

Highly Regioselective Palladium-Catalyzed Internal Arylation of Allyltrimethylsilane with Aryl Triflates

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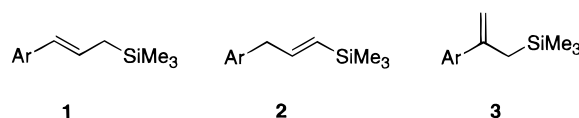
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Highly regioselective ligand-controlled Heck-arylation reactions of allyltrimethylsilane, delivering branched β -products, were performed in moderate to good yields. The high preference for internal over terminal double-bond arylation suggests a contribution from the β -cation-stabilizing effect of silicon. Microwave-promoted palladium-catalyzed coupling reactions proceeded with the same regioselectivity in six entries out of eight with the reaction times cut sharply down to 5–10 min.

Introduction

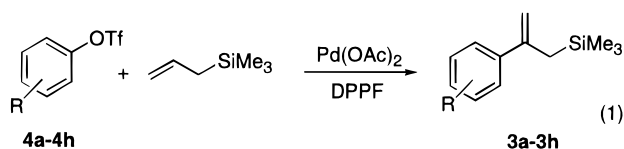
Allylsilanes are important intermediates in organic synthesis, and their utility is mainly attributed to the high regioselectivity obtained in reactions with electrophiles.^{1,2} Efficient synthetic methods for their preparation and functionalization are therefore desirable, and we previously extended the Heck reaction³ to include allylsilanes.⁴ Arylation of allyltrimethylsilane with iodobenzene under traditional Heck reaction conditions afforded **1** (Chart 1). We introduced silver additives as potential halide abstractors since we at that time hoped that the hyperconjugative stabilization of a cationic center β to the silicon might promote formation of **3**. The silver additive suppressed desilylation and enhanced the reaction rate considerably but was not preparatively useful since adding silver salts promoted internal arylation only to a minor extent. Instead, the double-bond isomer **2** was isolated as the major product.⁴ We have now devised a convenient and highly regioselective method for the preparation of a series of internally arylated allylsilanes **3**,⁵ which we suggest relies on the β -cation-stabilizing properties of silicon⁶ in combination with the bidentate ligand DPPF.⁷

Chart 1



Results

Eight aryltriflates **4a–h** were allowed to react with allyltrimethylsilane in fresh acetonitrile under Heck coupling conditions with palladium acetate and DPPF⁷ as the catalytic system and triethylamine or potassium carbonate as base. An internal arylation of allyltrimethylsilane was achieved predominantly, generating internally arylated compounds **3a–h** (eq 1). The corresponding terminally arylated compounds **1** were detected in small amounts in most, but not all, of the reactions. The preparative results are summarized in Table 1.



(1) (a) Chan, T. H.; Flemming, I. *Synthesis* **1979**, 761. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York 1983; p 173. (c) Hatanaka, Y.; Hiyama, T. *Synlett* **1991**, 845. Allylsilanes similar to 2-aryl-3-(trimethylsilyl)-1-propenes have been used for the synthesis of carbacephalams and HIV-1 protease inhibitors; see: (d) Oumoch, S.; Rousseau, G. *Bioorg. Med. Chem. Lett.* **1994**, *4*, 2841. (e) D'Aniello, F.; Taddei, M. *J. Org. Chem.* **1992**, *57*, 5247. Other recent applications of allylsilanes include: (f) Tietze, L. F.; Schimpf, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1089. (g) Singleton, D. A.; Waller, S. C.; Zhang, Z.; Frantz, D. E.; Leung, S. W. *J. Am. Chem. Soc.* **1996**, *118*, 9986. (h) Akiyama, T. *Synlett* **1996**, 1095. (i) Mayr, H.; Ofial, A. R. *J. Org. Chem.* **1996**, *61*, 5823. (j) Le Roux, C.; Dubac, J. *Organometallics* **1996**, *15*, 4646. (k) Yoshikawa, E.; Gevorgyan, V.; Asao, N.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6781.

(2) For regio- and stereochemical aspects of the palladium-catalyzed reactions of silanes, see: Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317.

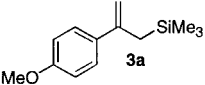
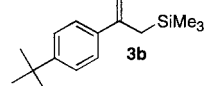
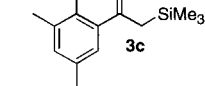
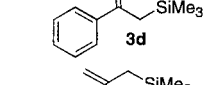
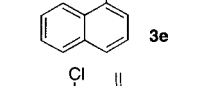
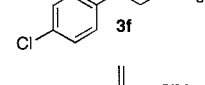
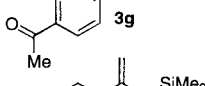
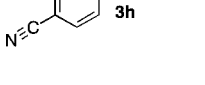
(3) (a) Heck, R. F. *Org. React.* **1982**, *27*, 345. (b) Heck, R. F. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 4, p 833. (c) de Meijere, A.; Meyer, F. E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379. (d) Cabri, W.; Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2. (e) Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley & Sons: Chichester 1995; p 125. (f) Jeffery, T. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press, Inc: Greenwich, 1996; Vol. 5, p 153.

(4) Karabelas, K.; Westerlund, C.; Hallberg, A. *J. Org. Chem.* **1985**, *50*, 3896.

The reaction proceeded with moderate to good yields with one exception (Table 1, entry 7). The use of the flexible bidentate ligand DPPF resulted in better selectivities than with DPPP.⁷ In the entries where moderate yields were isolated, the loss was mainly associated with desilylation and reduction. Desilylation,^{8,9} producing the

(5) For the preparation of **3d** by arylation of 1,3-bis(trimethylsilyl)-1-propene, see ref 4. For a selection of other methods for the preparation of **3**, see the following. Via organocerium: (a) Narayan, B. A.; Bunnelle, W. H. *Tetrahedron Lett.* **1987**, *28*, 6261. Via dithioacetals: (b) Ni, Z. J.; Luh, T. Y. *J. Chem. Soc., Chem. Commun.* **1988**, 15, 1011. (c) Wong, K. T.; Ni, Z. J.; Luh, T. Y. *J. Chem. Soc., Perkin Trans. 1* **1991**, 3113. Via organomagnesium and -derivates: (d) Hayashi, T.; Katsuro, Y.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 3915. (e) Fleming, I.; Pearce, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, *81*, 251. (f) Hayashi, T.; Fujiwa, T.; Okamoto, Y.; Katsuro, Y.; Kumada, M. *Synthesis* **1981**, *12*, 1001. (g) Barluenga, J.; Fernández-Simón, J. L.; Concellon, J. M.; Yus, M. *Tetrahedron Lett.* **1989**, *30*, 5927. (h) Kang, K. T.; Kim, S. S.; Lee, J. C. *Tetrahedron Lett.* **1991**, *32*, 4341. Via vinylboranes: (i) Rivera, I.; Soderquist, J. A. *Tetrahedron Lett.* **1991**, *32*, 2311. For another palladium catalyzed method of introducing residues internally, see: (j) Hojo, M.; Murakami, C.; Aihara, H.; Komori, E. i.; Kohra, S.; Tominaga, Y.; Hosomi, A. *Bull. Soc. Chim. Fr.* **1995**, *132*, 499.

Table 1. Internal Arylation of Allyltrimethylsilane*

Entry	Triflate	β -Product	Selectivity ^a 3/1	Isolated Yield 3+1
1	4a		97/3	42%
2	4b		94/6	47%
3	4c		100/0 ^b	60%
4	4d		95/5	67%
5	4e		98/2	77%
6	4f		98/2	85%
7	4g		94/6	31%
8	4h		100/0 ^b	59%

* Reactions were run on a 2.5 mmol scale in sealed Pyrex tubes under nitrogen atmosphere with 1 equiv of **4a–h**, 5 equiv of allyltrimethylsilane, 0.03 equiv of Pd(OAc)₂, 0.066 equiv of DPPF, and 2 equiv of base (Et₃N in entries 1–5, K₂CO₃ in entries 6–8) in 10 mL of fresh acetonitrile. Entries 1, 2, and 4–6 were conducted at 60 °C and entries 3, 7, and 8 at 80 °C. All reactions were completed in 20 h. ^a Determined by GC/MS. ^b Only product **3** was detected by GC/MS.

corresponding α -methylstyrenes, appeared in particular at higher reaction temperatures and the reduction of the aryl triflates, forming the analogous arenes, appeared mainly with the electron-deficient reactants¹⁰ **4f–h** (Table

(6) (a) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496. (b) Mayr, H.; Pock, R. *Tetrahedron* **1986**, *42*, 4211. (c) Lambert, J. B.; Wang, G. t.; Teramura, D. H. *J. Org. Chem.* **1988**, *53*, 5422. (d) Ibrahim, M. R.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 819. (e) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677. (f) Gabelica, V.; Kresge, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 3838 and references therein. (g) Chiavarino, B.; Crestoni, M. E.; Fornarini, S. *J. Am. Chem. Soc.* **1998**, *120*, 1523. Some recent examples where the β -effect has been utilized in organic synthesis: (h) Thorimbert, S.; Malacria, M. *Tetrahedron Lett.* **1996**, *37*, 8483. (i) Alvisi, D.; Blart, E.; Bonini, B. F.; Mazzanti, G.; Ricci, A.; Zani, P. *J. Org. Chem.* **1996**, *61*, 7139. (j) Miura, K.; Hondo, T.; Saito, H.; Ito, H.; Hosomi, A. *J. Org. Chem.* **1997**, *62*, 8292.

(7) DPPF = 1, 1'-bis(diphenylphosphino)ferrocene, DPPP = 1,3-bis(diphenylphosphino)propane. For a discussion of the properties of DPPF, see: Gan, K. S.; Hor, T. S. A. In *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, 1995; p 3.

(8) Initial screening experiments revealed that acetonitrile leads to a smaller extent of desilylation and better regioselectivities than other solvents (DMF, NMP, dioxane, and DMSO) for this particular reaction. For a recent discussion of the palladium-mediated mechanism of desilylation, see: LaPointe, A. M.; Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 906. See also ref 6h.

(9) As regards the desilylation process, a higher degree of desilylation takes place as the temperature rises but the desilylation is brought about in the product-forming stage of the reaction and does not change markedly thereafter, suggesting that the desilylation is palladium-mediated. See also refs 4 and 6h.

1, entries 6–8). The substitution of triethylamine in favor of an inorganic base¹¹ resulted in a suppression of reduction and a higher yield. The moderate yields encountered in reactions with 4-methoxy and 4-*tert*-butyl phenyl triflates (Table 1, entries 1 and 2) are partly due to the exchange of metal and phosphine bound aryl groups in the oxidative-addition complex,¹² as suggested by the formation of **3d** as a side product.

We observed that the reactions performed at 80 °C tended to result in improved regioselectivities as compared to the corresponding reactions at 60 °C, a phenomenon that prompted us to conduct the same coupling reaction with microwave flash heating.^{13,14} The microwave-promoted coupling reactions were completed in minutes instead of hours and proceeded smoothly, but an inferior regioselectivity was encountered with **4a** and **4b** as substrates, as compared with the standard thermal coupling reaction (Table 2). Notably, the reaction with the acetyl compound **4g** that delivered a relatively low regioselectivity with standard heating gave **3g** exclusively under microwave irradiation (Table 2, entry 7).

Discussion

Cabri et al. introduced the use of bidentate ligands for electronically controlled internal arylations of some selected electron-rich, acyclic olefins.¹⁵ This powerful means of regiocontrol was rationalized by assuming an involvement of a cationic organopalladium π -complex governing the regiochemical outcome.¹⁵ We believe that the high regioselectivity encountered with allyltrimethylsilane as substrate is influenced by a hyperconjugative stabilization of an electron-deficient center that develops β to the silicon atom during the course of the reaction¹⁶ (Scheme 1).

(10) (a) Cabri, W.; DeBernardinis, S.; Francalanci, F.; Penco, S.; Santi, R. *J. Org. Chem.* **1990**, *55*, 350. (b) Jutand, A.; Mosleh, A. *J. Org. Chem.* **1997**, *62*, 261.

(11) Cabri, W.; Candiani, I.; DeBernardinis, S.; Francalanci, F.; Penco, S.; Santi, R. *J. Org. Chem.* **1991**, *56*, 5796.

(12) (a) Andersson, C.-M.; Hallberg, A. *J. Org. Chem.* **1987**, *52*, 3529. (b) Kelkar, A. A.; Hanaoka, T.; Kubota, Y.; Sugi, Y. *J. Mol. Catal.* **1994**, *88*, L113. (c) Herrmann, W. A.; Brossmer, C.; Öfele, K.; Beller, M.; Fischer, H. *J. Organomet. Chem.* **1995**, *491*, C1–C4. (d) Morita, D. K.; Stille, J. K.; Norton, J. K. *J. Am. Chem. Soc.* **1995**, *117*, 8576 and references therein. (e) Herrman, W. A.; Brossmer, C.; Reisinger, C. P.; Riermeier, T. H.; Öfele, K.; Beller, M. *Chem. Eur. J.* **1997**, *1357*. (f) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441. For an alternative mechanism see: (g) Sakamoto, M.; Shimizu, I.; Yamamoto, A. *Chem. Lett.* **1995**, 1101.

(13) The microwave technique lends its efficiency mainly from the fact that a polar, homogeneous reaction mixture will be heated faster under microwave irradiation than under thermal heating. Apart from this, the boiling point elevation due to pressure in a closed Pyrex tube allows higher temperatures than are ordinarily feasible. (a) Hájek, M. *Collect. Czech. Chem. Commun.* **1997**, *62*, 347. Acetonitrile is known to be of sufficient polarity for efficient heating in microwave fields; see: (b) Stone-Elander, S.; Elander, N. *Appl. Radiat. Isot.* **1991**, *42*, 885. For a theoretical discussion of microwave irradiation, see: (c) Neas, E. D.; Collins, M. J. *Introduction to Microwave Sample Preparation*; Kingston, H. M., Jassie, L. B., Eds.; American Chemical Society: Washington, DC, 1988; p 7. For general references on microwave-assisted organic synthesis, see: (d) Mings, D. M. P.; Baghurst D. R. *Chem. Soc. Rev.* **1991**, *20*, 1. (e) Caddick, S. *Tetrahedron* **1995**, *51*, 10403. (f) Strauss, C. R.; Trainor, R. W. *Aust. J. Chem.* **1995**, *48*, 1665. (g) Galema, S. A. *Chem. Soc. Rev.* **1997**, *26*, 233. (h) Langa, F.; de la Cruz, P.; de la Hoc, A.; Diaz Ortiz, A.; Diez Barra, E. *Contemp. Org. Synth.* **1997**, 373.

(14) We have previously reported on the application of microwave irradiation in palladium-catalyzed synthesis. (a) Larhed, M.; Lindeberg, G.; Hallberg, A. *Tetrahedron Lett.* **1996**, *37*, 8219. (b) Larhed, M.; Hallberg, A. *J. Org. Chem.* **1996**, *61*, 9582. (c) Larhed, M.; Hoshino, M.; Hadida, S.; Curran, D. P.; Hallberg, A. *J. Org. Chem.* **1997**, *62*, 5583.

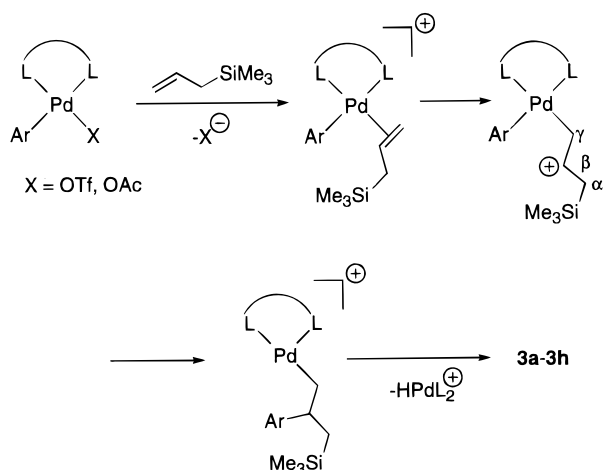
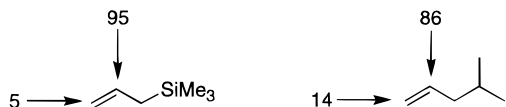
(15) Cabri, W.; Candiani, I.; Bedeschi, A.; Santi, R. *J. Org. Chem.* **1992**, *57*, 3558.

Table 2. Microwave-Promoted Internal Arylation^a

entry	triflate	product	reaction time (min)/ microwave power (W) ^b	selectivity ^c	yield (%) ^d
				3/1	3 + 1
1	4a	3a	5/50	78/22 ^e	34
2	4b	3b	5/50	88/12 ^f	69
3	4c	3c	5/50	93/7 ^e	66
4	4d	3d	5/50	92/8	62
5	4e	3e	5/50	97/3	66
6	4f	3f	7/50	97/3	54
7	4g	3g	7/60	100/0 ^g	48
8	4h	3h	10/50	100/0 ^g	28

^a Reactions were run on a 1.0 mmol scale in sealed Pyrex tubes with septa under nitrogen atmosphere and heated by means of microwave irradiation. Reactions were performed in 1.5 mL of fresh acetonitrile with 1 equiv of **4a–h**, 2.5 equiv of allyltrimethylsilane, 0.03 equiv of Pd(OAc)₂, 0.066 equiv of DPPF, and 2 equiv of Et₃N in entries 1–5 and 1.5 equiv of K₂CO₃ in entries 6–8.

^b Continuous irradiation (2450 MHz). ^c Determined by GC/MS. ^d GC/MS yield. ^e Three isomeric products detected by GC/MS. ^f Four isomeric products detected by GC/MS. ^g Only product **3** was detected by GC/MS.

Scheme 1**Scheme 2. Regioselectivity in the DPPF-Controlled Heck Reaction with Phenyl Triflate (**4d**)**

To assess the role of the β -effect, we conducted experiments where phenyl triflate (**4d**) was used as an arylating agent with 4-methyl-1-pentene, a compound chosen for its steric similarity to allyltrimethylsilane. An internal/terminal regioselectivity of 86/14 was observed,¹⁷ which is inferior as compared to the selectivity obtained with allyltrimethylsilane (Scheme 2).

Furthermore, a competitive experiment was conducted with allyltrimethylsilane (1 equiv), 4-methyl-1-pentene (1 equiv), and phenyl triflate (**4d**) (1 equiv). By ¹H NMR, we could detect 5.5 times more of arylated allyltrimethylsilane than arylated 4-methyl-1-pentene, despite the

(16) A similar β -stabilized cation complex has been suggested by Hosomi et al.; see ref 5j.

(17) According to GC/MS analyses, four compounds were formed. Hydrogenation, delivering two compounds, allowed determination of the regioselectivity ratio. See Phenylation of 4-Methyl-1-pentene in the Experimental Section.

1/1/1 ratio of reactants, revealing that allyltrimethylsilane was more reactive than 4-methyl-1-pentene.

The higher reactivity of allyltrimethylsilane compared to 4-methyl-1-pentene might be consistent with a reduced energy barrier mediated by the β -effect of silicon in a rate-determining insertion step.¹⁸ The preference for internal products to form even with the sterically hindered triflates **4c** and **4e** is compatible with the hypothesis that in the reactions proceeding via a cationic π -complex electronic factors predominate over steric.¹⁵

Tin is expected to exhibit a substantially more pronounced β -stabilizing effect than silicon.^{6c} Therefore, an even higher selectivity was expected with phenyl triflate (**4d**) and allyltrimethylstannane. A series of experiments with these reactants was performed, but we were unfortunately unable to trace any arylated allyltrimethylstannane from the reaction mixture. However, the predominant formation of α -methyl styrene in favor of the unbranched allyl compound suggests that internal arylation is predominant.¹⁹

Conclusion

The palladium-catalyzed, DPPF-controlled, internal arylation of allyltrimethylsilane constitutes an effective method for the preparation of 2-aryl-3-(trimethylsilyl)-1-propenes **3**. The method compares advantageously with other methods reported previously.⁵ We suggest that the superior regiocontrol as well as the faster rate of insertion of allyltrimethylsilane compared to 4-methyl-1-pentene is attributed to the β -effect of silicon. With microwave irradiation, the reaction times were reduced from up to 20 h to 5–10 min without seriously affecting the regiochemical control. Furthermore, we have now demonstrated that selective synthesis of three isomers (**1–3**) can be accomplished simply by modifying the original Heck reaction procedure.

Experimental Section

Procedures. ¹H and ¹³C NMR spectra were recorded in CDCl₃ at 270 and 67.8 MHz, respectively. Chemical shifts were reported as δ values (ppm) indirectly referenced to TMS by the solvent signal (CHCl₃) δ 7.26 and (CDCl₃) δ 77.0. Low-resolution mass spectra were recorded on a GC/MS instrument equipped with a HP-1 capillary column (25 m \times 0.22 mm) operating at an ionization potential of 70 eV. The oven temperature was 70–305 °C (gradient 20 °C/min). Isomers **1** and **3** were assumed to have identical GC/MS response factors. Elemental analyses were performed by Mikro Kemi AB, Uppsala, Sweden.

Microwave heating was carried out with a MicroWell 10 single-mode microwave cavity²⁰ from Labwell AB, Sweden, producing continuous irradiation at 2450 MHz. The microwave-assisted reactions were performed under nitrogen in oven-dried, heavy-walled Pyrex tubes²¹ (8 mL, l = 150 mm) sealed with a silicon septum. If overpressurization occurs this septum will burst.

(18) Cabri, W.; Candiani, I.; Bedeschi, A.; Penco, S.; Santi, R. *J. Org. Chem.* **1992**, *57*, 1481.

(19) The fact that minute amounts of the unbranched 3-aryl-1-propene, possibly derived from a concomitant Stille reaction, was observed by NMR made an accurate determination of the regiocontrol difficult. The heavier elements in the group (Sn and Pb) have been reported to be more easily displaced than the lighter elements (Si and Ge). For a discussion of this phenomenon, see ref 6c. Internally arylated allylstannane compounds are unstable; see: Desponds, O.; Schlosser, M. *J. Organomet. Chem.* **1991**, *93*.

(20) Stone-Elander, S. A.; Elander, N.; Thorell, J. O.; Solás, C.; Svennebrink, J. *J. Label. Compd. Radiopharm.* **1994**, *34*, 949.

(21) Pyrex tubes are recommended for microwave-assisted organic synthesis. Baghurst, D. R.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1992**, 1151.

Materials. Silica gel 60 (0.040–0.063 mm, E. Merck no 9385) and alumina gel 90 (0.063–0.200 mm, E. Merck no 101097, deactivated with 60 mL of water to 1000 g of aluminum gel) were used for chromatography. DPPF was purchased from Fluka and Pd(OAc)₂ from E. Merck. Allyltrimethylsilane and 4-methyl-1-pentene were obtained from Fluka and Aldrich, respectively. Acetonitrile (p.a.) was of commercial quality and taken from recently opened bottles.²² All other reagents were purchased from commercial suppliers and used without further purification. The aryl triflates were prepared from the corresponding phenols by a standard procedure using 2,4,6-collidine as base.²³ Products **1d**,²⁴ **3a**,^{5c} **3d**,^{5c} **3e**,^{5c} and **5**²⁵ were previously characterized.

General Procedure for Thermal Arylation Reactions of Allyltrimethylsilane (Table 1, Eq 1). A mixture of 2.50 mmol of aryl triflate **4a–h**, 0.0750 mmol (0.0168 g) of Pd(OAc)₂, 0.330 mmol (0.183 g) of DPPF, 12.5 mmol (1.43 g) of allyltrimethylsilane, 5.0 mmol (0.51 g) of triethylamine with triflates **4a–e**, and 3.75 mmol (0.518 g) of potassium carbonate with triflates **4f–h** and 10 mL of acetonitrile²² was heated under nitrogen in oven-dried, heavy-walled, and thin-necked Pyrex tubes, sealed with a Teflon stopcock on oil bath, **4a,b,d–f** at 60 °C and **4c,g,h** at 80 °C. Samples were periodically taken and partitioned between diethyl ether and water. The ethereal layers were dried over potassium carbonate before analysis by GC/MS. All reactions were completed after 20 h (>99% conversion of the aryl triflate). The reaction mixture was allowed to cool, diluted with water and extracted with diethyl ether. The combined organic layers were thereafter washed with brine and concentrated under reduced pressure. Products were subjected to purification by rapid silica column chromatography followed by bulb-to-bulb distillation under reduced pressure to give clear, sometimes slightly yellowish oils with a >95% purity of internally and terminally arylated products based on GC/MS analyses. The relatively low isolated yields connected with **3a,b,h** are partly due to the difficulty in getting pure fractions in the bulb-to-bulb distillation. The γ -products **1** were never produced in such yields that would make an isolation feasible. The true identity of **1d** was confirmed by comparison of spectroscopic data²⁴ and a GC/MS co-injection of a sample prepared by the Karabelas–Hallberg methodology.⁴

Phenylation of 4-Methyl-1-pentene (Scheme 2). The coupling of **4d** with 4-methyl-1-pentene was performed with 2.50 mmol (0.565 g) of **4d**, 12.5 mmol (1.05 g) of 4-methyl-1-pentene, 0.0750 mmol (0.0168 g) of Pd(OAc)₂, 0.330 mmol (0.183 g) of DPPF, and 5.0 mmol (0.51 g) of triethylamine dissolved in 10 mL of acetonitrile for 48 h at 60 °C. The workup was performed as described in the general procedure and purified on silica with isohexane as eluent. The isolated yield of phenylated products was 56%. A GC/MS analysis of the mixture of phenylated products revealed four compounds, which were reduced to two after hydrogenation over palladium in ethanol at atmospheric pressure.²⁶ The reported regioselectivity refers to the two isomers obtained after hydrogenation. The identity of the major unsaturated product proved to be 2-phenyl-4-methyl-1-pentene (**5**) by comparison with

spectral data,²⁵ and the minor unsaturated products were taken as cis and trans isomers of the 1-phenyl-4-methyl-1-pentene and 1-phenyl-4-methyl-2-pentene isomers.

Competitive Phenylation of Allyltrimethylsilane and 4-Methyl-1-pentene. The competitive experiment was performed with 1.00 mmol (0.226 g) of **4d**, 1.00 mmol (0.114 g) of allyltrimethylsilane, 1.00 mmol (0.0840 g) of 4-methyl-1-pentene, 0.030 mmol (0.00670 g) of Pd(OAc)₂, 0.132 mmol (0.0732 g) of DPPF, and 2.0 mmol (0.20 g) of Et₃N in 4 mL of acetonitrile. The reaction was performed at 60 °C. Workup was performed as described in the general procedure. The ratio of arylated allyltrimethylsilane in reference to arylated 4-methyl-1-pentene (5.5/1) was determined by ¹H NMR.

Deviations from the aforementioned reaction conditions will be given, when such deviations occur, in each description.

2-(2,4-Dichlorophenyl)-3-(trimethylsilyl)-1-propene (3f). Compound **3f** + **1f** (ratio 98/2) was obtained in 85% yield at 60 °C. The eluent was isohexane, and the products were further purified by bulb-to-bulb distillation (~110 °C at 10 mmHg): ¹H NMR (270 MHz, CDCl₃) δ 7.36 (d, J = 2.0 Hz, 1 H), 7.17 (d, J = 2.0 Hz, 1H), 7.15 (s, 1 H), 5.07 (m, 1 H), 4.88 (d, J = 1.7 Hz, 1 H), 2.01 (d, J = 1.0 Hz, 2 H), -0.09 (s, 9 H); ¹³C NMR (67.8 MHz, CDCl₃) δ 145.1, 141.7, 133.0, 132.6, 131.0, 129.2, 126.7, 114.5, 27.8, -1.9; MS m/z (relative intensity 70 eV) 258 (M⁺, 9), 243 (7), 73 (100). Anal. Calcd for C₁₂H₁₆Cl₂Si: C, 55.6; H, 6.2. Found: C, 55.7; H, 6.3.

General Procedure for Microwave-Promoted Arylation Reactions (Table 2). A mixture of 1.00 mmol of aryl triflate **4a–h**, 0.030 mmol (0.00670 g) of Pd(OAc)₂, 0.132 mmol (0.0732 g) of DPPF, 2.50 mmol (0.286 g) of allyltrimethylsilane, 0.150 g of internal standard (2,3-dimethylnaphthalene), 2.0 mmol (0.20 g) of triethylamine in entries 1–5 and 1.5 mmol potassium carbonate (0.17 g) in entries 6–8, and 1.5 mL of fresh acetonitrile was irradiated by microwaves in a Pyrex tube under nitrogen. For details, see Table 2. The reaction volume filled not more than one-fifth of the total volume of the tube, thereby allowing headspace for pressure to build up during the microwave treatment. All couplings with microwave irradiation were performed without stirring. The reaction mixtures were allowed to cool before the tubes were carefully opened in a fume cupboard. Small samples were removed, partitioned between diethyl ether and water, and dried by potassium carbonate before the organic phase was analyzed by GC/MS. The yield was determined by a GC/MS mean value of three injections after calibration curves made from pure **3a–h** and 2,3-dimethylnaphthalene as internal standard. In entries 1–3, where three or four arylated isomers were detected by GC/MS, the regioselectivities were calculated by dividing the area of the integrated peak of the major isomer (**3**) with those of the resulting peaks.

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Supporting Information Available: ¹H, ¹³C NMR spectra and MS data are available for all new compounds (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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