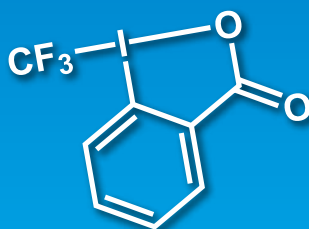
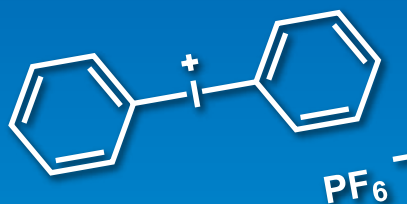
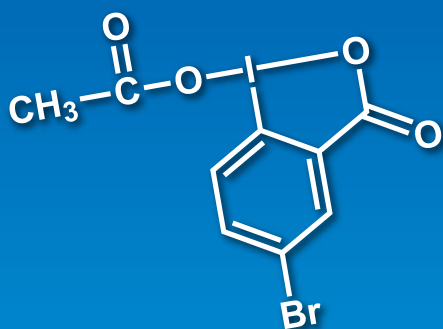


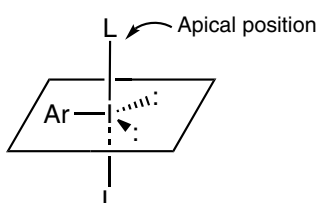
# Hypervalent Iodine Compounds



# 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 (PhI(OAc)<sub>2</sub>, **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.

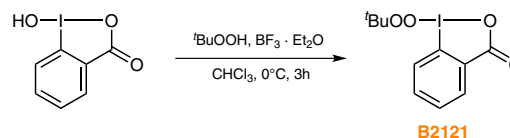


The stability and reactivity of hypervalent iodine compounds exhibit a greater dependence on the character of hypervalent bonds in the apical position. The hypervalent bonds in the apical position are easily cleaved, and the cleavage causes trivalent iodine with 10 electrons to be reduced to monovalent 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

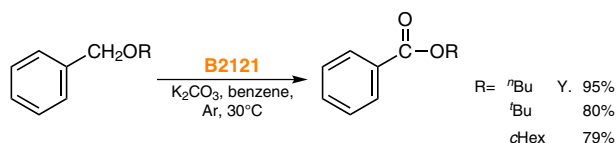
Ochiai and co-workers have also found that the ligand exchange of 1-hydroxy-1,2-benziodoxol-3-one with *tert*-butyl hydroperoxide affords 1-(*tert*-butylperoxy)-1,2-benziodoxoles-3-one (**B2121**) in the presence of Lewis acid. **B2121** is an interesting compound with a specific structure since it contains a *tert*-butylperoxy group and a trivalent iodine atom in the same molecule, both of which have oxidizing properties. Ochiai and

co-workers are investigating the efficacies of **B2121** as an oxidizing agent in further studies.<sup>2)</sup>

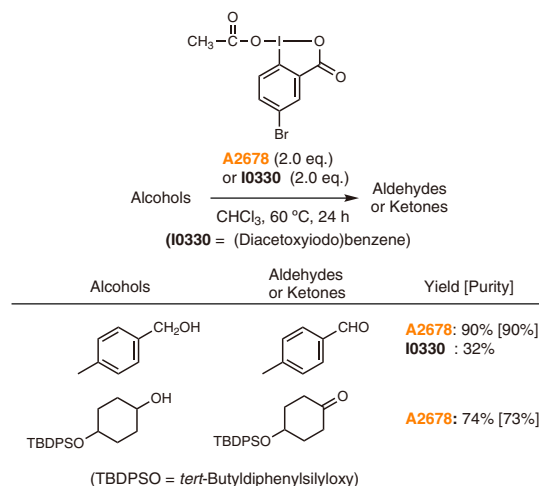


In one example of its useful property, **B2121** selectively oxidizes the benzylic methylene group of benzyl ether, and produces benzoic acid esters. The chemoselectivity of this reaction is high, and chemoselective oxidation at the benzylic site proceeds preferentially even in the presence of methoxymethyl group, silyl group, acetyl group, or tetrahydropyranyl group, and affords corresponding

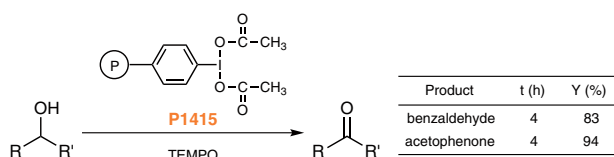
esters. Generally, the benzyl group is frequently used as a protecting group for alcohols. On the other hand, since esters are readily hydrolyzed to alcohols, **B2121** is a useful oxidative deprotecting reagent for benzyl group. The allyl group is also used as a protecting group for alcohols, **B2121** can afford acrylic acid esters selectively from allyl ethers. Furthermore, **B2121** can also be applied to the oxidation of sulfides, amines and amides, and it is expected to find use in many other field.



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>4)</sup>

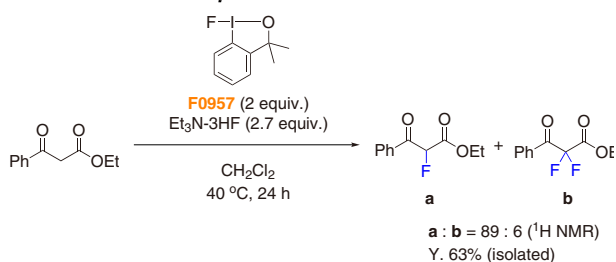


**P1415** can selectively oxidize primary alcohols to aldehydes, and secondary alcohols to ketones under mild conditions in the presence of TEMPO. After the reaction, the by-product, poly(4-iodostyrene), can be recovered by filtration, re-oxidized with peracetic acid, and reused. Therefore **P1415**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

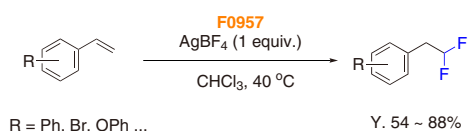
## Fluorinating Agents

1-Fluoro-3,3-dimethyl-1,2-benziodoxole (**F0957**) is an air- and moisture-stable compound developed by Stuart *et al.*<sup>5)</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.

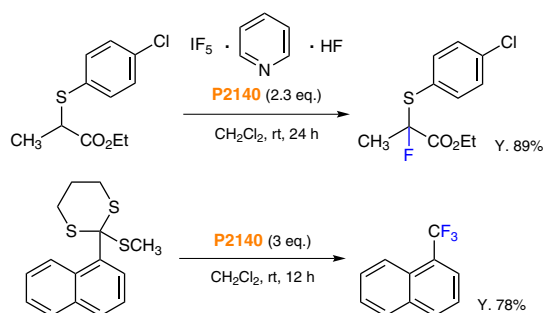
### Monofluorination of $\beta$ -ketoesters



### Difluorination of styrene derivatives

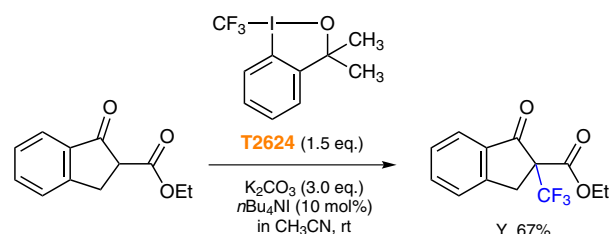


Hara Reagent (**P2140**), which was first reported by Hara *et al.*, is a novel fluorinating agent. **P2140** is a crystalline solid with air stability and non-hygroscopicity which makes it easier to handle. **P2140** can be applied to various fluorination reactions of sulfides.<sup>6)</sup> In addition, **P2140** iodofluorinates alkenes with stereo- and regioselectivity.



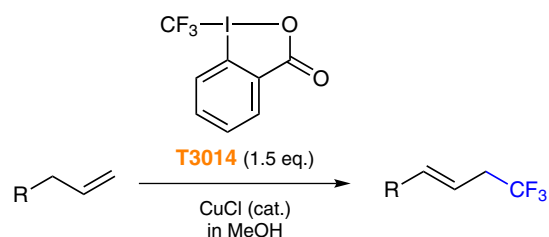
## Trifluoromethylating Agents

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>7)</sup>



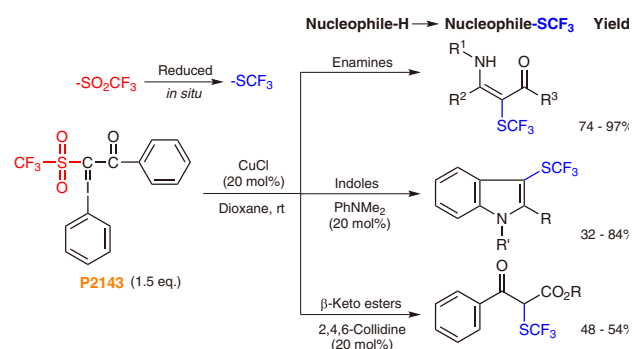
Togni Reagent II (**T3014**) is also an electrophilic trifluoromethylating agent, which was developed by Togni *et al.* **T3014** enables it to trifluoromethylate various substrates, as well as Togni Reagent. In particular, it has been reported that the reaction of **T3014** and olefins affords the corresponding allylic trifluoromethylated compounds.<sup>8)</sup>

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



## Trifluoromethylthiolating Agents

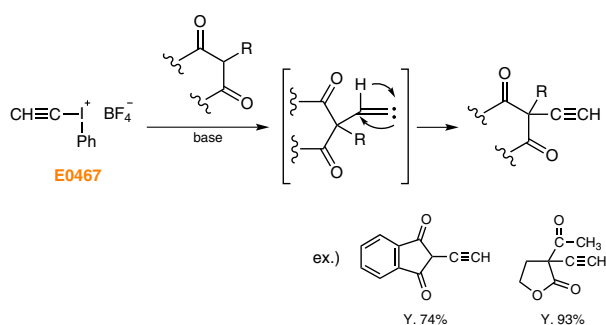
Shibata *et al.* have reported a electrophilic trifluoromethylthiolating reaction using Shibata Reagent II (**P2143**). **P2143** is electrophilic and reacts well with various nucleophiles to afford the CF<sub>3</sub>S-substituted products. The reaction process is assumed that a reactive trifluoromethylthio (CF<sub>3</sub>S-) species is generated from the trifluoromethanesulfonyl group by carbene-mediated *in situ* reduction catalyzed by a copper (I) salt in the presence of an amine. Trifluoromethylthiolated compounds have attracted special interest in the pharmaceutical and agrochemical industries.<sup>9)</sup>



## Ethynylation Reagents

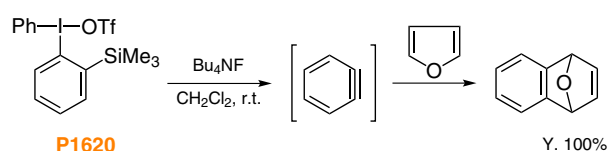
Ochiai and co-workers have developed alkynyliodonium tetrafluoroborate (**E0467**) prepared from alkynylsilanes and iodosobenzene in the presence of BF<sub>3</sub> and they reported its efficacy as electrophilic ethynylation reagents.<sup>10)</sup>

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 α-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>11)</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.



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# The list of products

We introduce our products according to their applications.

**Oxidizing Agents**

**Iodinating Agents**

**Fluorinating Agents**

**Trifluoromethylating Agents**

**Perfluoroalkylating Agents**

**Trifluoromethylthiolating Agents**

**Ethynylation Reagents**

**Arylation Reagents**

**Mesyloxylation Reagents**

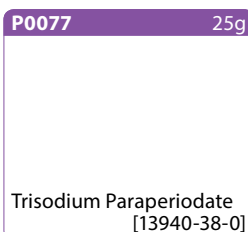
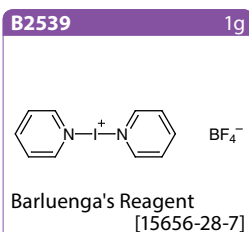
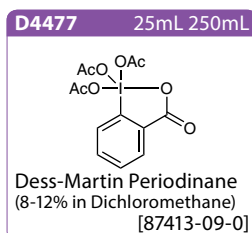
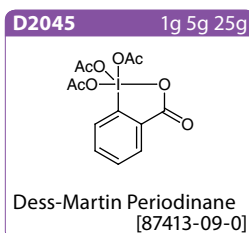
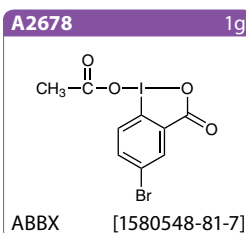
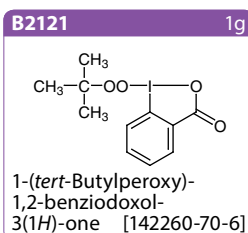
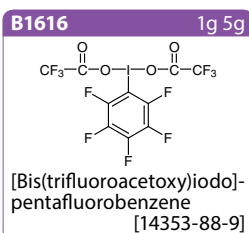
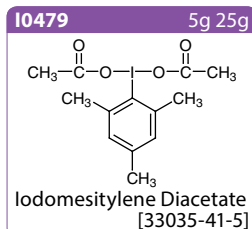
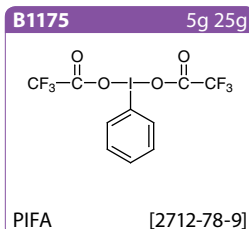
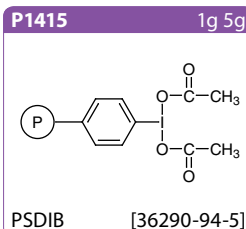
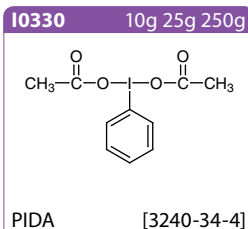
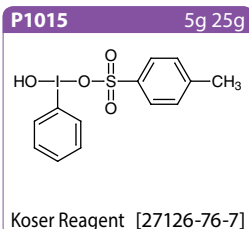
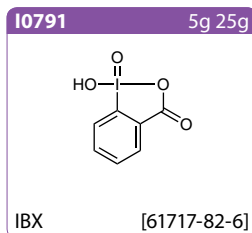
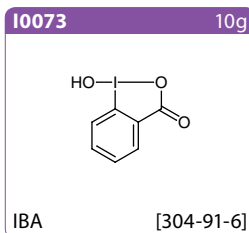
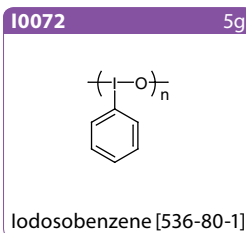
**Tosyloxylation Reagents**

**Condensation Reagents**

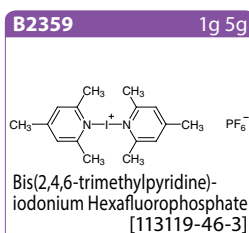
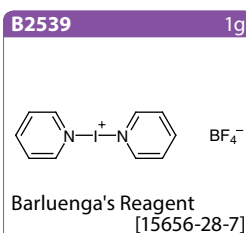
**Benzyne Precursors**

**Photo-Cationic Polymerization Initiators**

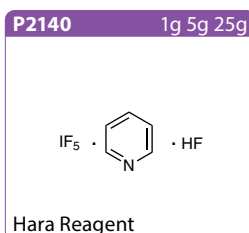
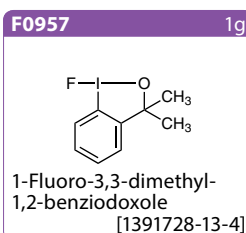
## Oxidizing Agents



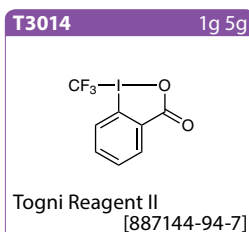
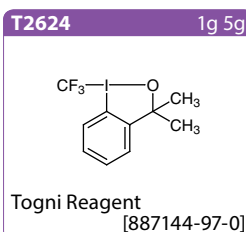
## Iodinating Agents



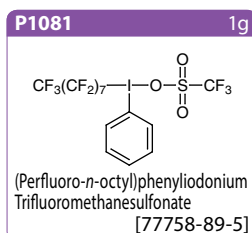
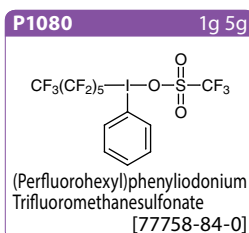
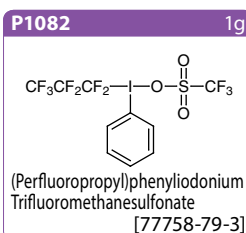
## Fluorinating Agents



## Trifluoromethylating Agents

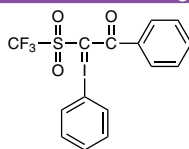


## Perfluoroalkylating Agents



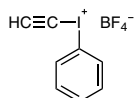
## Trifluoromethylthiolating Agents

P2143 1g 5g

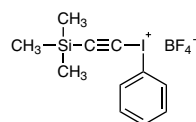

 Shibata Reagent II  
[1443036-49-4]

## Ethynylation Reagents

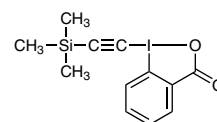
E0467 1g


 Ethynyl(phenyl)iodonium  
Tetrafluoroborate  
[127783-34-0]

P1239 1g

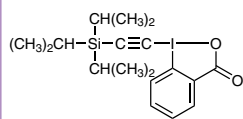

 Trimethylsilylethynyl(phenyl)-  
iodonium Tetrafluoroborate  
[127783-36-2]

T3272 1g 5g



TMS-EBX [181934-29-2]

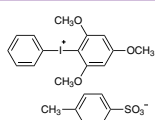
T3039 200mg 1g



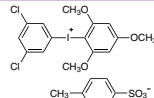
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## Arylation Reagents

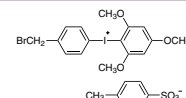
P2412 200mg 1g


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iodonium *p*-Toluenesulfonate  
[936326-60-2]

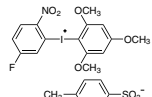
D5145 200mg 1g


 (3,5-Dichlorophenyl)-  
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[1868173-25-4]

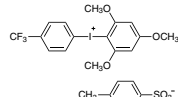
B5269 200mg


 [4-(Bromomethyl)phenyl]-  
(2,4,6-trimethoxyphenyl)-  
iodonium *p*-Toluenesulfonate  
[1453864-75-9]

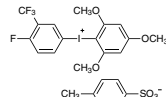
F1110 200mg


 (5-Fluoro-2-nitrophenyl)-  
(2,4,6-trimethoxyphenyl)-  
iodonium *p*-Toluenesulfonate  
[1868173-33-4]

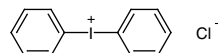
T3622 200mg 1g


 [4-(Trifluoromethyl)phenyl]-  
(2,4,6-trimethoxyphenyl)-  
iodonium Tosylate  
[1868173-15-2]

F1111 200mg

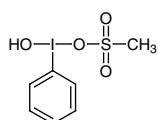

 [4-Fluoro-3-(trifluoromethyl)-  
phenyl]-(2,4,6-trimethoxyphenyl)-  
iodonium *p*-Toluenesulfonate  
[1868173-29-8]

D2356 5g 25g


 Diphenyliodonium  
Chloride [1483-72-3]

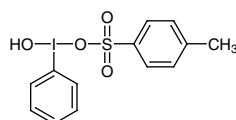
## Mesyloxylation Reagents

P1298 5g 25g


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

## Tosyloxylation Reagents

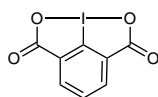
P1015 5g 25g



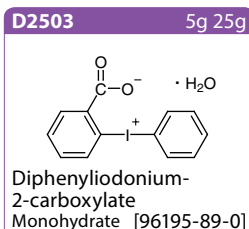
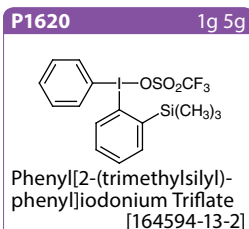
Koser Reagent [27126-76-7]

## Condensation Reagents

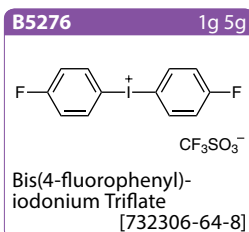
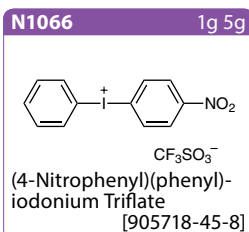
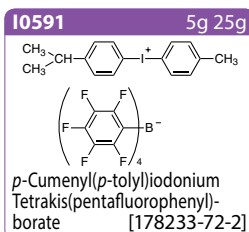
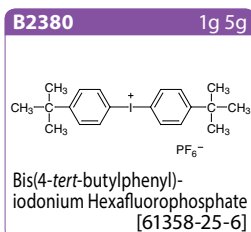
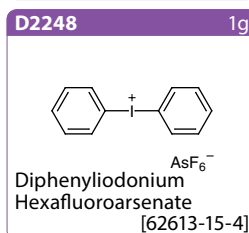
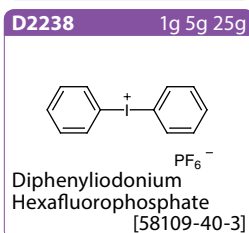
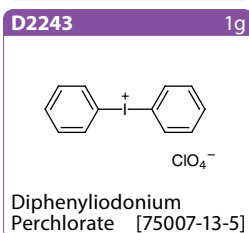
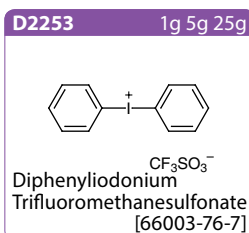
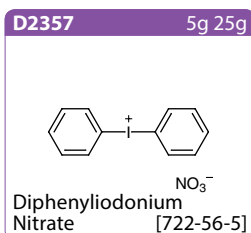
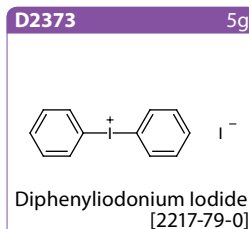
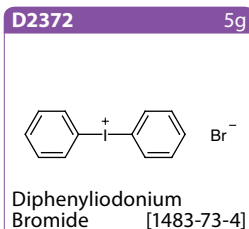
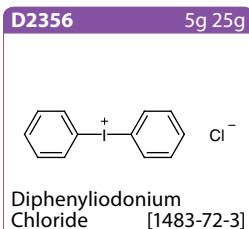
I0865 1g


 Iodosodilactone  
[2902-68-3]

## Benzyne Precursors



## Photo-Cationic Polymerization Initiators



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