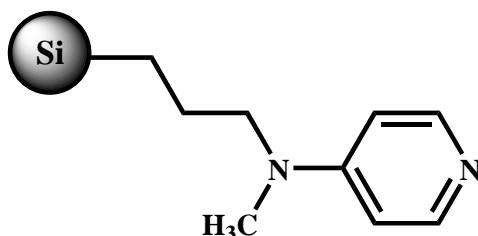
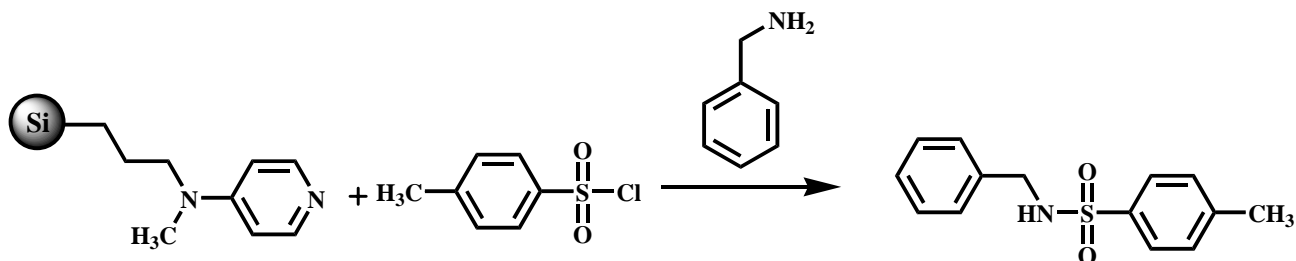


Use of *SiliaBond*[®] DMAP


SiliaBond[®] DMAP (or *Si*-DMAP) is the supported equivalent of 4-dimethylaminopyridine commonly used as a nucleophilic catalyst in a wide variety of reactions such as amidation or acetylation. These reactions are well known in organic synthesis and are very useful in various domains. *SiliaBond*[®] DMAP presents the advantage over its free counterpart as it can be removed by a simple filtration. One of the most important applications for this product is the "Catch and Release" for amide synthesis.

SiliaBond[®] DMAP can also be used in other types of reactions like esterification of alcohols and nucleophilic rearrangements.

 Sulfonamide synthesis using "Catch & Release" with *SiliaBond*[®] DMAP


Sample Procedure

 1) Catch of tosyl chloride

To a suspension of *SiliaBond*[®] DMAP (1.0 eq) in anhydrous DCM, is added tosyl chloride (2 eq.). The reaction mixture is stirred for one hour at room temperature, filtered and washed with anhydrous DCM. This "activated" *Si*-DMAP is immediately used for the second step without drying.

 2) Release of benzylsulfonamide

To the activated *Si*-DMAP obtained in the first step, is added benzylamine (0.65 eq. by considering an active DMAP loading of 60-70%) in anhydrous DCM, then reaction is stirred for 16 hours at room temperature. After completion, the reaction is filtered and the silica is washed with DCM. The benzylsulfonamide is obtained in 75-85% yield by concentration of the filtrate under vacuum. The amide presents a high purity (95-99%), which was evaluated by GC-FID in THF (inhibitor free).

Comparative results from GSK for amide products library using supported DMAP

A study was made at GSK (NC, USA) laboratory to compare the efficiency of polymer supported DMAP version to the silica supported one (**SiliaBond[®] DMAP**). Below are the yields that they observed for different compounds for the polymer (PS) and the silica (Si) supported DMAP. Results in red represents higher yield with the silica, in blue is for higher yield for the polymer, and in green comparable yields. In fact, **SiliaBond[®] DMAP** achieves higher efficiencies than the PS-DMAP product in most experiments as demonstrated below.

| PS | Si | PS | Si | PS | Si | PS | Si | PS | Si | PS | Si |
|--------------|---------------|--------------|---------------|---------------|---------------|---------------|---------------|--------------|---------------|---------------|---------------|
| 79.68 | 94.94 | 88.89 | 100.00 | 77.00 | 94.00 | 7.13 | 94.52 | 98.00 | 100.00 | 95.80 | 80.60 |
| 93.20 | 94.43 | 82.69 | 97.99 | 79.96 | 90.17 | 90.00 | 95.15 | 92.69 | 97.97 | 97.17 | 100.00 |
| 83.78 | 91.92 | 92.35 | 95.29 | 91.60 | 94.59 | 79.68 | 95.53 | 94.72 | 100.00 | 94.26 | 97.79 |
| 75.48 | 95.27 | 94.96 | 95.18 | 97.95 | 93.77 | 78.31 | 97.98 | 94.75 | 100.00 | 19.10 | 37.92 |
| 89.41 | 97.98 | 93.89 | 95.44 | 93.61 | 97.36 | 100.00 | 100.00 | 91.90 | 91.19 | 100.00 | 88.05 |
| 88.13 | 94.54 | 90.98 | 100.00 | 94.45 | 97.26 | 89.57 | 95.29 | 94.31 | 100.00 | 68.55 | 80.35 |
| 81.47 | 89.96 | 93.71 | 100.00 | 98.04 | 100.00 | 100.00 | 97.91 | 87.24 | 100.00 | 94.32 | 95.56 |
| 93.80 | 100.00 | 97.60 | 97.36 | 92.97 | 97.56 | 78.82 | 90.43 | 71.93 | 100.00 | 87.88 | 100.00 |
| 8.00 | 11.15 | 42.46 | 93.31 | 94.94 | 94.99 | 91.77 | 98.03 | 98.00 | 88.00 | 97.09 | 100.00 |
| 96.18 | 76.93 | 0.00 | 88.37 | 90.28 | 100.00 | 94.48 | 97.87 | 95.36 | 95.34 | 81.88 | 97.76 |
| 94.11 | 64.98 | 93.54 | 97.87 | 92.66 | 94.16 | 93.36 | 94.19 | 21.86 | 83.00 | 88.81 | 97.74 |
| 49.70 | 59.86 | 74.77 | 95.38 | 100.00 | 97.87 | 71.86 | 95.13 | 84.86 | 100.00 | 93.00 | 97.92 |
| 90.89 | 100.00 | 92.87 | 97.16 | 96.06 | 96.65 | 81.98 | 93.00 | 94.12 | 95.56 | 100.00 | 100.00 |
| 78.93 | 95.83 | 78.16 | 100.00 | 84.55 | 95.71 | 91.02 | 97.31 | 92.20 | 98.04 | 81.00 | 85.00 |
| 85.13 | 100.00 | 83.98 | 95.74 | 77.96 | 100.00 | 96.56 | 97.99 | 94.48 | 95.10 | 96.90 | 98.02 |
| 74.36 | 95.26 | 90.94 | 100.00 | 85.54 | 90.87 | 98.00 | 98.00 | 90.00 | 97.23 | 69.88 | 89.63 |