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An Efficient Asymmetric Cross-Coupling Reaction in Aqueous Media Mediated by Chiral Chelating Mono Phosphane Atropisomeric Biaryl Ligand

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Abstract: The enantiomerically pure ligand *BisNap*-Phos was obtained in a straightforward sequence of reactions beginning with inexpensive starting materials under the readily affordable conditions in high overall yield. An asymmetric *BisNap*-Phos-palladium complex-catalyzed Suzuki–Miyaura coupling leading to axially chiral biaryl compounds was described. The reactions were carried out under mild conditions in aqueous and organic media. A series of atropisomeric biaryls were synthesized with excellent yields and high enantioselectivities (up to 86% ee). The methodology provides an efficient and practical strategy for the synthesis of novel multifunctionalized axially chiral biaryl compounds under mild environmentally friendly and easily affordable conditions.

Keywords: Suzuki–Miyaura cross-coupling; atropisomeric compounds; chiral phosphines; biaryl ligands; C,P-complexation; asymmetric catalysis

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1. Introduction

The stereoselective formation of C-C bonds using chiral catalysts is one of the most common methods for the synthesis of optically pure compounds [1]. Among them, the sterically demanding Suzuki–Miyaura coupling reaction has been identified as one of the most powerful transformations in synthetic organic chemistry, especially in the synthesis of chiral, atropisomeric biaryls [2–6]. Some of the *ortho*-substituted biaryl compounds are biologically active [7–9], and many of them are efficient chiral ligand in homogenous catalysis [1,10–13]. Phosphine-based complexes with transition metals are the most common catalysts for the cross-coupling reactions [14–17]. The catalytic effectiveness of these ligands depends on the basicity of the phosphorus atom and the steric hindrance created by its substituent [18]. Over the past few years, many research groups have designed a series of new chiral ligands with C-P type complexation, e.g., S-Phos [16], which were extremely efficient even in demanding cases of cross-couplings in which sterically hindered substrates and inactivated aryl chlorides were coupled at an ambient temperature. Among the best ligands based on axially chiral biaryls motif are such monophosphines as MOP and MAP [17–23], which show great potential in asymmetric couplings. We have already reported a new straightforward approach to the synthesis of the new P,C-ligands *Nap*-Phos and *Sym*-Phos [17,23]. Their palladium complexes were highly active in such cross-couplings as Heck and Suzuki–Miyaura reactions. Cross-coupling reactions with *Sym*-Phos occur in mild conditions and run under aqueous or organic media [23].

Ligands for demanding couplings are shown in Figure 1.

Based on our experience in the field, we have synthesized sterically hindered and enantiomerically pure phosphine ligand *BisNap*-Phos (**10**) as an analogue of Sym-Phos [24].

Herein, we would like to present the use of chiral palladium complexes of *BisNap*-Phos as a catalyst in asymmetric Suzuki–Miyaura cross-coupling reactions run in environmentally friendly conditions.

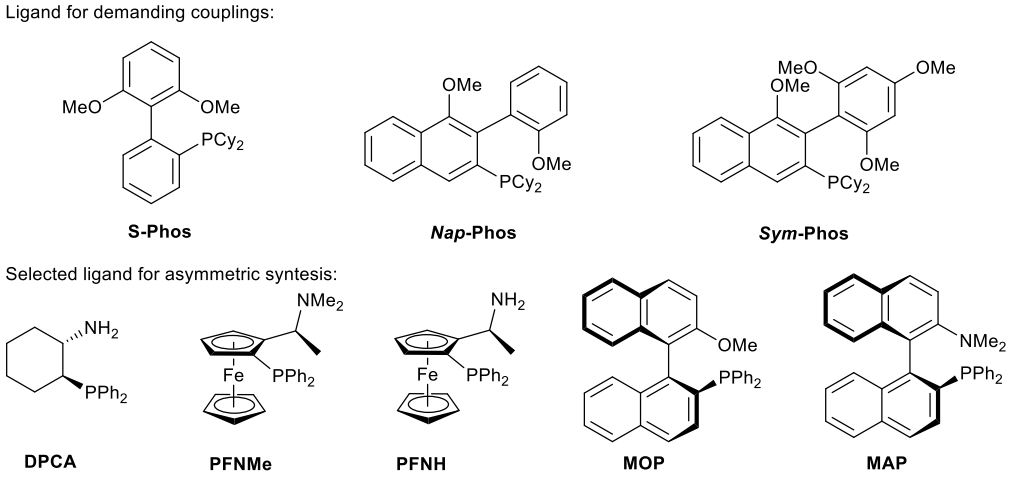
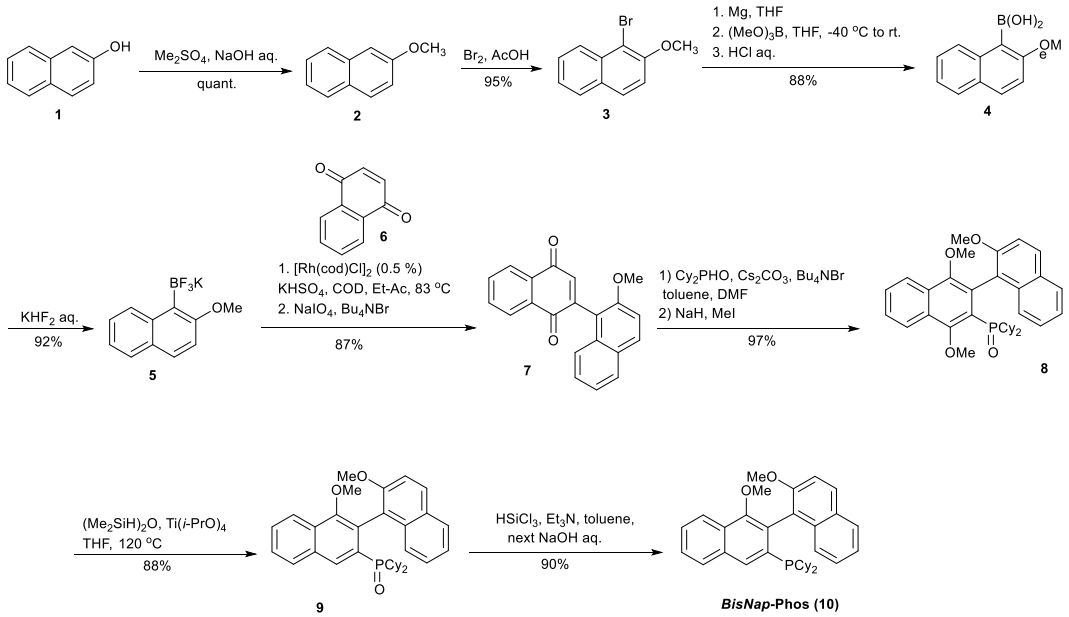


Figure 1. Highly efficient C,P-ligands and selected chiral ligands.

2. Results and Discussion

Racemic *BisNap*-Phos (**10**) was prepared in good overall yield by a multi-step procedure starting from 2-naphtol (Scheme 1).



Scheme 1. Synthesis of *BisNap*-Phos (**10**).

The synthesis of *BisNap*-Phos was designed similarly to the synthesis of *Sym*-Phos [23], starting from the readily available substrates naphthalen-2-ol, naphthoquinone, and dicyclohexylphosphine oxide. Enantiopure *BisNap*-Phos (**(*Sa*)-10** and **(*Ra*)-10**) were prepared after fractional crystallization of 1:1 complex of rac-*BisNap*-Phos oxide with TADDOL from the mixture ethanol/chloroform, followed by the reduction of corresponding enantiomer in mild conditions and without racemization by treatment with a mixture of $HSiCl_3/Et_3N$ in toluene. The absolute configuration of *BisNap*-Phos (**10**) was assigned by an X-ray analysis (Figure 2a, CCDC 2222975) of its palladium complex **12** with the second chiral nonracemic ligand (*S*)-*N*,*N*-dimethylnaphthylethylamine (**11**).

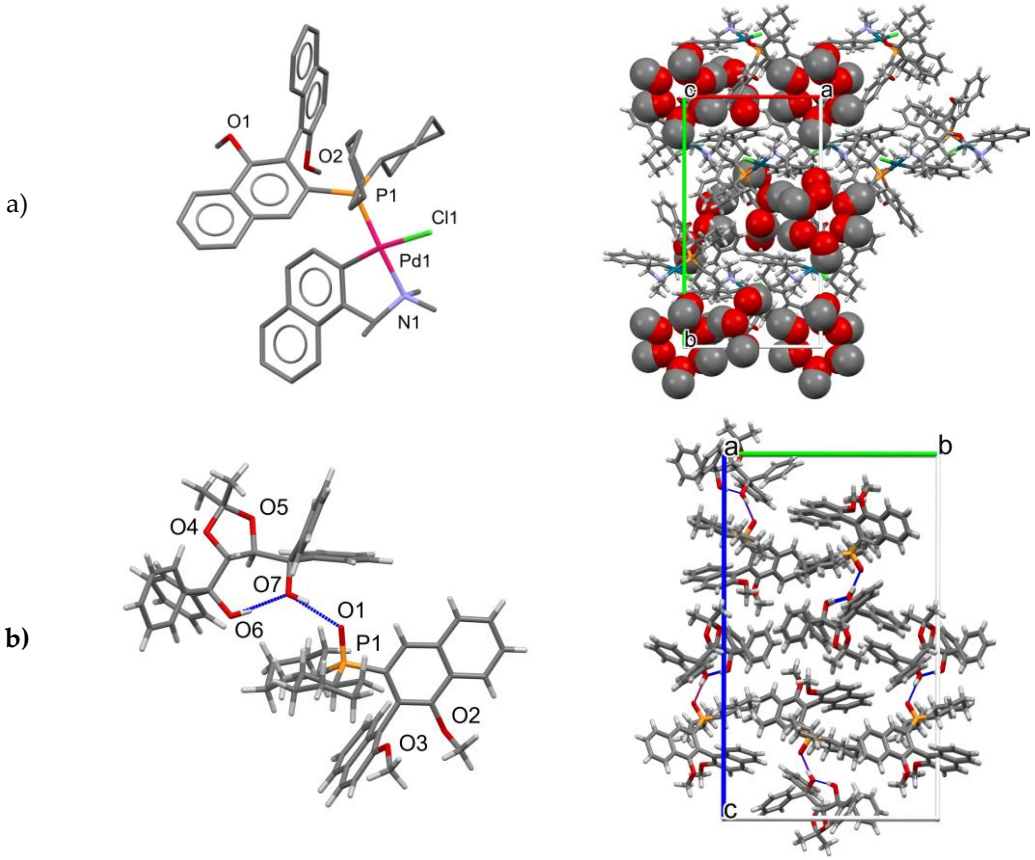
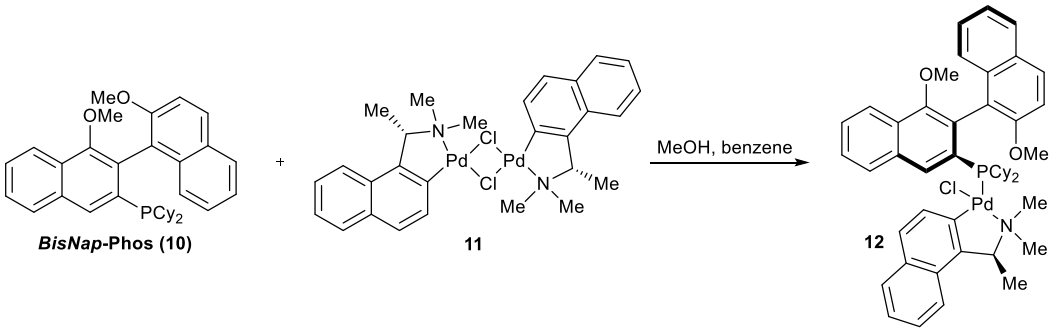


Figure 2. Molecular structure and crystal packing (**a**) of chiral palladium complex of *BisNap*-Phos and (**b**) of a cocrystal formed by compound **9** with TADDOL.

The compound **12** was obtained as presented in Scheme 2.



Scheme 2. Synthesis of chiral palladium complex of (***Sa***)-*BisNap*-Phos.

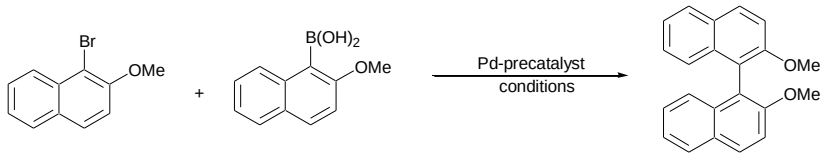
The coordination units of the studied Pd complex are hydrophobic outside, with the exception of the Cl atom. The strongest interactions between them are weak C–H . . . π contacts between phenyl rings. Such packing most probably facilitates the homochiral crystal formation due to the proper steric orientation of aromatic rings in the (*S,Sa)*- isomer. Because in the crystal net, there are still significantly large empty voids, which are stabilized by filling with hydrogen-bonded methanol and water molecules. The solvent molecules are located in special cages between the host molecules. The only contact with the coordination unit is with the hydrophilic Cl atom acting as a hydrogen bond acceptor from methanol molecule.

The diffraction experiment also confirmed the molecular structure of compound **(*Ra*)-9** (Figure 2b, CCDC No 2232483). Its stereochemistry was established owing to the presence of a TADDOL molecule with a known absolute configuration in this crystal. Both coformers

contact via O–H . . . O interaction, whereas the second TADDOL's OH group forms an intramolecular hydrogen bond.

Having the enantiopure ligand, we decided to investigate the catalytic activity of the palladium complex of *BisNap*-Phos and compare it with other ligands' complexes in the benchmark Suzuki–Miyaura coupling of 1-bromo-2-methoxy naphthalene **3** with 2-methoxynaphthalene-1-boronic acid **4**. We have reported previously [23] that the cross-coupling reactions could be successfully accomplished in water with the addition of small amounts of readily available surfactants, e.g., SDS and Brij, at low reaction temperature. Such environmentally friendly conditions were also applied in reactions mediated by *BisNap*-Phos-based catalysts. In the preliminary studies, we used the racemic and achiral ligands, since the chemical yields of the benchmark reactions, catalyzed by complexes of racemic and enantiomerically pure ligands, are known to be the same. As presented in Table 1, the best results (76% yield) were obtained when *BisNap*-Phos and *Sym*-Phos were used in the amount 4 mol% in a reaction run in an aqueous medium with the palladium precatalyst loading 2 mol% at 60 °C. In those benchmark experiments, the utilization of our ligands *BisNap*-Phos and *Sym*-Phos was even more efficient than the utilization of another ligand famous for its efficiency: S-Phos [16].

Table 1. Synthesis of 2,2-dimethoxy-1,1′-binaphthyl (**13**) mediated by different ligand complexes [a].



3 **4** **13**

Entry	Ligand (4 mol%)	T, [°C]	t, [h]	Yield [b], [%]
1	S-Phos	30	5	23
2	S-Phos	60	5	63
3	S-Phos	90	5	37
4	S-Phos	90	12	28
5	$PhPCy_2$	30	5	-
6	$PhPCy_2$	90	5	5
7	$PhPCy_2$	60	19	-
8	*rac-BisNap*-Phos	60	19	76 (70)
9	*Sym*-Phos	60	19	76

[a] Reaction conditions: **2** (0.5 mmol), **3** (0.7 mmol), K_2CO_3 (1.5 mmol), 0.3% SDS in H_2O (7.5 mL), $Pd(OAc)_2$ (2 %mol), L/Pd = 2, [b] yield by GC-MS, yield of isolated products presented in brackets.

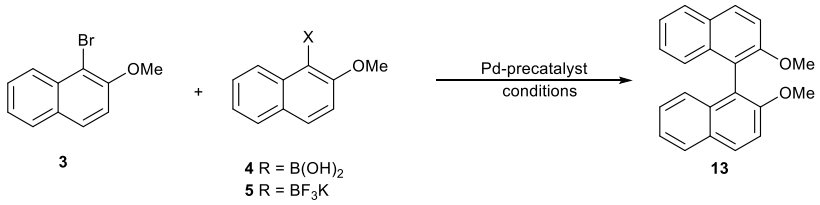
In the next step, the use of different palladium precatalysts was studied in the reaction of arylboronic acid **4** or potassium trifluorobarate **5** (Table 2). Higher yields (up to 97%) were obtained when boronic acid was used. As can be seen, the *Sym*-Phos ligand was more reactive in the reaction with potassium trifluorobarate **5** (Table 2, entry 6). After careful optimization of the palladium catalyst, *BisNap*-Phos/$PdCl_2(C_6H_5CN)_2$ was identified as the best complex (Table 2, entry 1).

In addition, the influence of the microwave (MW) radiation on the tested Suzuki–Miyaura reaction was examined. Benchmark reactions were conducted in toluene as a solvent at 160 °C with a short reaction time of up to 30 min. 2,2′-dimethoxy-1,1′-binaphthyl (**13**) was obtained in excellent yields (Table 3). Again, the use of *BisNap*-Phos/$PdCl_2(C_6H_5CN)_2$ as a catalyst led to the best yield of the product even without an argon atmosphere. The use of an increased amount of boronic acid (1.5 eq.) raised the overall yield up to 97% (Table 3, entry 5). All MW reactions were conducted in high-pressure-sealed vessels.

The advantages of *BisNap*-Phos were next demonstrated in the MW-promoted Suzuki–Miyaura coupling of boronic acid **4** and 1-bromo-2-methyl naphthalene (**14**). For this purpose, we used the $Pd(OAc)_2$—the metal source giving access to a precatalyst which is activated at lower temperature. The reaction with the *BisNap*-Phos/$Pd(OAc)_2$ catalyst

at 150 °C after 15–20 min. led to 2-methoxy-2′-methyl-1,1′-binaphthyl (**15**) in good yields (Table 4). In the case of the same reaction conducted in an oil bath without MW, we obtained product **15** with higher yield (76%) when prolonged to a 24 h reaction duration (Table 4, entry 4). Unfortunately, further extension of the reaction duration was not beneficial, because of the decomposition of a catalyst formed with *BisNap*-Phos and $Pd(OAc)_2$ to create palladium black.

Table 2. Effect of the precatalyst used in the synthesis of **13** [a].

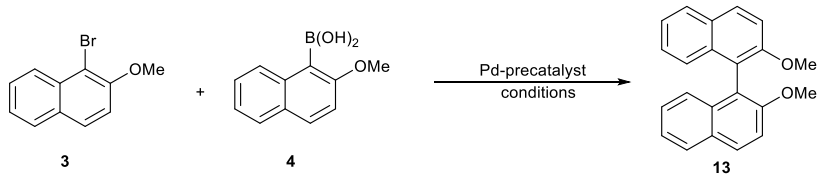


3 **4** R = $B(OH)_2$, **5** R = BF_3K **13**

Entry	Substrate	Catalyst (2 mol%)	Ligand (4 mol%)	t, [h]	Yield [b], [%]
1	**4**	$Pd(C_6H_5CN)_2Cl_2$	*rac-BisNap*-Phos	18	97 (86) [c]
2	**5**	$Pd(C_6H_5CN)_2Cl_2$	*rac-BisNap*-Phos	18	(56)
3	**4**	$Pd(OAc)_2$	*rac-BisNap*-Phos	19	76 (70)
4	**5**	$PdCl_2$	*rac-BisNap*-Phos	15	56 (50)
5	**5**	$Pd(CH_3CN)_2ClBF_4$	*Sym*-Phos	16	29 (28) [c]
6	**5**	$Pd(OAc)_2$	*Sym*-Phos	16	93 (88) [c]

[a] Reaction conditions: **3** (1 equiv.), **4** or **5** (1.2 equiv.), T = 60 °C, K_2CO_3 (3 equiv.), 0.3% SDS in H_2O, [b] yield determined by GC-MS analysis, yield of isolated products are presented in brackets, [c] Na_2CO_3 used as a base (3 equiv.).

Table 3. Synthesis of **13** under microwave conditions [a].



3 **4** **13**

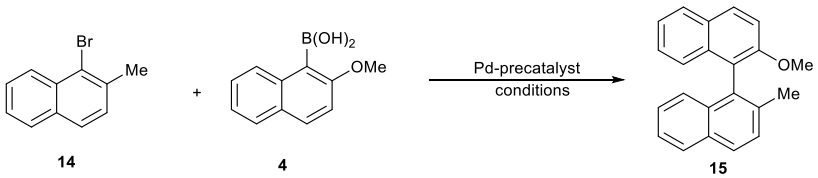
Entry	Catalyst (2 mol%)	Ligand (4 mol%)	t, [min]	T, [°C]	Yield [b], [%]
1	$Pd(OAc)_2$	S-Phos	15	160	Trace
2	$Pd_2(dba)_3$	*rac-BisNap*-Phos	30	160	61
3	$Pd(C_6H_5CN)_2Cl_2$	*rac-BisNap*-Phos	30	160	79
4	$Pd(C_6H_5CN)_2Cl_2$	*rac-BisNap*-Phos	15	160	86 [c]
5	$Pd(C_6H_5CN)_2Cl_2$	*rac-BisNap*-Phos	30	160	97 [c,d]
6	$Pd(C_6H_5CH_2CN)_2Cl_2$	*rac-BisNap*-Phos	30	160	76 [c,d]

[a] Reaction conditions: the reaction was carried out under an inert atmosphere, **3** (1 equiv.), **4** (1.2 equiv.), toluene, K_3PO_4 (3 equiv.), [b] yield of isolated product, [c] 2-methoxynapthylboronic acid (1.5 equiv.), [d] no protection by Ar atmosphere was applied.

Next, the optimization of the solvent for the synthesis of biaryl **15** in MW conditions was performed. As can be seen in Table 5, among tested aprotic solvents, the toluene was the best for this reaction and allowed it to achieve a 77% yield of the target product. In the reactions run in other tested solvents, a formation of palladium black was observed, which could be rationalized by the competitive reduction of the catalyst by the solvent used.

The usage of protic ethanol allowed a considerable decrease in the temperature of the MW-assisted couplings to 100 °C, with only slight yield deterioration, resulting in 54% (Table 6, entry 2).

Table 4. Synthesis of 2-methoxy-2′-methyl-1,1′-binaphthyl (**15**) under microwave conditions [a].



14 + **4** → **15**

Entry	Catalyst (2 mol%)	Ligand (4 mol%)	t, [min.]	Yield [b], [%]
1	$Pd(OAc)_2$	S-Phos	15	52
2	$Pd(OAc)_2$	*rac-BisNap*-SPhos	15	61
3	$Pd(OAc)_2$	*rac-BisNap*-SPhos	20	69
4	$Pd(OAc)_2$	*rac-BisNap*-SPhos	1440	76 [c]

[a] Reaction conditions: **14** (1 equiv.), **4** (1.2 equiv.), toluene, K_3PO_4 (3 equiv.), T = 150 °C. [b] yield of isolated product, [c] the reaction was carried out in an oil bath for 24 h.

Table 5. Effect of various solvents on the synthesis of **15** under microwave conditions [a].

Entry	Solvent	t, [min]	T, [°C]	Yield [b], [%]
1	dioxane	15	160	Trace
2	dioxane	25	160	60
3	toluene	15	150	61
4	toluene	20	150	77 (69) [c]
5	THF	15	100	27
6	acetone	15	150	Trace

[a] Reaction conditions: **14** (1 equiv.), **4** (1.2 equiv.), K_3PO_4 (3 equiv.), $Pd(OAc)_2$ (2 mol%), *rac-BisNap*-SPhos (4 mol%), [b] yield by GC-MS, [c] yield of isolated products presented in brackets.

Table 6. Synthesis of **15** in protic solvent under microwave conditions [a].

Entry	Base (3 equiv.)	Catalyst (2 %mol)	Ligand (4 %mol)	T, [°C]	Yield [b], [%]
1	K_2CO_3	$Pd(OAc)_2$	*rac-BisNap*-SPhos	100	52
2	K_2CO_3	$Pd(PhCH_2CN)_2Cl_2$	*rac-BisNap*-SPhos	100	54
3	Na_2CO_3	$Pd(OAc)_2$	*rac-BisNap*-SPhos	110	25
4	K_3PO_4	$Pd(OAc)_2$	*rac-BisNap*-SPhos	110	25

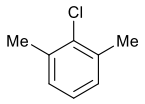
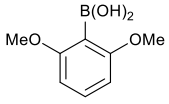
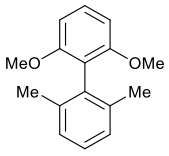
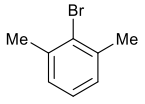
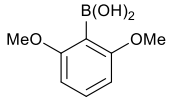
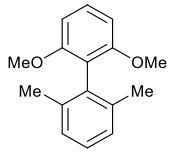
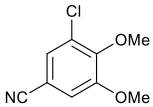
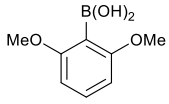
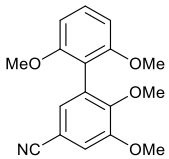
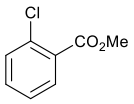
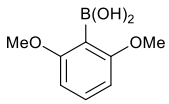
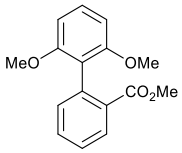
[a] Reaction conditions: **14** (1 equiv.), **4** (1.2 equiv.), ethanol, t = 20 min., [b] yield of isolated products.

Applying the optimized aqueous medium-mediated coupling reaction, as presented above, the synthesis of *ortho*-tetra and *ortho*-trisubstitued biaryls was carried out. The reactions of boronic acid **16** with different aryl halogens (**17-20**) led to obtaining the expected hindered biaryls with good yields of up to 87%, as presented in Table 7. The application of different halogens also influenced the reaction yields. As expected, the bromine derivatives were more reactive then their chloranalogues.

Having achieved an excellent procedure for the synthesis of racemic biaryls, we aimed to apply it to asymmetric Suzuki–Miyaura coupling leading to compound **15**. The efficiency of *BisNap*-Phos was compared with other commercially available chiral ligands. In the optimized conditions, (*S*)-*BisNap*-Phos was identified as the best ligand both in aqueous and non-aqueous media (Table 8). Its application allowed us to achieve an excellent yield and enantiomeric excess of binaphthyl **15** (up to 98% yield and 71% ee). The enantiomeric excess in all cases was determined by chiral HPLC. Notably, product **15** was obtained in two ways: by the reaction of bromide **14** with boronic acid **4**, and by the coupling of bromine **3** with boronic acid **24** with the same yield (98 %) and enantiomeric excess. We found that the application of the protective argon atmosphere and anhydrous conditions produce no benefits in comparison to the synthesis carried out without the protection in water. The proper selection of base used was also considered during the experiment design.

There is not clear rule allowing us to predict the best base and best solvent for a given reaction. Generally, some bases are associated with unipolar anhydrous solvents such as toluene (K_3PO_4), some with reactions conducted in an aqueous medium (Na_2CO_3, K_2CO_3), and some with polar aprotic solvents such as DMF and DME (Cs_2CO_3, CsF). Those empiric rules were used for the preliminary selection of the base. Nevertheless, our attempts to find confirmation of those assumptions did not bring unambiguous results.

Table 7. Synthesis of hindered *ortho*-substituted biaryls **21**–**23** in aqueous medium [a].

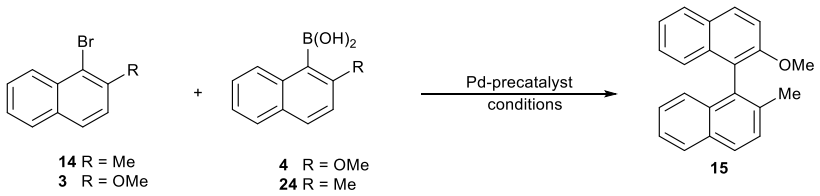
Entry	Ar-X (1 equiv.)	Ar-B(OH)$_2$ (1.5 equiv.)	Product	Yield [b], [%]
1	 **17**	 **16**	 **21**	40
2	 **18**	 **16**	 **21**	61
3	 **19**	 **16**	 **22**	56
4	 **20**	 **16**	 **23**	87 [c]

[a] Reaction conditions: 0.5 mol% $PdCl_2(C_6H_5CN)_2$, 1 mol% *rac-BisNa*p-Phos, 3 equiv. Na_2CO_3, 0.3% SDS in H_2O, t = 30 h, T = 60 °C; [b] isolated products yield, [c] 0.8 mol% $PdCl_2(C_6H_5CN)_2$, 1.9 mol% *rac-BisNap*-Phos, 3 equiv. Na_2CO_3, 0.3% SDS in H_2O, t = 30 h, T = 60 °C.

The coupling of bromine **14** and boronic acid **24** was studied next, which resulted in 2,2′-dimethyl-1,1′-binaphthyl **25**. The best yield (94%) of **25** was obtained using [Pd((*Ra*)-mop)$_2$]Cl_2 ligand, but the reaction with enantiopure (*Sa* or *Ra*)-*BisNap*-Phos ligand successfully led to product **25** with only slightly lower yields (up to 86%) and with the best enantioselecticity, up to 77% ee (Table 9). Again, the reactions run in aqueous media resulted in similar yields and stereoselectivities, as the reactions run under anhydrous and oxygen-free conditions.

(*Sa*)-*BisNap*-Phos was again determined to be the best ligand for the asymmetric synthesis of binaphthyl **13** in both aqueous and organic media (Table 10). Excellent yields were achieved in the reactions run both in anhydrous and in aqueous media, and higher enantiomeric excesses were achieved in reactions carried out in water. The utilization of potassium salt **5**, which is the obvious substitute for boronic acid **4**, was beneficial in the reactions run in aqueous media.

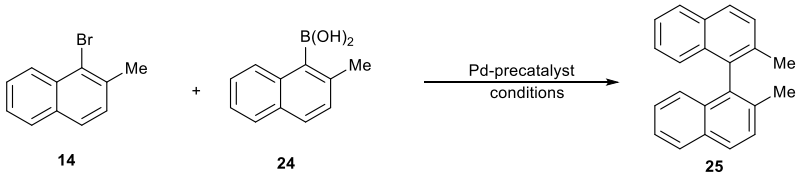
Table 8. Ligand activity in asymmetric synthesis of **15** [a].



Entry	Precatalyst	Solvent	Base	T [°C]	Yield [b], (ee), [%]
1	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	DME	Cs_2CO_3	80	73, (71 *S*)
2	[Pd(*R*)-binap]Cl_2	DME	Cs_2CO_3	80	Trace
3	[Pd(+)-diop]Cl_2	DME	Cs_2CO_3	80	Trace
4	[Pd((*R*)-mop)$_2$]Cl_2	DME	Cs_2CO_3	80	57 (56 *S*)
5	[Pd((*R*,*S*)-pfnme)$_2$]Cl_2	DME	Cs_2CO_3	80	14, (n/d)
6	[Pd((*R*,*S*)-pfnh)$_2$]Cl_2	DME	Cs_2CO_3	80	Trace
7	[Pd((*S*,*S*)-dpca)$_2$]Cl_2	DME	Cs_2CO_3	80	Trace
8	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	DME	CsF	80	88 (55 *S*)
9	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	0.3% SDS in H_2O	Na_2CO_3	60	98, (70 *S*)
10	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	0.3% SDS in H_2O	Na_2CO_3	60	98 (70 *S*) [c]
11	[Pd (*R*)-binap]Cl_2	DME	CsF	80	Trace
12	[Pd (*R*)-binap]Cl_2	Toluene	K_3PO_4	100	-
13	(*S*)-*BisNap*-Phos)$_2$ /$PdCl_2(C_6H_5CN)_2$	Toluene	K_3PO_4	150	98 (58 *S*)
14	[Pd(+)-diop]Cl_2	DME	CsF	80	Trace
15	(*R*)-PROPHOS /$PdCl_2(C_6H_5CN)_2$	DME	CsF	80	Trace
16	(+)-CHIRAPHOS /$PdCl_2(C_6H_5CN)_2$	DME	CsF	80	Trace

[a] Reaction conditions: **4** (1.2 equiv.), **14** (1 equiv.), $PdCl_2(C_6H_5CN)_2$ (2 mol%), Pd: P = 1: 2, base (3 equiv.), 16 h, [b] yield of isolated product, [c] **24** (1.2 equiv.), **3** (1 equiv.).

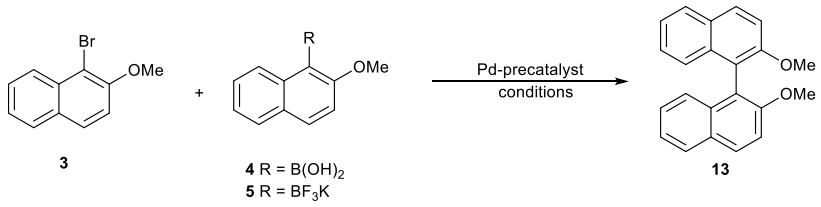
Table 9. Ligand activity in asymmetric synthesis of 2,2′-dimethyl-1,1′-binaphthyl (**25**) [a].



Entry	Precatalyst	Solvent	Base	T, [°C]	t, [h]	Yield [b], (ee), [%]
1	(*R*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	0.3% SDS in H_2O	Na_2CO_3	60	16	85 (77 S)
2	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	0.4% brij97 in H_2O	Na_2CO_3	60	16	84 (71 *R*)
3	[Pd(*R*)-binap]Cl_2	0.4% brij97 in H_2O	Na_2CO_3	60	16	Trace
4	[Pd((*R*,*S*)-pfnme)$_2$]Cl_2	0.4% brij97 in H_2O	Na_2CO_3	60	16	Trace
5	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	DME	CsF	65	144	86 (76 *R*)
6	[Pd(*R*)-binap]Cl_2	DME	CsF	65	144	15 (31 S)
7	[Pd(*R*)-binap]Cl_2	DME	K_3PO_4	100	16	Trace
8	[Pd((*R*,*S*)-pfnme)$_2$]Cl_2	DME	CsF	65	144	Trace [c]
9	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	DME	CsF	80	16	34 (n/d)
10	[Pd((*R*,*S*)-pfnh)$_2$]Cl_2	DME	CsF	80	16	-
11	[Pd((*R*)-mop)$_2$]Cl_2	DME	CsF	80	16	94 (60 *S*)
12	[Pd((*S*,*S*)-dpca)$_2$]Cl_2	DME	CsF	80	16	-

[a] Reaction conditions: **14** (1 equiv.), **24** (1.2 equiv.), $PdCl_2(C_6H_5CN)_2$ (2 mol%), ligand (4 mol% monophosphine or 2 mol% diphosphine), base (3 equiv.), catalysts were prepared in 0.25 mL THF; [b] isolated products yield, [c] $PdCl_2(C_6H_5CN)_2$ (3 mol%), ligand (6 mol%).

Table 10. Ligand activity in asymmetric synthesis of **13** [a].

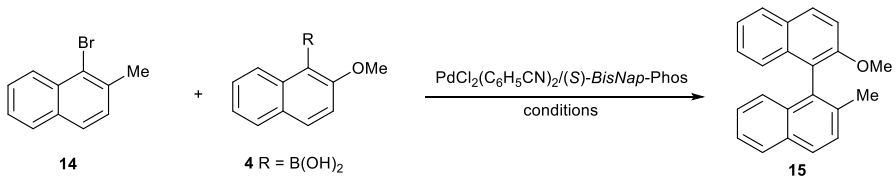


Entry	Precatalyst	Solvent	Base	T, [°C]	Yield [b], (ee), [%]
1	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	DME	Cs_2CO_3	80	67 (44 *R*)
2	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	0.4% brij 97 in H_2O	Na_2CO_3	60	62 (41 *R*) [c]
3	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	0.3% SDS in H_2O	Na_2CO_3	60	96 (47 *R*) [c]
4	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	0.3% SDS in H_2O	K_2CO_3	60	57 (36 *R*) [c]
5	[Pd(*R*)-binap]Cl_2	0.3% SDS in H_2O	Na_2CO_3	60	17 (24 *S*) [d]
6	[Pd(*R*)-binap]Cl_2	0.4% brij 97 in H_2O	Na_2CO_3	60	11 (22 *S*) [d]
7	[Pd(+)-diop]Cl_2	DME	Cs_2CO_3	80	-
8	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	Toluene	K_3PO_4	100	97 (36 *R*)
9	[Pd(*R*)-binap]Cl_2	Toluene	K_3PO_4	100	Trace

[a] Reaction conditions: **3** (1 equiv.), **4,5** (1.2 equiv.), $PdCl_2(C_6H_5CN)_2$ (2 mol%), Pd: P = 1: 2, base (3 equiv.), 24 h, [b] yield of isolated product, [c] **5** (1.2 equiv.) [d] 16 h.

The use of large amounts of expensive palladium catalysts is not acceptable in the case of practical synthesis. Thus, the optimization of the catalyst loading was performed to demonstrate the applicability of the approach. The reactions were caried out in grams scale. The reaction from 2.4 g of boronic acid **4** allowed to us reduce the quantity of palladium catalyst to 0.31 mol%, while the yields of the product and the stereoselectivity achieved were better than in small-scale syntheses (Table 11). A further decrease in the amount of palladium catalyst did not lead to an improved yield in the reaction. In all cases, enantiomeric excess reached 70% ee.

Table 11. Effect of catalyst amount in asymmetric synthesis of **15** [a].



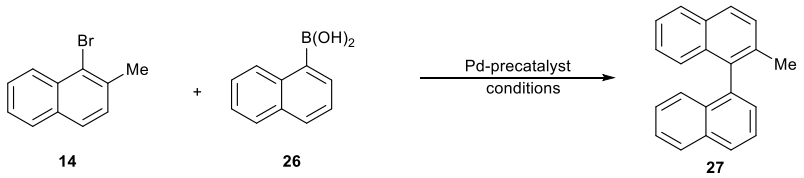
Entry	14	4	Pd, [mol%]	T, [h]	Yield [b], (ee), [%]
1	110 mg	152 mg	2.5	16	98 (70 *R*)
2	442 g	606 mg	1.25	24	88 (70 *R*)
3	884 g	1.2 g	0.62	24	93 (70 *R*)
4	1.8 g	2.4 g	0.31	32	98 (70 *R*)
5	3.5 g	4.8 g	0.15	24	84 (70 *R*)

[a] Reaction conditions: **14** (1 equiv.), **4** (1.2 equiv.), Na_2CO_3 (3 equiv.); $PdCl_2(C_6H_5CN)_2$: (*Sa*)-*BisNap*-Phos = 1:2; 60 °C; 0.3% SDS in H_2O, [b] yield of isolated product.

Next, the synthesis of chiral monosubstituted 1,1-binaphthyl was performed. 2-methyl-1,1′-binaphthyl (**27**) was obtained with an excellent yield, up to 100%, but with low enantioselectivity. Again, (*Sa*)-*BisNap*-Phos was the most efficient (37% ee, Table 12) ligand among other tested ligands. In this case, the reaction run in anhydrous conditions resulted in a higher yield of the product. This phenomenon could be rationalized by the fact that

the reactions leading to tris *ortho*-substituted biaryls are much less demanding, and the less active (i.e., more stable) bis-phosphine ligand complexes are already efficient enough to promote the reaction.

Table 12. Ligand activity in asymmetric synthesis of 2-methyl-1,1′-binaphthyl (**27**) [a].



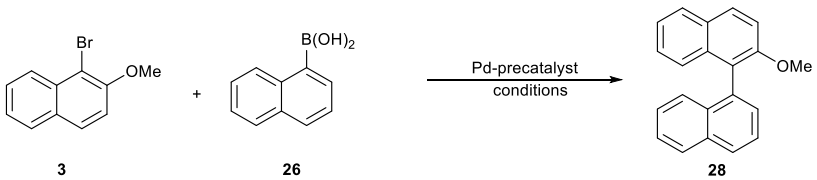
14 **26** **27**

Entry	Precatalyst	Solvent	Base	T, [°C]	Yield [b], (ee), [%]
1	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	DME	Cs_2CO_3	80	80 (37 *R*) [b]
2	[Pd(*R*)-binap]Cl_2	DME	Cs_2CO_3	80	100 [c] (11 *S*) [b]
3	[Pd(+)-diop]Cl_2	DME	Cs_2CO_3	80	-
4	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	0.4% brij97 in H_2O	Na_2CO_3	60	92 (n/d)
5	[Pd(*R*)-binap]Cl_2	0.4% brij97 in H_2O	Na_2CO_3	60	60 (n/d)

[a] Reaction conditions: **14** (1 equiv.), **26** (1.2 equiv.), $PdCl_2(C_6H_5CN)_2$ (2 mol%), ligand (4 mol% of *BisNap*-Phos or 2 mol% of diphosphines), base (3 equiv.), 16 h, [b] yield of isolated product, [c] conversion of **14**.

In the synthesis of methoxy substituted 1,1′-binaphthyl, the utilization of the [Pd(*R*)-binap]Cl_2 complex allowed it to achieve a higher yield, as well as stereoselectivity in the reaction run under anhydrous conditions (Table 13). Again, in the case of a less demanding synthesis such as this, the more stable bisphosphine-based catalyst allowed us to achieve an excellent yield of the reaction. At the same time, BINAP, as it is known, assures a great level of stereodifferentiation, which impacts the stereoselectivity of the reaction.

Table 13. Ligand activity in asymmetric synthesis of 2-methoxy-1,1′-binaphthyl (**28**) [a].



3 **26** **28**

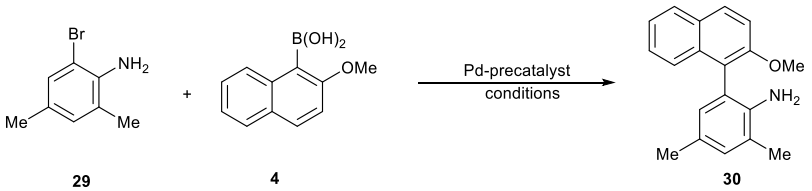
Entry	Precatalyst	Solvent	Base	T, [°C]	Yield [b], (ee), [%]
1	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	0.4% brij97 in H_2O	Na_2CO_3	60	92 (5 *S*) [c]
2	[Pd(*R*)-binap]Cl_2	0.4% brij97 in H_2O	Na_2CO_3	60	71 (7 *R*) [c]
3	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	DME	Cs_2CO_3	80	96 (6 *S*)
4	[Pd(*R*)-binap]Cl_2	DME	Cs_2CO_3	80	99 (43 *R*)
5	[Pd(+)-diop]Cl_2	DME	Cs_2CO_3	80	trace
6	[Pd(*R*)-binap]Cl_2	DME	Cs_2CO_3, $AgBF_4$ (6 mol%)	80	>99 (40 *R*)
7	[Pd(*R*)-binap]Cl_2	DME	Cs_2CO_3, Ag_3PO_4 (4 mol%)	80	99 (34 *R*)
8	[Pd(*R*)-binap]Cl_2	DME	Cs_2CO_3, Ag_3PO_4 (100 mol%)	80	48 (29 *R*)

[a] Reaction conditions: **2** (1 equiv.), **18** (1.2 equiv.), $PdCl_2(C_6H_5CN)_2$ (2 mol%), ligand (4 mol% of *BisNap*-Phos or 2 mol% of diphosphines), base (3 equiv.), 4 h, [b] yield of isolated product, [c] 16 h.

In the case of the highly coordinating substrate **29**, possessing an unprotected amino group, poor enantioselectivity was observed in the asymmetric synthesis leading to

product **30**, both in aqueous and anhydrous media. It was confirmed in the cases of utilization of all tested ligands (Table 14).

Table 14. Ligand activity in asymmetric synthesis of 1-(2-amino-3,5-dimethylphenyl)-2-methoxynaphthalene (**30**) [a].



29 **4** **30**

Entry	$PdCl_2(C_6H_5CN)_2$, Ligand/ Catalyst	Solvent	Base	T, [°C]	Yield [b], (ee), [%]
1	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	DME	Cs_2CO_3	80	86 (9)
2	[Pd(*R*)-binap]Cl_2	DME	Cs_2CO_3	80	48, (5)
3	[Pd(*R*)-binap]Cl_2	DMF	$K_3PO_4H_2O$	120	trace
4	[Pd(*R*)-binap]Cl_2	DMF	Cs_2CO_3	120	trace
5	[Pd(*R*)-binap]Cl_2	Toluene	K_3PO_4	100	trace
6	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	Toluene/H_2O = 3/2	Na_2CO_3	60	67, (1)
7	[Pd(*R*)-binap]Cl_2	Toluene/ H_2O = 3/2	Na_2CO_3	60	18 (7 by NMR)
8	[Pd(+)-diop]Cl_2	Toluene/ H_2O = 3/2	Na_2CO_3	60	trace
9	(*R*)-PROPHOS /$PdCl_2(C_6H_5CN)_2$	Toluene/ H_2O = 3/2	Na_2CO_3	60	-
10	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	0.4% Brij97 in H_2O	$Ba(OH)_2H_2O$	60	66, (1)
11	[Pd(*R*)-binap]Cl_2	0.4% Brij97 in H_2O	$Ba(OH)_2H_2O$	60	7 (9 by NMR)
12	(*R*)-Tol-BINAP /$PdCl_2(C_6H_5CN)_2$	0.4% Brij97 in H_2O	$Ba(OH)_2H_2O$	60	trace
13	[Pd(+)-diop]Cl_2	0.4% Brij97 in H_2O	$Ba(OH)_2H_2O$	60	trace
14	(*R*)-PROPHOS /$PdCl_2(C_6H_5CN)_2$	0.4% Brij97 in H_2O	$Ba(OH)_2H_2O$	60	21 (5 by NMR)

[a] Reaction conditions: **29** (1 equiv.), **4** (1.2 equiv.), $PdCl_2(C_6H_5CN)_2$ (2 mol%), ligand (4 mol% of *BisNap*-Phos or 2 mol% of diphosphines), base (3 equiv.), 16 h, [b] yield of isolated product.

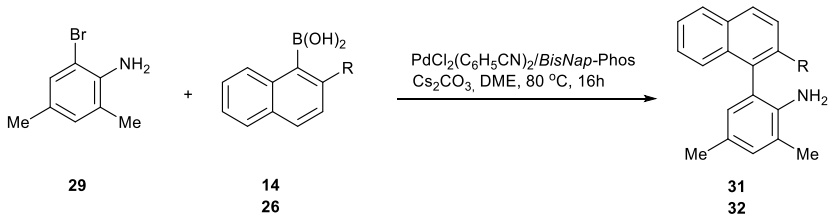
Some better selectivity was achieved when (*Sa*)-*BisNap*-Phos was used in the reaction between **29** and **31** carried out in anhydrous conditions, what one more time proved the high level of the ligand potency. Biaryl **31** was obtained with 19% ee (Table 15). The low enantioselectivity, observed in the cases of tris *ortho*-substituted synthetized biaryl, is probably caused by the low barrier of rotation [25].

We also found out that the coupling of phenanthrene bromide **33** with boronic acid **24** lead to the expected product **34** in excellent yields, both in anhydrous and aqueous conditions. Since the steric hindrance created by the phenanthrene motif is not essential, the BINAP could be used in this reaction, resulting in a comparable yield of the product **34**, as it was obtained in a reaction catalyzed by a complex of *BisNap*-Phos (Table 16), at a higher temperature. The stereoselectivity of the reactions was not high and the best results (35% ee) were achieved in the case of the *BisNap*-Phos catalyst-mediated reaction in anhydrous DME.

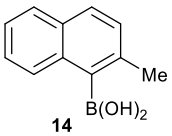
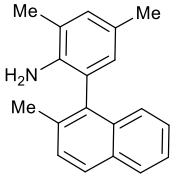
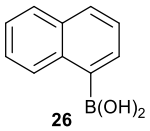
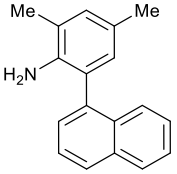
The substrates possessing mild coordinating functional groups were also used in coupling mediated by the *BisNap*-Phos complex caried out in aqueous media (Table 17).

In all studied cases, good to excellent yields of the coupling products were achieved, while the stereoselectivity of the reactions was dependent on the structure of the substrates, in which some steric hindrance created by the ortho-to-coupling position substituents and moderate coordinating ability of those substituents is required. Additionally, it seems that the products of low racemization energy [25] always formed in an almost racemic form. This observation can be explained considering the mechanistic studies of the reaction [26]. The studies indicated that the steric hindrance created by *ortho* substitutes is crucial at the reaction steps which define an absolute configuration of the coupling products.

Table 15. Asymmetric synthesis of biaryls **31** and **32** bearing unprotected amino groups [a].

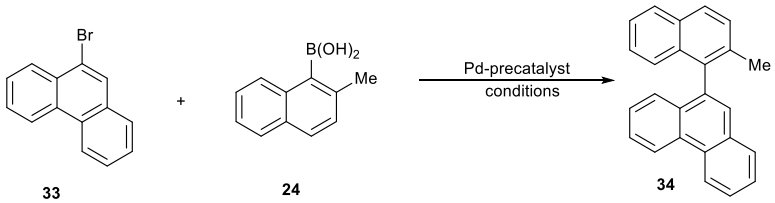


29 **14** **26** **31** **32**

Entry	Ar-B(OH)$_2$	Product	Yield [b], (ee), [%]
1	 **14**	 **31**	92 (19)
2	 **26**	 **32**	93 (4)

[a] Reaction conditions: $PdCl_2(C_6H_5CN)_2$ (2 mol%), *BisNap*-Phos (4 mol%), Cs_2CO_3, DME, 80 °C, 18 h. [b] yield of isolated product.

Table 16. Ligand activity in asymmetric synthesis of **34** [a].



33 **24** **34**

Entry	$PdCl_2(C_6H_5CN)_2$, Ligand/Catalyst	Solvent	Base	T, [°C]	Yield [b], (ee), [%]
1	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	DME	Cs_2CO_3	80	95, (35)
2	[Pd(*R*-)binap]Cl_2	DME	Cs_2CO_3	80	96, (10)
3	[Pd(*R*-)binap]Cl_2	Toluene	K_3PO_4	100	58 (10)
4	(*S*)-*BisNap*-Phos /$PdCl_2(C_6H_5CN)_2$	0.4% r-r Brij97 w H_2O	Na_2CO_3	60	92, (17)
5	[Pd(*R*-)binap]Cl_2	0.4% r-r Brij97 w H_2O	Na_2CO_3	60	> 99, (10)

[a] Reaction conditions: **33** (1 equiv.), **24** (1.2 equiv.), $PdCl_2(C_6H_5CN)_2$ (2 mol%), ligand (4 mol% of *BisNap*-Phos or 2 mol% of BINAP), base (3 equiv.), 16 h, [b] yield of isolated product.

Table 17. Synthesis of biaryls bearing mild-coordinating functional groups [a].

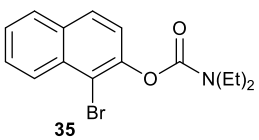
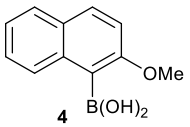
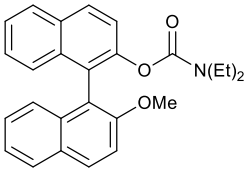
Entry	Ar-X	Ar-B(OH)$_2$	Product	Yield [b], (ee), [%]
1	 **35**	 **4**	 **36**	72 (59) [c]

Table 17. *Cont.*

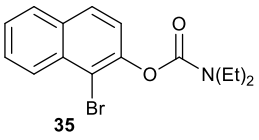
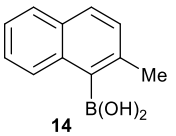
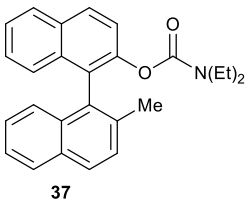
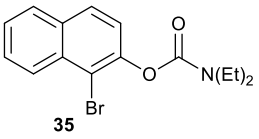
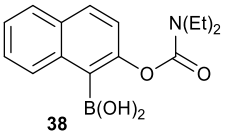
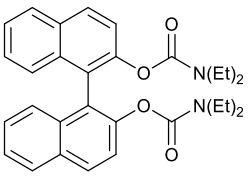
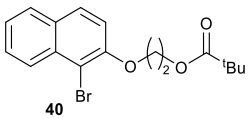
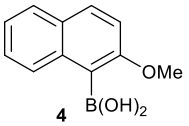
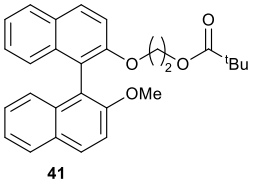
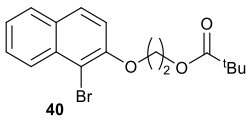
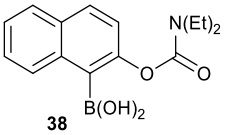
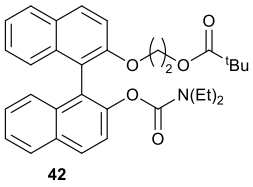
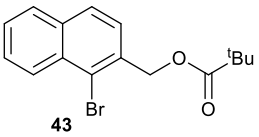
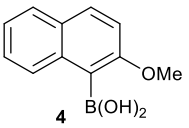
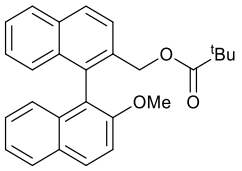
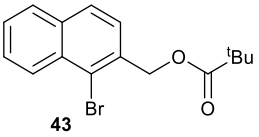
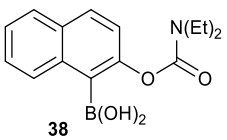
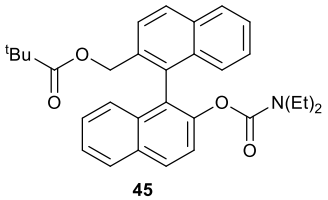
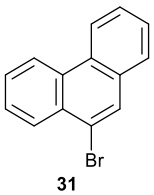
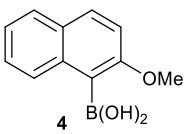
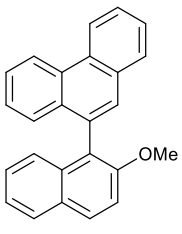
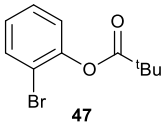
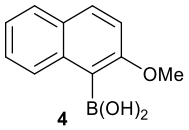
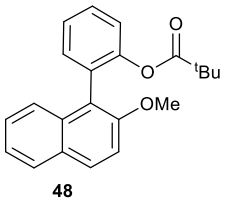
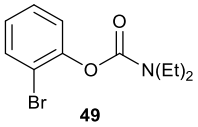
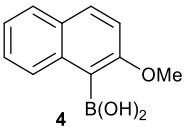
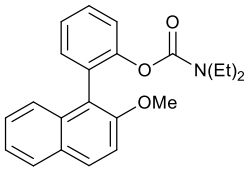
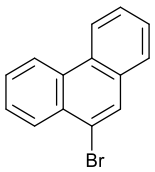
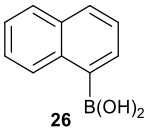
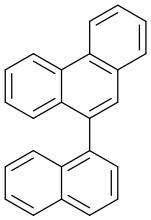
Entry	Ar-X	Ar-B(OH)$_2$	Product	Yield [b], (ee), [%]
2	 **35**	 **14**	 **37**	82 (67) [c]
3	 **35**	 **38**	 **39**	80 (50) [c]
4	 **40**	 **4**	 **41**	72 (36) [c]
5	 **40**	 **38**	 **42**	87 (36) [c]
6	 **43**	 **4**	 **44**	66 (86) [c]
7	 **43**	 **38**	 **45**	47 (76) [c]
11	 **31**	 **4**	 **46**	91 (5) [d]
12	 **47**	 **4**	 **48**	35 (3) [d]

Table 17. *Cont.*

Entry	Ar-X	Ar-B(OH)$_2$	Product	Yield [b], (ee), [%]
13	 **49**	 **4**	 **50**	85 (0) [d]
14	 **31**	 **26**	 **51**	98 (3) [d]

[a] Reaction conditions: $PdCl_2(C_6H_5CN)_2$ (2 mol%), *BisNap*-Phos (4 mol%), 18h; [b] isolated yield; [c] Na_2CO_3, H_2O, brij 97, 60 °C; [d] Na_2CO_3, H_2O, SDS, 60 °C.

Interestingly, carrying out the reactions in anhydrous media and protected with argon atmosphere had no benefits compared to the reactions in water without argon protection, if relatively air exposition-stable ligand *BisNap*-Phos was used.

3. Materials and Methods

3.1. General Information

The reagents were purchased from commercial suppliers and used without further purification. Solvents were dried and distilled under argon before use. All of the reactions involving the formation and further conversions of phosphines were carried out under argon atmosphere with attempted complete exclusion of air from the reaction vessels and solvents, including those used in the work-up. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV300 (1H 300 MHz, ^{31}P 121.5 MHz, ^{13}C NMR 75 MHz) and Bruker AV500 (^{1}H 500 MHz, ^{31}P 202 MHz, ^{13}C NMR 126 MHz) spectrometers (Bruker; Billerica, Ma., USA). All spectra were obtained in $CDCl_3$ solutions, unless mentioned otherwise, and the chemical shifts (δ) are expressed in ppm using internal reference to TMS and external reference to 85% H_3PO_4 in D_2O for ^{31}P. Coupling constants (*J*) are expressed in Hz. The abbreviations of signal patterns are as follows: s—singlet, d—doublet, t—triplet, q—quartet, m—multiplet, b—broad, and i—intensive. Elemental analyses were measured on the PerkinElmer CHN 2400. Optical rotations were measured in a 1 dm cell on a PerkinElmer 341LC digital polarimeter at ambient temperature. Thin-layer chromatography (TLC) was carried out on silica gel (Kieselgel 60, F254 on aluminum sheet, Merck KGaA, Darmstadt, Germany). All separations and purifications by column chromatography were conducted by using Merck silica gel 60 (230–400 mesh), unless noted otherwise.

3.2. Synthesis and Spectral Data

Synthesis of rac-dicyclohexyl(1′,2,4′-trimethoxy-5′,8′-dihydro-1,2′-binaphthalen-3′-yl)phosphane oxide (**8**).

A reactor equipped with a magnetic stirrer was charged with compound **7** (3 g, 9.6 mmol), obtained as presented [27], $CsCO_3$ (3.1 g, 9.6 mmol), Cy_2PHO (3 g, 14 mmol), Bu_4NHSO_4 (0.1g, 0.3 mmol), toluene (15 mL), and DMF (10 mL) Next, the reaction mixture was protected by an argon atmosphere, sealed with a glass stopper, and stirred at 35 °C for 96 h. After that time, the reaction mixture was cooled down to 0 °C, and CH_3I (2.3 mL, 5.2 g, 37 mmol) and K_2CO_3 (5.2 g, 37 mmol) were added. Protected by the argon atmosphere, the mixture was stirred in a closed reactor at 35 °C for 96 h. The obtained mixture was poured

on 100 g of ice, and carefully acidified with 1M HCl to an acidic pH. The crude product was extracted with DCM, dried with $MgSO_4$, and purified on a SiO_2 column eluted by a hexane: acetone (3: 1) mixture to afford 5.2g (97%) of pure compound **8**.

Alternatively, **8** could be obtained in a reaction catalyzed by $Bi(OTf)_3$ according to the following procedure. A reactor equipped with a magnetic stirrer was charged with compound **7** (0.5 g), Cy_2PHO (0.5 g), $Bi(OTf)_3$ (40 mg), and 10 mL of DMF. Next, the reaction mixture was protected by an argon atmosphere, sealed with a glass stopper, and stirred at 70 °C for 48 h. After that time, the reaction mixture was cooled down to 20 °C, and 10 mL of DMD, 50 mg of Bu_4NHSO_4, and $CsCO_3$ (0.3 g) were added, followed by the addition of 40% NaH (0.37g) realized in a small portion with respect to foaming H_2 gas. Once a liberation of H_2 was completed, 0.5 mL of CH_3I was added, the reactor sealed with a glass stopper, and the reaction mixture was stirred at 35 °C for 48 h. The obtained mixture was poured on 100 g of ice, and carefully acidified with 1M HCl to an acidic pH. The crude product was extracted with DCM, dried with $MgSO_4$, and purified on a SiO_2 column eluted by a hexane: acetone = 3: 1 mixture to afford 0.82 g (91%) of pure compound **8**.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96–2.16 (m, 22H), 3.45 (s, 3H), 3.86 (s, 3H), 4.14 (s, 3H), 7.17–7.28 (m, 3H), 7.34 (d, *J* = 9.2 Hz, 1H), 7.60–7.64 (m, 2H), 7.78–7.82 (m, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 8.16–8.21 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 25.7, 26.1, 26.2, 26.3, 26.5, 26.6, 26.7, 26.8, 26.8, 26.9, 27.0, 27.1, 39.4 (d, *J* = 18.0 Hz), 40.1 (d, *J* = 18.0 Hz), 55.3, 61.4, 62.4, 111.8, 119,8, 121.5, 122.3, 122.4, 123.7, 125.0, 125.3, 126.0, 126.9, 127.4, 128.0, 128.6, 129.1, 130.7, 131.2, 151.2, 154.2, 154.6.

^{31}P NMR (161 MHz, $CDCl_3$): δ 50.17 ppm.

HRMS (ESI): m/z = 557.3340 [C35H41O4P+H]+, m/z (teor.) = 557.3175

Synthesis of dicyclohexyl(1′,2-dimethoxy-5′,8′-dihydro-1,2′-binaphthalen-3′-yl)phosphane oxide (**9**).

A reactor equipped with a magnetic stirrer and reflux condenser connected to the argon line was charged with compound **8** (1.7 g, 3 mmol), 20 mL of THF, TMDS (1.7 mL, 1.3 g, 9.7 mmol), and $Ti(OiPr)_4$ (1 mL. 1 g, 3.5 mmol). The reaction was heated to afford a gentle reflux condition for 24 h and cooled down to ambient temperature. The solvents were evaporated off under the reduced pressure and the product **9** isolated on a SiO_2 column applied the gradient of eluents hexane:acetone = 6-3: 1 to afford 1.4g (88%) of pure compound **9**. Chiral chromatographic analysis of **9** was performed on HPLC-MS Column CHIRALPAK® AS-H, 250 × 4, 6 mm, 5 μm eluting with CH_3CN: H_2O = 50: 50 at flow 0.45 mL/min. which showed two signals at 8.07 min and 9.2 min with the same pseudomolecular ion mass 527 Da, which corresponds to the stereoisomers *R*- and *S*- of compound **9**.

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.13–1.68 (m, 22H), 3.56 (s, 3H), 3.90 (s, 3H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.23–7.36 (m, 1H), 7.31–7.36 (m, 1H), 7.42 (d, *J* = 9.1 Hz, 1H), 7.62–7.66 (m, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 9.0 Hz, 1H), 8.07–8.11 (m, 1H), 8.14–8.18 (m, 1H), 8.58 (d, *J* = 12.1 Hz, 1H),

^{13}C NMR (126 MHz, $CDCl_3$): δ 25.4, 25.5, 25.6, 25.8, 26.1, 26.2, 26.3, 26.5, 26.6, 26.7, 26.8, 36.7 (d, *J* = 3.7 Hz), 37.7 (d, *J* = 3.7 Hz), 55.8, 61.5, 112.3, 119.8, 122.6, 123.7, 126.0, 126.2, 126.7, 126.8, 128.8, 129.2, 130.2, 131.1, 132.2, 132.3, 133.4, 133.8, 134.2, 154.4, 154.6, 154.8.

^{31}P NMR (202 MHz, $CDCl_3$): δ 47.54 ppm.

Synthesis of rac-dicyclohexyl(1′,2-dimethoxy-5′,8′-dihydro-1,2′-binaphthalen-3′-yl) phosphane (***rac*-10**).

A reactor equipped with a magnetic stirrer and filled with argon was charged with compound **9** (0.5 g, 0.95 mmol), 20 mL of toluene, 10 mL of Et_3N, and 1 mL of $SiHCl_3$. The reactor was sealed with a glass stoper and the reaction mixture was stirred at 120 °C for 24 h. After that time, the reactor was cooled down to 0 °C, and 20 mL of toluene and 10 mL of 15% NaOH were added, maintaining the intense stirring. The formed organic phase was separated, washed with water, and dried by $MgSO_4$. The $MgSO_4$ was filtered off, and the solvent was completely evaporated off under reduced pressure. To the crude product, 15 mL of methanol was added, the air in the flask was replaced with argon, and the flask

was sealed with the glass stoper and heated at 90 °C to dissolve the crude product. The pure compound **10** (435 mg, 90%) was crystallized from the solution after 24 h, storing at 0 °C.

Starting from the enantiomerically pure **(*S*)-9**, the enantiomerically pure **(*S*)-10** was obtained $[\alpha]^{20}_{D}$ = +57.7 (*c* = 0.5, Et_2O). The spectral data of ***(Sa)*-10** were identical to those recorded for the racemic compound.

^{1}H NMR (500 MHz, $CDCl_3$): 1.02–1.90 (m, 22H), 3.49 (s, 3H), 3.88 (s, 3H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.28–7.31 (m, 2H), 7,41 (d, *J* = 8.8 Hz, 1H), 7.57–7.61 (m, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.96–8.02 (m, 3H), 8.19–8.23 (m, 1H).

^{13}C NMR (126 MHz, benzene d-6): 26.7, 27.1, 27.5, 27.6, 27.7, 27.8, 27.8, 27.8, 27.9, 29.9, 30.1, 30.2, 30.4, 30.5, 30.6, 30.7, 30.8, 34.9 (d, *J* = 17.8 Hz), 55.3, 61.0, 112.8, 121.8 (d, *J* = 6.9 Hz), 123.1, 123.5, 126.2, 126.5, 126.7, 127.8, 127.9, 128.1, 128.3, 128.6 (d, *J* = 3.4 Hz), 129.4, 129.8, 132.2, 132.6, 134.7, 134.8, 137.6, 137.8, 154.9, 155.0, 155.1.

^{31}P NMR (126 MHz, $CDCl_3$): δ −9.50 ppm.

Synthesis of palladium complex **12**.

A glass flask equipped with a magnetic stirrer was charged with 266 mg of palladium complex **(*S*)-11** dissolved in 6 mL of methanol and added to a stirring solution of 346 mg of ***rac*-10** in 12 mL of a benzene: methanol (1: 1) mixture. The air in the flask was replaced with argon, the flask was closed with a glass stopper, and the reaction mixture was stirred for 16 h at 50 °C. After the reaction completion, methanol was evaporated under reduced pressure and the product was purified by column chromatography eluted with a hexane: Et_2O: MeOH = 2: 1: 0.1 mixture to yield 55 mg of complex **12** as a mixture of diastereomers enriched with the less polar one. Next, the obtained product was crystallized twice with the same solvent mixture to yield 150 mg of a single diastereomer ***S,Sa*-12**. The relative configuration of the complex was determined by X-ray diffraction (Figure 2a, CCDC 2222975). Due to the restricted rotation of substituents in the complex, the ^{1}H and ^{13}NMR spectra of **12** contained unspecific very wide and not resolved signals:

^{31}P NMR (126 MHz, $CDCl_3$): δ = 73.89 ppm (wide).

MS (ESI): m/z = 850.27 [C48H56ClNO2PPd + H]+, m/z (teor.) = 850.28; and 814.29 [C48H55NO2PPd]+, m/z (teor.) = 814, 30. The isotopic profile of the signals corresponds to that theoretically calculated.

Synthesis of *(Sa)*-dicyclohexyl(1′,2-dimethoxy-5′,8′-dihydro-1,2′-binaphthalen-3′-yl) phosphane oxide (***(Sa)*-9**).

An amount of 150 mg of (***S,Sa*)-12** and 150 mg of dppe were dissolved in 30 mL of DCM. The reaction mixture was sealed and stirred at RT for 48 h, then heated at 100 °C for 20 min. 10 mL of 15% H_2O_2 was added and stirring continued for the next 4 h. The organic phase was separated and dried with $MgSO_4$ and the product was isolated by SiO_2 column chromatography eluting with a hexane: acetone (3: 1) mixture to afford 80 mg of (*Sa*)-**9**. The chiral HPLC-MS chromatogram recorder, with the application of CHIRALPAK® AS-H, 250 × 4, 6 mm, 5 µm column eluted with CH_3CN: water=50: 50 at flow 0.45 mL/min signal of enantiomer (*S*)- at 9.2 min, while the signal of enantiomer (*R*)-**9**- showed up at 8.0 min, was not presented. $[\alpha]^{20}_{D}$ = +67.7 (C = 1, DCM).

Separation of enantiomers of **9** by co-crystallization with TADDOL.

An amount of 4 g of racemic **9** and 3.5 g of (-)-TADDOL were dissolved in 60 mL of EtOH and 9 mL of $CHCl_3$, in a sealed glass pressure vial at 100 °C. The vial was allowed to cool down to ambient temperature. The crystalline complex was precipitated within 24 h with a yield of 1.6 g and $[\alpha]^{20}_{D}$ = +13.3 (*c* = 1, methanol). The diastereomeric excess of the obtained complex was measured by the NMR technique as reported [28]: 6 mg of complex and 35 mg of (*S*)-naproxen were dissolved in 1 mL of $CDCl_3$, and ^{31}P, ^{1}H spectra were recorded. The spectrum of racemic complex contains the signals at 52.0 and 51.9 ppm, with the single diastereomer (*S*)- at 51.9 ppm. Note that the chemical shifts of the signals corresponding to the enantiomer **9** are dependent on the concentration and the ratio of **9** to naproxen, so the assignment of the absolute configuration only through the NMR technique could not be precise if only a single enantiomer were present in the mixture. Pure **(*S*)-9** was obtained after a flash column separation of its complex with TADDOL eluting

with a hexane: acetone = 3: 1 mixture in a quantitative yield with $[\alpha]^{20}_{D}$ = + 67.7 (*c* = 1, DCM). Chromatographic analysis of **9** was performed on HPLC Column CHIRALPAK® AS-H, 250 × 4, 6 mm, 5 µm eluting with CH_3CN: water = 50: 50 at flow 0.45 mL/min; the enantiomer (*R*)- shows up at 8.07 min, and enantiomer (*S*)- at 9.2 min. The spectral data of (*S*a)-**9** were identical to those recorded for the racemic compound. The enantiomer (*R*a)-**9** could be obtained after the crystallization of the filtrate: the solution was evaporated under the reduced pressure and dissolved in acetone in a pressure vial to afford a 10% solution. The crystals of **(*R*a)-9** were formed upon cooling down to ambient temperature. In some experiments, complete enantiomer separation requires the recrystallization of the obtained crystals from the same solvent system.

General procedures for asymmetric synthesis of tetra-*ortho*-substituted biaryl compounds:

General procedure A: A 10 mL round-bottom flask equipped with a stirring bar was charged with 0.3% aqueous solution of SDS and base Na_2CO_3 (3 mmol). Next, *ortho*-substituted aryl bromide (1 mmol), *ortho*-substituted aryl boronic acid or its derivative (1.2 mmol), ligand *BisNap*-Phos (4 mol%), and the pre-catalyst $PdCl_2(C_6H_5CN)_2$ (2 mol%) were dissolved in a minimum amount of THF and added to the mixture. The reaction was stirred at 60 °C for 18 h, then extracted with DCM (3 × 10 mL), and the combined organic layer was dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the crude product was isolated by column chromatography.

General procedure B: A 10 mL round-bottom flask equipped with a stirring bar was charged with 0.3% aqueous solution of brij 97 and base Na_2CO_3 (3 mmol). Next, *ortho*-substituted aryl bromide (1 mmol), *ortho*-substituted aryl boronic acid or its derivative (1.2 mmol), ligand *BisNap*-Phos (4 mol%), and the pre-catalyst $PdCl_2(C_6H_5CN)_2$ (2 mol%) were dissolved in a minimum amount of THF and added to the mixture. The reaction was stirred at 60 °C for 18 h, then extracted with DCM (3 × 10 mL), and the combined organic layer was dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the crude product was isolated by column chromatography.

General procedure C: A 10 mL round-bottom flask equipped with a stirring bar was charged with anhydrous DME as a solvent and anhydrous Cs_2CO_3 (3 mmol). Next, *ortho*-substituted aryl bromide (1 mmol), *ortho*-substituted aryl boronic acid or it derivative (1.2 mmol), *BisNap*-Phos (4 mol%), and pre-catalyst $PdCl_2(C_6H_5CN)_2$ (2 mol%) were dissolved in a minimum amount of THF and added to the reaction mixture. The reaction was stirred at 80 °C for 18 h, then extracted with DCM (3 × 10 mL), and the combined organic layer was dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the crude product was isolated by column chromatography.

2,2′-dimethoxy-1,1′-binaphthyl (**13**).

The compound was synthesized according to General Procedure A and then purified by column chromatography on silica gel using hexane:acetone (6:1) as an eluent. The compound was obtained as colorless crystals. mp = 218.4–220.4 °C (lit. [29] mp = 223–227 °C). The enantiomeric excess was determined by LCMS using a reversed phase chiral column: AS-RH; Mobile phase: H_2O: CH_3CN (50: 50); Flow: 0.45; t(*R*) = 7.847 min. (73.5%); t(*S*) = 8.529 min., λ = 254 nm; and HPLC using a chiral column: OD-H; Mobile phase: hexane: ethanol (99.5: 0.5); Flow: 0.5 mL/min; t*(R)* = 18.609; t(*S*) = 20.334; λ = 254 nm. The specific rotation of the compound with an 47% ee (*R*) was $[\alpha]_D$ = +23.3 (*c* 1.0, $CHCl_3$) (lit. [29] $[\alpha]_D$ = + 57.54; *c* 1.0, $CHCl_3$). Yield: 96%. Elemental Analysis: found C, 84.05; H, 5.66; theoretical: C, 84.05; H, 5.77.

^{1}H NMR (500 Hz, $CDCl_3$): δ 3.78 (s, 6H, OCH_3), 7.10–7.12 (m, 2H), 7.21–7.23 (m, 2H), 7.31–7.34 (m, 2H), 7.47 (d, *J* = 9.1 Hz, 2HH), 7.87–7.89 (m, 2H), 7.99 (d, *J* = 8.8 Hz, 2H).

^{13}C NMR (126 Hz, $CDCl_3$): δ 56.9 (CH_3), 114.2, 119.6, 123.5, 125.2, 126.3, 127.9, 129.2, 129.4, 134.0, 155.0.

^{13}C NMR (DEPT 135, $CDCl_3$): δ 56.9 (CH_3), 114.2, 123.5, 125.2, 126.3, 127.9, 129.4.

2-methoxy-2′-methyl-1,1′-binaphthalene (**15**).

The compound was synthesized according to General Procedure A and then purified by column chromatography on silica gel using hexane:acetone = 9:1 as an eluent. The

compound was obtained as a yellowish solid. mp = 116–118 °C (lit.[30] mp = 119–120 °C). The enantiomeric excess was determined by LCMS using a reversed phase chiral column: AS-RH; Mobile phase: H_2O: CH_3CN (50: 50); Flow: 0.45; t(*S*) = 13.156 min.; t(*R*) = 14,070 min. (85%); λ = 254 nm. The specific rotation of the compound with an 70% ee (*R*) was $[\alpha]_D$ = +10.3 (*c* = 1.03, $CHCl_3$) (lit. [30] $[\alpha]_D$ = + 22.3; (*c* 1.3, $CHCl_3$, 92% ee). Yield: 98%. Elemental Analysis: found C, 88.25; H, 5.97; theoretical: C, 88.56; H, 6.08.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.11 (s, 3H, CH_3), 3.77 (s, 3H, OCH_3), 7.00–7.02 (m, 1H), 7.13–7.15 (m, 1H), 7.20–7.23 (m, 2H), 7.34 (ddd, *J* = 8.2, 6.6 and 1.3 Hz, 1H), 7.39 (ddd, *J* = 8.1, 6.7 and 1.3 Hz, 1H), 7.47 (d, *J* = 9.1 Hz, 1H), 7.53 (d, J = 8.2 Hz, 1H), 7.89 (dd, *J* = 8.4 and 3.9 Hz, 2H), 8.00 (d, *J* = 8.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 20.3 (CH_3), 56.6 (OCH_3), 113.8, 122.0, 123.6, 124.7, 125.1, 125.8, 126.5, 127.48, 127.9, 127.9, 128.7, 129.2, 129.4, 132.1, 132.3, 133.2, 133.6, 135.0.

^{13}C NMR (DEPT 135, $CDCl_3$): δ 20.3 (CH_3), 56.6 (OCH_3), 113.8, 123.6, 124.7, 125.1, 125.8, 125.8, 126.5, 127.5, 127.9, 127.9, 128.67, 129.4.

2,6-Dimethoxy-2′,6′-dimethyl-1,1′-biphenyl (**21**).

The compound was synthesized according to General Procedure A from chloride **17** or bromide **18** and then purified by column chromatography on silica gel using hexane: acetone (99.7: 0.3) as an eluent. The pure compound was isolated as colorless crystals. Mp = 108–110 °C (lit. [31] m.p. = 110–112 °C, crystallized from MeOH). Yield: 40–61%.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.01 (s, 6H, CH_3), 3.72 (s, 6H, OCH_3), 6.67 (d, *J* = 8.4 Hz, 2H), 7.15 (t, *J* = 8.42 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 8.2 Hz, 1H).

^{13}C NMR (126 MHz, DEPT 135, $CDCl_3$): δ 20.1 (CH_3), 55.8 (OCH_3), 103.9, 126.8, 127.0, 128.6.

5-Cyano-2,3,2′,6′-tetrametoxy-1,1′-biphenyl (**22**).

The compound was synthesized according to General Procedure A from chloride **19** and then purified by column chromatography on silica gel using hexane: acetone (6: 1) as an eluent. The pure compound was isolated as colorless crystals. Mp = 119–120 °C. Yield: 56%.

^{1}H NMR (^{1}H NMR (300.33 MHz, $CDCl_3$): δ 3.68 (s, 3H, OCH_3), 3.74 (s, 6H, OCH_3), 3.92 (s, 3H, OCH_3), 6.65 (d, *J* = 8.4 Hz, 2H), 7.13 (s, 2H), 7.31–7.36 (t, *J* = 8.2 Hz, 1H).

^{13}C NMR (75.52 MHz, $CDCl_3$): δ 55.8, 55.9, 60.5, 103.8, 104.1, 106.4, 113.9, 114.3, 119.2, 129.2, 129.6, 129.8, 151.7, 152.8, 157.7.

HRMS (ESI): m/z = 300.1227 [C17H17NO4+H]+, m/z (teor.) = 300.1230, diff. = −1.00 ppm.

2-Acetyl-2′,6′-dimethoxy-1,1′-biphenyl (**23**).

The compound was synthesized according to General Procedure A from chloride **20** and then purified by column chromatography on silica gel using hexane:ethyl acetate (9:1) as an eluent. The pure compound was isolated as colorless crystals. Mp = 51–52 °C (lit. [32] m.p. = 51–52 °C). Yield: 87%.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.64 (s, 3H, C(O)OCH_3), 3.71 (s, 6 H, OCH_3), 6.65 (d, *J* = 8.4 Hz, 2H, CH), 7.29 (t, *J* = 8.4 Hz, 1H), 7.34 (dd, *J* = 7.7, and 1.1 Hz, 1H), 7.40 (td, J = 7.7 and 1.5 Hz, 1H), 7.54 (td, *J* = 7.5 and 1.5 Hz, 1H), 7.96 (dd, *J* = 7.7 and 1.3 Hz, 1H).

^{13}C NMR (DEPT 135, $CDCl_3$): δ = 51.6 (C(O)OCH3), 55.8 (OCH3), 103.9, 126.9, 128.7, 129.6, 131.2, 132.4.

2,2′-dimethyl-1,1′-binaphthalene (**25**).

The compound was synthesized according to General Procedure A and then purified by column chromatography on silica gel using hexane as an eluent. The pure compound was a colorless oily liquid. The enantiomeric excess was determined by the specific rotation and then compared with the literature data. The specific rotation of the compound with an 77% ee (*S*) was $[\alpha]_D$ = +27.5 (*c* 1.025, $CHCl_3$), (lit. [30] $[\alpha]_D$ = +32.5 c = 0.8, $CHCl_3$, 90% ee (*S*)). The specific rotation of the compound with an 71% ee (*R*) was $[\alpha]_D$ = −24.4 (*c* 1.01, $CHCl_3$) (lit. [33] $[\alpha]_D$ = −40.0; *c* = 1.12; $CHCl_3$). Yield: 85%. Elemental Analysis: found C, 93.66; H, 5.79; theoretical: C, 93.99; H, 6.01.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.05 (s, 6H, CH_3), 7.05–7.07 (m, 2H), 7.22 (ddd, *J* = 8.4, 6.8 and 1.3 Hz, 2H), 7.41 (ddd, *J* = 8.1, 6.9 and 1.1 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.88–7.92 (m, 4H).

^{13}C NMR (126 MHz, CDCl3): δ = 20.0 (CH_3), 124.9, 125.6, 126.1, 127.4, 127.9, 128.7, 132.2, 132.7, 134.2,135.1.

^{13}C NMR (DEPT 135, CDCl3): δ = 20.0 (CH_3), 124.9, 125.6, 127.4, 127.9, 128.7.

2-methyl-1,1′-binaphthalene (**27**).

The compound was synthesized according to General Procedure C and then purified by column chromatography on silica gel using hexane as an eluent. The pure compound was isolated as colorless crystals. mp = 95.1 °C (lit. [34] mp = 82.8–87.1 °C). The enantiomeric excess was determined by HPLC using a chiral column: OJ-H, Mobile phase: hexane: isopropanol (80: 20); Flow: 1 mL/min; t(*R*) = 9.146 min. (68, 5%); t(*S*) = 12.253 min.; λ = 254 nm. The specific rotation of the compound with an 37% ee (*R*) was $[\alpha]_D = -17.8$ (*c* 1.0, $CHCl_3$), (lit. [35] $[\alpha]_D = -15.0$; *c* = 1.0, $CHCl_3$, λ = 589 nm, 49% ee). Yield: 80%. Elemental Analysis: found C, 93.66; H, 5.79; theoretical: C, 93.99; H, 6.01.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.12 (s, 3H, CH_3), 7.15–7.17 (m, 1H), 7.22–7.24 (m, 2H), 7.27–7.30 (m, 1H), 7.39 (dd, *J* = 6.9, and 1.3 Hz, 1H), 7.41 (ddd, *J* = 8.2, 6.6 and 1.3 Hz, 1H), 7.48 (ddd, *J* = 8.2, 6.6 and 1.6 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.63 (dd, *J* = 8.2 and 6.9 Hz, 1H), 7.89 (dd, *J* = 8.4 and 3.3 Hz, 2H), 7.97 (d, *J* = 8.2 Hz, 2H).

^{13}C NMR (126 MHz, CDCl3): δ 20.5 (CH_3), 124.8, 125.6, 125.9, 125.9, 126.0, 126.1, 126.3, 127.5, 127.6, 127.7, 127.8, 128.3, 128.6, 131.9, 132.6, 133.5, 133.7, 134.4, 136.0, 137.5.

^{13}C NMR (DEPT 135, $CDCl_3$): δ 20.5 (CH_3), 124.8, 125.6, 125.9, 125.9, 126.0, 126.1, 126.3, 127.5, 127.6, 127.7, 127.7, 128.2, 128.6.

2-methoxy-1,1′-binaphthalene (**28**).

The compound was synthesized according to General Procedure B and then purified by column chromatography on silica gel using hexane as an eluent. The pure compound was isolated as colorless crystals. Mp = 105.9 °C (lit. [36] mp = 109–110 °C - crystallized from MeOH). The enantiomeric excess was determined by HPLC using a chiral column: OJ-H, Mobile phase: hexane: isopropanol (95: 5); Flow: 1 mL/min; t(*S*) =16.607 min.; t(*R*) = 28.830 min. (67%); λ = 254 nm. The specific rotation of the compound with an 34% ee (*R*) was $[\alpha]_D = -16.5$ (*c* = 1.02, $CHCl_3$, λ = 589 nm), (lit. [35] (*S*) $[\alpha]_D = +8.0$; *c* = 1.0, $CHCl_3$, λ = 589 nm, 80% ee). Yield: 95%. HRMS (ESI): m/z = 285.1275 $[C_{21}H_{16}O+H]+$, m/z (teor.) = 285.1274, diff. = 0.35 ppm.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.78 (s, 3H, OCH_3), 7.16 (dd., *J* = 5.7 and 1.3 Hz, 2H), 7.23 (ddd, *J* = 8.2, 6.6 and 1.3 Hz, 1H), 7.29 (ddd, *J* = 8.1, 5.2 and 2.2 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.46 (dd, J = 6.9 and 1.3 Hz, 2H), 7.63 (dd, *J* = 8.2 and 6.9 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.94–8.01 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 56.8 (OCH_3), 113.8, 123.2, 123.5, 125.51, 125.58, 125.7, 125.9, 126.2, 126.3, 127.7, 127.8, 128.2, 128.4, 129.1, 129.5, 132.9, 133.7, 134.2, 134.5, 154.6.

^{13}C NMR (DEPT 135, $CDCl_3$): δ 56.8 (OCH_3), 113.8, 123.67, 125.5, 125.6, 125.7, 125.9, 126.2, 126.4, 127.7, 127.8, 128.2, 128.4, 129.5.

2-(2-methoxynaphthalen-1-yl)—4,6-dimethylaniline (**30**).

The compound was synthesized according to General Procedure C and then purified by column chromatography on silica gel using hexane as an eluent; when 2-methoxynaphthalene was removed from the column, the system was changed to hexane: acetone (98: 2). The pure compound was isolated as colorless crystals. Mp = 165.1 °C (DME). The enantiomeric excess was determined by HPLC using a chiral column: AS-H, Mobile phase: hexane: isopropanol (95: 5); Flow: 0.3 mL/min; t1 = 24.778 min. (54.5%); t2 = 26.990 min.; λ = 254 nm. Due to the low enantiomeric excess of the compound of 9%, specific rotation was not determined. Yield: 86%. Anal. calcd for $C_{19}H_{19}NO$: C 82.28; H, 6.90; N, 5.05. Found: C, 81.52; H, 6.80; N, 4.95.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.27 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 3.31 (s, 2 H, NH_2), 3.90 (s,3H, OCH_3), 6.82 (s, 1H), 7.02 (s, 1H), 7.35–7.39 (m, 2H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.44–7.46 (m, 1H), 7.84–7.86 (m, 1H), 7.93 (d, *J* = 8.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 17.9 (CH_3), 20.5 (CH_3), 56.8 (OCH_3), 113.9, 121.6, 121.8, 122.5, 123.7, 125.2, 126.6, 127.0, 127.8, 129.27, 129.4, 129.78, 130.6, 133.5, 140.3, 154.4.

^{13}C NMR (DEPT 135, $CDCl_3$): δ = 17.9 (CH_3), 20.5 (CH_3), 56.8 (OCH_3), 113.8, 123.7, 125.2, 126.6, 127.8, 129.4, 129.7, 130.6.

2,4-dimethyl-6-(2-methylnaphthalen-1-yl)aniline (**31**).

The compound was synthesized according to General Procedure C and then purified by column chromatography on silica gel using hexane as an eluent; when methylnaphthalene was removed from the column, the system was changed to hexane: acetone (99: 1). The pure compound was isolated as grayish crystals. Mp = 106.5 °C (DME). The enantiomeric excess was determined by HPLC using a chiral column: OD-H, Mobile phase: hexane: isopropanol (95: 5); Flow: 1 mL/min; t1 = 8.259 min.; t2 = 8.788 min. (59.5%); λ = 254 nm. The specific rotation of the compound with an 19% ee was $[\alpha]_D = -1.2$ (*c* = 1.0, $CHCl_3$, λ = 594 nm, 20 °C). Yield: 92%. Elemental Analysis: found C, 86.72; H, 7.30; N, 5.25; theoretical: C, 87.31; H 7.33; N, 5.36.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.26 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.20 (s, 2H, NH_2), 6.74 (s, 1H), 7.00 (s, 1H), 7.36 (ddd, *J* = 8.2, 6.6 and 1.3 Hz, 1H), 7.43–7.47 (m, 3H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.85–7.86 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 17.9 (CH_3), 20.4 (CH_3), 20.5 (CH_3), 122.8, 124.8, 125.0, 125.7, 126.1, 127.5, 127.8, 128.8, 128.9, 130.4, 132.3, 132.6, 134.7, 139.3.

^{13}C NMR (DEPT 135, $CDCl_3$): δ 17.9 (CH_3), 20.4 (CH_3), 20.5 (CH_3), 125.0, 125.7, 126.1, 127.5, 127.8, 128.8, 128.9, 130.4.

2,4-dimethyl-6-(naphthalen-1-yl)aniline (**32**).

The compound was synthesized according to General Procedure C and then purified by column chromatography on silica gel using hexane as an eluent; when naphthalene was removed from the column, the system was changed to hexane: acetone (99: 1). The pure compound was isolated as pinkish crystals. Mp = 127.8 °C (DME). The enantiomeric excess was determined by HPLC using a chiral column: OJ-H, Mobile phase: hexane:isopropanol (80: 20); Flow: 1 mL/min; t1 = 10.971 min (52%).; t2 = 13.418 min.; λ = 254 nm. Due to the low enantiomeric excess of the compound of 4%, specific rotation was not determined. Yield: 93%. Elemental Analysis: found C, 87.01 H, 6.85; N, 5.54; theoretical: C, 87.41; H, 6.93; N, 5.66.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.26 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.33 (s, 2H, NH_2), 6.88 (m, 1H), 7.01 (m, 1H), 7.43 (ddd, *J* = 8.2, 6.6 and 1.3 Hz, 1H), 7.46 (dd, *J* = 6.9 and 1.3 Hz, 1H), 7.51 (ddd, *J* = 8.2, 6.6 and 1.3 Hz, 1H), 7.56 (dd, *J* = 8.2 and 6.9 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.91 (dd, *J* = 15.1 and 8.2 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 17.8 (CH_3), 20.4 (CH_3), 122.5, 125.8, 125.8, 125.9, 126.2, 126.2, 127.1, 127.6, 127.8, 128.2, 129.4, 130.6, 131.8, 133.8, 137.4, 139.8.

^{13}C NMR (DEPT 135, $CDCl_3$): δ 17.8 (CH_3), 20.4 (CH_3), 125.8, 125.9, 126.2, 126.2, 127.6, 127.8, 128.2, 129.4, 130.6.

9-(2-methylnaphthalen-1-yl)phenanthrene (**34**).

The compound was synthesized according to General Procedure C and then purified by column chromatography on silica gel using hexane as an eluent. The pure compound was isolated as colorless crystals. mp = 145.7 °C (lit. [37] mp = 143–144 °C crystallized from EtOH-acetone). The enantiomeric excess was determined by HPLC using a chiral column: OJ-H, Mobile phase: hexane: isopropanol (95: 5); Flow: 1 mL/min; t1 = 11.078 min.; t2 = 16.962 min. (67%); λ = 254 nm. The specific rotation of the compound with an 35% ee was $[\alpha]_D = +55.4$ (*c* = 1.01, CHCl3, λ = 589 nm, 20 °C). Yield: 80%. Elemental Analysis: found C, 92.80; H, 5.81; theoretical: C, 94.30; H, 5.70.

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.20 (s, 3H, CH_3), 7.23 (ddd, *J* = 7.9, 6.6 and 1.3 Hz, 1H), 7.29–7.32 (m, 2H), 7.39–7.43 (m, 2H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.66–7.70 (m, 3H), 7.75 (ddd, *J* = 8.4, 6.9 and 1.4 Hz, 1H), 7.91–7.94 (m, 3H), 8.83–8.86 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 20.5 (CH_3), 122.6, 122.9, 124.8, 125.9, 126.2, 126.6, 126.6, 126.7, 126.8, 127.6, 127.8, 128.4, 128.6, 130.1, 131.7, 131.8, 132.0, 134.5, 135.9, 136.0.

^{13}C NMR (DEPT 135, $CDCl_3$): δ 20.5 (CH_3), 122.67, 122.9, 124.8, 125.9, 126.2, 126.5, 126.6, 126.7, 126.8, 127.6, 127.8, 128.4, 128.6.

2′-methoxy-[1,1′-binaphthalen]-2-yl diethylcarbamate (**36**).

The compound was synthesized according to General Procedure B and then purified by column chromatography on silica gel using hexane:acetone (9:1) as an eluent; when 2-methoxy naphthalene was removed from the column, the system was changed to hexane: acetone (6: 1). The pure compound was isolated as yellowish crystals. Mp = 110.7 °C. The enantiomeric excess was determined by HPLC using a chiral column: OJ-H, Mobile phase: hexane:ethanol (98: 2); Flow: 1 mL/min; t1 = 23.080 min.; t2 = 25.855 min. (79.5%); λ = 254 nm. The specific rotation of the compound with an 59% ee was $[\alpha]_D$ = +30.8 (*c* = 1.02, $CHCl_3$, λ = 589 nm). Yield: 72%. HRMS (ESI): m/z = 400.1925 [$C_{26}H_{25}NO_3$+H]+, m/z (theor.) = 400.1907, diff. = 5.00 ppm. Mobile phase: CH_3CN: H_2O (65: 35), Flow: 0.3 mL/min. Elemental Analysis: found C, 77.82; H, 6.22; N, 3.41 theoretical: C, 78.17; H, 6.31; N, 3.51.

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.43–0.46 (m, 3H, CH_3), 0.82–0.85 (m, 3H, CH_3), 2.68–2.69 (m, 2H, CH_2), 3.03–3.11 (m, 2H, CH_2), 3.76 (s, 3H, OCH_3), 7.19–7.21 (m, 1H), 7.24 (ddd, *J* = 8.51, 6.31 and 1.26 Hz, 1H, CH), 7.28 (dd, *J* = 4.4 and 0.9 Hz, 2H, CH_2), 7.31 (ddd, *J* = 8.1, 6.5 and 1.4 Hz, 1H), 7.42 (d, *J* = 9.1 Hz, 1H), 7.44 (dd, *J* = 7.9 and 4.1 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 13.0 (CH_3), 13.1 (CH_3), 41.2 (CH_2), 41.7 (CH2), 56.8 (OCH_3), 113.8, 118.5, 122.6, 123.6, 124.6, 125.0, 125.6, 126.0, 126.2, 126.5, 127.6, 1281, 128.7, 129.0, 129. 7, 131.4, 133.6, 133.9, 147.4, 153.5, 1554.0.

^{13}C NMR (DEPT 135, $CDCl_3$): δ 13.0 (CH_3), 13.1 (CH_3), 41.2 (CH_2), 41.7 (CH_2), 56.8 (OCH_3), 113.8, 122.6, 123.6, 125.0, 125.6, 126.0, 126.2, 126.5, 127.6, 128.1, 128.7, 129.7.

2′-methyl-[1,1′-binaphthalen]-2-yl diethylcarbamate (**37**).

The compound was synthesized according to General Procedure A and then purified by column chromatography on silica gel using hexane: acetone (9: 1) as an eluent. The pure compound was isolated as yellowish crystals. Mp = 100.5 °C. The enantiomeric excess was determined by HPLC using a chiral column: OJ-H, Mobile phase: hexane: isopropanol (95: 5); Flow: 1 mL/min; t1 = 8.204 min.; t2 = 10.755 min. (83.5%); λ = 254 nm. The specific rotation of the compound with an 67% ee was $[\alpha]_D$ = +65,4 (*c* = 1.105, $CHCl_3$, λ = 589 nm). Yield: 82%. HRMS (ESI): m/z = 370.1782 [$C_{26}H_{25}NO_2$+H]+, m/z (theor.) = 370.1802, diff. = −5.40 ppm.

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.35–0.38 (m, 3H, $N(CH_2CH_3)_2$), 0.81–0.83 (m, 3H, $N(CH_2CH_3)_2$), 2.11 (s, 3H, CH_3), 2.55–2.64 (m, 2H, CH_2), 3.01–3.07 (m, 2H, CH_2), 7.18–7.25 (m, 3H), 7.27–7.30 (m, 1H), 7.36–7.39 (m, 1H), 7.43–7.48 (m, 1H), 7.47 (d, *J* =8.4 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 12.9 ($N(CH_2CH_3)_2$), 12.9 $N(CH_2CH_3)_2$), 20.3 (CH_3), 41.2 ($N(CH_2CH_3)_2$), 41.7 ($N(CH_2CH_3)_2$), 122.7, 124.8, 125.2, 125.6, 125.9, 126.0, 126.5, 127.5, 127.5, 127.7, 128.1, 128.5, 128.7, 131.2, 131.5, 132.0, 133.1, 133.1, 135.3, 147.1, 153.4.

^{13}C NMR (DEPT 135, $CDCl_3$): δ 12.9 ($N(CH_2CH_3)_2$), 12.9 ($N(CH_2CH_3)_2$), 20.3 (CH_3), 41.2 ($N(CH_2CH_3)_2$), 41.7 ($N(CH_2CH_3)_2$), 122.7, 124.8, 125.2, 125.6, 125.9, 126.0, 126.5, 127.5, 127.7, 128.1, 128.5, 128.7.

2,2′-bis-[1,1′-binaphthalen]-2-yl *N*,*N*-diethylcarbamate (**39**).

The compound was synthesized according to General Procedure B and then purified by column chromatography on silica gel using hexane: acetone (9: 1) as an eluent. The pure compound was isolated as a yellowish solid. Mp = 66–68 °C (lit. [38] mp = 67–68 °C). The enantiomeric excess was determined by HPLC using a chiral column: OD-H, Mobile phase: hexane: ethanol (99.5: 0.5); Flow: 0.5 mL/min; t1 = 21.610 min.; t2 = 24.678 min. (75%); λ = 254 nm. The specific rotation of the compound with an 50% ee (*R*) was $[\alpha]_D$ = +62.0 (*c* = 0.995, $CHCl_3$, λ = 589 nm), (lit. [38] $[\alpha]_D$ = +117.0; *c* = 2.0, $CHCl_3$, λ = 589 nm). Yield: 80%. Elemental Analysis: found C, 73.83; H, 6.53; N, 5.61; theoretical: C, 74.36; H, 6.66; N, 5.78.

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.37–0.40 (m, 6H, CH_3), 0.84–0.87 (m, 6H, CH_3), 2.63–2.71 (m, 4H, CH_2), 2.99–3.13 (m, 4H, CH_2), 7.29 (ddd, *J* = 7.9, 6.6 and 1.3 Hz, 1H), 7.33–7.35 (m, 1H), 7.43 (ddd, *J* = 8.1, 6.7 and 1.3 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 12.9 (CH_3), 13.00 (CH_3), 41.3 (CH_2), 41.8 (CH_2), 122.5, 123.7, 125.2, 126.1, 126.4, 127.7, 128.8, 131.2, 133.4, 147.5, 153.3.

^{13}C NMR (DEPT 135, $CDCl_3$): δ 12.9 (CH_3), 13.00 (CH_3), 41.3 (CH_2), 41.8 (CH_2), 122.5, 125.2, 126.1, 126.4, 127.7, 128.8.

2-methoxy-2′-(2-pivaloyloxyethoxy)-1,1′-binaphthyl (**41**).

The compound was synthesized according to General Procedure B and then purified by column chromatography on silica gel using hexane: acetone (99: 1) as an eluent. The pure compound was isolated as an oily liquid. The enantiomeric excess was determined by HPLC using a chiral column: OD-H, Mobile phase: hexane: ethanol (99.5: 0.5); Flow: 0.5 mL/min; t1 = 20.882 min. (68%); t2 = 22.780 min.; λ = 254 nm. The specific rotation of the compound with an 36% ee was $[\alpha]_D$ = +13.7 (*c* = 1.015, $CHCl_3$, λ = 589 nm). Yield: 72%. HRMS (ESI): m/z = 451.1883 [$C_{28}H_{28}O_4$+Na]+, m/z (teor.) = 451.1880, diff. = 0.66 ppm

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.99 (s, 9H, CH3), 3.78 (s, 3H, OCH_3), 4.05–4.07 (m, 2H, CH_2), 4.10–4.19 (m, 2 H, CH_2), 7.11 (d, *J* = 16.4 Hz, 1H), 7.13 (d, *J* = 16.7 Hz, 1H), 7.19–7.25 (m, 2H), 7.30–7.33 (m, 1H), 7.33–7.37 (m, 1H), 7.46 (dd, *J* = 9.0 and 2.7 Hz, 2H), 7.87 (dd, *J* = 18.9 and 9.1 Hz, 2H), 7.97 (dd, J = 9.0 and 3.0 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 26.9 (CH_3), 38.5 ($C(CH_3)_3$), 56.7 (OCH_3), 63.0 (CH_2), 67.7 (CH_2), 113.9, 116.3, 119.2, 121.0, 123.4, 123.8, 125.1, 125.4, 126.3, 126.3, 127.8, 127.9, 129.1, 129.3, 129.4, 129.6, 133.9, 134,0, 153.9, 154.8, 178.3.

^{13}C NMR (DEPT 135, $CDCl_3$): δ 26.9 (CH_3), 56.7 (OCH_3), 63.0 (CH_2), 67.7 (CH_2), 113.9, 116.3, 123.4, 123.9, 125.1, 125.4, 126.3, 126.3, 127.8, 127.9, 129.4, 129.4.

2-((2′-((diethylcarbamoyl)oxy)-[1,1′-binaphthalen]-2-yl)oxy)ethyl pivalate (**42**).

The compound was synthesized according to General Procedure B and then purified by column chromatography on silica gel using hexane: acetone (95: 5) as an eluent. The pure compound was isolated as a yellowish solid. Mp = 91.8 °C. The enantiomeric excess was determined by HPLC using a chiral column: OJ-H, Mobile phase: hexane: ethanol (98: 2); Flow: 1 mL/min; t1 = 12.668 min.; t2 = 17.935 min. (68%); λ = 254 nm. The specific rotation of the compound with an 36% ee was [α] = + 19.9 (*c* = 1.005, $CHCl_3$, λ = 589 nm, 20 °C). Yield: 87%. Elemental Analysis: found C, 74.34; H, 6.74; N, 2.73; theoretical: C, 74.83; H, 6.87; N, 2.73.

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.42–0.45 (m, 3H, $N(CH_2CH_3)_2$), 0.80–0.82 (m, 3H, $N(CH_2CH_3)_2$), 1.01 (s, 9H, $(CH_3)_3$), 2.68–2.69 (m, 2H, $N(CH_2CH_3)_2$), 2.97–3.09 (m, 2H, $N(CH_2CH_3)_2$), 4.04–4.12 (m, 4H, OCH_2CH_2O), 7.23–7.26 (m, 2H), 7.28–7.29 (m, 2H), 7.35 (ddd, *J* = 7.9, 6.4 and 2.2 Hz, 1H), 7.42 (d, *J* = 9.0 Hz, 1H), 7.42–7.45 (m, 1H), 7.61 (d, *J* = 9.1 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.97 (t, *J* = 8.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 12.9 $N(CH_2CH_3)_2$), 13.1 $N(CH_2CH_3)_2$), 26.9(($CH_3)_3$), 38.5 ($C(CH_3)_3$), 41.2 $N(CH_2CH_3)_2$), 41.7 $N(CH_2CH_3)_2$), 62.9 (OCH_2CH_2), 67.6 (OCH_2CH_2), 115.7, 119.9, 122.5, 124.0, 124.4, 125.0, 125.7, 125.9, 126.1, 126.5, 127.5, 128.0, 128.7, 129.4, 129.6, 131.3, 133.5, 133.9, 147.4, 153.4, 153.9, 178.3.

^{13}C NMR (DEPT 135, $CDCl_3$): δ 12.9 $N(CH_2CH_3)_2$), 13.1 $N(CH_2CH_3)_2$), 26.9 (($CH_3)_3$), 41.2 $N(CH_2CH_3)_2$), 41.7 $N(CH_2CH_3)_2$), 62.9 (OCH_2CH_2), 67.6 (OCH_2CH_2), 115.7, 122.5, 124.0, 125.0, 125.7, 125.9, 126.1, 126.5, 127.5, 128.0, 128.7, 129.6.

(2-methoxy-1,1′-binaphthalen-2-yl)methyl 2,2′-dimethylpropanoate (**44**).

The compound was synthesized according to General Procedure B and then purified by column chromatography on silica gel using hexane: acetone (98: 2) as an eluent. The pure compound was isolated as an oily liquid. The enantiomeric excess was determined by HPLC using a chiral column: OD-H, Mobile phase: hexane: ethanol (98: 2); Flow: 0.5 mL/min; t1 = 7.395 min.; t2 = 7.865 min (93%); λ = 254 nm. The specific rotation of the compound with an 86% ee was $[\alpha]_D$ = −10.7 (*c* = 1.025, $CHCl_3$, λ = 589 nm). Yield: 66%. HRMS (ESI): m/z = 421.1827 [$C_{27}H_{26}O_3$+H]+, m/z (teor.) = 421.1774, diff. = 12.58 ppm.

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.07 (s, 9H, $(CH_3)_3$), 3.78 (s, 3H, OCH_3), 4.79 (d, *J* = 12.9 Hz, 1H, CH_2), 4.97 (d, *J* = 12.9 Hz, 1H, CH_2), 6.98–7.00 (m, 1H), 7.16–7.18 (m, 1H), 7.20 (ddd, *J* = 8.5, 6.9 and 1.3 Hz, 1H), 7.25 (ddd, *J* = 8.4, 6.8 and 1.3Hz, 1H), 7.32 (ddd,

J = 8.1, 6.9 and 1.3 Hz, 1H), 7.44–7.48 (m, 2H, CH), 7.69 (d, *J* = 8.5 Hz, 1H), 7.84–7.88 (m, 1H), 7.93 (d, *J* = 8.3Hz, 1H), 7.98–8.02 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 27.0 (CH_3), 38.7 ($C(CH_3)_3$) 56.4 (OCH_3), 64.8 (CH_2), 113.3, 119.7, 123.6, 125.1, 125.7, 125.9, 126.1, 126.2, 126.3, 126.7, 126.8, 127.2, 127.6, 127.8, 127.9, 128.0, 128.0, 128.1, 129.0, 129.4, 130.0 132.9, 133,0, 133.2, 133.2, 133.9, 154.4, 178.3.

^{13}C NMR (DEPT 135, $CDCl_3$): δ 27.0 (CH3), 56.4 (OCH3), 64.8 (CH2), 113.3, 123.6, 125.1, 125.7, 125.9, 126.2, 126.3, 126.7, 127.9, 128.0, 128.0, 130.0.

2-(2′-((diethylcarbamoyl)oxy)-[1.1′-binaphthalen]-2-yl)methyl pivalate (**45**).

The compound was synthesized according to General Procedure B and purified by column chromatography on silica gel using hexane: acetone (99: 1) as an eluent. The pure compound was isolated as colorless crystals. Mp = 69–72 °C. The enantiomeric excess was determined by HPLC using a chiral column: OD-H, Mobile phase: hexane: ethanol (98: 2); Flow: 1 mL/min; t1 = 7.861 min.; t2 = 8,513 min. (88%); λ = 254 nm. The specific rotation of the compound with a 76% ee was $[\alpha]_D$ = +31.5 (*c* = 1.0, $CHCl_3$, λ = 589 nm). Yield: 47%. Elemental Analysis: found C, 75.87; H, 6.80; N, 2.73; theoretical: C, 76.99; H, 6.88; N, 2.90.

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.37–0.40 (m, 3H, $N(CH_2CH_3)_2$), 0.78–0.81 (m, 3 H, $N(CH_2CH_3)_2$), 1.11 (s, 9H, $(CH_3)_3$), 2.65 (q, *J* = 6.9 Hz, 2H, $N(CH_2CH_3)_2$), 2.98–3.09 (m, 2H, $N(CH_2CH_3)_2$), 4.83 (d, *J* = 12.9 Hz, 1H, CH_2), 5.00 (d, *J* = 12.9 Hz, 1H, CH_2), 7.21–7.23 (m, 1H), 7.28–7.32 (m, 3H), 7.45–7.48 (m, 2H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.97 (t, *J* = 7.9 Hz, 2H), 8.02 (d, *J* = 8.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 12.9 $N(CH_2CH_3)_2$), 13.0 $N(CH_2CH_3)_2$), 27.1 (CH_3), 41. $N(CH_2CH_3)_2$), 41.8 $N(CH_2CH_3)_2$), 64.4 (CH2), 122.5, 125.4, 125.5, 125.7, 125.8, 126.0, 126.4, 126.6, 126.6, 127.6, 128.1, 128.3, 129.3, 131.4, 132.1, 132.7, 133.1, 133.3, 147.3, 178.1.

^{13}C NMR (DEPT 135, $CDCl_3$): δ 12.9 $N(CH_2CH_3)_2$), 13.0 $N(CH_2CH_3)_2$), 27.1 (CH_3), 41.2 $N(CH_2CH_3)_2$), 41.8 $N(CH_2CH_3)_2$), 64.4 (CH_2), 122.5, 125.4, 125.5, 125.8, 126.1, 126.4, 126.6, 126.6, 127.6, 128.1, 128.4, 129.3.

9-(2-methoxynaphthalen-1-yl)phenanthrene (**46**).

The compound was synthesized according to General Procedure C and then purified by column chromatography on silica gel using hexane as an eluent. The pure compound was isolated as colorless crystals. Mp = 184.9–187.7 °C. The enantiomeric excess was determined by HPLC using a chiral column: OJ-H, Mobile phase: hexane: ethanol (98: 2); Flow: 1 mL/min; t1 = 17.219 min. (52.5%); t2 = 26.766 min.; λ = 254 nm. Due to the low enantiomeric excess of the compound of 5%, specific rotation was not determined. Yield: 91%. HRMS (ESI): m/z = 335.1454 $[C_{25}H_{18}O+H]+$, m/z (teor.) = 335.1430, diff. = 7.16 ppm.

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.79 (s, 3H, CH_3), 7.21–7.24 (m, 1H), 7.28–7.30 (m, 1H), 7.34 (ddd, *J* = 8.2, 6.6 and 1.3 Hz, 1H), 7.39–7.40 (m, 2H), 7.49 (d, *J* = 9.1 Hz, 1H), 7.62–7.67 (m, 2H), 7.72 (ddd, *J* = 8.2, 6.9 and 1.3 Hz, 1H), 7.73 (s, 1H), 7.89–7.91 (m, 2H), 8.02 (d, *J* = 8.8 Hz, 1H), 8.80–8.83 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 56.8 (OCH_3), 113.8, 122.6, 122.8, 123.6, 125.5, 126.4, 126.5, 126.5, 126.6, 126.6, 126.8, 127.8, 128.7, 129.1, 129.6, 130.3, 131.9, 132.1, 134.3, 154.8.

^{13}C NMR (DEPT 135, $CDCl_3$): δ 56.8 (OCH_3), 113.8, 122.6, 122.8, 123.6, 125.5, 126.4, 126.5, 126.5, 126.6, 126.6, 126.8, 127.8, 128.7, 129.1, 129.6.

2-(2-methoxynaphthalen-1-yl)phenyl 2,2-dimethylpropanoate (**48**).

The compound was synthesized according to General Procedure A and then purified by column chromatography on silica gel using hexane:acetone (9:1) as an eluent. The pure compound was isolated as an oily liquid. The enantiomeric excess was determined using the europium tris [3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] as an optically active NMR shift reagent. Signals from which it was found that the compound exhibited an enantiomeric excess of 3% were 0.84 ppm and 0.86 ppm derived from hydrogen in the pivaloyl group. These signals were derived from split and shifted towards higher chemical shifts signal at 0.72 ppm. Yield: 35%. HRMS (ESI): m/z = 357.1439 $[C_{22}\ H_{22}O_3+Na]+$, m/z (teor.) = 357.1461, diff. = −6.16 ppm.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.73 (s, 9H, $(CH_3)_3$), 3.84 (s, 3H, OCH_3), 7.25–7.27 (m, 1H, CH), 7.32–7.36 (m, 3H), 7.37–7.38 (m, 3H), 7.47–7.49 (m, 1H), 7.79–7.81 (m, 1H), 7.88 (d, *J* = 8.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 26.5 (CH_3), 38.6, ($C(CH_3)_3$), 56.7 (OCH_3), 113.4, 120.4, 122.7, 123.5, 125.2, 125.6, 126.4, 127.6, 128.6, 128.8, 129.4, 129.5, 132.5, 133.5, 149.5, 154.2, 176.1.

^{13}C NMR (DEPT 135, $CDCl_3$): δ = 26.5 (CH_3), 56.7 (OCH_3), 113.4, 122.7, 123.5, 125.2, 125.6, 126.4, 127.6, 128.6, 129.4, 132.5.

2-(2-methoxynaphthalen-1-yl)phenyl diethylcarbamate (**50**).

The compound was synthesized according to General Procedure A and then purified by column chromatography on silica gel using hexane: acetone (9: 1) as an eluent. The pure compound was isolated as a colorless oily liquid. Using the HPLC method or chemical shift reagent europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate], the enantiomers were not distinguished. Yield: 85%. HRMS (ESI): m/z = 350.1750 [$C_{22}H_{23}NO_3$+H]+, m/z (teor.) = 350.1751, diff. = −0.29 ppm

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.46–0.49 (m, 3H, $N(CH_2CH_3)_2$), 0.80–0.84 (m, 3H, $N(CH_2CH_3)_2$), 2.67–2.71 (m, 2H, $N(CH_2CH_3)_2$), 3.00–3.12 (m, 2H, $N(CH_2CH_3)_2$), 3.83 (s, 3H, OCH_3), 7.30–7.36 (m, 5H), 7.42–7.49 (m, 3H, CH), 7.78–7.80 (m, 1H), 7.88 (d, *J* = 8.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 12.9 $N(CH_2CH_3)_2$), 13.2 $N(CH_2CH_3)_2$), 41.1 $N(CH_2CH_3)_2$), 41.7 $N(CH_2CH_3)_2$), 56.7 (OCH_3), 113.5, 120.9, 122.5, 123.0, 123.4, 124.8, 125.4, 126.3, 127.5, 128.4, 128.8, 128.9, 129.3, 131.03, 132.2, 133.5, 149.9, 153.3, 154.2.

^{13}C NMR (DEPT 135, 125.77 MHz, $CDCl_3$): δ 12.9 $N(CH_2CH_3)_2$), 13.2 $N(CH_2CH_3)_2$), 41.1 $N(CH_2CH_3)_2$), 41.6 $N(CH_2CH_3)_2$), 56.7 (OCH_3), 113.5, 123.0, 123.4, 124.8, 125.4, 126.3, 127.5, 128.4, 129.3, 132.2.

9-(naphthalen-1-yl)phenanthrene (**51**).

The compound was synthesized according to General Procedure C and then purified by column chromatography on silica gel using hexane as an eluent. The pure compound was isolated as colorless crystals. Mp = 115.9–117.2 °C (DME) (lit. [39] mp = 126–127 °C). The enantiomeric excess was determined by HPLC using a chiral column: AS-H, Mobile phase: hexane: isopropanol (90: 10); Flow: 0.2 mL/min; t1 = 26.394 min. (51%); t2 = 28.445 min.; λ = 254 nm. Due to the low enantiomeric excess of the compound of 3%, specific rotation was not determined. Yield: 98%. Elemental Analysis: found C, 93.74; H, 5.12 theoretical: C, 94.70; H, 5.30.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.31 (m, 1H, CH), 7.39–7.44 (m, 2H), 7.45–7.51 (m, 2H), 7.57–7.59 (m, 1H), 7.62–7.68 (m, 3H), 7.72–7.75 (m, 1H), 7.80 (s, 1H), 7.91–7.93 (m, 1H), 7.97–8.00 (m, 2H, CH), 8.82 (t, *J* = 8.8Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 122.6, 122.7, 125.4, 125.8, 126.0, 126.5, 126.5, 126.6, 126.7, 126.8, 127.4, 127.8, 128.0, 128.19, 128.4, 128.7 130.2, 130.3, 131.6, 132.1, 132.9, 133.5, 137.5, 137.1, 138.4.

^{13}C NMR (DEPT 135, $CDCl_3$): δ 122.6, 122.7, 125.4, 125.8, 126.0, 126.5, 126.5, 126.6, 126.7, 126.9, 127.4, 127.8, 128.0, 128.1, 128.4, 128.7.

X-ray crystal structure determination of Pd complex **(*S,Sa*)-12** and cocrystal of compound **9** with TADDOL.

The labeling scheme of atoms in coordination units of **(*S,Sa*)-12** is shown in Figure 3.

Crystal data for the Pd complex ***(S,Sa)*-12** and a cocrystal of compound **9** with TADDOL are provided in Tables 18–20.

Diffraction reflections were collected on Bruker Nonius Kappa CCD and on Xcalibur Sapphire2 diffractometers with Mo Kα radiation (0.71073 Å). The absorption corrections were applied by the multi-scan method from Blessing [40]. Crystal structure for compound **9** was refined with anisotropic non-hydrogen atoms. The proper configuration was established on the base of the synthesis route and the presence of the TADDOL molecule in the cocrystal structure.

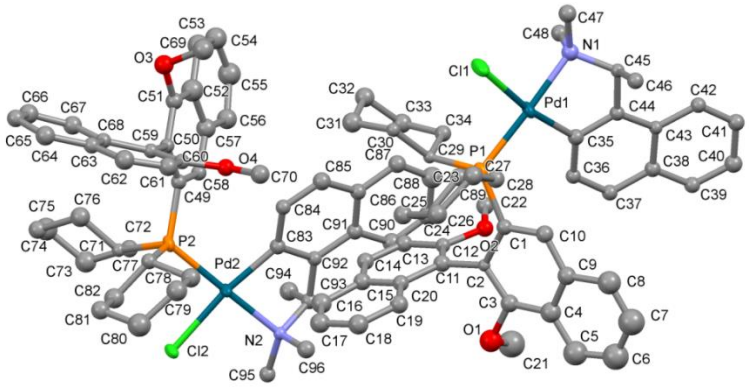


Figure 3. Labeling scheme of atoms in coordination units of Pd complex **12**. Hydrogen atoms and solvent molecules were omitted for clarity.

Table 18. Crystal data and structure refinement for Pd complex and cocrystal of **9** with TADDOL.

Formula	**$2(C_{48}H_{55}ClNO_2PPd)$, $9(CH_3OH)$, $2(H_2O)$**	**$C_{34}H_{39}O_3P$, $C_{31}H_{30}O_4$**
Formula weight	2005.75	993.17
Wavelength, temperature	0.71073 A, 100(2) K	0.71073 A, 293 (2) K
Crystal system, space group	Monoclinic, $P2_1$	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	a = 14.0761(1) Å b = 25.813(1) Å c = 14.586(1) Å beta = 90.26(1)°	a = 9.8002(6) Å b = 18.1101(10) Å c = 30.8874(18) Å
Volume	5299.7(4) $Å^3$	5482.0(6) $Å^3$
Z, Calculated density	2, 1.257 Mg/m^3	4, 1.203 Mg/m^3
Absorption coefficient	0.480 mm^{-1}	0.104 mm^{-1}
F(000)	2100	2120
Crystal size	0.28 × 0.10 × 0.05 mm	0.4 × 0.2 × 0.2 mm
Reflections collected / unique	15122 / 10364 [R_{int} = 0.0458]	46268 / 9878 [R_{int} = 0.0849]
Completeness to theta = 25.96	98.0 %	99.0%
Max. and min. transmission	0.986 and 0.891	0.975 and 0.979
Data / restraints / parameters	10364 / 10 / 545	9878 / 0 / 664
Goodness-of-fit on F^2	1.074	0.986
Final R indices [I>2sigma(I)]	R1 = 0.0585, wR2 = 0.1518	R_1 = 0.0608, wR_2 = 0.1326
R indices (all data)	R1 = 0.0605, wR2 = 0.1553	R_1 = 0.1003, wR_2 = 0.1529
Absolute structure parameter (Flack parameter)	0.03(5)	0.01(8)
Largest diff. peak and hole	0.833 and −0.791 e.$Å^{-3}$	0.51 and −0.31 e.$Å^{-3}$
CCDC No.	2222975	2232483

Table 19. Bond lengths (Å) and angles (°) for Pd complex and cocrystal of **9** with TADDOL.

Bond		**Bond**		**Angle**		**Angle**	
Pd complex							
C1-P1	1.83(2)	C49-P2	1.84(2)	C35-Pd1-N1	79.7(5)	C83-Pd2-N2	80.5(5)
C23-P1	1.87(2)	C71-P2	1.85(1)	C35-Pd1-P1	99.9(4)	C83-Pd2-P2	98.8(4)
C29-P1	1.88(1)	C77-P2	1.86(2)	N1-Pd1-P1	175.4(4)	N2-Pd2-P2	179.2(3)
P1-Pd1	2.275(4)	P2-Pd2	2.290(4)	C35-Pd1-Cl1	171.0(4)	C83-Pd2-Cl2	172.1(4)
Cl1-Pd1	2.391(4)	Cl2-Pd2	2.404(3)	N1-Pd1-Cl1	91.6(3)	N2-Pd2-Cl2	91.7(3)
N1-Pd1	2.12(1)	N2-Pd2	2.14(1)	P1-Pd1-Cl1	89.0(1)	P2-Pd2-Cl2	89.1(1)
C35-Pd1	2.00(1)	C83-Pd2	2.00(1)				
cocrystal with TADDOL							
P1-O1	1.501(3)	P1-C1	1.832(4)	P1-C29	1.820(5)	P1-C23	1.809(4)

Table 20. Intra- and intermolecular contacts in Pd complex and cocrystal of **9** with TADDOL.

D–H . . . A	D–H	D . . . A	H . . . A	Angle D–H . . . A
Pd complex				
C34-H34B...Pd1	0.99	3.33(1)	2.77	116.4
C46-H46C...Pd1	0.98	3.42(1)	2.92	112.0
C78-H78A...Pd2	0.99	3.41(1)	2.88	114.4
C94-H94A...Pd2	0.98	3.44(1)	2.94	112.1
C54–H54 . . . C38 [i]	0.95	3.69(2)	2.85	148
C54–H54 . . . C43 [i]	0.95	3.57(3)	2.68	156
C8–H8 . . . C55 [ii]	0.95	3.58(2)	2.78	142
C65–H65 . . . C5 [iii]	0.95	3.74(2)	2.85	157
C13–H13 . . . C86	0.95	3.62(2)	2.78	148
O12 . . . Cl1 [iv]		3.23(1)		
O11 . . . Cl2 [v]		3.16(1)		
O5 . . . O11		2.74(3)		
O6 . . . O5		2.84(4)		
O7 . . . O6 [i]		2.93(6)		
O8 . . . O7 [v]		2.52(5)		
O9 . . . O8		2.70(4)		
O10 . . . O9 [ii]		2.96(4)		
O13 . . . O12		2.74(2)		
O14 . . . O13 [vi]		2.83(4)		
cocrystal with TADDOL				
O6–H6A . . . O7	0.82	2.600(5)	1.785	172
O7–H7A . . . O1	0.82	2.602(4)	1.800	165

Symmetry codes: [i] 1 − x, −1/2 + y, 1 − z; [ii] 1 − x, 1/2 + y, 1 − z; [iii] −x, −1/2 + y, 1 − z; [iv] x, y, 1 + z; [v] 1 + x, y, z; [vi] 1 − x, −1/2 + y, 2 − z.

The compound **12** has the formula $2(C_{48}H_{55}ClNO_2PPd)$ $9(CH_3OH)$ $2(H_2O)$ and crystalizes in the monoclinic $P2_1$ space group as a solvate of a pure *(S,Sa)*-diastereoisomer with two neutral coordination units, nine methanol molecules, and two water molecules in the asymmetric part. Due to the very poor crystals of the Pd complex, only the Pd, P, and Cl atoms were refined anisotropically. Further calculations with all non-hydrogen atoms refined anisotropically presented no better solution. The hydrogen atoms in the coordination units were introduced at calculated positions and refined riding on their carrier atoms. The hydrogen atoms from solvent molecules were omitted due to the low quality of the experimental data. The absolute configuration of the chiral complex was confirmed by using the Flack parameter [41]. The supplementary crystallographic data for Pd complex **(*S*,*Sa*)-12** CCDC No. 2222975 and for the cocrystal of compound **(*Ra*)-9** with TADDOL CCDC No. 2232483 can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, accessed on 1 December 2022.

Crystal data for Pd complex **(*S*,*Sa*)-12** $C_{105}H_{130}Cl_2N_2O_{15}P_2Pd_2$ (M = 2005.75 g/mol): monoclinic, space group $P2_1$, a = 14.0761(1) Å, b = 25.813(1) Å, c = 14.586(1) Å, β = 90.26(1)°, V = 5299.7(4) Å^3, Z = 2, T = 100(2) K, μ(MoKα) = 0.480 mm^{-1}, *Dcalc* = 1.257 g/cm^3, 15122 reflections measured (2.8° ≤ 2Θ ≤ 51.92°), 10364 unique (R_{int} = 0.0458, R_{sigma} = 0.0526) which were used in all calculations. The final R_1 was 0.0585 (>2σ(I)) and wR_2 was 0.1553 (all data).

Crystal data for the cocrystal of compound **(*Ra*)-9** with TADDOL $C_{65}H_{69}O_7P$ (M =993.17 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 9.8002(6) Å, b = 18.1101(10) Å, c = 30.8874(18) Å, V = 5482.0(6) Å^3, Z = 4, T = 293(2) K, μ(MoKα) = 0.104 mm^{-1}, *Dcalc* = 1.203 g/cm^3, 46268 reflections measured (4.688° ≤ 2Θ ≤ 50.482°), 9878 unique (R_{int} = 0.0849, R_{sigma} = 0.0747), which were used in all calculations. The final R_1 was 0.0608 (I > 2σ(I)) and wR_2 was 0.1529 (all data).

4. Conclusions

In conclusion, new chiral non-racemic *(Sa)*- and *(Ra)*-*BisNap*-Phos ligands are easily available from inexpensive starting materials in straightforward synthesis performed under readily affordable conditions. The utilization of *BisNap*-Phos in Suzuki-Miyaura coupling was studied in detail, including the asymmetric version of this reaction. The effects of the catalyst, base, solvent, surfactant, and other reaction conditions were carefully evaluated. The palladium complexes of *BisNap*-Phos were highly catalytically active in aqueous and anhydrous mediums. A wide range of coupling products were obtained in excellent yields with good stereoselectivities (up to 86% ee). The *(Sa)*- and *(Ra)*-*BisNap*-Phos-based palladium catalysts appear to be more efficient than the catalysts based on commercially available ligands in the benchmark of asymmetric Suzuki–Miyaura couplings. Further applications of the *BisNap*-Phos in asymmetric catalysis are currently ongoing in our laboratory.

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Data Availability Statement: The data supporting reported results can be received from the Authors.

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Conflicts of Interest: The authors declare no conflict of interest.

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