**Synthesis of Phosphaisocoumarins via Ruthenium Catalysis**

**Significance:** Presented is the ruthenium-catalyzed C–H activation–cyclization of aryl phosphonic monoester and phosphinic acids resulting in phosphaisocoumarins. An extensive screening identified the witches’ brew shown to be ideal. The reason for the effectiveness of the mixture of Ag$_2$CO$_3$–AgOAc–KPF$_6$ is not identified. However, it was shown that in the absence of KPF$_6$ the reaction does proceed, albeit with lower yields (63% vs. 97%). AgOAc alone affords a comparable yield to the Ag$_2$CO$_3$–AgOAc mixture, although this was established early in the optimization study with only 2 mol% ruthenium catalyst. AgOAc alone was not used with a higher catalyst loading, leading to the extrapolation that the reaction may be successful without additional KPF$_6$ and Ag$_2$CO$_3$. The scope of the reaction was well studied and the yields range from moderate to good.

**Comment:** Heterocyclic phosphorus-containing compounds can have significant biological and pharmaceutical properties. The synthesis of phosphaisocoumarins has recently been reported using rhodium-catalyzed C–H activation–cyclization of alkyynes with organophosphorus compounds (Y. Unoh et al. Org. Lett. 2013, 15, 3258). The current report uses similar conditions, but with a less expensive ruthenium catalyst, albeit in a more complex overall reaction system. The reaction seems tolerant to electron-withdrawing and -donating groups on both alkyne and aryl phosphorus starting materials, although alkynes with strong electron-withdrawing groups were not tested. Some mechanistic studies were conducted using deuterium-labelled organophosphorus compounds, and a kinetic isotope effect ($k_H/k_D = 5.67$) was observed, indicating that C2–H bond cleavage is most likely involved in the rate-limiting step. A plausible mechanism was proposed, which does not include rationalization of the effect of the mixture of reagents involved in the reaction.