

Diastereoselective RRM and Natural Products

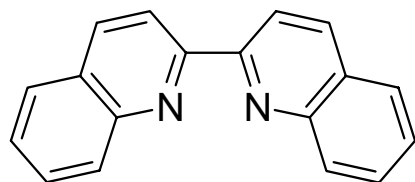
Siegfried Blechert

Department of Chemistry, TU Berlin – Berlin University of Technology, Germany

Among the different types of the metathesis reactions that have been developed, ring-rearrangement metathesis (RRM) has proven to be especially powerful [1]. Stereocenters are easily established in a ring and transferred to the side chain. The extension of the basic reaction by further metathesis steps allows the rapid construction of complex structures. We have developed a new concept of diastereoselective RRM leading to various carbo- and heterocycles in good to excellent stereoselectivities and conversions [2]. We observed a strong influence of the substitution pattern of the directing stereocentres on the configuration of the new stereocenters and on the conversions. Both depended also on the precatalysts applied. The flexibility of these principles as well as the application of the methodology in natural product synthesis will be presented [3].

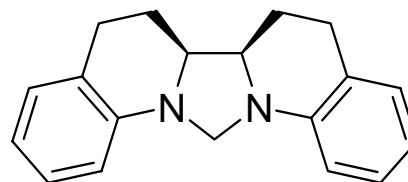
References:

1. Holub, N.; Blechert, S. *Chem. Asian J.* **2007**, in print.
2. Böhrsch, V., Neidhöfer, J., Blechert, S. *Angew. Chem. Int. Ed.* **2006**, *45*, 1302-1305.
3. Böhrsch, V., Blechert, S. *Chem. Commun.* **2006**, *45*, 18, 1968-1970.



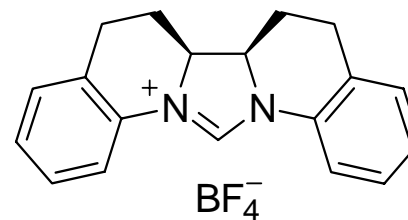
a) PtO_2 , H_2 ,
 CH_2Cl_2 , rt, 4 h
b) $\text{HC}(\text{OMe})_3$, HCOOH ,
toluene, 90°C , 8 h

60 %



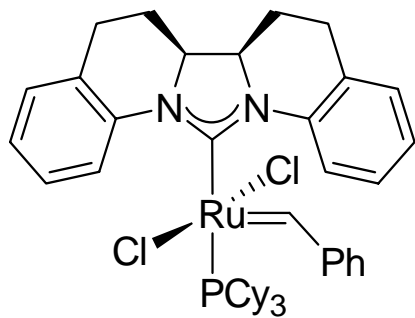
c) Ph_3CBF_4 ,
 CH_2Cl_2 , rt, 3 h

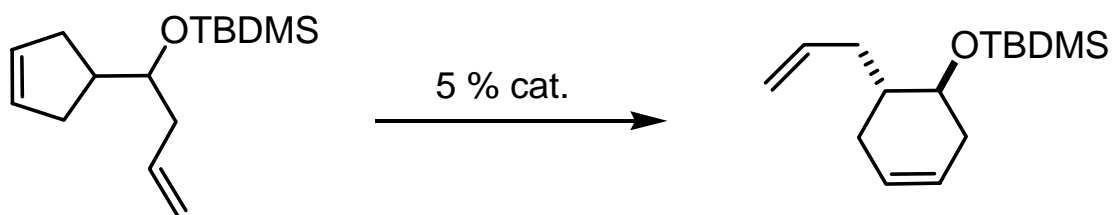
85 %



d) $\text{KOC}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$,
hexane
e) Grubbs I, 50°C , 16 h

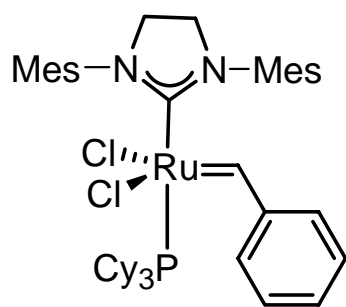
65 %



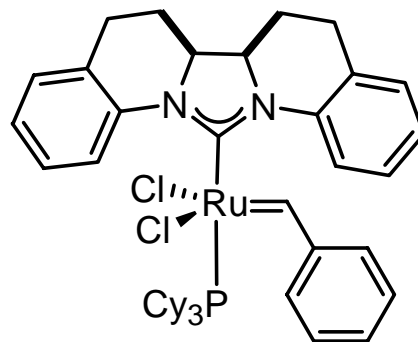


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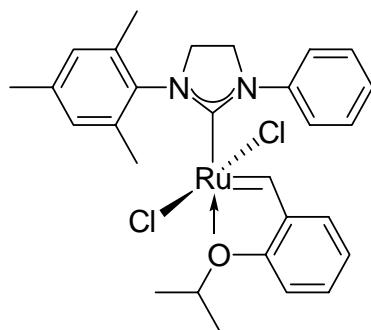
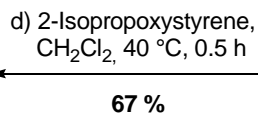
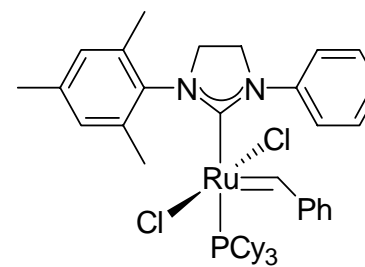
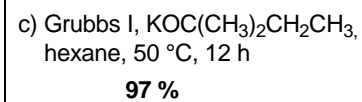
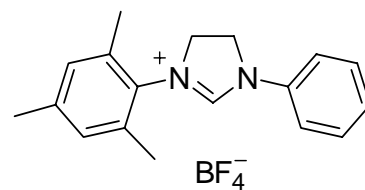
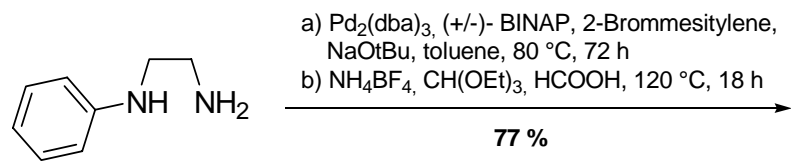
B: 9/1

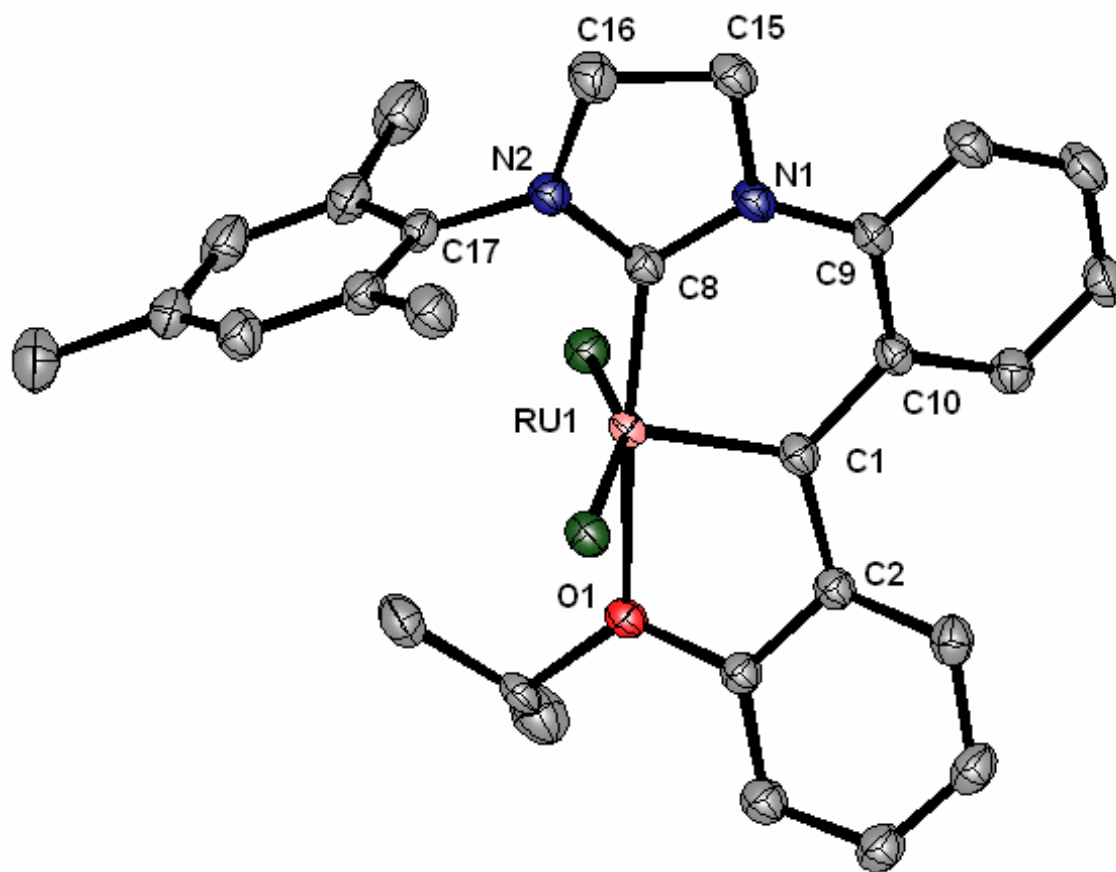


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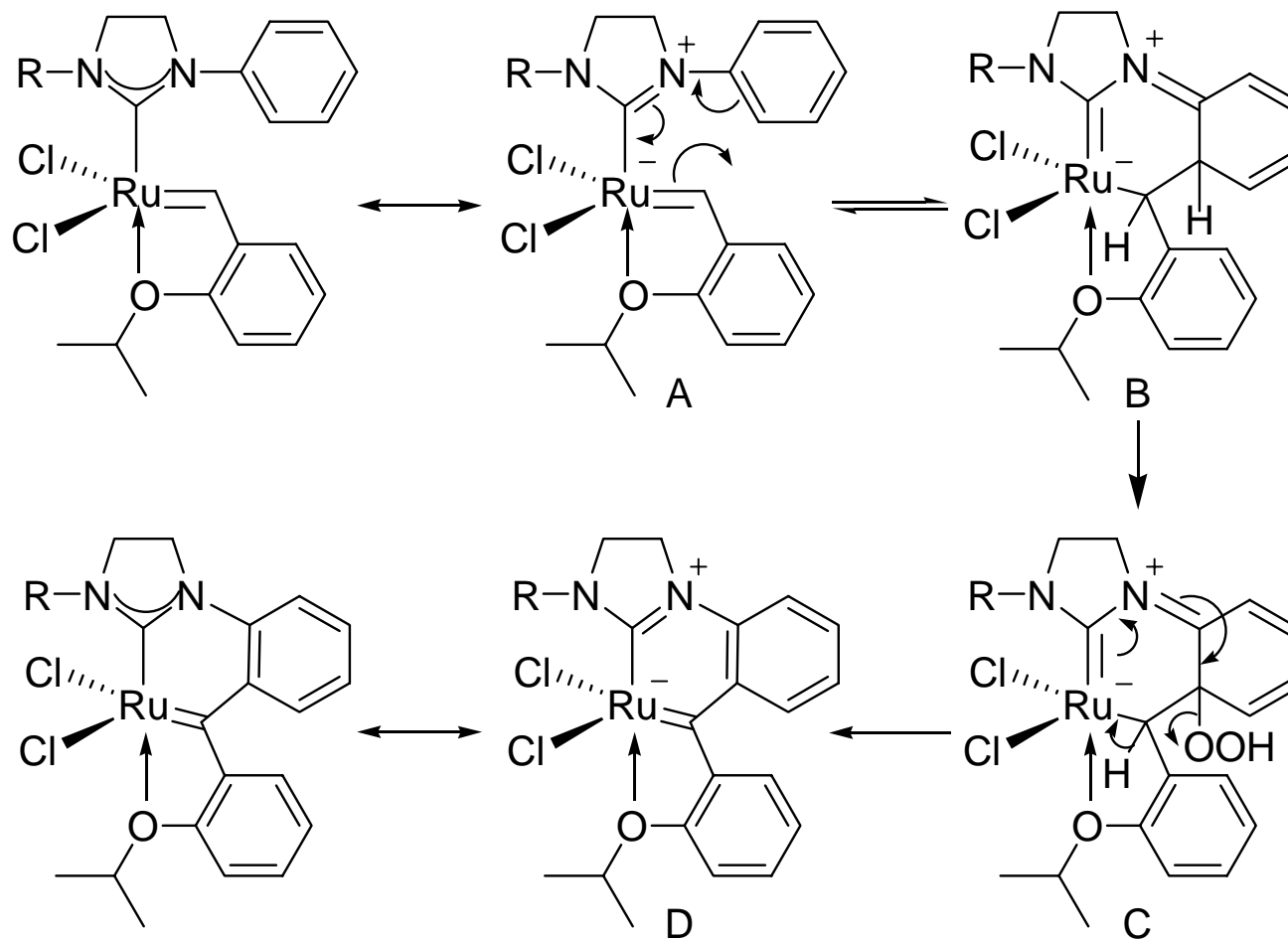


B

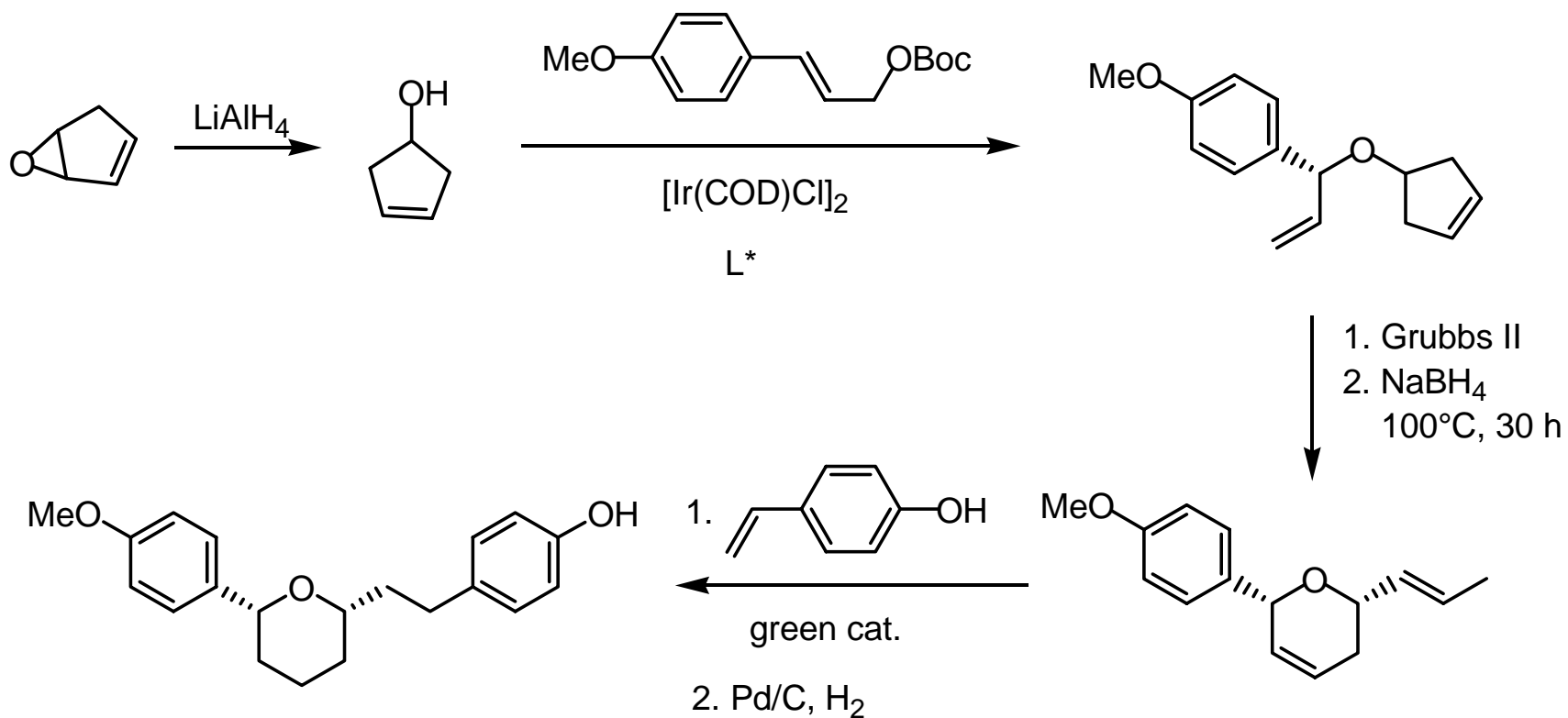




Proposed mechanism for the insertion



Synthesis of (-)-Centrolobine



Chem. Commun. 2006, 1968

