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Synthesis of α-Arylated Allylsilanes through Palladium-Catalyzed γ-Selective Allyl−Aryl Coupling

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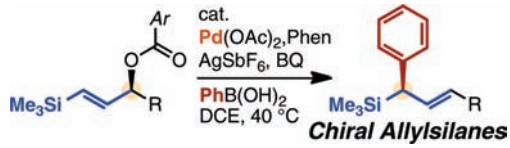
ABSTRACT



A palladium-catalyzed γ-selective allyl−aryl coupling between γ-silylated allylic esters and arylboronic acids produced α-arylated allylsilanes with *E*-alkene geometry. The reaction tolerated various functional groups in both the arylboronic acids and the allylic esters and afforded functionalized allylsilanes. The reaction of optically active allylic esters took place with excellent α-to-γ chirality transfer with *syn* stereochemistry to give chiral allylsilanes.

Allylsilanes are useful reagents for the stereoselective carbon−carbon bond formations.[1] The development of facile and efficient methods for the sythesis of allylsilanes is important. In particular, the preparation of enantiomerically enriched allylsilanes remains a challenge. Among a number of routes to allylsilanes,[2−13] two types of copper-mediated allylic substitution strategies, substitutions of γ-silylated allylic alcohol derivatives with organocopper reagents[14] and reactions of allylic alcohol derivatives with silylcuprate reagents,[15,16] are particularly efficient and versatile because the substrates and the reagents are readily available and the reactions are highly reliable in terms of product yield and stereoselectivity. Even these methods, however, are not secure from the problems of the incompatibility with functional groups because the organocopper reagents are prepared from basic organometallic reagents such as Grignard or organolithium reagents, and the silylcuprate reagents are also strongly basic.

(1) (a) Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293–1316. (b) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063–2192. (c) Chabaund, L.; James, P.; Landais, Y. *Eur. J. Org. Chem.* **2004**, 3173–3199.

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(3) For Pd-catalyzed hydrosilylations of 1,3-dienes, see: (a) Hayashi, T.; Kabeta, K.; Yamamoto, T.; Tamao, K.; Kumada, M. *Tetrahedron Lett.* **1983**, *24*, 5661–5664. (b) Hayashi, T.; Kebeta, K. *Tetrahedron Lett.* **1985**, *26*, 3023–3026. (c) Hayashi, T.; Hengrasmee, S.; Matsumoto, Y. *Chem. Lett.* **1990**, 1377–1380. (d) Hayashi, T.; Matsumoto, Y. *Tetrahedron: Asymmetry* **1990**, *1*, 151–154. (e) Hayashi, T.; Han, J. W.; Takeda, A.; Tang, J.; Nohmi, K.; Mukaide, K.; Tsuji, H.; Uozumi, Y. *Adv. Synth. Catal.* **2001**, *343*, 279–283.

(4) For Pd-catalyzed silylations of allylic substrates with disilanes, see: (a) Matsumoto, Y.; Ohno, A.; Hayashi, T. *Organometallics* **1993**, *12*, 4051–4055. (b) Hayashi, T.; Ohno, A.; Lu, S.; Matsumoto, Y.; Fukuyo, E.; Yanagi, K. *J. Am. Chem. Soc.* **1994**, *116*, 4221–4226. (c) Tsuji, Y.; Kajita, S.; Isobe, S.; Funato, M. *J. Org. Chem.* **1993**, *58*, 3607–3608. (d) Tsuji, Y.; Funato, M.; Ozawa, M.; Ogiyama, H.; Kajita, S.; Kawamura, T. *J. Org. Chem.* **1996**, *61*, 5779–5787. (e) Moser, R.; Nishikata, T.; Lipshutz, B. H. *Org. Lett.* **2010**, *12*, 28–31.

(5) For Pd-catalyzed hydrogenolysis of silyl-substituted allylic carbonates, see: Hayashi, T.; Iwamura, H.; Uozumi, Y. *Tetrahedron Lett.* **1994**, *35*, 4813–4816.

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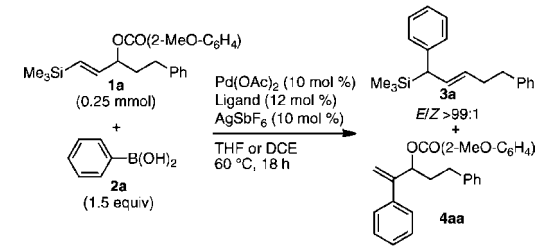
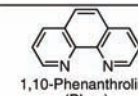
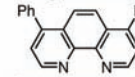
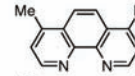
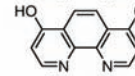
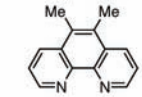
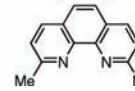
Herein, we report a palladium-catalyzed γ-selective allyl−aryl coupling between γ-trimethylsilyl-substituted allylic esters and arylboronic acids,[17−19] which appears to be a versatile route to α-arylated allylsilanes.[2,3b,5,7,8,14,15,16f] The reaction is compatible with various functional groups in both arylboronic acids and γ-silylated allylic esters, affording functionalized allylsilanes. Optically active allylic esters reacted with excellent α-to-γ chirality transfer with *syn* stereochemistry to give chiral allylsilanes.

In the studies to optimize reaction conditions, we used γ-trimethylsilyl-substituted allylic ester **1a** having an *o*-methoxybenzoyloxy leaving group.[20] The allylic ester **1a** was readily prepared in a three-step procedure involving an addition of lithium trimethylsilylacetylide to an aldehyde and Red-Al reduction[21] followed by acylation. Initially, **1a** and phenylboronic acid (**2a**) (1.5 equiv) were subjected to the standard reaction conditions for the palladium-catalyzed γ-selective allyl−aryl coupling between allylic ester and arylbornic acids [**1a**/**2a**/$Pd(OAc)_2$/1,10-phenanthroline/$AgSbF_6$ 1:1.5:0.1:0.12:0.1, 60 °C, 18 h].[17] The reactions afforded (*E*)-1-phenyl-2-alkenylsilane **3a** in 71 and 59% isolated yields in THF and $ClCH_2CH_2Cl$ (DCE), respectively (84 and 78% convn of **1a**), with excellent *E*/*Z* (>99:1) selectivity (Table 1, entries 1 and 2). Although no α-substitution product was formed, the reaction produced a smaller amount (12%) of desilylated exomethylene compound (**4aa**) having a phenyl group at the β-position with the acyloxy leaving group intact. Addition of a substoichiometric amount (20 mol %) of 1,4-benzoquinone (BQ) to the reaction mixture with DCE solvent resulted in complete consumption of **1a**, but failed to improve the yield of the coupling product **3a** (70% isolated yield) (entry 3, conditions A).[22] When the reaction was performed on a 2.7 mmol scale (1.0 g) under condition A, the coupling product **3a** was obtained in 68% isolated yield (**3a**/**4aa** 84:16).

Our ligand screening with substituted 1,10-phenanthrolines revealed that disubstitutions at the 4,7- or 5,6-positions have

Table 1. Optimization of Reaction Conditions[a]



entry	ligand	solvent	convn (%)	ratio of **3a**/**4aa**[c]	yield of **3a** (%)[d]	yield of **4aa** (%)[d]
1	 1,10-Phenanthroline (Phen)	THF	84	86:14	74 (71)	12
2		DCE	78	84:16	65 (59)	12
3[b]	Phen with BQ (20 mol %)	DCE (**Conditions A**)	100	85:15	78 (70)	14
4	 Bathophenanthroline (Bathophen)	THF (**Conditions B**)	62	>99:1	57 (52)	0
5		THF	64	95:5	60	3
6		THF	32	95:5	46	2
7		THF	50	94:6	45	3
8		THF	36	1:>99	0	16

[a] Conditions: $Pd(OAc)_2$ (10 mol %), ligand (12 mol %), $AgSbF_6$ (10 mol %), **1a** (0.25 mmol), **2a** (0.375 mmol), solvent (1.5 mL), 60 °C, 18 h. [b] Conditions: $Pd(OAc)_2$ (10 mol %), Phen (12 mol %), $AgSbF_6$ (10 mol %), BQ (20 mol %), **1** (0.25 mmol), phenylboronic acid (0.375 mmol), DCE (1.5 mL), 60 °C, 18 h. [c] Determined by ^1H NMR analysis of the crude materials. [d] NMR yield. The yield in parentheses was isolated yield.

(9) For silylene insertions into allylic ethers, see: Bourque, L. E.; Cleary, P. A.; Woerpel, K. A. *J. Am. Chem. Soc.* **2007**, *129*, 12602–12603.

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(11) For Ireland−Claisen rearrangements of (*Z*)-vinylsilanes, see: (a) Panek, J. S.; Clark, T. D. *J. Org. Chem.* **1992**, *57*, 4323–4326. (b) Sparks, M. A.; Panek, J. S. *J. Org. Chem.* **1991**, *56*, 3431–3438.

(12) For Wittig olefinations of α-silylaldehyde, see: Bhushan, V.; Lohray, B. B.; Enders, D. *Tetrahedron Lett.* **1993**, *34*, 5067–5070.

(13) For Rh- or Cu-catalyzed carbenoid insertions into Si−H bonds, see: (a) Davies, H. M.; Hansen, T.; Rutberg, J.; Bruzinski, P. R. *Tetrahedron Lett.* **1997**, *38*, 1741–1744. (b) Bulugahapitiya, P.; Landais, Y.; Parra-Rapado, L.; Planchenault, D.; Weber, V. *J. Org. Chem.* **1997**, *62*, 1630–1641. (c) Wu, J.; Chen, Y.; Panek, J. S. *Org. Lett.* **2010**, *12*, 2112–2115.

(14) For substitutions of γ-silylated allylic alcohol derivatives with organocopper reagents, see: (a) Smitrovich, J. H.; Woerpel, K. A. *J. Am. Chem. Soc.* **1998**, *120*, 12998–12999. (b) Smitrovich, J. H.; Woerpel, K. A. *J. Org. Chem.* **2000**, *65*, 1601–1614. (c) Kacprzynski, M. A.; May, T. L.; Kazane, S. A.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 4554–4558. See also: (d) Tanigawa, Y.; Fuse, Y.; Murahashi, S. *Tetrahedron Lett.* **1982**, *23*, 557–560.

(15) Fleming et al. developed the silylations of allylic alcohol derivatives with silylcuprate reagents, see: (a) Fleming, I.; Newton, T. W. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1805–1808. (b) Fleming, I.; Thomas, A. P. *J. Chem. Soc., Chem. Commun.* **1985**, 411–413. (c) Fleming, I.; Thomas, A. P. *J. Chem. Soc., Chem. Commun.* **1986**, 1456–1457. (d) Fleming, I.; Higgins, D.; Lawrence, N. J.; Thomas, A. P. *J. Chem. Soc., Perkin Trans. 1* **1992**, 3331–3349. (e) Dieter, R. K. *Modern Organocopper Chemistry*; Krause, N., Ed.; Wiley-VCH: Weinheim, Germany, 2002; pp 79−144.

(16) For other silylations of allylic substrates with silylcuprate reagents, see: (a) Laycock, B.; Kitching, W.; Wickham, G. *Tetrahedron Lett.* **1983**, *24*, 5785–5788. (b) Clive, D. L. J.; Zhang, C.; Zhou, Y.; Tao, Y. *J. Organomet. Chem.* **1995**, *489*, C35–C37. (c) Lipshuz, B. H.; Sclafani, J. A.; Takanami, T. *J. Am. Chem. Soc.* **1998**, *120*, 4021–4022. (d) Oestreich, M.; Auer, G. *Adv. Synth. Catal.* **2005**, *347*, 637–640. (e) Schmidtmann, E. S.; Oestreich, M. *Chem. Commun.* **2006**, 3643–3645. (f) Vyas, D. J.; Oestreich, M. *Chem. Commun.* **2010**, 568–570.

(17) For the Pd-catalyzed γ-selective and stereospecific allyl−aryl coupling between allylic esters and arylboronic acids, see: (a) Ohmiya, H.; Makida, Y.; Tanaka, T.; Sawamura, M. *J. Am. Chem. Soc.* **2008**, *130*, 17276–17277. (b) Ohmiya, H.; Makida, Y.; Li, D.; Tanabe, M.; Sawamura, M. *J. Am. Chem. Soc.* **2010**, *132*, 879–889.

(18) For an approach to allenylsilanes by the Rh-catalyzed coupling between propargylic carbonates and a silylboronate, see: Ohmiya, H.; Ito, H.; Sawamura, M. *Org. Lett.* **2009**, *11*, 5618–5620.

(19) For the Cu-catalyzed γ-selective and stereospecific allyl−aryl and allyl−alkyl couplings with organoboron compounds, see: (a) Ohmiya, H.; Yokokawa, N.; Sawamura, M. *Org. Lett.* **2010**, *12*, 2438–2440. (b) Ohmiya, H.; Yokobori, U.; Makida, Y.; Sawamura, M. *J. Am. Chem. Soc.* **2010**, *132*, 2895–2897.

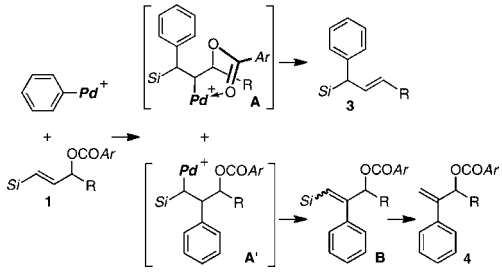
(20) For the screening of leaving groups, see Supporting Information. The superiority of this leaving group for the allyl−aryl coupling between γ-arylated allylic esters and arylboronic acids, see ref 17b.

(21) Jones, T. K.; Denmark, S. E. *Org. Synth.* **1985**, *64*, 182–185.

significant impacts on suppressing the β-phenylation. Most strikingly, the reaction with 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline) in the absence of BQ gave no β-phenylation product, but unfortunately the reaction stopped at a low conversion (62%) of **1a**, resulting in a moderate yield of the allylsilane **3a** (57% by ^{1}H NMR, 52% isolated, Table 1, entry 4, conditions B). The conversion and yield were not improved even with a prolonged reaction time. Smaller but still significant ligand effects in suppressing the β-phenylation were observed with 4,7-dimethyl-, 4,7-dihydroxy-, and 5,6-dimethyl-1,10-phenanthrolines (entries 5−7). In sharp contrast, 2,9-dimethylphenanthroline, which has an increased steric demand around the N,N′-coordination site, afforded only the β-phenylation product (**4aa**) in low yield (entry 8).

The formation of **4aa** can be explained by invoking the aryl−Pd insertion across the C−C double bond with the "reverse" site selectivity (Scheme 1). Thus, the reverse selectivity is induced by an interaction between the σ[C(γ)−Pd] and the σ*[Si−C(Me)] orbitals in the addition product **A′**. The β-hydride elimination of **A′** forms styrylsilane **B**: This process may be described as the elimination of H^+ and a Pd(0) species. Then, protodesilylation of **B** (with H^+ or $[Pd-H]^+$) gives the exomethylene compound **4**.[23] The pronounced substituent effects at the 4,7- and 5,6-positions of the phenanthroline ligands may be explained by the steric repulsion between the ligand substituents and the proximal Me_3Si group in **A′**.

Scheme 1. Possible Pathways to **3** and **4**



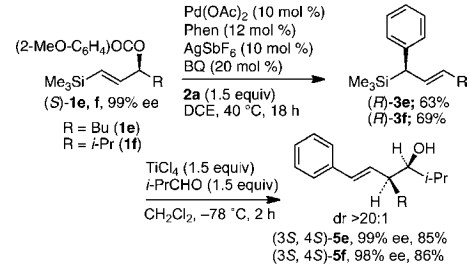
The γ-selective palladium-catalyzed reaction was capable of affording a variety of α-arylated allylsilanes (Table 2). All substrate combinations listed in Table 2 were subjected to both reaction conditions, conditions A (Pd/Phen/Ag/BQ/DCE) and conditions B (Pd/Bathophen/Ag/THF). While conditions A afforded higher yields of **3** in most cases (entries 1−7 and 9−12), the selectivity for **3** over **4** was generally higher with conditions B. It should be noted that the elimination of BQ (20 mol %) from conditions A resulted in a significant decrease in the yield of **3**. Since the side product (**4**) could easily be separated from the allylsilanes **3** by silica gel chromatography, conditions A seems to be more practical when higher isolated yields of **3** are obtained.

Table 2 illustrated that a variety of functional groups such as MeO, CF_3, Cl, ketone, aldehyde, thiophene, silyl ether, ester, and OH were compatible with the synthesis of α-arylated allylsilanes (entries 1−5 and 7−10). Importantly, the functional groups are tolerated in both allylic esters (**1**) and arylboronic acids (**2**). A heteroarylboronic acid such as 3-thiopheneboronic acid (**2h**) participated in the coupling (entry 7). The free hydroxy group in substrate **1d** did not inhibit the reaction, giving the corresponding hydroxylated allylsilane **3d** (entry 10). These functional groups in the substrates caused capricious effects on the yields of **3** and the **3**/**4** selectivities.

The tolerance of the reaction toward steric demand in both allylic esters (**1**) and arylboronic acids (**2**) is shown in Table 2, entries 6 and 11−13. *o*-Tolylboronic acid (**2g**) was coupled with **1a** albeit with a low yield (56%, entry 6, conditions A). The allylic esters **1e** and **1f** with Bu and bulkier *i*-Pr groups, respectively, instead of the phenylethyl group in **1a**, were phenylated at the α-position effectively (71 and 75%, entries 11 and 12, conditions A). The tertiary alcohol derivative **1g** was converted to γ,γ-disubstituted allylsilane **3g** with a moderate yield (61%, entry 13, conditions B).

The reaction of an optically active γ-silylated allylic ester (*S*)-**1e** (99% ee) and phenylboronic acid (**1a**) in the presence of $Pd(OAc)_2$, 1,10-phenanthroline, $AgSbF_6$, and BQ in DCE at 40 °C afforded the allylsilane **3e** in 63% yield (Scheme 2).

Scheme 2. Synthesis of Chiral Allylsilanes and Their Lewis-Acid-Mediated Addition to an Aldehyde



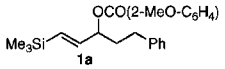
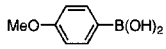
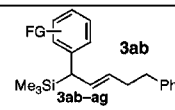
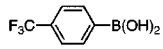
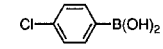
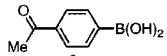
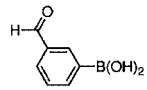
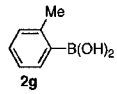
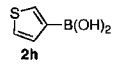
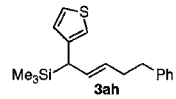
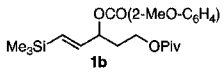
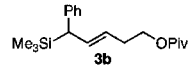
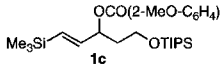
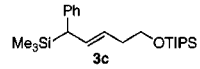
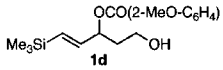
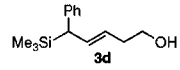
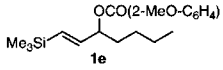
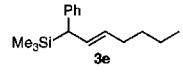
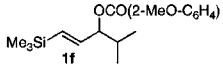
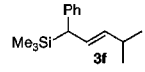
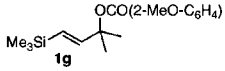
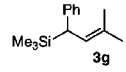
The subsequent addition of **3e** to isobutyraldehyde in the presence of $TiCl_4$ afforded homoallylic alcohol (3*S*,4*S*)-**5e** (99% ee) without a loss of enantiomeric purity.[1a,2a] The diastereomer ratio with respect to the consecutive stereogenic centers was >20:1 (*E*/*Z* > 99:1). Under the identical conditions, the reaction of (*S*)-**1f** (99% ee), which contains a bulkier α-*i*-Pr group, gave (*R*)-**3f** with 98% ee, suggesting that the α-to-γ chirality transfer is not significantly influenced by the steric demand of the α-substituent.

The 1,2-*syn*-selectivity for the arising stereogenic centers suggests that the addition of the allylsilanes **3e** and **3f** to the aldehyde proceeded through an acyclic antiperiplanar transition

(22) Generally, conditions A afforded higher yields of **3** than the conditions shown in Table 1, entry 1. For example, the reaction between **1a** and **2c** under the conditions shown in Table 1, entry 1, afforded the coupling product **3ac** in 51% isolated yield, while the conditions A afforded **3ac** in 82% (Table 2, entry 2).

(23) The styrylsilane **B** should be more susceptible to protonation−desilylation than **1** because the aryl group stabilizes a positive charge of the corresponding carbocation intermediate. The protodesilylation process may be mediated by Pd species, see: (a) Fillion, E.; Taylor, N. J. *J. Am. Chem. Soc.* **2003**, *125*, 12700–12701. (b) Busacca, C. A.; Swestock, J.; Johnson, R. E.; Bailey, T. R.; Musza, L.; Rodger, C. A. *J. Org. Chem.* **1994**, *59*, 7553–7556. (c) Farina, V.; Hossain, M. A. *Tetrahedron Lett.* **1996**, *37*, 6997–7000. (d) Gordillo, A.; de Jesús, E.; López-Mardomingo, C. *J. Am. Chem. Soc.* **2009**, *131*, 4584–4585.

Table 2. Synthesis of α-Arylated Allylsilanes (**3**) through Pd-Catalyzed Allyl−Aryl Coupling

entry	ester	arylboronic acid	allylsilane	conditions A[a] isolated yield of **3** (%)[c]	conditions A[a] ratio of **3**/**4**[d]	conditions B[b] isolated yield of **3** (%)[c]	conditions B[b] ratio of **3**/**4**[d]
1	 **1a**	 **2b**	 **3ab–ag**	62	71:29	30	92:8
2	**1a**	 **2c**	**3ac**	82	87:13	45	>99:1
3	**1a**	 **2d**	**3ad**	74	85:15	50	>99:1
4	**1a**	 **2e**	**3ae**	78	86:14	64	>99:1
5	**1a**	 **2f**	**3af**	68	87:13	61	>99:1
6	**1a**	 **2g**	**3ag**	56	81:19	35	>99:1
7	**1a**	 **2h**	 **3ah**	48	83:17	40	>99:1
8	 **1b**	**2a**	 **3b**	54	83:17	62	95:5
9	 **1c**	**2a**	 **3c**	66	79:21	42	92:8
10	 **1d**	**2a**	 **3d**	49	84:16	38	>99:1
11	 **1e**	**2a**	 **3e**	71	85:15	47	95:5
12	 **1f**	**2a**	 **3f**	75	84:16	65	87:13
13	 **1g**	**2a**	 **3g**	56	79:21	61	89:11

[a] Conditions A: $Pd(OAc)_2$ (10 mol %), Phen (12 mol %), $AgSbF_6$ (10 mol %), BQ (20 mol %), **1** (0.25 mmol), **2** (0.375 mmol), DCE (1.5 mL), 60 °C, 18 h. [b] Conditions B: $Pd(OAc)_2$ (10 mol %), Bathophen (12 mol %), $AgSbF_6$ (10 mol %), **1** (0.25 mmol), **2** (0.375 mmol), THF (1.5 mL), 60 °C, 18 h. [c] Isomeric ratio (E/Z > 99:1). Determined by ^1H NMR analysis of the crude materials. [d] Determined by ^1H NMR analysis of the crude materials.

state.[1a,2a] On the basis of the established 1,3-*anti* stereochemical pathway of Lewis-acid-mediated S_E' reactions of allylsilanes,[24] the absolute configuration of the chiral allylsilanes **3e** and **3f** was deduced to *R*. Accordingly, it revealed that α-to-γ chirality transfer in the Pd-catalyzed allyl−aryl coupling proceeded with *syn* stereochemistry. This stereochemistry coincides with the stereochemical outcome previously observed in the parent Pd-catalyzed allyl−aryl coupling, which can be rationalized by the C−C double bond insertion into the aryl−Pd bond and *syn*-β-acyloxy elimination with the assistance of intramolecular coordination of the acyloxy group to the palladium center.[17]

In conclusion, a palladium-catalyzed γ-selective allyl−aryl coupling between γ-trimethylsilyl-substituted allylic esters and arylboronic acids is a versatile, functional group-tolerable approach to α-arylated allylsilanes, while the yields are only moderate. The excellent α-to-γ chirality transfer with *syn*-stereochemistry allowed the preparation of chiral allylsilanes from optically active allylic esters.

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Supporting Information Available: Experimental details and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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