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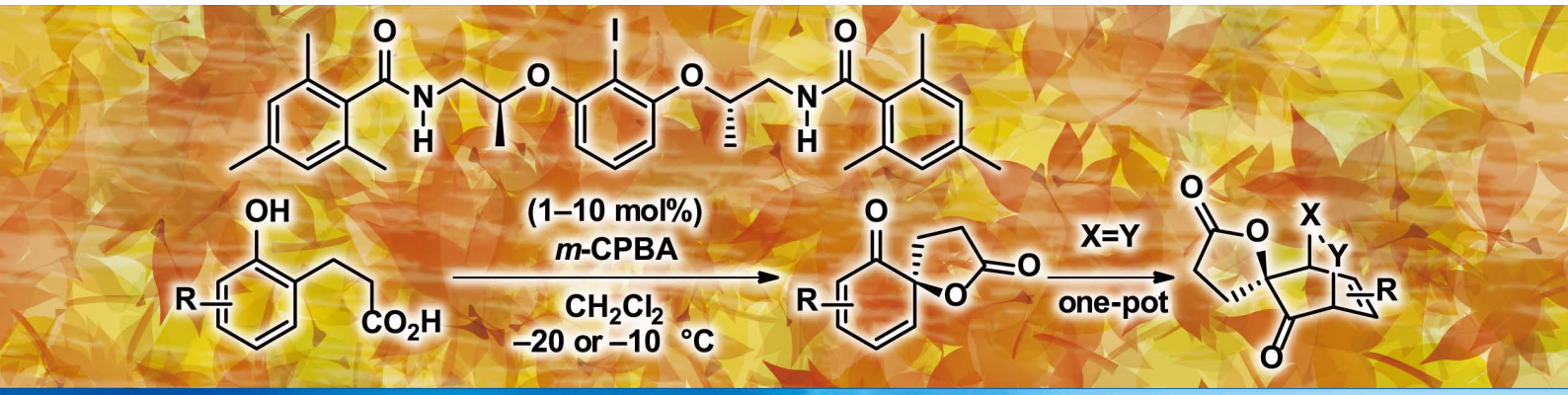

Contents

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Research Article

Designer C_2-symmetric Chiral Diamide-type Organoiodine Catalysts

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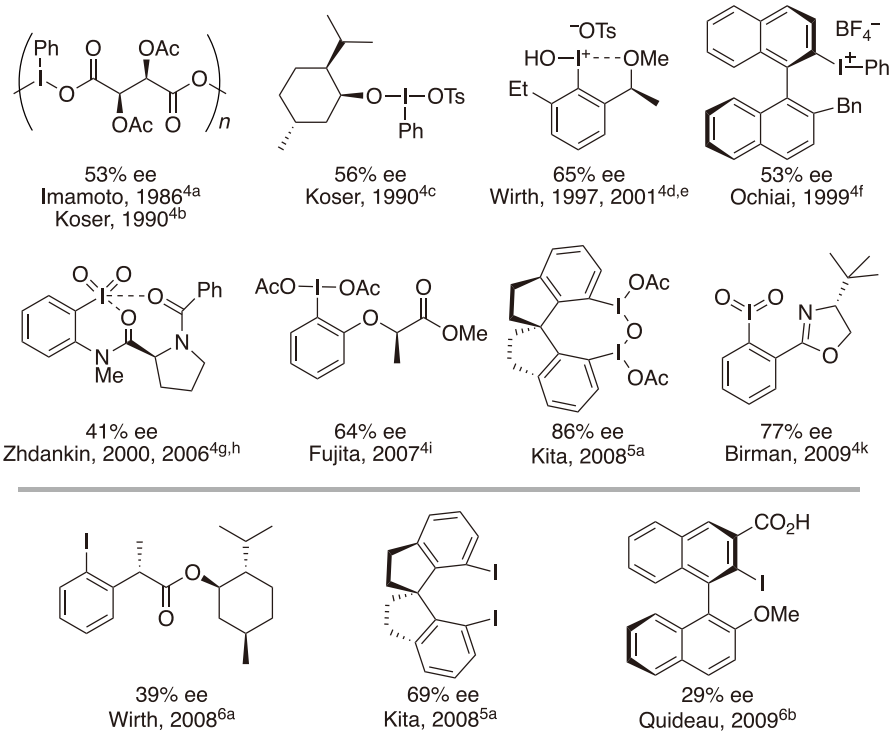
Abstract: As the global issues of environment, energy, and natural resource scarcity increase, the development of environmentally friendly and efficient catalytic methodologies of organic synthesis is strongly demanded for the sustainable advancement of material civilization. For this purpose, the use of toxic heavy metals and precious transition metals as reactants and/or catalysts should be avoided as much as possible in the synthesis of medicinal and pharmaceutical products. Over the past decades, iodine compounds have been the focus of great attention due to their mild and chemoselective oxidizing properties and their environmentally benign characteristics in contrast to toxic metal oxidants. Furthermore, the development of chiral hypervalent iodine-catalyzed enantioselective oxidative transformation is one of the most challenging areas in asymmetric organocatalysis. Here, we demonstrate the rational design of conformationally flexible chiral diamide-type C_2-symmetric organoiodine catalysis based on secondary nonbonding interactions for the enantioselective oxidative dearomatization of arenols. Several research groups have also reported highly enantioselective oxidative transformations using these conformationally flexible chiral organoiodine(III) catalysts or reagents. These examples highlight the substantial scope of conformationally flexible designer organoiodine(III) catalysis.

Keywords: *Chiral hypervalent iodine, catalyst, enantioselective oxidation, non-bonding interactions, conformationally flexible design*

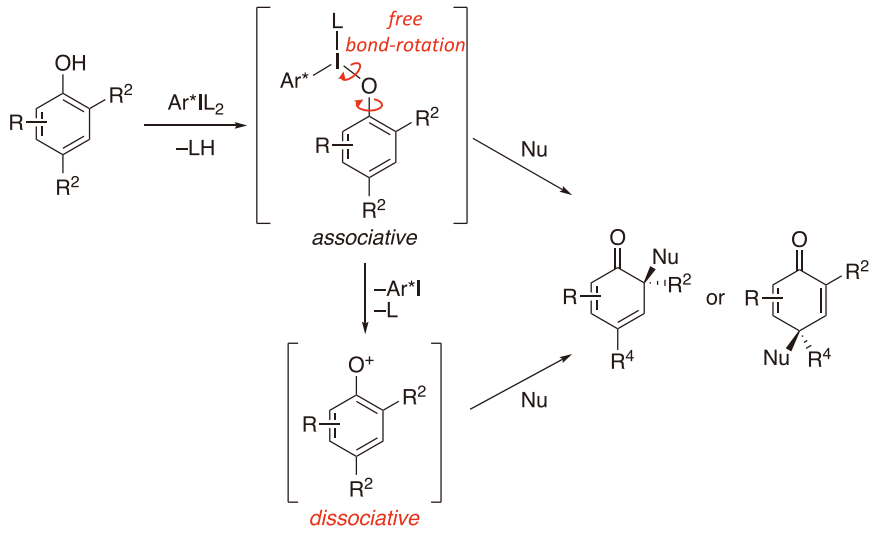
1. Introduction

The development of enantioselective hypervalent organoiodine catalysis is one of the most challenging areas in asymmetric synthesis.[1] The use of chiral hypervalent iodines has attracted great attention because of their chemoselective oxidizing properties and environmentally friendly characteristics, in contrast to toxic metal oxidants.[2] Representative examples of chiral hypervalent iodine reagents that were used for various asymmetric oxidations with the best enantioselectivities observed before our first report in 2010[3] are shown in **Scheme 1**.[4] However, the enantioselectivities of these reactions were moderate (<80%), except for Kita's reagent reported in 2008 with 86% ee,[5a] which was the highest asymmetric induction using chiral hypervalent iodines at that time. Additionally, there have been only a few examples of *in situ*-generated chiral hypervalent organoiodine (III or V) catalysts with *meta*-chloroperbenzoic acid (*m*-CPBA) as a terminal oxidant (**Scheme 1, bottom**).[5–8]

On the other hand, the enantioselective oxidative dearomatizative coupling of arenols is a useful strategy for the synthesis of various biologically active compounds.[9] The development of enantioselective oxidative dearomatization of arenols using chiral hypervalent iodine catalysis is one of the most challenging areas in asymmetric organocatalysis.[5,8,9] Especially, several researchers pointed out that it might be quite difficult to induce asymmetry via a chiral hypervalent iodine reagent because of the exclusive formation of phenoxenium ion via the dissociation of a chiral organoiodine(III) fragment during the reaction (Scheme 2).[5,10] Additionally, one might expect that asymmetric induction would be challenging even for associative pathways due to free rotation of C–O and I–O bonds in the intermediate and transition states.

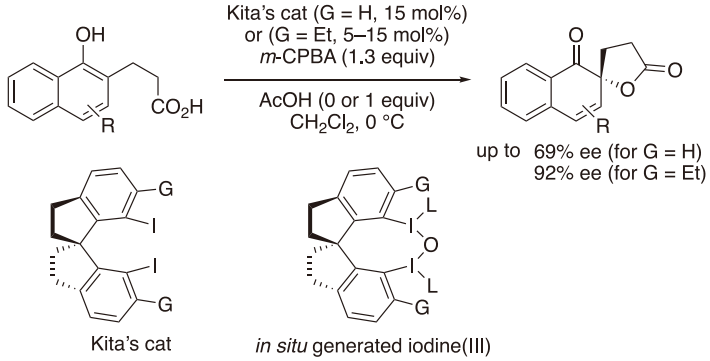


Scheme 1. Representative chiral organoiodine(III or V) reagents (top) and catalysts (bottom) reported before our first work in 2010.[4–6]



Scheme 2. Challenges in the hypervalent iodine-mediated enantioselective oxidative dearomatizative coupling of arenols.[5,10]

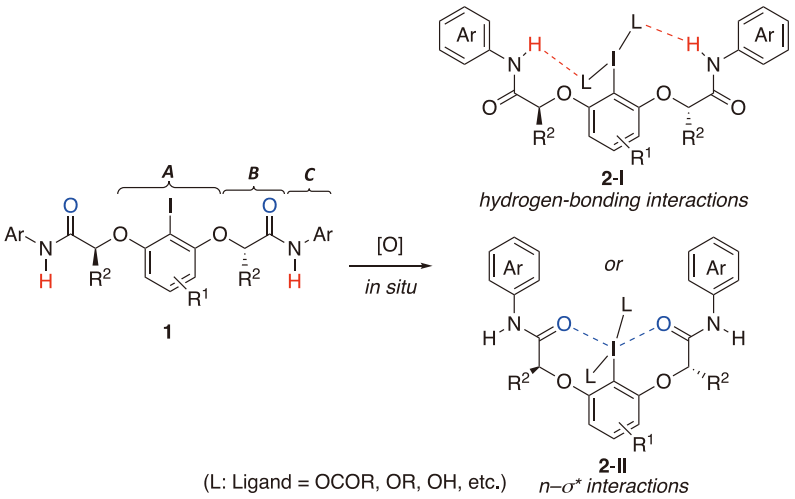
In 2008, Kita and colleagues overcame these difficulties for the first time.[5] They designed chiral organoiodines with a structurally rigid 1,1'-spirobiindane backbone, and applied it to the enantioselective oxidative dearomatization (oxidative spirolactonization, which was originally developed by Wood[11]) of 1-naphthol derivatives to the corresponding spirolactones with moderate enantioselectivity (up to 86% ee and 69% ee for stoichiometric and catalytic reactions, respectively) (**Scheme 3**).[5a] Later, the same research group succeeded in improving the enantioselectivities (up to 92% ee) by using *ortho*-modified spirobiindane catalyst.[5b] Notably, high levels of enantioselectivities were observed in halogenated solvents such as chloroform and dichloromethane. In sharp contrast, the use of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as a solvent gave racemic products. Additionally, the oxidation of 4-methoxy-substituted 1-naphthol afforded also a racemic product. These results might be explained by the stabilization of the phenoxenium ion (a dissociative intermediate) by polarizable solvents such as HFIP or resonance donation of alkoxy groups.



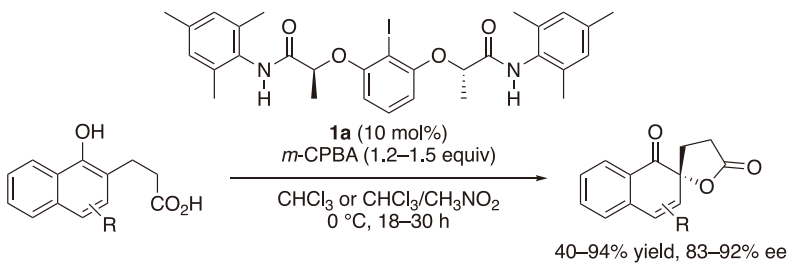
Scheme 3. Kita's structurally rigid chiral organoiodines for oxidative dearomatization of 1-naphthols.[5]

2. Design of 1st-Generation Organoiodine Catalysts

In sharp contrast to Kita's conformationally rigid design, we demonstrated the rational design of conformationally flexible hypervalent organoiodines as chiral catalysts based on secondary nonbonding interactions (i.e., intramolecular hydrogen-bonding interactions, etc.) for the same oxidative dearomatization reaction.[3,12] In 2010, we designed conformationally flexible C_2-symmetric chiral iodoarenes **1** consisting of three units: an iodoaryl moiety (**A**), chiral linkers (**B**), and subfunctional groups (**C**) (**Scheme 4**).[3] These units can be easily combined to give a wide variety of chiral iodoarenes **1**. Notably, the hypervalent iodines(III) **2** generated *in situ* from iodoarenes **1** were expected to exhibit intramolecular hydrogen-bonding interactions between the acidic hydrogen of C (N*H*Ar) and the ligand (L, such as an acetoxy group, alkoxy group, hydroxy group, etc.) of iodine(III) (**2-I**). Alternatively, intramolecular n–σ^* interactions between the electron-deficient iodine(III) center (σ^*_{C-I} orbital) of **A** and the Lewis-basic group of C (lone pair n), such as carbonyl groups, might also be generated (**2-II**). We envisioned that a suitable chiral environment might be constructed around the iodine(III) center of **2** via such non-covalent bonding intramolecular interactions. Our lactic acid-based[4i] 1st-generation catalyst **1a** (R^1, R^2, Ar = H, Me, Mes) could be successfully applied to the enantioselective oxidative dearomatization of 1-naphthol derivatives to the corresponding spirolactones with up to 92% ee (**Scheme 5**).[3]



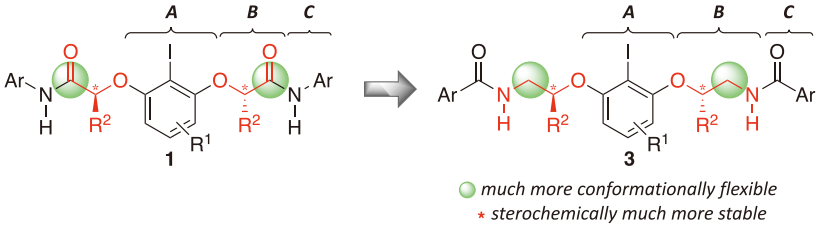
Scheme 4. Design of conformationally flexible 1st-generation chiral organoiodines **1**.[3]



Scheme 5. Enantioselective oxidative spirolactonization of 1-naphthol derivatives using 1st-generation organoiodine **1a**.[3]

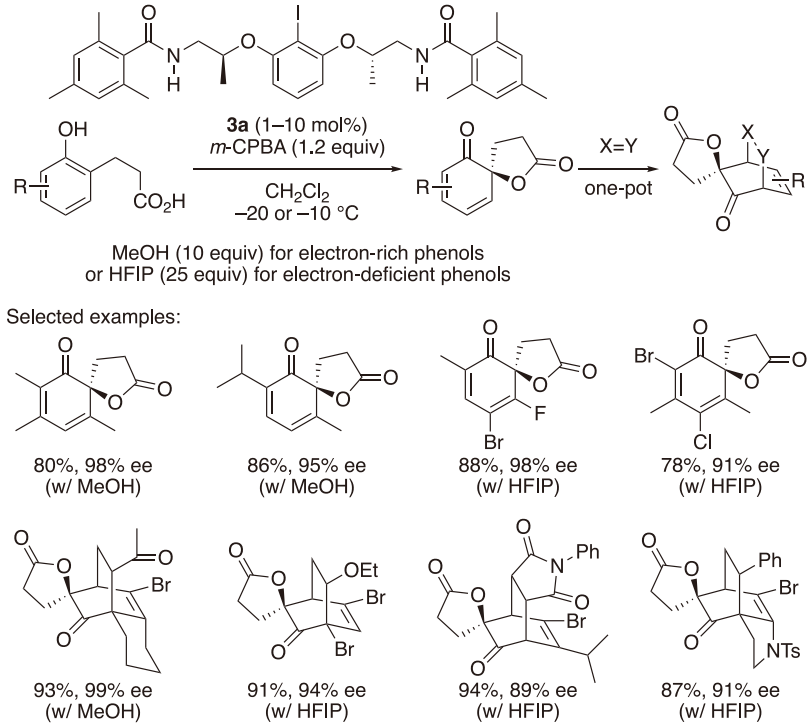
3. Design of 2nd-Generation Organoiodine Catalysts

However, lactic acid-based catalysts **1** were found to be insufficient for the oxidation of phenols, which were less reactive than 1-naphthols, with respect to not only reactivity but also enantioselectivity. To overcome these limitations, we designed new chiral organoiodines **3**, 2nd-generation catalysts, derived from 2-aminoalcohol instead of lactic acid as a chiral source (**Scheme 6**).[12] Because both **1** and **3** consist of 2-iodoresorcinol (**A**) and secondary amide (**C**) units, the acidic hydrogens are the same distance from the iodine center. On the other hand, because sp^2-hybridized carbonyl groups are moved to the outer sides, 2nd-generation catalysts **3** would be much more conformationally flexible. Moreover, **3** would be stereochemically much more stable than **1** for the same reason that the stereocenters are far from carbonyl groups.



Scheme 6. Design of 2nd-generation organoiodines **3** derived from 2-aminoalcohol as a chiral source.[12]

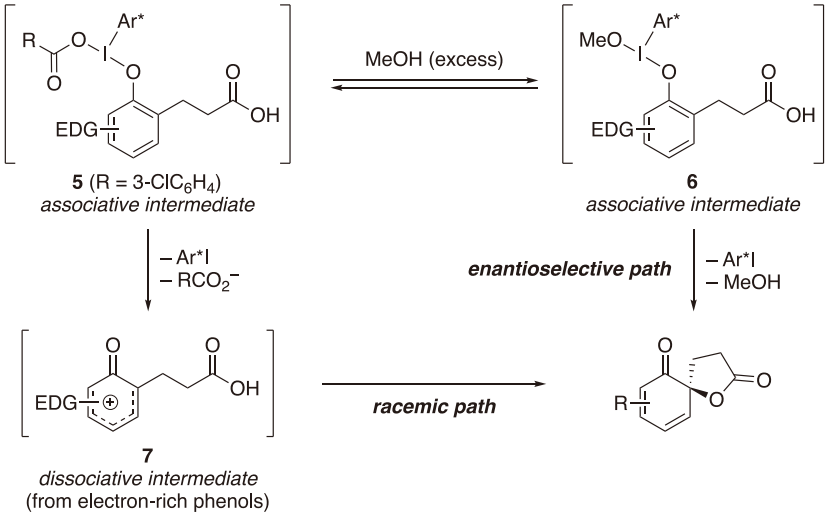
A catalyst loading of 1 to 10 mol% of **3a** (R^1, R^2, Ar = H, Me, Mes) was enough to give the desired cyclohexadienone spirolactones and the subsequent Diels–Alder adducts with excellent enantioselectivities up to 99% ee (**Scheme 7**).[12]



Scheme 7. Enantioselective oxidative spirolactonization of phenols using 2nd-generation catalysts **3a**.[12]

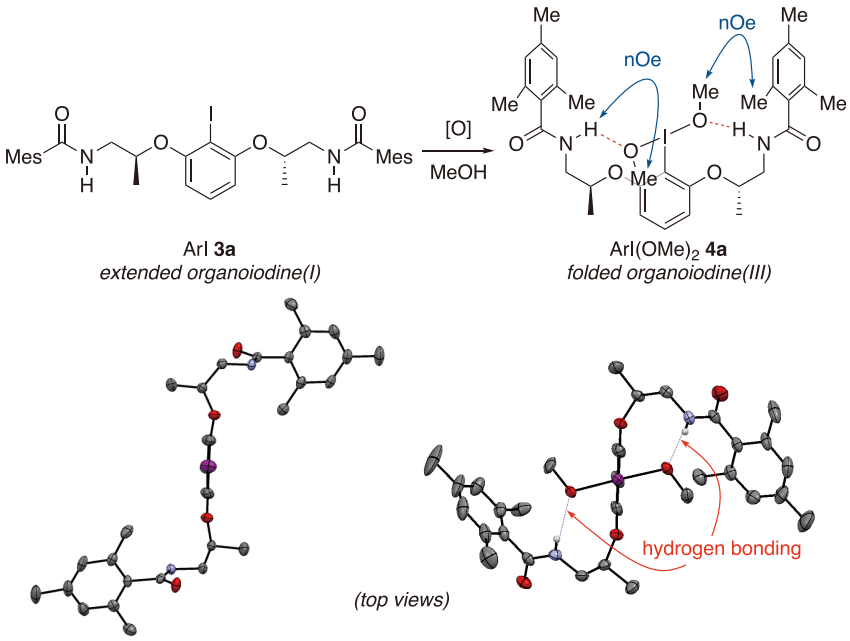
The additive effect of achiral alcohols such as methanol and HFIP was found to play a crucial role in the enantioselectivities and catalytic activities.[12] A plausible additive effect of methanol for the oxidation of electron-rich phenols is shown in **Scheme 8**. In the presence of excess amounts of methanol, methoxyphenoxy iodine(III) complex **6** might be generated from acyloxyphenoxy iodine(III) complex **5** via ligand exchanges under equilibrium. The oxidative cyclization reaction would then occur enantioselectively to produce enantio-enriched spirolactone (*enantioselective path*). In contrast, if the phenoxenium ion **7** is generated through dissociation of the iodoarene moiety ([Ar*I(OCOR')]–) from **5**, racemic spirolactone might be obtained (*racemic path*). Dissociative intermediate **7** might be generated more preferentially in the oxidation of more electron-rich phenols, due to stabilization of the cationic intermediates. The generation of **7** might be suppressed by the formation of **6**, since the leaving ability of an alkoxy ligand would be inferior to that of an acyloxy ligand. In fact, the

enantioselectivities were significantly improved with the use of methanol for the catalytic or stoichiometric oxidation of electron-rich phenols.[12] Additionally, control experiments suggest that methanol accelerates the oxidation reaction as a protic polar solvent and improves the enantioselectivity as a ligand of iodine(III). On the other hand, the beneficial effect of HFIP on the reactivity of hypervalent organoiodine-mediated reactions was investigated by Kita and colleagues.[13] However, according to previous works by both Kita[5] and our groups,[3] the enantioselectivities significantly dropped for the oxidation of highly reactive 1-naphthols in the presence of HFIP. In sharp contrast, HFIP did not reduce the enantioselectivities for the oxidation of *electron-deficient* phenols (**Scheme 7**).[12] This could be explained by the disfavoring of the dissociative path of electron-deficient phenols under these conditions.



Scheme 8. Additional methanol effect on the enantioselective dearomatization of electron-rich phenols.[12]

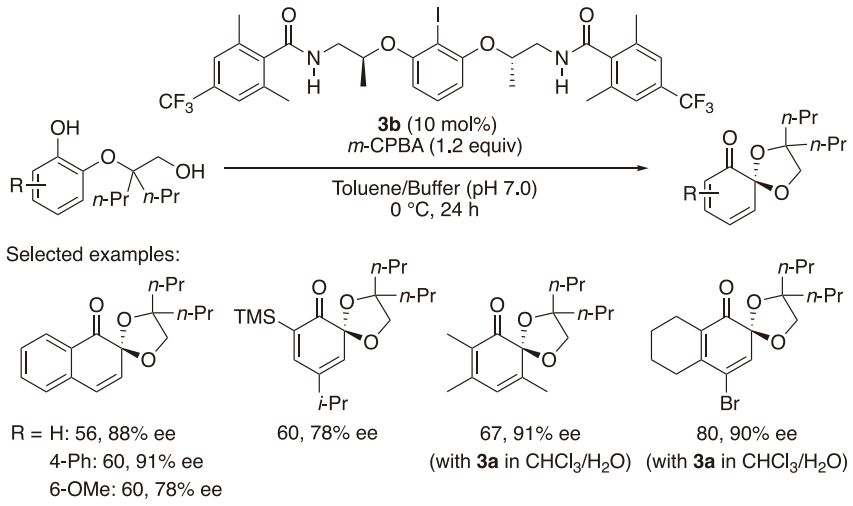
Furthermore, X-ray diffraction and NOE (Nuclear Overhauser Effect)–NMR analyses of *in situ*-generated organoiodine(III) **4a** showed that a suitable chiral environment around the iodine(III) center was constructed via intramolecular hydrogen-bonding interactions (**Scheme 9**).[12]



Scheme 9. X-ray structures of extended iodine(I) **3a** and folded iodine(III) **4a** and key NOE correlations of **4a**.[12]

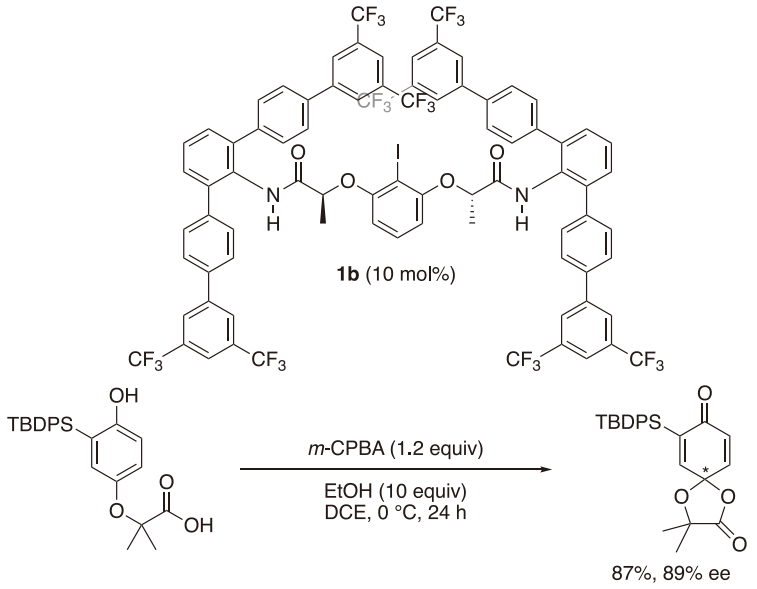
4. Application of Conformationally Flexible Organoiodine Catalysts for Enantioselective Oxidative Dearomatizative Spirolactonization

By using designer organoiodine catalysts **1** or **3**, we also achieved the first enantioselective oxidative dearomatization of *ortho*- and *para*-hydroquinone derivatives to give the corresponding masked benzoquinones[9] with high enantioselectivities (**Schemes 10 and 11**).[14] A tether strategy in which phenols were *O*-tethered to an acetic acid or ethanol unit at the *ortho*- or *para*-position realized rapid intramolecular cyclization enantioselectively prior to dissociation of the chiral iodine moiety. Interestingly, the use of slightly modified catalyst **3b** was found to be superior to the use of **3a**. Especially, this remote electronic effect was found to enhance enantioselectivity for the oxidation of phenols in a toluene–buffer (*p*H 7.0) biphasic solvent.



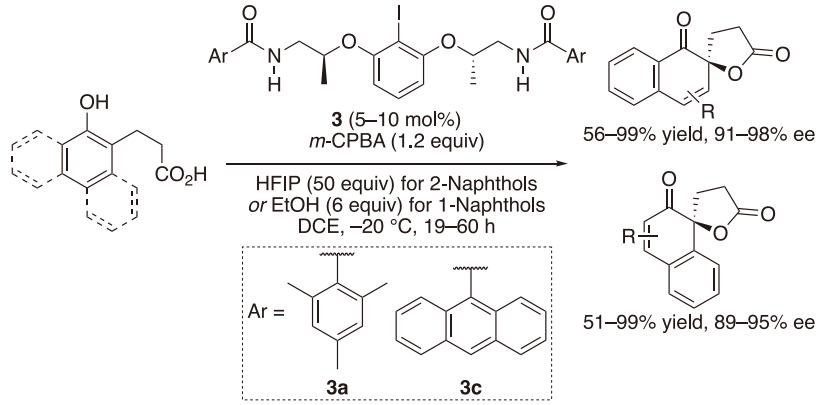
Scheme 10. Enantioselective oxidative spirolactonization of *ortho*-hydroquinones using organoiodines **3**.[14]

To achieve high enantioselectivity for the highly challenging *para*-cyclization reaction, in which the stereocenter developed far from the chiral environment created by phenoxide-bound iodine(III),[1e] we designed new lactic acid-derived catalysts **1b** bearing a deeper chiral cavity (**Scheme 11**).[14] The remote steric effects of these hydrogen bonding designer organoiodine catalysts enabled the high chemo- and enantioselectivity for the oxidative dearomatization of *para*-hydroquinone derivatives through an associative iodine(III)–phenoxide intermediate.



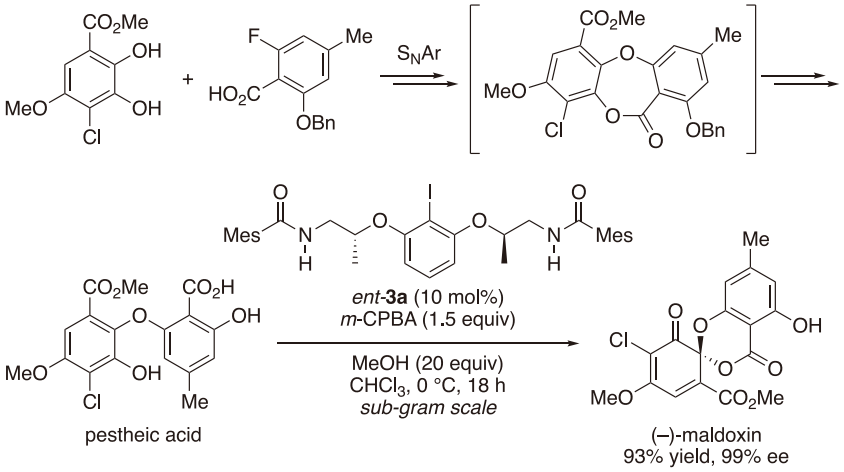
Scheme 11. Enantioselective oxidative spirolactonization of *para*-hydroquinones using organoiodine **1b**.[14]

Recently, we achieved a highly enantioselective oxidative dearomatization of 2-naphthol derivatives, which were found to be less reactive and selective by using 1st-generation catalysts **1**, by using our conformationally flexible organoiodine catalyst **3** **(Scheme 12)**.[15] Excellent enantioselectivities were also achieved for 1-naphthol derivatives that had previously[3] been obtained with lower enantioselectivities with lactic acid-based organoiodines **1**. Interestingly, the use of HFIP and methanol as additives was crucial to induce high enantioselectivity for 2-naphthol and 1-naphthols, respectively.



Scheme 12. Enantioselective oxidative spirolactonization of 1- and 2-naphthol derivatives using 2nd-generation catalysts **3**.[15]

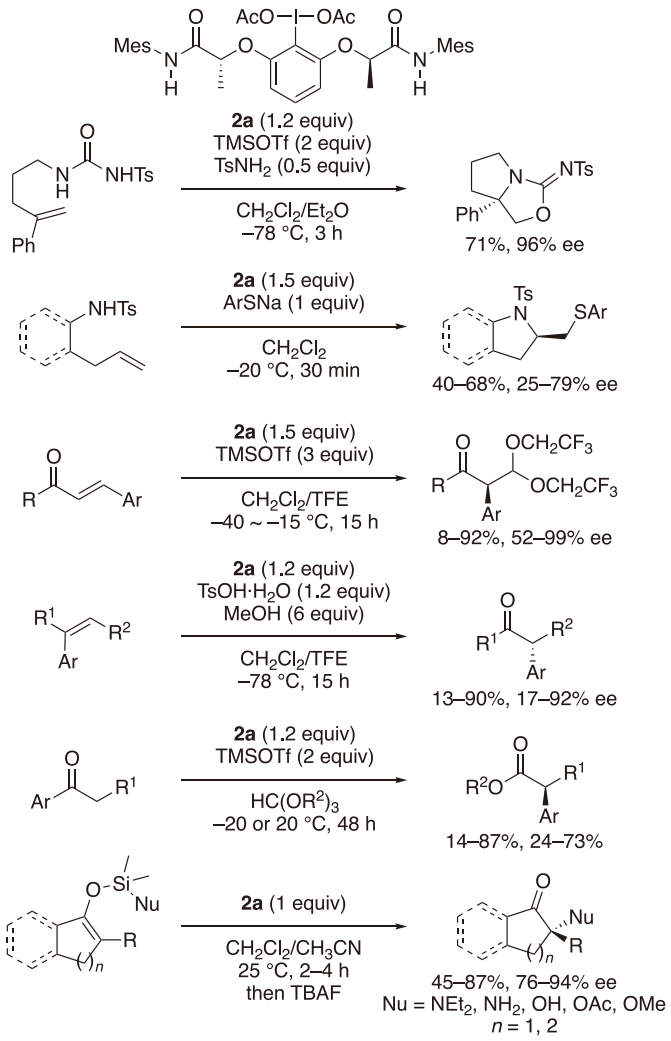
Recently, Suzuki, Tanino, Kobayashi and colleagues have successfully applied our organoiodine catalysis for the asymmetric synthesis of (−)-maldoxin (**Scheme 13**).[16] First, they achieved the total synthesis of pestheic acid based on an intramolecular S_NAr reaction without a nitro group, which has generally been required for the electrophilic substrates for S_NAr reactions. Then, a catalytic enantioselective oxidative dearomatization of pestheic acid in a sub-gram scale using organoiodine *ent*-**3a** in the presence of methanol as an additive gave enantiopure (−)-maldoxin in excellent yield.



Scheme 13. Asymmetric total synthesis of (–)-maldoxin using organoiodine catalysis.[16]

5. Application of Conformationally Flexible Organoiodine Catalysts for Various Reactionsn

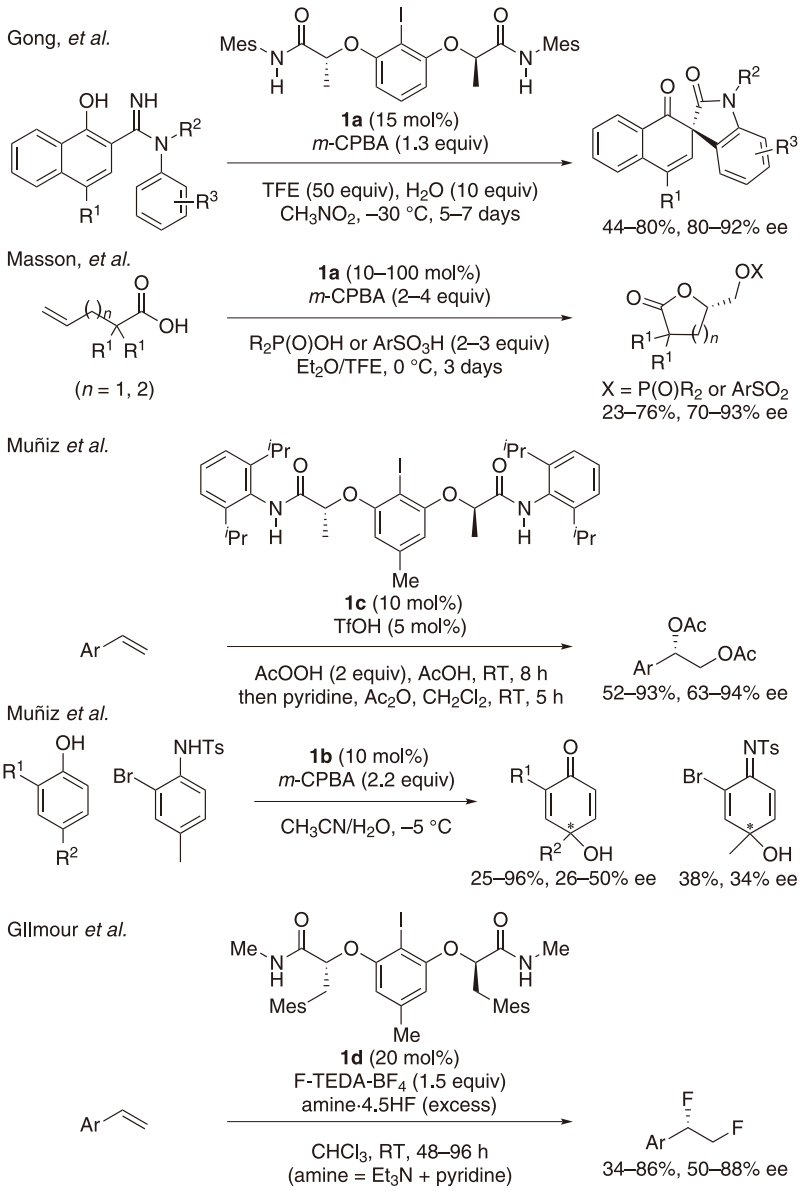
Our conformationally flexible 1st- and 2nd-generation organoiodines **1**–**3** could be successfully applied to a variety of enantioselective oxidative transformations as a reagent or catalyst.[17–19] Wirth's group reported a series of enantioselective oxidations including the oxyamination of homoallylic urea derivatives to isoureas,[17a] intramolecular thioamination of alkenes to pyrrolines or indolines,[17b] oxidative rearrangements of chalcones[17c] or 1,1-disubstituted alkenes[17d] to α-aryl ketones, oxidative rearrangement of arylketones in the presence of orthoesters to α-arylesters,[17e] and intramolecular enantioselective α-functionalization of carbonyl compounds through tethers between the nucleophile and silyl enol ethers,[17f] using our 1st-generation secondary bisamide reagent **2a**[3] **(Scheme 14)**.



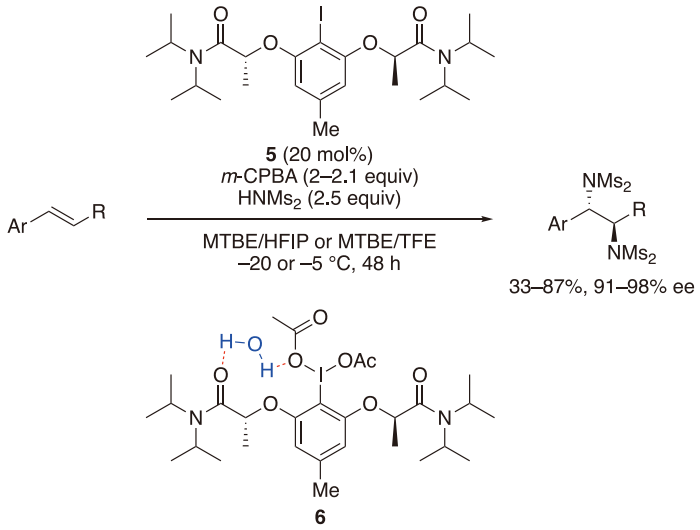
Scheme 14. Enantioselective oxidative transformations using 1st-generation organoiodine(III) reagent **2a** reported by Wirth's group.[17]

Enantioselective oxidations using catalytic amounts of lactic acid-based bisamides **1** with an oxidant were also achieved (**Scheme 15**).[18] Gong's group reported the **1a**-catalyzed dearomatizative cyclization of 1-hydroxy-*N*-aryl-2-naphthamide derivatives to generate all-carbon spiro-stereocenter using *m*-CPBA as a stoichiometric oxidant.[18a] Masson's group reported the **1a**-catalzyed enantioselective sulfonyl- or phosphoryl-oxylactonization of 4-pentenoic acids with *m*-CPBA to give the corresponding sulfonyloxy- or phosphoryloxy-γ-butyrolactones.[18b] On the other hand, Muñiz and colleagues reported the intermolecular vicinal diacetoxylation of terminal styrenes using structurally congested secondary bisamide **1c** as a catalyst in the presence of peracetic acid as an oxidant.[18c] As in our amino alcohol-derived organoiodines(III) **4**,[12] the authors have confirmed the folding structures as well as helical chirality of the corresponding iodine(III) by X-ray structural analysis.[18c] The same research group also reported the **1c**-catalyzed intermolecular dearomatization of phenols or anilines at the *para*-position using *m*-CPBA as an oxidant to give the corresponding *para*-quinols or imine with moderate enantioselectivity.[18d] On the other hand, Gilmour and colleagues reported the catalytic enantioselective vicinal difluorination of alkenes via in situ generation of an $ArIF_2$ species from the oxidation of bisamide **1d** with F-TEDA-BF_4 in the presence of an inexpensive HF–amine complex.[18e]

Muñiz and colleagues developed a tertiary bisamide **5** as a catalyst for the enantioselective intermolecular vicinal diamination of styrenes using *m*-CPBA as an oxidant (**Scheme 16**).[7p] Interestingly, a single crystal X-ray structural analysis of the corresponding iodine(III) **6** revealed the double hydrogen bonding via a water molecule, which might provide a useful explanation for the high enantioselectivity observed.

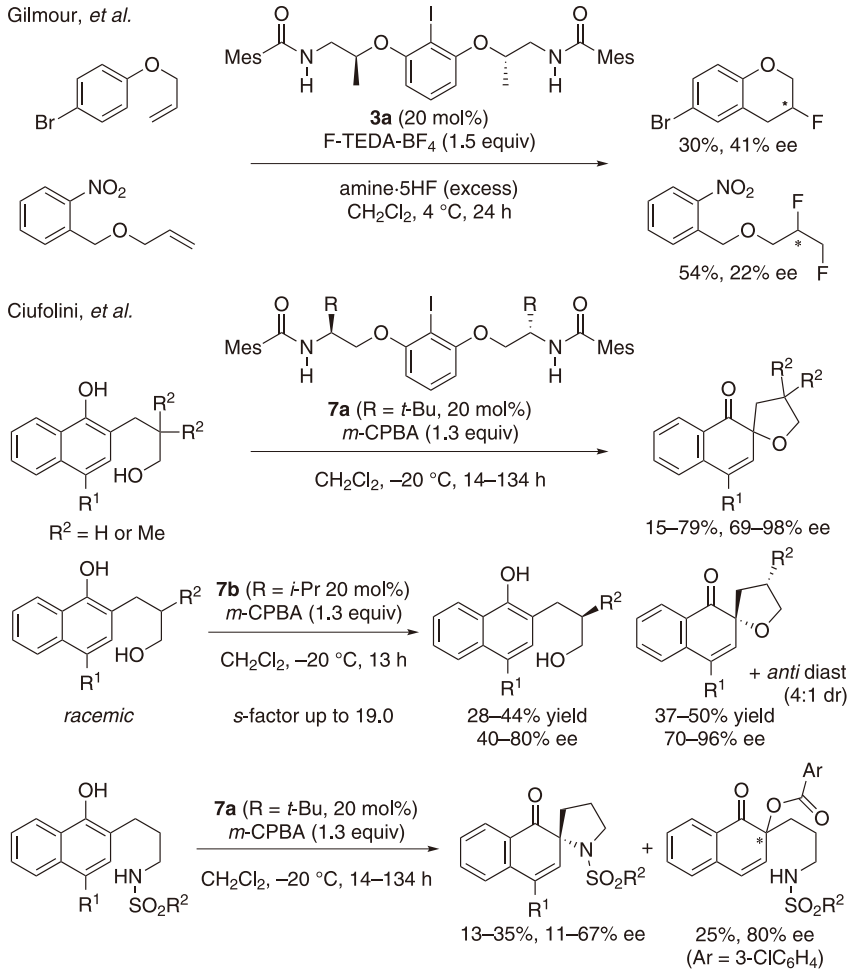


Scheme 15. Enantioselective oxidative transformations using lactic acid-based chiral bisamide catalysts **1**.[18]



Scheme 16. Enantioselective oxidative diamination of styrenes using tertiary bisamide catalyst **5** and structural analysis of the corresponding iodosoarene diacetate **6**.[7p]

On the other hand, 2nd-generation catalysts **3** or their analogues **6** have also been applied to enantioselective oxidations (**Scheme 17**).[19] Gilmour and colleagues reported the enantioselective vicinal difluorination or fluoro-cyclization of terminal alkenes using *in situ*-generated aryliodonium difluoride species from a catalytic amount of **3a** with F-TEDA-BF_4 as an oxidant in the presence of an excess amount of HF, albeit with only moderate enantioselectivity.[19a] Ciufolini and colleagues reported the enantioselective spiroetherification of 1-naphthol derivatives with *m*-CPBA as an oxidant to give the corresponding spiroethers with good to high enantioselectivity.[19b] Interestingly, catalyst **7a**, a structural analogue of our catalyst **3a**, was found to be superior to **3a** with respect to both stereoselectivity and reactivity for this particular reaction, especially under low catalyst-loading conditions.[19b] The same research group also reported the oxidative kinetic resolution of some 1-naphtholic alcohols using catalyst **7b** with an *S*-factor of up to 19.0.[19c] Recently, the same research group has also applied their catalyst **7a** to the enantioselective oxidative dearomatizative spiroamination of 1-naphtholic sulfonamides, albeit in moderate enantioselectivity and low yields.[19d] The low chemical yields were attributed to the generation of the intermolecular coupling product with *m*-CBA, a side-product derived from the oxidant used. Interestingly, this dearomatized *ortho*-acyl adduct could be obtained in significantly enantioenriched form.



Scheme 17. Enantioselective oxidative transformations using amino alcohol-derived chiral organoiodine catalysts **3** or **7**.[19]

6. Conclusion

In summary, we have demonstrated the rational design of conformationally flexible C_2-symmetric organoiodine catalysis based on secondary nonbonding interactions for the enantioselective oxidative dearomatization of arenol derivatives. Especially, we developed lactic acid-based 1st-generation and 2-amino alcohol-based 2nd-generation catalysts. Notably, Fujita and colleagues first introduced lactic acid as a chiral source for chiral hypervalent organoiodine(III) reagents.[4i] Although we have focused here on our diamide-type organoiodines, Fujita and colleagues have developed independently several lactic acid-based C_2-symmetric chiral organoiodines with diester functionality instead of diamides.[1h,4j] Several enantioselective oxidation reactions have also been developed by using these diester-type reagents or catalysts.[7,8] We hope that suitable catalysts may be found easily among those of both diamide- and diester-type catalysts for various further enantioselective oxidative transformations.

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Prof. Kazuaki Ishihara was born in Aichi, Japan, in 1963, and received his PhD from Nagoya University in 1991 under the direction of Professor Hisashi Yamamoto. He had the opportunity to work under the direction of Professor Clayton H. Heathcock at the University of California, Berkeley, as a visiting graduate student for three months in 1988. He was a JSPS Fellow under the Japanese Junior Scientists Program from 1989 to 1991. After completing his postdoctoral studies with Professor E. J. Corey at Harvard University, he returned to Japan and joined Professor H. Yamamoto's group at Nagoya University as an assistant professor in 1992, and became associate professor in 1997. In 2002, he was appointed to his current position as a full professor at Nagoya University. His research interests include asymmetric catalysis, biomimetic catalysis induced by artificial enzymes, dehydrative condensation catalysis towards green and sustainable chemistry, and acid–base combination chemistry. He has received numerous awards and honors for his work. His representative awards include: the Chemical Society of Japan Award (2018), the Scientists' Prize (The Commendation for Science and Technology by MEXT, 2017), the Synthetic Organic Chemistry Award (2016), the Society of Iodine Science Award (2015), the Ichimura Prizes in Technology–Contribution Prize (2013), the Yazaki Academic Award (2013), the Inoue Prize for Science (2011), and the Mukaiyama Award (2009).

Related Products

N,*N*′-[(2*S*,2′*S*)-[(2-Iodo-1,3-phenylene)bis(oxy)]bis(propane-2,1-diyl)]bis(mesitylamide)			200mg	I1122
(*R*,*R*)-2-Iodo-1,3-bis[1-(mesitylcarbamoyl)ethoxy]benzene			200mg	I0807
3-Chloroperoxybenzoic Acid (= *m*-CPBA)		25g	250g	C0357
1,1,1,3,3,3-Hexafluoro-2-propanol (= HFIP)	25g	100g	500g	H0424
Trimethylsilyl Triflate (= TMSOTf)	5g	25g	250g	T0871
p-Toluenesulfonamide (= $TsNH_2$)		25g	500g	T0281
2,2,2-Trifluoroethanol (= TFE)	25g	100g	500g	T0435
p-Toluenesulfonic Acid Monohydrate (= $TsOH{\cdot}H_2O$)		25g	500g	T0267
Tetrabutylammonium Fluoride (*ca*. 1mol/L in Tetrahydrofuran)	25mL	100mL	500mL	T1338
N-Fluoro-*N*′-(chloromethyl)triethylenediamine Bis(tetrafluoroborate) (= F-TEDA-BF_4)	5g	25g	100g	F0358
tert-Butyl Methyl Ether (= MTBE)		25mL	500mL	B0991

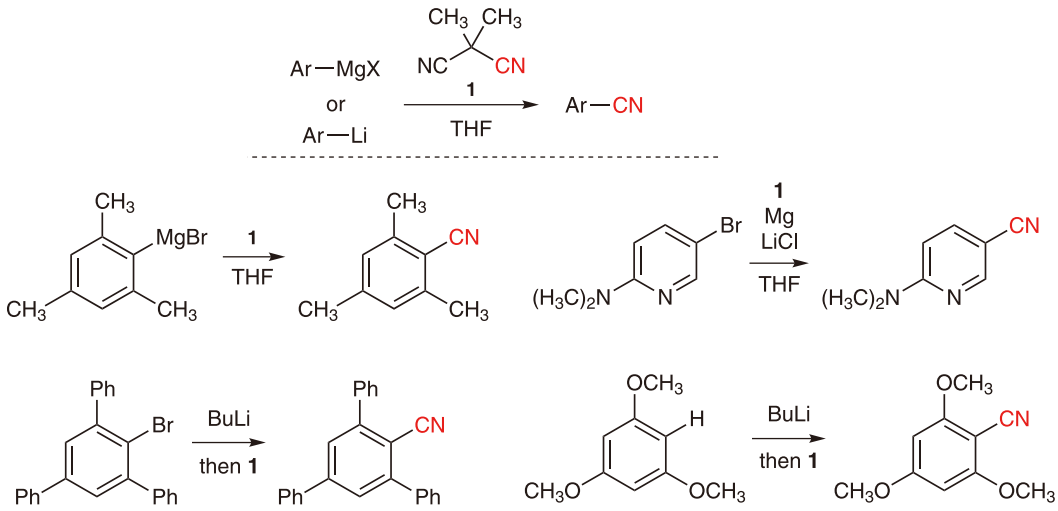
New Product Information

Low-Toxic Electrophilic Cyanating Reagent

Dimethylmalononitrile (1)

Product Number: **D5514**
5g

Dimethylmalononitrile (**1**) is a low-toxic electrophilic cyanating reagent and can introduce cyano groups into aromatic rings.[1,2] Aryl Grignard reagents (ArMgX) or aryllithiums (ArLi), derived from aryl halides (ArX), react with **1** to give cyano compounds (ArCN) in good yields. This reaction can be conducted under a transition metal free condition, and is applicable for various types of heteroaromatic or sterically hindered substrates. As cyano groups can be converted to other functional groups or scaffolds, further applications are anticipated to be reported.



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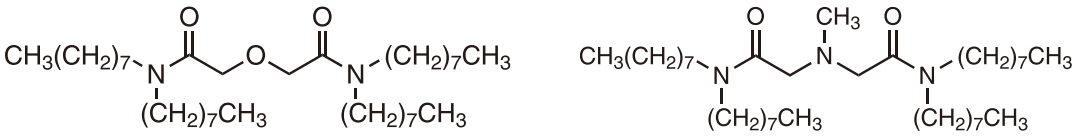
An Effective Extractant for Rare-Earth Elements

TODGA (1)

Product Number: **O0523**
250mg 1g

TODGA (**1**) is an effective extractant for rare-earth elements.[1] **1** is highly lipophilic and applicable to extraction of metals to the organic layer in the HNO_3(aq.)-*n*-dodecane system.[1,2] Due to the high extractability with **1** of hard metal ions such as rare-earth metals, **1** is evaluated as an extractant for the separating of rare-earth elements from high-level nuclear waste solutions at nuclear reactors.[3] On the other hand, MIDOA (**2**) is superior to extract soft metals, so they are complementarily utilized.[4]



1 **2**

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Related Product

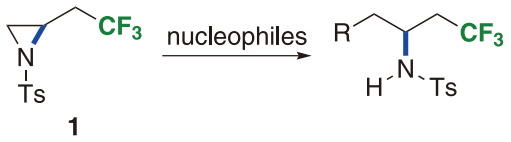
MIDOA (**2**)	1mL	5mL	M2476

Aziridine Derivative for the Synthesis of a Trifluoroalkylamine Moiety

1-Tosyl-2-(2,2,2-trifluoroethyl)aziridine (1)

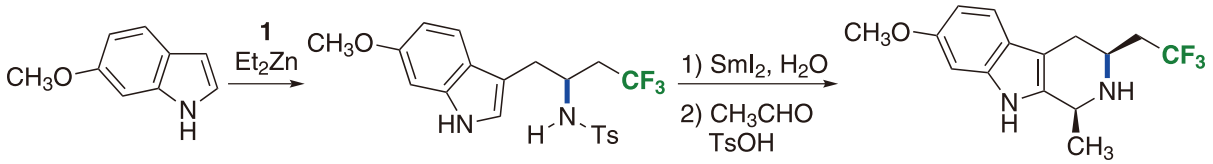
Product Number: **T3795**
200mg 1g

1-Tosyl-2-(2,2,2-trifluoroethyl)aziridine (**1**), which is utilized in the synthesis of trifluoroalkylamine derivatives, reacts with various carbon and nitrogen nucleophiles to provide ring-opening adducts with high regioselectivity and in high yields. Furthermore, when the indole adduct **2** is treated with acetaldehyde, the tetrahydroharmine derivative containing a fluorinated functional group (**3**) is afforded via a Pictet-Spengler reaction. **1** is anticipated to be used as a building block for fluoroamine synthesis and heterocycles for pharmaceutical and agrochemical research.



1

nucleophiles: Grignard reagents, ArO^-, ArS^-, $ArNH_2$, etc.



2 **3**

Reference

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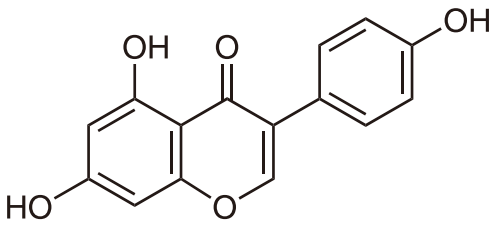
Related Product

Samarium(II) Iodide (*ca.* 0.1mol/L in Tetrahydrofuran)	25mL	100mL	S0494

Tyrosine Kinase Inhibitor: Genistein

Genistein (1)

Product Number: **G0272**
100mg 1g



1

Genistein (**1**) is a specific inhibitor of tyrosine-specific protein kinase and the inhibition manner to EGF receptor kinase by **1** is ATP-competitive but non-competitive with the substrate, histone H2B.[1] As shown in Table I, **1** inhibits autophosphorylation of EGF receptor more potently than other flavonoids and isoflavonoids.[1]

Interestingly, **1** inhibits DNA topoisomerase II on the DNA cleavage assay basis (Table II).[2] **1** also inhibits yeast α-glucosidase with a Ki value of 5.7×10^{-8} M.[3] The inhibition manner is non-competitive. **1** inhibits several enzymes in the following order of IC_{50}: α-glucosidase (50 nM), α-mannosidase (840 nM), β-mannosidase (4.5 μM), β- glucosidase (18 μM).

Table Ⅰ. Inhibition of genistein and related compounds to FGF receptor kinase[1]

Compounds	IC_{50} (μg/ml)
Genistein	0.7
Genistin	>100
Prunetin	4.2
Daidzein	>100
Biochanin A	26
Apigenin	25
Acacetin	40
Flavon	50
Xaempferol	3.2
Quercetin	5

Table Ⅱ. Inhibition of genistein to DNA topoisomerase II-mediated DNA cleavage activity[2]

Compounds	Formation of cleavable complex (μM)
Genistein	5
Genistin	50
Prunetin	>100
Biochanin A	>100
Apigenin	>100
Quercetin	>100

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MATERIALS

Highly Purified and Rapidly Soluble Crystalline Perovskite Precursors $MAPbI_3$-DMF and $FAPbI_3$

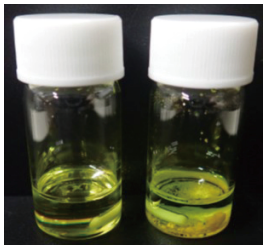
$MAPbI_3$-DMF (99.99%, trace metal basis) [for Perovskite precursor] 1g / 5g / 25g **[P2415]**
New **$FAPbI_3$** (99.99%, trace metal basis) [for Perovskite precursor] 1g / 5g / 25g **[P2417]**

Advantages

- Highly purified (99.99%) and rapidly soluble
- Ready-to-use crystalline solid for one-solution method
- Serves high PCE with reproducibility

$MAPbI_3$-DMF [P2415] and $FAPbI_3$ [P2417] are crystalline solids with high purity of 99.99% (trace metals basis). P2415 or P2417 is rapidly soluble compared with separate use of PbI_2 and MAI, or PbI_2 and FAI, respectively. These also show good solubility in DMSO. Wakamiya *et al.* have reported that P2415 can realize high power conversion efficiency (PCE) and reproducibility at a perovskite solar cell (PSC) device, and the low volatility of the pure DMSO solvent can extend the allowable time for antisolvent addition, and then can largely relax the time precision required for the antisolvent addition step.[1] On the other hand, they say that P2417 can be used with other cations Cs, MA, etc. forming mix-cation perovskites, and the PSC device can realize high efficiency and stability by an ambient air aging method.[2]

Rapid Dissolution



Left:
$MAPbI_3$-DMF [P2415]

Right:
MAI + PbI_2 (1:1)

1.5 mmol of 'MA/Pb' were added to 1 mL of DMSO and stirred for 3 min at room temp.

Left:
$FAPbI_3$ [P2417]

Right:
FAI + PbI_2 (1:1)

1.2 mmol of 'FA/Pb' were added to 1 mL of DMSO and stirred for 10 min at room temp.

PSC Device Performances

Table 1. (from Reference 1)
P2415 serves high PCE with reproducibility compared with MAI and PbI_2. (PCE = 19.8% (0.1 cm^2 cell), 14.2% (22 cm^2 cell))

$MAPbI_3$ source[*1]	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
$MAPbI_3$ DMF [P2415]	22.7	1.15	0.76	**19.8**
MAI + PbI_2	21.8	1.15	0.70	17.6

[*1] $MAPbI_3$ based Perovskite Solar Cell

Table 2. (from Reference 2)
P2417 is excellent precursor of FA containing perovskite layer. (Stable to long term storage as compared with FAI and PbI_2)

$FAPbI_3$ source[*2]	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
$FAPbI_3$[*3] **[P2417]**	23.7	1.11	0.78	**20.6**
FAI + PbI_2	23.0	1.11	0.75	19.4

[*2] $Cs_{0.05}FA_{0.80}MA_{0.15}PbI_{2.75}Br_{0.25}$ based Perovskite Solar Cell
[*3] Optimized device by ambient air aging method (see, Reference 2)

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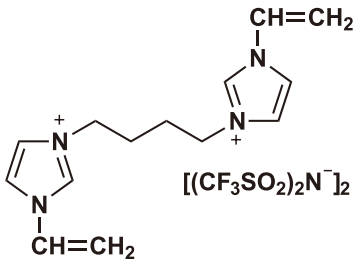
These products are commercialized by collaboration with Prof. Atsushi Wakamiya at Institute for Chemical Research, Kyoto University.

MATERIALS

Monomers for Poly(Ionic Liquid) Synthesis



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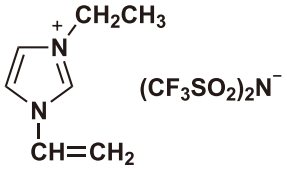
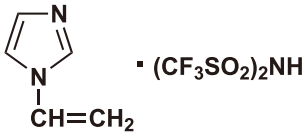
[B5421]



5g
[E1280]



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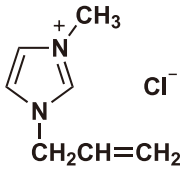

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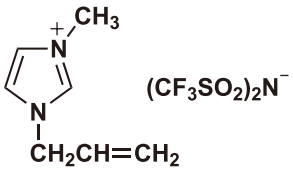

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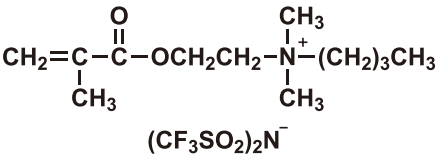

1g / 5g
New [M2987]

These chemicals bearing vinyl, allyl, or methacryl groups have been reported useful starting materials in the synthesis of polymers with properties as ionic liquids.

Applications

Polymeric electrolytes

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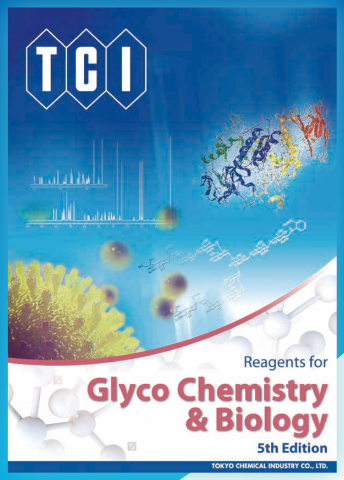

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