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Silylative Kinetic Resolution of Racemic 2,2-Dialkyl 5- and 6-Membered Cyclic Benzylic Alcohol Derivatives Catalyzed by Chiral Guanidine, (*R*)-*N*-Methylbenzoguanidine

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Abstract. Efficient silylative kinetic resolution of racemic 2,2-dialkyl 5- and 6-membered cyclic benzylic alcohols was achieved using diphenylmethylchlorosilane ($Ph_2MeSiCl$) or phenyldimethylchlorosilane ($PhMe_2SiCl$) as a silyl source catalyzed by chiral guanidine. The reaction could be applied to a broad range of 2,2-dialkyl 1-indanols with good *s*-values, irrespective of the electronic nature of the substituent on the aromatic ring of the substrates and the type of substituent at the C2-position. In addition, several 2,2-dimethyl 6-membered cyclic and heterocyclic alcohols could be adopted in the reaction.

Keywords: Guanidine; Indanols; Kinetic resolution; Organocatalysis; Silylation

The optically active 2,2-dimethyl 1-indanol moiety is frequently found in chiral catalysts such as the electrophilic selenium catalyst **1**[1] and organoiodine catalyst **2**[2] developed by Maruoka et al., as well as in biologically active compounds such as alcyopterosin I (**3**),[3] radulactone (**4**),[4] pterosin D (**5**),[5] and pterolactone A (**6**)[6] (Figure 1). Diastereomeric resolution techniques have been used obtain catalysts **1**[1] and **2**.[2] On the other hand, although Snyder et al. reported the first asymmetric synthesis of *ent*-alcyopterosin I *ent*-(**3**) by the asymmetric reduction of the corresponding ketone at the final step, the optical purity was only 57% ee (99% yield).[7,8] Two other methods— enantioselective reduction of *tert*-alkyl ketones using a chiral Ru complex as the catalyst, developed by Noyori et al.,[9] and (ii) chiral tartaric acid-derived borinic ester-catalyzed reduction developed by Singaram et al.[10]—were adopted for the same reaction, but the desired reaction did not occur in both cases.[7] Similarly, the first asymmetric synthesis of radulactone (**4**)[11] was achieved by the asymmetric reduction of the corresponding ketone via Corey-Bakshi-Shibata (CBS) reduction,[12] but the chemical yield was only 38% (87.2% ee). Thus, there are few options for practical asymmetric synthetic routes toward the chiral 2,2-dimethyl 1-indanol moiety.

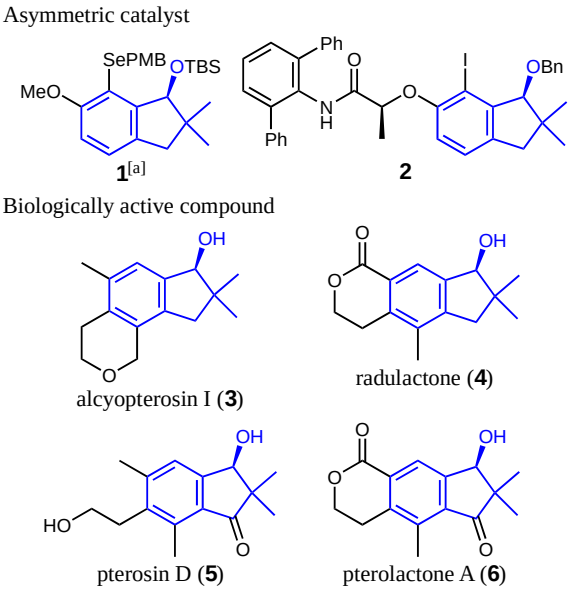

Figure 1. Representative compounds containing the 2,2-dimethyl 1-indanol moiety. [a] PMB: *p*-methoxybenzyl

On the other hand, kinetic resolution of racemic alcohols is well known as one of the most reliable and facile methods for providing optically active compounds, and much effort has been undertaken in this direction till date. The kinetic resolution of racemic β,β-disubstituted α-hydroxy-γ-butyrolactones by asymmetric carbamoylation,[13] acylation,[14] and silylation,[15] and the kinetic resolution of β,β-disubstituted α-hydroxy esters by asymmetric carbamoylation[16] have been reported. To the best of our knowledge, however, there are no examples of chemical or enzymatic methods for the efficient kinetic resolution of racemic 2,2-dialkyl 1-

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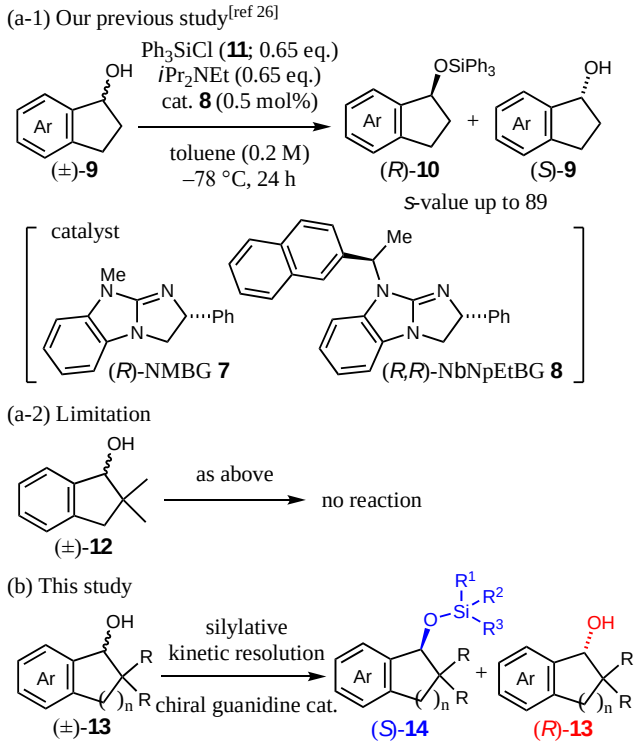
indanol derivatives in which there are no coordinating functional groups adjacent to the reaction sites.

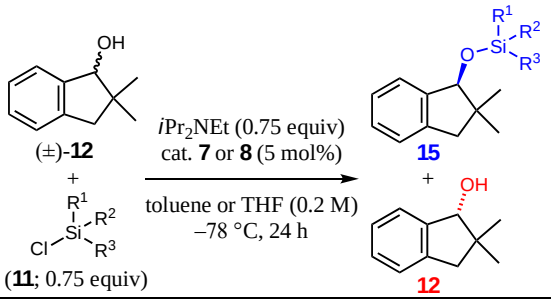
In recent years, kinetic resolution and desymmetrization by the catalytic asymmetric silylation reaction of alcohols have attracted attention as a new and powerful method for obtaining optically active compounds. This strategy has been extended to various substrates.[17–22] In our laboratory, chiral guanidine catalysts[23] **7** and **8** were found to be efficient for asymmetric silylation. We developed the first general method for the non-enzymatic kinetic resolution of racemic 1-indanol derivatives **9** with Ph_3SiCl (**11**) using **8** as the catalyst by asymmetric silylation, with a high *s*-value[24] of up to 89 (Scheme 1, (a-1)).[25] During the course of the examination of the substrate scope and limitations, we found that a broad range of 1-indanol derivatives **9** could be used in the reaction. However, no reaction occurred in the case of 2,2-dialkyl 1-indanol **12** (Scheme 1, (a-2)).[25] While the challenge with substrate **12** is the low reactivity resulting from the steric hindrance of the two substituents at C2, only a catalytic amount (0.5 mol%) is sufficient for the reaction of substrate **9**, which does not have any substituent at C2, as per our previous study. Therefore, we decided to re-examine the reaction to identify the suitable conditions for substrate **12**. Herein, we describe the first practical kinetic resolution of a variety of racemic 2,2-dialkyl 5- and 6-membered cyclic benzylic alcohol derivatives **13** with chlorosilanes by asymmetric silylation using chiral guanidine catalysts (Scheme 1 (b)).



Scheme 1. (a-1) Our previous study (a-2) limitation and (b) this study.

To optimize the reaction conditions, we first chose the racemic 2,2-dimethyl-1-indanol ((±)-**12**) as a model substrate and examined the combination of the chiral guanidine catalysts **7** and **8** with silyl chlorides **11** (Table 1). Since the reaction of **12** did not proceed when using a catalyst loading of 0.5 mol%,[25] we decided to increase the catalyst loading up to 5 mol% to improve the reactivity. No reaction occurred when using 0.75 equiv of Ph_3SiCl (**11a**) and *i*Pr_2NEt as a co-base in the presence of 5 mol% of **7** in toluene at –78 °C for 24 h under the previously established conditions[25] (entry 1). Upon replacing a phenyl group with a methyl group at one or two positions of silyl chloride **11a**, the reactions smoothly proceeded to give good *s*-values (entries 2 and 4). On the contrary, the reactions carried out using Et_3SiCl (**11d**) and Me_3SiCl (**11e**) with *tri*-alkyl substituents did not proceed or gave a moderate *s*-value (entries 8 and 9). From these results, it was evident that at least one phenyl substituent on the silyl chloride is essential for achieving high selectivity. The same trend was observed when using chiral guanidine catalyst **8** instead of **7**. While the reactions using **11a** and **11d** were unsuccessful (entries 10 and 14), those with **11b** and **11c** (entries 11 and 12) proceeded to completion. However, in all the cases, the selectivity was higher when using catalyst **7** than when using catalyst **8**. In particular, the combination of catalyst **8** and silyl chloride **11b** gave poor selectivity (entry 11). When the same reactions were carried out by changing the solvent from toluene to THF, the selectivity was improved in all cases (entries 2, 4, 12 versus 3, 5, 13).

Table 1. Optimization of the combination of catalyst and silyl chloride on reactivity and selectivity.

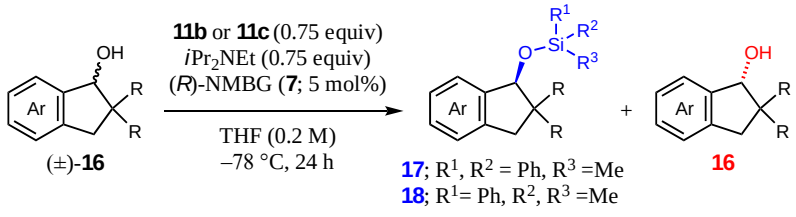


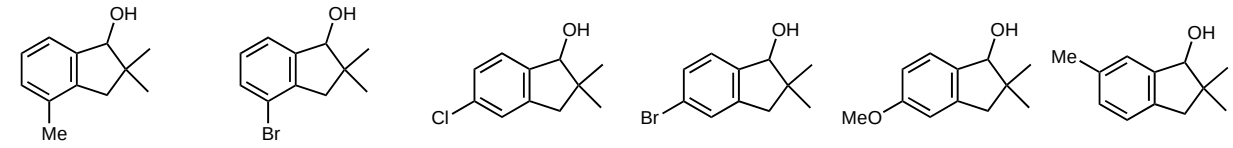
Entry	Cat.	Silyl reagent **11**	Conv[a] [%]	ee [%] (**15**; **12**)	*s*[a]
1	**7**	Ph_3SiCl (**11a**)	NR[b]	–; –	–
2	**7**	$Ph_2MeSiCl$ (**11b**)	62	58; 96	13.5
3[c]	**7**	**11b**	56	71; 89	17.7
4	**7**	$PhMe_2SiCl$ (**11c**)	65	52; 98	14.0
5[c]	**7**	**11c**	67	49; >99	>14.5
6[c,d]	**7**	**11c**	54	75; 87	19.5
7[c,e]	**7**	**11c**	32	87; 42	21.3
8	**7**	Et_3SiCl (**11d**)	NR[b]	–; –	–
9	**7**	Me_3SiCl (**11e**)	45	67; 55	8.7
10	**8**	Ph_3SiCl (**11a**)	NR[b]	–; –	–
11[f]	**8**	$Ph_2MeSiCl$ (**11b**)	35	53; 28	4.2
12	**8**	$PhMe_2SiCl$ (**11c**)	65	51; 95	10.3
13[c]	**8**	**11c**	58	67; 92	16.1
14	**8**	Et_3SiCl (**11d**)	NR[b]	–; –	–

[a] Conversions and *s*-values were calculated using Kagan's equation.[24] [b] No reaction. [c] THF was used as solvent. [d] 0.65 equiv of **11c** was used. [e] 0.48 equiv of **11c** was used. [f] Average of two reactions.

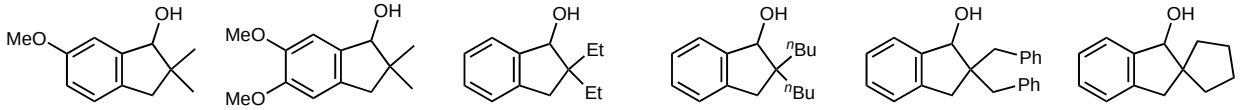
In the reaction using 0.75 equiv of **11c** with catalyst **7**, the conversion was much more than 50% to afford the corresponding (*R*)-**12** with >99% ee; hence, the exact *s*-value could not be evaluated (entry 5). Thus, the same reaction was carried out by decreasing the number of equivalents of **11c** from 0.75 to 0.65 and 0.48 for adjusting the conversion to about 50% in entries 6 and 7; high *s*-values were obtained in both cases. The absolute configuration of the recovered alcohol **12** was assigned (*R*)-configuration by comparison with its previously reported experimental optical rotation.[9]

To evaluate the scope and limitations of the reaction, we investigated the substituents at the C2-position and the effect of substituents on the aromatic ring on 1-indanols using two combinations of catalyst **7** and silyl chlorides **11b** or **11c** (Scheme 2). The reactions of 4-substituted 2,2-dimethyl-1-indanols **16a** and **16b** with **11b** and **11c** in the presence of **7** proceeded smoothly, with higher selectivity obtained when using **11b**. On the other hand, the reactions of 5-, 6-, and 5,6-substituted 2,2-dimethyl-1-indanols **16c**–**16h** gave better results when using **11c**, irrespective of the electronic nature of the substituents. Furthermore, in the case of 2,2-dialkyl substituents 1-indanols **16i**–**16l**, the suitable silyl chloride depended on the structure of the substrate. The reactions of **16i** with 2,2-diethyl substituents and **16k** with 2,2-dibenzyl ones afforded high *s*-values when using **11c** than when using **11b**. In the reaction of **16k** with **11b**, the conversion was low, probably because of the steric hindrance between the dibenzyl substituents and the two phenyl groups in the silyl reagent. Good selectivity was observed in the reactions of **16j** with 2,2-dibutyl substituents and spiro compound **17l** using **11b**.





16a → 17a +16a	16b→17b +16b	16c → 17c +16c	16d → 17d +16d	16e → 17e +16e	16f → 17f +16f
17a; 76% ee	17b; 75% ee	17c; 62% ee	17d; 56% ee	17e; 59% ee	17f; 70% ee
16a; 96% ee	16b; 90% ee	16c; 80% ee	16d; 86% ee	16e; 98% ee	16f; 83% ee
56% conv. *s* = 28	54% conv. *s* = 21	56% conv. *s* = 10	60% conv. *s* = 9	63% conv. *s* = 16	54% conv. *s* = 14
16a → 18a +16a	**16b→ 18b +16b**	**16c → 18c +16c**	**16d → 18d +16d**	**16e → 18e +16e**	**16f → 18f +16f**
18a; 60% ee	18b; 59% ee	18c; 48% ee	18d; 67% ee	18e; 57% ee	18f; 58% ee
16a; 98% ee	16b; 98% ee	16c; >99% ee	16d; 94% ee	16e; 99% ee	16f; 99% ee
62% conv. *s* = 18	62% conv. *s* = 17	67% conv. *s* > 14	58% conv. *s* = 17	64% conv. *s* = 17	63% conv. *s* = 17



16g → 17g +16g	16h → 17h +16h	16i → 17i +16i	16a → 17j +16j	16k → 17k +16k	16l → 17l +16l
17g; 75% ee	17h; 60% ee	17i; 62% ee	17j; 70% ee	17k; 70% ee	17l; 75% ee
16g; 79% ee	16h; 99% ee	16i; 92% ee	16j; >99% ee	16k; 8% ee	16l; 96% ee
52% conv. *s* = 17	62% conv. *s* = 18	60% conv. *s* = 13	59% conv. *s* > 29	11% conv. *s* = 6	56% conv. *s* = 27
16g → 18g +16g	**16a → 18h +16h**	**16a → 18i +16i**	**16a → 18j +16j**	**16a → 18k +16k**	**16a → 18l +16l**
18g; 61% ee	18h; 54% ee	18i; 55% ee	18j; 65% ee	18k; 88% ee	18l; 47% ee
16g; 98% ee	16h; 98% ee	16i; > 99% ee	16j; > 99% ee	16k; 81% ee	16l; 98% ee
62% conv. *s* = 18	64% conv. *s* = 14	65% conv. *s* > 17	61% conv. *s* > 23	48% conv. *s* = 37	68% conv. *s* = 12

Scheme 2. Silylative kinetic resolution of racemic 2,2-dialkyl 1-indanols.

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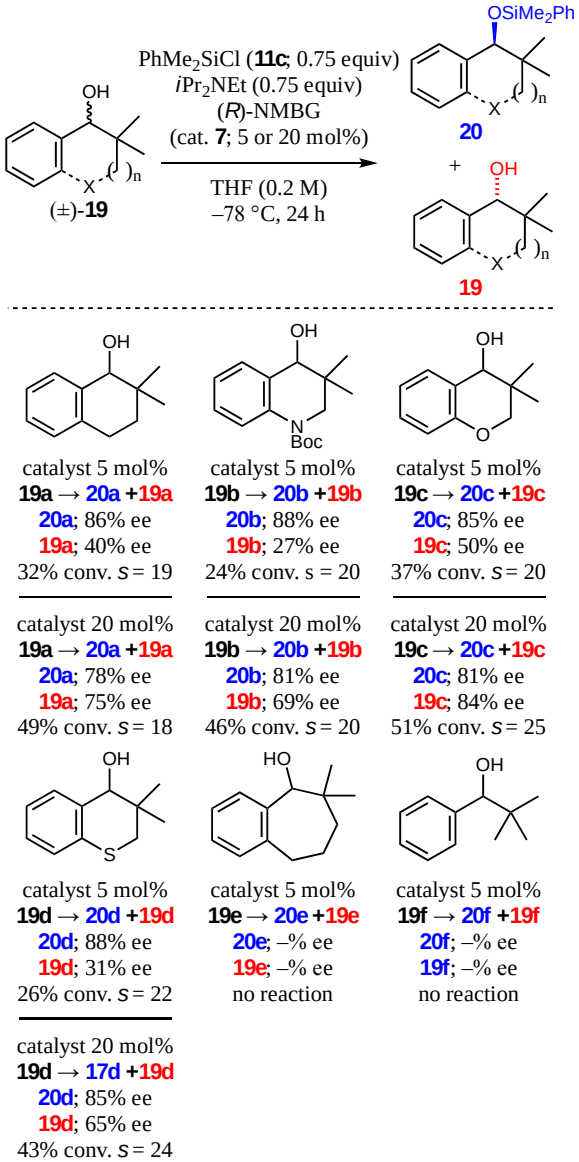
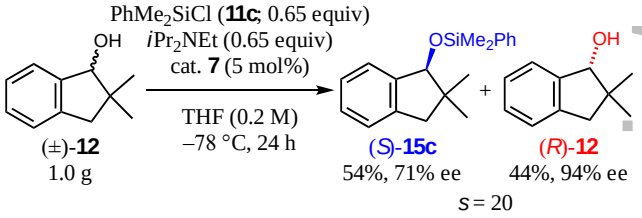
We next applied the reaction system to other 2,2-dimethyl substituted benzylic alcohols, including 6- and 7-membered cyclic and heterocyclic alcohols, as well as acyclic benzylic alcohols, to further expand the scope and limitations (Scheme 3). Since low reactivity was observed for a series of examined substrates, the reactions were carried out using $PhMe_2SiCl$ (**11c**) with less sterically hindered substituents as a silyl reagent. Under the optimized reaction conditions, the reaction of 2,2-dimethyl-substituted 6-membered cyclic and heterocyclic benzylic alcohols **19a**–**19d** proceeded to give 24%–37% conversion with high *s*-values. To increase the conversion, we carried out the same reactions by increasing the catalyst loading from 5 to 20 mol%. All the reactions showed improved conversion of up to about 50% conversion with the same high *s*-values. Unfortunately, the reactions of 7-membered cyclic alcohol **19e** and acyclic alcohol **19f** did not proceed, and the exact reason for this result is currently unknown.



Scheme 3. Silylative kinetic resolution of racemic 2,2-dimethyl-substituted benzylic alcohols.

To demonstrate the scalability of the reaction, we carried out the silylative kinetic resolution of (±)-**12** using **11c** on a 1 g scale, as shown in Scheme 4. The reaction proceeded smoothly, irrespective of the scale, to afford the silylated compound (*S*)-**15c** in 54% yield with 71% ee, and the recovered alcohol (*R*)-**12** in 44% yield with 94% ee, and high selectivity (*s* = 20). This result indicated the good practicality of the present reaction on a large scale.



Scheme 4. Gram-scale silylative kinetic resolution of (±)-**12** using $PhMe_2SiCl$ (**11c**).

In conclusion, we have developed an efficient method for the silylative kinetic resolution of racemic 2,2-dialkyl 5- and 6-membered cyclic benzylic alcohols using diphenylmethylchlorosilane ($Ph_2MeSiCl$) or phenyldimethylchlorosilane ($PhMe_2SiCl$) in the presence of chiral guanidine catalyst, (*R*)-*N*-methylbenzoguanidine ((*R*)-NMBG), with good *s*-values (up to 37). Although the kinetic resolution of neopentyl alcohols is generally challenging task due to their steric hindrance, we could overcome this issue by using the present reaction system. Further studies aimed at expanding the substrate scope of this reaction are in progress in our laboratory.

Experimental Section

Typical Procedure for the Silylative Kinetic Resolution of Racemic 2,2-Dialkyl 1-Indanols (Scheme 2): To a solution of racemic 4-methyl-2,3-dihydro-1*H*-indene-1-ol (±)-**16a** (52.8 mg, 0.30 mmol) in THF (1.5 mL) at room temperature were successively added (*R*)-NMBG **7** (3.7 mg, 14.8 μmol) and $^{i}Pr_2NEt$ (39.2 μL, 0.23 mmol). After cooling to –78 °C, $Ph_2MeSiCl$ (**11b**) (47.6 μL, 0.23 mmol) was added to the mixture. The reaction mixture was stirred for 24 h at the same temperature. Then it was quenched with saturated aqueous $NaHCO_3$ and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layer was dried over Na_2SO_4. After filtration of the mixture, and evaporated the solvent. The residue was purified by preparative thin layer chromatography on silica (hexane/EtOAc = 9/1) to afford the corresponding optically active (–)-**17a** and the recovered optically active (–)-**16a** [56% conversion, *s* = 28].

Enantiomeric excess of (–)-**17a** has been determined after desilylation into (+)-**16a** as followed: To a solution of the obtained silyl ether (–)-**17a** in THF (1.0 mL) at room temperature was added tetrabutylammonium fluoride (TBAF) (150 μL, 1.0 M in THF). The reaction mixture was stirred for 2 h and then it was quenched with saturated aqueous NH_4Cl at 0 °C and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layer was dried over Na_2SO_4. After filtration of the mixture, and evaporated the solvent. The residue was purified by preparative thin layer chromatography on silica gel (hexane/EtOAc = 9/1) to afford the desilylated (+)-**16a**.

Acknowledgements

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Silylative Kinetic Resolution of Racemic 2,2-Dialkyl 5- and 6-Membered Cyclic Benzylic Alcohol Derivatives Catalyzed by Chiral Guanidine, (*R*)-*N*-Methylbenzoguanidine

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