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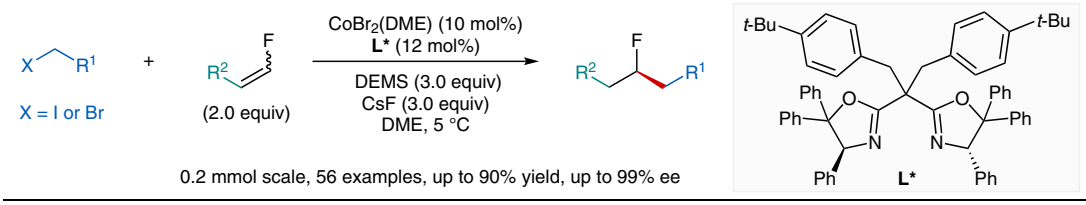
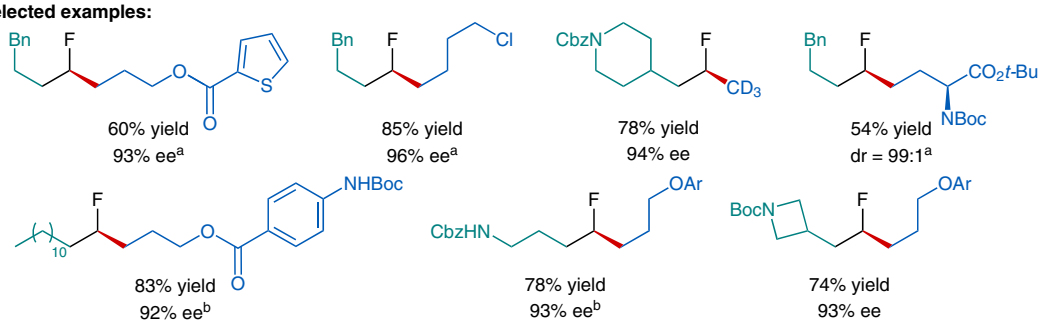
Cobalt-Catalysed Enantioselective C(sp^3)–C(sp^3) Coupling
Nat. Catal. **2021**, *4*, 901–911, DOI: 10.1038/s41929-021-00688-w.

Enantioselective Cobalt-Catalyzed Alkene Hydroalkylation

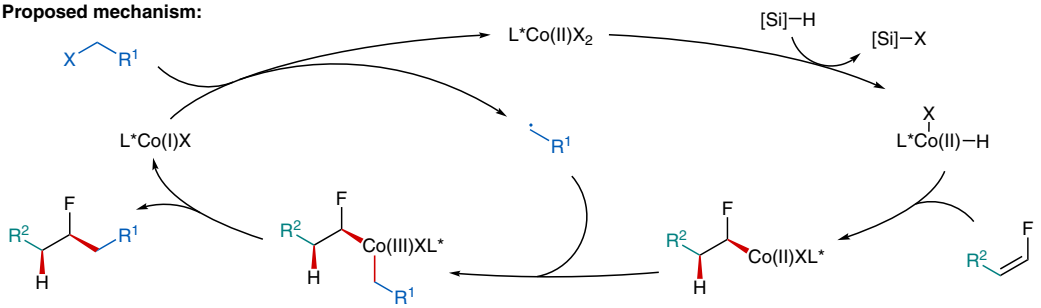


Selected examples:

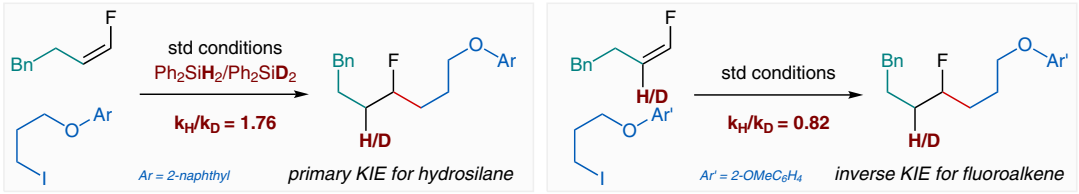


[a] from 1:5.3 (*Z*/*E*) monofluoroalkene, [b] from 19:1 (*Z*/*E*) monofluoroalkene, Ar = 2-naphthyl

Proposed mechanism:



Mechanistic studies:



Significance: A stereoselective Co-catalyzed C(sp^3)–C(sp^3) coupling reaction to access chiral fluoroalkanes has been developed. The reaction exhibits catalyst-controlled enantioselectivity, thereby removing the requirement for substrate auxiliaries. A series of mechanistic and computational studies were conducted to elucidate the mechanism for the transformation.

Comment: The reaction demonstrated high functional group compatibility with regards to both coupling partners. Radical clock experiments support a radical pathway from the alkyl halide. Kinetic studies suggest the reaction proceeds through an irreversible rate-limiting *syn*-hydrometalation of the Co–H intermediate across the π-system.

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Synfacts 2022, 18(01), 0037 Published online: 17.12.2021
DOI: 10.1055/s-0041-1737311; **Reg-No.:** L15422SF