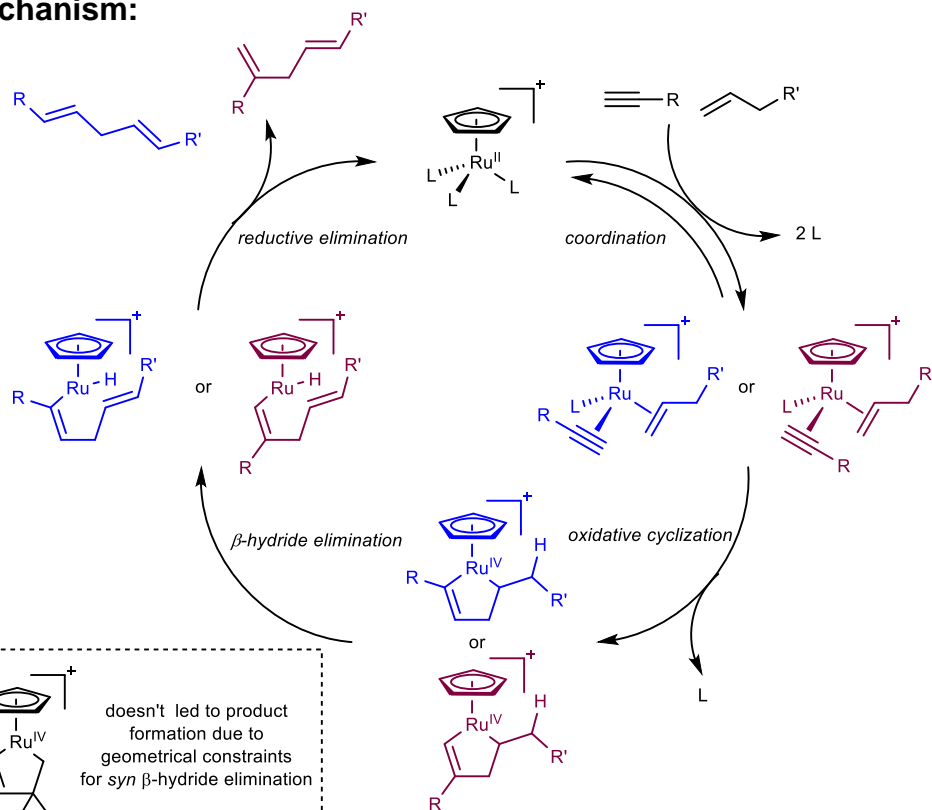


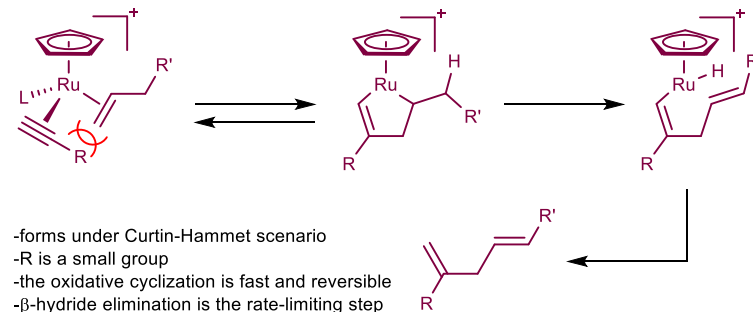
Trost, B. M. *Angew. Chem. Int. Ed.* **2005**, *44*, 6630 <https://doi.org/10.1002/anie.200500136>



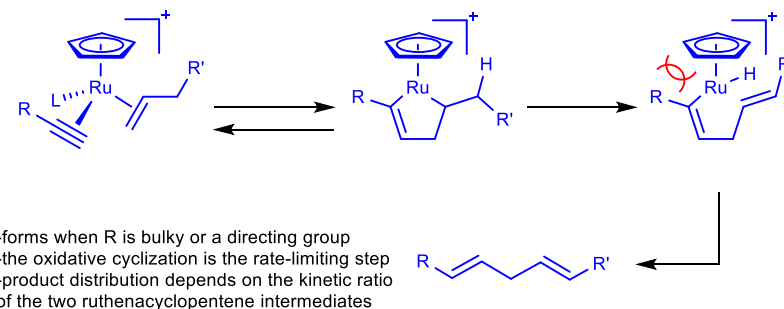
Mechanism:



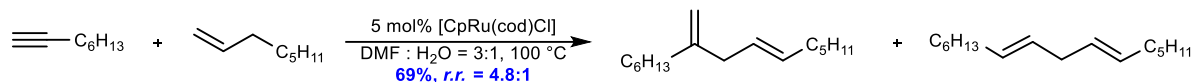
- The branched product is the thermodynamic product:



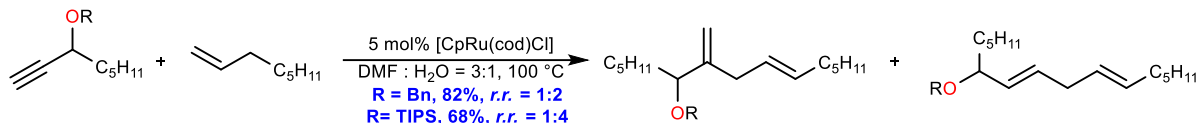
- The linear product is the kinetic product:



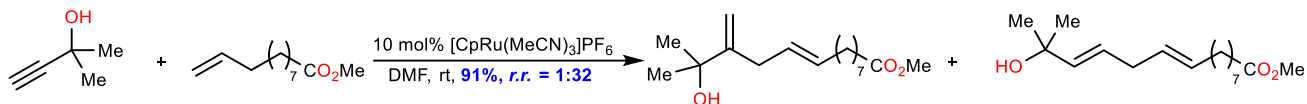
- Simple alkenes and alkynes provide branched products (Curtin-Hammet scenario):



- Bulky propargylic substituents favor the formation of the linear product (ruthenacycle formation is rate-limiting):

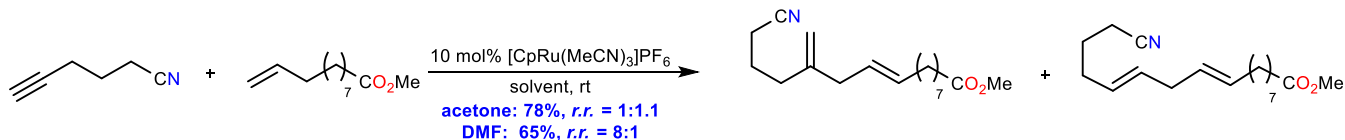


Trost, B. M. *J. Am. Chem. Soc.* **1993**, 115, 4361. <https://doi.org/10.1021/ja00063a064>



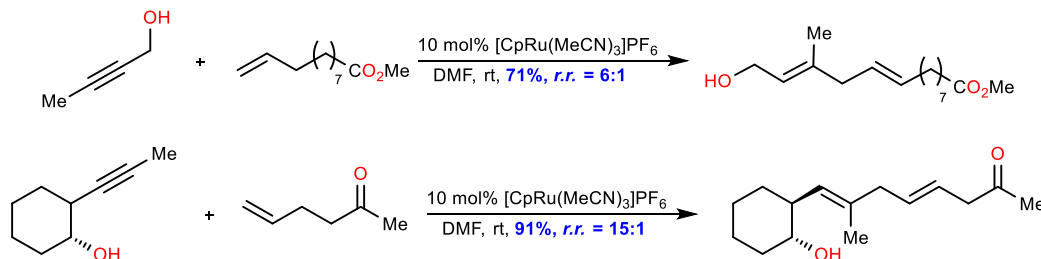
Trost, B. M. *J. Am. Chem. Soc.* **2001**, 123, 12504. <https://doi.org/10.1021/ja012009m>

- The solvent can also influence the outcome of the coupling (DMF ligates strongly to the catalyst, increasing its size)



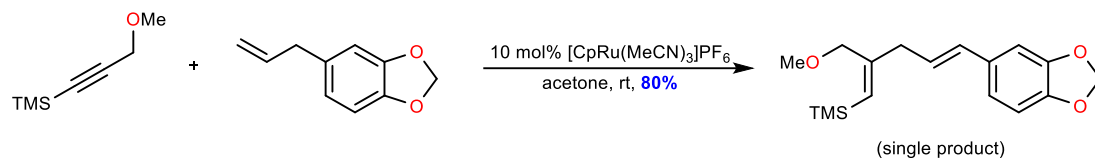
Trost, B. M. *Tetrahedron Lett.* **1999**, 40, 7739. [https://doi.org/10.1016/S0040-4039\(99\)01639-1](https://doi.org/10.1016/S0040-4039(99)01639-1)

- Propargylic and homopropargylic alcohols favor the formation of the linear product:



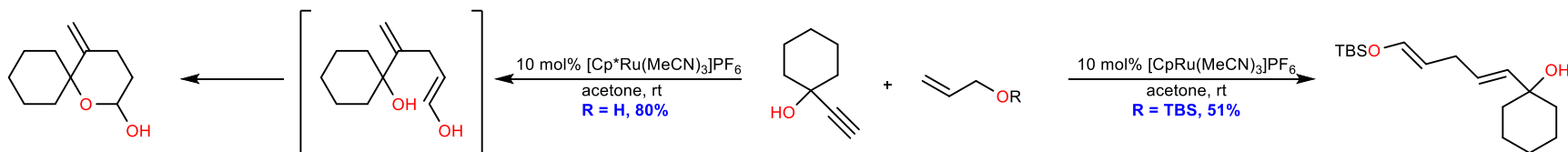
Trost, B. M. *Chem. Eur. J.* **2002**, 8, 2341. [https://doi.org/10.1002/1521-3765\(20020517\)8:10<2341::AID-CHEM2341>3.0.CO;2-A](https://doi.org/10.1002/1521-3765(20020517)8:10<2341::AID-CHEM2341>3.0.CO;2-A)

- Alkynyl silanes can be utilized to promote regioselectivity (acting as the bulky propargylic substituent):



Trost, B. M. *Org. Lett.* **2000**, 2, 1761. <https://doi.org/10.1021/ol0059504>

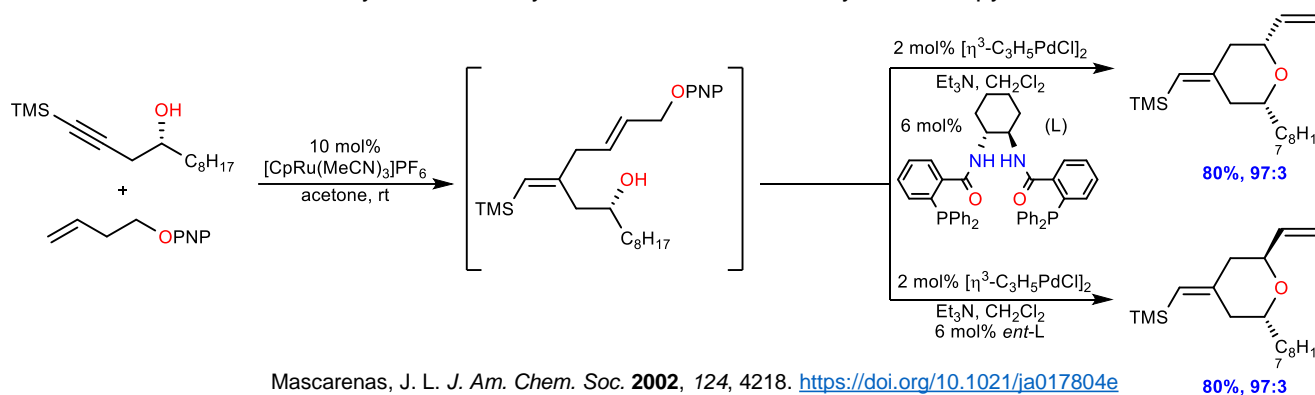
- Using the bulky Cp* ligand promotes the formation of the branched product:



Dixneuf, P. H. *J. Org. Chem.* **1999**, 64, 3524. <https://doi.org/10.1021/jo982300t>

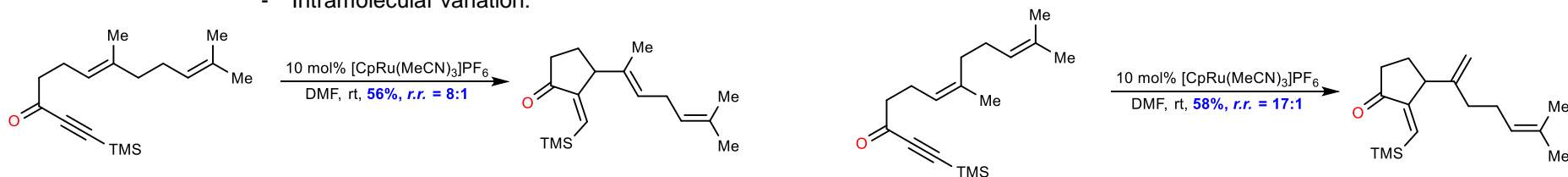
Trost, B. M. *J. Am. Chem. Soc.* **2001**, 123, 2897. <https://doi.org/10.1021/ja003870p>

- In combination with allyl-Pd chemistry, it can be utilized in the synthesis of pyrans:



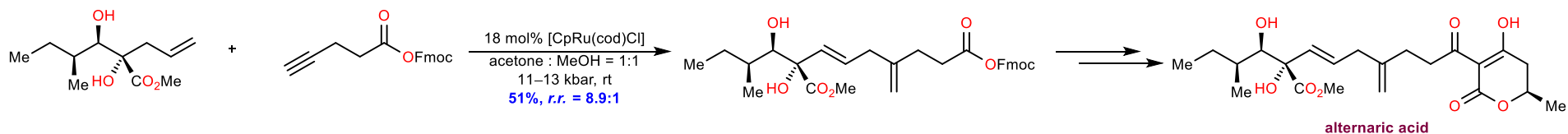
Mascarenas, J. L. *J. Am. Chem. Soc.* **2002**, 124, 4218. <https://doi.org/10.1021/ja017804e>

- Intramolecular variation:

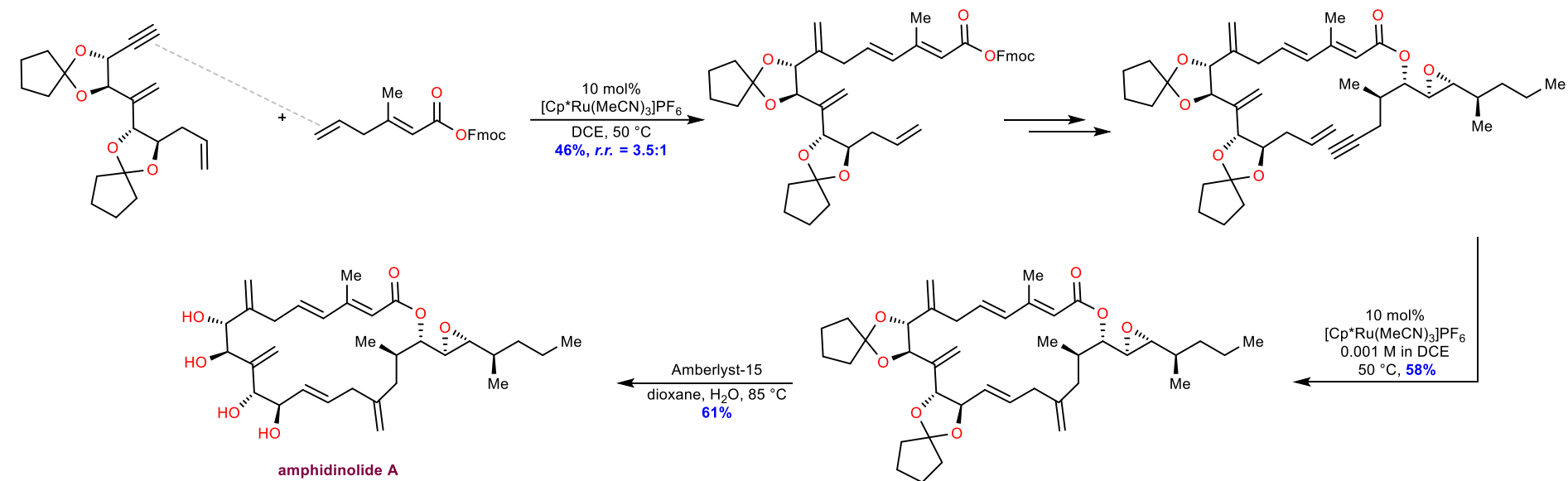


Trost, B. M. *J. Am. Chem. Soc.* **2000**, 122, 714. <https://doi.org/10.1021/ol0059504>

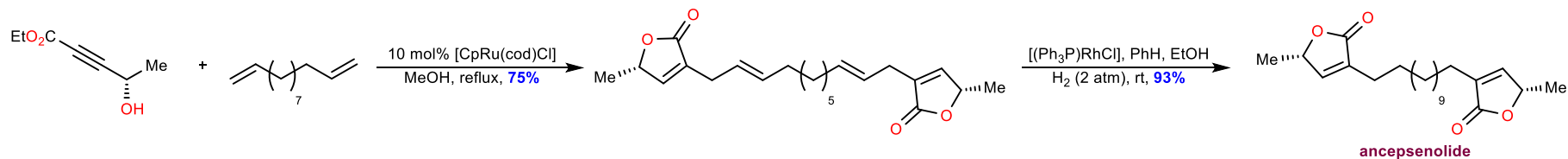
Selected examples in total synthesis



Trost, B. M. *J. Am. Chem. Soc.* **1998**, *120*, 9228. <https://doi.org/10.1021/ja981540n>

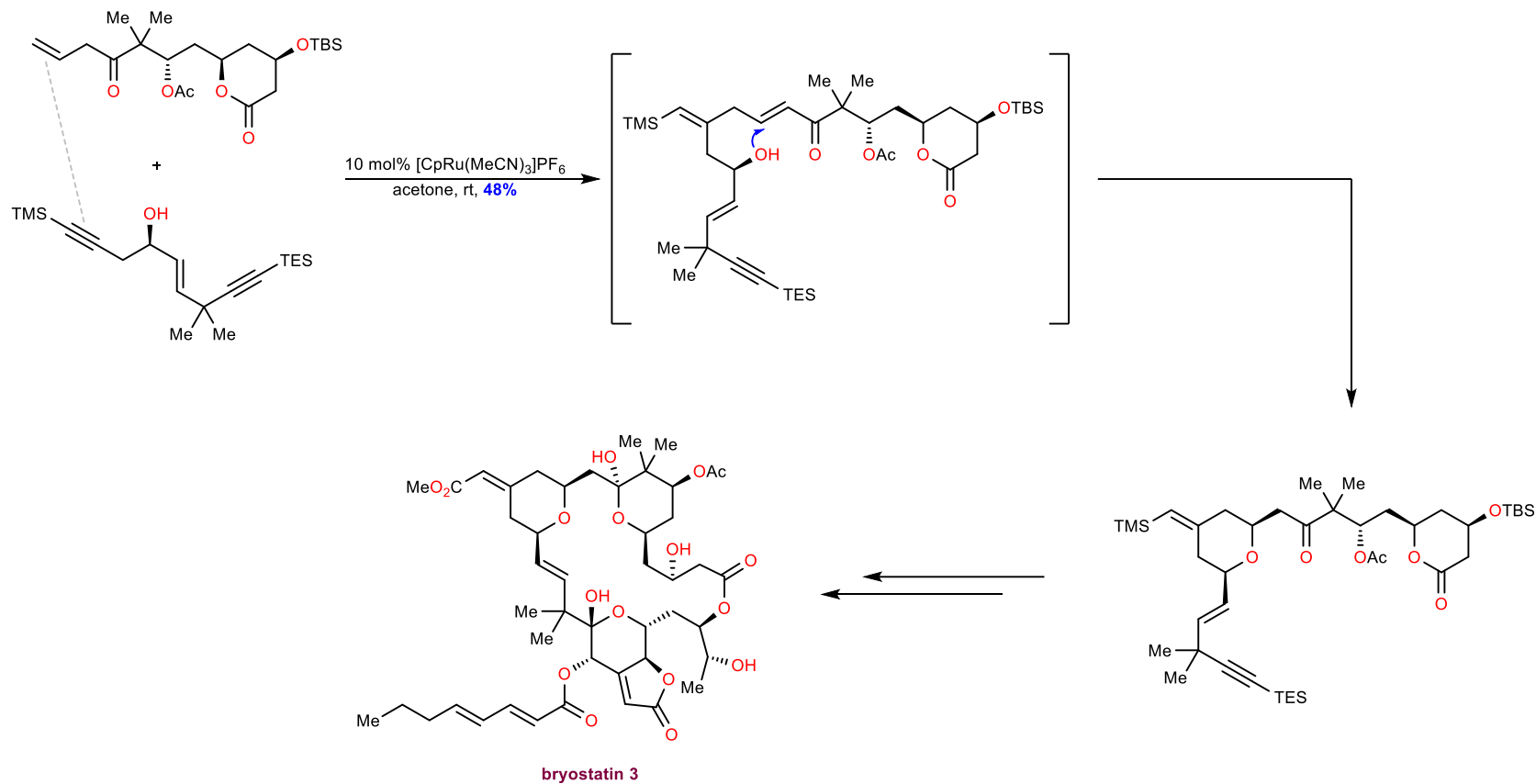


Trost, B. M. *J. Am. Chem. Soc.* **2002**, *124*, 12420. <https://doi.org/10.1021/ja0533646>



Trost, B. M. *J. Am. Chem. Soc.* **1994**, *116*, 4985 <https://doi.org/10.1021/ja00090a053>

Selected examples in total synthesis



Trost, B. M. *Science* **2020**, 368, 1007. <https://doi.org/10.1126/science.abb7271>