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Chiral α-branched mono phosphine auxiliaries, reversal of sense of asymmetric induction upon substitution

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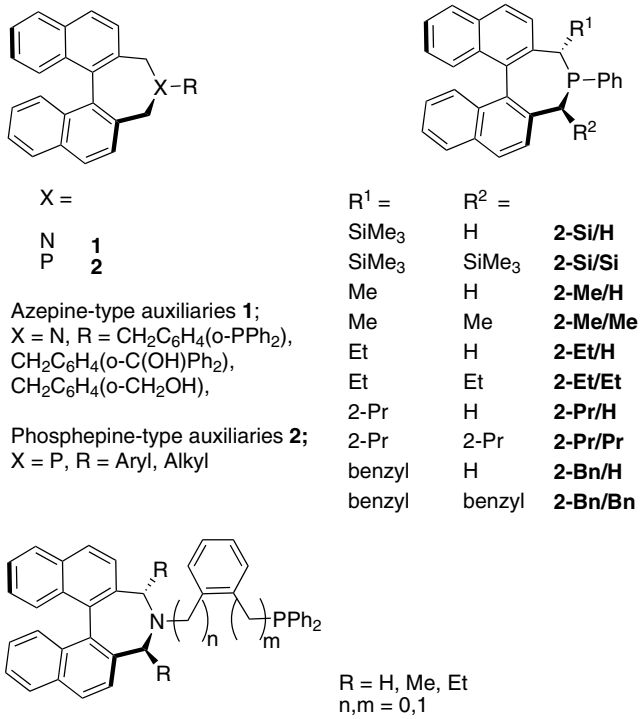
Abstract—A group of 10 (mono- or bis-) α-chiral mono phosphine ligands was synthesized from enantiopure phosphepine sulfide **3** by one or two subsequential highly diastereoselective α-deprotonation/alkylation steps, followed by desulfuration with Raney nickel. Their relative configuration was determined by X-ray crystal structure analysis. The new monophosphine ligands were tested in asymmetric hydrogenation, hydroboration, and Suzuki–Miyaura coupling showing asymmetric inductions up to 91% ee. In the case of hydrogenation, clear evidence was found that enantioselectivity is substantially controlled through α-C chirality rather than through biaryl chirality, which was demonstrated by a change of the sense of asymmetric induction upon change of substituents.

1. Introduction

2,2′-Bridged binaphthyl derivatives with a three atom bridge constitute a promising chiral motif for auxiliaries due to their rigidity and extended chiral bias. In particular, dinaphthoazepine **1**[1] and phosphepine units **2**[2] have been introduced as chiral modifiers in stoichiometric and catalytic asymmetric transformations. An amplification of steric interactions can be expected upon introduction of substituents into the 'pseudo' benzylic 3- and 5-positions. Substitution of **1** with Me or Et resulted indeed in improved enantioselectivity in the allylic alkylation of selected substrates.[3]

The successful use of monodentate P ligands in several types of catalytic reactions over the last few years,[4] has promoted the development of efficient methods for their (enantioselective) synthesis. Keeping in mind the successful application of numerous phospholane-type ligands[5] and recent reports on dinaphthophosphepines[6] in asymmetric catalysis, it seemed a promising concept to combine both structural features and investigate 3,5-disubstituted phosphepines **2** (Scheme 1).



Scheme 1.

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2. Results and discussion

2.1. Synthesis

Sulfide **3** was obtained from 2,2′-dimethyl-1,1′-binaphthyl in an one-pot reaction. The α,α′-dilithio compound prepared by reaction with *n*-BuLi/TMEDA was cyclized with Cl_2PPh[6] followed by treatment with sulfur to give 72% of **3**. With one exception, all α-disubstituted phosphepines were accessible from sulfide **3** via sequential deprotonation steps with *n*- or *t*-BuLi and subsequent reaction with TMS-Cl or appropriate alkyl iodides or benzyl bromide (Scheme 2). An attempted one-pot procedure with the formation of a dianion or using an in situ protocol[7] yielded a mixture of mono- and disubstituted products (Table 1, entries 2 and 3). A separation of mono substitution products **4-R/H** and **4′-R/H** was conveniently performed by column chromatography on silica gel with preferential elution of **4-R/H**. If steric bulkiness was moderate, both substitution steps proceeded with good yield and in a highly diastereoselective fashion to afford the α,α′-disubstituted phosphepines as single diastereomers with a mutual *trans* arrangement of substituents (Table 1 entries 4, 6, 9, and 12). We speculated that the stereoselectivity of each step is mainly controlled by steric interactions between the attacking Li base and H-3 of the naphthyl system resulting in exclusive introduction of substituents at the pseudo-axial positions. A similar selectivity was observed in the alkylation of analogous azepine-type ligands.[3] A less stringent stereocontrol exerted by the P-phenyl group was also operating as shown from a ~3:1 to 5:1 preference for the mono-substitution *trans* to the P-phenyl group. Table 1 summarizes yields of mono- and disubstituted phosphepine sulfides under various conditions. In the case of R = 2-Pr the reaction slowed down affording 68% and 15% of **4-Pr/H** and **4′-Pr/H**, respectively, together with some starting material. The second substitution step remained incomplete and gave a mixture of mono- (28 + 8%) and disubstituted (47%) products (entry 14). Attempts to introduce larger substituents such as *tert*-butyl or 1-adamantyl failed (entries 15 and 16). For the removal of sulfide, reducing agents such as $LiAlH_4$, Si_2Cl_6, $P(n\text{-}Bu)_3$, and Raney nickel have been employed frequently.[8] Due to the simplicity of the procedure, we gave preference to the latter method, which proceeded smoothly at room temperature. Compounds **2-Me/Me**, **2-Et/Et**, and **2-Bn/Bn** were obtained after chromatography on alumina under Ar or crystallization from hexane as moderately air sensitive powders in 78–88% yield. Compounds **2-Pr/H** and **2-Pr/Pr** were isolated as borane complexes. The same treatment of **4-Si/Si** resulted in significant decomposition.

Table 1. Synthesis of ligands

Entry	Procedure[a]	Electrophile	Yield		
			4-R/H	**4′-R/H**	**5-R/R**
1	A[b]	TMSCl	**72**%	22%	
2	A[c]	TMSCl	42%	12%	35%
3	A[d]	TMSCl	44%	4%	40%
4	B,C	TMSCl			**76**%
5	A	MeI	**70**%	27%	
6	B,C	MeI			**96**%[e]
7	A+B,C	MeI			94%[f]
8	A	EtI	62%	30%	
9	B,C	EtI			**95**%
10	A	BnBr	**76**%	20%	
11	B	BnBr			65%
12	C	BnBr			**71**%
13	A[g]	2-PrI	**68**%	15%	
14	A+B,C	2-PrI	28%	8%	**59**%
16	A[h]	*t*-BuI	n.r.	n.r.	
17	A[i]	1-adamantyl-Br	n.r.	n.r.	

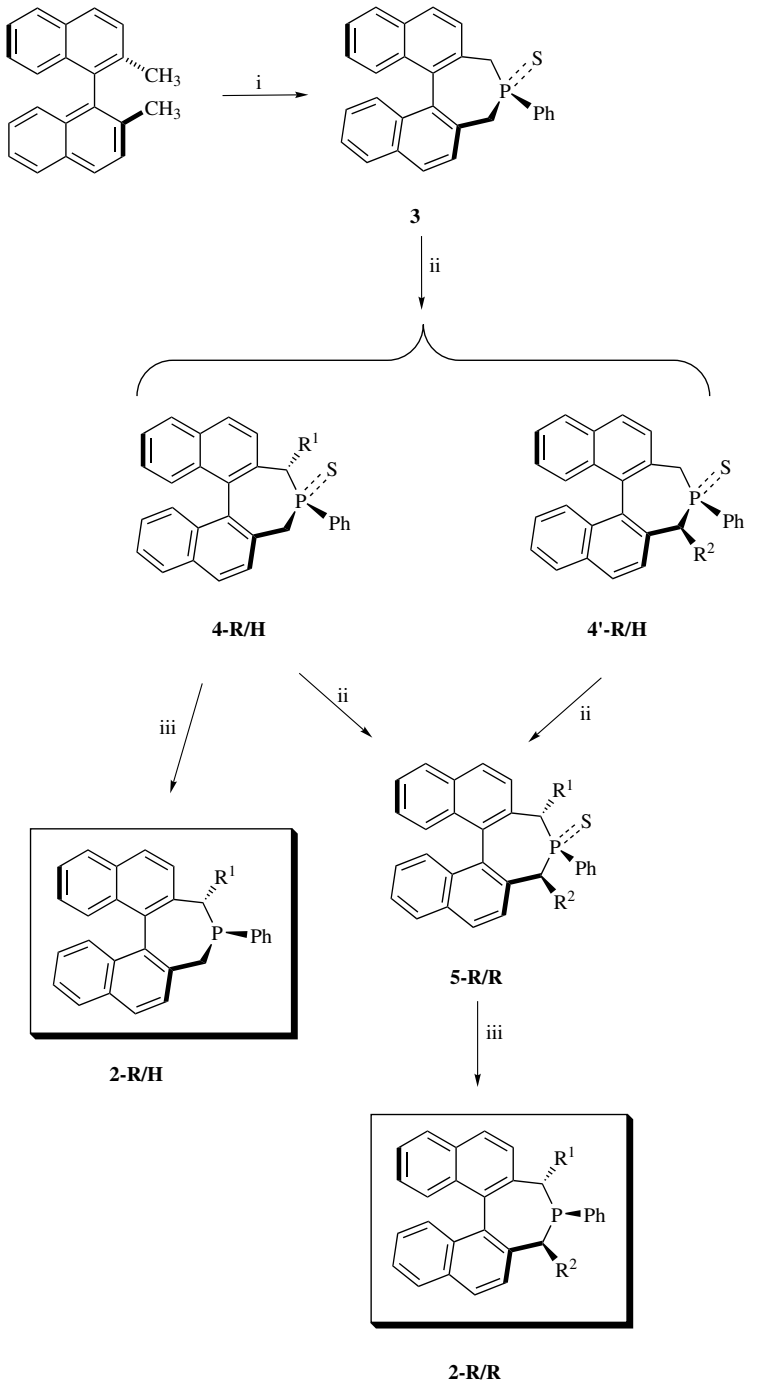
[a] See Experimental; A: **3**→**4**+**4′**, B: **4**→**5**, C: **4′**→**5**.
[b] With *n*-BuLi (1.1 equiv) and 5 equiv of electrophile.
[c] With *n*-BuLi (2.2 equiv) and 10 equiv of electrophile.
[d] In situ reaction with Li-TMP and TMSCl (6 equiv, −78 °C→rt).
[e] With separated isomers, total yield.
[f] Step 2 with mixture of isomers, yield after two steps.
[g] 15% of **3** recovered.
[h] 86% of **3** recovered.
[i] 80% of **3** recovered.

2.2. Crystal structures of (*rac*)-5-Me/Me and (*rac*)-4-Me/H

These two compounds were selected to determine by X-ray structure analysis, the relative stereochemistry of the disubstitution product and the predominating monosubstitution product with R = Me. Both structures showed similar biaryl angles of 71.43(2)° (**4-Me/H**) and 71.36(2)° (**5-Me/Me**), respectively. **4-Me/H** showed the Me group was located trans to the P-phenyl ring in a pseudo-axial position, pointing to the center of the opposite naphthyl ring (C22–C11 = 3.149 Å). Similarly, in **5-Me/Me**, a diaxial configuration of the Me groups was found (C22–C11 = 3.240 Å, C24–C1 = 3.092 Å). The proximity of methyl groups and the aromatic moiety are also reflected in ^{1}H-shift values for Me groups (0.93 and 0.73/1.11 ppm) (Fig. 1).

2.3. Asymmetric catalysis

Three types of catalytic reactions (Scheme 3) were performed to investigate the slope and limitations of new ligands. In all the experiments described below, ligands with an $(S)_a$-configuration were exclusively used. Hydrogenations under standard conditions were conducted with (*E*)-*N*-acetylcinnamic acid **6** [with the addition of $(i\text{-Pr})_2EtN$] or with the corresponding methyl ester **7** and 1 mol % of cationic Rh(I) complexes prepared in situ from $[Rh(COD)Cl]_2/NaClO_4$ or $Rh(COD)_2BF_4$ and the ligand in $MeOH/CH_2Cl_2$ (acid) or toluene (ester).[9] The results are summarized in Table 2. With equimolar mixtures of ligand/Rh, *N*-acetylphenylalanine **8** was obtained in moderate yield and low enantiomeric purity. With increasing bulkiness of substituents, the selectivity for the (*R*)-products changed to (*S*) indicating a mismatching of biaryl and centro-chirality in the auxiliary. Changing the ligand/Rh ratio to 2:1 not only improved the reactivity but also overbalanced the asymmetric induction of centro-chirality over axial-chirality to result in a maximum of 91% ee of (*S*)-**8** with ligand **2-Me/Me**. The effect of a counter ion and pressure seems negligible (entries 11–13). It is interesting to note that the presence of larger substituents had a detrimental effect on both reactivity and enantioselectivity. Similar



Scheme 2. Dinaphthoazepine and –phosphepine ligands. Reagents and conditions: (i) (1) *n*-BuLi, *n*-hexane 0 °C→rt; (2) Cl_2PPh; (3) S_8, THF, 50 °C. (ii) (1) *t*-BuLi, THF, −78→−40 °C; (2) RX, −78 °C. (iii) Raney-Ni, THF, rt.

trends were found for methyl (*E*)-*N*-acetylcinnamate **7** (entries 16–25) with a maximum asymmetric induction of 73% (entry 25). Competition experiments clearly indicate a higher reactivity of the unsubstituted phosphepine ligand with a factor ~100, which may be attributed to the preferred formation of species like Rh(**2-H/H**)$_n$ ($n = 1$ and 2) due to less steric hindrance and/or higher reactivity (entries 26 and 27).

Rhodium-catalyzed hydroboration[10] of styrene with catechol borane proceeded smoothly with all ligands **2** affording predominantly the branched product **10** (Table 3). Asymmetric inductions were comparably low with a maximum of 42% ee. The change of the product configuration with varying substituents is less pronounced than in the hydrogenation but may be also explained by the mismatching of configurations in the ligands.

Pd-mediated Ar–Ar′ coupling (Suzuki–Miyaura coupling[11]) of *ortho*-substituted aromates leads to inherently chiral biaryls providing sufficient steric restriction

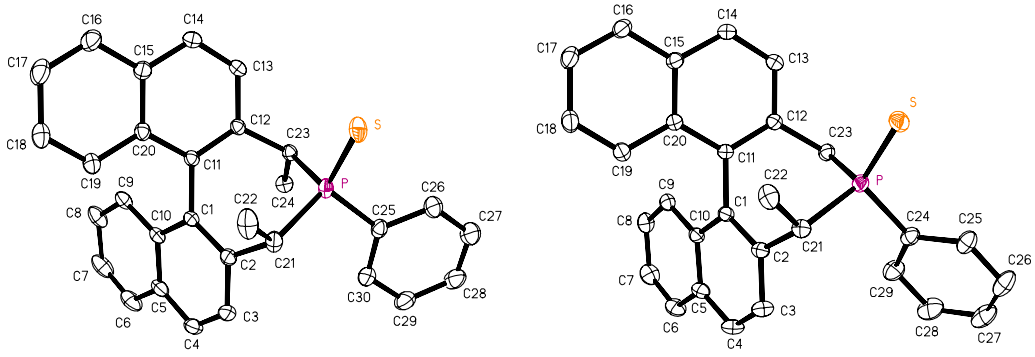
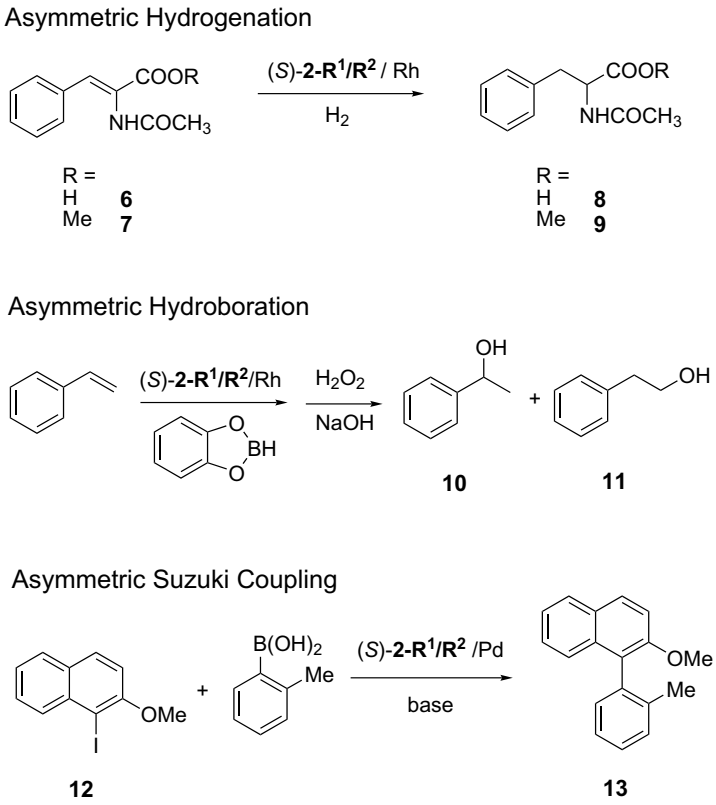


Figure 1. Crystal structures of *rac*-**5-Me/Me** (left hand side) and *rac*-**4-Me/H** (right hand side). In both cases structures with (S_a) configuration are depicted. H-atoms are omitted for clarity.



Scheme 3. Asymmetric transformations.

that take effect to prevent racemization.[12] This is usually the case when three or four *ortho*-substituents are present. The first attempts to couple 1-iodo-2-methoxynaphthalene with 2-methoxynaphthalene-1-boronic acid failed thus affording only traces of the desired biaryl.[13] This lack of reactivity was attributed to steric hindrance since the less sterically demanding *ortho*-tolyl boronic acid exhibited significantly higher reactivities with **12** to give **13** in up to 76% yield (with **2-Me/Me** and 5 mol % of CsF in DME at 70 °C). With other catalysts, isolated yields ranged between 21% and 46%. Generally, the asymmetric inductions were moderate, not exceeding 18%, and no clear dependence from catalyst structure could be observed (Table 4).

3. Conclusions

We were able to synthesize a group of (mono- or bis-) α-chiral monophosphine ligands by one or two subsequent diastereoselective α-deprotonation steps of a P-sulfide, followed by desulfuration with Raney nickel. Their relative configuration was determined by crystal structure analysis. This simple sequence constitutes a highly flexible modular approach to monophosphine ligands, since not only substituents R^1, R^2 but also substituents at P other than Ph can be introduced independently and with excellent control of stereoselectivity induced by the binaphthyl backbone. The new ligands were tested in three Rh- and Pd-catalyzed reactions

Table 2. Asymmetric hydrogenation

Entry	Substrate	Conditions	**2**-R^1/R^2	L/Rh	Conv. (%, NMR)	ee conf.	Pressure (bar)
1	**6**	A	H/H	1/1	99	90 (*R*)	3
2	**6**	A	Me/H	1/1	90	20 (*R*)	3
3	**6**	A	Bn/H	1/1	60	6 (*R*)	3
4	**6**	A	Et/H	1/1	68	35 (*S*)	3
5	**6**	A	Et/Et	1/1	71	30 (*S*)	3
6	**6**	A	H/H	2/1	99	91 (*R*)	3
7	**6**	A	Me/H	2/1	68	10 (*S*)	3
8	**6**	A	Et/H	2/1	99	45 (*S*)	3
9	**6**	A	Pr/H	2/1	98	12 (*S*)	3
10	**6**	A	Bn/H	2/1	23	34 (*S*)	3
11	**6**	A	Me/Me	2/1	99	**91** (*S*)	3
12	**6**	B	Me/Me	2/1	99	89 (*S*)	3
13	**6**	B	Me/Me	2/1	99	90 (*S*)	1.7
14	**6**	A	Et/Et	2/1	99	56 (*S*)	3
15	**6**	A	Bn/Bn	2/1	80	14 (*S*)	3
16	**7**	C	H/H	2/1	99	85 (*R*)	3
17	**7**	C	Me/H	2/1	99	27 (*S*)	1.7
18	**7**	C	Et/H	2/1	99	51 (*S*)	1.7
19	**7**	C	Bn/H	2/1	10	n.d.	3
20	**7**	C	Bn/H	2/1	10	n.d.	3
21	**7**	C	Me/Me	2/1	99	55 (*S*)	1.7
22	**7**	C	Me/Me	2/1	98	55 (*S*)	3
23	**7**	C	Et/Et	2/1	99	50 (*S*)	1.7
24	**7**	C	Et/Et	2/1	99	60 (*S*)	3
25	**7**	C	Bn/Bn	2/1	60	**73** (*S*)	3
26	**7**	C	Me/Me, H/H	1/1/1	99	83 (*R*)	3
27	**7**	C	Et/Et, H/H	1/1/1	99	83 (*R*)	3

All reactions were conducted at rt on a 1 mmol scale with 1 mol % of Rh; A: $[Rh(COD)Cl]_2$+$NaClO_4$, MeOH/CH_2Cl_2, B: $Rh(COD)_2BF_4$, MeOH/CH_2Cl_2, C: $Rh(COD)_2BF_4$, toluene; conversions were determined by ^1H NMR integration, ees by chiral HPLC on a Chiralcel OJ column after conversion to the methyl ester.

Table 3. Asymmetric hydroboration

Entry	**2**-R^1/R^2	L/Rh	Conv. (%, NMR)	**10**	
				Isol. yield	ee, config.
1	H/H	2/1	98	74	10 (*R*)
2	Me/H	1/1	98	56	7 (*S*)
3	Me/H	2/1	96	62	10 (*S*)
4	Et/H	2/1	98	80	31 (*S*)
5	Bn/H	2/1	98	57	6 (*S*)
6	Me/Me	2/1	98	73	**42** (*S*)
7	Et/Et	2/1	98	52	13 (*S*)
8	Bn/Bn	2/1	98	80	7 (*R*)

Table 4. Asymmetric Suzuki coupling[a]

Entry	**2**-R^1/R^2	Isol. yield of **13**	(sign of specific. rot.[b]) ee
1	H/H	46	(+) 8
2	Me/H	47	(+) 10
3	Et/H	32	(−) 2
4	Bn/H	28	(+) 6
5	Me/Me	76	(+) 12
6	Et/Et	21	(+) 18
7	Pr/Pr	42	(+) 14
8	Bn/Bn	56	(+) 14

[a] Reactions were conducted on a 0.1 mmol scale with 2 equiv of *o*-tolyl boronic acid, 5 mol % of $Pd(OAc)_2$ and 5 mol % of CsF in DME (70 °C, 16 h). The product was isolated by preparative TLC; ee was determined by chiral HPLC on a Chiralcel OD-H column; for details see Section 4.

[b] At 589 nm.

showing different degrees and even alternating the sense of asymmetric induction (compared to the parent compound **2-H/H**), which was attributed to mismatching stereogenic units being present in the auxiliary.

4. Experimental

4.1. General

Melting points were measured by Kofler melting point apparatus and are uncorrected. NMR: Bruker AM 400 spectrometer at 400.13 MHz (^1H), 100.61 MHz (^{13}C), and 161.98 MHz (^{31}P), respectively, in $CDCl_3$ if not otherwise noted; chemical shifts δ are reported in ppm rel to $CHCl_3$ (7.24 or 77.00 ppm, respectively) or rel to H_3PO_4 (85%). Coupling patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), p (pseudo), and b (broad). $^{13}C\{^1H\}$ NMR spectra are recorded in a *J*-modulated mode; signals are assigned as C, CH_2, and CH_3; undesignated signals refer to CH resonances. In spectral areas with extensive signal, overlapping multiplets could not be identified; those signals of unclear relationship are underlined, ignoring probable multiplet structures. MS: FINNIGAN MAT 8230 EI (70 eV). HRMS: FINNIGAN MAT 8230. For HPLC determination of chiral products a HP 1090 chromatograph equipped with a diode array detector was used. Optical rotations were measured with a Perkin–Elmer polarimeter 243 equipped with a 1 dm thermostated cell.

Petroleum ether (PE) and ethyl acetate (EA) were distilled, absolute THF and DME from sodium benzophenone ketyl, Et_2O and *n*-hexane from $LiAlH_4$. *n*-BuLi and *t*-BuLi were used as 1.6 molar (in *n*-hexane) and 1.7 molar (in pentane) solutions, respectively (Aldrich). Catecholborane was applied as a 1 molar solution in THF. TMSCl and benzylbromide were distilled. All other chemicals were of analytical grade and used without further purification.

4.2. Synthesis of ligands

4.2.1. (*S*)-4-Phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine sulfide 3. Crude (*S*)-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine in hexane as obtained from $PhPCl_2$ and (*S*)-2,2′-bis(lithiomethyl)-1,1′-binaphthyl–TMEDA complex [prepared from (*S*)-2,2′-dimethyl-1,1′-binaphthyl (33.4 mmol), *n*-BuLi (100 mmol), and TMEDA (100 mmol) according to Ref. 14] was concentrated to half of its volume. To this was added THF (60 mL) and sulfur powder (1.98 g, 62 mmol) and the reaction mixture stirred overnight at 50 °C. After adding water (4 mL), the mixture was concentrated and the residue dissolved in CH_2Cl_2 (200 mL). The organic layer was washed with H_2O (2×25 mL) and brine and dried over anhydrous Na_2SO_4. Removal of the solvent left the crude product, which was purified by chromatography (SiO_2, PE/CH_2Cl_2 = 50:50) to afford (*S*)-**3** as a white powder; yield 10.09 g [72% from (*S*)-2,2′-dimethyl-1,1′-binaphthyl]. White solid. Mp: 147–150 °C. ^{1}H NMR δ: 8.03 (d, $J = 8.3$ Hz, 1H); 7.96 (d, $J = 8.2$ Hz, 1H); 7.95 (d, $J = 8.2$ Hz, 1H); 7.87 (d, $J = 8.4$ Hz, 1H); 7.71 (dd, $J = 1.5$, 8.4 Hz, 1H); 7.62–7.27 (m, 9H); 7.21 (ddd, $J = 1.5$, 7.1, 8.4 Hz, 1H); 7.14 (d, $J = 8.1$ Hz, 1H); 7.10 (dd, $J = 1.0$, 8.2 Hz, 1H); 3.78 (dd, $J = 13.5$, 11.5 Hz, 1H); 3.31 (dd, $J = 14.4$, 18.6 Hz, 1H); 3.26 (dd, $J = 16.8$, 10.8 Hz, 1H); 3.16 (dd, $J = 13.1$, 13.3 Hz, 1H). ^{13}C NMR δ: 134.30 (d, $J = 3.5$ Hz, C); 133.60 (d, $J = 4.3$ Hz, C); 133.21 (d, $J = 3.0$ Hz, C); 132.97 (d, $J = 3.0$ Hz); 132.37 (d, $J = 1.7$ Hz); 132.11 (d, $J = 2.2$ Hz); 131.90 (d, $J = 3.0$ Hz); 131.38 (d, $J = 8.9$ Hz); 130.98 (d, $J = 67.5$ Hz); 130.95 (d, $J = 10.6$ Hz); 129.17; 128.98; 128.96 (d, $J = 2.1$ Hz); 128.57 (d, $J = 2.1$ Hz); 128.49 (d, $J = 1.3$ Hz); 128.45; 128.32; 128.27 (d, $J = 1.6$ Hz); 128.08 (d, $J = 4.3$ Hz); 127.14 (d, $J = 1.6$ Hz); 126.67; 126.58; 126.30 (d, $J = 1.3$ Hz); 126.00 (d, $J = 1.2$ Hz); 125.72 (d, $J = 1.3$ Hz); 42.58 (d, $J = 44.7$ Hz, CH_2); 38.45 (d, $J = 49.1$ Hz, CH_2). ^{31}P NMR δ: 63.43 (s). MS (200 °C) *m*/*z* (rel%): 420 (5, M^+). HRMS (EI): *m*/*z* calcd for $C_{28}H_{21}PS$ 420.1102, found: 420.1097. $[\alpha]_D^{20} = +99.6$ (*c* 0.59, $CHCl_3$).

4.2.2. (*S*,*S*$_a$,*R*$_p$)-3-Methyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine sulfide 4-Me/H and (*S*,*S*$_a$,*S*$_p$)-3-Methyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho-[2,1-*c*;1′,2′-*e*]phosphepine sulfide 4′-Me/H. *Typical procedure*: To a degassed solution of (*S*)-**3** (420 mg, 1 mmol) in dry THF (20 mL) was added dropwise *t*-BuLi solution (0.95 mL, 1.6 mmol) with stirring at −78 °C. The dark red solution was allowed to warm to −40 °C over 2 h and then again cooled to −78 °C. The appropriate electrophile (10 mmol) dissolved in dry THF (10 mL) was added over 15 min and the reaction allowed to come to rt and stirred for an additional hour. After quenching with a few drops of water the mixture was concentrated and the residue was dissolved in CH_2Cl_2 (50 mL). The organic phase was washed sequentially with water and brine and dried over Na_2SO_4. Removal of the solvent left the crude mixture of monomethylated products, which were separated by column chromatography (SiO_2; eluent CH_2Cl_2/PE; 30:70).

4-Me/H: yield: 304 mg (70%). Mp: 268–272 °C. ^{1}H NMR δ: 8.07–7.92 (m, 4H); 7.76–7.64 (m, 3H); 7.54–7.37 (m, 5H); 7.34–7.15 (m, 5H); 4.01 (dd, $J = 13.1$, 11.2 Hz, 1H); 3.14 (dd, $J = 13.1$, 13.0 Hz, 1H); 3.28 (dq, $J = 13.2$ Hz, 1H); 0.93 (dd $J = 17.4$, 7.5 Hz, 3H). ^{13}C NMR δ: 137.38 (d, $J = 6.8$ Hz, C); 134.05 (d, $J = 5.1$ Hz, C); 133.87 (d, $J = 2.3$ Hz, C); 133.16 (d, $J = 1.3$ Hz, C); 132.96 (C); 132.78 (d, $J = 2.1$ Hz, C); 132.55 (d, $J = 58.0$ Hz, C); 131.58 (d, $J = 3.0$ Hz); 130.93 (d, $J = 9.1$ Hz); 130.04 (d, $J = 6.0$ Hz); 129.03 (d, $J = 3.7$ Hz); 128.81 (d, $J = 2.5$ Hz); 128.49; 128.45 (d, $J = 1.7$ Hz); 128.36; 128.20 (d, $J = 9.4$ Hz, C); 128.18; 128.10; 128.44; 128.27; 128.94 (d, $J = 0.9$ Hz); 128.65 (d, $J = 1.4$ Hz); 126.10 (d, $J = 1.0$ Hz); 125.65 (d, $J = 1.8$ Hz); 45.84 (d, $J = 43.8$ Hz); 39.52 (d, $J = 45.4$ Hz, CH_2); 16.50 (d, $J = 2.4$ Hz, CH_3). ^{31}P NMR δ: 67.09 (s). MS (200 °C) *m*/*z* (rel%): 434 (22, M^+). HRMS: calcd for $C_{29}H_{23}PS$: 434.1258, found: 434.1267. $[\alpha]_D^{20} = +37.3$ (*c* 0.49, $CHCl_3$).

4′-Me/H: yield: 117 mg (27%). Mp: 242–256 °C. ^{1}H NMR δ: 8.01–7.88 (m, 6H); 7.65 (dd, $J = 1.0$, 8.4 Hz, 1H); 7.56 (d, $J = 8.4$ Hz, 1H); 7.48–7.38 (m, 5H); 7.26–7.15 (m, 3H); 7.04 (d, $J = 8.5$ Hz, 1H); 3.65–3.58 (m, 3H); 0.65 (dd, $J = 7.8$, 16.5 Hz, 3H). ^{13}C NMR δ: 135.68 (d, $J = 4.1$ Hz, C); 135.05 (d, $J = 6.7$ Hz, C); 133.35 (d, $J = 2.3$ Hz, C); 133.28 (d, $J = 3.6$ Hz, C); 133.17 (d, $J = 2.2$ Hz, C); 132.78 (d, $J = 2.1$ Hz, C); 132.71 (d, $J = 2.1$ Hz, C); 132.25 (d, $J = 9.1$ Hz); 131.75 (d, $J = 3.0$ Hz); 131.20 (d, $J = 64.3$ Hz, C); 130.78 (d, $J = 4.8$ Hz); 129.43 (d, $J = 10.3$ Hz, C); 128.85 (d, $J = 1.0$ Hz); 128.76; 128.29; 128.22 (d, $J = 13.5$ Hz); 128.17; 127.85 (d, $J = 4.6$ Hz); 127.15; 126.80; 126.50; 126.12; 126.06; 125.81; 51.12 (d, $J = 45.8$ Hz); 42.12 (d, $J = 49.0$ Hz, CH_2); 17.14 (d, $J = 3.9$ Hz, CH_3). ^{31}P NMR δ: 64.69 (s). MS (200 °C): *m*/*z* (rel%) 434 (100, M^+). HRMS: calcd for $C_{29}H_{23}PS$: 434.1258, found: 434.1265. $[\alpha]_D^{20} = +48$ (*c* 0.25, $CHCl_3$).

4.2.3. (*S*,*S*,*S*$_a$)-3,5-Dimethyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine sulfide 5-Me/Me. Yield: 430 mg (96%). Mp: 241–244 °C. ^{1}H NMR δ: 8.12–7.92 (m, 6H); 7.69 (d, $J = 8.7$ Hz, 1H); 7.64 (d, $J = 8.5$ Hz, 1H); 7.54–7.42 (m, 5H); 7.29–7.18 (m, 3H); 7.08 (d, $J = 8.5$ Hz, 1H); 3.70–3.55 (m, 2H); 1.11 (dd, $J = 17.6$, 7.7 Hz, 3H); 0.73 (dd, $J = 16.5$, 7.7 Hz, 3H). ^{13}C NMR δ: 136.68 (d, $J = 6.4$ Hz, C); 135.45 (d, $J = 3.5$ Hz, C); 134.37 (d, $J = 6.3$ Hz, C); 134.26 (d, $J = 1.3$ Hz, C); 134.09 (d, $J = 4.4$ Hz, C); 133.88 (d, $J = 2.1$ Hz, C); 133.55 (d, $J = 61.0$ Hz, C); 133.50 (d, $J = 2.1$ Hz, C); 133.21 (d, $J = 1.1$ Hz, C); 132.46 (d, $J = 8.7$ Hz); 131.91 (d, $J = 2.8$ Hz); 131.17 (d,

$J = 5.2$ Hz); 129.68 (d, $J = 6.8$ Hz); 129.39; 128.97 (d, $J = 1.1$ Hz); 128.74 (d, $J = 1.1$ Hz); 128.65; 128.46 (d, $J = 1.4$ Hz); 127.37; 127.15; 126.80 (d, $J = 0.7$ Hz); 126.72 (d, $J = 0.7$ Hz); 126.57; 126.18 (d, $J = 1.1$ Hz); 51.84 (d, $J = 44.1$ Hz); 43.75 (d, $J = 46.4$ Hz); 17.67 (d, $J = 1.8$ Hz, CH_3); 17.48 (d, $J = 3.8$ Hz, CH_3). ^{31}P NMR δ: 69.11 (s). MS (200 °C) *m/z* (rel%): 448 (100, M^+). HRMS: calcd for $C_{30}H_{25}PS$ 448.1415, found: 448.1426. $[\alpha]_D^{20} = +122$ (*c* 0.73, $CHCl_3$).

4.2.4. (*S*,S_a,R_p)-3-Ethyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine sulfide 4-Et/H. Yield: 278 mg (62%). Mp: 300–306 °C. ^{1}H NMR δ: 8.00–7.87 (m, 4H); 7.68–7.60 (m, 3H); 7.51–7.34 (m, 5H); 7.30–7.18 (m, 3H); 7.11(d, $J = 8.2$ Hz, 2H); 3.95 (dd, $J = 11.3$, 13.3 Hz, 1H); 3.07 (dd, $J = 12.9$, 13.0 Hz, 1H); 2.98 (m, 1H); 1.81 (m, 1H); 0.49 (m, 1H); 0.46 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR δ: 135.28 (d, $J = 6.8$ Hz, C); 133.95 (d, $J = 7.6$ Hz, C); 133.92 (d, $J = 2.3$ Hz, C); 133.89; (d, $J = 5.3$ Hz, C); 133.06 (d, $J = 2.0$ Hz, C); 132.95 (d, $J = 4.4$ Hz, C); 132.93 (d, $J = 1.7$ Hz, C); 132.75 (d, $J = 49.8$ Hz, C); 132.51 (C); 131.60 (d, $J = 2.8$ Hz); 131.28 (d, $J = 6.0$ Hz); 130.93 (d, $J = 9.1$ Hz); 128.93 (d, $J = 3.8$ Hz); 128.73 (d, $J = 2.3$ Hz); 128.50 (d, $J = 1.2$ Hz); 128.33; 128.27 (d, $J = 1.1$ Hz); 128.10 (d, $J = 0.9$ Hz); 126.94; 126.45 (d, $J = 1.0$ Hz); 126.43; 126.28; 126.13; 125.64 (d, $J = 1.2$ Hz); 53.26 (d, $J = 46.8$ Hz); 39.56 (d, $J = 49.2$ Hz, CH_2); 22.99 (d, $J = 2.4$ Hz, CH_2); 13.58 (d, $J = 13.4$ Hz, CH_3). ^{31}P NMR δ: 67.78 (s). MS (170 °C) *m/z* (rel%): 448 (27, M^+). HRMS: calcd for $C_{30}H_{25}PS$ 448.1415, found: 448.1422. $[\alpha]_D^{20} = +314$ (*c* 0.50, $CHCl_3$).

4.2.5. (*S*,S_a,S_p)-3-Ethyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine sulfide 4′-Et/H. Yield: 135 mg (30%). White foam. ^{1}H NMR δ: 8.01–7.87 (m, 6H); 7.63 (dd, $J = 0.8$, 8.4 Hz, 1H); 7.54 (d, $J = 8.4$ Hz, 1H); 7.50–7.39 (m, 5H); 7.28–7.15 (m, 3H); 7.02 (d, $J = 8.5$ Hz, 1H); 3.63–3.56 (m, 2H); 3.42 (m, 1H); 0.94 (m, 1H); 0.78 (m, 1H); 0.38 (dt, $J = 1.0$, 7.1 Hz, 3H). ^{13}C NMR δ: 135.46 (d, $J = 4.2$ Hz, C); 133.36 (d, $J = 2.2$ Hz, C); 133.14 (d, $J = 5.0$ Hz, C); 132.85 (d, $J = 3.0$ Hz, C); 132.80 (d, $J = 0.7$ Hz, C); 132.74 (d, $J = 2.2$ Hz, C); 132.71 (d, $J = 2.0$ Hz, C); 132.55 (d, $J = 9.1$ Hz); 132.08 (d, $J = 4.7$ Hz); 131.75 (d, $J = 2.9$ Hz); 131.02 (d, $J = 64.0$ Hz, C); 129.52 (d, $J = 10.5$ Hz, C); 128.78 (d, $J = 1.0$ Hz); 128.58; 128.28 (d, $J = 0.7$ Hz); 128.23 (d, $J = 1.4$ Hz); 128.10; 127.87 (d, $J = 2.9$ Hz); 127.05; 126.66; 126.43; 126.11; 126.05 (d, $J = 1.0$ Hz); 125.83 (d, $J = 0.7$ Hz); 59.12 (d, $J = 44.6$ Hz); 42.33 (d, $J = 41.6$ Hz, CH_2); 23.55 (d, $J = 7.7$ Hz, CH_2); 13.79 (d, $J = 12.0$ Hz, CH_3). ^{31}P NMR δ: 65.36 (s). MS (180 °C) *m/z* (rel%): 448 (100, M^+). HRMS: calcd for $C_{30}H_{25}PS$ 448.1415, found: 448.1406. $[\alpha]_D^{20} = +533$ (*c* 0.26, $CHCl_3$).

4.2.6. (*S*,*S*,S_a)-3,5-Diethyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine sulfide 5-Et/Et. Yield: 451 mg (95%). White solid. Mp: 229–233 °C. ^{1}H NMR δ: 8.02–7.90 (m, 6H); 7.58 (d, $J = 8.3$ Hz, 1H); 7.51 (d, $J = 8.3$ Hz, 1H); 7.48–7.38 (m, 5H); 7.27–7.14 (m, 3H); 6.98 (d, $J = 8.5$ Hz, 1H); 3.40–3.20 (m, 2H); 2.01 (m, 1H); 0.93 (m, 1H); 0.82 (m, 1H); 0.70 (m, 1H); 0.53 (t, $J = 7.1$ Hz, 3H) 0.35 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR δ: 134.86 (d, $J = 2.6$ Hz, C); 134.28 (d, $J = 6.6$ Hz, C); 133.49 (d, $J = 2.3$ Hz, C); 133.44 (d, $J = 2.3$ Hz, C); 133.40 (d, $J = 4.4$ Hz, C); 133.16 (d, $J = 2.1$ Hz, C); 133.13 (d, $J = 2.1$ Hz, C); 132.81 (d, $J = 0.9$ Hz, C); 132.35 (d, $J = 88.7$ Hz, C); 132.26 (d, $J = 8.7$ Hz); 132.06; 132.01; 131.49 (d, $J = 2.6$ Hz); 130.78 (d, $J = 7.0$ Hz); 128.54; 128.36; 128.31; 128.15; 128.09 (d, $J = 2.2$ Hz); 126.88; 126.54; 126.26; 126.17; 125.77; 59.79 (d, $J = 43.6$ Hz); 51.25 (d, $J = 45.8$ Hz); 24.41 (d, $J = 34.3$ Hz, CH_2); 24.39 (d, $J = 32.3$ Hz, CH_2); 13.40 (d, $J = 12.1$ Hz, CH_3); 13.26 (d, $J = 13.4$ Hz, CH_3). ^{31}P NMR δ: 70.29 (s). MS (180 °C) *m/z* (rel%): 476 (100, M^+). HRMS: calcd for $C_{32}H_{29}PS$ 476.1728, found: 476.1720. $[\alpha]_D^{20} = +143$ (*c* 0.69, $CHCl_3$).

4.2.7. (*S*,S_a,R_p)-3-Isopropyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine sulfide 4-*i*Pr/H. Yield: 314 mg (68%). Mp: 224–226 °C. ^{1}H NMR δ: 8.01 (d, $J = 8.3$ Hz, 1H); 7.95 (d, $J = 8.2$ Hz, 1H); 7.86 (d, $J = 8.3$ Hz, 1H); 7.73 (d, $J = 8.3$ Hz, 1H); 7.66 (d, $J = 11.3$ Hz, 1H); 7.64 (d, $J = 8.4$ Hz, 1H); 7.49–7.38 (m, 5H); 7.27–7.14 (m, 4H); 7.07 (d, $J = 8.4$ Hz, 1H); 3.91 (dd, $J = 12.7$, 12.7 Hz, 1H); 3.05 (dd, $J = 12.5$, 12.6 Hz, 1H); 2.92 (dd, $J = 9.9$, 12.1 Hz, 1H); 1.28 (m, 1H); 1.12 (d, $J = 6.1$ Hz, 3H); 0.27 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR δ: 136.53 (d, $J = 6.7$ Hz, C); 134.63 (d, $J = 68.1$ Hz, C); 134.53 (d, $J = 2.3$ Hz, C); 133.64 (d, $J = 5.1$ Hz, C); 133.11 (d, $J = 2.6$ Hz, C); 133.04 (d, $J = 1.4$ Hz, C); 132.61 (d, $J = 1.3$ Hz, C); 131.93 (d, $J = 2.6$ Hz); 131.86; 131.80 (d, $J = 0.9$ Hz); 131.42 (d, $J = 0.7$ Hz); 131.40; 130.64 (d, $J = 9.1$ Hz); 129.03 (d, $J = 3.8$ Hz); 128.70 (d, $J = 1.3$ Hz); 128.65 (d, $J = 1.1$ Hz); 128.38; 128.37 (d, $J = 9.5$ Hz, C); 128.25 (d, $J = 3.8$ Hz); 128.02; 127.10; 126.99; 126.39; 126.18; 125.95; 59.27 (d, $J = 45.3$ Hz); 40.61 (d, $J = 49.6$ Hz, CH_2); 29.17 (d, $J = 1.0$ Hz); 26.36 (CH_3); 23.15 (d, $J = 9.9$ Hz, CH_3). ^{31}P NMR δ: 65.41 (s). MS (150 °C) *m/z* (rel%): 462 (70, M^+). HRMS: calcd for $C_{31}H_{27}PS$ 462.1571, obsd 462.1566. $[\alpha]_D^{20} = +540$ (*c* 0.285, $CHCl_3$).

4.2.8. (*S*,*S*,S_a)-3,5-Diisopropyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine sulfide 5-*i*Pr/*i*Pr. Yield: 297 mg (59%). Mp: 256–265 °C. ^{1}H NMR δ: 8.11 (d, $J = 8.4$ Hz, 1H); 8.08 (d, $J = 7.5$ Hz, 1H); 8.01 (d, $J = 8.4$ Hz, 1H); 7.94–7.90 (m, 3H); 7.60 (dd, $J = 1.0$, 8.4 Hz, 1H); 7.51–7.40 (m, 6H); 7.30–7.14 (m, 4H); 3.22–3.14 (m, 2H); 1.41 (m, 1H); 1.11 (m, 1H); 1.04 (d, $J = 6.1$ Hz, 3H); 0.30 (d, $J = 6.4$ Hz, 3H); 0.29 (d, $J = 6.7$ Hz, 3H); −0.03 (d, $J = 6.1$ Hz, 3H). ^{13}C NMR δ: 135.98 (d, $J = 61.0$ Hz, C); 135.73 (d, $J = 6.6$ Hz, C); 135.18 (d, $J = 2.5$ Hz, C); 133.59 (d, $J = 6.4$ Hz, C); 133.41 (d, $J = 4.6$ Hz, C); 133.16 (d, $J = 2.2$ Hz, C); 132.96 (d, $J = 5.5$ Hz); 132.89 (d, $J = 0.7$ Hz, C); 132.46 (d, $J = 1.3$ Hz, C); 132.31 (d, $J = 2.5$ Hz, C); 132.07 (d, $J = 8.7$ Hz); 131.57 (d, $J = 2.9$ Hz); 131.39 (d, $J = 8.0$ Hz); 128.70; 128.46; 128.33; 128.16; 128.12; 127.72; 127.06; 126.17; 126.08; 125.68; 125.62; 69.95 (d, $J = 41.2$ Hz); 58.34 (d, $J = 45.1$ Hz); 29.83; 28.51 (d, $J = 4.0$ Hz); 26.60 (CH_3); 23.76 (CH_3); 23.70 (d, $J = 9.6$ Hz, CH_3); 22.77 (d, $J = 9.5$ Hz, CH_3). ^{31}P NMR δ: 65.57 (s). MS (180 °C)

m/*z* (rel%): 504 (100, M^+). HRMS: calcd for $C_{34}H_{33}PS$ 504.2041, found: 504.2048. $[\alpha]_D^{20} = +1524$ (*c* 0.1, $CHCl_3$).

4.2.9. (*S*,*S*$_a$,*R*$_p$)-3-Benzyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine sulfide 4-Bn/H. Yield: 388 mg (76%). Mp: 236–239 °C. ^{1}H NMR δ: 8.11 (d, $J = 8.3$ Hz, 1H); 8.03 (d, $J = 8.1$ Hz, 1H); 7.95 (d, $J = 8.1$ Hz, 1H); 7.82–6.63 (m, 4H); 7.58–7.49 (m, 3H); 7.44–7.20 (m, 6H); 7.01–6.97 (m, 3H); 6.85 (d, $J = 8.4$ Hz, 1H); 6.65–6.62 (m, 2H); 4.05 (dd, $J = 13.2$, 11.2 Hz, 1H); 3.52–3.31 (m, 2H); 3.19 (dd, $J = 12.9$, 13.0 Hz, 1H); 1.83 (m, 1H). ^{13}C NMR δ: 140.25 (d, $J = 14.0$ Hz, C); 135.11 (d, $J = 6.7$ Hz, C); 133.97 (C); 137.42 (d, $J = 51.7$ Hz, C); 133.16 (d, $J = 2.0$ Hz, C); 133.07; ($J = 2.0$ Hz, C); 132.91 (d, $J = 1.8$ Hz, C); 133.74 (d, $J = 51.7$ Hz, C); 133.16 (d, $J = 1.7$ Hz, C); 133.07 (d, $J = 2.0$ Hz, C); 132.91 (d, $J = 1.4$ Hz, C); 132.80 (C); 132.37 (d, $J = 2.8$ Hz, C); 131.73 (d, $J = 2.7$ Hz); 131.45 (d, $J = 5.7$ Hz); 130.95 (d, $J =$ 9.3 Hz); 129.18 (d, $J = 3.9$ Hz); 129.01 (d, $J = 2.3$ Hz); 128.71; 128.59 (d, $J = 1.1$ Hz); 128.35 (C); 128.28; 128.18; 128.09; 127.88; 127.07; 126.40; 126.18; 125.90 (d, $J = 1.1$ Hz); 125.77; 53.86 (d, $J = 45.0$ Hz); 39.66 (d, $J = 49.0$ Hz, CH_2); 35.72 (CH_2). ^{31}P NMR δ: 69.05 (s). MS (200 °C) *m*/*z* (rel%): 510 (75, M^+). HRMS: calcd for $C_{35}H_{27}PS$ 510.1571, obsd 510.1579. $[\alpha]_D^{20} = +324$ (*c* 0.30, $CHCl_3$).

4.2.10. (*S*,*S*$_a$,*S*$_p$)-3-Benzyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine sulfide 4′-Bn/H. Yield: 101 mg (20%). Mp: 257–261 °C. ^{1}H NMR δ: 8.07 (d, $J = 8.4$ Hz, 1H); 8.03–7.98 (m, 3H); 7.89 (d, $J =$ 8.1 Hz, 1H); 7.84 (d, $J = 8.4$ Hz, 1H); 7.64 (d, $J =$ 8.4 Hz, 1H); 7.53–7.39 (m, 5H); 7.36 (dd, $J = 0.9$, 8.4 Hz, 1H); 7.28 (ddd, $J = 1.6$, 7.2, 8.4 Hz, 1H); 7.20–7.14 (m, 2H); 7.07 (d, $J = 8.5$ Hz, 1H); 6.93–6.89 (m, 3H); 6.41–6.39 (m, 2H); 3.96–3.82 (m, 1H); 3.76 (d, $J = 17.7$ Hz, 1H); 3.69 (d, $J = 12.8$ Hz, 1H); 2.30 (m, 1H); 2.10 (m, 1H). ^{13}C NMR δ: 138.82 (d, $J =$ 13.1 Hz, C); 135.56 (d, $J = 3.9$ Hz, C); 133.32 (CH_2); 133.30 (CH_2); 132.92 (d, $J = 2.3$ Hz, C); 132.68 (C); 132.45 (d, $J = 9.1$ Hz); 132.08 (d, $J = 4.8$ Hz); 131.96 (d, $J = 2.9$ Hz); 131.08 (d, $J = 64.4$ Hz, C); 129.63 (d, $J = 10.6$ Hz); 129.10; 129.09; 128.49; 128.37; 128.33; 128.22; 128.02; 127.92; 128.79; *126.66*; *126.48*; *126.28*; *126.05*; 125.85; 58.91 (d, $J = 42.7$ Hz); 42.16 (d, $J = 49.0$ Hz, CH_2); 37.19 (d, $J = 2.1$ Hz, CH_2). ^{31}P NMR δ: 67.05 (s). MS (230 °C) *m*/*z* (rel%): 510 (100, M^+). HRMS: calcd for $C_{35}H_{27}PS$ 510.1571, obsd 510.1565. $[\alpha]_D^{20} = +397$ (*c* 0.49, $CHCl_3$).

4.2.11. (*S*,*S*,*S*$_a$)-3,5-Dibenzyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine sulfide 5-Bn/Bn. Yield: 426 mg (71%). Mp: 277–278 °C. ^{1}H NMR δ: 8.06–7.86 (m, 6H); 7.50–7.38 (m, 6H); 7.27–7.15 (m, 5H); 7.01–6.91 (m, 6H); 6.68–6.66 (m, 2H); 6.44–6.41 (m, 2H); 3.86 (m, 1H); 3.73 (m, 1H); 3.60 (m, 1H); 2.30 (m, 1H); 2.12 (m, 1H); 1.97 (m, 1H). ^{13}C NMR δ: 139.95 (d, $J = 14.4$ Hz, C); 138.35 (d, $J = 13.0$ Hz, C); 134.53 (d, $J = 2.5$ Hz); 134.01 (d, $J = 6.1$ Hz); 133.43 (d, $J = 4.4$ Hz); 133.32 (d, $J = 2.1$ Hz); 133.25 (C); 132.98 (d, $J = 61.0$ Hz, C); 132.95 (d, $J = 2.1$ Hz, C); 132.81 (d, $J = 1.0$ Hz, C); *132.33* (C); *132.28* (C); 132.18 (d, $J = 8.9$ Hz); 131.78 (d, $J = 2.6$ Hz); 131.05 (d, $J = 6.9$ Hz); 128.98; 128.64; 128.48; 128.46; 128.34; 128.27 (d, $J = 0.4$ Hz); 128.17; 127.91; 127.90; 127.69; 126.96 (d, $J = 0.4$ Hz); 126.42; 126.15 (d, $J = 0.4$ Hz); 126.03 (d, $J = 1.1$ Hz); 125.87; 59.54 (d, $J = 41.5$ Hz); 51.68 (d, $J = 43.6$ Hz); 37.37 (d, $J = 11.1$ Hz, CH_2); 37.28 (d, $J = 9.6$ Hz, CH_2). ^{31}P NMR δ: 72.91 (s). MS (electro spray) *m*/*z* (rel%): 623.2 (100, $M+Na^+$). HRMS (electro spray) $[M+Na]^+$: *m*/*z* calcd for $C_{42}H_{33}NaPS$ 623.1938, obsd 623.1932. $[\alpha]_D^{20} = +947$ (*c* 0.325, $CHCl_3$).

4.2.12. (*S*,*S*$_a$,*S*$_p$)-3-Methyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine 2-Me/H. *Typical procedure*: An excess of a slurry of freshly prepared Raney nickel in water (~1.5 g) was placed in a Schlenk tube and washed repeatedly with degassed THF. A THF solution of (*S*,*S*$_a$,*R*$_p$)-**4-Me/H** (434 mg, 1 mmol, 2 mL) was added under Ar and the mixture stirred overnight. Filtration through Celite and a short pad of alumina under Ar removed residues of Raney nickel. The filtrate was concentrated and the crude product purified by chromatography on alumina under Ar yielding 340 mg (85%) of (*S*,*S*$_a$,*S*$_p$)-**2-Me/H**. Mp: 102–105 °C. ^{1}H NMR δ: 7.90–7.84 (m, 3H); 7.73 (d, $J = 8.3$ Hz, 1H); 7.62 (dd, $J = 8.3$, 0.9 Hz, 1H); 7.39–7.36 (m, 2H); 7.26–7.17 (m, 9H); 6.95 (d, $J = 8.4$ Hz, 1H); 2.97–2.91 (m, 3H); 0.75 (dd, $J = 18.8$, 7.9 Hz, 3H). ^{13}C NMR δ: 139.76 (d, $J = 3.7$ Hz, C); 139.06 (d, $J = 20.8$ Hz, C); 134.45 (d, $J = 5.2$ Hz, C); 133.10 (d, $J = 1.3$ Hz, C); 133.05 (d, $J = 2.6$ Hz, C); 132.66; 132.65 (d, $J =$ 2.2 Hz, C); 132.60 (d, $J = 1.0$ Hz, C); 131.60 (d, $J =$ 18.8 Hz, C); 129.38; 128.87; 128.52 (d, $J = 1.2$ Hz); *128.26*; *128.25*; *128.19*; *127.99*; *127.76*; 127.42 (d, $J = 2.3$ Hz); 126.67; 126.57; 126.06; 125.75; 125.03; 125.01; 41.48 (d, $J = 18.8$ Hz); 31.96 (d, $J = 16.7$ Hz, CH_2); 20.92 (d, $J = 30.6$ Hz, CH_3). ^{31}P NMR δ: 18.57 (s). MS (160 °C): *m*/*z* (rel%) 402 (100, M^+). HRMS: calcd for $C_{29}H_{23}P$: 402.1537, found: 402.1542. $[\alpha]_D^{20} =$ −90 (*c* 0.545, $CHCl_3$).

4.2.13. (*S*,*S*,*S*$_a$)-3,5-Dimethyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine 2-Me/Me. Yield: 366 mg (88%). Mp: 212–215 °C. ^{1}H NMR δ: 7.92–7.86 (m, 4H); 7.63–7.52 (m, 4H); 7.40–7.30 (m, 5H); 7.16–7.13 (m, 4H); 3.47 (m, 1H); 3.38 (m, 1H); 0.92 (dd, $J = 7.8$, 20.2 Hz, 3H); 0.38 (dd, $J = 5.3$, 7.4 Hz, 3H). ^{13}C NMR δ: 141.23 (d, $J = 2.5$ Hz, C); 138.54 (d, $J =$ 25.5 Hz, C); 138.53 (d, $J = 1.0$ Hz, C); 134.65 (d, $J = 6.0$ Hz, C); 134.26 (C); 133.90 (C); 133.86 (d, $J = 2.7$ Hz, C); 132.74 (d, $J = 19.4$ Hz); 132.65 (C); 132.22 (C); 132.85 (d, $J = 3.0$ Hz); 128.74; 132.55; 128.42; 128.27 (d, $J = 5.2$ Hz); 128.17; 128.07; 127.85; 126.56; 126.47; 126.01; 125.95; 125.18; 125.13; 39.30 (d, $J =$ 20.4 Hz); 36.58 (d, $J = 19.8$ Hz); 22.31 (d, $J =$ 35.8 Hz, CH_3); 14.00 (d, $J = 3.4$ Hz, CH_3). ^{31}P NMR δ: 33.09 (s). MS (180 °C) *m*/*z* (rel%): 416 (100, M^+). HRMS: calcd for $C_{30}H_{25}P$ 416.1694, found: 416.1689. $[\alpha]_D^{20} = +95$ (*c* 0.55, $CHCl_3$).

4.2.14. (*S*,*S*$_a$,*S*$_p$)-3-Ethyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine 2-Et/H. Yield: 345 mg (83%). Mp: 125–127 °C. ^{1}H NMR δ: 7.91–7.87 (m, 3H); 7.76 (d, $J = 8.3$ Hz, 1H); 7.62 (dd, $J = 1.0$,

8.4 Hz, 1H); 6.96 (d, $J = 8.4$ Hz, 1H); 3.03–2.98 (m, 2H); 2.73 (m, 1H); 1.17 (m, 1H); 0.70 (m, 1H); 0.57 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR δ: 139.24 (C); 138.09 (d, $J = 3.1$ Hz, C); 136.36 (d, $J = 14.0$ Hz, C); 134.40 (d, $J = 4.9$ Hz, C); 134.02 (C); 133.52 (C); 132.98 (d, $J = 25.3$ Hz, C); 132.58 (C); 133.57 (d, $J = 2.2$ Hz, C); 132.48; 131.65 (d, $J = 18.8$ Hz); 130.42; 128.80; 128.47 (d, $J = 1.5$ Hz); 125.96; 125.75; 125.04; 124.99; 50.48 (d, $J = 19.3$ Hz); 31.78 (d, $J = 16.8$ Hz, CH_2); 28.01 (d, $J = 29.5$ Hz, CH_2); 14.19 (d, $J = 15.1$ Hz, CH_3). ^{31}P NMR δ: 15.09 (s). MS (180 °C) *m/z* (rel%): 416 (100, M^+). HRMS: calcd for $C_{30}H_{25}P$ 416.1694, found: 416.1699. $[\alpha]_D^{20} = +82$ (*c* 0.21, $CHCl_3$).

4.2.15. (*S*,*S*,*S*$_a$)-3,5-Diethyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine 2-Et/Et. Yield: 346 mg (78%). Mp: 174–177 °C. ^{1}H NMR δ: 7.94–7.88 (m, 4H); 7.59–7.56 (m, 4H); 7.38–7.28 (m, 5H); 7.17–7.11 (m, 4H); 3.20 (m, 1H); 3.04 (m, 1H); 1.30–1.26 (m, 2H); 0.91 (m, 1H); 0.82 (m, 1H); 0.62 (m, 1H); 0.60 (t, $J = 7.6$ Hz, 3H); 0.22 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR δ: 139.95 (d, $J = 2.3$ Hz, C); 138.31 (d, $J = 25.4$ Hz, C); 136.25 (d, $J = 0.7$ Hz, C); 134.58 (d, $J = 6.5$ Hz, C); 133.86 (C); 133.63 (C); 133.62 (C); 133.38 (d, $J = 20.4$ Hz); 132.66 (d, $J = 1.6$ Hz, C); 132.30 (C); 130.18 (d, $J = 3.2$ Hz); *129.93*; *128.60*; *128.41*; 128.19 (d, $J = 6.8$ Hz); 128.09; 127.99; 127.92; 126.70; 126.34; 125.86; 125.78; 125.19; 125.13; 47.55 (d, $J = 19.8$ Hz); 45.28 (d, $J = 19.3$ Hz); 29.51 (d, $J = 35.2$ Hz, CH_2); 21.22 (d, $J = 3.1$ Hz, CH_2); 14.12 (d, $J = 17.3$ Hz, CH_3); 13.68 (d, $J = 0.8$ Hz, CH_3). ^{31}P NMR δ: 31.51 (s). MS (160 °C) *m/z* (rel%): 444 (100, M^+). HRMS: calcd for $C_{32}H_{29}P$ 444.2007, found: 444.2014. $[\alpha]_D^{20} = +145$ (*c* 0.62, $CHCl_3$).

4.2.16. (*S*,*S*$_a$,*S*$_p$)-3-Isopropyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine borane complex 2-*i*Pr/H-BH$_3$. Yield: 309 mg (70%). Mp: 202–205 °C. ^{1}H NMR δ: 7.97 (d, $J = 8.4$ Hz, 1H); 7.93 (d, $J = 7.7$ Hz, 2H); 7.81 (d, $J = 8.4$ Hz, 1H); 7.69 (dd, $J = 1.3$, 8.4 Hz, 1H); 7.48–7.18 (m, 11H); 6.96 (d, $J = 8.2$ Hz, 1H); 3.37 (dd, $J = 12.6$, 16.4 Hz, 1H); 2.98 (dd, $J = 2.3$, 12.6 Hz, 1H); 2.69–2.64 (m, 2H); 0.93 (d, $J = 1.6$ Hz, 3H); 1.3–0.6 (bm, 3H); 0.33 (d, $J = 1.6$ Hz, 3H). ^{13}C NMR δ: 136.19 (d, $J = 8.3$ Hz, C); 134.10 (d, $J = 1.7$ Hz, C); 133.86 (d, $J = 4.4$ Hz, C); 133.14 (d, $J = 2.3$ Hz, C); 132.76 (d, $J = 52.4$ Hz, C); 131.92 (d, $J = 2.2$ Hz, C); 131.51 (d, $J = 8.1$ Hz); *131.25*; *131.23*; *131.20*; 131.16 (C); 129.12 (C); 128.90 (d, $J = 3.6$ Hz); 128.73 (d, $J = 1.4$ Hz); 128.61; 128.61; 128.51; 128.07 (d, $J = 5.1$ Hz); 126.88; 126.83 (d, $J = 1.2$ Hz); 126.34; 126.01; 125.52 (d, $J = 1.4$ Hz); 55.26 (d, $J = 24.2$ Hz); 31.86 (d, $J = 35.8$ Hz, CH_2); 29.20 (d, $J = 2.9$ Hz); 24.25 (CH_3); 23.54 (d, $J = 10.6$ Hz, CH_3). ^{31}P NMR δ: 42.20 (s). MS (130 °C) *m/z* (rel%): 430 (100, M^+-BH_3). HRMS: calcd for $C_{31}H_{27}P$ 430.1850, found: 430.1846. $[\alpha]_D^{20} = +222$ (*c* 0.34, $CHCl_3$).

4.2.17. (*S*,*S*,*S*$_a$)-3,5-Diisopropyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine borane complex 2-*i*Pr/*i*Pr-BH$_3$. Yield: 306 mg (65%) isolated as borane complex. Mp: 186–190 °C. ^{1}H NMR δ: 8.00–7.83 (m, 6H); 7.57 (d, $J = 8.3$ Hz, 1H); 7.49–7.35 (m, 6H); 7.26–7.20 (m, 2H); 7.16 (ddd, $J = 1.4$, 6.8, 8.0 Hz, 1H); 7.09 (d, $J = 8.5$ Hz, 1H); 4H; 3.11 (dd, $J = 6.5$, 10.8 Hz, 1H); 2.88 (dd, $J = 9.3$, 10.4 Hz, 1H); 1.20–1.17 (m, 2H); 0.94 (d, $J = 6.2$ Hz, 3H); 0.85 (bm, 3H); 0.33 (d, $J = 6.6$ Hz, 3H); 0.30 (d, $J = 6.6$ Hz, 3H); −0.02 (d, $J = 6.2$ Hz, 3H). ^{13}C NMR δ: 136.63 (d, $J = 8.2$ Hz, C); 134.86 (C); 134.82 (d, $J = 4.5$ Hz, C); 133.90 (d, $J = 4.5$ Hz, C); 133.40 (d, $J = 7.8$ Hz); 133.18 (C); 133.02 (d, $J = 30.7$ Hz, C); 132.78 (d, $J = 11.2$ Hz, C); 132.37 (C); 132.34 (d, $J = 5.9$ Hz); 132.21 (C); 131.37 (d, $J = 2.3$ Hz); 131.16 (d, $J = 4.5$ Hz); 128.57; 128.48; 128.40; 128.31; 128.20 (d, $J = 4.3$ Hz); 127.41; 126.85; 126.13; 125.95; 125.72; 125.65; 56.88 (d, $J = 28.7$ Hz); 53.82 (d, $J = 26.7$ Hz); 29.71 (d, $J = 3.7$ Hz); 27.75 (d, $J = 6.1$ Hz); 24.63 (CH_3); 23.66 (CH_3); 23.50 (d, $J = 0.4$ Hz, CH_3); 23.50 (d, $J = 4.4$ Hz, CH_3). ^{31}P NMR δ: 41.11 (bs). MS (150 °C) *m/z* (rel%): 472 (100, M^+-BH_3). HRMS: calcd for $C_{34}H_{33}P$ 472.2320, found: 472.2320. $[\alpha]_D^{20} = +184$ (*c* 0.12, $CHCl_3$).

4.2.18. (*S*,*S*$_a$,*S*$_p$)-3-Benzyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine 2-Bn/H. Yield: 377 mg (79%). Mp: 100–102 °C. ^{1}H NMR δ: 7.97 (d, $J = 8.4$ Hz, 1H); 7.93 (d, $J = 8.2$ Hz, 1H); 7.85 (d, $J = 8.2$ Hz, 1H); 7.70 (dd, $J = 1.0$, 8.4 Hz, 1H); 7.65 (d, $J = 8.23$ Hz, 1H); 7.44–6.98 (m, 14H); 6.78 (d, $J = 8.4$ Hz, 1H); 6.68–6.65 (m, 2H); 3.16 (m, 1H); 3.08–2.95 (m, 2H); 2.48 (m, 1H); 2.05 (m, 1H). ^{13}C NMR δ: 141.02 (d, $J = 13.5$ Hz, C); 138.91 (d, $J = 21.4$ Hz, C); 137.72 (d, $J = 3.6$ Hz, C); 134.37 (d, $J = 5.0$ Hz, C); 133.33 (C); 132.88 (C); 132.77 (C); 132.75 (d, $J = 2.2$ Hz, C); 132.59 (C); 132.50 (C); 131.65 (d, $J = 18.8$ Hz); 130.43; 128.94; 128.8; 128.72 (d, $J = 1.1$ Hz); 128.40; 128.30; 128.24; 127.97; 127.83; 127.63; 127.50 (d, $J = 2.5$ Hz); 127.06; 126.63; 126.07; 125.72 (d, $J = 5.1$ Hz); 125.22; 125.13; 50.46 (d, $J = 20.5$ Hz); 41.35 (d, $J = 31.4$ Hz, CH_2); 31.99 (d, $J = 16.7$ Hz, CH_2). ^{31}P NMR δ: 17.34 (s). MS (160 °C) *m/z* (rel%): 478 (21, M^+). HRMS: calcd for $C_{35}H_{27}P$ 478.1850, found: 478.1795. $[\alpha]_D^{20} = +163$ (*c* 0.38, $CHCl_3$).

4.2.19. (*S*,*S*,*S*$_a$)-3,5-Dibenzyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1′,2′-*e*]phosphepine 2-Bn/Bn. Yield: 488 mg (86%). Mp: 106–109 °C. ^{1}H NMR δ: 7.89–7.83 (m, 4H); 7.63 (ddd, $J = 1.5$, 6.7, 8.2 Hz, 2H); 7.48 (dd, $J = 1.2$, 8.4 Hz, 1H); 7.47–7.31 (m, 6H); 7.23 (d, $J = 3.3$ Hz, 2H); 7.13 (ddd, $J = 1.4$, 6.7, 8.1 Hz, 1H); 7.06–7.01 (m, 4H); 6.84–6.81 (m, 3H); 6.74–6.72 (m, 2H); 6.24–6.21 (m, 2H); 3.69 (m, 1H); 3.62 (m, 1H); 2.71 (m, 1H); 2.27 (m, 1H); 1.95 (m, 1H); 1.93 (m, 1H). ^{13}C NMR δ: 141.27 (d, $J = 2.3$ Hz, C); 140.74 (d, $J = 13.0$ Hz, C); 139.80 (d, $J = 2.2$ Hz, C); 138.18 (d, $J = 26.6$ Hz, C); 136.51 (C); 134.64 (d, $J = 6.2$ Hz, C); 134.19 (C); 133.40 (d, $J = 2.3$ Hz, C); 133.31 (C); 132.96 (d, $J = 20.0$ Hz); 132.45 (C); 130.27 (d, $J = 3.0$ Hz); 130.09; 128.85; 128.83; 128.72; 128.58 (d, $J = 6.8$ Hz); 128.25; 128.24; 128.20; 127.96; 127.86; 127.61; 127.43; 126.99; 125.94; 125.79; 125.78; 125.49; 125.45; 125.26; 47.11 (d, $J = 22.8$ Hz); 44.85 (d, $J = 21.0$ Hz); 42.87 (d, $J = 28.5$ Hz, CH_2); 33.54 (d, $J = 3.0$ Hz, CH_2). ^{31}P NMR δ: 36.21 (s). MS (230 °C)

m/z (rel%): 568 (100, M^+). HRMS: calcd for $C_{42}H_{33}P$ 568.2320, found: 568.2333. $[\alpha]_D^{20} = +417$ (*c* 0.51, $CHCl_3$).

4.3. Asymmetric hydrogenation (general procedure)

$Rh(COD)_2BF_4$ (2 mg, 0.5×10^{-5} mol, 1 mol % Rh) and ligand **2** (1×10^{-5} mol) were stirred in degassed toluene (1 mL) for 15 min and transferred via teflon canula to a 100 mL high-pressure glass tube under Ar. To this was added a degassed solution of substrate **7** (0.5 mmol) in toluene (7 mL) and the tube purged with H_2 and finally desired pressure was adjusted. After stirring for 20 h, the mixture was evaporated. Conversion was determinated by ^1H NMR and ee by chiral HPLC of the methylester on a Chiralcel OJ column (250×4.6 mm) with *i*-PrOH/*n*-hexane, 6:94 as the eluent at 40 °C with $v = 1.0$ mL min^{-1}; $t_R = 13.01$ min, $t_S = 19.03$ min, starting material: $t_3 = 27.02$ min.

4.4. Asymmetric hydroboration (general procedure)

A flame dried Schlenk tube was loaded with ligand **2** (3.8 or 7.6 μmol) and $Rh(COD)_2BF_4$ (1.5 mg, 3.8 μmol) and dry degassed THF (1.5 mL) was added under Ar at rt. The solution was stirred for 5 min and then cooled to 0 °C followed by the addition of styrene (43 μL, 0.38 mmol). Catecholborane (0.46 mL, 0.46 mmol) was added and the color of the solution changed from yellow to orange. Stirring was continued for 12 h at 5 °C. The reaction mixture was quenched upon addition of EtOH (2 mL) at 0 °C followed by NaOH solution (2.5 mL, 3 mol) and H_2O_2 (0.5 mL, 35%) and stirred vigorously for 0.5 h at rt. The mixture was extracted with diethyl ether (3×10 mL) and the combined organic phases washed with water and brine and dried over $MgSO_4$. The crude mixture of products was separated by chromatography (SiO_2, PE/diethyl ether, 50:50); Ee was determinated by HPLC with a Chiralcel OD-H column (250×4.6 mm) in *i*-PrOH/*n*-hexane (5:95); $t_R = 23.1$ min, $t_S = 29.5$ min.

4.5. Asymmetric Suzuki–Miyaura cross coupling (general procedure)

A flame dried Schlenk tube was charged with $Pd(OAc)_2$ (2.25 mg, 0.1 mmol, 5 mol %) and ligand **2** (0.02 mmol, 10 mol %) and filled with Ar. DME was added (0.5 mL) and the mixture was stirred for 15 min at rt and 5 min at 70 °C. To this was added iodide **12** (56.8 mg, 0.2 mmol) and *ortho*-tolyl boronic acid (54.4 mg, 2 equiv 0.4 mmol) dissolved in DME (1 mL) followed by CsF (76 mg, 0.5 mmol, 5 mol %) in water (0.05 mL). The reaction mixture was stirred at 70 °C for 16 h, cooled to rt and HCl (0.2 mL) and CH_2Cl_2 (5 mL) were added. The organic phase was washed with 1 M NaOH and water and dried with $MgSO_4$. After concentration, the residue was subjected to preparative TLC (PE/CH_2Cl_2, 80:20) to give **13**.[15] Ee was determinated by chiral HPLC using a Chiralcel OD-H column (250×4.6 mm) in *n*-hexane/*i*-PrOH (99.75:0.25); $v = 0.5$ mL min^{-1}, at 28 °C; $t_1 = 24.5$ min, $t_2 = 27.6$ min.

4.6. Crystal structure analysis

Colorless crystals of racemic samples of **4-Me/H** and **5-Me/Me** were obtained by diffusion of EtOAc into CH_2Cl_2 solutions. X-ray data were collected at $T = 173(2)$ K on a Bruker Smart APEX CCD area detector diffractometer with graphite monochromated MoKα radiation, $\lambda = 0.71073$ Å, using 0.3° ω-scan frames covering either a hemisphere (**4-Me/H**) or a complete sphere (**5-Me/Me**) of the reciprocal space. After data integration with program SAINT, corrections for absorption and $\lambda/2$-effects were applied with program SADABS.[16] The structures were solved with direct methods and then refined on F^2 with the program package SHELX97.[17] The non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogens were included in idealized positions. Complete structure data have been deposited.[18] Salient crystal data are as follows:

4-Me/H: $C_{29}H_{23}PS$, $M_r = 434.50$, monoclinic, space group $P2_1/c$ (no. 14), $T = 173(2)$ K, $a = 13.5899(9)$ Å, $b = 10.5222(7)$ Å, $c = 15.7802(10)$ Å, $\beta = 90.734(1)°$, $V = 2256.3(3)$ Å^3, $Z = 4$, $\rho_{calc} = 1.279$ g/cm^3, $\mu = 0.229$ mm^{-1}. Of 16988 reflections collected up to $\theta_{max} = 30°$, 6523 were independent, $R_{int} = 0.036$, and 5207 were observed ($I > 2\sigma(I)$); final *R* indices: $R_1 = 0.059$ (all data), $wR_2 = 0.135$ (all data). Selected bond lengths: P–C24 = 1.8143(15), P–C23 = 1.8286(15), P–C21 = 1.8624(15), P–S = 1.9478(5).

5-Me/Me: $C_{30}H_{25}PS$, $M_r = 448.53$, monoclinic, space group $C2/c$ (no. 15), $T = 173(2)$ K, $a = 17.6646(8)$ Å, $b = 10.7614(5)$ Å, $c = 25.2144(11)$ Å, $\beta = 102.539(1)°$, $V = 4678.8(4)$ Å^3, $Z = 8$, $\rho_{calc} = 1.273$ g/cm^3, $\mu = 0.223$ mm^{-1}. Of 29144 reflections collected up to $\theta_{max} = 30°$, 6800 were independent, $R_{int} = 0.019$, and 6128 were observed ($I > 2\sigma(I)$); final *R* indices: $R_1 = 0.043$ (all data), $wR_2 = 0.111$ (all data). Selected bond lengths P–C25 = 1.8136(12), P–C23 = 1.8463(10), P–C21 = 1.8631(12), P–S = 1.9618(4).

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