

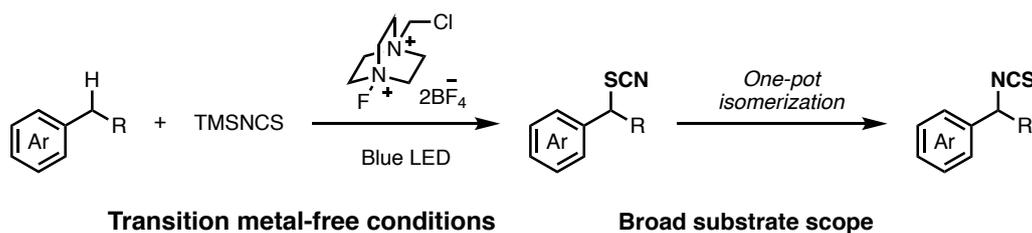
Photo-induced C–H bond thiocyanation and one-pot isomerization to isothiocyanates

○Maeda Bumpei,¹ Yusuke Aihara,² Ayato Sato,² Toshinori Kinoshita,² Kei Murakami¹
 (¹Graduate School of Science and Engineering, Kwansei Gakuin University, ²Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University)

Keywords: radical, thiocyanate, isothiocyanate, C–H bond activation, photo-irradiation

Thiocyanates and isothiocyanates are widely present in natural products and pharmaceuticals. They act not only as bioactive compounds but are also utilized as an organic synthetic toolbox. They are easily transformed into various functional groups such as heterocycles, sulfur-based, or nitrogen-based functional groups. Despite the various synthetic methods of thiocyanates have been developed such as substitution reactions or cyanations of thiols or disulfides, thiocyanations of unactivated aliphatic C–H bonds have been still challenging. Recently, two C–H thiocyanation reactions were reported: one is a copper-catalyzed reaction¹ and the other is AIBN-initiated reaction². Because the isomerization of thiocyanates into isothiocyanates can occur due to Lewis acid or heat, the substrate scopes of the reported methods were relatively limited. Thus, a novel C–H thiocyanation without transition metal in mild reaction conditions is required. The recent development of photo-induced reactions motivated us to develop a new C–H thiocyanation reaction with visible light irradiation³.

Herein, we describe a C–H thiocyanation using Selectfluor as a HAT reagent under visible light irradiation. We envisioned that the transition metal-free thiocyanation under mild conditions would be feasible with light irradiation. This reaction was applied to various substrates without isomerization. Additionally, we developed the one-pot synthesis of isothiocyanates following the corresponding C–H thiocyanation.



- 1) Cu-catalyzed reaction: Jiang, C.; Chen, P.; Liu, G. *CCS Chem.* **2020**, *2*, 1884–1893.
- 2) AIBN-initiated reaction with excess amount of substrate: Wu, D.; Duan, Y.; Liang, K.; Yin, H.; Chen, F.-C. *Chem. Commun.* **2021**, *57*, 9938–9941.
- 3) Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. *J. Org. Chem.* **2016**, *81*, 6898–6926.