Published in final edited form as:

J Am Chem Soc. 2016 March 9; 138(9): 2985–2988. doi:10.1021/jacs.6b01376.

Scalable, Metal- and Additive-Free, Photoinduced Borylation of Haloarenes and Quaternary Arylammonium Salts

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Abstract

We report herein a simple, metal- and additive-free, photoinduced borylation of haloarenes, including electron-rich fluoroarenes, as well as arylammonium salts directly to boronic acids. This borylation method has a broad scope and functional group tolerance. We show that it can be further extended to boronic esters, and carried out on gram scale as well as under flow conditions.

Aromatic boronic acids find increasingly important roles in the areas of synthetic organic chemistry,¹ catalysis,² molecular self-assembly,³ carbohydrate analysis,⁴ molecular sensing,⁵ materials science⁶ and medicinal chemistry.⁷ While the reaction of organomagnesium and organolithium reagents with trialkyl borates, first described by Khotinsky (RMgX)⁸ and Letsinger (RLi),⁹ remains in use, transition metal-catalyzed C–X¹⁰ and C–H-borylation¹¹ reactions have recently emerged as efficient alternatives that bypass air- and moisture-sensitive intermediates. In addition, transition metal-free, base-mediated borylation of iodo- and bromoarenes to arylboronic esters,¹² as well as the Sandmeyer-type borylation of anilines¹³ and electrophilic borylation of electron-rich arenes¹⁴ have been recently developed. These methods can be advantageous, since the use of heavy metals, expensive and air-sensitive catalysts and ligands can be avoided. However, the practicality and scalability of these methods may be limited by the narrow substrate scope and high molecular weight of the boron reagents.

Photochemical activation of molecules enables reactivity patterns that can be difficult to achieve from the ground states.¹⁵ A multitude of homolytic and heterolytic pathways that can be accessed from singlet and triplet excited states affords numerous synthetic possibilities. A number of photoinduced processes have been successfully adapted in the chemical industry (e.g. the Toray PNC process,¹⁶ rose oxide¹⁷ and vitamin D¹⁸ syntheses), pointing to the significant potential of photoinduced reactions.¹⁹

Photoinduced Ar–X bond dissociation is a key step in a number of important photochemical carbon–carbon and carbon–heteroatom bond-forming reactions, including nucleophilic substitution,²⁰ arylation,²¹ alkylation,²² and photocyclization²³ reactions.

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Supporting Information: Experimental and spectral details for all new compounds and all reactions reported. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Notes: The authors declare no competing financial interests.

We report herein that haloarenes, including electron rich fluoroarenes, as well as aryltrimethylammonium salts readily react with tetrahydroxydiboron (first introduced by Molander and Dreher for the Pd-, and later Ni-catalyzed borylations²⁴) and other diboron reagents to give aromatic boronic acids and esters under ultraviolet light in the absence of catalysts and additives in a scalable and practical manner in common grade solvents and without deoxygenation of the reaction mixtures (Figure 1).

Initial experiments showed that a reaction of bromobenzene with tetrahydroxydiboron in methanol under ultraviolet irradiation ($\lambda = 254$ nm) produced phenylboronic acid (**1**) in 92% yield after 3 h at 15 °C. The optimal temperature was 10–20 °C, with increased amounts of benzene observed at higher temperatures. The reaction did not proceed in the dark (see Table S1 in the SI) and showed a good quantum yield ($\Phi = 0.34$).

The preparative scope of the reaction was explored with a series of substituted bromoarenes. A diverse set of functional groups is well tolerated, including amide (**2**, 71%), phenol (**3**, 73%), arylacetate ester (**4**, 85%), thioether (**5**, 79% and **6**, 69%), and other functionalities (**7–25**). Both electron-releasing and electron-withdrawing substituents can be very well accommodated. Nitrogen-, oxygen-, and sulfur-containing heteroarylboronic acids were also prepared in high yields, as shown for products **7–11**. The boronic acids can be directly converted into the corresponding organotrifluoroborates as a part of the isolation procedure. For example, the borylation reaction of 3-bromoquinoline was followed by treatment of the reaction mixture with potassium difluoride²⁵ to give the corresponding trifluoroborate **11** in 81% yield.

Iodoarenes and chloroarenes were also successfully converted to boronic acids. The reactions with iodoarenes were very fast and produced the boronic acids (**12** and **13**) in high yields within 1 h. Chloroarenes reacted slower than bromoarenes (66% of **1** and 62% of **14** after 24 h). These observations are in accord with the increase in the bond dissociation energies (BDE) of the C₆H₅–X bonds (C–I 272, C–Br 336, C–Cl 400 kJ·mol⁻¹).²⁶ The differential reactivity of C–X bonds can be used for the chemoselective and high-yielding synthesis of haloarylboronic acids, as shown for **12**, **13**, **15** and **16**.

Boronic acids find increasing use in medicine,⁷ as exemplified by the fungal leucyl-tRNA synthetase inhibitor tavaborole (**16**, Table 1) that has recently been approved for treatment of onychomycosis.²⁷ Using the photoinduced borylation, **16** was prepared from the corresponding bromoarene in 73% yield after a simple work-up. Tavaborole was previously prepared using air- and moisture-sensitive reagents (NaH, *n*-BuLi, and B(O*i*Pr)₃).²⁸ The successful synthesis of **16** also indicates that an ortho-substituent is well-tolerated during the borylation event. Furthermore, good quantum efficiency of the borylation reaction enabled practical gram-scale syntheses of several representative boronic acids (**12**, **17**, **18** on 1.1–1.8 g scales) and trifluoroborate **7** (3 g) using simple quartz test-tubes and low intensity UV sources without deoxygenation of the reaction solutions.

Preliminary experiments also show that the reaction can be translated to a continuous flow process (**1**, 90% and **17**, 60%). Reaction mixtures typically remained homogeneous.

Monitoring of the borylation reactions by ^{11}B NMR indicated formation of trimethyl borate that may arise from solvolysis of B–X bond-containing inorganic byproducts of the reaction.

Fluorobenzene proved resistant to the borylation in line with the high BDE of the $\text{C}_6\text{H}_5\text{--F}$ bond ($526\text{ kJ}\cdot\text{mol}^{-1}$)²⁶ that exceeds the energy of absorbed light ($469\text{ kJ}\cdot\text{mol}^{-1}$). Remarkably, 4-fluoroaniline readily produced (4-aminophenyl)boronic acid that was isolated as trifluoroborate **25** in 53% yield, indicating that certain Ar–F bonds can be harnessed for the synthesis of boronic acids without the use of transition metals.²⁹ Similarly, 4-fluorophenol reacted smoothly to give boronic acid **3** in 69% yield (Table 2). Other fluoroarenes bearing electron-releasing substituents are also competent substrates (**26–30**). The procedure is particularly suitable for borylation of unprotected fluoroanilines and fluorophenols that have so far eluded C–F borylation. The reactivity observed for 4-fluoroaniline and other similar fluoroarenes in the photoinduced borylation reaction is consistent with the formation of the triplet aryl cation via the *heterolysis* of the C–F bond. This process is favored for the electron rich haloarenes and, unlike Ar–F homolysis, is greatly facilitated in polar protic solvents, as previously described by Albini, Fagnoni and Protti.³⁰ Indeed, the yield of the reaction of 4-fluorophenol with B_2pin_2 was solvent-dependent.

No reaction was observed in hexane after 2 h, and only 5% of the borylation product was formed in acetonitrile, while 20% of the borylation product was produced in methanol. This observation is in line with the experimental and computational data reported for the photoinduced heterolysis of 4-fluorophenol.³⁰ Although $\text{B}_2(\text{OR})_4$ generally behave as electrophiles, complexation with Lewis bases (e.g., fluoride, alkoxides, N-heterocyclic carbenes, 4-methylpyridine, and phosphines)³¹ produces nucleophilic $\text{sp}^2\text{--sp}^3$ Lewis base–diboron adducts that react with organic electrophiles in the absence of transition metal catalysts.³² It is possible that the photoheterolytically-produced fluoride ion forms a transient nucleophilic $\text{sp}^2\text{--sp}^3$ $\text{B}_2(\text{OR})_4\text{F}^-$ complex that then reacts with the triplet cation.³³ Interestingly, $\text{B}_2\text{pin}_2\text{F}^-$ adduct was proposed as an intermediate in the borylation of arenediazonium salts,^{13c} and $[\text{NMe}_4][\text{B}_2\text{pin}_2\text{F}]$ was subsequently shown to effect the diazonium borylation.^{31d} The photoinduced borylation of fluoroarenes is the first example of metal-free and direct conversion of fluoroarenes to arylboronic acids.

Encouraged by the outcome of the experiments with haloarenes, we turned our attention to the borylation of other carbon–heteroatom bonds. In particular, we focused on the Ar–N–borylation, since few methods are known for this transformation.^{13,34} Interestingly, aryltrimethylammonium iodides reacted rapidly and produced the corresponding boronic acids **1**, **14**, **18**, **23**, and **24** in 70–98% yields. In addition, ring scission of the cyclic salt **31** afforded boronic acid **32** in 69% yield (Table 3).

We next evaluated several diboron esters as counterparts in the reaction with haloarenes (Table 4). The borylation reactions with diboron esters derived from pinacol, neopentyl glycol, 1,1,3-trimethylethylene glycol, and 1,1,4,4-tetramethylethylene glycol delivered the corresponding phenylboronic esters **33–36** in high yields using acetonitrile as a solvent. The reaction scope was further tested with several bromoarenes with varied substitution patterns. In all cases the corresponding borolanes **37–40** were produced in excellent yields without any noticeable phototransposition.³⁵ Interestingly, the MIDA boronate ester **41** was also

prepared, indicating that bifunctional borylated arenes can be efficiently accessed using this method.

Although further work is necessary to clarify the mechanism, it is possible that homolytic substitution³⁶ in the diboron reagents and sp^2 - sp^3 Lewis base–diboron adducts by a photogenerated aryl radical and aryl triplet cation can be responsible for the observed reactivity.³³

In summary, this paper describes a simple, scalable, metal- and additive-free method of photoinduced borylation of haloarenes and quaternary arylammonium salts. The borylation produces aromatic boronic acids and esters in good to excellent yields under mild conditions and with formation of innocuous, easy-to-remove byproducts. The reaction is distinguished by a broad scope that includes electron-rich fluoroarenes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Financial support by the Welch Foundation (AX-1788), the NSF (CHE-1455061), the Max and Minnie Tomerlin Voelcker Fund, and UTSA is gratefully acknowledged. Mass spectroscopic analysis was supported by a grant from the NIMHD (G12MD007591).

References

1. (a) Suzuki, A.; Brown, HC. *Organic Syntheses Via Boranes*. Vol. 3. Aldrich Chemical Company; Milwaukee: 2003. (b) Hall, DG., editor. *Boronic Acids*. 2nd. Wiley-VCH; Weinheim: 2011. (c) Gutekunst WR, Baran PS. *Chem Soc Rev*. 2011; 40:1976–1991. [PubMed: 21298176]
2. (a) (b) Corey EJ. *Angew Chem, Int Ed*. 2002; 41:1650–1667. (c) Dimitrijevi E, Taylor MS. *ACS Catal*. 2013; 3:945–962. (d) Ishihara K. *Top Organomet Chem*. 2015; 49:243–270. (e) Taylor MS. *Acc Chem Res*. 2015; 48:295–305. [PubMed: 25493641]
3. (a) Fujita N, Shinkai S, James TD. *Chem Asian J*. 2008; 3:1076–1091. [PubMed: 18567041] (b) Mastalerz M. *Angew Chem, Int Ed*. 2010; 49:5042–5053.
4. (a) James TD, Shinkai S. *Top Curr Chem*. 2002; 218:159–200. (b) Jelinek R, Kolusheva S. *Chem Rev*. 2004; 104:5987–6015. [PubMed: 15584694] (c) Pal A, Berube M, Hall DG. *Angew Chem, Int Ed*. 2010; 49:1492–1495. (d) Hansena JS, Christensena JB, Petersena JF, Hoeg-Jensenb T, Norrild JC. *Sens Actuators, B*. 2012; 161:45–79.
5. (a) Wade CR, Broomsgrove AEJ, Aldridge S, Gabbaï FP. *Chem Rev*. 2010; 110:3958–3984. [PubMed: 20540560] (b) Wu X, Li Z, Chen XX, Fossey JS, James TD, Jiang YB. *Chem Soc Rev*. 2013; 42:8032–8048. [PubMed: 23860576] (c) Guan Y, Zhang Y. *Chem Soc Rev*. 2013; 42:8106–8121. [PubMed: 23860617] (d) You L, Zha D, Anslyn EV. *Chem Rev*. 2015; 115:7840–7892. [PubMed: 25719867] (e) Wu J, Kwon B, Liu W, Anslyn EV, Wang P, Kim JS. *Chem Rev*. 2015; 115:7893–7943. [PubMed: 25965103]
6. (a) Lorbach A, Huebner A, Wagner M. *Dalton Trans*. 2012; 41:6048–6063. [PubMed: 22546926] (b) Liu, J.; Lavigne, JJ. *Boronic Acids*. 2nd. Hall, DG., editor. Wiley-VCH; Weinheim: 2011. (c) Jäkle F. *Top Organomet Chem*. 2015; 49:297–325.
7. (a) Trippier PC, McGuigan C. *Med Chem Commun*. 2010; 1:183–198. (b) Yang, W.; Gao, W.; Wang, B. *Biological and Medicinal Applications of Boronic Acids*. In: Hall, DG., editor. *Boronic Acids*. Wiley-VCH; Weinheim: 2011. (c) Ban HS, Nakamura H. *Chem Rec*. 2015; 15:616–635. [PubMed: 25800654]
8. Khotinsky E, Melamed M. *Ber Dtsch Chem Ges*. 1909; 42:3090–3096.

9. Letsinger RL, Skoog IH. *J Org Chem*. 1953; 18:895–897.
10. (a) Ishiyama T, Murata M, Miyaura N. *J Org Chem*. 1995; 60:7508–7510. (b) Murata M, Watanabe S, Masuda Y. *J Org Chem*. 1997; 62:6458–6459. (c) Ishiyama T, Miyaura N. *J Organomet Chem*. 2000; 611:392–402. (d) Ishiyama, T.; Miyaura, N. *Boronic Acids*. 2nd. Hall, DG., editor. Wiley-VCH; Weinheim: 2011. (e) Chow WK, Yuen OY, Choy PY, So CM, Lau CP, Wong WT, Kwong FY. *RSC Adv*. 2013; 3:12518–12539.
11. (a) Cho JY, Tse MK, Holmes D, Maleczka RE, Smith MR. *Science*. 2002; 295:305–308. [PubMed: 11719693] (b) Mkhaliid IAI, Barnard JH, Marder TB, Murphy JM, Hartwig JF. *Chem Rev*. 2010; 110:890–931. [PubMed: 20028025] (c) Hartwig JF. *Acc Chem Res*. 2012; 45:864–873. [PubMed: 22075137] (d) Stahl T, Muether K, Ohki Y, Tatsumi K, Oestreich M. *J Am Chem Soc*. 2013; 135:10978–10981. [PubMed: 23855894]
12. (a) Yamamoto E, Izumi K, Horita Y, Ito H. *J Am Chem Soc*. 2012; 134:19997–20000. [PubMed: 23171366] (b) Nagashima Y, Takita R, Yoshida K, Hirano K, Uchiyama M. *J Am Chem Soc*. 2013; 135:18730–18733. [PubMed: 24266767] (c) Zhang J, Wu HH, Zhang J. *Eur J Org Chem*. 2013; 6263–6266. (d) Yamamoto E, Izumi K, Horita Y, Ukigai S, Ito H. *Top Catal*. 2014; 57:940–945. (e) Bose SK, Marder TB. *Org Lett*. 2014; 16:4562–4565. [PubMed: 25148202] (f) Yamamoto E, Ukigai S, Ito H. *Chem Sci*. 2015; 6:2943–2951. (g) Uematsu R, Yamamoto E, Maeda S, Ito H, Taketsugu T. *J Am Chem Soc*. 2015; 137:4090–4099. [PubMed: 25773395] (h) Bose SK, Deissenberger A, Eichhorn A, Steel PG, Lin Z, Marder TB. *Angew Chem, Int Ed*. 2015; 54:11843–11847.
13. (a) Mo F, Jiang Y, Qiu D, Zhang Y, Wang J. *Angew Chem, Int Ed*. 2010; 49:1846–1849. (b) Yu J, Zhang L, Yan G. *Adv Synth Catal*. 2012; 354:2625–2628. (c) Zhu C, Yamane M. *Org Lett*. 2012; 14:4560–4563. [PubMed: 22900887] (d) Qiu D, Jin L, Zheng Z, Meng H, Mo F, Wang X, Zhang Y, Wang J. *J Org Chem*. 2013; 78:1923–1933. [PubMed: 23106090] (e) Qiu D, Zhang Y, Wang J. *Org Chem Front*. 2014; 1:422–425. (f) Erb W, Hellal A, Albini M, Rouden J, Blanchet J. *Chem Eur J*. 2014; 20:6608–6612. [PubMed: 24737711] (g) Zhao CJ, Xue D, Jia ZH, Wang C, Xiao J. *Synlett*. 2014; 25:1577–1584.
14. (a) De Vries TS, Prokofjevs A, Vedejs E. *Chem Rev*. 2012; 112:4246–4282. [PubMed: 22519545] (b) Ingleson MJ. *Synlett*. 2012; 23:1411–1415. (c) Ingleson MJ. *Top Organomet Chem*. 2015; 49:39–71. (d) Warner AJ, Lawson JR, Fasano V, Ingleson MJ. *Angew Chem, Int Ed*. 2015; 54:11245–11249.
15. (a) Schutt, L.; Bunce, NG. *CRC Handbook of Organic Photochemistry and Photobiology*. 2nd. Horspool, WM.; Lenci, F., editors. CRC Press; Boca Raton: 2004. (b) Albini, A.; Fagnoni, M., editors. *Handbook of Synthetic Photochemistry*. Wiley-VCH; Weinheim: 2010. (c) Albini, A.; Fagnoni, M. *Photochemically-Generated Intermediates in Synthesis*. John Wiley & Sons, Inc; Hoboken: 2013.
16. (a) Pape M. *Pure Appl Chem*. 1975; 41:535–558. (b) Weissertal, K.; Arpe, HJ. *Industrial Organic Chemistry*. 3th. VCH; Weinheim: 1997. p. 254
17. Ravelli D, Protti S, Neri P, Fagnoni M, Albini A. *Green Chem*. 2011; 13:1876–1884.
18. (a) Zhu GD, Okamura WH. *Chem Rev*. 1995; 95:1877–1952. (b) Labler, L. *Ullmann's Encyclopedia of Industrial Chemistry*. 7th. Wiley-VCH; Weinheim: 2011. Vitamins 3, Vitamin D.
19. For recent examples, see: Yoshimura A, Takamachi Y, Han LB, Ogawa A. *Chem Eur J*. 2015; 21:1–5. Brimiouille R, Bauer A, Bach T. *J Am Chem Soc*. 2015; 137:5170–5176. [PubMed: 25806816] Mukhina OA, Kutateladze AG. *J Am Chem Soc*. 2016; doi: 10.1021/jacs.5b12690
20. (a) Bunnett JF. *Acc Chem Res*. 1978; 11:413–420. (b) Karapire, C.; Siddik, I. *CRC Handbook of Organic Photochemistry and Photobiology*. 2nd. Horspool, WM.; Lenci, F., editors. CRC Press; Boca Raton: 2004. (c) Uyeda C, Tan YC, Fu GC, Peters JC. *J Am Chem Soc*. 2013; 135:9548–9552. [PubMed: 23697882] (d) Tan YC, Munoz-Molina JM, Fu GC, Peters JC. *Chem Sci*. 2014; 5:2831–2835. (e) Li L, Liu W, Zeng H, Mu X, Cosa G, Mi Z, Li CJ. *J Am Chem Soc*. 2015; 137:8328–8331. [PubMed: 26086314]
21. (a) Dichiarante V, Fagnoni M, Albini A. *Angew Chem Int Ed*. 2007; 46:6495–6498. (b) Buden ME, Guastavino JF, Rossi RA. *Org Lett*. 2013; 15:1174–1177. [PubMed: 23463911] (c) Ruch J, Aubin A, Erbland G, Fortunato A, Goddard JP. *Chem Comm*. 2016; 52:2326–2329. [PubMed: 26728790]
22. (a) Mella M, Coppo P, Guizzardi B, Fagnoni M, Freccero M, Albini A. *J Org Chem*. 2001; 66:6344–6352. [PubMed: 11559185] (b) Guizzardi B, Mella M, Fagnoni M, Albini A. *Chem Eur*

- J. 2003; 9:1549–1555. [PubMed: 12658653] (c) Zheng XL, Yang L, Du WY, Ding AS, Guo H. Chem - Asian J. 2014; 9:439–442. [PubMed: 24288232]
23. (a) Grimshaw J, de Silva AP. Chem Soc Rev. 1981; 10:181–203.(b) Park YT, Song NW, Hwang CG, Kim KW, Kim D. J Am Chem Soc. 1997; 119:10677–10683.(c) Lu SC, Zhang XX, Shi ZJ, Ren YW, Li B, Zhang W. Adv Synth Cat. 2009; 351:2839–2844.
24. For Pd- and Ni-catalyzed borylation with tetrahydroxydiboron, see: Molander GA, Trice SLJ, Dreher SD. J Am Chem Soc. 2010; 132:17701–17703. [PubMed: 21105666] Molander GA, Trice SLJ, Kennedy SM, Dreher SD, Tudge MT. J Am Chem Soc. 2012; 134:11667–11673. [PubMed: 22769742] Molander GA, Trice SLJ, Kennedy SM. J Org Chem. 2012; 77:8678–8688. [PubMed: 22994557] Molander GA, Trice SL, Kennedy SM. Org Lett. 2012; 14:4814–4817. [PubMed: 22946672] Molander GA, Cavalcanti LN, Garcia-Garcia C. J Am Chem Soc. 2013; 78:6427–6439.
25. (a) Vedejs E, Chapman RW, Fields SC, Lin S, Schrimpf MR. J Org Chem. 1995; 60:3020–3027.(b) Molander GA, Ellis N. Acc Chem Res. 2007; 40:275–286. [PubMed: 17256882] (c) Darses S, Genet JP. Chem Rev. 2008; 108:288–325. [PubMed: 18095714] (d) Molander, GA.; Jean-Gérard, L. Boronic Acids. 2nd. Hall, DG., editor. Wiley-VCH; Weinheim: 2011.
26. Luo, YR. Comprehensive Handbook of Chemical Bond Energies. CRC Press; Boca Raton, FL: 2007.
27. (a) Baker SJ, Zhang YK, Akama T, Lau A, Zhou H, Hernandez V, Mao W, Alley MRK, Sanders V, Plattner JJ. J Med Chem. 2006; 49:4447–4450. [PubMed: 16854048] (b) Rock FL, Mao W, Yaremchuk A, Tukalo M, Crépin T, Zhou H, Zhang YK, Hernandez V, Akama T, Baker SJ, Plattner JJ, Shapiro L, Martinis SA, Benkovic SJ, Cusack S, Alley MRK. Science. 2007; 316:1759–1761. [PubMed: 17588934]
28. Gunasekera DS, Gerold DJ, Aalderks NS, Chandra JS, Maanu CA, Kiprof P, Zhdankin VV, Reddy MVR. Tetrahedron. 2007; 63:9401–9405.
29. For Ni-catalyzed borylation of fluoroarenes, see: Liu XW, Echavarren J, Zarate C, Martin R. J Am Chem Soc. 2015; 137:12470–12473. [PubMed: 26397717] Niwa T, Ochiai H, Watanabe Y, Hosoya T. J Am Chem Soc. 2015; 137:14313–14318. [PubMed: 26488683]
30. (a) Freccero M, Fagnoni M, Albini A. J Am Chem Soc. 2003; 125:13182–13190. [PubMed: 14570493] (b) Fagnoni M, Albini A. Acc Chem Res. 2005; 38:713–721. [PubMed: 16171314] (c) Dichiarante V, Fagnoni M. Synlett. 2008:787–800.(d) Raviola C, Ravelli D, Protti S, Albini A, Fagnoni M. Synlett. 2015; 26:471–478.
31. (a) Nguyen P, Dai C, Taylor NJ, Power WP, Marder TB, Pickett NL, Norman NC. Inorg Chem. 1995; 34:4290–4291.(b) Clegg W, Dai C, Lawlor FJ, Marder TB, Nguyen P, Norman NC, Pickett NL, Power WP, Scott AJ. J Chem Soc Dalton Trans. 1997:839–846.(c) Kleeberg C, Crawford AG, Batsanov AS, Hodgkinson P, Apperley DC, Cheung MS, Lin Z, Marder TB. J Org Chem. 2012; 77:785–789. [PubMed: 22126312] (d) Pietsch S, Neeve EC, Apperley DC, Bertermann R, Mo F, Qiu D, Cheung MS, Dang L, Wang J, Radius U, Lin Z, Kleeberg C, Marder TB. Chem Eur J. 2015; 21:7082–7098. [PubMed: 25877472]
32. (a) Lee KS, Zhugralin AR, Hoveyda AH. J Am Chem Soc. 2009; 131:7253–7255. [PubMed: 19432440] (b) Bonet A, Gulyas H, Fernandez E. Angew Chem, Int Ed. 2010; 49:5130–5134.(c) Bonet A, Pubill-Ulldemolins C, Bo C, Gulyas H, Fernandez E. Angew Chem, Int Ed. 2011; 50:7158–7161.(d) Wu H, Radomkit S, O'Brien JM, Hoveyda AH. J Am Chem Soc. 2012; 134:8277–8285. [PubMed: 22559866] (e) Bonet A, Sole C, Gulyas H, Fernandez E. Org Biomol Chem. 2012; 10:6621–6623. [PubMed: 22811000] (f) Sanz X, Lee GM, Pubill-Ulldemolins C, Bonet A, Gulyas H, Westcott SA, Bo C, Fernandez E. Org Biomol Chem. 2013; 11:7004–7010. [PubMed: 24056986] (g) Palau-Lluch G, Sanz X, La Cascia E, Civit MG, Miralles N, Cuenca AB, Fernandez E. Pure Appl Chem. 2015; 87:181–193.(h) Dewhurst RD, Neeve EC, Braunschweig H, Marder TB. Chem Comm. 2015; 51:9594–9607. [PubMed: 25912808]
33. See Scheme S1 and further discussion in the SI.
34. (a) Tobisu M, Nakamura K, Chatani N. J Am Chem Soc. 2014; 136:5587–5590. [PubMed: 24684671] (b) Hu J, Sun H, Cai W, Pu X, Zhang Y, Shi Z. J Org Chem. 2016; 81:14–24. [PubMed: 26628255]
35. Cameron KS, Pincock AL, Pincock JA, Thompson A. J Org Chem. 2004; 69:4954–4960. [PubMed: 15255721]

36. (a) Davies AG, Roberts BP, Scaiano JC. J Chem Soc B. 1971:2171–2176.(b) Nozaki K, Oshima K, Utimoto K. Bull Chem Soc Jpn. 1991; 64:403–409.(c) Brown HC, Midland MM. Angew Chem, Int Ed Engl. 1972; 11:692–700.(d) Ollivier C, Renaud P. Chem Rev. 2001; 101:3415–3434. [PubMed: 11840989]

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Figure 1. Photoinduced borylation

Table 1
Scope of the Photoinduced Reaction of Haloarenes with Tetrahydroxydiboron^a

^a Bromoarenes were used unless specified otherwise. Reaction conditions for small scale experiments: haloarene (0.6–1 mmol), tetrahydroxydiboron (1–1.6 mmol), CH₃OH (5–6 mL), 15 °C, 3–24 h, UV lamp (254 nm); then treatment with KHF₂ for ArBF₃K.

Table 2
Borylation of Fluoroarenes^a

^aReaction conditions: see footnote for Table 1.

Table 3
Borylation of Quaternary Arylammonium Salts^a

^aReaction conditions: see footnote for Table 1.

Table 4
Photoinduced Reaction of Haloarenes with Diboronic Esters^a

^aBromoarenes were used unless specified otherwise. Reaction conditions: haloarene (0.5–1 mmol), diboron ester (1–2 mmol), CH₃CN (6 mL), 15 °C, 4–14 h, UV lamp (254 nm). Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane.