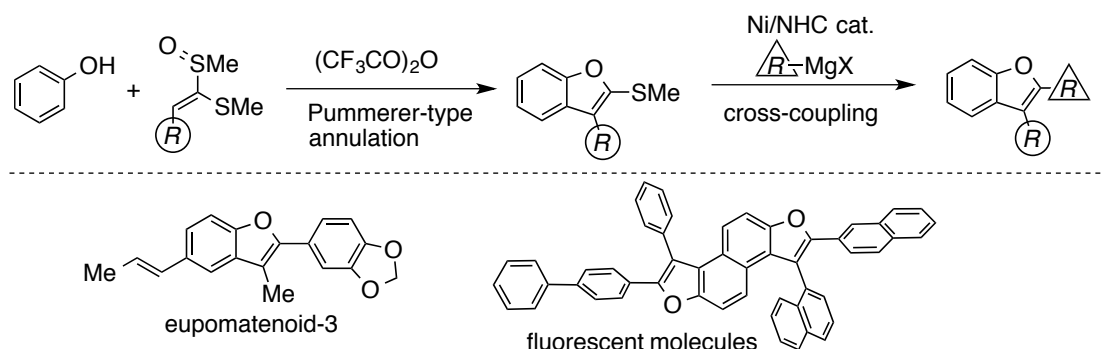


A Journey from Discovery of New Pummerer Chemistry to Catalytic C-S Bond Cleavage

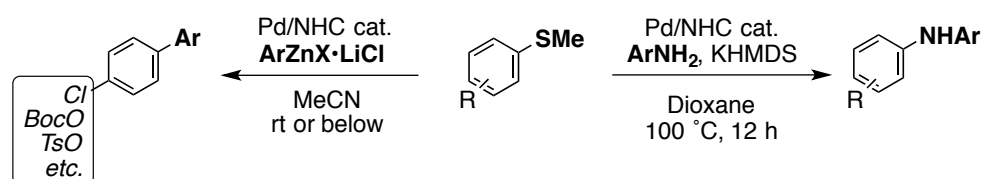
As represented by carbonyl umpolung, Swern oxidation, and sulfur ylide, organosulfur compounds have played important roles in organic synthesis through their intriguing reactivities that oxygen or halogen counterparts cannot show. Despite their stench, frequent catalyst poisoning, and poor atom economy, the unique reactivities of organosulfurs have been fascinating us enough to explore new transformations of organosulfurs from a modern viewpoint of organic chemistry. We are interested in how to tame organosulfur compounds (except for bad smells) to create new organic transformations.

Ketene dithioacetal monoxides (KDMs) are found to be interesting building blocks that enable direct transformation of phenols into benzofurans.^[1] Specifically, Pummerer-type reactions of phenols with KDMs with the aid of trifluoroacetic anhydride provide the corresponding 2-methylsulfanylbenzofurans. Subsequent rather difficult cross-coupling arylation at the methylthio group culminates in modular synthesis of multisubstituted benzofurans. This two-step approach to multisubstituted benzofurans is powerful enough to synthesize highly fluorescent benzofuran derivatives as well as naturally occurring Eupomatenoid family.



Scheme 1. Modular Synthesis of Benzofurans through Pummerer Annulation/Cross-Coupling

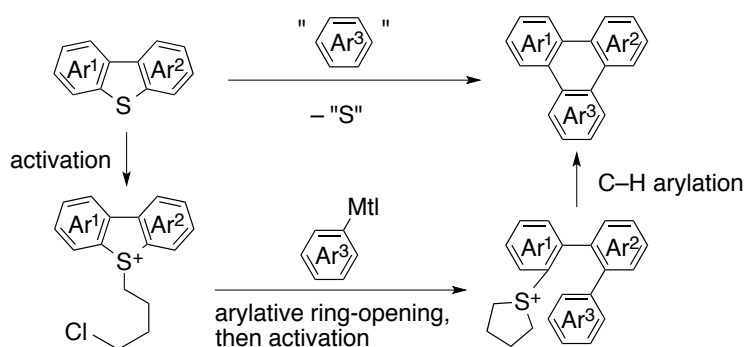
The difficulty we experienced in converting the 2-MeS substituent into an aryl group solicited us to explore reliable, general, and efficient catalytic transformations of sulfides. Accordingly, amination of aryl sulfides with amines^[2] and cross-coupling of aryl sulfides with arylzinc reagents^[3] have been invented. The former represents the first example of amination of sulfides and the latter is widest in generality in cross-coupling of sulfides.



Scheme 2. Palladium-Catalyzed Cross-Coupling of Aryl Sulfides

Aromatic skeletons are usually considered to be stable and to resist organic transformations. During the course of our research on organosulfur chemistry, we have invented a novel route to triphenylenes from readily available dibenzothiophenes through “aromatic metamorphosis”, which represents a transformation of an aromatic system to another through partial disassembly of the starting aromatic ring.^[4]

The aromatic metamorphosis begins with AgBF₄-mediated S_N2 reaction of dibenzothiophene with 1-bromo-4-chlorobutane to form the corresponding sulfonium salt. The sulfonium salt is reactive enough to undergo palladium-catalyzed arylative ring-opening with an arylboron compound for introducing the last benzene ring. The resulting chlorobutyl teraryl sulfide is then converted to the corresponding tetramethylene sulfonium salt by AgSbF₆-mediated intramolecular S_N2 reaction. The final step, i.e., ring-closure into triphenylenes, is achieved through unprecedented intramolecular direct C-H arylation with the sulfonium salt. Symmetrical as well as unsymmetrical triphenylenes of interest are synthesized in a tailor-made fashion in satisfactory overall yields.



Scheme 3. Palladium-Assisted Aromatic Metamorphosis of Dibenzothiophenes to Triphenylenes

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