Asymmetric Palladium-Catalyzed Annulation of Benzene-1,2-diols and Propargylic Carbonates

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The reaction of benzene-1,2-diol with various propargylic carbonates in the presence of a palladium catalyst and various chiral ligands afforded the corresponding 2-alkylidene-3-alkyl-2,3-dihydrobenzodioxins in quite good yields and enantioselectivities of up to 97%. The highest enantiomeric excesses were obtained using atropoisomeric diphosphanes as the chiral ligands; when Diop, BDPP and other ligands gave quite low enantioselectivities.

Introduction

There has been an increasing interest during the last few years in the synthesis of compounds containing the 1,4-benzodioxin and 1,4-benzodioxan structures. This is mainly due to the interesting biological activities displayed by some of these compounds, especially those found in nature.[1−5] While various 2-substituted 1,4-benzodioxans have been used as α- or β-blocking agents, as well as in antidepression or antihypertension therapy,[6−10] others exhibit antihyperglycemic properties[11] or act as inhibitors of 5-lipoxygenase.[12] These compounds are also interesting intermediates for useful synthetic transformations.[13−16]

Even though the access to 1,4-benzodioxin structures has been well documented in the literature,[13,17−25] synthetic routes to 2-alkylidene-1,4-benzodioxanes are not straightforward and often require a tedious multistep sequence.[26−34] In addition there is no example, to the best of our knowledge, of the asymmetric synthesis of 2-alkylidene-1,4-benzodioxanes, although these compounds are interesting precursors of chiral 1-alkyl-2,3-dihydro-1,4-benzodioxins. We reported recently a very easy access to various 2-alkylidene-2,3-dihydro-1,4-benzodioxins by a palladium-catalyzed reaction of propargylic carbonates with benzene-1,2-diols.[35,36] Since we postulated an η^3-allyl palladium species as an intermediate in this cyclization process and an intramolecular alkylation reaction as the key step, we expected that the concepts of asymmetric catalysis described by Trost et al.[37,38] in the case of η^3-allyl intermediates could be applied in our case. Little work has appeared in the literature on asymmetric intramolecular η^3-allyl palladium cyclization,[39−45] although good enantioselectivities have been reported in specific cases. We reported in a preliminary communication that the palladium-catalyzed annulation between benzene-1,2-diol and various propargylic carbonates occurred in an asymmetric way in the presence of a chiral ligand;[46] we describe in this paper a full account of our studies in this field.

Results and Discussion

In the asymmetric palladium-catalyzed alkylation starting from non-prochiral nucleophiles two reaction pathways can be envisioned:[37,38]
(i) the η^3-allyl intermediate has two identical geminal substituents at one terminus (C-1 or C-3) of the π-allyl complex, or
(ii) the η^3-allyl intermediate has two identical substituents at the two termini (C-1 and C-3) of the π-allyl complex

In order to apply these two cases to our palladium-catalyzed annulation between benzene-1,2-diol (**1**) and various propargylic carbonates, the propargylic carbonates used in this cyclization need to have the structures **2** and **9** in the first and second case, respectively.

A π-Allyl Intermediate with Identical Geminal Substituents at C-1 or C-3

The overall reaction is summarized in Scheme 1 and the general mechanism of annulation in this case is shown in Scheme 2. The racemic propargylic carbonate **2** used has two different substituents on the carbon bearing the carbonate function. Reaction of this racemic carbonate with a palladium complex bearing a chiral ligand gives two diastereoisomeric complexes **A₁** and **A₂** in a 1:1 ratio by an $S_{N'}2$ reaction.[47] Attack of the phenoxide, obtained by hydrogen exchange between the methoxide anion and benzene-1,2-

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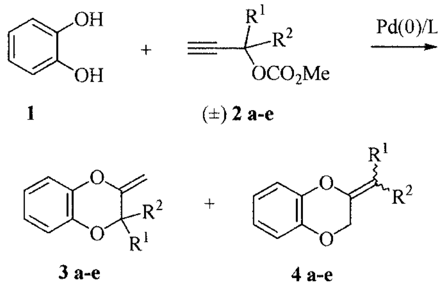
diol, at the central carbon of these σ-allenic palladium complexes affords the two stereoisomeric complexes **B$_1$** and **B$_2$**. Hydrogen exchange between the hydroxyl function and the carbenic palladium complex gives the new intermediates **C$_1$** and **C$_2$**, respectively, in equilibrium with the diastereoisomeric π-allyl complexes **D$_1$** and **D$_2$**; it should be noted here that this scheme is further complicated by *syn-anti* isomerization of these intermediates, which is not shown. These isomeric complexes, with two hydrogens on one terminus of the π-allyl intermediate, are in equilibrium with the σ-palladium complexes **C$_1$** and **C$_2$** via an η^3-σ-η^3 isomerization. Nucleophilic attack of the phenoxide at the more electrophilic terminus of the π-allyl intermediate affords the benzodioxin derivative **3**. If the rate of the σ-π-σ interconversion is fast compared to the rate of allylic alkylation, asymmetric cyclization can be expected.

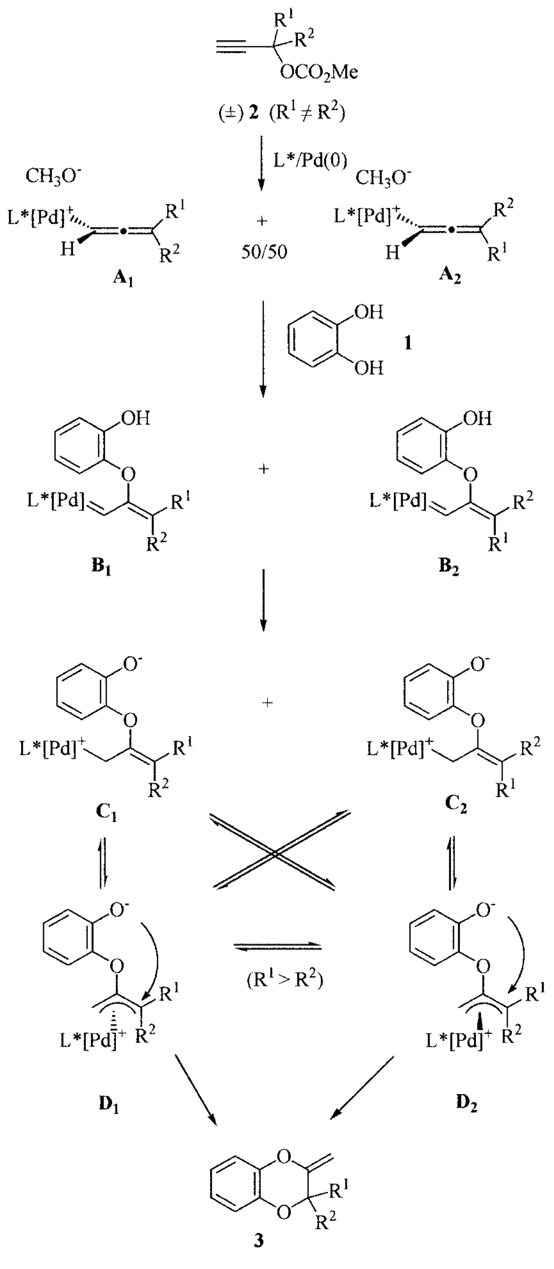


a R^1 = CH$_3$, R^2 = H
b R^1 = C$_5$H$_{11}$, R^2 = H
c R^1 = CH$_2$C$_6$H$_5$, R^2 = H
d R^1 = (CH$_3$)$_3$C, R^2 = H
e R^1 = CH$_3$, R^2 = C$_2$H$_5$

Scheme 1. Preparation of 2-alkylidene-3-alkyl-2,3-dihydrobenzodioxins **3a**−**e** and **4a**−**e**

We condensed four different racemic propargylic carbonates **2a**−**d** with benzene-1,2-diol (**1**) in the presence of palladium(0) and various chiral ligands. The results are summarized in Table 1.

In the condensation of carbonate **2a** with benzene-1,2-diol (**1**), 2-methyl-3-methylene-2,3-dihydro-1,4-benzodioxine (**3a**) was obtained as the major regioisomer whatever the phosphane used. However although high chemical yields were usually obtained, Chiraphos (Table 1, entry 1), phox (Table 1, entry 5) and the Trost ligand (Table 1, entry 7) gave very low chemical yields together with low to moderate enantioselectivities (*ee* up to 49% for phox). The chiral ligands BDPP (Table 1, entry 2) and Diop (Table 1, entry 3) gave high chemical yields in **3a**, but moderate enantioselectivities: 31 and 26%, respectively. The ferrocenylphosphane Josiphos gave an enantioselectivity up to 47%, but in 45% only yield (Table 1, entry 6). It should be noted that the monophosphane NMDPP gave **3a** in 72% yield with an *ee* of up to 48% (Table 1, entry 4). The highest enantioselectivities were obtained with the atropoisomeric ligands Binap, Biphemp, and MeOBiphep: 60% *ee*, 56% *ee*, and 78% *ee*, respectively, with quite good yields (Table 1, entries 8−10). In the case of MeOBiphep, lowering the reaction temperature to 0 °C increased the enantioselectivity of the cyclization in favor of **3a** to up to 82%, but lowered the yield of compounds **3a** and **4a** (40%) (Table 1, entry 11).



Scheme 2. General mechanism of asymmetric palladium-catalyzed annulation of benzene-1,2-diol (**1**) with racemic propargylic carbonates **2**

Using carbonate **2b** in this annulation reaction gave the cyclized products **3b** and **4b** in excellent chemical yields as a mixture (60−88% of **3b** and 40−12% of **4b** as a *Z*/*E* mixture). The cyclized product **3b** was obtained with low enantioselectivities using Diop or BDPP as the chiral ligands (Table 1, entries 12 and 13), whereas very high enantioselectivities were achieved using the atropoisomeric diphosphanes Binap, Biphemp, MeOBiphep, or TolBinap, as the chiral ligands — the highest value (90%) being obtained in the presence of MeOBiphep (Table 1, entries 14−17).

Table 1. Enantioselective palladium-catalyzed condensation of benzene-1,2-diol (**1**) with carbonates **2a**−**d**

Entry	Carbonate	Ligand[a]	Yield [%][b] (% **3**/% **4**)[c]	*ee* [%][c] of **3**
1	**2a**	(*S,S*)-Chiraphos	3	−
2	**2a**	(*S,S*)-BDPP	92 (94:6)	31 (−)
3	**2a**	(*R,R*)-Diop	92 (95:5)	26 (−)[d]
4	**2a**	NMDPP	90 (80:20)	48 (−)
5	**2a**	(*S*)-Phox	7 (89:11)	49 (−)
6	**2a**	(*R,S*)-Josiphos	45 (97:3)	47 (−)
7	**2a**	(*R,R*)-Trost ligand	10 (84:16)	25 (+)
8	**2a**	(*R*)-Binap	99 (81:19)	60 (−)
9	**2a**	(*S*)-Biphemp	98 (83:17)	56 (+)
10	**2a**	(*R*)-MeOBiphep	80 (77:23)	78 (−)
11	**2a**	(*R*)-MeOBiphep[e]	40 (80:20)	82 (−)[f]
12	**2b**	(*R,R*)-Diop	98 (88:12)	11 (+)
13	**2b**	(*S,S*)-BDPP	99 (82:18)	36 (+)
14	**2b**	(*R*)-Binap	99 (64:36)	82 (+)
15	**2b**	(*S*)-Biphemp	97 (63:37)	80 (−)[g]
16	**2b**	(*R*)-MeOBiphep	99 (60:40)	90 (+)[h]
17	**2b**	(*R*)-TolBinap	98 (72:28)	82 (+)
18	**2c**	(*R*)-Binap	81 (20:80)	67 (+)
19	**2c**	(*S*)-Biphemp	85 (20:80)	86 (−)[i]
20	**2c**	(*R*)-MeOBiphep	78 (20:80)	89 (+)[j]
21	**2d**	(*R*)-Binap[k]	99 (5:95)	86
22	**2d**	(*R*)-MeOBiphep[k]	99 (5:95)	90
23	**2e**	(*R*)-Binap	68 (100:0)	2 (+)[l]
24	**2e**	(*S*)-Biphemp	40 (100:0)	4 (−)[m]

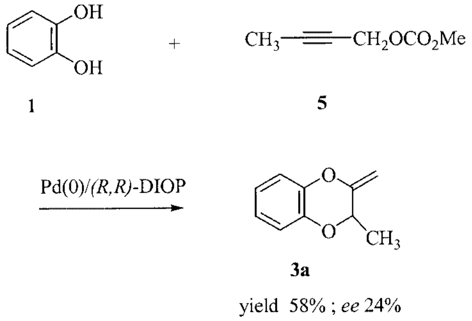
[a] See Exp. Sect for definitions of the ligands used. [b] After column chromatography. [c] Determined by GC or HPLC (see Exp. Sect.). [d] $[\alpha]_D^{25} = -13.5$ ($c = 1.2$, CH_2Cl_2). [e] Experiment performed at 0 °C. [f] $[\alpha]_D^{25} = -40.0$ ($c = 0.9$, CH_2Cl_2). [g] $[\alpha]_D^{25} = -58.1$ ($c = 0.7$, CH_2Cl_2). [h] $[\alpha]_D^{25} = +73.7$ ($c = 0.7$, CH_2Cl_2). [i] $[\alpha]_D^{25} = -50.8$ ($c = 1.0$, CH_2Cl_2). [j] $[\alpha]_D^{25} = +54.4$ ($c = 1.1$, CH_2Cl_2). [k] Experiment performed at 60 °C. [l] $[\alpha]_D^{25} = +3.7$ ($c = 0.8$, CH_2Cl_2). [m] $[\alpha]_D^{25} = -7.1$ ($c = 1.0$, CH_2Cl_2).

Condensation of propargylic carbonate **2c** with benzene-1,2-diol was performed in the presence of atropoisomeric ligands to give a mixture of compounds **3c** and **4c** in 78−85% chemical yield, the regioisomer **3c** being the minor one in this case (only 20% of the mixture) (Table 1, entries 18−20). However the obtained enantioselectivities were 67%, 86%, and 89%, in the presence of Binap, Biphemp, and MeOBiphep, respectively. The higher enantioselectivities obtained upon going from **2a** to **2b** and **2c** can be related to the increasing bulkiness of one of the substituents.

We also performed some experiments with the carbonate **2d** at reflux in THF in the presence of Binap and MeOBiphep (Table 1, entries 21 and 22); although the chemical yields of **3d** and **4d** were quantitative, and the enantioselectivities up to 86% and 90% *ee*, respectively, the amount of the regioisomer **4d** in the mixture was unfortunately only 5%.

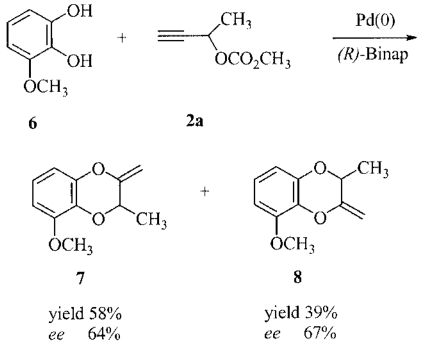
Finally we performed the cyclization of the tertiary carbonate **2e** with benzene-1,2-diol (**1**) in the presence of Binap and Biphemp (Table 1, entries 23 and 24); although the yields of cyclized product were moderate, we obtained only the regioisomer **3e**, as expected. Unfortunately, the creation of the quaternary asymmetric center occurred with practically no enantioselectivity, probably due to the very small differentiation between the methyl and the ethyl group.

The linear carbonate **5** was also used instead of the secondary carbonate **2a** in this palladium-catalyzed cyclization reaction in the presence of (*R,R*)-Diop as the ligand (Scheme 3). Compound **3a** was obtained with 58% yield and 24% enantioselectivity as the (−)-enantiomer. As we obtained the same enantioselectivity and configuration when starting from the linear or the branched carbonate **2a** and **5**, this is in agreement with the formation of a common intermediate, which is in this case the η^3-allyl complex **D**.



Scheme 3

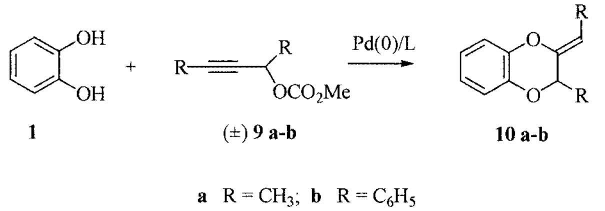
In order to determine the eventual influence of a substituent on the benzene-1,2-diol on the enantioselectivity, we performed one cyclization reaction at room temperature using 3-methoxybenzene-1,2-diol (**6**) as the nucleophile and (*R*)-Binap as the chiral ligand (Scheme 4). Regioisomers **7** and **8** were obtained in 58% and 39% yield, respectively, and practically the same enantioselectivity (64% and 67%, respectively), close to the values obtained using benzene-1,2-diol; the structures of compounds **7** and **8** were determined by NMR spectroscopy using an HMBC pulse sequence.



Scheme 4

π-Allyl Intermediates with Two Identical Substituents at C-1 and C-3

The overall reaction is shown in Scheme 5 and the general mechanism of annulation in this case is depicted in Scheme 6. Reaction of the racemic carbonate **9** with benzene-1,2-diol in the presence of a palladium complex of a chiral ligand afforded the stereoisomeric complexes $\mathbf{B_1}$ and $\mathbf{B_2}$ according to the mechanism shown in Scheme 2. Hydrogen exchange between the hydroxyl function and the carbenic palladium complex gave the new intermediates $\mathbf{C_1}$ and $\mathbf{C_2}$, each of which possesses a new asymmetric carbon center. However, these complexes are in equilibrium with the π-allyl complex **D** with two identical substituents on each terminus of the π-allyl intermediate, and whose palladium-allyl fragment therefore has a *meso* configuration. Again it should be noted that this reaction process is further complicated by *syn-anti* isomerization of this intermediate, which is not shown in the scheme. The nucleophilic attack of the phenoxide on one of the diastereotopic termini of the π-allyl intermediate afforded the benzodioxin derivative **10**.

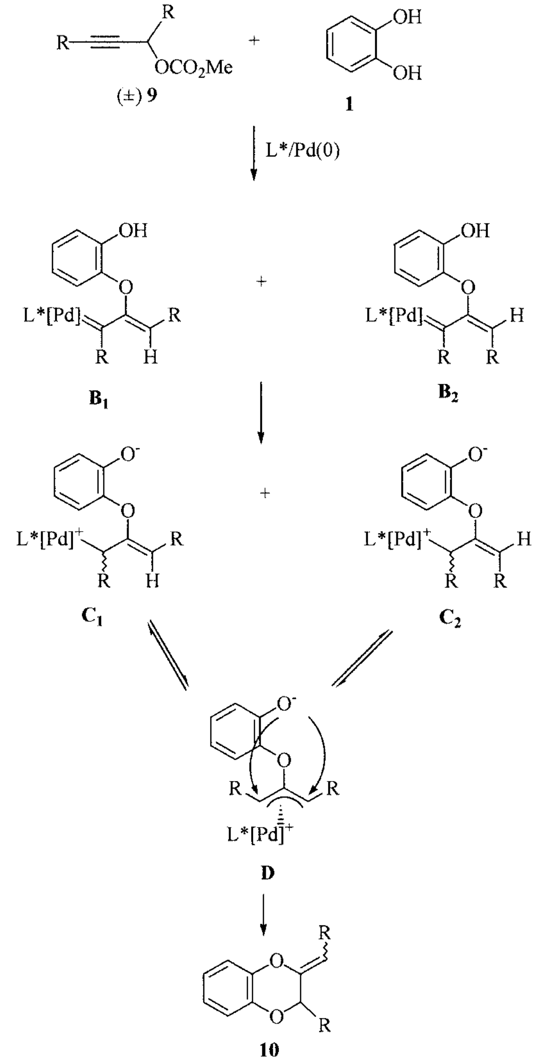


Scheme 5. Preparation of 2-alkylidene-3-alkyl-2,3-dihydrobenzodioxins **10a,b**

Two different racemic propargylic carbonates **9a**,**b** were condensed with benzene-1,2-diol (**1**) in the presence of palladium(0) and various chiral ligands (Scheme 5). The yields and enantioselectivities obtained are summarized in Table 2. Diop gave very disappointing enantioselectivities (*ee* up to only 28%) in this cyclization reaction (Table 2, entries 2 and 7). BDPP gave enantioselectivities up to 60% and 72% in the formation of **9a** and **9b**, respectively (Table 2, entries 1 and 6). The highest enantioselectivities were again obtained using the atropoisomeric diphosphanes as the chiral ligands. Dihydrobenzodioxin **10a** was obtained with enantioselectivities of up to 85%, 81%, and 90% using Binap, Biphemp, and MeOBiphep, respectively, as the ligand (Table 2, entries 3−5), and **10b** was obtained with enantioselectivities of up to 96%, 97%, 87%, and 87%, in the presence of Binap, Biphemp, MeOBiphep, and TolBinap respectively, as the ligand, (Table 2, entries 8−11). The highest enantioselectivities were obtained using carbonate **9b** instead of carbonate **9a**, and this can be related to the higher differentiation of the two diastereotopic termini of the π-allyl intermediate due to the different bulkiness of the phenyl and the methyl groups.

Conclusion

In conclusion, palladium-catalyzed annulation of benzene-1,2-diols and various propargylic carbonates afforded 2-alkylidene-3-alkyl-2,3-dihydrobenzo-1,4-dioxins in quite good yields and very high enantioselectivities of up to 97%. The highest chemical yields and enantioselectivities are obtained using atropoisomeric diphosphanes such as Binap,



Scheme 6. General mechanism of asymmetric palladium-catalyzed annulation of benzene-1,2-diol (**1**) with racemic propargylic carbonates **9**

Table 2. Enantioselective palladium-catalyzed condensation of benzene-1,2-diol (**1**) with carbonates **9a−b**

Entry	Carbonate	Ligand[a]	Yield [%][b] of **10**	*ee* [%][c] of **10**
1	**9a**	(*S,S*)-BDPP	98	60 (−)
2	**9a**	(*R,R*)-Diop	37	28 (−)
3	**9a**	(*R*)-Binap	99	85 (−)[d]
4	**9a**	(*S*)-Biphemp	26	81 (+)
5	**9a**	(*R*)-MeOBiphep	70	90 (−)[e]
6	**9b**	(*S,S*)-BDPP	99	72 (+)
7	**9b**	(*R,R*)-Diop	99	14 (+)
8	**9b**	(*R*)-Binap	98	96 (+)[f]
9	**9b**	(*S*)-Biphemp	95	97 (−)[g]
10	**9b**	(*R*)-MeOBiphep	99	87 (+)
11	**9b**	(*R*)-TolBinap	99	87 (+)

[a] See Exp. Sect for definitions of the ligands used. [b] After column chromatography. [c] Determined by GC or HPLC (see Exp. Sect.). [d] $[\alpha]_D^{25} = -18.3$ ($c = 0.8$, CH_2Cl_2). [e] $[\alpha]_D^{25} = -19.7$ ($c = 0.6$, CH_2Cl_2). [f] $[\alpha]_D^{25} = +43.4$ ($c = 1.5$, CH_2Cl_2). [g] $[\alpha]_D^{25} = -43.4$ ($c = 1.2$, CH_2Cl_2).

Biphemp, or MeOBiphep, as the chiral ligands. These are the highest *ee*'s reported for a palladium-catalyzed annulation reaction. Work is in progress in order to extend this methodology to other heteronucleophiles and to functionalize these compounds for their use in the synthesis of enantiopure compounds.

Experimental Section

General Remarks: ^{1}H (200 MHz) and ^{13}C NMR (50 MHz) spectra were obtained using a Bruker AM 300 spectrometer. Chemical shifts are reported with reference to $SiMe_4$ or $CDCl_3$ as an internal standard. The IR spectra were recorded on a Perkin−Elmer 681 instrument. Optical rotations were determined using a Perkin−Elmer 241 polarimeter. All reactions were monitored by thin-layer chromatography carried out on 0.25 mm silica gel plates (60 F-254, Merck). Compounds were exposed under UV light (254 nm). Column chromatography was carried out using Merck silica gel 60 (40−63 μm). Gas chromatography was realized on a Perkin−Elmer apparatus XL GC. HPLC analysis were performed on a Shimadzu apparatus LC-6A combined with a UV detector SPD-6A. Reactions involving palladium complexes were carried out in a Schlenk tube under an argon atmosphere. Tetrahydrofuran was distilled from sodium/benzophenone and stored under argon.

Compounds **2a**−**e**, **3a**−**e**, **4a**−**e**, **9a**−**b**, and **10a**−**b** have already been described.[36] (*S,S*)-Chiraphos [(2*S*,3*S*)-2,3-bis(diphenylphosphanyl)butane], (*S,S*)-BDPP [(2*S*,4*S*)-2,4-bis(diphenylphosphanyl)pentane], (*R,R*)-Diop [(2*R*,3*R*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphanyl)butane], (*R*)-Binap [(*R*)-2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl], (*R*)-TolBinap [(*R*)-2,2′-bis(di-*p*-toluylphosphanyl)-1,1′-binaphthyl], (*R,S*)-Josiphos [(*R*)-1-[(*S*)-2-(diphenylphosphanyl)ferrocenyl]ethyldicyclohexylphosphane], NMDPP [(1*S*,2*S*,5*R*)-1-diphenylphosphanyl)-2-isopropyl-5-methylcyclohexane], phox [(4*S*)-4,5-dihydro-2-[2-(diphenylphosphanyl)phenyl]-4-isopropyloxazole], and (*R,R*)-Trost ligand [(1*R*,2*R*)-1,2-bis{[2′-(diphenylphosphanyl)benzoyl]aminocyclohexane] were obtained from commercial sources.

(*S*)-Biphemp [(*S*)-6,6′-dimethyl-2,2′-bis(diphenylphosphanyl)-1,1′-biphenyl] and (*R*)-MeOBiphep [(*R*)-6,6′-dimethoxy-2,2′-bis(diphenylphosphanyl)-1,1′-biphenyl] were gifts from Dr. Schmid (Hofman La Roche, Basel, Swizerland).

General Procedure for the Palladium-Catalyzed Annulation Reaction: A mixture of $Pd_2(dba)_3$ (20.8 mg, 2.2×10^{-2} mmol) and the chiral ligand (9.1×10^{-2} mmol), in THF (7 mL) was stirred under a nitrogen atmosphere at room temperature for 30 min. This catalyst solution was added to a mixture of benzene-1,2-diol (100 mg, 0.9 mmol) and the corresponding propargylic carbonate (1.0 mmol). The resulting solution was stirred at room temperature for 24 h. The solvent was then evaporated and the residue chromatographed over silica eluting with petroleum ether/ethyl acetate[36] to afford the corresponding 2,3-dihydro-1,4-benzodioxin. The enantiomeric excesses of the obtained compounds were determined by gas chromatography on a chiral stationary-phase column Chiraldex^{TA} type B-PH (30 m × 0.32 mm) using helium as the carrier gas (1 mL/min), or by HPLC on a chiral column Chiralpak AD (25 cm × 4.6 mm).

2,3-Dihydro-2-methyl-3-methylene-1,4-benzodioxin (3a): GC, β-cyclodextrin column, 80 °C. (−)-isomer: $t_R = 40.1$ min; (+)-isomer: $t_R = 40.7$ min.

2,3-Dihydro-2-n-pentyl-3-methylene-1,4-benzodioxin (3b): HPLC (hexane). (+)-isomer: $t_R = 18.8$ min; (−)-isomer: $t_R = 20.4$ min.

2,3-Dihydro-2-benzyl-3-methylene-1,4-benzodioxin (3c): HPLC (hexane/*i*-propanol 96:4). (+)-isomer: $t_R = 44.8$ min; (−)-isomer: $t_R = 51.7$ min.

2,3-Dihydro-2-ethyl-2-methyl-3-methylene-1,4-benzodioxin (3d): HPLC (hexane). (+)-isomer: $t_R = 29.6$ min; (−)-isomer: $t_R = 30.5$ min.

2,3-Dihydro-5-methoxy-3-methyl-2-methylene-1,4-benzodioxin (7): GC, β-cyclodextrin, 115 °C. Isomers: $t_R = 42.2$ min and $t_R = 43.2$ min.

2,3-Dihydro-5-methoxy-2-methyl-3-methylene-1,4-benzodioxin (8): GC, β-cyclodextrin, 115 °C. Isomers: $t_R = 44.2$ min and $t_R = 45.2$ min.

2,3-Dihydro-3-ethylene-2-methyl-1,4-benzodioxin (10a): GC, β-cyclodextrin, 90 °C. (−)-isomer: $t_R = 45.8$ min; (+)-isomer: $t_R = 47.6$ min.

2,3-Dihydro-2-benzylidene-3-phenyl-1,4-benzodioxin (10b): HPLC (hexane/*i*-propanol 96:4), (−)-isomer: $t_R = 17.8$ min; (+)-isomer: $t_R = 19.3$ min.

2,3-Dihydro-5-methoxy-3-methyl-2-methylene-1,4-benzodioxin (7): $R_f = 0.22$ (eluent: petroleum ether/ethyl acetate, 50:1). IR: $\tilde{\nu}$ = 3040, 2980, 2930, 2820, 1650, 1590, 1485, 1460, 1250 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.58 (d, *J* = 6.6 Hz, 3 H, CH_3), 3.85 (s, 3 H, OCH_3), 4.41 (d, *J* = 2.2 Hz, 1 H, $=CH_2$), 4.56 (q, *J* = 6.6 Hz, 1 H, 3-H), 4.72 (d, *J* = 2.2 Hz, 1 H, $=CH_2$), 6.53 (dd, *J* = 8.1, 1.3 Hz, 1 H, H_{arom}), 6.60 (dd, *J* = 8.1, 1.3 Hz, 1 H, H_{arom}), 6.83 (t, *J* = 8.1 Hz, 1 H, H_{arom}) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.5 (CH_3), 56.2 (OCH_3), 69.4 (C-3), 89.9 ($=CH_2$), 105.4 (C_{arom}), 109.3 (C_{arom}), 121.4 (C_{arom}), 132.9 (C_{arom}), 143.4 (C_{arom}), 149.4 (C_{arom}), 154.2 (>C=) ppm.**2,3-Dihydro-5-methoxy-2-methyl-3-methylene-1,4-benzodioxin (8):** $R_f = 0.32$ (eluent: petroleum ether/ethyl acetate, 50:1). IR: $\tilde{\nu}$ = 3040, 2980, 2930, 2820, 1650, 1585, 1460, 1250 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.54 (d, *J* = 6.4 Hz, 3 H, CH_3), 3.88 (s, 3 H, OCH_3), 4.44 (d, *J* = 2.2 Hz, 1 H, $=CH_2$), 4.52 (q, *J* = 6.4 Hz, 1 H, 3-H), 4.85 (d, *J* = 2.2 Hz, 1 H, $=CH_2$), 6.54 (d, *J* = 8.5 Hz, 2 H, H_{arom}), 6.81 (t, *J* = 8.5 Hz, 1 H, H_{arom}) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.3 (CH_3), 56.2 (OCH_3), 69.1 (C-3), 90.3 ($=CH_2$), 105.0 (C_{arom}), 110.0 (C_{arom}), 121.1 (C_{arom}), 132.2 (C_{arom}), 143.9 (C_{arom}), 148.0 (C_{arom}), 153.8 (>C=) ppm. $C_{11}H_{12}O_3$ (192.22): calcd. C 68.72, H 6.30; found C 68.36, H 6.12.

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