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Asymmetric synthesis of 1,2-fluorohydrin: iridium catalyzed hydrogenation of fluorinated allylic alcohol†

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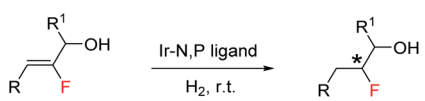
We have developed a simple protocol for the preparation of 1,2-fluorohydrin by asymmetric hydrogenation of fluorinated allylic alcohols using an efficient azabicyclo thiazole-phosphine iridium complex. The iridium-catalyzed asymmetric synthesis of chiral 1,2-fluorohydrin molecules was carried out at ambient temperature with operational simplicity, and scalability. This method was compatible with various aromatic, aliphatic, and heterocyclic fluorinated compounds as well as a variety of polyfluorinated compounds, providing the corresponding products in excellent yields and enantioselectivities.

Introduction

Despite the limited number of fluorinated natural products, the introduction of a fluorine atom into an organic molecule can have an immense impact in small molecule drug discovery.[1] Moreover, the stereocontrolled introduction of fluorine atoms into organic molecules can be expected to be the next chapter for the development of drugs possessing excellent bioactivity and bioavailability.[1b,c,e,2] However, current synthetic methodologies lack a waste-free and easy stereoselective approach for the construction of complex bioactive fluorinated molecules. Fluorohydrins[3] are well-known as an important subclass of organofluorine compounds. They serve as key intermediates in the synthesis of mono-fluorinated analogues for many bioactive compounds.[4] They are also used as derivatizing agents in determining enantiomeric composition by ^{19}F NMR spectroscopy.[5] Classic examples of drug molecules containing the 1,2-fluorohydrin substructure are fludrocortisone (the first fluorine-containing marketed drug);[6] anti-inflammatory corticosteroid diflupredate[7a–c] and antihepatitis C agent sofosbuvir.[7d] Along with steroid and nucleotide analogs a few alkaloid-derived fluorohydrins have also been reported.[7e] Nucleophilic opening of epoxides with various fluoride sources are one of the most reliable methods for fluorohydrin synthesis. The use of HF-based reagents (*e.g.*, Olah's reagent) as a fluoride source is particularly notable.[3b,8] Many of the existing methods for the synthesis of stereoselective fluorohydrins have economical or practical setbacks, often relating to the fluorinating agents. The lack of a general atom economical asymmetric process prompted us to devise a highly enantioselective synthetic method for the versatile generation of fluorohydrin molecules.

The asymmetric hydrogenation of olefins using iridium complexes without a coordinating group or a weakly coordinating group is one of the most fundamental and atom economical processes in synthetic organic chemistry.[9] For the trisubstituted olefins, the smallest substituent, which is hydrogen, determines which enantioface of the olefin preferentially coordinates to the Ir center. Since, H and F are both small substituents and almost of similar size, there is more than one possible orientation of the olefin for trisubstituted fluorinated allylic alcohols. This presents a significant challenge since it results in enantiomeric mixtures of the hydrogenated product.[10] Selectivity together with the frequent occurrence of defluorination (de-F) during hydrogenation and the electron-withdrawing property of fluorine makes trisubstituted fluorinated olefins an even more difficult substrate for hydrogenation.[11] Since olefins are inexpensive and widely available it led us to investigate the asymmetric hydrogenation of fluorinated allylic alcohols as a possible method to produce bio-relevant fluorohydrin compounds.[12] Recently, we reported the successful development of an efficient catalytic system for the enantioselective synthesis of fluorine motifs based on the highly selective hydrogenation of alkenyl fluorides.[10,12d,g] Our Ir-N,P



Scheme 1 Atom economical synthesis of asymmetric 1,2-fluorohydrin.

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† Electronic supplementary information (ESI) available: Experimental procedures, crystallography reports, and analytical data (PDF). CCDC 1976216 crystallographic data for **2n** (CIF). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0sc04032k

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catalyst was moderately successful for the asymmetric synthesis of fluorohydrins by hydrogenation, however it was limited to specific substrates[12a] or gave poor enantioselectivity with a high extent of de-F.[12b] With these limitations in mind, we set out to develop an efficient catalytic system for the atom economical asymmetric synthesis of fluorohydrins by hydrogenation of fluorinated allylic alcohols (Scheme 1).

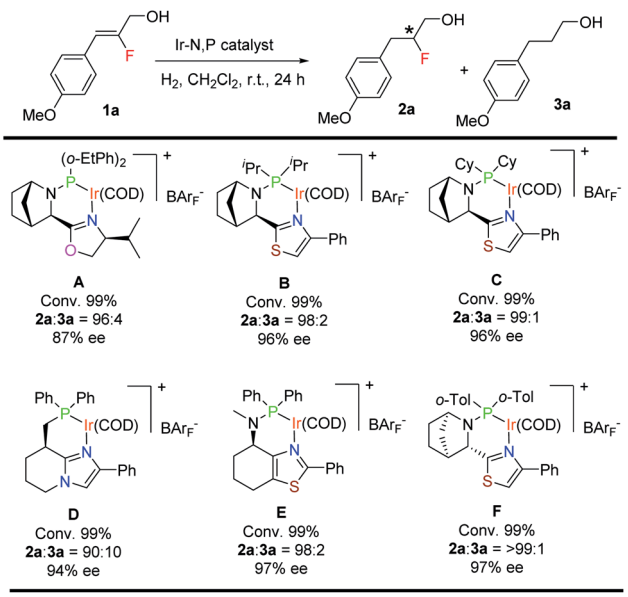
Results and discussion

For the asymmetric hydrogenation investigation reported here, we selected (*Z*)-2-fluoro-3-(4-methoxyphenyl)prop-2-en-1-ol (**1a**) as the model substrate and bicyclic oxazoline-*o*-Et-phenylphosphine iridium complex[12a] **A** as the catalyst using the following reaction conditions: 1 mol% catalyst, CH_2Cl_2, and 10 bar H_2. Substrate **1a** gave 99% conversion of the starting material along with slight de-F (4%) and very good enantioselectivity (87% ee) (Table 1). Catalysts having a thiazole backbone (catalyst **B** and catalyst **C**) led to an improved enantioselectivity of 96% ee with very minute de-F (1–2%). Further optimization of the heterocycle skeleton of the N,P-iridium complex involved changing thiazole to imidazole (catalyst **D**) which provided a comparable result but with 10% de-F. Catalyst **E** which was superior in our previous study[12a] on asymmetric hydrogenation of fluorinated allylic alcohol gave 97% ee with 2% de-F (more details, see: ESI†). We finally evaluated the effect of the substituent on phosphorous and replaced the two cyclohexyl groups with *ortho*-tolyl groups (catalyst **F**) and obtained the best result for **1a**: 99% conversion with excellent enantioselectivity (97%) and <1% of the de-F by-product.

Having successfully found a new effective catalyst containing a bicyclic thiazole backbone with *o*-tolyl substituents on phosphorus **F**, we carried out further optimization of the solvent, catalyst loading and hydrogen pressure (Table 2). Solvent screening with CH_2Cl_2, DCE and $PhCF_3$ proved that CH_2Cl_2 was the best in terms of reactivity, enantioselectivity and de-fluorination. When the H_2 pressure decreased from 10 bar (entry 1) to 4 bar (entry 4) using 1.0 mol% of catalyst **F** for 24 hours, conversion was not affected but de-F increased slightly to 2%. A decrease in the catalyst loading at 10 bar of H_2 pressure for substrate **1a** from 1.0 mol% (entry 1) to 0.5 mol% (entry 5) also increased the de-F to 4%. Hence, for substrate **1a** the optimal conditions for full conversion, good enantioselectivity and minimal de-F are a catalyst loading of 1.0 mol% (catalyst **F**) and 10 bar H_2 pressure for 24 hours (entry 1). It should be noted that almost no de-F product (<1%) was observed as a side reaction which is a recurring problem in hydrogenations of alkenyl fluorides.[11b]

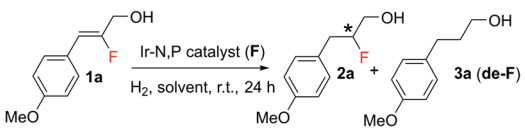
With the optimized reaction conditions established, we evaluated the hydrogenation of variously substituted (*Z*)-2-fluoro-3-phenylprop-2-en-1-ols **1** (Table 3). A variety of fluorinated allylic

Table 1 Evaluation of N,P-iridium catalysts in the asymmetric hydrogenation of **1a**[a]



[a] Reaction conditions: 0.05 mmol of **1a**, 1 mol% catalyst, 0.5 mL CH_2Cl_2, 10 bar H_2. Conversion was determined by ^{1}H-NMR spectroscopy. Enantiomeric excess was determined by SFC.

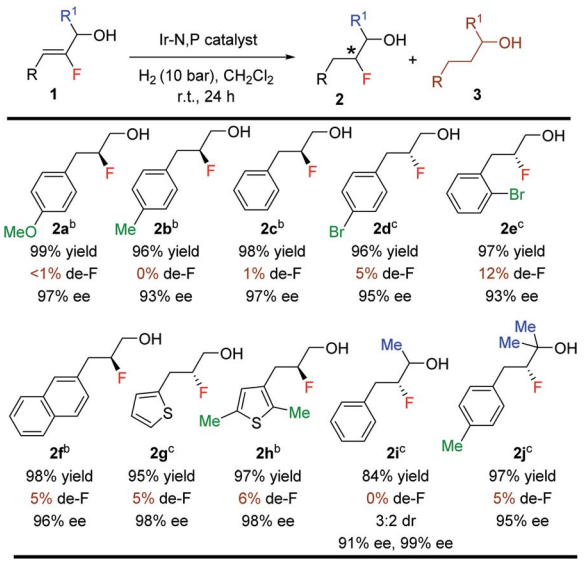
Table 2 Optimization of hydrogenation of vinyl fluoride **1a**[a]



Entry	Solvent	H_2 (bar)	Catalyst (mol%)	Conversion (%)	de-F (%)	ee (%)
1	CH_2Cl_2	10	1.0	99	<1	97
2	DCE	10	1.0	99	3	97
3	$PhCF_3$	10	1.0	98	3	97
4	CH_2Cl_2	4	1.0	99	2	97
5	CH_2Cl_2	10	0.5	99	4	97

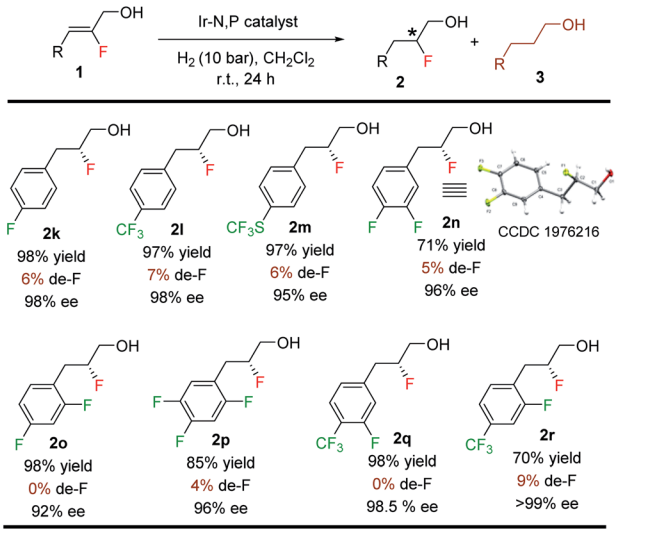
[a] Reaction conditions: 0.05 mmol of **1a**, 0.5 mL solvent. Conversion was determined by ^{1}H-NMR spectroscopy. Enantiomeric excess was determined by SFC.

Table 3 Hydrogenation of various fluorinated allylic alcohols[a]



[a] Reaction conditions: 0.25 mmol of substrate, 1 mol% catalyst, 2.0 mL CH_2Cl_2. [b] Catalyst **F**. [c] Catalyst ***ent*-F**. Yields are isolated hydrogenated product. Enantiomeric excess was determined by SFC or GC/MS using chiral stationary phases.

Table 4 Hydrogenation of various polyfluorinated allylic alcohols[a]



[a] Reaction conditions: 0.25 mmol of substrate, 1 mol% of catalyst ***ent*-F**, 2.0 mL CH_2Cl_2. Yields are isolated hydrogenated product. Enantiomeric excess was determined by SFC or GC/MS using chiral stationary phases.

alcohols were successfully hydrogenated to generate the desired products **2a–2e** in excellent yields and enantioselectivities. The (*Z*)-2-fluoro-3-phenylprop-2-en-1-ol substrates with either electron-donating or electron-withdrawing substituents at the *para* or *ortho* position of the aryl rings provided the desired products in high isolated yields (96–99%) and excellent enantioselectivities (93–97% ee). Replacing the phenyl group with 2-naphthyl or a heterocyclic (thienyl) substituent also yielded the desired products (**2f–2h**) in excellent yields (95–98%) and ees (96–98%). Next, we examined the secondary and tertiary vinyl-F alcohols and as expected, all gave satisfactory results. Again, very low de-F (0–12%) was observed in all examples, which underlines the effectiveness of this catalytic method.

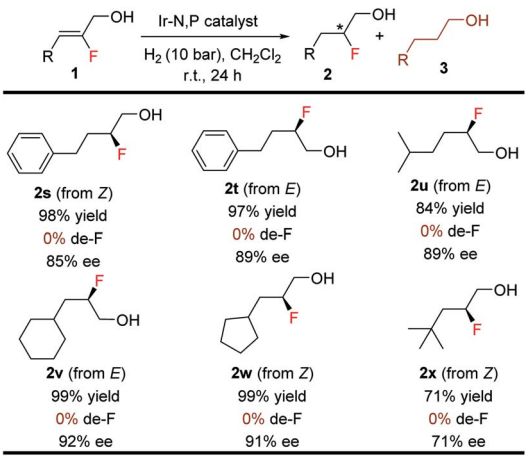
Since de-F during hydrogenation of alkenyl fluorides presents potential challenges,[11] various polyfluorinated allylic alcohols were hydrogenated under standard conditions (Table 4). For all examples, irrespective of the position of the fluorine or the trifluoromethyl substituent on the aromatic ring, we observed only traces of de-F products (0–9%) along with high yields (70–99%) and enantioselectivities (95–>99% ee) for the polyfluorinated 1,2-fluorohydrins.

The efficacy of this stereoselective 1,2-fluorohydrin synthesis was investigated by evaluating various aliphatic fluorinated allylic alcohols (Table 5). Gratifyingly, a number of aliphatic fluorinated allylic alcohols (**1s–1x**) were also efficiently hydrogenated in good to excellent yields (71–99%) with high enantioselectivities (71–92% ee). Interestingly, both isomers (*E* & *Z*) of 2-fluoro-4-phenylbut-2-en-1-ol were hydrogenated with excellent results. Various acyclic and cyclic primary, secondary, and tertiary aliphatic substituents afforded the anticipated product (**2s–2x**) without generating any problematic de-F.

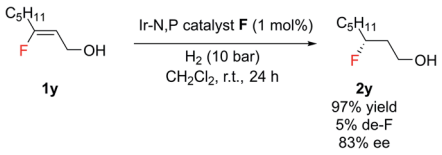
Notably, this method was amenable for (*Z*)-3-fluorooct-2-en-1-ol **1y**. The hydrogenated product **2y** was obtained in good ee (83%), where the chiral center containing fluorine is at the β position to the CH_2OH group (Scheme 2).

A preparative-scale production of chiral fluorohydrin under these reaction conditions was also carried out. Starting with 1.0 g of allylic alcohol **1c** and using 0.5 mol% of catalyst **F** under 10 bar H_2, the desired fluorohydrin **2c** was obtained in excellent 97% yield with 97% ee (Scheme 3).

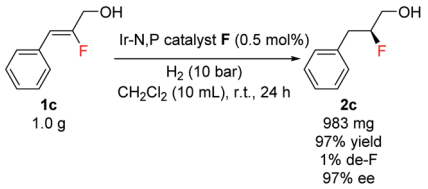
Table 5 Hydrogenation of various aliphatic fluorinated allylic alcohols[a]



[a] Reaction conditions: 0.25 mmol of substrate, 1 mol% catalyst **F**, 2.0 mL CH_2Cl_2. Yields are isolated hydrogenated product. Enantiomeric excess was determined by HPLC or GC/MS using chiral stationary phases.

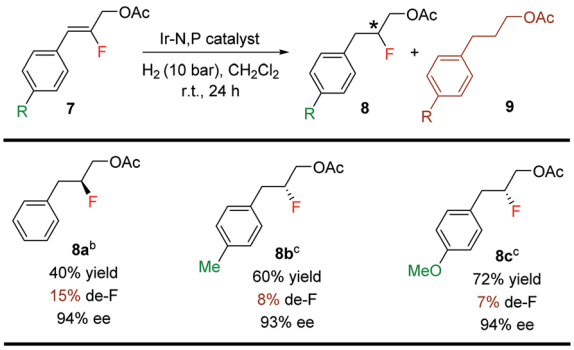


Scheme 2 Hydrogenation of (*Z*)-3-fluorooct-2-en-1-ol.



Scheme 3 Gram-scale production of chiral fluorohydrin.

Table 6 Hydrogenation of fluorinated allylic acetates[a]



[a] Reaction conditions: 0.25 mmol of substrate, 1 mol% catalyst, 2.0 mL CH_2Cl_2. [b] Catalyst **F**. [c] Catalyst ***ent*-F**. Yields are isolated hydrogenated product. Enantiomeric excess was determined by SFC or GC/MS using chiral stationary phases.

The enantioenriched 1,2-fluorohydrins can be transformed into a variety of many useful chiral fluorinated derivatives: acid **4**, aldehyde **5**, and sulfamate **6** were all obtained without any loss in enantiopurity (Scheme 4). The synthetic intermediate (*S*)-2-fluoro-3-phenylpropyl sulfamate **6** could be a potential key precursor for the synthesis of dapoxetine[13] analogs, a useful selective serotonin reuptake inhibitor (SSRI).

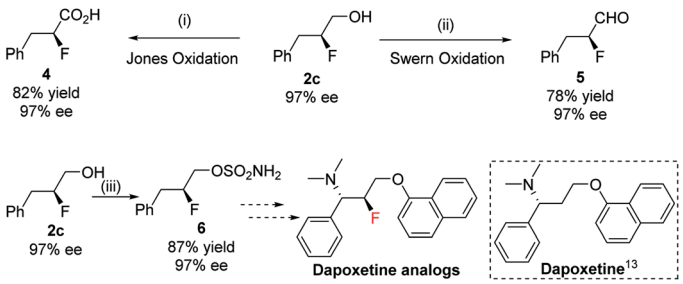
The Ir-complex (**F**) having the bicyclic thiazole backbone with *o*-tolyl substituents on phosphorus was also effective for fluorinated allylic acetates (**8a–8c**) (Table 6), giving good yields (40–72%) and enantioselectivities (93–94% ee), although at a higher level of defluorination.

Steric interactions between the olefin and the N,P-iridium catalyst controls the enantioselectivity of iridium-catalyzed asymmetric hydrogenations.[14,15] A quadrant model was developed[14] using catalyst **F** to explain the enantioselectivity and is similar to our earlier observations.[10] The Ir-N,P ligand (**F**) was positioned as depicted in Scheme 5a, with the iridium atom at the center of the four quadrants (Scheme 5b). The olefin (fluorinated allylic alcohol) coordinates vertically *trans* to phosphorus (Scheme 5c). The phenyl group on the thiazole moiety points outwards, making quadrant iii sterically hindered. One of the *o*-tolyl groups on the phosphorus atom also points slightly outwards, making quadrant ii the semi-hindered quadrant. Since quadrants i and iv do not experience obstructions from the ligand, they are considered open quadrants.

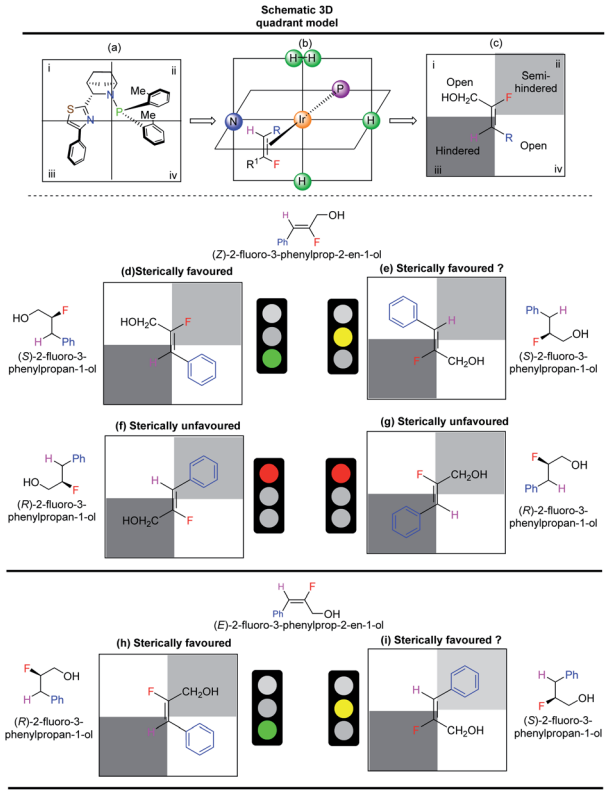
When the trisubstituted (*Z*)-fluoro alcohol **1c** is placed *trans* to phosphorus, such that the smallest substituent (H) occupies the hindered quadrant iii and the other small substituent (F) occupies the semi-hindered quadrant ii, this results in a favored arrangement (Scheme 5d). Since the H and F atoms are of similar size, another sterically favorable possible arrangement is to place fluorine in the sterically hindered quadrant iii (Scheme 5e). The two other possible arrangements are sterically not favored (Scheme 5f and g). Thus, based on the quadrant model, both sterically favored orientations of fluoro alcohol **1c** result in hydrogenation from the same face of the olefin. The predicted absolute configuration of hydrogenated product **2c** is *S*, which is in agreement as measured by the single crystal X-ray structure of similar compound **2n**.

The quadrant model also explains the lower enantioselectivity of the *E*-isomer of aromatic allylic alcohol. For (*E*)-fluoro alcohol **1c′**, the two sterically favored orientations (Scheme 5h and i) feature coordination from opposite faces, which results in the formation of a mixture of the *R* and *S* products.

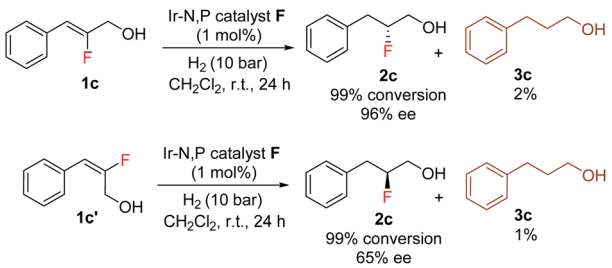
The enantioselectivity predictions using the quadrant model are in good agreement with the experimental results (Scheme 6) as the (*Z*)-fluoro alcohol **1c** provided product **2c** with high enantioselectivity (97% ee) while the *E* isomer gave the corresponding product **2c** in only 65% ee.



Scheme 4 Synthesis of chiral fluorine molecule having different functional groups. Conditions: (i) CrO_3, H_2SO_4, H_2O, acetone, 1 h, 0 °C; (ii) $(COCl)_2$, DMSO, TEA, 2 h, −78 to 0 °C; (iii) $ClSO_2NCO$, HCOOH, 0 °C – r.t.



Scheme 5 Determination of absolute configuration of olefin **1c** using catalyst **F**. (a–c) General fluorinated allylic alcohol in the selectivity model of the ligand; (d–g) four different products obtained by different possible coordination of *Z* isomer; (h and i) two different products obtained by different possible coordination of *E* isomer.



Scheme 6 Hydrogenation of both the *Z* and *E* isomer of vinyl fluoride olefin **1c**.

Conclusions

In summary, we have developed a general and efficient catalyst for the stereoselective synthesis of various fluorohydrins, which complements previous catalytic asymmetric syntheses of 1,2 fluorohydrins. This method is straightforward and also suppresses the problem of defluorination. The catalyst has been used effectively on various aromatic and aliphatic trisubstituted fluorinated allylic alcohols, providing chiral 1,2 fluorohydrins in excellent yields and enantioselectivities.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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