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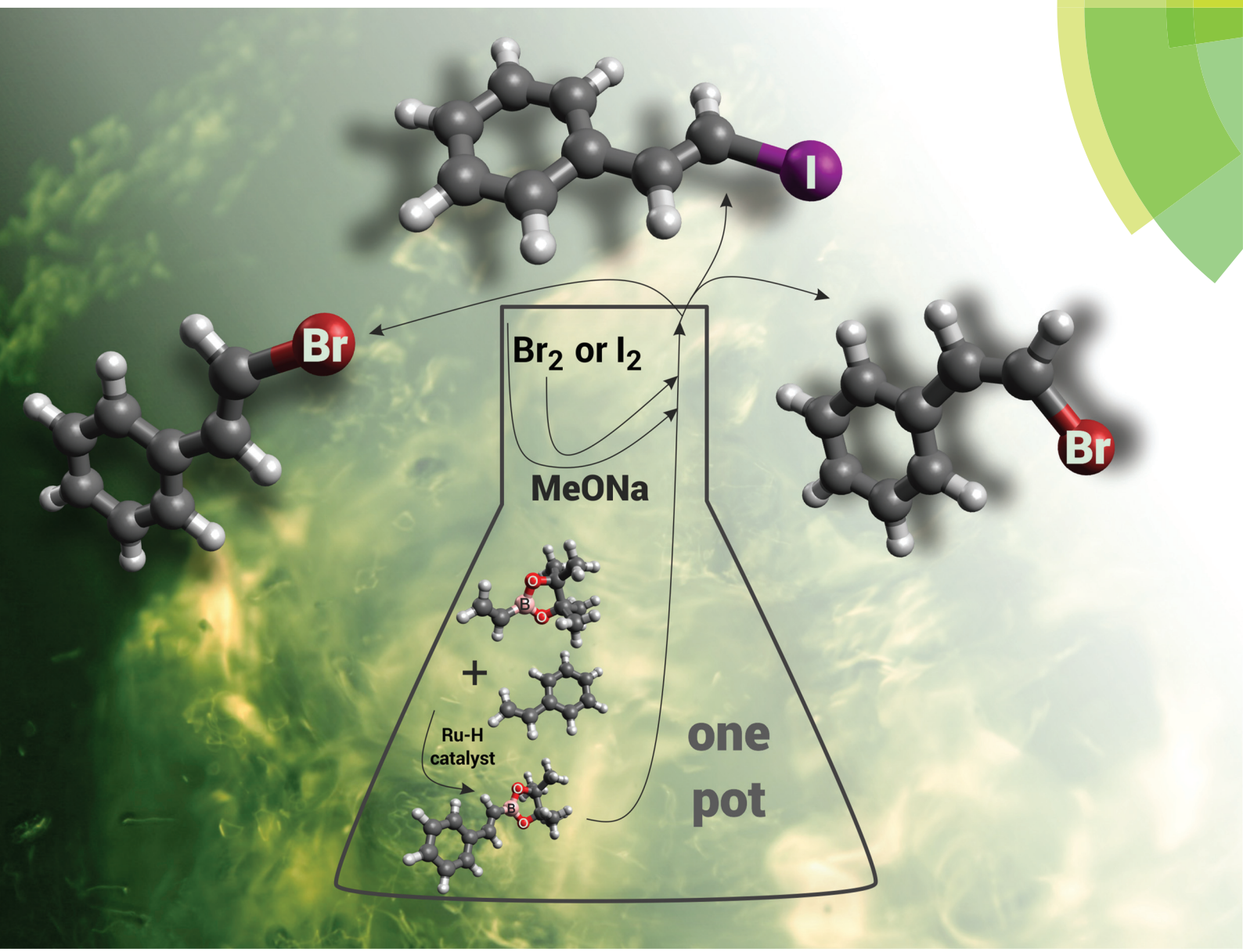

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PAPER
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A stereoselective synthesis of (*E*)- or (*Z*)-β-arylvinyl halides *via* a borylative coupling/halodeborylation protocol†

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A new stereoselective method for the synthesis of (*E*)-β-arylvinyl iodides and (*E*)- or (*Z*)-β-arylvinyl bromides from styrenes and vinyl boronates on the basis of a one-pot procedure *via* borylative coupling/halodeborylation is reported. Depending on the halogenating agent as well as the mode of the halodeborylation reaction, (*E*) or (*Z*) isomers are selectively formed.

Introduction

Transition metal catalyzed cross-coupling reactions, especially the Heck, Suzuki, Hiyama, Stille and Ullmann processes have been the most commonly used methods for generation of new C–C bonds.[1–3] These transformations predominantly use aryl or alkenyl halides as reagents and therefore the development of new synthetic protocols for their stereoselective synthesis is still of significant importance. β-Arylvinyl halides are vastly useful intermediates (coupling components) in organic chemistry, in the synthesis of unsaturated, conjugated products as well as natural compound analogues and are applied as precursors of vinyl anions or reagents in the Buchwald–Hartwig reaction.[4–7]

Over the past few decades, several routes to alkenyl halides with a specific stereoselectivity have been developed. β-Arylvinyl halides are classically prepared by the halodecarboxylation of cinnamic acid derivatives (Hunsdiecker reaction),[8–10] reduction of 1,1-dihalogenoalkenes[11,12] or olefination of aromatic aldehydes (Takai olefination).[13] Other effective methods leading to (*E*)-alkenyl halides are based on the catalytic *anti*-Markovnikov hydrobromination of alkynes, which occurs *via* the hydrocupration of alkynes, followed by bromination of the alkenyl copper intermediate,[14] homologation and further stereoselective elimination of benzyl bromides with dihalomethanes in the presence of a base[15] or intramolecular dehydration of bromohydrins using H-β zeolite as a catalyst.[16]

(*Z*)-β-Arylvinyl bromides can be synthesized by the Wittig olefination of an aldehyde with bromomethylene triphenylphosphorane,[17,18] by the reaction of aromatic aldehydes with α-bromomethyl sulfones (Julia olefination),[19] Pd-catalyzed debromination of 1,1-dibromo-1-alkenes by tributyltin hydride[20,21] or debrominative decarboxylation of *anti*-2,3-dibromo-3-arylpropanoic acids using *e.g.* NaN_3.[22,23]

Hydrometallation of alkynes followed by halogenation is another effective protocol used for the synthesis of (*E*)- or (*Z*)-alkenyl halides. Addition of the H–E bond (where E = Si, B, Sn, Zr) to alkynes leads to vinyl derivatives of these elements, which in the next step are stereospecifically substituted by a halogen atom using different halogenating agents.[24–30]

The most common methods used for the synthesis of alkenyl halides with different stereoselectivities are presented in Scheme 1.

The range of commercially available substituted styrenes is much wider than that of phenylacetylene analogues and therefore the methods for their application in the synthesis of metalloid-substituted compounds and further halodemetallation to the corresponding β-arylvinyl halides are important from the synthetic point of view (see Scheme 2). Terminal phenylacetylenes are often more expensive than their vinyl analogues, their preparation needs several steps and due to their tendency for dimerization and

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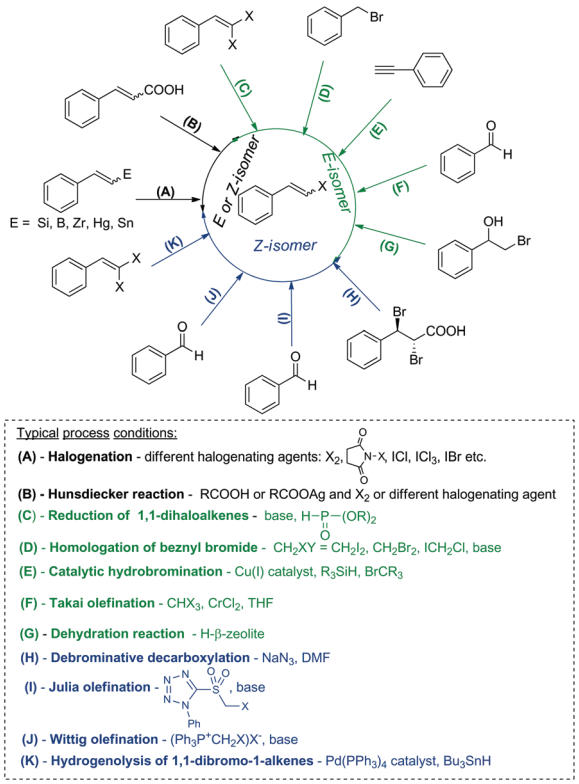


Scheme 1 Methods used for the synthesis of β-arylvinyl halides with different stereoselectivities.

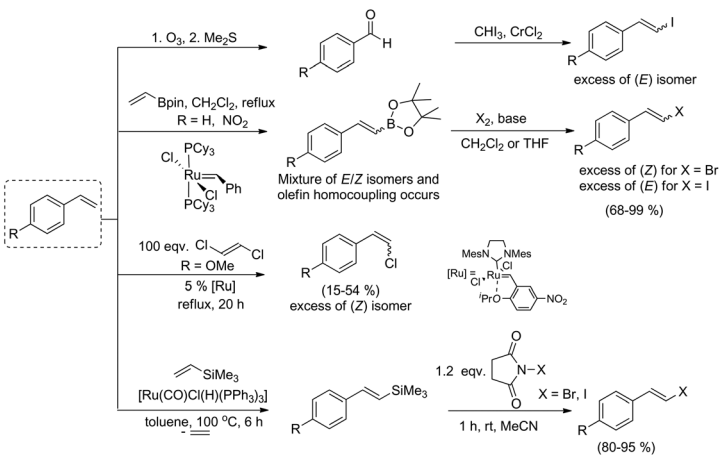
polymerization, they are less attractive in the synthesis. The formation of (*E*)-arylvinyl iodides and (*Z*)-arylvinyl bromides from styrenes in cross-metathesis with vinyl or 1-propenyl boronates, followed by the halogenation of alkenyl boronate intermediates was reported by Grubbs and co-workers.[31] β-Arylvinyl bromides were synthesized in a one-pot two-step procedure, while β-arylvinyl iodides were obtained only from isolated boronate intermediates. The cross-metathesis of 4-methoxystyrene with (*E*)-1,2-dichloroethene led to (*Z*)-4-methoxystyryl chloride as a main product.[32]

(*E*)-Vinyl iodides can be also prepared by a two-step procedure: oxidative cleavage of terminal olefins with ozone or OsO_4/$NaIO_4$ and Takai iodoolefination.[33,34]

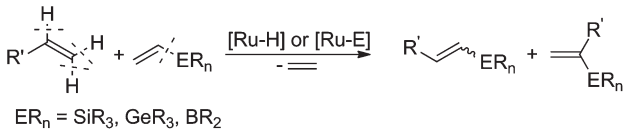
In 2009, our group reported an efficient method for the preparation of (*E*)-β-arylvinyl halides (bromides and iodides) in a one-pot procedure on the basis of a sequential silylative coupling reaction of vinylsilanes with styrenes and *N*-halosuccinimide-mediated halodesilylation (see Scheme 2).[35] Developed in our group, the silylative coupling reaction of olefins with vinylsilanes catalyzed by complexes with the Ru–H or Ru–Si bonds yields silyl-substituted alkenes with the simultaneous evolution of ethylene. The reaction occurs *via* activation of the C–Si bond in vinylsilane and C–H in olefin. Depending on the activation of different carbon–hydrogen bonds in olefin, (*E*), (*Z*) or *gem* isomers can be obtained. This mode of reactivity has also been extended to other vinyl metalloids: vinyl boronates and vinyl germanes.[36] Vinyl boronates give exclusively (*E*)-boryl-substituted ethenes in the reaction with styrenes and other olefins (see Scheme 3).[37]

The presented coupling reactions lead, in an easy and simple way, to metalloid-functionalized olefins, which can be used in many organic transformations. Our group has made a significant contribution to the development of one-pot procedures based on vinylsilanes in the preparation of organic compounds with various functional groups.[38–42]

Herein, we would like to report our investigation on the application of vinyl boronates as reagents for the synthesis of β-arylvinyl halides with (*E*) or (*Z*) geometry and propose new one-pot procedures for the preparation of such compounds *via* sequential borylative coupling and electrophilic halodeborylation reactions. This method constitutes an alternative for the synthesis of alkenyl halides according to the metathesis/halogenation or hydroboration/halogenation protocols, from easily accessible styrenes.



Scheme 2 The application of styrenes as reagents in the synthesis of β-arylvinyl halides.



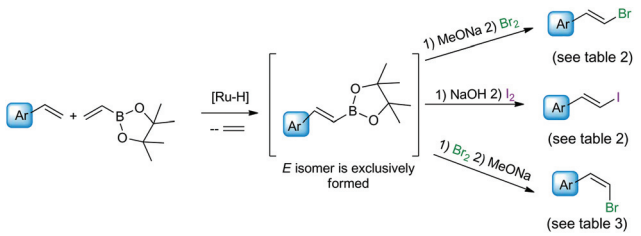
Scheme 3 Trans-metallation of olefins with vinyl metalloids.

Results and discussion

We have previously found that a borylative coupling of a series of substituted styrenes with vinyl boronates occurs with high regio- and stereoselectivity with the use of [Ru(CO)Cl(H)$(PCy_3)_2$] or [Ru(CO)Cl(H)$(PPh_3)_3$].[37] The first catalyst shows a much higher activity. (*E*)-2-Aryl-1-borylethenes were exclusively formed with quantitative yields, while no by-product of vinyl boronate homocoupling under the applied reaction conditions was observed.[37] This is an advantage when compared to the metathesis of analogous reagents carried out in the presence of a Grubbs catalyst (1st and 2nd generation), in which the homocoupling products of olefin and vinyl boronate were also detected.[31] The selectivity of metathesis was slightly lower compared to borylative coupling reaction and some amount of the (*Z*) isomer was formed. It means that the mixture of products obtained in the metathesis process after halodeborylation includes both isomers at different molar ratios.

For this reason, in our studies we decided to use borylative coupling – for the synthesis of (*E*)-2-aryl-1-borylethenes – as the first step of a sequential method for the preparation of β-arylvinyl halides (Scheme 4).

Commercially available, 4,4,5,5-tetramethyl-2-vinyl-1,3-dioxaborolane was used as a reagent for the borylative coupling of a group of styrenes, which had not been previously tested in this process. We found that only 1.1 molar excess of styrenes or even their equimolar amounts are enough to prevent vinyl boronate homocoupling, when 1 mol% of [Ru(CO)Cl(H)$(PCy_3)_2$] catalyst was used. Applying these conditions, the complete conversion of the reagents was observed after 5 h. The process was carried out in toluene at 80 °C, under an inert atmosphere. The formation of desired products, as well as the consumption of substrates, was monitored using GC and GC-MS analyses. ^{1}H NMR analysis showed that only the (*E*) isomer was formed in this catalytic transformation.



Scheme 4 A new synthetic protocol to (*E*)- or (*Z*)-β-arylvinyl halides *via* trans-metallation/halodemetallation reactions.

Three representatives of the obtained boryl-substituted ethenes were isolated to confirm the exact geometry of their structures and purity (see the ESI†). The rest of them were prepared *in situ* and were directly used in the halodeborylation process.

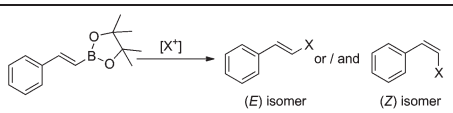
The excellent regio- and stereoselectivity of (*E*)-2-aryl-1-borylethene synthesis *via* borylative coupling is essential for the following halogenation process and for obtaining targeted β-arylvinyl halides with strictly defined configuration.

In the next step of the studies, the halodeborylation reaction (iododeborylation and bromodeborylation) was optimized using (*E*)-1-(4′,4′,5′,5′-tetramethyl)—1′,3′,2′-dioxaborolanyl-2-phenylethene and different halogenating agents: molecular I_2, Br_2 as well as NIS and NBS, applying the appropriate reaction conditions for both types of reagents (Table 1). Halodeborylations with molecular iodine or bromine were carried out in diethyl ether at 0 °C or −20 °C respectively, according to the procedure described by Brown's and co-workers (Table 1, entries 1, 2 and 4, 5).[43] We observed that depending on the order of addition of the base and halogen for the bromination process, the (*E*) or (*Z*) isomer was preferentially formed. When a base was added before Br_2 – the product was (*E*)-β-bromostyrene (Table 1, entry 4), while the opposite order of reagents led to (*Z*)-β-bromostyrene (Table 1, entry 5).

On the other hand, the iododeborylation of (*E*)-1-(4′,4′,5′,5′-tetramethyl)—1′,3′,2′-dioxaborolanyl-2-phenylethene irrespective of the order of addition of reagents, leads to (*E*)-β-iodostyrene. A slightly better yield of the reaction was obtained when the base was added before iodine (Table 1, entries 1 and 2).

We also observed that the rate of addition of halogen into the reaction mixture was essential for the process selectivity. When the reagent was added rapidly, the dihalogenated product was formed as well. A slight excess of halogen relative

Table 1 Influence of reaction parameters and the type of halogenating agents on the selectivity and productivity of halodeborylation reaction



Entry	[X$^+$]	Yield[g] [%]	Selectivity *E*/*Z*[h]
1[a]	I_2	100	1/0
2[b]	I_2	97	1/0
3[c]	NIS	94	1/0
4[d]	Br_2	100	1/0
5[e]	Br_2	99	1/20
6[f]	NBS	92	9/1

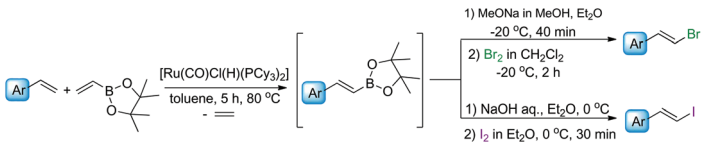
[a] 1. Et_2O, 3 M aq. NaOH, 0 °C. 2; I_2 in Et_2O, 30 min, 0 °C. [b] 1. I_2 in Et_2O, 30 min, 0 °C; 2. Et_2O, 3 M aq. NaOH, 0 °C. [c] 1.5 eq. of NIS, acetonitrile (0.1 M), rt. [d] 1. Et_2O, 3 M MeONa in MeOH, 40 min, −20 °C; 2. Br_2 in CH_2Cl_2, 2 h, −20 °C. [e] 1. Et_2O, Br_2 in CH_2Cl_2, −20 °C; 2. 3 M MeONa in MeOH, 2 h, −20 °C. [f] 1.5 eq. of NBS, acetonitrile (0.1 M), rt. [g] Reaction yields were calculated on the basis of GC analysis. [h] GC-MS and ^{1}H NMR were used for selectivity determination.

to the boronate reagent should be used during the entire process to prevent this side reaction. The temperature control is also important to obtain the desired monohalogenated product exclusively, and should be strictly maintained during the halogenation process.

Applying NIS or NBS as halogenating agents, β-arylvinyl halides were synthesized with the retention of configuration and with slightly lower yield compared to Brown's method (Table 1, entries 3 and 6).

The positive results on borylative coupling reaction as well as halodeborylation (bromodeborylation and iododeborylation), especially regarding the high efficiency and selectivity of both processes, encouraged us to check whether β-arylvinyl halides can be synthesized in one-pot protocol, without

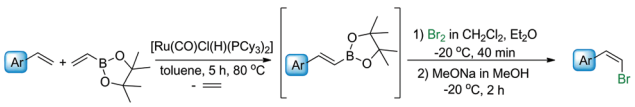
Table 2 Formation of (*E*)-β-arylvinyl halides *via* a one-pot procedure based on borylative coupling/halodeborylation reaction

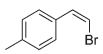
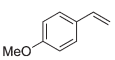
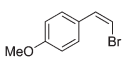
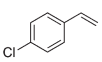
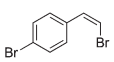
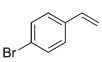
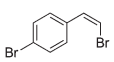


Entry	Ar	X_2	Yield [%]	Product		Selectivity (*E*)/(*Z*) [%]	Isolated yield [%]
1		Br_2	100		(**1a**)	1 : 0	87
2		I_2	100		(**1b**)	1 : 0	82
3		Br_2	98		(**2a**)	15 : 1	83
4		I_2	100		(**2b**)	1 : 0	84
5	MeO	Br_2	100	MeO	(**3a**)	20 : 1	76
6		I_2	100	MeO	(**3b**)	1 : 0	77
9	Br	Br_2	100	Br	(**4a**)	9 : 1	89
10		I_2	100	Br	(**4b**)	1 : 0	79
11	Br	Br_2	92	Br	(**5a**)	1 : 0	86
12		I_2	98	Br	(**5b**)	1 : 0	81
13	Cl	Br_2	99	Cl	(**6a**)	1 : 0	71
14		I_2	100	Cl	(**6b**)	1 : 0	63
15	Cl	Br_2	94	Cl	(**7a**)	20 : 1	67
16		I_2	100	Cl	(**7b**)	1 : 0	63
17		I_2	90		(**8b**)	1 : 0	58

Borylative coupling procedure: [Ru–H] : [ViB] : [olefin] = 10^{-2} : 1 : 1.1, toluene (0.5 M), 80 °C, 5 h. Bromodeborylation procedure: 1. MeONa (3 M in MeOH), Et_2O, 40 min, −20 °C; 2. [Borylated styrene] : [Br_2] = 1 : 1.6, Br_2 (1 M in CH_2Cl_2), −20 °C, 2 h. Iododeborylation procedure: 1. NaOH (3 M aq. solution), Et_2O, 0 °C; 2. [Borylated styrene] : [I_2] = 1 : 1.7, I_2 (1 M in Et_2O), 30 min, 0 °C. Reaction yields were calculated on the basis of GC analysis. GC-MS and ^{1}H NMR were used for selectivity determination.

Table 3 Synthesis of (*Z*)-β-arylvinyl bromides *via* a one-pot procedure from styrenes and vinyl boronate coupling and bromodeborylation



Entry	Ar	Yield [%]	Product		Selectivity (*E*)/(*Z*) [%]	Isolated yield [%]
1		98		(**9**)	0/1	84
2		93		(**10**)	0/1	61
3		100		(**11**)	1/8	89
4		96		(**12**)	1/8	82
5		98		(**13**)	1/8	84

Borylative coupling procedure: [Ru–H] : [ViB] : [olefin] = 10^{-2} : 1 : 1.1, toluene (0.5 M), 80 °C, 5 h. Bromodeborylation: 1. [Borylated styrene] : [Br_2] = 1 : 1.6, Br_2 (1 M in CH_2Cl_2), 0 °C, 40 min; 2. MeONa (3 M in MeOH), Et_2O, −20 °C, 2 h. Reaction yields were calculated on the basis of GC analysis. GC-MS and ^{1}H NMR were used for selectivity determination.

isolation and purification of intermediates – boryl-substituted ethenes.

In a typical procedure, the olefin, 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane, and 1 mol% of [Ru(CO)Cl(H)(PCy_3)$_2$] were dissolved in toluene (0.5 M), placed in a Schlenk's vessel fitted with a plug valve and heated up to 80 °C, under an inert atmosphere. After the total conversion of reagents, which was monitored by GC and GC-MS analyses, the reaction mixture was cooled down to −20 °C or 0 °C, diethyl ether was added and then depending on the protocol, bromine/iodine or the base was added firstly. (*E*)-β-Arylvinyl bromides and iodides were synthesized by the addition of a base – 3 M solution of sodium methoxide in methanol or sodium hydroxide in water, respectively – to the reaction mixture, followed by the dropwise injection of halogen dissolved in dichloromethane. The iodination was quenched with aqueous saturated solution of $Na_2S_2O_3$ and the products were separated using flash chromatography. A mixture of hexane with ethyl acetate at the ratio of 9/1 was used as an eluent. Pure (*E*)-β-arylvinyl bromides and (*E*)-β-arylvinyl iodides (Table 2, compounds **1–8(a and b)**) were obtained with high isolated yields (58–90%).

In the case of formation of (*Z*)-β-arylvinyl bromides, the procedure differs from that described above. Bromine was added to the reactor before the base (Table 3). The time of reaction and the whole isolation procedure were the same as that for the synthesis of (*E*) isomers. The isolated yields of the (*Z*)-β-bromostyrenes were similar to those of (*E*) isomers and varied between 61 and 89%.

It is worth emphasizing that all presented products can be prepared from commercially available reagents, without their preliminary purification. Due to the sensitivity of [Ru(CO)Cl(H)(PCy_3)$_2$] to air, it is recommended to carry out the borylative coupling reaction under an argon atmosphere in order to obtain total conversion of the reagents before deactivation of the catalyst. However, the halogenation processes were carried out in an air atmosphere. The most important factors affecting the effectiveness of the halodeborylation processes were temperature and the rate of halogen added to the reaction mixture.

Under optimal conditions, applying one-pot reaction sequences, a broad range of (*E*)-β-arylvinyl iodides and bromides as well (*Z*)-β-arylvinyl bromides, with miscellaneous substituents attached to the phenyl ring (such as –Me, –Ph, –OMe, –Br, –Cl) in different positions to the vinyl group, were successfully synthesized.

It should be noted that all presented compounds are interesting building blocks for organic synthesis, and can be modified by a wide spectrum of coupling reactions (Suzuki, Sonogashira, Hiyama *etc.*).

Conclusions

We have devised a one-pot protocol for the stereoselective synthesis of (*E*)-β-arylvinyl iodides, (*E*)-β-arylvinyl bromides and (*Z*)-β-arylvinyl bromides on the basis of highly selective catalytic borylative coupling/halodeborylation reactions. Commercially available substituted styrenes, much cheaper than the analogous terminal alkynes, were used as reagents in the protocols proposed. Not only the accessibility of substrates but also the higher selectivity of borylative coupling reaction *vs.* metathesis reaction is the reason why this method in an attractive alternative route for the synthesis of desired compounds from styrenes. Moreover, this methodology, compared to the protocol based on silylative coupling/halodesilylation reactions, offers a possibility for the synthesis of (*Z*)-β-arylvinyl

bromides, which cannot be obtained by the previously described Si-mediated reactions.

Experimental

Synthetic protocols

Borylative coupling. To a solution of $[Ru(CO)Cl(H)(PCy_3)_2]$ catalyst (0.01 mmol) in toluene in a Schlenk's vessel, both reagents: 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (1 mmol) and styrene (1.1 mmol) were added. The concentration of reagents in toluene was approximately 0.5 M. The reaction was carried out for 5 h at 80 °C under an argon atmosphere. The progress of the reaction was monitored by GC and GC-MS analyses. The solvent was evaporated and the crude product was isolated from the residue of the catalyst on silica gel using column chromatography and hexane/ethyl acetate (4/1) as the eluent. The product was analyzed on the basis of GC-MS and ^{1}H NMR. Only the (*E*) isomer was formed during the process. The spectral characterization of the boryl-substituted ethenes was in agreement with the literature.[44,45]

Synthesis of (*E*)-β-arylvinyl bromides

Procedure with Br_2. A solution of boryl-substituted styrene (1.0 mmol) in 2.5 ml Et_2O in a 50 mL round bottom flask was cooled down to −20 °C and 0.3 mL of sodium methoxide in methanol (3 M) was added dropwise. After 40 min, a 1 M solution of molecular bromine (266 mg, 1.6 mmol) in CH_2Cl_2 was added dropwise to have only a slight excess of a brominating agent to prevent the possibility of by-product (dibrominated compounds) formation. The reaction mixture was stirred at −20 °C for an additional 2 h and then the solvent was evaporated under reduced pressure. The crude product was isolated on silica gel using flash chromatography and hexane/ethyl acetate (9 : 1) as the eluent. The purity of the product was confirmed by GC-MS and ^{1}H NMR.

Procedure with NBS. *N*-Bromosuccinimide (0.31 g, 1.77 mmol) was added to the solution of boryl-substituted styrene (1.18 mmol) in MeCN (18 mL) and the suspension was stirred at room temperature for 24 h. The solvent was then evaporated and the mixture was extracted with *n*-hexane (30 mL). The organic layer was concentrated and the product was purified on silica gel using flash chromatography and hexane as the eluent. The purity of the product was confirmed by GC-MS and ^{1}H NMR.

One-pot procedure for the synthesis of (*E*)-β-arylvinyl bromides from styrenes. To a solution of 1 mol% $[Ru(CO)Cl(H)(PCy_3)_2]$ catalyst in toluene in the Schlenk's vessel under an argon atmosphere, both reagents: 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (1.0 mmol) and an appropriate styrene (1.1 mmol) were added. The reaction was carried out for 5 h at 80 °C. The progress of the reaction was monitored by GC and GC-MS analyses. After the reaction, the solution was cooled down to −20 °C and diethyl ether (2.0 mL) as well as 0.3 mL of an aqueous solution of sodium methoxide (3 M) were added dropwise. Molecular bromine (266 mg, 1.6 mmol) in CH_2Cl_2 was added dropwise to the reaction mixture to have only a slight excess of the brominating agent. The reaction was stirred for 2 h and then the solvent was evaporated under reduced pressure. The crude product was isolated on silica gel using flash chromatography and hexane/ethyl acetate (9 : 1) as the eluent. The purity of all obtained products were confirmed by GC-MS and ^{1}H NMR and the results were in agreement with the literature.[15,16,35]

(E)-β-Bromostyrene ***(1a)***.[35] Isolated yield: 87%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.66 (d, 1H, J_{H-H} = 14.0 Hz, HC═), 7.01 (d, 1H, J_{H-H} = 14.0 Hz, HC═), 7.12–7.29 (m, 5H, Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 106.7 (═CH–Br), 126.2, 128.4, 128.9, 136.0 (Ar), 137.3 (═CH–Ph) ppm; MS *m*/*z* (rel. int., %): 184($(M + 2)^+$, 47), 182(M^+, 48), 103(100), 77(60), 51(33).

(E)-β-Bromo(4-methylstyrene) ***(2a)***.[15] Isolated yield: 83%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.37 (s, 3H, CH_3), 6.74 (d, 1H, J_{H-H} = 14.0 Hz, HC═), 7.11 (d, 1H, J_{H-H} = 14.0 Hz, HC═), 7.16–7.18 (d, 2H, Ar), 7.22–7.24 (d, 2H, Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 21.7 (CH_3), 105.9 (═CH–Br), 126.5, 129.9, 133.5, 137.4 (Ar), 138.9 (═CH–Ar) ppm; MS *m*/*z* (rel. int., %): 198 ($(M + 2)^+$, 57), 196(M^+, 58), 117(100), 91(37), 63(20), 57(18) 51(12).

(E)-β-Bromo(4-methoxystyrene) ***(3a)***.[15] Isolated yield: 76%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.72 (s, 3H, OCH_3), 6.52 (d, 1H, J_{H-H} = 14.0 Hz, HC═), 6.76 (d, 2H, J_{H-H} = 8.7 Hz, Ar), 6.95 (d, 1H, J_{H-H} = 14.0 Hz, HC═), 7.14 (d, 2H, J_{H-H} = 8.7 Hz, Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 55.3 (OCH_3), 104.0 (═CH–Br), 114.2, 127.4, 128.8 (Ar), 136.6 (═CH–Ar), 159.7 (Ar) ppm; MS *m*/*z* (rel. int., %): 214($(M + 2)^+$, 97), 212(M^+, 100), 199(38) 197(40), 169(18), 171(17), 133(47), 118(27), 90(67), 77(16), 63(36).

(E)-β-Bromo(4-bromostyrene) ***(4a)***.[35] Isolated yield: 89%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.67 (d, 1H, J_{H-H} = 14.0 Hz, HC═), 6.93 (d, 1H, J_{H-H} = 14.0 Hz, HC═) 7.04 (d, 2H, Ar), 7.34 (d, 2H, Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 107.4 (═CH–Br), 122.2, 127.6, 132.0, 134.8 (Ar), 136.1 (═CH–Ar) ppm; MS *m*/*z* (rel. int., %): 264($(M + 2)^+$, 31), 262(M^+, 62), 181(33), 102(100), 75(31), 51(30).

(E)-β-Bromo(3-bromostyrene) ***(5a)***.[16] Isolated yield: 86%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.81 (d, 1H, J_{H-H} = 14.0 Hz, HC═), 7.05 (d, 1H, J_{H-H} = 14.0 Hz, HC═) 7.17–7.25 (m, 2H, Ar), 7.41–7.47 (m, 2H, Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 108.2 (═CH–Br), 122.9, 124.7, 129.0, 130.3, 131.2, 135.8 (Ar), 137.9 (═CH–Ar) ppm; MS *m*/*z* (rel. int., %): 264($(M + 2)^+$, 28), 262(M^+, 57), 181(24), 102(100), 75(26), 51(26).

(E)-β-Bromo(4-chlorostyrene) ***(6a)***.[35] Isolated yield: 71%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.78 (d, 1H, J_{H-H} = 14.0 Hz, HC═), 7.08 (d, 1H, J_{H-H} = 14.0 Hz, HC═) 7.23–7.33 (m, 4H, Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 107.0 (═CH–Br), 126.8, 128.9, 133.8, 134.1 (Ar), 135.6 (═CH–Ar) ppm; MS *m*/*z* (rel. int., %): 220($(M + 4)^+$, 36), 218($(M + 2)^+$, 72), 216(M^+, 34), 137(100), 102(68), 75(28).

(E)-β-Bromo(2-chlorostyrene) ***(7a)***.[16] Isolated yield: 67%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.72 (d, 1H, J_{H-H} = 14.0 Hz, HC═), 7.09–7.33 (m, 4H, Ar), 7.39 (d, 1H, J_{H-H} = 14.0 Hz, HC═) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 109.2 (═CH–Br), 126.9, 127.0, 129.4, 129.9, 132.5, 133.8 (Ar), 134.1 (═CH–Ar)

ppm; MS *m*/*z* (rel. int. %): 218($(M + 2)^+$, 26), 216(M^+, 21), 137(100), 101(53), 75(33), 51(19).

Synthesis of (*E*)-β-arylvinyl iodides

Procedure with I_2. To the solution of boryl-substituted styrene (1.18 mmol) in 1.5 mL Et_2O in a 50 mL round bottom flask 1.2 mL of aqueous solution of sodium hydroxide (3 M) was added dropwise at 0 °C. Subsequently, the solution of molecular iodine (500 mg, 1.97 mmol) in 3.6 mL of Et_2O was added dropwise to have only a slight excess of the iodinating agent to prevent the possibility of by-product formation (diiodized compounds). The reaction mixture was stirred for 30 minutes and then the excess of iodine was quenched with a saturated solution of sodium thiosulfate. The organic solution was separated and the aqueous solution was washed with diethyl ether. The combined organic layers were dried under magnesium sulfate. The solvent was evaporated and the crude product was isolated on silica gel using flash chromatography and hexane/ethyl acetate as the eluent (9 : 1). The purity of the product was confirmed by GC-MS and ^{1}H NMR.

Procedure with NIS. *N*-Iodosuccinimide (0.4 g, 1.77 mmol) was added to the solution of boryl-substituted styrene (1.18 mmol) in MeCN (18 mL) and the suspension was stirred at room temperature for 24 h. The solvent was then evaporated and the mixture was extracted with *n*-hexane (30 mL). The organic layer was concentrated and the product was purified on silica gel using flash chromatography and hexane/ethyl acetate as the eluent (9 : 1). The purity of the product was confirmed by GC-MS and ^{1}H NMR.

One-pot procedure for the synthesis of (*E*)-β-arylvinyl iodides from styrenes. To the solution of 1 mol% of $[Ru(CO)Cl(H)(PCy_3)_2]$ catalyst in toluene in the Schlenk's vessel under an argon atmosphere, both reagents: 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (1.0 mmol) and an appropriate styrene (1.1 mmol) were added. The reaction was carried out for 5 h at 80 °C. The progress of the reaction was monitored by GC and GC-MS analyses. After the reaction the solution was cooled down to 0 °C and diethyl ether (2.0 mL) as well as 1.2 mL of aqueous solution of sodium hydroxide (3 M) were added dropwise. To the reaction mixture, molecular iodine (431 mg, 1.7 mmol) in 3.1 mL of Et_2O was added dropwise to have only a small excess of the iodinating agent and to prevent the possibility of by-product formation. The reaction was stirred for further 30 minutes and then the excess of iodine was quenched with a saturated solution of sodium thiosulfate. The organic solution was separated and the aqueous phase was washed with diethyl ether. The combined organic layers were dried under magnesium sulfate. The solvent was evaporated and the crude product was isolated on silica gel using flash chromatography and hexane/ethyl acetate (9 : 1) as the eluent. The purity of the product was confirmed by GC-MS and ^{1}H NMR and the results were in agreement with the literature.[15,35,46]

(E)-β-Iodostyrene ***(1b)***.[35] Isolated yield: 82%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.83 (d, 1H, J_{H-H} = 14.9 Hz, HC=), 7.28–7.36 (m, 5H, Ar), 7.44 (d, 1H, J_{H-H} = 14.9 Hz, HC=) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 66.8 (=CH–I), 126.0, 128.4, 128.7, 137.7 (Ar), 145.0 (=CH–Ar) ppm; MS *m*/*z* (rel. int., %): 230(M^+, 100), 127(11), 103(83), 77(49).

(E)-β-Iodo(4-methylstyrene) ***(2b)***.[35] Isolated yield: 84%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.25 (s, 3H, CH_3), 6.65 (d, 1H, J_{H-H} = 14.9 Hz, HC=), 6.97–7.17 (m, 4H, Ar), 7.30 (d, 1H, J_{H-H} = 14.9 Hz, HC=) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 21.3 (CH_3), 75.4 (=CH–Br), 125.9, 129.4, 135.1, 138.4 (Ar), 144.9 (=CH–Ar) ppm; MS *m*/*z* (rel. int., %): 244(M^+, 100), 127(22), 115(78), 102(24).

(E)-β-Iodo(4-methoxystyrene) ***(3b)***.[35] Isolated yield: 77%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.85 (s, 3H, OCH_3), 6.67 (d, 1H, J_{H-H} = 14.9 Hz, HC=), 6.87–6.89 (d, 2H, Ar), 7.26–7.30 (d, 2H, Ar) 7.40 (d, 1H, J_{H-H} = 14.9 Hz, HC=) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 55.5 (OCH_3), 73.6 (=CH–I), 114.1, 127.8, 130.7 (Ar), 144.3 (=CH–Ar), 159.8 (Ar) ppm; MS *m*/*z* (rel. int., %): 260(M^+, 100), 133(47), 127(21), 118(20), 103(13), 89(28), 77(23), 63(25), 51(14).

(E)-β-Iodo(4-bromostyrene) ***(4b)***.[35] Isolated yield: 79%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.70 (d, 1H, J_{H-H} = 14.9 Hz, HC=), 6.99 (d, 2H, J_{H-H} = 8.4 Hz, Ar), 7.20 (d, 1H, J_{H-H} = 14.9 Hz, HC=), 7.29 (d, 2H, J_{H-H} = 8.4 Hz, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 77.6 (=CH–I), 122.4, 127.5, 131.9, 136.5 (Ar), 143.8 (=CH–Ar) ppm; MS *m*/*z* (rel. int., %): 310($(M + 2)^+$, 19), 308(M^+, 18), 183(16), 181(17), 127(12), 102(100), 75(40), 51(27).

(E)-β-Iodo(3-bromostyrene) ***(5b)***.[15] Isolated yield: 81%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.75 (d, 1H, J_{H-H} = 14.9 Hz, HC=), 7.00–7.10 (m, 2H, Ar) 7.20 (d, 1H, J_{H-H} = 14.9 Hz, HC=) 7.26–7.34 (m, 2H, Ar), ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 79.0 (=CH–I), 123.0, 124.7, 128.9, 130.3, 131.5, 139.5 (Ar), 143.4 (=CH–Ar) ppm; MS *m*/*z* (rel. int., %): 310($(M + 2)^+$, 40), 308(M^+, 39), 183(16), 181(17), 127(6), 102(100), 75(21), 51(12).

(E)-β-Iodo(4-chlorostyrene) ***(6b)***.[35] Isolated yield: 63%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.86 (d, 1H, J_{H-H} = 14.9 Hz, HC=), 7.22–7.25 (d, 2H, Ar) 7.30–7.33 (d, 2H, Ar), 7.40 (d, 1H, J_{H-H} = 14.9 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 77.6 (=CH–I), 127.2, 128.9, 134.2, 136.1 (Ar), 143.7 (=CH–Ar) ppm; MS *m*/*z* (rel. int., %): 264(M^+, 100), 137(83), 127(24), 102(93), 75(23).

(E)-β-Iodo(2-chlorostyrene) ***(7b)***.[46] Isolated yield: 63%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.78 (d, 1H, J_{H-H} = 14.9 Hz, HC=), 7.05–7.35 (m, 4H, Ar) 7.69 (d, 1H, J_{H-H} = 14.9 Hz, HC=) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 79.9 (=CH–I), 126.9, 127.1, 129.4, 129.9, 132.2, 135.8 (Ar), 141.4 (=CH–Ar) ppm; MS *m*/*z* (rel. int., %): 264(M^+, 37), 137(100), 127(25), 101(71), 75(50), 51(18).

(E)-1-Iodo-2-naphtylethene ***(8b)***.[15] Isolated yield: 58%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.87 (d, 1H, J_{H-H} = 14.6 Hz, HC=), 7.40–7.65 (m, 4H, napht.), 7.79–7.94 (m, 2H, napht.), 8.03–8.12 (m, 1H, napht.), 8.18 (d, J_{H-H} = 14.6 Hz, HC=), ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 79.4 (=CH–I), 123.7, 124.2, 125.6, 126.1, 126.5, 128.6, 128.8, 130.2, 133.5, 135.6 (Naph), 142.9 (=CH–Naph) ppm; MS *m*/*z* (rel. int., %): 280(M^+, 29), 153(100), 126(14).

Synthesis of (*Z*)-β-arylvinyl bromides

Procedure with Br_2. The solution of boryl-substituted styrene (1.0 mmol) in 2.5 mL Et_2O in a 50 mL round bottom flask was cooled down to −20 °C and the 1 M solution of molecular bromine (266 mg, 1.6 mmol) in CH_2Cl_2 was added dropwise to have only a slight excess of the brominating agent, to prevent the possibility of by-product (dibrominated compounds) formation. The reaction mixture was stirred for 40 min and then 0.3 mL of sodium methoxide in methanol (3 M) was added. The reaction was maintained at −20 °C for the next 2 h and then the solvent was evaporated under reduced pressure. The crude product was isolated on silica gel using flash chromatography and hexane/ethyl acetate as the eluent (9 : 1). The purity of the product was confirmed by GC-MS and ^{1}H NMR.

One-pot procedure for the synthesis of (*Z*)-β-arylvinyl bromides from styrenes. To a solution of 1 mol% of $[Ru(CO)Cl(H)(PCy_3)_2]$ catalyst in toluene in the Schlenk's vessel, both reagents: 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane (1.0 mmol) and an appropriate styrene (1.1 mmol) were added. The reaction was carried out for 5 h at 80 °C under an argon atmosphere. The progress of the reaction was monitored by GC and GC-MS analyses. After the reaction the solution was cooled down to −20 °C and 1 M solution of molecular bromine (266 mg, 1.6 mmol) in CH_2Cl_2 was added dropwise to the reaction mixture. The reaction mixture was stirred for 40 min and then 0.3 mL of sodium methoxide in methanol (3 M) was added. The reaction mixture was maintained at −20 °C for the next 2 h and then the solvent was evaporated under reduced pressure. The crude product was isolated on silica gel using flash chromatography and hexane/ethyl acetate (9 : 1) as the eluent. The purity of the product was confirmed by GC-MS and ^{1}H NMR and the results were in agreement with the literature.[19,23,47,48]

*(Z)-β-Bromostyrene (**9**).*[48] Isolated yield: 84%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.27 (d, 1H, J_{H-H} = 7.4 Hz, HC═), 5.89 (d, 1H, J_{H-H} = 7.4 Hz, HC═), 7.23–7.37 (m, 5H, Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 105.8 (═CH–Br), 128.0, 128.1, 128.9 131.9 (Ph), 134.9 (═CH–Ph) ppm; MS *m*/*z* (rel. int., %): 184($(M + 2)^+$, 46), 182(M^+, 47) 103(100), 77(58), 51(32).

*(Z)-β-Bromo(4-methylstyrene) (**10**).*[48] Isolated yield: 61%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.39 (3H, s, CH_3), 5.40 (1H, d, J_{H-H} = 7.4 Hz), 6.01 (1H, d, 1H J_{H-H} = 7,4 Hz), 7.16–7.31 (d, 2H, Ar), 7.37–7.40 (2H, d, Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 21.6 (CH_3), 105.3 (═CH–Br), 128.5, 128.9, 131.7 (Ar), 137.9 (═CH–Ar) ppm; MS *m*/*z* (rel. int., %): 198($(M + 2)^+$, 61), 196 (M^+, 62) 117(100), 91(41), 63(17), 57(13) 51(13).

*(Z)-β-Bromo(4-methoxystyrene) (**11**).*[19,48] Isolated yield: 89%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.84 (s, 3H), 5.40 (d, 1H, J_{H-H} = 7.3 Hz), 6.01 (d, 1H, J_{H-H} = 7.3 Hz), 6.90–6.95 (m, 2H, Ar), 7.36–7.44 (m, 2H, Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 55.0 (CH_3), 104.2 (═CH–Br), 112.9, 127.3, 130.3 (Ar), 132.6 (═CH–Ar), 159.9 (Ar) ppm; MS *m*/*z* (rel. int., %): 214($(M + 2)^+$, 97), 212(M^+, 100), 197(42), 169(18), 133(48), 118(28), 90(70), 77(18), 63(41).

*(Z)-β-Bromo(4-chlorostyrene) (**12**).*[48] Isolated yield: 82%; ^{1}H NMR (300 MHz, $CDCl_3$) – isolated yield: 82%; δ = 5.42 (d, 1H, J_{H-H} = 7.4 Hz, HC═), 6.02 (d, 1H, J_{H-H} = 7.4 Hz, HC═), 7.38–7.43 (d, 2H, Ar), 7.47–7.52 (d, 2H, Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 107.4 (═CH–Br), 128.1, 128.9, 131.0, 133.1 (Ar), 133.9 (═CH–Ar) ppm; MS *m*/*z* (rel. int., %): 220($(M + 4)^+$, 19), 218($(M + 2)^+$, 78), 216(M^+, 60), 137(100), 102(74), 75(43).

*(Z)-β-Bromo(4-bromostyrene) (**13**).*[23,47] Isolated yield: 84%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.52 (d, 1H, J_{H-H} = 7.9 Hz, HC═), 7.03 (d, 1H, J_{H-H} = 7.9 Hz, HC═), 7.21–7.41 (d, 2H, Ar), 7.47–7.61 (d, 2H, Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 108.1 (═CH–Br), 122.3, 127.5, 131.1, 131.2, 131.7, 136.9 (═CH–Ar) ppm; MS *m*/*z* (rel. int., %): 264($(M + 2)^+$, 29), 262(M^+, 63), 181(35), 102(100), 75(31), 51(27).

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Notes and references

1 *Metal-catalyzed Cross-coupling Reactions*, F. Diederich and P. J. Stang, ed, 2008.
2 H. Doucet, *Eur. J. Org. Chem.*, 2008, 2013–2030.
3 Q. Liao, Y. Wang, L. Zhang and C. Xi, *J. Org. Chem.*, 2009, **74**, 6371–6373.
4 M. S. Kabir, M. L. Van Linn, A. Monte and J. M. Cook, *Org. Lett.*, 2008, **10**, 3363–3366.
5 F. Besselievre, S. Piguel, F. Mahuteau-Betzer and D. S. Grierson, *Org. Lett.*, 2008, **10**, 4029–4032.
6 F. A. Davis, G. S. Lal and J. Wei, *Tetrahedron Lett.*, 1988, **29**, 4269–4272.
7 L. Jiang, G. E. Job, A. Klapars and S. L. Buchwald, *Org. Lett.*, 2003, **5**, 3667–3669.
8 J. Sinha, S. Layek, G. C. Mandal and M. Bhattacharjee, *Chem. Commun.*, 2001, 1916–1917.
9 C. Kuang, Q. Yang, H. Senboku and M. Tokuda, *Synthesis*, 2005, 1319–1325.
10 J. P. Das and S. Roy, *J. Org. Chem.*, 2002, **67**, 7861–7864.
11 S. Abbas, C. J. Hayes and S. Worden, *Tetrahedron Lett.*, 2000, **41**, 3215–3219.
12 H. Horibe, K. Kondo, H. Okuno and T. Aoyama, *Synthesis*, 2004, 986–988.
13 K. Takai, T. Ichiguchi and S. Hikasa, *Synlett*, 1999, 1268–1270.
14 M. R. Uehling, R. P. Rucker and G. Lalic, *J. Am. Chem. Soc.*, 2014, **136**, 8799–8803.

15 J. A. Bull, J. J. Mousseau and A. B. Charette, *Org. Lett.*, 2008, **10**, 5485–5488.
16 V. Pappula, R. R. Donthiri, C. M. Darapaneni and A. Subbarayappa, *Tetrahedron Lett.*, 2014, **55**, 1793–1795.
17 X. P. Zhang and M. Schlosser, *Tetrahedron Lett.*, 1993, **34**, 1925–1928.
18 G. Stork and K. Zhao, *Tetrahedron Lett.*, 1989, **30**, 2173–2174.
19 M.-E. Lebrun, P. Le Marquand and C. Berthelette, *J. Org. Chem.*, 2006, **71**, 2009–2013.
20 J. I. Uenishi, R. Kawahama, O. Yonemitsu and J. Tsuji, *J. Org. Chem.*, 1998, **63**, 8965–8975.
21 J. I. Uenishi, R. Kawahama, Y. Shiga, O. Yonemitsu and J. Tsuji, *Tetrahedron Lett.*, 1996, **37**, 6759–6762.
22 W. Xv, W. Zhang, F. Zhang and C. Kuang, *J. Chem. Res.*, 2014, **38**, 115–117.
23 C. Kuang, Q. Yang, H. Senboku and M. Tokuda, *Tetrahedron*, 2005, **61**, 4043–4052.
24 R. B. Miller and G. McGarvey, *J. Org. Chem.*, 1978, **43**, 4424–4431.
25 H. C. Brown, T. Hamaoka, N. Ravindran, C. Subrahmanyam, V. Somayaji and N. G. Bhat, *J. Org. Chem.*, 1989, **54**, 6075–6079.
26 H. C. Brown, T. Hamaoka and N. Ravindran, *J. Am. Chem. Soc.*, 1973, **95**, 5786–5788.
27 N. A. Petasis and I. A. Zavialov, *Tetrahedron Lett.*, 1996, **37**, 567–570.
28 A. Hamajima and M. Isobe, *Angew. Chem., Int. Ed.*, 2009, **48**, 2941–2945.
29 M.-F. Zou and M.-Z. Deng, *J. Org. Chem.*, 1996, **61**, 1857–1858.
30 Z. Huang and E.-I. Negishi, *Org. Lett.*, 2006, **8**, 3675–3678.
31 C. Morrill and R. H. Grubbs, *J. Org. Chem.*, 2003, **68**, 6031–6034.
32 V. Sashuk, C. Samojlowicz, A. Szadkowska and K. Grela, *Chem. Commun.*, 2008, 2468–2470.
33 C. A. Celatka and J. S. Panek, *Tetrahedron Lett.*, 2002, **43**, 7043–7046.
34 H. J. Kim, R. Pongdee, Q. Wu, L. Hong and H.-W. Liu, *J. Am. Chem. Soc.*, 2007, **129**, 14582–14584.
35 P. Pawluc, G. Hreczycho, J. Szudkowska, M. Kubicki and B. Marciniec, *Org. Lett.*, 2009, **11**, 3390–3393.
36 B. Marciniec, *Acc. Chem. Res.*, 2007, **40**, 943–952.
37 B. Marciniec, M. Jankowska and C. Pietraszuk, *Chem. Commun.*, 2005, 663–665.
38 P. Pawluc, W. Prukala and B. Marciniec, *Eur. J. Org. Chem.*, 2010, 219–229.
39 P. Pawluc, J. Szudkowska, G. Hreczycho and B. Marciniec, *J. Org. Chem.*, 2011, **76**, 6438–6441.
40 P. Pawluc, A. Franczyk, J. Walkowiak, G. Hreczycho, M. Kubicki and B. Marciniec, *Tetrahedron*, 2012, **68**, 3545–3551.
41 P. Pawluc, A. Franczyk, J. Walkowiak, G. Hreczycho, M. Kubicki and B. Marciniec, *Org. Lett.*, 2011, **13**, 1976–1979.
42 P. Pawluc, G. Hreczycho, J. Walkowiak and B. Marciniec, *Synlett*, 2007, 2061–2064.
43 H. C. Brown, T. Hamaoka and N. Ravindran, *J. Am. Chem. Soc.*, 1973, **95**, 6456–6457.
44 V. S. Rawat and B. Sreedhar, *Synlett*, 2014, 1132–1136.
45 C. Feng, H. Wang, L. Xu and P. Li, *Org. Biomol. Chem.*, 2015, **13**, 7136–7139.
46 J. J. Mousseau, J. A. Bull, C. L. Ladd, A. Fortier, D. S. Roman and A. B. Charette, *J. Org. Chem.*, 2011, **76**, 8243–8261.
47 S. H. Kim, H.-X. Wei, S. Willis and G. Li, *Synth. Commun.*, 1999, **29**, 4179–4185.
48 C. Kuang, H. Senboku and M. Tokuda, *Tetrahedron Lett.*, 2001, **42**, 3893–3896.