Preparation of optically active *n*-butyl(methyl)phenyl-, *tert*-butyl(methyl)phenyl- and isopropyl(methyl)phenylsilanes from the corresponding silyl chlorides using 2,2′-dihydroxy-1,1′-binaphthyls as resolving agents

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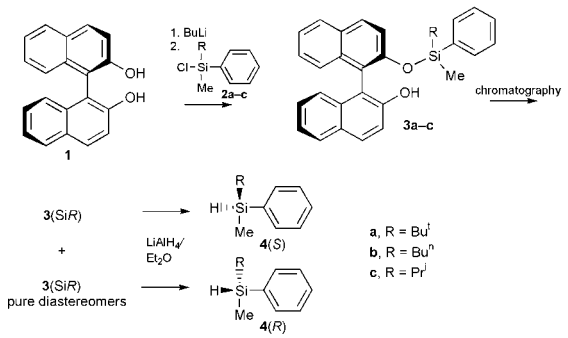
Enantiomeric silanes 4a, 4b and 4c were obtained from the corresponding racemic silyl chlorides *via* diastereomeric derivatives with (*R*)-[1,1′]binaphthalenyl-2,2′-diol; the optical purity of silanes 4a and 4c was determined (> 98% ee) by HPLC using a chiral cyclodextrin-based column.

Increasing attention has been recently paid to the preparation and synthetic applications of organosilicon compounds with a stereogenic silicon atom.[1,2] Chiral tri(alkyl/aryl)silanes appear to be the most important reagents and synthetic intermediates in this field, owing to their facile reactions with carbon–carbon multiple bonds[3] and easy transformations into other organosilicon compounds, among others, to silyl halides. The pioneering work on tri(alkyl/aryl)silane stereochemistry has been conducted long ago using methyl(naphthyl)phenylsilane[4,5] which is crystalline and relatively easy to obtain in an optically pure form. Some other optically active silanes (non-crystalline in the majority of cases when the naphthyl group is not present) have been prepared only recently. Masuda and coworkers[6] have reported the preparation of several optically active tri(alkyl/aryl)silanes by asymmetric synthesis involving chiral auxiliaries. It has been shown that enzymatic methods have a considerable potential in synthesis of optically active organosilicon compounds.[7–9] Since racemic silane derivatives are readily available, a racemate resolution may provide a convenient and amenable to large-scale approach to a variety of optically active silanes. Along such lines, a method for the preparation of enantiomers of *tert*-butyl(methyl)phenylsilane **4a** (Scheme 1) from racemic *tert*-butyl(methyl)phenylsilyl chloride **2a**, based upon resolution of a particular racemic intermediate with enantiomeric 2-aminobutanols has been developed in our laboratories.[10] However, all our attempts to extend this method to other alkyl/arylsilanes failed. In the search for a more general procedure for racemic silane resolution we have chosen enantiomeric [1,1′]binaphthalenyl-2,2′-diols (BINOLs) as the resolving agents. These easily accessible crystalline compounds have found broad application as ligands and chiral recognition agents;[11,12] however, to the best of our knowledge, their use as resolving agents has not been reported. We present here a method for the preparation of enantiomeric silanes **4a–c** with use of BINOLs. We also report the first direct determination of optical purity of silanes by GC with a chiral column, which provides an important tool for further work with optically active silanes.

Treatment of the lithium derivative of (*R*)-BINOL **1** with racemic *tert*-butyl(methyl)phenylsilyl chloride[7] **2a** yielded diastereomeric derivatives **3a** quantitatively. This diastereomer mixture was separated on a silica gel column to give pure crystalline diastereomers **3a**(Si*R)* and **3a**(Si*S*) and some mixed fraction.† Complete separation of **3a**(Si*R*) and **3a**(Si*S*) was achieved using preparative HPLC‡ and their yields and some physical data are given in Table 1. The absolute configuration of the diastereomer **3a**(Si*R*) (more mobile on chromatography) follows from its single crystal X-ray analysis,§ and a plot of the X-ray structure of **3a**(Si*R*) is shown in Fig. 1. In a similar manner BINOL derivatives of *n*-butyl(phenyl)methylsilane **3b** and phenyl(isopropyl)methylsilane **3c** were prepared and their respective diastereomers were separated by chromatography. The yields and some physical properties of these compounds are given in Table 1. Neither of the diastereomers of **3b** or **3c** could be obtained in crystalline form.



Scheme 1

Table 1 Preparation and some properties of 2′-alkyl(methyl)phenylsilanyloxy-[1,1′]binaphthalenyl-2-ols **3a–c** obtained from (*R*)-BINOL **1** and recemic alkyl(methyl)phenylsilyl chlorides **2a–c**

			More mobile isomer			Less mobile isomer		
R		Yield (%)	R_t/min	Mp/°C	Config.	R_t/min	Mp/°C	Config.
3a, Bu^t		95	19.73[a]	129–130	Si*R*	20.57[a]	133–134	Si*S*
3b, Bu^n		73	34.20[b]	—	Si*R*	39.92[b]	—	Si*S*
3c, Pr^i		84	16.15[a]	—	Si*R*	17.36[a]	—	Si*S*

[a] R_t refers to HPLC, analytical column,‡ eluent: 1% ethyl acetate in hexane. [b] Eluent: 0.5% ethyl acetate in hexane.

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Table 2 Preparation of optically active silanes by $LiAlH_4$ reduction of diastereomeric BINOL derivatives

	Si*R*			Si*S*		
R	Yield (%)	$[\alpha]_D(c)$	Ee (%)[a]	Yield (%)	$[\alpha]_D$ (*c*)‡	Ee (%)[a]
4a, Bu^t	78	−4.1(6.15)	> 98	83	+4.2(8.04)	> 98
4b, Bu^n	95	−6.2(6.50)	—	78	+6.5(7.10)	—
4c, Pr^i	82	−3.9(8.39)	98.7	80	+3.9(7.87)	98.2

[a] Determined by GC analysis using a chiral column (B-DM; ASTEC; 50 m × 0.32 mm; 100 kPa).

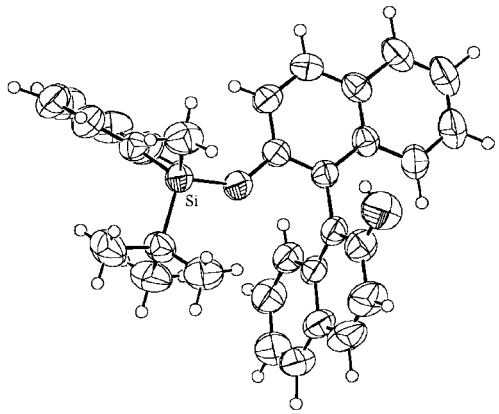
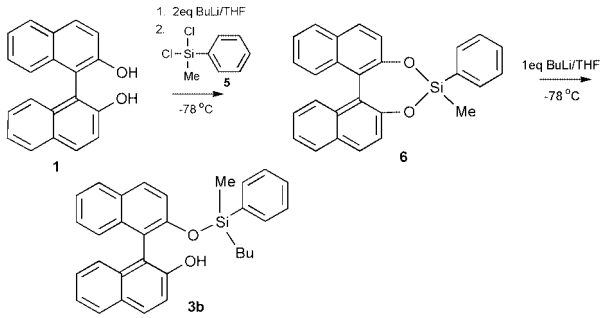


Fig. 1 X-Ray crystal structure of **3a**(Si*R*).

In order to generate optically active silane and to recover the BINOL, diastereomer **3a**(Si*R*) was reduced with $LiAlH_4$ in diethyl ether. Silane **4a**(*S*) was obtained in 83% yield, 95% ee. Specific rotation¶ and optical purity of this product (determined by GC analysis on a chiral column, *vide infra*) are presented in Table 2. Transformation of **3a**(Si*R*) into **4a**(*S*) indicates that $LiAlH_4$ reduction of the BINOL derivative occurred with retention of configuration around the Si atom, as expected by analogy to other O–Si derivatives.[13] Reduction of the more mobile diastereomer **3b**(Si*R*) afforded dextrorotatory silane **4b**(*S*).

Similarly, reduction of all other diastereomeric silyloxy derivatives afforded optically active silanes with yields and some properties compiled in Table 2. The optical purity of enantiomeric silanes **4c** was very high while the enantiomeric purity of **4b** could not be determined (*vide infra*). The absolute configuration of silanes **4b** and **4c** could not be determined by X-ray measurements. However, comparison with **4a** and some other silanes described[14] indicates an Si*S* configuration for the dextrorotatory enantiomers.

An attempt was made to use BINOL as a template for asymmetric synthesis of silanes. Treatment of *rac*-BINOL **1** (Scheme 2) with 2 mol equivalents of *n*-butyllithium followed by dichloro(methyl)phenylsilane (THF, −78 °C) gave an unstable intermediate which could not be isolated, presumably the [1,3,2]dioxasilepane derivative **6**. However, treatment of **6** *in situ* with 1 mol equivalent of *n*-butyllithium (THF, −78 °C) afforded **3b** as a mixture of diastereomers in a 1:1 ratio. Interestingly, stable [1,3,2]dioxasilepane derivatives with biphenyl frameworks have been prepared.[15]



Scheme 2

Determining the optical purity of silanes **4a**–**c** was crucial for their intended use in asymmetric synthesis. An attempt was made to apply several analytical methods, including HPLC on chiral columns and NMR measurements in the presence of shift reagents. Eventually, it was found that GC analysis using a commercial cyclodextrin-based chiral column (B-DM; ASTEC; 50 m × 0.32 mm) provided base-line separation of enantiomers **4a** at 70 °C [R_t = 75.51 min, (*R*); R_t = 77.00 min (*S*)] and **4c** at 120 °C [R_t = 25.37 min (*S*); R_t = 26.95 min (*R*)]. Conversely, silane **4b** bearing an *n*-butyl group showed no enantiomer separation even for a much longer retention time. To the best of our knowledge, GC chiral column separation of **4a** and **4c** represents the first direct determination of enantiomeric purity of tri(alkyl/aryl)silanes.

In conclusion, a method for preparation silanes **4a**–**c** of high enantiomeric purity has been developed. It has been shown that the enantiomeric purity of virtually unpolar silanes may be determined by GC using a cyclodextrin-based chiral column.

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Notes and references

† Important ^1H NMR data of new compounds (200 MHz, $CDCl_3$, δ/ppm): **3a**(Si*S*): 5.10 (s, 1, OH); 0.40 (s, 3, SiMe); **3a**(Si*R*) 4.9 7 (s, 1, OH); 0.46 (s, 3, SiMe); **3b**(Si*S*): 5.07 (s, 1, OH), 0.26 (s, 3, SiMe); **3b**(Si*R*): 5.03 (s, 1, OH), 0.26 (s, 3, SiMe); **3c**(Si*S*): 5.03 (s, 1, OH), 0.20 (s, 3H, SiMe); **3c**(Si*R*): 4.94 (s, 1, OH), 0.31 (s, 3H, SiMe).

‡ Analytical HPLC was performed using a Nucleosil 50-5 column (250 × 4.6 mm), flow rate 1 ml min^{-1}, UV detector (254 nm); preparative HPLC was carried out using a Nucleosil 50-7 column (three units in sequence 250 × 20 mm).

§ *Crystal data* for $C_{31}H_{30}O_2Si$ **3a**(Si*R*): M = 462.64, orthorhombic, space group $P2_12_12_1$, a = 8.3530(10), b = 13.3170(10), c = 23.5330(10) Å, U = 2617.7(4) $Å^3$; T = 293 K, Z = 4, μ(Cu-Kα) = 1.54 mm^{-1}. The final $wR(F^2)$ was 0.1063.

CCDC 182/1624. See http://www.rsc.org/suppdata/cc/b0/b001440k/ for crystallographic files in .cif format.

¶ Specific rotations were measured with a Perkin-Elmer Model 141 polarimeter using an 8 cm^3 capacity cell (10 cm path length) for hexane solutions of distilled samples. Distillation of silanes was required to remove solvents and other volatile impurities.

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