

## Protection

DUDLEY BENZYLATION  
REAGENT

TRICHLOROACETIMIDATE  
REAGENTS

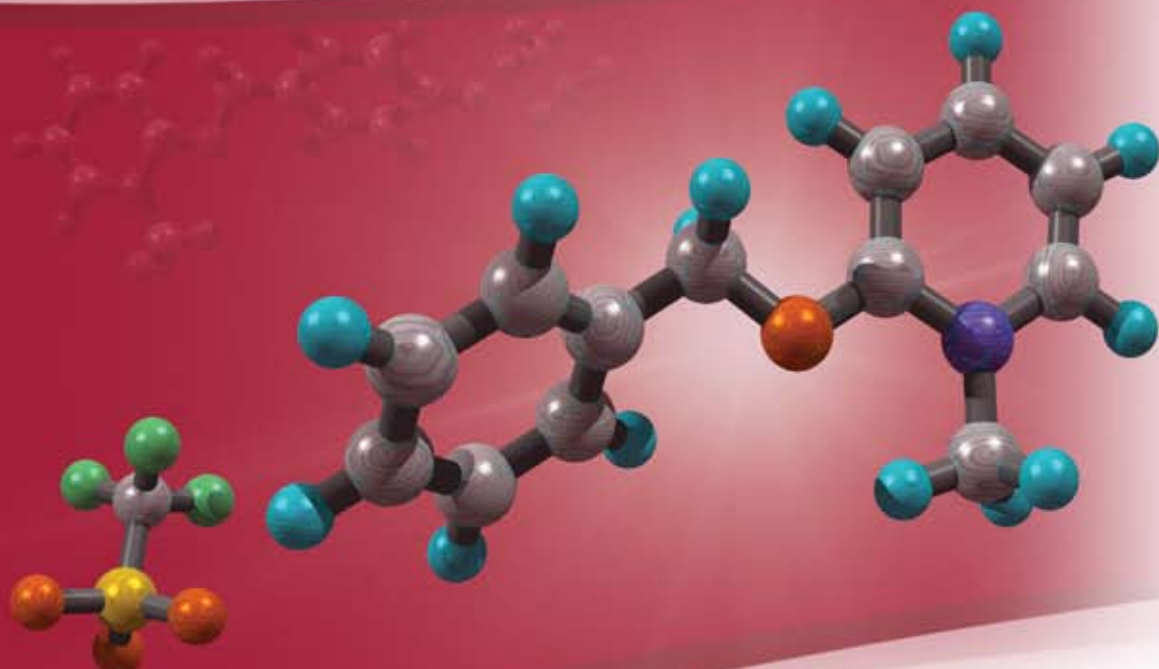
(2-TRIMETHYLSILYL)-  
ETHANESULFONYL  
REAGENTS

ETHYNYLNAPHTHALENES

FLUOROUS PROTECTING  
GROUPS

COMMON REAGENTS  
FOR PROTECTION

COMMON REAGENTS  
FOR DEPROTECTION



*2-Benzyloxy-1-methylpyridinium triflate: an air-stable pre-activated pyridinium salt for the mild benzylation of alcohols under neutral conditions.*

## Introduction

One of the common difficulties with natural product and other multi-step syntheses is the need to render one functional group inert to a particular reagent while keeping another group open for further chemical elaboration. Despite the great advances made in the involved syntheses of multifunctional products, selectivity in functional group transformations remains a critical issue in organic synthesis. Unfortunately for the synthetic chemist, there is no perfect protecting group applicable to any functional group in any situation. Thus, the need exists for the synthetic chemist to have a handy toolbox of selective and efficient protecting groups that can be applied and easily removed under a variety of conditions.

In this issue, we are pleased to introduce a few recent additions to the available protection reagents we offer. The Dudley Reagent is capable of benzylation of alcohols under neutral conditions. Allyl and 4-methoxybenzyl trichloroacetimidates are also commonly used to protect alcohols in various syntheses. Ethynyl naphthalenes offer sterically unobtrusive protection of hydroxyl groups on carbohydrates with orthogonal reactivity compared to benzyl ethers. The (2-trimethylsilyl)ethanesulfonyl (SES) group is used to protect amines via SES chloride; alternatively, SES-NH<sub>2</sub> can be used to introduce a SES-protected amine functionality directly into a molecule.

We also would like to introduce a variety of fluoros protecting groups to our protection line. Fluorous protecting groups serve dual purposes – they are able to both act as a protecting group as well as serve as a temporary fluoros tag that can facilitate product workup and purification throughout the synthesis. Finally, we have included the most popular reagents we offer for the protection of alcohols and amines.

For a complete listing of protection reagents, please visit [sigma-aldrich.com/protection](http://sigma-aldrich.com/protection). If you are unable to find the specific reagent for your research, "Please Bother Us" with your suggestions at [mredlich@sial.com](mailto:mredlich@sial.com), or contact your local Sigma-Aldrich office (see back cover).

## It's Here! The NEW 2007–2008 Aldrich Handbook of Fine Chemicals

...featuring over 35,000 listings including 2,000 new products.

Order your  
FREE copy today!

- ✓ 35,000 Chemical Listings
- ✓ 10,000 Structures
- ✓ 2,000 NEW Products
- ✓ 6,100 Citations
- ✓ 3,000 Application Notes
- ✓ Enhanced Application Index
- ✓ Advanced Product Tables



 **ALDRICH**  
Advancing Science

Call 1-800-325-3010 (USA) to order your copy or visit  
[sigma-aldrich.com/handbook34](http://sigma-aldrich.com/handbook34) today!

### About Our Cover

The cover graphic depicts the structure of the Dudley Benzylation Reagent, 2-benzyloxy-1-methylpyridinium triflate. This bench-stable, mild benzylation reagent protects alcohols under neutral conditions, and succeeds in cases where the benzyl trichloroacetimidate does not yield the desired product. Simply heating the alcohol in the presence of the salt provides the desired benzyl ether, and byproducts are easily removed from the reaction mixture.

 **ChemFiles**

Vol. 7 No. 3

**Aldrich Chemical Co., Inc.**  
**Sigma-Aldrich Corporation**  
6000 N. Teutonia Ave.  
Milwaukee, WI 53209, USA

#### To Place Orders

Telephone 800-325-3010 (USA)  
FAX 800-325-5052 (USA)

#### Customer & Technical Services

Customer Inquiries 800-325-3010  
Technical Service 800-231-8327  
SAFC™ 800-244-1173  
Custom Synthesis 800-244-1173  
Flavors & Fragrances 800-227-4563  
International 414-438-3850  
24-Hour Emergency 414-438-3850  
Web Site [sigma-aldrich.com](http://sigma-aldrich.com)  
Email [aldrich@sial.com](mailto:aldrich@sial.com)

#### Subscriptions

To request your **FREE** subscription to *ChemFiles*, please contact us by:

Phone: 800-325-3010 (USA)  
Mail: Attn: Marketing Communications  
Aldrich Chemical Co., Inc.  
Sigma-Aldrich Corporation  
P.O. Box 355  
Milwaukee, WI 53201-9358  
Email: [sams-usa@sial.com](mailto:sams-usa@sial.com)

International customers, please contact your local Sigma-Aldrich office. For worldwide contact information, please see back cover.

*ChemFiles* are also available in PDF format on the Internet at [sigma-aldrich.com/chemfiles](http://sigma-aldrich.com/chemfiles).

Aldrich brand products are sold through Sigma-Aldrich, Inc. Sigma-Aldrich, Inc. warrants that its products conform to the information contained in this and other Sigma-Aldrich publications. Purchaser must determine the suitability of the product for its particular use. See reverse side of invoice or packing slip for additional terms and conditions of sale.

All prices are subject to change without notice.

*ChemFiles* is a publication of Aldrich Chemical Co., Inc. Aldrich is a member of the Sigma-Aldrich Group. © 2007 Sigma-Aldrich Co.

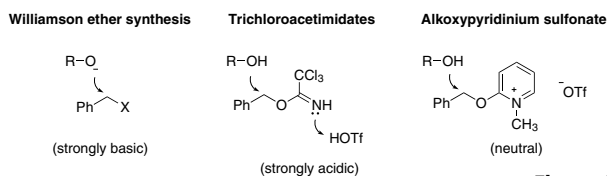
## Dudley Benzylation Reagent

Benzyl ethers and derivatives are among the most widely used protecting groups in organic synthesis. Cleavage can be effected under a variety of conditions including hydrogenolysis, oxidation, and acid decomposition. Typically, protection of alcohols in the form of a benzyl ether requires harsh reaction conditions. Williamson ether synthesis necessitates strongly basic conditions to generate an alkoxide nucleophile (**Figure 1**). Alternatively, trichloroacetimidate reagents can be employed in the presence of triflic acid (HOTf) as a promoter. Many complex alcohols are incompatible with these strongly basic or acidic conditions. For example,  $\beta$ -hydroxy esters are prone to elimination, epimerization at the  $\alpha$ -carbon, or retro-aldol reactions under acid or base catalysis. Additionally, resident protecting groups on the alcohol substrate may be incompatible with non-pH-neutral reactions. Under acidic conditions, trimethylsilyl (TMS) ethers are easily cleaved, while acetals can undergo migration in polyol systems. Bulkier silyl protecting groups can undergo migration in the presence of base.

Professor Gregory Dudley and co-workers at Florida State University have developed a pre-activated pyridinium salt for the mild benzylation of alcohols under neutral conditions.<sup>1</sup> The salt is bench-stable, can be handled in air (**Figure 2**), and simple reaction conditions are employed. Simply heating the alcohol in the presence of the salt provides the desired benzyl ether. Heterogeneous MgO serves to neutralize the mildly acidic hydroxypyridine generated during the protection reaction. The resultant pyridinone byproduct is water soluble, and thus, easily removed (**Scheme 1**).

As shown in **Table 1**, a variety of primary, secondary, and tertiary alcohols underwent clean and high-yielding benzylation. 1,2-Dichloroethane (DCE), benzene, toluene, and benzotrifluoride (BTF) are viable solvents for the reaction. BTF is a low-cost, moderately volatile solvent that is an environmentally friendly alternative to chlorinated solvents. Notably, the labile stereogenic center of optically pure methyl 3-hydroxy-2-methylpropionate survived the reaction conditions unaltered (entry 6). Trimethylsilylethanol (entry 7) is subject to Peterson elimination under acidic or basic conditions, and its benzyl ether had not been reported previously. Attempts to generate the benzyl ether derivative with benzyl trichloroacetimidate did not provide any of the desired product. However, use of the pyridinium reagent clearly provided the alcohol in 100% conversion.

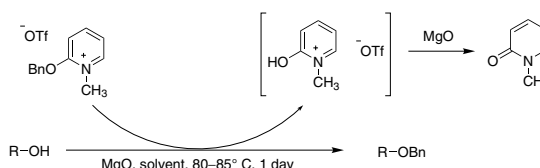
**References:** (1) (a) Poon, K. W. C.; Dudley, G. B. J. *Org. Chem.* **2006**, *71*, 3923. (b) Poon, K. W. C. et al. *Synlett* **2005**, 3142.



**Figure 1**



**Figure 2**



**Scheme 1**

Entry	Benylation Product	Solvent	<sup>1</sup> H NMR Yield (%)
1		DCE	67
2		benzene	93
3		toluene	91
4		BTF	>95
5		BTF	>95
6		BTF	85
7		BTF	100*
8		BTF	88
9		BTF	80

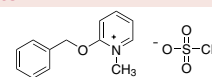
\*conversion

**Table 1**

### 2-Benzyloxy-1-methylpyridinium triflate

NEW

C<sub>14</sub>H<sub>14</sub>F<sub>3</sub>NO<sub>4</sub>S  
FW: 349.33  
[26189-59-3]



679674-1G	1 g
679674-5G	5 g

Ready to scale up? For competitive quotes on larger quantities or custom synthesis, contact SAFC™ at 1-800-244-1173 (USA), or visit safcglobal.com.

## Trichloroacetimidate Reagents

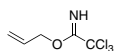
As described previously, trichloroacetimidates are also commonly employed as alcohol alkylation reagents, particularly when existing functionality is not acid sensitive.<sup>1</sup> Recent applications of allyl trichloroacetimidate include the synthesis of an allyl propargyl ether intermediate in the synthesis of the fused-ring alkaloid securinine,<sup>2</sup> preparation of fluorinated probes for protein kinase C (PKC),<sup>3</sup> and in the formal synthesis of the oxocene target Laurencin (Scheme 1).<sup>4</sup>

Likewise, 4-methoxybenzyl trichloroacetimidate has found extensive application for the protection of alcohols in the form of *p*-methoxybenzyl (PMB) ethers that are readily cleaved under oxidative conditions, typically dichlorodicyanoquinone (DDQ) or ceric ammonium nitrate (CAN). As shown in Scheme 2, 4-methoxybenzyl trichloroacetimidate was successfully applied in the selective preparation of chiral *syn*- or *anti*-diamines,<sup>5</sup> as well as in independent syntheses of bryostatin intermediates (Scheme 3).<sup>6,7</sup>

**References:** (1) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 3rd ed.; John Wiley & Sons: New York, 1999. (2) Honda, T. et al. *Org. Lett.* **2004**, *6*, 87. Attempted allylation with allyl bromide under basic conditions did not provide the desired compound. (3) Goekjian, P. G. et al. *J. Org. Chem.* **1999**, *64*, 4238. (4) Krüger, J.; Hoffmann, R. W. *J. Am. Chem. Soc.* **1997**, *119*, 7499. Attempted allylation under basic conditions resulted in silyl migration. (5) Ichikawa, Y. et al. *Org. Lett.* **2006**, *8*, 5737. (6) Manaviar, S. et al. *Org. Lett.* **2006**, *8*, 4477. (7) Keck, G. E. et al. *Org. Lett.* **2006**, *8*, 3667.

### O-Allyl 2,2,2-trichloroacetimidate, 96%

C<sub>5</sub>H<sub>6</sub>Cl<sub>3</sub>NO  
FW: 202.47  
[51479-73-3]

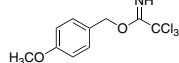


678414-5G

5 g

### 4-Methoxybenzyl-2,2,2-trichloroacetimidate

C<sub>10</sub>H<sub>10</sub>Cl<sub>3</sub>NO<sub>2</sub>  
FW: 282.55  
[89238-99-3]



679585-5G

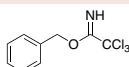
5 g

679585-25G

25 g

### Benzyl 2,2,2-trichloroacetimidate, 99%

C<sub>9</sub>H<sub>8</sub>Cl<sub>3</sub>NO  
FW: 252.52  
[81927-55-1]



140333-5G

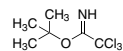
5 g

140333-25G

25 g

### tert-Butyl 2,2,2-trichloroacetimidate, 96%

C<sub>6</sub>H<sub>10</sub>Cl<sub>3</sub>NO  
FW: 218.51  
[98946-18-0]



364789-1G

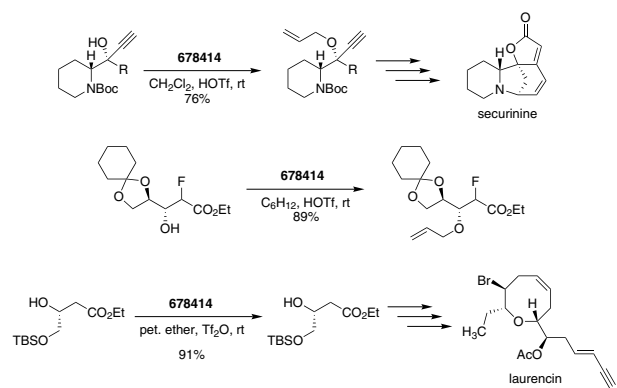
1 g

364789-5G

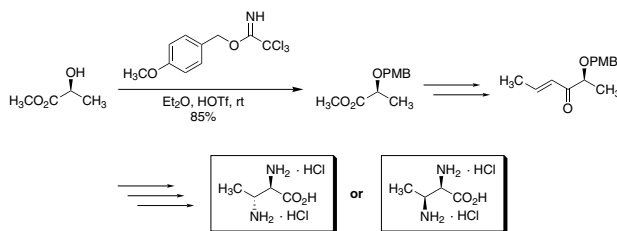
5 g

364789-25G

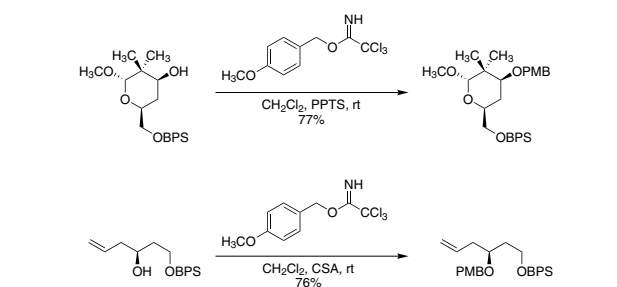
25 g



Scheme 1



Scheme 2



Scheme 3

Monthly Chemistry E-Newsletter  
Got ChemNews?  
sigma-aldrich.com/chemnews



TO ORDER: Contact your local Sigma-Aldrich office (see back cover), call 1-800-325-3010 (USA), or visit sigma-aldrich.com/chemicalsynthesis.

## (2-Trimethylsilyl)ethanesulfonyl Reagents

In 1986, Weinreb first reported the (2-trimethylsilyl)ethanesulfonyl (SES) group (**Figure 1**) as an alternative to a tosyl sulfonamide for mild sulfonyl protection of amines.<sup>1</sup> The SES-protected amines are stable compounds that can be readily cleaved by fluoride sources to regenerate the parent free amine and other volatile products, whereas the tosyl sulfonamide often proves difficult to deprotect.<sup>2</sup>

SES-Cl can be used to protect amino acids, and can be carried through syntheses as easily as Boc-, Fmoc-, or Z-protected amino acids. Boger and co-workers have recently employed SES-Cl to protect the amino side chain on D- or L-ornithine prior to protection of the carboxylic acid function (**Scheme 1**). Boger used these protected ornithines in their syntheses of Ramoplanin analogues<sup>3</sup> and the cyclic peptide of Chlorofusin.<sup>4</sup>

Ohno and Tanaka also used the SES protecting group in the palladium(0)-catalyzed synthesis of 1,4-oxazepines. The facile deprotection of the SES group compared to the tosyl group allowed for the creation of the heterocycle product bearing a free amino group (**Scheme 2**).<sup>5</sup>

In certain reactions, 2-(trimethylsilyl)ethanesulfonamide (SES-NH<sub>2</sub>), can be used to directly introduce a protected nitrogen-functionality into a substrate. One example is in the work of Bolm and Mancheño, who reported the use of SES-NH<sub>2</sub> in the iron-catalyzed imination of sulfoxides to yield sulfoximines (**Scheme 3**).<sup>6</sup>

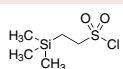
Lamaty and co-workers have employed SES-NH<sub>2</sub> in an aza-Baylis-Hillman reaction to prepare a series of SES-protected  $\beta$ -aminoesters. These  $\beta$ -aminoesters were then further elaborated to provide a series of 2,3-disubstituted pyrroles through a ring-closing metathesis protocol (**Scheme 4**).<sup>7</sup>

SES-NH<sub>2</sub> has also been used in the selective synthesis of various triazamacrocycles.<sup>8,9</sup> The macrocycles are constructed using a modular approach, which allows the researcher considerable control in the carbon bridge architecture of the macrocycle (**Scheme 5**).

**References:** (1) Weinreb, S. M.; Ralbovsky, J. L. "β-Trimethylsilyl ethanesulfonyl Chloride," in *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: Chichester, U.K., 1995, Vol. 7, p. 5255–5256. (2) Ribière, P. et al. *Chem. Rev.* **2006**, *106*, 2249. (3) (a) Rew, Y. et al. *J. Am. Chem. Soc.* **2004**, *126*, 1041. (b) Jiang, W. et al. *J. Am. Chem. Soc.* **2003**, *125*, 1877. (c) Jiang, W. et al. *J. Am. Chem. Soc.* **2002**, *124*, 5288. (4) Desai, P. et al. *Org. Lett.* **2003**, *5*, 5047. (5) Ohno, H. et al. *J. Am. Chem. Soc.* **2004**, *126*, 8744. (6) Mancheño, O. G.; Bolm, C. *Org. Lett.* **2006**, *8*, 2349. (7) Dederck, V. et al. *J. Org. Chem.* **2004**, *69*, 8372. (8) Masllorens, J. et al. *Tetrahedron* **2005**, *61*, 10105. (9) Parker, L. L. et al. *Tetrahedron* **2003**, *59*, 10165.

### 2-(Trimethylsilyl)ethanesulfonyl chloride

C<sub>5</sub>H<sub>13</sub>ClO<sub>2</sub>SSi  
FW: 200.76  
[106018-85-3]

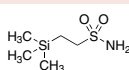


681334-1G

681334-5G

### 2-(Trimethylsilyl)ethanesulfonamide

C<sub>5</sub>H<sub>15</sub>NO<sub>2</sub>SSi  
FW: 181.33  
[125486-96-6]



681326-1G

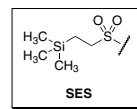
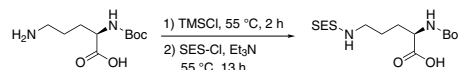
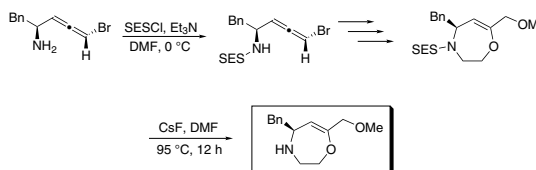


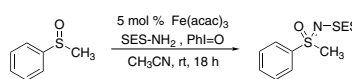
Figure 1



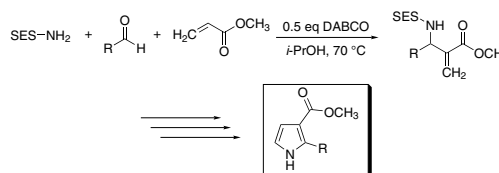
Scheme 1



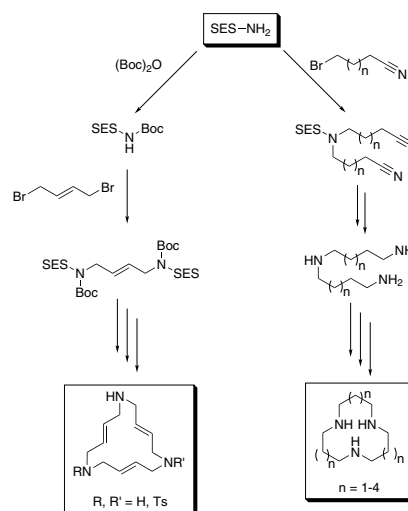
Scheme 2



Scheme 3



Scheme 4



Scheme 5

Order: 1.800.325.3010 Technical Service: 1.800.231.8327

(2-Trimethylsilyl)ethanesulfonyl Reagents

ALDRICH

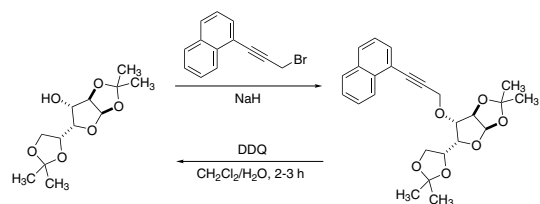
## Ethynynaphthalenes

Recent work by David Crich has been focused on the application of propargyl ethers as sterically unobtrusive donor protecting groups for  $\beta$ -mannosylation.<sup>1</sup> The propargyl ethers were easily introduced, and produced the desired effect on the stereoselectivity of the  $\beta$ -mannosylation reaction; however, they required an unwieldy two-step deprotection requiring the use of  $\text{OsO}_4$ . Further research elucidated the use of 3-(1-naphthyl)-2-propynyl ethers as a protecting group that retained the advantages of the propargyl ethers, yet were cleavable in a single step, orthogonal to benzyl ethers.<sup>2</sup>

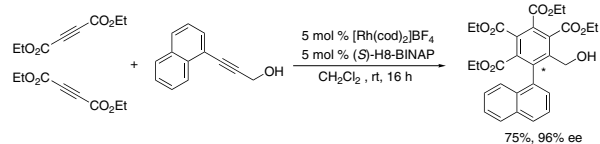
Hydroxy groups on a carbohydrate are easily alkylated with 1-(3-bromo-1-propynyl)naphthalene and sodium hydride to yield the propargyl ether. Subsequent deprotection is easily achieved by treatment with DDQ in wet dichloromethane over the course of 2-3 hours (**Scheme 1**). Furthermore, the propargyl ether proved to be exceptionally  $\beta$ -selective in glycosylations.

The hydroxy precursor, 3-(1-naphthyl)-2-propyn-1-ol is also useful as a building block. For example, a report from Tanaka details the use of 3-(1-naphthyl)-2-propyn-1-ol in a rhodium-catalyzed cross-cyclotrimerization with dimethyl acetylenedicarboxylate to furnish the axially chiral biaryl in good yield and excellent enantioselectivity (**Scheme 2**).<sup>3</sup>

**References:** (1) (a) Crich, D.; Jayalath, P. *Org. Lett.* **2005**, *7*, 2277. (b) Crich, D. et al. *J. Org. Chem.* **2006**, *71*, 3064. (2) Crich, D.; Wu, B. *Org. Lett.* **2006**, *8*, 4879. (3) Tanaka, K. et al. *Org. Lett.* **2005**, *7*, 3119.



**Scheme 1**

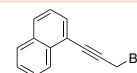


**Scheme 2**

### 1-(3-Bromo-1-propynyl)naphthalene

NEW

$\text{C}_{13}\text{H}_9\text{Br}$   
FW: 245.11  
[352035-98-4]



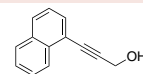
682756-1G

1 g

### 3-(1-Naphthyl)-2-propyn-1-ol

NEW

$\text{C}_{13}\text{H}_{10}\text{O}$   
FW: 182.22  
[16176-22-0]



682764-1G

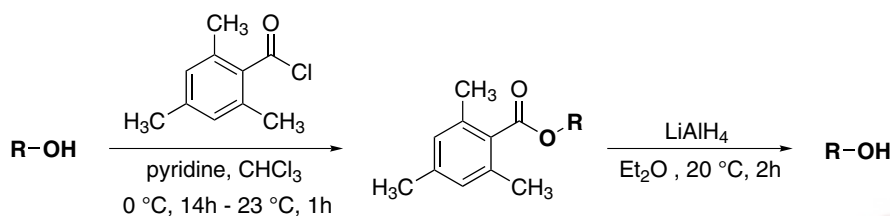
1 g

682764-5G

5 g

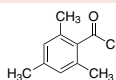
## 2,4,6-Trimethylbenzoyl chloride

Whereas acid chlorides might typically be thought of as building blocks, they can also be used to protect alcohols as their corresponding esters. 2,4,6-Trimethylbenzoyl chloride is a particularly useful acid chloride in this regard, as it forms the mesitoate esters. These esters are very stable to base hydrolysis, yet can be easily cleaved reductively with  $\text{LiAlH}_4$ .<sup>1,2</sup>



### 2,4,6-Trimethylbenzoyl chloride

$\text{C}_{10}\text{H}_{11}\text{ClO}$   
FW: 182.65  
[938-18-1]



682519-1G

1 g

682519-5G

5 g

**References:** (1) (a) Corey, E. J. et al. *J. Am. Chem. Soc.* **1969**, *91*, 4318. (b) Bolton, I. J. et al. *J. Chem. Soc. C* **1971**, 2944. (2) Greene, T. W.; Wuts, P. G. M. In *Protective Groups in Organic Synthesis*, 3rd ed.; John Wiley & Sons: New York, 1999; p.178-179.

## Fluorous Protecting Groups<sup>1</sup>

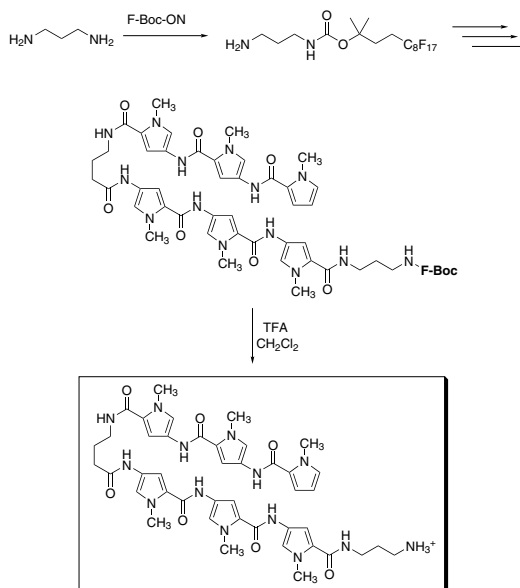
Fluorous protecting groups are able to serve multiple purposes at the same time. While acting as a regular protecting group for a specific functional group they also offer an ideal opportunity to introduce a temporary fluorous tag into a molecule. This tag can be carried through a multi-step synthesis procedure, and can facilitate product workup and purification after every synthetic step.

As a general guideline, fluorous-tagged products with high fluorine content (heavy fluorous products) are recommended for natural products or medicinal chemistry synthesis in combination with either liquid-liquid or fluorous solid-phase extraction (F-SPE). Homologous fluorous-tagged products with lower fluorine content (light fluorous compounds) are useful in either fluorous chromatography or fluorous mixture synthesis.<sup>2,3</sup> Products with smaller fluorous tags show increased solubility in organic solvents; therefore, fluorous solvents are not necessary during the reaction, and the fluorous phase (either solid or liquid) can be used only in the separation step. At the final stage of the synthesis the desired target molecule is deprotected by the same methods as the non-fluorous analogue.

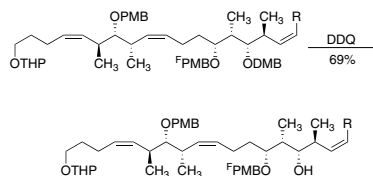
### F-Boc-ON

F-Boc-ON is the fluorous equivalent of 2-(*tert*-butoxycarbonyloxyimino)-2-phenylacetonitrile (Boc-ON) used in protecting amino groups in peptide synthesis or other functionalities in multi-step organic synthesis. Protection of the amino group with F-Boc-ON and deprotection are achieved under traditional reaction conditions, with the advantage that products containing the F-Boc group can easily be separated from organic reagents, reactants, or products by performing a quick fluorous solid-phase extraction over FluoroFlash® Silica Gel.<sup>4</sup>

In a recent example, F-Boc-ON was used for the preparation and isolation of DNA minor groove binding polyamides containing *N*-methylpyrrole. The authors found that the isolation of the fluorous intermediates in the synthetic scheme was advantageous when compared to conventional purification methods (Scheme 1).<sup>5</sup>



Scheme 1



Scheme 2

### F-PMB-OH

F-PMB-OH is the fluorous equivalent of *p*-methoxybenzyl alcohol (PMB-OH) used in protecting alcohols in multi-step organic synthesis. F-PMB can be deprotected either under typical acid or oxidizing conditions. The reactivity of F-PMB and conventional PMB are so similar that a 3,4-dimethoxybenzyl (DMB) protecting group has been selectively cleaved in the presence of both F-PMB and PMB (Scheme 2).<sup>6</sup>

### F-Trityl Alcohol and Chlorides

Several fluorous versions of trityl protecting groups are available from Sigma-Aldrich for the protection of alcohols, amines and carboxylates. These include F-Trt, F-MMT, and F-DMT that are analogous to the conventional trityl, monomethoxy trityl, and dimethoxy trityl groups and react analogously to their non-fluorous counterpart. Each of these groups is acid labile with the relative rate of deprotection being F-Trt < F-MMT < F-DMT. The F-DMT group has recently been used in oligonucleotide synthesis followed by purification through F-SPE.<sup>7</sup>

### F-Silanes

F-Silanes are the fluorous equivalent to a TIPS group. They exhibit properties similar to most silicon protecting groups and have been used in both parallel and fluorous mixture synthesis.<sup>8,9</sup> Tagging of an alcohol is accomplished by in situ activation of the F-silane to either the bromide or triflate followed by addition of the alcohol. Detagging of the F-silane is accomplished either by treatment with fluoride or acid.

### F-Benzyl Alcohol, F-Fmoc-Cl, F-Z-OSu

These reagents are the fluorous equivalents of their parent protecting groups and are fully compatible with the corresponding protection and deprotection methods conventionally associated with that group.

## Discover Sigma-Aldrich's Newest Web-Based Seminar

### Fluorous Chemistry for Synthesis, Separation, and Enrichment

- Featuring the latest innovative chemical synthesis technologies and products
- Access directly via your desktop browser
- Convenient navigation

#### Contents:

- Introduction
- Fluorous Separation Techniques
- Small Molecule Synthesis and Purification
- Fluorous Oligonucleotide, Peptide, and Carbohydrate Chemistry
- Fluorous Products Available Through Sigma-Aldrich

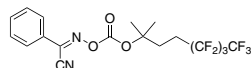


To view Sigma-Aldrich's Web-based chemistry seminar series, please visit [sigma-aldrich.com/cheminars](http://sigma-aldrich.com/cheminars).

## F-Protecting Groups

### 2-[(4,4,5,5,6,6,7,7,7-Nonafluoro-1,1-dimethylheptyloxy) carbonyloxyimino]-2-phenylacetonitrile, ≥ 97.0%

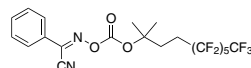
C<sub>18</sub>H<sub>15</sub>F<sub>9</sub>N<sub>2</sub>O<sub>3</sub>  
FW: 478.31



01382-1G-F 1 g

### 2-[(4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-1,1-dimethylnonyloxy) carbonyloxyimino]-2-phenylacetonitrile, ≥ 97.0%

C<sub>20</sub>H<sub>15</sub>F<sub>13</sub>N<sub>2</sub>O<sub>3</sub>  
FW: 578.32

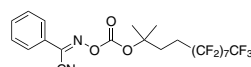


11807-1G-F 1 g

11807-5G-F 5 g

### 2-[(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoro-1,1-dimethylundecyloxy) carbonyloxyimino]-2-phenylacetonitrile, ≥ 97.0%

C<sub>22</sub>H<sub>15</sub>F<sub>17</sub>N<sub>2</sub>O<sub>3</sub>  
FW: 678.34  
[350716-42-6]

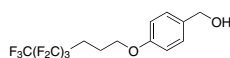


55118-1G-F 1 g

55118-5G-F 5 g

### 4-(4,4,5,5,6,6,7,7,7-Nonafluoroheptyloxy)benzyl alcohol, ≥ 97.0%

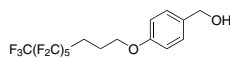
C<sub>14</sub>H<sub>13</sub>F<sub>9</sub>O<sub>2</sub>  
FW: 384.24



01452-1G-F 1 g

### 4-(4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononyloxy)benzyl alcohol, ≥ 97.0%

C<sub>16</sub>H<sub>13</sub>F<sub>13</sub>O<sub>2</sub>  
FW: 484.25

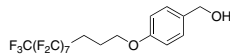


67772-1G-F 1 g

67772-5G-F 5 g

### 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecyloxy)benzyl alcohol, ≥ 97.0%

C<sub>18</sub>H<sub>13</sub>F<sub>17</sub>O<sub>2</sub>  
FW: 584.27

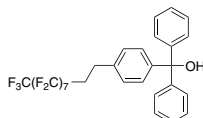


97071-1G-F 1 g

97071-5G-F 5 g

### 1-[4-(1H,1H,2H,2H-Perfluorodecyl)phenyl]-1,1-diphenylmethanol, 98%

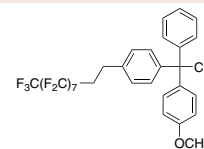
C<sub>29</sub>H<sub>19</sub>F<sub>17</sub>O  
FW: 706.43  
[649561-66-0]



672475-1G 1 g

### 1-(4-Methoxyphenyl)-1-[4-(1H,1H,2H,2H-perfluorodecyl)phenyl]-1-phenylmethyl chloride

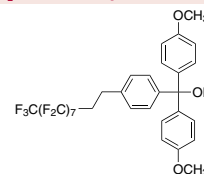
C<sub>30</sub>H<sub>20</sub>ClF<sub>17</sub>O  
FW: 754.91  
[865758-37-8]



672149-1G 1 g

### 1,1-Di-(4-methoxyphenyl)-1-[4-(1H,1H,2H,2H-perfluorodecyl)phenyl]methanol, 97%

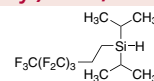
C<sub>31</sub>H<sub>23</sub>F<sub>17</sub>O<sub>3</sub>  
FW: 766.49  
[865758-47-0]



672696-1G 1 g

### Diisopropyl(3,3,4,4,5,5,6,6,6-nonafluorohexyl)silane, ≥ 95%

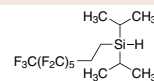
C<sub>12</sub>H<sub>19</sub>F<sub>9</sub>Si  
FW: 362.35  
[356056-13-8]



18976-1G-F 1 g

### Diisopropyl(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane, ≥ 95%

C<sub>14</sub>H<sub>19</sub>F<sub>13</sub>Si  
FW: 462.37  
[356056-14-9]

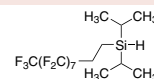


00454-1G-F 1 g

00454-5G-F 5 g

### Diisopropyl(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silane, ≥ 95%

C<sub>16</sub>H<sub>19</sub>F<sub>17</sub>Si  
FW: 562.38  
[356056-15-0]

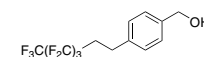


04537-1G-F 1 g

04537-5G-F 5 g

### 4-(3,3,4,4,5,5,6,6,6-Nonafluorohexyl)benzyl alcohol, ≥ 95%

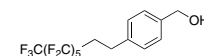
C<sub>13</sub>H<sub>11</sub>F<sub>9</sub>O  
FW: 354.21



08431-1G-F 1 g

### 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)benzyl alcohol, ≥ 97.0%

C<sub>15</sub>H<sub>11</sub>F<sub>13</sub>O  
FW: 454.23  
[356055-76-0]

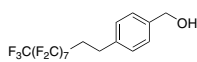


16638-1G-F 1 g

16638-5G-F 5 g

**4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Heptadecafluorodecyl) benzyl alcohol,  $\geq 98.0\%$** 

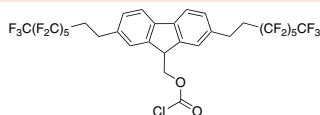
$C_{17}H_{11}F_{17}O$   
FW: 554.24  
[356055-77-1]



19563-1G-F 1 g  
19563-5G-F 5 g

**2,7-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-9-fluorenylmethoxycarbonyl chloride, 98% NEW**

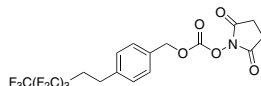
$C_{31}H_{17}ClF_{26}O_2$   
FW: 950.88



672262-1G 1 g

***N*-[4-(3,3,4,4,5,5,6,6-Nonafluorohexyl)benzyl oxycarbonyloxy]succinimide,  $\geq 95.0\%$** 

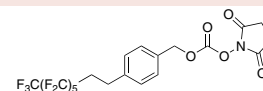
$C_{18}H_{14}F_9NO_5$   
FW: 495.29



00246-1G-F 1 g

***N*-[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)benzyl oxycarbonyloxy] succinimide,  $\geq 97.0\%$** 

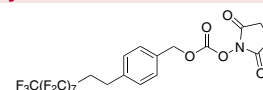
$C_{20}H_{14}F_{13}NO_5$   
FW: 595.31  
[556050-48-7]



05656-1G-F 1 g  
05656-5G-F 5 g

***N*-[4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Heptadecafluorodecyl) benzyl oxycarbonyloxy]succinimide,  $\geq 97.0\%$** 

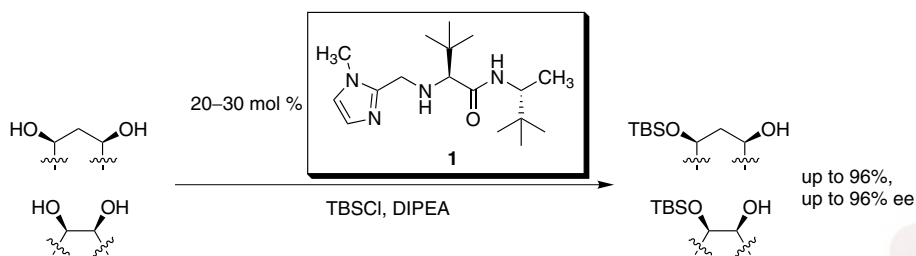
$C_{22}H_{14}F_{17}NO_5$   
FW: 695.32  
[556050-49-8]



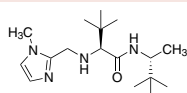
14944-1G-F 1 g  
14944-5G-F 5 g

**Hoveyda-Snapper Catalyst For Desymmetrization Of *meso*-Diols**

Professors Marc Snapper and Amir Hoveyda at Boston College have recently reported<sup>1</sup> the development of an amino-acid-based small molecule **1** capable of promoting asymmetric monosilylation of *meso*-1,2-diols. The catalyst is compatible with a variety of silyl chlorides and generally provides enantioselectivities above 88%, and the reactions do not require rigorous exclusion of air or moisture. Furthermore, the catalyst can be easily recovered in near-quantitative yield after use and subsequently reused with identical efficiency. This catalyst greatly increases the efficiency with which optically-enriched molecules can be prepared.

**(*S*)-*N*-[(*R*)-3,3-Dimethyl-2-butyl]-3,3-dimethyl-2-[(1-methyl-1*H*-imidazol-2-yl)methylamino]butanamide**

$C_{17}H_{32}N_4O$   
FW: 308.46



680826-1G 1 g

Reference: (1) Zhao, Y. et al. *Nature* **2006**, *443*, 67.

## Fluorous Separation Media

The separation of fluorous compounds by F-SPE (Fluorous Solid Phase Extraction) is a reliable and generic procedure that more greatly resembles filtration than chromatography. The quick separation depends primarily on the presence or absence of a light fluorous tag, not polarity or other molecular features that control traditional chromatography.<sup>10</sup> FluoroFlash® silica selectively retains fluorous molecules while non-fluorous compounds are not retained. The fluorous compounds can then be recovered easily through a simple solvent change. FluoroFlash® SPE cartridges are pre-packed in a variety of formats with a proprietary fluorous silica gel.

In **Figure 1**, a mixture of a non-fluorous dye (blue) and a fluorous dye (orange) are loaded on a fluorous adsorbent (left-hand test tube). The non-fluorous dye can be washed down with a fluorophobic solvent mixture like aqueous methanol (middle test tube). The fluorous dye remains on the adsorbent until the elution with a fluorophilic wash (e.g. with pure methanol, right-hand test tube). The colored dyes of this example were used to visualize the easy separation of a fluorous-tagged product from non-fluorous byproducts with F-SPE (Fluorous Solid Phase Extraction).

**References:** (1) The fluorous products featured here are manufactured by Fluorous Technologies, Inc. U.S. patents 6,156,896; 5,859,247; 5,777,121 and 6,673,539 may protect use of these compounds. (2) Zhang, Q. et al. *J. Am. Chem. Soc.* **2004**, *126*, 36. (3) Curran, D. P.; Oderaotshi, Y. *Tetrahedron* **2001**, *57*, 5243. (4) Curran, D. P. *Synlett* **2001**, 1488. (5) Mamidiyala, S. K.; Firestine, S. M. *Tet. Lett.* **2006**, *47*, 7431. (6) Curran, D. P.; Furukawa, T. *Org. Lett.* **2002**, *4*, 2233. (7) Pearson, W. H. et al. *J. Org. Chem.* **2005**, *70*, 7114. (8) Palmacci, E. R. et al. *Angew. Chem. Int. Ed.* **2001**, *40*, 4433. (9) Zhang, W. et al. *J. Am. Chem. Soc.* **2002**, *124*, 10443. (10) Zhang, W.; Curran, D. P. *Tetrahedron* **2006**, *62*, 11837. FluoroFlash® is a registered trademark of Fluorous Technologies, Inc.

## Fluorous Separation Media

**FluoroFlash® SPE Cartridges, 2 grams, 8 cc tube, particle size 40µm**

14196-1EA-F

**FluoroFlash® SPE Cartridges, 5 grams, 10 cc tube, particle size 40µm**

00866-1EA-F

**FluoroFlash® SPE Cartridges, 10 grams, 60 cc tube, particle size 40µm**

08967-1EA-F

**FluoroFlash® SPE Cartridges, 20 grams, 60 cc tube, particle size 40µm**

08966-1EA-F

**FluoroFlash® SPE Cartridges, 20 grams, 60 cc tube, particle size 40µm**

06961-1EA-F

**FluoroFlash® TLC Plates, with F254 indicator**

16888-1EA-F

**FluoroFlash® Silica Gel 40 µm, particle size ~40µm**

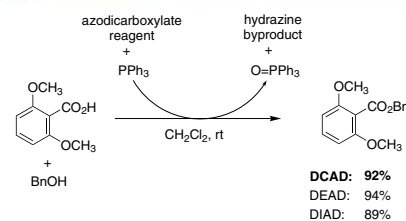
08965-1EA-F



**Figure 1**

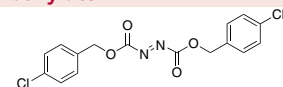
## Lipshutz DCAD Coupling Reagent

The Mitsunobu reaction is one of the most extensively used coupling reactions in organic synthesis and typically azodicarboxylate reagents such as DEAD or DIAD are employed. However, drawbacks such as low room temperature stability and difficulty in removing hydrazine byproducts detract from the practicability of these reagents. Recent work by Professor Bruce Lipshutz and co-workers details the development of a new azodicarboxylate for the Mitsunobu reaction.<sup>1</sup> DCAD is a solid reagent and can easily be stored and handled at room temperature, unlike the more common DEAD and DIAD reagents. DCAD exhibits comparable reactivity to DEAD in common Mitsunobu couplings; however, unlike DEAD, the reduced hydrazine byproduct of DCAD is easily removed by simple precipitation directly from the reaction mixture, and is easily recycled in high yield to regenerate DCAD.



### Di-(4-chlorobenzyl) azodicarboxylate

DCAD  
 C<sub>16</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub>  
 FW: 367.18



680850-1G 1 g  
 680850-10G 10 g

**References:** (1) Lipshutz, B. H. et al. *Org. Lett.* **2006**, *8*, 5069.

**TO ORDER: Contact your local Sigma-Aldrich office (see back cover), call 1-800-325-3010 (USA), or visit [sigma-aldrich.com/chemicalsynthesis](http://sigma-aldrich.com/chemicalsynthesis).**



## Common Reagents for Protection

### TMS

#### Chlorotrimethylsilane, redistillation, $\geq 99\%$

TMSCl	
C <sub>3</sub> H <sub>9</sub> ClSi	
FW: 108.64	
[75-77-4]	
386529-100ML	100 mL
386529-1L	1 L

#### Bromotrimethylsilane, 97%

TMSBr	
C <sub>3</sub> H <sub>9</sub> BrSi	
FW: 153.09	
[2857-97-8]	
194409-5G	5 g
194409-25G	25 g
194409-100G	100 g

#### Iodotrimethylsilane, 97%

TMSI	
C <sub>3</sub> H <sub>9</sub> I	
FW: 200.09	
[16029-98-4]	
195529-5G	5 g
195529-25G	25 g
195529-100G	100 g

#### Trimethylsilyl trifluoromethanesulfonate, 99%

TMS(OTf)	
C <sub>4</sub> H <sub>9</sub> F <sub>3</sub> O <sub>3</sub> SSi	
FW: 222.26	
[27607-77-8]	
225649-10G	10 g
225649-50G	50 g

#### N,O-Bis(trimethylsilyl)acetamide, synthesis grade

BSA	
C <sub>8</sub> H <sub>21</sub> NOSi <sub>2</sub>	
FW: 203.43	
[10416-59-8]	
128910-10ML	10 mL
128910-25ML	25 mL
128910-100ML	100 mL
128910-1L	1 L

#### N,O-Bis(trimethylsilyl)trifluoroacetamide, $\geq 99\%$

BSTFA	
C <sub>8</sub> H <sub>18</sub> F <sub>3</sub> NOSi <sub>2</sub>	
FW: 257.4	
[25561-30-2]	
155195-5G	5 g
155195-25G	25 g
155195-100G	100 g

#### N-Methyl-N-(trimethylsilyl)trifluoroacetamide, derivatization grade

MSTFA	
C <sub>9</sub> H <sub>12</sub> F <sub>3</sub> NOSi	
FW: 199.25	
[24589-78-4]	
394866-5ML	5 mL
394866-10X1ML	10 mL
394866-25ML	25 mL

### TBDMS

#### tert-Butyldimethylsilyl chloride, reagent grade, 97%

TBDMSCl	
C <sub>6</sub> H <sub>15</sub> ClSi	
FW: 150.72	
[18162-48-6]	
190500-5G	5 g
190500-25G	25 g
190500-100G	100 g
190500-1KG	1 kg
190500-10KG	10 kg

#### tert-Butyldimethylsilyl trifluoromethanesulfonate, reagent grade, 98%

TBDMS(OTf)	
C <sub>7</sub> H <sub>15</sub> F <sub>3</sub> O <sub>3</sub> SSi	
FW: 264.34	
[69739-34-0]	
226149-1G	1 g
226149-5G	5 g
226149-25G	25 g

#### N-tert-Butyldimethylsilyl-N-methyltrifluoroacetamide, > 97%

MTBSTFA	
C <sub>9</sub> H <sub>18</sub> F <sub>3</sub> NOSi	
FW: 241.33	
[77377-52-7]	
394882-5ML	5 mL
394882-10X1ML	10 mL
394882-25ML	25 mL
394882-100ML	100 mL

### TES

#### Chlorotriethylsilane, 99%

TESCl	
C <sub>6</sub> H <sub>15</sub> ClSi	
FW: 150.72	
[994-30-9]	
235067-5G	5 g
235067-25G	25 g

### TIPS

#### Triisopropylsilyl chloride, 97%

TIPSCl	
C <sub>9</sub> H <sub>21</sub> ClSi	
FW: 192.8	
[13154-24-0]	
241725-10G	10 g
241725-50G	50 g

#### Triisopropylsilyl trifluoromethanesulfonate, 97%

TIPS(OTf)	
C <sub>10</sub> H <sub>21</sub> F <sub>3</sub> O <sub>3</sub> SSi	
FW: 306.42	
[80522-42-5]	
248460-10G	10 g
248460-50G	50 g

**TBDPS****tert-Butyl(chloro)diphenylsilane, 98%**

TBDPSCI	
C <sub>16</sub> H <sub>19</sub> ClSi	
FW: 274.86	
[58479-61-1]	
195537-2G	2 g
195537-10G	10 g
195537-50G	50 g

**DTBS****Di-tert-butylsilyl bis(trifluoromethanesulfonate), 97%**

DTBS(OTf) <sub>2</sub>	
C <sub>10</sub> H <sub>18</sub> F <sub>6</sub> O <sub>6</sub> S <sub>2</sub> Si	
FW: 440.45	
[85272-31-7]	
262021-5G	5 g
262021-25G	25 g

**Boc****Di-tert-butyl dicarbonate, reagent grade, 97%**

Boc anhydride	
C <sub>10</sub> H <sub>18</sub> O <sub>5</sub>	
FW: 218.25	
[24424-99-5]	
199133-25G	25 g
199133-100G	100 g

**Di-tert-butyl dicarbonate, ReagentPlus®, 99%**

Boc anhydride	
C <sub>10</sub> H <sub>18</sub> O <sub>5</sub>	
FW: 218.25	
[24424-99-5]	
205249-10G	10 g
205249-50G	50 g
205249-100G	100 g
205249-1KG	1 kg
205249-15KG	15 kg

**2-(Boc-oxymino)-2-phenylacetonitrile, 99%**

Boc-ON	
C <sub>13</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>	
FW: 246.26	
[58632-95-4]	
193372-5G	5 g
193372-25G	25 g
193372-100G	100 g

**Fmoc****Fmoc chloride, 97%**

Fmoc-Cl	
C <sub>15</sub> H <sub>11</sub> ClO <sub>2</sub>	
FW: 258.7	
[28920-43-6]	
160512-1G	1 g
160512-5G	5 g
160512-25G	25 g

**Z/Cbz****Benzyl chloroformate, technical grade, 95%**

Z-Cl	
C <sub>8</sub> H <sub>7</sub> ClO <sub>2</sub>	
FW: 170.59	
[501-53-1]	
119938-5G	5 g
119938-100G	100 g

**Dibenzyl dicarbonate, 97%**

Z <sub>2</sub> O	
C <sub>16</sub> H <sub>14</sub> O <sub>5</sub>	
FW: 286.28	
[31139-36-3]	
311219-1G	1 g
311219-5G	5 g
311219-25G	25 g

**Bn****Benzyl chloride, ReagentPlus®, 99%**

BnCl	
C <sub>7</sub> H <sub>7</sub> Cl	
FW: 126.58	
[100-44-7]	
185558-50G	50 g
185558-250G	250 g
185558-1KG	1 kg
185558-2KG	2 kg
185558-4KG	4 kg

**Bz****Benzoyl chloride, ReagentPlus®, 99%**

BzCl	
C <sub>7</sub> H <sub>5</sub> ClO	
FW: 140.57	
[98-88-4]	
320153-1L	1 L

**MOM****Chloromethyl methyl ether, technical grade**

MOM-Cl	
C <sub>2</sub> H <sub>5</sub> ClO	
FW: 80.51	
[107-30-2]	
100331-25G	25 g
100331-100G	100 g

**MEM****2-Methoxyethoxymethyl chloride, technical grade**

MEM-Cl	
C <sub>4</sub> H <sub>9</sub> ClO <sub>2</sub>	
FW: 124.57	
[3970-21-6]	
357480-5G	5 g
357480-25G	25 g

**SEM****2-(Trimethylsilyl)ethoxymethyl chloride, technical grade**

SEM-Cl	
C <sub>6</sub> H <sub>15</sub> ClOSi	
FW: 166.72	
[76513-69-4]	
238902-1G	1 g
238902-5G	5 g
238902-25G	25 g

**TMSE****2-(Trimethylsilyl)ethanol, 99%**

TMSE-OH	
C <sub>5</sub> H <sub>14</sub> OSi	
FW: 118.25	
[2916-68-9]	
226890-1G	1 g
226890-10G	10 g
226890-50G	50 g

**Ms****Methanesulfonyl chloride,  $\geq 99.7\%$** 

MsCl	
CH <sub>3</sub> ClO <sub>2</sub> S	
FW: 114.55	
[124-63-0]	
471259-5ML	5 mL
471259-100ML	100 mL
471259-500ML	500 mL
471259-1L	1 L

**Ts****p-Toluenesulfonyl chloride, ReagentPlus<sup>®</sup>,  $\geq 99\%$** 

TsCl	
C <sub>7</sub> H <sub>7</sub> ClO <sub>2</sub> S	
FW: 190.65	
[98-59-9]	
240877-5G	5 g
240877-100G	100 g

**Trt****Trityl chloride, 98%**

Trt-Cl	
C <sub>19</sub> H <sub>15</sub> Cl	
FW: 278.78	
[76-83-5]	
T83801-25G	25 g
T83801-100G	100 g
T83801-500G	500 g

**PMB****4-Methoxybenzyl bromide**

PMB-Br	
C <sub>8</sub> H <sub>9</sub> BrO	
FW: 201.06	
[2746-25-0]	
561282-5G	5 g

**THP****3,4-Dihydro-2H-pyran, 97%**

C <sub>5</sub> H <sub>8</sub> O	
FW: 84.12	
[110-87-2]	
D106208-5ML	5 mL
D106208-100ML	100 mL
D106208-500ML	500 mL

**EtG****Ethylene glycol, ReagentPlus<sup>®</sup>,  $\geq 99\%$** 

C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	
FW: 62.07	
[107-21-1]	
102466-500ML	500 mL
102466-1L	1 L
102466-6X500ML	3000 mL
102466-4L	4 L
102466-20L	20 L

**Potassium Cyclopropyltrifluoroborate**

Cyclopropyl groups are found in a variety of natural products and are increasingly incorporated into pharmaceuticals such as the broad-spectrum antibiotic ciprofloxacin. Both the Charette<sup>1</sup> and Deng<sup>2</sup> groups have reported success in the cross-coupling of potassium cyclopropyltrifluoroborates with aryl bromides in the presence of common palladium catalysts. The trifluoroborate salts exhibit enhanced stability and more certain stoichiometry relative to their boronic acid counterparts. However, like boronic acids, post-reaction byproducts are easily removed. We are pleased to add this useful reagent to our ever-growing portfolio of organoboron compounds.

**Potassium cyclopropyltrifluoroborate**

C <sub>3</sub> H <sub>5</sub> BF <sub>3</sub> K	
FW: 147.98	
662984-1G	1 g
662984-5G	5 g

(1) Charette, A. B. et al. *Synlett* **2005**, 11, 1779. (2) Fang, G.-H. et al. *Org. Lett.* **2004**, 6, 357.

## Common Reagents for Deprotection

### Cesium fluoride, 99%

CsF	
FW: 151.9	
[13400-13-0]	
198323-25G	25 g
198323-100G	100 g

### Cesium fluoride, 99.9%

CsF	
FW: 151.9	
[13400-13-0]	
289345-5G	5 g
289345-25G	25 g
289345-100G	100 g

### Hydrogen fluoride pyridine, hydrogen fluoride ~70%, pyridine ~30%

HF	
FW: 20.01	
[62778-11-4]	
184225-25G	25 g
184225-100G	100 g

### Tetrabutylammonium fluoride hydrate, 98%

$C_{16}H_{36}FN \cdot xH_2O$	
FW: 261.46 (anhydrous basis)	
[22206-57-1]	
241512-10G	10 g
241512-100G	100 g

### Tetrabutylammonium fluoride solution, 1.0M tetrahydrofuran

$C_{16}H_{36}FN$	
FW: 261.46	
[429-41-4]	
216143-5ML	5 mL
216143-100ML	100 mL
216143-500ML	500 mL
216143-2L	2 L

### Tetramethylammonium fluoride, 97%

$C_4H_{12}FN$	
FW: 93.14	
[373-68-2]	
459135-1G	1 g
459135-5G	5 g

### 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone, 98%

$C_8Cl_2N_2O_2$	
FW: 227	
[84-58-2]	
D60400-5G	5 g
D60400-10G	10 g
D60400-100G	100 g

### Ammonium cerium(IV) nitrate, ACS reagent, $\geq 98.5\%$

$H_8CeN_8O_{18}$	
FW: 548.22	
[16774-21-3]	
215473-50G	50 g
215473-250G	250 g
215473-500G	500 g

### Ammonium cerium(IV) nitrate, 99.99%

$H_8CeN_8O_{18}$	
FW: 548.22	
[16774-21-3]	
431338-50G	50 g
431338-250G	250 g

### Boron tribromide solution, 1.0M dichloromethane

$BBr_3$	
FW: 250.52	
[10294-33-4]	
211222-100ML	100 mL
211222-800ML	800 mL
211222-2L	2 L

### Boron tribromide, ReagentPlus<sup>®</sup>, $\geq 99\%$

$BBr_3$	
FW: 250.52	
[10294-33-4]	
419508-100G	100 g
419508-500G	500 g

### *p*-Toluenesulfonic acid monohydrate, ReagentPlus<sup>®</sup>, 98.5%

$C_7H_8O_3S \cdot H_2O$	
FW: 190.22	
[6192-52-5]	
T35920-5G	5 g
T35920-100G	100 g
T35920-500G	500 g

# New Chiral Technologies from Sigma-Aldrich



## ChiroSolv™ Kits

ChiroSolv™ kits are 96-well format kits that enable rapid screening of resolving agents and solvents for chiral separation. Each of these ready-to-use disposable kits contains a combination of eight resolving agents and twelve solvents. Racemates that can be separated include: acids, bases, alcohols, amino acids, aldehydes, and ketones. Optimum resolution that typically requires over two months can be achieved within one day.

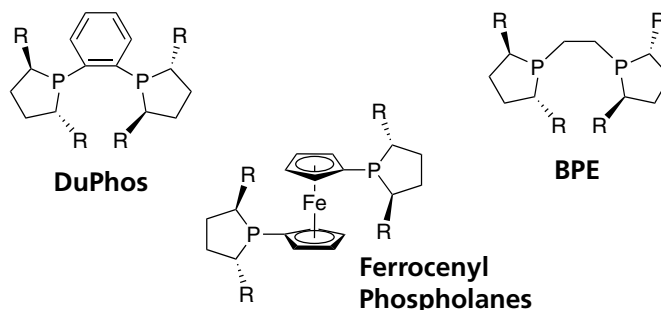
Available in three Acid Series kits (**681431**, **681423**, **681415**) and three Base Series kits (**681407**, **681393**, **681377**). For more information visit [sigma-aldrich.com/chirosolv](http://sigma-aldrich.com/chirosolv).

## Chiral Phospholane Ligands

Chiral phospholane ligands have been used extensively in transition metal-catalyzed asymmetric hydrogenations and other novel asymmetric reactions including [4+1] cycloadditions, imine alkylations, and allylboration.

Available in either enantiomeric form with Me, Et, and *i*-Pr substituents. For a detailed product listing, visit [sigma-aldrich.com/phospholane](http://sigma-aldrich.com/phospholane).

Chiral phospholane ligands are sold in collaboration with Kanata Chemical Technologies Inc. for research purposes only. These compounds were made and sold under license from E. I. Du Pont de Nemours and Company, which license does not include the right to use the compounds in producing products for sale in the pharmaceutical field.

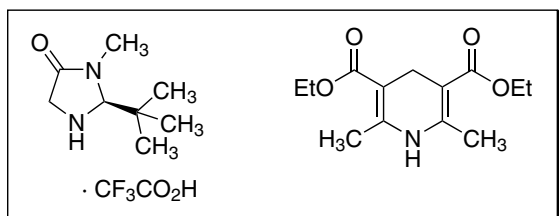


## MacMillan OrganoCatalysts™

Mac-H is a convenient formulation of the MacMillan Imidazolidinone OrganoCatalyst™ and Hantzsch ester for asymmetric reductions, effectively serving as "asymmetric hydrogenation in a bottle."

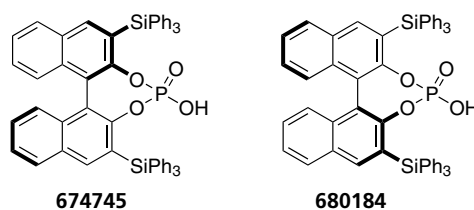
MacMillan TiPSY Catalysts have been used in the first direct enantioselective organocatalytic reductive amination reaction.

Mac-H



683558

MacMillan TiPSY Catalysts



To see our comprehensive solutions for chiral chemistry, visit [sigma-aldrich.com/gochiral](http://sigma-aldrich.com/gochiral).

**Argentina**

SIGMA-ALDRICH DE ARGENTINA S.A.  
Free Tel: 0810 888 7446  
Tel: (+54) 11 4556 1472  
Fax: (+54) 11 4552 1698

**Australia**

SIGMA-ALDRICH PTY LTD.  
Free Tel: 1800 800 097  
Free Fax: 1800 800 096  
Tel: (+61) 2 9841 0555  
Fax: (+61) 2 9841 0500

**Austria**

SIGMA-ALDRICH HANDELS GmbH  
Tel: (+43) 1 605 81 10  
Fax: (+43) 1 605 81 20

**Belgium**

SIGMA-ALDRICH NV/SA.  
Free Tel: 0800 14747  
Free Fax: 0800 14745  
Tel: (+32) 3 899 13 01  
Fax: (+32) 3 899 13 11

**Brazil**

SIGMA-ALDRICH BRASIL LTDA.  
Free Tel: 0800 701 7425  
Tel: (+55) 11 3732 3100  
Fax: (+55) 11 5522 9895

**Canada**

SIGMA-ALDRICH CANADA LTD.  
Free Tel: 1800 565 1400  
Free Fax: 1800 265 3858  
Tel: (+1) 905 829 9500  
Fax: (+1) 905 829 9292

**China**

SIGMA-ALDRICH (SHANGHAI)  
TRADING CO. LTD.  
Free Tel: 800 819 3336  
Tel: (+86) 21 6141 5566  
Fax: (+86) 21 6141 5567

**Czech Republic**

SIGMA-ALDRICH S.R.O.  
Tel: (+420) 246 003 200  
Fax: (+420) 246 003 291

**Denmark**

SIGMA-ALDRICH DENMARK A/S  
Tel: (+45) 43 56 59 10  
Fax: (+45) 43 56 59 05

**Finland**

SIGMA-ALDRICH FINLAND OY  
Tel: (+358) 9 350 9250  
Fax: (+358) 9 350 92555

**France**

SIGMA-ALDRICH CHIMIE S.à.r.l.  
Free Tel: 0800 211 408  
Free Fax: 0800 031 052  
Tel: (+33) 474 82 28 00  
Fax: (+33) 474 95 68 08

**Germany**

SIGMA-ALDRICH CHEMIE GmbH  
Free Tel: 0800 51 55 000  
Free Fax: 0800 64 90 000  
Tel: (+49) 89 6513 0  
Fax: (+49) 89 6513 1160

**Greece**

SIGMA-ALDRICH (O.M.) LTD.  
Tel: (+30) 210 994 8010  
Fax: (+30) 210 994 3831

**Hungary**

SIGMA-ALDRICH Kft  
Ingyenes zöld telefon: 06 80 355 355  
Ingyenes zöld fax: 06 80 344 344  
Tel: (+36) 1 235 9055  
Fax: (+36) 1 235 9050

**India**

SIGMA-ALDRICH CHEMICALS  
PRIVATE LIMITED  
Telephone  
Bangalore: (+91) 80 6621 9600  
New Delhi: (+91) 11 4165 4255  
Mumbai: (+91) 22 2570 2364  
Hyderabad: (+91) 40 6684 5488  
Fax  
Bangalore: (+91) 80 6621 9650  
New Delhi: (+91) 11 4165 4266  
Mumbai: (+91) 22 2579 7589  
Hyderabad: (+91) 40 6684 5466

**Ireland**

SIGMA-ALDRICH IRELAND LTD.  
Free Tel: 1800 200 888  
Free Fax: 1800 600 222  
Tel: (+353) 1 404 1900  
Fax: (+353) 1 404 1910

**Israel**

SIGMA-ALDRICH ISRAEL LTD.  
Free Tel: 1 800 70 2222  
Tel: (+972) 8 948 4100  
Fax: (+972) 8 948 4200

**Italy**

SIGMA-ALDRICH S.r.l.  
Numero Verde: 800 827018  
Tel: (+39) 02 3341 7310  
Fax: (+39) 02 3801 0737

**Japan**

SIGMA-ALDRICH JAPAN K.K.  
Tokyo Tel: (+81) 3 5796 7300  
Tokyo Fax: (+81) 3 5796 7315

**Korea**

SIGMA-ALDRICH KOREA  
Free Tel: (+82) 80 023 7111  
Free Fax: (+82) 80 023 8111  
Tel: (+82) 31 329 9000  
Fax: (+82) 31 329 9090

**Malaysia**

SIGMA-ALDRICH (M) SDN. BHD  
Tel: (+60) 3 5635 3321  
Fax: (+60) 3 5635 4116

**Mexico**

SIGMA-ALDRICH QUÍMICA, S.A. de C.V.  
Free Tel: 01 800 007 5300  
Free Fax: 01 800 712 9920  
Tel: 52 722 276 1600  
Fax: 52 722 276 1601

**The Netherlands**

SIGMA-ALDRICH CHEMIE BV  
Free Tel: 0800 022 9088  
Free Fax: 0800 022 9089  
Tel: (+31) 78 620 5411  
Fax: (+31) 78 620 5421

**New Zealand**

SIGMA-ALDRICH NEW ZEALAND LTD.  
Free Tel: 0800 936 666  
Free Fax: 0800 937 777  
Tel: (+61) 2 9841 0555  
Fax: (+61) 2 9841 0500

**Norway**

SIGMA-ALDRICH NORWAY AS  
Tel: (+47) 23 17 60 60  
Fax: (+47) 23 17 60 50

**Poland**

SIGMA-ALDRICH Sp. z o.o.  
Tel: (+48) 61 829 01 00  
Fax: (+48) 61 829 01 20

**Portugal**

SIGMA-ALDRICH QUÍMICA, S.A.  
Free Tel: 800 202 180  
Free Fax: 800 202 178  
Tel: (+351) 21 924 2555  
Fax: (+351) 21 924 2610

**Russia**

SIGMA-ALDRICH RUS, LLC  
Tel: +7 (495) 621 6037  
Fax: +7 (495) 621 5923

**Singapore**

SIGMA-ALDRICH PTE. LTD.  
Tel: (+65) 6779 1200  
Fax: (+65) 6779 1822

**South Africa**

SIGMA-ALDRICH  
SOUTH AFRICA (PTY) LTD.  
Free Tel: 0800 1100 75  
Free Fax: 0800 1100 79  
Tel: (+27) 11 979 1188  
Fax: (+27) 11 979 1119

**Spain**

SIGMA-ALDRICH QUÍMICA, S.A.  
Free Tel: 900 101 376  
Free Fax: 900 102 028  
Tel: (+34) 91 661 99 77  
Fax: (+34) 91 661 96 42

**Sweden**

SIGMA-ALDRICH SWEDEN AB  
Tel: (+46) 8 742 4200  
Fax: (+46) 8 742 4243

**Switzerland**

SIGMA-ALDRICH CHEMIE GmbH  
Free Tel: 0800 80 00 80  
Free Fax: 0800 80 00 81  
Tel: (+41) 81 755 2828  
Fax: (+41) 81 755 2815

**United Kingdom**

SIGMA-ALDRICH COMPANY LTD.  
Free Tel: 0800 717 181  
Free Fax: 0800 378 785  
Tel: (+44) 1747 833 000  
Fax: (+44) 1747 833 313  
SAFC (UK) Free Tel: 0800 71 71 17

**United States**

SIGMA-ALDRICH  
P.O. Box 14508  
St. Louis, Missouri 63178  
Toll-Free: 800 325 3010  
Toll-Free Fax: 800 325 5052  
Call Collect: (+1) 314 771 5750  
Tel: (+1) 314 771 5765  
Fax: (+1) 314 771 5757

**Internet**

sigma-aldrich.com

**World Headquarters**

3050 Spruce St., St. Louis, MO 63103  
(314) 771-5765  
sigma-aldrich.com

**Order/Customer Service** (800) 325-3010 • Fax (800) 325-5052

**Technical Service** (800) 325-5832 • sigma-aldrich.com/techservice

**Development/Bulk Manufacturing Inquiries SAFC™** (800) 244-1173

**The SIGMA-ALDRICH Group**

©2007 Sigma-Aldrich Co. All rights reserved.

SIGMA, SAFC, SAFC™, SIGMA-ALDRICH, ISOTEC, ALDRICH, FLUKA, SUPELCO, and ReagentPlus are trademarks belonging to Sigma-Aldrich Co. and its affiliate Sigma-Aldrich Biotechnology, L.P. Riedel-de Haën® trademark under license from Riedel-de Haën GmbH. Sigma brand products are sold through Sigma-Aldrich, Inc. Sigma-Aldrich, Inc. warrants that its products conform to the information contained in this and other Sigma-Aldrich publications. Purchaser must determine the suitability of the product(s) for their particular use. Additional terms and conditions may apply. Please see reverse side of the invoice or packing slip.



**SIGMA-ALDRICH**

*Accelerating Customers' Success  
through Leadership in Life Science,  
High Technology and Service*

**SIGMA-ALDRICH™**

3050 Spruce Street • St. Louis, MO 63103 USA

JJJ  
02177-503201  
0037