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One-Pot Cascade Hydration–Asymmetric Transfer Hydrogenation as a Practical Strategy to Construct Chiral β-Adrenergic Receptor Blockers

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The facile construction of biologically active β-adrenergic receptor agonists/blockers and analogues is a great fundamental and practical challenge in medical chemistry. Herein, we report a hydration–asymmetric transfer hydrogenation cascade to realize the one-pot enantioselective transformation of aromatic haloalkynes into chiral aromatic halohydrins, which can be converted readily into chiral β-adrenergicreceptor blockers. Such a one-pot cascade process involves the Au-catalyzed hydration of aryl-substituted haloalkynes to aryl-substituted α-halomethyl ketones and the Ru-catalyzed asymmetric transfer hydrogenation of aryl-substituted α-halomethyl ketones to aryl-substituted 2-haloethanols. The significant benefits of this procedure are that it provides chiral aromatic halohydrins in high yields, with excellent enantioselectivities, and a wide variety of functional groups are tolerated under mild conditions. The study described herein offers a useful approach to construct chiral β-adrenergic blockers, which is an attractive practical organic transformation that is performed in a one-pot manner.

Optically pure halohydrins, especially aryl-substituted 2-haloethanols as important synthetic motifs, have attracted great interest in medical chemistry.[1] Great achievements through the utilization of aryl-substituted 2-haloethanols as building blocks are well documented, as these building blocks can be readily converted into various β-adrenergic receptor agonists and blockers.[2] As shown in Figure 1, some prominent examples, such as nifenalol[2a,b] and pronethalol,[2b] are important medicines as β-adrenergic receptor blockers, whereas metaproterenol[2c] and fenoterol[2d] are β-adrenergic receptor agonists. Generally, the construction of aryl-substituted 2-haloethanols can be performed through two single-step reactions, in which hydration of haloalkynes gives α-halomethyl ketones and asymmetric transformation of the α-halomethyl ketones provides 2-haloethanols. Owing to the demands of atom economy and minimal workup procedures, the facile construction of aryl-substituted 2-haloethanols followed by their transformation into biologically active β-adrenergic receptor agonists or blockers is highly desirable.

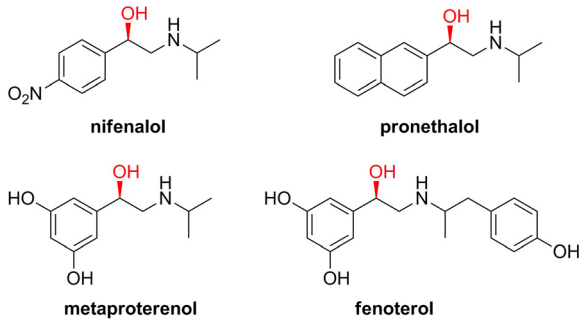

Figure 1. Important medicines prepared from aryl-substituted 2-haloethanols.

One-pot cascade reactions are atom economical, and they are well known to construct various valuable compounds with minimum isolation/purification processes.[3] As two classical reactions for the construction of aryl-substituted 2-haloethanols, the hydration of α-haloalkynes to 2-haloketones[4] and the asymmetric transfer hydrogenation (ATH) of 2-haloketones to chiral 2-haloethanols[5] have been extensively studied theoretically and practically. However, the one-pot direct transformation of alkynes into alcohols through a cascade process is still an unmet challenge,[6] and this can be mainly ascribed to complicated conflicts derived from intrinsic bimetallic incompatibility and extrinsic reaction conditions. So far, only one successful example of the one-pot enantioselective transformation of alkynes into chiral alcohols reported by Xiao's group has been realized, and the formic acid mediated alkyne-to-ketone transformation is performed with a subsequent enantio-relay-catalyzed ATH reaction to chiral alcohols (Scheme 1).[6a] However, this one-pot transformation of alkynes into alcohols is a two-step procedure. Clear drawbacks are that the first formic acid mediated alkyne-to-ketone transformation needs a high temperature (100 °C) to reach its hydrated completion, whereas the second ATH reaction must be controlled through adjustable pH values and an additional chiral catalyst. Notably, conflict of extrinsic reaction conditions and the incompatible nature of the chiral catalyst require the employment of a two-step procedure. Furthermore, the inherent nature of this one-pot transformation is intolerant to functional groups on the substrates, and haloalkynes cannot be converted into chiral halo alcohols. This limitation greatly hinders the practical application of this procedure for the construction of biologically active β-adrenergic receptor agonists or blockers. Thus, the development of

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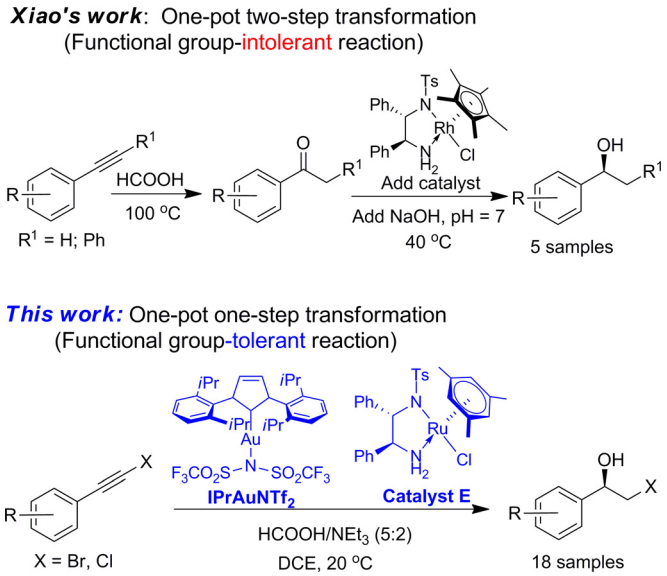


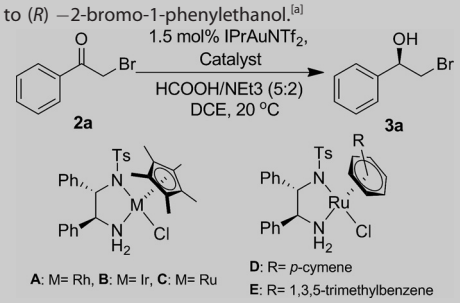
Scheme 1. One-pot organic transformation of alkynes into alcohols.

a one-pot, one-step cascade hydration–ATH reaction to overcome the intolerance of the substrate is of great fundamental and practical interest for the construction of chiral β-adrenergic receptor agonists or blockers from achiral haloalkynes.

To obtain compatible reaction conditions for the one-pot, one-step cascade hydration–ATH reaction of aromatic haloalkynes (Scheme 1) on the basis of our previous exploration in asymmetric catalysis,[7] two single-step catalytic reactions, the hydration of (bromoethynyl)benzene to 2-bromophenylethanone and the ATH reaction of 2-bromophenylethanone to (*R*)-2-bromophenylethanol, were investigated separately. In the first hydration reaction, owing to its air stability we used the highly efficient [2,5-bis(2,6-diisopropylphenyl)cyclopent-3-en-1-yl]{1,1,1-trifluoro-*N*-[(trifluoromethyl)sulfonyl]methylsulfonamido}gold ($IPrAuNTf_2$[8]) catalyst reported for the hydration of haloalkynes.[8a,b] Because of compatible considerations for the second ATH step, we systemically optimized the reaction conditions for the first hydration step[8a] through the addition of four common hydrogen sources ($HCOOH/NEt_3$, $HCOONa/H_2O$, *i*PrOH, and HCOOH) that are often employed in ATH reaction systems. In this process, the first hydration reaction step was performed through the use of 1,2-dichloroethane (DCE) as the solvent and with the hydrogen sources as additives in separate experiments; the mixtures were stirred at 20 °C for a certain amount of time in a parallel manner. With the use of the $HCOOH/NEt_3$ (5:2) azeotropic mixture and HCOOH as additives, enhanced yields (from 85%[8a] to more than 99%) were observed, and they were attributed possibly to acid-promoted acceleration of the reaction.[9] However, the use of HCOOH as an additive did not result in a chiral product in the second ATH reaction. Thus, the $HCOOH/NEt_3$ (5:2) azeotropic mixture was determined to be the optimal compatible solvent and the hydrogen source for the second ATH reaction. To our delight, in this case, the amount of $IPrAuNTf_2$ in the first hydration step could be halved (from 3.0 to 1.5 mol%) and quantitative hydration was still obtained.

In the case of the second ATH reaction step, we utilized the above optimal reaction conditions and screened the extensively studied Cp*M[(*S*,*S*)-TsDPEN] series **A**–**C** [η^5-Cp* = pentamethylcyclopentadiene; M = Ru, Rh, Ir; TsDPEN = *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine] and the areneRuTsDPEN series **D** and **E** (η^6-arene = *p*-cymene, 1,3,5-trimethylbenzene).[10,5d,j,k] In this optimization of the catalyst, the ATH reaction of 2-bromophenylethanone to (*R*)-2-bromophenylethanol was performed in the presence of the $IPrAuNTf_2$ (1.5 mol%) complex. As shown in Table 1, catalyst **E** produced the target (*R*)-2-bromophenylethanol product with the highest enantiomeric excess (*ee*) value in quantitative yield (Table 1, entry 5). Such an *ee* value was markedly better than those obtained with the Cp*MTsDPEN series (Table 1, entries 1–3) and slightly higher than that obtained with cymeneRuTsDPEN (Table 1, entry 4). Thereby, areneRuTsDPEN complex **E** (arene = 1,3,5-trimethylbenzene) was identified as the optimal catalyst for the second reaction.

Table 1. Optimization of catalysts for the ATH reaction of 2-bromoacetophenone to (*R*) −2-bromo-1-phenylethanol.[a]

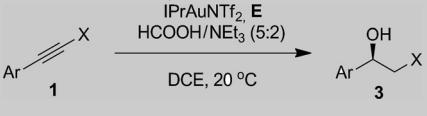


Entry	Catalyst	*t* [h]	Yield [%][b]	*ee* [%][c]
1	**A**	6	95	94
2	**B**	6	95	82
3	**C**	6	96	70
4	**D**	4	96	97
5	**E**	4	99	98

[a] Reactions were performed with 2-bromoacetophenone (0.30 mmol), water (0.90 mmol), $HCOOH/NEt_3$ (5:2, 0.75 mL, 9.0 mmol), $IPrAuNTf_2$ (4.50 μmol, 3.89 mg), and **E** (4.50 μmol, 2.80 mg) in DCE (3.0 mL) at 20 °C. [b] Yield of isolated product. [c] Determined by HPLC with a Daicel Chiralcel OD-H column.

Finally, the combination of both catalysts, $IPrAuNTf_2$ and **E**, in a one-pot cascade hydration–ATH process was explored. As expected, both $IPrAuNTf_2$ and **E** enabled the highly efficient hydration–ATH of (bromoethynyl)benzene; (*R*)-2-bromophenylethanol was afforded in 93% yield and the *ee* value was retained (Table 2, entry 1). To confirm that areneRuTsDPEN (**E**) was the optimal catalyst for the cascade reaction, the other three hydrogen sources ($HCOONa/H_2O$, *i*PrOH, and HCOOH) instead of the $HCOOH/NEt_3$ (5:2) azeotropic mixture were investigated under the same conditions. The cascade reaction with $HCOONa/H_2O$ as the hydrogen source did not occur, whereas that with *i*PrOH as the hydrogen source only gave (*R*)-2-bromophenylethanol in 42% yield with a very poor *ee* value. As pre-

Table 2. One-pot cascade hydration–ATH reactions of aromatic haloalkynes to chiral aromatic halohydrins.[a]



Entry	1	X	Ar	Yield [%][b]	*ee* [%][c]
1	**1a**	Br	Ph	93	98
2	**1b**	Br	4-MeC_6H_4	87	97
3	**1c**	Br	4-$MeOC_6H_4$	83	98
4	**1d**	Br	4-FC_6H_4	89	99
5	**1e**	Br	4-ClC_6H_4	90	98
6	**1f**	Br	4-BrC_6H_4	88	97
7	**1g**	Br	4-$O_2NC_6H_4$	81	95
8	**1h**	Br	4-$F_3CC_6H_4$	82	93
9	**1i**	Br	3-FC_6H_4	86	99
10	**1j**	Br	3-ClC_6H_4	89	95
11	**1k**	Br	3-BrC_6H_4	92	99
12	**1l**	Br	3,4-$Cl_2C_6H_3$	90	95
13	**1m**	Br	2-thienyl	92	99
14	**1n**	Br	2-naphthyl	78	97
15	**1o**	Cl	Ph	89	99
16	**1p**	Cl	4-FC_6H_4	94	97
17	**1q**	Cl	4-ClC_6H_4	92	98
18	**1r**	Cl	3,4-$F_2C_6H_3$	92	97

[a] Reactions were performed with haloalkyne (0.30 mmol), water (0.90 mmol), $HCOOH/NEt_3$ (5:2, 0.75 mL 9.0 mmol), $IPrAuNTf_2$ (4.50 μmol, 3.89 mg), and **E** (4.50 μmol, 2.80 mg) in DCE (3.0 mL) at 20 °C for 14 h. [b] Yield of isolated product. [c] Determined by HPLC with a Daicel Chiralcel OD-H, OJ-H, OB-H, or AS-H column.

sented in Xiao's report,[6a] the reaction with HCOOH as the hydrogen source afforded 2-bromophenylethanone in 98% yield as the intermediate; however, no target product was obtained. Notably, the cascade reaction in this case could be driven to completion to give the target (*R*)-2-bromophenylethanol product in 92% yield with 98% *ee* through adjustment of the pH value (pH 8.0) of the mixture by adding aqueous sodium hydroxide and by prolonging the reduction time; this suggests the benefit of this one-pot, one-step cascade hydration–ATH reaction. As a comprehensive result, the one-pot enantioselective cascade reaction with $IPrAuNTf_2$ (1.5 mol%) and areneRuTsDPEN (**E**, 1.5 mol%) as catalysts, $HCOOH/NEt_3$ (5:2) as the hydrogen source, and DCE as the solvent performed at 20 °C was determined as a compatible reaction system. More interestingly, in sharp contrast to Xiao's one-pot, two-step process, this one-pot, one-step cascade hydration–ATH reaction is also suitable for the substrates examined by Xiao, for which a representative substrate, ethynylbenzene, was converted smoothly into (*R*)-1-phenylethanol in 95% yield with 97% *ee*, which confirmed the superiority of this cascade hydration–ATH reaction.

Having established a clean cascade hydration–ATH reaction of (bromoethynyl)benzene to (*R*)-2-bromophenylethanol, the reaction time course was explored. As shown in Figure 2, the hydration of (bromoethynyl)benzene (**A**) proceeds fast with concomitant formation of 2-bromophenylethanone (**B**) in a maximum yield of 33%. Subsequently, the ATH reaction of 2-bromophenylethanone occurs quickly for the point at which

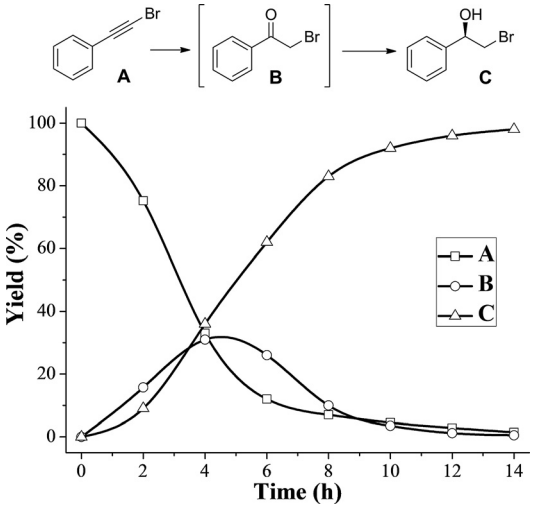


Figure 2. Time course of the transformation of (bromoethynyl)benzene into (*R*)-2-bromophenylethanone. Reactions were performed with (bromoethynyl)benzene (1 equiv.), $IPrAuNTf_2$ (1.5 mol%), **E** (1.5 mol%), and $HCOOH/NEt_3$ (5:2, 30 equiv.) at 20 °C.

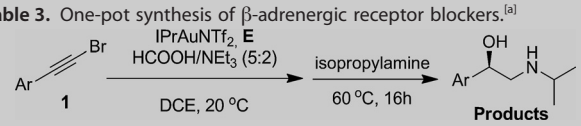
the maximum amount of **B** is produced to provide the target (*R*)-2-bromophenylethanone (**C**) product. Evidence to support this reaction time course came from a comparison of the two single-step reaction times and the cascade reaction time, for which the hydration of (bromoethynyl)benzene (**A**) to 2-bromophenylethanone (**B**) required 14 h and the ATH reaction of 2-bromophenylethanone (**B**) reached completion to (*R*)-2-bromophenylethanone within 4 h in two single-step reactions, whereas the total reaction time in the cascade hydration–ATH reaction was 14 h.

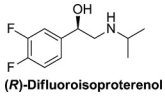
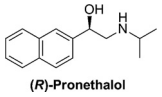
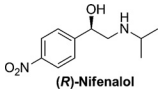
On the basis of this clean cascade hydration–ATH reaction, one-pot transformations of aryl-substituted haloalkynes into chiral aryl-substituted 2-haloethanols were investigated to test the general applicability of this procedure with a series of substrates. As shown in Table 2, in general, high yields and excellent enantioselectivities were obtained for all of the tested substrates. Also, the structures and electronic properties of substituents at the 3- and 4-positions of the Ar group did not affect significantly the enantioselectivities, and various electron-withdrawing and electron-donating substituents on the Ar group were equally efficient (Table 2, entries 2–12). Moreover, substrates bearing thienyl and naphthyl groups, 2-(bromoethynyl)thiophene (**1m**) and 2-(bromoethynyl)naphthalene (**1n**), were also converted smoothly into the corresponding bromohydrins in high yields with excellent enantioselectivities (Table 2, entries 13 and 14).

In addition to aromatic bromoalkynes, this cascade hydration–ATH reaction was also expanded to the one-pot transformations of aryl-substituted chloroalkynes; four representative aryl-substituted chloroalkynes were obtained successfully in high yields with excellent enantioselectivities (Table 2, entries 15–18). All these results indicate that this cascade hydration–ATH reaction could serve as a general approach to construct various optically pure halohydrins.

An important aim of this cascade hydration–ATH reaction was to realize the efficient preparation of biologically active

Table 3. One-pot synthesis of β-adrenergic receptor blockers.[a]



Entry	Product	Yield [%][b]	*ee* [%][c]
1	 (*R*)-Difluoroisoproterenol	86	99
2	 (*R*)-Pronethalol	71	99
3	 (*R*)-Nifenalol	78	99

[a] Reactions were performed with haloalkyne (0.30 mmol), water (0.90 mmol), $HCOOH/NEt_3$ (5:2, 0.75 mL 9.0 mmol), $IPrAuNTf_2$ (4.50 μmol, 3.89 mg), and **E** (4.50 μmol, 2.80 mg) in DCE (3.0 mL) at 20 °C for 14 h. After that, isopropylamine (53.10 mg, 0.90 mmol) was added, and the mixture was allowed to react at 60 °C for 16 h. [b] Yield of isolated product. [c] Determined by HPLC with a Daicel Chiralcel IC or AD-H column.

molecules that could be applied to the synthesis of β-adrenergic receptor blockers.[2b] As shown in Table 3, three chiral β-adrenergic receptor blockers, (*R*)-difluoroisoproterenol, (*R*)-nifenalol, and (*R*)-pronethalol, were readily synthesized in acceptable total yields with excellent enantioselectivities in a one-pot process involving the cascade hydration–ATH reaction followed by amination (a sequential reaction with isopropylamine). To demonstrate the practicality of this one-pot process, a gram-scale synthesis of (*R*)-difluoroisoproterenol was performed; the cascade hydration–ATH reaction of 4-(bromoethynyl)-1,2-difluorobenzene (**1 r**, 10.0 mmol) followed by reaction of the resulting halohydrin with isopropylamine (1.2 equiv.) gave (*R*)-difluoroisoproterenol in a total yield of 86% with 99% *ee*.[11]

In conclusion, through screening of compatible reaction conditions under which two organometallic complexes participate in a cascade process, we developed a one-pot, one-step cascade hydration–asymmetric transfer hydrogenation (ATH) reaction. As presented in this study, the cascade reaction involving the Au-catalyzed hydration of aryl-substituted haloalkynes to α-halomethyl ketones and the Ru-catalyzed ATH conversion of aryl-substituted α-halomethyl ketones into 2-haloethanols allowed the efficient construction of various aromatic halohydrins with up to 99% enantioselectivity under mild reaction conditions. Furthermore, taking use of the benefit of this cascade hydration–ATH reaction, we prepared three biologically active β-adrenergic receptor agonists through a one-pot sequential hydration–ATH and amination reaction to afford desirable chiral medicines in acceptable yields with excellent enantioselectivities. The study described herein offers an interesting approach for the practical construction of various biologically active molecules.

Acknowledgements

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Keywords: asymmetric catalysis · domino reactions · halohydrins · hydration · transfer hydrogenation

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