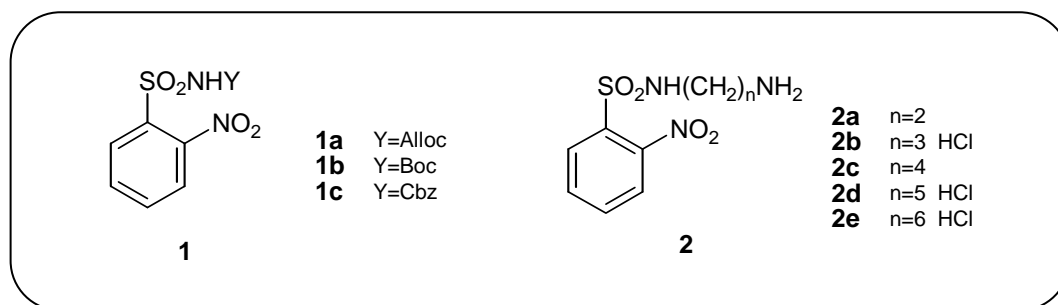
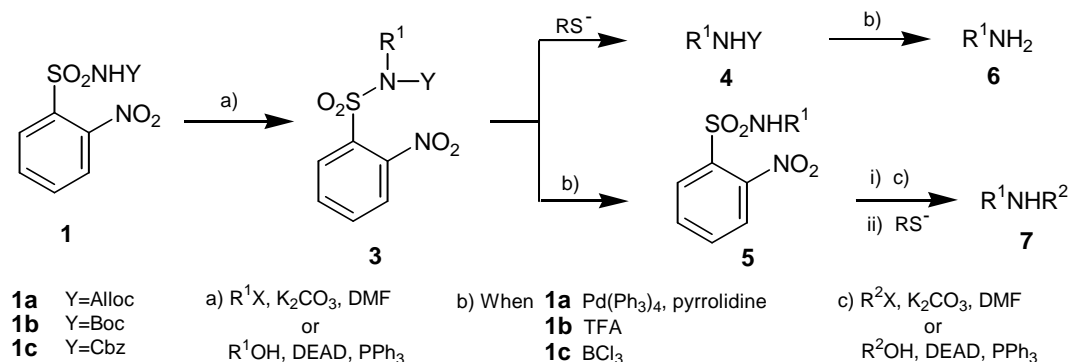


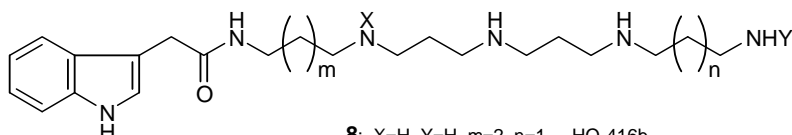
Useful Reagents for Primary and Secondary Amine and Polyamine Synthesis



Fukuyama and co-workers have demonstrated various reactions using the *N*-substituted sulfonamides **1** and **2**. Smooth reactions of **1** occur with alkyl halides under basic conditions and alcohols under Mitsunobu conditions to provide *o*-nitrobenzenesulfonyl (*o*-Ns) amines **3**.¹⁾ The various *o*-Ns amines (Alloc, Boc, Cbz) **3** obtained from these reactions can be selectively deprotected, under the appropriate conditions, to afford the monoprotected amines **4** and **5**. Furthermore, **4** can be converted to the primary amine **6** in high yield via a second deprotection. Compound **5** can be converted to the secondary amine **7** in high yields by repeating the alkylation and deprotection process.²⁾



Mono *o*-Ns protected diamines, **2**, are ideal starting materials for incorporation into polyamine chains. For example, total synthesis of spider toxins of HO-416b **8** and Agel-489 **9** using **2** was successfully accomplished by Fukuyama and co-workers.³⁾ Polyamine toxins derived from spider venom have been shown to be specific glutamate receptor blockers, known as antagonists. They are actively studied as tools for neurophysiology and as lead compounds for pharmaceutical and agrochemical agents. In addition, the applications to the total synthesis of lipogrammin-A, a macrocyclic polyamine using **2** has been reported.⁴⁾



8: X=H, Y=H, m=2, n=1 HO-416b
9: X=OH, Y=(CH₂)₃NH₂, m=1, n=2 Agel-489

Keywords : (*o*-Ns)amines, amine synthesis

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The *o*-Ns moiety acts as both a protecting and activating group for amino groups. The nitrogen-*o*-Ns bond is stable under acidic and basic conditions. The *o*-Ns group can be selectively and easily deprotected by thiols under basic conditions. Recently, applications of odorless thiols in this denosylation reaction have been investigating. For example, Matoba, *et al.* have reported useful denosylation reaction using 4-mercaptobenzoic acid as odorless aromatic thiol. The denosylation reaction is useful method for easy removing the by-products, and mild reaction conditions.⁵⁾ Further applications of **1** and **2** as useful building blocks in the synthesis of primary and secondary amines as well as polyamines are expected.

Products

A1632	<i>N</i> -Allyloxycarbonyl-2-nitrobenzenesulfonamide	(1a)		5g
B2303	<i>N</i> -(<i>tert</i> -Butoxycarbonyl)-2-nitrobenzenesulfonamide	(1b)	1g	5g
C1757	<i>N</i> -Carbobenzoxy-2-nitrobenzenesulfonamide	(1c)	5g	25g
A1627	<i>N</i> -(2-Aminoethyl)-2-nitrobenzenesulfonamide	(2a)		1g
A2268	<i>N</i> -(3-Aminopropyl)-2-nitrobenzenesulfonamide Hydrochloride	(2b)	1g	5g
A1630	<i>N</i> -(4-Aminobutyl)-2-nitrobenzenesulfonamide	(2c)		1g
A1661	<i>N</i> -(5-Aminopentyl)-2-nitrobenzenesulfonamide Hydrochloride	(2d)		1g
A1662	<i>N</i> -(6-Aminohexyl)-2-nitrobenzenesulfonamide Hydrochloride	(2e)		1g
N0142	2-Nitrobenzenesulfonyl Chloride		25g	500g

Denosylating Agents

B0041	Benzenethiol		25ml	500ml
M1294	4-Mercaptobenzoic Acid		5g	25g
M0058	2-Mercaptoethanol		25g	500g
M0052	Thioglycolic Acid		25g	500g

Related Products

D2479	Sodium Diformylamide			25g
I0497	Di- <i>tert</i> -butyl Iminodicarboxylate		5g	25g
I0510	<i>tert</i> -Butyl Methyl Iminodicarboxylate			5g
A1371	<i>N</i> -(<i>tert</i> -Butoxycarbonyl)-1,2-diaminoethane	1g	5g	25g
A1372	<i>N</i> -(<i>tert</i> -Butoxycarbonyl)-1,3-diaminopropane		1g	5g
A1373	<i>N</i> -(<i>tert</i> -Butoxycarbonyl)-1,4-diaminobutane	1g	5g	25g
A1374	<i>N</i> -(<i>tert</i> -Butoxycarbonyl)-1,5-diaminopentane		1g	5g
A1375	<i>N</i> -(<i>tert</i> -Butoxycarbonyl)-1,6-diaminohexane		1g	5g
C1511	<i>N</i> -Carbobenzoxy-1,2-diaminoethane Hydrochloride	1g	5g	25g
C1512	<i>N</i> -Carbobenzoxy-1,3-diaminopropane Hydrochloride		1g	5g
C1519	<i>N</i> -Carbobenzoxy-1,4-diaminobutane Hydrochloride		1g	5g
C1520	<i>N</i> -Carbobenzoxy-1,5-diaminopentane Hydrochloride		1g	5g
C1521	<i>N</i> -Carbobenzoxy-1,6-diaminohexane Hydrochloride		1g	5g

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