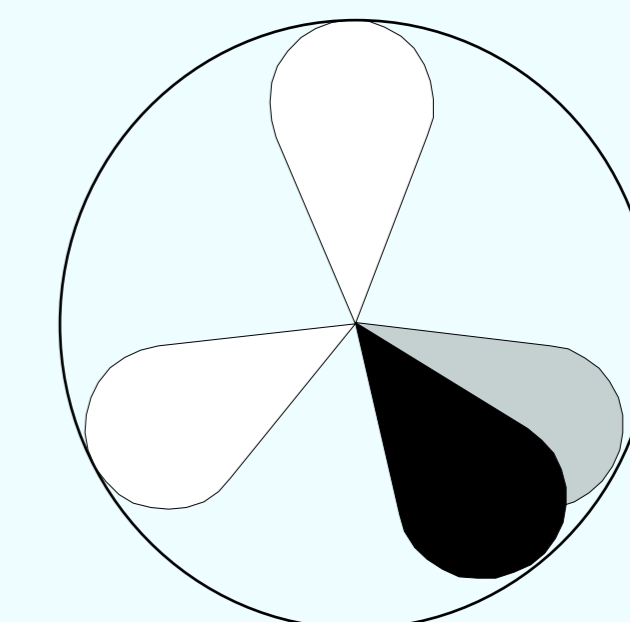


New Applications of Ruthenium-Based Metathesis Catalysts bearing N-Heterocyclic Carbene Ligands

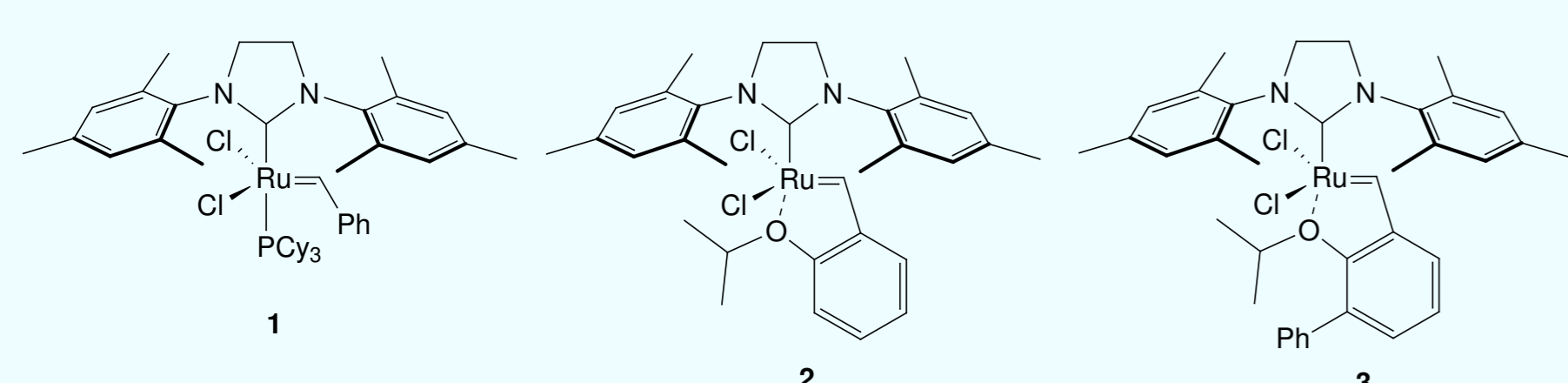


Metathesis of Substituted Olefins Using the "Second Generation" Ruthenium Catalysts. An Improved Catalyst for Alkyne Metathesis

Karol Grela*

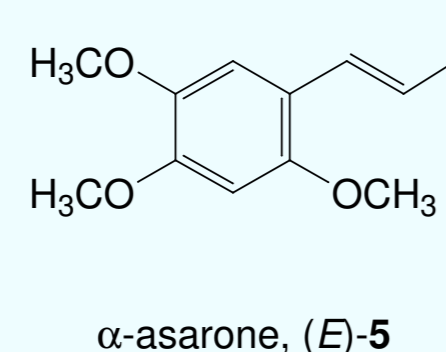
Institute of Organic Chemistry
Polish Academy of Sciences
grela@icho.edu.pl

1 "Second generation" Catalysts for Olefin Metathesis



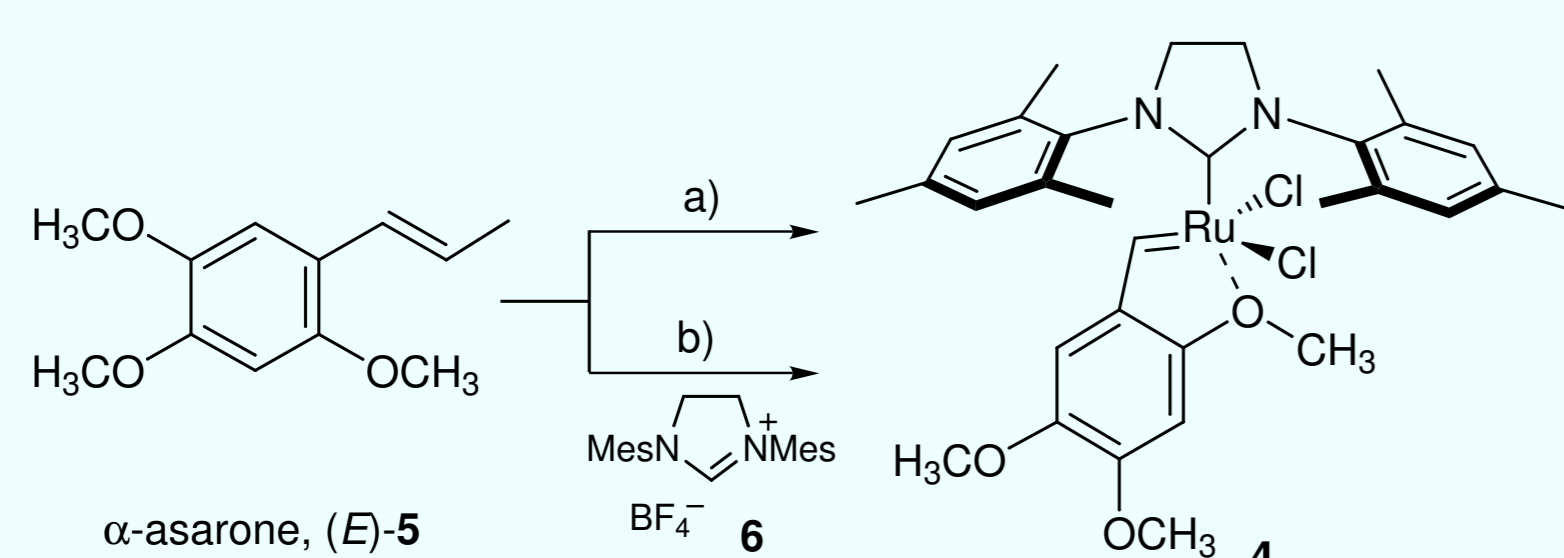
The development of well-accessible "second generation" metathesis catalysts combining high activity with an excellent tolerance to a variety of functional groups has been key to the widespread application of olefin metathesis in organic synthesis and polymer chemistry.

1.1 Good Bargain: An Inexpensive Air-Stable Ruthenium Metathesis Catalyst Derived from α -Asarone



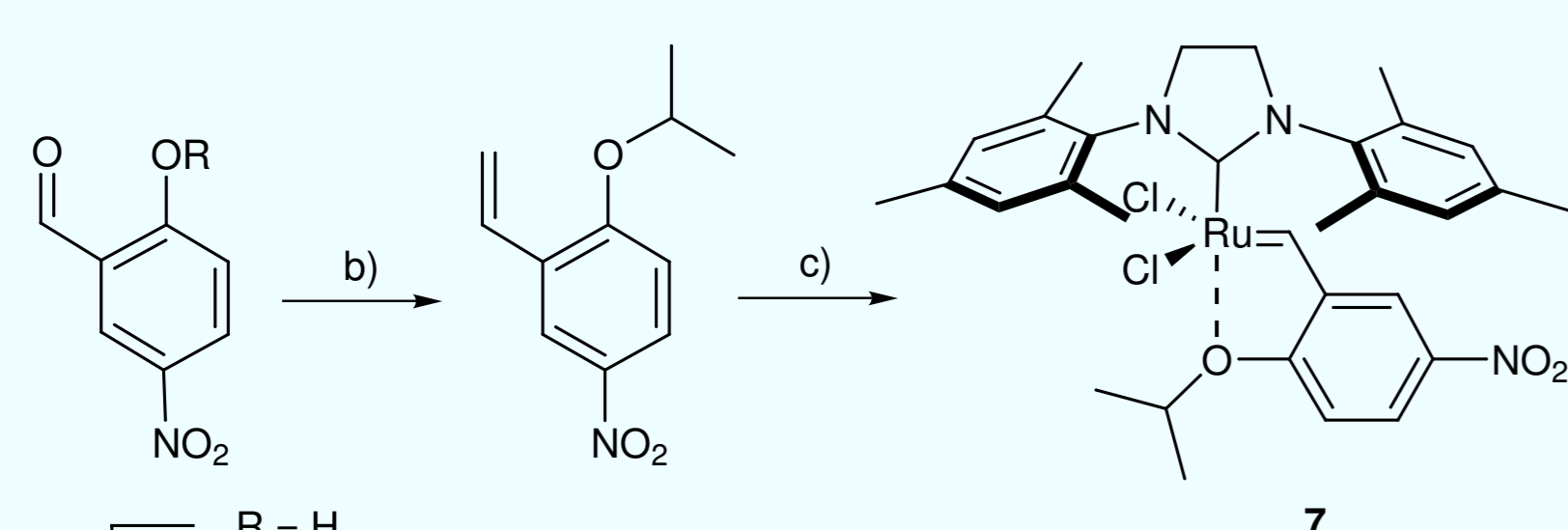
α -asarone, (E)-5

The recyclable and easy to obtain complex **4**, derived from inexpensive α -asarone ((E)-5 from *Asarum Europeanum*) can be successfully used in various types of metathesis (RCM, CM, enyne) as a cheaper and more potent substitute of the Hoveyda catalyst **2**. [*Eur. J. Org. Chem.* 2003, 963–966]



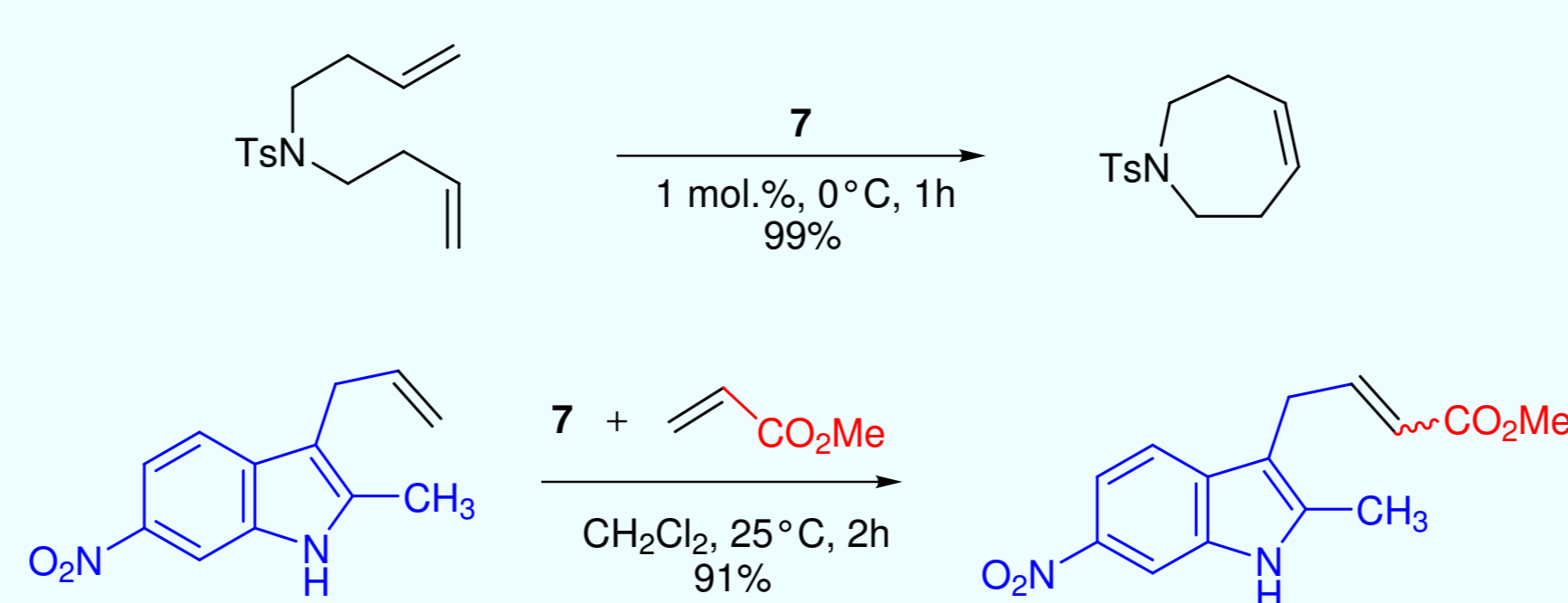
Reagents and conditions: a) 1, CuCl, CH₂Cl₂, 40°C, 91–96%; b) i) 6, C₃H₇OK, *n*-hexane, RT, 1h, then Cl₂(Cy)₂Ru=CHPh, 80°C, 30 min; ii) (E)-5, CuCl, CH₂Cl₂, 40°C, 82–89%

1.2 A New Highly Efficient Ruthenium Catalyst for Metathesis Reaction



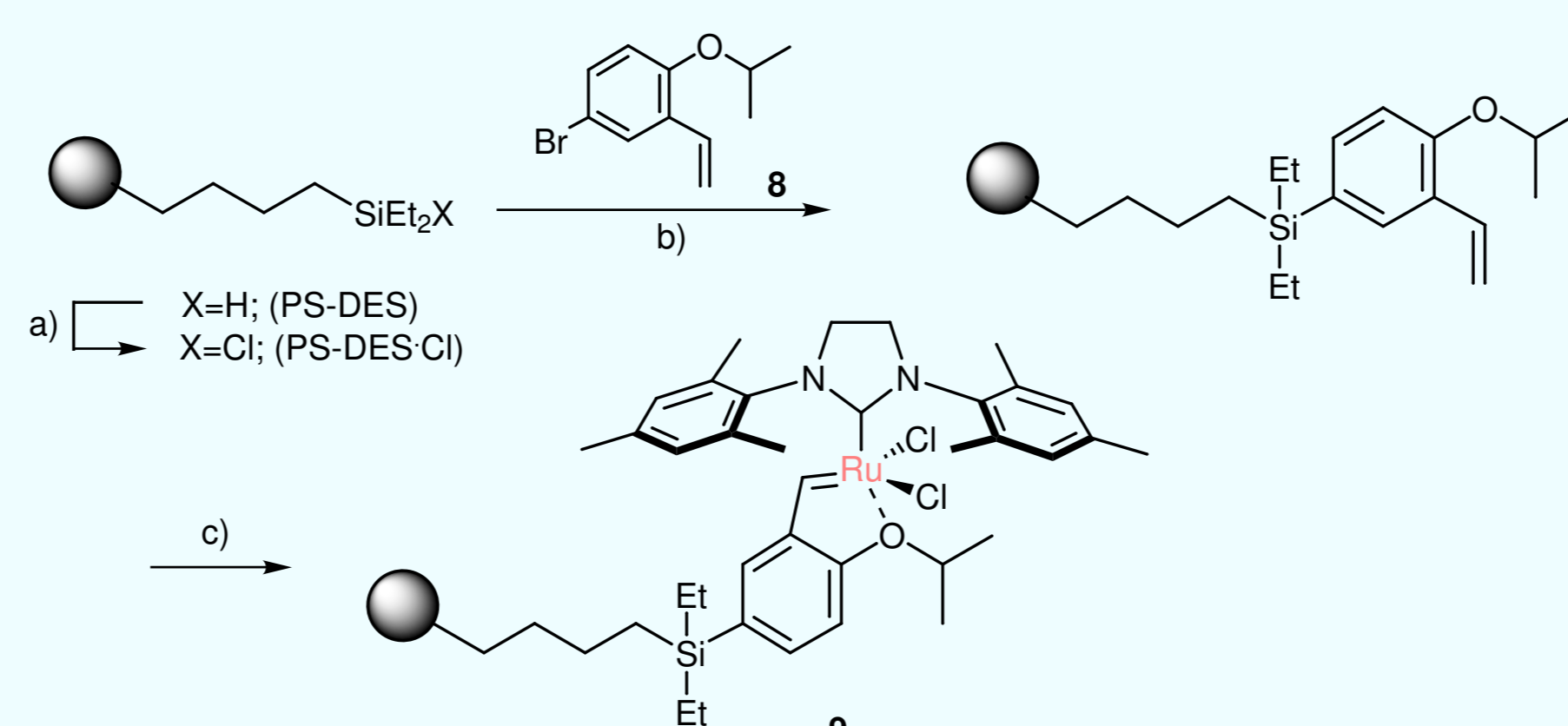
Reagents and conditions: a) iPrI, K₂CO₃, cat. Cs₂CO₃, DMF, 2d, RT, 86%; b) Ph₃P=CH₂, THF, –78 °C to RT, 1h, 57%; c) 1, CuCl, CH₂Cl₂, 30°C, 1h, 83%

We have shown that the Hoveyda-type catalysts can be significantly improved by changing electronic situation in the Ru-chelating isopropoxy-fragment. The introduction of the strong electron-withdrawing NO₂ group leads to complex **7** which is similarly stable but dramatically more reactive than the parent catalyst **2**. The highly active and easy to obtain in a three-step synthesis complex **7** is attractive from practical point of view. This catalyst operates in very mild conditions (0 °C to RT) and can be successfully applied in various types of metatheses (RCM, CM, enyne). [*Angew. Chem. Int. Ed.* 2002, 41, 4038–4040; (*Angew. Chem.* 2002, 114, 4210–4212)]



1.3 A PS-DES Immobilized Ruthenium Carbene

Despite the major advantages offered by the ruthenium catalysts bearing NHC-ligands, they share some disadvantages. Since metathesis reactions are expected to be used in pharmaceutical processes, the most undesirable feature of these complexes is that they decompose to form highly coloured ruthenium by-products, which are difficult to remove from the reaction products. From the point of view of chemical-economy recyclability is another important attribute. The need for further developments in this area led us to try yet another approach to efficiently immobilise a metathesis catalyst.



Reagents and conditions: a) 1, 3-dichloro-5,5-dimethylhydantoin, CH₂Cl₂, rt, 5h; b) 8, tBuLi, Et₂O, –78 °C then PS-DES-Cl, THF, –78 °C to rt, 24h; c) 1, CH₂Cl₂, rt, 24h, 4 times.

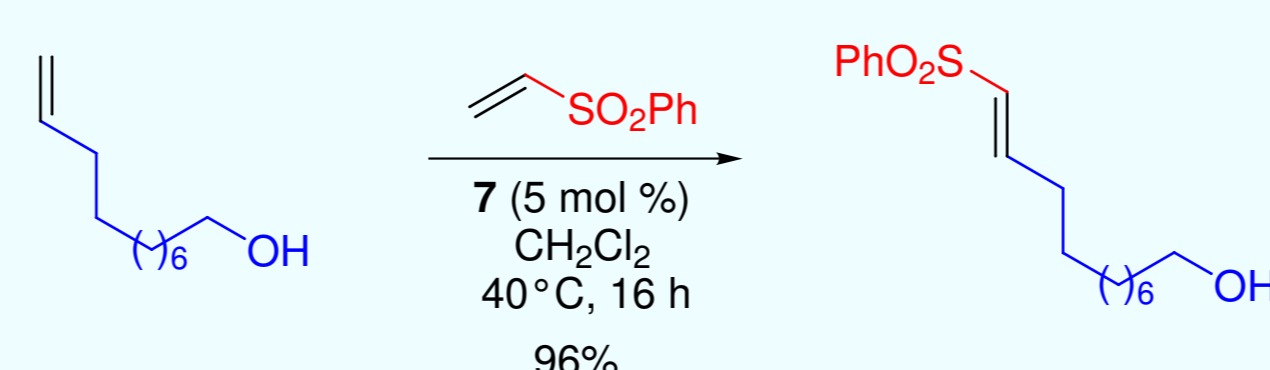
The catalyst **9** obtained as deep-green beads showing ruthenium loading of 0.22–0.35 mmol/g can be successfully applied for ring-closing metathesis leading to the formation of different carbo- and heterocycles of ring sizes 5–7 and 15–16. [*Tetrahedron Lett.* 2002, 43, 6425–6428]

2 Metathesis of Substituted Olefins

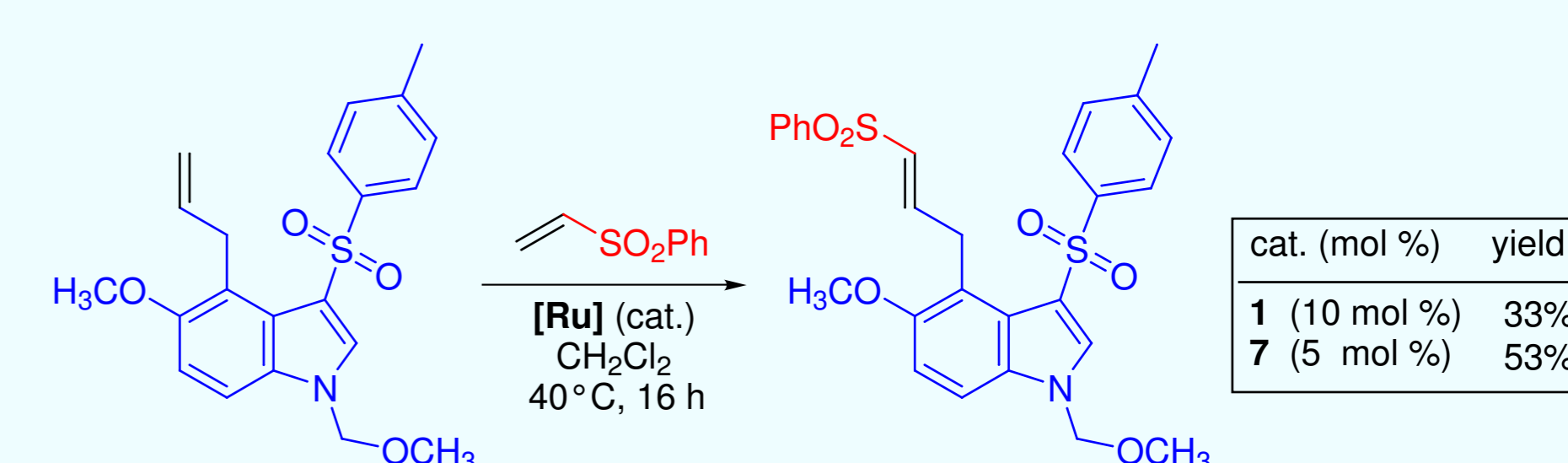


2.1 Cross-metathesis Reaction of Vinyl Sulfones

Substituted α,β -unsaturated sulfones are generally well accepted as useful intermediates in organic synthesis, *e.g.* as Michael acceptors and as 2π partners in cycloaddition reactions. Therefore, we decided to investigate the cross metathesis of readily available vinyl sulfones with terminal olefins.

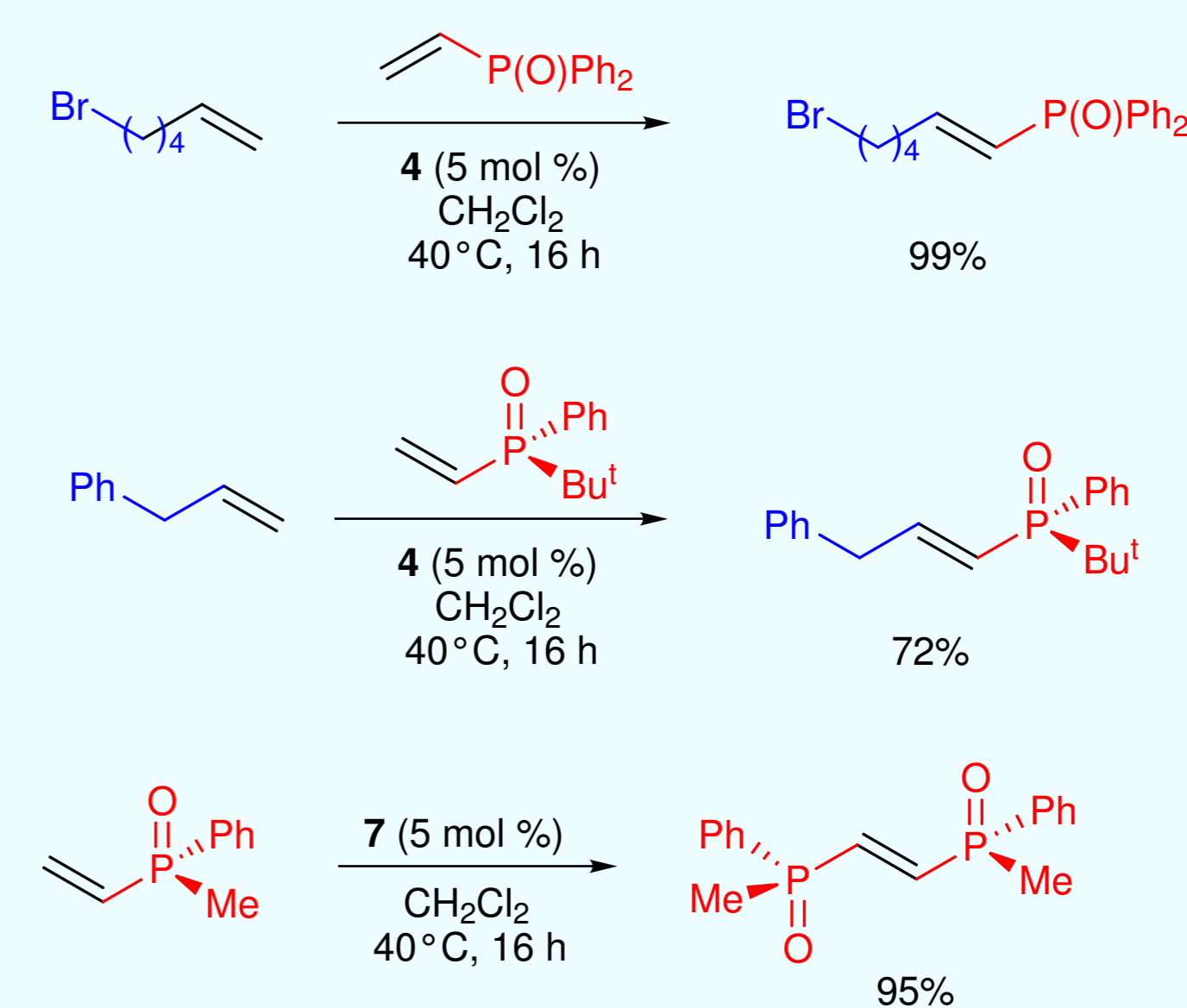


The reaction of *terminal* alkenes with phenyl vinyl sulfone proceeds smoothly to give the corresponding products in moderate to good yields. In all reported cases the (*E*)-alkene was the only isomer detected by GC/MS and NMR. [*Tetrahedron Lett.* 2001, 42, 6425–6428; *Tetrahedron* 2003, 59, 4525–4531]



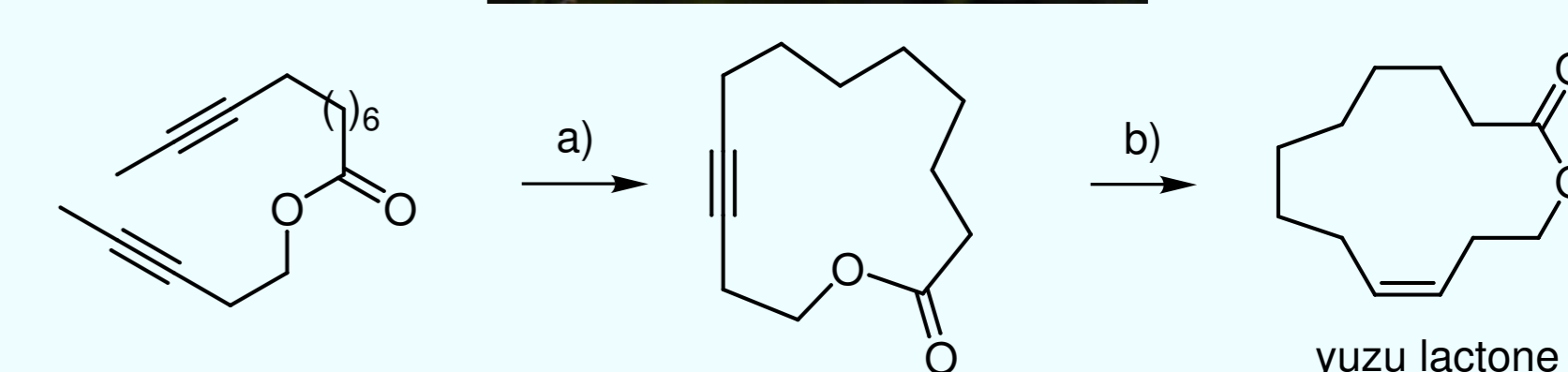
2.2 Synthesis of Substituted Vinylphosphine Oxides by Olefin Cross-Metathesis

Substituted vinylphosphine oxides have been prepared in good yield and exclusive (*E*)-olefin selectivity via olefin cross-metathesis. Metathesis of chiral vinylphosphine oxides proceeds without racemisation of the phosphorus chirality centre providing easy access to functionalised chiral nonracemic (*E*)-alkenylphosphine oxides. [*Org. Lett. in print*]



3 An Improved Catalyst for Alkyne Metathesis

An improved "instant" catalyst for ring closing alkyne metathesis reaction has been prepared. Catalyst formed in situ from molybdenum hexacarbonyl and 2-fluorophenol can be used without exclusion of air and moisture and shows high activity in metathesis of functionalized diynes. The high activity of 2-fluorophenol-based system can be seen from the stereoselective synthesis of yuzu lactone, the minty, camphor-like odoured macrolide isolated from flesh and peel of the Japanese citrus tree *Citrus juno* Tanaka (Yuzu). [*Org. Lett.* 2002, 4, 3747–3749]



Reagents and conditions: a) Mo(CO)₆, 2-fluorophenol, PhCl, reflux, 2h, 79%; b) Lindlar catalyst, quinoline, H₂ (1 atm), hexanes, 98%

4 Acknowledgments

This work was supported by the Volkswagen Foundation (Grant I/77 592) and the State Committee of Scientific Research (Grant No. 4 T09A 136 22).

