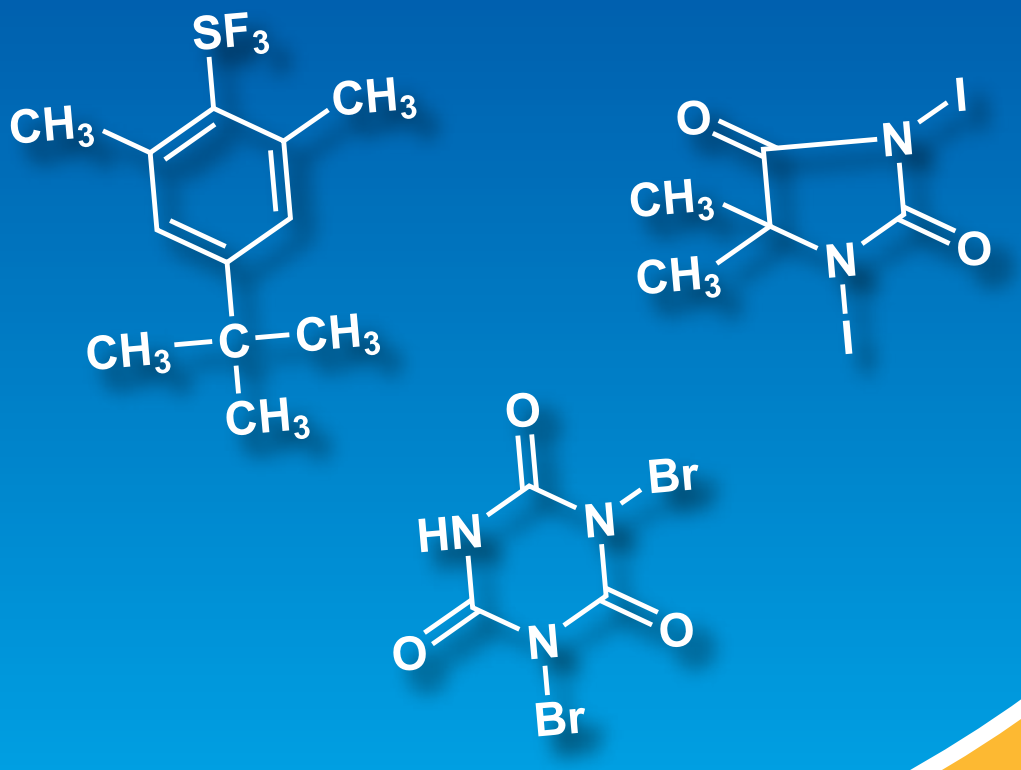
CHEMISTRY

Halogenation Reagents



Fluorinating Agents

Chlorinating Agents

Brominating Agents

Iodinating Agents

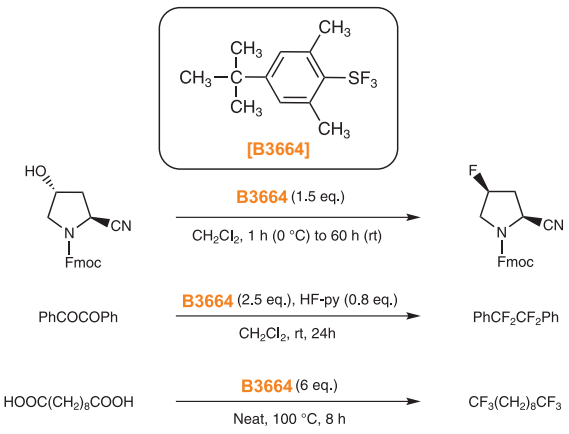
Halogenation Reagents

Halogenation is a basic and fundamental transformation in organic chemistry, and halogenated compounds are of extreme importance as building blocks in organic synthesis.

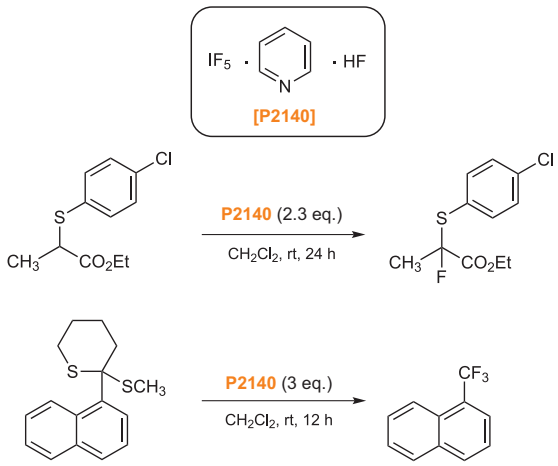
The development of modern coupling reactions, such as the Suzuki-Miyaura and Mizoroki-Heck reactions, have greatly increased the demand for halogenated compounds as starting materials.

On the other hand, introduction of fluorine into a certain position of bioactive compound such as a pharmaceutical and an agricultural chemical may remarkably reduce the toxicity of the compound, or improve the efficiency of medicine. This is due to the structurally mimic and blocking effect characterized by fluorine. In response to this situation, a number of novel halogenation reagents have been developed.

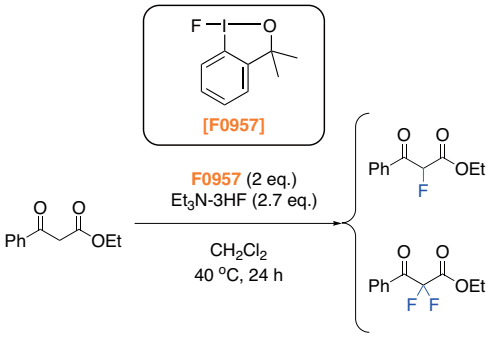
4-*tert*-Butyl-2,6-dimethylphenylsulfur trifluoride (FLUOLEAD™) **[B3664]** is introduced as below: **B3664** is a novel nucleophilic fluorinating agent which was first reported by Umemoto *et al.*[1] Differing from other existing fluorinating agents, such as DAST, **B3664** is a crystalline solid with high thermal stability and less fuming character, which makes it easier to handle. **B3664** fluorinates a hydroxyl or carbonyl group to afford the corresponding fluorinated compounds in good yields.[1]



IF_5-Pyridine-HF (Hara Reagent) **[P2140]** is also a novel fluorinating agent which was first reported by Hara *et al.*[2] **P2140** is a crystalline solid reagent with air stability and non-hygroscopicity, and can be used as an alternative reagent to IF_5 which is a unstable liquid in air. **P2140** can be applied to various fluorination reactions of sulfides as follows.



1-Fluoro-3,3-dimethyl-1,2-benziodoxole **[F0957]** is a hypervalent iodine derivative developed by Stuart *et al.*[3] **F0957** is stable to air and moisture and used as an electrophilic fluorinating reagent for a α-monofluorination of β-ketoesters in the presence of triethylamine trihydrofluoride.



Dibromoisocyanuric acid (DBI) **[D3753]** which was first reported by Gottardi, is a mild and highly effective brominating agent,[4a,b,c] and has superior brominating ability when compared with *N*-bromosuccinimide (NBS), which is frequently used in organic synthesis. For instance, nitrobenzene was converted to 3-bromonitrobenzene in 88% yield with **D3753** in conc. sulfuric acid in 5 min at 20 ºC,[4a] however, in only 70% yield with NBS in 50% sulfuric acid in 3 h at 85 ºC. Thus **D3753** has been widely used as an effective brominating agent.[4d,e]

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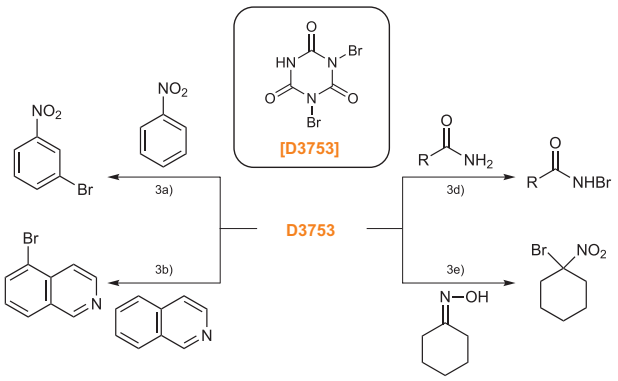
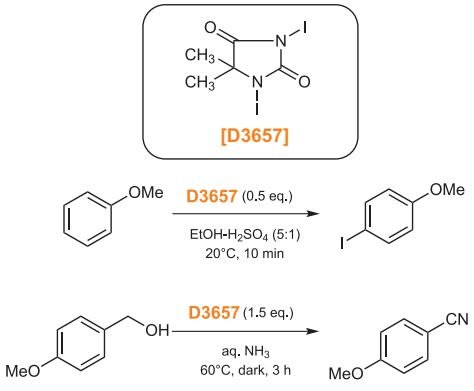


1,3-Diodo-5,5'-dimethylhidantoin (DIH) **[D3657]**, which was first reported by Orazi, is an useful iodinating agent.[5a] **D3657** has higher reactivity and selectivity than molecular iodine or *N*-iodosuccinimide (NIS), which are frequently used for iodination reactions. **D3657** reacts smoothly at room temperature with aromatic compounds in the presence of sulfuric acid to give the corresponding iodinate in a high regioselectivity and a high yield.[5b] And primary alcohols, and primary, secondary, and tertiary amines can be easily and efficiently converted into the corresponding nitriles in aqueous ammonia using **D3657**.[5c] In addition, dimethylhidantoin, which is formed after the reaction, can easily be removed by aqueous extraction.



TCI offers a variety of halogenation reagents other than the two items above. All the products are listed below.

References

1) T. Umemoto, R. P. Singh, Y. Xu, N. Saito, *J. Am. Chem. Soc.* **2010**, *132*, 18199.
2) a) S. Hara, M. Monoi, R. Umemura, C. Fuse, *Tetrahedron* **2012**, *68*, 10145.
b) M. Kunigami, S. Hara, *J. Fluorine Chem.* **2014**, *167*, 101.
c) T. Inoue, C. Fuse, S. Hara, *J. Fluorine Chem.* **2015**, *179*, 48.
d) M. Kunigami, S. Hara, *Carbohydr. Res.* **2015**, *417*, 78.
3) G. C. Geary, E. G. Hope, K. Singh, A. M. Stuart, *Chem. Commun.* **2013**, *49*, 9263.
4) a) W. Gottardi, *Monatsh. Chem.* **1968**, *99*, 815.
b) W. D. Brown, A. H. Gouliaev, *Synthesis* **2002**, 83.
c) S. C. Virgil, in *Encyclopedia of Reagents for Organic Synthesis*, ed. by L. A. Paquette, John Wiley & Sons, Chichester, **2001**, pp. 1560-1561.
d) Z. P. Demko, M. Bartsch, K. B. Sharpless, *Org. Lett.* **2000**, *2*, 2221.
e) T. R. Walters, W. W. Zajac Jr., J. M. Woods, *J. Org. Chem.* **1991**, *56*, 316.
5) a) O. O. Orazi, R. A. Corral, H. E. Bertorello, *J. Org. Chem.* **1965**, *30*, 1101.
b) V. K. Chaikovskii, V. D. Filimonov, A. A. Funk, V. I. Skorokhodov, V. D. Ogorodnikov, Russ. *J. Org. Chem.* **2007**, *43*, 1291.
c) S. Iida, H. Togo, *Tetrahedron* **2007**, *63*, 8274.

Fluorinating Agents

Nucleophilic Fluorinating Agents

P1888 500g

KHF_2

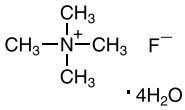
Potassium Hydrogenfluoride
CAS RN: 7789-29-9

C2204 25g 100g

CsF

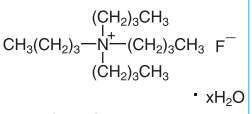
Cesium Fluoride
CAS RN: 13400-13-0

T2754 5g 25g



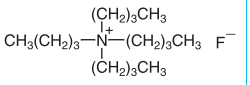
Tetramethylammonium Fluoride Tetrahydrate
CAS RN: 17787-40-5

T1037 25g 100g



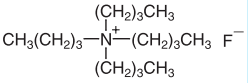
Tetrabutylammonium Fluoride Hydrate
CAS RN: 22206-57-1

T1339 25g 100g 500g



Tetrabutylammonium Fluoride (70-75% in Water)
CAS RN: 429-41-4

T1338 25mL 100mL 500mL



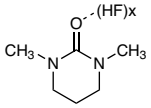
Tetrabutylammonium Fluoride (*ca.* 1mol/L in Tetrahydrofuran)
CAS RN: 429-41-4

T2022 10g

$(CH_3CH_2)_3N \cdot 3HF$

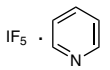
Triethylamine Trihydrofluoride
CAS RN: 73602-61-6

D5272 1g 5g



DMPU-HF Reagent
(HF 65%)
CAS RN: 287966-55-6

P2140 1g 5g



IF_5-Pyridine-HF
CAS RN: 2243786-10-7

T2026 10g

$(CH_3CH_2)_4NF \cdot 3HF$

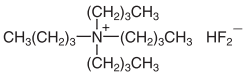
Tetraethylammonium Fluoride Trihydrofluoride
CAS RN: 42539-97-9

T2027 10g

$(CH_3CH_2)_4NF \cdot 4HF$

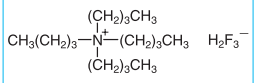
Tetraethylammonium Fluoride Tetrahydrofluoride
CAS RN: 145826-81-9

T1295 5g 25g



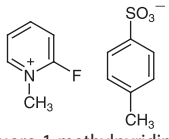
Tetrabutylammonium Bifluoride
CAS RN: 23868-34-0

T1635 5g 25g



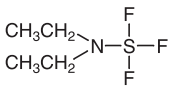
Tetrabutylammonium Dihydrogen Trifluoride
CAS RN: 99337-56-1

F0225 5g 25g



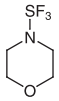
2-Fluoro-1-methylpyridinium *p*-Toluenesulfonate
CAS RN: 58086-67-2

D1868 5g 25g 100g



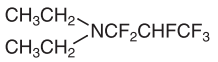
DAST
CAS RN: 38078-09-0

M1573 1g 5g



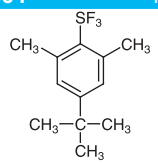
Morph-DAST
CAS RN: 51010-74-3

H0598 25g 100g 500g



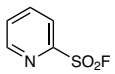
Ishikawa's Reagent
CAS RN: 309-88-6

B3664 1g 5g



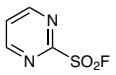
FLUOLEAD™
CAS RN: 947725-04-4

P2398 5g



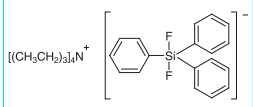
PyFluor
CAS RN: 878376-35-3

P2465 1g 5g



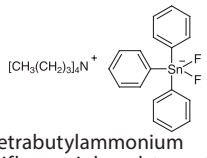
Pyrimidine-2-sulfonyl Fluoride
CAS RN: 35762-87-9

T1909 5g 25g



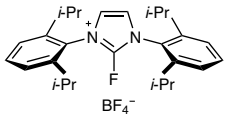
Tetrabutylammonium Difluorotriphenylsilicate
CAS RN: 163931-61-1

T1592 1g 5g



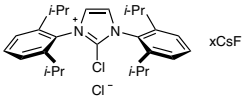
Tetrabutylammonium Difluorotriphenylstannate
CAS RN: 139353-88-1

B5480 200mg 1g



AlkylFluor™
CAS RN: 2043361-32-4

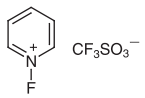
P2420 1g 5g



PhenoFluor™ Mix
CAS RN: 1648825-53-9

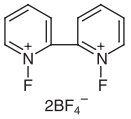
Electrophilic Fluorinating Agents

F0327 5g 25g



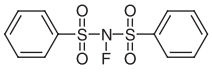
1-Fluoropyridinium Trifluoromethanesulfonate
CAS RN: 107263-95-6

D3812 1g 5g 25g 100g



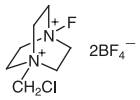
1,1'-Difluoro-2,2'-bipyridinium Bis(tetrafluoroborate)
CAS RN: 178439-26-4

F0335 1g 5g 25g



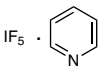
N-Fluorobenzenesulfonimide
CAS RN: 133745-75-2

F0358 5g 25g 100g



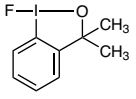
F-TEDA-BF_4
CAS RN: 140681-55-6

P2140 1g 5g



IF_5-Pyridine-HF
CAS RN: 2243786-10-7

F0957 1g



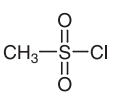
1-Fluoro-3,3-dimethyl-1,2-benziodoxole
CAS RN: 1391728-13-4

Chlorinating Agents

T2048 500mL

Thionyl Chloride (*ca.* 1mol/L in Dichloromethane)
CAS RN: 7719-09-7

M0094 25g 500g



Methanesulfonyl Chloride
CAS RN: 124-63-0

T0611 5g 25g

CCl_3SO_2Cl

Trichloromethanesulfonyl Chloride
CAS RN: 2547-61-7

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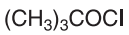
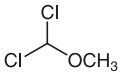
H0362 25g



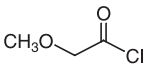
tert-Butyl Hypochlorite
CAS RN: 507-40-4

D1645 25g 100g 250g



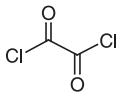
Dichloromethyl Methyl Ether
CAS RN: 4885-02-3

M0970 25g 100g 500g



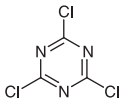
Methoxyacetyl Chloride
CAS RN: 38870-89-2

O0082 25g 100g 500g



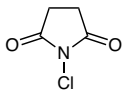
Oxalyl Chloride
CAS RN: 79-37-8

C0460 25g 500g



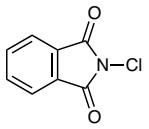
Cyanuric Chloride
CAS RN: 108-77-0

C0291 25g 100g 500g



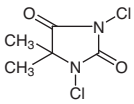
N-Chlorosuccinimide
(= NCS)
CAS RN: 128-09-6

C0802 25g 500g



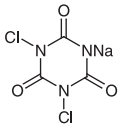
N-Chlorophthalimide
CAS RN: 3481-09-2

D1783 25g 100g 500g



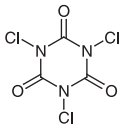
1,3-Dichloro-
5,5-dimethylhydantoin
CAS RN: 118-52-5

D1003 25g 500g



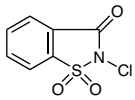
Sodium
Dichloroisocyanurate
CAS RN: 2893-78-9

T0620 25g 500g



Trichloroisocyanuric Acid
CAS RN: 87-90-1

C1674 5g 25g

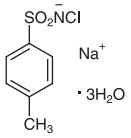


N-Chlorosaccharin
CAS RN: 14070-51-0

C0075 25g 100g 500g

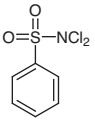
Chloramine B Hydrate
CAS RN: 304655-80-9

C0076 25g 500g



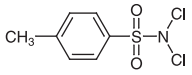
Chloramine T Trihydrate
CAS RN: 7080-50-4

D0317 5g 25g



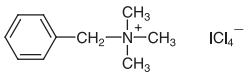
Dichloramine B
CAS RN: 473-29-0

D0318 25g 100g 500g



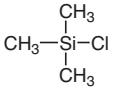
Dichloramine T
CAS RN: 473-34-7

B1543 5g



Benzyltrimethylammonium
Tetrachloroiodate
CAS RN: 121309-88-4

C0306 25mL 100mL 500mL



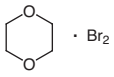
Trimethylsilyl Chloride
CAS RN: 75-77-4

Brominating Agents

B2414 90g 500g

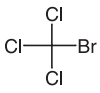
Bromine
CAS RN: 7726-95-6

B2719 5g 25g



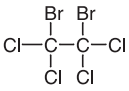
Bromine -
1,4-Dioxane Complex
CAS RN: 15481-39-7

B0662 25g 500g



Bromotrichloromethane
CAS RN: 75-62-7

D1987 25g

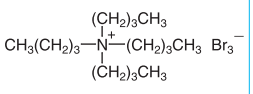


1,2-Dibromo-
1,1,2,2-tetrachloroethane
CAS RN: 630-25-1

T0038 5g 25g 100g 500g

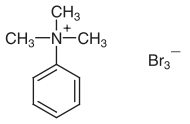
Carbon Tetrabromide
CAS RN: 558-13-4

T1284 25g 100g 500g



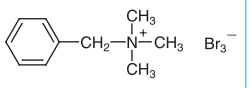
Tetrabutylammonium
Tribromide
CAS RN: 38932-80-8

P0928 25g 500g



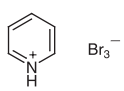
Trimethylphenylammonium
Tribromide
CAS RN: 4207-56-1

T1382 5g 25g



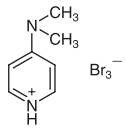
Benzyltrimethylammonium
Tribromide
CAS RN: 111865-47-5

P0825 25g 100g 500g



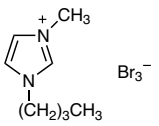
Pyridinium Bromide
Perbromide
CAS RN: 39416-48-3

D1787 5g 25g



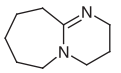
4-Dimethylaminopyridinium
Bromide Perbromide
CAS RN: 92976-81-3

B3596 5g



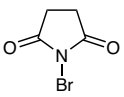
1-Butyl-3-methylimidazolium
Tribromide
CAS RN: 820965-08-0

D3976 5g



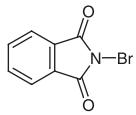
1,8-Diazabicyclo[5.4.0]-
7-undecene Hydrogen
Tribromide
CAS RN: 138666-59-8

B0656 25g 100g 500g



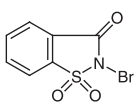
N-Bromosuccinimide
(= NBS)
CAS RN: 128-08-5

B1697 5g 25g



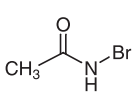
N-Bromophthalimide
CAS RN: 2439-85-2

B2152 5g 25g



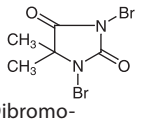
N-Bromosaccharin
CAS RN: 35812-01-2

B0530 5g 25g



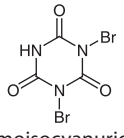
N-Bromoacetamide
CAS RN: 79-15-2

D1265 25g 500g



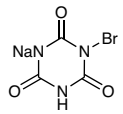
1,3-Dibromo-
5,5-dimethylhydantoin
CAS RN: 77-48-5

D3753 1g 5g 25g



Dibromoisocyanuric Acid
(= DBI)
CAS RN: 15114-43-9

B2148 25g



Monosodium Bromoisocyanurate
CAS RN: 164918-61-0

B2553 25mL 100mL

BBr_3

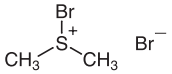
Boron Tribromide
(17% in Dichloromethane, *ca.* 1mol/L)
CAS RN: 10294-33-4

P1743 300g

PBr_3

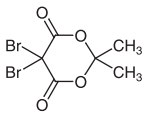
Phosphorus Tribromide
CAS RN: 7789-60-8

B3311 5g 25g



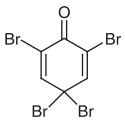
Bromodimethylsulfonium Bromide
CAS RN: 50450-21-0

D1710 5g 25g



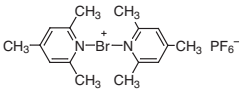
5,5-Dibromomeldrum's Acid
CAS RN: 66131-14-4

T1235 5g 25g



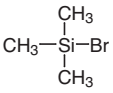
2,4,4,6-Tetrabromo-2,5-cyclohexadienone
CAS RN: 20244-61-5

B2358 1g 5g



Bis(2,4,6-trimethylpyridine)-bromonium Hexafluorophosphate
CAS RN: 188944-77-6

B1087 5mL 25mL 250mL



Trimethylsilyl Bromide
CAS RN: 2857-97-8

Iodinating Agents

I0604 25g 500g

I_2

Iodine
CAS RN: 7553-56-2

H1221 300mL

HI

Hydriodic Acid (57%)
CAS RN: 10034-85-2

C0936 10g

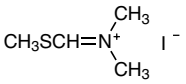
Carbon Tetraiodide
CAS RN: 507-25-5

C1190 1g 5g

ICH_2CH_2Cl

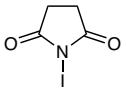
1-Chloro-2-iodoethane
CAS RN: 624-70-4

D4340 5g 25g



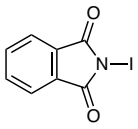
N,N-Dimethyl-*N*-(methylsulfanylmethylene)-ammonium Iodide
CAS RN: 29085-13-0

I0074 5g 25g 100g



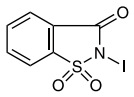
N-Iodosuccinimide
(= NIS)
CAS RN: 516-12-1

I1052 5g 25g



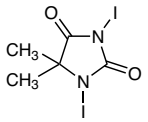
N-Iodophthalimide
CAS RN: 20919-42-0

I0784 5g



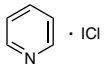
N-Iodosaccharin
CAS RN: 86340-94-5

D3657 5g 25g



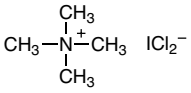
1,3-Diiodo-5,5-dimethylhydantoin (= DIH)
CAS RN: 2232-12-4

P2086 1g 5g



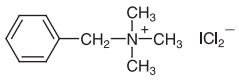
Pyridine Iodine Monochloride
CAS RN: 6443-90-9

T2717 5g



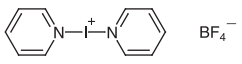
Tetramethylammonium Dichloroiodate
CAS RN: 1838-41-1

B1604 5g 25g



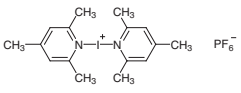
Benzyltrimethylammonium Dichloroiodate
CAS RN: 114971-52-7

B2539 1g



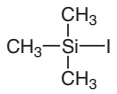
Bis(pyridine)iodonium Tetrafluoroborate
CAS RN: 15656-28-7

B2359 1g 5g



Bis(2,4,6-trimethylpyridine)-iodonium Hexafluorophosphate
CAS RN: 113119-46-3

I0308 5g 25g



Trimethylsilyl Iodide
CAS RN: 16029-98-4

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