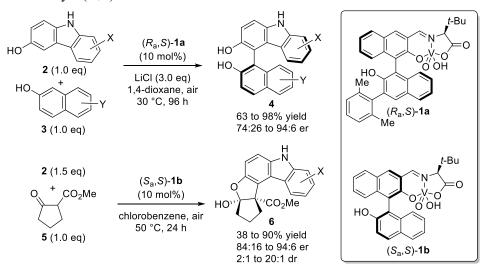
Chemo- and Enantioselective Hetero-coupling of 3-Hydroxycarbazoles Catalyzed by a Chiral Vanadium(V) Complexes

(¹*The Institute of Scientific and Industrial Research (ISIR)*, ²*Artificial Intelligence Research Center of ISIR, Osaka University*) \bigcirc Ganesh Tatya Kamble,¹ Makoto Sako,¹ Keigo Higashida,¹ Ankit Kumar,¹ Shinobu Takizawa,^{1,2} Hiroaki Sasai^{1,2}

Keywords: Vanadium; Hetero-coupling; Enantioselective Catalysis; Oxidative Coupling; Carbon-carbon Bond-formation

Optically active biarenol derivatives have played a significant role in asymmetric synthesis because of their high potential as chiral reagents and building blocks. Our group has previously reported a chiral vanadium(V) complex-mediated enantio- and regioselective oxidative homo-coupling reactions of monocyclic and polycyclic phenols including heterocycles to produce the axially chiral biarenols.¹

Herein, we report the first chiral vanadium(V) complex catalyzed oxidative shetero-couplings using 3-hydroxycarbazoles 2. Chiral vanadium catalyst $(R_{a,s}S)$ -1 $a^{2,3}$ was found to promote the coupling of 2 (1.0 eq) with 2-naphthols 3 (1.0 eq) under mild reaction conditions, affording the hetero-coupling products 4 without any formation of the corresponding homo-coupling products. In this presentation, highly chemo- and stereoselective cross-dehydrogenative couplings⁴ of 2 and β -ketoester 5 utilizing chiral vanadium catalyst $(S_{a,s}S)$ -1b will also be discussed.



Review: M. Sako, S. Takizawa, H. Sasai, *Tetrahedron* 2020, *76*, 131645. 2) M. Sako, Y. Takeuchi,
T. Tsujihara, J. Kodera, T. Kawano, S. Takizawa, H. Sasai, *J. Am. Chem. Soc.* 2016, *138*, 11481. 3) L.
Schober, M. Sako, S. Takizawa, H. Gröger, H. Sasai, *Chem. Commun.* 2020, *56*, 10151. 4) S. Narute,
D. Pappo, *Org. Lett.* 2017, *19*, 2917.