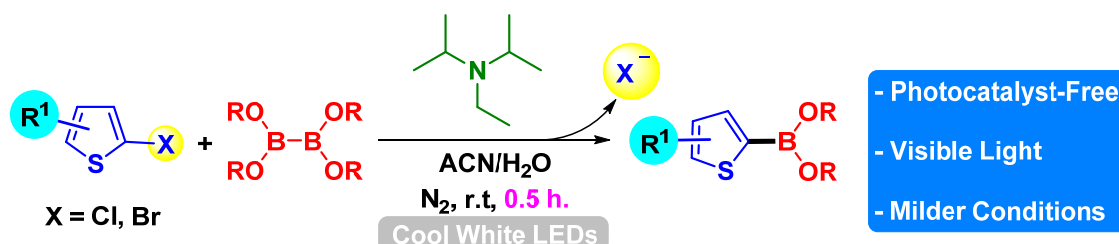


# BORYLATION OF THIOPHENES DRIVEN BY PHOTOCATALYST-FREE VISIBLE LIGHT

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Boron-containing thiophenes are important entities due to its applicability in the synthesis of pharmaceutical drugs such as Bruton's tyrosine kinase (BTK) inhibitor or fungicide agrochemical (Penthiopyrad) as well as the development of organic materials exhibiting photophysical and redox properties.[1] Reported methodologies for the synthesis of thiophenes containing boronates include the Miyaura borylation,[2] sequential lithiation/borylation,[3] the iridium-catalyzed borylation[4] or more recently the transition-metal-free formal thioboration.[5] However, these protocols somehow require conditions mostly complex (glovebox performance, high temperatures, synthesis of starting materials) and, therefore, the development of new strategies with milder conditions is warranted. Here, we show a promising and simple procedure employing visible light as energy source at room temperature and ambient pressure. All substrates are commercially available and, to our delight, no photocatalyst is required. Optimization, scope, derivatization and mechanism of the photoreaction will be discussed.



[1] (a) K. Meng, Z. Jiancun, W. Yonggang, T. Yong, L. Quing-Cong, W. Jun, W. Zhonghui, *WO* 2017/133630, **2017**; (b) P. Devendar, G. F. Yang, *Top. Curr. Chem.* **2017**, 375, 375-382; (c) M. Lepeltier, O. Lukyanova, A. Jacobson, S. Jeeva, D. F. Perepichka, *Chem. Commun.* **2010**, 46, 7007-7009; (d) Y. Ren, F. Jäkle, *Dalt. Trans.* **2016**, 45, 13996-14007.

[2] T. Ishiyama, M. Murata, N. Miyura, *J. Org. Chem.* **1995**, 60, 7508-7510.

[3] W. Li, D. P. Nelson, M. S. Jensen, R. S. Hoerrner, D. Cai, R. D. Larsen, P. J. Reider, *J. Org. Chem.* **2002**, 67, 5394-5397.

[4] (a) A. Ros, R. Fernández, J. M. Lassaletta, *Chem. Soc. Rev.* **2014**, 43, 3229-3243; (b) V.A. Kallepalli, K. A. Gore, F. Shi, L. Sánchez, G. Chotana, S. L. Miller, R. E. Maleczka, M. R. Smith, *J. Org. Chem.* **2015**, 80, 8341-8353.

[5] H. B. Abed, S. A. Blum, *Org. Lett.* **2018**, 20, 6673-6677.