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(*R*)-(+)-*N*-Methylbenzoguanidine ((*R*)-NMBG) catalyzed acylative kinetic resolution of racemic 3-hydroxy-3-aryl-propanoates

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ABSTRACT

(*R*)-(+)-*N*-methylbenzoguanidine ((*R*)-NMBG) functioned as an efficient acyl transfer catalyst for the acylative kinetic resolution of racemic β-hydroxy esters using cyclohexane carboxylic anhydride under mild reaction conditions. A *tert*-butyl ester moiety is necessary to achieve a high selectivity. The effects of the substituents on the aromatic rings of the substrates were systematically investigated, and diverse substrates participated in the reaction with good *s*-values (>20) irrespective of the type of substituents and their patterns, except for *o*-methoxy group.

The kinetic resolution (KR) of racemic secondary alcohols by asymmetric acylation is one of the more reliable and facile methods to obtain optically pure compounds. Therefore, much effort has been devoted to the development of efficient methods for KR. Although several enzymatic methods[1] have been developed to progress from laboratory scale to industrial scale, nonenzymatic chemical methods had not been reported till the middle of 1990s. The first nonenzymatic acylative KR of racemic alcohols was reported by Evans[2] and Vedejs[3] using a stoichiometric amount of chiral acylating agents. Shortly thereafter, pioneering studies on the catalytic acylative KR of alcohols were reported by the research groups of Vedejs,[4] Oriyama,[5] Fuji and Kawabata,[6] Fu,[7] and Miller.[8] The investigated substrates were mainly limited to racemic secondary benzylic alcohols, cycloalkanols, propargylic alcohols, and allylic alcohols till recently, even though several useful protocols for this purpose have been developed.[9] During the last decade, the KR of other more synthetically valuable substrates such as Morita–Baylis–Hillman adducts,[10] 2,2-difluoro-3-hydroxy-3-aryl-propanoates,[11] 2-hydroxyalkanoates,[12] 2-hydroxy-γ-butyrolactones,[13] 2-hydroxyphosphonates,[14] 1,2-azidoalcohols,[15] and 2-hydroxy-2-aryl-ethylphosphonates,[16] have been reported. On one hand, optically active β-hydroxy esters are frequently utilized as chiral building blocks for the synthesis of biologically active compounds[17] and pharmacologically active compounds.[18] Therefore, several asymmetric syntheses have been intensively developed for preparing these compounds, such as the asymmetric Mukaiyama aldol reaction using organometallic complexes[19] and organocatalysts,[20] the Reformatsky reaction,[21] and the asymmetric reduction of the corresponding β-keto esters.[22] The enzymatic KR of racemic aromatic β-hydroxy esters has been already developed.[18b,23] The first nonenzymatic acylative KR of racemic aromatic β-hydroxy esters was recently achieved by Dinér[24] using Fu's chiral planar ferrocenyl DMAP catalyst.[7] Previously, we achieved the KR of racemic benzylic alcohols (±)-**1** with free carboxylic acids by asymmetric esterification using pivalic anhydride as the coupling reagent catalyzed by (*R*)-*N*-methylbenzoguanidine ((*R*)-NMBG; **3**)) (Scheme 1, (1)).[25] Moreover, we achieved an efficient enantiodivergent synthesis of both the enantiomers of centrolobine using this protocol as the key step.[26] Thus, it was hypothesized that this protocol can also be applied to aromatic β-hydroxy esters (±)-**4** in the same manner (Scheme 1, (2)). Herein, we report the efficient acylative KR of various racemic 3-hydroxy-3-aryl-propanoates catalyzed by (*R*)-NMBG (**3**) as the chiral acyl transfer catalyst.

To explore a suitable acyl donor, the KR of racemic β-hydroxy ester (±)-**6** was selected as the model reaction and investigated using several types of carboxylic anhydrides catalyzed by (*R*)-NMBG (**3**) in Et_2O at room temperature for 24 h, the previously established conditions (Table 1).[25] The KR of (±)-**6** was carried out with diphenylacetic anhydride (DPHAA)[12b] (**8a**), and cyclohexane carboxylic anhydride (**8b**), both of which were efficient acyl components in a previous study;[25] the reactions smoothly proceeded with good *s*-values[27] (entries 1 and 2). Compared to

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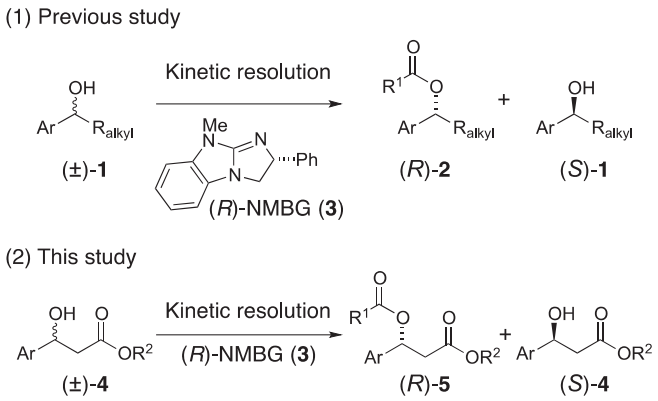
0040-4039/



Scheme 1. Previous study (**1**) and this study (**2**).

propionic anhydride (**8c**) and isobutyric anhydride (**8d**), the latter branched substituent showed better results than the former normal substituent (entries 3 and 4). In contrast, aromatic carboxylic anhydride **8e** with a very low *s*-value was not effective for the reaction (entry 5).

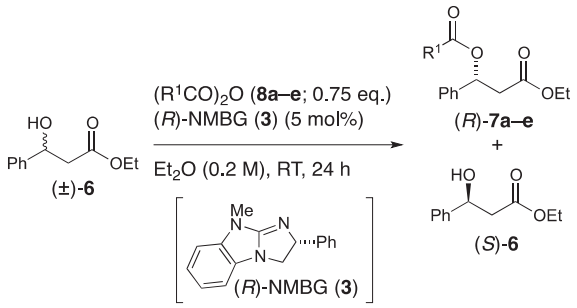
Next, to evaluate the effect of the structure of ester moiety on the substrates, the KR of diverse racemic β-hydroxy esters (±)-**9a**–**h** was investigated using both DPHAA (**8a**), and cyclohexane carboxylic anhydride (**8b**) under the abovementioned conditions (Table 2). First, the reaction was carried out using DPHAA (**8a**) (entries 1–8). The KR of **9a** and **9b** bearing normal substituents (R^2 = Et and Bn) on the ester moiety was carried out to afford good *s*-values (entries 1 and 2). On the other hand, the reaction of **9c**–**e** bearing disubstituted substituents (R^2 = ^{i}Pr, $CHPh_2$, and $^{c}C_6H_{11}$) showed better results (entries 3–5). The reaction of **9f** with a trisubstituted substituent (R^2 = ^{t}Bu) smoothly proceeded with a high *s*-value regardless of the steric effect (entry 6). When the methyl group(s) was replaced with a phenyl group(s) at the R^2 substituent of **9f**, the reactivity was enhanced; however, the selectivity decreased (entries 7 and 8). When anhydride **8b** was used, the same tendency was observed, and the selectivity slightly improved in the corresponding case of **8a** (entries 9–17). Among all the entries, the highest *s*-value was obtained in the reaction of **9f** with **8b** (entry 15). Under the conditions in entry 15, it was found that both the reactivity and selectivity decreased upon decreasing the catalyst loading from 5 to 2 mol % (entry 18). In an attempt to increase the reaction efficiency, the reaction time was prolonged to 48 h; however, the conversion was not significantly improved (entry 19).

With the optimized reaction conditions, three other types of isothiourea catalysts, (*R*)-BTM (**12**)[28] and (*R*)-HBTM (**13**),[28b,29] reported by Birman et al., and HBTM-2.1 (**14**),[30] reported by Smith et al., that served as efficient acyl transfer catalysts, were applied to the KR of (±)-**9f** (Table 3). The reaction of (±)-**9f** was carried out with 0.75 equiv of anhydride **8b** and a catalytic amount of (*R*)-BTM (**12**) to obtain a moderate *s*-value (entry 2). When the same reactions were conducted with (*R*)-HBTM (**13**) and HBTM-2.1 (**14**), both the reactions proceeded far beyond 50% conversion, affording the corresponding chiral alcohols **9f** in >99% ee (entries 3 and 5). Because the exact ee of **9f** could not be determined by HPLC analyses, the *s*-values were not evaluated under the conditions. Thus, the reactions were reinvestigated by reducing the amount of anhydride **8b** to 0.5 equiv. A moderate *s*-value was obtained using (*R*)-HBTM (**13**) (entry 4), and almost the same *s*-value was obtained in the case of (*R*)-NMBG (**3**) using HBTM-2.1 (**14**) (entry 6 vs entry 1).

To assess the generality of this novel method and systematically explore the electronic and steric effects on the aromatic rings of the substrates, a series of racemic β-hydroxy esters (±)-**15a**–**k** with carboxylic anhydride **8b** was investigated under the optimized reaction conditions (Table 4). The KR of **15a**–**c** with methyl substituents on the aromatic rings of the substrates smoothly proceeded in almost 50% conversion with good *s*-values in all the cases, irrespective of their positions (entries 1–3). Similarly, the KR of methoxy-substituted substrates **15d**–**f** was investigated; the reactions were influenced by the substitution patterns. The reaction of **15d** with an *ortho*-methoxy group resulted in poor reactivity and a low *s*-value (entry 4). On the other hand, the reactions of **15e** and **15f** with *meta*- and *para*-methoxy groups smoothly proceeded with good *s*-values, respectively (entries 5 and 6). The same tendency was observed in the case of chloro-substituted substrates **15g**–**i**, and better results were obtained compared to the corresponding cases of methoxy-substituted substrates (entries 7–11). The reactions of α- and β-naphthyl-substituted substrates **15j** and **15k** were also investigated; they afforded a high selectivity (entries 12–15).

In summary, we achieved the nonenzymatic acylative KR of β-hydroxy esters with cyclohexane carboxylic anhydride in the

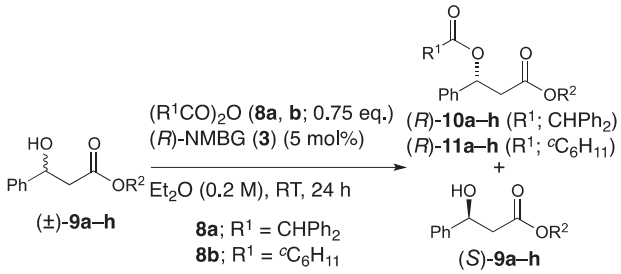
Table 1
(*R*)-NMBG catalyzed KR of (±)-**6** using various carboxylic anhydrides **8a**–**e**



Entry	R^1	Yield (**7**; **6**)[a] (%)	ee (**7**; **6**) (%)	*s*
1	Ph_2CH (**a**)	43; 46	83; 66	22
2	$^{c}C_6H_{11}$ (**b**)	41; 50	83; 80	26
3	Et (**c**)	32; 57	74; 44	10
4	^{i}Pr (**d**)	44; 33	72; 79	14
5	Ph (**e**)	19; 69	14; 2	1

[a] Isolated yield.

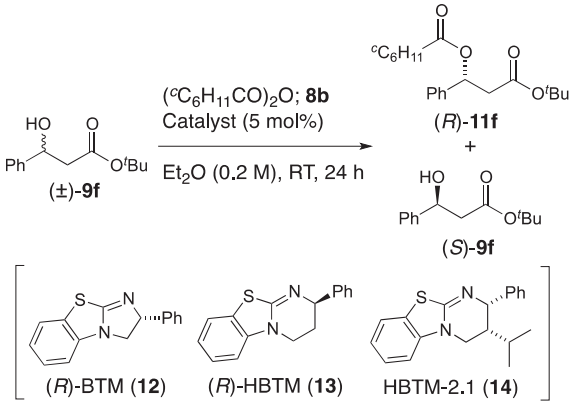
Table 2
Examination of the effect of the ester moiety



Entry	R^1, R^2	Yield (**10/11**; **9**)[a] (%)	ee (**10/11**; **9**) (%)	*s*
1[b]	$CHPh_2$, Et (**a**)	43; 46	84; 66	23
2	$CHPh_2$, Bn (**b**)	43; 52	84; 68	24
3	$CHPh_2$, ^{i}Pr (**c**)	36; 47	87; 68	29
4	$CHPh_2$, $CHPh_2$ (**d**)	41; 43	84; 91	37
5	$CHPh_2$, $^c C_6H_{11}$ (**e**)	41; 50	87; 70	29
6	$CHPh_2$, ^{t}Bu (**f**)	43; 40	89; 76	39
7	$CHPh_2$, $C(CH_3)_2Ph$ (**g**)	57; 38	68; 95	19
8	$CHPh_2$, $C(CH_3)Ph_2$ (**h**)	55; 43	60; 96	15
9[c]	$^c C_6H_{11}$, Et (**a**)	41; 50	83; 80	26
10	$^c C_6H_{11}$, Bn (**b**)	51; 48	82; 93	35
11	$^c C_6H_{11}$, ^{i}Pr (**c**)	50; 35	85; 94	43
12	$^c C_6H_{11}$, $CHPh_2$ (**d**)	55; 39	69; >99	ND[d]
13[e]	$^c C_6H_{11}$, $CHPh_2$ (**d**)	39; 51	82; 76	23
14	$^c C_6H_{11}$, $^c C_6H_{11}$ (**e**)	50; 38	85; 95	44
15	$^c C_6H_{11}$, ^{t}Bu (**f**)	48; 43	89; 91	54
16	$^c C_6H_{11}$, $C(CH_3)_2Ph$ (**g**)	53; 39	76; 94	24
17	$^c C_6H_{11}$, $C(CH_3)Ph_2$ (**h**)	57; 30	70; 97	22
18[f]	$^c C_6H_{11}$, ^{t}Bu (**f**)	25; 70	91; 31	28
19[g]	$^c C_6H_{11}$, ^{t}Bu (**f**)	31; 69	87; 38	22

[a] Isolated yield.
[b] Same as in Table 1, Entry 1.
[c] Same as in Table 1, Entry 2.
[d] Not determined.
[e] The reaction was carried out using 0.55 equiv of **8b**.
[f] The reaction was carried out using 2 mol % of **3** for 24 h.
[g] The reaction was carried out using 2 mol % of **3** for 48 h.

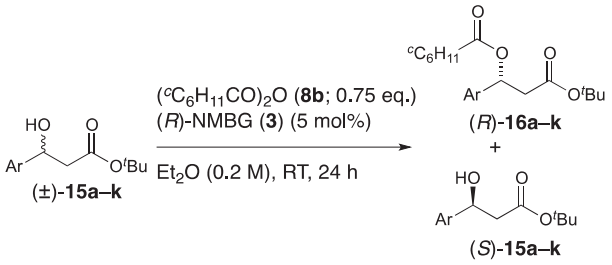
Table 3
Examination of the catalysts



Entry	Catalyst	Yield[a] (**11f**; **9f**) (%)	ee (**11f**; **9f**) (%)	*s*
1[b,c]	(*R*)-NMBG (**3**)	48; 43	89; 91	54
2[c]	(*R*)-BTM (**12**)	52; 48	75; 82	18
3[c]	(*R*)-HBTM (**13**)	70; 29	−40; >−99[d]	ND[e]
4[f]	(*R*)-HBTM (**13**)	44; 50	−72; −67[d]	12
5[c]	HBTM-2.1 (**14**)	65; 24	37; >99	ND[e]
6[f]	HBTM-2.1 (**14**)	38; 50	92; 71	51

[a] Isolated yield.
[b] Same as in Table 1, Entry 1.
[c] The reaction was carried out using 0.75 equiv of **8b**.
[d] Enantiomers.
[e] Not determined.
[f] The reaction was carried out using 0.50 equiv of **8b**.

Table 4
(*R*)-NMBG catalyzed KR of a variety of racemic aromatic β-hydroxy esters with anhydride **8b**



Entry	Ar	Yield (**16**; **15**)[a] (%)	ee (**16**; **15**) (%)	*s*
1	*o*-MeC_6H_4 (**a**)	47; 48	91; 84	55
2	*m*-MeC_6H_4 (**b**)	44; 47	89; 77	41
3	*p*-MeC_6H_4 (**c**)	49; 51	91; 88	59
4[b]	*o*-$MeOC_6H_4$ (**d**)	16; 81	77; 13	9
5	*m*-$MeOC_6H_4$ (**e**)	47; 47	87; 89	44
6	*p*-$MeOC_6H_4$ (**f**)	48; 52	87; 83	39
7	*o*-ClC_6H_4 (**g**)	44; 51	83; 75	24
8	*m*-ClC_6H_4 (**h**)	62; 38	60; >99	ND[c]
9[d]	*m*-ClC_6H_4 (**h**)	49; 46	88; 91	48
10	*p*-ClC_6H_4 (**i**)	59; 35	67; >99	ND[c]
11[d]	*p*-ClC_6H_4 (**i**)	50; 48	88; 92	53
12	α-Np (**j**)	48; 44	81; >99	ND[c]
13[d]	α-Np (**j**)	48; 44	90; 99	93
14	β-Np (**k**)	54; 46	82; >99	ND[c]
15[d]	β-Np (**k**)	50; 50	89; 93	60

[a] Isolated yield.
[b] Average of three runs.
[c] Not determined.
[d] The reaction was carried out using 0.55 equiv of **8b**.

presence of (*R*)-NMBG as an efficient chiral acyl transfer catalyst. Diverse optically active β-hydroxy esters were obtained from the reaction. Further studies on this method are underway in our laboratory to expand the substrate scope and apply this method to the synthesis of biologically active chiral compounds.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.09.014.

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