NICOLAUS COPERNICUS UNIVERSITY
IN TORUŃ

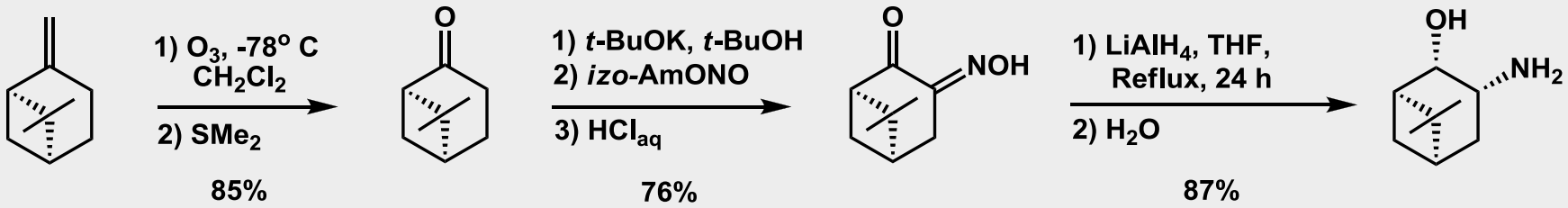
SYNTHESIS OF CHIRAL AMINES USING TERPENYL SPIROBORATE ESTERS AS CATALYSTS

Marta Ćwiklińska

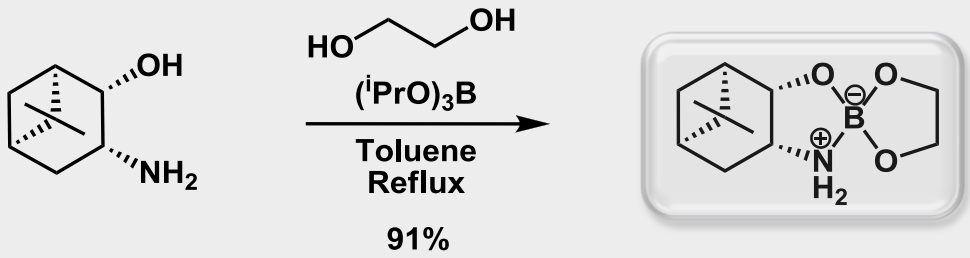
Marek P. Krzemiński

NICOLAUS COPERNICUS UNIVERSITY IN TORUŃ

Synthesis of spiroborate ester 1



m.p. 76-77 °C



1

m.p. 110-113 °C

^{11}B NMR [δ ppm]: 10,24 (s)

M. Krzemiński, A. Wojtczak, *Tetrahedron Lett.* **2005**, *46*, 8299.
C. M. Binder, A. Bautista, M. Zaidlewicz, M. Krzeminski, A. Oliver, B. Singaram, *J. Org. Chem.* **2009**, *74*, 2337.
M. P. Krzemiński, M. Ćwiklińska, *Tetrahedron Letters*, **2011**, *52*, 3919-3921.

Synthesis of imines

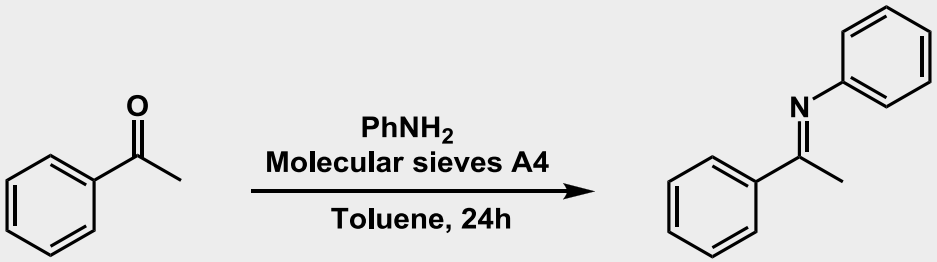
Synthesis of (*E*)-*N*-(1-phenylethylidene)methanamine (2)

(93%) (7%)

2

Cobas , A.; Guitian, E.; Castedo, L. *J. Org. Chem.*, **1993**, *58*, 3113.

Synthesis of (*E*)-*N*-(1-phenylethylidene)aniline (3)



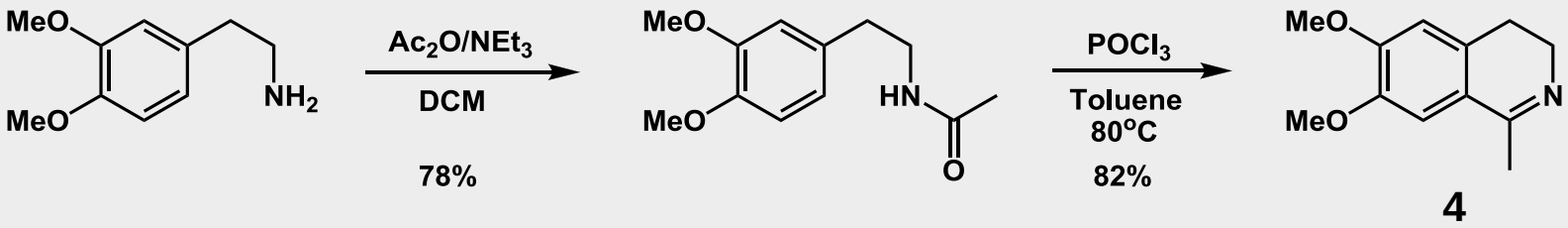
(> 99%)

3

Taguchi, K.; Westheimer, F. H. *J. Org. Chem.*, **1971**, *36*, 1570.

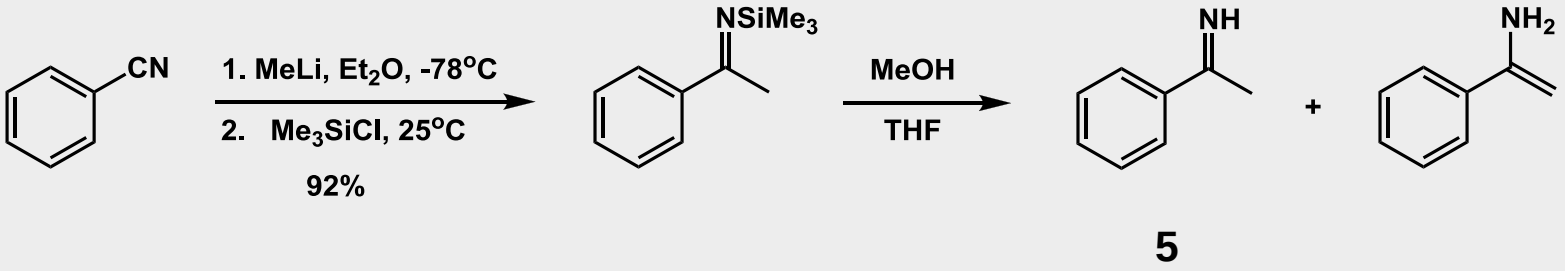
Synthesis of imines

Synthesis of 6,7-dimethoxy-1-methyl-3,4-dihydroisoquinoline (4)



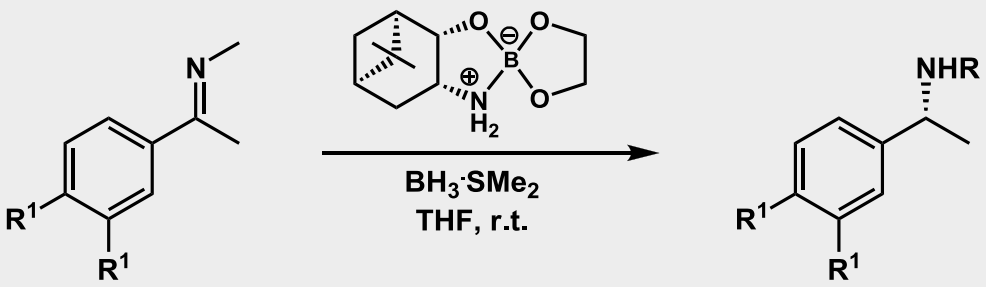
Whaley, W. M.; Govindachari, T. R. *Organic reaction Vol. VI*, John Wiley & Sons, New York, 1951, p. 74.

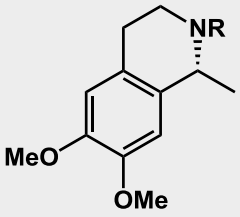
Synthesis of 1-phenylethanimine (5)



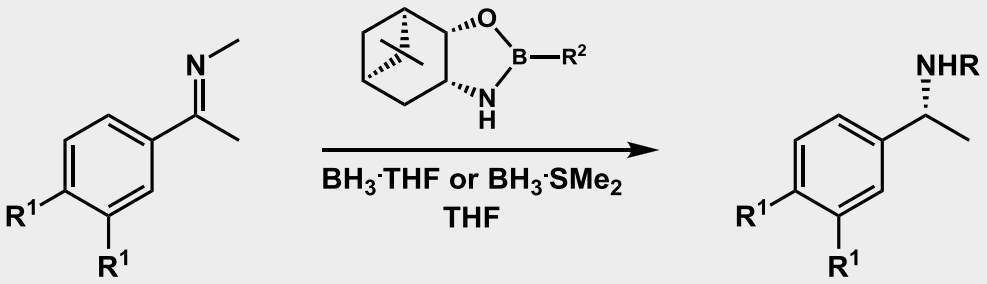
E. Canales, E. Hernandez, J.A. Soderquist, *J. Am. Chem. Soc.,* **2006**, *128*, 8712-8713
D. A. Cogan, J. A. Ellman, *J. Am. Chem. Soc.,* **1999**, *121*, 268-269.

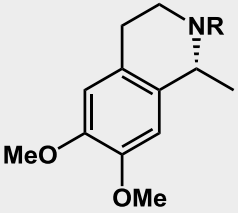
Borane reduction of imines 2-5 catalyzed by spiroborate ester 1



Imine	R	R¹	Yield, %	Ee, %
5	H	H	71	73
2	Me	H	84	50
3	Ph	H	90	11
4			71	93

Borane reduction of imines 2-4 catalyzed by oxazaborolidines



Imine	R	R^1	R^2	Yield, %	Ee, %
2	Me	H	H	77	50
3	Ph	H	H	29	3.1
3	Ph	H	-O^{i}Pr	93	2.2
4			-O^{i}Pr	56	0

Conclusions

- Spiroborate ester **1** was tested in borane reduction of prochiral cyclic and acyclic imines, and in all cases exhibited better catalytic ability than corresponding oxazaborolidines. Only for (*R*)-*N*-methyl-1-phenylethanamine obtained enantiomeric excess was identical (50 %).

- The best results were obtained for (*R*)-6,7-dimethoxy-1-methyl-1,2,3,4-tetrahydroisoquinoline (71 % of yield and 93 % ee).

- For the reduction of acetophenone derived imines, the substituent size on nitrogen atom in imine molecule was the dominant factor affecting the enantioselective reduction by the spiroborate catalyst. The smaller substituent occured the better results in enantioselectivity were received.

Marta Ćwiklińska
Marek P. Krzemiński

Nicolaus Copernicus University

In Toruń

Thank you for your attention