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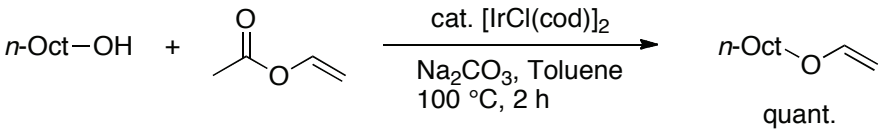
# Discussion Addendum for: Iridium-catalyzed Synthesis of Vinyl Ethers from Alcohols and Vinyl Acetate

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The synthesis of vinyl ethers by vinyl transfer from vinyl esters to alcohols constitutes the basis for much useful methodology. The originally reported iridium-catalyzed process provides a versatile and practical route to access vinyl alcohols.[2] This methodology was successfully expanded to facilitate allyl transfer from allyl acetates to alkyl alcohols, providing allyl ethers as products.[3] In addition, as a successful application of this protocol, the one-pot synthesis of γ,δ-unsaturated carbonyl compounds from allyl alcohols and vinyl acetates was achieved through in situ iridium-catalyzed formation of allylic vinyl ethers followed by Claisen rearrangement.[4] The above-mentioned advances will be summarized here.

## Scope of Allylation of Alcohols from Allyl Acetates

Vinyl ethers and allyl ethers are important classes of compounds that have been used in polymer synthesis and in the pharmaceutical chemistry,[5] as well as starting materials for Claisen rearrangements,[6] cycloadditions,[7] hydroformylations,[8] and Mizoroki-Heck reactions,[9] etc.

We found that the iridium cationic complex $[Ir(cod)_2]^+BF_4^-$ catalyzed the allylation of alcohols with allyl acetate to afford allyl ethers as products.[3] For instance, the reaction of allyl acetate with *n*-octyl alcohol in the presence of a catalytic amount of $[Ir(cod)_2]^+BF_4^-$ complex afforded allyl octyl ether in quantitative yield (Figure 1).


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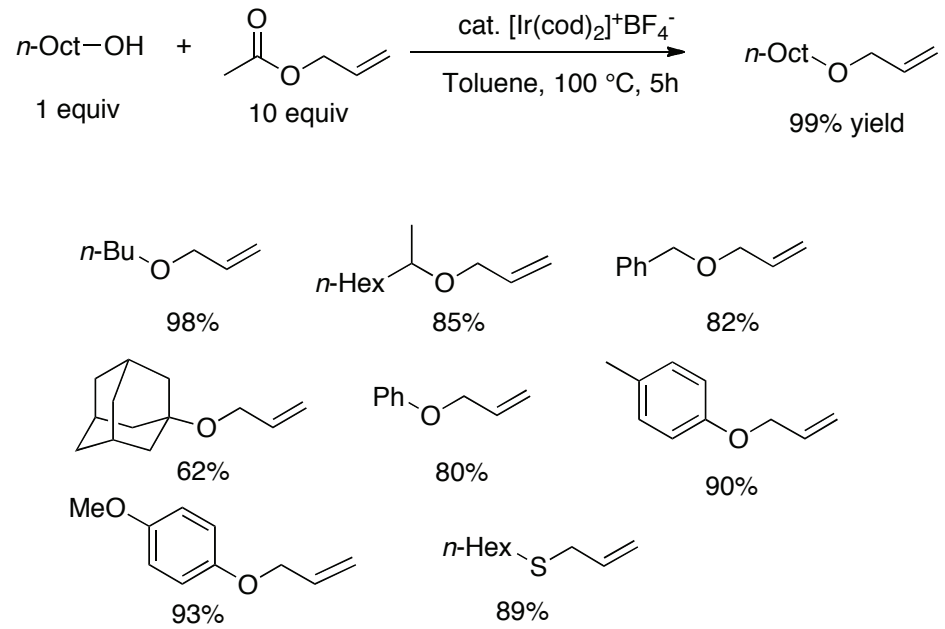


**Figure 1.** Ir-catalyzed reaction of *n*-octyl alcohol with allyl acetate to allyl octyl ether

## Application of the Vinyl Transfer Methodology in Organic Synthesis

We previously reported the rearrangement of allyl homoallyl ethers to γ,δ-unsaturated aldehydes induced by the $[IrCl(cod)]_2$ complex.[10] Therefore, this protocol would serve to a useful route for the formation of γ,δ-unsaturated carbonyl compounds from allyl alcohols with vinyl or isopropenyl acetate through the formation of vinyl ethers as the key intermediate.[4] For example, the reaction of *trans*-2-methyl-3-phenyl-2-propen-1-ol with isopropenyl acetate in the presence of $[IrCl(cod)]_2$ catalyst combined with $Cs_2CO_3$ at 100 °C for 3 h followed by heating at 140 °C for 15 h afforded 5-methyl-4-phenyl-5-hexen-2-one in 83% yield (Figure 2). The reaction is thought to proceed through the Claisen rearrangement of the in situ generated allylic vinyl ether.

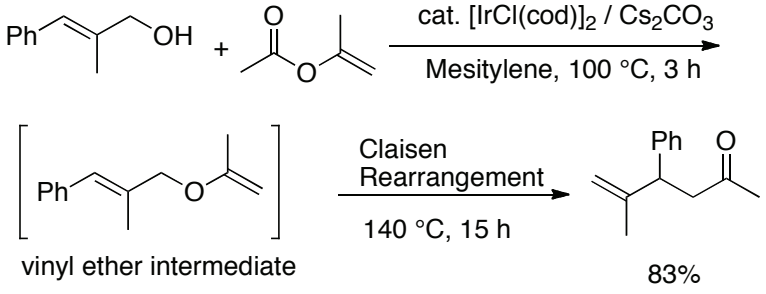


**Figure 2.** Ir-catalyzed one-pot synthesis of γ,δ-unsaturated carbonyl compounds

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