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Pd(II) complexes of monodentate deoxycholic acid derived binaphthyl diamido phosphites as chiral catalysts in the asymmetric Suzuki-Miyaura cross-coupling

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ABSTRACT

Chiral binaphthyl diamidophosphites derived from deoxycholic acid were synthesized and used as ligands for the preparation of mononuclear Pd(II) complexes, which were employed as catalysts in the asymmetric Suzuki-Miyaura cross-coupling of arylboronic acids with aryl bromides. Among the different reaction parameters, the substrate concentration emerged as being crucial for the outcome of the reaction: the reaction was faster in a concentrated reaction mixture, and could be performed at 0 °C, where the reaction promoted by the Pd-complexes was more enantioselective affording cross-coupling products with ee up to 70%.

1. Introduction

Asymmetric catalysis with transition metal complexes is a powerful method to obtain valuable enantiomerically enriched products with different structures:[1] as a matter of fact enantioselective oxidation,[2] hydrogenation[3] and C–C bond forming reactions[4] can be effectively performed under asymmetric metal catalysis conditions. In this research area, the enantiomerically pure ligand and its metal complexes play the main role for the chemical as well as stereochemical outcome of the reaction. For this reason, a great deal of synthetic effort has been made with regards to the design and achievement of enantiopure ligands and metal complexes leading to efficient and selective organic transformations. In this field, enantiopure phosphorus ligands have been successfully used in different metal catalyzed asymmetric reactions and, among them, monodentate phosphorus ligands with P-heteroatom bonds, such as phosphites,[5] phopsphoramidites,[6] phosphinites and phosphonites[7] represent good alternatives to the bidentate chiral phosphane ligands. This type of ligands can be obtained more easily than the bidentate ones, they are more stable than phosphanes and a great variety of structures are accessible, starting from amines or alcohols with different structural and stereochemical features. In addition, the convenient choice of the atoms bonded to the phosphorus (only oxygen, nitrogen and oxygen, carbon and oxygen) allows fine-tuning of the donor–acceptor characteristics of the phosphorus atom, which affect the coordination properties of the ligand.

Over the last ten years enantiopure diamidophosphites, which present two P–N bonds embedded in a phospholidine ring and an exocyclic P–O bond, have emerged as promising phosphorus ligands. The possibility of changing both nitrogen and oxygen substituents allows high control on the steric and electronic characteristics of these ligands. In addition, the presence of two substituted nitrogen atoms increases the steric hindrance and the electronic density of the phosphorus atom with respect to phosphites and phosphoramidites. Chiral diamidophosphites, both mono- and bidentate, have been used in different enantioselective C–C bond forming reactions, such as Pd-catalyzed allylic substitutions,[8] Pd-catalyzed cycloaddition,[9] Pd-catalyzed hydrovinylation,[10] Rh-catalyzed hydroformylation,[11] Cu and Rh-catalyzed conjugate addition of organometallic reagents to enones.[12] However, despite the success obtained in different Pd-catalyzed enantioselective reactions, to the best of our knowledge no examples concerning the use of diamidophosphite ligands in the Pd-catalyzed asymmetric Suzuki-Miyaura cross-coupling reaction have been reported in the literature, although this reaction has received a great deal of attention because of the interest in the biaryl reaction products, whose structural motif is present in chiral auxiliaries[1c] as well as in bioactive compounds.[13] Other types of chiral phosphorus

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ligands have been used with this aim, mainly bidentate ligands, such as bishydrazones[14] or phosphine–carbene ligands,[15] and bulky monophosphines.[16] Some years ago we demonstrated for the first time that chiral monophosphites can be used as enantioselective Pd-ligand in asymmetric Suzuki-Miyaura cross-coupling reactions.[17] These ligands were biaryl phosphites of deoxycholic acid and the success in the Suzuki-Miyaura reactions was linked to the bulkiness of the phosphites, which allow a monosubstituted catalytic Pd-complex to form in the reaction environment, believed crucial for the outcome of the reaction. Following our interest in deoxycholic acid derived chiral ligands to be used in asymmetric catalysis,[18] we envisaged that monodentate diamidophosphites with a binaphthyl diazaphospholidine moiety linked to the steroidal scaffold of deoxycholic acid could be interesting ligands for Pd-catalyzed asymmetric Suzuki-Miyaura cross-coupling reactions, aimed at obtaining optically active biaryl derivatives. Herein we describe the synthesis and characterization of the ligands **1a-b** and their disubstituted mononuclear Pd(II)-complexes ($PdCl_2L_2$) **2a-b** (Fig. 1), as well as the use of these Pd-complexes as catalytic precursors for the asymmetric Suzuki-Miyaura cross-coupling reaction.

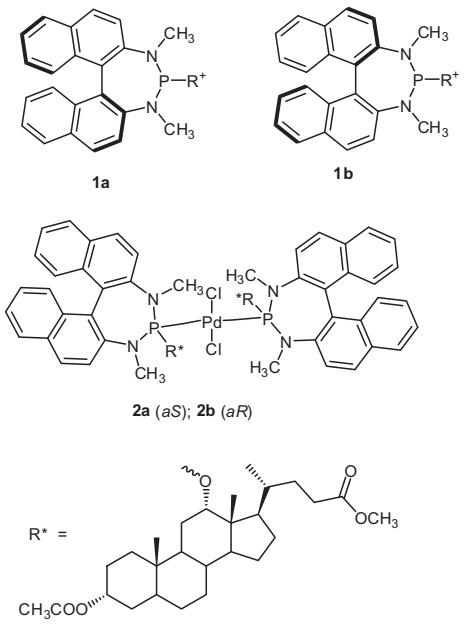


Figure 1. Structure of ligands and Pd(II) complexes.

2. Results and discussion

2.1. Synthesis and characterization of ligands and complexes

The diamido phosphites **1a-b** were synthesized in two consecutive steps by reacting methyl 3-acetyloxy-12-hydroxydeoxycholan-24-ate with PCl_3 in the presence of trimethylamine, and successive reaction of the crude bis-chlorophosphite with (*R*)- or (*S*)-*N*-*N*′-dimethyl-1,1′-binaphthalenediamine (DMBNDA) (Scheme 1) in boiling toluene, according to our previously described synthetic procedure.[18h]

The preparation and characterization of the new diamido phosphites **1a-b** are reported in the Experimental Section. The complexes **2a-b** of general formula $PdCl_2L_2$ were prepared by reacting two equivalents of ligand with $PdCl_2(PhCN)_2$ in toluene at room temperature (Scheme 2) for 15 min.

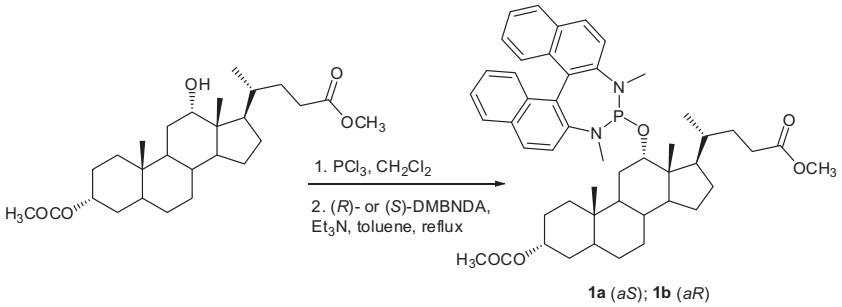
The Pd(II) complexes were obtained as yellow solids in almost quantitative yield. They are stable at room temperature under inert atmosphere and soluble in common organic solvents. They were fully characterized in solution by multinuclear (^1H, ^{31}P and ^{13}C) NMR spectroscopy: bidimensional ^1H–^{13}C HMBC, ^1H–^{13}C-HSQC, ^1H–^1H NOESY and ^1H–^1H COSY experiments were necessary to assign the majority of the signals.

The coordination of the ligand to the Pd center shifts the ^{31}P signal at higher fields in both the complexes (117.1 ppm for **2a** and 115.8 ppm for **2b**) with respect to the ^{31}P signal in the corresponding ligands (168.8 ppm for **1a** and 159.4 ppm for **1b**), probably because of the low σ-donor character of the ligands, as observed for other types of Pd(II) complexes with diamido phosphite ligands.[8e] Table 1 collects the signals of protons that are shifted because of the coordination of the ligand to the metal center: the different extent of the shift for corresponding protons of the two diastereomeric complexes is most likely the result of different arrangements of the ligands in the two complexes.

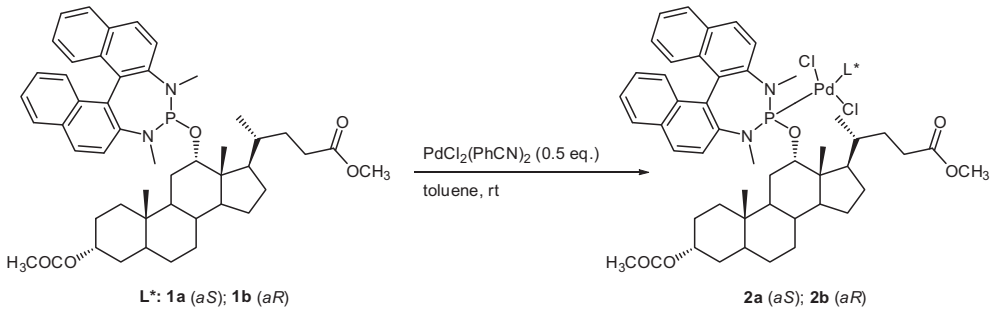
As far as the binaphthyl moiety is concerned, the coordination affects mainly the protons *a*, *b* and *a*′, *b*′, which are closer to the P atom. The extent of the shift upon coordination is higher for *a* than for *b* in both the complexes, most probably due to the higher distance of *b* from P, and hence from Pd. The coordination affects in different way the protons *a*′ and *b*′ of the two complexes: a low shift is observed for these protons when comparing **1a** and **2a**, whereas a shift comparable to that of protons *a* and *b* is detected when comparing **1b** and **2b**. Other significant differences were found for protons of the cholestanic backbone, which could be the result of conformational differences between the two complexes. The higher shifts observed for protons 1, 2 and 5 in passing from **1a** to **2a** can suggest the proximity of the Pd center to the A ring of the steroidal skeleton in **2a**, whereas the higher shifts of protons 12, 8 and 11 in going from **1b** to **2b** indicate that in complex **2b**, Pd is closer to the C ring of the cholestanic moiety.

2.2. Asymmetric Suzuki-Miyaura cross-coupling

The reaction between 1-bromo-2-methoxynaphthalene **3a** with *ortho*-tolylboronic acid **4a** (Scheme 3) promoted by the chiral Pd(II) complexes **2a-b** was chosen as the model system for screening the reaction conditions (Table 2).

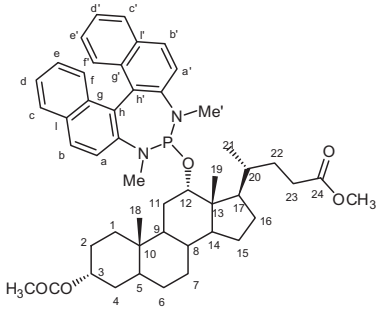


Scheme 1. Synthesis of ligands **1a** and **1b**.



Scheme 2. Synthesis of Pd (II)-complexes **2a** and **2b**.

Table 1
Chemical shift (ppm) for relevant protons in ligands and complexes



Protons	δ_H **1a**	δ_H **2a**	δ_H **1b**	δ_H **2b**
a	7.50	8.44	7.66	8.15
b	7.72	8.04	7.95	8.28
a′	7.41	7.53	7.78	8.58
b′	7.76	7.64	7.80	8.07
1	1.90, 1.01	0.04, −0.20	1.72, 0.89	1.15, 1.68
2	1.70, 1.42[a]	0.98, 0.67[a]	1.89, 1.74	1.86, 2.11
3	4.72	4.56	4.91	4.94
4	1.85, 1.69[a]	1.61, 1.39[a]	1.77, 1.55	1.52, 1.67
5	1.17	0.88	1.22	1.13
8	1.38	1.45	2.16	1.30
11	1.69, 1.33	0.76, 0.70	2.13, 1.35	1.74, 3.51
12	4.28	4.78	4.35	6.16
14	1.72	1.64	1.67	1.43
17	1.94	3.01	1.95	2.08
18	0.82	0.47	0.82	0.54
21	0.98	1.57	1.00	1.64
NMe	2.92	3.99	2.83	3.58
NMe′	2.89	3.67	3.03	3.53

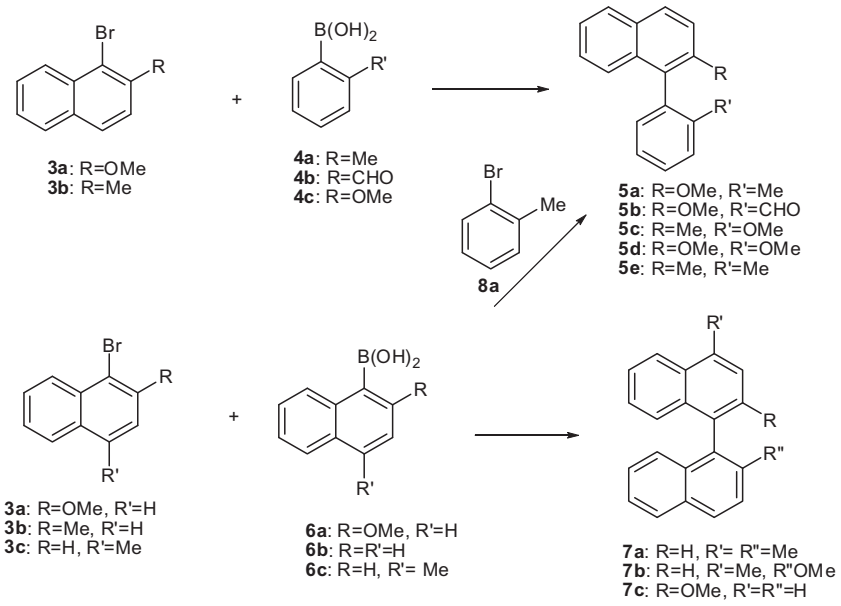
[a] These signals can be attributed both to protons 2 and 4.

Although most of the Suzuki-Miyaura cross-coupling reactions are carried out in organic solvent–water medium, both biphasic and homogeneous, dry solvents were used because of the water sensitivity of the Pd-complexes.

Dry reaction conditions affected the solubility of the bases, therefore the use of bases with some solubility in organic solvents, such as CsF or Cs_2CO_3, was mandatory: nevertheless the reaction mixtures were always suspensions.

At first the reaction was performed in toluene at 40 °C with 5% catalyst loading, using the complex **2a**, two equivalents of Cs_2CO_3, with an aryl bromide concentration of 0.02 M (entry 1): the reaction was complete in 14 h but the product was obtained with only 6% ee. Lowering the temperature slowed down the reaction rate, and did not improve the enantioselectivity (entry 2). The use of the diastereomeric complex **2b** gave the same results in terms of yield and reaction rate, both at 40 °C and at rt, but the enantioselectivity was much better: the cross-coupling product was obtained with 22% ee at 40 °C (entry 3) and with 25% ee. at rt.

These results point out the matched relationship between the (*R*)-absolute configuration of the biaryldiamido phosphite moiety and the stereochemistry of the cholestanic backbone. In addition, unlike that observed with the analogous binaphthyl phosphites, the absolute configuration of the product depends on the absolute configuration of the binaphthyl moiety of the ligand: the opposite prevailing enantiomer is obtained when using **2a** instead of **2b** (entries 1 and 3). This result indicates a different asymmetric induction mechanism for the catalytic precursors **2a-b** with respect to those obtained from the analogous phosphites.[17] Having established that **2b** gave the better enantioselectivities, optimization of the reaction conditions was carried out using this catalytic



Scheme 3. Asymmetric Suzuki-Miyaura biaryl coupling.

Table 2
Asymmetric Suzuki-Miyaura cross-coupling of **3a** and **4a**[a]

Run	Pd complex	Base	Solvent	Conc (M)	*T* (°C)	*t* (h)	Yield %[b]	ee %[c]	AC[d]
1	**2a**	Cs_2CO_3	Toluene	0.02	40	14	96	6	(−)
2	**2a**	Cs_2CO_3	Toluene	0.02	rt	48	96	7	(−)
3	**2b**	Cs_2CO_3	Toluene	0.02	40	14	96	22	(+)
4	**2b**	Cs_2CO_3	Toluene	0.02	rt	48	96	25	(+)
5	**2b**	CsF	Toluene	0.02	40	14	95	22	(+)
6	**2b**	CsF	Toluene	0.02	rt	48	94	27	(+)
7	**2b**	Cs_2CO_3	DME	0.02	rt	40	93	24	(+)
8	**2b**	Cs_2CO_3	THF	0.02	rt	40	94	22	(+)
9	**2b**	Cs_2CO_3	Toluene	0.1	rt	16	95	25	(+)
10	**2b**	Cs_2CO_3	Toluene	0.1	0	48	94	36	(+)

[a] The reactions were stopped at complete conversion of the substrate or when it did not proceed further.
[b] NMR yield.
[c] Enantiomeric excess (ee) determined by enantioselective HPLC (Chiralcel OJ, hexane/2-propanol 99/1, 1.0 mL/min, $T = 25°C$, $\lambda = 230$ nm).
[d] Sign of the specific rotation of the sample.

precursor. Changing the base from Cs_2CO_3 to CsF did not affect the yield or the enantioselectivity of the reaction to significant extent both at 40 °C and rt (entries 5 and 6). Similar results were obtained by changing the reaction solvent. The use of ether solvents, such as tetrahydrofuran or dimethoxyethane, gave the cross-coupling product in good yields in shorter reaction times (entries 7 and 8). It is conceivable that a coordinating solvent, THF or DME, can displace one ligand of the complex, giving rise to a monoligated species, which is slightly more active than the original complex,[17] but not more enantioselective. This species is less hindered and this can justify the higher reaction rate observed in coordinating solvents. Increasing the substrate concentration, in toluene as a solvent, had no influence on the enantioselectivity of the reaction (entries 4 and 9), but a higher reaction rate was observed, which gave complete conversion of the substrate at rt in only 16 h (entry 9). The increased rate allowed for the reaction to be carried out at lower temperature (entry 10), thus reaching the highest ee value of the product.

The optimized reaction conditions were used to screen different aryl bromides and different arylboronic acids in the reaction: the results are shown in Table 3.

When the reactions were performed at 0 °C, higher enantioselectivities than at rt were observed (entries 1 and 2, 6 and 7). However, as a consequence of the lower temperature the reaction slowed down and longer reaction times were required in order to obtain satisfactory yields of the products. At low temperatures, the arylboronic acids and the aryl bromides were less soluble, leading in some cases to low yields of the products (entries 5, 7, 12 and 14).

It was difficult to find a dependence of the outcome of the reaction only on the structural characteristics of the aryl bromide, as well as only on those of the aryl boronic acid: as a matter of fact, both reaction rate and enantioselectivity seem dependent on the combination aryl bromide—arylboronic acid. The 2-tolyl boronic acid **4a** gave a significantly lower reaction rate when coupled with **3b** (entry 9) than with **3a** (entry 2), but **3a** gave faster reactions when coupled with **4b**, **4c** and **6b** (entries 3, 4 and 11) than with **6c** (entries 13 and 14). The reaction between **3a** and **6b**, the aryl boronic acid devoid of substituent, was the fastest one, giving the product in 95% yield at 0 °C in only 24 hours of reaction (entry 11), suggesting that the steric hindrance near the boronic group can reasonably account for the reaction rate. At the same time, different enantioselectivities of the reaction were observed using the same aryl bromide (entries 1, 3, 4, 13) or the same aryl boronic acid (entries 2 and 9 or 5 and 7). The presence of a methoxy group near to the boronic moiety increases the enantioselectivity when the cross-coupling involves a 2-methyl substituted aryl bromide

Table 3
Asymmetric Suzuki-Miyaura cross-coupling with complex **2b**[a]

Run	ArBr	$ArB(OH)_2$	Ar-Ar	*T*	*t* (h)	Yield %[b]	ee %[c]	AC[d]
1	**3a**	**4a**	**5a**	rt	16	95	25	(+)
2	**3a**	**4a**	**5a**	0 °C	48	94	36	(+)
3	**3a**	**4b**	**5b**	rt	24	85	Racemic	
4	**3a**	**4c**	**5d**	rt	18	90	10	(−)
5	**3a**	**4c**	**5d**	0 °C	48	25[e]	12	(−)
6	**3b**	**4c**	**5c**	rt	48	56[e]	51	(−)
7	**3b**	**4c**	**5c**	0 °C	72	35[e]	70	(−)
8	**3b**	**6c**	**7a**	rt	48	95	13	(*R*)
9	**3b**	**4a**	**5e**	0 °C	72	75[e]	13	(−)
10	**3c**	**6a**	**7b**	rt	48	94	52	(*S*)
11	**3a**	**6b**	**7c**	0 °C	24	95	31	(*R*)
12	**8a**	**6a**	**5a**	0 °C	18	32[e]	40	(+)
13	**3a**	**6c**	**7b**	rt	48	88 (75[e])	17	(*S*)
14	**3a**	**6c**	**7b**	0 °C	72	38[e]	19	(*S*)

[a] All reactions were stopped at complete substrate conversion or when it did not proceed further.
[b] NMR yield.
[c] Enantiomeric excess (ee) determined by enantioselective HPLC (for conditions see experimental).
[d] Sign of the specific rotation of the sample or absolute configuration of the prevailing enantiomer, based on the elution order by comparison with the literature data.
[e] Isolated yield.

(entries 7, 12): the highest ee value was obtained when 2-methoxyphenyl boronic acid was reacted with 1-bromo-2-methylnaphthalene at 0 °C (entry 7). The reaction of 2-bromotoluene with 2-methoxy-1-naphthyl boronic acid (entry 12), a similar combination, gave the product with a lower ee, suggesting that also the size of the aryl moiety of the aryl boronic acid also plays an important role in determining the extent of the enantioselectivity. The ees of the products were still satisfactory when the 2-methoxy substituted aryl boronic acid was coupled with an aryl bromide where the methyl group was at the 4-position (entry 10), whereas the opposite combination, where the methoxy group was on the aryl bromide gave the same product but with very low ee (entries 13 and 14). The presence of a methoxy group both at the 2-position of the aryl bromide and the arylboronic acid decreased the enantioselectivity of the cross-coupling (entries 4 and 5), as did the presence of a methyl group at the same position on both the reactants (entry 9). The reaction exhibited a modest enantioselectivity when the 1-naphthyl boronic acid **6b**, devoid of substituent on the aryl moiety, was coupled with the 2-methoxy-1-bromonaphthalene **3a** (entry 11). By contrast the presence of a methyl group at the 4-position of the 1-naphthyl boronic acid (entries 8, 13, 14) or a formyl group at the 2-position of the aryl boronic acid (entry 3) decreased the enantioselectivity of the reaction. It should be noted that when the same cross-coupling product was prepared with the opposite combination of aryl bromide and aryl boronic acid (entries 2 and 12, 10 and 13), the same absolute configuration of the prevailing enantiomer was obtained in the presence of quite different yields (entries 2 and 12) and ees (entries 10 and 13). The different combination seems to influence the reaction rate or the extent of asymmetric induction but not its sense, which remains the same.

3. Conclusions

Pd(II) complexes of deoxycholic acid derived binaphthyl diamido phosphites have proven to work as chiral catalysts in the asymmetric Suzuki-Miyaura cross-coupling of aryl bromides with aryl boronic acids. A matched relationship between the stereochemistry of the bile acid and the (*R*)-absolute configuration of the binaphthyl diamido phosphite moiety was observed, and complex **2b** gave better enantioselectivities. This complex displayed high activity allowing the reactions to be performed at 0 °C, where the products were obtained in moderate to very good yields and with ees up to 70%.

4. Experimental

4.1. General

TLC analyses were performed on 60 F254 plates (0.2 mm) and chromatography purifications were carried out with silica gel (230–400 mesh) or with neutral alumina (Brockmann I). All reactions involving sensitive compounds were carried out under dry N_2, in flame-dried glassware. Toluene was refluxed over sodium-benzophenone and distilled before the use. *n*-Hexane, THF and DME were refluxed over potassium-benzophenone and distilled before the use. Dichloromethane, triethylamine and pyridine were refluxed over CaH_2 and distilled before the use. PCl_3 was distilled and dried with *freeze–pump–thaw* method before the use. Unless otherwise specified, the other compounds were commercially available and used as received. Methyl-3-acetyl-deoxycholan-24-ate was obtained as described previously and matched the reported characteristics.[18h]

^1H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ or benzene-d_6, on a Bruker AV-400 spectrometer (400.16 MHz for 1H) and the temperature was controlled to ±0.1 °C. ^1H and ^{13}C NMR chemical shifts (ppm) are referred to TMS as external standard, ^{31}P NMR chemical shifts (ppm) are referred to H_3PO_4 as external standard: the following abbreviations are used: singlet (s), doublet (d), double of doublets (dd), double double doublet (ddd), double triplet (dt), triplet of doublets (td), triplet (t), multiplet (m), broad (br). Enantiomeric excesses were determined by HPLC analysis on chiral stationary phase, using Chiracel OD-H and OJ as columns with hexane or hexane/^{i}PrOH mixtures as a mobile phase and UV detection at 230 or 254 nm. Elemental analyses were obtained using an Elementar Vario MICRO cube equipment.

4.2. General procedure for the synthesis of diamido phosphites

To a solution of methyl-3-acetyl-deoxycholan-24-ate (0.400 g, 0.9 mmol) in dry dichloromethane (5 ml), PCl_3 (0.24 ml, 2.7 mmol) was added under an inert atmosphere, and the reaction mixture was stirred at room temperature for 24 h. After removing the solvent under reduced pressure, the crude product was dissolved in dry toluene (2.5 ml) and a solution of *N*,*N*′-dimethyl-binaphtyldiamine (0.234 g, 0.75 mmol) and triethylamine (0.38 ml, 2.7 mmol) in dry toluene (2 ml) was added dropwise to this. After the addition, the reaction mixture was refluxed overnight. The mixture was cooled to room temperature and, after adding dry hexane (5 ml), was filtered under an inert atmosphere: the filtrate

was concentrated under vacuum and the crude product was purified by filtration under an inert atmosphere on a pad of neutral Al_2O_3 (3 g in a 2.5 cm diameter column) using dry dichloromethane as eluent, obtaining the pure diammido phosphite as a white amorphous solid.

4.2.1. Methyl-3α-acetyl-12α-[(*S*)-*N*,*N*-dimethylbinaphthyl]diazaphospholidine-5β-cholan-24-ate, 1a

0.382 g (0.48 mmol, 55 %); ^{1}H NMR (400 MHz, 298 K, C_6D_6), δ: 7.78 (d, $^3J_{HH}$ = 8.1 Hz, c′), 7.76 (d, $^3J_{HH}$ = 8.5 Hz, b′), 7.72 (d, $^3J_{HH}$ = 8.5 Hz, 1H, b), 7.68 (d, $^3J_{HH}$ = 8.1 Hz, 1H, c), 7.50 (d, $^3J_{HH}$ = 8.8 Hz, 1H, a),7.41 (d, $^3J_{HH}$ = 8.5 Hz, 1H, a′), 7.36 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 0.9 Hz, f′), 7.29 (dd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, f), 7.19 (ddd, $^3J_{HH}$ = 8.1, 6.9 Hz, $^4J_{HH}$ = 0.9 Hz, d′), 7.15 (ddd, $^3J_{HH}$ = 8.1, 6.8 Hz, $^4J_{HH}$ = 0.8 Hz, d), 6.93 (ddd, $^3J_{HH}$ = 8.9, 6.8 Hz, $^4J_{HH}$ = 1.2 Hz, e), 6.91 (ddd, $^3J_{HH}$ = 8.8, 6.9 Hz, $^4J_{HH}$ = 1.2 Hz, e′), 4.72 (m, 1H, 3), 4.28 (dt, $^3J_{HP}$ = 7.8 Hz, $^3J_{HH}$ = 2.6 Hz, 1H, 12), 3.40 (s, 3H, OCH_3), 2.92 (d, $^3J_{HP}$ = 9.1 Hz, 3H, NMe), 2.89 (d, $^3J_{HP}$ = 13.2 -Hz, 3H, NMe′), 2.24 (m, 1H, 23), 2.14 (m, 1H, 23), 1.96–1.78 (m, 6H, 1, 2/4, 8/9, 16, 17, 22), 1.76–1.56 (5H, 2′, 4′, 11, 6/7, 14), 1.51 (s, 3H, HCH_2(C=O)), 1.49–1.00 (m, 12H), 0.98 (d, $^3J_{HH}$ = 6.7 Hz, 3H, 21), 0.63 (s, 3H, 19), 0.82 (s, 3H, 18); ^{13}C{^{1}H} NMR (100 MHz, 298 K, C_6D_6), δ: 173.9 (24), 169.5 (C=O), 145.8 (d, J_{CP} = 7.5 Hz, h/i), 143.2 (d, $^5J_{CP}$ = 6.4 Hz, h′/i′), 133.8 (m), 133.4 (m′), 132.0 (g′), 131.6 (g), 129.3 (b), 128.52(b′), 128.46 (b′), 128.4 (c), 128.3 (d), 127.9 (f′), 127.3 (f), 126.2 (e), 126.1 (e′), 125.1 (d′), 124.2 (a′), 122.2 (a), 77.0 (d, $^2J_{CP}$ = 7.1 Hz, 12), 73.8 (3), 50.9 (OCH_3), 48.4 (14), 46.2 (17), 42.0 (5), 38.1 (d, $^2J_{CP}$ = 44.9 Hz, NMe′), 36.3 (20), 36.1 (d, $^2J_{CP}$ = 23.2 Hz, NMe), 35.9 (8/9), 35.2 (1), 34.2 (8/9), 32.5 (2/4), 31.3 (22), 31.1 (23), 27.9 (16), 27.8 (d, $^5J_{CP}$ = 5.2 Hz, 11), 27.5 (2/4), 27.3 (15), 26.9 (6/7), 24.4 (6/7), 23.2 (18), 21.0 (s, Me (C=O)), 18.2 (d, $^6J_{CP}$ = 9.6 Hz, 21), 12.9 (19); ^{31}P{^{1}H} NMR (161 MHz, 298 K, C_6D_6), δ: 168.8. Anal. Calcd. For $C_{49}H_{61}N_2O_5P$: C, 74.59; H, 7.79; N, 3.55. Found: C, 74.71; H, 7.76; N, 3.54.

4.2.2. Methyl-3α-acetyl-12α-[(*R*)-*N*,*N*-dimethylbinaphthyl]diazaphospholidine-5β-cholan-24-ate, 1b

0.313 g (0.40 mmol, 45 %). $[\alpha]_D^{25}$ = −198 (*c* 0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, 298 K, C_6D_6), δ: 7.95 (d, $^3J_{HH}$ = 8.6 Hz, b), 7.80–7.68 (m, 4H, a′, b′, c, c′), 7.66 (d, $^3J_{HH}$ = 8.6 Hz, a), 7.43 (d, $^3J_{HH}$ = 8.7 Hz, 1 H, f), 7.40 (d, $^3J_{HH}$ = 8.5 Hz, f′), 7.20–7.10 (m, 2H, d, d′), 6.99–6.87 (m, 2H, e, e′), 4.91 (m, 1H, 3), 4.35 (br s, 1H, 12), 3.40 (s, 3H, OCH_3), 3.03 (d, $^3J_{HP}$ = 7.6 Hz, 3H, NMe′), 2.83 (d, $^3J_{HP}$ = 12.5 Hz, 3H, NMe), 2.23 (m, 2H, 23,23′), 2.18–2.06 (m, 3H, 8,6,11), 2.01–1.59 (m, 9H, 1,17,9,2,2′,22,4,7,14), 1.81 (s, 3H, CH_3C=O), 1.60–0.86 (m, 11H, 4′,15,15′,20,16,16′,5,22′, 11′,1′,7′,6′), 1.00 (d, $^3J_{HH}$ = 6.5 Hz, 3H, 21), 0.82 (s, 3H, 18), 0.62 (s, 3H, 19). ^{13}C{^{1}H} NMR (100 MHz, 298 K, C_6D_6), δ: 173.5 (24), 169.7 (C=O), 145.4 (d, J_{CP} = 7.3 Hz, ì′), 143.0 (d, $^5J_{CP}$ = 6.7 Hz, i), 133.5 (g′), 133.1 (g), 131.8 (l′), 131.7 (l), 131.3 (h), 131.0 (h′), 129.1 (b′), 128.3 (b), 128.1 (c), 128.0 (c′), 127.5 (f), 127.1 (f′), 125.9 (e), 125.8 (e′), 124.8 (d), 124.7 (a), 124.5 (d′), 123.7 (a′), 77.5 (d, $^2J_{CP}$ = 14 Hz, 12), 73.8 (3), 50.7 (OCH_3), 47.9 (14), 47.1 (13), 46.2 (17), 41.6 (5), 38.0 (d, $^2J_{CP}$ = 43.0 Hz, NMe), 36.0 (20), 35.8 (d, $^2J_{CP}$ = 20.0 Hz, NMe′), 35.1 (1), 34.3 (10), 33.3 (9), 32.3 (4), 31.1 (23), 30.9 (22), 29.8 (8), 27.8 (7), 27.0 (2), 26.8 (6), 26.4 (d, $^5J_{CP}$ = 12.0 Hz, 11), 26.3 (16), 24.0 (15), 22.7 (18), 20.8 (Me(C=O)), 17.4 (21), 12.4 (19). ^{31}P{^{1}H} NMR (161 MHz, 298 K, C_6D_6), δ: 159.4. Anal. Calcd. for $C_{49}H_{61}N_2O_5P$: C, 74.59; H, 7.79; N, 3.55. Found: C, 74.50; H, 7.81; N, 3.56.

4.3. General procedure for the synthesis of complexes $PdCl_2L_2$

A solution of the ligand (0.5 mmol) in dry toluene (8 mL) was added to a red solution of $PdCl_2(PhCN)_2$ (0.25 mmol) in dry toluene (20 mL), which turned from red to yellow-orange. After 15 min stirring, the solvent was removed under reduced pressure and the yellow-orange solid was washed with n–hexane (3 × 4 mL) then dried under vacuum.

4.3.1. $PdCl_2$(1a)$_2$, 2a

850 mg (0.48 mmol, 96%) $[\alpha]_D^{31}$ = −211 (*c* 0.89, CH_2Cl_2). ^{1}H NMR (400 MHz, 298 K, C_6D_6), δ: 8.44 (d, $^3J_{HH}$ = 9.0 Hz, 1H, a), 8.04 (d, $^3J_{HH}$ = 9.0 Hz, 1H, b), 7.66 (d, $^3J_{HH}$ = 8.2 Hz, 1H, f′), 7.64 (d, $^3J_{HH}$ = 8.9 Hz, 1H, b′), 7.53 (d, $^3J_{HH}$ = 8.9 Hz, 1H, a′), 7.51 (d, $^3J_{HH}$ = 7.9 Hz, 1H, c), 7.21 (d, $^3J_{HH}$ = 8.4 Hz, 1H, c′), 7.15 (dd, $^3J_{HH}$ = 8.2, 7.2 Hz, 1H, e′), 7.07 (d, $^3J_{HH}$ = 8.8 Hz, 1H, f), 6.95 (dd, $^3J_{HH}$ = 7.9, 6.9 Hz, 1H, d), 6.84 (dd, $^3J_{HH}$ = 8.4, 7.2, 1H, d′), 6.73 (dd, $^3J_{HH}$ = 8.8, 6.9 Hz, 1H, e), 4.78 (m, 1H, 12), 4.56 (m, 1H, 3), 3.99 (t, $^3J_{HP}$ = 6.2 Hz, 3H, NMe), 3.67 (t, $^3J_{HP}$ = 5.9 Hz, 3H, NMe′), 3.43 (s, 3H, OCH_3), 3.01 (q, $^3J_{HH}$ = 9.6 Hz, 1H, 17), 2.60 (m, 1H, 23), 2.44 (m, 1H, 23), 2.07–0.62 (m, 27H), 1.57 (d, $^3J_{HH}$ = 6.3 Hz, 21), 0.58 (s, 3H, 19), 0.47 (s, 3H, 18), 0.04 (td, $^2J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 2.8 Hz, 1H, 1), -0.20 (d, $^2J_{HH}$ = 14.4 Hz, 1H, 1). ^{13}C{^{1}H} NMR (100 MHz, 298 K, C_6D_6), δ: 174.0 (24), 169.4 (C=O), 133.7 (g), 133.5 (g′), 131.8 (h), 131.7 (h′), 129.6 (b), 128.6 (b′, c, c′), 127.6 (f′), 127.3 (f), 126.6 (d′), 126.4 (e), 126.0 (e′), 124.8 (d), 123.2 (a′), 122.2 (a), 82.8 (t, $^2J_{cP}$ = 6.8 Hz, 12), 73.8 (3), 51.1 (OCH_3), 47.5 (14), 46.4 (17), 41.7 (5), 40.8 (t, $^2J_{CP}$ = 10.6 Hz, NMe′), 38.2 (t, $^2J_{CP}$ = 5.8 Hz, NMe), 36.0 (8/9), 35.9 (20), 34.9 (9/8), 34.2 (1), 32.6 (4), 32.2 (23), 31.7 (22), 27.43 (16), 27.37 (6/7), 26.3 (7/6), 25.8 (2), 24.2 (15), 23.0 (11), 22.6 (18), 21.2 (CH_3(C=O)), 18.9 (21), 12.8 (19). ^{31}P{^{1}H} NMR (161 MHz, 298 K, C_6D_6), δ: 117.1. Anal. Calcd. for $C_{98}H_{122}Cl_2N_4O_{10}P_2Pd$: C, 67.06; H, 7.01; N, 3.19. Found: C, 66.98; H, 6.99; N, 3.18.

4.3.2. $PdCl_2$(1b)$_2$, 2b

810 mg (0.46 mmol, 92%). $[\alpha]_D^{25}$ = +273 (*c* 1, CH_2Cl_2). ^{1}H NMR (400 MHz, 298 K, C_6D_6), δ: 8.58 (d, $^3J_{HH}$ = 8.8 Hz, 1H, a′), 8.28 (d, $^3J_{HH}$ = 8.7 Hz, 1H, b), 8.15 (d, $^3J_{HH}$ = 8.7 Hz, 1H, a), 8.07 (d, $^3J_{HH}$ = 8.8 Hz, 1H, b′), 7.91 (d, br.s., 1H, c′), 7.68 (d, $^3J_{HH}$ = 8.2 Hz, 1H, c), 7.30 (d, $^3J_{HH}$ = 8.3 Hz, 1H, f), 7.27 (d, $^3J_{HH}$ = 8.8 Hz, 1H, f′), 7.18 (t, $^3J_{HH}$ = 7.4 Hz, 1H, d′), 7.07 (ddd, $^3J_{HH}$ = 8.2, 6.9, 1.0 Hz, 1H, d), 6.91 (t, $^3J_{HH}$ = 7.4, Hz 1H, e′), 6.83 (ddd, $^3J_{HH}$ = 8.3, 6.9, 1.2 Hz, 1H, e), 6.16 (br.s., 1H, 12), 4.94 (m, 1H, 3), 3.58 (t, $^3J_{HP}$ = 4.6 Hz, 3H, NMe), 3.51 (t, $^3J_{HP}$ = 6.0 Hz, 3H, NMe′), 3.46 (s, 3H, OCH_3), 3.51 (m, 1H, 11), 2.51 (m, 1H, 23), 2.32 (m, 1H, 23′), 2.20–1.79 (m, 6H, 22,22′,17,2,2′,9), 1.76 (s, 3H, CH_3C=O), 1.75–1.61 (m, 3H, 1,4,11′), 1.64 (d, 1H, $^3J_{HH}$ = 4.0 Hz, 21), 1.61–1.01 (m, 10H, 4′,1′,5,6,8, 14,15,16,16′,20), 0.90–0.78 (m, 4H, 7,7′,15′,6′) 0.69 (s, 3H, 19), 0.54 (s, 3H, 18).

^{13}C{^{1}H} NMR (100 MHz, 298 K, C_6D_6), δ: 174.2 (24), 170.2 (C=O), 143.1 (i/i′), 142.8 (i/i′), 133.8 133.3, 133.2, 133.1 (g/g′/h/h′), 129.5, 129.4 (l/l′), 129.2 (b′), 129.1 (b), 129.0 (a′), 128.6 (c), 128.5 (c′), 127.9 (f), 127.7 (a), 127.5 (f′), 126.4 (e), 126.2 (e′), 126.1 (d), 125.5 (d′), 81.2 (12), 74.6 (3), 51.2 (OCH_3), 47.2 (17), 47.2 (13), 46.7 (14), 42.7 (NMe′), 42.4 (5), 40.3(NMe), 37.7 (20), 36.8 (8), 35.5 (9), 33.6 (4), 32.8 (23), 32.0 (10), 31.1 (22), 30.4 (11), 29.1 (1), 28.6 (2), 28.2 (16), 26.8 (15), 24.8 (6), 23.2 (18), 22.6 (18), 21.2 (CH_3(C=O)), 18.8 (21), 13.1 (19). ^{31}P{^{1}H} NMR (161 MHz, 298 K, C_6D_6), δ: 115.8. Anal. Calcd. for $C_{98}H_{122}Cl_2N_4O_{10}P_2Pd$: C, 67.06; H, 7.01; N, 3.19. Found: C, 67.12; H, 7.02; N, 3.18.

4.4. General procedure for Suzuki-Miyaura cross coupling reaction

A flame dried Schlenk was charged under an inert atmosphere with aryl bromide (0.5 mmol), aryl boronic acid (0.75 mmol) and **2b** (0.025 mmol, 5 mol %) dissolved in dry toluene (5 ml), then Cs_2CO_3 (1.25 mmol) was added. The mixture was stirred at room temperature or 0 °C until TLC analysis (hexane–CH_2Cl_2 8:2) showed complete substrate conversion or when it did not proceed further.

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The reaction was quenched with NH_4Cl solution, extracted with diethyl ether (3 × 10 mL) and the organic phase was dried over anhydrous Na_2SO_4. After removing the solvent at reduced pressure, the crude product was directly analysed by ^1H NMR and, if necessary, purified by column chromatography (SiO_2; hexane–CH_2Cl_2 8:2). The ee of the biaryl products were determined by HPLC on a chiral stationary phase.

4.4.1. (+)-2-Methoxy-1-(2-methylphenyl)-naphthalene, [19] 5a

From *ortho*-tolylboronic acid and 1-bromo-2-methoxynaphthalene after 16 h at RT. ^1H NMR (400 MHz, 298 K, $CDCl_3$), δ: 7.90 (d, 1H, J_{HH} = 9.2 Hz), 7.86–7.81 (m, 1H), 7.36–7.20 (m, 7H), 7.17 (d, 1H, J_{HH} = 5.0 Hz), 3.83 (s, 3H), 1.98 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, $CDCl_3$), δ: 153.6, 137.6, 136.1, 133.4, 130.8, 129.8, 128.9, 127.8. 127.5, 126.3, 125.6, 125.0, 124.5, 123.4, 113.6, 56.5, 19.7. HPLC: (Chiracel OJ, hexane/2-propanol 99:1, 1.0 mL/min, T = 25 °C, λ = 230 nm): t_1 = 8.4 min (major), t_2 = 11.5 min (minor).

4.4.2. 2-Methoxy-1-(2-formylphenyl)-naphthalene,[17] 5b

From 1-bromo-2-methoxynaphthalene and 2-formylphenylboronic acid after 24 h at rt. ^1H NMR (400 MHz, 298 K, $CDCl_3$), δ: 9.64 (s, 1H), 8.15 (dd, 1H, J_{HH} = 7.5, 3.9 Hz), 7.99 (d, 1H, J_{HH} = 9 Hz), 7.74 (t, 1H, J_{HH} = 7.5 Hz), 7.66 (dd, 1H, J_{HH} = 9.6 Hz, 3.3 Hz) 7.59 (t, 1H, J_{HH} = 6.9 Hz), 7.41–7.33 (m, 5H), 3.84 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, $CDCl_3$), δ: 192.8, 154.4, 140.6, 135.3, 134.1, 133.9, 132.6, 130.6, 129.2, 128.3, 128.2, 127.2, 125.1, 124.1, 120.3, 113.0, 56.6. HPLC (Chiralcel OJ, hexane/2-propanol 99:1 1.0 mL/min, T = 25 °C, λ = 230 nm): t_1 = 20.1 min (major), t_2 = 26.9 min (minor).

4.4.3. (−) 2-Methyl-1-(2-methoxyphenyl)-naphthalene, 5c

From 1-bromo-2-methylnaphthalene and 2-methoxyphenyl boronic acid, after 48 h at rt, the reaction mixture was purified giving 70 mg (0.28 mmol, 56%) of 2-methyl-1-(2-methoxyphenyl)-naphthalene. $[\alpha]_D^{25}$ = −3 (*c* 1, $CHCl_3$) for a sample with 51% ee. ^1H NMR (400 MHz, 298 K, $CDCl_3$), δ: 7.89 (d, 1H, J_{HH} = 8.0 Hz), 7.84 (d, 1H, J_{HH} = 8.0 Hz), 7.52–7.33 (m, 5H), 7.24–7.08 (m, 3H), 3.73 (s, 3H), 2.29 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, $CDCl_3$), δ: 157.4, 134.7, 133.9, 132.9, 132.0, 131.8, 128.8, 128.5, 128.3, 127.8, 127.2, 125.9, 125.7, 124.6, 120.7, 111.2, 55.5, 20.6. HPLC (Chiracel OJ, hexane:2-propanol 99.5:0.5, 0.7 ml/min, 230 nm) t_1 = 10.0 min (major), t_2 = 14.1 min (minor). Anal. Calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 86.98; H, 6.48.

4.4.4. (−) 2-Methoxy-1-(2-methoxyphenyl)-naphthalene,[17] 5d

From 1-bromo-2-methoxynaphthalene and 2-methoxyphenylboronic acid after 48 h at 0 °C, the reaction mixture was purified by column chromatography giving 33 mg (0.125 mmol, 25%) of 2-methoxy-1-(2-methoxyphenyl)-naphthalene as a white solid. ^1H NMR (400 MHz, 298 K, $CDCl_3$), δ: 7.88 (d, 1H, J_{HH} = 9.0 Hz), 7.80 (m, 1H), 7.45–7.28 (m, 5H), 7.21 (dd, 1H, J_{HH} = 7.2 Hz, 1.8 Hz), 7.07 (m, 2H), 3.84 (s, 3H), 3.70 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, $CDCl_3$), δ: 157.9, 154.4, 133.8, 132.5, 129.2, 128.9, 127.9, 126.2, 125.6, 125.4, 123.5, 122.4, 120.7, 114.4, 111.5, 108.0, 57.2, 55.9. HPLC (Chiralcel OJ, hexane/2-propanol 99:1 1.0 mL/min, T = 25 °C, λ = 230 nm): t_1 = 16.4 min (minor), t_2 = 21.7 min (major).

4.4.5. (−) 2-Methyl-1-(2-methylphenyl)-naphthalene,[20] 5e

From 1-bromo-2-methylnaphthalene and 2-tolyl boronic acid, after 72 h at 0 °C, the reaction mixture was purified by column chromatography giving 87 mg (0.37 mmol, 75%) of 2-methyl-1-(2-methylphenyl)-naphthalene. ^1H NMR (400 MHz, 298 K, $CDCl_3$), δ: 7.89 (d, J_{HH} = 8.1 Hz, 1H), 7.83 (d, J_{HH} = 8.4 Hz, 1H), 7.50–7.24 (m, 7H), 7.17 (d, J_{HH} = 7.0 Hz, 1H), 2.21 (s, 3H), 1.96 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, $CDCl_3$), δ: 139.2, 137.5, 136.8, 133.1, 132.6, 132.0, 130.0, 128.6, 127.8, 127.4, 127.1, 126.0, 125.9, 125.7, 124.8, 20.3, 19.5. HPLC (Chiracel OJ, hexane, 0.5 ml/min, T = 25 °C, 254 nm): t_1 = 12.5 min (major), t_2 = 19.5 min (minor).

4.4.6. (*R*)-2,4′-Dimethyl-1,1′-binaphthyl,[14] 7a

From 1-bromo-2-methylnaphthalene and 4-methyl-1-naphthaleneboronic acid, after 48 h at rt. ^1H NMR (400 MHz, 298 K, $CDCl_3$), δ: 8.10 (d, 1H, J_{HH} = 9.3 Hz), 7.89 (d, 1H, J_{HH} = 8.1 Hz), 7.87 (d, 1H, J_{HH} = 8.4 Hz), 7.57–7.15 (m, 9H), 2.83 (s, 3H), 2.13 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, $CDCl_3$), δ: 136.5, 135.9, 134.6, 134.0, 133.8, 133.0, 132.8, 132.2, 128.7, 127.9, 127.6, 126.8, 126.6, 126.5, 126.0, 125.9, 125.8, 124.9, 124.6, 20.7, 19.7. HPLC (Chiracel OJ, hexane/2-propanol 90:10, 1.0 mL/min, T = 25 °C, λ = 230 nm): t_1 = 4.7 min (major) and t_2 = 15.3 min (minor).

4.4.7. (*S*)-2-Methoxy-4′-methyl-1,1′-binaphthyl,[14] 7b

From 1-bromo-4′-methylnaphthalene and 2-methoxy-1-naphthaleneboronic acid, after 48 h at rt.

^1H NMR (400 MHz, 298 K, $CDCl_3$), δ: 7.92 (d, 1H, J_{HH} = 9.2 Hz), 7.86 (m, 1H), 7.41–7.26 (m, 9H), 7.21 (m, 1H), 3.80 (s, 3H), 2.85 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, $CDCl_3$), δ: 154.8, 134.6, 134.0, 133.1, 133.0, 132.9, 129.5, 128.2, 127.9, 126.9, 126.6, 126.5, 125.8, 125.7, 125.6, 124.5, 123.7, 114.0, 56.9, 19.8. HPLC (Chiracel OJ, hexane/2-propanol 90:10, 1.0 mL/min, T = 30 °C, λ = 227 nm): t_1 = 7.2 min (major) and t_2 = 29.3 min (minor).

4.4.8. (*R*)-2-Methoxy-1,1′-binaphthyl,[14] 7c

From 1-bromo-2-methoxynaphthalene and 1-naphthaleneboronic acid after 24 h at 0 °C. ^1H NMR (400 MHz, 298 K, $CDCl_3$), δ: 8.01–7.90 (m, 3H), 7.87 (d, 1H, J_{HH} = 8.1 Hz), 7.62 (t, 1H, J_{HH} = 6 Hz), 7.48–7.41 (m, 3H), 7.35–7.13 (m, 5H), 3.75 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, $CDCl_3$), δ: 154.8, 134.7, 134.4, 133.8, 133.1, 129.6, 129.2, 128.6, 128.4, 127.9, 127.8, 126.5, 126.3, 126.0, 125.8, 125.7, 125.6, 123.7, 123.4, 114.0, 56.9. HPLC (Chiracel OJ, hexane/2-propanol 95:5, 1.0 mL/min, T = 25 °C, λ = 230 nm): t_1 = 10.2 min (major) and t_2 = 15.7 min (minor).

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A. Supplementary data

Supplementary data (NMR spectra and 2D maps of all new compounds and HPLC chromatograms) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetasy.2017.09.012.

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