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Synthesis of Cyclic 1-Alkenylboronates via Zr-Mediated Double Functionalization of Alkynylboronates and Sequential Ru-Catalyzed Ring-Closing Olefin Metathesis

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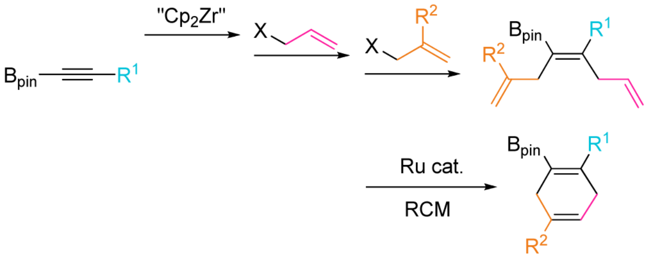
ABSTRACT



Synthesis of novel cyclic 1-alkenylboronates is accomplished through the zirconium-mediated regio- and stereoselective double functionalization of 1-alkynylboronates and the subsequent ruthenium-catalyzed ring-closing metathesis (RCM). The obtained substituted cyclic 1-alkenylboronates are transformed into *o*-terphenyl and triphenylene derivatives.

Cyclic alkenylboron compounds are highly valuable synthetic intermediates, particularly with regards to C–C bond formation through Pd-catalyzed Suzuki–Miyaura cross-coupling reactions,[1] giving rise to useful organic compounds showing biological activity such as Manzamine A and its derivatives.[2] Several synthetic routes to cyclic 1-alkenylboronates have been realized through Diels–Alder reactions of 1,3-dienyl-2-boronates with alkynes[3] or of 1-alkynylboronates with dienes,[4] halogen–boron exchange reactions,[5,6] and transition-metal-catalyzed dehydrogenative borylations of cyclic alkenes.[7] However, we often encounter difficulties in obtaining cyclic 1-alkenylboronates by utilizing transition-metal-catalyzed addition reactions of the boron-containing compounds to the internal alkynes[8] due to the less common availability

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(1) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483.

(2) Winkler, J. D.; Londregan, A. T.; Ragains, J. R.; Hamann, M. T. *Org. Lett.* **2006**, *8*, 3407–3409.

(3) Kamabuchi, A.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1993**, *34*, 4827–4828.

(4) Hilt, G.; Smolko, K. I. *Angew. Chem., Int. Ed.* **2003**, *42*, 2795–2797.

(5) Murata, M.; Oyama, T.; Watanabe, S.; Masuda, Y. *Synthesis* **2000**, 778–780.

(6) Takahashi, K.; Takagi, J.; Ishiyama, T.; Miyaura, N. *Chem. Lett.* **2000**, 126–127.

(7) (a) Olsson, V. J.; Szabó, K. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 6891–6893. (b) Kondoh, A.; Jamison, T. F. *Chem. Commun.* **2010**, *46*, 907–909.

(8) For examples of dimetalation of the internal alkynes, see: Silylborylation: (a) Nozaki, K.; Wakamatsu, K.; Nonaka, T.; Tuckmantel, W.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1986**, *27*, 2007–2010. (b) Suginome, M.; Nakamura, H.; Ito, Y. *Chem. Commun.* **1996**, 2777–2778. (c) Ohmura, T.; Oshima, K.; Suginome, M. *Chem. Commun.* **2008**, 1416–1418. Stannylborylation: (d) Sharma, S.; Oehlschlager, A. C. *Tetrahedron Lett.* **1988**, *29*, 261–264. (e) Onozawa, S.; Hatanaka, Y.; Sakakura, T.; Shimada, S.; Tanaka, M. *Organometallics* **1996**, *15*, 5450–5452. Diboration: (f) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018–11019. Thioborylation: (g) Ishiyama, T.; Nishijima, K.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 7219–7225.

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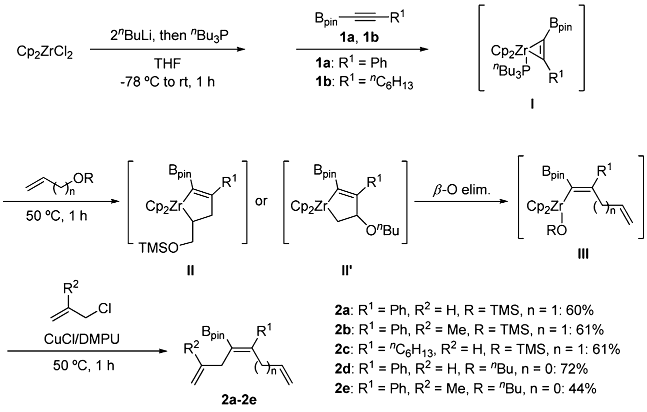
of cyclic alkynes[9] or benzyne[10] as the precursors. On the other hand, the versatility and synthetic applicability of the ring-closing olefin metathesis (RCM) reaction in the construction of functionalized carbocycles and heterocycles has been thoroughly demonstrated.[11] Along this line, recent advances in the synthesis of cyclic 1-alkenylboronates using the Ru-catalyzed RCM of dienylboronates provided cyclic 1-alkenylboronates with high versatility.[12] Recently, we have succeeded in the synthesis of various multisubstituted alkenylboronates regio- and stereoselectively, derived from alkynylboronates[13] and a low-valent ziroconocene complex.[14] Herein, we disclose that the cyclic 1-alkenylboronates are synthesized in high yields via RCM of highly allylated alkenylboronates given by double functionalization of 1-alkynylboronates as the starting materials.

The tetrasubstituted alkenylboronates **2a**−**2e** were prepared in good to excellent yields by the reaction of the starting 1-alkynylboronates **1a** and **1b** with the low-valent zirconocene complex, followed by sequential introduction of various allyl and/or vinyl moieties.[15] For instance, treatment of phenyl-substituted 1-alkynylboronate **1a** with $Cp_2ZrCl_2/2^n$BuLi (Negishi's reagent)[16] in the presence of P^nBu_3 afforded the stabilized zirconacyclopropene **I**,[17] which upon sequential double allylation generated **2a** in 60% yield with perfect stereoselectivity as shown in Scheme 1. To the best of our knowledge, zirconacyclopropenes as the intermediate species are believed to be fleeting and difficult to observe,[18] although related complexes are known.[19] Excellent selectivity forming **2** is attributed to the regioselective formation of zirconacyclopentene **II** (allyl) or **II′** (vinyl) bearing the boron moiety in the α-position, from which a smooth *β*-oxygen elimination gave rise to the alkenylzirconocene intermediate **III**.

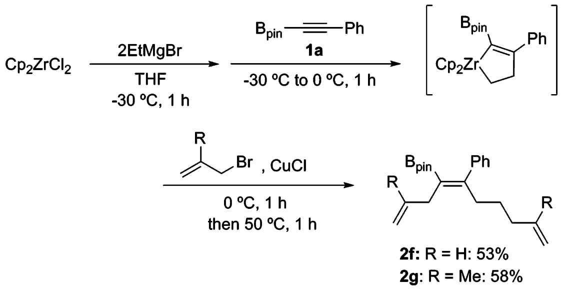
Similarly, analogous tetrasubstituted alkenylboronates **2b**−**2e** were obtained in moderate to high yields by double allylation or vinylation/allylation sequences. Perfect control of the stereochemistry of (*Z*)-alkenylboronates **2a**−**2e** is highly important for further cyclization reaction leading to the formation of the desired cyclic 1-alkenylboronates.

Scheme 1. Zirconocene-Mediated Synthesis of Tetrasubstituted Alkenylboronates **2a**−**2e**



Next our investigations focused on the regio- and stereoselective preparation of multisubstituted alkenylboronates through double allylation of zirconacyclopentenes (Scheme 2).[20] To our delight, upon treatment with Cp_2ZrCl_2/2EtMgBr (Takahashi's reagent),[21] 1-alkynylboronate **1a** afforded the zirconacyclopentene as an intermediate regioselectively, which was subjected to double allylation to give **2f** and **2g** in 53% and 58% yields, respectively. The obtained alkenylboronates **2a**−**2g** are fully characterized by GC-MS, ^{1}H, and ^{13}C{^{1}H} NMR spectra as well as elemental analyses.

Scheme 2. Synthesis of Tetrasubstituted Alkenylboronates **2f** and **2g** via Double Allylation of Zirconacyclopentene



With the doubly allylated alkenylboronate **2a** in hand, we next established the reaction conditions for RCM. The reactions were routinely carried out in the presence of 1−5 mol % of Grubbs second-generation catalyst **A**

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(9) Krebs, A.; Wilke, J. *Top. Curr. Chem.* **1983**, *109*, 189–233.

(10) Yoshida, H.; Okada, K.; Kawashima, S.; Tanio, K.; Ohshita, J. *Chem. Commun.* **2010**, *46*, 1763–1765.

(11) For recent reviews on olefin metathesis, see: (a) Cusak, A. *Chem.—Eur. J.* **2012**, *18*, 5800–5824. (b) Hassan, H. M. A. *Chem. Commun.* **2010**, *46*, 9100–9106. (c) van Otterlo, W. A. L.; de Koning, C. B. *Chem. Rev.* **2009**, *109*, 3743–3782. (d) Monfette, S.; Fogg, D. E. *Chem. Rev.* **2009**, *109*, 3783–3816. (e) Donohoe, T. J.; Fishlock, L. P.; Procopiou, P. A. *Chem.—Eur. J.* **2008**, *14*, 5716–5726.

(12) (a) Renaud, J.; Ouellet, S. G. *J. Am. Chem. Soc.* **1998**, *120*, 7995–7996. (b) Renaud, J.; Graf, C.-D.; Oberer, L. *Angew. Chem., Int. Ed.* **2000**, *39*, 3101–3104.

(13) For a recent review on alkynylboron compounds, see: Jiao, J.; Nishihara, Y. *J. Organomet. Chem.* **2012**, *721–722*, 3–16.

(14) (a) Nishihara, Y.; Miyasaka, M.; Okamoto, M.; Takahashi, H.; Inoue, E.; Tanemura, K.; Takagi, K. *J. Am. Chem. Soc.* **2007**, *129*, 12634–12635. (b) Nishihara, Y.; Okada, Y.; Jiao, J.; Suetsugu, M.; Lan, M.-T.; Kinoshita, M.; Iwasaki, M.; Takagi, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 8660–8664.

(15) Takahashi, T.; Kotora, M.; Kasai, K.; Suzuki, N. *Tetrahedron Lett.* **1994**, *35*, 5685–5688.

(16) Negishi, E.-i.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829–2832.

(17) Takahashi, T.; Suzuki, N.; Kageyama, M.; Kondakov, D. Y.; Hara, R. *Tetrahedron Lett.* **1993**, *34*, 4811–4814.

(18) For example: (a) Takahashi, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1987**, 623–626. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047–1058. (c) Johnson, S. A.; Liu, F.-Q.; Suh, M. C.; Zurcher, S.; Haufe, M.; Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 4199–4211. (d) Imabayashi, T.; Fujiwara, Y.; Nakao, Y.; Sato, H.; Sakaki, S. *Organometallics* **2005**, *24*, 2129–2140.

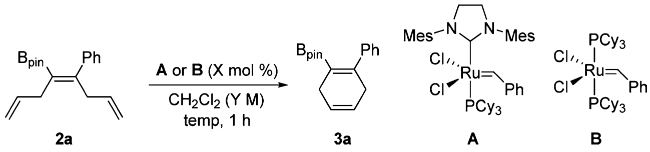
(19) Miller, A. D.; McBee, J. L.; Tilley, T. D. *J. Am. Chem. Soc.* **2008**, *130*, 4992–4999.

(20) Ben-Valid, S.; Quntar, A. A. A.; Srebnik, M. *J. Org. Chem.* **2005**, *70*, 3554–3559.

(21) Takahashi, T.; Nitto, Y.; Seki, T.; Saburi, M.; Negishi, E. *Chem. Lett.* **1990**, 2259–2262.

(Mes = 2,4,6-$Me_3C_6H_2$),[22] an efficient catalyst for RCM,[23] in CH_2Cl_2 at 25 or 40 °C. As shown in Table 1, the RCM catalyzed by Ru-complex **A** efficiently converted the substrate **2a** into the desired six-membered carbocyclic 1,4-cyclohexadienylboronate **3a** in 82% yield (Table 1, entry 1). Owing to a suppression of the intermolecular reaction, the diluted solution (0.01 M) of **2a** gave the better yield (Table 1, entry 2). A catalyst loading reduced to 1.0 mol % also generated **3a** in comparable yields (Table 1, entries 3 and 4). Finally, we found that the inexpensive first-generation Grubbs catalyst **B**[24] also furnished **3a** in 95% yield. This is the first example of the Ru-catalyzed RCM of tetrasubstituted alkenylboronates into cyclic 1-alkenylboronates bearing the substituents in the α-position of the boron functionality.

Table 1. Effect of Reaction Parameters on RCM of the Tetrasubstituted Alkenylboronate **2a**[a]

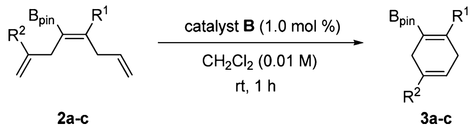


entry	catalyst	X (mol %)	Y (M)	temp (°C)	yield (%)[b]
1	**A**	5.0	0.10	40	82
2	**A**	5.0	0.01	40	94
3	**A**	1.0	0.01	40	92
4	**A**	1.0	0.01	25	99
5	**B**	1.0	0.01	25	95

[a] All reactions employed alkenylboronate **2a** (0.1 mmol). [b] GC yields.

Under the optimized reaction conditions, a series of alkenylboronates **2a**−**c** were subjected to the Ru-catalyzed RCM. The results are summarized in Table 2. The six-membered cyclic 1-alkenylboronates **3a**−**c** were formed in excellent yields. Since an RCM forming five- to seven-membered rings has been known to proceed,[11] we attempted the RCM of the synthesized tetrasubstituted alkenylboronate **2d** (for a five-membered ring) and **2f** (for an eight-membered ring). Unfortunately, however, no desired cyclic 1-alkenylboronates were isolated under the conditions described in Table 1. For example, when **2d** and **2f** were treated with catalyst **B**, the complete consumption of **2d** gave the complex mixture and the starting compound **2f** remained unreacted, respectively.

Table 2. Synthesis of Cyclic 1-Alkenylboronates **3a**−**c** via RCM of Alkenylboronates **2a**−**c**[a]



entry	substrate	product	yield (%)[b]
1	**2a**	**3a**	95
2	**2b**	**3b**	94
3	**2c**	**3c**	94

[a] All reactions employed alkenylboronates **2** (2.0 mmol) in CH_2Cl_2 (200 mL, 0.01 M) at rt. [b] Isolated yields.

The successful transformation of tetrasubstituted alkenylboronates **2** into six-membered cyclic ones **3** encouraged us to investigate the synthesis of 1,2-disubstituted 1,4-cyclohexadienes, *o*-terphenyls, and triphenylenes. In the field of organic materials science, the design and characterization of polycyclic aromatic hydrocarbons (PAHs), which exhibit superior electronic, optical, and/or self-assembling properties, have been studied intensively.[25] Hence, efficient synthetic methods leading to functionalized PAHs are expected to assist the rapid developments of PAH-based functional materials.[26] The Pd-catalyzed Suzuki−Miyaura cross-coupling reactions of **3a** with aryl iodides could be an efficient method for the formation of a wide variety of PAHs. The results of cross-couplings and the aromatization of **3a** are also summarized in Scheme 3. The resultant cyclic alkenylboronate **3a** was efficiently cross-coupled with various aryl iodides to give the corresponding 1,2-disubstituted 1,4-cyclohexadienes **4a**−**d** in excellent yields in the

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(22) (a) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953–956. (b) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546–2558. (c) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746–1787.

(23) (a) Yoshida, K.; Imamoto, T. *J. Am. Chem. Soc.* **2005**, *127*, 10470–10471. (b) Yoshida, K.; Kawagoe, F.; Iwadate, N.; Takahashi, H.; Imamoto, T. *Chem.—Asian J.* **2006**, *1*, 611–613. (c) Yoshida, K.; Horiuchi, S.; Iwadate, N.; Kawagoe, F.; Imamoto, T. *Synlett* **2007**, 1561–1564. (d) Yoshida, K.; Toyoshima, T.; Imamoto, T. *Chem. Commun.* **2007**, 3774–3776. (e) Yoshida, K.; Takahashi, H.; Imamoto, T. *Chem.—Eur. J.* **2008**, *14*, 8246–8261. (f) Yoshida, K.; Shishikura, Y.; Takahashi, H.; Imamoto, T. *Org. Lett.* **2008**, *10*, 2777–2780. (g) Yoshida, K.; Narui, R.; Imamoto, T. *Chem.—Eur. J.* **2008**, *14*, 9706–9713. (h) Yoshida, K.; Toyoshima, T.; Imamoto, T. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1512–1517. (i) Yoshida, K.; Kawagoe, F.; Hayashi, K.; Horiuchi, S.; Imamoto, T.; Yanagisawa, A. *Org. Lett.* **2009**, *11*, 515–518. (j) Takahashi, H.; Yoshida, K.; Yanagisawa, A. *J. Org. Chem.* **2009**, *74*, 3632–3640. (k) Yoshida, K.; Shida, H.; Takahashi, H.; Yanagisawa, A. *Chem.—Eur. J.* **2011**, *17*, 344–349. (l) Yoshida, K.; Hayashi, K.; Yanagisawa, A. *Org. Lett.* **2011**, *13*, 4762–4765.

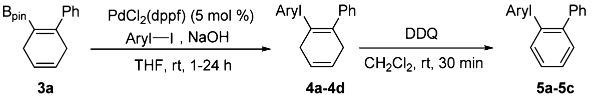
(24) (a) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100–110. (b) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039–2041.

(25) (a) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267–1300. (b) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718–747. (c) Wu, D.; Zhi, L.; Bodwell, G. J.; Cui, G.; Tsao, N.; Müllen, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 5417–5420. (d) Lorenz, U. J.; Solcà, N.; Lemaire, J.; Maitre, P.; Dopfer, O. *Angew. Chem., Int. Ed.* **2007**, *46*, 6714–6716. (e) Rouhanipour, A.; Roy, M.; Feng, X.; Räeder, H. J.; Müllen, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 4602–4604. (f) Kitagawa, Y.; Segawa, H.; Ishii, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 9133–9136.

(26) (a) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley: New York, 1997. (b) Boorum, M. M.; Scott, L. T. In *Modern Arene Chemistry*; Astruc, D., Ed.; Wiley-VCH: Weinheim, 2002: pp 20−31.

(27) For recent selected examples, see: (a) Lee, J. J.; Yamaguchi, A.; Alam, M. A.; Yamamoto, Y.; Fukushima, T.; Kato, K.; Takata, M.; Fujita, N.; Aida, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 8490–8494. (b) Osawa, T.; Kajitani, T.; Hashizume, D.; Ohsumi, H.; Sasaki, S.; Takata, M.; Koizumi, Y.; Saeki, A.; Seki, S.; Fukushima, T.; Aida, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 7990–7993. (c) Tatum, L. A.; Johnson, C. J.; Fernando, A. A. P.; Ruch, B. C.; Barakoti, K. K.; Alpuche-Aviles, M. A.; King, B. T. *Chem. Sci.* **2012**, *3*, 3261–3264. (d) Paquette, J. A.; Yardley, C. J.; Psutka, K. M.; Cochran, M. A.; Calderson, O.; Williams, V. E.; Maly, K. E. *Chem. Commun.* **2012**, *48*, 8210–8212.

Scheme 3. Synthesis of Symmetrical and Unsymmetrical 1,2-Diaryl-1,4-cyclohexadienes **4a**−**d** and *o*-Terphenyls **5a**−**c**

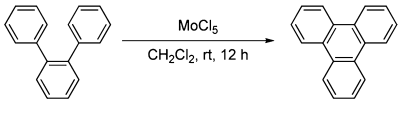


3a **4a-4d** **5a-5c**

4a: Aryl = Ph: 93%
4b: Aryl = 4-$MeOC_6H_4$: 84%
4c: Aryl = 4-$F_3CC_6H_4$: 91%
4d: Aryl = 2-ClC_6H_4: 79%

5a: Aryl = Ph: 93%
5b: Aryl = 4-$MeOC_6H_4$: 98%
5c: Aryl = 4-$F_3CC_6H_4$: 93%

Scheme 4. Synthesis of Triphenylene (**6**) by Oxidative Cyclization of **5a**



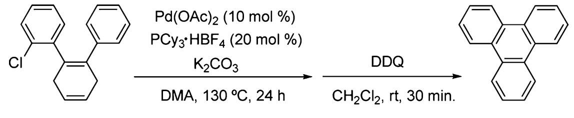
5a **6**: 33%

presence of a catalytic amount of $PdCl_2$(dppf) under the basic conditions. Furthermore, oxidation of the obtained **4a**−**c** with DDQ in CH_2Cl_2 furnished the *o*-terphenyls **5a**−**c** in 93, 98, and 93% yields, respectively.

Triphenylene derivatives are known to be applied to several functional organic materials such as the discotic liquid crystals.[27,28] When **5a** was treated with $MoCl_5$,[29] synthesis of triphenylene (**6**) was accomplished, albeit in 33% yield (Scheme 4).

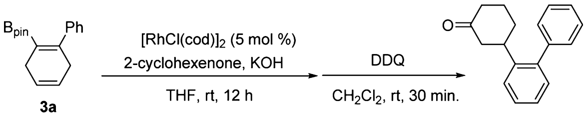
Since a direct oxidative cyclization of *o*-terphenyl was known to give a complex mixture due to the severe reaction conditions and the presence of many C−H bonds in the molecule,[26] selective synthesis of triphenylene (**6**) was examined by the Pd-catalyzed C−H functionalization of **4d**. The once isolated **4d** was treated with a catalytic amount of $Pd(OAc)_2$ under basic conditions,[30] followed by DDQ oxidation to give the desired products **6** in 63% yield (Scheme 5).

Scheme 5. An Alternative Synthesis of Triphenylenes (**6**) by Pd-Catalyzed Annulation via C−H Functionalization of **4d**



4d **6**: 63%

Scheme 6. Rhodium-Catalyzed 1,4-Addition of Cyclic Alkenylboronate **3a**



3a **7**: 49%

In order to demonstrate the utility of the synthesized cyclic 1-alkenylboronates, conjugate addition of **3a** to 2-cyclohexenone catalyzed by Rh was conducted and the subsequent DDQ oxidation in CH_2Cl_2 afforded **7** in 49% yield (Scheme 6).[31]

In summary, we have developed the regio- and stereoselective synthesis of tetrasubstituted alkenylboronates by a zirconocene-mediated stepwise allylation or vinylation of 1-alkynylboronates and zirconacyclopentene. The subsequent Ru-catalyzed RCM gave rise to the formation of six-membered cyclic 1-alkenylboronates that are not available by other methods. Current efforts to expand the scope of 1-alkynylboronates as well as to elucidate the application to the synthesis of various PAHs are in progress.

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Supporting Information Available. Copies of ^{1}H NMR and ^{13}C{^{1}H} NMR spectra for all the new compounds, as well as details on experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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(28) For recent reviews, see: (a) Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hagele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4832–4887. (b) Sergeyev, S.; Pisula, W.; Geerts, Y. H. *Chem. Soc. Rev.* **2007**, *36*, 1902–1929. (c) Kumar, S. *Chem. Soc. Rev.* **2006**, *35*, 83–109. (d) O'Neill, M.; Kelly, S. M. *Adv. Matter* **2003**, *15*, 1135–1146.

(29) King, B. T.; Kroulík, J.; Robertson, C. R.; Rempala, P.; Hilton, C. L.; Korinek, J. D.; Gortari, L. M. *J. Org. Chem.* **2007**, *72*, 2279–2288.

(30) For reviews, see: (a) Echavarren, A. M.; Gómez-Lor, B.; González, J. J.; de Frutos, Ó. *Synlett* **2003**, 585–597. (b) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174–238. (c) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147–1169.

(31) (a) Sakai, M.; Hayashi, H.; Miyaura, N. *Organometallics* **1997**, *16*, 4229–4231. (b) Takaya, Y.; Ogasawara, M.; Hayashi, T.; Sakai, M.; Miyaura, N. *J. Am. Chem. Soc.* **1998**, *120*, 5579–5580. (c) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829–2844.