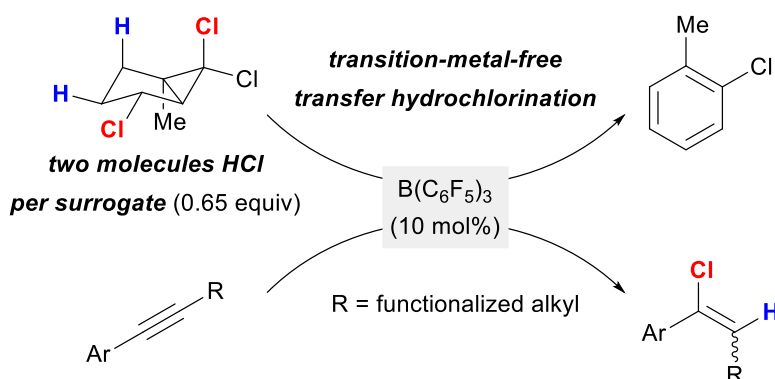


Metal-free transfer hydrochlorination of internal C–C triple bonds with a bicyclo[3.1.0]hexane-based surrogate releasing two molecules of hydrogen chloride

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Alkenyl chlorides are fundamental starting materials for the synthesis of complex molecules.^[1] Although a variety of methods for their synthesis exists, the hydrochlorination of alkynes is one of the most straightforward approaches while generating only minimal amounts of waste. The use of the toxic and corrosive gas hydrogen chloride however, is undesirable, particularly on a laboratory scale. Thus, transfer hydrochlorination which uses liquid or solid, non-corrosive surrogates has become an important field in organic chemistry. Our group has previously developed protocols for the ionic transfer hydroiodination^[2] and transfer hydrobromination^[3] but efforts to adapt the platform for transfer hydrochlorination failed.

Herein, we report the synthesis and application of a hydrochlorination reagent that transfers two molecules of HCl per molecule of surrogate to internal alkynes. Whereas the previously used surrogates for hydro(pseudo-)halogen transfer were based on a cyclohexa-1,4-diene core,^[4] bicyclo[3.1.0]hexanes are introduced as a new surrogate scaffold. Besides aromatization, strain release is leveraged as an additional driving force to transfer two molecules of HCl. The surrogate is activated under metal-free conditions using tris(pentafluorophenyl)borane (B(C₆F₅)₃) as catalyst and is eventually converted to a volatile byproduct of low molecular weight.

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