Experience at the University of Chicago

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Period: June 17th, 2025–September 14th, 2025

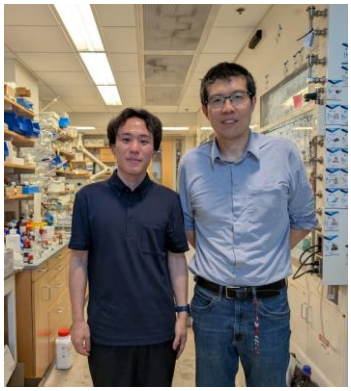
Country: United States of America

Institute: The University of Chicago

Advisor: Prof. Guangbin Dong

Research

I visited the Dong Group at the University of Chicago. Prof. Guangbin Dong is a leading researcher in the field of organometallic chemistry toward organic synthesis. He mainly focuses on carbon–carbon bond and carbon–hydrogen bond activation using transition-metal catalysts, and more recently he is interested in organic synthesis using boron reagents. He not only publishes many papers and receives many awards, but also is a good teacher. In December 2023, he came to Katsura Campus, Kyoto University, and gave us a six-hour lecture. At that time, I was really impressed by his chemistry and his personality. This is the reason why I wanted to do research in his group.



Prof. Dong and me on the first day

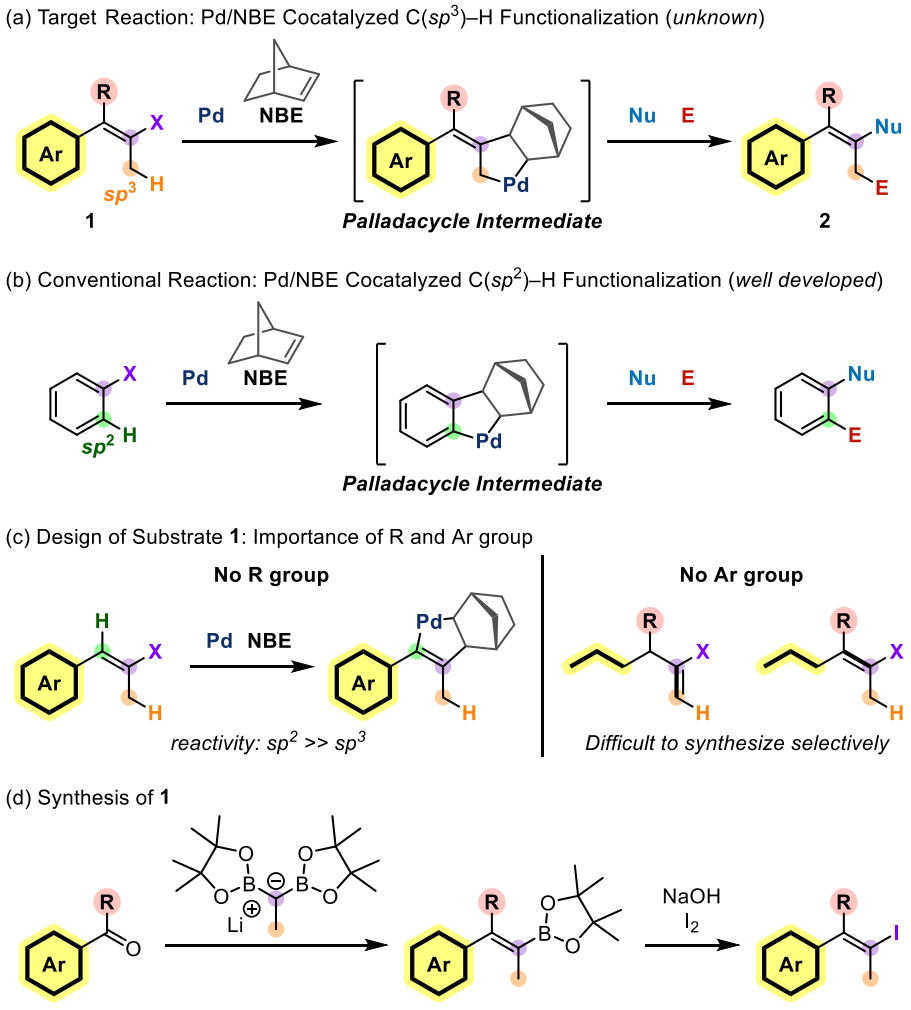
The lab is in this building on the fourth floor

Exhibition about the history of department of chemistry

My research project during this internship was to develop *ipso,α*-difunctionalization through C(sp^3)–H bond activation using palladium/norbornene cooperative catalysts (Scheme 1(a)). This was an independent project from other students and post-doctoral researchers, and a very challenging project because this reaction was a totally new type of molecular transformation. I thought that the same type of palladacycle intermediate as in conventional Pd/NBE cooperative catalysis was important for the success of the target reaction (Scheme 1(b)). I started screening the reaction conditions similar to those for *ipso,ortho*-difunctionalization of arenes, which the Dong group has developed. I designed the model substrate (**1**) to suppress undesired side reactions (Scheme 1(c)). The R-group highlighted in red was introduced to prevent C(sp^2)–H activation, which is more reactive than the target C(sp^3)–H

bond. The aryl group highlighted in yellow was introduced for facile synthesis of 1. After struggling for a few weeks, I succeeded in synthesizing **1a** (Scheme 1(d)), and then my project truly started.

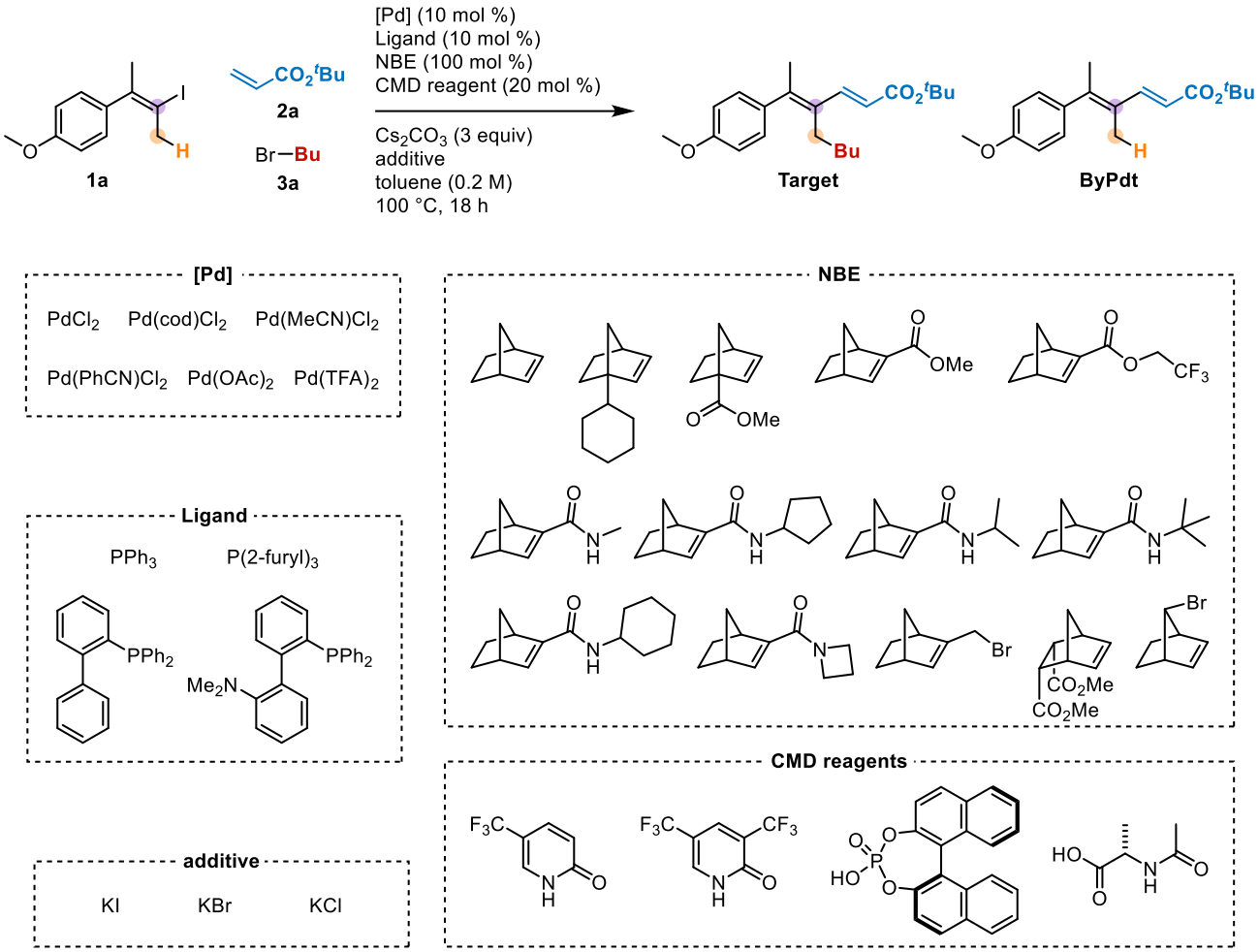
Scheme 1



Reaction optimization was performed under the conditions shown in Scheme 2. In almost all cases, the direct Heck product (**byPdt**) was the major product. Some palladium precursors were tested, affording only **byPdt**. Ligand had larger effects than palladium, indicating that Ph-DavePhos showed good reactivity. Next, I tested many structurally modified norbornenes (smNBEs). NBE had the largest effect in this reaction. 2-substituted NBEs and 7-Br NBE suppressed side reactions, such as reductive elimination or 3-exo-trig cyclization. In the case of CMD reagents, pyridone-type reagents afforded good results. Finally, some additives were tested, and they had negative effects on the reaction. Further optimization will be performed by other members in the Dong group.

Reaction set up

Scheme 2



Daily Life in Chicago

I stayed on the eastern side of Hyde Park, about a 20-minute walk from the lab. Although the southern part of Chicago is not said to be very safe, Hyde Park around the University of Chicago is relatively safe. This is because police officers are always standing along the streets, and police cars are always driving around Hyde Park. Therefore, I could work from early morning to late night Monday to Saturday. Since I spent so much time in the lab, I could make good friends there. I enjoyed not only eating lunch with them every day but also going sightseeing. One of the most impressive events was a group BBQ held at Prof. Dong's house. I talked with a guy who got his PhD in June and is now working at Merck & Co. He said to me, "Don't be shy. Age or rank are not important. Japanese people think too much about them." I was really impressed.

Summer is the best season to stay in Chicago. The temperature is around 25 °C and the humidity is lower than in Japan. I enjoyed walking along the

BBQ at Prof. Dong's house

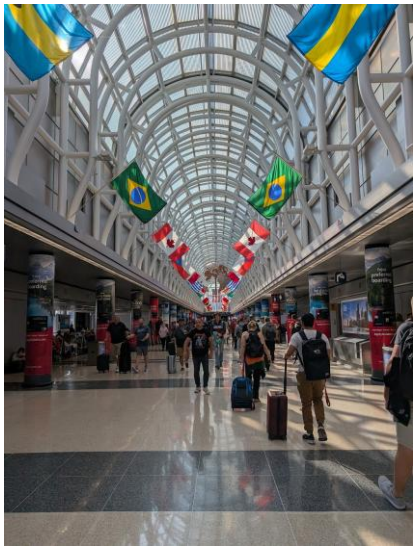
Downtown view from the Michigan lakeside

lakeside. I also visited tourist spots such as Shedd Aquarium, The Art Institute of Chicago, Navy Pier, and so on. The Chicago Cubs is a famous baseball team in Chicago, and they have two Japanese players, Seiya Suzuki and Shota Imanaga. I went to the ballpark nine times. I could watch Seiya's home run and sing "Go Cubs Go," which is sung when the Cubs win the game. Chicago is America's third-largest city, so it has many tourist attractions. I still have places I want to visit in Chicago, so I'd like to go there again someday.

Chicago Cubs

Acknowledgement

I would like to express my gratitude to the Shida Scholarship Program of Kyodai Collaborative for financial support. I couldn't have learned so many things and enjoyed daily life in a foreign country without this support.



O'Hare Airport, the last day