On the Mechanism of the Reductive Metallation of Asymmetrically Substituted Silyl Chlorides

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Keywords: Silicon / Lithiation / Radicals / Enantioselectivity / Asymmetric synthesis

An investigation of the stereochemical course of the reductive metallation of silyl chlorides with silicon-centred chirality has revealed two major events which are detrimental to stereoselection during silyl anion formation: (1) chloride-induced racemisation of silyl chlorides and (2) nonstereoselective formal dimerisation during metallation providing the corresponding disilane. In control experiments, the stereochemical course of these processes has been independently verified for the reductive metallation of the enantioenriched cyclic silyl chloride (Si*S*)-**7a** (R = H, *er* ≥ 88:12). A screening of several related derivatives of (Si*S*)-**7a** led to the sterically encumbered silyl chloride (Si*R*)-**7c** (R = *i*Pr, *er* ≥ 94:6) which displays some unique features. This structural modification prevents racemisation by lithium chloride ($T < -40$ °C) as well as dimerisation ($T < -100$ °C) thus allowing for the first generation of an asymmetrically substituted silyl anion (Si*S*)-**8c** (*er* = 74:26) by reductive metallation of a silyl chloride with silicon-centred chirality. Moreover, the enantiospecificity of the preparation of (Si*R*)-**7c** by chlorination [(Si*S*)-**9c** → (Si*R*)-**7c**] and its reduction with aluminium hydrides [(Si*R*)-**7c** → (Si*R*)-**9c**] have been unambiguously determined by X-ray crystallography as retention (≥99%) and inversion (≥99%), respectively.

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Introduction

Silyl metal compounds have gained substantial importance as silicon transfer reagents in synthetic organic, organometallic and polymer chemistry.[1−3] These organometallics frequently originate from the requisite silyllithium which in turn is easily accessible by reductive metallation of the corresponding silyl chloride.[4] Whereas achiral silyllithium compounds are well-established,[1] the chemistry of asymmetrically substituted, tetracoordinate silyllithium species has attracted relatively little attention. Nevertheless, metallated silyl anions with silicon-centred chirality are attractive organometallics with regards to their remarkably high configurational stability,[5] potential synthetic applications[1−3] and mechanistic properties.[6]

Until recently, the enantioselective preparation of asymmetrically substituted silyl anions remained an open challenge in organosilicon chemistry. In his seminal work, Sommer succeeded in the reductive cleavage of an enantiomerically enriched disilane with lithium metal thus providing the silyl anion with partial racemisation.[7a] Similar observations were made by Corriu who accessed an optically active silyl anion via a cobalt−lithium exchange reaction.[7b]

This long-standing problem was independently solved by Kawakami[8] and Strohmann[9] by way of two conceptually different strategies, namely (1) chemo-unselective tin−lithium exchange of chiral silyl stannane **1** (**1** → **6**, Scheme 1)[8] and (2) reductive metallation of the chiral disilane **3** using lithium metal (**3** → **6**, Scheme 1).[9] However, these fundamental approaches are afflicted with an intrinsic shortcoming which complicates synthetic applications since (almost) equimolar amounts of another organometallic **2** and **4**, respectively, are formed as by-products.

A straightforward methodology from a synthetic view for the generation of stereochemically *and* chemically uniform silyllithiums is therefore still not available. Herein, we wish to report our efforts towards accessing enantioenriched silyllithiums **6** from chiral silyl chlorides **5** by simple reductive metallation using lithium metal (**5** → **6**, Scheme 1). We anticipated that this approach would produce the silyl anion **6** along with lithium chloride as the only by-product. It should be noted that Kawakami has described the reductive metallation of an acyclic enantioenriched silyl chloride with silicon-centred chirality in a recent publication. The asymmetrically substituted silicon centre underwent complete racemisation during metallation, providing the silyl anion in racemic form.[8]

Although reductive lithiation of silyl chlorides is routinely employed for silyl anion generation, its mechanism has not been elucidated so far.[1] Occasional reports have indicated the subtle nature of the reductive metallation of triorganosilyl chlorides R_3SiCl[10] and amino-substituted

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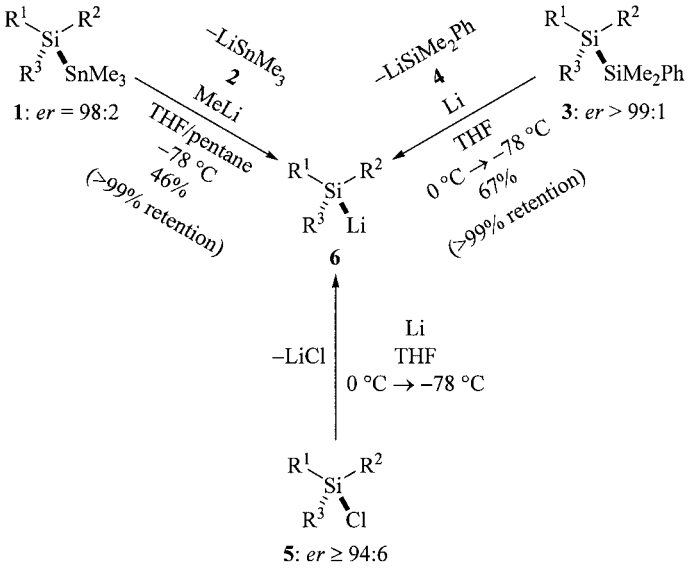
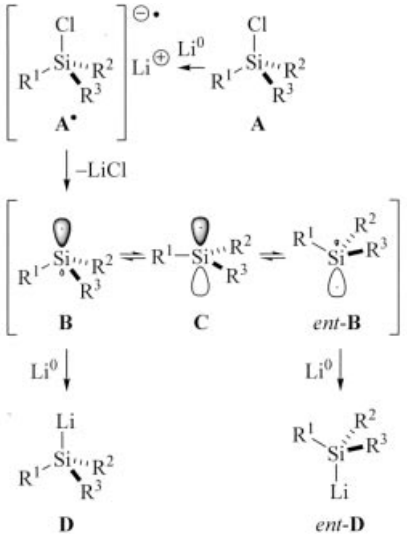


Scheme 1. Strategies for the enantioselective preparation of asymmetrically substituted silyl anions ($R^1 \neq R^2 \neq R^3$)

silyl chlorides $(Et_2N)_nPh_{3-n}SiCl$ (n = 1 and 2)[11] but without a detailed mechanistic understanding. Successful lithiation of R_3SiCl usually requires at least one aryl group at the silicon.[1a] A number of arylalkylsilyl chlorides having the general formula $Ph_{3-n}R_nSiCl$ (R = Me or *t*Bu, n = 0, 1, and 2) undergo reductive metallation in good yields.[1,10a] Conversely, treatment of trimethylsilyl chloride with lithium metal cleanly furnishes hexamethyldisilane rather than the desired silyllithium.[12] The peralkylated disilane is not reductively cleaved by elemental lithium or cognate reagents (LiN,[13a] LiDBB[13b] or LDMAN[13c]). However, metallation of $Ph_{3-n}R_nSiCl$ ($n \neq 3$) is known to proceed through disilanes which are subsequently cleaved under those reaction conditions.

These observations suggest that one or more aryl groups intervene in the reductive metallation of an intermediate disilane (or the silyl chloride itself) since an aryl group at silicon could potentially function as an electron acceptor. Nevertheless, we assume that the initial single electron transfer occurs into the σ*(Si–Cl) orbital (≡ LUMO). This hypothesis is consistent with experimental evidence that trialkylsilyl as well as arylalkylsilyl chlorides give the corresponding disilanes when treated with an electropositive metal. The fate of the initially formed radical anion $[R_3SiCl]^{\cdot -}$ is unknown but decomposition into a silyl radical $R_3Si^{\cdot}$ and a chloride anion Cl^- seems plausible. The silyl radical, $R_3Si^{\cdot}$, in turn is reduced by another equivalent of the electropositive metal providing a silyl anion R_3Si^- which formally dimerises together with unchanged silyl chloride. Alternatively, recombination of two molecules of $R_3Si^{\cdot}$ might also lead to the disilane intermediate. The mechanism of cleavage of the resultant disilane remains completely uncertain.

Based on these considerations, which involve the intermediacy of silyl radicals,[14] we have devised a working hypothesis (omitting disilane formation) for the reductive metallation of asymmetrically substituted silyl chlorides **A** (Scheme 2). Transfer of an electron into the σ*(Si–Cl) orbital of **A** provides silyl radical **B** and a chloride anion (**A** → **A**$^{\cdot}$ → **B**). Radical intermediate **B** with silicon-centred chirality is either prone to another electron capture forming **D** (**B** → **D**) or to racemisation *via* the vertex mechanism[14] (**B** → **C** → *ent*-**B**). Theoretical data predict a pyramidal configuration for silyl radicals with high inversion barriers[15] indicating that the second electron transfer (**B** → **D**) might occur prior to enantiomerisation (**B** → *ent*-**B**). Serious experimental data suggest the configurational stability of silyl radicals.[16] Therefore, the intermediacy of silyl radicals during metallation might not influence enantioselection.



Scheme 2. Vertex inversion of silyl radicals ($R^1 \neq R^2 \neq R^3$)

We selected cyclic silyl chloride (Si*S*)-**7a** (Figure 1) as a model substrate for two reasons, namely (1) chiral silyl chlo-

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rides for which practical syntheses are known[17,18] usually incorporate an α-naphthyl group (α-Np) which is an excellent electron acceptor.[8] (2) We reported a convergent and modular reaction sequence for a flexible preparation of chiral silanes with a 1,2,3,4-tetrahydro-1-silanaphthalene core.[19] This allows for straightforward access to (Si*S*)-**7a** and the related silanes *rac*-**7b** and (Si*R*)-**7c** (Figure 1).

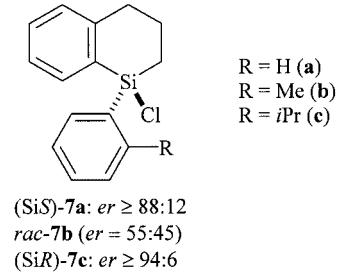
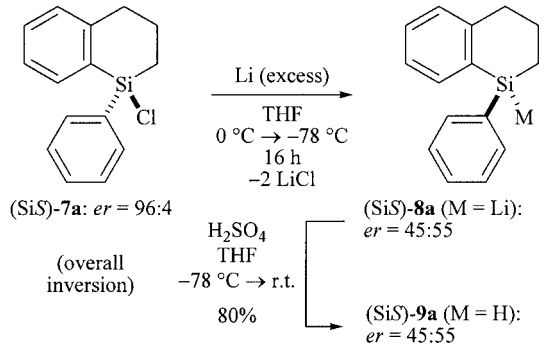


Figure 1. 1-Aryl-1-chloro-1,2,3,4-tetrahydro-1-silanaphthalenes **7**

Results and Discussion

First Generation Approach

We were pleased to find that treatment of (Si*S*)-**7a** (*er* = 96:4) with lithium metal under standard reaction conditions resulted in formation of the desired silyllithium (Si*S*)-**8a** in an isolated yield of 80% after protolysis (Scheme 3). Determination of the enantiomeric ratio after acidic workup [(Si*S*)-**8a** → (Si*S*)-**9a**] showed, however, that (Si*S*)-**8a** was nearly racemic. The slightly inverted absolute configuration of the isolated silane (Si*S*)-**9a** (*er* = 45:55) was rather puzzling assuming that protolysis proceeds with retention of stereochemistry.



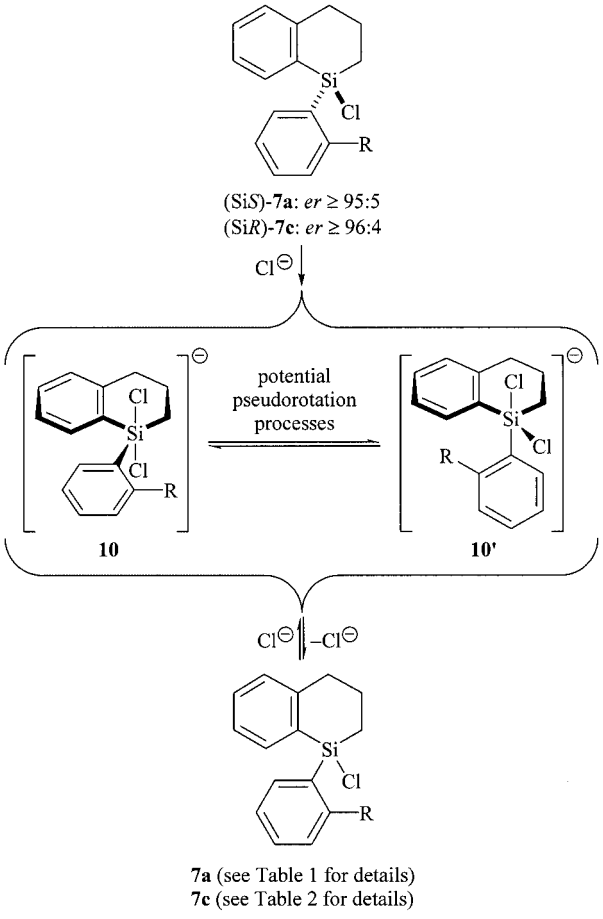
Scheme 3. Reductive metallation of (Si*S*)-**7a**

These results prompted us to further investigate the reaction pathway(s) of the reductive metallation with particular focus on the stereochemical consequences of two aspects, i.e. (1) does the lithium chloride "by-product" promote the racemisation of (Si*S*)-**7a** and (2) does this silyl anion formation [(Si*S*)-**7a** → (Si*S*)-**8a**, Scheme 3] proceed through a disilane?

Chloride-Induced Racemisation

Early investigations by Price using [^{36}Cl]-labelling techniques demonstrated a fast racemisation of optically active silyl chlorides by chloride anions.[20] Corriu[18a,18b] and, later, Bassindale[21] presented potential mechanistic rationales for these nucleophile-assisted racemisations based on kinetic[21b] and thermodynamic[21c] measurements.[22] However, these useful investigations have not provided a completely clear picture of the mechanism but have demonstrated the complexity of this process.[22,23]

As shown for the silyl chlorides **7**, we speculate that apical nucleophilic attack at silicon by chloride generates the achiral pentacoordinate silicon species **10** and equatorial attack provides **10′** (Scheme 4). Apart from reversible associative and dissociative processes, these pentacoordinate anions with a trigonal-bipyramidal geometry are prone to configurational isomerisation (**10**/**10′**). A recent study by Lammertsma elegantly showed that cyclic silanes undergo Berry pseudorotation![24]



Scheme 4. Plausible mechanisms for the chloride-induced racemisation of chiral silyl chlorides **7**

In order to examine the chloride-induced racemisation of (Si*S*)-**7a**, we observed (Si*S*)-**7a** with or without lithium chloride in THF (Table 1). After 1 h, treatment of the reaction mixture with lithium aluminium hydride[19] stereospecifically (≥95% inversion) furnished the corresponding silane (Si*S*)-**9a** in quantitative yield. This procedure allows for an indirect yet reliable determination of the enantiomeric ratio of silyl chloride (Si*S*)-**7a** by HPLC.

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Table 1. Chloride-induced racemisation of (Si*S*)-**7a**

Entry[a]	*er* (Si*S*)-**7a**	Solvent	Additive[b]	*T* [°C]	*er*[c] (Si*S*)-**9a**
1	96:4	THF	–	0	10:90
2	96:4	THF	LiCl	0	50:50
3	96:4	THF	LiCl	−78	50:50
4	92:8	THF	NaCl	−78	15:85
5	92:8	THF	KCl	−78	10:90
6	94:6	THF	LiF	−78	12:88
7	92:8	THF	LiBr	−78	12:88
8	94:6	THF	LiI	−78	32:68
9[d]	94:6	THF	$LiClO_4$	−78	50:50
10	94:6	THF	Li_2CO_3	−78	50:50
11	96:4	THF/Et_2O/pentane[e]	LiCl	−100	5:95

[a] Reactions were conducted with a substrate concentration of 0.15−0.25 M in degassed solvents and were kept at the indicated temperature for 1 h; reactions were terminated by addition of Et_2O followed by solid $LiAlH_4$ (≥95% inversion).[19] [b] 0.5 Equiv. of additive in the solvent prior to substrate addition. [c] Measured by HPLC using a Daicel Chiralcel OD-H column (*n*-heptane at 20 °C). [d] $LiClO_4$ led to almost complete decomposition of (Si*S*)-**7a** and only trace amounts of (Si*S*)-**9a** were isolated. [e] 4:1:1 mixture (Trapp mixture).

Although it has been reported that silyl chlorides racemise in THF,[25] racemisation of (Si*S*)-**7a** was marginal after 1 h and only occurred after prolonged reaction times (Table 1, Entry 1).[17a] In accordance with a systematic study by Sommer,[17a] solvents such as Et_2O and pentane also restrained racemisation and solvents with high dielectric constants such as acetonitrile led to rapid solvent-induced racemisation. However, all these solvents are unsuitable for reductive lithiation reactions.

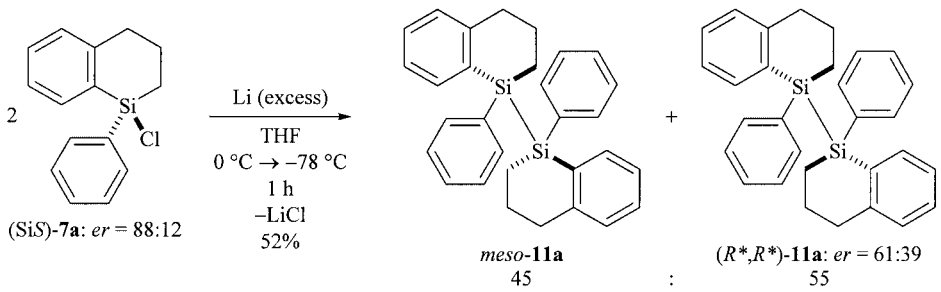
In contrast, addition of lithium chloride led to immediate racemisation at 0 °C and −78 °C (Table 1, Entries 2 and 3) whereas racemisation was only marginal with sodium and potassium chloride (Table 1, Entries 4 and 5). The degree of racemisation was somewhat dependent on the lithium halide but was not as clear cut as with lithium chloride (Table 1, Entries 6−8). These observations indicate a complex interplay of the inorganic salt (anion and cation), its solubility in THF and solvent-separated ion pairs. Interestingly, lithium perchlorate and carbonate led to complete racemisation (Table 1, Entries 9 and 10). If perchlorate and carbonate anions are considered inert and noncoordinating, the lithium counterion might also be involved in ionisation processes liberating chloride which will in turn promote racemisation.[17a,22,26]

It is noteworthy that no racemisation occurred in THF/Et_2O/pentane (4:1:1) (Trapp mixture[27]) at −100 °C (Table 1, Entry 11). We succeeded in performing the reductive metallation of (Si*S*)-**7a** using this solvent mixture. However, this metallation was sluggish and required stoichiometric amounts (100 mol %) of 4,4′-di-*tert*-butylbiphenyl (DBB). Nevertheless, this modification clearly affected the stereochemical outcome of the metallation of (Si*S*)-**7a** (Scheme 3) and provided almost racemic (Si*R*)-**9a** (*er* = 56:44) but with slight overall retention of stereochemistry. The dependence of the absolute configuration and enantiomeric ratio of **9a** on the reaction temperature and reducing species (lithium metal *versus* LiDBB) suggests that an additional reaction pathway occurs.

Formal Dimerisation: Disilane Formation

Disilanes have often been isolated quantitatively since the reductive cleavage of the silicon−silicon bond is the rate-determining step.[10a] We were able to isolate disilane **11a** as a mixture of all possible stereoisomers, *meso*-**11a** and (*R**,*R**)-**11a** (*er* = 61:39) in 52% yield when metallation of (Si*S*)-**7a** (*er* = 88:12) using lithium metal was terminated after 1 h (Scheme 5). The presence of **11a** has also been verified for the Trapp mixture at −100 °C. Compound **11a** was even formed at temperatures as low as −120 °C. Clearly, subsequent reductive cleavage of a mixture of achiral *meso*-**11a** and slightly enantiomerically enriched (*R**,*R**)-**11a** will only result in an almost racemic silyllithium **8a**.[28]

While we were performing these studies, Kawakami described the synthesis of a disilane (*er* = 75:25) by nucleo-



Scheme 5. Reductive metallation of (Si*S*)-**7a** accompanied by the formation of disilanes **11**

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philic chloride displacement of highly enantioenriched α-NpPhMeSiCl (*er* > 99:1) using α-NpPhMeSiLi (*er* = 91:9).[29] This reaction appears to proceed with predominant stereoretention at the former lithium-bearing silicon centre and with stereoinversion at the former electrophilic silicon centre. However, this transformation displays only moderate stereoselectivity, thereby confirming our findings.

In control experiments, precluding any diastereoselection, we treated highly enantioenriched (Si*S*)-**7a** (*er* = 96:4) with the achiral silyl anion **12** under the reaction conditions of reductive metallation (THF, −78 °C). Inverse as well as normal addition furnished disilane (Si*R*)-**13a** with clean inversion[8,25] of the configuration (Scheme 6). Notably, we were able to demonstrate that the substitution reaction is faster than the chloride-induced racemisation. In the case of the inverse addition protocol, the enantiomeric ratio of (Si*R*)-**13a** is dependent on the rate of addition of **12** which is accompanied by equimolar amounts of lithium chloride. Anion **12** is immediately consumed upon addition to silyl chloride (Si*S*)-**7a** yielding disilane (Si*R*)-**13a** along with unchanged (Si*S*)-**7a** and lithium chloride. If the addition of **12** is slow, chloride will partially racemise the unchanged (Si*S*)-**7a**. If addition of **12** is rapid, the stereochemical identity of (Si*S*)-**7a** is preserved. The normal addition protocol circumvents this side-reaction since (Si*S*)-**7a** and lithium chloride do not coexist under these circumstances. This is reflected by an almost perfect inversion (99%) of the configuration at silicon [(Si*S*)-**7a** with *er* = 96:4 → (Si*R*)-**13a** with *er* = 5:95].

We have drawn the following conclusions from these experiments. (1) Dimerisation during reductive metallation can be expected to produce predominantly the *meso*-configured (achiral) disilane. (2) The experimentally observed deviation from this stereoselectivity (Scheme 5) is partially due to chloride-induced racemisation which is significantly faster than the slow heterogeneous reductive metallation with solid lithium metal. (3) Dimerisation is faster than chloride-induced racemisation (Scheme 6).

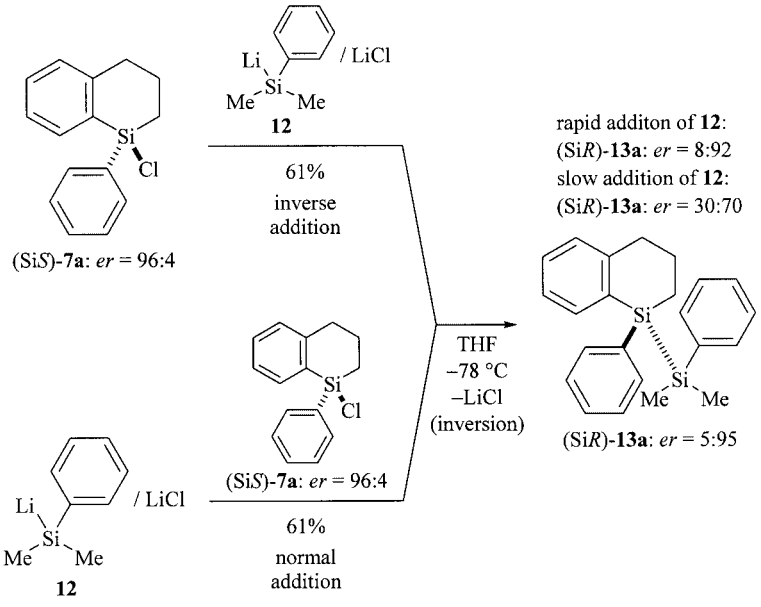
Second Generation Approach

These orientating investigations clearly reveal that an enantioselective reductive metallation of an asymmetrically substituted silyl chloride is impossible if the chiral silyl chloride is susceptible to chloride-induced racemisation and is able to formally dimerise.

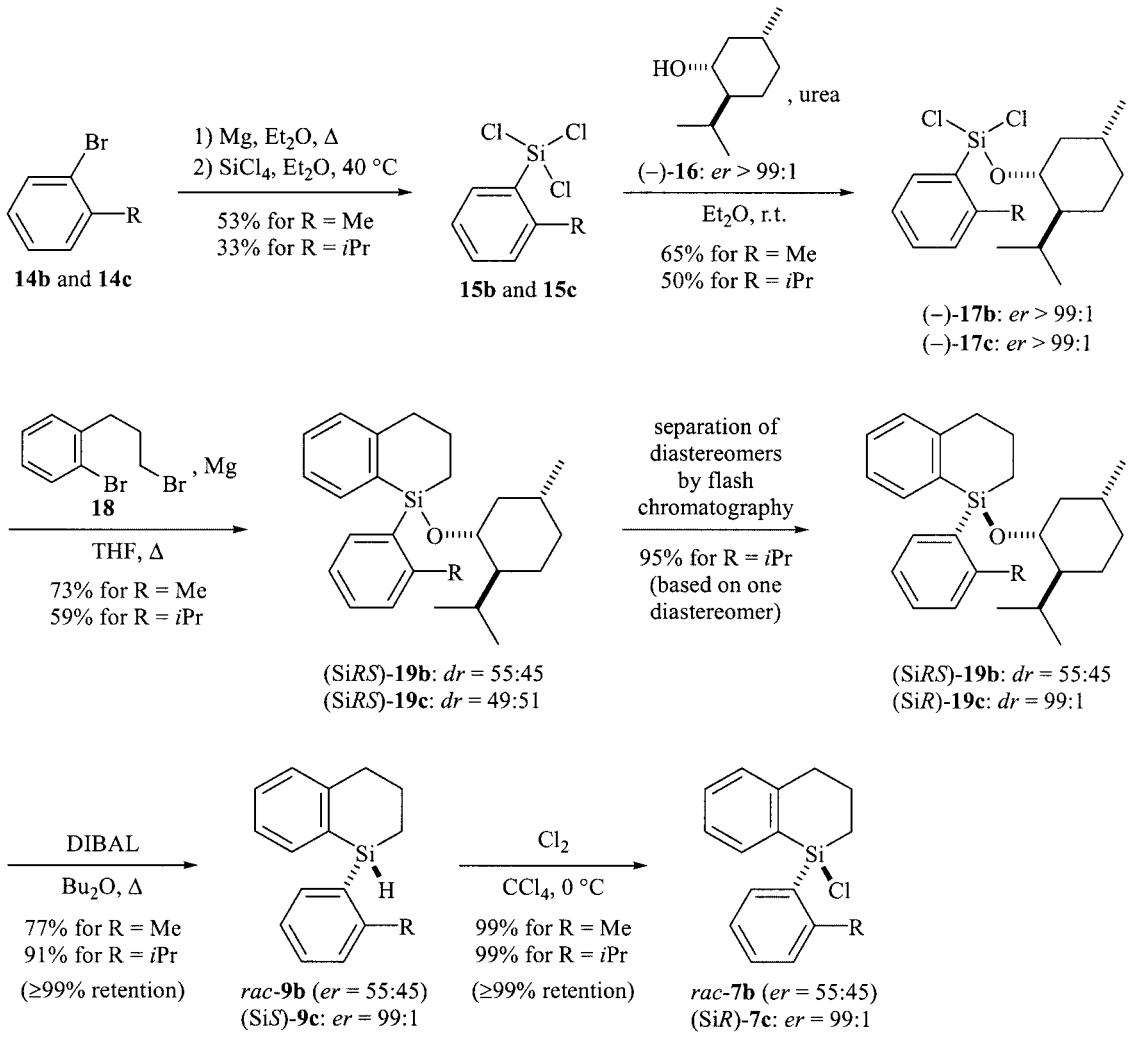
We became aware of an interesting observation reported by Fleming[10a,10b] whereby reductive metallation of $ArMe_2SiCl$ (Ar = Ph or *p*-Tolyl) is remarkably sensitive to the presence of substituents at the aryl moiety. Whereas phenyldimethylsilyl chloride is metallated providing the corresponding silyl anion, *p*-tolyldimethylsilyl chloride is selectively converted into its disilane which is *not* cleaved by lithium.[10b] Moreover, tris(*o*-tolyl)silyl chloride gives the silyllithium reagent without the formation of the disilane.[10c] These findings are extraordinarily significant for our problem since steric hindrance around the silicon centre seems to hamper disilane formation yet allows for the direct generation of the corresponding silyl anion.

Preparation of Sterically Hindered Silyl Chlorides

We decided to prepare these hindered silyl chlorides by gradually increasing the steric bulk of the exocyclic aryl substituent (**7b** and **7c**, Figure 1). Their syntheses are based on the Barbier reaction of chirally modified dichlorosilanes (−)-**17** and dibromide **18** (Scheme 7).[19] The required trichlorosilanes **15** were prepared from tetrachlorosilane and *ortho*-alkylated Grignard reagents derived from the corresponding aryl bromides **14**. Acceptable yields of analytically pure **15** were only achieved using Et_2O and not THF as the solvent since THF undergoes ring-opening with tetrachlo-



Scheme 6. Nucleophilic displacement at (Si*S*)-**7a** using the achiral silyl anion **12**



Scheme 7. Preparation of the sterically hindered silyl chlorides *rac*-**7b** and (Si*R*)-**7c**

rosilane. The dichlorosilanes (−)-**17** were obtained by maintaining **15** and (−)-menthol [(−)-**16**] in the presence of urea in Et_2O at room temperature. The Barbier reaction of (−)-**17** and **18** gave the cyclic silyl ethers (Si*RS*)-**19** in good yields. (Si*RS*)-**19** were purified by flash chromatography on silica gel and (Si*RS*)-**19c** was quantitatively separated into its diastereomers. Subsequent stereospecific reduction under forcing reaction conditions provided the silanes **9** in good to excellent yields. The enantiomeric ratio of (Si*S*)-**9c** (*er* = 99:1) was determined by HPLC by comparison with a racemic sample and agreed with the diastereomeric ratio of (Si*R*)-**19c** (*dr* = 99:1) which was determined by ^1H NMR spectroscopy. Chlorination of **9** using a saturated solution of chlorine in CCl_4 furnished the desired silyl chlorides **7** in quantitative yields. The enantiomeric ratio of (Si*R*)-**7c** was determined by HPLC after enantiospecific reduction (≥99% inversion) with lithium aluminium hydride.

The absolute configurations of (Si*S*)-**9c** and (Si*R*)-**7c** and, therefore, the stereochemical course of the chlorination [(Si*S*)-**9c** → (Si*R*)-**7c**] were unambiguously deduced by X-ray crystallography (Figure 2 and Figure 3).[30] Highly enantioenriched samples (*er* ≥ 99:1) of silane (Si*S*)-**9c** and silyl chloride (Si*R*)-**7c** were both crystallised from pentane at −30 °C. Silyl chloride (Si*R*)-**7c** was prepared from the

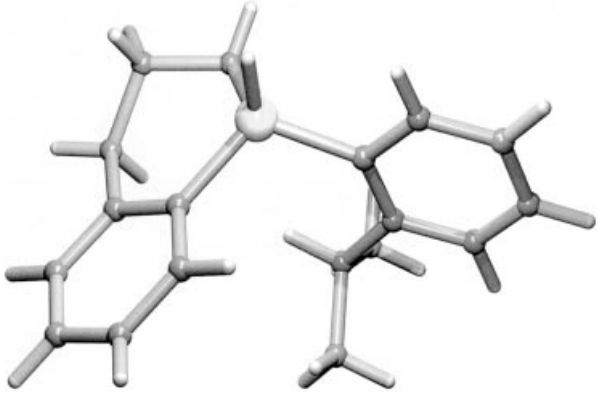


Figure 2. Molecular structure of (Si*S*)-**9c**

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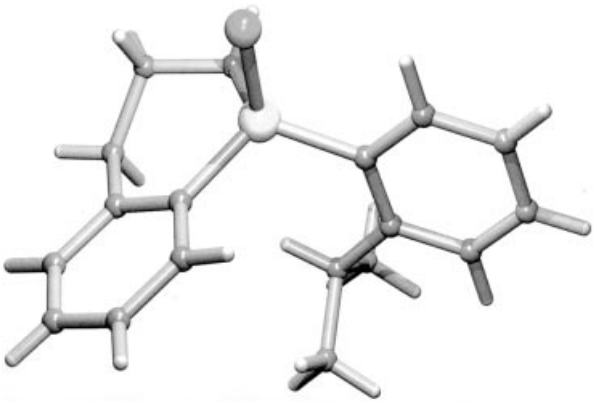


Figure 3. Molecular structure of (Si*R*)-**7c**

same batch of crystallised (Si*S*)-**9c**. These X-ray analyses are the first conclusive evidence for the stereoretentive nature of the chlorination and the stereoinvertive course of the reduction at an asymmetrically substituted silicon centre incorporated into a cyclic framework.

Chloride-Induced Racemisation

At first we performed two crucial experiments with (Si*R*)-**7c**. As predicted, (Si*R*)-**7c** showed almost perfect configurational stability when simply maintained in THF at room temperature (Table 2, Entry 1) but unlike (Si*S*)-**7a** (R = H) no chloride-induced racemisation was observed for (Si*R*)-**7c** (R = *i*Pr) in the presence of lithium chloride (Table 2, Entries 2 and 3). In order to verify this remarkable result, we investigated the racemisation of (Si*R*)-**7c** at several temperatures (Table 2, Entries 4−7). Substantial racemisation started to occur at temperatures above −60 °C whereas below this temperature, (Si*R*)-**7c** remained almost untouched by lithium chloride. Again, the corresponding bromide-induced racemisation was less pronounced (Table 2, Entry 8).

Table 2. Chloride-induced racemisation of (Si*R*)-**7c**

Entry[a]	*er* (Si*R*)-**7c**	Additive[b]	*T* [°C]	*er*[c] (Si*R*)-**9c**
1	97:3	−	20	4:96
2	97:3	LiCl	−100	4:96
3	97:3	LiCl	−78	4:96
4	97:3	LiCl	−60	9:91
5	97:3	LiCl	−40	20:80
6	94:6	LiCl	−20	47:53
7	97:3	LiCl	0	50:50
8	94:6	LiBr	−40	10:90
9	94:6	NBu_4Cl[d]	−78	50:50

[a] Reactions were conducted with a substrate concentration of 0.15−0.25M in degassed THF and were kept at the indicated temperature for 1 h; reactions were terminated by addition of Et_2O followed by solid $LiAlH_4$ (≥99% inversion).[19] [b] 0.5 Equiv. LiCl in solvent prior to substrate addition. [c] Measured by HPLC using a Daicel Chiralcel OD-H column (*n*-heptane at 10 °C). [d] Catalytic amounts, since only trace amounts of NBu_4Cl are soluble in THF.

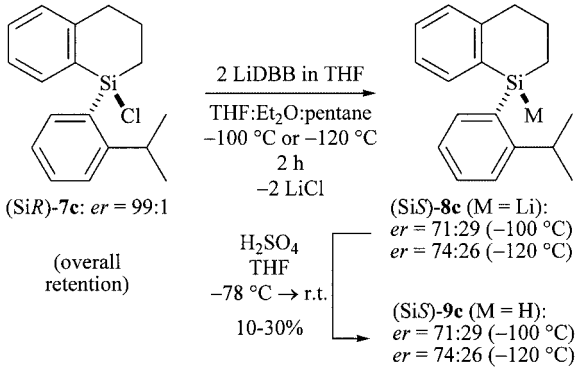
The additional *ortho*-substituent at the exocyclic aryl group in (Si*R*)-**7c** could hinder either nucleophilic attack of chloride[22] (from lithium chloride) or pseudorotational processes[24] (Scheme 4). The latter processes can be ruled out since complete racemisation occurred at −78 °C when tetra(*n*-butyl)ammonium chloride (NBu_4Cl) was used as the chloride source (Table 2, Entry 9). It seems that chloride is released from large aggregates of lithium chloride and THF.[31] In contrast, tetra(*n*-butyl)ammonium chloride provides a "naked" chloride anion with a large noncoordinating tetraalkylammonium counterion. Thus, higher temperatures are needed for nucleophilic attack of chloride derived from lithium chloride.

The molecular structure of (Si*R*)-**7c** (Figure 3) obtained from a single-crystal X-ray diffraction study illustrates the increased steric hindrance around the silicon centre. Although the exocyclic silicon−carbon bond freely rotates in solution, this might account for the unprecedented configurational stability of (Si*R*)-**7c**.

Enantiospecific Reductive Metallation

Treatment of silyl chloride (Si*R*)-**7c** with lithium in THF (0 °C → −78 °C, 16 h) resulted in a complex mixture of products after protolysis.[32] Silane **9c** (10−35%) was isolated along with minor amounts of the corresponding disilane ($C_{36}H_{42}Si_2$, *M* = 530.89 g/mol) which was unambiguously identified in the mass spectra (*m*/*z* = 530 [M^+]) of the crude reaction mixtures. Moreover, a major by-product (20%) which could not be isolated in analytically pure form indicated cleavage of an Si−C(sp^2) bond.

We were able to prevent disilane formation by performing the metallation with addition of preformed LiDBB in THF to a solution of (Si*R*)-**7c** in the Trapp mixture at −100 °C and −120 °C, respectively [(Si*R*)-**7c** → (Si*S*)-**9c**, Scheme 8]. These were the first metallations which provided the silyl anion (Si*S*)-**8c** with moderate stereoselectivity (*er* ≤ 74:26) with retention of the configuration at silicon. Unfortunately, a complex mixture of by-products was formed which we again believe to be the result of Si−C(sp^2) bond cleavage.



Scheme 8. Reductive metallation of (Si*R*)-**7c**

Strohmann has demonstrated the stereoselective transmetallation of silyllithiums with magnesium bromide furnishing the corresponding silylmagnesiums which are less

prone to racemisation.[9] Our efforts of transmetallating (Si*S*)-**8c** were most likely thwarted by remaining LiDBB.

Conclusion

In summary, we have conducted the first investigation of the stereochemical course of the reductive metallation of silyl chlorides with silicon-centred chirality. The present study has focussed on two out of several possible processes which are detrimental to enantioselection, namely halide-induced racemisation and formal dimerisation. Both reaction pathways were independently verified for silyl chloride (Si*S*)-**7a**. Interestingly, the stereoselectivity of the nucleophilic displacement of a Si−Cl bond is dependent on the order and rate of addition of the nucleophile. Structural modifications of the exocyclic aryl group in (Si*S*)-**7a** led to the sterically hindered silyl chloride (Si*R*)-**7c** which displays a remarkable peculiarity, i.e. (Si*R*)-**7c** is not racemised by lithium chloride in THF at temperatures below −40 °C. The absolute configuration of this highly configurationally stable silyl chloride (Si*R*)-**7c** has been determined by X-ray crystallography. Furthermore, the reductive metallation of (Si*R*)-**7c** does not proceed through a disilane intermediate at temperatures below −100 °C.

However, metallation of (Si*R*)-**7c** (*er* = 99:1) does not result in highly enantioenriched silyllithium (Si*S*)-**8c** (*er* = 74:26) even in the absence of chloride-induced racemisation and formal disilane formation. The experimental finding that treatment of (Si*R*)-**7c** with lithium or LiDBB leads to silicon−carbon bond cleavage, strongly indicates that the electron transfer is not as selective as suggested by Scheme 2. The use of enantioenriched, asymmetrically substituted silyl chlorides in reductive metallations indicates the complexity of this process and demanding mechanistic studies will be necessary for a more refined understanding.

In conclusion, by combining the restrained chloride-induced racemisation and inhibiting formal dimerisation, we accomplished the first enantioselective reductive metallation of a chiral silyl chloride. This conflicts with previous literature precedents.[8] Future work will be devoted to the design of chiral, nonracemic bridgehead silyl chlorides. Some achiral bi- and tricyclic derivatives have been successfully prepared by Sommer and Boudjouk.[33] Importantly, investigations concerning nucleophilic displacements at bridgehead silyl chlorides have indicated that stereoretention is favoured.[17a,33] This would remove the undesired influence of the above racemisation processes. If these structural modifications enable an efficient reductive metallation, the resultant asymmetrically substituted silyl anions might serve as interesting chiral silyl transfer reagents after transmetallation to copper.[2]

Experimental Section

General Remarks: Reagents obtained from commercial suppliers were used without further purification unless otherwise noted. All reactions were performed in flame-dried glassware under a static pressure of argon. Liquids were transferred with syringes or double-ended needles and all solvents were dried and distilled prior to use following standard procedures. Solvents (cyclohexane and *tert*-butyl methyl ether) for extractions and chromatography were distilled before use. Analytical thin-layer chromatography was performed on silica gel SIL G-25 glass plates and flash chromatography on silica gel (40−63 μm, 230−400 mesh, ASTM) using the indicated solvents. All stationary phases were obtained from Macherey−Nagel, Germany. High vacuum distillations (10^{-5} mbar) were performed using standard glassware and an Edwards turbo molecular pump. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker AM 400 and DRX 500 instruments. Analytical HPLC analysis on a chiral stationary phase using a Daicel Chiralcel OD-H column (*n*-heptane as solvent) or Daicel Chiralcel OJ-R column (MeCN:H_2O mixtures as solvent) provided baseline resolution of enantiomers.

General Procedure for the Reductive Metallation of 7 with Lithium Metal: Silyl chloride **7** was dissolved in THF (1 mL) and finely cut lithium wire (large excess) was added. After sonication at 0 °C and the appearance of a slightly red colour, the reaction mixture was cooled to −78 °C. The resultant silyl anion **8** was separated from the remaining lithium wire and H_2SO_4 in Et_2O (2 mL) was added followed by aqueous saturated $NaHCO_3$ (10 mL). The organic layer was separated and the aqueous phase extracted with *tert*-butyl methyl ether (3 × 30 mL), dried ($MgSO_4$) and the volatiles were evaporated under reduced pressure. Purification by flash chromatography on silica gel (cyclohexane) provided silane **9**. The enantiomeric ratio of **9a**[19] and **9c** was determined by HPLC.

General Procedure for the Reductive Metallation of 7 with LiDBB: Silyl chloride **7** was dissolved in THF/Et_2O/pentane, 4:1:1 (1 mL) and a freshly prepared solution of LiDBB (2 equiv.) was added at the indicated temperature. The reaction mixture was maintained at this temperature for the desired time and H_2SO_4 in Et_2O (2 mL) was then added followed by saturated aqueous $NaHCO_3$ (10 mL). The organic layer was separated and the aqueous phase extracted with *tert*-butyl methyl ether (3 × 30 mL), dried ($MgSO_4$) and the volatiles were removed under reduced pressure. Purification by flash chromatography on silica gel (cyclohexane) provided silane **9**. The enantiomeric ratio of **9a**[19] and **9c** was determined by HPLC.

Preparation of Disilanes *meso*-11a and (*R,*R**)-11a:** To silyl chloride (Si*S*)-**7a** (166 mg, 0.641 mmol, *er* = 88:12) in THF (1 mL) was added lithium wire (large excess). After sonication at 0 °C until a pale red colour appeared, the resultant reaction mixture was maintained at −78 °C for 1 h. After addition of H_2SO_4 in Et_2O (3 mL), the reaction mixture was allowed to warm to ambient temperature. Saturated aqueous $NaHCO_3$ (10 mL) was added and the aqueous layer extracted with *tert*-butyl methyl ether (3 × 50 mL). The combined organic phases were dried ($MgSO_4$) and the volatiles were evaporated under reduced pressure. Flash chromatography on silica gel (cyclohexane) provided **11a** as a mixture of *meso*-**11a** and (*R**,*R**)-**11a** (74.0 mg, 0.166 mmol, 52%, *meso*-**11a**: (*R**,*R**)-**11a** = 45:55) as a white solid. HPLC (Daicel Chiralcel OD-H column, column temperature 24 °C, solvent *n*-heptane/*i*PrOH, 199:1, flow rate 0.8 mL·min^{-1}): t_R = 12.54 min for *meso*-**11a**, t_R = 14.91 min (minor enantiomer) and t_R = 19.55 (major enantiomer). M.p. 104 °C (cyclohexane). R_f (cyclohexane) = 0.45. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.18−1.32 (m, 4 H), 1.71−1.98 (m, 4 H), 2.53−2.62 (m, 2 H), 2.70−2.80 (m, 2 H), 7.04−7.13 (m, 4 H), 7.19−7.32 (m, 12 H), 7.38 (d, *J* = 7.3 Hz, 1 H), 7.41 (dd, *J* = 7.7, *J* = 1.3 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 10.7, 11.5, 22.1, 22.5, 29.8, 35.3, 125.3, 125.4, 127.8, 127.9, 128.6, 128.8, 129.0,

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129.1, 129.2, 130.8, 131.3, 135.1, 135.2, 136.7, 136.9, 137.3, 137.4, 149.1, 149.4 ppm. IR (cuvette): $\tilde{\nu}$ = 3687 (m), 3026 (s), 2926 (w), 2401 (m), 2341 (m), 1522 (m), 1476 (m), 1426 (m), 1336 (w), 1225 (s), 1018 (m), 929 (s), 627 (m) cm^{-1}. LRMS (EI): *m*/*z* = 446 [M^+]. HRMS (EI): calcd. for $C_{30}H_{30}Si_2$: 446.1886; found 446.1886.

Preparation of (Si*R*)-13a. Inverse Addition: $Me_2PhSiCl$ (76.2 mg, 0.446 mmol) in THF (2 mL) was treated with lithium wire (large excess) at 0 °C and maintained at this temperature for 5 h. Silyl chloride (Si*S*)-**7a** (92.4 mg, 0.357 mmol) was dissolved in THF (1 mL), cooled to −78 °C and the freshly prepared $Me_2PhSiLi$ (**12**) in THF was added via syringe (rapid addition: 2.00 mL·min^{-1}; slow addition: 0.02 mL·min^{-1}). The reaction mixture was maintained at −78 °C for 1 h.

Normal Addition: $Me_2PhSiCl$ (19.8 mg, 0.116 mmol) in THF (1 mL) was treated with lithium wire (large excess) at 0 °C and maintained at this temperature for 5 h. The freshly prepared $Me_2PhSiLi$ (**12**) was separated from the remaining lithium metal and silyl chloride (Si*S*)-**7a** (24.3 mg, 0.0939 mmol) dissolved in THF (1 mL) was added via syringe. Both reactions were terminated by addition of aqueous saturated NH_4Cl (10 mL). The aqueous phase was separated and extracted with *tert*-butyl methyl ether (3 × 50 mL). The combined organic phases were dried ($MgSO_4$) and the volatiles were evaporated under reduced pressure. Flash chromatography on silica gel (cyclohexane) provided (Si*R*)-**13a** (77.9 mg, 0.217 mmol, 61%, *er* = 8:92) (*inverse addition*) and (20.4 mg, 0.0569 mmol, 61%, *er* = 5:95) (*normal addition*) as colourless oils. R_f (cyclohexane) = 0.46. $[\alpha]_D^{20}$ = −15.9, $[\alpha]_{578}^{20}$ = −16.7, $[\alpha]_{546}^{20}$ = −19.1, $[\alpha]_{436}^{20}$ = −35.7, $[\alpha]_{365}^{20}$ = −68.3 (*c* = 12.6, $CHCl_3$). HPLC (Daicel Chiralcel OJ-R column, column temperature 20 °C, solvent MeCN:H_2O = 75:25, flow rate 0.5 mL·min^{-1}): t_R = 14.03 min for (Si*R*)-**13a** (major enantiomer), t_R = 15.67 min for (Si*S*)-**13a** (minor enantiomer). ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.39 (s, 3 H), 0.45 (s, 3 H), 1.19 (t, *J* = 6.2 Hz, 2 H), 1.78−1.95 (m, 2 H), 2.57−2.63 (m, 1 H), 2.74−2.79 (m, 1 H), 7.10−7.17 (m, 2 H), 7.14−7.36 (m, 9 H), 7.38 (dd, *J* = 7.2, *J* = 1.2 Hz, 1 H), 7.41−7.42 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = −3.4, −2.8, 10.6, 22.3, 35.4, 125.3, 127.8, 127.9, 128.6, 128.7, 128.8, 129.1, 131.2, 134.2, 134.9, 136.5, 137.6, 138.7, 149.2 ppm. IR (cuvette): $\tilde{\nu}$ = 3690 (m), 3155 (m), 3054 (m), 2924 (s), 2857 (s), 2360 (m), 2253 (s), 1793 (m), 1428 (s), 1382 (m), 1246 (m), 1104 (m), 937 (m), 886 (m), 811 (w) cm^{-1}. LRMS (EI): *m*/*z* = 358 [M^+]. HRMS (EI): calcd. for $C_{23}H_{26}Si_2$: 358.1573; found 358.1577.

Trichloro(2-methylphenyl)silane (15b): A three-necked 250-mL flask equipped with a pressure-equalising dropping funnel, a reflux condenser and a magnetic stirrer bar was charged with magnesium turnings (8.76 g, 360 mmol, 1.37 equiv.) and was subsequently flame-dried (3 times) in vacuo. After filling with argon, Et_2O (60 mL) was added followed by dropwise addition of a solution of 1-bromo-2-methylbenzene (**14b**) (45.0 g, 31.5 mL, 263 mmol) in Et_2O (30 mL). Ice-cooling was needed at the beginning of the Grignard reaction in order to ensure a gentle reflux followed by heating at reflux for 1 h. The Grignard reagent was decanted from the excess magnesium and transferred to a pressure-equalising dropping funnel. A second three-necked flask (500 mL) equipped with the above pressure-equalising dropping funnel, a reflux condenser and a magnetic stirrer bar was charged with $SiCl_4$ (45.0 mL, 395 mmol, 1.50 equiv.). The Grignard reagent was added dropwise and the resultant reaction mixture was maintained for 2 h at 40 °C. The reaction mixture was allowed to return to ambient temperature and was filtered using Schlenk techniques. The filter cake was washed with Et_2O (3 × 20 mL) and the combined organic solvents were evaporated under reduced pressure. The crude product was distilled (93 °C at 8 mbar) affording **15b** (31.4 g, 139 mmol, 53%) as a colourless liquid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.34 (s, 3 H), 6.95−6.98 (m, 2 H), 7.13−7.17 (m, 1 H), 7.56 (d, *J* = 7.3 Hz, 1 H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 22.7, 125.6, 129.6, 131.3, 133.1, 134.8, 143.8 ppm. IR (cuvette): $\tilde{\nu}$ = 3854 (w), 3745 (w), 3058 (s), 2979 (s), 2931 (s), 2743 (w), 2671 (w), 2401 (m), 2361 (m), 1971 (m), 1935 (m), 1820 (m), 1700 (m), 1591 (s), 1567 (s), 1449 (s), 1385 (s), 1287 (s), 1216 (m), 1166 (m), 1133 (s), 1082 (s), 1033 (m), 987 (w), 929 (w), 772 (w) cm^{-1}. LRMS (EI): *m*/*z* = 224 [M^+]. $C_7H_7Cl_3Si$ (223.93): calcd. C 37.27, H 3.13; found C 37.29, H 2.93.

Trichloro(2-isopropylphenyl)silane (15c): According to the preparation of **15b**, magnesium turnings (1.42 g, 58.4 mmol, 1.16 equiv.) were flame-dried under vigorous stirring and Et_2O (30 mL) was added followed by dropwise addition of a solution of 2-isopropylbromobenzene (**14c**) (10.0 g, 50.2 mmol) in Et_2O (30 mL). The resultant reaction mixture was heated to reflux for 18 h. The Grignard reagent was then added dropwise to $SiCl_4$ (7.00 mL, 60.2 mmol, 1.20 equiv.) in Et_2O (30 mL) and maintained for 16 h at 40 °C. After the usual workup, the crude product was distilled (120 °C at 22 mbar) furnishing **15c** (4.14 g, 16.3 mmol, 33%) as a colourless liquid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.34 (d, *J* = 6.8 Hz, 6 H), 3.47 (sept, *J* = 6.8 Hz, 1 H), 7.29−7.88 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 24.2, 34.7, 125.9, 126.9, 133.4, 134.7, 155.5 ppm. IR (cuvette): $\tilde{\nu}$ = 3393 (m), 2969 (s), 2401 (m), 2253 (w), 1591 (m), 1540 (w), 1477 (s), 1435 (s), 1275 (m), 1213 (s), 1125 (s), 1069 (m), 1030 (w), 928 (w), 794 (m), 746 (w), 660 (w) cm^{-1}. LRMS (EI): *m*/*z* = 254 [M^+]. HRMS (EI): calcd. for $C_9H_{11}SiCl_3$: 251.9696; found 251.9690.

(−)-Dichloro-[(1*R*,2*S*,5*R*)-menthyloxy]-(2-methylphenyl)silane (17b): A three-necked 500-mL flask equipped with a pressure-equalising dropping funnel, a reflux condenser and a magnetic stirrer bar was charged with **15b** (31.4 g, 139 mmol) and urea (9.21 g, 153 mmol, 1.10 equiv.). At ambient temperature, a solution of (−)-menthol [(−)-**16**] (21.7 g, 139 mmol, 1.00 equiv.) and Et_2O (200 mL) was added dropwise over a period of 1 h. The reaction mixture was maintained at this temperature for 2 h followed by filtration using Schlenk techniques. The filter cake was washed with Et_2O (3 × 50 mL) and the filtrate was concentrated in vacuo. High vacuum distillation of the residue (135 °C at 6 × 10^{-5} mbar) provided dichlorosilane (−)-**17b** (31.4 g, 91.1 mmol, 65%) as a colourless liquid. $[\alpha]_D^{20}$ = −44.7, $[\alpha]_{578}^{20}$ = −46.3, $[\alpha]_{546}^{20}$ = −52.7, $[\alpha]_{436}^{20}$ = −87.8, $[\alpha]_{365}^{20}$ = −134 (*c* = 18.8, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.78 (d, *J* = 6.9 Hz, 3 H), 0.91 (d, *J* = 7.3 Hz, 3 H), 0.92 (d, *J* = 6.4 Hz, 3 H), 1.01 (dq, *J* = 12.5, *J* = 2.6 Hz, 2 H), 1.19 (dq, *J* = 12.0, *J* = 2.2 Hz, 1 H), 1.33 (dq, *J* = 12.5, *J* = 2.71 Hz, 1 H), 1.41−1.50 (m, 1 H), 1.63−1.68 (m, 2 H), 2.14−2.23 (m, 2 H), 2.60 (s, 3 H), 4.06 (dt, *J* = 10.3, *J* = 4.3 Hz, 1 H), 7.21 (d, *J* = 8.6 Hz, 2 H), 7.39 (t, *J* = 7.7 Hz, 1 H), 7.81 (d, *J* = 7.3 Hz, 1 H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 15.8, 21.3, 22.2, 22.7, 22.9, 25.5, 31.8, 34.4, 44.2, 49.7, 76.5, 125.2, 130.4, 130.7, 132.1, 135.1, 144.9 ppm. IR (cuvette): $\tilde{\nu}$ = 3013 (m), 2959 (s), 2871 (s), 2401 (m), 1593 (s), 1455 (s), 1386 (m), 1371 (m), 1286 (m), 1214 (w), 1136 (w), 879 (m), 756 (w) cm^{-1}. LRMS (CI/NH_3): *m*/*z* = 362 [[M + NH_4]$^+$]. $C_{17}H_{26}Cl_2OSi$ (345.38): calcd. C 59.12, H 7.59; found C 58.96, H 7.53.

(−)-Dichloro-(2-isopropylphenyl)-[(1*R*,2*S*,5*R*)-menthyloxy]silane (17c): According to the procedure for (−)-**17b**, a solution of (−)-menthol [(−)-**16**] (4.55 g, 29.1 mmol, 1.00 equiv.) and Et_2O (20 mL) was added dropwise to trichlorosilane **15c** (7.34 g, 29.0 mmol) and urea (1.91 g, 31.9 mmol, 1.10 equiv.) over a period of 1 h. The reaction mixture was maintained at this temperature for 3 h followed

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by filtration. The filter cake was washed with Et_2O (3 × 5 mL) and the filtrate was concentrated in vacuo. High vacuum distillation of the residue (160 °C at 6 × 10^{-5} mbar) provided dichlorosilane (−)-**17c** (5.44 g, 14.6 mmol, 50%) as a colourless viscous liquid. $[\alpha]_D^{20}$ = −50.0, $[\alpha]_{578}^{20}$ = −51.2, $[\alpha]_{546}^{20}$ = −58.9, $[\alpha]_{436}^{20}$ = −95.8, $[\alpha]_{365}^{20}$ = −144 (c = 16.8, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.79 (d, J = 6.8 Hz, 3 H), 0.81−0.87 (m, 1 H), 0.90 (d, J = 6.8 Hz, 3 H), 0.94 (d, J = 6.4 Hz, 3 H), 1.21 (q, J = 12.0 Hz, 1 H), 1.24−1.32 (m, 1 H), 1.28 (d, J = 1.7 Hz, 3 H), 1.30 (d, J = 2.2 Hz, 3 H), 1.31−1.36 (m, 1 H), 1.41−1.53 (m, 1 H), 1.64−1.72 (m, 2 H), 2.15−2.26 (m, 2 H), 3.45 (sept, J = 6.8 Hz, 1 H), 4.09 (ddd, J = 10.3, J = 4.3 Hz, 1 H), 7.23−7.83 (m, 4 H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 15.8, 21.3, 22.2, 22.9, 24.3, 24.4, 25.4, 31.7, 34.2, 34.4, 44.2, 49.7, 76.4, 125.6, 126.2, 132.4, 135.1, 155.5 ppm. IR (cuvette): $\tilde{\nu}$ = 3691 (w), 3308 (m), 3156 (m), 2963 (s), 2929 (s), 2871 (s), 2361 (s), 2255 (s), 1794 (w), 1650 (vw), 1561 (w), 1460 (m), 1384 (m), 1276 (vw), 1215 (w), 1126 (s), 1085 (m), 937 (m), 874 (m), 780 (m), 726 (w), 676 (m), 637 (w) cm^{-1}. LRMS (EI): m/z = 372 [M^+]. $C_{19}H_{30}Cl_2OSi$ (373.43): calcd. C 61.11, H 8.10; found C 61.28, H 7.96.

(Si*RS*)-1-[(1*R*,2*S*,5*R*)-Menthyloxy]-(2-methylphenyl)-1,2,3,4-tetrahydro-1-silanaphthalene [(Si*RS*)-19b]: A 250-mL three-necked flask equipped with a reflux condenser, a pressure-equalizing dropping funnel, an argon inlet and a magnetic stirrer bar was charged with magnesium turnings (6.60 g, 271 mmol, 9.00 equiv.). The flask was flame dried with vigorous stirring. After filling with argon, THF (50 mL) and 1,2-dibromoethane (1.10 mL, 11.2 mmol, 0.40 equiv.) were added. The magnesium turnings were treated with an equimolar mixture of dibromide **18** (8.40 g, 30.2 mmol) and (−)-**17b** (10.4 g, 30.2 mmol) in THF (50 mL) at reflux. The reaction mixture was maintained for a further 16 h at reflux and was then allowed to return to ambient temperature. Diluting with *n*-pentane (50 mL) resulted in additional precipitation of magnesium salts which were filtered and the volatiles were removed under reduced pressure. Flash chromatography on silica gel (cyclohexane−*t*-butyl methyl ether, 99:1) furnished (Si*RS*)-**19b** (8.63 g, 22.0 mmol, 73%) as a colourless oil. The diastereomeric ratio of 55:45 was determined from the ^{1}H NMR spectra by integration of the baseline separated doublets at δ = 0.33 and 0.61 ppm. R_f (cyclohexane) = 0.43. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.33 (d, J = 6.9 Hz, 1.65 H), 0.61 (d, J = 6.9 Hz, 1.35 H), 0.76 (d, J = 6.8 Hz, 1.65 H), 0.83 (d, J = 7.3 Hz, 1.35 H), 0.89 (d, J = 6.5 Hz, 1.35 H), 0.91 (d, J = 7.3 Hz, 1.65 H), 1.00 (ddd, J = 10.7, J = 1.3 Hz, 1 H), 1.08−1.37 (m, 6 H), 1.53−1.63 (m, 3 H), 1.72−1.78 (m, 0.45 H), 1.97−2.04 (m, 2 H), 2.18−2.24 (m, 0.55 H), 2.32 (s, 1.35 H), 2.34 (s, 1.65 H), 2.75−2.83 (m, 1 H), 2.86−2.94 (m, 1 H), 3.49−3.65 (m, 1 H), 7.11−7.27 (m, 4 H), 7.28−7.33 (m, 2 H), 7.47−7.50 (m, 1 H), 7.55−7.61 (m, 1 H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 14.0, 14.6, 15.7, 15.8, 21.5, 22.3, 22.5, 22.8, 23.0, 23.1, 25.1, 25.3, 27.0, 29.2, 29.8, 31.5, 34.6, 35.4, 36.0, 45.1, 45.8, 50.5, 50.6, 73.2, 73.5, 124.6, 124.7, 125.4, 125.5, 125.7, 126.6, 127.2, 128.3, 128.4, 128.5, 128.6, 128.8, 129.7, 129.9, 132.3, 132.7, 135.6, 135.7, 135.9, 136.3, 144.1, 149.7, 149.9 ppm. IR (cuvette): $\tilde{\nu}$ = 3687 (m), 3010 (s), 2928 (s), 2870 (m), 2401 (s), 2361 (s), 1928 (w), 1590 (m), 1521 (m), 1554 (s), 1371 (m), 1207 (w), 1099 (w), 974 (w), 929 (m), 868 (w) cm^{-1}. LRMS (CI/isobutene): m/z = 449 [[M + C_4H_9]$^+$]. $C_{26}H_{36}OSi$ (392.65): calcd. C 79.53, H 8.89; found C 79.58, H 9.24.

(Si*RS*)-1-(2-Isopropylphenyl)-1-[(1*R*,2*S*,5*R*)-menthyloxy]-1,2,3,4-tetrahydro-1-silanaphthalene [(Si*RS*)-19c]: By analogy with the procedure for (Si*RS*)-**19b**, magnesium turnings (0.99 g, 41 mmol, 9.0 equiv.) were flame dried under vigorous stirring. THF (10 mL) then 1,2-dibromoethane (0.17 mL, 1.67 mmol, 0.400 equiv.) were added. After a short period of heating at reflux, the magnesium was treated with an equimolar mixture of dibromide **18** (1.26 g, 4.53 mmol) and (−)-**17c** (1.14 g, 4.53 mmol) in THF (10 mL). Further heating at reflux was followed by the usual workup. Purification and quantitative separation of the diastereomers by flash chromatography on silica gel furnished (Si*R*)-**19c** (549 mg, 1.30 mmol, 29%) and (Si*S*)-**19c** (571 mg, 1.36 mmol, 30%) as viscous colourless oils. The diastereomeric ratios of 1:99 and 99:1, respectively, were determined from the ^{1}H NMR spectra by integration of the baseline separated doublets at δ = 0.35 and 0.61 ppm. Analytical data for (Si*R*)-**19c**: R_f (cyclohexane) = 0.41. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.35 (d, J = 6.9 Hz, 3 H), 0.81 (d, J = 6.9 Hz, 3 H), 0.88 (d, J = 6.4 Hz, 3 H), 0.94 (d, J = 6.9 Hz, 3 H), 1.07−1.15 (m, 3 H), 1.22 (d, J = 6.9 Hz, 3 H), 1.26−1.37 (m, 3 H), 1.48−1.67 (m, 3 H), 1.97−2.08 (m, 3 H), 2.19−2.26 (m, 1 H), 2.73−2.80 (m, 1 H), 2.87−2.93 (m, 1 H), 3.09 (sept, J = 6.7 Hz, 1 H), 3.46 (ddd, J = 10.3, J = 4.3 Hz, 1 H), 7.10−7.19 (m, 3 H), 7.24−7.30 (m, 2 H), 7.35 (t, J = 7.3 Hz, 1 H), 7.45 (d, J = 7.3 Hz, 1 H), 7.55 (dd, J = 6.0, J = 0.6 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ = 15.1, 15.7, 21.6, 22.5, 22.8, 23.2, 24.0, 24.7, 25.0, 31.7, 33.8, 34.6, 35.2, 45.7, 50.7, 73.1, 125.0, 125.2, 125.4, 128.5, 129.6, 130.0, 132.7, 134.7, 135.9, 136.2, 149.6, 155.6 ppm. IR (cuvette): $\tilde{\nu}$ = 3155 (w), 2927 (s), 2853 (s), 2341 (m), 2254 (m), 1793 (w), 1590 (w), 1560 (w), 1457 (m), 1384 (m), 1216 (w), 1081 (m), 972 (m), 904 (m), 776 (m) cm^{-1}. LRMS (CI/NH_3): m/z = 438 [[M + NH_4]$^+$]. $C_{28}H_{40}OSi$ (420.70): calcd. C 79.94, H 10.04; found C 79.94, H 9.58. Analytical data for (Si*S*)-**19c**: R_f (cyclohexane) = 0.39. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.61 (d, J = 6.9 Hz, 3 H), 0.75 (d, J = 6.4 Hz, 3 H), 0.77−0.88 (m, 2 H), 0.91 (d, J = 7.3 Hz, 3 H), 0.92 (d, J = 6.4 Hz, 3 H), 0.95−1.10 (m, 2 H), 1.22 (d, J = 6.5 Hz, 3 H), 1.24−1.32 (m, 2 H), 1.34−1.59 (m, 2 H), 1.72−1.77 (m, 1 H), 1.98−2.06 (m, 3 H), 2.29−2.36 (m, 1 H), 2.73−2.80 (m, 1 H), 2.85−2.92 (m, 1 H), 3.07 (sept, J = 6.9 Hz, 1 H), 3.53 (ddd, J = 9.9, J = 4.7 Hz, 1 H), 7.11−7.17 (m, 3 H), 7.28 (dt, J = 7.3, J = 7.3 Hz, 2 H), 7.35 (dt, J = 7.3, J = 1.7 Hz, 1 H), 7.48 (dd, J = 6.9, J = 0.9 Hz, 1 H), 7.59 (dd, J = 7.7, J = 1.7 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ = 14.8, 15.8, 21.6, 22.3, 22.8, 23.2, 24.3, 24.5, 25.3, 25.4, 29.8, 31.7, 33.8, 34.5, 35.4, 45.2, 76.3, 125.0, 125.2, 128.7, 129.6, 130.1, 133.2, 134.8, 135.9, 136.4, 149.3, 155.6 ppm.

***rac*-1-(2-Methylphenyl)-1,2,3,4-tetrahydro-1-silanaphthalene (*rac*-9b):** A 25-mL Schlenk flask equipped with a magnetic stirrer bar and a reflux condenser was charged with (Si*RS*)-**19b** (388 mg, 0.988 mmol) and di-*n*-butyl ether (8 mL). DIBAL (3.00 mL, 3.00 mmol, 3.00 equiv., 1M in hexane) was added and the reaction mixture was maintained at reflux for 16 h. The reaction mixture was allowed to return to ambient temperature and acetone (15 mL) was added followed by concentrated HCl (10 mL). After diluting with H_2O (20 mL), the organic layer was separated and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered and the volatiles were evaporated in vacuo. Purification by flash chromatography on silica gel (cyclohexane) provided the cyclic silane *rac*-**9b** (180 mg, 0.755 mmol, 77%) as a colourless liquid. The enantiomeric ratio of 55:45 was determined from HPLC by integration of baseline separated peaks which were assigned as the enantiomers by comparison with a racemic sample. R_f (cyclohexane) = 0.45. HPLC (Daicel Chiralcel OD-H column, column temperature 24 °C, solvent *n*-heptane, flow rate 0.5 mL·min^{-1}): t_R = 15.75 min (minor enantiomer), t_R = 19.98 min (major enantiomer). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.10−1.17 (m, 1 H), 1.32−1.35 (m, 1 H), 2.00−2.07 (m, 2 H), 2.43 (s, 3 H), 2.85−2.87 (m, 2 H), 5.02 (t, J = 2.8 Hz, 1 H), 7.12−7.41 (m, 8 H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$,

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125 MHz): δ = 9.5, 22.4, 22.7, 35.1, 125.1, 125.6, 128.9, 129.5, 129.6, 129.7, 130.0, 134.3, 136.2, 136.7, 144.2, 149.7 ppm. IR (cuvette): $\tilde{\nu}$ = 3687 (m), 3025 (s), 2927 (m), 2692 (m), 2401 (s), 2361 (m), 2124 (s), 1889 (w), 1521 (s), 1474 (m), 1435 (m), 1227 (s), 1140 (m), 1079 (w), 928 (s), 749 (w) cm^{-1}. LRMS (EI): *m*/*z* = 238 [M^+]. $C_{16}H_{18}Si$ (238.40): calcd. C 80.61, H 7.61; found C 80.75, H 7.88.

(Si*S*)-1-(2-Isopropylphenyl)-1,2,3,4-tetrahydro-1-silanaphthalene [(Si*S*)-9c]: According to the preparation of *rac*-**9b**, a solution of silyl ether (Si*R*)-**19c** (645 mg, 1.54 mmol, *dr* = 1:99) and di-*n*-butyl ether (20 mL) was treated with DIBAL (4.70 mL, 4.70 mmol, 3.00 equiv., 1M in hexane) at reflux for 16 h. After the usual workup with acetone (30 mL) and concentrated HCl (20 mL), the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 60 mL). Purification by flash chromatography on silica gel (cyclohexane) provided cyclic silane (Si*S*)-**9c** (373 mg, 1.40 mmol, 91%) as a colourless liquid. The enantiomeric ratio of 1:99 was determined from HPLC by integration of baseline separated peaks which were assigned as the enantiomers by comparison with a racemic sample. R_f (cyclohexane) = 0.45. $[\alpha]_D^{20}$ = +78.2, $[\alpha]_{578}^{20}$ = +82.7, $[\alpha]_{546}^{20}$ = +96.4, $[\alpha]_{436}^{20}$ = +177, $[\alpha]_{365}^{20}$ = +315 (*c* = 11.0, $CHCl_3$), HPLC (Daicel Chiralcel OD-H column, column temperature 10 °C, solvent *n*-heptane, flow rate 0.4 mL·min^{-1}): t_R = 16.43 min for (Si*S*)-**9c** (major enantiomer), t_R = 19.98 min for (Si*R*)-**9c** (minor enantiomer). ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.05−1.13 (m, 1 H), 1.10 (d, *J* = 6.9 Hz, 3 H), 1.29 (d, *J* = 6.9 Hz, 3 H), 1.33−1.41 (m, 1 H), 1.99−2.05 (m, 2 H), 2.84−2.87 (m, 2 H), 3.11 (sept, *J* = 6.9 Hz, 1 H), 5.03 (t, *J* = 3.4 Hz, 1 H), 7.10−7.40 (m, 8 H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 10.6, 22.6, 24.2, 24.6, 34.3, 35.1, 125.0, 125.4, 125.5, 128.9, 129.5, 130.3, 130.4, 133.3, 136.3, 136.8, 149.4, 155.5 ppm. IR (cuvette): $\tilde{\nu}$ = 3687 (m), 3010 (s), 2928 (s), 2401 (s), 2361 (s), 2123 (m), 1962 (w), 1928 (w), 1589 (m), 1522 (m), 1474 (m), 1435 (m), 1664 (m), 1224 (s), 1120 (w), 1076 (m), 1028 (w), 981 (w), 938 (m), 825 (w) cm^{-1}. LRMS (CI/NH_3): *m*/*z* = 267 [[M + H]$^+$]. $C_{18}H_{22}Si$ (266.45): calcd. C 81.14, H 8.32; found C 81.12, H 8.40.

(Si*R*)-1-(2-Isopropylphenyl)-1,2,3,4-tetrahydro-1-silanaphthalene [(Si*R*)-9c]: According to the preparation of (Si*S*)-**9c**, a solution of silyl ether (Si*S*)-**19c** (793 mg, 1.89 mmol, *dr* = 94:6) and di-*n*-butyl ether (25 mL) was treated with DIBAL (5.70 mL, 5.70 mmol, 3.00 equiv., 1M in hexane) at reflux for 16 h. The usual workup and purification by flash chromatography on silica gel (cyclohexane) gave cyclic silane (Si*R*)-**9c** (389 mg, 1.46 mmol, 77%) as a colourless liquid. The enantiomeric ratio of 94:6 was determined from HPLC by integration of baseline separated peaks which were assigned as the enantiomers by comparison with a racemic sample. $[\alpha]_D^{20}$ = −75.2, $[\alpha]_{578}^{20}$ = −78.8, $[\alpha]_{546}^{20}$ = −90.1, $[\alpha]_{436}^{20}$ = −166, $[\alpha]_{365}^{20}$ = −291 (*c* = 22.2, $CHCl_3$).

***rac*-1-Chloro-(2-methylphenyl)-1,2,3,4-tetrahydro-1-silanaphthalene (*rac*-7b):** A saturated solution of Cl_2 in CCl_4 (1 mL) was added dropwise to a vigorously stirred solution of *rac*-**9b** (138 mg, 0.580 mmol) in CCl_4 (4 mL) at 0 °C until a permanent pale yellow colour appeared. The reaction mixture was maintained for 2 min and a second portion of Cl_2 in CCl_4 (0.60 mL) was added. The yellow solution was purged with argon after 2 min. Evaporation of the solvent under high vacuum provided *rac*-**7b** (157 mg, 0.577 mmol, 99%) as a yellowish oil which was used without further purification. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.40−1.57 (m, 2 H), 2.06−2.16 (m, 2 H), 2.40 (s, 3 H), 2.79−2.87 (m, 1 H), 2.92−2.99 (m, 1 H), 7.18−7.26 (m, 4 H), 7.36 (t, *J* = 6.0 Hz, 2 H), 7.51 (d, *J* = 7.3 Hz, 1 H), 7.68 (d, *J* = 7.7 Hz, 1 H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 16.4, 22.1, 23.0, 34.7, 125.2, 126.2, 129.0, 130.3, 130.6, 130.9, 135.3, 136.3, 134.9, 148.9 ppm. IR (cuvette): $\tilde{\nu}$ = 3736 (w), 3677 (w), 3059 (m), 3010 (m), 2929 (s), 2863 (m), 2401 (m), 2361 (m), 1930 (w), 1824 (w), 1699 (w), 1590 (m), 1560 (m), 1521 (w), 1473 (m), 1437 (m), 1337 (w), 1269 (w), 1202 (m), 1131 (m), 1081 (m), 1029 (m), 974 (m), 916 (m), 799 (m), 690 (m) cm^{-1}. LRMS (EI): *m*/*z* = 272 [M^+]. HRMS (EI): calcd. for $C_{16}H_{17}ClSi$: 272.0788; found 272.0793.

(Si*R*)-1-Chloro-(2-isopropylphenyl)-1,2,3,4-tetrahydro-1-silanaphthalene [(Si*R*)-7c]: According to the procedure of *rac*-**7b**, a saturated solution of Cl_2 in CCl_4 (0.30 mL) was added to a solution of (Si*S*)-**9c** (40 mg, 0.15 mmol, *er* = 1:99) in CCl_4 (2 mL) at 0 °C. The reaction mixture was maintained for 2 min and a second portion of Cl_2 in CCl_4 (0.10 mL) was then added. The solution was purged with argon after 2 min. Evaporation of the solvent under high vacuum provided (Si*R*)-**7c** (44.7 mg, 0.148 mmol, 99%) as a colourless liquid which solidified upon standing at −30 °C in *n*-pentane. $[\alpha]_D^{20}$ = +24.5, $[\alpha]_{578}^{20}$ = +25.3, $[\alpha]_{546}^{20}$ = +29.6, $[\alpha]_{436}^{20}$ = +54.1, $[\alpha]_{365}^{20}$ = +91.1 (*c* = 25.7, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.00 (d, *J* = 6.9 Hz, 3 H), 1.30 (d, *J* = 6.9 Hz, 3 H), 1.38−1.46 (m, 1 H), 1.55−1.60 (m, 1 H), 2.07−2.20 (m, 2 H), 2.80−2.87 (m, 1 H), 2.95−3.00 (m, 1 H), 3.05 (sept, *J* = 6.9 Hz, 1 H), 7.19−7.27 (m, 3 H), 7.34−7.38 (m, 2 H), 7.47 (dt, *J* = 7.7, *J* = 1.7 Hz, 1 H), 7.53 (dd, *J* = 7.3, *J* = 1.3 Hz, 1 H), 7.70 (dd, *J* = 7.3, *J* = 1.3 Hz, 1 H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 17.3, 22.2, 24.0, 24.5, 34.7, 125.5, 125.8, 126.0, 128.9, 130.5, 131.2, 131.3, 131.6, 135.4, 136.3, 148.5, 155.4 ppm. IR (cuvette): $\tilde{\nu}$ = 3027 (m), 2903 (m), 2520 (m), 2360 (m), 2341 (s), 1793 (m), 1624 (m), 1540 (m), 1436 (m), 1216 (m), 1015 (m), 991 (m), 876 (w), 823 (m), 748 (m) cm^{-1}. LRMS (EI): *m*/*z* = 300 [M^+]. HRMS (EI): calcd. for $C_{18}H_{21}ClSi$: 300.1101; found 300.1108.

(Si*S*)-1-Chloro-(2-isopropylphenyl)-1,2,3,4-tetrahydro-1-silanaphthalene [(Si*S*)-7c]: According to the procedure for *rac*-**7b**, a saturated solution of Cl_2 in CCl_4 (0.20 mL) was added to a solution of (Si*R*)-**9c** (26.7 mg, 0.100 mmol, *er* = 96:4) in CCl_4 (1 mL) at 0 °C. The reaction mixture was maintained for 2 min and a second portion of Cl_2 in CCl_4 (0.05 mL) was then added. The solution was purged with argon after 2 min. Evaporation of the solvent at reduced pressure provided (Si*S*)-**7c** (29.8 mg, 0.0990 mmol, 99%) as a colourless liquid which solidified upon standing at −30 °C in *n*-pentane. $[\alpha]_D^{20}$ = −20.9, $[\alpha]_{578}^{20}$ = −22.9, $[\alpha]_{546}^{20}$ = −25.2, $[\alpha]_{436}^{20}$ = −46.2, $[\alpha]_{365}^{20}$ = −72.9 (*c* = 21.0, $CHCl_3$).

Acknowledgments

The research was supported by the Deutsche Forschungsgemeinschaft (Emmy Noether fellowship, Oe 249/2−2), the Fonds der Chemischen Industrie and the Wissenschaftliche Gesellschaft, Freiburg im Breisgau. The authors thank Ilona Hauser for skilful technical assistance, and Gerd Fehrenbach and Dr. Richard Krieger for performing the HPLC analyses. M. O. is indebted to Professor Reinhard Brückner for his continuous support. Generous donations of chemicals from Boehringer Ingelheim, Vienna, Austria, and Haarmann & Reimer, Holzminden, Germany are gratefully acknowledged.

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Received September 1, 2004

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