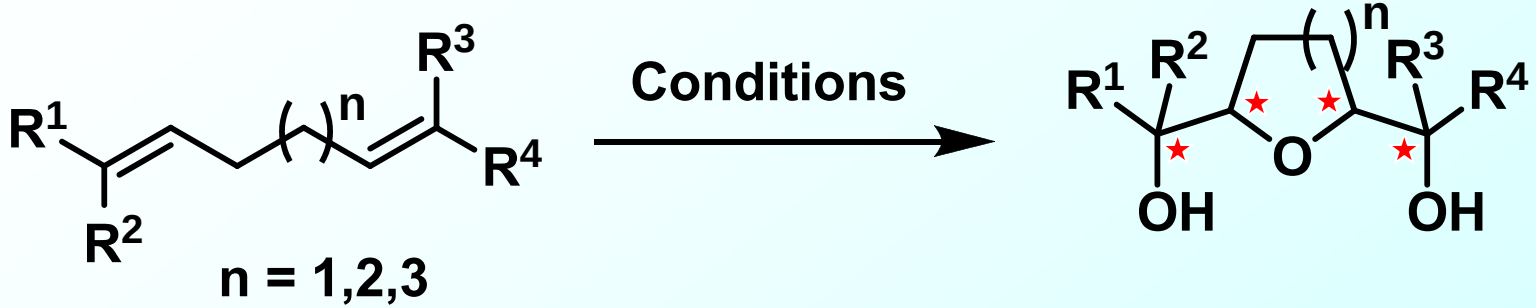
Oxidative Cyclization of Dienes mediated by Transition-Metal-Oxo Species.

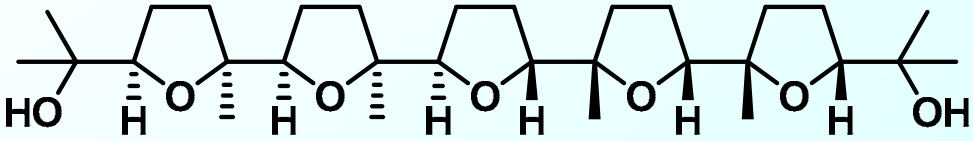
Mathieu Candy

Séminaire bibliographie STeRéO

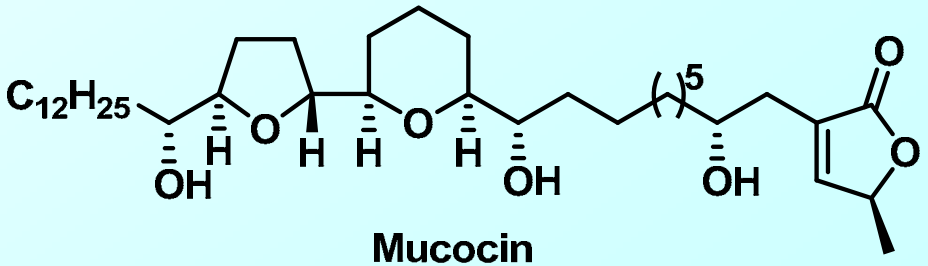
12 Novembre 2009

Introduction





glabrescol

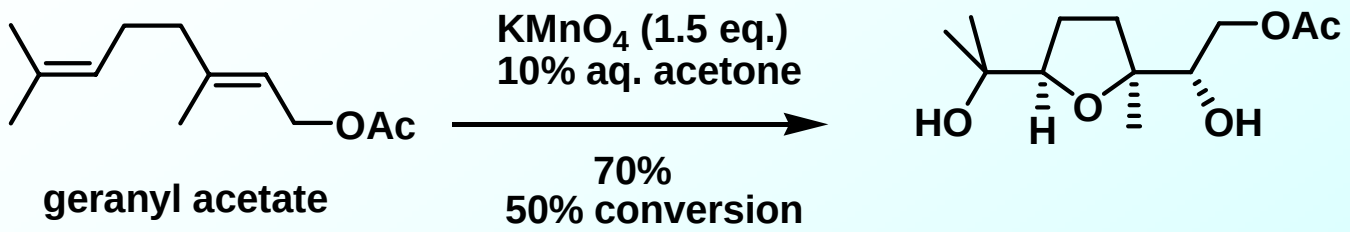


Mucocin

Piccialli, V. *Synthesis* **2007**, *17*, 2585.

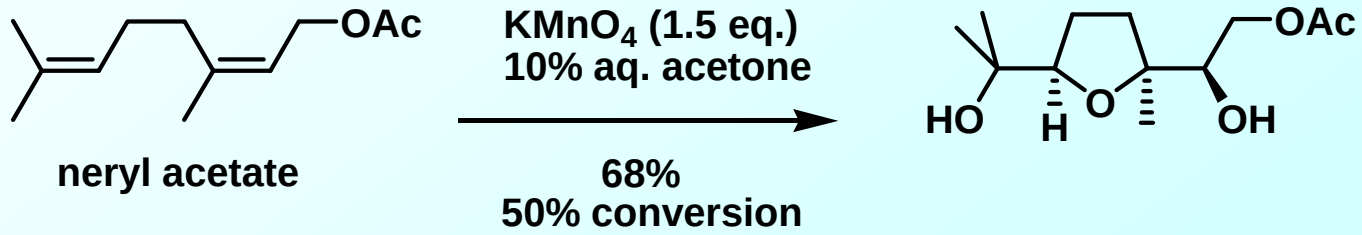
Contents

1.1 Formation of Tetrahydrofurans using $KMnO_4$



geranyl acetate

70%
50% conversion

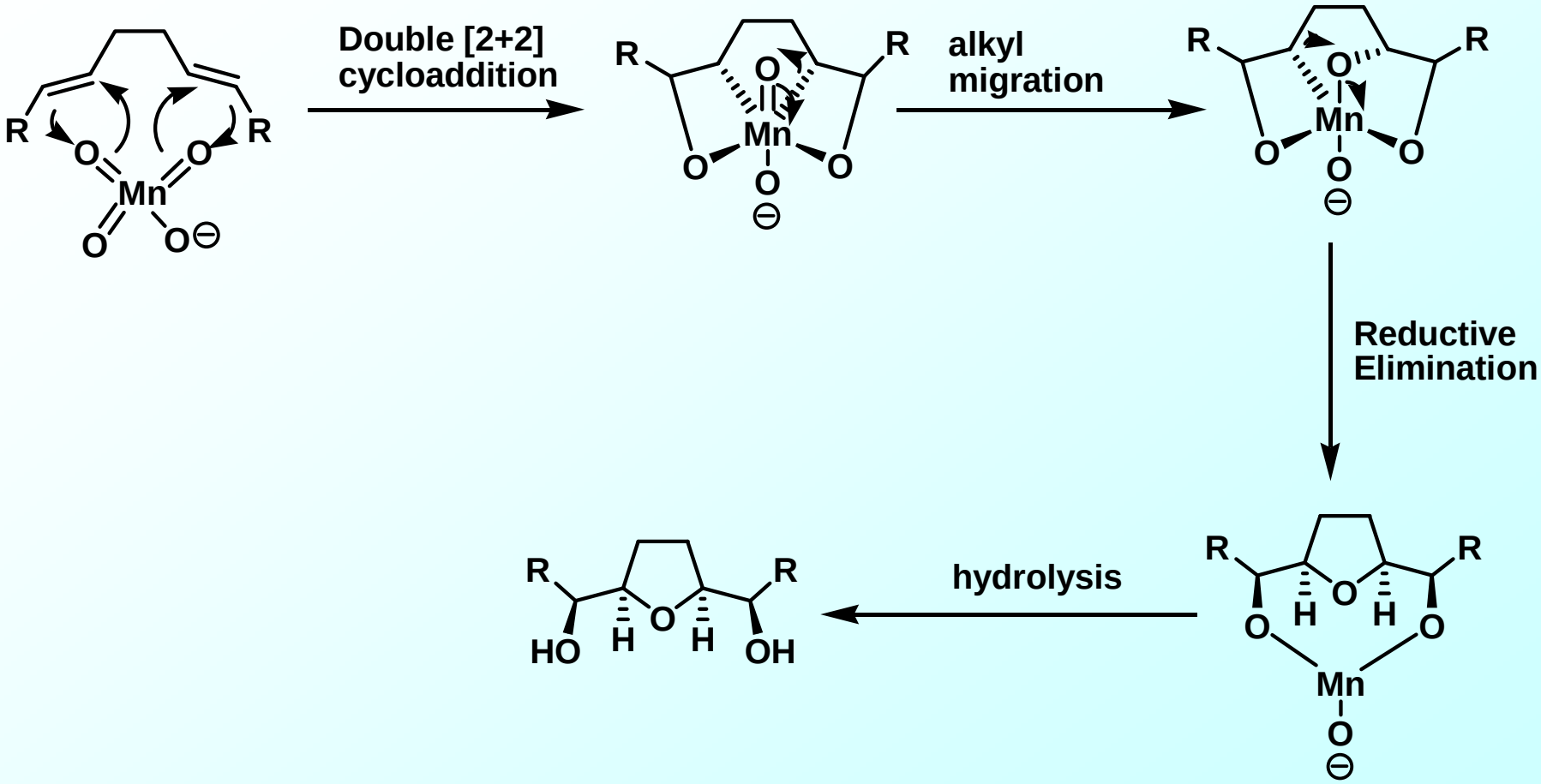


neryl acetate

68%
50% conversion

Klein, E.; Rojahn, W. *Tetrahedron* **1965***,* 21, 2353.
Kötz, A.*;* Steche, T. *J. Pratkt. Chem.* **1924**, 107, 3353.

1.1 Formation of Tetrahydrofurans using $KMnO_4$



Walba, D. M. et *al* . *J. Am. Chem. Soc.* **1979**, *101*, 4396.

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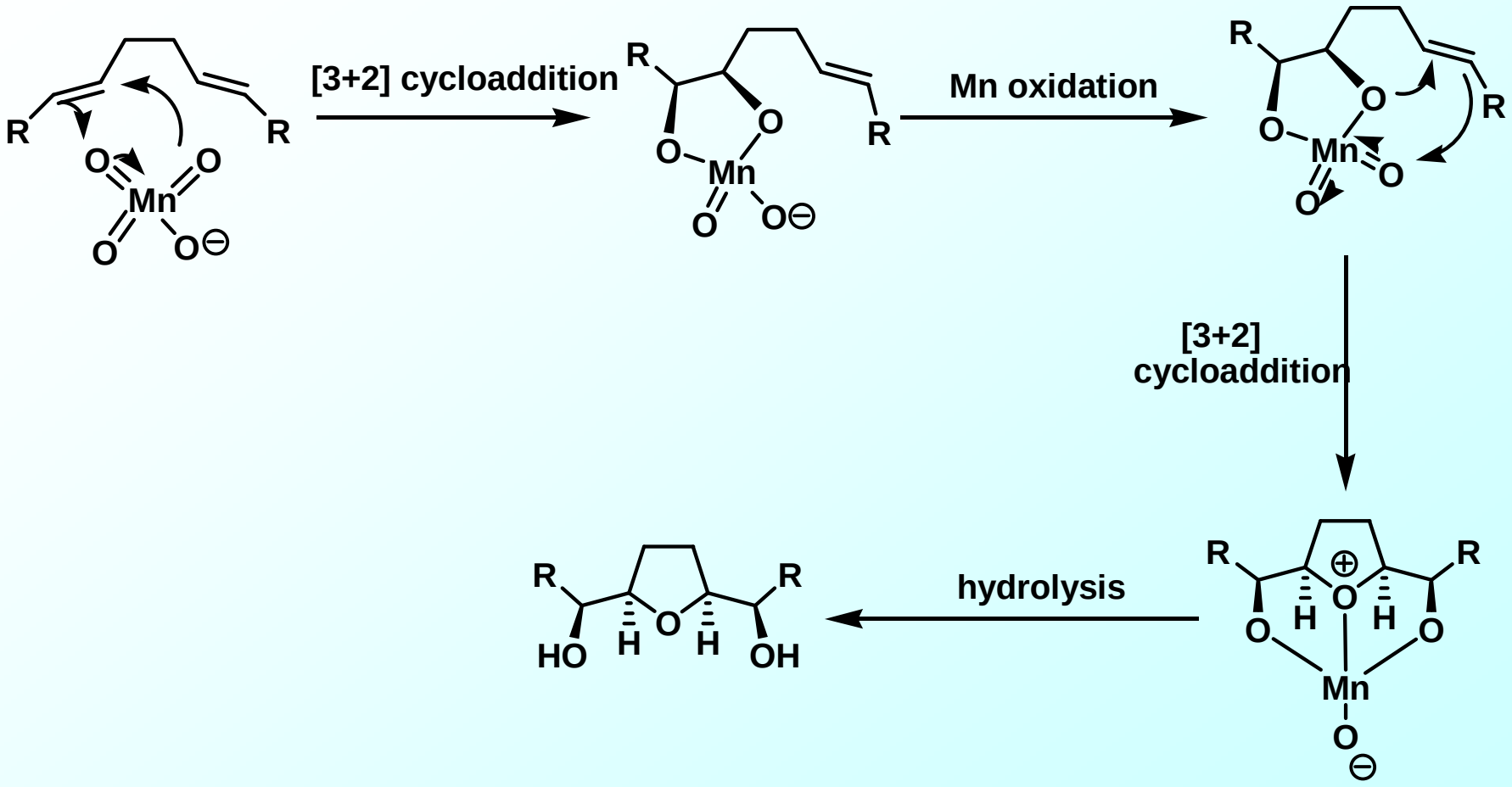
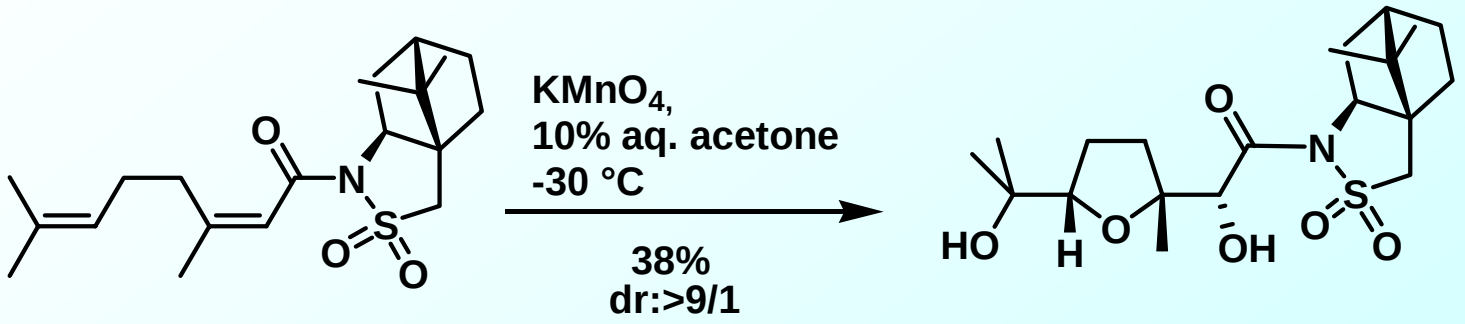


Baldwin, J.E. et *al* . *J. Chem. Soc. Chem. Commun.* **1979**, 918.

1.1 Formation of Tetrahydrofurans using $KMnO_4$



$KMnO_4$: Attack on the electron-deficient double bond

Walba, D. M. et *al* . *J. Am. Chem. Soc.* **1990**, *112*, 5624.

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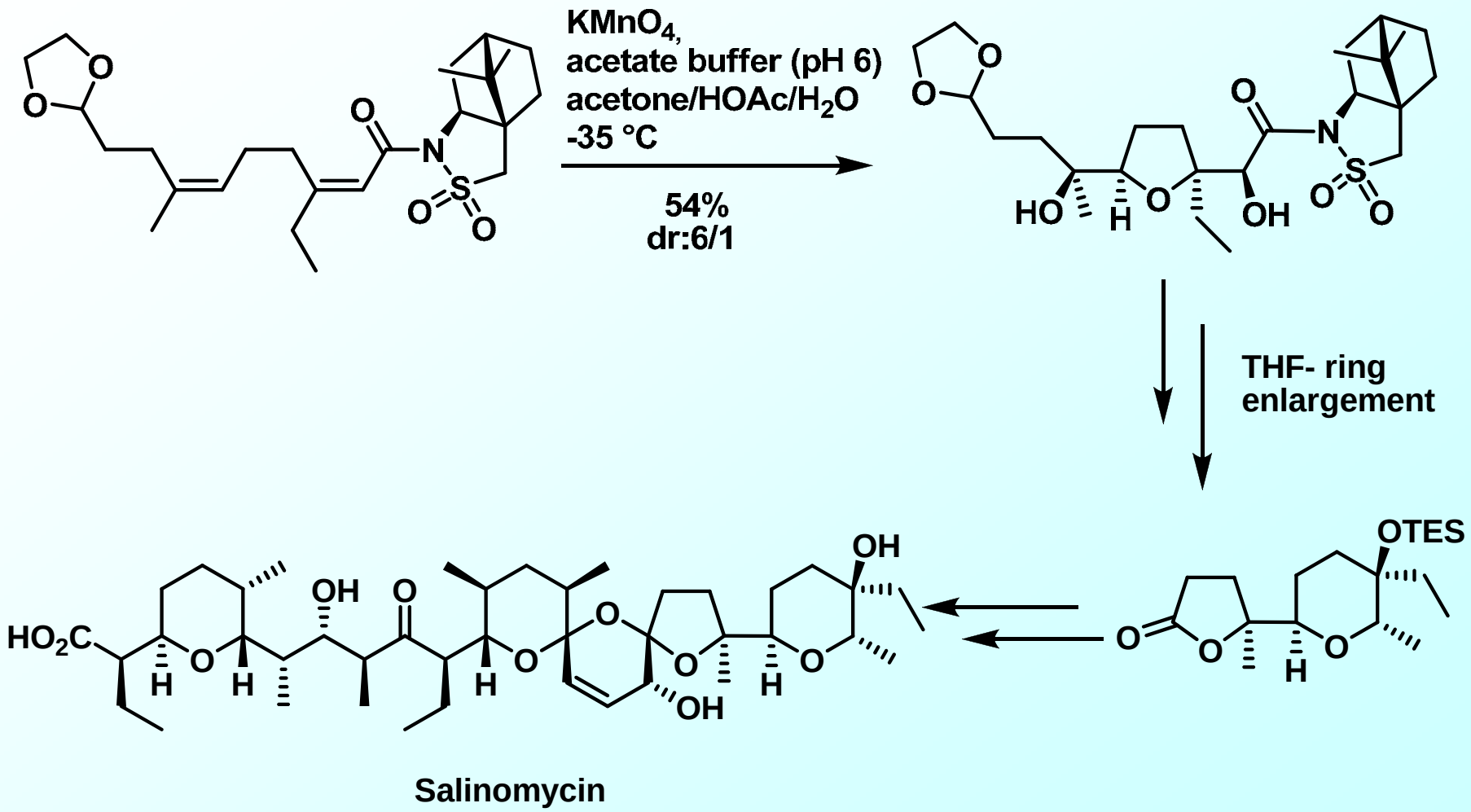
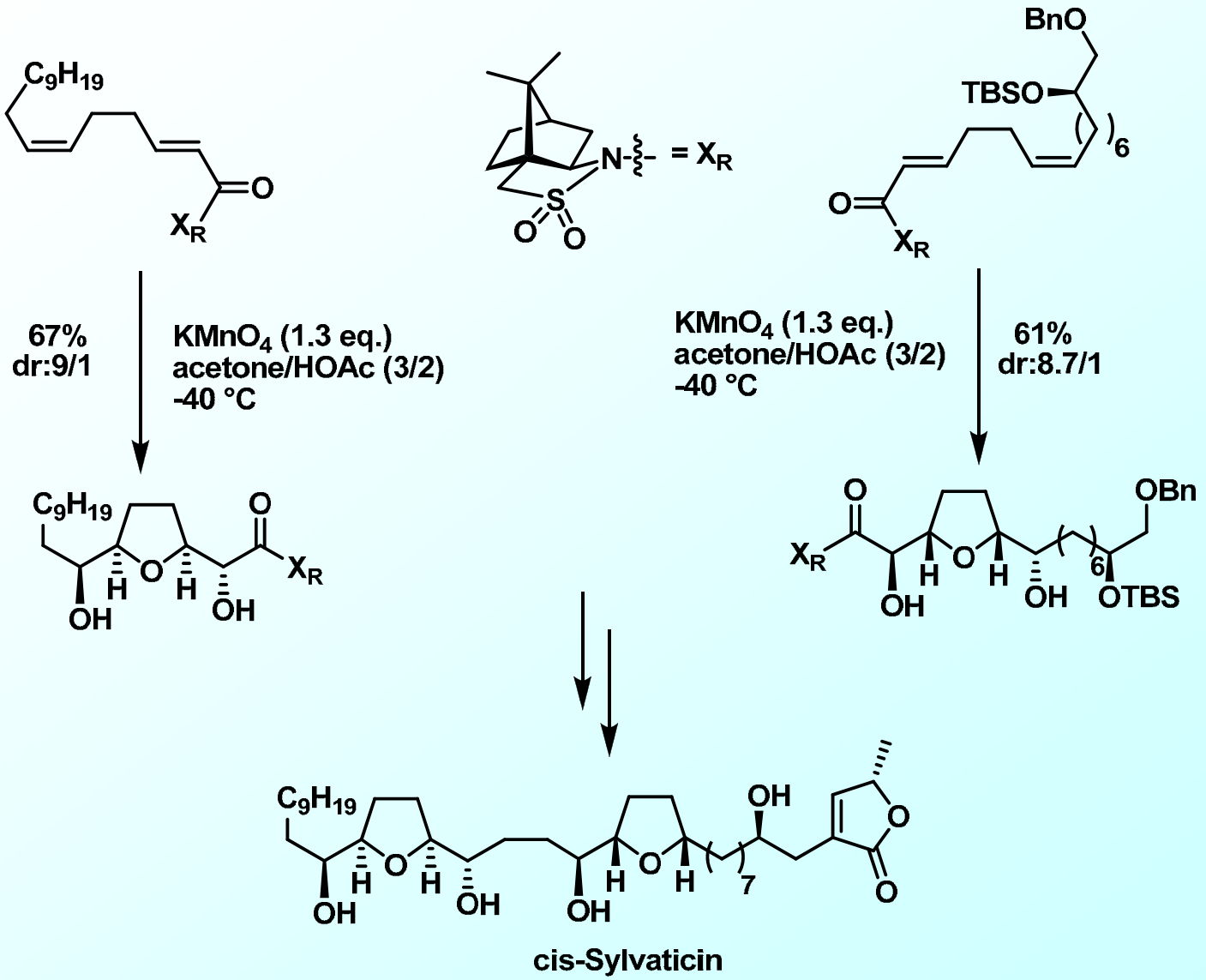


Salinomycin

Kocienski, P.J. et *al. J. Chem. Soc, Perkin Trans. 1* **1998**, 9.

1.1 Formation of Tetrahydrofurans using $KMnO_4$



Brown, R. C. D. et *al. Org. Lett.* **2008**, 2489.

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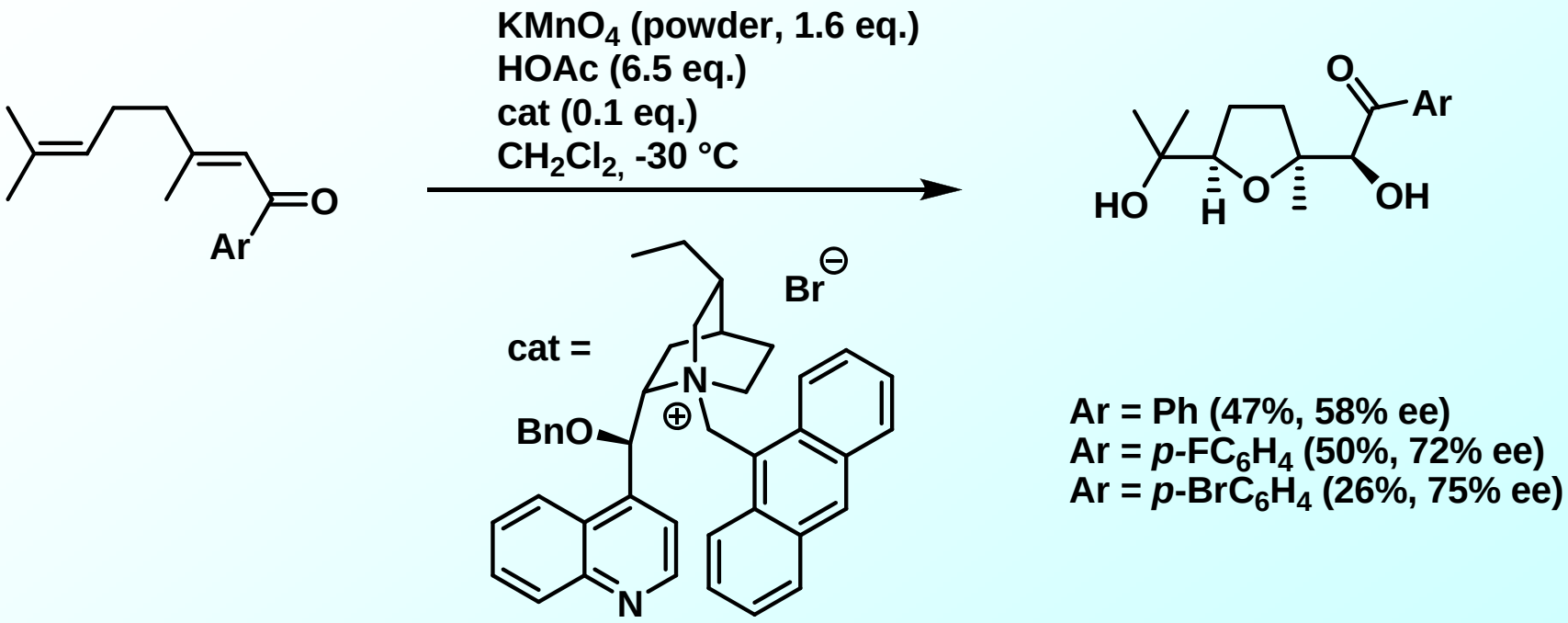
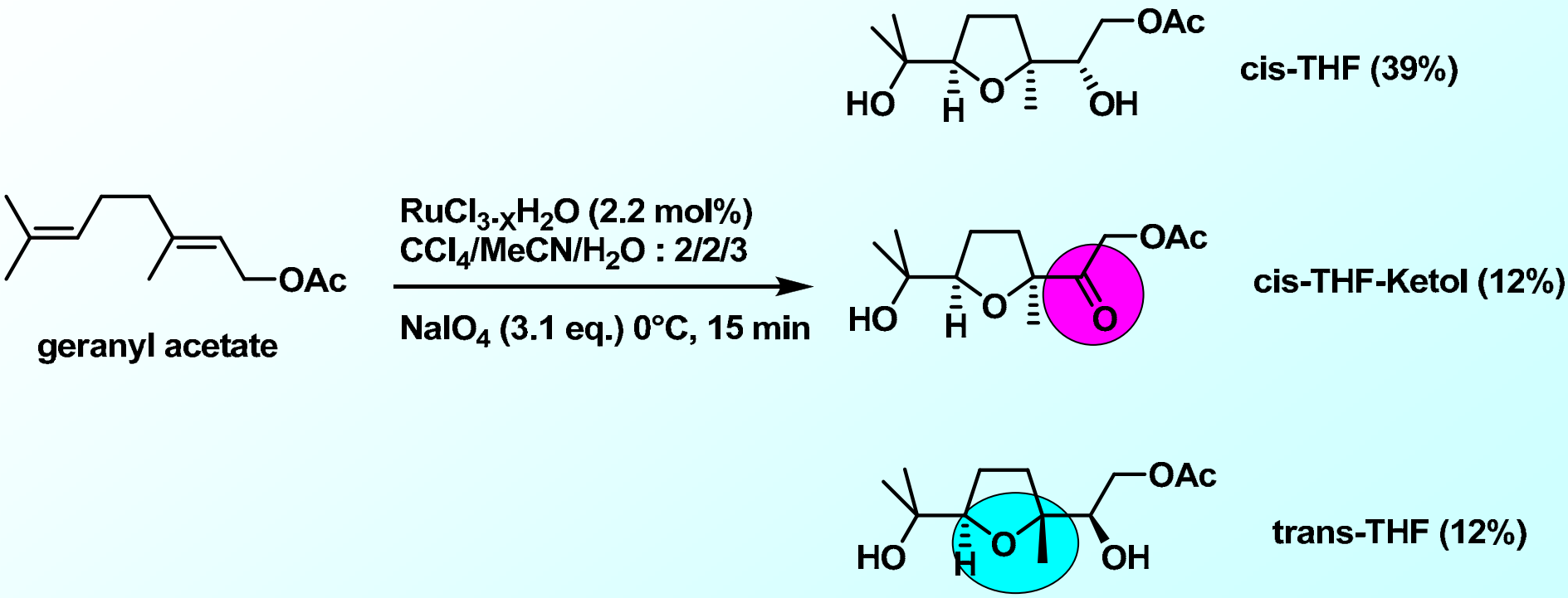


Ar = Ph (47%, 58% ee)
Ar = *p*-FC_6H_4 (50%, 72% ee)
Ar = *p*-BrC_6H_4 (26%, 75% ee)

The unique example of enantioselective oxidative cyclization !!!

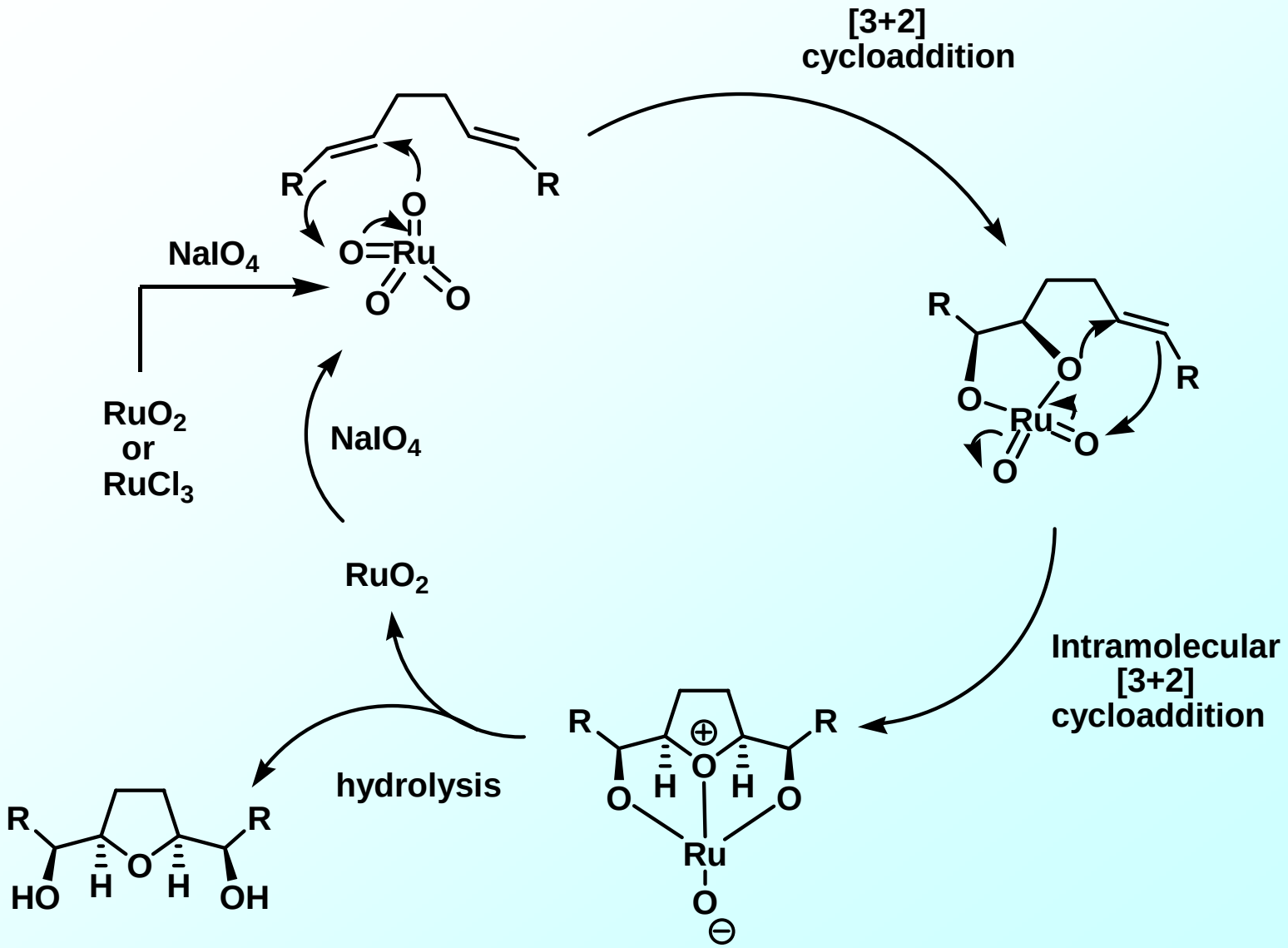
Brown, R. C. D. et *al. Angew. Chem. Int. Ed.* **2001**, *40,* 4496.

1.2 Formation of Tetrahydrofurans using Ru



Sharpless, K.. B. et *al. J. Org. Chem.* **1981**, *46,* 3936.

1.2 Formation of Tetrahydrofurans using Ru



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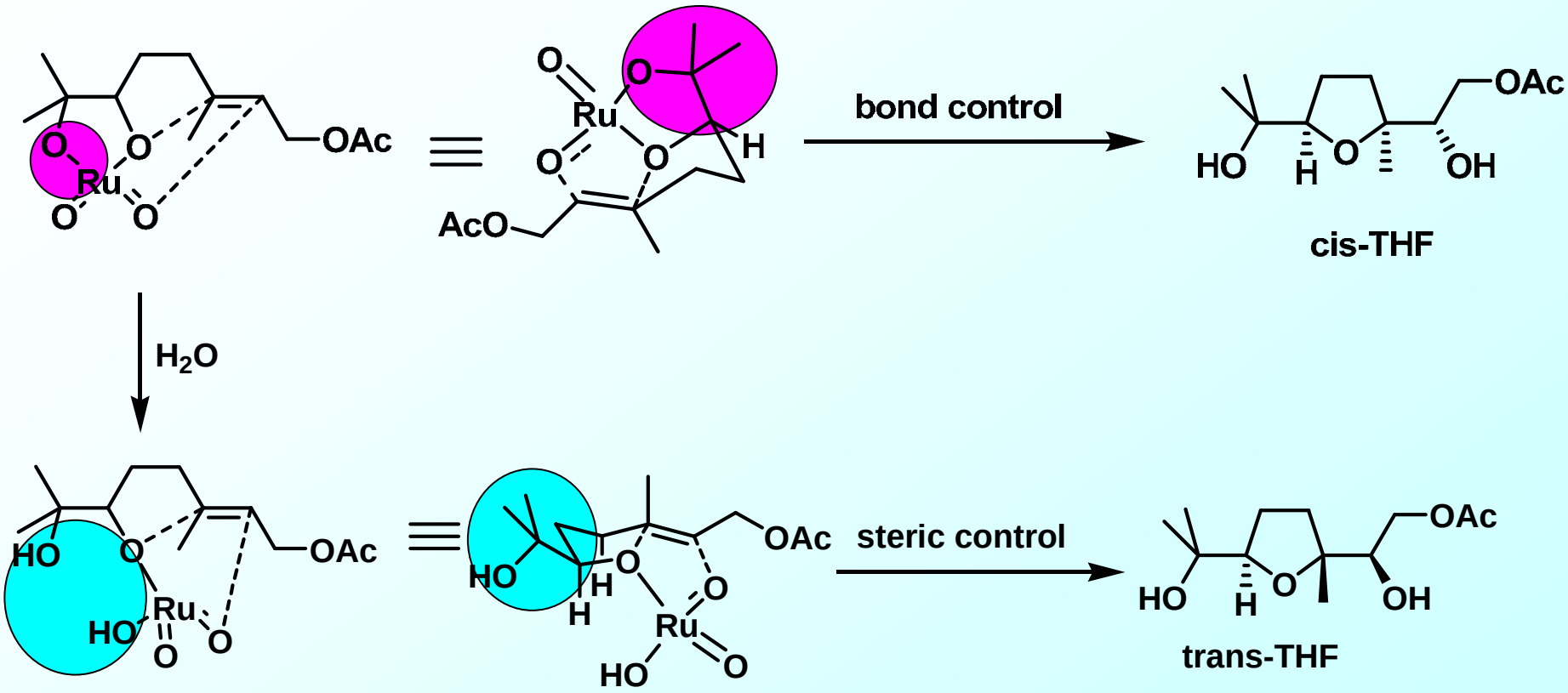

Piccialli, V. *et al. Tetrahedron* **2006**, *62*, 10989.

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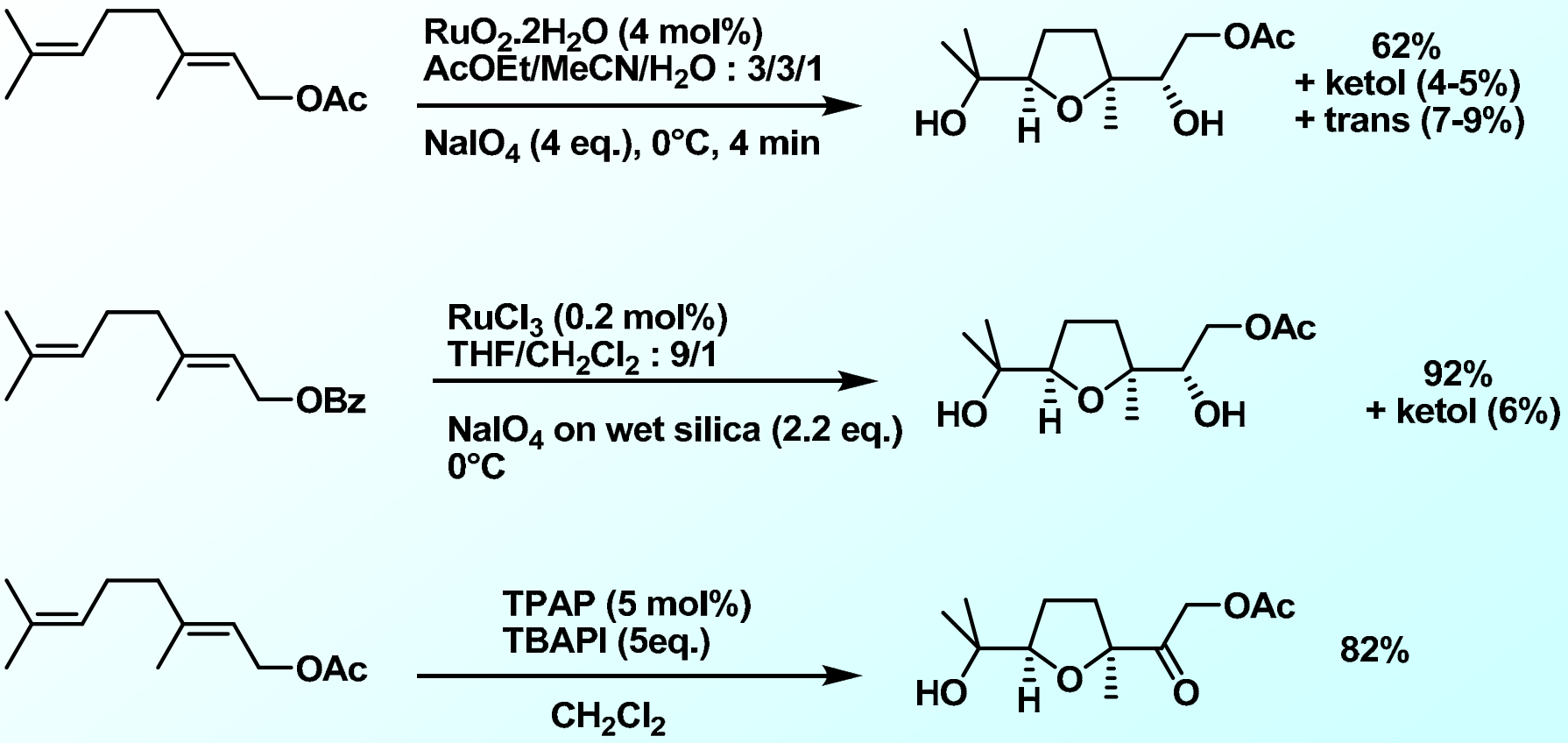
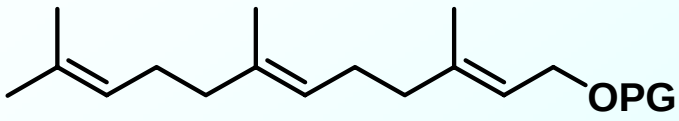


Piccialli, V. *et al. Tetrahedron Lett.* **2001**, *42*, 4695.
Stark, C. B. W. *et al. Synthesis* **2007**, 2751.
Piccialli, V. *et al. Tetrahedron Lett.* **2004**, *45*, 303.

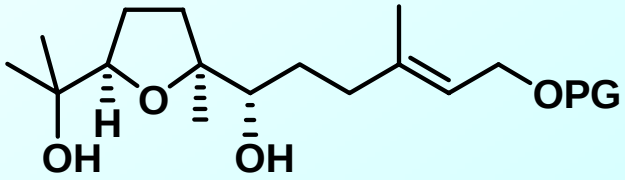
1.2 Formation of Tetrahydrofurans using Ru



PG = TBDPS, Bz, P-NO_2-Bz, Ac

$RuCl_3$ (1 mol%)
$NaIO_4$ on wet silica (3 eq.)
THF, RT

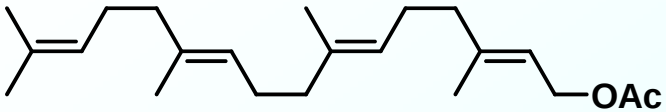
47-67%
+ 12-17% ketol



Ru : Attack on the electron-rich double bond

Stark, C. B. W. *et al. Org. Biomol. Chem.* **2007**, 5, 1605.

1.2 Formation of Tetrahydrofurans using Ru

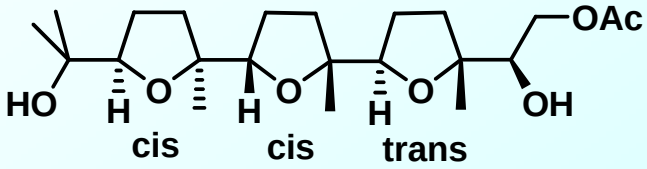


(E,E,E) geranylgeranyl acetate

Squalene

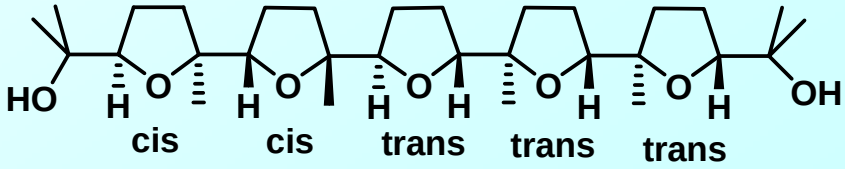
$RuO_2.2H_2O$ (20 mol%)
AcOEt/MeCN/H_2O : 3/3/1
$NaIO_4$ (6 eq.), 0°C, 30 min

30%



$RuO_2.2H_2O$ (20 mol%)
AcOEt/MeCN/H_2O : 3/3/1
$NaIO_4$ (8 eq.), 0°C, 30 min

45%



Piccialli, V. *et al. Tetrahedron Lett.* **2002**, *43*, 9265.

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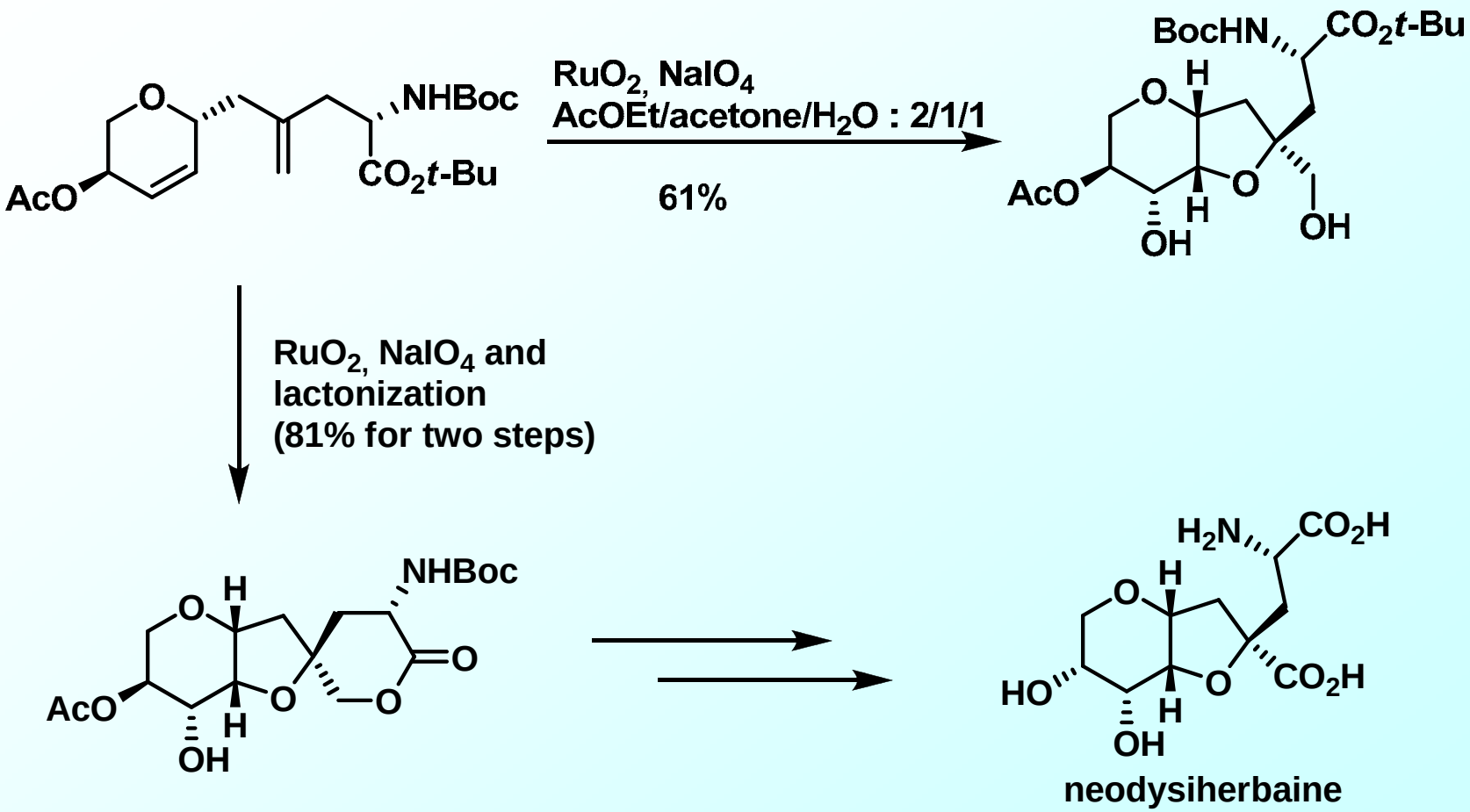
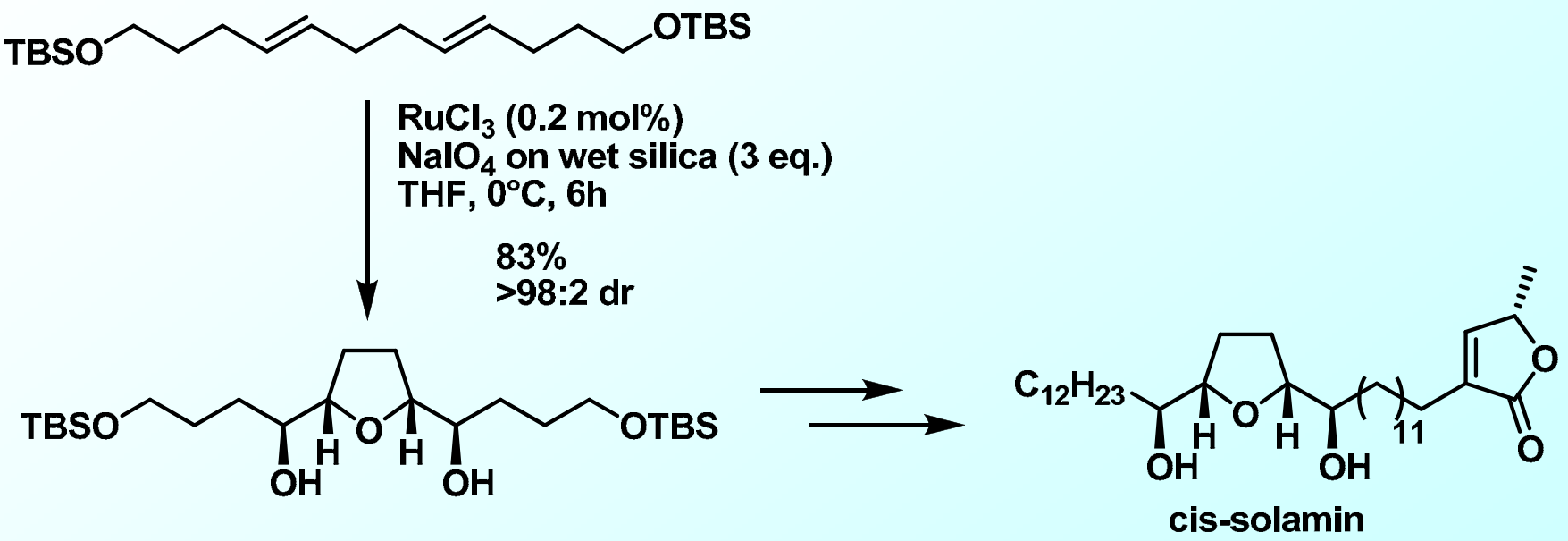


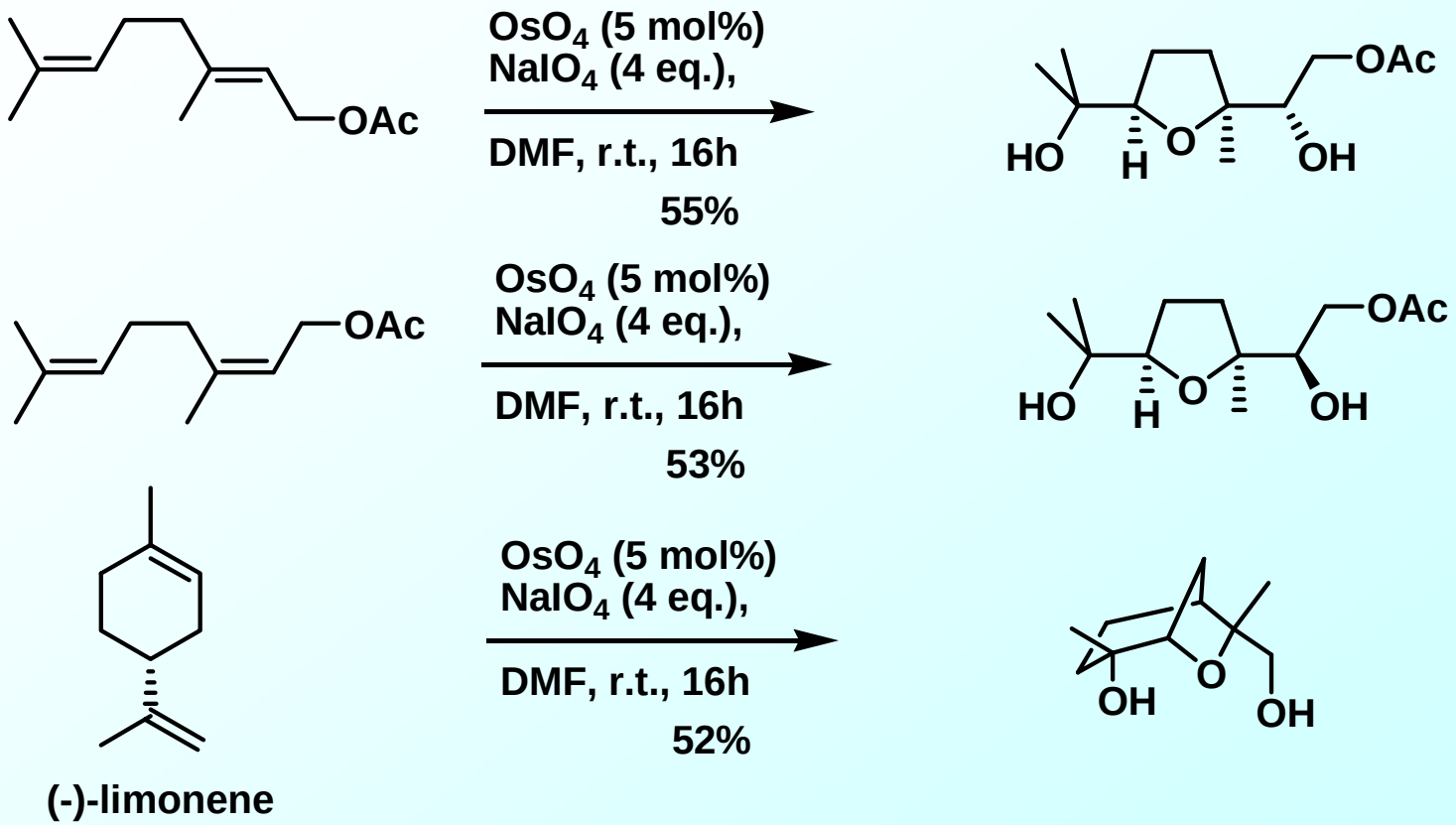
Lygo, B. et *al. Tetrahedron* Lett. **2005**, 46, 6629.

1.2 Formation of Tetrahydrofurans using Ru



Stark, C. B. W. *et al. Org. Lett.* **2006**, 8, 3433.

1.2 Formation of Tetrahydrofurans using Os



Piccialli, V. *et al. Tetrahedron Lett.* **1998**, *39*, 9781.

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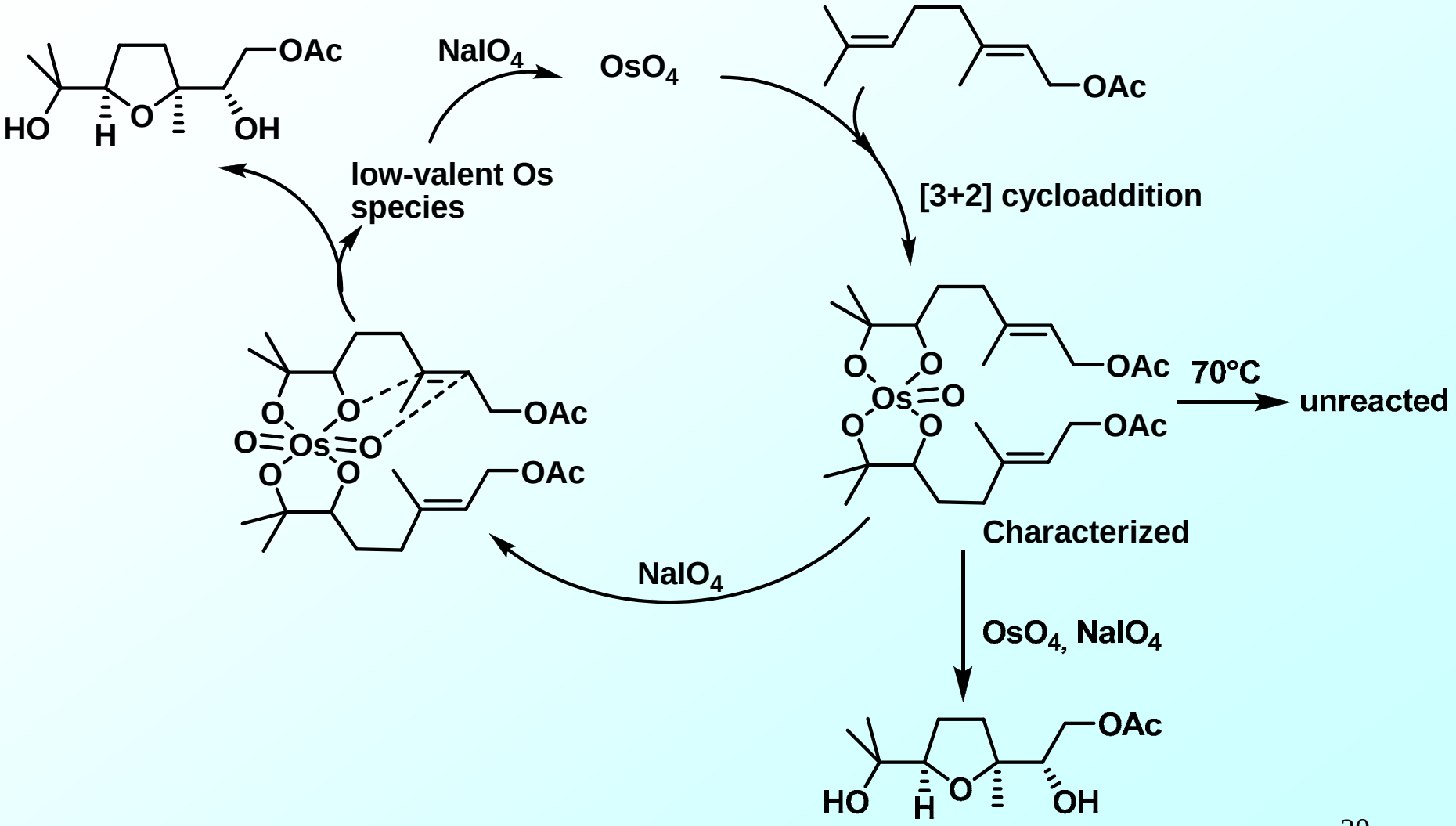

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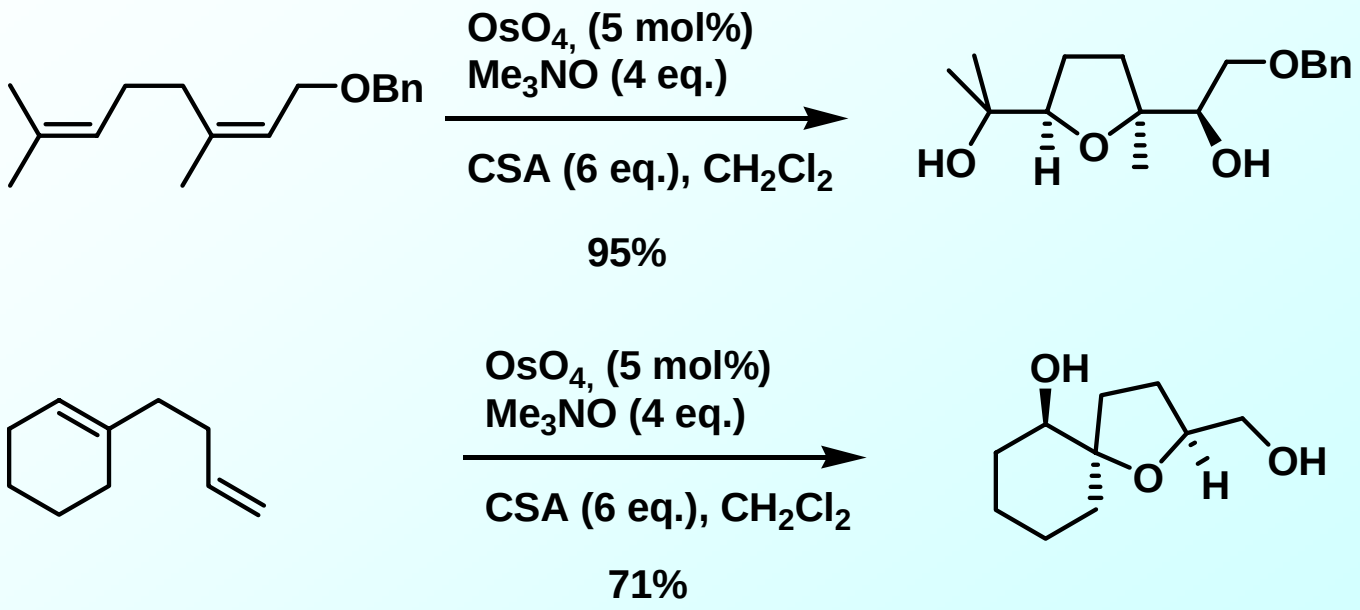

Donohoe, T. J. *et al. Angew. Chem. Int. Ed.* **2003**, *42*, 948.

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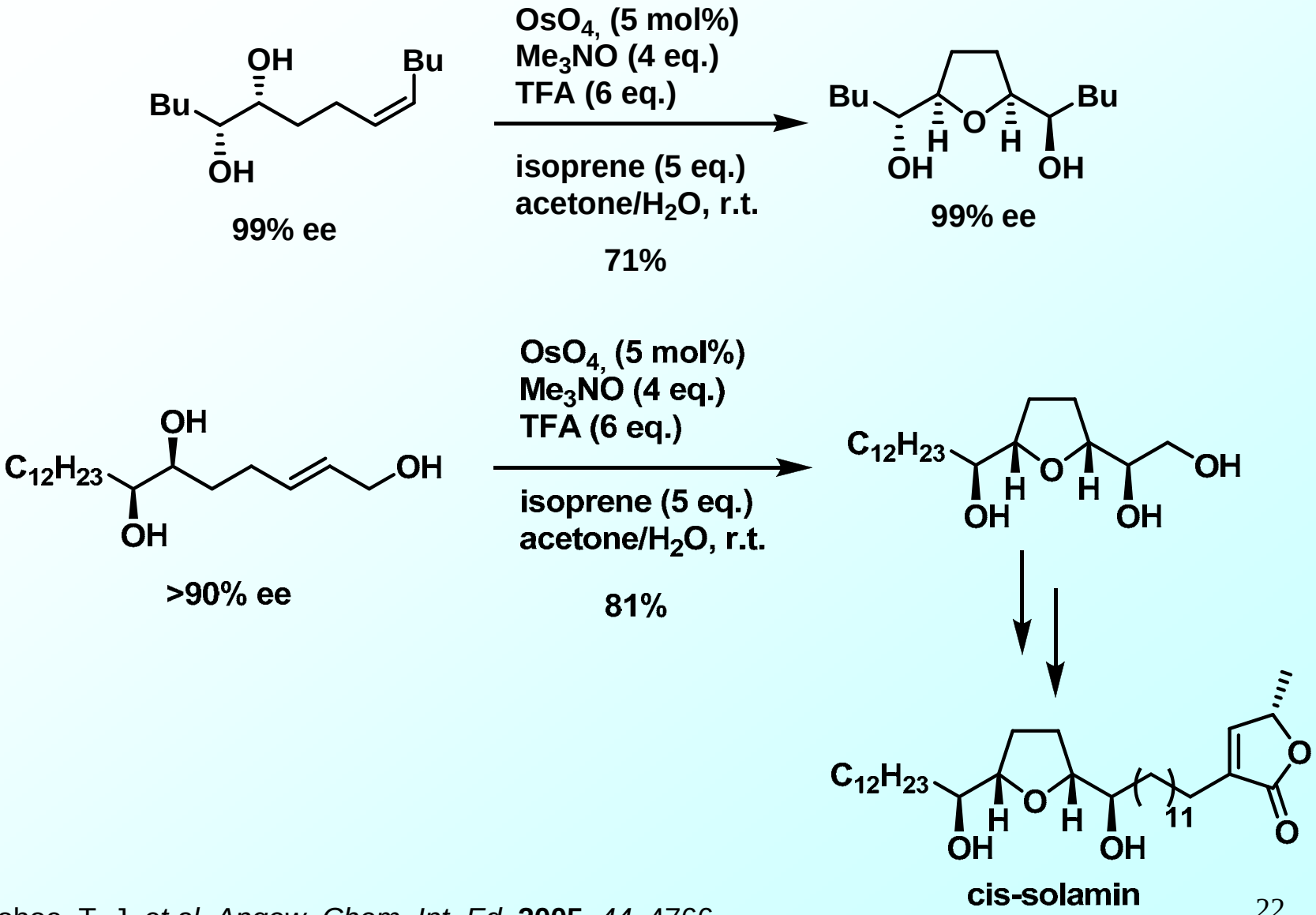
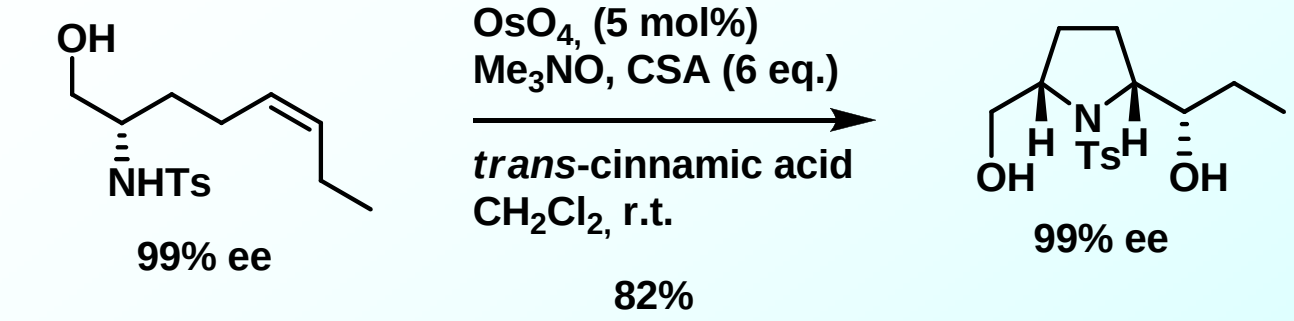
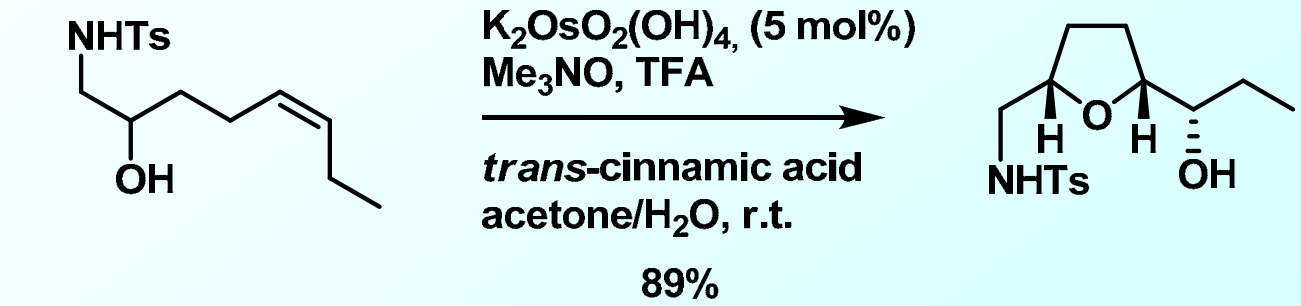
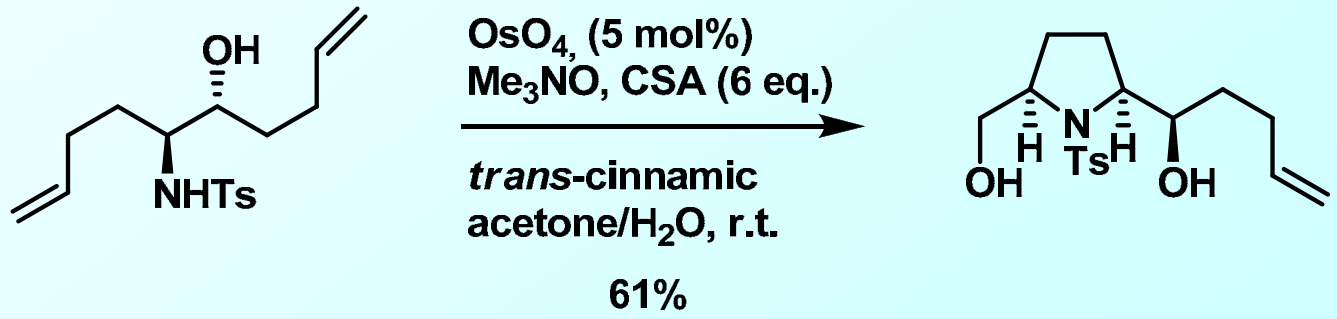


Donohoe, T. J. *et al. Angew. Chem. Int. Ed.* **2005**, *44*, 4766.

1.2 Formation of Pyrrolidines using Os

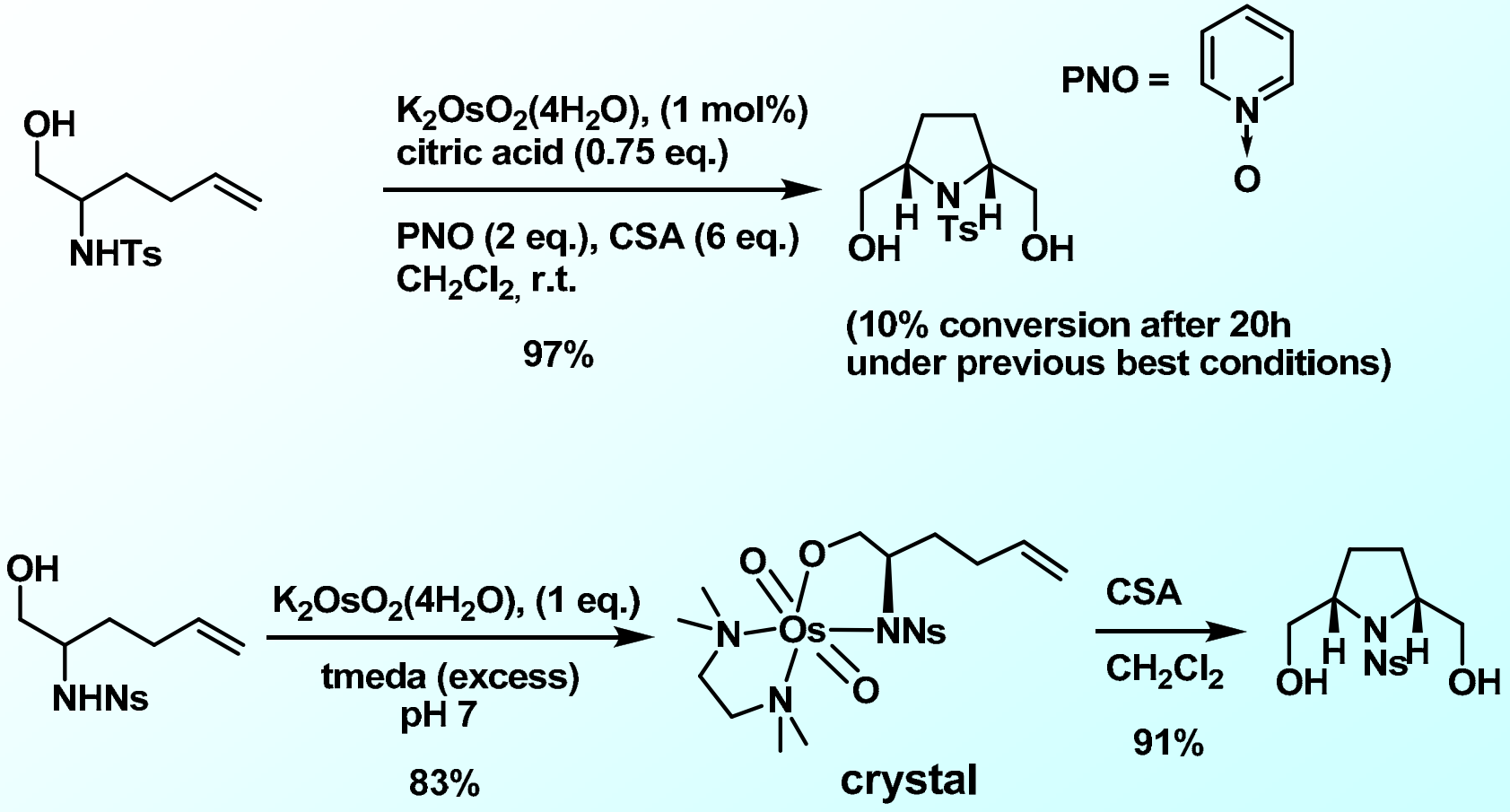






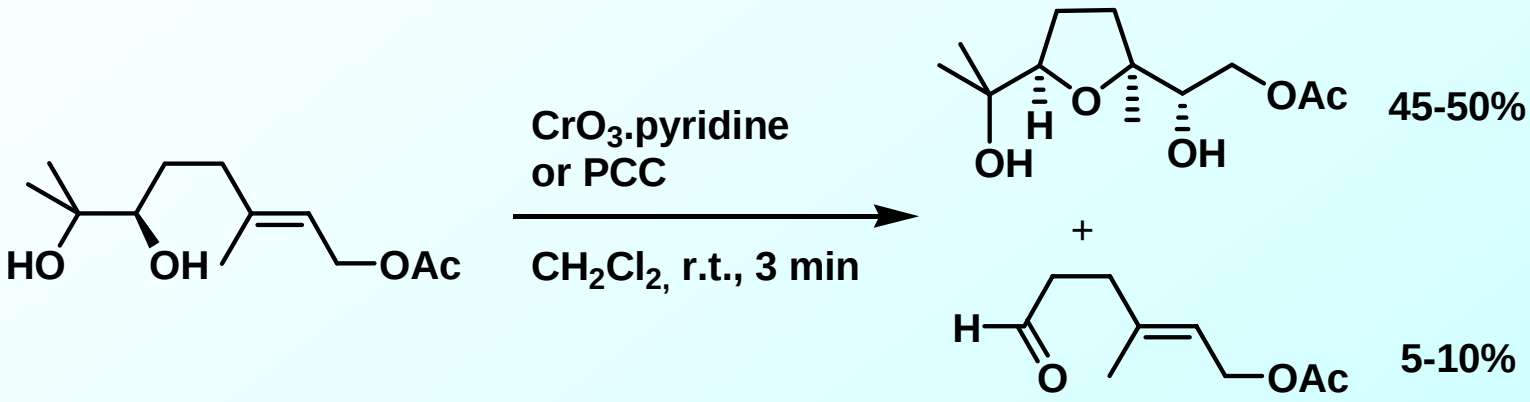
Donohoe, T. J. *et al. Angew. Chem. Int. Ed.* **2006**, *45*, 8025.

1.2 Formation of Pyrrolidines using Os



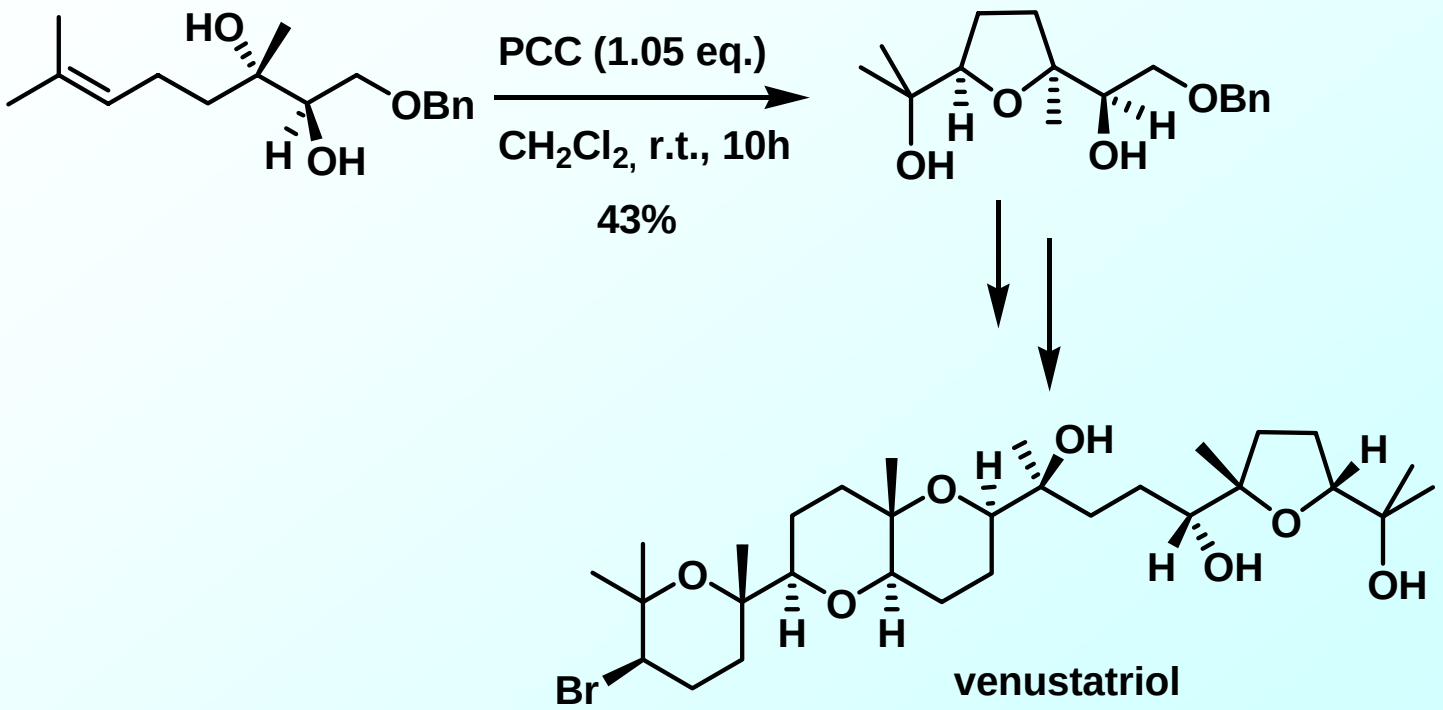
Donohoe, T. J. *et al. Angew. Chem. Int. Ed.* **2008**, *47*, 2872.

1.2 Formation of Tetrahydrofurans using Cr



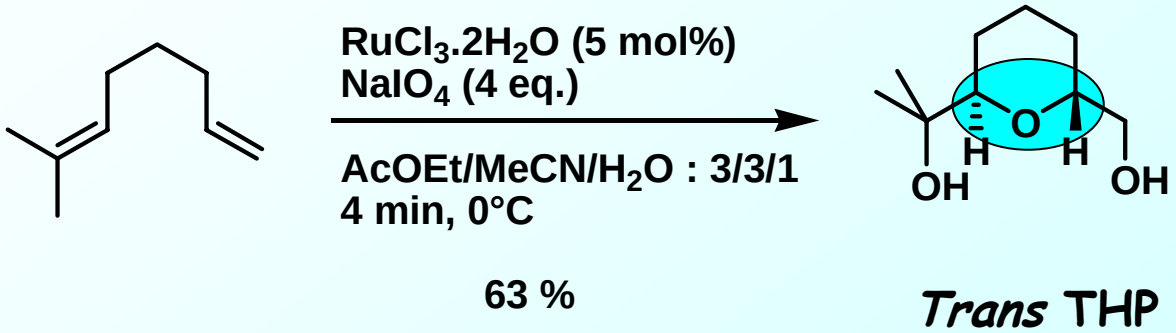
Casida, J. E. *et al. J. Agric. Food Chem.* **1974**, *22*, 379.
Walba, D. M. *et al. Tetrahedron Lett.***1982**, *23*, 727.

1.2 Formation of Tetrahydrofurans using Cr



Corey, E.J.; Ha, D. C. *Tetrahedron Lett.* **1988**, *29*, 3171.

2.1 Formation of Tetrahydropyrans using Ru



Piccialli, V. *Tetrahedron Lett.* **2000**, *41*, 3731.

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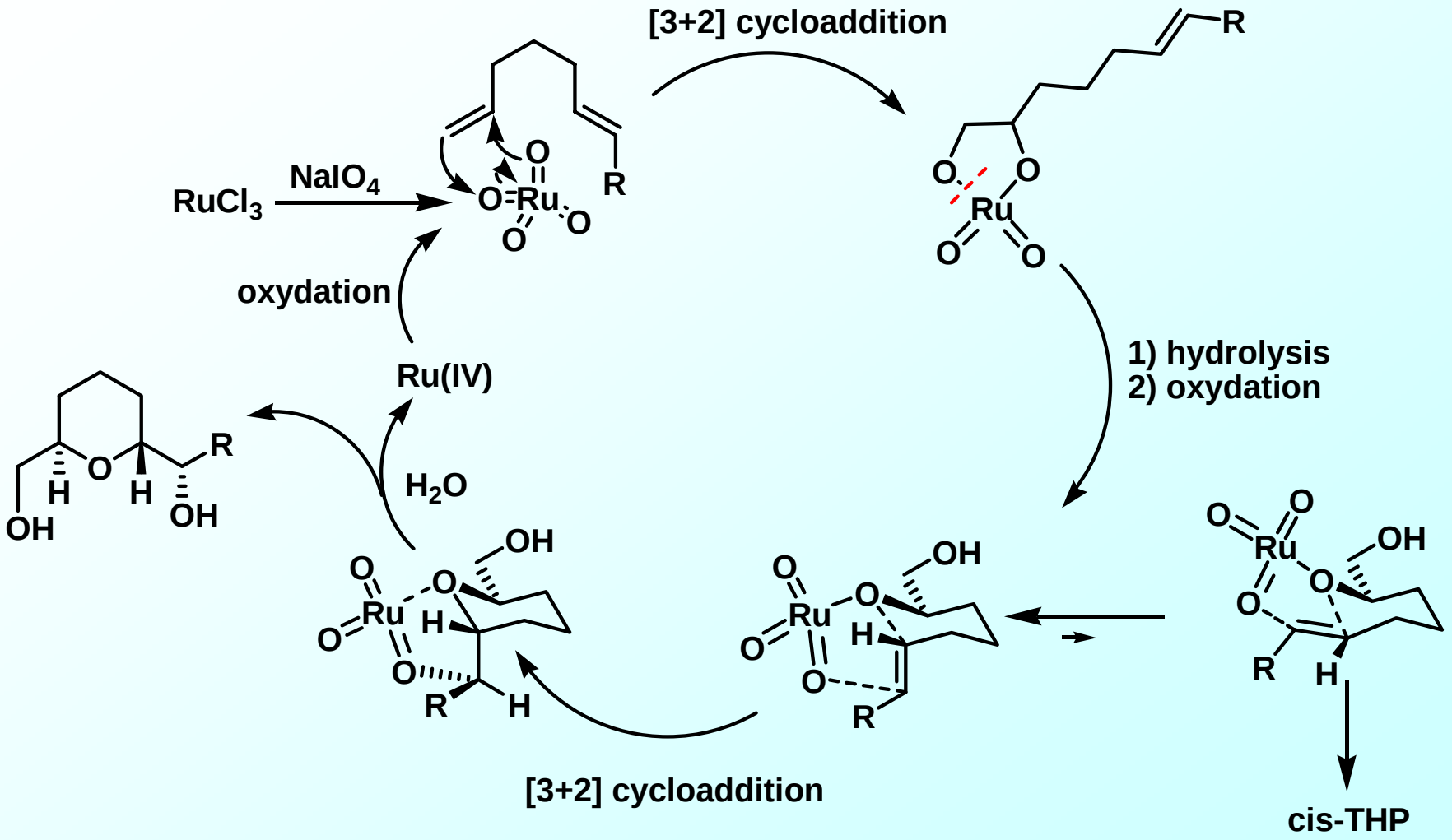

Piccialli, V. *Tetrahedron Lett.* **2000**, *41*, 3731.

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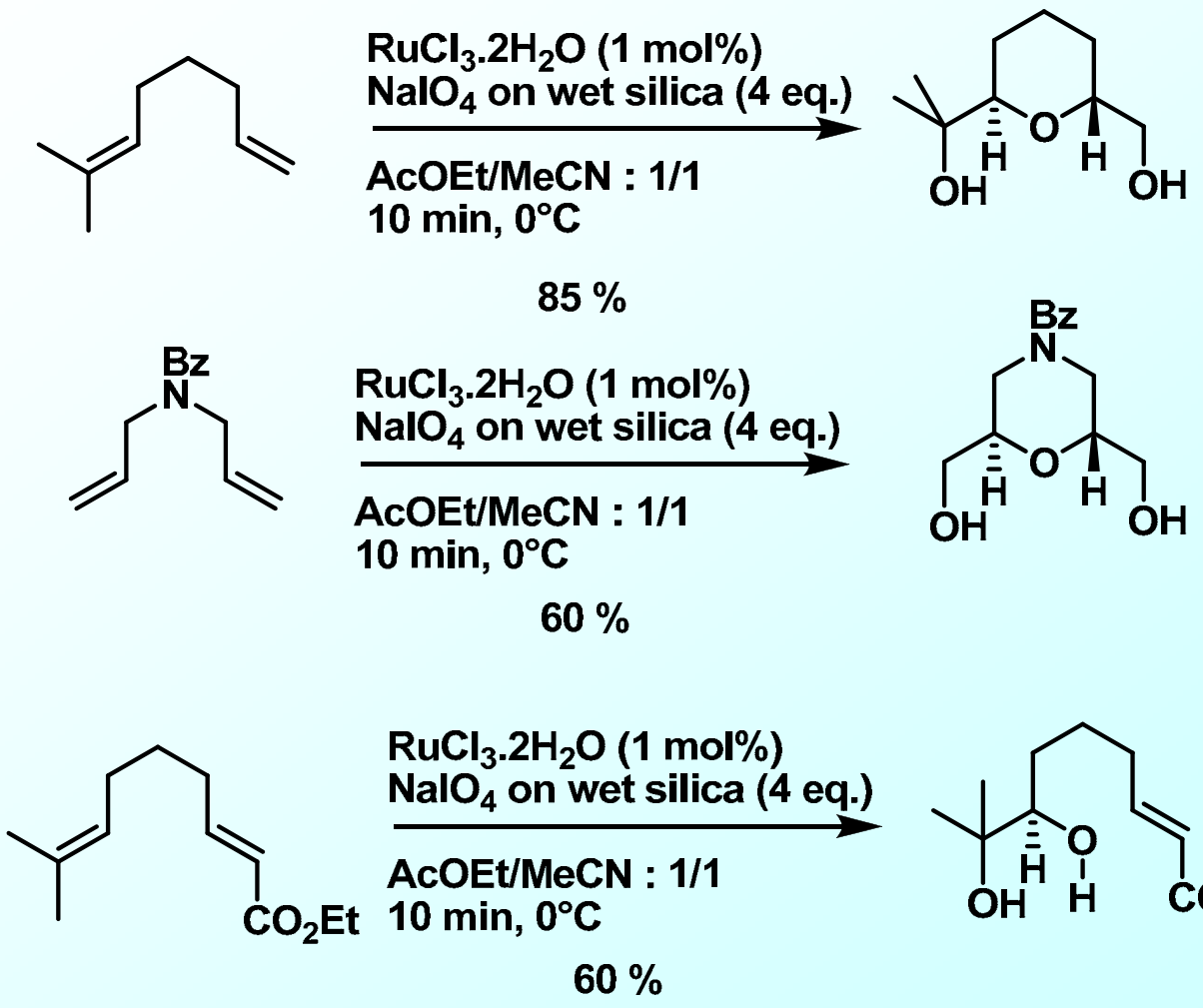
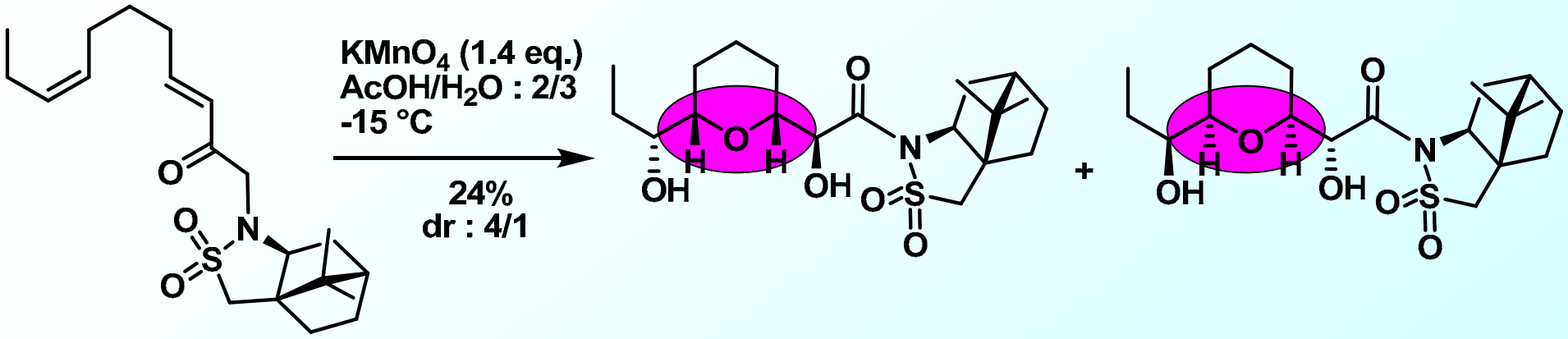
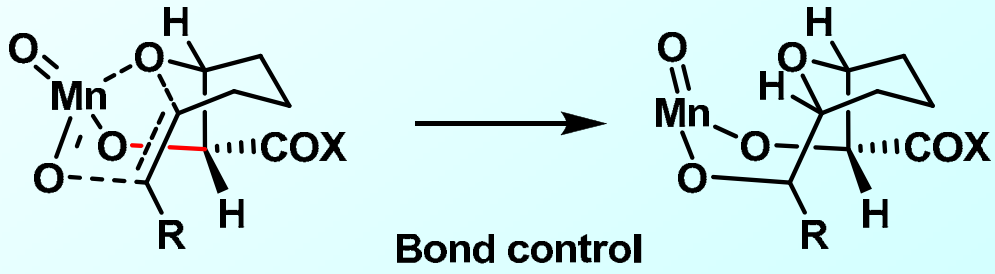


Stark, C. B. W *et al*. *Angew. Chem. Int. Ed.* **2006**, *45*, 6218.

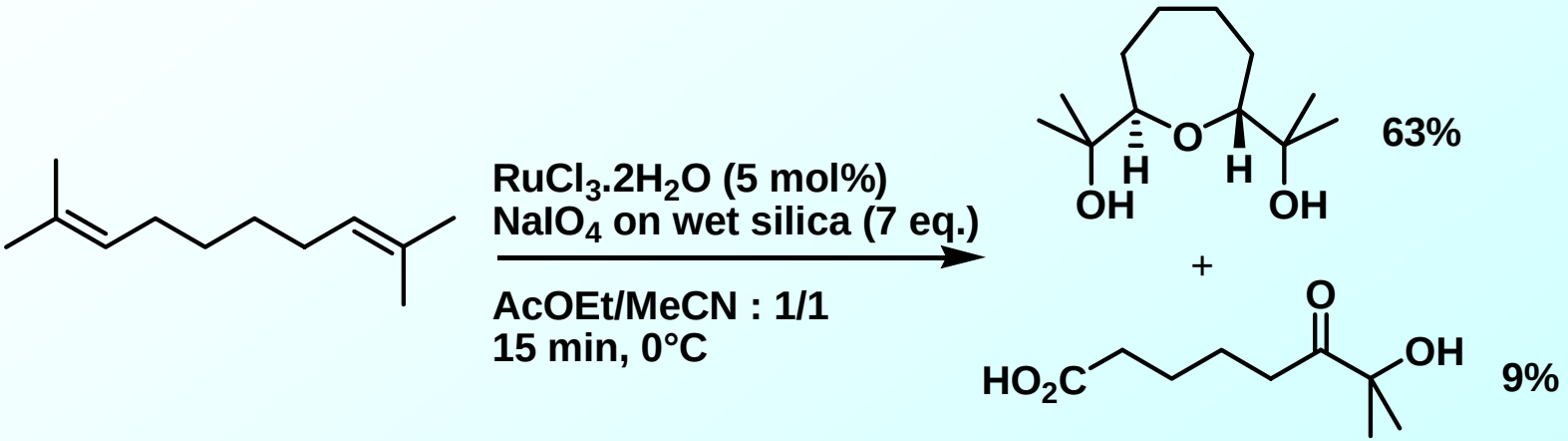
2.2 Formation of Tetrahydropyrans using $KMnO_4$





Brown, R. C. D.; Cecil, A. R. L. *Tetrahedron Lett.* **2004**, *45*, 7269.

3 Formation of Oxepanes



Piccialli, V. *et al. Tetrahedron Lett.* **2007**, *48*, 5131.

Conclusion

-Stereospecific and highly stereoselective process

-*Cis* THF

-*Cis* ($KMnO_4$) + *trans* (Ru) THP

-*Trans* oxepanes

-Only one example of enantioselective cyclization