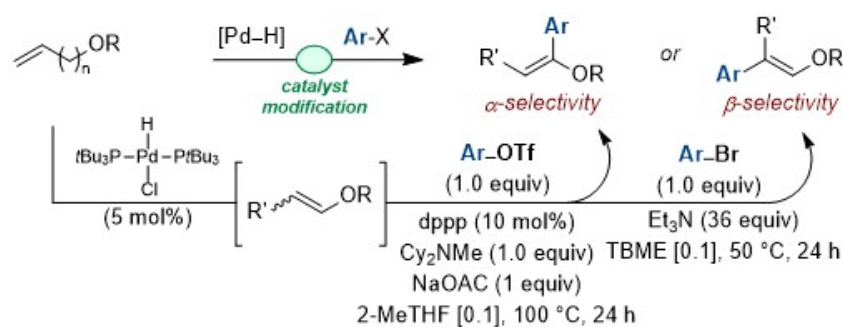


Assisted Tandem Pd Catalysis Enables Regiodivergent Heck Arylation of Transiently-Generated Substituted Enol Ethers

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The “one-pot” multi-step synthesis of organic molecules is considered an efficient and environmental-friendly approach since it prevents the use of several purification procedures and reduce the costs, time and chemical wastes.¹ For these reasons, numerous research groups have combined a metal-catalyzed olefin isomerization reaction with an additional chemical transformation performed in the same reaction vessel.²



Herein we describe an operationally-simple assisted tandem catalysis in which sensitive and unexplored 1,2-disubstituted vinyl ethers are formed *in-situ* by olefin migration and then regioselectively cross-coupled with a variety of aryl electrophiles. The isomerization is performed by means of a known [Pd(II)-H] catalysts which is subsequently reduced to [Pd(0)] by an organic base to initiate the Heck cross coupling.^{3,4} When the [Pd(II)-H] catalyst is modified by addition of a bisphosphine ligand (dppp), an organic base (Cy₂NMe), sodium acetate and aryl triflates are used as electrophiles, the α -arylation pathway is promoted preferentially. Instead the β -arylation pathway is favored for electron-deficient and electron-neutral aryl halides when the catalyst is simply modified by addition of an excess of an organic base (Et₃N). The products are generally obtained in good yield, regioselectivity and moderate stereoselectivity which is proposed to reflect the absence of stereocontrol in the isomerization step. The present methodology was further enriched by preliminary investigations which showed that high levels of stereoselectivity can be achieved either by ligand control or post-catalytic stereo-correction.

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