The synthesis of biaryl compounds by reaction of aryl halides with arylboronic acids, commonly referred to as the Suzuki coupling, 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.

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.
<table>
<thead>
<tr>
<th>Code</th>
<th>Formula</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>51,403-9</td>
<td>C₆H₆BF₂O₂</td>
<td><img src="image1.png" alt="Structure" /></td>
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<tr>
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<td>C₆H₆BNO₂</td>
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</tr>
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</tr>
<tr>
<td></td>
<td>5g 25g</td>
<td></td>
</tr>
</tbody>
</table>

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

References

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

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**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.
Aryl α-substituted proline analogs and γ-substituted pyroglutamates 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

### 52969
Boc-α-benzyl-DL-proline
500mg

### 90682
Boc-α-(2-bromobenzyl)-DL-proline
500mg

### 94866
Boc-α-(4-bromobenzyl)-DL-proline
500mg

### 90683
Boc-α-(2-chlorobenzyl)-DL-proline
500mg

### 90684
Boc-α-(3-chlorobenzyl)-DL-proline
500mg

### 30763
Boc-α-(2-diphenylmethyl)-DL-proline
500mg

### 74082
Boc-α-(4-fluorobenzyl)-DL-proline
500mg

### 68691
Boc-α-(4-methylbenzyl)-DL-proline
500mg

### 76501
Boc-α-(4-methylbenzyl)-DL-proline
500mg

### 36748
Boc-α-(1-naphthylmethyl)-DL-proline
500mg

### 95566
Boc-α-propyl-DL-proline
500mg

### 92392
(4R)-Boc-4-benzyl-L-pyroglutamic acid benzyl ester
500mg

### 51747
(4R)-Boc-4-benzyl-L-pyroglutamic acid
500mg

### 74624
(4R)-Boc-4-(2-bromobenzyl)-L-pyroglutamic acid benzyl ester
500mg

### 53371
(4R)-Boc-4-(2-bromobenzyl)-L-pyroglutamic acid benzyl ester
500mg

### 59703
(4R)-Boc-4-(4-methylbenzyl)-L-pyroglutamic acid benzyl ester
500mg
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

![Transition-Metal Catalysts](image)

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.

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.

### 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 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.

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- 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)

<table>
<thead>
<tr>
<th>Version</th>
<th>Standard Library (11,800 compounds)</th>
<th>Supplemental Library (3,500 compounds)</th>
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<tbody>
<tr>
<td>Single user, commercial</td>
<td>Z54,126-5</td>
<td>Z53,808-6</td>
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<tr>
<td>Single user, academic</td>
<td>Z54,138-9</td>
<td>Z53,818-3</td>
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<tr>
<td>Network version (1-10 users)</td>
<td>Z54,149-4</td>
<td>Z53,797-7</td>
</tr>
<tr>
<td>Demo program</td>
<td>Z54,159-1</td>
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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**

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

### Examples of products available for large-scale Suzuki coupling:

<table>
<thead>
<tr>
<th>Boronic Acid</th>
<th>CAS Number</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Hydroxyphenylboronic acid</td>
<td>52,396-8</td>
<td>500kg to MT</td>
</tr>
<tr>
<td>4-Methoxyphenylboronic acid</td>
<td>41,759-9</td>
<td>250-500kg</td>
</tr>
<tr>
<td>3-Aminophenylboronic acid hemisulfate</td>
<td>A7,175-1</td>
<td>50-100kg</td>
</tr>
<tr>
<td>2-Naphthaleneboronic acid</td>
<td>48,013-4</td>
<td>25-50kg</td>
</tr>
<tr>
<td>3-Formylphenylboronic acid</td>
<td>44,165-1</td>
<td>25kg</td>
</tr>
<tr>
<td>Tris(dibenzylideneacetone)dipalladium(0)</td>
<td>32,877-4</td>
<td>kg quantities</td>
</tr>
<tr>
<td>3-Methoxyphenylboronic acid</td>
<td>44,168-6</td>
<td>250-500kg</td>
</tr>
<tr>
<td>Phenylboronic acid, 97%</td>
<td>P2000-9</td>
<td>250kg</td>
</tr>
<tr>
<td>4-(Methylthio)phenylboronic acid</td>
<td>45,680-2</td>
<td>25-50kg</td>
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<tr>
<td>4-Chlorophenylboronic acid</td>
<td>41,754-8</td>
<td>25-50kg</td>
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<tr>
<td>4-Formylphenylboronic acid</td>
<td>43,196-6</td>
<td>25kg</td>
</tr>
<tr>
<td>Tetrakis(triphenylphosphine)Pd(0)</td>
<td>21,666-6</td>
<td>kg quantities</td>
</tr>
</tbody>
</table>

To obtain a quote or discuss your custom project, please call or visit us at www.sigma-aldrich.com/safc
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.
- Aldrich Catalog/Handbook [002]
- Aldrichimica Acta [014]
- Polymer Products CD - Catalog & Reference Guide [DGO]
- Dyes, Indicators & Intermediates [051]
- Fluka/Riedel-de-Haën® Catalog [003]
- CombiKits℠/Small Sample Service [CBJ]
- High-Purity Inorganics & Organometallics for Organic Synthesis [DVV]
- Products for NMR [DTW]
- Solvents for Scientific Research [BAO]
- Arylaldehydes [DUG]
- Fluka Peptide and Peptidomimetic Synthesis Reagents
- 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

Reference Books

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
Book Z28,778-4
CD-ROM Z28,779-2

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