

4-(Benzylamino)formoyldiphenylammonium Triflate (BDPAT): An Efficient, Recoverable Biphasic Catalyst For Esterification of Carboxylic Acids with Equimolar Amounts of Alcohols

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Abstract: Esterification of carboxylic acid with equimolar amounts alcohol can be efficiently catalyzed by biphasic 4-(benzylamino)formoyldiphenylammonium triflate (BDPAT, **3**) in good yield. The catalyst can be easily recovered without loss of activity.

Keywords: 4-(Benzylamino)formoyldiphenylammonium triflate, biphasic catalyst, esterification.

Esterification of carboxylic acid with alcohol is one of the most fundamental and important reactions in organic synthesis and a great number of methods have been developed¹. From a recent atom-economical standpoint, the uses of equimolar amounts of carboxylic acids and alcohols are strongly required. Mukaiyama and Shiina reported such direct esterification mediated by $\text{TiCl}_2(\text{ClO})_2$ and $\text{TiCl}(\text{OTf})_3$ reagents², which, however, necessitated more than equimolar amounts of anhydride and silyl dehydrating additives, respectively. More recently, Wakasugi found that diphenylammonium triflate (DPAT) could efficiently catalyze the esterification between equimolar amounts of carboxylic acids and alcohols in good yields under mild conditions³.

Facile catalyst separation and reuse are of prime importance in both industrial and academic settings. Although immobilization of the catalyst on a polymeric matrix can provide a simple solution to the recovery of the catalyst from the reaction medium, it needs more reaction steps for the synthesis of catalysts. Here, we report an efficient biphasic catalyst, 4-(benzylamino)formoyldiphenylammonium triflate (BDPAT, **3**), which could be recovered by simple liquid separation method, for the esterification between carboxylic acids with equimolar amounts of alcohols.

The preparation of the biphasic catalyst **3** is described in **Scheme 1**. Condensation of 4-iodobenzoic acid with benzylamine afforded the 4-iodobenzamide (**1**). Using Pd-catalyzed amination⁴, **1** coupled with 1.1 equiv. phenyl amine under 0.1 equiv. $\text{Pd}(\text{OAc})_2$ and 0.1 equiv. 1,1'-bis(diphenylphosphino)ferrocene (DPPF) in the presences of 2 equiv. Cs_2CO_3 to give biphenyl amine (**2**)⁵. Catalyst **3** was then readily prepared from **2** by treating with $\text{CF}_3\text{SO}_3\text{H}$.

Biphasic catalyst **3** was then used as catalyst for esterification between equimolar

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