Synthesis Y. Uozumi et al. Paper

Palladium-Catalyzed Asymmetric Suzuki–Miyaura Cross Coupling with Homochiral Phosphine Ligands Having Tetrahydro-1*H*-imidazo[1,5-*a*]indole Backbone

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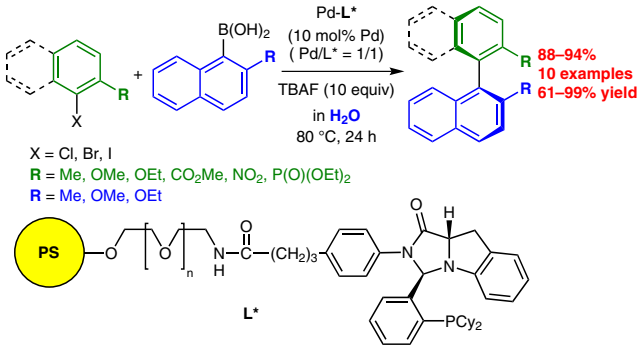
The authors would like to dedicate this article to Professor Dieter Enders on the occasion of his 70th birthday.



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Abstract Amphiphilic polystyrene-poly(ethylene glycol) resin-supported chiral imidazoindole phosphines (PS-PEG-L*), (3*R*,9a*S*)-2-aryl-3-(2-dialkylphosphino)phenyltetrahydro-1*H*-imidazo[1,5-*a*]indol-1-one, bearing PPh_2, P(*t*-Bu)$_2$, and P(*c*-Hex)$_2$ groups were designed and prepared with a view toward using them in aqueous heterogeneous asymmetric Suzuki–Miyaura biaryl coupling. The asymmetric coupling of 2-substituted 1-iodonaphthalenes and 2-substituted naphthalen-1-ylboronic acid took place in water under heterogeneous conditions in the presence of 10 mol% palladium of PS-PEG-L*-Pd complexes to give up to 94% ee of (*S*)-2,2′-disubstituted 1,1′-binaphthyls.

Key words asymmetric catalysis, biaryls, cross-coupling, palladium, Suzuki–Miyaura coupling, catalysis in water, heterogeneous catalysis

Catalytic asymmetric organic transformations have attracted significant interest due to their synthetic utility, and development of those catalyzed by transition metal complexes containing optically active ligands is one of the most exciting and challenging research subjects to date. Organophosphorus compounds having a homochiral backbone are recognized as one of the most versatile and successful classes of ligands in transition-metal-catalyzed asymmetric reactions. On the other hand, over the past two decades, we have demonstrated that a wide variety of organic transformations can be performed in water by use of amphiphilic polystyrene-poly(ethylene glycol) copolymer (PS-PEG) resin-supported transition metal catalysts, and therefore readily immobilizable chiral phosphine ligands are required for the realization of aqueous- and heterogeneous-switching of given catalytic asymmetric reactions.[1]

We have continued our efforts to develop new amphiphilic polymer resin-supported chiral phosphine ligands and found that those bearing tetrahydro-1*H*-imidazo[1,5-*a*]indol-1-one backbone (e.g., PS-PEG-**L*1**–**L*3**, Figure 1) are very effective for several types of aquacatalytic asymmetric reactions including palladium-catalyzed asymmetric π-allylic substitution, the Tsuji–Trost reaction,[2] and the cross-coupling of aryl halides and aryl boronic acids – the Suzuki–Miyaura coupling.[3] Here we describe in detail the development of the unimmobilized and immobilized chiral phosphine ligands bearing the tetrahydro-1*H*-imidazo[1,5-*a*]indol-1-one backbone (Figure 1) and their application to the asymmetric Suzuki–Miyaura coupling reaction.[4]

The triarylphosphine ligand, (3*R*,9a*S*)-3-[2-(diphenylphosphino)phenyl]-2-phenyltetrahydro-1*H*-imidazo[1,5-*a*]indol-1-one (**L*1**), the homogeneous counterpart of the

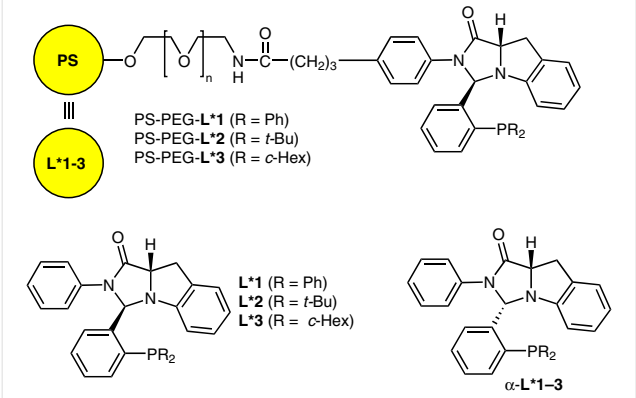
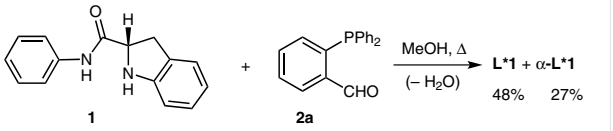


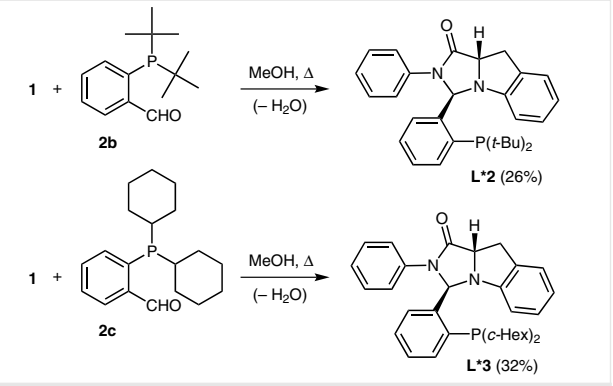
Figure 1 Tetrahydro-1*H*-imidazo[1,5-*a*]indolephosphines

polymeric ligand **PS-PEG-L*1**, was prepared from the (*S*)-indoline-2-carboxanilide **1** and 2-(diphenylphosphino)benzaldehyde (**2a**).[5] Thus, the reaction of anilide **1** and **2a** in refluxing methanol gave imidazoindolephosphine ligand **L*1** (48%) along with its diastereomeric isomer **α-L*1** (27%) (Scheme 1).



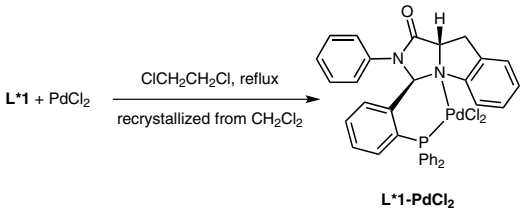
Scheme 1 Preparation of **L*1**

It has been reported that sterically demanding basic phosphine ligands having bulky alkyl P-substituents (e.g., *P*-*tert*-butyl, *P*-cyclohexyl) promote several palladium-catalyzed coupling reactions, including Suzuki–Miyaura coupling and Hartwig–Buchwald amination, of less reactive aryl chloride substrates.[6] 2-[Bis(*tert*-butyl)phosphino]phenyl and 2-[bis(cyclohexyl)phosphino]phenyl groups were readily introduced at the C3 position of the chiral imidazoindole skeleton via the condensation of indoline carboxanilide **1** with 2-[bis(*tert*-butyl)phosphino]benzaldehyde (**2b**) and 2-[bis(cyclohexyl)phosphino]benzaldehyde (**2c**), to afford the *P*-alkylimidazoindolephosphine ligands **L*2** and **L*3** in 26% and 32% yield, respectively (Scheme 2), while the minor diastereomeric isomers **α-L*2** and **α-L*3** were difficult to isolate because of their instability in air.



Scheme 2 Preparation of **L*2** and **L*3**

The coordination manner of the imidazoindolephosphine ligand to a transition metal was studied by X-ray crystal structure analysis of the parent palladium complex **L*1**-$PdCl_2$ (Scheme 3,Figure 2 A). The complex **L*1**-$PdCl_2$ was prepared by mixing **L*1** with palladium dichloride (L/Pd = 1.0:1.0) in refluxing dichloroethane and single crystals were obtained as yellow prisms by recrystallization from dichloromethane. The molecular structure is shown in Figure 2 A. The complex **L*1**-$PdCl_2$ adopts square planar geometry with a phosphorus atom, a nitrogen atom of indole ring (P,N-chelating fashion), and two chloride atoms. The bite angle of the imidazoindole phosphine ligand **L*1** to palladium ∠[N(1)-Pd-P] is 96.2° (Figure 2). As can be seen from the schematic structure of **L*1**-$PdCl_2$ complex shown in Figure 2 B, the fused benzene ring of the indole moiety and one of the *P*-phenyl groups are situated in the regions of the second and the fourth quadrants (from the view point of metal side) to construct the effective chiral surroundings.



Scheme 3 Preparation of **L*1**-$PdCl_2$

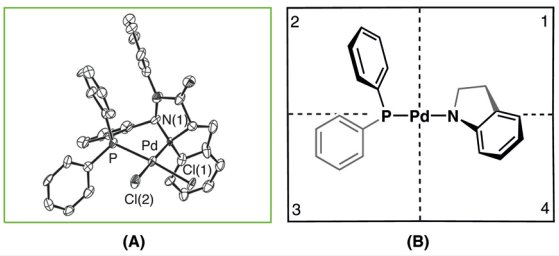
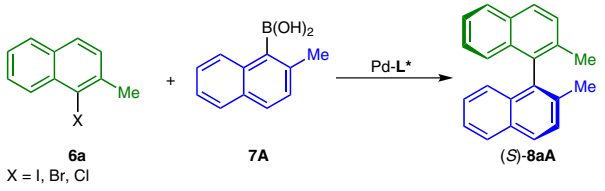


Figure 2 A: ORTEP drawing of L*1-$PdCl_2$. The ellipsoids are drawn at 30% probability level. All hydrogens are omitted for simplicity. B: Schematic structure of **L*1**-$PdCl_2$ from the view point of metal side. Two chloride ligands and a backside-half of **L*1** (-CON(C_6H_5)CHC_6H_4-) are omitted for simplicity. Selected bond length (Å): Pd–Cl(1) = 2.356(4), Pd–Cl(2) = 2.265(5), Pd–P = 2.231(4), Pd–N(1) = 2.12(1). Selected angles (degree): ∠[N(1)–Pd–P] = 96.2(2), ∠[Cl–Pd–Cl] = 91.1(2).

The enantio-inducing ability of the P,N-chelating tetrahydro-1*H*-imidazo[1,5-*a*]indolephosphine ligands was preliminarily examined for Suzuki–Miyaura biaryl coupling of **6a** and **7A** under homogeneous conditions.[7] The cross-coupling[8] of aryl halides and aryl boronic acids, the so-called Suzuki–Miyaura coupling, is one of the most versatile and successful synthetic tools for carbon–carbon bond formation. However, although axially chiral biaryls are highly accessible via this coupling only scattered attention has been paid to the asymmetric Suzuki–Miyaura biaryl coupling.[9] Representative results on the asymmetric coupling of **6a** and **7A** are shown in Table 1. Thus, the reaction of 1-iodo-2-methylnaphthalene (**6a-I**) and 2-methyl-1-naphthaleneboronic acid (**7A**) (5 equiv) was carried out in toluene in the presence of 10 mol% of $Pd(OAc)_2$ and imidazoindole-diphenylphosphine **L1** (Pd/P = 1:1) and K_3PO_4 (10 mol equiv) at 100 °C for 5 hours to give a quantitative yield of 2,2′-dimethyl-1,1′-binaphthyl (**8aA**). The enantiomeric purity and absolute configuration of **8aA** were determined by HPLC

analysis using a chiral stationary phase column and measurement of the specific rotation to be 90% ee (*S*) (Table 1, entry 1). Bromo- and chloronaphthalene **6a-Br** and **6a-Cl** exhibited lower reactivity (entries 2 and 3). The chemical yield and the enantiomeric purity of **8aA** were lowered with the imidazoindole-di(*tert*-butyl)phosphine **L2** to 78% yield and 86% ee, respectively (entry 4). Imidazoindole-di(cyclohexyl)phosphine **L3** was identified as the best ligand. Thus, starting with iodide **6a-I**, the chemical yield and the enantiomeric purity of binaphthyl **8aA** were 98% and 92% ee under similar conditions (entry 7). The palladium catalyst of **L3** was so catalytically active that the coupling took place at 60 °C to give 94% ee of **8** (24 h, 70% yield, entry 9). It is noteworthy that 1-chloro-2-methylnaphthalene (**6a-Cl**) also underwent the coupling with **7A** using the palladium-**L3** catalyst at 60 °C to afford 91% ee of **8aA**, though the chemical yield was modest (48%, entry 10).

Table 1 Palladium-Catalyzed Asymmetric Binaphthyl Coupling with Imidazoindolephosphines[a]



6a
X = I, Br, Cl

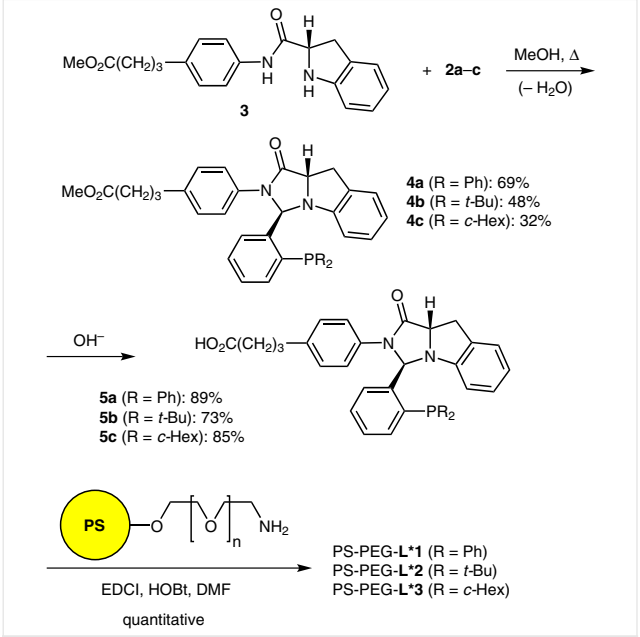
7A

(*S*)-**8aA**

Entry	Ligand	Halide	Yield (%)[b]	ee (%)[c]
1	**L1**	**6a-I**	98	90
2	**L1**	**6a-Br**	71	90
3	**L1**	**6a-Cl**	<2	N/A
4	**L2**	**6a-I**	78	86
5	**L2**	**6a-Br**	52	87
6	**L2**	**6a-Cl**	39	72
7	**L3**	**6a-I**	98	92
8	**L3**	**6a-Cl**	57	88
9[d]	**L3**	**6a-I**	70	94
10[d]	**L3**	**6a-Cl**	48	91

[a] Conditions: **6** (1.0 mmol), **7** (5.0 mmol), $Pd(OAc)_2$ (0.1 mmol), L* (0.1 mmol), K_3PO_4 (5.0 mmol), toluene (2 mL), 100 °C, 5 h, unless otherwise noted.
[b] Isolated yield.
[c] Determined by HPLC analysis using Chiralpack OD-H. $[\alpha]_D^{20}$ +32.5 (*c* 0.8 $CHCl_3$) for *S* of 94% ee. N/A: Not available.
[d] Carried out at 60 °C for 24 h.

With the encouraging results on the asymmetric biaryl coupling under homogeneous conditions in hand, we next examined the heterogeneous- and the aqueous-switching of the asymmetric coupling reaction. Thus, the imidazoindole phosphines were immobilized onto the amphiphilic polystyrene-poly(ethylene glycol) copolymer (PS-PEG)[10] resin by a butyryl amide tether. The imidazoindole ligands **4a–c** having an *N*-[4-(methoxycarbonylpropyl)phenyl] group were prepared by condensation of indoline carboxanilide **3** with 2-phosphinobenzaldehydes **2a–c** in 69%, 48%, and 32% yield, respectively, according to the procedures for the preparation of **L*** (Scheme 4). After alkaline hydrolysis of the ester groups of **4a**,**b**, and **c** (89%, 73%, and 85%, respectively), the resulting carboxylic acids **5a–c** were anchored onto PS-PEG amino resin by 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI·HCl) and 1-hydroxybenzotriazole (HOBt) in DMF. Negative Kaiser tests indicated that the condensation with **5a–c** were completed to form the corresponding PS-PEG resin-supported imidazoindolephosphine ligands, **PS-PEG-L*1**, **PS-PEG-L*2**, and **PS-PEG-L*3**, quantitatively. The gel-phase $^{31}P\{^1H\}$ NMR study of resin-supported phosphines were performed with MAS-NMR probe by use of the standard solution-phase parameters. A narrow singlet at δ = –19.7 was observed for the spectrum of **PS-PEG-L*1** in $CDCl_3$. The ^{31}P resonances of **PS-PEG-L*2** and **PS-PEG-L*3** were observed as narrow singlets at +12.5 ppm and –19.0 ppm, respectively.

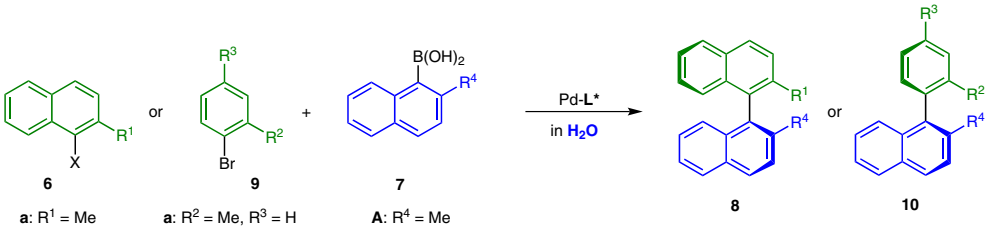


Scheme 4 Preparation of PS-PEG resin-supported imidazoindolephosphines

The asymmetric catalysis in water with a recyclable heterogeneous catalyst would approach what may be considered an ideal organic chemical process. Over the past ten years, we have demonstrated that a wide variety of non-asymmetric as well as asymmetric catalytic organic transformations can be performed in water by use of amphiphilic polystyrene-poly(ethylene glycol) copolymer (PS-PEG) resin-supported transition metal complexes and nanoparticles. Along the same line, the asymmetric Suzuki–Miyaura biaryl coupling was examined in water using amphiphilic resin-supported **PS-PEG-L***. We were pleased to find that the asymmetric Suzuki–Miyaura biaryl coupling took place

smoothly in water to provide good to excellent stereoselectivity with a wide substrate tolerance when a palladium complex of **PS-PEG-L*** was used in the presence of TBAF. Representative results are summarized in Table 2. Thus, the reaction of **6a-I** and **7A** was catalyzed with the amphiphilic polymeric **PS-PEG-L*3-Pd** to give a 95% yield of **8aA** with 94% ee (*S*), which was isolated via $scCO_2$ extraction from the catalyst resin beads followed by chromatographic purification (Table 2, entry 3). The coupling with PS-PEG-**L*1** and -**L*2** gave (*S*)-**8aA** with 90% and 86% ees, respectively, under otherwise the same conditions (entries 1 and 2). Coupling of naphthyl bromide **6a-Br** also proceeded smoothly with PS-PEG-**L*1-3** to give (*S*)-**8aA** in 71% (87% ee), 64% (88% ee), and 90% (88% ee) yield, respectively (entries 4–6). Recycle

Table 2 Palladium-Catalyzed Asymmetric Biaryl Coupling in Water with Supported Imidazoindolephosphines[a]



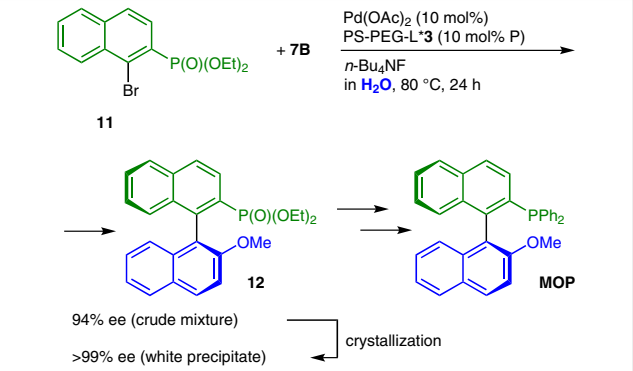
Entry	**6** or **9**	**7**	Product	Ligand	Yield (%)[b]	ee (%)[c]
1	**6a-I**	**7A**	**8aA**	PS-PEG-**L*1**	99	90 (*S*)
2	**6a-I**	**7A**		PS-PEG-**L*2**	85	86 (*S*)
3	**6a-I**	**7A**		PS-PEG-**L*3**	95	85 (*S*)
4	**6a-Br**	**7A**		PS-PEG-**L*1**	71	87 (*S*)
5	**6a-Br**	**7A**		PS-PEG-**L*2**	64	88 (*S*)
6	**6a-Br**	**7A**		PS-PEG-**L*3**	90	88 (*S*)
7	**6a-Br**	**7A**		(1st recycle)	88	88 (*S*)
8	**6a-Br**	**7A**		(2nd recycle)	86	88 (*S*)
9	**6a-Br**	**7A**		(3rd recycle)	89	87 (*S*)
10	**6a-Br**	**7A**		(4th recycle)	89	88 (*S*)
11	**6a-Cl**	**7A**		PS-PEG-**L*1**	<2	N/A
12	**6a-Cl**	**7A**		PS-PEG-**L*2**	40	80 (*S*)
13	**6a-Cl**	**7A**		PS-PEG-**L*3**	55	89 (*S*)
14	**6b-I**	**7A**	**8bA**	PS-PEG-**L*3**	85	92 (*R*)
15	**6b-Cl**	**7A**	**8bA**	PS-PEG-**L*3**	86	88 (*R*)
16	**6a-I**	**7C**	**8aC**	PS-PEG-**L*3**	93	92 (*R*)
17	**6c-I**	**7A**	**8cA**	PS-PEG-**L*3**	90	92 (*R*)
18	**6b-I**	**7C**	**8bC**	PS-PEG-**L*3**	90	92 (*S*)
19	**6c-I**	**7B**	**8cB**	PS-PEG-**L*3**	77	92 (*S*)
20	**6d-Br**	**7A**	**8dA**	PS-PEG-**L*3**	61	88 (*R*)
21	**9a**	**7A**	**10aA**	PS-PEG-**L*3**	96	92
22	**9b**	**7A**	**10bA**	PS-PEG-**L*3**	89	92
23	**9c**	**7A**	**10cA**	PS-PEG-**L*3**	93	94
24	**9d**	**7A**	**10dA**	PS-PEG-**L*3**	96	92 (*R*)

[a] All reactions were carried out in water at 80 °C for 24 h. Ratio of **6** (mol)/**7** (mol)/TBAF (mol)/$Pd(OAc)_2$ [or $PdCl_2(MeCN)_2$] (mol)/PS-PEG-L* (mol of P)/H_2O (L) = 1.0:5.0:10:0.1:0.1:20.
[b] Isolated yield.
[c] Determined by HPLC (Chiralpak OD-H or AD-H). The absolute configuration is shown in parentheses. N/A: Not available.

experiments of the supported catalyst **PS-PEG-L*3-Pd** were performed with **6a-Br**. The catalyst **PS-PEG-L*3-Pd** was readily recovered and reused 4 times without any reactivation of the recovered resin catalyst beads to give **8aA** in 88% average yield with an average stereoselectivity of 88% ee where no significant loss of catalytic activity or stereoselectivity was observed (entries 7–10). Coupling of naphthyl chloride **6a-Cl** took place with **PS-PEG-L*3-Pd** under similar conditions to give 89% ee of **8aA** (entry 13), whereas the reaction hardly proceeded with **PS-PEG-L*1** bearing a *P*-phenyl coordinating group (entry 11).

A series of unsymmetric binaphthyls were obtained in their enantioenriched forms via the asymmetric cross-coupling of various naphthyl halides **6** and naphthylboronic acids **7** having different 2-substitutents. Thus, the unsymmetric 2-methoxy-2′-methyl-1,1′-binaphthyl (**8bA**) was obtained with 92% ee and 88% ee from **6b-I** and **6b-Cl**, respectively (Table 2, entries 14 and 15). The coupling reaction of **6a-I** and **7C**, and that of the reverse combination (**6c-I** and **7A**) gave essentially the same results where both 92% ee of **8aC** (= **8cA**) was obtained in 93% and 90% isolated yield, respectively (entries 16 and 17). The asymmetric coupling of 1-iodo-2-methoxynaphthalene (**6b-I**) and 2-ethoxynaphthalene boronic acid (**7C**) gave an unsymmetric ether of binaphthol, 2-ethoxy-2′-methoxy-1,1′-binaphthyl (**8bC**) of 92% ee (entry 18). The reverse combination (**6c-I** and **7B**) also gave 92% ee of **8cB** (= **8bC**) (entry 19), where the chemical yield (77%) was slightly lower than that obtained from sterically less hindered 2-methoxynaphthyl **6b** (vs entry 18). Because of wide functional group tolerance of the Suzuki–Miyaura coupling, the asymmetric formation of biaryls bearing electrophilic groups was achieved under similar conditions. Thus, the reaction of 2-methoxycarbonyl-1-bromonaphthalene (**6d-Br**) with **7A** gave 2-methoxycarbonyl-2′-methyl-1,1′-binaphthyl (**8dA**) in 61% yield with 88% ee (entry 20). Bromobenzene **9** having appropriate *ortho*-substituents delivered the axially chiral phenylnaphthalene derivatives **10**. Thus, 2-bromotoluene (**9a**), 4-bromo-3-methylbenzonitrile (**9b**), methyl 4-bromo-3-methylbenzoate (**9c**), and 2-bromonitrobenzene (**9d**) underwent asymmetric coupling with **7A** in water to afford 89–96% yield of 1-(substituted aryl)-2-methylnaphthalenes **10aA**, **10bA**, **10cA**, and **10dA** with 92%, 92%, 94%, and 92% enantiomeric excess, respectively (entries 21–24), where the electrophilic substituents (e.g. CN, CO_2Me, NO_2) on the benzene rings of **9** were retained.

The stereoselective asymmetric biaryl coupling system was applied to the preparation of MOP ligand, which has previously been developed by Uozumi and Hayashi as an optically active monophosphine ligand. The reaction of phosphonate **11** and **7B** afforded diethyl 2′-methoxy-1,1′-binaphth-2-yl phosphonate (*S*)-**12**, a synthetic precursor of MOP ligands, in 70% isolated yield as a white precipitate. The enantiomeric purity of **12** was estimated to be ca. 94% ee before purification (as a crude residue), and was increased through purification to 99% ee (*S*) (Scheme 5).



Scheme 5 Application to MOP synthesis

In summary, a series of optically active P,N-chelating ligands bearing tetrahydro-1*H*-imidazo[1,5-*a*]indole backbone, were designed, prepared, and readily immobilized onto an amphiphilic polystyrene-poly(ethylene glycol) copolymer (PS-PEG) resin to afford PS-PEG resin-supported chiral phosphine ligands. Palladium complexes of the polymeric ligands exhibited good catalytic activity and enantioselectivity for a given reaction (e.g., Suzuki–Miyaura biaryl coupling) in water under heterogeneous conditions, where the fine tuning of the catalytic as well as enantioselective ability was realized by the introduction of several types of *P*-alkyl substituents. X-ray crystal structure analysis of the palladium complex **L*1**-$PdCl_2$ revealed that the imidazoindolephosphine coordinates to palladium(II) in a P,N-chelating fashion to construct the effective chiral environment.

All manipulations were performed under a N_2 atmosphere. H_2O was deionized with a Millipore system as a Milli-Q grade and was degassed by the freeze–pump–thaw method prior to use. NMR spectra were recorded at 25 °C on a JEOL JNM-A500 spectrometer (500 MHz for ^1H, 125 MHz for ^{13}C, 202 MHz for ^{31}P) or a JEOL JNM-AL400 spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C, 162 MHz for ^{31}P). ICP-AES analyses were performed on Leeman Labs Inc. Profile Plus using Pd standard solution (Kanto Chemical) as a standard. Melting points were determined using a Yanaco micro melting point apparatus MP-J3 and are uncorrected. ESI mass spectra were recorded on a JEOL JMS-T100LC spectrometer. The GC-MS was measured by an Agilent 6890 GC/5973N MS detector. IR spectra were obtained using a JASCO FT/IR-460 plus spectrophotometer in ATR mode. Optical rotations were recorded on a JASCO P-1020 polarimeter. PS-PEG amino-resin was purchased from RAPP POLYMERE™ (TentaGel®S NH_2, average diameter 0.90 mm, 1% divinylbenzene crosslinked, loading value of amino residue 0.2–0.3 mmol·g^{-1}).

Chiral Imidazoindolephosphines; (3*R*,9a*S*)-2-Phenyl-3-[2-(diphenylphosphino)phenyl]tetrahydro-1*H*-imidazo[1,5-*a*]indole-1-one (L*1); Typical Procedure

(*S*)-*N*-Phenylindoline-2-carboxamide (**1**; 338 mg, 1.0 mmol) and 2-(diphenylphosphino)benzaldehyde (**2a**; 580 mg, 2 mmol) were dissolved in MeOH (5 mL). The reaction mixture was heated to 80 °C in a sealed tube for 3 h. After cooling down to r.t., the mixture was extracted with EtOAc and concentrated. The resulting residue was chromatographed on silica gel (eluent: acetone/hexane = 1:5) to give a white solid; yield: 245 mg (48%).

[CAS Reg. No.: 375810-10-9]

Mp 94–96 °C; $[\alpha]_D^{19}$ +127 (*c* 0.7, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 8.0 Hz, 1 H), 7.41–7.32 (m, 15 H), 7.20–7.10 (m, 6 H), 7.03–6.93 (m, 2 H), 4.40 (d, *J* = 9.5 Hz, 1 H), 3.56 (d, *J* = 16.0 Hz, 1 H), 3.15 (dd, *J* = 9.5, 16.0 Hz, 1 H), 1.37 (d, *J* = 12.2 Hz, 9 H), 1.29 (d, *J* = 12.2 Hz, 9 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 174.3, 142.3–113.8 (C_{arom}, overlapped), 81.4 (d, $J_{C,P}$ = 24.9 Hz), 64.2, 31.5.

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ = –19.6.

MS (ESI-TOF): *m*/*z* = 533 $[M + Na]^+$.

(3*R*,9a*S*)-2-Phenyl-3-{2-[di(*tert*-butyl)phosphino]phenyl}tetrahydro-1*H*-imidazo[1,5-*a*]indole-1-one (L*2)

White solid; yield: 123 mg (26%); mp 102–104 °C; $[\alpha]_D^{21}$ +27.3 (*c* 0.7, $CHCl_3$).

IR (ATR): 2962, 2899, 1720, 1511, 1201 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 12.0 Hz, 1 H), 7.94 (d, *J* = 8.0 Hz, 1 H), 7.49–7.47 (m, 1 H), 7.36–7.35 (m, 1 H), 7.26–7.17 (m, 4 H), 7.12–7.07 (m, 2 H), 6.96–6.93 (m, 1 H), 6.80 (dd, *J* = 7.5 Hz, 1 H), 6.63 (dd, *J* = 7.5 Hz, 1 H), 4.85 (d, *J* = 8.0 Hz, 1 H), 4.65 (dd, *J* = 2.5, 12.0 Hz, 1 H), 3.74 (dd, *J* = 2.5, 16.5 Hz, 1 H), 3.87–3.32 (m, 1 H), 1.37 (d, *J* = 12.2 Hz, 9 H), 1.29 (d, *J* = 12.2 Hz, 9 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 175.8, 147.4, 138.9, 138.8, 138.6, 137.1, 135.5 (d, $J_{C,P}$ = 3.1 Hz), 131.8 (d, $J_{C,P}$ = 5.2 Hz), 130.3, 129.0 (d, $J_{C,P}$ = 21.7 Hz), 128.5, 128.2, 128.0, 126.2, 125.7 (d, $J_{C,P}$ = 2.0 Hz), 124.8, 124.6, 121.1, 121.0, 116.6, 77.5, 65.5, 33.1 (d, $J_{C,P}$ = 22.7 Hz), 32.6, d, $J_{C,P}$ = 19.6 Hz), 31.0 (d, $J_{C,P}$ = 15.5 Hz, 3 C), 30.8 (d, $J_{C,P}$ = 14.4 Hz, 3 C).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ = 12.8.

Anal. Calcd for $C_{30}H_{35}N_2OP$: C, 76.57; H, 7.50; N, 5.95. Found: C, 76.77; H, 7.29; N, 5.96

(3*R*,9a*S*)-2-Phenyl-3-[2-(dicyclohexylphosphino)phenyl]tetrahydro-1*H*-imidazo[1,5-*a*]indole-1-one (L*3)

White solid; yield: 169 mg (32%); mp 95–98 °C; $[\alpha]_D^{21}$ +49.2 (*c* 1.0, $CHCl_3$).

IR (ATR): 2928, 2881, 1690, 1258 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (dd, *J* = 2.5, 6.1 Hz, 1 H), 7.67–7.65 (m, 1 H), 7.59 (d, *J* = 7.0 Hz, 1 H), 7.48 (d, *J* = 8.5 Hz, 1 H), 7.38–7.30 (m, 3 H), 7.26–7.14 (m, 3 H), 7.04–7.01 (m, 1 H), 6.95 (t, *J* = 7.5 Hz, 1 H), 4.44 (d, *J* = 10.0 Hz, 1 H), 3.59 (d, *J* = 16.0 Hz, 1 H), 3.59 (d, *J* = 16.0 Hz, 1 H), 3.23 (dd, *J* = 10.0, 16.0 Hz, 1 H), 2.07–2.01 (m, 4 H), 1.82–1.59 (m, 8 H), 1.43–1.13 (m, 10 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 174.5, 152.0, 144.5 (d, $J_{C,P}$ = 20.6 Hz), 138.1, 135.3, 134.1, 134.0, 129.7, 128.9, 128.7, 128.2, 127.8, 125.3, 125.2, 124.9, 122.4, 120.4, 114.4, 114.2, 81.4 (d, $J_{C,P}$ = 31.0 Hz), 64.1, 51.4, 35.8 (d, $J_{C,P}$ = 9.3 Hz), 35.2 (d, $J_{C,P}$ = 9.3 Hz), 34.4, 33.2, 31.5, 30.8 (d, $J_{C,P}$ = 17.6 Hz), 30.6 (d, $J_{C,P}$ = 15.5 Hz), 29.7 (d, $J_{C,P}$ = 9.3 Hz), 29.6 (d, $J_{C,P}$ = 7.3 Hz), 27.1 (d, $J_{C,P}$ = 20.7 Hz), 27.0 (d, $J_{C,P}$ = 18.6 Hz), 26.9 (d, $J_{C,P}$ = 3.0 Hz).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ = –21.2.

Anal. Calcd for $C_{34}H_{39}N_2OP$: C, 78.13; H, 7.52; N, 5.36. Found: C, 78.18; H, 7.56; N, 5.40.

4-Methoxycarbonylpropyl Chiral Imidazoindolephosphines 4; (3*R*,9a*S*)-2-{[4-(Methoxycarbonylpropyl)phenyl]-3-(2-diphenylphosphino)phenyl}tetrahydro-1*H*-imidazo[1,5-*a*]indole-1-one (4a); Typical Procedure

(*S*)-2-{[4-(Methoxycarbonylpropyl]phenyl)aminocarbonyl}indoline (**3**; 676 mg, 2 mmol) and 2-(diphenylphosphino)benzaldehyde (**2a**; 1.16 g, 4 mmol) were dissolved in MeOH (5 mL). The reaction mixture was heated to 80 °C in a sealed tube for 48 h. After cooling to r.t., the mixture was extracted with EtOAc and concentrated. The resulting residue was chromatographed on silica gel (eluent: acetone/hexane = 1:2) to give colorless fine prisms; yield: 840 (69%); mp 115–117 °C; $[\alpha]_D^{21}$ –169 (*c* 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 6.5 Hz, 1 H), 7.43–7.13 (m, 18 H), 6.97–6.91 (m, 3 H), 4.37 (d, *J* = 8.5 Hz, 1 H), 3.64 (s, 3 H), 3.53 (d, *J* = 16.5 Hz, 1 H), 3.09 (dd, *J* = 8.5, 16.5 Hz, 1 H), 2.52 (t, *J* = 7.5 Hz, 2 H), 2.26 (t, *J* = 7.5 Hz, 2 H), 1.85 (quin, *J* = 7.5 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 174.1, 173.6, 142.3–113.5 (C_{arom}, overlapped), 81.4 (d, $J_{C,P}$ = 25.9 Hz), 64.1, 51.3, 34.3, 33.1, 31.4, 26.1.

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ = –18.9 (s).

MS (ESI-TOF): *m*/*z* = 633 $[M + Na]^+$.

(3*R*,9a*S*)-2-[4-(Methoxycarbonylpropyl)phenyl]-3-({2-[di(*tert*-butyl)phosphino]phosphino}phenyl)tetrahydro-1*H*-imidazo[1,5-*a*]indole-1-one (4b)

White solid; yield: 547 mg (48%); mp 125–127 °C; $[\alpha]_D^{21}$ +26.8 (*c* 1.0, $CHCl_3$).

IR (ATR): 2957, 2919, 1730, 1588, 1490 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15–8.13 (m, 1 H), 7.93 (d, *J* = 7.0 Hz, 1 H), 7.61 (d, *J* = 7.5 Hz, 1 H), 7.38–7.30 (m, 4 H), 7.25–7.16 (m, 3 H), 7.01–6.93 (m, 3 H), 4.35 (dd, *J* = 1.5, 9.5 Hz, 1 H), 3.62 (s, 3 H), 3.58 (d, *J* = 15.5 Hz, 1 H), 3.19 (dd, *J* = 10.0, 16.0 Hz, 1 H), 2.52 (t, *J* = 7.5 Hz, 2 H), 2.24 (t, *J* = 7.5 Hz, 2 H), 1.83 (quin, *J* = 7.5 Hz, 2 H), 1.25 (dd, *J* = 12.5, 17.5 Hz, 18 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 174.9, 173.8, 152.0, 144.6, 144.4, 138.1, 136.3, 135.3, 129.7, 129.0, 128.7, 127.5, 127.4, 125.3, 125.2, 124.9, 122.3, 121.2, 114.4, 114.2, 82.1 (d, $J_{C,P}$ = 35.2 Hz), 63.7, 51.4, 34.4, 33.2, 33.0 (d, $J_{C,P}$ = 7.3 Hz), 32.9, d, $J_{C,P}$ = 13.4 Hz), 31.3, 30.7 (d, $J_{C,P}$ = 14.4 Hz, 3 C), 30.6 (d, $J_{C,P}$ = 14.4 Hz, 3 C), 26.3.

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ = 7.4 (s).

Anal. Calcd for $C_{35}H_{43}N_2O_3P$: C, 73.66; H, 7.59; N, 4.91. Found: C, 74.00; H, 7.49; N, 4.96.

(3*R*,9a*S*)-2-(4-(Methoxycarbonylpropyl)phenyl)-3-(2-(cyclohexyl)phosphino)phosphino)phenyl)tetrahydro-1*H*-imidazo[1,5-*a*]indole-1-one (4c)

White solid; yield: 400 mg (32%); mp 118-120 °C; $[\alpha]_D^{21}$ +56.8 (*c* 1.1, $CHCl_3$).

IR (ATR): 3065, 2905, 1696, 1461 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 6.1 Hz, 1 H), 7.66 (m, 1 H), 7.56 (d, *J* = 7.2 Hz, 1 H), 7.39–7.29 (m, 4 H), 7.25–7.22 (m, 3 H), 7.16–6.93 (m, 2 H), 4.42 (d, *J* = 10.0 Hz, 1 H), 3.62 (s, 3 H), 3.58 (d, *J* = 15.9 Hz, 1 H), 3.22 (dd, *J* = 10.0, 15.9 Hz, 1 H), 2.52 (t, *J* = 7.3 Hz, 2 H), 2.07–

1.86 (m, 2 H), 2.24 (t, *J* = 7.3 Hz, 2 H), 2.07–1.99 (m, 3 H), 1.83 (quin, *J* = 7.3 Hz, 2 H), 1.73–1.71 (m, 2 H), 1.69–1.59 (m, 2 H), 1.41–1.11 (m, 14 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 174.5, 173.8, 152.0, 144.5 (d, $J_{C,P}$ = 20.7 Hz), 138.1, 135.3, 134.1, 134.0, 129.7, 128.9, 128.7, 128.2, 127.8, 125.3, 125.2, 124.9, 122.4, 120.4, 114.4, 114.2, 81.4 (d, $J_{C,P}$ = 31.0 Hz), 64.1, 51.4, 35.8 (d, $J_{C,P}$ = 9.3 Hz), 35.2 (d, $J_{C,P}$ = 9.3 Hz), 34.4, 33.2, 31.5, 30.8 (d, $J_{C,P}$ = 17.6 Hz), 30.6 (d, $J_{C,P}$ = 15.5 Hz), 29.7 (d, $J_{C,P}$ = 9.3 Hz), 29.6 (d, $J_{C,P}$ = 7.3 Hz), 27.2, 27.1 (d, $J_{C,P}$ = 20.7 Hz), 27.0 (d, $J_{C,P}$ = 18.6 Hz), 26.9 (d, $J_{C,P}$ = 3.0 Hz), 26.3, 26.2, 22.6.

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ = –21.2 (s).

Anal. Calcd for $C_{39}H_{47}N_2O_3P$: C, 75.21; H, 7.61; N, 4.50. Found: C, 75.18; H, 7.59; N, 4.53.

4-Hydroxycarbonylpropyl Chiral Imidazoindolephosphines 5; (3*R*,9a*S*)-2-{[4-(Hydroxycarbonylpropyl)phenyl]-3-(2-diphenylphosphino)phenyl}tetrahydro-1*H*-imidazo[1,5-*a*]indol-1-one (5a); Typical Procedure

To a solution of **4a** (421 mg, 0.7 mmol) in 1,4-dioxane (20 mL) was added aq 1 N NaOH (8 mL) at 0 °C. The reaction mixture was stirred at 25 °C for 10 h. The residual material was acidified with aq 5% HCl and extracted with Et_2O (3 ×). The combined extracts were dried (Na_2SO_4) and concentrated in vacuo. The resulting residue was chromatographed on silica gel (eluent: acetone/hexane = 1:2) to give colorless fine prisms; yield: 365 mg (89%).

[CAS Reg. No.: 338463-32-4]

Mp 112–115 °C; $[\alpha]_D^{21}$ –198.6 (*c* 1.0, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.7 (d, *J* = 7.9 Hz, 1 H), 7.36–7.15 (m, 20 H), 6.88–6.78 (m, 3 H), 4.34 (dd, *J* = 1.2, 9.8 Hz, 1 H), 3.48 (d, *J* = 16.5 Hz, 1 H), 3.23 (dd, *J* = 9.8, 16.5 Hz, 1 H), 2.46 (t, *J* = 7.2 Hz, 2 H), 2.23 (t, *J* = 7.2 Hz, 2 H), 1.78 (quin, *J* = 7.2 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 178.5, 174.2, 151.2–113.8 (C_{arom}, overlapped), 81.5 (d, $J_{C,P}$ = 25.8 Hz), 64.2, 34.3, 33.0, 31.6, 26.0.

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ = –19.6 (s).

MS (ESI-TOF): *m*/*z* = 619 $[M + Na]^+$.

(3*R*,9a*S*)-2-[4-(Hydroxycarbonylpropyl)phenyl]-3-{2-[di(*tert*-butyl)phosphino]phenyl}tetrahydro-1*H*-imidazo[1,5-*a*]indol-1-one (5b)

Starting from **4b** (285 mg, 0.5 mmol), **5b** was obtained as a white solid; yield: 202 mg (73%); mp 125–127 °C; $[\alpha]_D^{21}$ +28.8 (*c* 1.0, $CHCl_3$).

IR (ATR): 2962, 2360, 2341, 1735, 1510, 1365, 1232 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.34 (m, 1 H), 7.87 (m, 1 H), 7.66–7.47 (m, 6 H), 7.35–7.32 (m, 1 H), 7.17–6.96 (m, 3 H), 4.26 (dd, *J* = 1.0, 10.0 Hz, 1 H), 3.56 (d, *J* = 16.0 Hz, 1 H), 3.15 (dd, *J* = 10.0, 16.0 Hz, 1 H), 2.50 (t, *J* = 7.5 Hz, 2 H), 2.21 (t, *J* = 7.5 Hz, 2 H), 1.83 (quin, *J* = 7.5 Hz, 2 H), 1.44 (dd, *J* = 12.5, 17.5 Hz, 18 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 174.9, 173.8, 152.0, 144.6, 144.5, 138.2, 136.3, 135.4, 129.7, 129.0, 128.7, 127.6, 127.4, 125.3, 125.2, 124.9, 122.3, 121.2, 114.4, 114.2, 82.2 (d, $J_{C,P}$ = 35.0 Hz), 63.8 34.4, 33.2, 33.1 (d, $J_{C,P}$ = 7.3 Hz), 32.9, d, $J_{C,P}$ = 13.3 Hz), 31.3, 30.7 (d, $J_{C,P}$ = 14.4 Hz, 3 C), 30.6 (d, $J_{C,P}$ = 14.4 Hz, 3 C), 26.3.

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ = 7.4 (s).

Anal. Calcd for $C_{34}H_{41}N_2O_3P$: C, 73.36; H, 7.42; N, 5.03. Found: C, 73.66; H, 7.64; N, 4.96.

(3*R*,9a*S*)-2-[4-(Hydroxycarbonylpropyl)phenyl]-3-[2-(dicyclohexylphosphino)phenyl]tetrahydro-1*H*-imidazo[1,5-*a*]indol-1-one (5c)

Starting from **4c** (311 mg, 0.5 mmol), **5c** was obtained as a white solid; yield: 258 mg (85%); mp 121–123 °C; $[\alpha]_D^{21}$ +43.2 (*c* 0.9, $CHCl_3$).

IR (ATR): 3110, 2921, 1720 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 7.3 Hz, 1 H), 7.65 (m, 1 H), 7.54 (d, *J* = 7.2 Hz, 1 H), 7.35–7.31 (m, 4 H), 7.25–7.17 (m, 3 H), 7.00–6.95 (m, 2 H), 4.46 (d, *J* = 10.0 Hz, 1 H), 3.58 (d, *J* = 14.7 Hz, 1 H), 3.23 (dd, *J* = 10.0, 14.7 Hz, 1 H), 2.52 (t, *J* = 6.7 Hz, 2 H), 2.26 (t, *J* = 7.4 Hz, 2 H), 2.16–2.01 (m, 4 H), 1.83 (quin, *J* = 7.4 Hz, 2 H), 1.73–1.39 (m, 8 H), 1.34–1.10 (m, 12 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 178.8, 174.6, 152.1, 144.4 (d, $J_{C,P}$ = 21.7 Hz), 138.0, 135.2, 134.0, 129.5, 128.9, 128.7, 128.2, 127.7, 125.1, 125.0, 124.9, 122.3 121.0, 114.3, 114.2, 81.6 (d, $J_{C,P}$ = 31.0 Hz), 64.1, 35.8 (d, $J_{C,P}$ = 9.3 Hz), 35.3 (d, $J_{C,P}$ = 9.3 Hz), 34.3, 33.1, 31.5, 31.4, 30.9 (d, $J_{C,P}$ = 15.5 Hz), 29.7 (d, $J_{C,P}$ = 9.3 Hz), 29.6 (d, $J_{C,P}$ = 7.3 Hz), 27.2, 27.1 (d, $J_{C,P}$ = 20.7 Hz), 27.1 (d, $J_{C,P}$ = 18.3 Hz), 26.9 (d, $J_{C,P}$ = 3.0 Hz), 26.3, 26.1, 26.0, 22.6.

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ = –21.1 (s).

Anal. Calcd for $C_{38}H_{45}N_2O_3P$: C, 74.97; H, 7.45; N, 4.60. Found: C, 75.12; H, 7.40; N, 4.58.

PS-PEG Resin-Supported Chiral Imidazoindolephosphines (PS-PEG-L*); General Procedure

A Merrifield vessel was charged with PS-PEG-NH_2 [1.50 g, 0.40 mmol (total loading of amino residue)], **5** (0.80 mmol), EDCI·HCl (319 mg, 1.67 mmol), HOBt (300 mg, 2.20 mmol), and DMF (20.0 mL), and the reaction mixture was shaken on a wrist-action shaker at 25 °C for 24 h. Complete consumption of the primary amino residue of the resin was monitored by Kaiser test. The mixture was filtered and the resin was washed with DMF (5 × 20 mL) and EtOAc (5 × 20 mL). The resin was dried under reduced pressure to give **PS-PEG-L***.

PS-PEG-L*1

Yield: 1.72 g (99%); pale yellow resin.

^{31}P{^{1}H} NMR (SR-MAS NMR, 162 MHz): δ = –19.7.

PS-PEG-L*2

Yield: 1.68 g (98%); pale yellow resin.

^{31}P{^{1}H} NMR (SR-MAS NMR, 162 MHz) δ = 12.5.

PS-PEG-L*3

Yield: 1.70 g (98%); pale yellow resin.

^{31}P{^{1}H} NMR (MAS NMR, 162 MHz): δ = –19.0 (s).

Asymmetric Cross Coupling in Water; (*S*)-2,2′-Dimethyl-1,1′-binaphthyl (8aA); Typical Procedure

1-Iodo-2-methylnaphthalene (**6a**; 268 mg, 1 mmol), 1-(2-methylnaphthyl)boronic acid **7A** (930 mg, 5 mmol), **PS-PEG-L*1** (430 mg, 0.1 mmol P), $PdCl_2(MeCN)_2$ (34 mg, 0.1 mmol), and TBAF (260 mg, 10 mmol) were suspended in H_2O (20 mL), and the reaction mixture was stirred at 80 °C for 24 h under N_2. After cooling down to r.t., the mixture was filtered and the resin beads were washed with H_2O (3 × 20 mL). The resin beads were eluted with supercritical CO_2 until complete extraction of soluble organic materials. The crude residue was chromatographed on silica gel to give **8aA** as a colorless hard oil. The ee value of the product was determined by HPLC using a chiral sta-

tionary phase column (Chiralpak OD-H); yield: 280 mg (99%; Table 2, entry 1).

[CAS Reg. No.: 32587-64-7]

Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 7.9 Hz, 2 H), 7.88 (d, *J* = 7.9 Hz, 2 H), 7.51 (d, *J* = 8.5 Hz, 2 H), 7.38–7.41 (m, 2 H), 7.19–7.23 (m, 2 H), 7.04 (d, *J* = 8.5 Hz, 2 H), 2.03 (s, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 135.1 (2 C), 134.3 (2 C), 132.8 (2 C), 132.2 (2 C), 128.7 (2 C), 127.9 (2 C), 127.4 (2 C), 126.1 (2 C), 125.6 (2 C), 124.9 (2 C), 20.2 (2 C).

MS (EI+): *m*/*z* = 282 (M^+), 267 ($M^+ - CH_3$), 252 ($M^+ - C_2H_6$).

Optical property was measured with a sample of 94% ee (Table 1, entry 9); $[\alpha]_D^{20}$ +32.5 (*c* 0.8, $CHCl_3$) for (*S*) of 94% ee.[11] The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [chiralcel OD-H (250 mm), eluent; *n*-hexane, flow rate; 0.5 mL/min, t_R (major) = 20.0 min; t_R (minor) = 24.2 min] to be 94% ee.

(*R*)-2-Methoxy-2′-methyl-1,1′-binaphthyl (8bA)

White solid; yield: 253 mg (85%); mp 119–120 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.5 Hz, 1 H), 7.88–7.86 (m, 3 H), 7.50 (d, *J* = 7.9 Hz, 1 H), 7.45 (d, *J* = 9.2 Hz, 1 H), 7.38–7.35 (m, 1 H), 7.33–7.30 (m, 1 H), 7.21–7.18 (m, 2 H), 7.12 (d, *J* = 7.9 Hz, 1 H), 6.98 (d, *J* = 8.5 Hz, 1 H), 3.75 (s, 3 H), 2.09 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.4, 135.0, 133.6, 133.2, 132.3, 132.1, 129.3, 129.2, 128.6, 128.0, 127.9, 127.8, 127.5, 126.5, 125.8, 125.7, 125.1, 124.7, 123.6, 113.8, 56.6, 20.3.

MS (EI+): *m*/*z* = 298 (M^+), 268 ($M^+ - CH_2O$).

$[\alpha]_D^{20}$ +22.3 (*c* 1.3, $CHCl_3$). The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [chiralpac AD-H (500 mm), eluent; *n*-hexane/*i*-PrOH = 100:1, flow rate; 0.5 mL/min, t_R (major) = 65.4 min; t_R (minor) = 89.8 min] to be 92% ee. The absolute configuration was determined by the sign of the specific rotation.[12]

(*R*)-2-Ethoxy-2′-methyl-1,1′-binaphthyl (8aC)

Colorless needles; yield: 290 mg (93%); mp 71–72 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 9.2 Hz, 1 H), 7.87–7.84 (m, 3 H), 7.49 (d, *J* = 7.9 Hz, 1 H), 7.42 (d, *J* = 9.2 Hz, 1 H), 7.38–7.35 (m, 1 H), 7.33–7.30 (m, 1 H), 7.20–7.17 (m, 2 H), 7.13 (d, *J* = 8.5 Hz, 1 H), 6.99 (d, *J* = 8.5 Hz, 1 H), 4.10–3.99 (m, 2 H), 2.10 (s, 3 H), 1.05 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.8, 134.9, 133.8, 133.3, 132.5, 132.1, 129.2, 129.1, 128.6, 127.9, 127.8, 127.3, 126.4, 126.0, 125.7, 125.2, 124.6, 123.6, 122.9, 115.6, 64.9, 20.3, 15.0.

MS (EI+): *m*/*z* = 312 (M^+), 268 ($M^+ - C_2H_4O$).

$[\alpha]_D^{20}$ –5.4 (c 1.63, $CHCl_3$) for 92% ee. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [chiralpac AD-H (500 mm), eluent; *n*-hexane/*i*-PrOH = 95:5, flow rate; 0.5 mL/min, t_R (major) = 42.3 min; t_R (minor) = 54.9 min] to be 92% ee. The absolute configuration was determined by the sign of the specific rotation.

(*S*)-2-Ethoxy-2′-methoxy-1,1′-binaphthyl (8bC)

Colorless oil; yield: 294 mg (90%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 9.3 Hz, 1 H), 7.87–7.83 (m, 3 H), 7.48 (d, *J* = 8.3 Hz, 1 H), 7.39 (d, *J* = 8.8 Hz, 1 H), 7.36 (t, *J* = 7.3 Hz, 1 H), 7.31 (t, *J* = 7.6 Hz, 1 H), 7.19–7.16 (m, 2 H), 7.13 (d, *J* = 8.3 Hz, 1 H), 7.00 (d, *J* = 8.3 Hz, 1 H), 4.36 (q, *J* = 5.9 Hz, 2 H), 2.11 (s, 3 H), 0.90 (d, *J* = 5.9 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.2, 135.0, 133.9, 133.3, 132.6, 132.0, 129.3, 129.0, 128.6, 127.8, 127.7, 127.2, 126.3, 126.1, 125.6, 125.3, 124.5, 124.1, 123.7, 117.7, 71.7, 22.4, 22.3, 20.3.

MS (EI+): *m*/*z* = 328 (M^+).

$[\alpha]_D^{20}$ +50.1 (*c* 0.9, $CHCl_3$) for 90% ee. The absolute configuration was determined by the sign of the specific rotation.[13]

Methyl (*R*)-2′-Methyl-1,1′-binaphthyl-2-carboxylate (8dA)

[CAS Reg. No.: 113567-20-7]

Colorless prisms; yield: 200 mg (61%); mp 197–198 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00–7.86 (m, 4 H), 7.50 (d, *J* = 9.3 Hz, 1 H), 7.45 (d, *J* = 7.3 Hz, 1 H), 7.38–6.10 (m, 6 H), 3.73 (s, 3 H), 2.09 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.3, 154.4, 134.9, 133.6, 133.2, 132.3, 132.1, 129.3, 129.2, 128.6, 128.5, 127.9, 127.5, 127.4, 126.5, 125.8, 125.0, 124.7, 123.6, 122.0, 113.8, 56.6, 20.3.

MS (EI+): *m*/*z* = 326 (M^+).

$[\alpha]_D^{20}$ –53.2 (*c* 0.902, $CHCl_3$) for 88% ee. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [chiralpac AD-H (500 mm), eluent; *n*-hexane/*i*-PrOH = 95:5, flow rate; 0.5 mL/min, t_R (major) = 70.9 min; t_R (minor) = 77.9 min] to be 88% ee. The absolute configuration was determined by the sign of the specific rotation.[14]

2-Methyl-1-*o*-tolylnaphthalene (10aA)

[CAS Reg. No.: 93870-58-7]

Colorless oil; yield: 223 mg (96%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.5 Hz, 1 H), 7.77 (d, *J* = 8.5 Hz, 1 H), 7.41 (d, *J* = 8.5 Hz, 1 H), 7.39–7.22 (m, 6 H), 7.11 (d, *J* = 8.5 Hz, 1 H), 2.16 (s, 3 H), 1.91 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.2, 137.5, 136.8, 133.1, 132.5, 132.0, 130.0, 129.9, 128.6, 127.8, 127.4, 127.1, 125.9, 125.8, 125.7, 124.7, 20.3, 19.5.

MS (EI+): *m*/*z* = 232 (M^+).

$[\alpha]_D^{20}$ –92.7 (*c* 1.3, $CHCl_3$) for 92% ee. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [chiralcel OD-H (250 mm), eluent; *n*-hexane, flow rate; 0.5 mL/min, t_R (major) = 25.4 min; t_R (minor) = 28.1 min] to be 92% ee.

3-Methyl-4-(2-methylnaphthalen-1-yl)benzonitrile (10bA)

Colorless oil; yield: 229 mg (89%).

IR (ATR): 3122, 2965, 1511, 1220 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.5 Hz, 1 H), 7.82 (d, *J* = 8.5 Hz, 1 H), 7.67 (s, 1 H), 7.61 (m, 1 H), 7.44–7.41 (m, 2 H), 7.35–7.32 (m, 1 H), 7.24 (d, *J* = 8.5 Hz, 1 H), 7.09 (m, 1 H), 2.13 (s, 3 H), 1.95 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.7, 138.7, 135.4, 133.5, 132.7, 132.0, 131.7, 131.0, 129.8, 128.5, 128.1, 128.0, 126.4, 125.1, 124.9, 119.1, 111.4, 20.2, 19.3.

MS (EI+): *m*/*z* = 257 (M^+).

HRMS (EI+): *m*/*z* $[M]^+$ calcd for $C_{19}H_{15}N$: 257.1205; found: 257.1196.

$[\alpha]_D^{20}$ –52.3 (*c* 0.8, $CHCl_3$) for 92% ee. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [chiralcel OD-H (250 mm), eluent; *n*-hexane/*i*-PrOH = 98:2, flow rate; 0.5 mL/min, t_R (major) = 19.6 min; t_R (minor) = 24.4 min] to be 92% ee.

Methyl 3-Methyl-4-(2-methylnaphthalen-1-yl)benzoate (10cA)

White solid; yield: 363 mg (93%); mp 121–122 °C.

IR (ATR): 2931, 2977, 1691, 1511, 1420 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.94–7.84 (m, 3 H), 7.56 (d, *J* = 8.5 Hz, 1 H), 7.40 (d, *J* = 9.2 Hz, 1 H), 7.35–7.30 (m, 2 H), 7.22–7.13 (m, 2 H), 4.02 (s, 3 H), 2.19 (s, 3 H), 1.54 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.3, 153.7, 152.8, 134.3, 129.9, 129.4, 129.0, 127.8, 126.1, 125.8, 125.5, 123.9, 123.7, 121.9, 121.7, 118.1, 117.4, 55.8, 22.4, 20.3.

MS (EI+): *m*/*z* = 290 (M^+).

HRMS (EI+): *m*/*z* $[M]^+$ calcd for $C_{20}H_{18}O_2$: 290.1307; found: 290.1332.

$[\alpha]_D^{20}$ +52.6 (*c* 0.9, $CHCl_3$) for 94% ee. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [chiralcel AD-H (250 mm), eluent; *n*-hexane/*i*-PrOH = 98:2, flow rate; 0.5 mL/min, t_R (major) = 13.4 min; t_R (minor) = 11.8 min] to be 92% ee.

(*R*)-2-Methyl-1-(2-nitrophenyl)naphthalene (10dA)

White solid; yield: 252 mg (96%); mp 131–132 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.13 (m, 1 H), 7.84 (d, *J* = 7.9 Hz, 1 H), 7.80 (d, *J* = 7.9 Hz, 1 H), 7.74–7.71 (m, 1 H), 7.69–7.61 (m, 1 H), 7.41–7.25 (m, 4 H), 7.13 (d, *J* = 7.9 Hz, 1 H), 2.19 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 135.1, 134.7, 133.3, 133.0, 132.9, 132.1, 131.8, 128.6, 128.4, 128.2, 128.1, 128.0, 126.3, 125.0, 127.8, 124.4, 20.5.

MS (EI+): *m*/*z* = 263 (M^+).

$[\alpha]_D^{20}$ –101.0 (*c* 0.8, $CHCl_3$) for (*R*) of 92% ee {Lit.[15] $[\alpha]_D^{25}$ –95.0 (*c* 1.0, THF) for (*R*)}. The enantiomeric excess was determined by HPLC analysis using a chiral stationary phase column [chiralcel AD-H (250 mm), eluent; *n*-hexane, flow rate; 0.5 mL/min, t_R (major) = 35.9 min; t_R (minor) = 42.7 min] to be 92% ee. The absolute configuration was determined by the sign of the specific rotation.

Diethyl (*S*)-2′-Methoxy-1,1′-binaphthyl-2-ylphosphonate (12)

[CAS Reg. No.: 919491-25-1]

Colorless needles; yield: 295 mg (70%); mp 124–125 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.22 (m, 1 H), 8.01 (m, 2 H), 7.99 (d, *J* = 8.0 Hz, 1 H), 7.85 (d, *J* = 8.1 Hz, 1 H), 7.52 (m, 1 H), 7.45 (d, *J* = 9.0 Hz, 1 H), 7.28 (m, 3 H), 7.16 (m, 1 H), 6.87 (d, *J* = 8.4 Hz, 1 H), 3.77 (s, 3 H), 3.68 (m, 2 H), 3.56 (m, 2 H), 0.98 (t, *J* = 7.1 Hz, 3 H), 0.77 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.0, 140.5 (d, $J_{C,P}$ = 9.0 Hz), 134.8 (d, $J_{C,P}$ = 2.6 Hz), 133.8, 132.9 (d, $J_{C,P}$ = 16.3 Hz), 129.9, 128.9 (d, $J_{C,P}$ = 9.8 Hz), 128.6, 128.2, 128.0, 127.9, 127.6 (d, $J_{C,P}$ = 14.4 Hz), 127.3, 127.0 (d, $J_{C,P}$ = 18.1 Hz), 126.9, 126.4, 126.0, 123.5, 121.1 (d, $J_{C,P}$ = 5.5 Hz), 113.0, 61.8 (d, $J_{C,P}$ = 5.7 Hz), 61.7 (d, $J_{C,P}$ = 6.0 Hz), 56.2, 15.9 (d, $J_{C,P}$ = 6.5 Hz), 15.5 (d, $J_{C,P}$ = 6.9 Hz).

$^{31}P\{^1H\}$ NMR = 17.0.

$[\alpha]_D^{20}$ –19.5 (*c* 1.15, $CHCl_3$) for 86% ee (Lit.[16] $[\alpha]_D$+21.2 (*c* 1.015, $CHCl_3$) for (*R*) of >99% ee). The absolute configuration was determined by the sign of the specific rotation.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1589407. Included are NMR charts, HPLC data, and the CIF file of **L*1-PdCl$_2$**.

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