

Direct Transformation of Unreactive Chemical Bonds

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To understand of the intrinsic properties of the inert bonds and to meet the requirement of green and sustainable development for organic synthesis, Shi and coworkers made significant contributions in the field of C-H/O/C bond activations and developed efficient synthetic methodologies with high step- and atom- economy.

Due to their easy availability and inert reactivity, direct application of O-containing fine chemicals based on the activation of C-O bond is highly appealing and challenging. Shi and coworkers applied aryl/alkenyl carboxylates and phenolates as coupling partners into different transformations, which showed great potential for direct application of phenol derivatives in organic synthesis.¹ These results not only offer new strategies to construct useful compounds, but also open new windows for understanding the features of inert C-O bonds.

C-H activation is a hot topic providing methodologies to construct diverse organic molecules with high step and atom efficiency. The previous researches in C-H activation mostly focused on the mechanistic studies and cross couplings with organohalides/unsaturated bonds.² In Shi's studies, directing group-oriented strategy was successfully applied to approach regioselective C-H activation and the reaction was further extended to heterocycles and general arenes. New concept of oxidative coupling has been introduced to the field of C-H activation and highly selective halogenation, Suzuki-type coupling, Hiyama-type coupling, Kumada-type coupling, Tsuji-Trost-type alkylation based on C-H bond activation, even cross dehydrogenative arylation (CDA) of two arenes were developed.³ Later on, benzylic and allylic C-H activation was also established to construct C-C bonds.⁴ Afterwards, Shi has developed the late and noble transition metal catalysis (Pd, Ir, etc), normal transition metal catalysis (Co, Fe, Nb, Mo, etc)⁵ and even transition-metal free process for direct C-H transformations.⁶ Very recently, his group reported the beautiful and successful example for the direct addition of aryl C-H to aldehydes and aldimines with the decent studies on their mechanisms.⁷

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Research field:

C-O Activation, C-H Activation, Fixation of CO₂ and N₂, Activation of O₂

Selected Publications:

1. An efficient organocatalytic method for constructing biaryls through aromatic C-H activation. C.-L. Sun, H. Li, D.-G. Yu, M. Yu, X. Zhou, X.-Y. Lu, K. Huang, S.-F. Zheng, B.-J. Li, and Z.-J. Shi*, *Nat. Chem.* **2010**, 2, 1044-1048.
2. Direct Application of Phenolic Salts to Nickel-Catalyzed Cross-Coupling Reactions with Aryl Grignard Reagents. D.-G. Yu, B.-J. Li, S.-F. Zheng, B.-T. Guan, B.-Q. Wang and Z.-J. Shi*, *Angew. Chem. Int. Ed.* **2010**, 49, 4566-4570.
3. Cross-Coupling of Alkenyl/Aryl Carboxylates with Grignard Reagent via Fe-Catalyzed C-O Bond Activation. B.-J. Li, L. Xu, Z.-H. Wu, B.-T. Guan, C.-L. Sun, B.-Q. Wang, and Z.-J. Shi*, *J. Am. Chem. Soc.* **2009**, 131, 14656-14657.
4. Multiple C-H Activations To Construct Biologically Active Molecules in a Process Completely Free of Organohalogen and Organometallic Components. B.-J. Li, S.-L. Tian, Z. Fang, Z.-J. Shi*. *Angew. Chem. Int. Ed.* **2008**, 47, 1115-1119.
5. Ortho Arylation of Acetanilides via Pd(II)-Catalyzed C-H Functionalization. S. D Yang, B.-J. Li, X.-B. Wan, and Z.-J. Shi*. *J. Am. Chem. Soc.*, **2007**, 129, 6066 -6067.