Palladium-Catalyzed Three-Component Coupling Reaction of Allyl Carboxylates, Norbornenes and Diboronates Involving Sequential Olefins Insertion and Borylation Reaction

Zun Li,[a] Jia Zheng,[a] Chunsheng Li,[a] Wanqing Wu,[a] and Huanfeng Jiang*,[a]

*E-mail: jianghf@scut.edu.cn

[a] *Key Laboratory of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China.*

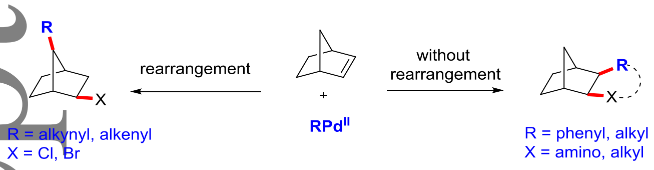
Cite this paper: *Chin. J. Chem.* **2019**, *37*, XXX—XXX. **DOI: 10.1002/cjoc.201900XXX**

Summary of main observation and conclusion An efficient Pd-catalyzed three-component coupling reaction of allyl carboxylates, norbornenes and diboronates is described, which allows efficient assembly of C(sp^3)–C(sp^3) and C(sp^3)–B bonds in a single process. Moreover, this approach shows advantages of good chemo- and regioselectivity, as well as good substrates suitability..

Background and Originality Content

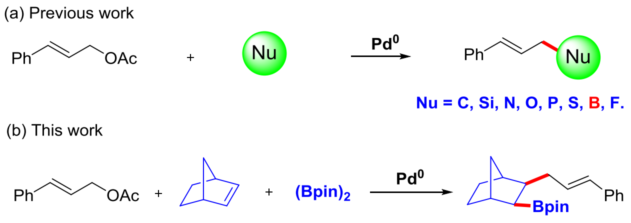
Norbornene derivatives, a group of inexpensive and practical organic molecules, are widely applied in the acquisition of biologically active molecules, functional polymers, solar-energy-storage materials and synthetic intermediates.[1] Consequently, turning norbornene derivatives into multiple new desired skeletons with high efficiency has emerged as an attractive goal in modern organic synthesis.[2] In recent years, continuous studies in the construction of C–C, C–N, C–X bonds by functionalization of norbornene derivatives in a two-molecule reaction systems have been carried out by our group (Scheme 1).[3] However, a palladium-catalyzed norbornene-involved three-component coupling reaction is relatively rare and still remains a challenging research area.[4]

Scheme 1 Constructing C–C, C–N, C–X bonds in two-molecule reactions



On the other hand, the use of various nucleophiles to capture σ-alkyl Pd(II)-intermediates has been demonstrated to be a facile route to construct various carbon-carbon bonds[5] or/and carbon-heteroatom bonds[6]. And several reports have elegantly demonstrated that σ-alkyl Pd(II)-intermediates can be readily trapped by B_2pin_2.[7] Meanwhile, π-allyl Pd(II)-intermediates are susceptible to take coupling reactions with nucleophiles to form C–C[8], C–Si[9], C–N[10], C–O[11], C–P[12], C–S[13], C–B[14] bonds (Scheme 2a). Based on our investigation into the insertion of norbornene derivatives in a palladium-catalyzed reaction system[2,3,15] and boration of alkenes[16], we anticipated that norbornenes can coordinate with π-allyl Pd(II)-intermediates to form σ-alkyl Pd(II) intermediates and they were stable enough to take subsequent conversion.[3a,4,5b,15,17] Therefore, we envisioned that a three-component coupling reaction of allyl carboxylates, norbornenes and boron nucleophiles can proceed smoothly under palladium catalysts. Accordingly, the coupling product of allyl carboxylate and boron nucleophile could be circumvented for the sake of the effective coordination between π-allyl Pd(II)-intermediates and norbornene. In this way, the reaction pathway can be diverted to difunctionalized products from the three components chemo- and regioselectively, which allows sequential construction of C(sp^3)-C(sp^3) bond and C(sp^3)-B bond in a single operation effectively (Scheme 2b).

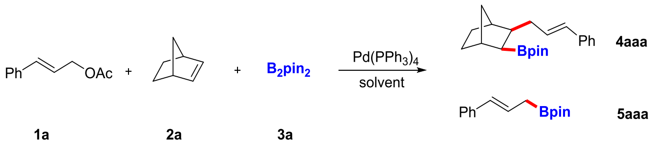
Scheme 2 Coupling of π-allyl Pd(II)-intermediate ornene.



Results and Discussion

Our initial investigations of this Pd-catalyzed olefin insertion and borylation reaction were commenced with 3-phenylallylacetate (**1a**), norbornene (**2a**) and bis(pinacolato)diboron (**3a**) as model substrates. Firstly, when the reaction was carried out in the presence of 5 mol% of $Pd(PPh_3)_4$ in toluene at 90 °C under N_2 atmosphere, the coupling products **4aaa** and **5aaa** could be detected by GC in less than 5% yield at the same time (Table 1, entry 1). Further investigation revealed that this coupling reaction was sensitive to solvents. Among them, 1,4-dioxane, DMF, DCE were not beneficial, and low efficiency of the desired product formation was observed (entries 2-4). Although DMSO, MeCN and $MeNO_2$ were able to promote the conversion well, the generation of two products was unselective (entries 5-7). To our delight, when alcohol solvents were examined, the reaction in ethanol, *n*-propanol mainly afforded **4aaa** (entries 8-9), while the one in *tert*-butanol mainly afforded **5aaa** (entry 10). Then, different temperatures were also tested (entries 11-14). Obviously, 90 °C was a suitable temperature relatively (entry 10). Further investigation on additives showed that alkaline additives largely inhibited the conversion (entries 15-

Table 1 Conditions optimization[a]

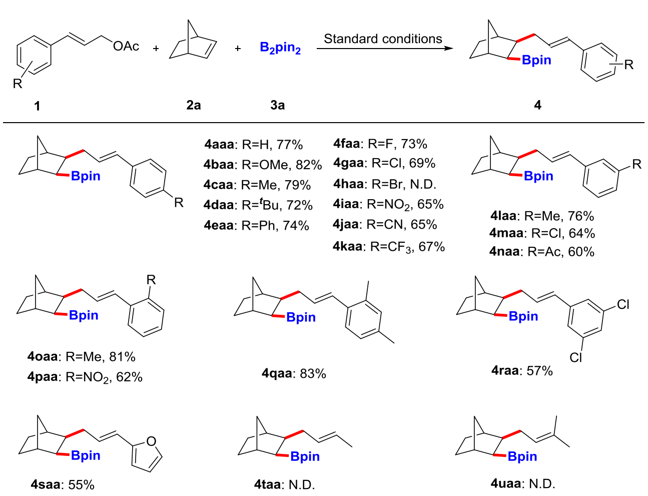


Entry	Solvent	Temperature (°C)	Additive (equiv)	GC Yield (%)[b]	
				4aaa	**5aaa**
1	Toluene	90	–	<5	<5
2	1,4-Dioxane	90	–	n.d.	<5
3	DMF	90	–	n.d.	n.d.
4	DCE	90	–	n.d.	0
5	DMSO	90	–	32	59
6	MeCN	90	–	44	42
7	$MeNO_2$	90	–	52	40
8	EtOH	90	–	61	15
9	*n*-PrOH	90	–	70	9
10	*tert*-BuOH	90	–	12	58
11	*n*-PrOH	70	–	62	13
12	*n*-PrOH	80	–	65	9
13	*n*-PrOH	100	–	55	27
14	*n*-PrOH	110	–	53	26
15	*n*-PrOH	90	NaOAc (1)	<5	n.d.
16	*n*-PrOH	90	K_2CO_3 (1)	13	7
17	*n*-PrOH	90	Cs_2CO_3 (1)	<5	26
18	*n*-PrOH	90	HOAc (1)	68	<5
19	*n*-PrOH	90	PivOH (1)	62	<5
20	*n*-PrOH	90	$Zn(OTf)_2$ (1)	76	n.d.
21	*n*-PrOH	90	$Zn(OTf)_2$ (0.2)	82(77)	n.d.
22[c]	*n*-PrOH	90	$Zn(OTf)_2$ (0.2)	84	n.d.

[a]Reaction conditions: (1) **1a** (0.2 mmol), **2a** (0.24 mmol), **3a** (0.24 mmol), $Pd(PPh_3)_4$ (5 mol%), solvent (1 mL), N_2 atmosphere, 12 h. [b]GC yield using dodecane as internal standard, n.d. = not detected. [c]1.5 equiv B_2pin_2 was added.

17), while acid additives promoted the transformation slightly (entries 18-19). Fortunately, when 1 equivalent of $Zn(OTf)_2$ was added, the reaction selectively afforded 4aaa with a 76% GC yield (entry 20). Efficient three-component coupling product formation was observed, giving the corresponding product **4aaa** in 82% yield when the amount of $Zn(OTf)_2$ was reduced to 0.2 equivalent (entry 21). Herein, we think that acids and $Zn(OTf)_2$ may play a role in inhibiting the production of by-product (**5aaa**). Subsequent experiment showed that GC yield of **4aaa** did not increase significantly when 1.5 equivalent of B_2pin_2 was added (entry 22). Above all, we determined the optimized conditions of the palladium-catalyzed three-component coupling reaction: allyl carboxylate (**1a**, 0.2 mmol), norbornene (**2a**, 1.2 equiv), bis(pinacolato)diboron (**3a**, 1.2 equiv), $Pd(PPh_3)_4$ (5 mol%), $Zn(OTf)_2$ (20 mol%), *n*-propanol (1 mL), N_2 atmosphere, 90 °C, 12 h. It is worth to mentioning that the transformation proved to be totally affording *exo*-product (confirmed by X-ray crystallography).[18]

Table 2 Substrate scope for allyl alkanoates **1**[a]



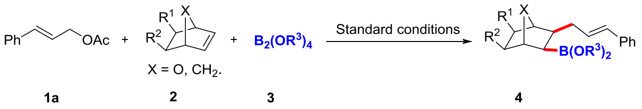
[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.24 mmol), **3a** (0.24 mmol), $Pd(PPh_3)_4$ (5 mol%), $Zn(OTf)_2$ (20 mol%) in 1 mL *n*-propanol at 90 °C, under N_2 atmosphere, for 12 h. N.D. = not detected.

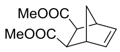
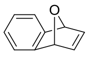
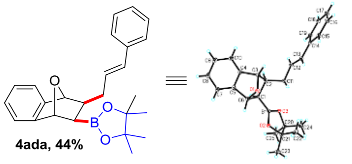
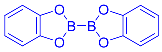
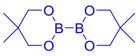
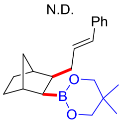
After the optimal conditions were determined, various 3-arylallylacetates were employed to explore the scope of this reaction firstly (Table 2). For the *para*-position of the phenyl ring, the substrates bearing electron-donating groups such as methoxy (**1b**), methyl (**1c**), *tert*-butyl (**1d**) and phenyl (**1e**) showed well tolerable and affording the desired products in 72-82% yields (**4baa-4eaa**). By contrast, the one bearing electron-withdrawing groups such as fluoro (**1f**), chloro (**1g**), nitro (**1i**), cyano (**1j**) and trifluoromethyl (**1k**) were converted to the desired products in 65-73 yields (**4faa, 4gaa, 4iaa, 4jaa, 4kaa**). It is worth noticing that the corresponding product of 4-bromo substituted substrate (**1h**) could not be obtained. And the result might be due to that the $C(sp^2)$-Br bond of the substrate (**1h**) would affect the oxidative addition of $C(sp^3)$-O bond. Pleasingly, *meta*- (**1l-1n**) and *ortho*-substituted 3-arylallylacetates (**1o-1p**) converted into the desired products in considerable yields successfully (**4laa-4paa**). Disubstituted substrates, such as 2,4-dimethyl substrate (**1qaa**) and 3,5-dichoro substituted substrate (**1raa**) could efficiently participate in this transformation giving **4qaa** and **4raa** in 83% yield and 57% yield respectively. To our delight, heteroaryl substrate (**1s**) was also tolerated in this protocol. Finally, the substrate gave no corresponding product when γ-position was replaced by methyl group (**1t**) or dimethyl group (**1u**), which might be owing to that the corresponding π-allyl Pd(II)-intermediate would undergo β-hydride elimination.[19]

In addition, different norbornene analogues **2** and boronates **3** were also investigated to explore the scope of this reaction under optimized conditions. As shown in Table 3, norbornadiene (**2b**) and 2,3-diester substituted norbornene (**2c**) could not undergo the transformation. Fortunately, the reaction of 1,2,3,4-tetrahydro-1,4-epoxynaphthalene (**2d**) afforded the desired product (entry 4, **4ada**) in 44% yield, which was unambiguously confirmed by X-ray crystallography.[18] We have also examined other boron nucleophiles such as 2,2'-biphenyl[*d*][1,3,2]dioxaborane (**3b**), 5,5,5',5'-tetramethyl-2,2'-co(1,3,2-dioxaborolane) (**3c**), wherein, **3b** could not convert to the desired product, and **3c** participated efficiently giving the desired product **4aac** in 77% yield.

Next, the substrate scope was further extended to other allyl compounds (Table 4). The substrates bearing formyl underwent this unique transformation smoothly, while the one bearing chloro (**1y**), bromo (**1z**) and *p*-methanesulfonyloxy (**1z^1**) group were not suitable, which can be attributed to its beneficial effect of the borylation step.[20]

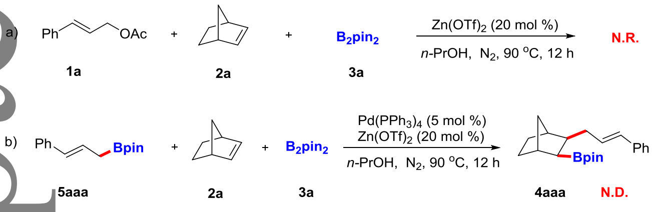
Table 3 Substrate scope for norbornene analogues **2** and diboronates **3**[a]



Entry	Norbornene analogues	Diboronates	Product	Yield
1	 **2b**	**3a**	N.D.	—
2	 **2c**	**3a**	N.D.	—
3	 **2d**	**3a**	 **4ada, 44%**	
4	 **2a**	 **3b**	N.D.	—
5	**2a**	 **3c**	 **4aac**	77%

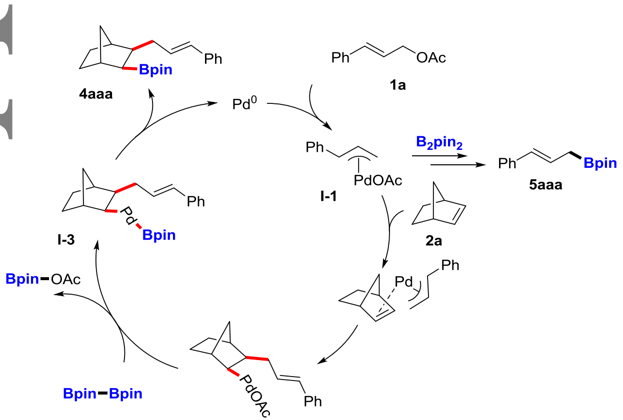
[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.24 mmol), **3a** (0.24 mmol), $Pd(PPh_3)_4$ (5 mol%), $Zn(OTf)_2$ (20 mol%) in 1 mL *n*-propanol at 90 °C, under N_2 atmosphere, for 12 h. N.D. = not detected.

Scheme 3. Mechanistic studies



To gain more insight into the mechanism, some control experiments were performed (Scheme 3). The starting material **1a** did not undergo this transformation without adding palladium catalysts, which indicated that $Pd(PPh_3)_4$ played a catalytic role in this reaction (Scheme 3, a). Moreover, when allyl carboxylate (**1a**) was replaced by the coupling product **5aaa**, the desired product **4aaa** could not be de-tected, indicating that **5aaa** could not be an intermediate of this process (Scheme 3, b).

Scheme 4 Tentative mechanism



On the basis of the above-mentioned results and previous reports[7,8,14-17,20,21], we proposed a tentative mechanism (Scheme 4). Firstly, oxidative addition of allyl carboxylate to Pd^0 formed π-allyl Pd(II)-intermediate **I-1**, followed by coordinating with norbornene **2a** and a *syn*-addition of **I-1** to carbon-carbon double bond to produce σ-alky Pd(II)-intermediate **I-2**. Then, **I-2** was captured by bis(pinacolato) -diboron **3a** to give σ-alkyl Pd(II)-intermediate **I-3**. Subsequent reductive elimination of **I-3** afforded **4aaa** and released Pd^0.

Conclusions

In summary, we have developed an efficient approach for the synthesis of 2-allylnorbornyl boronates via palladium-catalyzed three-component coupling reaction of allyl carboxylates, norbornenes and diboronates. The readily available starting materials, good selectivity and considerable yields make this protocol synthetically useful.

Experimental

In a 50 mL sealing tube equipped with a magnetic stirring bar and a reflux condenser was added allyl bis(pinacolato)diboron **3** (0.24 mmol), $Pd(PPh_3)_4$ (0.01 mmol, 5 mol%), $Zn(OTf)_2$ (0.04 mmol, 20 mol%), carboxylates **1** (0.2 mmol), a solution of norbornene **2** (0.24 mmol) and *n*-propanol (1 mL) under N_2 atmosphere at room temperature. The resulting mixture was stirred at 90 °C for 12 h. After the reaction mixture was cooled to room temperature, added 10 mL water, extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over $NaSO_4$, filtered and concentrated in vacuum to give the crude product. GC yields were determined by gas chromatography using decane as an internal standard. Purification was achieved by flash chromatography.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

Acknowledgement (optional)

The authors thank the National Program on Key Research Project (2016YFA0602900), the National Natural Science Foundation of China (21420102003), and Guangdong Province Science Foundation (2017B090903003) for financial support.

References

[1] (a) Tsubata, A.; Uchiyama, T.; Kameyama, A.; Nishikubo, T. *Macromolecules*. **1997**, *30*, 5649-5654; (b) Nishimura, I.; Kameyama, A.; Nishikubo, T. *Macromolecules*. **1998**, *31*, 2789- 2796; (c) Yoshida, Y.; Mohri, J.; Ishii, S.; Fujita, T. *J. Am. Chem. Soc.* **2004**, *126*, 12023-12032; (d) Holtsclaw, J.; Koreeda, M. *Org. Lett.* **2004**, *6*, 3719-3722; (e) Castagner, B.; Leighton, J. L. *Tetrahedron*. **2007**, *63*, 5895-5902; (f) Martins, A.; Mariampillai, B.; Lautens, M. *Top. Curr. Chem.* **2010**, *292*, 1-33; (g) Waibel, M.; Cramer, N. *Angew. Chem. Int. Ed.* **2010**, *49*, 4455-4458; (h) Nicolaou; K. C.; Ortiz, A.; Zhang, H. -J.; Lizos, D. E. *J. Am. Chem. Soc.* **2010**, *132*, 7138-7152; (i) Yanney, P. A. D. M. *Chem. Phys. Lett.* **2015**, *640*, 140-146.

[2] (a) Chauvet, F.; Heumann, A. and Waegell, B. *J. Org. Chem.* **1987**, *52*, 1916-1922; (b) Kinsella, M. A.; Kalish, V. J. and Weinreb, S. M. *J. Org. Chem*. **1990**, *55*, 105-111; (c) Yoshida, Y.; Mohri, J.; Ishii, S. and Fujita, T. *J. Am. Chem. Soc.* **2004**, *126*, 12023-12032; (d) Holtsclaw, J.; Koreeda, M. *Org. Lett.* **2004**, *6*, 3719-3722; (e) Gültekin, D. D.; Taskesenligil, Y.; Dastan, A.; Balci, M. *Tetrahedron*. **2008**, *64*, 4377-4383; (f) Larraufie, M. H.; Maestri, G.; Beaume, A.; Lacôte, E.;

Catellani, M. and Malacria, M. *Angew. Chem*. **2011**, *123*, 12461-12464; (g) Essiz, S.; Dalkilic, E.; Sari, O.; Dastan, A.; Balci, M. *Tetrahedron*. **2017**, *73*, 1640-1649; (h) Zanchin, G.; Pierro, I.; Parisini, E.; Rujas, J. M.; Ricci, G.; Leone, G. *J. Org. Chem*. **2018**, *861*, 142-150; (i) Zhu, W. -B.; Lü, X. -L.; Zhu, J. -H.; Cao, Q, -Y. *Chin. J. Org. Chem.* **2017**, *37*, 624-629.

[3] (a) Li, Y. -B.; Liu, X. -H.; Jiang, H. -F.; Liu, B. -F.; Chen, Z. -W.; and Zhou, P. *Angew. Chem. Int. Ed*. **2011**, *50*, 6341-6345; (b) Wu, W. Q.; Jiang, H. -F.; Gao, Y, Huang, H. -W.; Zeng, W. and Cao, D. -R.; *Chem. Commun*. **2012**, *48*, 10340-10342; (c) Gao, Y.; Huang, Y. -B.; Wu, W. -Q.; Huang, K. -F. and Jiang, H. -F.; *Chem. Commun*. **2014**, *50*, 8370-8373; (d) Huang, L. -B.; Wang, Q.; Wu, W. -Q. and Jiang, H. -F.; *Adv. Synth. Catal*. **2015**, *45*, 1949-1954.

[4] (a) Yang, K. and Song, Q. -L. *J. Org. Chem*. **2016**, *81*, 1000-1005; (b) Zhu, C. -L.; Chen, P. -Q.; Zhu, R.; Jiang, G. -B.; Lin, Z. -M.; Wu, W. -Q. and Jiang, H. -F. *Chem. Asian. J*. **2017**, *12*, 2991-2995.

[5] (a) Ma, S. M. and Lu, X. Y. *J. Org. Chem*. **1993**, *58*, 1245-1250; (b) Tsujihara, T.; Takenaka, K.; Onitsuka, K. Hatanaka, M. and Sasai, H. *J. Am. Chem. Soc*. **2009**, *131*, 3452-3453; (c) Chai, D. I.; Thansandote, P. and Lautens, M. *Chem. Eur. J*. **2011**, *17*, 8175-8188; (d) Ludlow, B. S.; Danielsson, J. and Somfai, P. *Adv. Synth. Catal*. **2012**, *354*, 205-216; (e) Wang, W.; Zhou, R.; Jiang, Z. -J.; Wang, X.; Fu, H. -Y.; Zheng, X. -L.; Chen, H. and Li, R. -X. *Eur. J. Org. Chem*. **2015**, 2579-2584; (f) Wu, X. -X.; Chen, W. -L.; Shen, Y.; Chen, S.; Xu, P. -F. and Liang, Y. -M. *Org. Lett*. **2016**, *18*, 1784-1787; (g) Coomber, C. E.; Benhamou, L.; Bucar, D. K.; Smith, P. D.; Porter, M. J. and Sheppard, T. D. *J. Org. Chem*. **2018**, *83*, 2495-2503.

[6] (a) Ji, J. -G.; Lu, X. -Y.; *Tetrahedron*. **1994**, *50*, 9067-9078; (b) Liu, H.; Li, C. -L.; Qiu, D.; Tong, X. -F. *J. Am. Chem. Soc*. **2011**, *133*, 6187-6193; (c) Huang, L. -B.; Wang, Q.; Liu, X. -H.; Jiang, H. -F. *Angew. Chem. Int. Ed*. **2012**, 51, 5696-5700; (d) Muriel, B.; Orcel, U. and Waser, J. *Org. Lett*. **2017**, *19*, 3548-3551.

[7] (a) Vachhani, D. D.; Butani, H. H.; Eycken, E. V. V. *Chem. Commun.* **2015**, 51, 14862-14865; (b) Nelson, H. M.; Williams, B. D.; Miro, J. and Toste, F. D. *J. Am. Chem. Soc.* **2015**, 137, 3213-3216; (c) Martínez, J. M.; Carrillo, V. L.; Buñuel, E.; Simancas, R. and Cárdenas, D. J. *J. Am. Chem. Soc.* **2007**, 129, 1874-1875; (d) Jiang, Z. -W.; Hou, W. -L.; Ni, C. -J.; Chen, J. -F.; Wang, D. and Tong, X. -F. *Chem. Commun.* **2017**, *53*, 4270-4273; (e) Ping, Y. -Y.; Li, Y. -X.; Zhu, J. -P. and Kong, W. -Q. *Angew. Chem. Int. Ed*. DOI:10.1002/ange.201806088.

[8] (a) Liao, M. -C.; Duan, X. -H. and Liang, Y. -M. *Tetrahedron. Lett*. **2005**, 46, 3469-3472; (b) Afewerki, S.; Ibrahem, I.; Rydfjord, J.; Breistein, P. and Córdova, A. *Chem. Eur. J*. **2012**, *18*, 2972-2977; (c) Fujita, T.; Yamamoto, T.; Morita, Y.; Chen, H.; Shimizu, Y. and Kanai, M. *J. Am. Chem. Soc*. **2018**, *140*, 5899-5903.

[9] (a) Tsuji, Y.; Funato, M.; Kawamura, T. *J. Org. Chem*. **1996**, *61*, 5779-5787; (b) Moser, R.; Nishikata, T. and Lipshutz, B. -H. *Org. Lett*. **2010**, 12, 28-31; (c) Selander, N.; Paasch, J. R. and Szabó, K. J. *J. Am. Chem. Soc*. **2011**, *133*, 409-411.

[10] (a) Feng, B.; Cheng, H. G.; Xiao, W. J. *Chem. Commun*. **2014**, *50*, 9550-9553; (b) Yin, P.; Wong, M. -Y.; Thamb, J. and Loh, T. P. *Org. Chem. Front*. **2014**, *1*, 1266-1269; (c) Chen, H. -J.; Yang, W. -F.; Wu, W. -Q. and Jiang, H. -F. *Org. Biomol. Chem*. **2014**, *12*, 3340-3343; (d) Wang, Y. -N.; Wang, B. -C.; Zhang, M. -M.; Gao, X. -W.; Li, T. -R.; Lu, L. -Q. and Xiao, W. -J. *Org. Lett*. **2017**, *19*, 4094-4097; (e) Gao, S.; Liu, H.; Yang, C.; Fu, Z. -Y.; Yao, H. -Q. and Lin, A. J. *Org. Lett*. **2017**, *19*, 4710-4713.

[11] (a) Baig, R. B. N. and Varma, R. S. *Green. Chem*. **2013**, *15*, 398-417; (b) Halder, M.; Islam, M. M.; Islam, S. M. *RSC Adv*. **2016**, *6*, 8282-8289; (c) Cazorla, C.; Billamboz, M.; Bricout, H.; Monflier, and Len, C. *Eur. J. Org. Chem*. **2017**, 1078-1085; (d) Rukkijakan, T.; Akkarasamiyo, S.; Sawadjoon, S. and Samec, J. S. M. *J. Org. Chem.* **2018**, *83*, 4099-4104.

[12] (a) Altamirano, K. B.; Montchamp, J. L. *Org. Lett*. **2006**, *8*, 4169-4171; (b) Butti, P.; Rochat, R.; Sadow, A. D.; Togni, A. *Angew. Chem. Int. Ed*. **2008**, *47*, 4878-4881; (c) Altamirano, K. B.; Thomas, I. A. and Montchamp, J. L. *J. Org. Chem*. **2008**, *73*, 2292-2301.

[13] (a) Tsutsumi, K.; Yabukami, T.; Fujimoto, K.; Kawase, T.; Morimoto, T. and Kakiuchi, K. *Organomet*. **2003**, *22*, 2996-2999; (b) Liu, W.; Zhao, X. -M.; Zhang, H. B.; Zhang, L. *Chem. Commun*. **2015**, *51*, 655-657.

[14] (a) Sebelius, S.; Olsson, V. J. and Szabó, K. J. *J. Am. Chem. Soc.* **2005**, *127*, 10478-10479; (b) Raducan, M.; Alam, R. and Szabó, K. J. *Angew. Chem. Int. Ed*. **2012**, *51*, 13050-13053; (c) Zhang, P.; Roundtree, I. A.; Morken, J. P. *Org. Lett*. **2012**, *14*, 1416-1419; (d) Mao, L. J.; Bertermnn, R.; Rachor, S. G.; Szbó, K. J. and Marder, T. B. *Org. Lett*. **2017**, *19*, 6590-6593.

[15] (a) Tsukada, N.; Sato, T.; Inoue, Y. *Tetrahedron. Lett*. **2000**, *41*, 4181-4184; (b) Walter, M. D.; Moorhouse, R. A.; Urbin, S. A.; White, P. S. and Brookhart, M. *J. Am. Chem. Soc*. **2009**, 131, 9055–9069.

[16] (a) Jia, T.; Cao, P.; Wang, B.; Lou, Y. -Z.; Yin, X. -M.; Wang, M. and Liao, J. J. Am. Chem. Soc. 2015, 137, 13760−13763; (b) Lee, J.; Radomkit, S.; Torker, S.; Pozo, J. and Hoveyda, A. H. *Nature. Com.* **2018**, *10*, 99–108.

[17] (a) Newman, S. G.; Lautens, M. *J. Am. Chem. Soc*. **2011**, *13,* 1778-1780; (b) Larraufie, M. H.; Maestri, G.; Beaume, A.; Derat, É.; Ollivier, C.; Fensterbank, L.; Courillon, C.; Lacôte, E. Catellani, M. and Malacria, M. *Angew. Chem. Int. Ed*. **2011**, *50*, 12253-12256; (c) Xiang, P.; Ye, Z. *J. Org. Chem*. **2015**, *798*, 429-436; (d) Chen, J.; Natte, K.; Wu, X. *J. Organomet. Chem*. **2016**, *803*, 9-12.

[18] Crystallographic data for **4ada** (CCDC 1848632) has been deposited with the Cambridge Crystallographic Data Centre.

[19] (a) Urata, H.; Suzuki, H.; Ikawa, T. *Bull. Chem. Soc. Jpn*. **1984**,*57*, 607-608; (b) Keinan, E.; Kumar, S. *J. Am. Chem. Soc*. **1994**, *116*, 11151-11152.

[20] Ishiyama, T.; Ahiko, T. A. and Miyaura, N. *Tetrahedron Lett.* **1996**, *37*, 6889-6892.

[21] (a) Tsuji, J.; Kiji, J.; Morikaw, M. *J. Am. Chem. Soc*. **1964**, *86,* 4350-4353; (b) Trost, B. M. *Tetrahedron*. **1977**, *33*, 2615-2649; (c) Trost, B. M. *Acc. Chem. Res*. **1980**, *13*, 385-393; (d) Tsuji, J. *Tetrahedron*. **1986**, *42*, 4361-4401; (d) Gavrilov, K. N.; Zheglov, S. V. *Adv. Synth. Catal*. **2010**, *352*, 2599-2610; (e) Pong, F. Y.; Mandal, S. and Sen, A. *Organomet*. **2014**, *33*, 7044-7051; (f) Zhang, P. S.; Pan, S. F.; Chen, W. Z.; Liu, M. C. and Wu, H. -Y. *J. Org. Chem*. **2018**, *83*, 3354-3360.

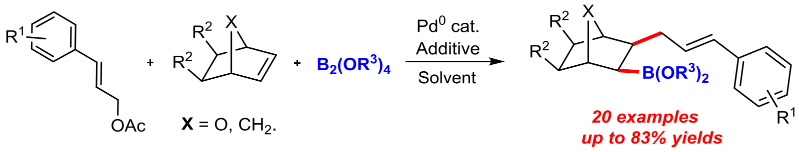
(The following will be filled in by the editorial staff)
Manuscript received: XXXX, 2019
Manuscript revised: XXXX, 2019
Manuscript accepted: XXXX, 2019
Accepted manuscript online: XXXX, 2019
Version of record online: XXXX, 2019

Entry for the Table of Contents

Page No.

Palladium-Catalyzed Three-Component Coupling Reaction of Allyl Carboxylates, Norbornenes and Diboronates Involving Sequential Olefins Insertion and Borylation Reaction

Zun Li, Jia Zheng, Chunsheng Li, Wanqing Wu, and Huanfeng Jiang*



20 examples
up to 83% yields

- ♦ Forming a stable σ-alkyl Pd^{II}-intermediate to couple with weak nucleophile – diboronates
- ♦ Efficient construction of C(sp^3)-C(sp^3) bond and C(sp^3)-B bond in a single reaction
- ♦ The coupling products of two components could be circumvented