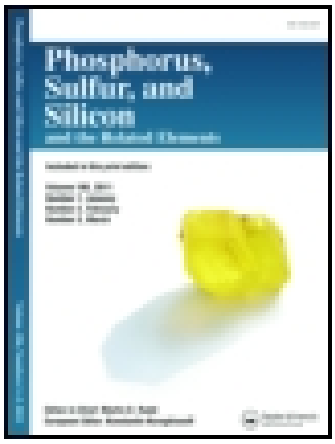

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A NEW EFFICIENT PROTOCOL FOR THE PREPARATION OF CHIRAL BISPHOSPHINES OF THE BICP FAMILY

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A NEW EFFICIENT PROTOCOL FOR THE PREPARATION OF CHIRAL BISPHOSPHINES OF THE BICP FAMILY

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A new procedure for the synthesis of chiral BICP ligands is described. The protocol involves the reaction of sodium diarylphosphide–borane complex with chiral 2,2′-bisbenzenesulfonyl-1,1′-dicyclopentane in toluene, followed by HBF_4·OMe_2-mediated BH_3 decomplexation.

Keywords: BICP; chiral bisphosphines; phosphine-borane

INTRODUCTION

Chiral phosphorus compounds, especially chelating bisphosphines, constitute one of the most important classes of ligands utilized in transition-metal-catalyzed asymmetric reactions.[1] The principal method for the synthesis of such bisphosphines involves the reaction of an appropriate homochiral bissulfonate (bismesylate, bistosylate) with an alkali diarylphosphide.[2] As the alkali diarylphosphides are very strong bases, usually poor yields are obtained for bisphosphines prepared via a nucleophilic substitution at an sp^3-carbon atom, due to a competing base-mediated elimination.[2] One such bisphosphine is Zhang's (2*R*,2′*R*)-bis(diphenylphosphino)-(1*R*,1′*R*)-dicyclopentane ((*R*,*R*)-BICP) (**1a**; Scheme 1), a chiral 1,4-bisphosphine with four stereogenic carbon centers in the backbone.[3] The original preparation of this ligand involved the reaction of the

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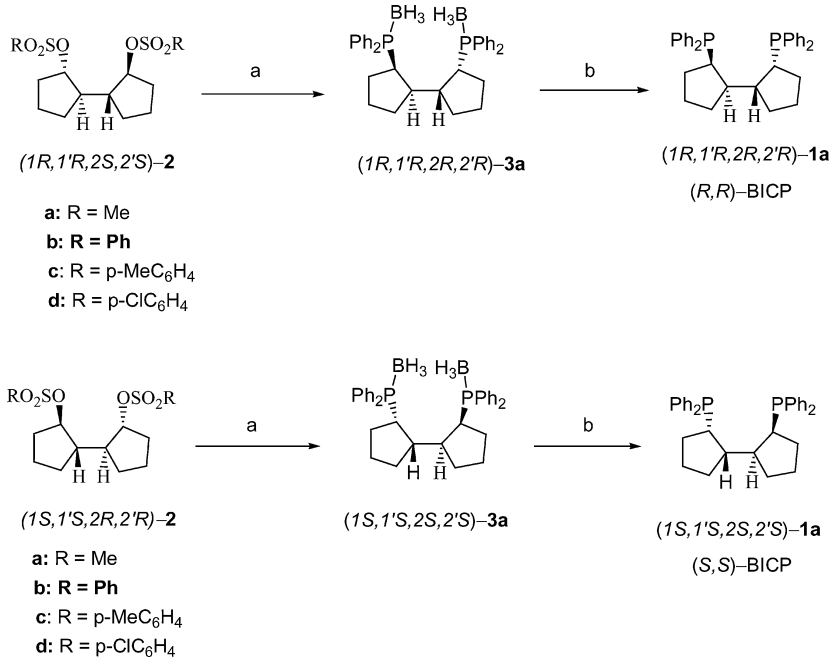


SCHEME 1 Synthesis of (*R*,*R*)-BICP and (*S*,*S*)-BICP. Reagents and conditions: a) NaOBu^t/BuLi, $Ar_2PH(BH_3)$, **2b**, toluene, 0°C to RT, 24 h, 50–51% yield; b) HBF_4xOMe_2, CH_2Cl_2, 0°C to RT, 24 h, >90% yield.

bismesylate obtained from (1*R*,1′*R*)-dicyclopentane-(2*S*,2′*S*)-diol* with lithium diphenylphosphide in tetrahydrofuran (THF).[3] This protocol affords (*R*,*R*)-BICP in only 20% yield after a tedious chromatographic purification. The Rh- and Ru-complexes of BICP provide excellent catalysts for asymmetric hydrogenation reactions.[3] Therefore, the development of a new, more practical synthesis of the ligand was necessary in order to enable its application in industrial processes.

In this article we describe a new higher yielding protocol for the preparation of BICP via the reaction of sodium diphenylphosphide-borane complex with the chiral bisbenzenesulfonate **2b** (Scheme 1). This procedure allows the large-scale synthesis of BICP (**1a**) as well as the preparation of new BICP-type ligands (**1b** and **1d**; Figure 1).

*One shortcoming for the general use of BICP as a ligand is that its original synthesis involves a hydroboration with Alpine-borane, which is only available as one isomer. We have solved this problem by developing a different synthetic sequence that affords both BICP enantiomers. The route involves an enzymatic kinetic resolution that gives both (1*R*, 1′*R*)-dicyclopentane-(2*S*, 2′*S*)-diol and (1*S*, 1′*S*)-dicyclopentane-(2*R*, 2′*R*)-diol. This route will be reported in due course.

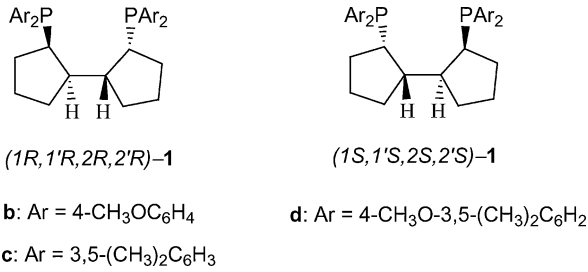


FIGURE 1 Chiral bisphosphine ligands of the BICP family.

RESULTS AND DISCUSSION

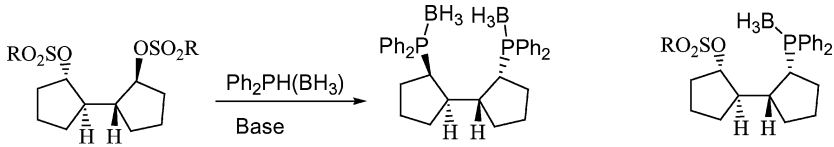
The great potential of phosphine–borane complexes for the synthesis of chiral phosphines was first recognized by Imamoto.[4] Since then a large number of ligands have been prepared via phosphine–boranes as synthetic vehicles.[5] The alkali anions derived from secondary phosphine–boranes display sufficient nucleophilicity in substitution reactions, but they are less basic than their corresponding borane-free counterparts. Therefore, their application is advantageous in order to avoid unwanted base-mediated eliminations.[5]

A few years ago Livinghouse reported a general protocol for the synthesis of homochiral bisphosphines that entails deprotonation of a secondary phosphine-borane complex with Bu^nLi in THF at $-78^\circ C$, followed by the addition of a DMF solution of the homochiral bis p-toluene sulfonate bistosylate of interest.[6] The desired chiral bisphosphine is then released from its bisborane complex by the tetrafluoroboric acid-dimethyl ether complex [$HBF_4 \cdot OMe_2$]–mediated BH_3 decomplexation.[6]

Our attempt to synthesize BICP using this protocol was not successful. The experiments where the bistosylate **2c**** was reacted (Scheme 1) with $LiPPh_2$-BH_3 in THF/DMF produced predominantly the mono phosphine–borane **4** (Table I, entries 1 and 2). Different solvents were then explored, and it was found that BICP–bisborane (**3a**) (Table I) was formed as the major product only when the reaction was carried out in toluene (Table I, entries 4–6). Thus, when the bistosylate **2c** was reacted with 3 equivalents of $LiPPh_2$-BH_3 in toluene, the corresponding BICP–bisborane (**3a**) was obtained in 35% yield after column chromatography. However, this reaction can be carried out only at low temperature ($-78^\circ C$) because at temperatures in the range of

In the screening experiments shown in Table 1 and discussed throughout the text (1*R*, 1′*R*, 2*S*, 2′*S*)-2** was used to give (*R*, *R*)-BICP.

TABLE I Selected Experiments Carried Out to Develop Conditions for the Synthesis of BICP



2 **3a** (bis) **4** (mono)

	Base	**2**	Equiv. Base	Solvent	T (°C)	Bis/Mono[a] (3a/4)
1	Bu^nLi	**2c**	2.2	THF/DMF	−78 to rt	Mono
2	Bu^nLi	**2a**	2.2	THF/DMF	−78 to rt	Mono
3	Bu^nLi	**2a**	2.2	THF	−78 to rt	3/1
4[b]	Bu^nLi	**2c**	2.4	PhMe	−78 to rt	Bis (35%)[c]
5	Bu^nLi	**2a**	2.2	MTBE	0 to rt	Mono
6	Bu^nLi	**2a**	2.2	Dioxane	rt	1/8
7	KOH	**2a**	2.2	MeOH	0 to rt	Mono
8	Pr^iMgCl	**2a**	2.2	THF/PhMe	0 to rt	NR
9	$KOBu^t$	**2a**	2.2	PhMe	0 to rt	Mono
10	$LiOBu^t$	**2a**	2.2	PhMe	0 to rt	Mono
11	$NaOBu^t$	**2a**	2.2	PhMe	0 to rt	1/3
12	$NaOBu^t$	**2b**	2.4	PhMe	0 to rt	1/2
13	$NaOBu^t$	**2b**	4.5	PhMe	0 to rt	9/1
14	$Bu^nLi/NaOBu^t$	**2b**	2.4	PhMe	0 to rt	3/1
15	$Bu^nLi/NaOBu^t$	**2b**	3	PhMe	0 to rt	>10/1 (50%)[d]
16	$Bu^nLi/NaOBu^t$	**2b**	4	PhMe	0 to rt	>10/1
17	$Bu^nLi/NaOBu^t$	**2d**	3	PhMe	0 to rt	>10/1
18	$Bu^nLi/NaOBu^t$	**2b**	3	PhMe/DMF	0 to rt	Mono
19	$Bu^nLi/NaOBu^t$	**2b**	3	THF/DMF	0 to rt	Mono
20	$Bu^nLi/KOBu^t$	**2b**	3	PhMe	0 to rt	Mono
21	$NaN(SiMe_3)_2$	**2b**	3	PhMe	0 to rt	1/1
22	NaOMe	**2b**	3	PhMe	0 to rt	Mono
23	NaH	**2b**	4.5	PhMe	0 to rt	NR
23	$NaOtC_5H_{11}$	**2b**	3	PhMe	0 to rt	1/8

[a]The ratio was determined by HPLC.
[b]The same conditions were used for performing the reaction with the **2a**, **2b**, and **2d**.
[c]Isolated yield by column chromatography.
[d]Isolated yield by crystallization from heptane.

−20°C to rt, $LiPPh_2$-BH_3 forms a viscous, sticky material in toluene that prevents efficient stirring of the reaction mixture. This makes the reaction inapplicable for scaleup. Therefore, we carried out experiments using other bases (Table I, entries 7–23). These experiments revealed that, unlike $LiPPh_2$-BH_3, $NaPPh_2$-BH_3 or $KPPh_2$-BH_3 form

solid suspensions in toluene at the temperature range between −20°C and rt without creating a problem for stirring. Of the bases examined, only Bu^tONa/Bu^nLi† gave BICP–bisborane (**3a**) as the major product in acceptable yields. An excess of 3 equivalents of the base and the secondary phosphine–borane was necessary to maximize the yield of BICP-bisborane. Higher excesses (Table I, entries 14–16) did not improve the yield. Under the best conditions found, Bu^tONa (3 equiv.) was suspended in dry toluene at 0°C and Bu^nLi (1.6 M in hexanes; 3 equiv.) was added. After stirring for 20 min at this temperature, a toluene solution of the chiral bisbenzenesulfonate **2b** was added at 0°C; the mixture was stirred at this temperature for 30 min and then at rt for 24 h. In this way, both enantiomers of BICP–bisborane (**3a**; Scheme 1) were obtained in 50–51% yield after crystallization from heptane. The reaction was carried out at up to 50 g scale. Similar yields were obtained when bistosylate **2c** or bis(*p*-chlorobenzene)sulfonate **2d** were used instead of bisbenzenesulfonate **2b**. These substrates are, however, significantly less soluble in toluene than the bisbenzenesulfonate and therefore are less applicable for a large-scale preparation. A lower yield in the reaction was obtained using **2a** as a substrate. Interestingly, when Bu^tOK/Bu^nLi (3 equivalents) was used as a base instead of Bu^tONa/Bu^nLi, monophosphine–borane **4** (Table I, entry 20) was obtained with very little formation of BICP–bisborane (**3a**).

The BH_3 decomplexation was easily carried out with $HBF_4{\cdot}OMe_2$ using the standard conditions developed by Livinghouse to give (*R,R*)-BICP or (*S,S*)-BICP (Scheme 1) in >90% yield.

The new procedure also allowed the preparation of new ligands of the BICP family (**1b**, **1d**; Figure 1) and the known bisphosphine **1c** in yields similar to those obtained for the parent ligand BICP. Ligands **1b** and **1d** are not accessible by the original Zhang protocol.

In summary, a new procedure for the synthesis of BICP has been developed. The procedure involves the reaction in toluene of bisbenzenesulfonate **2b** with $NaPPh_2$ (BH_3), derived from the secondary phosphine–borane and Bu^tONa/Bu^nLi, followed by the decomplexation of the resulting chiral BICP–bisborane with $HBF_4{\cdot}OMe_2$. Using this procedure, new ligands from the BICP family were obtained. In addition, the new protocol allows the synthesis of the BICP ligands on large scale.#

†For the application of Bu^tONa/Bu^nLi in organic synthesis see Schlosser [7].

#Both (*R, R*)-BICP and (*S, S*)-BICP were prepared using the new protocol and are now commercially available in research quantities from Strem.

EXPERIMENTAL

All experiments were performed under an argon atmosphere. Diphenylphosphine–borane complex and Bu^nLi (1.6 M in hexanes) were purchased from Aldrich (Milwaukee, WI, USA). Bu^tONa was purchased from Strem (Newburyport, MA, USA). Anhydrous solvents were used in all reactions. Bis(4-methoxyphenyl)phosphine-borane, bis(3,5-dimethylphenyl)phosphine-borane, and bis(4-methoxy-3,5-dimethylphenyl)phosphine-borane were prepared by known methods.[8] Chiral bissulfonates **2** were synthesized by reacting the corresponding diol with RSO_2Cl (2.1 equiv.) in THF in the presence of 3 equivalents of *N*-methylimidazole. Bissulfonates **2** were obtained in quantitative yields and used without purification. The enantiopurities of the bisphosphines were determined by chiral high performance liquid chromatography (HPLC) analysis.‡

(2*R*,2′*R*)-Bis(diphenylphosphino)-(1*R*,1′*R*)-dicyclopentane, Bisborane Complex (3a)[3]

$NaOBu^t$ (12.84 g, 0.134 mol) was suspended in dry toluene (100 ml). The mixture was cooled to 0°C and BuLi (1.6 M in hexane, 0.134 mol) was added via syringe. The yellow suspension was stirred at 0°C for 20 min. Diphenylphosphine-borane complex (26.73 g, 0.134 mol, 3 equiv.) was dissolved in 90 ml dry toluene, and the solution was added to the base ($NaOBu^t$/BuLi) at 0°C. The mixture was stirred for 20 min at 0°C (the color of the suspension turns white) and bisbenzenesulfonate **2b** (20.00 g, 0.0445 mol) in toluene (200 ml) was added. The mixture was stirred at 0°C for 1 h and then at room temperature for 24 h. The progress of the reaction was followed by ^{31}P NMR and HPLC. The mixture was washed with cold brine (300 ml). The water phase was back-extracted with CH_2Cl_2 (3 × 150 ml). The combined organic fractions were dried over Na_2SO_4. The solution was concentrated on a rotary evaporator to about 50 ml and dichloromethane (200 ml) was added. The solution was concentrated to about 50 ml and filtered through a plug of silica gel (100 g, washed after that with ~700 ml CH_2Cl_2). The solution was concentrated to about 50 ml and heptane (400 ml) was added. The mixture was concentrated to ~200 ml (white solid forms), stirred at 0°C for 1 h and filtered to give pure (*R*, *R*)-BICP-bisborane

‡The enantiopurity of each enantiomer of **1a** (>99% *ee*) was determined by chiral HPLC analysis (Chiralcel OD 250 × 4.6 mm column, 5% EtOH in hexane as an eluent, flow rate 1 ml/min, column temperature 30°C) of the corresponding bisphosphine oxides. The phosphine oxides were obtained by treating each of (*R*, *R*)-BICP and (*S*, *S*)-BICP with 3% H_2O_2 in toluene at 65°C and quenching the reaction with cold aqueous $Na_2S_2O_3$.

(**3a**) as a white solid (11.9 g, 50% yield). ^{1}H NMR ($CDCl_3$) δ 7.80–7.30 (m, 20H), 2.55–1.35 (m, 16H); ^{31}P NMR ($CDCl_3$) δ 17.68; ^{13}C NMR ($CDCl_3$) δ 133.43 (d, $J_{PC} = 8.5$ Hz), 132.25 (d, $J_{PC} = 8.5$ Hz), 132.08 (d, $J_{PC} = 50.0$ Hz), 130.67 (d, $J_{PC} = 2.1$ Hz), 130.57 (d, $J_{PC} = 2.1$ Hz), 129.71 (d, $J_{PC} = 56.5$ Hz), 128.39 (d, $J_{PC} = 9.4$ Hz), 128.29 (d, $J_{PC} = 9.1$ Hz), 46.28 (m), 36.26 (d, $J_{PC} = 30.6$ Hz), 31.35, 29.69, 22.68.

(2*S*,2′*S*)-Bis(diphenylphosphino)-(1*S*,1′*S*)-dicyclopentane, Bisborane Complex (3a)

Diphenylphosphine–borane complex (59.95 g, 0.3 mol) and (1*S*,1′*S*,2R, 2′*R*)-**2b** (45.00 g, 0.1 mol) were reacted as above to give after crystallization from heptane bisboronato-(*S*,*S*)-BICP (**3a**) as a white solid (27.2 g, 51%). Spectroscopic data the same as for the (*R*,*R*)-enantiomer.

(2*R*,2′*R*)-Bis[di(4-methoxyphenyl)phosphino]-(1*R*,1′*R*)-dicyclopentane, Bisborane Complex

Bis(4-methoxyphenyl)phosphine-borane complex (4.20 g, 0.0162 mol) and (*1R*,*1′R*,*2S*,*2′S*)-**2b** (2.44 g, 5.41×10^{-3} mol) were reacted as above to give, after purification by column chromatography (eluting with 30/70 hexane/CH_2Cl_2 first and then 10/90 hexane/CH_2Cl_2) and crystallization from heptane, 1.90 g of (*2R*,*2′R*)-bis[di(4-methoxyphenyl)phosphino]-(*1R*,*1′R*)-dicyclopentane, bisborane complex as a white solid (53%). ^{1}H NMR ($CDCl_3$) δ 7.65–6.88 (m, 16H), 3.93 (s, 6H), 3.81 (s, 6H), 2.48–1.41 (m, 16H); ^{31}P NMR ($CDCl_3$) δ 14.70; ^{13}C NMR ($CDCl_3$) δ 161.63 (d, $J_{PC} = 2.3$ Hz), 161.51 (d, $J_{PC} = 2.3$ Hz), 135.20 (d, $J_{PC} = 9.8$ Hz), 133.96 (d, $J_{PC} = 9.2$ Hz), 123.49 (d, $J_{PC} = 54.8$ Hz), 121.06 (d, $J_{PC} = 61.7$ Hz), 114.14 (d, $J_{PC} = 10.4$ Hz), 113.92 (d, $J_{PC} = 10.1$ Hz), 55.53, 55.26, 46.49, 36.69 (d, $J_{PC} = 32.5$ Hz), 31.50, 29.84, 22.68. HRMS calcd. for $C_{38}H_{50}B_2P_2O_4$: 654.3384; Found 654.3411.

(2*R*,2′*R*)-Bis[di(3,5-dimethylphenyl)phosphino]-(1*R*,1′*R*)-dicyclopentane, Bisborane Complex[3]

Bis(3,5-dimethylphenyl)phosphine-borane complex (3.93 g, 0.0153 mol) and (*1R*,*1′R*,*2S*,*2′S*)-2b (2.30 g, 5.11×10^{-3} mol) were reacted as above to give, after crystallization from heptane, bisboranato-(*2R*,*2′R*)-bis[di(3,5-dimethylphenyl)-phosphino]-(*1R*,*1′R*)-dicyclopentane as a white solid (1.76 g, 56%). ^{1}H NMR ($CDCl_3$) δ 7.36–7.03 (m, 12H), 2.41 (s, 12H), 2.31 (s, 12H), 2.54–1.25 (m,16H); ^{31}P NMR ($CDCl_3$) δ 17.05; ^{13}C NMR ($CDCl_3$) δ 137.93–129.30 (Ph), 46.33 (m), 35.44 (d, $J_{PC} =$ 30.9 Hz), 29.75, 22.95, 21.45, 21.25.

(2*S*,2′*S*)-Bis[di(4-methoxy-3,5-dimethylphenyl)-phosphino]-(1*S*,1′*S*)-dicyclopentane, Bisborane Complex

Bis(4-methoxy-3,5-dimethylphenyl)phosphine-borane complex (6.00 g, 0.019 mol) and (*1S*,*1′S*,*2R*,*2′R*)-**2b** (2.86 g, 6.35×10^{-3} mol) were reacted as above to give, after purification by column chromatography (eluting with 50/50 hexane/CH_2Cl_2 first and then 30/70 hexane/CH_2Cl_2) and crystallization from heptane, 2.70 g of (*2S*,*2′S*)-bis[di(4-methoxy-3,5-dimethylphenyl)phosphino]-(*1S*,*1′S*)-dicyclopentane, bisborane complex as a white solid (55%). ^{1}H NMR ($CDCl_3$) δ 7.39 (d, $J_{PH} = 10.1$ Hz, 4H, Ar), 7.13 (d, $J_{PH} = 9.8$ Hz, 4H, Ar), 3.78 (s, 6H, OCH_3), 3.72 (s, 6H, OCH_3), 2.46 (s, 12H, CH_3), 2.24 (s, 12H, CH_3), 2.48–1.27 (m, 16H, CH_2, CH); ^{13}P NMR ($CDCl_3$) δ 15.05; ^{13}C NMR ($CDCl_3$) δ 159.16, 134.04 (d, $J_{PC} = 9.2$ Hz), 132.73 (d, $J_{PC} = 8.6$ Hz), 131.43 (d, $J_{PC} = 10.7$ Hz), 131.01 (d, $J_{PC} = 10.4$ Hz), 127.26 (d, $J_{PC} = 50.9$ Hz), 124.62 (d, $J_{PC} = 58.9$ Hz), 59.68, 59.55, 46.3 (m), 35.70 (d, $J_{PC} = 31.4$ Hz), 31.22, 29.49, 23.01, 16.36, 16.17. HRMS calcd. for $C_{46}H_{66}B_2P_2O_4$: 766.4638; Found: 766.4695.

(2*R*,2′*R*)-Bis(diphenylphosphino)-(1*R*,1′*R*)-dicyclopentane ((*R*,*R*)-BICP) (1a)[3]

(*R*, *R*)-BICP-bisborane (**3a**) (10.45 g, 0.0196 mol) was dissolved in CH_2Cl_2 (60 ml), the solution was cooled to 0°C and tetrafluoroboric acid-dimethyl ether complex ($HBF_4 \cdot OMe_2$) (13.10 g, 0.098 mol, 5 equiv.) was added via syringe. The mixture was stirred at 0°C for 30 min and at room temperature for 24 h. The progress of the reaction was followed by ^{31}P NMR. It was then diluted with CH_2Cl_2 (60 ml) and treated with 2M NaOH (150 ml) (~30 equiv.) at 0°C. After 10 min stirring at 0°C, the two phases were separated and the water phase was back-extracted with CH_2Cl_2. The combined organic fractions were washed with water (100 ml) and dried over Na_2SO_4. The solution was concentrated to about 20 ml, and methanol (400 ml) was added. The solution was concentrated to ~150 ml, and the white solid was filtered (stable in air) and washed with MeOH (20 ml) to give 7.58 g pure BICP (77%). After concentration of the methanol filtrate to dryness and washing the solid with 20 ml cold heptane, an additional 1.78 g of BICP was isolated (94% combined yield). $[\alpha]_D^{20} = -44.5$ (c 0.58, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.43–7.21 (m, 20H), 2.49–1.37 (m, 16H); ^{31}P NMR ($CDCl_3$) δ −14.52; ^{13}C NMR ($CDCl_3$) δ 139.46–127.97 (Ph), 45.88 (dd, $J_{PC} = 12.3$ Hz, 12.3 Hz), 40.34 (d, $J_{PC} = 14.4$ Hz), 30.87 (dd, $J_{PC} = 6.4$ Hz, 4.0 Hz), 23.77 (d, $J_{PC} = 5.8$ Hz).

(2*S*,2′*S*)-Bis(diphenylphosphino)-(1*S*,1′*S*)-dicyclopentane ((*S*,*S*)-BICP) (1a)

(*S*,*S*)-BICP-bisborane (**3a**) (22.7 g, 0.0425 mol) and $HBF_4 \cdot OMe_2$ (56.8 g, 0.425 mol) were reacted as above to give after crystallization from methanol 19.2 g (90%) (*S*,*S*)-BICP as a white solid. $[\alpha]_D^{20} = +46.7$ (c 0.82, $CHCl_3$). The spectroscopic data are the same as for (*R*, *R*)-BICP. HRMS calcd. for $C_{34}H_{36}P_2$: 506.2292; Found: 506.2294.

(2*R*,2′*R*)-Bis[di(4-methoxyphenyl)phosphino]-(1*R*,1′*R*)-dicyclopentane (1b)

(2*R*,2′*R*)-Bis[di(4-methoxyphenyl)phosphino]-(1*R*,1′*R*)-dicyclopentane, bisborane complex (1.82 g, 2.78×10^{-3} mol) was dissolved in CH_2Cl_2 (30 ml) and treated with $HBF_4 \cdot OMe_2$ (3.72 g, 0.028 mol) as described above. The workup and purification were carried out as described for BICP. In this way, 1.32 g of pure **1b** (76%) was isolated. After concentration of the methanol filtrate to dryness an additional 0.33 g of bisphosphine was isolated (95% combined yield). $[\alpha]_D^{20} = -63.6$ (c 0.145, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.38–6.74 (m, 12 H), 3.84 (s, 6H), 3.75 (s, 6H), 2.40–1.34(m, 16H); ^{31}P NMR ($CDCl_3$) δ −19.01; ^{13}C NMR ($CDCl_3$) δ 159.90, 159.81, 135.27 (d, $J_{PC} = 15.0$ Hz), 134.99 (d, $J_{PC} = 13.5$ Hz), 130.59 (d, $J_{PC} = 10.1$ Hz), 130.28 (d, $J_{PC} = 10.1$ Hz), 113.82 (d, $J_{PC} = 8.2$ Hz), 113.70 (d, $J_{PC} = 8.9$ Hz), 55.15, 55.05, 45.95 (dd, $J_{PC} = 12.2$ Hz, 12.2 Hz), 40.67 (d, $J_{PC} = 13.0$ Hz), 30.91 (dd, $J_{PC} = 4.1$ Hz, 4.8 Hz), 23.60 (d, $J_{PC} = 5.1$ Hz). HRMS calcd. for $C_{38}H_{44}P_2O_4$: 626.2715; Found: 626.2688.

(2*R*,2′*R*)-Bis[di(3,5-dimethylphenyl)phosphino]-(1*R*,1′*R*)-dicyclopentane (1c)[3]

Bisboranato-(2*R*,2′*R*)-bis[di(3,5-dimethylphenyl)-phosphino]-(1*R*,1′*R*)-dicyclopentane (1.23 g, 1.91×10^{-3} mol) was dissolved in CH_2Cl_2 (30 ml) and treated with $HBF_4 \cdot OMe_2$ (2.55 g, 0.019 mol) as described above. The workup and purification were carried out as described for BICP. In this way 0.91 g pure **1c** (77%) was isolated. After concentration of the methanol filtrate to dryness an additional 0.19 g of bisphosphine was isolated (93% combined yield). ^{1}H NMR ($CDCl_3$) δ 7.17–6.88 (m, 12H), 2.34 (s, 12H), 2.18 (s, 12H), 2.40–1.23 (m, 16H); ^{31}P NMR ($CDCl_3$) δ − 16.63; ^{13}C NMR ($CDCl_3$) δ 139.77–130.04 (Ph), 47.36 (dd, $J_{PC} = 11.0$ Hz, 11.0 Hz), 39.14 (d, $J_{PC} = 13.7$ Hz), 30.82 (m), 22.41, 21.43, 21.28.

(2*S*,2′*S*)-Bis[di(4-methoxy-3,5-dimethylphenyl)-phosphino]-(1*S*,1′*S*)-dicyclopentane (1d)

(2*S*,2′*S*)-Bis[di(4-methoxy-3,5-dimethylphenyl)phosphino]-(1*S*,1′*S*)- dicyclopentane, bisborane complex (2.53 g, 3.3×10^{-3} mol) was dissolved in CH_2Cl_2 (30 ml) and treated with $HBF_4 \cdot OMe_2$ (4.43 g, 0.033 mol) as described above. The workup and purification were carried out as described for BICP. In this way, 1.79 g of pure **1d** (74%) was isolated. After concentration of the methanol filtrate to dryness, an additional 0.43 g of bisphosphine was isolated (91% combined yield). $[\alpha]_D^{20} = +102$ (c 0.205, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.24 (d, $J_{PH} = 8.1$ Hz, 4H, Ar), 6.98 (d, $J_{PH} = 7.7$ Hz, 4H), 3.73 (s, 6H), 3.68 (s, 6H), 2.26 (s, 12H), 2.24 (s, 12H), 2.39–1.19 (m, 16H); ^{31}P NMR ($CDCl_3$) δ -18.84; ^{13}C NMR ($CDCl_3$) δ 157.66, 157.41, 135.08 (d, $J_{PC} = 21.7$ Hz), 134.34 (d, $J_{PC} = 21.7$ Hz), 134.50, 133.37, 130.49 (d, $J_{PC} = 8.7$ Hz), 130.21 (d, $J_{PC} = 8.7$ Hz), 59.61, 59.54, 47.26 (dd, $J_{PC} = 11.4$ and 11.1 Hz), 39.74 (d, $J_{PC} = 13.1$ Hz), 30.47 (d, $J_{PC} = 6.9$ Hz), 22.29, 16.24, 16.10. HRMS calcd. for $C_{46}H_{60}P_2O_4$: 738.3967; Found: 738.3945.

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