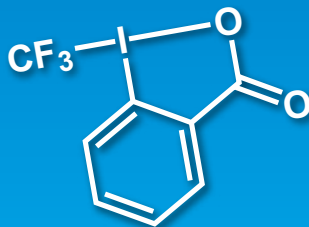
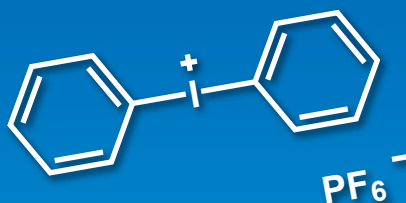
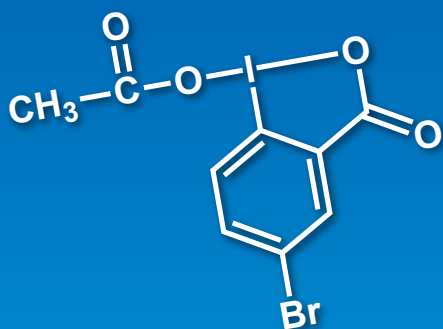




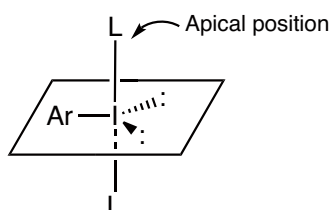
# Hypervalent Iodine Compounds



# Hypervalent Iodine Compounds

As Japan is not blessed with abundant natural resources, it is dependent on the importation of the majority of its raw materials from overseas. However, Japan can be proud of its production of iodine, where it is a leading world manufacturer. The present situation in Japan is that the produced and exported iodine products are low value-added products, and thus Japan still relies on the United States and Europe for importation of high value-added iodine products such as X-ray contrast medium or photosensitive agent for photographic film.

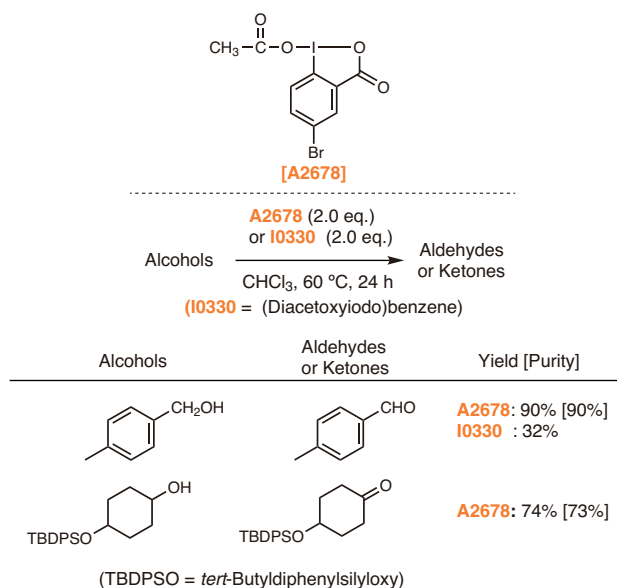
Iodine is atomic number 53, in the 5th period, Group VIIa, halogens of the periodic table. Iodine is a large-sized halogen element, easily polarizable, and low in electronegativity. It forms hypervalent iodine compound beyond the octet rule by readily extending its valence. For example, a hypervalent iodine compound with three ligands is a 10-I-3 type compound as shown in the figure. The central iodine atom forms a plane with two lone pairs and one s-bond, and furthermore, this iodine atom coordinates two ligands with larger electronegativity in an apical position orthogonal to the plane resulting in the formation of a linear three center-four electron bond. The I-L bond in the apical position is longer than the covalent bond. For example, the I-O bond lengths in (diacetoxyiodo)benzene ( $\text{PhI}(\text{OAc})_2$ , **[I0330]**) are longer than the sum of their covalent bond radii (1.99Å) and these bond lengths have a range of 2.15 - 2.16Å.



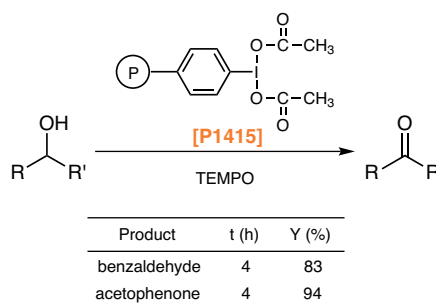
The stability and reactivity of hypervalent iodine compounds exhibit a greater dependence on the character of hypervalent bonds in the apical position. The hypervalent bonds in the apical position are easily cleaved, and the cleavage causes trivalent iodine with 10 electrons to be reduced to monovalent iodine of a more stable octet structure. For this reason it exhibits good elimination and oxidation rates and finds application in organic syntheses.<sup>1)</sup>

## ● Oxidizing Agents

ABBX **[A2678]** is a highly active trivalent iodine compound, developed by Togo *et al.*<sup>3)</sup> **A2678** oxidizes benzylic alcohols and aliphatic secondary alcohols to the corresponding aldehydes and ketones in good yields from simple extraction of the reaction mixture. 5-Bromo-2-iodobenzoic acid, formed as a co-product of this reaction, can be recovered by acidification of the aqueous layer.



The most common of the trivalent iodine compounds, (diacetoxyiodo)benzene **[I0330]** has been supported on a polymer. For example, Togo and co-workers have demonstrated several oxidation reactions using poly[4-(diacetoxyiodo)-styrene] **[P1415]**<sup>3)</sup>



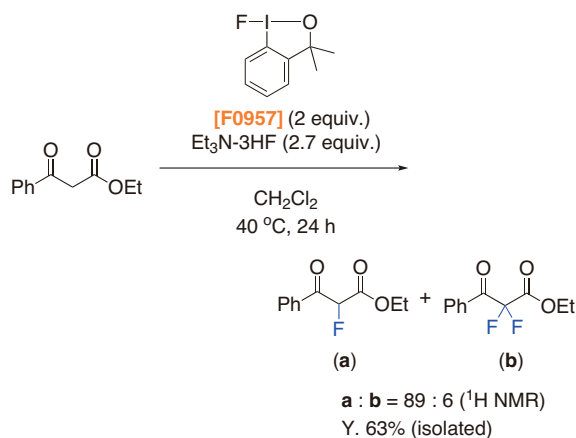
**P1415** can selectively oxidize primary alcohols to aldehydes, and secondary alcohols to ketones under mild conditions in the presence of TEMPO. After the reaction, the by-product, poly(4-iodostyrene), can be recovered by filtration, re-oxidized with peracetic acid, and reused. Therefore **P1415** is expected to be used as environmentally-friendly oxidation reagent in the future.

## ● Fluorinating Agents

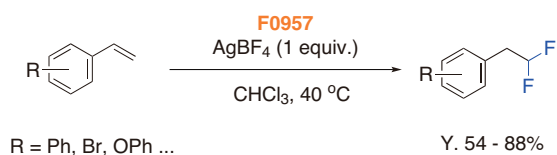
1-Fluoro-3,3-dimethyl-1,2-benziodoxole **[F0957]** is an air- and moisture-stable compound developed by Stuart *et al.*<sup>4)</sup> **F0957** is used as an electrophilic fluorinating agent for a  $\alpha$ -monofluorination of  $\beta$ -ketoesters in the presence of triethylamine trihydrofluoride. In this reaction, a difluorination reaction occurs by increasing the amounts of **F0957** with heating at 60 °C. On the other hand, Szabó *et al.* have reported a difluorination reaction of **F0957** with styrene derivatives.

They suggest that the reaction proceeds through the formation of a phenonium ion intermediate based on a deuterium-isotope-labelling experiment.

### Monofluorination of $\beta$ -ketoesters

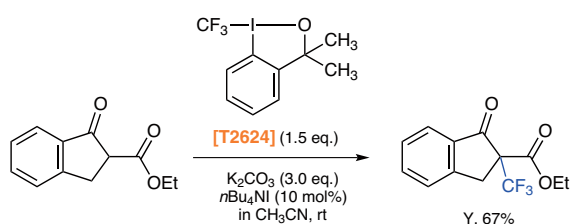


### Difluorination of styrene derivatives



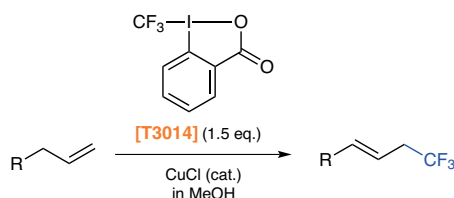
## Trifluoromethylating Agents

Togni Reagent **T2624** is an electrophilic trifluoromethylating agent developed by Togni and co-workers, which reacts with  $\beta$ -keto esters and  $\alpha$ -nitro esters to introduce a trifluoromethyl group on their  $\alpha$ -carbons. **T2624** also reacts with thiols and primary- and secondary phosphines to generate trifluoromethyl sulfides and trifluoromethyl substituted phosphines respectively. **T2624** can be applicable to various substrates.<sup>5)</sup>



Togni Reagent II **T3014** is also an electrophilic trifluoromethylating agent, which was developed by Togni *et al.* **T3014** enables it to trifluoromethylate various substrates, as well as Togni Reagent. In particular, it has been reported that the reaction of **T3014** and olefins affords the corresponding allylic trifluoromethylated compounds.<sup>6)</sup>

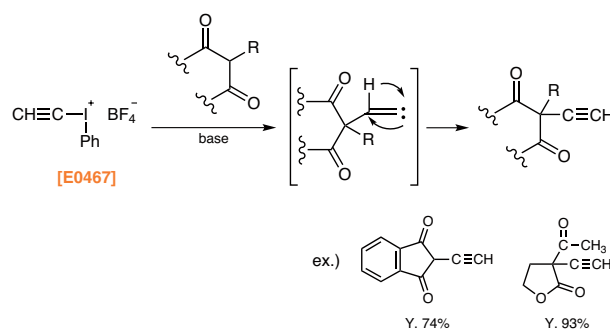
\***T3014** contains diatomaceous earth because of reducing explosibility.



## Ethynylation Reagents

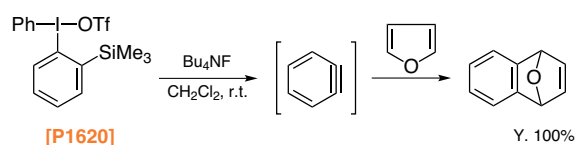
Ochiai and co-workers have developed alkynyliodonium tetrafluoroborate **E0467** prepared from alkynylsilanes and iodosobenzene in the presence of BF<sub>3</sub> and they reported its efficacy as electrophilic ethynylation reagents.<sup>7)</sup>

When **E0467** was reacted with enolates, alkylidene carbene was generated as an intermediate, and subsequently, an ethynylated product was obtained via 1,2-hydrogen rearrangement of the  $\alpha$ -hydrogen. This reaction proceeded under room temperature, and afforded ethynylated products in high yields. As for other electrophilic ethynylation reagents, ethynyl lead triacetate has been exploited, which is prepared from ethynyl(trimethyl)stannane and lead tetraacetate. However, preparation of this reagent requires the use of heavy metal compounds, which make it an unattractive procedure. The ethynylation procedure using this reagent requires careful control of the reaction conditions. The ethynylation method using **E0467** has been at the center of attention in many fields, as this method does not use highly toxic heavy metal compounds, and the reaction proceeds under mild conditions.



## Benzyne Precursors

Kitamura and co-workers have reported mild benzyne generation method using TMS-phenyliodonium compound **P1620**.<sup>8)</sup> According to the report, benzyne can be efficiently generated by treating **P1620** with Bu<sub>4</sub>NF. **P1620** is the excellent benzyne precursor which needs neither high temperature condition nor strong basic treatment in order to generate benzyne.

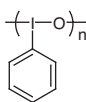


### References

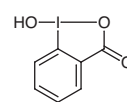
- 1) A. Varvoglis, *Synthesis* **1984**, 709; P. J. Stang, V. V. Zhdankin, *Chem. Rev.* **1996**, 96, 1123; V. V. Zhdankin, P. J. Stang, *Chem. Rev.* **2002**, 102, 2523.
- 2) M. Iinuma, K. Moriyama, H. Togo, *Eur. J. Org. Chem.* **2014**, 772.
- 3) H. Togo, S. Abe, G. Nogami, M. Yokoyama, *Bull. Chem. Soc. Jpn.* **1999**, 72, 2351; H. Togo, K. Sakuratani, *Kagaku to Kogyo (Chemistry and Chemical Industry)* **2002**, 55, 1018; H. Togo, K. Sakuratani, *Synlett* **2002**, 1966; Tokyo Kasei Kogyo, Jpn. Kokai Tokkyo Koho 2003-113131.
- 4) G. C. Geary, E. G. Hope, K. Singh, A. M. Stuart, *Chem. Commun.* **2013**, 49, 9263; N. O. Ilchenko, B. O. A. Tasch, K. J. Szabó, *Angew. Chem. Int. Ed.* **2014**, 53, 12897.
- 5) P. Eisenberger, S. Gischig, A. Togni, *Chem. Eur. J.* **2006**, 12, 2579; I. Kieltisch, P. Eisenberger, A. Togni, *Angew. Chem. Int. Ed.* **2007**, 46, 754; P. Eisenberger, I. Kieltisch, N. Armanino, A. Togni, *Chem. Commun.* **2008**, 1575.
- 6) P. Eisenberger, S. Gischig, A. Togni, *Chem. Eur. J.* **2006**, 12, 2579; X. Wang, Y. Ye, S. Zhang, J. Feng, Y. Xu, Y. Zhang, J. Wang, *J. Am. Chem. Soc.* **2011**, 133, 16410.
- 7) M. Ochiai, T. Ito, Y. Takaoka, Y. Masaki, M. Kunishima, S. Tani, Y. Nagao, *J. Chem. Soc. Chem. Commun.* **1990**, 118; M. Ochiai, *TCIMAIL*, **1999**, number 104, 2.
- 8) T. Kitamura, M. Yamane, *J. Chem. Soc. Chem. Commun.* **1995**, 983; T. Kitamura, M. Yamane, K. Inoue, M. Todaka, N. Fukatsu, Z. Meng, Y. Fujiwara, *J. Am. Chem. Soc.* **1999**, 121, 11674; T. Kitamura, M. Todaka, Y. Fujiwara, *Org. Synth.* **2002**, 78, 104.

## Oxidizing Agents

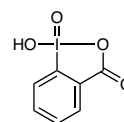
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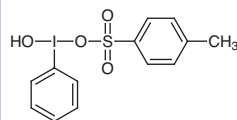
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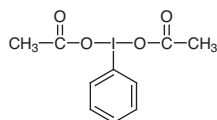
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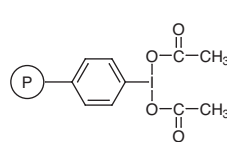
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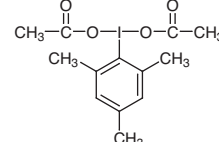
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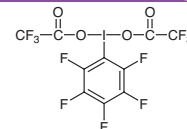
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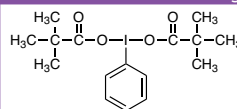
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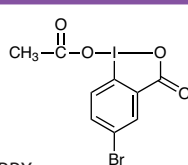
B1616 1g 5g

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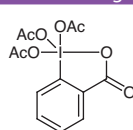
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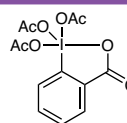
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ABBX  
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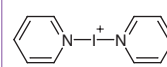
D2045 1g 5g 25g

Dess-Martin Periodinane  
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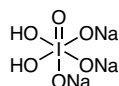
D4477 25mL 250mL

Dess-Martin Periodinane  
(8-12% in Dichloromethane)  
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B2539 1g

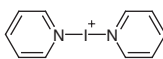
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P0077 25g

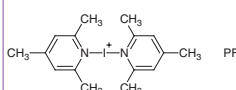
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## Iodinating Agents

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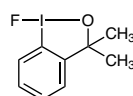
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Bis(2,4,6-trimethylpyridine)-  
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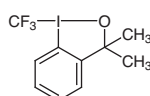
## Fluorinating Agents

F0957 1g

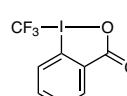
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## Trifluoromethylating Agents

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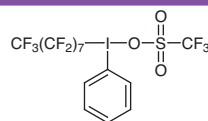
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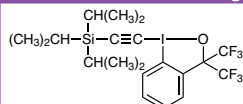
Togni Reagent II  
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## Perfluoroalkylating Agents

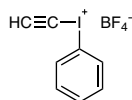
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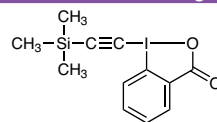
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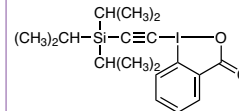
1-[2-(Triisopropylsilyl)ethynyl]-  
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**E0467** 1g


Ethynyl(phenyl)iodonium  
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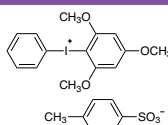
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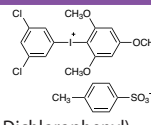
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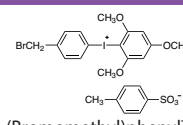
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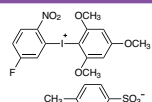
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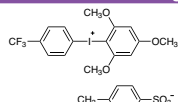
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**B5269** 200mg


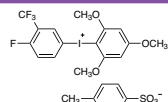
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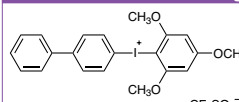
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**T3622** 200mg 1g


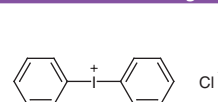
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(2,4,6-trimethoxyphenyl)-  
iodonium Tosylate  
CAS RN: 1868173-15-2

**F1111** 200mg 1g


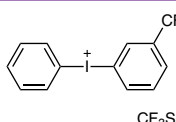
[4-Fluoro-3-(trifluoromethyl)-  
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**B5573** 200mg


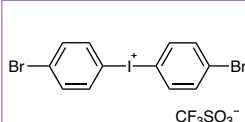
4-Biphenyl(2,4,6-trimethoxyphenyl)-  
iodonium Triflate  
CAS RN: 1868173-47-0

**D2356** 5g 25g


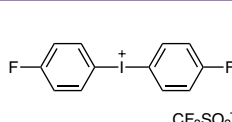
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Chloride  
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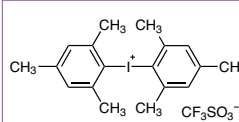
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**B5259** 1g 5g


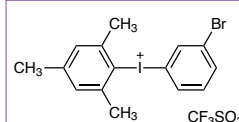
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**B5276** 1g 5g


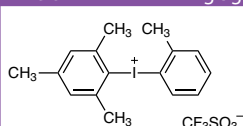
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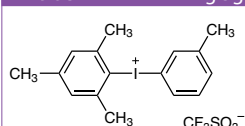
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**B5277** 1g 5g


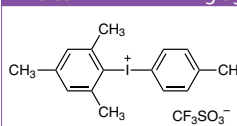
(3-Bromophenyl)(mesityl)-  
iodonium Triflate  
CAS RN: 1203709-76-5

**M2907** 1g 5g


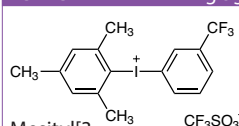
Mesityl(o-tolyl)iodonium  
Triflate  
CAS RN: 210823-54-4

**M2908** 1g 5g


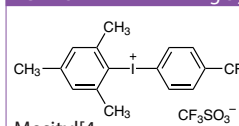
Mesityl(m-tolyl)iodonium  
Triflate  
CAS RN: 197245-87-7

**M2909** 1g 5g


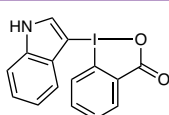
Mesityl(p-tolyl)iodonium  
Triflate  
CAS RN: 1204518-02-4

**T3445** 1g 5g


Mesityl[3-(trifluoromethyl)phenyl]-  
iodonium Triflate  
CAS RN: 1204518-08-0

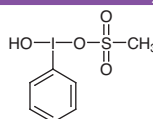
**T3446** 1g 5g


Mesityl[4-(trifluoromethyl)phenyl]-  
iodonium Triflate  
CAS RN: 1232133-62-8

**I1126** 250mg


N-H-IndoleBX  
CAS RN: 2130906-05-5

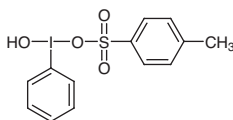
## Mesyloxylation Reagents

**P1298** 5g 25g


[Hydroxy(mesyloxy)iodo]-  
benzene  
CAS RN: 105551-42-6

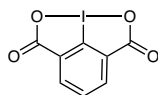
## Tosyloxylation Reagents

P1015 5g 25g

Koser Reagent  
CAS RN: 27126-76-7

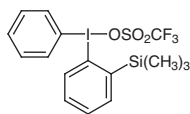
## Condensation Reagents

I0865 1g

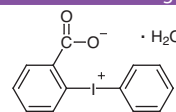
Iodosodilactone  
CAS RN: 2902-68-3

## Benzyne Precursors

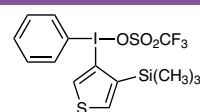
P1620 1g 5g

Phenyl[2-(trimethylsilyl)-phenyl]iodonium Triflate  
CAS RN: 164594-13-2

D2503 5g 25g

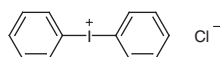
Diphenyliodonium-2-carboxylate Monohydrate  
CAS RN: 96195-89-0

P2097 200mg

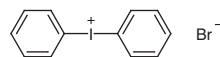
Phenyl[4-(trimethylsilyl)-3-thienyl]iodonium Triflate  
CAS RN: 175224-35-8

## Photo-Cationic Polymerization Initiators

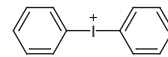
D2356 5g 25g

Diphenyliodonium Chloride  
CAS RN: 1483-72-3

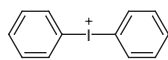
D2372 5g

Diphenyliodonium Bromide  
CAS RN: 1483-73-4

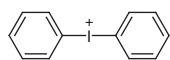
D2357 5g 25g

Diphenyliodonium Nitrate  
CAS RN: 722-56-5

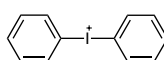
D2253 1g 5g 25g

Diphenyliodonium Trifluoromethanesulfonate  
CAS RN: 66003-76-7

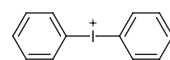
D2243 1g 5g

Diphenyliodonium Perchlorate  
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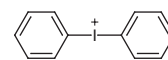
D5118 1g 5g

Diphenyliodonium Tetrafluoroborate  
CAS RN: 313-39-3

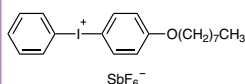
D2238 1g 5g 25g

Diphenyliodonium Hexafluorophosphate  
CAS RN: 58109-40-3

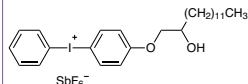
D2248 1g

Diphenyliodonium Hexafluoroarsenate  
CAS RN: 62613-15-4

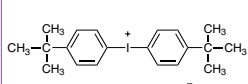
O0589 1g 5g

[4-(Octyloxy)phenyl]-(phenyl)iodonium Hexafluoroantimonate  
CAS RN: 121239-75-6

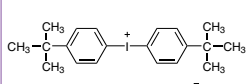
H1683 5g 25g

[4-[(2-Hydroxytetradecyl)-oxy]phenyl]phenyliodonium Hexafluoroantimonate  
CAS RN: 139301-16-9

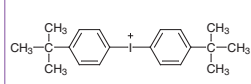
B6355 5g

Bis(4-tert-butylphenyl)-iodonium Chloride  
CAS RN: 5421-53-4

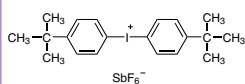
B5661 1g 5g

Bis(4-tert-butylphenyl)-iodonium Tetrafluoroborate  
CAS RN: 62051-09-6

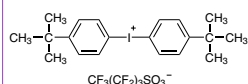
B2380 1g 5g

Bis(4-tert-butylphenyl)-iodonium Hexafluorophosphate  
CAS RN: 61358-25-6

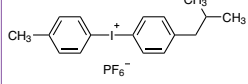
B6347 5g 25g

Bis(4-tert-butylphenyl)-iodonium Hexafluoroantimonate  
CAS RN: 61358-23-4

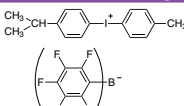
B6071 1g 5g

Bis(4-tert-butylphenyl)-iodonium Nonaflate  
CAS RN: 194999-85-4

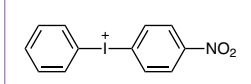
M3379 5g 25g

(4-Isobutylphenyl)(p-tolyl)-iodonium Hexafluorophosphate (ca. 70% in Propylene Carbonate)  
CAS RN: 344562-80-7

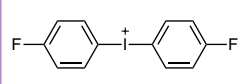
I0591 5g 25g

p-Cumenyl(p-tolyl)iodonium Tetrakis(pentafluorophenyl)-borate  
CAS RN: 178233-72-2

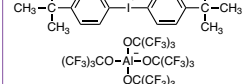
N1066 1g 5g

(4-Nitrophenyl)(phenyl)-iodonium Triflate  
CAS RN: 905718-45-8

B5276 1g 5g

Bis(4-fluorophenyl)-iodonium Triflate  
CAS RN: 732306-64-8

B5956 100mg 1g

Bis[4-(tert-butyl)phenyl]-iodonium Tetra(perfluoro-tert-butoxy)aluminate  
CAS RN: 2350272-68-1

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