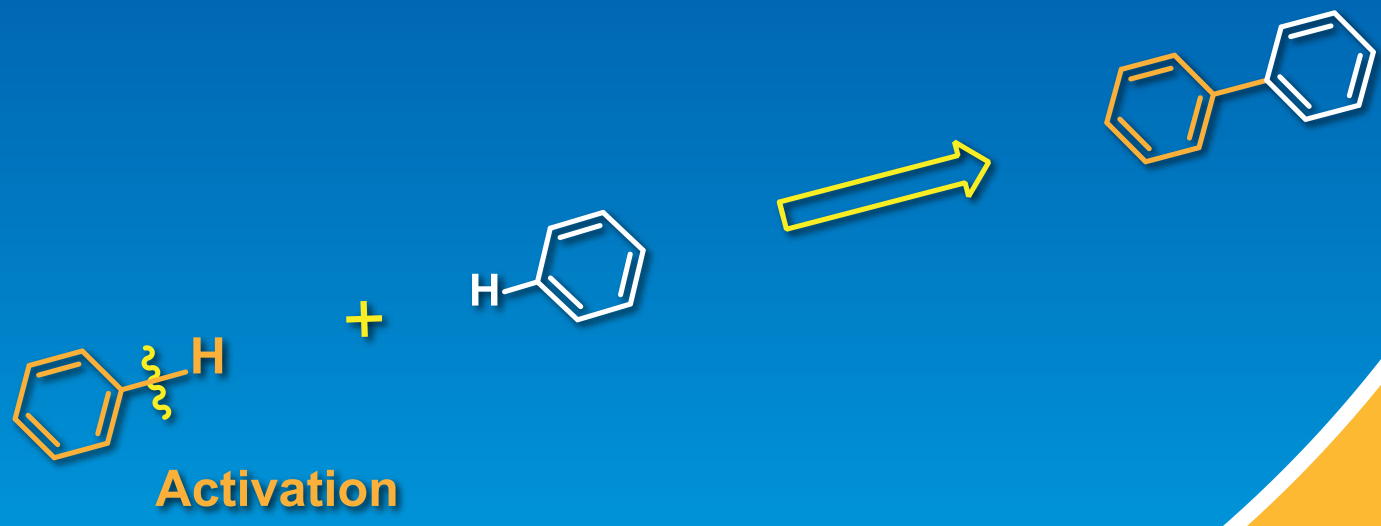
C-H Bond Activation Reaction



Metal Catalysts

Palladium Catalysts
Rhodium Catalysts
Iridium Catalysts
Ruthenium Catalysts
Copper Catalysts
Iron Catalysts
Nickel Catalysts
Gold Catalysts

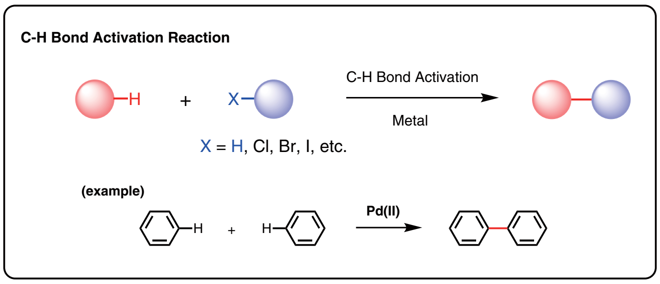
Ligands

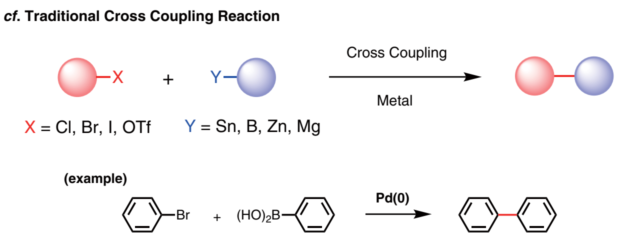
Directing Group Introducing Agents

Additives

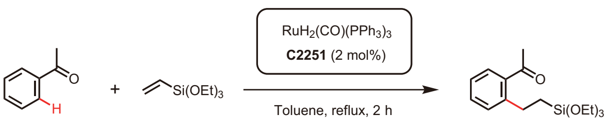
C-H Bond Activation Reaction

Recently, there have been a large number of reports on “C-H bond activation reaction”. C-H bond activation is a methodology for directly forming carbon-carbon bonds by activating a carbon-hydrogen bond, which is the most fundamental linkage in organic chemistry. Traditional cross coupling reactions have been one of the most useful synthetic methods for the formation of carbon-carbon bonds. However, the cross coupling reaction requires extra procedures for preparing organic halides (or triflates) compounds, and organic boron or metal compounds. On the other hand, the C-H bond activation can reduce these procedures, thus making this reaction a cost-effective and eco-friendly system.





C-H bonds generally have relatively high energy; therefore, the formation of a carbon-carbon or carbon-heteroatom bond by dissecting C-H bonds has been believed to be difficult. In 1993, Murai *et al*. reported the direct addition of C-H bonds of aromatic ketones to olefins in the presence of a catalytic amount of carbonyl(dihydrido)tris(triphenylphosphine)ruthenium(II) (**C2251**).[1] Since then, numerous examples of C-H bond activation have been reported.



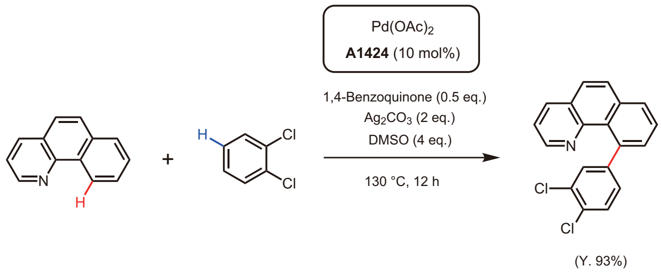
The reaction above proceeds without using halogenated compounds and organic boron or organic metal compounds. Thus, this system is cost-effective and eco-friendly.

In general, palladium(II), rhodium(I), iridium(I), ruthenium(II), copper(II), and iron(II) are widely used in C-H bond activation. There are a number of reports on C-H bond activation using these catalysts in the presence of appropriate ligands and activating reagents. In this brochure, some examples of C-H bond activation using palladium catalysts, iridium catalysts, and iron catalysts are shown as below.

● Pd(II) Catalysts

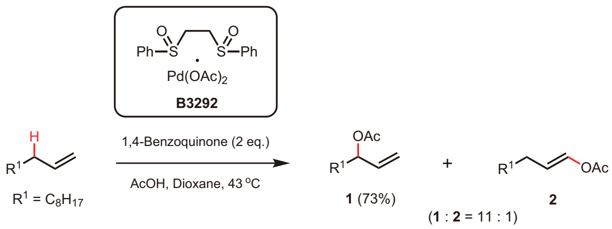
1) Regio-selective Coupling Reaction of 7,8-Benzoquinoline and Arene Compounds

Sanford *et al*. have reported the direct coupling reaction of 7,8-benzoquinoline and arene compounds using palladium acetate(II) (**A1424**).[2] In this reaction, a nitrogen atom of 7,8-benzoquinoline functions as a directing group to allow it to selectively introduce arenes at the C-10 position. Moreover, arene compounds also react with 7,8-benzoquinoline at the least sterically hindered positions. In this reaction system, 1,4-benzoquinone functions as a reaction promoter, and silver(I) carbonate oxidizes the generated Pd(0) species, which forms the Pd(II) / Pd(0) catalytic cycle.

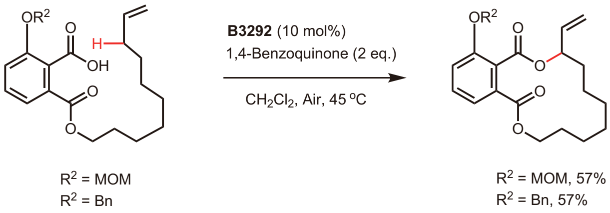


2) Allylic C-H Oxidation using “White Catalyst”

1,2-Bis(phenylsulfinyl)ethane palladium(II) diacetate (**B3292**) is a palladium catalyst, which was developed by M. C. White *et al.,* and named “White catalyst” after the developer. For an example of its characteristic reactivity differing from other homogeneous palladium catalysts, the allylic C-H oxidation reaction has been reported, in which an acetoxy group is introduced regioselectively into the allylic position.[3]

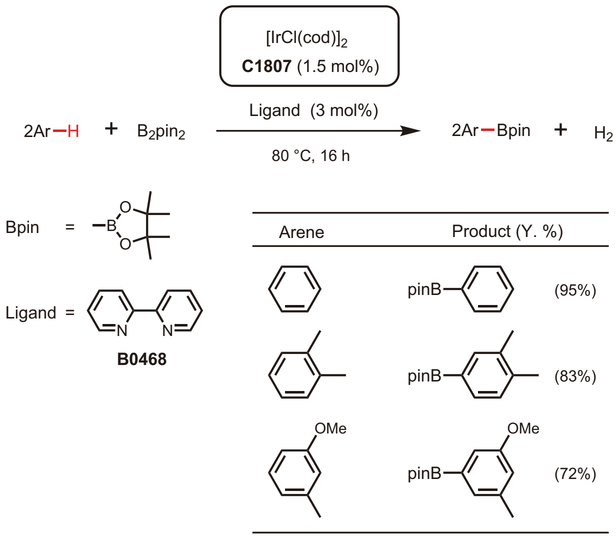


Moreover, White *et al.* have also reported the macrolactonization reaction of ortho-substituted salicylic acid substrates, applying the reaction into intramolecular allylic C-H oxidation, in which the corresponding 14-membered ring macrolides are obtained in moderate yields.[4)]



● Ir(I) Catalyst

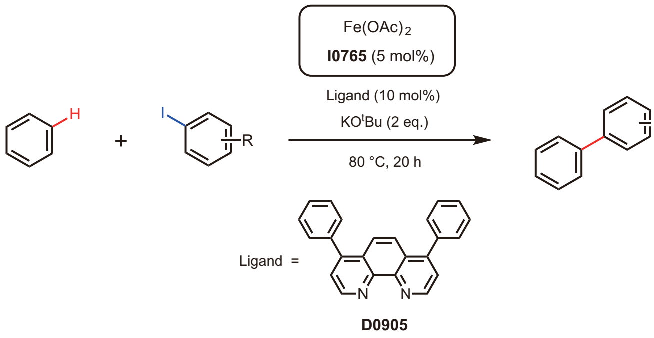
Miyaura, Ishiyama and Hargwig *et al.* have reported the direct C-H borylation in 2002.[5)] This reaction is the most famous and practical example of C-H bond activation using iridium catalysts. Aryl borates had been synthesized by the reaction of aryl lithium or magnesium reagents with trialkyl borates so far, however, their method allowed a one-step preparation of alkyl borates in a simple manner.

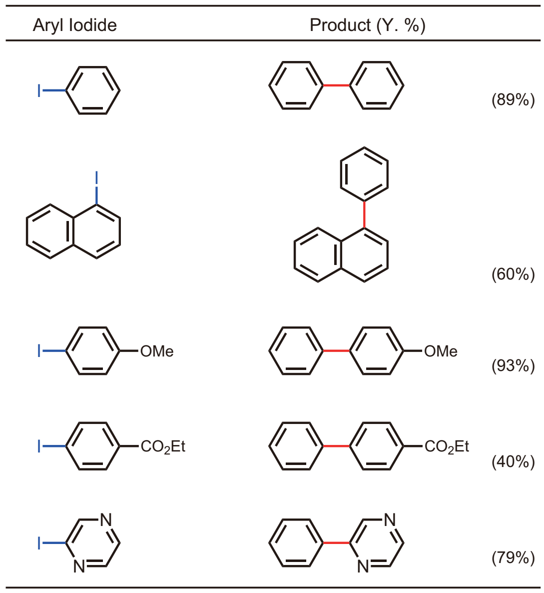


● Fe(II) Catalyst

Including palladium catalysts, which are frequently used for the Suzuki-Miyaura coupling reaction, transition metal catalysts, such as nickel or platinum, have been widely used for organic synthesis. However, the percentages of these metals in the earth's crust are extremely small, and their prices are rather expensive.[6)] On the other hand, iron is abundant and less expensive, and therefore, more and more chemists have focused their attention to organic synthesis using iron compounds as a catalyst. Cross coupling reactions using iron catalysts have been reported.[7)]

For an example of C-H activation using iron catalysts, Charette *et al.* have reported the direct coupling reaction of benzene with aryl iodides using iron(II) acetate (**I0765**).[8)] This reaction is highly cost-effective and environmentally friendly in the sense of using an iron catalyst, which is less expensive, and therefore, further development and applications are expected from the point of green chemistry.





Thus, C-H bond activation has been widely studied as a new methodology of carbon-carbon and carbon-heteroatom bond formations, following a cross coupling reaction and olefin metathesis.

TCI offers a variety of transition metal catalysts, ligands, and activating reagents readily available for C-H bond activation as below.

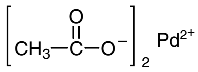
References

1) S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, *Nature* **1993,** *366*, 529.
2) K. L. Hull, M. S. Sanford, *J. Am. Chem. Soc*. **2007**, *129*, 11904.
3) M. S. Chen, N. Prabagaran, N. A. Labenz, M. C. White, *J. Am. Chem. Soc*. **2005**, *127*, 6970.
4) K. J. Fraunhoffer, N. Prabagaran, L. E. Sirois, M. C. White, *J. Am. Chem. Soc*. **2006**, *128*, 9032.
5) T. Ishiyama, J. Takagi, K. Ishida, N. Miyaura, N. R. Anastasi, J. F. Hartwig, *J. Am. Chem. Soc*. **2002**, *124*, 390.
6) J. Emsley, in *The Elements*, 3rd ed., Oxford Univ. Press, New York, **1998**.
7) T. Nagano, T. Hayashi, *Org. Lett*. **2004**, *6*, 1297; K. G. Dongo, H. Koh, M. Sau, C. L. L. Chai, *Adv. Synth. Catal*. **2007**, *349*, 1015; T. Hatakeyama, M. Nakamura, *J. Am. Chem. Soc*. **2007**, *129*, 9844.
8) F. Vallée, J. J. Mousseau, A. B. Charette, *J. Am. Chem. Soc*. **2010**, *132*, 1514.

Metal Catalysts

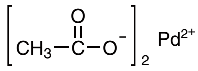
Palladium Catalysts

A1424 1g 5g



Palladium(II) Acetate [3375-31-3]

P2161 1g



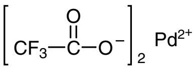
Palladium(II) Acetate(Purified) [3375-31-3]

P2106 1g 5g

$[Pd(CH_3COO)_2]_3$

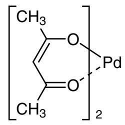
Palladium(II) Acetate Trimer [53189-26-7]

P1870 1g 5g



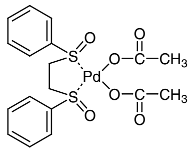
Palladium(II) Trifluoroacetate [42196-31-6]

B2018 1g 5g



Palladium(II) Acetylacetonate [14024-61-4]

B3292 200mg 1g



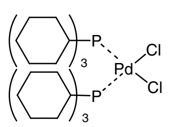
White Catalyst [858971-43-4]

B1676 1g 5g

$(CH_3CN)_2PdCl_2$

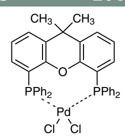
Bis(acetonitrile)palladium(II) Dichloride [14592-56-4]

B2055 1g 5g



Bis(tricyclohexylphosphine)-palladium(II) Dichloride [29934-17-6]

D4333 200mg 1g



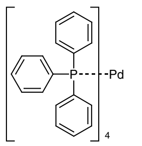
Dichloro[9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene]-palladium(II) [205319-10-4]

T3023 1g

$Pd(CH_3CN)_4(CF_3SO_3)_2$

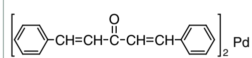
Tetrakis(acetonitrile)-palladium(II) Ditriflate [68569-14-2]

T1350 1g 5g 25g



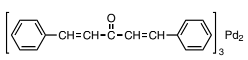
Tetrakis(triphenylphosphine)-palladium(0) [14221-01-3]

B1374 1g 5g



Bis(dibenzylideneacetone)-palladium(0) [32005-36-0]

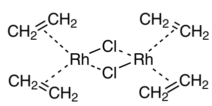
T2184 1g 5g



Tris(dibenzylideneacetone)-dipalladium(0) [51364-51-3]

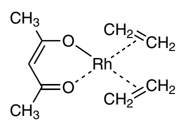
Rhodium Catalysts

C2461 200mg



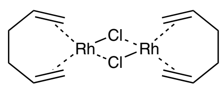
Chlorobis(ethylene)-rhodium(I) Dimer [12081-16-2]

A2100 200mg



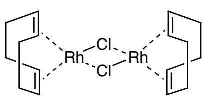
Acetylacetonatobis(ethylene)-rhodium(I) [12082-47-2]

C3194 100mg



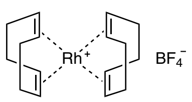
Chloro(1,5-hexadiene)-rhodium(I) Dimer [32965-49-4]

B1045 100mg 1g



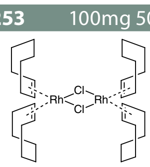
Chloro(1,5-cyclooctadiene)-rhodium(I) Dimer [12092-47-6]

B3961 100mg 1g



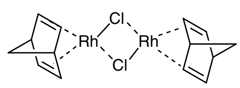
Bis(1,5-cyclooctadiene)-rhodium(I) Tetrafluoroborate [35138-22-8]

C2253 100mg 500mg



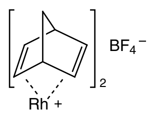
Chlorobis(cyclooctene)-rhodium(I) Dimer [12279-09-3]

N0453 100mg

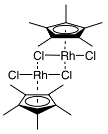


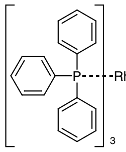
Norbornadiene Rhodium(I) Chloride Dimer [12257-42-0]

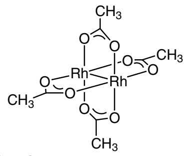
B2091 100mg

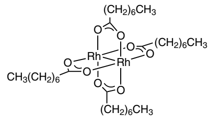


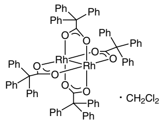
Bis[η-(2,5-norbornadiene)]-rhodium(I) Tetrafluoroborate [36620-11-8]

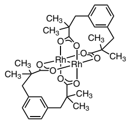
P1788 200mg 1g

(Pentamethylcyclopentadienyl)-rhodium(III) Dichloride Dimer [12354-85-7]

T0931 1g 5g

Tris(triphenylphosphine)rhodium(I) Chloride [14694-95-2]

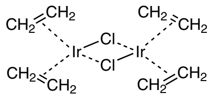
R0069 100mg 1g

Rhodium(II) Acetate Dimer [15956-28-2]

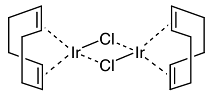
R0161 200mg 1g

Rhodium(II) Octanoate Dimer [73482-96-9]

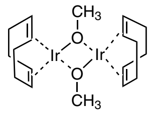
T1544 100mg

Tetrakis(triphenylacetato)-dirhodium(II) Dichloromethane Adduct [142214-04-8]

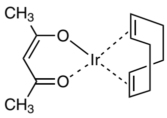
B4549 100mg

Bis[rhodium(α,α,α',α'-tetramethyl-1,3-benzenedipropionic Acid)] [819050-89-0]

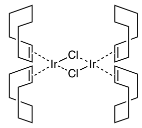
Iridium Catalysts

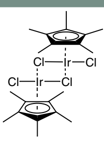
C3041 100mg

Chlorobis(ethylene)iridium(I) Dimer [39722-81-1]

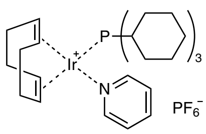
C1807 250mg 1g

Chloro(1,5-cyclooctadiene)-iridium(I) Dimer [12112-67-3]

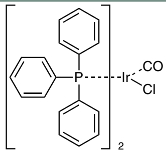
C2662 200mg 1g

(1,5-Cyclooctadiene)(methoxy)-iridium(I) Dimer [12148-71-9]

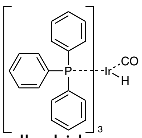
A2981 200mg 1g

(Acetylacetonato)-(1,5-cyclooctadiene)iridium(I) [12154-84-6]

C2985 200mg

Chlorobis(cyclooctene)-iridium(I) Dimer [12246-51-4]

P1763 1g

(Pentamethylcyclopentadienyl)-iridium(III) Dichloride Dimer [12354-84-6]

C2824 100mg

Crabtree's Catalyst [64536-78-3]

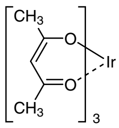
C2252 200mg 1g

Vaska's Catalyst [14871-41-1]

C3040 200mg 1g

Carbonylhydrido-tris(triphenylphosphine)-iridium(I) [17250-25-8]

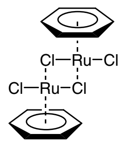
I0616 1g 5g

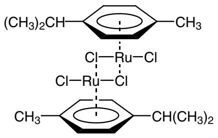
$IrCl_3 \cdot xH_2O$

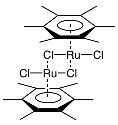
Iridium(III) Chloride Hydrate [14996-61-3]

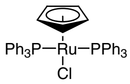
T2557 1g

Iridium(III) Acetylacetonate [15635-87-7]

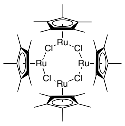
Ruthenium Catalysts

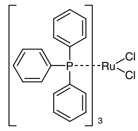
B1902 1g 5g

Benzeneruthenium(II) Chloride Dimer [37366-09-9]

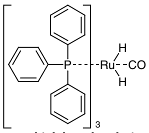
D2751 1g 5g

Dichloro(*p*-cymene)ruthenium(II) Dimer [52462-29-0]

H1010 1g

Dichloro(hexamethylbenzene)-ruthenium(II) Dimer [67421-02-7]

C2201 1g 5g

Cyclopentadienylbis(triphenyl-phosphine)ruthenium(II) Chloride [32993-05-8]

C3042 200mg 1g

Chloro(pentamethyl-cyclopentadienyl)ruthenium(II) Tetramer [113860-07-4]

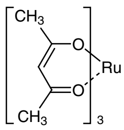
D1997 1g 5g

Tris(triphenylphosphine)-ruthenium(II) Dichloride [15529-49-4]

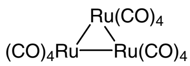
C2251 250mg 1g

Carbonyl(dihydrido)-tris(triphenylphosphine)-ruthenium(II) [25360-32-1]

R0074 1g 5g

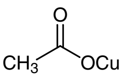
$RuCl_3$

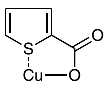
Ruthenium(III) Chloride [10049-08-8]

T2183 1g 5g

Ruthenium(III) Acetylacetonate [14284-93-6]

T2181 100mg 1g

Triruthenium Dodecacarbonyl [15243-33-1]

Copper Catalysts

A1540 5g 25g

Copper(I) Acetate [598-54-9]

C2312 1g 5g

Copper(I) 2-Thiophenecarboxylate [68986-76-5]

T2665 5g

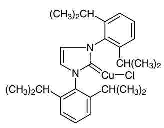
$(CH_3CN)_4Cu^+\ PF_6^-$

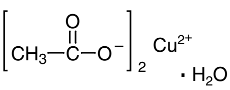
Tetrakis(acetonitrile)copper(I) Hexafluorophosphate [64443-05-6]

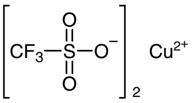
T2666 1g 5g 25g

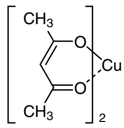
$(CH_3CN)_4Cu^+\ BF_4^-$

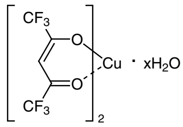
Tetrakis(acetonitrile)-copper(I) Tetrafluoroborate [15418-29-8]

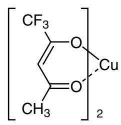
C2304 200mg 1g

Chloro[1,3-bis(2,6-diisopropyl-phenyl)imidazol-2-ylidene]-copper(I) [578743-87-0]

C2346 25g 500g

Copper(II) Acetate Monohydrate [6046-93-1]

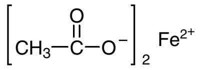
T1292 5g 25g

Copper(II) Trifluoromethanesulfonate [34946-82-2]

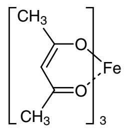
C0384 25g 250g

Copper(II) Acetylacetonate [13395-16-9]

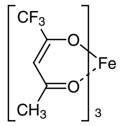
H0554 1g 5g

Copper(II) Hexafluoroacetyl-acetonate Hydrate [14781-45-4]

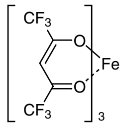
T0752 5g

Copper(II) Trifluoroacetylacetonate [23677-93-2]

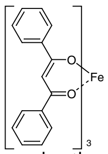
Iron Catalysts

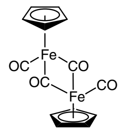
I0765 5g 25g

Iron(II) Acetate[3094-87-9]

I0079 25g 100g 500g

Iron(III) Acetylacetonate [14024-18-1]

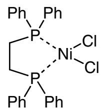
T0750 5g

Iron(III) Trifluoroacetylacetonate [28736-69-8]

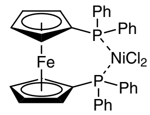
H0555 1g

Iron(III) Hexafluoroacetyl-acetonate [17786-67-3]

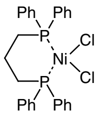
T1686 5g 25g

Tris(dibenzoylmethanato) Iron [14405-49-3]

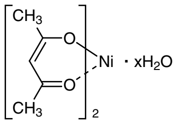
C1592 5g

Cyclopentadienyliron Dicarbonyl Dimer [12154-95-9]

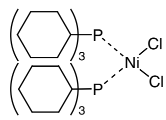
Nickel Catalysts

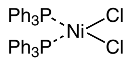
B2225 1g 5g 25g

[1,2-Bis(diphenylphosphino)-ethane]nickel(II) Dichloride [14647-23-5]

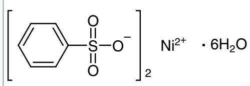
B2226 1g 5g

[1,1'-Bis(diphenylphosphino)-ferrocene]nickel(II) Dichloride [67292-34-6]

B1313 5g 25g

[1,3-Bis(diphenylphosphino)-propane]nickel(II) Dichloride [15629-92-2]

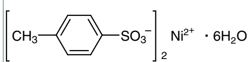
N0096 25g 100g 500g

Bis(2,4-pentanedionato)-nickel(II) Hydrate [3264-82-2]

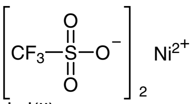
B3534 1g 5g

Bis(tricyclohexylphosphine)-nickel(II) Dichloride [19999-87-2]

B1571 10g 100g

Bis(triphenylphosphine)-nickel(II) Dichloride [14264-16-5]

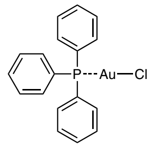
B0034 25g

Nickel(II) Benzenesulfonate Hexahydrate [39819-65-3]

N0850 25g 500g
$NiCl_2$
Nickel(II) Chloride Anhydrous [7718-54-9]

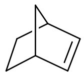
T0276 5g 25g

Nickel(II) *p*-Toluenesulfonate Hexahydrate [6944-05-4]

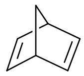
N0861 1g 5g

Nickel(II) Trifluoromethanesulfonate [60871-84-3]

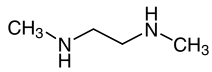
Gold Catalysts

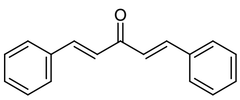
T2994 200mg 1g

(Triphenylphosphine)gold(I) Chloride [14243-64-2]

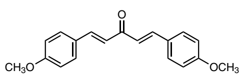
Ligands

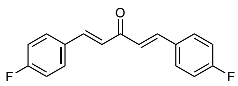
N0166 25g 400g

2-Norbornene [498-66-8]

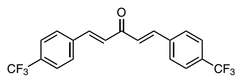
N0346 25mL 100mL 500mL

2,5-Norbornadiene (stabilized with BHT) [121-46-0]

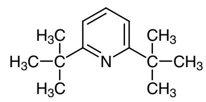
D0720 5mL 25mL

N,N'-Dimethylethylene-diamine [110-70-3]

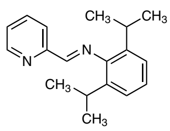
D0903 25g 250g

trans,trans-Dibenzylidene-acetone [35225-79-7]

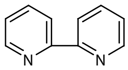
B4467 200mg 1g

trans,trans-Bis(4-methoxy-benzylidene)acetone [37951-12-5]

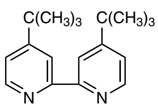
B2283 5g 25g

trans,trans-Bis(4-fluoro-benzylidene)acetone [53369-00-9]

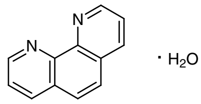
B4468 200mg 1g

trans,trans-Bis[4-(trifluoro-methyl)benzylidene]-acetone [103836-71-1]

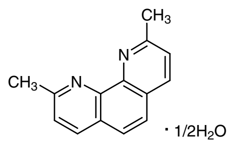
D1804 5g 25g

2,6-Di-*tert*-butylpyridine [585-48-8]

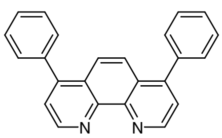
D4652 200mg 1g

trans-2,6-Diisopropyl-*N*-(2-pyridylmethylene)aniline [908294-68-8]

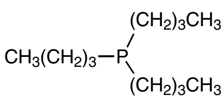
B0468 25g 100g 500g

2,2'-Bipyridyl [366-18-7]

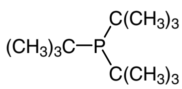
D3134 1g 5g

4,4'-Di-*tert*-butyl-2,2'-bipyridyl [72914-19-3]

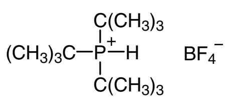
P0221 1g 25g

1,10-Phenanthroline Monohydrate [5144-89-8]

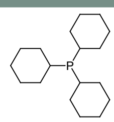
D0771 1g

Neocuproine Hemihydrate [34302-69-7]

D0905 1g 5g

Bathophenanthroline [1662-01-7]

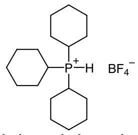
T0361 25mL 100mL 500mL

Tributylphosphine [998-40-3]

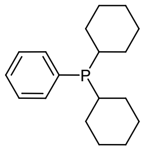
T1912 5g

Tri-*tert*-butylphosphine [13716-12-6]

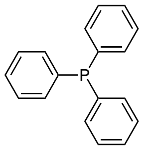
T2584 1g 5g

Tri-*tert*-butylphosphonium Tetrafluoroborate[131274-22-1]

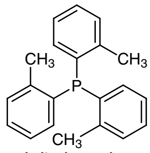
T1165 25mL

Tricyclohexylphosphine (contains Tricyclohexylphosphine Oxide) (*ca.* 18% in Toluene, *ca.* 0.60mol/L) [2622-14-2]

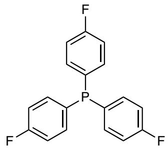
Please inquire for pricing and availability of listed products to our local sales representatives.

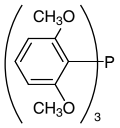
T2585 1g 5g

Tricyclohexylphosphonium Tetrafluoroborate [58656-04-5]

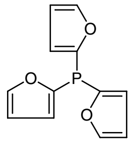
D2411 1g 5g

Dicyclohexylphenylphosphine [6476-37-5]

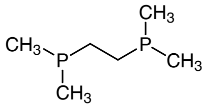
T0519 25g 100g 500g

Triphenylphosphine [603-35-0]

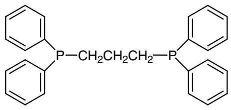
T1024 5g 25g

Tri(*o*-tolyl)phosphine [6163-58-2]

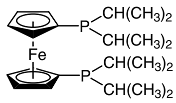
T2900 5g

Tris(4-fluorophenyl)phosphine [18437-78-0]

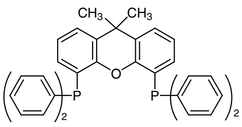
T1614 25g

Tris(2,6-dimethoxyphenyl)phosphine [85417-41-0]

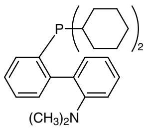
T1643 1g 5g

Tri(2-furyl)phosphine [5518-52-5]

B1174 100mg 1g

1,2-Bis(dimethylphosphino)ethane [23936-60-9]

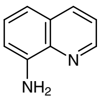
B1138 5g 25g

1,3-Bis(diphenylphosphino)propane [6737-42-4]

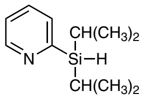
B2710 100mg 1g

1,1'-Bis(diisopropylphosphino)ferrocene [97239-80-0]

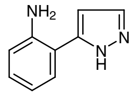
B2709 1g 5g 25g

4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene [161265-03-8]

D3389 1g 5g

2-(Dicyclohexylphosphino)-2'-(dimethylamino)biphenyl [213697-53-1]

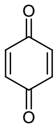
Directing Group Introducing Agents

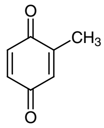
A0419 5g 25g 100g

8-Aminoquinoline [578-66-5]

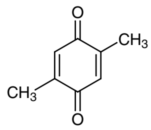
D4264 1g 5g

2-(Diisopropylsilyl)pyridine [1232692-92-0]

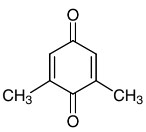
P1902 1g

2-(1*H*-Pyrazol-5-yl)aniline [111562-32-4]

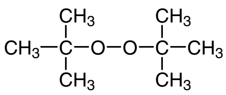
Additives

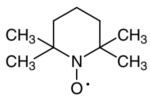
B0089 25g 100g 500g

1,4-Benzoquinone [106-51-4]

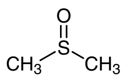
T1244 25g 500g

p-Toluquinone [553-97-9]

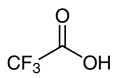
D0686 1g 5g 25g

p-Xyloquinone [137-18-8]

D2234 1g 5g 25g

2,6-Dimethyl-1,4-benzoquinone [527-61-7]

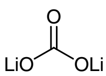
D3411 100mL

Di-*tert*-butyl Peroxide [110-05-4]

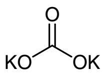
T1560 5g 25g

TEMPO Free Radical [2564-83-2]

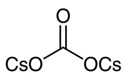
D0798 25g 500g

Dimethyl Sulfoxide [67-68-5]

T0431 25g 100g 500g

Trifluoroacetic Acid [76-05-1]

O0310 25g 500g
$2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$
Potassium Peroxymonosulfate [>45%(T) as $KHSO_5$] [37222-66-5]

L0224 25g 500g

Lithium Carbonate [554-13-2]

P1748 300g

Potassium Carbonate [584-08-7]

C2160 25g 100g

Cesium Carbonate [534-17-8]

T2052 100mL 500mL
$TiCl_4$
Titanium(IV) Chloride (14% in Dichloromethane, *ca.* 1.0mol/L) [7550-45-0]

T3238 100mL 500mL
$TiCl_4$
Titanium(IV) Chloride (*ca.* 19% in Toluene, *ca.* 1.0mol/L) [7550-45-0]

S0463 5g 25g
$AgSbF_6$
Silver Hexafluoroantimonate(V) [26042-64-8]

S0898 1g 5g
$Ag^+ \ (CF_3SO_2)_2N^-$
Silver Bis(trifluoromethanesulfonyl)imide [189114-61-2]

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