Highly Selective Palladium Catalyzed Kinetic Resolution and Enantioselective Substitution of Racemic Allylic Carbonates with Sulfur Nucleophiles: Asymmetric Synthesis of Allylic Sulfides, Allylic Sulfones, and Allylic Alcohols

Hans-Joachim Gais,* Thomas Jagusch, Nicole Spalthoff, Frank Gerhards, Michael Frank, and Gerhard Raabe[a]

Abstract: We describe the highly selective palladium catalyzed kinetic resolutions of the racemic cyclic allylic carbonates *rac*-**1a–c** and racemic acyclic allylic carbonates *rac*-**3aa** and *rac*-**3ba** through reaction with *tert*-butylsulfinate, tolylsulfinate, phenylsulfinate anions and 2-pyrimidinethiol by using *N*,*N*′-(1*R*,2*R*)-1,2-cyclohexanediylbis[2-(diphenylphosphino)-benzamide] (**BPA**) as ligand. Selectivities are expressed in yields and *ee* values of recovered substrate and product and in selectivity factors *S*. The reaction of the cyclohexenyl carbonate **1a** (≥99% *ee*) with 2-pyrimidinethiol in the presence of **BPA** was shown to exhibit, under the conditions used, an overall pseudo-zero order kinetics in regard to the allylic substrate. Also described are the highly selective palladium catalyzed asymmetric syntheses of the cyclic and acyclic allylic *tert*-butylsulfones **2aa**, **2b**, **2c**, **2d** and **4a–c**, respectively, and of the cyclic and acyclic allylic 2-pyrimidyl-, 2-pyridyl-, and 4-chlorophenylsulfides **5aa**, **5b**, **5ab**, **6aa–ac**, **6ba** and **6bb**, respectively, from the corresponding racemic carbonates and sulfinate anions and thiols, respectively, in the presence of **BPA**. Synthesis of the *E*-configured allylic sulfides **6aa**, **6ab**, **6ac** and **6bb** was accompanied by the formation of minor amounts of the corresponding *Z* isomers. The analogous synthesis of allylic *tert*-butylsulfides from allylic carbonates and *tert*-butylthiol by using **BPA** could not be achieved. Reaction of the cyclopentenyl esters *rac*-**1da** and *rac*-**1db** with 2-pyrimidinethiol gave the allylic sulfide **5c** having only a low *ee* value. Similar results were obtained in the case of the reaction of the cyclohexenyl carbonate *rac*-**1a** and of the acyclic carbonates *rac*-**3aa** and *rac*-**3ba** with 2-pyridinethiol and lead to the formation of the sulfides **5ab**, **6ab**, and **6bb**, respectively. The low *ee* values may be ascribed to the operating of a "memory effect", that is, both enantiomers of the substrate give the substitution product with different enantioselectivities. However, in the reaction of the racemic carbonate *rac*-**1a** as well as of the highly enriched enantiomers **1a** (≥99% *ee*) and *ent*-**1a** (≥99% *ee*) with 2-pyrimidinethiol the *ee* values of the substrates and the substitution product remained constant until complete conversion. Similar results were obtained in the reaction of the cyclic carbonates *rac*-**1a**, *ent*-**1a** (≥99% *ee*) and *ent*-**1c** (≥99% *ee*) with lithium *tert*-butylsulfinate. Thus, in the case of *rac*-**1a** and 2-pyrimidinthiol and *tert*-butylsulfinate anion as nucleophiles the enantioselectivity of the substitution step is, under the conditions used, independent of the chirality of the substrate; this shows that no "memory effect" is operating in this case. Hydrolysis of the carbonates *ent*-**1a–c**, *ent*-**3aa** and *ent*-**3ba**, which were obtained through kinetic resolution, afforded the enantiomerically highly enriched cyclic allylic alcohols **9a–c** (≥99% *ee*) and acyclic allylic alcohols **10a** (≥99% *ee*) and **10b** (99% *ee*), respectively.

Keywords: allylic compounds · asymmetric catalysis · asymmetric synthesis · kinetic resolution · palladium

Introduction

The separation of the enantiomers of a racemate (resolution) is an important technique for the attainment of enantioenriched compounds,[1] particularly on an industrial scale.[1d,e] Especially attractive resolution methods are those based on enantiomer selective reactions (kinetic resolution) employing chiral catalysts.[1, 2] While catalytic kinetic resolution has been for a long time the domain of enzymes,[1q,r] much progress has been made in the last decade towards the development of transition metal and small-molecule catalysts.[1h,m,n] In this context particularly interesting is the palladium-catalyzed reaction of racemic allylic esters with nucleophiles (Scheme 1),[3] which can not only provide an asymmetric synthesis of allylic compounds with complete conversion of

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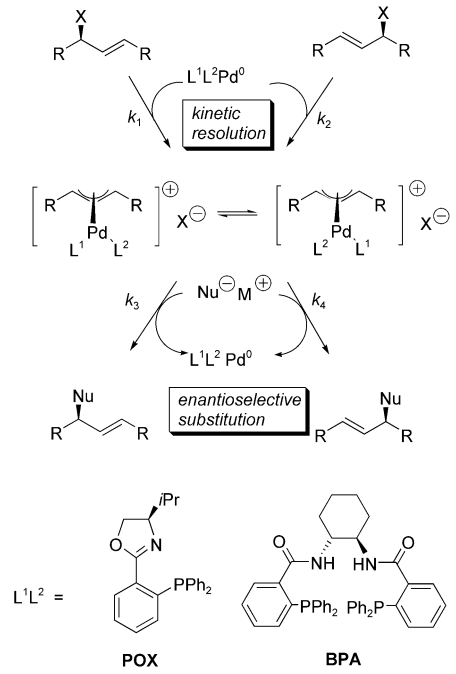


Scheme 1. Simplified mechanistic Scheme of the palladium(0) catalyzed reaction of racemic allylic substrates with nucleophiles (X = leaving group, Nu = nucleophile, M = metal).

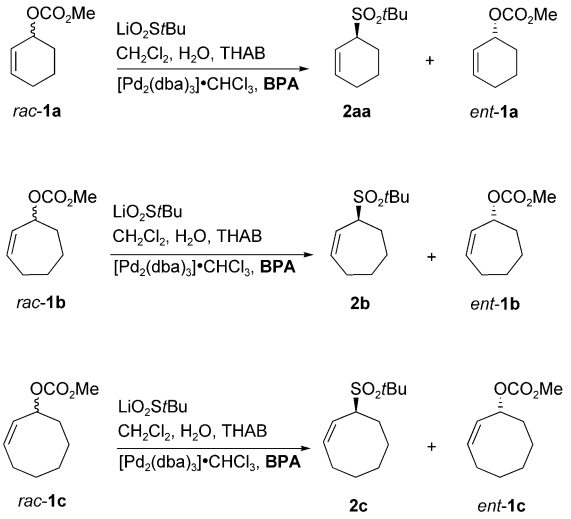
the substrate but, in principle, also kinetic resolution of the latter. According to a simplified mechanistic scheme[4a] both enantiomers of a symmetrically disubstituted substrate[4b] are converted by a chiral palladium(0) catalyst to the same set of equilibrating π-allyl palladium(II) intermediates;[4c] its reaction with the nucleophile affords the substitution product and the catalyst.[3, 5] While the second step, the enantioselective substitution, has been intensively studied,[3] it was only in the recent years that the first step, the kinetic resolution, has received attention. Kinetic resolution in palladium catalyzed allylic substitution was described for the first time by Hayashi et al. in 1986.[6] Reaction of an unsymmetrically disubstituted allylic ester with a carbon nucleophile in the presence of a chiral ferrocenylphosphane based palladium catalyst was found to proceed with a medium selective kinetic resolution. We reported in 1998[7] about the observation of high selectivities in both kinetic resolution and enantioselective substitution in the reaction of 1,3-diphenylpropenyl carbonate with lithium *tert*-butylsulfinate by using the chiral phosphinooxazoline ligand **POX**.[8, 3e,f] Determination of the stereochemical course of both processes revealed $k_1 > k_2$ and $k_3 > k_4$. Shortly afterwards we found[9] that the reaction of racemic 2-cyclohexenyl carbonate with 2-pyrimidinethiol in the presence of the chiral bisphosphinoamide ligand **BPA**[10, 3d] also proceeds with high enantioselectivities in both kinetic resolution and substitution and takes a similar stereochemical course. At the same time and subsequently several other groups also encountered kinetic resolution in the reaction of allylic substrates with carbon and oxygen nucleophiles by using chiral phosphanes including **BPA**.[11] These studies were mainly conducted in connection with the design of new chiral ligands for the palladium atom and were thus limited to certain substrates and nucleophiles. Based on our previous preliminary observations,[7, 9] we have been interested in the general synthetic and selectivity aspects of both the kinetic resolution and the enantioselective substitution of cyclic and acyclic substrates by using sulfur nucleophiles, as for example thiols and sulfinate anions, and **BPA** as ligand because of the following reasons. First, chiral allylic alcohols are synthetically highly useful[3a, 12] and the development of new methods for their kinetic resolution is currently a topic of much interest.[1h,m,n,q, 13] Following the invention of the highly efficient kinetic resolution of allylic alcohols through titanium-catalyzed epoxidation by Sharpless et al.,[14] a number of catalytic methods using transition-metal catalysts,[15] enzymes,[16] enzymes in combination with an achiral transition-metal catalyst,[17] and small-molecule catalysts[18] have been described. However, methods which provide for high selectivities in the kinetic resolution of both cyclic and acyclic allylic alcohols are still scarce. Second, allylic sulfides[19] and allylic sulfones[20] are valuable intermediates in organic synthesis[21] and the development of a method for the catalytic asymmetric synthesis of allylic sulfides and the widening of the scope of the palladium catalyzed asymmetric synthesis of allylic sulfones[7, 22–24] should greatly enhance the synthetic utility of these allylic sulfur compounds. For example, they could find interesting applications as for example in sigmatropic rearrangement, transition metal mediated substitution with organometallics[19, 20] and synthesis of chiral nonracemic sulfur stabilized allylic carbanions.[25] Third, it was of interest to see whether thiols can generally function as nucleophiles in the palladium catalyzed allylic substitution in the presence of chiral ligands including **BPA** and **POX**. Because of the pronounced thiophilicity of the palladium atom, coordination of the thiol to the palladium atom of the π-allyl intermediate[26] could occur leading to a retardation or even blocking of the catalytic cycle. The literature on the feasibility of a palladium catalyzed allylic substitution with thiols is ambiguous.[27] While several groups have described the successful utilization of thiols in the presence of achiral phosphanes,[27c–g] others reported about the failure to achieve an allylic substitution with thiols.[27a,b] Fourth, **BPA** was selected as ligand for the palladium atom because it provided high enantioselectivities in the substitution of a range of cyclic and acyclic substrates with various nucleophiles[3] including those based on sulfur.[7, 9, 22, 23, 28–30]

In this paper we describe both the highly selective kinetic resolution of cyclic and acyclic racemic allylic carbonates in reactions with sulfinate anions and thiols by using **BPA** and **POX** containing palladium catalysts, leading for example to highly enantioenriched allylic alcohols and the asymmetric synthesis of allylic sulfides and allylic sulfones.[31]

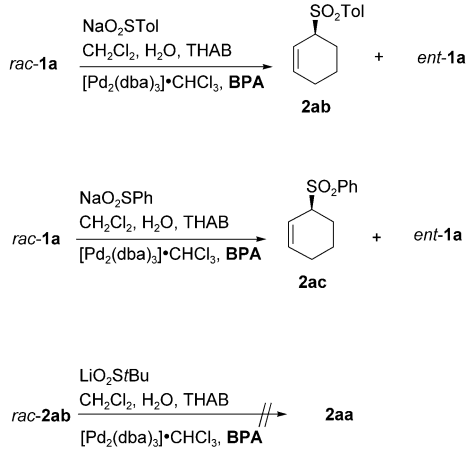
Results and Discussion

Kinetic resolution

Sulfinates and racemic allylic carbonates: The investigation of the kinetic resolution of allylic esters in their reaction with sulfinate anions was carried out with the racemic cyclohexenyl, cycloheptenyl and cyclooctenyl carbonates *rac*-**1a**, *rac*-**1b** and *rac*-**1c**, respectively (Schemes 2 and 3) and the

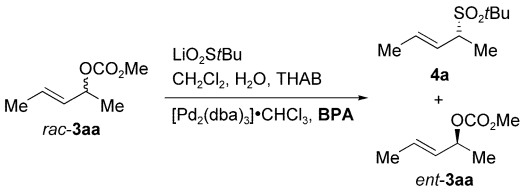


Scheme 2. Palladium-catalyzed kinetic resolution of cyclic carbonates with lithium *tert*-butylsulfinate.



Scheme 3. Palladium-catalyzed kinetic resolution of cyclic carbonates with aromatic sulfinate anions.

racemic acyclic carbonate *rac*-**3aa** (Scheme 4). Carbonates were chosen instead of acetates because of their higher reactivity in palladium-catalyzed substitution.[3a,g] Because of their different steric size and because of synthetic reasons, *tert*-butylsulfinate,[32] tolylsulfinate and phenylsulfinate anions were used. Most of the reactions studied were run with the *tert*-butylsulfinate anion because of 1) our interest in the utilization of enantioenriched allylic *tert*-butylsulfones as starting material for the synthesis of the corresponding chiral nonracemic allylic α-sulfonyl carbanions[25] and 2) the desire to determine the scope and limitation of sulfinate anions as



Scheme 4. Palladium-catalyzed kinetic resolution of a acyclic carbonate with lithium *tert*-butylsulfinate.

nucleophiles. The reactions were carried out at 0 °C at a 10 mmol scale under argon in a two-phase system composed of CH_2Cl_2 and water, containing Hex_4NBr (THAB) as a phase transfer catalyst, by using 2 equiv of the sulfinate salt, 1.5 mol % $[Pd_2(dba)_3]\cdot CHCl_3$ (dba = dibenzylideneacetone)[33] and 4.5 mol % **BPA**. The precatalyst and **BPA** were dissolved at 0 °C in CH_2Cl_2 and after a preformation time the allylic substrate was added. Then a cold solution of the sulfinate salt in a mixture of degassed water and CH_2Cl_2, containing THAB, was added. After GC analysis or ^{1}H NMR spectroscopy revealed an approximately 50 % conversion of the allylic substrates, the reactions were terminated by phase separation and stirring of the organic phase under air in order to destroy the catalyst. Carbonates and the sulfones were separated by chromatography and their *ee* values were determined either by GC or HPLC analysis using chiral stationary phase containing columns or by ^{1}H NMR spectroscopy in the presence of a chiral shift reagent.

As revealed by Table 1 both the kinetic resolution and the enantioselective substitution of the cyclic carbonates *rac*-**1a**–**c** in the reaction with lithium *tert*-butylsulfinate proceeded with high selectivities and afforded the highly enantioenriched carbonates *ent*-**1a**–**c** and sulfones **2aa**, **2b** and **2c**, respectively, in good yields (cf. Scheme 2). The selectivity of the kinetic resolution of the cyclooctenyl carbonate *rac*-**1c** was the highest. After an approximately 50 % conversion of the carbonate, the reaction with the sulfinate salt came practically to a complete halt (see below). The kinetic resolution of carbonate *rac*-**1c** was carried out with similar results on a 30 mmol and a 50 mmol scale by using only 0.9 mol % $[Pd_2(dba)_3]\cdot CHCl_3$ and 3 mol % **BPA**. We note that the faster reacting enantiomers of the carbonates *rac*-**1a**–**c** and the preferentially formed sulfones **2aa**, **2b** and **2c** have the same absolute configuration.[7]

Table 1. Palladium-catalyzed kinetic resolution of the cyclic carbonates *rac*-**1a**–**c** with lithium *tert*-butylsulfinate.[a]

Substrate	*t* [h]	Conv [%]	Carbonate	Yield [%]	*ee* [%]	Sulfone	Yield [%]	*ee* [%]
rac-**1a**	0.75	54	*ent*-**1a**	34	≥ 99	**2aa**	49	98
rac-**1b**	4	53	*ent*-**1b**	33	94	**2b**	46	95
rac-**1c**	24	58	*ent*-**1c**	34	≥ 99	**2c**	48	96

[a] 1.5 mol % $[Pd_2(dba)_3]\cdot CHCl_3$ and 4.5 mol % **BPA**.

In addition to lithium *tert*-butylsulfinate, sodium tolylsulfinate which is commercially available and sodium phenylsulfinate were applied as nucleophiles in the kinetic resolution of carbonate *rac*-**1a** (cf. Scheme 3). Table 2 shows that the kinetic resolution and enantioselective substitution of carbo-

Table 2. Palladium-catalyzed kinetic resolution of the cyclic carbonate *rac*-**1a** with sodium tolylsulfinate and sodium phenylsulfinate.[a]

Sulfinate salt	*t* [h]	Conv [%]	Carbonate	Yield [%]	*ee* [%]	Sulfone	Yield [%]	*ee* [%]
NaO_2STol	0.5	68	*ent*-**1a**	24	≥ 99	**2ab**	60	≥ 99
NaO_2SPh	0.5	62	*ent*-**1a**	27	≥ 99	**2ac**	56	≥ 99

[a] 1.5 mol % $[Pd_2(dba)_3]\cdot CHCl_3$ and 4.5 mol % **BPA**.

nate *rac*-**1a** by using the tolylsulfinate anion occurred with high selectivities and gave the highly enantioenriched carbonate *ent*-**1a** and sulfone **2ab** in good yields. Not surprisingly similar results were recorded by using sodium phenylsulfinate. Here too both the carbonate *ent*-**1a** and the sulfone **2ac** were obtained highly enantioenriched in good yields. These results show that the intermediate cyclic π-allyl-palladium complexes are readily substituted by sulfinate anions irrespective of their steric bulkiness.

It should be noted that sulfinate anions are ambident nucleophiles, which can react with the π-allyl intermediate not only at the sulfur atom with formation of an allylic sulfone but also at the oxygen atom with formation of an allylic sulfinate. However, the latter reaction is reversible and thus sulfinic esters are normally not isolated.[24, 34, 35] We were interested to see whether the reaction of the π-allyl intermediate with the sulfinate anion with formation of the sulfone is reversible. Therefore the racemic tolylsulfone *rac*-**2ab** was treated with lithium *tert*-butylsulfinate in the presence of $[Pd_2(dba)_3]\cdot CHCl_3$ and **BPA** under the same conditions used above. Even after a prolonged reaction time at room temperature or at reflux temperature formation of the *tert*-butylsulfone **2aa** could not be detected and tolylsulfone *rac*-**2ab** was recovered.

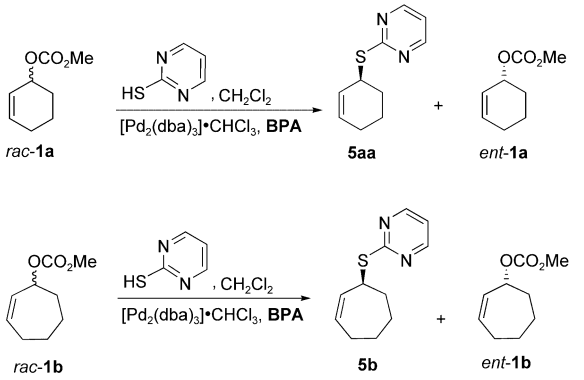
After having observed high selectivities in the kinetic resolution and enantioselective substitution of the cyclic carbonates *rac*-**1a–c** in reactions with sulfinate anions, the kinetic resolution of the acyclic carbonate *rac*-**3aa** by using lithium *tert*-butylsulfinate in the presence of **BPA** was studied under similar conditions (cf. Scheme 4). As revealed by Table 3 kinetic resolution and enantioselective substitution also occurred in this case with high selectivities and gave the highly enantioenriched carbonate *ent*-**3aa** and sulfone **4a** in good yields.

Table 3. Palladium-catalyzed kinetic resolution of the acyclic carbonate *rac*-**3aa** with lithium *tert*-butylsulfinate.[a]

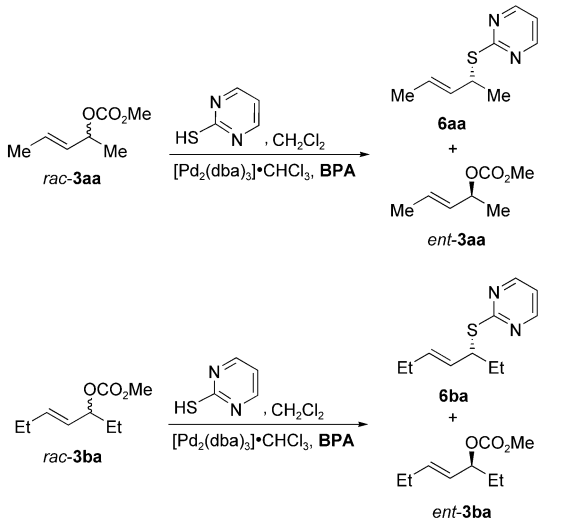
		Carbonate *ent*-**3aa**		Sulfone **4a**	
t [min]	Conv [%]	Yield [%]	*ee* [%]	Yield [%]	*ee* [%]
5	24	53	33	21	98
10	36	46	51	32	98
25	73	19	≥99	68	96

[a] 1.5 mol% $[Pd_2(dba)_3]\cdot CHCl_3$ and 4.5 mol% **BPA**.

2-Pyrimidinethiol and racemic allylic carbonates: A study of the palladium-catalyzed resolution of allylic substrates with thiols was undertaken in order to see whether they can function as nucleophiles and whether there is dependency of the selectivity of the kinetic resolution on the nucleophile. For the investigations the cyclic carbonates *rac*-**1a** and *rac*-**1b** and the acyclic carbonates *rac*-**3aa** and *rac*-**3ba** were selected as substrates and 2-pyrimidinethiol as nucleophile (Schemes 5 and 6). We had previously observed that 2-pyrimidinethiol is capable to act as a nucleophile in the palladium catalyzed allylic substitution in the presence of **BPA** in CH_2Cl_2 (see below).[22] 2-Pyrimidinethiol has only a low solubility (4.6 mmol L^{-1}) in CH_2Cl_2 at room temperature. Thus, in all reactions with 2-pyrimidinethiol in CH_2Cl_2 undissolved thiol was present until nearly all of the substrate was consumed.



Scheme 5. Palladium-catalyzed kinetic resolution of cyclic carbonates with thiols.



Scheme 6. Palladium-catalyzed kinetic resolution of acyclic carbonates with thiols.

The reactions were carried out at room temperature in CH_2Cl_2 under argon on a 10 mmol scale in substrate by using 2.5 or 5 mol% $[Pd_2(dba)_3]\cdot CHCl_3$, 5 or 11 mol% **BPA** and equimolar amounts of the thiol and they were terminated at approximately 50% conversion by filtration of the reaction mixture through Celite and stirring of the liquid phase under air. Carbonates and sulfides were separated by chromatography and their *ee* values were determined by GC or HPLC analysis on chiral stationary phases containing columns. Higher amounts of catalyst were required in all reactions with thiols as compared to those with sulfinate anions. The reactions of carbonates *rac*-**1a** and *rac*-**1b** with 2-pyrimidinethiol were highly selective in regard to the kinetic resolution and afforded the highly enantioenriched carbonates *ent*-**1a** and *ent*-**1b**, respectively and the enantioenriched sulfides **5aa** and **5b**, respectively, in good yields (cf. Scheme 5) (Table 4, entries 1 and 2). It should be noted that the *ee* values of the sulfides **5aa** and **5b** are significantly lower than that of the corresponding sulfones **2aa** and **2**. Kinetic resolution and substitution of the acyclic carbonates *rac*-**3aa** and *rac*-**3ba** with the thiol under the same condition used above proceeded with similar high selectivities and gave the highly enantioenriched carbonates *ent*-**3aa** and *ent*-**3ba**, respectively, and the enantioenriched sulfides **6aa** and **6ba**, respectively, in good

Table 4. Palladium-catalyzed kinetic resolution of the cyclic allylic carbonates *rac*-**1a** and *rac*-**1b** and of the acyclic allylic carbonates *rac*-**3aa** and *rac*-**3ba** with 2-pyrimidinethiol.

Entry	Substrate	*t* [h]	Conv [%]	Carbonate	Yield [%]	*ee* [%]	Sulfide	Yield [%]	*ee* [%]
1	*rac*-**1a**[a]	1.5	50	*ent*-**1a**	41	≥99	**5aa**	46	84
2	*rac*-**1b**[b]	3.5	50	*ent*-**1b**	39	97	**5b**	38	84
3	*rac*-**3aa**[a]	20	50	*ent*-**3aa**	36	≥99	**6aa**	36	93
4	*rac*-**3ba**[b]	48	50	*ent*-**3ba**	28	≥99	**6ba**	44	92

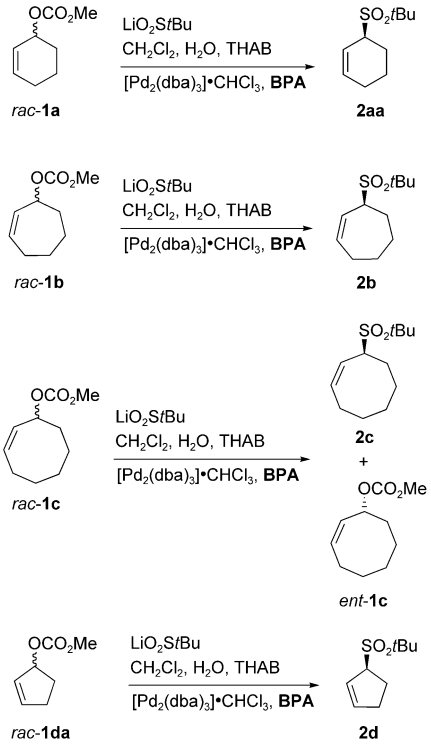
[a] 2.5 mol % $[Pd_2(dba)_3]\cdot CHCl_3$ and 5.5 mol % **BPA**. [b] 5 mol % $[Pd_2(dba)_3]\cdot CHCl_3$ and 11 mol % **BPA**.

yields (entries 3 and 4). NMR spectroscopy of the crude reaction mixtures indicated in no case the formation of side products. Deviations in the yields of carbonates and sulfides from the maximum yield of 50 % are most likely due to losses during work-up because of their volatility. The reactions of the cyclic carbonates *rac*-**1a** and *rac*-**1b** went to 50 % conversion of the substrates in much shorter reaction times as compared to the acyclic carbonates *rac*-**3aa** and *rac*-**3ba**.

Formation of sulfides **5aa**, **5b**, **6aa** and **6ba** rather than the isomeric *N*-allylic thiopyrimidones in the reaction of the allylic carbonates *rac*-**1a**, *rac*-**1b**, *rac*-**3aa** and *rac*-**3ba** with 2-pyrimidinethiol was revealed by an analysis of their ^{13}C NMR data in comparison with those of 2-(alkylthio)-pyrimdines/2-(alkylthio)-pyridines and the corresponding *N*-alkyl-thiopyrimidinones/*N*-alkyl-thiopyridones, which show characteristic differences.[27e,f, 36]

Asymmetric synthesis

Allylic sulfones: After having shown that in the reactions of the cyclic and acyclic carbonates with sulfinate anions in the presence of **BPA** the substitution of the corresponding π-allyl intermediates proceed with high enantioselectivities, it was of interest to see whether an asymmetric synthesis of the cyclic sulfones **2aa**, **2b**, **2c** and **2d** (Scheme 7) and of the acyclic sulfones **4a–c** (Schemes 8–11) could be achieved, requiring a complete transformation of the racemic substrates. Emphasis was placed on the asymmetric synthesis of *tert*-butylsulfones. The reactions of the cyclic carbonates *rac*-**1a–c** and *rac*-**1da** with lithium *tert*-butylsulfinate were carried out at room temperature on a 1–5 mmol scale in CH_2Cl_2/H_2O, containing THAB, by using 1.5 mol % $[Pd_2(dba)_3]\cdot CHCl_3$, 4.5 mol % **BPA** and 2 equiv of the sulfinate salt under otherwise the same conditions used in the corresponding kinetic resolutions. After TLC, ^1H NMR spectroscopy or GC analysis indicated complete conversion of the carbonate, the reaction mixture was exposed to air and the sulfone was isolated by chromatography. As shown by Table 5 the highly enantioenriched cyclohexenyl- and cycloheptenyl sulfones **2aa** and **2b**, respectively, were obtained in high yields (entries 1 and 2). In the case of the cyclooctenyl carbonate *rac*-**1c** the selectivity of the kinetic resolution was so high that even after a prolonged reaction time the conversion of the allylic substrate did not exceed 53 % (entry 3). Thus, the highly enantioenriched sulfone **2c** was isolated in only 44 % yield and the highly enantioenriched (≥99 % *ee*) carbonate *ent*-**1c** in 34 % yield. The reaction of the cyclopentenyl carbonate *rac*-**1da** with



Scheme 7. Asymmetric synthesis of cyclic sulfones.

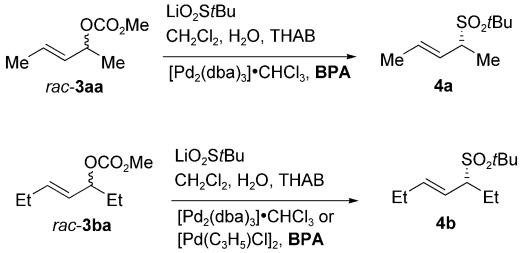
Table 5. Palladium-catalyzed asymmetric synthesis of ayclic allylic *S*-*tert*-butylsulfones.[a]

Entry	Carbonate	*t* [h]	Sulfone	Yield [%]	*ee* [%]
1	*rac*-**1a**	19	**2aa**	95	94
2	*rac*-**1b**	6	**2b**	89	93
3	*rac*-**1c**	52	**2c**	50	94
4	*rac*-**1d**	24	**2d**	76	89

[a] 1.5 mol % $[Pd_2(dba)_3]\cdot CHCl_3$ and 4.5 mol % **BPA**.

lithium *tert*-butylsulfinate gave sulfone **2d** with 89 % *ee* in 76 % yield (entry 4).

The reactions of the acyclic carbonates *rac*-**3aa** and *rac*-**3ba** with lithium *tert*-butylsulfinate were carried out in a similar way as those of the cyclic carbonates (Scheme 8). The acyclic



Scheme 8. Asymmetric synthesis of acyclic sulfones from carbonates.

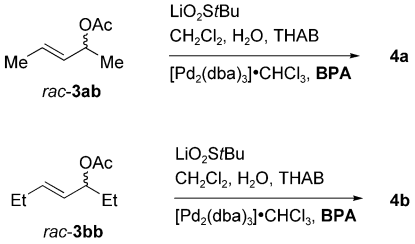
carbonates showed a higher reactivity than the cyclic carbonates *rac*-**1a–d**. After the complete conversion of the substrates the highly enantioenriched sulfones **4a** and **4b** were isolated in high yields (Table 6, entries 1 and 2). Formation of the corresponding (*Z*)-configured allylic sulfones was not observed. Occasionally, in palladium catalyzed

Table 6. Palladium-catalyzed asymmetric synthesis of acyclic allylic *S-tert*-butylsulfones.

Entry	Substrate	Precatalyst, mol%	Ligand, mol%	Solvent	*t* [h]	Conv [%]	Sulfone	Yield [%]	*ee* [%]
1	*rac*-**3aa**	$[Pd_2(dba)_3]\cdot CHCl_3$, 1.5	**BPA**, 4.5	CH_2Cl_2, H_2O, THAB	2	100	**4a**	98	98
2	*rac*-**3ba**	$[Pd_2(dba)_3]\cdot CHCl_3$, 1.5	**BPA**, 4.5	CH_2Cl_2, H_2O, THAB	2	100	**4b**	97	97
3	*rac*-**3ba**	$[Pd(C_3H_5)Cl]_2$, 3	**BPA**, 4.5	CH_2Cl_2, H_2O, THAB	6	100	**4b**	96	96
4	*rac*-**3ab**	$[Pd_2(dba)_3]\cdot CHCl_3$, 1.5	**BPA**, 4.5	CH_2Cl_2, H_2O, THAB	100	68	**4a**	51	98
5	*rac*-**3bb**	$[Pd_2(dba)_3]\cdot CHCl_3$, 1.5	**BPA**, 4.5	CH_2Cl_2, H_2O, THAB	48	53	**4b**	43	96
6	*rac*-**3ab**	$[Pd_2(dba)_3]\cdot CHCl_3$, 2	**POX**, 11	THF	48	55	*ent*-**4a**	55	58
7	*rac*-**3bb**	$[Pd_2(dba)_3]\cdot CHCl_3$, 1.5	**POX**, 6	THF	70	68	*ent*-**4b**	60	61
8	*rac*-**3cb**	$[Pd(C_3H_5)Cl]_2$, 1.5	**BPA**, 6	CH_2Cl_2, H_2O, THAB	48	70	**4c**	58	84

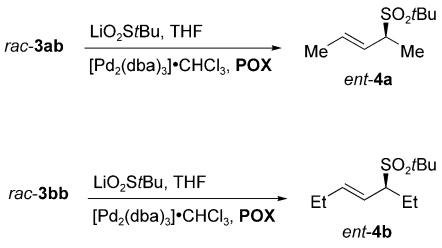
asymmetric synthesis of allylic sulfones and kinetic resolution by using $[Pd_2(dba)_3]\cdot CHCl_3$ as precatalyst separation of the substrate and the product or isolation of the product by chromatography was hampered by the presence of dibenzylideneacetone stemming from the precatalyst. Therefore the reaction of the carbonate *rac*-**3ba** with lithium *tert*-butylsulfinate was studied by using as precatalyst 3 mol% $[Pd(C_3H_5)Cl]_2$ (C_3H_5 = allyl)[37] and 4.5 mol% **BPA** under otherwise the same conditions used above. As indicated by Table 6 the reaction time for 100% conversion was longer but sulfone **4b** could be isolated with the same high *ee* value and in almost the same high yield (entry 3).

As noted previously[7] acetates *rac*-**3ab** and *rac*-**3bb** showed a much lower reactivity than the corresponding carbonates in the substitution with *tert*-butylsulfinate anion and a complete conversion of the substrates could not be achieved even after a longer reaction time (Scheme 9). Thus, at 68 and 53% conversion of *rac*-**3ab** and *rac*-**3bb** the yields of the sulfones **4a** and **4b**, respectively, were only 51 and 43%, respectively (entries 4 and 5). The enantioselectivities of the substitution were, however, the same as with the carbonates.



Scheme 9. Asymmetric synthesis of acyclic sulfones from acetates.

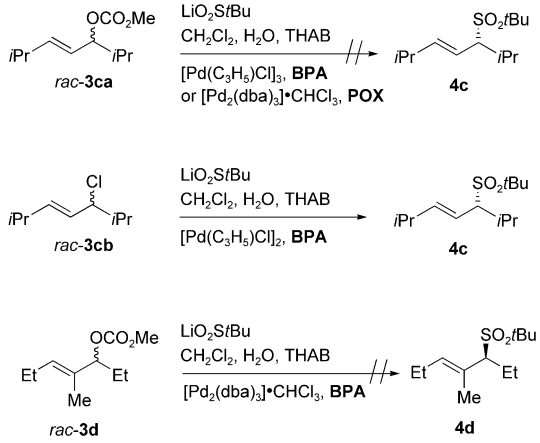
For comparison purposes the reaction of the acetates *rac*-**3ab** and *rac*-**3bb** with the *tert*-butylsulfinate anion in the presence of **POX** as ligand for the palladium atom was investigated (Scheme 10). We had previously observed that



Scheme 10. Asymmetric synthesis of acyclic sulfones by using **POX** as ligand.

the palladium-catalyzed reaction of racemic 1,3-diphenylpropenyl carbonate and acetate with lithium *tert*-butylsulfinate in THF in the presence of **POX** was highly enantioselective and gave the corresponding sulfone of 93% *ee*.[24] The reaction of acetates *rac*-**3ab** and *rac*-**3bb** with lithium *tert*-butylsulfinate in THF by using 2 or 1.5 mol% $[Pd_2(dba)_3]\cdot CHCl_3$ and 11 or 6 mol% **POX** could not be brought to completion and gave sulfones *ent*-**4a** and *ent*-**4b** only with 58 and 61% *ee*, respectively (entries 6 and 7). Thus, not only the substitutions of racemic alkyl substituted allylic substrates with tolylsulfinate anion but also those with *tert*-butylsulfinate anion catalyzed by the **POX** based palladium(0) catalyst show significantly lower enantioselectivities than those catalyzed by the **BPA** based catalyst. Because of the low enantioselectivity of the substitution, we did not investigate whether the low conversion was due at least in part to a kinetic resolution or to the low solubility of lithium *tert*-butylsulfinate in THF at room temperature (0.047 M).

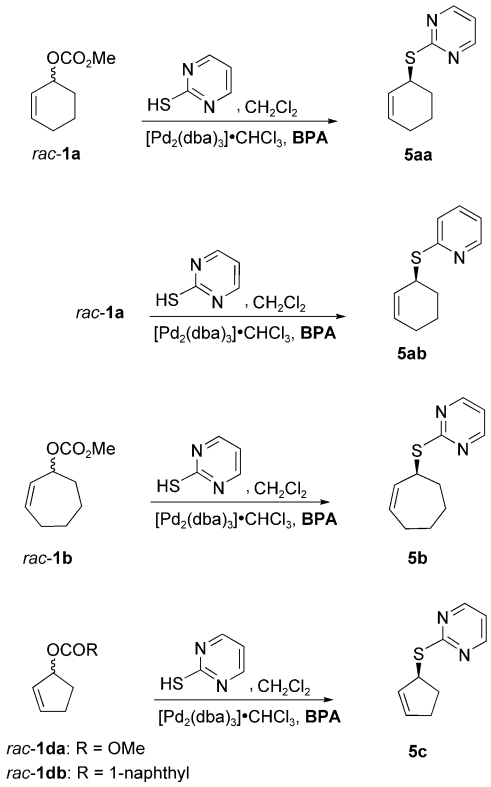
A substitution of the branched carbonate *rac*-**3ca** with *tert*-butylsulfinate anion by using either 1.5 mol% $[Pd_2(dba)_3]\cdot CHCl_3$ or 1.5 mol% $[Pd(C_3H_5)Cl]_2$ as precatalyst and 4.5 mol% **BPA** or 4.5 mol% **POX** as ligand could not be achieved (Scheme 11). However, reaction of chloride *rac*-**3cb** with lithium *tert*-butylsulfinate in the presence of 1.5 mol% $[Pd(C_3H_5)Cl]_2$ and 6 mol% **BPA** led to a 70% conversion of the allylic substrate and the branched sulfone **4c** of 84% *ee* was isolated in 58% yield (entry 8). The lower *ee* value of **4c** as compared to **4a** and **4b** was not due to a competing and hence non-selective uncatalyzed reaction of *rac*-**3cb** with the sulfinate anion as revealed by a control experiment. Another limitation of the palladium catalyzed allylic alkylation of



Scheme 11. Asymmetric synthesis of branched sulfones.

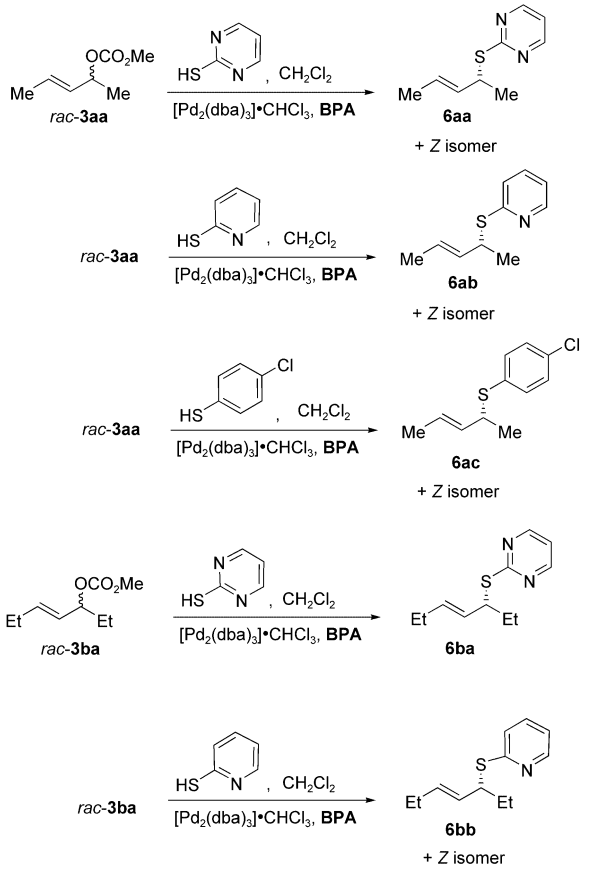
sulfinate anions was apparent in the case of the branched racemic carbonate *rac*-**3d** where a substitution with formation of sulfone **4d** could be accomplished neither with **BPA** nor with **POX** as ligand.

Allylic sulfides: After having recorded high enantioselectivities in the second step (cf. Scheme 1) of the reaction of racemic carbonates with 2-pyrimidinethiol in the presence of **BPA**, we investigated the asymmetric synthesis of the cyclic sulfides **5aa** and **5ab** (Scheme 12) and of the acyclic sulfides



Scheme 12. Asymmetric synthesis of cyclic sulfides.

6aa, **6ab**, **6ac**, **6ba** and **6bb** (Scheme 13), which requires a complete transformation of the corresponding racemic substrates. 2-Pyridinethiol and 4-chlorothiophenol were also included in this study, since we had observed previously that these two thiols are capable to act as nucleophiles in the palladium catalyzed allylic substitution in the presence of **BPA** as ligand. The reactions of the cyclohexenyl carbonate *rac*-**1a** with 2-pyrimidinethiol and 2-pyridinethiol were carried out on a 1-5 mmol scale in CH_2Cl_2 by using 5 mol% $[Pd_2(dba)_3]\cdot CHCl_3$, 11 mol% **BPA** and 1 equiv of the thiol under otherwise the same conditions used in the kinetic resolution. In contrast to 2-pyrimidinethiol, 2-pyridinethiol and 4-chlorothiophenol were completely soluble in CH_2Cl_2 under the conditions used. In order to achieve a complete conversion of both enantiomers of the carbonates, larger amounts of the precatalyst and the ligand were required as compared to the analogous reactions with sulfinate anions. After TLC indicated the complete conversion of the carbonate, the reaction mixture was exposed to air and the sulfide isolated by chromatography. As shown by Table 7 the



Scheme 13. Asymmetric synthesis of acyclic sulfides.

enantioenriched pyrimidyl sulfide **5aa** could be isolated in medium to good yield (entry 1). Interestingly, the corresponding pyridyl sulfide **5ab** derived from the reaction of *rac*-**1a** with 2-pyridinethiol had a much lower *ee* value (entry 2), which was not caused by a partial racemization of the sulfide during work-up as revealed by a control experiment. The reactions of the cycloheptenyl carbonate *rac*-**1b** with 2-pyrimidinethiol afforded the sulfide **5b** in a similar yield as in the cyclohexenyl case but with a lower *ee* value (entry 3).

Surprising results were obtained in the reaction of the cyclopentenyl esters *rac*-**1da** and *rac*-**1db** with 2-pyrimidine-

Table 7. Palladium-catalyzed asymmetric synthesis of cyclic and acyclic allylic sulfides.[a]

Entry	Substrate	Thiol	*t* [h]	Sulfide	*E*:*Z*	Yield [%]	*ee* [%]
1	*rac*-**1a**[a]	2-pyrimidinethiol	24	**5aa**	–	63	84
2	*rac*-**1a**[a]	2-pyridinethiol	27	**5ab**	–	64	55
3	*rac*-**1b**[a]	2-pyrimidinethiol	24	**5b**	–	61	84
4	*rac*-**1da**[b]	2-pyrimidinethiol	0.5	**5c**	–	80	34
5	*rac*-**1db**[b]	2-pyrimidinethiol	0.5	**5c**	–	96	36
6	*rac*-**3aa**[c]	2-pyrimidinethiol	48	**6aa**	29:1	72	89
7	*rac*-**3aa**[a]	2-pyridinethiol	48	**6ab**	15:1	87	68
8	*rac*-**3aa**[d]	4-chlorothiophenol	48	**6ac**	10:1	73	90
9	*rac*-**3ba**[a]	2-pyrimidinethiol	72	**6ba**	$\geq$99:1	64	91
10	*rac*-**3ba**[c]	2-pyridinethiol	72	**6bb**	16:1	24	50

[a] 5 mol% $[Pd_2(dba)_3]\cdot CHCl_3$ and 11 mol% **BPA**. [b] 2.5 mol% $[Pd_2(dba)_3]\cdot CHCl_3$ and 5.5 mol% **BPA**. [c] 5 mol% $[Pd_2(dba)_3]\cdot CHCl_3$ and 10 mol% **BPA**. [d] 5 mol% $[Pd_2(dba)_3]\cdot CHCl_3$ and 13 mol% **BPA**.

thiol (entries 4 and 5). Not only were the reaction times much shorter compared with the reaction of the cyclohexenyl analogues but also the *ee* values of the sulfide **5c**, which was isolated in high yields, were much lower.

The reactions of the acyclic carbonates *rac*-**3aa** and *rac*-**3ba** with 2-pyrimidinethiol, 2-pyridinethiol and 4-chlorothiophenol were carried out in a similar way as those of the cyclic carbonate (cf. Scheme 13). Table 7 shows that whereas pyrimidyl sulfides **6aa** and **6ba** were formed with high *ee* values (entries 6 and 9) the pyridyl sulfides **6ab** and **6bb** were obtained with low *ee* values (entries 7 and 10). Interestingly, the (*E*)-configured sulfides **6aa**, **6ab** and **6bb** contained minor amounts of the corresponding (*Z*)-configured isomers.[9] In the case of the sulfide **6ba** a contamination by the corresponding *Z* isomer could not be detected. Therefore the racemic *Z* isomer of **6ba** was prepared through reaction of carbonate *rac*-**3ba** with 2-pyrimidinethiol in the presence of $[Pd_2(dba)_3]\cdot CHCl_3$ and bis(diphenylphosphane)propane in CH_2Cl_2 at reflux, which yielded a mixture of *rac*-**6ba** and its *Z* isomer in a ratio of 9:1 in 55% yield. Both isomers were obtained pure by HPLC. Formation of the *Z* isomers of the allylic sulfides points to the existence of an equilibrium between the corresponding (*syn*,*syn*)- and (*anti*,*syn*)-configured π-allyl complexes (cf. Scheme 1), which are perhaps interconverting by a π–σ–π-isomerization mechanism.[38]

The palladium catalyzed asymmetric synthesis of allylic *tert*-butylsulfides from *tert*-butylthiol by using **BPA** as ligand failed. No sulfide formation was observed upon treatment of the carbonates *rac*-**1a** and *rac*-**3aa** with *tert*-butylthiol in CH_2Cl_2 in the presence of 5 mol% $[Pd_2(dba)_3]\cdot CHCl_3$ and 11 mol% **BPA** at room temperature. Formation of the allylic sulfides with pyrimidinethiol (pK_a 7.13[39a]), 4-chlorothiophenol (pK_a 7.06[39b]) and 2-pyridinethiol (pK_a 9.81[39c]) but not with *tert*-butylthiol (pK_a 11.05[39d]) may be related to their different acidity. The thiols are expected to react with the leaving group $MeOCO_2^-$ (pK_a 5.61[39e]) under deprotonation to give the corresponding thiolates, which ought to be the more reactive nucleophiles [Eq. (1)].

Furthermore the equilibrium between the leaving group and the thiol could be shifted to the side of the thiolate because of a decomposition of methyl carbonate with formation of carbon dioxide and methanol [Eq. (2)].[39e]

$$MeOCO_2^- + RSH \rightleftharpoons MeOCO_2H + RS^- \quad (1)$$

$$MeOCO_2H \rightarrow CO_2 + MeOH \quad (2)$$

Thus, because of a much lower acidity of *tert*-butylthiol, equilibrium may be unfavorable in this. Alternatively, reaction of a thiol with the **BPA** containing π-allyl intermediate could lead to the formation of an π-allyl–palladium complex containing the thiolate ligand at the palladium atom, whose stability in the case of *tert*-butylthiolate may be such as to prevent a catalytic cycle.

Aspects of kinetics

"Memory effect": Although **BPA** displays in solution time-average C_2 symmetry, its π-allyl palladium complexes do not (cf. Scheme 1).[40d,h] Nevertheless, both enantiomers of the symmetrically substituted substrate ought to be converted by the $Pd^0\cdot$**BPA** complex to the same set of equilibrating π-allyl palladium intermediates (see below). Thus the *ee* of the substitution product should be independent of the absolute configuration of the starting material. However, it has been reported that with **BPA** as ligand and certain racemic substrates, particularly cyclopentenyl esters, the two enantiomers of the substrate may give the substitution product of different *ee* values, a phenomenon termed as "memory effect".[40] Knowledge of the origins of this effect is of significant importance not only under mechanistic considerations but also for the application of palladium catalyzed allylic substitution in asymmetric synthesis, where a complete conversion of the racemic substrate to the product of high *ee* value is desired. The low *ee* values of sulfides **5ab**, **5c**, **6ab** and **6bb**, which were obtained through reaction of the cyclic esters *rac*-**1a**, *rac*-**1da** and *rac*-**1db** and of the acyclic esters *rac*-**3aa** and *rac*-**3ba**, respectively, with 2-pyrimidinethiol and 2-pyridinethiol, respectively, at higher catalyst loading could be ascribed to the operation of this effect. This would be supported by our observation that in the reaction of the racemic cyclopentenyl acetate with the thioacetate anion, which also proceeds under kinetic resolution, the faster reacting enantiomer gives the substitution product with high and the slow reacting enantiomer with low enantioselectivity.[30] Several explanations have been advanced as to the origins of the "memory effect", which are, however, still a matter of debate.[40] Recent investigations of the structures of the $Pd^0\cdot$**BPA** and symmetrically substituted π-allyl palladium(II)·**BPA** complexes had revealed in both cases monomer–oligomer equilibria, the components of which feature a P,P- as well as a P,O-coordination of the palladium atom.[40c,d] It has been suggested that in the case of **BPA** as ligand for the palladium atom the "memory effect" may be mainly due to 1) a combination of a difference in reactivity of the monomeric and oligomeric palladium(0) complexes towards the enantiomers of the substrate and 2) a difference in enantioselectivity of the reaction of the monomeric and oligomeric π-allyl intermediates with the nucleophile.[40c,d,f] This "oligomerization scheme" would also accommodate the observation that the catalyst concentration has an effect upon the *ee* value of the substitution product.[40d,e] In order to shed more light on the reaction of the racemic cyclic esters[11i] with the sulfur nucleophiles, the time dependencies of the conversion of the substrate and of the *ee* values of the substitution product in the reaction of the cyclohexenyl carbonate *rac*-**1a** with lithium *tert*-butylsulfinate (Figure 1, Table 8) (cf. Scheme 2) were followed by GC analysis according to the method of internal standard[41a] and by NMR spectroscopy and by GC analysis on chiral stationary phase containing columns, respectively. In addition to these two methods the method of enantiomer labeling,[41b–d] which does not require an internal standard, was also used for the determination of the concentration of the remaining substrate. This was done by the measurement of the *ee* values of the substrate before and after the addition of a certain amount of *rac*-**1a** by GC using a chiral stationary phase containing column.

While the *ee* value of the cyclohexenyl sulfone **2aa** remained practically constant until 50% conversion, that of

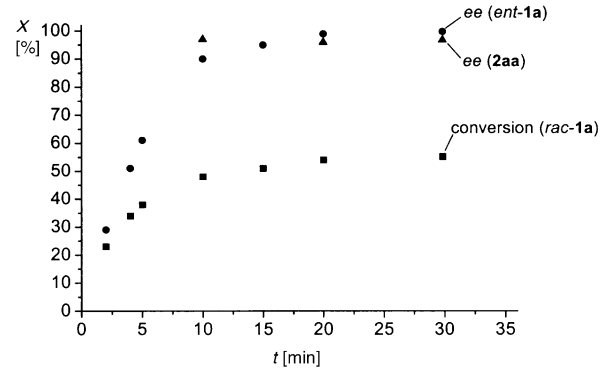
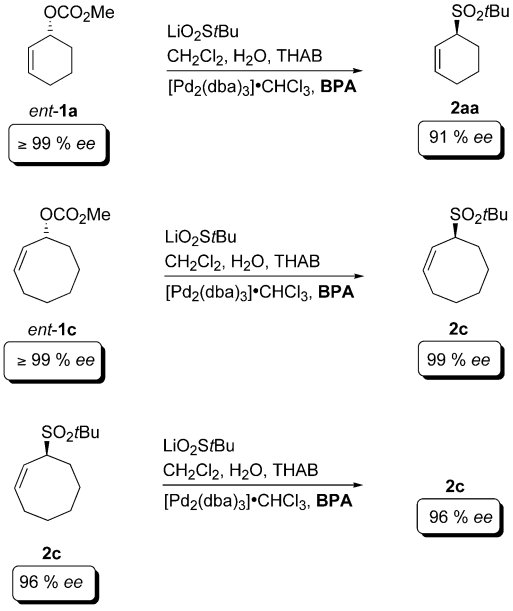


Figure 1. Time dependencies of *c* and *ee* (X) in the palladium-catalyzed kinetic resolution of carbonate *rac*-**1a** with lithium *tert*-butylsulfinate.

Table 8. Selectivity of the palladium-catalyzed kinetic resolution of the cyclic carbonate *rac*-**1a** with lithium *tert*-butylsulfinate.

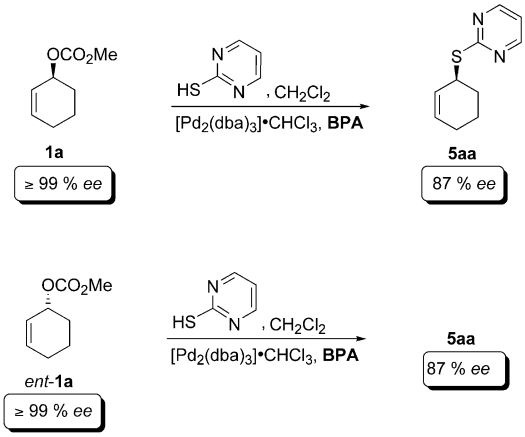
Entry	*t* [min]	Conv *rac*-**1a** [%]	*ee ent*-**1a** [%]	*S*
1	2	23	29	90
2	4	34	50	110
3	5	38	60	173
4	10	49	90	95
5	15	51	95	81
6	20	54	$\geq$99	61

carbonate *ent*-**1a** increased and reached 96% at approximately 50% conversion. Having obtained these results, cyclohexenyl carbonate *ent*-**1a** of $\geq$99% *ee* and cyclooctenyl carbonate *ent*-**1c** of $\geq$99% *ee*, both of which are the slow reacting enantiomers in the kinetic resolution of *rac*-**1a** and *rac*-**1c**, respectively, were submitted to the palladium-catalyzed reaction with lithium *tert*-butylsulfinate in the presence of **BPA** (Scheme 14). A complete conversion of the cyclohexenyl carbonate *ent*-**1a** to the *S* configured sulfone **2aa** of 91% *ee* took place. During the substitution reaction the *ee* values of carbonate *ent*-**1a** and sulfone **2aa** remained constant. The reaction of cyclooctenyl carbonate *ent*-**1c** with the sulfinate anion was very slow and only after a reaction time of 4 d could the formation of 4% of the *S* configured sulfone **2c** be detected by GC analysis. However, both the carbonate *ent*-**1c** and ulfone **2c** had an *ee* value of 99%. The observation of a constant *ee* value of the sulfone **2aa** up to 50% conversion of *rac*-**1a** and 100% conversion of *ent*-**1a** indicates that the enantioselectivity of the substitution step is independent of the chirality of the substrate, that is, no "memory effect" is operating. In a final experiment sulfone **2c** of 96% *ee* was treated with lithium *tert*-butylsulfinate in the presence of the precatalyst and **BPA**, which led to its recovery with 96% *ee*. Thus, once sulfone **2c** is formed through reaction of *rac*-**1c** with the sulfinate anion it does not suffer a partial racemization during the course of the reaction.



Scheme 14. Palladium catalyzed substitution of enantioenriched substrates with lithium *tert*-butylsulfinate.

The reactions of the racemic carbonate *rac*-**1a** and of the enantiomeric carbonates **1a** and *ent*-**1a** with 2-pyrimidinethiol in CH_2Cl_2 were studied next (cf. Schemes 5 and 15). The time



Scheme 15. Palladium catalyzed substitution of enantioenriched substrates with 2-pyrimidinethiol.

dependencies of the conversion of the substrates and of the *ee* values of the substrates and the sulfide were determined by GC analysis by the method of internal standard and GC analysis using a chiral stationary phase containing column, respectively (Table 9). As revealed by Figure 2 the *ee* value of sulfide **5aa** remained practically constant throughout the reaction and that of carbonate *ent*-**1a** increased with increasing conversion reaching at 50% conversion a value of 99%. In two further experiments the highly enantioenriched **1a** ($\geq$99% *ee*) and *ent*-**1a** ($\geq$99% *ee*), which were prepared

Table 9. Selectivity of the palladium-catalyzed kinetic resolution of the cyclic carbonate *rac*-**1a** with 2-pyrimidinethiol.

Entry	*t* [min]	Conv *rac*-**1a** [%]	*ee ent*-**1a** [%]	*S*
1	10	29	40	141
2	15	36	51	34
3	20	40	64	95
4	25	46	77	46
5	30	48	89	164
6	35	52	97	76
7	40	53	$\geq$99	80

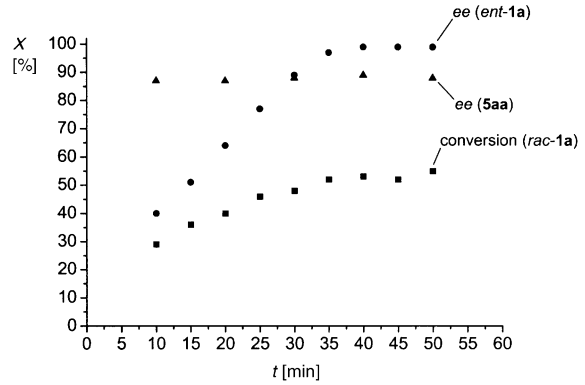


Figure 2. Time dependencies of *c* and *ee* (X) in the palladium-catalyzed kinetic resolution of carbonate *rac*-**1a** with 2-pyrimidinethiol.

through kinetic resolution of *rac*-**1a** by employing **BPA** and *ent*-**BPA**, were submitted separately to the reaction with the thiol in the presence of **BPA**. Both substitution reactions led to the formation of sulfide **5aa** of 87% *ee*. The *ee* values of sulfide **5aa** and carbonates **1a** and *ent*-**1a** remained practically constant throughout the reaction (Figure 3). These results show that not only in the reaction of the cyclohexenyl carbonate *rac*-**1a** with *tert*-butylsulfinate anion but also with 2-pyrimidinethiol no significant "memory effect" is operating. This is in contrast to the palladium-catalyzed reaction of *rac*-**1a** with thioacetate anion in the presence of **BPA**, where a powerful "memory effect" was observed.[30] However, in this case the catalyst loading was much higher.

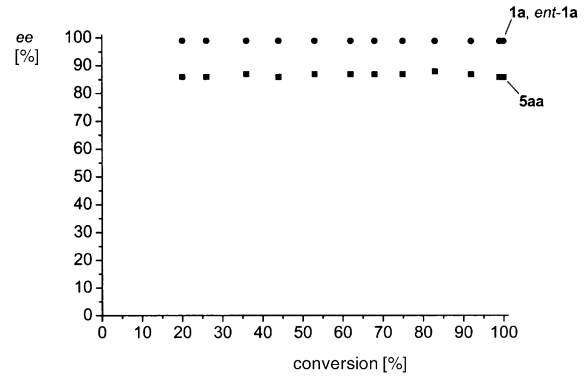


Figure 3. Time dependencies of *ee* in the palladium catalyzed reaction of **1a** and *ent*-**1a** with 2-pyrimidinethiol.

In summary, it seems that the magnitude of the "memory effect" depends not only on the substrate and the concentration of the catalyst but also on the nucleophile. Particularly illustrative examples are the reactions of the cyclopentenyl ester *rac*-**1da** with 2-pyrimidinethiol at higher (cf. Table 7, entry 4) and with *tert*-butylsulfinate anion (cf. Table 5) at lower catalyst concentration. While the reaction with the thiol delivered sulfide **5c** of 34% *ee*, that with the sulfinate ion gave sulfone **2d** of 89% *ee*.

Selectivity factor: All of the kinetic resolutions described above have been characterized in terms of the yields and *ee* values of the recovered substrate and the product. This seems particularly appropriate given that a major aim of this work was the synthetic exploitation of the palladium catalyzed kinetic resolution. In principle the efficiency of a kinetic resolution can also be described by the selectivity factor *S*, the ratio of the rate constants for the reactions of the enantiomers of the substrate with the catalyst.[1a,b, 42a] For a palladium catalyzed kinetic resolution of an allylic substrate obeying first-order kinetics with regard to the reaction of the substrate with the catalyst (unimolecularity) *S* can be calculated according to Equation (3), which contains as variables the conversion (*c*) and the *ee* value of the substrate (ee_s).[42b, 43] Application of Equation (3) requires, however, a determination of *c* and *ee* of the substrate with a precision not easily to obtain.[1a,o, 44]

$$S = \ln[(1-c)(1-ee_s)]/\ln[(1-c)(1+ee_s)] \quad (0<c<1,\ 0<ee_s<1 \qquad (3)$$

Small errors in the determination of *ee* and *c* can lead to major apparent changes of *S* with conversion, particularly in the case of high *S* values,[45] a problem which is often underestimated or even neglected in the measurement of *S*. However, the overall error can be reduced by analysis of a series of *ee* versus *c* values (see below).[11m]

Calculation of *S* for the kinetic resolution of the cyclohexenyl carbonate *rac*-**1a** with 2-pyrimidinethiol and lithium *tert*-butylsulfinate (cf. Figures 1 and 2) according to Equation (3) gave large values for pairs of *ee* versus *c* (cf. Tables 8 and 9); this indicates a high selectivity. This is in accordance with the isolation of *ent*-**1a** with high *ee* at approximately 50% conversion in the preparative experiments (cf. Tables 1, 2 and 4). However, Tables 8 and 9 also reveal major and irregular changes of *S* with conversion. Since our measurements of *ee* and *c* had a precision of only ± 0.5 and ± 1.0%, respectively, we ascribe the change of *S* with conversion mainly to errors in the determination of both values.[46] Nonlinear regression (Origin 6.1) of *S*[11m] (Tables 8 and 9) gave $S = 74 \pm 7$ for the kinetic resolution of *rac*-**1a** with lithium *tert*-butylsulfinate and $S = 77 \pm 11$ for the kinetic resolution of *rac*-**1a** with 2-pyrimidinethiol.

Overall kinetics: We have investigated the reactions of the enantiomerically highly enriched carbonates **1a** (≥ 99% *ee*) and *ent*-**1a** (≥ 99% *ee*) with 2-pyrimidinethiol in order to determine the dependency of the rate of the overall reaction on the concentration of the substrate. In the case of a first-order dependency on the substrate measurement of the rate constants would allow an alternative and direct determination of the selectivity factor *S*. Reactions were run in CH_2Cl_2 at 25 °C under argon with 1 mmol of carbonate ($c_o = 250$ mmol L^{-1}), 0.025 mmol $[Pd_2(dba)_3]\cdot CHCl_3$ ($c = 6.25$ mmol L^{-1}), 0.055 mmol of **BPA** ($c = 13.75$ mmol L^{-1}) and 1 mmol 2-pyrimidinethiol. Because of the low solubility of the thiol ($c = 4.6$ mmol L^{-1}), solid thiol was present and only at the very end of the reaction was a homogenous mixture formed. Therefore it is assumed that the concentration of the thiol in solution was not only rather low but also remained constant until nearly all of the substrate had been consumed. The progress of the reactions was monitored by GC using tetradecane as an internal standard. A plot of c/c_o of

the substrate versus log t[47] (Figure 4) and a plot of c versus t (Figure 5) for four half-lives of the reaction of **1a** indicated a pseudo-zero order kinetics in regard to the allylic substrate under the special conditions used, where the concentration of

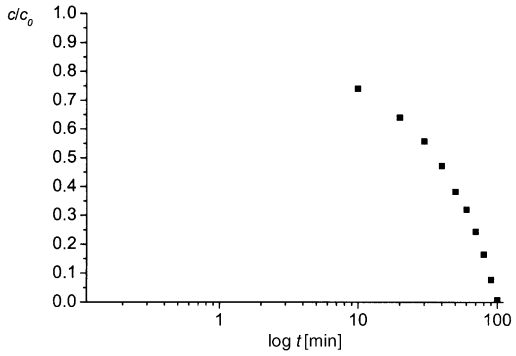


Figure 4. Time dependency of c of **1a** in the palladium catalyzed reaction with 2-pyrimidinethiol (c/c_o vs log t).

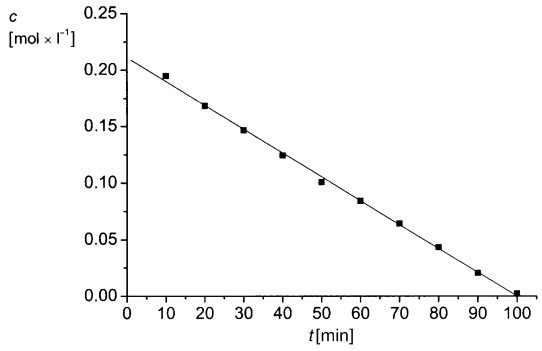
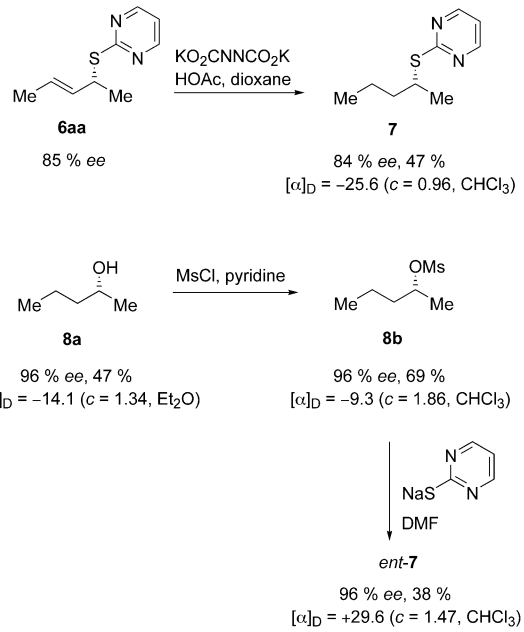


Figure 5. Time dependency of c of **1a** in the palladium catalyzed reaction with 2-pyrimidinethiol (c vs t).

the catalyst and the nucleophile remained constant. Thus in this particular case the rate of the overall catalytic reaction is independent of the substrate concentration. The reaction of *ent*-**1a** with 2-pyrimidinethiol, which was carried out under the same conditions as in the case of **1a** because of comparison, could be followed only for less than 1 half-live because of its slowness. Therefore the kinetic data obtained in this experiment did not allow for a determination of the order of the reaction of *ent*-**1a** with 2-pyrimidinethiol. The observation of a pseudo-zero order regime in the allylic substrate for the overall reaction of **1a** with 2-pyrimidinethiol implies that the rate-limiting step involves attack of the thiolate on the π-allyl intermediate. Both, pseudo-zero order[5a] and pseudo-first order kinetics[11c] with regard to the allylic substrate had been previously observed in palladium catalyzed allylic substitution with C-nucleophiles in the presence of chiral ligands other than **BPA**.

Determination of absolute configuration

The absolute configuration of sulfide **6aa** was determined by chemical correlation as shown in Scheme 16.[48] Reduction of sulfide **6aa** with diimide gave the saturated sulfide **7**. The (*R*)-configured alcohol **8a** of 96% *ee*[49] was converted via mesylate **8b** to the saturated sulfide *ent*-**7** of 96% *ee*. Since the acyclic sulfides **6aa**, **6ba**, **6ac**, **6ba** and **6bb** (see below) all have the same sign of optical rotation, the *R* configuration was also assigned to the later sulfides. The absolute configuration of the cyclohexenyl sulfide **5aa** had been assigned previously by chemical correlation.[28b] The *S* configuration was assigned to the cyclic sulfides **5b** and **5ab** (see below) on the basis that



Scheme 16. Determination of absolute configuration.

both have the same sign of optical rotation as **5aa** and the formation of the (*S*)-configured sulfones in the reaction of carbonates *rac*-**1a** and *rac*-**1b** with sulfinate anions (see below).

The absolute configuration of cyclooctenyl sulfone **4c** was determined by X-ray crystal structure analysis (Figure 6). By assuming that the substitution of carbonates *rac*-**1a–c** with *tert*-butylsulfinate anion in the presence of **BPA** all proceed with the same sense of asymmetric induction we assigned the *S* configuration to all of the sulfones **2aa**, **2ab**, **2ac**,[23a] **2b** and **2c**.

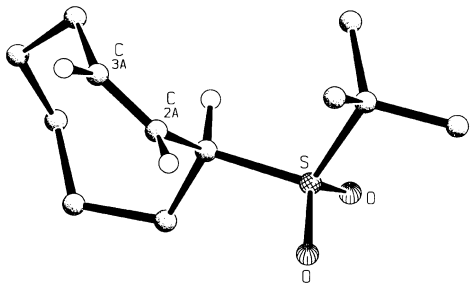
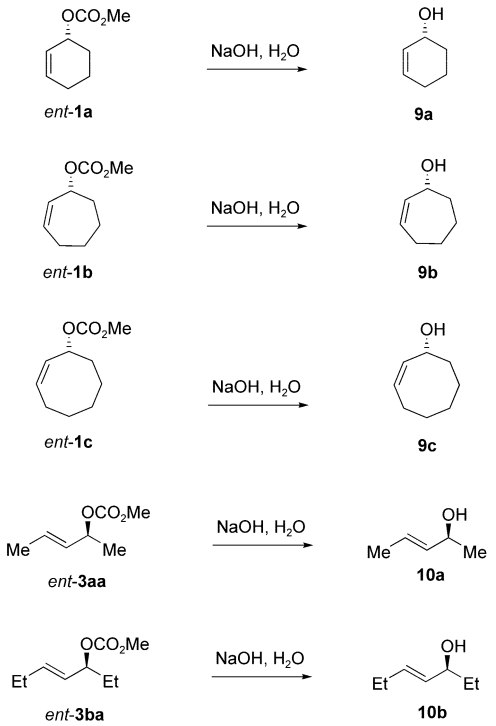


Figure 6. Structure of sulfone **2c** in the crystal.

Synthesis of highly enantioenriched allylic alcohols

The completion of the partial conversion of the racemic allylic alcohols *rac*-**1a–c**, *rac*-**3aa** and *rac*-**3ba** to the corresponding enantioenriched allylic alcohols via palladium-catalyzed res-

olution required the hydrolysis of the corresponding enantioenriched carbonates (Scheme 17). The reaction of the cyclic carbonates *ent*-**1a–c** and of the acyclic carbonates *ent*-**3aa** and *ent*-**3ba** with NaOH in water led to the isolation of the highly enantioenriched alcohols **9a–c**,[50a] **10a**[50b] and **10b**,[50c] respectively, in medium to high yields (Table 10). It should be noted that because of the high selectivity of the kinetic resolution of the racemic carbonates and because of



Scheme 17. Synthesis of enantiomerically highly enriched cyclic and acyclic allylic alcohols.

Table 10. Synthesis of highly enantioenriched cyclic and acyclic allylic alcohols.

Carbonate	Alcohol	Yield [%]	*ee* [%]	$[\alpha]_D^{22}$
ent-**1a**	**9a**	65	≥ 99	+110.8 ($c = 1.20$, CH_2Cl_2)
ent-**1b**	**9b**	94	≥ 99	+28.2 ($c = 1.03$, CH_2Cl_2)
ent-**1c**	**9c**	75	≥ 99	−52.4 ($c = 1.46$, CH_2Cl_2)
ent-**4a**	**10a**	90	≥ 99	−18.5 ($c = 1.05$, CH_2Cl_2)
ent-**4b**	**10b**	94	99	+4.0 ($c = 0.99$, CH_2Cl_2)

principle the alcohols **9a–c**, **10a** and **10b**, can be obtained in an enantiomeric purity not easily attainable by the known methods of asymmetric synthesis.[13] The absolute configurations of the alcohols **9a–c** and **10a** and thus of the carbonates *ent*-**1a–c** and *ent*-**3aa**, respectively, were determined by comparison of their chiroptical data with those reported in the literature.[50] Determination of the absolute configuration of alcohol **10b** and thus of carbonate *ent*-**3ba** was achieved through its hydrogenation to the corresponding saturated alcohol.[51, 52]

Conclusion

The palladium-catalyzed reactions of symmetrically disubstituted racemic allylic carbonates, being either cyclic or acyclic, with sulfinate anions and 2-pyrimidinethiol in the presence of **BPA** as ligand proceed with excellent levels of enantioselectivity in both kinetic resolution and substitution. The efficiencies of the kinetic resolutions are described in terms of *ee* values and yields of recovered substrates and substitution products rather than by the selectivity factors. This seems to be more appropriate given the problems associated with the accurate experimental measurement of the later. The statement of a selectivity factor based on the measurement of a single *ee* versus *c* pair and without error analysis may lead to questionable results, in particular in the case of high selectivities. However, a more reliable *S* value can be obtained by measurement and analysis of a series of *ee* versus *c* pairs. In accordance with previous observations the faster reacting enantiomer of the substrate and the preferentially formed substitution product have the same absolute configuration. While the kinetic resolution allows for the synthesis of enantiomerically highly enriched cyclic and acyclic allylic alcohols, the substitution provides for an asymmetric synthesis of enantiomerically highly enriched allylic sulfones, bearing various groups at the sulfur atom and allylic sulfides, carrying an aromatic group at the sulfur atom. The allylic substitutions with thiols required higher amounts of palladium catalyst as compared to those with sulfinate anions. Furthermore, sulfide formation in the presence of **BPA** was observed only with 2-pyrimidinethiol, 2-pyridinethiol and 4-chlorophenylthiol but not with *tert*-butylthiol. While the different pK_a values of the thiols used may play a decisive role, it can not be excluded that the formation of π-allyl palladium thiolate complexes is also an important factor in the palladium catalyzed allylic substitution with thiols. An equilibrium between a palladium thiolate complex and an π-allyl thiolate ion pair could perhaps account for the higher amount of catalyst required.

According to experiments with racemic and enantioenriched cyclohexenyl carbonate and *tert*-butylsulfinate anion and 2-pyrimidinethiol the *ee* value of the substitution product is independent of the chirality of the substrate, that is, no "memory effect" is operating. However, a "memory effect" seems to operate in the case of the reaction of the cyclohexenyl ester with 2-pyridinethiol and, in particular, in that of the cyclopentenyl esters with 2-pyrimidinethiol. Whether the formation of equilibrium mixtures of monomers and oligomers of the $Pd^0 \cdot$ **BPA** and π-allyl $Pd^{II} \cdot$ **BPA** complexes are mainly responsible for the "memory effect" remains to be seen.

Experimental Section

General: All reactions were carried out in absolute solvents under an argon atmosphere with syringe and Schlenk techniques in oven-dried glassware. CH_2Cl_2 was distilled under argon from CaH_2. The ligands **POX**[53] and **BPA**,[10] the precatalysts $[Pd_2(dba)_3] \cdot CHCl_3$[33] and $[Pd(C_3H_5)Cl]_2$,[37] and lithium *tert*-butylsulfinate[32] were prepared according to the literature. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR 300, Varian Gemini

300, Varian Inova 400 and Varian Unity 500 spectrometer. Chemical shifts (^{1}H, ^{13}C) are reported relative to Me_4Si ($\delta = 0$ ppm). Splitting patterns in the ^{1}H NMR spectra are designated as s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; quin, quintet; m, multiplet. ^{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 ATP pulse sequence. IR spectra were recorded with a Perkin–Elmer PE 1759-FT instrument. GC analyses were performed by using Chrompack CP-9000 [DB-5 (30 m, 0.32 mm; 50 kPa H_2); Macherey–Nagel Lipodex γ: octakis-(2,3-*O*-dipentyl-6-*O*-methyl)-γ-cyclodextrin (25 m, 0.25 mm; 100 kPa H_2); Macherey–Nagel Lipodex E: octakis-(2,6-di-*O*-pentyl-3-*O*-butyryl)-γ-cyclodextrin (25 m, 0.25 mm; 100 kPa H_2)] and Carlo Erba Mega Series 5300 [CP-Chirasil-Dex-CB (CP-βI-CB): permethyl-β-cyclodextrin (25 m, 0.25 mm; 100 kPa H_2); Hydrodex-β-6-TBDM: heptakis(2,3-di-*O*-methyl-6-*O*-*tert*-butyldimethylsilyl)-β-cyclodextrin (25 m, 0.25 mm, 100 kPa H_2)] instruments. GC-MS analyses were run on a Magnum Finnigan (HT-5: 25 m, 0.25 mm; 50 kPa He, CI, 40 eV, MeOH). HPLC analyses were performed on a Waters 600 (UV 485; RI 410) instrument with a Baker Chiralcel OD-H column. MS spectra were recorded on a Varian MAT 212S (EI, 70 eV) instrument. Only decisive signals of the MS spectra and those with an intensity higher than 10% are listed. Column chromatography was carried out on Merck silica gel 60, 0.063–0.200 mm. TLC was done with Merck silica gel 60 F_{254} aluminum plates. Elementary analyses were carried out by the microanalytical laboratories of the Institut für Organische Chemie at the RWTH Aachen. Optical rotary powers were measured on a Perkin–Elmer 241 instrument at approximately 22 °C.

X-ray Analyses: The crystal data and the most salient experimental parameters used in the X-ray measurement and in the crystal structure analysis are reported in Table 11. The crystal structure was solved using direct methods as implemented in the XTAL3.7 package of crystallographic routines.[54a] The molecular structure was visualized with the program SCHAKAL 92.[54b,c] The absolute configuration of **2c** as shown in Figure 6 has been determined by the method of Flack[54d] ($\chi_{abs} = 0.01(4)$).

Table 11. Crystal data and parameters of data collection for **2c**.

formula	$C_{12}H_{22}O_2S$
M_r	230.37
color and habit	colorless, irregular
crystal size [mm], ca.	0.3 × 0.3 × 0.3
crystal system	orthorhombic
space group	$P2_12_12_1$ (19)
a [Å]	6.051(2)
b [Å]	15.205(1)
c [Å]	27.643(3)
V [Å^3]	2543.3(9)
Z	2 × 4[a]
ρ_{calcd} [g cm^{-3}]	1.203
μ [mm^{-1}]	2.098
diffractometer	CDA4 Enraf-Nonius
T [K]	150
radiation	$Cu_{K\alpha}$
λ [Å]	1.54179
scan method	$\omega/2\theta$
Θ_{max} [°]	74.9
no. of data coll.[b]	6278
obsn criterion	$I > 2\sigma(I)$
refinement	on F
no. params refd	271
no. data obsd in refmnt	4803
R, R_w[c]	0.058/0.073
$\Delta(\rho)$ [e Å^{-3}]	−0.57/+0.79
GOF	2.627

[a] Two symmetrically independent species. [b] Friedel pairs collected. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{0.5}$; $w = 1/\sigma^2(F_o)$ where F_o and F_c are observed and calculated structure factors.

General procedure for the asymmetric synthesis of allylic sulfones and kinetic resolution of allylic carbonates with sulfinate anions (GP1): The precatalyst and ligand were placed in a Schlenk flask containing a stirring bar and the flask was evacuated and refilled with argon. Then the precatalyst and the ligand were dissolved under stirring through addition of CH_2Cl_2 or THF. The solution of $[Pd_2(dba)_3]\cdot CHCl_3$ and **BPA** initially attained a dark violet color which gradually changed to bright red-orange (approximately 15 min). Then the substrate was added. Stirring of the mixture was continued until the color of the solution had changed from red-orange to yellow (approximately 15 min). The sulfinate salt and THAB were placed in a second Schlenk flask which was evacuated and refilled with argon. Then the salt and the phase transfer catalyst were dissolved through addition of degassed water. Alternatively, a suspension of the sulfinate salt in THF was prepared in the same way. Both the solution containing the sulfinate salt and the solution containing the substrate were cooled in an ice bath and the solution or suspension of the sulfinate salt was added under argon with a syringe to the solution containing the catalyst and the substrate. Subsequently, the reaction mixture was either stirred at 0 °C or warmed to room temperature and stirred at this temperature for the time given and the progress of the reaction was monitored by TLC, GC or ^{1}H NMR spectroscopy. Then saturated aqueous NaCl was added and the mixture was stirred at room temperature under exposure to air for 1 h. Then CH_2Cl_2 was added and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Chromatography or kugelrohr distillation gave the sulfone and the allylic substrate. In kinetic resolution experiments stirring of the mixture under exposure to air was omitted.

Kinetic resolution of carbonate *rac*-1a with lithium-*tert*-butylsulfinate: **(*S*)-3-(2-methyl-propan-2-sulfonyl)-cyclohexene (2aa) and (*R*)-carbonic acid cyclohex-2-enyl methyl ester (*ent*-1a)**: Following GP1, a mixture of carbonate *rac*-**1a** (1.57 g, 10 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (155 mg, 0.15 mmol) and **BPA** (311 mg, 0.45 mmol) in CH_2Cl_2 (10 mL) was treated under stirring at 0 °C successively with a suspension of LiO_2StBu (2.56 g, 20 mmol) and THAB (360 mg, 0.8 mmol) in CH_2Cl_2 (15 mL) and degassed water (8 mL). Quenching of the mixture after stirring it at 0 °C for 45 min gave a mixture of carbonate *ent*-**1a** and sulfone **2aa** in a ratio of 46:54 (^{1}H NMR). Chromatography (hexane/EtOAc 7:1, 1% NEt_3) afforded sulfone **2aa** (999 mg, 49%) of 98% *ee* {^{1}H NMR, 400 MHz, $CDCl_3$, 30 mol%, [Eu(hfc)$_3$]}: δ (*t*Bu) (**2aa**) = 1.78, δ (*t*Bu) (*ent*-**2aa**) = 1.80] as a colorless solid and carbonate *ent*-**1a** (536 mg, 34%) of = 99% *ee* [GC, Lipodex E, t_R (*ent*-**1a**) = 13.3 min, t_R (**1a**) = 13.8 min] as a colorless oil.

Sulfone 2aa: $[\alpha]_D^{20} = -177.0$ ($c = 1.01$, CH_2Cl_2); m.p. 55 °C; the spectroscopic data were identical to those reported in the literature.[7]

Carbonate *ent*-1a: $[\alpha]_D^{20} = +168.0$ ($c = 1.73$, CH_2Cl_2); ^{1}H NMR (300 MHz, $CHCl_3$): δ = 1.56–2.16 (m, 6H), 3.77 (s, 3H), 5.09–5.14 (m, 1H), 5.78 (ddt, J = 10.0, 3.7, 2.0 Hz, 1H), 5.97 (dtd, J = 10.0, 3.7, 1.3 Hz, 1H); ^{13}C NMR (75 MHz, $CHCl_3$): δ = 18.6 (u), 24.9 (u), 28.2 (u), 54.5 (d), 71.9 (d), 125.0 (d), 133.3 (d), 155.5 (u); IR (neat): $\tilde{\nu}$ = 3084 (w), 3061 (w), 3030 (w), 2983 (w), 2937 (w), 1744 (s), 1496 (m), 1450 (m), 1371 (m), 1305 (m), 1255 (s), 1005 (m), 991 (m), 964 (m), 789 (m), 748 (m), 697 (m), 541 cm^{-1} (m); MS: *m*/*z* (%): 156 (11) [M^+], 111 (11), 97 (26), 84 (12), 81 (41), 80 (55), 79 (74), 77 (14), 74 (59), 59 (100), 53 (11), 46 (18), 45 (73); elemental analysis calcd (%) for $C_8H_{12}O_3$: C 61.52, H 7.74; found: C 61.34, H 7.79.

Kinetic resolution of carbonate *rac*-1b with lithium *tert*-butylsulfinate: **(*S*)-3-(2-methyl-propan-2-sulfonyl)-cycloheptene (2b) and (*R*)-carbonic acid cyclohept-2-enyl methyl ester (*ent*-1b)**: Following GP1, a mixture of carbonate *rac*-**1b** (1.77 g, 10 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (155 mg, 0.15 mmol) and **BPA** (311 mg, 0.45 mmol) in CH_2Cl_2 (10 mL) was treated under stirring at 0 °C successively with a suspension of LiO_2StBu (2.56 g, 20 mmol) and THAB (360 mg, 0.8 mmol) in CH_2Cl_2 (15 mL) and degassed water (8 mL). Quenching of the mixture after stirring it at 0 °C for 4 h gave a mixture of carbonate *ent*-**1b** and sulfone **2b** in a ratio of 47:53 (^{1}H NMR). Chromatography (hexane/EtOAc 7:1, 1% NEt_3) afforded sulfone **2b** (993 mg, 46%) of 95% *ee* {^{1}H NMR, 400 MHz, $CDCl_3$, 30 mol%, [Eu(hfc)$_3$]}: δ (*t*Bu) (**2b**) = 2.06, δ (*t*Bu) (*ent*-**2b**) = 2.21; GC, Lipodex-E, t_R (*ent*-**2b**) = 35.07 min, t_R (**2b**) = 34.58 min] as a colorless solid and carbonate *ent*-**1b** (580 mg, 33%) of 94% *ee* [GC, Lipodex E, t_R (*ent*-**1b**) = 20.78 min, t_R (**1b**) = 20.93 min] as a colorless oil. **Sulfone 2b**: $[\alpha]_D^{20} = -95.4$ ($c = 1.01$, CH_2Cl_2); m.p. 48 °C; the spectroscopic data were identical to those reported in the literature.[7]

Carbonate *ent*-1b: $[\alpha]_D^{20} = +33.2$ ($c = 1.29$, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34–2.30 (m, 8H), 3.77 (s, 3H), 5.26 (br d, J = 7.7 Hz, 1H), 5.56–5.76 (m, 1H), 5.79–5.90 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =

26.5 (u), 26.6 (u), 28.5 (u), 32.8 (u), 54.5 (d), 78.2 (d), 131.8 (d), 133.1 (d), 155.4 (u); IR (neat): $\tilde{\nu}$ = 2930 (m), 2857 (w), 1747 (s), 1444 (s), 1356 (w), 1326 (m), 1268 (s), 1203 (w), 1127 (w), 977 (m), 944 (m), 794 cm^{-1} (m); MS: *m*/*z* (%): 170 (2) [M^+], 95 (7), 94 (15), 79 (29), 77 (4), 67 (5), 59 (5), 55 (7); elemental analysis calcd (%) for $C_8H_{12}O_3$: C 63.51, H 8.29; found: C 63.30, H 8.26.

Kinetic resolution of carbonate *rac*-1c with lithium-*tert*-butylsulfinate: (*S*)-3-(2-methyl-propan-2-sulfonyl)-cyclooctene (2c) and (*R*)-carbonic acid cyclooct-2-enyl methyl ester (*ent*-1c)

On a 9.3 mmol scale: Following GP1, a mixture of carbonate *rac*-**1c** (1.71 g, 9.3 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (145 mg, 0.14 mmol) and **BPA** (288 mg, 0.42 mmol) in CH_2Cl_2 (10 mL) was treated under stirring at 0 °C successively with a suspension of LiO_2StBu (2.56 g, 20 mmol) and THAB (220 mg, 0.5 mmol) in CH_2Cl_2 (15 mL) and degassed water (8 mL). Quenching of the mixture after stirring it successively at 0 °C for 4 h and at room temperature for 20 h gave a mixture of carbonate *ent*-**1c** and sulfone **2c** in a ratio of 42:58 (^{1}H NMR). Chromatography (hexane/EtOAc 10:1, 1% NEt_3) furnished sulfone **2c** (1.03 g, 48%) of 96% *ee* [GC, Lipodex E, t_R (*ent*-**2c**) = 134.63 min, t_R (**2c**) = 134.96 min] as a colorless solid and carbonate *ent*-**1c** (584 mg, 34%) of ≥99% *ee* [GC, Lipodex E, t_R (*ent*-**1c**) = 21.97 min, t_R (**1c**) = 23.63 min] as a colorless oil.

Sulfone 2c: $[\alpha]_D^{20} = +135.4$ (c = 1.99, CH_2Cl_2); m.p. 55 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27–1.38 (m, 2H), 1.42 (s, 9H), 1.44–1.58 (m, 1H), 1.71–1.85 (m, 4H), 2.01–2.11 (m, 1H), 2.17–2.27 (m, 2H), 4.16–4.23 (m, 1H), 5.70 (m, 1H), 5.92 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.09 (u), 24.31 (d), 26.87 (u), 27.33 (u), 27.40 (u), 29.24 (u), 55.35 (d), 61.02 (u), 125.46 (d), 132.80 (d); GC-MS (EI, 70 eV) *m*/*z* (%): 231 (1.5) [M^+], 123 (100), 109 (18); IR (KBr): $\tilde{\nu}$ = 2925 (s), 2857 (s), 1479 (m), 1450 (m), 1395 (w), 1371 (w), 1305 (s), 1286 (s), 1263 (s), 1244 (s), 1222 (m), 1197 (m), 1110 (s), 1011 (w), 975 (w), 961 (w), 942 (w), 891 (w), 873 (w), 802 (w), 762 (m), 724 (m), 664 (s), 583 cm^{-1} (s); elemental analysis calcd (%) for $C_{12}H_{22}O_2S$: C 62.58, H 9.63; found: C 62.55, H 9.64.

***ent*-1c**: $[\alpha]_D^{20} = -78.4$ (c = 1.02, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35–1.45 (m, 1H), 1.47–1.75 (m, 6H), 1.94–2.03 (m, 1H), 2.09–2.18 (m, 1H), 2.20–2.30 (m, 1H), 3.77 (s, 3H), 5.48–5.56 (m, 2H), 5.66–5.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.27 (u), 25.82 (u), 26.36 (u), 28.80 (u), 34.99 (u), 54.56 (d), 76.42 (d), 130.12 (d), 130.13 (d), 155.34 (u); GC-MS (CI, 70 eV): *m*/*z* (%): 184 [M^+], 109 (100), 107 (17), 75; IR (capillary): $\tilde{\nu}$ = 2930 (s), 2858 (m), 1747 (s), 1443 (s), 1333 (m), 1305 (m), 1271 (s), 1149 (w), 1135 (w), 1021 (m), 993 (w), 950 (s), 794 (m), 757 (m), 723 cm^{-1} (w); elemental analysis calcd (%) for $C_{10}H_{16}O_3$: C 65.19, H 8.75; found C 65.21, H 8.63.

On a 30 mmol scale: Following GP1, a mixture of carbonate *rac*-**1c** (5.70 g, 31.0 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (310 mg, 0.30 mmol) and **BPA** (830 mg, 1.2 mmol) in CH_2Cl_2 (10 mL) was treated under stirring at 0 °C successively with a suspension of LiO_2StBu (7.70 g, 60 mmol) and THAB (650 mg, 1.5 mmol) in CH_2Cl_2 (50 mL) and degassed water (20 mL). Quenching of the mixture after stirring it at room temperature for 26 h gave a mixture of carbonate *ent*-**1c** and sulfone **2c** in a ratio of 42:58 (^{1}H NMR). Chromatography (hexane/EtOAc 10:1, 1% NEt_3) furnished sulfone **2c** (3.14 g, 44%) of 97% *ee* (GC, Lipodex E) as a colorless solid and carbonate *ent*-**1c** (2.34 g, 41%) of 95% *ee* (GC, Lipodex E) as a colorless oil.

On a 50 mmol scale: Following GP1, a mixture of carbonate *rac*-**1c** (9.80 g, 53.0 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (530 mg, 0.50 mmol), **BPA** (1.05 g, 1.5 mmol) and tetradecane (1.25 g, 6.3 mmol) in CH_2Cl_2 (50 mL) was treated under stirring at 0 °C successively with a suspension of LiO_2StBu (10.0 g, 78 mmol) and THAB (1.086 g, 2.5 mmol) in CH_2Cl_2 (75 mL) and degassed water (30 mL). Quenching of the mixture after stirring it at room temperature for 48 h gave a mixture of carbonate *ent*-**1c** and sulfone **2c** in a ratio of 42:58 (^{1}H NMR). Chromatography (hexane/EtOAc 10:1, 1% NEt_3) furnished sulfone **2c** (5.86 g, 48%) of 89% *ee* (GC Lipodex E). Crystallization from hexane/ethyl acetate gave sulfone **2c** (4.88 g, 40%) of ≥99% *ee* (GC, Lipodex E); $[\alpha]_D^{20} = 148.3$ (c = 2.81, CH_2Cl_2)) as a colorless solid. Besides sulfone **2c** carbonate *ent*-**1c** (3.81 g, 39%) of ≥99% *ee* (GC, Lipodex E) was isolated as a colorless oil.

Determination of the conversion in the kinetic resolution of carbonate *rac*-1a in the reaction with lithium *tert*-butylsulfinate by the method of internal standard: **BPA** (311 mg, 0.45 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (155 mg, 0.15 mmol) and tetradecane (253 mg, 1.27 mmol) were placed under argon in a Schlenk flask. Subsequently CH_2Cl_2 (10 mL) was added and the mixture was stirred at room temperature for 20 min and then cooled to 0 °C. In a second Schlenk flask were placed under argon LiO_2StBu (2.62 g, 20 mmol), THAB (300 mg, 0.7 mmol) and CH_2Cl_2 (20 mL) and the mixture was cooled to 0 °C and treated with degassed water (10 mL). Than the solution of the sulfinate salt was added to the solution containing the catalyst and the resulting mixture was treated with carbonate *rac*-**1a** (1.77 g, 11 mmol). The mixture was stirred at 0 °C and samples of the organic phase (0.1 mL) were withdrawn with a syringe after 2, 4, 5, 10, 15, 20 and 30 min under exposure to air and analyzed by GC. After a total reaction time of 45 min phases were separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Chromatography (hexane/EtOAc 7:1) afforded sulfone **2aa** (990 mg, 45%) of 96% *ee* [^{1}H NMR, 400 MHz, $CDCl_3$, 30 mol%, Eu(hfc)$_3$] as a colorless solid and carbonate *ent*-**1a** (498 mg, 29%) of ≥99% *ee* (GC, Lipodex E) as a colorless oil.

Substitution of carbonate *ent*-1a with lithium *tert*-butylsulfinate: Following GP1, **BPA** (16 mg, 2.3 μmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (8 mg, 0.77 μmol) and carbonate *ent*-**1a** (79 mg, 0.5 mmol) of ≥99% *ee* in CH_2Cl_2 (3 mL) were treated with LiO_2StBu (128 mg, 1 mmol) and THAB (13 mg, 2.99 μmol) in CH_2Cl_2 (3 mL) and degassed water (4 mL). Then the mixture was stirred at room temperature for 18 h. Chromatography (hexane/EtOAc 7:1) afforded sulfone **2aa** (88 mg, 87%) of 91% *ee* [^{1}H NMR, 400 MHz, $CDCl_3$, 30 mol% Eu(hfc)$_3$] as a colorless solid.

Substitution of carbonate *ent*-1c with lithium *tert*-butylsulfinate: Following GP1, **BPA** (31 mg, 0.045mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (15 mg, 0.015 mmol) and carbonate *ent*-**1c** (194 mg, 1.05 mmol) of 99% *ee* in CH_2Cl_2 (3 mL) were treated with LiO_2StBu (250 mg, 2.1 mmol) and THAB (22 mg, 0.05 mmol) in CH_2Cl_2 (3 mL) and degassed water (2 mL). Then the mixture was stirred at room temperature for 4 d. GC showed formation of 4.5% sulfone **2c** of 99% *ee* (GC, Lipodex E) and 95% carbonate *ent*-**1c** of 99% *ee* (GC, Lipodex E).

Kinetic resolution of carbonate *rac*-1a with sodium *p*-tolylsulfinate: (*S*)-3-(tolyl-sulfonyl)-cyclohexene (2ab) and (*R*)-carbonic acid cyclohex-2-enyl methyl ester (*ent*-1a): Following GP1, **BPA** (63 mg, 0.09 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (31 mg, 0.03 mmol) and *rac*-**1a** (313 mg, 2.0 mmol) in CH_2Cl_2 (6 mL) were treated with NaO_2STol (713 mg, 4 mmol) and THAB (45 mg, 0.1 mmol) in CH_2Cl_2 (6 mL) and degassed water (3 mL). After stirring the mixture at 0 °C for 30 min a mixture of carbonate *ent*-**1a** and sulfone **2ab** in a ratio of 32:68 was isolated. Chromatography (hexane/EtOAc 7:1) afforded sulfone **2ab** (234 mg, 60%) of ≥99% *ee* (HPLC, OD-H column) as a colorless solid and carbonate *ent*-**1a** (74 mg, 24%) of ≥99% *ee* (GC, Lipodex E) as a colorless oil. Sulfone **2ab**: m.p. 58 °C; $[\alpha]_D^{20} = -133.7$ (c = 1.02, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44–1.56 (m, 1H), 1.72–1.91 (m, 2H), 1.94–2.03 (m, 3H), 2.45 (s, 3H), 3.73 (m, 1H), 5.79 (dq, J = 10.1, 2.4 Hz, 1H), 6.06 (dq, J = 10.1, 2.2 Hz, 1H), 7.32–7.38 (pseudo-d, 2H), 7.74 (pseudo-d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.51 (u), 21.62 (d), 22.69 (u), 24.34 (u), 61.74 (d), 118.52 (d), 128.98 (d), 129.41 (d), 134.18 (u), 134.94 (d), 144.36 (u); MS: 236 (0.3) [M^+], 157 (39), 91 (7), 82 (10), 81 (100), 80 (13), 79 (22), 65 (7), 53 (6); IR (KBr): $\tilde{\nu}$ = 3038 (m), 2941 (m), 2864 (m), 2837 (m), 1596 (m), 1497 (m), 1449 (m), 1405 (w), 1288 (s), 1211 (w), 1185 (w), 1144 (s), 1086 (s), 1044 (m), 984 (m), 960 (w), 894 (m), 872 (m), 819 (s), 727 (w), 800 (m), 772 (w), 735 (m), 710 (s); elemental analysis calcd (%) for $C_{13}H_{16}O_2S$: C 66.07, H 6.82; found: C 65.90, H 6.91.

Kinetic resolution of carbonate *rac*-1a with sodium phenylsulfinate: (*S*)-3-(phenyl-sulfonyl)-cyclohexene (2ac) and (*R*)-carbonic acid cyclohex-2-enyl methyl ester (*ent*-1a): Following GP1, **BPA** (60 mg, 0.09 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (31 mg, 0.03 mmol) and *rac*-**1a** (316 mg, 2.0 mmol) in CH_2Cl_2 (6 mL) were treated with NaO_2SPh (656 mg, 4 mmol) and THAB (40 mg, 0.09 mmol) in CH_2Cl_2 (6 mL) and degassed water (4 mL). After stirring the mixture at 0 °C for 30 min a mixture of carbonate *ent*-**1a** and sulfone **2ac** in a ratio of 38:62 was isolated. Chromatography (hexane/EtOAc 7:1) afforded sulfone **2ac** (252 mg, 56%) of ≥99% *ee* [GC, Lipodex E, t_R (**3b**) = 27.0 min, t_R (**3b**) = 26.57, t_R (*ent*-**3b**) = 27.64 min] as a colorless oil and carbonate *ent*-**1a** (85 mg, 27%) of ≥99% *ee* (GC, Lipodex E).

Sulfone 2ac: $[\alpha]_D^{20} = -134.7$ (c = 1.02, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26–1.56 (m, 1H), 1.70–2.01 (m, 5H), 3.76 (m, 1H), 5.7–5.82 (dq, J = 10.0, 2.35 Hz, 1H), 6.05–6.13 (m, 1H), 7.53–7.69 (m, 3H), 7.86–7.90 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.55 (u), 22.75 (u), 24.43 (u), 61 85 (d), 118.53 (d), 129.08 (d), 129.20 (d), 133.76 (d), 135.43 (d).

Kinetic resolution of carbonate *rac*-3aa with lithium *tert*-butylsulfinate: (*R*,*E*)-4-(2-methyl-propan-2-sulfonyl)-2-pentene (4a) and (*S*,*E*)-carbonic acid pent-2-enyl methyl ester (*ent*-3aa): Following GP1, **BPA** (315 mg, 0.45 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (150 mg, 0.15 mmol) and *rac*-**3aa** (1.43 g, 9.92 mmol) in CH_2Cl_2 (10 mL) were treated with LiO_2StBu (2.50 g, 19.5 mmol) and THAB (380 mg, 0.87 mmol) in CH_2Cl_2 (20 mL) and degassed water (3 mL). Termination of the reaction after stirring the mixture at room temperature for 25 min gave a mixture of carbonate *ent*-**3aa** and sulfone **4a** in a ratio of 27:73. Chromatography (hexane/EtOAc 10:1) afforded sulfone **4a** (1.28 g, 68%) of 96% *ee* [GC, Lipodex E, t_R (**4a**) = 32.70 min, t_R (*ent*-**4a**) = 33.73 min] as a colorless solid and carbonate *ent*-**3aa** (270 mg, 19%) of ≥99% *ee* [GC, Lipodex E, t_R (**3aa**) = 5.95 min, t_R (*ent*-**3aa**) = 6.42 min] as a colorless oil. Carbonate *ent*-**3aa**: $[\alpha]_D^{20} = -64.3^\circ$ ($c = 0.90$, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.35$ (d, $J = 6.7$ Hz, 3H), 1.69 (ddd, $J = 6.4$, 1.7, 0.7 Hz, 3H), 3.76 (s, 3H), 5.15 (quin, $J = 6.4$ Hz, 1H), 5.50 (ddq, $J = 15.1$, 6.4, 1.7 Hz, 1H), 5.77 (dqd, $J = 15.4$, 6.4, 1.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 17.7$ (d), 20.4 (d), 54.5 (d), 75.5 (d), 129.1 (d), 130.3 (d), 155.2 (u); IR (neat): $\tilde{\nu} = 2983$ (m), 2958 (m), 2922 (w), 2857 (w), 1747 (s), 1678 (w), 1585 (w), 1444 (s), 1380 (m), 1330 (m), 1270 (s), 1172 (w), 1142 (w), 1125 (w), 1087 (w), 1038 (s), 1009 (w), 966 (m), 940 (m), 897 (m), 864 (m), 793 cm^{-1} (m); MS (EI): *m*/*z* (%): 144 (8) [M^+], 112 (10), 85 (28), 69 (100), 68 (24), 67 (32), 59 (17), 55 (16), 53 (13); elemental analysis calcd (%) for $C_7H_{12}O_3$: C 58.32, H 8.39; found: C 58.51, H 8.51.

Sulfone 4a: $[\alpha]_D^{20} = -11.2$ ($c = 2.81$, CH_2Cl_2). Following GP1, **BPA** (66 mg, 0.09 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (33 mg, 0.03 mmol) and *rac*-**3aa** (303 mg, 2.1 mmol) in CH_2Cl_2 (3 mL) were treated with LiO_2StBu (517 mg, 4 mmol) and THAB (45 mg, 0.1 mmol) in CH_2Cl_2 (3 mL) and degassed water (3 mL). Terminated of the reaction after stirring the mixture at room temperature for 5 min gave a mixture of carbonate *ent*-**3aa** and sulfone **4a** in a ratio of 76:24. Chromatography (hexane/EtOAc 10:1) afforded sulfone **4a** (85 mg, 21%) of 98% *ee* (GC, Lipodex E) as a colorless solid and carbonate *ent*-**3aa** (161 mg, 53%) of 33% *ee* (GC, Lipodex E) as a colorless oil.

General procedure for the kinetic resolution of allylic carbonates with thiols (GP2): The precatalyst and the ligand were placed in a Schlenk flask containing a stirring bar and the flask was evacuated and refilled with argon. Then precatalyst and ligand were dissolved under stirring by addition of CH_2Cl_2. Stirring was continued until the color of the solution had changed from dark violet to bright red-orange (approximately 15 min). Then the substrate was added. Stirring of the mixture was continued until the color of the solution had changed from red-orange to yellow (approximately 15 min). The thiol (and tetradecane as internal standard in the case to determine the conversion) were placed in a second Schlenk flask and the flask was evacuated and refilled with argon. Then the thiol was suspended by the addition of CH_2Cl_2. The mixture containing the catalyst and the substrate were added under argon and stirring with a cannula to the suspension of the thiol. The reaction mixture was stirred at room temperature for the time given and the reaction progress was monitored by TLC or GC. For work-up the mixture was filtered through Celite and washed with CH_2Cl_2 and concentrated in vacuo. Chromatography gave the sulfide and the carbonate.

Kinetic resolution of carbonate *rac*-3aa with 2-pyrimidinethiol: 2-((*R*,*E*)-1-methyl-but-2-enylsulfanyl)-pyrimidine (6aa) and (*S*)-carbonic acid methyl 1-methyl-but-2-enyl ester (*ent*-1a): Following GP2, a mixture of carbonate *rac*-**3aa** (1.44 g, 10 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (259 mg, 0.25 mmol) and **BPA** (380 mg, 0.55 mmol) in CH_2Cl_2 (20 mL) was treated with 2-pyrimidinethiol (1.12 g, 10 mmol) in CH_2Cl_2 (20 mL). After 20 h conversion of carbonate *rac*-**3aa** was approximately 50% and the reaction was terminated. Purification by flash chromatography (pentane/diethyl ether 20:1 → 3:1) gave sulfide **6aa** (649 mg, 36%) of 93% *ee* [GC, Lipodex γ, t_R (**6aa**) = 36.02 min, t_R (*ent*-**6aa**) = 36.08 min] and carbonate *ent*-**3aa** (519 mg, 36%) of ≥99% *ee* (GC, Lipodex E).

Sulfide 6aa: $[\alpha]_D^{20} = +188.1$ ($c = 1.06$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.51$ (d, $J = 7.0$ Hz, 3H), 1.69 (dm, $J = 5.7$ Hz, 3H), 4.47 (quin, $J = 6.7$ Hz, 1H), 5.64 (ddq, $J = 15.4$, 7.0, 1.3 Hz, 1H), 5.74 (dqd, $J = 15.1$, 5.7, 1.0 Hz, 1H), 6.94 (t, $J = 4.7$ Hz, 1H), 8.52 (d, $J = 4.7$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 17.8$ (d), 20.4 (d), 41.7 (d), 116.3 (d), 126.4 (d), 131.7 (d), 157.2 (d), 172.5 (u); IR (neat): $\tilde{\nu} = 3027$ (w), 2965 (w), 2924 (w), 1565 (s), 1547 (s), 1450 (m), 1426 (w), 1382 (s), 1188 (s), 1017 (w), 965 (w), 798 (w), 774 (m), 749 (m), 630 cm^{-1} (w); GC-MS (EI): *m*/*z* (%): 180 (10) [M^+], 151 (99), 147 (57), 113 (20), 112 (39), 84 (18), 79 (14), 69 (100), 68 (24), 67 (30), 59 (10), 57 (15), 53 (28), 52 (16); elemental analysis calcd (%) for $C_9H_{12}N_2S$: C 59.97, H 6.71, N 15.54; found: C 59.76, H 6.95, N 15.22.

Carbonate *ent*-3aa: $[\alpha]_D^{20} = -64.4^\circ$ ($c = 1.04$, $CHCl_3$).

Kinetic resolution of carbonate *rac*-3ba with 2-pyrimidinethiol: 2-((*R*,*E*)-1-ethyl-pent-2-enylsulfanyl)-pyrimidine (6ba) and (*S*)-carbonic acid 1-ethyl-pent-2-enyl methyl ester (*ent*-3ba): Following GP2, a mixture of carbonate *rac*-**3ba** (1.76 g, 10.3 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (517 mg, 0.5 mmol) and **BPA** (760 mg, 1.1 mmol) in CH_2Cl_2 (20 mL) was treated with 2-pyrimidinethiol (1.12 g, 10 mmol) in CH_2Cl_2 (20 mL) in CH_2Cl_2 (20 mL). After 2 d conversion of carbonate *rac*-**3ba** was approximately 50%. Purification by flash chromatography (pentane/diethyl ether 7:1 → 3:1) gave sulfide **6ba** (962 mg, 44%) of 92% *ee* [HPLC, Chiralcel OD-H column, hexane/*i*PrOH 95:5, t_R (**6ba**) = 10.13 min, t_R (*ent*-**6ba**) = 8.99 min] and carbonate *ent*-**3ba** (492 mg, 28%) of ≥99% *ee* [GC, Hydrodex-β-6-TBDM, t_R (*ent*-**3ba**) = 26.49 min].

Sulfide 6ba: $[\alpha]_D^{20} = +209.4$ ($c = 2.11$, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.95$ (t, $J = 7.4$ Hz, 3H), 1.02 (t, $J = 7.4$, 3H), 1.80–1.94 (m, 2H), 1.97–2.08 (m, 2H), 4.31 (td, $J = 8.2$, 6.0 Hz, 1H), 5.46 (ddt, $J = 15.1$, 8.5, 1.7 Hz, 1H), 5.77 (dtd, $J = 15.4$, 6.4, 0.7 Hz, 1H), 6.93 (t, $J = 4.8$ Hz, 2H), 8.49 (d, $J = 5.0$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 11.7$ (d), 13.6 (d), 25.4 (u), 27.8 (u), 48.7 (d), 116.3 (d), 128.2 (d), 134.5 (d), 157.1 (d), 172.5 (u); IR (neat): $\tilde{\nu} = 2964$ (m), 2932 (m), 2873 (w), 1565 (s), 1547 (s), 1460 (m), 1426 (w), 1382 (s), 1187 (s), 965 (w), 798 (w), 774 (m), 750 (m), 631 cm^{-1} (w); MS (EI): *m*/*z* (%): 208 (7) [M^+], 175 (19), 165 (35), 113 (30), 97 (11), 96 (19), 81 (22), 67 (11), 55 (100), 53 (14); elemental analysis calcd (%) for $C_{11}H_{16}N_2S$: C 63.42, H 7.74, N 13.45; found: C 63.38, H 7.70,N 13.29.

Carbonate *ent*-3ba: $[\alpha]_D^{20} = -60.2^\circ$ ($c = 1.31$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.91$ (t, $J = 7.4$ Hz, 3H), 0.99 (t, $J = 7.6$ Hz, 3H), 1.55–1.80 (m, 2H), 2.06 (quinm, $J = 7.5$ Hz, 2H), 3.76 (s, 3H), 4.95 (q, $J = 7.0$ Hz, 1H), 5.40 (ddt, $J = 15.4$, 7.9, 1.7 Hz, 1H), 5.81 (dtd, $J = 15.4$, 6.4, 0.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 9.5$ (d), 13.2 (d), 25.2 (u), 27.6 (u), 54.5 (d), 80.7 (d), 126.5 (d), 136.9 (d), 155.4 (u); IR (neat): $\tilde{\nu} = 2967$ (m), 2937 (m), 2879 (w), 2854 (w), 1749 (s), 1443 (s), 1383 (w), 1348 (m), 1265 (s), 1076 (w), 969 (m), 948 (s), 923 (m), 793 cm^{-1} (m); GC-MS (EI): *m*/*z* (%): 172 (3) [M^+], 143 (10), 99 (26), 97 (36), 96 (25), 81 (83), 79 (12), 71 (25), 69 (24), 68 (17), 67 (95), 59 (38), 57 (18), 55 (100), 54 (15), 53 (18), 45 (10); elemental analysis calcd (%) for $C_9H_{16}O_3$: C 62.77, H 9.36; found: C 62.56, H 9.65.

Determination of the conversion in the kinetic resolution of carbonate *rac*-1a in the reaction with 2-pyrimidinethiol by the method of internal standard: 2-((*S*)-cyclohex-2-enylsulfanyl)-pyrimidine (5aa) and (*R*)-carbonic acid cyclohex-2-enyl methyl ester (*ent*-1a): Following GP2, a mixture of carbonate *rac*-**1a** (1.52 g, 9.7 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (259 mg, 0.25 mmol) and **BPA** (380 mg, 0.55 mmol) containing tetradecane (252 mg, 1.27 mmol) in CH_2Cl_2 (20 mL) was treated with 2-pyrimidinethiol (1.12 g, 10 mmol) in CH_2Cl_2 (20 mL). Samples (0.1 mL) were taken with a syringe after 10, 15, 20, 25, 30, 35, 40, 45, 50 and 55 min and filtered under exposure to air through Celite. The Celite was washed with CH_2Cl_2 (2 mL) and the filtrate was analyzed by GC. After 60 min conversion of carbonate *rac*-**1a** was 50%. Purification by flash chromatography (pentane/diethyl ether 7:1 → 3:1) gave sulfide **5aa** (860 mg, 46%) of 84% *ee* [GC, CP-βI-CB, t_R (**5aa**) = 58.88, t_R (*ent*-**5aa**) = 58.72 min] as a colorless oil and the carbonate *ent*-**1a** (614 mg, 41%) of ≥99% *ee* (GC, Lipodex E) as a colorless oil.

Sulfide 5aa: $[\alpha]_D^{20} = -124.8$ ($c = 1.14$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.63–1.76$ (m, 1H), 1.79–1.99 (m, 2H), 2.03–2.16 (m, 3H), 4.53–4.56 (m, 1H), 5.78–5.92 (m, 2H), 6.96 (t, $J = 5.0$ Hz, 1H), 8.51 (d, $J = 5.0$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.8$ (u), 24.9 (u), 29.1 (u), 40.8 (d), 116.4 (d), 126.3 (d), 131.0 (d), 157.2 (d), 172.5 (u); IR (neat): $\tilde{\nu} = 2932$ (m), 2858 (w), 2834 (w), 1564 (s), 1547 (s), 1444 (m), 1428 (m), 1381 (s), 1255 (w), 1189 (s), 871 (w), 799 (w), 774 (m), 748 (m), 724 (w), 628 cm^{-1} (m); MS (EI): *m*/*z* (%): 192 (39) [M^+], 159 (87), 131 (16), 113 (96), 84 (13), 81 (63), 80 (66), 79 (100), 77 (26), 53 (28), 52 (12); elemental analysis calcd (%) for $C_{10}H_{12}N_2S$: C 62.47, H 6.29, N 14.57; found: C 62.18, H 6.39, N 14.60.

Carbonate *ent*-1a: $[\alpha]_D^{20} = +166.7$ ($c = 1.10$, $CHCl_3$).

Kinetic resolution of carbonate *rac*-1b with 2-pyrimidinethiol: 2-((*S*)-cyclohept-2-enylsulfanyl)-pyrimidine (5b) and (*R*)-carbonic acid cyclohept-2-enyl methyl ester (*ent*-1b): Following GP2, a mixture of carbonate *rac*-**1b** (828 mg, 4.9 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (259 mg, 0.25 mmol) and **BPA** (380 mg, 1.1 mmol) in CH_2Cl_2 (10 mL) was treated with 2-pyrimidinethiol (560 mg, 5 mmol) in CH_2Cl_2 (10 mL). After 3.5 h conversion of

carbonate *rac*-**1b** was approximately 50%. Purification by flash chromatography (pentane/diethyl ether 7:1) gave sulfide **5b** (380 mg, 38%) of 84% *ee* [GC, CP-βI-CB, t_R (**5b**) = 47.92, t_R (*ent*-**5b**) = 47.67 min] as a colorless oil and carbonate *ent*-**1b** (324 mg, 39%) of 97% *ee* (GC, Lipodex E) as a colorless oil. Sulfide **5b**: $[\alpha]_D^{20} = -157.5$ ($c = 1.42$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.50-2.27$ (m, 8H), 4.67–4.71 (m, 1H), 5.82–5.93 (m, 2H), 6.94 (t, $J = 4.7$ Hz, 1H), 8.51 (d, $J = 4.7$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 27.2$ (u), 27.2 (u), 28.4 (u), 32.3 (u), 44.9 (d), 116.3 (d), 131.7 (d), 134.0 (d), 157.2 (d), 172.5 (u); GC-MS (EI): *m*/*z* (%): 206 (19) [M^+], 174 (11), 173 (77), 163 (17), 145 (15), 137 (16), 114 (11), 113 (100), 112 (35), 95 (57), 94 (79), 91 (17), 84 (20), 80 (14), 79 (83), 77 (29), 67 (88), 65 (21), 57 (20), 55 (34), 53 (36), 52 (30); elemental analysis calcd (%) for $C_{11}H_{14}N_2S$: C 64.04, H 6.84, N 13.58; found: C 64.14, H 6.75, N 13.83.

Carbonate *ent*-1b: $[\alpha]_D^{20} = +34.1^\circ$ ($c = 0.99$, $CHCl_3$).

Determination of the conversion of carbonate 1a in the reaction with 2-pyrimidinethiol by the method of internal standard: **2-((*S*)-cyclohex-2-enylsulfanyl)-pyrimidine (5aa) and (*S*)-carbonic acid cyclohex-2-enyl methyl ester (1a)**: Following GP2, a mixture of carbonate **1a** (156 mg, 1 mmol) of ≥99% *ee*, $[Pd_2(dba)_3]\cdot CHCl_3$ (25.9 mg, 0.025 mmol) and **BPA** (38.0 mg, 0.055 mmol) in CH_2Cl_2 (2 mL) containing tertradecane (65 mg, 0.33 mmol) was treated with 2-pyrimidinethiol (112 mg, 1 mmol) in CH_2Cl_2 (2 mL) and samples were taken with a syringe after 20, 30, 40, 50, 60, 70, 80, 90, 100 and 110 min and filtered under exposure to air through Celite. The Celite was washed with CH_2Cl_2 (2 mL) and the filtrate was analyzed by GC.

Determination of the conversion of carbonate *ent*-1a in the reaction with 2-pyrimidinethiol by the method of internal standard: **2-((*S*)-cyclohex-2-enylsulfanyl)-pyrimidine (5aa) and (*R*)-carbonic acid cyclohex-2-enyl methyl ester (*ent*-1a)**: Following GP2, a mixture of carbonate **1a** (156 mg, 1 mmol) ≥99% *ee*, $[Pd_2(dba)_3]\cdot CHCl_3$ (25.9 mg, 0.025 mmol) and **BPA** (38.0 mg, 0.055 mmol) in CH_2Cl_2 (2 mL) containing tetradecane (65 mg, 0.33 mmol) was treated with 2-pyrimidinethiol (112 mg, 1 mmol) in CH_2Cl_2 (2 mL) and samples were taken with a syringe after 20, 30, 40, 50, 60, 70, 80, 90, 100 and 110 min and filtered under exposure to air through Celite. The Celite was washed with CH_2Cl_2 (2 mL) and the filtrate was analyzed by GC.

(*S*)-3-(2-Methyl-propan-2-sulfonyl)-cyclopentene (2d): Following GP1, a mixture of carbonate *rac*-**1da** (130 mg, 0.93 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (15 mg, 0.014 mmol) and **BPA** (31 mg, 0.045 mmol) in CH_2Cl_2 (2 mL) was treated under stirring at 0 °C with a suspension of LiO_2StBu (256 mg, 2 mmol) und THAB (24 mg, 0.055 mmol) in CH_2Cl_2 (3 mL). Then degassed water (3 mL) was added and the mixture was stirred at room temperature for 24 h. Chromatography (hexane/EtOAc 5:1) gave sulfone **2d** (133 mg, 76%) of 89% *ee* [GC, Lipodex E, t_R (**2d**) = 33.63 min, t_R (*ent*-**2d**) = 33.78 min; {^{1}H NMR, $CDCl_3$, 30 mol% [Eu(hfc)$_3$]}: δ (*t*Bu) (*ent*-**2d**) = 2.50, δ (*t*Bu) (**2d**) = 2.47] as a colorless solid. M.p. 58 °C; $[\alpha]_D^{20} = -192.6$ ($c = 1.02$, CH_2Cl_2).

(*S*)-3-(2-Methyl-propan-2-sulfonyl)-cyclohexene (2aa): Following GP1, a mixture of carbonate *rac*-**1a** (781 mg, 5.0 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (77 mg, 0.075 mmol) and **BPA** (155 mg, 0.22 mmol) in CH_2Cl_2 (30 mL) was treated under stirring at 0 °C with a suspension of LiO_2StBu (1.28 g, 10 mmol) und THAB (109 mg, 0.25 mmol) in CH_2Cl_2 (30 mL). Then degassed water (10 mL) was added and the mixture was successively stirred at 0 °C for 1 h and at room temperature for 18 h. Chromatography (hexane/EtOAc 7:1, 1% NEt_3) afforded sulfone **2aa** (960 mg, 95%) of 94% *ee* (400 MHz ^{1}H NMR, $CDCl_3$, 30 mol% [Eu(hfc)$_3$]) as a colorless solid.

(*S*)-3-(2-Methyl-propan-2-sulfonyl)-cycloheptene (2b): Following GP1, a mixture of carbonate *rac*-**1b** (172 mg, 1.0 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (15 mg, 0.015 mmol) and **BPA** (31.3 mg, 0.045 mmol) in CH_2Cl_2 (3 mL) was treated under stirring at 0 °C with a suspension of LiO_2StBu (256 mg, 2 mmol) und THAB (25 mg, 0.057 mmol) in CH_2Cl_2 (3 mL). Then degassed water (3 mL) was added and the mixture was successively stirred at 0 °C for 2 h and at room temperature for 4 h under ultrasonication. Chromatography (hexane/EtOAc 7:1, 1% NEt_3) afforded sulfone **2b** (192 mg, 89%) of 93% *ee* (GC, Lipodex E) as a colorless solid.

(*R*,*E*)-4-(2-Methyl-propan-2-sulfonyl)-2-pentene (4a)

From carbonate rac-3aa in the presence of BPA: Following GP1, a mixture of carbonate *rac*-**3aa** (144 mg, 1.0 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (15.5 mg, 0.015 mmol) and **BPA** (31.4 mg, 0.045 mmol) in CH_2Cl_2 (5 mL) was treated with a solution of THAB (70.0 mg, 0.16 mmol) and LiO_2StBu (260 mg, 2.0 mmol) in water (10 mL) and the resulting mixture was stirred at room temperature for 4 h. Chromatography (hexane/EtOAc 3:1) afforded sulfone **4a** (186 mg, 98%) of 98% *ee* (GC, Lipodex E) as a colorless oil.

From acetate rac-3 ab in the presence of BPA: Following GP1, a mixture of acetate *rac*-**3ab** (130 mg, 1.0 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (15.5 mg, 0.015 mmol) and **BPA** (31.4 mg, 0.045 mmol) CH_2Cl_2 (5 mL) was treated with a solution of THAB (70.0 mg, 0.16 mmol) and LiO_2StBu (260 mg, 2.0 mmol) in water (10 mL) and the mixture was stirred at room temperature for 94 h. Chromatography (hexane/EtOAc 3:1) afforded sulfone **4a** (98 mg, 51%) of 98% *ee* (GC, Lipodex E) as a colorless oil: $[\alpha]_D^{20} = -11.2$ (c = 1.00, EtOH).

From acetate rac-3 ab in the presence of POX: Following GP1, a mixture of acetate *rac*-**3ab** (2.00 g, 15.6 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (403 mg, 0.39 mmol) and **POX** (640 mg, 1.72 mmol) in THF (50 mL) was treated with a suspension of NaO_2StBu (4.50 g, 31.2 mmol) in THF (60 mL) and the mixture was stirred at room temperature for 48 h. Chromatography (hexane/EtOAc 4:1) gave sulfone *ent*-**4a** (1.62 g, 55%) of 58% *ee* (GC, Lipodex E) as a colorless oil: $[\alpha]_D^{20} = 4.3$ ($c = 1.30$, EtOH).

(*R*,*E*)-5-(2-Methyl-propan-2-sulfonyl)-3-heptene (4b)

From carbonate rac-3ba in the presence of BPA: Following GP1, a mixture of carbonate *rac*-**3ba** (172 mg, 1.0 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (15.5 mg, 0.015 mmol) and **BPA** (31.4 mg, 0.045 mmol) CH_2Cl_2 (10 mL) was treated with a solution of LiO_2StBu (256 mg, 2.0 mmol) and THAB (70 mg, 0.16 mmol) in water (5 mL) and the mixture was stirred at room temperature for 2 h. Chromatography (silica gel, hexane/EtOAc 3:1) afforded sulfone **4b** (214 mg, 97%) of 97% *ee* [GC, Lipodex E, t_R (*ent*-**4b**) = 31.60 min, t_R (**4b**) = 31.86 min] as a colorless oil: $[\alpha]_D^{20} = -31.4$ ($c = 1.00$, EtOH); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.94$ (t, $J = 7.4$ Hz, 3H), 1.03 (t, $J = 7.4$ Hz, 3H), 1.42 (s, 9H), 1.68 (m, 1H), 2.14 (m, 2H), 2.22 (m, 1H), 3.55 (dt, $J = 3.3$, 10.1 Hz, 1H), 5.45 (ddt, $J = 9.9$, 15.6, 1.6 Hz, 1H), 5.75 (dt, $J = 15.6$, 6.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 11.35$ (d), 13.58 (d), 20.97 (u), 25.10 (d), 26.13 (u), 62.20 (u), 65.34 (d), 124.46 (d), 139.48 (d); MS (EI, 70 eV) *m*/*z*: 219 (1) [M^+], 162 (5), 125 (5), 124 (5), 123 (100), 69 (6), 57 (5); IR (capillary): $\tilde{\nu} = 2980$ (s), 2940 (s), 1460 (m), 1280 (s), 1115 (s), 1015 (m), 975 (m), 800 (w), 720 (m), 660 cm^{-1} (m); elemental analysis calcd (%) for $C_{11}H_{22}O_2S$: C 60.51, H 10.16; found: C 60.62, H 10.48.

From carbonate rac-3 ba in the presence of BPA and [Pd(C$_3$H$_5$)Cl]$_2$: Following GP1, a mixture of carbonate *rac*-**3ba** (172 mg, 1.0 mmol), $[Pd(C_3H_5)Cl]_2$ (6.8 mg, 0.03 mmol) and **BPA** (31.4 mg, 0.045 mmol) in CH_2Cl_2 (10 mL) was treated with a solution of LiO_2StBu (256 mg, 2.0 mmol) and THAB (70 mg, 0.16 mmol) in water (5 mL) and the mixture was stirred at room temperature for 6 h. Chromatography (hexane/EtOAc 3:1) furnished sulfone **4b** (210 mg, 96%) of 96% *ee* (GC, Lipodex E) as a colorless oil: $[\alpha]_D^{20} = -31.2$ ($c = 1.32$, EtOH).

From acetate rac-3 bb in the presence of BPA: Following GP1, a mixture of acetate *rac*-**3bb** (157 mg, 1.0 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (15.5 mg, 0.015 mmol) and **BPA** (31.4 mg, 0.045 mmol) in CH_2Cl_2 (10 mL) was treated with a solution of LiO_2StBu (256 mg, 2.0 mmol) and THAB (70 mg, 0.16 mmol) in water (5 mL) and the mixture was stirred at room temperature for 48 h. Chromatography (hexane/EtOAc 3:1) afforded sulfone **4b** (95 mg, 43%) of 96% *ee* (GC, Lipodex E) as a colorless oil: $[\alpha]_D^{20} = -31.4$ ($c = 1.00$, EtOH).

Sulfone ent-4 b from acetate rac-3 bb in the presence of POX: Following GP1, a mixture of acetate *rac*-**3bb** (156 mg, 1.0 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (15.5 mg 0.015 mmol) and **POX** (22.0 mg, 0.06 mmol) in THF (10 mL) was treated with a suspension of $LiSO_2tBu$ (250 mg, 2.0 mmol) in THF (10 mL) and the mixture was stirred at room temperature for 70 h. Chromatography (hexane/EtOAc 3:1) gave sulfone *ent*-**4b** (130 mg, 60%) of 61% *ee* (GC, Lipodex E) as a colorless oil: $[\alpha]_D^{20} = 14.6$ ($c = 1.15$, THF).

(*S*,*E*)-2,6-Dimethyl-5-(2-methyl-propan-2-sulfonyl)-3-heptene (4c): Following GP1, a mixture of chloride *rac*-**3cb** (364 mg, 2.27 mmol), $[Pd(C_3H_5)Cl]_2$ (15.0 mg, 0.034 mmol) and **BPA** (94.0 mg, 0.136 mmol) in CH_2Cl_2 (20 mL) was treated with a solution of $LiSO_2tBu$ (600 mg, 4.56 mmol) and THAB (160 mg, 0.36 mmol) in water (15 mL) and the mixture was stirred at room temperature for 120 h. Chromatography (hexane/EtOAc 3:1) gave sulfone **4c** (330 mg, 58%) of 84% *ee* [GC, Lipodex E, t_R (*ent*-**4c**) = 76.13 min, t_R (**4c**) = 76.30 min] as a colorless oil: $[\alpha]_D^{20} = -6.35$ ($c = 1.15$, THF); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.93$ (d, $J = 7.1$ Hz, 3H), 1.03 (d, $J = 6.9$ Hz, 3H), 1.04 (d, $J = 6.6$ Hz, 6H), 1.4 (s, 9H), 2.41 (m, 1H), 2.71 (dh, $J = 6.9$, 2.8 Hz, 1H), 3.55 (m, 1H), 5.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 17.73$ (d), 21.62 (d), 22.00 (d), 22.39

(d), 24.71 (d), 27.49 (d), 31.65 (d), 62.36 (u), 66.42 (d), 119.31 (d), 145.26 (d); IR (capillary): $\tilde{\nu}$ = 2970 (s), 2930 (s), 1460 (s), 1280 (s), 1190 (m), 1120 (s), 980 (m), 800 (m), 695 (m), 635 (m), 560 (m), 490 cm^{-1} (w); MS (EI, 70 eV) *m/z*: 247 (2) [M^+], 126 (18), 125 (100), 124 (29), 109 (10), 95 (8), 83 (17), 69 (11); elemental analysis calcd (%) for $C_{13}H_{26}O_2S$: C 63.37, H 10.64; found: C 63.10, H 10.91.

General procedure for the asymmetric synthesis of sulfides by Pd-catalyzed allylic substitution of carbonates with thiols (GP3): The precatalyst and the ligand were placed in a Schlenk flask containing a stirring bar and the flask was evacuated and refilled with argon. Then precatalyst and ligand were dissolved under stirring by addition of CH_2Cl_2. The thiol was placed in a second Schlenk flask and the flask was evacuated and refilled with argon, then the carbonate was added. The thiol and carbonate were dissolved or suspended by the addition of CH_2Cl_2. Both solutions were degassed by three freeze-thaw cycles. Stirring was continued until the color of the solution had changed from dark violet to bright red-orange (approximately 15 min). The solution containing the catalyst and ligand was added under argon with a cannula to the solution or suspension of the thiol and the carbonate. This solution was stirred at the desired temperature. For work-up the reaction mixture was concentrated in vacuo and the sulfide was isolated by chromatography.

2-((*S*)-Cyclohex-2-enylsulfanyl)-pyrimidine (5aa): Following GP3, a mixture of carbonate *rac*-**1a** (187 mg, 1.2 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (51.8 mg, 0.05 mmol) and **BPA** (75.9 mg, 0.11 mmol) in CH_2Cl_2 (2.5 mL) was treated with 2-pyridinethiol (111 mg, 1 mmol) in CH_2Cl_2 (2.5 mL). After 24 h the reaction was stopped. Purification by flash chromatography (hexane/EtOAc 10:1) gave sulfide **5aa** (121 mg, 63%) of 84% *ee* (GC, CP-βI-CB).

2-((*S*)-Cyclohex-2-enylsulfanyl)-pyrimidine (5ab): Following GP3, a mixture of carbonate *rac*-**1a** (182 mg, 1.2 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (51.8 mg, 0.05 mmol) and **BPA** (75.9 mg, 0.11 mmol) in CH_2Cl_2 (2.5 mL) was treated with 2-pyridinethiol (111 mg, 1 mmol) in CH_2Cl_2 (2.5 mL). After 27 h the reaction was stopped. Purification by flash chromatography (hexane/EtOAc 40:1) gave sulfide **5ab** (122 mg, 64%) of 55% *ee* [GC, CP-βI-CB, t_R (**5ab**) = 26.05 min, t_R (*ent*-**5ab**) = 25.95 min]: $[\alpha]_D^{20} = -60.9$ (c = 1.82, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.62–1.74 (m, 1H), 1.78–1.95 (m, 2H), 2.02–2.14 (m, 3H), 4.56–4.62 (m, 1H), 5.77–5.90 (m, 2H), 6.96 (ddd, J = 7.4, 5.0, 1.0 Hz, 1H), 7.15 (dm, J = 8.0 Hz, 1H), 7.45 (td, J = 7.7, 2.0 Hz, 1H), 8.43 (dm, J = 5.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.8 (u), 24.9 (u), 29.3 (u), 39.9 (d), 119.4 (d), 122.4 (d), 126.9 (d), 130.5 (d), 135.9 (d), 149.4 (d), 159.2 (u); MS (EI): *m/z* (%): 191 (28) [M^+], 159 (10), 158 (91), 130 (14), 112 (100), 111 (27), 81 (40), 80 (37), 79 (65), 78 (31), 77 (20), 67 (27), 53 (15), 51 (16); IR (neat): $\tilde{\nu}$ = 3026 (m), 2993 (w), 2932 (s), 2858 (m), 2833 (m), 1579 (s), 1555 (s), 1453 (s), 1430 (m), 1414 (s), 1280 (w), 1255 (w), 1205 (w), 1146 (m), 1123 (s), 1041 (m), 997 (w), 986 (m), 871 (m), 756 (s), 724 (s), 638 (w), 619 cm^{-1} (w).; elemental analysis calcd (%) for $C_{11}H_{13}NS$: C 69.07, H 6.85, N 7.32; found: C 68.83, H 6.75, N 7.60.

2-((*S*)-Cyclohept-2-enylsulfanyl)-pyrimidine (5b): Following GP3, a mixture of carbonate *rac*-**1b** (170 mg, 1 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (51.8 mg, 0.05 mmol) and **BPA** (75.9 mg, 0.11 mmol) in CH_2Cl_2 (2 mL) was treated with 2-pyrimidinethiol (112 mg, 1 mmol) in CH_2Cl_2 (2 mL). After 24 h the reaction was stopped. Purification by flash chromatography (pentane/diethyl ethyl 7:1) gave sulfide **5b** (125 mg, 61%) of 84% *ee* (HPLC, Chiralcel OD-H column, hexane/*i*PrOH 98:2).

2-((*S*)-Cyclopent-2-enylsulfanyl))-pyrimidine (5c)

From rac-1da: Following GP3, a mixture of carbonate *rac*-**1da** (146 mg, 1.03 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (25.8 mg, 0.025 mmol, 2.5 mol%) and **BPA** (37.9 mg, 0.055 mmol) in CH_2Cl_2 (2 mL) was treated with 2-pyrimidinethiol (112 mg, 1 mmol) in CH_2Cl_2 (2 mL). After 35 min the reaction was complete. Purification by flash chromatography (hexane/EtOAc 7:1) gave sulfide **5c** (146 mg, 80%) of 34% *ee* [GC, Hydrodex-β-6-TBDM, t_R (*ent*-**5c**) = 59.99 min, t_R (**5c**) = 60.26 min]: $[\alpha]_D^{20} = -42.1$ (c = 1.41, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.91–1.98 (m, 1H), 2.30–2.53 (m, 3H), 4.78 (m, 1H), 5.81 (m, 1H), 5.89 (m, 1H), 6.88 (t, J = 4.9 Hz, 1H), 8.44 (d, J = 4.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.58 (u), 31.77 (u), 50.37 (d), 116.53 (d), 130.74 (d), 134.63 (d), 157.39 (d), 173.41 (u); IR (capillary): $\tilde{\nu}$ = 3056 (w), 2933 (m), 2849 (m), 1564 (s), 1546 (s), 1454 (w), 1427 (w), 1381 (s), 1347 (w), 1293 (w), 1254 (w), 1190 (s), 1018 (m), 980 (w), 910 (w), 799 (m), 773 (s), 747 (s), 630 (w), 475 cm^{-1} (w); MS (CI): *m/z* (%): 178 (46) [M^+], 145 (65), 113 (91), 112 (59), 69 (10), 67 (100), 66 (47), 65 (26), 53 (13), 52 (10); elemental analysis calcd (%) for $C_9H_{10}N_2S$: C 60.64, H 5.65, N 15.71; found: C 60.34, H 5.80, N 15.99.

From rac-1db: Following GP3, a mixture of ester *rac*-**1db** (243 mg, 1.02 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (25.8 mg, 0.025 mmol, 2.5 mol%) and **BPA** (37.9 mg, 0.055 mmol, 5.5 mol%) in CH_2Cl_2 (2 mL) was treated with 2-pyrimidinethiol (112 mg, 1 mmol) in CH_2Cl_2 (2 mL). After 30 min the reaction was complete. Purification by flash chromatography (hexane/EtOAc 7:1) gave sulfide **5c** (174 mg, 96%) of 36% *ee* (GC, Hydrodex-β-6-TBDM): $[\alpha]_D^{20} = -43.2$ (c = 1.13, $CHCl_3$).

2-((*R*,*E*)-1-Methyl-but-2-enylsulfanyl)-pyrimidine (6aa): Following GP3, a mixture of carbonate *rac*-**3aa** (173 mg, 1.2 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (51.8 mg, 0.05 mmol) and **BPA** (69.1 mg, 0.10 mmol) in CH_2Cl_2 (2.5 mL) was treated with 2-pyridinethiol (112 mg, 1 mmol) in CH_2Cl_2 (2.5 mL). After 2 d the reaction was stopped. Purification by flash chromatography (hexane/EtOAc 10:1) gave sulfide **6aa** (129 mg, 72%) of 89% *ee* [GC, Lipodex γ, t_R (**6aa**) = 36.02 min, t_R (*ent*-**6aa**) = 36.08 min] and a *E*/*Z* ratio of 29:1 (GC) as a colorless oil: $[\alpha]_D^{20} = +155.2$ (c = 2.02, $CHCl_3$).

2-((*R*,*E*)-1-Ethyl-pent-2-enylsulfanyl)-pyrimidine (6ba): Following GP3, a mixture of carbonate *rac*-**3ba** (207 mg, 1.2 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (51.8 mg, 0.05 mmol) and **BPA** (75.9 mg, 0.11 mmol) in CH_2Cl_2 (2.5 mL) was treated with 2-pyrimidinethiol (112 mg, 1 mmol) in CH_2Cl_2 (2.5 mL). After 3 d the reaction was stopped. Purification by flash chromatography (hexane/EtOAc 10:1) gave sulfide **6ba** (134 mg, 64%) of 91% *ee* [HPLC, Chiralcel OD-H-column, hexane/*i*PrOH 95:5, t_R (**6ba**) = 10.13 min, t_R (*ent*-**6ba**) = 8.99 min]: $[\alpha]_D^{20} = +210.9$ (c = 0.97, $CHCl_3$).

2-((*RS*,*Z*)-1-Ethyl-pent-2-enylsulfanyl)-pyrimidine (*rac*-6ab): Following GP3, a mixture of carbonate *rac*-**3ba** (310 mg, 1.8 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (31.1 mg, 0.03 mmol) and dppp (49.5 mg, 0.12 mmol) in CH_2Cl_2 (2.5 mL) was treated with 2-pyrimidinethiol (168 mg, 1.5 mmol) in CH_2Cl_2 (2.5 mL) and the mixture was heated at reflux for 3 d. Purification by chromatography (hexane/EtOAc 10:1) gave a mixture of *rac*-**6ab** and its *Z* isomer (173 mg, 55%) in a ratio of 9:1. HPLC (Merck, LiChrosorb, Si 60, 5 μm, hexane/EtOAc 9:1) afforded *rac*-**6ab** (100 mg) and its *Z* isomer (17 mg) as colorless oils. *Z* isomer: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.99 (t, J = 7.6 Hz, 3H), 1.01 (t, J = 7.4 Hz, 3H), 1.60–1.75 (m, 1H), 1.84–1.99 (m, 1H), 2.16–2.32 (m, 2H), 4.58–4.66 (m, 1H), 5.33 (ddt, J = 10.6, 10.6, 1.7 Hz, 1H), 5.77 (dtd, J = 10.7, 7.0, 0.7 Hz, 1H), 6.95 (t, J = 4.8 Hz, 2H), 8.49 (d, J = 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 11.74 (d), 14.15 (d), 21.23 (u), 28.47 (u), 44.15 (d), 116.28 (d), 128.50 (d), 134.49 (d), 157.06 (d), 172.51 (u); MS (EI): *m/z*: 208 (10) [M^+], 175 (22), 165 (42), 113 (42), 112 (10), 97 (11), 96 (24), 81 (32), 79 (13), 67 (13), 55 (100), 53 (16); IR (capillary): $\tilde{\nu}$ = 3306 (w), 2965 (s), 2932 (m), 2873 (m), 1565 (s), 1547 (s), 1461 (m), 1426 (w), 1382 (s), 1188 (s), 798 (m), 774 (m), 749 (m), 631 cm^{-1} (w).

2-((*R*,*E*)-1-Methyl-but-2-enylsulfanyl)-pyridine (6ab): Following GP3, a mixture of carbonate *rac*-**3aa** (173 mg, 1.2 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (51.8 mg, 0.05 mmol), **BPA** (75.9 mg, 0.11 mmol) and nBu$_4$NF (31.5 mg, 0.098 mmol) in CH_2Cl_2 (2.5 mL) was treated with 2-pyridinethiol (111 mg, 1 mmol) in CH_2Cl_2 (2.5 mL). After 2 d the reaction was stopped. Purification by flash chromatography (hexane/EtOAc 40:1) gave sulfide **6ab** (157 mg, 87%) of 68% *ee* [GC, Lipodex E, t_R (**6ab**) = 60.72 min, t_R (*ent*-**6ab**) = 60.33 min] and a *E*/*Z* ratio of 15:1 (^{1}H NMR) as a colorless oil: $[\alpha]_D^{20} = +100.0$ (c = 2.52, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.47 (d, J = 6.7 Hz, 3H), 1.66 (d, J = 6.7 Hz, 3H), 4.46 (quin, J = 6.8 Hz, 1H), 5.59 (dd, J = 15.5, 7 Hz, 1H), 5.66 (dq, J = 15.5, 5.8 Hz, 1H), 6.97 (ddd, J = 7.3, 4.7, 1.0 Hz, 1H), 7.16 (d, J = 8.1 Hz, 1H), 7.46 (td, J = 7.4, 2.0 Hz, 1H), 8.43 (dm, J = 4.7 Hz, 1H), ^{13}C NMR(75 MHz, $CDCl_3$): δ = 17.7 (d), 20.7 (d), 41.4 (d), 119.5 (d), 123.1 (d), 126.0 (d), 132.3 (d), 135.8 (d), 149.4 (d), 159.8 (u); IR (capillary): $\tilde{\nu}$ = 3067 (w), 3044 (w), 3025 (w), 2964 (m), 2920 (m), 2866 (w), 1578 (s), 1556 (s), 1452 (s), 1414 (s), 1377 (w), 1280 (w), 1148 (m), 1124 (s), 1088 (w), 1044 (m), 1017 (m), 985 (m), 964 (m), 758 (s), 725 (m), 620 (w), 481 cm^{-1} (w); GC-MS (EI): *m/z* (%): 179 (9) [M^+], 151 (10), 150 (100), 146 (30), 131 (14), 112 (19), 11 (43), 83 (12), 78 (23), 69 (58), 68 (12), 67 (51), 53 (13), 52 (10), 51 (22); elemental analysis calcd (%) for $C_{10}H_{13}NS$:C 67.00, H 7.32, N 7.81; found: C 66.96, H 7.40, N 8.04.

2-((*R*,*E*)-1-Ethyl-pent-2-enylsulfanyl)-pyridine (6bb): Following GP3, a mixture of carbonate *rac*-**3ba** (207 mg, 1.2 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (51.8 mg, 0.05 mmol) and **BPA** (69.0 mg, 0.10 mmol) in CH_2Cl_2 (2.5 mL) was treated with 2-pyridinethiol (112 mg, 1 mmol) in CH_2Cl_2 (2.5 mL). After 3 d the reaction was stopped. Purification by flash chromatography

(hexane/EtOAc 40:1) gave sulfide **6bb** (50 mg, 24%) of 50% *ee* [GC, Lipodex γ, t_R (**6bb**) = 67.22 min, t_R (*ent*-**6bb**) = 66.97 min] and a *E*/*Z* ratio of 16:1 (GC): $[\alpha]_D^{20} = +88.8$ ($c = 1.26$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.90$ (t, $J = 7.5$ Hz, 3H), 1.01 (t, $J = 7.5$ Hz, 3H), 1.72 (dquin, $J = 21.3$, 7.6 Hz, 1H), 1.78–1.87 (m, 1H), 1.95–2.02 (m, 2H), 4.22 (td, $J = 8.3$, 5.8 Hz, 1H), 5.39 (ddt, $J = 15.3$, 8.5, 1.5 Hz, 1H), 5.65 (dt, $J = 15.3$, 6.4 Hz, 1H), 6.97 (ddd, $J = 7.3$, 4.9, 1.1 Hz, 1H), 7.17 (dm, $J = 8.2$ Hz, 1H), 7.47 (dt, $J = 7.7$, 1.9 Hz, 1H), 8.44 (dm, $J = 4.9$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 11.8$ (d), 13.6 (d), 25.4 (u), 27.9 (u), 48.9 (d), 119.6 (d), 123.6 (d), 128.8 (d), 134.3 (d), 135.8 (d), 149.3 (d), 159.0 (u); IR (neat): $\tilde{\nu} = 3029$ (w), 2963 (s), 2931 (s), 2872 (m), 1564 (s), 1546 (s), 1459 (m), 1425 (w), 1381 (s), 1254 (w), 1187 (s), 964 (m), 797 (m), 774 (s), 749 (m), 630 cm^{-1} (m); MS (EI): *m*/*z* (%): 207 (14) [M^+], 192 (16), 178 (12), 174 (28), 164 (79), 112 (43), 111 (42), 97 (16), 96 (23), 83 (12), 81 (41), 79 (13), 78 (31), 74 (36), 73 (13), 67 (33), 61 (33), 59 (46), 55 (100), 53 (10), 51 (11), 45 (41); elemental analysis calcd (%) for $C_{12}H_{17}NS$: C 69.52, H 8.26, N 6.776; found: C 69.59, H 8.34, N 6.97.

1-Chloro-4-((*R*,*E*)-1-methyl-but-2-enylsulfanyl)-benzene (6ac): Following GP3, a mixture of carbonate *rac*-**3aa** (144 mg, 1 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (51.8 mg, 0.05 mmol) and **BPA** (90 mg, 0.13 mmol) in CH_2Cl_2 (2.5 mL) was treated with 4-chlorothiophenol (188 mg, 1.3 mmol) in CH_2Cl_2 (2.5 mL). After 2 d the reaction was stopped. Purification by flash chromatography (hexane/EtOAc 40:1) gave sulfide **15c** (155 mg, 73%) of 90% *ee* [GC, Lipodex γ, t_R (**6ac**) = 49.62 min, t_R (*ent*-**6ac**) = 49.44 min] and a *E*/*Z* ratio of 10:1 (^{1}H NMR) as a colorless oil: $[\alpha]_D^{20} = +35.7$ ($c = 1.45$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.34$ (d, $J = 7.0$ Hz, 3H), 1.61 (d, $J = 5.3$ Hz, 3H), 3.68 (quin, $J = 6.7$ Hz, 1H), 5.28–5.46 (m, 2H), 7.22–7.37 (m, 4H); ^{13}C NMR(75 MHz, $CDCl_3$): $\delta = 17.6$ (d), 20.6 (d), 46.2 (d), 126.3 (d), 128.7 (d), 132.5 (d), 133.1 (u), 133.6 (u), 134.2 (d); IR ($CHCl_3$): $\tilde{\nu} = 3023$ (w), 2970 (m), 2922 (m), 2866 (w), 1573 (w), 1476 (s), 1448 (s), 1389 (m), 1377 (m), 1261 (w), 1201 (m), 1095 (s), 1044 (w), 1013 (s), 963 (s), 821 (s), 746 (m), 554 (m), 502 cm^{-1} (m); MS (CI): *m*/*z* (%): 215 (^{37}Cl) (35) [M^++H], 214 (^{37}Cl) (19) [M^+], 213 (^{35}Cl) (100) [M^++H], 212 (^{35}Cl) (18) [M^+], 201 (22); elemental analysis calcd (%) for $C_{11}H_{13}ClS$: C 62.11, H 6.16; found: C 61.89, H 6.21.

(*R*)-Cyclohex-2-en-1-ol (9a): NaOH (5 g, 0.125 mol) in water (25 mL) was added to a solution of carbonate *ent*-**1a** (350 mg, 2.24 mmol) of ≥99% *ee* in MeOH (2 mL). The mixture was stirred at room temperature for 4 d after which time TLC indicated the complete consumption of the carbonate. The mixture was extracted with diethyl ether and the combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Chromatography (pentane/diethyl ether 7:1) afforded alcohol **9a** (143 mg, 65%) of ≥99% *ee* [GC, Lipodex E, t_R (**9a**) = 26.58 min, t_R (*ent*-**9a**) = 25.57 min] as a colorless oil: $[\alpha]_D^{20} = +110.8$ ($c = 1.20$, CH_2Cl_2).

(*R*)-Cyclohept-2-en-1-ol (9b): NaOH (10 g, 0.25 mol) in water (50 mL) was added to a solution of carbonate *ent*-**1b** (200 mg, 1.17 mmol) of ≥ 99% *ee* in MeOH (3 mL). The mixture was stirred at room temperature for 4 d after which time TLC indicated the complete consumption of the carbonate. The mixture was extracted with diethyl ether and the combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Chromatography (pentane/diethyl ether 7:1) afforded alcohol **9b** (126 mg, 94%) of ≥99% *ee* [GC, Lipodex γ, t_R (**7b**) = 12.36 min; Lipodex γ, t_R (**9b**) = 13.95 min, t_R (*ent*-**9b**) = 14.06 min] as a colorless oil: $[\alpha]_D^{20} = +28.2$ ($c = 1.03$, CH_2Cl_2).

(*R*)-Cyclooct-2-en-1-ol (9c): NaOH (10 g, 0.25 mol) in water (50 mL) was added to a solution of carbonate *ent*-**1c** (600 mg, 3.25 mmol) of ≥99% *ee* in MeOH (3 mL). The mixture was stirred at room temperature for 4 d after which time TLC indicated the complete consumption of the carbonate. The mixture was extracted with diethyl ether and the combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Chromatography (pentane/diethyl ether 7:1) afforded alcohol **9c** (308 mg, 75%) of ≥99% *ee* [GC, Lipodex-γ, t_R (**9c**) = 11.36 min; GC, Lipodex E: t_R (**9c**) = 8.44 min, GC, Lipodex-γ, t_R (**9c**) = 11.47 min, t_R (*ent*-**9c**) = 12.04 min] as a colorless oil: $[\alpha]_D^{20} = -52.4$ ($c = 1.46$, CH_2Cl_2).

(*S*,*E*)-Pent-3-en-2-ol (10a): NaOH (600 mg, 0.015 mol) in water (6 mL) was added to a solution of carbonate *ent*-**3aa** (288 mg, 2 mmol) of ≥99% *ee*. The mixture was stirred at room temperature for 2 d after which time TLC indicated the complete consumption of the carbonate. The mixture was extracted with diethyl ether and the combined organic phases were dried ($MgSO_4$). Concentration of the organic phase in vacuo afforded alcohol **10a** (155 mg, 90%) of ≥99% *ee* [GC, Lipodex E, t_R (**10a**) = 3.47 min] as a colorless oil: $[\alpha]_D^{20} = -18.57$ ($c = 1.05$, CH_2Cl_2).

(*S*,*E*)-Hept-4-en-3-ol (10b): NaOH (600 mg, 0.015 mol) in water (6 mL) was added to a solution of carbonate *ent*-**3ba** (344 mg, 2 mmol) of 99% *ee*. The mixture was stirred at room temperature for 4 d after which time TLC indicated the complete consumption of the carbonate. The mixture was extracted with diethyl ether and the combined organic phases were dried ($MgSO_4$). Concentration of the organic phase in vacuo and afforded alcohol **10b** (214 mg, 94%) of 99% *ee* [GC, Hydrodex-β-6-TBDM, t_R (**10b**) = 26.93 min, t_R (*ent*-**10b**) = 27.16 min] as a colorless oil: $[\alpha]_D^{20} = +4.04$ ($c = 0.99$, CH_2Cl_2).

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[2] While resolution by classical methods and by chromatography generally gives access to both enantiomers, kinetic resolution yields one enantiomer of the starting material and a product which may or may not be readily convertible to the other enantiomer of the starting material. Illustrative examples for the later aspect are the hydrolase catalyzed resolution of the acetates of racemic alcohols giving a mixture of the alcohol and the acetate[1q] and the transition metal catalyzed oxidative resolution of benzylic alcohols yielding a mixture of the alcohol and the ketone.[1n]

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[4] a) Although Scheme 1 shows only symmetrically substituted acyclic substrates, it is in priciple also valid for symmetrically substituted cyclic and for unsymmetrically substituted substrates. Scheme 1 is a simplified representation of the palladium-catalyzed allylic substitution because of the omission of the *syn*,*syn*- and *anti*,*syn*-isomerism of the π-allyl complexes as well as of the formation of contact ion pairs and the coordination of the leaving group or the nucleophile to the palladium atom with formation of neutral complexes; b) symmetri-

cally disubstituted allylic substrates are the most popular ones in palladium catalyzed allylic substitution because of the avoidance of otherwise difficult to control regioselectivity problems which generally arise with monosubstituted and unsymmetrically disubstituted substrates; c) complexes with **BPA** as ligand also do not exhibit C_2 symmetry (see text).

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