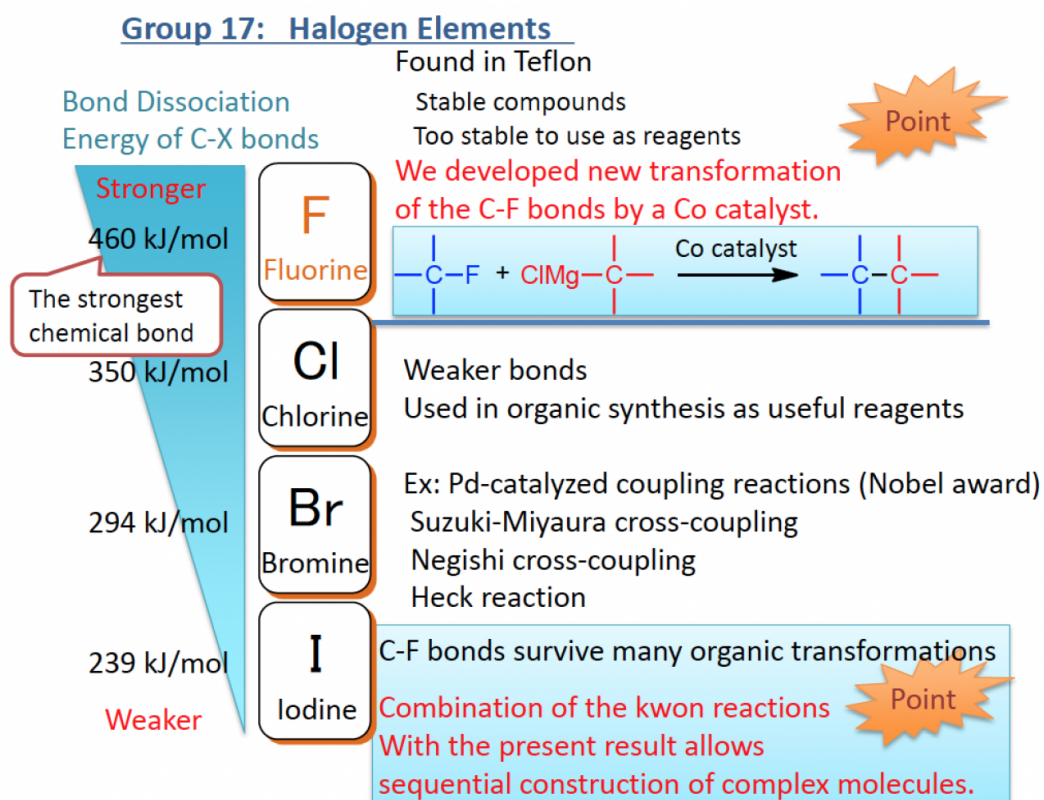


# Chemists build new chemical structures on unreactive bonds

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An outline of this research. Credit: Osaka University

Making complicated organic molecules is like solving a Rubik's cube. Organic chemists need to design sequences of reactions to carefully build up parts of a molecule, while maintaining the structure at other

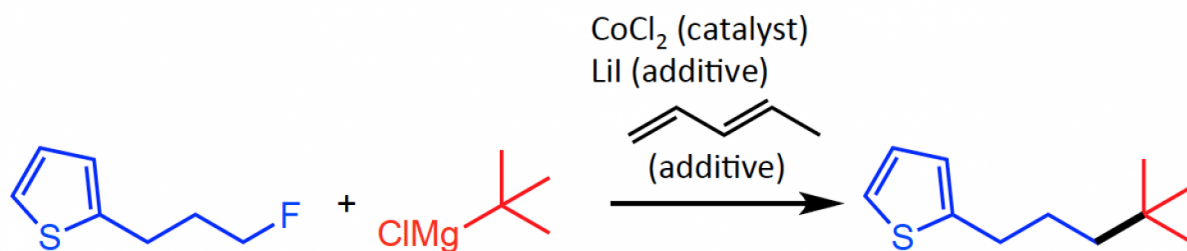
sites. Although chemists have developed many ingenious ways of performing chemical transformations, some chemical reactions remain out of reach.

At Osaka University, a team of organic chemists has now developed and enhanced a [chemical reaction](#) that allows controlled transformations of one of the toughest chemical bonds. "We previously developed a cobalt-catalyzed Grignard reaction for making hindered quaternary carbon centers. But that reaction also showed potential for modifying carbon-fluorine bonds. We tried many different additives and eventually found one that let us selectively build the same quaternary carbon-carbon bonds at carbon-fluorine sites," says first author Takanori Iwasaki.

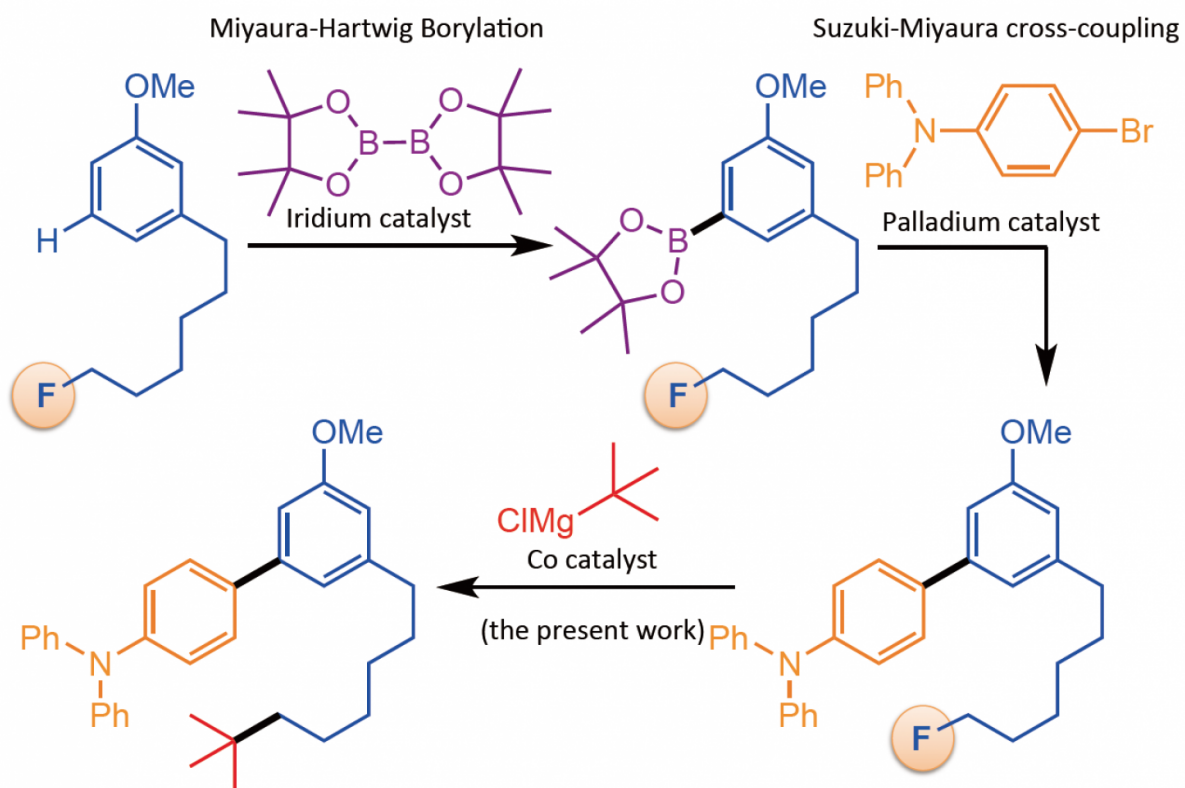
The Grignard reaction is a classic reaction in organic chemistry, useful for building the carbon skeleton of [molecules](#) by transforming carbon-halogen bonds into carbon-carbon bonds. Fluorine is also considered to be a halogen but the carbon-fluorine [bond](#) is among the strongest known and is usually unreactive to Grignard chemistry. Performing any kind of chemical reaction at carbon-fluorine bonds is difficult without affecting the rest of the molecule.

The Osaka team enhanced their catalytic system for performing difficult Grignard chemistry at very crowded, so-called quaternary carbon atoms. By adding a carefully selected additive to this catalytic system, they boosted its ability to work selectively on carbon-fluorine bonds.

"We have shown that this reaction is a very useful tool for sequentially changing parts of a molecule with great control," says group leader Nobuaki Kambe. "Our control over the chemistry of carbon-fluorine bonds should enable much more synthetic freedom for building complex carbon structures."



Co-catalyzed cross-coupling of alkyl fluorides with alkyl Grignard reagents.  
Credit: Osaka University



An iterative coupling reaction using the present catalytic system. Credit: Osaka University

**More information:** Takanori Iwasaki et al, Co-Catalyzed Cross-Coupling Reaction of Alkyl Fluorides with Alkyl Grignard Reagents, *Organic Letters* (2017). [DOI: 10.1021/acs.orglett.7b01370](https://doi.org/10.1021/acs.orglett.7b01370)

Provided by Osaka University

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