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Chiral Hypervalent Iodine(III) Catalyst Promotes Highly Enantioselective Sulfonyl- and Phosphoryl-oxylactonizations

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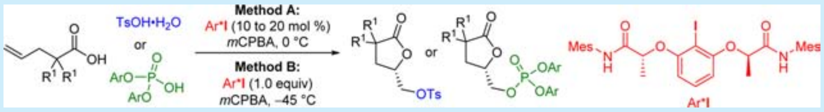
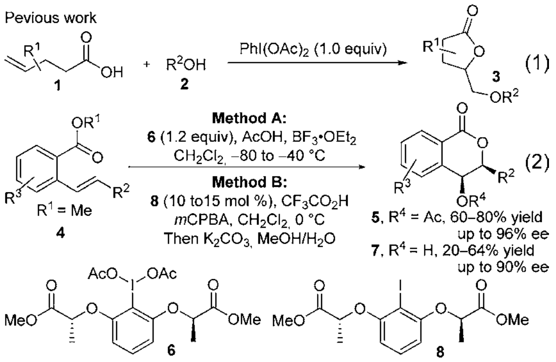
Supporting Information



ABSTRACT: An efficient enantioselective hypervalent iodine promoted oxylactonization of 4-pentenoic acids has been achieved using stoichiometric or a catalytic amount of chiral aryl-λ^3-iodane. This reaction provides straightforward access to a wide range of sulfonyloxy- and phosphoryloxy-γ-butyrolactones in respectable yields with moderate to excellent enantioselectivities.

Chiral γ-butyrolactones (dihydrofuran-2-ones) are prevalent motifs found in diverse biologically active natural and synthetic products.[1] In addition, γ-(hydroxymethyl)-γ-butyrolactones are valuable key building blocks for the synthesis of various natural products.[2] Among the reported approaches to γ-(oxymethyl)-γ-butyrolactones,[2,3] direct oxycyclization of 4-pentenoic acids mediated by hypervalent iodine(III) represents one of the most straightforward approaches starting from readily available precursors (Scheme 1, eq 1).[4] Surprisingly, in spite of recent impressive progress in asymmetric hypervalent iodine catalysis,[5,6] few efficient enantioselective oxylactonizations have to date been recorded. Fujita et al.[7] disclosed the first examples of enantioselective oxylactonization of *ortho*-alkenylbenzoate **4** using a stoichiometric amount of lactate-based aryl-λ^3-iodanes **6** leading to 6-*endo* δ-lactone **5** with excellent regio-, diastereo-, and enantioselectivity (Scheme 1, Method A, eq 2).[8] Three years later, the same group developed the first catalytic enantioselective hydroxylactonization of terminal akenes through the use of a combination of a stoichiometric amount of co-oxidant, namely *m*-chloroperbenzoic acid (*m*CPBA), and a catalytic amount of chiral iodoarene precursors **8** allowing *in situ* formation of the chiral hypervalent iodine catalyst (Scheme 1, Method B, eq 2). Although the δ-*syn*-hydroxylactones **7** were generally obtained with excellent enantioselectivity (up to 90% *ee*), moderate yields were observed due to the formation of a significant amount of racemic *anti*-products coming from a direct oxidation of **4** by *m*CPBA. Despite these advances, enantioselective cyclizations mediated by stoichiometric or catalytic amounts of hypervalent iodine have been limited to geometrically constrained substrates leading to endotype transformation and a related exotype cyclization of more flexible precursors, which would lead to valuable γ-butyrolactones, remains to be reported.[4g,i,6−9] Within this context and in conjunction with our interest in enantioselective hypervalent iodine(III) catalysis,[6b,10] we describe herein the first enantioselective sulfonyl- and phosphoryl-oxylactonization of nonrigid 4-pentenoic acid derivatives using stoichiometric or catalytic amounts of chiral hypervalent iodine precursors.

Scheme 1. Previous Oxylactonization Promoted by Aryl-λ^3-iodane



The chiral iodoarene **8**[7] was first examined in the γ-sulfonyloxylactonization of 4-pentenoic acid (**1a**) with *p*-toluenesulfonic acid (**2a**) in Et_2O at room temperature in combination with *m*CPBA (Table 1). Disappointingly, the recovered γ-tosyloxymethyl-γ-butyrolactone **3a** was obtained in low yield as a nearly racemic mixture, together with the epoxide adduct **12a** (50% yield, entry 1). Therefore, alternative chiral iodoarene precursors possessing different backbones were considered (entries 2−4). Axially chiral iodoarenes **9** and **10** developed by Kita[6d,g] and us,[6b] respectively, afforded **3a** as a major product in moderate enantioselectivity. Gratifyingly, we found that the flexible C_2-symmetric iodoarene **11a**[6e,f] afforded better enantioselectivity. Encouraged by this result, a variety of chiral iodoarenes **11**, built by modulating the steric properties of the secondary amide moiety, were prepared and evaluated in the model reaction (see Supporting Information (SI)). To our delight, precatalyst **11b**, incorporating a bulky 2,4,6-trimethyl phenyl group, furnished the γ-tosyloxymethyl-γ-butyrolactone **3a** with

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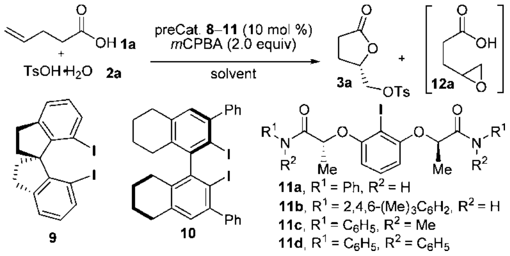
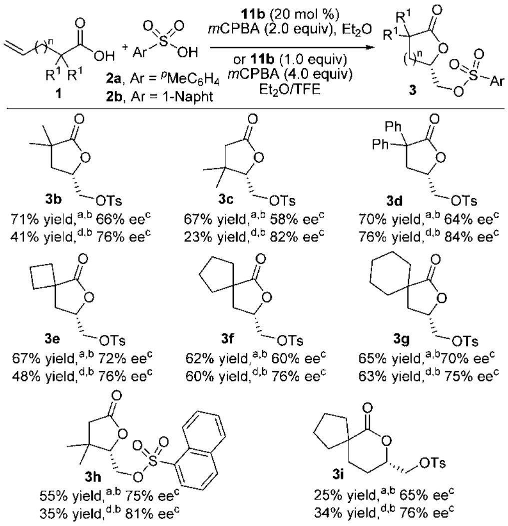
Table 1. Survey of Reaction Conditions[a]



entry	preCat.	solvent	t (°C)	yield (%)[b]	ee (%)[c]
1	**8**	Et_2O	rt	6	6[d]
2	**9**	Et_2O	rt	62	35[d]
3	**10**	Et_2O	rt	47	23[d]
4	**11a**	Et_2O	rt	50	44[d]
5	**11b**	Et_2O	rt	50	64[d]
6	**11c**	Et_2O	rt	49	45[d]
7	**11d**	Et_2O	rt	49	60[d]
8	**11b**	Et_2O	0	53	75[d,e]
9	**11b**	Et_2O/TFE (3/1)	0	72	68[d,e]
10	**11b**	Et_2O/TFE (9/1)	0	66	71[d,e]
11	**11b**	Et_2O	0	62	75[d,e,f]
12	**11b**	Et_2O	−30	24	74[d,f]
13	**11b**	Et_2O	−45	18	86[d,e,f]
14	**11b**	Et_2O/TFE (3/1)	−45	23	86[d,e,f]
15	**11b**	Et_2O/TFE (3/1)	−45	74	86[d,g]

[a] General conditions: **1a** (0.10 mmol), **2a** (0.30 mmol), preCat. **7**−**11** (0.01 mmol), and *m*CPBA (0.20 mmol), in 1.0 mL of solvent for 24 h. [b] Yields refer to chromatographically pure product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] For the determination of the absolute configuration (*S*), see SI. [e] For 72 h. [f] With 20 mol % of **11b**. [g] With **11b** (0.10 mmol) and *m*CPBA (0.40 mmol) in 2 mL of solvent for 120 h.

Scheme 2. Substrate Scope[a]



[a] General conditions: **1** (0.10 mmol), **2** (0.30 mmol), **11b** (0.02 mmol), and *m*CPBA (0.20 mmol), in Et_2O (1.0 mL) at 0 °C for 72 h. [b] Yields refer to chromatographically pure product. [c] *ee* determined by HPLC analysis on a chiral stationary phase. [d] With **11b** (0.10 mmol) and *m*CPBA (0.40 mmol), in Et_2O (2.0 mL) at −45 °C for 120 h.

higher enantioselectivity. Tertiary amide precatalysts **11c**−**d** were able to catalyze the tosyloxylactonization but with reduced asymmetric induction (entries 6 and 7). Among the solvents that were tested, Et_2O provided the highest level of enantioselectivity. Improvements in both yield and enantioselectivity were observed, when the reaction was performed at 0 °C. This condition minimizes the formation of **12a**. Addition of 2,2,2-trifluoroethanol (TFE) as a cosolvent,[11] which is well-known to improve the reactivity of the hypervalent iodine(III) catalyst, slightly increased the yield but slightly decreased the enantioselectivity (entries 9 and 10). Reactions with a 20 mol % catalyst loading resulted in a better yield than with a 10 mol % loading (entry 11). Interestingly, although the enantioselectivity improved at <0 °C, a significant decrease of the yield was observed even after prolonged reactions (entries 12 and 13). We first thought that this result possibly arose from heterogeneous reaction conditions. However, addition of TFE furnished a clear limpid solution at lower temperature, but gave similar results (entry 14). Other oxidants such as Oxone, H_2O_2, and Selectfluor were examined without much success. Although the use of a catalytic amount of a chiral hypervalent iodine has been recently reported at −50 °C,[6a] we found that under our experimental conditions (−45 °C), the iodoarene precatalyst **11b** is oxidized too slowly. Indeed, when 1 equiv of *in situ* preformed chiral hypervalent iodine was employed at −45 °C in Et_2O/TFE, the desired product was isolated in 74% isolated yield with 87% *ee* (entry 15).[7,12] These conditions while requiring a stoichiometric amount of **11b** allowed excellent enantioselectivity.

Having established two sets of optimum reaction conditions (catalytic and stoichiometric), we investigated the scope of the reaction by varying 4-pentenoic acids **1** (Scheme 2). When 2,2-dimethyl, 3,3-dimethyl and 2,2-diphenyl substituted 4-pentenoic acids **1b**, **1c**, and **1d** were submitted to the catalytic conditions, *γ*-lactone products **3b**, **3c**, and **3d** were obtained in respectable yields and enantioselectivities. These results indicate that the presence of *gem* disubstituents shows little effect on the course of this enantioselective reaction. Pleasingly, 1-allylcycloalkanecarboxylic acids **1e**−**g** were efficiently converted into the corresponding enantioenriched spiroproducts **3e**−**g**, an important structural motif present in a large number of pharmaceutical molecules.[13] The reaction with another sufonyl acid group, namely 1-naphthalenesulfonyl acid (**2b**), afforded the *γ*-1-naphthalenesulfonyloxylactone **3h** with similar enantioselectivity when compared to **2a**. We further examined the oxylactonization of larger ring systems. No cyclic product was isolated from 5-hexenoic acid, possibly due to the unfavorable entropical feature of the cyclization reaction. However, a positive Thorpe−Ingold effect was observed when gem-disubstituted 5-hexenoic acid **1i** was used as substrate leading to *δ*-oxylactone **3i** in good enantioselectivity albeit in moderate yield (65% *ee*, 28% yield). Evaluation of the scope of the enantioselective *γ*-sulfonyloxylactonization under the conditions involving a full equivalent of chiral iodoarene promotor **11b** (Et_2O/TFE (3/1), −45 °C) was next performed and resulted in improved enantioselectivity in each case, albeit in reduced yield as depicted in Scheme 2. For instance, **3d** was isolated in 84% *ee* instead of 64% *ee*.

After successful *γ*-sulfonyloxylactonization of different olefins, the *γ*-phosphoryloxylactonatization was also evaluated using **1a** as a model substrate with diphenyl phosphate **2c** (Table 2).[4j,e] The catalytic reaction conditions for tosyloxylactonization were tested, and the desired *γ*-phosphoryloxylactone **3j** was obtained in good enantioselectivity (76% *ee*) albeit with moderate yield (48% yield). However, to our delight, this novel phosphorylation was successful when TFE was used as cosolvent (entry 2),[11] providing the desired *γ*-lactone **3j** in much better yield without altering the enantioselectivity. Yield and enantioselectivity were further slightly improved by using 2 equiv of diphenyl phosphate and 1

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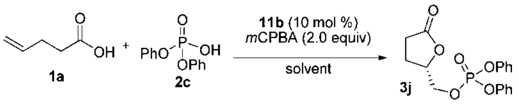
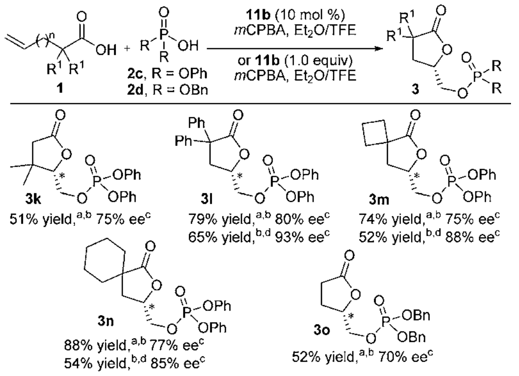
Table 2. Survey of Reaction Conditions[a,b]



entry	solvent	t (°C)	yield (%)[c]	ee (%)[d]
1	Et_2O	0	48	76
2	Et_2O/TFE (9/1)	0	66	71
3	Et_2O/TFE (9/1)	0	76	81[e]
4	Et_2O/TFE (3/1)	−45	67	94[f]

[a] Absolute configuration of **3j** was assigned by analogy with compound **3a**. [b] General conditions: **1a** (0.10 mmol), **2c** (0.30 mmol), **11b** (0.01 mmol), and *m*CPBA (0.20 mmol), in 1.0 mL of solvent for 72 h. [c] Yields refer to chromatographically pure product. [d] Determined by HPLC analysis on a chiral stationary phase. [e] With **2c** (0.20 mmol) and *m*CPBA (0.10 mmol). [f] With *m*CPBA (0.40 mmol) for 120 h.

Scheme 3. Substrate Scope



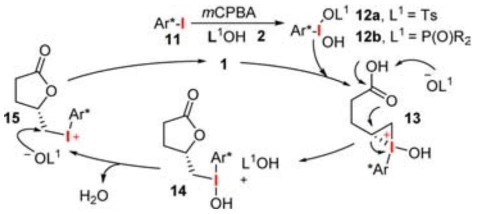
[a] General conditions: **1** (0.10 mmol), **2** (0.20 mmol), **11b** (0.01 mmol), and *m*CPBA (0.10 mmol), in Et_2O/TFE (9/1, 1.0 mL) at 0 °C for 72 h. [b] Yields referred to chromatographically pure product. [c] *ee* determined by HPLC analysis on a chiral stationary phase. [d] With **11b** (0.10 mmol) and *m*CPBA (0.40 mmol) in Et_2O/TFE (3/1, 2.0 mL) at −45 °C for 120 h.

equiv of *m*CPBA (entry 3). As previously, when the reaction was performed at −45 °C with a stoichiometric amount of **11b**, the reaction proceeded in much better selectivity leading to **3j** in 94% *ee* (entry 4).

To explore the scope and limitation of chiral hypervalent iodine-catalyzed oxycyclization, a variety of substrates were tested, and the results are listed in Scheme 3. It was found that the phosphoryloxylactonization of 4-pentenoic acids **1** generally gave higher enantioselectivity than the tosyloxylactonization. Notably, the *gem*-disubstituted lactones **3k–l** and spirolactones **3m–n** were obtained in good yields and enantioselectivities. 3,3-Dimethyl pent-4-enoic acids **1c** led to slightly reduced yields when compared to the sulfonyloxylactonization reaction. The nature of the phosphoric acid substantially influenced the enantioselective process. Indeed, as observed when comparing dibenzyl phosphate and diphenyl phosphate, the corresponding lactone **3o** was isolated in slightly lower enantioselectivity compared to lactone **3j**. Other reaction conditions, performed with 1 equiv of **11b** at −45 °C, were also examined leading to the corresponding 5-phosphoryloxy-4-pentanolactones **3l–n** in good to excellent enantioselectivity.

A plausible mechanism for this enantioselective organocatalyzed *γ*-oxylactonization process is proposed in Scheme 4.[3,4g,e] First, precursor **11** is *in situ* oxidized by *m*CPBA in the presence of sulfonic acid or phosphoric acid to generate the chiral aryl-λ^3-iodane **12**. While the exact structures of **12** await further study, **12a** and **12b** can exist as a hydroxy(tosyloxy)- and hydroxy(phosphoryloxy)iodoarene, respectively.[4g,e,14] Afterward, these hypervalent iodine(III) species **12** could undergo an electrophilic addition to the double bond forming chiral iodonium intermediate **13**.[4] Then, an intramolecular nucleophilic cyclization could occur to afford **14**. Finally, the *γ*-lactone **3** would be formed following the intermolecular nucleophilic addition of a sulfonyl or phosphoryl group, respectively. On the basis of the previous studies on the structures of chiral hypervalent iodine,[6e,f,15] an active catalyst with C_1-symmetry **12** stabilized by n−σ* interactions between the iodine(III) center and carbonyl oxygen of amide might be postulated (**13**, Figure 1).[16] In this proposed model, the chiral aryl-λ^3-iodanes **12** might hinder the *Si* face of an alkene to generate the (*R*)-iodonium intermediate **13**, which can undergo subsequent nucleophilic displacement of carboxylate with inversion of the chiral center to produce the enantioenriched (*S*)-lactone intermediate **14**.

Scheme 4. Plausible Reaction Mechanism



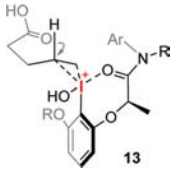


Figure 1. Plausible transition state.

In summary, we have described an enantioselective sulfonyl- and phoshoryl-oxy-lactonization of nonrigid 4-pentenoic acid derivatives using a stoichiometric or catalytic amount of chiral hypervalent iodine precursors. This method provides an efficient access to various interesting enantioenriched *γ*-lactones through a tandem sequence, in acceptable yields and moderate to excellent enantioselectivity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03631.

Detailed experimental procedures and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Seitz, M.; Reiser, O. *Curr. Opin. Chem. Biol.* **2005**, *9*, 285. (b) Hoffmann, H. M. R.; Rabe, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 94. (c) Koch, S. S. C.; Chamberlain, A. R. In *Studies in Natural Products Chemistry*; Atta-ur-Rahman, Ed.; Elsevier Science: New York, 1995; Vol. *16*, p 687.

(2) For selected examples, see: (a) Dey, S.; Karabal, P. U.; Sudalai, A. *Synth. Commun.* **2015**, *45*, 1559. (b) Kuilya, T. K.; Chatterjee, S.; Goswami, R. K. *Tetrahedron* **2014**, *70*, 2905. (c) Dake, G. R.; Fenster, E. E.; Patrick, B. O. *J. Org. Chem.* **2008**, *73*, 6711. (d) Deng, L. S.; Huang, X. P.; Zhao, G. *J. Org. Chem.* **2006**, *71*, 4625. (e) Wrona, I. E.; Gabarda, A. E.; Evano, G.; Panek, J. S. *J. Am. Chem. Soc.* **2005**, *127*, 15026. (f) Shiro, Y.; Kato, K.; Fujii, M.; Ida, Y.; Akita, H. *Tetrahedron* **2006**, *62*, 8687. (g) Hanessian, S.; Brassard, M. *Tetrahedron* **2004**, *60*, 7621. (h) Myers, A. G.; Siu, M.; Ren, F. *J. Am. Chem. Soc.* **2002**, *124*, 4230. (i) Gonzalez, I. C.; Forsyth, C. J. *J. Am. Chem. Soc.* **2000**, *122*, 9099. (j) Minehan, T. G.; Kishi, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 923. (k) Kobayashi, S.; Ueno, M.; Suzuki, R.; Ishitani, H.; Kim, H. S.; Wataya, Y. *J. Org. Chem.* **1999**, *64*, 6833. (l) Tanaka, M.; Tomioka, K.; Koga, K. *Tetrahedron* **1994**, *50*, 12829.

(3) (a) Louafi, F.; Lorion, M. M.; Oble, J.; Poli, G. *Synlett* **2015**, *26*, 2237. (b) Sanyal, I.; Barman, P. D.; Banerjee, A. K. *Tetrahedron Lett.* **2015**, *56*, 789. (c) Saikia, B.; Devi, T. J.; Barua, N. C. *Org. Biomol. Chem.* **2013**, *11*, 905. (d) Erdbrink, H.; Czekelius, C. *Synlett* **2013**, *24*, 2383. (e) Reddy, R. S.; Kiran, I. N. C.; Sudalai, A. *Org. Biomol. Chem.* **2012**, *10*, 3655. (f) Hamamoto, H.; Suzuki, Y.; Takahashi, H.; Ikegami, S. *Adv. Synth. Catal.* **2007**, *349*, 2685. (g) Jenkinson, S. F.; Harris, T.; Fleet, G. W. J. *Tetrahedron: Asymmetry* **2004**, *15*, 2667. (h) Chiacchio, U.; Rescifina, A.; Iannazzo, D.; Romeo, G. *J. Org. Chem.* **1999**, *64*, 28. (i) Ha, H. J.; Yoon, K. N.; Lee, S. Y.; Park, Y. S.; Lim, M. S.; Yim, Y. G. *J. Org. Chem.* **1998**, *63*, 8062. (j) Harcken, C.; Brückner, R.; Rank, E. *Chem. - Eur. J.* **1998**, *4*, 2342. (k) Ha, H. J.; Yoon, K. N.; Lee, S. Y.; Park, Y. S.; Lim, M. S.; Yim, Y. G. *J. Org. Chem.* **1998**, *63*, 8062. (l) Okabe, M.; Sun, R. C.; Zenchoff, G. B. *J. Org. Chem.* **1991**, *56*, 4392.

(4) Selected examples of carboxyloxylactonization: (a) Uyanik, M.; Suzuki, D.; Yasui, T.; Ishihara, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 5331. (b) Kang, Y. B.; Gade, L. H. *J. Am. Chem. Soc.* **2011**, *133*, 3658. (c) Zhu, M.; Sun, N. B.; Li, H.; Yan, Ji. *J. Heterocycl. Chem.* **2010**, *47*, 436. (d) Uyanik, M.; Yasui, T.; Ishihara, K. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 3848. (e) Zhou, Z. S.; He, X. H. *Tetrahedron Lett.* **2010**, *51*, 2480. (f) Dohi, T.; Takenaga, N.; Goto, A.; Maruyama, A.; Kita, Y. *Org. Lett.* **2007**, *9*, 3129. (g) Boye, A. C.; Meyer, D.; Ingison, C. K.; French, A. N.; Wirth, T. *Org. Lett.* **2003**, *5*, 2157. Selected examples of sulfonyloxylactonization: (h) Yan, J.; Wang, H.; Yang, Z.; He, Y. *Synlett* **2009**, 2669. (i) Shah, M.; Taschner, M. J.; Koser, G. F.; Rach, N. L. *Tetrahedron Lett.* **1986**, *27*, 4557. (j) Hu, J.; Zhu, M.; Xu, Y.; Yan, J. *Helv. Chim. Acta* **2014**, *97*, 137. Selected examples of phosphoryloxylactonization: (k) Zhou, Z. S.; He, X. H. *Tetrahedron Lett.* **2010**, *51*, 2480. (l) Koser, G. F.; Lodaya, J. T. S.; Ray, D. G.; Kokil, P. B. *J. Am. Chem. Soc.* **1988**, *110*, 2987. (m) Zhou, Z. S.; He, X. H. *J. Chem. Res.* **2014**, *38*, 630.

(5) For selected reviews on hypervalent iodine chemistry, see: (a) Ortiz, F. L.; Iglesias, M. J.; Fernández, I.; Sánchez, C. M. A.; Ruiz-Gómez, G. *Chem. Rev.* **2007**, *107*, 1580. (b) Ciufolini, M. A.; Braun, N. A.; Canesi, S.; Ousmer, M.; Chang, J.; Chai, D. *Synthesis* **2007**, 3759. (c) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2008**, *108*, 5299. (d) Quideau, S.; Pouységu, L.; Deffieux, D. *Synlett* **2008**, 467. (e) Ochiai, M.; Miyamoto, K. *Eur. J. Org. Chem.* **2008**, *2008*, 4229. (f) Dohi, T.; Kita, Y. *Chem. Commun.* **2009**, 2073. (g) Uyanik, M.; Ishihara, K. *Chem. Commun.* **2009**, 2086. (h) Ngatimin, M.; Lupton, D. W. *Aust. J. Chem.* **2010**, *63*, 653. (i) Liang, H.; Ciufolini, M. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 11849. (j) Fernández González, D.; Benfatti, F.; Waser, J. *ChemCatChem* **2012**, *4*, 955. (k) Yusubov, M. S.; Zhdankin, V. V. *Curr. Org. Synth.* **2012**, *9*, 247. (l) Farid, U.; Wirth, T. in *Asymmetric Synthesis II*; Christmann, M., Bräse, S., Eds.; Wiley−VCH: 2012; p 197. (m) Brown, M.; Farid, U.; Wirth, T. *Synlett* **2013**, *24*, 424. (n) Parra, A.; Reboredo, S. *Chem. - Eur. J.* **2013**, *19*, 17244. (o) Singh, F. V.; Wirth, T. *Chem. - Asian J.* **2014**, *9*, 950. (p) Kumar, R.; Wirth, T. *Top. Curr. Chem.* **2015**, *373*, 243. (q) Maertens, G.; L'Homme, C.; Canesi, S. *Front. Chem.* **2015**, *2*, 115. (r) Yoshimura, A.; Yusubov, M. S.; Zhdankin, V. V. *Org. Biomol. Chem.* **2016**, *14*, 4771. (s) Yoshimura, A.; Zhdankin, V. V. *Chem. Rev.* **2016**, *116*, 3328. (t) Berthiol, F. *Synthesis* **2015**, *47*, 587. (u) Jobin-Des Lauriers, A.; Legault, C. Y. *Asian J. Org. Chem.* **2016**, *5*, 1078.

(6) Examples of enantioselective oxidative lactonization: (a) Woerly, E. M.; Banik, S. M.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2016**, *138*, 13858. (b) Bekkaye, M.; Masson, G. *Synthesis* **2016**, *48*, 302. (c) Murray, S. J.; Ibrahim, H. *Chem. Commun.* **2015**, *51*, 2376. (d) Dohi, T.; Takenaga, N.; Nakae, T.; Toyoda, Y.; Yamasaki, M.; Shiro, M.; Fujioka, H.; Maruyama, A.; Kita, Y. *J. Am. Chem. Soc.* **2013**, *135*, 4558. (e) Uyanik, M.; Yasui, T.; Ishihara, K. *Tetrahedron* **2010**, *66*, 5841. (f) Uyanik, M.; Yasui, T.; Ishihara, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 2175. (g) Dohi, T.; Maruyama, A.; Takenaga, N.; Senami, K.; Minamitsuji, Y.; Fujioka, H.; Caemmerer, S. B.; Kita, Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 3787. (h) Guilbault, A.-A.; Basdevant, B.; Wanie, V.; Legault, C. Y. *J. Org. Chem.* **2012**, *77*, 11283. (i) Volp, K. A.; Harned, A. M. *Chem. Commun.* **2013**, *49*, 3001. (j) Brenet, S.; Berthiol, F.; Einhorn, J. *Eur. J. Org. Chem.* **2013**, 8094. (k) Rodriguez, A.; Moran, W. J. *Synthesis* **2012**, *44*, 1178.

(7) (a) Takesue, T.; Fujita, M.; Sugimura, T.; Akutsu, H. *Org. Lett.* **2014**, *16*, 4634. (b) Fujita, M.; Yoshida, Y.; Miyata, K.; Wakisaka, A.; Sugimura, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 7068.

(8) Shimogaki, M.; Fujita, M.; Sugimura, T. *Eur. J. Org. Chem.* **2013**, *2013*, 7128.

(9) Cao, Y.; Zhang, X.; Lin, G.; Zhang-Negrerie, D.; Du, Y. *Org. Lett.* **2016**, *18*, 5580.

(10) (a) Carboni, A.; Dagousset, G.; Magnier, E.; Masson, G. *Org. Lett.* **2014**, *16*, 1240. (b) Bekkaye, M.; Su, Y.; Masson, G. *Eur. J. Org. Chem.* **2013**, *2013*, 3978.

(11) Dohi, T.; Yamaoka, N.; Kita, Y. *Tetrahedron* **2010**, *66*, 5775.

(12) For recent selected examples using a stoichiometric amount of chiral hypervalent iodine, see: (a) Farid, U.; Wirth, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 3462. (b) Farid, U.; Malmedy, F.; Claveau, R.; Albers, L.; Wirth, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 7018. (c) Shimogaki, M.; Fujita, M.; Sugimura, T. *Angew. Chem., Int. Ed.* **2016**, *55*, 15797.

(13) For representative natural products bearing spirocyclic γ-lactones and derivatives, see: (a) Ghantous, A.; Gali-Muhtasib, H.; Vuorela, H.; Saliba, N. A.; Darwiche, N. *Drug Discovery Today* **2010**, *15*, 668. (b) Bunyapaiboonsri, T.; Yoiprommarat, S.; Intereya, K.; Rachtawee, P.; Hywel-Jones, N. L.; Isaka, M. *J. Nat. Prod.* **2009**, *72*, 756.

(14) (a) Mizar, P.; Laverny, A.; El-Sherbini, M.; Farid, U.; Brown, M.; Malmedy, F.; Wirth, T. *Chem. - Eur. J.* **2014**, *20*, 9910. (b) Pu, Y.; Gao, L.; Liu, H.; Yan, J. *Synthesis* **2012**, *44*, 99. (c) Hirt, U. H.; Schuster, M. F. H.; French, A. N.; Wiest, O. G.; Wirth, T. *Eur. J. Org. Chem.* **2001**, *2001*, 1569. (d) Hirt, U. H.; Spingler, B.; Wirth, T. *J. Org. Chem.* **1998**, *63*, 7674. (e) Koser, G. F.; Lodaya, J. S.; Ray, D. G.; Kokil, P. B. *J. Am. Chem. Soc.* **1988**, *110*, 2987. (f) Wirth, T.; Hirt, U. H. *Tetrahedron: Asymmetry* **1997**, *8*, 23. (g) Xia, M.; Chen, Z.-C. *Synth. Commun.* **1997**, *27*, 1315. (h) Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 2462. (i) Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1982**, *47*, 2487.

(15) (a) Haubenreisser, S.; Wöste, T. H.; Martínez, C.; Ishihara, K.; Muñiz, K. *Angew. Chem., Int. Ed.* **2016**, *55*, 413. (b) Wöste, T.; Muñiz, K. *Synthesis* **2016**, *48*, 816.

(16) The formation of a hydrogen bond between the amide and ligands attached to the iodine atom cannot be excluded (see SI and ref 15), although a comparable *ee* was observed in the case of tertiary amide precatalysts **11c** and **11d**.