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Zinc Catalysed Hydroboration of Terminal and Internal Alkynes

Souvik Mandal, Sayantan Mandal, K. Geetharani*^[a]

Abstract: A regioselective hydroboration of alkynes has been developed by using commercially available zinc triflate as a catalyst, in the presence of catalytic amount of NaBHEt₃. The reaction tolerates a wide range of terminal alkynes having several synthetically useful functional groups and proceeds regioselectively to furnish hydroborated products in moderate to excellent yields. This system shows moderate chemoselectivity towards terminal C=C bond over terminal and internal C=C bond and internal C=C bond.

Organoborane compounds emerged as a versatile synthetic intermediate in organic synthesis and it has been extensively used in medicinal chemistry, functional materials and pharmaceutical research.¹ Among them, vinyl boronate ester derivatives are well known for the construction of substituted olefins and dienyl moieties in organic synthesis via Suzuki-Miyaura cross coupling reaction.² Hydroboration of alkyne is one of the proficient techniques demonstrated for the synthesis of alkenyl boronates.³ Over the last decade, various transition metal catalysts as well as metal-free systems were extensively investigated for the stereo and regioselective hydroboration of alkynes.⁴⁻⁶ Transition metal complexes of Co, Ru, Rh, Pd and Ir, have been largely employed to achieve this transformation. However, recently, the first-row transition metals such as Fe, Co, Ni, Cu and Zn are becoming the primary choices of catalyst, as they are earth abundant, less expensive and less toxic.

Organozinc compounds were known to serve as a transmetalating regent in Negishi coupling type reactions,⁷ but the catalytic borylation using zinc as a catalyst has been hardly explored. In 2008 Nozaki and co-workers reported the first hydroboration of α , β -unsaturated ketone using borylzinc reagent (scheme 1a).8 Mankad and co-workers developed a series of bimetallic base metal catalyst that utilizes metal-metal cooperativity for photoinduced C-H borylation,⁹ in which, a Cu-Fe catalyst was found to be superior than the Zn-Fe catalyst. Along the same line, Uchiyama and co-workers reported diethylzinc catalysed borylation of aryl halides and borylzincation of benzynes.¹⁰ They have also demonstrated the borylzincation of terminal alkynes leading to alkenylboranate esters upon treating with water (scheme 1b). More recently, pioneering research concerning the zinc catalysed borylation reactions of alkyl halides,^{11a} aryl halide,^{11b} and dual C-X and C-H borylation of aryl halides,^{11c} have been reported by Marder and coworkers. Further, the dehydrogenative borylation of terminal

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alkynes with HBdan¹² (dan= 1,8-diaminonapthalene) and the borylation of aryl diazonium salt and aryltriazene with $B_2pin_2^{13}$ was achieved using $Zn(OTf)_2$ and $Zn(CIO_4)_2$ as a catalysts, respectively. Also, Aldridge and co-workers developed a palladium catalysed borylation of aryl halides and acyl chlorides using air stable zincboryl reagent.¹ NacnacZn-H (Nacnac N,N'-bis-2,6diisopropylphenyldiketiminate) catalysed hydrosilylation and hydroboration of N-heterocycles has been recently reported by Nikonov et al. (scheme 1c).¹⁵ During the preparation of this manuscript, Ingleson and co-workers reported zinc catalysed C-H borylation of terminal alkynes and the hydroboration of internal alkynes.¹⁶ Although there are excellent examples related to the Zn-catalysed borylation of organic substrates reported, the Zn-catalysed hydroboration of alkynes is scarcely explored. Herein, we are reporting a simple and efficient zinc catalyst for regioand chemoselective hydroboration of terminal alkynes. This approach is also applicable to internal alkynes.





We commenced our catalytic studies using phenylacetylene (**1a**) as a model substrate, pinacolborane (HBpin, 1.2 equiv) as the boron source, $Zn(OTf)_2$ as the catalyst. Reaction between **1a** and HBpin using $Zn(OTf)_2$ as a catalyst at room temperature did not induce any hydroboration reaction (Table 1, entry 1). When NaBHEt₃ was used as a hydride source, the hydroboration product **1b** was obtained in 14% yield (entry 2). Subsequent increment of temperature from room temperature to 80 °C increases the yield of the alkenyl boronate ester from 14% to 92% (entries 2-5). NaBH₄ as the hydride source yielded 80% of the product albeit with less regioselectivity (entry 6). Control experiments confirmed the essential role of the zinc catalyst (entry 7). While zinc dust only provided a trace amount of

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hydroborylated product (entry 8), $ZnCl_2$ and Znl_2 resulted comparable yields (entries 9 and 10). When the reaction was carried out at the catalyst loading of 2.5 mol% the yield decreases to 68%, however, increasing the catalyst loading did not significantly influence the product yield (entries 11 and 12). Changing the solvent from toluene to other polar solvents did not improve the yields (entries 13-15).

 Table 1 Optimisation of the reaction conditions for Zn catalysed hydroboration of phenylacetylene (1a).

+ 110/0	[cat.]	→ Bpin
т нв О	additive solvent	

entry	catalyst	additive	solvent	T (°C)	yield (%) ^[b]
1	Zn(OTf) ₂	-	toluene	RT	trace
2	Zn(OTf) ₂	NaBHEt₃	toluene	RT	14
3	Zn(OTf) ₂	NaBHEt₃	toluene	40	42
4	Zn(OTf) ₂	NaBHEt ₃	toluene	60	80
5	Zn(OTf) ₂	NaBHEt ₃	toluene	80	92
6	Zn(OTf) ₂	NaBH₄	toluene	80	80
7	-	NaBHEt ₃	toluene	80	11
8	Zn dust	NaBHEt₃	toluene	80	8
9	ZnCl₂	NaBHEt ₃	toluene	80	90
10	Znl ₂	NaBHEt₃	toluene	80	88
11 ^[c]	Zn(OTf) ₂	NaBHEt ₃	toluene	80	68
12 ^[d]	Zn(OTf) ₂	NaBHEt₃	toluene	80	91
13	Zn(OTf) ₂	NaBHEt ₃	THF	80	60
14	Zn(OTf) ₂	NaBHEt ₃	1,2-DME	80	67
15	Zn(OTf) ₂	NaBHEt ₃	Dioxane	80	75

[a] Standard conditions: **1a** (0.2 mmol), catalyst (5 mol %), additive (5 mol %), HBpin (1.2 equiv), solvent (1.0 mL) for 10 h unless otherwise stated. [b] Yields were determined by ¹H NMR using nitromethane as an internal standard. [c] 2.5 mol% of catalyst and 2.5 mol% of additive were used. [d]]10 mol% of catalyst and 10 mol% of additive were used.

Having identified the optimum conditions for hydroboration of phenylacetylene (1a) with 5 mol% Zn(OTf)₂, 5 mol% NaBHEt₃, 1.2 equiv of HBpin (see supporting information for details), we then explored the substrate scope. At first, the hydroboration reaction of several terminal and internal alkynes were examined (Table 2). Phenylacetylene derivatives having electron-donating (2a and 3a) and -withdrawing groups (4a and 5a) were efficiently hydroborylated to the corresponding alkenyl boronate ester in excellent yields (85-97%). We observed the good yield of hydroborated product for the sterically encumbered orthosubstituted substrate (6a). In the case of 1,4-diethynylbenzene, both mono- (7b, 58%) and di-hydroborated product (8b, 75%) can be obtained selectively by modifying the reaction conditions. The hydroboration of 3-ethynylpyridine (9a) and 3ethynylthiophene (10a) took place smoothly, affording the alkenyl boronate esters in good yields. Besides aromatic alkynes, the scope of the zinc catalyst system was extended to aliphatic terminal alkynes. The compounds 1-decyne (11a) as well as 1cyclohexyl-prop-2-yne (12a) gave the borylated products in yields up to 75%. Remarkably, alkynes having cyclic side chain (13a-15a) could also be easily transformed to the corresponding hydroborated products, despite their ring strain. The terminal C-C triple bond in 16a-18a was hydroborated preferentially over

the terminal C-C double bond, internal C-C triple bond and internal C-C double bond. Finally, we tested the efficiency of the hydroboration of the more Zn-catalysed challenging disubstituted alkynes. We were delighted to see the good yields of hydroborated products for symmetrical alkynes with either aryl (19a) or alkyl substituents (20a-21a). Unsymmetrical internal alkynes (22a-24a) were subjected to hydroboration reaction, the vinyl boronated esters were obtained in good yield with moderate regioselectivity. Moreover, when the substrate containing electron withdrawing groups, such as 4ethynylbenzonitrile, phenyl propargyl ether were used, trace amount of borylated products were observed. Using a substrate containing alcoholic moiety (9-ethynyl-9H-fluorenol) under the standard conditions employed, showed the incompatibility of the hydroxyl group.





Reaction conditions: [a] alkyne (1 mmol), $Zn(OTf)_2$ (5 mol%), NaBHEt₃ (5 mol%), HBpin (1.2 equiv), toluene (2 mL) for 10 h at 80 °C unless otherwise stated. Yields were determined by ¹H NMR, using nitromethane as an internal standard. Isolated yields were given in parentheses. [b] Isolated yield using ZnCl₂ (5 mol%) as a catalyst. [c] Reaction was performed using 10 mol% of Zn(OTf)₂ and NaBHEt₃, and 2.4 equiv of HBpin for 24 h. [d] Reaction was performed using 10 mol% of Zn(OTf)₂ and NaBHEt₃, and 2.4 equiv of HBpin for 24 h. [e] Reaction was performed using 2 equiv of HBpin. [f] Trace amount of bisborylated (alkene and alkyne hydroboration) product was observed by GC-MS analysis. [g] Trace amount of isomers of **17b** was observed by GC-MS analysis. [h] Reaction was performed using 1.5 equivalent of HBpin. [i] Ratio of the regioisomers was determined by ¹H NMR spectroscopy.

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Selective hydroboration of alkyne in the presence of other reducible functional groups is challenging and elusive. To probe the chemoselectivity of our catalyst system, a series of experiments were performed as shown in Scheme 2. The competitive intermolecular hydroboration reaction in the presence of equimolar amount of **1a**, **25a** and HBpin was performed using $Zn(OTf)_2$ as a catalyst (5 mol%). The results demonstrated that the presence of an alkene has little impact on hydroboration of terminal alkyne, and the desired alkenyl boronate ester was obtained in 55% yields (Scheme 2a). The competitive intermolecular hydroboration of internal and terminal alkynes was also conducted (Scheme 2b), and the ¹H NMR analysis shows moderate chemoselectivity towards terminal over the internal alkyne.

a)	Ph—=	+ Ph	Zn(OTf) ₂ (5 mol%) NaBHEt ₃ (5 mol%)	Ph Bpin +	Ph Bpin
	1a	25a 1	Foluene, 80 °C, 10 h	1b : 55%	25b : 5%
b)	Ph-==	+ Ph-=-	Zn(OTf) ₂ (5 mol%) Ph NaBHEt ₃ (5 mol%) HBpin (1.0 equiv	6) 6) Ph Bpin	+ Ph
	1a	19a	Toluene, 80 °C,	^{IO h} 1b : 51%	Pn 19b : 10%

To assess the regioselectivity of this method, deuterium labelling experiments were carried out using PhC=CD and HBpin. We observed a resonance at $\delta = 6.22$ ppm in the ²H NMR spectroscopy, indicating a *cis* orientation of deuterium and phenyl group in **1b-D** (Scheme 3a). Similarly, the regioselective hydroboration product (**1b-D'**) was obtained from the reaction of **1a** with DBpin, indicating the *cis* arrangement of deuterium and Bpin moiety, as the resonance observed at $\delta = 7.32$ ppm in ²H NMR spectrum (Scheme 3b).



Scheme 3. Deuterium labelling experiment: a) Hydroboration of 1a-D with HBpin. b) Hydroboration of 1a with DBpin

To shed light on the reaction mechanism, a series of stoichiometric experiments were performed. An equimolar amount of $Zn(OTf)_2$ with NaBHEt₃ was mixed, the formation of BEt₃ was observed by the ¹¹B NMR spectroscopy, however, several attempts to obtain a characterizable active species were not successful (scheme 4a). Subsequent addition of phenylacetylene (**1a**) resulted into the side on coordination of **1a** to the zinc center (species **B**, scheme 4a). Further addition of stoichiometric amount of HBpin led the quantitative yield of the desired product (scheme 4b). Based on these observations, it is possible that the mechanism of the present hydroboration reaction might proceed *via* alkenyl zinc intermediate where insertion of alkyne to Zn-H bond is likely to be the key step

(hydrozincation), similar to that of the previously reported hydroboration reactions. $^{\rm 4s,4u,6d,6i}$

On the other hand, Tsuchimoto *et al.* reported in the dehydrogenative borylation reaction that the $Zn(OTf)_2$ can activate the B-H bond, which initiates the evaluation of H₂ gas upon reaction with phenylacetylene.¹² Based on this preceding study, we monitored the stoichiometric reaction of **1a** with *in situ* generated active species **A** in a sealed system by ¹H NMR spectroscopy; we did not observe any production of H₂, which suggests that the deprotonation mechanism is not operated under our reaction conditions. Further, Marder *et al.* reported that the alkyl halide borylation catalysed by $ZnCl_2$ seems to involve one-electron processes.¹¹ Hence, we examined the hydroboration reaction in the presence of radical scavenger 9,10-dihydroanthracene, the desired product was obtained in good yield (see SI for details). This result excluded the possibility of a radical mechanism.



Scheme 4. Stoichiometric reaction between: a) zinc triflate and sodium triethylborohydride, and further with **1a**, b) **B** and HBpin.

In summary, we have demonstrated the utility of commercially available zinc triflate catalyst system in the hydroboration of a variety of internal and terminal alkynes. The wide substrate scope, functional group tolerability and chemoselectivity are some of the salient features of our system. Further studies on the mechanism and synthetic applications of this method are in progress in our laboratory.

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Conflict of interest

There is no conflict of interest to declare

Keywords: boronate ester • chemoselective • homogeneous catalysis • hydroboration • zinc

- D. G. Hall in Boronic Acids: Preparation, Applications in Organic Synthesis and Medicine, (Ed.: D. G. Hall), Wiley-VCH, Weinheim, Germany, 2011
- a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457-2483; b) C. E. Tucker, J. Davidson, P. Knochel, *J. Org. Chem.* **1992**, *57*, 3482-3485.

For internal use, please do not delete. Submitted_Manuscript

- a) T. Ishiyama, M. Murata, N. Miyaura, *J. Org. Chem.* **1995**, *60*, 7508-7510; b) J. Takagi, A. Kamon, T. Ishiyama, N. Miyaura, *Synlett* **2002**, *11*, 1880-1882; c) J. Takagi, K. Takahashi, T. Ishiyama, N. Miyaura, *J. Am. Chem. Soc.* **2002**, *124*, 8001-8006.
- [4] a) K. Semba, T. Fujihara, J. Terao, Y. Tsuji, Chem. Eur. J. 2012, 18, 4179-4184; b) S. Pereira, M. Srebnik, Organometallics 1995, 14, 3127-3128; c) S. Pereira, M. Srebnik, Tetrahedron Lett. 1996, 37, 3283-3286; d) T. Ohmura, Y. Yamamoto, N. Miyaura, J. Am. Chem. Soc. 2000, 122, 4990-4991; e) C. I. Lee, J. Zhou, O. V. Ozerov, J. Am. Chem. Soc. 2013, 135, 3560-3566; f) C. Gunanathan, M. Heolscher, F. Pan, W. Leitner, J. Am. Chem. Soc. 2012, 134, 14349-14352; g) B. Sundararaju, A. Fürstner, Angew. Chem. 2013, 125, 14300-14304; Angew. Chem. Int. Ed. 2013, 52, 14050-14054; h) M. Haberberger, S. Enthaler, Chem. Asian J. 2013, 8, 50-54; i) M. D. Greenhalgh, S. P. Thomas, Chem. Commun. 2013, 49, 11230-11232; j) V. S. Rawat, B. Sreedhar, Synlett 2014, 1132-1136; k) Q. Wang, S. E. Motika, N. G. Akhmedov, J. L. Petersen, X. Shi, Angew. Chem. 2014, 126, 5522-5526; Angew. Chem. Int. Ed. 2014, 53, 5418-5422; I) K. Wen, J. Chen, F. Gao, P. S. Bhadury, E. Fan, Z. Sun, Org. Biomol. Chem. 2013, 11, 6350-6356; m) S. Hong, W. Zhang, M. Liu, Z.-J. Yao, W. Deng, Tetrahedron Lett. 2016, 57, 1-4; n) G. A. Molander, N. M. Ellis, J. Org. Chem. 2008, 73, 6841-6844; o) H. E. Ho, N. Asao, Y. Yamamoto, T. Jin, Org. Lett. 2014, 16, 4670-4673; p) K. Shirakawa, A. Arase, M. Hoshi, Synthesis 2004, 1814-1820; q) N. W. J. Ang, C. S. Buettner, S. Docherty, A. Bismuto, J. H. Docherty, M. J. Cowley, S. P. Thomas, Synthesis 2018, 50, 803-808; r) Y. Wu, C. Shan, J. Ying, J. Su, J. Zhu, L. L. Liu, Y. Zhao, Green Chem. 2017, 19, 4169-4175; s) M. Magre, B. Maity, A. Falconnet, L. Cavallo, M. Rueping, Angew. Chem. 2019, 131, 7099-7103; Angew. Chem. Int. Ed. 2019, 58, 7025–7029; t) Y. Wang, R. Guan, P. Sivaguru, X. Cong, X Bi, Org. Lett. 2019, 21, 4035-4038; u) W. J. Jang, B-N. Kang, J. H. Lee, Y. M. Choi, C-H. Kimb, Jaesook Yun, Org. Biomol. Chem. 2019, 17, 5249-5252; v) R. Mamidala, V. K. Pandey, A. Rit, Chem. Commun. 2019, 55, 989-992; w) H.-Y. Tsai, M. Madasu, M. H. Huang, Chem. Eur. J. 2019, 25, 1300 - 1303
- [5] For review of hydroboration of C-C multiple bonds, see: a) M. Zaidlewicz, A. Wolan, M. Budny *in Comprehensive Organic Synthesis, Vol. 8* (Eds.: P. Knochel, G. A. Molander), Elsevier, Amsterdam, **2014**, pp. 877–963; b) N. Miyaura *in Catalytic Heterofunctionalization*, (Eds.: A. Togni, H. Grützmacher), Wiley-VCH, Weinheim, **2001**, pp. 1-46; c) C. M. Vogels, S. A. Westcott, *Curr. Org. Chem.* **2005**, *9*, 687-699; d) I. Beletskaya, A. Pelter, *Tetrahedron* **1997**, *53*, 4957-5026; e) R. Barbeyron, E. Benedetti, J. Cossy, J. J. Vasseur, S. Arseniyadis, M. Smietana, *Tetrahedron* **2014**, *70*, 8431-8452; f) D. Wei, C. Darce, *Chem. Rev.* **2019**, *119*, 2550–2610.
- a) J. S. McGough, S. M. Butler, I. A. Cade, M. J. Ingleson, Chem. Sci. [6] 2016, 7, 3384-3389; b) M. Fleige, J. Mobus, T. vom Stein, F. Glorius, D. W. Stephan, Chem. Commun. 2016, 52, 10830-10833; c) J. R. Lawson, L. C. Wilkins, R. L. Melen, Chem. Eur. J. 2017, 23, 10997-11000; d) A. Bismuto, S. P. Thomas, M. J. Cowley, Angew. Chem. 2016, 128,15582-15585; Angew. Chem. Int. Ed. 2016, 55, 15356-15359; e) Z. Yang, M. Zhong, X. Ma, K. Nijesh, S. De, P. Parameswaran, H. W. J. Roesky, J. Am. Chem. Soc. 2016, 138, 2548-2551; f) D. Franz, L. Sirtl, A. Pothig, S. Inoue, Z. Anorg. Allg. Chem. 2016, 642, 1245-1250; g) S. Liu, X. Zeng, B. Xu, Tetrahedron Lett. 2016, 57, 3706-3710; h) X. He, J. F. Hartwig, J. Am. Chem. Soc. 1996, 118, 1696-1702; i) S. Mandal, P. K. Verma, K. Geetharani, Chem. Commun. 2018, 54, 13690-13693; j) C. J. Major, K. L. Bamford, Z.-W. Qu, D. W. Stephan, Chem. Commun. 2019, 55, 5155-5158; k) A. Harinath, I. Banerjee, J. Bhattacharjee, Tarun K. Panda, New J. Chem. 2019, DOI: 10.1039/C9NJ01859J; I) Z.-C. Wang, M. Wang, J. Gao, S.-L. Shi, Y. Xu, Org. Chem. Front. 2019, DOI: 10.1039/C9Q000750D; m) F. Li, X. Bai, Y. Cai, H. Li, S.-Q. Zhang, F.-H. Liu, X. Hong, Y. Xu, S.-L. Shi, Org. Process Res. Dev. 2019, DOI: 10.1021/acs.oprd.9b00205.
- [7] a) E-i. Negishi, Acc. Chem. Res. 1982, 15, 340-348; b) E-i. Negishi, J. Orgmet. Chem. 1999, 576, 179-194; c) C. Han, S. L. Buchwald, J. Am. Chem. Soc. 2009, 131, 7532-7533.

For internal use, please do not delete. Submitted_Manuscript

- [8] T. Kajiwara, T. Terabayashi, M. Yamashita, K. Nozaki, Angew. Chem. 2008, 120, 6708-6712; Angew. Chem. Int. Ed. 2008, 47, 6606-6610.
- [9] T. J. Mazzacano, N. P. Mankad, J. Am. Chem. Soc. 2013, 135, 17258-17261.
- [10] Y. Nagashima, R. Takita, K. Yoshida, K. Hirano, M. Uchiyama, J. Am. Chem. Soc. 2013, 135, 18730-18733.
- [11] a) S. K. Bose, K. Fucke, L. Liu, P. G. Steel, T. B. Marder, Angew. Chem. 2014, 126, 1829-1834; Angew. Chem. Int. Ed. 2014, 53, 1799-1803; b)
 S. K. Bose, T. B. Marder, Org Lett. 2014, 16, 4562-4565; c) S. K. Bose,
 A. Deissenberger, A. Eichhorn, P. G. Steel, Z. Y. Lin, T. B. Marder, Angew. Chem. 2015, 127, 12009-12014; Angew. Chem. Int. Ed. 2015, 54, 11843-11847.
- [12] T. Tsuchimoto, H. Utsugi, T. Sugiura, S. Horio, Adv. Synth. Catal. 2015, 357, 77-82.
- [13] X. Qi, L. B. Jiang, C. Zhou, J. B. Peng, X. F. Wu, *Chemistry Open* 2017, 6, 345-349.
- [14] a) J. Campos, S. Aldridge, Angew. Chem. 2015, 127, 14365-14369;
 Angew. Chem. Int. Ed. 2015, 54, 14159-14163; b) J. Campos, A. Nova,
 E. L. Kolychev, S. Aldridge, Chem. Eur. J. 2017, 23, 12655–12667.
- [15] J. L. Lortie, T. Dudding, B. M. Gabidullin, I. G. Nikonov, ACS Catal. 2017, 7, 8454-8459.
- [16] R. J. Procter, M. Uzelac, J. Cid, P. J. Rushworth, M. J. Ingleson, ACS Catal. 2019, 9, 5760–5771.

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