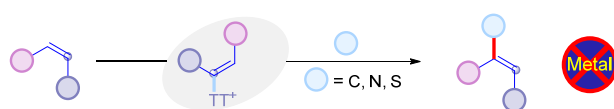


## TOC and Abstract



- unified protocol for intermolecular formal metal-free Heck-type reaction
- metal-free C-N, C-S, C-C bond-forming from *cine*-C-H bond
- internal & terminal, aryl & aliphatic alkenes

Herein, we report a unified protocol for metal-free *cine*-functionalizations of alkenes by thianthrenation. The reaction explores the new reactivity of alkenyl thianthrenium salts to form a new chemical bond at *cine*-position instead of *ipso*-position of vinyl thianthrenium salts. The reaction represents new metal-free reaction mode to functionalize *cine*-carbon of alkenyl thianthrenium salts, which is complementary to previous functionalization at *ipso*-carbon. The mild condition allows for the site-selective C-H functionalization of alkenes to forge C-S, C-N and C-C bonds with diverse nucleophiles.