様式３

# 論　文　内　容　の　要　旨

| 氏　名　（　Duona Fan　） | |
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| 論文題名 | Enantioselective Synthesis of NOBINs *via* Photo-induced Vanadium(V) Complex-Catalyzed Cross-coupling<br>（光誘導型バナジウム触媒クロスカップリングによるNOBINのエナンチオ選択的合成） |

論文内容の要旨

Biaryls are one of the most important chemical building blocks that are widely found in natural products, pharmaceuticals, organocatalysts and various materials. Among them, 2-amino-2'-hydroxy-1,1'-binaphthyls (NOBINs) are crucial axially chiral biaryls that serve as key precursors for chiral ligands in asymmetric catalysis. A synthesis of NOBIN and its derivatives by metal-mediated oxidative cross-couplings of 2-naphthols and 2-naphthylamines is considered to be the straightforward protocols for preparing these unsymmetric biaryl motifs. However, their approaches are limited due to the difficult controlling of cross-coupling selectivity. In addition, atom economy and sustainability issues have always remained a challenging part.

In recent, the new activation mode of substrates, such as photo-activation and electro-activation have been increasing immerged. These new activation modes combining with the traditional asymmetric catalysis have made new strategies with improved the efficiency of cross-coupling reactions and achievement of good selectivity. Considering the importance of discovering new catalytic strategies for the synthesis of NOBINs, this work herein brought up with a photo-induced asymmetric synthesis of NOBIN derivatives via vanadium(V) complex catalysis. A detailed study on cross-coupling between 2-naphthols or 3-phenanthrol and 2-naphthylamines using a mononuclear vanadium catalyst through LED light activation is discussed in **Chapter 2**.

In addition, I have also found the electrosynthesis of BINAMs (1,1'-binaphthalene-2,2'-diamines) and photoactivated C-N bonding reaction between arylamines and styrene during the optimizing processes for the synthesis of NOBINs. Therefore, these two developments, homo-coupling of naphthylamines by electro-activation and photoactivated C-N bonding formation are discussed in **Chapters 3 and 4**.

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# 論文審査の結果の要旨及び担当者

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## 論文審査の結果の要旨

軸性キラリティーを有するビナフチル骨格に、様々な官能基を任意の位置に導入したキラル有機化合物群は、不斉触媒の母核として有用であり、様々な機能性材料への応用が期待されている。学位申請者の范　多 納 氏は、電解酸化、または光照射条件下における光学活性卑金属触媒との共働活性化を検討し、2-amino-2’-hydroxy-1,1’-binaphthyls（NOBINs）骨格のエナンチオ選択的な新規構築法の開発に成功した。また、共働活性化条件を探索する中で、電解酸化による無触媒下での 1, 1’-binaphthalene-2, 2’-diamines（BINAMs）骨格の効率的構築法、及び光照射による無触媒下での炭素－窒素結合形成反法を見出している。共働活性化機構を明らかにするために DFT 計算、NMR・UV 等の測定結果を詳細に解析し、推定反応機構を示している。

よって、本論文は博士（理学）の学位論文として十分価値あるものと認める。