Synthesis of Chiral α-(*N*-Sulfoximido) Phosphines, Phosphine Oxides, and Phosphonates through Hydrophosphination and Hydrophosphorylation of *N*-Vinyl Sulfoximines

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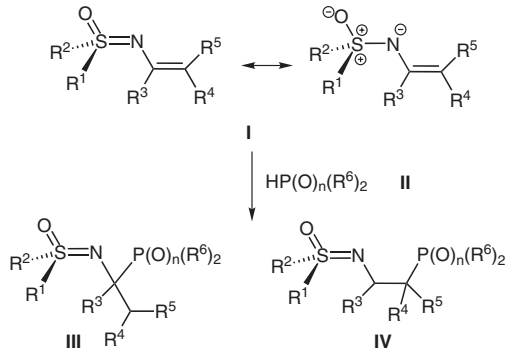
Dedicated to Professor Klaus Hafner on the occasion of his 80th birthday

Abstract: The reaction of *N*-vinyl sulfoximines with $HPPh_2$, $HP(O)Ph_2$, and $HP(O)(OMe)_2$ gave the corresponding α-(*N*-sulfoximido) phosphines, phosphine oxides, and phosphonates, respectively, with high regioselectivity in high yield. The *N*-vinyl sulfoximines showed an enamine-like regioselectivity in hydrophosphination and hydrophosphorylation (Pudovik reaction). While the acid-catalyzed hydrolysis of a cyclic *N*-vinyl sulfoximine gave the corresponding NH-sulfoximine and cyclohexanone, its hydroboration/oxidation afforded the corresponding *N*-(β-hydroxycyclohexenyl) sulfoximine. The structure of an α-(*N*-sulfoximido) phosphine was determined by X-ray crystal structure analysis.

Key words: Pudovik reaction, *N*-vinyl sulfoximines, hydrophosphination, hydrophosphorylation, phosphines, α-(*N*-sulfoximido) phosphines, α-(*N*-sulfoximido) phosphine oxides, α-(*N*-sulfoximido) phosphonates, hydroboration

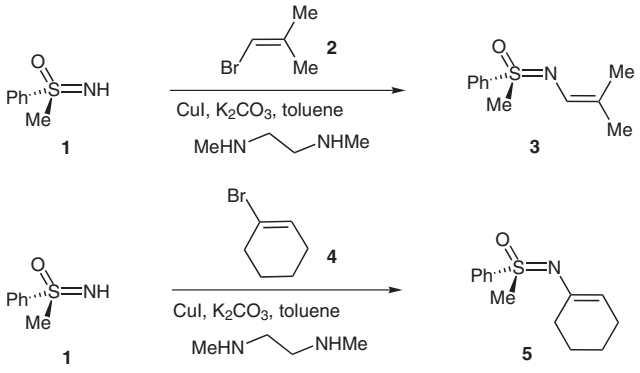
Sulfoximines have emerged as valuable chiral auxiliaries[1–4] and chiral ligands[5,6] for asymmetric synthesis. In addition sulfoximines have found important application as enzyme inhibitors[7] and peptidomimetics.[8] Recently, the *N*-vinyl sulfoximines **I** have been described, which are readily available through a palladium-catalyzed or copper-mediated coupling reaction of NH-sulfoximines with the corresponding vinyl halides or triflates (Scheme 1).[9]



Scheme 1

We decided to study the hydrophosphination and hydrophosphorylation (Pudovik reaction[10]) of *N*-vinyl sulfoximines **I** with phosphines **II**. The resulting α- or β-(*N*-sulfoximido) phosphines, phosphine oxides, and phosphonates **III** and **IV**, respectively, should both be of interest as new potential N,P-ligands for transition metals and analogues of α- and β-amino phosphonic acids. N,P-Ligands have found much application, for example, in transition-metal-catalyzed asymmetric synthesis.[11] Both α- and β-amino phosphonic acids are of significant interest as analogues of α- and β-amino acids.[12]

The *N*-vinyl sulfoximines **3**[9] and **5** of 95% purity were obtained through a copper-mediated coupling of the enantiopure *S*-configured sulfoximine **1**[13] with the corresponding bromides **2** and **4** in practically quantitative yields (Scheme 2). Despite their ready availability almost nothing was known about the reactivity of *N*-vinyl sulfoximines of type **I**. Specifically, the question whether they behave like enamines as hinted by the polar structure, which is according to ab initio calculations an appropriate representation of the electronic structure of the sulfoximine group,[14] or react as electron-withdrawing group activated alkenes, awaited experimental verification. Therefore, the reactivity of sulfoximine **5** towards water and acid was first investigated. The *N*-vinyl sulfoximine proved to be stable towards water in $CDCl_3$ at room temperature for at least 24 hours as shown by NMR spectroscopy and GC analysis. However, the addition of acetic acid to a mixture of **5** and water in $CDCl_3$ at room temperature resulted within one hour in a complete hydrolysis of the *N*-vinyl sulfoximine and gave sulfoximine **1** and ketone **6** (Scheme 3). Furthermore, an attempted chromatography of **3** and **5** on silica gel also led to a hydrolysis of the *N*-vinyl sulfoximines and the isolation of sulfoximine **1**.



Scheme 2

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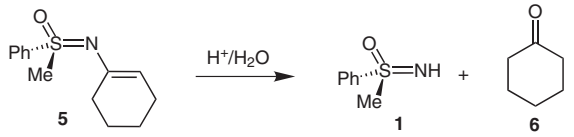
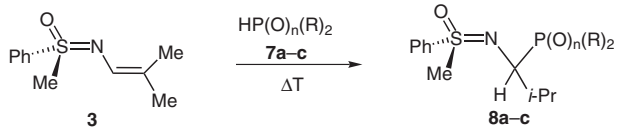


Scheme 3

Having established an enamine like reactivity of **5** towards H_2O/H^+, the reactions of the acyclic *N*-vinyl sulfoximine **3** with $HPPh_2$ (**7a**), $HP(O)Ph_2$ (**7b**) and $HP(O)(OMe)_2$ (**7c**) were studied. The treatment of **3** with 1.3 equivalents of neat **7a** at 100 °C for 48 hours resulted in complete conversion of the starting sulfoximine and gave, after the addition of BH_3·THF, a mixture of the diastereomeric α-(*N*-sulfoximido) phosphine–borane adducts (*S*)-**8aa**·BH_3 and (*R*)-**8ab**·BH_3 in a ratio of 1:1 in 87% yield (Scheme 4, Table 1). Crystallization and HPLC afforded the pure diastereomers (*S*)-**8aa**·BH_3 and (*R*)-**8ab**·BH_3. The configuration of (*S*)-**8aa**·BH_3 was determined by X-ray crystal structure analysis (Figure 1).[15]



a: n = 0, R = Ph, **b**: n = 1, R = Ph, **c**: n = 1, R = OMe

Scheme 4

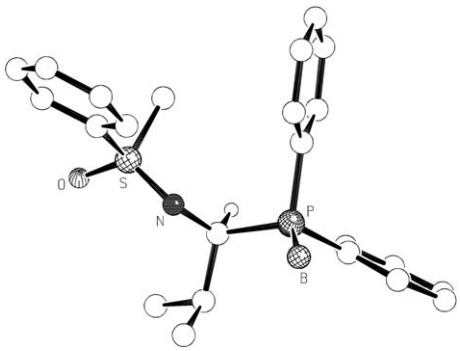


Figure 1 Structure of (*S*)-**8aa**·BH_3 in the crystal. Selected bonding parameters: S–O 1.447(2), S–N 1.517(1), C–P 1.851(2), P–B 1.929(2), S–N–C 120.9(1), P–C–N–S 130.1(1).

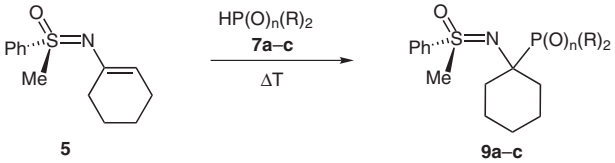
Table 1 Hydrophosphination and Hydrophosphorylation of the Acyclic *N*-Vinyl Sulfoximine **3**

Reagent	Products	Yield (%)	dr	Yield (%)	
				Major	Minor
$HPPh_2$	**8aa**, **8ab**[a]	87	1:1	40	38
$HP(O)Ph_2$	**8ba**, **8bb**	87	3:2	49	32
$HP(O)(OMe)_2$	**8ca**, **8cb**	99	3:2	56	40

[a] Isolated as the borane adduct.

A similar reaction of **3** with 1 equivalent of neat **7b** at 100 °C was complete after only 3 hours and gave a mixture of the diastereomeric α-(*N*-sulfoximido) phosphine oxides **8ba** and **8bb** in a ratio of 3:2 in 87% yield. Separation by HPLC furnished the pure diastereomers **8ba** and **8bb**. Finally, the treatment of **3** with 1.5 equivalents of neat **7c** at 100 °C for 23 hours gave a mixture of the diastereomeric α-(*N*-sulfoximido) phosphonates **8ca** and **8cb** in a ratio of 3:2 in 99% yield. Separation by HPLC afforded the pure diastereomers **8ca** and **8cb**. The addition of **7a–c** to **3** had occurred with high regioselectivity. The NMR spectra of the crude reaction mixtures gave no indication for the formation of regioisomers of type **IV**. Thus, the *N*-vinyl sulfoximine **3** showed in the Pudovik reaction with **7a–c** an enamine like reactivity[16] and gave the α-adducts of type **III** with high regioselectivity. The reactivity of **3** decreased in the order $HP(O)Ph_2 > HP(O)(OMe)_2 > HPPh_2$, which roughly parallels their acidity.[17]

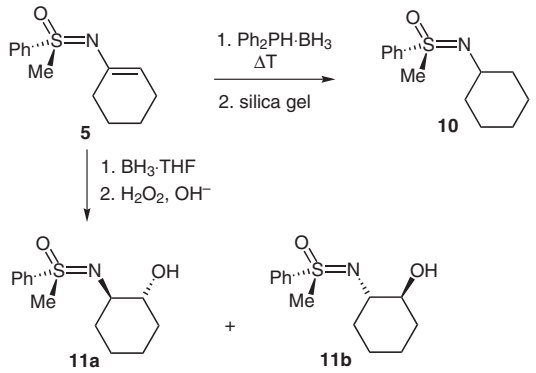
Next the reaction of the cyclic *N*-vinyl sulfoximine **5** with **7a–c** was studied. Surprisingly, the synthesis of phosphine **9a** from **5** and **7a** could not be achieved. The treatment of **5** with **7a** at 100 °C for a prolonged period of time resulted only in a low conversion of the vinyl sulfoximine to **9a** (10%) (Scheme 5). Attempts to achieve an addition of $HPPh_2$·BH_3 to the *N*-vinyl sulfoximine **5** also failed. Instead, the saturated sulfoximine **10** was directly isolated in 84% yield after chromatography of the crude reaction product on silica gel (Scheme 6). Treatment of **5** with BH_3·THF followed by an oxidation with H_2O_2 in the presence of NaOH gave the β-hydroxy sulfoximine **11** as a mixture of two diastereomers in a ratio of 2:1 in 71% yield. According to ^1H NMR spectroscopy, both diastereomers have the *trans*-configuration. These results show that BH_3 caused a highly regioselective hydroboration of the *N*-vinyl sulfoximine **5**. In contrast to **7a**, the reaction of **7b** with **5** at 100 °C proceeded cleanly and gave after a reaction time of 3 hours the α-(*N*-sulfoximido) phosphine oxide **9b** in 86% yield (Table 2). Similarly, the treatment of **5** with **7c** at 100 °C for 18 hours afforded the α-(*N*-sulfoximido) phosphonate **9c** in 96% yield. The addition of **7b** and **7c** to **5** proceeded with high regioselectivity according to NMR spectroscopy of the crude reaction mixtures.



a: n = 0, R = Ph, **b**: n = 1, R = Ph, **c**: **n** = 1, R = OMe

Scheme 5

Because of the ready synthesis of the functionalized *S*-methyl sulfoximines **8** and **9**, we became interested to see whether they can be derivatized at the methyl group through lithiation and to study the reaction of the lithiated derivatives with electrophiles.[1–3] Thus, treatment of sul-



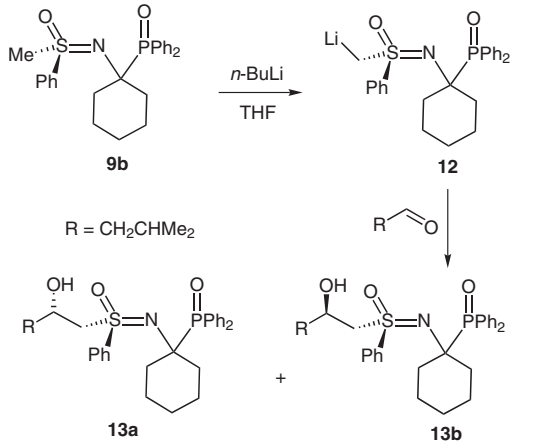
Scheme 6

Table 2 Hydrophosphorylation of the Cyclic *N*-Vinyl Sulfoximine **5**

Reagent	Product	Yield (%)
$HPPh_2$ (**7a**)	**9a**	–[a]
$HP(O)Ph_2$ (**7b**)	**9b**	86
$HP(O)OMe_2$ (**7c**)	**9c**	96

[a] Only a 10% conversion of **5** to **9a** was observed.

foximine **9b** with *n*-BuLi furnished the lithiomethyl derivative **12** which upon reaction with 3-methylbutanal afforded a mixture of the diastereomeric alcohols **13a** and **13b** in 83% yield (Scheme 7). The ratio of the diastereomers of **13**, the configuration of which was not determined, was 85:15. HPLC furnished the major diastereomer of **13** in 68% yield and the minor diastereomer of **13** in 4% yield.



Scheme 7

In conclusion, we have shown that the *N*-vinyl sulfoximines **3** and **5** readily undergo with high regioselectivity a noncatalyzed hydrophosphination and hydrophosphorylation with **7a–c** to give α-(*N*-sulfoximido) phosphines, phosphine oxides and phosphonates of type **III** in high yields. A complete conversion of **3** and **5** was only observed when the *N*-vinyl sulfoximines and the phosphines were heated without solvent at elevated temperatures. The asymmetric induction in the addition to the acyclic *N*-vinyl sulfoximine **3** was only low. It is not known, however, whether the addition of **7a–c** to **3** and **5** is kinetically or thermodynamically controlled since it might be reversible under the reaction conditions employed. The reaction of sulfoximines **3** and **5** with **7a–c** show the same regioselectivity as that of enamines. However, the Pudovik reaction of enamines has been studied only in a few cases and nothing is known about its mechanism.[16] It has been suggested that the addition of **7a–c** to imines, for example, takes place via a four-membered cyclic transition state.[10c] Therefore the addition of **7a–c** to **3** and **5** may occur by a similar mechanism. We found that the reaction of **3** and **5** with **7a–c** in the presence or in the absence of oxygen occurred with a similar high regioselectivity. Thus a radical mechanism for the reaction of **3** and **5** with **7a–c** seems unlikely. Because of the successful derivatization of sulfoximine **9b** at the *S*-methyl group via lithiation, the synthesis of interesting functionalized derivatives of **III** can be envisioned. Finally, it should be noted that hydroboration of **5** occurred readily and showed the same regioselectivity as that of enamines.[18] This suggests a perhaps facile route to cyclic *N*-(β-hydroxyalkyl) sulfoximines which are not easily accessible otherwise.[3a]

All reactions were carried out under argon with flame-dried glassware and dried solvents. Reactions involving oxygen sensitive phosphorus compounds were performed with degassed solvents (argon). Solvents were dried and purified by conventional methods before use. THF and toluene were freshly distilled from Na under N_2. Sulfoximine **1**,[13] the *N*-vinyl sulfoximine **3**[9] and bromide **4**[19] were synthesized according to the literature. All other chemicals were obtained from commercial sources. TLC was performed on silica gel 60 F_{254} aluminum sheets (Merck) with UV and iodine detection. Flash chromatography was performed on silica gel 60, 0.040–0.063 mm (Merck). Analytical HPLC was carried out on Waters 600 E UV 481 and Hewlett Packard HP 1050 instruments. Optical rotations were measured on a PerkinElmer P241 polarimeter. NMR spectra were recorded on Varian Mercury 300 and Varian Inova 400 instruments. Chemical shifts are reported relative to TMS. MS spectra were measured on a Finnigan SSQ 7000 (EI, 70 eV or CI, methane or isobutane) instrument and HRMS spectra on a Varian MAT 95 (EI, 70 eV) instrument. IR spectra were run on a Perkin Elmer FTIR 1760 S instrument. Microanalyses were obtained with a Vario EL element analyzer. Melting points were determined on a Leica melting point apparatus and are uncorrected.

(*S*)-*N*-Cyclohex-1-enyl-*S*-methyl-*S*-phenylsulfoximine (5)

A Schlenk flask was charged with CuI (1.03 g, 5.4 mmol), K_2CO_3 (1.49 g, 10.8 mmol), and (*S*)-*S*-methyl-*S*-phenylsulfoximine (**1**; 840 mg, 5.4 mmol). Subsequently, the flask was purged with argon and then toluene (50 mL), *N*,*N*′-dimethylethylenediamine (1.16 mL, 10.8 mmol), and bromide **4** (1.30 g, 8.1 mmol) were added. The mixture was heated under stirring for 20 h at 110 °C. Then, the mixture was cooled to r.t., Et_2O (50 mL) was added, and the mixture was filtered through a layer of Celite (1 cm) by washing with Et_2O (50 mL). Removal of the solvents under reduced pressure gave the *N*-vinyl sulfoximine **5** (1.25 g, 98%) as a yellow oil; $[\alpha]_D^{20}$ +137.6 (*c* 1.00, CH_2Cl_2).

IR (capillary): 2925 (s), 2839 (m), 1640 (m), 1444 (m), 1366 (w), 1243 (s), 1184 (s), 1093 (m), 1015 (m), 970 (m), 843 (w), 789 (m), 744 (s), 689 cm^{-1} (m).

^{1}H NMR (300 MHz, C_6D_6): δ = 1.24–1.47 (m, 2 H, CH_2), 1.50–1.60 (m, 2 H, CH_2), 1.76–2.05 (m, 2 H, CH_2), 2.28–2.35 (m, 2 H, CH_2), 2.65 (s, 3 H, SCH_3), 5.39–5.44 (m, 1 H, CH), 7.09–7.16 (m, 3 H, ArH), 7.88–7.97 (m, 2 H, ArH).

^{13}C NMR (75 MHz, C_6D_6): δ = 22.7 (CH_2), 23.7 (CH_2), 25.1 (CH_2), 32.1 (CH_2), 45.1 (SCH_3), 109.9 (CH), 128.6 (CH_{Ar}), 129.2 (CH_{Ar}), 132.5 (CH_{Ar}), 141.0 (C or C_{Ar}), 141.4 (C or C_{Ar}).

MS (EI, 70 eV): *m*/*z* (%) = 235 (M^+, 58), 234 (12), 173 (14), 172 (100), 157 (13), 145 (16), 144 (10), 141 (10), 140 (15), 130 (11), 125 (54), 124 (16).

Anal. Calcd for $C_{13}H_{17}NOS$ (235.10): C, 66.34; H, 7,28; N, 5.95. Found: C, 66.33; H, 7.37; N, 6.08.

(*S*)-1-*N*-[(*S*)-*S*-Methyl-*S*-phenylsulfonimidoyl]-*P*-diphenyl-*P*-(2-methylpropyl)-1-phosphine–Borane Adduct [(*S*)-8aa·BH_3] and (*R*)-1-*N*-[(*S*)-*S*-Methyl-*S*-phenylsulfonimidoyl]-*P*-diphenyl-*P*-(2-methylpropyl)-1-phosphine–Borane Adduct [(*R*)-8ab·BH_3]

A Schlenk tube (5 mL) with a screw cap was charged with the *N*-vinyl sulfoximine **3** (500 mg, 2.4 mmol) and $HPPh_2$ (**7a**; 578 mg, 3.1 mmol). The tube was purged with argon and the mixture was heated for 48 h at 100 °C. After the mixture had cooled to r.t., degassed CH_2Cl_2 (20 mL) was added and the solution was transferred to a Schlenk flask. Then borane (6 mL of 1 M in THF, 6.0 mmol) was added dropwise. After the mixture had stirred for 3 h at r.t., it was quenched by the dropwise addition of aq 2 M HCl (3 mL) under ice-bath cooling (formation of H_2 gas!). The mixture was diluted with CH_2Cl_2 (100 mL) and washed successively with aq $NaHCO_3$ (50 mL) and H_2O (50 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. Purification by flash chromatography (cyclohexane–EtOH, 80:20) gave the phosphine–borane adduct **8a**·BH_3 (859 mg, 87%) as a mixture of diastereomers in a ratio of 1:1 as a viscous colorless oil. Crystallization from cyclohexane–EtOH (92:8) furnished (*S*)-**8aa**·BH_3 (230 mg, 23%) as colorless crystals. The mother liquor was concentrated under reduced pressure. Separation by HPLC (Kromasil Si 100; 30 mm × 250 mm; cyclohexane–EtOH, 92:8; 20 mL/min) afforded (*R*)-**8ab**·BH_3 (378 mg, 38%) and (*S*)-**8aa**·BH_3 (168 mg, 17%) as colorless crystals.

(*R*)-**8aa**·BH_3

Mp 95 °C; $[\alpha]_D^{20}$ –39.3 (*c* 1.00, $CHCl_3$); R_f = 0.14 (cyclohexane–EtOH, 4:1).

IR ($CHCl_3$): 3017 (m), 2974 (w), 2853 (s), 2395 (w), 1459 (w), 1218 (s), 1151 (w), 1103 (w), 1049 (m), 879 (w), 823 (w), 787 (s), 734 (s), 670 cm^{-1} (s).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.60–1.60 (m, br, 3 H, BH_3), 0.85–0.94 (m, 6 H, CH_3), 2.29–2.41 (m, 1 H, CH), 3.05 (s, 3 H, SCH_3), 3.56–3.60 (m, 1 H, CH), 6.96–6.98 (m, 2 H, ArH), 7.24–7.31 (m, 2 H, ArH), 7.37–7.53 (m, 7 H, Ar), 7.65–7.72 (m, 2 H, ArH), 8.15–8.21 (m, 2 H, ArH).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 17.8 (CH_3), 22.9 (d, $J_{C,P}$ = 13.7 Hz, CH_3), 30.0 (d, $J_{C,P}$ = 7.6 Hz, CH), 45.6 (SCH_3), 62.6 (d, $J_{C,P}$ = 44.2 Hz, CHNP), 127.8, 127.91, 127.96, 128.05 and 128.15 (5 CH_{Ar}), 128.4 (C_{Ar}), 128.9 (CH_{Ar}), 130.1 (d, $J_{C,P}$ = 54.2 Hz, C_{Ar}), 130.6 (d, $J_{C,P}$ = 2.3 Hz, CH_{Ar}), 131.0 (d, $J_{C,P}$ = 3.2 Hz, CH_{Ar}), 132.4 (CH_{Ar}), 133.2 (d, $J_{C,P}$ = 8.4 Hz, CH_{Ar}), 134.5 (d, $J_{C,P}$ = 8.3 Hz, CH_{Ar}), 136.9 (C_{Ar}).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 22.3.

MS (EI, 70 eV): *m*/*z* (%) = 408 (M^+ – 1, 3), 211 (13), 210 (100), 141 (27).

Anal. Calcd for $C_{23}H_{29}BNOPS$ (409.18): C, 67.49; H, 7.14; N, 3.42. Found: C, 67.85; H, 6.84; N, 3.44.

(*S*)-**8ab**·BH_3

Mp 143 °C; $[\alpha]_D^{20}$ +58.0 (*c* 1.00, $CHCl_3$); R_f = 0.14 (cyclohexane–EtOH, 4:1).

IR ($CHCl_3$): 3061 (w), 2969 (w), 2926 (m), 2880 (w), 2388 (s), 2350 (m), 2285 (w), 1477 (m), 1436 (m), 1343 (w), 1249 (s), 1143 (s), 1106 (m), 1064 (m), 970 (w), 949 (m), 876 (w), 822 (w), 729 (s), 687 (s), 687 cm^{-1} (s).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.60–1.80 (m, br, 3 H, BH_3), 0.72–0.91 (m, 6 H, CH_3), 2.42–2.44 (m, 4 H, CH and SCH_3), 4.22–4.27 (m, 1 H, CH), 7.43–7.61 (m, 9 H, ArH), 7.67–7.81 (m, 4 H, ArH), 8.14–8.26 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.0 (d, $J_{C,P}$ = 1.8 Hz, CH_3), 23.2 (d, $J_{C,P}$ = 12.6 Hz, CH_3), 30.6 (d, $J_{C,P}$ = 7.8 Hz, CH), 43.7 (SCH_3), 61.0 (d, $J_{C,P}$ = 41.3 Hz, CHNP), 127.3 (CH_{Ar}), 127.5 (C_{Ar}), 128.2, 128.3, 128.4 and 128.6 (4 CH_{Ar}), 129.0 (CH_{Ar}), 130.7 (d, $J_{C,P}$ = 1.8 Hz, CH_{Ar}), 131.4 (d, $J_{C,P}$ = 1.7 Hz, CH_{Ar}), 132.7 (CH_{Ar}), 132.8 (CH_{Ar}), 134.9 ($J_{C,P}$ = 12.4 Hz, CH_{Ar}), 141.57 (C_{Ar}).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 25.7.

MS (EI, 70 eV): *m*/*z* (%) = 408 (M^+ – 1, 3), 211 (14), 210 (100), 141 (25).

Anal. Calcd for $C_{23}H_{29}BNOPS$ (409.18): C, 67.49; H, 7.14; N, 3.42. Found: C, 67.63; H, 6.90; N, 3.39.

(1*R*)-1-*N*-[(*S*)-*S*-Methyl-*S*-phenylsulfonimidoyl]-*P*-diphenyl-*P*-(2-methylpropyl)-1-phosphine Oxide [(1*R*)-8b] and (1*S*)-1-*N*-[(*S*)-*S*-Methyl-*S*-phenylsulfonimidoyl]-*P*-diphenyl-*P*-(2-methylpropyl)-1-phosphine Oxide [(1*S*)-8b]

A Schlenk tube (5 mL) with a screw cap was charged with the *N*-vinyl sulfoximine **3** (435 mg, 2.1 mmol) and $HP(O)Ph_2$ (**7b**; 420 mg, 2.1 mmol). The tube was carefully purged with argon and the mixture was heated for 3 h at 100 °C. Then the mixture was cooled to r.t. Purification by flash chromatography (EtOAc) gave the phosphine oxide **8b** (740 mg, 87%) as mixture of diastereomers in a ratio of 3:2. Separation by HPLC (cyclohexane–EtOH, 95:5); Kromasil Si 100-column, 30 mm × 250 mm; 20 mL/min) afforded the major diastereomer (423 mg, 49%) and the minor diastereomer (270 mg, 32%) as colorless crystals.

Major Diastereomer

Mp 143 °C; $[\alpha]_D^{20}$ –28.0 (*c* 1.00, CH_2Cl_2); R_f = 0.11 (EtOAc).

IR (KBr): 3058 (w), 2965 (m), 2869 (w), 2802 (w), 2344 (w), 1730 (w), 1583 (w), 1476 (w), 1441 (m), 1314 (w), 1247 (s), 1172 (s), 1097 (s), 950 (m), 874 (w), 837 (w), 747 (s), 695 cm^{-1} (s).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90–0.97 (m, 6 H, CH_3), 2.30–2.44 (m, 1 H, CH), 3.08 (s, 3 H, SCH_3), 3.41–3.48 (m, 1 H, CHNP), 6.95–6.99 (m, 2 H, ArH), 7.20–7.29 (m, 2 H, ArH), 7.40–7.56 (m, 7 H, ArH), 7.77–7.86 (m, 2 H, ArH), 8.16–8.25 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.3 (CH_3), 22.4 (d, $J_{C,P}$ = 13.1 Hz, CH_3), 29.1 (CH), 45.7 (SCH_3), 63.5 (d, $J_{C,P}$ = 90.9 Hz, CHNP), 128.0, 128.0, 128.1 and 128.2 (CH_{Ar}), 128.2 (CH_{Ar}), 129.1 (CH_{Ar}), 131.3 (CH_{Ar}), 131.5 (CH_{Ar}), 132.0 (d, $J_{C,P}$ = 8.4 Hz, CH_{Ar}), 132.6 (CH_{Ar}), 132.7 (CH_{Ar}), 133.2 and 134.4 (2 C_{Ar}), 136.8 (C_{Ar}).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 29.9.

MS (EI, 70 eV): *m*/*z* (%) = 412 (M^+ + 1, 1), 211 (13), 210 (100), 201 (13), 141 (34).

Anal. Calcd for $C_{23}H_{26}NO_2PS$ (411.14): C, 67.13; H, 6.37; N, 3.40. Found: C, 66.81; H, 6.53; N, 3.27.

Minor Diastereomer

Mp 184 °C; $[\alpha]_D^{20}$ +45.2 (*c* 1.00, CH_2Cl_2); R_f = 0.11 (EtOAc).

IR (KBr): 3058 (w), 2985 (w), 2965 (w), 2906 (m), 2876 (w), 1477 (m), 1439 (m), 1340 (w), 1248 (s), 1180 (s), 1142 (s), 1109 (s), 971 (m), 879 (m), 727 (s), 699 cm^{-1} (s).

^1H NMR (300 MHz, $CDCl_3$): δ = 0.80–0.92 (m, 6 H, CH_3), 2.25–2.38 (m, 1 H, CH), 2.46 (s, 3 H, SCH_3), 4.15–4.20 (m, 1 H, CHNP), 7.42–7.60 (m, 9 H, ArH), 7.78–7.92 (m, 4 H, ArH), 8.10–8.22 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.5 (CH_3), 22.5 (d, $J_{C,P}$ = 12.0 Hz, CH_3), 29.7 (d, $J_{C,P}$ = 3.0 Hz, CH), 44.3 (SCH_3), 60.5 (d, $J_{C,P}$ = 88.6 Hz, CHPN), 127.1 (CH_{Ar}), 128.0, 128.2, 128.3 and 128.5 (4 CH_{Ar}), 129.03 (CH_{Ar}), 131.3 (C_{Ar}), 131.5 and 131.6 (2 CH_{Ar}), 132.6 and 132.7 (2 CH_{Ar}), 134.0 (d, $J_{C,P}$ = 93.4 Hz, C_{Ar}), 142.6 (C_{Ar}).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 32.8.

MS (EI, 70 eV): *m/z* (%) = 412 (M^+ + 1, 1), 211 (13), 210 (100), 201 (14), 141 (35).

Anal. Calcd for $C_{23}H_{26}NO_2PS$ (411.14): C, 67.13; H, 6.37; N, 3.40. Found: C, 66.83; H, 6.14; N, 3.36.

(1*R*)-*P*-Dimethyl-1-*N*-[(*S*)-*S*-methyl-*S*-phenylsulfonimidoyl]-*P*-(2-methylpropyl)-1-phosphonate [(1*R*)-8c] and (1*S*)-*P*-Dimethyl-1-*N*-[(*S*)-*S*-methyl-*S*-phenylsulfonimidoyl]-*P*-(2-methylpropyl)-1-phosphonate [(1*S*)-8c]

A Schlenk tube (5 mL) with a screw cap was charged with the *N*-vinyl sulfoximine **3** (300 mg, 1.43 mmol) and $HP(O)(OMe)_2$ (**7c**; 236 mg, 2.15 mmol). The tube was carefully purged with argon and the mixture was heated for 23 h at 100 °C. Then the mixture was cooled to r.t. Purification by flash chromatography (cyclohexane–EtOH, 80:20) gave the phosphonate **8c** (450 mg, 99%) as a mixture of diastereomers in a ratio of 3:2. Separation by HPLC (cyclohexane–EtOH, 90:10; Kromasil Si 100-column, 30 mm × 250 mm; 15 mL/min) afforded the major diastereomer (254 mg, 56%) and the minor diastereomer (181 mg, 40%) as viscous oils.

Major Diastereomer

$[\alpha]_D^{20}$ +64.1 (*c* 1.00, CH_2Cl_2); R_f = 0.11 (cyclohexane–EtOH, 80:20).

IR ($CHCl_3$): 3446 (w), 2959 (s), 2853 (s), 1453 (m), 1246 (s), 1144 (m), 1038 (s), 973 (w), 884 (w), 823 (w), 749 (s), 691 cm^{-1} (w).

^1H NMR (400 MHz, $CDCl_3$): δ = 0.93–0.99 (m, 3 H, CH_3), 1.04 (d, J_3 = 6.6 Hz, 3 H, CH_3), 2.00–2.12 (m, 1 H, CH), 3.19 (s, 3 H, SCH_3), 3.50 (dd, J_3 = 4.1 Hz, $J_{H,P}$ = 14.3 Hz, 1 H, CHNP), 3.80 (d, $J_{H,P}$ = 14.1 Hz, 3 H, OCH_3), 3.85 (d, $J_{H,P}$ = 14.1 Hz, 3 H, OCH_3), 7.52–7.64 (m, 3 H, ArH), 8.00–8.05 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.4 (d, $J_{C,P}$ = 3.9 Hz, CH_3), 21.0 (d, $J_{C,P}$ = 13.7 Hz, CH_3), 30.3 (CH), 44.02 (SCH_3), 52.8 (d, $J_{C,P}$ = 7.2 Hz, OCH_3), 53.2 (d, $J_{C,P}$ = 7.2 Hz, OCH_3), 56.8 (d, $J_{C,P}$ = 161.0 Hz), 127.5 (CH_{Ar}), 128.9 (CH_{Ar}), 132.6 (CH_{Ar}), 140.5 (C_{Ar}).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.8.

MS (EI, 70 eV): *m/z* (%) = 320 (M^+ + 1, 1), 211 (14), 210 (100), 141 (52), 109 (10).

Anal. Calcd for $C_{13}H_{22}NO_4PS$ (319.10): C, 48.89; H, 6.94; N, 4.39. Found: C, 49.24; H, 7.05; N, 4.25.

Minor Diastereomer

$[\alpha]_D^{20}$ –65.5 (*c* 1.00, CH_2Cl_2); R_f = 0.11 (cyclohexane–EtOH, 80:20).

IR ($CHCl_3$): 3455 (w), 3062 (w), 2958 (s), 2875 (w), 1450 (m), 1244 (s), 1146 (m), 1038 (s), 978 (w), 881 (m), 823 (m), 789 (m), 749 (s), 691 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.04–1.07 (m, 3 H, CH_3), 1.10 (d, $J_{H,P}$ = 6.9 Hz, 3 H, CH_3), 2.20 (sept d, $J_{H,P}$ = 6.9 Hz, *J* = 3.3 Hz 1 H, H-2), 3.15 (s, 3 H, SCH_3), 3.32 (dd, *J* = 3.3 Hz, $J_{H,P}$ = 12.4 Hz, 1 H, H-1), 3.60–3.67 (m, 6 H, OCH_3), 7.52–7.64 (m, 3 H, ArH), 8.00–8.10 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.0 (CH_3), 20.1 (d, $J_{C,P}$ = 14.5 Hz, CH_3), 30.4 (CH), 45.8 (SCH_3), 52.5 (d, $J_{C,P}$ = 7.8 Hz, OCH_3), 52.71 (d, $J_{C,P}$ = 7.6 Hz, OCH_3), 57.1 (d, $J_{C,P}$ = 162.5 Hz), 128.5 (CH_{Ar}), 128.9 (CH_{Ar}), 132.6 (CH_{Ar}), 139.4 (C_{Ar}).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.1.

MS (EI, 70 eV): *m/z* (%) = 320 (M^+ + 1, 1.5), 211 (14), 210 (100), 141 (49), 109 (10).

Anal. Calcd for $C_{13}H_{22}NO_4PS$ (319.10): C, 48.89; H, 6.94; N, 4.39. Found: C, 48.49; H, 7.27; N, 4.56.

(*S*)-1-*N*-(*S*-Methyl-*S*-phenylsulfonimidoyl)-*P*-diphenyl-*P*-cyclohexyl-1-phosphine Oxide (9b)

A Schlenk tube (5 mL) with a screw cap was charged with the *N*-vinyl sulfoximine **5** (600 mg, 2.55 mmol) and $HP(O)Ph_2$ (**7b**; 516 mg, 2.55 mmol). After the tube was carefully purged with argon, the mixture was heated for 3 h at 100 °C. Then the mixture was cooled to r.t. Purification by flash chromatography (EtOAc) furnished the phosphine oxide **9b** (959 mg, 86%) as colorless crystals; mp 61 °C; $[\alpha]_D^{20}$ –27.7 (*c* 1.00, CH_2Cl_2); R_f = 0.29 (EtOH).

IR ($CHCl_3$): 3063 (w), 2938 (s), 2861 (m), 1441 (m), 1257 (s), 1163 (s), 1115 (m), 968 (w), 751 (s), 698 cm^{-1} (s).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.22–2.12 (m, 10 H, CH_2), 3.02 (s, 3 H, SCH_3), 7.14–7.30 (m, 4 H, ArH), 7.40–7.62 (m, 7 H, ArH), 7.96–8.03 (m, 2 H, ArH), 8.27–8.38 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (d, $J_{C,P}$ = 17.3 Hz, CH_2), 21.4 (CH_2), 25.0 (CH_2), 31.9 (CH_2), 34.0 (CH_2), 48.8 (SCH_3), 63.3 (d, $J_{C,P}$ = 92.2 Hz, C), 127.4 (CH_{Ar}), 127.9, 127.9, 128.0 and 128.1 (4 CH_{Ar}), 128.8 (CH_{Ar}), 130.8 (C_{Ar}), 131.1 (d, $J_{C,P}$ = 3.0 Hz, CH_{Ar}), 131.4 (d, $J_{C,P}$ = 2.4 Hz, CH_{Ar}), 132.0 (d, $J_{C,P}$ = 1.8 Hz, C_{Ar}), 132.2 (CH_{Ar}), 133.1, 133.2, 133.2 and 133.3 (4 CH_{Ar}), 144.2 (C_{Ar}).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 36.7.

MS (EI, 70 eV): *m/z* (%) = 237 (15), 236 (100), 202 (10), 201 (27), 172 (10), 96 (12), 91 (10).

MS (CI, Isobutane): *m/z* (%) = 439 (M^+ + 1, 30), 237 (15), 236 (100), 203 (63).

Anal. Calcd for $C_{25}H_{28}NO_2PS$ (437.16): C, 68.63; H, 6.45; N, 3.20. Found: C, 68.49; H, 6.41; N, 3.02.

***P*-Dimethyl-1-*N*-[(*S*)-*S*-methyl-*S*-phenylsulfonimidoyl]-*P*-cyclohexyl-1-phosphonate (9c)**

A Schlenk tube (5 mL) with a screw cap was charged with the *N*-vinyl sulfoximine **5** (100 mg, 0.42 mmol) and $HP(O)(OMe)_2$ (**7c**; 92 mg, 0.84 mmol). The tube was carefully purged with argon and the mixture was heated for 18 h at 100 °C. Then the mixture was cooled to r.t. Purification by flash chromatography (hexane–EtOH, 77:33) gave the phosphonate **9c** (137 mg, 96%) as a colorless viscous oil; $[\alpha]_D^{20}$ –21.0 (*c* 0.25, CH_2Cl_2); R_f = 0.20 (hexane–EtOH, 77:33).

IR ($CHCl_3$): 3002 (w), 2935 (s), 2853 (m), 1447 (m), 1285 (s), 1236 (s), 1166 (s), 1128 (m), 1067 (s), 1031 (s), 965 (w), 819 (s), 745 (s), 691 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.18–2.18 (m, 10 H, CH_2), 3.16 (s, 3 H, SCH_3), 3.65 (d, $J_{H,P}$ = 10.1 Hz, 3 H, OCH_3), 3.72 (d, $J_{H,P}$ = 10.1 Hz, 3 H, OCH_3), 7.48–7.58 (m, 3 H, ArH), 8.06–8.10 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8 (CH_2), 20.9 (CH_2), 25.5 (CH_2), 33.2 (CH_2), 33.8 (CH_2), 48.9 (SCH_3), 52.7 (d, $J_{C,P}$ = 7.8 Hz, OCH_3), 53.3 (d, $J_{C,P}$ = 7.8 Hz, OCH_3), 60.1 (d, $J_{C,P}$ = 158.6 Hz, CPN), 127.5 (CH_{Ar}), 128.8 (CH_{Ar}), 132.1 (CH_{Ar}), 144.4 (C_{Ar}).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 30.3.

MS (EI, 70 eV): *m*/*z* (%) = 237 (14), 236 (100), 96 (16).

MS (CI, Isobutane): *m*/*z* (%) = 346 (M + 1, 100), 236 (29).

HRMS-EI: *m*/*z* calcd for $C_{13}H_{18}NOS$ ($C_{15}H_{24}NO_4PS$ – $C_2H_6O_3P$): 236.110912; found: 236.110975 and for $C_2H_6O_3P$ ($C_{15}H_{24}NO_4PS$ – $C_{13}H_{18}NOS$): 109.005458; found: 109.005483.

(*S*)-*N*-Cyclohexyl-*S*-methyl-*S*-phenylsulfoximine (10)

A Schlenk tube (5 mL) with a screw cap was charged with the *N*-vinyl sulfoximine **5** (70 mg, 0.30 mmol) and $HPPh_2{\cdot}BH_3$ (80 mg, 0.40 mmol) was added. After the tube was carefully purged with argon, the mixture was heated for 19 h at 80 °C. Then the mixture was cooled to r.t. and applied to a silica gel column. Purification by flash chromatography (EtOAc) gave the sulfoximine **10** (59 mg, 84%) as a colorless viscous liquid; $[\alpha]_D^{20}$ –45.7 (*c* 1.00, CH_2Cl_2); R_f = 0.14 (EtOAc).

IR ($CHCl_3$): 3389 (w), 3017 (w), 2930 (s), 2854 (m), 1146 (m), 1232 (s), 1132 (m), 1082 (w), 971 (w), 885 (w), 754 (s), 669 cm^{-1} (m).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00–1.55 (m, 6 H, CH_2), 1.60–1.75 (m, 3 H, CH_2), 1.85–1.95 (m, 1 H, CH_2), 2.82–2.90 (m, 1 H, CH), 3.06 (s, 1 H, SCH_3), 7.51–7.64 (m, 3 H, ArH), 7.93–7.97 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.3 (CH_2), 25.5 (CH_2), 25.6 (CH_2), 36.4 (CH_2), 37.6 (CH_2), 45.7 (SCH_3), 54.1 (CH), 128.7 (CH_{Ar}), 129.1 (CH_{Ar}), 132.5 (CH_{Ar}), 140.7 (C_{Ar}).

MS (EI, 70 eV): *m*/*z* (%) = 237 (M^+, 49), 195 (12), 194 (100).

HRMS-EI: *m*/*z* calcd for $C_{13}H_{19}NOS$ [M]: 237.118737; found: 237.118643.

(*S*)-*N*-[(1*R*,2*R*)-2-Hydroxycyclohexyl]-*S*-methyl-*S*-phenylsulfoximine (11a) and (*S*)-*N*-[(1*S*,2*S*)-2-Hydroxycyclohexyl]-*S*-methyl-*S*-phenylsulfoximine (11b)

A Schlenk flask (50 mL) was charged with the *N*-vinyl sulfoximine **5** (100 mg, 0.42 mmol) and THF (10 mL) was added. Then the mixture was cooled to 0 °C and borane–THF complex (1.0 M in THF, 0.84 mL, 0.84 mmol) was added dropwise. The mixture was stirred first for 15 min at 0 °C and then for 2 h at r.t. After cooling the mixture to 0 °C, it was successively treated with aq NaOH (5 mL, 20%) and H_2O_2 (1 mL, 35%). Then the mixture was stirred for 2 h at r.t. It was then diluted with CH_2Cl_2 (20 mL), the organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (20 mL). The combined organic phases were washed with brine (10 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Purification and separation by flash chromatography (EtOH–cyclohexane, 1:4) gave the major diastereomer of **11** (44 mg, 41%) and the minor diastereomer of **11** (22 mg, 20%) as colorless oils.

Major Diastereomer

$[\alpha]_D^{20}$ +116.6 (*c* 1.00, CH_2Cl_2); R_f = 0.20 (EtOH–cyclohexane, 1:4).

IR (KBr): 3485 (m), 2930 (s), 2859 (s), 1447 (m), 1407 (w), 1234 (s), 1139 (s), 1079 (s), 988 (m), 961 (m), 899 (w), 842 (w), 788 (m), 747 (s), 690 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08–1.72 (m, 6 H, CH_2), 1.94–2.05 (m, 2 H, CH_2), 2.70–2.81 (m, 1 H, CHN), 3.04–3.15 (m, 4 H, SCH_3 and OH), 3.32–3.42 (m, 1 H, CHO), 7.49–7.66 (m, 3 H, ArH), 7.94–8.00 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.4 (CH_2), 24.9 (CH_2), 32.4 (CH_2), 34.9 (CH_2), 45.1 (SCH_3), 62.1 (CHN), 75.4 (CHO), 128.6 (Ar), 129.5 (Ar), 133.0 (Ar), 139.5 (Ar).

MS (EI, 70 eV): *m*/*z* (%) = 253 (M^+, 17), 194 (49), 142 (10), 141 (100), 140 (37), 125 (29), 114 (10).

HRMS-EI: *m*/*z* calcd for $C_{13}H_{19}NO_2S$: 253.113651; found: 253.113733.

Minor Diastereomer

$[\alpha]_D^{20}$ +42.2 (*c* 1.50, CH_2Cl_2); R_f = 0.13 (EtOH–cyclohexane, 1:4).

IR (KBr): 3504 (s), 3064 (w), 3013 (w), 2931 (s), 2859 (s), 1447 (m), 1406 (w), 1231 (s), 1137 (s), 1081 (s), 990 (s), 963 (m), 900 (w), 844 (m), 787 (m), 747 (s), 691 cm^{-1} (s).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01–1.80 (m, 7 H, CH_2), 1.97–2.05 (m, 1 H, CH_2), 2.52–2.64 (m, 1 H, CHN), 3.16 (s, 3 H, SCH_3), 3.26–3.34 (m, 1 H, CHO), 3.40–3.80 (br s, 1 H, OH), 7.54–7.68 (m, 3 H, ArH), 7.90–7.96 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.3 (CH_2), 25.0 (CH_2), 32.5 (CH_2), 34.6 (CH_2), 45.7 (SCH_3), 61.5 (CHN), 74.5 (CHO), 127.7 (Ar), 128.7 (Ar), 129.5 (Ar), 139.4 (Ar).

MS (EI, 70 eV): *m*/*z* (%) = 253 (M^+, 17), 194 (50), 142 (10), 141 (100), 140 (37), 125 (29), 124 (10).

HRMS-EI: *m*/*z* calcd for $C_{13}H_{19}NO_2S$: 253.113651; found: 253.113691.

1-*N*-(*S*)-[(2*S*,*S*)-2-Hydroxy-4-methylpentyl-*S*-phenylsulfonimidoyl]-*P*-diphenyl-*P*-cyclohexyl-1-phosphine Oxide (13a) and 1-*N*-(*S*)-[(2*R*,*S*)-2-Hydroxy-4-methylpentyl-*S*-phenylsulfonimidoyl]-*P*-diphenyl-*P*-cyclohexyl-1-phosphine Oxide (13b)

A Schlenk flask was charged with sulfoximine **9b** (100 mg, 0.23 mmol) and THF (5 mL) was added. After the solution was cooled to –78 °C, *n*-BuLi (1.6 M in hexane, 0.17 mL, 0.27 mmol) was added dropwise. The mixture was kept for 15 min at –78 °C and then 3-methylbutanal (50 μL, 0.46 mmol) was added. After stirring the mixture for 1 h at –78 °C, it was warmed to r.t. and stirred for 1 h. Then aq NH_4Cl (0.5 mL) and EtOAc (10 mL) were added and the organic phase was washed with H_2O (1 mL). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Purification by flash chromatography (EtOAc–cyclohexane, 1:1) gave the alcohol **13** (99 mg, 83%) as a mixture of two diastereomers in a ratio of 85:15. Separation by HPLC (EtOAc–cyclohexane, 1:1; Kromasil Si 100-column, 30 mm × 250 mm; 20 mL/min) afforded the major diastereomer of **13** (81 mg, 68%) and the minor diastereomer of **13** (5 mg, 4%) as colorless crystals.

Major Diastereomer

Mp 73 °C; $[\alpha]_D^{20}$ –8.2 (*c* 1.00, $CHCl_3$); R_f = 0.31 (EtOAc–cyclohexane, 1:1).

IR (KBr): 3505 (m), 3308 (s), 3058 (m), 2930 (s), 2864 (s), 1439 (s), 1288 (s), 1254 (s), 1156 (s), 1115 (s), 1018 (m), 895 (m), 747 (s), 723 (s), 697 cm^{-1} (s).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80–0.91 (m, 6 H, CH_3), 1.00–1.11 (m, 1 H, CH), 1.18–1.32 (m, 1 H, CH_2), 1.35–2.15 (m, 11 H, CH_2), 2.98–3.22 (m, 2 H, CH_2), 4.38–4.30 (m, 2 H, OH and CH), 7.25–7.35 (m, 3 H, ArH), 7.44–7.65 (m, 8 H, ArH), 7.87–7.99 (m, 2 H, ArH), 8.20–8.33 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 21.3 and 21.47 (3 CH_2), 21.8 (CH_3), 23.3 (CH_3), 24.1 (CH), 25.0 (CH_2), 32.7 (CH_2), 34.0 (CH_2), 45.8 (CH_2), 63.5 (d, $J_{C,P}$ = 90.3 Hz, CPN), 64.5 (CHO), 67.0 (CH_2), 127.8 (CH_{Ar}), 128.0, 128.1, 128.2 and 128.2 (4 CH_{Ar}), 128.9 (CH_{Ar}), 130.7 (C_{Ar}), 131.3 (CH_{Ar}), 131.6 (CH_{Ar}), 131.8 (d, $J_{C,P}$ = 38.7 Hz, C_{Ar}), 132.4 (CH_{Ar}), 133.0, 133.1, 133.2 (3 CH_{Ar}), 143.6 (C_{Ar}).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 37.2.

MS (EI, 70 eV): *m*/*z* (%) = 323 (33), 322 (100), 321 (15), 278 (42), 202 (19), 201 (43).

MS (CI, Isobutane): *m*/*z* (%) = 524 (M^+ + 1, 17), 323 (21), 322 (100), 203 (65).

HRMS-EI: *m/z* calcd for $C_{30}H_{38}NO_3PS$ ($C_{18}H_{28}NO_2S - C_{12}H_{10}OP$): 322.184077; found: 322.184045.

Minor Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.72 (d, J_3 = 6.9 Hz, 3 H, CH_3), 0.76 (d, J_3 = 6.6 Hz, 3 H, CH_3), 1.00–1.11 (m, 1 H, CH), 1.25–2.01 (m, 12 H, CH_2), 2.95–3.04 (d, J_3 = 4.0 Hz, 1 H, CH_2), 3.30–3.60 (m, 1 H, CH_2), 3.74–3.80 (m, 1 H, CH), 7.20–7.32 (m, 5 H, ArH), 7.48–7.65 (m, 6 H, ArH), 7.90–8.10 (m, 2 H, ArH), 8.22–8.34 (m, 2 H, ArH).

MS (EI, 70 eV): *m/z* (%) = 323 (23), 322 (100), 321 (27), 279 (16), 278 (78), 202 (31), 201 (65), 172 (12).

MS (CI, Isobutane): *m/z* (%) = 524 (M^+ + 1, 21), 405 (27), 323 (22), 322 (100), 203 (43).

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