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Synthesis of Allylsilanes and Dienylsilanes by a One-Pot Catalytic C−H Borylation−Suzuki−Miyaura Coupling Sequence

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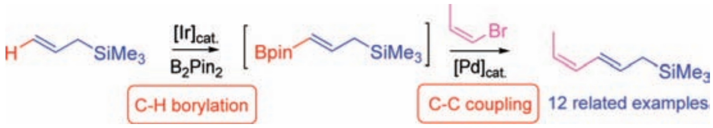
ABSTRACT

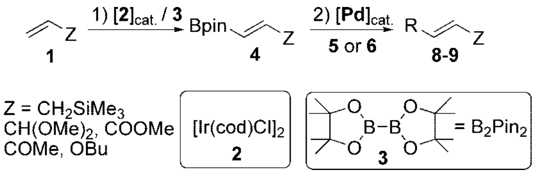


Allylsilane and various vinyl substrates undergo selective C−H bond functionalization based boronation reactions using iridium catalysis. The products were further reacted with aryl and vinyl halogenides in a one-pot sequence. This method is suitable for regio- and stereoselective synthesis of various allylsilanes and dienylsilanes.

Allyl and vinylsilanes have been widely applied as useful building blocks in complex organic transformations and natural product synthesis.[1] Therefore, development of new methods for selective synthesis of these species has attracted much interest in modern organic chemistry.[1h−p] In this respect, direct functionalization of allylsilanes offers a powerful approach for the synthesis of regio- and stereodefined derivatives.[1b,c]

Recent works by Marder, Hartwig, Miyaura, Smith, and their co-workers[2a−g] as well as our laboratory[2h] have demonstrated that organic substrates can be efficiently functionalized by C−H bond activation based borylation,[3a] which is often followed by a C−C bond formation reaction in a one-pot sequence.

We have envisaged that a similar strategy can also be employed for synthesis of functionalized allylsilanes starting from the parent compound **1a** (eq 1, Table 1).



(1)

Indeed, we have found that allylsilanes **8a−i** can be obtained from **1a** by employing a one-pot CH-borylation/CC-coupling sequence (entries 1−8). The iridium-catalyzed (**2**) regio- and stereoselective borylation of **1a** was performed at 80 °C (4 h) using **3** as boronate source. Subsequently, the in situ generated boronate **4a** was reacted with aryl (**5a−c**) and vinyl (**6a−e**) halogenides

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[1] (a) Fleming, I.; Barbero, A.; Walter, D *Chem. Rev* **1997**, *97*, 2063. (b) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: Chichester, 2002. (c) Sarkar, T. K. *Science of Synthesis, Houben-Weyl Methods of Molecular Transformations*; Fleming, I., Ed.; Thieme: Stuttgart, 2002; Vol. 4, p 837. (d) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375. (e) Chabaud, L.; James, P.; Landais, Y. *Eur. J. Org. Chem.* **2004**, 3173. (f) Chan, T. H. *Chem. Rev.* **1995**, *95*, 1279. (g) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (h) Kacprzynski, M. A.; May, T. L.; Kazane, S. A.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 4554. (i) Nakamura, S.; Uchiyama, M.; Ohwada, T. *J. Am. Chem. Soc.* **2005**, *127*, 13116. (j) Huber, J. D.; Perl, N. R.; Leighton, J. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 3037. (k) Auer, G.; Oestreich, M. *Adv. Synth. Catal.* **2005**, *347*, 637. (l) Karabelas, K.; Westerlund, C.; Hallberg, A. *J. Org. Chem.* **1985**, *50*, 3896. (m) Macsári, I.; Hupe, E.; Szabó, K. J. *J. Org. Chem.* **1999**, *64*, 9547. (n) Macsári, I.; Szabó, K. J. *Chem. Eur. J.* **2001**, *7*, 4097. (o) Barbero, A.; Cuadrado, P.; Fleming, I.; González, A. M.; Pulido, F. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, 327. (p) Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4962.

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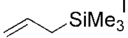
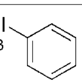
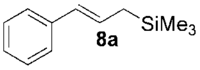
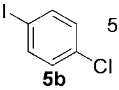
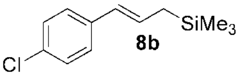
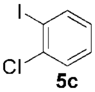
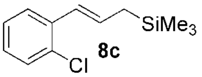
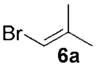
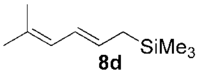
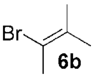
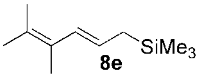
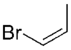
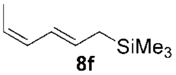
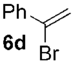
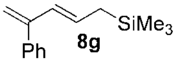
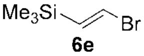
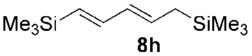
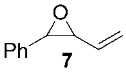
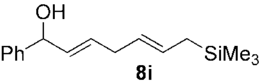
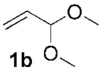
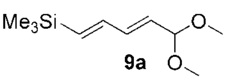
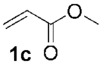
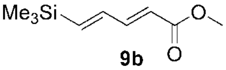
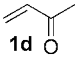
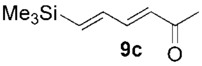
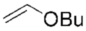
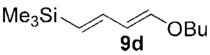
Table 1. Synthesis of Allyl- and Vinylsilanes via CH Borylation[a]

entry	substrates		cond.[b][°C / h]	products	yield[%][c]
1	 **1a**	 **5a**	50/16	 **8a**	56
2	**1a**	 **5b**	50/16	 **8b**	60
3	**1a**	 **5c**	60/16	 **8c**	57
4	**1a**	 **6a**	50/16	 **8d**	67
5	**1a**	 **6b**	50/16	 **8e**	73
6	**1a**	 **6c**	50/16	 **8f**	60
7	**1a**	 **6d**	50/7	 **8g**	59
8	**1a**	 **6e**	50/16	 **8h**	75
9	**1a**	 **7**	20/16[d]	 **8i**	55[e]
10	 **1b**	**6e**	50/16	 **9a**	75
11	 **1c**	**6e**	50/16	 **9b**	54
12	 **1d**	**6e**	40/16[f]	 **9c**	87
13	 **1e**	**6e**	50/16[f]	 **9d**	80

[a] The borylation reactions were carried out in neat **1a**−**e** (4−8 equiv) with diboronate **3** in the presence of catalyst **2** (2 mol %) at 80 °C for 4 h. [b] This step was followed by addition of **5** and **6**, Cs_2CO_3, and $Pd(PPh_3)_4$ (5 mol %) in a mixture of THF/water and stirring the mixture for the given times and temperatures. [c] Isolated yield. [d] Palladium pincer-complex catalyst (2.5 mol %) was used as catalyst in the second coupling step (see ref[4] and the Supporting Information). [e] This product was obtained in a 10:1 trans/cis ratio. [f] $Pd(OAc)_2$ (5 mol %) and dppf (10 mol %) were used instead of $Pd(PPh_3)_4$.

as well as vinyl epoxide derivative **7** under Suzuki−Miyaura conditions[3] affording allyl and dienyl silanes **8a**−**i**. To our delight, under similar reaction conditions, selective functionalization of several vinyl substrates **1b**−**e** could also be achieved. By employment of vinylsilane **6e** as coupling reagent, this reaction could be applied for synthesis of vinyl dienylsilanes **9a**−**d**. The regio- and stereoselectivity of the overall transformations is excellent, since only the formation of the trans-substituted linear products (**8** and **9**) (Table 1) was detected. The only exception was the reaction giving **8i** (entry 9), which resulted in about 10% of the cis isomer as well. The mild conditions employed in the one-pot sequence gave a high level of functional group tolerance as silyl, hydroxy, acetal vinyl ether, and carbonyl groups remained unchanged under the process.

The high regio- and stereoselectivity is a very attractive feature of the presented one-pot sequence. Although arylallylsilanes (such as **8a**−**c**) are relatively simple compounds, their synthesis is usually encumbered by rearrangement and desilylation processes.[1a–c,1] However, using the presented method, these side reactions can be completely avoided, and the corresponding arylallylsilanes (**8a**−**c**) can be prepared efficiently and with high selectivity (entries 1−3). Stereodefined allyl dienylsilanes are particularly useful synthons[1a–g,5] but also challenging synthetic targets. Considering the high selectivity of the presented borylation and coupling reactions (entries 4−9), these types of compounds can easily be obtained by the above methodology (eq 1). The employed one-pot approach is suitable for synthesis of both isolated (**8i**) and conjugated (**8d**−**g**) allyl dienylsilanes. Even dienes with different double-bond geometries (**8f**) could be prepared without any isomerization reactions (entry 6). The coupling reaction could also be smoothly performed in the presence of a bulky phenyl group affording **8g** in high selectivity (entry 7).

Silyl-substituted butadienes are useful substrates in Diels−Alder and related reactions.[1a–d,6] Due to the high selectivity of the borylation of **1b**−**e** and the subsequent coupling with vinyl bromide **6e**, these types of reagents are also easily accessible by the above-described C−H activation/C−C coupling sequence. Dienylsilanes **9c**,**d** are structurally interesting species, as in these compounds the linear conjugation is extended through three π-bonds.

Probably the most intriguing mechanistic feature of the presented one-pot reactions is the highly selective formation of vinyl boronate **4a** from the parent allylsilane **1a**. The regioselectivity of the C−H activation based borylation

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(2) (a) Mkhalid, I. A. I.; Coventry, D. N.; Albesa-Jove, D.; Batsanov, A. S.; Howard, J. A. K.; Perutz, R. N.; Marder, T. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 489. (b) Coapes, R. B.; Souza, F. E. Z.; Thomas, R. L.; Hall, J. J.; Marder, T. B. *Chem. Commun.* **2003**, 614. (c) Mkhalid, I. A. I; Coapes, B.; Edes, N.; Coventry, D. N.; Souza, F. E. S.; Thomas, R. L.; Hall, J. J.; Bi, S.-W.; Lin, Z.; Marder, T. B. *Dalton Trans.* **2008**, 1055. (d) Burgess, K.; van der Donk, W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 9350. (e) Tzschucke, C. C.; Murphy, J. M.; Hartwig, J. F. *Org. Lett.* **2007**, *9*, 761. (f) Boller, T. M.; Murphy, J. M.; Hapke, M.; Ishiyama, T.; Miyaura, N.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 14263. (g) Cho, J. Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E.; Smith, M. R. *Science* **2002**, *295*, 305. (h) Olsson, V. J.; Szabo, K. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 6891. (i) Brown, J. M.; Lloyd-Jones, G. C. *J. Am. Chem. Soc.* **1994**, *116*, 866.

(3) (a) Hall, D. G. *Boronic Acids*; Wiley: Weinheim, 2005. (b) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (c) Miyaura, N. *Top. Curr. Chem.* **2002**, *219*, 11.

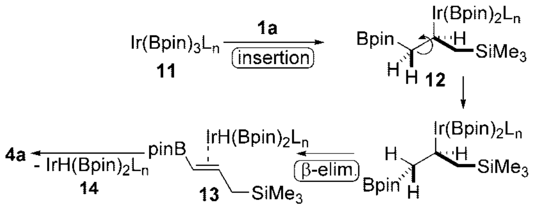
(4) Kjellgren, J.; Aydin, J.; Saltanova, I. V.; Wallner, O. A.; Szabo, K. *Chem. Eur. J.* **2005**, *11*, 5260.

(5) (a) Lee, T. W.; Corey, E. J *J. Am. Chem. Soc.* **2001**, *123*, 1872. (b) Meyers, C. Y.; Hua, D. H.; Peacock, N. J. *J. Org. Chem.* **1980**, *45*, 1721. (c) Yasuda, H.; Nishi, T.; Miyanaga, S.; Nakamura, A. *Organometallics* **1985**, *4*, 359.

(6) (a) Li, D.; Liu, G.; Hu, Q.; Wang, C.; Xi, Z. *Org. Lett.* **2007**, *9*, 5433. (b) Urabe, H.; Mitsui, K.; Ohata, S.; Sato, F. *J. Am. Chem. Soc.* **2003**, *125*, 6074. (c) Koreeda, M.; Ciufolini, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 2308. (d) Luh, T.-Y.; Wong, K.-T. *Synthesis* **1993**, 349.

(7) (a) Pereira, S.; Srebnik, M. *Organometallics* **1995**, *14*, 3127. (b) Morrill, C.; Grubbs, R. H. *J. Org. Chem.* **2003**, *68*, 6031. (c) Jankowska, M.; Pietraszuk, C.; Marciniec, B.; Zaidlewicz, M. *Synlett* **2006**, 1695.

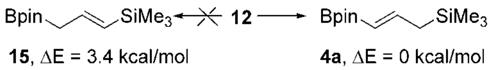
reactions is particularly difficult to control[2c,h] for linear alkenes comprising both sp^2 and sp^3 C−H bonds. This observation[2c,h] suggests that the selectivity of the C−H bond functionalization in **1a** is controlled by the steric or electronic effects of the silyl functionality.



(2)

We have found that the catalytic borylation of **1a** (step 1, eq 1) leads to formation of **4a** and its saturated counterpart, without formation of any other boronated products. Accordingly, one boronate group from **3** is used to form **4a**, whereas the other one is sacrificed for hydroboration of **1a**. Considering this, and our previous results[2h] on C−H bond activation−borylation reactions of cyclohexene using a similar catalytic system, we conclude that the borylation reaction probably proceeds via a dehydrogenative borylation mechanism (eq 2).[2b,c,i] This mechanism, reported by Marder,[2b,c] Lloyd-Jones,[2i] and Brown[2i] for rhodium-catalyzed C−H activation reactions, involves two steps: addition of the metal boronate complex to the double bond followed by β-hydride elimination. Accordingly, the corresponding mechanism involving **1a** is supposed to be started by addition of iridium tris-boryl complex[2d,f] **11** to the double bond of **1a** affording complex **12**. After a conformational change, β-hydride elimination occurs from the boronated carbon resulting in complex **13**. Subsequently, **4a** is released and the formed iridium−hydride complex **14** undergoes hydroboration with **1a** by regenerating the catalyst.

An interesting aspect is the selective formation of allylsilane **4a** instead of vinylsilane **15** in the β-hydride elimination step (eq 3). DFT calculations (B3PW91/6-31G**) show that the observed product **4a** is considerably (by 3.4 kcal/mol) more stable than its isoelectronic isomer **15**. This relatively large energy difference may explain the selective formation of **4a** in the C−H bond activation process. The surprisingly high stability of **4a** is probably due to the presence of favorable hyperconjugative interactions between the $B(p_{\pi^*})$ and $CC(\pi)$ as well as between the $C-Si(\sigma)$ and $CC(\pi^*)$ molecular orbitals. As there is no possibility for such type of electronic interactions in **15**, the relative thermodynamical stability of **4a** is higher.



(3)

It is very fortunate that the applied iridium catalyst does not induce cis−trans isomerization of **4a**−**e**, and thus, formation of these species is both stereo- and regioselective. Alternative methods for preparation of these types of vinylboronates involve hydroboration[7a] of alkynes or cross-metathesis,[7b,c] which often have selectivity issues.

In summary, we have devised a versatile one-pot protocol for regio- and stereoselective preparation of allylsilanes and vinyl dienylsilanes from easily accessible starting materials via a highly selective catalytic CH-borylation/CC-coupling sequence. The presented method opens operationally simple, new routes for preparation of densely functionalized allylsilanes and dienylsilanes, which are important building blocks in modern organic chemistry and natural product synthesis.[1,5,6]

Acknowledgment. This work was supported by the Swedish Research Council (VR).

Supporting Information Available: Experimental procedures, NMR data, as well as ^{1}H and ^{13}C NMR spectra of products **8a**−**i** and **9a**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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