Published in final edited form as:

Synlett. 2017 November ; 28(18): 2415–2420. doi:10.1055/s-0036-1588471.

Understanding Site Selectivity in the Palladium-Catalyzed Cross-Coupling of Allenylsilanolates

Scott E. Denmark and Andrea Ambrosi¹

University of Illinois at Urbana-Champaign, Department of Chemistry, 600 S Mathews Ave., Urbana, IL 61801, USA

Abstract

Allenylsilanolates can undergo cross-coupling at the α - or γ -terminus, and site selectivity appears to be determined by the intrinsic transmetalation mechanism. Fine-tuning of concentration, nucleophilicity, and steric bulk of the silanolate moiety allows for the selective formation of one isomer over the other. Whereas the α -isomer can be obtained in synthetically useful yield, the γ -isomer is favored only when employing reaction conditions that are inevitably associated with diminished reactivity.

Graphical Abstract

Keywords

allenes; cross-coupling; organosilanes; palladium; site selectivity; transmetalation

In recent years, the palladium-catalyzed cross-coupling of organosilanes has emerged as a valuable alternative to traditional cross-coupling methods involving organoboron, -tin, and -zinc reagents.^{2,3} In this context, ongoing efforts in these laboratories have helped establish the cross-coupling of organosilanol and -silanolate as a reliable and versatile synthetic method. The scope for the cross-coupling reaction encompasses a wide range of substrates. Indeed, aryl, heteroaryl, alkenyl, alkynyl, and allyl silanols/silanolates can be successfully coupled with several classes of aryl, heteroaryl, and alkenyl halides (Scheme 1).³

The cross-coupling of allylic silanolates is an interesting case because of the site-selectivity issue that arises.⁴ Allylsilanolates have the potential to react either at the α or γ position, and the selectivity can be controlled by the choice of ligand. For example, the γ -substituted

Correspondence to: Scott E. Denmark.

¹Current address: Gilead Sciences, Inc., Foster City, CA 94404, USA.

Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0036-1588471>.

product is formed with high selectivity when bulky trialkyl phosphines are used as the ligands (Scheme 2).⁵

By analogy to allylic nucleophiles, allenylsilanols (and allenylmetal species in general) also display site selectivity duality upon cross-coupling. Indeed, an allenylsilanolate **i** can react at the α -terminus, generating an allene **ii**, or at the γ -terminus, generating an alkyne **iii** (Scheme 3). Despite the potential for harnessing such dual behavior in synthetic methods, the cross-coupling of allenyl nucleophiles is an underdeveloped transformation. Only a handful of studies detail the use of allenylboron reagents in the context of the preeminent Suzuki–Miyaura reaction.⁶ In addition, other scattered reports have documented the palladium-catalyzed cross-coupling of allenyllithium,⁷ -copper,⁸ -magnesium,⁸ -zinc,^{8,9} and -tin¹⁰ reagents.

To the best of our knowledge, the cross-coupling of allenylsilanols and other allenylsilanes is unknown. Yet, the development of reaction conditions for the cross-coupling of this class of nucleophiles is a stimulating challenge, because of the intriguing stereochemical consequences that arise. The γ -selective cross-coupling of **i** will result in a product **iii** that necessarily contains a stereocenter if $R^1 \neq R^2$. In contrast to γ -substituted allenylsilanolates, in which the configuration of the newly formed stereocenter has to be formed by a chiral catalyst, allenylsilanolates such as **i** bear the advantage of being chiral reagents (again, if $R^1 \neq R^2$). Therefore, an enantioenriched allenylsilanolate **i** may, in principle, afford an enantioenriched cross-coupling product **iii** through an enantiospecific conversion of axial-to-central chirality elements.¹¹

The work presented in this article addresses the primary objective of developing the γ -selective cross-coupling of γ -disubstituted allenylsilanolates. Accordingly, the specific aims are: (1) to devise a convenient method for the synthesis of γ -disubstituted allenylsilanol/silanols (ideally, the synthetic route should be short, flexible, and amenable to the preparation of allenylsilanol as single enantiomers); (2) to optimize the γ -selective cross-coupling of allenylsilanolates, relying on the thorough mechanistic understanding of the transmetalation step for this class of nucleophiles.¹²

The synthesis of allenylsilanol **5** was accomplished through the sequence illustrated in Scheme 4. The synthetic route required the implementation of 2,4-dimethoxyphenyl (DMOP) as a novel silanol-masking group, easily cleaved under mild acidic conditions. Thus, silylation of 2-buten-1-ol with silyl chloride **1**, and further treatment with *t*-BuLi, triggered a reverse Brook rearrangement¹³ which afforded **2** in 72% yield. Mesylation of **2** and S_N2' displacement of the intermediate mesylate **3** with BnMgCl/CuCN provided allenylsilane **4** in 89% yield. The removal of the DMOP group was accomplished with one equivalent of dry HCl in Et₂O, followed by hydrolysis in aqueous media.¹⁴ The resulting allenylsilanol **5** was successfully deprotonated with NaH, KH, or *t*-BuLi to generate silanolates salts M^+5^- .

The study of the γ -selective cross-coupling of M^+5^- was undertaken through an extensive survey of ligands, palladium sources, and reaction conditions (Scheme 5). The reactions were run using 4-iodobenzotrifluoride (**6**, 0.05 mmol) as the cross-coupling partner, and

monitored by GC analysis.¹⁵ The amounts of residual silanol **5**, iodide **6**, α -product **7**, and γ -product **8** in the reaction mixtures were determined by integration of GC peaks relative to an internal standard (biphenyl).

Initially, $\text{Na}^+\text{5}^-$ and **6** were combined in the presence of $\text{Pd}(\text{dba})_2$ and a ligand in toluene at 40 °C (Table 1). In the absence of an added ligand, **7** was obtained in 20% conversion (Table 1, entry 1). The use of norbornadiene resulted in a 30% conversion into **7** and traces of the desired product **8** (Table 1, entry 2). Electron-rich aromatic phosphines did not have any beneficial impact (Table 1, entries 3–5), whereas the electron-deficient tri(pentafluorophenyl) phosphine appeared to improve conversion, giving 40% of **7** and 3% of **8** (Table 1, entry 6). The bulky, electron-rich aliphatic phosphonium salts **L1** and **L2** did not outperform any of the previous ligands in terms of conversion, but, significantly, **L1** afforded a more favorable α/γ ratio (83:17, Table 1, entries 7 and 8). With **L3**, however, the reaction did not proceed (Table 1, entry 9). The Buchwald-type phosphines SPhos and RuPhos provided **7** in low conversion (Table 1, entries 10 and 11) and caused significant protodesilylation. Ph_3As appeared to be the best ligand, as it afforded a mixture of α - and γ -products in an 81:19 ratio and overall 42% conversion (Table 1, entry 12). The reaction with Ph_3As was repeated on a 1.0 mmol scale, allowing for the isolation and full characterization of **7** (40%) and **8** (13%).

Having identified Ph_3As as a promising ligand, the effect of different palladium(0) and palladium(II) sources was evaluated next (Table 2). Palladium(0) complexes $\text{Pd}_2(\text{dba})_3$ and $\text{Pd}(4,4'\text{-CF}_3\text{-dba})_2$ maintained the levels of conversion observed for $\text{Pd}(\text{dba})_2$, but with a worse α/γ ratio (Table 2, entries 1 and 2). Allylpalladium chloride dimer (APC) caused a rapid consumption of the starting materials, with only 30% overall conversion into the products in a 83:17 α/γ ratio (Table 2, entry 3). $\text{PdCl}_2(\text{MeCN})_2$ and $\text{Pd}(\text{acac})_2$ provided a lower α/γ ratio (nearly 6:4) in 24% conversion (Table 2, entries 4 and 5). Finally, improved γ -selectivity was obtained with $\text{Pd}(\text{OAc})_2$ and $\text{Pd}(\text{OCOCF}_3)_2$, which afforded a nearly 1:1 mixture of products, albeit in low conversion (Table 2, 21%, entries 6 and 7).

From these results, it was concluded that the α -product **7** is generally preferred, regardless of the electronic and steric properties of the ligand. However, we were surprised to observe that, when the γ -product **8** is detected, the α/γ ratio decreases over the time, with the α -product being formed predominantly at the early stages of the reaction.

The fact that the α/γ ratio is not constant over the course of the reaction suggests a change in mechanism as the reaction progresses. Typically, this behavior originates from the accumulation of a byproduct which may provide an alternative mechanistic pathway. In the cross-coupling reaction under investigation, polysiloxanes and sodium iodide are obtained in stoichiometric amount from $\text{Na}^+\text{5}^-$ and **6**, whereas triphenylarsine oxide is generated substoichiometrically from the reduction of palladium(II) to palladium(0). In addition, the α -product **7** is accumulating in the reaction vessel. However, control experiments carried out by adding either NaI, $\text{Ph}_3\text{As=O}$, or **7** to the reaction mixture ruled out a substantial contribution of products/byproducts to the observed selectivity change.

Consequently, a different mechanistic hypothesis was formulated. We envisioned that an activated transmetalation pathway would account for the formation of the α -isomer, whereas a thermal transmetalation mechanism would lead to the γ -isomer (Scheme 6). Following oxidative addition (top right) and formation of the Si–O–Pd linkage in **iv** by iodide displacement, a thermal transmetalation event via an S_E' mechanism converts **iv** into propargylpalladium(II) complex **v**. The Si–O–Pd linkage is crucial in enabling this process, as intermediate **iv** is set for an intramolecular S_E' transmetalation via a favorable six-membered transition state.⁴ Reductive elimination from **v** generates the γ -product **8**. If another molecule of silanolate coordinates to the silicon center in **iv**, then activated transmetalation will take place from the hypercoordinate silanolate **vi**. A transmetalation event, proceeding via an S_E mechanism, will form allenylpalladium(II) intermediate **vii**. Reductive elimination will then lead to the α -product **7**.¹⁶

To test this hypothesis, other experimental variables had to be examined.

1. Silanolate concentration: A higher concentration of $\text{Na}^+\text{5}^-$ favors the formation of the pentacoordinate intermediate **vi** and therefore increases the preference for activated transmetalation, thus leading to a higher α selectivity. Indeed, the use of 3.9 equivalents of $\text{Na}^+\text{5}^-$ resulted in a 91:9 α/γ ratio, with 74% overall conversion after 18 h.
2. Effect of the cation: The nature of the cation M^+ determines the nucleophilicity of $\text{M}^+\text{5}^-$, which in turn affects the likelihood of an activated transmetalation.¹² Thus, $\text{Li}^+\text{5}^-$ is expected to be less nucleophilic than $\text{Na}^+\text{5}^-$, whereas $\text{K}^+\text{5}^-$ and $\text{Cs}^+\text{5}^-$ should be more nucleophilic, as the tightness of the ion pair decreases with the increasing ionic radius.¹⁷ As expected, the lithium silanolate $\text{Li}^+\text{5}^-$ afforded the γ -product **8** with high selectivity (Table 3, entry 1). However, the reaction was very slow even when the temperature was raised to 60 °C (Table 3, entry 2). This is not surprising, as the reduced nucleophilicity of $\text{Li}^+\text{5}^-$ also impacts the rate of formation of the Si–O–Pd linkage. Conversely, $\text{K}^+\text{5}^-$ provided high selectivity for the α -product and high conversion (88%, 93:7 α/γ ratio at 80 °C, Table 3, entry 4), in agreement with $\text{K}^+\text{5}^-$ being more nucleophilic than $\text{Na}^+\text{5}^-$. Finally, $\text{Cs}^+\text{5}^-$ was not preformed, but generated in situ by adding Cs_2CO_3 to the reaction mixture containing silanol **5**. The outcome was a 36% conversion to an 81:19 mixture favoring the α -product (Table 3, entry 5). This approach is not directly comparable to the previous cases, because, due to the insolubility of Cs_2CO_3 , the actual concentration of $\text{Cs}^+\text{5}^-$ in the reaction mixture is low.
3. Effect of the alkyl substituents on silicon: The possibility of achieving transmetalation through an activated pathway is also dependent upon the steric bulk around the silicon atom, as a more sterically encumbered environment disfavors the formation of a pentacoordinate intermediate **vi**.¹⁸ To establish the influence of increased steric bulk around silicon on the reactivity and selectivity, the diisopropyl sodium and potassium silanolates **9**[−] (and the silanol **9**, with Cs_2CO_3) were subjected to cross-coupling conditions (Table 4). Because the reaction of $\text{Na}^+\text{9}^-$ did not proceed at 40 °C (Table 4, entry 1), the temperature

was raised to 80 °C for the subsequent experiments. At that temperature, $\text{Na}^+\mathbf{9}^-$ afforded 7% of a 14:86 mixture favoring the γ -product (Table 4, entry 2). The more reactive $\text{K}^+\mathbf{9}^-$ gave higher conversion (39%), but with poorer selectivity (41:59). Lastly, the cesium silanolate generated in situ from $\mathbf{9}$ afforded 23% of the γ -isomer, in 12:88 α/γ ratio (Table 4, entry 4). As anticipated, the diisopropyl substrate $\mathbf{9}$ caused an overall improvement of the γ -selectivity, however, at the expense of reactivity.

The observation of γ -selectivity with the cesium silanolates requires additional explanation. Because the cesium silanolates $\text{Cs}^+\mathbf{5}^-$ and $\text{Cs}^+\mathbf{9}^-$ were not preformed stoichiometrically, but generated in situ by adding Cs_2CO_3 to the reaction mixture containing silanols $\mathbf{5}$ or $\mathbf{9}$, it is expected that the actual concentration of $\text{Cs}^+\mathbf{5}^-$ or $\text{Cs}^+\mathbf{9}^-$ be very low (thus favoring the formation of $\mathbf{8}$). As a consequence, the selectivity is determined by the subtle balance between the nucleophilicity and the actual concentration of the silanolate. For $\text{Cs}^+\mathbf{5}^-$, the selectivity is intermediate between that of $\text{Na}^+\mathbf{5}^-$ and $\text{K}^+\mathbf{5}^-$ (Table 3). With $\text{Cs}^+\mathbf{9}^-$, the bulkiness of the *i*-Pr groups greatly decreases the nucleophilicity of the silanolate, and the selectivity becomes comparable to that of $\text{Na}^+\mathbf{9}^-$ (Table 4).

In summary, through the evaluation of reaction conditions, a significant body of information was generated that helped gain insight into the mechanism of this transformation. The mechanistic hypothesis emerging from the experimental data was crucial in determining which factors should be adjusted to attain improved γ -selectivity. However, the reaction parameters that led to higher γ -selectivity also caused diminished reactivity. Even though the trends were successfully reversed in favor of the γ -isomer, the yields were always below the level required for synthetic utility (23% yield, 88:12 ratio for the γ -product, at best). On the other hand, the preference of γ -disubstituted allenylsilanolates to undergo cross-coupling at the α -terminus allowed for the quick identification of conditions for the α -selective coupling (up to 82% yield and 93:7 ratio for the α -product). Further investigation in our laboratories will address the substrate generality and stereospecificity of the α -selective cross-coupling of enantiomerically enriched allenylsilanolates.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Funding Information

We are grateful to the National Science Foundation (NSF CHE-1151566) for generous financial support. A.A. thanks the University of Illinois and Eli Lilly and Co. for graduate fellowships

References and Notes

- (a) Nakao Y, Hiyama T. Chem Soc Rev. 2011; 40:4893. [PubMed: 21755089] (b) Sore HF, Galloway WRJD, Spring DR. Chem Soc Rev. 2012; 41:1845. [PubMed: 22048071] (c) Chang, W-TT., Denmark, SE. Cross Coupling with Silicon Reagents: Arylsilanes. In: Molander, GA., editor. Science of Synthesis: Cross Coupling and Heck-Type Reactions. Thieme; Stuttgart: 2013. p. 383(d) Chang, W-TT., Denmark, SE. Cross Coupling with Silicon Reagents: Alkenylsilanes. In: Molander,

GA., editor. Science of Synthesis: Cross Coupling and Heck-Type Reactions. Thieme; Stuttgart: 2013. p. 431(e) Chang, W-TT., Denmark, SE. Cross Coupling with Silicon Reagents: Alkylsilanes. In: Molander, GA., editor. Science of Synthesis: Cross Coupling and Heck-Type Reactions. Thieme; Stuttgart: 2013. p. 443(f) Chang, W-TT., Denmark, SE. Cross Coupling with Silicon Reagents: Heteroarylsilanes. In: Molander, GA., editor. Science of Synthesis: Cross Coupling and Heck-Type Reactions. Thieme; Stuttgart: 2013. p. 495(g) Komiyama T, Minami Y, Hiyama T. ACS Catal. 2017; 7:631.

3. (a) Denmark SE, Regens CS. Acc Chem Res. 2008; 41:1486. [PubMed: 18681465] (b) Denmark SE, Liu JHC. Angew Chem Int Ed. 2010; 49:2978.(c) Chang WTT, Smith RC, Regens CS, Bailey AD, Werner NS, Denmark SE. Org React. 2011; 75:213.(d) Denmark SE, Ambrosi A. Org Process Res Dev. 2015; 19:982. [PubMed: 26478695]
4. Denmark SE, Werner NS. J Am Chem Soc. 2008; 130:16382. [PubMed: 18998687]
5. Denmark SE, Werner NS. Org Lett. 2011; 13:4596. [PubMed: 21830766]
6. (a) Locos OB, Dahms K, Senge MO. Tetrahedron Lett. 2009; 50:2566.(b) Radkowski K, Seidel G, Fürstner A. Chem Lett. 2011; 40:950.(c) Plunkett S, Dahms K, Senge MO. Eur J Org Chem. 2013:1566.(d) Yang Y, Szabó KJ. J Org Chem. 2016; 81:250. [PubMed: 26631028]
7. (a) Jeffery-Luong T, Linstrumelle G. Synthesis. 1982:738.(b) Hornillos V, Giannerini M, Vila C, Fananas-Mastral M, Feringa BL. Chem Sci. 2015; 6:1394. [PubMed: 29560227]
8. (a) Kleijn RH, Meijer J, Oostveen EA, Vermeer P. J Organomet Chem. 1982; 224:399.(b) de Graaf W, Boersma J, van Koten G, Elsevier CJ. J Organomet Chem. 1989; 378:115.
9. (a) Ruitenberk K, Kleijn H, Elsevier CJ, Meijer J, Vermeer P. Tetrahedron Lett. 1981; 22:1451.(b) Wang KK, Wang Z. Tetrahedron Lett. 1994; 35:1829.
10. (a) Badone D, Cardamone R, Guzzi U. Tetrahedron Lett. 1994; 35:5477.(b) Singh Aidhen I, Braslau R. Synth Commun. 1994; 24:789.(c) Kinderman, SS., Hiemstra, H. 3-Trimethylsilyl-1-propyne, Encyclopedia of Reagents for Organic Synthesis. John Wiley and Sons; New York: 2001. (d) Huang CW, Shanmugasundaram M, Chang HM, Cheng CH. Tetrahedron. 2003; 59:3635.(e) Kjellgren J, Sundén H, Szabó KJ. J Am Chem Soc. 2005; 127:1787. [PubMed: 15701014] (f) Mukai C, Takahashi Y. Org Lett. 2005; 7:5793. [PubMed: 16354068] (g) Williams DR, Shah AA. Chem Commun. 2010; 46:4297.(h) Mohamed YAM, Inagaki F, Takahashi R, Mukai C. Tetrahedron. 2011; 67:5133.
11. Marshall, JA., Gung, BW., Grachan, ML. Synthesis and Reactions of Allenylmetal Compounds, In Modern Allene Chemistry. Wiley-VCH; Weinheim: 2008. p. 493
12. (a) Tymonko SA, Smith RC, Ambrosi A, Denmark SE. J Am Chem Soc. 2015; 137:6192. [PubMed: 25945390] (b) Tymonko SA, Smith RC, Ambrosi A, Ober MH, Wang H, Denmark SE. J Am Chem Soc. 2015; 137:6200. [PubMed: 25945516]
13. Okada T, Oda N, Suzuki H, Sakaguchi K, Ohfuné Y. Tetrahedron Lett. 2010; 51:3765.
14. Analytical Data for Compound 5 ¹H NMR (500 MHz, C₆D₆): δ = 7.19–7.16 (m, 4 H), 7.09–7.04 (m, 1 H), 4.93 (h, *J* = 3.6 Hz, 1 H), 3.19 (dd, *J* = 14.6, 3.3 Hz, 1 H), 3.14 (dd, *J* = 14.6, 3.2 Hz, 1 H), 1.59 (d, *J* = 3.7 Hz, 3 H), 1.13 (s, 1 H), 1.01 (t, *J* = 7.9 Hz, 3 H), 1.00 (t, *J* = 7.9 Hz, 3 H), 0.67–0.59 (m, 4 H). ¹³C NMR (126 MHz, C₆D₆): δ = 210.9, 140.1, 129.3, 128.6, 126.6, 92.4, 80.0, 40.6, 17.7, 7.3, 7.2, 6.9, 6.9. HRMS (EI⁺): *m/z* calcd for C₁₅H₂₂OSi: 246.1440; found: 246.1436.
15. General Procedure for Cross-Coupling Experiments In a glove box, the Pd source and the ligand were added to an oven-dried 4 mL reaction vial containing a stir bar. A stock solution of 6 (0.05 mmol) and biphenyl in toluene (0.17 M) was added and the mixture stirred to homogenize. The vial was sealed with a septum screw cap, transferred outside the glove box and warmed to the indicated temperature. A solution of the silanolate in toluene (0.3–0.4 M) was then added via syringe. 50 µL aliquots were taken at the indicated time points, diluted with EtOAc (1 mL), quenched with acetate buffer (pH = 5), filtered through a silica plug, and analyzed by GC.
16. (a) This mechanistic hypothesis does not exclude the possibility of equilibration of v and vii. Under this circumstance, the α-product would be preferred. The presence of two substituents at the γ-terminus would decrease the rate of reductive elimination from v, and facilitate reductive elimination from vii. Moreover, it is known that reductive elimination to an sp² carbon is more facile than to an sp³ carbon, see ref. 16b. However, in the presence of a weakly coordinating ligand (such as triphenylarsine), reductive elimination is expected to be faster than the isomerization

between the short-lived intermediates v and vii, such that the transmetalation step is selectivity determining Low JJ, Goddard WA. J Am Chem Soc. 1986; 108:6115.

17. (a) Kurts AL, Macias A, Beletskaya I, Reutov OA. Tetrahedron. 1971; 27:4759.(b) Jones P, Harrison R, Wynne-Jones L. J Chem Soc, Perkin Trans 2. 1979:1679.
18. Denmark SE, Neuville L, Christy MEL, Tymonko SA. J Org Chem. 2006; 71:8500. [PubMed: 17064026]

Scheme 1.
Organosilanolate cross-coupling reaction

Scheme 2.
 γ -Selective cross-coupling of allylsilanolates

Scheme 3.

Site-selective cross-coupling of allenylsilanolates and stereochemical implications

Scheme 4.
Synthesis and deprotonation of allenylsilanol **5**

Scheme 5.
General cross-coupling reaction

Scheme 6.

Proposed catalytic cycle featuring a selectivity-determining transmetalation step

Table 1

Survey of Ligands

Entry	Ligand	Time (h)	Yield of 7 (%)	Yield of 8 (%)	α/γ
1	–	18	20	–	100:0
2	norbornadiene	18	30	1	97:3
3	Ph ₃ P	3	–	–	–
4	(4-MeO-C ₆ H ₄) ₃ P	3	–	–	–
5	(2-furyl) ₃ P	18	14	1	93:7
		1	28	–	100:0
6	(C ₆ F ₅) ₃ P	3	34	–	100:0
		18	40	3	93:7
		1	2	–	100:0
		3	7	1	88:12
7	 L1	18	10	v	83:17
		1	10	–	100:0
8	 L2	3	25	1	96:4
		18	36	3	95:5

Entry	Ligand	Time (h)	Yield of 7 (%)	Yield of 8 (%)	α/γ
9		3	—	—	—
10	L3	18	13	—	100:0
11		18	7	—	100:0
12		1	32	—	100:0
		3	34	2	94:6
		18	34	8	81:19

Table 2

Survey of Palladium Sources

Entry	Pd source	Time (h)	Yield of 7 (%)	Yield of 8 (%)	α/γ
1	$\text{Pd}_2(\text{dba})_3$	1	36	–	100:0
		18	37	5	88:12
2	$\text{Pd}(4,4'\text{-CF}_3\text{-dba})_2$	1	33	–	100:0
		18	34	4	89:11
3	APC	1	22	–	100:0
		18	25	5	83:17
4	$\text{PdCl}_2(\text{CH}_3\text{CN})_2$	1	12	1	92:8
		18	14	10	58:42
5	$\text{Pd}(\text{acac})_2$	1	15	–	100:0
		18	15	9	63:37
6	$\text{Pd}(\text{OAc})_2$	1	10	2	83:17
		18	10	10	50:50
7	$\text{Pd}(\text{OCOCF}_3)_2$	1	8	1	89:11
		18	10	11	48:52

Table 3

Effect of the Cation

Entry	Conditions	Time (h)	Yield of 7 (%)	Yield of 8 (%)	α/γ
1	Li ⁺ 5 ⁻ , 40 °C	18	1	5	17:83
2	Li ⁺ 5 ⁻ , 60 °C	1	–	5	0:100
		18	1	13	7:93
3	K ⁺ 5 ⁻ , 40 °C	1	35	–	100:0
		18	45	1	98:2
4	K ⁺ 5 ⁻ , 80 °C	1	57	1	98:2
		18	82	6	93:7
5	5, C ₅ H ₅ CO ₃ , 80 °C	18	29	7	81:19

Table 4

Effect of the Alkyl Substituents on Silicon

Entry	Pd source	Time (h)	Yield of 7 (%)	Yield of 8 (%)	α/γ
1	Na ⁺ 9 ⁻ , 40 °C	18	–	–	–
2	Na ⁺ 9 ⁻ , 80 °C	1	2	1	67:33
		1	131	23	14:86
3	K ⁺ 9 ⁻ , 80 °C	1	13	1	93:7
		18	16	23	41:59
4	9, Cs ₂ CO ₃ , 80 °C	18	1	1	50:50
		1	3	23	12:88