Titanocene-Catalyzed Pinacol Couplings: Reagent-Controlled Transition-Metal-Catalyzed Radical Reactions

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The titanocene-catalyzed pinacol coupling of aromatic aldehydes proceeding in good yields and with high diastereoselectivity under reagent control is described.

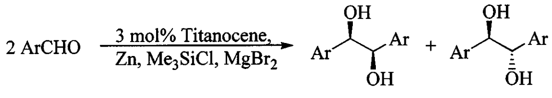
Introduction

The reductive coupling of carbonyl compounds, the pinacol coupling, is the most direct and efficient way to synthesize 1,2-diols by formation of the functionalized carbon−carbon bond.[1] The pinacol coupling is not only a shortcut of the alternative two-step sequence, i.e. McMurry coupling[2] and *syn,vic*-dihydroxylation.[3] More importantly, functional groups being sensitive to either or both of these two reactions can be tolerated if the pinacolization reagent is chosen carefully. Of the many stoichiometric reagents known to induce intermolecular dimerizations of aldehydes and ketones only few allow for highly diastereoselective coupling.[1] An enantioselective coupling has remained elusive so far. The reason for this is to be sought in the mechanism of the transformation. The reaction is generally thought to proceed via intermediate ketyl radicals formed by single electron transfer (SET) from low-valent transition-metal complexes, metal powders, or electrodes. The ketyl radicals can either dimerize,[4a][4b][4c] or add to a second equivalent of carbonyl compound with formation of an oxo radical that is subsequently reduced.[4d][4e][4f] Most of the SET reagents do, however, not allow for binding of both carbonyl partners in a stereodefined manner, thus not enabling effcient control of diastereoselectivity or enantioselectivity.

Among the rare examples of highly diastereoselective stoichiometric reagents are titanium(III) complexes, e.g. titanium trichloride and titanocene chloride.[5] This can be attributed to the dinuclear nature of these reagents and allows for binding of both carbonyl compounds and thus both formed ketyl radicals in the desired stereodefined manner. The repulsive steric interactions of the residues R of both aldehydes results in high diastereoselectivity in the formation of the 1,2-diols. However, the disadvantage of this otherwise efficient reaction is the inevitable use of stoichiometric amounts of the titanium complex. This is especially disadvantageous when more elaborate complexes are to be employed for achieving high enantio- or diastereoselectivity. Clearly, a reagent-controlled catalytic pinacol coupling would circumvent these problems.

An important recent development in this area has been the emergence of catalytic reactions from stoichiometric processes. Metal oxides or alkoxides, the products of additions to carbonyl groups are converted to metal chlorides by silylation with Me_3SiCl. The low-valent redox-active metal compound is then regenerated by in situ reduction with a readily available low-cost stoichiometric reductant, usually a metal powder. In this way the former stoichiometric reagent is essentially replaced by the readily available and cheap Me_3SiCl. The first succesful realization of this concept was a McMurry reaction catalytic in titanium.[6] Other examples are Nozaki-Hiyama couplings catalytic in chromium,[7] catalytic pinacol couplings,[8] and reactions catalytic in samarium diiodide.[9] In this full paper we wish to disclose our own results on the titanocene-catalyzed pinacol coupling. Our reaction shown in Figure 1 represents the so far only example of a catalytic pinacol coupling proceeding with high diastereoselectivity (> 95:5).

Figure 1. Titanocene-catalyzed pinacol coupling with Me_3SiCl



1
>95

2
<5

Results and Discussion

Titanocene Dichloride as SET Catalyst

Based on the ability of cyclopentadienyl-bonded titanium(III) complexes[5b] to induce stoichiometric pinacol couplings we anticipated the catalytic cycle depicted in Figure 1 to work.

There are, however, three points of concern that have to be carefully addressed: 1) reduction of titanocene dichloride has to be fast and quantitative to allow for efficient catalytic turn-over, 2) Me_3SiCl-induced pinacolization has to be sup-

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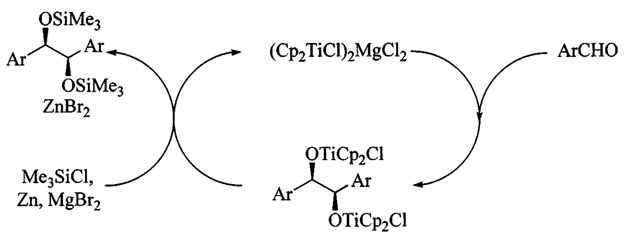
Figure 2. Catalytic cycle for titanocene-catalyzed pinacol coupling



pressed,[10] and 3) the right metal ion for the trimeric complex has to be utilized to achieve high diastereoselectivity.[11] We started our investigations with Zn powder, being known to efficiently reduce titanocene dichloride to the corresponding titanium(III) derivative over a wide range of temperatures as stoichiometric reductant[12] and Me_2SiCl_2 as highly active scavenger for the titanocene alkoxide in the presence of 10 mol-% of titanocene dichloride. Other metals, e.g. Mg, Mn, Al, turned out to be vastly inferior due to slow reduction and concomittant formation of benzyl alcohol. Further optimization studies are summarized in Table 1.

Table 1. Coupling of benzaldehyde (0.1 M in THF) in the presence of Me_2SiCl_2 or Me_3SiCl

Entry	Amount of catalyst [%]	t [h]	T [°C]	Yield [%]	**1**/**2**[a]
1a	10	1.2	0	93	86:14
1b	10	22	−40	92	70:30
1c	3	0.25	25	96	84:16[b]
1d	3	3	25	88	89:11[b][c]
1e	3	3	25	90	95:5[b][d]

[a] Determined by ^1H NMR of the crude mixture. – [b] 1.5 equiv. of Me_3SiCl. – [c] Slow addition of PhCHO and Me_3SiCl. – [d] Slow addition in the presence of $MgBr_2$.

Benzaldehyde coupling in the presence of Me_2SiCl_2 and 10 mol-% of titanocene dichloride gave complete conversion to products in less than 10 min. Me_3SiCl as additive also leads to clean formation of products. Me_3SiCl and Zn react to give the pinacols over 20 h ableit with low diastereoselectivity.[10] The catalytic acceleration of the reaction was thus significant as was the increase in diastereoselectivity. However, the upper limit for the formation of **1** and **2** in the stoichiometric reaction with zinc is 92:8[5b] indicating that some of the uncatalyzed pathway was still operating. To achieve useful levels of selectivity that are comparable to the stoichiometric parent system the following variations were investigated. To reduce interference of the noncatalyzed pathway to less significant levels both the aldehyde and Me_3SiCl were added slowly to a mixture of titanocene dichloride and Zn in THF. Indeed, selectivity increased and the yield remained high. Further improvement could be achieved by adding 1 equivalent of $MgBr_2$ to the benzaldehyde solution. This gave a tighter dimeric titanium complex by replacing Zn with Mg. A similar effect is known from stoichiometric reactions with titanocene(III) derivatives.[5b] $MgBr_2$ was prepared from 1,2-dibromoethane with Mg turnings. Homogeneous solutions of the salt could only be obtained when about 10% of benzene was added to the mixture.[13] Otherwise phase separation was observed. In this manner 2.5−3.0 M solutions of magnesium bromide in diethyl ether could be readily obtained. A mechanistically interesting feature of the reaction is that lowering the temperature led to a dramatically reduced diastereoselectivity of the reaction and pronouncedly longer reaction times. A reasonable explanation is that one step in the catalytic cycle was slow and that a less selective pathway was operating. Since both reduction of titanocene dichloride and the coupling are fast at and below room temperature it seems that silylation of the titanocene alkoxide to regenerate titanocene dichloride was slow.[7] Low diastereoselectivity can then be readily explained by uncatalyzed Me_3SiCl initiated coupling. At higher temperatures diastereoselectivity also decreased. Thus, 25° C seems to be the ideal temperature for conducting our titanocene-catalyzed pinacol coupling because all kinetic requirements for efficient catalysis are met. Clearly, this is preparatively convenient since no heating or cooling is required. It should be noted that only Me_3SiCl and the even more reactive silylating reagent Me_2SiCl_2 gave catalytic turn-over. Me_2tBuSiCl and less reactive reagents failed to yield substantial amounts of products. In other less polar solvent systems, e.g. Et_2O, CH_2Cl_2, or mixtures of the two, the catalyst and the zinc chloride formed in situ were insoluble. DMF or DMSO as solvents or cosolvents resulted in formation of substantial amounts of benzyl alcohol as by-product.

Under the optimized conditions a variety of symmetrical diols were synthesized in good yields and with high diastereoselectivities. The results of these investigations are summarized in Table 2. Functional groups interfering with McMurry couplings or dihydroxylation reactions such as chlorides, double bonds, phenolate esters and α,β-unsaturated esters are readily tolerated. Although initial experiments were performed on a small scale, the reaction can be readily scaled up and gives essentially the same results for 0.5, 5, and 50 mmol of substrate. In the latter case 374 mg of the catalyst were used. This compares favourably with the use of 24.9 g of titanocene dichloride in the stoichiometric reaction.[5b]

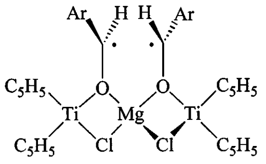
Table 2. Pinacol coupling of substituted aldehydes with 3 mol-% of Cp_2TiCl_2 under optimized conditions

Entry	Aryl	t [h]	Yield [%]	**1**/**2**[a]
2a	4-CH_3-C_6H_4	2.5	82	92:8
2b	4-Cl-C_6H_4	3	78	93:7
2c	3-Cl-C_6H_4	3	87	93:7[b]
2d	4-Vinyl-C_6H_4	2	91	92:8
2e	4-AcO-C_6H_4	3	83	92:8
2f	4-Crotonyloxy-C_6H_4	2	79	92:8
2g	2-Furyl	1.5	88	92:8

[a] Determined by ^1H NMR of the crude mixture after hydrolysis. – [b] Reaction also performed on a 50-mmol scale.

Mechanistically, it seems reasonable to assume that the catalytically active species is a dimeric titanium complex binding both ketyl radicals as indicated in Figure 3. The observed *syn* selectivity can then be readily explained by minimization of steric interference through *anti* orientation of the R groups in the complex.

Figure 3. Possible catalytically active species binding both ketyl radicals



rac-Ethylenebis(η^5-tetrahydroindenyl)titanium Dichloride (EBTHITiCl$_2$) as SET Catalyst

Although diastereoselectivity was high with titanocene dichloride from a synthetic point of view an improvement is still desirable. Also, it is worth knowing if structurally more demanding titanocene complexes can act as catalysts to induce enantioselectivity in future investigations. We thus decided to investigate the readily available EBTHITiCl$_2$ as catalyst shown in Figure 4.[14][15] Table 3 shows a summary of reactions performed under the optimized reaction conditions.

Figure 4. *rac*-EBTHITiCl$_2$ catalyst

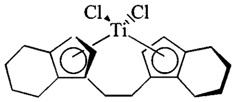


Table 3. Pinacol coupling of substitued aldehydes with 3 mol-% of *rac*-EBTHITiCl$_2$ under optimized conditions

Entry	Aryl	Yield [%]	**1/2**[a]
3a	C_6H_5	88	97:3
3b	4-C_6H_5-C_6H_4	79	98:2
3c	2-thienyl	79	98:2
3d	4-Br-C_6H_4	82	96:4
3e	4-Cl-C_6H_4	83	96:4
3f	3-Cl-C_6H_4	87	96:4
3g	4-Vinyl-C_6H_4	78	97:3
3h	4-Crotonyloxy-C_6H_4	81	97:3

[a] Determined by ^{1}H NMR of the crude mixture after hydrolysis.

Adding the reagents all at once resulted in inferior diastereoselectivity (**1/2** = 70:30) compared to the parent system titanocene dichloride. This indicates that silylation is slower using the sterically more demanding EBTHITiCl$_2$. However, once this observation was accounted for by careful slow addition, diastereoselectivity was significantly higher compared to titanocene dichloride. This demonstrates clearly that even though silylation is slowed down by steric congestion around titanium, the uncatalyzed pathway is not interfering to an important extent when proper reaction conditions are used. Here the optimal temperature for conducting the reaction is also 25° C. Thus, EBTHITiCl$_2$ constitutes a highly effective and diastereoselective catalyst for intermolecular pinacol couplings and is superior to all reagents known so far. The reaction represents a rare example of a transition-metal-catalyzed radical reaction proceeding with reagent control.[8c][18d][16] From these studies it has become clear that the reagent combination Zn/Me_3SiCl, when properly used, is a valuable stoichiometric reductive system for conducting titanocene-catalyzed redox reactions.

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Experimental Section

General: All reactions were performed in oven-dried (100°C) glassware under N_2. THF was freshly distilled from $LiAlH_4$. Me_2SiCl_2 and Me_3SiCl were distilled under N_2 immediately before use from CaH_2. Products were purified by flash chromatography[17] on Merck silica gel 50 (eluents given in brackets). Yields refer to analytically pure samples. Isomer ratios were determined from suitable ^{1}H-NMR integrals of cleanly separated signals. − ^{1}H NMR: [tetramethylsilane ($\delta = 0.00$) in the indicated solvent, $CHCl_3$ ($\delta = 7.26$) as internal standard in the same solvent] and ^{13}C NMR [tetramethylsilane ($\delta = 0.00$) in the indicated solvent or $CDCl_3$ ($\delta = 77.00$) and [D$_6$]DMSO ($\delta = 39.52$) as internal standards in the same solvent]; Bruker AMX 300 and Varian; integrals in accord with assignments, coupling constants are measured in Hz. − Combustion analyses: F. Hambloch, Institute of Organic Chemistry, University of Göttingen. − Mass spectra: G. Remberg, Institute of Organic Chemistry, University of Göttingen. − IR spectra: Perkin Elmer 1600 series FTIR as KBr pellets.

Table 1, Entry 1e: To titanocene dichloride (22.4 mg, 90 μmol) in THF (30 ml) was added Zn (196 mg, 3.0 mmol) and the mixture was stirred for 5 min. Benzaldehyde (300 μl, 3.0 mmol), $MgBr_2$ [1.8 ml of a 2.2 M solution in Et_2O containing 10% benzene (v/v), 4.0 mmol], and Me_3SiCl (570 μl, 4.5 mmol) were added in THF (15 ml) over 1.5 h and the mixture was stirred for 2 h. After addition of 2 M HCl (10 ml), stirring was continued for 15 min and the mixture extracted with *t*BuOMe (2× 50 ml). After washing with H_2O (20 ml), sat. $NaHCO_3$ (40 ml), H_2O (20 ml), and drying ($MgSO_4$), the crude product was purified by chromatography on silica gel (50% *t*BuOMe, 50% petroleum ether) to give 290 mg of 1,2-diphenyl-1,2-ethanediol as a 95:5 mixture of **1/2** (90%).

General Procedure for the Coupling in the Presence of Titanocene Dichloride: To a solution of titanocene dichloride (22.4 mg, 90 μmol) in dry THF (15 ml) under N_2 was added Zn (196 mg, 3.0 mmol) and the mixture was stirred until the red colour had faded and turned into lime green (typically 2−5 min). Then the aldehyde (3.0 mmol), Me_3SiCl (570 μl, 4.5 mmol) and $MgBr_2$ [1.8 ml of a 2.2 M solution in Et_2O containing 10% benzene (v/v), 4.0 mmol] in THF (15 ml) were added dropwise over 2 h. Stirring was continued for the indicated time and 2 M HCl (10 ml) was added). After 0.5 h, the mixture was extracted with *t*BuOMe (2 × 50 ml), washed with H_2O (20 ml), sat. $NaHCO_3$ (40 ml), H_2O (20 ml), and dried ($MgSO_4$). After evaporation of the solvent, the product was purified by chromatography on silica gel.

(R,R*)-1,2-Bis(4-methylphenyl)-1,2-ethanediol* (Table 2, entry 2a)[18]: After stirring for 2.5 h and silica gel chromatography (25% *t*BuOMe → 50% *t*BuOMe, 75% petroleum ether → 50% petroleum ether), 298 mg of 1,2-bis(4-methylphenyl)-1,2-ethanediol was obtained as a 92:8 mixture of **1/2** (82%).

(R,R*)-1,2-Bis(4-chlorophenyl)-1,2-ethanediol* (Table 2, entry 2b)[5a]:After stirring for 3 h and silica gel chromatography (40% *t*BuOMe → 60% *t*BuOMe, 60% petroleum ether → 40% petroleum ether), 331 mg of 1,2-bis(4-chlorophenyl)-1,2-ethanediol was obtained as a 93:7 mixture of **1/2** (78%).

(R,R*)-1,2-Bis(3-chlorophenyl)-1,2-ethanediol* (Table 2, entry 2c): After stirring for 3 h and silica gel chromatography (30% *t*BuOMe → 50% *t*BuOMe, 70% petroleum ether → 60% petroleum ether), 370 mg of 1,2-bis(3-chlorophenyl)-1,2-ethanediol was obtained as a 93:7 mixture of **1/2** (87%). Colorless crystals, m.p. 80°C. − IR (KBr): $\tilde{\nu}$ = 3380, 1575, 1475, 1200, 1080, 1000 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 2.82 (br. s, O*H*), 4.66 (s, C*H*OH), 6.92 (d, *J* = 7.6 Hz, 6-*H*, 2 H), 7.17 (dd, *J* = 7.5, 7.5 Hz, 5-*H*, 2 H), 7.24−7.21 (m, 2-*H*, 4-*H*, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 78.23 (*C*HOH), 125.15 (Ar−C-6), 126.89 (Ar-C-2), 128.26 (Ar-C-4), 129.39 (Ar-C-5), 134.19 (Ar-C-3), 141.49 (Ar-C-1). − $C_{14}H_{12}Cl_2O_2$ (283.2): calcd. C 59.39, H 4.27; found C 59.31, H 4.43. − For the minor diastereoisomer the following ^{1}H-NMR data are available from the spectrum of the mixture;[5b] other signals are overlapping. − ^{1}H NMR ($CDCl_3$): δ = 2.60 (br. s, O*H*), 4.82 (s, C*H*OH).

Reaction on 50-mmol Scale: To a solution of titanocene dichloride (374 mg, 1.5 mmol) in dry THF (250 ml) under N_2 was added Zn (3.272 g, 50 mmol) and the mixture was stirred until the red colour had faded and turned into lime green. Then the 3-chlorobenzaldehyde (5.63 ml, 50 mmol), Me_3SiCl (9.50 ml, 75 mmol), and $MgBr_2$ [30.3 ml of a 2.2 M solution in Et_2O containing 10% benzene (v/v), 67 mmol] were added dropwise in THF (250 ml) over 4 h. Stirring was continued for 4 h and 2 M HCl (100 ml) was added. After 0.5 h, the mixture was extracted with *t*BuOMe (2 × 500 ml), washed with H_2O (500 ml), sat. $NaHCO_3$ (100 ml), H_2O (500 ml), and dried ($MgSO_4$). After evaporation of the solvent, the product was purified by chromatography on silica gel (30% *t*BuOMe → 50% *t*BuOMe, 70% petroleum ether → 60% petroleum ether) to give 5.80 g of 1,2-bis(3-chlorophenyl)-1,2-ethanediol as a 92:8 mixture of **1/2** (82%).

(R,R*)-1,2-Bis(4-vinylphenyl)-1,2-ethanediol* (Table 2, entry 2d): After stirring for 2 h and silica gel chromatography (25% *t*BuOMe → 40% *t*BuOMe, 75% petroleum ether → 60% petroleum ether), 363 mg of 1,2-bis(4-vinylphenyl)-1,2-ethanediol was obtained as a 92:8 mixture of **1/2** (91%). Colorless crystals, m.p. 109°C. − IR (KBr): $\tilde{\nu}$ = 3380, 2350, 1630, 1405, 1035, 910 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 2.78 (br s, O*H*), 4.52 (s, C*H*OH), 5.08 (dd, *J* = 10.6, 1.1 Hz, $CH^Z{}_2CH$, 2 H), 5.56 (dd, *J* = 17.4, 1.1, $CH^E{}_2CH$, 2 H), 6.51 (dd, *J* = 17.4, 10.6 Hz, CH_2CH, 2 H), XX′ of AA′XX′ centred at 6.92, AA′ of AA′XX′ centred at 7.13. − ^{13}C NMR ($CDCl_3$): δ = 78.66 (*C*HOH), 113.80 (CH*C*H$_2$), 125.88, 127. 13, 136.39, 136.99, 139.90 (Ar-1-C). − $C_{18}H_{18}O_2$ (266.2) calcd. C 81.17, H 6.81; found C 81.08, H 6.82. − For the minor diastereoisomer the following ^{1}H-NMR data are available from the spectrum of the mixture;[5b] other signals are overlapping. − ^{1}H NMR ($CDCl_3$): δ = 2.10 (br. s, O*H*), 4.68 (s, C*H*OH), 5.09 (dd, *J* = 10.2, 1.1 Hz, $CH^Z{}_2CH$, 2 H), 5.59 (dd, *J* = 17.0, 1.1 Hz, $CH^E{}_2CH$, 2 H), 6.56 (dd, *J* = 17.0, 10.2 Hz, CH_2CH, 2 H), AA′ of AA′XX′ centred at δ = 7.20.

(R,R*)-1,2-Bis(4-acetoxyphenyl)-1,2-ethanediol* (Table 2, entry 2e): After stirring for 3 h and silica gel chromatography (100 ml of 50% *t*BuOMe, 50% petroleum ether; 100 ml of 90% *t*BuOMe, 10% EtOH, 100 ml of EtOH), 411 mg of 1,2-bis(4-acetoxyphenyl)-1,2-ethanediol was obtained as a 92:8 mixture of **1/2** (83%). Colorless crystals m.p. 190−192°C. − IR (KBr): $\tilde{\nu}$ 3145, 1750, 1605, 1510, 1400, 1370, 1215, 1060 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 2.28 (s, C*H*$_3$), 2.82 (br. s, O*H*), 4.70 (s, C*H*OH), XX′ of AA′XX′ centred at δ = 6.98, AA′ of AA′XX′ centred at δ = 7.15. − ^{13}C NMR ([D6] DMSO) δ = 20.74 (*C*H$_3$), 76.64 (*C*HOH), 120.44 (Ar-3-C), 127.95 (Ar-2-C), 139.77 (Ar-1-C), 149.12(Ar-4-C), 168.99 (CO). − $C_{18}H_{18}O_6$ (330.3) calcd. C 65.45, H 5.49; found C 65.40, H 5.75. For the minor diastereoisomer the following ^{1}H-NMR data are available from the spectrum of the mixture;[5b] other signals are overlapping. − ^{1}H NMR ($CDCl_3$): δ = 2.29 (s, C*H*$_3$), 4.72 (s, C*H*OH).

(R,R*)-1,2-Bis(4-crotonyloxyphenyl)-1,2-ethanediol* (Table 2, entry 2f): After stirring for 2 h and silica gel chromatography (25% *t*BuOMe → 50% *t*BuOMe, 75% petroleum ether → 50% petroleum ether), 453 mg of 1,2-bis(4-crotonyloxyphenyl)-1,2-ethanediol was obtained as a 92:8 mixture of **1/2** (79%). Colorless crystals m.p. 118°C. − IR (KBr): $\tilde{\nu}$ 3465, 1730, 1655, 1505, 1205, 910 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 1.96 (dd, *J* = 7.6, 1.5, C*H*$_3$), 2.78 (br. s, O*H*), 4.67 (s, C*H*OH), 6.51 (dq, *J* = 15.4, 1.6 Hz, COC*H*CH, 2 H), BB′ of AA′BB′ centred at δ = 7.00 (4 H), 7.11−7.21 (m, 6 H). − ^{13}C NMR ($CDCl_3$) δ = 18.21 (*C*H$_3$), 78.34 (*C*HOH), 121.22 (Ar-C-2), 121. 89 (CH*C*HCO), 127. 92 (Ar-C-3), 137.25 (Ar-C-1), 147.07 (Ar-C-4), 150.17 (*C*HCHCO), 164.76 (CO). − $C_{22}H_{22}O_6$ calcd. 382.1416; found 382.1416. − For the minor diastereoisomer the following ^{1}H-NMR data are available from the spectrum of the mixture;[5b] other signals are overlapping. − ^{1}H NMR ($CDCl_3$): δ = 4.81 (s, C*H*OH).

(R,R*)-1,2-Bis(2-furyl)-1,2-ethanediol* (Table 2, entry 2g)[18]: After stirring for 1.5 h and silica gel chromatography (25% *t*BuOMe → 50% *t*BuOMe, 75% petroleum ether → 50% petroleum ether), 256 mg of 1,2-bis(2-furyl)-1,2-ethanediol was obtained as a 92:8 mixture of **1/2** (88%).

General Procedure for the Coupling in the Presence of rac-EBTHITiCl$_2$: To a solution of $EBTHITiCl_2$ (34.2 mg, 90 μmol) in dry THF (15 ml) under N_2 was added Zn (196 mg, 3.0 mmol) and the mixture was stirred until the red colour had faded and turned into lime green. Then the aldehyde (3.0 mmol), Me_3SiCl (570 ml, 4.5 mmol), and $MgBr_2$ [1.8 ml of a 2.2 M solution in Et_2O containing 10% benzene (v/v), 4.0 mmol] were added dropwise over 2 h. Stirring was continued for 3 h and 2 M HCl (5 ml) was added. After 0.5 h, the mixture was extracted with *t*BuOMe (2 × 20 ml), washed with H_2O (20 ml), sat. $NaHCO_3$ (20 ml), H_2O (20 ml), and dried ($MgSO_4$). After evaporation of the solvent, the product was purified by chromatography on silica gel.

(R,R*)-1,2-Diphenyl-1,2-ethanediol* (Table 3, entry 3a): After chromatography on silica gel (50% *t*BuOMe, 50% petroleum ether), 283 mg of 1,2-diphenyl-1,2-ethanediol was obtained as a 97:3 mixture of **1/2** (88%).

(R,R*)-1,2-Bis(4′-biphenyl)-1,2-ethanediol* (Table 3, entry 3b)[19]: After chromatography on silica gel (40% *t*BuOMe → 70% *t*BuOMe, 60% petroleum ether → 30% petroleum ether), 434 mg of 1,2-bis(4′-biphenyl)-1,2-ethanediol was obtained as a 98:2 mixture of **1/2** (79%).

(R,R*)-1,2-Bis(2-thienyl)-1,2-ethanediol* (Table 3, entry 3c)[18]: After silica gel chromatography (40% *t*BuOMe → 60% *t*BuOMe, 60% petroleum ether → 40% petroleum ether), 268 mg of 1,2-bis(2-thienyl)-1,2-ethanediol was obtained as a 98:2 mixture of **1/2** (79%).

(R,R*)-1,2-Bis(4-bromophenyl)-1,2-ethanediol* (Table 3, entry 3d)[20]: After silica gel chromatography (50% *t*BuOMe → 70% *t*BuOMe, 50% petroleum ether → 30% petroleum ether), 458 mg of 1,2-bis(4-bromophenyl)-1,2-ethanediol was obtained as a 96:4 mixture of **1/2** (82%).

(R*,R*)-1,2-Bis(4-chlorophenyl)-1,2-ethanediol (Table 3, entry 3e): After silica gel chromatography (50% *t*BuOMe, 50% *t*BuOMe), 352 mg of 1,2-bis(4-chlorophenyl)-1,2-ethanediol was obtained as a 96:4 mixture of **1/2** (83%).

(R*,R*)-1,2-Bis(3-chlorophenyl)-1,2-ethanediol (Table 3, entry 3f): After silica gel chromatography (30% *t*BuOMe → 50% *t*BuOMe, 70% petroleum ether → 50% petroleum ether), 370 mg of 1,2-bis(3-chlorophenyl)-1,2-ethanediol was obtained as a 96:4 mixture of **1/2** (87%).

(R*,R*)-1,2-Bis(4-vinylphenyl)-1,2-ethandiol (Table 3, entry 3g): After silica gel chromatography (30% *t*BuOMe → 50% *t*BuOMe, 70% petroleum ether → 50% petroleum ether), 312 mg of 1,2-bis(4-vinylphenyl)-1,2-ethanediol was obtained as a 97:3 mixture of **1/2** (78%).

(R*,R*)-1,2-Bis(4-crotonyloxyphenyl)-1,2-ethanediol (Table 3, entry 3 h): After silica gel chromatography (30% *t*BuOMe → 50% *t*BuOMe, 70% petroleum ether → 50% petroleum ether), 464 mg of 1,2-bis(4-crotonyloxyphenyl)-1,2-ethanediol was obtained as a 97:3 mixture of **1/2** (81%).

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