

Cyclic Triolborate

Suzuki-Miyaura coupling reaction is carried out typically in the presence of a base and often in the coexistence of water as many boronic acids convert to cyclic anhydrides by dehydrotrimerization. However, since some boronic acids are hydrolyzed in basic aqueous solution, a large excess of boronic acids are often required.

Organic cyclid-triolborate salts are the ate complexed borate reagents developed by Miyaura, *et al.* There is no need to add bases in cross coupling reactions catalyzed by palladium. They may be used in aqueous and nonaqueous systems. They are also useful in *N*-arylation reaction with copper catalysts.

Reactions:

Suzuki-Miyaura Cross Coupling Reactions with Triolborate

Angew. Chem. Int. Ed., 47, 928-931 (2008).

Suzuki-Miyaura Cross Coupling Reactions using heterocyclic triolborates

$$Ar^{1} \xrightarrow{\bigcirc} O \xrightarrow{M^{\oplus}} + Ar^{2} - Br \xrightarrow{Pd(OAc)_{2}/PPh_{3}} Ar^{1} - Ar^{2}$$

Ar ¹	Ar ²	М	t[h]/T[°C]	Yield[%]
N	O ₂ N	Li	22/80	901)
N	Ac	Li	22/80	75 ¹⁾
N N	N	Li	22/80	70 ¹⁾
N ZZ	O ₂ N	Na	10/100	86
N X	O ₂ N	К	10/100	88

Suzuki-Miyaura Cross Coupling Reactions using various cyclic triolborates

$$Ar = B \xrightarrow{O} K^{\oplus} + Br$$
 $FG = Pd(OAc)_2$
 DMF/H_2O
 $Ar = B \xrightarrow{O} K^{\oplus} + Br$
 $Ar = B \xrightarrow{O} FG$

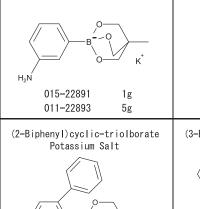
Ar	FG	t[h]/T[°C]	Yield(%)	Ar	FG	t[h]/T[°C]	Yield(%)
EI	MeO	3/rt.	quant.	OHC OHC	NO ₂	10/80	99
n Pr	MeO	4/rt.	99	- \\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	MeO	7/rt.	95
n Bu	MeO	5/rt.	94		MeO	5/rt.	98
The state of the s	MeO	5/rt.	92	آ 			
The state of the s	MeO	5/rt.	quant.	- F	MeO	5/rt.	quant.
Ph	MeO	6/rt.	99	F	MeO	5/rt.	quant.
C Y	MeO	5/rt.	95	CI	MeO	5/rt.	98
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	MeO	5/rt.	quant.	CI	MeO	5/rt.	98
NH ₂	MeO	8/rt.	quant.		NO ₂	5/100	98

## **Product List**

(2-Pyridine)cyclic-triolborate	(3-Pyridine)cyclic-triolborate	(4-Pyridine)cyclic-triolborate	2-(6-Fluoropyridine)cyclic-	
Lithium Salt	Potassium Salt	Sodium Salt	triolborate Lithium Salt	
B O Li*	N B O K	N	B O Li	
163-23761 1g	160-23771 1g	167–23781 1g	060-05621 1g	
169-23763 5g	166-23773 5g	163–23783 5g	066-05623 5g	
2-(6-Methoxypyridine)cyclic-	Phenylcyclic-triolborate Potassium	(3-Bromophenyl)cyclic-triolborate	(4-Bromophenyl)cyclic-triolborate	
triolborate Lithium Salt	Salt	Potassium Salt	Potassium Salt	
B O Li	B0 K ⁺	B	Br ————————————————————————————————————	
H ₃ C — O	[1014716-89-2]	Br		
137-16311 1g	166-24111 1g	024-16551 1g	028-16571 1g	
133-16313 5g	162-24113 5g	020-16553 5g	024-16573 5g	

## **Product List** (continued)

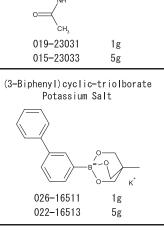
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(2-Fluorophenyl)cyclic-triolborate	(3-Fluorophenyl)cyclic-triolborate	(4-Fluorophenyl)cyclic-triolborate	(3,4-Difluorophenyl)cyclic-			
Potassium Salt	Potassium Salt	Potassium Salt	triolborate Potassium Salt			
B0 K*	B O K	F—————————————————————————————————————	F—————————————————————————————————————			
064-05521 1g	061–05531 1g	068-05541 1g	041-30841 1g			
060-05523 5g	067–05533 5g	064-05543 5g	047-30843 5g			
(3,5-Difluorophenyl)cyclic-	(3,4,5-Trifluorophenyl)cyclic-	(3-Chlorophenyl)cyclic-triolborate	(4-Chlorophenyl)cyclic-triolborate			
triolborate Potassium Salt	triolborate Potassium Salt	Potassium Salt	Potassium Salt			
B0 K	F B K	B O K	$a \longrightarrow B \xrightarrow{\circ} K^{*}$			
048-30851 1g	201–17481 1g	032–21281 1g	039–21291 1g			
044-30853 5g	207–17483 5g	038–21283 5g	035–21293 5g			
(2-Formy pheny )cyclic-triolborate	(4-Formylphenyl)cyclic-triolborate	cyclic-triolborate Sodium Salt	(4-Methylphenyl)cyclic-triolborate			
Sodium Salt	Sodium Salt		Potassium Salt			
O Na ⁺	OHC — B — O Na *	F ₃ C	H ₃ C			
065-05291 1g	068-05301 1g	021-16681 1g	134-16061 1g			
061-05293 5g	064-05303 5g	027-16683 5g	130-16063 5g			
(4-Ethylphenyl)cyclic-triolborate	(4-Propylphenyl)cyclic-triolborate	(4- <i>n-</i> ButyIphenyI)cyclic-triolborate	(4-VinyIphenyI)cyclic-trioIborate			
Potassium Salt	Potassium Salt	Potassium Salt	Potassium Salt			
8-00 K*	B N K	B-0-0-K,	B N K			
056-07861 1g	160-24011 1g	021-16561 1g	224-01841 1g			
052-07863 5g	166-24013 5g		220-01843 5g			
(3-Aminophenyl)cyclic-triolborate Potassium Salt	(2-Acetamidophenyl)cyclic- triolborate Sodium Salt					
00	BO Na ⁺	Reagent	Wako			



1g

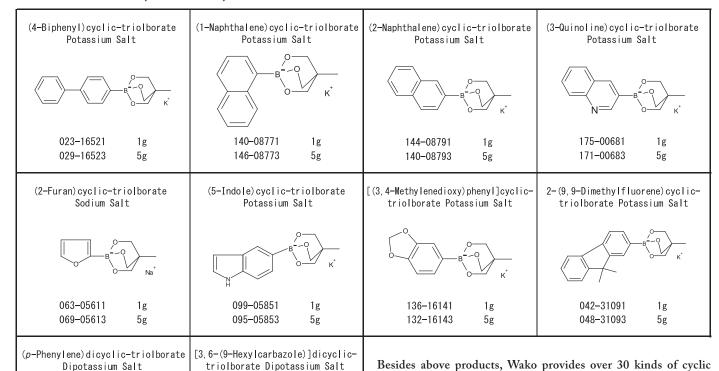
021-16321

027-16323





## **Product List** (continued)





080-09121

086-09123

1g

5g

#### Wako Pure Chemical Industries, Ltd.

www.wako-chem.co.jp

165-24201

161-24203

1g

5g

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Tel: 1-949-679-1700/ Fax: 1-949-679-1701

Boston Sale Office (Cambridge, MA):

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