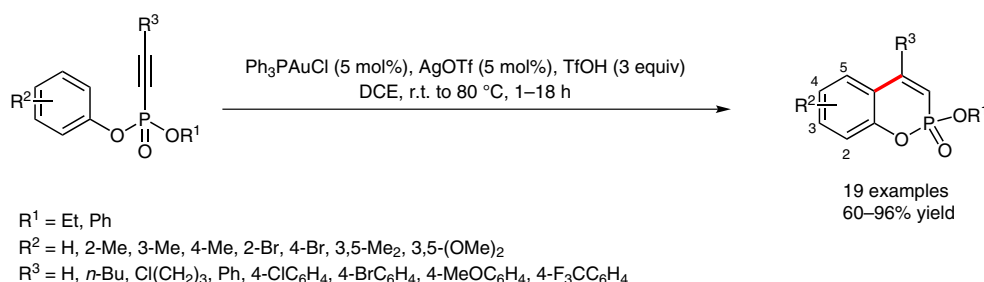


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 Gold-Catalyzed Hydroarylation of Aryl Alkynylphosphonates for the Synthesis of Phosphacoumarins  
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# Hydroarylation Approach to Phosphacoumarins



**Significance:** Reported is an intramolecular hydroarylation of aryl alkynylphosphonates catalyzed by gold–silver and resulting in the formation of phosphacoumarins. The starting materials are synthesized by the reaction of terminal alkynes with chlorophosphonates using a strong base (*n*-BuLi) at cryogenic temperatures. Optimization studies on the cyclization reaction using mixtures of different gold and silver salts led mostly to starting material recovery and/or isolation of  $\beta$ -keto-phosphonates. Trifluoromethanesulfonic acid (TfOH) as protic acid additive was unique in effecting the hydroarylation. Control experiments in the absence of gold, or in the absence of metals altogether, led to very poor yields of products. Surprisingly, no control experiment in the absence of silver was conducted. The substrate scope was well studied, except for absence of cases with  $R^2$  = electron-withdrawing groups. The yields seem to be consistently good.

**Comment:** Previous syntheses of phosphacoumarins, for example by the condensation of salicylaldehydes with diethylphosphonoacetates (C. H. Chen, J. L. Fox, J. L. Lippert *J. Heterocycl. Chem.* **1987**, 24, 931) suffer from deficiencies such as poorly available starting materials and harsh reaction conditions. The current methodology offers usage of reasonably mild catalytic conditions and readily available starting materials. The synthesis of the starting chlorophosphonates, which is not reported, does not seem to be too arduous an undertaking. Mechanistic studies hint at the involvement of an allene intermediate. Refreshingly, the authors conclude that more mechanistic elucidation has to be performed rather than draw the unsupported catalytic cycle pervasive in the current literature.

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