

The Cross-Coupling of Allylic Silanolate Salts with Aromatic Bromides

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The sodium salts of unsubstituted (allyl), substituted (crotyl), and α -stereogenic allylic silanols were synthesized and found to be stable, free-flowing powders that readily undergo palladium-catalyzed cross-coupling with a wide variety of aryl bromides to afford allylated arenes. Unsubstituted 2-propenyldimethylsilanolate cross-couples under ligand- and activator-free conditions to afford the desired products in 73-95% yield. Studies to determine allylic site-selectivity used substituted 2-butenyldimethylsilanolate and established that these reagents were mechanistically distinct from other allylic organometallic donors. Additionally, a remarkable influence of the π -acidic dibenzylideneacetone ligand led to high γ -selectivities in couplings with electron-rich and electron-poor aryl bromides, and heteroaromatic bromides in 40-83% yields. Chirality transfer experiments with scalemic, α -stereogenic allylic silanolates (94:6 er) revealed kinetic resolution through a highly ordered transmetalation event to produce allyl arenes of greater enantioenrichment (98:2 er). A unified mechanistic picture involving displacement, followed by intramolecular γ -transmetalation, and direct reductive elimination can rationalize all the observed trends.

