Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie
www.zaac.wiley-vch.de
RESEARCH ARTICLE
DOI: 10.1002/zaac.202300067

Stereochemically Pure *Si*-Chiral Aminochlorosilanes

Manuel Kümper,[a] Tobias Götz,[a] Noel Angel Espinosa-Jalapa,[a] Alexander Falk,[a] Robin Rothfelder,[a] and Jonathan O. Bauer*[a]

Silicon-based compounds with stereochemical information and convertible functional units are valuable building blocks in synthetic chemistry. *Si*-stereogenic aminochlorosilanes are built up by Si–N bond formation between an achiral dichlorosilane and a chiral enantiomerically pure primary amine. Both diastereomers could be isolated as stereochemically pure single-crystals by fractional crystallization and were analyzed by X-ray crystallography. Defined intermolecular interaction patterns were identified illustrating the role of N–H···π, C–H···π, and N–H···Cl contacts in the molecular crystalline packing arrangements. Stepwise functionalization of the silicon–chlorine and silicon–amine functions was carried out, demonstrating their potential for use as a chiral synthesis precursors. Via optically pure aminomethoxysilanes, enantiomerically enriched methoxysilanols, chloromethoxysilanes, and methoxysilanethiols were synthesized. The stereospecificity of the transformations was monitored. The (*R*)-BINOL-PSSLi method for determining the enantiomeric purity was found to be the tool of choice for acid-sensitive silanols and silanethiols.

Introduction

Silicon–chlorine and silicon–nitrogen functionalities play an important preparative role in a variety of chemical transformations[1] and applications,[2–4] such as protective group chemistry,[2] surface functionalization,[3] and functional polymers.[4] Silicon compounds that have a combination of methoxy and amino functions are also valuable synthetic building blocks.[5] The design of synthetic precursors and the investigation of their reactivity is therefore of great importance.[6] Given this synthetic versatility of chloro- and aminosilanes, stereochemically pure silicon-chiral compounds with different functional substitution patterns amenable to further transformations are desirable building blocks.[7] However, access routes to *Si*-stereogenic silanes with mixed halogen and nitrogen functions are often limited due to their increased Lewis acidity and the reactivity of Si–Hal and Si–N bonds towards nucleophiles.[7,8]

The coupling of (*S*)-(−)-1-phenylethylamine with a methoxysilane has been previously described.[5b] We recently reported the use of this chiral primary amine as an efficient chiral auxiliary in the preparation of enantiomerically pure aminophosphine sulfides featuring phosphorus-centered chirality.[9]

In the present work, we describe a facile route to diastereomerically pure silicon-stereogenic aminochlorosilanes. Si–NH bond formation between *tert*-butyldichlorophenylsilane and (*S*)-(−)-1-phenylethylamine followed by fractional crystallizations allowed complete separation of the two diastereomers of the aminochlorosilane. Because of their easy to substitute Si–Cl and Si–N bonds and the presence of a Brønsted acidic NH functionality, these compounds are promising bifunctional precursors for further functionalization reactions. In order to demonstrate their synthetic potential, stepwise transformation of their Si–Cl and Si–N bonds was carried out, ultimately leading to enantiomerically enriched silanols, chlorosilanes, and silanethiols.

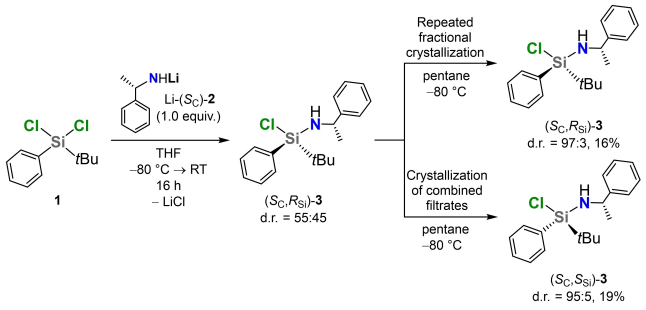
Results and Discussion

For our aim of providing silicon-based building blocks with silicon-centered chirality and both Si–Cl and Si–N bonds, we relied on a chiral auxiliary-based method originally developed by Kolodiazhnyi and co-workers for the desymmetrization of chlorophosphines.[10] Reaction of *tert*-butyldichlorophenylsilane (**1**) and freshly lithiated (*S*)-(−)-1-phenylethylamine [Li-(S_C)-**2**] led to the formation of the two *Si*-chiral diastereomers (S_C,S_{Si})-**3** and (S_C,R_{Si})-**3** (Scheme 1). The reaction resulted in a slight preference for the diastereomer (S_C,R_{Si})-**3** over (S_C,S_{Si})-**3** with a diastereomeric ratio of approximately 55:45 as determined by ^{1}H NMR spectroscopy.[11] Recrystallization from pentane at −80 °C gave a colorless solid enriched in the diastereomer (S_C,R_{Si})-**3**. After repeating the same recrystallization procedure three times on each isolated solid material, aminochlorosilane (S_C,R_{Si})-**3** could finally be obtained as a diastereomerically highly enriched crystalline solid (d.r. = 97:3) in 16% yield (Scheme 1), which was

[a] *M. Kümper, Dr. T. Götz, Dr. N. A. Espinosa-Jalapa, A. Falk, R. Rothfelder, Dr. J. O. Bauer*
Institut für Anorganische Chemie
Fakultät für Chemie und Pharmazie
Universität Regensburg
Universitätsstraße 31
D-93053 Regensburg, Germany
E-mail: jonathan.bauer@ur.de

Supporting information for this article is available on the WWW under https://doi.org/10.1002/zaac.202300067

Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie



Scheme 1. Synthesis of diastereomerically highly enriched *Si*-stereogenic aminochlorosilanes (S_C,R_{Si})-**3** and (S_C,S_{Si})-**3**. Diastereomeric ratios were determined according to ^{1}H NMR spectroscopy.

subjected to single-crystal X-ray sructural analysis (Figure 1 and Table 1).

Given the need for repeated recrystallizations to achieve stereochemically pure (S_C,R_{Si})-**3**, the high tendency of the other diastereomer (S_C,S_{Si})-**3** to precipitate was already apparent. This, however, offered the opportunity to also isolate the second diastereomer (S_C,S_{Si})-**3**, which was formed in sufficient quantity in the initial coupling reaction, by subjecting the combined (S_C,S_{Si})-**3**-enriched filtrates to the same conditions (solution of pentane, storage at −80 °C overnight). In fact, diastereomer (S_C,S_{Si})-**3** could also be obtained diastereomerically highly enriched (d.r. = 95:5) in 19% yield in form of single-crystals suitable for single-crystal X-ray diffraction analysis (Figure 1 and Table 1).

The absolute configurations at the stereogenic silicon center of (S_C,S_{Si})-**3** and (S_C,R_{Si})-**3**, respectively, were unequivocally assigned by single-crystal X-ray structural analysis (Figure 1 and Table 1). Both diastereomers crystallized in the orthorhombic crystal system, space group $P2_12_12_1$. As expected, the differences in the intramolecular bonding parameters of the two diastereomers are negligible. The arrangements around the nitrogen atom have a trigonal-planar geometry with an C11–N1–Si1 angle of 123.4(1)° or an C12–N1–Si1 angle of 123.8(1)°. The Si–Cl bond appears to be influenced by the presence of the Si–N bond. Compared to Cl–Si–O units,[6a,12] the Cl–Si–N unit in (S_C,S_{Si})-**3** and (S_C,R_{Si})-**3** shows a significantly elongated Si–Cl bond length of 2.0993(8) Å and 2.0927(7) Å, respectively (Figure 1).

However, there are interesting variations in the packing arrangement, which can be attributed to the different relative stereochemistry. The crystal structures of both diastereomers (S_C,S_{Si})-**3** and (S_C,R_{Si})-**3** clearly show anisotropic contributions in their weak intermolecular interaction patterns (Figure 2).[13] Intermolecular N–H···π interactions likely play an important role in the arrangement of the molecules in the crystal packing of (S_C,S_{Si})-**3**, with the shortest H···C contact (3.011 Å) found between the NH function and C17 of the phenyl ring of a chiral amine fragment (Figure 2, top). Considerably close edge-shifted C–H···π contacts[6b,14] were also found in the crystal structure of (S_C,S_{Si})-**3** between H18 and the acceptor atoms C14, C15, and C16, all belonging to a phenylethylamino moiety with distances of 2.812 Å (H18···C15), 2.903 Å (H18···C16), and 3.031 Å (H18···C14) (Figure 2, top). C–H···Cl interactions have been extensively discussed in the literature.[12,13,15] A comparatively short intermolecular C–H···Cl–Si contact (2.861 Å) was also found between H7 of a silicon-bound phenyl ring and the chlorine substituent in (S_C,S_{Si})-**3**.

In contrast to diastereomer (S_C,S_{Si})-**3**, the crystal structure of diastereomer (S_C,R_{Si})-**3** shows N–H···Cl hydrogen bonds with an H1···Cl1 distance of 2.921 Å and an N1–H1···Cl1 angle of 146.13° (Figure 2, bottom). Another striking difference in the intermolecular interaction pattern is the T-shaped π-stacking arrangement[16] between the silicon-bound phenyl ring of one molecule and the phenylethylamino group of another (Figure 2, bottom), which can also be considered as "aromatic donor–acceptor interactions".[17] Due to the high tendency of both diastereomers to crystallize, it can be assumed that the strength of the intermolecular interaction parameters is quite similar for both diastereomers.

The next step was to investigate whether the chlorine and amine functions can be successively substituted and whether these reactions occur stereospecifically. For this purpose, we

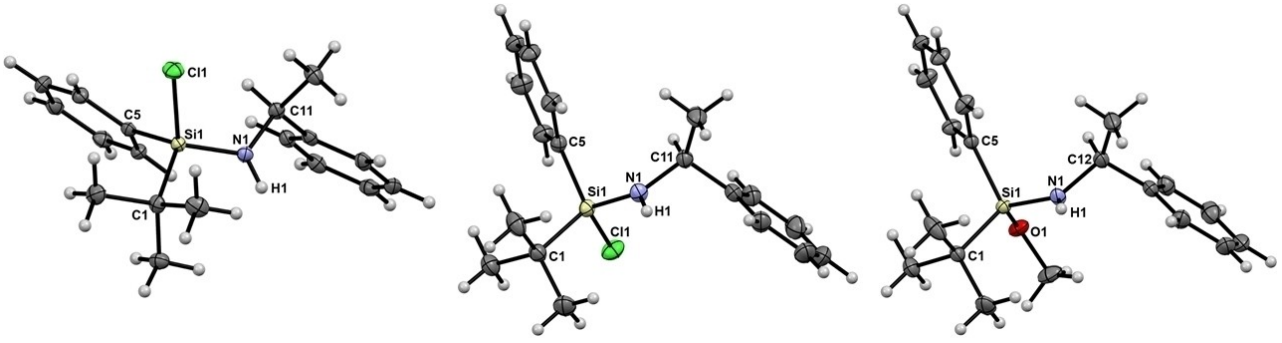


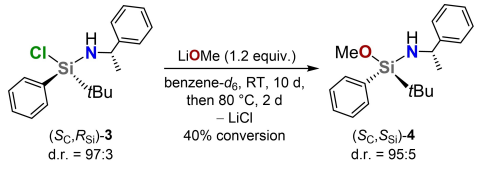
Figure 1. Molecular structures of compounds (S_C,S_{Si})-**3**, (S_C,R_{Si})-**3**, and (S_C,R_{Si})-**4** in the crystal (displacement ellipsoids set at the 50% probability level). Selected bond lengths/Å and angles/° of compound (S_C,S_{Si})-**3** (at 123 K): Si1–N1 1.704(2), Si1–Cl1 2.0993(8), N1–C11 1.477(3), Cl1–Si1–N1 111.88(8), C11–N1–Si1 123.6(1). Selected bond lengths/Å and angles/° of compound (S_C,R_{Si})-**3** (at 123 K): Si1–N1 1.692(1), Si1–Cl1 2.0927(7), N1–C11 1.476(2), Cl1–Si1–N1 111.82(7), C11–N1–Si1 123.4(1). Selected bond lengths/Å and angles/° of compound (S_C,R_{Si})-**4** (at 123 K): Si1–N1 1.699(1), Si1–O1 1.650(1), N1–C12 1.473(3), O1–Si1–N1 112.55(9), C12–N1–Si1 123.8(1).

Table 1. Crystal data and structure refinement of compounds (S_C,S_{Si})-**3**, (S_C,R_{Si})-**3**, and (S_C,R_{Si})-**4**.

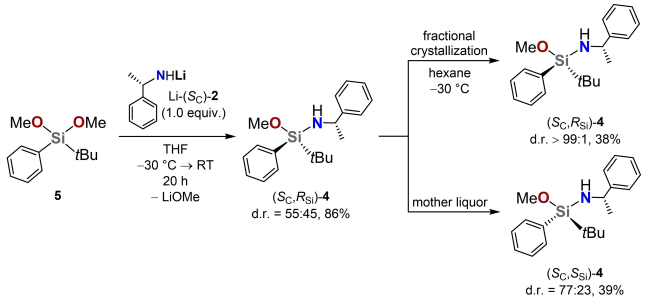
Compound	(S_C,S_{Si})-**3**	(S_C,R_{Si})-**3**	(S_C,R_{Si})-**4**
Formula	$C_{18}H_{24}ClNSi$	$C_{18}H_{24}ClNSi$	$C_{19}H_{27}NOSi$
M/g·mol^{-1}	317.92	317.92	313.50
T/K	123(1)	123.00(10)	122.98(10)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	7.38930(10)	6.32740(10)	6.23328(6)
b/Å	10.31930(10)	13.00500(10)	13.18420(12)
c/Å	22.4563(3)	21.6663(2)	22.0632(2)
V/Å^3	1712.35(4)	1782.87(4)	1813.17(3)
Z	4	4	4
Z'	1	1	1
Flack parameter	−0.002(9)	−0.001(4)	0.005(17)
ρ/g·cm^{-3}	1.233	1.184	1.148
μ/mm^{-1}	2.574	2.472	1.141
Crystal size/mm^3	0.24×0.17×0.08	0.17×0.09×0.05	0.53×0.2×0.18
λ/Å	1.54184	1.54184	1.54184
Radiation type	Cu K_α	Cu K_α	Cu K_α
θ range/°	3.937–66.967	3.964–73.174	3.906–66.891
Reflections, collected	13685	17299	15269
Reflections, independent	3048	3467	3222
Reflections with I > 2(I)	3006	3371	3209
R_{int}	0.0430	0.0250	0.0365
Parameters	194	198	212
Restraints	0	0	0
GooF	1.051	1.064	1.072
wR_2 (all data)	0.0757	0.0719	0.0738
wR_2	0.0755	0.0715	0.0738
R_1 (all data)	0.0288	0.0274	0.0286
R_1	0.0286	0.0265	0.0285
$\Delta\rho_{fin}$ (max/min)/e·Å^{-3}	0.267/−0.317	0.35/−0.20	0.16/−0.22

reacted the diastereomerically highly enriched aminochlorosilane (S_C,R_{Si})-**3** (d.r. = 97:3) with lithium methoxide in benzene at room temperature and monitored the course of the reaction by ^{1}H NMR spectroscopy. We observed the selective formation of a new species, albeit with a low conversion of 30% after 10 days (Scheme 2). Subsequent heating of the same sample at 80 °C for two days resulted in only a slight increase in conversion to 40%, but without any change in the product composition (Scheme 2).

To prove that the reactions proceeded chemoselectively with substitution of the Si–Cl function for a methoxy group and that the newly formed species can be assigned to the two corresponding diastereomers, we synthesized the two diastereomers of the aminomethoxysilane [(S_C,R_{Si})-**4** and (S_C,S_{Si})-**4**] via an alternative route (Scheme 3), which is similar to that



Scheme 2. Investigation of the chemoselectivity and stereospecificity of the reaction of *Si*-stereogenic aminochlorosilane (S_C,R_{Si})-**3** with lithium methoxide.



Scheme 3. Synthesis of diastereomerically pure and enriched *Si*-stereogenic aminomethoxysilanes (S_C,R_{Si})-**4** and (S_C,S_{Si})-**4**. Diastereomeric ratios were determined according to ^{1}H NMR spectroscopy.

described in Scheme 1 concerning the aminochlorosilanes. Reaction of *tert*-butyldimethoxyphenylsilane (**5**) with lithium (*S*)-(−)-1-phenylethylamide [Li-(S_C)-**2**] initially gave (S_C,R_{Si})-**4** and (S_C,S_{Si})-**4** in a diastereomeric ratio of 55:45 (Scheme 3), which was determined by ^{1}H NMR spectroscopy. Diastereomer (S_C,R_{Si})-**4** could be obtained in optically pure single-crystalline form in 38% yield after a single recrystallization from hexane at −30 °C. Accordingly, the mother liquor was enriched in diastereomer (S_C,S_{Si})-**4** (d.r. = 77:23). Compound (S_C,R_{Si})-**4** crystallized in the orthorhombic crystal system, space group $P2_12_12_1$ (Figure 1 and Table 1). The assigned absolute configuration at the stereogenic

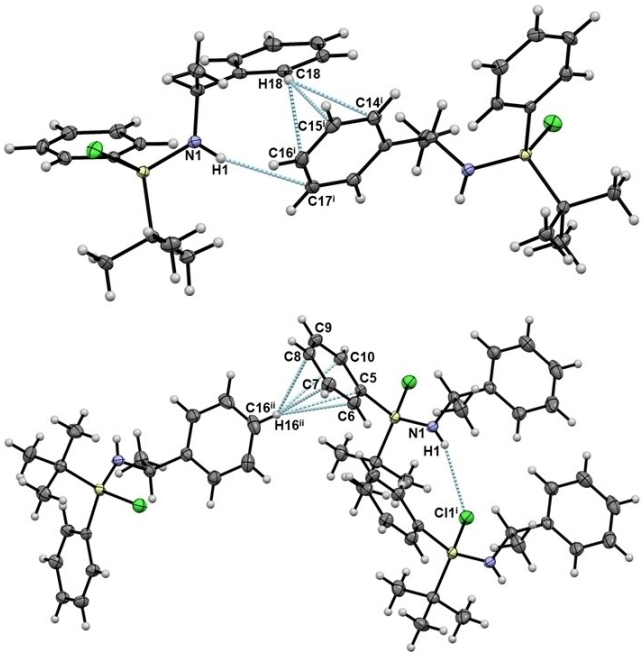


Figure 2. Part of the crystal structure of compounds (S_C,S_{Si})-**3** (top) and (S_C,R_{Si})-**3** (bottom) illustrating short intermolecular distances in characteristic supramolecular synthon units (displacement ellipsoids set at the 50% probability level). Selected intermolecular distances/Å and angles/° of (S_C,S_{Si})-**3** (at 123 K): H1···C17^{i} 3.011, H18···C14^{i} 3.031, H18···C15^{i} 2.812, H18···C16^{i} 2.903, N1–H1···C17^{i} 155.26, C18–H18···C14^{i} 130.89, C18–H18··· C15^{i} 155.91, C18–H18···C16^{i} 143.34. Symmetry transformations used to generate equivalent atoms: (i) −0.5+x, 0.5−y, 1−z. Selected intermolecular distances/Å and angles/° of (S_C,R_{Si})-**3** (at 123 K): H1···Cl1^{i} 2.921, H16^{ii}···C5 3.115, H16^{ii}···C6 3.122, H16^{ii}···C7 3.093, H16^{ii}···C8 3.042, H16^{ii}···C9 3.009, H16^{ii}···C10 3.046, N1–H1···Cl1^{i} 146.13, C16^{ii}–H16^{ii}···C5 159.53, C16^{ii}–H16^{ii}···C6 164.71, C16^{ii}–H16^{ii}···C7 153.87, C16^{ii}–H16^{ii}···C8 143.64, C16^{ii}–H16^{ii}···C9 141.45, C16^{ii}–H16^{ii}···C10 148.15. Symmetry transformations used to generate equivalent atoms: (i) −1+x, y, z; (ii) 1.5−x, 1−y, −0.5+z.

silicon center was *R*. By comparison with the NMR spectroscopic data of the diastereomers (S_C,R_{Si})-**4** and (S_C,S_{Si})-**4**, we could thus unambiguously show that the (S_C,R_{Si})-configured aminochlorosilane **3** (d.r. = 97:3) reacted chemoselectively and stereospecifically (with negligible loss of stereochemical integrity) with lithium methoxide with inversion of configuration at the stereogenic silicon center to the aminomethoxysilane (S_C,S_{Si})-**4** (d.r. = 95:5) (see Scheme 2). In this context, it is also worth mentioning that the unreacted starting material [(S_C,R_{Si})-**3**] showed no appreciable change in its diastereomeric purity. Furthermore, we have confirmed that a mixture of (S_C,S_{Si})-**3** and (S_C,R_{Si})-**3** (d.r. = 58:42) in the presence of lithium chloride in tetrahydrofuran showed no change in the diastereomeric ratio at room temperature. Also, in agreement with thermodynamic considerations from previous work, there was no evidence for a competing NH deprotonation by lithium methoxide.[5b] One reason for the low conversion could be aggregation effects, which can have a major impact on reactions involving metalated species.[5] The influence of mixed aggregates of lithium methoxide and lithium chloride, the latter being released during the substitution reaction, could also play a role.

It is significant that the crystal structure of the aminomethoxysilane (S_C,R_{Si})-**4** shows the same interaction patterns as found in the stereochemically related chlorine compound (S_C,R_{Si})-**3** (Figure 3). The NH group participates in a hydrogen bond, here with a methoxy oxygen atom as the acceptor (H1···O1 2.970 Å, N1–H1···O1 163.64°). Also clearly visible is the T-shaped π-stacking arrangement, which consists of the same aromatic molecular fragments as identified in compound (S_C,R_{Si})-**3**, albeit with slightly longer H···C contacts with distances between 3.192 Å (H17···C9) and 3.421 Å (H17···C6) compared to the H···C distances between 3.009 Å (H16···C9) and 3.122 Å (H16···C6) in (S_C,R_{Si})-**3**.

Having shown that the substitution of the chlorine atom from (S_C,R_{Si})-**3** was chemoselective and stereospecific, we next investigated the cleavage of the silicon-bound amine function starting from aminomethoxysilane (S_C,R_{Si})-**4**, which was available in stereochemically pure form and in sufficient quantities (Scheme 4). Mild acidic hydrolysis in a water/tetrahydrofuran mixture in the presence of ammonium chloride at room temperature over a period of 7 days was shown to proceed only with little loss of the stereochemical integrity at the silicon center. The methoxysilanol (S_{Si})-**6** was isolated in 78% yield and with a high enantiomeric ratio of e.r. = 95:5. Since the stereochemical course of the chemical transformation of Si–N to Si–O bonds by nucleophilic attack of hydroxy functions at a stereogenic silicon center has been extensively studied previously,[18] we therefore assumed with a high degree of certainty that the reaction occurred with inversion of configuration.

We also succeeded in converting the diastereomerically pure aminomethoxysilane (S_C,R_{Si})-**4** directly into the enantiomerically enriched chloromethoxysilane **7** (e.r. ≥ 80:20) with hydrogen chloride (Scheme 4). Starting from this intermediate

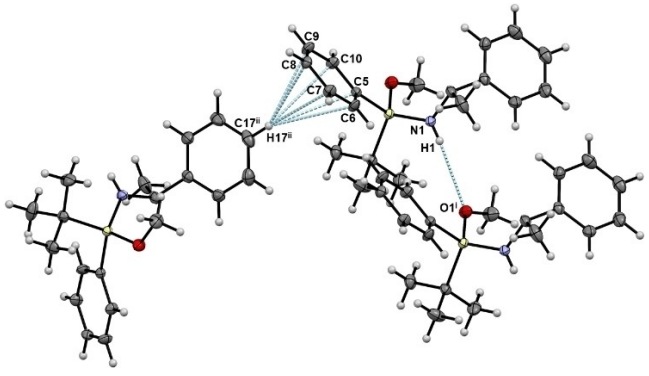
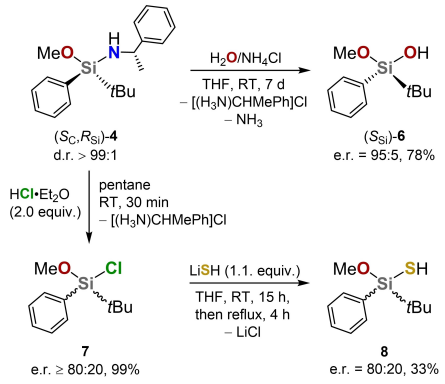


Figure 3. Part of the crystal structure of compound (S_C,R_{Si})-**4** illustrating short intermolecular distances in a characteristic supramolecular synthon unit (displacement ellipsoids set at the 50% probability level). Selected intermolecular distances/Å and angles/° (at 123 K): H1···O1^{i} 2.970, H17^{ii}···C5 3.388, H17^{ii}···C6 3.421, H17^{ii}···C7 3.363, H17^{ii}···C8 3.250, H17^{ii}···C9 3.192, H17^{ii}···C10 3.256, N1–H1···O1^{i} 163.64, C17^{ii}–H17^{ii}···C5 153.75, C17^{ii}–H17^{ii}···C6 162.74, C17^{ii}–H17^{ii}···C7 162.36, C17^{ii}–H17^{ii}···C8 153.78, C17^{ii}–H17^{ii}···C9 147.56, C17^{ii}–H17^{ii}···C10 147.72. Symmetry transformations used to generate equivalent atoms: (i) −1+x, y, z; (ii) 0.5−x, 1−y, −0.5+z.



Scheme 4. Conversions of diastereomerically pure aminomethoxysilane (S_C,R_{Si})-**4** to enantiomerically enriched methoxysilanol (S_{Si})-**6**, chloromethoxysilane **7**, and methoxysilanethiol **8**.

(**7**) we were then able to replace the chlorine substituent by a thiol group in a subsequent reaction with lithium hydrogen sulfide to open up access to enantiomerically enriched methoxysilanethiols (**8**, e.r. = 80:20, Scheme 4). Only little information is available about the stereochemical course at asymmerically substituted silicon centers in conversions from Si–N to Si–Cl[19] and form Si–Cl to Si–SH functions.[20] The information given in the literature does not allow any clear statement on inversion or retention processes in the reaction sequence from (S_C,R_{Si})-**4** via **7** to **8**.

The enantiomeric ratios of compounds (S_{Si})-**6** and **8** were determined by our recently reported NMR spectroscopic method using lithiated (*R*)-BINOL-dithiophosphoric acid [(*R*)-BINOL-PSSLi] as chiral shift reagent (for details, see the Supporting Information).[9] By applying this method to silanols and silanethiols, we were able to demonstrate that this practical tool can be used to determine the enantiomeric purity of chiral compounds that are sensitive towards Brønsted acids.

Conclusions

In conclusion, a facile route to bifunctional, stereochemically pure building blocks was opened by desymmetrizing coupling of a dichlorosilane with a chiral lithiated primary amine. Access to both diastereomers of the *Si*-stereogenic aminochlorosilane was achieved by repeated fractional crystallization. This class of compounds not only contains substitutable Si–Cl and Si–N bonds, but also a Brønsted acidic NH functionality capable of hydrogen-bonding or deprotonation and further functionalization. The potential of the new *Si*-stereogenic aminochlorosilanes was highlighted by the successive transformation of the Si–Cl and Si–N bonds through reactions with lithium methoxide, water, and lithium hydrogen sulfide to finally afford enantiomerically enriched methoxysilanols and methoxysilanethiols. Diastereomerically pure *Si*-stereogenic aminomethoxysilanes were also prepared using an independent synthetic route. The aminochlorosilanes (S_C,R_{Si})-**3** and (S_C,S_{Si})-**3** and the aminomethoxysilane (S_C,R_{Si})-**4** were investigated by single-crystal X-ray diffraction analysis and their anisotropic intermolecular interaction patterns in the molecular crystalline state analyzed and compared. For the stereochemically equivalent compounds (S_C,R_{Si})-**3** and (S_C,R_{Si})-**4**, the same supramolecular structural motifs, consisting of N–H···O/Cl hydrogen bonds and T-shaped π-stacking arrangements, were identified.

Experimental Section

General Remarks. All experiments were performed in an inert atmosphere of purified nitrogen by using standard Schlenk techniques or an MBraun Unilab 1200/780 glovebox. Glassware was heated at 140 °C prior to use. Pentane, diethyl ether, toluene, and tetrahydrofuran (THF) were dried and degassed with an MBraun SP800 solvent purification system. *n*-Butyllithium (2.5 M solution in hexane, Merck KGaA), *tert*-butyllithium (1.7 M solution in hexane, Merck KGaA), (*S*)-(−)-1-phenylethylamine [(S_C)-**2**] (98 %, Merck KGaA), (*S*)-(+)-3,3-dimethyl-2-butylamine (97 %, Sigma-Aldrich), hydrogen chloride (2.0 M solution in diethyl ether, Sigma-Aldrich) hydrogen sulfide (0.8 M solution in tetrahydrofuran, Sigma-Aldrich), methanol (dried over 3 Å molecular sieves), pyrrolidine (99 %, Sigma-Aldrich), trichlorophenylsilane (97 %, Alfa Aesar), and triethylamine (99 %, Merck KGaA) were used as received without further purification. (*R*)-BINOL-dithiophosphoric acid [(*R*)-BINOL-PSSH] (99 % ee) was synthesized according to a reported literature procedure.[9,21] *tert*-Butyldichlorophenylsilane (**1**)[22] and *tert*-butyldimethoxyphenylsilane (**5**)[23] were synthesized according to modified literature procedures. NMR Spectra were recorded in C_6D_6 ($\geq$ 99 %, Merck KGaA; dried over 3 Å molecular sieves and degassed by a standard freeze-pump-thaw procedure), $CDCl_3$ (99.8 %, Sigma-Aldrich; basified with Na_2CO_3 and dried over 3 Å molecular sieves) or CD_2Cl_2 ($\geq$ 99.8 %, Fluorochem; dried over 3 Å molecular sieves and degassed by a standard freeze-pump-thaw procedure). NMR spectra were either recorded on a Bruker Avance 300 (300.13 MHz), a Bruker Avance 400 (400.13 MHz) or on a Bruker Avance III HD 400 (400.13 MHz) at 25 °C. Chemical shifts (δ) are reported in parts per million (ppm). ^{1}H and ^{13}C{^{1}H} NMR spectra are referenced to tetramethylsilane ($SiMe_4$, δ = 0.0 ppm) as external standard, with the deuterium signal of the solvent serving as internal lock and the residual solvent signal as an additional reference. ^{29}Si{^{1}H} NMR spectra are referenced to $SiMe_4$ and ^{7}Li{^{1}H} NMR spectra to LiCl (1 M in D_2O). For the assignment of the multiplicities, the following abbreviations are used: b = broad signal, s = singlet, d = doublet, m = multiplet. High-resolution mass spectrometry was carried out on a Jeol AccuTOF GCX and an Agilent Q-TOF 6540 UHD spectrometer. Elemental analyses were performed on a Vario MICRO cube apparatus. Optical rotations were measured on an Anton Paar MCP 500 apparatus (concentration *c* in grams per 100 mL). The original NMR spectra can be found in the Supporting Information.

Single-Crystal X-Ray Diffraction Analysis. The crystals of compounds (S_C,S_{Si})-**3**, (S_C,R_{Si})-**3**, and (S_C,R_{Si})-**4** were selected and measured on a SuperNova Dualflex diffractometer equipped with a TitanS2 detector [(S_C,S_{Si})-**3** and (S_C,R_{Si})-**4**] or on a XtaLAB Synergy R, DW system equipped with a HyPix-Arc 150 detector [(S_C,R_{Si})-**3**]. The crystals were kept at T = 123(1) K during data collection. Data collection and reduction were performed with CrysAlisPro, Version 1.171.41.81a [(S_C,S_{Si})-**3**] or Version 1.171.43.36a [(S_C,R_{Si})-**3** and (S_C,R_{Si})-**4**].[24] For (S_C,S_{Si})-**3**, an empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK scaling algorithm was applied. For (S_C,R_{Si})-**3** and (S_C,R_{Si})-**4**, a numerical absorption correction based on Gaussian integration over a multifaceted crystal model, and an empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK scaling

algorithm was applied. Using Olex2,[25] the structures were solved with ShelXT[26] and a least-square refinement on F^2 was carried out with ShelXL.[27] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on the carbon atoms were located in idealized positions and refined isotropically according to the riding model. The hydrogen atoms on the nitrogen atoms were located from the difference Fourier map and refined without restraints. Figures 1, 2, and 3 were created using Mercury 4.1.0.[28]

Compound (S_C,S_{Si})-**3**: The asymmetric unit contains one molecule.

Compound (S_C,R_{Si})-**3**: The asymmetric unit contains one molecule.

Compound (S_C,R_{Si})-**4**: The asymmetric unit contains one molecule.

Syntheses. *tert-Butyldichlorophenylsilane (**1**).* *tert*-Butyllithium (73.0 mL of a 1.7 M solution in hexane, 124.0 mmol, 1.0 equiv.) was added dropwise to a solution of trichlorophenylsilane (20.0 mL, 124.0 mmol, 26.37 g, 1.0 equiv.) in pentane (120 mL) at −68 °C over a period of 30 min. The resulting white suspension was then allowed to slowly warm up to room temperature and kept stirring for 16 h. The mixture was then filtered through a fritted column layered with Celite® and the remaining solids washed with pentane (3×20 mL). The filtrates were collected and all volatiles removed in vacuo. The beige oily residue was purified by Kugelrohr distillation (100 °C oven temperature, $1.3\cdot10^{-2}$ mbar) to yield compound **1** as a colorless oil (24.61 g, 105.5 mmol, 88 %). ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 0.96 [s, 9H, C(C*H*$_3$)$_3$], 7.10 (m, 3H, H_{Ph}), 7.67 (m, 2H, H_{Ph}). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 298 K): δ 23.2 [s, *C*(CH$_3$)$_3$], 24.9 [s, C(*C*H$_3$)$_3$], 128.3 (s, C_{Ph}), 130.8 (s, C_{Ph}), 130.8 (s, C_{Ph}), 131.5 (s, C_{Ph}), 134.8 (s, C_{Ph}). ^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6, 298 K): δ 23.4 (s). HRMS (EI+): Calcd *m/z* for $C_{10}H_{14}Cl_2Si$ [M^+]: 232.0218. Found: 232.0242. CHN Analysis: Calcd for $C_{10}H_{14}Cl_2Si$: C, 51.50; H, 6.05. Found: C, 51.45; H, 5.85.

*Compounds (S_C,R_{Si})-**3** and (S_C,S_{Si})-**3**.* *n*-Butyllithium (4.40 mL of a 2.5 M solution in hexane, 11.0 mmol, 1.1 equiv.) was added dropwise to a solution of (*S*)-(−)-1-phenylethylamine [(S_C)-**2**] (1.28 mL, 1.21 g, 10.0 mmol, 1.0 equiv.) in tetrahydrofuran (30 mL) at room temperature and the mixture stirred for 10 min. The freshly prepared solution of lithium (*S*)-(−)-1-phenylethylamide [Li-(S_C)-**2**] was then added via cannula to a solution of *tert*-butyldichlorophenylsilane (**1**) (2.33 g, 10.0 mmol, 1.0 equiv.) in tetrahydrofuran (30 mL) at −80 °C. The mixture was stirred for 16 h while slowly warming up to room temperature. The formed solids were removed via cannula filtration and the filtrate was dried in vacuo. An aliquot of the crude sample was analyzed by ^{1}H NMR spectroscopy showing a diastereomeric ratio of d.r. = 55 : 45.

The crude mixture was dissolved in pentane (50 mL) and stored at −80 °C for one day resulting in the precipitation of a white solid. The solid was isolated by cannula filtration and the same recrystallization procedure repeated three times to yield the diastereomerically pure compound (S_C,R_{Si})-**3** as colorless crystals suitable for single-crystal X-ray diffraction analysis (503 mg, 1.6 mmol, 16 %, d.r. = 97 : 3). The filtrates were combined, dried in vacuo, again dissolved in pentane and stored at −80 °C for one day to obtain (S_C,S_{Si})-**3** as colorless crystals suitable for single-crystal X-ray diffraction analysis (601 mg, 1.9 mmol, 19 %, d.r. = 95 : 5).

*Compound (S_C,R_{Si})-**3**.* ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 0.96 [s, 9H, C(C*H*$_3$)$_3$], 1.24 (d, $^3J_{H-H}$ = 6.8 Hz, 3H, CHC*H*$_3$), 1.56 (d, $^3J_{H-H}$ = 10.7 Hz, 1H, N*H*), 4.13–4.22 (m, 1H, C*H*CH$_3$), 7.02–7.09 (m, 1H, H_{Ph}), 7.13–7.24 (m, 7H, H_{Ph}), 7.85–7.90 (m, 2H, H_{Ph}). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 298 K): δ 20.4 [s, *C*(CH$_3$)$_3$], 26.3 [s, C(*C*H$_3$)$_3$], 27.4 (s, CHCH$_3$), 51.6 (s, *C*HCH$_3$), 126.1 (s, C_{Ph}), 126.9 (s, C_{Ph}), 128.2 (s, C_{Ph}), 128.6 (s, C_{Ph}), 130.7 (s, C_{Ph}), 133.0 (s, C_{Ph}), 135.8 (s, C_{Ph}), 147.7 (s, C_{Ph}). ^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6, 298 K): δ 4.3 (s). $[\alpha]_D^{20} = -73.3°$ (*c* = 0.098, toluene).

*Compound (S_C,S_{Si})-**3**.* ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 0.99 [s, 9H, C(C*H*$_3$)$_3$], 1.31 (d, $^3J_{H-H}$ = 6.7 Hz, 3H, CHC*H*$_3$), 1.55 (d, $^3J_{H-H}$ = 11.5 Hz, 1H, N*H*), 4.03–4.16 (m, 1H, C*H*CH$_3$), 7.047.22 (m, 8H, H_{Ph}), 7.73–7.79 (m, 2H, H_{Ph}). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 298 K): δ 20.0 [s, *C*(CH$_3$)$_3$], 26.2 [s, C(*C*H$_3$)$_3$], 27.6 (s, CHCH$_3$), 51.5 (s, *C*HCH$_3$), 125.8 (s, C_{Ph}), 126.8 (s, C_{Ph}), 128.1 (s, C_{Ph}), 128.6 (s, C_{Ph}), 130.7 (s, C_{Ph}), 131.9 (s, C_{Ph}), 136.1 (s, C_{Ph}), 148.0 (s, C_{Ph}). ^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6, 298 K): δ 4.7 (s). HRMS (EI+): Calcd *m/z* for $C_{18}H_{25}ClNSi$ [$(M+H)^+$]: 317.13611. Found: 317.13421. CHN Analysis: Calcd for $C_{18}H_{24}ClNSi$: C, 68.00; H, 7.61; N, 4.41. Found: C, 67.98; H, 7.14; N, 4.23. $[\alpha]_D^{20} = -68.4°$ (*c* = 0.098, toluene).

*tert-Butyldimethoxyphenylsilane (**5**).* To a solution of *tert*-butyldichlorophenylsilane (14.00 g, 60 mmol) in hexane (150 mL) was added methanol (248 mmol, 10.0 mL) and triethylamine (144 mmol, 20.0 mL) at −50 °C. The resulting white suspension was then allowed to slowly warm up to room temperature and kept stirring for 4 h. The white suspension was then filtered through a fritted column layered with Celite® and the remaining solids washed with hexane (3×20 mL). The filtrates were collected and all volatiles removed in vacuo. The beige oily residue was purified by Kugelrohr distillation (70 °C oven temperature, $1.3\cdot10^{-2}$ mbar) to yield **5** as a colorless oil (11.84 g, 52.8 mmol, 88 %). ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 1.10 [s, 9H, C(C*H*$_3$)$_3$], 3.45 [s, 6H, Si(OC*H*$_3$)$_2$], 7.22 (m, 3H, H_{Ph}), 7.72 (m, 2H, H_{Ph}). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 298 K): δ 18.6 [s, *C*(CH$_3$)$_3$], 26.1 [s, C(*C*H$_3$)$_3$], 50.9 [s, Si(OCH$_3$)$_2$], 127.8 (s, C_{Ph}), 129.9 (s, C_{Ph}), 131.9 (s, C_{Ph}), 135.4 (s, C_{Ph}). ^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6, 298 K): δ −18.6 (s). HRMS (EI+): Calcd *m/z* for $C_{12}H_{20}O_2Si$ [M^+]: 224.12271. Found: 224.12305.

*Compounds (S_C,R_{Si})-**4** and (S_C,S_{Si})-**4**.* *n*-Butyllithium (18.4 mL of a 2.5 M solution in hexane, 45.96 mmol, 1.0 equiv.) was added dropwise to a solution of (*S*)-(−)-1-phenylethylamine [(S_C)-**2**] (5.9 mL, 5.57 g, 45.96 mmol, 1.0 equiv.) in tetrahydrofuran (60 mL) at −30 °C. The reaction mixture was then allowed to slowly warm up to room temperature and kept stirring for 1 h. The freshly prepared solution of lithium (*S*)-(−)-1-phenylethylamide [Li-(S_C)-**2**] was then added via cannula to a solution of **5** (10.31 g, 45.96 mmol, 1.0 equiv.) in tetrahydrofuran (40 mL) at −30 °C. The mixture was stirred for 15 h while slowly warming up to room temperature. Then all volatiles were removed in vacuo. The red oily residue was suspended in hexane (30 mL) and filtered through a fritted column layered with Celite®. The remaining solids were washed with hexane (3×20 mL). Then, the filtrates were collected and all volatiles removed in vacuo. An aliquot of the crude sample was analyzed by ^{1}H NMR spectroscopy showing a diastereomeric ratio of d.r. = 55 : 45. The crude oil was purified by Kugelrohr distillation (140 °C oven temperature, $1.3\cdot10^{-3}$ mbar) to yield (S_C,R_{Si})-**4**/(S_C,S_{Si})-**4** as a colorless oil (12.40 g, 39.5 mmol, 86 %, d.r. = 55 : 45).

The diastereomeric mixture (S_C,R_{Si})-**4**/(S_C,S_{Si})-**4** (12.40 g, 39.5 mmol, d.r. = 55 : 45) was dissolved in hexane (80 mL) at room temperature and the clear solution stored at −30 °C. Over a period of 3 d, colorless crystals were formed. The cold mother liquor was removed via suction filtration and the remaining crystalline material washed with cold (−30 °C) hexane (2×3 mL). Compound (S_C,R_{Si})-**4** was isolated as colorless crystals, suitable for single-crystal X-ray diffraction analysis, in diastereomerically pure form as confirmed by NMR spectroscopy (4.03 g, 12.86 mmol, d.r. > 99 : 1). The mother liquor and the hexane washings were collected, concentrated to 60 mL and stored at −80 °C to yield a white amorphous material over a period of one week. The cold mother liquor was removed via suction filtration and the amorphous material (d.r. = 82 : 18) dissolved in hexane (10 mL). The clear solution was then stored at −30 °C to yield again colorless crystals of compound (S_C,R_{Si})-**4** over a period of three days (1.44 g, 4.56 mmol, d.r. > 99 : 1, overall yield 38 %). The mother liquor and the hexane washings were again collected and all volatiles removed in vacuo to yield a pale beige

oily residue consisting of diastereomerically enriched compound (S_C,S_{Si})-**4** (5.62 g, 17.92 mmol, 39%, d.r. = 77:23).

*Compound (S_C,R_{Si})-**4**.* ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 1.02 [s, 9H, C(CH_3)$_3$], 1.29 (d, $^3J_{H-H}$ = 6.7 Hz, 3H, CHCH_3), 1.55 (d, $^3J_{H-H}$ = 11.4 Hz, 1H, N*H*), 3.27 (s, 3H, SiOCH_3), 4.14 (m, 1H, CHCH$_3$), 7.06 (m, 1H, H_{Ph}), 7.15 (m, 4H, H_{Ph}), 7.28 (m, 3H, H_{Ph}), 7.82 (m, 2H, H_{Ph}). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 298 K): δ 18.6 [s, C(CH$_3$)$_3$], 27.0 [s, C(CH_3)$_3$], 28.6 (s, CHCH_3), 50.8 (s, CHCH$_3$), 51.4 (s, SiOCH_3), 125.9 (s, C_{Ph}), 126.5 (s, C_{Ph}), 128.5 (s, C_{Ph}), 129.9 (s, C_{Ph}), 134.3 (s, C_{Ph}), 135.9 (s, C_{Ph}), 149.2 (s, C_{Ph}). ^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6, 298 K): δ −15.1 (s). HRMS (ESI +): Calcd *m/z* for $C_{19}H_{27}NOSi$ [M^+]: 314.1942. Found: 314.1935. CHN Analysis: Calcd for $C_{19}H_{27}NOSi$: C, 72.79; H, 8.68; N, 4.47. Found: C, 73.07; H, 8.35; N, 4.43. $[\alpha]_D^{20} = -48.9°$ (*c* = 0.106, toluene).

*Compound (S_C,S_{Si})-**4**.* ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 1.04 [s, 9H, C(CH_3)$_3$], 1.30 (d, $^3J_{H-H}$ = 6.7 Hz, 3H, CHCH_3), 1.49 (d, $^3J_{H-H}$ = 11.4 Hz, 1H, N*H*), 3.46 (s, 3H, SiOCH_3), 4.16 (m, 1H, CHCH$_3$), 7.08 (m, 1H, H_{Ph}), 7.16 (m, 7H, H_{Ph}), 7.63 (m, 2H, H_{Ph}). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 298 K): δ 18.4 [s, C(CH$_3$)$_3$], 26.8 [s, C(CH_3)$_3$], 28.2 (s, CHCH_3), 50.5 (s, CHCH$_3$), 51.1 (s, SiOCH_3), 125.4 (s, C_{Ph}), 126.3 (s, C_{Ph}), 127.5 (s, C_{Ph}), 128.3 (s, C_{Ph}), 129.5 (s, C_{Ph}), 133.3 (s, C_{Ph}), 135.7 (s, C_{Ph}), 148.8 (s, C_{Ph}). ^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6, 298 K): δ −14.9 (s).

*Reaction of compound (S_C,R_{Si})-**3** with lithium methoxide.* Compound (S_C,R_{Si})-**3** (0.070 g, 220 µmol, 1.0 equiv., d.r. = 97:3) and lithium methoxide (0.010 g, 264 µmol, 1.2 equiv.) were suspended in benzene-d_6 (1.0 mL). The suspension was stirred for 10 d at room temperature and then heated at 80 °C for 2 d, after which a conversion of 40% was achieved according to ^{1}H NMR spectroscopy. Comparison with the spectroscopic data of the independently synthesized compounds (S_C,R_{Si})-**4** and (S_C,S_{Si})-**4** showed the selective formation of compound (S_C,S_{Si})-**4** (d.r. = 95:5) (for details, see the Supporting Information).

*Verification of the configurational stability of (S_C,S_{Si})-**3** and (S_C,R_{Si})-**3**.* Compounds (S_C,S_{Si})-**3**/(S_C,R_{Si})-**3** (318 mg, 1.00 mmol, 1.0 equiv., d.r. = 58:42) and lithium chloride (127 mg, 3.00 mmol, 3.0 equiv.) were suspended in tetrahydrofuran (5 mL) and stirred for 16 h at room temperature. An aliquot of the crude sample was analyzed by ^{1}H NMR spectroscopy. No change in diastereomeric ratio was observed (for details, see the Supporting Information).

rac-tBuPhSi(OMe)(NC_4H_8). *n*-Butyllithium (16.8 mL of a 2.5 M solution in hexane, 42.0 mmol, 1.2 equiv.) was added dropwise to a solution of pyrrolidine (3.45 mL, 2.98 g, 42.0 mmol, 1.2 equiv.) in hexane (100 mL) at −30 °C. The resulting white suspension was then allowed to slowly warm up to room temperature and kept stirring for 1 h. Then, the mixture was added in one portion to a solution of **5** (7.85 g, 35.0 mmol, 1.0 equiv.) in hexane (40 mL) at room temperature. The resulting suspension was heated at reflux for 15 h. After cooling down to room temperature, the reaction mixture was filtered through a fritted column layered with Celite® and the remaining solid washed with hexane (2×20 mL). The filtrates were collected and all volatiles removed in vacuo. The crude oil was purified by Kugelrohr distillation (70 °C oven temperature, $1.3 \cdot 10^{-3}$ mbar) to yield *rac-t*BuPhSi(OMe)(NC_4H_8) as a colorless oil (8.11 g, 30.8 mmol, 88%). ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 1.12 [s, 9H, C(CH_3)$_3$], 1.51 (m, 4H, NCH_2CH_2), 3.01–3.12 (m, 4H, NCH_2CH_2), 3.46 (s, 3H, SiOCH_3), 7.24 (m, 3H, H_{Ph}), 7.72 (m, 2H, H_{Ph}). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 298 K): δ 19.1 [s, C(CH$_3$)$_3$], 26.7 (s, NCH_2CH_2), 26.9 [s, C(CH_3)$_3$], 48.1 (s, NCH_2CH_2), 50.4 (s, SiOCH_3), 127.6 (s, C_{Ph}), 129.3 (s, C_{Ph}), 134.4 (s, C_{Ph}), 135.5 (s, C_{Ph}). ^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6, 298 K): δ −14.4 (s). HRMS (EI +): Calcd *m/z* for $C_{15}H_{25}NOSi$ [M^+]: 263.16999. Found: 263.17030. CHN Analysis: Calcd for $C_{15}H_{25}NOSi$: C, 68.39; H, 9.57; N, 5.32. Found: C, 68.22; H, 9.40; N, 5.04.

*rac-tert-Butylmethoxyphenylsilanol (rac-**6**).* Water (2.0 mL, 111.1 mmol) and acetic acid (0.1 mL, 95 mg, 1.58 mmol) were added to a stirred solution of *rac-t*BuPhSi(OMe)(NC_4H_8) (5.75 g, 27.36 mmol) in tetrahydrofuran (60 ml) at −30 °C. The resulting mixture was then allowed to slowly warm up to room temperature and kept stirring for 36 h. Afterwards, diethyl ether (60 mL) and water (20 mL) were added. The organic phase was separated from the aqueous phase, washed with water (20 mL) and dried over magnesium sulfate. After filtration, all volatiles were removed in vacuo to yield *rac*-**6** as a colorless oil (4.72 g, 22.47 mmol, 82%). ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 1.06 [s, 9H, C(CH_3)$_3$], 3.42 (s, 3H, SiOCH_3), 3.66 (s, 1H, SiO*H*), 7.22 (m, 3H, H_{Ph}), 7.71 (m, 2H, H_{Ph}). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 298 K): δ 17.5 [s, C(CH$_3$)$_3$], 25.0 [s, C(CH_3)$_3$], 49.5 (s, SiOCH_3), 126.9 (s, C_{Ph}), 129.0 (s, C_{Ph}), 132.2 (s, C_{Ph}), 134.3 (s, C_{Ph}). ^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6, 298 K): δ −17.9 (s). HRMS (EI +): Calcd *m/z* for $C_{11}H_{18}O_2Si$ [M^+]: 210.10706. Found: 210.10663. CHN Analysis: Calcd for $C_{11}H_{18}O_2Si$: 62.81; H, 8.63. Found: 62.76; H, 8.54.

*(S_{Si})-tert-Butylmethoxyphenylsilanol [(S_{Si})-**6**].* Water (30 mL) and ammonium chloride (5.0 g) were added to a stirred solution of compound (S_C,R_{Si})-**4** (3.0 g, 9.56 mmol, d.r. > 99:1) in tetrahydrofuran (40 ml) at room temperature. The resulting biphasic system was kept stirring for 7 d. Afterwards, the organic phase was separated from the aqueous phase and dried over magnesium sulfate. After filtration, the solids were washed with diethyl ether (3×20 mL). Then, the filtrates were collected and all volatiles removed in vacuo to yield (S_{Si})-**6** as a colorless oil (1.56 g, 7.45 mmol, 78%, e.r. = 95:5). ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 1.07 [s, 9H, C(CH_3)$_3$], 2.82 (s, 1H, SiO*H*), 3.41 (s, 3H, SiOCH_3), 7.23 (m, 3H, H_{Ph}), 7.72 (m, 2H, H_{Ph}). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 298 K): δ 18.2 [s, C(CH$_3$)$_3$], 25.8 [s, C(CH_3)$_3$], 50.3 (s, SiOCH_3), 127.7 (s, C_{Ph}), 129.8 (s, C_{Ph}), 133.0 (s, C_{Ph}), 135.1 (s, C_{Ph}). $[\alpha]_D^{20} = -32.2°$ (*c* = 0.108, toluene).

*rac-tert-Butylchloromethoxyphenylsilane (rac-**7**).* Hydrogen chloride (4.8 mL of a 2.0 M solution in Et_2O, 9.48 mmol, 2.0 equiv.) was slowly added to a stirred solution of *rac-t*BuPhSi(OMe)(NC_4H_8) (1.25 g, 4.74 mmol, 1.0 equiv.) in pentane (60 mL) at −80 °C. A white solid precipitates immediately. The reaction mixture was allowed to slowly warm up to room temperature and kept stirring for 30 min. The mixture was then filtered through a fritted column layered with Celite® and the remaining solids washed with pentane (2×10 mL). The filtrates were collected and all volatiles removed in vacuo to yield *rac*-**7** as a colorless oil (1.08 g, 4.74 mmol, 99%). ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 1.05 [s, 9H, C(CH_3)$_3$], 3.34 (s, 3H, SiOCH_3), 7.17 (m, 3H, H_{Ph}), 7.68 (m, 2H, H_{Ph}).

*tert-Butylchloromethoxyphenylsilane (**7**).* Hydrogen chloride (6.9 mL of a 2.0 M solution in Et_2O, 13.10 mmol, 2.0 equiv.) was slowly added to a stirred solution of (S_C,R_{Si})-**4** (2.05 g, 6.55 mmol, 1.0 equiv., d.r. > 99:1) in pentane (100 mL) at −80 °C. A white solid precipitates immediately. The reaction mixture was allowed to slowly warm up to room temperature and kept stirring for 30 min. The mixture was then filtered through a fritted column layered with Celite® and the remaining solids washed with pentane (2×10 mL). The filtrates were collected and all volatiles removed in vacuo to yield **7** as a colorless oil (1.45 g, 6.55 mmol, 99%, e.r. ≥ 83:17). ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 1.04 [s, 9H, C(CH_3)$_3$], 3.35 (s, 3H, SiOCH_3), 7.17 (m, 3H, H_{Ph}), 7.67 (m, 2H, H_{Ph}). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 298 K): δ 20.3 [s, C(CH$_3$)$_3$], 25.0 [s, C(CH_3)$_3$], 51.1 (s, SiOCH_3), 127.9 (s, C_{Ph}), 130.6 (s, C_{Ph}), 131.0 (s, C_{Ph}), 134.8 (s, C_{Ph}). ^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6, 298 K): δ 3.3 (s). HRMS (EI +): Calcd *m/z* for $C_{11}H_{17}OClSi$ [M^+]: 228.07317. Found: 228.07354.

*rac-tert-Butylmethoxyphenylsilanethiol (rac-**8**).* *n*-Butyllithium (2.10 mL of a 2.5 M solution in hexane, 5.21 mmol, 1.1 equiv.) was slowly added to a solution of hydrogen sulfide (6.5 mL of a 0.8 M solution in tetrahydrofuran, 5.21 mmol, 1.1 equiv.) at 0 °C. The reaction mixture was then allowed to slowly warm up to room temperature and kept stirring for 20 min. The mixture was filtered and the solid washed with hexane (2×10 mL) Then, all volatiles

were removed in vacuo to yield LiSH as a white powder. A solution of *rac*-**7** (1.08 g, 4.74 mmol, 1.0 equiv.) in tetrahydrofuran (50 mL) was added to the freshly prepared LiSH at room temperature. The green-yellow suspension was kept stirring for 15 h and then heated at reflux for further 4 h. The mixture was cooled down to room temperature and all volatiles were removed in vacuo. The oily suspension was then diluted with hexane (50 mL) and filtered through a fritted column layered with Celite®. The remaining solids were washed with hexane (2×10 mL). Then, the filtrates were collected and all volatiles removed in vacuo. The crude oil was finally purified by silica gel flash column chromatography (EtOAc/hexane 2:8) (R_f = 0.4) to yield *rac*-**8** as a pale yellow oil (54 mg, 0.24 mmol, 5%). ^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K): δ 0.02 (s, 1H, Si*H*), 1.00 [s, 9H, C(CH_3)$_3$], 3.73 (s, 3H, SiOCH_3), 7.51 (m, 3H, H_{Ph}), 7.65 (m, 2H, H_{Ph}). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$, 298 K): δ 20.6 [s, C(CH_3)$_3$], 25.9 [s, C(CH_3)$_3$], 51.3 (s, SiOCH_3), 128.2 (s, C_{Ph}), 130.6 (s, C_{Ph}), 133.6 (s, C_{Ph}), 135.2 (s, C_{Ph}). ^{29}Si{^{1}H} NMR (79.49 MHz, $CDCl_3$, 298 K): δ 10.1 (s). CHN Analysis: Calcd for $C_{11}H_{18}OSSi$: C, 58.36; H, 8.01. Found: C, 58.79; H, 7.95.

tert-Butylmethoxyphenylsilanethiol (***8***). *n*-Butyllithium (2.90 mL of a 2.5 M solution in hexane, 7.03 mmol, 1.1 equiv.) was slowly added to a solution of hydrogen sulfide (9.0 mL of a 0.8 M solution in tetrahydrofuran, 7.03 mmol, 1.1 equiv.) at 0 °C. The reaction mixture was then allowed to slowly warm up to room temperature and kept stirring for 20 min. The mixture was filtered and the solid washed with hexane (2×10 mL) Then, all volatiles were removed in vacuo to yield LiSH as a white powder. A solution of **7** (1.45 g, 6.55 mmol, 1.0 equiv., e.r. ≥ 80:20) in tetrahydrofuran (50 mL) was added to the freshly prepared LiSH at room temperature. The green-yellow suspension was kept stirring for 15 h and then heated at reflux for further 4 h. The mixture was cooled down to room temperature and all volatiles were removed in vacuo. The oily suspension was then diluted with hexane (50 mL) and filtered through a fritted column layered with Celite®. The remaining solids were washed with hexane (2×10 mL). Then, the filtrates were collected and all volatiles removed in vacuo. The crude oil was finally purified by silica gel flash column chromatography (EtOAc/hexane 2:8) (R_f = 0.4) to yield **8** as a pale yellow oil (0.49 g, 2.16 mmol, 33%, e.r. = 80:20). ^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K): δ 0.01 (s, 1H, Si*H*), 0.84 [s, 9H, C(CH_3)$_3$], 3.44 (s, 3H, SiOCH_3), 7.25 (m, 3H, H_{Ph}), 7.51 (m, 2H, H_{Ph}). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$, 298 K): δ 20.5 [s, C(CH_3)$_3$], 25.9 [s, C(CH_3)$_3$], 51.6 (s, SiOCH_3), 128.0 (s, C_{Ph}), 130.4 (s, C_{Ph}), 133.2 (s, C_{Ph}), 134.9 (s, C_{Ph}). ^{29}Si{^{1}H} NMR (79.49 MHz, $CDCl_3$, 298 K): δ 9.4 (s). CHN Analysis: Calcd for $C_{11}H_{18}OSSi$: C, 58.36; H, 8.01. Found: C, 59.08; H, 8.05.

(R)-BINOL-PSSLi. *n*-Butyllithium (2 mL of a 2.5 M solution in hexane, 5.0 mmol, 1.0 equiv.) was added dropwise to a suspension of (*R*)-BINOL-dithiophosphoric acid [(*R*)-BINOL-PSSH] (1.90 g, 5.0 mmol, 1.0 equiv.) in hexane (120 mL) at −50 °C. The mixture was allowed to slowly warm up to room temperature. The resulting colorless solid was isolated by cannula filtration, washed with hexane (60 mL) and dried in vacuo to yield (*R*)-BINOL-PSSLi as a fine white powder (1.87 g, 4.83 mmol, 96%).

Determination of the enantiomeric ratios of compounds (S_{Si})-***6*** *and* ***8*** *using (R)-BINOL-PSSLi*. (*R*)-BINOL-PSSLi (92 mg, 0.23 mmol, 1.0 equiv.) and the respective silanol or silanethiol [*rac*-**6**, (S_{Si})-**6**, *rac*-**8**, or **8**] (0.23 mmol, 1.0 equiv.) were dissolved in CD_2Cl_2 (0.6 mL), the mixture transferred to a Young NMR tube and subjected to NMR spectroscopy. The enantiomeric ratios were determined by integration of the ^{1}H NMR signals of either the methoxy groups or the SH group, the latter at −50 °C (for details, see the Supporting Information).

rac-***6*** *in the presence of (R)-BINOL-PSSLi*. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 0.86 [s, 9H, C(CH_3)$_3$], 0.91 [s, 9H, C(CH_3)$_3$], 3.28 (s, 3H, OCH_3), 3.41 (s, 3H, OCH_3), 4.89 (bs, 2H, 2×O*H*), 7.27 (m, 8H, H_{Ar}), 7.38 (m, 6H, H_{Ar}), 7.48 (bt, $^3J_{HH}$ = 7.6 Hz, 4H, H_{Ar}), 7.53 (bd, $^3J_{H-H}$ = 8.7 Hz, 4H, H_{Ar}), 7.60 (m, 4H, H_{Ar}), 7.98 (bt, $^3J_{H-H}$ = 7.6 Hz, 8H, H_{Ar}). ^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6, 298 K): δ −15.0 (s), −14.8 (s). ^{31}P{^{1}H} NMR (162.04 MHz, CD_2Cl_2, 298 K): δ 127.5 (s). ^{7}Li{^{1}H} NMR (155.51 MHz, CD_2Cl_2, 298 K): δ 0.4 (s).

(S_{Si})-***6*** *(e.r. = 95:5) in the presence of (R)-BINOL-PSSLi*. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 0.90 [s, 9H, C(CH_3)$_3$], 3.35 (s, 3H, OCH_3, minor enantiomer), 3.43 (s, 3H, OCH_3), 5.00 (bs, 1H, O*H*), 7.31 (m, 5H, H_{Ar}), 7.40 (m, 4H, H_{Ar}), 7.51 (m, 4H, H_{Ar}), 7.61 (bd, $^3J_{H-H}$ = 7.0 Hz, 2H, H_{Ar}), 7.97 (bdd, $^3J_{H-H}$ = 8.6 Hz, $^3J_{H-H}$ = 5.2 Hz, 4H, H_{Ar}). ^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6, 298 K): δ −16.0 (s). ^{31}P{^{1}H} NMR (162.04 MHz, CD_2Cl_2, 298 K): δ 127.2 (s).

rac-***8*** in the *presence of (R)-BINOL-PSSLi*. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 0.26 (bs, 1H, Si*H*), 0.28 (bs, 1H, Si*H*), 1.01 [s, 18H, 2×C(CH_3)$_3$], 3.60 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 7.22 (m, 4H, H_{Ar}), 7.32 (m, 4H, H_{Ar}), 7.43 (m, 13H, H_{Ar}), 7.68 (m, 5H, H_{Ar}), 7.88–7.94 (m, 6H, H_{Ar}). ^{31}P{^{1}H} NMR (162.04 MHz, CD_2Cl_2, 298 K): δ 126.0 (s).

8 *(e.r. = 80:20) in the presence of (R)-BINOL-PSSLi*. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 0.27 (bs, 1H, Si*H*), 1.00 [s, 9H, C(CH_3)$_3$], 3.59 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3, minor enantiomer), 7.22 (m, 5H, H_{Ar}), 7.23 (m, 2H, H_{Ar}), 7.33 (m, 2H, H_{Ar}), 7.44 (m, 8H, H_{Ar}), 7.67 (m, 2H, H_{Ar}), 7.88–7.94 (m, 3H, H_{Ar}). ^{31}P{^{1}H} NMR (162.04 MHz, CD_2Cl_2, 298 K): δ 126.2 (s).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-2254809 [(S_C,S_{Si})-**3**], CCDC-2272120 [(S_C,R_{Si})-**3**], and CCDC-2272121 [(S_C,R_{Si})-**4**] (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was jointly supported by the Elite Network of Bavaria (ENB), the Bavarian State Ministry of Science and the Arts (StMWK), and the University of Regensburg (Project N-LW-NW-2016-366). Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

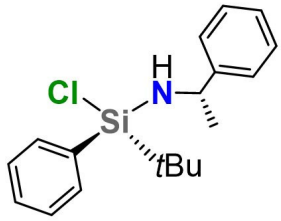
The data that support the findings of this study are available in the supplementary material of this article.

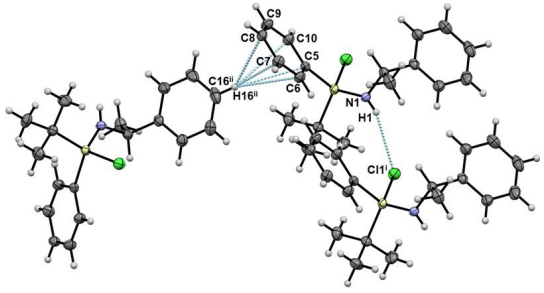
Keywords: Aminochlorosilanes · Chirality · Interaction patterns · Silanols · Silicon

[1] a) R. Wakabayashi, K. Kawahara, K. Kuroda, *Angew. Chem. Int. Ed.* **2010**, *49*, 5273–5277; *Angew. Chem.* **2010**, *122*, 5401–5405; b) R. Wakabayashi, Y. Sugiura, T. Shibue, K. Kuroda, *Angew.*

Chem. Int. Ed. **2011**, *50*, 10708–10711; *Angew. Chem.* **2011**, *123*, 10896–10899; c) P. Mizar, T. Wirth, *Angew. Chem. Int. Ed.* **2014**, *53*, 5993–5997; *Angew. Chem.* **2014**, *126*, 6103–6107; d) T. Götz, A. Falk, J. O. Bauer, *Chem. Eur. J.* **2022**, *28*, e202103531.
[2] P. G. M. Wuts, T. W. Greene, *Greene's Protective Groups in Organic Synthesis* (4th Ed.), John Wiley & Sons, Inc., Hoboken, New Jersey, USA, **2007**.
[3] a) T. Deschner, Y. Liang, R. Anwander, *J. Phys. Chem. C* **2010**, *114*, 22603–22609; b) S. P. Pujari, L. Scheres, A. T. M. Marcelis, H. Zuilhof, *Angew. Chem. Int. Ed.* **2014**, *53*, 6322–6356; *Angew. Chem.* **2014**, *126*, 6438–6474.
[4] a) U. Schubert, N. Hüsing, *Synthesis of Inorganic Materials* (4th Ed.), Wiley-VCH, Weinheim, Germany, **2019**; b) S. Ganachaud, S. Boileau, B. Boury, (Eds.), *Silicon Based Polymers: Advances in Synthesis and Supramolecular Organization*, Springer, Netherlands, **2008**.
[5] a) J. O. Bauer, C. Strohmann, *Chem. Commun.* **2012**, *48*, 7212–7214; b) M. Achternbosch, L. Zibula, J.-L. Kirchhoff, J. O. Bauer, C. Strohmann, *Inorg. Chem.* **2021**, *60*, 11562–11568.
[6] a) N. A. Espinosa-Jalapa, J. O. Bauer, *Z. Anorg. Allg. Chem.* **2020**, *646*, 828–834; b) J. O. Bauer, N. A. Espinosa-Jalapa, N. Fontana, T. Götz, A. Falk, *Eur. J. Inorg. Chem.* **2021**, 2636–2642.
[7] J. O. Bauer, C. Strohmann, *Eur. J. Inorg. Chem.* **2016**, 2868–2881.
[8] a) A. Kawachi, H. Maeda, K. Mitsudo, K. Tamao, *Organometallics* **1999**, *18*, 4530–4533; b) J. W. A. Kinnaird, P. Y Ng, K. Kubota, X. Wang, J. L. Leighton, *J. Am. Chem. Soc.* **2002**, *124*, 7920–7921.
[9] T. Huber, N. A. Espinosa-Jalapa, J. O. Bauer, *Chem. Eur. J.* **2022**, *28*, e202202608.
[10] O. I. Kolodiazhnyi, E. V. Gryshkun, N. V. Andrushko, M. Freytag, P. G. Jones, R. Schmutzler, *Tetrahedron: Asymmetry* **2003**, *14*, 181–183.
[11] Reaction of lithiated (*S*)-(+)-3,3-dimethyl-2-butylamine with *tert*-butyldichlorophenylsilane (**1**) gave a mixture of diastereomers with d.r. = 56:44 indicating that the chiral auxiliary has little effect on an initial preference for one diastereomer (for details, see the Supporting Information).
[12] J. O. Bauer, T. Götz, *Chemistry* **2021**, *3*, 444–453.
[13] M. A. Spackman, J. J. McKinnon, *CrystEngComm* **2002**, *4*, 378–392.
[14] a) T. Steiner, E. B. Starikov, A. M. Amado, J. J. C. Teixeira-Dias, *J. Chem. Soc. Perkin Trans. 2* **1995**, 1321–1326; b) C. A. Hunter, K. R. Lawson, J. Perkins, C. J. Urch, *J. Chem. Soc. Perkin Trans. 2* **2001**, 651–669; c) J. O. Bauer, *Z. Anorg. Allg. Chem.* **2021**, *647*, 1053–1057.
[15] a) R. Taylor, O. Kennard, *J. Am. Chem. Soc.* **1982**, *104*, 5063–5070; b) C. B. Aakeröy, T. A. Evans, K. R. Seddon, I. Pálinkó, *New J. Chem.* **1999**, 145–152; c) M. Liu, C. Yin, P. Chen, M. Zhang, S. Parkin, P. Zhou, T. Li, F. Yu, S. Long, *CrystEngComm* **2017**, *19*, 4345–4354.
[16] a) M. O. Sinnokrot, C. D. Sherrill, *J. Am. Chem. Soc.* **2004**, *126*, 7690–7697; b) S. Grimme, *Angew. Chem. Int. Ed.* **2008**, *47*, 3430–3434; *Angew. Chem.* **2008**, *120*, 3478–3483.
[17] C. R. Martinez, B. L. Iverson, *Chem. Sci.* **2012**, *3*, 2191–2201.
[18] a) M. Mewald, M. Oestreich, *Chem. Eur. J.* **2012**, *18*, 14079–14084; b) J. O. Bauer, C. Strohmann, *Angew. Chem. Int. Ed.* **2014**, *53*, 720–724; *Angew. Chem.* **2014**, *126*, 738–742.
[19] a) L. H. Sommer, J. D. Citron, C. L. Frye, *J. Am. Chem. Soc.* **1964**, *86*, 5684–5685; b) L. H. Sommer, J. D. Citron, *J. Am. Chem. Soc.* **1967**, *89*, 5797–5801.
[20] L. H. Sommer, J. McLick, *J. Am. Chem. Soc.* **1966**, *88*, 5359–5361.
[21] B.-Q. Gong, W.-Y. Chen, B.-F. Hu, *Phosphorus Sulfur Silicon Relat. Elem.* **1991**, *57*, 87–94.
[22] S. Scholz, I. Sänger, F. Schödel, M. Bolte, H.-W. Lerner, *Inorg. Chem. Commun.* **2014**, *44*, 50–52.
[23] K. Igawa, J. Takada, T. Shimono, K. Tomooka, *J. Am. Chem. Soc.* **2008**, *130*, 16132–16133.
[24] Rigaku Oxford Diffraction, CrysAlisPro Software System, **2020**.
[25] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
[26] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *A71*, 3–8.
[27] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3–8.
[28] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Crystallogr.* **2006**, *39*, 453–457.

Manuscript received: April 11, 2023
Revised manuscript received: June 30, 2023
Accepted manuscript online: July 3, 2023





*M. Kümper, Dr. T. Götz, Dr. N. A. Espinosa-Jalapa, A. Falk, R. Rothfelder, Dr. J. O. Bauer**