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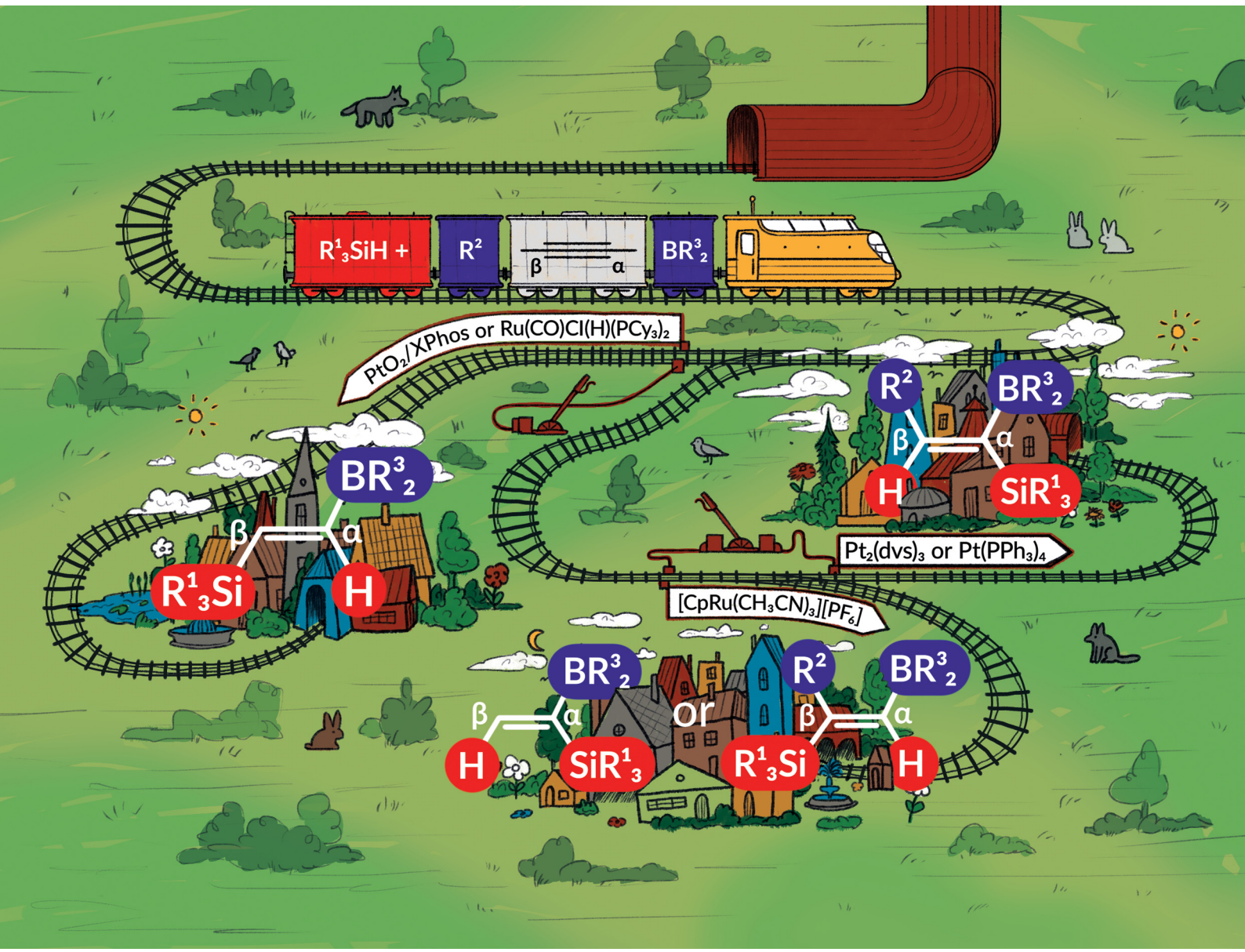

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Directed *cis*-hydrosilylation of borylalkynes to borylsilylalkenes†

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Hydrosilylation of borylalkynes to borylsilylalkenes (with a different arrangement of substituents) has been successfully developed. The *cis*-addition of SiH group to the C≡C bonds was directed by using a specific catalyst. The obtained products are crucial synthons for the introduction of the C=C bonds in organic synthesis.

Borylsilylalkenes are useful intermediates in organic synthesis because of their ability to achieve straightforward modification through a series of chemical transformations. The development of new and more efficient methodologies for the regio- and stereodefined synthesis of these compounds is one of the most challenging goals in modern organic and organometallic chemistry.

Such molecules combine the synthetic potential of both boryl and silyl groups bonded to sp^2-carbon and their different reactivities.[1] They can be converted into other functional groups (*e.g.*, halogen, aryl, alkenyl, hydroxyl, *etc.*) *via* demetallation processes (*e.g.*, palladium-catalyzed coupling reactions at the boryl (Suzuki–Miyaura)[2] or silyl (Hiyama)[3] fragment), or become reagents for the synthesis of saturated functional molecules.[4] They are considered precursors for the synthesis of di-, tri-, and tetrasubstituted alkenes present in many important pharmaceuticals (*e.g.*, anticancer drugs), bioactive natural compounds,[5] liquid crystals,[6] and dipeptide mimetics used in conformation studies of cyclic bioactive peptides.[7]

Methods for the synthesis of borylsilylalkenes include hydro-,[8] mono-,[9] di-,[10] and carboboration[11] of silylalkynes, silaboration of alkynes,[12] silylative coupling of vinylboranes with vinylsilanes,[13] hydrosilylation of borylalkynes,[8e,14] and others.[15] The detailed literature screening of the protocols for the synthesis of the analog isomers of borylsilylalkenes described in this work is presented in ESI† (Table S6, page 7 and Scheme S1, page 9).

In light of the constant very high interest in the synthesis of stereodefined functionalized alkenes and conjugated systems obtained by the transformation of boryl or silyl groups, herein we decided to test the hydrosilylation of borylalkynes. Hydrosilylation of the carbon–carbon triple bond (C≡C) is a straightforward, 100% atom efficient, industrially applied, repeatable method, which is easy to scale up and is based on commercially available reagents and catalysts.[16] Most importantly it gives the unique opportunity to obtain all possible isomers of *cis*-, and *trans*-addition of the SiH group to the C≡C bond. The R_3Si group can be bonded to both α and β-sp-carbons in terminal and internal alkynes. Different products can be obtained with the same set of reagents, but only by changing the type of catalyst and the reaction conditions. The versatility of this method is also a big synthetic challenge aimed at carrying out the process providing one product exclusively in each case.

Based on our experience[17] and the literature screening,[18] we tested a wide spectrum of catalytic systems (based on Ru, Rh, Ir, Pt) which allow *cis*- or *trans*-addition of the SiH bond to the terminal and internal C≡C. Catalysts dedicated to *trans*-additions (*e.g.*, $Ru{=}CHPh(Cl)_2(PCy_3)_2$, $[Cp^*Ru(MeCN)_3]PF_6$, $[(coe)_2IrCl]_2$[19] in the case of boryl derivatives (**2a–f**) led to the complex post-reaction mixtures containing predominantly *cis*-addition products. On the other hand, through careful catalyst selection, reaction optimization, and isolation of the resulting products, we achieved a family of borylsilylalkenes by the *cis*-hydrosilylations of the terminal and internal (boryl,silyl, aryl,alkyl)borylalkynes (**2a–f**) with a wide spectrum of silanes (**1a–g**) (Table 1).

We found that the reactions of ethynylborane (**2a**) with triethylsilane (**1a**), 1,1,1,3,5,5,5-heptamethyltrisiloxane (**1c**), and benzyldimethylsilane (**1f**) in the presence of PtO_2/XPhos (**I**) led to the formation of products **3** with a selectivity higher than 94%. In the case of the reaction with triphenylsilane (**1b**), the best results were obtained for Karstedt's catalyst (**II**)

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Table 1 Directed *cis*-hydrosilylation of borylalkynes **2a–f** with silanes **1a–g** in the presence of catalysts **I–V**

1a-f **2a-e** **3aa-fe** **4aa-fe** **5aa-fe**

SiR^1_3 = $SiEt_3$ (**1a**), $SiPh_3$ (**1b**), $SiMe(OSiMe_3)_2$ (**1c**), $SiMe_2(OEt)$ (**1d**), $SiMe_2Ph$ (**1e**), $SiMe_2Bn$ (**1f**), $Si(OSiMe_3)_3$ (**1g**)
R^2 = H, BR^3_2 = $(OC(CH_3)_2)_2$ (**2a**), R^2 = $B(OC(CH_3)_2)_2$, BR^3_2 = $(OC(CH_3)_2)_2$ (**2b**), R^2 = $SiMe_2(t\text{-Bu})$, BR^3_2 = $(OC(CH_3)_2)_2$ (**2c**),
R^2 = C_6H_5, BR^3_2 = $(OC(CH_3)_2)_2$ (**2d**), R^2 = CH_2OCH_3, BR^3_2 = $(OC(CH_3)_2)_2$ (**2e**), R^2 = *t*-Bu, BR^3_2 = $(OCH(CH_3)_2)_2$ (**2f**)

Entry	1	2	[M]	[1]:[2]:[M]	*t* [h]	Temp. [°C]	Solvent/atmosphere	Selectivity of **3**/**4**/**5** [%] NMR (GC-MS)	Isolated yield of **3** or **4** [%]
1	**1a**	**2a**	**I**	$1:1:10^{-2}$	48	60	THF/argon	**aa**, 96/4/0 (97/3/0)	93
2						100	THF/argon	**aa**, 100/0/0 (93/7/0)	
3[a]			**V**	$1:1:10^{-2}$	24	rt	DCM/argon	**aa**, 100/0/0 (100/0/0)	
4			**IV**	$1:1:2\times10^{-2}$	48	rt	DCM/argon	**aa**, 10/81/8 (11/80/9)	57
5	**1b**		**II**	$1:1:4\times10^{-4}$	48	100	Toluene/air	**ba**, 92/8/0 (92/8/0)	81
6			**IV**	$1:1:2\times10^{-2}$	24	rt	DCM/argon	**ba**, 0/100/0 (0/100/0)	72
7	**1c**		**I**	$1:1:10^{-2}$	24	100	THF/argon	**ca**, 94/6/0 (94/6/0)	91
8	**1f**		**I**	$1:1:10^{-2}$	24	100	THF/argon	**fa**, 95/5/0 (97/3/0)	86
9	**1a**	**2b**	**II**	$1:1:10^{-2}$	48	rt	Toluene/air	**ab**, 100/0/0 (99/0/1)	90
10			**III**	$1:1:10^{-2}$	120	rt	Toluene/air	**ab**, 100/0/0 (100/0/0)	
11	**1b**		**III**	$1:1:10^{-2}$	24	120	Toluene/air	**bb**, 100/0/0 (100/0/0)	98
12	**1c**		**III**	$1:1:10^{-2}$	24	60	Toluene/air	**cb**, 96/0/4 (96/0/4)	90
13	**1f**		**III**	$1:1:10^{-2}$	24	100	Toluene/air	**fb**, 100/0/0 (93/0/7)	91
14	**1a**	**2c**	**III**	$1:1:10^{-2}$	24	60	Toluene/air	**ac**, 0/100/0 (3/97/0)	89
15	**1b**		**II**	$1:1:4\times10^{-4}$	24	100	Toluene/air	**bc**, 0/100/0	93
16	**1c**		**III**	$1:1:10^{-2}$	24	60	Toluene/air	**cc**, 5/95/0	89
17	**1d**		**III**	$1:1:10^{-2}$	24	60	Toluene/air	**dc**, 0/100/0	91
18	**1e**		**II**	$1:1:4\times10^{-4}$	24	100	Toluene/air	**ec**, 0/100/0	89
19	**1f**		**II**	$1:1:4\times10^{-4}$	24	100	Toluene/air	**fc**, 0/100/0	91
20	**1a**	**2d**	**II**	$1:1:4\times10^{-4}$	48	rt	Toluene/air	**ad**, 18/82/0	76
21	**1b**		**III**	$1:1:10^{-2}$	48	120	Toluene/air	**bd**, 0/100/0	85
22	**1c**		**IV**	$1:1:2\times10^{-1}$	24	rt	Toluene/argon	**cd**, 84/7/9 (88/7/5)	79
22	**1e**		**II**	$1:1:4\times10^{-4}$	48	40	Toluene/air	**ed**, (8/85/7)	88
23	**1f**		**II**	$1:1:4\times10^{-4}$	48	rt	Toluene/air	**fd**, (3/94/3)	83
24			**IV**	$1:1:2\times10^{-1}$	24	rt	1,4-Dioxane/argon	**fd**, 89/0/11 (91/0/9)	86
25	**1g**		**IV**	$1:1:2\times10^{-1}$	24	rt	Toluene/argon	**gd**, 91/9/0 (97/0/3)	91
26	**1b**	**2e**	**III**	$1:1:10^{-2}$	24	120	Toluene/air	**be**, (14/86/0)	71
27	**1c**		**IV**	$1:1:2\times10^{-1}$	24	rt	Toluene/argon	**ce**, 100/0/0 (96/2/2)	89
28	**1f**		**II**	$1:1:4\times10^{-4}$	48	rt	Toluene/air	**fe**, 3/88/9 (7/85/8)	73
29			**IV**	$1:1:2\times10^{-1}$	24	rt	Toluene/argon	**fe**, (80/10/10)	70
30	**1g**		**IV**	$1:1:2\times10^{-1}$	24	rt	Toluene/argon	**ge**, 100/0/0 (100/0/0)	92
31	**1a**	**2f**	**II**	$1:1:10^{-2}$	24	rt	Toluene/air	**af**, 1/99/0 (3/97/0)	75

Complete conversion of **1a–g** for all tests was confirmed by ^{1}H NMR and GC-MS. Reaction conditions: *m***1a** = 0.0414 g, *m***1b** = 0.0934 g, *m***1c** = 0.0802 g, *m***1d** = 0.04 g, *m***1e** = 0.05 g, *m***1f** = 0.055 g, *m***1g** = 0.064 g, 2 ml of solvent. [a] $m\mathbf{1a}/V_{DCM}$ = 0.116 g ml^{-1}. For more detailed information please see the ESI. XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl, dvs = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, Cp = cyclopentadienyl, Cy = cyclohexyl.

($Pt_2(dvs)_3$). In all tests, product **3** was formed, from the *cis*-addition in which SiR_3 was added to the β-sp-carbon. In the literature, there is only one example of the hydrosilylation of ethynyl MIDA boronate ester (MIDA-*N*-methylimidodiacetic boronic acid ester) with benzyldimethylsilane (**1f**) used in excess (1.5 equiv.) in the presence of $PtCl_2$/XPhos. As a result, a product of *cis*-hydrosilylation was obtained selectively with a 91% yield.[14] Therefore, we recreated previously reported conditions for the reaction of borane (**2a**) with $HSiMe_2Bn$. Resulting from this, a complex mixture of products was observed (ESI,† Table S1, entry 25, page 2). This confirmed that the system proposed by us is much more efficient.

Screening different types of catalysts, we found that the reaction of borane **2a** with triethylsilane (**1a**) could also be performed at room temperature if $Ru(CO)Cl(H)(PCy_3)_2$ (**V**) was applied. Unfortunately, the reactions with the remaining silanes were less effective due to the lower conversion of the reagents. Attempts to solve these problems by increasing the reaction temperature resulted in the formation of side products.

On the other hand, the uses of $[CpRu(CH_3CN)_3][PF_6]$ (**IV**) in the reaction of (**2a**) with triethyl- (**1a**) and triphenylsilanes (**1b**) gave *gem*-isomers in high yields (products **4aa** and **4ba**). This proved that, with the same set of substrates and by changing the catalyst and reaction conditions we can direct the *cis*-hydrosilylation to various products. The attempt to obtain *cis*-isomer was unsuccessful.

In the next step of the study, hydrosilylation of internal symmetrical 1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-ethyne (**2b**) was performed. The best results were obtained in the presence of $Pt(PPh_3)_4$ (**III**). The results revealed that targeted product **4** was obtained, which contains two boryl groups and one silyl. Karstedt's (**II**) catalyst could also be used in the

modification of this borane but only when the reactions occurred at room temperature. With elevated temperatures, the formation of side/decomposition products was observed.

The same catalytic systems were used for hydrosilylation of 2-((*tert*-butyldimethylsilanyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2c**). Both of them were effective, and a higher temperature could be applied. The presence of a $SiMe_2(t\text{-Bu})$ group in the structure of the alkyne (**2c**) directed the addition of SiR_3 from silane, to the sp-carbon bonded to the boryl group. The attempt to obtain a second isomer **3** in the presence of $[CpRu(CH_3CN)_3][PF_6]$ (**IV**) was not successful. The uses of **IV** gave low conversions or led to complex mixtures of products.

The studies on the reactivity of 2-phenyl-1-ethynylboronic acid pinacol ester (**2d**) showed that hydrosilylation was the most efficient when Karstedt's (**II**) and $Pt(PPh_3)_4$ (**III**) catalysts were applied. With the set of silanes (**1a**, **1e–f**), products **4** were obtained, in which SiR_3 was attached to the α-sp-carbon bonded to the boryl group at the same time. The selectivity of these processes was in the range of 80–100%. Exclusive formation of product **4** was observed for $HSiPh_3$ (**1b**). The *cis*-additions to **2d** leading to products **3** occurred by the use of $[CpRu(CH_3CN)_3][PF_6]$ (**IV**). These products were formed with a selectivity of around 90%.

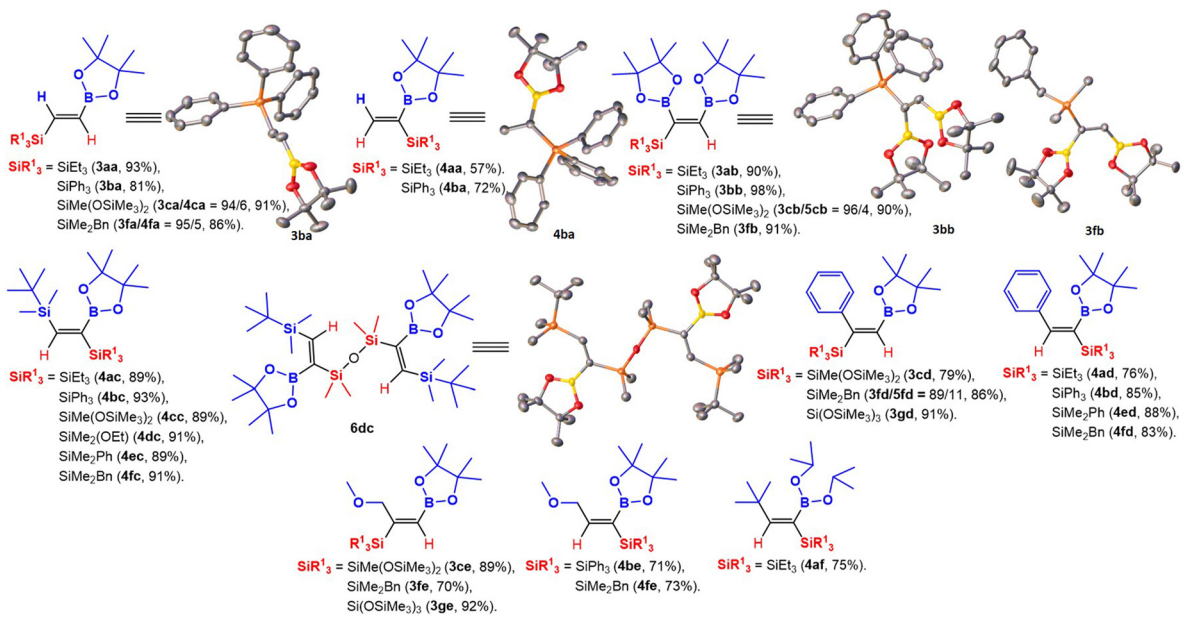
Similar results were found for 3-methoxy-1-propyn-1-ylboronic acid pinacol ester (**2e**). However, in this case, a much higher improvement in selectivity up to 100% was observed for silanes (**1c**, **1g**) with siloxy substituents.

Moreover, the (3,3-dimethyl-1-butynyl)boronic acid diisopropyl ester (**2f**) bearing *t*-Bu group and two isopropoxy groups, which are less stable than pinacol derivative, were tested. The reaction catalyzed by Karstedt's (**II**) catalyst gave product **4** with a high yield.

In the literature, hydrosilylation of 2-(hex-1-yn-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with an excess of silanes in the presence of $[CpRu(CH_3CN)_3][PF_6]$ (**IV**) in CH_2Cl_2 has been reported.[8e] Moreover, one example of the hydrosilylation of propynyl MIDA ester in the presence of $PtCl_2$/XPhos has also been described.[14] However, in both cases, excess of silane (1.5 equiv.) needed to be used since side products were obtained (ESI,† Table S5, entry 17, page 6). The stoichiometric procedures proposed by us herein lead to the selective formation of products of Si–H addition to the C≡C, which simplify the separation procedures of obtained products and are efficient for a wide spectrum of structurally different terminal and internal borylalkynes and silanes.

It is worth emphasizing that 29 compounds in total were synthesized, 25 of them for the first time (**3ca**, **3fa**, **3ab–cb**, **3fb**, **4ac–fc**, **3cd**, **3fd–gd**, **4ad–bd**, **4ed–fd**, **3ce**, **3fe–ge**, **4be**, **4fe**, **4af** and **6dc**). The obtained compounds were fully characterized by ^1H, ^{13}C, ^{29}Si, and GC-MS (or ESI MS). For compounds **3ba**, **4ba**, **3bb**, **3fb**, and **6dc** (which is a product of **4dc** condensation), crystal structures were obtained (Scheme 1). The compounds **3aa**, **4aa**, **3ba**, and **4ba** had previously been obtained *via* hydroboration,[8b–e] dehydrogenative borylation,[20] and silylboration[21] reactions with lower yields or in traces as side products (ESI,† Table S6, page 7).

In summary, we successfully obtained borylsilylalkenes by directed *cis*-hydrosilylation of a structurally different, wide group of borylalkynes with silanes (**1a–f**). The processes occurred by *cis*-addition of the Si–H bond across the carbon–carbon triple bond and led to products **3** or **4** depending on the specific catalyst and reaction conditions used. We proved that, compared to other synthetic methods which can be applied to obtain the targeted products, hydrosilylation is the most powerful method from those previously described and leads to the widest group of products with high yields, which are often not available in



Scheme 1 Structural formulas of obtained compounds with indicated isolated yields. Crystal structures of **3ba**, **4ba**, **3bb**, **3fb**, and **6dc** were confirmed by X-ray.

different protocols. Moreover, this process is a highly effective method for the synthesis of borylsilylalkenes with a diverse arrangement of substituents, which gives the possibility to use commercially available catalysts and substrates, carrying out the processes with a stoichiometric ratio of reagents. All these features will allow a further straightforward scaling up process. Finally, the obtained products constitute very useful synthons for the synthesis of substituted ethenes or complex materials by widely spread chemical transformation based on the modification of boryl, silyl, or sp^2-CH groups which can be performed one after another, based on the different reactivities of the boryl and silyl groups. Such synthons allow the synthesis of new molecules or known systems to be obtained using new approaches.

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Conflicts of interest

There are no conflicts to declare.

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