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Asymmetric iodine catalysis-mediated enantioselective oxidative transformations

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The implementation of chiral iodine catalysis has tremendously been developed in the field of asymmetric synthesis over the past decade. It enables the stereoselective creation of C–O as well as C–C, C–N and C–X (X = halogen) bonds through oxidative transformations. Thanks to the low toxicity and ease of handling of iodine compounds, this strategy offers many advantages over classical metal-catalyzed oxidations with chiral ligands. The approaches rely on iodine(I/III) or (–I/+I) catalysis by using a chiral aryliodine or ammonium iodide respectively in combination with a suitable terminal oxidant. As such, the design of iodine compounds with central, axial or even planar chirality has allowed us to achieve high enantioselectivities. The goal of this review is to cover the different chiral iodine compound-catalyzed oxidative transformations including α-functionalization of carbonyl compounds, dearomatization of phenol derivatives and difunctionalization of alkenes which should demonstrate that iodine catalysis has now found its place in the realm of asymmetric organocatalysis.

1. Introduction

Iodine catalysis has emerged as a versatile and eco-friendly strategy to perform oxidative transformations allowing for instant coupling with the formation of a C–O, C–N, C–C or C–X (X = halogen) bond.[1] In order to describe the mechanisms of such reactions, synthetic chemists frequently borrow the terms of oxidative additions, ligand exchanges and reductive eliminations to the field of metal-mediated processes. Nevertheless, iodine compounds are mild, stable, easy to handle and eco-compatible reagents, advantageously competing with heavy metals. As such, it is not surprising that iodine catalysis has attracted the interest of the synthetic community in the field

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Aurélie Claraz

Dr Aurélie Claraz received her Ph.D degree in organic chemistry in 2012 at Rouen (France) under the guidance of Dr Vincent Levacher. She joined the group of Pr. Petri Pihko at Jyväskylä (Finland) from 2013 to 2015 as a postdoctoral fellow. She then held a temporary assistant lecturer position in ChimieParisTech (France) working with Dr Sylvain Darses. After a second postdoctoral position in Pr. Janine Cossy's group (France), she was appointed at the CNRS as a research associate in Dr Géraldine Masson's group in November 2017. Her research interests lie mainly in the field of asymmetric organocatalysis with a special emphasis on organocatalyst design.

Géraldine Masson

Géraldine Masson received her PhD in 2003 from the Joseph Fourier University (France). She then moved to the University of Amsterdam (Holland) as a Marie Curie postdoctoral research fellow with Prof. Jan van Maarseveen and Prof. Henk Hiemstra. At the end of 2005, she was appointed "Chargé de Recherche" by the CNRS in the research group of Prof. Jieping Zhu at the Institut de Chimie des Substances Naturelles (ICSN), before initiating her independent career in 2011. She was promoted to Research Director of CNRS in 2014. Her group's research activities are directed toward the development of the design and the development of new catalytic methods for the synthesis of optically active molecules displaying biologically activities.

of asymmetric synthesis with the aim to develop a greener and more environmentally benign chemistry.[2] Until now, asymmetric iodine catalysis-mediated oxidative transformations have been relying on the catalytic use of either hypervalent organoiodine(III) reagents (also called λ^3-iodanes) or organic hypoiodites (I) as chiral oxidants. In the first case, chiral organoiodanes (III)[3] are generated *in situ* from aryliodine precatalysts and a stoichiometric amount of an achiral co-oxidant (Fig. 1). In 2005, Ochiai *et al.*[4] and Kita *et al.*[5] independently demonstrated the first catalytic use of a iodoarene in combination with *m*CPBA as a stoichiometric terminal oxidant.

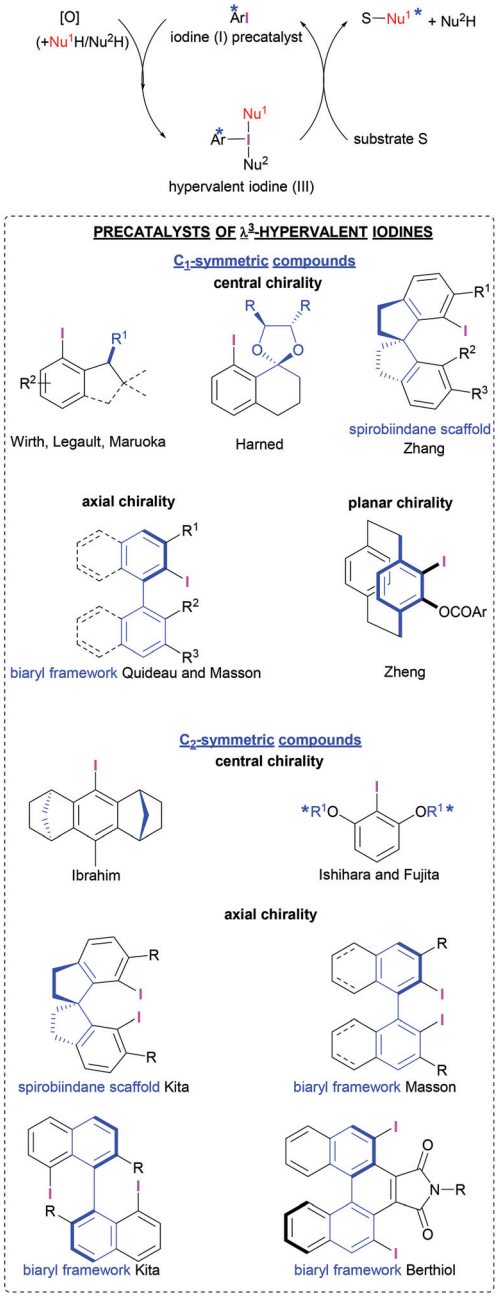


Fig. 1 Concept of iodine(I/III)-enabled enantioselective oxidative transformations and general structures of chiral aryliodine precatalysts.

Clearly, these seminal studies paved the way for iodine(I/III) catalysis, and in 2007, the first enantioselective catalytic transformation was reported by Wirth *et al.* for the α-oxytosylation of ketones by using an aryliodine species bearing a chiral moiety *ortho* to the iodine atom in the aromatic ring.[6] Since this original report, numerous chiral aryliodoarene-mediated enantioselective oxidative transformations through iodine(I/III) catalysis have been investigated.[7] Besides cost reductions and atom economical nature, the development of catalytic processes allows us to avoid the preliminary preparation and isolation of the chiral hypervalent organoiodine(III) reagent, since this reactive species is generated *in situ* from an aryliodine. Obviously, this feature can be advantageous during the design of new chiral precatalysts, especially for unstable hypervalent organoiodine(III) derivatives. The currently known enantiopure precatalysts of hypervalent organoiodine(III) compounds exhibit either C_1- or C_2-symmetry with central, axial or even planar chirality (Fig. 1).

On the other hand, chiral hypoiodites (I) are generated *in situ* from chiral organic iodides(–I) (typically chiral ammonium iodides that are traditionally used in asymmetric phase transfer catalysis),[8] and a stoichiometric amount of an achiral co-oxidant (Fig. 2).[9]

In both catalytic cycles depicted above, (re)oxidation of the iodine atom of a precatalyst from a low valent state to a higher oxidation state is the key step.[10] The choice of this stoichiometric achiral oxidant is critical for the success of the reaction. In an ideal fashion, it should not interact with the starting material or, at least, reoxidation of the precatalyst should be faster than the rates of undesired side reactions. In asymmetric processes, peroxides are the most commonly used oxidants that satisfy these requirements with more or less success.

To achieve cleaner reactions along with highest levels of enantiocontrol, a careful optimization of other classical reac-

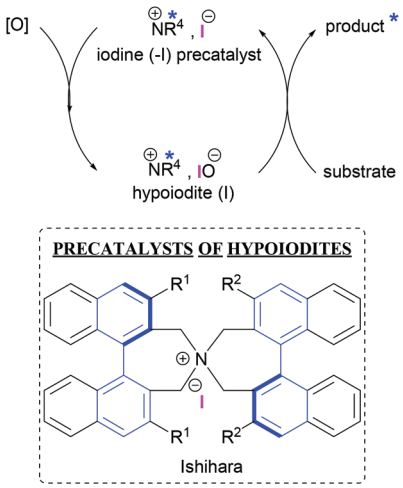


Fig. 2 Concept of iodine(–I/I)-enabled enantioselective oxidative transformations and general structure of chiral ammonium iodide precatalysts.

tion parameters such as solvent, temperature and the use of additives must be undertaken.

The focus of this review is to summarize the use of chiral iodine compounds in catalytic enantioselective oxidative processes with the aim of highlighting both catalyst design and synthetic applications. As such, we hope that this survey will help the reader in designing new chiral iodine precatalysts and applying those to new catalytic processes. For the sake of clarity, this review has been divided into different sections according to the kind of oxidative transformation considered:

a. α-functionalization of carbonyl compounds,

b. dearomatization of phenol derivatives,

c. functionalization of alkenes.

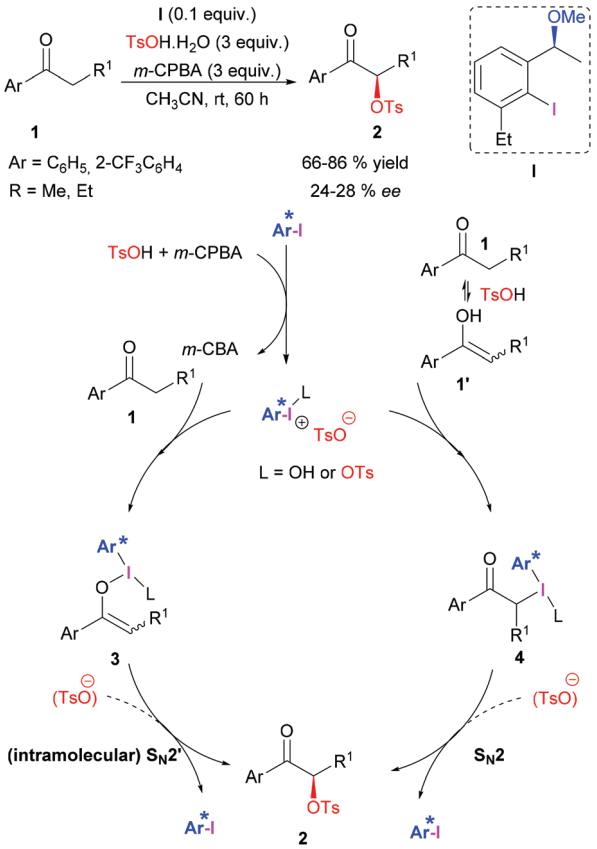
To help the reader, a color code has been used through all schemes and figures. Thus, on the precatalyst, pink, blue and green indicate the iodine atom, the enantiocontrol moiety and the chelating group respectively. The nucleophile and the formed bond are shown in red.

2. α-Functionalization of carbonyl compounds

Hypervalent iodine compounds enable the introduction of a nucleophile at the α-position of a carbonyl compound. As such, numerous efforts have been made towards the development of enantioselective versions to take advantage of this inversion of polarity (*umpolung* reaction).

2.1. α-Oxytosylation

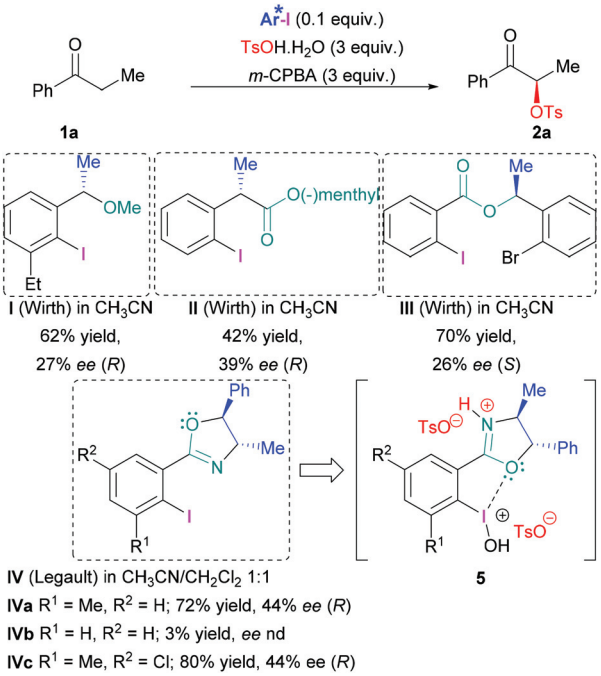
The enantioselective α-oxytosylation of ketones mediated by chiral hypervalent iodines gives access to synthetically useful enantioenriched carbonyl compounds. As mentioned above, the first catalytic enantioselective version of this reaction was reported in 2007 by Wirth *et al.* Inspired by the studies of Ochiai *et al.* who demonstrated the first catalytic racemic version of α-acetoxylation of ketones,[4] Wirth *et al.* employed organoiodane **I** with central chirality as the chiral inducer, *meta*-chloroperoxybenzoic acid (*m*CPBA) as the stoichiometric oxidant and *p*-toluenesulfonic acid monohydrate ($TsOH{\cdot}H_2O$) as a source of tosylate nucleophiles (Scheme 1).[6] In contrast to the process under stoichiometric conditions,[11] the catalytic transformation needs to be carried out at room temperature, which suggests that oxidation of the iodoarene is the rate determining step in the catalytic cycle. Noteworthily, no racemization of the product in the reaction medium was observed. Nevertheless, only moderate enantioselectivities were obtained in this difficult transformation. From a mechanistic point of view, the authors proposed the *in situ* generation of a chiral Koser's-type reagent from **I**, *m*CPBA and $TsOH{\cdot}H_2O$, furnishing either intermediate **3** or **4**. Subsequent nucleophilic addition of a tosylate anion on **3** (path A) or **4** (path B) *via* S_N2' and S_N2 type mechanisms would both provide enantioenriched ketone **2** along with the regeneration of aryliodine **I**. Interestingly, the reaction is generally clean and the α-oxybenzoyl ketones which would result from the nucleophilic addition of the *m*CBA by-product were not formed.



Scheme 1 First catalytic enantioselective α-oxytosylation of ketones.

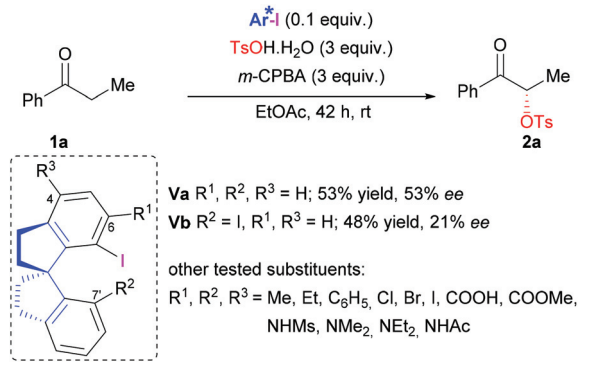
Importantly, the authors pointed out the need for a chelating group at the benzylic position on the *ortho* substituent of the iodine atom in **I** to get the highest possible levels of enantioselectivity. Based on this observation, they synthesized compound **II**, having a chiral ester moiety as the chelating function at the benzylic position instead of the methoxy group, and resulting in an increase of enantioselectivity up to 39% during the α-oxytosylation of propiophenone (Scheme 2).[12] In 2010, the same group prepared derivative **III**, bearing a chiral ester at the *ortho* position of iodine, and leading to lower enantioselectivity.[13]

In 2012, the group of Legault *et al.* developed chiral aryliodine **IVa** bearing a chiral oxazoline as a coordinating motif and a methyl at the *ortho* and *ortho*'-positions of iodine.[14] Premixing catalyst, substrate, and TsOH, followed by slow addition of *m*CPBA slightly enhanced both yield and selectivity during the α-oxytosylation of propiophenone. According to computational analyses, this procedure would favor the formation of the key reactive iodane **5** by minimizing *N*-oxidation of the oxazoline moiety through *N*-protonation.[15] Noteworthily, corresponding aryliodine **IVb** without the *ortho*'-methyl substituent is not able to promote the reaction as protonation of **IVb** is much more difficult. The best selectivity was finally obtained after the introduction of a chlorine atom *para* to iodine (**IVc**).



Scheme 2 New *ortho*-substituted iodobenzene precatalysts in α-oxytosylation.

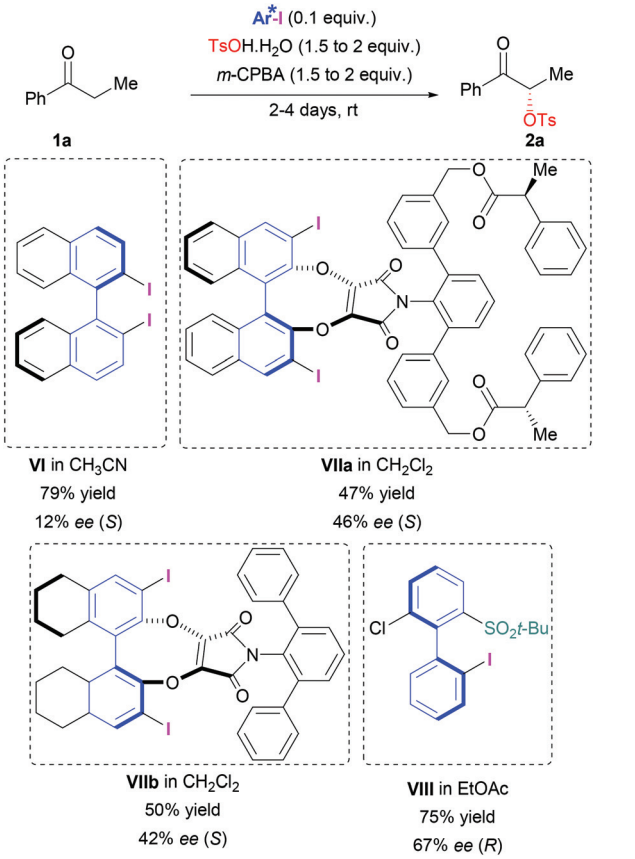
The enantiopure spirobiindane scaffold has also been exploited as a source of chirality in the α-oxytosylation of carbonyl compounds. In 2011, Zhang *et al.* synthesized chiral iodoarene **Va** in 7 steps (28% yields) from expensive commercially available (*S*)-1,10-spirobiindane-7,7′-diol.[16] In the presence of *m*CPBA as a stoichiometric oxidant in acetonitrile, the α-oxytosylation of propiophenone **1** afforded product **2** in 65% yield and 30% ee. The enantioselectivity was improved to 53% ee by simply switching the solvent from acetonitrile to ethyl acetate (Scheme 3). In contrast to Wirth's report, slight racemization of the product was observed in the reaction medium. It is worth mentioning that lower enantioselectivity was obtained with C_2-symmetrical chiral diiodoarene **Vb**. Introduction of other chelating and/or sterically demanding substituents on the spirobiindane scaffold close to the iodine atom (4-, 6-, and 7′-positions) did not improve the enantioselectivity. This reaction scope has been extended to other aromatic ketones and sulfonic acids, yielding the corresponding α-functionalized ketones with up to 56% ee.



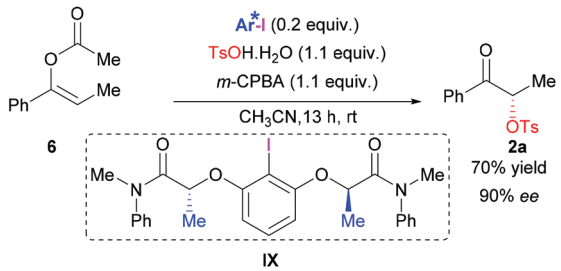
Scheme 3 Spirobiindane scaffold in the α-oxytosylation of ketones.

During their quest for a suitable precatalyst in the catalytic enantioselective α-oxytosylation of propiophenone, Wirth *et al.* tested 2,2′-diiodo-1,1′-binaphthyl (BINI) **VI**.[6] Poor enantioselectivity was obtained indicating that further tuning of this axially chiral backbone was required. In 2013, Berthiol *et al.* introduced new C_2-symmetric 3,3′-diiodo-BINOL-fused maleimide derivatives **VIIa**[17] and **VIIb**[18] that showed a stereochemical efficiency comparable to the best results previously reported (Scheme 4). In 2017, Masson *et al.* reported an axially chiral, non C_2-symmetric iodoarene **VIII** bearing a sulfone substituent as a potentially chelating group of the iodine atom. This catalyst afforded (*R*)-**2a** in 75% yield and 67% ee, which is the best enantioselectivity obtained up to date from **1a** under catalytic conditions.[19] Noteworthily, this catalyst is easily prepared in a few steps involving a palladium-catalyzed stereoselective cross-coupling.[20]

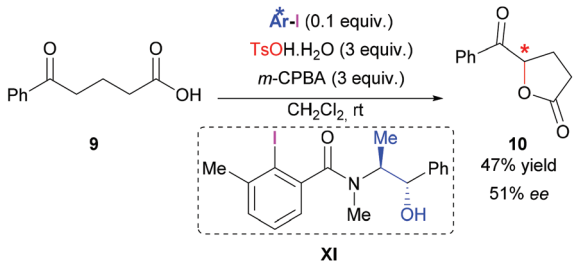
Despite the great advances which have been made, the direct α-oxytosylation of ketones still suffers from moderate enantioselectivities. The competition between the two different routes depicted in Scheme 1 might be responsible for



Scheme 4 Axially chiral biaryl precatalysts in the α-oxytosylation of ketones.



Scheme 5 α-Oxytosylation of enol acetates.



Scheme 7 Oxidative cyclization of 5-oxo-5-phenylpentanoic acid.

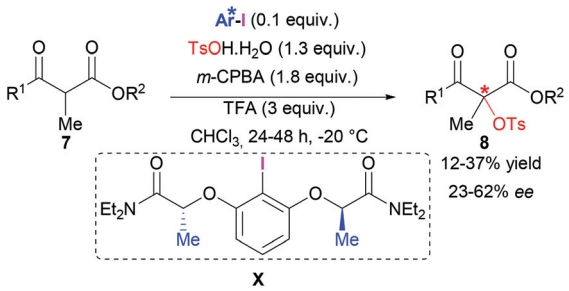
this limited enantiocontrol. Especially, the long distance between the iodoarene group in *O*-iodonium enolate **3** and the stereocenter formed can make efficient stereoinduction very difficult.[21] The lack of control in the geometry of enol **3** might also be problematic. To avoid the passage through the O-bonded intermediate **3** and favor the C-bonded intermediate **4**, Legault *et al.* considered α-oxytosylation of enolacetate **6** (Scheme 5). With such a strategy, C_2-symmetric 2-idodoresorcinol derivative **IX** offered the α-oxytosylated ketone **2** in good yield and with high enantioselectivity.[22] It is worth pointing out that very poor enantioselectivity was obtained during the direct α-oxytosylation of ketone **2** with the same kind of catalyst. This observation supports two different mechanisms for the α-oxytosylation of ketone and enol acetate: S_N2'-type reductive elimination of an *O*-enolate intermediate in the former case providing low enantiocontrol and highly enantioselective S_N2 substitution of a *C*-enolate in the latter case.[21]

In 2016, Xiong, Coeffard *et al.* investigated the α-oxytosylation of α-substituted β-ketoesters **7** by using C_2-symmetric iodoarene **IX** as a chiral precatalyst in combination with *m*CPBA as a stoichiometric oxidant at −20 °C in chloroform (Scheme 6).[23] Corresponding products **8** with a quaternary stereogenic center were obtained in poor yields albeit with respectable enantiomeric excesses (up to 37% yield and 62% ee). Interestingly, 3 equivalents of trifluoroacetic acid (TFA) as an additive were able to increase the enantioselectivity.[24]

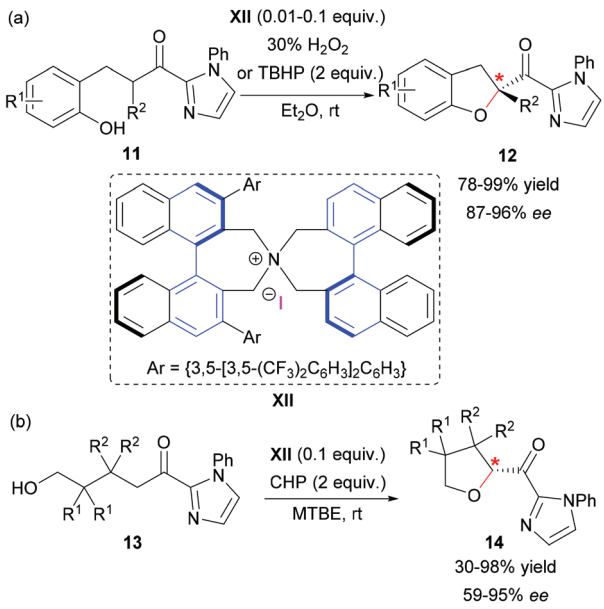
2.2. Intramolecular α-oxygenation

The hypervalent iodine catalyzed α-oxygenation of carbonyl compounds has been extended by Moran *et al.* to an intramolecular version *via* lactonization of 5-oxo-5-phenylpentanoic acid **9** (Scheme 7).[25] Inspired by the studies of Legault *et al.*,[14] the authors synthesized *ortho*-tolyliodine **XI** bearing a pseudoephedrine-based chiral amide as a chelating Lewis agent. In the presence of substoichiometric amounts of *m*CPBA and *p*TsOH, 5-benzoyldihydrofuran-2(3*H*)-one **10** was obtained with moderate yield and enantioselectivity.

In 2010, an elegant catalytic enantioselective oxidative cyclization of ketophenols **11** to the five-membered ring products 2-acyl-2,3-dihydrobenzofurans **12** was developed by Ishihara *et al.* (Scheme 8a). Excellent yields and enantioselectivities at very low catalyst loading were obtained. Their approach relied on the use of an *in situ* generated chiral hypoiodite $[IO]^-$ catalyst from the corresponding quaternary ammonium iodide pre-catalyst **XII** with hydrogen peroxide or *tert*-butyl hydroperoxide (TBHP) as an environmentally benign co-oxidant.[26] The unstable catalytically active species hypoiodite was detected using a series of Raman spectra unveiling an unprecedented I(−I/+I) asymmetric catalysis.[27] This method has been extended to the less favorable six-membered ring oxidative cyclization to access 2-acyl-chromane derivatives.[27] In a similar fashion, highly enantioenriched 2-acyl tetrahydrofuran derivatives **14**



Scheme 6 α-Oxytosylation of α-substituted β-ketoesters.

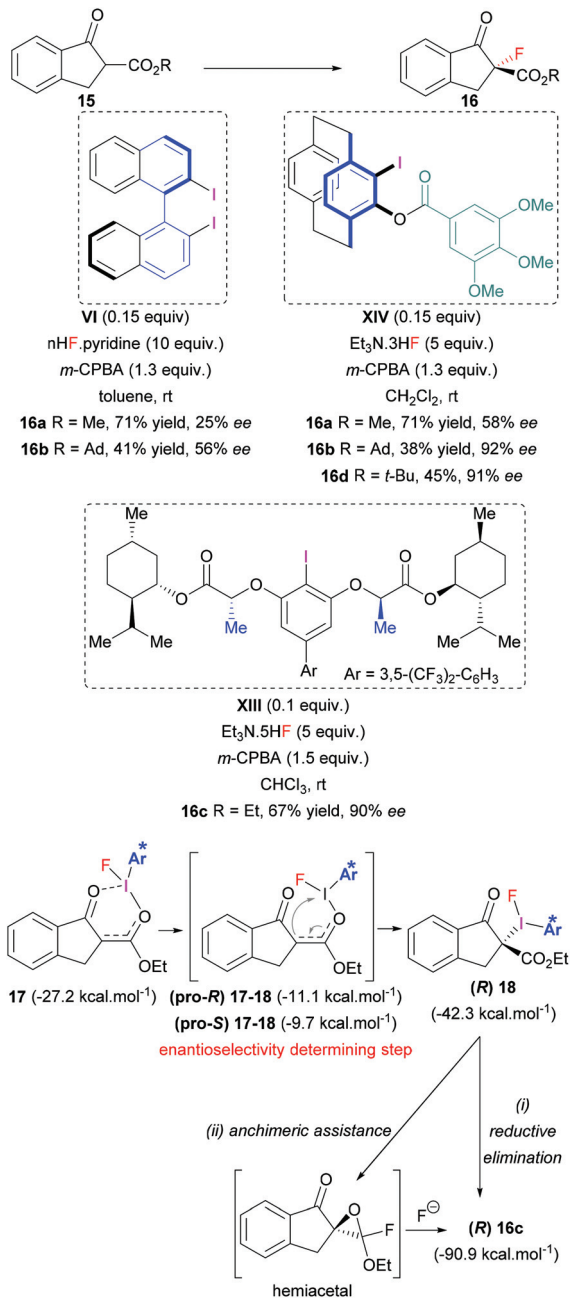


Scheme 8 *In situ* generated chiral hypoiodite-catalyzed oxidative cyclization.

have been obtained *via* cycloetherification of corresponding δ-hydroxyketones **13** using cumene hydroperoxide (CHP) as a stoichiometric co-oxidant (Scheme 8b).[28]

2.3. α-Fluorination

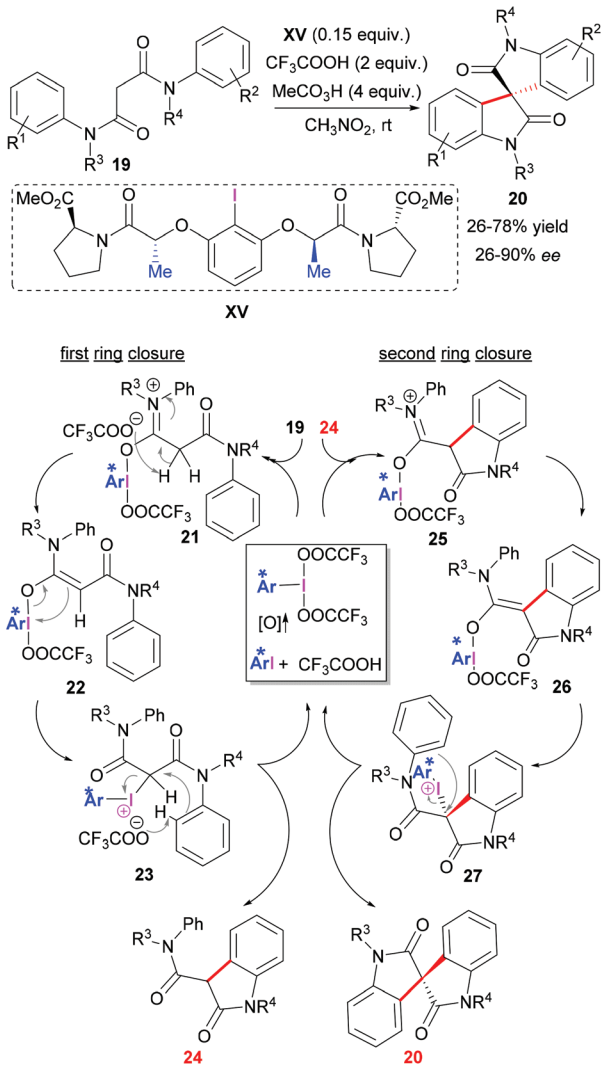
A chiral iodoarene-catalyzed asymmetric nucleophilic α-fluorination of indanone-based β-ketoesters **15** has been initially reported by Kita, Shibata *et al.* using C_2-symmetric axially chiral precatalyst **VI** in combination with *m*CPBA as a stoichiometric oxidant and *n*HF·pyridine as a fluorine source (Scheme 9).[29] Moderate enantioselectivity was obtained with methyl ester **15a**, whereas sterically demanding adamantyl ester **15b** afforded a higher enantiomeric excess (56% ee *vs.* 25% ee). A breakthrough has been very recently achieved by Rueping *et al.* by using chiral iodoarenes derived from 2-iodoresorcinol and lactate scaffolds with triethylamine pentahydrofluoride as the fluorine source.[30] More particularly, the authors developed the flexible C_2-symmetrical menthol ester derivative **XIII** bearing a 3,5-bis(trifluoromethyl)-phenyl group *para* to iodine providing fluorinated product **16** in good yields and with high enantioselectivities. Noteworthily, all catalysts tested derived from (*S*)-lactic acid furnished the same major enantiomer of product **16** regardless of the configuration of the chiral alcohol at the end of the resorcinol arms. This observation highlights the significance of the lactate moiety in enantiocontrol. The chiral iodoresorcinol derivative lacking C_2-symmetry proved to be inferior. In parallel to Rueping's work, Lu, Zheng *et al.* designed a novel planar chiral iodoarene **XIV** based on [2,2]-paracyclophane and bearing a benzoyl group as a potentially coordinating function of the *ortho*-iodine atom. Triethylamine trihydrofluoride (TEA·3HF) was selected as the fluorine source. It is worth mentioning that a positive effect on the enantioselectivity was observed with the introduction of methoxy-groups on the phenyl ring of the benzoyl.[31] In line with experimental observations, these three research groups assumed *in situ* generation of Ar*-I-F_2 from Ar*-I, *m*CPBA and HF along with the activation of this key chiral reactive species by an excess of HF. Based on DFT calculations, Rueping *et al.* proposed a mechanism with formation of an O-bonded hypervalent iodine intermediate **17**.[30] Migration of the aryl iodonium from the *O*-ester enolate to the α-C atom would lead to intermediate **18** *via* the transition state **17** → **18** and yield the α-fluorinated product through reductive elimination. The competitive α-hydroxylation of the carbonyl compounds is responsible for the moderate yield. Transition state **17** → **18** is anticipated to be the enantioselectivity-determining step. Formation of (*R*)-**18** is favored as transition state (pro-*R*) **17** → **18** was found to be 1.4 kcal mol^{-1} lower in energy than transition state (pro-*S*) **17** → **18**. Subsequently, according to DFT calculations, two pathways have been proposed by the authors to account for the formation of α-fluorinated (*R*)-product **16** with the retention of the configuration from (*R*)-**18**: (i) reductive elimination or (ii) elimination of ArI *via* anchimeric assistance of the ester group affording an intermediate hemiacetal (with inversion of configuration) which would undergo opening of the epoxide ring by a nucleophilic attack of the fluorine anion (with a second inversion of configuration).



Scheme 9 α-Fluorination of indanone derivatives.

Although most hypervalent iodine(III)-catalyzed asymmetric oxidative coupling protocols enable the formation of C–X bonds (X = O, N, F), an elegant intramolecular $C(sp^2)$–$C(sp^3)$ coupling reaction of N^1,N^3-diphenylmalonamide **19** was achieved by Gong *et al.* in 2014 (Scheme 10).[32] This transformation provided access to biologically important spirobisoxindoles **20** with a quaternary carbon stereogenic center in good yields and with good enantiomeric excesses. The best reaction conditions involved the use of ethaneperoxoic acid ($MeCO_3H$)

2.4. Spirocyclization through $C(sp^2)$–$C(sp^3)$ coupling



Scheme 10 Spirocyclisation through two sequential C–C cyclizing couplings.

as the stoichiometric oxidant in nitromethane with C_2-symmetric iodoresorcinol derivative **XV** as a precatalyst. Notably, the tertiary (*S*)-proline amide on **XV** (at the end of the resorcinol arms) played a key role in inducing the highest enantioselectivities compared to secondary amides, carboxylic acids or esters. However, only a small mismatched-effect was observed with the (*R*)-proline amide derivative indicating that the chiral lactate moiety is responsible for the enantiocontrol. Moreover, the addition of 2 equivalents of trifluoroacetic acid enhanced the catalytic performances in terms of both yield and enantioselectivity. To shed light on the reaction mechanism and the origin of the stereoselectivities, computational studies were undertaken by Sunoj *et al.*[33] Based on DFT calculations, the authors proposed a mechanism in which the *in situ* generation of the key chiral hypervalent iodine intermediate Ar*-I(TFA)$_2$ was the initial step. Ligand exchange with the nitrogen atom of incoming dianilide substrate **19** followed by pseudo-intramolecular deprotonation of **21** by the leaving trifluoroacetate anion generated *O*-iodonium enolate **22**. The ensuing *O* to *C*-aryliodonium migration leads to *C*-iodonium enolate **23** with a lower energy. Intramolecular Friedel–Crafts reaction assisted by the trifluoroacetate anion allowed the formation of the first oxindole ring **24** with concomitant regeneration of precatalyst **XV**. The second ring formation would be enabled by a similar reaction sequence yielding spirobisoxindole **20**. It is worth mentioning that the direct ring closure from *O*-iodonium **22** and **26** was calculated to be of higher energy, indicating that formation of *C*-iodonium enolates **23** and **27** might occur. As chiral information of intermediate **24** is lost during the second catalytic cycle, the stereoselectivity of the reaction is solely governed during the second ring closure. More precisely, the 1,3-migration of the chiral aryl iodonium from *O* to *C*-enolate (**26** → **27**) is the stereocontrolling step of the reaction. The transition states leading to (*S*)-product **20** were found to be 2.1 kcal mol^{-1} lower than those leading to the (*R*)-product, which is in good agreement with the experimentally obtained enantioselectivity. Noteworthily, in the preferred conformer of key chiral hypervalent iodine intermediate Ar*-I(TFA)$_2$, resorcinol arms were found to organize in a C_2-symmetric helical assembly with a right-handed P helicity in which the two trifluoroacetate ligands form a network of nonconvalent interactions with the chiral arms.

3. Dearomatization of phenol derivatives

The asymmetric dearomatization of phenol derivatives is of particular interest for the synthetic community as it can be a pivotal step in the total synthesis of natural products. Chiral hypervalent organoiodine reagents are organo-oxidants of choice to perform this transformation enantioselectively.[34] They can be generated *in situ* from a catalytic amount of chiral iodoarene and *m*CPBA as a stoichiometric oxidant. The ligand exchange between the phenol and *in situ* generated iodine(III) would furnish phenoxy-λ^3-chiral aryliodoarene **28** (Fig. 3). Subsequently, two mechanisms are generally considered: direct attack of the nucleophile *via* a S_N2'-type substitution (associative path) or formation of phenoxenium ion **29**, which is trapped by the nucleophile (dissociative path). The key requirement to successively achieve asymmetric induction is to find reaction conditions (catalyst, solvent, additive *etc.*) capable of favoring the associative mechanism.

3.1. Intramolecular transformations

The intramolecular dearomatization of phenol derivatives provides a straightforward way to spirocyclic compounds. The asymmetric dearomatization of propanoic acid substituted 1-naphthol **30** to spirolactone **31** has been intensively studied as a model reaction for the design of new aryliodine precatalysts. Indeed, precatalysts which exhibits either C_1- or C_2-symmetry and central or axial-chirality have been developed to achieve the highest enantioselectivity (Scheme 11).

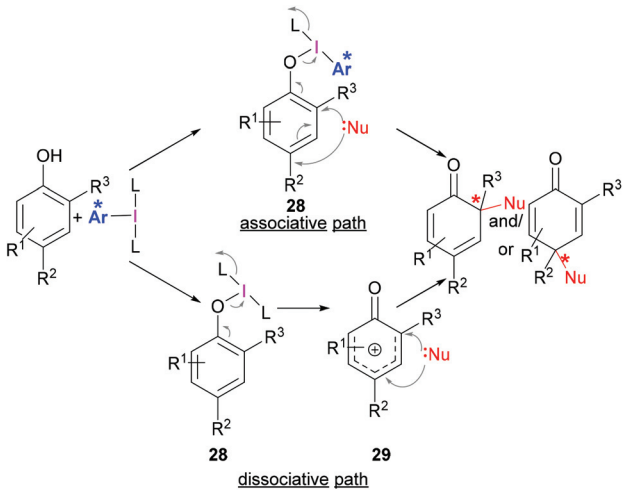


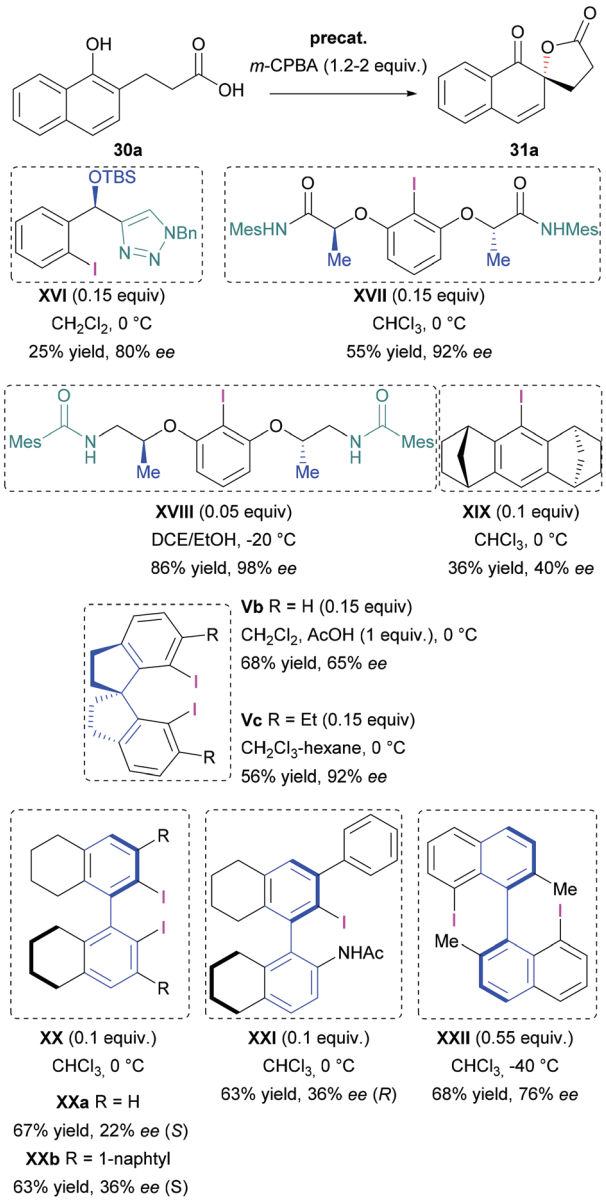
Fig. 3 Proposed mechanisms for organoiodane-mediated phenol dearomatization.

In 2017, Nachtsheim and Pericàs *et al.* reported a new C_1-symmetric triazole-based chiral iodoarene (**XVI**).[35] This catalyst was prepared thanks to an enzymatic kinetic resolution followed by a copper-catalyzed azide–alkyne cycloaddition and provided spirolactone **31a** in moderate yield and with good enantioselectivity.

Ishihara *et al.* developed conformationally flexible C_2-symmetric chiral iodoarenes **XVII** derived from lactate as a source of chirality affording spirolactone **31a** in good yield and with high enantioselectivity (55% and 92% ee).[36] More recently, an enhancement of the yield and the enantioselectivity was achieved by the same group by using catalyst **XVIII** derived from chiral amino-alcohol at low loadings.[37] X-ray and NMR analyses of *in situ* generated organoiodine(III) species from **XVIII** showed that intramolecular hydrogen-bonding interactions between acidic amido protons and ligands of iodine(III) allowed the construction of a suitable chiral environment around the iodine(III) center.[38]

An original C_2-symmetric iodoarene **XIX** with central chirality based on the rigid all-carbon *anti*-dimethanoanthracene framework displayed lower activity and selectivity.[39] However, a rigid C_2-symmetric aryliodine **Vb** based on the axially chiral spirobiindane scaffold was disclosed by Kita *et al.* in 2008. Cyclized product **31a** has been obtained with good enantioselectivity using this catalyst.[40] An enhancement of the enantioselectivity was observed with **Vc** *via* the introduction of ethyl-substituents at the *ortho*-positions of the iodine atoms, presumably due to an extension of the surroundings around the reactive sites.[41]

In 2016, Masson *et al.* explored axially chiral 1,1′-binaphthalene framework and derivatives for the development of novel chiral iodoarenes prepared from commercially available (*R*)-1,1′-binaphthyl-2,2′-diamine (BINAM).[42] Spirolactone **31a** was obtained with a small enantiomeric excess with H_8-BINI **XXa**. Introduction of 1-naphthyl substituents at the 3,3′-positions (**XXb**) exerted a slightly beneficial effect on enantioselectivity.



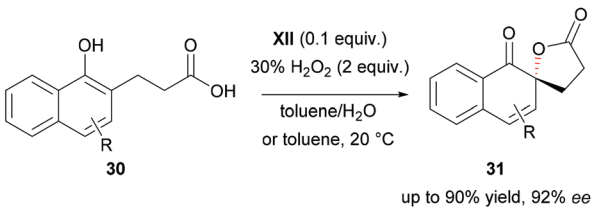
Scheme 11 Asymmetric dearomatization of propanoic acid substituted 1-naphthol **30a**.

Interestingly, a non C_2-symmetric iodoarene precatalyst (**XXI**) harboring an amide group at the 2′-position afforded spirolactone **31a** with poor enantioselectivity but with an inversion of configuration. By analogy with Ishihara and Wirth's catalysts, additional non-covalent interactions between the amide group and the iodine(III) center or its ligands may be responsible of this reversal through a different transition state. Kita *et al.* designed a new type of chiral 1,1′-binaphthalene (**XXII**) substituted with the iodine atoms at the 8,8′-positions which dramatically improved the enantioselectivity, but at the price of a high catalyst loading (0.55 equiv.).[43] This precatalyst bearing the iodine atoms within the major groove of the naphthalene rings has been synthesized by a nickel-catalyzed reductive homocoupling, enantiomeric resolution of the obtained

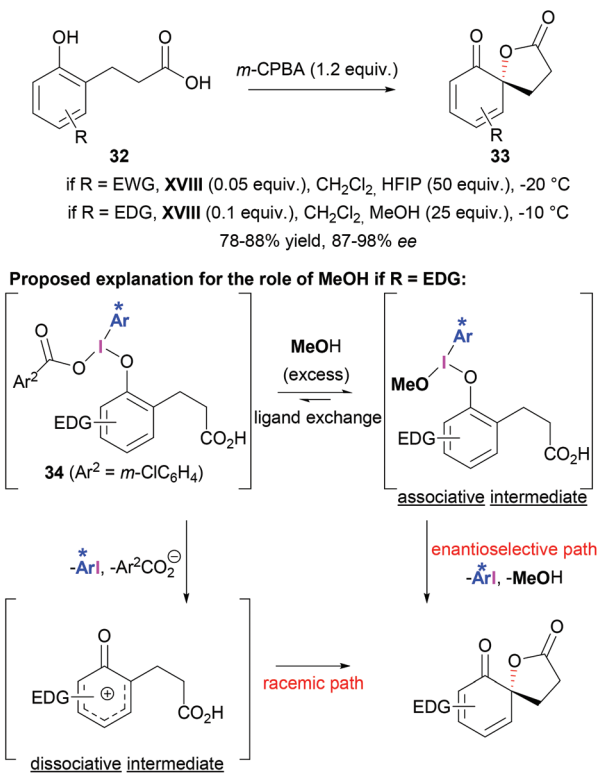
racemic diamine on preparative HPLC with a chiral stationary phase column, followed by Sandmeyer-type iodination.

In 2015, Ishihara *et al.* reported the application of their strategy of *in situ* generated-chiral ammonium hypoiodite from the corresponding chiral ammonium iodide and hydrogen peroxide as a stoichiometric oxidant to the catalytic spirolactonization of 1-naphthol derivatives with good yields and good enantioselectivities at room temperature (Scheme 12).[44] The use of hydrogen-peroxide as a stoichiometric oxidant offers the advantage of generating only water as a by-product instead of *m*CBA, but limited the scope of the transformation to 3 or 4-substituted naphthols.

In 2013, Ishihara *et al.* investigated oxidative cyclization dearomatization of phenol derivatives **32** by using precatalyst **XVIII** (Scheme 13).[38] In the case of poorly reactive electron-deficient phenols, the addition of 50 equivalents of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) was required and it dramatically



Scheme 12 Hypoiodite-catalyzed asymmetric dearomatization of 3 or 4 substituted 1-naphthol derivatives **30**.

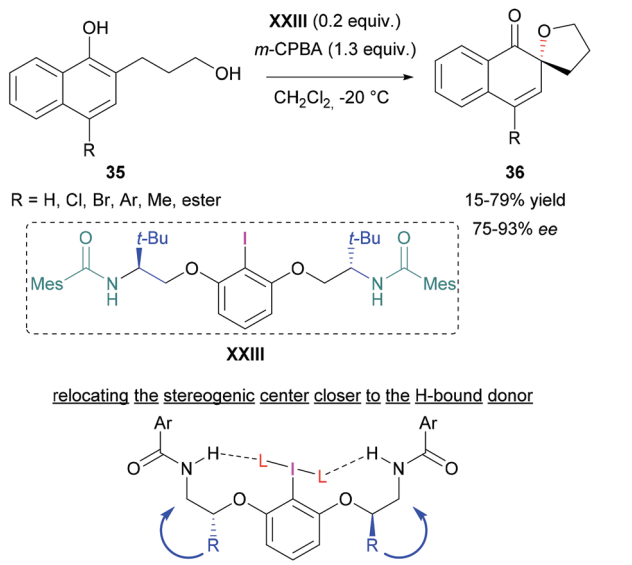


Scheme 13 Spirocyclization of phenols.

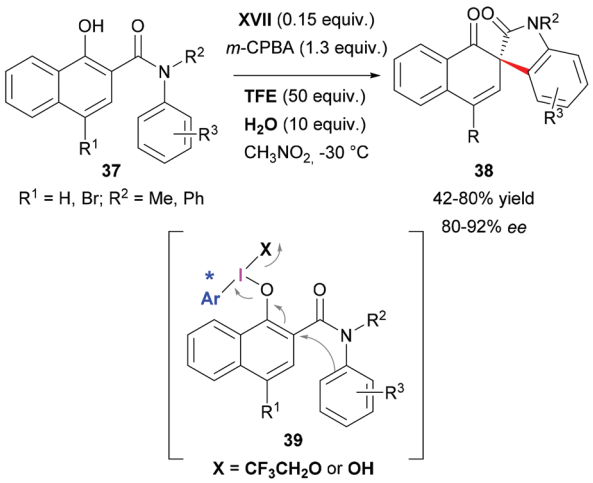
enhanced the efficiency of the process.[45] In contrast, addition of 25 equivalents of methanol was necessary in the case of highly reactive electron-rich phenols to presumably ensure a ligand exchange from acyloxyphenoxyiodine(III) **34**. This protocol would slow down the racemic dissociative pathway and would favor the enantioselective associative pathway as the methoxy ligand is a poorer leaving group than the carboxylate ligand. Under these conditions, high yields and excellent enantioselectivities were obtained in both cases. Noteworthily, this protocol has proved to be also very efficient for the spirolactonization of poorly reactive 2-naphthol derivatives[37] and for dearomatization of *ortho*- and *para*-hydroquinone derivatives allowing the construction of *ortho*- and *para*-benzoquinones.[46]

In 2017, Ciufolini *et al.* described the hypervalent-iodine catalyzed enantioselective oxidative cycloetherification reaction of naphtholic alcohols **35** (Scheme 14).[47] The design of a new precatalyst was required as these substrates are less reactive than the corresponding carboxylic acids. In this context, a variant of Ishihara's catalyst was examined. Considering that intramolecular H-bonding between the secondary amide NH group and the ligand of iodine III is the key feature in these types of catalysts, the authors relocated the stereogenic center closer to the iodine atom. As a result, **XXIII** provided spiro compounds **36** in high yields and with excellent enantioselectivities. This procedure has been extended to the oxidative cyclization of naphtholic sulfonamides with good enantioselectivity.

In their continuous efforts to exploit chiral hypervalent iodine catalysis for the creation of C–C bonds, Gong *et al.* disclosed a highly enantioselective dearomatizative spirocyclization of 1-hydroxy-*N*-aryl-2-naphthamide derivatives **37**, providing access to spiroxindoles derivatives **38** with good yields and enantioselectivity.[48] Precatalyst **XVII** was the aryliodine of choice for this transformation in the presence of *m*CPBA as a stoichiometric oxidant. The reaction would proceed through



Scheme 14 A modification of Ishihara's type catalysts for the spirocyclization of naphtholic alcohols.



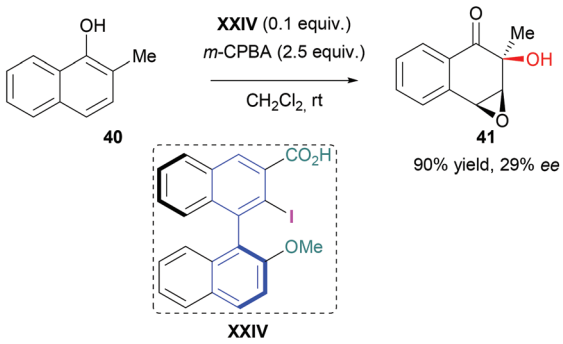
Scheme 15 Oxidative C–C coupling-enabled naphthol dearomatization.

the formation of phenoxy-λ^3-iodine species **39**, which would undergo intramolecular S_N2'-like Friedel–Crafts substitution. The addition of a mixture of trifluoroethanol and water was critical for the improvement of both yields and enantioselectivity (Scheme 15).[45] As previously suggested by Ishihara *et al.*, these additives would facilitate ligand exchanges to favor the enantioselective associative pathway over the racemic dissociative pathway.

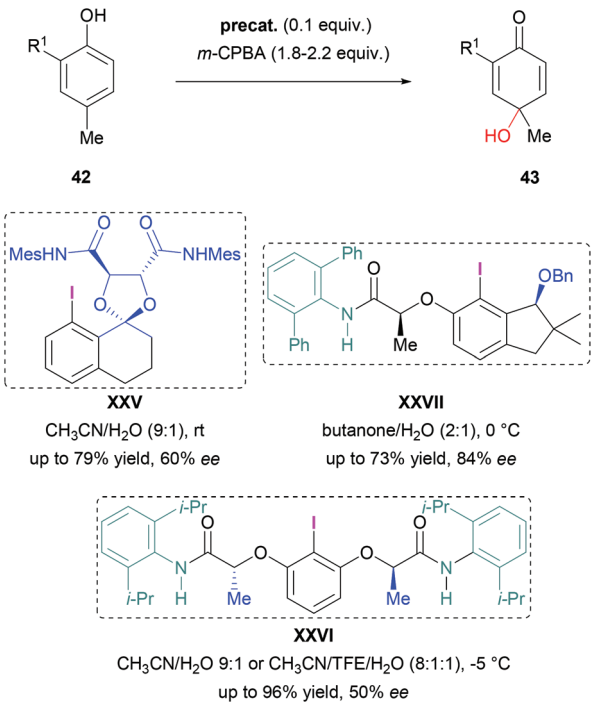
3.2. Intermolecular transformations

Asymmetric intermolecular phenol dearomatization is a highly challenging task as this transformation can easily proceed through a racemic dissociative pathway.[49] Quideau *et al.* have pioneered catalytic enantioselective hydroxylative phenol dearomatization.[50] Axially chiral monoiodobinaphthyl **XXIV** was used in the presence of a stoichiometric amount of *m*CPBA to convert 2-methylnaphthol **40** to epoxy *ortho*-quinol **41** in good yield and with moderate enantioselectivity. Unfortunately, epoxidation of the *ortho*-quinol by the stoichiometric oxidant cannot be avoided. Secondary I···O interactions between the iodine(III) atom and the methoxy group and/or the carboxylic acid function were assumed, but the real nature (λ^3 or λ^5) of reacting hypervalent iodine involved in this transformation could not be determined with certainty (Scheme 16).

Hypervalent iodine-catalyzed intermolecular dearomatization of phenol can also enable the introduction of a nucleophile at the *para* position of the hydroxyl group. Designing an enantioselective version of such a reaction seems to be even more arduous, as the creation of the stereogenic center occurs quite far away from the chiral environment (namely the phenoxy-λ^3-chiral aryliodane). To address this challenge, Harned *et al.* designed C_1-symmetric chiral iodine **XXV** derived from 8-iodotetralone and tartaric acid for the 4-hydroxylation of phenols **42** in the presence of *m*CPBA as the stoichiometric oxidant (Scheme 17).[51] The resulting 2,5-cyclohexanedienones **43** were obtained in moderate yields and with enantioselectivity up to 60% ee. In 2017, Muñiz *et al.* proposed the



Scheme 16 Intermolecular naphthol dearomatization.



Scheme 17 4-Hydroxylation of phenols.

use of C_2-symmetric lactic amide **XXVI** (Ishihara's type precatalyst), which exhibited slightly lower stereoselectivities for the same transformation.[52] Very recently, Maruoka *et al.* developed C_1-symmetric indanol-based chiral organoiodine **XXVII** allowing the access to 2,5-cyclohexadienones **43** with the highest level of enantioselectivity reported to date.[53] Importantly, on this catalyst, the chiral indanol moiety is responsible for the enantiocontrol of the process as both enantiomers of the lactate moiety provided the same major enantiomer of the product.

4. Functionalization of alkenes

Hypervalent iodine-mediated asymmetric difunctionalization of alkenes is a useful strategy for the preparation of polysubsti-

tuted molecules with the creation of one or two vicinal stereogenic centers from either two identical or different nucleophiles.[54]

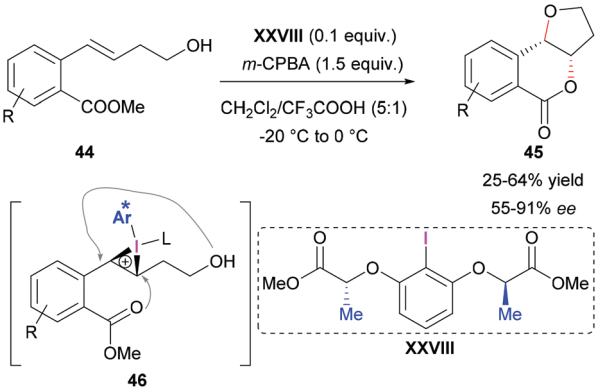
4.1. Intramolecular version

In its intramolecular version, such a reaction enables the construction of polysubstituted heterocycles in one step.

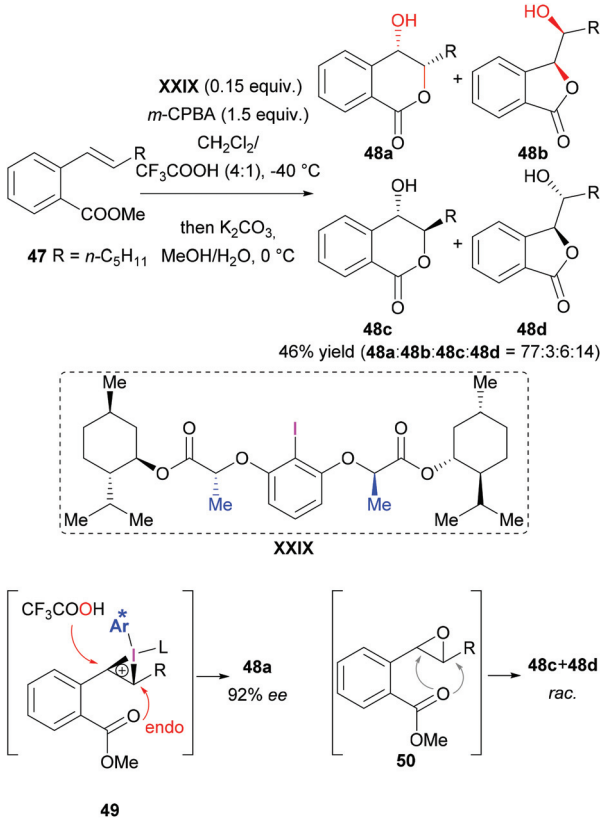
4.1.1. Lactonization. The first example of a catalytic difunctionalization of alkenes mediated by chiral hypervalent iodine has been reported by Fujita *et al.* In their original reports, the authors disclosed an oxidative double cyclization of 2-(4-hydroxybut-1-enyl)benzoates **44** (Scheme 18).[55] By using precatalyst **XXVIII**, *m*CPBA as the terminal oxidant and trifluoroacetic acid as an activator, the dihydrofuran-fused isochromanones **45** were obtained in moderate yields with enantioselectivities up to 91% ee. The reaction would proceed through the diastereofacial attack of the chiral iodane on the double bond to form iodonium **46**. The latter would undergo nucleophilic substitutions by the internal hydroxy and carboxymethyl groups with an inversion of configuration. The competitive direct oxidation of the double bond by *m*CPBA is responsible for the moderate yields.

The background oxidation with *m*CPBA has been well identified by the same research group in the hypervalent-iodine catalyzed trifluoroacetoxylactonisation of *ortho*-alk-1-enylbenzoates **47** (Scheme 19).[56] In this process, the catalytic oxidation mediated by chiral hypervalent iodine(III) species gives enantioenriched *syn*-products **48a** and **48b** *via* ring opening of iodonium **49**, while the direct oxidation with *m*CPBA delivers racemic *anti*-products **48c** and **48d** *via* opening of epoxide **50**. Good 6-*endo* regioselectivity and high enantioselectivity were obtained on *cis*-isochromanone **48a** with pre-catalyst **XXIX**. On this catalyst, the chiral menthol group seems to bring only more steric hindrance at the end of the resorcinol arm and the enantioselectivity of the process is governed by the lactate moiety. Unfortunately, the competitive background oxidation with *m*CPBA of the electron-rich internal double bond significantly affected the yield.

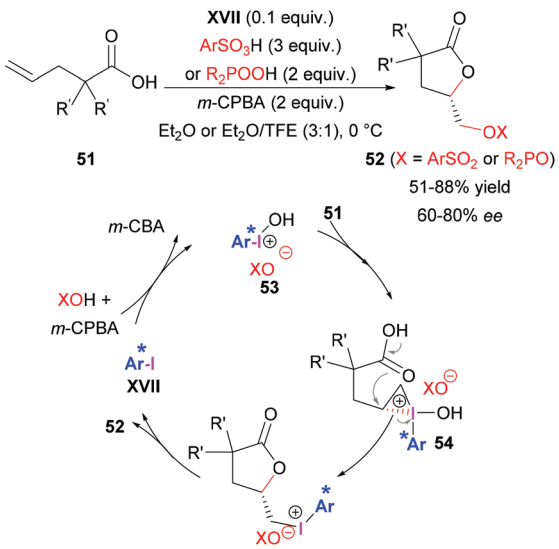
In 2017, Masson *et al.* reported a tosyloxy- and phosphoryloxy-lactonization of flexible 4-pentenoic acid derivatives **51**



Scheme 18 Oxidative double cyclization.



Scheme 19 Oxy-lactonization of *ortho*-alk-1-enylbenzoates **47**.



Scheme 20 Tosyloxy- and phosphoryloxy-lactonization of flexible 4-pentenoic acid **51**.

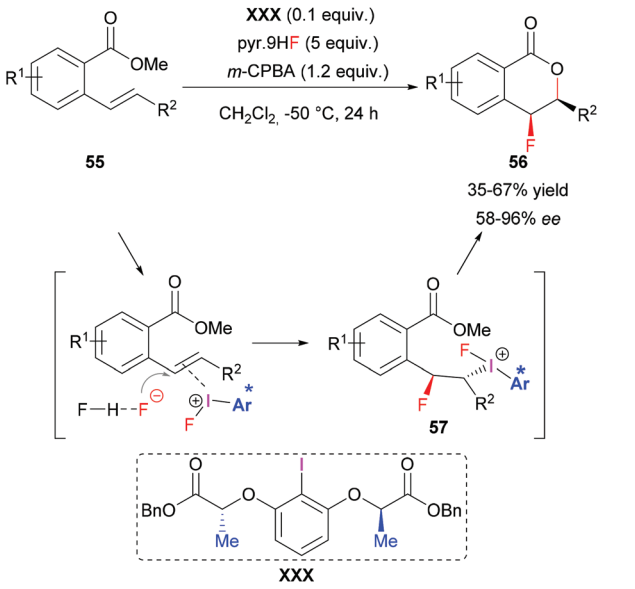
(Scheme 20).[57] By using **XVII** and a stoichiometric amount of *m*CPBA in the presence of sulfonic or phosphoric acid, excellent *exo* selectivity was observed, providing access to valuable γ-butyrolactones **52** with good yields and good enantioselectivities. To minimize the competitive direct oxidation of

the terminal double bond by *m*CPBA, the reaction needs to be carried out at 0 °C. Addition of 2,2,2-trifluoroethanol (TFE) as a cosolvent was required to improve the yield of phosphoryloxycyclization.[45] From a mechanistic point of view, the authors proposed *in situ* generation of intermediate **53** from precatalyst **XVII**, *m*CPBA and the acid. Electrophilic attack of the double bond by this chiral λ^3-aryliodane would furnish chiral aryliodonium **54**. Intramolecular nucleophilic attack of the carboxy group with *exo* selectivity followed by substitution of the iodonium with the sulfonyl or phosphoryl group would afford γ-lactone **52**.

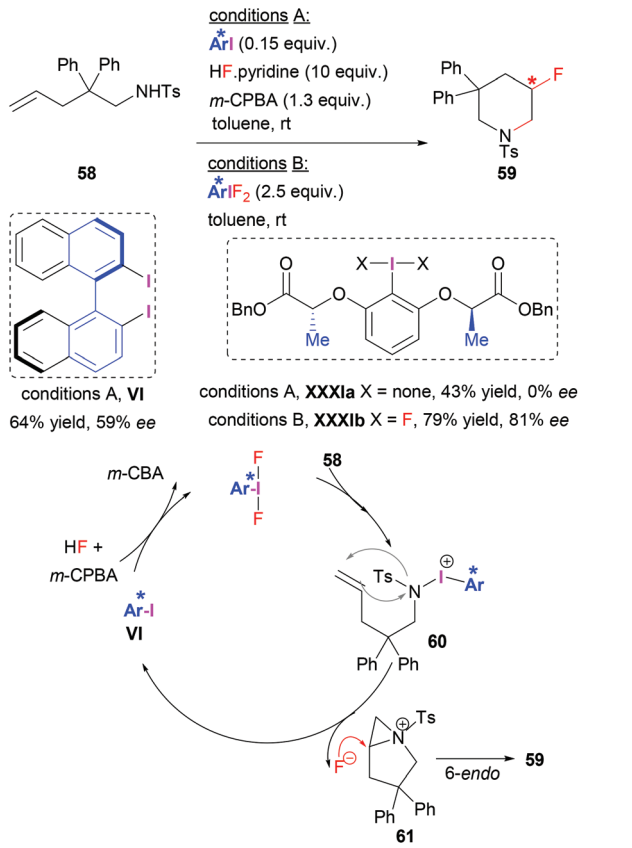
The hypervalent iodine catalyzed fluorolactonization of *ortho*-alk-1-enylbenzoates **55** has been investigated by Jacobsen *et al.* (Scheme 21).[58] This method used HF·pyridine as a nucleophilic fluoride source with chiral precatalyst **XXX** and *m*CPBA, affording 3-alkyl-4-fluoroisochromanones **56** as a single *syn* diastereoisomer with moderate yields and high enantioselectivities. Noteworthily, the obtained regioselectivity (formation of the 6-membered ring) is complementary to that established in asymmetric fluorolactonization with an electrophilic fluoride source. This regioselectivity is explained by the activation of the alkene by hypervalent iodine followed by the addition of the fluoride anion onto the benzylic carbon, furnishing *anti*-vicinal fluoroiodonium intermediate **57**. The latter would undergo intramolecular nucleophilic substitution by the carboxymethyl group with an inversion of configuration providing *syn*-diastereoisomer **56**.

4.1.2. Formation of aza-heterocycles. Kita, Shibata *et al.* developed the chiral aryl iodine-catalyzed intramolecular aminofluorination of ω-amino-alkene **58** using *m*CPBA as a stoichiometric terminal oxidant and HF·pyridine as a nucleophilic fluoride source.[29] This transformation enabled the formation of 2-fluoropiperidine **59** with moderate yield and enantioselectivity. According to the observed 6-*endo* selectivity of the process, the aminofluorination would proceed through oxidation of the sulfonamide by *in situ* generated $ArIF_2$, furnishing electrophilic species **60**. The latter would react with the double bond to release the precatalyst and concomitantly form intermediate aziridinium **61**. The latter would undergo nucleophilic attack of the fluoride on the tertiary carbon to deliver *endo*-type cyclized product **59**. The best aryliodine precatalyst evaluated was C_2-symmetric axially chiral BINI **VI**. Strikingly, while a stoichiometric amount of chiral aryliodonium difluoride **XXXIb** has been reported to give **59** with 81% ee,[59] no enantioselectivity was observed with parent aryliodine **XXXIa** under catalytic conditions. This observation suggests different types of mechanisms between the catalytic and stoichiometric processes (Scheme 22).

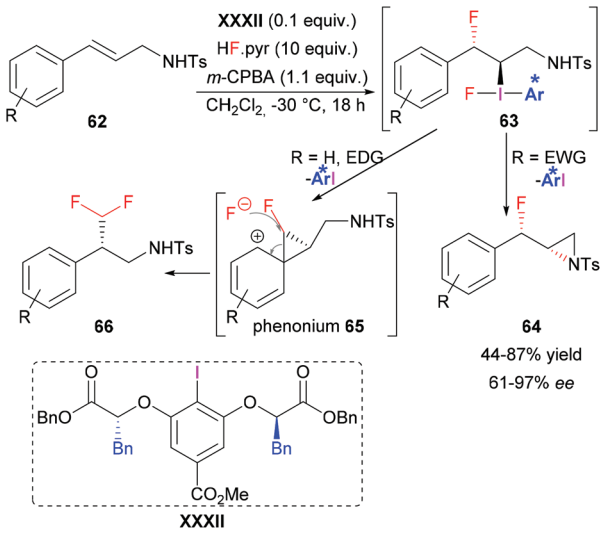
Very recently, the highly enantioselective *syn*-β-fluoroaziridination of cynnamyltosylamide **62** was disclosed by Jacobsen *et al.* (Scheme 23).[60] The optimal reaction conditions are similar to those previously reported by the group for fluorolactonization (see section 4.1.1) with **XXXII** as the precatalyst of choice. In contrast to the above fluoropiperidination reported by Kita, Shibata *et al.*, the reaction would be initiated by the oxidation of the electron-rich internal alkene by *in situ* generated $ArIF_2$ furnishing an electrophilic iodonium. Nucleophilic attack by the excess of fluoride would generate *anti*-vicinal fluoroiodonium **63**, which would be intra-



Scheme 21 Hypervalent iodine catalysed asymmetric 6-*endo*-type-fluorolactonization.



Scheme 22 Access to enantioenriched 3-aminopiperidine **59**.



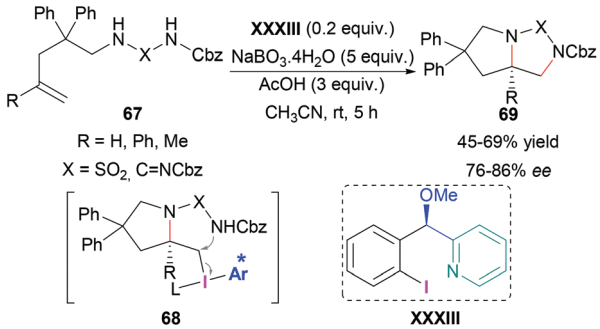
Scheme 23 Synthesis of *syn*-β-fluoroaziridines and competitive rearrangement.

molecularly trapped by the sulfonamide to give fluoroaziridines **64**. This reaction sequence accounts for the total *syn*-selectivity. The process is limited to electron deficient cinnamyl tosylamides since substrates lacking electron withdrawing substituents gave rise to 1,1-difluoromethylated products **66** *via* phenonium ion **65** (Scheme 23, R = H, EDG). Carbonyl-based protected amines (carbamates, amides) led to the formation of 1,2-oxy-fluorinated products *via* intramolecular nucleophilic attack of the carbonyl oxygen on fluoroiodonium rather than nitrogen.

In 2014, Wirth *et al.* reported an elegant intramolecular diamination of homoallylic guanidine and diaminosulfone derivatives **67**.[61] In this transformation, the two attacking nucleophiles are on the substrate. Activation of the double bond by hypervalent iodine triggered the first nucleophilic attack of one nitrogen to the more substituted carbon. S_N2-type nucleophilic substitution of the resulting hypervalent moiety (intermediate **68**) delivered bicyclic molecules **69**. While poor enantioselectivity was obtained with the flexible C_2-symmetric Ishihara's type catalyst, the design of a much more rigid catalyst **XXXIII** featuring a pyridine moiety attached to a chiral benzylic center afforded the diamines with up to 86% ee. The pyridine nitrogen would coordinate iodine(III). The authors did not rule out also a possible coordination of the oxygen atom belonging to the methoxy group to iodine(III). It is worth pointing out that sodium perborate in the presence of acetic acid as an activator was the stoichiometric oxidant of choice with this catalyst instead of commonly employed *m*CPBA (Scheme 24).

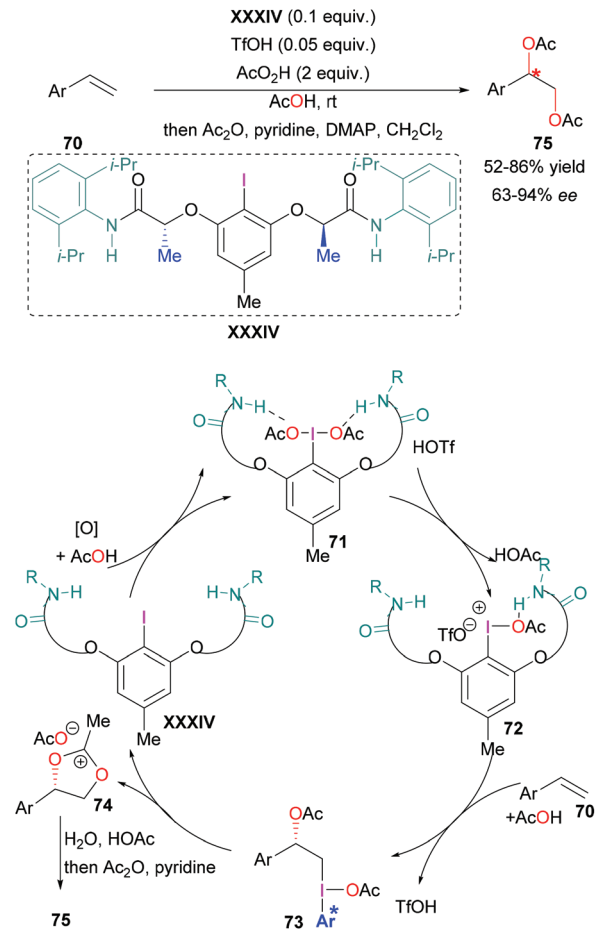
4.2. Intermolecular version

4.2.1. Dioxygenation. In 2016, Muñiz *et al.* reported the first intermolecular asymmetric alkene dioxygenation under hypervalent iodine catalysis.[62] By using C_2-symmetric bislactamide **XXXIV**, peracetic acid as the terminal oxidant and triflic



Scheme 24 Intramolecular diamination leading to a dicyclized product.

acid as a Brønsted acid co-catalyst in acetic acid, vicinal diacetoxylation of terminal styrenes **70** took place in good yields with up to 94% ee (Scheme 25). X-ray analyses and ^{1}H-NMR spectroscopy of the corresponding diacetate iodonium to **XXXIV** unveiled hydrogen bonding between the amide NH groups of the arms and ligand acetoxy, resulting in the creation of a supramolecular helical chirality around the central iodine(III) atom. These observations confirmed the concept of

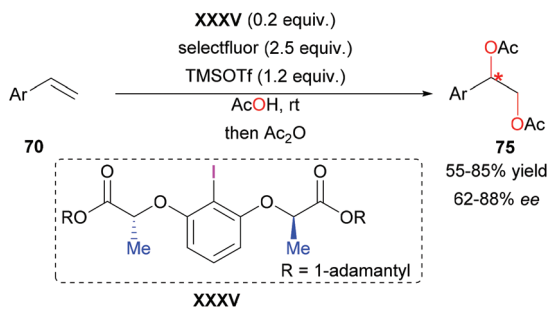


Scheme 25 Diacetoxylation of styrene.

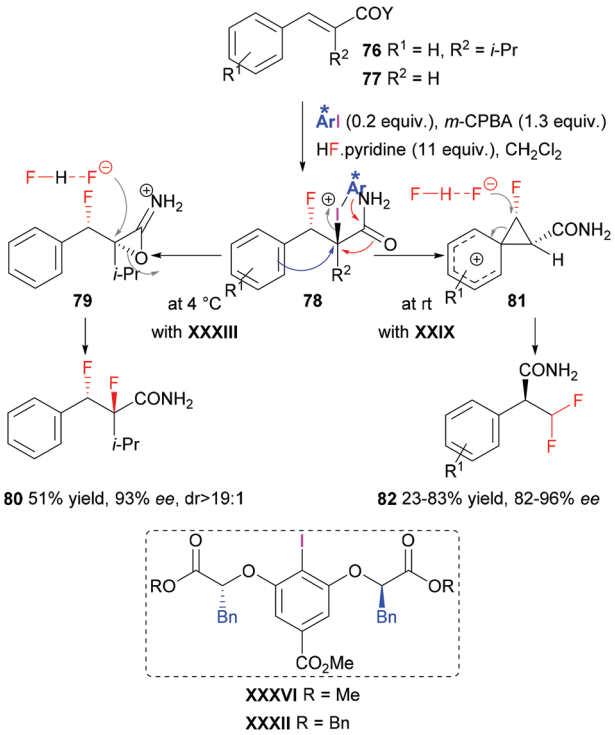
intramolecular hydrogen bonding interactions previously introduced by Ishihara *et al.*[36] in the conformationally flexible enantioselective organoiodine catalysis and was also first demonstrated by the same group using X-ray (solid state) and NMR analyses (solution state) of diacetoxyaryliodine derived from **XVIII** (see section 3.1).[38] From a mechanistic point of view, the catalytic cycle would start with the oxidation of **XXXIV** by peracetic acid in acetic acid to generate intermediate diacetoxyiodonium **71**. Addition of triflic acid would allow the formation of a more reactive cationic catalyst state **72**[63] which no longer exhibits C_2-symmetry. Upon oxidation of the styrene and subsequent nucleophilic attack of acetate, intermediate **73** would be formed. Intramolecular nucleophilic addition of the acetate would regenerate catalyst **XXXIV** along with the formation of dioxolonium **74**. The latter would undergo ring opening by acetate or hydrolysis to provide vicinally dioxygenated product **75** upon treatment with acetic anhydride.

Muñiz *et al.* also demonstrated the use of bislactate **XXXV** to efficiently catalyze vicinal diacetoxylation of external and internal styrenes with up to 96% ee (Scheme 26).[64] This protocol relies on the use of Selectfluor as the terminal oxidant (to avoid epoxidation of the alkene observed with the commonly employed peracids) and a stoichiometric amount of trimethylsilyltriflate as an iodonium co-activator.

4.2.2. Difluorination. In 2016, Jacobsen *et al.* described asymmetric vicinal difluorination of trisubstituted cinnamide derivative **76** in 93% ee and with excellent *anti*-diastereoselectivity using resorcinol-based diester **XXXVI** (Scheme 27, left part).[65] In combination with *m*CPBA as the stoichiometric oxidant and pyridine·9HF as the nucleophilic fluorine source, the *in situ* generated reactive iodoarene difluoride would activate the internal alkene. Nucleophilic fluorination at the benzylic carbon would lead to *anti*-fluoroalkyl iodonium(III) intermediate **78**. Anchimeric nucleophilic assistance by the neighboring amide group (red arrows) would allow the second fluorination to take place *via* intermediate **79** with an overall total *anti*-diastereoselectivity to afford 1,2-difluorinated product **80**. In the case of disubstituted cinnamide derivatives **77** (R^2 = H), fluoroalkyl iodonium(III) intermediate **78** would preferentially undergo aryl migration (blue arrows) *via* phenonium ion **81** to afford *gem*-difluoro compounds **82** in good yields and with excellent enantioselectivities using precatalyst



Scheme 26 Diacetoxylation of styrene with bis-lactate **XXXV** and Selectfluor.

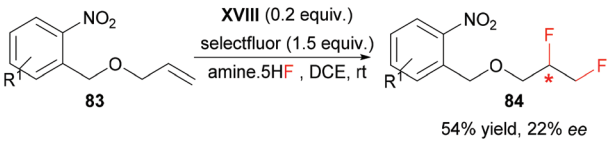


Scheme 27 Vicinal and geminal difluorination of alkenes.

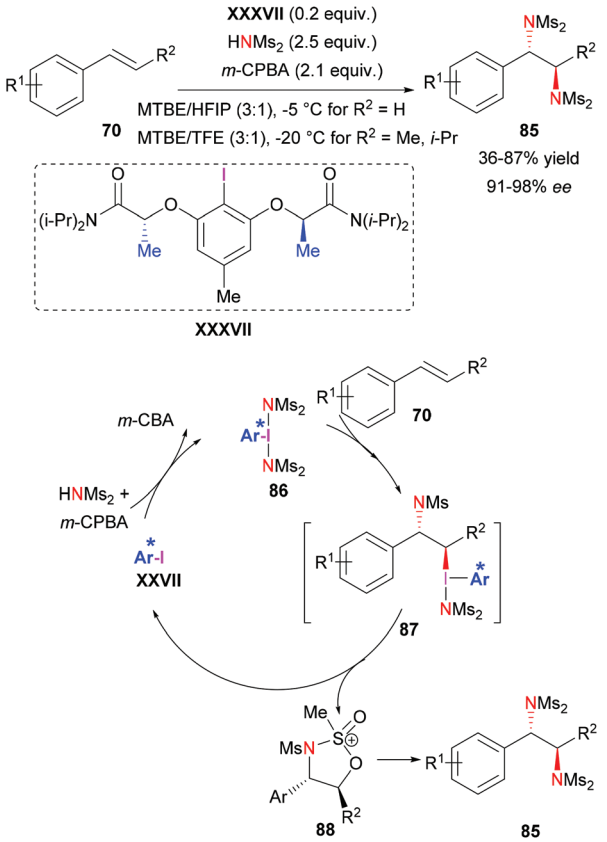
XXXII (Scheme 27, right part).[66] This elegant migratory geminal difluorination has been extended to secondary and tertiary cinnamate ester derivatives. It is worth mentioning that, in both transformations, higher enantioselectivities were obtained with aryl iodine bearing benzylic *versus* aliphatic substituents at the stereogenic centers probably due to attractive π-cation interactions in the transition states.

Gilmour *et al.* reported vicinal difluorination of terminal aliphatic alkene **83** with modest yield and enantioselectivity using catalyst **XVIII**, Selectfluor as the stoichiometric oxidant and amine·5HF (Scheme 28).[67]

4.2.3. Diamination. In 2017, Muñiz *et al.* reported an iodine(I/III)-catalyzed enantioselective vicinal diamination of internal and external styrenes using *m*CPBA as a terminal oxidant and bismesylimide as a nitrogen source (Scheme 29).[68] The undesired epoxidation background reaction was advantageously reduced when an MTBE/HFIP or MTBE/TFE solvent combination was used at low temperatures. Tertiary amide iodoresorcinol derivative **XXXVII** was the catalyst of choice to provide diamines **85** in good yields and with excellent enantioselectivity. Since the previously observed



Scheme 28 Difluorination of terminal aliphatic alkene **83**.



Scheme 29 Vicinal diaminations of alkenes.

supramolecular arrangement of resorcinol derivatives with secondary amides through intramolecular hydrogen-bonding is not directly possible with this tertiary amide version, the intervention of water for the formation an analogous helical framework through intermolecular hydrogen-bonding has been proposed. From a mechanistic point of view, the authors suggested the initial formation of key reactive catalyst diaminoiodonium **86** which would activate the alkene. Subsequent nucleophilic addition of the bismesylimide on the benzylic carbon would give *anti*-vicinal aminoalkyliodonium(III) **87**. Intramolecular displacement of the iodonium by the bisulfonimide with an inversion of configuration would liberate the catalyst and generate cyclic intermediate **88**. Ring opening of this intermediate would allow the second C–N bond formation with second inversion of configuration, which would account for the *anti*-diastereoselectivity observed in diamine products **85**.

5. Conclusions

The blossoming research field of asymmetric iodine catalysis has been summarized. Since the pioneering iodoarenes of Wirth *et al.* with a chiral coordinating group *ortho* to the iodine atom, we have seen that a handful of chiral aryliodines has been developed and used efficiently as precatalysts of hypervalent iodine(III) to perform oxidative transformations with high enantiocontrol. Although the flexible and easily tunable C_2-symmetric resorcinol derivative seems to be a privileged structure in many transformations, other compounds with central, axial or planar chirality have also appeared to be suitable precatalysts. Chiral quaternary ammonium iodides have also been ingeniously employed as precursors of hypoiodites for iodine (−I/+I) catalysis. Both such catalytic systems have proven to be ideal methods for α-functionalization of carbonyl compounds, dearomatization of phenol derivatives and functionalization of alkenes with different types of nucleophiles (in an intra- or intermolecular way) with high enantioselectivities. Moreover, recent mechanistic investigations *via* X-ray, NMR and computational analysis have shed light on the structures of the reactive catalysts and the intermediates involved in the catalytic cycles. These insights are expected to contribute in the near future to the design of new chiral iodine compounds and their applications in new asymmetric reactions.

Conflicts of interest

There are no conflicts to declare.

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