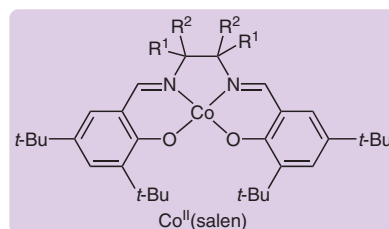
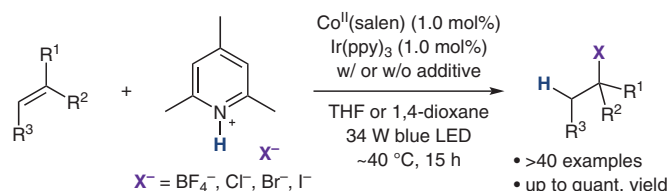


Hydrohalogenation of Alkenes Using Collidine-HX Salts under Dual Cobalt and Photoredox Catalysis



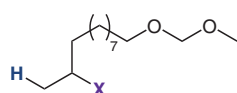
Hydrofluorination
additive
n-Bu₄NOTf (10 mol%)
H₂O (1.0 equiv)

Hydrochlorination
additive
n-Bu₄NOTf (10 mol%)

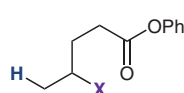
Hydrobromination
additive
w/o

Hydroiodination
additive
w/o

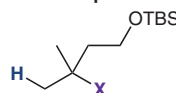
Selected examples:



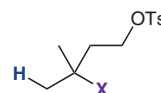
X = F: 46% yield
X = Cl: 76% yield
X = Br: >99% yield
X = I: 85% yield



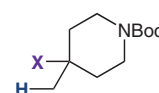
X = F: 0% yield
X = Cl: 96% yield
X = Br: 78% yield
X = I: 87% yield



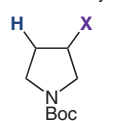
X = F: 77% yield
X = Cl: 65% yield
X = Br: 93% yield



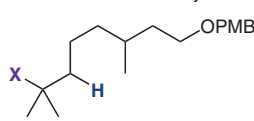
X = F: 71% yield
X = Cl: 95% yield
X = Br: >99% yield



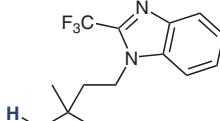
X = F: 85% yield
X = Cl: >99% yield
X = Br: 94% yield



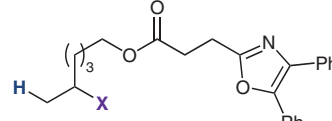
X = F: 12% yield
X = Cl: 80% yield
X = Br: 80% yield
X = I: 44% yield



X = F: 23% yield
X = Cl: 93% yield
X = Br: 95% yield

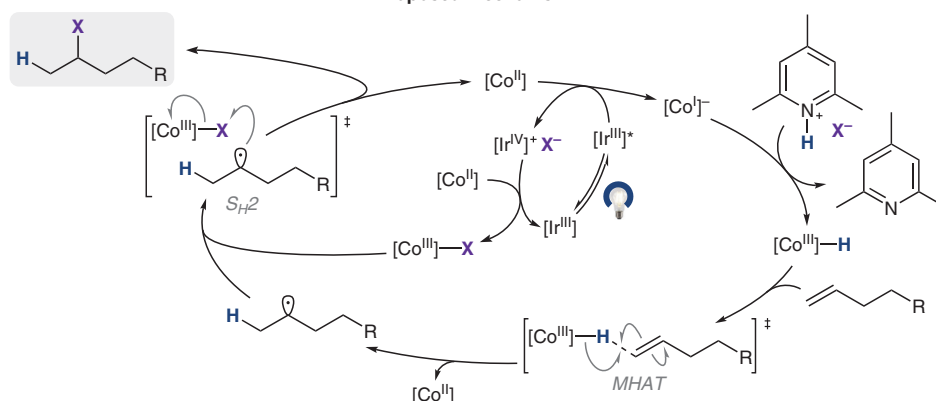


X = F: 97% yield
X = Cl: 56% yield
X = Br: 99% yield



X = F: 47% yield
X = Cl: 53% yield
X = Br: 89% yield

Proposed mechanism:



Significance: A dual photoredox- and cobalt-catalyzed protocol for the hydrohalogenation of aliphatic alkenes using inexpensive and safe-to-handle collidine salts as HX surrogates is disclosed.

Comment: This dual catalysis exploits a radical-based umpolung strategy, in which a proton and a halide anion are converted into a nucleophilic hydrogen radical and an electrophilic halogen radical, respectively.