Highly Selective Olefin-Assisted Pd(II)-Catalyzed Oxidative Alkynylation of Enallenes


Significance: Molecules containing multiple unsaturated bonds represent a versatile class of compounds for synthetic organic chemists. In particular, enyne motifs have been of special interest because of their prevalence in natural and biologically active compounds and their value as building blocks. In this work, the authors disclose the synthesis of this class of compounds by using a selective olefin-assisted palladium-catalyzed oxidative alkynylation of enallenes with terminal alkynes as quenching agents.

Comment: Enallenes reacted with a number of terminal alkynes in the presence of Pd(OAc)$_2$ using 1,4-benzoquinone as oxidant. The resulting trienynes were obtained in moderate to good yields, essentially as a single stereoisomer. The presence of a pendant alkene moiety was found to be necessary for both reactivity and selectivity. Scalability of this protocol was demonstrated by performing a gram-scale reaction. The use of a catalytic amount of oxidant and an electron-transfer mediator under oxygen atmosphere in a biomimetic approach was also successful.

Use of an electron-transfer mediator:

Selected examples: