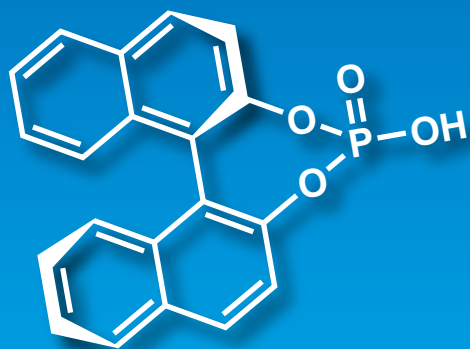
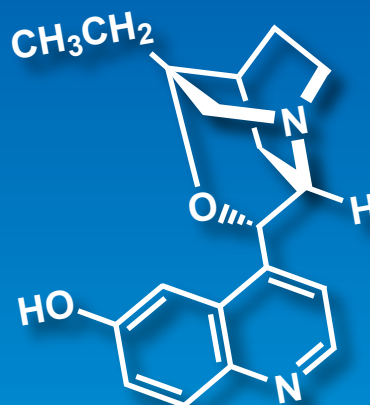
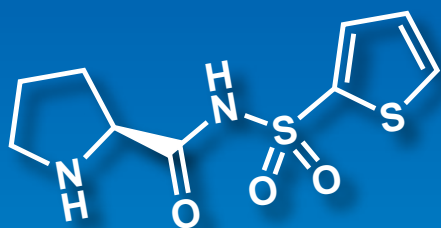
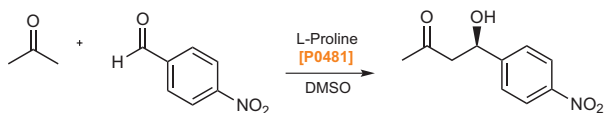


Asymmetric Organocatalysts

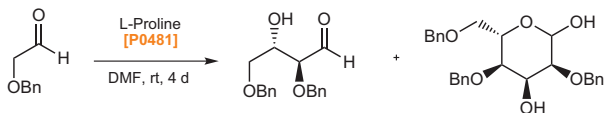


Asymmetric Organocatalysts

Asymmetric organocatalysis has emerged as a powerful synthetic tool that is complementary to metal-catalyzed reactions. Pioneering work in this area dates back to the 1970s in which Eder *et al.* and Hajos *et al.* separately reported an intramolecular asymmetric aldol reaction which employed L-proline [P0481] as catalyst.^{1,2)} This reaction was considered to be a special case at that time. Later in 2000, List *et al.* reported an L-proline-catalyzed intermolecular asymmetric aldol reaction.³⁾ The same year, MacMillan *et al.* documented the first highly enantioselective amine-catalyzed Diels-Alder reaction.⁴⁾ These reports received a great deal of attention and the research in the area of asymmetric organocatalysts has since thrived.⁵⁾

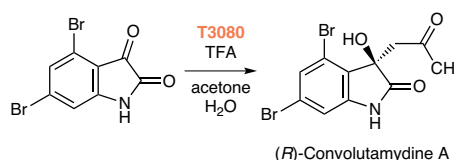
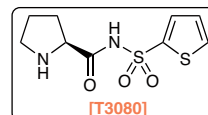


Later, the significance of these proline-catalyzed reactions was luminously demonstrated by MacMillan for the application to carbohydrate synthesis.⁶⁾ Córdova *et al.* reported a proline-catalyzed asymmetric conversion of protected glycol aldehydes into hexoses in one step.⁷⁾

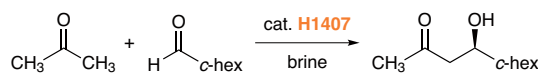
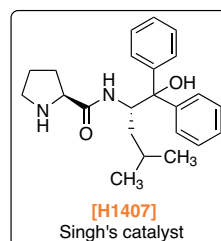


Compared with conventional transition metal complex catalysts, asymmetric organocatalysts offer several advantages including operational simplicity, their availability, and low toxicity which confer a direct benefit in the production of pharmaceuticals and contribution to green chemistry.

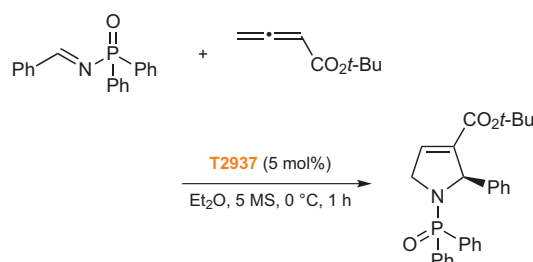
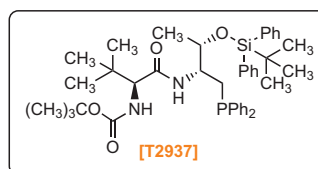
In the initial spectacular advances in asymmetric organocatalysis, proline and its analogues have been predominantly employed. Generally organocatalytic aldol reactions with ketones as acceptors require high catalyst loadings, however a recent development in this area enables the reaction with a lower catalyst loading. Nakamura *et al.* reported the enantioselective synthesis of (*R*)-convolutamydine by using 5 mol% of newly developed novel *N*-heteroaryl-sulfonylprolinamide [T3080].⁸⁾ In this reaction, amounts of the catalyst can be reduced to 0.5 mol% with retention of the enantioselectivity even though the time takes longer to complete the reaction.



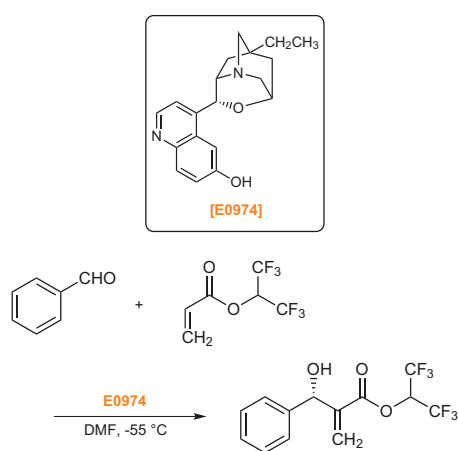
Singh *et al.* also developed a new class of proline-based organocatalysts and reported asymmetric direct aldol reactions with excellent enantioselectivities (>99% ee). A variety of ketones and aldehydes could be employed using 0.5 mol% of catalyst [H1407].⁹⁾



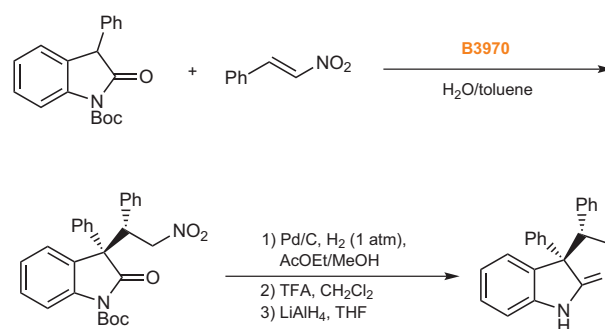
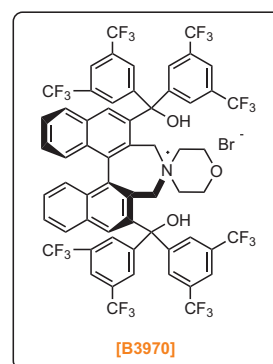
Due to the various advantages including ready availability and versatility, the asymmetric reactions using other amino acids as organocatalysts were also intensively studied. More recently, the group of Lu explored the possibility of deriving a wide array of novel multifunctional organocatalysts from amino acid structural scaffolds.¹⁰⁾ The new catalyst, dipeptide-derived phosphine [T2937], was proven to promote enantioselective [3+2] cycloadditions of allenes to acrylates or acrylamides.



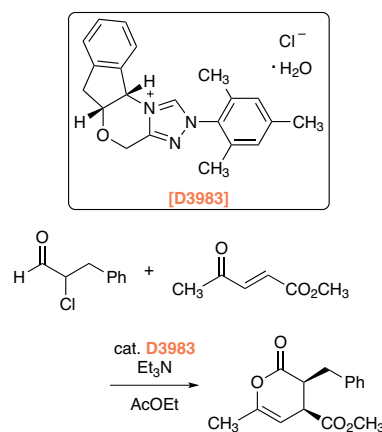
Cinchona alkaloids and their derivatives have been intensively used as chiral ligands for metal-catalyzed reactions or as organocatalysts as demonstrated in Sharpless asymmetric dihydroxylation with an OsO_4 -cinchona alkaloids complex.¹¹⁾ It is considered as one of the most privileged chiral inducers. Cinchona alkaloids-derived catalysts could be effectively applied for nearly all classes of organic reactions. The quinuclidinyl moiety as a tertiary amine could serve as an active center for Brønsted base catalysis, Lewis base catalysis, and nucleophilic catalysis. Upon alkylation of the quinuclidine nitrogen, the resulting ammonium salts could serve as phase transfer catalysts, another class of organic catalysis. Hatakeyama, Ishihara, *et al.* have developed α -isocupreine (α -ICPN) [E0974], a pseudoenantiomer of β -isocupreidine [I0728] and reported the application to an efficient asymmetric Morita-Baylis-Hillman (MBH) reaction.¹²⁾



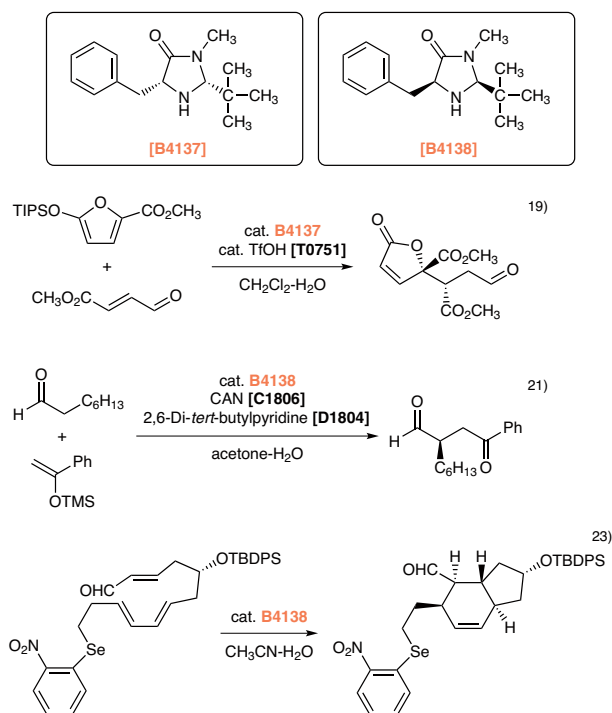
Since the pioneering work on asymmetric synthesis of amino acids using *N*-benzyl cinchoninium halide as a chiral phase transfer catalyst in 1980s,¹³⁾ numerous cinchona alkaloids-derived chiral phase-transfer catalysts have been developed.¹⁴⁾ In the late 1990s, a totally new aspect on the design of chiral phase-transfer catalyst, based on the C_2 -symmetrical chiral binaphthyl moiety, has emerged.¹⁵⁾ The ongoing efforts towards the simplification of the catalyst have led to the novel catalyst which could be employed under even milder conditions with excellent enantioselectivities. Maruoka *et al.* reported an enantioselective conjugate addition of 3-substituted oxindoles to Michael acceptors under neutral conditions in a water-rich solvent in the presence of a newly developed morpholine-derived chiral phase-transfer catalyst [B3970] without base additives.¹⁶⁾



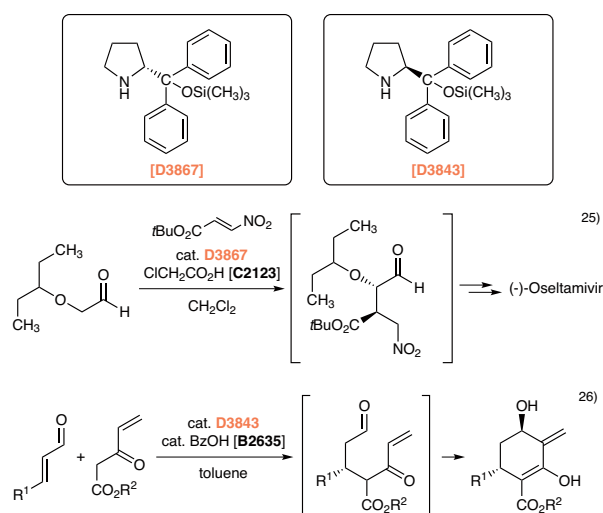
Nucleophilic carbene is an emerging class of asymmetric organocatalysis. Since the report of the first asymmetric intramolecular Stetter reaction by Enders *et al.*, there have been many reports on asymmetric carbon-carbon bond formation reactions *via* umpolung of aldehydes mediated by *N*-heterocyclic carbene (NHC) catalysts.¹⁷⁾ Bode *et al.* have reported highly enantioselective Diels-Alder reactions to afford dihydropyridinones using an NHC catalyst [D3983] generated *in situ*.¹⁸⁾



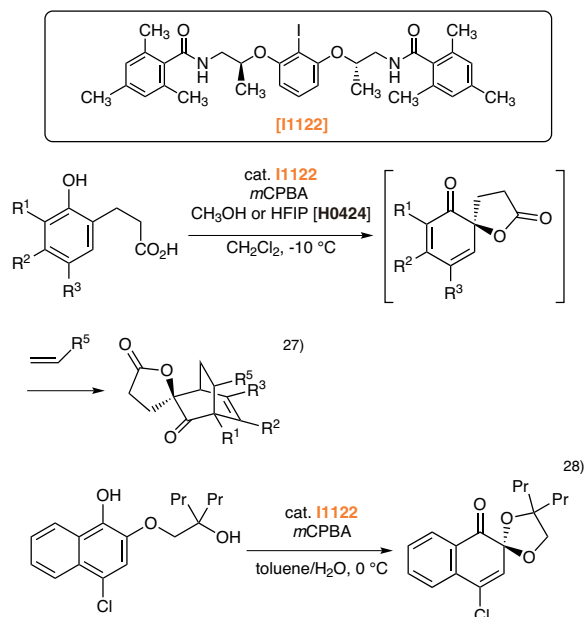
The imidazolidinone derivatives [B4137] [B4138] are asymmetric organocatalysts developed by MacMillan *et al.* To date, various types of asymmetric reactions using **B4137** and **B4138** have been reported, such as Mukaiyama-Michael addition,¹⁹⁾ epoxidation of α,β -unsaturated aldehydes,²⁰⁾ 1,3-addition of aldehydes,²¹⁾ and the Diels-Alder reaction.²²⁾ The desired products are realized in high yields and selectivity in all the cases. These reactions are often utilized in total syntheses of natural products to construct complex condensed-ring structures such as in spinosyn.²³⁾ Thus, **B4137** and **B4138** are powerful tools and their use in new asymmetric reactions is anticipated.



The two prolinol derivatives **D3867** and **D3843**, known as Hayashi-Jørgensen catalysts are utilized in various types of asymmetric reactions. For instance, Hayashi *et al.* have reported an asymmetric Michael addition of nitroalkenes and aldehydes, which gives *syn* adducts with high enantio- and diastereoselectivities.²⁵⁾ Furthermore, utilizing this reaction as a key early-stage step allowed them to achieve a short synthesis of the anti-flu drug oseltamivir phosphate.²⁵⁾ Additionally, Jørgensen's group have reported a tandem Michael/intramolecular Morita-Baylis-Hillman reaction to afford cyclohexanone derivatives.²⁶⁾



Ishihara's group has developed a new iodoarene catalyst **[I1122]** for the enantioselective spiroactonization.²⁷⁾ The given spiroactone has a diene moiety, so that it affords an optically active fused ring compound in one-pot synthesis through Diels-Alder reaction with an olefin. Furthermore, **I1122** is also utilized in the construction of asymmetric cyclic acetals.²⁸⁾



References

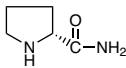
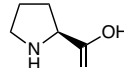
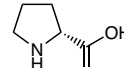
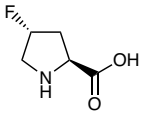
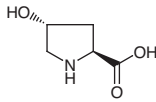
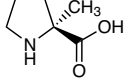
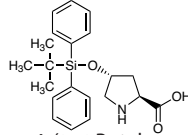
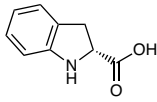
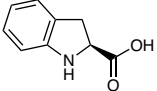
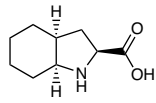
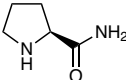
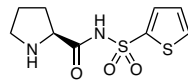
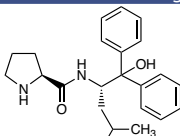
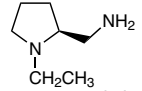
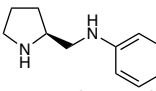
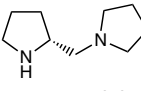
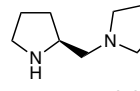
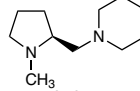
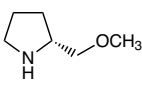
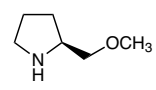
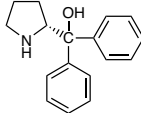
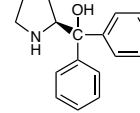
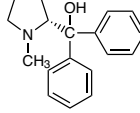
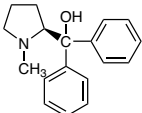
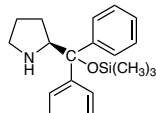
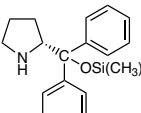
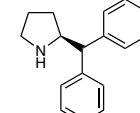
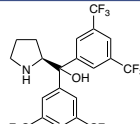
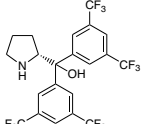
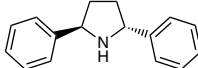
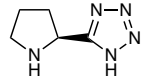

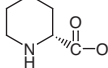
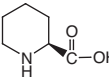
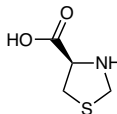
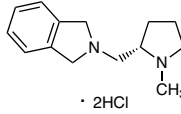
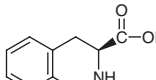
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The list of products

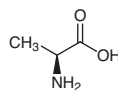
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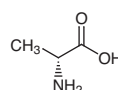
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Amino Acids	8
Cinchona Alkaloids	8
Chiral Imidazolidinones	9
Chiral Oxazaborolidines	9
Chiral Isothioureas	9
Chiral Diols	9
Chiral Phosphoric Acids	10
Chiral Sulfonic Acids	10
Chiral Amines	10
Chiral Ammonium Salts	10
Chiral <i>N</i>-Heterocyclic Carbenes (NHC)	10
Others	11

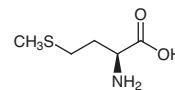
Prolines, Proline Analogs

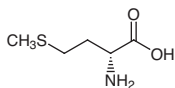
		P2083 1g 5g  D-Prolinamide CAS RN: 62937-45-5	P0481 25g 250g  L-Proline CAS RN: 147-85-3	P0994 5g 25g  D-Proline CAS RN: 344-25-2
F0818 50mg  trans-4-Fluoro-L-proline CAS RN: 2507-61-1	H0296 5g 25g 100g  trans-4-Hydroxy-L-proline CAS RN: 51-35-4	M2077 1g 5g  α-Methyl-L-proline CAS RN: 42856-71-3	B3440 1g 5g  trans-4-(tert-Butyl-diphenylsilyloxy)-L-proline CAS RN: 259212-61-8	I0589 1g  (R)-(+)-Indoline-2-carboxylic Acid CAS RN: 98167-06-7
I0395 1g 5g  (S)-(-)-Indoline-2-carboxylic Acid CAS RN: 79815-20-6	O0370 1g 5g  (2S,3aS,7aS)-Octahydro-1H-indole-2-carboxylic Acid CAS RN: 80875-98-5	P1382 1g 5g 25g  L-Prolinamide CAS RN: 7531-52-4	T3080 100mg  N-(2-Thiophenesulfonyl)-L-prolinamide CAS RN: 1089663-51-3	H1407 200mg 1g  Singh's Catalyst CAS RN: 910110-45-1
A1301 1g 5g  (S)-(-)-2-Aminomethyl-1-ethylpyrrolidine CAS RN: 22795-99-9	A0945 1g 5g  (S)-(+)-2-(Anilinomethyl)pyrrolidine CAS RN: 64030-44-0	P1925 1g  (R)-(-)-1-(2-Pyrrolidinylmethyl)pyrrolidine CAS RN: 60419-23-0	P1241 1g 5g  (S)-(+)-1-(2-Pyrrolidinylmethyl)pyrrolidine CAS RN: 51207-66-0	M1183 1g 5g  (S)-(-)-1-Methyl-2-(1-piperidinomethyl)pyrrolidine CAS RN: 84466-85-3
M1169 1g 5g  (R)-2-(Methoxymethyl)pyrrolidine CAS RN: 84025-81-0	M1161 1g 5g  (S)-2-(Methoxymethyl)pyrrolidine CAS RN: 63126-47-6	D2365 1g 5g  (R)-(+)-α,α-Diphenyl-2-pyrrolidinemethanol CAS RN: 22348-32-9	D2735 1g 5g  (S)-(-)-α,α-Diphenyl-2-pyrrolidinemethanol CAS RN: 112068-01-6	H0784 100mg 1g 5g  (R)-(-)-2-[Hydroxy(diphenyl)methyl]-1-methylpyrrolidine CAS RN: 144119-12-0
H0768 100mg 1g 5g  (S)-(+)-2-[Hydroxy(diphenyl)methyl]-1-methylpyrrolidine CAS RN: 110529-22-1	D3843 1g 5g  (S)-Hayashi-Jorgensen Catalyst CAS RN: 848821-58-9	D3867 1g 5g  (R)-Hayashi-Jorgensen Catalyst CAS RN: 943757-71-9	D3804 1g  (S)-(-)-2-(Diphenylmethyl)pyrrolidine CAS RN: 119237-64-8	B5701 1g  (S)-α,α-Bis[3,5-bis(trifluoromethyl)phenyl]-2-pyrrolidinemethanol CAS RN: 848821-76-1
B5882 1g 5g  (R)-Bis[3,5-bis(trifluoromethyl)phenyl]pyrrolidin-2-yl)methanol CAS RN: 948595-00-4	D3185 100mg  (2R,5R)-2,5-Diphenylpyrrolidine CAS RN: 155155-73-0	P1784 100mg 500mg  (S)-5-(Pyrrolidin-2-yl)-1H-tetrazole CAS RN: 33878-70-5	A1043 100mg 1g  L-Azetidine-2-carboxylic Acid CAS RN: 2133-34-8	P1830 5g 25g  D-Pipecolic Acid CAS RN: 1723-00-8
P1404 1g 5g  L-Pipecolic Acid CAS RN: 3105-95-1	T0219 25g 500g  L-Thioprolin CAS RN: 34592-47-7	M1995 1g 5g  (S)-2-[(1-Methyl-2-pyrrolidinyl)methyl]isoindoline Dihydrochloride	T1515 5g 25g  (S)-(-)-1,2,3,4-Tetrahydroisoquinoline-3-carboxylic Acid CAS RN: 74163-81-8	

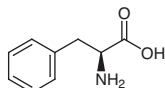
Amino Acids

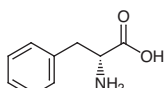
A0179 25g 250g

 L-Alanine
CAS RN: 56-41-7

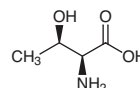
A0177 5g 25g

 D-Alanine
CAS RN: 338-69-2

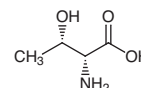
M0099 25g 100g 500g

 L-Methionine
CAS RN: 63-68-3

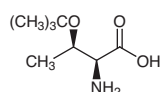
M0102 1g 5g 25g

 D-Methionine
CAS RN: 348-67-4

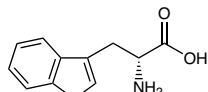
P0134 25g 250g

 L-Phenylalanine
CAS RN: 63-91-2

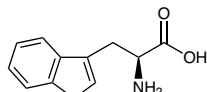
P0135 5g 25g

 D-Phenylalanine
CAS RN: 673-06-3

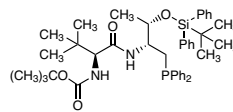
T0230 25g 100g 500g

 L-(-)-Threonine
CAS RN: 72-19-5

T0228 25g 100g 500g

 D-(+)-Threonine
CAS RN: 632-20-2

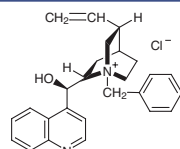
B3398 1g 5g

 O-tert-Butyl-L-threonine
CAS RN: 4378-13-6

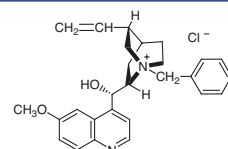
T0539 5g 25g

 D-Tryptophan
CAS RN: 153-94-6

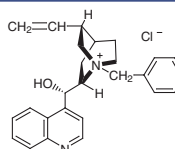
T0541 25g 100g

 L-Tryptophan
CAS RN: 73-22-3

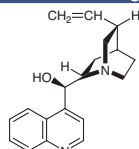
T2937 100mg

 O-TBDPS-D-Thr-N-Boc-
L-tert-Leu-Diphenylphosphine
CAS RN: 1264520-63-9

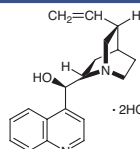
Cinchona Alkaloids

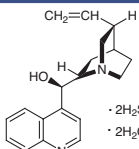
B1683 10g

 N-Benzylcinchonidinium Chloride
CAS RN: 69257-04-1

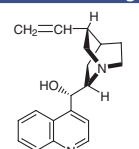
B1684 5g

 N-Benzylquinidininium Chloride
CAS RN: 77481-82-4

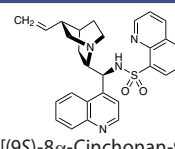
B1689 5g

 N-Benzylcinchoninium Chloride
CAS RN: 69221-14-3

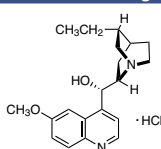
C0347 25g 100g

 Cinchonidine
CAS RN: 485-71-2

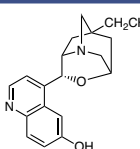
C0348 25g

 Cinchonidine Dihydrochloride
CAS RN: 24302-67-8

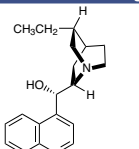
C0349 25g 500g

 Cinchonidine Sulfate Dihydrate
CAS RN: 524-61-8

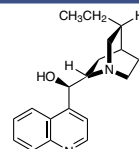
C0350 25g 200g

 Cinchonine
CAS RN: 118-10-5

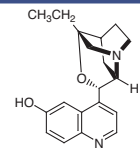
C2728 100mg

 N-[(9S)-8α-Cinchonan-9-yl]-
quinoline-8-sulfonamide
CAS RN: 1440939-88-7

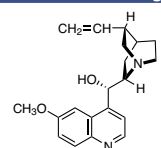
H0752 25g 250g

 Hydroquinidine Hydrochloride
CAS RN: 1476-98-8

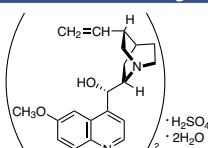
E0974 100mg

 α-Isocupreine
CAS RN: 1476067-44-3

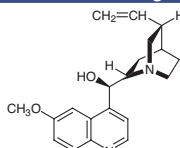
H1701 1g 5g

 Hydrocinchonine
CAS RN: 485-65-4

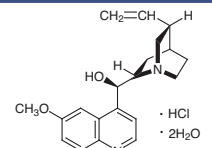
H1702 1g 5g

 Hydrocinchonidine
CAS RN: 485-64-3

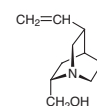
I0728 1g

 β-Isocupreidine
CAS RN: 253430-48-7

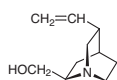
Q0006 5g 25g

 Quinidine
CAS RN: 56-54-2

Q0010 5g 25g

 Quinidine Sulfate Dihydrate
CAS RN: 6591-63-5

Q0028 25g 100g

 Quinine
CAS RN: 130-95-0

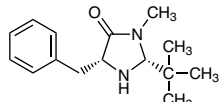
Q0030 25g

 Quinine Hydrochloride Dihydrate
CAS RN: 6119-47-7

Q0074 100mg 1g

 Quincorine
CAS RN: 207129-35-9

Q0076 100mg 1g

 Quincoridine
CAS RN: 207129-36-0

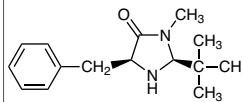
Chiral Imidazolidinones

B4137 200mg 1g



(2R,5R)-(+)-2-tert-Butyl-3-methyl-5-benzyl-4-imidazolidinone
CAS RN: 390766-89-9

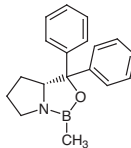
B4138 200mg 1g



(2S,5S)-(-)-2-tert-Butyl-3-methyl-5-benzyl-4-imidazolidinone
CAS RN: 346440-54-8

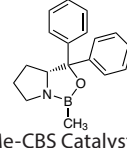
Chiral Oxazaborolidines

D2130 1g 5g



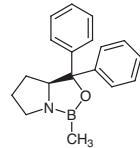
(R)-Me-CBS Catalyst
CAS RN: 112022-83-0

D5911 5mL 25mL



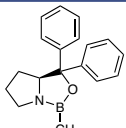
(R)-Me-CBS Catalyst
(ca. 1mol/L in Toluene)
CAS RN: 112022-83-0

D2131 1g 5g



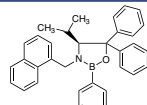
(S)-Me-CBS Catalyst
CAS RN: 112022-81-8

D5912 5mL 25mL



(S)-Me-CBS Catalyst
(ca. 1mol/L in Toluene)
CAS RN: 112022-81-8

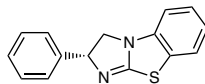
I0801 10mL



(S)-4-Isopropyl-3-(1-naphthylmethyl)-2,5,5-triphenyl-1,3,2-oxazaborolidine
CAS RN: 850661-66-4

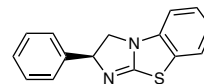
Chiral Isothioureas

B3296 200mg 1g 5g



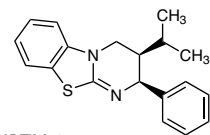
(+)-BTM
CAS RN: 885051-07-0

B3549 1g



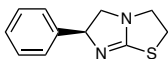
(-)-BTM
CAS RN: 950194-37-3

D4808 50mg 200mg



HBTM-2.1
CAS RN: 1203507-02-1

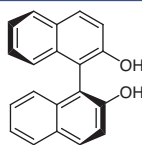
T1215 10g 25g



(-)-Tetramisole Hydrochloride
CAS RN: 16595-80-5

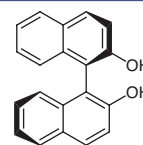
Chiral Diols

B1100 1g 5g 25g



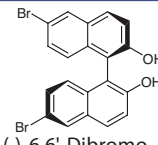
(S)-(-)-1,1'-Bi-2-naphthol
CAS RN: 18531-99-2

B1142 1g 5g 25g



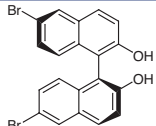
(R)-(+)-1,1'-Bi-2-naphthol
CAS RN: 18531-94-7

D2729 1g



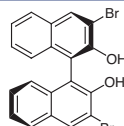
(R)-(-)-6,6'-Dibromo-1,1'-bi-2-naphthol
CAS RN: 65283-60-5

D2730 1g 5g



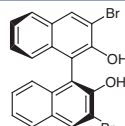
(S)-(+)-6,6'-Dibromo-1,1'-bi-2-naphthol
CAS RN: 80655-81-8

D2810 1g 5g



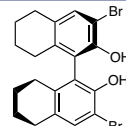
(R)-3,3'-Dibromo-1,1'-bi-2-naphthol
CAS RN: 111795-43-8

D2811 1g 5g



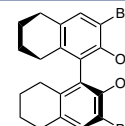
(S)-3,3'-Dibromo-1,1'-bi-2-naphthol
CAS RN: 119707-74-3

D4418 1g 5g



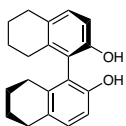
(R)-(+)-3,3'-Dibromo-5,5',6,6',7,7',8,8'-octahydro-1,1'-bi-2-naphthol
CAS RN: 65355-08-0

D5107 1g



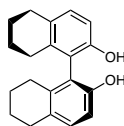
(S)-3,3'-Dibromo-1,1'-bi-2-naphthol
CAS RN: 765278-73-7

O0282 1g 5g 25g



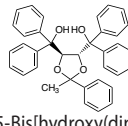
(R)-(+)-5,5',6,6',7,7',8,8'-Octahydro-1,1'-bi-2-naphthol
CAS RN: 65355-14-8

O0283 1g 5g



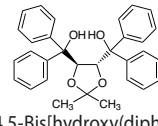
(S)-(-)-5,5',6,6',7,7',8,8'-Octahydro-1,1'-bi-2-naphthol
CAS RN: 65355-00-2

B1615 1g



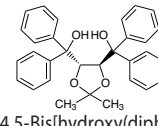
(+)-4,5-Bis(hydroxy(diphenyl)methyl)-2-methyl-2-phenyl-1,3-dioxolane
CAS RN: 109306-21-0

B1614 1g 5g



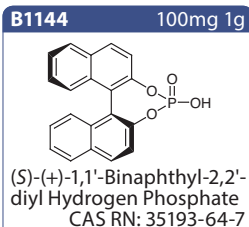
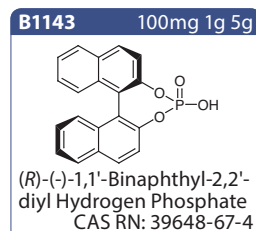
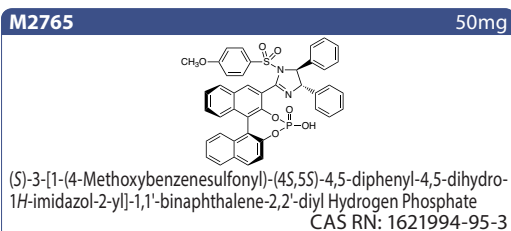
(-)-4,5-Bis(hydroxy(diphenyl)methyl)-2,2-dimethyl-1,3-dioxolane
CAS RN: 93379-48-7

B2048 1g 5g

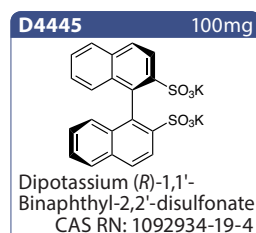
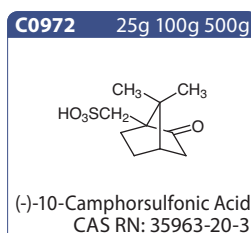
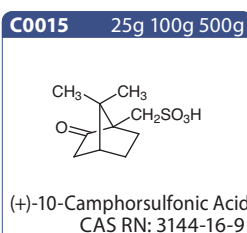


(+)-4,5-Bis(hydroxy(diphenyl)methyl)-2,2-dimethyl-1,3-dioxolane
CAS RN: 93379-49-8

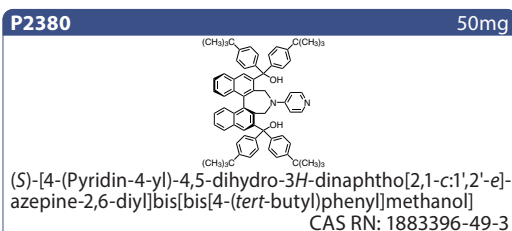
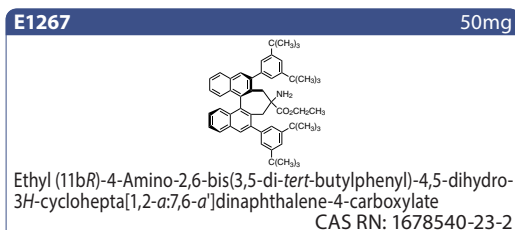
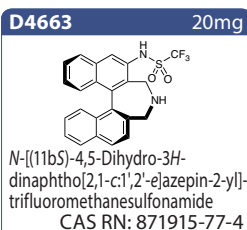
Chiral Phosphoric Acids



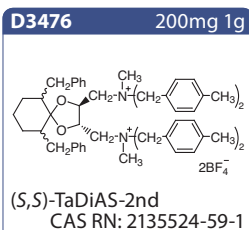
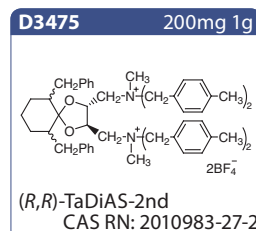
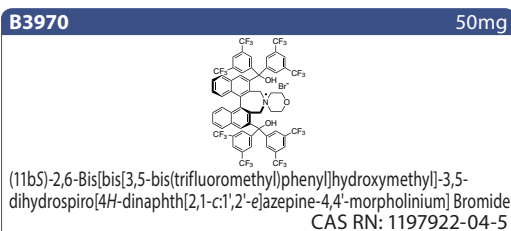
Chiral Sulfonic Acids



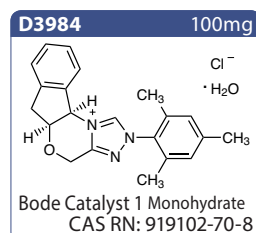
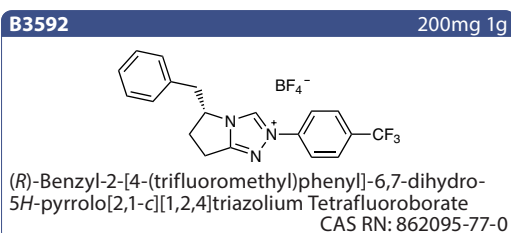
Chiral Amines



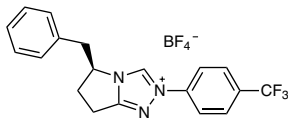
Chiral Ammonium Salts



Chiral N-Heterocyclic Carbenes (NHC)

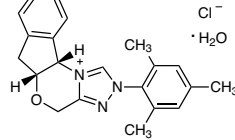


B3593 200mg 1g



(S)-Benzyl-2-[4-(trifluoromethyl)phenyl]-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazolium Tetrafluoroborate

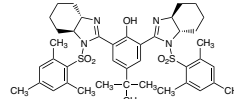
D3983 100mg



Bode Catalyst 2 Monohydrate
CAS RN: 903571-02-8

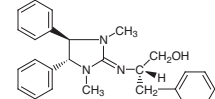
Others

B6146 50mg



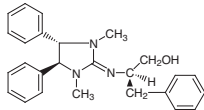
(-)-4-tert-Butyl-2,6-bis[(4S,5S)-4,5-tetramethylene-1-(2,4,6-trimethylbenzenesulfonyl)imidazolin-2-yl]phenol
(contains 5% Dichloromethane at maximum)
CAS RN: 2102316-91-4

D2898 100mg



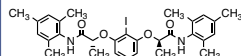
(4R,5R)-1,3-Dimethyl-4,5-diphenyl-2-[(S)-1-benzyl-2-hydroxyethylimino]imidazolidine
CAS RN: 337308-63-1

D2899 100mg



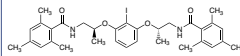
(4S,5S)-1,3-Dimethyl-4,5-diphenyl-2-[(R)-1-benzyl-2-hydroxyethylimino]imidazolidine
CAS RN: 210468-90-9

I0807 200mg



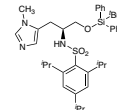
(R,R)-2-Iodo-1,3-bis[1-(mesityl-carbamoyl)ethoxy]benzene
CAS RN: 1226896-38-3

I1122 200mg



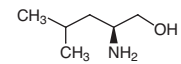
N,N'-[(2S,2'S)-[(2-Iodo-1,3-phenylene)bis(oxy)]bis(propane-2,1-diyl)]bis(mesitylamide)
CAS RN: 1399008-27-5

T2223 100mg



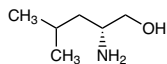
N²-(2,4,6-Triisopropylbenzenesulfonyl)-O-(tert-butyl)diphenylsilyl)-n-methyl-L-histidinol
CAS RN: 787554-04-5

L0137 5mL 25mL



L-(+)-Leucinol
CAS RN: 7533-40-6

L0236 1g 5g



D-(-)-Leucinol
CAS RN: 53448-09-2

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