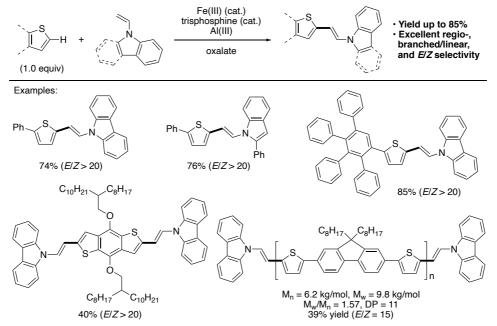
Iron-Catalyzed Oxidative C–H Alkenylation of Thiophene Compounds

(¹ Molecular Technology Innovation, Department of Chemistry, The University of Tokyo) O Takahiro Doba, ¹ Rui Shang, ¹ Eiichi Nakamura¹

Keywords: Iron Catalysis; Oxidative C-H Alkenylation; Thiophene, Enamine; Donor Material

Transition-metal-catalyzed oxidative C–H alkenylation (Fujiwara-Moritani type reaction) has attracted much attention as one of the most straightforward methods to synthesize alkenyl compounds. However, the scope of alkenes has long been limited to electron-deficient alkenes such as acrylates and styrenes,¹ and there are only a limited number of reports with electron-rich alkenes.²

Herein, we report that electron-rich vinylcarbazoles and vinylindoles react with thiophene compounds using Fe(III) as a catalyst, trisphosphine as a ligand, Al(III) as a base, and oxalate³ as a mild oxidant. This reaction gives direct access to donor materials containing unique enaminyl thiophene structures⁴ with controlled regio-, branched/linear, and E/Z selectivity. Moreover, this method is applicable to the synthesis of a vinylcarbazole-endcapped thiophene polymer. Deuterium exchange between two substrates indicated that enamines react through an electrophilic metalation mechanism rather than a carbometallation mechanism.



1) P. Wang et al. Nature **2017**, 551, 489. 2) W. Lin et al. ACS Catal. **2018**, 8, 8070. 3) T. Doba et al. Nat. Catal. **2021**, 4, 631. 4) M. Tanaka et al. Jpn. Kokai Tokkyo Koho JP 2010126571 A June 10, 2010.