One-pot synthesis of substituted styrenes from vicinal dibromoalkanes and arylboronic acids

A. A. Tikhonov,[a] A. A. Vasil´ev,[b]★ M. V. Chirskaya,[c] M. I. Struchkova,[b] N. L. Merkulova,[c] and S. G. Zlotin[b]

[a]*Moscow Chemical Lyceum 1303,*
4 Tamozhennyi pr., 111033 Moscow, Russian Federation
[b]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 135 5328. E-mail: vasiliev@ioc.ac.ru
[c]*ChemBridge Corp.,*
1 ul. Malaya Pirogovskaya, 119435 Moscow, Russian Federation.
Fax: +7 (495) 956 4948

Dehydrobromination of vicinal dibromoalkanes in systems comprising 1,2-dimethoxyethane, *N*-butyl-*N*´-methylimidazolium tetrafluoroborate (or tetrabutylammonium bromide), and a base with subsequent palladium-catalyzed cross-coupling of the thus formed bromoalkenes with arylboronic acids furnished substituted styrenes.

Key words: styrenes, bromoalkenes, boronic acids, cross-coupling, the Suzuki reaction, bromination, dehydrobromination, ionic liquids.

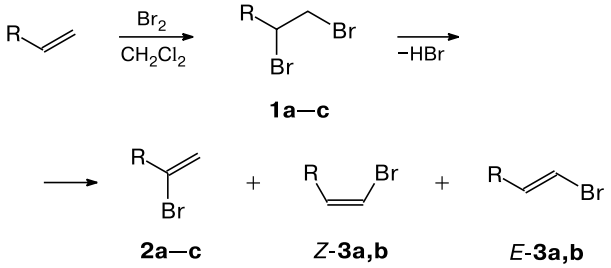
Among numerous methods for the synthesis of styrenes, reactions catalyzed by transition metal complexes (the Suzuki,[1] Heck,[2] and Stille[3] reactions) are of particular interest. From the preparative point of view, the first of them is the most convenient due to its lower substrate dependence, as well as to the fact that boron-containing secondary products formed in the course of the process can be easily separated from the cross-coupling products. One of the versions of the Suzuki reaction consists of the coupling of alkenyl halides with arylboron derivatives. For the synthesis of starting alkenyl halides,[4] it is convenient to make use of dehydrobromination of available vicinal dibromoalkanes with bases.

In the present work, we studied the possibility of synthesis of various styrenes using a one-pot sequence of two reactions, *viz.*, dehydrobromination of vicinal dibromoalkanes and the Suzuki cross-coupling of the thus formed bromoalkenes. This approach, when the same base is used in both stages of the process, makes it possible to avoid the bromoalkene isolation step, which considerably simplifies the procedure and in number of cases ensures the higher yields of the products. It should be taken into account that the media used for dehydrobromination must be compatible with the conditions of the second stage of cross-coupling.

Obviously, the selectivity of dehydrobromination of vicinal dibromoalkanes is a crucial factor that determines the preparative value of the method. Usually, a mixture of regio- and stereoisomers is formed in this reaction,[5] however, for some dibromides the selective formation of one of them is possible.[6] Recently, we have found[7] that dehydrobromination of 1-(2,3-dibromopropyl)cyclohexanol with K_2CO_3 in an ionic liquid, *N*-butyl-*N*´-methylimidazolium tetrafluoroborate ([bmim][BF_4]), proceeded regio- and stereoselectively with the formation of (*E*)-1-(3-bromoprop-2-en-1-yl)cyclohexanol.

In order to investigate the factor of 1,2-dibromoalkane structure and reaction conditions, we studied the dehydrobromination of model 1,2-dibromohexane (**1a**), 1,2-dibromo-1-cyclohexylethane (**1b**), and 1,2-dibromo-1-phenylethane (**1c**) in several systems, including ionic liquids (Scheme 1, Table 1).

Scheme 1



R = Bu (**a**), *cyclo*-C_6H_{11} (**b**), Ph (**c**)

It turned out that dehydrobromination of compounds **1a,b** with potassium carbonate or potassium phosphate in

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 116—123, January, 2007.

Table 1. Dehydrobromination of vicinal dibromides **1a—c** up to 100% conversion under various conditions

Entry	Dibromide	Base*	Solvent (catalyst**)	*T*/°C	*t*/h	Product composition (mol.%)	
						2	*Z*-**3** + *E*-**3**
1	**1a**	K_2CO_3	DMSO	20	24	—	—
2		K_2CO_3	DMSO	55	168	39	29 + 32
3		K_3PO_4	DMF	100	2	44	28 + 28
4		K_3PO_4	DMA	110	4.5	49	26 + 25
5		K_2CO_3	[bmim]BF_4	20	48	59	18 + 23
6		K_3PO_4	[bmim]BF_4	20	24	69	13 + 18
7		K_3PO_4	DME ([bmim]BF_4)	20	48	65	18 + 17
8		K_3PO_4	DME (Bu_4NBr)	70	4	53	25 + 22
9		KOH	DME ([bmim]BF_4)	20	3	73	13 + 14
10	**1b**	K_2CO_3	DMSO	20	24	—	—
11		K_2CO_3	[bmim]BF_4	20	72	98	2
12		K_3PO_4	DME ([bmim]Cl)	70	4	71	8 + 21
13	**1c**	K_3PO_4	DME ([bmim]BF_4)	70	3	100	—

* 4 equiv.
** ~30 mol.%.

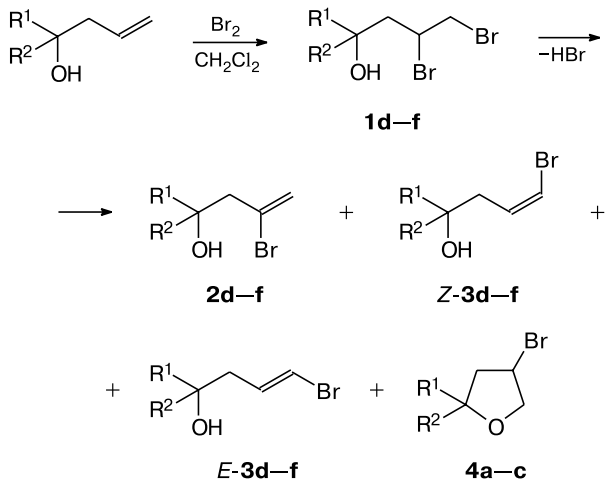
polar aprotic solvents, such as DMSO, DMF, and dimethylacetamide (DMA), proceeded effectively only at the temperatures ~100 °C (see Table 1, entries *1—4*). The use of potassium carbonate in [bmim]BF_4 enabled us to remarkably increase the rate of the reaction and to lower its temperature (see Table 1, entries *5* and *11*; *cf.* Ref. 7). High yields of the products were obtained by carrying out the reaction in 1,2-dimethoxyethane (DME) in the presence of ~30 mol.% of imidazolium ([bmim]BF_4, [bmim]Cl) or tetraalkylammonium (Bu_4NBr) salts (see Table 1, entries *7—9*, *12*, *13*). These additives apparently serve as phase transfer catalysts, since without them the process does not take place. The catalytic version of the reaction seems more preferable, since it allows one to diminish the consumption of expensive organic salts. The rate of dehydrobromination increases on moving from K_2CO_3 or K_3PO_4 to more basic potassium hydroxide (see Table 1, entry *9*).

The usual products of the reaction under consideration are mixtures of isomers **2**, *Z*-**3** and *E*-**3**. The content of isomer **2** increases in the series of starting dibromides **1a** < **1b** < **1c** so that in the latter case α-bromostyrene **2c** becomes the only dehydrobromination product (see Table 1, entry *13*).

The fraction of type **3** bromoalkenes grows higher for the dehydrobromination of 1,2-dibromoalkanes **1d—f** bearing hydroxyl group in position 4 (Scheme 2, Table 2). The process, however, is accompanied by cyclization into 3-bromotetrahydrofuran derivatives **4** (*cf.* Ref. 7).

The dehydrobromination media can, in principle, be used for the further cross-coupling of bromoalkenes thus formed with arylboronic acids. For example, the cross-coupling in Na_2CO_3—DME—H_2O in the presence of $Pd(PPh_3)_4$ [8] as well as in DMF in the presence

Scheme 2



R^1 = H, R^2 = C_6H_{13} (**1d—3d**, **4a**); $R^1 + R^2$ = $(CH_2)_5$ (**1e—3e**, **4b**); $R^1 + R^2$ = $(CH_2)_4$ (**1f—3f**, **4c**)

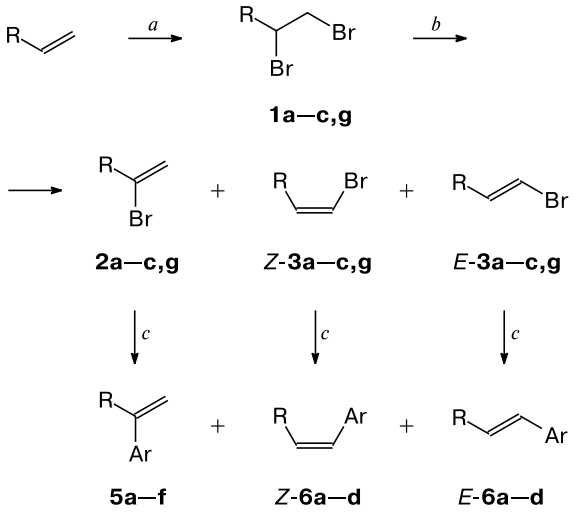
of $Pd(OAc)_2$ and powdered solid inorganic bases[9,10] were described. It is known that imidazolium salts, form-

Table 2. Dehydrobromination of hydroxyl-containing dibromo derivatives **1d—f** in [bmim]BF_4 (4 equiv. K_2CO_3, 20 °C, conversion 100%)

Entry	Compound	R^1, R^2	*t*/h	Product composition (mol.%)			
				2	*Z*-**3**	*E*-**3**	**4**
1	**1d**	H, C_6H_{13}	4	7	7	16	70
2	**1e**	$(CH_2)_5$	4	5	11	56	28
3	**1f**	$(CH_2)_4$	1	7	9	59	25

ing catalytically active complexes with palladium compounds,[11] have a beneficial effect on the process of cross-coupling. In fact, addition of arylboronic acids together with palladium catalyst into *in situ* formed mixture of dehydrobromination products **2**, *Z*-**3** and *E*-**3** effected the cross-coupling reaction leading to styrenes **5** and **6** (Scheme 3).

Scheme 3



1—3: R = Bu (**a**), *cyclo*-C_6H_{11} (**b**), Ph (**c**), Pr^i (**g**)

5, **6**	R	Ar	Yield (%)
a	Bu	Ph	63 (**5** + **6**)
b	Bu	4-$MeOC_6H_4$	75 (**5** + **6**)
c	*cyclo*-C_6H_{11}	4-$MeOC_6H_4$	69 (**5** + **6**)
d	Pr^i	4-$MeOC_6H_4$	64 (**5** + **6**)
e	Ph	4-$MeOC_6H_4$	54 (**5**)
f	Ph	Ph	51 (**5**)

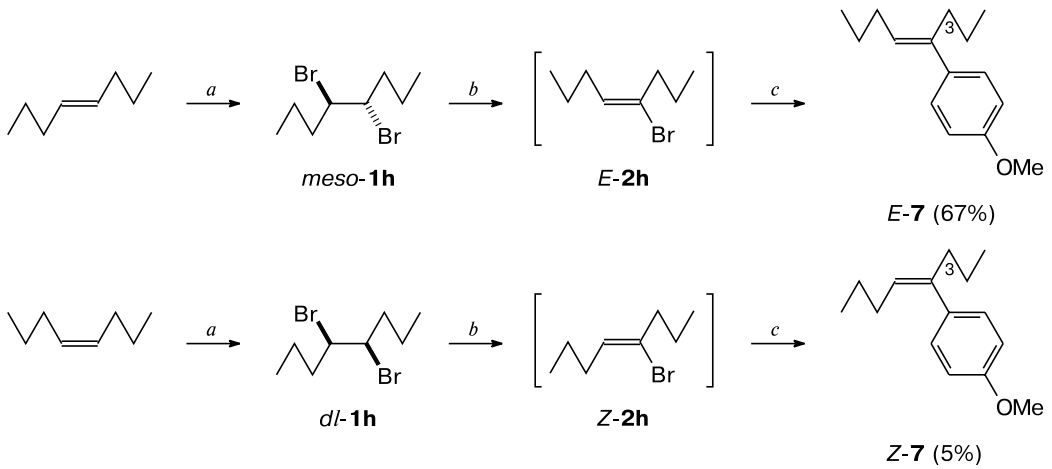
Reagents and conditions: *a*. Br_2, CH_2Cl_2. *b*. K_3PO_4, [bmim]BF_4, DME, 55 °C, 3 h. *c*. $ArB(OH)_2$, $Pd(PPh_3)_4$.

The isomeric composition of products **5** and **6** corresponds to the isomeric composition of dehydrobromination products **2** and **3** (see Table 1). From dibromide **1c**, individual 1,1-disubstituted alkenes **5e,f** were obtained. The reactions in DME—[bmim]BF_4 (see Experimental, method *A*) proceeded chemoselectively with the formation of cross-coupling products, whereas in DMF (method *B*, see Ref. 10), according to chromato-mass spectrometry data, the formation of considerable amount of biaryls (due to homodimerization of arylboronic acids) and dienes (due to homodimerization of alkenyl bromides) was observed. The preparative experiments were carried out according to method *A*, the main reaction products were identified by GC-MS and ^1H and ^{13}C NMR spectra.

The described sequence of reactions of symmetrical *meso*-4,5-dibromooctane (*meso*-**1h**), obtained by bromination of *trans*-oct-4-ene, leads to individual bromoalkene *E*-**2h** and, correspondingly, to styrene *E*-**7** with *cis*-orientation of propyl groups at the double bond in 67% yield (Scheme 4; for the stereochemistry of bromination—dehydrobromination of *cis*- and *trans*-alkenes see Ref. 12). For *dl*-4,5-dibromooctane (*dl*-**1h**), obtained from *cis*-oct-4-ene, dehydrobromination to bromoalkene *Z*-**2h** proceeds quite effectively (GLC data). However, subsequent cross-coupling of this compound with 4-methoxyphenylboronic acid gives the styrene derivative *Z*-**7** in 5% yield only. This apparently occurs due to the steric hindrance, created by propyl group *cis* to the bromine atom. The configurations of compounds **7** were unambiguously proved by ^{13}C NMR data: the allylic C(3) atom in *E*-**7** isomer resonates at δ 32.2, whereas the analogous signal for isomer *Z*-**7** is observed at δ 41.5 (the effect of steric compression).

By analogy, *trans*-1,2-dibromocyclooctane (**1i**) was transformed into individual *cis*-1-phenylcyclooct-1-ene (**8**) in 65% yield (Scheme 5). It is known that interme-

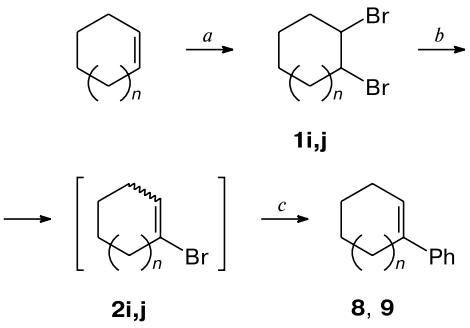
Scheme 4



Reagents and conditions: *a*. Br_2, CH_2Cl_2. *b*. K_3PO_4, [bmim]BF_4, DME, 55 °C, 3 h. *c*. 4-$MeOC_6H_4B(OH)_2$, $Pd(PPh_3)_4$.

diate 1-bromocyclooct-1-ene (**2i**), resulted from the dehydrobromination of compound **1i**, has *cis*-configuration, since the *trans*-elimination of HBr would have led to the strained *trans*-1-bromocyclooctene (*cf.* Ref. 13). Bromination of a mixture of *cis*- and *trans*-cyclododecenes leads to a diastereomeric mixture of 1,2-dibromocyclododecanes (**1j**), dehydrobromination of which gives a mixture of *cis*- and *trans*-1-bromocyclododec-1-enes (**2j**). It so happened that only *cis*-isomer with more sterically accessible bromine atom reacts with the phenylboronic acid. The configuration of product **9** has been ascertained by comparison of ^{1}H NMR characteristic signals with those of the authentic sample, prepared by dehydration of 1-phenylcyclododecanol.[14] Dehydrobromination of *trans*-1,2-dibromocyclohexane under investigated conditions actually does not occur (*cf.* Refs 13, 15).

Scheme 5

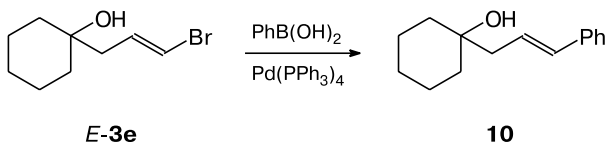


n = 3 (**1i**, **2i**, **8**), 7 (**1j**, **2j**, **9**)

Reagents and conditions: *a*. Br_2, CH_2Cl_2. *b*. K_3PO_4, $[bmim]BF_4$, DME, 55 °C, 3 h. *c*. $PhB(OH)_2$, $Pd(PPh_3)_4$.

Attempted one-pot sequence of dehydrobromination and cross-coupling starting from 4-hydroxy-1,2-dibromoalkanes **1d—f** leads to the formation, along with the target styrenes, a considerable amount of byproducts (^{1}H NMR data), which are difficult to separate by column chromatography. In this case, it is reasonable to make phenylboronic acid react with the preliminarily purified bromoalkene, for example, *E*-**3e**. As a result, styrene derivative **10** was obtained in 47% yield (Scheme 6). It should be noted that the alternative synthesis of alcohols of type **10** by reaction of carbonyl compounds with organoelement cinnamyl derivatives is accompanied as a rule by allylic rearrangement of the nucleophilic component.[16]

Scheme 6



In the conclusion, we have studied the scope of one-pot procedure for the synthesis of substituted styrenes, which includes the sequence of dehydrobromination of vicinal dibromoalkanes and cross-coupling of bromoalkenes thus formed with arylboronic acids. In a number of cases, this approach makes easier the preparative synthesis of different styrenes. It should be noted that earlier the similar approach has been described only for the 1,2-dibromo-3,3,3-trifluoropropane[17] and 1,2-dibromoethane,[18] which form individual dehydrobromination products.

Experimental

NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13 (^{1}H) and 75.47 (^{13}C) MHz) in $CDCl_3$. Chromato-mass spectra were taken with Agilent Technologies 85973 Network instrument (EI, 70 eV), connected with Agilent Technologies 6890 chromatograph (HP-5MS 30000×0.25 mm capillary column, the temperature of injector and flame-ionization detector of 280 °C, temperature programming: 60→300 °C (5 min), then 10 deg min^{-1}, helium as the carrier gas, 2 mL min^{-1}). During the analysis the total ionic current and the signals of the flame-ionization detector were recorded. The GLC-analysis was performed with Chrom-5 instrument (2×2500 mm column, SE-30 on Chromaton N-AW-DMCS, the thermostat temperature (depending on the nature of the analyzed compound) varied in the range of 130—180 °C, the injector and detector temperature — 250 °C).

N-Butyl-*N*′-methylimidazolium chloride ([bmim]Cl)[19] and *N*-butyl-*N*′-methylimidazolium tetrafluoroborate ($[bmim]BF_4$)[20] were obtained by known procedures and before use were pre-dried for 8—10 h at 50 °C (~1 Torr). Potassium carbonate was calcined in air. Solvents were dried by standard methods. Potassium phosphate, 4-methoxyphenylboronic acid, and *trans*-oct-4-ene were purchased from Aldrich, phenylboronic acid and cyclododecene, from Acros, vinylcyclohexane, from Fluka, and were used without further purification. Hex-1-ene and styrene (Reakhim) were redistilled before use. *cis*-Oct-4-ene was obtained by partial hydrogenation of oct-4-yne (1 atm H_2, Raney Ni, 5% pyridine in EtOH). Column chromatography was performed on Silica gel (Merck).

Dec-1-en-4-ol, 1-allylcyclohexanol, and 1-allylcyclopentanol were obtained by modified procedure.[21] To a flask with 50 mmol of carbonyl compound, 50 mL of THF, 5 g (77 mmol) of zinc dust, and ~1 mL of allyl bromide, 1—2 drops of acetic acid were added with stirring to initiate the reaction. After the exothermic stage was over, the rest allyl bromide was added (total of 9.1 g, 6.5 mL, 75 mmol). The mixture was stirred for 2—3 h until complete conversion of the carbonyl compound (GLC-control). The mixture was quenched with 5% H_2SO_4, light petroleum was added, and this was filtered through a glass filter. The organic layer was separated and washed several times with saturated $NaHCO_3$ solution until the aqueous layers became clear. The organic layer was dried with $MgSO_4$, concentrated and the residue was distilled *in vacuo*. The physical and chemical data of compounds obtained corresponded to those reported in the literature.[21,22]

Dec-1-en-4-ol. The yield was 3.78 g (48%), b.p. 105 °C (15 Torr).

1-Allylcyclohexanol. The yield was 4.48 g (64%), b.p. 80 °C (10 Torr).

1-Allylcyclopentanol. The yield was 5.4 g (43%), b.p. 70—80 °C (15 Torr).

Vicinal dibromides 1a—j (general procedure). To a solution of an olefin (1 mmol) in CH_2Cl_2 (3 mL), bromine (192 mg, 0.062 mL, 1.2 mmol) in CH_2Cl_2 (2 mL) was added at 0—5 °C under stirring until the color persisted. An aqueous solution of $Na_2S_2O_3$ and $NaHCO_3$ was added to the mixture, which was stirred for another 15—20 min. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2, the extracts were dried with $CaCl_2$ or Na_2SO_4 and concentrated *in vacuo*. The residue was used in the next stage without additional purification.

Dehydrobromination of vicinal dibromides 1a—j (general procedure). To a mixture of vicinal dibromide **1** (1 mmol) and [bmim]BF_4 (1 g), freshly powdered K_2CO_3 (552 mg, 4 mmol) was added under stirring and the mixture was stirred at the temperature indicated in Tables 1 and 2. Periodically, aliquots were withdrawn, which were suspended in water, extracted with hexane, and the extracts were analyzed by GLC to monitor the conversion of starting dibromide **1** and the isomeric composition of the products formed. Reaction with the use of other solvents and bases were carried out similarly. The duration and temperatures of the reactions as well as the isomeric compositions of the products formed are given in Tables 1 and 2. After complete conversion of dibromide **1**, the mixture was diluted with water, extracted with hexane, the extract was dried and concentrated *in vacuo*. The residue was analyzed by ^{1}H NMR and, if needed, purified by distillation and/or by column chromatography.

Bromohexenes 2a and 3a. 2-Bromohex-1-ene (**2a**). ^{1}H NMR, characteristic signals, δ: 2.44 (t, 2 H, =C—CH_2, J = 7.4 Hz); 5.39, 5.55 (both s, 1 H each, $=CH_2$). (*Z*)-1- Bromohex-1-ene (*Z*-**3a**). ^{1}H NMR, characteristic signals, δ: 2.21 (br.q, 2 H, =C—CH_2, J = 7.4 Hz). (*E*)-1-Bromohex-1-ene (*E*-**3a**). ^{1}H NMR, characteristic signals, δ: 2.06 (br.q, 2 H, =C—CH_2, J = 7.4 Hz). The spectral characteristics are in agreement with those described in the literature.[5a]

Bromo cyclohexyl ethylenes 2b and 3b. Mixture of isomers, b.p. 80—82 °C (15 Torr). Found (%): C, 50.60; H, 7.04. $C_8H_{13}Br$. Calculated (%): C, 50.81; H, 6.93. 1-Bromo-1-cyclohexylethylene (**2b**). ^{1}H NMR, characteristic signals, δ: 2.18 (m, 1 H, =C—CH); 5.38, 5.56 (both s, 1 H each, $=CH_2$). ^{13}C NMR, δ: 25.7 (C(4)$_{cyclo\text{-}C_6H_{11}}$); 25.9 (C(3)$_{cyclo\text{-}C_6H_{11}}$, C(5)$_{cyclo\text{-}C_6H_{11}}$); 32.1 (C(2)$_{cyclo\text{-}C_6H_{11}}$, C(6)$_{cyclo\text{-}C_6H_{11}}$); 48.5 (C(1)$_{cyclo\text{-}C_6H_{11}}$); 114.0 ($=CH_2$); 141.2 (=C). (*Z*)-1-Bromo-2-cyclohexylethylene (*Z*-**3b**). ^{1}H NMR, characteristic signals, δ: 2.53 (m, 1 H, =C—CH); 5.93 (t, 1 H, =CH, J = 7.4 Hz); 6.05 (d, 1 H, =CH, J = 7.4 Hz). (*E*)-1-Bromo-2-cyclohexylethylene (*E*-**3b**). ^{1}H NMR, characteristic signals, δ: 2.02 (m, 1 H, =C—CH); 6.00 (d, =CH, J = 13.6 Hz); 6.15 (dd, =CH, J = 13.6 Hz, J = 7.3 Hz). (*E*,*Z*)-Isomers **3b**. ^{13}C NMR, characteristic signals without assignment, δ: 25.5, 31.6, 32.2, 38.8, 41.7, 103.0, 105.4, 140.1, 143.6.

Dehydrobromination of 1,2-dibromodecan-4-ol (1d). Using K_2CO_3 in [bmim]BF_4 gave a mixture of 3-bromo-5-hexyltetrahydrofuran (**4a**) and bromodec-1-en-4-ols **2d** and **3d** (7 : 3). After workup and column chromatography 110 mg (47%) of tetrahydrofuran **4a** and 45 mg (19%) of mixture of alcohols **2d** and **3d** were obtained.

Bromodec-1-en-4-ols 2d, 3d. Oil. Found (%): C, 51.46; H, 7.97. $C_{10}H_{19}BrO$. Calculated (%): C, 51.08; H, 8.14. ^{1}H NMR spectrum of the mixture consisted of the following groups of overlapped signals of the three isomers, δ: 0.89 (m, 3 H, Me); 1.26—1.74 (m, 11 H, CH_2, OH). 2-Bromodec-1-en-4-ol (**2d**). ^{1}H NMR, characteristic signals, δ: 2.51 (dd, 1 H, =C—CH_2, J = 14.4 Hz, J = 8.3 Hz); 2.57 (dd, 1 H, =C—CH_2, J = 14.4 Hz, J = 3.9 Hz); 3.93 (m, 1 H, OCH); 5.53, 5.69 (both s, 1 H each, $=CH_2$). ^{13}C NMR, δ: 14.0 (Me); 22.6, 25.5, 29.2, 31.8, 36.4 (all CH_2); 49.4 (=C—$\underline{C}H_2$); 69.1 (OCH); 119.5 ($=CH_2$); 130.9 (=CBr). (*Z*)-1-Bromodec-1-en-4-ol (*Z*-**3d**). ^{1}H NMR, characteristic signals, δ: 2.06—2.40 (m, 2 H, =C—CH_2); 3.76 (m, 1 H, OCH); 6.18—6.27 (m, 2 H, CH=CH). (*E*)-1-Bromodec-1-en-4-ol (*E*-**3d**). ^{1}H NMR, characteristic signals, δ: 2.06—2.40 (m, 2 H, =C—CH_2); 3.67 (m, 1 H, OCH); 6.14 (d, 1 H, =CH, J = 13.5 Hz); 6.23 (dt, 1 H, =CH, J = 13.5 Hz, J = 7.3 Hz). ^{13}C NMR, δ: 14.0 (Me); 22.7, 25.5, 29.7, 31.9, 36.8 (all CH_2); 40.7 (=C—$\underline{C}H_2$); 70.5 (OCH); 106.7 (=CHBr); 134.3 (=CH).

3-Bromo-5-hexyltetrahydrofuran (4a). Mixture of two diastereomers (3 : 1), oil, b.p. 95 °C (1 Torr). Found (%): C, 51.06; H, 8.21; Br, 33.66. $C_{10}H_{19}BrO$. Calculated (%): C, 51.08; H, 8.14; Br, 33.98. ^{1}H NMR spectrum of the mixture consisted of the following groups of overlapped signals of both diastereomers, δ: 0.88 (t, Me, J = 6.9 Hz); 1.22—1.78 (m, 10 H, CH_2). Major diastereomer. ^{1}H NMR, characteristic signals, δ: 2.00 (ddd, 1 H, CH_2, J = 13.7 Hz, J = 9.1 Hz, J = 6.6 Hz); 2.33 (ddd, 1 H, CH_2, J = 13.7 Hz, J = 5.9 Hz, J = 2.4 Hz); 4.01 (dd, 1 H, OCH_2, J = 10.5 Hz, J = 3.7 Hz); 4.19 (m, 1 H, CHBr); 4.30 (dd, 1 H, OCH_2, J = 10.5 Hz, J = 5.1 Hz); 4.44 (m, 1 H, OCH). ^{13}C NMR, δ: 14.0 (Me); 22.5, 26.1, 29.3, 31.7, 35.0, 43.0 (all CH_2); 47.1 (CHBr); 76.1 (OCH_2); 78.5 (OCH). Minor diastereomer. ^{1}H NMR, characteristic signals, δ: 1.95 (m, 1 H, CH_2); 2.63 (dt, 1 H, CH_2, J = 13.7 Hz, J = 6.9 Hz); 3.88 (quint, 1 H, CHBr, J = 6.9 Hz); 3.98—4.06 (m, 2 H, OCH_2); 4.35 (m, 1 H, OCH). ^{13}C NMR, δ: 14.0 (Me); 22.5, 26.0, 29.2, 31.7, 35.8, 42.7 (all CH_2); 44.9 (CHBr); 75.5 (OCH_2); 79.6 (OCH).

Dehydrobromination of 1-(2,3-dibromopropyl)cyclohexanol (1e) gave products **2e**, **3e**, and **4b**, the spectral characteristics of which agreed with those described earlier.[7]

Dehydrobromination of 1-(2,3-dibromopropyl)cyclopentanol (1f) gave products **2f**, **3f**, and **4c**. After column chromatography tetrahydrofuran **4c** and mixture of alcohols **2f** and **3f** were obtained.

1-(Bromopropenyl)cyclopentanols 2f and 3f. Found (%): C, 46.70; H, 6.33. $C_8H_{13}BrO$. Calculated (%): C, 46.85; H, 6.39. ^{1}H NMR spectrum of the mixture consisted of the following groups of overlapped signals of the three isomers, δ: 1.53—1.88 (m, CH_2 of cyclopentane). 1-(2-Bromoprop-2-en-1-yl)cyclopentanol (**2f**). ^{1}H NMR, characteristic signals, δ: 2.79 (s, 2 H); 5.60, 5.70 (both s, 1 H each). ^{13}C NMR, characteristic signals, δ: 23.5, 39.6, 51.8 (all CH_2); 120.7 ($=CH_2$); 129.1 (=C). (*Z*)-1-(3-Bromoprop-2-en-1-yl)cyclopentanol (*Z*-**3f**). ^{1}H NMR, characteristic signals, δ: 2.53 (d, 2 H, J = 5.6 Hz). ^{13}C NMR, characteristic signals, δ: 39.7, 41.4 (both CH_2); 109.8 (=CHBr); 131.2 (=CH). (*E*)-1-(3-Bromoprop-2-en-1-yl)cyclopentanol (*E*-**3f**). ^{1}H NMR, characteristic signals, δ: 2.33 (d, 2 H, J = 7.6 Hz); 6.14 (d, 1 H, J = 13.6 Hz); 6.29 (dt, 1 H, J = 13.6 Hz, J = 7.6 Hz). ^{13}C NMR, δ: 23.7, 39.4, 44.6 (all CH_2); 81.3 (COH); 106.9 (=CHBr); 134.1 (=CH).

3-Bromo-1-oxaspiro[4.4]nonane (4c). Oil, b.p. 101—103 °C (15 Torr). Found (%): C, 46.91; H, 6.46; Br, 38.82. $C_8H_{13}BrO$. Calculated (%): C, 46.85; H, 6.39; Br, 38.96. ^{1}H NMR, δ: 1.46—1.81 (m, 7 H); 1.99 (m, 1 H); 2.25 (dd, 1 H, J = 13.9 Hz, J = 4.9 Hz); 2.47 (dd, 1 H, J = 13.9 Hz, J = 7.3 Hz); 3.93 (dd, 1 H, J = 10.0 Hz, J = 5.1 Hz); 4.14 (dd, 1 H, J = 10.0 Hz, J = 5.6 Hz); 4.37 (m, 1 H). ^{13}C NMR, δ: 23.6, 24.0, 38.6, 38.7 (all CH_2); 45.5 (CHBr); 46.7 (CH_2); 74.7 (OCH_2); 91.4 (OC).

One-pot synthesis of styrenes from vicinal dibromides (general procedure). ***A.*** To a solution of 1.5 mmol of vicinal dibromide in 4.5 mL of DME, [bmim]BF_4 (100 mg, 0.44 mmol) (or equimolar amount of the other phase transfer catalyst) and 1.274 g (6 mmol) of K_3PO_4 were added. The mixture was refluxed with stirring for 1—2 h until complete conversion of starting dibromide (GLC control). Oxygen was removed from the mixture by several cycles of evacuation (before vigorous boiling of the solvent started) and filling with argon. After addition of $Pd(PPh_3)_4$ (40 mg, 2.3 mol.%) the reaction mixture was stirred for 30—40 min and then 1.5 mmol of the corresponding arylboronic acid and 3 mL of water were added, and the mixture was refluxed for 4—6 h under argon. The mixture was cooled, diluted with water, and the organic components were extracted with benzene. The extracts were dried with Na_2SO_4 and concentrated *in vacuo*. Column chromatography of the residue (1—3% of ethyl acetate in hexane as the eluent) gave the mixtures of corresponding isomeric styrenes, which we were not able to separate by this method. The yields were 50—75%.

B. A mixture of dibromide **1** (1 mmol) and K_3PO_4 (848 mg, 4 mmol) in DMF (2 mL) was heated to ~100 °C and stirred until complete conversion of starting compound **1** (2—4 h). The mixture was cooled and deoxygenated by triple sequential evacuation and filling with argon, then $Pd(OAc)_2$ (10 mg, 4.5 mol.%) and 1.2 mmol of the corresponding arylboronic acid were added. The reaction mixture was stirred for 4—5 h at ~90 °C, diluted with water, and the organic components were extracted with benzene. The extract was dried, filtered through a short pad of silica and analyzed by chromato-mass spectrometry.

Phenylhexenes 5a and 6a. Total yield was 151 mg (63%). ^{1}H NMR spectrum of the mixture consisted of the following groups of overlapped signals of the three isomers, δ: 0.97 (t, 3 H, Me, J = 6.6 Hz); 1.35—1.57 (m, 4 H, CH_2); 7.21—7.53 (m, 5 H, Ph). 2-Phenylhex-1-ene (**5a**). ^{1}H NMR, characteristic signals, δ: 2.58 (t, 2 H, =C—CH_2, J = 7.9 Hz); 5.13, 5.33 (both s, 1 H each, =CH_2). MS, m/z: 160 $[M]^+$. (*Z*)-1-Phenylhex-1-ene (*Z*-**6a**). ^{1}H NMR, characteristic signals, δ: 2.41 (br.q, 2 H, =C—CH_2, J = 7.2 Hz); 5.74 (dt, 1 H, =CH, J = 11.8 Hz, J = 7.2 Hz); 6.48 (d, 1 H, =CH, J = 11.2 Hz). MS, m/z: 160 $[M]^+$. (*E*)-1-Phenylhex-1-ene (*E*-**6a**). ^{1}H NMR, characteristic signals, δ: 2.27 (br.q, 2 H, =C—CH_2, J = 7.2 Hz); 6.29 (dt, 1 H, =CH, J = 15.8 Hz, J = 6.6 Hz); 6.46 (d, 1 H, =CH, J = 15.8 Hz). MS, m/z: 160 $[M]^+$. The spectral characteristics of the compounds obtained were in agreement with those described in the literature.[23]

(4-Methoxyphenyl)hexenes 5b and 6b. Total yield was 214 mg (75%). ^{1}H NMR spectrum of the mixture consisted of the following groups of overlapped signals of the three isomers, δ: 0.93 (t, 3 H, Me, J = 7.4 Hz); 1.30—1.52 (m, 4 H, CH_2); 3.83 (s, 3 H, OMe); 6.89 (d, 2 H, H arom., J = 8.8 Hz). 2-(4-Methoxyphenyl)hex-1-ene (**5b**). ^{1}H NMR, characteristic signals, δ: 2.50 (t, 2 H, =C—CH_2, J = 7.4 Hz); 5.00, 5.22 (both s, 1 H each, =CH_2); 7.38 (d, 2 H, H arom., J = 8.8 Hz). ^{13}C NMR, δ: 14.0 (q); 22.5, 30.6, 35.2 (all t); 55.3 (q); 110.5 (t); 113.7, 127.2 (both d); 134.0, 148.1, 159.0 (all s). MS, m/z: 190 $[M]^+$. (*Z*)-1-(4-Methoxyphenyl)hex-1-ene (*Z*-**6b**). ^{1}H NMR, characteristic signals, δ: 2.35 (br.q, 2 H, =C—CH_2, J = 6.6 Hz); 5.60 (dt, 1 H, =CH, J = 11.8 Hz, J = 7.4 Hz); 6.36 (d, 1 H, =CH, J = 11.8 Hz); 7.25 (d, 2 H, H arom., J = 8.8 Hz). ^{13}C NMR, δ: 14.0 (q); 22.5, 28.5, 32.3 (all t); 55.3 (q); 113.7, 128.2, 130.0, 131.7 (all d); 130.5, 158.1 (both s). MS, m/z: 190 $[M]^+$. (*E*)-1-(4-Methoxyphenyl)hex-1-ene (*E*-**6b**). ^{1}H NMR, characteristic signals, δ: 2.22 (br.q, 2 H, =C—CH_2, J = 6.6 Hz); 6.11 (dt, 1 H, =CH, J = 15.4 Hz, J = 7.4 Hz); 6.35 (d, 1 H, =CH, J = 15.4 Hz). MS, m/z: 190 $[M]^+$. The spectral characteristics of the compounds obtained were in agreement with those described in the literature.[23]

Cyclohexyl 4-methoxyphenyl ethylenes 5c and 6c. Total yield was 224 mg (69%). ^{1}H NMR spectrum of the mixture consisted of the following groups of overlapped signals of the three isomers, δ: 1.10—1.44, 1.64—1.92 (both m, 5 H each, CH_2); 3.82 (s, 3 H, OMe); 6.87, 7.29 (both d, 2 H each, H arom., J = 8.6 Hz). 1-Cyclohexyl-1-(4-methoxyphenyl)ethylene (**5c**). ^{1}H NMR, characteristic signals, δ: 2.44 (m, 1 H, =C—CH); 4.96, 5.10 (both s, 1 H each, =CH_2). ^{13}C NMR, δ: 26.6, 27.0, 32.9 (all CH_2); 42.6 (CH); 55.3 (OMe); 109.1 (=CH_2); 113.5, 127.6 (both =CH arom.); 135.3 (=C arom.); 154.3 (=C olefin); 158.8 (=C—O). MS, m/z: 216 $[M]^+$. (*Z*)-2-Cyclohexyl-1-(4-methoxyphenyl)ethylene (*Z*-**6c**). ^{1}H NMR, characteristic signals, δ: 2.58 (m, 1 H, =C—CH); 5.42 (dd, 1 H, =CH, J = 11.8 Hz, J = 9.6 Hz); 6.26 (d, 1 H, =CH, J = 11.8 Hz). MS, m/z: 216 $[M]^+$. (*E*)-2-Cyclohexyl-1-(4-methoxyphenyl)ethylene (*E*-**6c**). ^{1}H NMR, characteristic signals, δ: 2.12 (m, 1 H, =C—CH); 6.05 (dd, 1 H, =CH, J = 16.2 Hz, J = 6.6 Hz); 6.31 (d, 1 H, =CH, J = 16.2 Hz). MS, m/z: 216 $[M]^+$. The spectral characteristics of the compounds obtained were in agreement with those described in the literature.[24]

(4-Methoxyphenyl)-3-methylbut-1-enes 5d and 6d. Total yield was 169 mg (64%). ^{1}H NMR spectrum of the mixture consisted of the following groups of overlapped signals of the three isomers, δ: 1.14 (d, 6 H, *gem*-Me, J = 6.6 Hz); 3.84 (s, 3 H, OMe); 6.89, 7.33 (both d, 2 H each, H arom., J = 8.6 Hz). 2-(4-Methoxyphenyl)-3-methylbut-1-ene (**5d**). ^{1}H NMR, characteristic signals, δ: 2.84 (sept, 1 H, =C—CH, J = 6.6 Hz); 5.00, 5.14 (both s, 1 H each, =CH_2). ^{13}C NMR, δ: 22.2 (*gem*-Me); 32.4 (CH); 55.3 (OMe); 108.8 (=CH_2); 113.6, 127.7 (both =CH arom.); 136.0 (=C arom.); 155.2 (=C olefin); 158.9 (=C—O). MS, m/z: 176 $[M]^+$. (*Z*)-1-(4-Methoxyphenyl)-3-methylbut-1-ene (*Z*-**6d**). ^{1}H NMR, characteristic signals, δ: 5.42 (t, 1 H, =CH, J = 11.0 Hz); 6.27 (d, 1 H, =CH, J = 11.0 Hz). MS, m/z: 176 $[M]^+$. (*E*)-1-(4-Methoxyphenyl)-3-methylbut-1-ene (*E*-**6d**). ^{1}H NMR, characteristic signals, δ: 6.09 (dd, 1 H, =CH, J = 16.2 Hz, J = 6.6 Hz); 6.32 (d, 1 H, =CH, J = 16.1 Hz). MS, m/z: 176 $[M]^+$. The spectral characteristics of the compounds obtained were in agreement with those described in the literature.[24,25]

1-(4-Methoxyphenyl)-1-phenylethylene (5e). The yield was 170 mg (54%). ^{1}H NMR, δ: 3.85 (s, 3 H); 5.40, 5.42 (both s, 1 H each); 6.89, 7.31 (both d, 2 H each, J = 8.8 Hz); 3.37 (m, 5 H). ^{13}C NMR, δ: 55.3 (OMe); 112.8 (=CH_2); 113.6, 127.6, 128.1, 128.3, 129.3 (all =CH); 134.1, 141.9, 149.6 (all =C); 159.4 (=C—O). The spectral characteristics of the compounds obtained were in agreement with those described in the literature.[18,26]

1,1-Diphenylethylene (5f). The yield was 138 mg (51%). ^{1}H NMR, δ: 5.57 (s, 2 H); 7.38—7.50 (m, 10 H). ^{13}C NMR, δ: 114.2 (=CH_2); 127.6, 128.1 (CH arom.); 141.4 (C arom.); 150.0 (=C). The spectral characteristics were in agreement with those described in the literature.[27]

(*E*)-4-(4-Methoxyphenyl)oct-4-ene (*E*-7). The yield was 220 mg (67%). ^{1}H NMR, δ: 0.96, 1.04 (both t, 3 H each, J = 7.4 Hz); 1.44, 1.54 (both sext, 2 H each, J = 7.4 Hz); 2.24 (q, 2 H, J = 7.4 Hz); 2.53 (t, 2 H, J = 7.4 Hz); 3.85 (s, 3 H); 5.67 (t, 1 H, J = 6.6 Hz); 6.91, 7.35 (both d, 2 H each, J = 8.8 Hz). ^{13}C NMR, δ: 13.9 (2 Me); 21.8, 23.1, 30.6 (all CH_2); 32.2 (C(3)H_2); 55.1 (OMe); 113.4, 127.3, 127.8 (all =CH); 136.0, 139.3 (both =C); 158.3 (=C—O). MS, m/z: 218 $[M]^+$. The spectral characteristics were in agreement with those described in the literature.[28]

(*Z*)-4-(4-Methoxyphenyl)oct-4-ene (*Z*-7). The yield was 16 mg (5%). ^{1}H NMR, δ: 0.86, 0.88 (both t, 3 H each, J = 7.4 Hz); 1.27—1.42 (m, 4 H); 1.94 (q, 2 H, J = 7.4 Hz); 2.30 (t, 2 H, J = 7.4 Hz); 3.83 (s, 3 H); 5.42 (t, 1 H, J = 7.4 Hz); 6.88, 7.07 (both d, 2 H each, J = 8.8 Hz). ^{13}C NMR, δ: 13.5, 13.8 (both Me); 21.2, 23.3, 30.9 (all CH_2); 41.5 (C(3)H_2); 55.1 (OMe); 113.3, 127.1, 129.4 (all =CH); 133.8, 140.2 (both =C); 158.0 (=C—O). The spectral characteristics were in agreement with those described in the literature.[29]

(*E*)-1-Phenylcyclooctene (8). The yield was 181 mg (65%). ^{1}H NMR, δ: 1.41—1.84 (m, 8 H); 2.33, 2.67 (both m, 2 H each); 6.06 (t, 1 H, J = 8.3 Hz); 7.18—7.52 (m, 5 H). ^{13}C NMR, δ: 26.1, 26.9, 27.4, 28.5, 29.4, 30.0 (all CH_2); 125.7, 126.4, 127.9, 128.2 (all =CH); 140.2, 143.2 (both =C). MS, m/z: 186 $[M]^+$. The spectral characteristics were in agreement with those described in the literature.[30]

(*E*)-1-Phenylcyclododecene (9). The chromato-mass spectrometry data showed the following composition of the reaction product: cyclododecene ($[M]^+$ 166) 12%, *Z*-**2j** ($[M]^+$ 244 for ^{79}Br) 38%, *E*-**2j** ($[M]^+$ 244) 8%, **9** ($[M]^+$ 242) 41%. For identification of the target component of the mixture, an independent synthesis[14] of (*E*,*Z*)-1-phenylcyclododecenes (9 : 1) was performed. (*E*)-Isomer. ^{1}H NMR, δ: 1.26—1.38 (m, 2 H); 1.42—1.62 (m, 12 H); 1.62—1.74 (m, 2 H); 2.38 (q, 2 H, C(3)H_2, J = 7.4 Hz); 2.70 (t, 2 H, C(12)H_2, J = 7.4 Hz); 5.69 (t, 1 H, C(2)H, J = 8.1 Hz); 7.30 (m, 1 H, H arom.); 7.35 (m, 4 H, H arom.). ^{13}C NMR, δ: 22.4, 22.5, 24.3, 24.4, 24.8, 24.9, 25.3, 25.4, 25.6 (all CH_2); 27.4 (C(12)H_2); 126.3, 126.7, 128.0 (all CH arom.); 130.2 (C(2)H); 140.4 (C arom.); 143.4 (C(1)). (*Z*)-Isomer. ^{1}H NMR, characteristic signals, δ: 2.14 (m, 2 H, C(3)H_2); 2.56 (m, 2 H, C(12)H_2); 5.86 (t, 1 H, C(2)H, J = 8.1 Hz). ^{13}C NMR, δ: 23.2, 23.8, 24.0, 24.3, 26.1, 26.3, 27.2, 27.6, 29.1 (all CH_2); 37.0 (C(12)H_2); 126.2, 127.9, 128.3 (all CH); 138.4, 140.8 (both C).

1-[(2*E*)-3-Phenylprop-2-en-1-yl]cyclohexanol (10). A mixture of 1-[(2*E*)-(3-bromoprop-2-en-1-yl)]cyclohexanol (*E*-**3e**) (365 mg, 1.67 mmol) and $Pd(PPh_3)_4$ (40 mg, ~2 mol.%) in DME (2 mL) was stirred for 40 min under argon (during this time, the dark yellow precipitate formed). Then phenylboronic acid (244 mg, 2.0 mmol) was added in one portion under argon followed by a degassed solution of Na_2CO_3 (0.54 g) in water (2.1 mL). The mixture was refluxed with stirring for 6 h while precipitation of palladium black was observed. The mixture was cooled, diluted with water, and the organic components were extracted with benzene. The extracts were dried with Na_2SO_4 and concentrated *in vacuo*. Column chromatography of the residue (1→5% gradient of ethyl acetate in hexane as the eluent) gave 170 mg (47%) of compound **10** as a viscous solidifying oil. ^{1}H NMR, δ: 1.20—1.80 (m, 11 H); 2.39 (d, 2 H, J = 7.4 Hz); 6.31 (dt, 1 H, J = 15.4 Hz, J = 7.4 Hz); 6.48 (d, 1 H, J = 15.4 Hz); 7.18—7.43 (m, 5 H). ^{13}C NMR, δ: 22.1, 25.7, 37.4, 45.9 (all CH_2); 71.5 (OC); 125.3, 126.1, 127.1, 128.4, 133.5 (all =CH); 137.3 (=C). The spectral characteristics were in agreement with those described in the literature.[31]

This work was financially supported by the Russian Federation President Council for Grants (Program for Support of the Leading Scientific Schools of the Russian Federation, Grant No. NSh-1802.2003.3), the Presidium of the Russian Academy of Sciences (Program for Basic Research), and the Russian Foundation for Basic Research (Project No. 06-03-32603).

References

1. N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457; A. Suzuki, in *Metal-Catalyzed Cross-Coupling Reactions*, Eds F. Diederich and P. J. Stang, Wiley—VCH, Weinheim, 1998, 49; S. Kotha, K. Lahiri, and D. Kashinath, *Tetrahedron*, 2002, **58**, 9633.
2. S. Brase and A. de Meijere, in *Metal-Catalyzed Cross-Coupling Reactions*, Eds F. Diederich and P. J. Stang, Wiley—VCH, Weinheim, 1998, 99; I. P. Beletskaya and A. V. Cheprakov, *Chem. Rev.*, 2000, **100**, 3009.
3. T. N. Mitchell, in *Metal-Catalyzed Cross-Coupling Reactions*, Eds F. Diederich and P. J. Stang, Wiley—VCH, Weinheim, 1998, 167; V. Farina, V. Krishnamurthy, and W. J. Scott, *The Stille Reaction*, Wiley, New York, 1998.
4. R. C. Larock, *Comprehensive Organic Transformations. A Guide to Functional Group Preparations*, 2nd ed., Wiley, New York, 1999, 258; 659.
5. (a) E. V. Dehmlow and M. Lissel, *Liebigs Ann. Chem.*, 1980, 1; (b) A. Medlik-Balan and J. Klein, *Tetrahedron*, 1980, **36**, 299; (c) E. V. Dehmlow, R. Thieser, Y. Sasson, and R. Neumann, *Tetrahedron*, 1986, **42**, 3569; (d) E. K. Starostin, M. A. Lapitskaya, A. V. Ignatenko, K. K. Pivnitsky, and G. I. Nikishin, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 78 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 81].
6. P. Bapseres and R. Quelet, *C. R.*, 1950, **230**, 969; R. Knorr, J. Ruhdorfer, P. Böhrer, H. Bronberger, and E. Räpple, *Liebigs Ann. Chem.*, 1994, 433; I. J. Solomon and R. Filler, *J. Am. Chem. Soc.*, 1963, **85**, 3492; G. Huett and S. I. Miller, *J. Am. Chem. Soc.*, 1961, **83**, 408; Z. Rappoport, P. Shulman, and M. Thuval, *J. Am. Chem. Soc.*, 1978, **100**, 7041; S. P. Götzoe and D. Seebach, *Chimia*, 1996, **50**, 20; M. Büchner, A. Nixdorf, and H.-F. Grützmacher, *Chem. Eur. J.*, 1998, **4**, 1799.
7. M. V. Chirskaya, A. A. Vasil´ev, N. L. Sergovskaya, S. V. Shorshnev, and S. I. Sviridov, *Tetrahedron Lett.*, 2004, **45**, 8811.
8. N. Miyaura, T. Yanagi, and A. Suzuki, *Synth. Commun.*, 1981, **11**, 513; S. Gronowitz, V. Bobosik, and K. Lawitz, *Chem. Scr.*, 1984, **23**, 120; B. I. Alo, A. Kandil, P. A. Patil, M. J. Sharp, M. A. Siddiqui, and V. Snieckus, *J. Org. Chem.*, 1991, **56**, 3763.

9. N. A. Bumagin, V. V. Bykov, and I. P. Beletskaya, *Dokl. Akad. Nauk SSSR*, 1990, **315**, 1133 [*Dokl. Chem.*, 1990, **315**, 354 (Engl. Transl.)]; V. V. Bykov, N. A. Bumagin, and I. P. Beletskaya, *Dokl. Akad. Nauk*, 1995, **340**, 775 [*Dokl. Chem.*, 1995 (Engl. Transl.)]; N. A. Bumagin and V. V. Bykov, *Tetrahedron*, 1997, **53**, 14437.
10. A. S. Burukin, A. A. Vasiliev, N. L. Merkulova, M. I. Struchkova, and S. G. Zlotin, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 114 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 118].
11. C. J. Mathews, P. J. Smith, and T. Welton, *Chem. Commun.*, 2000, 1249; C. W. K. Gstöttmayr, V. P. W. Böhm, E. Herdtweck, M. Grosche, and W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1363; O. Navarro, H. Kaur, P. Mahjoor, and S. P. Nolan, *J. Org. Chem.*, 2004, **69**, 3173; H. Lebel, M. K. Janes, A. B. Charette, and S. P. Nolan, *J. Am. Chem. Soc.*, 2004, **126**, 5046; K. Arentsen, S. Caddick, F. G. N. Clocke, A. P. Herring, and P. B. Hitchcock, *Tetrahedron Lett.*, 2004, **45**, 3511.
12. M. Lepingle, *Bull. Soc. Chim. Fr.*, 1926, **39**, 741; W. G. Young, R. T. Dillon, and H. J. Lucas, *J. Am. Chem. Soc.*, 1929, **51**, 2528; F. G. Bordwell and P. S. Landis, *J. Am. Chem. Soc.*, 1957, **79**, 1593.
13. B. S. Bandodakar and G. Nagendrappa, *Synthesis*, 1990, 843.
14. N. Han, X. Lei, and N. J. Turro, *J. Org. Chem.*, 1991, **56**, 2927.
15. W. E. Billups, G.-A. Lee, B. E. Arney, and K. H. Whitmire, *J. Am. Chem. Soc.*, 1991, **113**, 7980; G. Ndebeka, S. Raynal, and P. Caubere, *J. Org. Chem.*, 1980, **45**, 5394.
16. M. Mladenova, B. Blagoev, M. Gaudemar, F. Gaudemar-Bardone, and J. Y. Lallemand, *Tetrahedron*, 1981, **37**, 2157; T. Tabuchi, J. Inanaga, and M. Yamaguchi, *Tetrahedron Lett.*, 1986, **27**, 1195; Y. Rollin, S. Derien, E. Dunach, C. Gebehenne, and J. Perichon, *Tetrahedron*, 1993, **49**, 7723.
17. R. Pan, X. Liu, and M. Deng, *J. Fluor. Chem.*, 1999, **95**, 167.
18. V. R. Lando and A. L. Monteiro, *Org. Lett.*, 2003, **5**, 2891.
19. J. S. Wilkes, J. A. Levisky, R. A. Wilson, and C. L. Hussey, *Inorg. Chem.*, 1982, **21**, 1263.
20. P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. De Souza, and J. Dupont, *Polyhedron*, 1996, **15**, 1217.
21. B. C. Ranu, A. Majee, and A. R. Das, *Tetrahedron Lett.*, 1995, **36**, 4885.
22. S. R. Wilson and M. E. Guazzaroni, *J. Org. Chem.*, 1989, **54**, 3087; P. Jones and P. Knochel, *J. Org. Chem.*, 1999, **64**, 186.
23. I. N. N. Namboothiri and A. Hassner, *J. Organomet. Chem.*, 1996, **518**, 69.
24. J.-T. Liu, Y.-J. Jang, Y.-K. Shih, S.-R. Hu, C.-M. Chu, and C.-F. Yao, *J. Org. Chem.*, 2001, **66**, 6021.
25. K. J. Davis, U. T. Bhalerao, and B. V. Rao, *Synth. Commun.*, 1999, **29**, 1679.
26. J. Pfeiffer, M. Nieger, and K. H. Dötz, *Eur. J. Org. Chem.*, 1998, 1011.
27. J. J. Eisch, Y. Qian, and M. Singh, *J. Organomet. Chem.*, 1996, **512**, 207.
28. T. Hayashi, K. Inoue, N. Taniguchi, and M. Ogasawara, *J. Am. Chem. Soc.*, 2001, **123**, 9918.
29. E. Comer and M. G. Organ, *J. Am. Chem. Soc.*, 2005, **127**, 8160.
30. M. Christl, D. Moigno, E.-M. Peters, K. Peters, and H. H. von Schnering, *Liebigs Ann. Chem. Recl*, 1997, 1791.
31. L. Li and N. Navasero, *Org. Lett.*, 2004, **6**, 3091.

Received March 28, 2006;
in revised form November 24, 2006