Heterogeneous Enantioselective Hydrogenation of Activated Ketones Catalyzed by Modified Pt-Catalysts: A Systematic Structure-Selectivity Study

Christian Exner,[a] Andreas Pfaltz,*[,a] Martin Studer,[b] Hans-Ulrich Blaser*[b]

[a] University of Basel, Department of Chemistry, St. Johanns-Ring 19, 4056 Basel, Switzerland
Fax: (+41)-61-267-1103, e-mail: Andreas.Pfaltz@unibas.ch
[b] Solvias AG, P. O. Box, 4002 Basel, Switzerland
Fax: (+41)-61-686-6100, e-mail: Hans-Ulrich.blaser@solvias.com

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Abstract: A systematic structure-selectivity study was carried out for the enantioselective hydrogenation of activated ketones with chirally modified Pt/Al_2O_3 catalysts. For this, 18 modifiers containing an extended aromatic system able to form a strong adsorption complex with the Pt surface, and a suitable chiral group with an amino function capable to interact with the keto group of the substrate (**HCd**, **Qd**, **HCn**, **Qn**, and semi-synthetic derivatives, as well as synthetic analogues) were prepared and tested on 8 different activated ketones in AcOH and toluene under standard conditions. It was found that relatively small structural changes of the substrate and/or modifier structures strongly affected the enantioselectivity, and that no "best" modifier exists for all substrates. The highest ees for all substrates were obtained with quinuclidine-derived modifiers in combination with naphthalene or quinoline rings, either in AcOH (substrates **1**–**5** and **8**, all carrying an sp^3 carbon next to the keto group) or toluene (**6** and **7**, with an sp^2 carbon next to the ketone). The presence and nature of the substituent R' at the quinuclidine significantly affected the ee (positive and negative effects). Certain combinations of an aromatic system and an amino function were preferred: For the quinuclidine moiety, quinoline and to a somewhat lesser extent naphthalene were a better match, while for the pyrrolidinylmethyl group anthracene was better suited. Methylation of the OH group often had a positive effect for hydrogenations in AcOH but not in toluene. With the exception of **8**, higher ees were obtained for the **Cd**/**Qn** series [leading to (*R*)-products] than for the **Cn**/**Qd** series [leading to (*S*)-products]. In several cases, opposite structure-selectivity trends were detected when comparing reactions in toluene and AcOH, indicating a significant influence of the solvent.

Keywords: enantioselective hydrogenation of ketones; heterogeneous modified catalyst; modifier; Pt-*Cinchona*; structure-ee relationship

Introduction

Empirical structure-selectivity correlations are an important tool for understanding and developing enantioselective catalysts. This is even more so for heterogeneous systems because of a serious lack of understanding of their mode of action. A significant shortcoming of most published studies in this area is the usually narrow range of substrates and reaction conditions employed. Due to an often high substrate specificity, this can severely limit the value of such investigations.

The hydrogenation of activated ketones with a chirally modified platinum catalyst is the most thoroughly investigated asymmetric heterogeneous catalytic process.[1] The effect of the modifier structure on the enantioselectivity has been studied extensively for the hydrogenation of the model substrate ethyl pyruvate and it has been demonstrated that an effective modifier must have two structural elements:[2] an (extended) aromatic system which is able to form a strong adsorption complex with the Pt surface, and a suitable chiral group with an amino function able to interact with the keto group of the substrate. For different types of activated ketones, the most selective modifiers up to now have been shown to be the naturally occurring cinchonidine **Cd** and its pseudo-enantiomer cinchonine **Cn** (with different relative configurations at C_8 and C_9) leading to the corresponding (*R*)- and (*S*)-alcohols, respectively (Figure 1). Generally, the (*S*)-enantiomer is formed with a lower ee compared to the (*R*)-enantiomer. The difference can be small to medium as shown for **1** and **2**, but is very significant in other cases.

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To the best of our knowledge, no systematic study comparing different modifiers for various activated ketones has been carried out. In most cases, only ethyl or methyl pyruvate was tested, and if other substrates were used, usually only one modifier was investigated. Furthermore, much more data are available for modifiers of the cinchonidine series than for the pseudo-enantiomeric cinchonine modifiers. Here we report a systematic study of 18 modifiers with 8 substrates in 2 solvents carried out under standard conditions. Evaluation of the results has led to empirical structure-selectivity relationships for various ketone/modifier combinations which show some general trends not documented so far.

Results and Discussion

Our study addressed three questions: i) What are the effects of varying the aromatic moiety (presence of N, R″, size) and the amino function (R′ at C-3, bicycle *vs.* monocycle)? ii) Is it possible to find a "best modifier" for a series of activated ketones for producing either the (*R*)- or the (S)-alcohol in high ees? iii) What is the effect of the substrate structure, especially the different functional groups adjacent to the keto group?

For this purpose we investigated 18 different modifiers (**HCd**, **Qd**, **HCn**, **Qn**, semi-synthetic derivatives, as well as synthetic analogues, many of them new, see Figures 1 and 2) for the hydrogenation of eight ketones (Figure 1). Six aliphatic ketones **1**–**5** and **8** carrying an sp^3 and two aromatic ketones **6** and **7** carrying an sp^2 carbon next to the C=O function were chosen. As activating groups, ester, acid and acetal functions were investigated. Acetic acid and toluene were used as solvents. Under our standard conditions, the conversions were 90–100% for the keto esters and the keto acid. Because of this, a discussion of the effect of the modifier structure on the reaction rates and acceleration factors is not possible. Lower conversions were usually obtained with keto acetals, but even here they were always > 20%. Selected enantioselectivities are summarized in Table 1. Since for practical reasons the standard reaction conditions chosen for our investigation differ from the optimized ones described in refs.[3–9] (Figure 1), our ees usually did not reach the best literature values. We are aware that changes in the reaction conditions (p, T and especially modifier concentration) can affect different substrate-modifier combinations differently. However, the fact that we observed the same trends as described in refs.[3–9] gives us confidence that the main effects are really due to an inherent structure-selectivity correlation and are not much distorted by unsuitable reaction conditions.

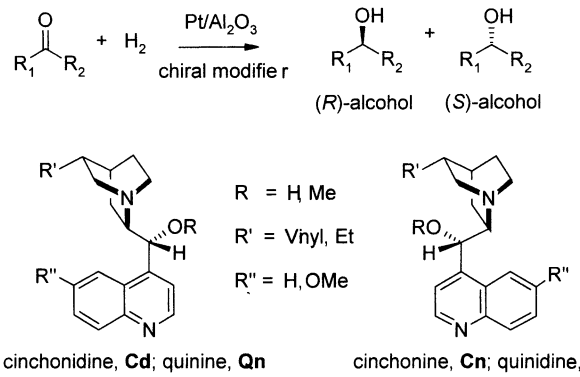
For reasons of clarity, only the series for the solvent giving higher enantioselectivity is depicted in Table 1 (a complete list of ees is given in the supporting information) with the exception of **5**. Here, the results for both solvents are given because the highest ees are obtained in toluene but the averages are higher in AcOH. In the upper part, results with modifiers based on the pseudo-enantiomeric **Cd** and **Cn**, and in the lower part with synthetic modifiers [only (*S*)-series at C-OH] are shown. Besides these, a variety of other modifiers was tested like the corresponding ***threo*-QQ**, **QN** and **QA**, **MeO-isoCn**, 2-quinolinyl and 1-anthracenyl derivatives. In all cases, the ees were much lower than those described here and these results will not be discussed further.

First conclusions can be drawn by cursory inspection of Table 1: i) The highest enantioselectivities for different substrates were obtained with different modifiers, there is definitively no "best modifier" for all substrates.

Table 1. Selected ee values for various combinations of substrates, modifiers and solvents [upper part left column % ee for (*S*)-, right column % ee for (*R*)-product; lower part % ee for (*S*)-product; **bold:** highest ee for a particular substrate].

Substrate/solvent Modifier	**1** AcOH	**2** AcOH	**3** AcOH	**4** AcOH	**5** AcOH	**5** toluene	**6** toluene	**7** toluene	**8** AcOH	Average
HCn/HCd	84/88	78/81	78/91	64/70	54/69	58/78	78/89	47/80	60/69	68/**81**
IsoCn/isoCd	88/88	81/80	82/93	67/**84**	62/65	**71**/**80**	80/**91**	55/**83**	64/34	**74**/79
MeOCn/MeOHCd	85/91	81/88	**93**/97	59/69	62/72	18/54	31/55	0/0	75/44	55/62
Qd/Qn	86/93	66/85	66/83	49/62	34/60	23/23	52/87	9/34	46/36	50/63
IsoQd/isoQn	84/88	76/78	81/72	60/58	39/49	40/56	66/84	9/32	51/33	58/63
MeOQd/MeOQn	**90**/**94**	82/**90**	92/**98**	73/69	61/**76**	4/23	8/45	0/0	**77**/64	53/60
(1*S*,2*R*)-(+)-QQ	82	78	69	61	58	66	**90**	**72**	59	72
(1*S*,2*R*)-(+)-QN	88	**86**	84	**74**	**67**	35	70	19	**70**	66
(1*S*,2*R*)-(+)-QA	79	63	80	56	54	32	60	3	31	51
(*S*)-(+)-PQ	70	57	8	30	29	31	52	43	34	41
(*S*)-(+)-PN	73	58	54	51	42	42	74	32	29	52
(*S*)-(+)-PA	76	71	70	61	51	69	84	n.a.	29	66
Average	82/*84*	73/*76*	71/*75*	59/*62*	51/58	41/*49*	62/*73*	26/*36*	52/*44*	58/63

Reaction conditions: 1.0 mg modifier, 10 mg 5% Pt/Al_2O_3 (JM 94), 1.0 mL solvent, 0.1 mL substrate, 50 bar H_2, 25 °C, 1 h. Reactions were carried out in glass vials (4 parallel experiments in a 50-mL autoclave).



	R_1	R_2	% ee (S)	Lit.	% ee (R)	Lit.
1	Me	COOEt	94	[3b]	98	[4]
2	$Ph(CH_2)_2$	COOEt	92	[4]	96	[4]
3	Me	$CH(OMe)_2$	88	[5]	97	[5]
4	$MeCOCH_2$	COOEt	63	[6]	78	[6]
5	$PhCOCH_2$	COOEt	59	[6]	86	[6]
6	Ph	COOMe	57[a]	[4]	98[a]	[7]
7	Ph	$CH(OEt)_2$	n.d.	-	81	[8]
8	$Ph(CH_2)_2$	COOH	32	[9]	85	[9]

Figure 1. Structure and numbering of substrates, structure of cinchona modifiers, and highest ees reported in the literature. [a] Only results for the corresponding ethyl ester reported.

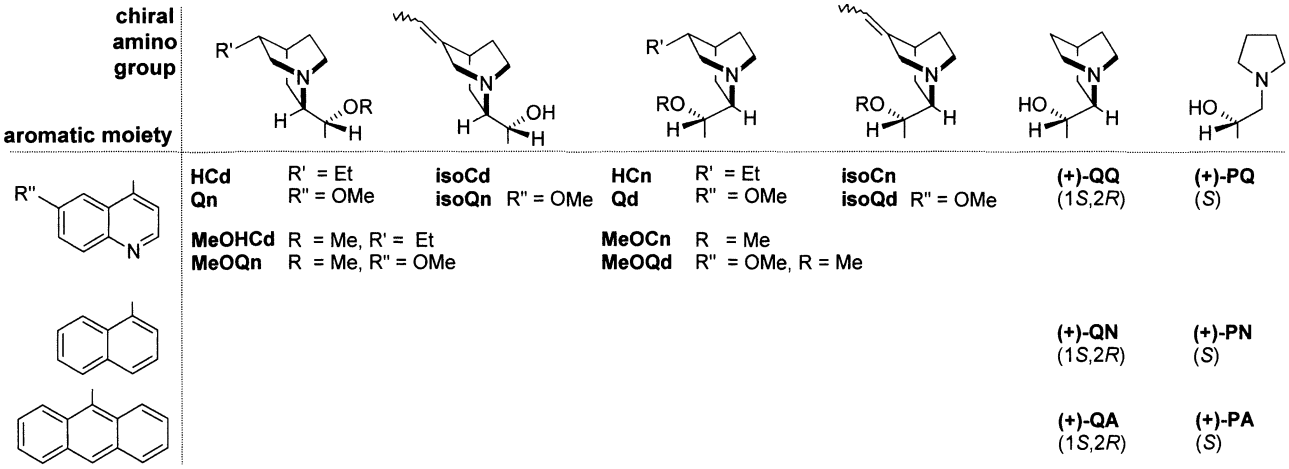


Figure 2. Structural elements (unless indicated otherwise, R and R″ = H, R′ = vinyl) and abbreviation of modifiers (**Cd** cinchonidine, **Cn** cinchonine, **Qn** quinine, **Qd** quinidine).

ii) It was confirmed that the **Cn**/**Qd** derivatives as well as the corresponding synthetic analogues with (*S*)-configuration at C-OH always give an excess of the (*S*)-enantiomer, whereas **Cd**/**Qn** derivatives always give predominantly the (*R*)-alcohol. iii) For ester and acetal substrates, *Cinchona*-derived modifiers were generally superior for the (*R*)-alcohols, whereas the highest ees for (*S*)-products were often observed with the synthetic modifiers. iv) The preferred solvent for the alkyl ketones **1**–**5** and **8** was found to be AcOH, whereas aryl ketones **6** and **7** gave higher ees in toluene. v) In general, **HCd** and **isoCd** were better modifiers for the *R*-series, while **isoCn** and **QQ** were better for the *S*-series. vi) With the exception of **8**, higher ees were obtained for the **Cd**/**Qn** series [(*R*)-products] than for the **Cn**/**Qd** series. vi) The highest ees were obtained with the aliphatic ketones **1**–**3**.

Specific Modifier Structure-Selectivity Effects

In order to analyze the effects of the various structural elements in more detail, we compared different pairs of modifiers in which only one element was changed and plotted the *ee differences* (ee obtained with the upper modifier minus ee obtained with the lower modifier) for all substrates in both toluene and acetic acid as depicted in Figures 3–7. We will discuss one analysis in more detail and summarize the others in analogy.

In order to analyze the effect of *R′ at the quinuclidine system* we compared **HCn** with **(+)-QQ**, **isoCn** with **(+)-QQ**, and **HCn** with **isoCn** for the (*S*)-series (Figure 3a), and **HCd** with **(−)-QQ**, **isoCd** with **(−)-QQ**, and **HCd** with **isoCd** for the (*R*)-series (Figure 3b). The left parts of Figure 3a and Figure 3b allow a comparison of R′ = Et and H, respectively. For the (*S*)-alcohols in toluene, the derivative with R′ = Et gave significantly lower ees than the modifier with R′ = H, whereas no uniform trend was observed in AcOH; for the (*R*)-products the Et substituent was superior in both solvents. The two middle parts allow a comparison of R′ = vinylidene and H, respectively. R′ = vinylidene instead of H gave mixed results for the (*S*)-products in toluene but, except for one substrate had a positive effect in AcOH. The two right parts finally allow a comparison of R′ = ethyl and

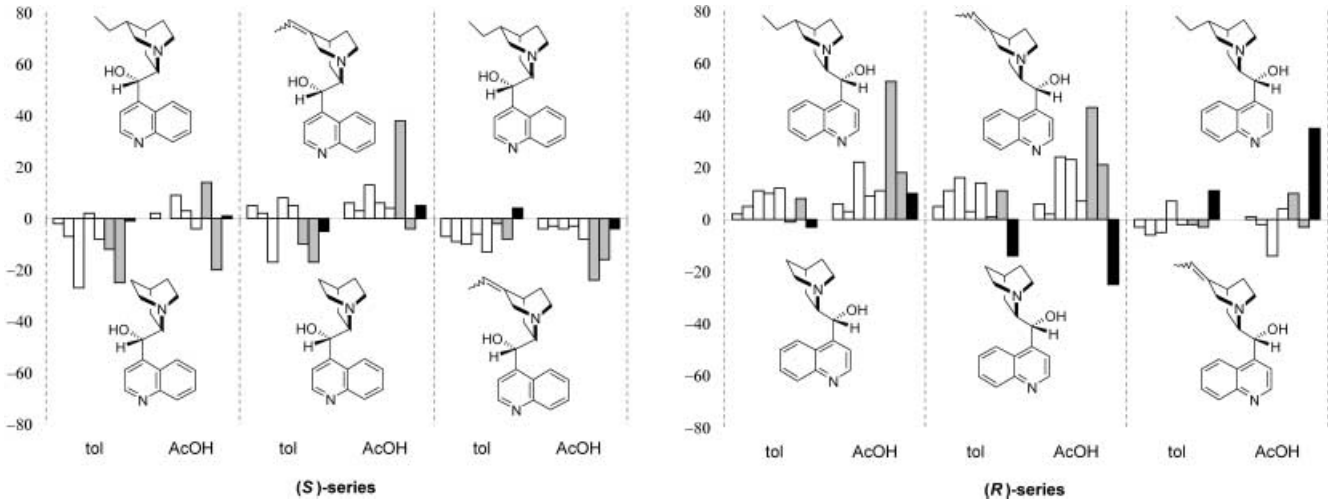


Figure 3. Effect of the nature of R' on enantioselectivity. The first five bars (white) always represent **1**–**5** (aliphatic substrates), the next two bars (gray) represent **6** and **7** (aromatic substrates), the black bar represents **8** (free acid). Y axis:Δee (%) of the two modifiers depicted. Figure 3a (left): (*S*)-series. Figure 3b (right): (*R*)-series.

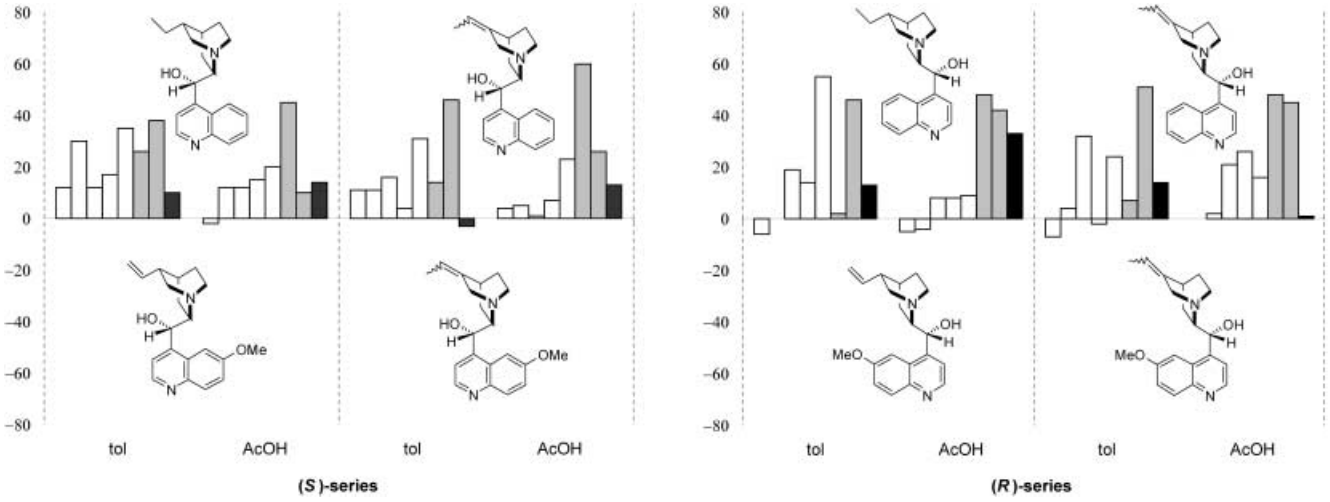


Figure 4. Effect of varying R″ on enantioselectivity.

vinylidene, respectively. R′ = Et instead of vinylidene had (with the notable exception of **8** in toluene) a negative effect for the (*S*)- and mixed effects for the (*R*)-products. From these comparisons we conclude that the modifiers with R′ = Et or vinyl are superior for producing (*R*)-alcohols, while for (*S*)-alcohols the ees usually increase in the order vinylidene > H > Et. This means that the presence of an R' substituent has a positive effect on the ee in the **Cd**/**Qn** series, while it has a negative effect in the **Cn**/**Qd** series. The same results were seen with the analogous **Qn** and **Qd** derivatives (no details shown, averages see Table 1).

The effect of *R''* *at the quinoline moiety* (Figure 4) can be summarized as follows: the unsubstituted **Cn** and **isoCn** derivatives (Figure 4, left) generally gave a much better performance than their counterparts carrying a methoxy group on the quinoline system. A similar picture emerged for **HCd** and **isoCd** (Figure 4, right). In a few cases a weak inverse effect was found, especially for **1** and **2** in AcOH. Independent experiments showed, however, that this was due to an artifact. Because of the high rates obtained with, e.g., the HCd/ethyl pyruvate/AcOH combination, this reaction was diffusion limited in our experimental set-up, whereas the slower combination Qn/ethyl pyruvate/AcOH was not. Since it is well known that lowering the hydrogen concentration (e.g., by diffusion limitation) decreases the enantioselectivity,[10,11] this explains the lower ee observed for HCd than for Qn. Control experiments with better mass transfer indeed gave higher ees for HCd.

The effect of O-*methylation* (R = Me) can be seen in Figure 5. In toluene, the non-methylated derivatives usually gave a significantly higher ee for the (*R*)- as well as for the (*S*)-products. In AcOH the methoxy deriva-

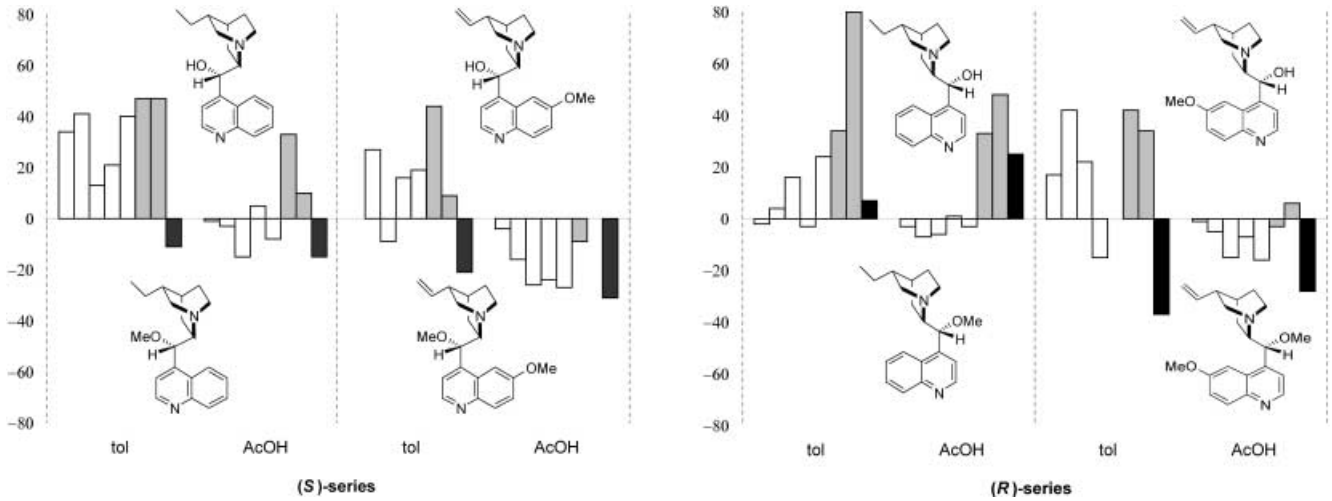


Figure 5. Effect of varying R on enantioselectivity.

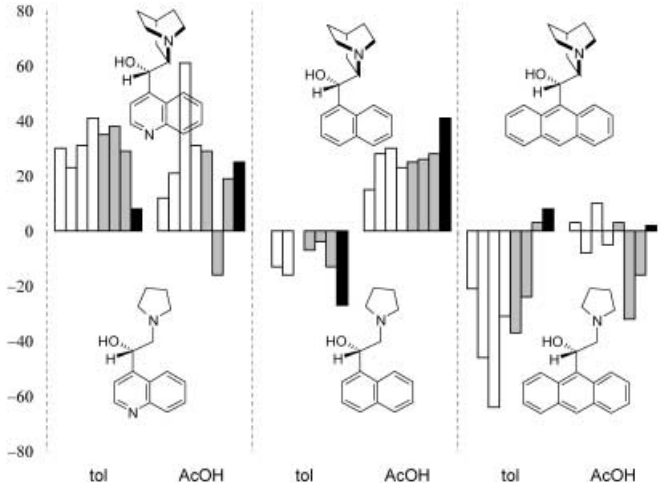


Figure 6. Effect of varying the amino function with different aromatic rings on enantioselectivity [(S)-series].

tives were generally better for the aliphatic ketones **1**–**5**, whereas for the other substrates both negative and positive effects were observed, strongly depending on the nature of R″ at the quinoline system.

As shown in Table 1, the highest ees for each substrate were obtained with quinuclidine-derived modifiers in combination with naphthalene or quinoline rings. Figure 6 shows the performance of different *amino function/aryl group* combinations. Here, modifiers with an *N*-pyrrolidinylmethyl group are compared with their quinuclidine analogues. The quinuclidine/quinoline combination gave higher ees in both solvents with only one exception. With naphthalene-derived modifiers, quinuclidine was superior in toluene while in AcOH the inverse effect was observed. Surprisingly, the quinuclidine ring in combination with anthracene was generally inferior in both solvents.

Finally, the effect of *replacing quinoline by anthracene or naphthalene* is depicted in Figure 7. With quinucli-

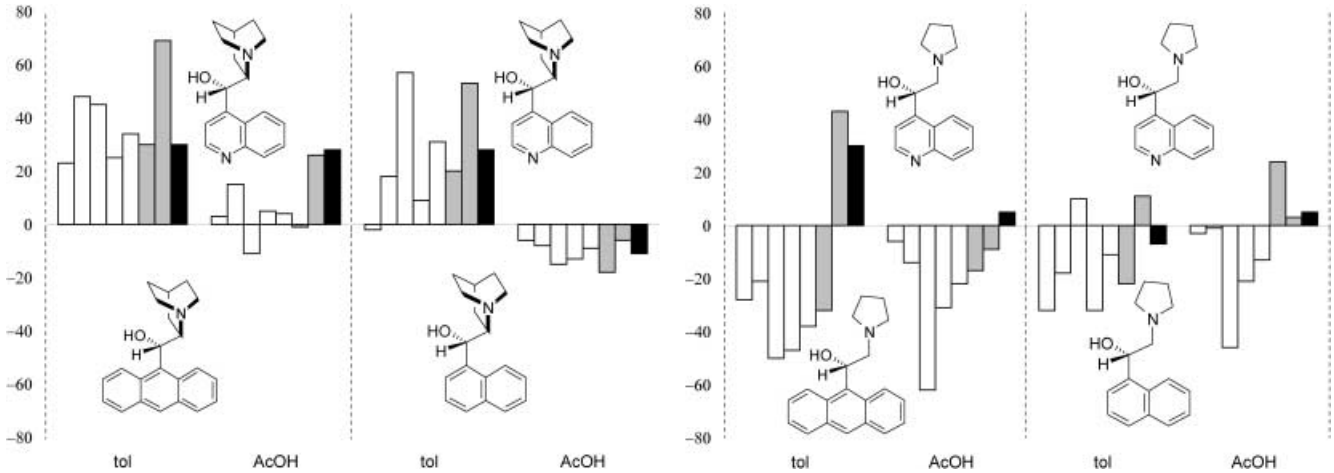


Figure 7. Effect of the aromatic moiety on enantioselectivity. Left part modifiers with quinuclidine, right part with *N*-pyrrolidinemethyl [(*S*)-series].

dine as chiral amino function, quinoline (toluene) or naphthalene (AcOH) were usually the best choice, while the ees with anthracene were generally lower. With the *N*-pyrrolidinylmethyl moiety, however, either anthracene or, somewhat less pronounced, naphthalene showed a better over-all performance than quinoline.

From these data, the following conclusions can be drawn

- It was confirmed that the presence of an extended aromatic system with a chiral group carrying an amino function are necessary but not sufficient prerequisites for high ees.
- For every substrate the highest ees were obtained with quinuclidine-derived modifiers in combination with naphthalene or quinoline rings.
- The substituent R' at the quinuclidine system has a more important influence than previously thought and can significantly affect the ee compared to the unsubstituted derivatives (positive and negative effects!).
- Both bicyclic and tricyclic aromatic systems rings can lead to high ees. For the sterically more demanding and more rigid quinuclidine, quinoline and to some lesser extent naphthalene were a better match, while for anthracene the smaller pyrrolidinylmethyl group was superior. The combination of the previously identified "best structural elements" anthracene and quinuclidine does not give the highest ees.
- **HCd** and **HCn** derivatives usually gave higher ees than the corresponding **Qn** and **Qd** which carry a methoxy substituent at the quinoline system.
- Methylation of the OH group often had a positive effect for hydrogenations in AcOH but not in toluene.

While this study was not designed to answer mechanistic questions, we would nevertheless like to briefly address the structure of the activated complex formed between the functionalized ketone and the modifier. There is sufficient evidence that the productive activated complex is created by the adsorbed modifier forming an H bond between the amino moiety and the carbonyl oxygen of the adsorbed ketone.[1,2,3c] For the combination of ethyl pyruvate and cinchonidine (and also some simpler synthetic modifiers) evidence from calculations[3c] and synthetic variations[12–14] have led to the proposal that for an optimal complex, the modifier has to be able to adopt the open(3) conformation as depicted in Figure 8a. Our results are basically compatible with this proposal, even though it is not possible to interpret the sometimes very strong influence of R, R', R″, the substrate structure and the solvent with this simple model.

Earlier it was found that synthetic modifiers with the larger anthracene gave higher ees in combination with a pyrrolidinylmethyl[2a] or piperidine-derived moiety.[14] It was suggested that the open(4) conformation (as depicted for **Cd** in Figure 8b), which might lead to lower ees, is not possible in this case.[2a] In addition, the adsorption of the modifier on the Pt surface might also be stronger. It was therefore disappointing that anthracene gave much lower ees when combined with quinuclidine than either quinoline or naphthalene. The reason for this is most likely that the very rigid quinuclidine moiety cannot adopt an optimal conformation when attached to the anthracene group, maybe because of unfavorable interactions with the hydrogen atom in the 1′ position (see Figure 8c). With the much smaller and more flexible pyrrolidinylmethyl group such interactions are less likely, and the beneficial effect of the large aromatic anthracene dominates.

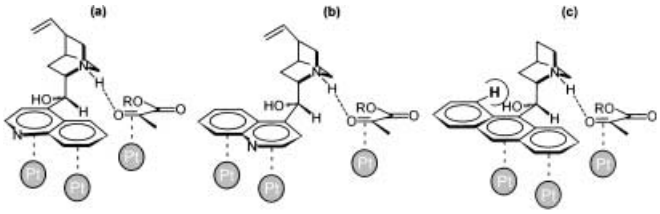


Figure 8. Activated complex between cinchona type modifiers and *trans* α-keto ester adsorbed on the Pt surface.[1,2,3c] **(a) Cd** in the open(3) conformation, **(b) Cd** in the open(4) conformation, **(c) QA**, open(3) conformation.

Specific Modifier Structure-Selectivity Effects

a) Substrates carrying an sp^3 carbon next to the activated ketone (aliphatic ketones)

For the monoketones **1**–**3** the highest enantioselectivities were always observed in AcOH with ees well above 80%: Relatively high ees could be achieved with most modifiers. The ees were somewhat lower for the diketones **4** and **5** and they seemed to be more sensitive to the combination of modifier and solvent. For **5**, the average ee was higher in AcOH but the highest ees were obtained in toluene. In all cases, the best modifiers were either derived from the natural alkaloids or closely related synthetic analogues like **QN**. While the differences between the two pseudo-enantiomers were usually not very large, *O*-methylation generally had a small beneficial effect in AcOH.

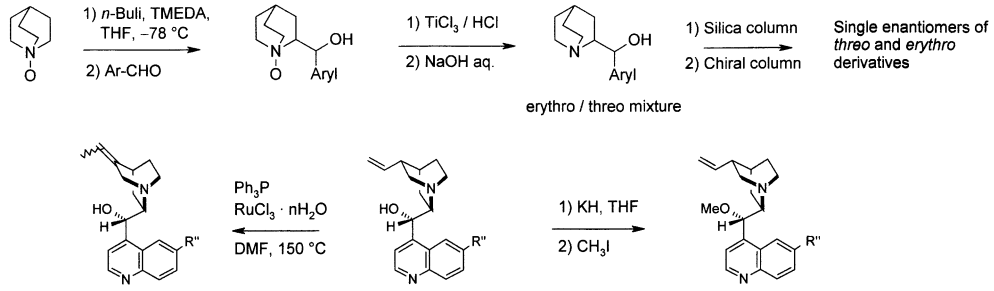
b) Substrates carrying an sp^2 carbon next to the activated ketone (aromatic ketones)

The trends observed for **6** and **7** were different compared to **1**–**5**. Here, the highest ees were observed in toluene, usually with the iso-derivatives or the closely related **QQ**. In contrast to **1**–**5**, the ees showed enormous fluctuations when applying different modifiers. While

the **HCn/HCd** and the **isoCN/isoCd** series gave high ees, derivatives carrying a methoxy group at the quinoline ring or at the stereogenic center led to much lower ees (sometimes zero!). The differences between the pseudo-enantiomers were also larger than for the aliphatic substrates.

c) Free ketoacid ***8***

In general, **8** showed a similar behavior as **1**–**5**, with relatively small ee variations for different modifiers. Interestingly, the (*S*)-series gave higher ees here in contrast to all other substrates. However, it has to be noted that AcOH and toluene might not be the best solvent for **8**. Previous studies suggested an isopropanol/water mixture to be the optimum for keto acids.[9]



Scheme 1. Synthesis of the modifiers.

Conclusion

Our systematic structure-selectivity study revealed the very high substrate specificity of this catalytic system and should be taken as a warning to propose a general reaction mechanism based on just a few isolated observations. Obviously, relatively small structural changes in substrate and/or modifier can strongly affect the enantioselectivity but to a varying degree and often in opposite manner for different substrates or when comparing reactions in toluene and AcOH. This indicates that the interactions between the substrate and the modifier depend on many factors. Nevertheless, we did find some common trends and our data serve as a good basis to select the optimal modifier for a particular transformation. Moreover, some of the new modifier-substrate combinations gave significantly higher ees than previously reported, especially for the (*S*)-products. Our results should also be a useful basis for further optimization of the modifier structure as well as the development of modifiers for other substrates.

Experimental Section

Synthesis of the Modifiers

HCn and **HCd** were synthesized according to ref.[2b] and **PQ**, **PN** and **PA** according to ref.[2a] All synthetic derivatives carrying a quinuclidine group were synthesized according to Scheme 1 (upper part), all methylated derivatives according to Scheme 1 (lower part, right side) and all isomerized derivatives according to Scheme 1 (lower part, left side). For a detailed description of the synthesis and the characterization of the modifiers, see supporting information.

Typical Hydrogenation Experiment

1.00 mg modifier, 10 mg catalyst [5% Pt/Al_2O_3 (JMC 94), pretreated for 2 h at 400 °C under hydrogen], 1.00 mL solvent and 100 μL substrate (**2**–**6**), 100 mg substrate (**7**, **8**) or 250 μL substrate (**1**) were placed into a 3-mL glass vial equipped with a magnetic stirring bar. Four such vials (three tests and one reference experiment) were placed into a 50-mL autoclave thermostatted at 25 °C. The autoclave was closed, purged with argon (3 times) and hydrogen (3 times) and then pressurized to 50 bar hydrogen pressure. The reactions were started by turning the magnetic stirrer on (1100 rpm). After 1 h, the pressure was released, and the autoclave was purged with argon (3 times). The vials were discharged, and the reaction mixtures were filtered through disk filters and analyzed. For analytical methods, see supporting material.

Acknowledgements

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