

Asymmetric Intermolecular Pauson–Khand Reaction of Symmetrically Substituted Alkynes

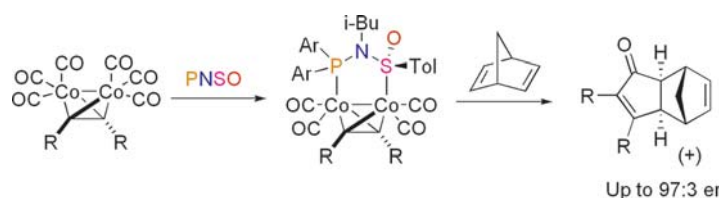
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ABSTRACT



The asymmetric intermolecular Pauson–Khand reaction of symmetric alkynes has been accomplished for the first time. *N*-Phosphino-*p*-tolylsulfonamide (PNSO) ligands have been identified as efficient ligands in this process. The chirality of the cobalt *S*-bonded sulfinyl moiety was found to direct olefin insertion into one of the two possible cobalt–carbon bonds in the alkyne complex. Reaction of symmetric alkynes allows for a simplified experimental protocol since there is no need for separation of diastereomeric complexes.

Since its discovery, the Pauson–Khand reaction (PKR) has attracted the interest of the community of chemists because it provides the most simple and attractive access to cyclopentenone compounds, which in turn are valuable synthetic intermediates.^{1,2} The use of cobalt,^{3,4} rhodium,⁵ iridium,⁶ and titanium⁷ complexes has allowed the development of efficient asymmetric intramolecular versions of this process. Although great advances have been made in this field, one major challenge remains,⁸ namely the use of symmetrically substituted alkynes in an enantioselective intermolecular process. From the synthetic point of view, an intermolecular reaction offers a clear advantage over an intramolecular one:

from three simple components (alkene, alkyne, CO) it provides high added-value molecules in a single step.

The standard methodology used in the asymmetric cobalt-mediated intermolecular PKR relies on the use of chiral phosphines and terminal alkynes.⁹ The reaction of a chiral phosphine with a terminal dicobalt–alkyne complex provides two diastereomers. Once these are separated, olefin reaction with each diastereomer usually leads to the corresponding PKR product in high optical purity. The success of this approach depends on two

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