Synthetic Methods

International Edition: DOI: 10.1002/anie.201604527
German Edition: DOI: 10.1002/ange.201604527

Direct Cross-Couplings of Propargylic Diols

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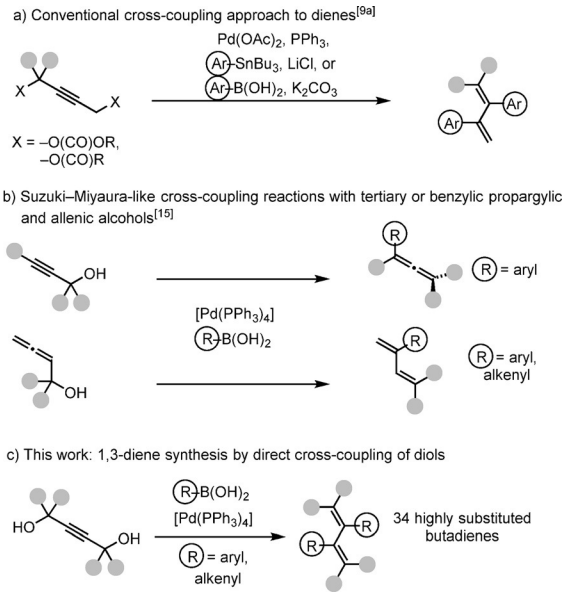
Abstract: *[Pd(PPh$_3$)$_4$] catalyzes a Suzuki–Miyaura-like twofold cross-coupling sequence between underivatized propargylic diols and either aryl or alkenyl boronic acids to furnish highly substituted 1,3-dienes. Thus, 2,3-diaryl-1,3-butadienes and their dialkenic congeners ([4]dendralenes) are delivered in a (pseudo)halogen-free, single-step synthesis which supersedes existing methods. Allenols are also readily formed. Treatment of these single- and twofold cross-coupled products with acid leads to remarkably short syntheses of highly-substituted benzofulvenes and aryl indenes, respectively.*

1,3-Dienes[1] are indispensable in chemical synthesis,[2] ubiquitous in functional materials and devices,[3] and feature prominently in biologically active natural products.[4] Accordingly, numerous techniques to synthesize the 1,3-diene motif featuring various substitution patterns have been devised.[5–13] Cross-coupling reactions grant facile access to many butadiene substitution patterns. Thus, Böhmer and Grigg employed twofold Stille or Suzuki–Miyaura reactions to convert propargylic dicarbonates into 2,3-diaryl-1,3-butadienes bearing up to two additional substituents (Scheme 1 a).[9a] General and efficient methods for the synthesis of more highly substituted 1,3-butadienes remain elusive, however, with existing methods being severely limited in scope and/or involving lengthy preparations.[14]

The group of Yoshida and Ihara has shown that certain propargylic and allenic alcohols are competent substrates in Suzuki–Miyaura-like cross-coupling reactions with boronic acids (Scheme 1 b).[15,16] These intriguing transformations suggested the possibility of not just an exceptionally step-economical synthesis of 1,3-dienes[17] but one that would be ideally suited to the synthesis of otherwise inaccessible, highly substituted congeners. Herein we show that bench-stable, inexpensive, and readily available propargylic diols[18] and boronic acids can indeed participate in a versatile one-step, double Suzuki–Miyaura cross-coupling sequence, thus delivering highly substituted 1,3-butadienes (Scheme 1 c). We also report convenient syntheses of substituted allenic alcohols, benzofulvenes, and aryl indenes based upon this technology.

Employing 2,5-dimethylhex-3-yne-2,5-diol (**1**) and phenyl boronic acid as initial cross-coupling partners, we were delighted to observe the formation of the hexasubstituted 1,3-butadiene **2a** (see Table 1) in the presence of [Pd(PPh$_3$)$_4$]



Scheme 1. The new synthesis of 1,3-butadienes and the most relevant published work. a) A more conventional cross-coupling approach using esters and carbonates. b) Reported Suzuki–Miyaura reactions with alcohol substrates. c) The present approach, delivering highly substituted dienes from readily available propargylic diols in one step.

as catalyst and toluene as solvent. Interestingly, the reaction proceeded less quickly but more cleanly in either the presence of water or a pH 7 aqueous buffer (see the Supporting Information for complete optimization details). These optimized reaction conditions were effective with a broad range of functionalized boronic acids (Table 1), including mono- to multi-carbocyclic aromatic and heteroaromatic derivatives which are electron-rich, neutral, or electron-poor. Under slightly modified reaction conditions, similar success was obtained with alkenyl boronic acids, thus furnishing highly substituted [4]dendralenes (**2u–w**), a family of substances for which, until now, no general synthetic route has been reported.[19] In fact, all but one of the twenty three compounds in Table 1 are new, highlighting both the paucity of highly substituted 1,3-butadienes in the literature and the utility of this new method.

We next probed the effect of substituents on the diol. 1,3-Butadienes were readily prepared from symmetrical diols bearing cycloalkyl substituents (Table 2, entry 1), and unsymmetrical diols featuring either phenyl or (cyclo)alkyl substituents (entries 2–5). When using a diol precursor carrying one secondary propargylic alcohol, high selectivity for the *E* stereoisomer of the product 1,3-butadiene was observed (entry 3). For diols containing a single primary alcohol, cross-coupling *without* allylic transposition was observed as a very

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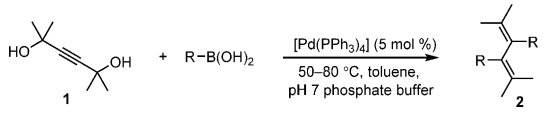
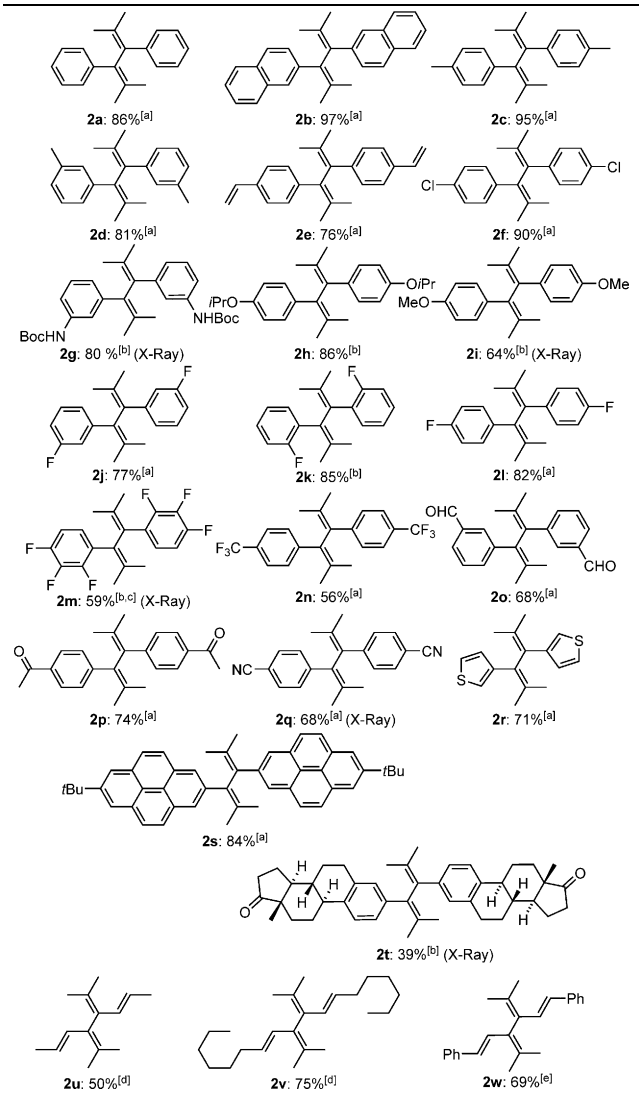
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201604527.

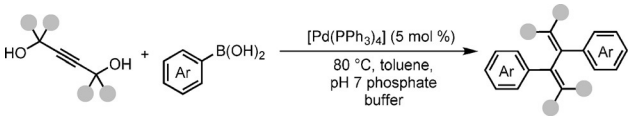
Table 1: Direct twofold cross-couplings between aryl- and alkenylboronic acids and 2,5-dimethylhex-3-yne-2,5-diol.

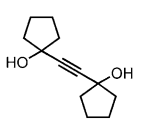
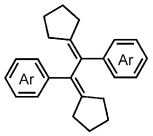
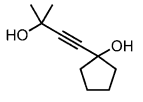
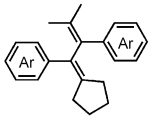
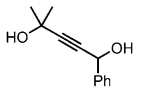
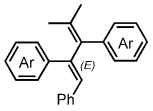
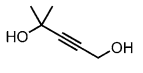
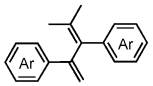
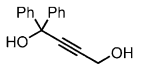
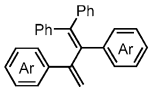




[a] Standard reaction conditions: **1** (0.35 mmol), boronic acid (1.05 mmol), $[Pd(PPh_3)_4]$ (0.018 mmol), toluene (3.5 mL, 0.1 M), pH 7 Na_2HPO_4/NaH_2PO_4 buffer (0.50 mL), 80°C, 16–24 h. [b] Standard reaction conditions, modified concentration: toluene (1.8 mL, 0.2 M), pH 7 Na_2HPO_4/NaH_2PO_4 buffer (0.25 mL). [c] Yield measured by ^{1}H NMR spectroscopy using an internal standard. [d] Reaction conditions: diol (0.35 mmol), boronic acid (1.05 mmol), $[Pd(PPh_3)_4]$ (0.018 mmol), toluene (1.8 mL, 0.2 M), 50°C, 48–72 h. [e] Reaction conditions: diol (0.35 mmol), boronic acid (1.05 mmol), $[Pd(PPh_3)_4]$ (0.018 mmol), toluene (1.8 mL, 0.2 M), 60°C, 72 h. Boc = *tert*-butoxycarbonyl.

Table 2: Direct twofold cross-couplings between propargylic diols and arylboronic acids to form 3,4-diarylated-1,3-butadienes.



Entry[a]	Substrate	Product	Ar	Yield [%]
1			**3a,** Ar = 4-FC_6H_4 **3b,** Ar = 4-MeC_6H_4 **3c,** Ar = 4-O*i*PrC_6H_4	94% 83% 84%[b]
2			**4a,** Ar = 4-CNC_6H_4 **4b,** Ar = 2-Naphthyl	81% 80%
3			**5a,** Ar = 3-MeC_6H_4 **5b,** Ar = 3-FC_6H_4	71 (13:1)[c] 72 (7.0:1)[c]
4			**6a,** Ar = 4-AcC_6H_4 **6b,** Ar = 4-$OMeC_6H_4$	73 (13:1)[d] 71 (12:1)[b,d]
5			**7a,** Ar = C_6H_5 **7b,** Ar = 4-vinylC_6H_4	61 (4.0:1)[d] 67 (5.7:1)[d]

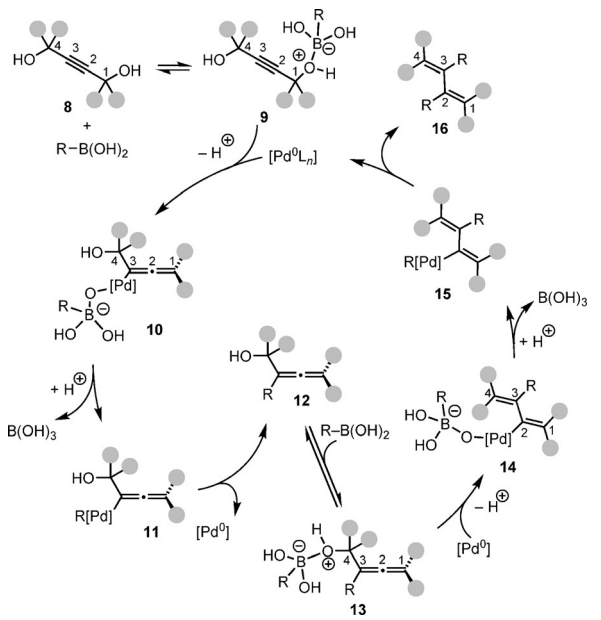
[a] Standard reaction conditions: diol (0.35 mmol), boronic acid (1.05 mmol), $[Pd(PPh_3)_4]$ (0.018 mmol), toluene (3.5 mL, 0.1 M), pH 7 Na_2HPO_4/NaH_2PO_4 buffer (0.50 mL), 80°C, 16 h, unless otherwise noted. [b] Standard reaction conditions, modified concentration: toluene (1.8 mL, 0.2 M), pH 7 Na_2HPO_4/NaH_2PO_4 buffer (0.25 mL). [c] *E*/*Z* ratio, by ^{1}H NMR spectroscopic analysis of the crude reaction mixture. [d] A minor allene regioisomer was also observed, see Ref. [20]. The ratio of 1,3-butadiene to allene (quoted in parentheses) was obtained by ^{1}H NMR spectroscopic analysis of the crude reaction mixture.

minor pathway in one case (entry 4). The quantity of this allenic product[20] increased when bulkier groups at the substituted side of the diol were used (entry 5). Unsubstituted but-2-yne-1,4-diol gave no trace of 1,3-butadiene products.[21]

A plausible mechanism for the twofold Suzuki–Miyaura cross-coupling is presented in Scheme 2.[22] Formation of an activated Lewis acid/base complex (**9**) likely facilitates oxidative insertion of palladium(0) into the propargylic C–O bond of the diol **8**. This insertion can occur at either C3 or C1 (with or without propargylic transposition) to deliver one of two regioisomers, or an η^3 complex. We suspect that transposition occurs to deliver the least sterically hindered possibility, namely the allenic σ-palladium complex **10**. Reductive elimination of transmetalated complex **11** provides the product of the first cross-coupling cycle, **12**, which can be isolated if the reaction is halted at low conversion. We speculate that the second cross-coupling (i.e., **12**→**16**) proceeds by a similar activated Lewis acid/base complex (**13**) via the least sterically demanding intermediates **14** and **15**.[23]

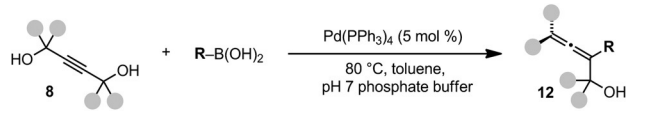
The 1,3-butadienes **16** are not always the major products from these reactions. Bulky substituents on either the precursor diol (Table 3, entries 1–3) or on the boronic acid (entries 4 and 5) result in the generation of the allenols **12**. The second cross-coupling reaction (i.e. **12**→**16**, Scheme 2) presumably stalls in these cases because of increased steric hindrance about the remaining alcohol functional group.

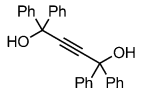
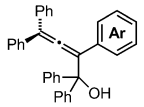
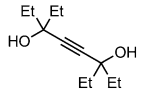
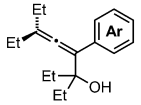
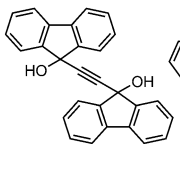
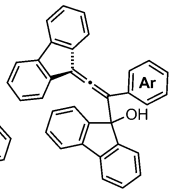
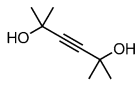
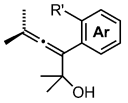
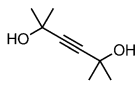
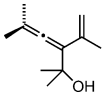
Simply adding a Brønsted acid to the reaction mixture, upon completion of the cross-coupling reaction, permits



Scheme 2. Possible mechanism for the twofold cross-coupling reaction.

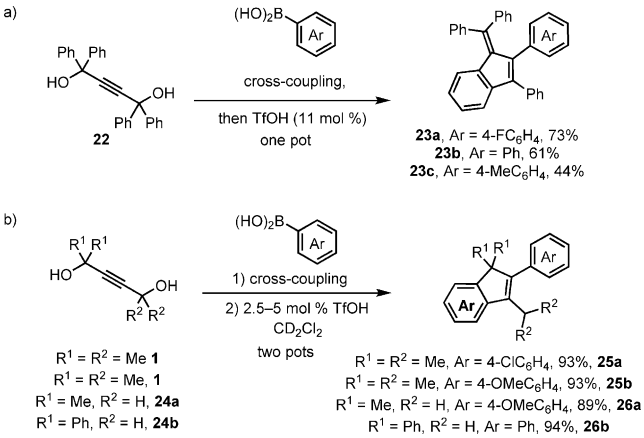
Table 3: Synthesis of allenols from boronic acids and propargylic diols.



Entry[a]	Substrate	Product	R	Yield [%]
1			**17a**, Ar = Ph **17b**, Ar = 4-FC$_6$H$_4$ **17c**, Ar = 4-MeC$_6$H$_4$	67[b] 81[b] 59[b]
2			**18a**, Ar = 3-MeC$_6$H$_4$ **18b**, Ar = 4-Cl-C$_6$H$_4$	67[c] 75[c]
3			**19**, Ar = 4-MeC$_6$H$_4$	68[c]
4			**20a**, Ar = 2-MeC$_6$H$_4$ **20b**, Ar = 2-FC$_6$H$_4$ **20c**, Ar = 2-Np **20d**, Ar = 2-ClC$_6$H$_4$	68 56[c] 73 46
5			**21**, R = –C(CH$_3$)=CH$_2$	57[d]

[a] Standard reaction conditions: diol (0.35 mmol), boronic acid (1.05 mmol), [Pd(PPh$_3$)$_4$] (0.018 mmol), toluene (3.5 mL, 0.1 M), pH 7 Na_2HPO_4/NaH_2PO_4 buffer (0.50 mL), 80 °C, 40 h; unless otherwise noted. [b] See the Supporting Information for single-crystal X-ray diffraction analysis and CCDC numbers. [c] Standard reaction conditions, 20 h. [d] Reaction conditions: diol (0.35 mmol), boroxine pyridine complex (1.05 mmol), [Pd(PPh$_3$)$_4$] (0.018 mmol), toluene (1.8 mL, 0.2 M), 55 °C, 72 h.

a one-pot synthesis of benzofulvenes from propargylic diols (Scheme 3a).[24] Similar treatment of the products of twofold cross-coupling led to a clean and completely regioselective 4π electrocyclization/Friedel–Crafts cyclization to form highly substituted indenes (Scheme 3b).[25]



Scheme 3. Synthesis of benzofulvenes and indenes from propargylic diols. a) Reaction conditions: cross-coupling as in Table 3, then CH_2Cl_2 (2 mL), TfOH (11 mol%), 0 °C, 5 min. b) Reaction conditions: butadiene (0.157 mmol), CD_2Cl_2 (1 mL), TfOH (2.5–5.0 mol%), 0 °C, 5 min. Tf = trifluoromethanesulfonyl.

In conclusion, a step-economical and functional-group-tolerant method for the synthesis of tetra-, penta-, and hexasubstituted 1,3-butadienes has been devised. The Suzuki–Miyaura twofold cross-coupling of propargylic diols supersedes previous approaches involving halides or pseudohalides, which are necessary within the constraints of a traditional cross-coupling paradigm, and significantly broadens the scope of 1,3-dienes available by synthesis. We anticipate that this simple new method, and the related syntheses of allenyl alcohols, benzofulvenes, and indenes also reported herein, will find broad application in synthesis.

Experimental Section

A 10 mL Schlenk flask containing a magnetic stirrer bar, the propargylic diol (0.35 mmol, 1.0 mol. equiv), [Pd(PPh$_3$)$_4$] (0.018 mmol, 20 mg, 0.05 mol. equiv), and the boronic acid (1.1 mmol, 3.0 mol. equiv), was evacuated and then refilled with argon three times before toluene (3.5 mL, 0.1 M) and pH 7 Na_2HPO_4/NaH_2PO_4 buffer (0.5 mL) was added. The flask was immersed in an oil bath (80 °C) and sealed. After 16 hours the flask was cooled to room temperature, opened, and diethyl ether (15 mL) and 1 M aq. NaOH (15 mL) were added. The layers were separated and the aqueous layer was extracted a second time with diethyl ether (15 mL). The combined organic extracts were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. This crude reaction residue was purified by flash chromatography.

Acknowledgments

This work was supported by the Australian Research Council.

Keywords: alkenes · allenes · cross-coupling · palladium · synthetic methods

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 9244–9248
Angew. Chem. **2016**, *128*, 9390–9394

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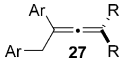

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Received: May 10, 2016
Published online: July 4, 2016

