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Pd-Catalyzed Synthesis of Vinyl Arenes from Aryl Halides and Acrylic Acid

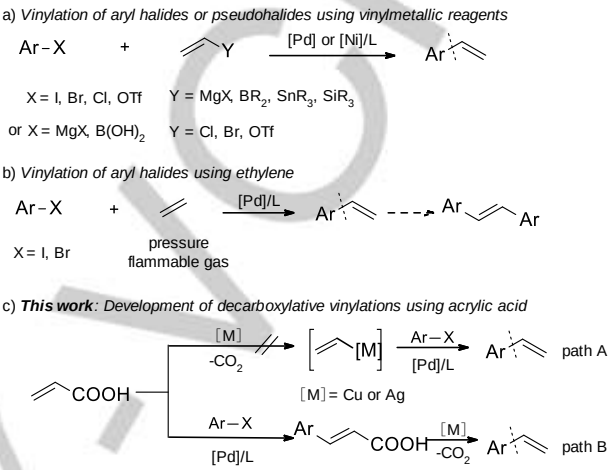
Yang Gao,[a] Yang Ou and Lukas J. Gooßen*

Abstract: Acrylic acid is presented as an inexpensive, non-volatile vinylating agent in a palladium-catalyzed decarboxylative vinylation of aryl halides. The reaction proceeds via a Heck reaction of acrylic acid, immediately followed by protodecarboxylation of the cinnamic acid intermediate. The use of the carboxylate group as a deciduous directing group ensures high selectivity for monoarylated products. The vinylation process is generally applicable to diversely substituted substrates. Its preparative utility is shown by the synthesis of drug-like molecules and the gram-scale preparation of key intermediates in drug synthesis.

Substituted styrenes are key building blocks in organic synthesis, and are widely used in the manufacturing of fine chemicals[1] and polymers.[2] Moreover, the vinyl group can be used as a hub for further functionalization, e.g. by olefin metathesis,[3] carboxylation,[4] (asymmetric) hydrofunctionalization,[5] or heterocycle synthesis.[6] However, whereas expedient methods exist to introduce substituted alkenyl arenes, e.g. *α,β*-unsaturated carbonyl compounds or stilbenes,[7] the introduction of vinyl groups into functionalized molecules is not at all trivial.

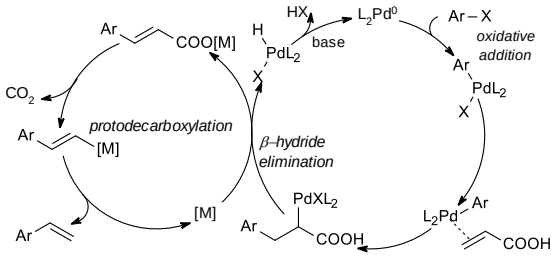
Established methods to access these products include the dehydration or Hoffmann elimination of a saturated precursor,[8] carbonyl olefination, [9] and partial reduction of terminal alkynes.[10] However, these methods are limited by the availability of suitable precursors. Arguably, the most versatile synthetic entry to vinyl arenes is the reaction of aryl halides or pseudohalides with organometallic magnesium-,[11] boron-,[12] tin-,[13] or silicon-based [14] vinylating reagents (Scheme 1a). However, these reagents all have their individual drawbacks, including their high price, and limited stability or functional group compatibility. The coupling of vinyl halides with preformed aryl–metal species suffers from the limited structural availability of the latter.[15] Therefore, a new, generally applicable vinylation agent with the potential to avoid stoichiometric organometallic reagents is highly desirable.

The Heck reaction of aryl halides with ethylene would constitute a particularly straightforward and inexpensive route to vinyl arenes despite the difficult handling of this gaseous reagent.[16] However, the competing double arylation with formation of stilbenes is hard to suppress due to the low solubility of ethylene in organic solvents and the high reactivity of the styrene intermediates towards coupling with aryl halides. Nevertheless reasonable selectivities for monoarylated products have been reported using excess ethylene (Scheme 1b).[17]



Scheme 1. Strategies for the vinylation of aryl halides.

We reasoned that acrylic acid, produced on an annual scale of more than a million tons, would be an ideal vinylating agent, since it is inexpensive, non-toxic, non-volatile and easy to handle.[18] However, all attempts to apply the decarboxylative cross-coupling pathway established for biaryl synthesis to acrylic acid – i.e. decarboxylation of a copper acrylate and transfer of the vinyl group to an arylpalladium complex – have been frustrated by the low reactivity of acrylic acid towards decarboxylation (Scheme 1c, path A).[19] Still, we reasoned that the targeted decarboxylative vinylation might be possible via an alternative pathway, in which the carboxylate acts as a deciduous directing group (Scheme 1c, path B).[20]



Scheme 2. Mechanistic outline for the envisioned processes.

Scheme 2 details the mechanistic blueprint for this approach. The electron-withdrawing COOH group should facilitate a Heck-type vinylation of aryl halides with acrylic acid leading to the corresponding cinnamate. Cinnamic acid derivatives have a strong tendency towards protodecarboxylation,[21] a reaction that has been described as early as 1865[22] and has been led to

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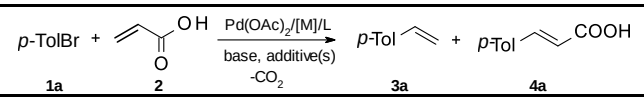
synthetic maturity by Abbott and Johnson.[23] The key requirements of an effective catalyst system for the desired transformation were identified to be that it (1) is just active enough to catalyze the vinylation with acrylic acid, (2) does not mediate any further coupling of the aryl bromide with styrenes or cinnamic acids, (3) effectively promotes the protodecarboxylation of cinnamic acids but not that of acrylic acid, and (4) operates under sufficiently mild conditions to avoid unwanted oxidation or polymerization of substrates and products. In an ideal case, the decarboxylation would be promoted by the same palladium catalyst that mediates the cross-coupling step.[24]

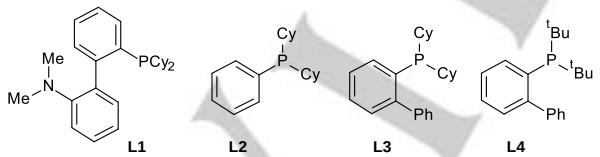
In the search for a catalyst system that fulfills the above requirements, 4-bromotoluene (**1a**) and acrylic acid (**2**) were chosen as model substrates, and various bases, ligands, and additives were systematically investigated (Table 1).

Table 1. Optimization of the vinylation conditions.[a]



1a 2 3a 4a

	Ligand	Base	Additive(s)	T (°C)	**3a** (%)	**4a** (%)
1[b]	PPh_3	Et_3N	$Cu(OH)_2$/1,10-Phen	120	6	5
2[c]	"	"	AgOAc/K_2CO_3	"	6	63
3	"	"	–	"	18	29
4	"	$NH(^iPr)_2$	–	"	18	35
5	"	TMEDA	–	"	31	46
6	"	PMDTA	–	"	38	45
7	L1	"	–	"	70	23
8	L2	"	–	"	66	20
9	L3	"	–	"	64	19
10	L4	"	–	"	22	56
11	L1	"	–	130	76	12
12	**L1**	**"**	**TBAB**	**"**	**86**	**0**

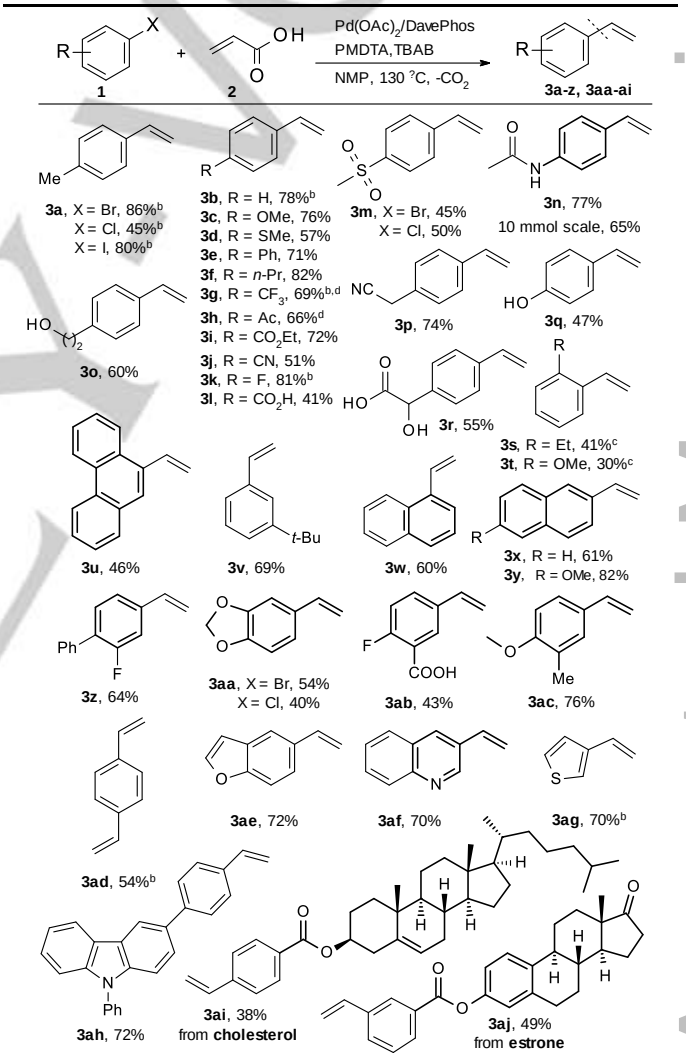


L1 L2 L3 L4

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.75 mmol), $Pd(OAc)_2$ (10 mol%), ligand (20 mol%), base (3 equiv.), NMP (2 mL), 12 h, yields determined by ^1H NMR spectroscopy using dibromomethane as an internal standard. [b] $Cu(OH)_2$ (10 mol%), 1,10-Phen (10 mol%). [c] AgOAc (10 mol%), K_2CO_3 (15 mol%). 1,10-Phen = 1,10-phenanthroline, TBAB = tetrabutylammonium bromide, NMP = *N*-methylpyrrolidone, TMEDA = *N,N,N′,N′*-tetramethylethylenediamine, PMDTA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine.

Control experiments demonstrate that state-of-the-art Pd/Ag or Pd/Cu decarboxylative cross-coupling catalysts are almost ineffective (entries 1 and 2). Under classical Mizoroki-Heck conditions, the desired styrene **3a** was obtained in encouraging yields along with 4-methylcinnamic acid (**4a**) as the main byproduct (entry 3). The selectivity for the decarboxylated product **3a** could be improved by the right choice of base. Whereas inorganic bases such as $NaHCO_3$ or K_2CO_3 gave unsatisfactory results (see Table S2 in SI), amines and multidentate amines such as TMEDA and PMDTA, in particular, shifted the selectivity towards the desired product (entries 3-6). The ligand at the palladium center is also decisive. The use of Buchwald-type ligands sharply increased not only the conversion but also the selectivity in favor of the desired product **3a** versus the cinnamate **4a** (entries 7-10). Best results were obtained with DavePhos (**L1**). Increasing the temperature to 130 °C led to further improved yields (entry 11).

Table 2. Scope of the reaction with regard to the aryl halide substrate [a]



[a] Reaction conditions: **1a** (0.5 mmol), **2** (0.75 mmol), $Pd(OAc)_2$ (10 mol%), DavePhos (20 mol%), PMDTA (3 equiv.), TBAB (1 equiv.), NMP (2 mL), 130 °C, 12 h, isolated yields. X = Br unless otherwise noted. [b] ^1H NMR yield. [c] 140 °C. [d] *n*-Bu_4PBr (1.0 equiv.).

Since the formation of palladium black was observed during the reaction, various additives known to stabilize Pd were tested. In this context, tetra-*n*-butylammonium bromide (TBAB) was best at suppressing the precipitation of Pd, which is in line with

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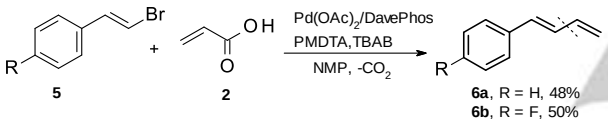
previous investigations on this reagent in Heck reactions by Jeffery et al.[25] Thus, **3a** was obtained in 86% yield (entry 12), without even trace formation of **4a** (see also Table S3 in SI).

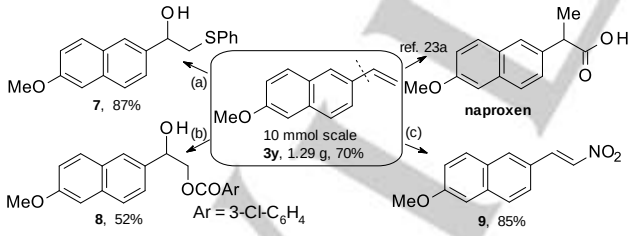
We next investigated the scope of the decarboxylative vinylation. As can be seen from Table 2, the reaction protocol is widely applicable to electron-rich and electron-deficient aryl bromides bearing a wide variety of functional groups, such as ether, ester, carbonyl, thioether, sulfone, cyano, trifluoromethyl, and acetamido groups. Substituents in *ortho*-, *meta*-, and *para*-position are tolerated. However, the yields of *ortho*-substituted vinyl arenes were somewhat lower, presumably due to steric hindrance. Even sensitive functionalities such as acidic -COOH and -OH groups did not interfere with the reaction. The decarboxylation process is highly chemoselective, affecting neither benzoic nor aliphatic carboxylate groups in the substrates (**3l**, **3ab**, **3r**).[26] 1,4-Divinylbenzene was obtained when using the corresponding dihaloarene as substrate (**3ad**). Heteroaryl bromides were also smoothly converted, as demonstrated by the synthesis of vinyl furan, quinolone, thiophene and carbazole derivatives (**3ae**-**3ah**).

The reaction can also be used for the vinylation of alkenyl bromides, providing convenient access to valuable dienyl arenes (Scheme 3).[27]



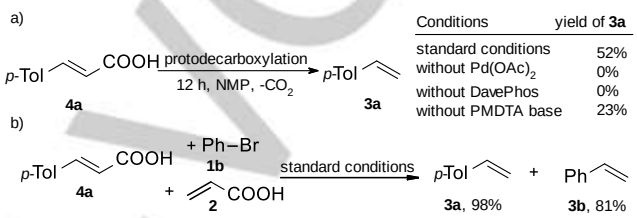
Scheme 3. Vinylation of alkenyl bromides.

The synthetic value of vinyl arenes is illustrated by the follow-up reactions summarized in Scheme 4. Vinyl arene **3y** was synthesized from the corresponding aryl bromide in 70% yield on gram scale, and was then further derivatized via hydrodroxythiolation, hydroxyacyloxylation, and nitration.[28] Hydrocarboxylation of **3y** furnished naproxen, a nonsteroidal anti-inflammatory drug.[29]



Scheme 4. Synthetic applications. (a) PhSH, ^{t}BuOLi, in EtOH, air, r.t.; (b) *m*-CPBA in DCM, r.t.; (c) $AgNO_2$, TEMPO in DCE, 70 °C.

A series of experiments were conducted to elucidate the reaction mechanism. A kinetic profile of the vinylation of **1a** showed that the substrates are rapidly consumed and that the postulated cinnamic acid intermediate **4a** indeed builds up in solution (Figure S1 in SI). In the course of the reaction, **4a** is gradually consumed and the styrene product **3a** is formed. Another control experiment confirmed that **4a** is converted into **3a** under the decarboxylative vinylation conditions (Scheme 5a). Further experiments revealed that both Pd and the P-ligand are essential for both the cross-coupling and the protodecarboxylation. This is in line with Croatt's mechanistic proposal for the Pd/phosphine-catalyzed protodecarboxylation of polyenoic acids,[24] which involves a reversible Michael addition of the phosphine to the unsaturated carboxylates. Interestingly, decarboxylation of **4a** gave higher yields when it was added to a decarboxylative cross-coupling of an aryl bromide and acrylic acid (Scheme 5b). This suggests that the aryl bromide keeps the Pd catalyst in oxidation state +2, which is likely to be the one required for the protodecarboxylation step. All findings are consistent with the proposed catalytic cycle (Scheme 2).



Scheme 5. Mechanistic studies.

In conclusion, utilizing carboxylates as deciduous directing group opens up a convenient synthetic access to substituted styrenes from widely available aryl halides and inexpensive and easy-to-handle acrylic acids. Key features of the Pd-catalyst system are that it favors the arylation of acrylic acid over that of the styrene product and that it facilitates decarboxylation of the cinnamic acids before an unwanted second arylation can occur.

Experimental Section

An oven-dried 20 mL vial was charged with $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), DavePhos (40.2 mg, 0.10 mmol) and TBAB (163 mg, 0.5 mmol) and closed with a septum cap. Under argon, NMP (2.0 mL), aryl bromide (0.5 mmol, 1 equiv.), PMDTA (0.32 mL, 1.5 mmol), and acrylic acid (52 µL, 0.75 mmol) were added, and the mixture was stirred at 130 °C for 12 h. The resulting mixture was washed with 1 M LiCl (15 mL) and 1 M HCl and the aqueous layer was extracted 3 times with diethyl ether (10 mL). The combined organic phases were dried over $MgSO_4$, filtered, and the volatiles removed in vacuo. The residue was purified by column chromatography (SiO_2, pentane/ethyl acetate gradient).

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Keywords: palladium • acrylic acid • aryl halides • vinylation • decarboxylative coupling

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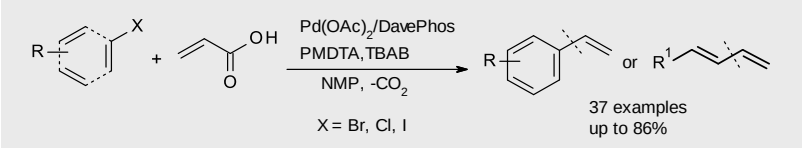

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Pd-Catalyzed Synthesis of Vinyl Arenes from Aryl Halides and Acrylic Acid

Acrylic acid has been utilized as an inexpensive, non-volatile vinylating agent in a palladium-catalyzed decarboxylative coupling with aryl halides. The reaction proceeds via a Heck reaction of the acrylic acids and consecutive protodecarboxylation of the resulting cinnamic acids. It is widely applicable to a wide range of functionalized molecules leading exclusively to monoarylated compounds.