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Metal-free and Redox-neutral Conversion of Organotrifluoroborates to Radicals Enabled by Visible Light

Wenbo Liu,^[a] Peng Liu,^{[a], [b]} Leiyang Lv,^[a] and Chao-Jun Li*^[a]

Abstract: Converting organoboron compounds to corresponding radicals has broad synthetic applications in organic chemistry. To achieve these transformations, various strong oxidants such as $Mn(OAc)_3$, $AgNO_3/K_2S_2O_8$ and $Cu(OAc)_2$ in stoichiometric amount are required through single electron transfer mechanism. Herein, we establish a distinct strategy to generate both aryl and alkyl radicals with organotrifluoroborates as the precursors via the S_H2 process. This strategy is enabled by using water as the solvent and visible light as the energy input and diacetyl as the promoter in the absence of any metal catalyst or redox reagent, thereby eliminating the metal waste. To demonstrate its synthetic utility, an efficient acetylation to prepare valuable aryl (alkyl) methyl ketones is developed and applications to construct other C-C, C-I, C-Br, C-S bonds are also feasible. Experimental evidences suggest that triplet diacetyl serves as the key intermediate in this process.

Organoboron compounds are versatile in organic synthesis. Early boron chemistry mainly focused on organoboranes, which carry some limitations including: (1) they are pyrophoric, which makes them difficult to handle; (2) in most cases, only one substituent in the boranes is delivered into the products, which reduces the atom economy especially when the organoboranes are valuable. In this regard, organoboronic acids, esters and trifluoroborates are more advantageous because of their stability, low toxicity, and ease of preparation, storage and handling.^[1] Many elegant and powerful reactions involving these boron compounds have been established including Suzuki cross coupling,^[2] Petasis reaction,^[3] Chan-Lam coupling^[4] and the Hayashi-Miyaura reaction,^[5] in which the boron compounds serve as the nucleophiles. Besides the nucleophiles, organoboron compounds can also be the precursors of radicals.^[6]

Radicals are important intermediates in organic synthesis.^[7] Approaches that generate radicals from readily available precursors are highly desirable. Benefited from the Suzuki coupling and other boron-based reactions, numerous organoboronic acids and trifluoroborates have been commercialized and readily accessible. Thus, developing efficient

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Figure 1. Traditional approaches to convert boron compounds to radicals and this work.

methods that convert these boron compounds to radicals is significant. Hitherto, the main strategy to convert these boron compounds to radicals is through the single electron transfer (SET) mechanism with transition metals as the oxidants. For example, Demir reported that aryl boronic acids were converted to aryl radicals in the presence of $Mn(OAc)_3$ at high temperature.^[8] Baran showed that aryl boronic acids and trifluoroborates were oxidized to aryl radicals by AgNO₃/K₂S₂O₈ at room temperature.^[9] In addition to aryl boronic compounds, alkyl counterparts can also be oxidized to the corresponding alkyl radicals with suitable oxidants. For instance, Fensterbank and Molander demonstrated that alkyl trifluoroborates were oxidized to alkyl radicals with stoichiometric amount of Cu(OAc)₂ (Figure 1a top).^[10] Nonetheless, the engagement of stoichiometric strong metalbased oxidants not only significantly limits the functional group compatibility but also generates large amounts of waste, which provokes serious environmental concerns. Upon these issues, Akita, Molander and others introduced photo-redox catalysts to oxidize alkyl trifluoroborates to alkyl radicals, thereby eliminating the generation of metal wastes (Figure 1a bottom).^[11] However, due to higher oxidative potential, these benign photo-redox protocols fail to transform aryl trifluoroborates into radicals although the more reactive aryl (triol)borate can be oxidized under photo-redox conditions as demonstrated by Akita.^[11c] Moreover, through using the Lewis base catalysis strategy, Ley has reported that electron-rich aryl boronic acids can be converted into the aryl radicals under photo-redox conditions.^[12] In this context, we wish to report a general approach to convert both aryl/alkyl trifluoroborates to the aryl/alkyl radicals promoted by visible light without any photo-redox catalyst or strong oxidants. This approach via the bimolecular homolytic substitution (S_H2) mechanism both acquires practical advantages and provides a complementary mechanistic alternative to SET. The success of

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this protocol hinges upon using water as the solvent and diacetyl as the visible light responsive promoter (Figure 1b).

Our work was inspired by the well-established organoborane chemistry, which engages the S_H2 at the boron center initiated by an oxygen radical (Figure 2a).^[13] However, this S_H2 process is only applicable to the highly reactive pyrophoric organoboranes and the specialized catechol boronic esters. Regular boronic acids and esters, particularly aryl boronic acids and esters, are not suitable ^[6, 14] because: (1) the conjugation of two oxygen lone pairs with the empty p orbital of boron atom decreases the Lewis acidity of aryl boronic acid (and ester); (2) a high energy barrier needs to overcome to generate the highly reactive aryl radical (Figure 2b). Upon these challenges, we hypothesized that ArBF₂, which can be generated from ArBF₃ salt in situ,^[15] might be sufficiently reactive towards oxygen radical to undergo the S_H2 process due to its stronger Lewis acidity (Figure 2c). With these concerns in mind and motivated by Davies' seminal investigation on triplet ketones,^[16] we envisioned that organotrifluoroborate might interact with the triplet diacetyl to produce the radicals via the S_H2 process.

(a) Oxygen radical reacting with organoborane to produce radical via $\rm S_{H}2$

$$\begin{array}{ccc} R & R & R^{1} & R^{1$$

Ar

(b) Challenges related with aryl boron compounds to undergo $\rm S_{\rm H}2$

$$Ar - B' + R^{1}O + R^{1}O + R^{1}O + OR + OR$$

(1) Low Lewis acidity of B in aryl boronic acids (2) High energy barrier to generate aryl radical

(c) Research proposal: ArBF₂ with triplet ketone to aryl radical via S_H2



Figure 2. Research design. (a) Oxygen radical reacting with organoborane via S_H2 process to form radical, (b) challenges to convert aryl boronic compounds via S_H2 process, (c) research proposal to convert aryl trifluoroborates to aryl radicals via triplet diacetyl promoted by visible light.

To evaluate this hypothesis shown in Figure 2c, we selected diacetyl as the photo-sensitizer because: (1) it is visible light sensitive; (2) it is cheap and readily available and (3) it is nontoxic since it is widely exploited as the food additive. In addition, water was chosen as the solvent because: (1) water is not a hydrogen donor for radical and (2) the hydrophobic effect^[17] would favor the interaction between the triplet ketone and ArBF2. Based on the persistent radical effect [18], TEMPO was added to trap the radical intermediate, thereby serving as a convenient and reliable indicator of the radical intermediate via forming the TEMPO/radical adduct. The compact fluorescence lamp (CFL) was chosen as the light source and the reaction temperature was selected as 4 °C to alleviate the potential protodeboronation.^[19] When 4-biphenyltrifluoroborate was subjected to the test conditions, it was found that the biphenyl/TEMPO adduct can be detected in 56% yield (Scheme 1). Control experiments showed that no radical adduct was formed without diacetyl (Scheme 1). These two experiments suggest the generation of aryl radical from aryl trifluoroborate under the light irradiation assisted by diacetyl. In contrast, other common boronic compounds including biphenyl boronic acid, pinacol ester and MIDA ester cannot form the corresponding radical under these conditions, thereby signifying



Scheme 1. Radical trapping experiments with TEMPO.

Table	1.	Synthesis	of	aryl	(alkyl)	methyl	ketone	from
trifluoro	bor	ate and diac	etyl	3	- 40.1			



[a] Reactions were performed at 0.1 mmol scale unless otherwise specified, with 1.5 equivalent of AcOH, 1 mL water at 4 °C under the irradiation of 2 x 34 Watts household CFL lamp for 24 hours unless otherwise specified. All the yields refer to the isolated average yields of two parallel runs. [b] Under Condition B (See SI)

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the importance of F atom in this triplet diacetyl engaged S_{H2} process. Moreover, other water-insoluble diketones such as 2,3-hexanedione and 3,4-hexanedione cannot promote the generation of radical, which implies the unique reactivity of diacetyl in this process (Scheme 1).

To evaluate the synthetic utility of this approach generating radicals, we turned attention to the radical addition of diacetyl because this will represent an interesting reaction, in which diacetyl serves both as radical promoter and reactant.^[20] Therefore, it can be envisioned that at least two equivalents of diacetyl are needed since one equivalent acts as the radical promoter and the other as the acylation reagent. More significantly, the prepared aryl (alkyl) methyl ketones from the radical addition are highly useful intermediates to heterocycles, fragrances, resins and a wide range of drug candidates.^[21] Previous approaches towards these compounds are comprised of cross couplings, Wacker oxidation and alkyne hydration, which require either transition metal catalysts or sensitive or toxic reagents.^[22] Therefore, an efficient approach to prepare these methyl ketones with environmentally benign trifluoroborates and diacetyl would be more advantageous. Towards this goal and extensive optimization, we following found that 4biphenyltrifluoroborate, as the model substrate, can be acetylated in 86% yield under visible light irradiation in water [23] (Please see SI for details).

With the optimized conditions identified, we subsequently examined the scope of this mild acetylation protocol. As shown in Table 1, a wide range of aryl and alkyl trifluoroborates can be acetylated under the standard conditions in good to excellent yields (35% - 90%). Various functional groups, including (-OPh, -OBn, -Cl, -Br, -F, -CF₃ and ketone) are also compatible with the conditions. Remarkably, aryl trifluoroborates, benzylic and nonactivated primary as well as the secondary alkyl trifluoroborates can all be employed in this acetylation. The broad scope is complementary to the related elegant photo-redox approach disclosed by Molander and co-workers.^[24] To highlight the practicality of this method, the gram scale synthesis was performed (entries 8 & 13 in Table 1). It is noteworthy that during the scope investigation, trace amount of a by-product (< 5%) was always observed along with the desired methyl ketones as shown in Table 1.[25]

To further investigate the functional group tolerance of this reaction, we also performed the parallel reactions in the presence of a wide variety of additives (see SI), known as "robustness screen".^[26] These results demonstrate that the presence of an alkene, alkyne, alcohol, ketone, aldehyde, ester, amide and aryl iodide has little or no impact on this reaction since the desired product can be obtained in comparable vields and the additives can be recovered in > 76% vields. Notably, considering that this reaction employs water as the solvent and visible light as the energy input in the absence of any toxic transition metal catalysts at low temperature, we envisioned that this approach may find potential application in chemical biology. As a preliminary study, we found three types of important molecules (i.e. amino acid, glucose and uridine), which comprise three fundamental biomacromolecules (i.e. protein, sugar and nucleic acids), can all be tolerated under the standard conditions. However, among all additives, an exception is nitrobenzene, which completely inhibits the reaction.

It is fully expected that this acetylation would further upgrade the versatility of organotrifluoroborates even though they have already found extensive applications in organic synthesis.[15b-d, 27] To elucidate this argument, we have prepared a wide array of important synthons from organotrifluoroborate with the acetylation as the key steps (please see SI). For example, 4biphenyltrifluoroborate was converted into the ester via the combination of acetylation and oxidation. Moreover, a new aromatization reaction was developed through a cascade acetvlation and aldol condensation. Furthermore. the trifluoroborate can be transformed into the carboxylic acid by this acetylation, followed by oxidation. Finally, vinyl triflate, as a versatile intermediate in various cross-couplings, was prepared from the trifluoroborate. These examples suggest the unique roles of this acetylation in diversifying organotrifluoroborate.

To explore further preparative potential of this approach forming radicals in different contexts, we found that other bonds including C-C, C-S, C-I, C-Br can be constructed in presence of the radical trapping reagents in synthetically useful yields without optimization (Scheme 2). Control experiments suggest that light irradiation and diacetyl are indispensable for all these transformations, which rule out the ionic pathway. These examples corroborate the synthetic potential of this new method to convert trifluoroborates to radicals and further optimization are undergoing. Preliminary optimization results suggest that upon removing the acetic acid additive, increasing the temperature to rt and the radical trapping reagents to 2 equivalents, 4bromobiphenyl and 4-iodobiphenyl can be obtained in 84% and 90% yield, respectively.



Scheme 2. Synthetic application of this approach to generate radicals in other contexts (all the yields are not optimized).

Based on our hypothesis in Figure 2c, the triplet diacetyl is the key initiator for the S_H2 process. To collect evidences of this hypothesis, spectroscopic investigations and control experiments were performed. It was found that in contrast to diacetyl, diethyl oxalate and ethyl pyruvate cannot initiate this process, which is consistent with the UV-Vis study because only diacetyl displays notably absorption in the visible light region ($\lambda > 405$ nm) (Figure 3a). The intensive absorption of visible light would excite diacetyl to its triplet state rather than diethyl oxalate and ethyl pyruvate. In addition, as known triplet quenchers of diacetyl,^[28] pyrene significantly retards this reaction and oxygen completely inhibits it, both of which imply the engagement of the triplet diacetyl (Figure 3b & 3c).

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Figure 3. Mechanistic investigation. (a) UV-Vis spectroscopic analysis, (b) triplet quencher pyrene retards the reaction, (c) triplet quencher oxygen completely inhibits the reaction.

In summary, a general and convenient approach to produce radicals from organotrifluoroborates promoted by visible light has been established. This approach utilizes the triplet diacetyl to activate organotrifluoroborate and proceeds under mild conditions strong redox-reagents, thereby avoiding without the stoichiometric metal waste. To demonstrate its synthetic utility, an acetylation of organotrifluoroborates has been developed. Moreover, the application in other contexts to synthesize carboncarbon and carbon-heteroatom bonds is also viable. This mild and environmentally friendly approach to generate radicals is anticipated to find applications in other radical engaged reactions.

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[1]	D. G. Hall, in <i>Boronic Acids</i> , Wiley-VCH Verlag GmbH & Co. KGaA, 2011 , pp. 1-133.
[2]	N. Miyaura, A. Suzuki, Chem. Rev. 1995, 95, 2457-2483.
[3]	N. R. Candeias, F. Montalbano, P. M. S. D. Cal, P. M. P. Gois, Chem.

- Rev. 2010, 110, 6169-6193. X. Qiao, P. Y. S. Lam, Synthesis 2011, 829-856. [4]
- T. Hayashi, K. Yamasaki, Chem. Rev. 2003, 103, 2829-2844.
- [5] [6] C. Ollivier, P. Renaud, Chem. Rev. 2001, 101, 3415-3434.

- [7] a) M. Yan, J. C. Lo, J. T. Edwards, P. S. Baran, J. Am. Chem. Soc. 2016, 138, 12692-12714; b) M. R. Heinrich, Chem. Eur. J. 2009, 15, 820-833; c) W. Liu, X. Yang, Y. Gao, C.-J. Li, J. Am. Chem. Soc. 2017, 139, 8621-8627
 - a) A. S. Demir, Ö. Reis, M. Emrullahoglu, J. Org. Chem. 2003, 68, 578-580; b) A. Dickschat, A. Studer, Org. Lett. 2010, 12, 3972-3974.
 - a) I. B. Seiple, S. Su, R. A. Rodriguez, R. Gianatassio, Y. Fujiwara, L. Sobel, P. S. Baran, J. Am. Chem. Soc. 2010, 132, 13194-13196; b) J. W. Lockner, D. D. Dixon, R. Risgaard, P. S. Baran, Org. Lett. 2011, 13, 5628-5631.
- a) G. Sorin, R. Martinez Mallorquin, Y. Contie, A. Baralle, M. Malacria, J.-P. Goddard, L. Fensterbank, *Angew. Chem. Int. Ed.* **2010**, *49*, 8721-8723; b) G. A. Molander, V. Colombel, V. A. Braz, [10] Org. Lett. 2011, 13, 1852-1855; c) M. Presset, N. Fleury-Brégeot, D. Oehlrich, F. Rombouts, G. A. Molander, J. Org. Chem. 2013, 78, 4615-4619.
- a) J. K. Matsui, D. N. Primer, G. A. Molander, Chem. Sci. 2017, 8, [11] 3512-3522; b) D. R. Heitz, K. Rizwan, G. A. Molander, *J. Org. Chem.* 2016, *81*, 7308-7313; c) Y. Yasu, T. Koike, M. Akita, *Adv. Synth. Catal.* **2012**, *354*, 3414-3420; d) H. Huang, G. Zhang, L. Gong, S. Zhang, Y. Chen, *J. Am. Chem. Soc.* **2014**, *136*, 2280-2283; e) T. Koike, M. Akita, Synlett 2013, 24, 2492-2505; f) K. Miyazawa, Y. Yasu, T. Koike, M. Akita, Chem. Commun. 2013, 49, 7249-7251; g) M. Kazuki, K. Takashi, A. Munetaka, Adv. Synth. Catal. 2014, 356, 2749-2755; h) Y. Li, K. Miyazawa, T. Koike, M. Akita, Org. Chem. Front. 2015, 2, 319-323;
 - F. Lima, U. K. Sharma, L. Grunenberg, D. Saha, S. Johannsen, J. Sedelmeier, E. V. Van der Eycken, S. V. Ley, *Angew. Chem. Int. Ed.* 2017, 56, 15136-15140.
- a) A. G. Davies, B. P. Roberts, Acc. Chem. Res. 1972, 5, 387-392; [13] b) P. J. Krusic, J. K. Kochi, J. Am. Chem. Soc. 1969, 91, 3942-3944; c) A. G. Davies, B. P. Roberts, Nature 1971, 229, 221-223; d) C. Carra, J. C. Scaiano, Eur. J. Org. Chem. 2008, 2008, 4454-4459.
- a) V. Darmency, P. Renaud, in *Top. Curr. Chem.* (Ed.: A. Gansäuer), Springer Berlin Heidelberg, Berlin, Heidelberg, **2006**, pp. 71-106; b) J. A. Baban, N. J. Goodchild, B. P. Roberts, J. Chem. Soc., Perkin Trans. 2 1986, 157-161. [15]
 - a) E. Vedejs, R. W. Chapman, S. C. Fields, S. Lin, M. R. Schrimpf, J. Org. Chem. 1995, 60, 3020-3027; b) G. A. Molander, N. Ellis, Acc. Chem. Res. 2007, 40, 275-286; c) S. Darses, J.-P. Genet, Eur. J. Org. Chem. 2003, 2003, 4313-4327; d) S. Darses, J.-P. Genet, Chem. Rev. 2008, 108, 288-325; e) A. J. J. Lennox, G. C. Lloyd-Jones, J. Am. Chem. Soc. 2012, 134, 7431-7441.
 - A. G. Davies, D. Griller, B. P. Roberts, J. C. Scaiano, J. Chem. Soc. D 1971, 196-197
- [17] D. C. Rideout, R. Breslow, J. Am. Chem. Soc. 1980, 102, 7816-7817. [18] a) H. Fischer, Chem. Rev. 2001, 101, 3581-3610; b) T. Vogler, A.
- Studer, Synthesis 2008, 1979-1993. [19]
- P. A. Cox, A. G. Leach, A. D. Campbell, G. C. Lloyd-Jones, J. Am. Chem. Soc. 2016, 138, 9145-9157. a) W. G. Bentrude, K. R. Darnall, J. Am. Chem. Soc. 1968, 90, 3588-[20]
- 3589; b) I. Tabushi, S. Kojo, K. Fukunishi, J. Org. Chem. 1978, 43, 2370-2374; c) A. Citterio, M. Serravalle, E. Vismara, Tetrahedron Lett. 1982, 23, 1831-1834; d) S. Kim, Adv. Synth. Catal. 2004, 346, 19-32. [21]

H. Siegel., M. Eggersdorfer, in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH: Germany, 2000, pp. 187-207. a) S. D. Ramgren, N. K. Garg, Org. Lett. 2014, 16, 824-827; b) C. E.

- Russell, L. S. Hegedus, J. Am. Chem. Soc. 1983, 105, 943-949; c) A. Hallberg, L. Westfelt, B. Holm, *J. Org. Chem.* **1981**, *46*, 5414-5415; d) H. B. Kwon, B. H. McKee, J. K. Stille, *J. Org. Chem.* **1990**, 55, 3114-3118; e) M. Tanaka, Synthesis 1981, 1981, 47-48; f) B. W. Michel, A. M. Camelio, C. N. Cornell, M. S. Sigman, J. Am. Chem. Soc. 2009, 131, 6076-6077; g) T. Mitsudome, T. Umetani, N. Nosaka, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, Angew. Chem. Int. Ed. 2006, 45, 481-485; h) T. Tachinami, T. Nishimura, R. Ushimaru, R. Noyori, H. Naka, J. Am. Chem. Soc. 2013, 135, 50-53; i) S. Liang, J. Jasinski, G. B. Hammond, B. Xu, Org. Lett. 2015, 17. 162-165.
- [23] The beneficial effect of acetic acid in this acetylation may be attributed to the fact that protonation of diacetyl can increase its electrophilicity since aryl and alkyl radicals are nucleophilic. [24]
- J. Amani, E. Sodagar, G. A. Molander, Org. Lett. 2016, 18, 732-735. [25] Please see SI for the possible mechanism to generate this byproduct
- a) K. D. Collins, F. Glorius, Acc. Chem. Res. 2015, 48, 619-627; b) [26] K. D. Collins, F. Glorius, Nat. Chem. 2013, 5, 597-601;
- [27] a) G. A. Molander, D. E. Petrillo, J. Am. Chem. Soc. 2006, 128, 9634-9635; b) G. A. Molander, D. J. Cooper, J. Org. Chem. 2007, 72, 3558-3560; c) G. A. Molander, L. N. Cavalcanti, J. Org. Chem. 2011, 76, 623-630; d) G. A. Molander, L. N. Cavalcanti, J. Org. Chem. 2011, 76, 7195-7203;
- [28] H. L. J. Bäckström, K. Sandros, Acta Chem. Scand. 1958, 12, 823-832

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Converting organoboron compounds to corresponding radicals has broad synthetic applications in organic chemistry. To achieve these transformations, various strong oxidants such as $Mn(OAc)_3$, $AgNO_3/K_2S_2O_8$ and $Cu(OAc)_2$ in stoichiometric amount are required through single electron transfer mechanism. Herein, we establish a distinct strategy to generate both aryl and alkyl radicals with organotrifluoroborates as the precursors via the S_{H2} process. This strategy is enabled by using water as the solvent and visible light as the energy input and diacetyl as the promoter in the absence of any metal catalyst or redox reagent, thereby eliminating the metal waste. To demonstrate its synthetic utility, an efficient acetylation to prepare valuable aryl (alkyl) methyl ketones is developed and applications to construct other C-C, C-I, C-Br, C-S bonds are also feasible. Experimental evidences suggest that triplet diacetyl serves as the key intermediate in this process.