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Palladium-catalyzed stereoselective synthesis of *E*- and *Z*-1,1-diaryl or triarylolefins

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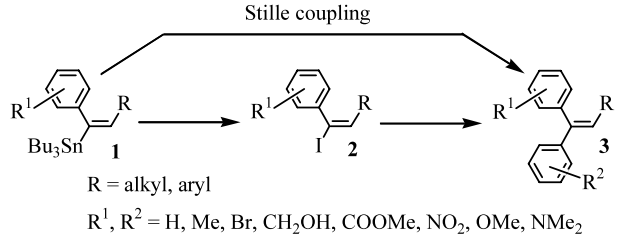
Abstract—A stereoselective and flexible synthesis of various *E*- and *Z*-1,1-diaryl and triarylolefins **3** was achieved from readily available vinylstannanes **1** via stereospecific iodo-destannylation and subsequent palladium-catalyzed Negishi-type cross-coupling reaction with arylzinc reagents under mild conditions.

Trisubstituted arylated olefins has attracted considerable attention of organic chemists in recent years not only for their interesting physical properties,[1] but also for their occurrence in natural and biological active substances. In this respect, the growing interest in arylated olefin derivatives of general structure **3** (Scheme 1) is connected with the hormonal,[2] retinoidal,[3] antimitotic,[4] antiviral[5] and anticonvulsant[6] activities. Despite their broad applications, the search for more simple and efficient methods for the stereocontrolled synthesis of trisubstituted arylated olefins bearing non-identical aromatic rings remains an ongoing challenge in the area of synthetic organic chemistry.

Several synthetic methods have been developed for the preparation of **3** such as Wittig-type reactions,[7] McMurry coupling of carbonyl compounds,[8] Heck reactions,[9] or palladium-catalyzed coupling reactions of organometallic reagents with organic halides[10] particularly, those involving sequential arylation of 1,1-dihaloalkenes using Grignard[11] or arylstannane[12] derivatives. While these reactions are suitable methods, many of them either display low stereoselectivity when olefins bear non-identical aromatic rings or do not tolerate sensitive functionality and/or requires harsh conditions (high temperatures, long reaction times). A stereoselective protocol for the synthesis of triaryl olefins has been reported which is based on the palladium-catalyzed hydroarylation of disubstituted alkynes.[13] However, in many instances, a lack of regioselectivity was observed from unsymmetrical alkynes and a mixture of regioisomers was obtained except in the case of hydroarylation of unsymmetrical alkynes conjugated to an electron withdrawing group such as arylpropiolamides[14] and related compounds.[15] More recently, 2-pyridyldimethyl(vinyl)silane has been successfully used as synthetic precursors of triaryl olefins by the palladium-catalyzed sequential double-Heck/Hiyama coupling reactions.[16]



Scheme 1.

We had previously reported an unprecedented *ortho*-directing effect (ODE) in unsymmetrical substituted arylalkynes[17] or diarylalkynes[18] which promotes regioselective addition of tributyltin hydride to the triple bond to afford efficiently disubstituted vinylstannane derivatives **1**. An important aspect of our ongoing research on the synthetic utility of these disubstituted vinylstannanes as intermediates in organic synthesis is their elaboration via further coupling under palladium catalysis into trisubstituted arylated olefins **3**. Consequently, our goal during this work was to provide a clean, high-yielding and general synthesis of trisubstituted arylated olefins **3** of defined configuration by direct coupling of **1** with aryl halides (Stille reaction) or

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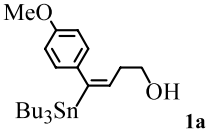
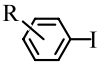
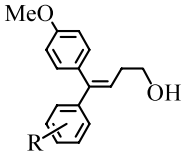
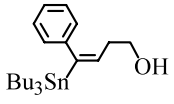
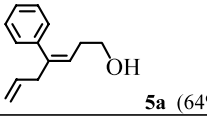
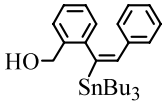
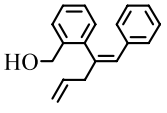
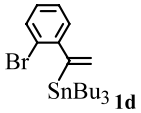
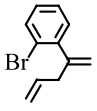
via coupling of the corresponding vinyl iodides **2** with organometallic reagents (Scheme 1). The results of this study are reported now.

Although Stille coupling of vinylstannanes with organic halides have already been established as an efficient method for the formation of carbon–carbon bonds, the coupling reactions in the case of sterically hindering 1-substituted vinylstannanes is well known to be sluggish[19] and often require specific conditions for different substrates. Thus several reported Stille conditions were examined for the coupling of **1** with aryl iodides using various combinations of Pd/solvent/additive mixtures (e.g. $Pd(PPh_3)_4$, $PdCl_2L_2$ (L: MeCN or PPh_3), $Pd(dba)_2$/$(furyl)_3P$, $AsPh_3$, Ar_3P with or without CuI). After much study,[20] it was found that the use of CuI as co-catalyst, which may facilitate the rate-determining transmetallation step, in combination with palladium catalyst that incorporate bulky phosphines resulted in optimal conditions. Thus, in the presence of $Pd(dba)_2$ (5 mol%), P(*o*-Tol)$_3$ (10 mol%), CuI (10 mol%) in refluxing acetonitrile for 15 h the reaction of **1a** (1.5 equiv.) having a free hydroxyl group[21] with 4-iodo-nitrobenzene **4a** afforded the coupling product **3a** in 66% yield (Table 1, entry 1). Unfortunately, under these conditions, all our attempts to prepare trisubstituted olefins **3b–c** from unreactive aryl iodides such as hindered *ortho*-substituted aryl iodides (i.e. **4b**) or deactivated aryl iodides bearing an electron-donating group (i.e. **4c**) resulted in unsatisfactory yields (27–42%, entries 2 and 3). It may be pointed out that Stille coupling of α-substituted vinyl stannanes **1b–d** with highly reactive organic halides such as allylic bromide in the presence of $Pd(dba)_2$ (5 mol%) and PPh_3 (10 mol%) in refluxing THF provided the allylated products **5a–c** in moderate to good yields (44–75%, entries 4–6).

Difficulties in obtaining trisubstituted arylated olefins **3** in good yields by direct coupling of sterically encumbered α-substituted vinyl stannanes **1** with unreactive aryl iodides led us to explore their halodestannylation chemistry and subsequent palladium-catalyzed cross-coupling reaction with various organometallic reagents (Mg, Zn, Sn…). Of particular interest, our attention was drawn to arylzinc derivatives (Negishi reaction)[22] since they are mild nucleophiles, well-known for their compatibility with most functional groups and are good candidates for transmetallations to organopalladium(II) complexes.

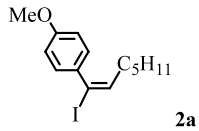
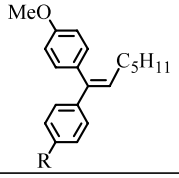
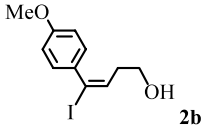
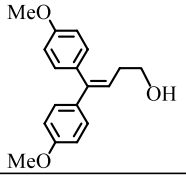
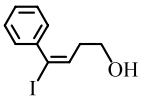
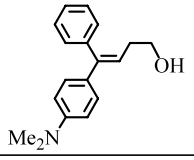
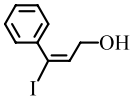
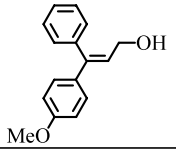
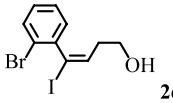
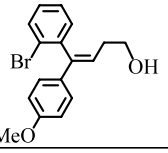
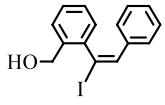
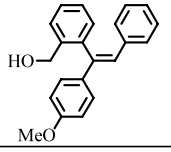
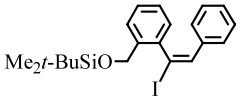
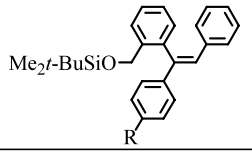
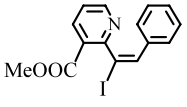
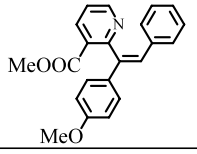
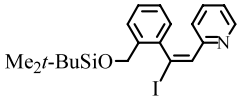
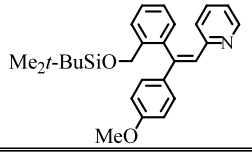
Stereospecific iodo-destannylation of α-substituted vinyl stannanes **1** with ca. 1 equiv. of iodine in dichloromethane at 20°C allows cleanly and rapidly the synthesis of the corresponding *E*-vinyl iodides[23] **2** as a single isomer, an interesting class of compounds which has been difficult to obtain in a stereoselective manner.[24] These latter are suitable electrophiles for further cross-coupling reactions. Thus, reaction of **2** with arylzinc chlorides in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$ (5%) occurs rapidly in THF at room temperature and provided in excellent yields within 2 to 4 h, the corresponding trisubstituted arylated olefins **3** as isomerically pure materials.[23] The coupling reaction was effective with either (*E*)-α-iodo substituted styrenes **2a–e** or (*E*)-iodostilbenes **2f–i**. As shown in Table 2, the reaction tolerates sensitive func-

Table 1. Palladium-catalyzed Stille coupling reaction of vinyl stannanes **1** with organic halides

Entry	Vinyl stannane 1[a]	Organic halide	Conditions[b]	Coupled product
1	 **1a**	 **4a**: R = *p*-NO_2	A	 **3a**: R = *p*-NO_2 (66%)[c]
2		**4b**: R= *o*-CO_2Me	A	**3b**: R= *o*-CO_2Me (27%)
3		**4c**: R = *p*-OMe	A	**3c**: R = *p*-OMe (42%)
4	 **1b**		B	 **5a** (64%)
5	 **1c**		B	 **5b** (44%)
6	 **1d**		B	 **5c** (75%)

[a] Prepared from the corresponding alkynes according to ref 17 and 18.
[b] Conditions A: 1.5 equiv of **1a**, 1 equiv of **4**, 5 mol% $Pd(dba)_2$, 10 mol% P(*o*-Tol)$_3$, 10 mol% CuI, MeCN, 80°C, 15 hrs. Conditions B: 1 equiv of **1b-d**, 5 equiv of allyl bromide, 5 mol% $Pd(dba)_2$, 10 mol% PPh_3, THF, 60°C.
[c] Obtained as a 8:92 mixture of *E:Z*-isomers determined by ^1H NMR.

Table 2. Palladium-mediated cross coupling reaction between arylzinc chlorides[a] and trisubstituted vinyl iodides **2**

Entry	Vinyl iodide 2[b]	Yields (%)[c]	Arylated alkene 3[b]	Yields (%)[d]
1 2	 **2a**	80	 **3a**: R = OMe **3b**: R = NMe_2	89 93
3	 **2b**	79	 **3c**	92[e]
4	 **2c**	80	 **3d**	93[e]
5	 **2d**	78	 **3e**	92[e]
6	 **2e**	77	 **3f**	94[e]
7	 **2f**	89	 **3g**	63[e,f]
8 9	 **2g**	93	 **3h**: R = H **3i**: R = OMe	80 93
10	 **2h**	78[g]	 **3j**	73[h]
11	 **2i**	89	 **3k**	94

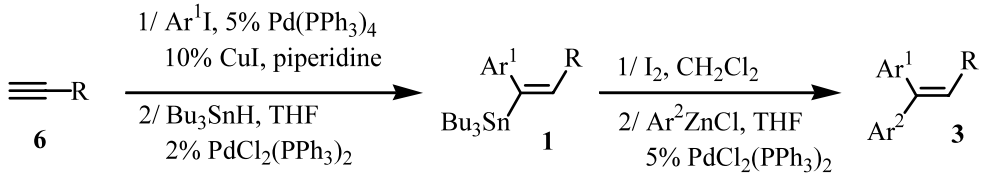
[a]/ All reactions were performed with 2 equiv of ArZnCl prepared from ArMgCl, 5 mol% of $PdCl_2(PPh_3)_2$ in THF at 20°C. For a general procedure see ref [25].
[b]/ All new compounds exhibited satisfactory spectral properties and isomeric purity (>95%) except if otherwise indicated.
[c]/ Isolated yield based on **1**.
[d]/ Isolated yield based on **2**.
[e]/ 3 equiv of ArZnCl were used.
[f]/ Obtained as a 35:65 mixture of *E*:*Z*-isomers determined by ^1H NMR.
[g]/ Isolated in a 93:7 mixture of *E*:*Z*-isomers determined by ^1H NMR.
[h]/ Isolated in a 7:93 mixture of *E*:*Z*-isomers determined by ^1H NMR.

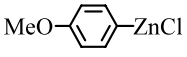
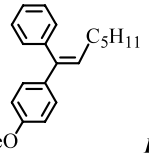
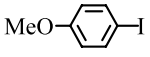
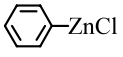
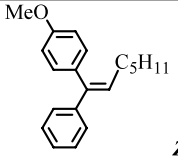
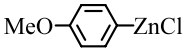
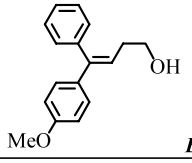
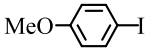
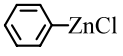
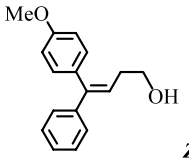
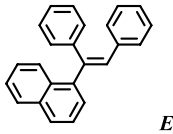
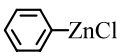
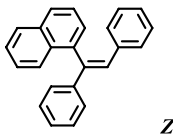
tional groups in the substrates and was even successful in the absence of hydroxy protecting groups (entries 3–6) except in the case of vinyl iodide **2f**. The coupling reaction from **2f** demonstrated the need for protecting the benzylic alcohol function. Indeed, without protection, the product of the reaction **3g** is mainly obtained as a mixture of *E* and *Z*-isomers (*E*/*Z*: 35/65, entry 7). However, when the same reaction was conducted from the corresponding silyloxy derivatives **2g**, triaryl olefins **3h** and **3i** were formed in high yields as a single isomer (entries 8 and 9).

The flexibility of this procedure was further demonstrated by the synthesis of both *E*- and *Z*-isomers of trisubstituted arylated olefins **3** in an independent fashion as illustrated in Table 3. The installation of aromatic groups at the desired olefins carbon can be achieved by simply changing the order of addition of aromatic groups. Thus, starting from terminal alkyne **6** this four-step sequence afforded the desired *E*- and *Z*-isomers of arylated olefins **3** in good overall yields. It may be pointed out that in the conversion of **1** to **3**, the intermediate vinyl iodides **2** could be used in the further coupling step without purification.

The favorable results obtained above in the alkenyl-aryl coupling reactions prompted us to study and compare related procedures particularly those involving aryl Grignard reagents, arylstannanes and arylboranes. Several points are worth noting from the above results summarized in Table 4. More reactive organometallics

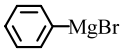
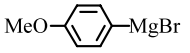
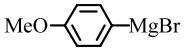
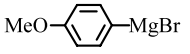
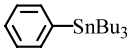
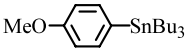
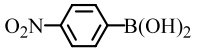
Table 3. Synthesis of *E*- and *Z*-1,1-diaryl or triarylolefins **3**[a]



Entry	R	Ar^1I	Ar^2ZnCl	Arylated olefin 3 (Yield)[b]
1	C_5H_{11}			 ***E*-3l** (76%)
2	C_5H_{11}			 ***Z*-3l** (74%)
3	$(CH_2)_2OH$			 ***E*-3m** (75%)
4	$(CH_2)_2OH$			 ***Z*-3m** (76%)
5	C_6H_5			 ***E*-3n** (77%)
6	C_6H_5			 ***Z*-3n** (79%)

[a]/ All new compounds exhibited satisfactory spectral properties and isomeric purity (>95%).
[b]/ Isolated overall yield based on **1**.

Table 4. Palladium-catalyzed arylation of vinyl iodides **2** with aryl Grignard, arylstannane or arylboronic acid reagents

Entry	Vinyl iodide 2	ArM	Conditions[a]	Arylated olefin 3	Yield (%)[b]
1	**2a**		A	***Z*-3l**	71[c]
2	**2a**		A	**3a**	75[c]
3	**2c**		A	***E*-3m**	33[c,d]
4	**2g**		A	**3i**	89
5	**2b**		B	***Z*-3m**	79
6	**2c**		B	***E*-3m**	81
7	**2b**		C	**3o**	62

[a]/ Conditions A: 2 equiv of ArMgBr, 1 equiv of **2**, 5 mol% $PdCl_2(PPh_3)_2$, THF, 20°C 2 to 3h. Conditions B: 2 equiv of $ArSnBu_3$, 1 equiv of **2**, 5 mol% $Pd(dba)_2$, 10 mol% $AsPh_3$, 10 mol% CuI, NMP, 20°C, 15 h. Conditions C: 1.2 equiv of $ArB(OH)_2$, 5 mol% $Pd(PPh_3)_4$, DME, 2 equiv Na_2CO_3, 90°C, 15 h.

[b]/ Isolated yield based on **2**.

[c]/ Coupling product was contamined with 15 to 20% of 1,2-diarylstilbenes.

[d]/ 3 equiv of ArMgBr were used.

such as organomagnesium derivatives suffer from a moderate functional tolerance when compared to organozinc compounds. Moreover, in most cases studied the cross coupling products were contaminated with 15–20% of 1,2-diarylstilbenes arising probably from metal–halogen exchange reaction[26] (Table 4 entries 1–3). With less reactive organometallic species such as arylstannane or arylboronic acid compounds (entries 5–7), the coupling can occur stereospecifically to produce the desired arylated olefins **3** in good yields. It should be pointed out that for efficient coupling, Suzuki reaction typically requires heating to ~90°C for several hours, whereas Stille reaction proceed at room temperature.

In summary, we have developed a stereoselective and flexible sequence that allows synthesis of both configurationally pure *E*- and *Z*-functionalized 1,1-diaryl and triarylolefins from readily available vinylstannanes. The sequence involved in the coupling step the use of organozinc reagents at room temperature which have significant practical advantages relative to those that require elevated temperatures.

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23. The isomeric purity after purification by flash chromatography was >95% since examination of the ^{13}C and ^{1}H NMR spectra of the products indicated the presence of one isomer in each cases.
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25. Typical procedure: To a stirred solution of vinyl stannane **1** (1 equiv.) in dry CH_2Cl_2 (2 mL per mmol of substrate) was added at 0°C sublimed finely divided I_2 (1.05 equiv.) and the dark wine solution was vigorously stirred at room temperature until all of the substrate had been consumed. Saturated aqueous $Na_2S_2O_3$ was added to remove excess of iodine followed by potassium fluoride aqueous solution. After stirring at room temperature for 1 h, the resulting white precipitate of tributyltin fluoride was removed by filtration and the filtrate was extracted with ether. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated (the crude vinyl iodide **2** could be used in the further step without purification). Filtration through silica gel afforded pure vinyl iodide **2**.
2b: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.47 (2H, d, $J=8.9$ Hz), 6.84 (2H, d, $J=8.9$ Hz), 6.49 (1H, t, $J=7.6$ Hz), 3.81 (3H, s), 3.65 (2H, t, $J=6.3$ Hz), 2.27 (2H, q, $J=7.6$ Hz), 1.48 (1H, br.s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.2, 138.9, 134.0, 130.0, 113.6, 97.6, 61.5, 55.3, 35.4.
2c: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.30 to 7.17 (5H, m), 6.47 (1H, t, $J=7.5$ Hz), 3.57 (2H, t, $J=6.4$ Hz), 2.20 (2H, q, $J=7.5$ Hz), 1.89 (1H, br.s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 141.3, 139.2, 128.5, 128.1, 128.0, 97.0, 61.2, 35.2.
To a solution of vinyl iodide **2**, $PdCl_2(PPh_3)_2$ (5 mol%) in THF was added at room temperature ArZnCl (2 equiv.) prepared by transmetallation from the corresponding Grignard reagent (2 equiv.) and anhydrous $ZnCl_2$ (2.1 equiv.). The reaction was stirred at room temperature and monitored by TLC until complete consumption of starting materials (2 to 4 h). The reaction was hydrolyzed at 0°C with aqueous HCl (1N), extracted with Et_2O, the organic extract was dried over $MgSO_4$ and the solvent was removed in vacuo. Pure arylated olefin was isolated by simple filtration through silica gel.
***E*-3m**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.46 to 7.35 (3H, m), 7.26 to 7.20 (4H, m), 6.86 (2H, d, $J=9.0$ Hz), 6.08 (1H, t, $J=7.6$ Hz), 3.83 (3H, s), 3.73 (2H, t, $J=6.6$ Hz), 2.42 (2H, q, $J=7.6$ Hz), 1.94 (1H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.7, 143.5, 140.0, 135.0, 129.7, 128.2, 128.1, 126.9, 123.4, 113.4, 62.5, 55.2, 33.2.
***Z*-3m**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.18 (5H, m), 7.05 (2H, d, $J=8.3$ Hz), 6.84 (2H, d, $J=8.3$ Hz), 6.00 (1H, t, $J=7.3$ Hz), 3.76 (3H, s), 3.66 (2H, t, $J=6.5$ Hz), 2.36 (2H, q, $J=7.0$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.5, 143.4, 142.7, 132.1, 130.9, 127.9, 127.2, 126.9, 125.1, 113.5, 62.3, 55.0, 33.2.
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