

Functionalization of Styrenes by Copper-Catalyzed Borylation/*ortho*-Cyanation and Silver-Catalyzed Annulation Processes

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Abstract: An efficient two-step method for the assembly of indanone derivatives starting from a simple vinyl arene has been developed. The sequence first involves addition of bis(pinacolato)diboron (B_2Pin_2) and *N*-cyano-*N*-phenyl-*p*-methylbenzenesulfonamide (NCTS) to a broad range of styrenes by utilizing IMesCuCl as catalyst. This step simultaneously accomplishes hydroboration of the alkene and *ortho* cyanation of the benzene unit. The products thus obtained are further functionalized by a $AgNO_3$ /Selectfluor-mediated coupling of the BPin and cyano functionalities to annulate a new five-membered ring. This combined two-step sequence provides a versatile method for the site-selective derivatization of a broad range of vinyl arene substrates.

Styrene and its derivatives serve as inexpensive and widely available feedstock reagents for organic synthesis.^[1] Despite the numerous directed C–H functionalization processes that have been developed for the derivatization of aromatic subunits, simple vinyl groups, such as that found in styrene, have rarely been employed as a handle for the manipulation of aromatic core structures.^[2] Furthermore, annulation methods involving styrene, where the vinyl group is incorporated within a new ring fused to the existing aromatic core, are especially challenging given the barrier for dearomatization, which arene annulation processes typically require.^[3,4] The copper-catalyzed cyanoborylation reaction of vinyl naphthalenes, recently reported by Yang and Buchwald^[5] and computationally evaluated by Yang and Liu,^[6] is a highly attractive catalytic process, in that simple vinyl arene units may be derivatized through a formal hydroboration of the alkene and *ortho* cyanation of the aromatic core.^[7] We envisioned that developing a borylation/*ortho*-cyanation procedure that is general across a broad range of styrene derivatives, and then utilizing the functionality rich products thus obtained, could serve as a platform for creating a versatile suite of styrene derivatization methods. In particular, the sequential installation of an alkylborane and nitrile to a simple vinyl arene followed by an ensuing cyclization process presents the opportunity to introduce a new ring fused to the original vinyl arene core. Herein we describe the implementation of this strategy, including the development of a styrene cyanoborylation process with a broad substrate

scope, and the discovery of a method for the annulation of cyclopentanone units through a silver-mediated coupling of the alkylborane and nitrile.

In the course of exploring the development of regioselective addition processes of alkenes, we examined the copper-catalyzed functionalization of styrene with B_2Pin_2 and Ph(Ts)N–CN (**1**).^[8,9] This process affords the product **2** through a sequence where *ortho* cyanation and alkene borylation occurs, accompanied by the formation of the simple hydroboration product **3**. Whereas initial reports of this process with vinyl naphthalenes involved copper catalysts of bidentate phosphines,^[5] our explorations focused on the use of *N*-heterocyclic carbene (NHC) ligands. By using IPrCuCl as the catalyst, a screen of *tert*-butoxide bases identified *t*BuOLi as the base of choice (Table 1, entries 1–3). A screen of several NHC ligands showed IMes to be the optimum choice, with efficiencies dropping substantially as ligand sterics were increased (entries 4–7). Copper(II) precatalysts were effective, although less efficient than preformed Cu^I/NHC complexes (entries 8 and 9). Toluene was slightly less effective as a solvent compared with THF (entry 10). Further optimization of the THF procedure, using 4 Å molecular sieves and slow addition of styrene and **1**, led to optimal reaction conditions, thus affording **2** in an

Table 1: Cu/NHC-catalyzed cyanoborylation of styrene.

Entry	CuL	Base	Solvent	2 Yield [%] ^[a]	3 Yield [%] ^[a]
1	IPrCuCl	<i>t</i> BuOK	THF	18	34
2	IPrCuCl	<i>t</i> BuONa	THF	23	15
3	IPrCuCl	<i>t</i> BuOLi	THF	47	22
4	IMesCuCl	<i>t</i> BuOLi	THF	78	21
5	SIMesCuCl	<i>t</i> BuOLi	THF	50	29
6	ICyCuCl	<i>t</i> BuOLi	THF	7	38
7	CuCl/IPr*OMe	<i>t</i> BuOLi	THF	trace	trace
8	CuBr ₂ /IMes	<i>t</i> BuOLi	THF	63	10
9	CuOTf ₂ /IMes	<i>t</i> BuOLi	THF	37	25
10	IMesCuCl	<i>t</i> BuOLi	toluene	61	19
11 ^[b]	IMesCuCl	<i>t</i> BuOLi	THF	92 (84 ^[c])	5 (<5 ^[c])

[a] Determined by ¹H NMR analysis by using CH₂Br₂ as an internal standard. [b] Reaction was conducted with 4 Å molecular sieves with slow addition of styrene and **1**. [c] Yield of isolated product shown within parentheses. ICy = 1,3-bis(cyclohexyl)imidazol-2-ylidene, IMes = 1,3-bis(mesityl)imidazol-2-ylidene, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, IPr*OMe = 1,3-bis[2,6-bis(diphenylmethyl)-4-methoxyphenyl]imidazol-2-ylidene, SIMes = 1,3-bis(mesityl)-4,5-dihydroimidazol-2-ylidene, THF = tetrahydrofuran, Ts = 4-toluenesulfonyl.

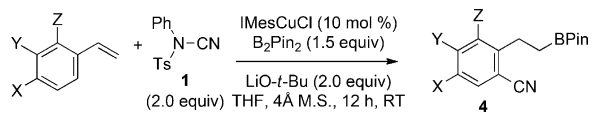
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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201507303>.

84% yield upon isolation, and with only trace amounts of **3** (entry 11). This optimized protocol was used in the remainder of our studies.

The efficiency of the cyanoborylation was explored across a range of substituted styrenes. With styrene itself, exclusive *ortho* cyanation was observed, and no evidence for the *meta* or *para* isomers was obtained (Table 2, entry 1). Similarly,

Table 2: IMesCuCl-catalyzed cyanoborylation of substituted styrenes.



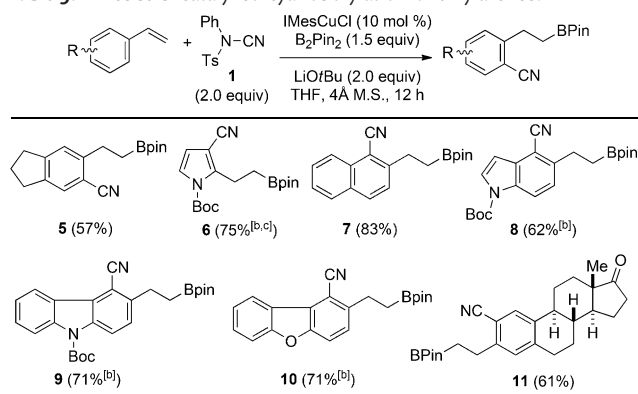
Entry	X	Y	Z	Yield [%] ^[a]
1	H	H	H	84
2	F	H	H	81
3	Cl	H	H	45
4	Me	H	H	81
5	<i>t</i> Bu	H	H	84
6	Ph	H	H	79
7	CH ₂ OTBS	H	H	72
8	CH(OEt) ₂	H	H	81
9	1-propenyl ^[b]	H	H	65 ^[c]
10	H	Me	H	65 (10:1)
11	H	CH ₂ OTBS	H	67 (10:1)
12	H	Br	H	78 (> 20:1)
13	H	OMe	H	71 (5:1) ^[c]
14	H	H	Me	67%

[a] Yield of the isolated product is reported. For entries 10–13, the major isomer is isomer **4** and the minor isomer corresponds to cyanation at the more hindered position *ortho* to both the boroalkyl group and the Y substituent. [b] A 1:1 *E/Z* mixture of the 1-propenyl substituent was used. [c] The BPin derivative was oxidized to the corresponding alcohol with NaOH and H₂O₂. The overall yield for the cyanoborylation and oxidation is shown. M.S. = molecular sieves, TBS = *tert*-butyldimethylsilyl.

with *para*-substituted styrenes, cyanation *ortho* to the vinyl group was exclusively observed, and the procedure cleanly tolerated fluoro, chloro, methyl, *tert*-butyl, phenyl, silyloxy-methyl, and acetal-containing substituents (entries 2–8). Yields were uniformly high aside from the chlorostyrene substrate, which proceeded in modest yield (entry 3). Notably, a 1-propenyl substituent was tolerated, with the procedure being highly chemoselective for addition to the vinyl substituent (entry 9). To examine *meta*-substitution patterns on the styrene, examples were conducted with methyl, silyloxymethyl, bromo, and methoxy substituents *meta* to the vinyl group (entries 10–13). In these cases, cyanation at the least hindered position *ortho* to the vinyl functionality was favored, with a minor isomer being derived from cyanation of the more hindered site *ortho* to the two substituents. Finally, a styrene bearing an *ortho*-methyl substituent was exclusively cyanated *ortho* to the vinyl functionality (entry 14). Notably, despite the higher activation barriers predicted for isolated styrenes compared with the corresponding vinylnaphthalenes,^[6] a broad range of borylation/*ortho*-cyanations of simple styrenes are available at room temperature by using the IMesCuCl catalyst system.

To further elucidate the scope and regioselectivity, a number of heteroaromatic and polycyclic substrates were

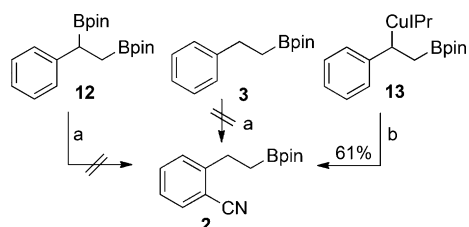
Table 3: IMesCuCl-catalyzed cyanoborylation of vinylenes.^[a]



[a] Regioisomers shown were obtained with > 97:3 selectivity. Yields are those of the isolated products. [b] The BPin derivative shown was oxidized to the corresponding alcohol with NaOH and H₂O₂. The overall yield for the cyanoborylation and oxidation is shown. [c] The BPin oxidation process was accompanied by an N to O Boc migration.

examined in the transformation. A dihydroindene derivative and the *N*-Boc derivative of 2-vinylpyrrole both underwent highly regioselective cyanation at the least-hindered *ortho*-position (Table 3; **5** and **6**). However, 2-vinylnaphthalene underwent highly regioselective cyanation at the more hindered C1-position (**7**) and an *N*-Boc indole bearing a 5-vinyl group similarly underwent highly regioselective cyanation at the 4-position (**8**). These observed regioselectivities with substrates that possess extended conjugation are consistent with the related transformations reported by Yang and Buchwald,^[5] where exclusive cyanation in naphthalenes occurred at the C1-position, and were explained through computational studies from Yang and Liu.^[6] Carbazoles were also effective substrates, with cyanation of the *N*-Boc derivative of 3-vinylcarbazole selectively occurring at the C4-position (**9**). Similarly, a dibenzofuran substrate underwent regioselective cyanation at the C1-position (**10**). Finally, regioselective derivatization of an estrone-derived substrate bearing a vinyl group at the C3-position was accomplished, with installation of the cyano group occurring exclusively at the C2-position (**11**). Thus, a broad range of substrates, including simple substituted styrenes, naphthalenes, and mono- and polycyclic heteroaromatics may be regioselectively derivatized in efficient catalytic processes at room temperature.

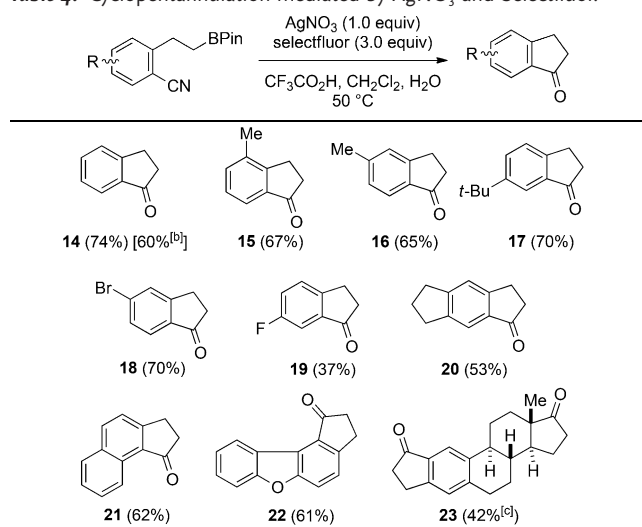
While significant insights have been provided into the mechanism of the borylation/*ortho*-cyanation of vinylnaphthalenes,^[5,6] we sought to gain evidence for the reactive intermediate involved in the functionalization of simple styrenes. Authentic samples of either the bis(borylated) derivative **12** or alkylborane **3**, when subjected to the optimized reaction conditions for styrene derivatization, failed to produce **2** (Scheme 1). However, subjecting independently synthesized benzylic copper species **13**^[10] to the reaction conditions produced **2** in 61% yield upon isolation. The conversion of **13** into **2** proceeded similarly in either the presence or absence of IMesCuCl. These observations, in combination with previously obtained insights, provide strong evidence for the intermediacy of benzylic copper intermediates in the borylation/*ortho*-cyanation process.



Scheme 1. Evidence for cyanation of a benzylic copper intermediate. a) **1** (2.0 equiv), IMesCuCl (10 mol%), LiOtBu (2.0 equiv), THF, RT, 12 h. b) **1** (2.0 equiv), LiOtBu (2.0 equiv), THF, RT, 12 h.

The multifunctional borylated/*ortho*-cyanated products derived from this regioselective styrene derivatization method hold considerable promise in subsequent functionalization processes. Among the strategies examined, attempts to fluorinate the BPin derivatives using a recently developed silver-catalyzed fluorination procedure provided an unexpected and interesting outcome. Following the protocol developed by Li for the fluorination of alkyl BPin derivatives,^[11] **2** was treated with AgNO₃ and Selectfluor in CF₃CO₂H/H₂O/CH₂Cl₂ at 50 °C. While fluorination was not observed, the outcome instead involved the efficient annulation of a five-membered ring at the sites where the boroethyl and cyano functional groups were positioned in the substrate. While AgNO₃ loadings of 20 mol% were effective in catalyzing the process, slightly higher yields were typically obtained with a full equivalent of AgNO₃. The method allows efficient synthesis of indanones from styrenes by combining the attributes of the copper-catalyzed styrene borylation/*ortho*-cyanation procedure with the AgNO₃/Selectfluor-promoted annulation method. The process is efficient for the direct synthesis of 1-indanone (**14**; Table 4) from styrene and for the conversion of a substituted styrene (entry 14, Table 2) into 4-methyl-1-indanone (**15**, Table 4) and for the conversion of a substituted styrene (entry 14, Table 2) into 4-methyl-1-indanone (**15**, Table 4). Similarly, indanones substituted at the C-5- or C-6-positions (**16** and **17**) may be obtained with exceptional regiocontrol, simply by starting with the appropriate monosubstituted styrene (entries 5 and 10, Table 2), over the two-step functionalization/annulation

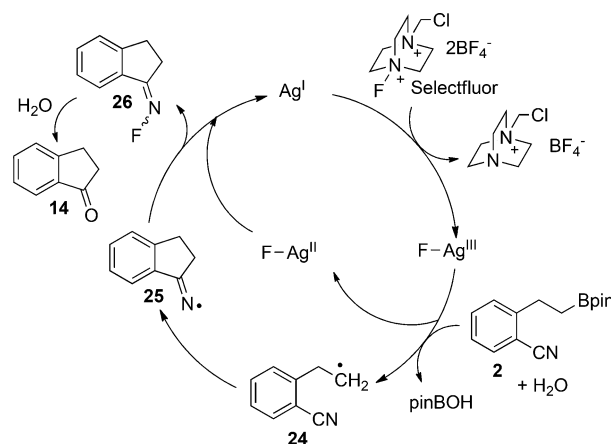
Table 4: Cyclopentannulation mediated by AgNO₃ and Selectfluor.^[a]



[a] Yields are those of the isolated products. [b] 0.2 Equiv. of AgNO₃ was used. [c] 0.5 Equiv. of AgNO₃ was used.

sequence. The method is tolerant of bromo- and fluoroarenes, as evidenced by the production of products **18** and **19** (Table 4), albeit in reduced yield in the case of the fluoroarene. The procedure is amenable to more complex ring systems as evidenced by efficient and completely regioselective annulation of a five-membered ring to a dihydroindene (**20**), naphthalene (**21**), dibenzofuran (**22**), or steroid framework (**23**) utilizing the BPin derivatives **5**, **7**, **10**, and **11** (Table 3) derived from simple vinyl arene substrates. Substrates bearing N-Boc functionality were not tolerated by the acidic reaction medium required for annulation.

Mechanistic studies from the group of Li have elucidated the nature of the silver-catalyzed radical fluorination of alkylboronates using Selectfluor.^[11] The process was proposed to involve generation of a Ag^{III}F species, which oxidizes alkyl(BPin) derivatives to produce carbon-centered radicals as intermediates during the fluorination process. Although several examples of chemoselective fluorination in the presence of nitriles were described, the specific arrangement of cyano and BPin functional groups provided by the copper-catalyzed styrene derivatization method described here leads to cyclization rather than fluorination (Table 4). On the basis of the Li precedent, we propose that Ag^{III}-mediated oxidation of the alkyl(BPin) species **2** generates the homobenzylic radical **24**,^[12] which undergoes cyclization onto the nitrile to afford the nitrogen-centered radical **25** (Scheme 2). The species **25** then likely reacts with Ag^{II}F to regenerate the Ag^I catalyst and **26**, which undergoes hydrolysis under the acidic reaction conditions to produce the observed product **14**. Whereas catalyzed intermolecular additions of aryl boronic acid derivatives to nitriles have been described as a method to generate aryl ketones,^[13] we are unaware of strategies that allow alkyl boronic acid derivatives to participate in processes of this type. A number of attractive radical cyclization methods and photocatalytic cross-couplings involving alkyltrifluoroborates have been recently described,^[14] but the corresponding methods involving BPin additions are currently underdeveloped.^[15] The advances described here, involving the cyclization of alkylBPin derivatives with nitriles, thus provide an important complement to previously developed radical cyclization processes involving alkylborane precursors.



Scheme 2. Mechanism of AgNO₃/Selectfluor-mediated cyclization.

In summary, an efficient process has been developed for the bis(functionalization) of styrenes, wherein the vinyl unit undergoes formal hydroboration simultaneously along with *ortho* cyanation of the arene. The process proceeds at room temperature, and tolerates a broad range of substituted styrenes. The *ortho* cyanation is highly selective for the least substituted *ortho* position, with the exception of polycyclic substrates with extended conjugation, in which case the cyanation occurs adjacent to the ring juncture. The products obtained are derivatized through a novel AgNO₃/Selectfluor-mediated radical cyclization, thus resulting in the installation of a fused five-membered ring ketone. The combination of these procedures provides a novel method for the cyclopentannulation of styrenes, where only a simple vinyl substituent is required at the site of ring installation.

Acknowledgements

The authors wish to thank the National Science Foundation (CHE-1265491) for support of this research. Michael Gilbert is thanked for assistance with NMR experiments.

Keywords: annulations · copper · cyclizations · radicals · silver

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 12683–12686
Angew. Chem. **2015**, *127*, 12874–12877

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Received: August 5, 2015

Published online: August 31, 2015