Extended Umpolung: Aromatic, Nitrogen, Phosphorus, and Beyond

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The development of new bond forming strategies is the most fundamental but the most important research subject in synthetic organic chemistry. In general, chemists understand the polarity of two organic fragments and successfully connect one to the other. Namely, one is a negatively polarized nucleophile, and the other is a positively polarized electrophile. Such nucleophilic or electrophilic character is fundamentally dependent on the inherent polarity of functional groups or elements themselves. However, if the inherent polarity is inverted, highly challenging bond-forming reactions can be achieved. This polarity inversion concept is known as *umpolung* and was originally proposed by Corey and Seebach, where the inherently electrophilic aldehyde was inverted to the nucleophilic acyl fragment via dithioacetalization/deprotonative electrophilic substitution/deprotonation sequence.[1]

Our research group focused on the conceptual extension of *umpolung* and successfully developed several new bond forming reactions based on the concept of *extended umpolung*: i) copper-promoted oxidative aromatic C–H coupling via aromatic umpolung,[2] ii) highly selective copper-catalyzed electrophilic amination reactions via nitrogen umpolung,[3] and iii) electrophilic phosphination reactions via Tf_2O-mediated phosphorus umpolung.[4]

Here, recent advances, particularly, highly chemo- and stereoselective alkoxylation reactions based on oxygen umpolung will be presented.

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