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Synthesis of Phosphanyl Sulfoximines Through Phospha-Michael Reaction of Alkenyl Sulfoximines and Their Evaluation as Chiral Bidentate 1,5-N,P Ligands for Palladium in Asymmetric Allylic Alkylation

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The intermolecular phospha-Michael reaction of cyclic and acyclic alkenyl sulfoximines proceeds readily and yields the corresponding phosphanyl sulfoximines in good yield. The asymmetric induction provided by sulfoximine group in C–P bond formation is apparently only low. The configuration of three phosphanyl sulfoximine–boranes has been determined by X-ray crystal structure analysis. The ability of the phosphanyl sulfoximines to act as ligand in Pd-catalyzed asymmetric allylic alkylation was studied with pairs of diastereomeric cyclic and acyclic derivatives carrying different substituents at the N atom. This study showed that the substituent at the N atom and both the chirality of the backbone and sulfoximine group play a crucial role in determining the enantioselectivity of the allylic alkylation. The Pd-catalyzed reaction of the racemic 1,3-diphenylallyl acetate with the malonate anion in the presence of a cyclic *N*-benzyl-substituted phosphanyl sulfoximine gives the corresponding malonate with 97 % *ee* in 98 % yield. The similar alkylation with dialkyl-substituted allylic acetates proceeds only with medium enantioselectivity. The bidentate 1,5-N,P-coordination of the Pd atom by the phosphanyl sulfoximine was confirmed by NMR experiments of a π-1,3-diphenylallyl-Pd^{II} complex containing a cyclohexyl phosphanyl sulfoximine as ligand. The cyclohexane ring of the free cyclic phosphanyl sulfoximines adopts in solution and in the crystal a conformation in which the sulfoximine and phosphanyl group are both in a pseudo axial position. The coordination of the ligand to the Pd atom causes an inversion of the cyclohexane ring, which places the two groups in equatorial position.

Introduction

The sulfonimidoyl group has gained a firm place as chiral auxiliary in asymmetric synthesis.[1,2] Its versatility stems from an almost unique combination of features including configurational stability, carbanion stabilization, nucleofugacity, nucleophilicity, Brønsted and Lewis basicity, and activation in *ortho*-lithiation. In recent years sulfoximines have found interest as chiral ligands in asymmetric transition metal catalysis.[3] Amongst the various sulfoximines which have been designed for transition metals[4] the aryl phosphanyl sulfoximine **I**[5] and alkyl phosphanyl sulfoximine **II**[6] (Figure 1)[7,8] showed considerable promise as 1,4-N,P ligands in Ir-catalyzed asymmetric hydrogenation[4n,4o,5] and Pd-catalyzed allylic alkylation.[5,6] We envisioned the synthesis and study of acyclic and cyclic phosphanyl sulfoximines of type **V** and **VI**, respectively, as potential ligands for transition metals. Phosphanyl sulfoximines **V** and **VI**, which have besides the chiral sulfoximine group also a chiral backbone, could serve as bidentate 1,5-N,P ligands for transition metals. The 1,4-N,P ligands **I** and **II** probably form chelates of type **III** and **IV**, respectively, which are expected to possess a relatively low S–N rotational barrier.[8b,8c] This provides conformational flexibility for the S(O)Ar(R) group being placed in close proximity to the metal atom. In contrast, the phosphanyl sulfoximines **V** and **VI** are in principle capable to give chelates of type **VII** and **VIII**, respectively, the S atom of which is part of the six-membered ring. Incorporation of the chiral sulfoximine group into the ring of **VII** and **VIII** could perhaps allow an efficient transmission of the effects exerted by the substituents of the backbone via the N- and P atom across the metal atom to its organic residues. In this context the nature of the group R^1, which is in close proximity to the metal atom, could be of special importance. While its steric size might be significant in the transmission of the substituent effects, its electronic nature will affect the Lewis basicity of the sulfoximine group.[1] Formation of N,P chelates of type **VII** and **VIII** and not O,P chelates should be preferred because of the higher propensity of the N atom of sulfoximines to bind Lewis and Brønsted acids.[1,8b] The variation of the substituents R^1, R^2 and R^3 of **V** and ring size of **VI** could provide a synthetic means to perhaps influence the performance of the ligand.[9] A large number of bidentate N,P ligands have been synthesized and successfully applied

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in asymmetric transition metal catalysis[9] and particularly in Pd-catalyzed allylic alkylation[10b,10d,11] However, N,P ligands of type **V** and **VI** carrying three consecutive stereogenic centers in the single bond[7] composed backbone connecting the N- and P atom are rare.[12] Previously, we had studied the potential of the Pd-catalyzed allylic alkylation in asymmetric C–S and C–O bond formation and kinetic resolution.[13] Therefore, we were primarily interested in the evaluation of phosphanyl sulfoximines of type **V** and **VI** as N,P ligands for the Pd atom. We envisioned a synthesis of phosphanyl sulfoximines **V** and **VI** through a phospha-Michael reaction (PMR) of the corresponding alkenyl sulfoximines with an alkali phosphide. While mainly intramolecular MRs of alkenyl sulfoximines with O-,[14] N-,[15] S-[16] and C-nucleophiles[17] are well documented, only one example of a intermolecular PMR of a vinyl sulfoximine had been described.[6] Therefore, the evaluation of the potential of the PMR for the synthesis of phosphanyl sulfoximines was of interest. In this paper we describe the synthesis of phosphanyl sulfoximines of type **V** and **VI** through PMR of alkenyl sulfoximines and their evaluation as ligands in Pd^0-catalyzed allylic alkylation[18] together with a NMR spectroscopic determination of the mode of their coordination to the Pd atom.

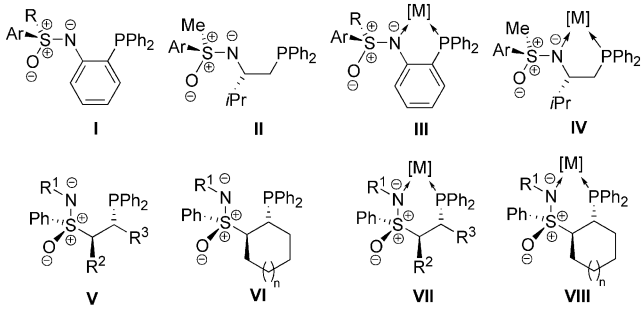
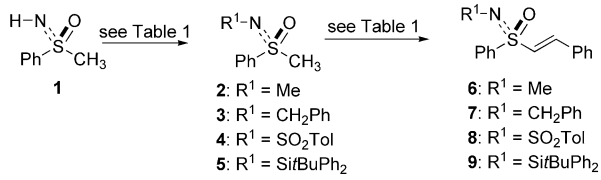


Figure 1. 1,4- and 1,5-N,P-Phosphanyl sulfoximines and their metal chelates.

Results and Discussion

Acyclic Alkenyl Sulfoximines

The substituent R^1 at the N atom of **V** and **VI** was expected to be of importance for the performance of the phosphanyl sulfoximines as ligands for the Pd atom. The ability of sulfoximines **V** and **VI** to function as a 1,5-N,P chelate ligand will strongly depend on the Lewis basicity of the N atom. While alkyl groups at the N atom enhance the Lewis basicity of the sulfoximine group, electron-withdrawing substituents have the opposite effect.[1] Steric effects exerted by the substituent at the N atom of **V** and **VI** could also influence their coordinating ability. Based on these considerations the methyl, benzyl, *p*-tolysulfonyl and *tert*-butyldiphenylsilyl group were selected as substituents at the N atom of the phosphanyl sulfoximines. The acyclic alkenyl sulfoximines **6**–**9** were prepared starting from the NH-sulfoximine **1** in two steps including a functionalization at the N atom followed by an addition/elimination sequence (Scheme 1, Table 1). Sulfoximine **1** in turn is readily available in enantiomerically pure form through an efficient resolution with 10-camphorsulfonic acid following the method of half-quantity.[19]



Scheme 1. Synthesis of the alkenyl sulfoximines **6**–**9** starting from sulfoximine **1**.

Table 1. Synthesis of the *N*-substituted *S*-methyl sulfoximines (MS) **2**–**5** and alkenyl sulfoximines (AS) **6**–**9**.

R^1	MS	Conditions	Yield (%)	AS	Yield (%)
Me	**2**	HCHO, HCO_2H, H_2SO_4, reflux, 3 d	93	**6**[a]	88
CH_2Ph	**3**	$PhCH_2Br$, KH, Bu_4NBr, DME, room temp., 1 h	90	**7**[a]	91
SO_2Tol	**4**	$TolSO_2Cl$, pyridine, room temp., 12 h	92	**8**[a]	92
Si*t*BuPh$_2$	**5**	*t*BuPh$_2$SiCl, ImH, DMF, 0 °C to room temp., 7 h	96	**9**[a]	85

[a] 1. *n*BuLi, THF, –78 °C; 2. PhCHO, –78 °C; 3. $ClCO_2Me$, –78 °C to room temp.; 4. DBU, –78 °C to room temp.

While the *N*-methyl sulfoximine **2** was prepared in 93% yield through Eschweiler–Clark methylation of **1**,[20] its benzylation using a slightly modification of the literature protocol afforded the *N*-benzyl sulfoximine **3**[21] in 90% yield. Tosylation of sulfoximine **1** with tosyl chloride in pyridine furnished the *N*-tolylsulfonyl sulfoximine **4**[22] in 92% yield, and silylation of **1** with *t*BuPh$_2$SiCl and imidazole in dimethylformamide (DMF) gave the *N*-silyl sulfoximine **5**[23] in 96% yield. The addition/elimination route[24,25] was selected of the various methods available for the synthesis of alkenyl sulfoximines,[1] because of its simplicity and high yield. The one pot procedure involved the lithiation of the *S*-methyl sulfoximines **2**–**5** with *n*BuLi and the treatment of the corresponding carbanions with benzaldehyde, which gave the corresponding alkoxides as mixtures of epimers.[23,26] The alkoxides were not isolated but treated with $ClCO_2Me$, which afforded the corresponding carbonates. Treatment of the carbonates without prior isolation with 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) furnished the corresponding alkenyl sulfoximines **6**–**9** as *E*-isomers in 85–92% yield.[27,28]

Cycloalkenyl Sulfoximines

A synthesis of cycloalkenyl sulfoximines of type **IX** (Figure 2) was not available at the beginning of our investigation. Two approaches to sulfoximines **IX** were envisioned. Route A features the construction of the carbocycle of **IX**

through a cycloalkylation of the *S*-methyl sulfoximine **XII** with dihalide **XIII** to yield sulfoximine **XI**.[29] Halogenation of **XI** with formation of halide **X**[30] and its subsequent elimination could afford the alkenyl sulfoximine **IX**. While the α-halogenation of sulfoximines had been described, nothing was known, however, about the feasibility of an elimination of α-halo sulfoximines with formation of the corresponding alkenyl sulfoximines. Route B encompasses the synthesis of the ω-chloro(bromo)alkenyl sulfoximine **XV** by the addition/elimination route from sulfoximine **XII** and the ω-halo aldehyde **XVI**. Lithiation of **XV** and cyclization of the α-lithioalkenyl sulfoximine **XIV** could afford **IX**.[31] Following route A, cycloalkylation of sulfoximine **2** upon the successive reaction with 1.2 equiv. of *n*BuLi and 1.2 equiv. of 1,5-dibromopentane gave the cyclohexyl sulfoximine **10** in 50% yield together with 50% of the starting sulfoximine **2** (Scheme 2).[29,30] The successive treatment of sulfoximine **10** with 1.2 equiv. of *n*BuLi and 2 equiv. of 1,2-dibromo-1,1,2,2-tetrachloroethane afforded an inseparable 55:45 mixture of the α-chloro and α-bromo sulfoximines **11** and **12**, respectively, in 91% total yield. The mixture of **11** and **12** was then subjected to a treatment with *t*BuOK in THF. Unfortunately, this gave only traces of the desired alkenyl sulfoximine. Instead, sulfinamide **13** and the cyclohexyl sulfoximine **10** were isolated as the major products. Formation of the sulfinamide and the cyclohexyl sulfoximine can be ascribed to an elimination of **11** and **12** with formation of 1-chloro(bromo)cyclohexene (not isolated) and a halophilic reaction,[32] respectively.

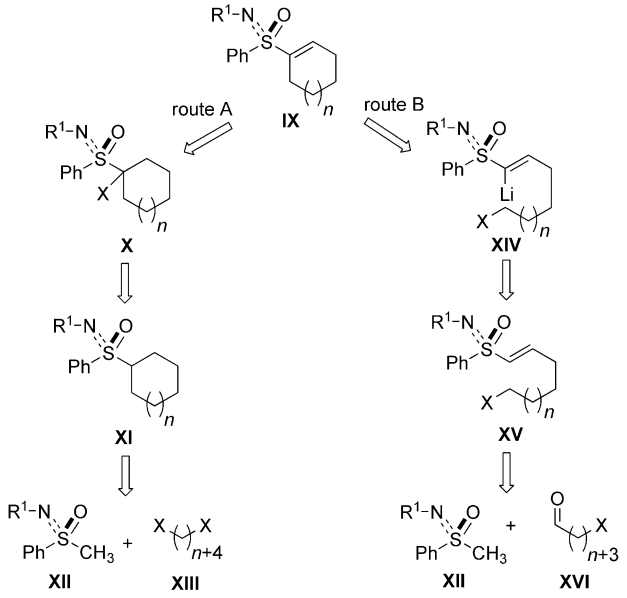
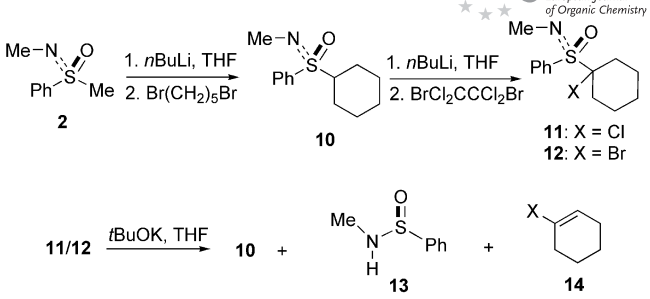
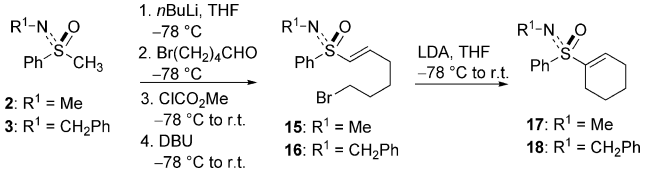


Figure 2. Retrosynthesis of the cycloalkenyl sulfoximines.

Following the alternative route B, sulfoximines **2** and **3** were successively treated with *n*BuLi, 5-bromopentanal, $ClCO_2Me$ and DBU, which afforded the corresponding 6-bromoalkenyl sulfoximines **15** and **16** in 83% and 77% yield, respectively (Scheme 3). Reaction of the 6-bromoalkenyl sulfoximines **15** and **16** with 1 equiv. of LDA[33] furnished the corresponding cycloalkenyl sulfoximines **17** and **18** in 80% and 92% yield, respectively.



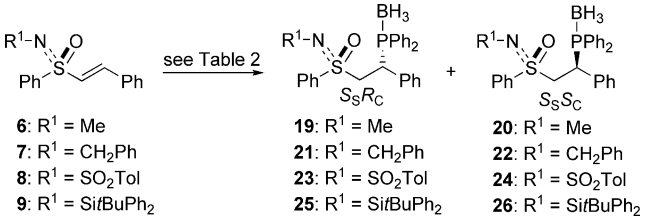
Scheme 2. Attempted synthesis of a cycloalkenyl sulfoximine through α-halogenation and elimination.



Scheme 3. Synthesis of the cycloalkenyl sulfoximines through α-lithiation and cyclization of the 6-bromoalkenyl sulfoximines.

PMR of Alkenyl Sulfoximines

Having the desired alkenyl and cycloalkenyl sulfoximines in hand, their PMR was investigated. The treatment of the alkenyl sulfoximine **6** with 1.1 equiv. of $KPPh_2$ at –78 °C in THF and the subsequent successive addition of 2 equiv. of MeOH, 2.2 equiv. of BH_3·THF and HCl (method A) gave the phosphane–borane **19** as a single diastereomer in but only 18% yield (Scheme 4, Table 2, entry 1). Better yields were obtained by using $HPPh_2$ and 10 mol-% of *t*BuOK (method B). The alkenyl sulfoximine **6** furnished under these conditions a mixture of the diastereomeric phosphane–boranes **19** and **20** in a ratio of 78:22 in 78% yield (entry 2). The alkenyl sulfoximines **7**–**9** afforded under the same conditions the corresponding phosphane–boranes **21**–**26** in good yields as mixtures of diastereomers (entries 3–5). The diastereomeric phosphane–boranes were separated by crystallization and/or chromatography. The absolute configuration of phosphane–boranes *ent*-**20**[34] and **25** was determined by X-ray crystal structure analysis (see below). Characteristic shift differences of the signals of the Ph group at the stereogenic C atom were observed in the ^1H



Scheme 4. PMR of the alkenyl sulfoximines **6**–**9**.

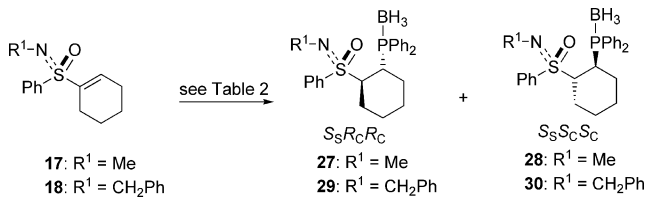
NMR spectra of the S_SR_C- and S_SS_C-configured phosphane–boranes, which allowed a configurational assignment of **19**–**24**.

Table 2. PMR of the alkenyl sulfoximines **6**–**9** and cycloalkenyl sulfoximines **17** and **18**.

Entry	Starting material	R^1	Method[a]	Phosphanyl sulfoximine	*dr*[b]	Yield (%)
1	**6**	Me	A	**19**, **20**	≥ 98:2	18, 0
2	**6**	Me	B	**19**, **20**	78:22	61, 17
3	**7**	CH_2Ph	B	**21**, **22**	64:36	53, 25
4	**8**	SO_2Tol	B	**23**, **24**	27:73	18, 51
5	**9**	$SitBuPh_2$	B	**25**, **26**	58:42	40, 32
6	**17**	Me	B	**27**, **28**	50:50	35, 46
7	**18**	CH_2Ph	B	**29**, **30**	50:50	41, 39
8	**18**	CH_2Ph	C	**29**, **30**	25:75	[c]

[a] A: *i*. 1.1 equiv. $KPPh_2$, –78 °C, 30 min. *ii*. 2 equiv. MeOH, –78 °C, 2 h. *iii* BH_3·THF, 0 °C, 2 h. *iv*. 1 N HCl until pH 5 was reached. B: 1.1 equiv. $HPPh_2$, 0.1 equiv. *t*BuOK, room temp., 1–2 h. *ii*. 2.2 equiv. BH_3·THF, 0 °C, 1 h. *iii*. 1 N HCl until pH 5. C: 2 equiv. $HPPh_2$, 1.9 equiv. *n*BuLi, –78 °C, 1 h. *ii*. 1.9 equiv. (±)-10-camphorsulfonic acid, –78 °C. *iii*. 2.2 equiv. BH_3·THF, 0 °C. *iv*. 1 N HCl until pH 5 was reached. [b] The ratio S_SR_C/S_SS_C and $S_SR_CR_C/S_SS_CS_C$ was determined by chiral HPLC (see Exp. Sect.) or ^1H NMR spectroscopy. [c] Not determined.

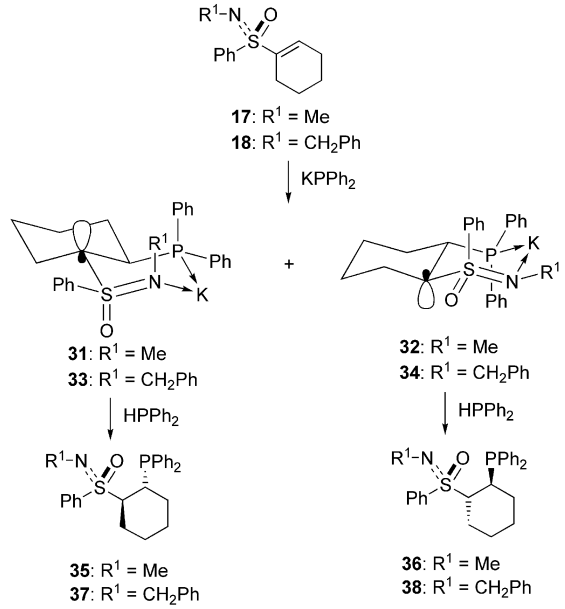
Gratifyingly, the cycloalkenyl sulfoximine **17** also underwent a PMR upon the treatment with $HPPh_2$ and *t*BuOK (Scheme 5, entry 6) and gave the two *trans*-configured diastereomeric phosphane–boranes **27** and **28** in a ratio of 50:50 (^1H NMR) in 35% and 46% yield, respectively, after separation by chromatography. The similar PMR of the benzyl-substituted cycloalkenyl sulfoximine **18** with $HPPh_2$ according to method B afforded a 50:50 mixture of the diastereomeric phosphane–boranes **29** and **30** (entry 7). Separation by chromatography gave **29** and **30** in 41% and 39% yield, respectively. The reaction of **18** with $LiPPh_2$ at low temperature according to method C, which included the use of 2 equiv. of $HPPh_2$ and 1.9 equiv. of *n*BuLi, furnished the phosphane–boranes **29** and **30** in a ratio of 25:75 (entry 8). In no experiment with **17** and **18** was the formation of the other two possible diastereomers observed. The absolute configuration of the $S_SR_CR_C$-configured phosphane–borane **29** was determined by X-ray crystal structure analysis (see below). The configuration of the phosphane–boranes **21**–**24** was assigned based on characteristic ^1H NMR shift differences between the $S_SR_CR_C$- and $S_SS_CS_C$-configured diastereomers (see below).



Scheme 5. PMR of the cycloalkenyl sulfoximines **17** and **18**.

The sulfonimidoyl group of the alkenyl sulfoximines apparently exerts, irrespective of its N-substituent, only a low degree of asymmetric induction in the addition of $MPPh_2$ to the double bond. However, it cannot be excluded that C–P bond formation was reversible under the conditions applied and the PMR was thus under thermodynamic control. While the nearly unselective formation of the phosphanyl sulfoximines was unsatisfying in synthetic terms, it provided a most welcome tool to study the influence of the configuration of the sterogenic centers upon the asymmetric induction in allylic alkylation (see below).

The highly selective formation of the *trans*-configured cyclic phosphanyl sulfoximines **35**–**38** in the reaction of the corresponding cycloalkenyl sulfoximines with $HPPh_2$ according to method B can be rationalized as follows. The addition of $KPPh_2$ to the double bond of **17** and **18** is unselective giving the potassium α-sulfonimidoyl carbanion salts **31** and **33** and their diastereomers **32** and **34**, respectively (Scheme 6). Based on the current knowledge of the structure of α-sulfonimidoyl carbanion salts,[35] the potassium salts are expected to adopt a structure which is characterized by (1) a pyramidalized anionic C atom, (2) the lack of a C–K bond and (3) a six-membered ring, in which the K atom is coordinated by the P and N atom. Because of steric effects, the bicyclic ring system with the bridgehead anionic C atom adopts the *trans*-configuration. Protonation of carbanions **31**–**34** should occur preferentially from the direction of the pyramidalization giving the corresponding *trans*-configured phosphanyl sulfoximines **35**–**38**.



Scheme 6. Stereochemical course of the PMR of the cycloalkenyl sulfoximines **17** and **18** (coordination of the K atom by THF not shown).

X-ray Crystal Structure Analysis of Phosphanyl Sulfoximine–Boranes

The absolute configuration of the phosphane–boranes *ent*-**20**, **25** and **29** was determined by X-ray crystal structure

analysis.[36] The acyclic phosphanyl *N*-methyl sulfoximine–borane **20** (Figure 3) and phosphanyl *N*-silyl sulfoximine–borane **25** (Figure 4) adopt in the crystal almost an *anti* conformation at the C_a–C_b bond as revealed by S–C_a–C_b–P dihedral angles of 165.4° and 145.7°, respectively. In the crystal, the six-membered ring of the cyclic phosphanyl *N*-benzyl sulfoximine–borane **29** has a distorted chair-like conformation, in which the sulfoximine and the phosphanyl group adopt a pseudo axial position (Figure 5). The S–C_a–C_b–P and H_a–C_a–C_b–H_b dihedral angles are 140.7° and 82°, respectively. The sulfoximine group of **29** adopts a C_a-S conformation in the crystal, in which the smaller O atom points towards the cyclohexane ring and the larger phenyl- and *N*-benzyl group are orientated in the opposite direction.

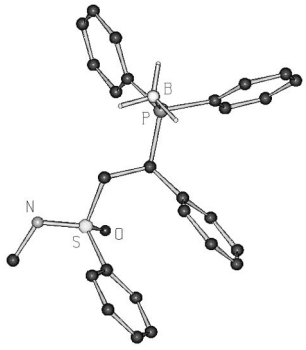


Figure 3. Structure of the acyclic phosphanyl *N*-methyl sulfoximine–borane *ent*-**20** in the crystal. Selected bond lengths: S–O 1.455(2), S–N 1.521(4), C–S 1.797(4), P–B 1.923(3), C–P 1.853(5).

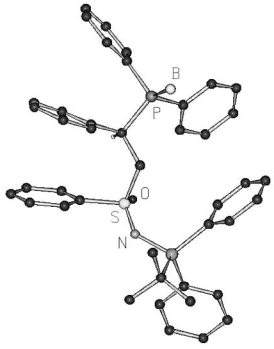


Figure 4. Structure of the acyclic phosphanyl *N*-silyl sulfoximine–borane **25** in the crystal. Selected bond lengths: S–O 1.453(4), S–N 1.489(4), C–S 1.796(5), P–B 1.913(5), C–P 1.858(4).

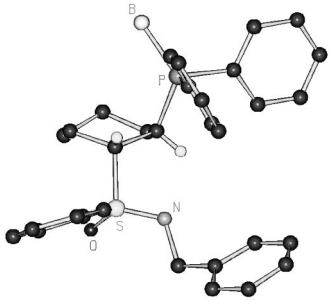
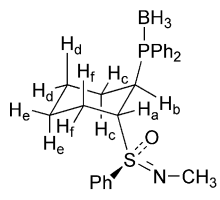


Figure 5. Structure of the cyclic phosphanyl *N*-benzyl sulfoximine–borane **29** in the crystal. Selected bond lengths: S–O 1.434(4), S–N 1.492(4), C–S 1.830(5), P–B 1.927(6), C–P 1.841(4).

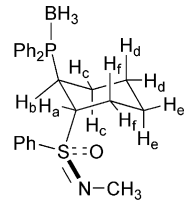
NMR Spectroscopy of Cyclic Phosphane–Boranes

It was of interest to see whether the cyclohexane ring of the cyclic phosphane–boranes **27**–**30** adopts in solution a similar conformation as the one of the phosphane–borane **29** in the crystal. A bidentate coordination of the Pd atom by the phosphanyl sulfoximines **35**–**38** would require an inversion of the chair-like conformation of the cyclohexane ring, bringing the phosphanyl and sulfoximine group in a pseudo equatorial position. Thus, NMR spectroscopy of the free ligands **35**–**38** and their Pd^0 or Pd^{II} allyl complexes could provide a means to prove a 1,5-N,P chelation of the Pd atom. The ^{1}H NMR spectra of **27**–**30** showed no measurable coupling between H_a and H_b and the COESY spectra revealed the absence of a correlation peak between both H atoms. A NOE was observed between H_a and H_b of the phosphane–boranes **27** and **28** (**29** and **30** were not investigated). Both signals of H_a and H_b of the phosphane–boranes **27**–**30** appeared as a doublet of doublet and both showed a coupling with the P atom and the neighboring protons H_{fax} and H_{cax}, respectively. The couplings $^3J(H_a,H_{feq})$ and $^3J(H_b,H_{ceq})$ were not observed, which are therefore smaller than 2 Hz. The *J* values of **27** and **28** are shown in Figure 6. These results are in accordance with a dihedral angle between H_a and H_b of approximately 80°. Thus, the phosphanyl sulfoximines **27**–**30** adopt in solution a similar conformation as **29** in the crystal, in which both the sulfoximine and phosphanyl group are in a pseudo axial position and the S–C_a–C_b–P dihydral angle is approximately 140°.



27

$^3J(H_a,H_b)$ < 2 Hz
$^3J(H_b,H_{ceq})$ < 2 Hz
$^3J(H_a,H_{feq})$ < 2 Hz
$^3J(H_a,H_{fax})$ = 5.5 Hz
$^3J(H_b,H_{cax})$ = 6.0 Hz
$^2J(P,H_b)$ = 19.5 Hz
$^3J(P,H_a)$ = 13.7 Hz



28

$^3J(H_a,H_b)$ < 2 Hz
$^3J(H_b,H_{ceq})$ < 2 Hz
$^3J(H_a,H_{feq})$ < 2 Hz
$^3J(H_a,H_{fax})$ = 5.1 Hz
$^3J(H_b,H_{cax})$ = 6.7 Hz
$^2J(P,H_b)$ = 19.0 Hz
$^3J(P,H_a)$ = 13.7 Hz

Figure 6. Coupling constants of the cyclic phosphane–boranes **27** and **28**.

A major difference was observed between the ^{1}H NMR spectra of the $S_SR_CR_C$-configured phosphane–boranes **27** and **29** and those of the corresponding $S_SS_CS_C$-configured phosphane–boranes **28** and **30**. In the case of the $S_SR_CR_C$-configured phosphane–boranes **27** and **29**, the signal of H_b appeared at δ = 4.57 ppm and 4.70 ppm, respectively, which is close to the average value found for the acyclic phos-

phane–boranes (δ =4.5 ppm). In contrast, the signal of H_b of the $S_SS_CS_C$-configured phosphane–boranes **28** and **30** appeared at δ = 3.53 ppm and 3.70 ppm, respectively. In addition, the signal of H_{feq} of the $S_SR_CR_C$-configured sulfoximines **27** and **29** experienced a high-field shift of 0.73 ppm and 0.79 ppm, respectively, relative to those of **28** and **30**. The high-field displacements of the signal of H_b of **28** and **30** and that of H_{feq} of **27** and **29** are most likely due to the anisotropic effect of the phenyl group at the S atom. Sulfoximines **27**–**30** adopt a C_a-S conformation in which the smallest substituent, the O atom, points below the cyclohexane ring because of a minimization of steric interaction (Figure 7 and cf. Figure 5). While the phenyl group of the $S_SS_CS_C$-configured sulfoximines **28** and **30** points towards H_b, that of the $S_SR_CR_C$-configured sulfoximines **27** and **29** points towards H_{feq}.

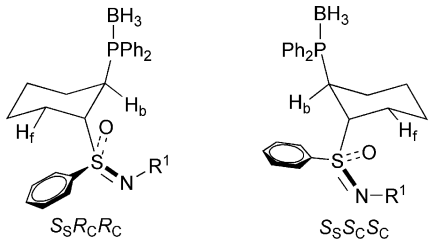
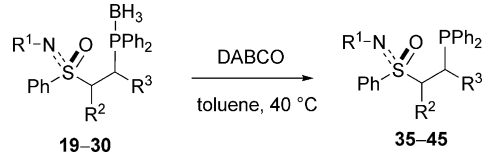


Figure 7. C_a-S Conformation of the sulfoximine group of the cyclic phosphane–boranes **27**–**30**.

Deboronation of Phosphane–Boranes

The free acyclic and cyclic phosphanyl sulfoximines **39**–**45** and **35**–**38**, respectively, were obtained through treatment of the corresponding phosphane–boranes **19**–**26** and **27**–**30** with 1.05 equiv. of 1,4-diazabicyclo[2.2.2]octane (DABCO) in dry degassed toluene at 40 °C (Table 3).

Table 3. Deboronation of phosphane–boranes **19**–**30** with formation of the corresponding phosphanyl sulfoximines **39**–**45** and **35**–**38**.

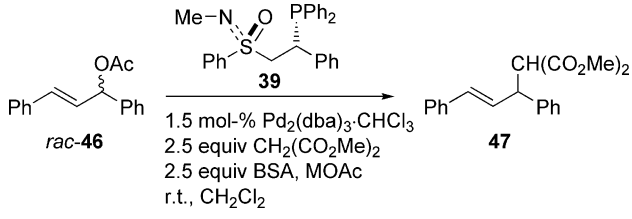


Phosphane–borane	Phosphanyl sulfoximine	R^1	R^2	R^3	Config.	Yield (%)
19	**39**	Me	H	Ph	S_SR_C	96
20	**40**	Me	H	Ph	S_SS_C	94
21	**41**	CH_2Ph	H	Ph	S_SR_C	98
22	**42**	CH_2Ph	H	Ph	S_SS_C	94
23	**43**	SO_2Tol	H	Ph	S_SR_C	94
25	**44**	Si*t*BuPh$_2$	H	Ph	S_SR_C	92
26	**45**	Si*t*BuPh$_2$	H	Ph	S_SS_C	93
27	**35**	Me	–(CH$_2$)$_4$–		$S_SR_CR_C$	97
28	**36**	Me	–(CH$_2$)$_4$–		$S_SS_CS_C$	91
29	**37**	CH_2Ph	–(CH$_2$)$_4$–		$S_SR_CR_C$	97
30	**38**	CH_2Ph	–(CH$_2$)$_4$–		$S_SS_CS_C$	93

Deboronation of the acyclic phosphane–boranes **19**–**26** was slower (2 h) than that of the cyclic phosphane–boranes **27**–**30** (1 h). The progress of the deboronation was monitored by ^{31}P NMR spectroscopy. The corresponding phosphanes **35**–**45** were isolated in high yield by filtration of the crude reaction mixture through a plug of silica gel and removal of the solvent in vacuo. Phosphanes **35**–**45** are sensitive towards dioxygen.

Palladium-Catalyzed Allylic Alkylation with Phosphanyl Sulfoximines as Ligands

The acyclic phosphanyl sulfoximines **39**–**44** and the cyclic phosphanyl sulfoximines **35**–**38** were tested as ligands in the Pd^0-catalyzed asymmetric allylic alkylation of racemic 1,3-diphenylallyl acetate *rac*-**46** by using 1.5 mol-% of $Pd_2(dba)_3$·$CHCl_3$ and 3 mol-% of the ligand. Acetate *rac*-**46** was selected because of its general use as standard for the evaluation of ligands for the Pd atom.[10,11] The dimethyl malonate anion served as nucleophile, which was generated by using the combination of dimethyl malonate, bis(trimethylsilyl)acetamide (BSA) and a catalytic amount of MOAc.[37] The Pd^0·phosphanyl sulfoximine complexes were prepared by heating the corresponding phosphanyl sulfoximines and $Pd_2(dba)_3$·$CHCl_3$ at 40 °C for 2 h. In preliminary experiments the S_SR_C-configured phosphanyl-*N*-methylsulfoximine **39** was used as ligand. The variation of the ligand-to-palladium ratio affected the yield as well as the *ee* value of malonate (*R*)-**47** (Scheme 7, Table 4, entries 1–3). At a ligand-to-palladium ratio of 1:1 malonate (*R*)-**47** was isolated in 40% yield with 63% *ee* (entry 3). While an increase of the ratio led to a much higher yield of malonate (*R*)-**47**, its *ee* value dramatically decreased (entry 2). At a ligand-to-palladium ratio of 0.66:1 malonate (*R*)-**47** was isolated in only 12% yield but with an *ee* value of 61% (entry 1). A full conversion of acetate *rac*-**46** was achieved by using Li^+ instead of K^+ as counterion (entry 5). The use of the NBu_4^+ as counterion resulted in a lower enantioselectivity of the alkylation (entry 4).



Scheme 7. Pd-catalyzed allylic alkylation of acetate *rac*-**46** with phosphanyl sulfoximine **39** as ligand.

The pronounced dependency of the enantioselectivity and yield on the ligand-to-metal ratio can be rationalized by a mechanistic scheme which was previously proposed in order to explain similar ligand-to-palladium effects in the case of a phosphanyl-oxazoline ligand.[38] Accordingly, a

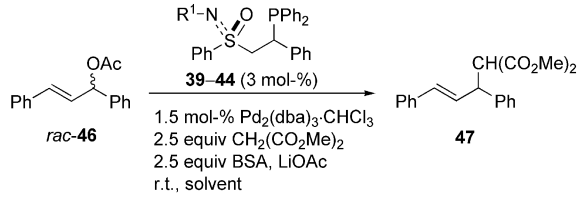
Table 4. Effect of the ligand to Pd^0 ratio and cation on the Pd-catalyzed allylic alkylation of acetate *rac*-**46** with phosphanyl sulfoximine **39** as ligand.

Entry	**39**/Pd^{0}[a]	M	**47**		
			Yield (%)	*ee*[b]	Config.[c]
1	0.66:1	K	12	61	*R*
2	2.2:1	K	96	46	*R*
3	1:1	K	40	63	*R*
4	1:1	NBu_4	54	43	*R*
5	1:1	Li	96	65	*R*

[a] 3 mol-% of Pd^0 was used. [b] The *ee* value of malonate **47** was determined by chiral HPLC. [c] The absolute configuration of malonate **47** was determined by comparison of the optical rotation with the literature value.

chelated π-allyl-Pd complex predominates at ligand-to-metal ratios of 1:1 or 0.66:1, which reacts with the nucleophile with medium enantioselectivity. At a ligand-to-metal ratio of 2.2:1 a second π-allyl-Pd complex with two molecules of **39** coordinated via the P atom to the Pd atom is formed in considerable amounts, which reacts faster but with lower enantioselectivity.

Interestingly, application of the diastereomeric S_SS_C-configured phosphanyl sulfoximine **40** as ligand gave the (*S*)-configured malonate (*S*)-**47** in 40% yield with only 10% *ee* (Scheme 8, Table 5, entry 2). This results shows that not only the stereogenic C atom but also the stereogenic S atom plays an important role in the enantioselectivity and activity of the catalyst. The N-substituent has also a significant effect on the selectivity of the catalyst. While the alkylation in the presence of the *N*-methyl-substituted phosphanyl sulfoximine **39** gave malonate (*R*)-**47** with 65% *ee*, that with the *N*-benzyl-substituted phosphanyl sulfoximine **41** gave (*R*)-**47** in almost quantitative yield with 82% *ee* (entries 1 and 3). The decrease of the reaction temperature to –1 °C led to a reduced conversion but higher enantioselectivity (entry 7). An increase of the catalyst loading had only a minor effect on the yield of malonate (*R*)-**47** (entry 8). The S_SS_C-configured *N*-benzyl-substituted phosphanyl sulfoximine **42** gave a more active catalyst as compared the S_SS_C-configured *N*-methyl ligand **40**. Here, malonate (*S*)-**47** was isolated in 72% yield with an *ee* value of 40% (entry 4). Table 5 reveals that there are matched and mismatched ligands as far as the configuration of the stereogenic centers is concerned. The S_CR_C-configured ligands **39** and **41** provided for a significantly higher degree of asymmetric induction than the corresponding diastereomers **40** and **42**. Interestingly, the *N*-tolylsulfonyl and *N*-silyl-substituted phosphanyl sulfoximines **43** and **44**, respectively, gave catalysts of much lower efficiency in terms of yield and enantioselectivity (entries 5 and 6) as compared to those containing the corresponding phosphanyl *N*-alkyl sulfoximines as ligands. This can be ascribed to a different mode of coordination of the Pd^0 atom by the two types of ligands. While the *N*-alkyl-substituted phosphanyl sulfoximines should have a strong Lewis basic N atom, the *N*-tolylsulfonyl and *N*-silyl-substituted phosphanyl sulfoximines should contain a weak Lewis basic N atom.[1] Hence, the former two phosphanyl sulfoximines will have a high and the later two only a low tendency to act as bidentate ligands for the Pd atom. A screening of several solvents showed CH_2Cl_2 to be the best one in terms of activity of the catalyst (entries 3, 9 and 10).



Scheme 8. Pd-catalyzed allylic alkylation of acetate *rac*-**46** with acyclic phosphanyl sulfoximines as ligand.

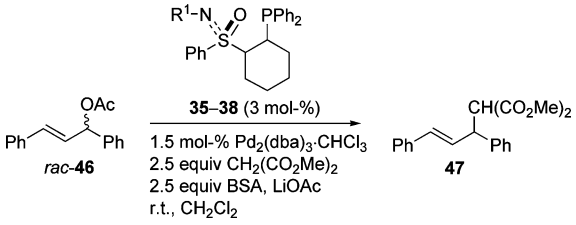
Table 5. Pd-catalyzed allylic alkylation of acetate *rac*-**46** under variation of the acyclic phosphanyl sulfoximine.

Entry	Ligand[a]	R^1	Config.	Solvent	**47**		
					Yield (%)	*ee*	Config.
1	**39**	Me	S_SR_C	CH_2Cl_2	96	65	*R*
2	**40**	Me	S_SS_C	CH_2Cl_2	40	10	*S*
3	**41**	CH_2Ph	S_SR_C	CH_2Cl_2	98	82	*R*
4	**42**	CH_2Ph	S_SS_C	CH_2Cl_2	72	40	*S*
5[b]	**43**	SO_2Tol	S_SR_C	CH_2Cl_2	17	5	*S*
6	**44**	Si*t*BuPh$_2$	S_SS_C	CH_2Cl_2	5	15	*R*
7[c]	**41**	CH_2Ph	S_SR_C	CH_2Cl_2	40	89	*R*
8[d]	**41**	CH_2Ph	S_SR_C	CH_2Cl_2	57	90	*R*
9	**41**	CH_2Ph	S_SR_C	CH_3CN	28	69	*R*
10	**41**	CH_2Ph	S_SR_C	$PhCH_3$	5	88	*R*

[a] L/Pd ratio 1:1. [b] KOAc was used instead of LiOAc. [c] Carried out at –1 °C. [d] Carried out at –1 °C using 6 mol-% of Pd and ligand.

Having recorded promising enantioselectivities with the acyclic phosphanyl sulfoximines, it was of interest to test the cyclic phosphanyl sulfoximines. These phosphanyl sulfoximines should show a higher tendency to form a chelate with the Pd atom provided the cyclohexane ring can undergo the required conformational change (cf. Figure 5). Application of the phosphanyl *N*-methyl sulfoximine **35** in the reaction of *rac*-**46** with the malonate anion, under same conditions as before, gave malonate (*R*)-**47** in almost quantitative yield with 86% *ee* (Scheme 9, Table 6, entry 1). The doubling of the ligand-to-metal ratio had no bearing on the efficiency of the alkylation (entry 2). The use of K^+ instead of Li^+ as counterion did not influence the yield or the enantioselectivity (entry 3). The Pd-catalyzed reaction of *rac*-**46** with the malonate anion in the presence of the diastereomeric $S_SS_CS_C$-configured ligand **36** gave malonate (*S*)-**47** in 95% yield with only 73% *ee* (entry 4). The lower enantioselectivity reflects, as in the case of the acyclic phosphanyl sulfoximines, the influence of the chirality of the sulfoximine group on the enantioselectivity. Interestingly, the use of the phosphanyl *N*-benzyl sulfoximine **37** resulted in a higher enantioselectivity of the reaction of *rac*-**46** with the malonate anion. With the $S_SR_CR_C$-configured ligand **37** malonate (*R*)-**47** was isolated in 95% yield with 97% *ee* (entry 5). In addition, with this ligand the alkylation reaction was much faster than with all other ligands tested so far. The reaction was complete at room temperature within

50 min using 3 mol-% of the catalyst. The reaction of acetate *rac*-**46** with the malonate anion in the presence of the $S_SS_CS_C$-configured phosphanyl sulfoximine **38** furnished the *S*-configured malonate (*S*)-**47** in 96% yield with only 79% *ee* (entry 7). These results show that the chiral backbone of the ligand is the key factor determining the enantioselectivity of the alkylation. However, the chirality of the sulfoximine group and the N-substituent also exert a strong effect.



Scheme 9. Cyclic phosphanyl sulfoximines in Pd-catalyzed allylic alkylation of acetate **46**.

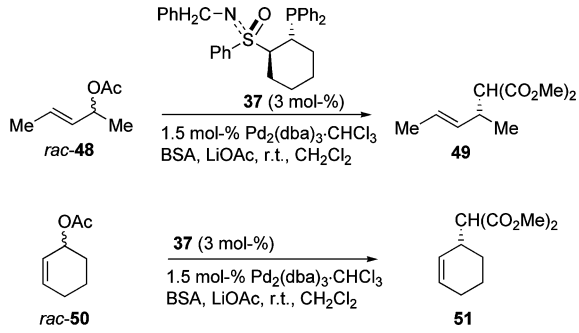
Table 6. Pd-catalyzed allylic alkylation of acetate *rac*-**46** with cyclic phosphanyl sulfoximines as ligand.

Entry	Ligand	R^1	Config.	Ligand/Pd	**47**		
					Yield (%)	*ee*%	Config.
1	**35**	Me	$S_SR_CR_C$	1:1	97	86	*R*
2	**35**	Me	$S_SR_CR_C$	2:1	95	86	*R*
3[a]	**35**	Me	$S_SR_CR_C$	1:1	96	86	*R*
4	**36**	Me	$S_SS_CS_C$	1:1	95	73	*S*
5	**37**	CH_2Ph	$S_SR_CR_C$	1:1	98	97	*R*
6[b]	**37**	CH_2Ph	$S_SR_CR_C$	1:1	96	95	*R*
7	**38**	CH_2Ph	$S_SS_CS_C$	1:1	96	79	*S*
8[b]	**38**	CH_2Ph	$S_SS_CS_C$	1:1	96	79	*S*

[a] KOAc was used instead of LiOAc. [b] Prepared in situ from the phosphane–borane with DABCO.

The above discussed alkylation experiments were run with the pure phosphanyl sulfoximines. Because of their ready reaction with dioxygen, it was of interest to see whether the same results in allylic alkylation could be achieved with a phosphanyl sulfoximine generated in situ through deboronation of the corresponding phosphane–borane. Phosphane **37** was generated upon treatment of the phosphane–borane **29** with DABCO and the crude ligand was reacted in the standard fashion with $Pd_2(dba)_3{\cdot}CHCl_3$, *rac*-**46** and the nucleophile. The *R*-configured malonate (*R*)-**47** was isolated after 1 h reaction time in 96% yield with 95% *ee* (entry 6). Similar results were obtained by using the crude diastereomeric $S_SS_CS_C$-configured phosphanyl sulfoximine **38** (entry 8). Thus, the presence of $DABCO{\cdot}BH_3$ does not impair the activity of the catalyst in the allylic alkylation investigated.

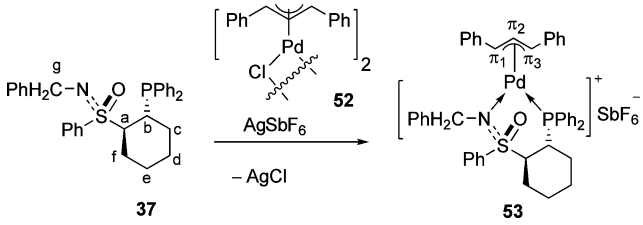
Phosphanyl sulfoximine **37**, which showed the highest enantioselectivity in the allylic alkylation of *rac*-**46** with the malonate anion, was also tested as ligand in the reaction of the racemic dimethyl-substituted allylic acetate *rac*-**48** (Scheme 10). The *R*-configured malonate (*R*)-**49** was isolated after a reaction time of 3.5 h in 95% yield with 59% *ee*. Thus, the allylic alkylation with the diphenyl- and dimethyl-substituted allylic acetates *rac*-**46** and *rac*-**48**, respectively, in the presence of ligand **37** proceeded with the same sense of asymmetric induction. The alkylation with the cyclic allylic acetate *rac*-**50** in the presence of ligand **37** gave after 24 h reaction time the *R*-configured malonate (*R*)-**51** in 70% yield with 36% *ee*. It is interesting to note that in the alkylation of the malonate anion with diphenyl- and dialkyl-substituted allylic substrates the cyclic phosphanyl sulfoximine **37** shows in regard to the degree of asymmetric induction a similar behavior as the [(diphenylphosphanyl)-phenyl]oxazolines.[10b]



Scheme 10. Asymmetric allylic alkylation of acetates *rac*-**48** and *rac*-**50** using phosphanyl sulfoximine **37** as ligand.

Mode of Coordination of the Cyclic Phosphanyl Sulfoximine to the Pd Atom in the π-1,3-Diphenylallyl-Pd^{II} Complex

The π-1,3-diphenylallyl-Pd^{II} complex **53** containing the cyclic phosphanyl sulfoximine **37** as ligand was synthesized upon the successive treatment of the π-1,3-diphenylallyl–Pd^0 complex **52**[39] with 1 equiv. of phosphanyl sulfoximine **37** and $AgSbF_6$ (Scheme 11). Complex **53** and phosphanyl sulfoximine **37** were studied by NMR spectroscopy in order to reveal the mode of coordination of the phosphanyl sulfoximine to the Pd atom. Selected NMR spectroscopic data of phosphanyl sulfoximine **37** and complex **53** are listed in Table 7. The ^1H, ^{13}C and ^{31}P NMR spectra of the free ligand **37** were fully assigned by $^1H,^1H$-, $^1H,^{13}C$- and $^{31}P,^{13}C$-correlation, DEPT and NOE experiments.



Scheme 11. Synthesis of the π-1,3-diphenylallyl-Pd^{II} complex **53**.

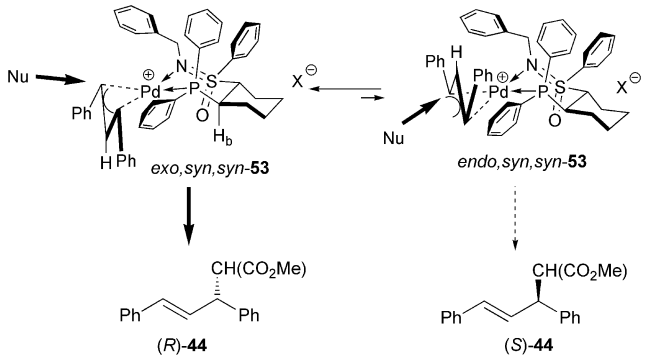
While the signal of C_a of **37** appeared at δ = 59.4 ppm, that of C_b showed up at δ = 29.4 ppm. The chemical shifts of both signals are typical for sp^3-hybridized C atoms in α-position of a sulfoximine and diphenylphosphanyl group, respectively. Both the C_a- and C_b atom are coupled with the P atom and their signals appeared as doublets. Characteristic shift differences were observed between the ^{31}P, ^1H and

Table 7. Selected ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopic data of phosphanyl sulfoximine **37** and the π-allyl complex **53**.

	37[a]			**53**[b]		
Atom	δ_P	δ_H	δ_C	δ_P	δ_H	δ_C
a		3.15	59.4(d)		5.10	63.8(d)
b		4.14	29.4(d)		3.12	28.0(d)
g		3.97	46.0(s)		2.55	47.8(s)
g		4.30			3.40	
π_1		–	–		6.80[c]	106(d)
π_2		–	–		6.60[c]	110
π_3		–	–		4.11[d]	67
P	13.1(s)			22.7(s)		
Coupling constants						
$^3J(H_a,H_b)$	< 2			11		
$^2J(P,C_{\pi1})$	–			17		
$^3J(H_{\pi2},H_{\pi3})$	–			10.4		
$^3J(P,H_{\pi1})$	–			[d]		
$^3J(H_{\pi2},H_{\pi3})$	–			[d]		

[a] In $CDCl_3$. [b] In $[D_8]$THF. [c] Multiplicity could not be determined. [d] Could not be determined because of signal overlap.

^{13}C NMR spectra of complex **53** and those of the phosphanyl sulfoximine **37**. The ^{31}P signal of complex **53** experienced a low-field displacement, which is typical for a P atom coordinated to a Pd atom.[40] While the signal of the H_a atom of complex **53** was shifted to low field, that of the H_b atom was displaced to high-field. The signals of H_a and H_b of complex **53** were assigned by $^1H,^{13}C$-correlation. The displacements of the signals of **53** as compared to **37** gave a first indication of an inversion of the conformation of the cyclohexane ring of the coordinated ligand. The cyclohexane ring of phosphanyl sulfoximine **37** has a conformation being close to that of the corresponding phosphane–borane **29** as indicated by the absence of a coupling between H_a and H_b [$^3J(H_a,H_b) < 2$ Hz]. Consequently, both the sulfoximine and phosphanyl group of the free ligand **37** adopt an almost axial position. A change of the conformation of the cyclohexane ring of the ligand upon coordination to the Pd atom in complex **53** is indicated by a $^3J(H_a,H_b)$ value of 11 Hz for complex **53**. This value translates into H_a–C_a–C_b–H_b and S–C_a–C_b–P dihedral angles of approximately 180° and 60°, respectively. Thus, in complex **53** both the sulfoximine and phosphanyl group occupy an almost equatorial position at the cyclohexane ring. The inversion of the conformation of the cyclohexane is most easily explained by a coordination of both the sulfoximine and phosphanyl group in **53** to the Pd atom. Thus, phosphanyl sulfoximine **37** acts as a bidentate ligand for the Pd atom with formation of a six-membered 1,5-N,P chelate in complex **53**. Compound **53** showed the charateristic chemical shifts and couplings expected for the 1,3-diphenylallyl group (cf. Table 7).[41] Eight different stereoisomers of the π-allyl-Pd complex **53** are conceivable, depending on the configuration of the 1,3-diphenylallyl moiety and its orientation relative to the ligand. These isomers include *endo*,*syn*,*syn*-**53**, *exo*,*syn*,*syn*-**53**, *endo*,*syn*,*anti*-**53** and *exo*,*syn*,*anti*-**53**, *exo*,*anti*,*syn*-**53**, *endo*,*anti*,*syn*-**53**, *exo*,*anti*,*anti*-**53** and *endo*,*anti*,*anti*-**53**.[42] Unfortunately, the NMR spectroscopic data of **53** did allow only a partial assignment of the configuration of the 1,3-diphenylallyl group because of overlap of signals. In addition, the NOE experiments were not capable to differentiate between the *exo* and *endo* orientation of the allyl group because of the same reason. A complete NMR spectroscopic characterization of **53** would have required the synthesis and NMR study of derivatives of the complex specifically labeled at the various phenyl groups. This effort was not undertaken, however, mainly because of the relatively low efficiency of ligand **37** in the allylic alkylation of *rac*-**48** and *rac*-**50** and the wealth of structural information on 1,3-diphenylallyl-Pd^{II} complexes containing other N,P ligands.[41] Based on the literature data on 1,3-diphenylallyl-Pd^{II} complexes[41] and the preliminary NMR spectroscopic data of **53** the most likely candidates for the major isomer of **53** are *endo*,*syn*,*syn*-**53** and *exo*,*syn*,*syn*-**53**, in which the 1,3-diphenylallyl group has the *syn*,*syn*-configuration and adopts either the *endo*- or *exo*-configuration relative to the ligand (Scheme 12). The ^{31}P NMR spectrum of the crude complex **53** at room temperature exhibited three signals in a ratio of 96:2:2. Although the minor components were not identified, this observation could indicate the presence of three isomers of **53**, which are in slow equilibrium with each other. Scheme 12 depicts models of *endo*,*syn*,*syn*-**53** and *exo*,*syn*,*syn*-**53** assuming that the six-membered heterocyclic ring adopts a chair-like conformation.



Scheme 12. Alleged structure of the π-allyl complexes *exo*,*syn*,*syn*-**53** and *endo*,*syn*,*syn*-**53** and their proposed reaction with the malonate anion (Nu).

Complex *endo*,*syn*,*syn*-**53** should be thermodynamically disfavored because of a steric interaction between the phenyl rings of the allyl and diphenylphosphanyl group. Thus, the most stable isomer of complex **53** in solution should be *exo*,*syn*,*syn*-**53**, in which the 1,3-diphenylallyl group has the *syn*,*syn*-configuration and adopts the sterically less hindered *exo*-position. The NMR spectroscopic data revealed the *syn*-orientation of $H_{\pi2}$ and the phenyl group at $C_{\pi3}$ (cf. Table 7). Although the orientation of $H_{\pi2}$ and the phenyl group at $C_{\pi1}$ could not be determined, the notion of the major isomer of **53** having the *syn*,*anti*-configuration is less likely.

Selectivity Model

Reaction of *exo*,*syn*,*syn*-**53** with the malonate anion at the C atom *trans* to the P atom is expected to be faster

than that of *endo*,*syn*,*syn*-**53** at this position. Attack of the nucleophile at the C atom of *endo*,*syn*,*syn*-**53** in *trans* position to the P atom should be hampered because of steric interactions between the phenyl rings of (1) the allyl and phosphanyl group and (2) the benzyl and allyl group. This model is based on the assumptions that (1) the attack of the nucleophile at the allylic C atom in *trans*-position to the P atom is kinetically preferred and (2) the more stable complex is the most reactive one. While such a preference for a *trans*-P-attack had been generally observed in π-allyl-Pd complexes containing other N,P ligands,[43] an unidentified minor isomer of **53** could in principle be more reactive.

Conclusions

The PMR of the substituted cyclic and acyclic alkenyl sulfoximines with $HPPh_2$/*t*BuOK proceeded readily and gave the corresponding phosphanyl sulfoximines in high yield. The sulfoximine group apparently provides only a low asymmetric induction in the addition of the P-nucleophile to the double bond. The cyclic phosphanyl sulfoximines are efficient ligands in the Pd-catalyzed asymmetric allylic alkylation of 1,3-diphenylallyl acetate with the malonate anion. However, the enantioselectivity of the allylic alkylation of alkyl-substituted allylic acetates with these ligands was only medium. The cyclohexane ring of the cyclic phosphanyl sulfoximines undergoes upon coordination of the ligand to the Pd atom an inversion, which brings the sulfoximine and phosphanyl group from a pseudo-axial position in the free ligand to a pseudo-equatorial position in the coordinated ligand. Formation of a 1,5-N,P chelate is the driving force for this conformational change.

Experimental Section

Experimental Procedures: Reactions involving dioxygen and water sensitive compounds were carried out under an argon or nitrogen atmosphere using standard Schlenk, cannula and syringe techniques in oven-dried glassware. Sulfoximine **1** was prepared according to the literature.[19,44] All reagents employed were obtained from commercial suppliers. *t*BuOK was purified by sublimation and benzaldehyde by distillation. Diisopropylamine was distilled from CaH_2. *n*BuLi was received as a 1.6 M solution in *n*-hexane and standardized using either diphenylacetic acid or phenanthroline and benzyl alcohol. BH_3·THF was received as a 1 M solution in THF. All other chemicals were used as received without further purification. Toluene was distilled from sodium, and CH_2Cl_2 was distilled from CaH_2. THF and Et_2O were distilled from sodium-benzophenone ketyl. All anhydrous solvents were degassed via three freeze-thaw cycles and stored in a Schlenk flask closed with two Glindemann® sealings and PARAFILM®M. Flash column chromatography was performed on E. Merck silica gel 60, 0.040–0.063 mm. Thin layer chromatography (TLC) was performed on E-Merck precoated alumina sheets (silica gel 60 F_{254}). Development of TLC was done either by UV-light (λ = 254 nm) or *p*-anisaldehyde, phosphomolybdic acid, potassium permanganate and/or ninhydrin. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on Varian (Gemini 300, Mercury 300, Inova 400) instruments. Chemical shifts are given in ppm relative to tetramethylsilane (^1H: δ = 0.00 ppm, ^{13}C: δ = 0.00 ppm) as internal reference, or to residual solvents signals (tetrahydrofuran: ^1H: δ = 1.73 and 3.58 ppm, ^{13}C: δ = 25.4 and 67.6 ppm; chloroform: ^1H: δ = 7.26 ppm, ^{13}C: δ = 77.0 ppm; CH_2Cl_2: ^1H: δ = 5.32 ppm, ^{13}C: δ = 53.8 ppm) for ^1H and ^{13}C spectra, and to H_3PO_4 as external reference for ^{31}P spectra. The coupling constants are given in Hertz. The multiplicity of the signals was denoted as follow: s = singlet, d = doublet, t = triplet, b = broad signal, and combinations thereof. Assignment of the peaks in the ^1H NMR spectra was made by GMQCOSY, GNOE, or GTOCSY experiments. Assignment of the peaks in the ^{13}C NMR spectra was made by APT, DEPT and HETCOR experiments. IR spectra were recorded on a Perkin–Elmer PE 1760 FT spectrometer as KBr pellets or in solution. Absorptions are given in cm^{-1} in a range of 4000 to 850 cm^{-1}, and the following abbreviations are used to describe their relative intensity: w = weak, m = medium, s = strong. Mass spectra were recorded on a Varian Mat 212 S and Finnigan MAT 312 for ionization through EI (Electronic impact, 70 eV) and CI (chemical ionization, 100 eV). ESI (electrospray ionization) and ESI-MS/MS were recorded on a Thermo Finnigan LCQ DECA XPlus instrument. Only peaks of $m/z > 80$ and an intensity > 10%, except decisive ones, are given. High resolution mass spectrometry (HRMS) was done with a Finnigan MAT 95 (EI) or Micromass LCT (LC-TOF-HRMS, column Acquit UPLC BEH C_{18}) intrument. Analytical HPLC were performed with Millipore Waters (UV-481) and Hewlett–Packard HP 1050 instruments. Elemental analyses were done with a Heraeus CHN-Rapid instrument. Optical rotations were measured with a Perkin–Elmer Polarimeter PE 241 and given in grad × mL/dm × g, and the concentration *c* in g/100 mL. The measurements were run at approximately 22 °C. Melting points were measured in an open glass capillary using a Büchi 510 melting point apparatus SMP-20 and are uncorrected.

General Procedure for the Preparation of Acyclic Alkenyl Sulfoximines (Method A). (+)-(*E*)-{2-[(*S*)-*N*-Benzyl-*S*-phenylsulfonimidoyl]alkenyl}benzene (7): In a round-bottom Schlenk flask, sulfoximine **3** (2.30 g, 9.38 mmol) was dissolved in anhydrous THF (30 mL) and the mixture was cooled to –78 °C. A solution of *n*BuLi (16.45 mL, 10.32 mmol) was added dropwise to the mixture, and the resulting yellow mixture was stirred for 30 min. Benzaldehyde (1.10 g, 10.32 mmol) was added within 5 min and the colorless mixture was stirred at the same temperature for 1 h. Then the mixture was treated with $ClCO_2Me$ (980 mg, 10.32 mmol) and it was warmed to room temperature. After the mixture was stirred for 1 h, it was cooled to –78 °C and DBU (1.57 g, 10.32 mmol) was added dropwise. The mixture was warmed to room temperature and it was stirred overnight. The heterogeneous mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc (4 × 30 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by column chromatography (cyclohexane/EtOAc, 85:15) afforded the alkenyl sulfoximine **7** (3.84 g, 91%) as pale yellow solid. Crystallization by layering *n*-hexane on the top of a saturated solution of the crude mixture in CH_2Cl_2 afforded **7** as fine white needles; m.p. 101 °C. $[\alpha]_D$ = +24.0 (c = 1.00, CH_2Cl_2). ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.22 (d, J = 14.6 Hz, 1 H, NCH_2), 4.35 (d, J = 14.6 Hz, 1 H, NCH_2), 6.88 (d, J = 15.3 Hz, 1 H, SC*H*), 7.22 (m, 1 H, Ar), 7.34 (m, 5 H, Ar), 7.44 (m, 4 H, Ar), 7.56 (m, 4 H, Ar and S-CH=C*H*), 8.01 (m, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 47.2 (CH_2), 126.5 (CH), 127.6 (CH), 127.8 (CH), 128.3 (CH), 128.4 (CH), 128.7 (CH), 129.0 (CH), 129.3 (CH), 130.8 (CH), 132.7 (CH), 132.8 (C), 140.1 (C), 141.5 (C), 142.6 (CH) ppm. IR (KBr): $\tilde{\nu}$ = 2882 (s), 1240 (s), 1122 (s), 1074 (s) cm^{-1}. MS (CI, CH_4): m/z (%) = 334 (100) [M^+ + 1], 229 (13), 208 (12), 91 (10). HRMS: calcd. for $C_{21}H_{19}NOS$:

333.1187; found 333.1188. $C_{21}H_{19}NOS$ (333.4): calcd. C 75.64, H 5.74, N 4.20; found C 75.70, H 5.71, N 4.19.

(+)-(*E*)-{2-[(*S*)-*N*-Methyl-*S*-phenylsulfonimidoyl]alkenyl}benzene (6): According to method A, the alkenyl sulfoximine **6** was prepared starting from sulfoximine **2** (4.05 g, 23.93 mmol), *n*BuLi (16.45 mL, 26.29 mmol), benzaldehyde (2.79 g, 26.29 mmol), $ClCO_2Me$ (2.49 g, 26.29 mmol) and DBU (4.00 g, 26.29 mmol) in THF (60 mL). Purification by column chromatography (cyclohexane/EtOAc, 3:2) afforded the alkenyl sulfoximine **6** (5.42 g, 88%) as colorless oil, which crystallized at –26 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.81 (s, 3 H, NCH_3), 6.88 (d, J = 15.3 Hz, 1 H, SCH), 7.37 (m, 3 H, CH-*m*-Ph and CH-*p*-Ph), 7.47 (m, 2 H, CH-*o*-Ph), 7.50–7.62 (m, 4 H, S-*o*-Ph and S-*p*-Ph and S-CH=CH), 7.96 (m, 2 H, S-*m*-Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.5 (CH_3, NCH_3), 127.4 (CH, S-CH), 128.4 (CH), 128.7 (CH), 129.0 (CH), 129.4 (CH) (CH-*o*-Ph, CH-*m*-Ph, S-*o*-Ph and S-*m*-Ph), 130.8 (CH), 132.7 (CH) (CH-*p*-Ph and S-*p*-Ph), 132.8 (C, CH-*i*-Ph), 139.4 (C, S-*i*-Ph), 142.6 (CH, S-CH=CH) ppm.

(–)-(*E*)-{2-[(*S*)-*N*-(*p*-Tolylsulfonyl)-*S*-phenylsulfonimidoyl]alkenyl}-benzene (8): According to method A, the alkenyl sulfoximine **8** was prepared starting from sulfoximine **4** (6.80 g, 22.0 mmol), *n*BuLi (15.3 mL, 24.2 mmol), benzaldehyde (2.57 g, 24.2 mmol), $ClCO_2Me$ (2.28 g, 24.2 mmol) and DBU (3.69 g, 24.2 mmol) in THF (60 mL). Purification by column chromatography (cyclohexane/EtOAc/CH_2Cl_2, 13:6:1) afforded the alkenyl sulfoximine **8** (5.42 g, 88%) as white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3 H, Ph-CH_3), 6.90 (d, J = 15.1 Hz, S-CH), 7.23 (m, 2 H, Ph), 7.34–7.47 (m, 4 H, Ph), 7.52–7.67 (m, 5 H, Ph and S-CH=CH), 7.86 (m, 2 H), 8.01 (m, 2 H, Ph) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.5 (CH_3), 125.5 (CH), 126.8 (CH), 127.7 (CH), 128.9 (CH), 129.1 (CH), 129.3 (CH), 129.6 (CH), 131.7 (CH), 131.8 (C), 134.0 (CH), 138.7 (C), 140.8 (C), 142.8 (C), 143.9 (CH) ppm.

(–)-(*E*)-{2-[(*S*)-*N*-(*tert*-Butyldiphenylsilyl)-*S*-phenylsulfonimidoyl]-alkenyl}benzene (9): According to method A, the alkenyl sulfoximine **9** was prepared starting from sulfoximine **5** (6.00 g, 15.24 mmol), *n*BuLi (10.5 mL, 16.77 mmol), benzaldehyde (1.78 g, 16.77 mmol), $ClCO_2Me$ (1.59 g, 16.77 mmol) and DBU (2.55 g, 16.77 mmol). Purification by column chromatography (cyclohexane/EtOAc, 12:1) afforded the alkenyl sulfoximine **9** (6.23 g, 85%) as colorless oil, which solidified upon standing at 4 °C. White solid; m.p. 69 °C. $[\alpha]_D$ = –62.3 (c = 1.30, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13 [s, 9 H, C(CH_3)$_3$], 6.63 (d, J = 15.2 Hz, 1 H, SCH), 7.19 (m, 2 H, Ph), 7.28 (m, 9 H, Ph), 7.42 (m, 4 H, Ph and S-CH=CH), 7.75 (m, 4 H, Ph), 7.93 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.5 (C), 27.2 (CH_3), 127.32 (CH), 127.34 (CH), 127.36 (CH), 128.2 (CH), 128.7 (CH), 128.8 (CH), 128.91 (CH), 128.93 (CH), 130.2 (CH), 131.8 (CH), 132.0 (CH), 132.9 (C), 135.61 (CH), 135.64 (CH), 136.3 (C), 136.4 (C), 138.8 (CH), 144.3 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3048 (m), 2952 (m), 2928 (m), 2887 (m), 2853 (m), 1616 (m), 1578 (w), 1472 (w), 1445 (m), 1425 (m), 1390 (w), 1283 (s), 1185 (w), 1140 (s), 1103 (s), 1025 (m), 999 (w), 965 (m), 870 (m), 820 (s) cm^{-1}. MS (CI, CH_4): m/z (%) = 482 (16) [M^+ + 1], 425 (11), 424 (34), 406 (10), 405 (29), 404 (100), 105 (17), 61 (11). HRMS: calcd. for $C_{26}H_{22}NOSSi$ [$M^+ - C_4H_9$]: 424.1191; found 424.1195. $C_{30}H_{31}NOSSi$ (481.19): calcd. C 74.80, H 6.49, N 2.91; found C 74.83, H 6.78, N 2.76.

{1-Chlorocyclohexyl[(*S*)-*N*-methylsulfonimidoyl]}benzene (11) and {1-Bromocyclohexyl[(*S*)-*N*-methylsulfonimidoyl]}benzene (12): In a round-bottom Schlenk flask, sulfoximine **10** (178 mg, 750 μmol) was dissolved in anhydrous THF (2 mL). The solution was cooled to –15 °C and *n*BuLi (0.51 mL, 816 μmol) was added dropwise. The yellow mixture was stirred for 30 min and a solution of 1,2-dibromotetrachloroethane (490 mg, 1.50 mmol) in anhydrous THF (2 mL) was added dropwise. After the mixture was stirred for 45 min, it was warmed to room temperature and stirred overnight. Then the mixture was quenched with saturated aqueous NH_4Cl, and the aqueous layer was extracted with Et_2O (4× 5 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by column chromatography (cyclohexane/EtOAc, 85:15) afforded a mixture of the chloro sulfoximine **11** and bromo sulfoximine **12** (202 mg, 91%) in a ratio 45:55. GC: R_t(**11**) = 10.6 min, R_t(**12**) = 11.1 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (m, 1 H), 1.60–1.80 (m, 6 H), 1.90–2.40 (m, 4 H), 2.80 (s)/2.81 (s, 3 H), 7.53–7.70 (m, 3 H), 7.90–8.00 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (CH_2), 21.7 (CH_2), 22.5 (CH_2), 24.3 (CH_2), 30.1 (CH_3), 30.3 (CH_3), 32.3 (CH_2), 33.38 (CH_2), 33.42 (CH_2), 34.5 (CH_2), 86.8 (C), 89.6 (C), 128.6 (CH), 128.7 (CH), 132.2 (CH), 132.3 (CH), 133.1 (CH), 133.2 (CH), 133.3 (C) ppm.

11: GC–MS (EI): m/z (%) = 118 (15), 116 (35), 81 (100).

12: GC–MS (EI): m/z (%) = 162 (17), 160 (17), 81 (100).

(*S*,*E*)-(*N*-Methyl-6-bromohex-1-enylsulfonimidoyl)benzene (15): According to method A, the alkenyl sulfoximine **15** was prepared starting from sulfoximine **2** (540 mg, 3.19 mmol), *n*BuLi (2.19 mL, 3.50 mmol), 5-bromopentanal (580 mg, 3.51 mmol), $ClCO_2Me$ (332 mg, 3.51 mmol) and DBU (486 mg, 3.51 mmol). Purification by column chromatography (cyclohexane/EtOAc, 3:2) afforded a pale yellow oil consisting of the alkenyl sulfoximine **15** (2.65 g, 83%) and an unidentified side product. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.63 (m, 2 H, CHCH$_2$CH_2), 1.85 (m, 2 H, BrCH$_2$CH_2), 2.27 (m, 2 H, CHCH_2), 2.73 (s, 3 H, NCH_3), 3.38 (t, J = 6.8 Hz, 2 H, BrCH_2), 6.34 (dt, J = 15.1, J = 1.7 Hz, 1 H, SCH), 6.85 (dt, J = 15.1, J = 6.8 Hz, 1 H, SCHCH), 7.56 (m, 3 H, S-*o*-Ph and S-*p*-Ph), 7.87 (m, 2 H, S-*m*-Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.2 (CH$_2$, CHCH$_2$CH_2), 29.4 (CH$_3$, NCH_3), 30.5 (CH$_2$, CHCH_2), 32.0 (CH$_2$, BrCH$_2$CH_2), 33.0 (CH$_2$, BrCH_2), 128.7 (CH, S-*m*-Ph), 129.3 (CH, S-*o*-Ph), 130.8 (CH, SCH), 132.6 (CH, S-*p*-Ph), 139.3 (C, S-*i*-Ph), 145.7 (CH, SCH=CH) ppm.

(*S*,*E*)-(*N*-Benzyl-6-bromohex-1-enylsulfonimidoyl)benzene (16): According to method A, the alkenyl sulfoximine **16** was prepared starting from sulfoximine **3** (4.32 g, 17.6 mmol), *n*BuLi (12.1 mL, 19.3 mmol), 5-bromopentanal (3.19 g, 19.3 mmol), $ClCO_2Me$ (1.83 g, 19.3 mmol) and DBU (2.89 mL, 19.7 mmol). Purification by column chromatography (cyclohexane/EtOAc, 3:1) afforded a pale yellow oil consisting of the alkenyl sulfoximine **16** (5.0 g, 77%) and an unidentified side product. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49 (m, 2 H, CHCH$_2$CH_2), 1.82 (m, 2 H, BrCH$_2$CH_2), 2.23 (m, 2 H, CHCH_2), 3.35 (t, J = 6.6 Hz, 2 H, BrCH_2), 4.12 (d, J = 14.6 Hz, 1 H, NCH_2), 4.26 (d, J = 14.6 Hz, 1 H, NCH_2), 6.37 (dt, J = 15.1, J = 1.4 Hz, 1 H, SCH), 6.88 (dt, J = 15.1, J = 6.6 Hz, 1 H, SCHCH), 7.20 (m, 1 H, NCH$_2$-*p*-Ph), 7.29 (m, 2 H, NCH$_2$-*m*-Ph), 7.38 (m, 2 H, NCH$_2$-*o*-Ph), 7.54 (m, 3 H, S-*o*-Ph and S-*p*-Ph), 7.91 (m, 2 H, S-*m*-Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.7 (CH$_2$, CHCH$_2$CH_2), 30.4 (CH$_2$, CHCH_2), 31.8 (CH$_2$, BrCH$_2$CH_2), 33.0 (CH$_2$, BrCH_2), 47.0 (CH$_2$, NCH_2), 126.3 (CH, NCH$_2$-*p*-Ph), 127.3 (CH, NCH$_2$-*m*-Ph), 128.0 (CH, NCH$_2$-*o*-Ph), 128.4 (CH, S-*m*-Ph), 129.5 (CH, S-*o*-Ph or S-*p*-Ph), 130.8 (CH, S-CH), 132.4 (CH, S-*o*-Ph or S-*p*-Ph), 139.6 (C, S-*i*-Ph), 141.2 (C, NCH$_2$-*i*-Ph), 145.6 (CH, S-CH=CH) ppm. MS (CI, CH_4): m/z (%) = 394 (88), 392 (100) [M^+ + 1], 390 (10), 350 (16), 349 (11), 348 (46), 312 (13), 268 (11), 266 (13), 125 (13), 91 (20).

General Procedure for the Preparation of Cyclic Alkenyl Sulfoximines (Method B). (+)-(*S*)-[*N*-Methyl-(*S*-cyclohex-1-ene)sulfonimidoyl]benzene (17): In a round-bottom Schlenk flask, freshly dis-

tilled diisopropylamine (1.91 mL, 13.73 mmol) was dissolved in anhydrous THF (450 mL). The solution was cooled to –78 °C and *n*BuLi (8.58 mL, 13.73 mmol) was added dropwise. After the mixture was stirred for 15 min, it was warmed to room temperature for 5 min and then cooled to –78 °C. A solution of 6-bromosulfoximine **15** (4.21 g, 13.31 mmol) in THF (450 mL), which was previously cooled to –78 °C, was added to the solution of LDA within 5 min via a double-ended cannula. After the yellow mixture was stirred for 40 min, it was warmed to 0 °C. Then the mixture was quenched with saturated aqueous NH_4Cl. The organic layer was separated, and the aqueous layer was extracted with EtOAc (4 × 300 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by column chromatography (cyclohexane/EtOAc, 3:2) afforded the alkenyl sulfoximine **17** (2.50 g, 80%) as white solid; m.p. 49 °C. $[\alpha]_D$ = +31.1 (*c* = 0.26, Et_2O). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.47–1.70 (m, 4 H, C*H*$_2$), 2.06 (m, 1 H, C*H*$_2$), 2.22–2.38 (m, 3 H, C*H*$_2$), 2.76 (s, 3 H, NC*H*$_3$), 7.02 (m, 1 H, SCC*H*), 7.53 (m, 3 H, *Ph*), 7.86 (m, 2 H, *Ph*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9 (CH_2), 22.1 (CH_2), 23.6 (CH_2), 25.7 (CH_2), 29.4 (CH_3), 128.80 (CH), 128.82 (CH), 132.1 (CH), 138.0 (C), 138.2 (CH), 138.5 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3060 (w), 2935 (s), 2867 (m), 2801 (m), 1444 (s), 1341 (w), 1244 (s), 1148 (s), 1110 (m), 1081 (m), 1048 (w), 1022 (w), 937 (m), 864 (m) cm^{-1}. MS (CI, CH_4): *m*/*z* (%) = 236 (18) [M^+ + 1], 235 (93) [M^+], 234 (10), 139 (11), 129 (11), 126 (11), 125 (25), 110 (100), 109 (16), 97 (13), 81 (58), 80 (6), 79 (45), 78 (19), 77 (33), 69 (15), 68 (18). HRMS: calcd. for $C_{13}H_{17}NOS$: 235.1031; found 235.1031.

(–)-(*S*)-[*N*-Benzyl-(*S*-cyclohex-1-ene)sulfonimidoyl]benzene (18): According to method B, the cycloalkenyl sulfoximine **18** was prepared starting from 6-bromosulfoximine **16** (3.73 g, 9.51 mmol) in THF (330 mL), diisopropylamine (1.37 mL, 9.70 mmol) and *n*BuLi (6.06 mL, 9.70 mmol) in THF (240 mL). Purification by column chromatography (cyclohexane/EtOAc, 85:15) afforded the alkenyl sulfoximine **18** (2.74 g, 92%) as white solid; m.p. 61–62 °C. $[\alpha]_D$ = –0.80 (*c* = 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.45–170 (m, 4 H, C*H*$_2$), 2.08 (m, 1 H, C*H*$_2$), 2.20–2.41 (m, 3 H, C*H*$_2$), 4.18 (d, *J* = 14.9 Hz, 1 H, NC*H*$_2$), 4.27 (d, *J* = 14.9 Hz, 1 H, NC*H*$_2$), 7.09 (m, 1 H, SCC*H*), 7.21 (m, 1 H, NCH$_2$*Ph*), 7.30 (m, 2 H, NCH$_2$*Ph*), 7.41–7.60 (m, 5 H, S*Ph* and NCH$_2$*Ph*), 7.91 (m, 2 H, S*Ph*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9 (CH_2), 22.2 (CH_2), 23.7 (CH_2), 25.8 (CH_2), 46.9 (CH_2), 126.3 (CH), 127.4 (CH), 128.1 (CH), 128.99 (CH), 129.00 (CH), 132.4 (CH), 138.63 (C), 138.74 (CH), 138.86 (C), 141.8 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3379 (w), 3062 (m), 3021 (w), 2934 (s), 2859 (m), 1641 (w), 1491 (w), 1445 (m), 1352 (w), 1257 (s), 1135 (s), 1078 (m), 1024 (w), 909 (m) cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 312 (100) [M^+ + 1]. HRMS: calcd. for $C_{19}H_{21}NOS$: 311.1344; found 311.1345.

General Procedure for the Preparation of Phosphane–Boranes (Method C). (+)-Diphenyl{(1*S*)-1-phenyl-2-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]ethyl}phosphane–Borane (20) and (–)-Diphenyl{(1*R*)-1-phenyl-2-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]ethyl}phosphane–Borane (19): In a round-bottom Schlenk flask, the alkenyl sulfoximine **6** (400 mg, 1.55 mmol) was dissolved in anhydrous and degassed THF (12 mL). Then diphenylphosphane (335 mg, 1.70 mmol) and *t*BuOK (17 mg, 170 μmol) were successively added at room temperature. The mixture was stirred at room temperature until TLC indicated a complete conversion of the alkenyl sulfoximine **6** (1 to 2 h). Then the mixture was cooled to 0 °C and BH_3·THF (3.41 mL, 3.41 mmol) was added dropwise. The mixture was warmed to room temperature and after 1 h it was cooled to 0 °C. 1 M H_2SO_4 (CAUTION: gas evolution) was added carefully until a pH of 5 was reached. Then the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. A mixture of the diastereomeric phosphane–boranes **19** and **20** in a ratio of 78:22 [Chiral OD-H column, detector 254 nm, *n*-heptane/2-propanol, 98:2, flow: 0.75 mL/min, 36 bar, R_t(**19**) = 22.4 min; R_t(**20**) = 27.1 min] was obtained. Purification by column chromatography (cyclohexane/EtOAc, 4:1) afforded the phosphane–borane **20** (122 mg, 17%) as white foam and phosphane–borane **19** (430 mg, 61%) as white crystalline solid. Layering *n*-hexane on the top of a saturated solution of a mixture of both isomers in CH_2Cl_2 gave the phosphane–borane **19** as colorless single crystals suitable for X-ray analysis.

19: M.p. 117 °C. $[\alpha]_D$ = –116.5 (*c* = 1.19, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.4–1.4 (br. s, 3 H, B*H*$_3$), 2.51 (s, 3 H, NC*H*$_3$), 3.63 (ddd, *J* = 15.1, $^3J_{P,H}$ = 10.2, *J* = 1.6 Hz, 1 H, SC*H*$_2$), 4.06 (ddd, *J* = 15.1, *J* = 11.8, $^3J_{P,H}$ = 1.9 Hz, 1 H, SC*H*$_2$), 4.46 (ddd, $^2J_{P,H}$ = 15.1, *J* = 11.8, *J* = 1.6 Hz, 1 H, SCH$_2$C*H*), 6.79 (m, 4 H), 6.89 (m, 1 H), 7.13–7.23 (m, 6 H), 7.29 (m, 2 H), 7.37 (m, 2 H), 7.59 (m, 3 H), 8.01 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.3 (CH_3, NC*H*$_3$), 38.0 [d, ^1J(P,C) = 28.8 Hz, CH, SCH$_2$*C*H], 56.7 (d, $^2J_{P,C}$ = 7.9 Hz, CH_2, SC*H*$_2$), 125.9 (d, $^1J_{P,C}$ = 51.6 Hz, 1 C, *i*-Ph), 127.0 (d, $^1J_{P,C}$ = 54.9 Hz, 1 C, *i*-Ph), 127.3 (d, $J_{P,C}$ = 2.4 Hz, CH), 127.6 (d, $J_{P,C}$ = 1.9 Hz, CH), 128.2 (d, $J_{P,C}$ = 10.1 Hz, CH), 128.9 (CH), 129.1 (CH), 129.4 (d, $J_{P,C}$ = 9.7 Hz, CH), 130.0 (d, $J_{P,C}$ = 4.2 Hz, CH), 131.2 (d, $J_{P,C}$ = 1.7 Hz, CH), 131.8 (C), 132.1 (d, $J_{P,C}$ = 1.8 Hz, CH), 132.4 (CH), 132.5 (d, $J_{P,C}$ = 8.8 Hz, CH), 133.2 (d, $J_{P,C}$ = 8.6 Hz, CH), 136.8 (C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 25.48 (br. s) ppm. IR (KBr): $\tilde{\nu}$ = 3908 (w), 3654 (w), 3465 (m), 3055 (m), 2974 (w), 2932 (m), 2871 (m), 2802 (m), 2383 (s), 2348 (s), 2274 (w), 1583 (w), 1491 (m), 1438 (m), 1403 (w), 1267 (m), 1236 (s), 1142 (s), 1104 (s), 1064 (s), 997 (w), 916 (m), 855 (s), 823 (m) cm^{-1}. MS (CI, CH_4): *m*/*z* (%) = 456 (1) [M^+ + 1], 300 (23), 299 (100), 298 (24), 289 (11), 184 (14), 156 (54), 125 (28). $C_{27}H_{29}BNOPS$ (457.38): calcd. C 70.90, H 6.39, N 3.06; found C 71.04, H 6.51, N 2.86.

20: M.p. 53–55 °C. $[\alpha]_D$ = +142.9 (*c* = 1.80, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.3–1.4 (br. s, 3 H, B*H*$_3$), 2.61 (s, 3 H, NC*H*$_3$), 3.54 (ddd, *J* = 14.9, $^3J_{P,H}$ = 10.3, *J* = 1.5 Hz, 1 H, SC*H*$_2$), 3.98 (ddd, *J* = 14.9, *J* = 11.8, $^3J_{P,H}$ = 1.9 Hz, 1 H, SC*H*$_2$), 4.39 (ddd, $^2J_{P,H}$ = 16.3, *J* = 11.8, *J* = 1.3 Hz, 1 H, SCH$_2$C*H*), 6.88 (m, 2 H), 6.92 (m, 2 H), 7.04 (m, 1 H), 7.14–7.34 (m, 7 H), 7.37–7.60 (m, 6 H), 7.87 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.4 (CH_3, NC*H*$_3$), 38.9 (d, $^1J_{P,C}$ = 28.7 Hz, CH, SCH$_2$*C*H), 56.7 (d, $^2J_{P,C}$ = 8.0 Hz, CH_2, SC*H*$_2$), 125.9 (d, $^1J_{P,C}$ = 51.6 Hz, 1 C, *i*-Ph), 127.1 (d, $^1J_{P,C}$ = 56.0 Hz, 1 C, *i*-Ph), 127.5 (d, $J_{P,C}$ = 2.9 Hz, CH), 127.7 (d, $J_{P,C}$ = 2.4 Hz, CH), 128.2 (d, $J_{P,C}$ = 10.1 Hz, CH), 128.9 (CH), 129.1 (CH), 129.7 (d, $J_{P,C}$ = 9.2 Hz, CH), 130.0 (d, $J_{P,C}$ = 4.3 Hz, CH), 131.2 (d, $J_{P,C}$ = 2.4 Hz, CH), 131.9 (d, $J_{P,C}$ = 2.4 Hz, CH), 132.4 (C), 132.5 (CH), 132.6 (d, $J_{P,C}$ = 8.8 Hz, CH), 133.2 (d, $J_{P,C}$ = 8.5 Hz, CH), 138.0 (C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 26.11 (br. s) ppm. IR (KBr): $\tilde{\nu}$ = 3460 (w), 2922 (m), 2805 (w), 2375 (s), 1971 (w), 1900 (w), 1814 (w), 1673 (w), 1585 (m), 1483 (m), 1438 (s), 1245 (s), 1128 (s), 1063 (s), 915 (m), 855 (w) cm^{-1}. MS (ESI-MS, MeOH): *m*/*z* (%) = 458 (100) [M^+ + 1], 443 (28), 333 (12), 319 (24), 305 (32), 299 (44), 289 (38), 156 (28). $C_{27}H_{29}BNOPS$ (457.38): calcd. C 70.90, H 6.39, N 3.06; found C 71.01, H 6.36, N 3.06.

(–)-Diphenyl{(1*R*)-1-phenyl-2-[(*S*)-*N*-benzyl-*S*-phenylsulfonimidoyl]-ethyl}phosphane–Borane (21) and (+)-Diphenyl{(1*S*)-1-phenyl-2-[(*S*)-*N*-benzyl-*S*-phenylsulfonimidoyl]ethyl}phosphane–Borane (22): According to method C, the phosphane–boranes **21** and **22** were prepared starting from the alkenyl sulfoximine **7** (700 mg, 2.10 mmol), diphenylphosphane (453 mg, 2.31 mmol) and *t*BuOK

(22 mg, 0.21 mmol) in THF (18 mL). After the complete conversion of sulfoximine **7**, BH_3·THF (4.62 mL, 4.62 mmol) was added. Work up after the mixture was stirred for 1 h gave a mixture of **21** and **22** in a ratio of 64:36 [chiralpack-IA column, detector 230 nm, *n*-heptane/2-propanol, 85:15, flow: 0.75 mL/min, 32 bar, R_t(**22**) = 14.90 min; R_t(**21**) = 21.28 min]. Purification by column chromatography (cyclohexane/EtOAc, 85:15) afforded the phosphane–borane **21** (592 mg, 53%) as white crystalline solid and the phosphane–borane **22** (277 mg, 25%) as white foam. Layering *n*-hexane on the top of a saturated solution of both isomers in CH_2Cl_2 gave the phosphane–borane **21** as fine white needles.

21: M.p. 140 °C. $[a]_D$ = –140.3 (*c* = 1.03, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.4–1.5 (br. s, 3 H, BH_3), 3.70 (ddd, *J* = 14.8, $^3J_{P,H}$ = 10.1, *J* = 1.4 Hz, 1 H, SCH_2), 3.98 (d, *J* = 14.6 Hz, 1 H, NCH_2Ph), 4.04 (d, *J* = 14.6 Hz, 1 H, NCH_2Ph), 4.08 (ddd, *J* = 14.8, *J* = 11.8, $^3J_{P,H}$ = 1.8 Hz, 1 H, SCH_2), 4.54 (ddd, $^2J_{P,H}$ = 16.7, *J* = 11.8, *J* = 1.4 Hz, 1 H, SCH$_2$C*H*), 6.83 (m, 4 H), 6.93 (m, 1 H), 7.13–7.35 (m, 13 H), 7.44 (m, 2 H), 7.53–7.63 (m, 3 H), 8.01 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.9 (d, $^1J_{P,C}$ = 29.8 Hz, CH, SCH$_2$*C*H), 46.9 (CH$_2$, N*C*H$_2$Ph), 56.3 (d, $^2J_{P,C}$ = 8.4 Hz, CH$_2$, S*C*H$_2$), 125.8 (d, $^1J_{P,C}$ = 51.9 Hz, 1 C, *i*-Ph), 126.3 (CH), 127.0 (d, $^1J_{P,C}$ = 54.2 Hz, 1 C, *i*-Ph), 127.10 (CH), 127.13 (CH), 127.4 (d, $J_{P,C}$ = 2.3 Hz, CH), 128.0 (CH), 128.3 (d, $J_{P,C}$ = 9.9 Hz, CH), 128.7 (CH), 128.8 (CH), 129.1 (d, $J_{P,C}$ = 9.9 Hz, CH), 129.7 (d, $J_{P,C}$ = 4.6 Hz, CH), 130.9 (d, $J_{P,C}$ = 2.3 Hz, CH), 131.82 (C), 131.85 (CH), 132.2 (CH), 132.3 (d, $J_{P,C}$ = 9.1 Hz, CH), 133.0 (d, $J_{P,C}$ = 9.1 Hz, CH), 137.5 (C),141.0 (C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 25.75 (br. s) ppm. IR (KBr): $\tilde{\nu}$ = 3866 (w), 3466 (w), 3047 (m), 2927 (m), 2879 (w), 2842 (m), 2363 (s), 2341 (s), 1555 (w), 1492 (w), 1439 (m), 1387 (w), 1251 (s), 1201 (m), 1136 (s), 1072 (s), 920 (m), 862 (w), 819 (w) cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 534 (1) [M$^+$ + 1], 533 (1), 530 (7), 300 (23), 299 (100), 298 (25), 289 (4), 233 (9), 232 (56). $C_{33}H_{33}BNOPS$ (534.47): calcd. C 74.30, H 6.24, N 2.63; found C 74.04, H 6.45, N 2.62.

22: M.p. 94 °C. $[a]_D$ = +103.6 (*c* = 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.35–1.40 (br. s, 3 H, BH_3), 3.60 (ddd, *J* = 14.8, *J* = 10.6, $^3J_{P,H}$ = 1.4 Hz, 1 H, SCH_2), 4.00 (d, *J* = 14.9 Hz, 1 H, NCH_2Ph), 4.06 (ddd, *J* = 14.8, $^3J_{P,H}$ = 11.6, *J* = 1.7 Hz, 1 H, SCH_2), 4.16 (d, *J* = 14.9 Hz, 1 H, NCH_2Ph), 4.57 (ddd, $^2J_{P,H}$ = 16.5, *J* = 10.6, *J* = 1.7 Hz, 1 H, SCH$_2$C*H*), 6.88 (m, 2 H), 6.95 (m, 2 H), 7.05 (m, 1 H), 7.12–7.32 (m, 12 H), 7.40 (m, 1 H), 7.48 (m, 4 H), 7.56 (m, 1 H), 7.92 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.7 (d, $^1J_{P,C}$ = 28.9 Hz, CH, SCH$_2$*C*H), 46.4 (CH$_2$, N*C*H$_2$Ph), 57.1 (d, $^2J_{P,C}$ = 8.2 Hz, CH$_2$, S*C*H$_2$), 125.6 (d, $^1J_{P,C}$ = 51.7 Hz, 1 C, *i*-Ph), 126.2 (CH), 126.9 (d, $^1J_{P,C}$ = 54.6 Hz, 1 C, *i*-Ph), 127.0 (CH), 127.2 (d, $J_{P,C}$ = 2.9 Hz, CH), 127.6 (d, $J_{P,C}$ = 2.4 Hz, CH), 127.9 (CH), 128.0 (d, $J_{P,C}$ = 10.1 Hz, CH), 128.72 (CH), 128.76 (CH), 129.0 (d, $J_{P,C}$ = 9.6 Hz, CH), 129.8 (d, $J_{P,C}$ = 4.3 Hz, CH), 131.0 (d, $J_{P,C}$ = 2.3 Hz, CH), 131.8 (d, $J_{P,C}$ = 2.3 Hz, CH), 132.2 (C), 132.39 (d, $J_{P,C}$ = 8.9 Hz, CH), 132.44 (CH), 133.0 (d, $J_{P,C}$ = 8.5 Hz, CH), 138.3 (C), 141.1 (C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 26.38 (br. s) ppm. IR (KBr): $\tilde{\nu}$ = 3052 (m), 2919 (m), 2847 (m), 2365 (s), 2344 (s), 1815 (w), 1582 (w), 1484 (m), 1439 (s), 1247 (s), 1117 (s), 1061 (s), 920 (m), 820 (w) cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 534 (20) [M$^+$ + 1], 533 (10), 532 (19), 300 (20), 299 (100), 298 (24), 289 (12), 288 (11), 279 (4), 233 (10), 232 (69), 187 (11), 106 (15), 105 (10). $C_{33}H_{33}BNOPS$ (534.47): calcd. C 74.30, H 6.24, N 2.63; found C 74.27, H 6.08, N 2.50.

(–)-Diphenyl{(1*S*)-1-phenyl-2-[(*S*)-*N*-(*p*-tolylsulfonyl)-*S*-phenylsulfonimidoyl]ethyl}phosphane–Borane (24) and (+)-Diphenyl{(1*R*)-1-phenyl-2-[(*S*)-*N*-(*p*-tolylsulfonyl)-*S*-phenylsulfonimidoyl]ethyl}-phosphane–Borane (23): According to method C, the phosphane–boranes **24** and **23** were prepared starting from alkenyl sulfoximine **8** (2.0 g, 5.03 mmol), diphenylphosphane (1.03 g, 5.5 mmol) and *t*BuOK (56 mg, 500 μmol) in THF (60 mL). After the complete conversion of sulfoximine **8**, BH_3·THF (11 mL, 11 mmol) was added. Work up after the mixture was stirred for 1 h gave a mixture of **24** and **23** in a ratio of 73:27 [Kromasil Si 100 column, detector 254 nm, cyclohexane/EtOAc/CH_2Cl_2, 11:2:0.5, flow: 1 mL/min, 30 bar, R_t(**23**) = 8.49 min; R_t(**24**) = 11.07 min]. The crude mixture was dissolved in CH_2Cl_2 and silica gel was added before the evaporation so that the crude mixture was adsorbed on silica gel. The loaded silica gel was placed on top of a column containing silica gel. Purification by column chromatography (cyclohexane/EtOAc/CH_2Cl_2, 11:2:1) afforded in the first collected fractions the phosphane–borane **23**, which was contaminated with the phosphane–borane **24**. After evaporation of the solvents, the residue was dissolved in the minimum amount of CH_2Cl_2 and *n*-hexane was layered on the top of the saturated solution. The phosphane–borane **23** crystallized at –26 °C as colorless needles (540 mg, 18%). The major isomer was eluted with $CHCl_3$ to yield the phosphane–borane **24**, which was contaminated with the phosphane–borane **23**. After evaporation of the solvents, the residue was dissolved in the minimum amount of CH_2Cl_2 and *n*-hexane was layered on the top of the saturated solution. The phosphane–borane **24** crystallized in CH_2Cl_2 at 4 °C as woolly solid (1.53 g, 51%).

24: M.p. 196 °C. $[a]_D$ = –86.7 (*c* = 0.97, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.4–1.4 (br. s, 3 H, BH_3), 2.37 (s, 3 H, H_3C-Ph-SO$_2$), 4.14 (ddd, *J* = 14.8, *J* = 11.4, $^3J_{P,H}$ = 2.4 Hz, 1 H, SCH_2), 4.24 (ddd, *J* = 14.8, $^3J_{P,H}$ = 8.6, *J* = 2.3 Hz, 1 H, SCH_2), 4.45 (ddd, $^2J_{P,H}$ = 16.1, *J* = 11.4, *J* = 2.3 Hz, 1 H, SCH$_2$C*H*), 6.73 (m, 2 H), 6.80 (t, *J* = 7.7 Hz, 2 H), 6.93 (m, 1 H), 7.13–7.24 (m, 8 H), 7.28–7.44 (m, 4 H), 7.64 (m, 5 H), 8.01 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5 (CH$_3$, H$_3$*C*-Ph-SO$_2$), 37.8 (d, $^1J_{P,C}$ = 28.3 Hz, CH, SCH$_2$*C*H), 57.8 (d, $^2J_{P,C}$ = 9.2 Hz, CH$_2$, S*C*H$_2$), 125.0 (d, $^1J_{P,C}$ = 51.8 Hz, 1 C, *i*-Ph), 126.2 (d, $^1J_{P,C}$ = 55.0 Hz, 1 C, *i*-Ph), 126.3 (CH), 127.54 (CH), 127.57 (CH), 127.59 (CH), 128.1 (d, *J* = 10.1 Hz, CH), 128.8 (CH), 128.9 (CH), 129.3 (d, *J* = 9.8 Hz, CH), 129.5 (d, *J* = 4.2 Hz, CH), 130.6 (C), 131.2 (d, *J* = 2.4 Hz, CH), 132.2 (d, *J* = 2.3 Hz, CH), 132.3 (d, *J* = 9.0 Hz, CH), 133.0 (d, *J* = 8.6 Hz, CH), 133.4 (CH), 136.6 (C), 140.3 (C), 142.5 (C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 26.27 (br. s) ppm. IR (KBr): $\tilde{\nu}$ = 3924 (m), 3653 (w), 3463 (m), 3056 (m), 2922 (w), 2410 (m), 1597 (w), 1493 (w), 1436 (m), 1398 (m), 1316 (s), 1239 (s), 1182 (w), 1154 (s), 1104 (s), 1067 (s), 1018 (w), 996 (w), 911 (m), 813 (m) cm^{-1}. MS (CI, CH_4): *m*/*z* (%) = 597 (2) [M$^+$ + 1], 596 (5) [M$^+$ – 1], 299 (30), 187 (23), 173 (10), 172 (100), 155 (11), 133 (15), 111 (48), 109 (25), 105 (97), 91 (12), 88 (3), 87 (12).

23: M.p. 122 °C. $[a]_D$ = +162.35 (*c* = 0.85, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.4–1.4 (br. s, 3 H, BH_3), 2.37 (s, 3 H, H_3C-Ph-SO$_2$), 3.90 (ddd, *J* = 14.7, $^3J_{P,H}$ = 8.2, *J* = 2.1 Hz, 1 H, SCH_2), 4.33 (ddd, *J* = 14.7, *J* = 12.2, $^3J_{P,H}$ = 3.0 Hz, 1 H, SCH_2), 4.58 (ddd, $^2J_{P,H}$ = 16.1, *J* = 12.2, *J* = 2.1 Hz, 1 H, SCH$_2$C*H*), 6.84 (m, 4 H), 6.98 (m, 1 H), 7.13–7.27 (m, 8 H), 7.30 (m, 1 H), 7.44 (m, 1 H), 7.47–7.64 (m, 5 H), 7.76 (m, 2 H), 8.05 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.5 (CH$_3$, H$_3$*C*-Ph-SO$_2$), 39.1 (d, $^1J_{P,C}$ = 28.0 Hz, CH, SCH$_2$*C*H), 59.1 (d, $^2J_{P,C}$ = 9.8 Hz, CH$_2$, S*C*H$_2$), 124.8 (d, $^1J_{P,C}$ = 51.7 Hz, 1 C, *i*-Ph), 126.0 (d, $^1J_{P,C}$ = 50.5 Hz, 1 C, *i*-Ph), 126.3 (CH), 127.5 (d, $J_{P,C}$ = 2.6 Hz, CH), 127.6 (d, $J_{P,C}$ = 1.9 Hz, CH), 127.8 (CH), 128.1 (d, $J_{P,C}$ = 10.2 Hz, CH), 128.9 (CH), 129.0 (CH), 129.1 (d, $J_{P,C}$ = 9.8 Hz, CH), 129.8 (d, $J_{P,C}$ = 4.1 Hz, CH), 130.3 (C), 131.2 (d, $J_{P,C}$ = 2.0 Hz, CH), 132.1 (d, $J_{P,C}$ = 2.0 Hz, CH), 132.4 (d, $J_{P,C}$ = 8.9 Hz, CH), 133.3 (d, $J_{P,C}$ = 8.7 Hz, CH), 133.6 (CH), 137.2 (C), 140.5 (C), 142.6 (C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 26.17 (br. s) ppm. IR (KBr): $\tilde{\nu}$

= 3676 (w), 3652 (w), 3593 (w), 3447 (m), 3060 (m), 2924 (m), 2392 (s), 1597 (w), 1493 (m), 1440 (m), 1399 (w), 1315 (s), 1226 (m), 1152 (s), 1091 (s), 1063 (s), 1021 (w), 997 (w), 911 (m), 816 (m) cm^{-1}. MS (CI, CH_4): *m*/*z* (%) = 596 (2) [M^+ + 1], 299 (9), 291 (17), 290 (10), 289 (34), 187 (31), 185 (10), 172 (61), 133 (15), 11 (30), 109 (30), 106 (8), 105 (100), 101 (16), 91 (13), 87 (26), 85 (10), 61 (21). Elemental analysis of a mixture of isomers **23** and **24**: $C_{33}H_{33}BNO_3PS_2$ (597.17): calcd. C 66.33, H 5.57, N 2.34; found C 66.34, H 5.45, N 2.23.

(+)-Diphenyl{(*S*)-1-phenyl-2-[(*S*)-*N*(-*tert*-butyldiphenylsilyl)-*S*-phenylsulfonimidoyl]ethyl}phosphane–Borane (26) and (–)-Diphenyl{(*R*)-1-phenyl-2-[(*S*)-*N*-(*tert*-butyldiphenylsilyl)-*S*-phenylsulfonimidoyl]ethyl}phosphane–Borane (25): According to method C, the phosphane–boranes **25** and **26** were prepared starting from the alkenyl sulfoximine **9** (2.0 g, 4.16 mmol), diphenylphosphane (851 mg, 4.57 mmol) and *t*BuOK (46 mg, 410 μmol) in THF (70 mL). After the complete conversion of sulfoximine **9**, BH_3·THF (9.2 mL, 9.2 mmol) was added. Work-up after the mixture was stirred for 1 h gave a mixture of **25** and **26** in a ratio of 58:42 [chiralpack-IA column, detector 254 nm, *n*-heptane/2-propanol, 95:5, flow: 0.6 mL/min, 31 bar, R_t(**25**) = 12.31 min; R_t(**26**) = 19.53 min]. Purification by column chromatography (cyclohexane/EtOAc, 93:7) afforded a mixture of **25** and **26** (2.27 g, 80%) as sticky oil. The mixture was dissolved in hot *n*-heptane/2-propanol (95:5). After a few days at room temperature, colorless crystals were formed, which were collected and analyzed by HPLC. The ratio of **25** and **26** was 98.5:1.5. The crystals were once again dissolved in hot *n*-heptane/2-propanol (95:5) and after a few days the crystals were collected and analyzed. The phosphane–borane **25** (1.14 g, 40%, *dr* ≥ 99:1) was obtained as colorless single crystals suitable for X-ray crystal structure analysis. The first mother liquor (enriched in the minor isomer **26**) was concentrated, and the residue was dissolved in hot *n*-heptane/2-propanol (95:5). After two crystallizations at 4 °C, the minor isomer **26** was isolated (920 mg, 32%, *dr* ≥ 99:1) as colorless single crystals suitable for X-ray crystal structure analysis.

26: M.p. 135 °C. $[\alpha]_D$ = +115.2 (*c* = 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.4–1.2 (br. s, 3 H, BH_3), 0.99 [s, 9 H, C(CH_3)$_3$], 3.38 (ddd, *J* = 14.6, $^3J_{P,H}$ = 10.3, *J* = 1.2 Hz, 1 H, SCH_2), 4.03 (ddd, *J* = 14.6, *J* = 11.8, $^3J_{P,H}$ = 1.7 Hz, 1 H, SCH_2), 4.43 (dd, $^2J_{P,H}$ = 16.5, *J* = 11.8, *J* = 1.2 Hz, 1 H, SCH$_2$C*H*), 6.61 (m, 2 H), 6.76 (t, *J* = 7.7 Hz, 2 H), 6.90 (m, 1 H), 6.99 (t, *J* = 7.8 Hz, 2 H), 7.11 (m, 4 H), 7.17–7.36 (m, 11 H), 7.39 (m, 1 H), 7.48 (m, 1 H), 7.63 (m, 2 H), 7.76 (4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.4 [C, Si*C*(CH$_3$)$_3$], 27.1 [CH$_3$, SiC(*C*H$_3$)$_3$], 39.2 (d, $^1J_{P,C}$ = 28.7 Hz, CH, SCH$_2$*C*H), 59.9 (d, $^2J_{P,C}$ = 6.8 Hz, CH$_2$, S*C*H$_2$), 125.8 (d, $^1J_{P,C}$ = 51.3 Hz, 1 C, *i*-Ph), 126.98 (d, $^1J_{P,C}$ = 54.6 Hz, 1 C, *i*-Ph), 127.00 (d, $J_{P,C}$ = 3.0 Hz, CH), 127.1 (CH), 127.26 (CH), 127.28 (CH), 127.35 (CH), 127.90 (CH), 127.93 (d, $J_{P,C}$ = 9.9 Hz, CH), 128.77 (CH), 128.82 (CH), 129.0 (d, $J_{P,C}$ = 9.6 Hz, CH), 129.6 (d, $J_{P,C}$ = 4.3 Hz, CH), 130.9 (d, $J_{P,C}$ = 2.4 Hz, CH), 131.3 (C), 131.50 (CH), 131.55 (d, $J_{P,C}$ = 2.2 Hz, CH), 132.3 (d, $J_{P,C}$ = 8.8 Hz, CH), 132.8 (d, $J_{P,C}$ = 8.4 Hz, CH), 135.40 (CH), 135.44 (CH), 135.82 (C),135.83 (C),142.7 (C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 25.42 (br. s) ppm. IR (KBr): ṽ = 3058 (m), 2929 (m), 2889 (m), 2853 (m), 2385 (m), 2343 (m), 1585 (w), 1483 (m), 1435 (m), 1320 (m), 1262 (m), 1149 (m), 1103 (m), 1060 (m), 999 (m), 906 (w), 819 (m) cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 682 (15) [M^+ + 1], 681 (14) [M^+], 680 (23) [M^+ – 1], 380 (18), 300 (22), 299 (100), 298 (25), 289 (12).

25: M.p. 124 °C. $[\alpha]_D$ = –86.6 (*c* = 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.4–1.2 (br. s, 3 H, BH_3), 0.98 [s, 9 H, C(CH_3)$_3$], 3.38 (ddd, *J* = 14.7, *J* = 10.9, $^3J_{P,H}$ = 1.3 Hz, 1 H, SCH_2), 3.92 (ddd, *J* = 14.7, $^3J_{P,H}$ = 11.7, *J* = 1.5 Hz, 1 H, SCH_2), 4.49 (br. dd, $^2J_{P,H}$ = 16.7, *J* = 10.9 Hz, 1 H, SCH$_2$C*H*), 6.72 (m, 2 H), 6.84 (t, *J* = 7.8 Hz, 2 H), 6.94 (m, 1 H), 7.04 (m, 2 H), 7.09–7.23 (m, 7 H), 7.27 (m, 4 H), 7.34 (m, 1 H), 7.43 (m, 4 H), 7.53 (m, 3 H), 7.62 (m, 2 H), 7.89 (m, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.3 [C, Si*C*(CH$_3$)$_3$], 27.1 [CH$_3$, SiC(*C*H$_3$)$_3$], 38.1 (d, $^1J_{P,C}$ = 28.8 Hz, CH, SCH$_2$*C*H), 60.1 (d, $^2J_{P,C}$ = 6.5 Hz, CH$_2$, S*C*H$_2$), 126.0 (d, $^1J_{P,C}$ = 51.6 Hz, 1 C, *i*-Ph), 126.99 (CH), 127.01 (CH), 127.15 (CH), 127.18 (CH), 127.21 (d, $^1J_{P,C}$ = 54.4 Hz, 1 C, *i*-Ph), 127.3 (d, $J_{P,C}$ = 2.5 Hz, CH), 128.0 (d, $J_{P,C}$ = 10.1 Hz, CH), 128.1 (CH), 128.66 (CH), 128.74 (CH), 129.0 (d, $J_{P,C}$ = 9.7 Hz, CH), 129.6 (d, $J_{P,C}$ = 4.4 Hz, CH), 130.9 (d, $J_{P,C}$ = 2.4 Hz, CH), 131.54 (CH), 131.56 (d, $J_{P,C}$ = 4.0 Hz, CH), 131.9 (C), 132.3 (d, $J_{P,C}$ = 8.8 Hz, CH), 132.9 (d, $J_{P,C}$ = 8.4 Hz, CH), 135.26 (CH), 135.31 (CH), 135.7 (C), 135.8 (C), 143.0 (C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 26.05 (br. s) ppm. IR (KBr): ṽ = 3059 (m), 2929 (m), 2889 (m), 2853 (m), 2385 (m), 2343 (m), 1969 (w), 1585 (w), 1483 (m), 1435 (m), 1320 (m), 1262 (m), 1149 (m), 1103 (m), 1060 (m), 999 (m), 906 (w), 819 (m), 771 (m), 732 (s), 695 (s), 598 (m), 526 (m), 491 (m) cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 683 (5) [M^+ + 2], 682 (15) [M^+ + 1], 681 (14) [M^+], 680 (23), 380 (18), 300 (21), 299 (100), 298 (25). Elemental analysis of a mixture of isomers 25 and 26: $C_{42}H_{45}BNOPSSi$ (681.75): calcd. C 73.99, H 6.65, N 2.05; found C 74.04, H 6.69, N 2.01.

(+)-Diphenyl{(1*R*,2*R*)-2-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]cyclohexyl}phosphane–Borane (27) and (–)-Diphenyl{(1*S*,2*S*)-2-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]cyclohexyl}phosphane–Borane (28): According to method C, the phosphane–boranes **27** and **28** were prepared starting from the alkenyl sulfoximine **17** (375 mg, 1.59 mmol), diphenylphosphane (330 mg, 1.77 mmol) and *t*BuOK (18 mg, 590 μmol) in THF (12 mL). After complete conversion of sulfoximine **17**, BH_3·THF (3.45 mL, 3.45 mmol) was added. Work-up after the mixture was stirred for 1 h gave a mixture of **27** and **28** in a ratio of 1:1 (determined by ^{1}H NMR). Purification by column chromatography (cyclohexane/EtOAc, 85:15) afforded the phosphane–borane **27** (240 mg, 35%) as white crystalline solid and the phosphane–borane **28** (315 mg, 46%) as white foam.

27: M.p. 72 °C. $[\alpha]_D$ = +70.8 (*c* = 0.12, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.60–1.40 (br. s, 3 H, BH_3), 1.50 (m, 2 H), 1.63 (m, 1 H), 1.77 (br. d, *J* = 15.0 Hz, 1 H), 1.90–2.24 (m, 4 H), 2.67 (s, 3 H, NCH_3), 3.17 (br. dd, $^3J_{P,H}$ = 13.8, *J* = 5.8 Hz, 1 H, SC*H*), 4.57 (br. dd, $^2J_{P,H}$ = 19.6, *J* = 6.2 Hz, 1 H, SCHC*H*P), 7.49 (m, 11 H), 7.86 (m, 2 H), 8.14 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.5 (CH$_2$), 20.8 (CH$_2$), 21.8 (CH$_2$), 22.0 (d, *J* = 1.7 Hz, CH$_2$), 26.0 (d, $^1J_{P,C}$ = 30.7 Hz, CH, SCH*C*HP), 29.6 (CH$_3$, N*C*H$_3$), 58.5 (d, $^2J_{P,C}$ = 7.7 Hz, CH, S*C*H), 128.4 (d, $^1J_{P,C}$ = 56.7 Hz, 1 C, *i*-Ph), 128.5 (d, $J_{P,C}$ = 9.8 Hz, CH), 128.70 (d, $J_{P,C}$ = 10.0 Hz, 1 C), 128.72 (d, $^1J_{P,C}$ = 54.0 Hz, 1 C, *i*-Ph), 129.2 (CH), 129.7 (CH), 131.13 (CH), 131.17 (CH), 132.5 (CH), 132.6 (d, $J_{P,C}$ = 8.9 Hz, CH), 133.0 (d, $J_{P,C}$ = 8.6 Hz, CH), 136.8 (C, S*i*-Ph) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 21.98 (br. s) ppm. IR (capillary, dissolved in $CHCl_3$): ṽ = 3881 (w), 3836 (w), 3674 (w), 3632 (w), 3450 (w), 3058 (w), 3012 (w), 2935 (m), 2871 (m), 2804 (w), 2391 (s), 1560 (w), 1441 (m), 1247 (s), 1137 (s), 1105 (s), 1068 (s), 1002 (m), 868 (m), 832 (w) cm^{-1}. MS (ESI–MS, MeOH): *m*/*z* (%) = 458 [M^++23] (98), 434 [M^+ – 1] (100). $C_{25}H_{31}BNOPS$ (435.37): calcd. C 68.97, H 7.18, N 3.22; found C 68.62, H 6.97, N 2.94.

28: M.p. 48 °C. $[\alpha]_D$ = –15.9 (*c* = 1.90, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.60–1.70 (br. s, 3 H, BH_3), 1.58 (m, 3 H), 1.96 (m, 2 H), 2.25 (m, 1 H), 2.34–2.53 (m, 2 H), 2.62 (s, 3 H, NCH_3), 3.11 (br. dd, $^3J_{P,H}$ = 13.7, *J* = 5.4 Hz, 1 H, SC*H*), 3.53 (br.

dd, $^2J_{P,H}$ = 19.1, J = 6.6 Hz, 1 H, SCHC*H*P), 7.26 (m, 2 H), 7.36–7.60 (m, 11 H), 7.74 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0 (CH_2), 21.2 (CH_2), 21.8 (CH_2), 22.1 (CH_2), 27.7 (d, $^1J_{P,C}$ = 29.6 Hz, CH, SCH*C*HP), 29.7 (CH_3, N*C*H$_3$), 58.9 (d, $^2J_{P,C}$ = 7.4 Hz, CH, S*C*H), 127.8 (d, $^1J_{P,C}$ = 54.3 Hz, 1 C, *i*-Ph), 127.9 (d, $^1J_{P,C}$ = 53.0 Hz, 1 C, *i*-Ph), 128.8 (d, $J_{P,C}$ = 9.6 Hz, CH), 128.9 (d, $J_{P,C}$ = 9.8 Hz, CH), 129.5 (CH), 129.9 (CH), 131.1 (d, $J_{P,C}$ = 1.8 Hz, CH), 131.5 (d, $J_{P,C}$ = 1.8 Hz, CH), 132.5 (d, $J_{P,C}$ = 8.1 Hz, CH), 132.63 (CH), 132.63 (d, $J_{P,C}$ = 7.8 Hz, CH), 136.8 (C, S*i*-Ph) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 21.53 (br. s) ppm. IR (capillary, dissolved in $CHCl_3$): $\tilde{\nu}$ = 3940 (w), 3882 (w), 3834 (w), 3783 (w), 3662 (w), 3534 (w), 3444 (m), 3160 (w), 3058 (w), 2935 (w), 2806 (w), 2393 (s), 2280 (w), 1590 (w), 1440 (s), 1301 (w), 1234 (s), 1138 (s), 1105 (s), 1070 (s), 862 (m) cm^{-1}. MS (ESI–MS, MeOH): *m*/*z* (%) = 460 (100), 458 [M$^+$+23] (90), 434 [M$^+$ – 1] (80). $C_{25}H_{31}BNOPS$ (435.37): calcd. C 68.97, H 7.18, N 3.22; found C 69.12, H 7.26, N 3.03.

(+)-Diphenyl{(1*R*,2*R*)-2-[(*S*)-*N*-benzyl-*S*-phenylsulfonimidoyl]cyclohexyl}phosphane–Borane (29) and (–)-Diphenyl{(1*S*,2*S*)-2-[(*S*)-*N*-benzyl-*S*-phenylsulfonimidoyl]cyclohexyl}phosphane–Borane (30): According to method C, the phosphane–boranes **29** and **30** were prepared starting from the alkenyl sulfoximine **18** (1.14 g, 3.66 mmol), diphenylphosphane (718 mg, 3.86 mmol) and *t*BuOK (40 mg, 356 μmol) in THF (40 mL). After the complete conversion of sulfoximine **18**, BH_3·THF (8 mL, 8 mmol) was added. Work-up after the mixture was stirred for 1 h gave a mixture of **29** and **30** in a ratio of 1:1 (determined by ^{1}H NMR). Purification by column chromatography (cyclohexane/EtOAc, 9:1) afforded the phosphane–borane **29** (768 mg, 41%) as white crystalline solid, and the phosphane–borane **30** (730 mg, 39%) as white foam. The isomer **29** was crystallized from Et_2O at –26 °C, which gave colorless single crystals suitable for X-ray crystal structure analysis.

29: M.p. 124 °C. $[\alpha]_D$ = +50.4 (c = 0.80, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.6–1.45 (br. s, 3 H, B*H*$_3$) 1.45–1.68 (m, 3 H), 1.74 (m, 1 H), 1.92–2.32 (m, 4 H), 3.26 (dd, $^3J_{P,H}$ = 13.5, J = 5.5 Hz, 1 H, SC*H*), 3.91 (d, J = 14.3 Hz, 1 H), 4.30 (d, J = 14.3 Hz, 1 H), 4.70 (dd, $^2J_{P,H}$ = 19.5, J = 6.3 Hz, 1 H, SCHC*H*P), 7.27 (m, 3 H), 7.34–7.50 (m, 10 H), 7.55 (m, 3 H), 7.83 (m, 2 H), 8.06 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.5 (CH_2), 20.9 (CH_2), 21.9 (CH_2), 22.1 (d, $^2J_{P,C}$ = 1.7 Hz, CH_2, PCH*C*H$_2$), 26.3 (d, $^1J_{P,C}$ = 30.5 Hz, CH, SCH*C*HP), 47.1 (CH_2, N*C*H$_2$Ph), 58.7 (d, $^2J_{P,C}$ = 7.7 Hz, CH, S*C*H), 126.3 (CH), 127.4 (CH), 128.0 (CH), 128.3 (d, $^1J_{P,C}$ = 51.9 Hz, 1 C, *i*-Ph), 128.5 (d, $J_{P,C}$ = 9.7 Hz, CH), 128.60 (d, $^1J_{P,C}$ = 54.2 Hz, 1 C, *i*-Ph), 128.66 (d, $J_{P,C}$ = 9.9 Hz, CH), 129.1 (CH), 129.5 (CH), 131.0 (d, $J_{P,C}$ = 2.0 Hz, CH), 131.1 (d, $J_{P,C}$ = 2.1 Hz, CH), 132.46 (d, $J_{P,C}$ = 9.0 Hz, CH), 132.53 (CH), 132.9 (d, $J_{P,C}$ = 8.7 Hz, CH), 137.2 (C, S*i*-Ph), 141.7 (C, NCH$_2$*i*-Ph) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 21.61 (br. s) ppm. IR (KBr): $\tilde{\nu}$ = 3794 (w), 3685 (w), 3434 (m), 3051 (m), 2931 (m), 2855 (m), 2344 (w), 1611 (m), 1438 (s), 1258 (s), 1203 (m), 1123 (m), 1061 (m), 1001 (w), 880 (m), 832 (m) cm^{-1}. MS (CI, CH_4): *m*/*z* (%) = 510 (2) [M$^+$ – 1], 280 (18), 279 (100), 278 (25), 232 (86). $C_{31}H_{35}BNOPS$ (511.47): calcd. C 72.80, H 6.90, N 2.74; found C 72.60, H 6.99, N 2.62.

30: M.p. 59–61 °C. $[\alpha]_D$ = –14.5 (c = 1.03, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.6–1.51 (br. s, 3 H, B*H*$_3$), 1.51–1.71 (m, 3 H), 1.94 (m, 1 H), 2.09 (m, 1 H), 2.27 (m, 1 H), 2.37–2.58 (m, 2 H), 3.15 (dd, $^3J_{P,H}$ = 13.7, J = 5.2 Hz, 1 H, SC*H*), 3.70 (dd, $^2J_{P,H}$ = 19.0, J = 6.3 Hz, 1 H, SCHC*H*P), 3.96 (d, J = 14.8 Hz, 1 H, NC*H*$_2$), 4.24 (d, J = 14.8 Hz, 1 H, NC*H*$_2$), 7.19 (m, 1 H), 7.28 (m, 4 H), 7.33–7.50 (m, 8 H), 7.53–7.64 (m, 5 H), 7.77 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9 (CH_2), 21.1 (CH_2), 21.9 (d, $^2J_{P,C}$ = 2.3 Hz, CH_2, PCH*C*H$_2$), 22.2 (CH_2), 27.5 (d, $^1J_{P,C}$ = 29.8 Hz, CH, SCH*C*HP), 47.0 (CH_2), 59.3 (d, $^2J_{P,C}$ = 7.4 Hz, CH, S*C*H), 126.1 (CH), 127.0 (CH), 127.65 (d, $^1J_{P,C}$ = 52.6 Hz, 1 C, *i*-Ph), 127.74 (d, $^1J_{P,C}$ = 54.6 Hz, 1 C, *i*-Ph), 127.9 (CH), 128.6 (d, $J_{P,C}$ = 9.9 Hz, CH), 128.7 (d, $J_{P,C}$ = 9.9 Hz, CH), 129.2 (CH), 129.5 (CH), 130.9 (d, $J_{P,C}$ = 3.1 Hz, CH), 131.2 (d, $J_{P,C}$ = 2.3 Hz, CH), 132.41 (d, $J_{P,C}$ = 8.4 Hz, CH), 132.42 (d, $J_{P,C}$ = 8.4 Hz, CH), 132.5 (CH), 137.2 (C, S*i*-Ph), 141.4 (C, NCH$_2$*i*-Ph) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 21.70 (br. s) ppm. IR (KBr): $\tilde{\nu}$ = 3944 (m), 3930 (m), 3899 (m), 3696 (s), 3677 (s), 3612 (m), 3073 (m), 3052 (m), 2903 (m), 2871 (m), 2382 (s), 1619 (m), 1491 (w), 1438 (s), 1201 (m), 1126 (s), 1062 (s) cm^{-1}. MS (CI, isobutane): *m*/*z* (%) = 511 (7) [M$^+$], 510 (18) [M$^+$ – 1], 280 (18), 279 (92), 278 (22), 267 (14), 233 (15), 232 (100), 106 (13). HRMS (ESI-TOF): calcd. for $C_{31}H_{36}BNOPS$ [M$^+$ + H]: 512.2348; found 512.2349.

General Procedure for the Preparation of Phosphanyl Sulfoximines (Method D): (–)-Diphenyl{(1*R*)-1-phenyl-2-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]ethyl}phosphane (39): To a solution of the phosphane–borane **19** (100 mg, 218 μmol) in anhydrous and degassed toluene (3 mL) contained in a round-bottom Schlenk flask was added DABCO (26 mg, 228 μmol) at room temperature. The solution was heated at 40 °C for 2 h and the solvent was removed under reduced pressure to give a sticky solid. A short chromatographic column equipped with a Schlenk adaptor on the top and a 100 mL round-bottom Schlenk flask at the bottom was filled with silica gel. The column was kept under high vacuum for 5 min and filled with argon. This was repeated 4 times. The silica gel was wetted with Et_2O/CH_2Cl_2 (97:3) by applying a low argon pressure on the top of the column and low vacuum at the Schlenk flask. Then the sticky solid was dissolved in a minimum amount of CH_2Cl_2, and the solution was loaded on the top of the column using a syringe. The column was eluted with approximately 25 mL of Et_2O/CH_2Cl_2 (97:3) using a syringe and collected in a Schlenk flask. The Schlenk flask was disconnected from the column and the solvent was removed under high vacuo, which gave phosphane **39** (93 mg, 96%) as white solid; m.p. 146 °C. $[\alpha]_D$ = –58.0 (c = 0.10, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, NC*H*$_3$), 3.52 (ddd, J = 14.8, $^3J_{P,H}$ = 7.5, J = 1.9 Hz, 1 H, SC*H*$_2$), 3.77 (ddd, J = 14.8, J = 11.9, $^3J_{P,H}$ = 2.0 Hz, 1 H, SC*H*$_2$), 4.04 (ddd, J = 11.9, $^2J_{P,H}$ = 3.3, J = 1.9 Hz, 1 H, SCH$_2$C*H*), 6.66 (m, 2 H), 6.76 (m, 3 H), 6.91 (m, 2 H), 7.00 (m, 2 H), 7.08 (m, 3 H), 7.22 (m, 1 H), 7.35 (m, 5 H), 7.55 (2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.2 (CH_3, N*C*H$_3$), 38.4 (d, $^1J_{P,C}$ = 17.7 Hz, CH, SCH$_2$*C*H), 57.0 (d, $^2J_{P,C}$ = 24.1 Hz, S*C*H$_2$), 125.1 (d, $J_{P,C}$ = 2.5 Hz, CH), 126.6 (d, $J_{P,C}$ = 1.0 Hz, CH), 126.7 (d, $J_{P,C}$ = 6.7 Hz, CH), 127.45 (CH), 127.48 (CH), 127.7 (d, $J_{P,C}$ = 5.8 Hz, CH), 127.8 (d, $J_{P,C}$ = 4.9 Hz, CH), 127.9 (CH), 128.7 (CH), 130.8 (CH), 131.8 (d, $^2J_{P,C}$ = 18.2 Hz, CH, P*o*-Ph), 132.98 (d, $^2J_{P,C}$ = 21.0 Hz, CH, P*o*-Ph), 132.99 (d, $^1J_{P,C}$ = 11.2 Hz, 1 C, *i*-Ph), 134.0 (d, $^1J_{P,C}$ = 15.6 Hz, 1 C, *i*-Ph), 135.8 (d, $^2J_{P,C}$ = 8.1 Hz, 1 C, PCH*i*-Ph), 136.1 (C) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 1.47 (s) ppm.

(+)-Diphenyl{(1*S*)-1-phenyl-2-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-ethyl}phosphane (40): According to method D, phosphane **40** was prepared from the phosphane–borane **20** (100 mg, 218 μmol) and DABCO (26 mg, 228 μmol) in toluene (3 mL) at 40 °C for 2 h. Purification by column chromatography afforded phosphane **40** (93 mg, 94%) as white solid; m.p. 111–113 °C. $[\alpha]_D$ = +120.7 (c = 0.14, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.58 (s, 3 H, NC*H*$_3$), 3.48 (ddd, J = 14.5, $^3J_{P,H}$ = 7.6, J = 1.4 Hz, 1 H, SC*H*$_2$), 3.78 (ddd, J = 14.5, J = 12.0, $^3J_{P,H}$ = 2.3 Hz, 1 H, SC*H*$_2$), 3.90 (ddd, J = 12.0, $^2J_{P,H}$ = 2.9, J = 1.4 Hz, 1 H, SCH$_2$C*H*), 6.91 (m, 4 H), 7.05 (m, 5 H), 7.15 (m, 1 H), 7.29–7.44 (m, 7 H), 7.46–7.55 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.4 (CH_3, N*C*H$_3$),

39.9 (d, $^1J_{P,C}$ = 18.6 Hz, CH, SCH$_2$*C*H), 58.3 (d, $^2J_{P,C}$ = 23.5 Hz, CH$_2$, S*C*H$_2$), 126.4 (d, *J* = 2.5 Hz, CH), 127.7 (d, *J* = 6.5 Hz, CH), 127.9 (d, *J* = 1.2 Hz, CH), 128.4 (CH), 128.6 (d, *J* = 7.6 Hz, CH), 128.8 (CH), 128.9 (CH), 129.2 (CH), 129.6 (CH), 132.2 (CH), 132.7 (d, $^2J_{P,C}$ = 17.9 Hz, CH, P*o*-Ph), 133.94 (d, $^1J_{P,C}$ = 17.1 Hz, 1 C, *i*-Ph), 134.03 (d, $^2J_{P,C}$ = 21.1 Hz, CH, P*o*-Ph), 135.0 (d, $^1J_{P,C}$ = 16.4 Hz, 1 C, *i*-Ph), 137.3 (d, $^2J_{P,C}$ = 7.8 Hz, 1 C, PCH*i*-Ph), 137.8 (C) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ = 2.30 (s) ppm.

(–)-Diphenyl{(1*R*)-1-phenyl-2-[(*S*)-*N*-benzyl-*S*-phenylsulfonimidoyl]-ethyl}phosphane (41): According to method D, phosphane **41** was prepared from the phosphane–borane **21** (178 mg, 333 μmol) and DABCO (41 mg, 365 μmol) in toluene (5 mL) at 40 °C for 2 h. Purification by column chromatography afforded phosphane **41** (169 mg, 98%) as white solid; m.p. 157–158 °C. $[a]_D$ = –92.2 (*c* = 0.40, CH$_2$Cl$_2$). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.67 (ddd, *J* = 14.7, $^3J_{P,H}$ = 7.6, *J* = 1.6 Hz, 1 H, SC*H*$_2$), 3.87 (d, *J* = 14.7 Hz, 1 H, NC*H*$_2$Ph), 3.90 (ddd, *J* = 14.7, *J* = 12.0, $^3J_{P,H}$ = 2.0 Hz, 1 H, SC*H*$_2$), 4.01 (d, *J* = 14.7 Hz, 1 H, NC*H*$_2$Ph), 3.67 (ddd, *J* = 12.0, $^2J_{P,H}$ = 4.6, *J* = 1.6 Hz, 1 H, SCH$_2$C*H*), 6.76 (m, 2 H), 6.87 (m, 3 H), 6.96 (m, 2 H), 7.06 (m, 2 H), 7.11–7.26 (m, 8 H), 7.32 (m, 1 H), 7.43 (m, 3 H), 7.48 (m, 2 H), 7.63 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 39.4 (d, $^1J_{P,C}$ = 17.9 Hz, CH, SCH$_2$*C*H), 46.2 (CH$_2$, N*C*H$_2$Ph), 58.4 (d, $^2J_{P,C}$ = 24.0 Hz, CH$_2$, S*C*H$_2$), 126.10 (CH), 126.12 (CH), 127.2 (CH), 127.69 (CH), 127.71 (d, $J_{P,C}$ = 6.9 Hz, CH), 127.9 (CH), 128.4 (CH), 128.5 (CH), 128.7 (d, $J_{P,C}$ = 7.6 Hz, CH), 128.8 (d, $J_{P,C}$ = 6.6 Hz, CH), 128.9 (CH), 129.7 (CH), 132.0 (CH), 132.8 (d, $^2J_{P,C}$ = 18.1 Hz, CH, P*o*-Ph), 133.99 (d, $^1J_{P,C}$ = 17.7 Hz, 1 C, *i*-Ph), 134.01 (d, $^2J_{P,C}$ = 20.9 Hz, CH, P*o*-Ph), 135.1 (d, $^1J_{P,C}$ = 16.0 Hz, 1 C, *i*-Ph), 137.0 (d, $^2J_{P,C}$ = 7.9 Hz, 1 C, PCH*i*-Ph), 137.8 (C), 141.2 (C) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ = 1.67 (s) ppm.

(+)-Diphenyl{(1*S*)-1-phenyl-2-[(*S*)-*N*-benzyl-*S*-phenylsulfonimidoyl]-ethyl}phosphane (42): According to method D, phosphane **42** was prepared from the phosphane–borane **22** (100 mg, 188 μmol) and DABCO (23 mg, 205 μmol) in toluene (3 mL) at 40 °C for 2 h. Purification by column chromatography afforded phosphane **42** (92 mg, 94%) as white solid; m.p. 129 °C. $[a]_D$ = +117.27 (*c* = 0.11, CH$_2$Cl$_2$). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.47 (ddd, *J* = 14.6, $^3J_{P,H}$ = 7.8, *J* = 1.4 Hz, 1 H, SC*H*$_2$), 3.78 (ddd, *J* = 14.6, *J* = 12.0, $^3J_{P,H}$ = 1.9 Hz, 1 H, SC*H*$_2$), 3.87 (d, *J* = 14.8 Hz, 1 H, NC*H*$_2$Ph), 4.01 (br. d, *J* = 12.0 Hz, 1 H, SCH$_2$C*H*), 4.07 (d, *J* = 14.8 Hz, 1 H, NC*H*$_2$Ph), 6.80–6.90 (m, 4 H), 6.92–7.02 (m, 5 H), 7.05–7.15 (m, 2 H), 7.19 (m, 4 H), 7.25 (m, 4 H), 7.32 (m, 1 H), 7.39 (m, 3 H), 7.50 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 38.8 (d, $^1J_{P,C}$ = 18.6 Hz, CH, SCH$_2$*C*H), 45.5 (CH$_2$, N*C*H$_2$Ph), 57.7 (d, $^2J_{P,C}$ = 23.0 Hz, CH, S*C*H$_2$), 125.1 (CH), 125.3 (d, $J_{P,C}$ = 2.6 Hz, CH), 126.0 (CH), 126.7 (d, $J_{P,C}$ = 6.5 Hz, CH), 126.84 (CH), 126.85 (CH), 127.4 (CH), 127.6 (d, $J_{P,C}$ = 7.4 Hz, CH), 127.7 (CH), 127.8 (d, $J_{P,C}$ = 6.4 Hz, CH), 128.0 (CH), 128.6 (CH), 131.2 (CH), 131.7 (d, $^2J_{P,C}$ = 17.9 Hz, CH, P*o*-Ph), 132.94 (d, $^1J_{P,C}$ = 17.3 Hz, 1 C, *i*-Ph), 133.02 (d, $^2J_{P,C}$ = 21.0 Hz, CH, P*o*-Ph), 134.0 (d, $^1J_{P,C}$ = 16.4 Hz, 1 C, *i*-Ph), 136.3 (d, $J_{P,C}$ = 7.9 Hz, 1 C, PCH*i*-Ph), 137.6 (C), 140.3 (C) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ = 2.42 (s) ppm.

(+)-Diphenyl{(1*R*)-1-phenyl-2-[(*S*)-*N*-(*p*-tolylsulfonyl)-*S*-phenylsulfonimidoyl]ethyl}phosphane (43): According to method D, phosphane **43** was prepared from the phosphane–borane **23** (46 mg, 77 μmol) and DABCO (11 mg, 98 μmol) in toluene (5 mL) at 40 °C for 2 h. Purification by column chromatography afforded phosphane **43** (42 mg, 94%) as white solid; m.p. 145 °C. $[a]_D$ = +56.0 (*c* = 0.1, CH$_2$Cl$_2$). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.35 (s, 3 H, SO$_2$-*p*C*H*$_3$Ph), 3.77 (ddd, *J* = 14.4, $^3J_{P,H}$ = 6.1, *J* = 2.0 Hz, 1 H, SC*H*$_2$), 4.02 (dt, *J* = 12.3, $^2J_{P,H}$ = 2.2 Hz, 1 H, SCH$_2$C*H*), 4.17 (ddd, *J* = 14.4, *J* = 12.3, $^3J_{P,H}$ = 2.7 Hz, 1 H, SC*H*$_2$), 6.82 (m, 2 H), 6.90 (m, 2 H), 6.97 (m, 3 H), 7.06 (m, 2 H), 7.17 (m, 3 H), 7.31–7.48 (m, 5 H), 7.53 (m, 3 H), 7.60 (m, 2 H), 7.74 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 21.4 (CH$_3$, SO$_2$-*p*C*H*$_3$Ph), 40.0 (d, $^1J_{P,C}$ = 20.2 Hz, CH, SCH$_2$*C*H), 60.7 (d, $^2J_{P,C}$ = 25.9 Hz, CH$_2$, S*C*H$_2$), 126.4 (CH), 126.7 (d, $J_{P,C}$ = 2.4 Hz, CH), 127.8 (d, $J_{P,C}$ = 6.6 Hz, CH), 127.99 (CH), 128.03 (CH), 128.66 (CH), 128.76 (CH), 128.77 (CH), 128.84 (CH), 128.9 (CH), 130.0 (CH), 132.7 (d, $^2J_{P,C}$ = 18.2 Hz, CH, P*o*-Ph), 133.1 (d, $^1J_{P,C}$ = 16.8 Hz, 1 C, *i*-Ph), 133.6 (CH), 134.20 (d, $^2J_{P,C}$ = 21.7 Hz, CH, P*o*-Ph), 134.23 (d, $^1J_{P,C}$ = 15.7 Hz, 1 C, *i*-Ph), 135.6 (d, $^2J_{P,C}$ = 7.8 Hz, 1 C, PCH*i*-Ph), 137.1 (C), 140.6 (C), 142.3 (C) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ = 3.39 (s) ppm.

(–)-Diphenyl{(*R*)-1-phenyl-2-[(*S*)-*N*-(*tert*-butyldiphenylsilyl)-*S*-phenylsulfonimidoyl]ethyl}phosphane (44): According to method D, phosphane **44** was prepared starting from the phosphane–borane **25** (80 mg, 117 μmol) and DABCO (15 mg, 134 μmol) in toluene (2.5 mL) at 40 °C for 2 h. Purification by column chromatography afforded phosphane **44** (72 mg, 92%) as sticky syrup. $[a]_D$ = –61.3 (*c* = 0.16, CH$_2$Cl$_2$). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.99 [s, 9 H, C(C*H*$_3$)$_3$], 3.38 (ddd, *J* = 14.4, $^3J_{P,H}$ = 8.4, *J* = 1.1 Hz, 1 H, SC*H*$_2$), 3.67 (m, 1 H, SC*H*$_2$), 3.17 (m, 1 H, SCH$_2$C*H*), 6.66 (m, 2 H), 6.88 (m, 5 H), 7.04 (m, 4 H), 7.11–7.29 (m, 7 H), 7.30–7.45 (m, 6 H), 7.50–7.62 (m, 6 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 19.3 [C, *C*(CH$_3$)$_3$], 27.1 [CH$_3$, C(*C*H$_3$)$_3$], 39.6 (d, $^1J_{P,C}$ = 18.1 Hz, CH, SCH$_2$*C*H), 62.3 (d, $^2J_{P,C}$ = 21.1 Hz, CH$_2$, S*C*H$_2$), 126.0 (d, $J_{P,C}$ = 2.5 Hz, CH), 126.9 (CH), 127.0 (CH), 127.2 (CH), 127.6 (CH), 127.7 (d, $J_{P,C}$ = 6.6 Hz, CH), 128.0 (CH), 128.4 (CH), 128.5 (CH), 128.59 (CH), 128.65 (d, $J_{P,C}$ = 2.9 Hz, CH), 129.4 (CH), 131.3 (CH), 132.8 (d, $^2J_{P,C}$ = 18.1 Hz, CH, P*o*-Ph), 133.9 (d, $^2J_{P,C}$ = 20.5 Hz, CH, P*o*-Ph), 134.1 (d, $^1J_{P,C}$ = 9.2 Hz, 1 C, *i*-Ph), 135.2 (d, $^1J_{P,C}$ = 16.0 Hz, 1 C, *i*-Ph), 135.34 (CH), 135.37 (CH), 135.5 (C), 136.0 (C), 136.1 (C), 137.2 (d, $^2J_{P,C}$ = 8.1 Hz, 1 C, PCH*i*-Ph), 143.4 (C) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ = 2.26 (s) ppm.

(+)-Diphenyl{(*S*)-1-phenyl-2-[(*S*)-*N*-(*tert*-butyldiphenylsilyl)-*S*-phenylsulfonimidoyl]ethyl}phosphane (45): According to method D, phosphane **45** was prepared starting from the phosphane–borane **26** (118 mg, 173 μmol) and DABCO (21 mg, 187 μmol) in toluene (3 mL) at 40 °C for 2 h. Purification by column chromatography afforded phosphane **45** (107 mg, 93%) as white foam; m.p. 76 °C. $[a]_D$ = +109.0 (*c* = 0.1, CH$_2$Cl$_2$). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.04 [s, 9 H, C(C*H*$_3$)$_3$], 3.39 (ddd, *J* = 14.4, $^3J_{P,H}$ = 7.6, *J* = 1.3 Hz, 1 H, SC*H*$_2$), 3.76 (ddd, *J* = 14.4, *J* = 12.1, $^3J_{P,H}$ = 2.1 Hz, 1 H, SC*H*$_2$), 4.09 (m, 1 H, SCH$_2$C*H*), 6.60 (m, 2 H), 6.81 (m, 2 H), 6.89 (m, 3 H), 7.04 (m, 4 H), 7.15 (m, 1 H), 7.18–7.46 (m, 14 H), 7.64 (m, 2 H), 7.74 (m, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 19.4 [C, *C*(CH$_3$)$_3$], 27.2 [CH$_3$, C(*C*H$_3$)$_3$], 40.6 (d, $^1J_{P,C}$ = 18.3 Hz, CH, SCH$_2$*C*H), 62.0 (d, $^2J_{P,C}$ = 21.5 Hz, CH$_2$, S*C*H$_2$), 126.0 (d, $J_{P,C}$ = 2.5 Hz, CH), 127.0 (CH), 127.2 (CH), 127.5 (CH), 127.6 (CH), 127.7 (d, $J_{P,C}$ = 6.7 Hz, CH), 127.8 (CH), 128.4 (CH), 128.5 (CH), 128.60 (CH), 128.62 (CH), 128.67 (d, $J_{P,C}$ = 2.2 Hz, CH), 129.4 (CH), 131.3 (CH), 132.9 (d, $^2J_{P,C}$ = 18.3 Hz, CH, P*o*-Ph), 133.9 (d, $^2J_{P,C}$ = 20.8 Hz, CH, P*o*-Ph), 134.2 (d, $^1J_{P,C}$ = 17.2 Hz, 1 C, *i*-Ph), 135.2 (d, $^1J_{P,C}$ = 16.1 Hz, 1 C, *i*-Ph), 135.43 (CH), 135.46 (CH), 136.0 (C), 136.1 (C), 136.6 (d, $^2J_{P,C}$ = 7.9 Hz, 1 C, PCH*i*-Ph), 142.9 (C) ppm. ^{31}P NMR (162 MHz, CDCl$_3$): δ = 2.43 (s) ppm.

(+)-Diphenyl{(1*R*,2*R*)-2-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]cyclohexyl}phosphane (35): According to method D, phosphane **35** was prepared starting from the phosphane–borane **27** (112 mg, 258 μmol) and DABCO (32 mg, 285 μmol) in toluene (3 mL) at

40 °C for 1 h. Purification by column chromatography afforded phosphane **35** (105 mg, 97%) as white solid; m.p. 122 °C. $[\alpha]_D$ = +207.0 (c = 0.10, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (br. d, J = 14.3 Hz, 1 H), 1.56 (br. d, J = 10.3 Hz, 2 H), 1.81–2.36 (m, 5 H), 2.68 (s, 3 H, NCH_3), 3.04 (br. t, J = 6.5 Hz, 1 H, SCH), 3.94 (br. s, 1 H, SCHCHP), 7.31 (m, 6 H), 7.49 (m, 5 H), 6.65 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0 (CH_2), 21.2 (d, $J_{P,C}$ = 8.2 Hz, CH_2), 21.8 (d, $J_{P,C}$ = 5.1 Hz, CH_2), 22.7 (d, $J_{P,C}$ = 11.2 Hz, CH_2), 29.7 (CH_3, NCH_3), 30.4 (d, $^1J_{P,C}$ = 14.0 Hz, CH, SCHCHP), 60.4 (d, $^2J_{P,C}$ = 17.6 Hz, CH, SCH), 128.2 (d, $J_{P,C}$ = 7.7 Hz, CH), 128.4 (d, $J_{P,C}$ = 7.5 Hz, CH), 128.8 (CH), 128.96 (CH), 128.97 (CH), 129.6 (CH), 132.1 (CH), 133.5 (d, $J_{P,C}$ = 15.1 Hz, CH), 133.7 (d, $J_{P,C}$ = 15.2 Hz, CH), 136.2 (d, $^1J_{P,C}$ = 44.6 Hz, 1 C, *i*-Ph), 136.3 (d, $^1J_{P,C}$ = 46.4 Hz, 1 C, *i*-Ph), 137.5 (C, S*i*-Ph) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = –12.79 (s) ppm.

(–)-Diphenyl{(1*S*,2*S*)-2-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]cyclohexyl}phosphane (36): According to method D, phosphane **36** was prepared starting from the phosphane–borane **28** (71 mg, 163 μmol) and DABCO (20 mg, 178 μmol) in toluene (2.5 mL) at 40 °C for 1 h. Purification by column chromatography afforded phosphane **36** (63 mg, 91%) as sticky syrup. $[\alpha]_D$ = –11.4 (c = 0.22, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 (m, 1 H), 1.64 (m, 2 H), 1.91 (m, 1 H), 1.99–2.22 (m, 2 H), 2.55 (m, 1 H), 2.60 (s, 3 H, NCH_3), 2.70 (br. d, J = 14.2 Hz, 1 H), 2.91 (br. t, J = 6.1 Hz, 1 H, SCH), 2.99 (br. s, 1 H, SCHCHP), 7.01 (m, 2 H), 7.09 (m, 2 H), 7.23 (m, 1 H), 7.29 (m, 3 H), 7.36 (m, 2 H), 7.43 (m, 2 H), 7.58 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3 (d, $J_{P,C}$ = 7.8 Hz, CH_2), 21.61 (d, $J_{P,C}$ = 3.4 Hz, CH_2), 21.63 (CH_2), 22.2 (d, $J_{P,C}$ = 12.0 Hz, CH_2), 29.7 (CH_3, NCH_3), 31.3 (d, $^2J_{P,C}$ = 15.6 Hz, CH, SCHCHP), 60.0 (d, $^1J_{P,C}$ = 16.9 Hz, CH, SCH), 128.3 (d, $J_{P,C}$ = 7.6 Hz, CH), 128.4 (d, $J_{P,C}$ = 7.9 Hz, CH), 128.9 (CH), 129.0 (CH), 129.1 (CH), 129.8 (CH), 132.1 (CH), 133.2 (d, $J_{P,C}$ = 17.0 Hz, CH), 133.4 (d, $J_{P,C}$ = 17.6 Hz, CH), 135.4 (d, $^1J_{P,C}$ = 15.1 Hz, 1 C, *i*-Ph), 135.5 (d, $^1J_{P,C}$ = 14.8 Hz, 1 C, *i*-Ph), 136.9 (C, S*i*-Ph) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = –13.67 (s) ppm.

(+)-Diphenyl{(1*R*,2*R*)-2-[(*S*)-*N*-benzyl-*S*-phenylsulfonimidoyl]cyclohexyl}phosphane (37): According to method D, phosphane **37** was prepared starting from phosphane–borane **29** (200 mg, 391 μmol) and DABCO (48 mg, 428 μmol) in toluene (6 mL) at 40 °C for 1 h. Purification by column chromatography afforded phosphane **37** (189 mg, 97%) as white solid; m.p. 129 °C. $[\alpha]_D$ = +78.0 (c = 0.10, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.38 (m, 1 H), 1.58 (m, 2 H), 1.80 (br. d, J = 14.9 Hz, 1 H), 1.93 (m, 1 H), 2.06 (m, 1 H), 2.18 (m, 1 H), 2.38 (m, 1 H), 3.15 (m, 1 H, SCH), 3.97 (d, J = 15.0 Hz, 1 H, NCH_2Ph), 4.14 (br. s, 1 H, SCHCHP), 4.32 (d, J = 15.0 Hz, 1 H, NCH_2Ph), 7.23–7.38 (m, 9 H), 7.43 (m, 4 H), 7.51 (m, 3 H), 7.64 (m, 2 H), 7.72 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.8 (CH_2), 20.1 (d, $J_{P,C}$ = 8.0 Hz, CH_2), 20.8 (d, $J_{P,C}$ = 5.0 Hz, CH_2), 21.7 (d, $J_{P,C}$ = 11.0 Hz, CH_2), 29.4 (d, $^1J_{P,C}$ = 13.8 Hz, CH, SCHCHP), 46.0 (CH_2, NCH_2Ph), 59.4 (d, $^2J_{P,C}$ = 18.0 Hz, CH, SCH), 125.0 (CH), 126.0 (CH), 126.8 (CH), 127.3 (d, $J_{P,C}$ = 7.7 Hz, CH), 127.4 (d, $J_{P,C}$ = 7.4 Hz, CH), 127.92 (CH), 127.97 (CH), 128.04 (CH), 128.7 (CH), 131.1 (CH), 132.2 (d, $J_{P,C}$ = 10.6 Hz, CH), 132.4 (d, $J_{P,C}$ = 11.2 Hz, CH), 135.1 (d, $^1J_{P,C}$ = 30.7 Hz, 1 C, *i*-Ph), 135.3 (d, $^1J_{P,C}$ = 32.1 Hz, 1 C, *i*-Ph), 136.6 (C, S*i*-Ph), 141.0 (C, NCH_2*i*-Ph) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = –13.09 (s) ppm. MS (CI, isobutane): m/z (%) = 498 (4) [M^+ + 1], 391 (6), 268 (20), 267 (100), 266 (7). HRMS (ESI-TOF): calcd. for $C_{31}H_{34}NOPS$ [M^+ + H]: 498.2015; found 498.2009.

(–)-Diphenyl{(1*S*,2*S*)-2-[(*S*)-*N*-benzyl-*S*-phenylsulfonimidoyl]cyclohexyl}phosphane (38): According to method D, phosphane **38** was prepared starting from the phosphane–borane **30** (78 mg, 153 μmol) and DABCO (18 mg, 160 μmol) in toluene (2.5 mL) at 40 °C for 1 h. Purification by column chromatography afforded phosphane **38** (71 mg, 93%) as white solid; m.p. 89 °C. $[\alpha]_D$ = –34.0 (c = 0.10, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 (m, 1 H), 1.57–1.73 (m, 2 H), 1.93 (m, 1 H), 2.15 (m, 2 H), 2.58 (m, 1 H), 2.76 (m, 1 H), 2.98 (m, 1 H, SCH), 3.13 (br. s, 1 H, SCHCHP), 3.91 (d, J = 14.8 Hz, 1 H, NCH_2Ph), 4.23 (d, J = 14.8 Hz, 1 H, NCH_2Ph), 7.09 (m, 4 H), 7.17 (m, 1 H), 7.20–7.49 (m, 12 H), 7.56–7.65 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.3 (d, $J_{P,C}$ = 7.6 Hz, CH_2), 20.5 (CH_2), 20.8 (d, $J_{P,C}$ = 4.8 Hz, CH_2), 21.3 (d, $J_{P,C}$ = 11.8 Hz, CH_2), 30.1 (d, $^1J_{P,C}$ = 15.5 Hz, CH, SCHCHP), 46.0 (CH_2, NCH_2Ph), 59.4 (d, $^2J_{P,C}$ = 17.1 Hz, CH, SCH), 125.0 (CH), 126.1 (CH), 126.8 (CH), 127.3 (d, $J_{P,C}$ = 7.7 Hz, CH), 127.4 (d, $J_{P,C}$ = 7.8 Hz, CH), 127.45 (d, $J_{P,C}$ = 7.5 Hz, CH), 127.93 (CH), 127.98 (CH), 128.05 (CH), 128.7 (CH), 131.2 (CH), 132.2 (d, $J_{P,C}$ = 10.6 Hz, CH), 132.4 (d, $J_{P,C}$ = 11.5 Hz, CH), 134.4 (d, $^1J_{P,C}$ = 33.1 Hz, 1 C, *i*-Ph), 134.6 (d, $^1J_{P,C}$ = 33.1 Hz, 1 C, *i*-Ph), 136.8 (C, S*i*-Ph), 140.7 (C, NCH_2*i*-Ph) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = –13.48 (s) ppm.

General Procedure for the Allylic Alkylation (Method E). (+)-Dimethyl 2-[(*R*,*E*)-1,3-Diphenylallyl]malonate [(*R*)-47]: In a round-bottom Schlenk flask, $Pd_2(dba)_3{\cdot}CHCl_3$ (7.4 mg, 7 μmol) and phosphane **37** (7.1 mg, 14 μmol) were dissolved in anhydrous and degassed CH_2Cl_2 (2 mL). Then the mixture was heated at reflux for 1 h. After the mixture was warmed to room temperature, it was transferred to a Schlenk flask containing acetate *rac*-**46** (120 mg, 480 μmol). The volume of the mixture was adjusted to 3 mL through addition of CH_2Cl_2 and the mixture was treated subsequently with dimethyl malonate (138 μL, 1.19 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (320 μL, 1.19 mmol) and lithium acetate (1 mg). After the mixture was stirred for 50 min (complete conversion of acetate *rac*-**46** by TLC), it was quenched with water (3 mL) and extracted with EtOAc (3 × 3 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by column chromatography (cyclohexane/EtOAc, 9:1) gave malonate (*R*)-**47** (151 mg, 98%) with 97% *ee* {HPLC: chiralcel-OD-H column, detector 254 nm, *n*-heptane/2-propanol, 95:5, flow: 0.75 mL/min, 40 bar, R_t[(*R*)-**47**] = 15.28 min; R_t[(*S*)-**47**] = 19.53 min} as colorless viscous oil, which solidified upon standing.

(+)-(*R*)-(*E*)-Dimethyl 2-(Pent-3-en-2-yl)malonate [(*R*)-49]: According to method E, malonate (*R*)-**49** was prepared starting from acetate *rac*-**48** (61 mg, 480 μmol), phosphane **37** (7.1 mg, 14 μmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (7.4 mg, 7 μmol), dimethyl malonate (138 μL, 1.19 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (320 μL, 1.19 mmol) and lithium acetate (1 mg). After the mixture was stirred for 3.5 h (complete conversion of acetate *rac*-**48** according to TLC), it was quenched and submitted to work-up. Purification by column chromatography (*n*-pentane/Et_2O, 8:1) gave malonate (*R*)-**49** (90 mg, 95%) with 59% *ee* {GC: β-cyclodextrin CP column, R_t[(*S*)-**49**] = 32.82 min; R_t[(*R*)-**49**] = 32.92 min} as colorless viscous oil.

(+)-(*R*)-Dimethyl 2-(Cyclohex-2-enyl)malonate [(*R*)-51]: According to method E, malonate (*R*)-**51** was prepared starting from acetate *rac*-**50** (61 mg, 480 μmol), phosphane **37** (7.1 mg, 14 μmol), $Pd_2DBA_3{\cdot}CHCl_3$ (7.4 mg, 7 μmol), dimethyl malonate (138 μL, 1.19 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (320 μL, 1.19 mmol) and lithium acetate (1 mg). After the mixture was stirred for 24 h (complete conversion according to TLC), it was quenched and submitted to work-up. Purification by column chromatography (*n*-pentane/Et_2O, 10:1) gave malonate (*R*)-**51** (71 mg, 70%) with 36% *ee* {GC: β-cyclodextrin CP column, R_t[(*S*)-**51**] = 25.30 min; R_t[(*R*)-**51**] = 25.48 min} as colorless viscous oil.

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