Significance: Reported is a palladium-catalyzed synthesis of N-aryl indoles from the reaction of diarylamines with olefins by a hydroamination–C–H activation route. In recent years, the traditional methods, for example, the venerable century-old Fischer indole synthesis, among other textbook reactions, have been superceded by a barrage of methodologies based on transition-metal-catalyzed heteroannulation processes originating with Larock, with significant contributions by Buchwald, Ackermann, Glorius, Fagnou, among others (see: Angew. Chem. Int. Ed. 2013, 52, 3434; J. Am. Chem. Soc. 2012, 134, 9098; Angew. Chem. Int. Ed. 2013, 52, 12426). The present methodology takes advantage of the Fujiwara–Moritani reaction (hydroamination of olefins) together with a precedented aryl C–H activation to achieve the N-aryl indole synthesis. Although a comparison to another ruthenium-based photocatalytic method is given, the significance of the present route in assessment to plethora of recently similar established methods is unfortunately not made and would require reading of about 30 references cited in this report.

Comment: The scope of the reaction is defined mainly with styrenes with a few cases of other aliphatic olefins included. The yields of products are modest to good with noticeably lower yields with stericly demanding styryl systems. N-Aryl variation to heterocyclic substituted aryls and pyridyl may be obtained albeit also with lower yields. For unsymmetrical diaryl amines, the regioselectivity of C–H activation–annulations occurs towards the EWG aryl ring. Based on the achieved regioselectivity pattern, a mechanism of initial orthopalladation (for EWG aryls) and initial N-palladation (for EDG aryls) is proposed. The reaction of prototype diphenylamine in the absence of styrene reactant partner in D2O afforded diphenylamine deuterated in all ortho- and para-positions (75–80% d-incorporation), which suggests reversible electrophilic palladation and raises the question of validity to name this a C–H activation process. However, the absence of para-deuterated product in the presence of the styrene co-reactant is good evidence for Pd being trapped by initial N-coordination. Furthermore, putative 2-aminostilbene and indolenine intermediates were shown to be converted into indole products under the given conditions. This is a useful beginning of a mechanistic study whose elaboration is promised.