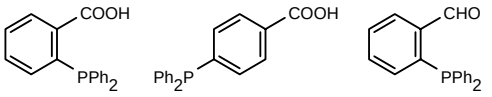
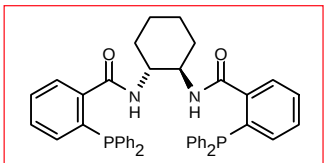
Triaryl Phosphines for Asymmetric Catalysis



45,488-5 **40,159-5** **32,620-8**

Professor Barry Trost and co-workers at Stanford University have recently reported progress in the area of enantioselective allylic substitutions.[1] Their methods employ chiral ligands (e.g., **1**) constructed from a chiral diamine and 2-(diphenylphosphino)benzoic acid. With a palladium source, a "chiral pocket" forms about the metal center, leading to high enantioselectivities in ensuing reactions. Much of the early work was performed with *meso*-2-cycloalkene-1,4-diols as substrates[2], and has since been extended to dihydrofurans.[3] High selectivities have also been reported for acyclic substrates.[4] Nitrogen nucleophiles (heterocycles, azide, phthalimide) work well, as do sulfur nucleophiles[5] and malonate anions.[4] Trost's group has synthesized an impressive array of products using this methodology: carbonucleosides (e.g., carbovir),[6] nucleosides,[3] (–)-epibatidine,[7] (+)-polyoxaminic acid,[4] and chiral vinyl glycinol.[8]



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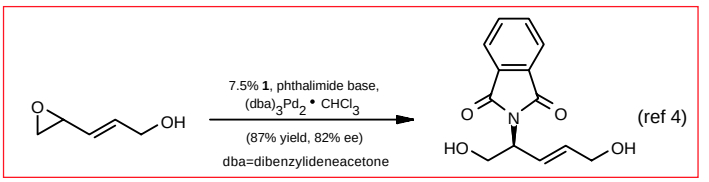
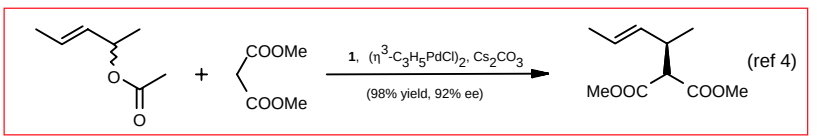
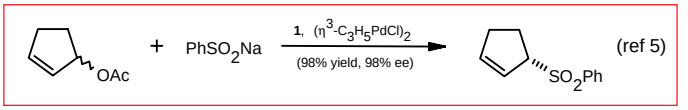
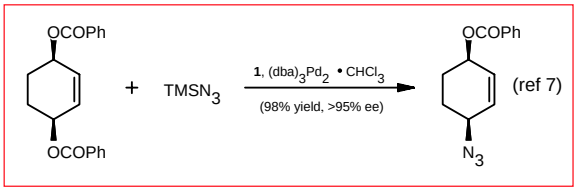


Aldrich now manufactures 2-(diphenylphosphino)benzoic acid, as well as 4-(diphenylphosphino)benzoic acid and 2-(diphenylphosphino)benzaldehyde. Trost and Krische have used 2-(diphenylphosphino)benzoic acid in an intramolecular Alder ene reaction.[9] Schiff bases derived from 2-(diphenylphosphino)benzaldehyde, as well as chiral acetals, have been used as optically active ligands in palladium-catalyzed, asymmetric substitution reactions.[10,11]







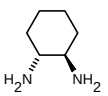
References: (1) For reviews see: Trost, B.M. *Acc. Chem. Res.* **1996**, *29*, 355; Trost, B.M.; Van Vranken, D.L. *Chem. Rev.* **1996**, *96*, 395. (2) Trost, B.M. et al. *J. Am. Chem. Soc.* **1992**, *114*, 9327. (3) Trost, B.M.; Shi, Z. *ibid.* **1996**, *118*, 3037. (4) Trost, B.M. et al. *ibid.* **1996**, *118*, 6520. (5) Trost, B.M. et al. *ibid.* **1995**, *117*, 9662. (6) Trost, B.M. et al. *ibid.* **1992**, *114*, 8746. (7) Trost, B.M.; Cook, G.R. *Tetrahedron Lett.* **1996**, *37*, 7485. (8) Trost, B.M.; Bunt, R.C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 99. (9) Trost, B.M.; Krische, M.J. *J. Am. Chem. Soc.* **1996**, *118*, 233. (10) Brunner, H.; Fuerst, J. *Inorg. Chim. Acta* **1994**, *220*, 63. (11) Frost, C.G.; Williams, J.M.J. *Synlett* **1994**, 551.

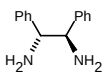
45,488-5 **2-(Diphenylphosphino)benzoic acid,** 97% NEW! **1g; 5g**

40,159-5 **4-(Diphenylphosphino)benzoic acid,** 97% NEW! **1g; 5g**

32,620-8 **2-(Diphenylphosphino)benzaldehyde,** 97% **1g**

Chiral Diamines





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