

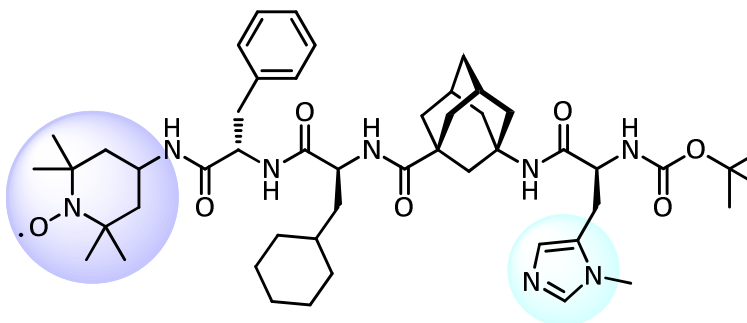
EN ROUTE TO MULTICATALYSIS:

Kinetic Resolution of *trans*-Cycloalkane-1,2-diols
via Oxidative Esterification and Alcohol Cross-Coupling

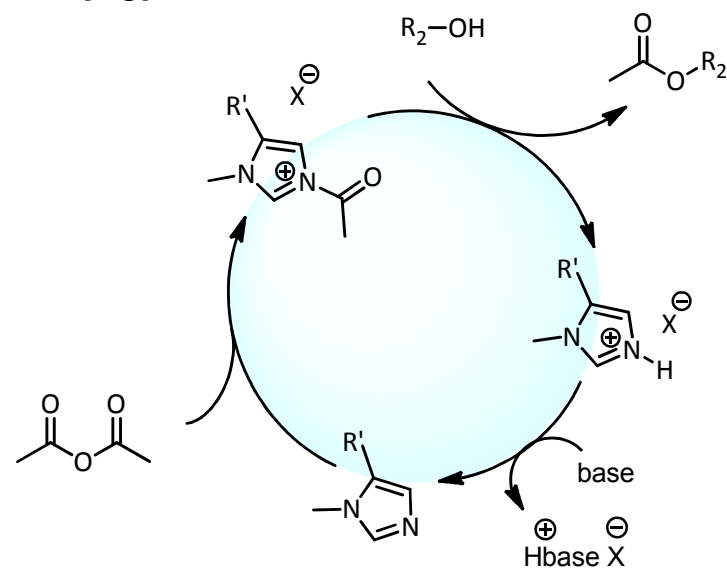
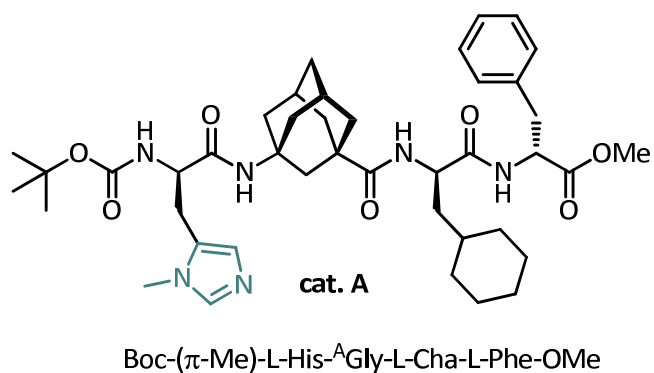
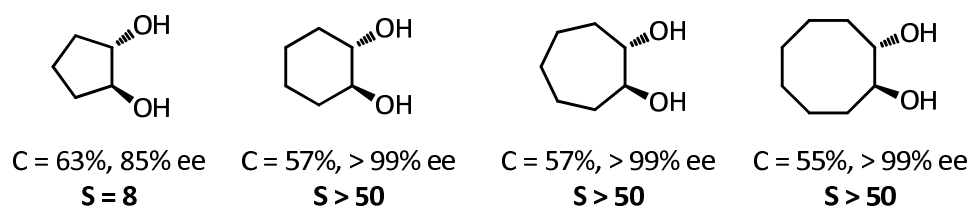
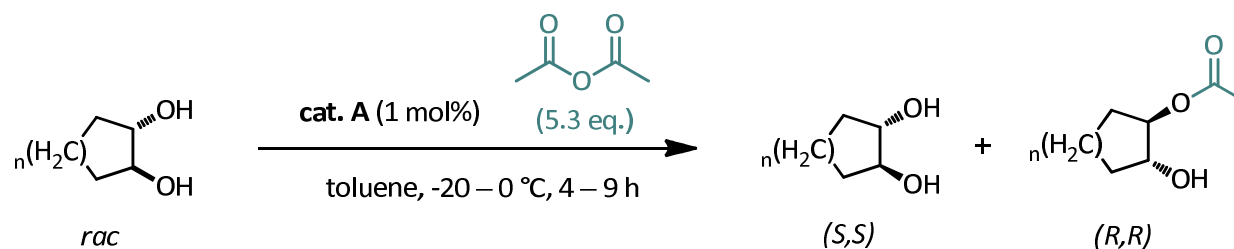
14.03.2014

Christine Hofmann

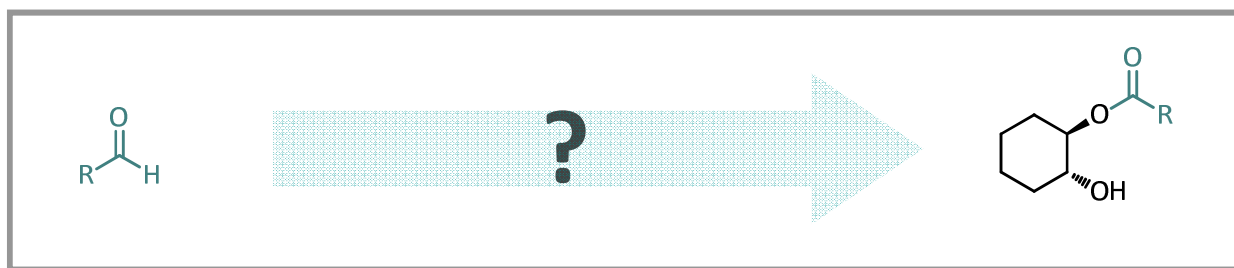
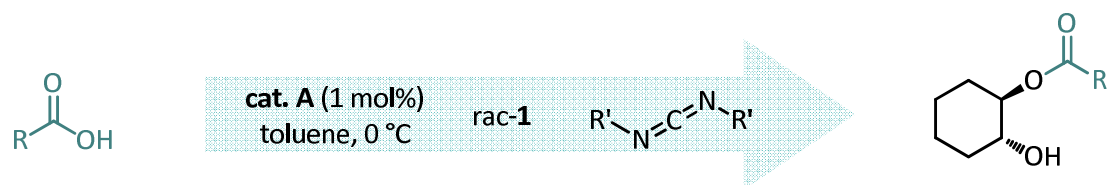
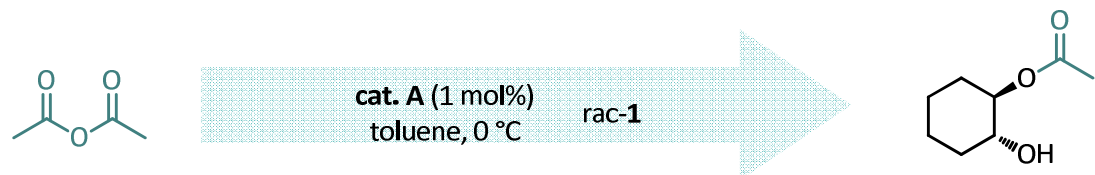
*Institute of Organic Chemistry
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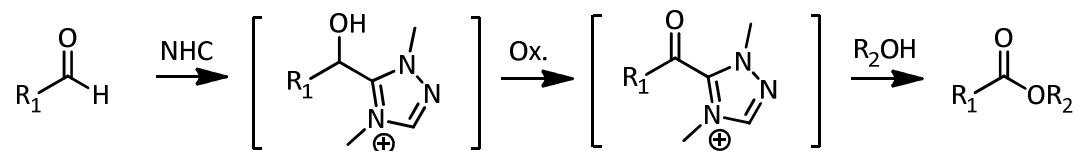
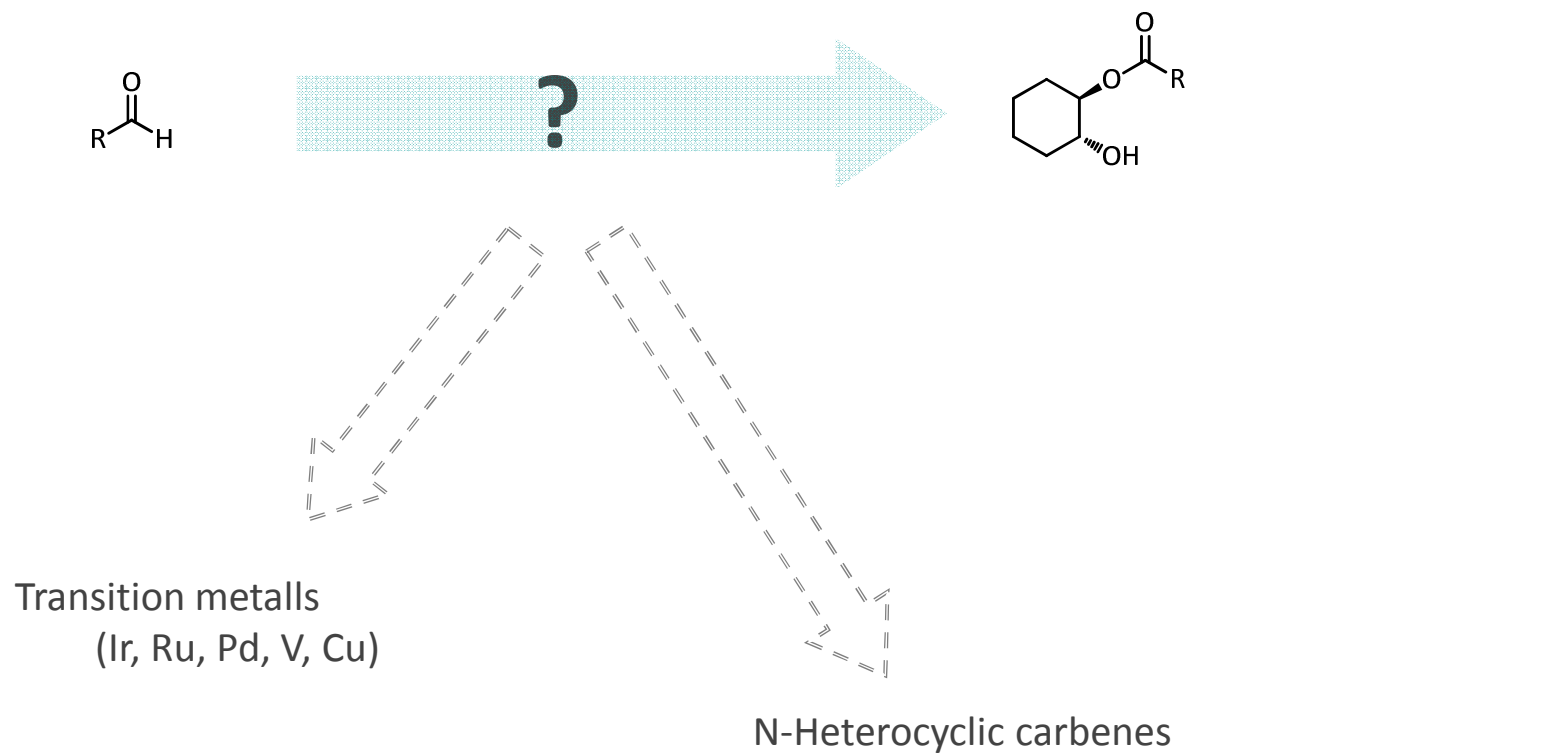
Introduction: Kinetic Resolution of *trans*-Cycloalkane-1,2-diols



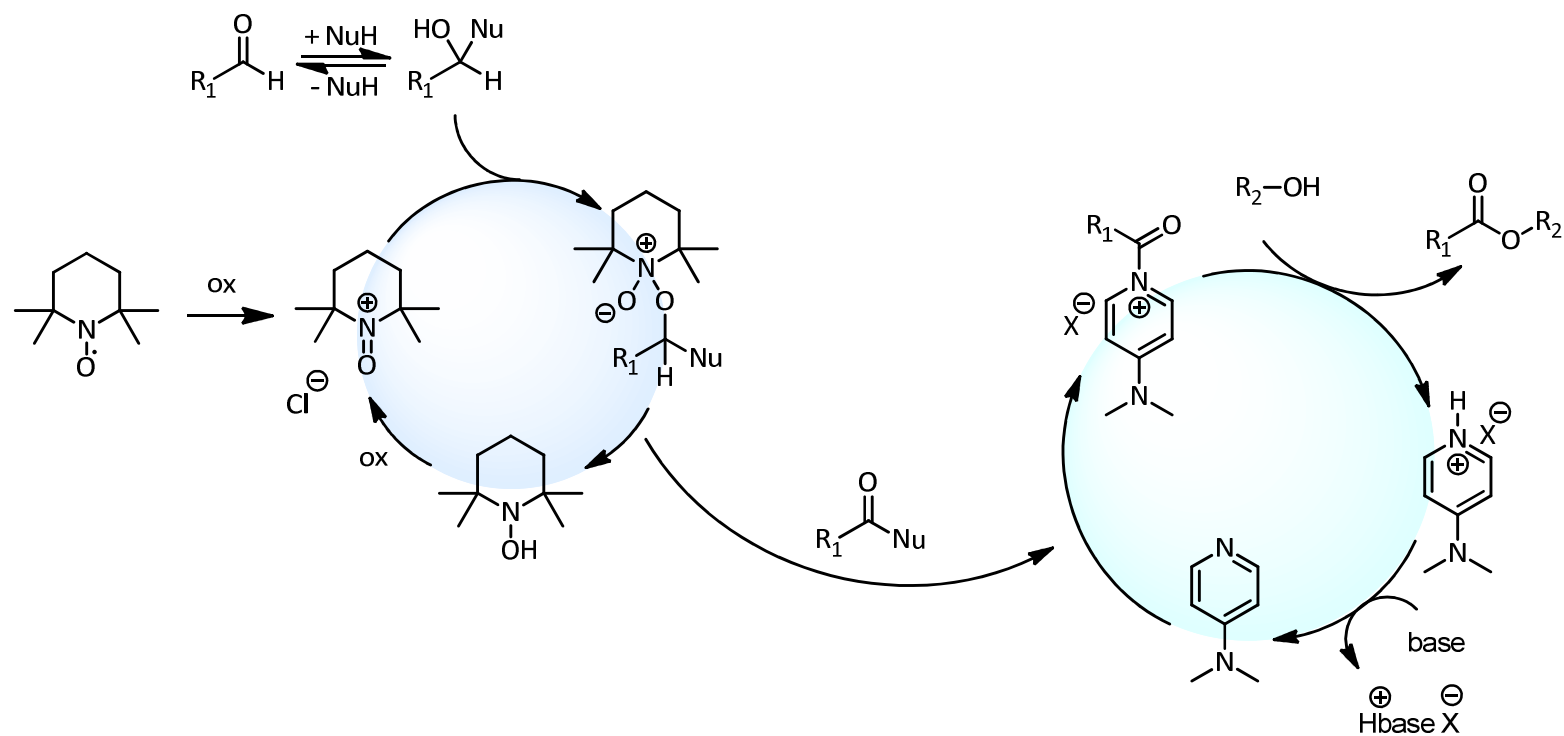
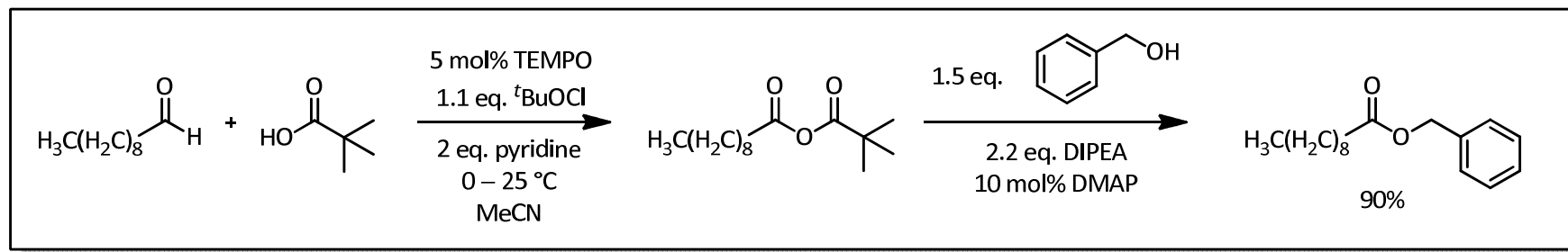
Part I: Motivation



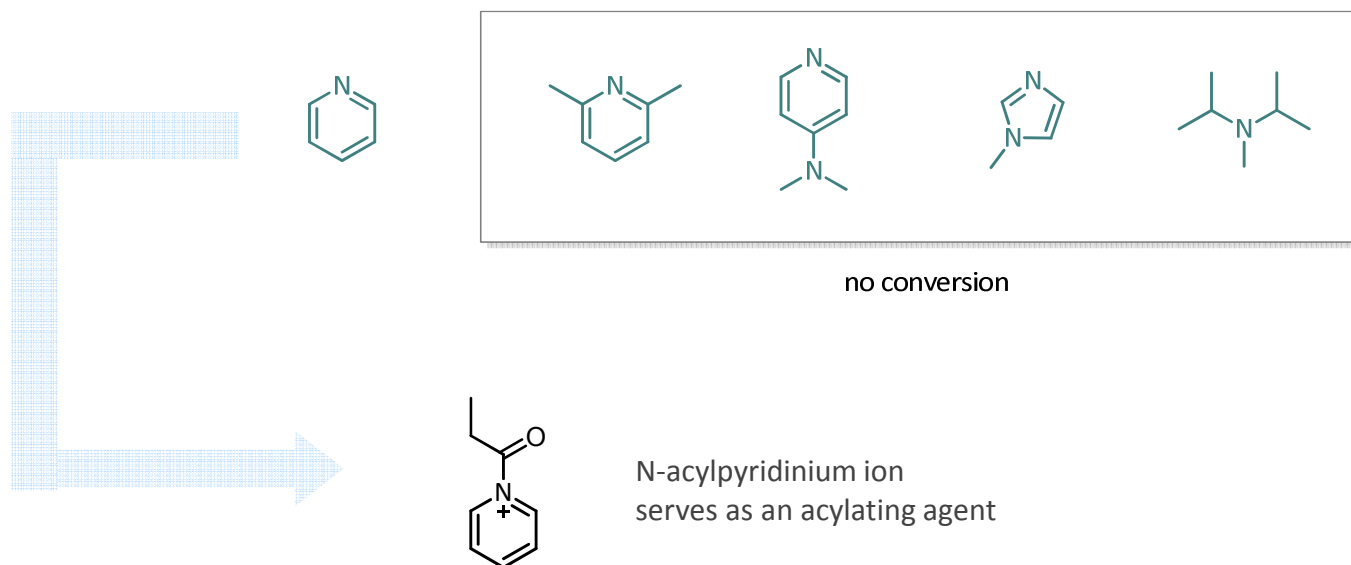
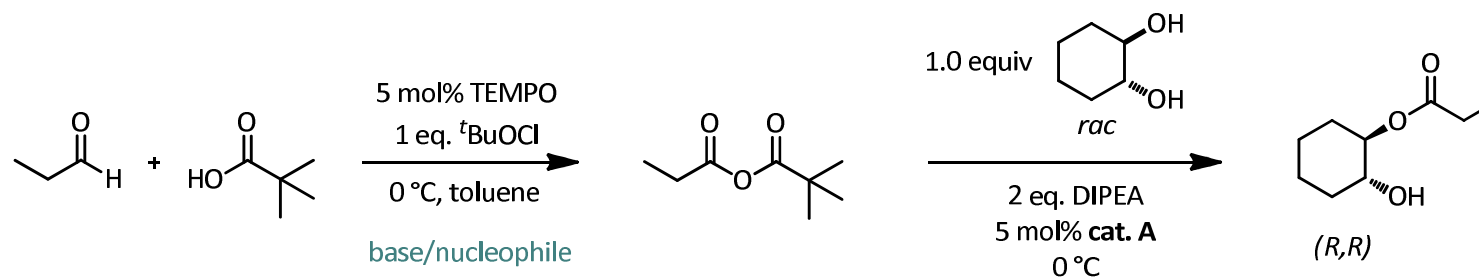
Oxidative Esterification



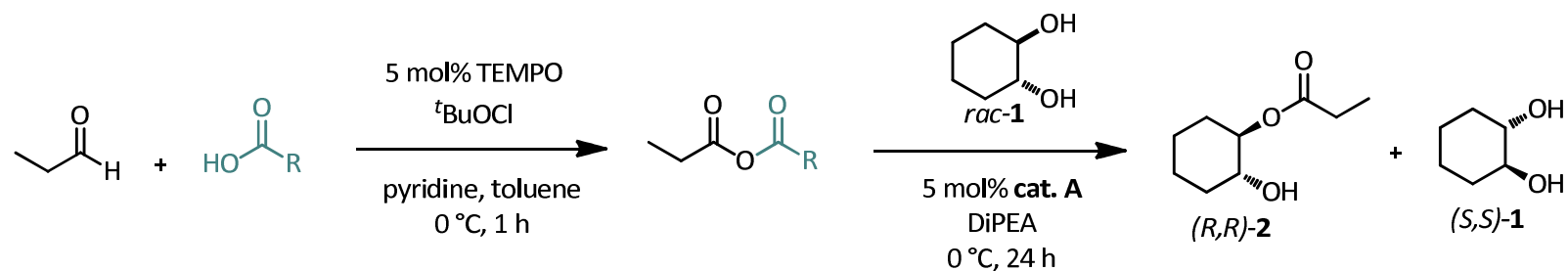
“Szpilman ester”



Optimization Studies I: The Role of Pyridine

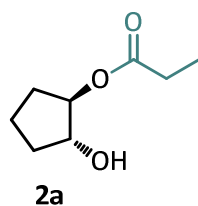
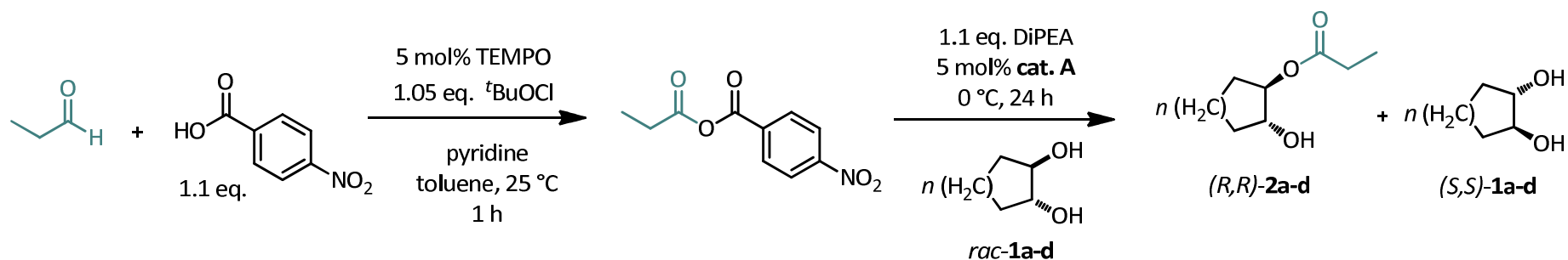


Optimization Studies II: Acid Screening

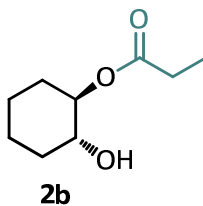


pK_a	~ 13.5	~ 13.0	~ 11.5	~ 10.0	~ 9.5	9.0
Conv.	12%	23%	27%	28%	38%	49%
ee(1)	12%	27%	28%	29%	48%	81%
ee(2)	92%	90%	78%	73%	78%	86%
S	27	25	11	13	9	33

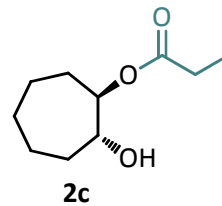
Substrate Scope: Diols



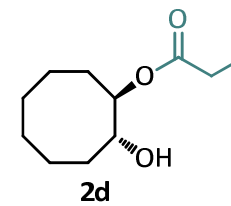
C = 70%
ee(**1a**) = 76%
ee(**2a**) = 31%
S = 4



C = 47%
1b, 46%, ee = 81%
2b, 43%, ee = 88%
S = 39

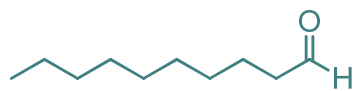
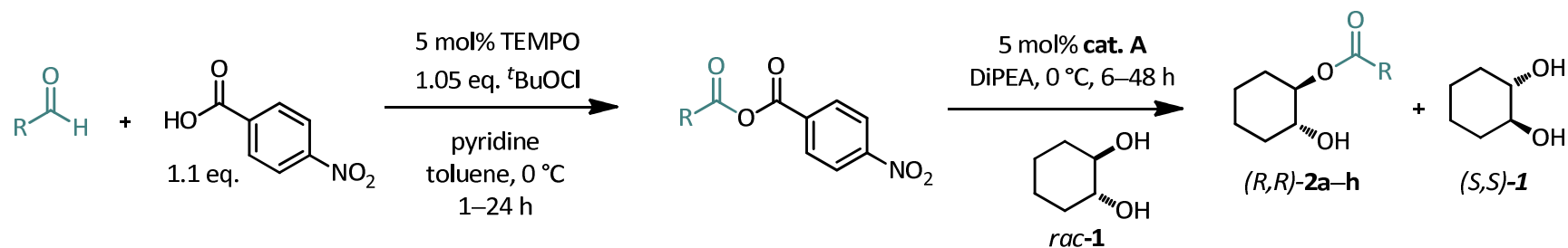


C = 49%
1c, 48%, ee = 86%
2c, 43%, ee = 88%
S = 43

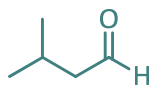


C = 50%
1d, 39%, ee = 94%
2d, 47%, ee = 93%
S > 50

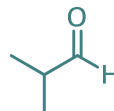
Various Aldehydes



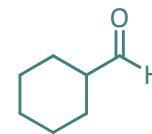
C = 47%
1, 48%, ee = 79%
2a, 42%, ee = 88%
S = 38



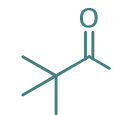
C = 48%
1, 43%, ee = 76%
2b, 46%, ee = 82%
S = 24



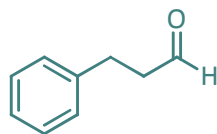
C = 44%
1, 43%, ee = 72%
2c, 40%, ee = 90%
S = 40



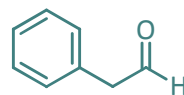
C = 46%
1, 41%, ee = 52%
2d, 39%, ee = 62%
S = 7



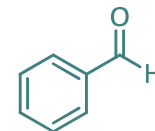
C = 4%
1, ee = 79%
2e, ee = 90%
S = 25



C = 50%
1, 44%, ee = 85%
2f, 44%, ee = 82%
S = 27

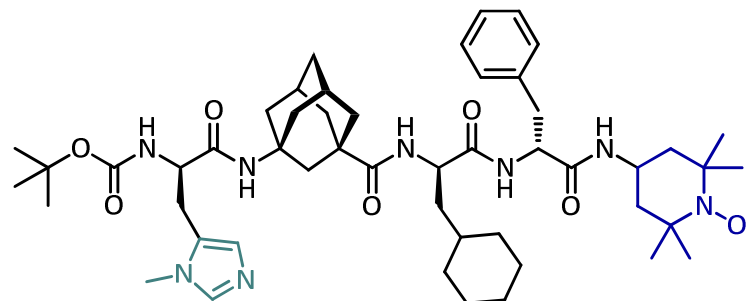


C = 35%
1, 58%, ee = 50%
2g, 27%, ee = 93%
S = 47

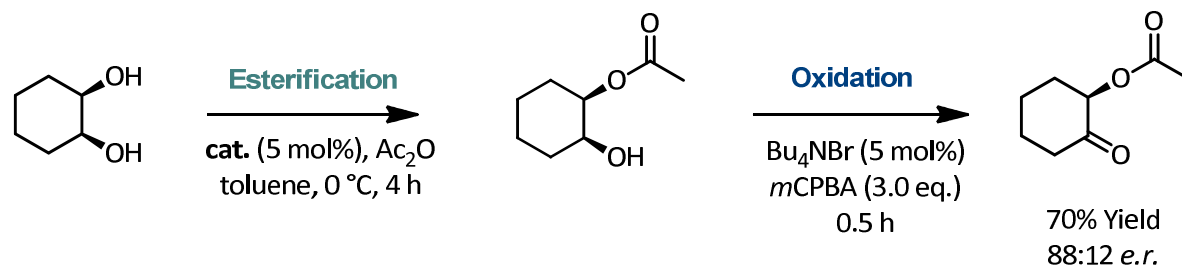


C = 7%
1, ee = 6%
2h, ee = 78%
S = 9

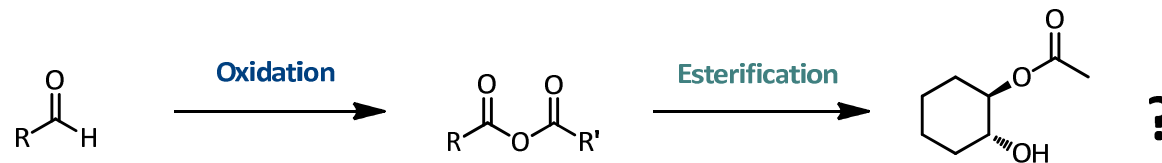
Motivation II



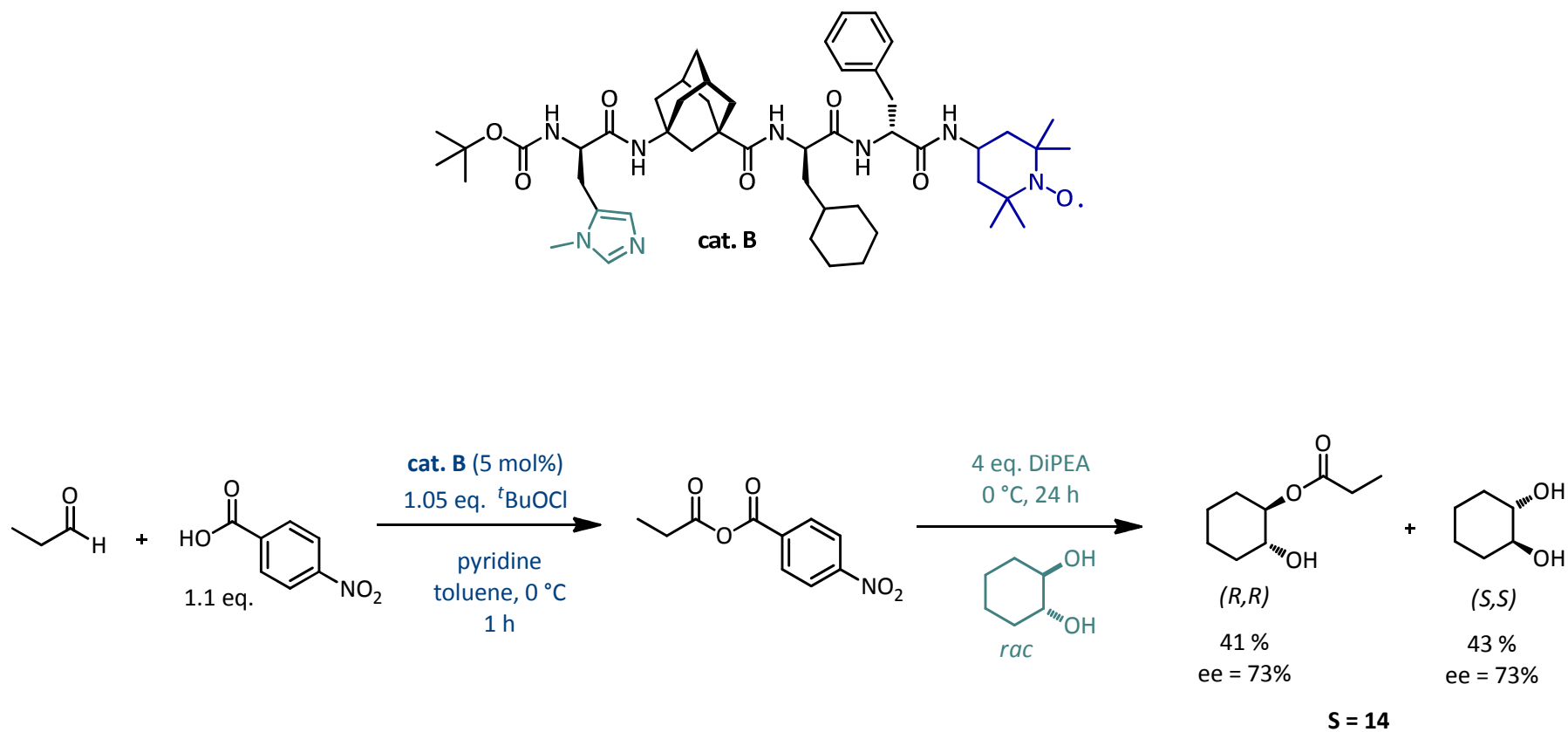
Previous work: Desymmetrization of *meso*-diol



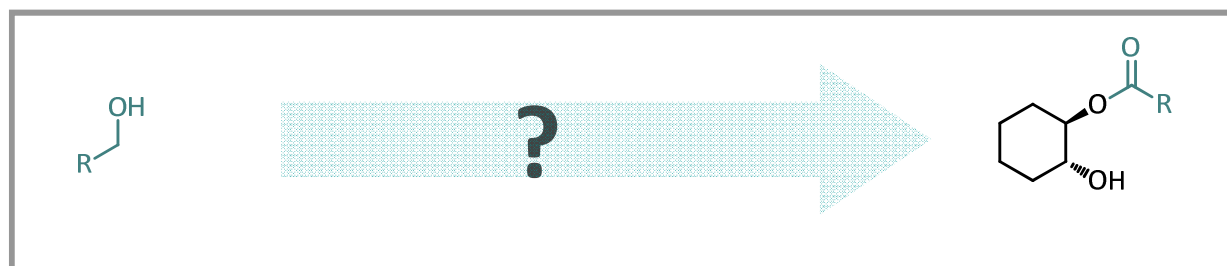
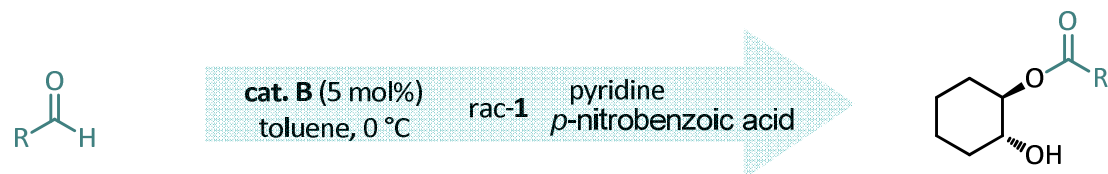
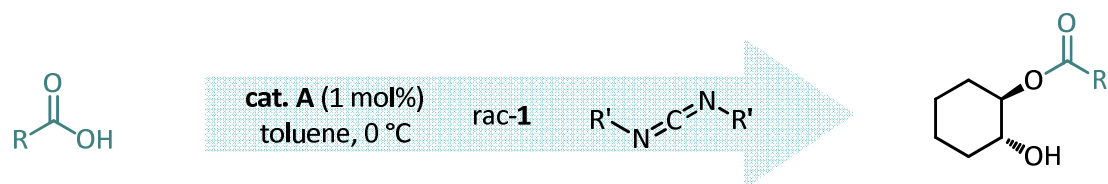
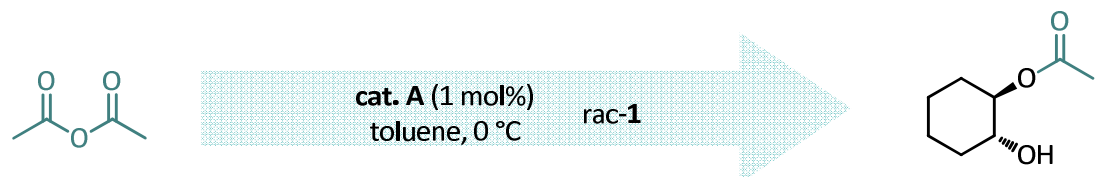
This work: Oxidative esterification of diol



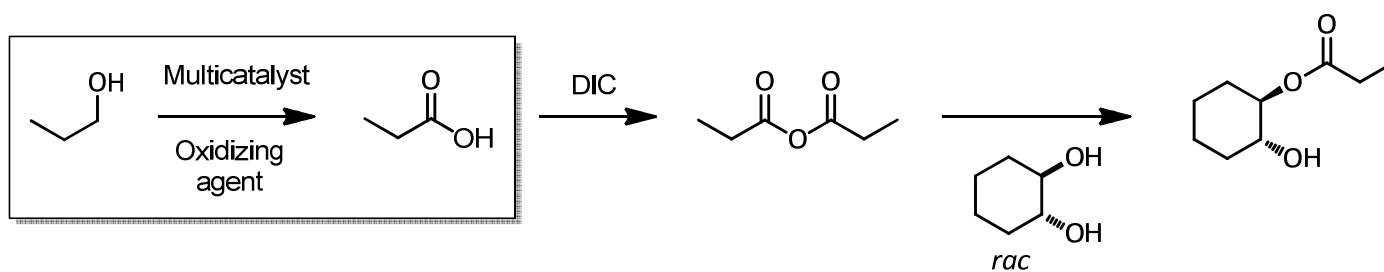
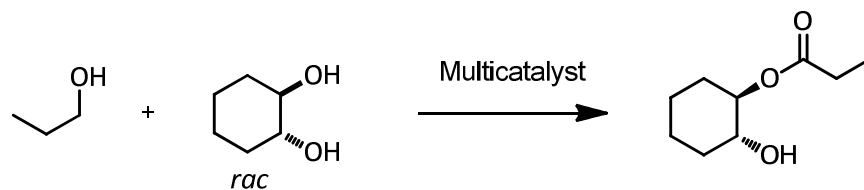
Multicatalytic System



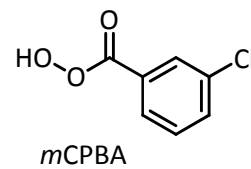
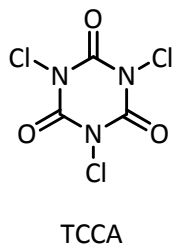
Part II: Motivation



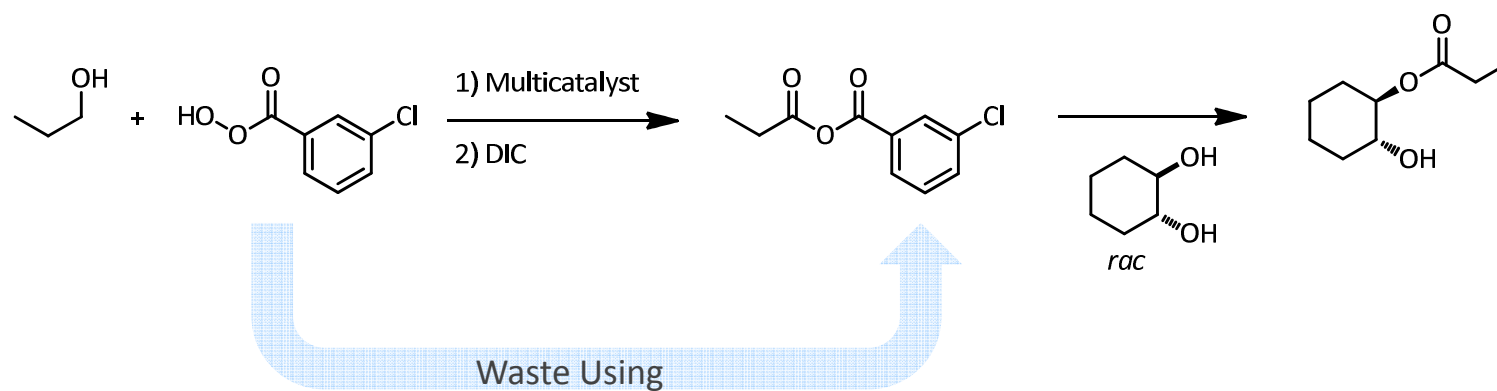
Enantioselective Alcohol Cross-Coupling



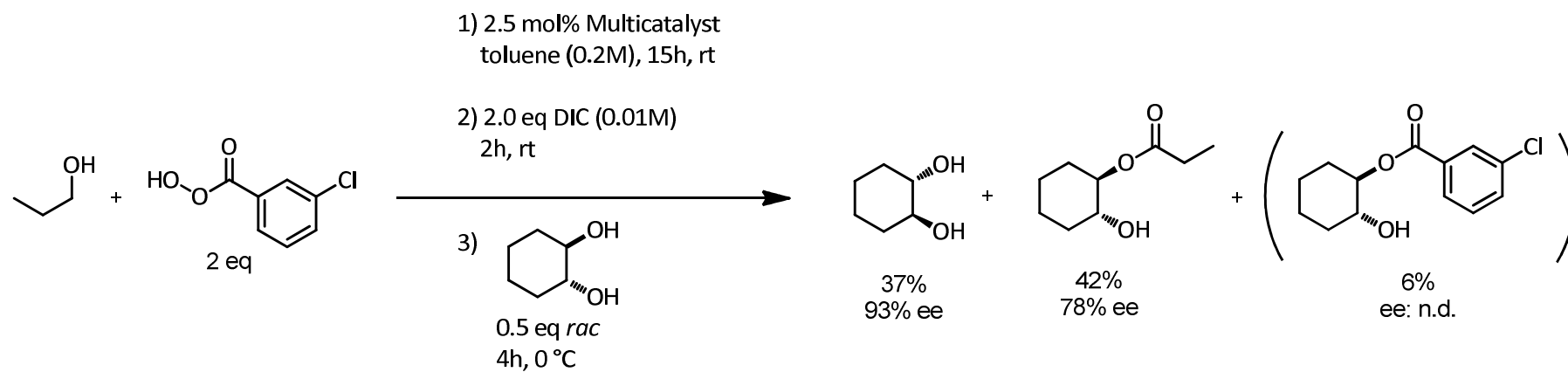
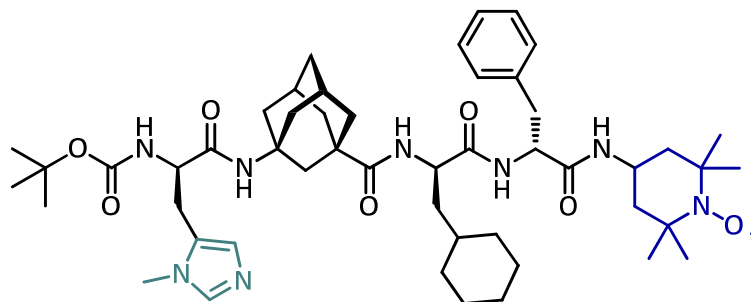
Oxidation agents



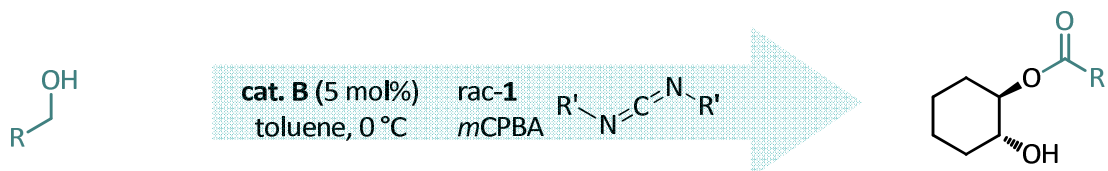
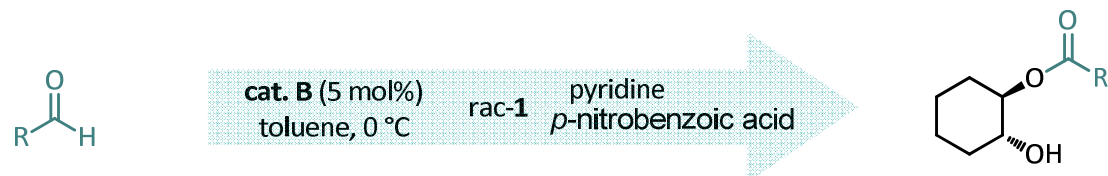
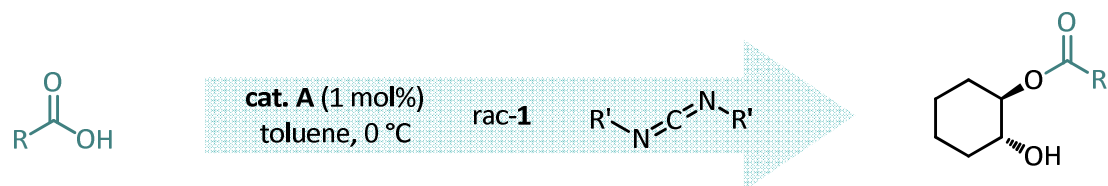
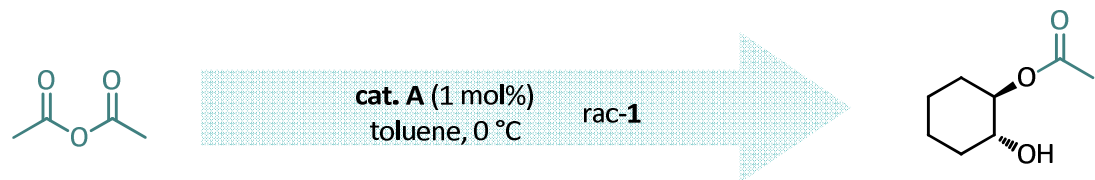
Enantioselective Alcohol Cross-Coupling



Enantioselective Alcohol Cross-Coupling



Summary



Thank you for your attention!