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Palladium-Catalyzed Stereoselective Synthesis of (*E*)-Stilbenes via Organozinc Reagents and Carbonyl Compounds

Jin-Xian Wang,^{a, b,*} Kehu Wang,^a Lianbiao Zhao,^a Hongxia Li,^a Ying Fu,^a and Yulai Hu^a

^a Institute of Chemistry and Department of Chemistry, Northwest Normal University, 805, An Ning Road (E.), Lanzhou 730070, People's Republic of China
Fax: (+86)-931-776-8159; e-mail: wangjx@nwnu.edu.cn

^b State Key Laboratory of Applied Organic Chemistry, Lanzhou University
Lanzhou 730000, People's Republic of China

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Abstract: In the presence of a catalytic amount of PdCl₂(PPh₃)₂ and a silylating agent, organozinc halides reacted with carbonyl compounds to give the corresponding (*E*)-stilbenes in good to excellent yields under mild conditions. The reaction mechanism is briefly discussed.

Keywords: carbonyl compounds; catalyst; organozinc halides; palladium; (*E*)-stilbenes

Introduction

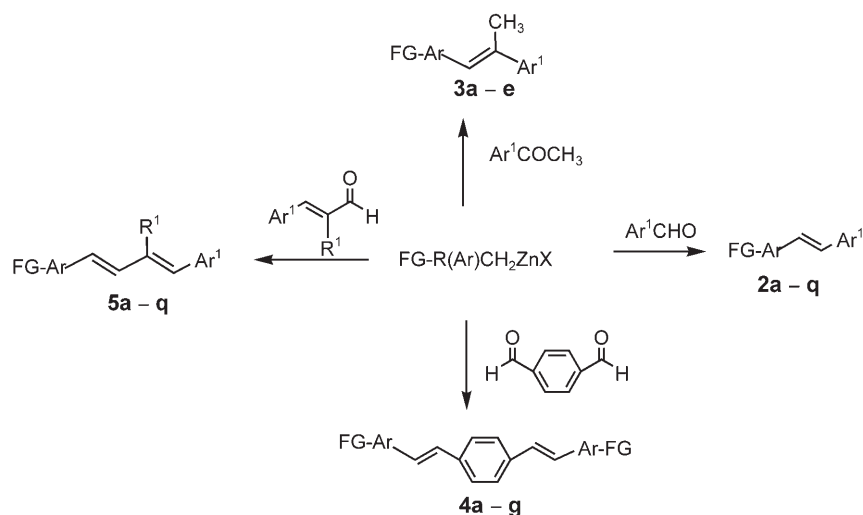
Stilbenes are important synthetic precursors to phenanthrene alkaloids^[1] as well as enantiomerically pure 1,2-diphenylethane-1,2-diamines,^[2] and diols.^[3] They are also used as optical brighteners^[4] and therapeutic agents for liver disorders. Many methods have been described for the synthesis of stilbenes.^[5] The reduction, dehydrogenation, and elimination reactions leading to stilbenes without formation of new carbon-carbon bonds are known to be very convenient methods. Synthetically more important are the dimerization reactions: oxidative or eliminative dimerization of a suitable methylarene often constitutes the method of the choice for the preparation of a symmetrical stilbene. Meerwein arylation^[6] and Heck reaction^[7] are prominent examples for the synthesis of stilbenes from arenes and styrenes. Moreover, condensation reactions of a nucleophilic with an electrophilic arylmethyl compound including the Knoevenagel-type reaction and the very general Wittig and Wittig–Horner reactions^[8] are also well known methods. Recently, a new procedure for the synthesis of stilbenes *via* reaction of aldehyde tosylhydrazones with stabilized carbonions,^[9] or benzotriazole-stabilized carbanions,^[10] or trimethyl borate/lithium *tert*-butoxide^[11] has been reported. We also have reported^[12] that the nitro group of 1-aryl-2-nitroethenes can

be substituted by organozinc halides under the catalysis of Ni(acac)₂ and a tertiary amine to give 1-aryl-1-alkenes in excellent yields. In addition, we have reported^[13] that stereoselectively alkenylated compounds can be obtained from substituted aromatic aldehydes by reaction with organozinc halides in the presence of catalytic amount of NiCl₂(PPh₃)₂ or CoCl(PPh₃)₃ and a silylating agent. However, we have found that this reaction is sensitive to the molecular structure of the carbonyl compounds. When NiCl₂(PPh₃)₂ or CoCl(PPh₃)₃ were employed as a catalyst, aromatic ketones, *p*-benzenedialdehyde etc. would undergo several side reactions.

We have now found that the (*E*)-stilbenes can be obtained from carbonyl compounds and arylmethylzinc halides in the presence of a catalytic amount of PdCl₂(PPh₃)₂ using a silylating agent. In this paper, we report the synthesis of (*E*)-stilbenes from organozinc reagents and carbonyl compounds. The reactions are shown in Scheme 1.

Results and Discussion

Various kinds of transition metal complex were employed as catalyst for the synthesis of (*E*)-2-chlorostilbenes from 2-chlorobenzaldehyde with benzylzinc chloride, and the results are summarized in Table 1.



Scheme 1.

Table 1. Optimized conditions for the synthesis of (*E*)-stilbenes *via* the addition-elimination of benzylzinc chloride to 2-chlorobenzaldehydes.^[a]

Entry	Catalyst [mol %]	Lewis acid	Solvent	<i>T</i> [°C]	Time [h]	Yield [%] ^[b]
1	PdCl ₂ (PPh ₃) ₂ (3.0)	Me ₃ SiCl	THF	−18→r.t.	8	89
2	PdCl ₂ (PPh ₃) ₂ (2.0)	Me ₃ SiCl	THF	−18→r.t.	8	91
3	PdCl ₂ (PPh ₃) ₂ (2.0)	Me ₃ SiCl	THF	r.t.	8	70
4	PdCl ₂ (PPh ₃) ₂ (2.0)	Me ₃ SiCl	THF	0	8	84
5	PdCl ₂ (PPh ₃) ₂ (2.0)	none	THF	−18→r.t.	8	90 ^[c]
6	PdCl ₂ (PPh ₃) ₂ (0)	Me ₃ SiCl	THF	−18→r.t.	8	0
7	PdCl ₂ (PPh ₃) ₂ (2.0)	Me ₃ SiCl	THF	−18→r.t.	3	70
8	PdCl ₂ (PPh ₃) ₂ (2.0)	Me ₃ SiCl	THF	−18→r.t.	6	86
9	PdCl ₂ (PPh ₃) ₂ (2.0)	Me ₃ SiCl	DMF	−18→r.t.	8	85
10	PdCl ₂ (PPh ₃) ₂ (2.0)	Me ₃ SiCl	CH ₃ CN	−18→r.t.	8	78
11	PdCl ₂ (PPh ₃) ₂ (2.0)	Me ₃ SiCl	C ₆ H ₆	−18→r.t.	8	61
12	PdCl ₂ (PPh ₃) ₂ (2.0)	AlCl ₃	THF	−18→r.t.	8	69
13	PdCl ₂ (PPh ₃) ₂ (2.0)	BF ₃ ·OEt ₂	THF	−18→r.t.	8	78
14	PdCl ₂ (2.0)	Me ₃ SiCl	THF	−18→r.t.	8	86
15	Ni(acac) ₂ (3.0)/Et ₃ N	Me ₃ SiCl	THF	−18→r.t.	8	78
16	CoCl(PPh ₃) ₃ (3.0)	Me ₃ SiCl	THF	−18→r.t.	8	83
17	NiCl ₂ (PPh ₃) ₂ (3.0)	Me ₃ SiCl	THF	−18→r.t.	8	81

^[a] All reactions were conducted on a scale of 11 mmol benzylzinc chloride with 10 mmol 2-chlorobenzaldehyde, and 20 mmol Lewis acid in 20 mL solvent.

^[b] Yields of isolated products.

^[c] Product is the corresponding diphenylethanol.

PdCl₂(PPh₃)₂ was fairly superior to PdCl₂, CoCl(PPh₃)₃, NiCl₂(PPh₃)₂, and Ni(acac)₂/Et₃N (Table 1, entries 2, 14, 15, 16, and 17). In the absence of PdCl₂(PPh₃)₂, the reaction was not successful (Table 1, entry 6). The amount of PdCl₂(PPh₃)₂ affected the yield, and the use of 2 mol % of the catalyst based on 2-chlorobenzaldehyde gave the best result. Furthermore, the reaction was influenced markedly by the solvent. When THF, DMF, CH₃CN, and benzene were employed as the solvent in the reaction of benzylic zinc chloride with 2-chlorobenzaldehyde in

the presence of 2% PdCl₂(PPh₃)₂ and Me₃SiCl, the yields of the corresponding (*E*)-stilbene were 91, 85, 78, and 61%, respectively (Table 1, entries 2, 9, 10, and 11). THF was found to be the best solvent.

We have also investigated the effects of time and temperature on the reaction. It was found that a high yield of (*E*)-stilbene could be obtained at −18°C to room temperature for 8 h (Table 1, entries 2, 3, 4, 7, and 8). In the absence of Me₃SiCl, the olefination reactions was not successful. For example, no olefinic product was isolated after the reaction of 2-chloro-

Table 2. Synthesis of (*E*)-stilbenes *via* addition-elimination of organozinc reagents to aromatic aldehydes.^[a]

Entry	R (Ar)	R ¹	X	Product ^[b]	Yield [%] ^[c]
1	H	H	Cl		2a ^[14] 90
2	H	H	Br		2a ^[14] 85
3	3-Br	H	Br		2b ^[15] 81
4	4-Cl	H	Br		2c ^[16] 86
5	4-Br	H	Br		2d ^[15] 88
6	4-Br	4-OMe	Br		2e 89
7	H	4-OH	Br		2f ^[17] 85
8	3-Cl	H	Br		2g ^[18] 84
9	H	2-OH	Br		2h ^[19] 78
10	H	2-OMe	Br		2i ^[16] 85
11	H	4-OMe	Br		2j ^[20] 91
12	H	3,5-(OMe) ₂ -4-OH	Cl		2k 73
13	H	4-OCH ₂ Ph	Cl		2l 86
14	H	2,4-(NO ₂) ₂	Cl	no reaction	
15	H	2-OCH ₂ Ph	Cl		2m 75
16	H	2,6-Br ₂ -4-OH	Cl		2n 68
17	3-Br	4-OMe	Br		2o 82

Table 2. (Continued)

Entry	R (Ar)	R ¹	X	Product ^[b]	Yield [%] ^[c]
18	3-Br	3-OMe-4-OH	Br		78
19	(β-naphthyl)	H	Br		74

^[a] All reactions were conducted on a scale of 10 mmol aldehydes with 11 mmol organozinc reagent, 0.2 mmol [PdCl₂(PPh₃)₂], and 20 mmol Me₃SiCl in 20 mL THF at −18°C to room temperature for 8 h.

^[b] All products were characterized by melting point, IR, ¹H NMR ¹³C NMR, MS and elemental analyses.

^[c] Yields of isolated products.

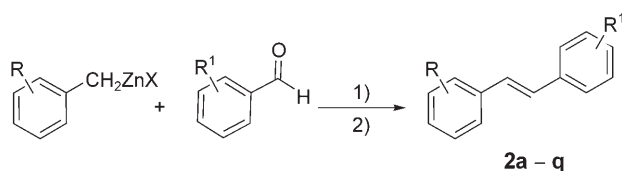
benzaldehyde and PhCH₂ZnCl without Me₃SiCl. The products were the corresponding 1,2-diphenethyl alcohol (Table 1, entry 5).

In order to determine the scope and limitation of this new method for the synthesis of (*E*)-stilbenes, various aldehydes were allowed to react with organozinc reagents in the presence of THF catalyzed by PdCl₂(PPh₃)₂ using a silylation agent were examined as shown in Table 2.

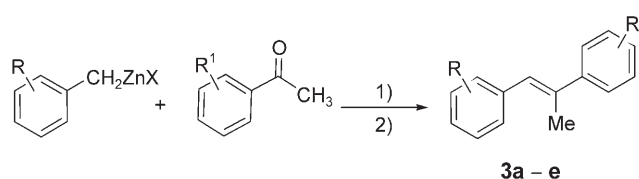
We have also found that the reaction of substituted aromatic aldehydes with benzylzinc chlorides or bromides in the presence of catalytic amount of PdCl₂(PPh₃)₂ also gave the corresponding (*E*)-stilbenes in good to excellent yields. The reactions are shown in Scheme 2 and the results are summarized in Table 2 (68–90%, entries 1–13 and 15–19).

Various substituents on the phenyl ring, either electron-withdrawing or electron-donating, such as chloro, bromo, methoxy, benzyloxy, and hydroxy, could be tolerated and had little effect on the yields except for the case of 2,4-dinitrobenzaldehyde which gave no olefination product (Table 2, entries 3–13, 15–18, and 14). Aromatic ketones also reacted with benzylzinc chlorides or bromides similarly giving the corresponding substituted (*E*)-stilbenes in excellent yields (Scheme 3, and Table 3). The *p*-benzenedialdehyde reacted similarly and provided the corresponding substituted (*E,E*)-distylbenzene in excellent yields (Scheme 4, and Table 4).

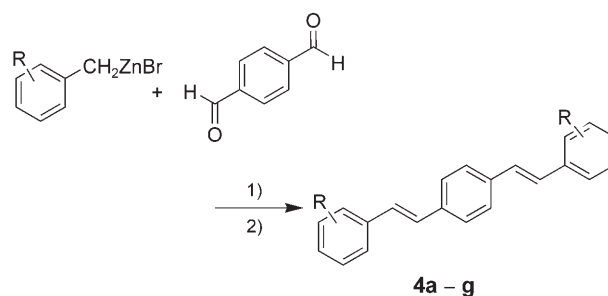
Unsaturated aldehydes, such as phenylacrylic aldehyde, reacted similarly and provided the correspond-



Scheme 2. Reagents and conditions: 1) [PdCl₂(PPh₃)₂], Me₃SiCl, THF, −18°C to room temperature; 2) saturated NH₄Cl solution.



Scheme 3. Reagents and conditions: 1) [PdCl₂(PPh₃)₂], Me₃SiCl, THF, −28°C to room temperature; 2) saturated NH₄Cl solution.

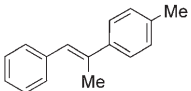
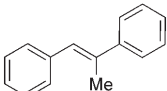
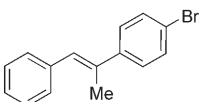
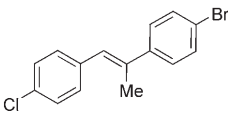
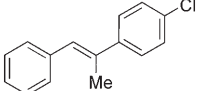


Scheme 4. Reagents and conditions: 1) [PdCl₂(PPh₃)₂], Me₃SiCl, THF, −18°C to room temperature; 2) saturated NH₄Cl solution.

ing substituted (*1E,3E*)-1,4-diphenyl-1,3-butadiene in excellent isolated yields (Scheme 5, and Table 5). One feature of this reaction that makes it a particularly attractive synthetic procedure is its regioselectivity. The double bond is formed between the carbonyl carbon atom of the carbonyl compounds and the carbon atom of organozinc reagents. Another feature of this reaction is its stereoselectivity. In all cases only the (*E*)-stilbenes were formed. The (*E*)-stilbene can be detected by ¹H NMR, ¹³C-NMR, MS and elemental analysis.

Based on our experimental results and other related studies,^[26,27] we propose the general reaction mechanism shown in Scheme 6. The first step of this mechanism is the reaction of PdCl₂L₂ with organozinc reagent or zinc powder to form [Pd(0)L₂] and then [Pd(0)L₂] reacts with ArCH₂ZnX **1** to give

Table 3. Palladium-catalyzed stereoselective olefination of benzylzinc bromides with aromatic ketones,^[a]

Entry	R	R ¹	Product ^[b]	Yield [%] ^[c]
1	4-CH ₃	H		78
2	H	H		72
3	H	4-Br		75
4	4-Cl	4-Br		76
5	H	4-Cl		81

^[a] All reactions were conducted on the following scale: 10 mmol substituted acetophenones with 11 mmol benzylzinc bromides, 2 mmol % [PdCl₂(PPh₃)₂] and 20 mmol Me₃SiCl in 20 mL THF at -28 °C to room temperature.

^[b] All products were characterized by melting point, IR, ¹H NMR ¹³C NMR, MS and elemental analyses.

^[c] Yields of isolated products.

[ArCH₂PdXL₂] **6**. The second step is the 1,2-addition of **6** to an aromatic aldehyde, which is activated by chlorotrimethylsilane,^[28] to give palladium complex **7**. The loss of the [PdXCIL₂] **8** from **7** in the presence of the chlorotrimethylsilane yields a secondary silyl ether **9**, which has been isolated. Compound **9** can also be detected in the reaction by GC-MS. Loss of the Me₃SiOH from **9** gives the final product (*E*)-stilbenes **2**. The [PdXCIL₂] **8** in the presence of ArCH₂ZnX **1** gives [Pd⁰L₂] and the catalyst is thus regenerated.

Conclusions

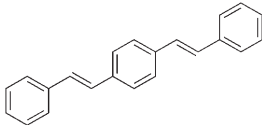
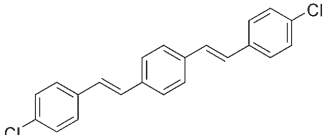
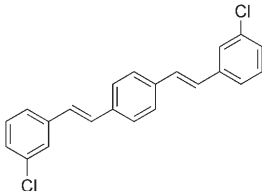
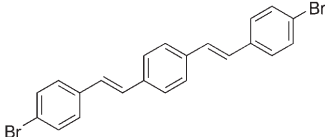
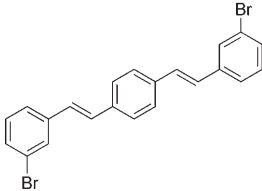
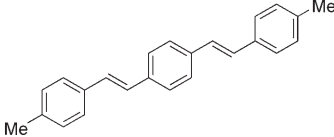
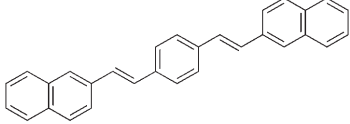
In conclusion, we found that the reaction between organozinc halide and carbonyl compound is actually a competitive reaction. When catalysts, reagents, reaction conditions and material ratio are changed, the types of reactions change accordingly. They range from dialkylation reaction, stereoselective olefination reaction, to an addition reaction. We have developed a new and convenient method for an efficient and highly stereoselective synthesis of (*E*)-stilbenes from the corresponding carbonyl compounds with benzylic zinc halides in the presence of catalytic amount of PdCl₂(PPh₃)₂ using a silylating agent in THF under mild conditions. The main advantages of this new method are mild reaction conditions, high stereoselectivity, tolerance of unsaturated double bonds and sub-

stituents, simple operation and excellent yields of the products. This method offers the possibility for the formation of carbon-carbon double bonds and the synthesis of the natural active products.

Experimental Section

All reactions were carried out in over-dried glassware under argon or nitrogen. All substrates and reagents were obtained commercially except for the organozinc reagents and catalysts, which were prepared by standard procedures.^[29,30] THF was distilled from sodium/benzophenone. ¹H NMR spectra were recorded on a Bruker AM 400 MHz or a Bruker AC-E 200 MHz spectrometers in CDCl₃ with TMS as an internal standard. ¹³C NMR spectra were obtained on a Bruker AM-400 operating at 100 MHz or a Bruker AC-E 200 operating at 50 MHz in CDCl₃ with TMS as an internal standard. IR spectra were recorded on an Alpha Centauri FI-IR spectrometer. Mass spectra were recorded on an HP 5988 A and GC/MS/DS instrument. Elemental analyses were carried out on a Carlo-Erba 1106 instruments. The stereochemistries of the product stilbenes were determined by comparison of the ¹H NMR spectra with those reported in the literature and GC/MS analyses on an HP-6890/HP-5973 gas chromatograph equipped with a 30 m × 0.25 mm HP-5 MS capillary column and a flame ionization detector.

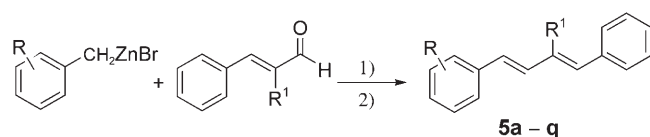
Table 4. Palladium-catalyzed stereoselective olefination of benzylzinc bromides with *p*-benzenedialdehyde.^[a]

Entry	R (Ar)	Product ^[b]	Yield [%] ^[c]
1	H		78
2	4-Cl		73
3	3-Cl		89
4	4-Br		82
5	3-Br		70
6	4-CH ₃		71
7	β -C ₁₀ H ₇		80

^[a] All reactions were conducted on the following scale: 10 mmol substituted *p*-benzenedialdehyde with 11 mmol benzylzinc bromides, 2 mmol % [PdCl₂(PPh₃)₂] and 20 mmol Me₃SiCl in 20 mL THF at –18 °C to room temperature.

^[b] All products were characterized by melting point IR, ¹H NMR, ¹³C NMR, MS and elemental analyses.

^[c] Yields of isolated products.



Scheme 5. Reagents and conditions: 1) [PdCl₂(PPh₃)₂], Me₃SiCl, THF, –18 °C to room temperature; 2) saturated NH₄Cl solution.

General Procedure

Benzylzinc halides (11 mmol) was prepared according to Knochel's procedure.^[29] PdCl₂(PPh₃)₂ (0.2 mmol) and THF (2 mL) were mixed and heated at 60 °C for 10 min in over-dried glassware under argon or nitrogen. The solution of benzylzinc halide in THF was added at room temperature, and the resulting mixture was cooled to –18 °C (for aromatic aldehydes and unsaturated aldehydes or –28 °C for aromatic ketones). A solution of the carbonyl compound (10 mmol) and Me₃SiCl (2.18 g, 20 mmol) in THF (10 mL) was added dropwise. Then the temperature was allowed to rise to room temperature. After stirring for 8 h, saturated NH₄Cl solution (10 mL) and Et₂O (10 mL) were added and

Table 5. Palladium-catalyzed stereoselective olefination of benzylzinc bromides with α,β -unsaturated aldehydes.^[a]

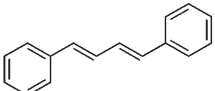
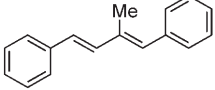
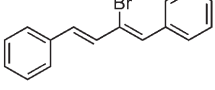
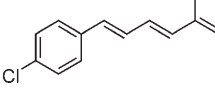
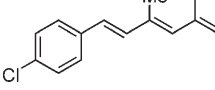
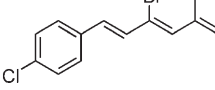
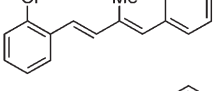
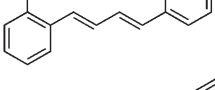
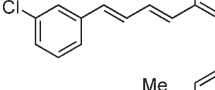
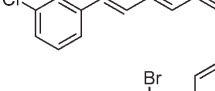
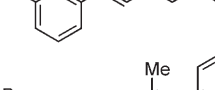
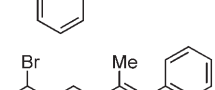
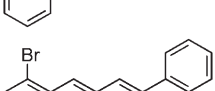
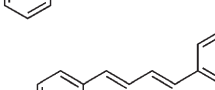
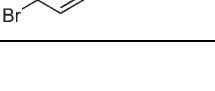
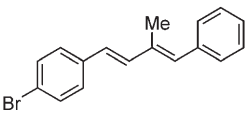
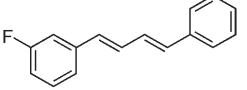
Entry	R	R ¹	Product ^[b]	Yield [%] ^[c]
1	H	H		76
2	H	CH ₃		91
3	H	Br		61
4	4-Cl	H		85
5	4-Cl	CH ₃		94
6	4-Cl	Br		63
7	2-Cl	CH ₃		55
8	2-Cl	H		51
9	3-Cl	H		50
10	3-Cl	CH ₃		69
11	3-Cl	Br		65
12	3-Br	CH ₃		72
13	2-Br	CH ₃		67
14	2-Br	H		75
15	4-Br	H		90

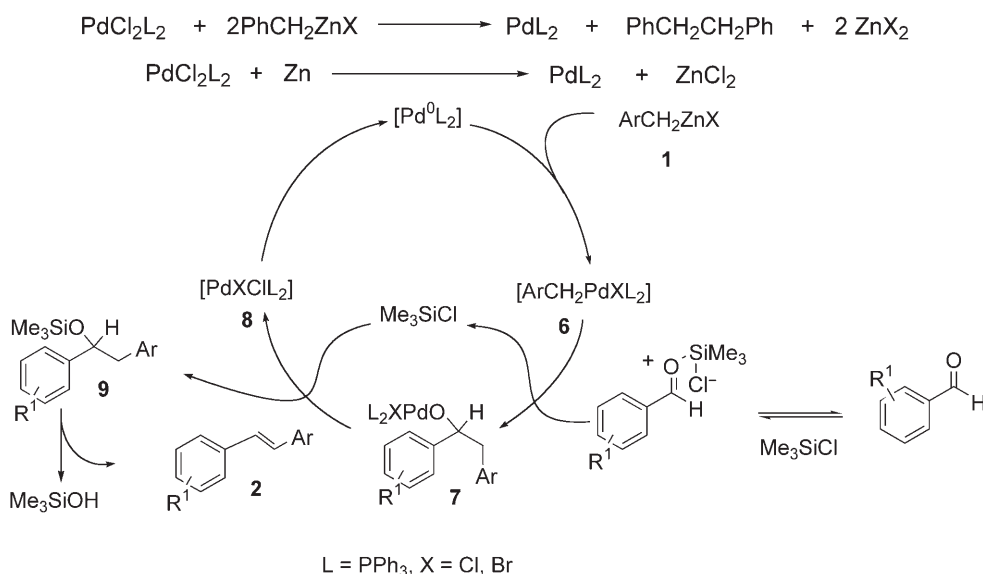
Table 5. (Continued)

Entry	R	R ¹	Product ^[b]	Yield [%] ^[c]
16	4-Br	CH ₃		85
17	3-F	H		63

^[a] All reactions were conducted on the following scale: 10 mmol substituted cinnamaldehydes with 11 mmol benzylzinc bromide, 2 mmol % [PdCl₂(PPh₃)₂] and 20 mmol Me₃SiCl in 20 mL THF at -18 °C to room temperature.

^[b] All products were characterized by melting point IR, ¹H NMR, ¹³C NMR, MS, and elemental analyses.

^[c] Yields of isolated products.



Scheme 6. The general reaction mechanism of palladium-catalyzed stereoselective olefination of organozinc reagents with carbonyl compounds.

the mixture was stirred for 10 min. The organic layer was separated, dried over anhydrous MgSO₄ and concentrated. The product was isolated from the crude reaction mixture by chromatography on a silica gel column using petroleum/ethyl acetate as an eluent.

Most of the products are known, except for **2e**, **2k**, **2l**, **2m**, **2n**, **2o**, **2p** in Table 2, **3a–e** in Table 3, **4c**, **4e**, **4g** in Table 4, and **5b–h**, **5j–q** in Table 5. All new compounds were characterized by IR, ¹H NMR, ¹³C NMR, MS, and elemental analysis.

Supporting Information

Details of the characterization of all new compounds can be founded in the Supporting Information.

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