

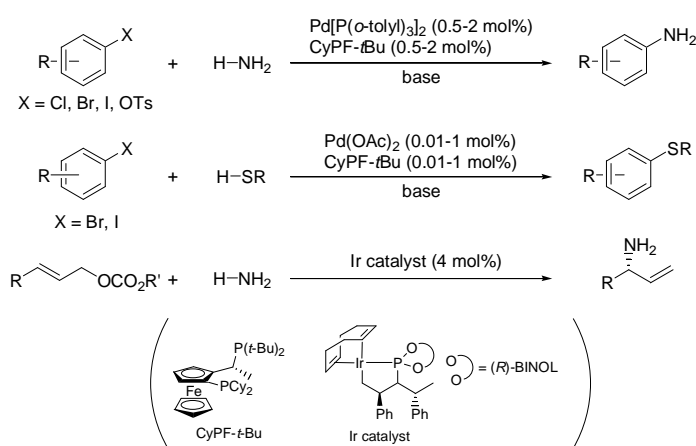
# The Report of Study in “Transition-Metal Catalyzed Cleavage and Addition of $sp^3$ Carbon-Sulfur Bonds to Alkynes”

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I had joined Professor John F. Hartwig's group at University of Illinois in Illinois from 5/May to 21/July. He's one of the most famous chemists in organic chemistry and his representative development, cross-coupling of organohalides with amines (“Buchwald-Hartwig cross coupling”), is widely used by both academics and industrials. His researches are a variety of topics in organometallic chemistry; catalytic and mechanistic studies of carbon-heteroatom and carbon-carbon bond forming cross couplings, carbon-hydrogen bond activation, asymmetric allylic substitution, amination of olefin, and so on. His recent reports are shown in Scheme 1.



**Scheme 1.** Hartwig's recent reports

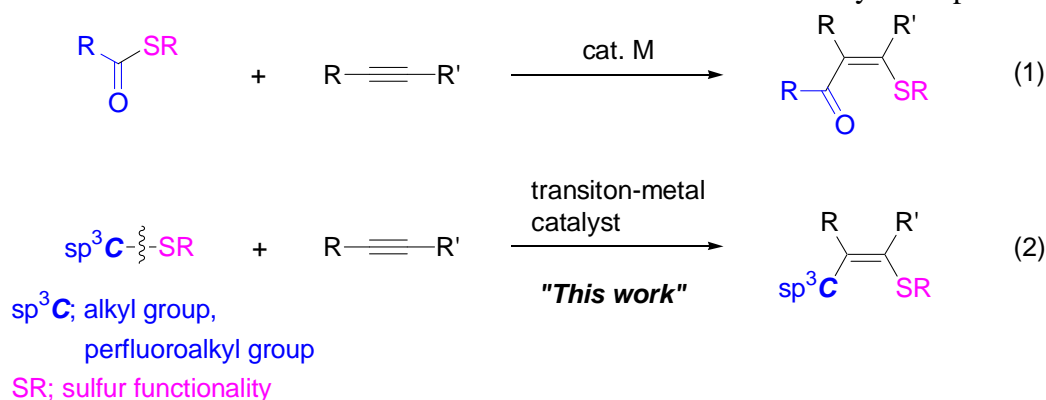
## My Research Content

The development of addition reactions of carbon-heteroatom bonds across carbon-carbon unsaturated bonds has been one of the most important subjects in synthetic chemistry. Our effort has focused on development of transition-metal catalyzed insertion of carbon-sulfur bonds to carbon-carbon unsaturated bonds and I have already discovered the addition reaction of thioesters to alkynes to produce vinylsulfides (Eq. 1).

Although we and other groups have reported some direct carbon-sulfur bond activations and additions to

alkynes, transition-metal catalyzed reactions employing  $sp^3$ -carbon-sulfur bonds as reaction centers are much less explored. To the best of my knowledge, there is no report of the intermolecular version. One reason of this problem is that effective mechanistic information about the reaction of  $sp^3$  carbon-sulfur bonds with transition-metal complexes has not been attracted presumably due to a lack of a good reaction system. So, the development of this reaction remains as a challenging theme.

During my stay in this group, I aimed to get a key to achieving a novel transition-metal catalyzed  $sp^3$  carbon-sulfur bond alkyl and perfluoroalkyl groups,



activation and addition to alkynes (Eq. 2). Especially, I wanted to extract mechanistic information pertaining to such reaction because John F. Hartwig's group has an eminent technique with organometallic chemistry. While for confidentiality reasons I'm unable to explain concrete experimental contents and data, effective results for the achievement of my purpose were obtained.

### General Impression of Illinois

I have lived in Urbana city at Illinois, which is a peaceful town. Around of my apartment, there are many restaurant, shops and supermarket, so I enjoyed spending my life (and, of course, research).

Herein I want to introduce three pictures. Picture 1 shows the landmark of University of Illinois, statue of Alma Mater. At a commencement day, many alumni and alumnae take a commemorative photo with the statue. Picture 2 shows the 'strong' water tower in Chicago. This monument is a sole survivor of all building at the time from Chicago's massive fire. At the weekend before I returned to Japan, I went Chicago with three Japanese Post-doctors. At that time, I took the water tower's picture. Chicago is a giant city and many high-rise buildings stand. Final, picture 3 shows me (left) and Prof. John F. Hartwig (right). He's a great gentleman and always has excellent ideas of chemistry. I've been able to spend lab's life with unlimited fun due to him and lab partners.

### Acknowledgment

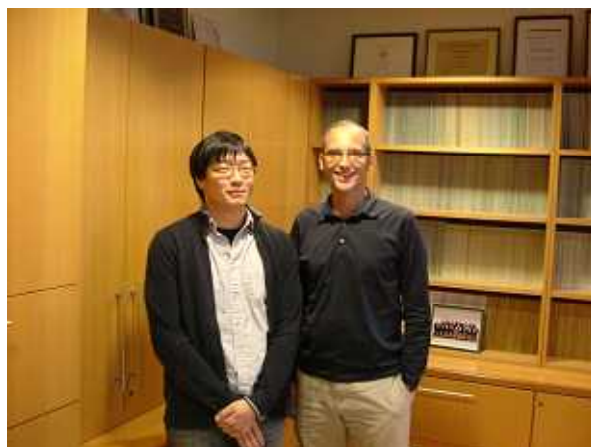
I would like to thank the great support of my stay in Illinois by GCOE program, as well as the supervision of Prof. John F. Hartwig and lab partners.



**Picture 1.** Alma Mater and a Church



**Picture 2.** Water Tower in Chicago



**Picture 3.** Prof. John F. Hartwig and Me.