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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


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 product C that depended on the ligand. When the ligand was small [(2-Tol)3P], 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.

**Comment:** The fate of the syn-carbopalladation product C depended on the ligand. When the ligand was small [(2-Tol)3P], 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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