Palladium(0)-Catalyzed Enantioselective *O,S*-Rearrangement of Racemic *O*-Allylic Thiocarbamates: A New Entry to Enantioenriched Allylic Sulfur Compounds

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Reaction of (±)-(*E*)-pent-3-en-2-ol, (±)-(*E*)-hept-4-en-3-ol, (±)-(*E*)-2,6-dimethylhept-4-en-3-ol, (±)-cyclohex-2-en-1-ol, and (±)-cyclohept-2-en-1-ol with methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *tert*-butyl, and benzyl isothiocyanate gave the corresponding racemic *O*-allylic thiocarbamates of medium to good thermal stability in good yields. The palladium(0)-catalyzed rearrangement of the (±)-(*E*)-pent-3-en-2-ol-, (±)-(*E*)-hept-4-en-3-ol-, (±)-cyclohex-2-en-1-ol-, and (±)-cyclohept-2-en-1-ol-derived *O*-allylic thiocarbamates at room temperature in methylene chloride by using $Pd_2(dba)_3{\cdot}CHCl_3$ (dba = dibenzylideneacetone) as precatalyst and (+)-(1*R*,2*R*)-1,2-bis-*N*-((2-(diphenylphosphino)benzoyl)-1,2-diaminocyclohexane as ligand for the palladium atom proceeded quantitatively and gave the corresponding acyclic (*R*)-configured *S*-allylic thiocarbamates and the cyclic (*S*)-configured *S*-allylic thiocarbamates with ee values ranging from 85% to ≥99% in yields of 76−94%. Rearrangement of the *O*-allylic thiocarbamates carrying a methyl group at the N atom not only was the fastest but also proceeded with the highest enantioselectivity. No rearrangement was observed under these conditions in the case of the racemic *N*-methyl *O*-allylic thiocarbamate derived from (±)-2,6-dimethylhept-4-en-3-ol, which has a branched carbon skeleton. (*S*)-Cyclohex-2-enethiol of 97% ee was obtained through hydrolysis of the corresponding *N*-methyl *S*-allylic thiocarbamate. 2-((*R*)-(*E*)-1-Methylbut-2-enylsulfanyl)pyrimidine of 91% ee and 2-((*S*)-cyclohex-2-enylsulfanyl)pyrimidine of 97% ee were synthesized in one synthetic operation from the corresponding *N*-methyl *S*-allylic thiocarbamates and 2-chloropyrimidine. Similarly, (*S*)-cyclohex-2-enylsulfanyl)benzene of 97% ee was obtained in one synthetic operation from the corresponding *N*-methyl *S*-allylic thiocarbamate through a palladium(0)-catalyzed substitution of iodobenzene in the presence of a base. The palladium(0)-catalyzed enantioselective rearrangement of *O*-allylic carbamates to *S*-allylic carbamates has been extended from the solution phase to the solid phase by using a methyl thioisocyanate polystyrene resin. In the case investigated the enantioselectivity of the rearrangement on the solid phase was considerably lower than that in solution.

Introduction

Exploitation of the synthetic potential of chiral allylic sulfides and thiolo esters through, for example, [2,3]-[1−8] and [3,3]-sigmatropic rearrangement[9−13] and copper-mediated substitution with organometallics[14−16] is hampered by the lack of general methods for their enantioselective synthesis. We have recently described the successful application of the palladium(0)-catalyzed allylic alkylation to the enantioselective synthesis of allylic heteroaryl sulfides from the corresponding racemic allylic acetates or carbonates and heteroaryl thiols.[17,18] This method, however, seems to be restricted to the allylic alkylation of heteroaryl thiols since alkyl and aryl thiols showed in our hands only a low reactivity. It occurred to us that a perhaps general access to chiral allylic sulfur compounds might be opened if a similar catalytic enantioselective synthesis of allylic thiols could be developed because of the ready alkylation,[19,20] arylation,[21−23] heteroarylation,[19,20] and acylation[19,20] of the latter at the S

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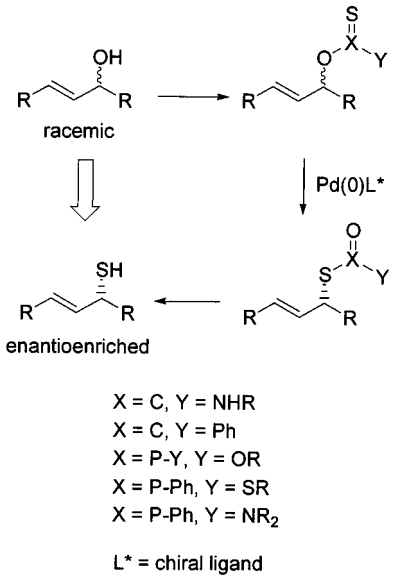
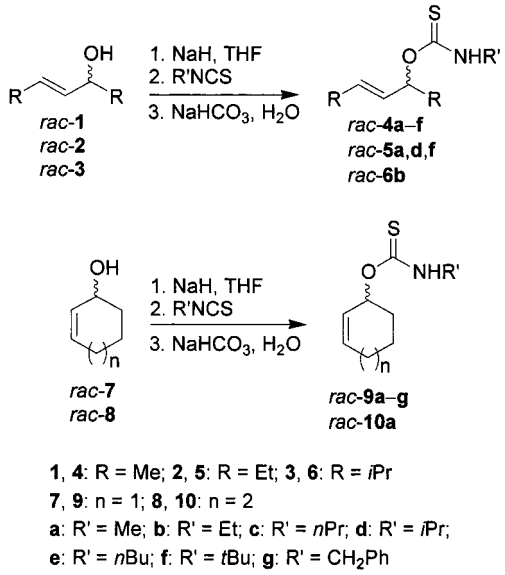
Scheme 1



Scheme 2



atom. The facile palladium(0)/triphenylphosphane-catalyzed rearrangement of racemic *O*-allylic thiocarbamates,[21] thioesters,[24] phosphorothionates,[25] and phosphonothionates[25] with formation of the corresponding racemic *S*-allylic derivatives suggested a perhaps efficient enantioselective synthesis of *S*-allylic thiocarbamates, thioesters, phosphorothionates, and phosphonothionates from racemic allylic alcohols by using a chiral phosphane for the palladium atom (Scheme 1).[26] If successful, the ready conversion of these *S*-allylic derivatives to the corresponding allylic thiols[21] and the manifold ways available for a derivatization of the latter would thus provide for an entry to the various chiral allylic sulfur compounds. Of the transformations depicted in Scheme 1, the rearrangement of N-monosubstituted *O*-allylic thiocarbamates to the corresponding *S*-allylic thiocarbamates seemed to be the most attractive for the following reasons. First, racemic N-monosubstituted *O*-allylic carbamates are easily accessible from the corresponding racemic allylic alcohols and isothiocyanates.[21] Second, chiral *S*-allylic thiocarbamates themselves are expected to be useful starting materials in enantioselective CC bond formation with copper organyls. Third, chiral *S*-allylic thiocarbamates show promise as starting materials for the synthesis of configurationally stable chiral (α-thioallyl)lithium compounds.[27]

Herein, we describe an efficient palladium-catalyzed enantioselective synthesis of symmetrically 1,3-disubstituted cyclic and acyclic *S*-allylic thiocarbamates from the corresponding racemic allylic alcohols through an *O,S*-transposition in solution and on the solid phase and their conversion to enantioenriched allylic thiols and sulfides.[28]

Results and Discussion

Synthesis of Racemic *O*-Allylic Thiocarbamates. The acyclic *O*-allylic thiocarbamates *rac*-**4a**−**f**, *rac*-**5a,d,f**, and *rac*-**6b** as well as the cyclic *O*-allylic thiocarbamates *rac*-**9a**−**g** and *rac*-**10a** were readily prepared from the racemic allylic alcohols *rac*-**1**−**3**, *rac*-**7**, and *rac*-**8**, respectively, and the corresponding isothiocyanates at 0 °C in THF in 71−93% yield (Scheme 2). *O*-Allylic thiocarbamates are in general thermally unstable, suffering a [3,3]-sigmatropic rearrangement at ambient temperatures to the corresponding *S*-allylic thiocarbamates.[21,27] While the enantioenriched *O*-allylic thiocarbamates yield the enantioenriched *S*-allylic thiocarbamates, the racemic compounds afford the racemic rearrangement products. Thus, for the attempted palladium-catalyzed enantioselective rearrangement of racemic *O*-allylic thiocarbamates, a sufficient thermal stability will be of utmost importance. While the cyclohexenyl and cycloheptenyl derivatives *rac*-**9a**−**g** and *rac*-**10a** were stable at room temperature, *O*-allylic thiocarbamates derived from cyclopent-2-en-1-ol suffered a partial rearrangement already during their synthesis and are, thus, not suitable for the present purpose.[29] The acyclic *O*-allylic thiocarbamates showed an intermediate thermal stability at room temperature, which posed, however, no obstacle to their synthesis except chromatographic purification, where a partial rearrangement occurred. However, we found that for the subsequent palladium-catalyzed rearrangement the purity of the crude *O*-allylic thiocarbamates was in all cases high enough to render a chromatographic purification superfluous (vide infra). The ^{1}H NMR spectra (300−500 MHz) and the ^{13}C NMR spectra (75−125 MHz) of the *O*-allylic thiocarbamates *rac*-**4a**−**e**, *rac*-**5a,d**, *rac*-**6b**, *rac*-**9a**−**e,g**, and *rac*-**10a** in $CDCl_3$ showed at room temper-

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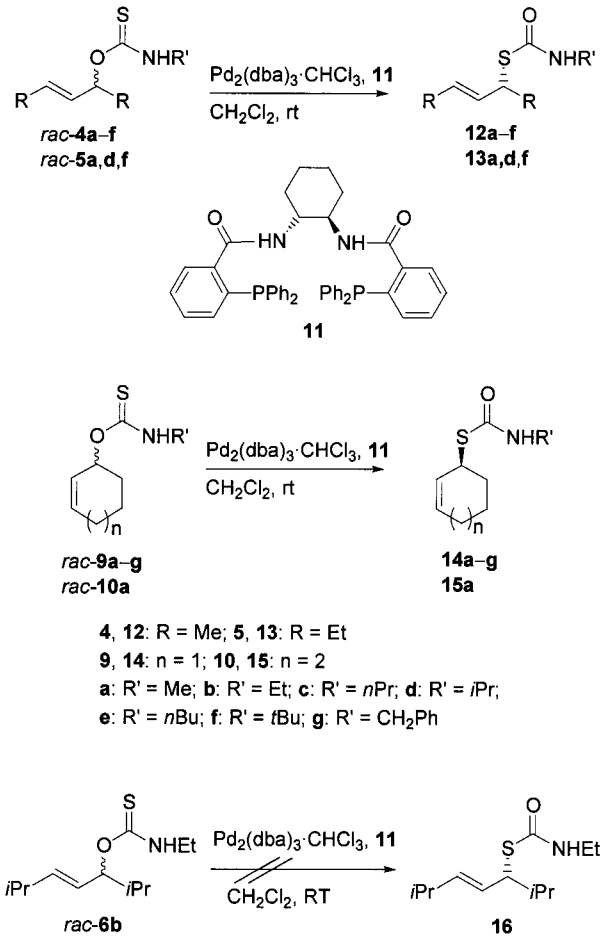
Scheme 3



ature the presence of two isomers in ratios of 1.1:1 to 1.4:1. We ascribe to the isomers the structures of the two C(S)−N conformers, which are observable under these conditions because of a restricted rotation around the C(S)−N bond of the thiocarbamate group.[30,31] Such a phenomenon was, however, not manifested in the NMR spectra of the *N*-*tert*-butylthiocarbamates *rac*-**4f** and *rac*-**9f**, which may be due to an extreme equilibrium position in these cases.

Palladium-Catalyzed Rearrangement. Since we and others had observed high enantioselectivities in the palladium(0)-catalyzed allylic alkylation of sulfinates[18,33−36] and thiols[17,18] with racemic acyclic and cyclic allylic acetates and carbonates by using the chiral bisphosphane **11**[32] (Scheme 3) as ligand for the palladium atom, this phosphane was also used in the palladium(0)-catalyzed rearrangement of the acyclic and cyclic allylic *O*-thiocarbamates shown in Scheme 3. Besides the alteration of the carbon skeleton, the substituent at the N atom of the

Table 1. Palladium(0)-Catalyzed Rearrangement of the Racemic Acyclic *O*-Allylic Thiocarbamates *rac*-4a−f and *rac*-5a,d,f

entry	substrate	Pd(0)/**11** (mol %)	*t* (h)	convn (%)	product	yield (%)	ee (%)
1	*rac*-**4a**	2.5/3	15	100	**12a**	92	91
2	*rac*-**4b**	2.5/3	16	100	**12b**	92	92
3	*rac*-**4c**	2.5/3	16	100	**12c**	89	90
4	*rac*-**4d**	2.5/3	20	100	**12d**	93	90
5	*rac*-**4e**	2.5/3	48	100	**12e**	89	85
6	*rac*-**4f**	2.5/3	24	100	**12f**	76	85
7	*rac*-**5a**	7.5/9	15	100	**13a**	92	91
8	*rac*-**5d**	7.5/9	5	100	**13d**	86	86
9	*rac*-**5f**	7.5/9	15	100	**13f**	91	64

O-allylic carbamates was also varied to study its possible influence on the enantioselectivity and, in particular, on the rate of the rearrangement. To avoid problems of regioselectivity, the investigations of the palladium-catalyzed rearrangement of *O*-allylic thiocarbamates were begun with substrates which are symmetrically 1,3-disubstituted.

Acyclic Carbamates. The (±)-(*E*)-pent-3-en-2-ol-derived racemic *O*-allylic thiocarbamates *rac*-**4a**−**f**, which carry a methyl, an ethyl, an *n*-propyl, an isopropyl, an *n*-butyl, and a *tert*-butyl group at the N atom, suffered at room temperature in methylene chloride in the presence of $Pd_2(dba)_3$·$CHCl_3$ (dba = dibenzylideneacetone) (1.25 mol %) and bisphosphane **11** (3 mol %) after a reaction time of 15−48 h a quantitative and enantioselective rearrangement to the *S*-allylic thiocarbamates **12a**−**f** (Table 1). The *S*-allylic carbamates **12a**−**f** were isolated after purification by chromatography with ee values varying from 85−92% in yields of 76−92%. Rearrangement of carbamate *rac*-**4a**, which carries the least sterically demanding methyl group at the N atom, proceeded the most efficiently in terms of enantioselectivity and reaction rate (Table 1, entry 1). No differences in regard to enantioselectivity, reaction time, and yield were observed whether the *O*-allylic carbamates were purified by chromatography prior to rearrangement or used as the crude material obtained in the previous step.

In the case of (±)-(*E*)-hept-4-en-3-ol the rearrangement of the *O*-allylic carbamates *rac*-**5a,d,f**, which bear a methyl, an isopropyl, and a *tert*-butyl group at the N atom, was studied (cf Table 1). Here too, the rearrangement of *rac*-**5a,d** in the presence of $Pd_2(dba)_3$·$CHCl_3$ (3.75 mol % Pd) and bisphosphane **11** (9 mol %) in methylene chloride at room temperature proceeded quantitatively and enantioselectively to afford the *S*-allylic thiocarbamates **13a,d** with ee values of 86% and 91%, respectively. As observed in the case of the *N*-methyl derivative *rac*-**4a**, rearrangement of the *N*-methyl derivative *rac*-**5a** not only was the fastest but also occurred with the highest enantioselectivity (Table 1, entry 7). We noticed, however, that for the rearrangement of the (±)-(*E*)-hept-4-en-3-ol-derived thiocarbamates *rac*-**5a,d** larger quantities of the precatalyst and longer reaction times were required than in the case of the (±)-(*E*)-pent-3-en-2-ol-derived thiocarbamates *rac*-**4a**−**f**. The influence of the substituent at the N atom on the rearrangement either thermally or palladium catalyzed was most noticeable in the case of the *N*-*tert*-butylthiocarbamate *rac*-**5f**. While a complete conversion of *rac*-**5f** was observed after a reaction time of 15 h, the ee value of the *S*-allylic thiocarbamate **13f** was only 64%. A control experiment with *rac*-**5f** under the same conditions but without the precatalyst revealed, however, a competing thermal rearrangement of this

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Table 2. Palladium(0)-Catalyzed Rearrangement of the Racemic Cyclic *O*-Allylic Thiocarbamates *rac*-9a−g and *rac*-10a

entry	substrate	Pd(0)/**11** (mol %)	*t* (h)	convn (%)	product	yield (%)	ee (%)
1	*rac*-**9a**	1.25/1.5	0.5	100	**14a**	94	97
2	*rac*-**9b**	1.25/1.5	2	100	**14b**	96	95
3	*rac*-**9c**	1.25/1.5	2	100	**14c**	94	99
4	*rac*-**9d**	1.25/1.5	2	100	**14d**	92	92
5	*rac*-**9e**	2.5/3	16	100	**14e**	93	99
6	*rac*-**9f**	1.25/1.5	16	100	**14f**	92	97
7	*rac*-**9g**	2.5/3	3	100	**14g**	91	99
8	*rac*-**10a**	1.25/1.5	5	100	**15a**	94	92

O-allylic thiocarbamate to *rac*-**13f**, which had occurred to an extent of 50% after 15 h.

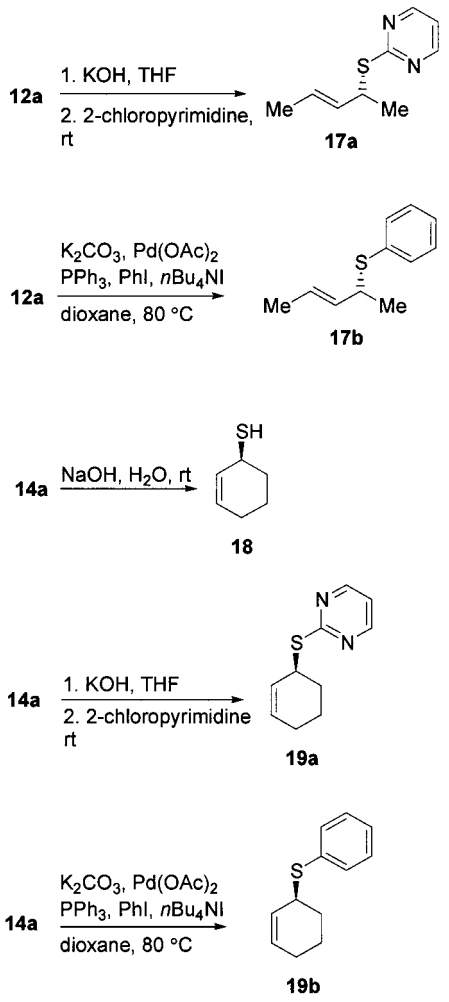
To determine the scope and limitation of the palladium-catalyzed rearrangement of *O*-allylic thiocarbamates under the influence of bisphosphane **11**, the (±)-(*E*)-2,6-dimethylhept-4-en-3-ol-derived *O*-allylic thiocarbamate *rac*-**6b**, which has a branched allylic carbon skeleton and bears an ethyl group at the N atom, was investigated. Under the conditions employed for the rearrangement of the aforementioned *O*-allylic thiocarbamates, no conversion of *rac*-**6b** could be observed. Even the extension of the reaction time to 40 h and the use of 3.8 mol % $Pd_2(dba)_3$·$CHCl_3$ and 9 mol % **11** did not lead to a rearrangement of *rac*-**6b** under formation of the *S*-allylic thiocarbamate **16**.

Cyclic Carbamates. The palladium-catalyzed rearrangement of the (±)-cyclohex-2-en-1-ol-derived racemic *O*-allylic thiocarbamates *rac*-**9a**−**g**, which bear a methyl, an ethyl, an *n*-propyl, an isopropyl, an *n*-butyl, a benzyl, and a *tert*-butyl group at the N atom, proceeded faster and with higher enantioselectivities than that of the acyclic *O*-allylic thiocarbamates. After reaction times of 0.5−16 h the *S*-allylic thiocarbamates **14a**−**g** were obtained in yields of 92−94% having ee values of 92% to ≥99% (Table 2). In the case of the *N*-*n*-propyl derivative **14c** and the *N*-*n*-butyl derivative **14e** (Table 2, entries 3 and 5), the respective enantiomers could not be detected by GC analysis on a cyclodextrin column. Conversion of the starting material was in all cases quantitative. Except in the case of the thiocarbamate *rac*-**9e**, which carries an *n*-butyl group at the N atom (Table 2, entry 5), complete rearrangement occurred by using only 0.62 mol % $Pd_2(dba)_3$·$CHCl_3$ and 1.5 mol % bisphosphane **11**. Increasing the size of the substituent at the N atom of the cyclohexenyl derivatives *rac*-**9a**−**g** led, as in the case of the acyclic *O*-allylic thiocarbamates, to an increase in the reaction time.

The palladium-catalyzed rearrangement of the (±)-cyclohept-2-en-1-ol-derived racemic *O*-allylic thiocarbamate *rac*-**10a**, which bears a methyl group at the N atom, occurred with high enantioselectivity and gave with high yield the corresponding *S*-allylic derivative **15a** (Table 2, entry 7). The rate and the enantioselectivity of the rearrangement of *rac*-**10a** were, however, somewhat lower than those of the corresponding six-membered *O*-allylic carbamate *rac*-**9a** (Table 2, entry 1).

While the NMR spectra of the *O*-allylic thiocarbamates *rac*-**4a**−**e**, *rac*-**5a,d**, *rac*-**6b**, *rac*-**9a**−**e,g**, and *rac*-**10a** in $CDCl_3$ showed, as aforementioned, two sets of signals, those of the isomeric *S*-allylic thiocarbamates did not show such a phenomenon. This may be attributed to the lower C(O)−N rotational barrier of S-substituted thiocarbamates as compared to the isomeric O-substituted thiocarbamates.[31]

Scheme 4



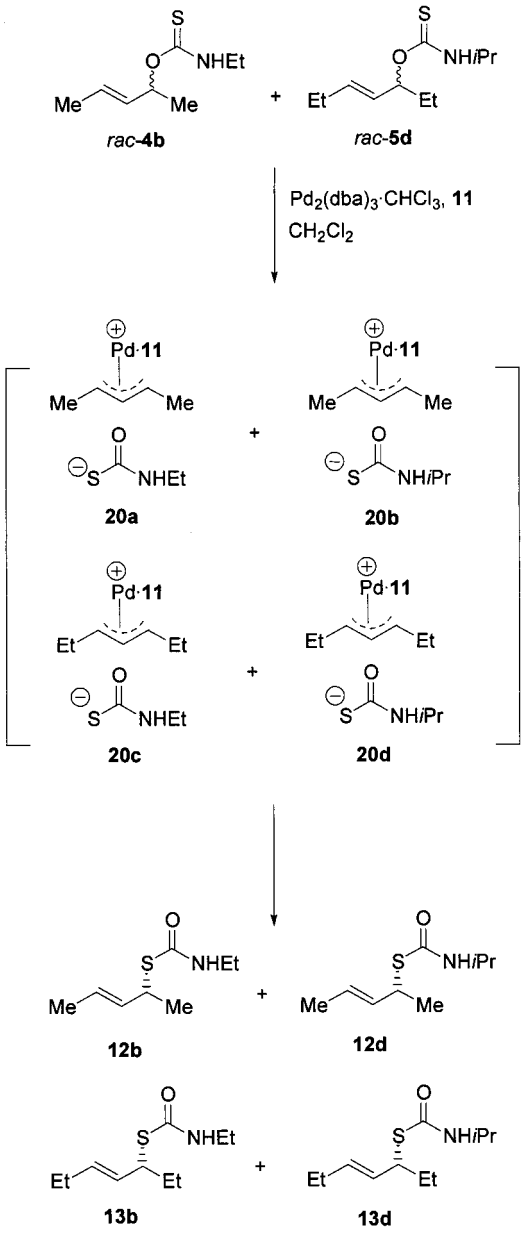
Mechanistic Consideration. The absolute configuration of the acyclic allylic *S*-thiocarbamate **12a** was determined by chemical correlation with sulfide **17a** of known (*R*) configuration[17] as shown in Scheme 4. Thus, thiocarbamate **12a** was cleaved with potassium hydroxide at room temperature in THF under formation of the corresponding allylic thiol, which was not isolated but converted directly upon treatment with 2-chloropyrimidine to sulfide **17a** of 92% ee, which was isolated in 95% yield (Scheme 4). Since the *S*-allylic thiocarbamates **12a**−**f** and **13a,d,f** all have the same sign of optical rotation, the (*R*) configuration was also assigned to the other acyclic *S*-allylic thiocarbamates. The absolute configuration of the cyclic *S*-allylic thiocarbamate **14a** was determined by its conversion to the allylic thiol **18** (64% yield, 97% ee) of known (*S*) configuration[12] with sodium hydroxide at room temperature in water. Since the *S*-allylic thiocarbamates **14a**−**f** and **15a** also all have the same sign of optical rotation, the (*S*) configuration was also assigned to the other cyclic *S*-allylic thiocarbamates. Functionalization of **12a** at the S atom with formation of **17a** was carried out not only under stereochemical but also under synthetic aspects. Application of this procedure to the cyclic *S*-allylic thiocarbamate **14a** afforded without isolation of **18** sulfide **19a** of 97% ee in 80% yield. Finally, the *S*-allylic thiocarbamates **12a** and **14a** were converted to the phenyl sulfides **17b** and **19b**, respectively, through a palladium-catalyzed substitution of iodobenzene.[21] Thus, treatment of **12a** and **14a** with

K_2CO_3 and iodobenzene at 80 °C in dioxane in the presence of $Pd(OAc)_2$, PPh_3, and nBu_4NI afforded sulfide **17b** of 92% ee in 56% yield and sulfide **19b** of 97% ee in 75% yield, respectively.

The sense of asymmetric induction of the palladium-catalyzed rearrangement of the cyclic and acyclic *O*-allylic thiocarbamates in the presence of bisphosphane **11** is the same as in the palladium-catalyzed substitutions of the corresponding cyclic and acyclic racemic allylic carbonates and acetates with sulfinates and thiols in the presence of this bisphosphane.[17,18,33−36] Also the degree of asymmetric induction is comparable in both cases. On the basis of these results and those obtained previously in the palladium(0)-catalyzed rearrangement of cyclic and acyclic *O*-allylic thiocarbamates[21] and of the other *O*-allylic derivatives listed in Scheme 1 in the presence of achiral phosphanes,[24,25] it is, thus, proposed that the catalytically active chiral palladium(0) catalyst formed from $Pd_2(dba)_3{\cdot}CHCl_3$ and **11** reacts with the racemic *O*-allylic thiocarbamate under formation of a chiral cationic π-allylpalladium(II) complex,[37] which possesses as counterion the corresponding thiocarbamate ion (Scheme 5). Substitution of the π-allylpalladium(II) complex by the thiocarbamate ion gives the *S*-allylic thiocarbamate and the palladium(0) catalyst. A verification of this ionization−substitution mechanism was done by submitting two different *O*-allylic thiocarbamates, for example, *rac*-**4b** and *rac*-**5d**, which differ not only in their carbon skeleton but also in the substituent at the N atom, to a crossover experiment. If the rearrangement occurs as proposed via an ionization−substitution mechanism, formation of four different ion pairs and, thus, of four different rearrangement products would be expected. Thus, a mixture of the racemic *O*-allylic thiocarbamates *rac*-**4b** and *rac*-**5d** in a ratio of 1:1 was treated with 2.5 mol % $Pd_2(dba)_3{\cdot}CHCl_3$ and 6 mol % bisphosphane **11** in methylene chloride at room temperature. Rearrangement was complete after 16 h, and a mixture of the four *S*-allylic thiocarbamates **12b,d** and **13b,d** in a ratio of 30:20:18:30 was isolated in practically quantitative yield. These results can be rationalized by the formation of intermediates **20a**−**d** and, thus, support further the notion of a mechanism for the palladium(0)-catalyzed rearrangement of the *O*-allylic thiocarbamates, which includes besides a number of further important steps not depicted in the simplified Scheme 5[38−45] an ionization followed by a substitution.

Extension to the Solid Phase. We were interested to see whether polymer-bound *O*-allylic thiocarbamates could also be submitted to a highly enantioselective palladium-catalyzed rearrangement in the presence of ligand **11**. Thus, the *O*-allylic thiocarbamate resin **22** was synthesized by treatment of methyl isothiocyanate resin **21** with alcohol *rac*-**7** (4 equiv of the corresponding sodium salt) at room temperature in THF (Scheme 6). Loading of resin **21** with formation of resin **22** could easily be followed by IR spectroscopy by using the disappearance of the strong heterocumulene absorptions of **21** at 2100 and 2170 cm^{-1} and the appearance of the strong N−H and C═S absorptions of **22** at 3400 and 1150 cm^{-1}, respectively. Resin-bound *O*-allylic thiocarbamate **22** was submitted to a palladium-catalyzed rearrangement with 5 mol % $Pd_2(dba)_3{\cdot}CHCl_3$ and 6 mol % bisphosphane **11** at room temperature in methylene chloride with formation of the resin-anchored *S*-allylic thiocarbamate **24**. Resin **24** was cleaved with KOH at room temperature to afford the thiol **18**, which was not isolated but converted upon treatment with 2-chloropyrimidine, as described above, to sulfide **19a**. Sulfide **19a** of 66% ee was isolated in 34% overall yield, based on resin **21**. Similarly, resin **24** was treated with K_2CO_3 and iodobenzene at 80 °C in dioxane in the presence of Pd-

Scheme 5



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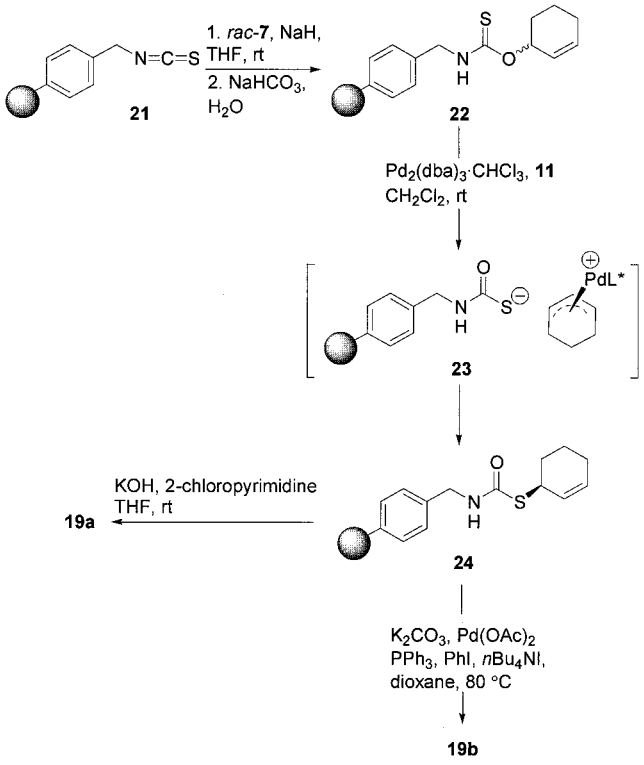
Scheme 6



$(OAc)_2$, PPh_3, and nBu_4NI, which afforded sulfide **19b** of 64% ee in 24% overall yield, based on **21**. Thus, the palladium-catalyzed rearrangement of polymer-bound racemic *O*-allylic thiocarbamate **22** in the presence of ligand **11**, which involves presumably formation of ion pair **23** and a substitution of the cationic palladium complex by the polymer-bound nucleophile, proceeded readily but with a significantly lower enantioselectivity. The lower enantioselectivity was not caused by a competing thermal sigmatropic and, thus, unselective rearrangement of **22** with formation of **24**, containing the racemic *S*-allylic thiocarbamte, under the conditions employed. This was demonstrated through a control experiment in which resin **22** was kept at room temperature in THF for the time required for its palladium-catalyzed rearrangement in the presence of **11** followed by a treatment with KOH and 2-chloropyrimidine. Formation of *rac*-**19a** could not be observed under these conditions.

Conclusions

In summary, the quantitative palladium(0)-catalyzed rearrangement of racemic acyclic and cyclic *O*-allylic thiocarbamates, which are easily accessible from the corresponding racemic allylic alcohols and isothiocyanates, in the presence of bisphosphane **11** as ligand for the palladium atom afforded with high enantioselectivities and yields the corresponding *S*-allylic thiocarbamates. The *S*-allylic thiocarbamates are easily converted to the corresponding enantioenriched allylic thiols, which can be used as starting material for the syntheses of enantioenriched sulfides and presumably also for that of other allylic sulfur compounds. The sense of asymmetric induction in the rearrangement of the *O*-allylic thiocarbamates in the presence of **11** is the same as in the palladium-catalyzed substitution of the corresponding racemic allylic acetates and carbonates with external sulfur nucleophiles by using this ligand. Furthermore, the degree of asymmetric induction in palladium-catalyzed rearrangement and substitution is nearly the same. This and further evidence point to an ionization−substitution mechanism for the rearrangement involving an π-allylpalladium(II) complex ligated by **11** as intermediate. Unfortunately, the mode of the coordination of bisphosphane **11** to the palladium atom in the π-allylpalladium(II) complex being the decisive one for the formation of the substitution product is not known at present.[32,42−45] As a consequence rationalization of the asymmetric induction on the basis of a substrate model is hampered. Finally, a major difference between the palladium-catalyzed rearrangement described herein and the substitution with external nucleophiles is that in the former case the counterion of the π-allylpalladium(II) complex is also the nucleophile, whose concentration does not exceed the concentration of the palladium(0) precatalyst and is, thus, much lower than in substitution. The palladium-catalyzed rearrangement has thus far only been carried out with *O*-allylic thiocarbamates, which are symmetrically 1,3-disubstituted, and by using bisphosphane **11** as ligand. Palladium(0) complexes with **11** as ligand are apparently not capable of catalyzing the rearrangement of acyclic *O*-allylic thiocarbamates having a branched carbon skeleton. This is in accordance with previous results obtained in the palladium-catalyzed substitution of allylic acetates and carbonates having such a carbon skeleton in the presence of **11**.[32,46] An enantioselective rearrangement of such *O*-allylic thiocarbamates may perhaps be achieved by using chiral phosphinoferrocenyl[47] or phosphinooxazoline ligands.[48] A principle limitation of the method described for the synthesis of enantioenriched *S*-allylic thiocarbamates seems to be the inaccessibility of the cyclopentenyl derivatives because of their limited thermal stability. In this case a palladium(0)-catalyzed enantioselective allylic substitution of the acetate or carbonate of racemic cyclopent-2-en-1-ol with potassium thioacetate or thiobenzoate in the presence of **11** can perhaps be applied[49,50] for the synthesis of enantioenriched cyclopent-2-ene-1-thiol. All the other cyclic and acyclic *O*-allylic thiocarbamates investigated showed a sufficient thermal stability.

Palladium-catalyzed rearrangement of the polymer-bound *O*-allylic thiocarbamate in the presence of ligand **11** and the subsequent cleavage of the polymer-bound *S*-allylic thiocarbamate to the thiol and its functionalization proceeded in the case investigated with medium to good overall yields. The enantioselectivity, however, was markedly lower. The reasons for the lower selectivity are difficult to discern at present.

Currently we are extending our studies to the enantioselective rearrangement of monosubstituted and branched *O*-allylic thiocarbamates.

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Experimental Section

General Methods. All reactions were carried out in absolute solvents under argon with syringe and Schlenk techniques in oven-dried glassware. THF and ether were distilled under argon from sodium/lead alloy in the presence of benzophenone, and CH_2Cl_2 was distilled from calcium hydride. Bisphosphane **11**[51] and $Pd_2(dba)_3$·$CHCl_3$[52] were prepared according to literature procedures. The racemic acyclic alcohols were prepared by standard procedures from the corresponding unsaturated aldehydes via Grignard reaction, and the racemic cyclic alcohols were synthesized from the corresponding alkenes via Wohl−Ziegler bromination followed by a substitution of the thus obtained allylic bromides with aqueous $NaHCO_3$. The isothiocyanates were obtained from commercial sources. The methyl isothiocyanate polystyrene resin (loading 1.9 mmol/g) was obtained from Novabiochem, Germany. Column chromatography: Merck silica gel 60 (0.063−0.100 mm). Optical rotations: Perkin-Elmer model 241, measurements made at approximately 22 °C, specific rotations in grad·mL/dm·g, *c* in g/100 mL. Kugelrohr distillations were carried out in a Büchi GKR 50 apparatus. ^{1}H and ^{13}C NMR: Varian VXR 300, Varian Gemini 300, Varian Inoca 400, and Varian Unity 500. Peaks in the ^{13}C NMR spectra are denoted as "u" for carbons with zero or two attached protons or "d" for carbons with one or three attached protons, as determined from the APT pulse sequence. GC analyses: Chrompack CP-9000 (CP-Sil-8, 30 m × 0.32 mm; 75 kPa of H_2). IR spectra were recorded with a Perkin-Elmer PE 1759 FT instrument, and only peaks of $\nu > 700$ cm^{-1} are listed. GC−MS was run with a Magnum Finnigan (CP-Sil-8-MS, 25 m × 0.25 mm; 11 psi of He, CI, 40 eV, MeOH) instrument, and only peaks of $m/z > 70$ and intensity >10%, except decisive ones, are listed. Elemental analysis: Microanalytical Laboratory of the Institut für Organische Chemie of the RWTH Aachen.

General Procedure for the Synthesis of *O*-Allylic Thiocarbamates (GP1). A solution of the allylic alcohol (22.5 mmol) in THF (10 mL) was slowly added at 0 °C to an argon-purged suspension of NaH (1.00 g, 25 mmol, 60% in mineral oil) in THF (10 mL). After the suspension was stirred at 0 °C for 1 h, a solution of the isothiocyanate (22.6 mmol) in THF (5 mL) was added via syringe. The mixture was then stirred for an additional hour and subsequently quenched through the addition of saturated aqueous $NaHCO_3$ (10 mL). The aqueous phase was then extracted with ethyl acetate (3 × 10 mL), and the combined organic phases were dried ($MgSO_4$). Concentration of the organic phases in vacuo and purification of the residue by chromatography (pentanes/ether, 3:1) gave the *O*-allylic carbamate.

(±)-Methylthiocarbamic Acid *O*-((*E*)-1-Methylbut-2-enyl) Ester (*rac*-4a). Following GP1, the reaction of alcohol *rac*-**1** (1.94 g, 22.5 mmol) with methyl isothiocyanate (1.62 g, 22.6 mmol) gave thiocarbamate *rac*-**4a** (2.61 g, 73%) as an orange oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34/1.40 (d, J = 6.4 Hz, 3 H, CHCH_3), 2.84/3.75 (d, J = 5.0 Hz, 3 H, NHCH_3), 1.70 (dd, J = 7.5, 0.7 Hz, 3 H, CHCH_3), 5.54 (ddq, J = 15.1, 6.4, 1.7 Hz, 1 H, =CH), 5.71 (dqd, J = 15.1, 7.7, 1.7 Hz, 1 H, =CH), 4.52 (dq, J = 6.7, 6.7 Hz, 1 H, CHO), 6.69/7.43 (br ds, 1 H, NH) (conformer ratio 1.1:1); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.74 (d), 20.31 (d), 31.63 (d), 76.71 (d), 128.21 (d), 130.43 (d), 189.26 (u), 190.42 (u); IR (film) ν 3297 (m), 3029 (w), 2965 (m), 2932 (m), 2856 (m), 1659 (w), 1530 (s), 1447 (s), 1413 (m), 1360 (s), 1219 (s), 1154 (s), 1065 (m), 1027 (s), 965 (m), 903 (w), 818 (w) cm^{-1}; MS (CI) m/z (relative intensity) 160 [M$^+$ + 1] (27), 126 (12), 102 (40), 92 (51). Anal. Calcd for $C_7H_{13}NOS$ (159.25): C, 52.79; H, 8.23; N, 8.80. Found: C, 52.39; H, 8.52; N, 9.07.

(±)-Methylthiocarbamic Acid *O*-((*E*)-1-Ethylpent-2-enyl) Ester (*rac*-5a). Following GP1, reaction of alcohol *rac*-**2** (5.13 g, 45.0 mmol) with methyl isothiocyanate (3.33 g, 45.6 mmol) gave thiocarbamate *rac*-**5a** (6.14 g, 73%) as an orange oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (dt, J = 13.7, 7.3 Hz, 3 H, CHCH_3), 0.99 (dt, J = 7.33, 7.3 Hz, 3 H, CHCH_3), 1.59−1.85 (m, 2 H, CH_2), 2.02−2.11 (m, 2 H, CH_2), 2.86/3.07 (J = 4.89 Hz, 3 H, NHCH_3), 5.41 (ddt, J = 15.6, 7.0, 1.5 Hz, 1 H, =CH), 5.74−5.85 (m, 2 H, =CH, CHO), 6.47/7.42 (br ds, 1 H, NH) (conformer ratio 1.2:1); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.49 (d), 13.33 (d), 25.37 (u), 27.61 (u), 29.43 (d), 31.72 (d), 81.93 (d), 83.62 (d), 126.47 (d), 126.74 (d), 136.32 (d), 136.48 (d), 189.47 (u), 190.73 (u); IR (film) ν 3285 (s), 2966 (s), 2936 (s), 2876 (m), 1662 (m), 1529 (s), 1456 (s), 1361 (s), 1280 (m), 1217 (s), 1154 (s), 1137 (s), 1067 (m), 1053 (s), 967 (s), 935 (m) cm^{-1}; MS (CI) m/z (relative intensity) 188 [M$^+$ + 1] (11), 97 (26), 96 (19), 81 (13). Anal. Calcd for $C_9H_{17}NOS$ (187.10): C, 57.71; H, 9.15; N, 7.48. Found: C, 57.39; H, 8.88; N, 7.77.

(±)-Ethylthiocarbamic Acid *O*-((*E*)-1-Isopropyl-4-methylpent-2-enyl) Ester (*rac*-6b). Following GP1, reaction of alcohol *rac*-**3** (1.88 g, 13.2 mmol) with ethyl isothiocyanate (1.22 g, 14.0 mmol) gave thiocarbamate *rac*-**6b** (2.69 g, 89%) as a pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88−1.02 (m, 12 H, CH(CH_3)$_2$), 1.18/1.22 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 1.91−2.06 (m, 1 H, CH(CH$_3$)$_2$), 2.25/2.38 (m, 1 H, CH(CH$_3$)$_2$), 3.33 (m, 1 H, CH_2CH$_3$), 3.58 (m, 1 H, CH_2CH$_3$), 5.33 (ddd, J = 15.4, 7.4, 1.4 Hz, 1 H, =CH), 5.63−5.77 (m, 2 H, =CH, CHO), 6.33/7.32 (br ds, 1 H, NH) (conformer ratio 1.2:1); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.86 (d), 14.38 (d), 17.74 (d), 17.84 (d), 18.20 (d), 18.28 (d), 22.21 (d), 30.85 (d), 32.17 (d), 32.25 (d), 37.85 (d), 39.89 (d), 84.67 (d), 86.67 (d), 122.27 (d), 122.43 (d), 142.23 (d), 142.43 (d), 188.67 (u), 189.42 (u); IR (film) ν 3301 (s), 2961 (s), 2932 (s), 2871 (s), 1655 (s), 1520 (s), 1464 (s), 1404 (m), 1384 (s), 1367 (m), 1334 (m), 1298 (m), 1207 (s), 1154 (m), 1122 (m), 1094 (m), 1059 (w), 970 (s), 855 (m), 737 (w) cm^{-1}; MS (CI) m/z (relative intensity) 230 [M$^+$ + 1] (15), 158 (20), 125 (15), 124 (29), 115 (32), 109 (36), 106 (16), 83 (11), 81 (45), 79 (13), 72 (11), 70 (10), 69 (100). Anal. Calcd for $C_{12}H_{23}NOS$ (229.15): C, 62.83; H, 10.11; N, 6.11. Found: C, 63.21; H, 9.99; N, 6.51.

(±)-Methylthiocarbamic Acid *O*-(Cyclohex-2-enyl) Ester (*rac*-9a). Following GP1, reaction of alcohol *rac*-**7** (2.21 g, 22.5 mmol) with methyl isothiocyanate (1.65 g, 22.6 mmol) gave thiocarbamate *rac*-**9a** (2.76 g, 71%) as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.60−2.18 (m, 6 H, CH_2), 2.87/3.07 (d, 3 H, J = 5.0 Hz, CH_3), 5.75−5.88 (m, 2 H, =CH, CHO), 5.93−6.04 (m, 2 H, CH=CH), 6.56/7.21 (br ds, 1 H, NH) (conformer ratio 1.4:1); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.93 (u), 24.92 (u), 28.3 (u), 29.51 (d), 31.70 (d), 73.76 (d), 75.46 (d), 125.52 (d), 132.98 (d), 190.04 (u); IR (film) ν 3280 (m), 3029 (m), 2937 (s), 2864 (m), 1726 (w), 1656 (m), 1531 (s), 1531 (s), 1444 (s), 1395 (m), 1365 (s), 1217 (s), 1152 (s), 1096 (m), 1043 (m), 1006 (m), 949 (m), 927 (m), 726 (m) cm^{-1}; MS (CI) m/z (relative intensity) 172 [M$^+$ + 1] (63), 92 (100), 81 (75), 43 (100). Anal. Calcd for $C_8H_{13}NOS$ (171.07): C, 56.10; H, 7.65; N, 8.18. Found: C, 56.00; H, 7.81; N, 8.45.

(±)-Methylthiocarbamic Acid *O*-(Cyclohept-2-enyl) Ester (*rac*-10a). Following GP1, reaction of alcohol *rac*-**8** (1.12 g, 10.0 mmol) with methyl isothiocyanate (0.80 g, 11.0 mmol) gave thiocarbamate *rac*-**10a** (1.46 g, 79%) as colorless crystals: mp 49 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28−1.54 (m, 1 H, CH_2), 1.62−1.82 (m, 3 H, CH_2), 1.84−2.31 (m, 4 H, CH_2), 2.88/3.09 (m, 3 H, CH_3), 5.64−5.93 (m, 2 H, CH=CH), 5.99 (m, 1 H, CHO), 6.58/7.42 (br ds, 1 H, NH) (conformer ratio 1.3:1); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 26.07 (u), 26.14 (u), 26.60 (u), 28.44 (u), 29.46 (d), 31.65 (d), 32.71 (u), 80.03 (d), 81.54 (d), 131.04 (d), 131.58 (d), 132.76 (d), 133.31 (d), 189.82 (u), 190.01 (u); IR (KBr) ν 3248 (s), 3030 (w), 2970 (m), 2918 (s), 2886 (m), 2853 (m), 1655 (w), 1545 (s), 1442 (s), 1359 (s), 1301 (w), 1219 (s), 1156 (s), 1123 (m), 1073 (s), 1055 (s), 979 (s), 927 (m), 897 (w), 864 (w), 831 (m), 787 (m), 723 (m), 686 (s) cm^{-1}; GC−MS (CI) m/z (relative intensity) 186 [M$^+$] (19), 95 (77), 94 (27), 93 (15), 92 (100), 91 (18), 79 (24), 77 (10), 67 (46), 65 (11), 58 (37). Anal. Calcd for $C_8H_{13}NOS$ (185.09): C, 58.34; H, 8.16; N, 7.56. Found: C, 58.26; H, 8.19; N, 7.55.

General Procedure for the Palladium-Catalyzed Rearrangement of *O*-Allylic Thiocarbamates (GP2). Ligand **11** and precatalyst $Pd_2(dba)_3$·$CHCl_3$ were placed in a Schlenk flask, and CH_2Cl_2 (10 mL) was added at room temperature.

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After formation of the palladium−ligand complex, which is indicated by the development of an orange color of the solution, the allylic *O*-thiocarbamate (1.00 mmol) was added and the mixture was stirred at room temperature. After TLC indicated a complete consumption of the starting material, the mixture was quenched through the addition of saturated aqueous NaCl (10 mL). After the mixture was stirred for 30 min, the layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by chromatography (hexanes/ethyl acetate, 3:1) gave the pure *S*-allylic thiocarbamate.

Methylthiocarbamic Acid *S*-((*R*)-(*E*)-1-methylbut-2-enyl) Ester (12a). Following GP2, rearrangement of thiocarbamate *rac*-**4a** (159 mg, 1.00 mmol) in the presence of ligand **11** (21 mg, 0.03 mmol) and $Pd_2(dba)_3$·$CHCl_3$ (13 mg, 0.013 mmol) gave after a reaction time of 16 h thiocarbamate **12a** (146 mg, 92%) as a pale yellow oil: 91% ee (GC, octakis(2,3-*O*-dipentyl-6-*O*-methyl)-γ-cyclodextrin column, t_R(**12a**) = 48.9 min, t_R(*ent*-**12a**) = 48.8 min); $[\alpha]^{20}_D$ +97.4 (*c* 13.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.42 (d, *J* = 7.1 Hz, 3 H, CHC*H*$_3$), 1.70 (dd, *J* = 6.0, 1.0 Hz, 3 H, CHC*H*$_3$), 2.85 (d, *J* = 4.7 Hz, 3 H, NHC*H*$_3$), 4.52 (dqd, *J* = 7.1, 7.1, 1.0 Hz, 1 H, CHS), 5.23−5.41 (m, 1 H, NH), 5.53 (ddq, 1 H, *J* = 15.1, 7.1, 1.4 Hz, =CH), 5.67 (dqd, *J* = 15.1, 6.4, 1.1 Hz, 1 H, =CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.71 (d), 21.18 (d), 27.67 (d), 41.65 (d), 125.75 (d), 132.17(d), 167.42 (u); IR (film) ν 3315 (s), 3026 (m), 2964 (m), 2936 (m), 2879 (m), 1740 (m), 1727 (m), 1655 (s), 1523 (s), 1449 (s), 1413 (m), 1375 (m), 1227 (s), 1203 (s), 1160 (m), 1046 (m), 1016 (m), 965 (m), 819 (m), 734 (m) cm^{-1}; MS (CI) *m*/*z* (relative intensity) 160 [M^+ + 1] (27), 126 (12), 102 (40), 92 (51), 69 (46). Anal. Calcd for $C_7H_{13}NOS$ (159.25): C, 52.79; H, 8.23; N, 8.80. Found: C, 52.55; H, 8.21; N, 9.18.

Methylthiocarbamic Acid *S*-((*R*)-(*E*)-1-Ethylpent-2-enyl) Ester (13a). Following GP2, rearrangement of thiocarbamate *rac*-**5a** (187 mg, 1.00 mmol) in the presence of ligand **11** (63 mg, 0.09 mmol) and $Pd_2(dba)_3$·$CHCl_3$ (39 mg, 0.038 mmol) gave after a reaction time of 16 h thiocarbamate **13a** (172 mg, 92%) as a pale yellow oil: 91% ee (GC, octakis(2,3-*O*-dipentyl-6-*O*-methyl)-γ-cyclodextrin column, t_R(**13a**) = 50.1 min, t_R(*ent*-**13a**) = 49.9 min); $[\alpha]^{20}_D$ +85.4 (*c* 11.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 (dt, *J* = 15.1, 6.3 Hz, 6 H, CH_2CH_3), 0.63−1.77 (m, 2 H, CH_2CH_3), 2.03 (dqd, *J* = 7.4, 7.4, 1.4 Hz, 2 H, CH_2CH_3), 2.86 (d, *J* = 4.9 Hz, 3 H, NHC*H*$_3$), 3.92 (dt, *J* = 7.4, 7.4 Hz, 1 H, CHS), 5.38 (ddt, *J* = 15.1, 8.5, 1.6 Hz, 1 H, =CH), 5.71 (dt, br ds, *J* = 15.1, 6.3 Hz, 2 H, =CH, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.74 (d), 13.58 (d), 25.37 (u), 27.79 (d), 28.54 (u), 48.82 (d), 129.01 (d), 134.06 (d), 167 (u); IR (film) ν 3315 (s), 3028 (w), 2964 s), 2933 (s), 2874 (m), 1654 (s), 1520 (s), 1461 (m), 1413 (m), 1379 (w), 1306 (w), 1224 (s), 1161 (m), 1011 (m), 965 (m), 818 (m) cm^{-1}; MS (CI) *m*/*z* (relative intensity) 188 [M^+ + 1] (9), 92 (14), 81 (20). Anal. Calcd for $C_9H_{17}NOS$ (187.10): C, 57.71; H, 9.15; N, 7.48. Found: C, 57.49; H, 9.38; N, 7.73.

Methylthiocarbamic Acid *S*-((*S*)-Cyclohex-2-enyl) Ester (14a). Following GP2, rearrangement of thiocarbamate *rac*-**9a** (171 mg, 1.00 mmol) in the presence of ligand **11** (10.5 mg, 0.0125 mmol) and $Pd_2(dba)_3$·$CHCl_3$ (6.5 mg, 0.0075 mmol) gave after a reaction time of 30 min thiocarbamate **14a** (161 mg, 94%) as colorless crystals: 97% ee (GC, octakis(2,3-*O*-dipentyl-6-*O*-methyl)-γ-cyclodextrin column, t_R(**14a**) = 103.3 min, t_R(*ent*-**14a**) = 103.2 min); mp 51 °C; $[\alpha]^{20}_D$ −260.0 (*c* 10.9, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.63−2.10 (m, 6 H, CH_2), 2.86 (d, *J* = 5.0 Hz, 3 H, NHC*H*$_3$), 4.19 (m, 1 H, CHS), 5.53 (br ds, 1 H, NH), 5.66−5.73 (m, 1 H, =CH), 5.82 (dtd, *J* = 8.4, 3.7, 1.7 Hz, 1 H, =CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.74 (u), 24.76 (u), 27.79 (d), 30.42 (u), 40.91 (d), 126.78 (d), 130.62 (d), 167.84 (u); IR (KBr) ν 3676 (w), 3650 (w), 3630 (w), 3282 (s), 3028 (s), 2930 (s), 2906 (s), 2853 (s), 2832 (s), 2666 (w), 2477 (w), 1645 (s), 1526 (s), 1459 (s), 1443 (s), 1430 (s), 1408 (s), 1387 (s), 1348 (s), 1325 (s), 1305 (s), 1230 (s), 1200 (s), 1158 (s), 1081 (s), 1037 (s), 1011 (s), 997 (s), 918 (m), 870 (s), 826 (s), 751 (s), 724 (s) cm^{-1}; MS (CI) *m*/*z* (relative intensity) 172 [M^+ + 1] (54), 92 (100), 81 (73), 77 (5). Anal. Calcd for $C_8H_{13}NOS$ (171.07): C, 56.10; H, 7.65; N, 8.18. Found: C, 55.94; H, 7.85; N, 7.96.

Methylthiocarbamic Acid *S*-((*S*)-Cyclohept-2-enyl) Ester (15a). Following GP2, rearrangement of thiocarbamate *rac*-**10a** (185 mg, 1.00 mmol) in the presence of ligand **11** (21.0 mg, 0.03 mmol) and $Pd_2(dba)_3$·$CHCl_3$ (13.0 mg, 0.012 mmol) gave after a reaction time of 5 h thiocarbamate **15a** (173 mg, 94%) as colorless crystals: 92% ee (GC, heptakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)-β-cyclodextrin column, t_R(**15a**) = 70.4 min, t_R(*ent*-**15a**) = 69.8 min); mp 38 °C; $[\alpha]^{20}_D$ −262.0 (*c* 10.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.49−1.69 (m, 2 H, CH_2), 1.72−1.98 (m, 4 H, CH_2), 2.13−2.20 (m, 2 H, CH_2), 2.87 (dd, 3 H, *J* = 4.7, 2.2 Hz, CH_3), 4.37 (m, 1 H, CHS), 5.40 (br ds, 1 H, NH), 5.80 (m, 2 H, CH=CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.05 (u), 27.20 (u), 27.77 (d), 28.28 (u), 33.34 (u), 44.93 (d), 131.75 (d), 133.52 (d), 167.50 (u); IR (KBr) ν 3332 (s), 3019 (m), 2924 (s), 2849 (m), 2732 (s), 1645 (s), 1522 (s), 1445 (m), 1413 (m), 1385 (w), 1228 (s), 1206 (s), 1161 (m), 1069 (w), 1052 (w), 1011 (m), 958 (m), 889 (w), 838 (w), 821 (s), 788 (m), 692 (m) cm^{-1}; GC−MS (CI) *m*/*z* (relative intensity) 186 [M^+ + 1] (37), 96 (13), 95 (83), 94 (26), 93 (19), 92 (100), 79 (14), 67 (33), 58 (39). Anal. Calcd for $C_8H_{13}NOS$ (185.09): C, 58.34; H, 8.16; N, 7.56. Found: C, 58.45; H, 8.11; N, 7.41.

2-((*R*)-(*E*)-1-Methylbut-2-enylsulfanyl)pyrimidine (17a). 2-Chloropyrimidine (399 mg, 3.5 mmol), KOH (196 mg, 3.5 mmol), and THF (30 mL) were placed in a flask, and thiocarbamate **12a** (500 mg, 3.1 mmol) was added. After the mixture was heated at reflux for 16 h, the solid was removed by filtration and the filtrate was concentrated in vacuo. Purification of the residue by Kugelrohr distillation gave sulfide **17a** (530 mg, 95%) as a colorless oil: 91% ee (GC, octakis(2,3-di-*O*-pentyl-6-*O*-methyl)-γ-cyclodextrin column, t_R(**17a**) = 36.03 min, t_R(*ent*-**17a**) = 36.15 min); $[\alpha]^{20}_D$ +124.3 (*c* 12.4, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52 (d, *J* = 6.7 Hz, 3 H, CHC*H*$_3$), 1.68 (dd, *J* = 7.4, 1.0 Hz, 3 H, CHC*H*$_3$), 4.48 (dqd, *J* = 6.7, 6.7, 0.7 Hz, CHS), 5.58−5.82 (m, 2 H, CH=CH), 6.95 (t, *J* = 4.7 Hz, 1 H, Ar), 8.50 (d, *J* = 4.7 Hz, 2 H, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.81 (d), 20.37 (d), 41.65 (d), 116.36 (d), 126.40 (d), 131,71 (d), 157.15 (d), 172.39 (u).

2-((*R*)-(*E*)-1-Methylbut-2-enylsulfanyl)benzene (17b). A solution of the *S*-allylic thiocarbamate **12a** (159 mg, 1 mmol) and PhI (187 mg, 1 mmol) in dioxane (5 mL) was added under argon to K_2CO_3 (180 mg, 1.3 mmol), $Pd(OAc)_2$ (23 mg, 0.1 mmol), PPh_3 (79 mg, 0.3 mmol), and nBu$_4$NI (369 mg, 1.0 mmol). After the mixture was heated at reflux for 3 h, hexane (30 mL) was added following cooling of the mixture to room temperature. Then the mixture was filtered, and the organic phase was washed with water, dried (MgSO4), and concentrated in vacuo. Kugelrohr distillation of the residue gave sulfide **19b** (99 mg, 56%) as a colorless oil: 92% ee (GC, octakis(2,3-*O*-dipentyl-6-*O*-methyl)-γ-cyclodextrin column, t_R(**17b**) = 29.6 min, t_R(*ent*-**17b**) = 29.3 min)); $[\alpha]^{20}_D$ +34.2 (*c* 9.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (d, 3 H, *J* = 6.9 Hz, CH_3), 1.60 (dm, 3 H, *J* = 5.0 Hz, CH_3), 3.73 (dq, 1 H, *J* = 6.9 Hz, CHS), 5.32−5.47 (m, 2 H, =CH), 7.17−7.28 (m, 4 H, Ph), 7.35−7.39 (m, 1 H, Ph); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 17.55 (d), 20.70 (d), 45.69 (d), 125.75 (d), 126.71 (d), 128 (d), 132.51 (d), 134.97 (u); IR (KBr) ν 3760 (s), 3073 (m), 3058 (m), 3023 (m), 2970 (s), 2920 (s), 2865 (m), 1665 (w), 1584 (s), 1478 (s), 1448 (s), 1375 (s), 1200 (m), 1154 (m), 1091 (m), 1058 (m), 1044 (m), 1017 (s), 962 (s), 746 (s), 692 (s) cm^{-1}; GC−MS (Cl) *m*/*z* (relative intensity) 178 [M^+, 13), 177 (37), 110 (23), 109 (16), 69 (100), 65 (11). Anal. Calcd for $C_{11}H_{14}S$ (179.29): C, 74.10; H, 7.91. Found: C 74.22; H 7.98.

***(S)*-Cyclohex-2-enethiol (18).** To an aqueous solution of NaOH (10 mL, 5%) was added thiocarbamate **14a** (1.71 g, 10 mmol). After the mixture was stirred at room temperature for 16 h, it was neutralized with 2 N HCl and then extracted with diethyl ether (3 × 10 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by Kugelrohr distillation gave thiol **18** (889 mg, 64%) as a colorless oil: 97% ee (GC, octakis(2,3-*O*-dipentyl-6-*O*-methyl)-γ-cyclodextrin column, t_R(**18**) = 6.7 min, t_R(*ent*-**18**) = 6.5 min); $[\alpha]^{20}_D$ −271.3 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.57−1.66 (m, 1 H, CH_2), 1.66−1.77 (m, 1 H, CH_2),

1.68 (d, J = 8.3 Hz, 1 H, SH), 1.79−2.12 (m, 1 H, CH_2), 3.45−3.57 (m, 1 H, CHS), 5.65−5.78 (m, 2 H, CH=CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.37 (u), 24.61 (u), 33.42 (u), 34.99 (d), 127.89 (d), 130.61 (d); IR (film) ν 3025 (s), 2937 (s), 2859 (s), 2834 (s), 1644 (w), 1442 (s), 1431 (s), 1390 (w), 1351 (w), 1341 (w), 1305 (w), 1258 (m), 1232 (m), 1210 (m), 1186 (w), 1149 (w), 1085 (w), 1041 (m), 1000 (m), 987 (w), 934 (m), 903 (m), 875 (m), 854 (w), 833 (m), 731 (s), 721 (s), 703 (m) cm^{-1}; MS (CI) m/z (relative intensity) 114 [M^+] (16), 98 (18), 84 (35), 83 (21), 82 (13), 81 (39), 55 (15), 43 (100). Anal. Calcd for $C_6H_{10}S$ (114.05): C, 63.10; H, 8.83. Found: C, 62.89; H, 8.64.

Crossover Experiment. Following GP2, rearrangement of a mixture of thiocarbamates *rac*-**4b** (87 mg, 0.50 mmol) and *rac*-**5d** (108 mg, 0.50 mmol) in the presence of ligand **11** (42 mg, 0.06 mmol) and precatalyst $Pd_2(dba)_3$•$CHCl_3$ (26 mg, 0.025 mmol) gave after a reaction time of 16 h a mixture of **12b**, **12d**, **13b**, and **13d** in a ratio of 30:20:18:30 according to GC (t_R(**12b**) = 8.08 min, t_R(**12d**) = 8.15 min, t_R(**13b**) = 8.99 min, t_R(**13d**) = 9.07 min) and GC−MS.

Loading of the Methyl Isothiocyanate Resin 21 with Alcohol *rac*-7. A solution of alcohol *rac*-**7** (294 mg, 3 mmol) in THF (10 mL) was slowly added at 0 °C to an argon-purged suspension of NaH (140 mg, 3.5 mmol, 60% in mineral oil) in THF (10 mL). After the suspension was stirred at 0 °C for 1 h, it was slowly added via syringe to a suspension of the methyl isothiocyanate resin **21** (390 mg, loading 1.9 mmol/g) in THF (5 mL). The suspension was stirred at 20 °C for 16 h, and then saturated aqueous $NaHCO_3$ (10 mL) was added. Then resin **22** was filtered, washed with H_2O (10 mL) and alternately two times with THF (10 mL) and methanol (10 mL), and freeze-dried.

Pd-Catalyzed Rearrangement of Resin-Bound O-Allylic Thiocarbamate 22. Ligand **11** (31.1 mg, 0.045 mmol) and $Pd_2(dba)_3$•$CHCl_3$ (19.6 mg, 0.019 mmol) were placed in a Schlenk flask, and at room temperature CH_2Cl_2 (10 mL) was added. After the development of an orange color, indicating formation of the palladium−ligand complex, the solution was added via syringe to the *O*-allylic thiocarbamate resin **22**, obtained as described above, and the resulting suspension was stirred at room temperature for 16 h. Subsequently, resin **24** was filtered, alternately washed with CH_2Cl_2 and methanol (2 × 10 mL), and freeze-dried.

(−)-2-((*S*)-Cyclohex-2-enylsulfanyl)pyrimidine (19a). KOH (250 mg, 8 mmol), 2-chloropyrimidine (250 mg, 4 mmol), and resin **24**, obtained as described above, in THF (10 mL) were placed in a Schlenk flask. After the suspension was stirred at room temperature for 16 h, it was filtered and the residue was washed with THF (10 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by chromatography (hexanes/ethyl acetate, 3:1) gave sulfide **19a** (49.0 mg, 34% yield, based on **21**) of 66% ee (GC) as a colorless oil.

(−)-((*S*)-Cyclohex-2-enylsulfanyl)benzene (19b). K_2CO_3 (135 mg, 1.0 mmol), $Pd(OAc)_2$ (17.3 mg, 0.075 mmol), PPh_3 (59 mg, 0.23 mmol), Bu_4NI (277 mg, 0.75 mmol), and resin **24**, obtained as described above, were placed under argon in a Schlenk flask. Then a solution of PhI (140 mg, 1.0 mmol) in dioxane (5 mL) was added, and the mixture was heated at reflux for 5 h. Hexane (5 mL) was added following cooling of the suspension to room temperature. The suspension was filtered, and the residue was washed with hexane (20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by chromatography (hexanes/ethyl acetate, 3:1) gave sulfide **19b** (34.2 mg, 24% yield, based on **21**) of 64% ee (GC) as a colorless oil.

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Supporting Information Available: Full experimental details and ^{1}H NMR, ^{13}C NMR, IR, MS, and analytical data of the *O*-allylic thiocarbamates *rac*-**4b**−**f**, *rac*-**5d,f**, and *rac*-**9b**−**g**, the *S*-allylic thiocarbamates **12b**−**f**, **13d,f**, and **14b**−**g**, and the sulfides **19a,b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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