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A Highly Selective Ferrocene-Based Planar Chiral PIP (Fc-PIP) Acyl Transfer Catalyst for the Kinetic Resolution of Alcohols

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Abstract: Novel planar chiral ferrocene nucleophilic catalysts (Fc-PIP) containing both central and planar chiral elements were designed and synthesized for catalytic enantioselective acyl transfer of secondary alcohols. A remarkably efficient catalyst with high selectivity factors (up to $S = 1892$) was identified. Comparing the combination of central and planar chirality revealed a strong requirement for the "matched" chiral elements, indicating that the stereogenic center of the imidazole rings should present itself on the same face as the ferrocenyl fragment; otherwise, the catalyst is completely inactive. An exclusively stacked transition state that accounts for the high selectivity of the kinetic resolution of secondary alcohols is proposed. Notably, this newly designed catalyst family is suitable for the catalytic kinetic resolution of bulky arylalkyl carbinols, producing esters with extremely high ee (>99%).

In view of the importance of chiral bulky arylalkyl carbinols in asymmetric organic synthesis and their synthetic difficulty,[1] the catalyst reported herein provides important access to bulky alcohols in high optical purity.

Since the pioneering work of Vedejs in nonenzymatic catalytic kinetic resolution (KR)[2] of secondary alcohols using chiral phosphine[2a] and chiral 4-dimethylaminopyridine (DMAP) equivalents[2b] as nucleophilic acyl transfer catalysts, asymmetric nucleophilic acyl transfer catalysis for catalytic KR has been further developed.[3,4] Fu's planar chiral DMAP equivalent is an exemplary system of exquisite design (Figure 1)[4a,b] that is highly effective for catalytic KR, with selectivity factors (S) ranging from 32 to 95; the highest S value ($S = 95$) was obtained when bulky (*rac*)-phenyl-*tert*-butyl carbinol was employed as a substrate. These ferrocenyl-based systems rapidly became the gold standard in catalytic KR.[4c] Thereafter, several chiral DMAP-like catalysts incorporating elements of central,[4d,k,5] axial,[6] and pseudoplanar[7] chirality have been developed that show selectivity factors comparable to those of the earlier planar chiral DMAP equivalents. An important breakthrough was presented by Birman and co-workers,[8] who described another class of simple nucleophile design that incorporates a dihydroimidazole moiety along with the parent pyridine to generate the 2,3-dihydroimidazo[1,2-*a*]pyridine (DHIP) scaffold. Among those reported, the catalyst CF_3-PIP[8a] proved to be particularly effective in the catalytic KR of benzylic alcohols with excellent S values (up to 85). The high selectivity factors were reasoned to be due to the $\pi-\pi$ and cation$-\pi$ interactions between the pyridinium ring of the N-acylated catalyst and the arene ring of the alcohol. On the basis of this hypothesis, catalysts Cl-PIQ[8b] and BTM[8c] with extended π systems were developed (Figure 1), and the enhanced $\pi-\pi$ and cation$-\pi$ interactions[9]

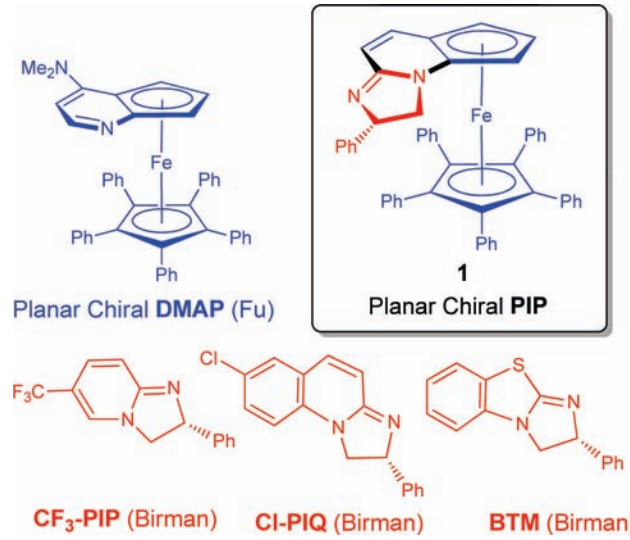

Figure 1. Representative nucleophilic catalysts and the design of planar chiral PIP **1**.

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were found to be extremely effective improvements for the catalytic KR of various secondary alcohols, with selectivity factors up to 117 and 355 respectively. Since cation$-\pi$ interactions have been invoked to explain the selectivity of nucleophilic catalysis[5b,d,10] and demonstrated to exert intramolecular control in flexible-sensor systems,[11,12] it is reasonable to expect that such phenomena may be operating here, although Houk and co-workers[13] elucidated a subtle interplay between steric and electronic effects that revealed CH$-\pi$ interactions to play an important role in some catalytic systems as well. While there have been reports dedicated to uncovering the origins of enantioselectivity in catalytic KR, the goal of unambiguous elucidation of the origin of enantioselectivity still remains.[14]

Encouraged by the success of the combination of planar chirality and central chirality in asymmetric catalysis,[15] we set out to develop the new class of planar chiral ferrocene nucleophilic catalysts **1**, which combine aspects from planar chiral DMAP and chiral imidazole catalysts (Figure 1).

Herein, we describe these new nonenzymatic nucleophilic catalysts **1** and their application to catalytic KR of arylalkyl carbinols with selectivity factors up to an impressive value of 1892, which is comparable to that achievable with enzymes. This new catalyst construct also serves as a good model for the elucidation of the experimental rationale of the importance of the $\pi-\pi$ and cation$-\pi$ interactions in delineating the control of stereoselection. Unlike enzymes, the general class of synthetic catalyst defined here can operate over a wide temperature range, is tolerant of a variety of solvent conditions, and offers wider substrate scope. The catalyst system described herein offers hitherto unachievable enzyme-like selectivity factors from a synthetic catalyst, and in view of the advantages of synthetic catalysts, this system can truly supplant enzyme-mediated reactions.

Birman[14,16] has discussed how the phenyl group on the stereogenic center of their imidazole rings exerts its stereochemical influence primarily through discriminating between the two faces of the carbonyl group of the in situ-generated amide in its transition state of acyl transfer. Although good empirical evidence was offered, it is generally difficult to ascribe the level of stereoselection to any one factor, since it is inherently difficult to corroborate computational and experimental observations.[14a] As with existing rationales for stereoselection in planar chiral nucleophilic catalysis,[4a] it is apparent that our system also benefits from the steric influence of the pentaphenyl floor, i.e., the "bottom" face is completely blocked by the η^5-C_5Ph_5 moiety.

The synthesis of desired planar chiral PIP **1** was accomplished as shown in Figure 2. In the case of **1a** as an example, the catalyst synthesis was conducted as follows: The preparation of racemic **3** according to Fu's protocol[4a] followed by the Pd-catalyzed C$-$N coupling of (*S*)-4-phenyloxazolidin-2-one to **3** gave two chromatographically separable diastereoisomers, (S,S_p)- and (S,R_p)-**4a** in 45 and 47% yield, respectively (92% overall yield). Hydrolysis of the resultant isomers in the presence of methanolic sodium hydroxide afforded the corresponding alcohols, which were then treated with $MsCl/Et_3N$ without further purification to furnish the two diastereoisomers (S,S_p)- and (S,R_p)-**1a** in 83 and 85% yield, respectively. The relative configurations of two isomers were assigned on the basis of the X-ray diffraction analysis of the isomer (S,S_p)-**1a** (Figure 2 inset).

With the eight planar chiral PIP derivatives ***S_p*-1a$-$d** and ***R_p*-1a$-$d** in hand, we proceeded to investigate their catalytic behavior in the catalytic KR of ($\pm$)-1-phenylpropanol under Birman's optimal resolution conditions at 0 °C;[8a] the results are summarized in Table 1. Surprisingly, only one compound, namely, ***R_p*-1a** ($S = 27$), gave catalytic results with S values comparable to those of the systems of Birman and Fu. In contrast, ***S_p*-1a** was completely catalytically inactive for acyl transfer even after a prolonged reaction time. These findings clearly indicated that the phenyl group attached to the stereogenic center of ***S_p*-1a** is bulky enough to shield the entire top face from effective acyl transfer.

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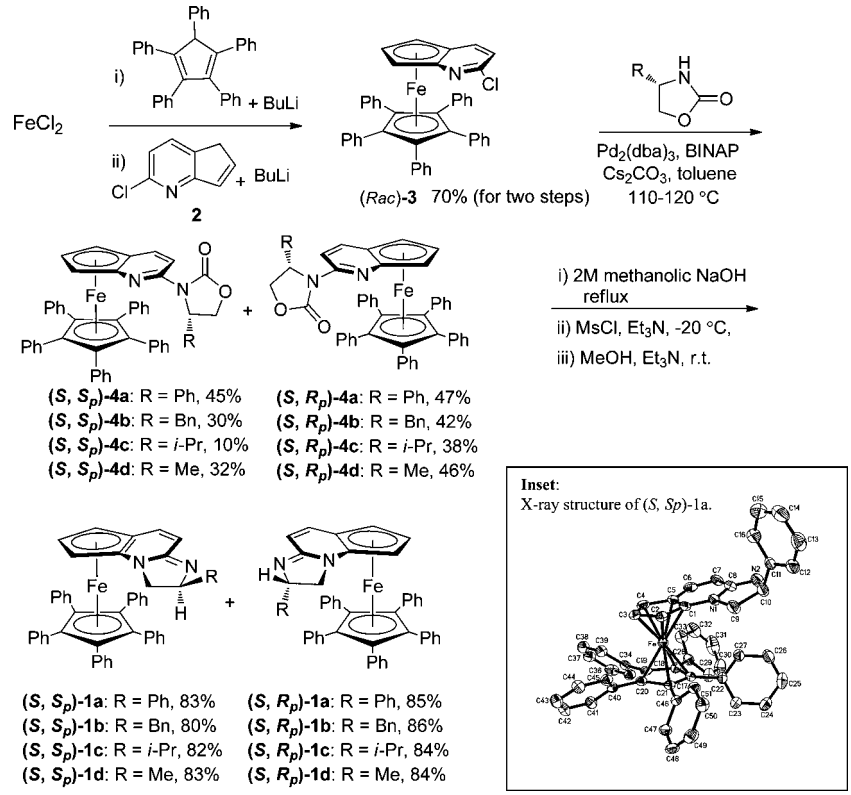
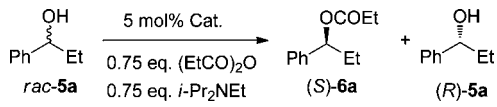


Figure 2. Synthesis of planar chiral PIP catalysts **1a**−**d**.

Table 1. Screening and Optimization of Planar Chiral PIP Catalysts **1a**−**d** in the KR of (±)-1-Phenylpropanol[a]



entry	catalyst	solvent	*t* (h)	**6a** ee (%)[b]	**5a** ee (%)[b]	C_{HPLC} (%)[c]	*S*[c]
1	S_p-**1a**	$CHCl_3$	10	ND[d]	–	–	–
2	S_p-**1a**	$CHCl_3$	24	ND[d]	–	–	–
3	R_p-**1a**	$CHCl_3$	7	77.2	94.2	55	27
4	S_p-**1b**	$CHCl_3$	10	ND[d]	–	–	–
5	R_p-**1b**	$CHCl_3$	7	35.4	95.9	73	7
6	S_p-**1c**	$CHCl_3$	10	ND[d]	–	–	–
7	R_p-**1c**	$CHCl_3$	7	1	4.4	81.5	1
8	S_p-**1d**	$CHCl_3$	10	3.8	0.7	15.8	1
9	R_p-**1d**	$CHCl_3$	7	68.5	64.9	48.7	10
10	R_p-**1a**	CH_2Cl_2	7	76.4	84.4	52.5	20
11	R_p-**1a**	$CHCl_3$	7	77.2	94.2	55.0	27
12	R_p-**1a**	*tert*-amyl alcohol	7	92.5	21.5	18.9	31
13	R_p-**1a**	THF	7	85.2	88.0	50.8	36
14	R_p-**1a**	Et_2O	7	92.3	71.1	43.5	53
15	R_p-**1a**	toluene	7	85.7	97.9	53.3	58
16	R_p-**1a**	toluene[e]	13	96.3	55.2	36.5	92
17	R_p-**1a**	toluene[f]	24	97.5	44.9	31.5	125
18	R_p-**1a**	toluene[g]	7	91.6	76.7	45.6	53
19	R_p-**1a**	toluene[h]	7	82.2	74.0	47.3	23
20	R_p-**1a**	toluene[i]	7	75.1	96.7	56.3	28

[a] Conditions: 0.4 M 1-phenylpropanol and 5 mol % catalyst at 0 °C. [b] Determined by chiral HPLC. [c] Calculated from the ee of the ester and unreacted alcohols. [d] Not determined. [e] The reaction was conducted at −20 °C. [f] The reaction was conducted at −40 °C. [g] Using 2 mol % catalyst R_p-**1a** instead. [h] Using 2 mol % catalyst R_p-**1a** and acetic anhydride instead. [i] Using 2 mol % catalyst R_p-**1a** and isobutyric anhydride instead.

According to Birman's computational study,[14a] a *splayed* transition state in the system they studied was found to be 7.6 kcal/mol less stable than that of a stacked transition state. A plausible transition state, TS I, is shown in Figure 3; such a transition state exhibits a favorable cation−π interaction and minimal steric interactions and is in complete agreement with the experimental observations of this report. As such, a stacked transition state can be considered as the exclusive reaction manifold, as supported by the fact S_p-**1a** was completely catalytically inactive. The use of this rationale and these observations serves to further elucidate Birman's PIP,[8a] PIQ,[8b] and BTM[8c] systems: where similar facial selectivity can now be deduced, the $\pi-\pi$ and cation−π interactions of the stacked conformer are the main factors for attaining the high selectivity. The one face is essentially completely blocked by the phenyl substituent, and the selectivity results from favoring a stacked transition state over a splayed one. However, these interpretations suggest that any bulky group in place of the phenyl group in R_p-**1** would give the same levels of selectivity factor, but catalysts R_p-**1c**,**d** bearing alkyl groups exhibited drastically

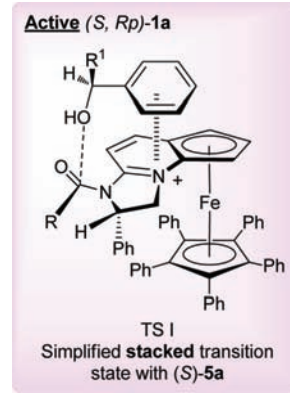
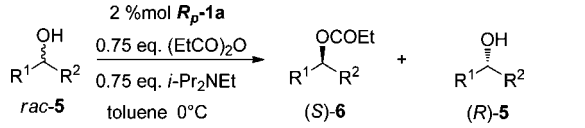


Figure 3. Possible transition state for catalysts (***S***, R_p)-**1a** interacting with (*S*)-**5a**.

Table 2. Scope and Generality of the R_p-**1a**-Catalyzed KR of Secondary Alcohols



entry	R^1	R^2	t (h)	**6** ee (%)	**5** ee (%)	C_{HPLC} (%)	S^c
1	Ph	Me	8	83.0	87.6	51.3	31 (33)
2	Ph	Et	7	85.7	97.9	53.3	58 (41)
3	Ph	*i*-Pr	8	92.4	92.3	50.0	84 (59)
4	Ph	*t*-Bu	10	99.1	81.1	45.0	534 (117)
5[a]	Ph	*t*-Bu	18	99.5	72.1	42.0	801
6[b]	**Ph**	***t*-Bu**	**24**	**99.8**	**62.0**	**38.3**	**1892**
7	*o*-OMePh	Me	8	94.1	54.5	36.7	57
8	*m*-OMePh	Me	8	86.9	90.1	50.9	44
9	*p*-OMePh	Me	8	86.1	83.9	49.3	35
10	1-naphthyl	Me	7	86.1	94.1	52.2	47
11	*p*-ClPh	Me	8	85.1	92.7	52.1	41
12	*p*-BrPh	Me	8	82.5	94.6	53.4	37
13	styryl	Me	8	85.2	36.1	29.7	18

[a] Reaction run using 5 mol % R_p-**1a** at −20 °C. [b] Reaction run using 5 mol % R_p-**1a** at −40 °C. [c] Data in parentheses are *S* values for Birman's Cl-PIQ.[14]

reduced selectivity factors, suggesting a noninnocent role of the aromatic appendage, such as the difference in forming the enantioselectively favored conformation upon acylation of the catalyst.[16]

While newly synthesized planar chiral catalyst R_p-**1a** was an effective catalyst for the KR of (±)-1-phenylpropanol, the structural novelty as well as the potential application in model studies to elucidate origins of the enantioselectivity prompted us to further optimize the resolution conditions.

Screening of solvents (Table 1, entries 10−15) revealed that toluene gives the best selectivity factor ($S = 58$), which is higher than the value $S = 41$ obtained with Cl-PIQ.[8b] Further optimization (Table 1, entries 15−17) revealed that a much higher selectivity factor $S = 125$ was obtained when the reaction was performed at −40 °C, although a concomitant loss in activity was apparent (Table 1, entry 17). Decreasing the catalyst loading to 2 mol % gave a similar selectivity and slightly lower conversion (Table 1, entry 18). Use of acetic anhydride as the electrophile source led to reduced selectivity (Table 1, entry 19), and in contrast to Birman's result,[8c] the bulkier isobutyric anhydride also resulted in lower selectivity (Table 1, entry 20).

The above optimization led us to established that 2 mol % R_p-**1a**/$(EtCO)_2O$ (0.75 equiv)/i-Pr_2NEt (0.75 equiv)/toluene/0 °C were the optimal reaction conditions for catalytic KR. With these conditions, the generality and substrate scope were probed. A series of arylalkyl carbinols were screened, and from Table 2 it can be seen that kinetic resolution proceeded smoothly under the optimal reaction conditions for all of the arylalkyl carbinols tested. Selectivity factors ranging from 31 to 534 were observed, and notably, this is the first example of a catalytic KR of secondary alcohols with a selectivity factor $S > 500$ where the resultant ester was obtained in >99% ee, which is comparable only to enzymatic catalysis. Furthermore, it was found that our new catalyst has a significant steric effect on the alkyl part of alcohols, and bulkier alkyl groups gave higher selectivity factors (Table 2, entries 1−4). To our delight, exploiting the improved selectivity at lower temperatures further raised the *S* value to 801 at −20 °C and amazingly to 1892 at −40 °C (Table 2, entries 5 and 6).

According to Birman's computational study,[14a] steric interactions between the alkyl group and the virtually coplanar ortho hydrogen of the phenyl group can account for the observed stereochemical outcome, thus explaining the enantioselectivity trends we observed with the size of the alkyl group.

In conclusion, we have developed a remarkably effective planar chiral PIP catalyst for the enantioselective acyl transfer of secondary alcohols to achieve selectivity factors up to $S = 1892$. Notably, this newly designed catalyst, R_p-**1a**, is suitable for the catalytic KR of bulky arylalkyl carbinols to afford the corresponding esters with with high ee (99.8%) and *S* values (up to 1892). It is notable that the enzymatic catalytic KR of bulky arylalkyl carbinols has not been reported.[17] Our new catalytic system provides a competitive and attractive synthetic method for obtaining highly optical pure bulky alcohols.[1] Further applications of R_p-**1a** to various substrates and catalytic processes, especially involving bulky arylalkyl carbinols, are ongoing in our laboratory.

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Supporting Information Available: Synthetic procedures for planar chiral PIPs **1a**−**d** and corresponding spectral data; X-ray analysis data for (S,S_p)-**1a** (CIF); general experimental procedures; and HPLC data analysis for all kinetic resolutions of *rac*-**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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