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Asymmetric Bromine–Lithium Exchange: Application toward the Synthesis of New Biaryl-Diphosphine Ligands

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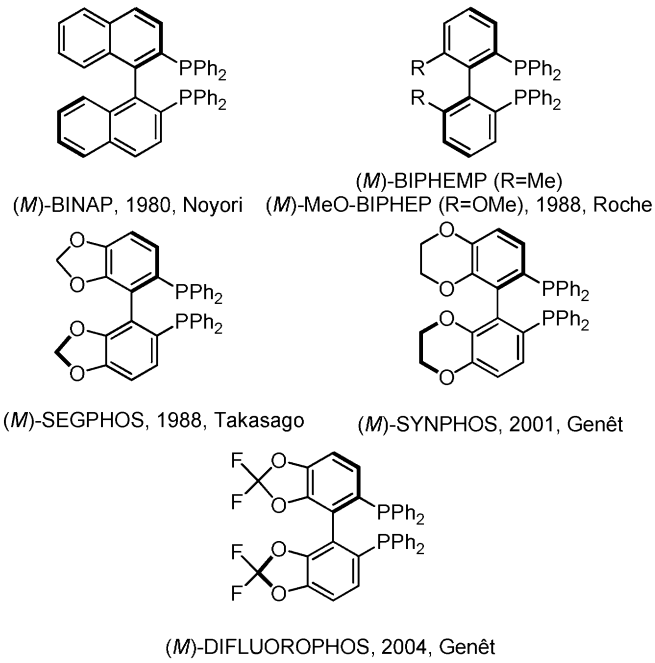
Abstract: The desymmetrization of the prochiral tetrabromobiphenyl *via* asymmetric bromine–lithium exchange as a key step of synthesis of novel biphenyl-diphosphine ligands is reported. This new approach allows an easy access to twelve new enantiomerically pure atropisomeric ligands in one- to three-step reactions in good to excellent yields.

Keywords: asymmetric bromine–lithium exchange; atropoisomeric ligands; catalytic phosphination; dihedral angles; diphosphines

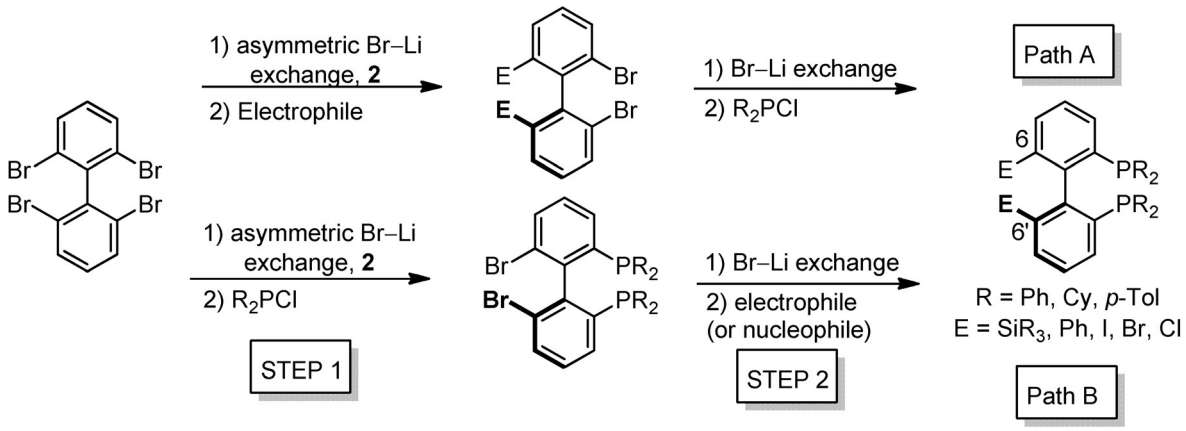
Biaryl-diphosphine-based ligands are well-known in the literature to be efficient bidentate ligands for Rh(I)-[1] and Ru(II)-catalyzed[2] asymmetric hydrogenation reactions providing high levels of enantioselectivity and isolated yields. To name a few (Scheme 1), BINAP was the first biaryl-diphosphine ligand bearing a binaphthyl backbone synthesized by Noyori et al. in 1980[1a] (Nobel Prize for Chemistry in 2001). A few years later, Cereghetti et al.,[3] at the pharmaceutical company Roche, patented BIPHEMP and *MeO*-BIPHEP. In 1998, the Japanese company Takasago developed SEGPHOS,[4] a new diphosphine ligand bearing a dioxolane backbone. In 2001, Genêt et al. synthesized the dioxane derivative of SEGPHOS, SYNPHOS.[5] And finally, Genêt and co-workers developed the difluorodioxolane analogue of SEGPHOS, DIFLUOROPHOS.[6]

Compared to the binaphthyl core, the biphenyl one offers a tremendous advantage: positions 6 and 6′ can be easily functionalized. By changing the steric bulk of the substituent pattern at positions 6 and 6′, the dihedral angle of the biphenyl core can be modulated. Indeed, it is a key parameter for the ligand efficiency based on yield and chiral induction in asymmetric transformations (hydrogenations, cross-couplings).[4b–7] Based on this property, we were interested to introduce various halogen, silyl, aryl and alkyl groups in positions 6 and 6′ such as R = TMS, TES, Br, Cl, I, Ph and C_4H_8 (butane bridge) which can modulate this angle. We were also interested to study the introduction of both R′ = PPh_2, PCy_2 and P(*p*-tolyl)$_2$ in order to determine their influence on the ligand properties (Scheme 2).

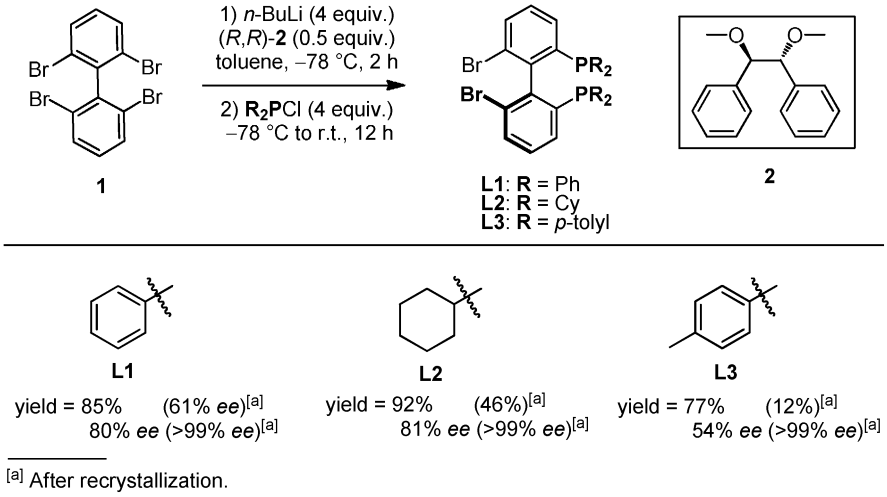
The afore-mentioned properties and our ongoing research program on asymmetric Br–Li exchange[8] prompted us to elaborate a novel two-step synthetic



Scheme 1. Various biaryl-diphoshine-based ligands of the literature.



Scheme 2. General structure of new biaryl-diphosphine ligands **L**, and ways to synthesize them.

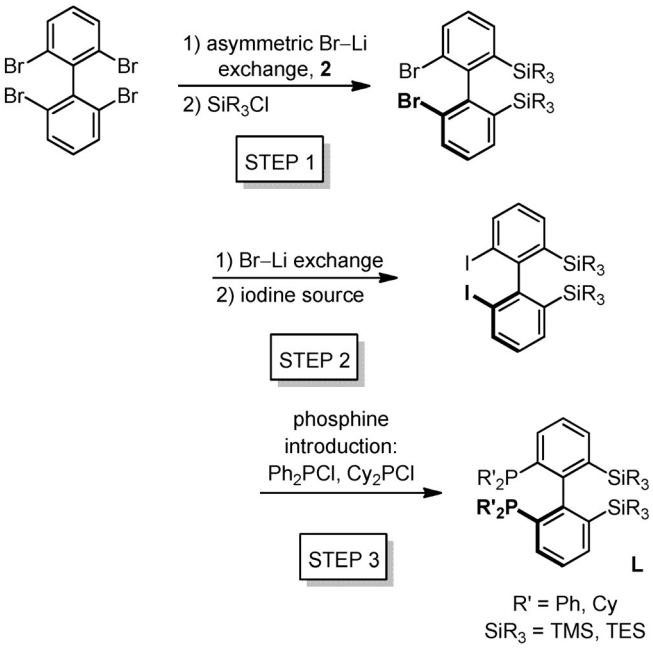


Scheme 3. The one-step synthetic protocol to atropisomeric 6,6′-dibromo-2,2′-diphosphine ligands **L1**, **L2** and **L3**.

protocol to prepare atropoisomeric 6,6′-dibromo-2,2′-diphosphine ligands based on the desymmetrization of prochiral tetrabromobiphenyl substrate **1**. The synthesis of the target atropisomeric biphenyl-diphosphine ligands by our strategy entails an asymmetric transformation of **1** *via* asymmetric Br–Li exchange using (1*R*,2*R*)-1,2-dimethoxy-1,2-diphenylethane **2** as chiral catalyst[8b] and appropriate P-electrophiles such as chlorodiphenylphosphine, chlorodicyclohexylphosphine and chlorodi(*p*-tolyl)phosphine. In fact there are two possible pathways for the synthesis of the desired new 6,6′-disubstituted atropisomeric phosphines (Scheme 2). In path A, the desired substituent is first introduced. After a second Br–Li exchange, the P-electrophile is added. There are potential problems with the second lithiation including identification of optimal conditions and avoiding racemization. Therefore, for some ligands, it was preferable to first introduce the P-electrophile (path B), and the other electrophile after the second lithiation. The second step could also be changed to a nucleophilic substitution of the two Br atoms.

A first simple application was the one-step synthesis of the brominated ligands **L1**, **L2** and **L3** (Scheme 3).

The desymmetrization protocol[8b] performed very well and gave access to three new dibromo-bisphosphino-biphenyl atropisomeric ligands **L1**, **L2** and **L3**. Asymmetric phosphination of **1** by chlorodiphenylphosphine and chlorodicyclohexylphosphine gave bisphosphines **L1** and **L2** with 80% *ee* and 81% *ee* (in 85% and 92% isolated yields respectively, see Scheme 3). Further increase of the enantiopurity of products **L1** and **L2** was possible by fractional recrystallization from acetone of the corresponding phosphines with *ee* up to >99% (in 61% and 46% yields, Scheme 3). The phosphination of dilithiated species **1** by chloro(di-*p*-tolyl)phosphine proceeded effectively to afford **L3** in 77% isolated yield (but with 54% *ee*). Further increase of the enantiopurity of product

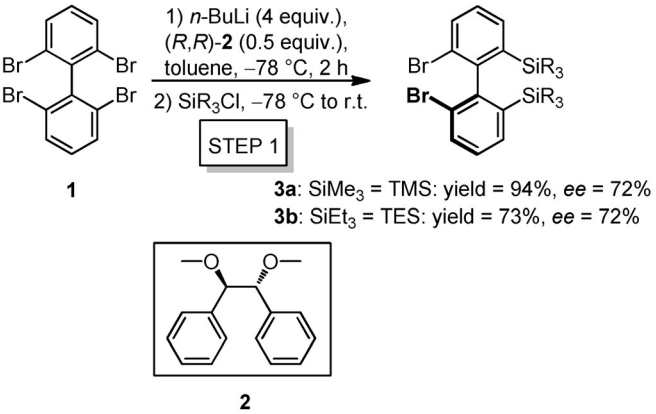


Scheme 4. Proposed chemical pathway to new silyl-diphosphine ligands.

L3 was also possible by recrystallization from methanol with *ee* up to >99% (in 12% yield, Scheme 3).

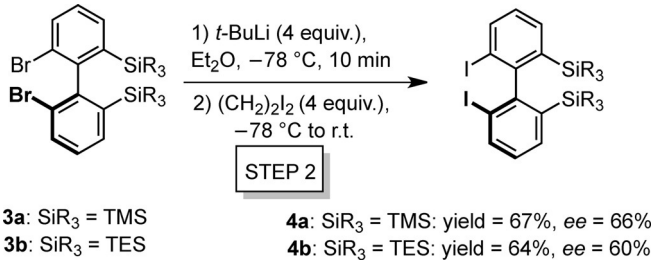
Considering the synthesis of silyl-diphosphine ligands, we had to deal with many problems. The best route was the three-step sequence in Scheme 4. In fact, it was found that the phosphination step (step 3) needed to be done on the diiodide counterpart instead of the dibromide.

The synthesis started with step 1, the asymmetric Br–Li exchange procedure, under the standard conditions previously developed in our laboratory[8b] using chiral diether **2** as reference ligand, followed by an electrophilic quench with the appropriate silyl derivatives such as trimethylsilyl (TMS) and triethylsilyl (TES): good levels of enantioselectivity (up to 72%) and high isolated yields (up to 94%) were obtained (Scheme 5).



Scheme 5. Asymmetric Br–Li exchange procedure and electrophilic quench.

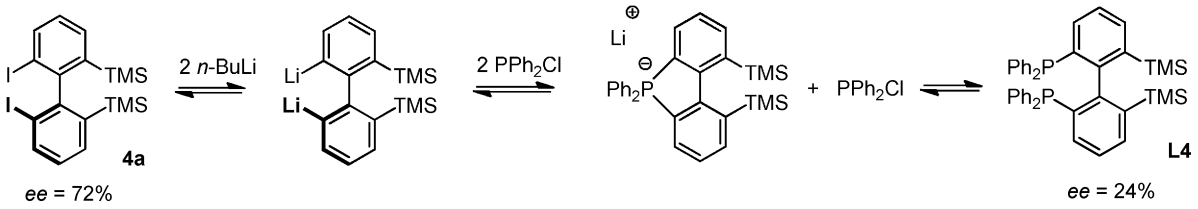
Then, a second Br–Li exchange for step 2, using *t*-BuLi instead of *n*-BuLi was performed in order to introduce the iodine atoms on the biaryl skeleton. We observed that the second Br–Li exchange in THF gave a mixture of silylated compounds. According to the literature,[9] a silyl migration could have occurred in THF at −78 °C in the presence of an organolithium reagent because of the possible generation of a silicate intermediate in polar solvents such as THF. Instead, using diethyl ether led to a clean reaction, by disfavouring the thermodynamic stability of the silicate complex. The iodine introduction was also problematic: the electrophilic quench of the highly reactive dilithiated species had to be performed with diiodoethane and not molecular iodine (Scheme 6). Excess of molecular iodine favoured iododesilylation as a side reaction.



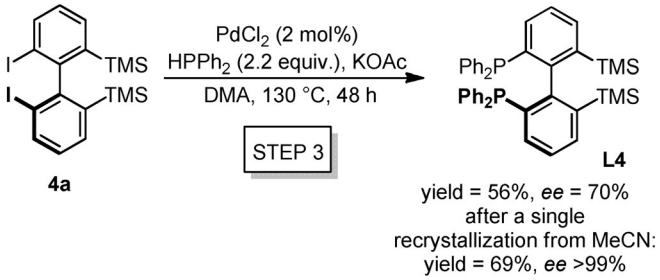
Scheme 6. Iodination procedure.

The planned phosphination step was based on an I–Li exchange, followed by the needed P-electrophile. However, the reaction with Ph_2PCl resulted in poor yield, and more importantly, a serious loss of *ee*, from 72% to 24%. This phenomenon may be ascribed to the formation of an ate-complex which appeared to be highly problematic in terms of optical purity conservation[10] (Scheme 7).

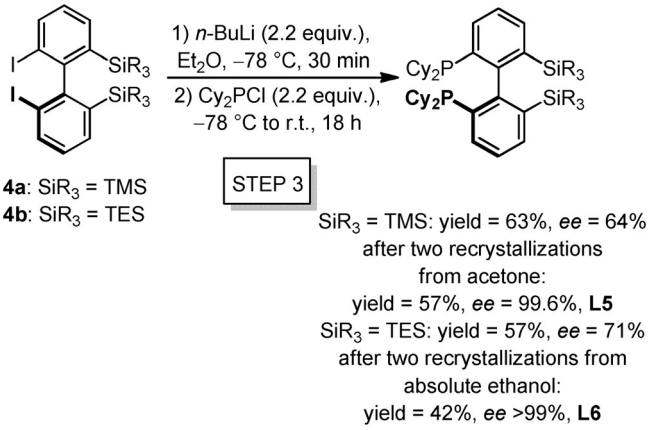
Finally, a different phosphination procedure was applied for the introduction of the diphenylphosphine motif. For step 3, we investigated the utilization of the palladium-catalyzed phosphination developed by Leroux et al.[11] on trisubstituted biaryls. Under the described conditions, the phosphination of (*M*)-(6,6′-diiodo-[1,1′-biphenyl]-2,2′-diyl)bis(trimethylsilane) **4a** provided a poor reaction conversion (50%) with a low isolated yield (27%) for the desired product. After much experimentation (for details, see Table 3 in the Supporting Information), it was found that simply replacing $Pd(OAc)_2$ by $PdCl_2$ provided complete conversion, with 56% isolated yield (Scheme 8). In addition, it was satisfying to note that no erosion of the enantiomeric excess was detected under those harsh reaction conditions. A single recrystallization procedure from acetonitrile led to the ligand **L4** of in-



Scheme 7. Possible ate-complex generated during the quench with Ph_2PCl.



Scheme 8. Pd-catalyzed phosphination procedure.

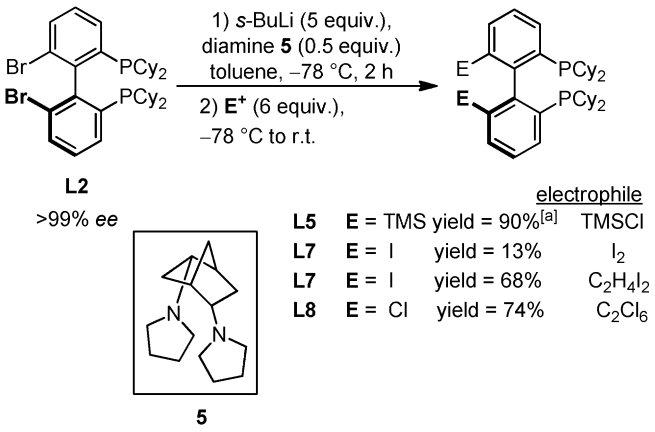


Scheme 9. Procedure for the introduction of dicyclohexylphosphine.

terest in good yield (69%) and perfect optical purity (>99%).

The synthesis of the dicyclohexyl analog was also of interest due to the abundance of these groups in asymmetric catalysis. In this perspective, we thought about the introduction of the dicyclohexylphosphine by iodine–lithium exchange on the previously synthesized intermediates **4a** and **4b**. In fact, considering the stabilization of the potential ate-complex by the diphenylphosphine moieties, it would not be the case with the corresponding saturated phosphine electrophile dicyclohexylphosphine chloride. We thus applied the planned conditions used for the introduction of dicyclohexylphosphine (step 3) to generate two new silyl-diphosphine ligands **L5** and **L6** (Scheme 9).

According to path B (Scheme 2), which gave us access to **L2**, we decided to apply the second Br–Li exchange as a tool for direct modification of the 6,6′-

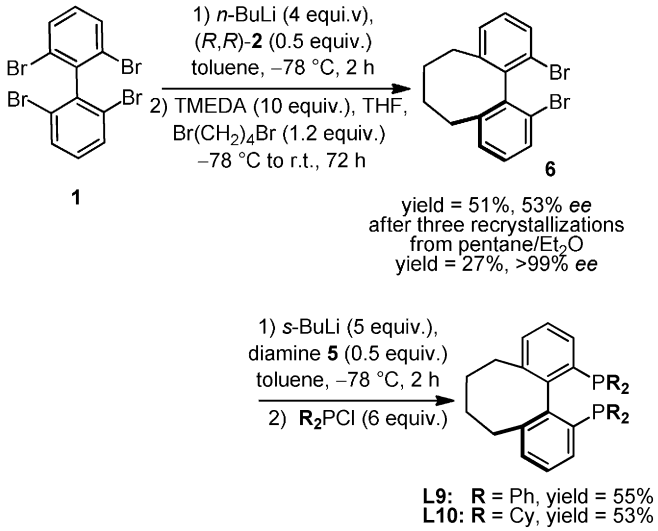


[a] Decrease of enantiopurity from >99% *ee* to 90% *ee*.

Scheme 10. Direct functionalization of the 6,6′-bromines of ligand **L2**.

bromines of the diphosphine **L2**. Unfortunately, the standard reaction conditions described above (*t*-BuLi in Et_2O), gave the product in low yield with almost complete racemization. For that reason an evaluation of the optimal conditions for this transformation was performed. Finally, after screening of many parameters (solvent, organolithium reagent and additive influence), we found the following optimized conditions (Scheme 10).

Performing a second Br–Li exchange in toluene with 5 equiv. of *s*-BuLi and in the presence of 0.5 equiv. of the diamine 2,5-di(pyrrolidin-1-yl)bicycle[2.2.1]heptane **5** as ligand, which was previously identified as efficient Br–Li exchange catalyst,[12] led to the target compound **L5**, in one step with 90% yield and 90% *ee*. After two recrystallizations from acetone, the enantiomericaly pure (>99% *ee*) diphosphine **L5** was obtained in 72% yield (Scheme 10). The developed strategy for the direct functionalization of 6,6′-dibromo-positions employed for **L5** synthesis was also successfully applied to the synthesis of **L7** and **L8** in good yields (68 and 74%, respectively), without optical purity erosion. As before (Scheme 6), we observed that the electrophilic source of iodine played an essential role in terms of the degradation of the yield of ligand **L7**: diiodoethane instead of molecular iodine has to be used.

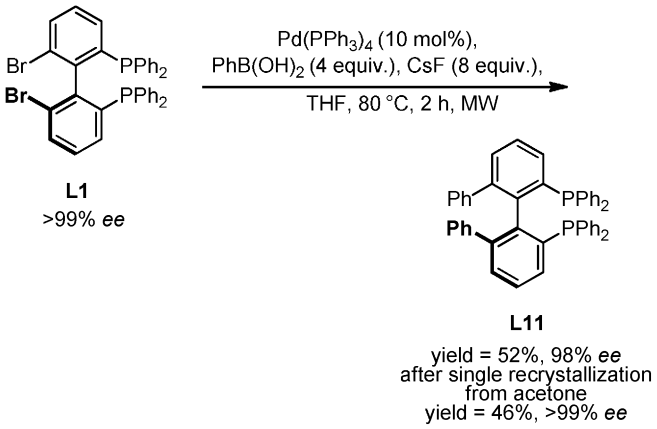


Scheme 11. Synthesis of **L9** and **L10** bearing the butane bridge.

Considering the synthesis of ligands with small dihedral angles, we proposed to introduce a rigid butane bridge. A closely related idea has been applied to the synthesis chiral biaryl C_n-TunaPhos ligands with a wide range of dihedral angles.[13] In our case, we decided to install the alkyl bridge, which could be realized *via* a double S_N2 reaction, by quenching the dilithiated species with the appropriate dihaloalkane. According to path A, this step was followed by a phosphination procedure (Scheme 11).

We chose 1,4-dibromobutane as the appropriate electrophile to construct the chiral precursor **6**. The desymmetrization step was realized under the standard conditions using the chiral ligand **2**.[8b] Due to the fact that no expected product was detected in toluene, the addition of TMEDA and THF as co-solvents was required. However, the expected product **6** was obtained after 72 h in good yield (51%) but with only 53% *ee*. Finally, we were pleased to find that the enantiomeric excess of product **6** could be easily improved by recrystallization from a (1:1) mixture of pentane/ether to >99% *ee*. The phosphination of precursor **6** in the presence of diamine **5** led to the formation of the desired ligands **L9** and **L10** in 55% and 53% yield respectively (Scheme 11).

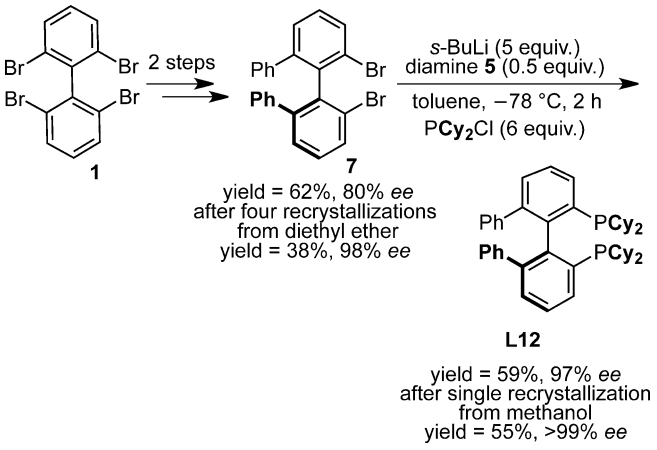
We next concentrated our efforts on the preparation of other ligands containing aryl substituents at the 6,6′-positions of the biphenyl core. Their introduction should be possible following a classic Suzuki coupling of **L1** and **L2** with the corresponding arylboronic acid (Scheme 12). Our initial attempt to couple **L1** and phenylboronic acid, using $Ba(OH)_2$ as a base, was quite disappointing (for details, see Table 11 in the Supporting Information). Only traces of the desired product **L11** were detected. The use of CsF as a base and $Pd(PPh_3)_4$ as palladium source afforded the desired ligand **L11** with a moderate yield of 40% after a long reaction time (72 h). Therefore, we decided to perform the reaction under microwave irradiation to promote the introduction of the phenyl rings. In this case, we observed, after 2 h, full conversion with good isolated yield (52%) and slight enantiopurity erosion (98% *ee*) for the formation of **L11**.



Scheme 12. Synthesis of ligand **L11**.

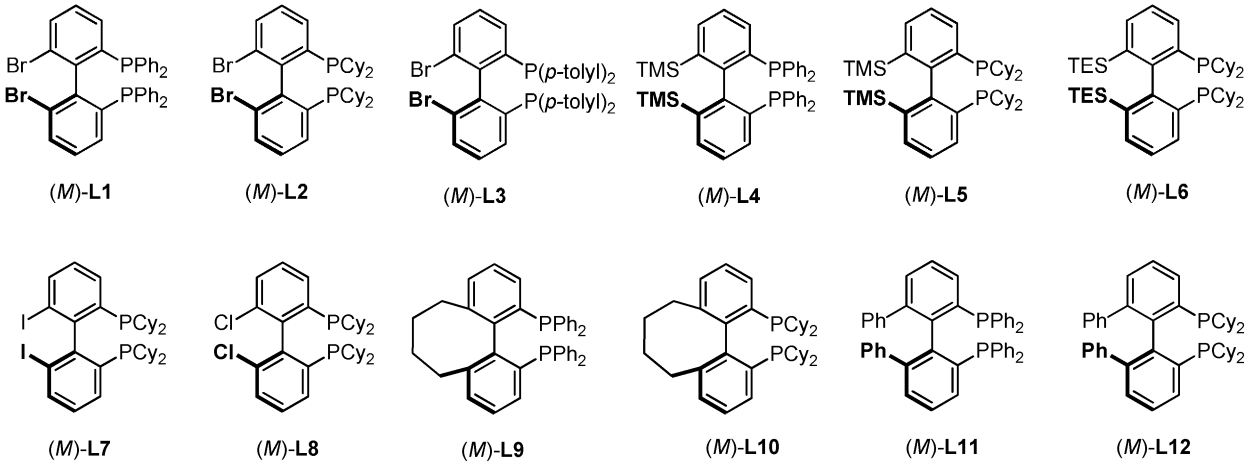
The Suzuki coupling of **L2** with phenylboronic acid was also tried. Unfortunately, an inseparable mixture of products was obtained. Considering that the synthesis of compound **7** was previously reported by our group,[8b] we decided to prepare the ligand **L12** according to a stepwise methodology starting with the enantiomerically enriched compound **7** presented as in Scheme 13.

A recrystallization of **7** from diethyl ether led to increase the optical purity of **7** from 80% up to 98% *ee*. Finally reaction of **7** with *s*-BuLi in the presence of diamine **5** followed by phosphination with chlorodiphenylphosphine gave the desired ligand **L12** in 55% yield as a single enantiomer (ee > 99%).



Scheme 13. Synthesis of ligand **L12**.

Table 1. Rationalization of dihedral angle and P_1–P_2 distance values.



Entry	L*	Dihedral angle [°]	P_1–P_2 distance [Å]	Entry	L*	Dihedral angle [°]	P_1–P_2 distance (Å)
1	(*M*)-**BINAP**	88.33 (1)	4.218 (2)	7	(*M*)-**L7**	83.40 (1)	3.777 (1)
2	(*M*)-**L1**	83.20 (7)	3.6946 (7)	8	(*M*)-**L8**	79.05 (4)	3.7459 (5)
3	(*M*)-**L2**	78.67 (5)	3.7345 (6)	9	(*M*)-**L9**	72.73 (5)	3.5922 (5)
4	(*M*)-**L4**[a]	82.86 (4)	3.6264 (6)	10	(*M*)-**L10**[a]	70.07 (5)	3.5429 (4)
5	(*M*)-**L5**[a]	79.84 (3)	3.4423 (4)	11	(*M*)-**L11**	64.14 (4)	3.4054 (5)
6	(*M*)-**L6**[a]	85.34 (6)	3.1755 (5)	12	(*M*)-**L12**[a]	100.25 (6)	4.403 (1)

[a] Dihedral angles and P_1–P_2 distances determined for *rac*-crystals

Having in hand a library of various diphosphine (diarylphosphine and dicyclohexylphosphine) ligands (**L1** to **L12**, Table 1), we were interested to have a first view on the impact of the ligand backbone (silyl, aryl, alkyl and halogen) on the dihedral angle and the P_1–P_2 distance compared to the (*M*)-BINAP values.[14]

In the Table 1, we compared the dihedral angles and P_1-–P_2 distances of ligands **L1**–**L12**, which were analyzed by X-ray diffraction, with (*M*)-BINAP as a reference (a comprehensive listing of the X-ray data of ligands **L1**–**L12** is included in the Supporting Information).[15] The size of the substituents on positions 6 and 6′ of the biaryl (**L5** *vs.* **L6**: 79.84° *vs.* 85.34°) and the substitution pattern on the phosphorus atoms (**L5** *vs.* **L4**: 3.4423 Å *vs.* 3.6264 Å) have a direct impact on the dihedral angle and P_1–P_2 distance values. A small effect of halogen atoms exchanged at the 6,6′-positions (**L2**, **L7** and **L8**) on the distance between the phosphorus atoms was observed. The dihedral angles of **L9** and **L10**, in which rotation of the sp^2–sp^2 bond is restricted by a butane bridge are lower and close to the calculated dihedral angles of C_2-TunaPhos (74°).[13] As can be seen from the ORTEP molecular structure of ligand **L12** (see Figure 11 in the Supporting Information), the edge orientation of the phenyl rings on positions 6,6′ is responsible for the dihedral angle increase up to 100.25°. Surprisingly, a very small dihedral angle in **L11** ligand (64.14°) is detected due to the face orientation of 6,6′-diphenyl substituents. Important variations were also noticed compared to the reference values measured for (*M*)-BINAP (entry 1, Table 1). Therefore, it will be interesting to see the influence of those parameters in metal-catalyzed hydrogenation reactions.

In conclusion, we have demonstrated that the asymmetric bromine–lithium exchange was successfully applied to the synthesis of new chiral biphenyl-diphosphine ligands bearing various substituents at positions 6 and 6′ and phosphines. Twelve ligands (**L1** to **L12**) were synthesized in good overall yield and perfect optical purity (*ee* > 99%). Further investigations are currently ongoing with this new ligand family on metal-catalyzed hydrogenation reactions and preliminary results will be communicated in due time.

Experimental Section

General Procedure of Br–Li Exchange

To a flame-dried Schlenck tube were added 256 mg (1.06 mmol, 0.5 equiv.) of chiral ligand (1*R*,2*R*)-1,2-dimethoxy-1,2-diphenylethane **2** followed by 20 mL of dry toluene. The resulting mixture was cooled to −78 °C during 10 min. Then 2.92 mL (4.68 mmol, 4 equiv.) of *n*-BuLi (1.6 M in hexanes) were added and an additional time of 10 min was respected. Finally, 1 g (2.12 mmol, 1 equiv.) of the substrate 2,2′,6,6′-tetrabromo-1,1′-biphenyl **1**, previously dis-

solved in 10 mL of dry toluene was added to the medium. The reaction was carried out during 2 h at −78 °C. Then it was quenched with 4 or 5 equiv. of the appropriate electrophile at −78 °C, and finally allowed to reach room temperature during 2 h. Then it was quenched with water and followed by an extraction with EtOAc. The combined organic fractions were dried over sodium sulfate, filtered and concentrated under reduced pressure followed by silica gel flash chromatography or crystallization.

Acknowledgements

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