Asymmetric Catalysis

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Stereoarrayed CF_3-Substituted 1,3-Diols by Dynamic Kinetic Resolution: Ruthenium(II)-Catalyzed Asymmetric Transfer Hydrogenation

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Abstract: *CF_3-substituted 1,3-diols were stereoselectively prepared in excellent enantiopurity and high yield from CF_3-substituted diketones by using an ansa-ruthenium(II)-catalyzed asymmetric transfer hydrogenation in formic acid/triethylamine. The intermediate mono-reduced alcohol was also obtained in very high enantiopurity by applying milder reaction conditions. In particular, $CF_3C(O)$-substituted benzofused cyclic ketones underwent either a single or a double dynamic kinetic resolution during their reduction.*

Progress towards advanced asymmetric synthetic methodologies broadens the access to diversified fluorine-containing chiral structures with novel properties.[1] For example, the side-chain of the selective monoamine oxidase A inhibitor, befloxatone, features a stereogenic α-trifluoromethyl hydroxymethyl moiety,[2a] and an α-trifluoromethyl 1,3-glycolyl stereotriad is embedded in an intermediate of the NMR molecular probe, ^{19}F-labeled bafilomycin A_1, a vacuolar-type ATPase inhibitor[2b] (Figure 1). The stereoarrangement in befloxatone allows formation of strong hydrogen bonds between the hydroxy group and the enzyme active site, hence increasing the desirable interaction versus that of the nonfluorinated isosteric analogue. Indeed, alcohols having a CF_3 substituent in close proximity to the hydroxy function possess an enhanced Brønsted acid character owing to the characteristic electron-withdrawing property of perfluoroalkyl chains. An ensuing potential application of these fluorine-containing alcohols would be as organocatalysts in organic transformations or as ligands in coordination chemistry.[3] In particular, CF_3-substituted 1,3-diols could offer an interesting opportunity, however a literature search revealed very few known related compounds in optically active form.[4] Clearly, the access to such enantiopure diols is still a challenge and it has prompted our interest in this research area.

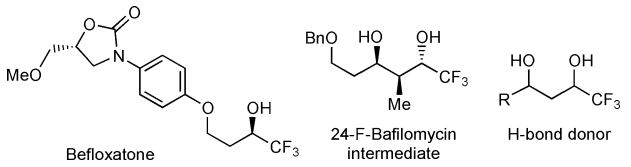

Figure 1. Examples of chiral CF_3-substituted alcohols.

Highlighted in 2006 was our report on the efficient access to α-substituted α-fluoroalkyl carbinols (monoalcohols) by asymmetric transfer hydrogenation (ATH) of the corresponding ketones using HCO_2H/Et_3N mixtures.[5] Our first-generation Noyori-type chiral ATH catalysts (**A**; $[Ru^{II}(R_2NSO_2DPEN)(\eta^6\text{-arene})]$; $R_2NSO_2DPEN = (S,S)$- or (R,R)-*N*-(dialkylsulfamoyl)-1,2-diphenylethylenediamine; Figure 2) enabled the preparation, at 25 °C, of fluorinated alcohols in high enantiomeric excesses (94–99 %) and yields (> 98 %) by employing a substrate/catalyst molar ratio (S/C) of 200. Moreover, our recently developed second- and third-generation ansa-Ru^{II}-type complexes (**B**, **C**, and **D**) proved to be very effective in the ATH of diaryl diketones.[6]

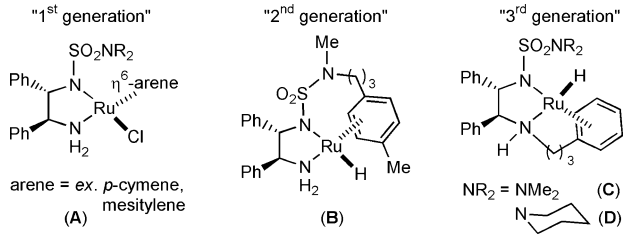

Figure 2. Enantiopure *N*-R_2NSO_2-[(*S*,*S*)-DPEN]-based ruthenium(II) complexes.

Hereafter, we present our investigation results on the preparation of CF_3-substituted 1,3-diols by employing **B** and **D**, which incorporate respectively enantiopure DPEN-SO_2N-(Me)$(CH_2)_3(\eta^6$-Tol) and piperidino-SO_2DPEN-$(CH_2)_3(\eta^6$-Ph) conjugate ligands. The advantage of these advanced ruthenium(II) catalyst designs resides in their enhanced activity and longevity over that of the first-generation. They are generated in situ from the shelf-stable μ-chlorido ruthenium(II) dimers upon treatment with the HCO_2H/Et_3N medium.

Readily prepared in high yields by Claisen condensation of the aryl ketone with ethyl trifluoroacetate, the basic test substrate 4,4,4-trifluoro-1-phenyl-1,3-butanedione (**1a**) was subjected to ATH in HCO_2H/Et_3N (5:2) using **D**. Because of

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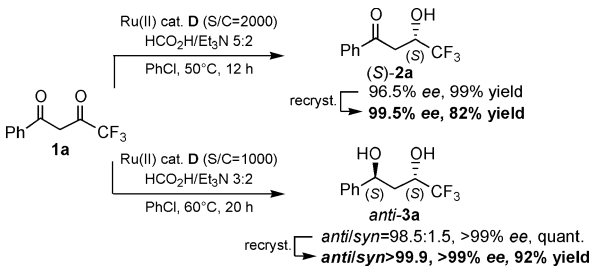
the dissymmetry of this activated 1,3-diketone, the reduction to either the monoalcohol (*S*)-**2a** or diol *anti*-**3a** was deemed possible (Scheme 1). Both catalyst loading (S/C = 2000) and



Scheme 1. The ansa-Ru^{II}-catalyzed ATH of 4,4,4-trifluoro-1-phenyl-1,3-butanedione (**1a**).

temperature (50 °C) proved to be crucial for the complete regioselectivity and high enantioselectivity (up to 96.5 % *ee* attained) for the $CF_3C(O)$ reduction. (*S*)-4,4,4-Trifluoro-3-hydroxy-1-phenylbutan-1-one [(*S*)-**2a**] was isolated in 99.5 % *ee* and 82 % yield after recrystallization from heptane/toluene.[7] Applying a S/C = 1000 in HCO_2H/Et_3N (3:2) at 60 °C, 4,4,4-trifluoro-1-phenylbutan-1,3-diol (**3a**) was quantitatively formed in a 98.5:1.5 *anti*/*syn* ratio and with 99 % *ee* [*anti*-(*S*,*S*)]. Recrystallization from hexane/EtOAc led to the stereopure diol. Noteworthy, (*R*)-**2a** was prepared in 93 % *ee* by a copper(I)-catalyzed asymmetric cross-coupling of 3-oxo-3-phenylpropionic acid with the hazardous CF_3CHN_2,[8] while an enzymatic resolution-based multistep synthesis provided (*R*)-**2a** and *anti*-**3a** in 92 % *ee* and 96 % *de* (*S*,*S*), respectively.[4a] Nevertheless, to the best of our knowledge no metal-catalyzed asymmetric reduction has been described so far for such diketones.

As suggested by Noyori et al.[9] and by us[5a] for aryl ketones and trifluoromethyl ketones, respectively, the stereochemical control is enforced by either a stabilizing CH–π or CH–F attractive electrostatic interaction. In the present case, the CH–F interaction overrides the CH–π interaction in the first step, thus leading to the intermediate formation of (*S*)-**2a** on the way to *anti*-**3a** (Figure 3).

Investigating different media for this reduction versus neat HCO_2H/Et_3N revealed the beneficial use of a cosolvent, such as PhCl, EtOAc, or 1,2-dichloroethane, and HCO_2H/Et_3N (3:2) as the hydrogen donor (for details see the Supporting Information).

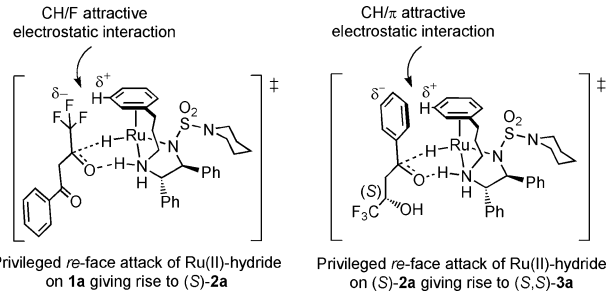
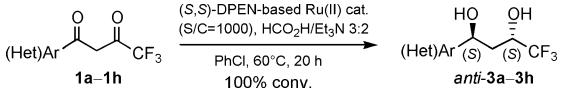


Figure 3. Proposed transition states of the two-step ATH of **1a** with **D**.

Accordingly, a series of 4,4,4-trifluoro-1-(het)aryl-1,3-butanediones (**1b–h**) was screened for this transformation (Table 1). The corresponding diols *anti*-**3b–h** were obtained in

Table 1: The ansa-Ru^{II}-catalyzed ATH of various 4,4,4-trifluoro-1-(het)aryl-1,3-butanediones (**1**).[a]



(Het)Ar	Cat.	*anti*/*syn*[b]	*ee* [%][b]
Ph (**1a**)	**B**	97:3	98
Ph (**1a**)	**D**	98.5:1.5 (>99.9)	99 (>99.9)
o-HO-Ph (**1b**)[c]	**D**	98.5:1.5 (>99.9)	>99 (>99.9)
p-MeO-Ph (**1c**)	**D**	98.5:1.5 (>99.9)	99 (>99.9)
p-Cl-Ph (**1d**)	**D**	98:2 (>99.9)	>99 (>99.9)
1-Naph (**1e**)	**B**	98:2	98.5
1-Naph (**1e**)	**D**	98.5:1.5 (>99.9)	97 (>99.9)
2-Naph (**1f**)	**D**	98.5:1.5 (>99.9)	>99 (>99.9)
2-Furyl (**1g**)	**D**	99:1 (>99.9)	>99 (>99.9)
2-Thienyl (**1h**)	**D**	99:1 (>99.9)	>99.9 (>99.9)

[a] ATH of **1** (1 mmol) was carried out in PhCl (1 mL) with the ruthenium(II) catalyst (S/C = 1000 for **D** and S/C = 100 for **B**) using HCO_2H/Et_3N 3:2 (0.5 mL). Conversion (100 %) and *anti*/*syn* ratio were determined by ^{19}F NMR spectroscopy, and the *ee* values were determined by chiral-phase HPLC or GC. Yields of isolated product ranged between 95 and 99 %. [b] The *anti*/*syn* ratio and *ee* values given within parentheses were obtained after recrystallization. [c] Reaction using HCO_2H/Et_3N (5:2; 0.5 mL) at 50 °C. ^{19}F NMR spectroscopy indicated formation of a side-product in 5 mol %.

> 99.9 % *ee* and high yields (95–99 %) upon isolation. The tabulated results demonstrate the tolerance of aromatic ring substituents (electron rich or electron poor). The *o*-hydroxyphenyl diketone **1b** necessitated, for optimum results, the use of HCO_2H/Et_3N (5:2) at 50 °C because a slightly lower *anti*/*syn* ratio (97:3) and a higher amount of side-products (12 %) resulted otherwise. Selected diketones (**1e** and **1h**) were reduced as was **1a** to the monoalcohols [(*S*)-**2e** and (*S*)-**2h**}] which were formed in high enantioselectivity (≥ 97 % *ee*) and virtually quantitative yield.[10] A facile single recrystallization afforded the stereopure carbinols (*S*)-**2**.

What precedes clearly demonstrates the new practical and simple access to a large variety of unknown CF_3-substituted 1,3-glycols in high stereopurity by applying the present ansa-Ru^{II}-catalyzed asymmetric reduction.

To explore the substrate scope, we shifted to more rigid 1,3-diketones such as α-$CF_3C(O)$-substituted benzofused five- to seven-membered cyclic ketones (**1i–t**). These ketones are based on 1-indanone, α-tetralone, (thio-) chroman-4-one,

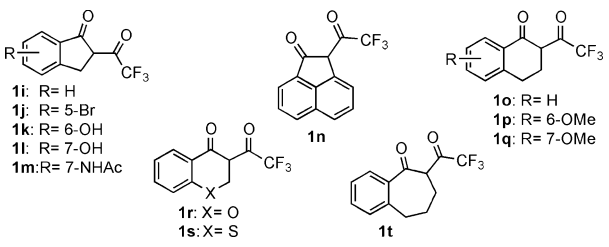
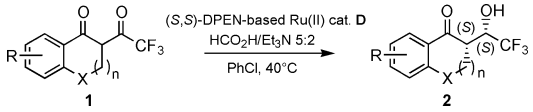


Table 2: The **D**-catalyzed ATH of selected benzofused cyclic ketones **1** to the monoalcohols **2**.[a]

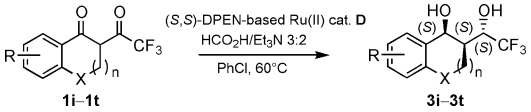


1 **2**

			2[b]			**2**[c]	
1	S/C	*t* [h]	d.r.	*ee* [%]	Yield [%]	d.r.	*ee* [%]
1i	2000	26	96:4	97.5	90	>99:9	99.5
1j	2000	26	96:4	97.5	92	>99:1	>99.9
1l	1000[d]	15	97:3	>99.9	84	>99:1	>99.9
1m	2000	30	98:2	>99	88	>99:1	>99.9
1o	1000	20	89:11	72	70	>99:1	>99
1s	2000	20	86:14	75	51	99:1	64

[a] ATH of **1** (1.0 mmol) was carried out at 40 °C in PhCl (1 mL) using **D** with HCO_2H/Et_3N (5:2; 0.5 mL). 100% conversion. Yields of isolated products ranged between 94 and 100%. Conversion and d.r. values were determined by ^{19}F NMR spectroscopy. The *ee* values were determined by chiral-phase HPLC. [b] Crude reaction mixture. [c] After recrystallization. [d] EtOAc (1 mL) was used as cosolvent.

Table 3: The **D**-catalyzed ATH of benzofused cyclic ketones **1** to the diols **3**.[a]



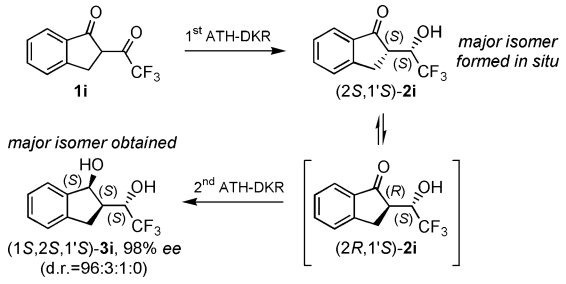
1i–1t **3i–3t**

1	S/C	*t* [h]	Conv. [%]	d.r.	*ee* [%][b]
1i	1000	24	100	96:3:1:0	98 (>99.9)
1j	1000	24	100	97:3:0:0	>99 (>99.9)
1k	1000	24	100	91:7:2:0	99.5
1k	1000[c]	24	100	95:4:1:0	99.5
1l	1000	24	95	74:18:5:3	96.5
1l	500[c]	24	>99	96:2:2:0	>99.9
1m	500	24	100	97:3:0:0	98.5 (>99.9)
1n	1000	18	100	6:3:91:0	99.5
1o	1000	24	100	0:92:7:1	>99.9
1p	500	24	>99	0:96:1:3	>99.9
1q	1000	24	95	0:93:7:0	>99.9
1r	100	2.5	100[f]	0:95:5:0	>99.9
1s	1000	24	100	2:86:10:3	>99.9
1t	500	18	100	10:90:0:0	73

[a] ATH of **1** (1.0 mmol) was carried out at 60 °C in PhCl (1 mL) using **D** with HCO_2H/Et_3N (3:2; 0.5 mL). Conversions and d.r. values were determined by ^{19}F NMR spectroscopy. The *ee* values of the major diastereomer were determined by chiral-phase HPLC and the d.r. values correspond to the ratios of the four signals, going in an upfield direction, corresponding to the diastereomers. Yields of isolated products were 1–4% lower than conversion. [b] The *ee* values within parentheses were obtained after recrystallization (d.r. >99.9 for all). [c] EtOAc used as a cosolvent. [f] ^{19}F NMR spectroscopy indicated the formation of side-products in 23 mol%.

and 1-suberone. A dynamic kinetic resolution (DKR) was expected to occur in these cases.[11] Thus, the reduction was conducted at 40 °C by employing **D** with a S/C = 2000 in HCO_2H/Et_3N (5:2) and PhCl as cosolvent (Table 2). To favor the formation of the diol **3**, the reaction temperature was increased to 60 °C and a higher catalyst loading was used (Table 3).

Interestingly, racemic 2-trifluoroacetyl-1-indanone (**1i**) was reduced quantitatively to the corresponding monoalcohol **2i** with a d.r. value of 96:4 [97.5% *ee* for (2*S*,1′*S*)-**2i**; Scheme 2], hence validating the occurrence of a DKR. The absolute configuration was assigned by analogy to that of (2*S**,1′*S**)-**2s** as determined by X-ray analysis.[12] This stereochemistry can be rationalized by the attack of the ruthenium(II) hydride on the $CF_3C(O)$ *re*-face, and formation of the equilibrium mixture wherein (2*S*,1′*S*)-**2i** is predominant. Notably, heating the stereopure (2*S*,1′*S*)-**2i** at 40 °C in a mixture of HCO_2H/Et_3N (5:2) and PhCl, in the absence of **D** resulted in a 96:4 mixture of (2*S*,1′*S*)-**2i** and (2*R*,1′*S*)-**2i**. This d.r. value was attained within 25 minutes and remained constant after several days of heating, while in HCO_2H/Et_3N (3:2) and PhCl the same equilibrium was established within 10 minutes at 40 °C. A d.r. value of 94:6 resulted from heating at 60 °C.



Scheme 2. Consecutive ATH/DKRs of 2-trifluoroacetyl-1-indanone (**1i**) using **D** at 60 °C.

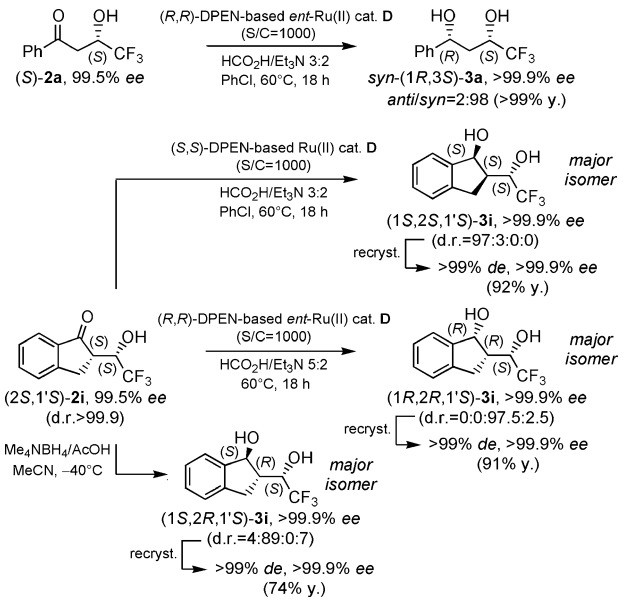
Though the ATH of the 7-OH-substituted **1l** or the 7-NHAc-substituted **1m** led to high diastereo- and enantioselectivities, the former performed better with a higher catalyst loading (S/C = 1000) and with EtOAc as a cosolvent. Also, five-membered benzofused cyclic ketones (**1i–m**) afforded better results than their six-membered homologues (**1o** and **1s**). Here as well, recrystallization of the 1-indanone-derived monoalcohol allowed isolation of the stereopure compounds (2*S*,1′*S*)-**2**.

When targeting diols (**3**) with the three contiguous stereocenters, the formation of 2^3 stereoisomers are theoretically possible. However, we were delighted to confirm by ^{19}F NMR spectroscopy the formation in all cases of one major diastereomer (86–97% yield) in greater than or equal to 99% *ee*, except for the seven-membered cyclic compound **1t**, which led to a product with only 73% *ee* (Table 3). The indicated d.r. value corresponds to the ratios of the four ^{19}F NMR signals, going in an upfield direction, corresponding to the diastereomers. X-ray analyses of **3j** and **3s** revealed their (1*S*,2*S*,1′*S*) absolute configuration.[12] This data demonstrates the manifestation of a second DKR whereby the methine configuration (in the cycle) of **2** en route to **3** is inverted (Scheme 2 for **3i**).[13]

The created stereochemistry at the benzylic carbon (C1) is governed by the handedness of **D** (see Figure 3), while the C2 configuration is impacted by outwards orientation of the peripheral $CH(OH)CF_3$ group, thus minimizing the steric interference in the second transition state.

The ATH of **1k** and **1l** needed EtOAc as a cosolvent to achieve the maximum diastereo- and enantioselectivities, and the latter required a higher catalyst loading (S/C = 500) for complete conversion (for a comprehensive study see the Supporting Information). Here as well, the five-membered benzofused cyclic ketones (**1i–n**) outperformed their six-membered cyclic higher homologues (**1o–t**). And for the 4-chromanone-derived substrate **1r**, minimizing the side-product formation necessitated the use of S/C = 100.

Moreover, access to the complementary *syn* diols *syn*-**3** was demonstrated on two representative cases starting from the stereopure monoalcohols **2** and resorting to the antipode *ent*-**D** for the ATH of the aroyl function (Scheme 3). Thus, the



Scheme 3. Access to the complementary *syn*-diols *syn*-**3a** and *syn*-**3i** by switching to *ent*-**D** for the ATH of the aroyl function (the second reduction step) and diastereoselective reduction using Me_4NBH_4/AcOH.

acyclic (*S*)-**2a** and the cyclic (2*S*,1′*S*)-**2i** β-hydroxy-ketones afforded the stereoisomers (1*R*,3*S*)-**3a** [*anti*/*syn* = 2:98, > 99.9 % *ee* (*syn*)] and (1*R*,2*R*,1′*S*)-**3i** [d.r. = 0:0:97.5:2.5, > 99.9 % *ee* (major)], respectively. Interestingly, (1*S*,2*R*,1′*S*)-**3i** [> 99 % *de*, > 99.9 % *ee*] was accessed by Me_4NBH_4/AcOH reduction in MeCN at −40 °C and subsequent recrystallization from $CHCl_3$/hexane. Their absolute configurations were confirmed by X-ray analysis.[12] Note that in contrast to the double ATH/DKR of **1i** employing either **D** or *ent*-**D**, the methine configuration (in the cycle) of **2i** en route to **3i** is not inverted in these steps.

Finally, the ATH (S/C = 2000) of **1i** on a 10 gram scale led successfully to (2*S*,1′*S*)-**2i** in 99.5 % *ee* and 92 % yield after a single recrystallization from cyclohexane. Also, the ATH of (2*S*,1′*S*)-**2i** on a 4 gram scale using **D** and *ent*-**D** yielded the corresponding diastereomeric diols (1*S*,2*S*,1′*S*)-**3i** (d.r. = 96.5:3:0.5:0; > 99.9 % *ee*) and (1*R*,2*R*,1′*S*)-**3i** (d.r. = 0:0:97.5:2.5; > 99.9 % *ee*), and upon recrystallization the stereopure compound was obtained.

In conclusion, we have presented a new, efficient, and practical ansa-Ru^{II}-catalyzed enantio- and diastereoselective ATH to the carbinols **2** and **3**. The latter are formed by an unprecedented double ATH/DKR in the case of $CF_3C(O)$-substituted benzofused cyclic ketones. The present methodology definitely expands and enriches the area of fluorine research, and the generated compounds, having excellent enantiopurity, may be further elaborated to increase molecular complexity.

Acknowledgments

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Keywords: alcohols · asymmetric catalysis · enantioselectivity · kinetic resolution · ruthenium

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[13] Notably, taking however into account the relative group priorities according to the CIP stereochemistry rules, an *S* absolute configuration for the methine of the cycle is encountered in both compounds.

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