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Rapid Access to Borylated Thiophenes Enabled by Visible Light

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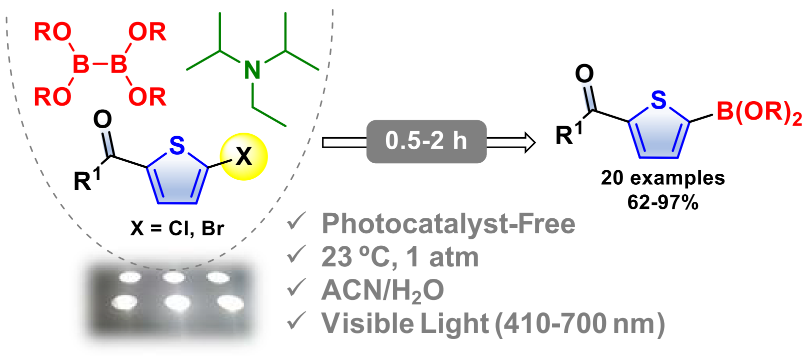
Supporting Information



ABSTRACT: Boron-containing thiophenes are important entities in organic/medicinal chemistry as well as in material science. In this Letter, a novel, straightforward, and fast procedure for their production employing visible light as an energy source at room temperature and ambient pressure is reported. All substrates are commercially available, and the process does not require the use of any external photocatalyst.

Organoboron compounds play a key role as intermediate targets in organic/medicinal chemistry and material science[1] due to their versatility and environmentally benign and user-friendly characteristics. Sophisticated and elegant methods have been reported for the insertion of boryl groups into organic molecules, including recent advances in the transition-metal-catalyzed or UV-photoinduced borylation of alkanes, arenes, heteroarenes, fused arenes, olefins, and other substrates.[2] Among these products, borylated heteroarene rings are considered important building blocks for subsequent derivatization.[3] Of particular interest is the fast production of C−C bonds for the preparation of bioactive molecules.[1b,4]

In this context, boron-containing thiophenes are important scaffolds, for example, in conjugated materials[5] showing organic electronic applications[6] or the fabrication of light-emitting diodes[7] or even in antimicrobial activity.[8] Early reports on synthesizing 2-thiophenyl boronate esters used stoichiometric or catalytic metalation protocols.[9] In 1995, Miyaura et al. published the Pd-catalyzed reaction between tetraalkoxydiboron reagents with haloarenes to form arylboronates, including the 3-iodobenzothiophene (Scheme 1a).[10] Later, Li et al. reported an efficient alternative for producing some arylboronic acids using a lithium−halogen exchange with an *in situ* quench with borate (Scheme 1b).[11] Regarding iridium-catalyzed reactions, Sawamura et al. realized an ester-directed borylation on a silica-supported iridium complex (Scheme 1c, top reaction),[12] whereas Smith et al. showed an alternative strategy that included a sequential diborylation/monodeborylation pathway to obtain boron-containing thiophenes (Scheme 1c, bottom reaction).[13] Recently, Blum et al. discovered a simple and transition-metal-free protocol to exclusively produce 3-borylated thiophene derivatives (Scheme 1d).[14] All of these methodologies somehow require mostly

Scheme 1. Strategies Related to the Borylation of Thiophenes

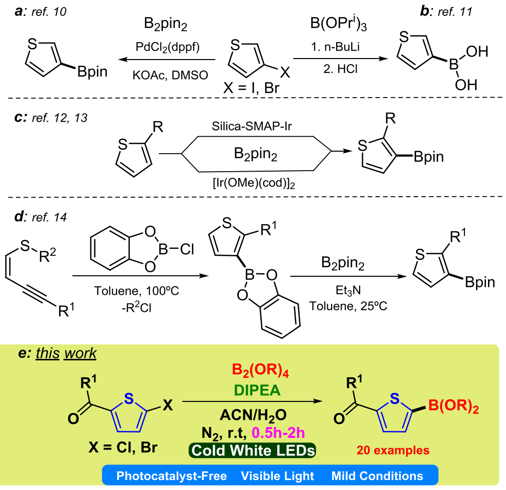


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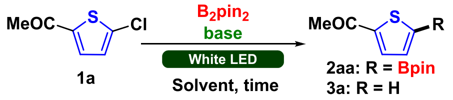
Table 1. Searching for the Optimal Conditions[a]



no.	solvent	base	time (h)	conv. (%)[b]	2aa/3a	yield (%)[b]
1[c]	ACN	DIPEA	6	27	75/25	22
2	ACN	DIPEA	6	100	85/15	53
3	ACN		6	0		0
4[d]	ACN	DIPEA	overnight	0		0
5	MeOH	DIPEA	6	52	44/56	8
6	DMF	DIPEA	6	9		0
7[e]	**ACN-H_2O**	**DIPEA**	**0.5**	**100**	**92/8**	**84**[f].
8	ACN-H_2O	DIPEA[g]	0.5	61	89/11	51
9	ACN-H_2O	DIPEA[h]	0.5	100	84/16	58
10[i]	ACN-H_2O	DIPEA	0.5	74	80/20	31
11[j]	ACN-H_2O	DIPEA	0.5	85	88/12	45
12	ACN-H_2O	Et_3N	0.5	68	87/13	56
13	ACN-H_2O	DIPA	0.5	71	92/8	63
14	ACN-H_2O	DBU	0.5	86	90/10	63
15	ACN-H_2O	DABCO	0.5	10	85/15	10
16	ACN-H_2O	Ph_3N	0.5	3		0
17	ACN-H_2O	pyridine	0.5	0		0
18[k]	**ACN-H_2O**	**DIPEA**	**0.5**	**100**	**85/15**	**80**
19[l]	**ACN-H_2O**	**DIPEA**	**0.5**	**100**	**85/15**	**76**

[a] **1a** (0.08 mmol), B_2pin_2 (1.6 mmol), and base (0.12 mmol) in 3 mL of N_2/solvent; irradiation (cold-white LED), 23 °C. [b] GC-FID yields of **2aa**. [c] With DCA (10 mol %). [d] Heating (50 °C) in dark. [e] ACN−H_2O (9:1 v/v). [f] Isolated yield. [g] DIPEA (0.08 mmol). [h] DIPEA (0.16 mmol). [i] B_2pin_2 (0.4 mmol). [j] B_2pin_2 (0.8 mmol). [k] Using 2-acetyl-5-bromothiophene (0.08 mmol). [l] Using 2-acetyl-5-iodothiophene (0.08 mmol).

complex conditions, such as the performance of the reaction in a glovebox, the employment of high temperatures or iridium precatalysts, the preliminary synthesis of the starting materials, or sometimes the need for prolonged reaction times. To reduce costs and unwarranted residues in the final products, the development of new and "greener" strategies with milder conditions is highly desired.

Herein we report as a proof of concept a straightforward, rapid, and photocatalyst-free process to fabricate borylated thiophenes using visible light under mild conditions (Scheme 1e). This reaction implies the *in situ* generation of a ground-state complex that is capable of absorbing light in the visible region, initiating the process.

In view of the successful merging of visible-light excitation for chemical transformations[15] and inspired by our previous experience,[16] we commenced with a reaction of 2-acetyl-5-chlorothiophene (**1a**) and bis(pinacolato)diboron (B_2pin_2) in the presence of Hünig's base (diisopropylethylamine, DIPEA) and catalytic amounts of 9,10-dicyanoanthracene (DCA) using cold-white LEDs (Table 1, entry 1). The expected product **2aa** was obtained in moderate yield after the incomplete conversion of **1a**. Surprisingly, a control experiment in the absence of DCA afforded the complete conversion of **1a** together with adduct **2aa** in good yield (Table 1, entry 2). No product formation was detected in the absence of base or after heating the reaction mixture to 50 °C overnight in the dark (Table 1, entries 3 and 4), demonstrating that both components (base and light) were essential for this photochemical protocol. Changes in solvent conditions did not improve the results (Table 1, entries 5 and 6).

On the basis of the literature data,[17] we performed the reaction using an acetonitrile (ACN)/water mixture as the solvent, anticipating that the process could be accelerated. Indeed, the complete conversion of **1a** was observed after 30 min of irradiation, leading to product **2aa** in excellent yield and with high selectivity (Table 1, entry 7). Varying the amount of DIPEA or B_2pin_2 did not gain better outputs of the reaction in terms of the conversion and yield (Table 1, entries 8−11). Changing the base under optimal conditions presented good results when triethylamine (Et_3N), diisopropylamine (DIPA), 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU), or 1,4-diazabicyclo[2.2.2]octane (DABCO) was used (Table 1, entries 12−15), whereas the reaction did not occur with triphenylamine (Ph_3N) or pyridine (Table 1, entries 16 and 17). Finally, the procedure was applied to the thioaryl bromide or iodide derivative, and excellent results were also obtained (Table 1, entries 18 and 19).

To better understand this methodology, absorptivity measurements of different mixtures under reaction conditions were carried out (Figure 1). Before irradiation, new bands at ca. 400 and 550 nm were clearly observed when the three ingredients (**1a** + B_2pin_2 + DIPEA) were present, and, indeed, the solution turned red (Figure 1, inset). This fact, together with the colorless mixtures to the naked eye for the rest of combinations (Figure 1, inset), pointed to the formation of a complex in the ground state with remarkable absorbance in the visible region, which allowed the initiation of the investigated reaction.

To shed light on the nature of this complex, NMR experiments were conducted (Figure 2). First, the ^{11}B NMR spectrum of B_2pin_2 showed its characteristic δ at 31 ppm. However, a new species was observed (δ 22.5 and 20) when DIPEA or DIPEA/**1a** was added, which was safely ascribed to the sp^3−sp^2 diboron **A** (Figure 2a).[2n,17,18] Thus the treatment of B_2pin_2 in water with Hünig's base gave rise to **A** and the cationic protonated DIPEA. Furthermore, the interaction between B_2pin_2 and **1a** did not take place, and **2aa** was not detected in the three-component mixture (Figure 2a),

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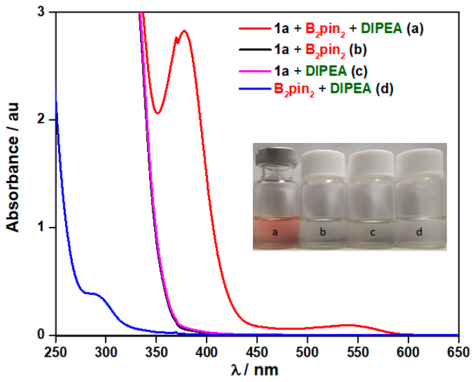


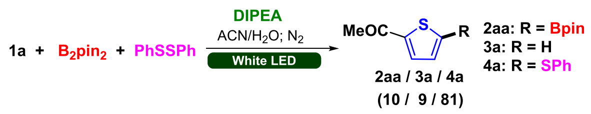
Figure 1. UV−vis absorption spectra. Inset: photographs of different solutions. Conditions: **1a** (0.08 mmol), B_2pin_2 (0.16 mmol), and DIPEA (0.12 mmol); solvent: ACN/H_2O (9/1 v/v) in a total volume of 3 mL under an air atmosphere.

supporting the notion that light was a crucial parameter for the reaction (see Table 1, entries 3 and 4).

Besides, the ^{13}C NMR spectroscopic analysis of the starting material **1a** in the absence/presence of B_2pin_2 + DIPEA was achieved (Figure 2b). Interestingly, in addition to the carbonyl signal (δ 192), a new weakly shifted peak appeared in the mixture, suggesting the possibility of a hydrogen-bonding equilibrium between **A** and the C=O group of **1a**. Moreover, the quaternary carbon in the α position and the CH in the β position related to the C=O group were somehow affected due to this presumably noncovalent interaction (Figure 2b). Assuming that this hydrogen-bonding interaction between **1a** and **A** could induce some effects on aromatic substituents, the most relevant part of the ^1H NMR spectra (Figure 2c) showed a weak shift of the CH resonances of the thiophene core. The foregoing experimental results pointed out the formation of a three-component complex in the ground state, where the carbonyl group played a pivotal role in this type of processes. To support this hypothesis, several carbonyl-free thiophenes were submitted to visible-light irradiation under the standard conditions. As expected, no conversion of the starting material was observed, even after 6 h of reaction. (See the details in the SI.)

With these data in hand, we proposed the following reaction mechanism (Figure 2d). After the formation of intermediate **A**, a hydrogen-bonding interaction with **1a** occurs, affording a new complex **B** that might tentatively be responsible for the red color of the solution. Hence, under visible-light irradiation, complex **B** is promoted to its excited state (**B***). This species is now capable of oxidizing DIPEA (this pathway is feasible based on theoretical calculations; data not shown), and, after a fast splitting of the C−Cl bond, the thiophene radical intermediate **C** is generated, which was confirmed by PhSSPh[19] trapping (Scheme 2). Now, **C** would react with **A** to lead to the desired

Scheme 2. Trapping of Thiophene Radical



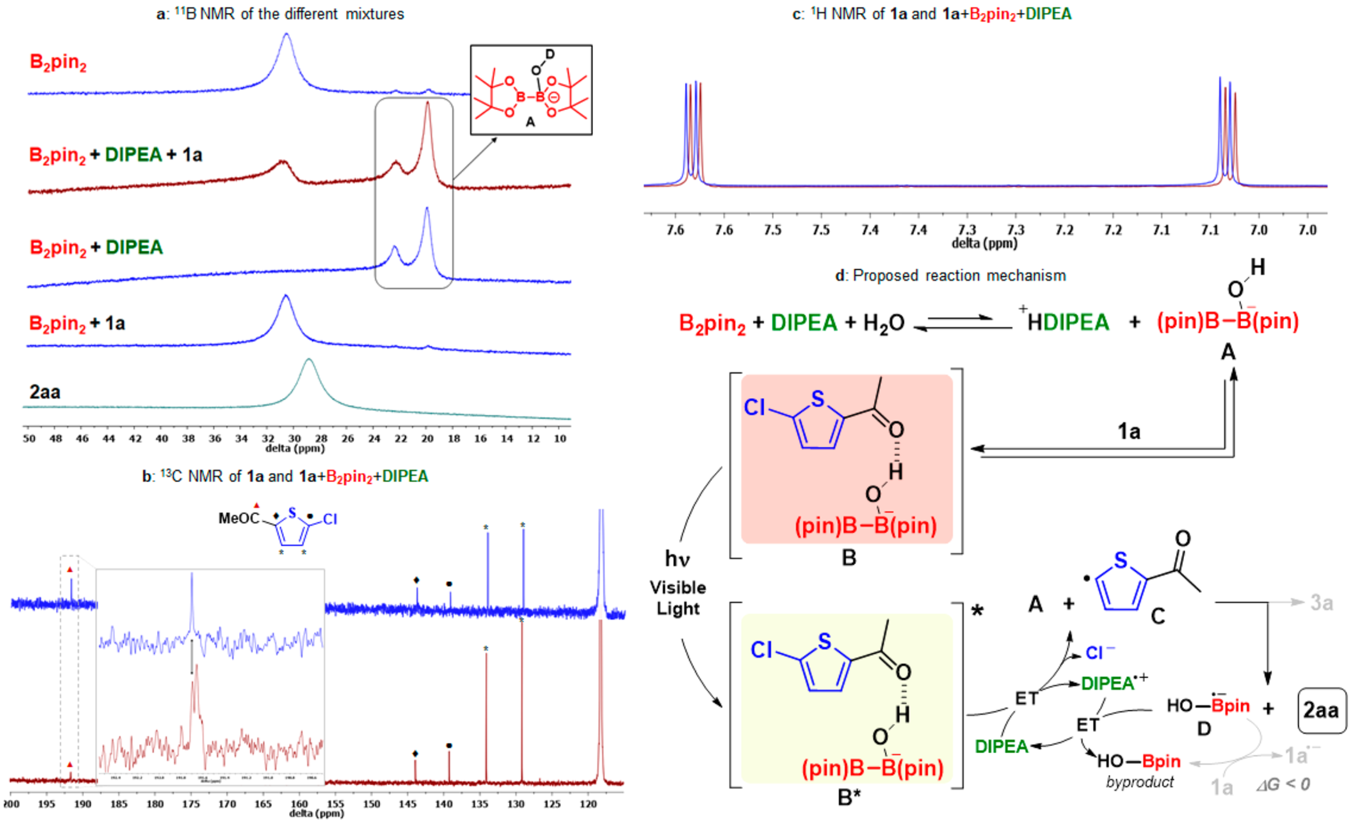


Figure 2. (a) ^{11}B NMR spectra in CD_3CN/D_2O (9/1 v/v), (b) ^{13}C NMR spectra of **1a** (top) and **1a** + B_2pin_2 + DIPEA (bottom) in CD_3CN/D_2O (9/1 v/v), (c) ^1H NMR spectra of **1a** (blue) and **1a** + B_2pin_2 + DIPEA (red) in CD_3CN/D_2O (9/1 v/v), and (d) proposed reaction mechanism.

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2aa and the boryl radical anion **D**.[18b,20] Finally, one single electron transfer (SET) from **D** to the DIPEA radical cation would provide OH-Bpin as the byproduct,[2n] which hydrolyzes to volatile products upon workup.[21] Importantly, the role of DIPEA could be two-fold because it can act as (i) a base and (ii) a photoreductant in the electron transfer process.

To further rationalize the proposed reaction mechanism, computational studies under the framework of the density functional of theory (DFT) were performed. (See the SI for computational details.) Thus different alternatives for complex **B** were first computed. (See Figure S1.) From this preliminary screening, the proposed structure of **B** including a hydrogen bond between **A** and **1a** was found to be the predominant one that was fully in agreement with the experimental data (NMR and UV−vis). Then, the electronic absorption spectrum of **B** was calculated using 6-31+G** as the basis set together with a variety of functionals. (See the SI.) Although a similar qualitative trend was found, the B3LYP functional showed the best theoretical−experimental relationship. As depicted in Figure 3a, the absorption spectrum of **B** in acetonitrile was dominated by the thiophene-type transition at 292 nm that thoroughly matches with the computed value for **1a** (292 nm; experimental value: 289 nm). Interestingly, two additional small absorption bands at longer wavelengths appeared for **B** (Figure 3b) at 543 and 423 nm, with an oscillator strength of *f* = 0.00001 and 0.0005, respectively; this finding differed from the **1a** absorption spectrum where these two bands were not found. Therefore, a good correlation could be established between the results from the UV−vis measurements and the computational data. In addition, the electronic transition at 423 nm might imply the movement of an electron from the B_2pin_2 moiety to the thiophene unit (Figure 3c,d).

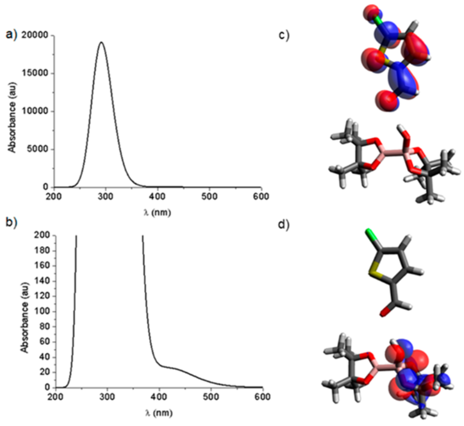
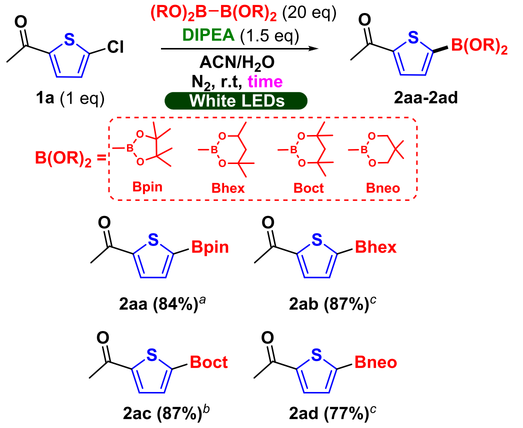


Figure 3. (a) Absorption spectrum and (b) detail of **B** computed using B3LYP/6-31+G** in acetonitrile. Orbitals involved in the transition at 423 nm (c) LUMO and (d) HOMO−1.

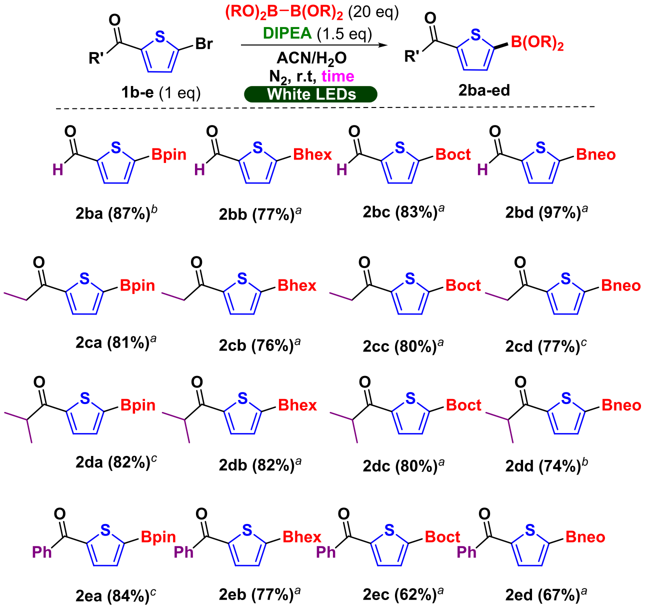
Scheme 3. Substrate Scope for Borylated Thiophenes[a]



[a]**1a** (1 equiv), $(OR)_2B-B(OR)_2$ (20 equiv), and DIPEA (1.5 equiv). Full conversion of **1a** in all cases; GC-FID yields of products. [b]0.5 h of irradiation time. [c]1 h of irradiation time. [d]2 h of irradiation time.

Having established the optimal conditions and understood the method, we next conducted the substrate scope using different diboron derivatives (Scheme 3). After cold-white LED irradiation, full conversion of the starting thiophene material **1a** was effectively observed in all cases, and high yields of products (**2aa−ad**) were obtained. It is noteworthy that the borylation reactions magnificently occurred using other diboron esters as counterparts such as 1,1,3-trimethylethylene glycol (Bhex), 1,1,4,4,-tetramethylethylene glycol (Boct), and neopentyl glycol (Bneo), delivering the corresponding thiophene boronic esters in high yield under very mild conditions. To strongly support this proof of concept and demonstrate the versatility of the protocol, we proceeded to investigate the reaction, combining several commercially available thiophene derivatives and the diboron compounds previously employed (Scheme 4). Gratifyingly, all tested reactions worked perfectly under the optimal conditions, and the desired products (**2ba−ed**) were obtained in high yield and with high selectivities. Therefore, these types of thiophene−boronates can be easily prepared at shorter irradiation times (ranging from 0.5 to 2 h), making this protocol feasible for a late-stage functionalization of boron-based compounds for the synthesis of more complex organic molecules.

Scheme 4. Versatility Screening for Photocatalyst-free Visible-Light Thiophene Borylations[a]



[a]**1** (1 equiv), $(OR)_2B-B(OR)_2$ (20 equiv), and DIPEA (1.5 equiv). Full conversion of **1** in all cases; GC-FID yields of products. [b]0.5 h of irradiation time. [c]1 h of irradiation time. [d]2 h of irradiation time.

In conclusion, fast access to borylated-like thiophenes by means of visible light (cold-white LEDs) as an energy source has been reported. This photocatalyst-free reaction is proposed to proceed via the *in situ* formation of a ground-state complex that, after visible-light absorption, evolves to the formation of the corresponding borylation of the thiophene core. The mechanistic aspects have been demonstrated by spectroscopic measurements and theoretical calculations, and the scope and the versatility of the procedure have been successfully proven. This work constitutes a new, mild strategy for affording boron-containing thiophenes that should be of potential application extending beyond borylation. Finally, this challenged coupling offers a novel route toward synthetic highly valuable heteroarene boronates with a new, likely exploitable mechanistic paradigm.[22]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01076.

> Experimental details, general procedure, optimization of reaction conditions, GC-FID chromatograms, characterization of products, computational information, and spectroscopic data of all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) *Boronic Acids: Preparation and Applications in Organic Synthesis and Medicine*; Hall, D. G., Ed.; Wiley-VCH: Weinheim, Germany, 2005. (b) Miyaura, N.; Suzuki, A. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. *Chem. Rev.* **1995**, *95*, 2457−2483. (c) Miyaura, N. Organoboron Compounds. *Top. Curr. Chem.* **2002**, *219*, 11−59. (d) Yan, J.; Fang, H.; Wang, B. H. Boronolectins and fluorescent boronolectins: an examination of the detailed chemistry issues important for the design. *Med. Res. Rev.* **2005**, *25*, 490−520.

(2) For metal-catalyzed reactions, see: (a) Thongpaen, J.; Manguin, R.; Dorcet, V.; Vives, T.; Duhayon, C.; Mauduit, M.; Baslé, O. Visible light induced Rhodium(i)-catalyzed C−H borylation. *Angew. Chem., Int. Ed.* **2019**, *58*, 15244−15248. (b) Iqbal, S. A.; Cid, J.; Procter, R. J.; Uzelac, M.; Yuan, K.; Ingleson, M. J. Acyl-directed ortho-borylation of anilines and C7 borylation of indoles using just bbr$_3$. *Angew. Chem., Int. Ed.* **2019**, *58*, 15381−15385. (c) Haldar, C.; Emdadul Hoque, Md.; Bisht, R.; Chattopadhyay, B. Concept of Ir-catalyzed CH bond activation/borylation by noncovalent interaction. *Tetrahedron Lett.* **2018**, *59*, 1269−1277. (d) Yan, G.; Huang, D.; Wu, X. Recent advances in C−B bond formation through a free radical pathway. *Adv. Synth. Catal.* **2018**, *360*, 1040−1053. (e) Cuenca, A. B.; Shishido, R.; Ito, H.; Fernández, E. Transition-metal-free B−B and B−interelement reactions with organic molecules. *Chem. Soc. Rev.* **2017**, *46*, 415−430. (f) Xu, L.; Wang, G.; Zhang, S.; Wang, H.; Wang, L.; Liu, L.; Jiao, J.; Li, P. Recent advances in catalytic C−H borylation reactions. *Tetrahedron* **2017**, *73*, 7123−7157. (g) Ros, A.; Fernández, R.; Lassaletta, J. M. Functional group directed C−H borylation. *Chem. Soc. Rev.* **2014**, *43*, 3229−3243. (h) Hartwig, J. F. Borylation and silylation of C−H bonds: a platform for diverse C−H bond functionalizations. *Acc. Chem. Res.* **2012**, *45*, 864−873. (i) Hartwig, J. F. Regioselectivity of the borylation of alkanes and arenes. *Chem. Soc. Rev.* **2011**, *40*, 1992−2002. (j) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. C−H Activation for the construction of C−B bonds. *Chem. Rev.* **2010**, *110*, 890−931. For UV-photoinduced reactions see: (k) Mfuh, A. M.; Doyle, J. D.; Chhetri, B.; Arman, H. D.; Larionov, O. V. Scalable, Metal- and Additive-Free, Photoinduced Borylation of Haloarenes and Quaternary Arylammonium Salts. *J. Am. Chem. Soc.* **2016**, *138*, 2985−2988. (l) Mfuh, A. M.; Nguyen, V. T.; Chhetri, B.; Burch, J. E.; Doyle, J. D.; Nesterov, V. N.; Arman, H. D.; Larionov, O. V. Additive- and Metal-Free, Predictably 1,2- and 1,3-Regioselective, Photoinduced Dual C−H/C−X Borylation of Haloarenes. *J. Am. Chem. Soc.* **2016**, *138*, 8408−8411. (m) Chen, K.; Cheung, M. S.; Lin, Z.; Li, P. Metal-free borylation of electron-rich aryl (pseudo)halides under continuous-flow photolytic conditions. *Org. Chem. Front.* **2016**, *3*, 875−879. (n) Chen, K.; Zhang, S.; He, P.; Li, P. Efficient metal-free photochemical borylation of aryl halides under batch and continuous-flow conditions. *Chem. Sci.* **2016**, *7*, 3676−3680.

(3) (a) Rygus, J. P. G.; Crudden, C. M. Enantiospecific and Iterative Suzuki−Miyaura Cross-Couplings. *J. Am. Chem. Soc.* **2017**, *139*, 18124−18137. (b) Crudden, C. M.; Ziebenhaus, C.; Rygus, J. P. G.; Ghozati, K.; Unsworth, P. J.; Nambo, M.; Voth, S.; Hutchinson, M.; Laberge, V. S.; Maekawa, Y.; Imao, D. Iterative protecting group-free cross-coupling leading to chiral multiply arylated structures. *Nat. Commun.* **2016**, *7*, 11065. (c) Close, A. J.; Kemmitt, P.; Mark Roe, S.; Spencer, J. Regioselective routes to orthogonally-substituted aromatic MIDA boronates. *Org. Biomol. Chem.* **2016**, *14*, 6751−6756. (d) Li, J.; Ballmer, S. G.; Gillis, E. P.; Fujii, S.; Schmidt, M. J.; Palazzolo, A. M. E.; Lehmann, J. W.; Morehouse, G. F.; Burke, M. D. Synthesis of many different types of organic small molecules using one automated process. *Science* **2015**, *347*, 1221−1226. (e) Xu, L.; Zhang, S.; Li, P. Boron-selective reactions as powerful tools for modular synthesis of diverse complex molecules. *Chem. Soc. Rev.* **2015**, *44*, 8848−8858. (f) Duret, G.; Quinlan, R.; Bisseret, P.; Blanchard, N. Boron chemistry in a new light. *Chem. Sci.* **2015**, *6*, 5366−5382. (g) Li, J.; Grillo, A. S.; Burke, M. D. From Synthesis to Function via Iterative Assembly of N-Methyliminodiacetic Acid Boronate Building Blocks. *Acc. Chem. Res.* **2015**, *48*, 2297−2307.

(4) (a) Lennox, A. J. J.; Lloyd-Jones, G. C. Selection of boron reagents for Suzuki−Miyaura coupling. *Chem. Soc. Rev.* **2014**, *43*, 412−443. (b) Molander, G. A.; Canturk, B. Organotrifluoroborates and Monocoordinated Palladium Complexes as Catalysts-A Perfect Combination for Suzuki−Miyaura Coupling. *Angew. Chem., Int. Ed.* **2009**, *48*, 9240−9261. (c) Martin, R.; Buchwald, S. L. Palladium-Catalyzed Suzuki−Miyaura Cross-Coupling Reactions Employing Dialkylbiaryl Phosphine Ligands. *Acc. Chem. Res.* **2008**, *41*, 1461−1473. (d) Darses, S.; Genet, J.-P. Potassium Organotrifluoroborates: New Perspectives in Organic Synthesis. *Chem. Rev.* **2008**, *108*, 288−325.

(5) Ren, Y.; Jäkle, F. Merging thiophene with boron: new building blocks for conjugated materials. *Dalton Trans.* **2016**, *45*, 13996−14007.

(6) (a) Branger, C.; Lequan, M.; Lequan, R. M.; Barzoukas, M.; Fort, A. Boron derivatives containing a bithiophene bridge as new materials for non-linear optics. *J. Mater. Chem.* **1996**, *6*, 555−558. (b) Noda, T.; Shirota, Y. 5,5‘-Bis(dimesitylboryl)-2,2‘-bithiophene and 5,5”-Bis(dimesitylboryl)-2,2‘:5‘,2”-terthiophene as a novel family of electron-transporting amorphous molecular materials. *J. Am. Chem.*

Soc. **1998**, *120*, 9714−9715. (c) Yuan, Z.; Collings, J. C.; Taylor, N. J.; Marder, T. B.; Jardin, C.; Halet, J.-F. Linear and Nonlinear Optical Properties of Three-Coordinate Organoboron Compounds. *J. Solid State Chem.* **2000**, *154*, 5−12.

(7) (a) Noda, T.; Ogawa, H.; Shirota, Y. A blue-emitting organic electroluminescent device using a novel emitting amorphous molecular material, 5,5′-bis(dimesitylboryl)-2,2′-bithiophene. *Adv. Mater.* **1999**, *11*, 283−285. (b) Ji, L.; Edkins, R. M.; Sewell, L. J.; Beeby, A.; Batsanov, A. S.; Fucke, K.; Drafz, M.; Howard, J. A. K.; Moutounet, O.; Ibersiene, F.; Boucekkine, A.; Furet, E.; Liu, Z.; Halet, J.-F.; Katan, C.; Marder, T. B. Experimental and Theoretical Studies of Quadrupolar Oligothiophene-Cored Chromophores Containing Dimesitylboryl Moieties as π-Accepting End-Groups: Syntheses, Structures, Fluorescence, and One- and Two-Photon Absorption. *Chem. - Eur. J.* **2014**, *20*, 13618−13635.

(8) Bailey, P. J.; Cousins, G.; Snow, G. A.; White, A. J. Boron-containing antibacterial agents: effects on growth and morphology of bacteria under various culture conditions. *Antimicrob. Agents Chemother.* **1980**, *17*, 549−553.

(9) (a) Krause, E.; Renwanz, G. New metallic derivates of thiophene. III. Germanium, antimony, tellurium and boron thienyls. *Ber. Dtsch. Chem. Ges. B* **1932**, *65*, 777−784. (b) Johnson, J. R.; Campen, M. G. V.; Grummitt, O. Organoboron Compounds. II. The Reducing Action of Some Organoboronic Acids. *J. Am. Chem. Soc.* **1938**, *60*, 111−115. (c) Kabalka, G. W.; Sastry, U.; Sastry, K. A. R.; Knapp, F. F.; Srivastava, P. C. Synthesis of arylboronic acids via the reaction of borane with arylmagnesium halides. *J. Organomet. Chem.* **1983**, *259*, 269−274.

(10) Ishiyama, T.; Murata, M.; Miyaura, N. Palladium(0)-catalyzed cross-coupling reaction of alkoxydiboron with haloarenes: a direct procedure for arylboronic esters. *J. Org. Chem.* **1995**, *60*, 7508−7510.

(11) Li, W.; Nelson, D. P.; Jensen, M. S.; Hoerrner, R. S.; Cai, D.; Larsen, R. D.; Reider, P. J. An Improved Protocol for the Preparation of 3-Pyridyl- and Some Arylboronic Acids. *J. Org. Chem.* **2002**, *67*, 5394−5397.

(12) Kawamorita, S.; Ohmiya, H.; Sawamura, M. Ester-directed regioselective borylation of heteroarenes catalyzed by a silica-supported Iridium complex. *J. Org. Chem.* **2010**, *75*, 3855−3858.

(13) Kallepalli, V. A.; Gore, K. A.; Shi, F.; Sánchez, L.; Chotana, G.; Miller, S. L.; Maleczka, R. E.; Smith, M. R. Harnessing C−H borylation/deborylation for selective deuteration, synthesis of boronate esters, and late stage functionalization. *J. Org. Chem.* **2015**, *80*, 8341−8353.

(14) Bel Abed, H.; Blum, S. A. Transition-Metal-Free Synthesis of Borylated Thiophenes via Formal Thioboration. *Org. Lett.* **2018**, *20*, 6673−6677.

(15) Selected examples: (a) Maiti, B.; Abramov, A.; Pérez-Ruiz, R.; Díaz Díaz, D. The prospect of photochemical reactions in confined gel media. *Acc. Chem. Res.* **2019**, *52*, 1865−1876. (b) Zhou, Q.-Q.; Zou, Y.-Q.; Lu, L.-Q.; Xiao, W.-J. Visible-Light-Induced organic photochemical reactions through energy-transfer pathways. *Angew. Chem., Int. Ed.* **2019**, *58*, 1586−1604. (c) *Visible Light Photocatalysis in Organic Chemistry*; Stephenson, C. R. J., Yoon, T. P., MacMillan, D. W. C., Eds.; Wiley-VCH: Weinheim, Germany, 2018. (d) Savateev, A.; Antonietti, M. Heterogeneous organocatalysis for photoredox chemistry. *ACS Catal.* **2018**, *8*, 9790−9808. (e) Marzo, L.; Pagire, S. K.; Reiser, O.; Koenig, B. Visible-Light photocatalysis: does it make a difference in organic synthesis? *Angew. Chem., Int. Ed.* **2018**, *57*, 10034−10072. (f) Romero, N. A.; Nicewicz, D. A. Organic photoredox catalysis. *Chem. Rev.* **2016**, *116*, 10075−10166. (g) Prier, C.; Rankic, D.; MacMillan, D. W. C. Visible light photoredox catalysis with transition metal complexes: applications in organic synthesis. *Chem. Rev.* **2013**, *113*, 5322−5363.

(16) Neumeier, M.; Sampedro, D.; Májek, M.; de la Peña O'Shea, V. A.; Jacobi von Wangelin, A.; Pérez-Ruiz, R. Dichromatic photocatalytic substitutions of aryl halides with a small organic dye. *Chem. - Eur. J.* **2018**, *24*, 105−108.

(17) Jiang, M.; Yang, H.; Fu, H. Visible-Light photoredox borylation of aryl halides and subsequent aerobic oxidative hydroxylation. *Org. Lett.* **2016**, *18*, 5248−5251.

(18) (a) Candish, L.; Teders, M.; Glorius, F. Transition-Metal-Free, visible-light-enabled decarboxylative borylation of aryl n-hydroxyphthalimide esters. *J. Am. Chem. Soc.* **2017**, *139*, 7440−7443. (b) Wang, J.; Qin, T.; Chen, T.; Wimmer, L.; Edwards, J. T.; Cornella, J.; Vokits, B.; Shaw, S. A.; Baran, P. S. Nickel-Catalyzed cross-coupling of redox-active esters with boronic acids. *Angew. Chem.* **2016**, *128*, 9828−9831. (c) Thorpe, S. B.; Calderone, J. A.; Santos, W. L. Unexpected Copper(II) catalysis: catalytic amine base promoted β-borylation of α,β-unsaturated carbonyl compounds in water. *Org. Lett.* **2012**, *14*, 1918−1921. (d) Power, P. P. Persistent and stable radicals of the heavier main group elements and related species. *Chem. Rev.* **2003**, *103*, 789−810.

(19) Majek, M.; von Wangelin, A. J. Organocatalytic visible light mediated synthesis of aryl sulfides. *Chem. Commun.* **2013**, *49*, 5507−5509. Mixtures of **2aa**, dehalogenated product **3a**, and the aryl sulfide derivative **4a** were hence observed in the crude reaction, where **4a** was the major product (selectivity **2aa**/**3a**/**4a** 10/9/81), unambiguously proving the involvement of the thiophene radical.

(20) Hu, D.; Wang, L.; Li, P. Decarboxylative borylation of aliphatic esters under visible-light photoredox conditions. *Org. Lett.* **2017**, *19*, 2770−2773.

(21) According to theoretical calculations (see the details in the SI), the ΔG_{ET} value associated with the electron transfer from **D** to **1a** has been found to be −0.78 eV, which indicates that a radical chain might occur in this process.

(22) Friese, F. W.; Studer, A. New avenues for C-B bond formation via radical intermediates. *Chem. Sci.* **2019**, *10*, 8503−8518.