

Gold-Catalyzed [3+2] Carbocycloaddition Reaction of Pinacol Alkenylboronates: Stereospecific Synthesis of Boryl-Functionalized Cyclopentene Derivatives

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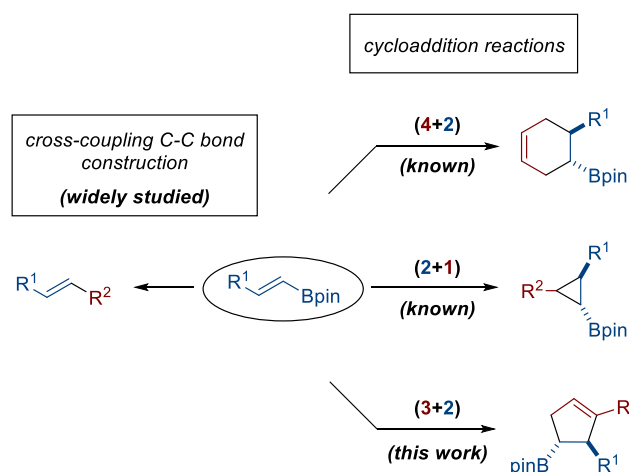
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Abstract: Gold-catalysis has enabled new synthetic opportunities in the chemistry of vinylidazo compounds. Herein, we report the gold-catalyzed reaction of stabilized vinylidazo compounds with pinacol alkenylboronates to provide boryl-functionalized cyclopentene derivatives through a formal [3+2] carbocycloaddition reaction, a very unusual pathway in alkenylboronate chemistry. This reaction proceeds with high regio- and stereoselectivity. The synthetic usefulness of the resulting borylated cyclopentene derivatives toward the synthesis of densely functionalized cyclopentanoids is also demonstrated.

Alkenylboronic acid esters are a class of particularly useful organoboron reagents,^[1] given their wide availability and unique reactivity profiles. In particular, their ability to engage in palladium-catalyzed Suzuki-Miyaura cross-coupling reactions has made them very popular.^[2] Alkenylboronates also serve as C2 partners in [n+2] carbocycloaddition reactions.^[3] Such protocols are of interest due to the great synthetic versatility offered by the boronate function installed in the resulting cycloadducts, that can easily be transformed into a range of functional groups through well-established procedures.^[4] In this regard, the reaction of vinyl boronic pinacol esters with a variety of cyclic and acyclic dienes under thermal conditions afforded the corresponding [4+2] cycloadducts, which could then be converted into the corresponding cyclohexenols.^[5] The [2+1] cycloaddition reaction of alkenylboronic acid esters with several carbene precursors has also been investigated, providing an efficient approach to boryl-substituted cyclopropane derivatives.^[6] Recently, this cyclopropanation has been performed in an enantioselective fashion.^[7] In sharp contrast, [3+2] carbocycloaddition reactions of alkenylboronates remain a largely uncharted area, in part due to the narrow arsenal of suitable precursors or synthetic equivalents for the C3 unit.^[8] In this regard, we and others have recently reported coinage metal-catalyzed [3+2] carbocycloaddition reactions between vinylidazo compounds and unsaturated substrates.^[9,10] On the basis of these precedents, we surmised

that the reaction of vinylidazo compounds with alkenylboronates could follow a similar pathway, thus providing access to synthetically useful boryl-substituted cyclopentene derivatives, which could be subsequently transformed into further interesting products. Herein, we report the realization of this goal; specifically, we describe the gold(I)-catalyzed [3+2] cycloaddition reaction of alkenylboronates with alkenyldiazo compounds leading to boryl-functionalized cyclopentenones.^[11,12] A preliminary study on the synthetic utility of these cyclopentene derivatives has also been carried out. This [3+2] cycloaddition/derivatization sequence provides convenient access to densely functionalized cyclopentene motifs that are prevalent in numerous natural and synthetic bioactive molecules.



Scheme 1. Reactivity profiles of alkenylboronates.

At the outset, ethyl 2-diazo-3-enoate (**1a**) was reacted in 1,2-dichloroethane (DCE) with commercially available (*E*)-styryl pinacolboronate (**2a**, 2 equiv) in the presence of a catalytic amount (5 mol%) of several transition-metal complexes (Table 1).

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Notably, catalysts based on rhodium or copper failed to give any cycloaddition product (entries 1 and 2). We therefore decided to evaluate gold complexes as catalysts in the model reaction (entries 3-12). As proof of our concept, various gold complexes proved capable of promoting the formation of the [3+2] cycloadduct **3aa**, albeit in low isolated yield (20-26%, entries 4-7). We then tested different reaction conditions using [IPrAu(CH₃CN)][SbF₆] as the catalyst. In this case, while the use of dichloromethane as the solvent was found to slightly improve the yield (30%, entry 8), the use of THF or hexane led to a total shutdown in reactivity (entries 9 and 10). To our delight, slow addition over 30 minutes (syringe pump) of the diazo reagent to a solution of alkenylboronate and catalyst led to a significant increase in yield of the target **3aa** (73% after chromatographic purification, entry 11). Under these slow addition conditions, the catalyst loading could be reduced to 2.5 mol%, affording **3aa** with no loss in yield (75%, entry 12).

Interestingly, this [3+2] cycloaddition reaction took place with complete regio- and stereoselectivity. The relative configuration of compound **3aa** was established to be *trans* by X-ray diffraction.^[13]

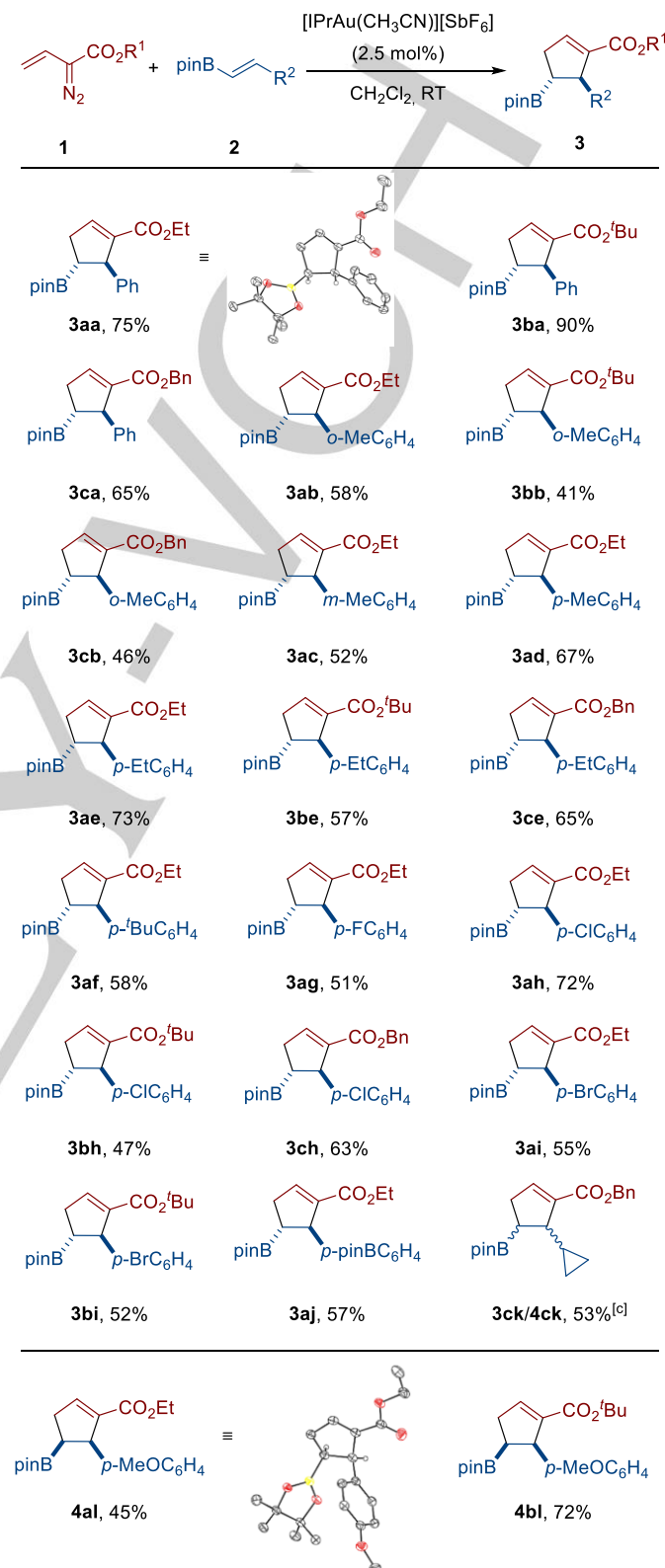
Table 1. Screening of reaction conditions.^[a]

Entry ^[a]	ML _n	Solvent	x mol%	3aa [%] ^[b]
1	Rh ₂ (OAc) ₄	DCE	5.0	-
2	[Cu(CH ₃ CN)][BF ₄]	DCE	5.0	-
3 ^[c]	(ArO) ₃ PAuNTf ₂	DCE	5.0	-
4 ^[d]	JohnPhosAuNTf ₂	DCE	5.0	20
5	IPrAuNTf ₂	DCE	5.0	20
6 ^[e]	[IPrAu(CH ₃ CN)][BAR ^f ₄]	DCE	5.0	24
7	[IPrAu(CH ₃ CN)][SbF ₆]	DCE	5.0	26
8	[IPrAu(CH ₃ CN)][SbF ₆]	CH ₂ Cl ₂	5.0	30
9	[IPrAu(CH ₃ CN)][SbF ₆]	THF	5.0	-
10	[IPrAu(CH ₃ CN)][SbF ₆]	hexane	5.0	-
11 ^[f]	[IPrAu(CH ₃ CN)][SbF ₆]	CH ₂ Cl ₂	5.0	73
12 ^[f]	[IPrAu(CH ₃ CN)][SbF ₆]	CH ₂ Cl ₂	2.5	75

[a] Reactions performed on a 0.15 mmol scale. [b] Isolated yield after chromatographic purification (Florisil; hexanes/ethyl acetate 20:1). [c] Ar = 2,4-^tBu₂C₆H₃. [d] JohnPhos = 2-(di-*tert*-butylphosphino)biphenyl. [e] [BAR^f₄] = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate. [f] Slow addition of **1a** over 30 min.

With suitable reaction conditions in hand, we next evaluated the scope of this gold-catalyzed [3+2] cycloaddition reaction (Table 2).

Table 2. Gold-catalyzed [3+2] cycloaddition reaction of vinyl diazocompounds **1** and alkenylboronates **2**: Substrate scope.^[a,b]



[a] Reaction conditions: **1** (0.15 mmol), **2** (0.30 mmol, 2 equiv.), [IPrAu(CH₃CN)][SbF₆] (2.5 mol%), CH₂Cl₂, RT. [b] Isolated yields. [c] Isolated as an inseparable 2:1 mixture of *trans* and *cis* isomers.

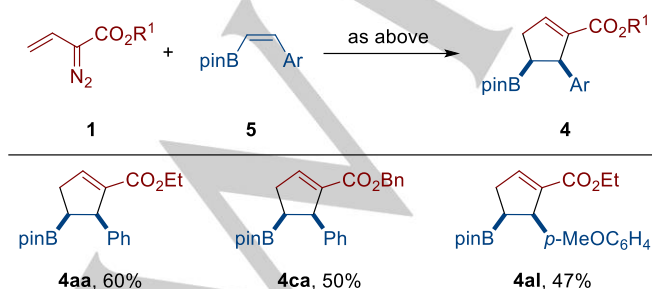
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Thus, by following the slow addition protocol developed for the model reaction, vinyl diazo compounds **1b** ($R^1 = t\text{Bu}$) and **1c** ($R^1 = \text{Bn}$) were reacted with (*E*)-styryl pinacolboronate (**2a**) to give cyclopentene derivatives **3ba** and **3ca** in 90% and 65% yield, respectively.

A variety of aryl-substituted *E*-alkenylboronates **2** ($R^2 = \text{Ar}$) were then evaluated for their suitability in this reaction.^[14] First, we found that substitution at the *ortho* and *meta* position of the aromatic ring of the alkenylboronate is well tolerated, providing the corresponding cyclopentene derivatives **3ab-3cb** and **3ac** in moderate to good yields (49–72%). An array of *para* alkyl-substituted alkenylboronates also proved to be suitable reaction partners for this [3+2] cycloaddition, furnishing the desired cycloadducts in similarly good yields (57–73%). Likewise, alkenylboronates containing halogen groups at the arene moiety were perfectly compatible with the present protocol, affording the respective products in comparable yields. Of particular interest is that alkenylboronate **2j** ($R^2 = 4\text{-pinBC}_6\text{H}_4$) could be also used as a counterpart in this gold-catalyzed cycloaddition reaction providing the expected functionalized cyclopentene derivative **3aj** containing two different C-B linkages in a synthetically useful yield. It is worth noting that all of these transformations involving aryl-substituted *E*-alkenylboronates proceed with complete regio- and stereoselectivity with exclusive formation of the *trans* cycloadduct.^[15] In contrast, the reaction with alkenylboronate **2k** ($R^2 = \text{cyclopropyl}$) was more sluggish, furnishing the corresponding cyclopentenenes **3ck/4ck** in 53% yield as a 2:1 mixture of *trans* and *cis* isomers.^[16]

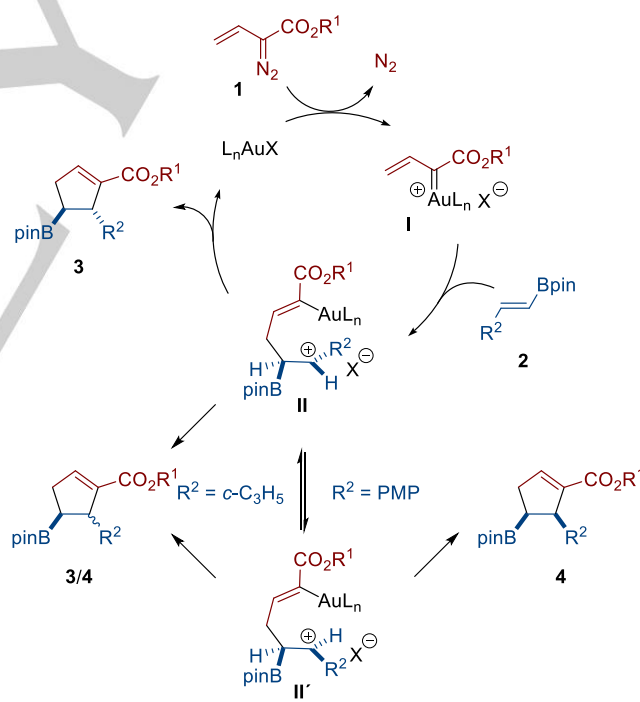
To our surprise, the reaction of vinyl diazo compound **1a** and (*E*)-4-methoxystyryl pinacolboronate (**2l**, $R^2 = 4\text{-MeOC}_6\text{H}_4$) under the standard conditions did not provide the expected *trans*-configured [3+2] adduct. Instead, cyclopentene derivative **4al** with a *cis*-arrangement of the C4 and C5 groups was formed, albeit in moderate yield. The structure of compound **4al** was confirmed by X-ray crystallography.^[13] The same stereochemical outcome was found in the reaction of alkenylboronate **2l** and vinyl diazo compound **1b** ($R^1 = t\text{Bu}$) with formation of *cis*-configured cycloadduct **4bl** as the only cyclization product.^[17]

We next evaluated *Z*-alkenyl boronates under our reaction conditions (Scheme 2). Here, we were pleased to find that treatment of vinyl diazo compounds **1a** ($R^1 = \text{Et}$) and **1c** ($R^1 = \text{Bn}$) with (*Z*)-styryl pinacolboronate (**5a**, $\text{Ar} = \text{Ph}$) led to cycloadducts **4aa** and **4ca**, respectively, as single *cis* isomers in moderate yields. A similar stereochemical outcome was observed in the reaction of diazo compound **1a** with (*Z*)-4-methoxystyryl pinacolboronate (**5b**, $\text{Ar} = 4\text{-MeOC}_6\text{H}_4$) affording cyclopentene derivative **4al**.



Scheme 2. Gold-catalyzed reaction of vinyl diazoacetates **1** and *cis*-configured alkenylboronates **5**.

Building on previous gold-catalyzed transformations of vinyl diazo compounds, a likely mechanistic pathway for the formation of boryl-functionalized cyclopentene derivatives **3** and **4** is proposed in Scheme 3. The process would be initiated by generation of gold vinylcarbene intermediate **I** with concomitant dinitrogen release. The enhanced vinylogous reactivity of type **I** intermediates has been widely documented. Accordingly, attack of the alkenylboronate at the vinylogous position of the gold carbene would generate cationic intermediate **II**, which would then undergo a cyclization reaction and liberate the final cyclopentene **3**. A fast cyclization event would account for the high stereospecificity found in most cases in the formation of compounds **3**. In contrast, alkenylboronates with strongly electron-donating groups, such as *c*-C₃H₅ (**2k**) or 4-MeOC₆H₄ (**2l**), would generate a more stable cationic intermediate with a lifetime long enough for carbon-carbon bond rotation to occur prior to the cyclization event. Consequently, for the cyclopropyl substituted intermediate, the participation in the cyclization reaction of conformers **II** and **II'** would lead to the observed mixture of stereoisomers. A similar substitution effect has been observed in some gold catalyzed rearrangements of 1,6-enynes involving cationic intermediates.^[18] The exclusive formation of the *cis*-isomer **4** in the reaction of alkenylboronate **2l** ($R^2 = \text{PMP}$) could be explained in terms of a stabilizing aryl-boron interaction in conformation **II'**.^[19]

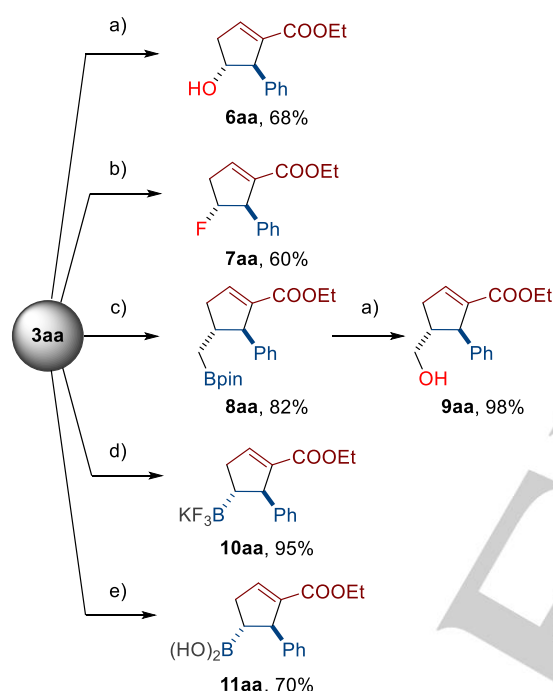


Scheme 3. Proposed mechanism for the gold-catalyzed reaction of vinyl diazo compounds **1** and alkenylboronates **2**.

Finally, to demonstrate the synthetic utility of the boryl-functionalized cyclopentene derivatives available through our methodology, we investigated follow-up chemistry using compound **3aa** as the model substrate (Scheme 4). For example, oxidation of **3aa** with NaBO₃ afforded the hydroxylated product **6aa** in 68% yield. In agreement with ample precedents on related oxidations, this transformation occurred with retention of the

configuration. Moreover, fluorination of borylated substrate **3aa** in the presence of AgNO₃ and Selectfluor^[20] proceeded readily to afford the expected fluorination product **7aa** in moderate yield, albeit as a 4:1 mixture of *trans* and *cis* isomers.^[21,22] Furthermore, subjecting **3aa** to the conditions of a Matteson homologation^[23] led to boronic ester **8aa** in good yield, which in turn could be converted into the corresponding primary alcohol **9aa** in almost quantitative yield. Finally, using well-established methodologies boronate **3aa** could be transformed into trifluoroborate salt **10aa** and boronic acid **11aa** in good yields.

The selected transformations involving the C-B bond displayed in Scheme 4, along with many other potential reactions of the unsaturated ester moiety, clearly showcase the synthetic potential of the cyclopentene derivatives reported in this study.



Scheme 4. Preliminary study on synthetic utility of borylated cyclopentene derivatives. Reaction conditions: a) NaBO₃ (4 equiv), Et₂O; then NaOH (2.5 equiv), H₂O, RT, overnight; b) Selectfluor (3 equiv), TFA (4 equiv), AgNO₃ (20 mol %), CH₂Cl₂, H₂O, 50 °C; c) CH₂Br₂, BuLi, Et₂O, -78 °C; d) KHF₂ (2.25 equiv), MeOH, RT, 30 min; e) NaIO₄ (2 equiv), NH₄Cl (2 equiv), acetone/H₂O, RT, 24 h.

In summary, we have developed a convenient synthesis of cyclopentenyl boronic esters through gold-catalyzed [3+2] cycloaddition reaction of vinyl diazo compounds with alkenylboronates. The reaction proceeds in good yields with complete regio- and stereoselectivity. Preliminary studies demonstrated that adducts produced by our protocol are useful synthetic intermediates as the boronate moiety can be transformed easily into a range of functional groups through well-established procedures, providing facile access to densely functionalized cyclopentene derivatives. Further investigation into the development of new synthetic applications of this cycloaddition reaction, as well as the development of an asymmetric variant, are currently ongoing in our laboratories.

Acknowledgements

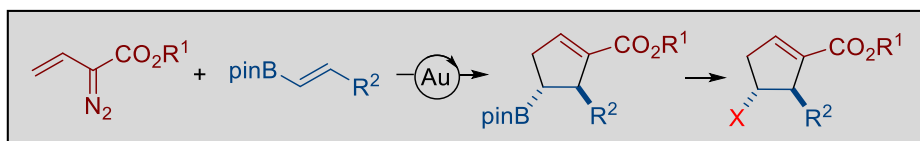
Financial support from Agencia Estatal de Investigación (AEI) and Fondo Europeo de Desarrollo Regional (FEDER) (grant CTQ2016-76840-R) is gratefully acknowledged. K. Y. was supported by a Japan Public-Private Partnership Student Study Abroad Program TOBITATE Young Ambassador Program. E. L. thanks the Consejería de Educación y Cultura, Principado de Asturias, for a predoctoral fellowship (Severo Ochoa Program). P. B. thanks the Spanish MINECO for a Ramón y Cajal contract (RyC-2016-20951). We are also grateful to Prof. J. M. González for interesting discussions.

Keywords: alkenylboronates • [3+2] cycloaddition • cyclopentenes • diazo compounds • gold catalysis

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- [13] CCDC numbers 1986202 (**3aa**) and 1986206 (**4al**), contain the supplementary crystallographic data for these structures. These data are provided free of charge by the Cambridge Crystallographic Data Centre.
- [14] Our studies indicate that an aryl group on the β -position of the alkenylboronate is paramount to reaction success. In fact, the parent alkenylboronate (4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane) and a representative α -aryl-substituted alkenylboronate (4,4,5,5-tetramethyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane) failed to undergo the present cycloaddition reaction.
- [15] β -Aryl-substituted alkenylboronates bearing strong electron-withdrawing groups such as *p*-nitrophenyl or pentafluorophenyl were not suitable substrates.
- [16] Other β -alkyl-substituted alkenyl boronates (R^2 = propyl, isopropyl, cyclohexyl) were found to be unsuitable substrates providing complex mixtures of products.
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Entry for the Table of Contents



An efficient gold-catalyzed [3+2] cycloaddition of vinyl diazoacetates and vinyl boronates has been developed. The boryl-substituted cyclopentene derivatives are obtained with complete regio- and stereoselectivity and can easily be converted into densely substituted cyclopentene derivatives by well-established methodologies.

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