

Vol. 2, No. 1



ChemFiles

Boronic Acids

Boronic Acid Esters

Diboron Esters

CombiKits™

Prolines & Pyroglutamates

Transition-Metal Catalysts

Palladium Scavengers

FT-NMR Libraries on CD-ROMs

Large-Scale Suzuki Coupling

Reference Books

Products for Suzuki Coupling

 **ALDRICH®**

Suzuki Coupling Reagents

Essential Tools for Today's Synthetic Chemist

The synthesis of biaryl compounds by reaction of aryl halides with arylboronic acids, commonly referred to as the Suzuki coupling,¹ is an important area of growth. Of the wide variety of cross-coupling reactions, Suzuki coupling is the most general and widely used. Arylboronic acids are the favored reagents due to their stability, low toxicity, and limited side reactions. This brochure contains a comprehensive selection of boronic acids, boronic acid esters, diboron esters, and transition-metal catalysts useful for the Suzuki coupling reaction. New offerings are added monthly; if you don't see the material you need for your research, please call us at 1-800-231-8327 (USA) or your local office. Your new product suggestions, as always, are welcome and appreciated.

For additional technical information, please phone our Technical Services Department at 1-800-231-8327 (USA) or inquire via the Web at www.sigma-aldrich.com.

Boronic Acids

Aldrich is pleased to present its complete selection of boronic acids, the building blocks of the Suzuki coupling reaction. Most boronic acids readily undergo dehydration reactions to give a cyclic (trimer) anhydride. Our selection of boronic acids may contain varying amounts of this cyclic anhydride. Fortunately, the acid and the anhydride work equally well in the Suzuki coupling reactions; thus, the two forms are generally regarded as equivalent.

55,656-4
C₃H₈BBrO₂

New!



1g
5g

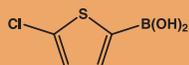
55,659-9
C₃H₆BClO₂

New!



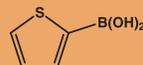
1g
5g

49,993-5
C₄H₄BClO₂S



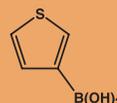
5g

43,683-6
C₄H₄BO₂S



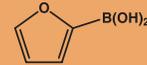
1g
5g

43,684-4
C₄H₄BO₂S



1g
5g

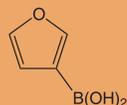
46,491-0
C₄H₄BO₃



1g
10g

51,216-8
C₄H₄BO₃

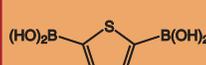
New!



1g

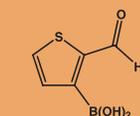
47,031-7
C₄H₄B₂O₄S

New!



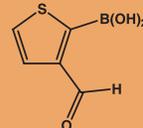
5g

49,990-0
C₅H₆BO₃S



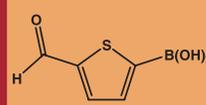
1g
5g

49,991-9
C₅H₆BO₃S



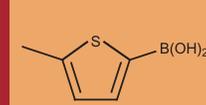
1g
5g

51,405-5
C₅H₆BO₃S



1g
5g

51,219-2
C₅H₇BO₂S



1g
5g

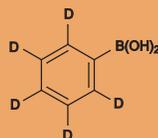
56,279-3
C₅H₁₀BClO₂

New!



1g
10g

51,786-0
C₆H₂BD₄O₂



1g

46,509-7
C₆H₂BF₄O₂



5g

52,409-3
C₆H₄BF₃O₂

New!



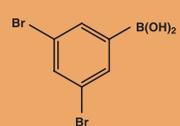
5g

52,410-7
C₆H₄BF₃O₂



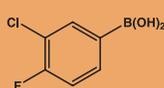
1g
5g

49,950-1
C₆H₃BBr₂O₂



1g
5g

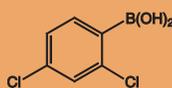
51,223-0
C₆H₅BClFO₂



5g

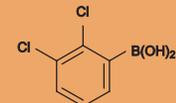
52,138-8
C₆H₅BCl₂O₂

New!



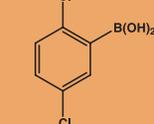
5g

51,404-7
C₆H₅BCl₂O₂



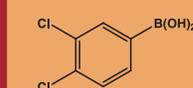
5g
25g

51,231-1
C₆H₅BCl₂O₂



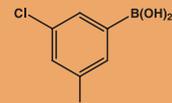
5g

47,191-7
C₆H₅BCl₂O₂



5g
25g

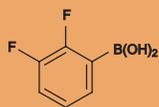
44,520-7
C₆H₅BCl₂O₂



5g
25g

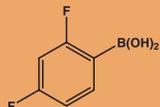
To order: contact your local Sigma-Aldrich office or call 1-800-558-9160 (USA) or visit our Web site at www.sigma-aldrich.com

51,403-9
C₆H₅BF₂O₂



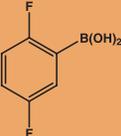
5g
25g

46,507-0
C₆H₅BF₂O₂



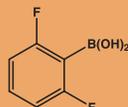
5g
25g

51,402-0
C₆H₅BF₂O₂



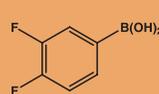
5g
25g

47,079-1
C₆H₅BF₂O₂



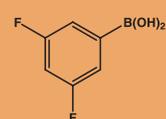
1g
10g

46,508-9
C₆H₅BF₂O₂



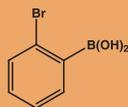
5g
25g

47,192-5
C₆H₅BF₂O₂



5g
25g

47,380-4
C₆H₆BBrO₂



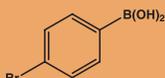
5g
25g

44,162-7
C₆H₆BBrO₂



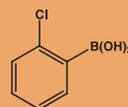
1g
5g

B7,595-6
C₆H₆BBrO₂



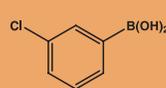
1g
5g

44,521-5
C₆H₆BClO₂



1g
5g

41,752-1
C₆H₆BClO₂



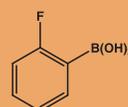
1g
10g

41,754-8
C₆H₆BClO₂



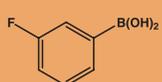
1g
10g
25g

44,522-3
C₆H₆BFO₂



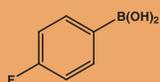
1g
10g

44,164-3
C₆H₆BFO₂



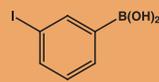
1g
10g

41,755-6
C₆H₆BFO₂



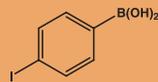
1g
5g

44,167-8
C₆H₆BIo₂



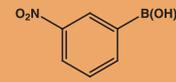
5g
25g

47,193-3
C₆H₆BIo₂



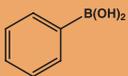
5g
25g

32,510-4
C₆H₆BNO₄



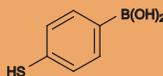
1g
5g

P2,000-9
C₆H₇BO₂



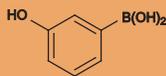
10g
50g

52,401-8
C₆H₇BO₂S



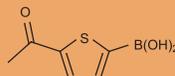
1g
5g

52,396-8
C₆H₇BO₃



1g
10g

49,992-7
C₆H₇BO₃S



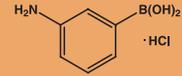
5g
25g

A7,175-1
C₆H₈BNiO₂



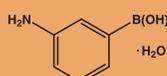
5g
25g

41,070-5
C₆H₉BCINO₂



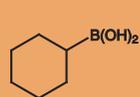
1g
5g

28,751-2
C₆H₁₀BNO₃



1g
5g

55,658-0
C₆H₁₃BO₂



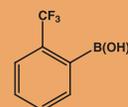
5g
10g

55,655-6
C₆H₁₃BO₂



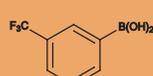
1g
5g

44,519-3
C₇H₆BF₃O₂



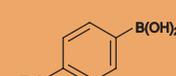
1g
10g

43,203-2
C₇H₆BF₃O₂



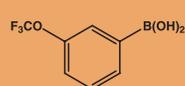
1g
5g

43,932-0
C₇H₆BF₃O₂



1g
5g

51,012-2
C₇H₆BF₃O₃



5g

51,013-0
C₇H₆BF₃O₃



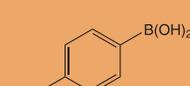
5g

51,301-6
C₇H₆BNO₂



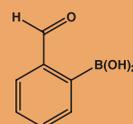
1g
5g

52,141-8
C₇H₆BNO₂



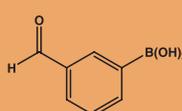
1g
10g

43,195-8
C₇H₇BO₃



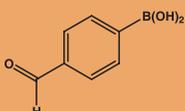
1g
5g

44,165-1
C₇H₇BO₃



1g
5g

43,196-6
C₇H₇BO₃



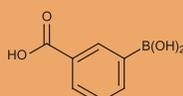
1g
5g

49,999-4
C₇H₇BO₄



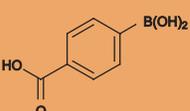
1g
5g

45,676-4
C₇H₇BO₄



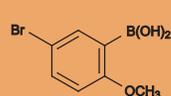
1g
10g

45,677-2
C₇H₇BO₄



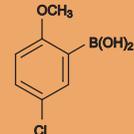
1g
10g

51,270-2
C₇H₈BBrO₃



5g

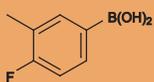
51,224-9
C₇H₈BClO₃



5g

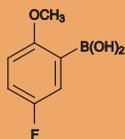
Ready to scale up? For larger quantities, please contact Sigma-Aldrich Fine Chemicals at 1-800-336-9719 (USA) or your local office

48,356-7
C₇H₈BF₂O₂



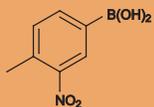
5g
25g

48,354-0
C₇H₈BF₃O₃



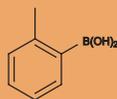
5g
25g

52,147-7
C₇H₈BNO₄



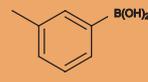
1g
5g

39,360-6
C₇H₈BO₂



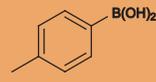
1g
5g

39,361-4
C₇H₈BO₂



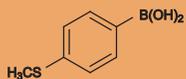
1g
5g

39,362-2
C₇H₈BO₂



1g
10g

45,680-2
C₇H₈BO₂S



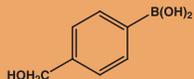
1g
5g

51,283-4
C₇H₈BO₃



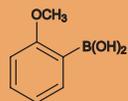
1g
10g

51,233-8
C₇H₈BO₃



1g
10g

44,523-1
C₇H₈BO₃



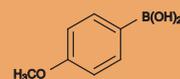
1g
5g

44,168-6
C₇H₈BO₃



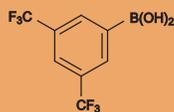
1g
10g

41,759-9
C₇H₈BO₃



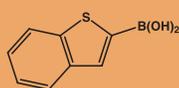
1g
5g

47,107-0
C₈H₅BF₂O₂



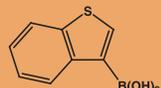
5g

49,997-8
C₈H₇BO₂S



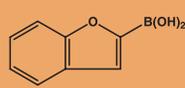
5g
25g

51,211-7
C₈H₇BO₂S



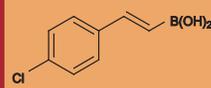
5g
25g

49,994-3
C₈H₇BO₃



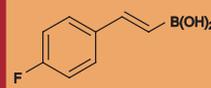
5g
25g

52,356-9
C₈H₈BClO₂



1g
10g

51,897-2
C₈H₈BF₂O₂



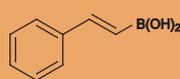
1g
10g

41,758-0
C₈H₈BO₂



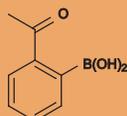
1g
5g

47,379-0
C₈H₈BO₂



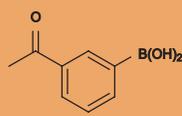
5g
25g

47,080-5
C₈H₈BO₃



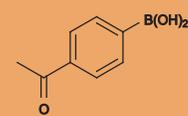
5g
25g

47,081-3
C₈H₈BO₃



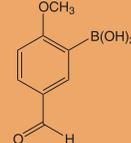
5g
25g

47,082-1
C₈H₈BO₃



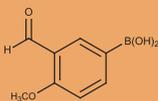
5g
25g

51,225-7
C₈H₈BO₄



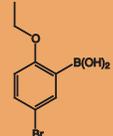
5g

51,286-9
C₈H₈BO₄



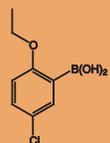
5g
25g

51,282-6
C₈H₁₀BBrO₃



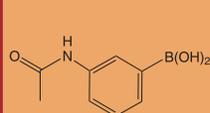
1g
5g

54,254-7
C₈H₁₀BClO₃



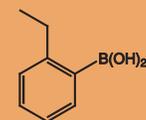
5g

56,601-2
C₈H₁₀BNO₃



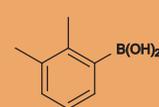
1g

52,152-3
C₈H₁₁BO₂



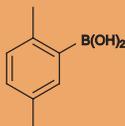
10g

48,350-8
C₈H₁₁BO₂



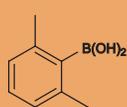
5g
25g

48,351-6
C₈H₁₁BO₂



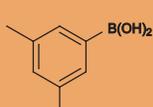
5g
25g

48,006-1
C₈H₁₁BO₂



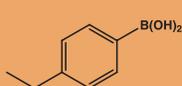
5g
25g

48,008-8
C₈H₁₁BO₂



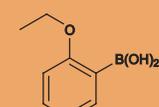
5g
25g

49,953-6
C₈H₁₁BO₂



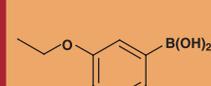
5g
25g

45,552-0
C₈H₁₁BO₃



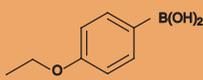
1g
10g

44,163-5
C₈H₁₁BO₃



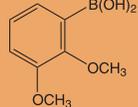
1g
5g

45,553-9
C₈H₁₁BO₃



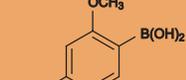
1g
10g

55,773-0
C₈H₁₁BO₄



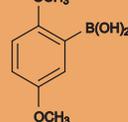
5g

48,348-6
C₈H₁₁BO₄



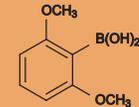
1g
10g

48,349-4
C₈H₁₁BO₄



5g
25g

48,009-6
C₈H₁₁BO₄



5g
25g

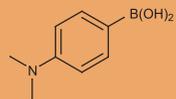
48,011-8
C₈H₁₁BO₄



5g
25g

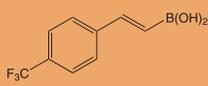
To order: contact your local Sigma-Aldrich office or call 1-800-558-9160 (USA)
or visit our Web site at www.sigma-aldrich.com

48,353-2
C₈H₁₂BNO₂



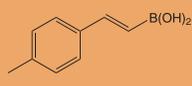
1g
5g

51,902-2
C₉H₈BF₃O₂



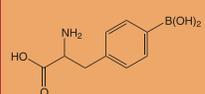
1g
5g

56,813-9
C₉H₁₁BO₂



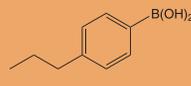
1g
5g

51,268-0
C₈H₁₂BNO₄



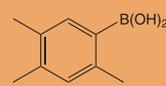
1g

52,150-7
C₉H₁₃BO₂



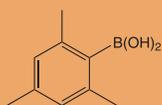
10g

54,232-6
C₉H₁₃BO₂



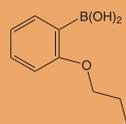
5g

54,231-8
C₉H₁₃BO₂



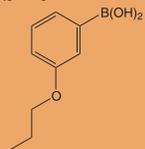
5g

55,772-2
C₉H₁₃BO₃



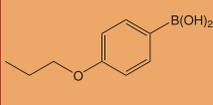
5g

55,771-4
C₉H₁₃BO₃



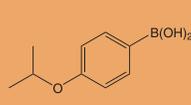
5g

55,770-6
C₉H₁₃BO₃



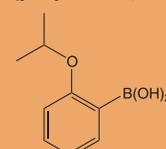
5g

54,247-4
C₉H₁₃BO₃



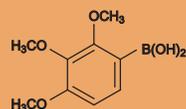
1g
10g

54,246-6
C₉H₁₃BO₃



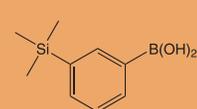
1g
10g

51,228-1
C₉H₁₃BO₅



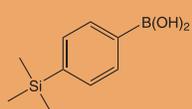
5g

52,366-6
C₉H₁₅BO₂Si



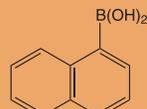
1g
5g

52,367-4
C₉H₁₅BO₂Si



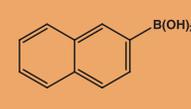
1g
5g

N25-7
C₁₀H₉BO₂



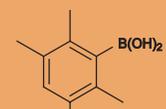
5g
25g

48,013-4
C₁₀H₉BO₂



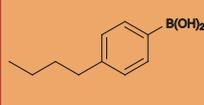
5g
25g

52,151-5
C₁₀H₁₅BO₂



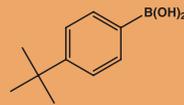
5g
25g

52,149-3
C₁₀H₁₅BO₂



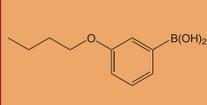
1g
5g

48,005-3
C₁₀H₁₅BO₂



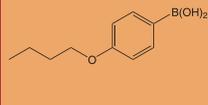
5g
25g

54,249-0
C₁₀H₁₅BO₃



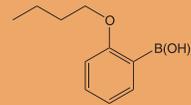
1g
10g

54,250-4
C₁₀H₁₅BO₃



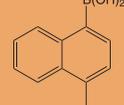
1g
10g

54,248-2
C₁₀H₁₅BO₃



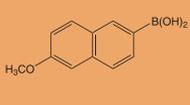
1g
10g

52,145-0
C₁₁H₁₁BO₂



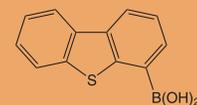
10g

52,189-2
C₁₁H₁₁BO₃



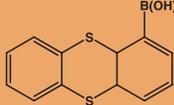
5g

49,998-6
C₁₂H₉BO₂S



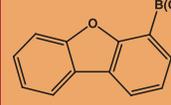
1g
5g

51,221-4
C₁₂H₉BO₂S₂



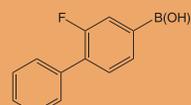
5g

49,995-1
C₁₂H₉BO₃



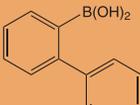
5g

51,210-9
C₁₂H₁₀BFO₂



5g

54,220-2
C₁₂H₁₁BO₂



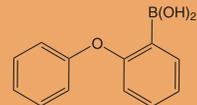
5g

48,345-1
C₁₂H₁₁BO₂



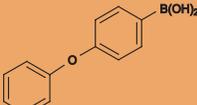
5g
25g

52,148-5
C₁₂H₁₁BO₃



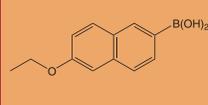
10g

48,014-2
C₁₂H₁₁BO₃



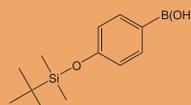
5g
25g

52,190-6
C₁₂H₁₃BO₃



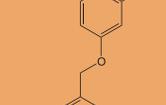
5g

52,404-2
C₁₂H₂₁BO₃Si



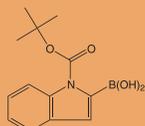
1g
5g

52,633-9
C₁₃H₁₃BO₃



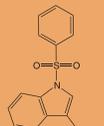
5g
25g

56,233-5
C₁₃H₁₆BNO₄



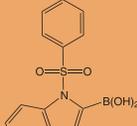
1g

56,387-0
C₁₄H₁₂BNO₄S



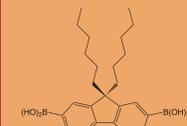
1g

56,386-2
C₁₄H₁₂BNO₄S



1g

56,633-0
C₂₅H₃₆B₂O₄



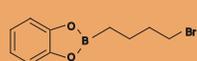
1g
5g

Ready to scale up? For larger quantities, please contact Sigma-Aldrich Fine Chemicals at 1-800-336-9719 (USA) or your local office

Boronic Acid Esters

The synthesis of biaryl compounds via the Suzuki coupling reaction has become more commonplace now that many arylboronic acids are readily available. Several years ago, Miyaura et al. demonstrated the utility of cyclic pinacol esters of arylboronic acids in Suzuki coupling reactions.^{2,3} Aldrich is pleased to offer the following arylboronic acid pinacol esters as part of a growing line of reagents used in the Suzuki coupling reaction.

51,368-7
C₁₀H₁₂BBrO₂



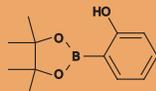
50g

56,814-7
C₁₀H₂₁BO₂



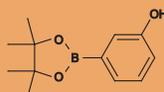
1g
5g

52,255-4
C₁₂H₁₇BO₃



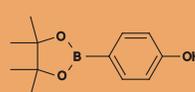
1g
5g

52,256-2
C₁₂H₁₇BO₃



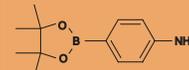
1g
5g

52,257-0
C₁₂H₁₇BO₃



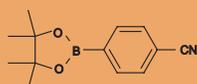
1g
5g

51,875-1
C₁₂H₁₈BNO₂



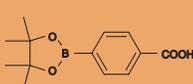
1g
5g

52,755-6
C₁₃H₁₆BNO₂



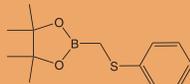
1g
5g

51,349-0
C₁₃H₁₇BO₄



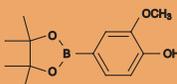
5g

56,815-5
C₁₃H₁₉BO₂S



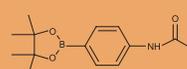
1g
5g

51,878-6
C₁₃H₁₉BO₄



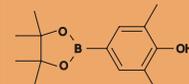
1g
5g

51,877-8
C₁₄H₂₀BNO₃



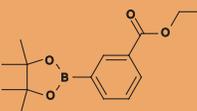
1g
5g

51,879-4
C₁₄H₂₁BO₃



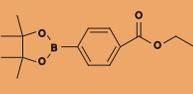
1g
5g

52,754-8
C₁₅H₂₁BO₄



1g
5g

52,756-4
C₁₅H₂₁BO₄



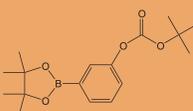
1g
5g

54,062-5
C₁₅H₂₇BO₄



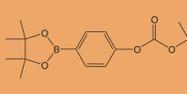
1g

56,582-2
C₁₇H₂₅BO₅



1g
5g

56,594-6
C₁₇H₂₅BO₅



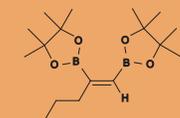
1g
5g

56,235-1
C₁₇H₂₈BNO₄



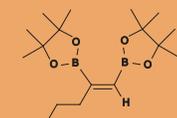
1g
5g

52,990-7
C₁₇H₃₂B₂O₄



1g
5g

52,760-2
C₁₈H₃₄B₂O₄



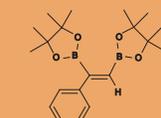
1g
5g

52,989-3
C₁₉H₃₆B₂O₄



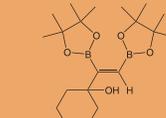
1g
5g

52,757-2
C₂₀H₃₀B₂O₄



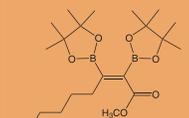
1g
5g

52,761-0
C₂₀H₃₆B₂O₅



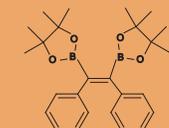
1g
5g

52,759-9
C₂₁H₃₈B₂O₆



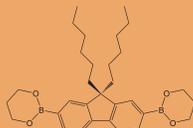
1g
5g

52,758-0
C₂₆H₃₄B₂O₄



1g
5g

56,668-3
C₃₁H₄₄B₂O₄



1g
5g

References

- (1) Miyaura, N. et al. *Synth. Commun.* **1981**, *11*, 513.
- (2) Ishiyama, T. et al. *Tetrahedron Lett.* **1997**, *38*, 3447.
- (3) Ishiyama, T. et al. *J. Org. Chem.* **1995**, *60*, 7508.
- (4) Pietrre, S.R.; Baltzer, S. *Tetrahedron Lett.* **1997**, *38*, 1197.
- (5) Brown, S.D.; Armstrong, R.W. *J. Am. Chem. Soc.* **1996**, *118*, 6331.
- (6) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147.
- (7) Stanforth, S. *Tetrahedron* **1998**, *54*, 263.
- (8) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

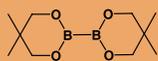
To order: contact your local Sigma-Aldrich office or call 1-800-558-9160 (USA)
or visit our Web site at www.sigma-aldrich.com

Diboron Esters

The following diboron esters are versatile reagents that couple with organic triflates² and halides³ to give the corresponding boronic esters, which are readily converted to arylboronic acids. This route and the subsequent Suzuki coupling reaction can be run under mild conditions, thus permitting the use of cyano-, ester-, carbonyl-, and nitro-substituted aryl rings. The wide variety of arylboronic acids available via these diboron esters also makes this class of compounds suitable for solid-phase combinatorial studies.^{4,5}

51,880-8

$C_{10}H_{20}B_2O_4$



1g
5g

47,328-6

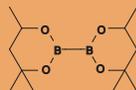
$C_{12}H_8B_2O_4$



1g
5g

52,568-5

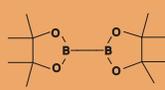
$C_{12}H_{24}B_2O_4$



1g
5g

47,329-4

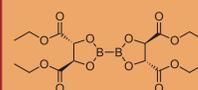
$C_{12}H_{24}B_2O_4$



1g
5g

52,716-5

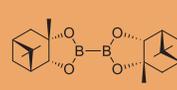
$C_{16}H_{24}B_2O_{12}$



1g
5g

52,714-9

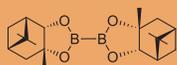
$C_{20}H_{32}B_2O_4$



1g
5g

52,713-0

$C_{20}H_{32}B_2O_4$



1g
5g

For references see Boronic Acid Esters section.



CombiKits™ is a trademark of Sigma-Aldrich Co.

For more information on this unique service, please call us at 800-333-7306 (USA) or e-mail us at bwandler@sial.com. In Europe, e-mail us at smarsden@eurnotes.sial.com.

Aldrich Offers CombiKits™

The emerging importance of combinatorial and high-throughput methods in chemistry has resulted in a need for specialized kits of chemicals. We are able to provide a variety of these kits by combining Aldrich's vast chemical inventory and our customized weighing process. Some of our more popular kits have included carboxylic acids, arylboronic acids, amines, and alcohols; we are now pleased to add isocyanates to this list.

Key Features Include:

Flexibility

- ❖ Ideal for high-throughput or combinatorial chemistry; available in vials or titerplates

No Minimum Order

- ❖ Service as diverse as your needs

Reduces Waste

- ❖ Little or no unused product to store or dispose

Saves Time

- ❖ Less time weighing reagents, more time doing research

NOW AVAILABLE: Easy-to-Order, Ready-to-Use, Preselected CombiKits™

R75,012-3 CombiKits™ - Boronic Acids/Boron Pinacol Esters for combinatorial chemistry - 1 mmol	1 kit
R75,015-8 CombiKits™ - Boronic Acids/Boron Pinacol Esters for combinatorial chemistry - 5 mmol	1 kit
R75,011-5 CombiKits™ - Isocyanates for combinatorial chemistry - 1 mmol	1 kit
R75,013-1 CombiKits™ - Isocyanates for combinatorial chemistry - 5 mmol	1 kit

We can create a kit tailored to your specific requirements.

Ready to scale up? For larger quantities, please contact Sigma-Aldrich Fine Chemicals at 1-800-336-9719 (USA) or your local office



AKIRA SUZUKI

Professor of Chemistry

Kurashiki University of Science and the Arts

Organic Syntheses via Boranes

Volume 3: Suzuki Coupling
Akira Suzuki & Herbert C. Brown



251,430-6

Available April 2002

Call to place your advance order now!

Also available

Organic Syntheses via Boranes Vol. 1 Z40,094-7
Herbert C. Brown

Organic Syntheses via Boranes Vol. 2: Recent Developments
Herbert C. Brown, Marek Zaidlewicz Z40,095-5

To order: contact your local sigma-aldrich office or call
1-800-558-9160 (USA) or visit our Web site at www.sigma-aldrich.com

Professor Akira Suzuki received his Ph.D. degree (1959) from Hokkaido University, Sapporo, Japan, where he later became a professor in the Department of Applied Chemistry (1973–94). In 1963–65, Dr. Suzuki worked as a postdoctoral associate in Professor Herbert C. Brown's research group investigating the stereochemistry of the hydroboration reaction. He was a visiting professor at several universities, including the University of Wales in 1988 and Purdue University in 2001. After his retirement from Hokkaido University in 1994, Professor Suzuki became a professor of chemistry at Okayama University of Science and was later appointed Professor at Kurashiki University of Science and the Arts in 1995. He has received numerous awards, including: Testimonial from the Korean Chemical Society (1987), the Chemical Society of Japan Award (1989), the H. C. Brown Lecturer Award (Purdue University, 2000), the 2001 Distinguished Lecturer Award (Queen's University, Canada, and Pfizer), and was made an Honorary Member of the Argentine Organic Chemistry Society in 2001.

Professor Suzuki's contributions to organoborane chemistry involve the discovery and development of new synthetic methodologies using organoboron compounds. The formation of organic radicals from organoboranes in the presence of catalytic amounts of oxygen was first discovered in the course of cooperative work with Professor Brown's research group. Professor Suzuki was also instrumental in the utilization of organoboron compounds as carbanions in synthesis. Organoboranes are also useful as a source of carbocations under electrochemical conditions, although a limited number of examples have been reported. More recent work by Suzuki and coworkers revolves around palladium catalyzed cross-coupling reactions of various organoboron compounds with a number of organic electrophiles in the presence of bases. This reaction has become known as the Suzuki Coupling and is the focus of this book.

Cyclic Aryl-Substituted Amino Acid Derivatives

Aryl α -substituted proline analogs and γ -substituted pyrrolidines are valuable building blocks in both medicinal and peptide chemistry. Through Suzuki coupling technology, they can be used as starting materials in the conversion of aryl bromides into biaryl compounds. These products have also found uses in peptide chemistry for the introduction of diversity and structural constraints in peptidomimetics.

58147	Boc- α -allyl-DL-proline	500mg	95566	Boc- α -propyl-DL-proline	500mg
52969	Boc- α -benzyl-DL-proline	500mg	92392	(4R)-Boc-4-benzyl-L-pyrrolidinic acid	500mg
90682	Boc- α -(2-bromobenzyl)-DL-proline	500mg	51747	(4R)-Boc-4-benzyl-L-pyrrolidinic acid benzyl ester	500mg
94866	Boc- α -(4-bromobenzyl)-DL-proline	500mg	74624	(4R)-Boc-4-(2-bromobenzyl)-L-pyrrolidinic acid benzyl ester	500mg
90683	Boc- α -(2-chlorobenzyl)-DL-proline	500mg	53371	(4R)-Boc-4-(4-bromobenzyl)-L-pyrrolidinic acid benzyl ester	500mg
90684	Boc- α -(3-chlorobenzyl)-DL-proline	500mg	59703	(4R)-Boc-4-(4-methylbenzyl)-L-pyrrolidinic acid benzyl ester	500mg
30763	Boc- α -(diphenylmethyl)-DL-proline	500mg			
74082	Boc- α -(4-fluorobenzyl)-DL-proline	500mg			
68691	Boc- α -methyl-DL-proline	500mg			
76501	Boc- α -(4-methylbenzyl)-DL-proline	500mg			
36748	Boc- α -(1-naphthylmethyl)-DL-proline	500mg			

To order: contact your local Sigma-Aldrich office or call 1-800-558-9160 (USA)
or visit our Web site at www.sigma-aldrich.com

Transition-Metal Catalysts

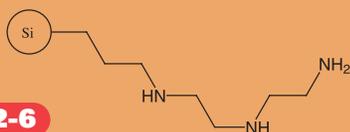
A variety of transition-metal catalysts for the Suzuki coupling reaction are available from Aldrich. The majority of these catalysts are palladium- and nickel-based, typically utilizing phosphine-derived ligands.⁶⁻⁸

47,055-4	[1,1'-Bis(diphenylphosphino)ferrocene]dichloronickel(II), 97%	1g
37,967-0	[1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II), complex with CH ₂ Cl ₂	1g; 5g
40,323-7	Dichlorobis(tricyclohexylphosphine)palladium(II), 95%	1g
45,304-8	Dichlorobis(tri- <i>o</i> -tolylphosphine)palladium(II), 97%	1g; 5g
20,867-1	Dichlorobis(triphenylphosphine)palladium(II), 98%	1g; 5g; 25g
41,274-0	Dichlorobis(triphenylphosphine)palladium(II), 99.99%	250mg; 1g
20,586-9	Palladium(II) acetate, 98%	1g; 2g; 10g
37,987-5	Palladium(II) acetate, 99.98%	1g; 5g
21,666-6	Tetrakis(triphenylphosphine)palladium(0), 99%	1g; 5g; 25g
32,877-4	Tris(dibenzylideneacetone)dipalladium(0)	500mg; 5g; 50g
36,631-5	Tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct	250mg; 1g

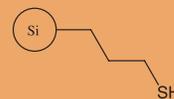
For references see *Boronic Acid Esters* section.

Palladium Scavengers

Scavenger resins have been commercially available for several years. Most of these scavengers have been used to sequester organic functionalities from solution in order to ease the purification process upon completion of the synthesis. Now, Aldrich is introducing a new class of quenching reagents: **palladium scavengers on silica gel**.

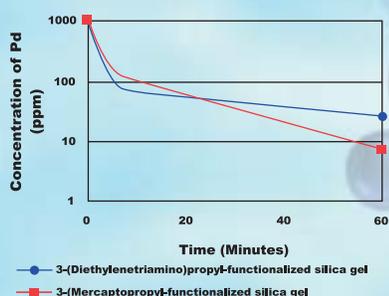


3-(Diethylenetriamino)propyl-functionalized silica gel
5g 25g 100g



3-Mercaptopropyl-functionalized silica gel
5g 25g 100g

Scavenging of Palladium



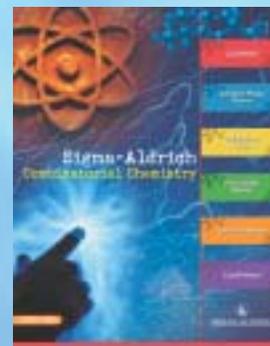
Conditions:

In separate flasks, two solutions of Pd(OAc)₂ (1000 ppm Pd) were prepared in THF. While stirring at room temperature, four equivalents of each of the silica-based scavengers were added to their respective flasks. As illustrated in the graph, the palladium was successfully scavenged from the solution within minutes. Simple filtration of the bound palladium allows for its recovery.

For the advantages of functionalized silica gels over polystyrene supports, please visit our Web site at www.sigma-aldrich.com/combichem and click on Solution-Phase Resins.

For questions regarding these scavengers or other resins, please contact the product manager at 414-298-6330, or via e-mail at mmcnello@sial.com.

If you would like more information regarding supported reagents, request your 2001-2002 Sigma-Aldrich Combinatorial Chemistry catalog today. This catalog features everything you need for polymer-assisted organic synthesis, parallel synthesis, and high-throughput screening. This catalog is also available via our Web site at www.sigma-aldrich.com/combichem.



Larger quantities are available from SiliCycle, Inc.

Ready to scale up? For larger quantities, please contact Sigma-Aldrich Fine Chemicals at 1-800-336-9719 (USA) or your local office

Introducing...

NEW Electronic FT-NMR Libraries from Aldrich!

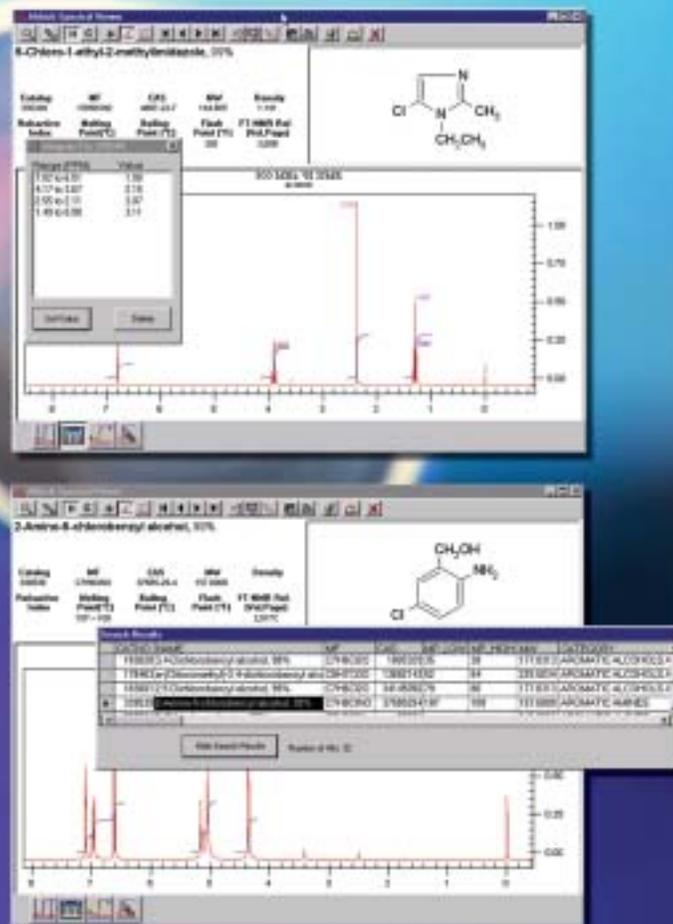
The Aldrich FT-NMR Library with Spectral Viewer on CD-ROM is an electronic book that contains high-resolution 300MHz ^1H and 75MHz ^{13}C spectra for the more than 11,800 compounds found in the printed version of *The Aldrich Library of ^{13}C and ^1H FT-NMR Spectra*. A supplemental library is also available that includes spectra for 3,500 additional compounds not included in the original printed version. Order both the standard and the supplemental library for access to spectra on over 15,000 compounds.

Features:

- Displays ^1H and ^{13}C spectra, integral, chemical structure, and technical data
- Text Searching by Chemical Name, Aldrich Catalog Number, CAS Number, and Molecular Formula
- Advanced data field searching on Chemical Category and physical properties such as Boiling Point, Melting Point, Density, Flash Point, Molecular Weight, and Refractive Index
- Spectra processing using Zoom, Peak Integration, and Peak Labeling
- Print spectra, structure, technical data, integral table and peak listing
- Export spectra to a file (Bitmap, Metafile, or JPEG formats) or to the clipboard (Bitmap or Metafile formats)
- Web link button provides additional technical data from the Sigma-Aldrich Website

Ideal for:

- ✓ Teaching students NMR spectral interpretation
- ✓ Referencing spectra for comparison studies and the identification of unknown compounds
- ✓ Exporting spectra quickly for presentations and papers



Minimum system requirements: Pentium® 200MHz, Windows® 95/98/ME/NT4-SP5/2000, CD-ROM drive, 600MB hard disk space, 64MB RAM. (PC ONLY)

Version	Standard Library (11,800 compounds) Cat. No.	Supplemental Library (3,500 compounds) Cat. No.
Single user, commercial	Z54,126-5	Z53,808-6
Single user, academic	Z54,138-9	Z53,818-3
Network version (1-10 users)	Z54,149-4	Z53,797-7
Demo program	Z54,159-1	—

Aldrich is a registered trademark of Sigma-Aldrich Co. Chemical Abstracts is a registered trademark of the American Chemical Society. Pentium is a registered trademark of Intel Corp. Windows is a registered trademark of Microsoft Corp.

SPECIAL OFFER—Receive a FREE supplemental library if you buy and register the standard product before 10/31/2002!

To order: contact your local Sigma-Aldrich office or call 1-800-558-9160 (USA) or visit our Web site at www.sigma-aldrich.com

Suzuki Coupling in Large Scale at Sigma-Aldrich Fine Chemicals

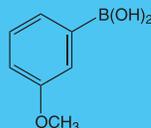
Suzuki coupling is rapidly moving from the laboratory to process R&D and large-scale manufacturing. Sigma-Aldrich Fine Chemicals is poised to meet that increasing demand:

- Active process development program to manufacture many of our 200+ boronic acids and coupling catalysts in large scale
- Capacity and expertise in low-temperature, air-sensitive chemistry, and cross-coupling syntheses up to multi-ton scale at our Sheboygan, WI plant
- Experience in custom synthesis

Examples of products available for large-scale Suzuki coupling:



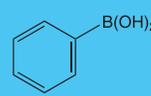
52,396-8 [87199-18-6]
3-Hydroxyphenylboronic acid
500kg to MT MDL# 1074603



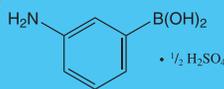
44,168-6 [10365-98-7]
3-Methoxyphenylboronic acid
250-500kg MDL# 161359



41,759-9 [5720-07-0]
4-Methoxyphenylboronic acid
250-500kg MDL# 39139



P2000-9 [98-80-6]
Phenylboronic acid, 97%
250kg MDL# 2013



A7,175-1 [66472-86-4]
3-Aminophenylboronic acid hemisulfate
50-100kg MDL# 13111



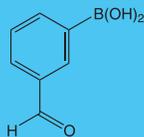
45,680-2 [98546-51-1]
4-(Methylthio)phenylboronic acid
25-50kg MDL# 93410



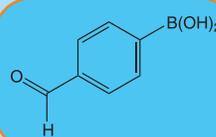
48,013-4 [32316-92-0]
2-Naphthaleneboronic acid
25-50kg MDL# 236051



41,754-8 [1679-18-1]
4-Chlorophenylboronic acid
25-50kg MDL# 39137



44,165-1 [87199-16-4]
3-Formylphenylboronic acid
25kg MDL# 161356



43,196-6 [87199-17-5]
4-Formylphenylboronic acid
25kg MDL# 151823

$\text{Pd}_2(\text{dba})_3$

32,877-4 [52409-22-0]
Tris(dibenzylideneacetone)dipalladium(0)
kg quantities MDL# 13310

$\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$

21,666-6 [14221-01-3]
Tetrakis(triphenylphosphine)Pd(0)
kg quantities MDL# 10012

To obtain a quote or discuss your custom project, please call or visit us at www.sigma-aldrich.com/safc

France
tel. 33 4 74 82 28 82
fax 33 4 74 82 28 90

Germany
tel. 49 89 6513 1900
fax 49 89 6513 1919

Italy
tel. 3902 33 41 7350
fax 3902 33 41 7201

Japan
tel. 81 3 5821 3171
fax 81 3 5614 6279

Switzerland
tel. 41 81 755 2732
fax 41 81 755 2770

U.K.
tel. 44 1202 712222
fax 44 1202 740171

USA
tel. 314 534 4900
fax 314 652 0000


SIGMA-ALDRICH
FINE CHEMICALS

Tell Us About Yourself

Name _____
Organization _____
Department _____ Mail Stop _____
Address _____ Bldg/Rm # _____
City _____ State _____ Country _____ Postal Code _____
Phone _____ Fax _____
E-mail _____

Place Printed Label Here

1. Where do you currently purchase your products for Suzuki Coupling?

Aldrich [1AA] Other _____

2. Please check any of the following FREE catalog and literature pieces that you would like to receive.

- | | |
|---|---|
| <input type="checkbox"/> Aldrich Catalog/Handbook [002] | <input type="checkbox"/> Aldrichimica Acta [014] |
| <input type="checkbox"/> Polymer Products CD - Catalog & Reference Guide [DGQ] | <input type="checkbox"/> Dyes, Indicators & Intermediates [051] |
| <input type="checkbox"/> Combinatorial Chemistry [EDZ] | <input type="checkbox"/> Fluka/Riedel-de-Haën® Catalog [003] |
| <input type="checkbox"/> High-Purity Inorganics & Organometallics for Organic Synthesis [DVV] | <input type="checkbox"/> CombiKits™/Small Sample Service [CBJ] |
| <input type="checkbox"/> Arylaldehydes [DUG] | <input type="checkbox"/> Products for NMR [DTW] |
| <input type="checkbox"/> Fluka Peptide and Peptidomimetic Synthesis Reagents | <input type="checkbox"/> Solvents for Scientific Research [BAO] |
| | <input type="checkbox"/> Aldrich Glassware [044] |

3. Would you like to receive a FREE CD-ROM with product listings from the Sigma-Aldrich Library of Rare Chemicals?

Yes [DDH] No

Combikits and eBookshelf are trademarks of Sigma-Aldrich Co.

BU9

Reference Books

New!

Handbook of Organopalladium Chemistry for Organic Synthesis

Ei-ichi Negishi, John Wiley & Sons, New York, NY, 2002, 1,392pp. Hardcover.
This handbook is the most comprehensive and authoritative reference available on organopalladium reagents and catalysts. The material is organized according to reaction type, rather than type of organopalladium compound.

Z51,386-5

Organoboranes for Syntheses

P.V. Ramachandran and H.C. Brown, Eds., Oxford University Press, New York, NY, 2001, 264pp. Hardcover.

This book examines the recent advances in the art of organic synthesis via organoboranes. The volume includes a wide range of topics in asymmetric synthesis, such as reduction, aldol reaction, allylboration, homologation, and cyclopropanation. Additional subjects include Suzuki coupling, amino acid synthesis, fluoro-organic synthesis, boron catalysts for stereoselective transformations, heterocyclic synthesis, and novel borohydride reagents.

Z51,374-1

Contemporary Boron Chemistry

M. Davidson et al., Eds., The Royal Society of Chemistry, Cambridge, UK, 2000, 538pp. Hardcover.

Covers boron chemistry with applications in polyolefin catalysis; medicine; materials and polymers; boron cluster chemistry, including carboranes and metal-containing clusters; organic and inorganic chemistry of species containing 1 or 2 boron atoms; and theoretical studies of boron-containing compounds. New materials with novel optical and electronic properties are also discussed.

Z52,633-9

Handbook of Palladium-Catalyzed Organic Reactions

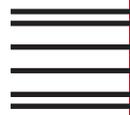
J.-L. Malleron, J.-C. Fiaud, and J.-Y. Legros, Academic Press, San Diego, CA, 1997, 304pp. Comb-bound.

Detailed descriptions of the main types of reactions that are catalyzed by palladium. Includes the catalytic cycles and mechanisms for each class of reactions.

Book Z28,778-4

CD-ROM Z28,779-2

For a complete list of titles available from Sigma-Aldrich, please visit our eBookShelf™ at: www.sigma-aldrich.com/books

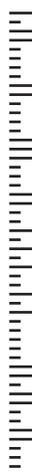
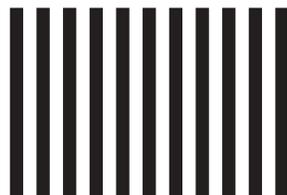


BUSINESS REPLY MAIL
FIRST-CLASS MAIL PERMIT NO. 3038 ST. LOUIS, MO

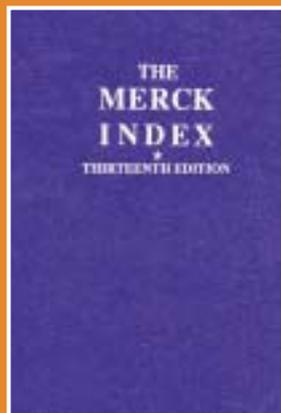
POSTAGE WILL BE PAID BY ADDRESSEE

SIGMA
P.O. BOX 14508
ST. LOUIS, MO, USA 63178-9916

NO POSTAGE
NECESSARY IF
MAILED IN THE
UNITED STATES



The Merck **INDEX**



13th ed., Merck & Co.,
Rahway, NJ, 2001,
1,741pp. Hardcover.

The **NEW** thirteenth edition contains over 10,000 monographs on chemicals, biologicals, and drugs, and provides a variety of information such as CAS registry numbers, molecular weights, physical properties,

toxicity data, descriptions of commercial uses, and references to the scientific and patent literature. Includes an organic name reaction section and a name index with over 50,000 names.

Z52,876-5

Sigma-Aldrich Worldwide Locations

Argentina

Sigma-Aldrich de Argentina SA
Phone: 54 11 4556 1472
Fax: 54 11 4552 1698
E-mail: info-argentina@sial.com

Australia

Sigma-Aldrich Pty. Ltd.
Phone: 61 2 9841 0555
Fax: 61 2 9841 0500
E-mail: ausmail@sial.com

Austria

Sigma-Aldrich Handels GmbH
Phone: 43 1 605 8110
Fax: 43 1 605 8120
E-mail: sigma@sigma.co.at

Belgium

Sigma-Aldrich N.V./S.A.
Phone: 32 3 899 1301
Fax: 32 3 899 1311
E-mail: becustsv@eurnotes.sial.com

Brazil

Sigma-Aldrich Brasil Ltda.
Phone: 55 11 3732 3100
Fax: 55 11 3733 5151
E-mail: sigmabr@sial.com

Canada

Sigma-Aldrich Canada Ltd.
Phone: (905) 829-9500
Fax: (905) 829-9292
E-mail: canada@sial.com

Czech Republic

Sigma-Aldrich s.r.o.
Phone: 420 2 2176 1111
Fax: 420 2 2176 3300
E-mail: czecustsv@eurnotes.sial.com

Denmark

Sigma-Aldrich Denmark A/S
Phone: 45 43 565900
Fax: 45 43 565905
E-mail: denorder@eurnotes.sial.com

Finland

Sigma-Aldrich Finland YA-Kemia Oy
Phone: 358 9 350 9250
Fax: 358 9 350 92555
E-mail: finorder@eurnotes.sial.com

France

Sigma-Aldrich Chimie S.a.r.l
Phone: 33 4 74 822888
Fax: 33 4 74 956808
E-mail: fradvsv@eurnotes.sial.com

Germany

Sigma-Aldrich Chemie GmbH
Phone: 49 89 6513 0
Fax: 49 89 6513 1169
E-mail: deorders@eurnotes.sial.com

Greece

Sigma-Aldrich (O.M.) Ltd.
Phone: 30 10 994 8010
Fax: 30 10 994 3831
E-mail: groustsv@eurnotes.sial.com

Hungary

Sigma-Aldrich Kft
Phone: 36 1 269 6474
Fax: 36 1 235 9050
E-mail: info@sigma.sial.hu

India

Sigma-Aldrich Foreign Holding Company
Phone: 91 80 852 4222
Fax: 91 80 852 4214
E-mail: india@sial.com

Ireland

Sigma-Aldrich Ireland Ltd.
Phone: 353 1 404 1900
Fax: 353 1 404 1910
E-mail: eicustsv@eurnotes.sial.com

Israel

Sigma-Aldrich Israel Ltd.
Phone: 972 8 948 4222
Fax: 972 8 948 4200
E-mail: hexter@sigma.co.il

Italy

Sigma-Aldrich S.r.l.
Phone: 39 02 33417 310
Fax: 39 02 38010 737
E-mail: itorder@eurnotes.sial.com

Japan

Sigma-Aldrich Japan K.K.
Phone: 81 3 5821 3111
Fax: 81 3 5821 3170

Korea

Sigma-Aldrich Korea
Phone: 82 31 329 9000
Fax: 82 31 329 9090
E-mail: hojoo@sial.com

Malaysia

Sigma-Aldrich (M) Sdn. Bhd.
Phone: 60 3 5635 3321
Fax: 60 3 5635 4116
E-mail: sam@sial.com

Mexico

Sigma-Aldrich Quimica, S.A. de C.V.
Phone: 52 722 276 1600
Fax: 52 722 276 1601
E-mail: mexico@sial.com

Netherlands

Sigma-Aldrich Chemie B.V.
Phone: 31 78 620 5411
Fax: 31 78 620 5421
E-mail: nlcustsv@eurnotes.sial.com

Norway

Sigma-Aldrich Norway AS
Phone: 47 23 176 000
Fax: 47 23 176 010
E-mail: nortech@sial.com

Poland

Sigma-Aldrich Sp. z o.o.
Phone: 48 61 823 2481
Fax: 48 61 823 2781
E-mail: plcustsv@eurnotes.sial.com

Portugal

Sigma-Aldrich Quimica, S.A.
Phone: 351 1 924 2555
Fax: 351 1 924 2610
E-mail: poorders@eurnotes.sial.com

Rep. of Singapore

Sigma-Aldrich Pte., Ltd.
Phone: 65 271 1089
Fax: 65 271 1571
E-mail: sapl@sial.com

Russia

OOO SAF-LAB
Phone: 7 095 975 3321
Fax: 7 095 975 4792
E-mail: techcare@sial.com

South Africa

Sigma-Aldrich (Pty) Ltd
Phone: 27 11 397 8886
Fax: 27 11 397 8859
E-mail: rsa@sial.com

Spain

Sigma-Aldrich Quimica S.A.
Phone: 34 91 661 9977
Fax: 34 91 661 9642
E-mail: esorders@eurnotes.sial.com

Sweden

Sigma-Aldrich Sweden AB
Phone: 46 8 742 4200
Fax: 46 8 742 4243
E-mail: sweorder@eurnotes.sial.com

Switzerland

Fluka Holding AG
Phone: 41 81 755 2511
Fax: 41 81 756 5449
E-mail: fluka@sial.com

United Kingdom

Sigma-Aldrich Company Ltd.
Phone: 44 1202 733114
Fax: 44 1202 715460
E-mail: ukcustsv@eurnotes.sial.com

United States

Aldrich
Phone: (414) 273-3850
Fax: (414) 273-4979
E-mail: aldrich@sial.com
Sigma
Phone: (314) 771-5765
Fax: (314) 771-5757
E-mail: sigma@sial.com



P.O. Box 355
Milwaukee, WI 53201
USA

Return Service Requested



For Development/Manufacturing Quantities
Contact your local Sigma-Aldrich office
and ask for Sigma-Aldrich Fine Chemicals

For Quantity Pricing/Standing Orders
Contact your local Sigma-Aldrich office



World Headquarters • 3050 Spruce St., St. Louis, MO 63103 • (314) 771-5750 • <http://www.sigma-aldrich.com>

The
SIGMA-ALDRICH
Family

SIGMA
Biochemicals and
Reagents for Life
Science Research

ALDRICH
Organics and
Inorganics for
Chemical Synthesis

Fluka
Specialty Chemicals
and Analytical
Reagents for Research

Riedel-de Haen
Laboratory Chemicals
and Reagents for
Research and Analysis

SUPELCO
Chromatography
Products for Analysis
and Purification

ISOTEC INC.
Promoting Research
and Discovery

Sigma-Aldrich Research is the research sales and marketing division of Sigma-Aldrich, Inc. Sigma-Aldrich Fine Chemicals is the development and manufacturing division of Sigma-Aldrich, Inc.

©2002 Sigma-Aldrich Co. Printed in USA. 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(s) for their particular use. Additional terms and conditions may apply. Please see reverse side of the invoice or packing slip.

SIGMA and are registered trademarks of Sigma-Aldrich Co. Riedel-de Haën®: trademark under license from Riedel-de Haën GmbH.