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Synthesis of Acrylonitriles *via* Mild Base Promoted Tandem Nucleophilic Substitution-Isomerization of α-Cyanohydrin Methanesulfonates

Shiwen Liu,[a] Lingling Meng,[a] Xiaojun Zeng,[b] Gerald B. Hammond,*[,c] and Bo Xu*[,b]

[a] *College of Textiles and Clothing & Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province, Yancheng Institute of Technology, Yancheng, Jiangsu 224003, China*
[b] *Key Laboratory of Science and Technology of Eco-Textiles, Ministry of Education, College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, China*
[c] *Department of Chemistry, University of Louisville, Louisville, Kentucky 40292, United States*

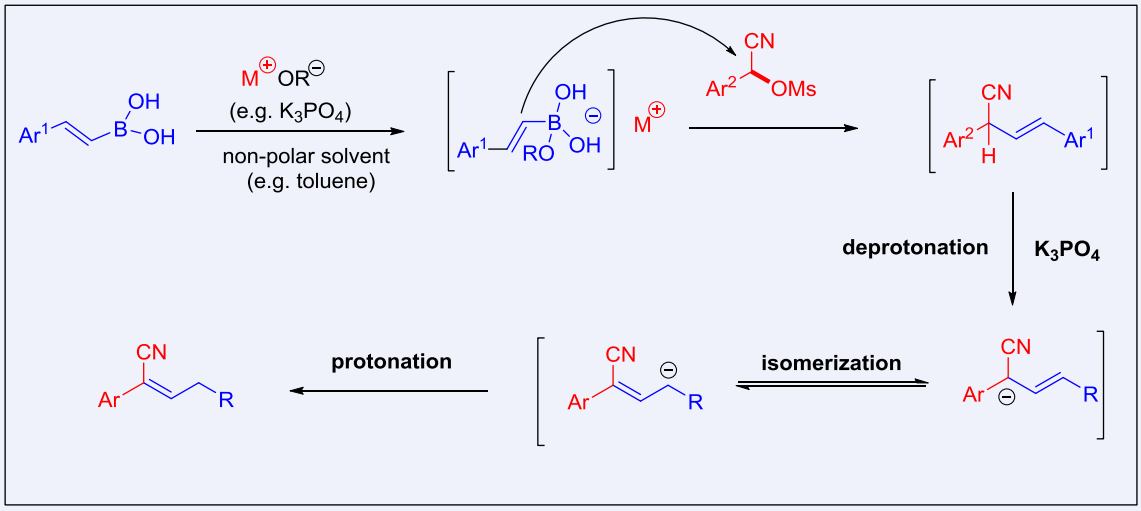
Keywords

Acrylonitriles | Nucleophilic substitution | Isomerization | α-Cyanohydrin methanesulfonates | Alkenyl boronic acids

Main observation and conclusion

We have developed an efficient synthesis of acrylonitriles *via* mild base promoted tandem nucleophilic substitution-isomerization of α-cyanohydrin methanesulfonates with alkenylboronic acids. This transition metal-free protocol works under simple and mild conditions and offers good chemical yields for a wide range of substrates and demonstrates good functional group tolerance.

Comprehensive Graphic Content



*E-mail: bo.xu@dhu.edu.cn; gb.hammond@louisville.edu

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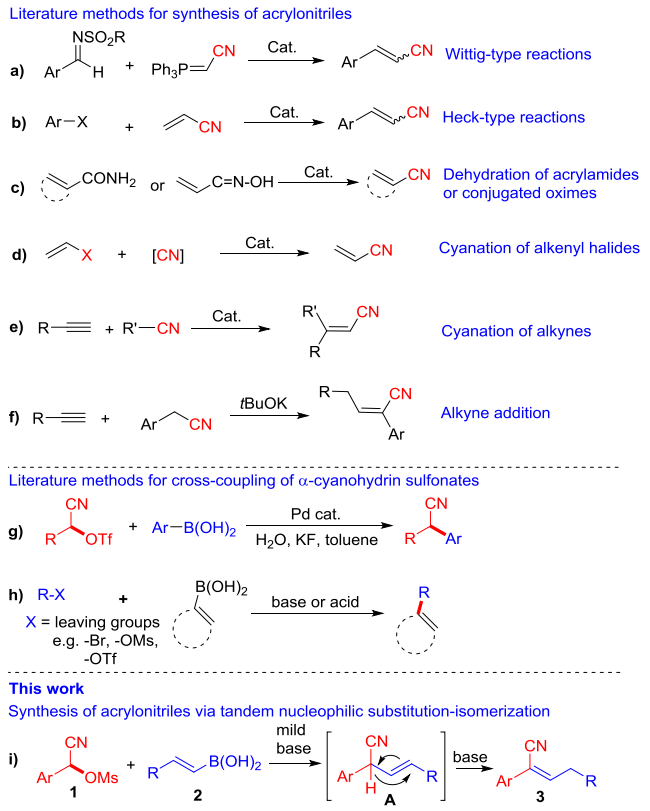
Background and Originality Content

Nitriles are important targets and highly useful building blocks which can be transformed to many functionalities such as carboxylic acids,[1] amines[2] and aldehydes.[3] More specifically, acrylonitriles involved in various transformations, such as Michael addition,[4] Diels-Alder cycloadditions[5] and cross-couplings.[6] Besides, acrylonitriles remain one of commonly used monomers for preparation of plastics, acrylic fibers and polyacrylonitrile.[7] Moreover, the acrylonitrile motif represents a common structural motif frequently found in many pharmaceuticals and natural products such as Entacapone (agent for Pakinson's disease), CC-5079 (antitumor agent), Rilpivirine (reverse transcriptase inhibitor).[8] Thus, their efficient synthesis has been a longstanding goal of organic synthesis.

Traditional methods for the synthesis of acrylonitriles are based on the classical Knoevenagel condensations,[9] Wittig-type reactions[10] (Scheme 1a), Heck or oxidative Heck-type reactions[11] (Scheme 1b), dehydration of acrylamides or conjugated oximes (Scheme 1c),[12] cyanation of alkenyl halides (Scheme 1d),[13] cyanation of alkynes (Scheme 1e)[11c,14] and allylic cyanation.[15] However, these methods usually suffer from poor substrate scope and/or low *E*/*Z* selectivity. Recently, Jiang and coworkers reported an efficient base promoted addition of arylacetonitriles to terminal alkynes[16] (Scheme 1f), providing a straightforward and transition metal-free protocol for the preparation of acrylonitriles although strong base (KO*t*Bu) was needed. On the other hand, Pd catalyzed Suzuki cross-coupling of organoboronic acids with α-cyanohydrin triflates has been reported by Falck and coworkers (Scheme 1g).[17] Also, metal-free Suzuki type cross-couplings[18] of alkenyl or aryl boronic acids have been well explored by groups of Tang,[19] Wang,[20] Huang,[21] Ryu[22] and us[23] (Scheme 1h).

Scheme 1 Literature background

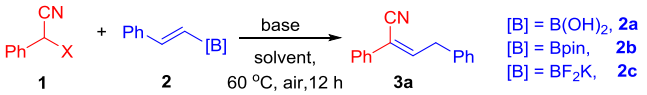


Based on these pioneering works, we envisioned a new synthesis of acrylonitriles *via* a tandem nucleophilic substitution-isomerization protocol (Scheme 1i). First, a mild base promoted nucleophilic substitution of α-cyanohydrin methanesulfonates by alkenylboronic acids generates intermediate **A**, then a base promoted isomerization of **A** leads to the formation of acrylonitriles **3**. Because only mild bases are needed, this tandem protocol may offer wide substrates scope and good functional group tolerance.

Results and Discussion

As shown in Table 1, firstly, we investigated the reactions of α-CN benzyl electrophiles (**1a**—**1c**) containing various leaving groups with alkenylboronic acid **2a** in the presence of weak base K_3PO_4 at room temperature. Both bromide **1a** and tosylate **1b** did not give any product. To our delight, the coupling product **3a** was obtained in 89% yield when α-cyanohydrin methanesulfonate **1c** was used. On the other hand, no reaction occurred when less reactive alkenylboronic ester **2b** or potassium alkenyltrifluoroborate **2c** was used. Screening of bases of different strength revealed that weaker bases (K_2CO_3, NaF, KF, K_3PO_4) could give moderate to good yields and were better than stronger bases (*t*BuOK, NaOMe) probably due to the strong binding effect to the cation. Besides, comparison of different cations showed that the transformation hardly proceeded when using LiF as base. Moreover, changing the solvent from low polar solvents to more polar solvents such as DMF, THF resulted in significant decrease of the chemical yields.

Table 1 Optimization of reaction conditions[a]



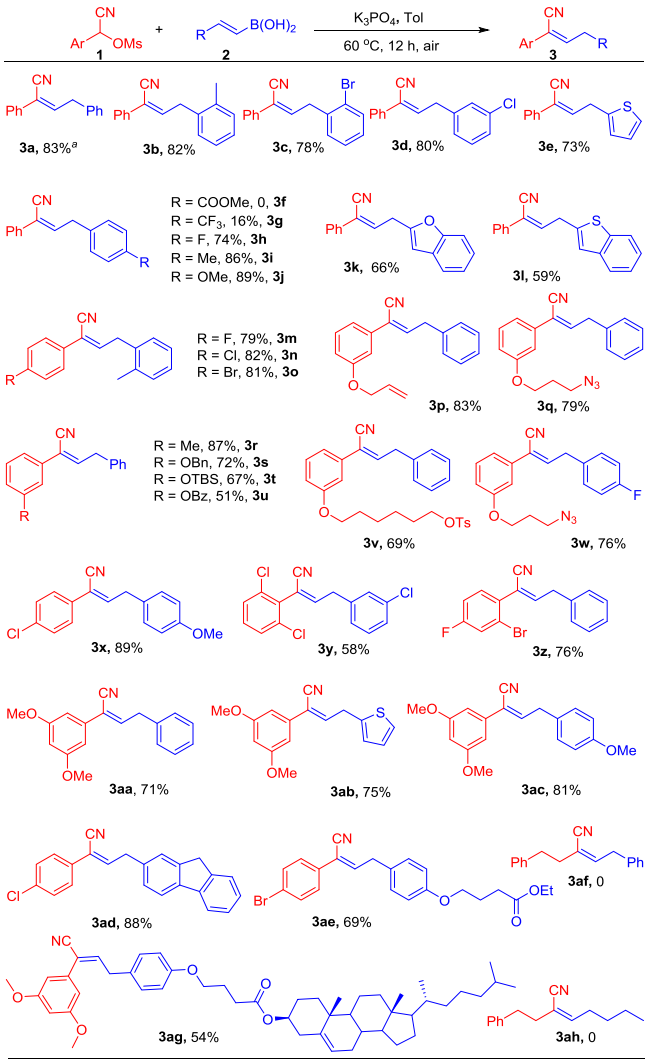
1 2 3a

entry	X	2	base	solvent	Yield[b]/%
1	Br	**2a**	K_3PO_4	toluene	0
2	OTs	**2a**	K_3PO_4	toluene	0
3	OMs	**2a**	K_3PO_4	toluene	89
4	OMs	**2b**	K_3PO_4	toluene	0
5	OMs	**2c**	K_3PO_4	toluene	0
6	OMs	**2a**	K_2CO_3	toluene	76
7	OMs	**2a**	LiF	toluene	8
8	OMs	**2a**	NaF	toluene	59
9	OMs	**2a**	KF	toluene	79
10	OMs	**2a**	CsF	toluene	44
11	OMs	**2a**	NaOH	toluene	65
12	OMs	**2a**	NaOMe	toluene	33
13	OMs	**2a**	KO*t*Bu	toluene	45
14	OMs	**2a**	K_3PO_4	DCE	67
15	OMs	**2a**	K_3PO_4	THF	32
16	OMs	**2a**	K_3PO_4	DMF	0

[a] Conditions: **1** (0.1 mmol), **2** (0.15 mmol), base (0.2 mmol) in solvent (1 mL), 60 °C, 12 h. [b] All yields are determined by GC-MS.

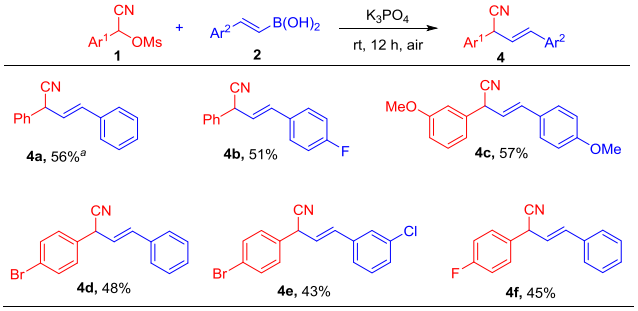
With the optimized reaction conditions in hand, we examined the substrate scope of acrylonitrile **3** synthesis (Table 2). Firstly, we investigated the scope of alkenylboronic acids. Diverse alkenylboronic acids could couple with α-cyanohydrin methanesulfonate **1a** smoothly in moderate to excellent yields (Table 2, **3a**—**3l**). For substituents at the *ortho*, *meta* or *para* positions of

Table 2 Scope for synthesis of acrylonitriles[a]



[a] Conditions: **1** (0.1 mmol), **2** (0.15 mmol), K_3PO_4 (0.2 mmol) in toluene (1 mL), 60 °C, 12 h. All yields are isolated yields.

Table 3 Scope for synthesis of α-alkenyl nitriles[a]



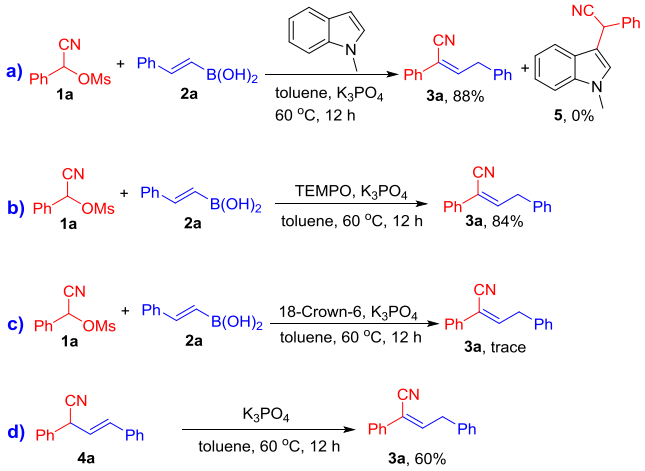
[a] Conditions: **1** (0.1 mmol), **2** (0.15 mmol), K_3PO_4 (0.2 mmol) in toluene (1 mL), rt, 12 h. All yields are isolated yields.

the phenyl ring in **2**, including halides (F, Cl and Br) (Table 2, **3c**—**3d**, **3h**), alkyl (Table 2, **3b**), high yields were obtained regardless. Besides, alkenyl boronic acids **2** containing a thiophene, benzothiophene, benzofuran or fluorene moieties (Table 2, **3e**, **3k**, **3l**, **3ad**) all are suitable substrates. For electron-donating substituents at the phenyl ring in **2** (Table 2, **3j**, **3ae**), good yields were obtained, while electron-withdrawing substituents like COOMe or CF_3 led to sluggish reactions due to their low nucleophilicity (Table 2, **3f**, **3g**). Next, we aimed to investigate the scope of α-cyanohydrin methanesulfonate **1**. For halogen substituents (F, Cl and Br) at *para* positions of the phenyl ring in **1** (Table 2, **3m**—**3o**), good yield was obtained. Besides, the reaction system tolerated diverse functional groups including methyl, allyl, benzyl, azide, tosylate, benzoyl and silyl groups (Table 2, **3p**—**3w**). Additionally, disubstituted α-cyanohydrin methanesulfonates were also suitable substrates (Table 2, **3y**—**3ac**). Moreover, even for **1** containing complex natural product like skeleton (Table 2, **3ag**), this protocol also worked very well. However, aliphatic α-cyanohydrin methanesulfonates (Table 2, **3af**) and alkyl alkenylboronic acid (Table 2, **3ah**) did not work under the same conditions due to less reactivity.

Remarkably, diverse coupling products **4** were obtained at room temperature (Table 3). These results indicated that acrylonitriles **3** were probably transformed from coupling products **4**. It should be also noted that our metal-free protocol is orthogonal towards the classic transitional metal catalyzed Suzuki reaction. For example, reactive aryl bromides (Table 3, **4d**, **4e**) showed no reactivity towards alkenylboronic acids in our conditions.

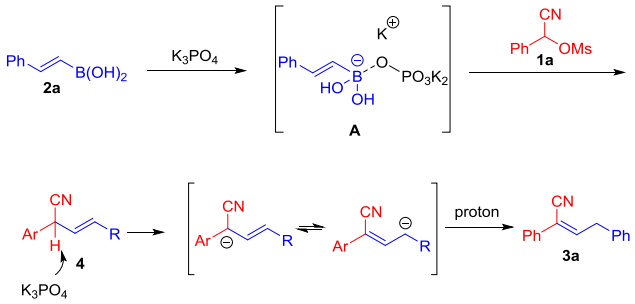
Then, we moved our focus to the investigation of possible reaction pathway (Scheme 2). The reaction was not affected by both TEMPO (2,2,6,6-tetramethyl-1-piperinedinyloxy, a radical quencher) and *N*-methylindole (an electron-rich aromatic) (Scheme 2, **a**—**b**).[19a,20,22a] These results indicated that both radical intermediate and cationic intermediate were not likely and the reaction may not go through a radical mechanism or an S_N1 like mechanism. Furthermore, only trace product was detected when using K^+ chelator (18-crown-6) (Scheme 2, c), which indicated that K^+ played an extremely important role, even participating in this transformation. Besides, under the optimized conditions, compound **4a** can be converted into **3a** in 60% yield, which suggested that nucleophilic substitution product **4a** was formed firstly in this transformation, and then was transformed into more stable acrylonitriles **3a**.

Scheme 2 Investigation of reaction pathways



Based on above experimental results, we propose a possible mechanism (Scheme 3). Firstly, the base (K_3PO_4) attacks the organoboronic acid **2a** to form an ate type complex **A**, whose anionic nature leads to enhanced nucleophilicity.[24] In this process, K^+ plays an important role in the formation of ion pair organic compound intermediate **A**. On the other hand, formation of ion pair organic compound intermediate **A** could enhance the nucleophilicity of alkenyl boronic acids. Then complex **A** reacting with the sp^3-carbon electrophile **1a** to give intermediate **4** *via* an S_N2 pathway. Then, in the presence of base, a deprotonation/isomerization/protonation of **4** gives the thermodynamic product **3a**. Remarkably, only (*Z*)-2,3-disubstituted acrylonitriles could be

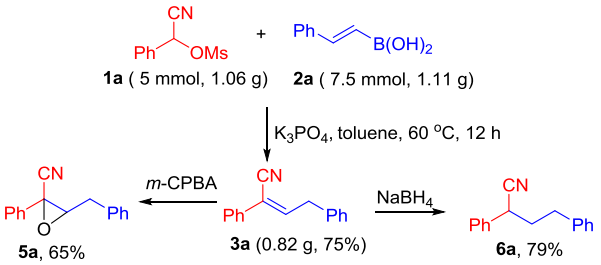
Scheme 3 Proposed mechanism



obtained without any (*E*)-isomers, probably due to the steric effect of aromatics.

Additionally, our methodology can be used in larger scale synthesis without complications (Scheme 4). Also, the obtained **3a** can be selectively reduced to give **6a** in 79% yield using the simple reductant – $NaBH_4$.[25] Moreover, the epoxidation of **3a** led to the formation of an epoxide **5a** in 65% yield.[26]

Scheme 4 Gram-scale synthesis and further synthetic manipulations



Conclusions

In conclusion, we have developed an efficient cross-coupling between alkenylboronic acids and α-cyanohydrin methanesulfonate. Acrylonitriles can be accessed under simple and mild conditions with good chemical yields and good functional group tolerance for a wide range of substrates. Other transition metal-free systems are currently being investigated in our laboratory and will be communicated in due course.

Experimental

Procedure for cross-coupling reaction: An oven-dried vial was charged with α-cyano methanesulfonate (0.1 mmol), alkenylboronic acids (0.15 mmol), K_3PO_4 (0.2 mmol). Tol (1 mL) was added and the mixture was stirred at 60 centigrade for 12 h under air. After that, water was added and the aqueous phase was extracted with ethyl acetate (3 × 3 mL). The combined organic layers were dried over Na_2SO_4 and then concentrated. The crude product was purified by silica gel column chromatography.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.202000579.

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References

[1] (a) Daw, P.; Sinha, A.; Rahaman, S. M. W.; Dinda, S.; Bera, J. K. Bifunctional Water Activation for Catalytic Hydration of Organonitriles. *Organometallics* **2012**, *31*, 3790–3797; (b) Kumar, S.; Dixit, S. K.; Awasthi, S. K. An efficient one pot method for synthesis of carboxylic acids from nitriles using recyclable ionic liquid [bmim]HSO_4. *Tetrahedron Lett.* **2014**, *55*, 3802–3804.

[2] (a) Schafer, C.; Ellstrom, C. J.; Cho, H.; Torok, B. Pd/C-Al-water facilitated selective reduction of a broad variety of functional groups. *Green Chem.* **2017**, *19*, 1230–1234; (b) Ji, P.; Manna, K.; Lin, Z.; Feng, X.; Urban, A.; Song, Y.; Lin, W. Single-Site Cobalt Catalysts at New $Zr_{12}(\mu_3\text{-}O)_8(\mu_3\text{-}OH)_8(\mu_2\text{-}OH)_6$ Metal-Organic Framework Nodes for Highly Active Hydrogenation of Nitroarenes, Nitriles, and Isocyanides. *J. Am. Chem. Soc.* **2017**, *139*, 7004–7011; (c) Arup, M.; Dipankar, S.; Yehoshoa, B. D.; David, M. Low-Pressure Hydrogenation of Nitriles to Primary Amines Catalyzed by Ruthenium Pincer Complexes. Scope and mechanism. *ChemCatChem* **2017**, *9*, 559–563.

[3] Lichtenecker, R. J. Synthesis of aromatic 13C/2H-[small alpha]-keto-acid precursors to be used in selective phenylalanine and tyrosine protein labelling. *Org. Biomol. Chem.* **2014**, *12*, 7551–7560.

[4] (a) Fleming, F. F.; Wang, Q. Unsaturated Nitriles: Conjugate Additions of Carbon Nucleophiles to a Recalcitrant Class of Acceptors. *Chem. Rev.* **2003**, *103*, 2035–2078; (b) Prakasham, A. P.; Gangwar, M. K.; Ghosh, P. Michael addition of cyclic β-oxo ester and α-methyl cyano ester substrates with activated olefins by iron complexes of benzimidazole derived *N*-heterocyclic carbene ligands. *J. Organomet. Chem.* **2018**, *859*, 106–116; (c) Kowalkowska, A.; Jończyk, A.; Maurin, J. K. Domino Reaction of Pyrrolidinium Ylides: Michael Addition/[1,2]-Stevens Rearrangement. *J. Org. Chem.* **2018**, *83*, 4105–4110.

[5] Chittimalla, S. K.; Liao, C.-C. Diels-Alder reactions of masked o-benzoquinones with acrylonitrile. *Tetrahedron* **2003**, *59*, 4039–4046.

[6] Kise, N.; Hamada, Y.; Sakurai, T. Electroreductive coupling of aromatic ketones, aldehydes, and aldimines with α,β-unsaturated esters: Synthesis of 5-aryl substituted γ-butyrolactones and lactams. *Tetrahedron* **2017**, *73*, 1143–1156.

[7] Karp, E. M.; Eaton, T. R.; Nogue, V. S. I.; Vorotnikov, V.; Biddy, M. J.; Tan, E. C. D.; Brandner, D. G.; Cywar, R. M.; Liu, R. M.; Manker, L. P.; Michener, W. E.; Gilhespy, M.; Skoufa, Z.; Watson, M. J.; Fruchey, O. S.; Vardon, D. R.; Gill, R. T.; Bratis, A. D.; Beckham, G. T. Renewable acrylonitrile production. *Science* **2017**, *358*, 1307.

[8] (a) Fleming, F. F.; Yao, L.; Ravikumar, P. C.; Funk, L.; Shook, B. C. Nitrile-Containing Pharmaceuticals: Efficacious Roles of the Nitrile Pharmacophore. *J. Med. Chem.* **2010**, *53*, 7902–7917; (b) Miller, J. S.; Manson, J. L. Designer Magnets Containing Cyanides and Nitriles. *Acc. Chem. Res.* **2001**, *34*, 563–570; (c) Penthala, N. R.; Sonar, V. N.; Horn, J.; Leggas, M.; Yadlapalli, J. S. K. B.; Crooks, P. A. Synthesis and evaluation of a series of benzothiophene acrylonitrile analogs as anticancer agents. *MedChemComm* **2013**, *4*, 1073–1078; (d) Bach, A.; Stuhr-Hansen, N.; Thorsen, T. S.; Bork, N.; Moreira, I. S.; Frydenvang, K.; Padrah, S.; Christensen, S. B.; Madsen, K. L.; Weinstein, H.; Gether, U.; Stromgaard, K. Structure-activity relationships of a small-molecule inhibitor of the PDZ domain of PICK1. *Org. Biomol. Chem.* **2010**, *8*, 4281–4288.

[9] (a) D'Sa, B. A.; Kisanga, P.; Verkade, J. G. Direct Synthesis of α,β-Unsaturated Nitriles Catalyzed by Nonionic Superbases. *J. Org. Chem.* **1998**, *63*, 3961–3967; (b) Li, G.; Xiao, J.; Zhang, W. Efficient

and reusable amine-functionalized polyacrylonitrile fiber catalysts for Knoevenagel condensation in water. *Green Chem.* **2012**, *14*, 2234–2242.

[10] (a) Maryanoff, B. E.; Reitz, A. B. The Wittig olefination reaction and modifications involving phosphoryl-stabilized carbanions. Stereochemistry, mechanism, and selected synthetic aspects. *Chem. Rev.* **1989**, *89*, 863–927; (b) Staden, L. F. v.; Gravestock, D.; Ager, D. J. New developments in the Peterson olefination reaction. *Chem. Soc. Rev.* **2002**, *31*, 195–200; (c) Zhang, T. Y.; O'Toole, J. C.; Dunigan, J. M. An efficient and practical synthesis of diphenyl cyanomethylenephosphonate: Applications to the stereoselective synthesis of cis-α,β-unsaturated nitriles. *Tetrahedron Lett.* **1998**, *39*, 1461–1464; (d) Fang, F.; Li, Y. A.; Tian, S. K. Stereoselective Olefination of *N*-Sulfonyl Imines with Stabilized Phosphonium Ylides for the Synthesis of Electron-Deficient Alkenes. *Eur. J. Org. Chem.* **2011**, *2011*, 1084–1091; (e) Palomo, C.; Aizpurua, J. M.; Garcia, J. M.; Ganboa, I.; Cossio, F. P.; Lecea, B.; Lopez, C. A new version of the Peterson olefination using bis(trimethylsilyl)methyl derivatives and fluoride ion as catalyst. *J. Org. Chem.* **1990**, *55*, 2498–2503.

[11] (a) Bumagin, N. A.; More, P. G.; Beletskaya, I. P. Synthesis of substituted cinnamic acids and cinnamonitriles *via* palladium catalyzed coupling reactions of aryl halides with acrylic acid and acrylonitrile in aqueous media. *J. Organomet. Chem.* **1989**, *371*, 397–401; (b) Ruan, J.; Li, X.; Saidi, O.; Xiao, J. Oxygen and Base-Free Oxidative Heck Reactions of Arylboronic Acids with Olefins. *J. Am. Chem. Soc.* **2008**, *130*, 2424–2425; (c) Huang, X.; Li, X.; Jiao, N. Copper-catalyzed direct transformation of simple alkynes to alkenyl nitriles *via* aerobic oxidative *N*-incorporation. *Chem. Sci.* **2015**, *6*, 6355–6360.

[12] (a) Kazuaki, I.; Yoshiro, F.; Hisashi, Y. Rhenium(VII) Oxo Complexes as Extremely Active Catalysts in the Dehydration of Primary Amides and Aldoximes to Nitriles. *Angew. Chem. Int. Ed.* **2002**, *41*, 2983–2986; (b) Kazuya, Y.; Hiroshi, F.; Yoshiyuki, O.; Miyuki, K.; Noritaka, M. A Tungsten–Tin Mixed Hydroxide as an Efficient Heterogeneous Catalyst for Dehydration of Aldoximes to Nitriles. *Angew. Chem. Int. Ed.* **2007**, *46*, 3922–3925; (c) Zhou, S.; Addis, D.; Das, S.; Junge, K.; Beller, M. New catalytic properties of iron complexes: dehydration of amides to nitriles. *Chem. Commun.* **2009**, 4883–4885.

[13] (a) Stuhl, L. S. Reaction of $[Co(CN)_5]^{3-}$ with alkenyl halides in an aprotic medium. *J. Org. Chem.* **1985**, *50*, 3934–3936; (b) Pradal, A.; Evano, G. A vinylic Rosenmund-von Braun reaction: practical synthesis of acrylonitriles. *Chem. Commun.* **2014**, *50*, 11907–11910; (c) Ahuja, B. B.; Sudalai, A. Cu-catalyzed debrominative cyanation of gem-dibromoolefins: a facile access to [small alpha],[small beta]-unsaturated nitriles. *Org. Biomol. Chem.* **2015**, *13*, 5918–5923.

[14] (a) Nakao, Y.; Yukawa, T.; Hirata, Y.; Oda, S.; Satoh, J.; Hiyama, T. Allylcyanation of Alkynes: Regio- and Stereoselective Access to Functionalized Di- or Trisubstituted Acrylonitriles. *J. Am. Chem. Soc.* **2006**, *128*, 7116–7117; (b) Nakao, Y.; Yada, A.; Ebata, S.; Hiyama, T. A Dramatic Effect of Lewis-Acid Catalysts on Nickel-Catalyzed Carbocyanation of Alkynes. *J. Am. Chem. Soc.* **2007**, *129*, 2428–2429; (c) Nakao, Y.; Hirata, Y.; Hiyama, T. Cyanoesterification of 1,2-Dienes: Synthesis and Transformations of Highly Functionalized α-Cyanomethylacrylate Esters. *J. Am. Chem. Soc.* **2006**, *128*, 7420–7421; (d) Yoshiaki, N.; Yasuhiro, H.; Masaaki, T.; Tamejiro, H. Nickel/BPh_3-Catalyzed Alkynylcyanation of Alkynes and 1,2-Dienes: An Efficient Route to Highly Functionalized Conjugated Enynes. *Angew. Chem.* **2008**, *120*, 391–393; (e) Yoshiaki, N.; Yasuhiro, H.; Masaaki, T.; Tamejiro, H. Nickel/BPh_3-Catalyzed Alkynylcyanation of Alkynes and 1,2-Dienes: An Efficient Route to Highly Functionalized Conjugated Enynes. *Angew. Chem. Int. Ed.* **2008**, *47*, 385–387; (f) Hirata, Y.; Yukawa, T.; Kashihara, N.; Nakao, Y.; Hiyama, T. Nickel-Catalyzed Carbocyanation of Alkynes with Allyl Cyanides. *J. Am. Chem. Soc.* **2009**, *131*, 10964–10973; (g) Bürger, M.; Röttger, S. H.; Loch, M. N.; Jones, P. G.; Werz, D. B. Pd-Catalyzed Cyanoselenylation of Internal Alkynes: Access to Tetrasubstituted Selenoenol Ethers. *Org. Lett.* **2020**, *22*, 5025–5029.

[15] Qin, C.; Jiao, N. Iron-Facilitated Direct Oxidative C−H Transformation of Allylarenes or Alkenes to Alkenyl Nitriles. *J. Am. Chem. Soc.* **2010**, *132*, 15893–15895.

[16] Qi, C. R.; Peng, Y. B.; Ouyang, L.; Ren, Y. W.; Jiang, H. F. Base-Promoted Addition of Arylacetonitriles to Terminal Alkynes: Regio- and Stereoselective Access to Disubstituted Acrylonitriles. *Adv. Synth. Catal.* **2017**, *359*, 1339–1350.

[17] He, A.; Falck, J. R. Stereospecific Suzuki Cross-Coupling of Alkyl α-Cyanohydrin Triflates. *J. Am. Chem. Soc.* **2010**, *132*, 2524–2525.

[18] Ortega, V.; del Castillo, E.; Csákÿ, A. G. Transition-Metal-Free Stereocomplementary Cross-Coupling of Diols with Boronic Acids as Nucleophiles. *Org. Lett.* **2017**, *19*, 6236–6239.

[19] (a) Li, C.; Zhang, Y.; Sun, Q.; Gu, T.; Peng, H.; Tang, W. Transition-Metal-Free Stereospecific Cross-Coupling with Alkenylboronic Acids as Nucleophiles. *J. Am. Chem. Soc.* **2016**, *138*, 10774–10777; (b) Tian, D.; Li, C.; Gu, G.; Peng, H.; Zhang, X.; Tang, W. Stereospecific Nucleophilic Substitution with Arylboronic Acids as Nucleophiles in the Presence of a CONH Group. *Angew. Chem. Int. Ed.* **2018**, *57*, 7176–7180.

[20] Wu, G.; Xu, S.; Deng, Y.; Wu, C.; Zhao, X.; Ji, W.; Zhang, Y.; Wang, J. Coupling of arylboronic acids with benzyl halides or mesylates without adding transition metal catalysts. *Tetrahedron* **2016**, *72*, 8022–8030.

[21] He, Z.; Song, F.; Sun, H.; Huang, Y. Transition-Metal-Free Suzuki-Type Cross-Coupling Reaction of Benzyl Halides and Boronic Acids *via* 1,2-Metalate Shift. *J. Am. Chem. Soc.* **2018**, *140*, 2693–2699.

[22] (a) Ueda, M.; Nishimura, K.; Ryu, I. Transition-Metal-Free Suzuki-Miyaura Coupling Reaction of Arylpropar-gylic Bromides with Aryl- and Alkenylboronic Acids. *Synlett* **2013**, *24*, 1683–1686; (b) Mitsuhiro, U.; Daiki, N.; Takahiro, M.; Ilhyong, R. Transition-Metal-Catalyst-Free Cross-Coupling Reaction of Secondary Propargylic Acetates with Alkenyl- and Arylboronic Acids. *Eur. J. Org. Chem.* **2017**, *2017*, 7040–7045.

[23] Liu, S.; Zeng, X.; Hammond, G. B.; Xu, B. Mild Base Promoted Nucleophilic Substitution of Unactivated sp^3-Carbon Electrophiles with Alkenylboronic Acids. *Adv. Synth. Catal.* **2018**, *360*, 3667–3671.

[24] Miyaura, N.; Suzuki, A. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. *Chem. Rev.* **1995**, *95*, 2457–2483.

[25] Kulp, S. S.; Caldwell, C. B. Reduction of .alpha.,.beta.-diarylacrylonitriles by sodium borohydride. *J. Org. Chem.* **1980**, *45*, 171–173.

[26] García Ruano, J. L.; Fajardo, C.; Fraile, A.; Martín, M. R. *m*-CPBA/KOH: An Efficient Reagent for Nucleophilic Epoxidation of gem-Deactivated Olefins. *J. Org. Chem.* **2005**, *70*, 4300–4306.

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CORRIGENDUM

Synthesis of Acrylonitriles *via* Mild Base Promoted Tandem Nucleophilic Substitution-Isomerization of α-Cyanohydrin Methanesulfonates

Shiwen Liu, Lingling Meng, Xiaojun Zeng, Gerald B. Hammond,* and Bo Xu*

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