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Copper-Catalyzed *gem*-Difluoroolefination of Diazo Compounds with $TMSCF_3$ via C–F Bond Cleavage
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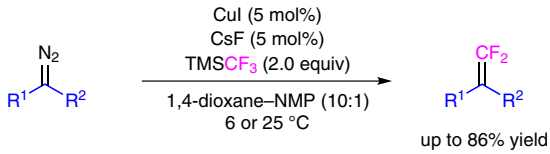
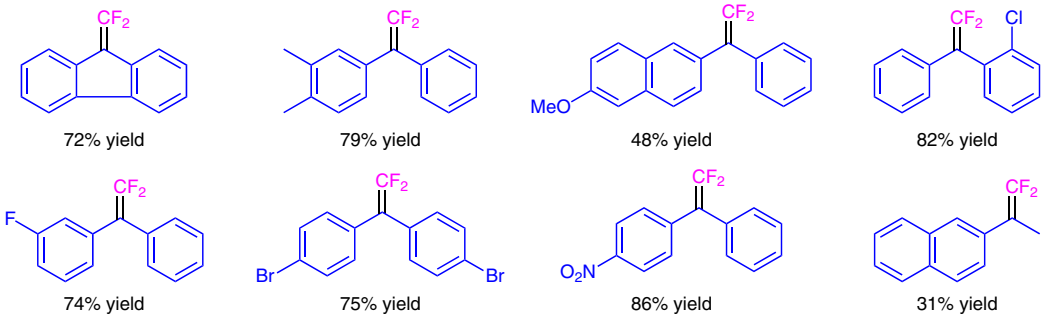
gem-Difluoroolefination of Diazo Compounds with $TMSCF_3$ Catayzed by Copper

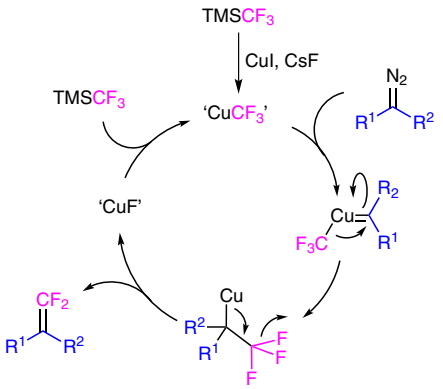


R^1 = Ph, naphthyl derivatives, 4-MeC_6H_4, 3,4-$(Me)_2C_6H_3$, 4-*n*-BuC_6H_4, 4-*t*-BuC_6H_4, 4-$MeOC_6H_4$, 4-$(Me)_2NC_6H_4$, 3-FC_6H_4, 4-FC_6H_4, 3-ClC_6H_4, 3,4-$Cl_2C_6H_3$, 4-ClC_6H_4, 4-BrC_6H_4, 4-$F_3CC_6H_4$, 4-$O_2NC_6H_4$
R^2 = Ph, 2-EtC_6H_4, 3-$PhOC_6H_4$, 4-$(Me)_2NC_6H_4$, 2-FC_6H_4, 4-FC_6H_4, 2-ClC_6H_4, 4-BrC_6H_4, Me
R^1, R^2 = fluorene derivative

Selected examples:



Proposed mechanism:



Significance: Hu and co-workers report the copper-catalyzed synthesis of 1,1-difluoroalkenes via a *gem*-difluoroolefination reaction. The actual reagent '$CuCF_3$' is formed in situ with a stoichiometric amount of $TMSCF_3$ and catalytic amounts of CuI and CsF. Various diazo compounds are transformed into their corresponding difluorovinyl derivatives in high yield.

Comment: Standard approaches for the olefin synthesis, such as the olefin metathesis using 1,1-difluoroethane and a ruthenium carbene catalyst, have not been successful in introducing the $C{=}CF_2$ moiety. This difluorovinyl functionality may be further transformed into tri- and difluoromethyl, monofluoroalkenyl, and difluoromethylenyl groups.

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