Iminophosphorane-Catalyzed Enantioselective Ketimine Nitro-Mannich Reaction

Significance: Dixon and co-workers report a new class of bifunctional Brønsted base/H-bond donor organocatalyst. The catalyst (bifunctional iminophosphorane, BIMP) can be applied to the ketimine nitro-Mannich reaction, generating β-nitroamines in good to excellent yields and enantioselectivities.

Comment: The authors developed a new catalyst motif consisting of a triarylaminophosphorane moiety as a Brønsted base and a thiourea moiety as an H-bond donor. The catalyst can be easily synthesized via Staudinger reaction of an organoazide and a triarylphosphine. The efficiency of the catalyst was demonstrated by the application to the first catalytic enantioselective addition of nitromethane to ketone-derived imines under metal-free conditions. The reaction can be scaled up to multigrams and gives access to enantiomerically pure quaternary α-amino acids.