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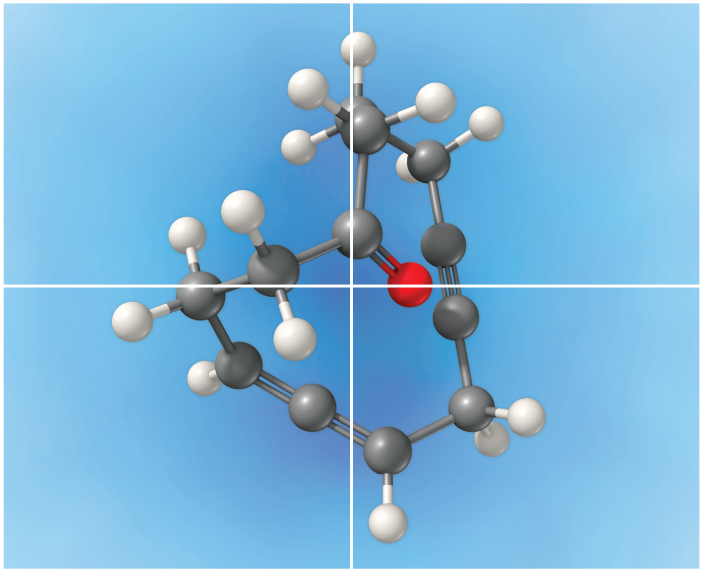

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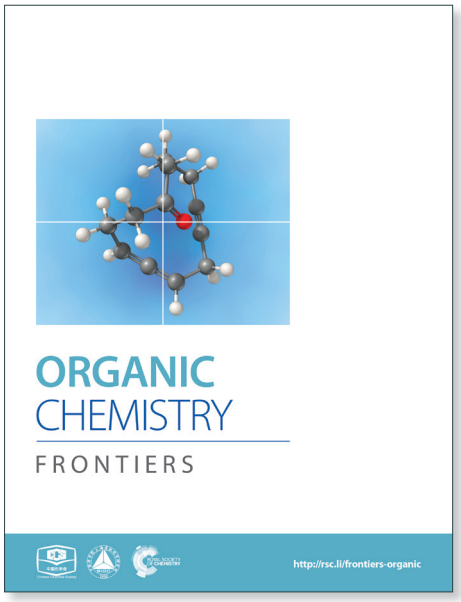

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Research Article

Atroposelective synthesis of axially chiral P,S-ligands based on Arynes

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Dedicated to Professor Ei-ichi Negishi for his 80th birthday

The first atropo-selective aryl-aryl coupling based on arynes in presence of a *tert*-butylsulfinyl group as chiral auxiliary on the aryllithium nucleophile is described. The approach allows for the efficient access to a novel family of atropo-enantiopure biphenyl-based phosphine-thioether ligands. The new *P,S* heterodonor ligands were assessed in model palladium-catalyzed allylic substitution reactions.

Introduction

The importance of biaryls in natural products, drugs, catalysis, and organic materials has led to the development of numerous strategies for their synthesis, especially in the case of atropo-enriched biaryls.[1, 2] In our laboratory, we developed the potential of the old reaction of an aryllithium and an *ortho*-dihaloarene bearing at least one exchangeable halogen, leading to functionalizable 2-halobiaryls.[3-6] We studied its regioselectivity[4-8] and applied it to the synthesis of various C_1-symmetric phosphorus ligands.[9-12] Recently, we described the use of this so-called 'ARYNE coupling' in the modular synthesis of highly atropo-enriched biphenyls (Scheme 1),[13] following Clayden's 'traceless resolving agent' method based on sulfoxides.[14, 15] We started from achiral or racemic polyhalobiphenyls obtained by 'ARYNE coupling', which were then desymmetrized or deracemized. We showed that 2,2',6-tribromo-1,1'-biphenyl could serve as a platform for accessing atropo-enriched biphenyls, variously derivatizable in positions 2, 2' and 6. In the present paper, we report now on an improved alternative method, where axial stereoenrichment is installed during the aryl-aryl coupling step by means of a covalently attached chiral sulfoxide auxiliary, i.e. an atropo-diastereoselective 'ARYNE coupling'.

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Results and discussion

In the target transformation, the position of the chiral auxiliary would be key for an efficient atropo-selective coupling. On the one hand, the auxiliary could be located on the aryllithium nucleophile, closest to the reacting center, namely *ortho* to lithium. Using a chiral coordinating group in *ortho* position would produce a more rigid metallacycle, increasing the chances for a high stereoinduction. On the other hand, if the aryne bears the auxiliary *ortho* to the triple bond, complex regioselectivity issues could arise due to steric and electronic effects of the aryne substituents,[7] including the chiral auxiliary. In particular, a lithium-coordinating auxiliary could favor addition of the nucleophile alternately on both termini of the triple bond depending on the reaction conditions, as shown by Meyers,[16-18] leading to competing kinetic and thermodynamic controls. Consequently, we chose to locate the chiral auxiliary on the nucleophile. The already proposed mechanism[5] would be modified as depicted in Scheme 2. Diastereoselection could proceed either by a favored approach of the aryne to the chiral nucleophile **B**, or by formation of the more stable atropo-diastereomer of the resulting biaryllithium **F**, depending on the early or late nature of the transition state. Arynes being high energy intermediates, and considering the successful prediction of the regioselectivity of nucleophilic addition onto arynes based on the ground state distortion model,[19-24] it is much probable that the transition state would be early. This implies in our case that atropo-diastereoselection arises from the dissymmetric approach of the arylmetal to the aryne.

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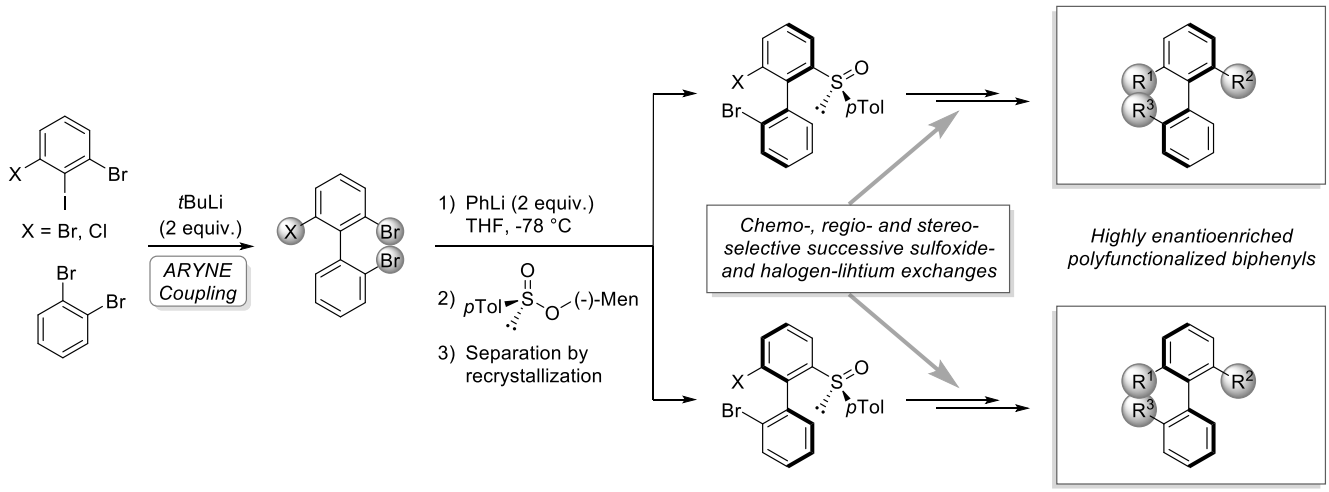
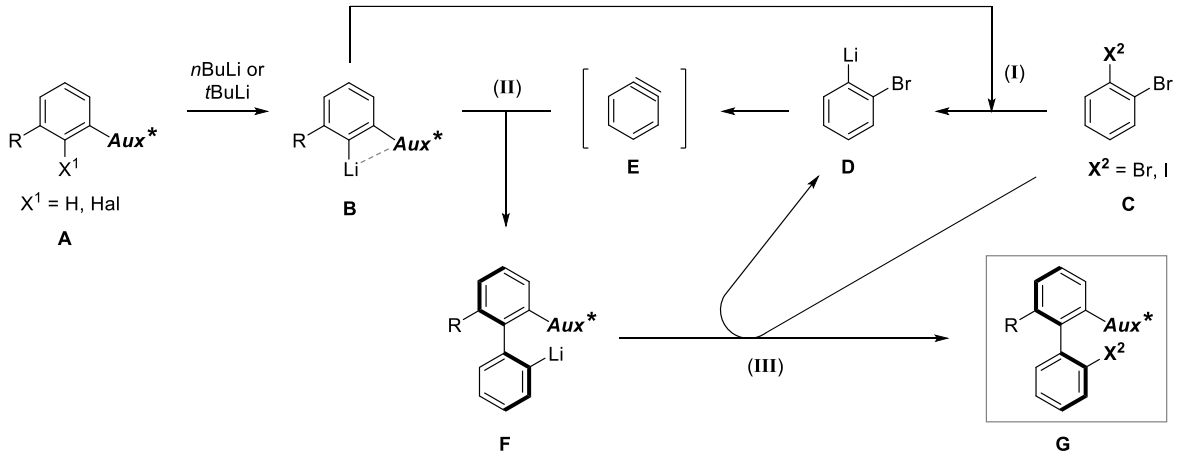


Scheme 1 Post-'ARYNE coupling' desymmetrization (X =Br) or deracemization (X = Cl) and functionalization of biphenyls.



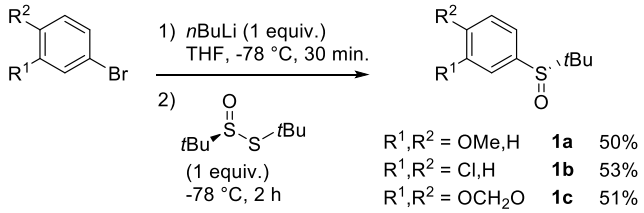
Scheme 2 Proposed mechanism of the atropo-diastereoselective 'ARYNE coupling' (*Aux** = coordinating chiral auxiliary).

Due to the successful results obtained in the literature using sulfoxides as chiral auxiliaries in directed lithiation-diastereoselective trapping sequences on aromatic compounds,[25-34] as well as in our precedent work,[35-40] and due to the robustness of the *tert*-butyl sulfinyl group, we chose the latter as stereoinducer in our targeted transformation.

Atropo-diastereoselective 'ARYNE coupling' with aryl tert-butyl sulfoxides

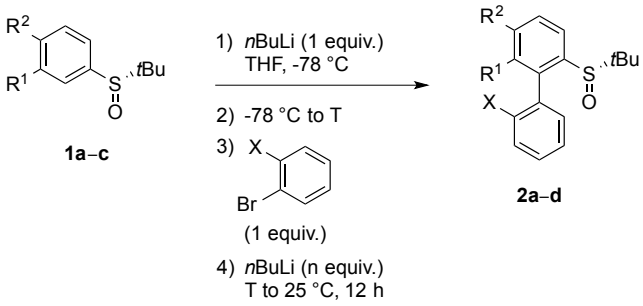
Aryl *tert*-butyl sulfoxides **1a–c** were therefore prepared following Ellman's method,[41, 42] after enantioselective oxidation of di-*tert*-butyl disulfide and treatment with the desired aryllithium reagents (Scheme 3). Sulfoxide **1a** was chosen as test substrate in the 'ARYNE coupling' with 1,2-dibromobenzene due to its easy access, its completely regioselective lithiation with *n*BuLi,[43, 44] and the ease of detection of its derivatives by ^{1}H and ^{13}C NMR thanks to the OMe signals. Preliminary experiments showed that in the previously reported conditions (treatment of the pronucleophile with *n*BuLi at -78 °C, followed by addition of 1,2-dibromobenzene at -78 °C and stirring while warming up to room temperature no coupling product was obtained (Table 1, entry 1). We suspected a lack of reactivity of the lithiated arylsulfoxide in the halogen/lithium exchange with 1,2-dibromobenzene (stage (**I**) in Scheme 2). Accordingly, 0.2 equivalents of *n*BuLi were added after introduction of the benzyne precursor so as to trigger the generation of *ortho*-bromo-lithiobenzene and the chain reaction (Table 1, entry 2). Here again, the formation of the coupling product was not observed, and only the starting sulfoxide, 1,2-dibromobenzene and its homocoupling product, 2,2'-dibromobiphenyl, were recovered. Increasing the temperature before introduction of 1,2-dibromobenzene for a facile elimination of LiBr did not lead to the desired biarylsulfoxide either (entry 3). Finally, in

order to facilitate further the formation of the aryne, in both stages (**I**) and (**III**) of the mechanism (Scheme 2), 1,2-dibromobenzene was replaced with 1-bromo-2-iodobenzene, since halogen/lithium exchanges are faster with iodine than with bromine. In that case, starting from sulfoxides **1a–c**, the corresponding coupling products **2b–d** were indeed obtained, in various yields and atropo-selectivities (Table 1, entries 4–6). Only one diastereomer of **2b** could be isolated in 20% yield from the complex mixture, although formation of the other atropo-isomer could not be ruled out (entry 4). The benzodioxole analogue **2d** was obtained in a ca. 1:1 diastereomeric ratio, yet with a good 82% yield (entry 6). Most interestingly, biaryl **2c** could be obtained with a promising diastereomeric ratio of 79:21, and the atropo-diastereomers could be separated by column chromatography with respective yields of 40% and 11% (entry 5). After recrystallization from ethyl acetate, the absolute configuration of the major isomer could be determined by X-ray diffraction crystallography and was shown to be (S_S,a*S*) (Figure 1).[45] We could moreover show that each atropo-diastereomer of **2c** was obtained with high enantioenrichment (e.r. = 97:3 for (S_S,a*S*)-**2c**, 99:1 for (S_S,a*R*)-**2c**) by chiral SFC analysis after synthesis of both racemic diastereomers starting from (±)-di-*tert*-butyl-thiosulfinate, confirming the configurational stability of the sulfinyl auxiliary during the 'ARYNE coupling'.



Scheme 3 Synthesis of the starting aryl *tert*-butyl sulfoxides.

Table 1 Atropo-diastereoselective 'ARYNE coupling' of aryl *tert*-butyl sulfoxides.

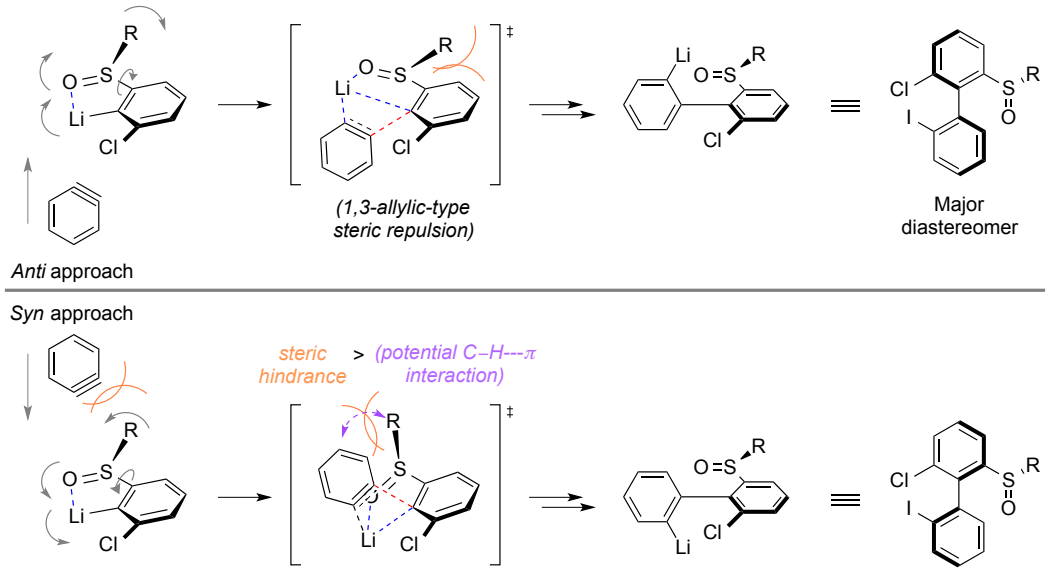


Entry	S.M.	R^1	R^2	T (°C)	X	Product	n	Yield (%)[a]	d.r.[b]
1	**1a**	OMe	H	-78	Br	**2a**	0	0	—
2	**1a**	OMe	H	-78	Br	**2a**	0.2	0	—
3	**1a**	OMe	H	-35	Br	**2a**	0.2	0	—
4	**1a**	OMe	H	-78	I	**2b**	0.2	20[c]	100:0[c]
5	**1b**	Cl	H	-78	I	**2c**	0.2	51	79:21[d]
6	**1c**	OCH_2O		-78	I	**2d**	0.2	82	54:46

[a] Combined yield of both atropo-diastereomers. [b] Diastereomeric ratio measured by ^{1}H NMR of the crude mixture. [c] Only one atropo-diastereomer could be isolated, whose configuration could not be ascertained; formation of the other atropo-isomer could not be ruled out. [d] The absolute configuration of the major atropo-diastereomer was shown to be (S_S,a*S*) (see text).

Figure 1 X-ray diffraction of the major atropo-diastereomer **(*S*S,*aS*)-2c**.[45]

The stereochemical outcome of the 'ARYNE coupling' could be explained by the following considerations (Scheme 4). During the attack of the aryllithium nucleophile onto the aryne, both aromatic rings should be perpendicular to minimize steric interactions. Due to the strong lithium-coordinating property of sulfinyl groups, the *ortho*-lithioaryl sulfoxide intermediate forms a metallacycle, where the *tert*-butyl substituent and the non-bonding electron pair point away from each side of the benzene ring, respectively towards the top and the bottom in Scheme 4. If the aryne approaches the carbon-lithium bond *anti* to the *t*Bu group, i.e. from the bottom face, the sulfinyl group is forced to rotate "clockwise" in the transition state, thus pushing the *tert*-butyl towards the *ortho*-proton. This 1,3-allylic-type repulsion would hence defavor the *anti* transition state. On the other hand, in the *syn* approach, the rotation of the sulfinyl moiety would be "counter-clockwise", pushing the *t*Bu group into a pseudo-axial position. Despite the flatness of the aryne positioned perpendicularly to the aryllithium, the *t*Bu/aryne steric repulsion would dramatically increase the energy of the *syn* transition state. A weak stabilizing electrostatic interaction between the π cloud of the aryne and the C–H bonds of the *t*Bu group, whose electron density is affected by the electron-withdrawing sulfinyl function,[46] could be expected and would oppose to the steric repulsion. Given the unambiguous absolute configuration of the major atropo-diastereomer (Figure 1), it appears that both this potential stabilizing C–H---π interaction and the 1,3-allylic-type repulsion of the *anti* approach are overpowered by the *t*Bu/aryne repulsion in the *syn* approach. Nevertheless, the imperfect stereoselectivity observed in this reaction may be due to a delicate balance between these various steric and stereoelectronic parameters. This could be also suggested by the poor stereoselectivity of the coupling leading to **2d**, which could be ascribed to a competitive coordination of lithium to the oxygen atoms of the dioxole motif, thus upsetting the relative weight of stabilizing or destabilizing interactions discussed above.



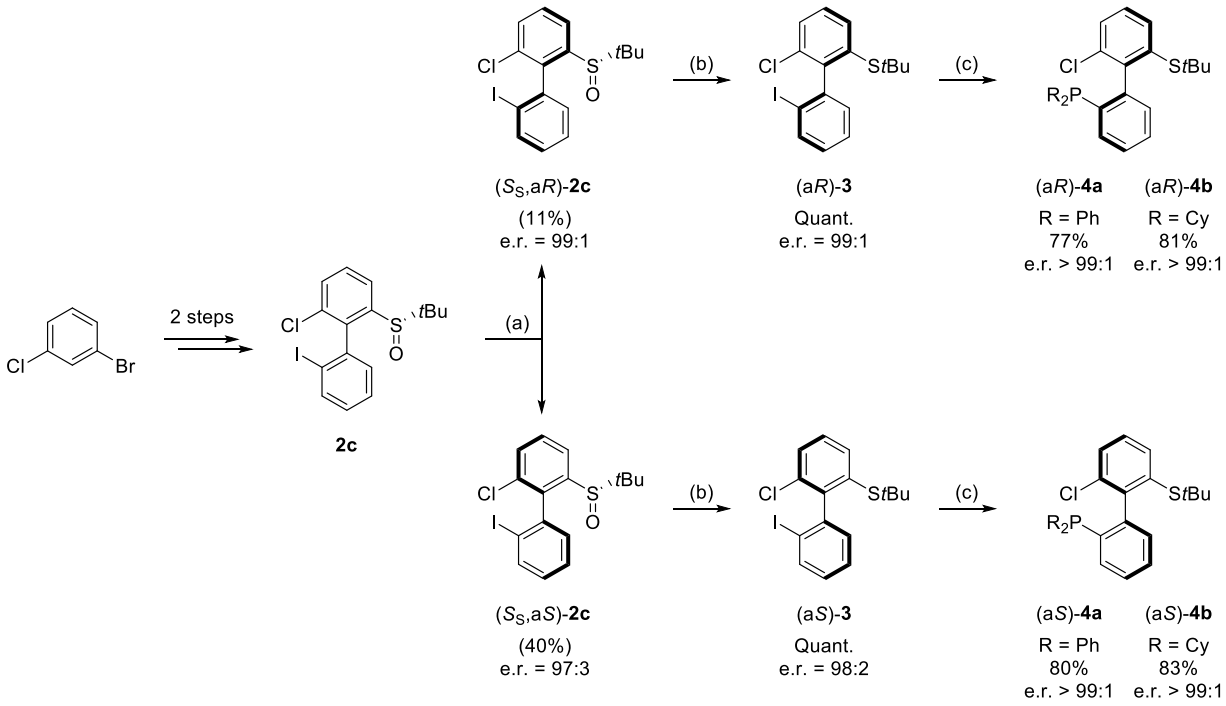
Scheme 4 Stereochemical rationale for the atropo-diastereoselective 'ARYNE coupling' of aryl *tert*-butyl sulfoxides (R = *t*Bu).

Synthesis of P,S ligands and evaluation in catalysis

As **2c** bears a functionalisable iodo substituent *ortho* to the biphenyl junction, and as both of its atropo-diastereomers are separable by column chromatography, we reasoned that it could be easily converted into a set of enantiomeric *P,S* ligands. Indeed, the strong affinity of phosphorus and sulfur for transition metals has motivated the synthesis of many phosphine-thioether bidentate ligands.[47, 48] Yet, among them, very few are based on an atropo-enriched 1,1'-biaryl-2,2'-diyl

phosphine-thioether backbone, and the latter are exclusively binaphthyl-derived ligands.[49-58] We were hence interested in the properties of atropo-enriched biphenyl-linked phosphine-thioethers derived from **2c**.

Each atropomer of sulfoxide **2c** was therefore converted into the corresponding thioether, before undergoing iodine/lithium exchange with *t*BuLi and trapping with chlorodiphenyl– or chlorodicyclohexylphosphine (Scheme 5). Gratifyingly, the corresponding biarylphosphines were obtained without loss of atropo-enrichment. The enantiomeric purity of sulfides **3** and of *P,S* ligands **4a,b** was determined by SFC by comparison with the racemic counterparts obtained by a similar synthesis starting from racemic di-*tert*-butyl thiosulfinate. The retention of axial configuration was confirmed by X-ray diffraction analysis of monocrystals of compound (a*S*)-**4a** (Figure 2).[45]



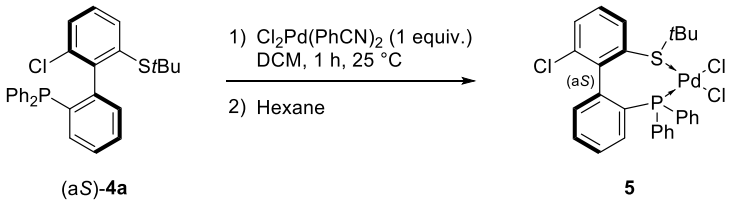
(a) Separation by silica gel column chromatography. (b) TFAA (5 equiv.), NaI (3 equiv.), acetone, -40 °C, 30 min. (c) *i*. *t*BuLi (2 equiv.), THF, -100 °C, 5 min.; *ii*. $ClPR_2$ in toluene, -100 to 25 °C.

Scheme 5 Synthesis of atropo-enantiopure biphenylic P,S ligands.

Figure 2 X-ray diffraction of (a*S*)-**4a**.[45]

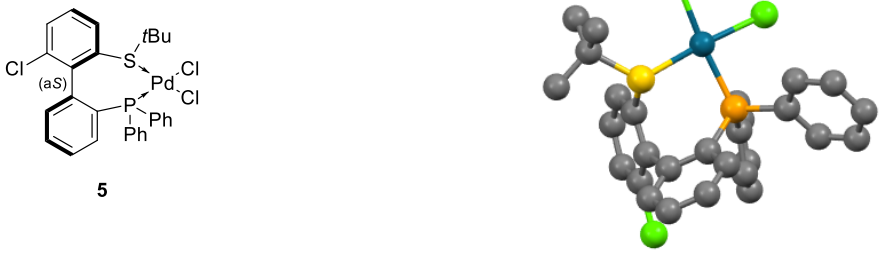
The coordination of (a*S*)-**4a** with a transition metal was then studied by reacting it with bis(benzonitrile)dichloropalladium (Scheme 6). The expected complex ((a*S*)-**4a**)$PdCl_2$ (**5**) was indeed obtained and characterized by ^{1}H, ^{13}C and ^{13}C NMR as well as HRMS. A clear shift in ^{31}P NMR from -14.1 ppm (free ligand **4a**) to +29.4 ppm in **5** attested the coordination of the phosphine moiety to palladium. Similarly, the singlet corresponding to the protons of the *tert*-butyl group moved downfield, from 1.12 to 1.63 ppm, indicative of electron depletion at sulfur and hence of coordination of the thioether to the metal. Additionally, the ^{13}C NMR signal of the quaternary carbons in the *t*Bu group moved upfield from 47.4 ppm in **4a** to 30.4 ppm in **5**, which is coherent with back-donation from the metal. The structure of complex **5** was further unambiguously determined by X-ray diffraction analysis of single crystals of **5** (Figure 3).[45] The metal is effectively chelated by the bidentate ligand, affording a distorted square-planar geometry. The Cl-Pd-Cl angle is almost equal to 90° (89.60°), but other angles deviate from the ideal case; the P-Pd-S and P-Pd-Cl3 angles are smaller than 90° (respectively 87.61° and 87.97°), while the S-

Pd-Cl2 angle is 95.59°, i.e. wider than a right angle. These distorsions are explained in part by the difference in *trans* influence between the phosphine and thioether moieties; indeed, the Pd-Cl2 bond measures 2.339 Å and the Pd-Cl3 one 2.316 Å, demonstrating the stronger *trans* influence of the phosphine. Last but not least, the axial configuration of the free ligand is preserved in complex **5**, and coordination of sulfur to palladium is effected so as to place the *t*Bu group in an equatorial position, away from the phenyl substituents at phosphorus.



(a*S*)-**4a** **5**

Scheme 6 Synthesis of a palladium complex from atropo-enantiopure P,S ligand (a*S*)-**4a**.

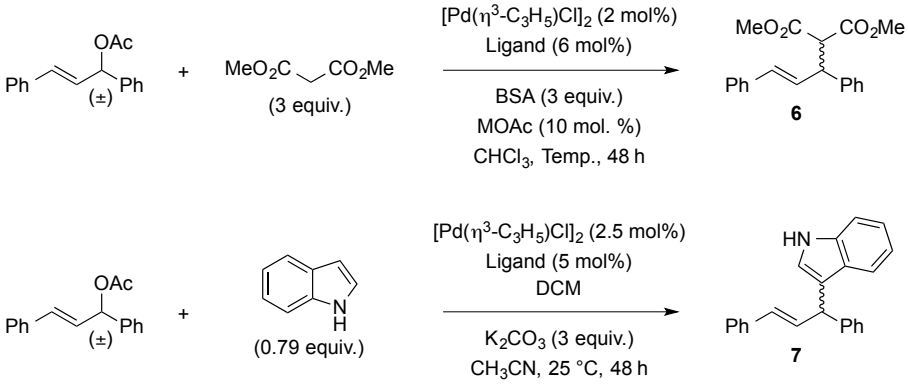


5

Figure 3 X-ray diffraction of **5**.[45]

As palladium-catalyzed asymmetric allylic substitution constitutes a benchmark reaction for the assessment of chiral bidentate ligands, compounds **4a,b** were evaluated in the reaction of 1,3-diphenylallyl acetate with dimethyl malonate and indole (Table 2). In the reaction with dimethyl malonate, ligands (a*S*)-**4a** and (a*S*)-**4b** gave similar results in terms of yield and enantioselectivity (entries 1–2), indicating negligible influence of the phosphorus substituents. Both enantiomers of ligand **4b** also gave similar results as expected (entries 2–3). Running the reaction at higher temperature (25 °C instead of 10 °C) did not bring any improvement (entry 4), but a slight increase in enantioselectivity was observed when diminishing the reaction temperature to -25 °C (entry 5). On the other hand, switching from potassium to lithium in the acetate salt proved markedly advantageous, as it increased the e.r. from 90:10 (80% ee) to 97:3 (94% ee) at 25 °C, and from 93:7 (86% ee) to 99:1 (98% ee) at -25 °C (entries 4–7). For comparison purposes, binaphthyl-derived phosphine-thioether ligands afforded 68–96% yield and 7-96% ee in the same reaction.[56] Ligand (a*S*)-**4a** was also evaluated in the reaction with indole, using Hoshi and Hajiwara *et al.*'s conditions developed for related Sulfur-MOP ligands.[58] In our case (entry 8), 83% yield and 92:8 e.r. (i.e. 84% ee) were achieved, which compares honorably with the cited Sulfur-MOP ligands (58– 89% yield and 48–92% ee).

Table 2 Evaluation of ligands **4a,b** in palladium-catalyzed asymmetric allylic substitution.



Entry	Ligand	Product	MOAc	T (°C)	Yield (%)[a]	e.r. (abs. config.)[b,c]
1	(a*S*)-**4a**	**6**	KOAc	10	98	90:10 (*R*)
2	(a*S*)-**4b**	**6**	KOAc	10	99	91:9 (*R*)
3	(a*R*)-**4b**	**6**	KOAc	10	93	90:10 (*S*)
4	(a*S*)-**4a**	**6**	KOAc	25	99	90:10 (*R*)
5	(a*S*)-**4a**	**6**	KOAc	-25	99	93:7 (*R*)
6	(a*S*)-**4a**	**6**	LiOAc	25	99	97:3 (*R*)
7	(a*S*)-**4a**	**6**	LiOAc	-25	99	99:1 (*R*)
8	(a*S*)-**4a**	**7**	—	25	83	92:8

[a] Isolated yield. [b] Enantiomeric ratio measured by chiral SFC analysis. [c] When possible, absolute configuration was assigned by comparison with literature data.

Conclusions

This work describes the first attempt at developing an unprecedented asymmetric version of the so-called 'ARYNE coupling', i.e. the coupling of an aryllithium and an aryne generated *in situ* from an *ortho*-dihaloarene by halogen/lithium exchange in a chain reaction. A *tert*-butylsulfinyl group was used as chiral auxiliary on the aryllithium nucleophile. In one case, both atropo-diastereomers of the resulting 2-(*tert*-butylsulfinyl)-6-chloro-2-iodo-1,1'-biphenyl could be separated by column chromatography, and derivatized into atropo-enantiopure biphenyl-based phosphine-thioether ligands. The latter are the first of their kind in the family of phosphine-thioethers, where congeners had been built up to now from a binaphthyl scaffold. The new *P,S* heterodonor ligands were assessed in model palladium-catalyzed allylic substitution reactions, where they showed comparable efficiency with regard to their binaphthyl homologues of the literature. Other developments of the atropo-diastereoselective 'ARYNE coupling' will soon be reported.

Experimental section

General information

Starting materials, if commercially available, were purchased and used as received after check of the purity. When known compounds had to be prepared according to literature procedures, pertinent references are given. Air and moisture-sensitive materials were stored in Schlenk tubes under argon. Et_2O, 1,4-dioxane and THF were dried by distillation over sodium/benzophenone after the characteristic blue color of sodium diphenyl ketyl (benzophenone sodium "radical –anion") had been found to persist. CH_2Cl_2 was dried over CaH_2 under argon. Diisopropylamine and triethylamine were dried over KOH under argon. Melting ranges (m.p.) given were found to be reproducible after recrystallization, unless stated otherwise ("decomp."), and are uncorrected. Thin-Layer chromatography (TLC) was carried out on 0.25 mm Merck silica-gel (60-F254). Column chromatography was carried out on silica gel by using MERCK silica (40-63µm). *n*-Butyllithium (1.6 M in hexanes, Aldrich), was used as solution and its concentration was determined following the Wittig-Harborth Double Titration method ((total base) - (residual base after reaction with 1,2-dibromoethane)). NMR-spectra were recorded on Bruker Avance300 (^{1}H NMR= 300 MHz, ^{13}C NMR= 75.5 MHz) and Bruker Avance400 (^{1}H NMR= 400MHz, ^{13}C NMR= 100.6 MHz). Chemical shifts were referred on partial deuterated chloroform ($\delta[^1H]$ = 7.26 and accordingly $\delta[^{13}C]$ = 77.16 ppm) and given in ppm on the δ-scale. Multiplicities were abbreviated as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Coupling constants were given in Hz. The spectra were processed with the programs Bruker TOPSIN 2.1 or MestReNova 5.2.5. Mass spectra and elementary analysis were carried out by the Analytical Service of the University of Strasbourg. The angles of rotation were measured on a Perkin Elmer Polarimeter 341 and denoted as specific rotations: $[\alpha]_D^{20}$. Crystal X-ray diffraction analysis was carried out by the Radiocrystallography Service of the University of Strasbourg.

General procedure for the synthesis of *tert*-butylsulfinyl benzene derivatives

At -78 °C, *n*-butyllithium (1.6 M in hexanes, 1.1 equiv., 12.5 mL, 20.0 mmol) was added dropwise to a solution of the substrate (1 equiv., 20.0 mmol) in THF (100 mL, C = 0.2 mol/L). The resulting mixture was stirred for 30 min at -78 °C and a solution of (*S*)-*tert*-butyl-*tert*-butanethiosulfinate (1 equiv., 3.89 g, 20.0 mmol) in THF (18 mL, C = 1.1 mol/L) was added. The resulting mixture was stirred for 2 h at -78 °C and then MeOH was added (100 mL) at -78 °C, followed by water (100 mL) at 25 °C. The aqueous and organic layers were separated and the aqueous layer was extracted with ethyl acetate (3 × 100 mL). The combined organic layers were dried over Na_2SO_4, filtered and evaporated to dryness.

(*S*)-1-(*tert*-Butylsulfinyl)-3-methoxybenzene (1a).[59, 36, 60] The product was prepared according to the general procedure and starting from 1-bromo-3-methoxybenzene (1 equiv., 3.74 g, 20.0 mmol). Purification by column chromatography on silica gel (eluent: cyclohexane/AcOEt (7/3)) afforded (*S*)-1-(*tert*-butylsulfinyl)-3-methoxybenzene **1a** as a colorless solid (2.12 g, 10.0 mmol, 50%): Mp = 79-81 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.38 (app. t, *J* = 7.9 Hz, 1 H), 7.21-7.17 (m, 1 H), 7.10 (d, *J* = 7.9 Hz, 1 H), 7.02 (dd, *J* = 8.3, 2.3 Hz, 1 H), 3.86 (s, 3 H, OMe), 1.18 (s, 9 H, S(O)CMe_3) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 159.8 (C_{IV}, COMe), 141.4 (C_{IV}, CS(O)CMe_3), 129.2, 118.7, 117.5, 110.7, 56.0 (C_{IV}, S(O)CMe_3), 55.6 (OMe), 22.9 (3 C, S(O)CMe_3) ppm; Elemental analysis calcd. (%) C 62.23, H 7.60; found C 62.47, H 7.57; $[\alpha]_D^{20}$ = -33.7 (c 1, $CHCl_3$).

(*S*)-1-(*tert*-Butylsulfinyl)-3-chlorobenzene (1b). The product was prepared according to the general procedure and starting from 1-bromo-3-chlorobenzene (1 equiv., 2.35 mL, 20.0 mmol). Purification by column chromatography on silica gel (eluent: cyclohexane/AcOEt (7/3)) afforded (*S*)-1-(*tert*-butylsulfinyl)-3-chlorobenzene **1b** as a colorless solid (2.30 g, 10.6 mmol, 53%): Mp = 115-117 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.63-7.57 (m, 1 H), 7.51-7.37 (m, 3 H), 1.19 (s, 9 H, S(O)CMe_3) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 142.3 (C_{IV}, CS(O)CMe_3), 135.0 (C_{IV}, CCl), 131.3, 129.5, 126.2, 124.5, 56.3 (C_{IV}, S(O)CMe_3), 22.8 (3 C, SOCMe_3) ppm; Elemental analysis calcd. (%) C 55.42, H 6.05; found C 55.74, H 6.12. $[\alpha]_D^{20}$ = -151.7 (c 1, $CHCl_3$). ee > 99% (SFC, CHIRALCEL OD-H).

(*S*)-5-(*tert*-Butylsulfinyl)benzo[*d*][1,3]dioxole (1c).[60] The product was prepared according to the general procedure and starting from 5-bromobenzo[*d*][1,3]dioxole (1 equiv., 2.41 mL, 20.0 mmol). Purification by column chromatography on silica gel (eluent: cyclohexane/AcOEt (7/3)) afforded (*S*)-5-(*tert*-butylsulfinyl)benzo[*d*][1,3]dioxole **1c** as a colorless solid (2.31 g, 10.2 mmol, 51%): Mp = 67-69 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.04 (d, *J* = 1.5 Hz, 1 H), 6.97 (dd, *J* = 8.1, 1.5 Hz, 1 H), 6.82 (d, *J* = 8.1 Hz, 1 H), 5.98 (s, 2 H, OCH_2O), 1.09 (s, 9 H, S(O)CMe_3) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 150.3 (C_{IV}), 148.1 (C_{IV}), 133.1 (C_{IV}, CS(O)CMe_3), 121.1, 108.1, 106.4, 101.8 (C_{II}, OCH_2O), 55.9 (C_{IV}, S(O)CMe_3), 22.8 (3 C, S(O)CMe_3) ppm.; Elemental analysis calcd. (%) C 58.38, H 6.24; found C 58.32, H 6.23. $[\alpha]_D^{20}$ = -39.4 (c 1, $CHCl_3$).

2-((*S*)-*tert*-Butylsulfinyl)-2'-iodo-6-methoxy-1,1'-biphenyl (2b). *n*-Butyllithium (1.6 M in hexanes, 1 equiv., 688 µL, 1.10 mmol) was added to a solution of (*S*)-1-(*tert*-butylsulfinyl)-3-methoxybenzene **1a** (1 equiv., 234 mg, 1.10 mmol) in THF (5.5 mL, C = 0.2 mol/L) at -78 °C. 1-Bromo-2-iodobenzene (1 equiv., 141 µL, 1.10 mmol) was added at -78 °C, followed by *n*-butyllithium (1.6 M in hexanes, 0.2 equiv., 138 µL, 0.220 mmol). The reaction mixture was allowed to reach 25 °C during 12 h and water was added (5 mL). The aqueous and organic layers were separated and the aqueous layer was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over Na_2SO_4, filtered and evaporated to dryness. The crude mixture was purified by column chromatography on silica gel (eluent: pentane/AcOEt (2/1)). Only one *atropo*-diastereoisomer of **2b** was isolated as a pale yellow oil (91.1 mg, 0. 220 mmol, 20%). Attempt to obtain correct elemental analysis failed probably due to the enclosure of solvent in the oil: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.95 (dd, *J* = 7.9, 1.0 Hz, 1 H), 7.62 (dd, *J* = 7.9, 1.5 Hz, 1 H), 7.57 (app. t, *J* = 7.9 Hz, 1 H), 7.36 (app. td, *J* = 7.6, 1.0 Hz, 1 H), 7.14 (m, 2 H), 7.06 (app. td, *J* = 7.6, 1.7 Hz, 1 H), 3.74 (s, 3 H, OMe), 1.06 (s, 9 H, S(O)CMe_3) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 156.2 (C_{IV}), 141.6 (C_{IV}), 139.2, 139.1 (C_{IV}), 133.4, 133.2 (C_{IV}), 129.5, 129.3, 127.0, 119.1, 114.0, 102.0 (C_{IV}, CI), 57.5 (C_{IV}, S(O)CMe_3), 56.2 (OMe), 23.6 (3 C, S(O)CMe_3) ppm.

2-(*tert*-Butylsulfinyl)-6-chloro-2'-iodo-1,1'-biphenyl ((*S*$_S$,a*R*)-2c and (*S*$_S$,a*S*)-2c). *n*-Butyllithium (1.6 M in hexanes, 1 equiv., 688 µL, 1.10 mmol) was added to a solution of (*S*)-1-(*tert*-butylsulfinyl)-3-chlorobenzene **1b** (1 equiv., 238 mg, 1.10 mmol) in THF (2.2 mL, C = 0.5 mol/L) at -78 °C. 1-Bromo-2-iodobenzene (1 equiv., 141 µL, 1.10 mmol) was added at -78 °C followed by *n*-butyllithium (1.6 M in hexanes, 0.2 equiv., 138 µL, 0.220 mmol). The reaction mixture was allowed to reach 25 °C during 12 h. Water was added (2 mL). The aqueous and organic layers were separated and the aqueous layer was extracted with ethyl acetate (3 × 2 mL). The combined organic layers were dried over Na_2SO_4, filtered and evaporated to dryness. A mixture of two atropo-diastereomers **2c** was obtained with a diastereomeric excess of 57%. The crude mixture was purified by column chromatography on silica gel (eluent: pentane/AcOEt (7/3)) (235 mg, 0.561 mmol, 51%): Elemental analysis calcd. (%) C 45.89, H 3.85; found C 45.79, H 3.90. Atropo-diastereoisomer **(*S*$_S$,a*R*)-2c** (colorless solid) (50.7 mg, 0.121 mmol, 11%): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.94 (app. td, *J* = 7.5, 1.8 Hz, 2 H), 7.65-7.53 (m, 2 H), 7.48-7.38 (m, 2 H), 7.10 (app. td, *J* = 8.1, 2.1 Hz, 1 H), 1.12 (s, 9 H, S(O)CMe_3) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 142.8 (C_{IV}), 141.9 (C_{IV}), 139.8, 139.8 (C_{IV}), 134.9 (C_{IV}), 132.3, 132.3, 129.9, 129.6, 128.2, 126.2, 102.1 (C_{IV}, CI), 57.4 (C_{IV}, S(O)CMe_3), 23.6 (3 C, S(O)CMe_3) ppm. ee = 97% (SFC, CHIRALCEL OD).

Atropo-diastereoisomer **(*S*$_S$,a*S*)-2c** (crystallization from ethyl acetate, colorless crystal) (184 mg, 0.439 mmol, 40%): Mp = 130-132 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.98 (app. d, *J* = 8.1 Hz, 1 H), 7.94 (dd, *J* = 7.8, 1.2 Hz, 1 H), 7.68-7.63 (m, 1 H), 7.56 (app. t, *J* = 7.8 Hz, 1 H), 7.42 (app. t, *J* = 7.8 Hz, 1 H), 7.21-7.05 (m, 2 H), 1.08 (s, 9 H, S(O)CMe_3) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 143.0 (C_{IV}), 142.1 (C_{IV}), 140.2 (C_{IV}), 139.4, 134.1 (C_{IV}), 133.1, 132.5, 130.0, 129.6, 127.4, 125.9, 100.9 (C_{IV}, CI), 57.9 (C_4, S(O)CMe_3), 23.5 (3 C, S(O)CMe_3) ppm; $[\alpha]_D^{20}$ = -264.1 (c 1, $CHCl_3$). ee = 94% (SFC, CHIRALCEL OD).

5-((*S*)-*tert*-Butylsulfinyl)-4-(2-iodophenyl)benzo[*d*][1,3]dioxole ((*S*$_S$,a*R*)-2d and (*S*$_S$,a*S*)-2d)). *n*-Butyllithium (1.6 M in hexanes, 1 equiv., 688 µL, 1.10 mmol) was added to a solution of (*S*)-5-(*tert*-butylsulfinyl)benzo[*d*][1,3]dioxole **1c** (1 equiv., 249 mg, 1.10 mmol) in THF (2.2 mL, C = 0.5 mol/L) at -78 °C. 1-Bromo-2-iodobenzene (1 equiv., 141 µL, 1.10 mmol) was added at -78 °C followed by *n*-butyllithium (1.6 M in hexanes, 0.2 equiv., 138 µL, 0.220 mmol). The reaction mixture was allowed to reach 25 °C during 12 h. Water was added (2 mL). The aqueous and organic layers were separated and the aqueous layer was extracted with ethyl acetate (3 × 2 mL). The combined organic layers were dried over Na_2SO_4, filtered and evaporated to dryness. A mixture of two atropo-diastereomers **(*S*$_S$,a*S*)-2d** and **(*S*$_S$,a*R*)-2d** was obtained as a colorless solid with a diastereomeric excess of 8%. The crude mixture was purified by column chromatography on silica gel (eluent: pentane/AcOEt (7/3)) (385 mg, 0.899 mmol, 82%): Elemental analysis calcd. (%) C 47.67, H 4.00; found C 47.99, H 4.22. Fractions of pure atropo-diastereomer 2 could be obtained after several purifications by column chromatography, allowing for attribution of NMR signals to each diastereomer.

Atropo-diastereoisomer 1: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.96 (dd, *J* = 7.8, 1.0 Hz, 1 H), 7.54 (d, *J* = 8.1 Hz, 1 H), 7.50

(dd, J = 6.3, 1.5 Hz, 1 H), 7.43 (app. td, J = 7.5, 1.1 Hz, 1 H), 7.09-7.02 (m, 2 H), 6.08 (AB, $\Delta\nu_{AB}$ = 15.0 Hz, J = 1.3 Hz, 2 H, OCH_2O), 1.06 (s, 9 H, S(O)CMe_3) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 149.9 (C_{IV}), 145.2 (C_{IV}), 139.9, 137.1(C_{IV}), 133.2(C_{IV}), 131.8, 129.9, 128.0, 125.0 (C_{IV}), 122.2, 108.7, 102.0 ($C_{II,}$ OCH_2O), 100.9 (C_{IV}, CI), 57.2 (C_{IV}, S(O)$\underline{C}Me_3$), 23.2 (3 C, S(O)C$\underline{Me_3}$) ppm.

Atropo-diastereomer 2: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.99 (dd, J = 8.1, 1.2 Hz, 1 H), 7.55 (d, J = 8.4 Hz, 1 H), 7.41 (app. td, J = 7.5, 1.2 Hz, 1 H), 7.24 (dd, J = 7.5, 1.5 Hz, 1 H), 7.10 (app. td, J = 7.8, 1.8 Hz, 1H), 7.05 (d, J = 8.1 Hz, 1 H), 6.02 (AB, $\Delta\nu_{AB}$ = 7.1 Hz, J = 1.2 Hz, 2 H, OCH_2O), 1.03 (s, 9 H, S(O)CMe_3) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 150.2 (C_{IV}), 145.3 (C_{IV}), 139.6, 137.3 (C_{IV}), 132.6 (C_{IV}), 132.4, 130.0, 127.6, 125.2 (C_{IV}), 121.9, 108.5, 102.0 ($C_{II,}$ OCH_2O), 101.4 (C_{IV}, CI), 57.4 (C_{IV}, S(O)$\underline{C}Me_3$), 23.3 (3 C, S(O)C$\underline{Me_3}$) ppm.

***tert*-Butyl(6-chloro-2'-iodo-(1,1'-biphenyl)-2-yl)sulfane ((a*S*)-3 and (a*R*)-3).** At -40 °C, a solution of trifluoroacetic anhydride (5 equiv., 334 µL, 2.40 mmol) in acetone (1.2 mL, C = 2 mol/L) was added slowly *via* cannula to a stirred solution of the substrate (1 equiv., 200 mg, 0.480 mmol) and sodium iodide (3 equiv., 216 mg, 1.44 mmol) in acetone (4.8 mL, C = 0.1 mol/L). After 30 min, the solution was allowed to reach 25 °C. After dropwise addition of a saturated aqueous solution of sodium sulfite (2 mL) and a saturated aqueous solution of sodium hydrogencarbonate (2 mL), the organic and aqueous layers were separated and the aqueous layer was extracted with dichloromethane (3 × 5 mL). The combined organic layers were dried over Na_2SO_4, filtered and evaporated to dryness. The crude mixture was purified by column chromatography on silica gel (eluent: cyclohexane): Mp = 55-57 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.93 (dd, J = 7.5, 0.6 Hz, 1 H), 7.64 (dd, J = 7.5, 0.9 Hz, 1 H), 7.49-7.37 (m, 2 H), 7.31 (app. t, J = 8.1 Hz, 1 H), 7.17 (dd, J = 7.5, 1.5 Hz, 1 H), 7.08 (app. td, J = 7.8, 1.5 Hz, 1 H), 1.26 (s, 9 H, $SCMe_3$) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 147.1 (C_{IV}), 143.9 (C_{IV}), 138.6, 135.9 (C_{IV}), 135.1, 134.3 (C_{IV}), 130.9, 129.3, 129.0, 128.5, 127.4, 101.2 (C_{IV}, CI), 47.6 (C_{IV}, S$\underline{C}Me_3$), 31.7 (3 C, SC$\underline{Me_3}$) ppm; Elemental analysis calcd. (%) C 47.72, H 4.00; found C 47.78, H 4.10.

Synthesis of **(a*S*)-3**: The product was prepared according to the general procedure and starting from (a*S*)-2-((*S*)-*tert*-butylsulfinyl)-6-chloro-2'-iodo-1,1'-biphenyl **(S_S,a*S*)-2c**. Purification by column chromatography afforded **(a*S*)-3** as a colorless solid (191 mg, 0.474 mmol, 99%). $[\alpha]_D^{20}$ = -127.5 (c 1, $CHCl_3$). ee = 96 % (SFC, CHIRALCEL OJ-H).

Synthesis of **(a*R*)-3**: The product was prepared according to the general procedure and starting from (a*R*)-2-((*S*)-*tert*-butylsulfinyl)-6-chloro-2'-iodo-1,1'-biphenyl **(S_S,a*R*)-2c**. Purification by column chromatography afforded **(a*R*)-3** as a colorless solid (191 mg, 0.474 mmol, 99%). ee = 98% (SFC, CHIRALCEL OJ-H).

(2'-(*tert*-Butylthio)-6'-chloro-(1,1'-biphenyl)-2-yl)diphenylphosphine ((a*S*)-4a and (a*R*)-4a)). *tert*-Butyllithium (1.7 M in pentane, 2 equiv., 294 µL, 0.500 mmol) was added to a solution of the substrate (1 equiv., 100 mg, 0.250 mmol) in THF (0.5 mL, C = 0.5 mol/L) at -100 °C. After 5 min, a solution of chlorodiphenylphosphine (1 equiv., 44.9 µL, 0.250 mmol) in toluene (0.25 mL, C = 1mol/L) was added. The reaction mixture was allowed to reach 25 °C and water was added (0.5 mL). The organic and aqueous layers were separated and the aqueous layer was extracted with dichloromethane (3 × 1 mL). The combined organic layers were dried over Na_2SO_4, filtered and evaporated to dryness. The crude mixture was purified by chromatography on silica gel (eluent: cyclohexane): Mp = 131-133 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.61 (d, J = 7.5 Hz, 1 H), 7.42 (app. td, J = 7.5, 1.2 Hz, 1 H), 7.37-7.17 (m, 15 H), 1.23 (s, 9 H, $SCMe_3$) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 145.0 (C_{IV}, d, J = 24.1 Hz), 144.1 (C_{IV}, d, J = 4.9 Hz), 138.0 (C_{IV}, d, J = 7.7 Hz), 137.6 (C_{IV}, d, J = 9.3 Hz), 136.9 (C_{IV}, d, J = 9.0 Hz), 136.5 (C_{IV}, d, J = 1.4 Hz), 134.9 (C_{IV}, d, J = 1.1 Hz), 134.2 (d, J = 1.2 Hz), 134.1, 134.0, 133.9, 133.7, 133.5, 130.7 (d, J = 4.8 Hz), 128.7, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 47.4 (C_{IV}, d, J = 1.7 Hz, S$\underline{C}Me_3$), 31.5 (3 C, SC$\underline{Me_3}$) ppm; ^{31}P NMR (161 MHz, $CDCl_3$): δ = -14.11 ppm; Elemental analysis calcd. (%) C 72.95, H 5.68; found C 72.52, H 5.72.

Synthesis of **(a*S*)-4a**: The product was prepared according to the general procedure and starting from (a*S*)-*tert*-butyl(6-chloro-2'-iodo-(1,1'-biphenyl)-2-yl)sulfane **(a*S*)-3**. Purification by column chromatography afforded **(a*S*)-4a** as a colorless solid (88.5 mg, 0.192 mmol, 77%). $[\alpha]_D^{20}$ = -117.8 (c 1, $CHCl_3$). ee > 99% (SFC, CHIRALPAK AZ).

Synthesis of **(a*R*)-4a**: The product was prepared according to the general procedure and starting from (a*R*)-*tert*-butyl(6-chloro-2'-iodo-(1,1'-biphenyl)-2-yl)sulfane **(a*R*)-3**. Purification by column chromatography afforded **(a*R*)-4a** as a colorless solid (92.2 mg, 0.200 mmol, 80%). ee > 99% (SFC, CHIRALPAK AZ).

(2'-(*tert*-Butylthio)-6'-chloro-(1,1'-biphenyl)-2-yl)dicyclohexylphosphine ((a*S*)-4b and (a*R*)-4b). *tert*-Butyllithium (1.7 M in pentane, 2 equiv., 294 µL, 0.500 mmol) was added to a solution of the substrate (1 equiv., 100 mg, 0.250 mmol) in THF (0.5 mL, C = 0.5 mol/L) at -100 °C. After 5 min, a solution of chlorodicyclohexylphosphine (1 equiv., 55.2 µL, 0.250 mmol) in toluene (0.25 mL, C = 1 mol/L) was added. The reaction mixture was allowed to reach 25 °C and water was added (0.5 mL). The organic and aqueous layers were separated and the aqueous layer was extracted with dichloromethane (3 × 1 mL). The combined organic layers were dried over Na_2SO_4, filtered and evaporated to dryness. The crude mixture was purified by chromatography on silica gel (eluent: cyclohexane): Mp = 55-57 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.58 (dd, J = 7.8, 1.2 Hz, 1 H), 7.56-7.52 (m, 1 H), 7.41 (dd, J = 7.8, 1.2 Hz, 1 H), 7.38-7.34 (m, 2 H), 7.28-7.24 (m, 1 H), 7.21-7.15 (m, 1 H), 1.85-1.45 (m, 11 H), 1.39-0.96 (m, 11 H), 1.18 (s, 9 H, $SCMe_3$) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 145.8 (C_{IV}, d, J = 29.3 Hz), 145.3 (C_{IV}, d, J = 5.6 Hz), 136.8 (C_{IV}, d, J = 18.9 Hz), 136.0 (C_{IV}, d, J = 2.1 Hz), 134.8, 134.6 (C_{IV}, d, J = 0.9 Hz), 132.0 (d, J = 2.9 Hz), 131.4 (d, J = 6.0 Hz), 129.1, 127.8, 127.3, 126.7, 47.3 (C_{IV}, d, J = 3.1 Hz, S$\underline{C}Me_3$), 34.7 (d, J = 15.2 Hz), 33.3 (d, J = 13.7 Hz), 31.5 (3 C, SC$\underline{Me_3}$), 30.6 (C_{II}, d, J = 13.2 Hz), 29.8-29.6 (C_{II}, m), 27.7-27.3 (C_{II}, m), 26.5 (C_{II}, d, J = 8.2 Hz) ppm; ^{31}P NMR (161 MHz, $CDCl_3$): δ = -9.89 ppm; Elemental analysis calcd. (%) C 71.09, H 8.10; found C 71.01, H 8.19.

Synthesis of **(a*S*)-4b**: The product was prepared according to the general procedure and starting from (a*S*)-*tert*-butyl(6-chloro-2'-iodo-(1,1'-biphenyl)-2-yl)sulfane **(a*S*)-3**. Purification by column chromatography afforded **(a*S*)-4b** as a colorless solid (98.4 mg, 0.208 mmol, 83%). $[\alpha]_D^{20}$ = -125.2 (1 c, $CHCl_3$). ee > 99 % (SFC, CHIRALPAK AD).

Synthesis of **(a*R*)-4b**: The product was prepared according to the general procedure and starting from (a*R*)-*tert*-butyl(6-chloro-2'-iodo-(1,1'-biphenyl)-2-yl)sulfane **(a*R*)-3**. Purification by column chromatography afforded **(a*R*)-4b** as a colorless solid (96.0 mg, 0.203 mmol, 81%). ee > 99 % (SFC, CHIRALPAK AD).

Complex [(a*S*-4a)PdCl$_2$] (5). Ligand **(a*S*)-4a** (1 equiv., 46.1 mg, 0.100 mmol) and bis(benzonitrile)palladium dichloride (1 equiv., 38.4 mg, 0.100 mmol) were dissolved in dichloromethane (1 mL) under an argon atmosphere and the reaction mixture was stirred for 1 h at 25 °C. Degassed hexane (5 mL) was then slowly added, which led to the precipitation of **5**. The precipitate was filtered and washed with hexane to afford **5** as an orange powder. The single crystals for X-ray diffraction were obtained by recrystallization from dichloromethane and toluene (1:4). Complex **5** and one molecule of toluene crystallize in the same packing: ^{1}H NMR ($CDCl_3$, 400 MHz) (Complex **5** + toluene): δ = 8.07 (d, *J* = 7.6 Hz, 1 H), 7.83-7.71 (m, 4 H), 7.67 (app. t, *J* = 7.6 Hz, 1 H), 7.54-7.36 (m, 5 H), 7.35 (dd, *J* = 7.2, 3.6 Hz, 1 H), 7.30-7.22 (m, 4 H), 7.21-7.13 (m, 4 H), 7.00-6.93 (m, 2 H), 2.36 (s, 3 H, Me of toluene), 1.63 (s, 9 H, $SCMe_3$) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz) (Complex **5** + toluene): δ = 141.25 (C_{IV}, d, *J* = 7.1 Hz), 137.9 (C_{IV} of toluene), 136.9 (C_{IV}, d, *J* = 2.0 Hz), 136.2, 136.0, 134.6 (d, *J* = 11.2 Hz), 134.3 (C_{IV}), 134.1 (d, *J* = 7.1 Hz), 132.6, 131.8-131.7 (m), 131.5-131.4 (m), 130.2, 129.6, 129.5, 129.0, 128.7, 128.5, 128.5, 128.4, 128.2, 127.6 (C_{IV}, d, *J* = 9.2 Hz), 127.2, 125.3, 123.5 (C_{IV}), 122.9 (C_{IV}), 30.4 ($S\underline{C}Me_3$ + $SC\underline{Me}_3$), 21.5 (Me of toluene) ppm; ^{31}P NMR (161 MHz, $CDCl_3$): δ = +29.35; HRMS [M + Na]$^+$ for $C_{28}H_{26}Cl_3PPdSNa$ calcd. 658.949; found 658.949.

Dimethyl (1,3-diphenyl-2-propen-1-yl)malonate (6). *General procedure.* To a solution of allylpalladium chloride dimer [Pd(η^3-C_3H_5)Cl]$_2$ (2 mol%, 2.93 mg, 8.00×10^{-3} mmol) in chloroform (1.6 mL) was added the ligand (6 mol%, 0.0240 mmol) under an argon atmosphere, and the reaction mixture was stirred at 25 °C for 30 min. A solution of 1,3-diphenylpropenyl acetate (1 equiv., 101 mg, 0.400 mmol) in chloroform (0.8 mL, C = 0.5 mol/L) was added, followed by the addition of the base (10 mol%, 0.0400 mmol) at temperature T. The reaction mixture was then stirred for a further 5 min under the temperature T. Afterwards, dimethyl malonate (3 equiv., 137 µL, 1.20 mmol) and *N*,*O*-bis(trimethylsilyl) acetamide (BSA) (3 equiv., 294 µL, 1.20 mmol) were added. The reaction mixture was stirred for 48 h at the temperature T. The reaction mixture was then quenched by the addition of a saturated aqueous solution of NH_4Cl (2 mL) and the product extracted with dichloromethane (3 × 2 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* to yield the crude product, which was purified by flash chromatography (eluent: pentane/AcOEt (8/2)): Mp = 48-51 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.35-7.17 (m, 10 H), 6.48 (d, *J* = 15.6 Hz, 1 H), 6.33 (dd, *J* = 15.6, 8.4 Hz, 1 H), 4.27 (dd, *J* = 10.8, 8.8 Hz, 1 H), 3.96 (d, *J* = 10.8 Hz, 1 H), 3.71 (s, 3 H, OMe), 3.52 (s, 3 H, OMe) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 168.2 (C_{IV}, C=O), 167.8 (C_{IV}, C=O), 140.2 (C_{IV}), 136.8 (C_{IV}), 131.9, 129.1, 128.7, 128.5, 127.9, 127.6, 127.2, 126.4, 57.7, 52.6, 52.5, 49.2 ppm. Determination of enantioenrichment by chiral SFC (CHIRALPAK AD column).

(*E*)-3-(1,3-Diphenylallyl)-1H-indole (7). A Schlenk tube was charged with the ligand (5 mol%, 0.0310 mmol) and allylpalladium chloride dimer [Pd(η^3-C_3H_5)Cl]$_2$ (2.5 mol%, 5.85 mg, 0.0155 mmol), evacuated and backfilled with argon (3 cycles), and then dichloromethane (0.2 mL) was added. After stirring at 25 °C for 20 min, 1,3-diphenylpropenyl acetate (1.27 equiv., 200 mg, 0.787 mmol) and acetonitrile (6.6 mL) were added to the mixture, which was stirred for 30 min. Then, indole (1 equiv., 72.6 mg, 0.620 mmol) and K_2CO_3 (3 equiv., 257 mg, 1.86 mmol) were added to the mixture. After being stirred at 25 °C for 8 h, the reaction mixture was quenched with water (4 mL) and diluted with ethyl acetate (5 mL). The organic layer was washed with water (2 × 5 mL) and once with brine (5 mL). The combined aqueous solutions were extracted with ethyl acetate (3 × 5 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: pentane/AcOEt (8/2)): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.94 (bs, 1 H), 7.44 (d, *J* = 8.0 Hz, 1 H), 7.39-7.14 (m, 12 H), 7.06-7.00 (m, 1 H), 6.89 (dd, *J* = 2.4, 0.8 Hz, 1 H), 6.73 (dd, *J* = 16.0, 7.6 Hz, 1 H), 6.44 (d, *J* = 16.0 Hz, 1 H), 5.12 (d, *J* = 7.2 Hz, 1 H) ppm; ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 143.4 (C_{IV}), 137.5 (C_{IV}), 136.7 (C_{IV}), 132.5, 130.6, 128.5, 128.5, 128.4, 127.2, 126.8 (C_{IV}), 126.4, 126.3, 122.6, 122.1, 119.9, 119.5, 118.8 (C_{IV}), 111.1, 46.2 ppm. Determination of enantioenrichment by chiral SFC (CHIRALCEL OD column).

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