

# International Internship at ETH Zürich

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under supervision of Prof. Christophe Copéret

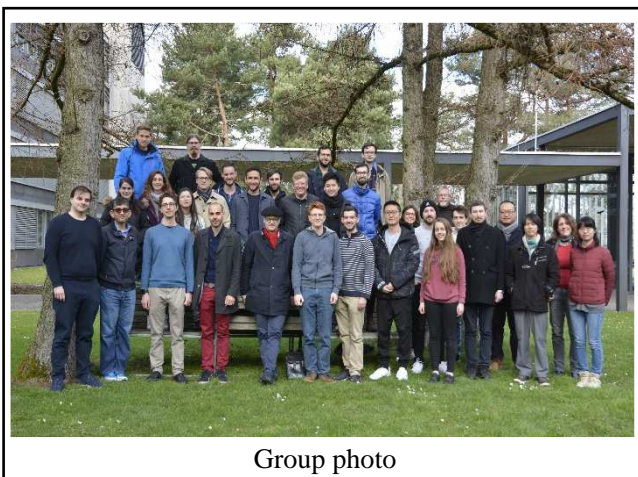
## 1. Research

### 1-1. ETH Zürich

Located in Switzerland, ETH Zürich is full of students from all over the world, and all lectures in graduate course are given in English. I could enjoy impressive presentations by foreign professors invited frequently. There was also abundant resource of research: analytical instruments, experimental devices, free license of computer applications, as well as plenty of financial support such as cheap tuition and discount at cafeteria. ETH Zürich is one of the best universities to study and do research, I guess (except for bad location of Hönggerberg campus on a hill).



### 1-2. Copéret Group

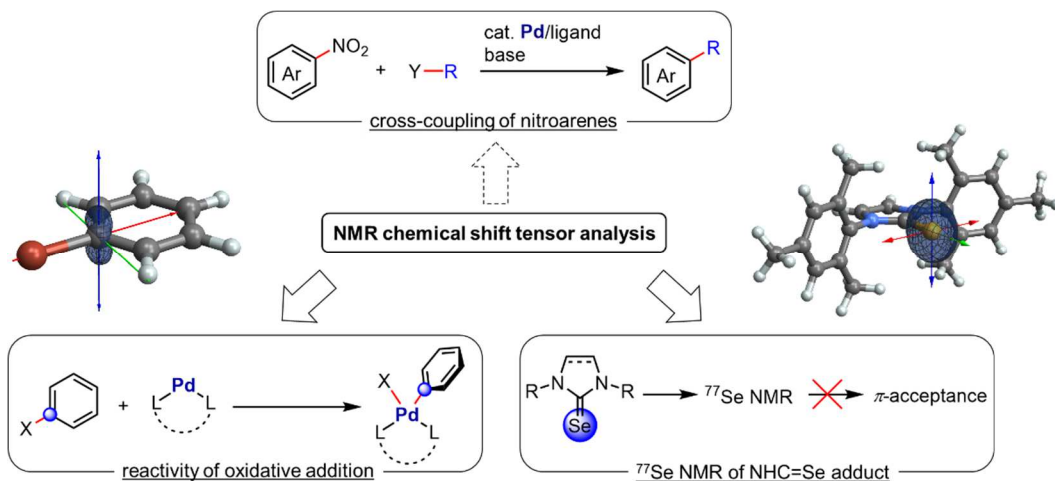


This group works on various topics such as heterogeneous catalyst grafted on support, solid-state NMR technique, and computation chemistry. Although Christophe seemed the only one to have a comprehensive grasp for these research themes, it was a great opportunity for me to get exposure to this diversity. I always had difficulties in discussion with students from unfamiliar backgrounds, but such communication was a good

training for me to improve my English skill and extend my knowledge of chemistry.

### 1-3. Research Project

Being interested in a unique calculation of solid-state NMR (ssNMR) chemical shift in Copéret group, I tried to apply this technique to my PhD project, cross-coupling reactions of nitroarenes. ssNMR gives access to the chemical shift tensor and to the anisotropic electron distribution around a nucleus, which can be useful to probe the symmetry and the energy of molecular frontier orbitals. My first attempt was to clarify key orbital interactions during the catalytic cycle and hence requirements for an ideal catalyst by calculating the chemical shift tensor of each intermediate and transition state. Unfortunately, obtained results were not insightful enough to improve the original catalytic systems. Apart from this project, however, I successfully found a good correlation between one of the principal components of chemical shift tensors at ipso carbon of substituted benzene (Ph-X) and the reactivity of Ph-X bond towards the oxidative addition to Pd(0) species. Further investigation suggested the importance of energetically high-lying  $\pi$ -system during the oxidative addition, which has been commonly ignored. This result also stimulated me to study  $\pi$ -acceptor character of ligands by using the same methodology. One big finding here was the truth of  $^{77}\text{Se}$  NMR analysis in the evaluation of  $\pi$ -accepting ability of *N*-heterocyclic carbenes (NHCs). This method is known as one of the most useful techniques to assess  $\pi$ -acidity of NHCs, which was proven to be unreliable. In a series of research at ETH, I learned a lot about advantages and disadvantages of computation and ssNMR analysis.



### 2. Life

This stay was my first challenge to live alone, but it was not necessary to be anxious about it at all. My flat was in a kind of student dormitory and nicely located in the eastern part of beautiful Lake Zürich, which impressed me every day on my way to and back from the lab. It was around 50-minutes way by train and bus via Oerlikon, where I could get everything I need in the stay at a reasonable price.

Switzerland is surrounded by natural beauties. I enjoyed hiking and skiing in great mountains as well as sightseeing at many fascinating cities on weekends. The location of Switzerland also enabled me to travel around Europe, though I lost some opportunities unfortunately because of accidents including a huge strike at Paris, severe flood in Venice, and a pandemic corona virus.



Ski trip to Andermatt.



Beutiful scenery at Meienfeld.

### 3. Acknowledgement

I appreciate Mazume Research Encouragement Prize in Kyoto University for the financial support. Here I also would like to say thank you to Prof. Christophe Copéret for his kind acceptance and supervision, Ms. Andrea Mark-Fischer for her help during my stay, and members of the group, especially my mentor Mr. Christopher Gordon, for pleasant time.