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Facile synthesis of enantiomerically pure *tert*-butyl(methyl)phenylsilanes

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Abstract

A method for the preparation of both enantiomers of *tert*-butyl(methyl)phenylsilane **2** is presented. Racemic *tert*-butyl(methyl)phenylsilyl chloride **3** was allowed to react with (*R*)-(−)-2-amino-1-butanol **4** to give hydrochloride **5**. Diastereomer separation via treatment of the respective free amine **6** with 0.5 mol equivalent of HCl in hexane-2-propanol yielded crystalline diastereomerically pure hydrochloride (*R*)Si-**5**. The corresponding free amine (*R*)Si-**6** was reduced with $LiAlH_4$ to give (*S*)-**2**. The mother liquors obtained after separation of (*R*)Si-**5** on treatment with oxalic acid provided a crystalline salt that eventually afforded (*R*)-**2**. The optical purity of (*S*)-**2** (98% ee) was documented by its reaction (hydrosilylation) with propargylic alcohol derivative **10** and HPLC analysis of product **11** using a chiral column.

1. Introduction

Nonracemic organosilicon compounds with an asymmetric silicon atom may potentially serve as auxiliaries or reagents for enantioselective synthesis. However, chiral silicon derivatives have been little exploited as compared to organosulfur or organophosphorus compounds in which the heteroatom provides the stereogenic centre. To date, one of the main reasons for the limited interest in this area of organosilicon chemistry lies, apparently, in the inaccessibility of appropriate optically active compounds. In spite of recent efforts towards a practical synthesis of chiral organosilicon compounds,[1–3] only methyl(1-naphthyl)phenylsilane **1** (Fig. 1) and congeners are readily available in enantiomeric form by the classical Sommer procedure involving separation of diastereomeric methyl(1-naphthyl)phenyl[(−)-menthoxy]silanes[4,5] or by a catalytic method developed by Corriu and coworkers.[6] For both methods

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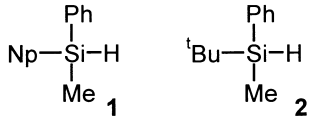


Figure 1.

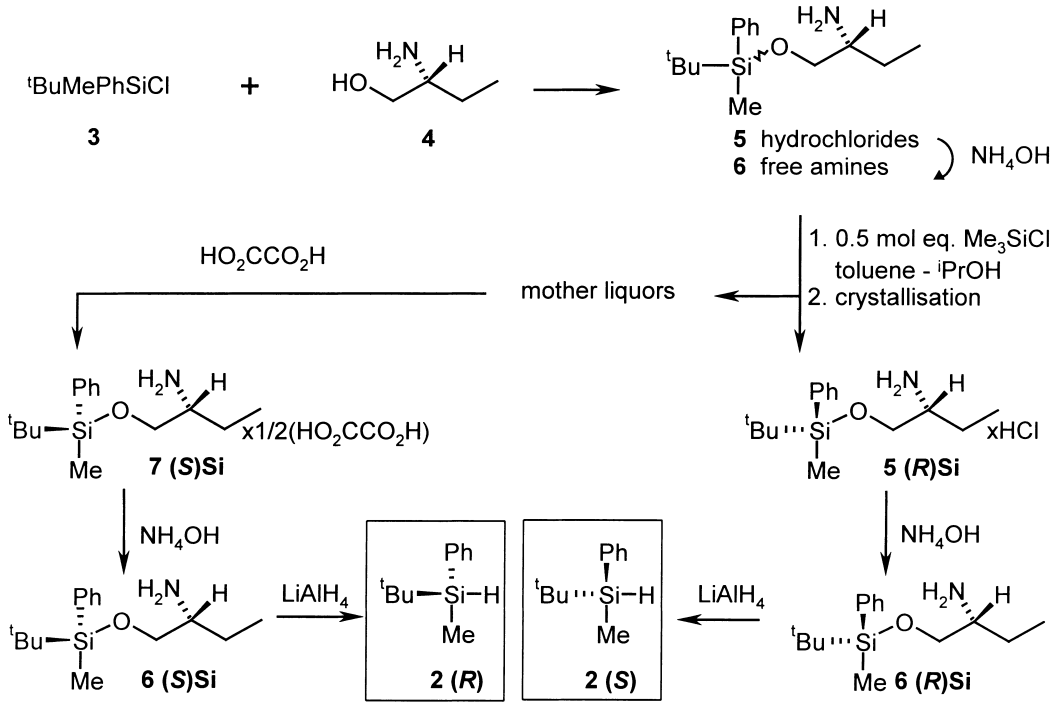
it is crucial that methyl(1-naphthyl)phenylsilane and many of its derivatives retaining the 1-naphthyl substituent at the silicon atom occur as crystalline solids. Some reactions of nonracemic **1** and its derivatives that have been examined with respect to asymmetric induction provided only moderate encouragement for further investigation[7–12] [an exception is the methylation of optically active *tert*-butyl 2-(methylnaphthylphenylsilyl)acetate which occurs with 9:1 diastereoselectivity[13]]. However, the relatively low level of asymmetric induction in reactions involving **1** may by attributed to the lack of differentiation of the two bulky aromatic substituents, the 1-naphthyl and phenyl groups. In this connection, it was considered to be of interest to develop a practical synthesis of a silane with more pronounced alteration in the steric bulk of the substituents at the silicon atom and to scrutinise its application as a tool in asymmetric synthesis. Transformations of silanes to other silyl derivatives, such as silyl halides and silyl alkoxides are well known. Enantiomeric *tert*-butyl(methyl)phenylsilanes **2** were chosen as targets in the initial studies. Racemic *tert*-butyl(methyl)phenylsilane may be easily prepared[14,15] from commercially available dichloro(methyl)phenylsilane. Nonracemic *tert*-butyl(methyl)phenylsilane ($[\alpha]_D^{20}$ −0.65 or +0.65) has been prepared with the use of optically active borneol as a chiral agent ($[\alpha]_D^{20}$ +1.20) or by a method involving hydrosilylation of benzophenone in the presence of a chiral catalyst.[16] However, the specific rotation of the described material was low, the enantiomeric excess was not determined and the assignment of the absolute configuration was speculative.

2. Results and discussion

Our preliminary attempts to separate *tert*-butyl(methyl)phenylmenthoxysilanes by crystallisation or chromatography failed. We then turned our attention to amino alcohols as resolving agents, reasoning that even if their *O*-silyl derivatives will not crystallise instantly, the presence of the amine function will provide a handle for chemical modifications and consequently allow the generation of crystalline derivatives [(+)-ephedrine had been utilised[6] in the synthesis of the optically active methyl(1-naphthyl)phenylsilane but in a quite different way]. 2-Amino-1-butanol, which is commercially available in both enantiomeric forms, was chosen as potentially one of the most advantageous resolving agents. Reaction of (*R*)-(−)-2-amino-1-butanol **4** (97% ee) (Scheme 1) with racemic *tert*-butyl(methyl)phenylsilyl chloride **3** in dry toluene yielded a mixture of diastereomeric amino silyloxy derivatives **5** as hydrochlorides.

These hydrochlorides were partly crystalline, however, all attempts to isolate pure crystalline material proved futile. It appeared likely that only one of the diastereomeric hydrochlorides had crystallised. The mixture of hydrochlorides was thus transformed into the respective free amine **6** which was purified by distillation (89% yield). Treatment of **6** in hexane–2-propanol with 0.5 mol equivalents of HCl (generated in situ from Me_3SiCl) indeed gave crystalline hydrochloride (*R*)Si-**5** that could be easily separated by filtration and purified further. The hydrochloride thus obtained (25% yield) was transformed into the free base (*R*)Si-**6** (an oil) and then into the *N*-acetyl derivative **8** (Fig. 2).

^{1}H NMR analysis of the latter showed that it is diastereomerically pure (see experimental section). Some other crystalline amides were also prepared, of which *p*-nitrobenzyl derivative (*R*)Si-**9** provided crystals suitable for X-ray analysis (long needles from 1-chlorobutane). The absolute configuration of the silicon atom in the derivative (*R*)Si-**9** was revealed by a single crystal X-ray analysis. The structure of



Scheme 1.

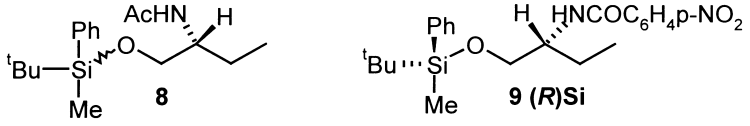


Figure 2.

(*R*)Si-**9** is represented in Fig. 3. It shows that with use of (*R*)-(−)-2-amino-1-butanol and crystallisation of the respective hydrochloride, the diastereomer **5** with (*R*)-configuration of the Si atom is obtained.

Diastereomerically pure aminosilane (*R*)Si-**6** was treated with lithium aluminium hydride in diethyl ether. The apolar product was collected and distilled to give silane **2** (75% yield) as a colourless oil ($[\alpha]_D^{20}$ +4.24 (hexane)). As it has been demonstrated that lithium aluminium hydride reduction of alkoxysilanes occurs with retention of configuration at the silicon atom,[4,17] the (*S*) configuration at the silicon atom has been attributed to the product, i.e. **2**(*S*). As regards the relationship between the absolute configuration of *tert*-butyl(methyl)phenylsilane and the direction of its specific rotation, the suggestion of the previous workers[16] has been confirmed.

At this stage, a relatively simple approach to optically active silane (*S*)-**2** was achieved. The overall efficiency of the method suffered, however, from processing of only one enantiomer of the starting racemic *tert*-butyl(methyl)phenylsilyl chloride **3**. A further improvement would be a method that would allow purification of the major diastereomer of aminosilane **6** remaining after separation of crystalline diastereomeric hydrochloride (*R*)Si-**5**. It was eventually found that the mother liquors from precipitation of the (*R*)Si-**5**, after drying and treatment with an excess of anhydrous oxalic acid in 2-propanol, afford crystalline oxalate (*S*)Si-**7** that can be isolated by filtration (33% yield from **6**). Recrystallisation from chloroform and decomposition of the salt with ammonium hydroxide gives the free base (*S*)Si-**6** ($[\alpha]_D^{20}$ −53.44).

For larger scale preparations, a restriction of the developed procedure may come from the use of 2-

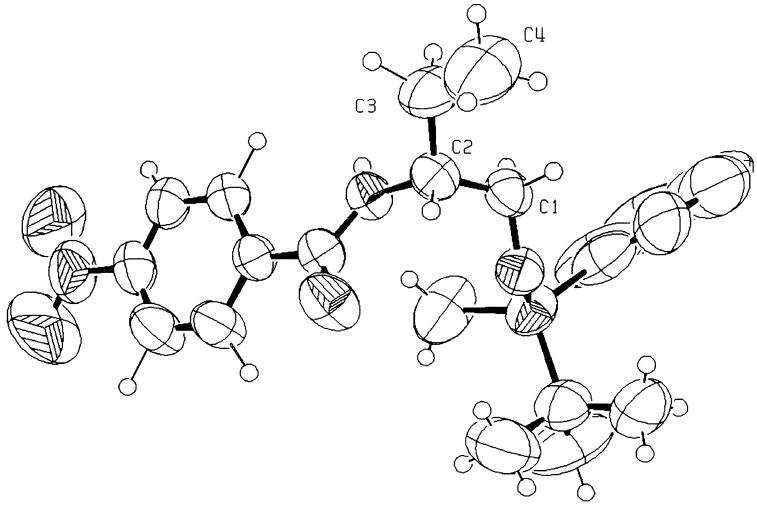
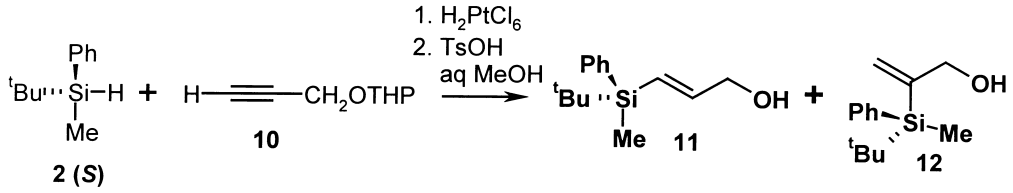


Figure 3.

amino-1-butanols of 97% ee, which, although available in both enantiomeric forms (Aldrich), is relatively expensive. (*R*)-(−)-2-Amino-1-butanol of only 80% ee (Fluka) is approximately 100 times cheaper. Fortunately, application of the latter reagent to the above described procedure gave the respective silanes with no decrease in the enantiomeric excess, but with a somewhat lower overall yield.

With enantiomeric silanes **2** showing a high specific rotation in hand, we faced the problem of determining the enantiomeric excess. Some separation of enantiomers was observed on a Chiralcel® OJ column (Daicel Chemical Industries, Tokyo, 25×0.46 cm, hexane, t_R ca. 12 min, 0.5 ml/min; no separation occurred on a Chiralcel OD-H column). However, the separation was not sufficient for any quantitative conclusions. Screening of NMR spectra of **2** with chiral shift reagents was equally unfruitful. After this failure of direct methods, we turned our attention to chemical reactions. Our previous experience[18] has shown that enantiomeric vinylsilanes **11** are very well suited to HPLC analysis on a chiral column. Hydrosilylation of protected propargyl alcohol **10** with (*S*)-**2** ($[\alpha]_D^{20}$ +4.24) in the presence of H_2PtCl_6 followed by hydrolysis of the protecting group in the reaction product gave a mixture of regioisomeric vinylsilanes **11** and **12** in a ratio of 2:3, which were separated on a silica gel column (Scheme 2). The minor isomer was identical to **11** prepared via another route.[18] Its HPLC analysis using a Chiralcel OD-H column indicated the presence of only one enantiomer. We conclude that the starting material consisted of one enantiomer within the limit of error of the HPLC analysis which we estimate at 2%. It is noteworthy that hydrosilylation of ethylene derivatives has been shown[19] to occur with retention of configuration at the silicon atom. In conclusion, the synthesis of epimeric (*R*)- and (*S*)-*tert*-butyl(methyl)phenylsilanes **2** starting from racemic *tert*-butyl(methyl)phenylsilyl chloride and involving separation of the corresponding diastereomeric 2-amino-butan-1-ol derivatives, has been achieved. It has been shown that hydrosilylation of a propargyl alcohol derivative **10** with enantiomeric *tert*-butyl(methyl)phenylsilane affords product **11** of 98% ee.



Scheme 2.

3. Experimental

3.1. General

Melting points were determined on a Kofler hot-stage melting point apparatus. ^{1}H and ^{13}C NMR spectra were performed in $CDCl_3$ on a Varian Gemini 200 MHz spectrometer and multiplicities were assigned using DEPT techniques. All chemical shifts are quoted on the δ scale relative to internal tetramethylsilane. Optical rotations were measured on a Perkin–Elmer model 141 polarimeter at the concentration (g/100 ml) indicated. Chiral HPLC analyses were performed using a Shimadzu LC-8A chromatograph provided with an SPD-6A variable λ detector and fitted with a Chiralcel OD-H column (25×0.46 cm). Conditions A: hexane as eluent, flow 0.5 ml/min, λ=254 nm. Conditions B: hexane:2-propanol (9:1) as eluent, flow 0.5 ml/min, λ=254 nm. Elemental analyses were carried out by the Microanalysis Service of the Institute of Organic Chemistry, Warsaw.

3.2. tert-*Butylchloro(methyl)phenylsilane* ***3***

The procedure of Tacke[20] was simplified: in a two-necked flask provided with a reflux condenser was placed dichloro(methyl)phenylsilane (2 ml, 2.319 g, 12.1 mmol), and a 1.7 M solution of *tert*-butyllithium in pentane (Aldrich, 8 ml, 13.6 mmol) was added through a septum, all at once. The flask was immersed in a cold water bath and the reaction mixture was stirred for 24 h. The resulting slurry was concentrated on a rotary evaporator and then distilled in a Kugelrohr apparatus at 8 torr. A fraction collected at 120–150°C consisted of chloride **3** (2.291 g, 89% yield from $MePhSiCl_2$); δ_H 0.66 (3H, s, CH_3Si), 0.98 (9H, s, $(CH_3)_3C$), 7.41 (3H, m), 7.61 (2H, m).

3.3. 2-(R)-*Amino-1-(*tert-*butylmethylphenylsilyloxy)butane* ***6***

A mixture of silyl chloride **3** (3.459 g, 16.7 mmol), (*R*)-(−)-2-amino-1-butanol **4** (Aldrich, 97% ee, 1.570 g, 17.6 mmol), and dry toluene (5 ml) was stirred at 95–100°C (oil bath) for 24 h. The slurry was diluted with toluene (5 ml), cooled to rt and treated with 3 ml of 25% aqueous ammonia and 3 ml of water. After stirring for 2 h, the organic phase was separated, dried with anhydrous sodium sulfate and concentrated in vacuo. Kugelrohr distillation (175°C at 22 torr) afforded **6** as a colourless liquid (3.511 g, 82% based on silyl chloride **3**); δ_H 0.37 (3H, s, $SiCH_3$), 0.91 (9H, s, $SiC(CH_3)_3$), 0.93 (3H, m, CH_3), 1.1–1.6 (2H, bm, CH_2), 2.8 (1H, m, CHN), 3.3–3.5 (1H, m, CHO), 3.55–3.67 (1H, m, CHO), 7.38 (3H, m, Ph), 7.55 (2H, m, Ph).

3.4. 2-(R)-*Amino-1-(*tert-*butylmethylphenyl-Si(*R*)-silyloxy)butane hydrochloride (*R*)-Si-* ***5***

Trimethylchlorosilane (923 mg, 8.50 mmol) was added in one portion to a solution of aminosiloxane **6** (4.371 g, 16.47 mmol) in 2-propanol (4.5 ml). At first the mixture remained liquid then turned gelatinous.

The flask was placed in an oil bath maintained at 70°C. When a clear solution resulted it was diluted with hexane (18 ml). The heating was turned off and the mixture was stirred magnetically while the bath temperature gradually dropped. After crystals appeared, the flask was placed in a refrigerator for several hours. The crystals were collected and washed three times with a cold mixture of hexane:2-propanol (4:1, 10 ml in total), and air-dried for 24 h. Product (*R*)S-**5i** was obtained (1.768 g, 36% from aminosiloxane **6**), m.p. 186–188°C, $[\alpha]_D^{20}$ +31.7 (c 11.16, $CHCl_3$).

A sample of this material (11 mg) was acetylated (Ac_2O, Et_3N, CH_2Cl_2, 2 h at rt) and its diastereomeric purity was determined by ^1H NMR; the integration ratio of CH_3CON signals at δ 1.92 and δ 2.00 was 95:5, respectively. The remaining part of the product (1.757 g) was recrystallised twice from hexane:chloroform (7:3, 35 ml) yielding 1.148 g (65%) of crystals, m.p. 193–194°C, $[\alpha]_D^{20}$ +34.48 (c 10.92, $CHCl_3$); δ_H 0.41 (3H, s, CH_3Si), 0.93 [9H, s, $(CH_3)_3C$], 0.98 (3H, t, J=7 Hz, CH_3), 1.7–2.1 (2H, bm, CH_2), 3.2 (1H, m, CHN), 3.80 (2H, dq, J_1=11 Hz, J_2=4.3 Hz, CH_2O), 7.37 (3H, m, Ph), 7.55 (2H, m, Ph), 8.55 (3H, m, H_3N^+); δ_C −7.49 (CH_3Si), 10.06 (CH_3), 18.33 [$(CH)_3C$], 22.60 (CH_2), 25.89 [$(CH_3)_3C$], 54.91 (CHN), 82.27 (CH_2O), 96.11, 127.72, 129.58, 134.48. Anal. calcd for $C_{15}H_{28}ClNOSi$: C, 59.67%; H, 9.35%; Cl, 11.74%; N, 4.64%. Found: C, 59.60%; H, 9.57%; Cl, 11.89%; N, 4.61%.

The procedures in Sections 3.3 and 3.4 were then repeated using (*R*)-(−)-2-amino-1-butanol of 80% ee (Fluka). Since this reagent contains some water which cannot be removed by a standard distillation, it was diluted with four parts of benzene, stirred overnight with calcium hydride and then distilled under reduced pressure. Reaction of purified aminobutanol (1.665 g, 18.7 mmol) with silyl chloride **3** (3.796 g, 17.8 mmol) yielded aminosiloxane **6** (4.152 g, 88%), which in turn gave hydrochloride (*R*)Si-**5**, (1.768 g, 36%). Two recrystallisations of the product from toluene (9 ml per gram) provided pure product (1.497 g, total yield 32% based on **6**).

*3.5. 2-(*R*)-Amino-1-[*tert*-butyl(methyl)phenyl-Si(*R*)-silyloxy]butane (*R*)Si-**6***

The purified hydrochloride (*R*)Si-**5** (1.124 g) was suspended in dichloromethane (10 ml), treated with 25% aqueous ammonia solution (0.5 ml) and diluted with water (0.5 ml). The mixture was stirred at rt for 2 h, then the organic phase was separated, washed with water, dried with sodium sulfate and concentrated in vacuo. Kugelrohr distillation of the residue (150°C at 2 torr) afforded (*R*)Si-**6** as a colourless liquid, 941 mg (95%), $[\alpha]_D^{20}$ +38.89 (c 13.2, hexane). Anal. calcd for $C_{15}H_{27}NOSi$: C, 67.87%; H, 10.25%; N, 5.28%. Found: C, 67.50%; H, 10.51%; N, 5.42%.

3.6. tert-*Butyl(methyl)phenylsilane (*S*)-**2***

To a suspension of lithium aluminium hydride (150 mg) in ether (10 ml), a solution of the siloxyamine (+)-**6** (1.047 g) in ether (10 ml) was added dropwise. After stirring for 24 h at rt, methanol (1 ml) was added carefully, followed by 10% hydrochloric acid (20 ml). The organic phase was washed successively with water and saturated sodium hydrogen carbonate solution, dried with sodium sulfate, and concentrated on the rotary evaporator (rt water bath). The residue was filtered through a short silica gel column in hexane solution; Kugelrohr distillation of the concentrated eluent (115°C at 22 torr) afforded silane (*S*)-**2** as a colourless liquid, 100% pure by GLC, 528 mg (yield 75%), $[\alpha]_D^{20}$ +4.24 (c 8.04, hexane); δ 0.33 (3H, d, J=3.9 Hz, CH_3Si), 0.93 [9H, s, $(CH_3)_3C$], 4.13 (1H, q, J=3.9 Hz, SiH), 7.2–7.7 (5H, m, aromatic).

3.7. 2-(R)-Amino-1-[tert-butyl(methyl)phenyl-Si(S)-silyloxy]butaneoxalate (S)Si-7

The filtrate and washings from the first precipitation of the hydrochloride (*R*)Si-**5** were concentrated in vacuo. The semisolid residue was stirred with dichloromethane (3 ml), conc. ammonia solution (1 ml) and water (1 ml) until two liquid phases formed. Hexane (10 ml) was added and stirring was continued for about 5 min. The organic phase was separated, washed with brine, dried with sodium sulfate and concentrated in vacuo. The residue (2.295 g) was dissolved in 2-propanol (7 ml). The solution was warmed to 80°C and treated with anhydrous oxalic acid (387 mg, 4.28 mmol) in 2-propanol (4 ml). The mixture was cooled with stirring and then set aside in the refrigerator. Crystals were collected, washed with cold 2-propanol (total 10 ml) and air-dried. The product (*S*)Si-**7** was obtained (1.676 g, 33% from **6**), m.p. 167–169°C. To determine its diastereomeric purity, a sample (14 mg) was converted to the *N*-acetyl derivative (see above). ^{1}H NMR showed a mixture of 12% of the (*R*)Si diastereomer (CH_3CON signal at δ 1.92). The bulk of the product (1.662 g) was then recrystallised twice from 2-propanol to give pure (*S*)Si-**7** (577 mg), m.p. 170–173°C, $[\alpha]_D^{20}$ −31.3 (c 9.1, MeOH). Anal. calcd for $C_{32}H_{56}N_2O_6Si_2$: C, 61.89%; H, 9.09%; N, 4.51%. Found: C. 61.72%; H, 9.05%; N, 4.43%.

3.8. 2-(R)-Amino-1-[tert-butyl(methyl)phenyl-(S)-silyloxy]butane (S)Si-6

The oxalate (*S*)Si-**7** (242 mg, 0.39 mmol) was suspended in dichloromethane (3 ml) and stirred with 25% ammonia solution (0.2 ml) diluted with water (0.4 ml) until the solid had disappeared completely. Usual work-up followed by a Kugelrohr distillation (155°C at 3 torr) afforded (*S*)Si-**6** as a colourless liquid, 172 mg (83%), $[\alpha]_D^{20}$ −53.44 (c 8.94, $CHCl_3$).

3.9. tert-Butyl(methyl)phenylsilane (R)-2

Reduction of (*S*)Si-**8** (170 mg, 0.64 mmol) with lithium aluminium hydride (60 mg, 1.58 mmol) in ether (total volume 4 ml) and work-up were performed as above. Kugelrohr distillation (105°C at 19 torr) afforded (*R*)-**2** as a colourless liquid, 80 mg (69.9%), $[\alpha]_D^{20}$ −4.1 (c 6.15, hexane).

3.10. Hydrosilylation of propargylic derivative 10 with silane (S)-2

The hydrosilylation catalyst was prepared by dissolving $H_2PtCl_6 \cdot H_2O$ (Fluka, 50 mg) in 2-propanol (1 ml).

A mixture of silane (*S*)-**2** (186 mg, 1.04 mmol), protected propargylic alcohol **10** (179 mg, 1.28 mmol) and the catalyst (two drops) was stirred at 50°C for 48 h under argon. The solution was diluted with hexane (1 ml), the cloudy mixture was put on a short silica gel column and the THP-protected products were eluted with hexane:ethyl acetate (9:1). The corresponding fractions were combined, concentrated, dissolved in methanol (10 ml) and treated with a few crystals of *p*-toluenesulfonic acid. After 2 h at rt, an excess of potassium carbonate was added, the mixture was evaporated to dryness and the residue was chromatographed on silica with hexane–ethyl acetate. The fraction consisting of pure **11** (40 mg) was analysed on a Chiralcel OD-H column; only one enantiomer **11** was detected (t_R=16.7 min, hexane:2-propanol 9:1, 0.5 ml/min), identical with an authentic sample.[18]

3.11. N-{2-(R)-1-[tert-Butyl(methyl)phenyl-Si(R)-silyloxy]}butyl-4-nitrobenzamide (R)Si-9

Compound (*R*)Si-**6** (117 mg, 0.44 mmol), dissolved in benzene (2 ml) and pyridine (0.2 ml), was allowed to react with 4-nitrobenzoyl chloride (105 mg, 0.57 mmol) for 1 h at rt. The excess reagent was decomposed with water (1.5 ml). Work-up followed by chromatography on silica with hexane–ethyl acetate afforded pure amide (*R*)Si-**9**, 157 mg, m.p. 123–124°C (long needles from 1-chlorobutane); δ_H 0.39 (3H, s, CH_3Si), 0.92 [9H, s, $(CH_3)_3C$], 1.01 (3H, t, J=7.5 Hz, CH_3), 1.75 (2H, m, CH_2), 3.82 (2H, m, CH_2O), 4.15 (1H, m, CHN), 6.4 (1H, m, NH), 7.35 (3H, m), 7.5 (2H, m), 7.74 (2H, d, J=9 Hz), 8.23 (2H, d, J=9 Hz). Crystal data: colourless orthorhombic crystal (0.25×0.3×0.45 mm); empirical formula, $C_{22}H_{30}N_2O_4Si$ (f_w 414.57); space group $P2_12_12_1$; *a*=9.5140(10) Å, *b*=12.6970(10) Å, *c*=20.1500(10) Å, *V*=2434.1(3) Å^3, D_{calc}=1.131 g/cm^3; α=β=γ=90°; Cu-Kα radiation (1.54184 Å) at 293 K.

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