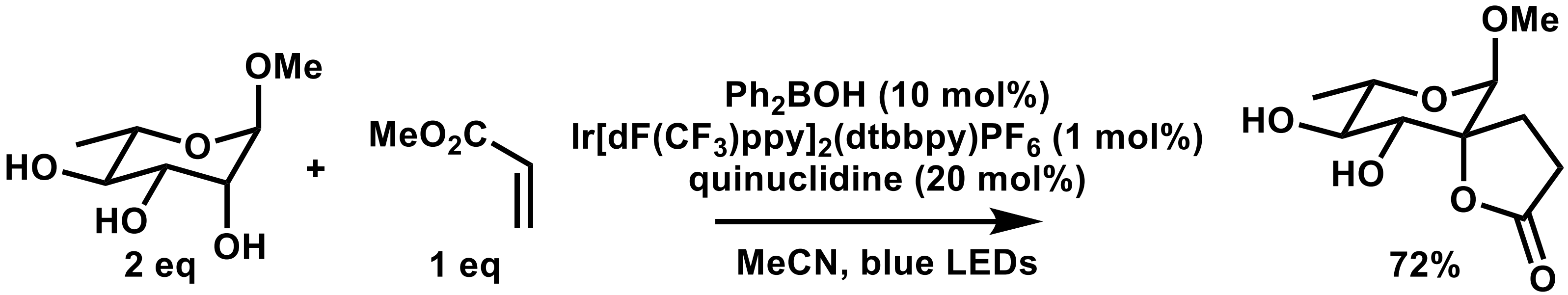


Entry	Substrate	Product	Yield
1			52%
2			30% (d.r. = 2:1)
3			46%

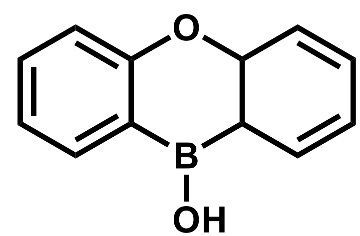
manno- and galactopyranosides did not undergo selective alkylation

1) Wan, I. C.; Witte, M. D.; Minnaard, A. J. *Chem. Commun.* **2017**, *53*, 4926.

Investigation for conditions (1)



Entry	Change(s) to conditions	Yield
1	Ph_2BOH omitted	5% with a mixture of C-H alkylation products
2	Ir cat. omitted	no reaction
3	quinuclidine omitted	<5%
4	Minnaard conditions	5%
5	A used in place of Ph_2BOH	55%
6	$Bu_4N^+BzO^-$ (20 mol%)* in place of quinuclidine	<5%
7	Methyl thioglycolate (20 mol%)** in place of quinuclidine	<5%

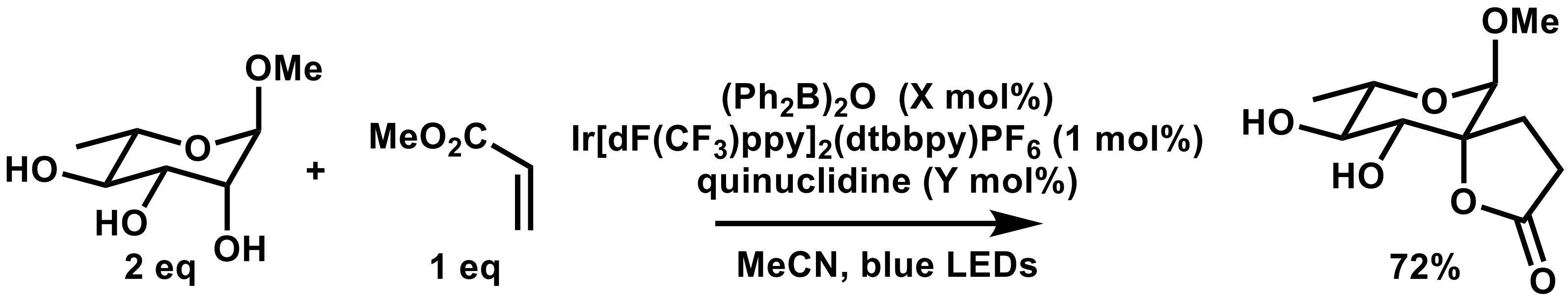


A

*O-H BDE: 111 kcal/mol
**S-H BDE: 87 kcal/mol
(N-H BDE: 99 kcal/mol)

1) Dimakos, V.; Su, H. Y.; Garrett, G. E.; Taylor, M. S. *J., Am. Chem. Soc.* **2019**, *141*, 5149.

Investigation for conditions (2)



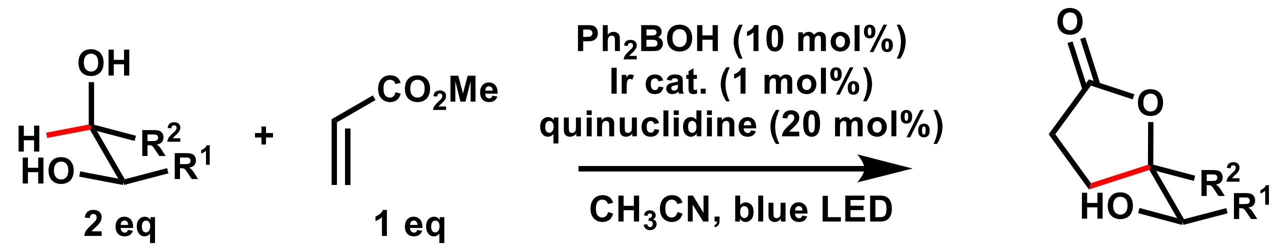
		$(Ph_2B)_2O$ (mol%)		
		2.5	5	10
quinuclidine (mol%)	10	43%	<5%	<5%
	20	54%	72%	20%
	40	41%	43%	53%

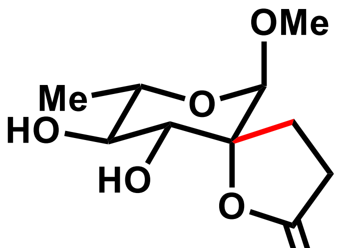
Roughly 10 mol % excess of quinuclidine relative to $(Ph_2B)_2O$ was optimal

Dual role for quinuclidine as ・Brønsted base (to promote borinic acid–diol complexation)
・HAT mediator.

1) Dimakos, V.; Su, H. Y.; Garrett, G. E.; Taylor, M. S. *J., Am. Chem. Soc.* **2019**, *141*, 5149.

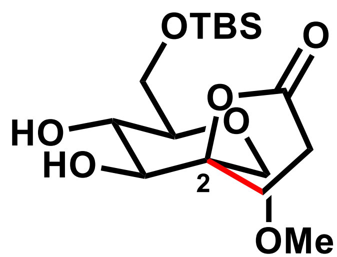
Substrate Scope (1)



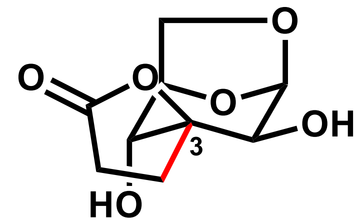


72% (5%)[a]

Rhamnopyranoside

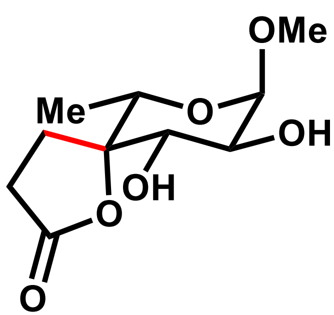


68% (14%)[a]



68% (9%)[a]

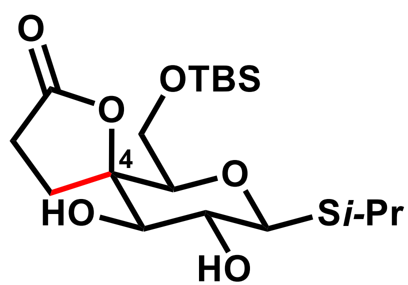
Mannopyranoside



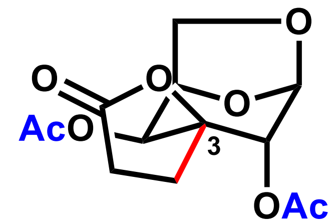
62% (C4:C3 = 5.3:1)

20% (C4:C3 = 1:1.2)[a]

Fucopyranoside



54%[c] (<5%)[a]



54% (d.r. = 6:1)[d]

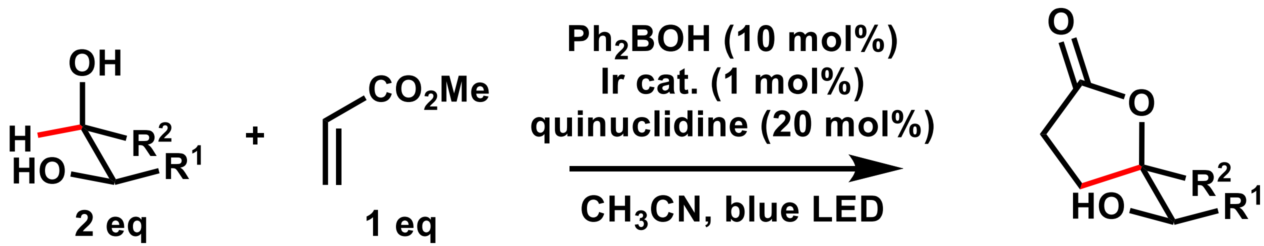
18% (d.r. = 0.6:1)[a]

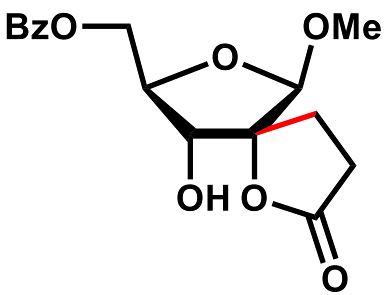
Galactopyranoside

[a]without Ph_2BOH. [c]1.0 eq of pyranoside.
[d]2.0 eq of acrylate. acylation prior to isolation

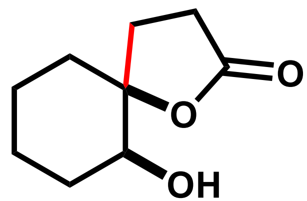
1) Dimakos, V.; Su, H. Y.; Garrett, G. E.; Taylor, M. S. *J., Am. Chem. Soc.* **2019**, *141*, 5149.

Substrate Scope (2)

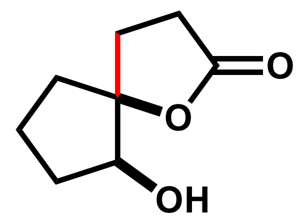




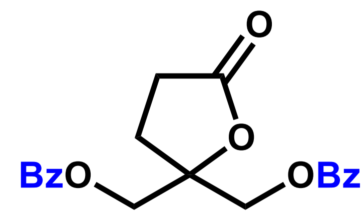
54%[b,c] (6%)[a]



57% (d.r. = 11:1)
68% (d.r. = 1.7:1)[a]

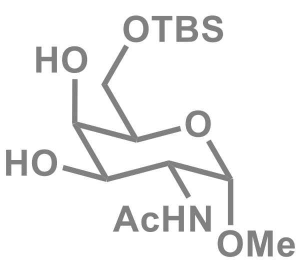


63%[c] (35%)[a]

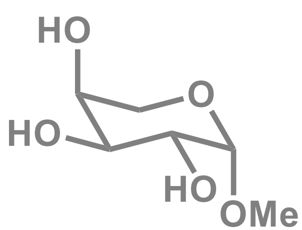


57%[d] (23%)[a]

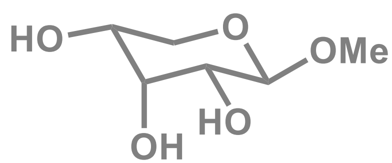
[a]without Ph_2BOH. [b]2.0 eq of acrylate. [c]Amberlyst prior to isolation.
[d]1.0 eq of quinuclidine. acylation prior to isolation.



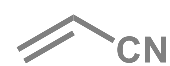
α-D-*N*-acetyl galactosamine



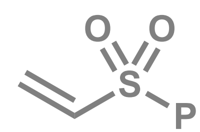
β-L-arabino pyranoside



β-D-ribo pyranoside



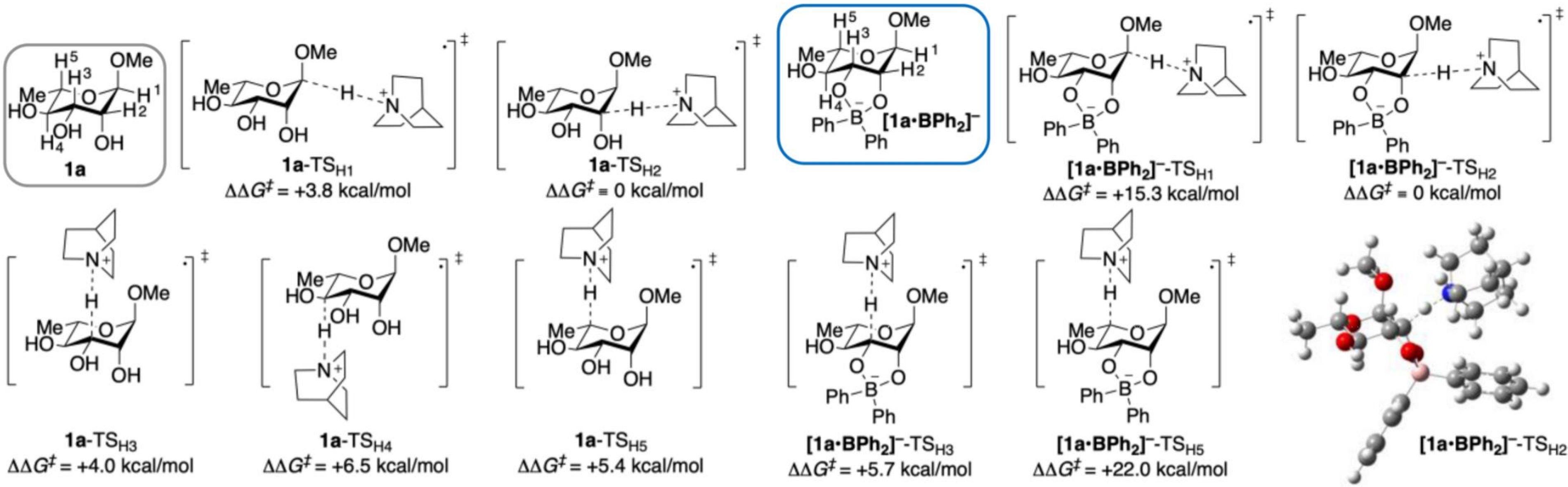
acrylonitrile



phenyl vinyl sulfone

1) Dimakos, V.; Su, H. Y.; Garrett, G. E.; Taylor, M. S. *J., Am. Chem. Soc.* **2019**, *141*, 5149.

Calculation for Site-selectivity

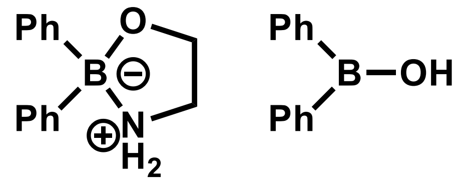


rhamnopyranoside **1a**				diphenylborinate [**1a**·BPh$_2$]$^-$			
BDE (kcal/mol)		ΔΔG‡ for HAT (kcal/mol)		BDE (kcal/mol)		ΔΔG‡ for HAT (kcal/mol)	
position	BDE	transition state	ΔΔG‡	position	BDE	transition state	ΔΔG‡
H-1	89.2	**1a**-TS$_{H1}$	+3.8	H-1	91.2	[**1a**·BPh$_2$]$^-$-TS$_{H1}$	+15.3
H-2	89.6	**1a**-TS$_{H2}$	0.0	H-2	85.1	[**1a**·BPh$_2$]$^-$-TS$_{H2}$	0.0
H-3	90.2	**1a**-TS$_{H3}$	+4.0	H-3	86.0	[**1a**·BPh$_2$]$^-$-TS$_{H3}$	+5.7
H-4	87.4	**1a**-TS$_{H4}$	+6.5	H-4	85.7	[**1a**·BPh$_2$]$^-$-TS$_{H4}$	–
H-5	91.7	**1a**-TS$_{H5}$	+5.4	H-5	91.8	[**1a**·BPh$_2$]$^-$-TS$_{H5}$	+22.0

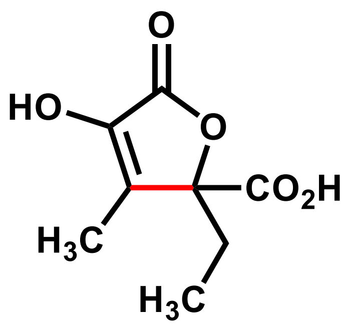
The gas-phase DFT calculations (B97-D3/Def2-TZVP) were carried out using Gaussian 16.

1) Dimakos, V.; Su, H. Y.; Garrett, G. E.; Taylor, M. S. *J., Am. Chem. Soc.* **2019**, *141*, 5149.

Summary

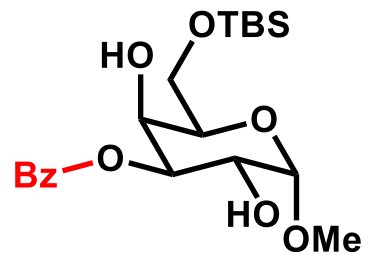


Aldol reaction with pyruvic acid

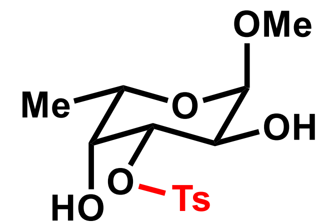


90%

Acylation, sulfonylation and alkylation of carbohydrates

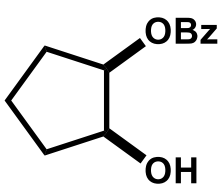


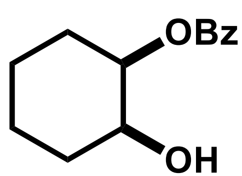
95%



97%

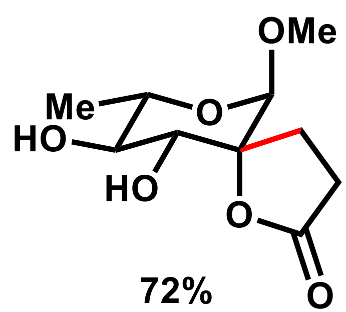
Highselectivity of diols





8 : 1

C-H Alkylation of Carbohydrates



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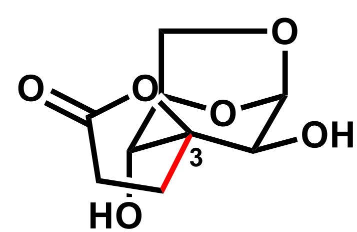

68%

1) Dimakos, V.; Su, H. Y.; Garrett, G. E.; Taylor, M. S. *J., Am. Chem. Soc.* **2019**, *141*, 5149.