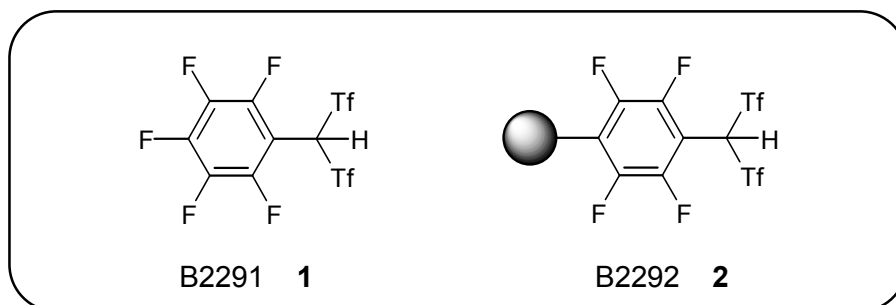
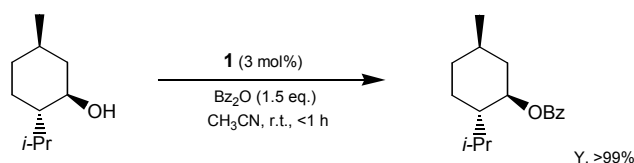


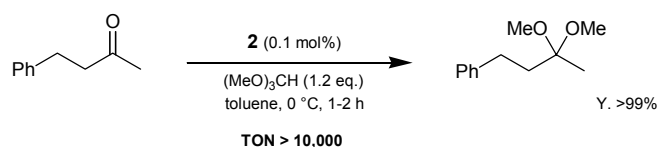
Super Brønsted Acid



Products **1** and **2** are a super Brønsted acid and a polymer-supported super Brønsted acid, which are developed by Ishihara, Yamamoto and co-workers. These products have two trifluoromethanesulfonyl groups which are strong electron-withdrawing groups and one perfluorophenyl group on the methine carbon. The acidity of the proton on the methine carbon is remarkably high, and both products are utilized as excellent acid catalyst in various reactions.^{1a)} For example, **1** has a $pK_a = 1.5$ (in CD_3CO_2D) and it has been reported to be useful for the acylation of (-)-menthol.



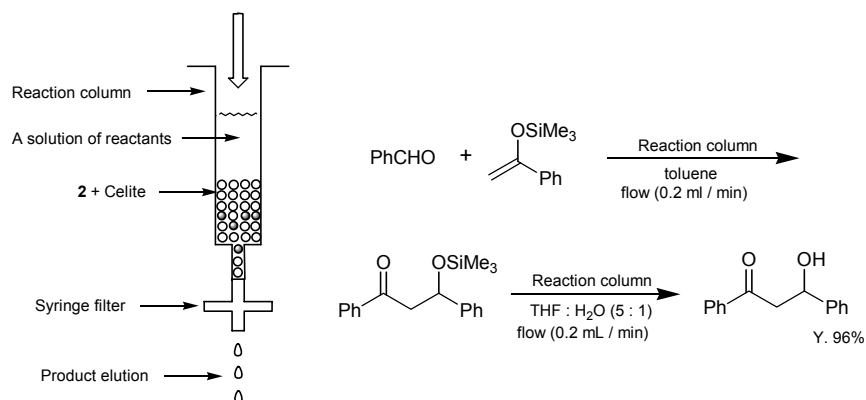
2 is effectively swollen by both polar and nonpolar organic solvents, and it possesses high catalytic activity. It is used as a solid acid catalyst which can be recovered and reused. For example, in the acetalization of benzylacetone, it is quantitatively recovered after the reaction by simple filtration and it can be reused more than 10 times without loss of activity. The turnover number (TON) is greater than 10,000.^{1a)}



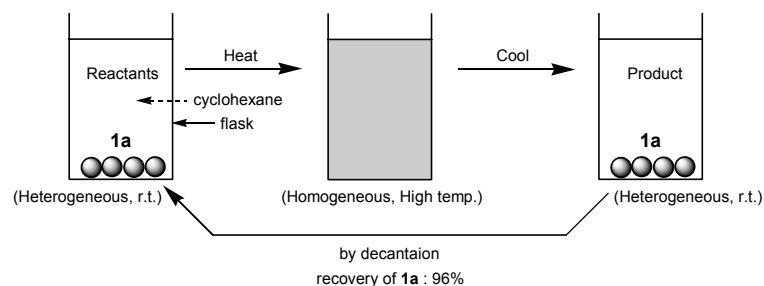
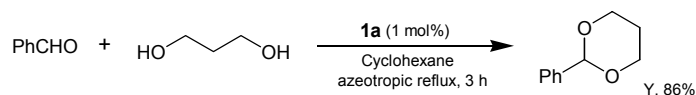
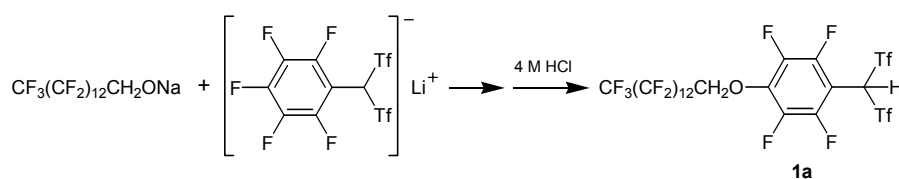
Another application for **2** that has been reported is its use in a packed reaction column.^{1b)} The reaction column is a rather simple system that consists of a disposable syringe packed with a mixture of **2** and Celite. Since the catalytic activity of **2** is quite high, it is possible to perform various acid-promoted reactions in high yield and in a single pass requiring just a short reaction time. For example, the Mukaiyama aldol reaction can be successfully performed by passing a mixed solution of benzaldehyde and the silylenol ether of acetophenone into the reaction column just once. The resulting silyl ether of the aldol product is again put through the reaction column as an aqueous THF solution, and hydrolysis progresses smoothly to give the desired aldol product in 96% yield over the 2-steps of procedures. Furthermore, the conversions into acetals and esters also progress readily, thereby making it a very useful reagent for functional group conversions of samples prior to NMR, HPLC and GC analyses. This reaction column can also be coupled to a pump to establish a continuous-flow reaction system.

Keyword : super brønsted acid

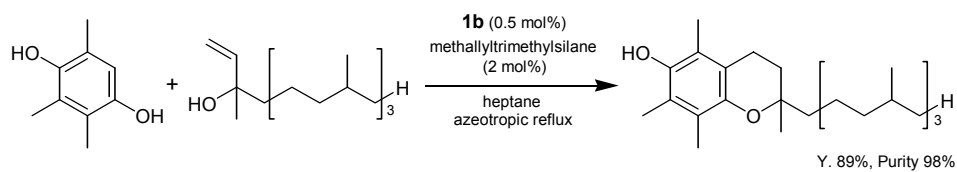
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The lithio product of **1** is known to undergo nucleophilic substitution at the *para*-position. Thus it is possible to create further designs. For example, 1*H*,1*H*-perfluorotetradecyloxy group was introduced at the *para*-position to obtain a product with a high fluororous property, which can be used as a fluororous super Brønsted acid catalyst **1a**.^{1c)} During the acetalization of benzaldehyde, **1a** dissolves in cyclohexane when it is heated to reflux, and function as a catalyst. After the reaction, **1a** precipitates upon cooling to room temperature, allowing it to be recovered and reused. As described herein, when **1a** is utilized as homogeneous catalyst, its activity is higher than the solid catalyst **2**; furthermore it can also be recovered as a solid catalyst, and there are advantages that it can be recovered and reused the catalyst without fluororous solvents.



The trimethylsilyl pentafluorophenylbis(trifluoromethanesulfonyl)methide [$(\text{C}_6\text{F}_5\text{CTf}_2)\text{SiMe}_3$] **1b** prepared from **1** and allyltrimethylsilane is utilized as a super Lewis acid catalyst in the regioselective condensation of trimethylhydroquinone with isophytol.^{1d)} When the acidity of **1** is compared with TfOH and Tf₂NH, the order of Brønsted acidity is TfOH > Tf₂NH > **1**, however, when the Lewis acidity of the trimethylated forms of these compounds was compared, the order of Lewis acidity becomes **1b** > Tf₂NSiMe₃ > TfOSiMe₃. It is anticipated that the conjugate base of **1** ($\text{C}_6\text{F}_5\text{C}^-\text{Tf}_2$) will find utility as a bulky counter anions.



B2291 1-[Bis(trifluoromethanesulfonyl)methyl]-2,3,4,5,6-pentafluorobenzene (1) 1g 100mg
 B2292 Bis(trifluoromethanesulfonyl)methyltetrafluorophenyl Polystyrene Resin (2) 100mg

References

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 - e) K. Ishihara, H. Yamamoto, *TCI MAIL*, **2002**, *115*, 2.