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Asymmetric Transfer Hydrogenation of (Hetero)arylketones with Tethered Rh(III)−*N*-(*p*-Tolylsulfonyl)-1,2-diphenylethylene-1,2-diamine Complexes: Scope and Limitations

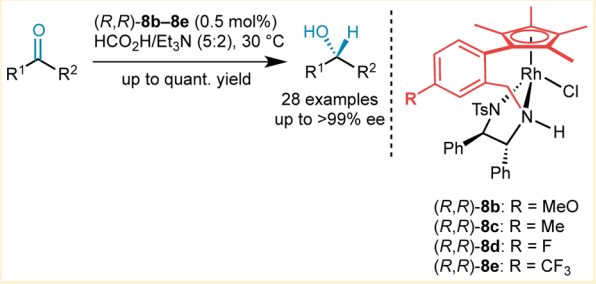
Long-Sheng Zheng,[†] Quentin Llopis,[†] Pierre-Georges Echeverria,[†] Charlène Férard,[†] Gérard Guillamot,[‡] Phannarath Phansavath,*[,†] and Virginie Ratovelomanana-Vidal*[,†]

[†]Institut de Recherche de Chimie Paris, PSL Research University, Chimie ParisTech-CNRS, 75005 Paris, France

[‡]PCAS, 23 rue Bossuet, Z.I. de la vigne aux Loups, 91160 Longjumeau, France

Supporting Information

ABSTRACT: A series of new tethered Rh(III)/Cp* complexes containing the *N*-(*p*-tolylsulfonyl)-1,2-diphenylethylene-1,2-diamine ligand have been prepared, characterized, and evaluated in the asymmetric transfer hydrogenation (ATH) of a wide range of (hetero)aryl ketones. The reaction was performed under mild conditions with the formic acid/triethylamine (5:2) system as the hydrogen source and provided enantiomerically enriched alcohols with good yields and high to excellent enantioselectivities. Although the nature of the substituents on the phenyl tethering ring did not alter the stereochemical outcome of the reaction, complexes bearing electron-donating groups exhibited a higher catalytic activity than those having electron-withdrawing groups. A scale-up of the ATH of 4-chromanone to the gram scale quantitatively delivered the reduced product with excellent enantioselectivity, demonstrating the potential usefulness of these new complexes.



INTRODUCTION

Because enantiomerically pure alcohols are important synthetic building blocks in the manufacturing of pharmaceuticals, flavors, and fragrances, significant efforts have been made to develop efficient and atom-economical stereoselective processes for the synthesis of these compounds.[1] In this area, transition-metal-catalyzed asymmetric transfer hydrogenation (ATH) is one of the most powerful and useful methods for the generation of enantiomerically enriched secondary alcohols from the corresponding prochiral ketones, owing not only to its high performance in terms of activity and selectivity, but also to its operational simplicity.[2] Moreover, a variety of convenient, safe, and inexpensive non-H_2 hydrogen sources can be used for this reaction, typically 2-propanol, formic acid/triethylamine mixtures, or formate salts. Since the seminal report in 1995 by Noyori and Ikariya of the [RuCl(η^6-arene)(*N*-TsDPEN)] complexes **1**[3] (named Noyori catalysts; TsDPEN = *N*-(*p*-tosylsulfonyl)-1,2-diphenylethylene-1,2-diamine), ruthenium-based catalysts have been widely used in the ATH of ketones and imines (Figure 1). Rhodium and iridium derivatives **2** and **3**, respectively, bearing Cp* as a ligand in place of the benzene ring were also studied and successfully employed for these transformations.[1a,2h,4] Numerous investigations aimed at diversifying the ligands were undertaken to achieve more efficient catalytic performances, and various derivatives of the Noyori catalysts have been reported.[2] Notably, Wills et al. introduced a series of ruthenium complexes **4** and **5** bearing a tether between the η^6-arene and the diamine unit,[5] and developed the isoelectronic Rh(III) derivatives **6**,[6] **7**,[7] and **8a**,[8] which proved effective for the asymmetric catalytic reduction of imines and functionalized ketones.

As part of our ongoing studies toward the development of efficient catalysts for the asymmetric reduction of unsaturated compounds,[9] we reported the synthesis and catalytic performances of the rhodium(III)−TsDPEN-based tethered catalyst **8b** bearing a methoxy group on the tethering phenyl ring (Figure 1).

This new complex showed a good catalytic behavior in the asymmetric transfer hydrogenation of ketones[10] and α-amino β-keto ester hydrochlorides.[11] Following these initial reports, we now describe herein the synthesis, characterization, and evaluation of the novel Rh−TsDPEN-based tethered complexes **8c**−**8e** having electron-donating methyl and electron-withdrawing fluorine and trifluoromethyl substituents, respectively, on the 2-benzyl tether (Figure 1). To evaluate the electronic effect of the 2-benzyl tether substituent on the catalytic performance of the resulting complexes, a complete comparative study of the Wills complex **8a**[8] and complexes **8b**−**8e** in the ATH of a wide range of aromatic ketones is disclosed.

RESULTS AND DISCUSSION

Novel complexes (*R*,*R*)-**8b**−**8e** were prepared from commercially available 2-bromo-5-methoxybenzaldehyde (**9**), 2-bromo-5-methylbenzaldehyde (**10**), 2-bromo-5-fluorobenzaldehyde

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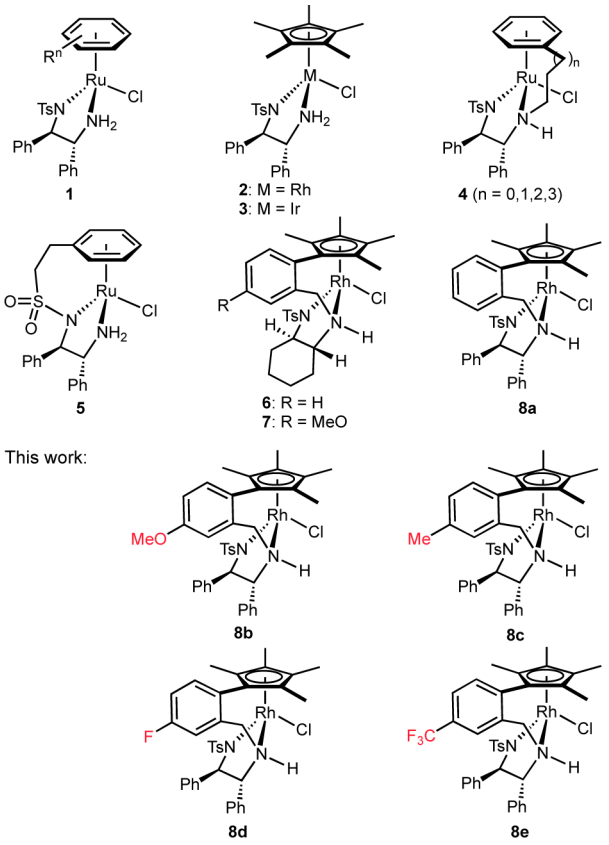
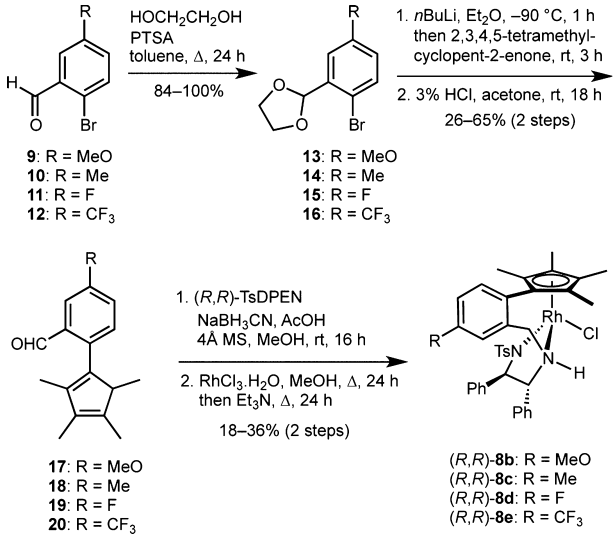


Figure 1. Transition-metal complexes used in ATH.

(**11**), and 2-bromo-5-(trifluoromethyl)benzaldehyde (**12**), which were protected as their 1,3-dioxolane derivatives **13**–**16** (Scheme 1).

Scheme 1. Synthesis of Complexes (*R*,*R*)-8b–8e



Treatment of these compounds with *n*-BuLi followed by addition of 2,3,4,5-tetramethylcyclopent-2-enone furnished the corresponding alcohols, which were then subjected to 3% hydrochloric acid in acetone. The latter conditions led to both deprotection of the aldehyde function and dehydration of the tertiary alcohol, providing compounds **17**–**20**. Subsequent reductive amination using (*R*,*R*)-TsDPEN in the presence of sodium cyanoborohydride then delivered the corresponding diamines, and the targeted complexes (*R*,*R*)-**8b**–**8e** were obtained through heating the latter in refluxing methanol in the presence of rhodium(III) chloride followed by treatment with triethylamine. The four complexes were isolated after flash chromatography as orange solids and as single diastereomers, whereas their structures were confirmed by X-ray crystallographic analysis in the case of (*R*,*R*)-**8b**, (*R*,*R*)-**8c**, and (*R*,*R*)-**8d** (Figures 2–4).[12]

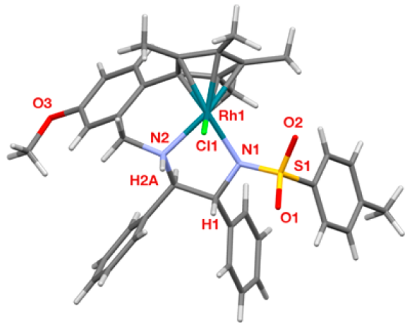


Figure 2. X-ray structure of complex (*R*,*R*)-**8b**.[12]

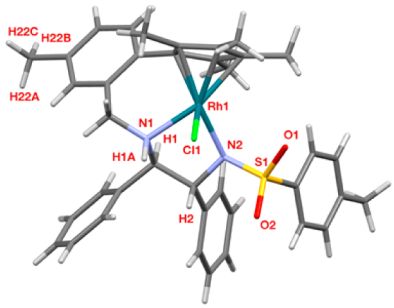


Figure 3. X-ray structure of complex (*R*,*R*)-**8c**.[12]

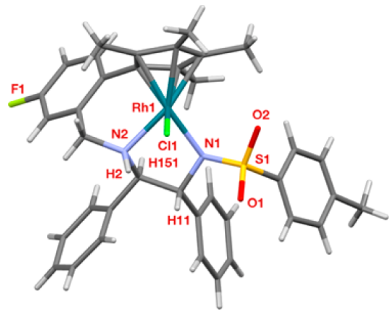


Figure 4. X-ray structure of complex (*R*,*R*)-**8d**.[12]

Evaluation of these complexes started with the ATH of acetophenone as the standard substrate using (*R*,*R*)-**8b** in combination with various hydrogen donor systems (Table 1). The reaction was carried out at 24–30 °C with 0.5 mol % of (*R*,*R*)-**8b**. A comparison of various hydrogen donor sources highlighted the choice of a formic acid/triethylamine (5:2) system in preference to sodium hypophosphite, ammonium formate, or an *i*-PrOH/*t*-BuOK system. Indeed, in the presence of a formic acid/triethylamine (5:2) system, a full conversion was attained within 5 h, and the reduced compound, (*R*)-1-phenylethanol, was obtained with a very high enantiomeric excess of 98% (entry 1). On the other hand, in the presence of sodium hypophosphite, the conversion dramatically decreased to

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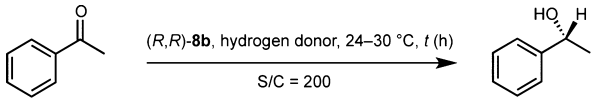
Table 1. Optimization of the Reaction Conditions for the ATH of Acetophenone with (*R*,*R*)-8b[a]



entry	hydrogen donor	*t* (h)	conversion[b] (%)	ee[c] (%)
1	HCO_2H/Et_3N (5:2)[d]	5	100	98
2	$NaH_2PO_2{\cdot}H_2O$[e]	29	7	
3	HCO_2NH_4[f]	29	53	98
4	*i*-PrOH/*t*-BuOK[g]	29		

[a]Reaction conditions: acetophenone (126 μL, 1.08 mmol), (*R*,*R*)-**8b** (4 mg, 0.0054 mmol). [b]Determined by ^{1}H NMR of the crude product. [c]Determined by HPLC analysis. [d]A 580 μL volume of HCO_2H/Et_3N (5:2). [e]$NaH_2PO_2{\cdot}H_2O$ (2.7 mmol), THF used as a solvent. [f]HCO_2NH_4 (2.4 mmol), CH_2Cl_2 used as a solvent. [g]*i*-PrOH (0.026 mmol) in *t*-BuOK (11 mL).

7% (entry 2). In the same manner, an unsatisfactory conversion of 53% was observed with ammonium formate (entry 3). Upon using the *i*-PrOH/*t*-BuOK system as the reducing agent, only degradation products were formed (entry 4). Finally, the optimized reaction conditions for the ATH of acetophenone with (*R*,*R*)-**8b** were set as follows: 0.5 mol % concentration of tethered Rh complex (*R*,*R*)-**8b** in neat HCO_2H/Et_3N (5:2) at 24−30 °C. With this optimized set of conditions in hand, and to establish the scope and limitations of the (*R*,*R*)-**8b**−**8e**-catalyzed ATH reaction, a series of aryl ketones were first examined (Table 2). A comparison with the rhodium complex (*R*,*R*)-**8a**[8] was carried out as well. It should be noted that, with the exception of four substrates (entries 1, 3, 10, and 11) indicated in Table 2, none of the ketones described in this paper have been previously reduced using the Wills complex (*R*,*R*)-**8a** so that the range of ketones has been consistently expanded in this comparative study.

Acetophenone underwent a faster reduction with (*R*,*R*)-**8b** and (*R*,*R*)-**8c** than with the other parent complexes (*R*,*R*)-**8a**, (*R*,*R*)-**8d**, and (*R*,*R*)-**8e**, excellent yields and enantioselectivities being observed in all cases (entry 1). The ATH of propiophenone proceeded similarly except for (*R*,*R*)-**8e**, which failed to afford complete conversion even after a prolonged reaction time of 96 h, and with a significantly higher catalytic activity observed for complexes (*R*,*R*)-**8b** and (*R*,*R*)-**8c**, which gave full conversions in only 6 h as compared to 22 h with (*R*,*R*)-**8a** (entry 2). On the other hand, 2-chloroacetophenone was readily reduced with all five complexes with ee values ranging from 95% to >99% (entry 3). The catalytic reduction of acetophenones bearing substituents in the para or meta positions of the phenyl ring led to high levels of stereoselectivity as well (entries 4−7), with a higher catalytic activity observed with (*R*,*R*)-**8b** and (*R*,*R*)-**8c** (entries 4 and 5), whereas complex (*R*,*R*)-**8e** led only to 62−64% conversions after 100−110 h of reaction for 4-(benzyloxy)acetophenone and 3,5-dimethoxyacetophenone (entries 6 and 7). In contrast, lower enantiofacial discriminations were observed for aryl ketones possessing an ortho substituent as for 2-bromoacetophenone (entry 8, 64−71% ee) and 1-acetonaphthone (entry 10, 78−85% ee). In both instances, compared to complex (*R*,*R*)-**8a**, slightly higher ee values could be attained with complexes (*R*,*R*)-**8b**, (*R*,*R*)-**8c**, and (*R*,*R*)-**8d** (entries 8 and 10). Whereas fair enantioselectivities were reached within a short reaction time for 4-nitroacetophenone (88% ee, entry 9), polycyclic aryl ketones afforded uniformly high enantioinductions with ee values ranging from 92% to >99% (entries 11−16). A gram-scale ATH of 4-chromanone was also carried out with complex (*R*,*R*)-**8b** under the standard conditions and furnished quantitatively the desired (*R*)-chroman-4-ol with the same enantiomeric purity (>99% ee, cf. entry 14).

Additionally, we studied the ATH of a highly electron-rich aryl ketone bearing a morpholine substituent in the para position. Although this challenging family of substrates was recently efficiently reduced through ATH with tethered ruthenium−TsDPEN catalysts,[13] no example of catalytic reduction with a rhodium catalyst has been reported to our knowledge. The use of complexes (*R*,*R*)-**8a** and (*R*,*R*)-**8b** under the defined standard conditions smoothly afforded the desired reduced compound in quantitative yield and with an excellent enantiopurity (entry 17). It appears from this survey that complexes (*R*,*R*)-**8a**−**8e** exhibited comparable stereoselectivities, providing the corresponding alcohols with mainly high enantioselectivities for para- and meta-substituted ketones (ee values up to >99%), whereas lower enantioinductions were observed for the ortho-substituted compounds. Of note, a lower catalytic activity was displayed by complex (*R*,*R*)-**8e**, possessing an electron-withdrawing trifluoromethyl substituent, which generally required longer reaction times.

To test the substrate scope further, we next explored the (*R*,*R*)-**8a**−**8e**-mediated ATH of heteroaryl and alkyl ketones (Table 3). The former compounds underwent the catalytic reduction in good yields, with systematically high asymmetric inductions observed with all the examined tethered Rh(III)/Cp* complexes, for (*R*)-1-(2-furyl)ethanol, (*R*)-1-(2-thienyl)ethanol, (1*R*)-1-(benzofuran-2-yl)ethanol, and (*R*)-1-(2-pyridyl)ethanol (entries 1−4). With regard to nonaromatic ketones, β-tetralone yielded moderate ee values (80−83%, entry 5), whereas high stereoselectivities were obtained for the ATH of acetylcyclohexane (entry 6, 93−95% ee), albeit lower ee values of 84 and 87% were respectively observed using parent tethered rhodium complexes.[6,7]

In addition, because the catalytic asymmetric reduction of unsymmetrical benzophenones has been less investigated,[14] we were keen to evaluate the catalytic performance of our new complexes in the ATH of these more challenging substrates wherein a catalyst has to discriminate structural differences in the two aromatic moieties (Scheme 2). Interestingly, the tethered Rh−TsDPEN complexes (*R*,*R*)-**8a** and (*R*,*R*)-**8b** operated efficiently under the standard reaction conditions, and 4-nitrobenzophenone underwent the ATH with satisfactory enantiomeric excesses of 84% and 83%, respectively (Scheme 2). On the other hand, the asymmetric transfer hydrogenation proceeded with low enantioinductions for 4-chlorobenzophenone and 4-methoxybenzophenone. Unsurprisingly, the highest stereoselectivity was observed with the ortho-substituted substrate 2-methylbenzophenone, which was converted into the corresponding alcohol in 99% ee.

The ATH reaction was also carried out with a 1,4-diaryl diketone (Scheme 3). Thus, 1,4-diphenyl-1,4-butanedione was successfully reduced with (*R*,*R*)-**8b** under the standard conditions, giving the corresponding (1*R*,4*R*)-1,4-diphenyl-1,4-butanediol with a very high *dl*/*meso* ratio (96:4) and an excellent enantioselectivity (>99% ee).

When the reaction was performed with (*R*,*R*)-**8a**, an incomplete conversion was observed even after a prolonged reaction time of 48 h (48% conversion, 41% isolated yield), whereas the stereochemical outcome remained unchanged. This compound is a precursor of (2*R*,5*R*)-diphenylpyrrolidine, which is commonly used in asymmetric organocatalytic reactions.[15]

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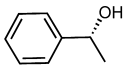
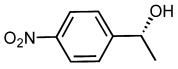
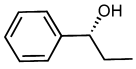
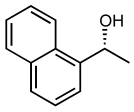
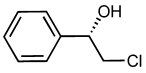
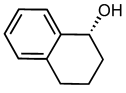
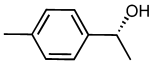
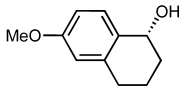
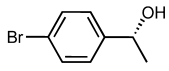
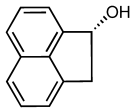
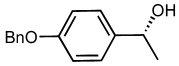
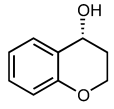
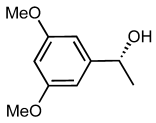
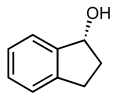
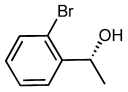
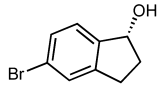
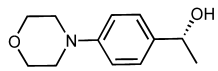
Table 2. Asymmetric Transfer Hydrogenation of Aryl Ketones Mediated by Complexes (*R*,*R*)-8a−8e[a]

Entry/ATH product[b]	Cat. 8	Time [h]	Yield [%][c]	ee [%][d]	Entry/ ATH product[b]	Cat. 8	Time [h]	Yield [%][c]	ee [%][d]
1 	**8a**[e]	10	100	98	9 	**8a**	1	99	88
	8b	5	99	98		**8b**	0.5	99	88
	8c	8.5	99	97		**8c**	1	99	88
	8d	22	97	98		**8d**	0.5	99	88
	8e	24	99	98		**8e**	2.5	99	88
2 	**8a**	22	90	98	10 	**8a**[e]	8	35	80
	8b	6	79	97		**8b**	27	94	82
	8c	6	100	97		**8c**	30	100	84
	8d	30	100	97		**8d**	39	98	85
	8e	96	(89)	97		**8e**	110	(68)	78
3[f] 	**8a**[e]	2	100	99.6	11 	**8a**[e]	9	100	99.9
	8b	1.5	99	99		**8b**	7	92	>99
	8c	1	93	95		**8c**	9	100	>99
	8d	4	95	95		**8d**	39	98	>99
	8e	5	88	95		**8e**	24	100	99
4 	**8a**	22	100	98	12 	**8a**	48	97	>99
	8b	7	98	98		**8b**	29	72	>99
	8c	7	93	97		**8c**	24	100	99
	8d	27	97	98		**8d**	96	(94)	92
	8e	96	90	98		**8e**	96	(81)	99
5 	**8a**	22	97	95	13 	**8a**	24	62	98
	8b	3	99	96		**8b**	5.5	95	98
	8c	24	99	94		**8c**	22	100	97
	8d	30	99	94		**8d**	22	100	97
	8e	96	91	95		**8e**	55	76	98
6[g] 	**8a**	22	100	98	14 	**8a**	6	100	99
	8b	23	97	99		**8b**	4	100	>99
	8c	39	100	99		**8c**	4.5	100	>99
	8d	48	84	99		**8d**	10	100	>99
	8e	110	(64)	98		**8e**	96	79	>99
7 	**8a**	7	99	96	15 	**8a**	7	97	>99
	8b	2	90	96		**8b**	5.5	100	>99
	8c	2.5	100	94		**8c**	5	100	>99
	8d	72	100	94		**8d**	7	100	>99
	8e	100	(62)	96		**8e**	6.5	99	99
8 	**8a**	22	88	64	16 	**8a**	23	95	99
	8b	27	98	70		**8b**	22	79	>99
	8c	30	99	65		**8c**	4	100	>99
	8d	88	93	71		**8d**	6	100	>99
	8e	110	(82)	66		**8e**	65	84	>99
					17[g] 	**8a**	30	99	99
						8b	30	99	99

[a]Reaction conditions: ketone (0.8 mmol) in neat HCO_2H/Et_3N (5:2) (430 μL), (*R*,*R*)-**8a−8e** (0.004 mmol, 0.5 mol %), 24−30 °C. Except where indicated, complete conversions were observed. [b]Absolute configuration assigned by comparing the optical rotation with literature data and on the basis of the general trends in enantioselectivity observed for the Rh-catalyzed ATH of ketones. [c]Isolated yields after filtration through a short pad of silica gel. Values in parentheses refer to incomplete conversions. [d]Determined by HPLC or SFC analysis. [e]Results described by Wills et al.[8] Conversion is reported in place of yield. [f]Ethyl acetate was used as a cosolvent to allow solubilization of the reaction mixture. [g]Dichloromethane was used as a cosolvent to allow solubilization of the reaction mixture.

CONCLUSION

In conclusion, the synthesis, characterization, and evaluation of novel tethered Rh(III) complexes (*R*,*R*)-**8b−8e** having electron-donating groups as well as electron-withdrawing substituents on the tethering phenyl ring were successfully accomplished. These new complexes showed high stability and

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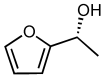
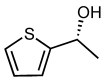
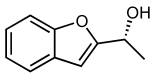
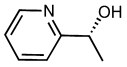
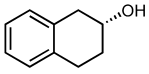
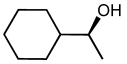
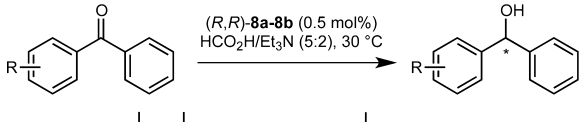
Table 3. (*R*,*R*)-8a−8e-Mediated ATH of Heteroaryl and Aliphatic Ketones[a]

Entry/ATH product[b]	Cat. **8**	Time [h]	Yield [%][c]	ee [%][d]
1 	**8a**	5.5	82	99
	8b	5.5	100	98
	8c	8	100	>99
	8d	27	92	>99
	8e	24	85	99
2 	**8a**	23	100	99
	8b	23	76	98
	8c	17	98	99
	8d	20	100	99
	8e	65	84	>99
3 	**8a**	5.5	100	97
	8b	3	100	98
	8c	3	100	98
	8d	3.5	100	99
	8e	6.5	100	98
4 	**8a**	6	89	97
	8b	4.5	99	94
	8c	6.5	100	96
	8d	9	98	99
	8e	24	70	96
5 	**8a**	24	53	81
	8b	3	96	83
	8c	3	100	83
	8d	27	100	80
	8e	30	89	80
6 	**8a**	22	71[e]	94[f]
	8b	7	68[e]	95[f]
	8c	7	73[e]	93[f]
	8d	30	72[e]	94[f]
	8e	24	58[e]	94[f]

[a]Reaction conditions: see Table 2. [b]Absolute configuration assigned by comparing the optical rotation with literature data. [c]Isolated yields after filtration through a pad of silica gel. [d]Determined by HPLC or SFC analysis. [e]Isolated yield (two steps) after conversion of the alcohol into the benzoyl ester. [f]Determined by HPLC on the related benzoyl ester.

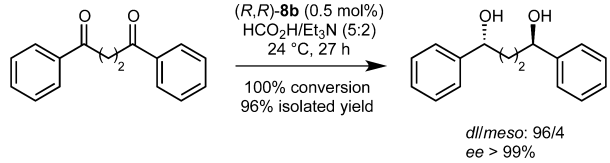
Scheme 2. (*R*,*R*)-8a−8b-Mediated ATH of Diaryl Ketones



R	t	(*R*,*R*)-**8a**	(*R*,*R*)-**8b**
p-NO_2	32 h	52% yield, 84% ee (*S*)	92% yield, 83% ee (*S*)
p-Cl	30 h	100% yield, 54% ee (*S*)	99% yield, 50% ee (*S*)
p-MeO	7 d	79% yield, 9% ee (*R*)	72% yield, 9% ee (*R*)
o-Me	7 d	60% yield, >99% ee (*S*)	65% yield, 99% ee (*S*)

were easy to handle. As far as the synthesis, characterization, and applications of novel tethered Rh(III) complexes is concerned, a complete comparative study of the catalytic performances of complexes (*R*,*R*)-**8b**−**8e** was conducted. This study demonstrated that these complexes exhibited excellent activities for the asymmetric transfer hydrogenation of a wide range of functionalized ketones. In this survey, the catalytic performance of the Wills complex (*R*,*R*)-**8a** was also evaluated on a broad scope of

Scheme 3. (*R*,*R*)-8b-Mediated ATH of 1,4-Diphenyl-1,4-butanedione



new substrates. Selectivities obtained with complexes (*R*,*R*)-**8b**−**8e** were comparable to those obtained with (*R*,*R*)-**8a** or slightly higher in a few instances, and with a better catalytic activity observed in several cases. A wide range of (hetero)aryl ketones underwent the (*R*,*R*)-**8b**−**8e**-promoted ATH using formic acid/triethylamine with high levels of enantioselectivities under mild reaction conditions at a low catalyst loading. The scope of the prochiral ketones for the ATH promoted by tethered Rh−TsDPEN/Cp* complexes has been consistently expanded, including notably unsymmetrical benzophenones, a highly electron-rich acetophenone bearing a morpholine substituent, and a highly electron-poor aryl ketone possessing a nitro substituent. Moreover, 1,4-diphenyl-1,4-butanedione was efficiently reduced upon using the Rh−TsDPEN complex (*R*,*R*)-**8b** into the enantiomerically pure 1,4-diphenyl-1,4-butanediol, a valuable intermediate in the preparation of the (2*R*,5*R*)-diphenylpyrrolidine organocatalyst. In addition, the ATH of 4-chromanone was performed with (*R*,*R*)-**8b** on the gram scale without a detrimental impact on the yield and the stereochemical outcome of the reaction, demonstrating the potential usefulness of these new complexes.

EXPERIMENTAL SECTION

Synthesis of Complexes (*R*,*R*)-8b−8e. *Compound* ***13***.[16] A mixture of 2-bromo-5-methoxybenzaldehyde (**9**) (5.0 g, 23.2 mmol), ethylene glycol (3.1 mL, 56.6 mmol), and *p*-toluenesulfonic acid (56 mg, 0.32 mmol) in toluene (40 mL) was refluxed in a Dean−Stark apparatus using an oil bath for 24 h. The cooled mixture was washed with H_2O and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated. Purification of the residue by flash chromatography (SiO_2, petroleum ether/EtOAc = 95/5) afforded **13** (6.01 g, quantitative) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, J = 8.8 Hz, 1H), 7.15 (d, J = 3.1 Hz, 1H), 6.78 (dd, J = 8.8, 3.1 Hz, 1H), 6.04 (s, 1H), 4.18−4.03 (m, 4H), 3.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 137.3, 133.6, 116.6, 113.1, 112.9, 102.4, 65.4 (2C), 55.5. MS (DCI/NH_3): m/z = 259 $[M + H]^+$.

Compound ***14***.[17] Following the general procedure described for **13**, and starting from 2-bromo-5-methylbenzaldehyde (**10**) (4.2 g, 21.3 mmol), compound **14** (4.8 g, 92%) was obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52−7.32 (m, 2H), 7.03 (dd, J = 8.2, 2.3 Hz, 1H), 6.06 (s, 1H), 4.31−3.93 (m, 4H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.5, 136.2, 132.8, 131.6, 128.5, 119.7, 102.8, 65.6 (2C), 21.1. MS (DCI/NH_3): m/z = 244 $[M + H]^+$.

Compound ***15***.[18] Following the general procedure described for **13**, and starting from 2-fluoro-5-methylbenzaldehyde (**11**) (5.0 g, 25.0 mmol), compound **15** (5.2 g, 84%) was obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (dd, J = 8.8, 5.1 Hz, 1H), 7.32 (dd, J = 9.3, 3.1 Hz, 1H), 6.94 (ddd, J = 8.8, 7.8, 3.1 Hz, 1H), 6.03 (d, J = 1.3 Hz, 1H), 4.27−3.94 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.1 (d, J_{CF} = 247.3 Hz), 139.1 (d, J_{CF} = 6.2 Hz), 134.3 (d, J_{CF} = 7.6 Hz), 117.8 (d, J_{CF} = 22.7 Hz), 116.9 (d, J_{CF} = 3.2 Hz), 115.2 (d, J_{CF} = 24.4 Hz), 102.1, 65.6 (2C). MS (DCI/NH_3): m/z = 248 $[M + H]^+$.

Compound ***16***.[19] Following the general procedure described for **13**, and starting from 2-bromo-5-(trifluoromethyl)benzaldehyde (**12**) (5.0 g, 19.8 mmol), compound **16** (5.8 g, 99%) was obtained as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00−7.78 (m, 1H), 7.78−7.62 (m, 1H), 7.47 (dt, J = 8.3, 1.5 Hz, 1H), 6.09 (s, 1H), 4.33−3.89 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.1, 133.7,

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130.2 (q, J_{CF} = 33.0 Hz), 127.2 (q, J_{CF} = 3.9 Hz), 125.0 (q, J_{CF} = 3.6 Hz), 123.8 (q, J_{CF} = 272.5 Hz), 102.0, 65.7 (2C). MS (DCI/NH_3): m/z = 299 $[M + H]^+$.

Compound ***17***.[7] To a solution of **13** (6.0 g, 23.2 mmol) in Et_2O (42 mL) was added dropwise *n*-BuLi (9.7 mL, 2.5 M in hexane, 24.4 mmol) at −90 °C. After 1 h at this temperature, 2,3,4,5-tetramethylcyclopent-2-enone (3.7 mL, 24.4 mmol) was added dropwise and the reaction, was allowed to warm to rt and stirred for 3 h. Toluene and water (30 mL/30 mL) were added, and the aqueous layer was extracted with toluene. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated to afford the crude alcohol. THF (140 mL), acetone (18 mL), and 3% aqueous HCl solution (60 mL) were added, and the mixture was stirred overnight at rt. Toluene was added, and the organic layer was washed with H_2O and then brine, dried over $MgSO_4$, filtered, and concentrated. The crude residue was purified by flash chromatography (SiO_2, petroleum ether/EtOAc = 98/2) to give **17** (3.9 g, 65%) as a bright yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.81 (br s, 1H), 7.44 (dd, J = 2.3, 0.8 Hz, 1H), 7.15−7.14 (m, 2H), 3.88 (s, 1H), 3.87 (s, 3H), 1.92 (s, 3H), 1.85 (s, 3H), 1.71 (s, 3H), 0.93 (d, J = 7.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.9, 158.3, 141.8 (2C), 138.2, 135.3, 134.5, 132.0, 121.8 (2C), 109.0, 55.5 (2C), 14.2, 12.3, 11.9, 11.0. MS (DCI/NH_3): m/z = 257 $[M + H]^+$.

Compound ***18***. Following the general procedure described for **17**, and starting from **14** (4.8 g, 19.6 mmol), compound **18** (2.6 g, 55%) was obtained as a bright yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.87 (br s, 1H), 7.90−7.66 (m, 1H), 7.40 (dd, J = 7.8, 2.0 Hz, 1H), 7.13 (d, J = 7.8 Hz, 1H), 3.20 (br s, 1H), 2.42 (s, 3H), 1.94 (s, 3H), 1.87 (s, 3H), 1.73 (s, 3H), 0.95 (d, J = 7.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.2, 144.4, 141.9, 139.3, 138.8, 137.1, 136.5, 134.5, 134.4, 130.8, 127.3, 52.5, 21.0, 14.2, 12.4, 11.9, 11.1. HRMS (ESI/ion trap): m/z $[M + Na]^+$ calcd for $C_{17}H_{20}ONa$ 263.1406, found 263.1408.

Compound ***19***. Following the general procedure described for **17**, and starting from **15** (5.2 g, 21.0 mmol), compound **23** (2.5 g, 49%) was obtained as a bright yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.80 (br s, 1H), 7.62 (dd, J = 8.9, 2.6 Hz, 1H), 7.37−7.16 (m, 2H), 3.18 (br s, 1H), 1.93 (s, 3H), 1.86 (s, 3H), 1.71 (s, 3H), 0.94 (d, J = 7.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.9, 161.7 (d, J_{CF} = 247.9 Hz), 145.1 (d, J_{CF} = 19.4 Hz), 142.4, 139.9 (d, J_{CF} = 14.0 Hz), 137.6, 136.2, 134.6, 132.8 (d, J_{CF} = 6.5 Hz), 121.0 (d, J_{CF} = 22.1 Hz), 113.1 (d, J_{CF} = 22.0 Hz), 52.6 14.2, 12.4, 12.0, 11.1. HRMS (ESI/ion trap): m/z $[M + Na]^+$ calcd for $C_{16}H_{17}FONa$ 267.1156, found 267.1157.

Compound ***20***. Following the general procedure described for **17**, and starting from **16** (5.2 g, 17.5 mmol), compound **20** (1.4 g, 26%) was obtained as a bright yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.87 (br s, 1H), 8.30−8.10 (m, 1H), 7.79 (ddd, J = 8.1, 2.1, 0.8 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 3.26 (br s, 1H), 1.96 (s, 3H), 1.87 (s, 3H), 1.74 (s, 3H), 0.96 (d, J = 7.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.6, 145.1, 143.5, 137.5, 134.9, 134.8, 131.7, 131.6, 129.6 (q, J_{CF} = 3.2 Hz), 129.1 (q, J_{CF} = 33.6 Hz), 124.6 (q, J_{CF} = 3.7 Hz), 123.9 (q, J_{CF} = 272.2 Hz), 52.5, 14.1, 12.6, 12.0, 11.1. MS (DCI/NH_3): m/z = 295 $[M + H]^+$. HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{17}H_{18}F_3O$ 295.1304, found 295.1310.

*Complex (R,R)-***8b**. To a solution of compound **17** (538 mg, 2.1 mmol) in dry MeOH (24 mL) was added (*R*,*R*)-TsDPEN (900 mg, 2.5 mmol) followed by the addition of 700 mg of molecular sieves (4 Å) and 2 drops of glacial acetic acid. The mixture was stirred at rt for 5 h, then $NaBH_3CN$ (170 mg, 2.7 mmol) was added, and the reaction was stirred overnight at rt. After removal of the molecular sieves and evaporation of MeOH, the residue was dissolved in EtOAc (40 mL). The organic layer was washed with saturated $NaHCO_3$ and then brine, dried over $MgSO_4$, filtered, and concentrated. Purification of the residue by flash chromatography (SiO_2, pentane/EtOAc = 9/1 to 8/2) afforded the diamine (786 mg, 60%) as a white solid. To a solution of the diamine (740 mg, 1.2 mmol) in MeOH (28 mL) was added $RhCl_3{\cdot}H_2O$ (255 mg, 1.2 mmol), and the reaction mixture was heated under reflux using an oil bath for 23 h. Et_3N (340 μL, 2.4 mmol) was then added, and the mixture was refluxed for a further 20 h and concentrated. The residue was triturated with H_2O, and the solid was filtered, washed with H_2O, and dried under vacuum. Purification of the black solid by flash chromatography (SiO_2, EtOAc/cyclohexane = 1/1 to EtOAc/MeOH = 95/5) afforded (*R*,*R*)-**8b** (455 mg, 50%) as an orange solid. Mp: >260 °C dec. R_f = 0.51 (CH_2Cl_2/MeOH = 9/1, UV, $KMnO_4$). $[\alpha]_D^{25}$ = −154.4 (c = 0.12, $CHCl_3$). IR (neat): 2360, 2339, 1608, 1513, 1489, 1455, 1397, 1372, 1277, 1239, 1131, 1098, 1086, 1040, 1023, 940, 895, 812, 796, 766, 700, 682, 661, 646, 635, 622, 606 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 8.5 Hz, 1H), 7.27 (d, J = 8.6 Hz, 2H), 7.19−7.16 (m, 3H), 7.02 (dd, J = 8.4, 2.5 Hz, 1H), 6.73 (d, J = 8.0 Hz, 2H), 6.70 (d, J = 7.3 Hz, 2H), 6.59 (t, J = 7.8 Hz, 2H), 6.48 (d, J = 7.4 Hz, 2H), 6.42 (br d, J = 2.4 Hz, 2H), 4.98 (d, J = 12.4 Hz, 1H), 4.32 (d, J = 11.0 Hz, 1H), 4.22 (dd, J = 14.0, 2.9 Hz, 1H), 3.73 (s, 3H), 3.60 (d, J = 14.0 Hz, 1H), 3.26 (t, J = 12.4 Hz, 1H), 2.17 (s, 3H), 2.09 (s, 3H), 1.97 (s, 3H), 1.83 (s, 3H), 1.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 142.3, 139.0, 138.6, 137.5, 135.7, 131.2, 128.8, 128.7, 127.9, 127.7, 127.1, 126.2, 118.6, 117.0, 115.0, 106.4 (d, J_{CRh} = 6.6 Hz), 99.2 (d, J_{CRh} = 6.6 Hz), 97.0 (d, J_{CRh} = 8.8 Hz), 88.7 (d, J_{CRh} = 9.5 Hz), 80.6 (d, J_{CRh} = 8.0 Hz), 75.9, 69.8, 55.5, 52.5, 21.3, 10.8, 10.7, 10.4, 8.3. HRMS (ESI/ion trap): m/z $[M - Cl]^+$ calcd for $C_{38}H_{40}N_2O_3RhS$ 707.1809, found 707.1813.

*Complex (R,R)-***8c**. Following the general procedure described for (*R*,*R*)-**8b**, and starting from **18** (546 mg, 2.3 mmol), complex (*R*,*R*)-**8c** (590 mg, 36%, 2 steps) was obtained as an orange solid. Mp: 274 °C dec. R_f = 0.58 (CH_2Cl_2/MeOH = 9/1, UV, $KMnO_4$). $[\alpha]_D^{25}$ = −112 (c = 0.15, $CHCl_3$). IR (neat): 1456, 1277, 1133, 1107, 1085, 1036, 1021, 938, 894, 809, 751, 701, 682, 670, 661, 647, 601 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.23 (m, 5H), 7.23−7.06 (m, 3H), 6.81−6.66 (m, 5H), 6.59 (dd, J = 8.2, 7.1 Hz, 2H), 6.48 (d, J = 7.6 Hz, 2H), 4.99 (d, J = 12.8 Hz, 1H), 4.30 (d, J = 11.0 Hz, 1H), 4.20 (dd, J = 14.0, 3.3 Hz, 1H), 3.62 (d, J = 14.0 Hz, 1H), 3.25 (dd, J = 12.8, 10.9 Hz, 1H), 2.29 (s, 3H), 2.17 (s, 3H), 2.09 (s, 3H), 1.98 (s, 3H), 1.82 (s, 3H), 1.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 139.9, 139.1, 138.7, 135.9, 135.8, 132.4, 130.3, 129.8, 128.7, 127.9, 127.8, 127.0, 126.2, 123.9, 106.3 (d, J_{CRh} = 6.1 Hz), 99.5 (d, J_{CRh} = 7.0 Hz), 97.2 (d, J_{CRh} = 9.0 Hz), 88.2 (d, J_{CRh} = 9.2 Hz), 80.9 (d, J_{CRh} = 8.6 Hz), 75.9, 69.9, 52.2, 21.3, 21.2, 10.8, 10.6, 10.4, 8.3. HRMS (ESI/ion trap): m/z $[M - Cl]^+$ calcd for $C_{38}H_{40}N_2O_2RhS$ 691.1860, found 691.1870.

*Complex (R,R)-***8d**. Following the general procedure described for (*R*,*R*)-**8b**, and starting from **19** (555 mg, 2.3 mmol), complex (*R*,*R*)-**8d** (297 mg, 19%, 2 steps) was obtained as an orange solid. Mp: 280 °C dec. R_f = 0.55 (CH_2Cl_2/MeOH = 9/1, UV, $KMnO_4$). $[\alpha]_D^{25}$ = −151 (c = 0.14, $CHCl_3$). IR (neat): 1736, 1608, 1585, 1511, 1492, 1455, 1373, 1275, 1235, 1216, 1158, 1132, 1023, 940, 894, 868, 852, 842, 811, 793, 779, 757, 730, 699, 677, 657, 645, 636, 607 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (dd, J = 8.5, 5.5 Hz, 1H), 7.33−7.10 (m, 7H), 6.74 (d, J = 8.0 Hz, 3H), 6.71−6.55 (m, 4H), 6.48 (d, J = 7.3 Hz, 2H), 5.04 (d, J = 12.8 Hz, 1H), 4.32 (d, J = 10.9 Hz, 1H), 4.22 (d, J = 14.2 Hz, 1H), 3.64 (d, J = 14.3 Hz, 1H), 3.34−3.13 (m, 1H), 2.17 (s, 3H), 2.10 (s, 3H), 1.98 (s, 3H), 1.83 (s, 3H), 1.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8 (d, J_{CF} = 251.3 Hz), 142.1, 139.2, 138.7 (d, J_{CF} = 7.7 Hz), 138.4, 135.4, 131.9 (d, J_{CF} = 8.4 Hz), 129.0, 128.9, 128.6, 127.9, 127.7, 127.1, 127.0, 126.3, 123.1 (d, J_{CF} = 3.2 Hz), 118.7 (d, J_{CF} = 22.3 Hz), 116.8 (d, J_{CF} = 21.4 Hz), 106.5 (d, J_{CRh} = 6.4 Hz), 99.9 (d, J_{CRh} = 7.0 Hz), 96.0 (d, J_{CRh} = 9.2 Hz), 88.2 (d, J_{CRh} = 9.5 Hz), 81.1 (d, J_{CRh} = 8.5 Hz), 76.3, 69.9, 52.2, 21.3, 10.8, 10.6, 10.4, 8.3. HRMS (ESI/ion trap): m/z $[M - Cl]^+$ calcd for $C_{37}H_{37}FN_2O_2RhS$ 695.1609, found 695.1616.

*Complex (R,R)-***8e**. Following the general procedure described for (*R*,*R*)-**8b**, and starting from **20** (656 mg, 2.2 mmol), compound (*R*,*R*)-**8e** (310 mg, 18%, 2 steps) was obtained as an orange solid. Mp: 284 °C dec. R_f = 0.56 (CH_2Cl_2/MeOH = 9/1, UV, $KMnO_4$). $[\alpha]_D^{25}$ = −172 (c = 0.14, $CHCl_3$). IR (neat): 2359, 2341, 1329, 1275, 1168, 1132, 1082, 938, 906, 896, 881, 870, 808, 791, 766, 756, 713, 699, 687, 679, 671, 659, 641, 622, 614, 605 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 8.2 Hz, 2H), 7.23−7.09 (m, 4H), 6.73 (d, J = 8.0 Hz, 2H), 6.76−6.66 (m, 3H), 6.65−6.54 (m, 2H), 6.47 (d, J = 7.6 Hz, 2H), 5.04 (d, J = 12.7 Hz, 1H), 4.35 (d, J = 10.9 Hz, 1H), 4.26 (dd, J = 14.0, 3.3 Hz, 1H), 3.73 (d, J = 14.1 Hz, 1H), 3.19 (dd, J = 12.7, 10.9 Hz, 1H), 2.17 (s, 3H), 2.10 (s, 3H), 1.98 (s, 3H), 1.83 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 139.2, 138.1, 137.0, 135.1, 131.8 (q, J_{CF} = 33.2 Hz), 131.5, 131.3, 130.7, 129.1, 128.9, 128.6, 128.6 (q, J_{CF} = 3.2 Hz), 127.8, 127.6, 127.1, 126.5 (q, J_{CF} = 3.2 Hz), 126.3, 123.3 (q, J_{CF} = 272.7 Hz), 106.5 (d, J_{CRh} = 6.3 Hz), 100.1 (d, J_{CRh} = 7.0 Hz), 95.5 (d, J_{CRh} = 9.2 Hz),

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87.8 (d, J_{CRh} = 9.1 Hz), 81.4 (d, J_{CRh} = 8.4 Hz), 76.4, 69.5, 52.1, 21.2, 10.6, 10.5, 10.3, 8.2. HRMS (ESI/ion trap): m/z $[M - Cl]^+$ calcd for $C_{38}H_{37}F_3N_2O_2RhS$ 745.1577, found 745.1585.

General Procedure for the ATH of Ketones with Complexes (*R,R*)-8a−8e. To a round-bottom tube containing complex (*R,R*)-**8** (4 μmol, 0.5 mol %) was added at room temperature a HCO_2H/Et_3N (5:2) azeotropic mixture (430 μL, 7.2 mmol), and three vacuum/argon cycles were used to ensure an inert atmosphere. The orange mixture was stirred for 10−15 min before the ketone (0.8 mmol) was added. The reaction mixture was stirred at 24−30 °C until the starting material was consumed as determined by TLC, and then the reaction mixture was purified by filtration through a pad of silica gel using pentane/EtOAc (8:2). The filtrate was concentrated under vacuum to give the reduced product. Enantiomeric excess was determined by SFC (Chiralpak OD-H and Chiralpak AD-H, AS-H, IA, IC, or ID) or HPLC (Chiralpak IB, IC, or ID column) analysis.

(R)-1-Phenylethanol.[8] Yield: 96 mg, 98%. Pale yellow oil. $[\alpha]_D^{20}$ = +45.5 (*c* = 1.0, $CHCl_3$, 98% ee), lit.[8] $[\alpha]_D^{26}$ = +45.4 (*c* = 0.5, $CHCl_3$, 98% ee). Enantiomeric excess determined by HPLC analysis on a Daicel Chiralpak IB column (0.46 × 25 cm), hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 215 nm, t_R = 7.38 min (*R*), 8.04 min (*S*). MS (DCI/NH_3): m/z = 140 $[M + NH_4]^+$.

(R)-1-Phenylpropan-1-ol.[20] Yield: 98 mg, 90%. Pale yellow oil. $[\alpha]_D^{25}$ = +45 (*c* = 1.0, $CHCl_3$, 98% ee), lit.[20] $[\alpha]_D^{20}$ = +44.5 (*c* = 1.0, $CHCl_3$, 97% ee). Enantiomeric excess determined by SFC analysis on a Daicel Chiralpak OD-H column (0.46 × 25 cm), $scCO_2$/MeOH = 95/5, 4.0 mL/min, *P* = 150 bar, λ = 215 nm, t_R = 2.07 min (*R*), 2.44 min (*S*). MS (DCI/NH_3): m/z = 154 $[M + NH_4]^+$.

(S)-2-Chloro-1-phenylethan-1-ol.[21] Yield: 119 mg, 95%. Colorless oil. $[\alpha]_D^{25}$ = +56 (*c* = 1.09, $CHCl_3$, 95% ee), lit.[21] $[\alpha]_D^{20}$ = +57.8 (*c* = 1.0, $CHCl_3$, 96.6% ee). Enantiomeric excess determined by SFC analysis on a Daicel Chiralpak OD-H column (0.46 × 25 cm), $scCO_2$/MeOH = 95/5, 4.0 mL/min, *P* = 150 bar, λ = 215 nm, t_R = 2.52 min (*S*), 3.38 min (*R*). MS (DCI/NH_3): m/z = 174 $[M + NH_4]^+$.

(R)-1-(p-Tolyl)ethan-1-ol.[22] Yield: 109 mg, 100%. Pale yellow oil. $[\alpha]_D^{25}$ = +53 (*c* = 0.94, $CHCl_3$, 98% ee), lit.[22] $[\alpha]_D^{20}$ = +55.4 (*c* = 1.01, $CHCl_3$, 98.7% ee). Enantiomeric excess determined by HPLC analysis on a Daicel Chiralpak ID column (0.46 × 25 cm), hexane/*i*-PrOH = 97/3, 0.5 mL/min, λ = 215 nm, t_R = 18.77 min (*R*), 19.97 min (*S*). MS (DCI/NH_3): m/z = 119 $[M + H - H_2O]^+$.

(R)-1-(4-Bromophenyl)ethan-1-ol.[23] Yield: 159 mg, 99%. Colorless oil. $[\alpha]_D^{25}$ = +35 (*c* = 1.17, $CHCl_3$, 96% ee), lit.[23] $[\alpha]_D^{22}$ = +34.8 (*c* = 1.03, $CHCl_3$, 97% ee). Enantiomeric excess determined by HPLC analysis on a Daicel Chiralpak IB column (0.46 × 25 cm), hexane/*i*-PrOH = 95/5, 0.5 mL/min, λ = 215 nm, t_R = 15.09 min (*S*), 15.83 min (*R*). MS (DCI/NH_3): m/z = 202 $[M + NH_4 - H_2O]^+$.

(R)-1-(4-(Benzyloxy)phenyl)ethan-1-ol.[24] Yield: 182 mg, 100%. White solid. $[\alpha]_D^{25}$ = +33 (*c* = 1.09, $CHCl_3$, 99% ee), lit.[24] $[\alpha]_D^{25}$ = −31.8 (*c* = 1.2, $CHCl_3$, > 99% ee, (*S*)-isomer). Enantiomeric excess determined by SFC analysis on a Daicel Chiralpak OD-H column (0.46 × 25 cm), $scCO_2$/MeOH = 98/2, 2.0 mL/min, *P* = 150 bar, λ = 215 nm, t_R = 39.24 min (*S*), 42.59 min (*R*). MS (DCI/NH_3): m/z = 211 $[M + H - H_2O]^+$.

(R)-1-(3,5-Dimethoxyphenyl)ethan-1-ol.[25] Yield: 144 mg, 99%. Colorless oil. $[\alpha]_D^{25}$ = +31 (*c* = 0.95, $CHCl_3$, 96% ee), lit.[25] $[\alpha]_D^{20}$ = −32.7 (*c* = 2.0, $CHCl_3$, 97% ee, (*S*)-isomer). Enantiomeric excess determined by SFC analysis on a Daicel Chiralpak OD-H column (0.46 × 25 cm), $scCO_2$/MeOH = 95/5, 4.0 mL/min, *P* = 150 bar, λ = 215 nm, t_R = 3.11 min (*R*), 3.49 min (*S*). MS (DCI/NH_3): m/z = 183 $[M + H]^+$.

(R)-1-(2-Bromophenyl)ethan-1-ol.[26] Yield: 142 mg, 88%. Colorless oil. $[\alpha]_D^{25}$ = +40 (*c* = 0.99, $CHCl_3$, 64% ee), lit.[26] $[\alpha]_D^{24}$ = +32.7 (*c* = 0.8, $CHCl_3$, 64% ee). Enantiomeric excess determined by SFC analysis on a Daicel Chiralpak ID column (0.46 × 25 cm), $scCO_2$/MeOH = 90/10, 4.0 mL/min, *P* = 150 bar, λ = 215 nm, t_R = 1.27 min (*R*), 1.50 min (*S*). MS (DCI/NH_3): m/z = 218 $[M + NH_4]^+$.

(R)-1-(4-Nitrophenyl)ethan-1-ol.[27] Yield: 132 mg, 99%. Yellow oil. $[\alpha]_D^{22}$ = +34.9 (*c* = 1.0, $CHCl_3$, 88% ee); lit.[27] $[\alpha]_D^{23}$ = +33.7 (*c* = 1.0, $CHCl_3$, 85% ee). Enantiomeric excess determined by SFC analysis on a Daicel Chiralpak AS-H column (0.46 × 25 cm), $scCO_2$/MeOH = 95/5, 2.0 mL/min, *P* = 100 bar, λ = 215 nm, t_R = 6.30 min (*R*), 7.33 min (*S*). MS (DCI/NH_3): m/z = 185 $[M + NH_4]^+$.

(R)-1-(Naphthalen-1-yl)ethan-1-ol.[28] Yield: 135 mg, 98%. Colorless oil. $[\alpha]_D^{20}$ = +46.6 (*c* = 1.0, $CHCl_3$, 85% ee), lit.[28] $[\alpha]_D^{22}$ = +55.1 (*c* = 1.0, $CHCl_3$, 92% ee). Enantiomeric excess determined by SFC analysis on a Daicel Chiralpak OD-H column (0.46 × 25 cm), $scCO_2$/MeOH = 95/5, 4.0 mL/min, *P* = 150 bar, λ = 215 nm, t_R = 7.65 min (*S*), 11.48 min (*R*). MS (DCI/NH_3): m/z = 155 $[M + H - H_2O]^+$.

(R)-1,2,3,4-Tetrahydro-1-naphthol.[5f] Yield: 141 mg, 100%. Colorless oil. $[\alpha]_D^{25}$ = −30 (*c* = 0.94, $CHCl_3$, 99% ee), lit.[5f] $[\alpha]_D^{30}$ = −30.7 (*c* = 1.02, $CHCl_3$, 99.2% ee). Enantiomeric excess determined by SFC analysis on a Daicel Chiralpak OD-H column (0.46 × 25 cm), $scCO_2$/MeOH = 95/5, 3.0 mL/min, *P* = 150 bar, λ = 215 nm, t_R = 3.80 (*S*), 4.20 min (*R*). MS (DCI/NH_3): m/z = 131 $[M + H - H_2O]^+$.

(R)-6-Methoxy-1,2,3,4-tetrahydro-1-naphthol.[29] Yield: 165 mg, 100%. Colorless oil. $[\alpha]_D^{25}$ = −22 (*c* = 0.92, $CHCl_3$, > 99% ee), lit.[29] $[\alpha]_D^{21}$ = −17.2 (*c* = 1.19, $CHCl_3$, 92% ee). Enantiomeric excess determined by SFC analysis on a Daicel Chiralpak AD-H column (0.46 × 25 cm), $scCO_2$/MeOH = 90/10, 3.0 mL/min, *P* = 150 bar, λ = 215 nm, t_R = 5.37 min (*S*), 6.23 min (*R*). MS (DCI/NH_3): m/z = 161 $[M + H - H_2O]^+$.

(R)-1,2-Dihydroacenaphthylen-1-ol.[30] Yield: 129 mg, 95%. White solid. $[\alpha]_D^{25}$ = −1.4 (*c* = 0.92, $CHCl_3$, 98% ee), lit.[30,31] $[\alpha]_D^{20}$ = −1.4 (*c* = 0.5, $CHCl_3$, 98.2% ee). Enantiomeric excess determined by SFC analysis on a Daicel Chiralpak OD-H column (0.46 × 25 cm), $scCO_2$/*i*-PrOH = 93/7, 4.0 mL/min, *P* = 150 bar, λ = 215 nm, t_R = 8.17 min (*S*), 8.99 min (*R*). MS (DCI/NH_3): m/z = 153 $[M + H - H_2O]^+$.

(R)-Chroman-4-ol.[21] Yield: 120 mg, 100%. White solid. $[\alpha]_D^{25}$ = +68 (*c* = 0.93, $CHCl_3$, > 99% ee), lit.[21] $[\alpha]_D^{20}$ = +66.9 (*c* = 1.0, $CHCl_3$, 99.1% ee). Enantiomeric excess determined by SFC analysis on a Daicel Chiralpak AD-H column (0.46 × 25 cm), $scCO_2$/MeOH = 97/3, 3.0 mL/min, *P* = 150 bar, λ = 215 nm, t_R = 10.59 min (*S*), 11.25 min (*R*). MS (DCI/NH_3): m/z = 133 $[M + H - H_2O]^+$.

(R)-2,3-Dihydro-1H-inden-1-ol.[2] Yield: 107 mg, 100%. White solid. $[\alpha]_D^{25}$ = −33 (*c* = 0.85, $CHCl_3$, > 99% ee), lit.[21] $[\alpha]_D^{22}$ = +29.3 (*c* = 0.967, $CHCl_3$, > 99% ee, (*S*)-isomer). Enantiomeric excess determined by HPLC analysis on a Daicel Chiralpak IB column (0.46 × 25 cm), hexane/*i*-PrOH = 98/2, 1.0 mL/min, λ = 215 nm, t_R = 14.86 (*S*), 16.43 min (*R*). MS (DCI/NH_3): m/z = 117 $[M + H - H_2O]^+$.

(R)-5-Bromo-2,3-dihydro-1H-inden-1-ol.[32] Yield: 170 mg, 100%. White solid. $[\alpha]_D^{25}$ = −16 (*c* = 0.92, $CHCl_3$, > 99% ee), lit.[32] $[\alpha]_D^{25}$ = +15.8 (*c* = 1.0, $CHCl_3$, 98.1% ee, (*S*)-isomer). Enantiomeric excess determined by SFC analysis on a Daicel Chiralpak AD-H column (0.46 × 25 cm), $scCO_2$/MeOH = 90/10, 3.0 mL/min, *P* = 150 bar, λ = 215 nm, t_R = 5.92 (*S*), 8.21 min (*R*). MS (DCI/NH_3): m/z = 195 $[M + H - H_2O]^+$.

(R)-1-(4-Morpholinophenyl)ethan-1-ol.[33] Yield: 164 mg, 99%. White solid. $[\alpha]_D^{22}$ = + 43.9 (*c* = 1.16, $CHCl_3$, 99% ee); lit.[33] $[\alpha]_D^{25}$ = + 45.9 (*c* = 1.0, $CHCl_3$, 93% ee). Enantiomeric excess determined by HPLC analysis on a Daicel Chiralpak IC column (0.46 × 25 cm), hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 215 nm, t_R = 24.81 min (*S*), 31.01 min (*R*). MS (DCI/NH_3): m/z = 208 $[M + H]^+$.

(R)-1-(2-Furyl)ethanol.[34] Yield: 89 mg, 99%. Colorless oil. $[\alpha]_D^{25}$ = +20.0 (*c* = 0.79, $CHCl_3$, > 99% ee), lit.[34] $[\alpha]_D^{25}$ = +20.7 (*c* = 1.0, $CHCl_3$, 99% ee). Enantiomeric excess determined by HPLC analysis on a Daicel Chiralpak IC column (0.46 × 25 cm), hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 215 nm, t_R = 9.17 min (*S*), 9.90 min (*R*). MS (DCI/NH_3): m/z = 95 $[M + H - H_2O]^+$.

(R)-1-(2-Thienyl)ethanol.[35] Yield: 102 mg, 100%. Colorless oil. $[\alpha]_D^{25}$ = +23 (*c* = 0.91, $CHCl_3$, 99% ee), lit.[35] $[\alpha]_D^{20}$ = +21.6 (*c* = 1.0, $CHCl_3$, 98% ee). Enantiomeric excess determined by SFC analysis on a Daicel Chiralpak ID column (0.46 × 25 cm), $scCO_2$/MeOH = 93/7, 3.0 mL/min, *P* = 150 bar, λ = 215 nm, t_R = 2.07 min (*R*), 2.35 min (*S*). MS (DCI/NH_3): m/z = 111 $[M + H - H_2O]^+$.

(R)-1-(Benzofuran-2-yl)ethanol.[36] Yield: 129 mg, 100%. White solid. $[\alpha]_D^{25}$ = +18 (*c* = = 0.88, $CHCl_3$, 97% ee), lit.[36] $[\alpha]_D^{23}$ = +18 (*c* = 3.0, $CHCl_3$, 96% ee). Enantiomeric excess determined by HPLC analysis on a Daicel Chiralpak ID column (0.46 × 25 cm), hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 215 nm, t_R = 9.48 min (*R*), 10.11 min (*S*). MS (DCI/NH_3): m/z = 145 $[M + H - H_2O]^+$.

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(R)-1-(2-Pyridyl)ethanol.[37] Yield: 98 mg, 100%. Pale yellow oil. $[\alpha]_D^{25}$ = +21 (*c* = 0.99, $CHCl_3$, 96% ee), lit.[37] $[\alpha]_D^{20}$ = +26.6 (*c* = 1.0, $CHCl_3$, 97.3% ee). Enantiomeric excess determined by HPLC analysis on a Daicel Chiralpak ID column (0.46 × 25 cm), hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 215 nm, t_R = 15.23 min (*S*), 17.10 min (*R*). MS (DCI/NH_3): *m*/*z* = 124 $[M + H]^+$.

(R)-1,2,3,4-Tetrahydro-2-naphthol.[5e] Yield: 119 mg, 100%. Pale yellow oil. $[\alpha]_D^{25}$ = +53 (*c* = 0.88, $CHCl_3$, 81% ee), lit.[5e] $[\alpha]_D^{23}$ = +52.7 (*c* = 0.37, $CHCl_3$, 88% ee). Enantiomeric excess determined by SFC analysis on a Daicel Chiralpak AD-H column (0.46 × 25 cm), $scCO_2$/*i*-PrOH = 90/10, 3.0 mL/min, *P* = 150 bar, λ = 215 nm, t_R = 4.76 min (*S*), 5.19 min (*R*). MS (DCI/NH_3): *m*/*z* = 166 $[M + NH_4]^+$.

(R)-1-Cyclohexylethanol.[38] Yield: 80 mg, 100%. Colorless oil. $[\alpha]_D^{25}$ = +2.1 (*c* = 3.5, $CHCl_3$, 94% ee), lit.[38] $[\alpha]_D^{23}$ = +3.51 (*c* = 3.1, $CHCl_3$, 95% ee). Enantiomeric excess determined on the benzoate derivative by HPLC analysis on a Daicel Chiralpak ID column (0.46 × 25 cm), hexane/*i*-PrOH = 97/3, 0.5 mL/min, λ = 215 nm, t_R = 8.87 min (*S*), 9.37 min (*R*). MS (DCI/NH_3): *m*/*z* = 146 $[M + NH_4]^+$.

(S)-(4-Nitrophenyl)(phenyl)methanol.[39] Yield: 169 mg, 92%. White solid. $[\alpha]_D^{22}$ = + 70.0 (*c* = 1.0, $CHCl_3$, 83% ee); lit.[39] $[\alpha]_D^{22}$ = +71.0 (*c* = 0.27, $CHCl_3$, 92% ee). Enantiomeric excess determined by HPLC analysis on a Daicel Chiralpak IA column (0.46 × 25 cm), hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t_R = 12.17 min (*R*), 14.49 min (*S*). MS (DCI/NH_3): *m*/*z* = 247 $[M + NH_4]^+$.

(S)-(4-Chlorophenyl)(phenyl)methanol.[39] Yield: 173 mg, 99%. White solid. $[\alpha]_D^{22}$ = + 10.9 (*c* = 2.0, $CHCl_3$, 50% ee); lit.[39] $[\alpha]_D^{20}$ = + 8.0 (*c* = 1.51, $CHCl_3$, 48% ee). Enantiomeric excess determined by HPLC analysis on a Daicel Chiralpak IA column (0.46 × 25 cm), hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t_R = 12.92 min (*R*), 14.01 min (*S*). MS (DCI/NH_3): *m*/*z* = 201 $[M + H - H_2O]^+$.

(R)-(4-Methoxyphenyl)(phenyl)methanol.[39] Yield: 123 mg, 72%. White solid. $[\alpha]_D^{22}$ = +2.1 (*c* = 1.65, $CHCl_3$, 9% ee); lit.[39] $[\alpha]_D^{20}$ = +1.5 (*c* = 1.08, $CHCl_3$, 5% ee). Enantiomeric excess determined by HPLC analysis on a Daicel Chiralpak IA column (0.46 × 25 cm), hexane/*i*-PrOH = 90/10, 0.8 mL/min, λ = 254 nm, t_R = 13.37 min (*R*), 14.37 min (*S*). MS (DCI/NH_3): *m*/*z* = 197 $[M + H - H_2O]^+$.

(S)-Phenyl(o-tolyl)methanol.[40] Yield: 103 mg, 65%. White solid. $[\alpha]_D^{22}$ = +8.2 (*c* = 2.0, $CHCl_3$, 99% ee); lit.[40] $[\alpha]_D^{20}$ = +7.3 (*c* = 0.735, $CHCl_3$, 98% ee). Enantiomeric excess determined by HPLC analysis on a Daicel Chiralpak IC column (0.46 × 25 cm), hexane/*i*-PrOH = 98/2, 0.6 mL/min, λ = 254 nm, t_R = 28.8 min (*S*), 32.6 min (*R*). MS (DCI/NH_3): *m*/*z* = 181 $[M + H - H_2O]^+$.

(1R,4R)-1,4-Diphenylbutan-1,4-diol.[41] Yield: 186 mg, 96%. White solid. $[\alpha]_D^{25}$ = +51 (*c* = 1.1, $CHCl_3$, > 99% ee), lit.[41] $[\alpha]_D^{25}$ = +58 (*c* = 1.02, $CHCl_3$, 99% ee). Enantiomeric excess determined by SFC analysis on a Daicel Chiralcel OD-H column (0.46 × 25 cm), $scCO_2$/MeOH = 95/5, 4 mL/min, *P* = 150 bar, λ = 215 nm, t_R = 22.13 min (*R*,*R*), 25.69 min (*meso*), 28.08 min (*S*,*S*). MS (DCI/NH_3): *m*/*z* = 242 $[M + H - H_2O]^+$.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00436.

Crystallographic data for **8b** (CIF)
Crystallographic data for **8c** (CIF)
Crystallographic data for **8c** (CIF)
^1H and ^{13}C NMR spectra of all compounds, HPLC and SFC chromatograms of the ATH products, and thermal ellipsoid plots for the crystal structures of **8b**–**8d** (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: phannarath.phansavath@chimie-paristech.fr.
*E-mail: virginie.vidal@chimie-paristech.fr.

ORCID

Virginie Ratovelomanana-Vidal: 0000-0003-1167-1195

Notes

The authors declare no competing financial interest.

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