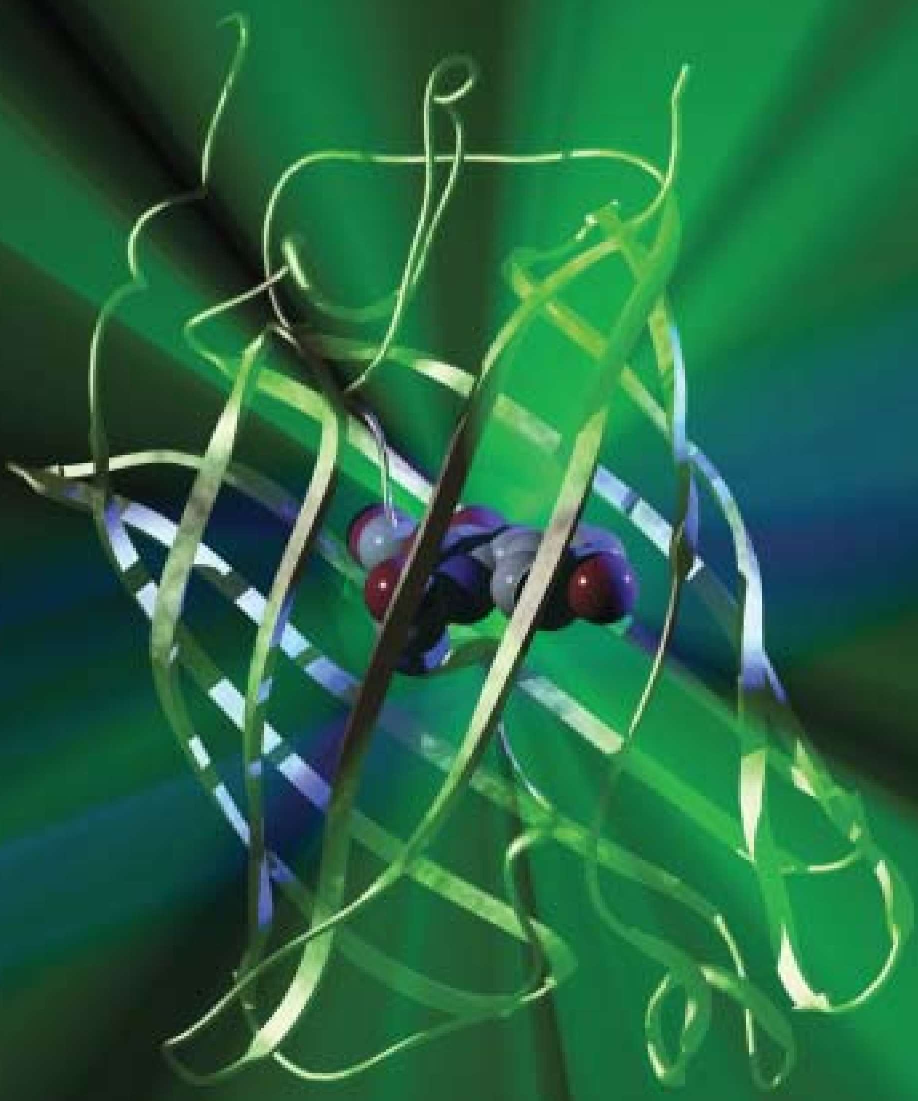
ChemFiles

Unnatural Amino Acids II

Vol.2, No.4

- Cyclic Amino Acids
- Diamino Acids
- β-Amino Acids and Homo-Amino Acids
- Alanine Derivatives
- Phenylalanine-Derivatives
- Proline and Pyroglutamine Derivatives



The latest Update on New Tools for Drug Discovery

Fluka

Unnatural Amino Acids II

What is New?

Fluka is very pleased to highlight in this ChemFiles issue a completely new overview of our fast-growing product range of unnatural amino acids. Please contact your local Sigma-Aldrich office (see back cover) or download a copy from the web at www.sigma-aldrich.com, if you would like to receive a hard copy of our first brochure using these "Innovative tools for your research in Drug Discovery." (ChemFile Vol. 1 No. 5)

"One-stop shopping"

Fluka offers you all the tools you need for synthesizing peptides, from basics such as coupling reagents expanding to a range of around 600 unnatural amino acids. In this brochure you will find an overview of more than 90 New and unique building blocks for peptide-analogues and peptidomimetics research.

Content of this ChemFile

Fluka is pleased to discuss in this ChemFile the following topics:

- **Cyclic Amino Acids**
- **Diamino Acids**
- **β-Amino Acids and Homo Amino Acids**
- **Alanine Derivatives**
- **Phenylalanine Boronic Acids**
- **Proline and Pyroglutamine Derivatives**

New offerings in this rapidly expanding field are added monthly!

At Sigma-Aldrich we are committed to supplying you with reliable products, new technologies and unsurpassed service. A strong example of this commitment is the introduction of several thousands of new products every year. Please take a look at www.sigma-aldrich.com/flukanew for a regular update on the latest Fluka products. When you cannot find the amino acid you are looking for, we welcome your input and will use it to broaden our product range even further. Please contact us at Flukatec@eurnotes.sial.com with new suggestions!

Prices: **all presented prices can be subject to changes. Please contact your local Sigma-Aldrich Office (see back cover) or check our web site for local price information.**

ChemFiles on the web

Please take a look at the whole range of our ChemFiles brochures at www.sigma-aldrich.com/chemfiles. When you prefer to obtain a paper copy of these brochures, please contact your local Sigma-Aldrich Office (see back cover).

CombiChem Catalog on the web

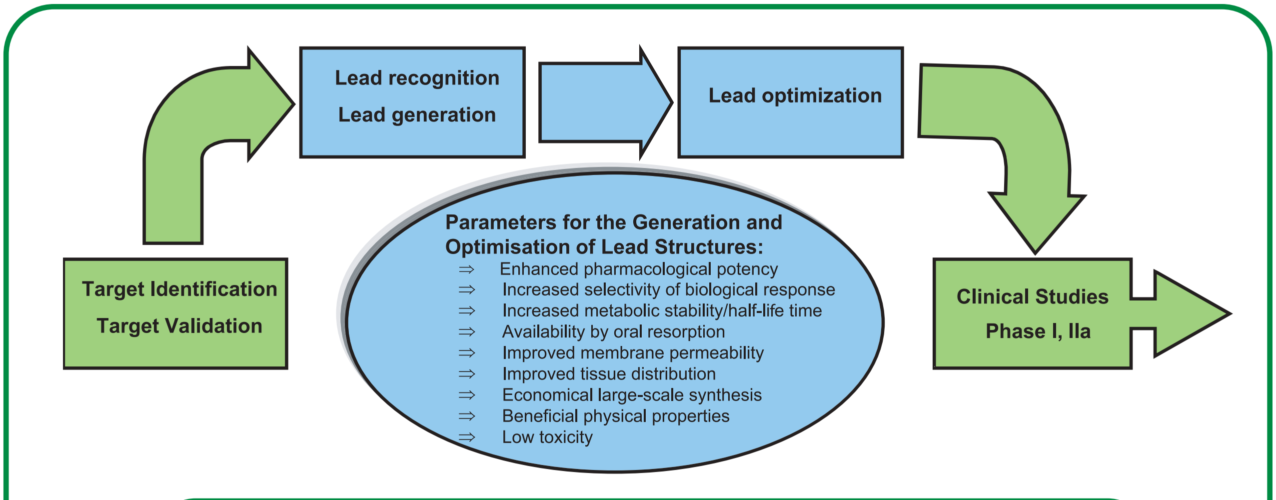
Sigma-Aldrich is the market leader when it comes to supplying building blocks, resins and other tools to the combinatorial chemistry market. Please take a look at our web site at www.sigma-aldrich.com/combichem for the electronic version of the combichem catalog.

Front picture presents a Green Fluorescent Protein, made by A. Tepper, University of Leiden, The Netherlands

"Are you interested in synthesizing "FUNCTION"?

"The essential step in combinatorial chemistry is not the synthesis; rather it is finding a target, based on specific properties. Combinatorial synthetic research is an adaption to what nature has been doing all the time: synthesis followed by selection, as opposed to synthesis by design. The aim of combinatorial chemistry is primarily discovering a molecule, whereas that of chemical synthesis is constructing a molecule."

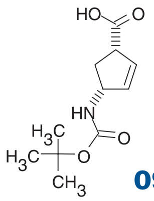
REFERENCE: Albert Eschenmoser, Chem. Intell. **2000**, *6*, 6.



The Drug-Discovery Process

Unnatural amino acids, utilized as building blocks, conformational constraints, molecular scaffolds or pharmacologically active products, represent a nearly infinite array of diverse structural elements for the development of new leads in peptidic and non-peptidic compounds. Small-molecule combinatorial libraries containing unnatural amino acid residues already show remarkable impact on drug discovery processes.[1-5] Novel short-chain peptide ligand mimetics with both enhanced biological activity and proteolytic resistence are drug candidates in todays R&D pipelines of many pharmaceutical companies. Optimized and fine-tuned analogues of peptidic substrates, inhibitors or effectors are also excellent analytical tools for investigating signal transduction pathways or gene regulation.

REFERENCES: [1] Bunin, B.A. et al., *Annu. Rep. Med. Chem.* **1999**, *34*, 267. [2] Floyd, C. D. et al., *Prog. Med. Chem.* **1999**, *36*, 91. [3] Borman, S. *Chem. Eng. News* **1999**, 77, 33. [4] Brown, R. K. *Modern Drug Discovery* **1999**, *2*, 63. [5] Borman, S. *Chem. Eng. News* **2000**, *78*, 53.



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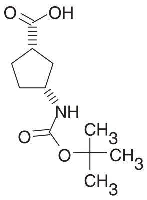

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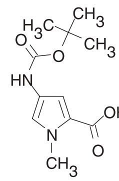

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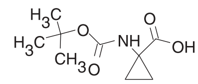

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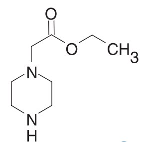

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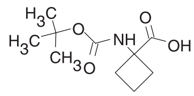

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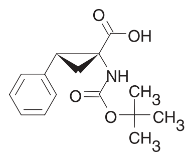

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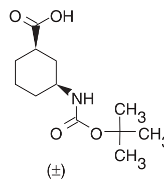

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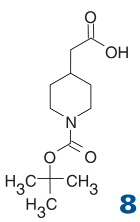

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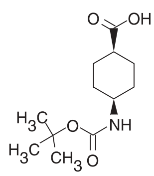

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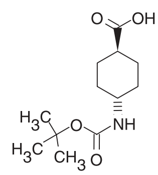


89798

39977	**1-(BOC-amino)cyclopropanecarboxylic acid**				**250 mg**
	>98.0%	**$C_9H_{15}NO_4$**	**M_r 201.22**	**[88950-64-5]**	**1 g**
68822	**1-(Fmoc-amino)-cyclopropanecarboxylic acid**				**250 mg**
	~97%	**$C_{19}H_{17}NO_4$**	**M_r 323.35**	**[126705-22-4]**	**1 g**
73823	**(1*R*,2*R*)-*cis*-1-(BOC-amino)-2-phenylcyclopropanecarboxylic acid**				**500 mg**
	~98%	**$C_{15}H_{19}NO_4$**	**M_r 277.32**	**[180322-86-5]**	
89954	**(1*S*,2*R*)-*trans*-1-(Boc-amino)-2-phenylcyclopropanecarboxylic acid**				**500 mg**
	~98%	**$C_{15}H_{19}NO_4$**	**M_r 277.32**	**[151910-11-1]**	
73251	**(1*R*,2*S*)-*trans*-1-(Boc-amino)-2-phenylcyclopropanecarboxylic acid**				**500 mg**
	~98%	**$C_{15}H_{19}NO_4$**	**M_r 277.32**	**[24205-60-5]**	
68823	**1-(Boc-amino)cyclobutanecarboxylic acid**			**Boc-cyclovaline**	**500 mg**
	>98.0%	**$C_{10}H_{17}NO_4$**	**M_r 215.25**	**[120728-10-1]**	
39978	**1-(Fmoc-amino)cyclobutanecarboxylic acid**			**Fmoc-cyclovaline**	**100 mg**
	~97%	**$C_{20}H_{19}NO_4$**	**M_r 337.38**		**500 mg**
09784	**(1*S*,3*R*)-(+)-3-(Boc-amino)cyclopentanecarboxylic acid**				**500 mg**
	~98%	**$C_{11}H_{19}NO_4$**	**M_r 229.28**	**[261165-05-3]**	
09781	**(1*S*,4*R*)-(-)-4-(Boc-amino)-2-cyclopentene-1-carboxylic acid**				**500 mg**
	>98.0%	**$C_{11}H_{17}NO_4$**	**M_r 227.26**	**[151907-79-8]**	
09782	**(1*R*,4*S*)-(+)-4-(Boc-amino)-2-cyclopentene-1-carboxylic acid**				**500 mg**
	>98.0%	**$C_{11}H_{17}NO_4$**	**M_r 227.26**	**[151907-80-1]**	

80393	*cis*-3-(Boc-amino)cyclohexanecarboxylic acid				500 mg
	>98.0%	$C_{12}H_{21}NO_4$	M_r 243.30	[222530-33-8]	
88412	*cis*-4-(Boc-amino)cyclohexanecarboxylic acid				500 mg
	>98.0%	$C_{12}H_{21}NO_4$	M_r 243.30	[53292-90-3]	
93265	*cis*-4-(Fmoc-amino)cyclohexanecarboxylic acid				500 mg
	>98.0%	$C_{22}H_{23}NO_4$	M_r 365.42	[147900-45-6]	
89798	*trans*-4-(Boc-amino)cyclohexanecarboxylic acid				500 mg
	>98.0%	$C_{12}H_{21}NO_4$	M_r 243.30	[53292-89-0]	
83067	*trans*-4-(Fmoc-amino)cyclohexanecarboxylic acid				500 mg
	>98.0%	$C_{22}H_{23}NO_4$	M_r 365.42	[147900-46-7]	
78324	1-Boc-(*S*)-azetidine-2-carboxylic acid				500 mg
	>98.0%	$C_9H_{15}NO_4$	M_r 201.22	[51077-14-6]	
70238	1-Fmoc-(*S*)-azetidine-2-carboxylic acid				500 mg
	>97.0%	$C_{19}H_{17}NO_4$	M_r 323.34	[136552-06-2]	
81964	1-Boc-4-piperidylacetic acid				500 mg
	>98.0%	$C_{12}H_{21}NO_4$	M_r 243.30	[157688-46-5]	
17852	4-(Boc-amino)-1-methylpyrrole-2-carboxylic acid				1 g
	>99.0%	$C_{11}H_{16}N_2O_4$	M_r 240.26	[77716-11-1]	

Books

Fmoc Solid Phase Peptide Synthesis: A Practical Approach

W.C. Chan and P.D. White, Eds., Oxford University Press, New York, NY, 2000, 376pp. Hardcover.

Covers not only the essential procedures for the production of linear peptides but also more advanced techniques for preparing cyclic, side-chain modified, phospho- and glycopeptides. Many other methods also deserving attention have been included: convergent peptide synthesis; peptide-protein conjugation; chemoselective ligation; and chemoselective purification.

Z42,426-9

A Practical Guide to Combinatorial Chemistry

A.W. Czarnik and S.H. DeWitt, Eds., American Chemical Society, Washington, DC, 1997, 450pp. Hardcover.

A practical guide for both newcomers and specialists in small-molecule combinatorial chemistry. Tutorial-style chapters review computational tools to analyze molecular diversity, methods of solid-phase peptide and small-molecule synthesis, and approaches to synthesizing solid- and solution-phase libraries.

Z40,842-5

Combinatorial Peptide and Nonpeptide Libraries: A Handbook

G. Jung, John Wiley & Sons, New York, NY, 1997, 545pp. Hardcover.

The use of combinatorial chemistry and peptide libraries in drug screening and development is a new and rapidly expanding technology. This first handbook on the topic contains background information and step-by-step experimental procedures.

Z28,816-0

Compendium of Chiral Auxiliary Applications, 3-volume set

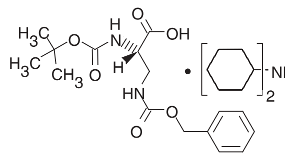
Greg Roos, Sultan Qaboos University, Sultanate of Oman · Hardback
1612 Pages · Academic Press · Published December 2001

This is the first major reference work of its kind to look logically and sequentially at Chiral Auxiliaries, investigating their properties and applications in diastereoselective synthesis.

- Fully cross-referenced to enable comparative selection of auxiliaries to be made dependent on target application
- Includes more than 13,000 auxiliary reaction applications with complete reaction details for each auxiliary.

Z51,324-5

For full details, including more description, condensed table of contents and 6-page detailed contents as pdf file, visit www.sigma-aldrich.com/chiralbook



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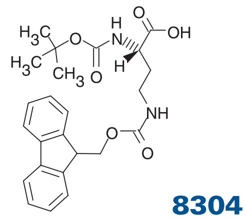

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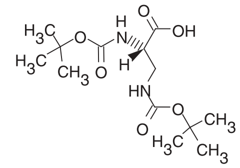

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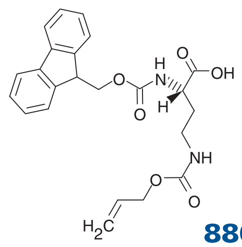

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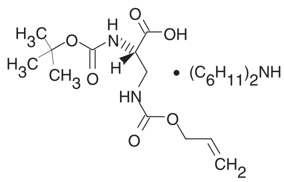
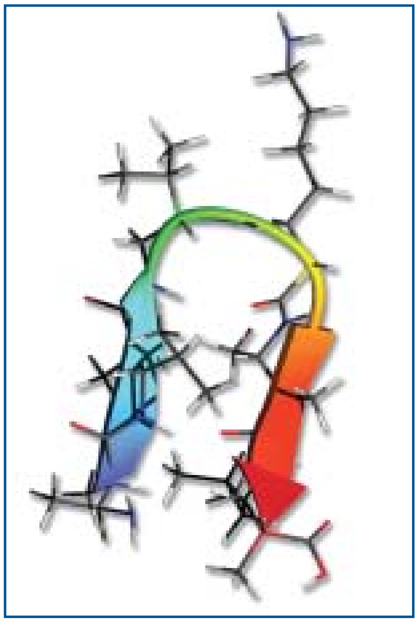


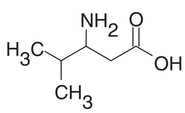
94572

32840	H-DL-Dap-OH dihydrochloride		DL-2,4-Diaminobutyric acid dihydrochloride			1 g
	>99.0%	$C_4H_{10}N_2O_2$•2HCl	M_r 191.06	[65427-54-5]		5 g
76179	H-D-Dap-OH HCl		D-2,3-Diaminopropionic acid monohydrochloride			1 g
	>99.0%	$C_3H_8N_2O_2$•HCl	M_r 140.57	[6018-56-0]		5 g
73031	Boc-Dap(Fmoc)-OH		N_α-Boc-N_β-Fmoc-L-2,3-diaminopropionic acid			500 mg
	>98.0%	$C_{23}H_{26}N_2O_6$	M_r 426.46	[122235-70-5]		2.5 g
86283	Boc-Dap(Boc)-OH DCHA		N_α,N_β-Di-Boc-L-2,3-diaminopropionic acid Dicyclohexylamine salt			
	~97%	$C_{13}H_{24}N_2O_6$•$C_{12}H_{23}N$	M_r 485.66	[201472-68-6]		500 mg
						2.5 g
94572	Boc-Dap(Alloc)-OH DCHA		N_β-Alloc-N_α-Boc-L-2,3-diaminopropionic acid Dicyclohexylamine salt			
	>97.0%	$C_{12}H_{20}N_2O_6$	M_r 288.30	[204197-28-4]		1 g
						5 g
76289	Boc-Dap(Z)-OH DCHA		N_α-Boc-N_β-Z-L-2,3-diaminopropionic acid			500 mg
	>98.0%	$C_{16}H_{22}N_2O_6$•$C_{12}H_{23}N$	Mr 519.68	[65710-58-9]		2.5 g
74242	Fmoc-Dap(Z)-OH		N_α-Fmoc-N_β-Z-L-2,3-diaminopropionic acid			500 mg
	~97%	$C_{26}H_{24}N_2O_6$	M_r 460.48	[204316-36-9]		
96414	Z-Dap(Fmoc)-OH		N_α-Z-N_β-Fmoc-L-2,3-diaminopropionic acid			500 mg
	>98.0%	$C_{26}H_{24}N_2O_6$	M_r 460.48	[142855-80-9]		
74391	Fmoc-Dap(Fmoc)-OH		N_α,N_β-di-Fmoc-L-2,3-diaminopropionic acid			500 mg
	>97.0%	$C_{33}H_{28}N_2O_6$	M_r 548.59	[201473-90-7]		
83041	Boc-Dab(Fmoc)-OH		N_γ-Fmoc-N_α-Boc-L-2,4-diaminobutyric acid			250 mg
	>98.0%	$C_{24}H_{28}N_2O_6$	M_r 440.49	[117106-21-5]		1 g
81717	Boc-Dab(Alloc)-OH DCHA		N_γ-Alloc-N_α-Boc-L-2,4-diaminobutyric acid Dicyclohexylamine salt			
		$C_{13}H_{22}N_2O_6$•$C_{12}H_{23}N$	M_r 483.65	[327156-92-3]		1 g
						5 g
88645	Fmoc-Dab(Alloc)-OH		N_γ-Alloc-N_α-Fmoc-L-2,4-diaminobutyric acid			1 g
	>98.0%	$C_{23}H_{24}N_2O_6$	M_r 424.45	[204316-32-5]		5 g

β-Amino Acids and Homo Amino Acids



In the past few years β-peptides and other β-amino acid containing oligomers have emerged as very promising tools in medicinal chemistry, as they exhibit remarkable biological activity together with an extraordinary biological stability.[1] β-Peptides have shown to be stable to common peptidases for at least two days.[2] Recently, a cyclic β-tetrapeptide was synthesized with biological activity similar to somatostatine, an important endogenous neurotransmitter and inhibitor of hormone secretion.[3] Systematic replacement of an α-amino acid by an β-amino acid residue resulted in a hybrid oligopeptide which binds to major histocompatibility complex (MHC) proteins, while showing enhanced stability towards proteolysis.[4,5] Another important aspect of β-peptide oligomers is their ability to fold into well defined and stable helical-, turn- and pleated sheet-conformations in solution.[6-9] The picture aside shows a β-peptide forming a two-stranded β-pleated sheet connected by a hairpin turn. This sheet-and-turn structure was created and analysed by NMR in solution by Seebach and coworkers. It complements the similar structure described by Gelmann *et al.*[10] by revealing the opposite orientation of the net dipole. Further remarkable applications of β-amino acids are the use as protease inhibitors,[11] precursors for antibiotics[12] and building blocks in cryptophycins.[13,14]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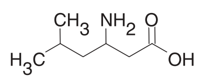
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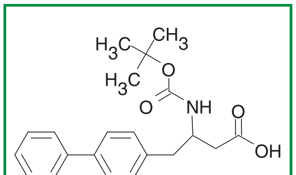
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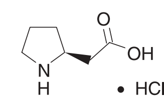
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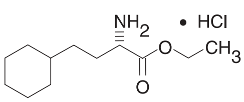
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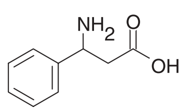
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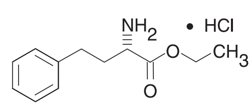
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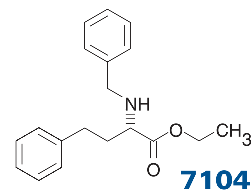
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03768	**H-L-β-Homopro-OH HCl**		**(*S*)-2-(2-Pyrrolidinyl)acetic acid hydrochloride**		**250 mg**
	>98.0%	**$C_6H_{11}NO_2$•HCl**	**M_r 129.16**	**[56633-75-1]**	**1 g**
17988	**H-DL-β-Leu-OH**		**(±)-3-Amino-4-methylpentanoic acid**		**1 g**
	>98.0%	**$C_6H_{13}NO_2$**	**M_r 131.17**	**[5699-54-7]**	**5 g**
21625	**H-DL-β-Homoleu-OH**		**(±)-3-Amino-5-methylcaproic acid**		**1 g**
	>99.0%	**$C_7H_{15}NO_2$**	**M_r 145.20**	**[3653-34-7]**	**5 g**
71552	**H-DL-β-Phe-OH**		**(±)-3-Amino-3-phenylpropionic acid**		**1 g**
	~99%	**$C_9H_{11}NO_2$**	**M_r 165.19**	**[614-19-7]**	**5 g**

REFERENCES: [1] Borman, S. *Chem. Eng. News* **1999**, 77, 27. [2] Seebach, D. Matthews, J. L. *Chem Comm.* **1997**, 2015. [3] Seebach D. et al., *Angew. Chem. Int Ed.* **1999**, *38*, 1223. [4] Rognan, D. et. al., *J. Med. Chem.* **1999**, *42*, 2318. [5] Rognan, D. et. al., *J. Biol. Chem.* **2001**, *27*, 24525. [6] Seebach, D. et al., *Angew. Chem.* Int Ed. **1999**, *38*, 1595. [7] Gademann, K. et al., *Helv. Chim. Acta* **1999**, *82*, 1. [8] Gellman, S. H. et al., *J. Am. Chem. Soc.* **1999**, *121*, 6206. [9] Gellman, S. H. et al., *J. Am. Chem. Soc.* **1999**, *121*, 7574. [10] Gellman, S. H. et al., *J. Am. Chem. Soc.* **1998**, *120*, 10555. [11] Takashiro et al., *Bioorg.& Med. Chem.* **1999**, *7*, 2063. [12] Tymiak, A. A. et al., *J. Org. Chem.* **1989**, *54*, 1149. [13] Eggen, M. et al., *Org. Lett.* **2001**, *12*, 1813. [14] White, J. D. *J. Org. Chem.* **1999**, *64*, 6206.

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β-Amino Acids and Homo Amino Acids

continued

79995*	**L-Homophe-OEt HCl**				10 g
	>98.0%	$C_{12}H_{17}NO_2$•HCl	M_r 243.73	[90891-21-7]	100 g
75854*	**D-Homophe-OEt HCl**				10 g
	>98.0%	$C_{12}H_{17}NO_2$•HCl	M_r 243.73	[90940-54-8]	100 g
71044*	**N-Benzyl-L-Homophe-OEt HCl**				10 g
	>98.0%	$C_{19}H_{23}NO_2$•HCl	M_r 333.86		100 g
75664*	**N-Benzyl-D-Homophe-OEt HCl**				10 g
	>98.0%	$C_{19}H_{23}NO_2$•HCl	M_r 333.86		100 g
41844	**(±)-3-(Boc-amino)-4-(4-biphenylyl)butyric acid**				500 mg
	>98.0%	$C_{21}H_{25}NO_4$	M_r 355.43		
23704	**(±)-3-Amino-4-(4-biphenylyl)butyric acid hydrochloride**				250 mg
	>98.0%	$C_{16}H_{17}NO_2$•HCl	M_r 291.78		1 g
70031*	**(+)-Ethyl (*S*)-2-amino-4-cyclohexylbutyrate hydrochloride**				10 g
	>98.0%	$C_{12}H_{23}NO_2$•HCl	M_r 249.78		100 g
78706*	**(-)-Ethyl (*R*)-2-amino-4-cyclohexylbutyrate hydrochloride**				10 g
	>98.0%	$C_{12}H_{23}NO_2$•HCl	M_r 249.78		100 g
68289	**3-Amino-4,4,4-trifluorobutyric acid**				500 mg
	>98.0%	$C_4H_6F_3NO_2$	M_r 157.09	[584-20-3]	

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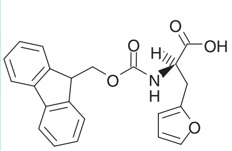
Alanine Derivatives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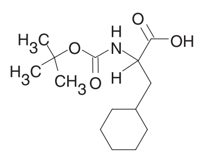
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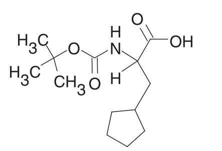
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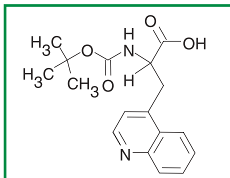
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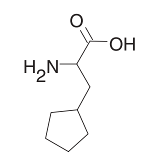
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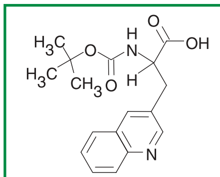
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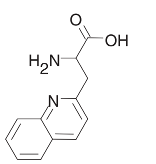
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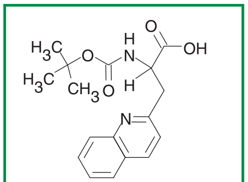
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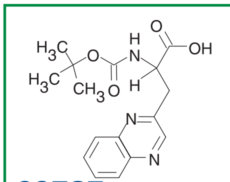
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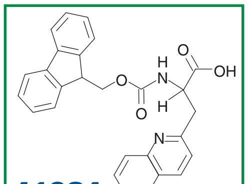
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09806	**Fmoc-3-(2-furyl)-D-Ala-OH**				
	> 98.0%	$C_{22}H_{19}NO_5$	M_r 377.40	[220497-85-8]	500 mg
42284	**Boc-3-cyclopentyl-DL-Ala-OH**				250 mg
	> 98.0%	$C_{13}H_{23}NO_4$	M_r 257.33		1 g
32762	**Fmoc-3-cyclopentyl-DL-Ala-OH**		Fmoc-3-cyclopentyl-DL-alanine		500 mg
	> 98.0%	$C_{23}H_{25}NO_4$	M_r 379.46		
38473	**3-Cyclopentyl-DL-Ala-OH**				250 mg
	>98.0%	$C_8H_{15}NO_2$	M_r 157.21	[96539-87-6]	1 g
39327	**Boc-DL-Cha-OH**		Boc-3-cyclohexyl-DL-alanine		250 mg
	>98.0%	$C_{14}H_{25}NO_4$	M_r 271.36	[144186-13-0]	1 g
44056	**Fmoc-DL-Cha-OH**		Fmoc-3-cyclohexyl-DL-alanine		250 mg
	~98.0%	$C_{24}H_{27}NO_4$	M_r 393.48	[188632-07-7]	1 g
49665	**Boc-3-(4-quinolyl)-DL-Ala-OH**				500 mg
	~97.0%	$C_{17}H_{20}N_2O_4$	M_r 316.36		

Alanine Derivatives

25886	**3-(4-quinolyl)-DL-Ala-OH dihydrochloride dihydrate**				500 mg
	>98.0%	$C_{12}H_{12}N_2O_2 \cdot 2HCl.2H_2O$	M_r 325.19		
51236	**Boc-3-(3-quinolyl)-DL-Ala-OH**				1 g
	>97.0%	$C_{17}H_{20}N_2O_4$	M_r 316.36		
56918	**Boc-3-(2-quinolyl)-DL-Ala-OH**				250 mg
	~97.0%	$C_{17}H_{20}N_2O_4$	M_r 316.36		1 g
41984	**Fmoc-3-(2-quinolyl)-DL-Ala-OH**				250 mg
	~98.0%	$C_{27}H_{22}N_2O_4$	M_r 438.48		1 g
52949	**3-(2-quinolyl)-DL-Ala-OH**				250 mg
	>98.0%	$C_{12}H_{12}N_2O_2$	M_r 216.24	[123761-12-6]	1 g
69787	**Boc-3-(2-quinoxalyl)-DL-Ala-OH**				500 mg
	>98.0%	$C_{16}H_{19}N_3O_4$	M_r 317.34		

Phenylalanine Boronic Acids

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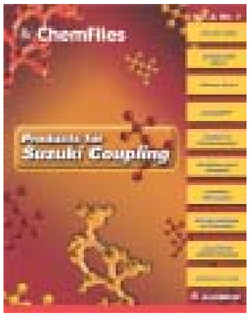

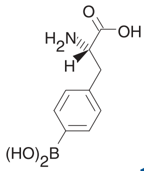

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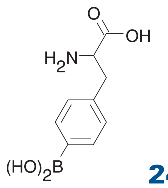

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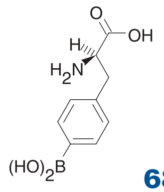

68047

17755	**4-Borono-L-phenylalanine**				250 mg
	~97%	$C_9H_{12}BNO_4$	M_r 209.01	[76410-58-7]	
68047	**4-Borono-D-phenylalanine**				250 mg
	>98.0%	$C_9H_{12}BNO_4$	M_r 209.01	[90580-64-6]	
24946	**4-Borono-DL-phenylalanine**				100 mg
	>97.0%	$C_9H_{12}BNO_4$	M_r 209.01	[90580-64-6]	500 mg

Proline and Pyroglutamine Derivatives

95471	**Boc-Thi-OH**	(-)-(*R*)-Boc-4-thiazolidinecarboxylic acid		(-)-Boc-L-thiaproline	1 g
	>99.0%	$C_9H_{15}NO_4S$	M_r 233.29	[51077-16-8]	5 g
94703	**Fmoc-Thi-OH**	(-)-(*R*)-Fmoc-4-thiazolidinecarboxylic acid		(-)-Fmoc-L-thiaproline	1 g
	>99.0%	$C_{19}H_{17}NO_4S$	M_r 355.41	[133054-21-4]	5 g
30763	**Boc-α-(diphenylmethyl)-DL-Pro-OH**				500 mg
	>90.0%	$C_{23}H_{27}NO_4$	M_r 381.47		
36748	**Boc-α-(1-naphthylmethyl)-DL-Pro-OH**				500 mg
	~98%	$C_{21}H_{25}NO_4$	M_r 355.43		

Please see the following page for structures

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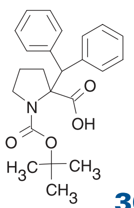
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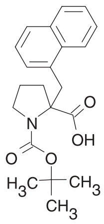
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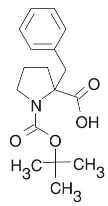
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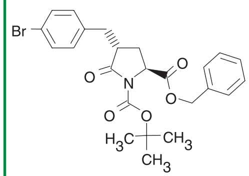
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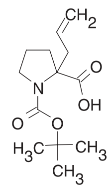
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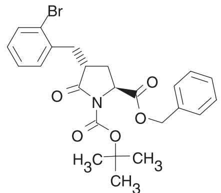
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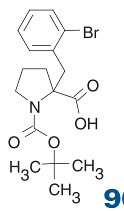
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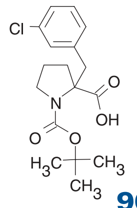
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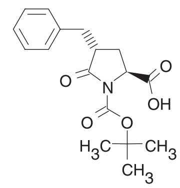
92392

68691	**Boc-α-Me-DL-Pro-OH** **~98%** **$C_{11}H_{19}NO_4$**	**M_r 229.28**	**[203869-80-1]**	**500 mg**
95566	**Boc-α-propyl-DL-Pro-OH** **>90.0%** **$C_{13}H_{23}NO_4$**	**M_r 257.33**		**500 mg**
58147	**Boc-α-allyl-DL-Pro-OH** **~98%** **$C_{13}H_{21}NO_4$**	**M_r 255.31**	**[315234-49-2]**	**500 mg**
52969	**Boc-α-benzyl-DL-Pro-OH** **~98%** **$C_{17}H_{23}NO_4$**	**M_r 305.37**		**500 mg**
74082	**Boc-α-(4-fluorobenzyl)-DL-Pro-OH** **~98%** **$C_{17}H_{22}FNO_4$**	**M_r 323.36**		**500 mg**
94866	**Boc-α-(4-bromobenzyl)-DL-Pro-OH** **~98%** **$C_{17}H_{22}BrNO_4$**	**M_r 384.27**		**500 mg**
76501	**Boc-α-(4-methylbenzyl)-DL-Pro-OH** **~98%** **$C_{18}H_{25}NO_4$**	**M_r 319.40**		**500 mg**
90682	**Boc-α-(2-bromobenzyl)-DL-Pro-OH** **~98%** **$C_{17}H_{22}BrNO_4$**	**M_r 384.27**		**500 mg**
90683	**Boc-α-(2-chlorobenzyl)-DL-Pro-OH** **~98%** **$C_{17}H_{22}ClNO_4$**	**M_r 339.82**		**500 mg**
90684	**Boc-α-(3-chlorobenzyl)-DL-Pro-OH** **~98%** **$C_{17}H_{22}ClNO_4$**	**M_r 339.82**		**500 mg**
92392	**(4*R*)-Boc-4-benzyl-Pyr-OH** **~97%** **$C_{17}H_{21}NO_5$**	**(4*R*)-Boc-4-benzyl-L-pyroglutamic acid** **M_r 319.36**		**500 mg**
51747	**(4*R*)-Boc-4-benzyl-Pyr-OBzl** **~98%** **$C_{24}H_{27}NO_5$**	**(4*R*)-Boc-4-benzyl-L-pyroglutamic acid benzyl ester** **M_r 409.48**	**[203645-44-7]**	**500 mg**
53371	**(4*R*)-Boc-4-(4-bromobenzyl)-Pyr-OBzl** **~98%** **$C_{24}H_{26}BrNO_5$**	**(4*R*)-Boc-4-(4-bromobenzyl)-L-pyroglutamic acid benzyl ester** **M_r 488.38**		**500 mg**
59703	**(4*R*)-Boc-4-(4-methylbenzyl)-Pyr-OBzl** **~98%** **$C_{25}H_{29}NO_5$**	**(4*R*)-Boc-4-(4-methylbenzyl)-L-pyroglutamic acid benzyl ester** **M_r 423.51**		**500 mg**
74624	**(4*R*)-Boc-4-(2-bromobenzyl)-Pyr-OBzl** **~98%** **$C_{24}H_{26}BrNO_5$**	**(4*R*)-Boc-4-(2-bromobenzyl)-L-pyroglutamic acid benzyl ester** **M_r 488.38**		**500 mg**

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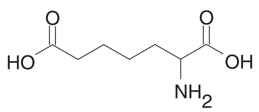
Other Amino Acid Building Blocks



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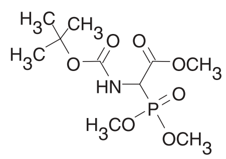

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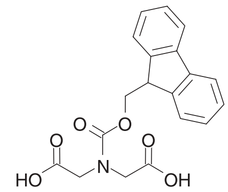

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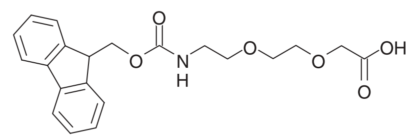

95003

09659	(±)-Boc-2-phosphonoglycine trimethyl ester				1 g
	>98.0%	$C_{10}H_{20}NO_7P$	M_r 297.24	[89524-98-1]	5 g
17856	N-Fmoc-iminodiacetic acid				1 g
	>99.0%	$C_{19}H_{17}NO_6$	M_r 355.35	[112918-82-8]	5 g
09256	(±)-2-Aminoheptanedioic acid			(±)-2-Aminopimelic acid	1 g
	>97.0%	$C_7H_{13}NO_4$	M_r 175.19	[627-76-9]	5 g
95003	{2-[2-(Fmoc-amino)ethoxy]ethoxy}acetic acid			8-(Fmoc-amino)-3,6-dioxaoctanoic acid	
	~97%	$C_{21}H_{23}NO_6$	M_r 385.41	[166108-71-0]	500 mg

Coupling Reagents

Fluka is a global supplier of the highest quality coupling reagents, available from research to large-scale quantities. We focus on a broad assortment of versatile peptide coupling reagents, carbodiimides and additives for achieving fast, efficient, selective and racemization-free amidation in a wide variety of solvent systems.

Carbodiimides

The most popular *in-situ* condensing agents are the carbodiimides.[1-3] The reaction of a carboxylic acid with a carbodiimide is believed to involve a labile O-acylisourea (see figure).

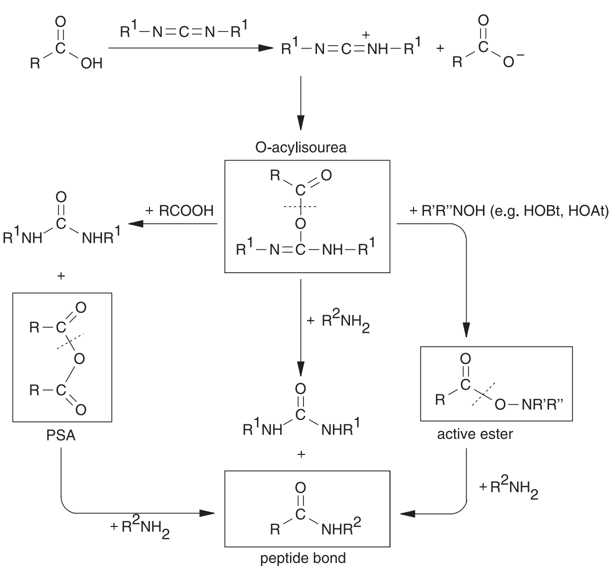

Figure: Mechanism of Peptide bond formation through carbodiimide activation

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N,N´-dicyclohexylcarbodiimide (DCC) is extensively used in Boc/Bzl-peptide synthesis, because the dicyclohexylurea (DCU) by-product is easily removed from the reaction vessel in presence of trifluoroacetic acid during the Boc-deprotection protocol. In the Fmoc/t-Bu chemistry, diisopropylcarbodiimide gives rise to a more DMF-soluble urea by-product and is therefore highly recommended.[4,5] N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (WSC, EDC) is widely used in solution phase, as it generates a urea by-product which can be easily removed from the reaction medium by extraction with water.[6,7]

Another important water-soluble carbodiimide is N-cyclohexyl-N'-(2-morpholinoethyl)carbodiimide-methyl-p-toluenesulfonate (CMC).[8,9] A major drawback of the cabodiimide procedure is the dehydration of side-chain carboxamides of Asn- and Gln-residues to the corresponding nitriles. This problem is completely avoided when using carbodiimides in combination with additives like hydroxylamine derivatives, such as 1-hydroxybenzotriazole (HOBt)[10] or 7-aza-1-hydroxybenzotriazole (HOAt).[11-13] These additives lead to an efficient suppression of racemization and total exclusion of dehydration of carboxamide residues while generating highly active ester species. Carbodiimide-mediated activation is achieved without base catalysis otherwise responsible for considerable rates of racemization in sensitive Fmoc-Cys(Trt)-OH residue.[14,15]

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Coupling Reagents-Product List

36650	N,N'-Dicyclohexylcarbodiimide (DCC)				100 g
	~99%	$C_{13}H_{22}N_2$	M_r 206.33	[538-75-0]	500 g
					2.5 kg
36651	N,N'-Dicyclohexylcarbodiimide solution, ~1 M in NMP				100 ml
36652	N,N'-Dicyclohexylcarbodiimide solution, ~1 M in dichloromethane				100 ml
38370	N,N'-Diisopropylcarbodiimide				25 ml
	>98.0%	$C_7H_{14}N_2$	M_r 126.20	[693-13-0]	100 ml
					500 ml
34640	N,N'-Di-tert-butylcarbodiimide				5 ml
	>99.0%	$C_9H_{18}N_2$	M_r 154.26	[691-24-7]	25 ml
03449	N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (WSC, EDC)				1 g
	>99.0%	$C_8H_{17}N_3$•HCl	M_r 191.70	[25952-53-8]	5 g
					25 g
39391	N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide (WSC, EDC)				10 ml
	>97.0%	$C_8H_{17}N_3$	M_r 155.24	[1892-57-5]	50 ml
29469	N-Cyclohexyl-N'-(2-morpholinoethyl)carbodiimide methyl-p-toluenesulfonate (CMC)				5 g
	>99.0%	$C_{14}H_{26}N_3O$•$C_7H_7O_3S$	M_r 423.58	[2491-17-0]	25 g
29470	N-Cyclohexyl-N'-(2-morpholinoethyl)carbodiimide methyl-p-toluenesulfonate (CMC)				5 g
	>97.0%				25 g

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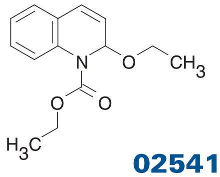

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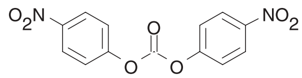

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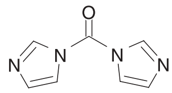

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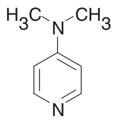

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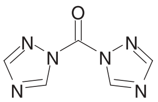

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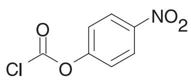

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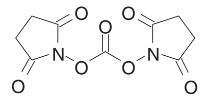
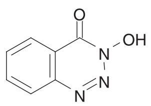


43720

02541	**2-Ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ)**				10 g
	>99.0%	$C_{14}H_{17}NO_3$	M_r 247.30	[16357-59-8]	50 g
21860	**1,1'-Carbonyldiimidazole (CDI)**				5 g
	~97%	$C_7H_6N_4O$	M_r 162.15	[530-62-1]	25 g
					100 g
21861	**1,1'-Carbonyldi(1,2,4-triazole) (CDT)**				5 g
	~95%	$C_5H_4N_6O$	M_r 164.13	[41864-22-6]	25 g
15118	**Bis(4-nitrophenyl) carbonate**				10 g
	>97.0%	$C_{13}H_8N_2O_7$	M_r 304.21	[5070-13-3]	50 g
23240	**4-Nitrophenyl chloroformate**				10 g
	>97.0%	$C_7H_4ClNO_4$	M_r 201.57	[7693-46-1]	50 g
					250 g
43720	**Di(N-succinimidyl) carbonate (DSC)**				5 g
	>97%	$C_9H_8N_2O_7$	M_r 256.17	[74124-79-1]	25 g
29224	**4-Dimethylaminopyridine (DMAP)**				10 g
	>99.0%	$C_7H_{10}N_2$	M_r 122.17	[1122-58-3]	50 g
					250 g
39405	**4-Dimethylaminopyridine (DMAP)**				10 g
	>98.0%				50 g
					250 g

54804	**1-Hydroxybenzotriazole hydrate (HOBt)**				100 g
	>99.0%	$C_6H_5N_3O \cdot aq$	M_r 135.13	[123333-53-9]	250 g
54802	**1-Hydroxybenzotriazole hydrate (HOBt)**				10 g
	>98.0%				50 g
					250 g
54810	**1-Hydroxybenzotriazole solution (HOBt)**			~1 M in NMP	100 ml
					500 ml
12815	**1-Hydroxybenzotriazole solution (HOBt), ≤ 0.1% water**			~0.2 M in DMSO/NMP	50 ml



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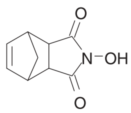

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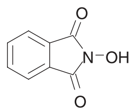

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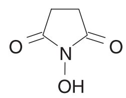

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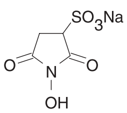

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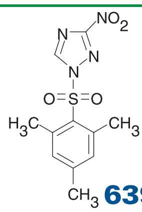

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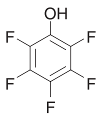

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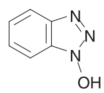

54802

37305	**3,4-Dihydro-3-hydroxy-4-oxo-1,2,3-benzotriazine (Dhbt)**				10 g
	>98.0%	$C_7H_5N_3O_2$	M_r 163.14	[28230-32-2]	50 g
					250 g
56480	**N-Hydroxysuccinimide (HOSu)**				25 g
	>97.0%	$C_4H_5NO_3$	M_r 115.09	[6066-82-6]	100 g
					1 kg
56485	**N-Hydroxysulfosuccinimide sodium salt (Sulfo-NHS)**				250 mg
	>98.5%	$C_4H_4NNaO_6S$	M_r 217.13	[106627-54-7]	1 g
					5 g
56191	**N-Hydroxyphthalimide**				100 g
	>98.0%	$C_8H_5NO_3$	M_r 163.13	[524-38-9]	500 g
56055	**N-Hydroxy-5-norbornene-2,3-dicarboxylic acid imide (HONB)**				10 g
	>98.0%	$C_9H_9NO_3$	M_r 179.18	[21715-90-2]	50 g
63941	**1-(2-Mesitylenesulfonyl)-3-nitro-1H-1,2,4-triazole (MSNT)**				1 g
	>98.0%	$C_{11}H_{12}N_4O_4S$	M_r 296.31	[74257-00-4]	5 g
76740	**2,3,4,5,6-Pentafluorophenol (Pfp-OH)**				5 g
	>99.0%	C_6HF_5O	M_r 184.07	[771-61-9]	25 g

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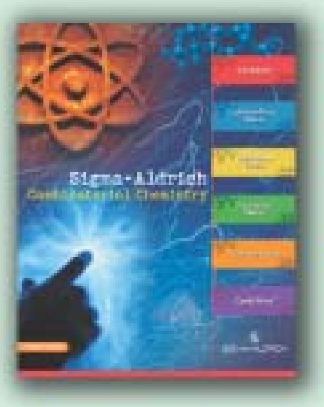

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Preloaded Resins Introduction

Fluka offers a comprehensive collection of high quality polystyrene and Tentagel® resins (which are composites of polyethylene oxide grafted to a low cross-linked polystyrene matrix) with Fmoc-amino acids derivatives, pre-attached to the most commonly used linker systems. These resins are used for the synthesis of free and protected peptide acids.

Gel-type polystyrene resins cross-linked with 1% DVB are ideally suited for batchwise peptide synthesis in the most commonly used solvents, e.g. DMF, DCM and NMP.[1, 2] The polymer beads show good swelling properties in these solvents, i.e. the polymer matrix contributes only to a small volume of the interior of each resin bead compared to the solvent. This allows for an unhindered, fast contact between the growing peptide chains and dissolved reagents, maximizing diffusion rates. Troublesome interactions of the growing peptide chains are successfully reduced.[3,4]

Among gel type supports, Tentagel® resins offer the following benefits:[5,6]

- *Equal distribution of functional groups and homogenicity of binding sites throughout a highly solvated and inert polymer network, ideal for the assembly of large molecules such as peptides*
- *Properties of the polymers are highly dominated by those of polyethylene oxide (hydrophilic as well as hydrophobic), which contributes 50-70 % (w:w) of the polymer*
- *Improved physico-chemical behaviour resulting in consistent and almost solvent-independent swelling properties*
- *Tentagels® are applicable in almost all solvent systems due to their solubility in a broad range of solvents*
- *The kinetic behaviour of reactive sites, located at the end of the spacer arms, corresponds with those in solution state*
- *Tentagel® resins allow the use of solid phase magic angle spinning MAS ^{1}H-NMR as well as gel-phase ^{13}C-NMR spectroscopic techniques for analysis of resin functionalities and resin-bound molecules. Easy and fast determination of functional groups can be accomplished by IR-spectroscopy, in particular by Fourier transform (FT) techniques on flattened beads*

ABBREVIATIONS:
DMF (dimethylformamide), DCM (dichloromethane), NMP (N-methylpyrrolidone), TFA (trifluoroacetic acid), HFIP (hexafluoroisopropanol), DVB (divinylbenzene), PS (polystyrene), Trt (trityl), TFE (trifluoroethanol)

The narrow size distribution of the 90 µm Tentagel® S beads together with their excellent pressure stability and the overall high diffusion rates make such resins ideally suited for both batch and continuous-flow peptide synthesis. TFA-labile Wang resin is the standard support for batch synthesis of peptide acids following Fmoc/tBu protection scheme.[7,8] The Fmoc-amino acids are coupled to the 4-hydroxymethyl phenoxyacetic acid linkers in such a way that epimerisation and dipeptide formation is minimized. The extraordinary mild cleavage conditions for highly acid-labile 2-chlorotrityl and 4-carboxytrityl resins enable the isolation of fully protected peptide fragments for convergent syntheses and selective side-chain derivatisations.[9-11] The large steric impediment of the trityl functionality effectively suppresses diketopiperazine (DKP) formation in the synthesis of prolyl peptides.[12] C-terminal Cys- and His-residues are introduced to trityl resins avoiding any racemization, thus resulting in enantiomeric pure products. As the amino acids attached to 2-chlorotrityl resin are N-terminal-free, these resins are ready for the coupling reactions without any deprotecting pre-treatments.

	Wang resin	2-chlorotrityl-resin 4-carboxytrityl-resin
Strategy	Fmoc	Fmoc
Cleavage	95 % TFA	1. HOAc/TFE /DCM (1:1:8; v:v:v) 2. HFIP/DCM (1:4; v:v) 3. 0,5 % TFA/DCM (v:v)
Target	Free peptide acids	Fully protected peptide acids

REFERENCES: [1] W. C. Chan and P. D. White (Eds), Fmoc Solid Phase Peptide Synthesis, A Practical Approach, Oxford University Press, New York, NY, 2000. [2] Meldal, M., in *Methods Enzymol.*, Vol. 289 *(Solid-Phase Peptide Synthesis)*, (G. B. Fields, ed.), Academic Press, San Diego **1997**, 83. [3] Sarin, V. K. et al., *J. Am. Chem. Soc.*, **1984**, *106*, 7845. [4] Pugh, K.C., *Int. J. Peptide Protein Res.*, **1992**, *40*, 208; [5] Bayer, E., *Angew. Chem.* **1991**, *103*, 117. [6] Rapp, W. et al., in *Peptides, Chemistry, Structure and Biology, Proc. 14th Am. Pept. Symp.,* (P. T. P. Kaumaia, R. S. Hodges, eds), Mayflower, England, **1996**, 313, 319, 321. [7] Wang, S. S., *J. Am. Chem. Soc.* **1973**, *95*, 1328. [8] Guy, C. A., Fields, G. B., in *Methods Enzymol.*, Vol. 289 *(Solid-Phase Peptide Synthesis)*, (G. B. Fields, ed.), Academic Press, San Diego **1997**, 29. [9] Barlos, K. et al., Int. *J. Pept. Protein Res.* **1991**, *37*, 513. [10] E. Bayer et al. in *Peptides, Chemistry, Structure and Biology, Proc. 13th Am. Pept. Symp.*, (R. S. Hodges, J. A. Smith, eds),ESCOM, Leiden **1994**, 156. [11] Bollhagen, R. et al., *J. Chem. Soc, Chem. Commun.*, **1994**, 2559. [12] G. Grübler et al. in *Innovations and Perspectives in Solid Phase Synthesis,3rd* International Symposium (R. Epton, ed.), Mayflower Worldwide, Birmingham **1994**, 517.

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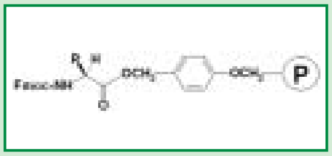
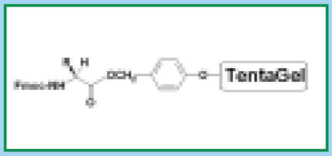
Wang Resin



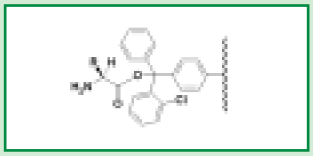
PS crosslinked with 1% DVB
100-200 mesh;
* 200-400 mesh
~0.4-0.8 mmol/g resin
packages: 1 g, 5 g

Tentagel® S PHB Resin



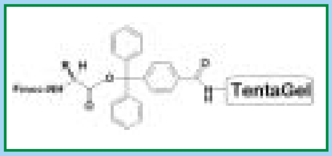
POE grafted to low crosslinked PS matrix ; particle size: 90 mm
~0.1-0.3 mmol/g resin
packages: 1 g, 5 g

2-chlorotrityl Resin



PS crosslinked with 1% DVB
100-200 mesh;
* 200-400 mesh
~0.6-1.2 mmol/g resin
packages: 1 g, 5 g

Tentagel® STrt Resin



POE grafted to low crosslinked PS matrix; particle size: 90 µm
~0.1-0.3 mmol/g resin
packages: 1 g, 5 g

	Wang Resin No	Wang Resin Residue	Tentagel® S PHB Resin No	Tentagel® S PHB Resin Residue	2-chlorotrityl Resin No	2-chlorotrityl Resin Residue	Tentagel® STrt Resin No	Tentagel® STrt Resin Residue
Ala	47644	Fmoc-Ala-	86367	Fmoc-Ala-	80929	H-Ala-	86408	Fmoc-Ala-
Arg	47362	Fmoc-Arg(Pbf)-	86381	Fmoc-Arg(Pbf)-	88619	H-Arg(Pbf)-	86442	Fmoc-Arg(Pbf)-
	47665	Fmoc-Arg(Pmc)-	86369	Fmoc-Arg(Pmc)-	72859	H-Arg(Pmc)-	86411	Fmoc-Arg(Pmc)-
Asn	47388	Fmoc-Asn(Trt)-	86378	Fmoc-Asn(Trt)-	94636	H-Asn(Trt)-	86412	Fmoc-Asn(Trt)-
Asp	47646*	Fmoc-Asp(OtBu)-	86379	Fmoc-Asp(OtBu)-	92368	H-Asp(OtBu)-	86413	Fmoc-Asp(OtBu)-
Cys	47613*	Fmoc-Cys(Acm)-	86383	Fmoc-Cys(Acm)-	94399	H-CysAcm)-	86414	Fmoc-Cys(Acm)-
			86384	Fmoc-Cys(tBu)-			86415	Fmoc-Cys(tBu)-
	47651*	Fmoc-Cys(StBu)-	86385	Fmoc-Cys(S-tBu)-			86416	Fmoc-Cys(S-tBu)-
	18606	Fmoc-Cys(Trt)-	86386	Fmoc-Cys(Trt)-	90254	H-Cys(Trt)-	86417	Fmoc-Cys(Trt)-
Gln	47402	Fmoc-Gln(Trt)-	86388	Fmoc-Gln(Trt)-	95256	H-Gln(Trt)-	86419	Fmoc-Gln(Trt)-
Glu	47658*	Fmoc-Glu(OtBu)-	86389	Fmoc-Glu(OtBu)-	82201	H-Glu(OtBu)-	86421	Fmoc-Glu(tBu)-
Gly	47659*	Fmoc-Gly-	86391	Fmoc-Gly-	92681	H-Gly-	86422	Fmoc-Gly-
His	42237	Fmoc-His(Trt)-	86392	Fmoc-His(Trt)-	93216	H-His(Trt)-	86423	Fmoc-His(Trt)-
Ile	47661*	Fmoc-Ile-	86393	Fmoc-Ile-	82914	H-Ile-	86424	Fmoc-Ile-
Leu	47662*	Fmoc-Leu-	86394	Fmoc-Leu-	82938	H-Leu-	86425	Fmoc-Leu-
Lys	47647*	Fmoc-Lys(Boc)-	86395	Fmoc-Lys(Boc)-	89861	H-Lys(Boc)-	86426	Fmoc-Lys(Boc)-
Met	47663*	Fmoc-Met-	86396	Fmoc-Met-	76215	H-Met-	86427	Fmoc-Met-
	47338	Fmoc-D-Met-						
Phe	47666*	Fmoc-Phe-	86399	Fmoc-Phe-	73771	H-Phe-	86431	Fmoc-Phe-
	47379	Fmoc-D-Phe-						
Pro	47667*	Fmoc-Pro-	86401	Fmoc-Pro-	94077	H-Pro-	86433	Fmoc-Pro-
Ser	47648*	Fmoc-Ser(tBu)-	86402	Fmoc-Ser(tBu)-	73571	H-Ser(tBu)-	86434	Fmoc-Ser(tBu)-
	47403	Fmoc-Ser(Trt)-						
Thr	47652*	Fmoc-Thr(tBu)-	86403	Fmoc-Thr(tBu)-	72574	H-Thr(tBu)-	86435	Fmoc-Thr(tBu)-
Trp	55606	Fmoc-Trp(Boc)-	86418	Fmoc-Trp(Boc)-	80539	H-Trp(Boc)-	86443	Fmoc-Trp(Boc)-
	47668*	Fmoc-Trp-	86404	Fmoc-Trp-	86436	Fmoc-Trp-	47404	Fmoc-D-Trp-
Tyr	47654*	Fmoc-Tyr(tBu)-	86405	Fmoc-Tyr(tBu)-	71025	H-Tyr(tBu)-	86437	Fmoc-Tyr(tBu)-
Val	47669*	Fmoc-Val-	86406	Fmoc-Val-	86557	H-Val-	86438	Fmoc-Val-
	47407	Fmoc-D-Val-						

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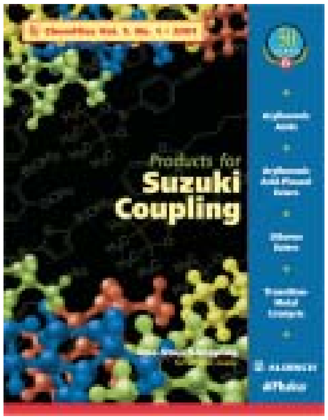

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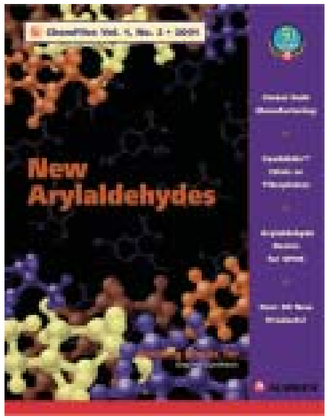

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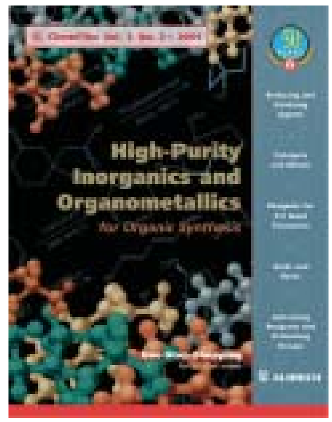

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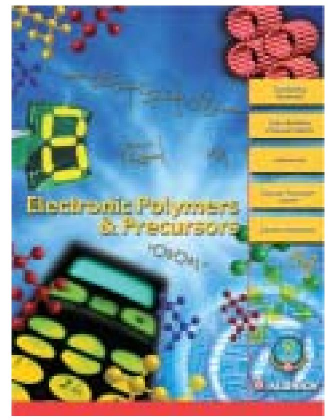

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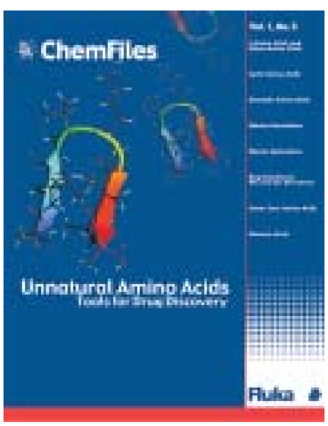

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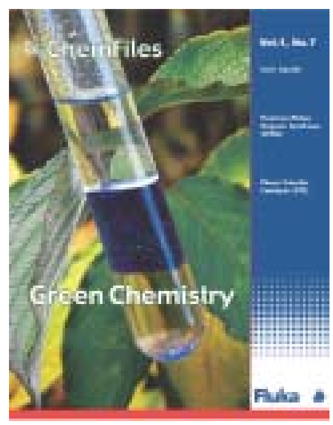

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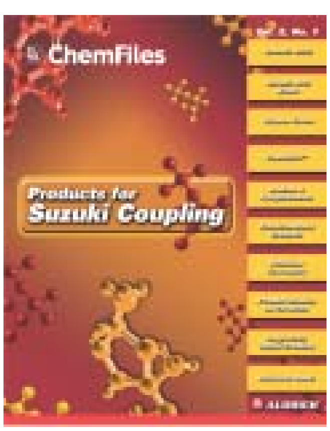
Green Chemistry



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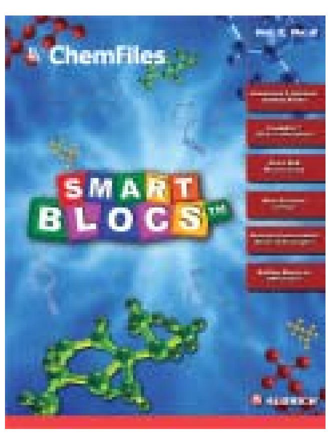

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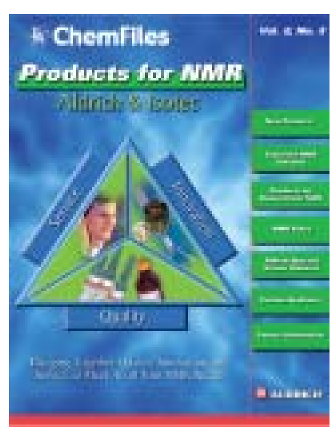

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