

Optically active *P*-chiral phosphinoselenoic amides: stereochemical outcome at the *P*-stereogenic center in the synthesis of these substances and their characterization

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Abstract—A variety of optically active *P*-chiral phosphinoselenoic amides were synthesized with high efficiency by reacting racemic *P*-chiral phosphinoselenoic chlorides with optically active lithium amides. Some of the diastereomers of the amides were separated by column chromatography on silica gel. The absolute configurations of the phosphinoselenoic amides were determined by X-ray molecular structure analyses. Optically active *P*-chiral phosphinoselenoic chlorides were also reacted with optically active lithium amide. The reaction proceeded predominantly with inversion of configuration, but also involved retention of stereochemistry at the phosphorus atom during the substitution reaction.

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1. Introduction

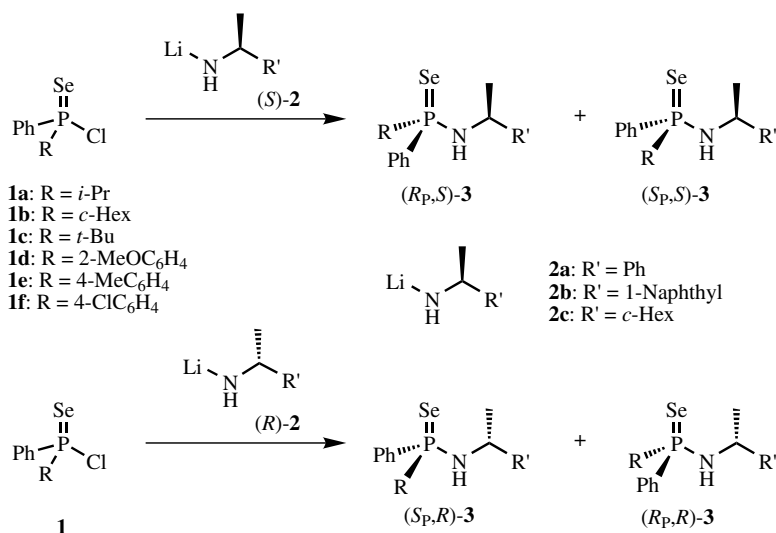
Optically active *P*-chiral organophosphorus compounds are an important class of compound¹ because of their wide applicability as optically active ligands for transition metal complexes.² *P*-Chiral derivatives bearing heteroatom-containing substituents have also been the focus of considerable attention. In the syntheses of these compounds, the stereochemical outcome of *P*-stereogenic centers in the substitution reaction of *P*-chiral precursors, such as chlorophosphines, chlorophosphine boranes, phosphinic and phosphinothioic halides, is also of interest. For example, the reaction of racemic *P*-chiral chlorophosphines with optically active α -methylbenzylamine takes place with asymmetric induction at the phosphorus atom to give diastereomerically enriched aminophosphines.³ Amination of an optically active *P*-chiral chlorophosphine borane with a disodium salt of ethylenediamine proceeds with inversion of configuration at the phosphorus atom.⁴ The reaction of optically active *P*-chiral phosphinic bromide and phosphinothioic chloride with pyrrole is not completely stereoselective.⁵ In each example however, only one of the amines reacted with one of the *P*-chiral precursors, and only limited derivatives were prepared. Over the course of

our studies on phosphinoselenoic acid derivatives,^{6–8} we have established an efficient synthetic method for the preparation of *P*-chiral phosphinoselenoic chlorides in both racemic⁷ and optically active forms.⁸ We also elucidated the diastereoselectivity of their reactions with lithium amides leading to the first optically active *P*-chiral phosphinoselenoic amides.⁷ We herein report the details of the stereochemical course of the substitution reaction of *P*-chiral phosphinoselenoic chlorides with lithium amides.

2. Results and discussion

Initially, the synthesis of optically active *P*-chiral phosphinoselenoic amides was carried out by reacting racemic *P*-chiral phosphinoselenoic chlorides **1** with optically active lithium amides **2** (Scheme 1, Table 1). For example, a THF solution of lithium (*S*)-1-phenylethylamide **2a** was added to a THF solution of *P*-isopropyl-*P*-phenylphosphinoselenoic chloride **1a**, and the reaction mixture stirred for 2 h. After the usual workup, a diastereomeric mixture of phosphinoselenoic amides **3a** was obtained in a ratio of 44:56. The two diastereomers were separated by column chromatography on silica gel, and optically active *P*-chiral phosphinoselenoic amides (*R_P*,*S*)-**3a** and (*S_P*,*S*)-**3a** were obtained in respective yields of 36% and 46% (entry 1). A similar reaction of phosphinoselenoic chlorides **1b–f** with the lithium

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Scheme 1.

Table 1. Synthesis of optically active *P*-chiral phosphinoselenoic amides^a

Entry	1	(<i>S</i>)- 2	R	R'	3	Diastereomeric ratio ^b	Yield ^c (%) (<i>R_p,S</i>)/(<i>S_p,S</i>)
1	1a	2a	<i>i</i> -Pr	Ph	3a	44/56	36/46
2	1b	2a	<i>c</i> -Hex	Ph	3b	41/59	37/50
3	1c	2a	<i>t</i> -Bu	Ph	3c	38/62	34/51
4	1d	2a	2-MeOC ₆ H ₄	Ph	3d	58/42	72 ^d
5	1e	2a	4-MeC ₆ H ₄	Ph	3e	52/48	76 ^d
6	1f	2a	4-ClC ₆ H ₄	Ph	3f	48/52	87 ^d
7	1a	2b	<i>i</i> -Pr	1-Naphthyl	3g	38/62	38/53
8	1b	2b	<i>c</i> -Hex	1-Naphthyl	3h	39/61	34/41
9	1c	2b	<i>t</i> -Bu	1-Naphthyl	3i	35/65	36/56
10	1a	2c	<i>i</i> -Pr	<i>c</i> -Hex	3j	49/51	40/41
11	1b	2c	<i>c</i> -Hex	<i>c</i> -Hex	3k	49/51	44/46
12	1c	2c	<i>t</i> -Bu	<i>c</i> -Hex	3l	49/51	42/43

^a Phosphinoselenoic chlorides **1** were reacted with lithium amides (*S*)-**2** (1 equiv) in THF at room temperature for 2 h.

^b Diastereomeric ratios were determined based on the integration of NMR spectra of the crude reaction mixtures.

^c Isolated yields.

^d Not separated.

amide **2a** gave phosphinoselenoic amides **3b–f** as diastereomeric mixtures in good yields. Although the diastereomeric mixtures of diaryl derivatives **3d–f** were not separated (entries 4–6), diastereomeric mixtures of alkyl–phenyl derivatives **3b** and **3c** were successfully separated by column chromatography on silica gel (entries 2 and 3). Lithium (*S*)-1-(1-naphthyl)ethyl **2b** and (*S*)-1-cyclohexylethylamides **2c** were also used as optically active lithium amides, and various optically active *P*-chiral phosphinoselenoic amides **3g–l** were obtained with high efficiency (entries 7–12). Antipodal phosphinoselenoic amides (*S_p,R*)-**3** and (*R_p,R*)-**3** were also obtained by reacting chlorides **1** with lithium (*R*)-amides in a similar manner. The resulting amides **3** were stable under air and toward water.

The ratios of the diastereomers of amides **3** were slightly influenced by the substituents on the phosphorus atom of **1**, and the substituents on the nitrogen atom of **2** also had an affect on the ratios of the diastereomers. The reaction of chlorides **1a–c** with lithium 1-cyclohexyleth-

ylamide **2c** gave equimolar amounts of mixtures of diastereomers **3j–l** (entries 10–12), whereas asymmetric induction was observed for the reaction of chlorides **1a–c** with lithium 1-phenylethyl- **2a** and 1-(1-naphthyl)ethylamides **2b** (entries 1–3 and 7–9). The equivalence of chlorides **1** and lithium amides **2** did not greatly affect the ratio of the diastereomers. When 10 equiv of lithium 1-phenylethylamide **2a** were reacted with phosphinoselenoic chloride **1c**, phosphinoselenoic amides (*R_p,S*)-**3c** and (*S_p,S*)-**3c** were obtained in a ratio of 41:59. The reaction of 10 equiv of phosphinoselenoic chloride **1c** with lithium amide **2a** also gave amide **3c** in a ratio of 43:57.

The absolute configurations of (*R_p,S*)-*P*-*tert*-butyl-*P*-phenyl-*N*-(1-phenylethyl)phosphinoselenoic amide (*R_p,S*)-**3c** and (*R_p,S*)-*N*-(1-cyclohexylethyl)-*P*-*tert*-butyl-*P*-phenylphosphinoselenoic amide (*R_p,S*)-**3l** were determined by X-ray molecular structure analyses, and those of other derivatives were assigned based on the similarities of their spectroscopic properties with **3c**

Table 2. Selected physical properties of optically active *P*-chiral phosphinoselenoic amides

Entry	3	R_f^a	$[\alpha]_D^{20b}$	^{31}P (ppm) ^c	^{77}Se (ppm) ^c
1	(<i>R</i> _P , <i>S</i>)- 3a	0.4	−44	74.1	−386.8
	(<i>S</i> _P , <i>S</i>)- 3a	0.3	−55	75.0	−368.0
2	(<i>R</i> _P , <i>S</i>)- 3b	0.4	−40	70.2	−363.5
	(<i>S</i> _P , <i>S</i>)- 3b	0.3	−37	70.8	−342.9
3	(<i>R</i> _P , <i>S</i>)- 3c	0.4	−40	79.0	−369.2
	(<i>S</i> _P , <i>S</i>)- 3c	0.3	−62	81.3	−335.4
4	(<i>R</i> _P , <i>S</i>)- 3g	0.3	−28	73.8	−414.3
	(<i>S</i> _P , <i>S</i>)- 3g	0.2	+15	75.5	−371.2
5	(<i>R</i> _P , <i>S</i>)- 3h	0.3	−13	69.8	−390.6
	(<i>S</i> _P , <i>S</i>)- 3h	0.2	+27	71.4	−346.3
6	(<i>R</i> _P , <i>S</i>)- 3i	0.3	−13	78.3	−388.5
	(<i>S</i> _P , <i>S</i>)- 3i	0.2	−18	82.0	−336.9
7	(<i>R</i> _P , <i>S</i>)- 3j	0.4	−33	72.7	−391.3
	(<i>S</i> _P , <i>S</i>)- 3j	0.3	+25	73.4	−382.2
8	(<i>R</i> _P , <i>S</i>)- 3k	0.4	−33	68.6	−368.1
	(<i>S</i> _P , <i>S</i>)- 3k	0.3	+31	69.1	−358.3
9	(<i>R</i> _P , <i>S</i>)- 3l	0.4	−32	77.4	−367.0
	(<i>S</i> _P , <i>S</i>)- 3l	0.3	+18	78.4	−353.6

^a CH₂Cl₂/hexane = 1:1 (v/v).^b *c* 1.0, CH₂Cl₂.^c Measured in CDCl₃.

and **3l** (Table 2). Products **3** with lower polarities were assigned as (*R*_P,*S*)-isomers and their signals in ^{31}P NMR spectra were always at lower fields than those of the products with higher polarities, which were assigned as (*S*_P,*S*)-isomers. A similar trend was observed for the signals of (*R*_P,*S*)-**3** in ^{77}Se NMR spectra.

ORTEP drawings of phosphinoselenoic amides (*R*_P,*S*)-**3c**⁷ and (*R*_P,*S*)-**3l** are shown in Figures 1 and 2. The phosphorus atoms adopted slightly distorted tetrahedral structures. The P–Se bond lengths in (*R*_P,*S*)-**3c** (2.118 Å) and (*R*_P,*S*)-**3l** (2.113 Å) were slightly longer than that in phosphinoselenoic chloride (2.081 Å) and close to those in phosphinochalcogenoselenoic acid esters (2.103, 2.099 Å).^{6b} The N–H group in (*R*_P,*S*)-**3c** interacted with the selenium atom of an adjacent molecule. The H···Se distance was 3.06 Å, and the NH···Se motif was almost linear, as evidenced by a bond angle of 172°. These results suggest that intermolecular hydrogen bonding is present in the form NH···Se.

Finally, optically active *P*-chiral phosphinoselenoic chlorides were reacted with optically active lithium amide (Scheme 2). The reaction of (*R*)-phosphinoselenoic chloride (*R*)-**1c** with lithium (*S*)-1-phenylethyl amide gave phosphinoselenoic amide (*R*_P,*S*)-**3c** and (*S*_P,*S*)-**3c** in a ratio of 11:89. On the other hand, reaction of (*S*)-phosphinoselenoic chloride (*S*)-**1c** with lithium (*S*)-1-phenylethyl amide gave (*R*_P,*S*)-**3c** and (*S*_P,*S*)-**3c** in a ratio of 62:38. The sum of the ratios (73:127) of (*R*_P,*S*)-**3c** and (*S*_P,*S*)-**3c** in these reactions was in good agreement with the ratio of (*R*_P,*S*)-**3c** and (*S*_P,*S*)-**3c** (38:62) observed in Table 1. These results suggest that the decrease in the diastereomeric ratio is not due to the configurational instability of the chloride **1c** under these reaction conditions. If it was, the ratio of the two diastereomers would be nearly the same in these reactions. Furthermore, when the diastereomers were heated for 2 h, no epimerization occurred. Therefore,

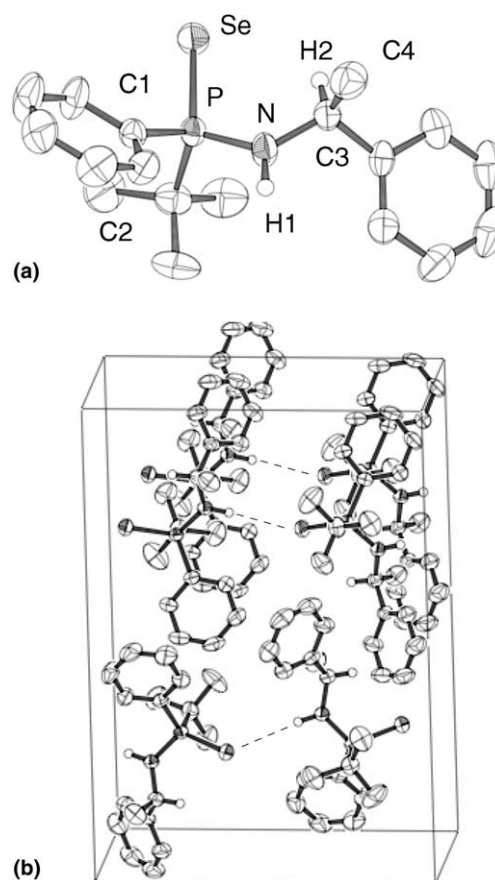


Figure 1. (a) ORTEP drawing of (*R*_P,*S*)-**3c** with thermal ellipsoid plot (50% probability). Hydrogen atoms (except for H1 and H2) are omitted for clarity. Selected bond lengths (Å): P–Se, 2.1180(7); P–N, 1.652(2). Selected bond angles (°): Se–P–N, 113.00(8); Se–P–C1, 110.75(9); Se–P–C2, 112.47(10); N–P–C1, 105.7(1); N–P–C2, 106.8(1); C1–P–C2, 107.7(1); P–N–C3, 126.2(2); Se–P–N–C3, −12.0(3). (b) Crystal packing diagram (Hydrogen bonds are shown as dashed lines). Distance between Se···H: 3.06 Å; angle of Se···HN: 172°.

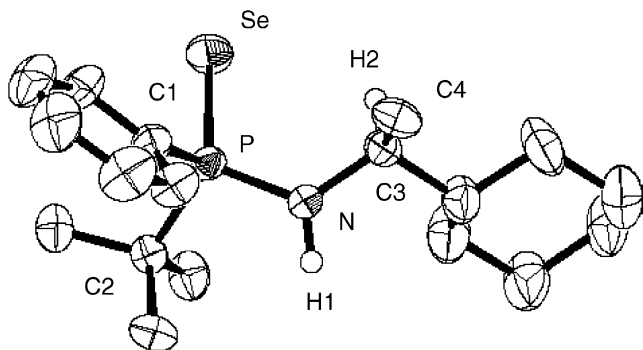


Figure 2. ORTEP drawing of (*R_p,S*)-**3l** with thermal ellipsoid plot (50% probability). Hydrogen atoms (except for H1 and H2) are omitted for clarity. Selected bond lengths (Å): P–Se, 2.1134(7); P–N, 1.656(3). Selected bond angles (°): Se–P–N, 112.74(9); Se–P–C1, 111.7(1); Se–P–C2, 112.70(9); N–P–C1, 110.5(1); N–P–C2, 104.5(1); C1–P–C2, 104.1(1); P–N–C3, 124.1(2); Se–P–N–C3, 32.4(3).

the substitution reaction of (*R*)-**1c** with the lithium amide (*S*)-**2a** proceeds exclusively with inversion of configuration at the phosphorus center. Similarly, inversion is predominant at the phosphorus center for the reaction of (*S*)-**1c**. However, these reactions also involve retention of the stereochemistry of phosphorus atom of **1c**. In particular, it is more important in the latter case. No clear experimental results are currently available to explain this point. However, lithium amide **2a** may approach the phosphorus atom of chloride **1c** from the P–Cl bond. Alternatively, the reaction may involve pseudorotation of the pentavalent adducts between the optically active chloride **1c** and lithium amide **2a**. In any case, the asymmetric induction observed in Table 1 is not due to the kinetic resolution of racemic chlorides **1** with enantiomerically pure lithium amides **2**.

3. Conclusion

We successfully synthesized optically active *P*-chiral phosphinoselenoic amides from racemic *P*-chiral phosphinoselenoic chlorides and optically active lithium

amides, and their stereoisomers were isolated in a pure form. Recently, optically active *P*-achiral phosphinothioic,⁹ and phosphinoselenoic amides¹⁰ have successfully been used in transition metal-catalyzed asymmetric reactions. The optically active amides synthesized herein may also be suitable optically active ligands.

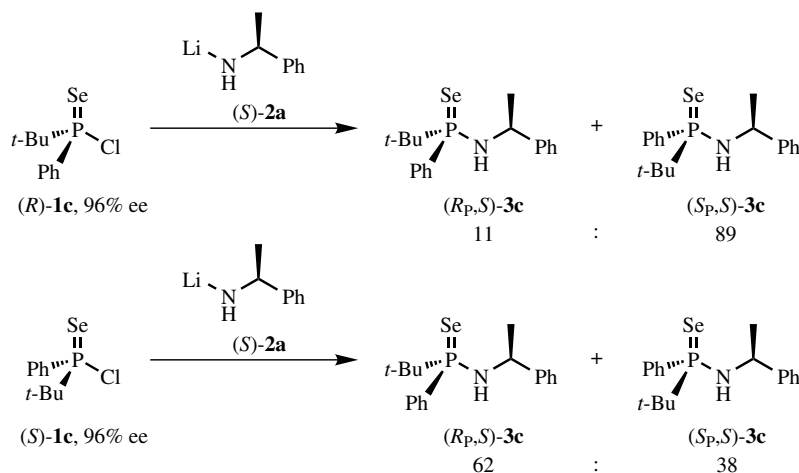
4. Experimental

4.1. General

All reactions were carried out under an argon atmosphere. Dehydrated THF was purchased from Kanto Chemical Co., Inc. and used as received. ¹H NMR, ¹³C NMR, ³¹P NMR, and ⁷⁷Se NMR spectra were recorded on JEOL α-400 spectrometer in CDCl₃, using TMS (0.0 ppm) or CHCl₃ (7.24 ppm) for ¹H NMR and CDCl₃ for ¹³C NMR as internal references, 85% H₃PO₄ for ³¹P NMR and Me₂Se for ⁷⁷Se NMR as external references. Melting points were determined using a Yanagimoto melting point apparatus and are uncorrected. The mass spectra (MS) were taken on Shimadzu GCMS QP1000 (EI mode). The high resolution mass spectroscopy (HRMS) was taken on JEOL JMS-GCmate II GCMS System. Elemental analyses were carried out by Elemental Analysis Center of Kyoto University. Optical rotations were measured using a Jasco P-1020 polarimeter with a 1 dm cell.

4.2. Synthesis of optically active *P*-chiral phosphinoselenoic amides **3**

4.2.1. A representative procedure for the synthesis of *P*-(1-methylethyl)-*P*-phenyl-*N*-(1-phenylethyl)phosphinoselenoic amide **3a.** To a solution of (*S*)-1-phenylethylamine (0.28 mL, 2.2 mmol) in THF (5 mL) was added BuLi (1.6 mol/L hexane solution, 1.25 mL, 2.0 mmol) at 0 °C, and the reaction mixture stirred at that temperature for 10 min. To a solution of *P*-(1-methylethyl)-*P*-phenylphosphinoselenoic chloride **1a** (0.531 g, 2.00 mmol) in THF (5 mL) was added the reaction mix-



Scheme 2.

ture at 0 °C, and the mixture stirred at room temperature for 2 h. The mixture was extracted with CH₂Cl₂ (50 mL), and the organic layer washed with water (50 mL × 2), dried over MgSO₄ and filtered off. After the solvent was removed, the residue was purified by column chromatography on silica gel using *n*-C₆H₁₄/CH₂Cl₂ as eluent to give 0.252 g (36%) of (*R*_P,*S*)-**3a** as a colorless solid and 0.323 g (46%) of (*S*_P,*S*)-**3a** as a colorless solid. (*R*_P,*S*)-**3a**: $[\alpha]_{\text{D}}^{20} = -44$ (*c* 1.0, CH₂Cl₂). Mp 65–67 °C (decomp). ¹H NMR (400 MHz, CDCl₃): δ 0.86 (dd, *J* = 7.0 Hz, *J*_{HP} = 20.3 Hz, 3H), 1.13 (dd, *J* = 6.8 Hz, *J*_{HP} = 19.5 Hz, 3H), 1.29 (d, *J* = 6.3 Hz, 3H), 1.99 (s, 1H), 2.18–2.31 (m, 1H), 4.64–4.72 (m, 1H), 7.24–7.54 (m, 8H), 8.02–8.07 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 16.5, 16.6, 24.8 (d, *J*_{CP} = 3.3 Hz), 32.6 (d, *J*_{CP} = 61.2 Hz), 52.3, 126.5, 127.3, 128.2 (d, *J*_{CP} = 11.6 Hz), 128.6, 131.7 (d, *J*_{CP} = 2.5 Hz), 132.2 (d, *J*_{CP} = 10.8 Hz), 133.1, 145.0 (d, *J*_{CP} = 7.4 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 74.1 (*J*_{PSe} = 745.6 Hz). ⁷⁷Se NMR (76 MHz, CDCl₃): δ -386.8 (d, *J*_{SeP} = 745.6 Hz). MS (EI): *m/z* 351 (M⁺). Anal. Calcd for C₁₇H₂₂NPSe: C, 58.29; H, 6.33; N, 4.00. Found: C, 58.28; H, 6.20; N, 3.94. (*S*_P,*S*)-**3a**: $[\alpha]_{\text{D}}^{20} = -55$ (*c* 1.0, CH₂Cl₂). Mp 89–91 °C (decomp). ¹H NMR (400 MHz, CDCl₃): δ 0.93 (dd, *J* = 6.8 Hz, *J*_{HP} = 20.5 Hz, 3H), 1.22 (dd, *J* = 6.8 Hz, *J*_{HP} = 19.0 Hz, 3H), 1.53 (d, *J* = 6.8 Hz, 3H), 2.22–2.33 (m, 1H), 2.35 (s, 1H), 4.29–4.37 (m, 1H), 7.12–7.23 (m, 5H), 7.26–7.31 (m, 2H), 7.37–7.41 (m, 1H), 7.74–7.80 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 16.5, 25.5 (d, *J*_{CP} = 4.1 Hz), 32.0 (d, *J*_{CP} = 61.2 Hz), 52.3, 126.3, 127.0, 127.9 (d, *J*_{CP} = 12.4 Hz), 128.3, 131.0 (d, *J*_{CP} = 82.7 Hz), 131.5 (d, *J*_{CP} = 3.3 Hz), 132.5 (d, *J*_{CP} = 10.8 Hz), 144.7 (d, *J*_{CP} = 5.8 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 75.0 (*J*_{PSe} = 744.2 Hz). ⁷⁷Se NMR (76 MHz, CDCl₃): δ -368.0 (d, *J*_{SeP} = 744.2 Hz). MS (EI): *m/z* 351 (M⁺). Anal. Calcd for C₁₇H₂₂NPSe: C, 58.29; H, 6.33; N, 4.00. Found: C, 58.25; H, 6.28; N, 3.99. (*S*_P,*R*)-**3a**: $[\alpha]_{\text{D}}^{20} = +44$ (*c* 1.0, CH₂Cl₂). (*R*_P,*R*)-**3a**: $[\alpha]_{\text{D}}^{20} = +53$ (*c* 1.0, CH₂Cl₂).

4.2.2. P-Cyclohexyl-P-phenyl-N-(1-phenylethyl)phosphinoselenoic amide 3b. (*R*_P,*S*)-**3b**: A colorless solid. $[\alpha]_{\text{D}}^{20} = -40$ (*c* 1.0, CH₂Cl₂). Mp 75–77 °C (decomp). ¹H NMR (400 MHz, CDCl₃): δ 0.89–1.85 (m, 11H), 1.21 (d, *J* = 6.8 Hz, 3H), 2.25 (s, 1H), 4.57–4.65 (m, 1H), 7.16–7.20 (m, 1H), 7.26 (t, *J* = 7.8 Hz, 2H), 7.33–7.44 (m, 5H), 7.94–7.98 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 24.6 (d, *J*_{CP} = 3.3 Hz), 25.5, 25.9 (d, *J*_{CP} = 14.9 Hz), 26.0 (d, *J*_{CP} = 14.9 Hz), 26.1, 26.3, 42.4 (d, *J*_{CP} = 59.5 Hz), 52.0, 126.6, 127.3, 128.0 (d, *J*_{CP} = 12.4 Hz), 128.5, 131.6 (d, *J*_{CP} = 2.5 Hz), 132.3 (d, *J*_{CP} = 9.9 Hz), 132.6 (d, *J*_{CP} = 81.9 Hz), 145.0 (d, *J*_{CP} = 6.6 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 70.2 (*J*_{PSe} = 739.6 Hz). ⁷⁷Se NMR (76 MHz, CDCl₃): δ -363.5 (d, *J*_{SeP} = 739.6 Hz). MS (EI): *m/z* 391 (M⁺). Anal. Calcd for C₂₀H₂₆NPSe: C, 61.54; H, 6.71; N, 3.59. Found: C, 61.34; H, 6.73; N, 3.54. (*S*_P,*S*)-**3b**: A colorless solid. $[\alpha]_{\text{D}}^{20} = -37$ (*c* 1.0, CH₂Cl₂). Mp 82–84 °C (decomp). ¹H NMR (400 MHz, CDCl₃): δ 1.06–1.95 (m, 11H), 1.47 (d, *J* = 6.8 Hz, 3H), 2.37 (s, 1H), 4.21–4.31 (m, 1H), 7.06–7.41 (m, 8H), 7.65–7.70 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 25.5 (d, *J*_{CP} = 4.1 Hz),

25.6, 25.9 (d, *J*_{CP} = 15.7 Hz), 26.00, 26.01 (d, *J*_{CP} = 14.9 Hz), 26.2, 42.1 (d, *J*_{CP} = 60.4 Hz), 52.1, 126.2, 126.9, 127.7 (d, *J*_{CP} = 12.4 Hz), 128.3, 130.5, 131.4 (d, *J*_{CP} = 2.5 Hz), 132.6 (d, *J*_{CP} = 10.8 Hz), 144.7 (d, *J*_{CP} = 5.8 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 70.8 (*J*_{PSe} = 739.6 Hz). ⁷⁷Se NMR (76 MHz, CDCl₃): δ -342.9 (d, *J*_{SeP} = 739.6 Hz). MS (EI): *m/z* 391 (M⁺). Anal. Calcd for C₂₀H₂₆NPSe: C, 61.54; H, 6.71; N, 3.59. Found: C, 61.56; H, 6.87; N, 3.38. (*S*_P,*R*)-**3b**: $[\alpha]_{\text{D}}^{20} = +39$ (*c* 1.0, CH₂Cl₂). (*R*_P,*R*)-**3b**: $[\alpha]_{\text{D}}^{20} = +35$ (*c* 1.0, CH₂Cl₂).

4.2.3. P-(1,1-Dimethylethyl)-P-phenyl-N-(1-phenylethyl)phosphinoselenoic amide 3c. (*R*_P,*S*)-**3c**: A colorless solid. $[\alpha]_{\text{D}}^{20} = -40$ (*c* 1.0, CH₂Cl₂). Mp 128–130 °C (decomp). ¹H NMR (400 MHz, CDCl₃): δ 1.11 (d, *J*_{HP} = 17.1 Hz, 9H), 1.32 (d, *J* = 6.8 Hz, 3H), 2.40 (s, 1H), 4.78–4.87 (m, 1H), 7.26–7.53 (m, 8H), 8.06–8.11 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 24.5, 25.0, 35.6 (d, *J*_{CP} = 56.2 Hz), 52.5, 126.6, 127.3, 127.7 (d, *J*_{CP} = 11.6 Hz), 128.7, 131.5 (d, *J*_{CP} = 3.3 Hz), 132.4 (d, *J*_{CP} = 78.6 Hz), 133.3 (d, *J*_{CP} = 9.9 Hz), 145.3 (d, *J*_{CP} = 7.4 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 79.0 (*J*_{PSe} = 750.2 Hz). ⁷⁷Se NMR (76 MHz, CDCl₃): δ -369.2 (d, *J*_{SeP} = 750.2 Hz). MS (EI): *m/z* 365 (M⁺). Anal. Calcd for C₁₈H₂₄NPSe: C, 59.34; H, 6.64; N, 3.84. Found: C, 59.23; H, 6.49; N, 3.71. (*S*_P,*S*)-**3c**: A colorless solid. $[\alpha]_{\text{D}}^{20} = -62$ (*c* 1.0, CH₂Cl₂). Mp 104–106 °C (decomp). ¹H NMR (400 MHz, CDCl₃): δ 1.19 (d, *J*_{HP} = 17.1 Hz, 9H), 1.61 (d, *J* = 6.3 Hz, 3H), 2.29 (s, 1H), 4.40–4.50 (m, 1H), 7.19–7.38 (m, 8H), 7.47–7.73 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 25.0, 25.8 (d, *J*_{CP} = 3.3 Hz), 35.2 (d, *J*_{CP} = 56.2 Hz), 52.3, 126.2, 126.9, 127.3 (d, *J*_{CP} = 12.4 Hz), 128.4, 130.2 (d, *J*_{CP} = 81.1 Hz), 131.3 (d, *J*_{CP} = 2.5 Hz), 133.8 (d, *J*_{CP} = 10.8 Hz), 145.1 (d, *J*_{CP} = 5.8 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 81.3 (*J*_{PSe} = 741.1 Hz). ⁷⁷Se NMR (76 MHz, CDCl₃): δ -335.4 (d, *J*_{SeP} = 741.1 Hz). MS (EI): *m/z* 365 (M⁺). Anal. Calcd for C₁₈H₂₄NPSe: C, 59.34; H, 6.64; N, 3.84. Found: C, 59.18; H, 6.60; N, 3.80. (*S*_P,*R*)-**3c**: $[\alpha]_{\text{D}}^{20} = +40$ (*c* 1.0, CH₂Cl₂). (*R*_P,*R*)-**3c**: $[\alpha]_{\text{D}}^{20} = +60$ (*c* 1.0, CH₂Cl₂).

4.2.4. P-(2-Methoxyphenyl)-P-phenyl-N-(1-phenylethyl)phosphinoselenoic amide 3d. A pale-yellow oil. ³¹P NMR (162 MHz, CDCl₃): δ 56.1 (*J*_{PSe} = 750.2 Hz), 56.2 (*J*_{PSe} = 750.2 Hz). ⁷⁷Se NMR (76 MHz, CDCl₃): δ -260.0 (d, *J*_{SeP} = 750.2 Hz), -257.8 (d, *J*_{SeP} = 750.2 Hz). MS (EI): *m/z* 399 (M⁺).

4.2.5. P-(4-Methylphenyl)-P-phenyl-N-(1-phenylethyl)phosphinoselenoic amide 3e. A pale-yellow oil. ³¹P NMR (162 MHz, CDCl₃): δ 54.1 (*J*_{PSe} = 745.6 Hz), 54.8 (*J*_{PSe} = 745.6 Hz). ⁷⁷Se NMR (76 MHz, CDCl₃): δ -265.1 (d, *J*_{SeP} = 745.6 Hz), -259.1 (d, *J*_{SeP} = 745.6 Hz). MS (EI): *m/z* 415 (M⁺).

4.2.6. P-(4-Chlorophenyl)-P-phenyl-N-(1-phenylethyl)phosphinoselenoic amide 3f. A pale-yellow oil. ³¹P NMR (162 MHz, CDCl₃): δ 55.1 (*J*_{PSe} = 757.7 Hz), 55.6 (*J*_{PSe} = 757.7 Hz). ⁷⁷Se NMR (76 MHz, CDCl₃): δ -258.3 (d, *J*_{SeP} = 757.7 Hz), -255.4 (d, *J*_{SeP} = 757.7 Hz). MS (EI): *m/z* 419 (M⁺).

4.2.7. *P*-(1-Methylethyl)-*N*-[1-(1-naphthyl)ethyl]-*P*-phenylphosphinoselenoic amide **3g.** (*R_P,S*)-**3g**: A pale-yellow solid. $[\alpha]_{\text{D}}^{20} = -28$ (*c* 1.0, CH₂Cl₂). Mp 109–111 °C (decomp). ¹H NMR (400 MHz, CDCl₃): δ 0.82 (dd, *J* = 6.8 Hz, *J*_{HP} = 20.0 Hz, 3H), 1.07 (dd, *J* = 6.8 Hz, *J*_{HP} = 19.0 Hz, 3H), 1.37 (d, *J* = 6.3 Hz, 3H), 2.12–2.25 (m, 1H), 2.55 (s, 1H), 5.49–5.58 (m, 1H), 7.43–7.62 (m, 7H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 8.03–8.09 (m, 2H), 8.38 (d, *J* = 8.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 16.4, 16.5, 23.5, 32.5 (d, *J*_{CP} = 61.2 Hz), 48.2, 123.2, 123.9, 125.3, 125.8, 126.4, 128.1, 128.1 (d, *J*_{CP} = 12.4 Hz), 128.7, 130.5, 131.6 (d, *J*_{CP} = 2.5 Hz), 131.9 (d, *J*_{CP} = 10.8 Hz), 133.4 (d, *J*_{CP} = 80.2 Hz), 133.9, 140.3 (d, *J*_{CP} = 8.3 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 73.8 (*J*_{PSe} = 745.6 Hz). ⁷⁷Se NMR (76 MHz, CDCl₃): δ -414.3 (d, *J*_{SeP} = 745.6 Hz). MS (EI): *m/z* 401 (M⁺). HRMS was performed on the mixture of diastereomers. HRMS (EI): *m/z* calcd for C₂₁H₂₄NPSe (M⁺) 401.0812, found 401.0823. (*S_P,S*)-**3g**: A pale-yellow solid. $[\alpha]_{\text{D}}^{20} = +15$ (*c* 1.0, CH₂Cl₂). Mp 82–84 °C (decomp). ¹H NMR (400 MHz, CDCl₃): δ 0.95 (dd, *J* = 6.8 Hz, *J*_{HP} = 20.0 Hz, 3H), 1.26 (dd, *J* = 6.8 Hz, *J*_{HP} = 19.0 Hz, 3H), 1.67 (d, *J* = 6.3 Hz, 3H), 2.25–2.38 (m, 1H), 2.57 (s, 1H), 5.10–5.21 (m, 1H), 7.10–7.15 (m, 2H), 7.23–7.28 (m, 1H), 7.29–7.34 (m, 1H), 7.37–7.42 (m, 2H), 7.55 (d, *J* = 6.9 Hz, 1H), 7.67–7.72 (m, 3H), 7.77–7.84 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 16.5, 16.6, 25.9 (d, *J*_{CP} = 3.3 Hz), 32.2 (d, *J*_{CP} = 61.2 Hz), 48.7, 123.1, 123.2, 125.3, 125.5, 125.8, 127.6, 127.8 (d, *J*_{CP} = 12.4 Hz), 128.7, 130.0, 130.9 (d, *J*_{CP} = 82.7 Hz), 131.4 (d, *J*_{CP} = 2.5 Hz), 132.3 (d, *J*_{CP} = 10.8 Hz), 133.7, 140.9 (d, *J*_{CP} = 5.0 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 75.5 (*J*_{PSe} = 744.2 Hz). ⁷⁷Se NMR (76 MHz, CDCl₃): δ -371.2 (d, *J*_{SeP} = 744.2 Hz). MS (EI): *m/z* 401 (M⁺). (*S_P,R*)-**3g**: $[\alpha]_{\text{D}}^{20} = +26$ (*c* 1.0, CH₂Cl₂). (*R_P,R*)-**3g**: $[\alpha]_{\text{D}}^{20} = -14$ (*c* 1.0, CH₂Cl₂).

4.2.8. *P*-Cyclohexyl-*N*-[1-(1-naphthyl)ethyl]-*P*-phenylphosphinoselenoic amide **3h.** (*R_P,S*)-**3h**: A pale-yellow solid. $[\alpha]_{\text{D}}^{20} = -13$ (*c* 1.0, CH₂Cl₂). Mp 52–54 °C (decomp). ¹H NMR (400 MHz, CDCl₃): δ 0.92–1.94 (m, 11H), 1.37 (d, *J* = 6.3 Hz, 3H), 2.52 (s, 1H), 5.49–5.58 (m, 1H), 7.45–7.60 (m, 6H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 7.3 Hz, 1H), 8.04–8.09 (m, 2H), 8.41 (d, *J* = 8.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 23.5, 25.5, 25.9 (d, *J*_{CP} = 14.9 Hz), 25.9, 26.0 (d, *J*_{CP} = 15.7 Hz), 26.2, 42.4 (d, *J*_{CP} = 60.4 Hz), 48.2, 123.4, 123.9, 125.3, 125.9, 126.4, 128.1 (d, *J*_{CP} = 12.4 Hz), 128.2, 128.7, 130.6, 131.6 (d, *J*_{CP} = 2.5 Hz), 132.2 (d, *J*_{CP} = 9.9 Hz), 133.4 (d, *J*_{CP} = 81.9 Hz), 134.0, 140.4 (d, *J*_{CP} = 8.3 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 69.8 (*J*_{PSe} = 744.2 Hz). ⁷⁷Se NMR (76 MHz, CDCl₃): δ -390.6 (d, *J*_{SeP} = 744.2 Hz). MS (EI): *m/z* 441 (M⁺). Anal. Calcd for C₂₄H₂₈NPSe: C, 65.45; H, 6.41; N, 3.18. Found: C, 65.18; H, 6.24; N, 3.17. (*S_P,S*)-**3h**: A pale-yellow solid. $[\alpha]_{\text{D}}^{20} = +27$ (*c* 1.0, CH₂Cl₂). Mp 48–50 °C (decomp). ¹H NMR (400 MHz, CDCl₃): δ 1.10–1.70 (m, 8H), 1.68 (d, *J* = 6.7 Hz, 3H), 1.83–1.86 (m, 1H), 1.99–2.07 (m, 2H, CH₂), 2.59 (s, 1H), 5.12–5.22 (m, 1H), 7.04–7.11 (m, 2H), 7.20–7.42 (m, 4H), 7.56 (d, *J* = 7.3 Hz,

1H), 7.68 (dt, *J* = 2.9, 7.3 Hz, 3H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 25.6, 25.8, 25.88 (d, *J*_{CP} = 12.4 Hz), 25.92 (d, *J*_{CP} = 12.4 Hz), 26.0, 26.3, 42.3 (d, *J*_{CP} = 60.4 Hz), 48.4, 123.1, 123.2, 125.2, 125.4, 125.8, 127.5, 127.6 (d, *J*_{CP} = 12.4 Hz), 128.6, 129.9, 130.2, 131.2, 132.4 (d, *J*_{CP} = 10.8 Hz), 133.6, 140.9 (d, *J*_{CP} = 5.0 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 71.4 (*J*_{PSe} = 738.1 Hz). ⁷⁷Se NMR (76 MHz, CDCl₃): δ -346.3 (d, *J*_{SeP} = 738.1 Hz). MS (EI): *m/z* 441 (M⁺). Anal. Calcd for C₂₄H₂₈NPSe: C, 65.45; H, 6.41; N, 3.18. Found: C, 65.17; H, 6.37; N, 3.15. (*S_P,R*)-**3h**: $[\alpha]_{\text{D}}^{20} = +13$ (*c* 1.0, CH₂Cl₂). (*R_P,R*)-**3h**: $[\alpha]_{\text{D}}^{20} = -27$ (*c* 1.0, CH₂Cl₂).

4.2.9. *P*-(1,1-Dimethylethyl)-*N*-[1-(1-naphthyl)ethyl]-*P*-phenylphosphinoselenoic amide **3i.** (*R_P,S*)-**3i**: A pale-yellow solid. $[\alpha]_{\text{D}}^{20} = -13$ (*c* 1.0, CH₂Cl₂). Mp 155–157 °C (decomp). ¹H NMR (400 MHz, CDCl₃): δ 1.06 (d, *J*_{HP} = 17.1 Hz, 9H), 1.40 (d, *J* = 6.8 Hz, 3H), 2.50 (s, 1H), 5.61–5.69 (m, 1H), 7.48–7.59 (m, 6H), 7.68 (d, *J* = 6.8 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 8.08–8.13 (m, 2H), 8.46 (d, *J* = 8.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 23.1, 24.9, 35.7 (d, *J*_{CP} = 56.2 Hz), 48.6, 123.2, 124.3, 125.3, 125.9, 126.5, 127.6 (d, *J*_{CP} = 11.6 Hz), 128.2, 128.7, 130.7, 131.5 (d, *J*_{CP} = 2.5 Hz), 132.7 (d, *J*_{CP} = 78.6 Hz), 133.2 (d, *J*_{CP} = 9.9 Hz), 134.0, 140.4 (d, *J*_{CP} = 9.1 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 78.3 (*J*_{PSe} = 745.6 Hz). ⁷⁷Se NMR (76 MHz, CDCl₃): δ -388.5 (d, *J*_{SeP} = 745.6 Hz). MS (EI): *m/z* 415 (M⁺). Anal. Calcd for C₂₂H₂₆NPSe: C, 63.77; H, 6.32; N, 3.38. Found: C, 63.50; H, 6.30; N, 3.35. (*S_P,S*)-**3i**: A pale-yellow solid. $[\alpha]_{\text{D}}^{20} = -18$ (*c* 1.0, CH₂Cl₂). Mp 145–147 °C (decomp). ¹H NMR (400 MHz, CDCl₃): δ 1.22 (d, *J*_{HP} = 17.0 Hz, 9H), 1.74 (d, *J* = 6.8 Hz, 3H), 2.49 (s, 1H), 5.19–5.30 (m, 1H), 7.03 (dt, *J* = 3.4, 7.8 Hz, 2H), 7.18–7.27 (m, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.63–7.83 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 25.0 (d, *J*_{CP} = 1.7 Hz), 26.1 (d, *J*_{CP} = 1.7 Hz), 35.3 (d, *J*_{CP} = 56.2 Hz), 48.7, 122.7, 123.3, 125.3, 125.5, 125.8, 127.2 (d, *J*_{CP} = 12.4 Hz), 127.5, 128.5, 129.9, 130.2 (d, *J*_{CP} = 81.9 Hz), 131.2 (d, *J*_{CP} = 2.5 Hz), 133.5 (d, *J*_{CP} = 10.8 Hz), 133.7, 141.3 (d, *J*_{CP} = 5.8 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 82.0 (*J*_{PSe} = 744.2 Hz). ⁷⁷Se NMR (76 MHz, CDCl₃): δ -336.9 (d, *J*_{SeP} = 744.2 Hz). MS (EI): *m/z* 415 (M⁺). Anal. Calcd for C₂₂H₂₆NPSe: C, 63.77; H, 6.32; N, 3.38. Found: C, 63.54; H, 6.22; N, 3.37. (*S_P,R*)-**3i**: $[\alpha]_{\text{D}}^{20} = +12$ (*c* 1.0, CH₂Cl₂). (*R_P,R*)-**3i**: $[\alpha]_{\text{D}}^{20} = +16$ (*c* 1.0, CH₂Cl₂).

4.2.10. *N*-(1-Cyclohexylethyl)-*P*-(1-methylethyl)-*P*-phenylphosphinoselenoic amide **3j.** (*R_P,S*)-**3j**: A colorless solid. $[\alpha]_{\text{D}}^{20} = -33$ (*c* 1.0, CH₂Cl₂). Mp 105–107 °C (decomp). ¹H NMR (400 MHz, CDCl₃): δ 0.82 (d, *J* = 5.4 Hz, 3H), 0.83 (dd, *J* = 6.8 Hz, *J*_{HP} = 20.5 Hz, 3H), 0.90–1.13 (m, 5H), 1.17 (dd, *J* = 6.8 Hz, *J*_{HP} = 18.5 Hz, 3H), 1.33–1.40 (m, 1H), 1.59–1.69 (m, 5H), 2.16 (s, 1H), 2.20–2.30 (m, 1H), 3.19–3.28 (m, 1H), 7.34–7.42 (m, 3H), 7.89–7.94 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 16.4, 16.6, 19.2 (d, *J*_{CP} = 2.5 Hz), 26.1, 26.2, 26.4, 27.8, 29.3, 32.0 (d, *J*_{CP} = 62.0 Hz), 44.3 (d, *J*_{CP} = 5.8 Hz), 52.4 (d, *J*_{CP} = 2.3 Hz), 127.9 (d, *J*_{CP} = 12.4 Hz), 131.3 (d, *J*_{CP} = 2.5 Hz), 131.9 (d,

$J_{CP} = 9.9$ Hz), 133.4 (d, $J_{CP} = 79.4$ Hz). ^{31}P NMR (162 MHz, CDCl_3): δ 72.7 ($J_{\text{PSe}} = 741.1$ Hz). ^{77}Se NMR (76 MHz, CDCl_3): δ -391.3 (d, $J_{\text{SeP}} = 741.1$ Hz). MS (EI): m/z 357 (M^+). The elemental analysis was performed on a mixture of diastereomers. Anal. Calcd for $\text{C}_{17}\text{H}_{28}\text{NPSe}$: C, 57.30; H, 7.92; N, 3.93. Found: C, 57.00; H, 7.81; N, 3.86. (*S_p,S*)-**3j**: A pale-yellow oil. $[\alpha]_{\text{D}}^{20} = +25$ (c 1.0, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3): δ 0.73–1.30 (m, 6H), 0.82 (dd, $J = 6.8$ Hz, $J_{\text{HP}} = 20.5$ Hz, 3H), 1.05 (d, $J = 6.8$ Hz, 3H), 1.15 (dd, $J = 6.8$ Hz, $J_{\text{HP}} = 19.0$ Hz, 3H), 1.44–1.56 (m, 5H), 1.95 (s, 1H), 2.20–2.34 (m, 1H), 3.02–3.13 (m, 1H), 7.34–7.41 (m, 3H), 7.90–7.95 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 16.3, 16.4, 18.8 (d, $J_{CP} = 3.3$ Hz), 26.0, 26.2, 26.3, 27.5, 29.3, 31.8 (d, $J_{CP} = 62.0$ Hz), 44.1 (d, $J_{CP} = 5.0$ Hz), 52.9 (d, $J_{CP} = 2.5$ Hz), 127.8 (d, $J_{CP} = 12.4$ Hz), 131.3 (d, $J_{CP} = 2.5$ Hz), 132.1 (d, $J_{CP} = 10.8$ Hz), 132.3 (d, $J_{CP} = 82.7$ Hz). ^{31}P NMR (162 MHz, CDCl_3): δ 73.4 ($J_{\text{PSe}} = 742.7$ Hz). ^{77}Se NMR (76 MHz, CDCl_3): δ -382.2 (d, $J_{\text{SeP}} = 742.7$ Hz). MS (EI): m/z 357 (M^+). (*S_p,R*)-**3j**: $[\alpha]_{\text{D}}^{20} = +33$ (c 1.0, CH_2Cl_2). (*R_p,R*)-**3j**: $[\alpha]_{\text{D}}^{20} = -25$ (c 1.0, CH_2Cl_2).

4.2.11. *P*-Cyclohexyl-*N*-(1-cyclohexylethyl)-*P*-phenylphosphinoselenoic amide **3k.** (*R_p,S*)-**3k**: A colorless solid. $[\alpha]_{\text{D}}^{20} = -33$ (c 1.0, CH_2Cl_2). Mp 92–94 °C (decomp). ^1H NMR (400 MHz, CDCl_3): δ 0.82 (d, $J = 6.8$ Hz, 3H), 0.85–1.28 (m, 9H), 1.37–1.48 (m, 3H), 1.59–1.66 (m, 7H), 1.77–1.80 (m, 1H), 1.89–1.98 (m, 2H), 2.14 (s, 1H), 3.18–3.29 (m, 1H), 7.34–7.42 (m, 3H), 7.88–7.93 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 19.1 (d, $J_{CP} = 2.5$ Hz), 25.6, 25.8, 25.9, 26.1, 26.2, 26.26, 26.30, 26.4, 27.9, 29.4, 42.1 (d, $J_{CP} = 61.2$ Hz), 44.3 (d, $J_{CP} = 6.6$ Hz), 52.2 (d, $J_{CP} = 1.7$ Hz), 127.8 (d, $J_{CP} = 11.6$ Hz), 131.2 (d, $J_{CP} = 2.5$ Hz), 132.1 (d, $J_{CP} = 10.8$ Hz), 133.4 (d, $J_{CP} = 80.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3): δ 68.6 ($J_{\text{PSe}} = 739.6$ Hz). ^{77}Se NMR (76 MHz, CDCl_3): δ -368.1 (d, $J_{\text{SeP}} = 739.6$ Hz). MS (EI): m/z 397 (M^+). Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{NPSe}$: C, 60.60; H, 8.14; N, 3.53. Found: C, 60.40; H, 8.12; N, 3.51. (*S_p,S*)-**3k**: A colorless solid. $[\alpha]_{\text{D}}^{20} = +31$ (c 1.0, CH_2Cl_2). Mp 118–120 °C (decomp). ^1H NMR (400 MHz, CDCl_3): δ 0.77–2.02 (m, 23H), 1.17 (d, $J = 6.8$ Hz, 3H), 3.08–3.17 (m, 1H), 7.40–7.48 (m, 3H), 7.93–7.99 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 18.8 (d, $J_{CP} = 2.5$ Hz), 25.5, 25.7, 25.8, 26.0, 26.06, 26.12, 26.2, 26.4, 27.4, 29.4, 42.0 (d, $J_{CP} = 61.2$ Hz), 44.1 (d, $J_{CP} = 5.8$ Hz), 52.2, 127.8 (d, $J_{CP} = 12.4$ Hz), 131.3, 132.3 (d, $J_{CP} = 82.7$ Hz), 133.0 (d, $J_{CP} = 9.9$ Hz). ^{31}P NMR (162 MHz, CDCl_3): δ 69.1 ($J_{\text{PSe}} = 738.1$ Hz). ^{77}Se NMR (76 MHz, CDCl_3): δ -358.3 (d, $J_{\text{SeP}} = 738.1$ Hz). MS (EI): m/z 397 (M^+). Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{NPSe}$: C, 60.60; H, 8.14; N, 3.53. Found: C, 60.31; H, 8.20; N, 3.49. (*S_p,R*)-**3k**: $[\alpha]_{\text{D}}^{20} = +33$ (c 1.0, CH_2Cl_2). (*R_p,R*)-**3k**: $[\alpha]_{\text{D}}^{20} = -31$ (c 1.0, CH_2Cl_2).

4.2.12. *N*-(1-Cyclohexylethyl)-*P*-(1,1-dimethylethyl)-*P*-phenylphosphinoselenoic amide **3l.** (*R_p,S*)-**3l**: A colorless solid. $[\alpha]_{\text{D}}^{20} = -32$ (c 1.0, CH_2Cl_2). Mp 106–108 °C (decomp). ^1H NMR (400 MHz, CDCl_3): δ 0.90 (d, $J = 6.3$ Hz, 3H), 0.97–1.29 (m, 5H), 1.11 (d,

$J_{\text{HP}} = 16.6$ Hz, 9H), 1.53–1.73 (m, 6H), 2.18 (s, 1H), 3.37–3.48 (m, 1H), 7.35–7.42 (m, 3H), 7.90–7.94 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 19.1 (d, $J_{CP} = 1.7$ Hz), 24.9 (d, $J_{CP} = 1.6$ Hz), 26.26, 26.34, 26.5, 28.0, 29.5, 35.2 (d, $J_{CP} = 57.9$ Hz), 44.3 (d, $J_{CP} = 6.6$ Hz), 52.7 (d, $J_{CP} = 2.5$ Hz), 127.4 (d, $J_{CP} = 12.4$ Hz), 131.1 (d, $J_{CP} = 2.5$ Hz), 132.4, 133.2 (d, $J_{CP} = 10.8$ Hz). ^{31}P NMR (162 MHz, CDCl_3): δ 77.4 ($J_{\text{PSe}} = 745.6$ Hz). ^{77}Se NMR (76 MHz, CDCl_3): δ -367.0 (d, $J_{\text{SeP}} = 745.6$ Hz). MS (EI): m/z 371 (M^+). Anal. Calcd for $\text{C}_{18}\text{H}_{30}\text{NPSe}$: C, 58.37; H, 8.16; N, 3.78. Found: C, 58.38; H, 8.17; N, 3.76. (*S_p,S*)-**3l**: A colorless solid. $[\alpha]_{\text{D}}^{20} = +18$ (c 1.0, CH_2Cl_2). Mp 91–93 °C (decomp). ^1H NMR (400 MHz, CDCl_3): δ 0.87–1.34 (m, 5H), 1.13 (d, $J_{\text{HP}} = 17.1$ Hz, 9H), 1.18 (d, $J = 6.8$ Hz, 3H), 1.54–1.91 (m, 7H), 3.32–3.39 (m, 1H), 7.38–7.47 (m, 3H), 7.95–8.01 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 18.5 (d, $J_{CP} = 3.3$ Hz), 24.9, 26.2, 26.3, 26.4, 27.2, 29.7, 35.2 (d, $J_{CP} = 57.1$ Hz), 44.2 (d, $J_{CP} = 5.0$ Hz), 52.9 (d, $J_{CP} = 1.7$ Hz), 127.3 (d, $J_{CP} = 11.6$ Hz), 131.2 (d, $J_{CP} = 2.5$ Hz), 131.6 (d, $J_{CP} = 81.1$ Hz), 133.3 (d, $J_{CP} = 9.9$ Hz). ^{31}P NMR (162 MHz, CDCl_3): δ 78.4 ($J_{\text{PSe}} = 741.1$ Hz). ^{77}Se NMR (76 MHz, CDCl_3): δ -353.6 (d, $J_{\text{SeP}} = 741.1$ Hz). MS (EI): m/z 371 (M^+). Anal. Calcd for $\text{C}_{18}\text{H}_{30}\text{NPSe}$: C, 58.37; H, 8.16; N, 3.78. Found: C, 58.35; H, 7.99; N, 3.77. (*S_p,R*)-**3l**: $[\alpha]_{\text{D}}^{20} = +32$ (c 1.0, CH_2Cl_2). (*R_p,R*)-**3l**: $[\alpha]_{\text{D}}^{20} = -18$ (c 1.0, CH_2Cl_2).

4.3. X-ray crystallographic analysis of (*R_p,S*)-**3l**

A well shaped orthorhombic crystal of (*R_p,S*)-**3l** was obtained by recrystallization from hot hexane. A colorless block crystal of $\text{C}_{18}\text{H}_{30}\text{NPSe}$ having approximate dimensions of 0.34 × 0.29 × 0.11 mm was mounted on a glass fiber. All measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71070$ Å) at 223 K. Crystal data and refinement details: space group $P2_12_12_1$ (#19); $a = 9.3381(7)$, $b = 11.7960(9)$, $c = 17.557(1)$ Å, $V = 1933.9(3)$ Å 3 , $Z = 4$, $D_{\text{calcd}} = 1.272$ g/cm 3 ; $F(000) = 776.00$; $\mu(\text{Mo K}\alpha) = 20.20$ cm $^{-1}$; 15,843 reflections measured, 4413 observed ($I > 2\sigma(I)$); 191 variables; $R = 0.060$, $R_w = 0.092$, $\text{GOF} = 1.08$. The absolute configuration was determined by the Flack parameter method. Crystallographic data for (*R_p,S*)-**3l** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC-281479. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [fax: +44 1223 336 003; e-mail: deposit@ccdc.cam.ac.uk].

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