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# Imidodiphosphoric acid catalysis

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## 1. Introduction

The past decade has seen substantial growth in chiral phosphoric acid catalysis, particularly with 1,1′-binaphthalene-2,2′-diol (BINOL) and related axially-chiral ligands. With a wide range of derivatives and broad applicability, these catalysts have demonstrated versatility and tunability.[1] For instance, simple conversion of the phosphoric acid to an *N*-sulfonyl phosphoramide results in an eight million-fold increase in acidity.[2] In addition to singly axially chiral phosphoric acids, a subgroup of catalysts possessing multiple chiral axes has been reported.[3] These species are suggested to improve selectivity through cooperative interactions between their acid and/or stereogenic backbones.[1b] The combination of these concepts resulted in the formation of imidodiphosphoric acids (IDPAs) (Fig. 1).

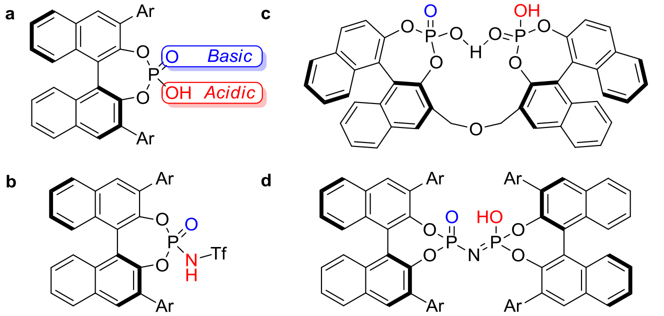
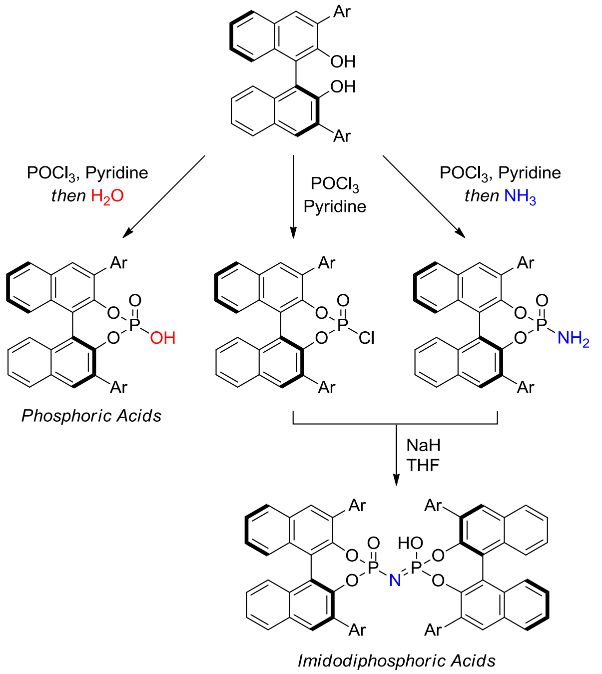


**Fig. 1.** Synergy of concepts leading to BINOL-derived imidodiphosphoric acid catalysts. **a**, phosphoric acid. **b**, *N*-sulfonyl phosphoramide. **c**, diphosphoric acid with two axes of chirality. **d**, imidodiphosphoric acid.

### 1.1. Imidodiphosphoric acids

IDPAs are prepared from the same BINOL-derivatives as their parent phosphoric acids, requiring only two additional steps in their synthesis (Scheme 1).[4]



**Scheme 1.** Typical syntheses of BINOL-derived chiral phosphoric and imidodiphosphoric acids.

Steric interactions from the 3,3′-substituents preclude rotation about the P–N bond(s), reducing the number of both conformers and catalytically active sites to one. With the addition of a deep chiral cavity around the active site, these factors severely limit the possible orientations of coordinated substrates leading to high degrees of stereoinduction (Fig. 2).[4a]

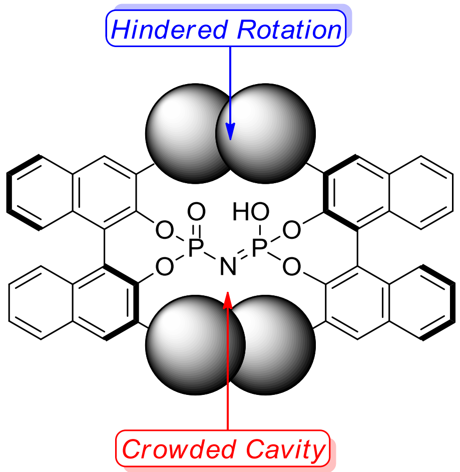


**Fig. 2.** Conformational and steric effects of 3,3′-substituents.

### 1.2. Focus of this report

This report outlines the applications of imidodiphosphoric acid in organocatalysis. Emphasis is on proposed rationales for the observed reactivities/selectivities. Where appropriate, the imidodiphosphoric acid catalysed reaction is contrasted with select competing or complementary catalytic methodologies. Sections are divided according to reaction types: acetalizations, sulfoxidations, functionalization of indoles/pyrroles, and miscellanea. Several existing reviews directly address specific reactions and are suggested for further reading in their relevant sections. Fig. 3 summarizes the imidodiphosphoric acids highlighted in this report.

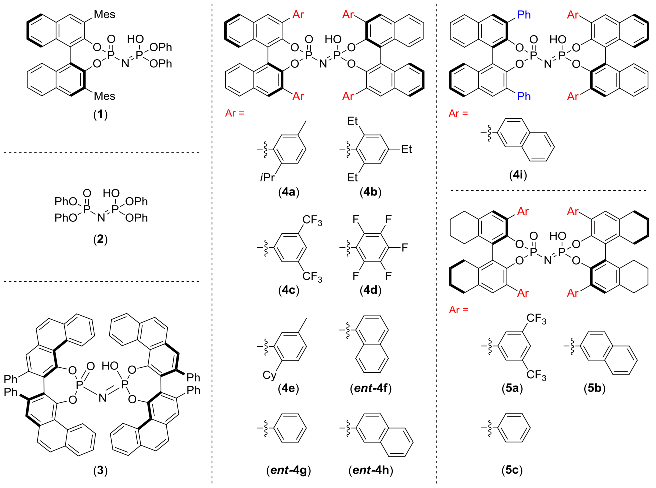


**Fig. 3.** Imidodiphosphoric acids highlighted in this report.

## 2. Acetalization reactions

### 2.1. *N*,*O*-Acetalizations

Although not the primary focus of the work, the initial use of imidodiphosphoric acids as catalysts was reported by List et al. in 2010 (Scheme 2).[5]