

# Division of Synthetic Chemistry

## – Synthetic Organic Chemistry –

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### Scope of Research

Our group has been carrying out innovative research on the organic synthesis by designing catalysts and chemical reactions as well as molecules. Our current research projects include (1) radical-mediated organocatalysis such as N-heterocyclic carbene catalysis or organophotoredox catalysis; (2) reductive umpolung reactions; and (3) boron-based new molecules.

#### KEYWORDS

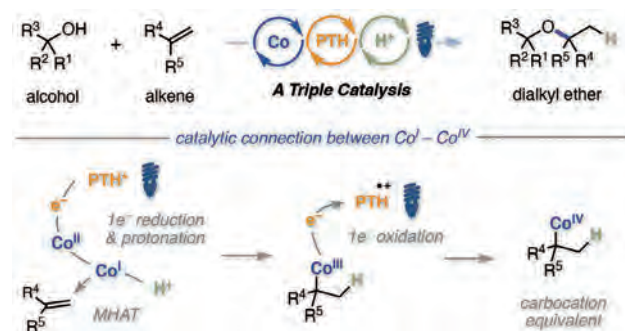
Synthetic Reactions  
Photoredox Catalysis  
Organocatalysis  
Radical Reaction  
Boron Molecule

### Recent Selected Publications

Kodo T.; Nagao K.; Ohmiya H., Organophotoredox-Catalyzed Semipinacol Rearrangement via Radical-Polar Crossover, *Nat. Commun.*, **13**, 2684 (2022).  
Nakagawa M.; Matsuki Y.; Nagao K.; Ohmiya H., A Triple Photoredox/Cobalt/Brønsted Acid Catalysis Enabling Markovnikov Hydroalkoxylation of Unactivated Alkenes, *J. Am. Chem. Soc.*, **144**, 7953-7959 (2022).  
Matsuki Y.; Ohnishi N.; Kakeno Y.; Takemoto S.; Ishii T.; Nagao K.; Ohmiya H., Aryl Radical-Mediated N-Heterocyclic Carbene Catalysis, *Nat. Commun.*, **12**, 3848 (2021).  
Sato Y.; Nakamura K.; Sumida Y.; Hashizume D.; Hosoya T.; Ohmiya H., Generation of Alkyl Radical through Direct Excitation of Boracene-Based Alkylborate, *J. Am. Chem. Soc.*, **142**, 9938-9943 (2020).  
Shibutani S.; Kodo T.; Takeda M.; Nagao K.; Tokunaga N.; Sasaki Y.; Ohmiya H., Organophotoredox-Catalyzed Decarboxylative C(sp<sup>3</sup>)-O Bond Formation, *J. Am. Chem. Soc.*, **142**, 1211-1216 (2020).

## A Triple Photoredox/Cobalt/Bronsted Acid Catalysis Enabling Markovnikov Hydroalkoxylation of Unactivated Alkenes

We demonstrate Markovnikov hydroalkoxylation of unactivated alkenes using alcohols through a triple catalysis consisting of photoredox, cobalt, and Brønsted acid catalysts under visible light irradiation. The triple catalysis realizes three key elementary steps in a single catalytic cycle: (1) Co(III) hydride generation by photochemical reduction of Co(II) followed by protonation, (2) metal hydride hydrogen atom transfer (MHAT) of alkenes by Co(III) hydride, and (3) oxidation of the alkyl Co(III) complex to alkyl Co(IV). The precise control of protons and electrons by the three catalysts allows the elimination of strong acids and external reductants/oxidants that are required in the conventional methods.

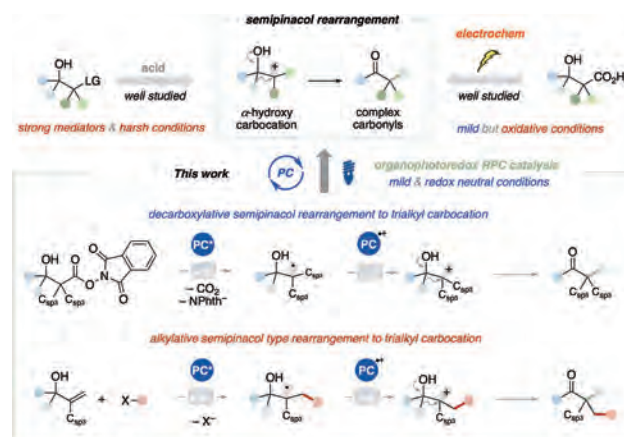


**Figure 1.** A Triple Photoredox/Cobalt/Bronsted Acid Catalysis Enabling Markovnikov Hydroalkoxylation of Unactivated Alkenes.

## Organophotoredox-Catalyzed Semipinacol Rearrangement via Radical-Polar Crossover

Over the past century, significant progress in semipinacol rearrangement involving 1,2-migration of  $\alpha$ -hydroxy carbocations has been made in the areas of catalysis and total synthesis of natural products. To access the  $\alpha$ -hydroxy carbocation intermediate, conventional acid-mediated or electrochemical approaches have been employed. However, the photochemical semipinacol rearrangement has been underdeveloped. Herein, we report the organophotoredox-catalyzed semipinacol rearrangement via radical-polar crossover (RPC). A phenothiazine-based organophotoredox catalyst facilitates the generation of an  $\alpha$ -hydroxy non-benzylic alkyl radical followed by oxidation to the corresponding carbocation, which can be exploited to undergo the semipinacol rearrangement. As a result, the photo-

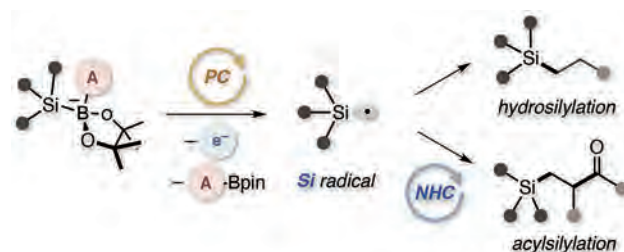
chemical approach enables decarboxylative semipinacol rearrangement of  $\beta$ -hydroxycarboxylic acid derivatives and alkylative semipinacol type rearrangement of allyl alcohols with carbon electrophiles, producing  $\alpha$ -quaternary or  $\alpha$ -tertiary carbonyls bearing  $sp^3$ -rich scaffolds.



**Figure 2.** Organophotoredox-catalyzed semipinacol rearrangement via radical-polar crossover.

## Organic Photoredox-Catalyzed Silyl Radical Generation from Silylboronate

A visible-light-driven silyl radical generation method from silylboronates has been developed. The activation of silylboronates with a catalytic amount of mild base promoted the single-electron oxidation process to form silyl radicals. Facile single electron transfer for the borate form readily occurred without hydrogen atom transfer for hydrosilane in the presence of various photoredox catalysts. Combining this protocol with radical-mediated N-heterocyclic carbene catalysis enabled the acylsilylation of alkenes *via* a radical relay process with silyl radical generation. Furthermore, the recent advanced methods for the synthesis of silylboronates significantly improved the utility of this silyl radical generation process.



**Figure 3.** Organic Photoredox-Catalyzed Silyl Radical Generation from Silylboronate.