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$B(C_6F_5)_3$-Catalyzed Reduction of Ketones and Imines Using Silicon-Stereogenic Silanes: Stereoinduction by Single-Point Binding

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We recently employed a silicon-stereogenic silane as a stereochemical probe to clarify the mechanism of the $B(C_6F_5)_3$-catalyzed hydrosilylation of ketones. When using a prochiral ketone, reasonable stereoinduction was seen, originating from the stereogenicity at the silicon atom, a chirality transfer from silicon to carbon through single-point binding of the chiral silane to the carbonyl oxygen atom. In the present investigation, we further elaborated on this remarkable observation by systematic variation of the ketone substitution pattern. We then included prochiral imines as well to test for diastereocontrol. Unexpectedly, these substance classes, ketones and imines, yielded diametrically opposed results in the reduction with a silicon-stereogenic silane. While the level of diastereoselection was decent in the C=O reduction ($dr \approx 80:20$), no asymmetric induction was detected in the C=NR reduction. On the basis of these experimental data and our previous mechanistic insight, we propose different reaction pathways for the reduction step of these related $B(C_6F_5)_3$ catalyses. Aside from these mechanistic implications, we also report an unusual 1,6- rather than conventional 1,2-reduction of a sterically encumbered diaryl-substituted ketone.

Introduction

Reductive processes are among the standard transformations in organic synthesis. Over the course of decades, target molecules of increasing complexity as well as a general demand of catalytic and selective methods maintained considerable interest in procedures for the reduction of unsaturated bonds.[1] Within this broad area, hydrosilylation chemistry making use of the hydridic character of silanes is attractive, simply because of their availability, handling and chemical stability.[2] Upon activation of either the Si–H bond or a C=O or C=NR functional group with catalytic or stoichiometric amounts of a mediator, silanes serve as hydride sources. While a major portion of known processes are transition metal-catalyzed,[3] Lewis acid-promoted protocols are less developed.[4] A major breakthrough using the latter activation strategy was achieved by Piers et al. by showing that the electron-deficient borane $B(C_6F_5)_3$[5] (**1**) facilitates the hydrosilylation of carbonyl compounds at low catalyst loading and ambient temperature.[6] Based on comprehensive mechanistic investigations, Piers et al. proposed a counterintuitive three-step mechanism (Scheme 1).[7]

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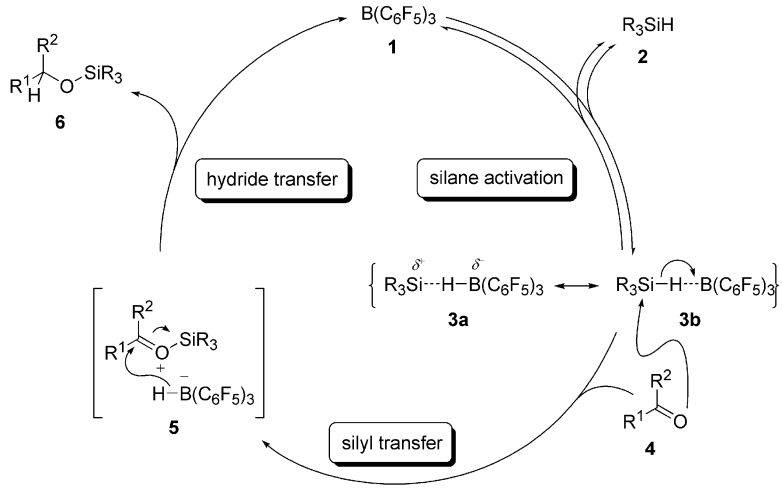
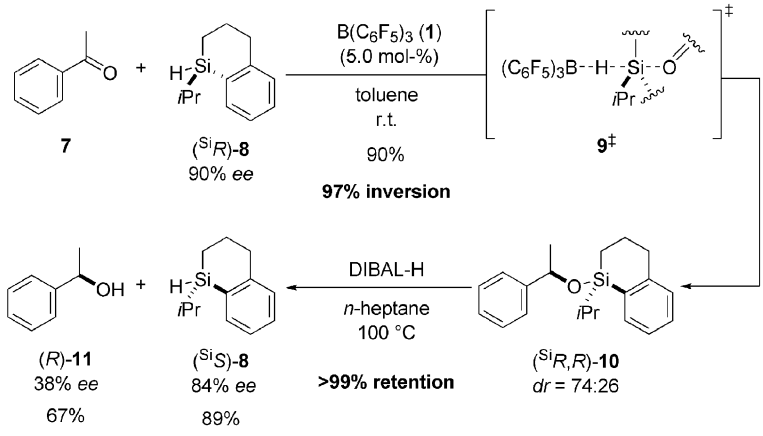
The catalysis commences with reversible coordination of the strong Lewis acid **1** to the Si–H bond of silane **2** (**1**→**3**). The resonance structures **3a** and **3b** of the thus-formed intermediate rationalize the capability of **1** to abstract a hydride upon further activation of the Si–H bond. Transfer of the silicon group to the Lewis basic carbonyl oxygen atom of **4** then produces the ion pair **5** (**3**→**5**), which collapses through hydride transfer from the borohydride to the electrophilic carbon atom of the carboxonium ion (**5**→**1**).

Later, Piers et al. also employed the Si–H bond activation by $B(C_6F_5)_3$ (**1**) in the reduction of imines[8a] and in the dehydrogenative coupling of alcohols and silanes.[8b] Nevertheless, the authors stated that it would need a silicon-stereogenic silane to finally settle the mechanism(s) for C=O and C=NR reduction.[7] Intrigued by the current progress in metal-free dihydrogen activation using hindered Lewis bases and **1** or $B(C_6F_5)_3$-derived Lewis acids (frustrated Lewis pairs, FLPs),[9–12] we anticipated an analogy of H–H and Si–H bond activation by **1**. The $B(C_6F_5)_3$-catalyzed hydrogenation of C=N bonds lent further support.[11g,11h] The expectant, far-reaching mechanistic implications for both processes prompted us to examine the $B(C_6F_5)_3$-catalyzed hydrosilylation of C=O groups utilizing a silicon-stereogenic silane as a stereochemical probe (Scheme 2).[13,14]

We learned that, from our family of silicon-stereogenic silanes,[15] merely isopropyl-substituted silanes, e.g. (^{Si}R)-**8**, would participate in the $B(C_6F_5)_3$-catalyzed reduction. With acetophenone (**7**) as the prochiral carbonyl compound, the silicon ether (^{Si}R,*R*)-**10** is produced in a diastereomeric ratio



Scheme 1. Catalytic cycle of the $B(C_6F_5)_3$-catalyzed hydrosilylation of carbonyl compounds.



Scheme 2. Two-step stereochemical analysis of the $B(C_6F_5)_3$-catalyzed hydrosilylation of acetophenone (**7**).

of 74:26. Stereospecific cleavage of the Si–O bond proceeded with retention of the configuration at the silicon atom,[16] liberating silane (^{Si}S)-**8** with overall inversion of the configuration. Alcohol (*R*)-**11** was isolated in 38% *ee*, which agrees with the *dr* = 74:26 for (^{Si}R,*R*)-**10** and 90% *ee* for (^{Si}R)-**8**. While this Walden inversion clearly confirmed the S_N2-Si mechanism passing through transition state **9**‡, it is noteworthy that (^{Si}R,*R*)-**10** was obtained in decent diastereomeric ratio. Remarkably, asymmetric induction originates from the chiral silicon entity by single-point binding to the carbonyl oxygen atom. In combination with the steric bulk of the borohydride, this results in reasonable discrimination of the diastereotopic faces of activated **7**. That situation is a rare example for an intramolecular chirality transfer from silicon to carbon.[17] To the best of our knowledge, there exists only a single other report on the enantioselective preparation of alcohols by carbonyl reduction with a chiral silane.[18] In contrast to the present report, the approach by Fry et al. hinges upon Lewis base activation (cesium fluoride) of the silane. The poor levels of enantioselection (≤13% *ee*) along with almost completeley racemized silane after reductive Si–O bond cleavage – yet with inversion of the configuration at the silicon atom – strongly indicates the involvement of hypervalent silicon intermediates. These are prone to racemization by pseudorotational processes (cf. **9**‡ in Scheme 2, no racemization seen in hypervalent transition states).

Our research, devoted to the $B(C_6F_5)_3$-catalyzed reduction of carbonyl compounds using silicon-stereogenic silanes, allowed for a refined mechanistic understanding. In this full account, we present our synthetic efforts to further illuminate the structural features of the prochiral ketone required to impart diastereocontrol. Moreover, we also apply this chemistry to prochiral imines, and experimental observations made in those reductions suggest differing mechanisms for carbonyl and imine hydrosilylation.

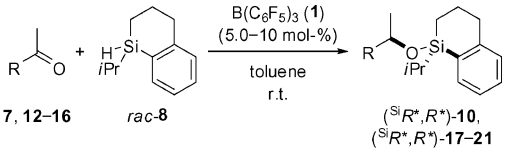
Results and Discussion

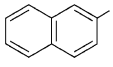
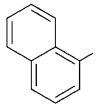
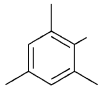
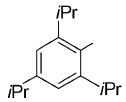
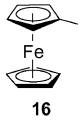
Reduction of C=O Bonds

An initial silane screening had revealed that *tert*-butyl-substituted silanes were inert towards $B(C_6F_5)_3$ (**1**).[13] Therefore, all reactions were performed with less hindered silane *rac*-**8**, decorated with an isopropyl substituent. As shown previously (Scheme 2), the reduction of **7** at ambient temperature afforded ($^{Si}R^*,R^*$)-**10** in a diastereomeric ratio of 74:26 (Table 1, entry 1).[19] The reaction rate decreased markedly at lower reaction temperatures, and diastereoselection remained the same. Replacing the phenyl group by either 2- or 1-naphthyl groups had no effect, affording diasteromeric ratios of 73:27 for ($^{Si}R^*,R^*$)-**17** and 77:23 for ($^{Si}R^*,R^*$)-**18** (Table 1, entries 2 and 3). A further increase of the steric demand as in 2,4,6-trimethylacetophenone (**14**) or 2,4,6-triisopropylacetophenone (**15**) had only little effect, producing ($^{Si}R^*,R^*$)-**19** and ($^{Si}R^*,R^*$)-**20** in *dr* = 80:20 and 81:19, respectively (Table 1, entries 4 and 5). For **15**, double the amount of **1** was needed to secure full conversion. In fact, the reactivity of these sterically shielded carbonyl groups is noteworthy, as there exists only a handful of protocols for their hydrosilylation.[20] An electron-rich methyl ketone, e.g. **16**, was unreactive at room temperature, and completely decomposed at elevated temperature (Table 1, entry 6); 2,4,6-trimethoxyacetophenone (not shown) furnished a complex product mixture.

Cyclic ketones, 1-indanone (**22**) and 1-tetralone (**23**), displayed unexpected reactivity. Both reacted sluggishly, and diastereomeric ratios were poor, even though these carbonyl compounds are conformationally less flexible (Table 2, entries 1 and 2).

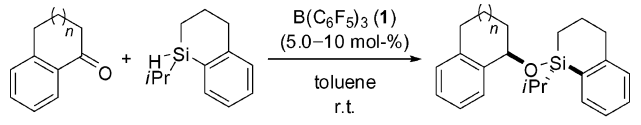
Table 1. Diastereoselective hydrosilylation of prochiral ketones using silicon-stereogenic silane *rac*-**8**: acyclic methyl ketones.[a]



Entry	R	*t* [h]	*dr*[b]	*C* [%][c]	Product	Yield [%][d]
1	 **7**	4	76:24	>99	($^{Si}R^*,R^*$)-**10**	82
2	 **12**	4	73:27	>99	($^{Si}R^*,R^*$)-**17**	54
3	 **13**	16	77:23	>99	($^{Si}R^*,R^*$)-**18**	63
4	 **14**	14	80:20	>99	($^{Si}R^*,R^*$)-**19**	87
5[e]	 **15**	17	81:19	>99	($^{Si}R^*,R^*$)-**20**	63
6[e,f]	 **16**	15	–[f]	>99	($^{Si}R^*,R^*$)-**21**	–[f]

[a] All reactions were performed using a slight excess of the ketone (1.05 equiv.). [b] Determined by ^{1}H NMR spectroscopy or GLC analysis. [c] Conversion of silane, as monitored by GLC using *n*-decane as internal standard. [d] Isolated yield after flash chromatography. [e] 10 mol-% of **1**. [f] Reaction at 70 °C. The reaction conditions lead to elimination products.

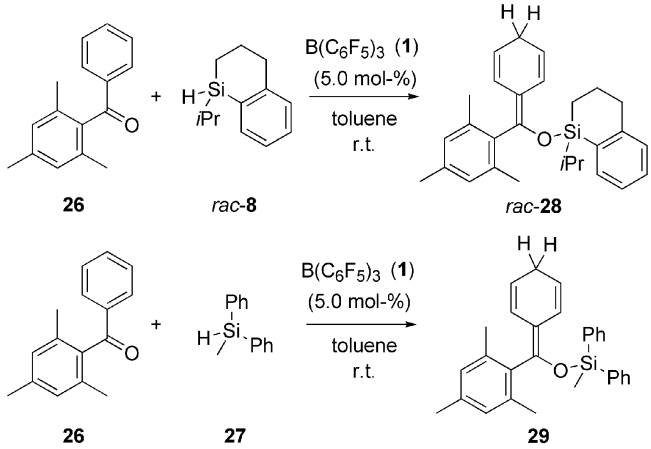
Table 2. Diastereoselective hydrosilylation of prochiral ketones using silicon-stereogenic silane *rac*-**8**: cyclic ketones.[a]



Entry	Ketone	*n*	*t* [h]	*dr*[b]	*C* [%][c]	Product	Yield [%]
1	**22**	0	20	60:40	36	($^{Si}R^*,R^*$)-**24**	n.d.
2[d]	**23**	1	14	75:25	>99	($^{Si}R^*,R^*$)-**25**	–[e]

[a] Both reactions were performed using a slight excess of the ketone (1.05 equiv.). [b] Determined by ^{1}H NMR spectroscopy. [c] Conversion of silane, as monitored by GLC using *n*-decane as internal standard. [d] 10 mol-% of **1**. [e] Not obtained in analytically pure form. n.d. = not determined.

While a number of alkyl aryl ketones performed well (Table 1), we discovered that certain diaryl-substituted ketones adopt an unprecedented reaction pathway (Scheme 3). Treatment of prochiral ketone **26**, decorated with mesityl and phenyl groups, with cyclic silane *rac*-**8** in



Scheme 3. $B(C_6F_5)_3$-catalyzed hydrosilylation of **26**: observation of an unusual 1,6-reduction.

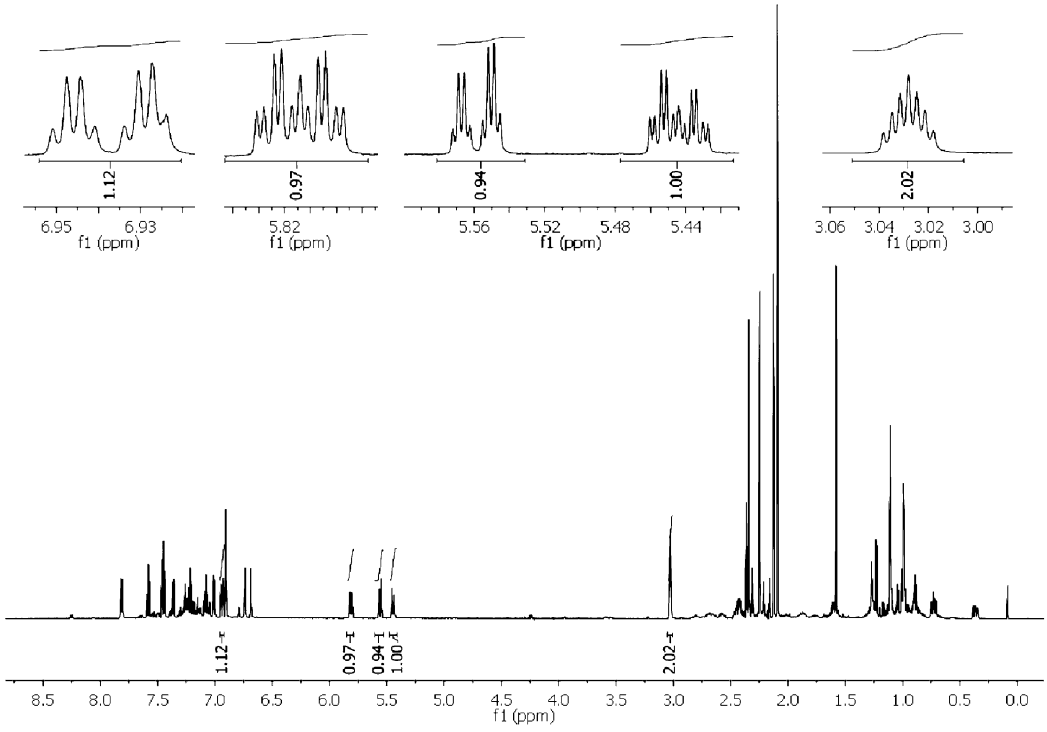
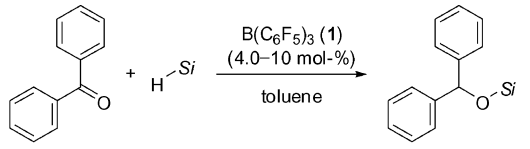


Figure 1. ^{1}H NMR spectra of the *rac*-**28**: 1,6- rather than 1,2-reduction.

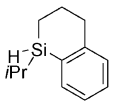
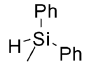
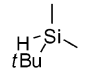
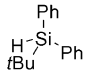
the presence of $B(C_6F_5)_3$ (**1**) yielded an unexpected product, *rac*-**28**. The same outcome was seen with acyclic (less hindered) silane **27**. The ^{1}H NMR spectra of the crude reaction mixture showed no methyne signal, diagnostic for 1,2-reduction. Instead, three well-defined signals appeared between 5.43 ppm and 5.84 ppm, and subsequent correlation spectroscopy revealed that the spin system of these three signals is completed by signals at δ = 3.03 ppm and 6.94 ppm (Figure 1). In conjunction with the observed integration of 1:1:1:1:2, this set of data is in agreement with an unusual 1,6-reduction. We conclude that the carbonyl group flanked by the methyl groups cannot undergo 1,2-reduction for steric reasons, and borohydride reduction must occur in an 1,6-fashion. Unfortunately, any attempts to isolate the proposed products, *rac*-**28** and **29**, or to further react **29** with benzaldehyde in a $B(C_6F_5)_3$-catalyzed vinylogous Mukaiyama aldol reaction[21] were unfruitful.

Encouraged by these findings, we set out to examine its generality. For this, we selected benzophenone (**30**) as substrate. Reaction with *rac*-**8** as well as **27** resulted in 1,2-reduction, affording conventional silicon ethers *rac*-**33** and **34** (Table 3, entries 1 and 2). We therefore hoped that sterically hindered, *tert*-butyl-substituted silanes **31** and **32** would bring about 1,6-reduction yet again these emerged as unreactive (Table 3, entries 3–6). As mentioned before (vide supra), we assume that a bulky *tert*-butyl group attached to the silicon atom thwarts activation of the Si–H bond by $B(C_6F_5)_3$ (**1**).[22]

Table 3. Silane substitution pattern in the hydrosilylation of benzophenone (**30**).



30 *rac*-**8** and **27**, **31**–**32** *rac*-**33** and **34**–**36**

Entry	Silane	*T* [°C]	*t* [h]	Product	Yield [%][b]
1	 *rac*-**8**	r.t.	18.5	*rac*-**33**	88
2	 **27**	r.t.	1	**34**	80
3	 **31**	r.t.	14	**35**	–[c]
4	 **32**	r.t.	15	**36**	–[c]
5		60	24	**36**	–[c]
6		100	26	**36**	–[c]

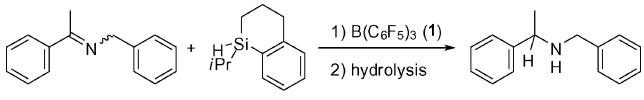
[a] All reactions were performed using a slight excess of the ketone (1.05 equiv.). [b] Isolated yield after flash chromatography. [c] No product formation.

Reduction of C=N Bonds

The reduction of several aryl methyl ketones was accomplished in moderate diastereomeric ratios (Table 1). We reasoned that improved stereocontrol might be possible when using imines with different R groups at the nitrogen atom. In contrast to Si–O bond formation in the reduction of C=O groups, the Si–N linkage formed in the C=NR reduction is prone to facile hydrolysis. Isolation of diastereomers will therefore be difficult. The level of asymmetric induction must be determined from the enantiomeric excess of the thus-formed amine, which in turn requires the use enantiomerically pure silane (^{Si}R)-**8**.

We began our investigation with the identification of a practical reaction protocol by reducing imine (*E*/*Z*)-**37** (*E*:*Z* = 92:8) with racemic silane *rac*-**8**. According to Piers et al.,[8] the high-yielding reduction of **37** with Me_2PhSiH using 5.0 mol-% of **1** was complete after 2 h at ambient temperature. Conversely, the reaction with *rac*-**8** at elevated temperature, higher catalyst loading, and prolonged reaction time provided only trace amounts of the desired amine **38** (Table 4, entry 1). A further increase of the reaction temperature to 100 or 140 °C resulted in no improvement (Table 4, entries 2 and 3). We then added **1** in stoichiometric quantities, finally resulting in 84% conversion after 40 h at 75 °C and 38% yield after hydrolysis on silica gel (Table 4, entry 4).

Table 4. B(C_6F_5)$_3$-mediated hydrosilylation of imine (*E*/*Z*)-**37** using silane *rac*-**8**: variation of the reaction conditions.[a]



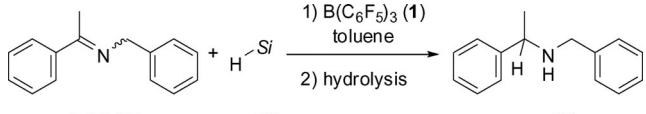
(*E*/*Z*)-**37** *E*:*Z* = 92:8 *rac*-**8** *rac*-**38**

Entry	B(C_6F_5)$_3$ (**1**) [mol-%]	Solvent	*T* [°C]	*t* [h]	*C* [%][b]	Yield [%]
1	5.00	toluene	70	24	<5	traces
2	10.0	toluene	100	24	n.d.	traces
3	10.0	xylene	140	44	<5	traces
4	100	toluene	75	40	84	38%[c]

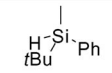
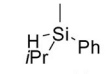
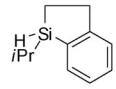
[a] All reactions were performed using a slight excess of the silane (1.05–1.20 equiv.). [b] Conversion of silane, as monitored by GLC using *n*-decane or biphenyl as internal standard, neglecting silanol and disiloxane formation; determination based of consumption **37** failed because of complexation with **1**. [c] Isolated yield after flash chromatography; n.d. = not determined.

For this reason, we asked ourselves whether related silicon-stereogenic silanes would display improved reactivity. Yet again, no conversion was observed for *tert*-butyl-substituted *rac*-**39** (Table 5, entry 1). In turn, corresponding isopropyl-substituted *rac*-**40** reacted in the presence of stoichiometric amounts of B(C_6F_5)$_3$ (**1**) (Table 5, entry 2); with catalytic amounts of **1**, we merely obtained traces of amine *rac*-**38**. Silanes with the silicon atom embedded into a five- or even four-membered ring are subtantially more reactive due to *strain-release Lewis acidity*.[23] Our indane-derived silane *rac*-**41** might therefore contribute the reactivity necessary for turnover at lower temperature. Indeed, GLC analysis showed 51% conversion (Table 5, entry 3) along with a white precipitate, the imine–borane complex.[24]

Table 5. B(C_6F_5)$_3$-mediated hydrosilylation of imine (*E*/*Z*)-**37**: variation of the silicon-stereogenic silane.[a]



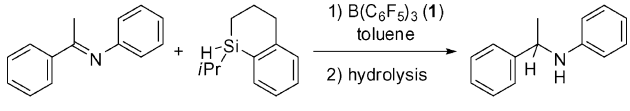
(*E*/*Z*)-**37** *rac*-**39** *rac*-**40** *rac*-**41** *rac*-**38**

Entry	Silane	B(C_6F_5)$_3$ (**1**) [mol-%]	*T* [°C]	*t* [h]	*C* [%][b]	Yield [%]
1	 *rac*-**39**	10.0	70	24	0	–
2	 *rac*-**40**	100	75	24	83	50%[c]
3	 *rac*-**41**	100	r.t.	16	51	–[d]

[a] All reactions were performed using a slight excess of the silane (1.05–1.20 equiv.). [b] Conversion of silane, as monitored by GLC using *n*-decane as internal standard, neglecting silanol and disiloxane formation; determination based of consumption **37** failed because of complexation with **1**. [c] Isolated yield after flash chromatography. [d] Product formation detected by GLC but the product was not isolated.

We learned from our experiments that benzyl-substituted imine **37** tends to form a stable complex with B(C_6F_5)$_3$ (**1**), thereby preventing catalytic turnover. Piers et al. had reported that less Lewis basic imines are more reactive due to their lower affinity towards adduct formation.[6–8] We therefore replaced the benzyl with a phenyl group as in imine **42**. We were pleased to find that borane **1** (10.0 mol-%) catalyzed the reduction of **42**; conversion was dependent on the

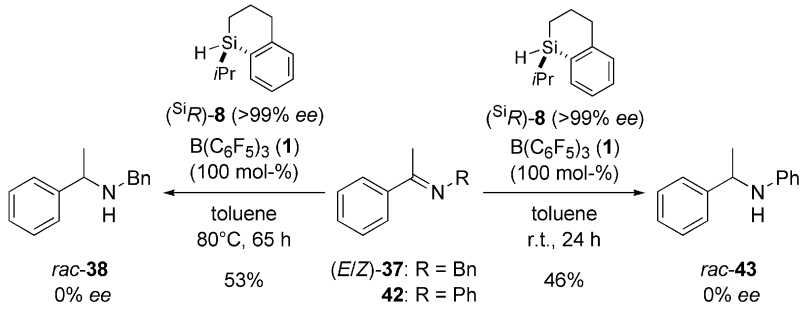
Table 6. B(C_6F_5)$_3$-mediated hydrosilylation of imine **42**: variation of the reaction conditions.



42 *rac*-**8** *rac*-**43**

Entry	B(C_6F_5)$_3$ (**1**) [mol-%]	*T* [°C]	*t* [h]	*C* [%][b]	Yield [%]
1	10.0	70	67	47	–[c]
2	10.0	100	90	69	–[c]
3	100	r.t.	40	>99	46%[d]

[a] All reactions were performed using a slight excess of the silane (1.05–1.20 equiv.). [b] Conversion of silane, as monitored by GLC using *n*-decane as internal standard, neglecting silanol and disiloxane formation; determination based of consumption **42** failed because of complexation with **1**. [c] Product formation detected by GLC but the product was not isolated. [d] Isolated yield after flash chromatography.



Scheme 4. $B(C_6F_5)_3$-catalyzed reduction of imines **37** and **42** with enantio-enriched silane (^{Si}R)-**8** (>99% *ee*).

reaction temperature (Table 6, entries 1 and 2). A stoichiometric run provided *rac*-**43** in 46% isolated yield at full conversion (Table 3, entry 3).

Having optimized reaction conditions for the $B(C_6F_5)_3$-mediated reduction of imines **37** and **42** with silicon-stereogenic silane **8**, the next logical step was to use virtually enantiopure silane (^{Si}R)-**8** (>99% *ee*). Analysis of enantiomeric excesses of amine **38** and **43** would then disclose the chirality transfer from silicon to carbon. Both reactions were performed using the previously elaborated protocols (see Tables 4 and 6), affording amines **38** and **43** in 53% and 46% chemical yields, respectively (Scheme 4). To our surprise, we obtained both amines as racemic mixtures!

This unexpected stereochemical outcome suggests that the asymmetrically substituted silicon atom might not be in the proximity of the imine carbon atom in the stereochemistry-determining borohydride reduction. The mechanism of imine reduction (with hindered silanes) might therefore be subtly different from carbonyl reduction (**5**, Figure 2).[13] It must be noted though that, based on NMR measurements, Piers et al. had already postulated ion pair **44** to be a pivotal intermediate in the $B(C_6F_5)_3$-catalyzed activation of (non-hindered) Me_2PhSiH in the presence of an imine (Figure 2).[8] We assume, however, that the encumbered borohydride cannot transfer a hydride onto a hindered silylated iminium ion (as in **44**). Instead, another molecule of the imine, likely to be activated by complexation with Lewis acid **1**, is prone to hydride transfer (**45**, Figure 2). This situation accounts for the absence of any stereoinduction of the silicon-stereogenic entity. We do believe that carbonyl and imine reduction differ in the irreversible reduction step (at least) when using our silicon-stereogenic silanes.

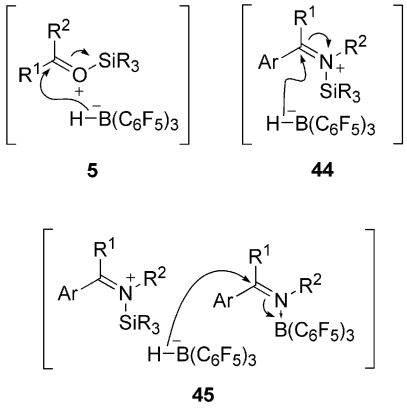


Figure 2. Origin of the chirality transfer from silicon to carbon.

Conclusions

In the synthetic portion of this paper, we explored the level of diastereoselectivity in the reagent-controlled $B(C_6F_5)_3$-catalyzed reduction of prochiral carbonyl compounds using a silicon-stereogenic silane as the sole source of stereochemical information. Our investigation demonstrate that a diastereomeric ratio of 80:20 is the norm for aryl methyl ketones, which is remarkable in the sense that the carbonyl group is activated through single-point binding of a chiral silicon entity.[17] Moreover, we disclosed an unusual 1,6-reduction of a borohydride when using sterically congested ketones.

The mechanistic portion derived from the unexpected observation that the $B(C_6F_5)_3$-mediated reduction of prochiral imines with silicon-stereogenic silane **8** proceeded without any stereoinduction. We rationalize the conflicting results for C=O and C=NR reduction by different hydride transfer steps (Figure 2). Carbonyl reduction passes through ion pair **5** with a chiral oxonium ion while imine reduction involves two discrete activated imines, out of which the achiral imine–borane complex is less hindered and more reactive (**45**, Figure 2).

Experimental Section

General Information: $B(C_6F_5)_3$ (**1**),[25] *rac*-**8** and (^{Si}R)-**8**,[14b] ketones **15**,[26] **16**[27] and **26**,[28] silanes **31**[29] and **32**,[30] imines (*E*/*Z*)-**37**[31] and **42**,[32] silicon-stereogenic silanes *rac*-**39**[33] and *rac*-**41**[34] were prepared according to known procedures. All reactions were performed in flame-dried Schlenk tubes under a static pressure of argon using conventional Schlenk technique or a glovebox. Liquids and solutions were transferred with syringes. Solvents were dried prior to use by continuous distillation from the following drying agents: sodium/benzophenone (for toluene and xylene), potassium/benzophenone (for THF) and potassium (for *n*-hexane). Melting points were determined by means of a Thompson Scientific melting point apparatus (uncorrected values). Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} glass plates (purchased from Merck); for flash column chromatography Merck's silica gel 60 (40–63 μm, 230–400 mesh, ASTM) was em-

ployed; cyclohexane/*tert*-butyl methyl ether (TBME) or cyclohexane/ethyl acetate solvent mixtures were used as eluents. ^1H, ^{13}C and ^{29}Si NMR spectra were recorded in $CDCl_3$ or C_6D_6 on Bruker AV 300, Bruker AV 400, Varian INOVA 500 and Varian Unity plus 600 spectrometers. GLC analyses were performed using a Shimadzu GC-17A equipped with a SE-54 capillary column (30 m × 0.32 mm, 0.25 μm, N_2 carrier gas, 250 °C injection temperature, detector temperature 300 °C; temperature program: start temperature 40 °C for 1 min, heat rate 10 °C min^{-1}, 280 °C end temperature for 10 min). HPLC analysis was performed with an Agilent 1200 instrument on a chiral stationary phase using a Daicel Chiralcel OD-H column (*n*-heptane/*i*PrOH as a solvent). Mass spectra were recorded with Waters Micromass Quattromicro (GC-MS/EI) or Bruker Daltronics Micro-TOF (ESI-MS). IR spectra were recorded on a Varian 3100 FT-IR instrument equipped with an ATR unit. Elemental analyses were conducted on a Vario EL III instrument from Elementaranalysensysteme GmbH (Hanau, Germany). Analytical data for ($^{Si}R^*$,R^*)-**10** was included in a preliminary report.[13]

General Procedure for the Hydrosilylation of Ketones (GP 1): A Schlenk tube is charged with $B(C_6F_5)_3$ (**1**) (0.04–0.10 equiv.) in a glovebox. After connection to an argon/vacuum manifold, the solid is dissolved in anhydrous degassed toluene forming a colorless solution. Subsequently, solutions of the ketone (1.05 equiv.) and the silane (1.00 equiv.) in toluene are added dropwise via syringe. The resulting solution (0.1 M in silane) is maintained at ambient temperature until complete consumption of the reactants (1.00 to 18.5 h) as monitored by GLC. After addition of cyclohexane (10 mL) and a small portion of silica gel the solvents are evaporated. Purification by flash column chromatography on silica gel (mixtures of cyclohexane/*tert*-butyl methyl ether) affords the analytically pure products as colorless, highly viscous oils or solids.

($^{Si}R^*$,R^*)-1-Isopropyl-1-(1-naphth-2-ylethoxy)-1-silatetraline [($^{Si}R^*$,R^*)-17]: See Table 1, entry 2. According to GP 1, starting from **12** (71.5 mg, 0.420 mmol), *rac*-**8** (74.5 mg, 0.400 mmol), and $B(C_6F_5)_3$ (**1**) (11.1 mg, 0.0217 mmol) compound ($^{Si}R^*$,R^*)-**17** (78 mg, 54%, *dr* = 73:27 by GLC) was obtained as a colorless, highly viscous oil. R_f = 0.57 (cyclohexane/*tert*-butyl methyl ether = 24:1). GLC (SE-54): t_R = 24.5 (minor diastereomer), 24.7 min (major diastereomer). NMR spectroscopic data for major diastereomer: ^1H NMR (400 MHz, $CDCl_3$): δ = 0.65 (ddd, *J* = 15.0, *J* = 7.9, *J* = 4.3 Hz, 1 H), 0.75 (ddd, *J* = 15.0, *J* = 10.4, *J* = 4.7 Hz, 1 H), 0.86–1.23 (m, 7 H), 1.42 (d, *J* = 6.6 Hz, 3 H), 1.58–1.72 (m, 1 H), 1.76–1.93 (m, 1 H), 2.57 (ddd, *J* = 16.0, *J* = 9.6, *J* = 2.9 Hz, 1 H), 2.62–2.72 (m, 1 H), 4.92 (q, *J* = 6.4 Hz, 1 H), 7.13 (d, *J* = 7.2 Hz, 1 H), 7.25 (dd, *J* = *J* = 7.2 Hz, 1 H), 7.32 (ddd, *J* = *J* = 7.5, *J* = 1.6 Hz, 1 H), 7.40–7.49 (m, 3 H), 7.64–7.84 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.8, 14.2, 17.1, 17.2, 23.1, 27.1, 35.5, 71.2, 123.7, 124.2, 125.4, 125.6, 126.0, 127.8, 128.0, 128.1, 128.5, 129.7, 132.1, 132.8, 133.4, 134.7, 144.2, 150.1 ppm. NMR spectroscopic data for minor diastereomer: ^1H NMR (400 MHz, $CDCl_3$): δ = 0.86–1.23 (m, 9 H), 1.47 (d, *J* = 6.6 Hz, 3 H), 1.76–1.93 (m, 1 H), 1.94–2.01 (m, 1 H), 2.62–2.72 (m, 1 H), 2.79 (ddd, *J* = 15.9, *J* = 7.3, *J* = 2.9 Hz, 1 H), 4.99 (q, *J* = 6.8 Hz, 1 H), 7.03 (dd, *J* = *J* = 7.3 Hz, 1 H), 7.11 (d, *J* = 7.5 Hz, 1 H), 7.20–7.28 (m, 1 H), 7.36 (dd, *J* = 7.3, *J* = 1.3 Hz, 1 H), 7.40–7.49 (m, 3 H), 7.64–7.84 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.5, 14.1, 17.1, 17.3, 23.1, 27.0, 35.6, 71.3, 123.8, 124.2, 125.2, 125.5, 126.0, 127.7, 127.9, 128.1, 128.6, 129.5, 131.5, 132.8, 133.4, 134.8, 144.0, 150.1 ppm. IR (ATR): $\tilde{\nu}$ = 3055 (m), 2923 (m), 2862 (m), 1602 (w), 1086 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{24}H_{28}OSiNa$ [[M + Na]$^+$]: 383.1802; found 383.1801. $C_{24}H_{28}OSi$ (360.56): calcd. C 79.95, H 7.83; found C 80.04, H 7.95.

($^{Si}R^*$,R^*)-1-Isopropyl-1-(1-naphth-1-ylethoxy)-1-silatetraline [($^{Si}R^*$,R^*)-18]: See Table 1, entry 3. According to GP 1, starting from **13** (68.7 mg, 0.404 mmol), *rac*-**8** (66.5 mg, 0.350 mmol), and $B(C_6F_5)_3$ (**1**) (10.4 mg, 0.0203 mmol) compound ($^{Si}R^*$,R^*)-**18** (79 mg, 63%, *dr* = 77:23 by ^1H NMR spectroscopy) was obtained as a colorless, highly viscous oil. R_f = 0.60 (cyclohexane/*tert*-butyl methyl ether = 24:1). GLC (SE-54): t_R = 24.0 (minor diastereomer), 24.1 min (major diastereomer); NMR spectroscopic data for major diastereomer: ^1H NMR (400 MHz, $CDCl_3$): δ = 0.59 (ddd, *J* = 15.1, *J* = 7.9, *J* = 4.2 Hz, 1 H), 0.74 (ddd, *J* = 15.1, *J* = 10.4, *J* = 4.7 Hz, 1 H), 1.00 (d, *J* = 7.0 Hz, 3 H), 1.14 (d, *J* = 6.8 Hz, 3 H), 1.15–1.25 (m, 1 H), 1.53 (d, *J* = 6.4 Hz, 3 H), 1.59–1.68 (m, 1 H), 1.75–1.86 (m, 1 H), 2.58 (ddd, *J* = 15.9, *J* = 9.5, *J* = 3.1 Hz, 1 H), 2.68 (ddd, *J* = 15.9, *J* = 7.5, *J* = 3.0 Hz, 1 H), 5.48 (q, *J* = 6.2 Hz, 1 H), 7.15 (d, *J* = 7.5 Hz, 1 H), 7.28 (dd, *J* = *J* = 7.2 Hz, 1 H) 7.35 (ddd, *J* = *J* = 7.4, *J* = 1.6 Hz, 1 H), 7.40–7.51 (m, 3 H), 7.76–7.81 (m, 3 H), 7.79–7.84 (m, 1 H), 8.00 (dd, *J* = 6.8, *J* = 2.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.6, 14.2, 17.1, 17.2, 23.2, 26.6, 35.5, 68.9, 122.9, 123.6, 125.3, 125.4, 125.7 (2×), 127.3, 128.6, 128.9, 129.7, 130.0, 132.1, 133.9, 134.7, 142.5, 150.5 ppm. NMR spectroscopic data for minor diastereomer: ^1H NMR (400 MHz, $CDCl_3$): δ = 0.86–1.11 (m, 8 H), 1.15–1.25 (m, 1 H), 1.57 (d, *J* = 6.4 Hz, 3 H), 1.86–1.96 (m, 1 H), 1.96–2.08 (m, 1 H), 2.63–2.73 (m, 1 H), 2.80 (ddd, *J* = 16.1, *J* = 7.2, *J* = 2.9 Hz, 1 H), 5.58 (q, *J* = 6.4 Hz, 1 H), 7.00 (dd, *J* = 7.4 Hz, 1 H), 7.11 (d, *J* = 7.5 Hz, 1 H), 7.23 (ddd, *J* = *J* = 7.5, *J* = 1.4 Hz, 1 H), 7.40–7.51 (m, 3 H), 7.76–7.81 (m, 3 H), 7.79–7.84 (m, 1 H), 7.97 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.5, 14.1, 17.1, 17.3, 23.1, 26.6, 35.6, 69.0, 122.9, 123.6, 125.2 (2×), 125.6, 125.7, 127.4, 128.6, 128.9, 129.5, 130.0, 131.5, 133.9, 134.8, 142.3, 150.0 ppm. IR (ATR): $\tilde{\nu}$ = 3052 (w), 2923 (m), 2863 (m), 1590 (w), 1092 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{24}H_{28}OSiNa$ [[M + Na]$^+$]: 383.1802; found 383.1813. $C_{24}H_{28}OSi$ (360.56): calcd. C 79.95, H 7.83; found C 80.01, H 7.82.

($^{Si}R^*$,R^*)-1-Isopropyl-1-(1-mesitylethoxy)-1-silatetraline [($^{Si}R^*$,R^*)-19]: See Table 1, entry 4. According to GP 1, starting from **14** (71.1 mg, 0.438 mmol), *rac*-**8** (74.4 mg, 0.400 mmol), and $B(C_6F_5)_3$ (**1**) (10.4 mg, 0.0203 mmol) compound ($^{Si}R^*$,R^*)-**19** (123 mg, 87%, *dr* = 80:20 by ^1H NMR spectroscopy) was obtained as a colorless, highly viscous oil. R_f = 0.16 (cyclohexane/*tert*-butyl methyl ether = 98:2). GLC (SE-54): t_R = 21.8 min (both diastereomers). NMR spectroscopic data for major diastereomer: ^1H NMR (500 MHz, $CDCl_3$): δ = 0.52 (dddd, *J* = 15.0, *J* = 8.2, *J* = 4.2, *J* = 0.9 Hz, 1 H), 0.74 (ddd, *J* = 15.0, *J* = 10.4, *J* = 4.6 Hz, 1 H), 0.95–1.14 (m, 7 H), 1.41 (d, *J* = 6.8 Hz, 3 H), 1.47–1.56 (m, 1 H), 1.75–1.83 (m, 1 H), 1.95–2.50 (br. s, 9 H), 2.59 (ddd, *J* = 16.0, *J* = 9.2, *J* = 3.2 Hz, 1 H), 2.61 (ddd, *J* = 16.0, *J* = 7.6, *J* = 3.3 Hz, 1 H), 5.12 (q, *J* = 6.8 Hz, 1 H), 6.76 (br. s, 2 H), 7.13 (d, *J* = 7.5 Hz, 1 H), 7.25 (dd, *J* = *J* = 7.2 Hz, 1 H), 7.32 (ddd, *J* = *J* = 7.5, *J* = 1.6 Hz, 1 H), 7.64 (dd, *J* = 7.2, *J* = 1.6 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.0, 14.3, 17.1, 17.2, 20.4, 20.9, 23.1 (2×), 35.6, 68.2, 125.4, 128.7, 129.6, 129.9, 132.0, 134.6, 135.5, 136.0, 138.3, 150.1 ppm. NMR spectroscopic data for minor diastereomer: ^1H NMR (500 MHz, $CDCl_3$): δ = 0.83–0.92 (m, 1 H), 0.95–1.14 (m, 8 H), 1.45 (d, *J* = 6.8 Hz, 3 H), 1.85–1.95 (m, 1 H), 1.95–2.50 (br. s, 10 H), 2.68 (ddd, *J* = 15.9, *J* = 9.8, *J* = 2.9 Hz, 1 H), 2.82 (ddd, *J* = 16.0, *J* = 7.4, *J* = 2.8 Hz, 1 H), 5.15 (q, *J* = 6.8 Hz, 1 H), 6.73 (br. s, 2 H), 6.98 (dd, *J* = *J* = 7.5 Hz, 1 H), 7.11 (d, *J* = 7.5 Hz, 1 H), 7.17 (dd, *J* = 7.5, *J* = 1.6 Hz, 1 H), 7.24 (ddd, *J* = *J* = 7.5, *J* = 1.6 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.7, 14.0, 17.1, 17.2, 20.4, 20.9, 23.2, 23.3, 35.7, 68.3, 125.2, 128.3, 129.6, 129.9, 131.6, 134.8, 135.5, 135.7, 138.3, 150.3 ppm. IR (ATR): $\tilde{\nu}$ = 2923 (s), 2863 (m), 1612 (w), 1085 (s) cm^{-1}. HRMS (ESI): calcd. for

$C_{23}H_{32}OSiNa$ [[M + Na]$^+$]: 375.2115; found 375.2120. $C_{23}H_{32}OSi$ (352.59): calcd. C 78.35, H 9.15; found C 78.01, H 9.28.

($^{Si}R^*,R^*$)-1-Isopropyl-1-[1-(1,4,6-triisopropyl)phenylethoxy]-1-silatetraline [($^{Si}R^*,R^*$)-20]: See Table 1, entry 5. According to GP 1, starting from **15** (104 mg, 0.420 mmol), *rac*-**8** (74.4 mg, 0.400 mmol), and $B(C_6F_5)_3$ (**1**) (20.4 mg, 0.0398 mmol) compound ($^{Si}R^*,R^*$)-**20** (101 mg, 63%, *dr* = 81:19 by ^{1}H NMR spectroscopy) was obtained as a white solid. M.p. 97–98 °C (cyclohexane/*tert*-butyl methyl ether); R_f = 0.77 (cyclohexane/*tert*-butyl methyl ether = 24:1). GLC (SE-54): t_R = 23.4 min (both diastereomers). NMR spectroscopic data for major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.58 (ddd, *J* = 14.9, *J* = 8.5, *J* = 4.3 Hz, 1 H), 0.77 (ddd, *J* = 15.0, *J* = 10.2, *J* = 4.7 Hz, 1 H), 0.90–1.32 (m, 25 H), 1.48 (d, *J* = 6.6 Hz, 3 H), 1.61–1.72 (m, 1 H), 1.78–1.97 (m, 1 H), 2.53–2.76 (m, 3 H), 2.84 (sept, *J* = 7.0 Hz, 1 H), 4.04–4.22 (br. s, 1 H), 5.32 (q, *J* = 6.7 Hz, 1 H), 6.85 (br. s, 1 H), 7.03 (br. s, 1 H), 7.13 (d, *J* = 7.5 Hz, 1 H), 7.24 (dd, *J* = *J* = 7.2 Hz, 1 H), 7.31 (ddd, *J* = *J* = 7.5, *J* = 1.6 Hz, 1 H), 7.63 (dd, *J* = 7.2, *J* = 1.5 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.1, 14.5, 17.1, 17.2, 23.1, 23.7 (2×), 24.1, 24.2, 25.1 (2×), 25.8, 28.5, 28.9, 34.1, 35.5, 66.8, 120.3, 123.2, 125.3, 128.9, 129.5, 132.2, 134.7, 136.3, 144.2, 146.9, 148.9, 150.4 ppm. NMR spectroscopic data for minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90–1.32 (m, 27 H), 1.53 (d, *J* = 6.6 Hz, 3 H), 1.78–1.97 (m, 1 H), 1.99–2.16 (m, 1 H), 2.53–2.76 (m, 3 H), 2.84 (sept, *J* = 7.0 Hz, 1 H), 4.04–4.22 (br. s, 1 H), 5.36 (q, *J* = 6.7 Hz, 1 H), 6.78 (br. s, 1 H), 6.97 (dd, *J* = *J* = 7.5 Hz, 1 H), 7.06 (br. s, 1 H), 7.10 (d, *J* = 7.5 Hz, 1 H), 7.17–7.22 (m, 1 H), 7.52 (d, *J* = 7.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.6, 14.2, 17.0, 17.1, 23.1, 23.7 (2×), 24.0, 24.2, 25.1 (2×), 25.9, 28.5, 28.9, 34.1, 35.7, 66.8, 120.3, 123.2, 125.2, 128.3, 129.4, 132.0, 134.8, 136.3, 144.2, 146.8, 148.9, 150.1 ppm. IR (ATR): $\tilde{\nu}$ = 2956 (m), 2865 (m), 1608 (w) 1461 (m), 1073 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{29}H_{44}OSiNa$ [[M + Na]$^+$]: 459.3504; found 459.3504. $C_{29}H_{44}OSi$ (436.75): calcd. C 79.75, H 10.15; found C 79.51, H 10.25.

***rac*-1-(Benzhydryloxy)-1-isopropyl-1-silatetraline (*rac*-33):** See Table 3, entry 1. According to GP 1, starting from **30** (76.4 mg, 0.420 mmol), *rac*-**8** (74.6 mg, 0.400 mmol), and $B(C_6F_5)_3$ (**1**) (20.6 mg, 0.0402 mmol) compound *rac*-**33** (129 mg, 88%) was obtained as a colorless, viscous oil. R_f = 0.52 (cyclohexane/*tert*-butyl methyl ether = 24:1); GLC (SE-54): t_R = 24.3 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.64 (dddd, *J* = 15.0, *J* = 8.0, *J* = 4.3, *J* = 0.8 Hz, 1 H), 0.79 (ddd, *J* = 15.1, *J* = 10.4, *J* = 4.7 Hz, 1 H), 1.00 (d, *J* = 6.6 Hz, 3 H), 1.08–1.21 (m, 4 H), 1.52–1.70 (m, 1 H), 1.73–1.93 (m, 1 H), 2.58 (ddd, *J* = 15.9, *J* = 9.2, *J* = 3.4 Hz, 1 H), 2.67 (ddd, *J* = 16.1, *J* = 6.9, *J* = 3.4 Hz, 1 H), 5.66 (s, 1 H), 7.07–7.14 (m, 2 H), 7.16–7.34 (m, 11 H), 7.40–7.46 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.1, 14.3, 17.1, 17.2, 22.9, 35.5, 76.8, 125.3, 126.4, 126.8, 126.9, 127.2, 128.2, 128.3, 128.6, 129.6, 131.2, 134.9, 145.0 (2×), 150.4 ppm. IR (ATR): $\tilde{\nu}$ = 3060 (w), 2923 (m), 2863 (m), 1590 (w) 1454 (m), 1059 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{28}OSiNa$ [[M + Na]$^+$]: 395.1802; found 395.1794. $C_{25}H_{28}OSi$ (372.57): calcd. C 80.59, H 7.57; found C 80.37, H 7.75.

(Benzhydryloxy)methyldiphenylsilane (34): See Table 3, entry 2. According to GP 1, starting from **30** (76.5 mg, 0.420 mmol), Ph_2MeSiH (**27**) (72.8 mg, 0.404 mmol), and $B(C_6F_5)_3$ (**1**) (7.9 mg, 0.015 mmol) compound **34** (123 mg, 80%) was obtained as a white solid. M.p. 72–73 °C (cyclohexane/*tert*-butyl methyl ether). R_f = 0.56 (cyclohexane/*tert*-butyl methyl ether = 24:1). GLC (SE-54): t_R = 25.2 min. ^{1}H NMR (300 MHz, C_6D_6): δ = 0.52 (s, 3 H), 5.96 (s, 1 H), 7.03–7.11 (m, 2 H), 7.12–7.20 (m, 3 H), 7.20–7.28 (m, 7 H), 7.38–7.46 (m, 4 H), 7.65–7.76 (m, 4 H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = –2.1, 77.7, 126.9, 127.4, 128.2, 128.6, 130.1, 134.9, 136.6, 145.1 ppm. IR (ATR): $\tilde{\nu}$ = 3069 (w), 1491 (m), 1054 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{26}H_{24}OSiNa$ [[M + Na]$^+$]: 403.1487; found 403.1489. $C_{26}H_{24}OSi$ (380.55): calcd. C 82.06, H 6.36; found C 81.89, H 6.18.

Modified Two-Step Procedure for the Preparation of *rac*-40[33]

***rac*-Isopropylmethoxymethylphenylsilane:** To a solution of dimethoxymethylsilane (3.65 g, 20.0 mmol, 1.00 equiv.) in THF (150 mL) was added *i*PrMgCl (17.4 mL of a 2.30 M solution in Et_2O, 40.0 mmol, 2.00 equiv.) at ambient temperature. The resulting solution was heated at reflux for 18 h, forming a white precipitate. After cooling to 0 °C, H_2O (50 mL) was added carefully. The organic layer was separated and the aqueous layer was extracted with Et_2O (4 × 75 mL). The combined organic layers were washed with brine (50 mL) and dried with Na_2SO_4. Evaporation of the solvent under reduced pressure gave the title compound (3.78 g, 97%) as sligthy yellow liquid, which was used without further purification. GLC (SE-54): t_R = 9.8 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.36 (s, 3 H), 0.96 (d, *J* = 7.0 Hz, 3 H), 1.03 (d, *J* = 6.9 Hz, 3 H), 1.10–1.22 (m, 1 H), 3.48 (s, 3 H), 7.34–7.43 (m, 3 H), 7.51–7.61 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –6.9, 13.8, 16.9, 17.0, 51.2, 127.9, 129.7, 134.2, 135.9 ppm. ^{29}Si NMR (60 MHz, $CDCl_3$): δ = 9.97 ppm. IR (ATR): $\tilde{\nu}$ = 3022 (w), 2956 (m), 2865 (m), 1464 (m) 1087 (s) cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{19}OSiNa$ [[M + Na]$^+$]: 217.1019; found 217.1006.

***rac*-Isopropylmethylphenylsilane (*rac*-40):** To a solution of *rac*-isopropylmethoxymethylphenylsilane (1.95 g, 10.0 mmol, 1.00 equiv.) in *n*-hexane (50 mL) was added DIBAL-H (15.0 mL of a 1.00M solution in *n*-hexane, 15.0 mmol, 1.50 equiv.) within 20 min at 0 °C. After stirring for an additional 12 h at ambient temperature, the reaction was neutralized by addition of 2N HCl (pH = 7) and H_2O (50 mL) at 0 °C. The phases were separated and the aqueous layer was extracted with Et_2O (4 × 50 mL). The combined organic layers were washed with brine (10 mL) and dried with Na_2SO_4. After evaporation of the solvent under reduced pressure, the crude reaction mixture was purified by flash chromatography on silica gel (4 × 22 cm, cyclohexane, 40 mL, #3–6) to yield *rac*-**40** (865 mg, 54%) as a colorless liquid. R_f = 0.71 (pentane). GLC (SE-54): t_R = 7.9 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.36 (d, *J* = 3.8 Hz, 3 H), 1.00–1.16 (m, 7 H), 4.24 (qd, *J* = 3.8, *J* = 2.3 Hz, 1 H), 7.34–7.45 (m, 3 H), 7.53–7.60 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –7.7, 12.6, 18.0, 18.3, 127.9, 129.3, 134.8, 136.0 ppm. ^{29}Si NMR (60 MHz, $CDCl_3$): δ = –6.38 ppm. IR (ATR): $\tilde{\nu}$ = 3020 (w), 2941 (w), 2864 (m), 2110 (s) cm^{-1}. HRMS (GC-MS/EI): calcd. for $C_{10}H_{16}Si$ [M$^+$]: 164.1021; found 164.1055. $C_{10}H_{16}Si$ (164.32): calcd. C 73.09, H 9.81; found C 72.85, H 10.14.

***rac*-*N*-Benzyl-1-(1-phenylethyl)amine (*rac*-38):** A solution of silane (^{Si}R)-**8** (114 mg, 0.600 mmol, 1.20 equiv., >99% *ee*) in toluene (1 mL) was added to a solution of $B(C_6F_5)_3$ (**1**) (256 mg, 0.500 mmol, 1.00 equiv.) in toluene (4 mL). The clear solution was heated to 75 °C and a solution of imine (*E*/*Z*)-**37** (105 mg, 0.500 mmol, 1.00 equiv.) in toluene (1 mL) was added dropwise within 5 min. The yellowish solution was maintained at 80 °C for 65 h. After cooling to ambient temperature, the solution was directly purified by flash chromatography on silica gel (4 × 7 cm, 10 mL, cyclohexane/ethyl acetate = 9:1→3:1, #17–31) to yield amine *rac*-**38** (56 mg, 53%, 0% *ee*) as a slightly yellow oil. R_f = 0.12 (cyclohexane/EtOAc = 4:1). GLC (SE-54): t_R = 15.9 min. HPLC (Daicel Chiralcel OD-H, column temperature = 20 °C, *n*-heptane:*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 230 nm): t_R = 7.0 [(*R*)-**38**], 7.6 min [(*S*)-**38**].[35] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38 (d, *J* = 6.7 Hz, 3 H), 1.76 (br. s, 1 H, N*H*), 3.61 (d, *J* = 13.2 Hz,

1 H), 3.67 (d, J = 13.2 Hz, 1 H), 3.83 (q, J = 6.8 Hz, 1 H), 7.20–7.47 (m, 10 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.6, 51.8, 57.6, 126.8, 127.0, 127.4, 128.3, 128.5, 128.6, 140.7, 145.7 ppm. HRMS (ESI): calcd. for $C_{15}H_{17}NNa$ [[M + Na]$^+$]: 234.1253; found 234.1235. The analytical data agreed with those reported previously.[35]

***rac*-*N*-Phenyl-1-(1-phenylethyl)amine (*rac*-43):** A solution of silane (^{Si}*R*)-**8** (114 mg, 0.600 mmol, 1.20 equiv., >99% *ee*) in toluene (1 mL) was added to a solution of B(C_6F_5)$_3$ (**1**) (256 mg, 0.500 mmol, 1.00 equiv.) in toluene (4 mL). A solution of imine **42** (105 mg, 0.500 mmol, 1.00 equiv.) in toluene (1 mL) was then added dropwise in 5 min. The yellowish solution was maintained at ambient temperature for 24 h and directly purified by flash column chromatography (silica, 4×7 cm, 10 mL, cyclohexane/ethyl acetate = 19:1, #23–27). Further purification by flash chromatography (silica 2.5×22 cm, 10 mL, cyclohexane/ethyl acetate = 95:5, #8–9) yielded amine *rac*-**43** (45 mg, 46%, 0% *ee*) as a slightly yellow oil. R_f = 0.62 (cyclohexane/EtOAc = 3:1). GLC (SE-54): t_R = 15.7 min. HPLC (Daicel Chiralcel OD-H, column temperature = 20 °C, *n*-heptane:*i*PrOH = 90:10, flow rate = 0.8 mL/min, λ = 230 nm): t_R = 7.9 [(*S*)-**43**], 9.7 min [(*R*)-**43**].[35] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.53 (d, J = 6.8 Hz, 3 H), 4.20 (br. s, 1 H) 4.50 (q, J = 6.7 Hz, 1 H), 6.48–6.56 (m, 2 H), 6.66 (tt, J = 7.3, J = 1.0 Hz, 1 H), 7.03–7.17 (m, 2 H), 7.20–7.28 (m, 1 H), 7.29–7.42 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.1, 53.7, 57.6, 113.6, 117.5, 126.0, 127.0, 128.8, 129.3, 145.2, 147.2 ppm. HRMS (ESI): calcd. for $C_{14}H_{15}NH$ [[M + H]$^+$]: 198.1277; found 198.1292. The analytical data agreed with those reported previously.[35]

Supporting Information (see also the footnote on the first page of this article): NMR spectroscopic data as well as (if available) HPLC and GLC traces of new compounds.

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