Enantioselective Vicinal Diacetoxylation of Alkenes under Chiral Iodine(III) Catalysis

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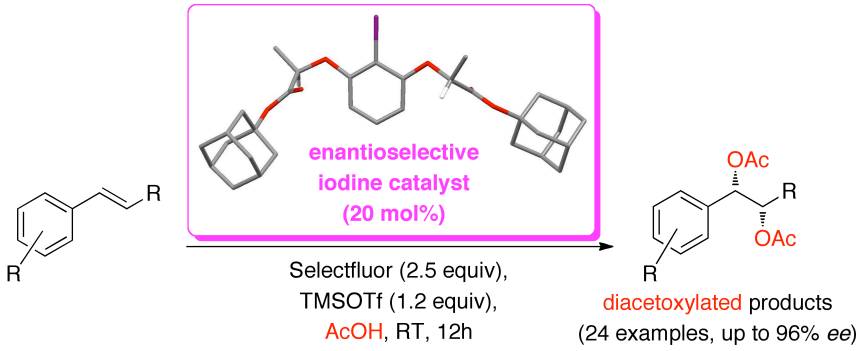
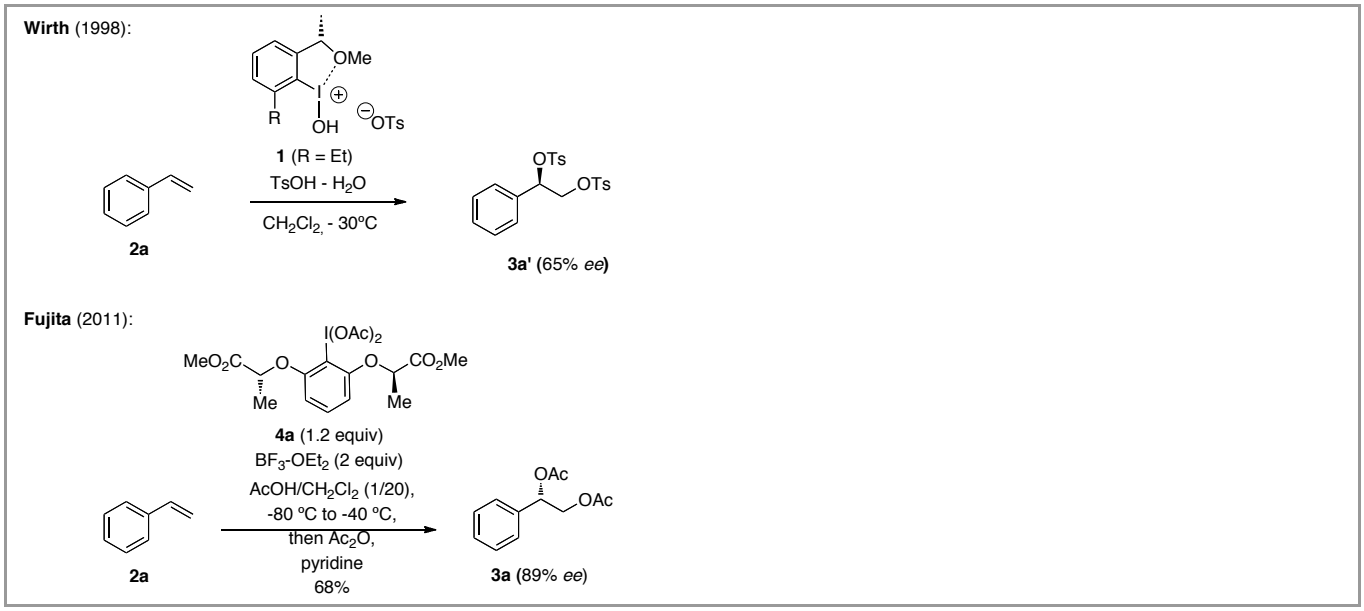


Abstract A procedure for the intermolecular enantioselective dioxygenation of alkenes under iodine(III) catalysis has been developed. This protocol employs Selectfluor as the terminal oxidant together with a defined C2-symmetric aryl iodide as the organocatalyst. This enantioselective reaction proceeds under mild conditions and converts a series of terminal and internal styrenes into the corresponding vicinal diacetoxylation products with up to 96% *ee*.

Key words Alkenes, Chirality, Diacetoxylation, Hypervalent Iodine, Oxidation, Selectfluor.

As a synthetic concept, the vicinal difunctionalization of alkenes allows for a rapid structural and functional diversification of simple alkene moieties within a single operation.[2] Among the many examples of this type of reactions, the development of processes that proceed entirely under intermolecular reaction control is of particular challenge. While this field has been largely dominated by enantioselective transition metal catalysis such as the seminal osmium-based dihydroxylation and aminohydroxylation processes developed by Sharpless,[3] chiral non-racemic iodine(III) reagents[4] have recently emerged as potentially versatile alternatives.[5] Based on earlier work on defined iodine(III) reagents for selective dioxygenation of alkenes,[5c,6] the development of the corresponding enantioselective dioxygenation reactions was pioneered and extensively investigated by Wirth.[7] These reactions made use of defined chiral iodine(III) reagents such as **1**, and the oxidation of styrene **2a** led to formation of the corresponding ditosylation product **3a'** with up to 65% ee (Scheme 1). The appearance of the chiral bislactate derived iodine(III) oxidant **4a** has greatly advanced the inherent synthetic possibilities,[5,8] and, based on this reagent, an enantioselective diacetoxylation of **2a** subsequently led to formation of the corresponding diacetoxylated product **3a** in up to 89% *ee* (Scheme 1).[9] A related diamination[10] was also developed using stoichiometric amounts of **4a**. Moreover, an amide derivative of **4a** promoted an oxygenative rearrangement reaction,[11a] an Umpolung functionalization of silylated enolethers[11b] and asymmetric Kita-spirolactonization reactions.[11c-f] In addition, important contributions were also achieved in the field of related intramolecular enantioselective reactions of alkene oxidation.[5,12,13] In the case of the latter, Fujita recently reported that such oxidations could also be conducted with catalytic amounts of **4a** in the presence of *m*CPBA as terminal oxidant.[5,14,15]



Scheme 1 Intermolecular vicinal dioxygenation reactions of styrene with stoichiometric amounts of hypervalent iodine(III) promoters.

However, despite the fact that dioxygenation belongs to the most extensively investigated reactions in iodine(III)-mediated oxidation of alkenes,[16] the development of corresponding reaction conditions for strictly intermolecular difunctionalization under iodine(III) catalysis represents an ongoing challenge.[17]

This is a noteworthy observation, in particular when taking into account the potential that a metal-free process would have for applications in fields such as biological and medicinal synthesis, where the avoidance of metal contamination is of major importance. We have recently introduced new derivatives of chiral hypervalent iodine reagents of the Ishihara motif, which led to catalyst structures based on effective hydrogen bonding (Figure 1).[18]

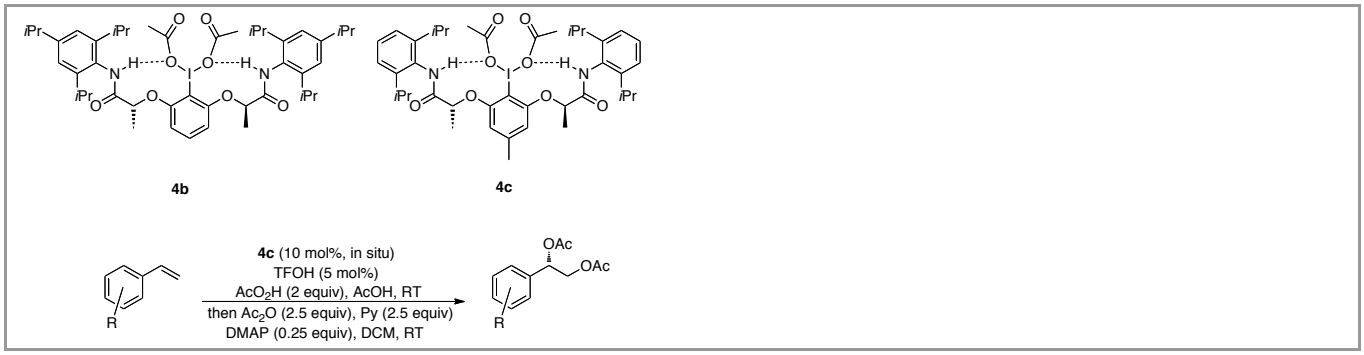


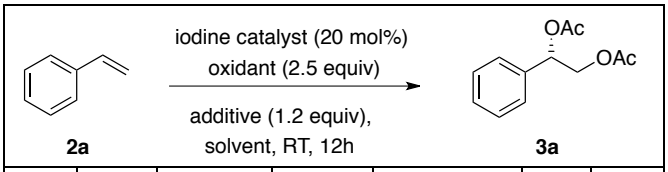
Figure 1 Intramolecular hydrogen-bonding properties of chiral hypervalent iodine compounds **4b,c** and catalytic enantioselective diacetoxylation of styrenes.

These compounds indeed enabled the catalytic enantioselective diacetoxylation of styrenes under intermolecular reaction control in up to 94% ee. Despite the success of these new catalysts, we remained curious to explore whether the parent diesters such as **4a** could be employed as catalysts as well. We here report the development of suitable conditions for such an enantioselective diacetoxylation of alkenes using catalytic amounts of an iodine(I/III) catalysis with **4a** and related derivatives.

Although different oxygen sources such as perchlorate, trifluoroacetate and tosylate have become available,[16] we were particularly drawn to the development of a dioxygenation reaction using the more common acetate as nucleophile. Such a process would be based on chiral derivatives of the fundamental $PhI(OAc)_2$ reagent. Its notoriously low reactivity towards alkenes is usually attributed to the diminished electrophilicity of the central iodine(III) atom. In an elegant study, Gade and Kang demonstrated that Brønstedt activation of $PhI(OAc)_2$ with triflic acid represents a powerful tool to accelerate the overall diacetoxylation process.[19,20] Attempts to devise conditions for diacetoxylation reactions that are catalytic in iodine reagent have met with certain success,[21] however, the potential contribution of background reactivity to the overall product formation[22] remains an issue. Obviously, the use of a chiral iodine reagent would provide the possibility to employ enantioselectivity as a tool to unambiguously proof the catalytic performance of the aryl iodine. Our approach to develop an enantioselective diacetoxylation of alkenes was started from **4a** as catalyst source and with styrene as standard alkene (Table 1). Our initial attempts on the use of peracids as terminal oxidants[15] for the present case of an intermolecular dioxygenation were quickly abandoned. In agreement with the earlier conclusion from Gade and Kang on achiral iodines,[22] that due to similar kinetics, iodine(III) catalysis and stoichiometric oxidation by the stoichiometric oxidant itself compete for the alkene oxidation, aldehyde formation and other degradation products were observed. For the chiral reagent **4a**, reactions in the presence of *m*-chloroperbenzoic

acid (*m*CPBA), peracetic acid or sodium hypochlorite lead to no diacetoxylation of styrene **2a** to the expected product **3a**, regardless whether potential activating additives were added (Table 1, entries 1-5).

Table 1 Optimization of the catalytic enantioselective diacetoxylation.

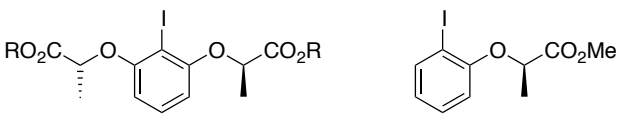


2a **3a**

Entry	Iodine Cat.	Oxidant	Additive	Solvent	Yield [%] [a]	*Ee* [%] [b]
1	**4a**	*m*CPBA	-	$AcOH/CH_2Cl_2$	n.c. [c]	-
2	**4a**	*m*CPBA	TFA	CH_2Cl_2	n.c.	-
3	**4a**	AcO_2H	-	AcOH	n.c.	-
4	**4a**	AcO_2H	TMSOTf	AcOH	n.c.	-
5	**4a**	NaOCl	TMSOTf	AcOH	n.c.	-
6	**4a**	Selectfluor	-	AcOH	n.c.	-
7	**4a**	Selectfluor	TfOH	AcOH	63	0
8	**4a**	Selectfluor	MsOH	AcOH	38	0
9	**4a**	Selectfluor	TMSOTf	AcOH	67	68
10	**4a**	Selectfluor	TMSOAc	AcOH	n.c.	-
11	**4a**	Selectfluor	TMSOAc, TfOH	AcOH	69	72
12	**4a**	Selectfluor	TMSOTf	$AcOH/ CH_2Cl_2$	n.c.	-
13	**4a**	Selectfluor	TMSOTf	$AcOH/ CHCl_3$	n.c.	-
14	**4a**	Selectfluor	TMSOTf	$AcOH/(CH_2Cl)_2$	n.c.	-
15	**4a**	Selectfluor	TMSOTf	$AcOH/CCl_4$	n.c.	-
16	**5a**	Selectfluor	TMSOTf	AcOH	64	74
17	**5e**	Selectfluor	TMSOTf	AcOH	67	52
18	**5b**	Selectfluor	TMSOTf	AcOH	47	78
19	**5c**	Selectfluor	TMSOTf	AcOH	63	78
20	**5d**	Selectfluor	TMSOTf	AcOH	66	80

[a] Isolated yield after treatment with acetic anhydride. [b] Determined by chiral HPLC analysis (OD-H column). [c] n.c. = no conversion to **3a** was observed.

We thus changed our approach and employed Selectfluor, which is known for its ability to promote stoichiometric iodine(III) formation from the corresponding aryliodides.[8c,23] While reagent **4a** itself cannot promote a catalytic diacetoxylation of styrene in the sole presence of Selectfluor (entry 6), addition of triflic acid demonstrated that turn-over can be achieved, although the desired product **3a** was formed as racemate (entry 7). Less acid strength as with methyl sulfonic acid results in a decrease in yield (entry 8). Finally, addition of TMS triflate gave a catalytic reaction that formed a product with 68% ee (entry 9). Changing the additive to TMS acetate shut down the reaction (entry 10), while the additional presence of triflic acid reactivated the enantioselective catalysis (entry 11). Attempts to carry out the reaction in solvent mixtures were not successful (entries 12-15). The reaction was then further developed exploring the potential of different *in situ* generated hypervalent iodine compounds. When starting the reaction from the corresponding iodine(I) compound **5a** (Figure 1), an efficient catalysis was observed (entry 16). A related catalyst **5e** with a single lactate side chain gave similar yield, but decreased *ee* (entry 17). A useful increase in enantioselectivity to 78% *ee* was observed for the *tert*-butyl ester **5b**, although the chemical yield decreased. The latter was attributed to a potential incompatibility of the *tert*-butyl ester with the TMS additive. Consequently the new adamantyl derivatives **5c** and **5d** were synthesized and structurally characterized (Figure 3).[23]



5a: R = Me,
5b: R = *t*Bu,
5c: R = 2-adamantyl
5d: R = 1-adamantyl

5e

Figure 2 Chiral iodine(I) catalysts: structures

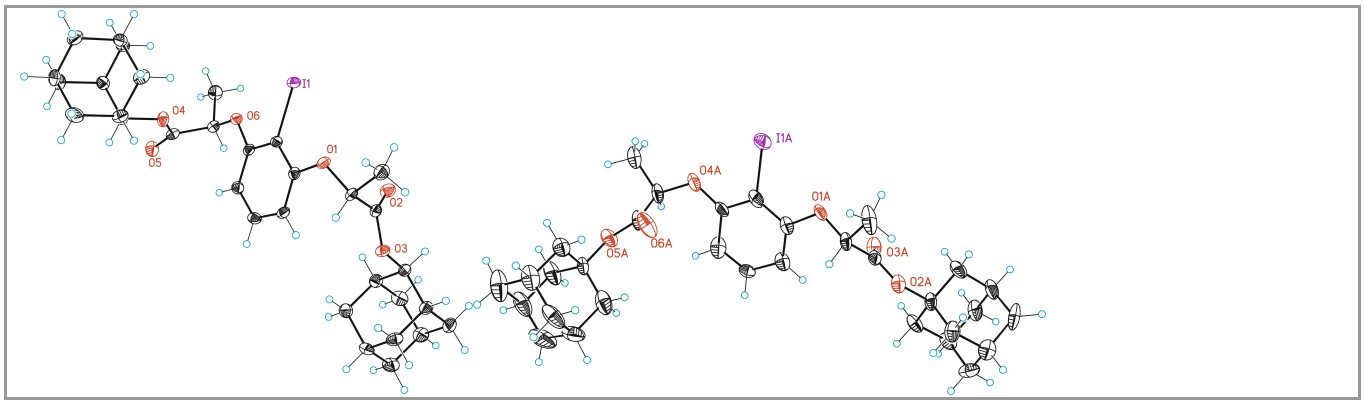
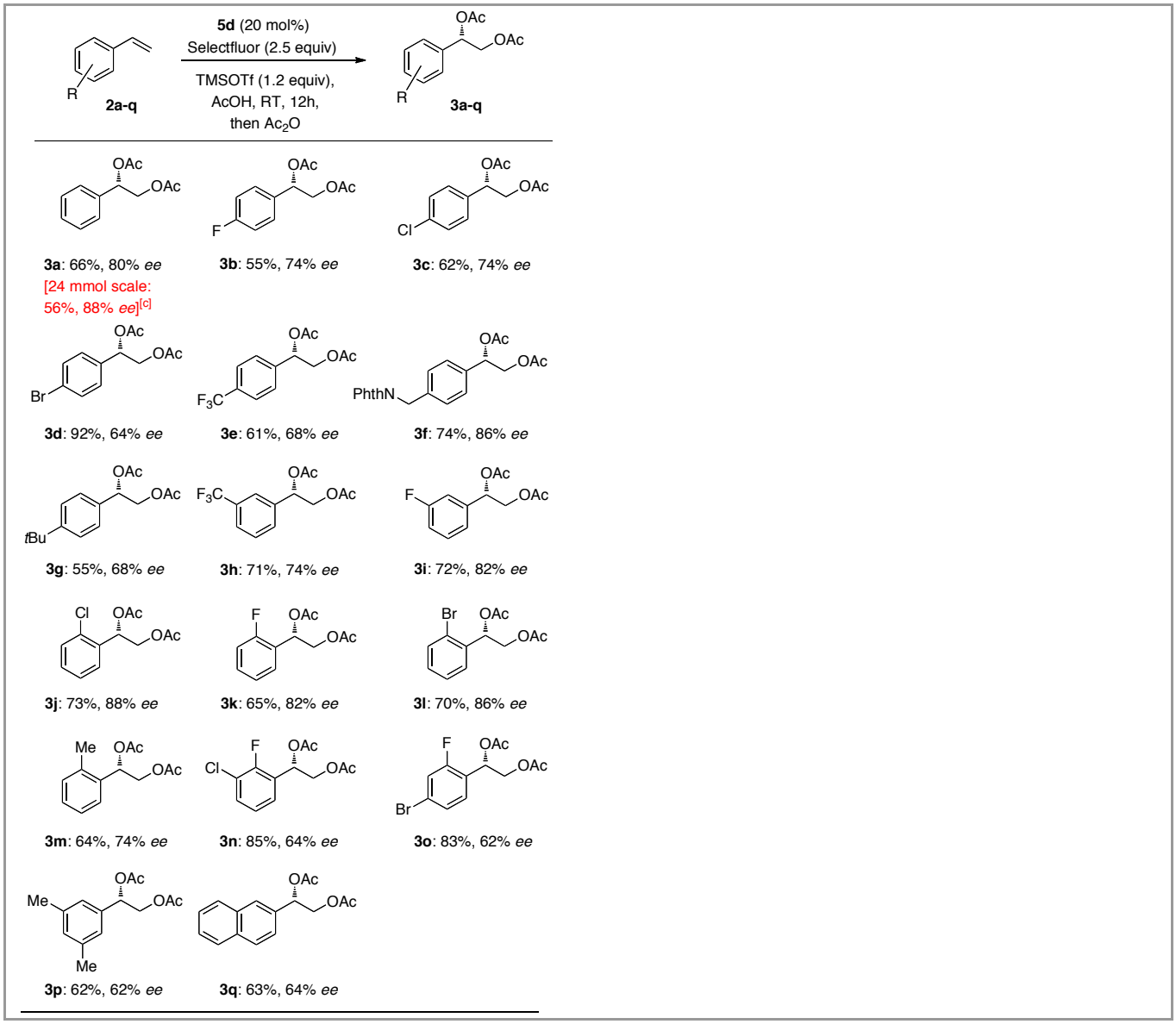


Figure 3 Solid state structures of compounds **5c** (top) and **5d** (bottom).

They demonstrated to be efficient catalysts giving the diacetoxylation product in up to 80% *ee* (entries 19, 20). In particular, compound **5d** displayed significantly higher stability than the *tert*-butyl ester **5b**, and could be recovered in over 95% isolated yield after the oxidation catalysis. In all these cases, in order to account for a uniform product, the crude reaction mixtures were treated with acetic anhydride prior to analysis of product **3a** (cf. footnote a)

The reaction is general for a range of styrenes. Table 2 displays 17 examples of different styrenes **2a-q** that could be converted into the corresponding diacetoxylation products **3a-q** in an enantioselective manner. These examples demonstrate a higher substrate scope than reported for the stoichiometric reaction.[9] The high robustness of the reaction conditions was further demonstrated for a 24 mmol scale diacetoxylation of **2a**, which provided 2.99 g of the corresponding product **3a**.



Scheme 2 Scope of the iodine(III)-catalyzed enantioselective diacetoxylation of styrenes. [a] Isolated yield after purification. [b] *Ee* determination at the stage of free diols by HPLC on chiral stationary phase. [c] 24 h Reaction time.

Apart from styrene itself, several *para*-substituted arenes **2b-g** underwent diacetoxylation in good yields and with 64-86% *ee*. An exception was encountered for the case of 4-methoxy styrene, which suffered from degradation under the present conditions. Other successful examples include the *meta*- and *ortho*-substituted products **3h-m**, which formed with up to 88% *ee*. Higher-substituted styrenes **2n-q** led to formation of the corresponding diacetoxylation products **3n-q** with good enantioselectivities of 62-64% *ee*. The enantioselectivity values obtained from such room temperature catalyses are noteworthy when compared to the outcome of the parent stoichiometric reaction, which was conducted at a temperature range between −80 and −40 °C.[9] They are only slightly lower than the ones for the presently best enantioselective catalysis based on compounds **4b,c**.[18]

A mechanistic context for this intermolecular enantioselective iodine(III)-catalyzed dioxygenation reaction is discussed in Figure 4. The reaction starts with the Selectfluor-mediated oxidation of the iodine(I) species Ar*I to the corresponding cationic iodine(III) catalyst state **A**, which in the presence of trimethylsilyl acetate and triflic acid generates the catalyst state **B**. Since the reaction proceeds in acetic acid as solvent, this pathway could initially proceed through the formation of the corresponding diacetoxy iodine(III) species, which upon protonolysis by triflic acid will ultimately generate **B**. In any case, the presence of both the TMS group for removal of the fluoride and HOTf for the formation of a cationic catalyst state are required. In agreement with the data from Gade on the achiral reaction,[19] **B** should represent the active catalyst involved in the alkene oxidation. This was corroborated by a stoichiometric control experiment on diacetoxylation of styrene **2a** with **4a** together with 1.1 equivalents of TMS triflate in acetic acid at room temperature (Scheme 3), which gave **3a** (56% yield, 73% *ee*) in a comparable outcome to the results from catalysis (Table 1, entry 11: 69% yield, 72% *ee*). Upon oxidation of the styrene, the iodo-oxygenated intermediate **C** is formed, from which the iodine(I) catalyst is regenerated upon an intramolecular reductive displacement by the acetyl group forming the resulting dioxolonium derivative **D**. It had previously been discussed[16] that such an intermediate **D** can undergo ring opening by acetate through a Prèvost mechanism[25] or through water addition to form a hydroxyacetate **6** within a Woodward pathway.[26] It should also be noted that both pathways from **D** release one equivalent of

triflic acid. However, the reaction does not proceed with catalytic amounts of HOTf, which should be the result of neutralization through the tertiary quinuclidinium amine that is generated from Selectfluor within the oxidation step.

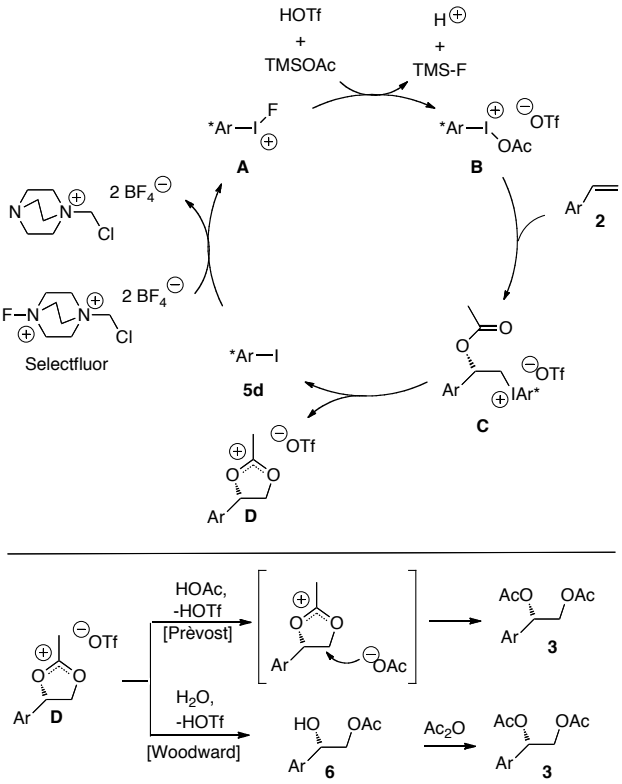
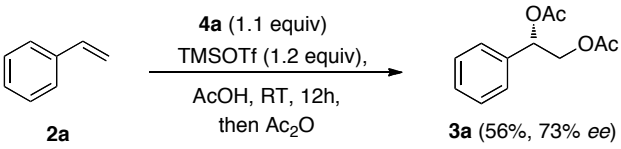
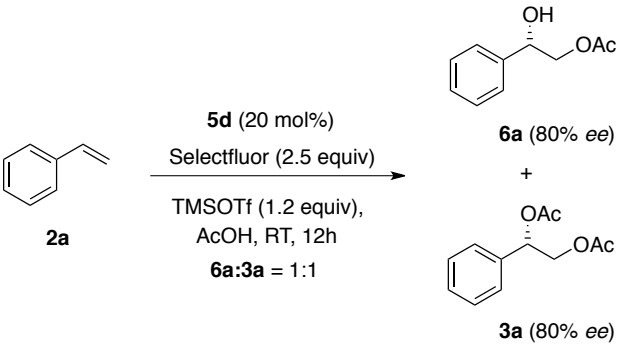


Figure 4 Catalytic cycle for the enantioselective diacetoxylation of styrenes.



Scheme 3 Stoichiometric control experiment



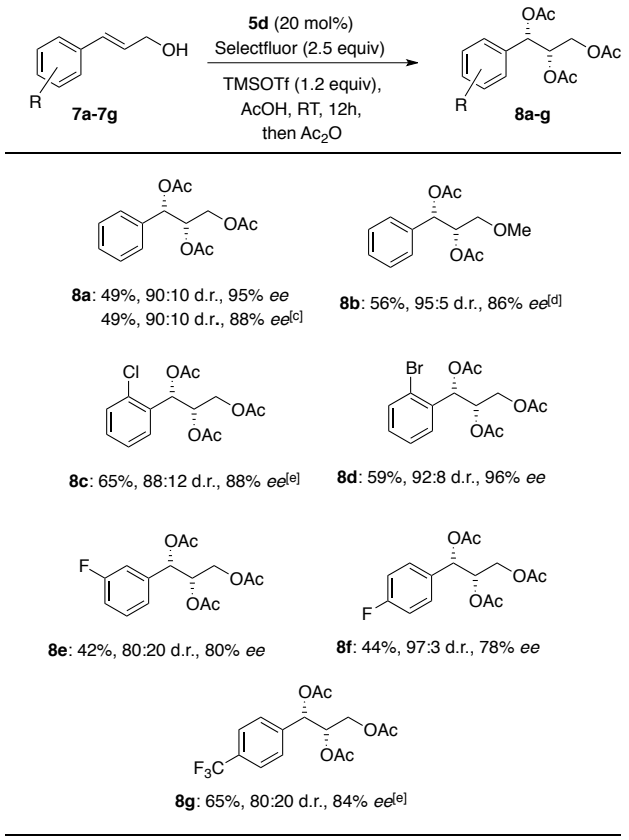
Scheme 4 Control experiment on the initial product distribution for terminal alkene oxidation.

To gain further insight on the involved intermediates in the dioxygenation, we isolated the direct reaction products from catalytic dioxygenation of styrene **2a** (Scheme 4). In this case, the crude reaction mixture contained both the diacetoxylation product **3a** as well as the regioselectively formed 1-hydroxy, 2-acetoxy product **6a**, indicating that two different pathways are competent under the reaction conditions. The diacetate **3a** was isolated as the (*S*)-enantiomer in 42% yield with 80% *ee*, while the equally (*S*)-configured hydroxyacetate **6a** was formed in 40% yield and with 80% ee as determined after conversion to the diacetate **3a**.

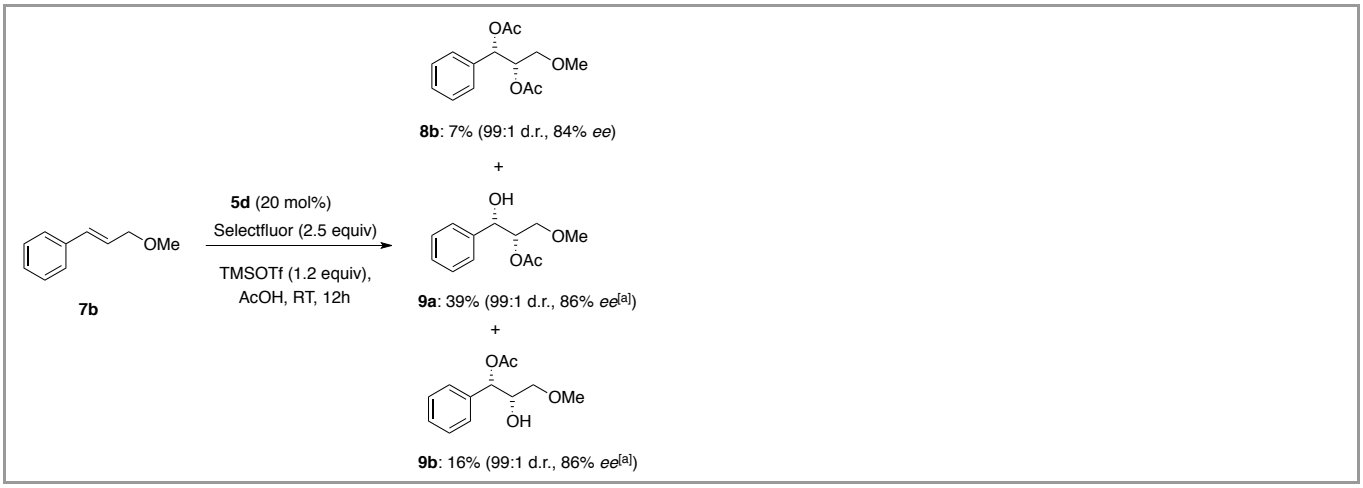
The fact that the two compounds **3a** and **6a** form with identical absolute configuration and identical enantiomeric excess is important. To account for the observed (*S*)-configuration of the diacetoxylation product through a Prèvost pathway, an opening of intermediate **D** at

the homobenzylic position is required. While this is not entirely impossible, it appears highly improbable. In fact, a Prèvost mechanism was suggested to be involved in the stoichiometric dioxygenation, which provided the expected (*R*)-stereochemistry.[9] The present observation on the stereochemical outcome suggests that a Prèvost mechanism is not involved in this transformation and product **3a** should form through a different pathway (vide infra).

The present conditions for catalytic enantioselective diacetoxylation reaction could also be extended to the substrate class of internal alkenes., which are beyond the scope of our earlier catalysts **4b,c**. While β-methyl styrene did not display any reactivity under the present standard catalytic conditions, cinnamic alcohol and its derivatives were found to be suitable substrates (Scheme 5). This observation is reminiscent of the earlier report on stoichiometric reactivity[9] and appears to be the consequence of an electronic effect of the allylic oxygen. For example, cinnamyl alcohol **7a** gave the corresponding oxidation product **8a** with a 90:10 diastereomeric ratio in favor of the *like*-product **8a**, which formed with 95% *ee*. The same product could be obtained from the acetoxylated alcohol leading to an identical product formation with 88% *ee*. This somewhat lower induction may be the result of the presence of a sterically more demanding acetoxy substituent retarding the face selection. The corresponding cinnamyl methyl ether led to a 95:5 diastereomeric ratio in favor of the *like*-product **8b**, which formed in 86% *ee.* From this observation, possible hydrogen bonding from the free OH in **8a** appears not to play an essential role in the reaction. Finally, substituted free cinnamyl alcohols **7d-g** gave the corresponding *like*-diacetoxylation products **8d-g** in good to very good diastereoselectivities and with 78-96% *ee*.



Scheme 5 Scope of the iodine(III)-catalyzed enantioselective diacetoxylation of styrenes. [a] Isolated yield after purification. [b] *Ee* determination by HPLC on chiral stationary phase.[21] [c] from cinnamyl acetate **7a'**. [d] from cinnamyl methyl ether **7b**. [e] with **5b** as catalyst



Scheme 6 Control experiment for the reaction outcome in the dioxygenation of internal alkenes. [a] ee determined after conversion to **8b**

While the crude product was usually directly transformed by treatment with acetic anhydride to furnish single diacetate products **8** in all cases from Table 3, we also again investigated the initial formation of different dioxygenation products for cinnamyl methyl ether **7b** (Scheme 6). After direct work-up, the crude reaction product was identified to consist of a mixture of the diacetoxylation product **8b** in 7% and with 84% *ee*, together with 55% of the two hydroxylated products **9a** and **9b** in a 70:30 ratio. After separation of the two compounds and their conversion into **8b** by acetoxylation with acetic anhydride, an identical 86% *ee* was determined for both samples. This outcome confirms a *like*-configuration for products **9a,b** and suggests the dominance of a Woodward pathway in the cases of internal alkenes **7a-g** and **7a'**.

In addition, the observed *like*-configuration for product **8b** is inconsistent with the potential involvement of a Prèvost mechanism, as the underlying opening of the corresponding cationic dioxolanyl intermediate should generate the opposite diastereoisomer of an *unlike*-configuration.

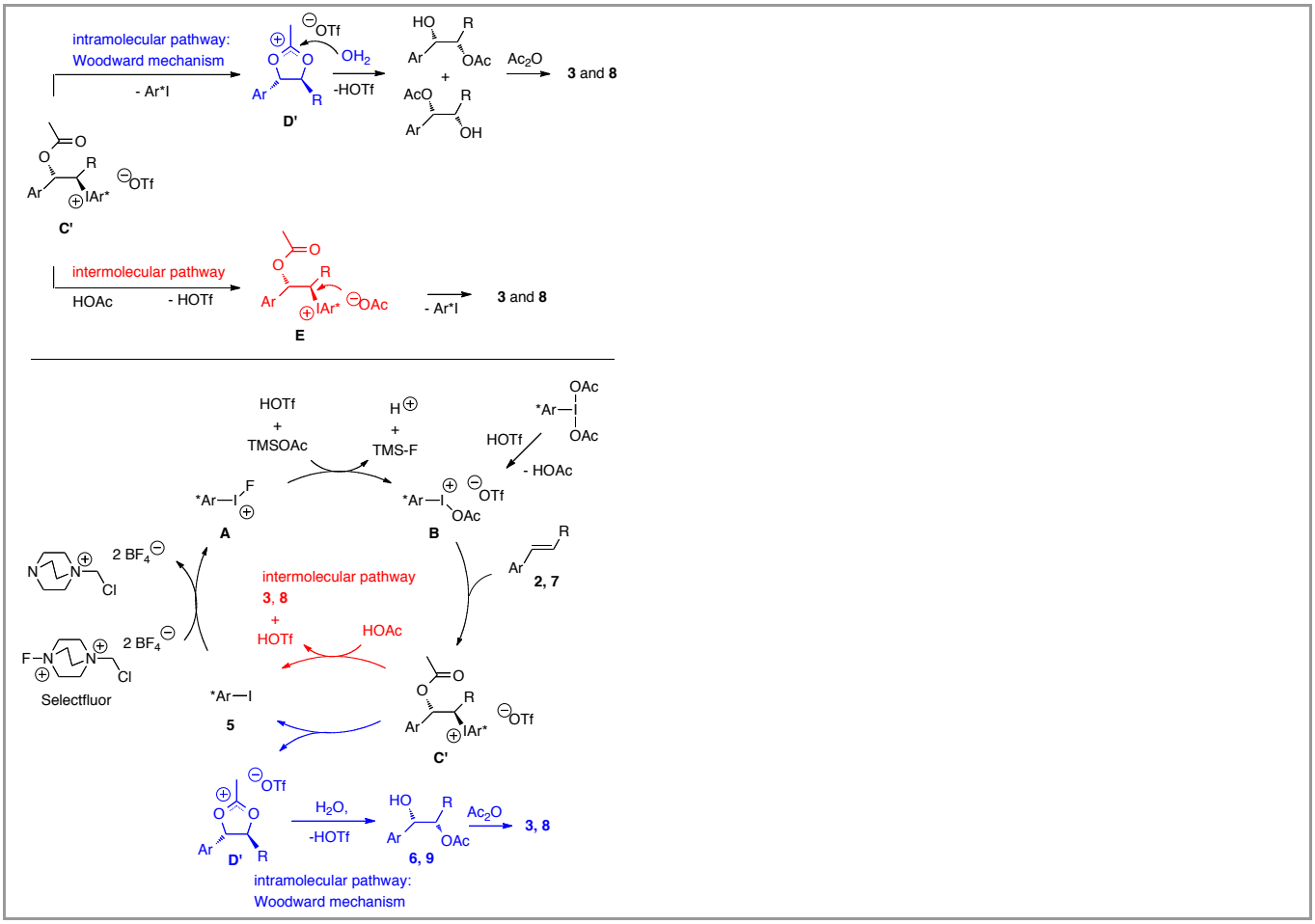


Figure 5 Mechanistic conclusion: Competing pathways in the enantioselective catalytic diacetoxylation of alkenes and overall catalytic cycle for diacetoxylation of terminal (R = H) and internal alkenes.

As a result, it must be concluded that Prèvost pathways are entirely absent in the present oxidative difunctionalization of styrenes. Instead, a direct reductive elimination of the iodine(III) moiety in intermediate **C'** appears to be taking place. Such a process involves an intermolecular S_N2-displacement **E** of the iodine(III) nucleophuge[27] through acetate or acetic acid at stage **C'**, which competes with the intramolecular displacement that forms the dioxolonium intermediate **D'**. Such a direct nucleophilic substitution at the alkyl-iodine(III) group is in agreement with related investigation on ditosylation reactions.[6,7a,16c,28] In these cases, the tosyl group does not engage in an intramolecular iodine displacement leading to a stereochemical outcome that perfectly resembles the one from the present diacetoxylation.[28]

For steric reasons, such direct iodine for acetate exchange at stage **E** has a higher chance to proceed for styrene derivatives, where the S_N2 reaction proceeds at a primary center (R = H). In contrast, for cinnamyl derivatives, the Woodward pathway is largely dominating. Since both pathways lead to stereochemically uniform products, the relative participation of each of the enantioconvergent pathway does not alter the overall enantiomeric excess of the product. Figure 5 displays the full catalytic cycle based on all data including control experiments and stereochemical conclusions.

In summary, we have developed a second protocol for an iodine(III)-catalyzed enantioselective vicinal dioxygenation of alkenes under intermolecular reaction control. The reaction proceeds under mild conditions, extends the substrate class to β-substituted styrenes and provides the corresponding oxidation products with up to 96% *ee*. The two successful realizations of catalytic dioxygenation with **4b,c** and now **5d** should be instructive for the development of similar iodine(I/III)-catalyzed enantioselective difunctionalization reactions of alkenes.[29]

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General. All solvents, reagents and all deuterated solvents were purchased from Aldrich and Acros. Column chromatography was performed with silica gel (Merck, type 60, 0.063-0.20 mm). NMR spectra were recorded on a Bruker Avance 300 MHz, 400 MHz or 500 MHz spectrometer, respectively. All chemical shifts in NMR experiments are reported in ppm downfield from TMS. The following calibrations were used: $CDCl_3$ δ = 7.26 and 77.16 ppm; DMSO-d_6 δ = 2.50 and 39.52 ppm. MS (ESILCMS) experiments were performed using an Agilent 1100 HPLC with a Bruker micro-TOF instrument (ESI). Unless otherwise stated, a Supelco C8 (5 cm x 4.6 mm, 5 µm particles) column was used with a linear elution gradient from 100% H_2O (0.5% HCO_2H) to 100% MeCN in 13 min at a flow rate of 0.5 mL/min. MS (EI) and HRMS experiments were performed on a Kratos MS 50 within the service departments at ICIQ. Melting points were determined with a Buchi Melting Point B-540 apparatus. IR spectra were taken with a Bruker Alpha instrument in the solid state. Specific optical rotation values were measured with a Polarimeter JascoP1030 equipped with a 100 mm cell. HPLC measurements were carried out on a Knauer Wellchrome (injection valve A0258, pump K-100, solvent organizer K-1500, UV-detector K-2600). The respective chiral stationary phase and exact conditions are specified for each individual compound within the compound characterization section. Diastereomeric ratios were determined by achiral gas chromatography on an Agilent Technologies 7890A gas chromatograph equipped with an Agilent J&W HP-5 column.

Synthesis and availability of styrenes **2a-q**, diacetoxylation products **3a-q** and the corresponding free diols were reported previously.[18] (*E*)-1-Phenyl-3-methoxypropene (**7b**),[30] (*E*)-3-(2-chlorophenyl)prop-2-en-1-ol (**7c**),[31a] (*E*)-3-(2-bromophenyl)prop-2-en-1-ol (**7d**),[31b] (*E*)-3-(3-fluorophenyl)prop-2-en-1-ol (**7e**),[31c] (*E*)-3-(4-fluorophenyl)prop-2-en-1-ol (**7f**),[31d] (*E*)-3-(4-trifluoromethylphenyl) prop-2-en-1-ol (**7g**)[31e] were synthesized according to a literature protocol.[32] Products **8a**,**b** were reported previously.[33]

Procedures

General Procedure for the diacetoxylation of alkenes catalyzed by hypervalent iodine reagents. A Pyrex tube equipped with a stir bar was charged with the respective iodine(I)- or iodine(III)-compound (0.040 mmol, 20 mol%) and AcOH (4 mL). The addition of the respective alkene (0.20 mmol, 1.0 equiv) was followed by subsequent addition of Selectfluor® (0.50 mmol, 2.5 equiv) and TMSOTf (0.24 mmol, 1.2 equiv). The tube was sealed and the reaction mixture was stirred at ambient temperature for 12 h. The reaction mixture was poured into a separating funnel containing CH_2Cl_2 and H_2O. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 three times. The combined organic layers were washed with H_2O and brine once each. Drying the organic phase over Na_2SO_4 and filtration was followed by removal of the solvents under reduced pressure. The residue was dissolved in CH_2Cl_2 (0.35 mL) and, depending on whether a styrene- or a cinnamyl alcohol-derivative was used as starting material, DMAP (0.050–0.070 mmol, 0.25–0.35 equiv), pyridine (0.50–0.70 mmol, 2.5–3.5 equiv) and Ac_2O (0.50–0.70 mmol, 2.5–3.5 equiv) were added. After stirring at room temperature for 5 h, HCl (1M) and H_2O were added and the aqueous phase was extracted with CH_2Cl_2 three times. After drying over Na_2SO_4 and removing the solvent under reduced pressure, the crude product was purified by flash column chromatography on silica gel using hexane:ethyl acetate mixtures. In order to determine the enantiomeric excesses in case of styrene-derivatives as starting materials, the pure product was dissolved in MeOH (0.1M). Addition of K_2CO_3 (1.5 equiv) was followed by stirring at ambient temperature for 4 h. MeOH was removed under reduced pressure after acidification with HCl (1M). Extraction of the aqueous layer with CH_2Cl_2 three times, drying the combined organic layers over Na_2SO_4 and evaporation of the solvent yielded the corresponding diol, which was submitted to HPLC analysis. In the case of cinnamyl alcohol derived starting materials, enantiomeric excesses were determined at the stage of the acetoxylated products.

(*S*)-1-Phenylethane-1,2-diol-1,2-diacetate (3a): Isolated yield: 29.4 mg (66%). HPLC-conditions for free diol: OD-H, hexane:^{i}PrOH = 95:5, 0.7 mL/min, t_R = 24.9 (minor), 27.3 (major): 80% *ee.*
(*S*)-1-(4-Fluorophenyl)ethane-1,2-diol-1,2-diacetate (3b): Isolated yield: 26.4 mg (55%). HPLC-conditions for free diol: OD-H, hexane:^{i}PrOH = 95:5, 1 mL/min, t_R = 17.1 (minor), 18.5 (major): 74% *ee*.
(*S*)-1-(4-Chlorophenyl)ethane-1,2-diol-1,2-diacetate (3c): Isolated yield: 32 mg (62%). HPLC-conditions for free diol: OD-H, hexane:^{i}PrOH = 95:5, 1 mL/min, t_R = 18.2 (minor), 19.8 (major): 74% *ee*.
(*S*)-1-(4-Bromophenyl)ethane-1,2-diol-1,2-diacetate (3d): Isolated yield: 55.4 mg (92%). HPLC-conditions for free diol: OD-H, hexane:^{i}PrOH = 95:5, 0.5 mL/min, t_R = 39.9 (minor), 43.2 (major): 64% *ee*.
(*S*)-1-(4-Trifluoromethylphenyl)ethane-1,2-diol-1,2-diacetate (3e): Isolated yield: 35.4 mg (61%). HPLC-conditions for free diol: OD-H, hexane:^{i}PrOH = 95:5, 0.5 mL/min, t_R = 34.8 (minor), 36.5 (major): 68% *ee*.
(*S*)-4-(Phthaloylmethylenephenyl)ethane-1,2-diol-1,2-diacetate (3f): Isolated yield: 56.4 mg (74%). HPLC-conditions for free diol: IA, hexane:^{i}PrOH = 93:7, 1 mL/min, t_R = 90.3 (major), 101.6 (minor): 86% *ee*.
(*S*)-1-(4-*tert*-Butylphenyl)ethane-1,2-diol-1,2-diacetate (3g): Isolated yield: 30.6 mg (55%). HPLC-conditions for free diol: OD, hexane:^{i}PrOH = 98:2, 0.8 mL/min, t_R = 48.7 (minor), 52.6 (major): 68 *ee*.
(*S*)-1-(3-Trifluoromethylphenyl)ethane-1,2-diol-1,2-diacetate (3h): Isolated yield: 41.3 mg (71%). HPLC-conditions for free diol: OD-H, hexane:^{i}PrOH = 95:5, 0.7 mL/min, t_R = 19.8 (minor), 22.3 (major): 74 *ee*.
(*S*)-1-(3-Fluorophenyl)ethane-1,2-diol-1,2-diacetate (3i): Isolated yield: 34.6 mg (72%). HPLC-conditions for free diol: OD-H, hexane:^{i}PrOH = 95:5, 1 mL/min, t_R = 16.0 (minor), 17.7 (major): 82% *ee*.

(*S*)-1-(2-Chlorophenyl)ethane-1,2-diol-1,2-diacetate (3j): Isolated yield: 37.5 mg (73%). HPLC-conditions for free diol: OD-H, hexane:^{i}PrOH = 95:5, 1 mL/min, t_R = 13.4 (minor), 17.5 (major): 88% *ee.*
(*S*)-1-(2-Fluorophenyl)ethane-1,2-diol-1,2-diacetate (3k): Isolated yield: 31 mg (65%). HPLC-conditions for free diol: OD-H, hexane:^{i}PrOH = 95:5, 1 mL/min, t_R = 12.7 (minor), 15.2 (major): 82% *ee.*
(*S*)-1-(2-Bromophenyl)ethane-1,2-diol-1,2-diacetate (3l): Isolated yield: 42.2 mg (70%). HPLC-conditions for free diol: OD-H, hexane:^{i}PrOH = 95:5, 0.7 mL/min, t_R = 21.3 (minor), 27.9 (major): 86% *ee.*
(*S*)-1-(2-Methylphenyl)ethane-1,2-diol-1,2-diacetate (3m): Isolated yield: 30.2 mg (64%). HPLC-conditions for free diol: OD-H, hexane:^{i}PrOH = 95:5, 0.7 mL/min, t_R = 21.9 (minor), 27.9 (major): 74% *ee.*
(*S*)-1-(3-Chloro-2-fluorophenyl)ethane-1,2-diol-1,2-diacetate (3n): Isolated yield: 46.7 mg (85%). HPLC-conditions for free diol: OD-H, hexane:^{i}PrOH = 95:5, 0.7 mL/min, t_R = 20.0 (minor), 25.8 (major): 64% *ee.*
(*S*)-1-(4-Bromo-2-fluorophenyl)ethane-1,2-diol-1,2-diacetate (3o): Isolated yield: 53 mg (83%). HPLC-conditions for free diol: OD-H, hexane:^{i}PrOH = 95:5, 0.7 mL/min, t_R = 20.1 (minor), 22.8 (major): 62% *ee.*
(*S*)-1-(3,5-Dimethylphenyl)ethane-1,2-diol-1,2-diacetate (3p): Isolated yield: 31 mg (62%). HPLC-conditions for free diol: OD-H, hexane:^{i}PrOH = 95:5, 0.7 mL/min, t_R = 19.2 (minor), 22.3 (major): 62% *ee.*
(*S*)-1-(2-Naphthyl)ethane-1,2-diol-1,2-diacetate (3q): Isolated yield: 34.3 mg (63%). HPLC-conditions for free diol: OD-H, hexane:^{i}PrOH = 90:10, 0.95 mL/min, t_R = 14.6 (minor), 17.7 (major): 64% *ee*.
(1*S*,2*S*)-1,2,3-Propanetriol-1-phenyl-1,2,3-triacetate (8a): Isolated yield: 28.8 mg (49%). HPLC-conditions: OJ, hexane:^{i}PrOH = 85:15, 1.0 mL/min, t_R = 23.2 (major), 32.9 (minor): 88% *ee.*
(1*S*,2*S*)-3-Methoxy-1-phenyl-1,2-propanediol-1,2-diacetate (8b): Isolated yield: 30 mg (56%). HPLC-conditions: IC, hexane:^{i}PrOH = 95:5, 0.5 mL/min, t_R = 23.7 (minor), 27.3 (major): 86% *ee.*

(*R*,*R*)-1,3-Di(1-(2-adamantoxycarbonyl)ethoxy)-2-iodobenzene (5c)

According to a procedure of Breit[34] a solution of *N*,*N*-dicyclohexylcarbodiimide (706 mg, 3.42 mmol, 2.60 equiv) in CH_2Cl_2 (4.4 mL) was added to a suspension of (2*R*,2'*R*)-2,2'-(2-iodo-1,3-phenylene)bis(oxy)dipropanoic acid (500 mg, 1.32 mmol), 1-adamantanol (881 mg, 5.79 mmol, 4.40 equiv) and DMAP (106 mg, 0.870 mmol, 0.660 equiv) in CH_2Cl_2 (6.6 mL) at 0ºC. Stirring was continued for 12 h, while the reaction mixture was allowed to warm to room temperature slowly. A small amount of silica gel was added to the reaction mixture, the solvent was removed under reduced pressure and the crude product was submitted to flash column chromatography using hexane:ethyl acetate = 12:1 as eluent. Washing the obtained compound with pentane yielded the pure product (604 mg, 71%) as a white crystalline solid.

m.p.: 136ºC.

$[\alpha]_D^{25}$ = –39.1 (*c* = 0.115, $CHCl_3$).

IR (ATR): ν/cm^{-1} = 2989, 2903, 2852, 2673, 2119, 1736, 1719, 1587, 1458, 1374, 1344, 1277, 1252, 1217, 1200, 1182, 1135, 1098, 1067, 1041, 1016, 977, 964, 933, 903, 860, 817, 798, 764, 753, 703, 675, 647, 626, 607, 575, 508, 456, 412

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 1.37–2.01 (m, 28H), 1.71 (d, *J* = 6.5 Hz, 6H), 4.80 (q, *J* = 4.6 Hz, 2H), 4.94–4.97 (m, 2H), 6.39 (d, *J* = 8.6 Hz, 2H), 7.10 (t, *J* = 8.2 Hz, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ/ppm = 18.8, 27.0, 27.2, 31.6, 31.8, 31.8, 32.0, 36.3, 36.4, 37.4, 74.4, 78.3, 80.6, 106.7, 129.5, 158.4, 171.2.

HRMS: calcd for $C_{32}H_{41}INaO_6^+$: 671.1840, found: 671.1846.

(*R*,*R*)-1,3-Di(1-(1-adamantoxycarbonyl)ethoxy)-2-iodobenzene (5d)

According to the procedure described above for compound **5c**,[21] the title compound was obtained as a white crystalline solid (76%).

m.p.: 153 ºC.

$[\alpha]_D^{25}$ = –27.9 (*c* = 0.1, $CHCl_3$) .

IR (ATR): ν/cm^{-1} = 2985, 2907, 2852, 2117, 1746, 1586, 1458, 1374, 1349, 1315, 1288, 1250, 1201, 1180, 1126, 1101, 1069, 1046, 1021, 966, 940, 916, 899, 876, 831, 761, 752, 725, 701, 642, 606, 589, 525, 467, 453, 407

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 1.62–1.64 (m, 12H), 1.66 (d, *J* = 6.8 Hz, 6H), 2.03–2.09 (m, 12H), 2.12–2.16 (m, 6H), 4.63 (q, *J* = 6.5 Hz, 2H), 6.37 (d, *J* = 8.2 Hz, 2H), 7.12 (t, *J* = 7.9 Hz, 1H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ/ppm = 18.7, 31.0, 36.2, 41.3, 74.6, 80.6, 82.1, 106.7, 129.3, 158.5, 170.7.

HRMS: calcd for $C_{32}H_{41}INaO_6^+$: 671.1840, found: 671.1840.

(1*S*,2*S*)-1,2,3-Propanetriol-1-(2-chlorophenyl)-1,2,3-triacetate (8c)

Synthesized according to the general procedure. Isolated yield: 43 mg (65%).

IR (ATR): ν/cm^{-1} = 2958, 2926, 2854, 1742, 1475, 1442, 1370, 1209, 1126, 1042, 960, 865, 760, 741, 710, 689, 602, 568, 546, 475, 459, 415.

^{1}H-NMR (500 MHz, $CDCl_3$): δ/ppm = 1.99 (s, 3H), 2.05 (s, 3H), 2.12 (s, 3H), 4.04 (dd, *J* = 11.8, 6.6 Hz, 1H), 4.27 (dd, *J* = 11.8, 4.5 Hz, 1H), 5.55 (ddd, *J* = 6.6, 5.3, 4.5 Hz, 1H), 6.41 (d, *J* = 5.3 Hz, 1H), 7.23–7.29 (m, 2H), 7.35–7.40 (m, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ/ppm = 20.8, 20.8, 21.0, 62.2, 70.6, 71.1, 127.1, 128.3, 129.9, 130.0, 133.0, 134.1, 169.5, 169.9, 170.6.

HRMS: calcd for $C_{15}H_{17}ClNaO_6^+$: 351.0606, found: 351.0602.

HPLC-conditions: OJ, hexane:^{i}PrOH = 85:15, 0.5 mL/min, t_R = 35.3 (major), 45.7 (minor).

(1*S*,2*S*)-1,2,3-Propanetriol-1-(2-bromophenyl)-1,2,3-triacetate (8d)

Synthesized according to the general procedure. Isolated yield: 44 mg (59%).

IR (ATR): ν/cm^{-1} = 3423, 2961, 1744, 1470, 1438, 1370, 1210, 1122, 1043, 1021, 961, 865, 759, 737, 686, 603, 567, 545, 470, 453.

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 1.99 (s, 3H), 2.05 (s, 3H), 2.12 (s, 3H), 4.07 (dd, *J* = 11.8, 6.6 Hz, 1H), 4.27 (dd, *J* = 11.8, 5.0 Hz, 1H), 5.55 (ddd, *J* = 6.7, 5.0, 5.0 Hz, 1H), 6.37 (d, *J* = 5.0 Hz, 1H), 7.15–7.19 (m, 1H), 7.28–7.32 (m, 1H), 7.36–7.39 (m, 1H), 7.54–7.56 (m, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ/ppm = 20.7, 20.9, 20.9, 62.2, 71.1, 72.8, 122.9, 127.6, 128.6, 130.2, 133.3, 135.8, 169.5, 169.8, 170.6.

HRMS: calcd for $C_{15}H_{17}BrNaO_6^+$: 395.0101, found: 395.0110.

HPLC-conditions: IB, hexane:^{i}PrOH = 95:5, 0.3 mL/min, t_R = 28.6 (major), 30.3 (minor).

(1*S*,2*S*)-1,2,3-Propanetriol-1-(3-fluorophenyl)-1,2,3-triacetate (8e)

Synthesized according to the general procedure. Isolated yield of a 4:1 diastereomeric mixture: 26.2 mg (42%).

IR (ATR): ν/cm^{-1} = 3441, 2962, 1742, 1617, 1593, 1490, 1450, 1371, 1210, 1145, 1079, 1044, 969, 947, 912, 872, 792, 768, 732, 702, 648, 602, 522, 485, 448, 409.

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 2.05 (s, 3H), 2.05 (s, 3H), 2.10 (s, 3H), 3.82 (dd, *J* = 12.1, 5.7 Hz, 1H), 4.28 (dd, *J* = 12.1, 4.0 Hz, 1H), 5.39 (ddd, *J* = 6.6, 5.7, 3.9 Hz, 1H), 5.94 (d, *J* = 6.6 Hz, 1H), 6.99–7.09 (m, 2H), 7.12–7.14 (m, 1H), 7.30–7.35 (m, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ/ppm = 20.8, 20.8, 21.0, 62.1, 72.2, 73.3 (d, *J* = 1.8 Hz), 114.3 (d, *J* = 23.0 Hz), 116.0 (d, *J* = 20.0 Hz), 122.9 (d, *J* = 3.1 Hz), 130.5 (d, *J* = 8.3 Hz), 138.7 (d, *J* = 7.3 Hz), 163.0 (d, *J* = 246.9 Hz), 169.8, 170.0, 170.5.

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = –112.1.

HRMS: calcd for $C_{15}H_{17}FNaO_6^+$: 335.0901, found: 335.0912.

HPLC-conditions: IB, hexane:^{i}PrOH = 95:5, 0.5 mL/min, t_R = 16.0 (minor), 18.3 (major).

(1*S*,2*S*)-1,2,3-Propanetriol-1-(4-fluorophenyl)-1,2,3-triacetate (8f)

Synthesized according to the general procedure. Isolated yield: 27.5 mg (44%).

IR (ATR): ν/cm^{-1} = 2959, 1740, 1607, 1512, 1434, 1371, 1211, 1160, 1044, 961, 837, 788, 730, 689, 647, 603, 544, 501, 435.

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 2.05 (s, 3H), 2.05 (s, 3H), 2.08 (s, 3H), 3.80 (dd, *J* = 12.1, 5.8 Hz, 1H), 4.26 (dd, *J* = 12.1, 3.8 Hz, 1H), 5.40 (ddd, *J* = 7.1, 5.7, 3.7 Hz, 1H), 5.94 (d, *J* = 7.1 Hz, 1H), 7.02–7.08 (m, 2H), 7.32–7.37 (m, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ/ppm = 20.8, 20.9, 21.1, 62.2, 72.3, 73.3, 115.9 (d, *J* = 21.7 Hz), 129.2 (d, *J* = 8.4 Hz), 132.0 (d, *J* = 3.3 Hz), 163.0 (d, *J* = 248.4 Hz), 169.8, 170.1, 170.5.

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = –112.5.

HRMS: calcd for $C_{15}H_{17}FNaO_6^+$: 335.0901, found: 335.0900.

HPLC-conditions: IB, hexane:^{i}PrOH = 95:5, 0.5 mL/min, t_R = 16.6 (minor), 19.0 (major).

(1*S*,2*S*)-1,2,3-Propanetriol-1-(4-trifluoromethylphenyl)-1,2,3-triacetate (8g)

Synthesized according to the general procedure. Isolated yield of a 4:1 diastereomeric mixture: 47 mg (65%).

IR (ATR): ν/cm^{-1} = 2958, 1742, 1622, 1422, 1372, 1324, 1212, 1164, 1122, 1066, 1044, 1017, 962, 839, 765, 749, 697, 602, 531, 454, 432.

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 2.04 (s, 3H), 2.04 (s, 3H), 2.11 (s, 3H), 3.82 (dd, *J* = 12.2, 5.7 Hz, 1H), 4.30 (dd, *J* = 12.2, 4.2 Hz, 1H), 5.42 (ddd, *J* = 6.5, 5.8, 4.1 Hz, 1H), 6.00 (d, *J* = 6.6 Hz, 1H), 7.47–7.49 (m, 2H), 7.61–7.63 (m, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ/ppm = 20.8, 20.8, 21.0, 62.0, 72.0, 73.3, 123.9 (q, *J* = 272.6 Hz), 125.8 (q, *J* = 3.8 Hz), 127.6, 131.2 (q, *J* = 32.8 Hz), 140.2 (q, *J* = 1.3 Hz), 169.7, 169.9, 170.5.

^{19}F-NMR (282 MHz, $CDCl_3$): δ/ppm = – 62.9.

HRMS: calcd for $C_{16}H_{17}F_3NaO_6^+$: 385.0869, found: 385.0876.

HPLC-conditions: IB, hexane:^{i}PrOH = 95:5, 0.5 mL/min, t_R = 16.3 (minor), 26.8 (major).

(1*S*,2*S*)-3-methoxy-1-phenyl-1,2-propanediol-2-acetate (9a) and (1*S*,2*S*)-3-Methoxy-1-phenyl-1,2-propanediol-1-acetate (9b)

These compounds were synthesized according to the general procedure, but without acetoxylation using acetic anhydride. Separation by column chromatography from the corresponding bisacetate **8b** afforded the pure compound. Combined isolated yield: 27.8 mg (55%).

IR (ATR, both regioisomers): ν/cm^{-1} = 3455, 3033, 2927, 1737, 1495, 1453, 1372, 1231, 1197, 1127, 1081, 1025, 985, 952, 916, 871, 850, 762, 732, 701, 622, 540, 495, 448.

major regioisomer:

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 2.12 (s, 3H), 2.33 (bs, 1H), 3.17 (dd, *J* = 9.8, 5.6 Hz, 1H), 3.30–3.34 (m, 1H), 3.31 (s, 3H), 4.00 (ddd, *J* = 7.3, 5.6, 3.3 Hz, 1H), 5.84 (d, *J* = 7.5 Hz, 1H), 7.28–7.40 (m, 5H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ/ppm = 21.3, 59.3, 72.8, 73.3, 76.8, 127.3, 128.6, 128.7, 137.5, 170.4.

minor regioisomer:

^{1}H-NMR (400 MHz, $CDCl_3$): δ/ppm = 2.08 (s, 3H), 2.33 (bs, 1H), 3.33 (s, 3H), 3.38 (dd, *J* = 10.8, 4.1 Hz, 1H), 3.55 (dd, *J* = 10.7, 4.1 Hz, 1H), 5.00 (d, *J* = 5.9 Hz, 1H), 5.14 (ddd, *J* = 5.7, 4.4, 3.8 Hz, 1H), 7.28–7.40 (m, 5H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ/ppm = 21.2, 59.5, 71.7, 73.7, 75.9, 126.7, 128.3, 128.7, 140.2, 170.8.

HRMS, both regiosisomers: calcd for $C_{12}H_{16}NaO_4^+$:247.0946, found: 247.0941.

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Supporting Information

Supporting Information is provided as pdf and contains detailed description on the synthesis of chiral iodine reagents, X-ray data and reproduction of ^{1}H, ^{13}C and ^{19}F spectra of new products.

Primary Data

No.

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Biosketches

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