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Synthesis of Conjugated Boron-Enynes *via cis*-Alkynylboration of Terminal Alkynes

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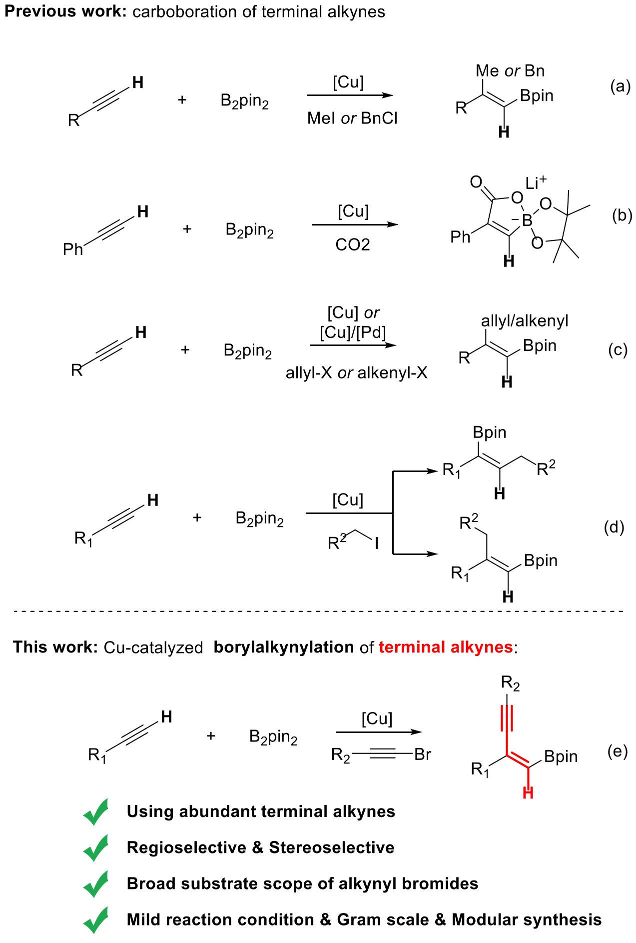
Abstract. A unique and practical Cu-catalyzed *cis*-alkynylboration of terminal alkynes with diboron reagents and bromoalkynes has been realized. This process enables the convenient synthesis of a large variety of trisubstituted enynylboronates under mild reaction conditions with broad functional-groups compatibility, high regioselectivity and stereoselectivity. The usability and practicability of this process was further demonstrated by the successful modular synthesis of enediynes.

Keywords: copper catalysis; carboborylation; regio- and stereoselectivity; *cis*-alkynylboration; enynylboronates

Alkenylboronates units are valuable synthetic building blocks whose C-B bond can be transformed into C-C or C-X bond to give multisubstituted alkenes.[1] Many approaches have been developed for the synthesis of alkenylboronates,[2] such as metal exchange reactions with organolithium or Grignard reagents and borylation reactions of alkynes.[3,4,5] Among the methods reported, copper-catalyzed carboboration reaction of alkynes with bis(pinacolato)-diboron [$B_2(pin)_2$] and subsequent interception of the putative β-boryl alkenyl-copper intermediate species with carbon based electrophiles, which appears to be the most straightforward and effective method to obtain tri- and tetra-substituted alkenylboronates, have received increasing interest.[6,7,8,9] Copper-catalyzed carboboration of internal alkynes involving boracarboxylation,[6a] alkylboration,[6b-h] arylboration[6i,6j] and alkynylboration[6m] have been extensively established for synthesis of tetra-substituted alkenylboronates, but only few examples of carboboration of terminal alkynes were reported. For examples, Tortosa's and Yoshida's group pioneered Cu-catalyzed methylboration and benzylboration of activated terminal alkynes (Scheme 1, a).[7] Hou's group reported a Cu-catalyzed boracarboxylation of phenylacetylene, only one example was given in this paper (Scheme 1, b).[6a] Then, Cu- or Cu/Pd catalyzed allylboration[8] and alkenylboration[6k] of terminal alkynes synthesis of skipped and conjuction dienes were realized (Scheme 1, c). Moreover, our group reported a regiodivergent copper-catalyzed alkylboration of unactivated terminal alkynes,[9] anti-markovnikov and markovnikov alkylboration products were obtained by using two different ligands (Scheme 1, d). To the best of our knowledge, alkynylboration of terminal alkynes has not been reported to date.

On the other hand, enynes are widely used for designing nanostructures, polymer synthesis and organic synthesis.[10] Although, transition-metal-catalyzed cross-dimerization of alkynes, Suzuki, Sonogashira-coupling reaction and alkynylboration of internal alkynes have been developed toward the synthesis of enynes.[4f-h,6m,11] The search for new synthetic approaches to enyne compounds is still a challenging issue in chemical synthesis. Taking into account our ongoing interest in the development of new boration/functionalization reactions of C-C unsaturated bonds[9,12] and the important of enynes units in organic synthesis, we envisioned that alkynylboration of terminal alkynes could be applied to rapidly synthesis trisubstituted enynylboronates which were inaccessible by previous methods. To achieve this idea, two formidable challenges should be overcome. The first challenge is the reactivity, regioselectivity and stereoselectivity.[13] Athough the carboboration of terminal alkynes has been studied, until now alkynylboration of terminal alkynes have never been reported to access conjugated enynes scaffolds. The second challenge is to prevented the side reactions, including the Cadiot-Chodkiewicz reaction[14] and the further boration of the enyne[15] products, which were also catalyzed by copper catalyst under base condition.

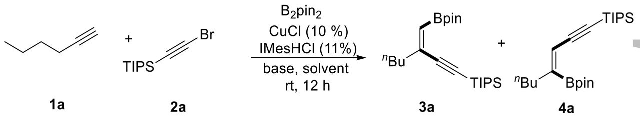
Herein, we report an example of copper-catalyzed *cis*-alkynylboration of terminal alkynes with B_2pin_2 and bromoalkynes synthesis of conjugated boron-enynes (Scheme 1, e). This reaction presents an efficient route to construct C(sp)-C(sp^2) and C(sp^2)-B bond in a single step with tolerance of a broad range of substituted alkynes. Subsequent manipulations of the boron-enynes products proved to be efficient access to a variety of high-value products.



Scheme 1. Scheme Caption.

We initially used 1-hexyne, bis(pinacolato)diboron (B_2in_2) and triisopropylsilylethynyl bromide as model substrates, and systematically screened the influence of all reaction parameters to attempt the alkynylboration reaction. when the substrates were treated with the conditions: CuCl, dppbz, and LiO^{t}Bu in THF at room temperature for 12 h, which were used in our previous alkylboration reaction,[9] we are pleased to found that the target alkynylboration product **3a** was obtained in 27% yield with moderate anti-Markovnikov regioselectivity (**3a** : **4a** = 5:1, entry 1).Then we explored the effects of other ligands on this reaction. Unfortunately, when Dppf, IPr·HCl, which are superior in the migratory insertion of CuBpin complexes across alkynes, were used, alkynylboration was completely suppressed. It's found that IMes·HCl was the optimal ligand for the transformation, the alkynylboration product **3a** was obtained in 45% yield with moderate anti-Markovnikov regioselectivity (**3a** : **4a** = 6:1, entry 9). Then, the influences of various bases were tested, indicated that a mild base LiOTMS (lithium trimethylsilanolate, $LiOSiMe_3$, p*Ka′*= 12.7)[16] was the optimal choice, whereas other bases such as NaO^{t}Bu, KO^{t}Bu, K_2CO_3 and Cs_2CO_3 afforded the desired product in diminished yields with slightly lower regioselectivity. We tentatively suggest that the increase in regioselectivity observed with the LiOTMS are due to its increased size. Moreover, when we used the precatalyst IMesCuCl instead of CuCl and IMes·HCl, the yield of **3a** was slightly improved (entry 15). Gratifyingly, when dioxane was used as solvent, the yield of product **3a** was promoted to 80% with higher regioselectivity (r.r. = 15:1). The loading of the catalyst (IMesCuCl) could be reduced to 2 mol % without influencing the conversion effect significantly.

Table 1. Optimization of reaction conditions.[a]



entry	Ligand	Base	Yield [%]	r.r. [b]
1	DppBz	LiO^{t}Bu	27	5:1
2	DMAP	LiO^{t}Bu	10	1.5:1
3	Dppe	LiO^{t}Bu	23	5:1
4	PCy_3	LiO^{t}Bu	20	6:1
5	PPh_3	LiO^{t}Bu	< 2	-
6	1,10-phen	LiO^{t}Bu	< 2	-
7	Dppf	LiO^{t}Bu	< 2	-
8	I^{i}Pr·HCl	LiO^{t}Bu	5	2:1
9	IMes·HCl	LiO^{t}Bu	45	6:1
10	IMes·HCl	NaO^{t}Bu	37	5:1
11	IMes·HCl	KO^{t}Bu	31	5:1
12	IMes·HCl	Cs_2CO_3	34	6:1

13	IMes·HCl	K_2CO_3	40	6:1
14	IMes·HCl	LiOTMS	72	12:1
15[c]	IMesCuCl	LiOTMS	77	12:1
16[d]	IMesCuCl	**LiOTMS**	**87 (80^{e})**	**15:1**
17[d], [f]	IMesCuCl	LiOTMS	84 (76^{e})	15:1

[a] Reaction conditions: alkyne **1a** (0.2 mmol), $(Bpin)_2$ (0.3 mmol), **2a** (0.4 mmol), CuCl (0.02 mmol), ligand (0.022 mmol), base (0.4 mmol), and THF (1 mL) were stirred at room temperature for 12 h.

[b] Determined by GC analysis.

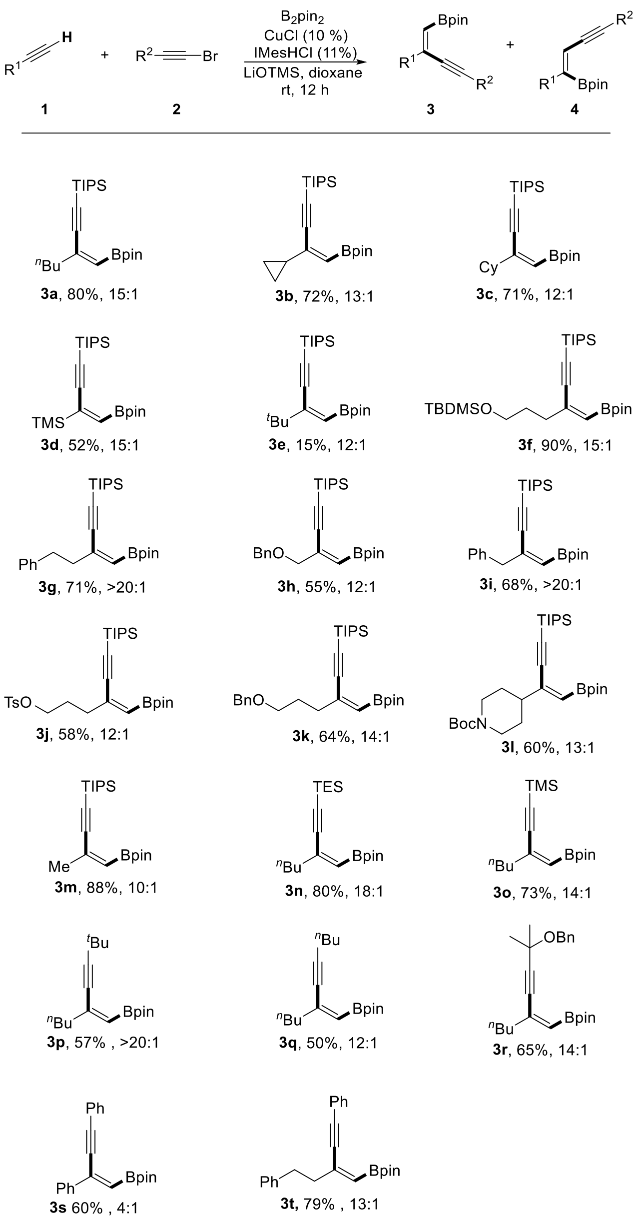
[c] IMesCuCl instead of CuCl and IMes·HCl.

[d] Dioxane was used instead of THF.

[e] Isolated yield.

[f] 2 mol% of IMesCuCl was used. B_2pin_2 = bis(pinacolato)-diboron.

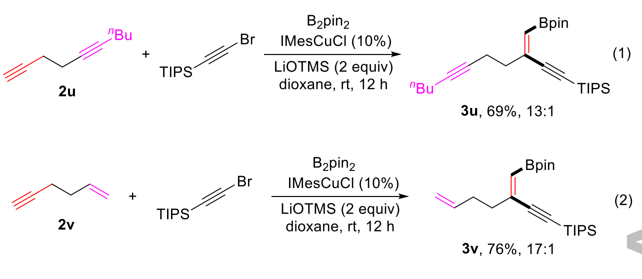
Table 2. Substrates scope.[a]



3a, 80%, 15:1
3b, 72%, 13:1
3c, 71%, 12:1
3d, 52%, 15:1
3e, 15%, 12:1
3f, 90%, 15:1
3g, 71%, >20:1
3h, 55%, 12:1
3i, 68%, >20:1
3j, 58%, 12:1
3k, 64%, 14:1
3l, 60%, 13:1
3m, 88%, 10:1
3n, 80%, 18:1
3o, 73%, 14:1
3p, 57% , >20:1
3q, 50%, 12:1
3r, 65%, 14:1
3s 60% , 4:1
3t, 79% , 13:1

[a] Reaction conditions: alkynes (0.2 mmol), B_2pin_2 (0.3 mmol), haloalkynes (0.4 mmol), IMesCuCl (0.02 mmol), and LiOTMS (0.4 mmol) were stirred in dioxane (1 mL) at room temperature for 12 h. *r.r.* was determined by GC analysis. Isolated yield.

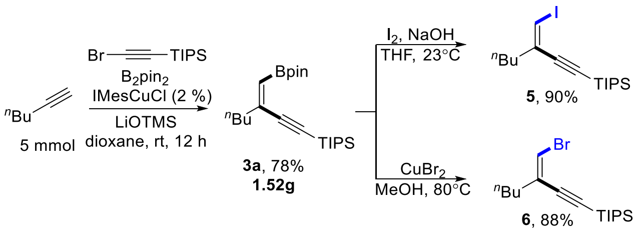
With the optimized reaction conditions in hand, we sought to examine the scope of copper-catalyzed alkynylboration with a wide scope of terminal alkynes. As shown in Table 2, these alkynes could be converted to the desired products smoothly in all case with excellent regioselectivities and acceptable isolated yields (up to 90%). The reaction of cyclopropyl and cyclohexyl acetylene proceeded smoothly under the standard conditions (**3b**, **3c**). The introduce of a bulky TMS group led to a less reactive substrate, the desired product **3d** could be formed in 52 % yield. Under the same conditions, the substrate with ^{t}Bu group afforded **3e** in only 15% yield. This result shows the substituents at the alkyne have a large effect on the reactivity of the alkynylboration, larger steric hindrance substituents at alkynyl reduces the catalytic efficiency. Under the mild reaction conditions, this alkynylboration reaction showed good compatibility with many synthetically relevant functional groups such as ether (**3f**, **3h**, **3k**), ester (**3j**), and carbamate (**3l**). Remarkably, propyne, which is manufactured on a huge scale by the petrochemical industry, successfully gave out alkynylboration product in good yield of 88% (**3m**). Then, we investigated the scope of bromoalkynes. A variety of silylated alkynylbromides were well tolerated in this reaction (**3n**, **3o**). In addition, this reaction proceeded well with aromatic (**3s**, **3t**) and aliphatic alkynylbromides bearing different functional groups, offering products bearing a ^{t}Bu group (**3p**, 57%) or protected alcohols (**3r**, 65%).



Scheme 2. Intramolecular competitive experiments.

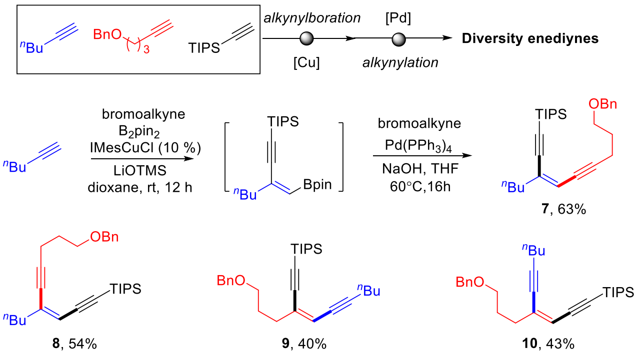
Regarding to the chemoselectivity of this alkynylboration reaction, it exhibited that in the case of substrate with both terminal and internal alkynes, the former is much more reactive. Thus, when **2u** was treated with the reaction conditions (Scheme 2, eq 1), we observed only the alkynylboration at the terminal alkyne with excellent regioselectivity (69%, 13:1), whereas the transformation at the internal alkyne did not take place. The similar chemoselectivity was also found in substrate **2v** with both terminal alkyne and terminal alkene (Scheme 2, eq 2), the alkynylboration occurred exclusively at the position of the terminal alkyne, which was consistent with our previous work.[9]

Gram-scale synthesis of boron-enynes **3a** was carried out to test the scalability of the transformation. The alkynylboration of **1a** on a 5.0 mmol scale afforded **3a** in 78% yield (Scheme 3). To test the synthetic utility of this copper-catalyzed *cis*-alkynylboration reaction, alkenylhalogenation products (**5, 6**) were obtained with the halogenation of the vinylboronic ester.[9]



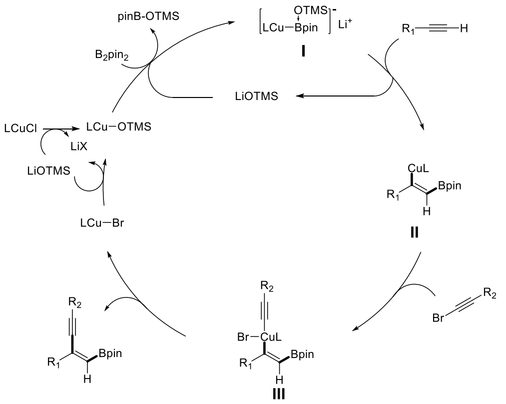
Scheme 3. Gram-scale experiment and derivatization of product.

Considering that enediynes units are widely existed in natural compounds and nanostructures,[17] we exploited the synthetic application of the alkynylboration process for modular synthesis enediynes by using three simple alkynes (Scheme 4). As an example, coupling of 1-hexyne with triisopropylsilylethynyl bromide resulted in the formation of boron-enyne. Through further Pd-catalyzed alkynylation, target enediynes unit **7** was made in 63% yield in two-steps. Other enediynes (**8, 9**, and **10**) can also be obtained in the same way.



Scheme 4. Modular synthesis of enediynes from three simple alkynes.

Based on previous work, we propose a plausible catalytic cycle for borylalkynylation of terminal alkynes as illustrated in Scheme 5. First, IMesCuOTMS complex was generated from the reaction of IMesCuCl with LiOTMS. Then σ-bond metathesis with pinB-Bpin generates borylcopper species **I** with an 'ate'-salt form under excess base condition (see SI for more information).[18] An 'ate'-salt form borylcopper species may be the real catalyst in this borylalkynylation. Subsequent insertion of the terminal alkyne into the Cu-B bond of **I** with high regioselective furnishes a *β*-boryl vinylcopper intermediate **II**. Then oxidative addition with the bromoalkyne to form intermediate **III**, which undergoes a reductive elimination to furnish the desired alkynylboration product along with the regeneration of the Cu$^{(I)}$ catalyst.



Scheme 5. Plausible catalytic cycle.

In summary, we described a copper-catalyzed alkynylboration of terminal alkynes for the first time. The present reaction provided convenient and efficient access to a large variety of functionalized conjugated boron-enynes under mild reaction conditions which exhibited well functional groups compatibility with excellent regio-selectivity. This process would be an important supplement to previous alkynylboration reactions.

Experimental Section

A 10 mL Schlenk tube equipped with a magnetic stirrer was charged with IMesCuCl (10 mol%, 0.02 mmol), LiOTMS (2.0 equiv., 0.4 mmol) and B_2pin_2 (1.5 equiv., 0.3 mmol). The tube was evacuated and backfilled with argon for three times, and then dioxane (1 mL) was added. After stirring for 5 min, the alkyne **1** (0.2 mmol) and bromoalkyne **2** (2.0 equiv., 0.4 mmol) was added by syringe under argon. The reaction mixture was stirred at room temperature for 12 h. Then EtOAc and water were added and the layers were separated. The aqueous phase was extracted with EtOAc (x2) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to give the enynylboronates **3**.

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References

[1] a) M. Kischkewitz, K. Kischkewitz, C. Mück-Lichtenfeld, A. Studer, *Science* **2017**, *355*, 936-938; b) M. Althaus, A. Mahmood, J. R. Suarez, S. P. Thomas, V. K. Aggarwal, *J. Am. Chem. Soc.* **2010**, *132*, 4025-4028; c) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, 95, 2457-2483; d) T. Hayashi, K. Yamasaki, *Chem. Rev.* **2003**, *103*, 2829-2844; e) J.-X. Qiao, P. Y. S. Lam, *Synthesis* **2011**, *6*, 829-856.

[2] a) J. R. Coombs, L. Zhang, J. P. Morken, *Org. Lett.* **2015**, *17*, 1708-1711; b) S. Tanaka, Y. Saito, T. Yamamoto, T. Hattori, *Org. Lett.* **2018**, *20*, 1828-1831; c) T. Ohmura, Y. Takasaki, H. Furukawa, M. Suginome, *Angew. Chem., Int. Ed.* **2009**, *48*, 2372-2375; d) J. Takaya, N. Kirai, N. Iwasawa, *J. Am. Chem. Soc.* **2011**, *133*, 12980-12983; e) W. B. Reid, J. J. Spillane, S. B. Krause, D. A. Watson, *J. Am. Chem. Soc.* **2016**, *138*, 5539-5542; f) M. Morimoto, T. Miura, M. Murakami, *Angew. Chem., Int. Ed.* **2015**, *54*, 12659-12663; g) C. Wang, C. Z. Wu, S. Ge, *ACS Catal.*, **2016**, *6*, 7585-7589; h) H. Wen, L. Zhang, S. Zhu, G. Liu, Z. Huang, *ACS Catal.* **2017**, *7*, 6419-6425; i) L. Zhang, Z. Huang, *J. Am. Chem. Soc.* **2015**, *137*, 15600-15603; j) T. J. Mazzacano, N. P. Mankad, *ACS Catal.* **2016**, *7*, 146-149.

[3] For reviews on borylation of alkynes, see: a) J. Yun, *Asian J. Org. Chem.* **2013**, *2*, 1016-1025; b) R. Barbeyron, E. Benedetti, J. Cossy, J. J. Vasseur, S. Arseniyadis, M. Smietana, *Tetrahedron.* **2014**, *70*, 8431-8452; c) K. Semba, T. Fujihara, J. Terao, Y. Tsuji, *Tetrahedron.* **2015**, *71*, 2183-2197; d) H. Yoshida, *ACS Catal.* **2016**, *6*, 1799-1811; e) M. Suginome, *Chem. Rec.* **2010**, *10*, 348-358; f) T. Fujihara, K. Semba, J. Terao, Y. Tsuji, *Catal. Sci. Technol.* **2014**, *4*, 1699-1709; g) Y. Shimizu, M. Kanai, *Tetrahedron Lett.* **2014**, *55*, 3727-3737; h) Y. Tsuji, T. Fujihara. *Chem. Rec.* **2016**, *16*, 2294-2313; i) E. C. Neeve, S. J. Geier, I. A. I. Mkhalid, S. A. Westcott, T. B. Marder, *Chem. Rev.* **2016**, *116*, 9091-9161; j) D. Hemming, R. Fritzemeier, S. A. Westcott, W. L. Santos, P. G. Steel, *Chem. Soc. Rev.* **2018**, *47*, 7477-7494.

[4] a) M. Suginome, A. Yamamoto, M. Murakami, *J. Am. Chem. Soc.* **2003**, *125*, 6358-6359; b) M. Suginome, A. Yamamoto, M. Murakami, *Angew. Chem., Int. Ed.* **2005**, *44*, 2380-2382; c) M. Daini, A. Yamamoto, M. Suginome, *J. Am. Chem. Soc.* **2008**, *130*, 2918-2919; d) S. Mannathan, M. Jeganmohan, C.-H. Cheng, *Angew. Chem., Int. Ed.* **2009**, *48*, 2192-2195; e) N. Nakagawa, T. Hatakeyama, M. Nakamura, *Chem. - Eur. J.* **2015**, *21*, 4257-4261; f) A. Yamamoto, M. Suginome, *J. Am. Chem. Soc.* **2005**, *127*, 15706-15707; g) M. Suginome, M. Shirakura, A. Yamamoto, *J. Am. Chem. Soc.* **2006**, *128*, 14438-14439; h) M. Nogami, K. Hirano, M. Kanai, C. Wang, T. Saito, K. Miyamoto, A. Muranaka, M. Uchiyama, *J. Am. Chem. Soc.* **2017**, *139*, 12358-12361.

[5] a) D. X. Li, Y. E. Kim, J. Yun, *Org. Lett.*, **2015**, *17*, 860-863; b) Q. Feng, K. Yang, Q. Song, *Chem. Commun.* **2015**, *51*, 15394-15397; c) H. Yoshida, Y. Takemoto, K. Takaki, *Chem. Commun.* **2015**, *51*, 6297-6300; d) A. Verma, R. F. Snead, Y. Dai, C. Slebodnick, Y. Yang, H. Yu, Y. Fu, W. L. Santos, *Angew. Chem., Int. Ed.* **2017**, *56*, 5111-5115; e) A. J. Jordan, P. K. Thompson, J. P. Sadighi, *Org. Lett.* **2018**, *20*, 5242-5246; f) E. Chong, S. A. Blum, *J. Am. Chem. Soc.* **2015**, *137*, 10144-10147; g) H. Yoshida, S. Kawashima, Y. Takemoto, K. Okada, J. Ohshita, K. Takaki, *Angew. Chem., Int. Ed.* **2012**, *51*, 235-238.

[6] a) L. Zhang, J. Cheng, B. Carry, Z. Hou, *J. Am. Chem. Soc.* **2012**, *134*, 14314-14317; b) P. Liu, Y. Fukui, P. Tian, Z.-T. He, C.-Y. Sun, N.-Y. Wu, G.-Q. Lin, *J. Am. Chem. Soc.* **2013**, *135*, 11700-11703; c) C.-C. Tai, M.-S. Yu, Y.-L. Chen, W.-H. Chuang, T.-H. Lin, G. P. A. Yap, T.-G, Ong, *Chem. Commun.* **2014**, *50*, 4344-4346; d) Y. D. Bidal, F. Lazreg, C. S. J. Cazin, *ACS Catal.* **2014**, *4*, 1564-1569; e) K. Kubota, H. Iwamoto, E. Yamamoto, H. Ito, *Org. Lett.* **2015**, *17*, 620-623; f) T. Itoh, Y. Shimizu, M. Kanai, *J. Am. Chem. Soc.* **2016**, *138*, 7528-7531; g) S. Liu, X. Zeng, B. Xu, *Adv. Synth. Catal.* **2018**, *360*, 3249-3253; h) S. H. Kim-Lee, I. Alonso, P. Mauleón, R. G. Arrayás, J. C. Carretero, *ACS Catal.*, **2018**, *8*, 8993-9005; i) Y.-Q. Zhou, W. You, K. B. Smith, M. K. Brown, *Angew. Chem., Int. Ed.* **2014**, *53*, 3475-3479; j) K. Semba, M. Yoshizawa, Y. Ohtagaki, Y. Nakao, *Bull. Chem. Soc. Jpn.* **2017**, *90*, 1340-1343; k) Nuria Vázquez-Galinñanes, M. Fañanás-Mastral, *ChemCatChem* **2018**, *10*, 4817-4820; l) L.-J. Cheng, N. P. Mankad, *Angew. Chem., Int. Ed.* **2018**, *57*, 10328-10332; More recently, Yun's group reported an example of Cu-catalyzed borylalkynylation of internal alkynes for synthesis of tetrasubstituted enynylboronates. Only aryl substituted internal alkynes were used in their transformation: m) J. T. Han, J. Yun, *Org. Lett.* **2018**, *20*, 2104-2107.

[7] a) R. Alfaro, A. Parra, J. Alemán, J. L. G. Ruano, M. Tortosa, *J. Am. Chem. Soc.* **2012**, *134*, 15165-15168; b) H. Yoshida, I. Kageyuki, K. Takaki, *Org. Lett.*

2013, *15*, 952-955; c) B. Mun, S. Kim, H. Yoon, K. H. Kim, Y. Lee, *J. Org. Chem*. **2017**, *82*, 6349-6357.

[8] a) H.-Y. Bin, X. Wei, J. Zi, Y.-J. Zuo, T.-C. Wang, C.-M. Zhong, *ACS Catal*. **2015**, *5*, 6670-6679; b) J. Mateos, E. Rivera-Chao, M. Fañanás-Mastral, *ACS Catal*. **2017**, *7*, 5340-5344; c) E. Rivera-Chao, M. Fañanás-Mastral, *Angew. Chem., Int. Ed.* **2018**, *57*, 9945-9949.

[9] W. Su, T.-J. Gong, Q. Zhang, Q. Zhang, B. Xiao, Y. Fu, *ACS Catal*. **2016**, *6*, 6417-6421. One more example of copper-catalyzed alkylboration of terminal alkynes was shown by Kanai's group, see ref. 6f for details.

[10] a) J. Roncali, *Chem. Rev.* **1997**, *97*, 173-206; b) P. Wessig, G. Müller, *Chem. Rev*. **2008**, *108*, 2051-2063; c) P. Lan, L. E. White, E. S. Taher, P. E. Guest, M. G. Banwell, A. C. Willis, *J. Nat. Prod.* **2015**, *78*, 1963-1968; d) E. Negishi, L. Anastasia, *Chem. Rev.* **2003**, *103*, 1979-2018; e) R. Chinchilla, C. Nájera, *Chem. Rev.*, **2007**, *107*, 874-922; f) O. Rivada-Wheelaghan, S. Chakraborty, L. J. Shimon, Y. Ben-David, D. Milstein, *Angew. Chem., Int. Ed.* **2016**, *55*, 6942-6945; g) L. Cornelissen, M. Lefrancq, O. Riant, *Org. Lett.* **2014**, *16*, 3024-3027; h) H.-D. Xu, R.-W. Zhang, X. Li, S. Huang, W. Tang, W.-H. Hu, *Org. Lett.* **2013**, *15*, 840-843; i) Z. Yan, X.-A. Yuan, Y. Zhao, C. Zhu, J. Xie, *Angew. Chem., Int. Ed.* **2018**, *57*, 12906-12910; j) C, Ye, B, Qian. Y. Li, M. Su, D. Li, H. Bao, *Org. Lett*. **2018**, *20*, 3202-3205.

[11] a) B. M. Trost, J. T.Masters, *Chem. Soc. Rev*. **2016**, *45*, 2212-2238; b) R. Chinchilla, C. Najera, *Chem. Rev*. **2007**, *107*, 874-922.

[12] a) W. Su, T.-J. Gong, X. Lu, M.-Y. Xu, C.-G. Yu, Z.-Y. Xu, H.-Z. Yu, B. Xiao, Y. Fu, *Angew. Chem., Int. Ed.* **2015**, *54*, 12957-12961; b) L. Li, T.-J. Gong, X. Lu, B. Xiao, Y. Fu, *Nat. Commun.* **2017**, *8*, 345; c) T.-J. Gong, S.-H. Yu, K. Li, W. Su, X. Lu, B. Xiao, Y. Fu, *Chem.-Asian J.* **2017**, *12*, 2884-2888; d) S.-J. He, B. Wang, X. Lu, T.-J. Gong, Y.-N. Yang, X.-X. Wang, Y. Wang, B. Xiao, Y. Fu, *Org. Lett.* **2018**, *20*, 5208-5212.

[13] a) H. Jang, A. R. Zhugralin, Y. Lee, A. H. Hoveyda, *J. Am. Chem. Soc.* 2011, 133, 7859-7871; b) C. Gunanathan, M. Hölscher, F. Pan, W. Leitner, *J. Am. Chem. Soc*. **2012**, *134*, 14349-14352; c) W. J. Jang, W. L. Lee, J. H. Moon, J. Y. Lee, J. Yun, *Org. Lett.* **2016**, *18*, 1390-1393.

[14] a) G. Evano, N. Blanchard, M. Toumi, *Chem. Rev.* **2008**, *108*, 3054-3131; b) K. S. Sindhu, A. P. Thankachan, P. S. Sajitha, G. Anilkumar, *Org. Biomol. Chem.* **2015**, *13*, 6891-6905.

[15] a) F. Meng, F. Haeffner, A. H. Hoveyda, *J. Am. Chem. Soc*. **2014**, *136*, 11304-11307; b) D.-W. Gao, Y. Xiao, M. Liu, Z. Liu, M. K. Karunananda, J. S. Chen, K. M. Engle, *ACS Catal*. **2018**, *8*, 3650-3654; c) X.-C. Gan, Q. Zhang, X.-S. Jia, L. Yin, *Org. Lett.* **2018**, *20*, 1070-1073; d) Y. Huang, J. Pozo, S. Torker, A. H. Hoveyda, *J. Am. Chem. Soc.* **2018**, *140*, 2643-2655; e) H. L. Sang, S. Yu, S. Ge, *Org. Chem. Front.* **2018**, *5*, 1284-1287.

[16] Blaschette, A.; Bressel, B. *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 175-178.

[17] a) U. Galm, M. H. Hager, S. G. Van Lanen, J. Ju, J. S. Thorson, B. Shen, *Chem. Rev*. **2005**, *105*, 739-758; b) K. C. Nicolaou, W.-M. Dai. *Angew. Chem., Int. Ed.* **1991**, *30*, 1387-1416.

[18] L. Dang, Z. Lin, T. B. Marder, *Chem. Commun.* **2009**, 3987-3995.

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Synthesis of Conjugated Boron-Enynes via cis-Alkynylboration of Terminal Alkynes

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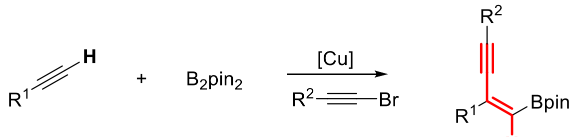

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