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Silylative Kinetic Resolution of Racemic 1-Indanol Derivatives Catalyzed by Chiral Guanidine

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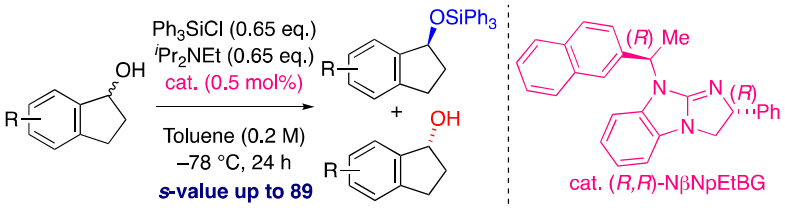
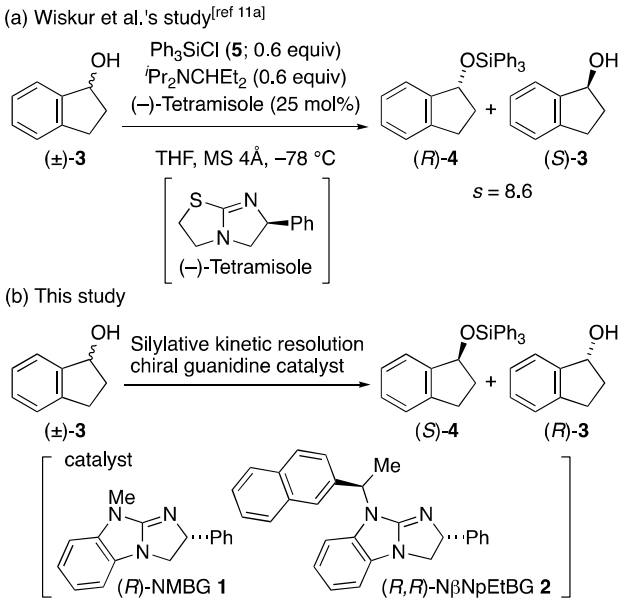
Supporting Information Placeholder



ABSTRACT: Efficient kinetic resolution of racemic 1-indanol derivatives was achieved using triphenylchlorosilane by asymmetric silylation in the presence of chiral guanidine catalysts. The chiral guanidine catalyst, [(*R,R*)-NβNpEtBG] was found to be highly efficient as only 0.5 mol% catalyst loading was sufficient to catalyze the reaction of various substrates with appropriate conversion and high *s*-values (up to 89). This catalyst system was successfully applied to the gram-scale silylative kinetic resolution of racemic 1-indanol with high selectivity.

The kinetic resolution of racemic alcohols by enantioselective acylation using enzyme[1] and chiral nucleophilic organocatalysis[2,3] has been intensively developed and widely utilized from laboratory to industrial scale. Alternatively, kinetic resolution of racemic alcohols by enantioselective silylation using non-enzymatic catalysts[4] has been drawing much attention, as silyl ethers are ubiquitous hydroxyl protecting groups in organic chemistry.[5] In 2001, Ishikawa and co-workers first reported the asymmetric silylation of racemic alcohols using chlorosilanes in the presence of stoichiometric amounts of chiral guanidines.[6] Oestreich and co-workers reported the diastereoselective dehydrogenative coupling of racemic alcohols with silicon-stereogenic silanes to achieve kinetic resolution.[7] However, these examples required stoichiometric amounts of chiral sources. In a breakthrough study by Hoveyda and Snapper in 2006, the catalytic asymmetric silylation of alcohols was achieved using an amino-acid-based chiral imidazole catalyst.[8,9] Tan and co-workers reported the successful enantioselective desymmetrization and divergent resolution of alcohols using chlorosilanes and scaffolding organocatalysts.[10] In 2011, Wiskur and co-workers reported the silylative kinetic resolution of monofunctional secondary alcohols and α-hydroxy carbonyl compounds[11] using chiral isothiourea catalysts, which were also revealed to serve as efficient acyl transfer catalysts for asymmetric acylation.[12] Although significant advances have been made in the chiral silylation of alcohols, many of the examples require a relatively large catalyst loading (≥ 20 mol%). Song and co-workers reported the enantioselective silylation of benzylic alcohols using 1,1,1,3,3,3-hexamethyldisilazane (HMDS) with an extremely low loading (1 ppm) of a BINOL-based polyether catalyst.[13] List and co-workers also reported the asymmetric silylation of alcohols with HMDS using a chiral Brønsted acid catalyst.[14] Dehydrogenative Si-O coupling has been achieved by Oestreich and co-workers, who used transition metal catalysis with donor-functionalized alcohols,[15] and various kinds of alcohols.[16]

Scheme 1. Previously reported study (a) and this study (b)

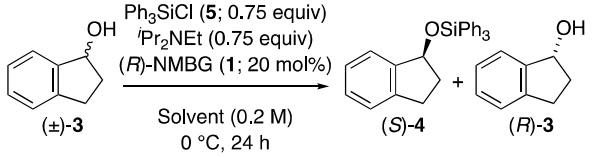


In our research group, chiral guanidine-based catalyst (*R*)-*N*-methylbenzoguanidine ((*R*)-NMBG **1**) was found to facilitate efficient acyl transfer for the kinetic resolution of racemic benzylic alcohols via asymmetric esterification, in the pres-

ence of pivalic anhydride.[17] To demonstrate an application of this protocol, we achieved an enantiodivergent synthesis of both enantiomers of centrolobine using the developed catalyst in the synthetic key step.[18] Furthermore, we recently reported the acylative kinetic resolution of racemic aromatic β-hydroxy esters with cyclohexanecarboxylic anhydride in the presence of (*R*)-NMBG **1** and its derivative (*R,R*)-*N*-(1-(β-naphthyl)ethyl)benzoguanidine ((*R,R*)-NβNpEtBG **2**).[19] Considering Wiskur et al.'s asymmetric silylation utilizing an isothiourea-based catalyst (Scheme 1 (a)),[11a] we anticipated that our guanidine-based catalyst could also be a promising candidate for asymmetric silylation (Scheme 1 (b)).

Optically active 1-indanol derivatives are important chiral building blocks for the synthesis of biologically active compounds,[20] with asymmetric reduction of prochiral carbonyl compounds being the most common method of synthesis.[21] Although several enzymatic[21] and dynamic kinetic resolution strategies using synergistic enzyme and metal catalyst systems[22] have been reported, the organocatalyzed acylative kinetic resolution of racemic 1-indanol (**3**) has remained a challenge.[11a] Moreover, only one study[16] has been recently published describing a practical method for the silylative kinetic resolution of racemic **3** exceeding an *s*-value[24] of 20.[11a] Therefore, we became interested in the development of an efficient method for accessing chiral 1-indanols. Here we report the first practical kinetic resolution of a variety of racemic 1-indanol derivatives with chlorosilanes by asymmetric silylation using guanidine-type catalysts (Scheme 1 (b)).

Table 1. Solvent effect on the kinetic resolution of *rac*-1-indanol ((±)-3) by asymmetric silylation



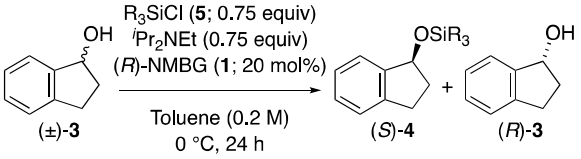
Entry	Solvent	Conv. [%][a]	ee (**4**; **3**) [%]	*s*-value[a]
1	MeCN	1	66; 0.9	5.0
2	DMF	NR[b]	–; –	–
3	Hexane	43	33; 25	2.5
4	Toluene	62	53; 86	8.4
5	Et_2O	55	53; 65	6.1
6	THF	57	58; 78	8.7
7	CH_2Cl_2	60	48; 73	6.0
8	$(CH_2Cl)_2$	43	58; 44	5.7
9	EtOAc	54	57; 68	7.3

[a] Conversions and *s*-values were calculated using Kagan's equation.[24] [b] No reaction.

In light of Wiskur et al.'s study, racemic 1-indanol ((±)-**3**) was chosen as a model substrate to facilitate direct comparison with reported results. First, we examined solvent effects on the silylative kinetic resolution of **3** with 0.75 equiv of Ph_3SiCl (**5**) as a silylation reagent and $^iPr_2NEt$ as a co-base in the presence of 20 mol% of (*R*)-NMBG **1** at 0 °C for 24 h (Table 1). The reactivity appeared to be influenced by the polarity of the solvent, as high-polarity solvents such as MeCN and DMF led to negligible conversion or no reaction (entries 1 and 2). In contrast, the reaction proceeded smoothly with good conversion (43–62%) in a number of other commonly used organic solvents (entries 3–9). Both toluene and THF gave high *s*-values (8.4 and 8.7, respectively); however, considering both reactivity and selectivity, toluene was selected as the most suitable solvent and was adopted for the remainder of the study.

To evaluate the effect of the silyl chloride substitution on selectivity, five silyl chlorides **5a**–**5e** were applied to the silylative kinetic resolution of (±)-**3** under the above mentioned conditions (Table 2). Upon substitution of a phenyl group for a methyl group at one or two positions, selectivity decreased (entries 2 and 3), although reactivity did not diminish. When the reaction was carried out using alkyl substituted silyl chlorides such as **5d** and **5e**, the reaction appeared to be influenced by steric effects: the triethyl substituted **5d** showed fair reactivity but a low *s*-value, and the *tert*-butyl dimethyl substituted **5e** resulted in no reaction (entries 4 and 5). Among all the entries, the highest *s*-value was obtained when using **5a** (entry 1).

Table 2. Effect of silyl chloride substituents on reactivity and selectivity

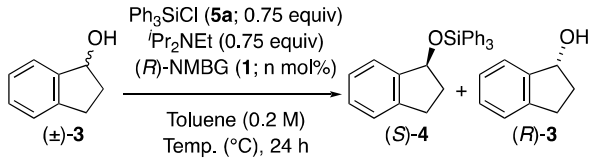


Entry	R_3SiCl **5**	Conv [%][a]	ee (**4**; **3**) [%]	*s*-value[a]
1[b]	Ph_3SiCl (**5a**)	62	53; 86	8.4
2	$Ph_2MeSiCl$ (**5b**)	62	42; 69	4.8
3	$PhMe_2SiCl$ (**5c**)	66	24; 46	2.4
4	Et_3SiCl (**5d**)	60	31; 47	2.9
5	$^tBuMe_2SiCl$ (**5e**)	NR[c]	–; –	–

[a] Conversions and *s*-values were calculated using Kagan's equation.[24] [b] Same as in Table 1, entry 4. [c] No reaction.

To further optimize the reaction conditions, we examined the temperature effect and catalyst loading for the same reaction (Table 3). As the conversion exceeded 50% when the reaction was performed at 0 °C (entry 1), it was proposed that even lower reaction temperatures could be trialed. With each decrease in reaction temperature (–20, –40, and –78 °C), there was an increase in the *s*-value with no effect on reactivity (entries 2–4). The reaction was then carried out by incrementally decreasing the catalyst loading from 20 mol% to 10, 5, and 1 mol% (entries 5–7). Interestingly, conversion was maintained in each case, and generally, each decrease in catalyst loading resulted in an increase in *s*-value. Although the exact reason was not clear, with 1 mol% of the catalyst, the reaction gave the highest conversion (68%), affording the recovered alcohol (*R*)-**3** in >99% ee. Since the *s*-value was not evaluated under the conditions (entry 7), for convenience, it was calculated the minimum value of >13 using the ee of the recovered alcohol as 99%. The reaction was further investigated by reducing the equivalents of **5** and $^iPr_2NEt$ to 0.65, which resulted in a higher *s*-value than that for entry 6 at 5 mol% catalyst loading (entry 8). In line with the noted trend, the reaction was repeated at a low catalyst loading of 0.5 mol%, which gave the highest *s*-value (entry 9, $s = 23$), the as same as entry 8. As expected, the control reaction performed in the absence of chiral catalyst **1** gave no appreciable background reaction (entry 10).

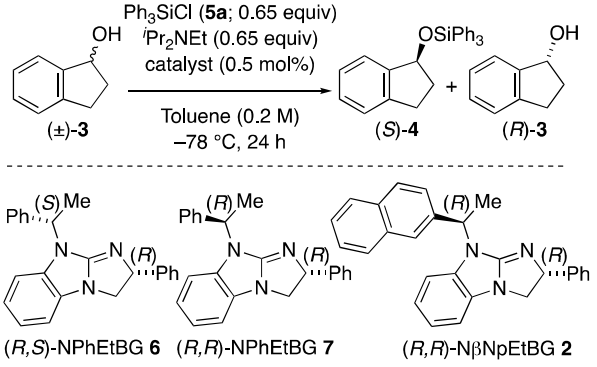
Table 3. Examination of temperature and catalyst loading on conversion and selectivity



Entry	n [mol%]	Temp. [°C]	Conv. [%][a]	ee (**4**; **3**) [%]	*s*-value[a]
1[b]	20	0	62	53; 86	8
2	20	–20	57	61; 80	10
3	20	–40	62	59; 96	14
4	20	–78	63	58; 98	17
5	10	–78	61	64; 98	20
6	5	–78	60	65; 99	23
7[c]	1	–78	68	47; >99	>13
8[d]	1	–78	59	68; 98	23
9[d]	0.5	–78	59	68; 98	23
10	–[g]	–78	<1[h]	–; –	–

[a] Conversions and *s*-values were calculated using Kagan's equation.[24] [b] Same as in Table 1, entry 4. [c] Average of two reactions. [d] Using 0.65 equiv of **5** and $^{i}Pr_2NEt$. [g] Without catalyst. [h] Determined by ^1H NMR analysis of the crude reaction mixture using 1-bromonaphthalene as an internal standard.

Table 4. Examination of chiral guanidine catalysts



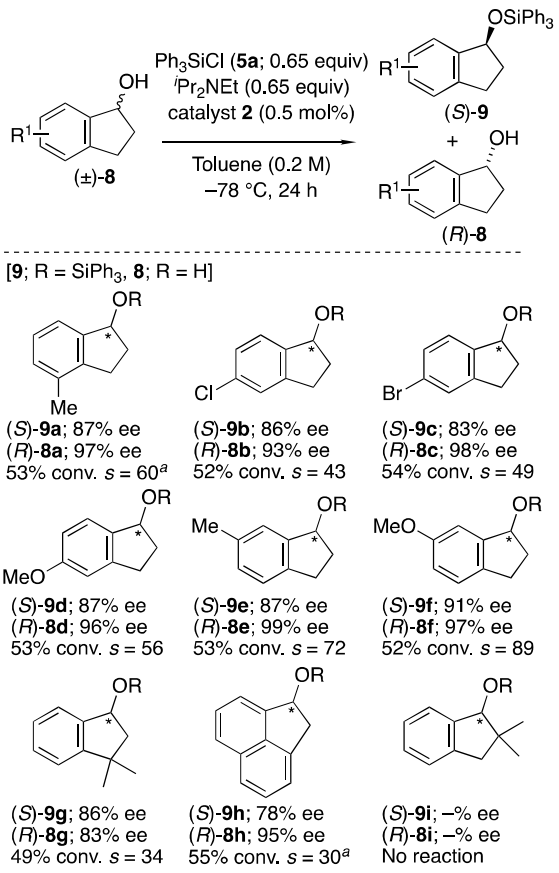
Entry	Catalyst	Conv. [%][a]	ee (**4**; **3**) [%]	*s*-value[a]
1[b]	**1**	59	68; 98	23
2	(*R,S*)-NPhEtBG **6**	54	62; 72	9
3	(*R,R*)-NPhEtBG **7**	57	64; 85	12
4	(*R,R*)-NβNpEtBG **2**	53	82; 92	32

[a] Conversions and *s*-values were calculated using Kagan's equation.[24] [b] Same as in Table 3, entry 9.

With the optimized reaction conditions in hand, we attempted to further improve the selectivity. Thus, three further guanidine catalysts, (*R,S*)-NPhEtBG **6**, (*R,R*)-NPhEtBG **7**, and (*R,R*)-NβNpEtBG **2** (previously reported by our research group in application to acylative kinetic resolution),[18] were applied to the silylative kinetic resolution of (±)-**3** (Table 4). Comparison of the performance of diastereomeric catalysts (*R,S*)-NPhEtBG **6** and (*R,R*)-NPhEtBG **7** revealed that the (*R,R*)-configuration led to better results (entries 2 and 3). However, the selectivity of both catalysts was much lower than that of catalyst **1** (entry 1). Because of the higher performance of the (*R,R*)-stereochemistry at the two stereogenic centers in the catalyst, we next applied (*R,R*)-NβNpEtBG **2** to the same reaction. The reaction proceeded smoothly to afford the highest *s*-value (entry 4).

To assess the generality of this novel method, we screened several racemic 1-indanol derivatives **8a**–**8h** under the optimized reaction conditions, using 0.5 mol% loading of (*R,R*)-NβNpEtBG **2** (Scheme 2). However, the reactions of 4-substituted 1-indanol **8a** and the fused aromatic 1-indanol derivative **8h** were performed in THF due to the poor solubility of them in toluene. Interestingly, 4-substituted **8a**, 5-substituted **8b**–**8d**, and 6-substituted 1-indanols **8e** and **8f**, proceeded with 52–54% conversion, and consistently high *s*-values were obtained in every case, irrespective of the substitution pattern and the electronic nature of the substituents. In terms of selectivity, 6-substituted 1-indanols **8e** and **8f** outperformed the rest, with outstanding *s*-values of 72 and 89 respectively. The reactions of 4- and 5-substituted 1-indanols **8a**–**8d** proceeded smoothly, resulting in *s*-values ranging from 43 to 60. The reaction of 3,3-disubstituted 1-indanol **8g** and the fused aromatic 1-indanol derivative **8h** also afforded good *s*-values. Unfortunately, the reaction of 2,2-disubstututed 1-indanol **8i** did not proceed, probably because of the steric hindrance of the 2,2-dimethyl groups.

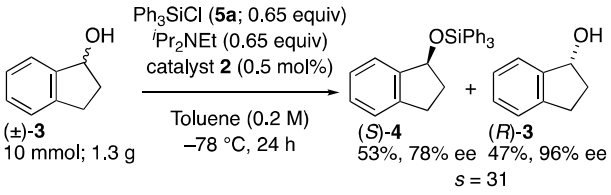
Scheme 2. Silylative kinetic resolution of racemic 1-indanol derivatives



[a] THF was used as solvent.

To elucidate the scalability of this method, a gram-scale silylative kinetic resolution of racemic 1-indanol (**3**) was performed, as shown in Scheme 3. The reaction carried out on a 10-mmol scale under the optimized reaction conditions proceeded smoothly to afford the silyl ether (*S*)-**4** in 53% yield and 78% ee, along with the recovered alcohol (*R*)-**3** in 47% yield, 96% ee, and high selectivity. This result indicates the potential utility of the present method for furnishing chiral indanol derivatives on a large scale.

Scheme 3. Gram-scale kinetic resolution of racemic 1-indanol (3)



In conclusion, we have developed a general method for the non-enzymatic kinetic resolution of racemic 1-indanol derivatives with triphenylchlorosilane catalyzed by chiral guanidine, (*R,R*)-*N*-(1-(β-1-naphthyl)ethyl)benzoguanidine [(*R,R*)-NβNpEtBG], with high *s*-values (up to 89). The catalyst was found to be a highly efficient, as only 0.5 mol% catalyst loading and slightly excess amount of silylchloride (0.65 equiv) were required to achieve ≈50% conversion. This protocol was also extended to the gram-scale silylative kinetic resolution of racemic 1-indanol with high selectivity. Although the non-enzymatic kinetic resolution of racemic 1-indanol has presented a historically challenging issue in organic chemistry, we have developed a highly promising method to overcome this challenge. Further studies are in progress in our laboratory to explore the scope and limitation of this reaction, and to further develop novel chiral catalysts that will be reported in due course.

EXPERIMENT SECTION

General Information. ^{1}H and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS) or chloroform (in chloroform-d) as internal standard. Electrospray ionization mass (ESI-MS) spectra were recorded on a Bruker microTOFII-SHIY3 mass spectrometer (Bruker, Billerica, MA) using the positive mode ESI-TOF method for acetonitrile solutions and sodium formate as the reference. Thin layer chromatography was performed on Wakogel B5F. All reactions were carried out under nitrogen atmosphere in dried glassware. Dichloromethane and dichloroethane were distilled from diphosphorus pentoxide, then calcium hydride, and dried over MS 4Å. EtOAc was distilled from diphosphorus pentoxide and dried over MS 4Å. Hexane, toluene, diethyl ether, THF, MeCN, and *N,N*-dimethylformamide were distilled from calcium hydride, and dried over MS 4Å. 1-Indanol ((±)-**3**) was purchased from Wako Pure Chemical Industries Ltd. and Tokyo Chemical Industry Co., Ltd. Ph_3SiCl (**5a**) was purchased from Tokyo Kasei Kogyo Co., Ltd. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted.

Racemic 1-indanols **8a**, **8b**, **8c**, **8d**, **8e**, **8g**, **8h** were prepared by the reduction of the corresponding commercially available ketones. Racemic 1-indanols **8f** and **8i** were prepared by the reduction of the corresponding synthesized ketones.

Typical Procedure for the Preparation of Racemic 1-Indanols 8a–8e, 8g, 8h (Scheme 2):

To a solution of 4-methyl-1-indanone (307.1 mg, 2.10 mmol) in MeOH (4.2 mL) and CH_2Cl_2 (4.2 mL) at 0 °C was added $NaBH_4$ (95.1 mg, 2.51 mmol). The reaction mixture was stirred for 30 min at room temperature and then it was quenched with saturated aqueous NH_4Cl at 0 °C. 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 evaporation of the solvent, the crude product was purified by column chromatography on silica (hexane/EtOAc = 4/1) to afford 4-methyl-1-indanol (**8a**) (285.4 mg, 92%).

Preparation of Racemic 8f (Scheme 2):

To a solution of 6-hydroxy-1-indanone (296 mg, 2.00 mmol) in DMF (4.0 mL) at 0 °C was added NaH (60%, 120 mg, 3.00 mmol). The reaction mixture was stirred for 30 min and then MeI (187 μL, 3.00 mmol) was added to the mixture. The whole mixture was stirred for 20.5 h at room temperature and then it was quenched with saturated aqueous NH_4Cl at 0 °C and diluted with H_2O and EtOAc. After the extraction with EtOAc, the combined organic layer was dried over Na_2SO_4, filtered, and evaporated the solvent. The residue was purified by column chromatography on silica (hexane/EtOAc = 9/1) to afford 6-methoxy-1-indanone as a white solid (318 mg, 98% yield), which was subsequently reduced by the above method using $NaBH_4$ to afford **8f** (275 mg, 95% yield, 1.77 mmol scale).

Preparation of Racemic 8i (Scheme 2):

According to the literature procedure,[25] to a solution of 1-indanone (463 mg, 3.50 mmol) in THF (7.0 mL) at 0 °C was added NaH (60%, 701 mg, 17.5 mmol). The reaction mixture was stirred for 10 min at room temperature and then MeI (187 μL, 3.00 mmol) was added to the mixture at 0 °C. The whole mixture was stirred for 0.5 h at 40 °C and continued stirring for 3 h at room temperature. Then it was quenched with saturated aqueous H_2O at 0 °C and diluted with EtOAc. After the extraction with EtOAc, the combined organic layer was dried over Na_2SO_4, filtered, and evaporated the solvent. The residue was semi-purified by column chromatography on silica (hexane/EtOAc = 9/1) to afford 3,3-dimethyl-1-indanone as a pale yellow oil, which was subsequently reduced by the above method using $NaBH_4$ to afford **8i** (485 mg, 85% yield for 2 steps).

^{1}H NMR ($CDCl_3$): δ 7.40–7.34 (m, 1H), 7.26–7.16 (m, 3H), 4.68 (d, *J* = 5.0 Hz, 1H), 2.79 (d, *J* = 15.5 Hz, 1H), 2.67 (d, *J* = 15.5 Hz, 1H), 1.84 (br s, 1H), 1.19 (s, 3H), 1.04 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 144.4, 141.8, 128.0, 126.5, 125.0, 124.4, 83.5, 44.8, 44.5, 26.7, 21.4.

Typical Procedure for the Silylative Kinetic Resolution of Racemic 1-Indanol (Table 4, entry 4):

To a solution of racemic 1-indanol (±)-**3** (134.0 mg, 1.00 mmol) in toluene (5.0 mL) at room temperature were successively added (*R,R*)-NβNpEtBG **2** (2.0 mg, 5.1 μmol) and ^{i}Pr$_2$NEt (113 μL, 0.65 mmol). After cooling to –78 °C, Ph_3SiCl (**5a**) (191.9 mg, 0.65 mmol) was added to the mixture. The reaction mixture was stirred for 24 h at the same temperature and then it was quenched with saturated aqueous $NaHCO_3$ and diluted with EtOAc. After the extraction with EtOAc, the combined organic layer was dried over Na_2SO_4, filtered, and evaporated the solvent. The residue was purified by preparative thin layer chromatography on silica (hexane/EtOAc = 4/1) to afford the corresponding optically active (*S*)-**4** and the recovered optically active (*R*)-**3** [53% conversion, *s* = 32].

Enantiomeric excess of (*S*)-**4** has been determined after desilylation into (*S*)-**3** as followed: To a solution of the obtained silyl ether (*S*)-**4** in THF (2.0 mL) at room temperature was added TBAF (1.5 mL, 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. After the extraction with EtOAc, the combined organic layer was dried over Na_2SO_4, filtered, and evaporated the solvent. The residue was purified by preparative thin layer chromatography on silica (hexane/EtOAc = 1/1) to afford the desilylated (*S*)-**3**.

Gram-scale kinetic resolution of racemic 1-indanol (3) (Scheme 3):

To a solution of racemic 1-indanol ((±)-**3**) (1.34 g, 10.0 mmol) in toluene (50 mL) at room temperature were successively added (*R,R*)-NβNpEtBG **2** (19.5 mg, 0.05 mmol) and ^{i}Pr$_2$NEt (1.13 mL, 6.50 mmol). After cooling to –78 °C, Ph_3SiCl (**5a**) (1.92 mg, 6.50 mmol) was added to the mixture. The reaction mixture was stirred for 24 h at

the same temperature and then it was quenched with saturated aqueous $NaHCO_3$ and diluted with EtOAc. After the extraction with EtOAc, the combined organic layer was dried over Na_2SO_4, filtered, and evaporated the solvent. The residue was purified by column chromatography on silica (hexane/EtOAc = 20/1 to 9/1) to afford the corresponding optically active (*S*)-**4** (2.08 g, 53% yield, 78% ee) and the recovered optically active (*R*)-**3** (630 mg, 47% yield, 96% ee) [*s* = 31]. Enantiomeric excess of (*S*)-**4** has been determined after desilylation into (*S*)-**3**.

[Optically Active (*R*)-Alcohols **3**, and **8a**–**8h**]

(*R*)-2,3-dihydro-1*H*-inden-1-ol ((*R*)-3)[11a]
[Table 4, Entry 4, 92% ee]: HPLC (CHIRALCEL OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.5 mL/min): t_R = 27.3 min (3.9%), t_R = 31.0 min (96.1%); ^{1}H NMR ($CDCl_3$): δ 7.43–7.39 (m, 1H), 7.30–7.21 (m, 3H), 5.22 (t, *J* = 6.0 Hz, 1H), 3.05 (ddd, *J* = 16.0, 8.5, 5.0 Hz, 1H), 2.81 (dt, *J* = 16.0, 7.5 Hz, 1H), 2.52–2.42 (m, 1H), 2.19 (br s, 1H), 1.99–1.88 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 144.9, 143.2, 128.2, 126.6, 124.8, 124.1, 76.3, 35.8, 29.7.
Absolute configuration was determined by the comparison of the HPLC retention time in Ref. 1.

(*R*)-4-methyl-2,3-dihydro-1*H*-inden-1-ol ((*R*)-8a)[26]
[Scheme 2, 97% ee]: $[\alpha]_D^{24}$ = –11.4 (*c* 1.46, $CHCl_3$); lit.,[26] $[\alpha]_D^{23}$ = –36.3 (*c* 1.5, $CHCl_3$), 99% ee for *R*; HPLC (CHIRALPAK OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.65 mL/min): t_R = 23.9 min (1.7%), t_R = 30.0 min (98.3%); ^{1}H NMR ($CDCl_3$): δ 7.26 (d, *J* = 7.0 Hz, 1H), 7.18 (dt, *J* = 7.5, 7.0 Hz, 1H), 7.10 (d, *J* = 7.0 Hz, 1H), 5.24 (dd, *J* = 6.0, 5.5 Hz, 1H), 2.98 (ddd, *J* = 16.0, 8.5, 5.0 Hz, 1H), 2.73 (ddd, *J* = 16.0, 8.0, 7.0 Hz, 1H), 2.54–2.44 (m, 1H), 2.29 (s, 3H), 2.07 (br s, 1H), 1.99–1.90 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 144.7, 142.1, 134.2, 129.0, 126.9, 121.5, 76.6, 35.3, 28.4, 18.7.

(*R*)-5-chloro-2,3-dihydro-1*H*-inden-1-ol ((*R*)-8b)[27]
[Scheme 2, 93% ee]: $[\alpha]_D^{22}$ = –19.2 (*c* 0.74, $CHCl_3$); lit.,[27] $[\alpha]_D^{25}$ = +30.10 (*c* 1.0, $CHCl_3$), 99% ee for *S*; HPLC (CHIRALCEL OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.5 mL/min): t_R = 27.0 min (92.8%), t_R = 30.1 min (7.2%); ^{1}H NMR ($CDCl_3$): δ 7.30 (d, *J* = 8.5 Hz, 1H), 7.24–7.15 (m, 2H), 5.17 (t, *J* = 6.0 Hz, 1H), 3.00 (ddd, *J* = 16.0, 9.0, 5.0 Hz, 1H), 2.78 (dt, *J* = 16.0, 7.5 Hz, 1 H), 2.54–2.41 (m, 1H), 2.16 (br s, 1H), 1.99–1.87 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 145.2, 143.4, 134.0, 126.9, 125.3, 125.0, 75.6, 36.0, 29.6.

(*R*)-5-bromo-2,3-dihydro-1*H*-inden-1-ol ((*R*)-8c)[28]
[Scheme 2, 98% ee]: $[\alpha]_D^{22}$ = –19.6 (*c* 1.00, $CHCl_3$); lit.,[28] $[\alpha]_D^{25}$ = +15.8 (*c* 1.0, $CHCl_3$), 98.1% ee for *S*; HPLC (CHIRALCEL OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.5 mL/min): t_R = 29.7 min (1.0%), t_R = 31.7 min (99.0%); ^{1}H NMR ($CDCl_3$): δ 7.42–7.31 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 1H), 5.22–5.09 (m, 1H), 3.08–2.93 (m, 1H), 2.85–2.71 (m, 1H), 2.53–2.40 (m, 1H), 2.35 (br s, 1H), 1.99–1.83 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 145.6, 143.9, 129.7, 128.0, 125.7, 122.2, 75.6, 35.9, 29.6.

(*R*)-5-methoxy-2,3-dihydro-1*H*-inden-1-ol ((*R*)-8d)[27]
[Scheme 2, 96% ee]: $[\alpha]_D^{25}$ = –21.8 (*c* 1.23, $CHCl_3$); lit.,[27] $[\alpha]_D^{25}$ = +27.6 (*c* 1.0, $CHCl_3$), 99% ee for *S*; HPLC (CHIRALCEL OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.6 mL/min): t_R = 39.7 min (1.8%), t_R = 42.9 min (98.2%); ^{1}H NMR ($CDCl_3$): δ 7.30 (d, *J* = 9.5 Hz, 1H), 6.78 (d, *J* = 6.0 Hz, 2H), 5.17 (dd, *J* = 6.0, 5.0 Hz, 1H), 3.79 (s, 3H), 3.03 (ddd, *J* = 16.0, 8.5, 5.5 Hz,1 H), 2.78 (ddd, *J* = 16.0, 8.5, 6.5 Hz, 1H), 2.52–2.39 (m, 1H), 2.05 (br s, 1H), 1.99–1.89 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 160.1, 145.2, 137.3, 125.0, 112.9, 109.7, 75.7, 55.3, 36.2, 29.9.

(*R*)-6-methyl-2,3-dihydro-1*H*-inden-1-ol ((*R*)-8e)[26]
[Scheme 2, 99% ee]: $[\alpha]_D^{22}$ = –48.0 (*c* 1.00, $CHCl_3$); lit.,[26] $[\alpha]_D^{23}$ = –36.3 (*c* 1.5, $CHCl_3$), 99% ee for *R*; HPLC (CHIRALCEL OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.5 mL/min): t_R = 23.5 min (0.7%), t_R = 25.6 min (99.3%); ^{1}H NMR ($CDCl_3$): δ 7.24 (s, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 5.20 (t, *J* = 6.0 Hz, 1H), 2.78 (ddd, *J* = 16.0, 8.5, 5.0 Hz, 1H), 2.78 (dt, *J* = 16.0, 8.0 Hz, 1H), 2.52–2.43 (m, 1H), 2.37 (s, 3H), 2.11 (br s, 1H), 1.99–1.89 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 145.1, 140.2, 136.3, 129.1, 124.7, 124.5, 76.3, 36.1, 29.3, 21.2.

(*R*)-6-methoxy-2,3-dihydro-1*H*-inden-1-ol ((*R*)-8f)[29]
[Scheme 2, 97% ee]: $[\alpha]_D^{23}$ = –32.8 (*c* 1.42, $CHCl_3$); lit.,[29] $[\alpha]_D^{23}$ = –20.0 (*c* 0.5, $CHCl_3$), 94% ee for *R*; HPLC (CHIRALCEL OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.6 mL/min): t_R = 32.2 min (1.5%), t_R = 35.3 min (98.5%); ^{1}H NMR ($CDCl_3$): δ 7.14 (d, *J* = 8.5 Hz, 1H), 6.95 (d, *J* = 2.0 Hz, 1H), 6.82 (dd, *J* = 8.5, 3.0 Hz, 1H), 5.18 (dd, *J* = 7.0, 6.5 Hz, 1H), 3.80 (s, 3H), 2.96 (ddd, *J* = 15.5, 9.0, 4.5 Hz, 1H), 2.74 (dt, *J* = 15.5, 8.0 Hz, 1H), 2.54–2.44 (m, 1H), 2.11 (br s, 1H), 1.98–1.88 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 158.9, 146.3, 135.0, 125.4, 114.9, 108.7, 76.5, 55.4, 36.4, 28.9.

(*R*)-3,3-dimethyl-2,3-dihydro-1*H*-inden-1-ol ((*R*)-8g)[30]
[Scheme 2, 83% ee]: $[\alpha]_D^{21}$ = –15.5 (*c* 1.37, $CHCl_3$); lit.,[30] $[\alpha]_D^{25}$ = –27.1 (*c* 0.11, $CHCl_3$), 90% ee for *R*; HPLC (CHIRALCEL OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.5 mL/min): t_R = 18.3 min (8.6%), t_R = 20.8 min (91.4%); ^{1}H NMR ($CDCl_3$): δ 7.39 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.31 (dt, *J* = 1.0, 7.0 Hz, 1H), 7.26 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 5.30–5.21 (m, 1H), 2.38 (dd, *J* = 13.0, 7.0 Hz, 1H), 2.14 (br s, 1H), 1.84 (dd, *J* = 13.0, 6.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 151.8, 143.6, 128.5, 126.9, 124.1, 122.2, 74.4, 51.8, 42.2, 29.9, 29.8.

(*R*)-1,2-dihydroacenaphthylen-1-ol ((*R*)-8h)[11a]
[Scheme 2, 95% ee]: HPLC (CHIRALCEL OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.65 mL/min): t_R = 45.4 min (2.3%), t_R = 52.2 min (97.7%); ^{1}H NMR ($CDCl_3$): δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.59–7.46 (m, 3H), 7.30 (d, *J* = 7.0 Hz, 1H), 5.66 (s, 1H), 3.74 (ddd, *J* = 17.5, 7.0, 1.0 Hz, 1H), 3.18 (dd, *J* = 17.5, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 145.6, 141.5, 137.1, 131.1, 128.2, 128.0, 124.9, 122.7, 120.3, 120.0, 74.2, 41.7.
Absolute configuration was determined by the comparison of the HPLC retention time in Ref. 1.

[Optically Active (*S*)-Silyl Ethers **4**, and **9a**–**9h**]

(*S*)-((2,3-dihydro-1*H*-inden-1-yl)oxy)triphenylsilane ((*S*)-4)[11a]
[Table 4, Entry 4, 82% ee]: Enantiomeric excess of (*S*)-**4** has been determined after desilylation into (*S*)-**3**; HPLC (CHIRALCEL OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.5 mL/min): t_R = 28.1 min (90.8%), t_R = 32.1 min (9.2%); ^{1}H NMR ($CDCl_3$): δ 7.93–7.81 (m, 6H), 7.62–7.48 (m, 9H), 7.39–7.24 (m, 4H), 5.69–5.59 (m, 1H), 3.20–3.08 (m, 1H), 2.90–2.77 (m, 1H), 2.48–2.36 (m, 1H), 2.31–2.15 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 145.0, 142.8, 135.5, 134.6, 130.0, 127.84, 127.76, 126.4, 124.6, 124.4, 77.4, 36.3, 29.7.

(*S*)-((4-methyl-2,3-dihydro-1*H*-inden-1-yl)oxy)triphenylsilane ((*S*)-9a)
[Scheme 2, 87% ee]: $[\alpha]_D^{25}$ = –29.6 (*c* 1.0, $CHCl_3$); white solid; Mp: 52–53 °C; IR (KBr): 1117, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.77–7.70 (m, 6H), 7.52–7.46 (m, 3H), 7.46–7.39 (m, 6H), 7.15–7.03 (m, 3H), 5.52 (t, *J* = 6.5 Hz, 1H), 2.98 (ddd, *J* = 16.0, 9.0, 3.5 Hz, 1H), 2.64 (dt, *J* = 16.0, 8.0 Hz, 1H), 2.36–2.25 (m, 3H), 2.28 (s, 3H), 2.27–2.06 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 144.8, 141.7, 135.6, 134.7, 133.9, 130.0, 128.6, 127.8, 126.6, 121.8, 77.7, 35.7, 28.4, 18.7; Anal. Calcd for $C_{28}H_{26}OSi$: C, 82.71; H, 6.45. Found: C, 82.63; H, 6.27.
Enantiomeric excess of (*S*)-**9a** has been determined after desilylation into (*S*)-**8a**; HPLC (CHIRALCEL OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.65 mL/min): t_R = 23.8 min (93.6%), t_R = 30.6 min (6.4%).

(*S*)-((5-chloro-2,3-dihydro-1*H*-inden-1-yl)oxy)triphenylsilane ((*S*)-9b)
[Scheme 2, 86% ee]: $[\alpha]_D^{22}$ = –40.9 (*c* 1.00, $CHCl_3$); white solid; Mp: 95–96 °C; IR (KBr): 1119, 716, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.75–7.66 (m, 6H), 7.52–7.45 (m, 3H), 7.45–7.38 (m, 6H), 7.20 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 5.44 (dd, *J* = 6.5, 6.0 Hz, 1H), 3.00 (ddd, *J* = 16.0, 8.5, 4.0 Hz, 1H), 2.70 (dt, *J* = 16.0, 8.0, 8.0 Hz, 1H), 2.36–2.24 (m, 1H), 2.19–2.06 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 144.9, 143.6, 135.5, 134.4, 133.5, 130.1, 127.9, 126.6,

125.5, 124.8, 76.7, 36.3, 29.6; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{27}H_{23}ClOSiNa$ 449.1099; Found 449.1097.
Enantiomeric excess of (*S*)-**9b** has been determined after desilylation into (*S*)-**8b**; HPLC (CHIRALCEL OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.5 mL/min): t_R = 26.9 min (3.6%), t_R = 29.3 min (96.4%).

(*S*)-((5-bromo-2,3-dihydro-1*H*-inden-1-yl)oxy)triphenylsilane ((*S*)-9c)
[Scheme 2, 83% ee]: $[\alpha]_D^{22}$ = –39.0 (*c* 1.00, $CHCl_3$); white solid; Mp: 80–81 °C; IR (KBr): 1119, 710, 700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.74–7.65 (m, 6H), 7.51–7.44 (m, 3H), 7.44–7.37 (m, 6H), 7.34 (s, 1H), 7.30–7.23 (m, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 5.41 (dd, *J* = 7.0, 6.0 Hz, 1H), 2.99 (ddd, *J* = 16.0, 9.0, 4.0 Hz, 1H), 2.69 (dt, *J* = 16.0, 8.0 Hz, 1H), 2.32–2.22 (m, 1H), 2.16–2.04 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 145.3, 144.1, 135.5, 134.4, 130.1, 129.5, 127.9, 127.8, 125.9, 121.7, 76.8, 36.3, 29.6; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{27}H_{23}BrOSiNa$ 493.0594; Found 493.0596.
Enantiomeric excess of (*S*)-**9c** has been determined after desilylation into (*S*)-**8c**; HPLC (CHIRALCEL OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.5 mL/min): t_R = 29.2 min (91.5%), t_R = 31.9 min (8.5%).

(*S*)-((5-methoxy-2,3-dihydro-1*H*-inden-1-yl)oxy)triphenylsilane ((*S*)-9d)
[Scheme 2, 87% ee]: $[\alpha]_D^{24}$ = –31.8 (*c* 1.03, $CHCl_3$); white slurry; IR (KBr): 1090, 741, 704 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.76–7.68 (m, 6H), 7.51–7.45 (m, 3H), 7.45–7.38 (m, 6H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.78 (s, 1H), 6.73 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.47 (t, *J* = 6.0 Hz, 1H), 3.81 (s, 3H), 3.04 (ddd, *J* = 16.0, 9.0, 4.5 Hz, 1H), 2.71 (dt, 16.0, 8.0 Hz, 1H), 2.36–2.24 (m, 1H), 2.18–2.06 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 159.9, 144.8, 137.3, 135.5, 134.7, 129.9, 127.8, 125.3, 112.6, 109.6, 76.9, 55.3, 36.5, 30.0; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{26}O_2SiNa$ 445.1594; Found 445.1599.
Enantiomeric excess of (*S*)-**9d** has been determined after desilylation into (*S*)-**8d**; HPLC (CHIRALCEL OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.6 mL/min): t_R = 39.9 min (93.5%), t_R = 44.5 min (6.5%).

(*S*)-((6-methyl-2,3-dihydro-1*H*-inden-1-yl)oxy)triphenylsilane ((*S*)-9e)
[Scheme 2, 87% ee]; $[\alpha]_D^{23}$ = –31.0 (*c* 1.00, $CHCl_3$); white solid; Mp: 91–92 °C; IR (KBr): 1115, 708 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.78–7.71 (m, 6H), 7.53–7.46 (m, 3H), 7.46–7.39 (m, 6H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.92 (s, 1H), 5.48 (t, *J* = 6.5 Hz, 1H), 2.99 (ddd, *J* = 16.0, 8.5, 3.5 Hz, 1H), 2.69 (dt, *J* = 16.0, 8.0 Hz, 1H), 2.34 –2.25 (m, 1H), 2.30 (s, 3H), 2,16–2.05 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 145.1, 139.8, 135.9, 135.6, 134.7, 130.0, 128.6, 127.8, 125.1, 124.3, 77.4, 36.5, 29.3, 21.2; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{26}OSiNa$ 429.1645; Found 429.1638.
Enantiomeric excess of (*S*)-**9e** has been determined after desilylation into (*S*)-**8e**; HPLC (CHIRALCEL OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.5 mL/min): t_R = 23.4 min (93.7%), t_R = 26.0 min (6.3%).

(*S*)-((6-methoxy-2,3-dihydro-1*H*-inden-1-yl)oxy)triphenylsilane ((*S*)-9f)
[Scheme 2, 91% ee]: $[\alpha]_D^{22}$ = –48.6 (*c* 1.00, $CHCl_3$); white solid; Mp: 60–62 °C; IR (KBr): 1115, 702 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.79–7.69 (m, 6H), 7.58–7.38 (m, 9H), 7.11 (d, *J* = 7.5 Hz, 1H), 6.83–6.75 (m, 1H), 6.64 (s, 1H), 5.48 (dd, *J* = 6.0, 5.0 Hz, 1H), 3.64 (s, 3H), 3.02–2.89 (m, 1H), 2.66 (dt, *J* = 16.0, 8.0 Hz, 1H), 2.43–2.30 (m, 1H), 2.22–2.09 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 158.7, 146.4, 135.6, 134.7, 134.6, 130.0, 127.9, 125.2, 114.8, 108.8, 77.5, 55.3, 36.7, 28.9; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{26}O_2SiNa$ 445.1594; Found 445.1595.
Enantiomeric excess of (*S*)-**9f** has been determined after desilylation into (*S*)-**8f**; HPLC (CHIRALCEL OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.6 mL/min): t_R = 31.5 min (95.5%), t_R = 36.5 min (4.5%).

(*S*)-((3,3-dimethyl-2,3-dihydro-1*H*-inden-1-yl)oxy)triphenylsilane ((*S*)-9g)
[Scheme 2, 86% ee]: $[\alpha]_D^{22}$ = –18.4 (*c* 0.90, $CHCl_3$); white solid; Mp: 89–91 °C; IR (KBr): 1117, 700 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.75–7.68 (m, 6H), 7.50–7.44 (m, 3H), 7.44–7.38 (m, 6H), 7.30–7.24 (m, 1H), 7.20–7.10 (m, 3H), 5.51 (t, *J* = 6.5 Hz, 1H), 2.16 (ddd, *J* = 12.5, 7.0, 2.0 Hz, 1H), 2.03 (ddd, *J* = 12.5, 6.0, 2.0 Hz, 1H), 1.42 (d, *J* = 1.0 Hz, 3H), 1.14 (d, *J* = 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 151.5, 143.7, 135.6, 134.6, 130.0, 128.2, 127.8, 126.6, 124.5, 122.0, 75.4, 51.7, 42.1, 29.72, 29.68; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{29}H_{28}OSiNa$ 443.1802; Found 443.1805.
Enantiomeric excess of (*S*)-**9g** has been determined after desilylation into (*S*)-**8g**; HPLC (CHIRALCEL OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.5 mL/min): t_R = 18.3 min (92.9%), t_R = 21.1 min (7.1%).

(*S*)-((1,2-dihydroacenaphthylen-1-yl)oxy)triphenylsilane ((*S*)-9h)[11a]
[Scheme 2, 78% ee]: Enantiomeric excess of (*S*)-**9h** has been determined after desilylation into (*S*)-**9h**; HPLC (CHIRALCEL OD-3, *i*-PrOH/hexane = 1/30, flow rate = 0.65 mL/min): t_R = 45.5 min (89.0%), t_R = 54.9 min (11.0%); ^1H NMR ($CDCl_3$): δ 7.82–7.75 (m, 6H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.55–7.41 (m, 11H), 7.27–7.18 (m, 2H), 6.03 (d, *J* = 7.0 Hz, 1H), 3.62 (dd, *J* = 17.5, 7.0 Hz, 1H), 3.42 (d, *J* = 17.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 145.6, 141.7, 137.3, 135.6, 134.4, 131.1, 130.1, 127.9, 124.4, 122.6, 120.5, 119.3, 75.4, 42.0.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Copy of ^1H- and ^{13}C-NMR, and Copy of HPLC Analyses (PDF)

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Notes

The authors declare no competing financial interest.

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