We have recently shown that the unprecedented PCl_2-catalyzed cycloisomerization of allenye systems is a highly versatile tool for obtaining products that cannot be attainable with other metals. Simple adjustment of the allene or alkyne substitution can direct the reactivity in a completely selective manner and give birth to important carbocyclic platforms: hydridienes, cyclic vinylallenes, and trienes.

The gold catalysis has provided deeper insight into the mechanism of the cycloisomerization of allenyne. Because no standard metallacyclic route could be envisaged, two unusual mechanistic pathways which take into account the presence of cationic intermediates have been proposed: a 1,5-proton shift for the Alder-ene products and a 1,5-hydride shift for the vinyl allenes. We also found evidence for an intriguing halide effect that completely alters the cycloisomerisation process.

Finally, we will present an expedient method for the synthesis of polycyclic compounds from propargyl acetates or vinyl allenes involving up to three Au(I)-catalyzed elemental steps: 3,3-rearrangement, metalla-Nazarov reaction, and electrophilic cyclopropanation.

These rearrangements proceed with chirality transfer and have been applied to the synthesis of a natural product.

Date: 24th November 2010 (Wednesday)
Time: 11am – 12.30pm
Venue: NTU SPMS CBC Building Level 2, Conference Room
Host: Nanyang Professor Koichi Narasaka