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Access to Enantiomerically Pure *P*-Stereogenic Primary Aminophosphine Sulfides under Reductive Conditions

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Abstract: Stereochemically pure phosphines with phosphorus-heteroatom bonds and *P*-centered chirality are a promising class of functional building blocks for the design of chiral ligands and organocatalysts. A route to enantiomerically pure primary aminophosphine sulfides was opened through stereospecific reductive C–N bond cleavage of phosphorus(V) precursors by lithium in liquid ammonia. The chemoselectivity of the reaction as a function of reaction time, substrate pattern, and chiral auxiliary was investigated. In the presence of exclusively aliphatic groups bound to the phosphorus atom, all competing reductive side reactions are totally prevented. The absolute configurations of all *P*-stereogenic compounds were determined by single-crystal X-ray diffraction analysis. Their use as synthetic building blocks was demonstrated. The lithium salt of (*R*)-BINOL-dithiophosphoric acid proved to be a useful stereochemical probe to determine the enantiomeric purity. Insights into the coordination mode of the lithium-based chiral complex formed in solution was provided by NMR spectroscopy and DFT calculations.

Introduction

Phosphorus-stereogenic phosphines play a central role in asymmetric transition-metal catalysis[1] and have also been used as organocatalysts.[2] Since the seminal work on phosphine ligands with phosphorus-centered chirality by Knowles and co-workers in the late 1960s and 1970s,[3] numerous synthetic methods for the preparation of *P*-stereogenic compounds have been reported.[4] Many synthetic routes to fully carbon-substituted phosphines with stereogenic phosphorus(III) and (V) centers start from tetravalent phosphine-borane adducts[5] or phosphine sulfides and make use of a desymmetrization through kinetically controlled asymmetric deprotonation.[6] Strategies based on a thermodynamic dynamic resolution via lithiated phosphine boranes and sulfides were also reported.[7] Over the past few decades, further elegant routes toward *P*-chiral compounds have been developed. Prominent examples among them are the dynamic kinetic asymmetric oxidation of trivalent phosphines[8] and the (−)-menthol-mediated dynamic kinetic resolution of *P*-stereogenic phosphine oxides.[9] Enantioselective transition-metal-catalyzed procedures have increasingly gained in importance over the past years.[10–12] These processes are essentially based on catalytic asymmetric C–P cross-coupling reactions of secondary phosphines[10] and secondary phosphine oxides,[11] or rely on desymmetrization reactions.[12] Asymmetric organocatalytic variants of desymmetrization and coupling reactions also demonstrate the enormous research output in this field.[13]

Access strategies to *P*-stereogenic P(III) and P(V) phosphines containing additional phosphorus-heteroatom bonds are very desirable due to their great potential for the design of new types of chiral ligand systems[1] and organocatalysts.[2] However, enantiomerically pure *P*-chiral compounds in which the stereogenic phosphorus atom is directly linked to other reactive functionalities are rare and their synthesis strategies strongly limited in terms of functional group compatibility and substrate scope. Chiral auxiliary-based methods,[14] which often involve the separation of mixtures of diastereomers, are still an integral part in synthesizing structurally versatile *P*-stereogenic compounds, as these methods have the advantage of providing stereochemically pure phosphine precursors for targeted subsequent transformations.[15] In particular, *P*-stereogenic phosphinic acid and aminophosphine derivatives have proven to be highly efficient intermediates,[16] which have contributed significantly to the emergence of new areas of application in recent times.[17] Riera, Verdaguer, and co-workers opened direct access to enantiomerically pure *P*-chiral borane-protected primary aminophosphines (**A**, Figure 1, a) by reductive C–N bond cleavage of diasteromerically pure (*S*)-(−)-1-arylethylamino-functionalized phosphine borane precursors.[17d] Their method relies on the important previous work of Kolodiazhnyi et al., who already reported the diastereoselective synthesis of the used precursors.[18]

The $N–P^{+}–O^{-}$ bonding motif received much attention in asymmetric Brønsted acid[19] and Lewis base organocatalysis[20] and became a central structural feature in the catalyst design. Han et al. reported a chiral auxiliary-based multistep synthesis

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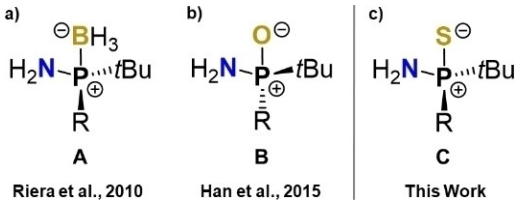


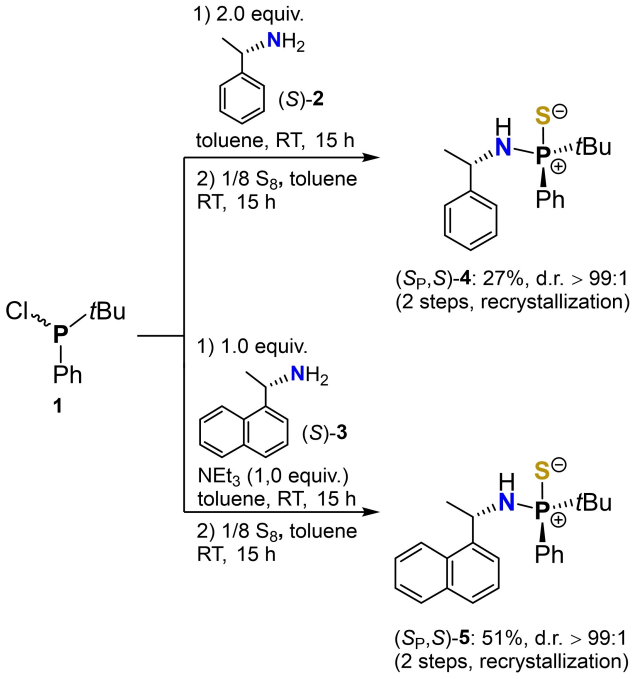
Figure 1. Previously reported enantiomerically pure *P*-stereogenic primary aminophosphines. a) Borane-protected aminophosphines (**A**).[17d] b) Aminophosphine oxides (**B**).[17j] c) Aminophosphine sulfides (**C**) reported herein.

of enantiomerically pure primary aminophosphine oxides (**B**) via benzoxazaphosphinine-2-oxide templates (Figure 1, b).[17j] This is a modification of the widely used[17c,e,g] stereoselective strategy originally developed by Jugé[21] in the way of introducing an inverted reactivity of the P–N and P–O bonds of the cyclic chiral intermediate.[15e,17j] Compounds **B** turned out to be valuable precursors for the design of new organocatalysts.[17j] However, their use in catalyst development is strongly limited probably due to the lack of convenient asymmetric synthesis methods.[22] In the context of our work on heterocyclic ring systems,[23] we became interested in stereochemically pure *P*-stereogenic phosphine sulfide moieties. Notably, we found no report in the literature of enantiomerically pure primary aminophosphine sulfides (**C**) exhibiting an $H_2N–P^+–S^-$ structural motif (Figure 1, c).

Herein, we report our studies on the reductive C–N bond cleavage of stereochemically pure *P*-stereogenic phosphorus(V) precursors by lithium dissolved in liquid ammonia to provide enantiomerically pure primary aminophosphine sulfides. We thoroughly investigated the competition between C–N bond cleavage, Birch-type reduction, P–Ph cleavage, and desulfurization in aromatic and aliphatic phosphine sulfides depending on the reaction time and the chiral auxiliary used. The use of the enantiomerically pure primary aminophosphine sulfides as synthetic building blocks was shown in an example. We also introduced a practical method to determine the enantiomeric purity of primary aminophosphine sulfides using the lithium salt of (*R*)-BINOL-dithiophosphoric acid [(*R*)-BINOL-PSSLi]. NMR spectroscopy accompanied by computational investigations of the chiral complex formed in solution provided important insights into the interplay of hydrogen-bonding and coordinative metal-ligand interactions. To the best of our knowledge, this is the first report on the synthesis of enantiomerically pure *P*-stereogenic primary aminophosphine sulfides.

Results and Discussion

In order to provide suitable stereochemically pure *P*-stereogenic precursors, we resorted to a chiral auxiliary-based method developed by Kolodiazhnyi and co-workers.[18] We first reacted racemic *tert*-butylchlorophenylphosphine (**1**) with (*S*)-(−)-1-phenylethylamine [(*S*)-**2**] and (*S*)-(−)-1-(1-naphthyl)ethylamine [(*S*)-**3**] (Scheme 1). It is known that the coupling of both racemic phosphorus(III) and phosphorus(V) chlorides with chiral amines



Scheme 1. Synthesis of the stereochemically pure phosphorus(V) precursors (S_P,*S*)-**4** and (S_P,*S*)-**5**.

and alcohols leads to unequal mixtures of both diastereomers,[17d,18,22b,24] which strongly depends on the reaction conditions.[18,24b] The phosphorus(III) intermediates were not isolated and reacted directly with elemental sulfur in a second step to compounds **4** and **5**, respectively. The diastereomeric ratios of the auxiliary-substituted phosphine sulfides were determined by means of ^{31}P and ^{1}H NMR spectroscopy. The phenyl-substituted compounds (S_P,*S*)-**4** and (S_P,*S*)-**5** were obtained in a diastereomeric ratio of 6:1 and 12:1, respectively. After fractional crystallization, the main diastereomer was obtained in stereochemically pure form for both derivatives **4** and **5**, and with overall yields of 27% [(S_P,*S*)-**4**] and 51% [(S_P,*S*)-**5**].

The absolute configuration at the stereogenic phosphorus center was determined to be S_P for both compounds by single-crystal X-ray structural analysis. Diastereomer (S_P,*S*)-**4** crystallized in the orthorhombic crystal system, space group $P2_12_12_1$, and diastereomer (S_P,*S*)-**5** in the monoclinic crystal system, space group $P2_1$ (Figure 2).

In a next step, we investigated whether a selective reductive C–N bond cleavage can be applied to the stereochemically pure phenylethyl- and naphthylethyl-substituted phosphorus(V) starting compounds (S_P,*S*)-**4** and (S_P,*S*)-**5**. At first glance, this seems to be challenging under these strongly reducing conditions as these types of compounds might also be sensitive to reduction of the phosphorus(V) center in addition to the possibility of a Birch-type reduction of the phosphorus-bound phenyl ring or even full cleavage of the P–Ph moiety. For this purpose, we first reacted compound (S_P,*S*)-**4** in a solution of lithium in liquid ammonia in the presence of *tert*-butanol for either one, two, or three minutes before quenching the reaction

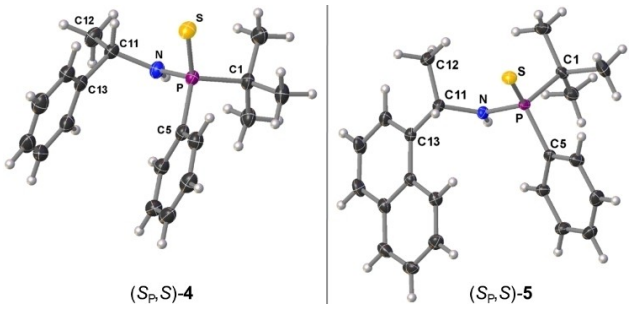


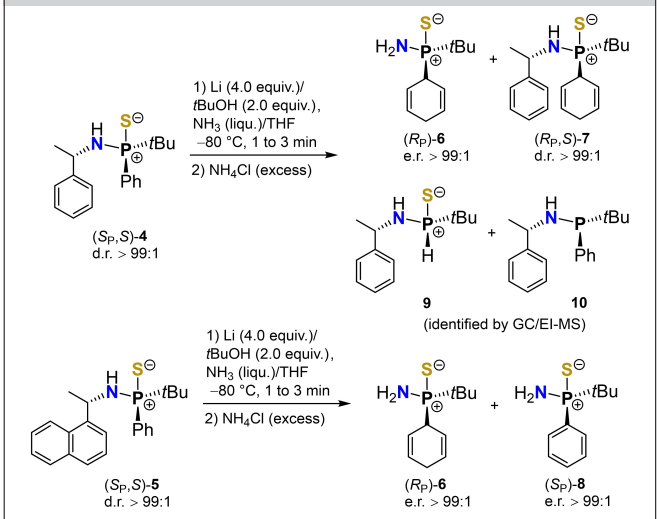
Figure 2. Molecular structures of compounds (S_P,S)-**4** and (S_P,S)-**5** in the crystal (displacement ellipsoids set at the 50% probability level).

with ammonium chloride (Table 1). We could unequivocally identify and fully characterize two main products, (R_P)-**6** and (R_P,S)-**7**, both now having a cyclohexadienyl ring bound to the phosphorus atom. Their ratios, determined by ^{31}P NMR spectroscopy, depended sensitively on the reaction time. Apparently, the Birch-type reduction[25] of the phenyl ring attached to the phosphorus atom occurs before the reductive C–N bond cleavage, a finding consistent with the observation on (*S*)-(−)-1-phenylethylamino-substituted phosphine boranes.[17d] Hence, starting from the phenylethyl-substituted phosphine sulfide (S_P,S)-**4**, the product of selective C–N bond cleavage with a still intact P–Ph group [(S_P)-**8**] was never observed. Since the phosphorus atom is unaffected in the reactions toward (R_P)-**6** and (R_P,S)-**7**, we expected the formation of both compounds to occur with retention of configuration at the stereogenic phosphorus atom. We were indeed able to isolate single crystals of (R_P,S)-**7** and (R_P)-**6** to confirm the proposed absolute configuration at the phosphorus atom by single-crystal X-ray diffraction analysis (Figure 3, top). Both compounds crystallized in the orthorhombic crystal system, space group $P2_12_12_1$.

The Birch-type reduction of phosphorus-bound phenyl rings by metals dissolved in liquid ammonia has previously been studied on phosphine boranes, which was often accompanied by P–Ph cleavage as the most important side reaction.[26] In fact, during the reaction of compound (S_P,S)-**4** with lithium/*tert*-butanol in liquid ammonia, two additional products, **9** and **10**, were obtained in a ratio of approximately 1.5:1, which remained almost constant over all reaction times between 1 to 3 min (Table 1). Species **9** and **10** together accounted for about 41% of the total products formed (for details, see the Supporting Information). GC/EI-MS analysis indicated that compound **9** was the product of a P–Ph bond cleavage, and **10** the desulfurized phosphorus(III) species. The P–S bond cleavage of phosphine sulfides by alkali metals in liquid ammonia is known.[27] The transfer of an electron from the π* orbital of a phenyl substituent to the σ* orbital of the P–S bond was thought to be an important step in the mechanism.[28] In both compounds **9** and **10**, the chiral auxiliary is still attached to the phosphorus atom. Apparently, the formation of these products competes with the Birch-type reduction of the phosphorus-bound phenyl ring right at the beginning of the reaction. Remarkably, as the reaction proceeds, the product composition depends only on the rate of the subsequent reductive C–N bond cleavage of (R_P,S)-**7**, leading to (R_P)-**6**.

The envisioned product (S_P)-**8** as a result of selective C–N bond cleavage was only formed when using the (*S*)-(−)-1-(1-naphthyl)ethylamino-substituted phosphine (S_P,S)-**5** (Table 1). One reason may be the different reduction potentials of the phenyl and naphthyl groups of (S_P,S)-**4** and (S_P,S)-**5**, respectively,

Table 1. Time-dependent product ratios formed under the reductive conditions for the cleavage of the chiral auxiliary.



Starting material	(S_P,S)-**4**		
Reaction time [min]	1	2	3
Ratio (R_P)-**6**/(R_P,S)-**7**/**9**/**10**	13:49:21:17	37:22:26:15	41:15:27:17
Starting material	(S_P,S)-**5**		
Reaction time [min]	1	2	3
Ratio (R_P)-**6**/(S_P)-**8**	34:66	38:62	53:47

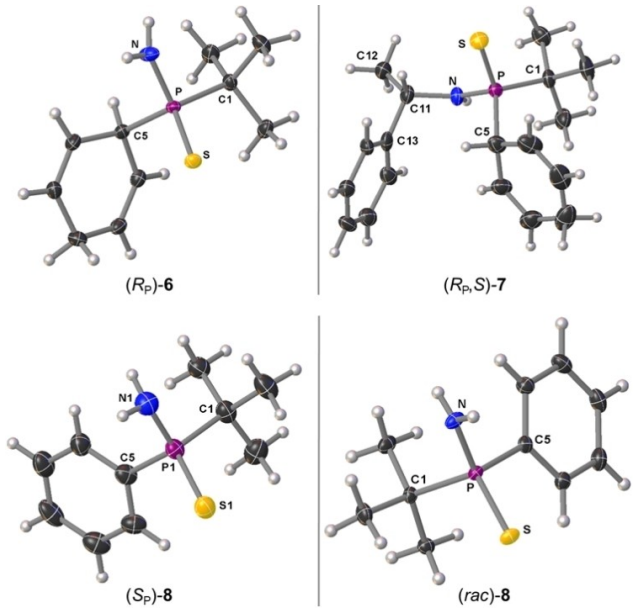


Figure 3. Molecular structures of compounds (R_P)-**6** and (R_P,S)-**7** (top), and (S_P)-**8** and (*rac*)-**8** (bottom) in the crystal (displacement ellipsoids set at the 50% probability level).

in terms of the initial formation of the radical anions.[29] Another explanation might be the higher stability of the 1-(1-naphthyl)ethide anion over the 1-phenylethide anion, which are both formed as a result of the reductive C–N bond cleavage.[29] However, different from what was described for P(III) phosphine boranes,[17d] the phenyl ring of P(V) phosphine sulfides was not necessarily spared from the Birch-type reduction just by using the naphthylethyl fragment within the intramolecular auxiliary. The longer the substrate was exposed to the reductive conditions, the more the product ratio (R_P)-**6**/(S_P)-**8** was shifted toward the Birch-type-reduced product (R_P)-**6** (34:66 after 1 min, 53:47 after 3 min) (Table 1). Smaller amounts of unspecified by-products were obtained from the reaction of compound (S_P,*S*)-**5** with lithium/*tert*-butanol in liquid ammonia, which, however, show ^{31}P NMR signals in a chemical shift range similar to that of compounds **9** and **10**.

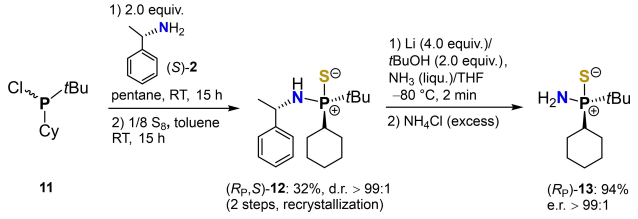
Also for compound (S_P)-**8** the absolute configuration at the stereogenic phosphorus atom could be unambiguously assigned and confirmed by single-crystal X-ray structural analysis (monoclinic crystal system, space group $P2_1$) (Figure 3, bottom). The racemic form of the compound [(*rac*)-**8**] was synthesized separately for determining the stereochemical purity of (S_P)-**8** (see below). The molecular structure of (*rac*)-**8** was also determined by single-crystal X-ray crystallography (monoclinic crystal system, space group $P2_1/n$) (Figure 3, bottom).

Although the use of the (1-naphthyl)ethylamino-patterned starting material (S_P,*S*)-**5** does in fact result in much faster C–N bond cleavage and hence reasonable amounts of the desired primary aminophenylphosphine (S_P)-**8**, the chemoselectivity of the reaction using phosphine sulfides with a phosphorus-bound phenyl group appears to be difficult to control and extremely short reaction times are required to suppress the undesired Birch-type reduction of the phenyl ring. Moreover, phosphorus(V) compounds appear to be generally more susceptible to Birch-type reduction or P–Ph cleavage by alkali metals dissolved in liquid ammonia than phosphorus(III) compounds.

We therefore set out to investigate how phosphorus(V) sulfides with only aliphatic groups bound to the phosphorus atom react under these strongly reductive conditions. For this purpose, we synthesized the cyclohexyl derivative (R_P,*S*)-**12** in two steps starting from *tert*-butylchlorocyclohexylphosphine (**11**) and (*S*)-(−)-1-phenylethylamine [(*S*)-**2**] by using the same proven methodology as outlined above (Scheme 2). Compound (R_P,*S*)-**12** was initially obtained in a diastereomeric ratio of 3:1. Recrystallization provided the diastereomerically pure precursor in 32% overall yield. Surprisingly, by replacing the phenyl group with a cyclohexyl group, the subsequent reaction of compound (R_P,*S*)-**12** with lithium in liquid ammonia proceeded with excellent chemoselectivity and led exclusively to the stereospecific C–N bond cleavage to give the desired product (R_P)-**13** in enantiomerically pure form and in a high yield of 94%. The complete absence of a P–S bond cleavage in the case of fully aliphatic substitution patterns impressively shows that a phosphorus-bound aryl group is indeed required for initiating a desulfurization process.

The stereoisomers (R_P,*S*)-**12** and (R_P)-**13** could be obtained in single-crystalline form and subjected to single-crystal X-ray structure analysis for confirming the absolute configuration at the stereogenic phosphorus atom. Compound (R_P,*S*)-**12** crystallized in the orthorhombic crystal system, space group $P2_12_12_1$, and the cleavage product (R_P)-**13** in the trigonal crystal system, space group $P3_2$ (Figure 4).

In order to determine the enantiomeric purity of compounds (S_P)-**8** and (R_P)-**13**, we first attempted a method that has previously been used for the NMR spectroscopic determination of the enantiomeric purity of silyl pyridines.[30] This method is based on the use of (*R*)-BINOL-dithiophosphoric acid [(*R*)-BINOL-PSSH][31] as Brønsted acidic chiral shift reagent. After preparation of the respective racemic compounds (*rac*)-**8** and (*rac*)-**13**, we tested the ability of (*R*)-BINOL-PSSH as stereochemical probe for our new *P*-stereogenic primary aminophosphine sulfides. However, diastereotopic discrimination could not be achieved for the racemic mixtures either in the ^{1}H or the ^{31}P NMR spectra, which is probably due to the low basicity of the H_2N–P^+–S^- unit. We therefore adapted the procedure for our aminophosphine sulfides by using the lithiated (*R*)-BINOL-dithiophosphoric acid [(*R*)-BINOL-PSSLi] (Scheme 3). Apparently, the lithium ion has an important structure-stabilizing effect and consequently leads to significant ^{1}H and ^{31}P NMR spectroscopic discrimination between the two diastereomers formed when the racemic compounds are used. The formation of a structure like **D** in dichloromethane solution was supported by quantum chemical calculations on the M062X/6-31+G(d) level of theory[32] using the polarizable continuum model (PCM)[33] (solvent: dichloromethane). The calculated structure **D**-Cy (R = cyclohexyl) of [(*R*)-BINOL-PSSLi·(R_P)-**13**] exhibits the lowest energy among all optimized, plausible structures in dichloromethane (for details, see the Supporting Information). It shows



Scheme 2. Stereospecific, reductive C–N bond cleavage of (R_P,*S*)-**12** to enantiomerically pure *P*-chiral primary aminophosphine sulfide (R_P)-**13**.

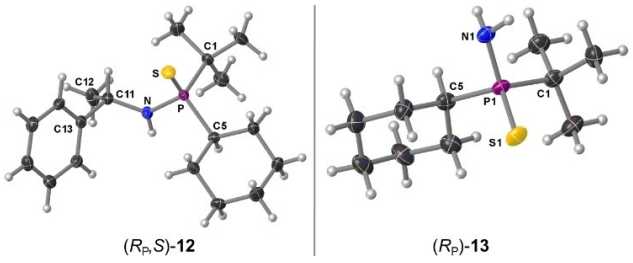
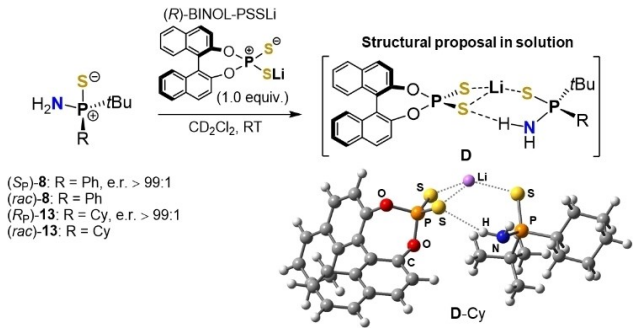


Figure 4. Molecular structures of compounds (R_P,*S*)-**12** and (R_P)-**13** in the crystal (displacement ellipsoids set at the 50% probability level).



Scheme 3. Determination of the enantiomeric purity of primary aminophosphine sulfides by NMR spectroscopy using lithiated (*R*)-BINOL-PSSH as chiral probe (top). Calculated model (**D**-Cy) of the structural proposal **D** (bottom) [M062X/6-31 + G(d); PCM solvent: dichloromethane].[32,33]

that the interplay of both coordinative and hydrogen-bonding interactions may play an important role in the formation of a rigid structure required for efficient diastereotopic discrimination (Scheme 3). A tetrahedral coordination of the lithium center and all coordination modes with an involved $H_2N\cdots Li$ interaction turned out to be energetically less favorable than structure **D**-Cy.

In **D**-Cy, the lithium center is coordinated in a trigonal-pyramidal fashion by three sulfide donor atoms. The NH_2 function appears to be involved in the structure formation via a weak N–H···S hydrogen bond. The ^{1}H NMR spectrum of compound (R_P)-**13** in the presence of (*R*)-BINOL-PSSLi in dichloromethane shows a slightly downfield-shifted NH_2 signal at 2.35 ppm compared to the broad signal of the pure compound (R_P)-**13** ($\delta = 2.12$ ppm). For compound (*rac*)-**8**, which actually shows a broad NH_2 signal at $\delta = 2.60$ ppm in dichloromethane, the presence of (*R*)-BINOL-PSSLi even leads to a splitting of the NH_2 group into two sharp slightly downfield-shifted signals at 2.69 and 2.74 ppm, probably corresponding to the two diagnostic diastereomers. These findings support an involvement of the primary amino group in the complex formation, presumably through weak hydrogen-bonding interaction with a sulfide acceptor of the dithiophosphoric acid unit according to the proposed model **D**.[34] For comparison, the NH signal of the lithium amide (*rac*)-**13**-Li in dichloromethane is considerably highfield-shifted to 0.24 ppm. Therefore, complete deprotonation of the amino function along with an HN···Li interaction in the reaction of the aminophosphine sulfide with (*R*)-BINOL-PSSLi can be excluded. This is also in accordance with acidity considerations (higher Brønsted acidity of the P–SH compared to the NH_2 function). In this context, it seems logical that the same result is also obtained if the reaction is carried out vice versa, that is, the respective lithium amide and (*R*)-BINOL-PSSH are reacted.

We also examined the sodium and potassium salts of (*R*)-BINOL-dithiophosphoric acid as well as the monolithiated (*R*)-BINOL for their ability to discriminate between the two enantiomers of *P*-stereogenic aminophosphine sulfides. However, this resulted in either no splitting at all [in the case of (*R*)-BINOL-Li] or only insufficient splitting [when using (*R*)-BINOL-PSSNa and (*R*)-BINOL-PSSK].

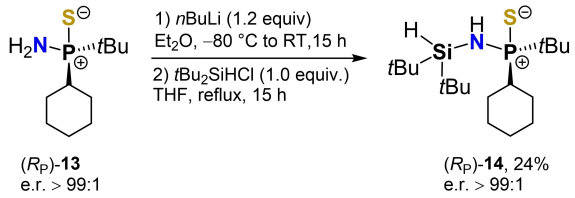
The ^{7}Li NMR spectrum of the complex formed from (*rac*)-**13** and (*R*)-BINOL-PSSLi in dichloromethane shows a signal at $\delta =$ 0.4 ppm. In order to strengthen our structural hypothesis in solution, we performed DFT calculations on the ^{7}Li NMR chemical shift for the computed complexes on the M062X/6-311 + G(2d,p)//M062X/6-31 + G(d) level of theory[32] using the gauge-independent atomic orbital (GIAO)[35] method (for details, see the Supporting Information). The calculated ^{7}Li NMR chemical shift of $\delta = 0.3$ ppm for **D**-Cy fits perfectly with the experimentally measured shift. Based on all spectroscopic and computational data, we can indeed consider complex **D** as a plausible structural proposal in dichloromethane solution (Scheme 3).

Finally, the ^{1}H and ^{31}P NMR spectra of the enantiomerically pure samples in the presence of (*R*)-BINOL-PSSLi nicely proved the stereospecificity of the reductive C–N bond cleavage and hence the enantiomeric ratios of e.r. > 99:1 of the primary aminophosphine sulfides (S_P)-**8** and (R_P)-**13** (for details, see the Supporting Information). This method, based on the lithium salt of (*R*)-BINOL-PSSH, can be a valuable spectroscopic tool for determining the enantiomeric purity of weakly basic chiral compounds or chiral substances that are sensitive to Brønsted acids.

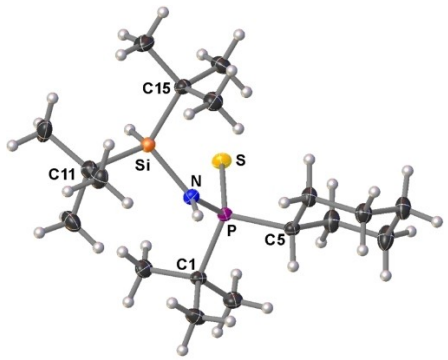
The *P*-stereogenic primary aminophosphine sulfides represent a valuable class of functional precursors that can be added to the molecular repertoire for the synthesis of new phosphine-based asymmetric catalyst systems. In order to demonstrate the applicability for further functionalization, we performed an N–Si coupling through lithiation of the enantiomerically pure compound (R_P)-**13** followed by reaction with di-*tert*-butylchlorosilane (Scheme 4). The Si–H bond of the resulting *N*-hydrosilyl-substituted phosphine sulfide (R_P)-**14** has great synthetic potential for carrying out further transformations.[23,36] Stereochemically pure compound (R_P)-**14** was isolated in single-crystalline form from a diethyl ether solution (24% yield) and characterized by single-crystal X-ray crystallography (orthorhombic crystal system, space group $P2_12_12_1$) (Figure 5).

Conclusion

In conclusion, easy synthetic access to enantiomerically pure *P*-stereogenic primary aminophosphine sulfides was opened. By a



Scheme 4. Functionalization of the primary amino group of enantiomerically pure (R_P)-**13** through lithiation and reaction with a chlorohydrosilane. The yield refers to crystalline material obtained directly from the mother liquor.



(R_P)-**14**

Figure 5. Molecular structure of compound (R_P)-**14** in the crystal (displacement ellipsoids set at the 50% probability level).

sequence of P–N coupling of racemic chlorophosphines with a chiral amine, separation of the diastereomers, and subsequent reductive C–N bond cleavage in solutions of lithium in liquid ammonia, enantiomerically pure primary aminophosphine sulfides [(R_P)-**6**, (S_P)-**8**, and (R_P)-**13**] were obtained for the first time. The competition between reductive C–N bond cleavage, Birch-type reduction, P–Ph cleavage, and desulfurization when using phenyl-substituted phosphine sulfides depending on the reaction time and the chiral auxiliary used was investigated in detail. Undesirable reductive side reactions during the cleavage of the chiral auxiliary can be completely avoided by exclusively using aliphatic substitution patterns as shown for a cyclohexyl-substituted derivative. The absolute configuration of all *P*-stereogenic compounds was determined by single-crystal X-ray crystallography and the enantiomeric purity of the primary aminophosphine sulfides determined by NMR spectroscopy using the lithium salt of (*R*)-BINOL-dithiophosphoric acid [(*R*)-BINOL-PSSLi] as an efficient chiral shift reagent. This method could be particularly useful for weakly basic or Brønsted acid-sensitive chiral substances. NMR spectroscopic and computational studies on a plausible [(*R*)-BINOL-PSSLi·(R_P)-**13**] complex in solution provided important insights into structure-forming coordination principles. The *P*-stereogenic primary aminophosphine sulfides can provide a basis for the design of new chiral ligands and organocatalysts. First steps in this direction were shown by the successful functionalization of the primary amino function by a hydrosilyl moiety.

Experimental Section

Original NMR spectra, details on the time-dependent product ratios formed under reductive conditions, details on the determination of the enantiomeric ratios, X-ray crystallographic data, and details on quantum chemical calculations are provided in the Supporting Information.

Deposition Numbers 2201330 [for (S_P,*S*)-**4**], 2201331 [for (S_P,*S*)-**5**], 2201332 [for (R_P)-**6**], 2201333 [for (R_P,*S*)-**7**], 2201334 [for (S_P)-**8**], 2201335 [for (*rac*)-**8**], 2201336 [for (R_P,*S*)-**12**], 2201337 [for (R_P)-**13**], 2202270 [for (R_P)-**14**] contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

General Remarks: All experiments were performed in an inert atmosphere of purified nitrogen by using standard Schlenk techniques or an MBraun Unilab 1200/780 glovebox. Glassware was heated at 140 °C prior to use. Dichloromethane (DCM), diethyl ether, hexane, pentane, tetrahydrofuran (THF), and toluene were dried and degassed with an MBraun SP800 solvent purification system. Ammonia (anhydrous, Staub & Co.), ammonium chloride (≥ 99.8%, Merck KGaA), *tert*-butanol (anhydrous, ≥99.5%, Merck KGaA), *n*-butyllithium (2.5 M or 1.6 M solution in hexane, Merck KGaA), *tert*-butyllithium (1.6 M solution in pentane, Merck KGaA), dichlorocyclohexylphosphine (95%, Merck KGaA), dichlorophenylphosphine (97%, Merck KGaA), di-*tert*-butylchlorosilane (97%, Merck KGaA), (*S*)-(−)-1-phenylethylamine [(*S*)-**2**] (98%, Merck KGaA), (*S*)-(−)-1-(1-naphthyl)ethylamine [(*S*)-**3**] (≥99%, Merck KGaA), lithium (granules, 99%, Merck KGaA), sulfur (99%, Merck KGaA), triethylamine (≥99%, Merck KGaA), (*R*)-(+)-1,1′-bi-2-naphthol (99%, Merck KGaA), phosphorus(V) sulfide (99%, Merck KGaA), and *m*-xylene (≥99%) were used as received without further purification. (*R*)-BINOL-dithiophosphoric acid [(*R*)-BINOL-PSSH] (99% ee) was synthesized according to a reported literature procedure.[31] *tert*-Butylchlorophenylphosphine (**1**)[37] and *tert*-butylchlorocyclohexylphosphine (**11**)[38] were synthesized according to modified literature procedures; the new protocols are presented herein. Compound (S_P,*S*)-**4** has been reported previously.[18] C_6D_6 (≥99%, Merck KGaA) and CD_2Cl_2 (≥99.8%, Fluorochem) were dried over 3 Å molecular sieves and degassed by a standard freeze-pump-thaw procedure. NMR spectra were either recorded on a Bruker Avance 400 (400.13 MHz) or on a Bruker Avance III HD 400 (400.13 MHz) at 25 °C. Chemical shifts (δ) are reported in parts per million (ppm). ^{1}H and ^{13}C{^{1}H} NMR spectra are referenced to tetramethylsilane ($SiMe_4$, $\delta = 0.0$ ppm) as external standard, with the deuterium signal of the solvent serving as internal lock and the residual solvent signal as an additional reference. ^{31}P{^{1}H} NMR spectra are referenced to 85% H_3PO_4, ^{29}Si{^{1}H} NMR spectra to $SiMe_4$, and ^{7}Li{^{1}H} NMR spectra to LiCl (1 M in D_2O). Hydrogen and carbon atoms of aromatic rings are denoted as H_{ar} and C_{ar}, respectively, or specified with the subscripts i = ipso, o = ortho, m = meta, and p = para. For the assignment of the multiplicities, the following abbreviations are used: s = singlet, d = doublet, m = multiplet, br = broad signal. Elemental analyses were performed on a Vario MICRO cube apparatus. High-resolution mass spectrometry was carried out on a Jeol AccuTOF GCX and an Agilent Q-TOF 6540 UHD spectrometer. The original NMR spectra and details on the determination of the enantiomeric purity can be found in the Supporting Information.

Single-crystal X-Ray Diffraction: The crystals were selected and measured either on an Xcalibur Gemini Ultra diffractometer, equipped with a TitanS2 detector [(S_P,*S*)-**4** and (R_P,*S*)-**7**], an XtaLAB Synergy R, DW system, equipped with a HyPix-Arc 150 detector [(S_P,*S*)-**5**, (R_P)-**6**, (*rac*)-**8**, and (R_P)-**14**], or on a SuperNova Dualflex diffractometer, equipped with a TitanS2 detector [(S_P)-**8**, (R_P,*S*)-**12**, and (R_P)-**13**]. The crystals were kept at T = 123(1) K [(S_P,*S*)-**4**, (S_P,*S*)-**5**, (R_P,*S*)-**7**, (S_P)-**8**, (R_P,*S*)-**12**, (R_P)-**13**, and (R_P)-**14**] or 100(1) K [(R_P)-**6** and (*rac*)-**8**] during data collection. Data collection and reduction were performed with CrysAlisPro, Version 1.171.41.83a [(S_P,*S*)-**4**, (S_P,*S*)-**5**, (R_P,*S*)-**7**, (R_P)-**6**, (*rac*)-**8**, (R_P,*S*)-**12** and (R_P)-**14**] or Version 1.171.41.90a [(S_P)-**8** and (R_P)-**13**].[39] For all compounds a numerical absorption correction based on Gaussian integration over a multifaceted crystal model, and an empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK scaling algorithm was applied. Using Olex2,[40] the structures were solved with ShelXT[41] and a least-square refinement on F^2 was carried out with ShelXL.[42] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were located in

idealized positions and refined isotropically according to the riding model. Hydrogen atoms at the nitrogen atoms in compounds (S_P,S)-**4**, (S_P,S)-**5**, (R_P,S)-**7**, and (R_P,S)-**12** were located in idealized positions and refined isotropically according to the riding model. Hydrogen atoms at the nitrogen atoms in compounds (R_P)-**6**, (S_P)-**8**, (*rac*)-**8**, (R_P)-**13**, and (R_P)-**14** were located from the difference Fourier map and refined without restraints. The hydrogen atom at the silicon atom was located from the difference Fourier map and refined without restraints. All figures were created with Olex2.[40] X-ray crystallographic data can be found in the Supporting Information.

Compound (S_P,S)-**4**: The asymmetric unit contains one molecule.

Compound (S_P,S)-**5**: The asymmetric unit contains one molecule.

Compound (R_P)-**6**: The asymmetric unit contains one molecule.

Compound (R_P,S)-**7**: The asymmetric unit contains one molecule. The phenyl moiety (C14, C15, C16, C17, C18) is disordered over two positions and split into two parts with occupancies of 66:34. SIMU and SADI restraints were used to model this disorder.

Compound (S_P)-**8**: The asymmetric unit contains four molecules. DFIX and DANG restraints were used for this structure.

Compound (*rac*)-**8**: The asymmetric unit contains one molecule.

Compound (R_P,S)-**12**: The asymmetric unit contains one molecule.

Compound (R_P)-**13**: The asymmetric unit contains three molecules. One of the cyclohexyl moieties (C25, C26, C27, C28) is disordered over two positions and split into two parts with occupancies of 50:50. SIMU and SADI restraints were used to model this disorder.

Compound (R_P)-**14**: The asymmetric unit contains one molecule.

DFT Calculations: Optimization and additional harmonic vibrational frequency analyses were performed with the software package Gaussian 09 (Revision E.01) on the M062X/6-31+G(d) level of theory[32] without symmetry restrictions applying the Polarizable Continuum Model (PCM)[33] [solvent: dichloromethane for **D**-Cy, **E**-Cy, **F**-Cy, **G**-Cy, and **H**-Cy, tetrahydrofuran for $(LiCl{\cdot}THF)_2$]. The GJF input files and the figures of the optimized structures were created with the program GaussView version 5.0.9.[43] For the ground state structures, the vibrational frequency analysis showed no imaginary frequency in the harmonical approximation. The relative energies (ΔG) of the computed structures are given based on the sum of electronic and thermal free energies (Gibbs energies) at 298.15 K in kJ mol^{-1}. The Hartree units were converted as follows: 1 Hartree = 2625.4995 kJ mol^{-1}.[44] The total electronic energies (SCF), the sum of electronic and zero-point energies (ZPE), the sum of electronic and thermal free energies (Gibbs energies) at 298.15 K, ^{7}Li GIAO magnetic shieldings together with the derived ^{7}Li NMR chemical shifts, and the Cartesian coordinates of the optimized structures can be found in the Supporting Information. The ^{7}Li NMR chemical shift calculations were performed with the software package Gaussian 09 (Revision E.01) on the M062X/6-311+G(2d,p) level of theory[32] applying the Gauge-Independent Atomic orbital (GIAO)[35] method on the M062X/6-31+G(d)-optimized structures. The ^{7}Li NMR chemical shifts of **D**-Cy, **E**-Cy, **F**-Cy, **G**-Cy, and **H**-Cy were calculated relative to that of $(LiCl{\cdot}THF)_2$ ($\delta = 0.5$ ppm, measured in THF).[45] The existence of the dimeric structure [$(LiCl{\cdot}THF)_2$] of LiCl in THF solution is very well supported by work from Stalke[46] and Reich.[47]

Syntheses: *tert-Butylchlorophenylphosphine (**1**).* *tert*-Butyllithium (60.0 mL of a 1.6 M solution in pentane, 96.0 mmol, 1.0 equiv.) was slowly added to a solution of dichlorophenylphosphine (17.2 g, 96.0 mmol, 1.0 equiv.) in pentane (150 mL) at −80 °C. The reaction mixture was allowed to slowly warm to room temperature and stirred for 15 h. The precipitated lithium chloride was filtered off via cannula filtration. Then, all volatiles of the filtrate were removed under vacuum. Compound **1** was obtained as a yellowish liquid (14.4 g, 71.7 mmol, 75 %). ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 0.93 [d, $^3J_{H\text{-}P}$ = 13.5 Hz, 9H, PC(CH_3)$_3$], 7.09–7.05 (m, 3H, H_{ar}), 7.58–7.53 (m, 2H, H_{ar}). ^{31}P{^{1}H} NMR (162.04 MHz, C_6D_6, 298 K): δ 108.3. ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 298 K): δ 25.2 [d, $^2J_{C\text{-}P}$ = 17.8 Hz, PC(CH_3)$_3$], 34.2 [d, $^1J_{C\text{-}P}$ = 29.9 Hz, P*C*(CH_3)$_3$], 128.1 (d, $^3J_{C\text{-}P}$ = 8.5 Hz, C_m), 130.3 (s, C_p), 132.2 (d, $^2J_{C\text{-}P}$ = 25.4 Hz, C_o), 136.1 (d, $^1J_{C\text{-}P}$ = 40.8 Hz, C_i).

*Compound (S_P,S)-**4***: Compound (*S*)-**2** (2.43 mL, 2.28 g, 18.84 mmol, 2.0 equiv.) was added to a solution of compound **1** (1.89 g, 9.42 mmol, 1.0 equiv.) in toluene (50 mL) at room temperature. After stirring for 15 h, the solids were filtered off by transferring the liquid phase via cannula filtration directly into another Schlenk tube filled with sulfur (0.30 g, 9.42 mmol, 1.0 equiv.). The reaction mixture was stirred at room temperature for 15 h. Then, all volatiles were removed under vacuum. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the crude product showed the formation of the desired product (S_P,S)-**4** in a 6:1 diastereomeric ratio. The crude product was recrystallized from toluene/hexane at 25 °C. Compound (S_P,S)-**4** (0.82 g, 2.58 mmol, 27 % overall yield, d.r. > 99:1) was obtained as colorless crystals suitable for single-crystal X-ray diffraction analysis. ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 1.05 [d, $^3J_{H\text{-}P}$ = 16.3 Hz, 9H, PC(CH_3)$_3$], 1.52 (d, $^4J_{H\text{-}P}$ = 6.7 Hz, 3H, CHCH_3), 2.33–2.29 (m, 1H, N*H*), 4.62-4.52 (m, 1H, *CH*CH$_3$), 7.10–6.92 (m, 8H, H_{ar}), 7.88–7.83 (m, 2H, H_{ar}). ^{31}P{^{1}H} NMR (162.04 MHz, C_6D_6, 298 K): δ 80.7. ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 298 K): δ 24.9 [d, $^2J_{C\text{-}P}$ = 1.4 Hz, PC(CH_3)$_3$], 26.2 (d, $^3J_{C\text{-}P}$ = 2.8 Hz, CH*C*H$_3$), 35.2 [d, $^1J_{C\text{-}P}$ = 66.7 Hz, P*C*(CH_3)$_3$], 51.5 (d, $^2J_{C\text{-}P}$ = 1.5 Hz, *C*HCH$_3$), 126.5 (s, C_{ar}), 127.0 (s, C_{ar}), 127.6 (d, $^2J_{C\text{-}P}$ = 12.0 Hz, C_o), 128.6 (s, C_{ar}), 131.1 (d, $^4J_{C\text{-}P}$ = 2.9 Hz, C_p), 132.0 (d, $^1J_{C\text{-}P}$ = 91.4 Hz, PC_i), 134.1 (d, $^3J_{C\text{-}P}$ = 10.0 Hz, C_m), 146.0 (d, $^3J_{C\text{-}P}$ = 6.1 Hz, CC_i). HR(ESI)-MS: Calcd *m/z* for $C_{18}H_{25}NPS$ [$(M+H)^+$]: 318.1440. Found: 318.1441. CHN Analysis: Calcd for $C_{18}H_{24}NPS$: C, 68.11; H, 7.62; N, 4.41. Found: C, 68.27; H, 7.51; N, 4.42.

*Compound (S_P,S)-**5***: Compound **1** (0.48 g, 2.39 mmol, 1.0 equiv.) was added to a solution of compound (*S*)-**3** (0.38 mL, 0.41 g, 2.39 mmol, 1.0 equiv.) and triethylamine (0.33 mL, 0.24 g, 2.39 mmol, 1.0 equiv.) in toluene (7 mL) at room temperature. After stirring for 15 h, the solids were filtered off by transferring the liquid phase via cannula filtration directly into another Schlenk tube filled with sulfur (0.08 g, 2.39 mmol, 1.0 equiv.). The reaction mixture was stirred at room temperature for 15 h. Then, all volatiles were removed under vacuum. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the crude product showed the formation of the desired product (S_P,S)-**5** in a 12:1 diastereomeric ratio. The crude product was recrystallized from toluene/hexane at −25 °C. Compound (S_P,S)-**5** (0.45 g, 1.22 mmol, 51 % overall yield, d.r. > 99:1) was obtained as pale beige crystals suitable for single-crystal X-ray diffraction analysis. ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 1.06 [d, $^3J_{H\text{-}P}$ = 16.3 Hz, 9H, PC(CH_3)$_3$], 1.67 (d, $^4J_{H\text{-}P}$ = 6.7 Hz, 3H, CHCH_3), 2.32 (m, 1H, N*H*), 5.37–5.48 (m, 1H, *CH*CH$_3$), 6.76–6.72 (m, 2H, H_{ar}), 6.85–6.81 (m, 1H, H_{ar}), 7.02–6.97 (m, 1H, H_{ar}), 7.14–7.12 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 1H, H_{ar}), 7.35–7.32 (m, 1H, H_{ar}), 7.45–7.44 (d, $^3J_{H\text{-}H}$ = 7.1 Hz, 1H, H_{ar}), 7.59 (dd, $^3J_{H\text{-}H}$ = 8.0, $^4J_{H\text{-}H}$ = 4.9 Hz, 2H, H_{ar}), 7.69 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 1H, H_{ar}), 7.82–7.77 (m, 2H, H_{ar}). ^{31}P{^{1}H} NMR (162.04 MHz, C_6D_6, 298 K): δ 81.2. ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 298 K): δ 24.9 [d, $^2J_{C\text{-}P}$ = 1.4 Hz, PC(CH_3)$_3$], 26.5 (d, $^3J_{C\text{-}P}$ = 1.8 Hz, CH*C*H$_3$), 35.3 [d, $^1J_{C\text{-}P}$ = 66.6 Hz, P*C*(CH_3)$_3$], 47.9 (s, *C*HCH$_3$), 122.8 (s, C_{ar}), 123.8 (s, C_{ar}), 125.6 (s, C_{ar}), 125.8 (s, C_{ar}), 126.3 (s, C_{ar}), 127.5 (d, $^2J_{C\text{-}P}$ = 12.0 Hz, C_o), 127.9 (s, C_{ar}), 128.9 (s, C_{ar}), 130.7 (s, C_{ar}), 131.1 (d, $^4J_{C\text{-}P}$ = 2.9 Hz, C_p), 131.9 (d, $^1J_{C\text{-}P}$ = 91.7 Hz, PC_i), 133.8 (d, $^3J_{C\text{-}P}$ = 10.0 Hz, C_m), 134.4 (s, C_{ar}), 142.4 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, CC_i). HR(ESI)-MS: Calcd *m/z* for $C_{22}H_{27}NPS$ [$(M+H)^+$]: 368.1596. Found: 368.1598. CHN Analysis: Calcd $C_{22}H_{26}NPS$: C, 71.90; H, 7.13; N, 3.81. Found: C, 71.64; H, 7.00; N, 3.74.

*General procedure for the reductive C–N bond cleavage of compounds (S_P,S)-**4** and (S_P,S)-**5***: Ammonia (5 mL) was condensed into a flask

containing lithium (9.0 mg, 1.28 mmol, 4.0 equiv.) at −80 °C. The mixture was stirred for 5 to 10 min while turning into a dark blue solution. Meanwhile, a solution of either (S_P,S)-**4** (0.102 g, 0.32 mmol, 1.0 equiv.) or (S_P,S)-**5** (0.118 g, 0.32 mmol, 1.0 equiv.) and *tert*-butanol (0.06 mL, 0.64 mmol, 2.0 equiv.) in THF (2.5 mL) was prepared and then added to the solution of lithium in liquid ammonia in one portion. After stirring for 1, 2, or 3 min (see Table 1), the mixture was quenched with ammonium chloride. Reaction times longer than 3 min up to 10 min led to a significant increase in undesired by-products. After quenching, the cooling bath was removed allowing ammonia to evaporate. The crude mixture was extracted with diethyl ether (1×5 mL, 2×2.5 mL) and the solids removed via cannula filtration. All volatiles were removed under vacuum and the ratios of the products [(R_P)-**6**/(R_P,S)-**7**/**9**/**10** or (R_P)-**6**/(S_P)-**8**, depending on the starting compound used] in the crude mixture determined by $^{31}P\{^1H\}$ NMR spectroscopy (see Table 1 in the paper and the Supporting Information). Separation attempts using Kugelrohr distillation were challenging and mostly resulted in mixed fractions of the products. However, very few crystals of pure (R_P)-**6**, (S_P)-**8**, and (R_P,S)-**7**, suitable for single-crystal X-ray diffraction analysis, could be obtained. Crystals of (R_P)-**6** were obtained from the crude reaction mixture of the reduction of (S_P,S)-**4** after 3 min reaction time. The crude product mixture was dissolved in diethyl ether (5 mL) and the solvent was slowly evaporated from a half-sealed vial at room temperature for two days until colorless crystalline needles of (R_P)-**6** were formed. Crystals of (R_P,S)-**7** were obtained from the crude reaction mixture of the reduction of (S_P,S)-**4** after 1 min reaction time. The crude product was dissolved in diethyl ether (2 mL) and the solvent was slowly evaporated from a half-sealed vial at room temperature for two days until colorless crystalline blocks of (R_P,S)-**7** were formed. Crystals of (S_P)-**8** were obtained from the crude reaction mixture of the reduction of (S_P,S)-**5** after 1 min reaction time. After dissolving the crude product in dichloromethane (2 mL), the solution was slowly layered with pentane (4 mL) and stored at −35 °C in a sealed vial for four weeks until colorless crystalline blocks of (S_P)-**8** were formed. The crystalline material of compounds (R_P)-**6**, (R_P,S)-**7**, and (S_P)-**8** was sufficient to obtain all analytical data (NMR spectroscopy, elemental analysis, high-resolution mass spectrometry, and X-ray crystallography). The enantiomeric purity of crude compound (S_P)-**8** was determined by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy in the presence of (*R*)-BINOL-PSSLi (99% ee) in CD_2Cl_2 (for details, see the Supporting Information). Compounds **9** and **10** were identified by GC/EI-MS analysis. For this purpose, a diethyl ether extract of the crude mixture of the reaction of compound (S_P,S)-**4** with lithium/*tert*-butanol in liquid ammonia after 3 min reaction time was subjected to GC/EI-MS analysis.

*Compound (R_P)-**6***: ^1H NMR (400.13 MHz, C_6D_6, 298 K): δ 1.09 [d, $^3J_{H\text{-}P}$ = 16.0 Hz, 9H, PC(CH_3)$_3$], 1.60 (br, 2H, NH_2), 2.36–2.32 (m, 1H, C*H*), 2.41–2.38 (m, 1H, C*H*), 3.41–3.30 (m, 1H, C*H*), 5.58-5.52 (m, 1H, C*H*), 5.66–5.61 (m, 1H, C*H*), 5.80–5.76 (m, 1H, C*H*), 6.04–5.99 (m, 1H, C*H*). $^{31}P\{^1H\}$ NMR (162.04 MHz, C_6D_6, 298 K): δ 81.2. $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 298 K): δ 55.9 [d, $^2J_{C\text{-}P}$ = 0.9 Hz, PC(CH$_3$)$_3$], 26.7 (d, $^4J_{C\text{-}P}$ = 6.1 Hz, CH_2), 37.3 [d, $^1J_{C\text{-}P}$ = 59.2 Hz, P*C*(CH$_3$)$_3$], 43.7 (d, $^1J_{C\text{-}P}$ = 53.5 Hz, PCH), 123.3 (d, $^3J_{C\text{-}P}$ = 6.5 Hz, *C*H), 123.6 (d, $^3J_{C\text{-}P}$ = 7.2 Hz, *C*H), 126.7 (d, $^2J_{C\text{-}P}$ = 10.0 Hz, *C*H), 127.5 (d, $^2J_{C\text{-}P}$ = 9.9 Hz, *C*H). HR(ESI)-MS: Calcd *m/z* for $C_{10}H_{19}NPS$ [(M + H)$^+$]: 216.0970. Found: 216.0973. CHN Analysis: Calcd for $C_{10}H_{18}NPS$: C, 55.79; H, 8.43; N, 6.51. Found: C, 56.36; H, 8.28; N, 6.27.

*Compound (R_P,S)-**7***: ^1H NMR (400.13 MHz, C_6D_6, 298 K): δ 1.17 [d, &bk$^3J_{H\text{-}P}$ = 15.9 Hz, 9H, PC(CH_3)$_3$], 1.35 (d, $^4J_{H\text{-}P}$ = 6.8 Hz, 3H, CHCH_3), 2.04–1.87 (m, 1H, N*H*), 2.27–2.14 (m, 2H, CH_2), 3.39–3.26 (m, 1H, C*H*), 5.08–4.97 (m, 1H, C*H*), 5.45–5.39 (m, 2H, C*H*), 5.88-5.83 (m, 1H, C*H*), 5.98–5.92 (m, 1H, C*H*), 7.05–7.01 (m, 1H, H_{ar}), 7.12–7.08 (m, 2H, H_{ar}), 7.23–7.20 (m, 2H, H_{ar}). $^{31}P\{^1H\}$ NMR (162.04 MHz, C_6D_6, 298 K): δ 82.6. $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 298 K): δ 25.5 (d, $^3J_{C\text{-}P}$ = 4.5 Hz, CHCH$_3$), 26.2 [s, PC(CH_3)$_3$], 26.5 (d, $^4J_{C\text{-}P}$ = 6.0 Hz, CH_2), 38.0 [d, $^1J_{C\text{-}P}$ = 59.7 Hz, P*C*(CH$_3$)$_3$], 43.9 (d, $^1J_{C\text{-}P}$ = 53.7 Hz, PCH), 50.6 (d, $^3J_{C\text{-}P}$ = 1.5 Hz, *C*HCH$_3$), 123.5 (d, $^3J_{C\text{-}P}$ = 7.3 Hz, *C*H), 123.6 (d, $^3J_{C\text{-}P}$ = 6.2 Hz, *C*H), 126.3 (d, $^2J_{C\text{-}P}$ = 10.0 Hz, *C*H), 126.8 (s, C_{ar}), 127.1 (d, $^2J_{C\text{-}P}$ = 9.7 Hz, *C*H), 127.2 (s, C_{ar}), 128.7 (s, C_{ar}), 146.5 (d, $^3J_{C\text{-}P}$ = 3.5 Hz, *C*C$_i$). HR(ESI)-MS: Calcd *m/z* for $C_{18}H_{27}NPS$ [(M + H)$^+$]: 320.1596. Found: 320.1594. CHN Analysis: Calcd for $C_{18}H_{26}NPS$: C, 67.68; H, 8.20; N, 4.38. Found: C, 67.62; H, 8.26; N, 4.38.

*Compound (S_P)-**8***: ^1H NMR (400.13 MHz, C_6D_6, 298 K): δ 0.98 [d, $^3J_{H\text{-}P}$ = 16.7 Hz, 9H, PC(CH_3)$_3$], 1.76 (br, 2H, NH_2), 7.07–7.04 (m, 3H, H_{ar}), 7.91–7.86 (m, 2H, H_{ar}). $^{31}P\{^1H\}$ NMR (162.04 MHz, C_6D_6, 298 K): δ 75.4. $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 298 K): δ 24.7 [d, $^2J_{C\text{-}P}$ = 2.0 Hz, PC(CH$_3$)$_3$], 35.6 [d, $^1J_{C\text{-}P}$ = 67.5 Hz, P*C*(CH$_3$)$_3$], 127.9 (d, $^2J_{C\text{-}P}$ = 11.8 Hz, C_o), 131.2 (d, $^4J_{C\text{-}P}$ = 2.9 Hz, C_p), 133.2 (d, $^3J_{C\text{-}P}$ = 9.8 Hz, C_m), 133.2 (d, $^1J_{C\text{-}P}$ = 88.8 Hz, PC_i). GC/EI-MS: *m/z* (%) = 213 (21) [M$^{+\bullet}$], 157 (53) [(M − C_4H_8)$^{+\bullet}$], 156 (24) [(M - C_4H_9)$^{+\bullet}$], 124 (100) [$H_2NPPh^{+\bullet}$]. CHN Analysis: Calcd for $C_{10}H_{16}NPS$: C, 56.32; H, 7.56; N, 6.57. Found: C, 56.40; H, 7.51; N, 6.52.

*Compound (rac)-**8***: A solution of compound **1** (4.41 g, 22.0 mmol, 1.0 equiv.) in diethyl ether (50 mL) was cooled to −80 °C and ammonia was condensed into the solution. The reaction mixture was allowed to slowly warm to room temperature and stirred for 15 h. The formed precipitate was filtered off via cannula filtration and all volatiles of the filtrate were removed under vacuum. The crude intermediate was dissolved in pentane (50 mL), added to a flask loaded with sulfur (0.70 g, 22.0 mmol, 1.0 equiv.), and stirred for 15 h yielding a colorless suspension. The liquid phase was removed via cannula filtration and the remaining solid extracted with dichloromethane. Then, all volatiles were removed under vacuum to yield (*rac*)-**8** as a colorless solid (1.35 g, 6.33 mmol, 29% overall yield). Crystals suitable for single-crystal X-ray diffraction analysis were obtained by recrystallization from dichloromethane/pentane at room temperature. ^1H NMR (400.13 MHz, C_6D_6, 298 K): δ 0.98 [d, $^3J_{H\text{-}P}$ = 16.7 Hz, 9H, PC(CH_3)$_3$], 1.79 (br, 2H, NH_2), 7.08–7.05 (m, 3H, H_{ar}), 7.91–7.86 (m, 2H, H_{ar}). $^{31}P\{^1H\}$ NMR (162.04 MHz, C_6D_6, 298 K): δ 75.4. $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 298 K): δ 24.7 [d, $^2J_{C\text{-}P}$ = 2.0 Hz, PC(CH$_3$)$_3$], 35.6 [d, $^1J_{C\text{-}P}$ = 67.3 Hz, P*C*(CH$_3$)$_3$], 127.9 (d, $^2J_{C\text{-}P}$ = 11.8 Hz, C_o), 131.2 (d, $^4J_{C\text{-}P}$ = 2.9 Hz, C_p), 133.0 (d, $^1J_{C\text{-}P}$ = 89.3 Hz, PC_i), 133.2 (d, $^3J_{C\text{-}P}$ = 9.8 Hz, C_m). ^1H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 1.15 [d, $^3J_{H\text{-}P}$ = 16.9 Hz, 9H, PC(CH_3)$_3$], 2.60 (br, 2H, NH_2), 7.54–7.45 (m, 3H, H_{ar}), 7.93–7.98 (m, 2H, H_{ar}). $^{31}P\{^1H\}$ NMR (162.04 MHz, CD_2Cl_2, 298 K): δ 76.4. $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 298 K): δ 25.0 [d, $^2J_{C\text{-}P}$ = 2.0 Hz, PC(CH$_3$)$_3$], 36.0 [d, $^1J_{C\text{-}P}$ = 66.7 Hz, P*C*(CH$_3$)$_3$], 128.4 (d, $^2J_{C\text{-}P}$ = 11.9 Hz, C_o), 131.9 (d, $^4J_{C\text{-}P}$ = 2.9 Hz, C_p), 132.8 (d, $^1J_{C\text{-}P}$ = 89.6 Hz, PC_i), 133.2 (d, $^3J_{C\text{-}P}$ = 9.8 Hz, C_m). HR(ESI)-MS: Calcd *m/z* for $C_{10}H_{17}NPS$ [(M + H)$^+$]: 214.0814. Found: 214.0814. CHN Analysis: Calcd for $C_{10}H_{16}NPS \cdot 0.05\ CH_2Cl_2$: C, 55.49; H, 7.46; N, 6.44. Found: C, 55.71; H, 7.07; N, 6.38.

*Compound **9***: $^{31}P\{^1H\}$ NMR (162.04 MHz, C_6D_6, 298 K): δ 66.1. GC/EI-MS [80 °C (1 min) - 320 °C (15 min) with 25 °C·min^{-1}], (70 eV, t_R = 7.02 min): *m/z* (%) for $C_{12}H_{20}NPS$: 241 (2) [M$^{+\bullet}$], 208 (16) [{C_8H_9(NH)P*t*Bu}$^{+\bullet}$], 184 (29) [(M−C_4H_9)$^{+\bullet}$], 120 (100) [($C_8H_{10}N$)$^{+\bullet}$], 105 (85) [(C_8H_9)$^{+\bullet}$], 77 (22) [(C_6H_5)$^{+\bullet}$], 57 (38) [(C_4H_9)$^{+\bullet}$].

*Compound **10***: $^{31}P\{^1H\}$ NMR (162.04 MHz, C_6D_6, 298 K): δ 47.5. GC/EI-MS [80 °C (1 min)–320 °C (15 min) with 25 °C·min^{-1}], (70 eV, t_R = 7.47 min): *m/z* (%) for $C_{18}H_{24}NP$: 285 (8) [M$^{+\bullet}$], 228 (55) [(M−C_4H_9)$^{+\bullet}$], 124 (88) [(C_6H_7NP)$^{+\bullet}$], 105 (100) [(C_8H_9)$^{+\bullet}$], 77 (13) [(C_6H_5)$^{+\bullet}$].

*tert-Butylchlorocyclohexylphosphine (**11**)*: *tert*-Butyllithium (2.97 mL of a 1.6 M solution in pentane, 4.76 mmol, 1.0 equiv.) was slowly added to a solution of dichlorocyclohexylphosphine (0.88 g, 4.76 mmol, 1.0 equiv.) in pentane (10 mL) at −80 °C. The reaction

mixture was allowed to slowly warm to room temperature and stirred for 15 h. The precipitated lithium chloride was filtered off via cannula filtration. Then, all volatiles of the filtrate were removed under vacuum. Compound **11** was obtained as a yellowish liquid (0.72 g, 3.48 mmol, 73%). ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 1.05 [d, $^3J_{H\text{-}P}$ = 12.2 Hz, 9H, PC(CH_3)$_3$], 1.22–1.10 (m, 4H, CH_2), 1.38–1.24 (m, 2H, CH_2), 1.50–1.46 (m, 1H, CH_2), 1.61-1.54 (m, 1H, CH_2), 1.68–1.64 (m, 2H, CH_2), 2.09–2.05 (m, 1H, PC*H*). ^{31}P{^{1}H} NMR (162.04 MHz, C_6D_6, 298 K): δ 137.8. ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 298 K): δ 26.2 [d, $^2J_{C\text{-}P}$ = 1.1 Hz, PC(CH_3)$_3$], 26.5 (s, CH_2), 26.7 (s, CH_2), 26.9 (s, CH_2), 33.5 [d, $^1J_{C\text{-}P}$ = 33.5 Hz, PC(CH_3)$_3$], 39.2 (d, $^1J_{C\text{-}P}$ = 37.9 Hz, PCH). GC/EI-MS: *m/z* (%) = 206 (8) [$M^{+\bullet}$], 83 (14) [$C_6H_{11}{}^{+\bullet}$], 57 (100) [$C_4H_9{}^{+\bullet}$].

*Compound (R_P,S)-**12***: Compound (*S*)-**2** (4.24 mL, 3.99 g, 32.96 mmol, 2.0 equiv.) was added to a solution of compound **11** (3.41 g, 16.48 mmol, 1.0 equiv.) in pentane (40 mL) at room temperature. After stirring for 15 h, the solids were filtered off by transferring the liquid phase via cannula filtration directly into another Schlenk tube filled with sulfur (0.53 g, 16.48 mmol, 1.0 equiv.). The reaction mixture was stirred at room temperature for 15 h. Then, all volatiles were removed under vacuum. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the crude product showed the formation of the desired product (R_P,*S*)-**12** in a 3:1 diastereomeric ratio. The crude product was recrystallized from toluene/hexane at −25 °C. Compound (R_P,*S*)-**12** (1.70 g, 5.25 mmol, 32% overall yield, d.r. > 99:1) was obtained as colorless crystals suitable for single-crystal X-ray diffraction analysis. ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 0.87–0.96 (m, 3H, CH_2), 1.11 [d, $^3J_{H\text{-}P}$ = 15.4 Hz, 9H, PC(CH_3)$_3$], 1.18–1.29 (m, 1H, CH_2), 1.35 (d, $^4J_{H\text{-}P}$ = 6.8 Hz, 3H, CHCH_3), 1.38–1.44 (m, 2H, CH_2), 1.48-1.65 (m, 5H, CH_2, PC*H*), 1.94–1.98 (m, 1H, N*H*), 4.94-5.04 (m, 1H, *CH*CH$_3$), 7.03–7.07 (m, 1H, H_{ar}), 7.13–7.15 (m, 2H, H_{ar}), 7.21–7.23 (m, 2H, H_{ar}). ^{31}P{^{1}H} NMR (162.04 MHz, C_6D_6, 298 K): δ 89.1. ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 298 K): δ 25.8 (d, $^3J_{C\text{-}P}$ = 4.4 Hz, CH_2), 25.9 [d, $^2J_{C\text{-}P}$ = 1.1 Hz, PC(CH_3)$_3$], 26.0 (d, $^4J_{C\text{-}P}$ = 1.7 Hz, CH_2), 26.9 (d, $^2J_{C\text{-}P}$ = 10.7 Hz, CH_2), 27.0 (d, $^2J_{C\text{-}P}$ = 9.7 Hz, CH_2), 27.4 (d, $^3J_{C\text{-}P}$ = 3.4 Hz, CH_2), 28.7 (d, $^3J_{C\text{-}P}$ = 1.4 Hz, CHCH_3), 36.8 [d, $^1J_{C\text{-}P}$ = 61.3 Hz, PC(CH_3)$_3$], 40.6 (d, $^1J_{C\text{-}P}$ = 57.8 Hz, PCH), 50.8 (d, $^2J_{C\text{-}P}$ = 1.2 Hz, CHCH$_3$), 126.9 (s, C_{ar}), 127.1 (s, C_{ar}), 128.7 (s, C_{ar}), 146.7 (d, $^3J_{C\text{-}P}$ = 3.6 Hz, PC_i). HR(ESI)-MS: Calcd *m/z* for $C_{18}H_{31}NPS$ [$(M+H)^+$]: 324.1909. Found: 324.1914. CHN Analysis: Calcd for $C_{18}H_{30}NPS$: C, 66.84; H, 9.35; N, 4.33. Found: C, 66.75; H, 9.12; N, 4.22.

*Compound (R_P)-**13***: Ammonia (5 mL) was condensed into a flask containing lithium (24 mg, 3.48 mmol, 4.0 equiv.) at −80 °C. The mixture was stirred for 10 min while turning into a dark blue solution. Meanwhile, a solution of compound (R_P,*S*)-**12** (0.28 g, 0.87 mmol, 1.0 equiv.) and *tert*-butanol (0.17 mL, 1.74 mmol, 2.0 equiv.) in THF (5 mL) was prepared and then added to the solution of lithium in liquid ammonia in one portion. After stirring for 2 min, the mixture was quenched with ammonium chloride and the cooling bath removed allowing ammonia to evaporate. The crude mixture was extracted with diethyl ether (1×10 mL, 2×5 mL) and the solids were removed via cannula filtration. Then, all volatiles were removed under vacuum and the gel-like substance purified via Kugelrohr distillation (100–120 °C oven temperature, $1.0\cdot10^{-2}$ mbar). Compound (R_P)-**13** (0.18 g, 0.82 mmol, 94%, e.r. > 99:1) was obtained as a colorless solid. Crystals suitable for single-crystal X-ray diffraction analysis were obtained from diethyl ether by slow evaporation of the solvent. The enantiomeric purity of crude compound (R_P)-**13** was determined by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy in the presence of (*R*)-BINOL-PSSLi (99% ee) in CD_2Cl_2 (for details, see the Supporting Information). ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 1.06 [d, $^3J_{H\text{-}P}$ = 15.5 Hz, 9H, PC(CH_3)$_3$], 1.09–1.06 (m, 2H, CH_2), 1.48–1.42 (br, 2H, NH_2), 1.52-1.49 (m, 1H, CH_2), 1.66–1.56 (m, 7H, CH_2), 1.91–1.88 (m, 1H, PC*H*). ^{31}P{^{1}H} NMR (162.04 MHz, C_6D_6, 298 K): δ 85.4. ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 298 K): δ 25.7 [d, $^2J_{C\text{-}P}$ = 1.4 Hz, PC(CH_3)$_3$], 26.0 (d, $^3J_{C\text{-}P}$ = 1.6 Hz, CH_2), 26.6 (d, $^2J_{C\text{-}P}$ = 14.4 Hz, CH_2), 26.8 (d, $^2J_{C\text{-}P}$ = 13.5 Hz, CH_2), 28.3 (s, CH_2), 30.2 (s, CH_2), 36.2 [d, $^1J_{C\text{-}P}$ = 61.3 Hz, PC(CH_3)$_3$], 38.6 (d, $^1J_{C\text{-}P}$ = 58.2 Hz, PCH). ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 1.23 [d, $^3J_{H\text{-}P}$ = 15.8 Hz, 9H, PC(CH_3)$_3$], 1.38-1.26 (m, 3H, CH_2), 1.57–1.41 (m, 2H, CH_2), 1.71–1.67 (m, 1H, PC*H*), 1.92–1.79 (m, 3H, CH_2), 2.02–1.93 (m, 2H, CH_2), 2.12 (br, 2H, NH_2). ^{31}P{^{1}H} NMR (162.04 MHz, CD_2Cl_2, 298 K): δ 86.7. ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, 298 K): δ 25.9 [d, $^2J_{C\text{-}P}$ = 1.4 Hz, PC(CH_3)$_3$], 26.3 (d, $^3J_{C\text{-}P}$ = 1.6 Hz, CH_2), 26.8 (d, $^2J_{C\text{-}P}$ = 14.5 Hz, CH_2), 27.1 (d, $^2J_{C\text{-}P}$ = 12.8 Hz, CH_2), 27.2 (d, $^3J_{C\text{-}P}$ = 4.0 Hz, CH_2), 28.7 (s, CH_2), 36.5 [d, $^1J_{C\text{-}P}$ = 60.7 Hz, PC(CH_3)$_3$], 38.6 (d, $^1J_{C\text{-}P}$ = 58.1 Hz, PCH). HR(ESI)-MS: Calcd *m/z* for $C_{10}H_{23}NPS$ [$(M+H)^+$]: 220.1283. Found: 220.1276. CHN Analysis: Calcd for $C_{10}H_{22}NPS$: C, 54.76; H, 10.11; N, 6.39. Found: C, 55.21; H, 10.46; N, 6.15.

*Compound (rac)-**13***: A solution of compound **11** (1.02 g, 4.93 mmol, 1.0 equiv.) in pentane (15 mL) was cooled to −80 °C and ammonia was condensed into the solution. The reaction mixture was allowed to slowly warm to room temperature and stirred for 15 h. The formed precipitate was filtered off via cannula filtration and the filtrate directly transferred into a Schlenk tube loaded with sulfur (0.16 g, 4.93 mmol, 1.0 equiv.) at room temperature. The reaction mixture was stirred for 15 h. All volatiles were removed under vacuum and the remaining solid extracted with diethyl ether. Then, all volatiles were removed under vacuum to yield (*rac*)-**13** as a colorless liquid (0.50 g, 2.28 mmol, 46% overall yield). ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 1.07 [d, $^3J_{H\text{-}P}$ = 15.6 Hz, 9H, PC(CH_3)$_3$], 1.07–1.03 (m, 2H, CH_2), 1.54–1.47 (br, 2H, NH_2), 1.68-1.60 (m, 6H, CH_2), 1.95–1.75 (m, 3H, PC*H*/CH_2). ^{31}P{^{1}H} NMR (162.04 MHz, C_6D_6, 298 K): δ 85.4. ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 298 K): δ 25.7 [d, $^2J_{C\text{-}P}$ = 1.4 Hz, PC(CH_3)$_3$], 26.0 (d, $^3J_{C\text{-}P}$ = 1.6 Hz, CH_2), 26.6 (d, $^2J_{C\text{-}P}$ = 14.4 Hz, CH_2), 26.8 (d, $^2J_{C\text{-}P}$ = 13.5 Hz, CH_2), 28.3 (s, CH_2), 30.2 (s, CH_2), 36.2 [d, $^1J_{C\text{-}P}$ = 61.3 Hz, PC(CH_3)$_3$], 38.6 (d, $^1J_{C\text{-}P}$ = 58.2 Hz, PCH). HR(ESI)-MS: Calcd *m/z* for [$(M+H)^+$]: 220.1283. Found: 220.1276. CHN Analysis: Calcd for $C_{10}H_{22}NPS$: C, 54.76; H, 10.11; N, 6.39. Found: C, 55.12; H, 10.59; N, 6.09.

*Compound (rac)-**13**-Li*: *n*-Butyllithium (0.44 mL of a 2.5 M solution in hexane, 1.09 mmol, 1.0 equiv.) was added dropwise to a solution of (*rac*)-**13** (0.24 g, 1.09 mmol, 1.0 equiv.) in pentane (20 mL) at −30 °C. The suspension was allowed to slowly warm to room temperature and then stirred for 15 h. The remaining solid was filtered off and dried under vacuum to yield (*rac*)-**13**-Li as a colorless solid (0.17 g, 0.75 mmol, 69%). ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 0.24 (d, $^2J_{H\text{-}P}$ = 12.3 Hz, 1H, N*H*), 1.20 [d, $^3J_{H\text{-}P}$ = 15.1 Hz, 9H, PC(CH_3)$_3$], 1.46–1.25 (m, 5H, CH_2), 1.68 (d, $^2J_{H\text{-}P}$ = 11.3 Hz 1H, PC*H*), 1.88–1.78 (m, 3H, CH_2), 2.02–1.90 (m, 1H, CH_2), 2.19–2.05 (m, 1H, CH_2). ^{31}P{^{1}H} NMR (162.04 MHz, CD_2Cl_2, 298 K): δ 92.6. ^{7}Li{^{1}H} NMR (155.51 MHz, CD_2Cl_2) δ 1.13. ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, 298 K): δ 26.0 [s, PC(CH_3)$_3$], 26.6 (s, CH_2), 27.6 (s, CH_2), 29.7 (s, CH_2) 30.3 (s, CH_2), 37.4 [d, $^1J_{C\text{-}P}$ = 52.7 Hz, PC(CH_3)$_3$], 40.0 (d, $^1J_{C\text{-}P}$ = 49.2 Hz, PCH).

*Compound (R_P)-**14***: *n*-Butyllithium (0.22 mL of a 1.6 M solution in hexane, 0.55 mmol, 1.2 equiv.) was added to a solution of compound (R_P)-**13** (100 mg, 0.46 mmol, 1.0 equiv., e.r. > 99:1) in diethyl ether (2 mL) at −80 °C. The reaction mixture was allowed to slowly warm to room temperature and stirred for 15 h. The resulting colorless solution was again cooled to −80 °C and di-*tert*-butylchlorosilane (82 mg, 0.46 mmol, 1.0 equiv.), dissolved in diethyl ether (3 mL), was added. The reaction mixture was allowed to slowly warm to room temperature and stirred for 15 h. Since no reaction occurred, the solvent was changed to THF (5 mL) and the reaction mixture was heated at reflux for 15 h turning into a yellow solution. Then, all volatiles were removed under vacuum and the crude product was extracted with diethyl ether. Colorless crystals of compound (R_P)-**14** (40 mg, 0.11 mmol, 24%) suitable for single-crystal X-ray diffraction analysis were obtained by slow crystallization from the diethyl ether solution at −25 °C. ^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ 1.07–1.03 (m, 3H, CH_2), 1.08 [s, 9H, SiC(CH_3)$_3$], 1.12 [s,

9H, SiC(CH_3)$_3$], 1.17 [d, $^3J_{H\text{-}P}$ = 15.5 Hz, 9H, PC(CH_3)$_3$], 1.53–1.40 (m, 4H, CH_2), 1.70–1.64 (m, 2H, CH_2/N*H*), 1.84-1.74 (m, 1H, C*H*), 2.12–2.08 (m, 1H, CH_2), 2.28–2.23 (m, 1H, CH_2), 4.65–4.63 (m, 1H, Si*H*). ^{31}P{^{1}H} NMR (162.04 MHz, C_6D_6, 298 K): δ 85.1. ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 298 K): δ 20.0 [d, $^3J_{C\text{-}P}$ = 2.4 Hz, SiC(CH_3)$_3$], 20.1 [d, $^3J_{C\text{-}P}$ = 0.9 Hz, SiC(CH_3)$_3$], 26.2 [d, $^2J_{C\text{-}P}$ = 1.4 Hz, PC(CH_3)$_3$], 27.3 (d, $^3J_{C\text{-}P}$ = 2.3 Hz, CH_2), 27.4 (d, $^2J_{C\text{-}P}$ = 3.3 Hz, CH_2), 29.1 (d, $^2J_{C\text{-}P}$ = 3.4 Hz, CH_2), 29.1 [s, SiC(CH_3)$_3$], 29.2 [s, SiC(CH_3)$_3$], 29.3 (d, $^3J_{C\text{-}P}$ = 2.4 Hz, CH_2), 38.2 [d, $^1J_{C\text{-}P}$ = 59.7 Hz, PC(CH_3)$_3$], 42.9 [d, $^1J_{C\text{-}P}$ = 56.9 Hz, PCH]. ^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6, 298 K): δ 4.5 (d, $^2J_{C\text{-}P}$ = 6.5 Hz). HR(ESI)-MS: Calcd *m/z* for $C_{18}H_{41}NPSSi$ [(M + H)$^+$]: 362.2461. Found: 362.2464. CHN Analysis: Calcd for $C_{18}H_{40}NPSSi$: C, 59.78; H, 11.15; N, 3.87. Found: C, 59.29; H, 11.03; N, 3.42.

*Determination of the enantiomeric ratios of compounds (S_P)-**8** and (R_P)-**13** using (R)-BINOL-PSSLi*: *n*-Butyllithium (0.06 mL of a 2.5 M solution in hexane, 0.14 mmol, 1.0 equiv.) was added to a suspension of (*R*)-BINOL-PSSH (53 mg, 0.14 mmol, 1.0 equiv.) in pentane (20 mL) at −30 °C. The mixture was allowed to slowly warm to room temperature. The resulting colorless solid was filtered off, washed with pentane and dried under vacuum. Then, the freshly prepared sample of (*R*)-BINOL-PSSLi and the respective primary aminophosphine sulfide [(*rac*)-**8**, (S_P)-**8**, (*rac*)-**13**, or (R_P)-**13**] (0.14 mmol, 1.0 equiv.) were dissolved in CD_2Cl_2 (0.5 mL), the mixture transferred to a Young NMR tube and subjected to ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. The enantiomeric ratios were determined by integration of either the ^{1}H NMR signals of the *tert*-butyl groups or the ^{31}P{^{1}H} NMR signals. For details, see the Supporting Information.

*(rac)-**8** in the presence of (R)-BINOL-PSSLi*: ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 0.97 [d, 9H, $^3J_{H\text{-}P}$ = 17.2 Hz, PC(CH_3)$_3$], 1.00 [d, 9H, $^3J_{H\text{-}P}$ = 17.2 Hz, PC(CH_3)$_3$], 2.69 (s, 2H, NH_2), 2.74 (s, 2H, NH_2), 7.23–7.20 (m, 7H, H_{ar}), 7.33–7.31 (m, 7H, H_{ar}), 7.42–7.36 (m, 7H, H_{ar}), 7.48–7.44 (m, 14H, H_{ar}), 7.81–7.72 (m, 5H, H_{ar}), 7.94–7.91 (m, 14H, H_{ar}). ^{31}P{^{1}H} NMR (162.04 MHz, CD_2Cl_2, 298 K): δ 77.3 (s, 1P, S*P*N), 77.5 (s, 1P, S*P*N), 126.3 (s, 2P, O_2PS_2).

*(S_P)-**8** in the presence of (R)-BINOL-PSSLi*: ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 1.07 [d, 9H, $^3J_{H\text{-}P}$ = 17.2 Hz, PC(CH_3)$_3$], 2.82 (s, 2H, NH_2), 7.26–7.23 (m, 17H, H_{ar}), 7.36–7.34 (m, 17H, H_{ar}), 7.47–7.44 (m, 17H, H_{ar}), 7.53–7.51 (m, 17H, H_{ar}), 7.97–7.92 (m, 34H, H_{ar}). ^{31}P{^{1}H} NMR (162.04 MHz, CD_2Cl_2, 298 K): δ 77.3 (s, 1P, S*P*N), 127.8 (s, O_2PS_2).

*(rac)-**13** in the presence of (R)-BINOL-PSSLi*: ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 1.04 [d, 9H, $^3J_{H\text{-}P}$ = 16.3 Hz, PC(CH_3)$_3$], 1.05 [d, 9H, $^3J_{H\text{-}P}$ = 16.3 Hz, PC(CH_3)$_3$], 1.25–1.10 (m, 6H, CH_2), 1.43–1.26 (m, 4H, CH_2), 1.61–1.58 (m, 2H, 2×C*H*), 1.78–1.64 (m, 7H, CH_2), 1.95–1.80 (m, 3H, CH_2), 2.52 (s, 4H, 2×NH_2), 7.27–7.24 (m, 4H, H_{ar}), 7.40–7.37 (m, 4H, H_{ar}), 7.48–7.45 (m, 4H, H_{ar}), 7.60–7.58 (m, 4H, H_{ar}), 7.97–7.95 (m, 4H, H_{ar}), 8.01–7.99 (m, 4H, H_{ar}). ^{31}P{^{1}H} NMR (162.04 MHz, CD_2Cl_2, 298 K): δ 88.5 (s, 1P, S*P*N), 88.6 (s, 1P, S*P*N), 122.5 (s, 2P, O_2PS_2). ^{7}Li{^{1}H} NMR (155.51 MHz, CD_2Cl_2, 298 K): δ 0.4.

*(R_P)-**13** in the presence of (R)-BINOL-PSSLi*: ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 1.11 [d, 9H, $^3J_{H\text{-}P}$ = 16.1 Hz, PC(CH_3)$_3$], 1.45–1.17 (m, 5H, CH_2), 1.63–1.60 (m, 1H, C*H*), 1.79–1.70 (m, 3H, CH_2), 1.93–1.80 (m, 2H, CH_2), 2.35 (s, 2H, NH_2), 7.29–7.23 (m, 2H, H_{ar}), 7.40–7.34 (m, 2H, H_{ar}), 7.49–7.43 (m, 2H, H_{ar}), 7.58–7.51 (m, 2H, H_{ar}), 8.01–7.89 (m, 4H, H_{ar}). ^{31}P{^{1}H} NMR (162.04 MHz, CD_2Cl_2, 298 K): δ 87.9 (s, 1P, S*P*N), 126.3 (s, 1P, O_2PS_2).

Preparation of (R)-BINOL-PSSNa and (R)-BINOL-PSSK: A suspension of benzyl sodium (0.18 g, 1.6 mmol, 1.0 equiv.) or benzyl potassium (0.17 g, 1.3 mmol, 1.0 equiv.) in hexane (20 mL) was added to a suspension of (*R*)-BINOL-PSSH (1.6 or 1.3 mmol, 1.0 equiv.) in hexane (30 mL) at −30 °C. The mixture was allowed to slowly warm to room temperature and stirred for 48 h. Then, the resulting colorless solid was filtered off, washed with hexane and dried under vacuum to yield (*R*)-BINOL-PSSNa (0.58 g, 1.45 mmol, 91 %) and (*R*)-BINOL-PSSK (0.46 g, 1.10 mmol, 85 %), respectively. The reagents were used directly.

Preparation of monolithiated (R)-BINOL: *n*-Butyllithium (1.0 mL of a 2.5 M solution in hexane, 2.5 mmol, 1.0 equiv.) was added to a suspension of (*R*)-BINOL (0.69 g, 2.5 mmol, 1.0 equiv.) in hexane (60 mL) at −30 °C. The mixture was allowed to slowly warm to room temperature and stirred for 48 h. Then, the resulting colorless solid was filtered off, washed with hexane and dried under vacuum to yield monolithiated (*R*)-BINOL (0.67 g, 2.3 mmol, 92 %). The reagent was used directly.

Investigation of (R)-BINOL-PSSNa, (R)-BINOL-PSSK, and monolithiated (R)-BINOL for use as chiral shift reagents: Freshly prepared (*R*)-BINOL-PSSNa, (*R*)-BINOL-PSSK, or monolithiated (*R*)-BINOL (0.14 mmol, 1.0 equiv.) and (*rac*)-**8** (29 mg, 0.14 mmol, 1.0 equiv.) were dissolved in CD_2Cl_2 (0.5 mL), the mixture transferred to a Young NMR tube and subjected to ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. With (*R*)-BINOL-PSSNa and (*R*)-BINOL-PSSK, no sufficient diastereotopic discrimination was achieved. With monolithiated (*R*)-BINOL, no diastereotopic discrimination was achieved. For details, see the Supporting Information.

*(rac)-**8** in the presence of (R)-BINOL-PSSNa*: ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 1.03 [d, 18H, $^3J_{H\text{-}P}$ = 17.1 Hz, PC(CH_3)$_3$], 2.61 (s, 2H, NH_2), 2.67 (s, 2H, NH_2), 7.22–7.18 (m, 7H, H_{ar}), 7.53-7.32 (m, 23H, H_{ar}), 7.76–7.71 (m, 3H, H_{ar}), 7.90–7.82 (m, 12H, H_{ar}). ^{31}P{^{1}H} NMR (162.04 MHz, CD_2Cl_2, 298 K): δ 76.6 (s, 1P, S*P*N), 76.6 (s, 1P, S*P*N), 130.1 (s, 2P, O_2PS_2).

*(rac)-**8** in the presence of (R)-BINOL-PSSK*: ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ 1.10 [d, 9H, $^3J_{H\text{-}P}$ = 17.0 Hz, PC(CH_3)$_3$], 1.10 [d, 9H, $^3J_{H\text{-}P}$ = 17.0 Hz, PC(CH_3)$_3$], 2.76 (br, 4H, 2×NH_2), 7.20–7.16 (m, 6H, H_{ar}), 7.55-7.32 (m, 28H, H_{ar}), 7.94–7.85 (m, 16H, H_{ar}). ^{31}P{^{1}H} NMR (162.04 MHz, CD_2Cl_2, 298 K): δ 76.4 (s, 2P, S*P*N), 130.4 (s, 2P, O_2PS_2).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article

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