

SESSION II: SPEAKER ABSTRACTS

C–H to C–N Cross-coupling of Sulfonamides with Olefins

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Due to the ubiquity of C–N bonds in natural products and pharmaceuticals, the cross-coupling of nitrogen functionality with hydrocarbons under fragment coupling conditions (1 equivalent) stands to significantly impact chemical synthesis. Whereas significant progress has been made in cross-couplings of amines with aryl halides to form C(sp²)–N bonds, the development of analogous C(sp³)–N coupling reactions remains an elusive goal. Herein, we disclose a C(sp³)–N fragment coupling reaction between abundant terminal olefins and *N*-triflyl protected aliphatic and aromatic amines via Pd(II)/sulfoxide-oxazoline (SOX) catalyzed intermolecular allylic C–H amination. A range of (52) allylic amines are furnished in good yields (avg. 76%) and excellent regio- and stereoselectivity (avg. >20:1 linear:branched, >20:1 *E:Z*). For the first time, a variety of singly activated aromatic and aliphatic nitrogen nucleophiles, including ones with stereochemical elements, can be used in fragment coupling stoichiometries for intermolecular C–H amination reactions. Mechanistic studies reveal that the SOX ligand framework is uniquely effective at promoting functionalizations with such alkyl amine nucleophiles in the absence of any other activators.

