DOI: 10.1002/asia.200700262

Highly Enantioselective Reactions of Configurationally Labile Epimeric Diamine Complexes of Lithiated *S*-Benzyl Thiocarbamates

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Abstract: Substitution reactions that employ primary-carbamoyl-protected arylmethanethiols are described. The enantiodetermining step was found to occur in the post-deprotonation step as a dynamic thermodynamic resolution with a chiral bis(oxazoline) ligand. The configurationally labile lithium complexes were trapped with various electrophiles to yield different substitution products in good to excellent yields and enantiomeric excesses. The absolute configurations of the substitution products were determined, and the stereochemical pathway of the substitution reaction was elucidated for different classes of electrophiles. The temperature-dependent epimerization process was monitored by ^{1}H and ^{6}Li NMR spectroscopy.

Keywords: asymmetric synthesis · bis(oxazoline) ligands · carbanions · dynamic thermodynamic resolution · lithium

Introduction

Within the field of enantioselective synthesis, the use of chiral α-heterosubstituted organolithium compounds still present a challenging crucial issue: Once these compounds have been generated in an asymmetric fashion by using chiral base systems, their configurational stability decides whether they can be advantageously utilized in enantioselective synthesis.[1] Reaction of the lithiated species with different electrophiles normally proceeds stereospecifically. Therefore, the enantioenrichment of the whole reaction is determined either within the deprotonation step itself (kinetic resolution or enantiotopic differentiation) and/or by the character of the lithiated species and its behavior within the post-deprotonation step (dynamic kinetic resolution or dynamic thermodynamic resolution).[2] Within the last three decades, many substrates have been investigated for their use in enantioselective synthesis and, thereby, for their configurational stability.[3,4]

It was found in 1980 that α-alkoxyalkyl lithium compounds (**1**) are configurationally stable.[3a] The same holds true for α-substituted chiral 1-carbamoyloxyallyl lithium (**2**),[3b] α-substituted chiral 1-carbamoyloxybenzyl lithium (**3**),[3c–f] and, generally, chiral 1-carbamoyloxyalkyl lithium compounds (**4**) (Scheme 1).[3g] Furthermore, some *N*-Boc-α-aminoalkyl lithium compounds, such as pyrrolidines **5** and allylamines **6**, were found to exhibit the desired configurational stability.[4]

A completely different situation is often found for α-thio- or α-seleno-substituted organolithium derivatives.[5–7] Once the lithium-bearing chiral center has been formed, in many cases it starts to epimerize even at temperatures of −78 °C and below.[5,6] Only very few α-thio-substituted compounds are known that exhibit lithiated carbanions that are considerably stable configurationally, namely, α-silylated α-thioalkyl lithium **7**,[8] α-methylated α-thiobenzyl lithium **8**,[9] and cyclic α-thioallyl lithium derivative **9**.[10] For these three cases, configurational stability most likely originates from the branching substituents at the chiral center, thus enhancing the barrier of epimerization as proposed by Hoffmann and co-workers.[6,11] The apparent absence of epimerization of the lithiated *S*-prolinyl thiocarbamate **10** is due to the fact that the *S*,*S* epimer is highly favored both kinetically and thermodynamically.[12]

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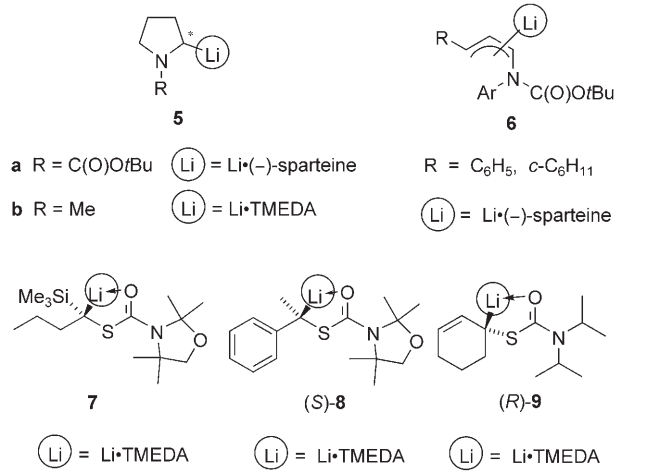
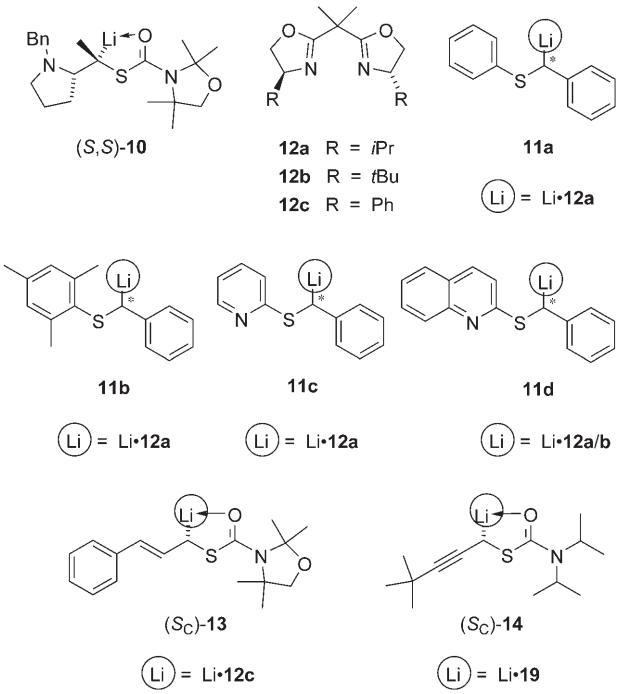
	R	R′	X	Li
1	alkyl	H	OCH_2OCH_3	Li•$(OEt_2)_n$
2	(*E*)-CH=CH-CH_3	CH_3	$OC(O)N(iPr)_2$	Li•TMEDA
3	C_6H_5	CH_3	$OC(O)N(iPr)_2$	Li•TMEDA
4	alkyl	H	$OC(O)NR_2$	Li•TMEDA or Li•(−)-sparteine



Scheme 1. Different configurationally stable chiral lithium compounds. TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

In the case of configurationally labile lithiated species, one has to rely on the mechanisms of enantioenrichment that occur in the post-deprotonation step to gain synthetically useful application of these compounds. Different mechanisms have been found by investigations of several aryl benzyl sulfides **11** by Toru and co-workers (Scheme 2).[13] By using chiral bis(oxazoline) ligands such as **12** in the deprotonation sequence of sulfides **11**, very highly enantioenriched α-substituted benzyl thiols were obtained. In our group, bis(oxazoline) **12c** was used in the substitution of *S*-cinnamyl

Abstract in German: Die asymmetrische Deprotonierung prochiraler *S*-Benzylthiocarbamate wird beschrieben und untersucht. Die Enantiomerenanreicherung entsteht im Post-Deprotonierungsschritt mittels dynamisch-thermodynamischer Resolution unter Verwendung eines chiralen Bis(oxazolin)-Liganden. Die bei −30 °C konfigurationslabilen Diaminkomplexe equilibrieren und können mit verschiedenen Elektrophilen abgefangen werden. So werden in sehr guten Ausbeuten hoch enantiomerenangereicherte α-substituierte *S*-Benzylthiocarbamate erhalten. Die Absolutkonfiguration und der stereochemische Verlauf der Substitutionsreaktionen werden aufgeklärt. Zudem wird die Temperaturabhängige Epimerisierung mittels ^{1}H- und ^{6}Li-NMR-Spektroskopie verfolgt und visualisiert.



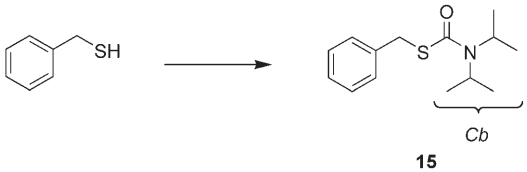
Scheme 2. The different configurationally labile chiral lithium compounds and ligands employed.

thiocarbamate **13**,[14b] whereas (−)-sparteine (**19**) was successfully applied in the case of configurationally labile *S*-2-alkynyl thiocarbamate **14**.[14a]

Herein we present a reliable method of synthesizing highly enantioenriched secondary *S*-benzyl thiocarbamates from primary prochiral *S*-benzyl thiocarbamates. We investigated the configurational stability of the lithium complexes, the mechanism of enantioenrichment, and the stereochemical pathway of the substitution reactions.

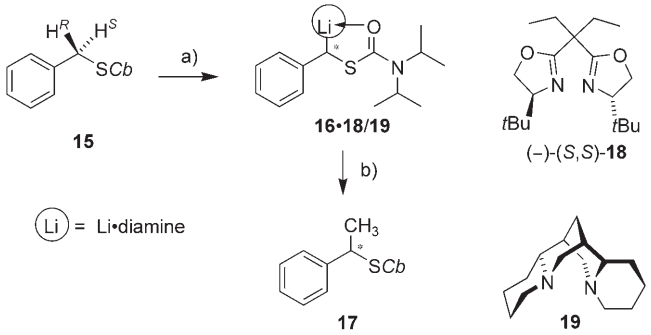
Results and Discussion

S-Benzyl thiocarbamate **15** was synthesized from phenylmethanethiol by carbamoylation with sodium hydride as the base[15] in 92 % yield (Scheme 3).[16,17]



Scheme 3. Synthesis of *S*-benzyl thiocarbamate **15**. Reaction conditions: NaH, *Cb*Cl, THF, room temperature, 2 days, 92 %.

Thiocarbamate **15** was deprotonated by using 1.2 equivalents of *sec*-butyllithium in toluene in the presence of 1.2 equivalents of different tertiary chiral diamines (Scheme 4). With achiral TMEDA and methyl iodide as the



Scheme 4. Deprotonation of *S*-benzyl thiocarbamate **15**. Reaction conditions: a) Diamine, *s*BuLi, toluene, $T_{deprot} = -78\,°C$, $t_{deprot} = 2$ h; b) MeX (X = I, OTf), toluene, −78 °C. Tf = trifluoromethanesulfonyl.

electrophile in the first reaction, the desired racemic methylation product *rac*-**17** was obtained in 94% yield after 2 h of deprotonation at −78 °C (Table 1, entry 1).[17] We then used chiral bis(oxazoline) (−)-(*S*,*S*)-**18**[18] as a chiral diamine at −78 °C under the same reaction conditions. We obtained only moderate yields, and the product could not be completely purified (Table 1, entries 2 and 3). When the electrophile was changed to methyl triflate, we obtained the pure product (−)-(*S*)-**17**, but yields and enantioselectivity were not improved (Table 1, entry 4). By utilizing the same conditions as before, but with (−)-sparteine (**19**) as the chiral diamine, (−)-(*S*)-**17** was obtained in 59% yield, albeit with a slightly better but still poor enantioselectivity of 16% *ee* (Table 1, entry 5).

Table 1. Results of the first deprotonation–methylation experiments of **15**.[a]

Entry	Diamine	ElX	**17** [%]	*ee* [%]	$[\alpha]_D^{20}$ of **17** in $CHCl_3$ (*c*)
1	TMEDA	MeI	94	*rac*	–
2	**18**	MeI	63[b]	n.d.	n.d.
3[c]	**18**	MeI	77[b]	n.d.	n.d.
4	**18**	MeOTf	31	19	n.d.
5	**19**	MeOTf	59	16	−6.6 (0.98)

[a] $T_{deprot} = -78\,°C$, $t_{deprot} = 2$ h. [b] Product contaminated with substrate; ratio determined by GC analysis (HP 1701). [c] Reaction time prolonged to 4 h. n.d. = not determined.

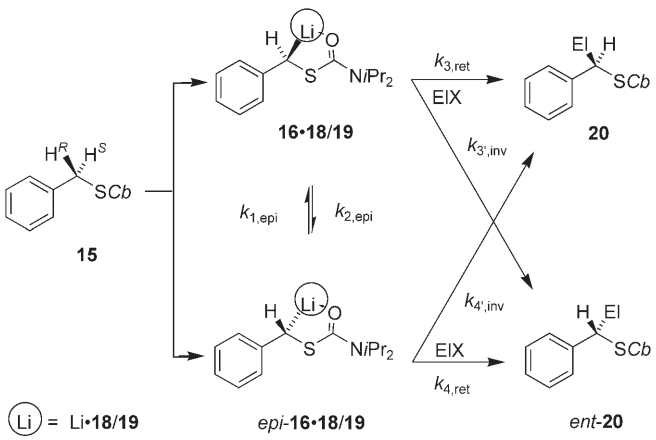
Out of this series of experiments, several questions arose:

1) Do the complexes **16·18** and **16·19** epimerize?
2) Is the enantiotopic discrimination by bis(oxazoline) **18** simply bad and frozen in the configurationally stable complex **16·18**?
3) Is there a good enantiotopic discrimination with (−)-sparteine (**19**) that is later destroyed by epimerization?
4) Can epimerization conditions be achieved that favor one of the diastereomeric complexes, which can then be trapped with different electrophiles?

Some control experiments were performed. The results obtained are outlined in Table 2. A longer deprotonation time at −78 °C yielded the methylated *S*-thiocarbamate (−)-(*S*)-**17** in a significantly increased yield of 67% (Table 2, entry 1). The enantiomeric excess remained unchanged and was found to be 19% *ee*. Deprotonation at −30 °C for 12 h and trapping of the lithiated species at −78 °C with methyl triflate yielded (−)-(*S*)-**17** in 98% yield and with 96% *ee* (Table 2, entry 2). These two key experiments showed the main reaction features at once: The enantioselectivity originates from the post-deprotonation step through dynamic thermodynamic resolution.[2] There was an equilibrium of epimeric complexes at higher temperatures (−30 °C), and one of the epimeric complexes was strongly favored when chiral bis(oxazoline) **18** was used. Upon cooling the reaction mixture, the equilibration slowed, and the ratio of epimeric complexes seems to be frozen on the timescale set by the reaction of the complex with the electrophile used, that is, $k_{1/2epi} \ll k_{3/4ret/inv}$ (Scheme 5). No precipitation formed by a crystallizing lithium species was observed during the experiments. The complexes remained in solution and equilibrated without an asymmetric transformation of the second order.[19]

Table 2. Deprotonation experiments of **15** performed in order to identify the enantiodeterming step.

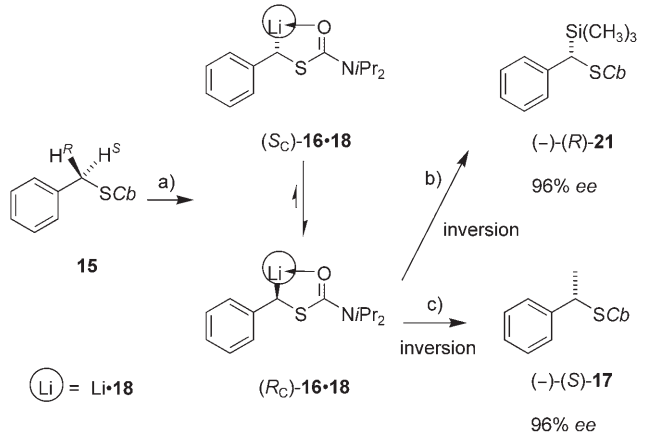
Entry	Diamine	T_{deprot} [°C]	t_{deprot} [h]	ElX	Yield [%] (product)	*ee* [%]	$[\alpha]_D^{20}$ in $CHCl_3$ (*c*)
1	**18**	−78	5	MeOTf	67 (**17**)	19	−12.9 (1.05)
2	**18**	−30	13	MeOTf	98 (**17**)	96	−147.4 (1.36)
3	**19**	−78	2	MeOTf	59 (**17**)	16	n.d.
4	**19**	−30	14	MeOTf	92 (ent-**17**)	17	n.d.
5	**18**	−30	12	TMSCl	90 (**21**)	96	−166.5 (1.01)
6	**18**	−30	4	TMSCl	82 (**21**)	94	−162.4 (0.97)
7	**18**	−78	0.5	TMSCl in situ	52 (ent-**21**)	28	+50.8 (0.72)
8	**19**	−78	0.5	TMSCl in situ	66 (**21**)	16	n.d.



Scheme 5. Kinetic description of the reaction of the epimeric complexes **16·18/19**. ElX = electrophile.

An experiment with (−)-sparteine (**19**) as a chiral ligand under the same reaction conditions as before clearly indicates that the corresponding lithium complexes also equilibrate at −30 °C (Table 2, entry 4). Compared to the substitution at −78 °C (**17**: 59 %, 16 % *ee*; Table 2, entry 3), *ent*-**17** was obtained in 92 % yield and with 17 % *ee*. In contrast to the result with the bis(oxazoline) **18**, none of the epimeric complexes was strictly favored, which rules out (−)-sparteine (**19**) as the chiral diamine of choice.

By using **18** and trimethylsilyl chloride as the electrophile and employing the same reaction conditions as before (4 h at −30 °C), the silylated *S*-benzyl thiocarbamate (−)-(*R*)-**21** was obtained in 90 % yield and with 96 % *ee* (Scheme 6 and



Scheme 6. Silylation and methylation of *S*-benzyl thiocarbamate **15**. Reaction conditions: a) **18**, *s*BuLi, toluene, −30 °C, 12 h; b) Me_3SiCl, toluene, −78 °C, 2 h, 90 %; c) MeOTf, toluene, −78 °C, 2 h, 98 %.

Table 2, entry 5). This shows that the enantioenrichment is independent of the electrophile, thus excluding a dynamic kinetic resolution in the substitution step and thereby proving the proposed mechanism of enantioenrichment. Essentially the same results were obtained when the deprotonation time was shortened to 4 h at −30 °C (Table 2, entry 6). To estimate the kinetic enantiotopic differentiation of (−)-sparteine (**19**) and bis(oxazoline) **18**, in situ experiments were performed: (−)-Sparteine (**19**) showed poor enantiotopic differentiation as silane (−)-(*R*)-**21** was formed with a poor enantiomeric excess of 16 % *ee* (Table 2, entry 8). Nevertheless, this result underlines the fact that the complexes must be configurationally stable at −78 °C as the enantioenrichment did not change when the complexes were stirred for a while before being trapped with an electrophile (Table 2, entry 3). Silane (+)-(*S*)-**21** was formed by employing bis(oxazoline) **18** in the in situ procedure (Table 2, entry 7). The low enantiomeric excess of 28 % *ee* indicates poor kinetic enantiotopic differentiation by **18** as well. Besides, the formation of the enantiomer (+)-(*S*)-**21** in the in situ trapping experiment with bis(oxazoline) **18** serves as the final proof for dynamic thermodynamic resolution as the enantiodetermining step. This is in contrast to the findings of Toru and co-workers with regard to the enantiodetermining step in the substitution sequences that employ lithiated benzyl phenyl sulfides **11a/b**:[13a] dynamic kinetic resolution takes place there. The difference is attributed to the dipole-stabilizing effect of the carbamate group.

Assignment of Absolute Configurations and Elucidation of the Stereochemical Pathways

Single crystals of the methylated benzyl thiocarbamate (−)-(*S*)-**17** were obtained and analyzed by X-ray crystal-structure analysis with anomalous dispersion. We thus assigned the *S* configuration of the stereogenic carbon atom (Figure 1). From single crystals of silane (−)-(*R*)-**21**, which were suitable for X-ray analysis with anomalous dispersion, we determined the stereogenic centre of the silane to be *R*-configured (Figure 2). As it is known that both silylation

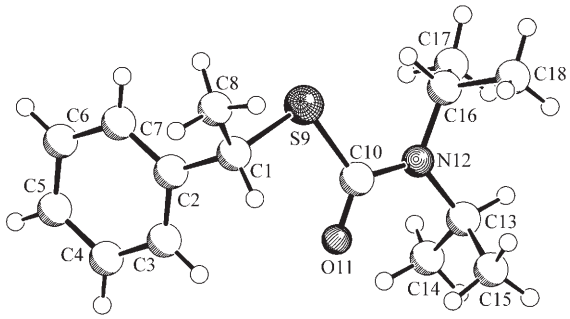


Figure 1. X-ray crystal structure of (−)-(*S*)-**17**.[20]

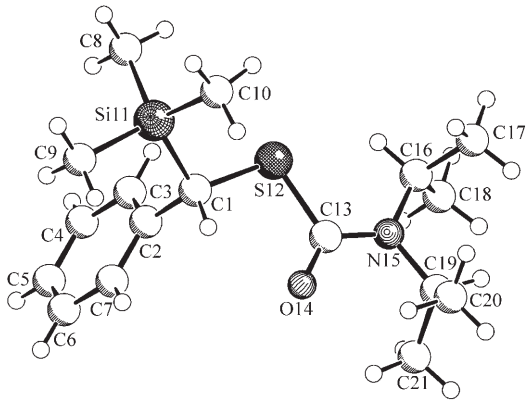


Figure 2. X-ray crystal structure of (−)-(*R*)-**21**.[21]

and methylation on mesomerically stabilized α-thioorganolithium compounds usually take place with inversion of configuration,[9,10a,b,14] the benzylic carbon atom of the favored epimeric complex is considered to have the *R* configuration (Scheme 6).[22]

Extension of the Methodology

We extended this methodology by successfully employing various electrophiles. It was possible to determine both the enantiomer ratio and the absolute stereochemistry of the

various substitution products as outlined in Table 3. Like the silylation described above, stannylation worked well with a good yield and an excellent enantiomeric excess of 98% *ee* (Table 3, entry 1). Trapping of the lithiated species with gaseous carbon dioxide yielded the corresponding ester (−)-(*R*)-**23** in 90% yield after the resulting acid was methylated with diazomethane (Table 3, entry 2). When methyl chloroformate was used as the electrophile, the same product, (−)-(*R*)-**23**, was obtained in 99% yield and essentially the same enantiomeric excess of 95% *ee* (Table 3, entry 3). We obtained suitable crystals of (−)-(*R*)-**23** for X-ray analysis with anomalous dispersion from the reaction with methyl chloroformate. The configuration of the stereogenic benzylic carbon atom in (−)-(*R*)-**23** was determined to be *R* (Figure 3), which shows that both the acid chloride and the carbon dioxide reacted with inversion of configuration.

Table 3. Further substitution reactions with *S*-benzyl thiocarbamate **15** and bis(oxazoline) **18**.

Entry	ElX	Conf. of **16**	Yield [%] (product)	*ee* [%]	$[\alpha]_D^{20}$ in $CHCl_3$ (*c*)	Conf. of product[a]
1	Bu_3SnCl	R_C	78 (**22**)	98	−42.6 (0.96)	*S*
2[b]	CO_2	R_C	53 (**23**)	98	−157.4 (1.10)	*R*
3	ClC(O)OMe	R_C	99 (**23**)	95	n.d.	*R*
4[c]	$(H_3C)_3CCHO$	R_C	13 (**24**)	94	−74.0 (0.1)	*R*,*S*
			45 (**24**)	94	−147.1 (1.04)	*R*,*R*
5[d]	H_5C_6CHO	R_C	48 (**25**)	97	−20.3 (0.45)	*R*,*S*
			33 (**25**)	96	−121.1 (0.57)	*R*,*R*
6	$(H_5C_6)_2CO$	R_C	99 (**26**)	98	+57.5 (0.96)	*R*

[a] All the electrophiles used so far reacted with inversion of configuration. [b] The acid was converted into the ester with diazomethane prior to the determination of the enantiomeric excess. [c] Diastereomer ratio = 1:3. [d] Diastereomer ratio = 1:1.5.

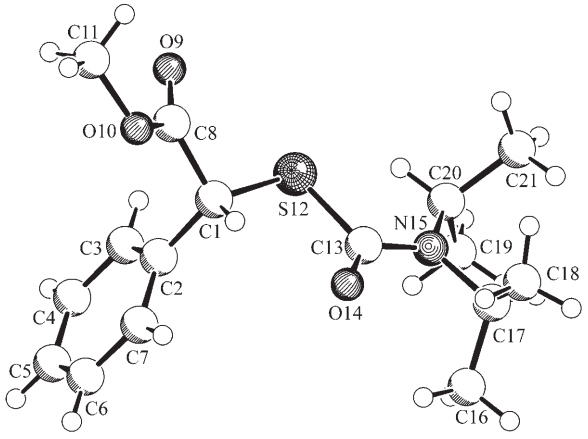


Figure 3. X-ray crystal structure of (−)-(*R*)-**23**.[23]

Aliphatic and aromatic aldehydes were successfully employed as well (Table 3, entries 4 and 5). Separation of the diastereomers of **24** and **25** was achieved in both cases by simple column chromatography on silica gel.

Furthermore, one diastereomer from the reaction of (R_C)-**16** with pivaldehyde formed single crystals suitable for X-ray analysis (Figure 4). The benzylic carbon atom in (−)-(*R*,*R*)-**24** is *R*-configured. This indicates a reaction under inversion of configuration for the aliphatic aldehyde. The same stereochemical course is proven for the addition of the aromatic aldehyde by the crystal structure obtained from the benzaldehyde adduct (−)-(*R*,*S*)-**25** (Figure 5).

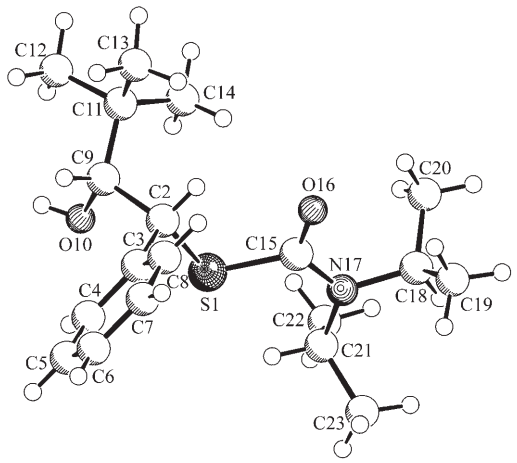


Figure 4. X-ray crystal structure of (−)-(*R*,*R*)-**24**.[24]

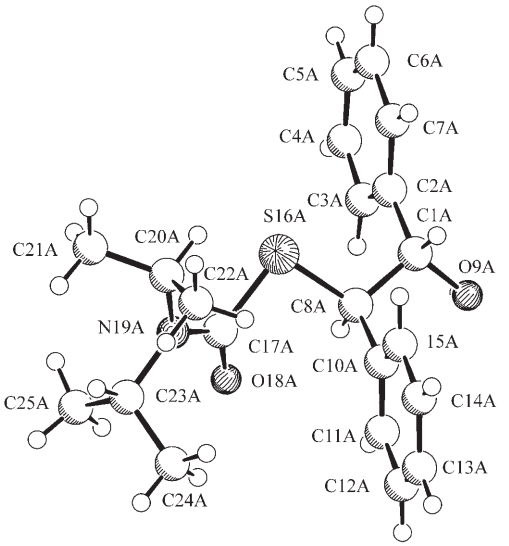


Figure 5. X-ray crystal structure of (−)-(*R*,*S*)-**25**.[26]

It was also possible to obtain the crystal structure of the benzophenone adduct (+)-(*R*)-**26** (Figure 6), which was formed in 99% yield and with 98% *ee* (Table 3, entry 6). We concluded from the *R*-configured stereogenic carbon

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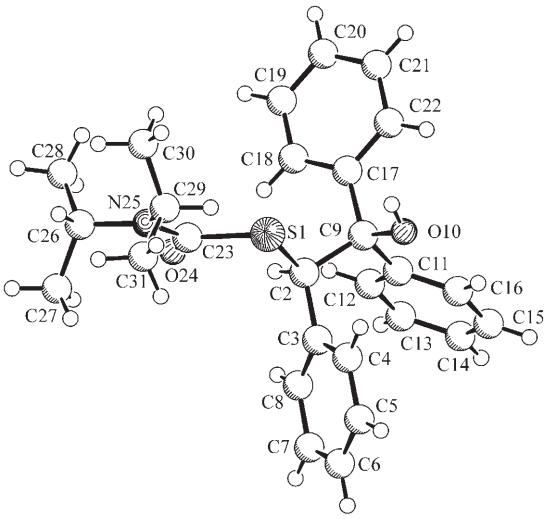


Figure 6. X-ray crystal structure of (+)-(*R*)-**26**.[27]

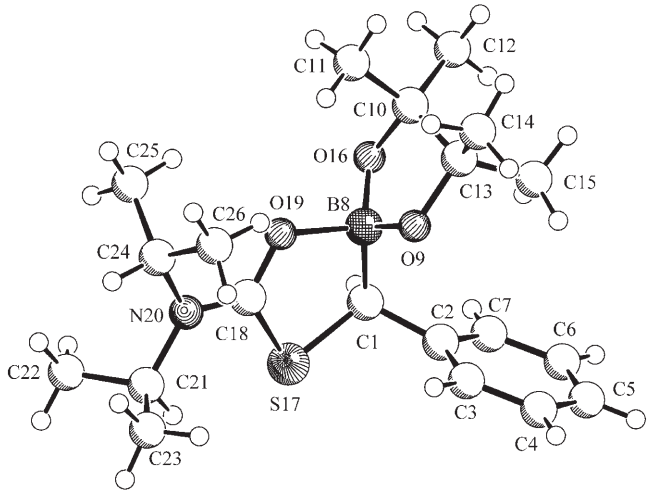


Figure 7. X-ray crystal structure of *rac*-**30**.[29]

atom that an inversion of configuration must have occurred in the reaction. There are no hints that a single-electron-transfer (SET) mechanism took place with benzophenone as the electrophile.[25]

Allyl bromide, acetone, and the pinacol-derived boronate **27** turned out to be more problematic electrophiles. With allyl bromide, the enantioenriched allylated *S*-thiocarbamate (−)-(*R*)-**28** was obtained in only 20% yield (Table 4, entry 2). Nevertheless, the enantiomeric excess of 82% *ee* was good. When the racemic complex was trapped under the same conditions, the allylation product *rac*-**28** was isolated in 97% yield (Table 4, entry 1).

Table 4. Further substitution reactions with *S*-thiocarbamate **15**.

Entry	Diamine	T_{deprot} [°C]	t_{deprot} [h]	ElX	Conf. of **16**	Yield [%] (product)	*ee* [%]	$[\alpha]_D^{20}$ in $CHCl_3$ (*c*)	Conf. of product[a]
1	TMEDA	−78	2	H_2CCHCH_2Br	*rac*	97 (**28**)	*rac*	–	–
2	**18**	−30	4		R_C	20 (**28**)	82	−170.4 (1.03)	*S*
3	TMEDA	−78	2	$(H_3C)_2CO$	*rac*	30 (**29**)	*rac*	–	–
4	**18**	−30	4		R_C	0	–	–	–
5	TMEDA	−78	2		*rac*	62 (**30**)	*rac*	–	–
6	**18**	−30	4	*i*PrO–B(O)(O)	R_C	19 (**30**)	58	+50.9 (0.95)	*S*
				(**27**)					

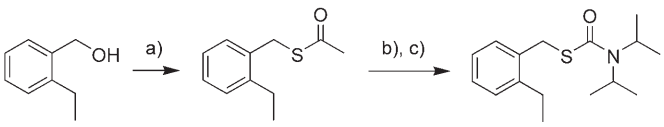
[a] All the electrophiles used so far reacted with inversion of configuration.

Acetone did not add to the chiral organolithium complex (R_C)-**16**·**18** at all; trapping of the racemic lithium complex resulted in the desired alcohol *rac*-**29** in a moderate yield of 30% (Table 4, entries 3 and 4).

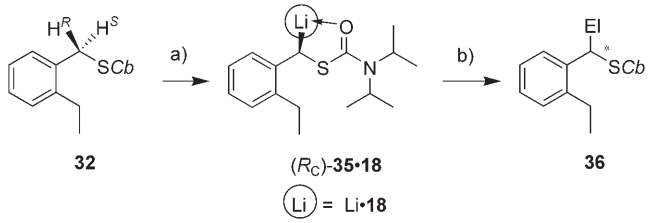
A very similar situation to that with allyl bromide emerged when borate **27** was used (Table 4, entries 5 and 6). Borane (+)-(*S*)-**30** was obtained in low yield (19%) and with a moderate enantiomeric excess of 58% *ee*. It was not possible to determine the absolute stereochemistry by X-ray analysis as only the racemic form of the enantioenriched sample of (+)-(*S*)-**30** crystallized (Figure 7). We assumed a reaction with inversion of configuration, as this stereospecificity was observed in our group for this boronate when it was used as an electrophile in the substitution reaction of an α-lithiated unsaturated *O*-carbamate.[28]

To demonstrate some generality, we trapped the sterically more demanding *S*-benzyl thiocarbamate **32**, which bears an ethyl moiety in the *ortho* position. *ortho*-Ethyl-substituted *S*-benzyl thiocarbamate **32** was obtained in three steps, starting with *ortho*-ethyl benzyl alcohol **33**, which was thioesterified under Mitsunobu reaction conditions[30] to yield thioester **34** in 78% yield (Scheme 7). Reductive cleavage of **34** directly followed by carbamoylation[14] afforded the *o*-substituted *S*-benzyl thiocarbamate **32** in 89% yield over two steps.

We trapped lithiated *S*-thiocarbamate **32** by using the same reaction conditions as before (Scheme 8). At first, we applied trimethylchlorosilane as the electrophile, but to our surprise, we could not get the desired silane **36a** even when the reac-



Scheme 7. Synthesis of *S*-benzyl thiocarbamate **32**. Reaction conditions: a) Ph_3P, DIAD, $H_3CC(O)SH$, THF, 0°C, 78%; b) $LiAlH_4$, Et_2O, −30°C; c) NaH, *Cb*Cl, THF, room temperature, 2 days, 89%. DIAD = diisopropyl azodicarboxylate.



Scheme 8. Trapping of *S*-benzyl thiocarbamate **32**. Reaction conditions: a) **18**, *s*BuLi, toluene, −30 °C, 4 h; b) ElX, toluene, −78 °C, 2 h. **36a**: El = Me_3Si; **36b**: El = C(O)OMe; **36c**: El = $Ph_2C(OH)$.

Table 5. Further substitution reactions with *S*-thiocarbamate **32**.

Entry	Diamine	ElX	Conf. of **35**	Yield [%] (product)	*ee* [%]	$[\alpha]_D^{20}$ in $CHCl_3$ (*c*)	Conf. of product[a]
1	TMEDA	Me_3SiCl	*rac*	0 (**36a**)	–	–	–
2	**18**		R_C	0 (**36a**)	–	–	–
3	*i*Pr-**18**[b]		R_C	0 (**36a**)	–	–	–
4	**18**	ClC(O)OMe	R_C	58 (**36b**)	36	−64.1 (0.91)	*R*
5	**18**	$(H_5C_6)_2CO$	R_C	84 (**36c**)	99	+10.7 (1.03)	*R*

[a] All the electrophiles used so far reacted with inversion of configuration. [b] The *tert*-butyl residue was exchanged for an isopropyl residue to decrease steric demand.

tion conditions were changed (Table 5, entries 1–3). Warming to room temperature upon reaction with trimethylchlorosilane did not deliver the product either.

Nevertheless, trapping with methyl chloroformate and benzophenone worked well and yielded the desired substitution products (−)-(*R*)-**36b** and (+)-(*S*)-**36c**, respectively, in satisfying to good yields (Table 5, entries 4 and 5). The enantioselectivity in the case of the acid chloride was surprisingly low. As a reason, we assumed that racemization of **36b** caused by basic species in the reaction mixture occurred, which deprotonated the ester already formed as it is even more acidic than the starting compound **32**. With benzophenone, an excellent enantiomeric excess of 99% *ee* for **36c** resulted. The stereochemistry was assigned in analogy to the results obtained for the substitution of *S*-benzyl thiocarbamate **15**.

NMR Spectroscopic Investigations

If the epimeric complexes are configurationally stable at low temperatures (−78 °C) but equilibrate at higher temperatures (−30 °C), it should be possible to follow this epimerization process by means of NMR spectroscopy.[31,32] We expected to see signals for two species at lower temperatures, an increase in intensity for one group of signals with a corresponding decrease in intensity for the other group upon warming the sample, and finally, at higher temperatures, a single set of signals belonging to one single epimeric complex within the sample.

The following NMR spectroscopic experiment was performed: *S*-benzyl thiocarbamate **15** was deprotonated in [D_8]toluene at −78 °C in the presence of 1.1 equivalents each of bis(oxazoline) **18** and *n*Bu^{6}Li (see Experimental Section for details). The sample was directly subjected to NMR spectroscopy, during which it was kept first at −60 °C. The first ^{1}H NMR spectrum taken of this sample showed the well-known signals of the substrate and the diamine, as well as a new set of double signals. A second ^{1}H NMR spectrum taken after five minutes at −60 °C showed only the new double dataset (Figure 8). Within this dataset, the phenyl protons of the two epimeric complexes appear separately and can be distinctly identified; the result is 10 distinguishable signals. From the TOCSY experiments, the signals can be unambiguously assigned to the respective diastereomeric complexes. One set of signals has only half the intensity of the other, which indicates a diastereomer ratio of the epimeric complexes of about 2:1. The same ratio can be deduced from the ^{6}Li NMR spectrum of this sample at this temperature, in which two peaks were detected (Figure 10). Cooling of the sample to −80 °C did not affect the diastereomer ratio, which was deduced from both ^{1}H and ^{6}Li NMR spectra within the limits of accuracy (Figures 9 and 10).

Warming of the sample to −50 °C started the epimerization process, which was accelerated by further heating. After about 2 h at −50 to −40 °C, the sample was complete-

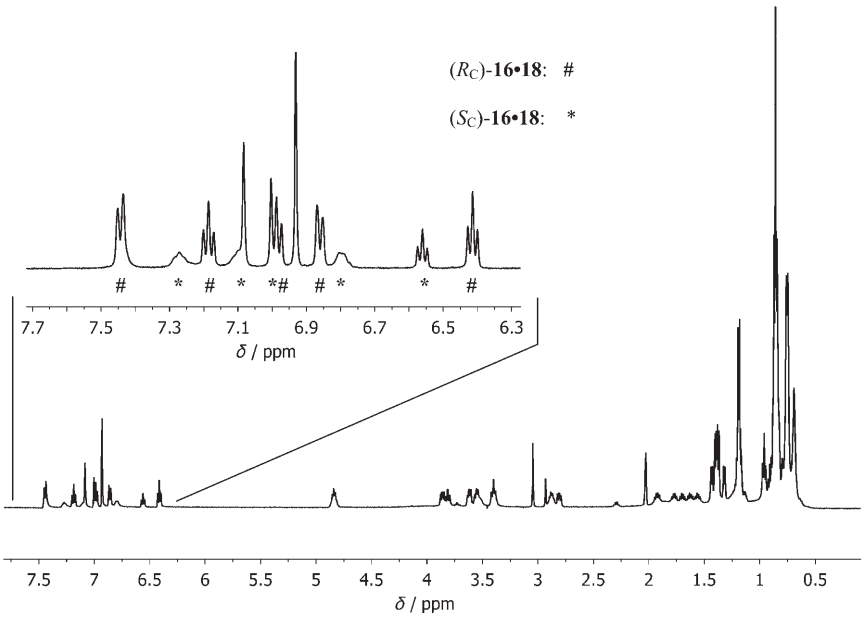


Figure 8. ^{1}H NMR spectrum of the 2:1 mixture of the epimeric complex **16**·**18** at −60 °C.

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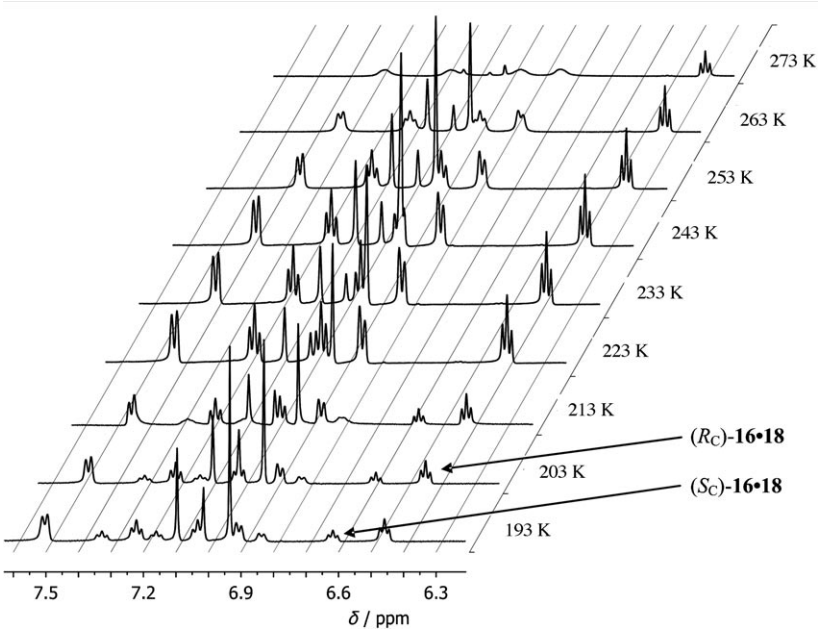


Figure 9. ^{1}H NMR spectra of the 2:1 mixture of the epimeric complex **16·18** (6.3–7.6 ppm) at different temperatures.

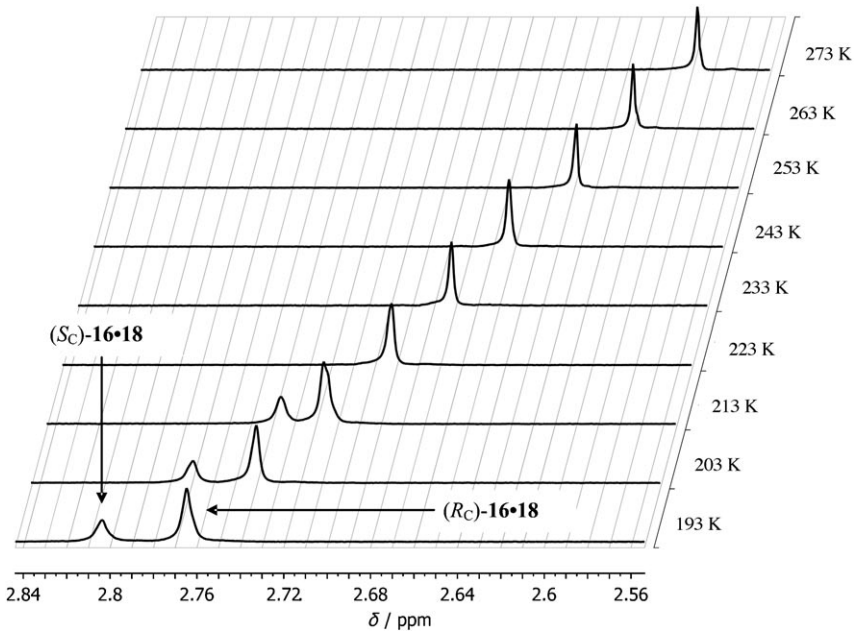
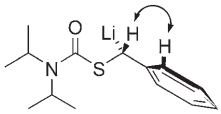


Figure 10. ^{6}Li NMR spectra of the 2:1 mixture of the epimeric complex **16·18** at different temperatures.

ly equilibrated in the NMR tube. Only one set of signals remained, which indicates a diastereomer ratio of $\geq$95:5. When the sample was cooled again, this diastereomer ratio did not change.

On the basis of the ^{13}C NMR spectrum, an η^1-bound species must be assumed. The signal of the lithium-bearing benzylic carbon atom appeared as a triplet ($^{1}J_{Li,C}$ = 3.5 Hz). As this is the only triplet in the spectrum, the lithium atom cannot be η^2- or η^3-bound. Besides, a monomeric complex species is most likely. The structure of the whole complex must be considerably rigid at −60 °C to −80 °C. This can be concluded from the distinct signals of the phenylic protons, which indicate, on the NMR timescale, a fixed position of the phenyl ring. Further proof for this statement can be given by an NOE enhancement of the signal of the remaining benzylic proton: for this purpose, a 1D NOESY experiment was conducted.[33] Selective irradiation at the frequency of the benzylic proton produced a single signal for one of the *ortho* protons of the phenyl ring (compare Scheme 9). This hindered rotation of the phenyl ring most probably originates from the ligand in the complex, which exhibits a great steric influence on the rotation of that ring.



Scheme 9. NOE experiment with (R_C)-**16·18** (ligand not shown for simplicity).

The NMR spectroscopic investigations clearly underline the statements deduced from the substitution experiments described above. Although the sample used for NMR spectroscopy equilibrated within less than 2 h at −50 to −40 °C, we recommend that the lithiated species is stirred in the reaction flask at higher temperatures of −30 °C for at least 3 h to ensure that epimerization is completed.

Conclusions

We have presented a novel methodology for the synthesis of highly enantioenriched, differently substituted *S*-benzyl thiocarbamates **20**. We demonstrated that substitution reactions with different types of electrophiles proceed under strict inversion of configuration. As the thiocarbamates can be deprotected,[8] this lithiation protocol can be used for the syn-

thesis of differently substituted highly enantioenriched secondary arylmethanethiols. NMR spectroscopic investigations of the epimeric complexes visualized and confirmed the temperature-dependent epimerization process, which indicates an η^1-bound lithium species.

Experimental Section

General Remarks

All reactions were performed under argon atmosphere. Details regarding purification of solvents, reagents, and a list of the applied analysis systems can be found in the preceding paper in this issue.[3i] TMEDA was distilled from powdered CaH_2 and stored under argon. Pivaldehyde, benzaldehyde, and acetone were distilled prior to use. Borate **27** was used without purification. E = Et_2O, P = pentane, TBME = *tert*-butyl methyl ether. HPLC: Waters 600E multisolvent delivery system and 996 PDA detector or Knauer Smartline UV detector 2600, Pump 1000 and Manager 5000 or Agilent Technologies 1200 Series (Bin Pump, ALS, TCC, DAD). NMR spectroscopic investigations were performed on a Varian Inova 500-MHz spectrometer. Crystallographic data: Datasets were collected on a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction DenzoSMN,[34] absorption correction SORTAV,[35] Denzo,[36] structure solution SHELXS-97,[37] structure refinement SHELXL-97,[38] graphics SCHAKAL.[39]

Syntheses

15: NaH (60% in mineral oil, 920 mg, 23 mmol, 1.15 equiv) was suspended in dry THF (30 mL). The mixture was cooled to 0°C, and phenylmethanethiol (2.48 g, 20 mmol, 1.0 equiv) dissolved in dry THF (5 mL) was slowly added. After evolution of hydrogen stopped, a solution of *N,N*-diisopropylcarbamoyl chloride (3.76 g, 23 mmol, 1.15 equiv) in dry THF (10 mL) was added such that the reaction temperature did not rise. The reaction mixture was allowed to warm to room temperature and was stirred at this temperature for 2 days. Afterwards, the reaction flask was immersed in an ice bath, and water (25 mL) and HCl (2 N, 3 mL) were added to give a clear yellowish solution. *tert*-Butyl methyl ether (TBME; 50 mL) was added, and after separation of phases, the aqueous phase was extracted with TBME (3×20 mL). The combined organic layers were washed successively with saturated $NaHCO_3$ and brine. After drying over anhydrous $MgSO_4$, filtering through glass wool, and removal of the solvent, the crude product was subjected to column chromatography (E/P = 1:15) to afford pure *N,N*-diisopropylthiocarbamic acid *S*-benzyl ester (**15**; 4.63 g, 18.4 mmol, 92%) as a white crystalline solid. R_f = 0.47 (E/P = 1:1); t_R = 13.4 min (HP-5); m.p.: 65°C (Et_2O); IR (ATR): $\tilde{\nu}$ = 3030 (m, C–H_{arom}), 2997, 2973, 2936, 2876 (s, C–H_{aliph}), 1647 (s, C=O), 1494 (m), 1458 (s), 1369 (m), 1288 (s), 1209 (s), 1152 (m), 1115 (m), 1033 (s), 912 (m), 818 (s), 776 (s), 706 (s), 667 (s), 624 cm^{-1} (s); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.56 (br s, 12H, $((H_3C)_2HC)_2N$), 3.74 (br s, 1H, $((H_3C)_2HC)_2N$), 4.34 (br s, 1H, $((H_3C)_2HC)_2N$), 4.38 (s, 2H, $CH_{benzylic}$), 7.43–7.63 ppm (m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.5 ($((H_3C)_2HC)_2N$), 34.4 ($C_{benzylic}$), 48.4 ($((H_3C)_2HC)_2N$), 126.9, 128.5, 129.0, 138.1 (Ph), 165.0 ppm (NC=O); MS (EI, 70 eV): *m/z* (%) = 251 (36) $[M]^+$, 151 (6), 128 (66) $[Cb]^+$, 95 (18), 86 (100), 57 (42); elemental analysis: calcd (%) for $C_{14}H_{21}NOS$ (251.39): C 66.89, H 8.42, N 5.57; found: C 66.86, H 8.52, N 5.50.

34: DIAD (3.34 g, 16.5 mmol, 1.1 equiv) was added in a dropwise manner to a solution of PPh_3 (4.33 g, 16.5 mmol, 1.1 equiv) in THF (30 mL) at 0°C over a period of 30 min, and the reaction mixture was stirred for 60 min under argon atmosphere. A white precipitate was formed. A mixture of (2-ethylphenyl)methanol (2.04 g, 15 mmol, 1.0 equiv) and thioacetic acid (1.25 g, 16.5 mmol, 1.1 equiv) in THF (8 mL) of was added dropwise over a period of 5 min, and the mixture was stirred at 0°C for 1 h followed by 3 h (until the formation of a clear solution) at room temperature. The solvent was evaporated under vacuum, and pentane (100 mL) was added to the reaction mixture. The precipitated triphenylphosphine oxide was filtered off, and the crude product was subjected to column chromatography (E/P = 1:50→1:30) to afford pure **34** (2.28 g, 11.7 mmol, 78%) as a slightly yellowish oil. R_f = 0.54 (E/P = 1:8); t_R = 9.1 min (HP-5); IR (ATR): $\tilde{\nu}$ = 3063, 3020 (m, C–H_{arom}), 2967, 2934, 2874 (ms, C–H_{aliph}), 1690 (s, C=O), 1491 (m), 1453 (s), 1427 (m), 1353 (m), 1133 (s), 1102 (m), 1056 (m), 956 (s), 891 (m), 812 (m), 756 (m), 731 (m), 690 (s), 632 cm^{-1} (s); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.23 (t, $^3J_{C,H}$ = 7.5 Hz, 3H, H_3CCH_2), 2.33 (s, 3H, $C(O)CH_3$), 2.66 (q, $^3J_{C,H}$ = 7.5 Hz, 2H, H_3CCH_2), 4.16 (s, 2H, $CH_{benzylic}$), 7.08–7.30 ppm (m, 4H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.1 (H_3CCH_2), 25.5 (H_3CCH_2), 30.1 ($CH_3(O)C$), 30.9 ($C_{benzylic}$), 126.2, 127.8, 128.6, 130.2, 134.4, 142.4 (Ph), 195.2 ppm (C=O); MS (EI, 70 eV): *m/z* (%) = 194 (18) $[M]^+$, 176 (3), 165 (2), 151 (4), 135 (5), 118 (100), 104 (8), 91 (17), 71 (16), 57 (27), 43 (47); elemental analysis: calcd (%) for $C_{11}H_{14}OS$ (194.29): C 68.00, H 7.48; found: C 67.98, H 7.48.

32: A solution of **34** (2.20 g, 11.3 mmol, 1.0 equiv), obtained as above, in Et_2O (20 mL) was added in a dropwise manner at −30°C to a well-stirred suspension of $LiAlH_4$ (0.47 g, 12.4 mmol, 1.1 equiv) in Et_2O (30 mL). The resulting solution was stirred at −30°C for 60 min (TLC control). Afterwards, the reaction flask was cooled to 0°C, and the reaction was quenched by careful addition of water (10 mL). After filtration of the aluminum salts followed by evaporation of the solvent from the filtrate, the crude thiol was obtained as a colorless liquid. The thiol was used in the subsequent step without further purification. A solution of the crude thiol in anhydrous THF (10 mL) was added to a stirred suspension of NaH (60% in mineral oil, 0.59 g, 14.7 mmol, 1.3 equiv) in anhydrous THF (30 mL). The resulting solution was stirred at room temperature for 15 min, and a solution of *N,N*-diisopropylcarbamoyl chloride (2.4 g, 14.7 mmol, 1.3 equiv) in anhydrous THF (10 mL) was added. This mixture was stirred at room temperature for 2 days. The reaction flask was then cooled to 0°C, and water (10 mL) and HCl (2 N, 3 mL) were slowly injected into the flask. The layers were separated, and the aqueous layer was extracted with TBME (3×20 mL). The collective organic phase was dried over anhydrous $MgSO_4$, filtered through glass wool, and concentrated under reduced pressure to give the crude thiocarbamate, which was subjected to column chromatography (E/P = 1:30) to furnish *N,N*-diisopropylthiocarbamic acid *S*-(2-ethyl-benzyl) ester **32** (2.80 g, 10.1 mmol, 89%) as a colorless oil. R_f = 0.41 (E/P = 1:15); t_R = 13.7 min (HP-5); IR (ATR): $\tilde{\nu}$ = 3063 (m, C–H_{arom}), 2970, 2934, 2874 (s, C–H_{aliph}), 1653 (s, NC=O), 1491 (m), 1454 (s), 1421 (s), 1373 (m), 1281 (s), 1232 (m), 1211 (s), 1151 (m), 1113 (m), 1037 (s), 912 (m), 820 (s), 757 (s), 730 (s), 667 (s), 631 cm^{-1} (s); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.24 (t, $^3J_{C,H}$ = 8.2 Hz, 3H, H_3CCH_2), 1.28 (br s, 12H, $((H_3C)_2HC)_2N$), 2.72 (q, $^3J_{C,H}$ = 8.2 Hz, 2H, H_3CCH_2), 3.53 (br s, 1H, $((H_3C)_2HC)_2N$), 4.12 (br s, 1H, $((H_3C)_2HC)_2N$), 4.16 (s, 2H, $CH_{benzylic}$), 7.08–7.36 ppm (m, 4H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7 (H_3CCH_2), 20.3 ($((H_3C)_2HC)_2N$), 25.5 (H_3CCH_2), 32.2 ($C_{benzylic}$), 47.9 ($((H_3C)_2HC)_2N$), 126.0, 127.5, 128.5, 130.4, 134.9, 142.8 (Ph), 165.4 ppm (NC=O); MS (EI, 70 eV): *m/z* (%) = 279 (31) $[M]^+$, 204 (1), 160 (2), 136 (3), 128 (73) $[Cb]^+$, 104 (4), 86 (100), 58 (8); elemental analysis: calcd (%) for $C_{16}H_{25}NOS$ (279.44): C 68.77, H 9.02, N 5.01; found: C 68.60, H 9.13, N 4.91.

General procedure for the asymmetric deprotonation of **15** and **32** (GPA): *S*-Benzyl thiocarbamate **15** or **32** (75 mg/84 mg, 0.30 mmol, 1.0 equiv) was dissolved in toluene (3 mL), the appropriate ligand **18** or **19** (0.36 mmol, 1.2 equiv) was added, and the reaction flask was cooled to −78°C. *s*BuLi (1.2–1.3 M in hexane/cyclohexane = 92:8, 0.36 mmol, 1.2 equiv) was injected into this mixture in a dropwise manner. The reaction mixture was stirred at −78°C for 5 min before it was warmed to −30°C and stirred at this temperature for 4 h. Upon cooling to −78°C again, the appropriate electrophile (0.45–1.5 mmol, 1.5–5.0 equiv) was injected, and the reaction mixture was stirred for 4–12 h until no more starting material was detected by TLC. The reaction was then quenched with methanol (0.5 mL) followed by water (1 mL) and HCl (2 N, 0.5 mL). The layers were separated, and the aqueous layer was extracted with TBME (3×10 mL). The collective organic phase was washed with saturated $NaHCO_3$, dried over anhydrous $MgSO_4$, filtered through glass wool, and concentrated under reduced pressure to give the crude product. The crude product was subjected to column chromatography (E/P) to afford the pure products.

General procedure for the nonstereoselective deprotonation of **15** and **32** (GPB): *S*-Benzyl thiocarbamate **15** or **32** (125 mg/140 mg, 0.50 mmol, 1.0 equiv) was dissolved in Et_2O (5 mL). TMEDA (70 mg, 0.60 mmol, 1.2 equiv) was added, and the reaction flask was cooled to −78 °C. Afterwards, *s*BuLi (1.2–1.3 M in hexane/cyclohexane = 92:8, 0.60 mmol, 1.2 equiv) was injected in a dropwise manner, and the reaction mixture was stirred at −78 °C for 2 h. The appropriate electrophile (0.6–1.5 mmol, 1.2–3.0 equiv) was then injected, and the reaction mixture was stirred for 2–4 h until no more starting material was detected by TLC. Workup and purification were performed as described in GPA.

17: (−)-(*S*)-*N*,*N*-Diisopropylthiocarbamic acid *S*-(1-phenylethyl) ester: White solid, yield: 98 %. $R_f = 0.44$ (E/P = 1:8); $t_R = 13.4$ (HP-5), 19.9 min (HP1701); m.p.: 74 °C (Et_2O); $[\alpha]_D^{20} = -147.4$ ($c = 1.36$, $CHCl_3$); IR (ATR): $\tilde{\nu} = 3029$ (m, C−H_{arom}), 2974, 2929, 2869 (s, C−H_{aliph}), 1648 (s, NC=O), 1494 (m), 1470 (s), 1452 (m), 1420 (m), 1371 (m), 1280 (s), 1212 (s), 1152 (m), 1113 (m), 1081 (m), 1039 (s), 962 (m), 911 (s), 817 (s), 760 (s), 692 (s), 666 (s), 624 (s), 576 cm^{-1} (m); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.21$ (br d, $^3J_{N,H} = 7.2$ Hz, 12 H, $((H_3C)_2HC)_2N$), 1.64 (d, $^3J_{C,H} = 7.6$ Hz, 3 H, CH_3), 3.71 (br s, 2 H, $((H_3C)_2HC)_2N$), 4.64 (q, $^3J_{C,H} = 7.6$ Hz, 1 H, $CH_{benzylic}$), 7.05–7.39 ppm (m, 5 H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 20.5 ($((H_3C)_2HC)_2N$), 23.1 (CH_3), 43.7 ($C_{benzylic}$), 47.9 ($((H_3C)_2HC)_2N$), 126.9, 127.3, 128.3, 143.3 (Ph), 164.8 ppm (NC=O); MS (ESI): $m/z =$ 288.1393 $[M+H]^+$; elemental analysis: calcd (%) for $C_{15}H_{23}NOS$ (265.42): C 67.88, H 8.73, N 5.28; found: C 67.89, H 8.83, N 5.33; HPLC: CHIRA GROM 1 (2 × 250 mm), $\lambda = 210$ nm, *n*-hexane/*i*PrOH = 10000:1, 0.3 mL min^{-1}, $t_R(+) = 11.3$ min, $t_R(-) = 13.2$ min, 96 % *ee* (with **18**; Table 2, entry 2).

21: (−)-(*R*)-*N*,*N*-Diisopropylthiocarbamic acid *S*-(1-phenyl-1-trimethylsilanylmethyl) ester: According to GPA, white solid, yield: 90 %. $R_f = 0.48$ (E/P = 1:8); $t_R = 14.3$ min (HP-5); m.p.: 86 °C (Et_2O); $[\alpha]_D^{20} = -166.5$ ($c =$ 1.01, $CHCl_3$); IR (ATR): $\tilde{\nu} = 3078$, 3024 (m, C−H_{arom}), 2969, 2894 (s, C−H_{aliph}), 1653 (s, NC=O), 1486 (m), 1450 (m), 1423 (s), 1370 (m), 1279 (s), 1246 (m), 1214 (m), 1152 (m), 1115 (m), 1037 (s), 914 (m), 860 (s), 838 (s), 819 (s), 735 (s), 697 (s), 664 (m), 624 cm^{-1} (s); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.06$ (s, 9 H, $(H_3C)_3Si$), 1.24 (br d, $^3J_{N,H} = 7.2$ Hz, 6 H, $((H_3C)HC(CH_3))_2N$), 1.32 (br d, $^3J_{N,H} = 7.2$ Hz, 6 H, $((H_3C)HC(CH_3))_2N$), 3.88 (br s, 2 H, $((H_3C)_2HC)_2N$), 4.07 (s, 1 H, $CH_{benzylic}$), 7.05–7.42 ppm (m, 5 H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -2.6$ ($(H_3C)_3Si$), 20.2 ($((H_3C)_2HC)_2N$), 35.9 ($C_{benzylic}$), 48.0 ($((H_3C)_2HC)_2N$), 125.0, 127.8, 127.9, 142.6 (Ph), 165.1 ppm (NC=O); MS (ESI): $m/z = 324.1806$ $[M+H]^+$, 346.1631 $[M+Na]^+$; elemental analysis: calcd (%) for $C_{17}H_{29}NOSSi$ (323.57): C 63.10, H 9.03, N 4.33; found: C 63.05, H 9.01, N 4.18; HPLC: CHIRA GROM 1 (2 × 250 mm), $\lambda = 210$ nm, *n*-hexane/*i*PrOH = 10000:1, 0.2 mL min^{-1}, $t_R(+) = 19.4$ min, $t_R(-) = 21.2$ min, 96 % *ee* (with **18**; Table 2, entry 5).

In situ experiment with **18**: *S*-Benzyl thiocarbamate **15** (125 mg, 0.3 mmol, 1.0 equiv), bis(oxazoline) **18** (116 mg, 0.36 mmol, 1.2 equiv), and trimethylsilyl chloride (65 mg, 0.6 mmol, 2 equiv) were dissolved in dry toluene (3 mL). The reaction flask was cooled to −78 °C, *s*BuLi (1.2–1.3 M in hexane/cyclohexane = 92:8, 0.60 mmol, 1.2 equiv) was injected in a dropwise manner, and the reaction mixture was stirred for 30 min. The reaction was then quenched with methanol (0.5 mL) followed by water (1 mL) and HCl (2 N, 0.5 mL). Workup was performed according to GPA. Yield: 52 %. $[\alpha]_D^{20} = +50.8$ ($c = 0.72$, $CHCl_3$); HPLC: CHIRA GROM 1 (2 × 250 mm), $\lambda = 210$ nm, *n*-hexane/*i*PrOH = 10000:1, 0.2 mL min^{-1}, $t_R(+) = 19.4$ min, $t_R(-) = 21.2$ min, 28 % *ee*.

In situ experiment with **19**: *S*-Benzyl thiocarbamate **15** (125 mg, 0.3 mmol, 1.0 equiv), (−)-sparteine (**19**; 84 mg, 0.36 mmol, 1.2 equiv), and trimethylsilyl chloride (65 mg, 0.6 mmol, 2 equiv) were subjected to reaction as described above. Yield: 66 %. HPLC: CHIRA GROM 1 (2 × 250 mm), $\lambda = 210$ nm, *n*-hexane/*i*PrOH = 10000:1, 0.2 mL min^{-1}, $t_R(+) =$ 19.4 min, $t_R(-) = 21.2$ min, 16 % *ee*.

22: (−)-(*S*)-*N*,*N*-Diisopropylthiocarbamic acid *S*-(1-phenyl-1-tributylstannnylmethyl) ester: Colorless liquid, yield: 78 %. $R_f = 0.41$ (E/P = 1:20); $t_R = 14.3$ min (HP-5); $[\alpha]_D^{20} = -42.6$ ($c = 0.96$, $CHCl_3$); IR (ATR): $\tilde{\nu} = 3054$, 3023 (m, C−H_{arom}), 2955, 2971, 2853 (s, C−H_{aliph}), 1626 (s, NC=O), 1490 (m), 1451 (m), 1422 (s), 1376 (m), 1286 (s), 1212 (m), 1151 (m), 1115 (m), 1075 (s), 1036 (s), 960 (m), 912 (m), 874 (s), 823 (s), 776 (m), 733 (m), 695 (s), 669 (m), 633 cm^{-1} (m); ^1H NMR (300 MHz, $CDCl_3$): $\delta =$ 0.81–0.91 (m, 9 H, $(H_3C(CH_2)_3)_3Sn$), 1.11–1.69 (m, 30 H, $((H_3C)HC(CH_3))_2N$, $(H_3C(CH_2)_3)_3Sn$), 3.52 (br s, 1 H, $((H_3C)_2HC)_2N$), 4.22 (br s, 1 H, $((H_3C)_2HC)_2N$), 4.06 (s, 1 H, $CH_{benzylic}$), 6.94–7.36 ppm (m, 5 H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 10.9$ ($(H_3CCH_2CH_2CH_2)_3Sn$), 13.5 ($(H_3C(CH_2)_3)_3Sn$), 20.4 ($((H_3C)_2HC)_2N$), 27.1 ($(H_3CCH_2CH_2CH_2)_3Sn$), 28.5 ($(H_3CCH_2CH_2CH_2)_3Sn$), 30.4 ($C_{benzylic}$), 48.2 ($((H_3C)_2HC)_2N$), 124.6, 126.5, 128.5, 145.4 (Ph), 166.9 ppm (NC=O); MS (ESI): $m/z = 542.2456$ $[M+H]^+$, 564.2284 $[M+Na]^+$; elemental analysis: calcd (%) for $C_{26}H_{47}NOSSn$ (540.43): C 57.78, H 8.77, N 2.59; found: C 57.85, H 8.90, N 2.47; HPLC: Chiralcel OD-H (4.6 × 250 mm), $\lambda = 210$ nm, *n*-hexane/*i*PrOH = 400:1, 1.0 mL min^{-1}, $t_R(+) = 30.1$ min, $t_R(-) = 36.0$ min, 98 % *ee* (with **18**; Table 3, entry 1).

23: With gaseous carbon dioxide as electrophile: As described in GPA, the lithiated species were generated and equilibrated by employing **18**. As the electrophile, dried and precooled gaseous carbon dioxide was bubbled through the reaction mixture over a period of 10–15 min. After a further 1 h of stirring at −78 °C, the reaction was carefully quenched with methanol (0.5 mL) and water (1 mL). Workup was performed as described in GPA. The crude acid was directly dissolved in Et_2O, and a solution of diazomethane in Et_2O was added at room temperature until the yellowish color of the reaction mixture remained. The solution was stirred for 1 h. To destroy the remaining diazomethane, silica gel was added, and the suspension was stirred for a further 1 h. The solvent was removed under reduced pressure, and the crude product was thus adsorbed onto silica gel. This mixture was directly subjected to column chromatography (E/P = 1:3) to yield (−)-(*R*)-*N*,*N*-diisopropylcarbamoylsulfanylphenylacetic acid methyl ester (**23**) as a white crystalline solid. Yield: 53 %. $R_f = 0.13$ (E/P = 1:8); $t_R = 14.7$ min (HP-5); m.p.: 51 °C (Et_2O); $[\alpha]_D^{20} = -157.4$ ($c = 1.10$, $CHCl_3$); IR (ATR): $\tilde{\nu} = 3086$, 3063, 3031 (m, C−H_{arom}), 2973, 2952, 2880, 2841 (s, C−H_{aliph}), 1742 (s, C=O), 1656 (s, NC=O), 1496 (m), 1453 (m), 1422 (m), 1371 (m), 1284 (s), 1211 (s), 1152 (m), 1036 (s), 1011 (m), 912 (m), 819 (s), 733 (m), 698 (s), 668 (m), 625 cm^{-1} (s); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.23$ (br s, 12 H, $((H_3C)_2HC)_2N$), 3.31–3.97 (br s, 2 H, $((H_3C)_2HC)_2N$), 3.67 (s, 3 H, CH_3O), 5.22 (s, 1 H, $CH_{benzylic}$), 7.11–7.41 ppm (m, 5 H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.3$ ($((H_3C)_2HC)_2N$), 48.5 ($((H_3C)_2HC)_2N$), 52.0 (CH_3O), 52.9 ($C_{benzylic}$), 128.2, 128.6, 128.8, 135.1 (Ph), 163.1 (NC=O), 171.6 ppm (C=O); MS (ESI): $m/z = 332.1287$ $[M+Na]^+$; elemental analysis: calcd (%) for $C_{16}H_{23}NO_3S$ (309.42): C 62.11, H 7.49, N 4.53; found: C 61.85, H 7.69, N 4.44; HPLC: Chiralcel OD-H (4.6 × 250 mm), $\lambda = 210$ nm, *n*-hexane/*i*PrOH = 120:1, 1.0 mL min^{-1}, $t_R(+) = 6.7$ min, $t_R(-) = 9.4$ min, 99 % *ee* (with **18**; Table 3, entry 2).

23: With methyl chloroformate as electrophile: According to GPA with methyl chloroformate as electrophile and **18** as chiral ligand, (−)-(*R*)-**23** was obtained as a white crystalline solid. Yield: 99 %. HPLC: Chiralcel OD-H (4.6 × 250 mm), $\lambda = 210$ nm, *n*-hexane/*i*PrOH = 120:1, 1.0 mL min^{-1}, $t_R(+) = 6.7$ min, $t_R(-) = 9.4$ min, 96 % *ee*.

24: *N*,*N*-Diisopropylthiocarbamic acid *S*-(2-hydroxy-3,3-dimethyl-1-phenylbutyl) ester: According to GPA, diastereomeric species (−)-(*R*,*S*)-**24** and (−)-(*R*,*R*)-**24** were generated and separated by column chromatography on silica gel with E/P = 1:4 as eluent.

(−)-(*R*,*S*)-**24**: White crystalline solid, yield: 13 %. $R_f = 0.32$ (E/P = 1:4); $t_R = 16.5$ min (HP-5); m.p.: 113 °C (Et_2O); $[\alpha]_D^{20} = -74.0$ ($c = 0.10$, $CHCl_3$); IR (ATR): $\tilde{\nu} = 3459$ (OH), 3061, 3029 (m, C−H_{arom}), 2971, 2950, 2868 (s, C−H_{aliph}), 1619 (s, NC=O), 1465 (m), 1452 (m), 1424 (s), 1371 (m), 1285 (s), 1240 (m), 1207 (m), 1151 (m), 1079 (m), 1069 (m), 1036 (s), 1013 (m), 913 (m), 821 (s), 741 (s), 697 (s), 637 (m), 625 cm^{-1} (s); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.74$ (s, 9 H, $(H_3C)_3C$), 1.19 (br s, 12 H, $((H_3C)_2HC)_2N$), 2.17 (br s, 1 H, HO), 3.47 (br s, 1 H, $((H_3C)_2HC)_2N$), 3.71 (br s, 1 H, C*H*(OH)), 3.97 (br s, 1 H, $((H_3C)_2HC)_2N$), 4.87 (d, $^3J_{C,H} =$ 2.4 Hz, 1 H, $CH_{benzylic}$), 7.11–7.25 (m, 3 H, Ph), 7.39–7.46 ppm (m, 2 H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.6$ ($((H_3C)_2HC)_2N$), 26.7 ($(H_3C)_3C$), 35.9 ($(H_3C)_3C$), 48.5 ($((H_3C)_2HC)_2N$), 51.9 ($C_{benzylic}$), 82.6 (CH(OH)), 127.3, 128.2, 129.9, 139.6 (Ph), 164.1 ppm (NC=O); MS (ESI): $m/z = 338.2156$ $[M+H]^+$, 360.1973 $[M+Na]^+$, 697.4050 $[2M+Na]^+$; elemental analysis: calcd (%) for $C_{19}H_{31}NO_2S$ (337.52): C 67.61, H 9.26, N 4.15; found: C 67.45, H 9.20, N 3.82; HPLC: Chiralcel OD-H

(4.6×250 mm), λ=210 nm, *n*-hexane/*i*PrOH=120:1, 1.0 mL min^{-1}, $t_R(+)$=7.3 min, $t_R(-)$=9.7 min, 94% *ee* (with **18**; Table 3, entry 4).

(−)-(*R*,*R*)-**24**: White crystalline solid, yield: 45%. R_f=0.23 (E/P=1:4); t_R=16.6 min (HP-5); m.p.: 134 °C (Et_2O); $[\alpha]_D^{20}=-147.1$ (*c*=1.04, $CHCl_3$); IR (ATR): $\tilde{\nu}$=3462 (OH), 3059, 3028 (m, C−H$_{arom}$), 2969, 2902, 2869 (s, C−H$_{aliph}$), 1617 (s, NC=O), 1453 (m), 1425 (s), 1370 (m), 1285 (s), 1240 (m), 1207 (m), 1151 (m), 1114 (m), 1079 (s), 1035 (s), 914 (m), 884 (s), 822 (s), 776 (m), 741 (s), 698 (s), 670 (m), 626 cm^{-1} (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.79 (s, 9H, $(H_3C)_3C$), 1.19 (br s, 12H, $((H_3C)_2HC)_2N$), 3.28 (br s, 1H, HO), 3.44 (br s, 1H, $((H_3C)_2HC)_2N$), 3.61 (br s, 1H, C*H*(OH)), 4.04 (br s, 1H, $((H_3C)_2HC)_2N$), 4.81 (d, $^3J_{C,H}$=7.2 Hz, 1H, CH$_{benzylic}$), 7.09–7.34 ppm (m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.5 ($((H_3C)_2HC)_2N$), 26.8 ($(H_3C)_3C$), 36.7 ($(H_3C)_3C$), 48.2 ($((H_3C)_2HC)_2N$), 52.8 (C$_{benzylic}$), 82.1 (CH(OH)), 127.2, 128.1, 128.6, 142.4 (Ph), 166.6 ppm (NC=O); MS (ESI): *m*/*z*=338.2150 $[M+H]^+$, 360.1967 $[M+Na]^+$, 697.4034 $[2M+Na]^+$; elemental analysis: calcd (%) for $C_{19}H_{31}NO_2S$ (337.52): C 67.61, H 9.26, N 4.15; found: C 67.60, H 9.42, N 4.12; HPLC: Chiralcel OD-H (4.6×250 mm), λ=210 nm, *n*-hexane/*i*PrOH=120:1, 1.0 mL min^{-1}, $t_R(+)$=7.2 min, $t_R(-)$=9.7 min, 94% *ee* (with **18**; Table 3, entry 4).

25: *N*,*N*-Diisopropylthiocarbamic acid *S*-(2-hydroxy-1,2-diphenylethyl) ester: According to GPA, diastereomeric species (−)-(*R*,*S*)-**25** and (−)-(*R*,*R*)-**25** were generated and separated by column chromatography on silica gel with E/P=1:4 as eluent.

(−)-(*R*,*S*)-**25**: Colorless, highly viscous oil, yield: 48%. R_f=0.57 (E/P=1:1); t_R=22.4 min (HP-5); $[\alpha]_D^{20}=-20.3$ (*c*=0.45, $CHCl_3$); IR (ATR): $\tilde{\nu}$=3341 (OH). 3066, 3030 (m, C−H$_{arom}$), 2974, 2941, 2891 (s, C−H$_{aliph}$), 1611 (s, NC=O), 1473 (m), 1452 (s), 1430 (s), 1375 (m), 1295 (s), 1209 (s), 1154 (m), 1136 (m), 1079 (m), 1062 (m), 1037 (s), 1002 (m), 913 (m), 821 (s), 757 (m), 733 (s), 697 (s), 676 (m), 634 (m), 571 cm^{-1} (m); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.31 (br s, 12H, $((H_3C)_2HC)_2N$), 3.13 (br s, 1H, HO), 3.56 (br s, 1H, $((H_3C)_2HC)_2N$), 4.20 (br s, 1H, $((H_3C)_2HC)_2N$), 5.04 (d, $^3J_{C,H}$=5.5 Hz, 1H, CH$_{benzylic}$), 5.22 (d, $^3J_{C,H}$=5.5 Hz, 1H, C*H*(OH)), 7.07–7.36 ppm (m, 10H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.5 ($((H_3C)_2HC)_2N$), 48.4 ($((H_3C)_2HC)_2N$), 55.6 (C$_{benzylic}$), 77.5 (CH(OH)), 127.2, 127.4, 127.5, 127.5, 128.0, 129.5, 137.6, 140.5 (Ph), 164.6 ppm (NC=O); MS (ESI): *m*/*z*=358.1868 $[M+H]^+$, 380.1660 $[M+Na]^+$; elemental analysis: calcd (%) for $C_{21}H_{27}NO_2S$ (357.51): C 70.55, H 7.61, N 3.92; found: C 70.42, H 7.91, N 3.76; HPLC: Chiralcel OD-H (4.6×250 mm), λ=210 nm, *n*-hexane/*i*PrOH=150:1, 1.0 mL min^{-1}, $t_R(-)$=29.8 min, $t_R(+)$=40.0 min, 97% *ee* (with **18**; Table 3, entry 5).

(−)-(*R*,*R*)-**25**: White solid, yield: 33%. R_f=0.51 (E/P=1:1); t_R=19.6 min (HP-5); m.p.: 80 °C (Et_2O); $[\alpha]_D^{20}=-121.1$ (*c*=0.57, $CHCl_3$); IR (ATR): $\tilde{\nu}$=3426 (O−H), 3064, 3028 (m, C−H$_{arom}$), 2970, 2932, 2868 (s, C−H$_{aliph}$), 1630 (s, NC=O), 1493 (m), 1452 (m), 1425.0 (m), 1373 (m), 1331 (m), 1286 (s), 1211 (m), 1156 (m), 1115 (m), 1089 (m), 1035 (s), 913 (m), 875 (m), 817 (s), 746 (m), 741 (s), 705 (s), 665 (m), 627(s), 589 cm^{-1} (m); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.32 (br s, 12H, $((H_3C)_2HC)_2N$), 3.07 (br s, 1H, $((H_3C)_2HC)_2N$), 4.67 (br s, 1H, $((H_3C)_2HC)_2N$), 4.72 (br s, 1H, HO), 4.86 (d, $^3J_{C,H}$=9.4 Hz, 1H, CH$_{benzylic}$), 4.95 (br d, 1H, C*H*(OH)), 7.08–7.36 ppm (m, 10H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.4 ($((H_3C)_2HC)_2N$), 48.2 ($((H_3C)_2HC)_2N$), 57.1 (C$_{benzylic}$), 79.2 (CH(OH)), 126.9, 127.3, 127.4, 127.8, 128.4, 128.7, 138.5, 142.3 (Ph), 167.1 ppm (NC=O); MS (ESI): *m*/*z*=358.1839 $[M+H]^+$, 380.1657 $[M+Na]^+$, 737.3412 $[2M+Na]^+$; elemental analysis: calcd (%) for $C_{21}H_{27}NO_2S$ (357.51): C 70.55, H 7.61, N 3.92; found: C 70.52, H 7.67, N 3.94; HPLC: Chiralcel OD-H (4.6×250 mm), λ=210 nm, *n*-hexane/*i*PrOH=150:1, 1.0 mL min^{-1}, $t_R(+)$=38.8 min, $t_R(-)$=47.5 min, 96% *ee* (with **18**; Table 3, entry 5).

26: (+)-(*R*)-*N*,*N*-Diisopropylthiocarbamic acid *S*-(2-hydroxy-1,2,2-triphenylethyl) ester: White solid, yield: 99%. R_f=0.38 (E/P=1:4); t_R=25.2 min (HP-5); m.p.: 154 °C (Et_2O); $[\alpha]_D^{20}=+57.5$ (*c*=0.96, $CHCl_3$); IR (ATR): $\tilde{\nu}$=3453 (O−H), 3061, 3032 (m, C−H$_{arom}$), 2991, 2970, 2932, 2871 (s, C−H$_{aliph}$), 1622 (s, NC=O), 1495 (m), 1448 (s), 1421 (s), 1282 (s), 1207 (s), 1150 (m), 1091 (m), 1056 (m), 1033 (s). 910 (m), 820 (s), 792 (m), 748 (m), 724 (s), 697 (s), 664 (m), 625 (m), 592 cm^{-1} (m); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.79–1.56 (br m, 12H, $((H_3C)_2HC)_2N$), 3.00 (s, 1H, HO), 3.41 (br s, 1H, $((H_3C)_2HC)_2N$), 4.01 (br s, 1H, $((H_3C)_2HC)_2N$), 5.86 (s, 1H, CH$_{benzylic}$), 6.93–7.43 (m, 13H, Ph), 7.65–7.74 ppm (m, 2H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.4 ($((H_3C)_2HC)_2N$), 48.2 (br, $((H_3C)_2HC)_2N$), 57.6 (C$_{benzylic}$), 82.6 ($(C(Ph)_2(OH))$, 125.9, 126.1, 126.4, 126.7, 126.8, 127.7, 127.9, 130.1, 140.0, 144.6, 146.1 (Ph), 163.8 ppm (NC=O); MS (ESI): *m*/*z*=434.2148 $[M+H]^+$, 465.1968 $[M+Na]^+$, 889.4025 $[2M+Na]^+$; elemental analysis: calcd (%) for $C_{27}H_{31}NO_2S$ (433.61): C 74.79, H 7.21, N 3.23; found: C 74.43, H 7.18, N 3.05; HPLC: Chiralcel OD-H (4.6×250 mm), λ=210 nm, *n*-hexane/*i*PrOH=100:1, 1.0 mL min^{-1}, $t_R(-)$=7.8 min, $t_R(+)$=8.8 min, 98% *ee* (with **18**; Table 3, entry 6).

28: *N*,*N*-Diisopropylthiocarbamic acid *S*-(1-phenylbut-3-enyl) ester: *rac*-**28**: Colorless oil, yield: 97%. R_f=0.56 (E/P=1:4); t_R=13.7 min (HP-5); IR (ATR): $\tilde{\nu}$=3064, 3029 (m, C−H$_{arom}$), 2997, 2973, 2934 (s, C−H$_{aliph}$), 1651 (s, NC=O), 1493 (m), 1453 (m), 1421 (s), 1371 (m), 1334 (m), 1277 (s), 1211 (m), 1150 (m), 1113 (m), 1035 (s), 992 (m), 912 (m), 819 (s), 766 (m), 731 (s), 697 (s), 667 (m), 623 cm^{-1} (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.24 (br s, 12H, $((H_3C)_2HC)_2N$), 2.62–2.96 (m, 2H, $H_2CCHCH_AH_B$), 3.78 (br s, 2H, $((H_3C)_2HC)_2N$), 4.62 (dd, $^3J_{C,H}$=8.6, 8.6 Hz, 1H, CH$_{benzylic}$), 4.95 (dd, $^3J_{C,H}$=10.4, 1.3 Hz, 1H, $H_{trans}H_{cis}CCHCH_AH_B$), 5.01 (dd, $^3J_{C,H}$=17.1 Hz, $^2J_{C,H}$=1.3 Hz, 1H, $H_{trans}H_{cis}CCHCH_AH_B$), 5.60–5.78 (m, 1H, H_2CCHCH_2), 7.15–7.40 ppm (m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.2 ($((H_3C)_2HC)_2N$), 41.6 (H_2CCHCH_2), 46.7 ($((H_3C)_2HC)_2N$), 47.9 (C$_{benzylic}$), 117.0 (H_2CCHCH_2), 127.0, 128.1, 128.4 (Ph), 135.3 (H_2CCHCH_2), 141.8 (Ph), 164.7 ppm (NC=O); MS (ESI): *m*/*z*=292.1718 $[M+H]^+$, 314.1547 $[M+Na]^+$; elemental analysis: calcd (%) for $C_{17}H_{25}NOS$ (291.45): C 70.06, H 8.65, N 4.81; found: C 69.86, H 8.74, N 4.74.

(−)-(*S*)-**28**: Colorless liquid, yield: 20%. $[\alpha]_D^{20}=-170.4$ (*c*=1.03, $CHCl_3$); HPLC: CHIRA GROM 2 (2×250 mm), λ=210 nm, *n*-hexane/*i*PrOH=4000:1, 0.3 mL min^{-1}, $t_R(+)$=9.0 min, $t_R(-)$=16.6 min, 82% *ee* (with **18**; Table 4, entry 2).

29: *rac*-*N*,*N*-Diisopropylthiocarbamic acid *S*-(2-hydroxy-2-methyl-1-phenylpropyl) ester: Colorless oil, yield: 30%. R_f=0.24 (E/P=1:1); t_R=15.4 min (HP-5); IR (ATR): $\tilde{\nu}$=3425 (O−H), 3060 (m, C−H$_{arom}$), 2972, 2933, 2877 (s, C−H$_{aliph}$), 1632 (s, NC=O), 1493 (m), 1452 (m), 1423.0 (s), 1370 (s), 1332 (m), 1278 (s), 1210 (m), 1150 (m), 1113 (m), 1035 (s), 956 (m), 911 (m), 817 (s), 739 (s), 701 (s), 666 (m), 631(s), 542 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.15 (s, 3H, $(H_3C)_2C(OH)$), 1.22 (br s, 12H, $((H_3C)_2HC)_2N$), 1.22 (s, 3H, $(H_3C)_2C(OH)$), 2.85 (br s, 1H, HO), 3.41 (br s, 1H, $((H_3C)_2HC)_2N$), 4.18 (br s, 1H, $((H_3C)_2HC)_2N$), 4.63 (s, 1H, CH$_{benzylic}$), 7.14–7.32 ppm (m, 5H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ=20.5 ($((H_3C)_2HC)_2N$), 26.0 ($(H_3C_A)_2C(OH)$), 29.1 ($(H_3C_B)_2C(OH)$), 48.7 ($((H_3C)_2HC)_2N$), 60.0 (C$_{benzylic}$), 73.2 ($((H_3C)_2C(OH))$), 127.1, 128.0, 129.4, 140.1 (Ph), 165.6 ppm (NC=O); MS (ESI): *m*/*z*=310.1841 $[M+H]^+$, 332.1661 $[M+Na]^+$, 641.3417 $[2M+Na]^+$; elemental analysis: calcd (%) for $C_{17}H_{27}NO_2S$ (309.47): C 65.98, H 8.79, N 4.53; found: C 65.99, H 8.79, N 4.31.

30: *N*,*N*-Diisopropylthiocarbamic acid *S*-[1-phenyl-1-(4,4,5,5-tetramethyl-[1.3.2]dioxaborolan-2-yl)methyl] ester: *rac*-**30**: White crystalline solid, yield: 62%. R_f=0.14 (E/P=1:1); t_R=16.3 min (HP-5); m.p.: 114 °C; IR (ATR): $\tilde{\nu}$=3058, 3025 (m, C−H$_{arom}$), 2972, 2926, 2854 (s, C−H$_{aliph}$), 1585 (s, NC=O), 1495 (m), 1452 (m), 1423 (s), 1375 (s), 1347 (s), 1325 (s), 1243 (m), 1202 (s), 1129 (s), 1089 (s), 1034 (s), 968 (m), 952 (m), 923 (m), 881 (m), 842 (m), 811 (m), 764 (s), 695 (s), 647 (m), 596 cm^{-1} (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.89 (s, 6H, $(H_3C)_2C$), 1.05 (s, 6H, $(H_3C)_2C$), 1.21–1.29 (m, 6H, $((H_3C)HC(CH_3))_2N$), 1.41–1.51 (m, 6H, $((H_3C)HC(CH_3))_2N$), 3.64 (sept, 1H, $((H_3C)_2HC)_2N$), 3.80 (s, 1H, CH$_{benzylic}$), 4.01 (sept, 1H, $((H_3C)_2HC)_2N$), 7.05–7.32 ppm (m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ=19.8, 19.9, 20.5, 20.7 ($(H_3C_{A/B})_2CC(H_3C_{A/B})_2$), 24.8 ($((H_3C)HC(CH_3))_2N$), 24.9 ($((H_3C)HC(CH_3))_2N$), 49.1 (C$_{benzylic}$), 53.0 ($((H_3C)_2HC)_2N$), 80.0 ($(H_3C)_2CC(H_3C)_2$), 125.3, 127.7, 128.7, 140.8 (Ph), 178.3 ppm (NC=O); MS (ESI): *m*/*z*=378.2283 $[M+H]^+$, 400.2102 $[M+Na]^+$; elemental analysis: calcd (%) for $C_{20}H_{32}BNO_3S$ (377.35): C 63.66, H 8.55, N 3.71; found: C 63.57, H 8.54, N 3.67.

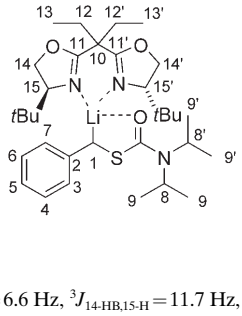
(+)-(*S*)-**30**: White crystalline solid, yield: 19%. $[\alpha]_D^{20}=+50.9$ (*c*=0.95, $CHCl_3$); 58% *ee* (^{1}H NMR (300 MHz, C_6D_6, 50 mol% (+)-Pr(hfc)$_3$): δ=4.89 ppm (CH$_{benzylic}$; $\Delta\delta$=0.03 ppm), (+)/(−)=3.9:1.0) (with **18**; Table 4, entry 6).

36b: (−)-(*R*)-*N*,*N*-Diisopropylcarbamoylsulfanyl-(2-ethylphenyl)acetic acid methyl ester: White crystalline solid, yield: 58%. R_f=0.69 (E/P=

1:1); $t_R = 13.3$ min (HP-5); $[\alpha]_D^{20} = -64.1$ ($c = 0.91$, $CHCl_3$); IR (ATR): $\tilde{\nu} =$ 3032 (m, C–H_{arom}), 2974, 2948, 2877 (s, C–H_{aliph}), 1745 (s, C=O), 1646 (s, NC=O), 1488 (m), 1454 (m), 1419 (m), 1369 (m), 1211 (s), 1199 (m), 1050 (s), 1018 (m), 1053 (m), 1007 (m), 877 (m), 826 (s), 727 (m), 670 (s), 668 (m), 542 cm^{-1} (m); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.25$ (t, $^3J_{C,H} = 7.2$ Hz, 3H, H_3CCH_2), 1.27 (br s, 12H, $((H_3C)_2HC)_2N$), 2.78 (q, $^3J_{C,H} = 7.2$ Hz, 2H, CH_3CH_2), 3.48 (br s, 2H, $((H_3C)_2HC)_2N$), 3.71 (s, 3H, CH_3O), 3.99 (br s, 2H, $((H_3C)_2HC)_2N$), 5.51 (s, 1H, $CH_{benzylic}$), 7.08–7.53 ppm (m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.4$ (H_3CCH_2), 20.2 ($((H_3C)_2HC)_2N$), 26.1 (H_3CCH_2), 47.9 (CH_3O), 49.8 ($((H_3C)_2HC)_2N$), 52.9 ($C_{benzylic}$), 126.3, 128.4, 128.7, 129.2, 132.6, 142.7 (Ph), 164.1 (NC=O), 171.8 ppm (C=O); MS (ESI): $m/z = 338.1786$ $[M+H]^+$, 360.1601 $[M+Na]^+$, 697.3308 $[2M+Na]^+$; elemental analysis: calcd (%) for $C_{18}H_{27}NO_3S$ (337.48): C 64.08, H 8.06, N 4.15; found: C 64.00, H 7.96, N 4.07; HPLC: Chiralcel OD-H (4.6×250 mm), $\lambda = 210$ nm, *n*-hexane/*i*PrOH = 95:5, 1.0 mL min^{-1}, $t_R(+) = 7.8$ min, $t_R(-) = 9.0$ min, 36% *ee* (with **18**; Table 5, entry 6).

36c: (+)-(*R*)-*N*,*N*-Diisopropylthiocarbamic acid *S*-[1-(2-ethylphenyl)-2-hydroxy-2,2-diphenylethyl] ester: White foam, yield: 84%. $R_f = 0.42$ (E/P = 1:2); $t_R = 21.1$ min (HP-5); $[\alpha]_D^{20} = +10.7$ ($c = 1.03$, $CHCl_3$); IR (ATR): $\tilde{\nu} = 3524$ (O–H), 3057 (m, C–H_{arom}), 2973, 2933, 2882 (s, C–H_{aliph}), 1627 (s, NC=O), 1488 (m), 1445 (s), 1425 (s), 1283 (s), 1210 (m), 1155 (s), 1116 (m), 1034 (s), 902 (m), 822 (s), 750 (s), 727 (m), 698 (s), 667 (m), 656 (m), 624 (m), 599 cm^{-1} (m); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.06$ (t, $^3J_{C,H} =$ 7.6 Hz, 3H, H_3CCH_2), 1.03–1.42 (br m, 12H, $((H_3C)_2HC)_2N$), 2.18–2.36 (m, 1H, $CH_3CH_AH_B$), 2.68–2.82 (m, 1H, $CH_3CH_AH_B$), 3.28 (br s, 1H, HO), 3.37 (br s, 1H, $((H_3C)_2HC)_2N$), 4.04 (br s, 1H, $((H_3C)_2HC)_2N$), 6.05 (s, 1H, $CH_{benzylic}$), 6.93–7.76 ppm (m, 14H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.3$ (H_3CCH_2), 20.1 ($((H_3C)_2HC)_2N$), 24.9 (H_3CCH_2), 48.1 (br, $((H_3C)_2HC)_2N$), 52.2 ($C_{benzylic}$), 82.2 ($C(Ph)_2(OH)$), 122.7, 125.1, 126.6, 126.8, 126.9, 126.9, 127.0, 127.2, 127.4, 127.8, 130.9, 138.0, 142.1, 144.0, 146.0 (Ph), 163.8 ppm (NC=O); MS (ESI): $m/z = 484.2278$ $[M+Na]^+$, 945.4665 $[2M+Na]^+$; elemental analysis: calcd (%) for $C_{29}H_{35}NO_2S$ (461.66): C 75.45, H 7.64, N 3.03; found: C 75.45, H 7.59, N 2.92; HPLC: Chiralcel OD-H (4.6×250 mm), $\lambda = 210$ nm, *n*-hexane/*i*PrOH = 100:1, 0.5 mL min^{-1}, $t_R(-) = 7.8$ min, $t_R(+) = 8.2$ min, 97% *ee* (with **18**; Table 5, entry 5).

Preparation of the NMR sample of **16·18**: A flame-dried rubber-sealed NMR tube (0.5×18 cm^2, round-bottomed) was filled with argon. A solution of *n*Bu^{6}Li (1.08 mL, 1.03 M) was injected. The solvent was removed under reduced pressure to yield pure *n*Bu^{6}Li in the NMR tube. In a flame-dried and argon-filled flask, a mixture of **15** (25 mg, 0.10 mmol, 1.0 equiv) and **18** (35 mg, 0.11 mmol, 1.1 equiv) were dissolved in dry [D$_8$]toluene (1 mL). This solution was cooled to −78 °C for 10 min before it was transferred into the previously prepared and now equally cooled NMR tube containing *n*Bu^{6}Li.



(*R*$_C$)-**16·18**: ^1H NMR (500 MHz, [D$_8$]toluene, −50 °C): $\delta = 0.75$ (s, 9H, *t*BuH_A), 0.76 (s, 9H, *t*BuH_B), 0.80–0.91 (m, 9H, 9-H_A, 9-H_B, 13-H), 0.96 (t, $^3J_{12'\text{-H},13'\text{-H}} = 7.3$ Hz, 3H, 13′-H), 1.36 (d, $^3J_{8'\text{-H},9'\text{-H}} = 6.7$ Hz, 3H, 9′-H_A), 1.39 (d, $^3J_{8'\text{-H},9'\text{-H}} = 6.6$ Hz, 3H, 9′-H_B), 1.52–1.62 (m, 1H, 12′-H_A), 1.65–1.73 (m, 1H, 12-H_A), 1.73–1.82 (m, 1H, 12′-H_B), 1.86–1.95 (m, 1H, 12-H_B), 2.82 (dd, $^3J_{14\text{-HA},15\text{-H}} = 6.6$ Hz, $^3J_{14\text{-HB},15\text{-H}} = 11.7$ Hz, 1H, 15-H), 2.91 (sept, $^3J_{C,H} = 6.7$ Hz, 1H, 8′-H), 3.02 (s, 1H, 1-H), 3.41 (pseudo t, $^3J_{14'\text{-H},15'\text{-H}} = {}^3J_{14'\text{-HA},14'\text{-HB}} = 9.9$ Hz, 1H, 14′-H_A), 3.54–3.60 (m, 1H, 14′-H_B), 3.60–3.66 (m, 1H, 14-H_A), 3.81 (pseudo t, $^3J_{C,H} = 9.9$ Hz, 1H, 14-H_B), 3.85 (dd, $^3J_{14'\text{-HA},15'\text{-H}} = 6.4$ Hz, $^3J_{14'\text{-HB},15'\text{-H}} =$ 10.4 Hz, 1H, 15′-H), 4.84 (sept, $^3J_{8\text{-H},9\text{-HA}} = {}^3J_{8\text{-H},9\text{-HB}} = 6.5$ Hz, 1H, 8-H), 6.39 (pseudo t, $^3J_{4\text{-H},5\text{-H}} = {}^3J_{5\text{-H},6\text{-H}} = 7.3$ Hz, 1H, 5-H), 6.84 (d, $^3J_{3\text{-H},4\text{-H}} =$ 7.8 Hz, 1H, 3-H), 6.97 (pseudo t, $^3J_{C,H} = 7.3$ Hz, 1H, 4-H), 7.17 (pseudo t, $^3J_{6\text{-H},7\text{-H}} = 7.5$ Hz, 1H, 6-H), 7.41 ppm (d, $^3J_{C,H} = 7.5$ Hz, 1H, 7-H); the signal at 3.02 ppm showed an NOE enhancement with the signal at 6.84 ppm; ^{13}C NMR (125 MHz, [D$_8$]toluene, −50 °C): $\delta = 9.4$ (C13′), 10.5 (C13), 19.7 (C_B9), 19.9 (C_A9), 20.8 (C_A9′), 21.2 (C_B9′), 25.2 ($(H_3C)_3C$), 25.6 ($(H_3C)_3C$), 29.1 (C12′), 32.7 (t, $^1J_{Li,C} = 3.5$ Hz, C1), 33.3 ($(H_3C)_3C$), 33.4 (C12), 34.0 ($(H_3C)_3C$), 46.2 (C8), 48.3 (C8′), 49.2 (C10), 67.7 (C14′), 69.5 (C14), 72.3 (C15), 75.3 (C15′), 110.6 (C5), 116.9 (C7), 119.3 (C3), 128.0 (C3), 128.9 (C6), 157.1 (C2), 167.0 (C11), 168.3 (C11′), 184.0 ppm (NC=O); ^6Li NMR (125 MHz, [D$_8$]toluene, −50 °C): $\delta = 2.74$ ppm (s).

(*S*$_C$)-**16·18**: ^1H NMR (500 MHz, [D$_8$]toluene, −50 °C): selected signals from the epimeric mixture of complexes: $\delta = 2.93$ (s, 1H, 1-H), 6.56 (pseudo t, $^3J_{4\text{-H},5\text{-H}} = {}^3J_{5\text{-H},6\text{-H}} = 7.5$ Hz, 1H, 5-H), 6.80 (br s, 1H, 3-H), 7.01 (br s, 1H, 4-H), 7.10 (br s, 1H, 6-H), 7.27 ppm (br s, 1H, 7-H); ^{13}C NMR (125 MHz, [D$_8$]toluene, −50 °C): selected signals from the epimeric mixture of complexes: $\delta = 31.9$ (t, C1), 111.4 (C5), 116.7 (C7), 155.6 (C2), 166.8 (C11), 168.8 (C11′), 184.1 ppm (NC=O); ^6Li NMR (125 MHz, [D$_8$]toluene, −50 °C): from the epimeric mixture of complexes: $\delta =$ 2.77 ppm (s).

Acknowledgements

Generous support by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 424), Fonds der Chemischen Industrie, the International NRW Graduate School of Chemistry, Münster (Germany), and the Japan Society for the Promotion of Science (stipends for H.L.) is gratefully acknowledged. Excellent experimental assistance by Mrs. Cornelia Weitkamp is acknowledged as well.

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[20] X-ray crystal-structure analysis for (*S*)-**17**: $C_{15}H_{23}NOS$, $M_r = 265.40$, colorless crystals, $0.40 \times 0.40 \times 0.05$ mm^3, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 8.6763(5)$, $b = 10.4289(7)$, $c = 17.2086(10)$ Å, $V = 1557.11(16)$ Å^3, $\rho_{calcd} = 1.132$ g cm^{-3}, $\mu = 17.50$ cm^{-1}, empirical absorption correction ($0.541 \le T \le 0.918$), $Z = 4$, $\lambda = 1.54178$ Å, $T = 223$ K, ω and ϕ scans, 7424 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.60$ Å^{-1}, 2691 independent ($R_{int} = 0.059$) and 2517 observed reflections ($I \le 2\sigma(I)$), 168 refined parameters, $R_1 = 0.050$, $wR_2 = 0.129$, Flack parameter 0.05(3), max. residual electron density 0.24 (-0.19) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms. CCDC-657931 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at http://www.ccdc.cam.ac.uk/data_request/cif.

[21] X-ray crystal-structure analysis for (*R*)-**21**: $C_{17}H_{29}NOSSi$, $M_r = 323.56$, colorless crystals, $0.40 \times 0.25 \times 0.10$ mm^3, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 7.096(1)$, $b = 10.806(1)$, $c = 25.318(1)$ Å, $V = 1941.4(3)$ Å^3, $\rho_{calcd} = 1.107$ g cm^{-3}, $\mu = 2.28$ cm^{-1}, empirical absorption correction ($0.914 \le T \le 0.978$), $Z = 4$, $\lambda = 0.71073$ Å, $T = 198$ K, ω and ϕ scans, 10686 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.66$ Å^{-1}, 4556 independent ($R_{int} = 0.041$) and 3783 observed reflections ($I \le 2\sigma(I)$), 197 refined parameters, $R_1 = 0.039$, $wR_2 = 0.080$, Flack parameter $-0.01(7)$, max. residual electron density 0.21 (-0.21) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms. CCDC-657927 contains the supplementary crystallographic data for this paper.

[22] In an attempt to obtain further hints regarding the stereochemical course of the silylation reaction, a destannylation experiment was performed, which employed stannane (−)-(*S*)-**22** as substrate, bis(oxazoline)**18** as diamine ligand, *sec*-butyllithium as base, and a 10:1 mixture of toluene and diethyl ether as solvent. After the stannane was stirred at −78 °C in the presence of the diamine and the base for 2 h, trimethylsilyl chloride (2 equiv) was added as electrophile. Silane **21** was not obtained. Instead, stannane **22** was recovered essentially quantitatively. Changing the solvent system or working without ligands did not affect the outcome of the experiment. These unsuccessful destannylations correspond to our previous findings with α-stannylated *S*-2-alkynyl thiocarbamates: R. Otte, D. Hoppe, unpublished results.

[23] X-ray crystal-structure analysis for (*R*)-**23**: $C_{16}H_{23}NO_3S$, $M_r = 309.41$, colorless crystals, $0.25 \times 0.20 \times 0.10$ mm, triclinic, space group *P*1 (No. 1), $a = 7.5139(1)$, $b = 7.8544(1)$, $c = 7.9183(1)$ Å, $\alpha = 107.268(1)$, $\beta = 94.691(1)$, $\gamma = 103.611(1)$°, $V = 427.89(1)$ Å^3, $\rho_{calcd} = 1.201$ g cm^{-3}, $\mu = 17.55$ cm^{-1}, empirical absorption correction ($0.668 \le T \le 0.844$), $Z = 1$, $\lambda = 1.54178$ Å, $T = 223$ K, ω and ϕ scans, 3820 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.60$ Å^{-1}, 1765 independent ($R_{int} = 0.030$) and 1743 observed reflections ($I \le 2\sigma(I)$), 195 refined parameters, $R_1 = 0.045$, $wR_2 = 0.122$, Flack parameter 0.03(2), max. residual electron density 0.27 (-0.25) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms. CCDC-657932 contains the supplementary crystallographic data for this paper.

[24] X-ray crystal-structure analysis for (*R*,*R*)-**24**: $C_{19}H_{31}NO_2S$, $M_r = 337.51$, colorless crystals, $0.40 \times 0.35 \times 0.30$ mm^3, monoclinic, space group $P2_1$ (No. 4), $a = 11.406(1)$, $b = 15.187(2)$, $c = 11.744(2)$ Å, $\beta = 93.54(1)$°, $V = 2030.4(5)$ Å^3, $\rho_{calcd} = 1.104$ g cm^{-3}, $\mu = 14.73$ cm^{-1}, empirical absorption correction ($0.590 \le T \le 0.666$), $Z = 4$, $\lambda = 1.54178$ Å, $T = 223$ K, ω and ϕ scans, 28092 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.60$ Å^{-1}, 7042 independent ($R_{int} = 0.038$) and 6924 observed reflections ($I \le 2\sigma(I)$), 431 refined parameters, $R_1 = 0.040$, $wR_2 = 0.109$, Flack parameter 0.012(12), max. residual electron density 0.30 (-0.14) e Å^{-3}, two almost identical molecules in the asymmetric unit, hydrogen atoms calculated and refined as riding atoms. CCDC-657928 contains the supplementary crystallographic data for this paper.

[25] Clear changes in the color of the reaction mixture may indicate a radical reaction pathway involving SET. This was not observed here.

[26] X-ray crystal-structure analysis for (*R*,*S*)-**25**: $C_{21}H_{27}NO_2S$, $M_r = 357.50$, colorless crystals, $0.25 \times 0.15 \times 0.10$ mm^3, monoclinic, space group $P2_1$ (No. 4), $a = 12.2635(3)$, $b = 18.9572(4)$, $c = 17.7404(6)$ Å, $\beta = 98.641(1)$°, $V = 4077.50(19)$ Å^3, $\rho_{calcd} = 1.165$ g cm^{-3}, $\mu = 15.02$ cm^{-1}, empirical absorption correction ($0.705 \le T \le 0.864$), $Z = 8$, $\lambda = 1.54178$ Å, $T = 223$ K, ω and ϕ scans, 29202 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.60$ Å^{-1}, 10152 independent ($R_{int} = 0.114$) and 7296 observed reflections ($I \le 2\sigma(I)$), 921 refined parameters, $R_1 = 0.072$, $wR_2 = 0.178$, Flack parameter 0.06(3), max. residual electron density 0.56 (-0.46) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms; molecule A (C1,C8): *S*,*R*; the other three: *R*,*S*. CCDC-657933 contains the supplementary crystallographic data for this paper.

[27] X-ray crystal-structure analysis for (*R*)-**26**: $C_{27}H_{31}NO_2S \cdot {}^1/_2C_4H_{10}O$, $M_r = 470.65$, colorless crystals, $0.45 \times 0.35 \times 0.30$ mm^3, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 14.5564(2)$, $b = 16.2223(3)$, $c = 22.9980(4)$ Å, $V = 5430.71(16)$ Å^3, $\rho_{calcd} = 1.151$ g cm^{-3}, $\mu = 12.57$ cm^{-1}, empirical absorption correction ($0.602 \le T \le 0.704$), $Z = 8$, $\lambda = 1.54178$ Å, $T = 223$ K, ω and ϕ scans, 86326 reflections collected ($\pm h$, $\pm k$, $\pm l$), $(\sin\theta)/\lambda = 0.60$ Å^{-1}, 9827 independent ($R_{int} = 0.066$) and 9333 observed reflections ($I \le 2\sigma(I)$), 591 refined parameters, $R_1 = 0.045$, $wR_2 = 0.117$, Flack parameter 0.014(13), max. residual electron density 0.44 (-0.28) e Å^{-3}, hydrogen atoms calculated and

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Received: August 22, 2007
Published online: December 7, 2007

