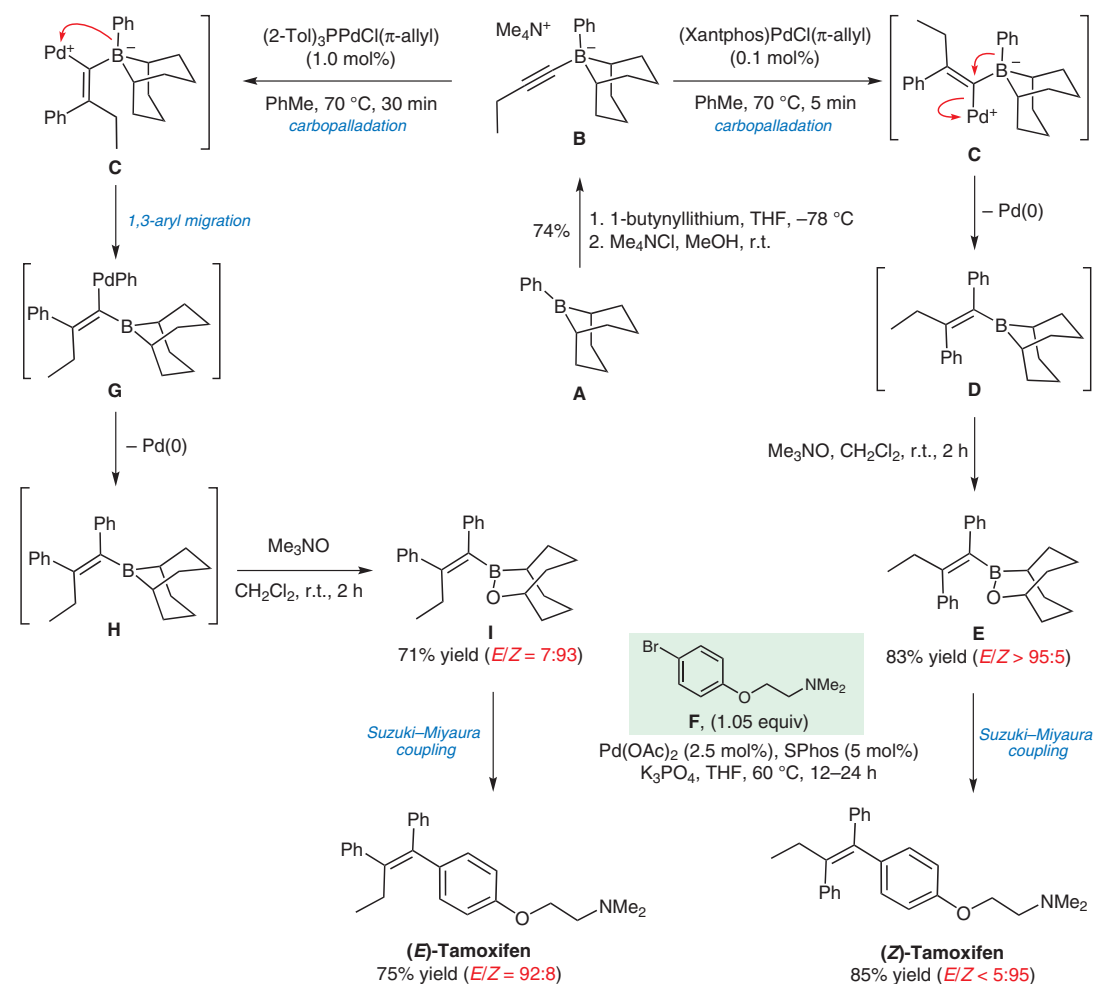


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Stereoselective Synthesis of (*E*)-(Trisubstituted Alkenyl)borinic Esters: Stereochemistry Reversed by Ligand in the Palladium-Catalyzed Reaction of Alkynylborates with Aryl Halides

*Org. Lett.* **2009**, *11*, 5434-5437.

## Synthesis of (*E*)- and (*Z*)-Tamoxifen



**Significance:** (*Z*)-Tamoxifen is used for the treatment of estrogen receptor positive breast cancer. The synthesis depicted features a *syn*-carbopalladation of alkynyl borate **B** followed by a 1,2-aryl migration (**C** → **D**) to generate a trisubstituted alkenylborane in high yield and stereoselectivity. Oxidation of the alkenylborane **D** with  $\text{Me}_3\text{NO}$  afforded the alkenylborinic ester **E** that participated in an efficient Suzuki-Miyaura coupling to give (*Z*)-tamoxifen.

**Comment:** The fate of the *syn*-carbopalladation product **C** depended on the ligand. When the ligand was small [ $(2\text{-Tol})_3\text{P}$ ], a 1,3-aryl migration took place (**C** → **G**) to generate the alkenylborane **H** after reductive elimination. Alkenylborane **H** was converted into (*E*)-tamoxifen as shown. The borate derived from **B** is stable towards air and moisture. A further 14 examples of the synthesis of alkenylborinic esters via the 1,2-aryl migration pathway are presented.

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**SYNFACT**  
of the month

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