

#### Catalysts

- $[\text{RhOH}(\text{S-BINAP})_2]_2$ ,  
 $[\text{RhOMe}(\text{S-BINAP})_2]_2$ ,  
and Catalyst Precursors
- Cobalt Oxazoline  
Palladacycles
- $\text{Rh}_2(\text{esp})_2$
- Palladium Catalysts

#### Ligands

- N-Heterocyclic  
Carbene (NHC) Ligands
- ChiralQuest  
Phosphine Ligands

#### Suzuki Coupling

- Potassium  
Trifluoroborate Salts

## Introduction

During the past two decades, catalytic synthetic methods have generated intense research efforts in the quest to provide scientists with the tools required to perform C–C and C–X (X = O, N) bond-forming reactions in an efficacious, atom-economical fashion. Such research efforts have created an extensive library of highly active catalysts that facilitate the synthesis of target molecules in greater complexity and in fewer steps. Thus, the efficient constructive capacity found in recent catalyzed methodologies has been a determining factor in the process design of fine chemical and pharmaceutical building blocks and has resulted in the replacement of linear-designed, stoichiometric organic transformations that lack catalyst mediation (**Scheme 1**).<sup>1</sup> Furthermore, the field of catalytic, asymmetric synthesis has evolved to its current technologically advanced state, rendering oxidation and reduction processes, such as hydroformylation and hydrogenation, amenable to industrial scale design, i.e., the highly selective and active chiral ruthenium catalyst utilized in the reduction of a Lipitor® side-chain precursor (**Scheme 2**).<sup>2</sup>

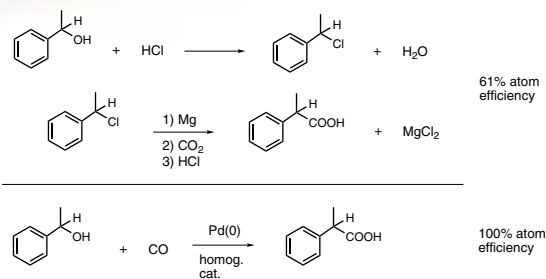
This edition of *ChemFiles* describes new and improved applications within the field of catalysis. Sigma-Aldrich is proud to offer cutting-edge catalysts and ligands for the expeditious construction of complex carbon and heteroatom architectures. In many cases, the methodologies illustrated herein exhibit high levels of chemo-, regio-, and stereoselectivity. These exciting new reagents will challenge the researcher to pursue the syntheses of increasingly elaborate target molecules. For a complete listing of products organized along the lines of stereoselective transformations and general catalysis, please visit [sigma-aldrich.com/catalysis](http://sigma-aldrich.com/catalysis).

## 1. Catalysts

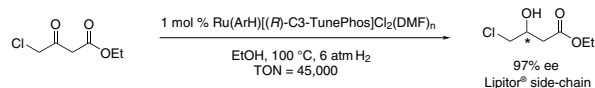
### [RhOH((S)-BINAP)]<sub>2</sub> (**1**), [RhOMe((S)-BINAP)]<sub>2</sub> (**2**), and Catalyst Precursors

In the late 1990s, the Hayashi group successively developed rhodium-based catalysts applied in the asymmetric, conjugate addition of arylboronic acids to C=C bonds.<sup>3</sup> They utilized Rh-BINAP catalysts to effect several advantages over other enantioselective 1,4-addition reactions: 1) high selectivities (>95% ee) have been attained; 2) the reaction is performed in an aqueous environment; 3) the reaction temperature is not low (60–90 °C) and thus is advantageous for process design; 4) a multitude of aryl and alkenyl groups can be incorporated; and 5) a variety of electron-deficient olefins can be effectively coupled with boronic acids in an asymmetric fashion.

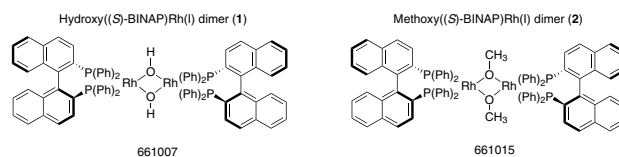
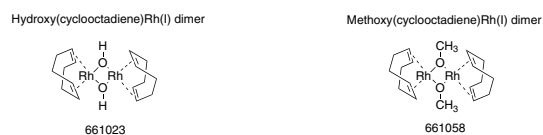
We are now pleased to offer the latest technology from Hayashi, including both the pre-catalysts suitable for facile conversion into the active species, as well as the catalysts themselves (**Scheme 3**). Rh-dimer catalysts **1** and **2** offer additional benefits over their monomeric counterparts: 1) the reaction is carried out at ambient temperatures, which limits the amount of boron reagent needed by eliminating decomposition at higher temperatures; 2) the yield of 1,4-addition product is typically higher due to a reduction of arylboronic acid hydrolysis; and 3) the enantioselectivities are always higher in reactions catalyzed by [RhOH((S)-BINAP)]<sub>2</sub> and [RhOMe((S)-BINAP)]<sub>2</sub> than by Rh(acac)(BINAP).<sup>4</sup> In general, the Hayashi system displays impressive levels of enantiocontrol in the reactions of both acyclic and cyclic enones of varying electronic character, affording highly enantioenriched products in excellent yields (**Scheme 4, Table 1**).



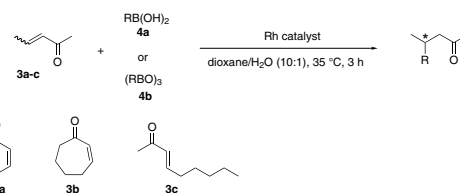
**Scheme 1**



**Scheme 2**



**Scheme 3**



**Scheme 4**

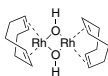
Entry	<b>3</b>	<b>4</b>	Catalyst	Temp (°C)	Time (h)	Yield (%)	% ee
1	<b>3a</b>	<b>4a</b>	Rh(acac)(BINAP)	40	5	<2	-
2	<b>3a</b>	<b>4a</b>	<b>1</b>	35	3	96	99.3
3	<b>3b</b>	<b>4a</b>	Rh(acac)(BINAP)	100	5	51	93
4	<b>3b</b>	<b>4b</b>	<b>1</b>	35	3	94	96.3
5	<b>3c</b>	<b>4a</b>	Rh(acac)(BINAP)	100	5	88	92
6	<b>3c</b>	<b>4b</b>	<b>1</b>	35	3	92	97.8

**Table 1**

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**Hydroxy(cyclooctadiene)Rhodium(I) Dimer**

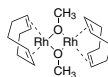
C<sub>16</sub>H<sub>26</sub>O<sub>2</sub>Rh<sub>2</sub>  
FW: 516.33



661023-1G 1 g

**Methoxy(cyclooctadiene)Rhodium(I) Dimer**

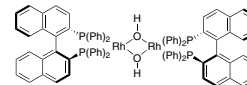
C<sub>18</sub>H<sub>30</sub>O<sub>2</sub>Rh<sub>2</sub>  
FW: 544.38



661058-1G 1 g

**Hydroxy((S)-BINAP)Rhodium(I) Dimer**

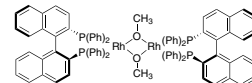
C<sub>88</sub>H<sub>66</sub>O<sub>2</sub>P<sub>4</sub>Rh<sub>2</sub>  
FW: 1485.17



661007-1G 1 g

**Methoxy((S)-BINAP)Rhodium(I) Dimer**

C<sub>90</sub>H<sub>70</sub>O<sub>2</sub>P<sub>4</sub>Rh<sub>2</sub>  
FW: 1513.22



661015-1G 1 g

**Cobalt Oxazoline Palladacycles: COP-Cl (5) and COP-OAc (6)**

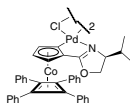
Overman and co-workers have successfully synthesized dimeric cobalt catalysts that effectively promote the asymmetric rearrangement of allylic trichloroacetimidates to allylic trichloroacetamides.<sup>5</sup> The rationale for this transformation is obvious as it grants ready access to valuable allylic amines of high enantiopurity, following the removal of the trichloroacetyl group under acidic, basic, or reductive conditions (**Scheme 5**). The high levels of asymmetry induced by COP catalysts in the preparation of chiral allylic amines can be carried forth into low-molecular weight compounds such as (*S*)-Vigabatrin, a GABA aminotransaminase inhibitor.<sup>6</sup> Sigma-Aldrich has already introduced COP-Cl (**5**), and now has commercialized the acetate-bridged COP dimer **6**, which has enhanced performance characteristics versus COP-Cl due to its increased solubility in non-chlorinated solvents (**Scheme 6**).

COP-OAc also catalyzes the asymmetric rearrangement of prochiral (*Z*)-allylic trichloroacetimidates in the presence of carboxylic acids to the corresponding chiral allylic esters with high enantiopurities (**Scheme 7**).<sup>7</sup> The scope of the reaction when utilizing an *n*-propyl-substituted allylic imidate at ambient temperature includes a wide range of aliphatic and aromatic carboxylic acids with high enantioselectivities of 3-acyloxy-1-alkene products (93–99%, **Table 2**). Good yields (60–98%) of the chiral allylic alcohols and heteroatom substituent tolerance on the allylic imidate ensure that this methodology will be attractive for broader application on the pathway to natural product synthesis.

Another promising feature of this catalyst system is found in the recent literature, wherein COP-OAc dimer **6** promotes the intramolecular aminopalladation of allylic *N*-tosylcarbamates to afford highly enantioenriched 2-vinylloxazolidin-2-ones.<sup>8</sup> The COP-OAc catalyst exhibits superior activity and avoids the use of silver salts for pre-activation, thereby leveraging a distinct advantage over the earlier catalyst models studied by Overman. Furthermore, crude allylic *N*-tosylcarbamate reagents can be prepared *in situ* following the addition of an allylic alcohol to an *N*-sulfonylisocyanate and subsequently cyclized with excellent selectivity (**Scheme 8**).

**COP-Cl Catalyst**

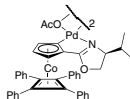
C<sub>78</sub>H<sub>66</sub>Cl<sub>2</sub>Co<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Pd<sub>2</sub>  
FW: 1464.98  
[612065-01-7]



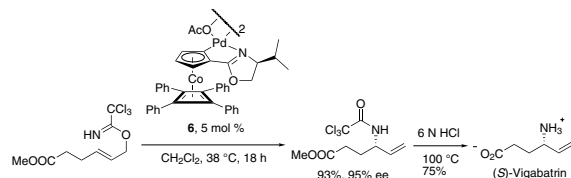
646636-250MG 250 mg  
646636-1G 1 g

**(S)-(+)-COP-OAc Catalyst**

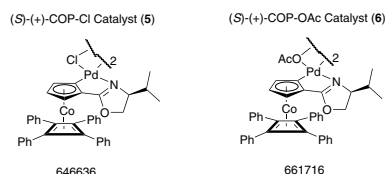
C<sub>82</sub>H<sub>72</sub>O<sub>6</sub>N<sub>2</sub>Co<sub>2</sub>Pd<sub>2</sub>  
FW: 1512.06  
[222400-03-5]



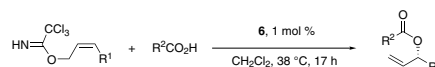
661716-250MG 250 mg  
661716-1G 1 g



Scheme 5



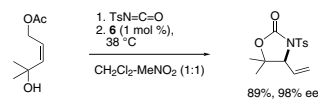
Scheme 6



Scheme 7

Entry	R <sup>1</sup>	R <sup>2</sup>	Catalyst	Temp (°C)	Time (h)	Yield (%)	% ee
1	<i>n</i> -Pr	Me	<b>6</b>	23	17	88	94 ( <i>R</i> )
2	<i>n</i> -Pr	C <sub>6</sub> H <sub>4</sub> ( <i>p</i> -NO <sub>2</sub> )	<b>6</b>	23	26	60	94
3	<i>n</i> -Pr	C <sub>6</sub> H <sub>4</sub> ( <i>o</i> -MeO)	<b>6</b>	23	10	92	>99
4	<i>n</i> -Pr	2-naphthyl	<b>6</b>	23	17	87	96
5	<i>i</i> -Bu	Me	<b>6</b>	23	14	96	93
6	CH <sub>2</sub> OPMB	Me	<b>6</b>	23	16	93	>99

Table 2



Scheme 8



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### Rh<sub>2</sub>(esp)<sub>2</sub> (7): An Exceptionally Efficient and Selective Catalyst for C–H Amination

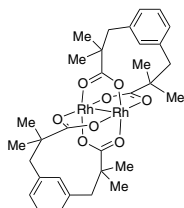
By substituting tetramethylated *m*-benzenedipropionic acid **8** via a decarboxylative metathesis of Rh<sub>2</sub>(OAc)<sub>4</sub> (**Scheme 9**), the Du Bois group at Stanford has improved the catalytic performance of Rh with respect to the oxidative C–H activation of sulfamate, sulfamide, carbamate, urea, and guanidine substrates through nitrene insertion.<sup>9</sup> High yields of tri- and tetrasubstituted amines were found by conducting the reactions under slow addition of the oxidant PhI(O<sub>2</sub>CtBu)<sub>2</sub>, which is an easily prepared, stable, and unlike PhI(OAc)<sub>2</sub>, more soluble in non-polar solvents, effective oxidant for C–H amination. The proclivity of unactivated methylene groups to undergo C–H amination is a result of the catalyst's robust nature. Substrates with 3° C–H bonds are fully converted to the desired heterocycle at catalyst loadings as low as 0.15 mol %. This exceptional improvement in catalyst turnover is illustrated in **Scheme 10**, wherein five times the amount of the isosteric Rh<sub>2</sub>(O<sub>2</sub>CtBu)<sub>4</sub> must be applied in the intramolecular conversion of sulfamates to heterocycles to afford comparable product yields.

Du Bois and co-workers have also employed this highly efficient catalyst for the oxidative cyclization of sulfamide, urea, and guanidine substrates. Most impressively, Rh<sub>2</sub>(esp)<sub>2</sub> has been found to facilitate the intermolecular C–H insertion into a range of benzylic and 3° substrates with 2,2,2-trichloroethylsulfamate as the *N*-atom source (**Scheme 11**). These reactions are generally performed with limiting amounts of starting material, a feature that distinguishes the Rh<sub>2</sub>(esp)<sub>2</sub>-catalyzed process from other intermolecular amination methods with Mn, Fe, Ru, and Cu. By employing this methodology, rapid access to amino alcohols, amino acids, and diamines is afforded.<sup>10</sup>

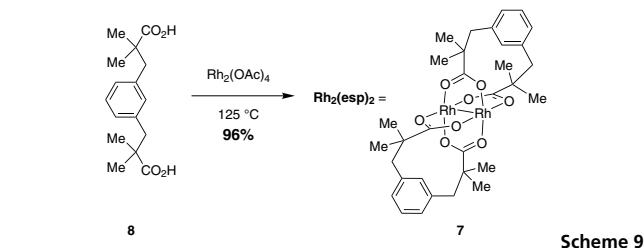
This new oxidative strategy offers the unique ability to control chemo-, regio-, and diastereoselective transformations for the preparation of 1,3-diamines, amino alcohols, and β-amino acids. The Du Bois group has developed this C–H amination for use in the total synthesis of (–)-tetrodotoxin (TTX), a highly efficacious blowfish poison.<sup>11</sup> The densely functionalized, oxygenated cyclohexanone framework of TTX illustrates the difficult challenge in its attempted synthesis, of which only two successful strategies have been employed prior to this report.<sup>12,13</sup> Stereospecific C–H bond amination using an appropriately configured 1° carbamate was used to install a C–N bond in asymmetric fashion at a late stage in the total synthesis of (–)-TTX (**Scheme 12**).<sup>14</sup> These C–H activation methods and catalysts described by the Stanford group now offer a powerful tool for synthetic chemists to apply for the construction of functionalized amine frameworks.

#### Bis-[rhodium(α,α,α',α'-1,3-benzenedipropionic acid)]

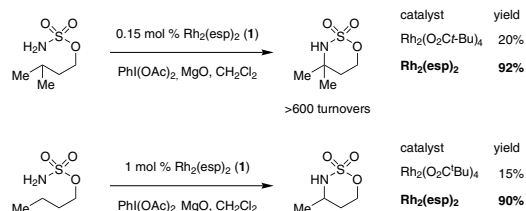
C<sub>32</sub>H<sub>40</sub>O<sub>8</sub>Rh<sub>2</sub>  
FW: 758.47



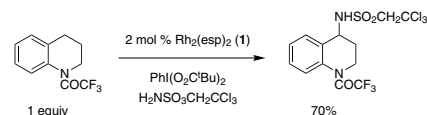
662623-100MG	100 mg
662623-500MG	500 mg



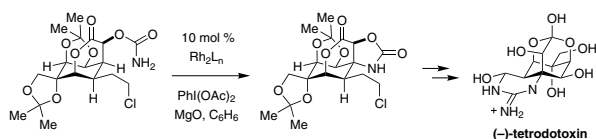
Scheme 9



Scheme 10



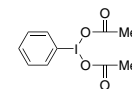
Scheme 11



Scheme 12

#### (Diacetoxyiodo)benzene

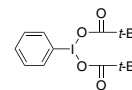
C<sub>10</sub>H<sub>11</sub>O<sub>4</sub>  
FW: 322.10  
[3240-34-4]



178721-5G	5 g
178721-25G	25 g
178721-100G	100 g

#### Bis(*tert*-butylcarbonyloxy)iodobenzene

C<sub>16</sub>H<sub>23</sub>O<sub>4</sub>  
FW: 406.26  
[57357-20-7]



662283-5G	5 g
662283-25G	25 g
662283-100G	100 g

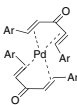
## Palladium Catalysts: Pd(dmdba)<sub>2</sub> and Pd EnCat™ Systems

C–C coupling reactions are arguably the most powerful transformations in synthetic organic chemistry, as simple molecules can be expeditiously converted into architecturally diverse structures. Among C–C bond forming reactions, the great importance of palladium catalysts has encouraged scientists to search for very active and, at the same time, stable palladium complexes that may advance research scale Heck, Suzuki, and Sonogashira processes to the industrial arena.<sup>15</sup> The cross-coupling of aryl halides and boronic acids in an efficient and selective manner, known as the Suzuki–Miyaura reaction,<sup>16</sup> represents one benchmark that a new Pd catalyst must be applied toward prior to entry into industrial process applications.

Pd<sub>2</sub>(dba)<sub>3</sub> is the most commonly used non-phosphine based Pd(0) precursor because of its air stability and proclivity to undergo dibenzylidene ligand dissociation, thus granting Pd faster access into the catalytic cycle. Fairlamb and co-workers have explored varying the π-electron accepting characteristics of the dba ligand and thus affected the Pd–η<sup>2</sup>-dba bond strength (**Scheme 13**).<sup>17</sup> They found that electron donating groups on the dba ligand decreased the magnitude of ligand back-bonding, thus increasing the concentration of the most reactive Pd(0) species in solution. This is the greatest advantage over Pd<sub>2</sub>(dba)<sub>3</sub> and is directly translated into improved catalyst activity and product yields in the reactions of various aryl chlorides with arylboronic acids (**Scheme 14**, **Table 3**).

### Bis(3,5,3',5'-dimethoxydibenzylideneacetone)palladium(0)

C<sub>42</sub>H<sub>44</sub>O<sub>10</sub>Pd  
FW: 815.21  
[811862-77-8]



656933-1G	1 g
656933-5G	5 g

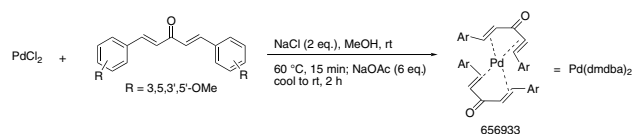
Another goal that Pd catalysts must achieve before industrial applications can be realized involves the recovery and reuse of the catalyst, because homogeneous palladium catalysts contaminate products, process equipment, and waste streams necessitating costly clean-up procedures. Furthermore, the loss of catalyst during the reaction and reaction work-up limits catalyst activity (TONs) and has proven to be cost prohibitive with respect to process scale. Sigma-Aldrich has addressed these issues by offering Pd EnCat™ catalysts, wherein the metal is microencapsulated within a polyurea matrix thereby preventing Pd leaching. The advantage of Pd EnCat™ catalysts are numerous: 1) low, residual metal levels in crude product (usually <10 ppm before purification); 2) easy recovery of catalyst; 3) compatibility of immobilized metal with various ligands to effect C–C bond forming reactions; 4) safer and easier to handle than Pd/C for hydrogenation; and 5) efficiency and economy gains through recovery and recycling. The range of processes mediated by Pd EnCat™ catalysts is well documented including Suzuki, Heck, carbonylation, and Stille couplings, to reductions of carbonyls, alkenes, and epoxides via hydrogenation (**Scheme 15**). Sigma-Aldrich carries a full line of Pd EnCat™ catalysts licensed through Reaxa and available with co-encapsulated phosphine ligands, thereby facilitating the removal of Pd metal and the ligand.

### Pd EnCat™ 30, loading: 0.4 mmol/g Pd

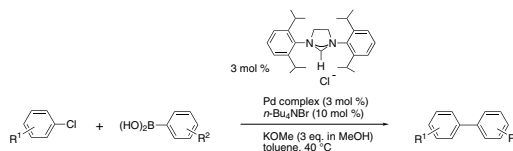
644714-1G	1 g
644714-10G	10 g
644714-100G	100 g

### Pd EnCat™ 40, loading: 0.4 mmol/g Pd

644722-1G	1 g
644706-10G	10 g
644706-100G	100 g



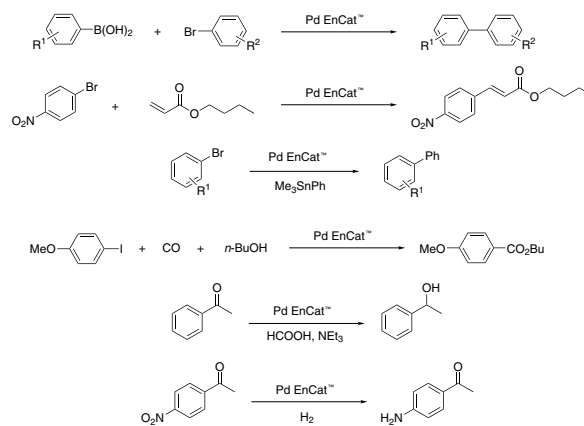
Scheme 13



Scheme 14

Entry	R <sup>1</sup> Ar-Cl	R <sup>2</sup> PhB(OH) <sub>2</sub>	% Conversion	
			Pd <sub>2</sub> (dba) <sub>3</sub>	Pd(dmdba) <sub>2</sub>
1	4-NO <sub>2</sub>	H	80	89
2	4-COMe	H	61	79
3	4-Me	4-OMe	83	89
4	4-OMe	H	63	83

Table 3



Scheme 15

### Pd EnCat™ TPP30, loading: 0.4 mmol/g Pd, Pd 1.0, TPP 0.8

644706-1G	1 g
644706-10G	10 g
644706-100G	100 g

### Pd EnCat™ TOTP30, loading: 0.4 mmol/g Pd, Pd 1.0, TOTP 0.5

644692-1G	1 g
644692-10G	10 g
644692-100G	100 g



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**Pd(II) EnCat™ BINAP30, loading: 0.39 mmol/g Pd, Pd 1.0, BINAP 0.25**

658693-1G	1 g
658693-10G	10 g
658693-100G	100 g

**2. Ligands****N-Heterocyclic Carbene (NHC) Ligands**

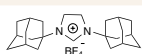
Rapid progress in cross-coupling reactions of unactivated substrates catalyzed by metal complexes has transformed the chemical marketplace through introduction of an extensive library of achiral and chiral phosphine ligands. The positive effects of phosphine ligands are exemplified in the numerous reports of highly efficient systems in terms of turnovers and selectivities applied to traditional industrial processes such as hydrogenation. However, the disadvantages in the high cost of producing tertiary (especially chiral) phosphines and their degradative tendency in converting to phosphine oxides have only now been addressed by the rich field of NHC ligands utilized in homogeneous catalysis.<sup>18</sup>

The advantages of N-heterocyclic carbenes as ancillary ligands are: 1) they are stronger  $\sigma$ -donors than phosphines, enabling favorable rates of palladium catalyzed oxidative addition of aryl chlorides; 2) the strong metal-carbenic bond of the NHC complex favors tight binding kinetics, therefore lessening ligand dissociation; 3) the presence of sterically encumbering groups bound to the *N*-atoms facilitate reductive elimination of the product from palladium; and 4) the activity of NHC ligands can be modified by the introduction of electronic directing substituents remotely, as witnessed in the synthesis of benzimidazolines that contain electronically dissimilar groups on the aromatic backbone.<sup>19</sup>

A wide range of NHC ligands that exhibit high activities in various important organic transformations when combined with metal pre-catalysts are now commercially available. NHC imidazolidine ligands with sterically encumbering groups such as mesityl, isopropyl, and adamantyl have been used in the Pd-catalyzed cyclization of anilides,<sup>20</sup> amination of aryl chlorides,<sup>21</sup> arylation with ester enolates to afford  $\alpha$ -aryl esters,<sup>22</sup> Sonogashira reactions of unactivated alkyl bromides,<sup>23</sup> and the ruthenium-catalyzed RCM reaction (Schemes 16–20).<sup>24</sup> This last example shows the power of NHC ligands to stabilize the metal active species in solution and thus imparts the ability of the catalyst to effect RCM on highly substituted and electron-poor olefinic reactants to yield tetrasubstituted products. Such pronounced reactivity was the exclusive domain of the Shrock alkylidene catalysts.<sup>25</sup> However, use of these imidazolidines leads to an improvement in performance over early ruthenium metathesis catalysts and provides additional stability features versus the Shrock system. Our goal at Sigma-Aldrich is to accelerate cutting-edge research projects in NHC ligand mediated chemistry. To this end, we are the first to offer a ligand kit composed of a diverse set of sterically demanding NHC ligands.

**1,3-Bis(1-adamantyl)imidazolium tetrafluoroborate**

C<sub>23</sub>H<sub>33</sub>BF<sub>4</sub>N<sub>2</sub>  
FW: 424.33  
[286014-42-4]



660035-1G	1 g
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**1,3-Di-isopropyl-imidazol-2-ylidinium tetrafluoroborate**

C<sub>9</sub>H<sub>17</sub>N<sub>2</sub> · BF<sub>4</sub>  
FW: 240.05  
[286014-34-4]



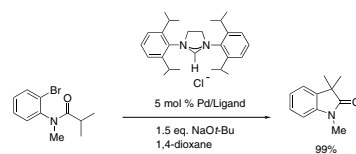
660019-1G	1 g
660019-5G	5 g

**Pd(0) EnCat™ 30NP, wet, nanoparticulate, loading: 0.4 mmol/g Pd**

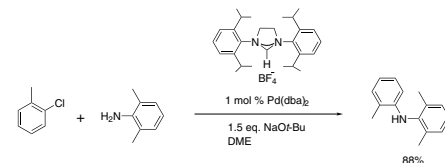
653667-1G	1 g
653667-10G	10 g
653667-100G	100 g

**Pd EnCat™ Kit**

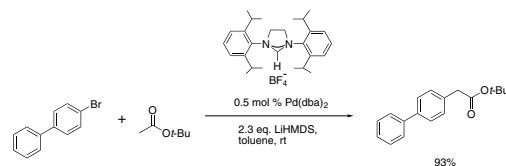
659959-1EA	1 kit
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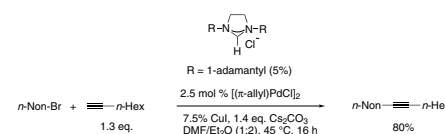
Scheme 16



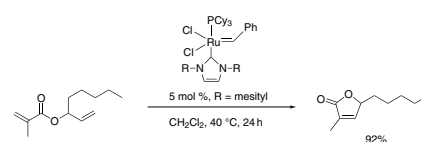
Scheme 17



Scheme 18



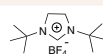
Scheme 19



Scheme 20

**1,3-Bis-(tert-butyl)-4,5-dihydro-1H-imidazolium tetrafluoroborate**

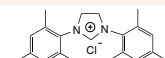
C<sub>11</sub>H<sub>23</sub>N<sub>2</sub> · BF<sub>4</sub>  
FW: 270.12  
[137581-21-6]



659991-1G	1 g
659991-5G	5 g

***N,N'*-(2,4,6-Trimethyl)dihydroimidazolium chloride**

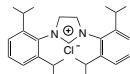
C<sub>21</sub>H<sub>27</sub>ClN<sub>2</sub>  
FW: 342.91



656631-1G	1 g
656631-5G	5 g

***N,N'*-(2,6-Diisopropylphenyl)dihydroimidazolium chloride**

C<sub>27</sub>H<sub>39</sub>ClN<sub>2</sub>  
 FW: 427.06  
 [258278-25-0]



656623-1G	1 g
656623-5G	5 g

**ChiralQuest Phosphine Ligands**

The field of asymmetric catalysis has been primarily represented by methodologies that have focused on incorporating hydrogen in a stereoselective manner into achiral molecules, especially in industrial applications. It is well known that hydrogen is the most common constituent in the immense realm of stereogenicity. Catalytic asymmetric hydrogenations are among the most widely used industrial catalytic processes due to their high turnover rates, efficiency, atom economy, and inexpensive material costs. Transition metal complexes associated with chiral phosphorus ligands are the preeminent choice of catalysts for asymmetric hydrogenation as a result of the tremendous efforts of researchers worldwide. The requirement of an electron-rich chiral phosphine ligand is at the core of this transformation.

Professor Xumu Zhang at Penn State has made remarkable advances by creating a toolbox of chiral phosphines that can be used on a variety of substrates, some of which have been historically resistant to facile hydrogenation.<sup>26</sup> Furthermore, an additional benefit in some reductions is reduced catalyst loading due to increased turnover numbers (TON). Sigma-Aldrich is pleased to announce an agreement with ChiralQuest to distribute research quantities of a series of Zhang's chiral phosphines and metal-ligand complexes for catalytic asymmetric hydrogenations (**Schemes 21–25**).

C3-TunePhos, a member of the atropisomeric aryl bisphosphine ligand family with tunable dihedral angles, provides comparable or superior enantioselectivities and catalytic abilities to BINAP in Ru-catalyzed asymmetric hydrogenation of β-ketoesters, cyclic β-(acylamino) acrylates, and α-phthalimide ketones (**Scheme 21**).

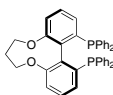
A highly electron-donating, low molecular weight, and rigid *P*-chiral bisphospholane ligand, TangPhos proves highly efficient in the rhodium-catalyzed hydrogenation of a variety of functionalized olefins such as α-dehydroamino acids, α-arylamides, β-(acylamino)-acrylates, itaconic acids, and enol acetates (**Schemes 22–23**).

Binapine, a highly electron-donating rigid ligand, demonstrates excellent enantioselectivity and reactivity, with TON up to 10,000 for the asymmetric hydrogenation of *Z*-β-aryl(β-acylamino) acrylates (**Scheme 24**).

(*R*)-Binaphane shows excellent enantioselectivity (up to >99% ee) for hydrogenation of *E/Z*-isomeric mixtures of β-substituted arylamides (**Scheme 25**).

**(*R*)-C<sub>3</sub>-TunePhos**

C<sub>39</sub>H<sub>32</sub>O<sub>2</sub>P<sub>2</sub>  
 FW: 594.62  
 [301847-89-2]



650862-100MG	100 mg
650862-500MG	500 mg

**(*S,S',R,R'*)-TangPhos**

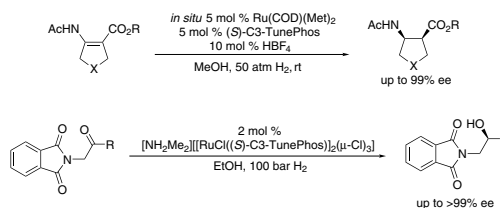
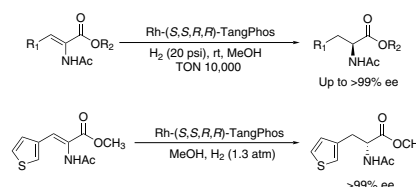
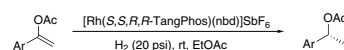
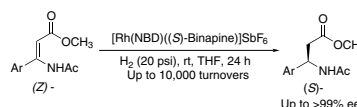
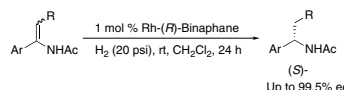
C<sub>16</sub>H<sub>32</sub>P<sub>2</sub>  
 FW: 286.37  
 [470480-32-1]



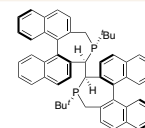
650889-100MG	100 mg
650889-500MG	500 mg

**NHC Ligands Kit**

662232-1EA 1 kit

**Scheme 21****Scheme 22****Scheme 23****Scheme 24****Scheme 25****(*S*)-Binapine**

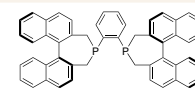
C<sub>52</sub>H<sub>48</sub>P<sub>2</sub>  
 FW: 734.89  
 [610304-81-9]



650870-100MG	100 mg
650870-500MG	500 mg

**(*R*)-Binaphane**

C<sub>50</sub>H<sub>36</sub>P<sub>2</sub>  
 FW: 698.77  
 [253311-88-5]



650854-100MG	100 mg
650854-500MG	500 mg



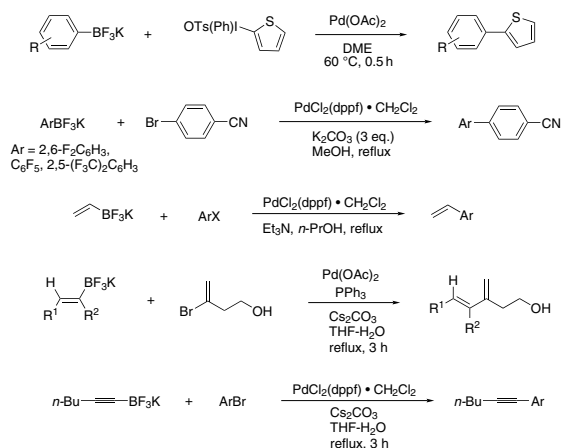
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### 3. Suzuki Coupling

#### Potassium Trifluoroborate Salts

Boronic acids, boronate esters, and organoboranes have been utilized for many years as the primary boron source in Suzuki–Miyaura-type reactions. These organoboron reagents have inherent limitations including: 1) boronic acids are often difficult to purify and have uncertain stoichiometry; 2) the boronate esters lack atom-economy and thus detract market value; and 3) boranes are limited by their hydroboration method of preparation, are air-sensitive, and lack functional-group compatibility.

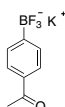
Potassium trifluoroborates are a special class of organoboron reagents that offer several advantages over the corresponding boronic acids and esters in that they are moisture- and air-stable, and are remarkably compliant with strong oxidative conditions. The epoxidation of C=C bonds in unsaturated alkyl- or aryltrifluoroborates proceeds with full conversion and selectivity, avoiding degradation of the boron functionality. Trifluoroborates are versatile coupling partners and are present as reagents in a vast array of C–C bond forming reactions (Scheme 26).<sup>27</sup> We have partnered with Gary Molander at the University of Pennsylvania in a collaborative effort to provide trifluoroborate salts, thereby expanding the palette of available boron reagents for cross-coupling reactions.



Scheme 26

#### Potassium 4-acetylphenyltrifluoroborate, 97%

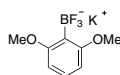
C<sub>8</sub>H<sub>7</sub>BF<sub>3</sub>KO  
FW: 226.05  
[252726-24-2]



657050-1G	1 g
657050-5G	5 g

#### Potassium 2,6-dimethoxyphenyltrifluoroborate, 95%

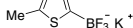
C<sub>8</sub>H<sub>8</sub>BF<sub>3</sub>KO<sub>2</sub>  
FW: 244.06



657085-1G	1 g
657085-5G	5 g

#### Potassium 5-methyl-2-thiophenyltrifluoroborate, 95%

C<sub>5</sub>H<sub>5</sub>BF<sub>3</sub>KS  
FW: 204.06



654949-1G	1 g
654949-5G	5 g

#### Potassium vinyltrifluoroborate, 95%

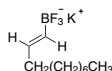
C<sub>2</sub>H<sub>3</sub>BF<sub>3</sub>K  
FW: 133.95  
[13682-77-4]



655228-1G	1 g
655228-5G	5 g

#### Potassium trans-1-decyltrifluoroborate, 95%

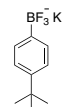
C<sub>10</sub>H<sub>19</sub>BF<sub>3</sub>K  
FW: 246.16



637882-1G	1 g
637882-5G	5 g

#### Potassium 4-tert-butylphenyltrifluoroborate, 95%

C<sub>10</sub>H<sub>13</sub>BF<sub>3</sub>K  
FW: 240.11



654728-1G	1 g
654728-10G	5 g

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

C<sub>6</sub>H<sub>3</sub>BF<sub>5</sub>K  
FW: 219.99



656992-1G	1 g
656992-5G	5 g

#### Potassium 4-methoxyphenyltrifluoroborate, 95%

C<sub>7</sub>H<sub>7</sub>BF<sub>3</sub>KO  
FW: 214.03  
[192863-36-8]



579068-1G	1 g
579068-5G	5 g

#### Potassium 4-chlorophenyltrifluoroborate, 95%

C<sub>6</sub>H<sub>4</sub>BClF<sub>3</sub>K  
FW: 218.45  
[661465-44-7]



657077-1G	1 g
657077-5G	5 g

#### Potassium 3-formylphenyltrifluoroborate, 95%

C<sub>7</sub>H<sub>5</sub>BF<sub>3</sub>KO  
FW: 212.02



657093-1G	1 g
657093-5G	5 g

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- (2) (a) Lipitor® sales surpassed \$10.8 billion USD in 2004, making it the top-selling drug in the world. Lipitor is a registered trademark of Pfizer, Inc. (b) (*R*)-C<sub>3</sub>-TunePhos is a member of the Sigma-Aldrich family of chiral phosphine ligands and licensed from ChiralQuest.
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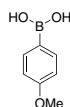


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# Boronic Acids and Esters

## 4-Methoxyphenylboronic acid

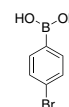
**417599**  
 $C_7H_9BO_3$   
 FW: 151.96  
 [5720-07-0]



1 g  
 5 g  
 25 g

## 4-Bromophenylboronic acid

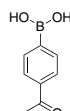
**B75956**  
 $C_6H_6BBrO_2$   
 FW: 200.83  
 [5467-74-3]



1 g  
 5 g

## 4-Acetylphenylboronic acid

**470821**  
 $C_8H_9BO_3$   
 FW: 163.97  
 [149104-90-5]



5 g  
 25 g

## Phenylboronic acid, 95%

**P20009**  
 $C_6H_7BO_2$   
 FW: 121.93  
 [98-80-6]



10 g  
 50 g  
 250 g

## Methylboronic acid, 97%

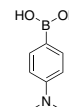
**165336**  
 $CH_3BO_2$   
 FW: 59.86  
 [13061-96-6]



1 g  
 5 g

## 4-(Dimethylamino)phenylboronic acid

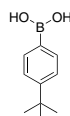
**483532**  
 $C_8H_{12}BNO_2$   
 FW: 165.00  
 [28611-39-4]



1 g  
 5 g  
 25 g

## 4-tert-Butylphenylboronic acid

**480053**  
 $C_{10}H_{15}BO_2$   
 FW: 178.04  
 [123324-71-0]



5 g  
 25 g

## Butylboronic acid, 97%

**163244**  
 $C_4H_{11}BO_2$   
 FW: 101.94  
 [4426-47-5]



1 g  
 5 g  
 25 g

## o-Tolylboronic acid

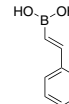
**393606**  
 $C_7H_9BO_2$   
 FW: 135.96  
 [16419-60-6]



1 g  
 5 g  
 25 g

## trans-2-Phenylvinylboronic acid, 97%

**473790**  
 $C_8H_9BO_2$   
 FW: 147.97  
 [6783-05-7]



5 g  
 25 g

## 3-Methoxyphenylboronic acid

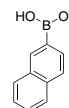
**441686**  
 $C_7H_9BO_3$   
 FW: 151.96  
 [10365-98-7]



1 g  
 10 g

## Naphthalene-1-boronic acid

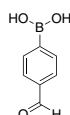
**N257**  
 $C_{10}H_9BO_2$   
 FW: 171.99  
 [13922-41-3]



5 g  
 25 g

## 4-Formylphenylboronic acid

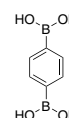
**431966**  
 $C_7H_7BO_3$   
 FW: 149.94  
 [87199-17-5]



1 g  
 5 g  
 25 g

## Benzene-1,4-diboronic acid

**417130**  
 $C_6H_6B_2O_4$   
 FW: 165.75  
 [4612-26-4]



5 g  
 25 g

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Cat. No.

#### Homogeneous Pd Catalysts I<sup>a</sup>

PdCl<sub>2</sub> • Pd(OAc)<sub>2</sub> • Pd<sub>2</sub>(dba)<sub>3</sub> • Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> • Pd(PPh<sub>3</sub>)<sub>4</sub> • [Pd(allyl)Cl]<sub>2</sub> • Pd(dppf)Cl<sub>2</sub>

659975-1EA

#### Heterogeneous Pd Catalysts I<sup>a</sup>

Palladium, 10 wt. % on activated carbon • Palladium, 10 wt. % (dry) on activated carbon • Palladium, 10 wt. % on Al<sub>2</sub>O<sub>3</sub> • Palladium, 5 wt. % on BaSO<sub>4</sub> • Palladium, 5 wt. % on CaCO<sub>3</sub>, lead-poisoned (Lindlar Catalyst) • Palladium hydroxide, 20 wt. % palladium on carbon

659967-1EA

#### Pd EnCat<sup>TMa</sup>

Pd EnCat<sup>TM</sup> 30 • Pd EnCat<sup>TM</sup> 40 • Pd EnCat<sup>TM</sup> TPP30 • Pd EnCat<sup>TM</sup> TOTP30 • Pd EnCat<sup>TM</sup> BINAP30 • Pd EnCat<sup>TM</sup> 30 NP

659959-1EA

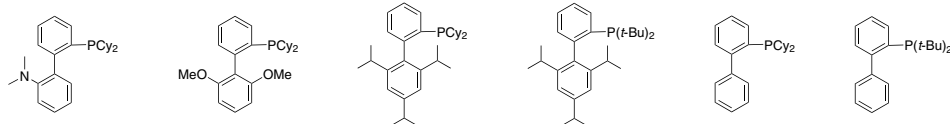
#### Phosphine Ligands I<sup>a</sup>

PPh<sub>3</sub> • PCy<sub>3</sub> • P(*t*-Bu)<sub>3</sub>H•BF<sub>4</sub> • P(*o*-tolyl)<sub>3</sub> • P(2-Furyl)<sub>3</sub> • dppp • dppf

659940-1EA

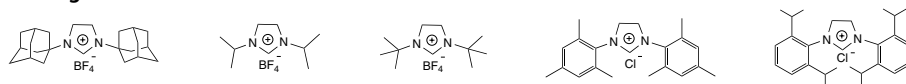
#### Buchwald Ligands Kit I<sup>a</sup>

659932-1EA



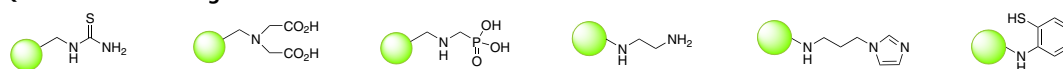
#### NHC Ligands I<sup>a</sup>

662232-1EA



#### QuadraPure<sup>TM</sup> Scavengers<sup>b</sup>

659428-1EA



<sup>a</sup>1-g sampler bottles. <sup>b</sup>5-g sampler bottles.

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SIGMA-ALDRICH DE ARGENTINA, S.A.  
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Fax: +420 246 003 291

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Fax: 23 17 60 50

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SIGMA-ALDRICH Sp. z o.o.  
Tel: +4861 829 01 00  
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Free Fax: 800 202178  
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SIGMA-ALDRICH CHEMIE LLC  
Swiss Free Call: 0800 80 00 80  
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P.O. Box 14508  
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Call Collect: 314-771-5750  
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