

#### Catalysts

- Gold Catalysts
- Dinuclear Zinc Catalysts

#### Cycloaddition Reagents

- 1-(2-Methoxyethoxy)-1-vinylcyclopropane

#### Suzuki Coupling

- Boronate Esters
- Potassium Organotrifluoroborates

#### Other Reagents

- Diazald<sup>®</sup>
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## Introduction

The past decade has witnessed tremendous advances in the synthetic methods for C–C bond formation. The source of these advances is due to several factors including the development and commercialization of powerful catalyst/ligand combinations, the creation of robust and reliable protocols for cross-coupling, the ready accessibility to an ever-expanding toolbox of organometallic reagents, and the improvement of stoichiometric C–C bond-forming reagents such as chiral auxiliaries.

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### About Our Cover

The cover graphic depicts the structure of a proline-derived ligand developed by the Trost group at Stanford University. Hydrogen atoms have been omitted for clarity. Exposure of this ligand to diethylzinc results in the generation of a powerful catalyst capable of performing a variety of synthetically useful C–C bond forming reactions in an asymmetric fashion. This system efficiently catalyzes aldol condensations, Henry reactions, alkynylation, Mannich-type reactions, and desymmetrizations.

## ChemFiles

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## Catalysts

### Gold Catalysts

Prior to the 1980s, gold was regarded as having little catalytic activity. Recent advancements, spearheaded by F. Dean Toste (University of California, Berkeley) and others, have propelled gold into the forefront of transition metal catalysis. In particular, phosphine-ligated gold(I) complexes have recently emerged as powerful C–C bond forming catalysts, capable of performing a variety of reactions under mild conditions. The list of useful C–C bond construction methods includes cyclopropanations, enyne isomerizations, Rautenstrauch rearrangements, ene reactions, and ring expansions. Typically, the catalyst system relies on a phosphine gold(I) chloride complex in combination with a silver salt co-catalyst to generate the active species *in situ* (**Scheme 1**).

#### Cyclopropanation

Toste and co-workers successfully demonstrated that a variety of olefins undergo stereoselective cyclopropanation with propargyl esters in the presence of  $\text{Ph}_3\text{PAuSbF}_6$  (generated *in situ* from  $\text{PPh}_3\text{AuCl}$  and  $\text{AgSbF}_6$ , **Scheme 2**).<sup>1</sup> This reaction shows a preference for *cis*-selectivity and therefore complements the *trans*-selectivity observed in transition metal-catalyzed cyclopropanation of olefins using  $\alpha$ -diazoacetates. A diverse set of complex vinylcyclopropanes was synthesized using this methodology (**Figure 1**).

#### Isomerization of 1,5-Enynes

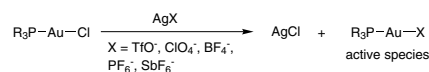
In the presence of gold(I), a range of 1,5-enynes rearrange to give bicyclo[3.1.0]hexenes in a high-yielding, stereocontrolled fashion.<sup>2</sup> The isomerization conditions accommodate diverse substitution patterns about the enyne, and moreover, can be conducted under “open-flask” conditions. The catalyst system utilizes  $\text{Ph}_3\text{PAuCl}$  in combination with  $\text{AgBF}_4$ ,  $\text{AgPF}_6$ , or  $\text{AgSbF}_6$  co-catalysts. While this method allows for access to simple bicyclic hydrocarbons (**Scheme 3**), complex heteroatom-rich cyclopropanes can also be prepared in high-yield and with superb diastereocontrol (**Scheme 4**). This latter example also illustrates the efficient chirality transfer that takes place in the isomerization process.

#### Rautenstrauch Rearrangement

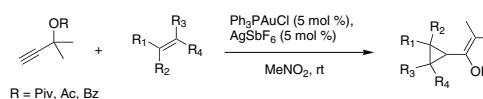
The Rautenstrauch rearrangement of 1,4-enynes provides efficient access to a diverse portfolio of functionalized cyclopentenones. Historically, the Pd-catalyzed reaction was limited to the preparation of achiral cyclopentenones, substituted at the 2 and 3 positions. Recent advances in gold(I) catalysis by Toste and co-workers have significantly broadened the scope of this synthetically useful rearrangement.<sup>3</sup> For example, chiral 1-ethynyl-2-propenyl pivalates efficiently rearrange in an enantioselective fashion and under mild conditions (**Scheme 5**). For optically pure pivalates, the *in situ*-generated catalyst  $\text{Ph}_3\text{PAuSbF}_6$  is most effective for transfer of the resident substrate chirality to the cyclopentenone product.  $\text{Ph}_3\text{PAuOTf}$  (also generated *in situ*) is adequate for Rautenstrauch rearrangement of racemic pivalates.

#### Conia-Ene Reactions

The thermal cyclization of  $\epsilon$ -acetylenic carbonyl compounds (Conia-ene reaction) provides access to methylenecyclopentanes without the need for deprotonation. However, the synthetic utility of this reaction is limited due to the high temperatures required. Toste has reported a mild catalytic version of this reaction that proceeds under neutral conditions at ambient temperatures.<sup>4</sup> The treatment of  $\beta$ -ketoesters containing tethered alkynes with  $\text{Ph}_3\text{PAuOTf}$  rapidly provides the corresponding vinylidenecyclopentanes in excellent conversion (**Scheme 6**, **Table 1**). This isomerization can also be performed at reduced



Scheme 1



Scheme 2

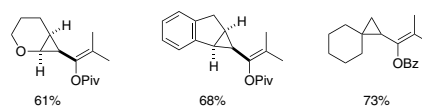
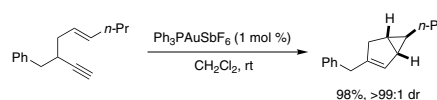
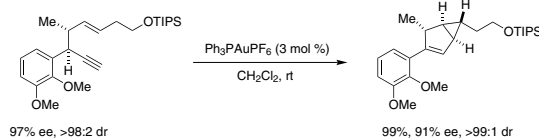


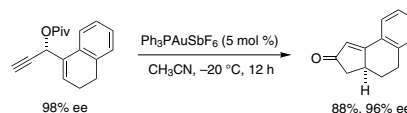
Figure 1



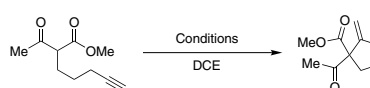
Scheme 3



Scheme 4



Scheme 5



Scheme 6

Entry	Conditions	Temp (°C)	Time	Conversion (%)
1	$\text{Ph}_3\text{PAuCl}$ (10 mol %)	60	6 h	0
2	$\text{Ph}_3\text{PAuOTf}$ (10 mol %)	23	<15 min	>95
3	$[(\text{Ph}_3\text{PAu})_3\text{O}]\text{BF}_4$ (1 mol %)	60	1 h	0
4	$[(\text{Ph}_3\text{PAu})_3\text{O}]\text{BF}_4$ (1 mol %), 5% TfOH	23	<15 min	>95

Table 1

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catalyst loadings by using the oxonium catalyst,  $[(\text{Ph}_3\text{PAu})_2\text{O}]\text{BF}_4$ , in the presence of acid. This methodology was applied to the synthesis of a variety of architecturally intriguing cyclopentanes (Scheme 7).

### 5-endo-dig Carbocyclizations

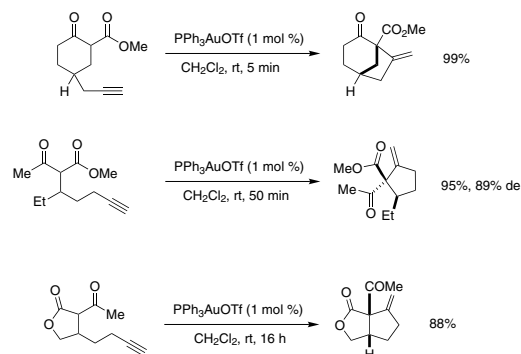
While the gold(I)-catalyzed Conia-ene cycloisomerization is limited to terminal  $\epsilon$ -alkynes, the related 5-endo-dig reaction allows for cyclization onto nonterminal  $\delta$ -alkynes providing cyclopentene derivatives.<sup>5</sup> While this synthetic methodology can be applied to simple bicyclic molecules, it can also be used in the preparation of *N*-heterocycles and halogenated cyclopentenes (Scheme 8).

### Propargyl Claisen Rearrangement

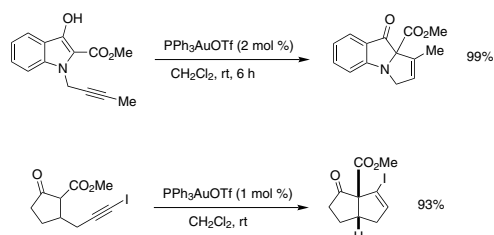
The Claisen rearrangement is one of the most powerful methods for C–C bond formation in the organic chemist's toolbox. The isolable oxonium gold catalyst,  $[(\text{Ph}_3\text{PAu})_2\text{O}]\text{BF}_4$ , provides access to a variety of homoallylic alcohols via a rapid two-step, one-pot sequence of a Claisen rearrangement of a propargyl vinyl ether, followed by reduction of the aldehyde functionality (Scheme 9, Table 2).<sup>6</sup> The reactions are generally high-yielding, and additionally, the catalyst system also shows a good ability to relay resident substrate chirality into the allene products (Scheme 10).

### Other Gold-Catalyzed Reactions

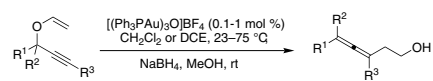
The facile and high-yielding ring expansion of 1-alkynylcycloalkanols to the corresponding 2-alkylidenecycloalkanones is catalyzed by several gold catalysts, including in situ-generated  $\text{Ph}_3\text{PAuSbF}_6$ . Treatment of 1-(phenylethynyl)cyclopropanol with  $\text{Ph}_3\text{PAuSbF}_6$  gives exclusively the (*E*)-benzylidenecyclobutanone in high yield (Scheme 11).<sup>7</sup> Using the same catalyst, pyrroles can be prepared by an intramolecular acetylenic Schmidt reaction of homopropargyl azides (Scheme 12).<sup>8</sup>



Scheme 7



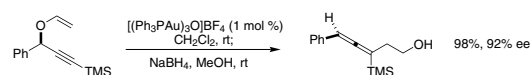
Scheme 8



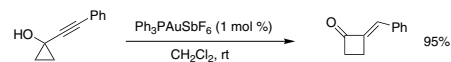
Scheme 9

Entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Time	Yield (%)
1	Ph	H	(CH <sub>2</sub> ) <sub>3</sub> OTBS	0.5 h	89%
2	2-Br-C <sub>6</sub> H <sub>4</sub>	H	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	6.5 h	96%
3	Ph(CH <sub>2</sub> ) <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	1 h	91%
4	—(CH <sub>2</sub> ) <sub>5</sub> —		(CH <sub>2</sub> ) <sub>3</sub> Ph	1 h	61%

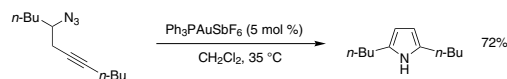
Table 2



Scheme 10



Scheme 11



Scheme 12

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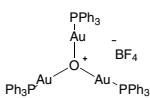
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NEW

$C_{54}H_{45}Au_3BF_4OP_3$   
FW: 1480.56



665142-250MG	250 mg	45.00
665142-1G	1 g	140.00

**Chloro(triphenylphosphine)gold(I), 99.9+%**

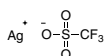
$C_{18}H_{16}AuClP$   
FW: 495.71  
[14243-64-2]



254037-500MG	500 mg	111.50
254037-5G	5 g	449.00

**Silver trifluoromethanesulfonate, ≥99%**

$CAgF_3O_3S$   
FW: 256.94  
[2923-28-6]



176435-1G	1 g	18.90
176435-10G	10 g	64.50
176435-25G	25 g	138.00

**Silver tetrafluoroborate, 98%**

$AgBF_4$   
FW: 194.67  
[14104-20-2]



208361-1G	1 g	18.50
208361-10G	10 g	75.80
208361-50G	50 g	272.00

**Silver hexafluorophosphate, 98%**

$AgF_6P$   
FW: 252.83  
[26042-63-7]



227722-1G	1 g	36.80
227722-10G	10 g	189.00
227722-50G	50 g	729.00

**Silver hexafluoroantimonate(V), 98%**

$AgF_6Sb$   
FW: 343.62  
[26042-64-8]



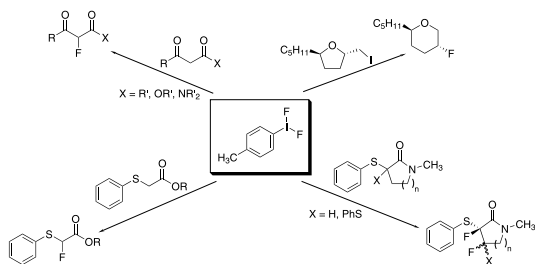
227730-1G	1 g	15.80
227730-5G	5 g	41.70
227730-25G	25 g	169.50

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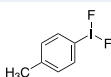
The importance of selectively fluorinating compounds in medicinal chemistry, biology, and organic synthesis is well appreciated and provides a major impetus to the discovery of new and mild fluorinating agents that can operate safely and efficiently. Elemental fluorine and many electrophilic fluorinating agents have been used in synthesis; however, most of these fluorinating agents are highly aggressive, unstable, and require special equipment and care for safe handling. Sigma-Aldrich is pleased to offer the following alternatives, which lack these drawbacks.

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**4-Iodotoluene difluoride**

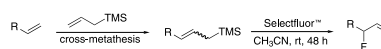
$CH_3C_6H_4IF_2$   
FW: 256.03  
[371-11-9]



651117-1G	1 g	\$32.80
651117-5G	5 g	112.50

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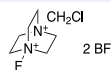
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**References:** (1) Yoshida, M. et al. *Arkivoc* [Online] **2003**(vi), 36. (2) Inagaki, T. et al. *Tetrahedron Lett.* **2003**, *44*, 4117. (3) Motherwell, W. B., et al. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2809. (4) Greaney, M. F. et al. *Tetrahedron Lett.* **2001**, *42*, 8523. (5) For a review, see Singh, R. P.; Shreeve, J. M. *Acc. Chem. Res.* **2004**, *37*, 31. (6) Thibaudeau, S.; Gouverneur, V. *Org. Lett.* **2003**, *5*, 4891.

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$C_7H_{14}B_2ClF_9N_2$   
FW: 354.26  
[140681-55-6]



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## Dinuclear Zinc Catalysts

The aldol reaction is arguably one of the most important C–C bond forming reactions in the synthesis of complex molecules. While the classical version is highly atom economical, it suffers from chemo- and regioselectivity problems. In the case of more selective, contemporary versions, nearly all of the reactions require pre-formation of an enolate, enol, or an equivalent thereof (e.g., silyl enol ethers in the Mukaiyama protocol). Generation of these species requires stoichiometric amounts of an adjunct reagent, decreasing from the overall atom efficiency of the process. Barry Trost and co-workers at Stanford University have developed a powerful catalyst technology that eliminates the requirement for pre-formation of a nucleophilic species. Moreover, aldol condensations, and variants thereof, can be performed in a highly asymmetric fashion. The catalyst system utilizes a proline-derived ligand in combination with  $\text{Et}_2\text{Zn}$  (2 equivalents) to generate an active dinuclear zinc species in situ (**Scheme 13**).

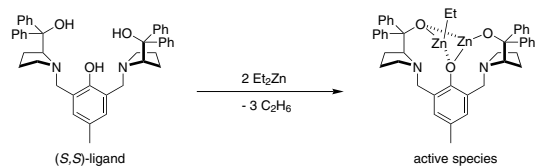
The first demonstration of this catalyst was in the condensation of aryl methyl ketones with aldehydes.<sup>9</sup> For example, the aldol product between isobutyraldehyde and acetophenone was obtained in good yield and in excellent optical purity (**Scheme 14**).

In a similar fashion, use of acetone as the nucleophilic aldol component provides access to a variety of chiral  $\beta$ -hydroxyacetones (**Scheme 15**).<sup>10</sup>

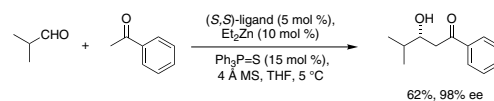
Trost's catalytic asymmetric aldol reaction is applicable to  $\alpha$ -hydroxyketone donors, giving synthetically useful polyoxygenated products in a stereocontrolled fashion. The reactions proceed at room temperature in high-yield with good diastereoselectivity in favor of the *syn*-diol adduct.<sup>11</sup> This methodology was utilized in the synthesis of the natural product (+)-boronolide (**Scheme 16**).<sup>12</sup>

Similarly,  $\alpha$ -hydroxyketones undergo imine addition in the presence of the dinuclear zinc catalyst. This Mannich-type reaction is highly diastereo- and enantioselective, giving *syn*-1,2-amino alcohols in very good yield.<sup>13</sup> Both glyoxalate imines and aldimines are active substrates in the imine aldol reaction (**Scheme 17**).

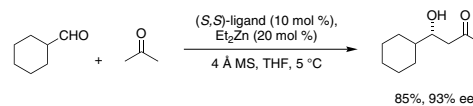
Despite tremendous potential, the instability of methyl vinyl ketone and its aldol adducts has hampered its use in synthesis. Recently, the Trost group reported the general catalytic asymmetric aldol reaction using methyl vinyl ketone in combination with the dinuclear zinc catalyst (**Scheme 18**).<sup>14</sup>



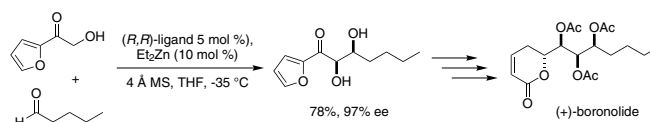
Scheme 13



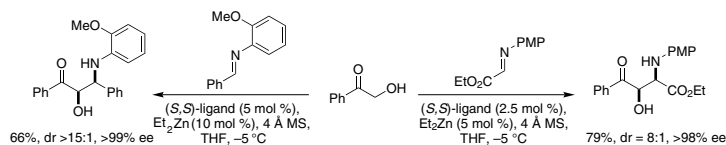
Scheme 14



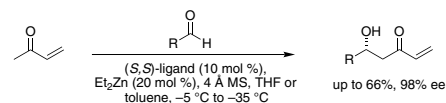
Scheme 15



Scheme 16



Scheme 17



Scheme 18

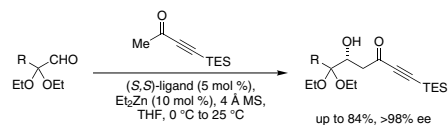
Until the recent development of the zinc catalyst system, the use of methyl ynone in aldol additions was also virtually unknown. Addition of methyl ynone to  $\alpha$ -ketal aldehydes occurs smoothly to give highly functionalized alkyne building blocks (**Scheme 19**).<sup>15</sup> This strategy was used to install the C9 stereochemistry in the formal synthesis of the cytotoxic phosphate ester fostriecin (**Figure 2**).<sup>16</sup>

The nitroaldol (Henry) reaction is an atom economical approach to  $\beta$ -hydroxynitroalkanes that are useful intermediates in the preparation of nitrogen-containing natural products. The asymmetric synthesis of both (-)-denopamine and (-)-arbutamine relied on the dinuclear zinc-catalyzed addition of nitromethane to benzaldehyde derivatives (**Scheme 20**).<sup>17</sup>

Chiral propargylic alcohols are easily accessed in high enantiomeric excess by Zn-catalyzed addition of terminal alkynes to unsaturated aldehydes. This reaction tolerates a variety of alkyne substituents (e.g., Ph, TMS, CO<sub>2</sub>Et, and CH(OEt)<sub>2</sub>), as well as both aryl- and  $\alpha,\beta$ -unsaturated aldehydes (**Scheme 21**).<sup>18</sup> In this case, a third equivalent of Et<sub>2</sub>Zn is necessary for the formation of the zinc acetylide nucleophile.

Finally, the Trost catalyst system efficiently desymmetrizes *meso*-2-arylpropane-1,3-diols in high-yield with an excellent degree of stereodiscrimination.<sup>19</sup> Of the derivatizing agents explored, vinyl benzoate proved most effective in the desymmetrization reaction (**Scheme 22**).

Sigma-Aldrich is pleased to announce an agreement with Professor Barry Trost to distribute this versatile ligand for research applications in Zn-mediated asymmetric C–C bond forming reactions (**Scheme 23**).



Scheme 19

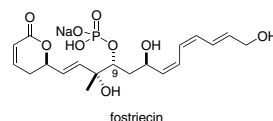
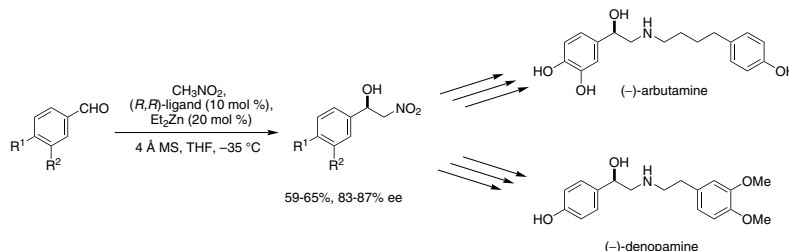
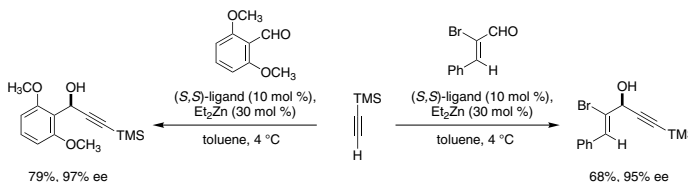


Figure 2



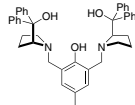
Scheme 20



Scheme 21

**(R,R)-2,6-Bis((2-(hydroxydiphenylmethyl)-1-pyrrolidiny)methyl)-4-methylphenol** NEW

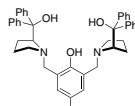
C<sub>43</sub>H<sub>46</sub>N<sub>2</sub>O<sub>3</sub>  
FW: 638.84



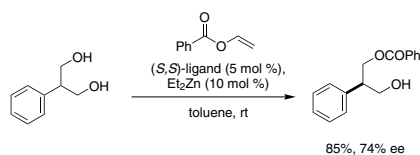
667625-1G	1 g	20.50
667625-5G	5 g	81.20

**(S,S)-2,6-Bis((2-(hydroxydiphenylmethyl)-1-pyrrolidiny)methyl)-4-methylphenol** NEW

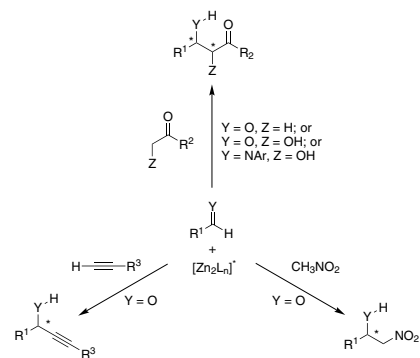
C<sub>43</sub>H<sub>46</sub>N<sub>2</sub>O<sub>3</sub>  
FW: 638.84



668370-1G	1 g	20.50
668370-5G	5 g	81.20



Scheme 22



Scheme 23

Ready to scale up? For competitive quotes on larger quantities or custom synthesis, contact SAFC™ at 1-800-244-1173 (USA), or visit [www.safcglobal.com](http://www.safcglobal.com).

## Cycloaddition Reagents

### 1-(2-Methoxyethoxy)-1-vinylcyclopropane

Vinylcyclopropanes (VCPs) are excellent scaffolds for construction of seven-membered and bicyclic ring systems. Paul Wender, of Stanford University, has developed a simple but versatile VCP reagent (1-(2-methoxyethoxy)-1-vinylcyclopropane,

**Figure 3**) capable of participating in a variety of rhodium-catalyzed cycloaddition reactions.

Exposure of the VCP reagent to alkynes in the presence of catalytic  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  results in the expeditious formation of substituted cycloheptenones via [5+2] cycloaddition (**Scheme 24**, **Table 3**).<sup>20</sup> The reaction is tolerant to a variety of functional groups (OH, NHTs,  $\text{CO}_2\text{H}$ ), as well as both mono- and disubstituted acetylenes. The combination of rapid reaction times, low catalyst loadings, and the ability to perform the reaction on a significant scale (100 mmol), make this method of cycloheptenone formation extraordinarily cost-effective.

Using similar conditions, Wender expanded the scope of this methodology to perform three-component [5+2+1] cycloadditions by performing the reaction under mild CO pressure.<sup>21</sup> With the presence of CO, an intermediate cyclooctadienone is formed by CO insertion. This species rapidly undergoes transannular closure. Subsequent hydrolysis of the enol ether furnishes the observed bicyclo[3.3.0]octenone (**Scheme 25**). This general method was used to prepare an array of bicyclooctenes in good to excellent yield (**Table 4**). Notably, the cycloaddition occurs with complete regioselectivity and with tolerance of heteroatom-containing functional groups.

A final elaboration of this methodology was achieved by use of phenylacetylenes in a non-polar solvent system to give hydroxyindanones (**Scheme 26**).<sup>22</sup> With this relatively simple change, a two-fold CO insertion occurs, resulting in a net four-component [5+1+2+1] cycloaddition!

Lastly, the scope of this general class of reactions was broadened to include other  $\pi$ -systems. Specifically, allenes participate in intermolecular [5+2] cycloadditions with the VCP reagent to give cycloheptanone derivatives (**Scheme 27**).<sup>23</sup>

### 1-(2-Methoxyethoxy)-1-vinylcyclopropane

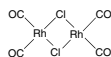
$\text{C}_8\text{H}_{14}\text{O}_2$   
FW: 142.20  
[278603-80-8]



666246-1G 1 g 65.00

### $\mu$ -Dichlorotetracarbonyldirrhodium(I), 97%

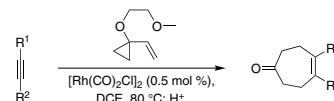
$\text{C}_4\text{Cl}_2\text{O}_4\text{Rh}_2$   
FW: 388.76  
[14523-22-9]



209031-250MG 250 mg 53.50  
209031-1G 1 g 180.50



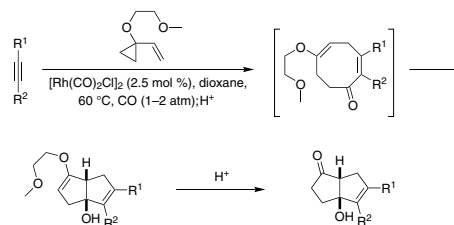
Figure 3



Scheme 24

Entry	R <sup>1</sup>	R <sup>2</sup>	Time	Yield (%)
1	H	H	2 h	75%
2	H	$\text{CO}_2\text{Me}$	10 min	84%
3	$\text{CO}_2\text{Et}$	$\text{CO}_2\text{Et}$	1 h	96%
4	H	$\text{CH}_2\text{OH}$	25 min	82%
5	H	$\text{CH}_2\text{NPhth}$	11 min	97%
6	H	1-cyclohexenyl	7 h (rt)	85%

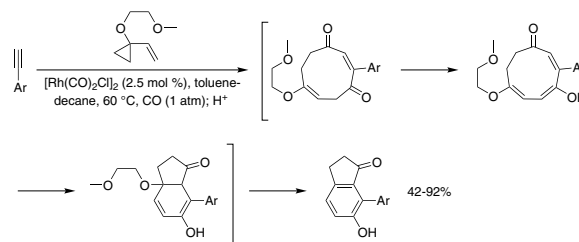
Table 3



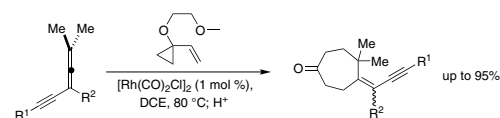
Scheme 25

Entry	R <sup>1</sup>	R <sup>2</sup>	Time	Yield (%)
1	$\text{C}(\text{O})\text{CH}_3$	Et	20 h	97%
2	$\text{C}(\text{O})\text{NH}_2$	Ph	40 h	96%
3	CHO	Ph	26 h	69%
4	$\text{CO}_2\text{Et}$	TMS	26 h	67%

Table 4



Scheme 26



Scheme 27

# MacMillan Imidazolidinone OrganoCatalysts™

## Metal-Free Asymmetric Catalysis

### Product Highlights

- Superior enantiocontrol in numerous transformations
- High activities at low catalyst loadings
- Extraordinary functional group tolerance
- Asymmetric  $\alpha$ -fluorination employed in natural product synthesis

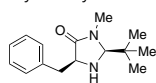
MacMillan and co-workers have created chiral imidazolidinone organo-catalysts that function as the linchpin in a variety of directed enantioselective organic reactions, including the enamine-catalyzed  $\alpha$ -chlorination and 1,3-dipolar cycloaddition of aldehydes. Sigma-Aldrich is pleased to offer six imidazolidinone organocatalysts in our collaboration with Materia, Inc. that mediate rapid and enantiocontrolled C–F and C–H bond formation. In the former process, catalyst **1** was utilized in low (5 mol %) loadings in the first example of organocatalytic advanced enantioselective  $\alpha$ -fluorination of aldehydes to afford a broad spectrum of highly enantioenriched alcohols.



References: (a) MacMillan, D. W. et al. *J. Am. Chem. Soc.* **2000**, 122, 9874. (b) MacMillan, D. W. et al. *J. Am. Chem. Soc.* **2005**, 127, 8826.

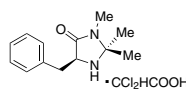
#### (2*S*,5*S*)-(-)-2-*tert*-Butyl-3-methyl-5-benzyl-4-imidazolidinone, 97%

**NEW**  
 (2*S*,5*S*)-2-*tert*-Butyl-3-methyl-5-phenylmethyl-4-imidazolidinone  
 $C_{15}H_{22}N_2O$   
 FW: 246.35  
 [346440-54-8]  
 663107-500MG 500 mg \$60.00  
 663107-1G 1 g 95.00



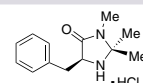
#### (5*S*)-2,2,3-Trimethyl-5-benzyl-4-imidazolidinone dichloroacetic acid

**NEW**  
 $C_{15}H_{20}Cl_2N_2O_3$   
 FW: 347.24  
 663085-500MG 500 mg \$55.00  
 663085-2G 2 g 150.00



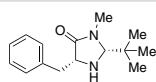
#### (5*S*)-2,2,3-trimethyl-5-phenylmethyl-4-imidazolidinone monohydrochloride, 97%

**NEW**  
 $C_{13}H_{18}N_2O \cdot HCl$   
 FW: 254.76  
 [278173-23-2]  
 569763-500MG 500 mg \$30.00  
 569763-2G 2 g 80.00



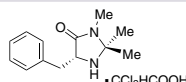
#### (2*R*,5*R*)-(-)-2-*tert*-Butyl-3-methyl-5-benzyl-4-imidazolidinone, 97%

**NEW**  
 $C_{15}H_{22}N_2O$   
 FW: 246.35  
 [390766-89-9]  
 663093-500MG 500 mg \$60.00  
 663093-1G 1 g 95.00



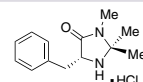
#### (5*R*)-2,2,3-Trimethyl-5-benzyl-4-imidazolidinone dichloroacetic acid

**NEW**  
 $C_{15}H_{20}Cl_2N_2O_3$   
 FW: 347.24  
 663077-500MG 500 mg \$55.00  
 663077-2G 2 g 150.00



#### (5*R*)-2,2,3-trimethyl-5-phenylmethyl-4-imidazolidinone monohydrochloride, 97%

**NEW**  
 $C_{13}H_{18}N_2O \cdot HCl$   
 FW: 254.76  
 [323196-43-6]  
 663069-500MG 500 mg \$30.00  
 663069-2G 2 g 80.00



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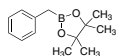
## Suzuki Coupling

### Boronate Esters

C–C bond formation via the Suzuki–Miyaura reaction is one of the most powerful and thoroughly explored facets of Pd-catalyzed cross-coupling. The boron-based nucleophiles utilized in this reaction offer distinct advantages over other organometallic coupling reagents. Both boronic acids and boronate esters are highly nucleophilic, exhibit a broad range of functional group tolerance, and are substantially less toxic than heavy metal organometallic reagents such as organotin.

#### Benzylboronic acid pinacol ester, 96%

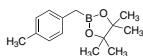
$C_{13}H_{19}BO_2$   
FW: 218.10  
[87100-28-5]



659207-1G	1 g	35.00
659207-10G	10 g	200.00

#### 4-Methylbenzylboronic acid pinacol ester, 97% NEW

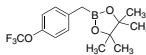
$C_{14}H_{21}BO_2$   
FW: 232.13  
[356570-52-0]



663298-1G	1 g	38.00
663298-5G	5 g	125.00

#### 4-(Trifluoromethoxy)benzylboronic acid pinacol ester, 97% NEW

$C_{14}H_{18}BF_3O_3$   
FW: 302.10  
[475250-46-5]



662879-5G	5 g	125.00
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#### Cyclopropylboronic acid pinacol ester, 96%

$C_9H_{17}BO_2$   
FW: 168.04  
[126689-01-8]



659851-1G	1 g	67.50
659851-5G	5 g	225.00

#### Isopropenylboronic acid pinacol ester, 95% NEW

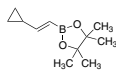
$C_9H_{17}BO_2$   
FW: 168.04  
[126726-62-3]



663212-5G	5 g	75.00
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#### trans-2-Cyclopropylvinylboronic acid pinacol ester, 96%

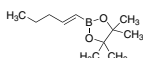
$C_{11}H_{19}BO_2$   
FW: 194.08  
[849061-99-0]



653942-1G	1 g	29.50
653942-5G	5 g	98.30

#### trans-1-Pentenylboronic acid pinacol ester, 97%

$C_{11}H_{21}BO_2$   
FW: 196.09  
[161395-96-6]

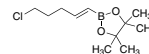


665169-1G	1 g	36.00
665169-5G	5 g	120.00

Sigma-Aldrich is pleased to offer the following boronate esters as part of our growing portfolio of reagents used in the Suzuki coupling reaction. Included in this listing are five novel 2-pyridylboronate esters. While most pyridylboronate esters readily undergo hydrolysis, those ligated to *N*-phenyldiethanolamine are stable reagents amenable to long-term storage. Most importantly, they exhibit high activity in cross-coupling reactions.<sup>24</sup>

#### trans-5-Chloro-1-penteneboronic acid pinacol ester, 97%

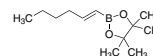
$C_{11}H_{20}BClO_2$   
FW: 230.54  
[154820-95-8]



652067-5G	5 g	47.80
652067-25G	25 g	166.50

#### trans-1-Hexenylboronic acid pinacol ester, 97% NEW

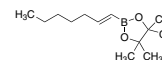
$C_{12}H_{23}BO_2$   
FW: 210.12  
[126688-97-9]



663743-1G	1 g	36.00
663743-5G	5 g	120.00

#### trans-1-Heptenylboronic acid pinacol ester, 97% NEW

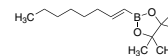
$C_{13}H_{25}BO_2$   
FW: 224.15  
[169339-75-7]



662992-5G	5 g	100.00
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#### trans-1-Octenylboronic acid pinacol ester, 95% NEW

$C_{14}H_{27}BO_2$   
FW: 238.17  
[83947-55-1]



663050-1G	1 g	40.00
663050-10G	10 g	225.00

#### 1-Phenylvinylboronic acid pinacol ester, 96%

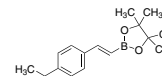
$C_{14}H_{19}BO_2$   
FW: 230.11  
[78782-27-1]



659193-1G	1 g	37.50
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#### trans-2-(4-Ethylphenyl)vinylboronic acid pinacol ester, 97% NEW

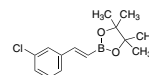
$C_{16}H_{23}BO_2$   
FW: 258.16



662798-1G	1 g	90.00
662798-5G	5 g	300.00

#### trans-2-(3-Chlorophenyl)vinylboronic acid pinacol ester, 97%

$C_{14}H_{18}BClO_2$   
FW: 264.56  
[871125-84-7]

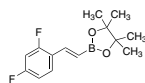


665533-1G	1 g	90.00
665533-5G	5 g	300.00

**trans-2-(2,4-Difluorophenyl)vinylboronic acid pinacol ester, 96%**

NEW

C<sub>14</sub>H<sub>17</sub>BF<sub>2</sub>O<sub>2</sub>  
FW: 266.09  
[736987-78-3]

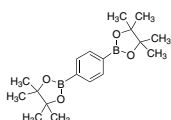


664871-1G	1 g	50.00
664871-5G	5 g	190.00

**1,4-Benzenediboronic acid dipinacol ester, 97%**

NEW

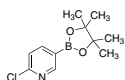
C<sub>18</sub>H<sub>28</sub>B<sub>2</sub>O<sub>4</sub>  
FW: 330.03  
[99770-93-1]



663816-5G	5 g	87.50
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**6-Chloropyridine-3-boronic acid pinacol ester, 97%**

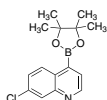
C<sub>11</sub>H<sub>10</sub>BClNO<sub>2</sub>  
FW: 239.51  
[444120-94-9]



659843-1G	1 g	75.00
659843-5G	5 g	250.00

**7-Chloroquinoline-4-boronic acid pinacol ester, 90%**

C<sub>15</sub>H<sub>11</sub>BClNO<sub>2</sub>  
FW: 289.56  
[871125-83-6]



658596-1G	1 g	114.50
-----------	-----	--------

**1-(Phenylsulfonyl)-3-indoleboronic acid pinacol ester, 97%**

C<sub>20</sub>H<sub>22</sub>BN<sub>2</sub>O<sub>4</sub>S  
FW: 383.27  
[870717-93-4]



654280-1G	1 g	75.00
654280-5G	5 g	250.00

**2-Pyridineboronic acid N-phenylethanolamine ester**

C<sub>15</sub>H<sub>17</sub>BN<sub>2</sub>O<sub>2</sub>  
FW: 268.12  
[662138-96-7]



647284-1G	1 g	19.70
647284-5G	5 g	77.90
647284-10G	10 g	140.50

**4-Methyl-2-pyridineboronic acid N-phenylethanolamine ester**

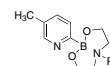
C<sub>16</sub>H<sub>19</sub>BN<sub>2</sub>O<sub>2</sub>  
FW: 282.15  
[849100-03-4]



648841-5G	5 g	68.90
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**5-Methyl-2-pyridineboronic acid N-phenylethanolamine ester**

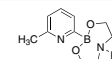
C<sub>16</sub>H<sub>19</sub>BN<sub>2</sub>O<sub>2</sub>  
FW: 282.15



648825-1G	1 g	47.80
648825-5G	5 g	188.00

**6-Methyl-2-pyridineboronic acid N-phenylethanolamine ester**

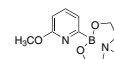
C<sub>16</sub>H<sub>19</sub>BN<sub>2</sub>O<sub>2</sub>  
FW: 282.15



648817-1G	1 g	18.00
648817-5G	5 g	72.10

**6-Methoxy-2-pyridineboronic acid-N-phenylethanolamine ester**

C<sub>16</sub>H<sub>19</sub>BN<sub>2</sub>O<sub>3</sub>  
FW: 298.14



649155-1G	1 g	47.50
649155-5G	5 g	187.50

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## Potassium Organotrifluoroborates

Boronic acids, boronate esters, and organoboranes have typically been the boron-based reagents of choice in Suzuki–Miyaura cross-coupling reactions. While in many instances these reagents provide suitable results, each has inherent limitations. Organoboranes are limited by their hydroboration method of preparation, and hence suffer from functional group incompatibility. Boronic acids may have indeterminate stoichiometry as a result of partial cyclodehydration, and moreover can be difficult to purify. While boronate esters don't suffer these drawbacks, they lack atom economy and are more costly.

Potassium organotrifluoroborates are an attractive alternative to other boron-based reagents. The air- and moisture-stable salts are readily accessible by a variety of high-yielding methods. The tractable, crystalline solids are suitable for storage for extended periods of time. The post-reaction byproducts (salts) are readily separated from the desired product. Most importantly, these novel nucleophiles perform as well as boronic acids and esters in cross-coupling and other important reactions. Additionally, the  $\text{BF}_3\text{K}$  moiety is compatible with sensitive functional groups and is tolerant to "hostile" reaction conditions such as epoxidation,<sup>25</sup> ozonolysis,<sup>26</sup> osmylation,<sup>26</sup> and metal-halogen exchange (Scheme 28).<sup>26</sup> Sigma-Aldrich has partnered with Gary Molander at the University of Pennsylvania in a collaborative effort to provide an array of potassium organotrifluoroborates, thereby expanding the toolbox of available boron reagents.

Potassium organotrifluoroborates exhibit superb behavior in the Suzuki–Miyaura reaction and provide a powerful method for the construction of important structural motifs including functionalized alkenes and arenes; 1,3-dienes; styrenes; biaryls; and complex heterocyclic natural products.

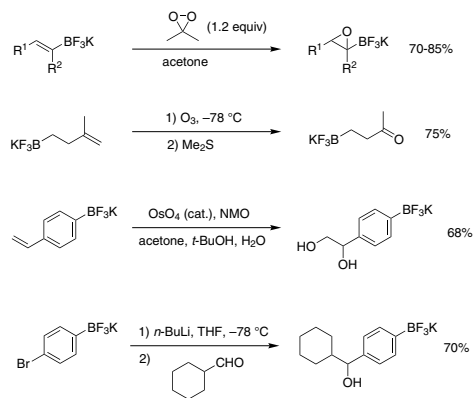
The Molander group successfully demonstrated facile bond formation between alkyltrifluoroborates and alkenyl triflates (Scheme 29).<sup>27</sup> Presence of water was found to be essential, and use of  $\text{Cs}_2\text{CO}_3$  was more effective than other bases (e.g.,  $\text{K}_2\text{CO}_3$ ,  $\text{K}_3\text{PO}_4$ ,  $\text{CsOH}$ ,  $\text{NaOAc}$ , or  $\text{KOH}$ ).

Application of these conditions to the cross-coupling of alkyltrifluoroborates and aryl bromides or triflates gave excellent results, providing access to a myriad of functionalized arenes (Scheme 30).<sup>27,28</sup>

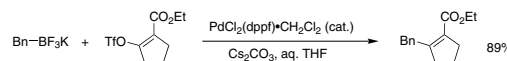
The stereospecificity of this reaction is illustrated by cross-coupling of alkene partners, giving synthetically versatile 1,3-dienes (Scheme 31).<sup>29</sup> Access to any one of the four possible geometrical isomers is achieved simply by choosing the appropriate trifluoroborate nucleophile and alkenyl bromide.

Vinylation of arenes by alkenyltrifluoroborates has proven to be a very general reaction. Aryl bromides, iodides, and triflates all perform well, giving functionalized styrene derivatives in good-to-excellent yields (Scheme 32).<sup>30,31</sup>

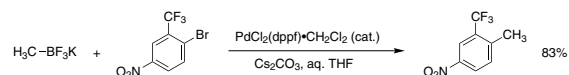
Until recently, biaryl coupling of trifluoroborates was limited to the use of more reactive aryl coupling partners: aryl triflates, iodides, and bromides.<sup>32–34</sup> Buchwald et al. were able to assemble sterically-congested biphenyls using ordinarily unreactive aryl chlorides (Scheme 33).<sup>35</sup> This was achieved by the use of *S*-Phos as a ligand additive to the reaction mixture.



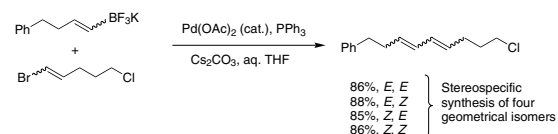
Scheme 28



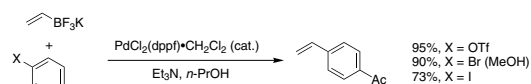
Scheme 29



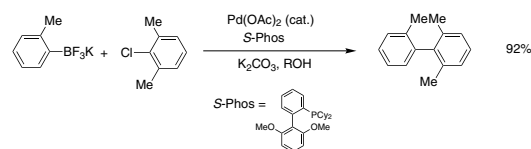
Scheme 30



Scheme 31

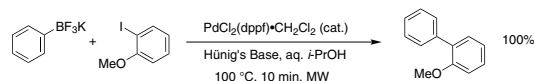


Scheme 32



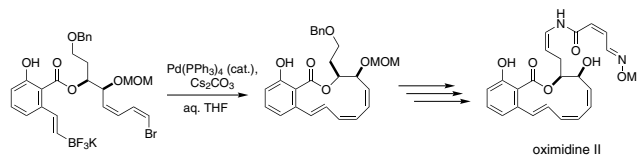
Scheme 33

Kabalka and co-workers have also made headway in the field of biaryl coupling by employing microwave synthesis.<sup>36</sup> Use of microwaves dramatically reduced reaction times relative to the thermal reaction. Aryl iodides containing electron-withdrawing groups or electron-donating groups worked equally well (**Scheme 34**).



Scheme 34

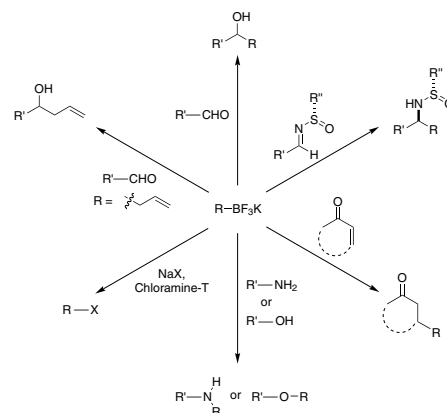
Lastly, the Molander group demonstrated the generality of potassium organotrifluoroborate cross-coupling in the preparation of the salicylate enamide natural product oximidine II (**Scheme 35**).<sup>37</sup> The key ring-closure step utilized an intramolecular C–C bond formation between a potassium styryltrifluoroborate and a 1-bromo-1,3-diene to give the desired macrolide framework.



Scheme 35

In addition to Suzuki–Miyaura cross-coupling, potassium organotrifluoroborates participate in other synthetically useful reactions such as 1,2-addition to aldehydes<sup>38</sup> and sulfinimines;<sup>39</sup> conjugate addition to enones;<sup>38,40</sup> C–N bond formation;<sup>41</sup> halogenation;<sup>42</sup> and allylation<sup>43</sup> (**Scheme 36**).

For further information about potassium organotrifluoroborates, please view our Cheminars™ at [sigma-aldrich.com/cheminars](http://sigma-aldrich.com/cheminars).



Scheme 36

#### Potassium hydrogenfluoride solution, 3 M in water

NEW

HF <sub>2</sub> K		
FW: 78.10		
[7789-29-9]	KHF <sub>2</sub>	
663883-25ML	25 mL	12.50
663883-100ML	100 mL	19.00
663883-500ML	500 mL	38.00

#### Potassium methyltrifluoroborate

NEW

CH <sub>3</sub> BF <sub>3</sub> K		
FW: 121.94		
	CH <sub>3</sub> BF <sub>3</sub> K	
637890-1G	1 g	35.00
637890-5G	5 g	110.00

#### Potassium butyltrifluoroborate, 95%

NEW

C <sub>4</sub> H <sub>9</sub> BF <sub>3</sub> K		
FW: 164.02		
[444343-55-9]	H <sub>3</sub> C(CH <sub>2</sub> ) <sub>3</sub> BF <sub>3</sub> K	
660094-1G	1 g	18.50
660094-5G	5 g	62.50

#### Potassium benzyltrifluoroborate, 95%

C <sub>7</sub> H <sub>7</sub> BF <sub>3</sub> K		
FW: 198.03		
[329976-73-0]	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> BF <sub>3</sub> K	
563056-1G	1 g	65.00
563056-5G	5 g	220.00

#### Potassium vinyltrifluoroborate, 95%

NEW

C <sub>2</sub> H <sub>3</sub> BF <sub>3</sub> K		
FW: 133.95		
[13682-77-4]	CH <sub>2</sub> =CHBF <sub>3</sub> K	
655228-1G	1 g	25.00
655228-5G	5 g	83.20

#### Potassium *trans*-1-decenyltrifluoroborate, 95%

C <sub>10</sub> H <sub>19</sub> BF <sub>3</sub> K		
FW: 246.16		
[479678-72-3]	H <sub>3</sub> C(CH <sub>2</sub> ) <sub>8</sub> CH=CHBF <sub>3</sub> K	
637882-1G	1 g	35.00
637882-5G	5 g	110.00

#### Potassium *trans*-styryltrifluoroborate

C <sub>8</sub> H <sub>7</sub> BF <sub>3</sub> K		
FW: 210.05		
[201852-49-5]	C <sub>6</sub> H <sub>5</sub> CH=CHBF <sub>3</sub> K	
576158-1G	1 g	38.20
576158-5G	5 g	120.00

#### Potassium phenyltrifluoroborate, 95%

C <sub>6</sub> H <sub>5</sub> BF <sub>3</sub> K		
FW: 184.01		
[153766-81-5]	C <sub>6</sub> H <sub>5</sub> BF <sub>3</sub> K	
563951-1G	1 g	33.10
563951-5G	5 g	105.00

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**Potassium *p*-tolyltrifluoroborate**

C<sub>7</sub>H<sub>7</sub>BF<sub>3</sub>K  
FW: 198.03  
[216434-82-1]



571555-1G	1 g	39.70
571555-5G	5 g	125.00

**Potassium 4-acetylphenyltrifluoroborate, 97%**

C<sub>8</sub>H<sub>7</sub>BF<sub>3</sub>KO  
FW: 226.05  
[252726-24-2]



657050-1G	1 g	25.00
657050-5G	5 g	83.20

**Potassium 4-carboxyphenyltrifluoroborate, 97%**

C<sub>7</sub>H<sub>5</sub>BF<sub>3</sub>KO<sub>2</sub>  
FW: 228.02  
[850623-38-0]



657069-1G	1 g	24.00
657069-5G	5 g	80.00

**Potassium 4-(trifluoromethyl)phenyltrifluoroborate, 96%**

C<sub>7</sub>H<sub>4</sub>BF<sub>6</sub>K  
FW: 252.01  
[166328-08-1]



576131-1G	1 g	39.70
576131-5G	5 g	125.00

**Potassium 3-hydroxyphenyltrifluoroborate, 96%**

C<sub>6</sub>H<sub>5</sub>BF<sub>3</sub>KO  
FW: 200.01  
[871231-45-7]



659746-1G	1 g	24.00
659746-5G	5 g	80.00

**Potassium 3-fluorophenyltrifluoroborate, 96%**

C<sub>6</sub>H<sub>4</sub>BF<sub>4</sub>K  
FW: 202.00  
[267006-24-6]



659770-1G	1 g	24.00
659770-5G	5 g	80.00

**Potassium 2,4-difluorophenyltrifluoroborate, 95%**

C<sub>6</sub>H<sub>3</sub>BF<sub>5</sub>K  
FW: 219.99  
[871231-41-3]



656992-1G	1 g	28.10
656992-5G	5 g	93.60

**Potassium 4-bromophenyltrifluoroborate**

C<sub>6</sub>H<sub>4</sub>BBrF<sub>3</sub>K  
FW: 262.90  
[374564-35-9]



571547-1G	1 g	38.20
571547-5G	5 g	120.00

**Potassium 2-naphthalenetri-fluoroborate**

C<sub>10</sub>H<sub>7</sub>BF<sub>3</sub>K  
FW: 234.07  
[668984-08-5]



657018-1G	1 g	28.10
657018-5G	5 g	93.60

**Potassium 3,4-(methylenedioxy)phenyltrifluoroborate, 97%**

C<sub>7</sub>H<sub>5</sub>BF<sub>3</sub>KO<sub>2</sub>  
FW: 228.02  
[871231-46-8]



659754-1G	1 g	24.00
659754-5G	5 g	80.00

**Potassium 5-methyl-2-thiophenetri-fluoroborate, 95%**

C<sub>5</sub>H<sub>5</sub>BF<sub>3</sub>KS  
FW: 204.06  
[871231-40-2]



654949-1G	1 g	28.10
654949-5G	5 g	93.60

**Stabilized 2-Iodoxybenzoic Acid (SIBX)**

Since 1994,<sup>1</sup> 2-iodoxybenzoic acid (IBX) has been well recognized as a very powerful and selective oxidizing agent. Similar to the Dess–Martin periodinane, IBX is an environmentally benign alternative to metal-based oxidizing agents. However, IBX is not often used due to the fact that it is an impact-sensitive explosive material, which prevents its shipping and transport, as well as its application in industry.<sup>2</sup> Sigma-Aldrich is pleased to introduce a stabilized formulation of IBX (SIBX) that displays none of the explosive properties of IBX, while maintaining excellent reactivity and selectivity.

**SIBX has demonstrated use in the:**

- Oxidation of alcohols to carbonyl compounds.<sup>3</sup>
- Oxidative demethylation of 2-methoxyphenols.<sup>3</sup>
- Oxidative dearomatization of 2-alkylphenols into orthoquinols (alternative to Barton or Adler oxidations).<sup>4</sup>

**2-Iodoxybenzoic acid, stabilized (45 wt. % IBX)**

C<sub>7</sub>H<sub>5</sub>IO<sub>4</sub>  
FW: 280.02  
[61717-82-6]



661384-1G	1 g	27.50
661384-10G	10 g	195.00

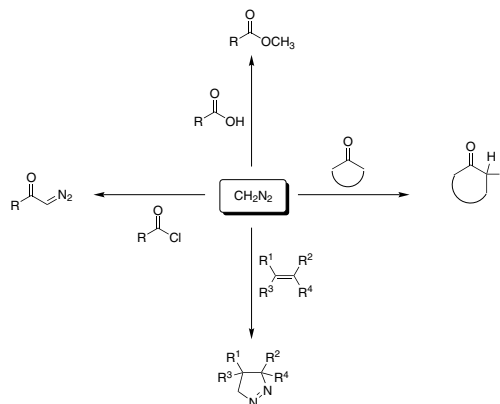
(1) Frigerio, M.; Santagostino, M. *Tetrahedron Lett.* **1994**, *35*, 8019. (2) Plumb, J. B.; Harper, D. J. *Chem. Eng. News* **1990**, *68*, 3. (3) Ozanne, A. et al. *Org. Lett.* **2003**, *5*, 2903. (4) Quideau, S. et al. *Arkivoc*, **2003**, 6, 106.

## Other Reagents

### Diazald®

Diazomethane is an extremely versatile reagent for the preparation of both C–O and C–C bonds.<sup>44</sup> It is one of the most common methylating reagents for carboxylic acids and has found extensive application in the alkylation of phenols, enols, and heteroatoms, such as nitrogen and sulfur. Diazomethane has also been used in cycloalkanone ring expansion, preparation of  $\alpha$ -diazo ketones from carboxylic acid halides, and pyrazoline formation (Scheme 37).

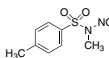
Due to the toxicity and unstable nature of diazomethane, all reactions involving its preparation and use should be carried out using proper precautions.<sup>45</sup> Sigma-Aldrich is pleased to offer Diazald® as the preferred diazomethane precursor, as well as a variety of specialized glassware for safe generation of this versatile reagent. Diazomethane can be conveniently prepared and purified as a solution in a variety of scales (1 to 300 mmol), depending on the glassware kit chosen.



Scheme 37

#### Diazald®, 99%

C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>S  
FW: 214.24  
[80-11-5]



D28000-25G	25 g	14.00
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#### Diazald® Kit with Clear-Seal® joints

Z100250-1KT	564.00
-------------	--------

#### Diazald® Kit with System 45® compatible connections

Z419761-1SET	635.00
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#### Mini Diazald® Kit with ST/NS 19/22 Clear-Seal® joints

Z108898-1EA	267.50
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#### Mini Diazald® Kit with ST/NS 19/26 Clear-Seal® joints

Z202509-1EA	268.50
-------------	--------

#### Macro Diazald® Kit with ST/NS 24/40 Clear-Seal® joints

Z108510-1KT	854.00
-------------	--------

#### Macro Diazald® Kit with ST/NS 29/32 Clear-Seal® joints

Z203076-1KT	1155.00
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### Diethyl Azodicarboxylate (DEAD)

Due to stricter safety regulations, shipment of diethyl azodicarboxylate (DEAD, Figure 4) as a dry reagent is prohibited in the United States. Sigma-Aldrich has achieved full compliance with UN and U.S. DOT safety regulations, and is pleased to offer this extremely versatile reagent as a stable and safe 40% solution in toluene.

The most widespread application of DEAD is as an activating reagent in the Mitsunobu reaction. Under the Mitsunobu protocol, numerous transformations are possible including stereochemical inversion of secondary alcohols, aminations, and macrolactonizations. For example, Fürstner's total synthesis of (–)-balanol relied on the preparation of a chiral azide intermediate available from the corresponding stereoinverted alcohol (Scheme 38).<sup>46</sup>

Keck utilized the DEAD-assisted Mitsunobu esterification to prepare a crucial intermediate in the synthesis of the antiviral alkaloid, 7-deoxypancratistatin (Scheme 39).<sup>47</sup>

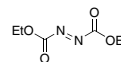
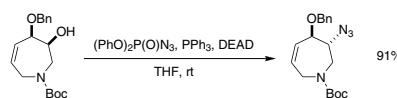
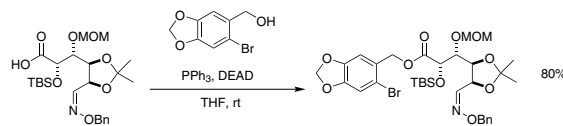


Figure 4



Scheme 38



Scheme 39

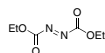
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The azo-linkage in DEAD is also an active Michael acceptor. In the presence of a copper(II) salicylaldehyde catalyst,  $\beta$ -ketoesters add cleanly to DEAD, giving the corresponding hydrazone derivative (Scheme 40).<sup>48</sup> In a similar fashion, copper(II) salts also catalyze the addition of boronic acids to DEAD in essentially quantitative yield.<sup>49</sup>

In addition to C–O and C–N bond formation, DEAD can be used in the construction of C–C bonds. Optically active 3-aryl-3-substituted propanoic acids can be readily prepared in excellent enantiomeric excess from chiral secondary benzylic alcohols (Scheme 41).<sup>50</sup>

#### Diethyl azodicarboxylate solution, 40 wt. % in toluene

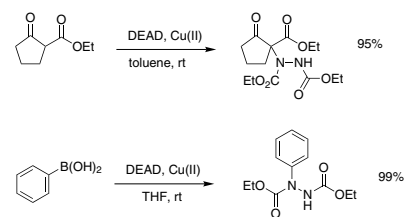
$C_6H_{10}N_2O_4$   
FW: 174.15  
[1972-28-7]



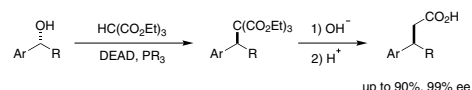
563110-100G	100 g	98.80
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#### Diethyl azodicarboxylate, polymer-bound

561851-1G	1 g	60.00
561851-5G	5 g	200.00
561851-25G	25 g	900.00



Scheme 40



Scheme 41

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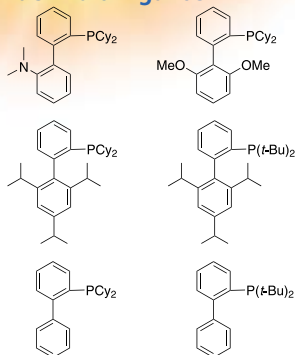
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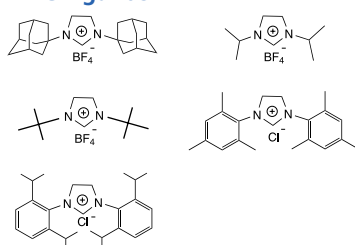
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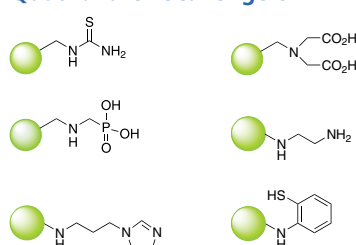
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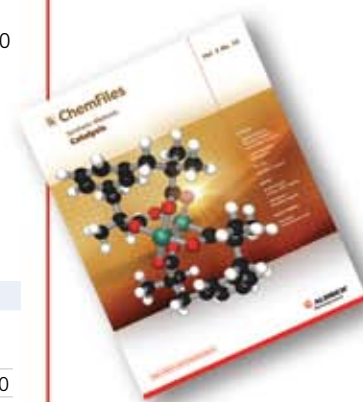
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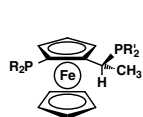


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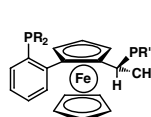
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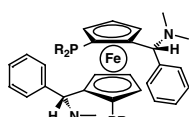
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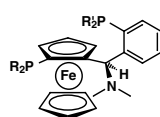
Josiphos



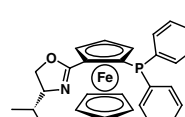
Walphos



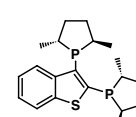
Mandypfos



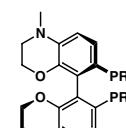
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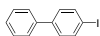
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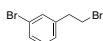
C<sub>12</sub>H<sub>9</sub>I  
FW: 280.10  
[1591-31-7]



637769-5G	5 g	\$87.40
637769-25G	25 g	327.50

## 3-Bromophenethyl bromide, 97%

C<sub>8</sub>H<sub>8</sub>Br<sub>2</sub>  
FW: 263.96  
[40422-70-6]



653802-1G	1 g	\$20.00
653802-10G	10 g	110.00

## 5-Bromo-6-bromomethyl-1,3-benzodioxole, 96%

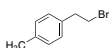
C<sub>8</sub>H<sub>6</sub>Br<sub>2</sub>O<sub>2</sub>  
FW: 293.94  
[5434-47-9]



653748-5G	5 g	\$30.70
653748-25G	25 g	109.00

## 4-Methylphenethyl bromide, 97%

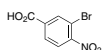
C<sub>9</sub>H<sub>11</sub>Br  
FW: 199.09  
[6529-51-7]



653810-1G	1 g	\$22.50
653810-5G	5 g	75.00

## 3-Bromo-4-nitrobenzoic acid, 97%

C<sub>7</sub>H<sub>4</sub>BrNO<sub>4</sub>  
FW: 246.01  
[101420-81-9]



659304-1G	1 g	\$52.50
659304-5G	5 g	186.00

## 4-Bromo-3-iodotoluene, 97%

C<sub>7</sub>H<sub>6</sub>BrI  
FW: 296.93



659312-1G	1 g	\$26.50
659312-5G	5 g	92.60

## 3-Iodo-4-nitrotoluene, 97%

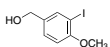
C<sub>7</sub>H<sub>6</sub>INO<sub>2</sub>  
FW: 263.03  
[52488-29-6]



659320-5G	5 g	\$55.60
659320-25G	25 g	195.00

## 3-Iodo-4-methoxybenzyl alcohol, 97%

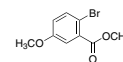
C<sub>8</sub>H<sub>9</sub>IO<sub>2</sub>  
FW: 264.06



659339-1G	1 g	\$20.30
659339-10G	10 g	109.00

## Methyl 2-bromo-5-methoxybenzoate, 97%

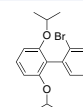
C<sub>9</sub>H<sub>9</sub>BrO<sub>3</sub>  
FW: 245.07  
[35450-36-3]



659290-5G	5 g	\$43.20
659290-25G	25 g	151.00

## 2-Bromo-2',6'-diisopropoxy-1,1'-biphenyl, 95%

C<sub>18</sub>H<sub>21</sub>BrO<sub>2</sub>  
FW: 349.26  
[870703-70-1]



660221-5G	5 g	\$31.80
660221-25G	25 g	106.00

## 2-Fluoro-5-iodopyridine, 97%

C<sub>5</sub>H<sub>3</sub>FIN  
FW: 222.99  
[171197-80-1]



660043-1G	1 g	\$15.50
660043-10G	10 g	85.00

## 5-Bromo-2-(trifluoromethyl)pyridine, 97%

C<sub>6</sub>H<sub>3</sub>BrF<sub>3</sub>N  
FW: 225.99  
[436799-32-5]



661104-500MG	500 mg	\$50.00
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## 3-Bromo-5-(trifluoromethyl)pyridine, 97%

C<sub>6</sub>H<sub>3</sub>BrF<sub>3</sub>N  
FW: 225.99  
[436799-33-6]



661112-500MG	500 mg	\$52.00
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## 2-Bromo-6-(trifluoromethyl)pyridine, 97%

C<sub>6</sub>H<sub>3</sub>BrF<sub>3</sub>N  
FW: 225.99  
[189278-27-1]



661147-500MG	500 mg	\$54.50
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## 2-Bromo-5-(trifluoromethyl)pyridine, 97%

C<sub>6</sub>H<sub>3</sub>BrF<sub>3</sub>N  
FW: 225.99  
[50488-42-1]



661120-1G	1 g	\$38.00
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## 5-Bromo-3-nitropyridine-2-carbonitrile, 95%

C<sub>6</sub>H<sub>2</sub>BrN<sub>3</sub>O<sub>2</sub>  
FW: 228.00  
[573675-25-9]



662968-5G	5 g	\$45.00
662968-25G	25 g	152.50

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