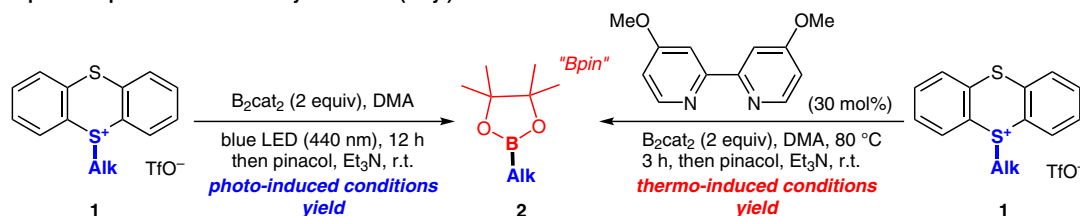
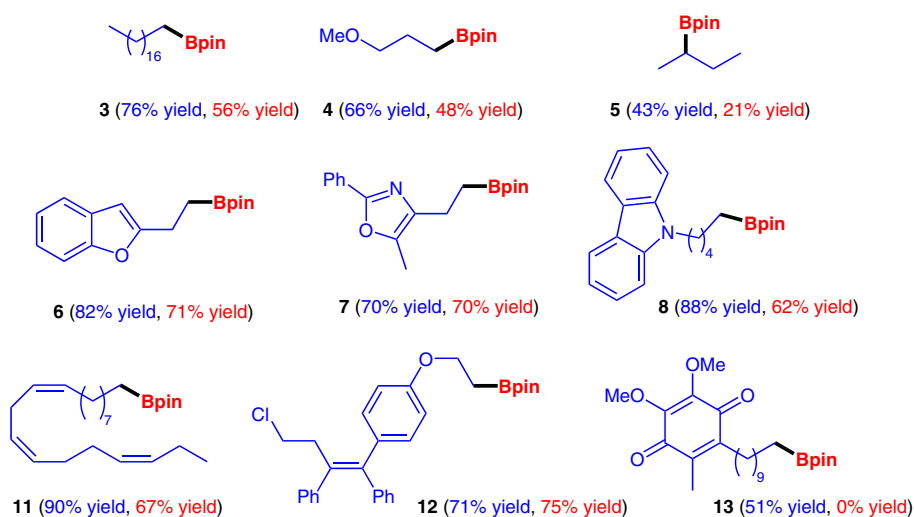


Single-Electron Reduction of Sulfonium Salts for the Generation of Nonstabilized Alkyl Radicals

Optimized protocols for the borylation of *S*-(alkyl) thianthrenium salts:



Examples:



Significance: Although several reports describe single-electron transfer (SET) induced transformations of sulfonium salts to form aryl radicals, the analogous generation of alkyl radicals, particularly nonstabilized ones, from sulfonium salts is synthetically challenging. Taking inspiration from the *S*-adenosylmethionine (SAM) superfamily of enzymes that catalyze the formation of alkyl radicals from sulfonium salts in nature, the current report describes a mild photoredox-mediated approach for the generation of these species from *S*-alkylthianthrenium salts and their subsequent reaction to either form a diverse array of alkyl boronates or to participate in C–C bond-forming reactions.

Comment: The *S*-alkylthianthrenium salts were synthesized on a gram-scale by a one-pot method involving sequential treatment of the corresponding alcohols with Tf_2O and thianthrene; the product structure was confirmed by single-crystal X-ray crystallography. Model studies on the desulfurative borylation demonstrated that this transformation could be achieved under both photoinduced and Lewis base catalyzed thermal conditions, although the nature of the sulfonium salt was critical for success. Typically, the photochemical process led to better yields than the Lewis base system, with subtle differences in substrate reactivity also being observed (see 13). The alkyl radicals generated were also shown to engage in a range of C–C bond-forming processes; mechanistic studies suggested the intermediacy of an electron donor–acceptor complex.