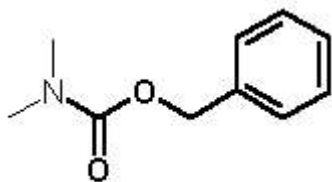


Organic Chemistry Portal

Reactions >> Protecting Groups >> Stability

Benzyl carbamates

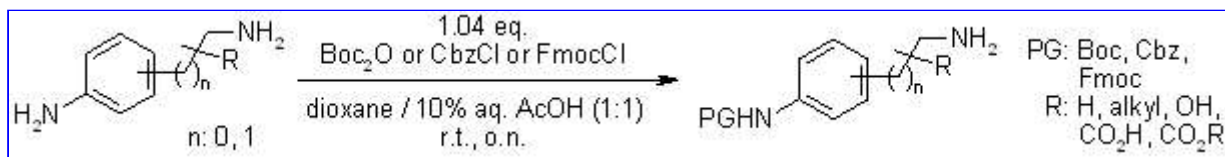
Cbz-NR₂ / Z-NR₂

T. W. Green, P. G. M. Wuts,
Protective Groups in Organic Synthesis,
 Wiley-Interscience, New York, **1999**, 531-537, 736-739.

Stability

H₂O:	pH < 1, 100°C	pH = 1, RT	pH = 4, RT	pH = 9, RT	pH = 12, RT	pH > 12, 100°C
Bases:	LDA	NEt ₃ , Py	t-BuOK	Others:	DCC	SOCl ₂
Nucleophiles:	RLi	RMgX	RCuLi	Enolates	NH ₃ , RNH ₂	NaOCH ₃
Electrophiles:	RCOCl	RCHO	CH ₃ I	Others:	:CCl ₂	Bu ₃ SnH
Reduction:	H ₂ / Ni	H ₂ / Rh	Zn / HCl	Na / NH ₃	LiAlH ₄	NaBH ₄
Oxidation:	KMnO ₄	OsO ₄	CrO ₃ / Py	RCOOH	I ₂ , Br ₂ , Cl ₂	MnO ₂ /CH ₂ Cl ₂

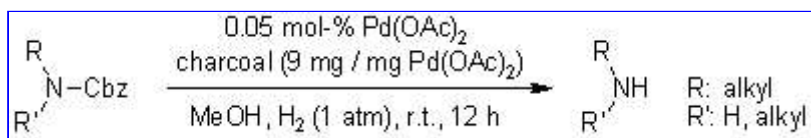
Protection of Amino Groups



A simple and efficient protection procedure is general and regioselective for the preparation of mono-*N*-Boc, *N*-Cbz, *N*-Fmoc or *N*-Alloc aromatic amines in high yield without affecting aliphatic amino groups and other functionalities.

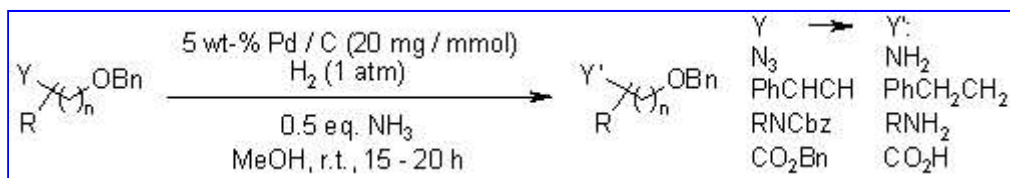
V. Perron, S. Abbott, N. Moreau, D. Lee, C. Penney, B. Zacharie, *Synthesis*, **2009**, 283-289.

Deprotection



In situ preparation of an active Pd/C catalyst from Pd(OAc)₂ and charcoal in methanol enables a simple, highly reproducible protocol for the hydrogenation of alkenes and alkynes and for the hydrogenolysis of *O*-benzyl ethers. Mild reaction conditions and low catalyst loadings, as well as the absence of contamination of the product by palladium residues, make this a sustainable, useful process.

F.-X. Felpin, E. Fouquet, *Chem. Eur. J.*, **2010**, 12440-12445.



Ammonia, pyridine and ammonium acetate were extremely effective as inhibitors of Pd/C catalyzed benzyl ether hydrogenolysis. While olefin, Cbz, benzyl ester and azide functionalities were hydrogenated smoothly, benzyl ethers were not

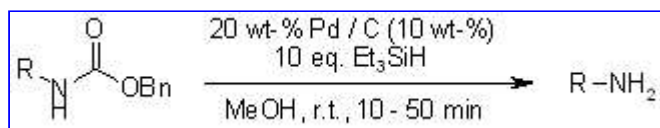
cleaved.

H. Sajiki, *Tetrahedron Lett.*, **1995**, 36, 3465-3468.



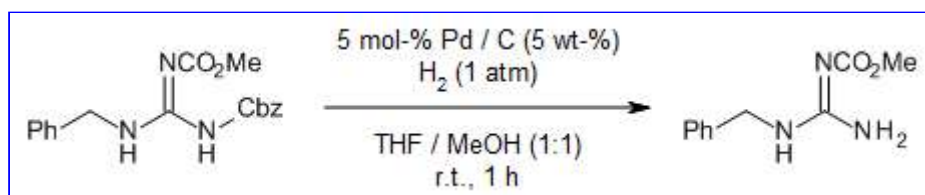
A generally applicable method for the introduction of gaseous hydrogen into a sealed reaction system under microwave irradiation allows the hydrogenation of various substrates in short reaction times with moderate temperatures between 80 °C and 100 °C with 50 psi of hydrogen.

G. S. Vanier, *Synlett*, **2007**, 131-135.



In situ generation of molecular hydrogen by addition of triethylsilane to palladium on charcoal results in rapid and efficient reduction of multiple bonds, azides, imines, and nitro groups, as well as deprotection of benzyl and allyl groups under mild, neutral conditions.

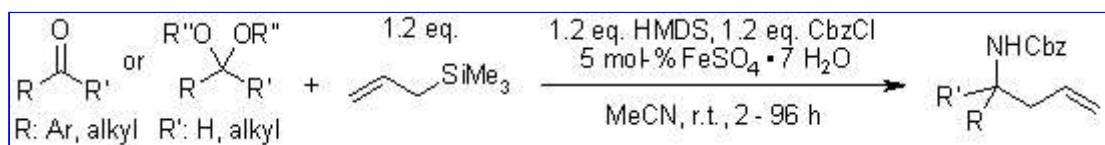
P. K. Mandal, J. S. McMurray, *J. Org. Chem.*, **2007**, 72, 6599-6601.



Various thioureas derived from primary amines and carbamoyl-protected isothiocyanates react with the Burgess reagent to give the corresponding guanidines via either a stepwise or one-pot procedure. A selective deprotection of the *N,N'*-diprotected guanidines affords *N*-monoprotected guanidines.

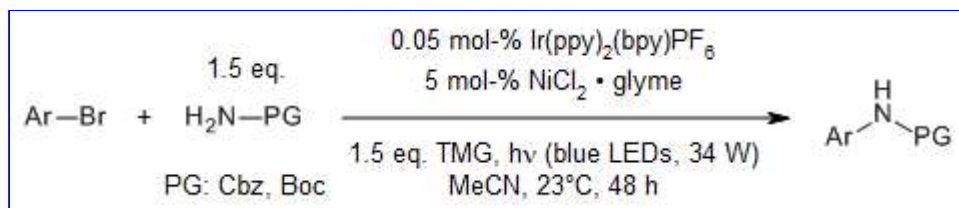
T. Maki, T. Tsuritani, T. Yasukata, *Org. Lett.*, **2014**, 16, 1868-1871.

Other Syntheses of Cbz-Protected Amino Groups



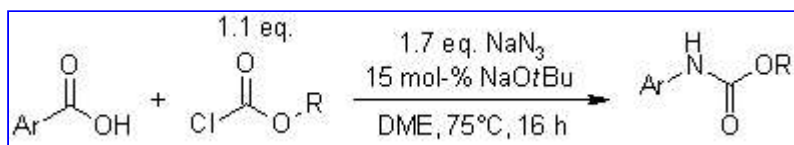
An efficient catalytic four-component reaction of carbonyl compounds, benzyl chloroformate, 1,1,1,3,3,3-hexamethyldisilazane, and allyltrimethylsilane provides Cbz-protected homoallylic amines in the presence of 5 mol% of iron(II) sulfate heptahydrate as an inexpensive and environmentally friendly catalyst.

Q.-Y. Song, B.-L. Yang, S.-K. Tian, *J. Org. Chem.*, **2007**, 72, 5407-5410.



A highly efficient Ni(II)-catalyzed photoredox N-arylation of Cbz-amines/Boc-amines with aryl electrophiles at room temperature provides a wide variety of *N*-aromatic and *N*-heteroaromatic carbamate products that find use in the synthesis of several biologically active molecules. The reaction offers a viable alternative to traditional palladium-catalyzed Buchwald-Hartwig reaction.

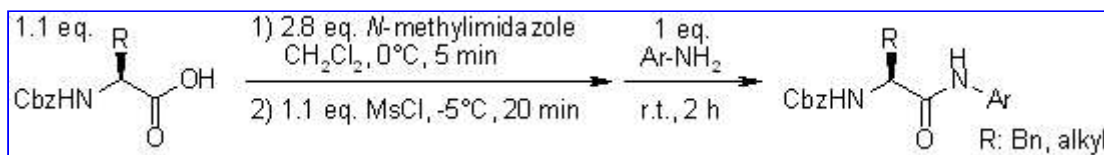
L. R. Reddy, S. Kotturi, Y. Waman, V. R. Reddy, C. Patel, A. Kobarne, S. Kuttappan, *J. Org. Chem.*, **2018**, 83, 13854-13860.



The reaction of di-*tert*-butyl dicarbonate or a chloroformate and sodium azide with an aromatic carboxylic acid produces the corresponding acyl azide. The acyl azide undergoes a Curtius rearrangement to form an isocyanate derivative which is trapped either by an alkoxide or by an amine to form the aromatic carbamate or urea.

H. Lebel, O. Leogane, *Org. Lett.*, **2006**, *8*, 5717-5720.

Cbz-Protected Amino-Groups in Multi-step Syntheses



N-Cbz-protected amino acids reacted with various aryl amines in the presence of methanesulfonyl chloride and *N*-methylimidazole in dichloromethane to give the corresponding arylamides in high yields without racemization under these mild conditions.

L. Mao, Z. Wang, Y. Li, X. Han, W. Zhou, *Synlett*, **2011**, 129-133.