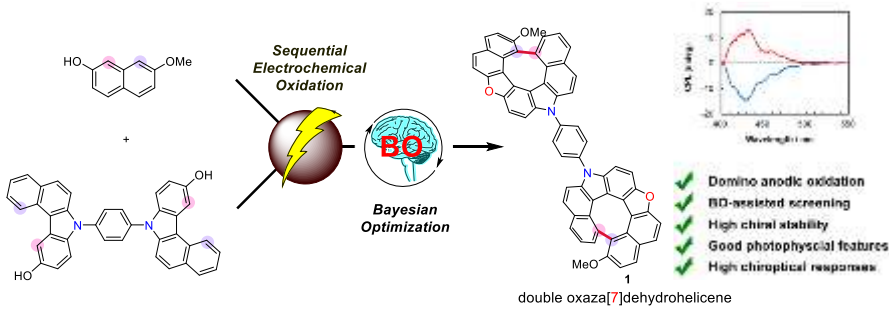
Form 3

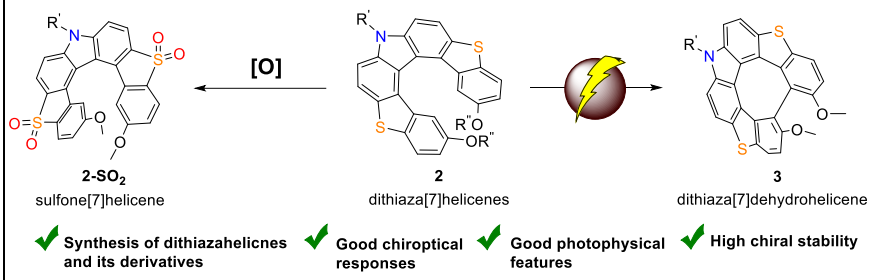
Abstract of Thesis

Name (MEGHNA SASI)	
Title	Synthesis, Structure, and (Chir)optical Features of Hetero[7]helicenes and Hetero[7]dehydrohelicenes（ヘテロ[7]ヘリセンおよびヘテロ[7]デヒドロヘリセンの合成とその構造およびキロプティカル特性に関する研究）

Heterohelicenes, featuring helical structures formed by *ortho*-fused aromatic rings, have recently attracted significant attention for their potential applications in asymmetric catalysis, polymers, molecular machines, molecular recognition, organic electronics, and chiroptical devices.[1] However, the impact of various structural modifications on their overall optical behaviors remains an ambiguous area that requires further investigation. This PhD thesis, titled "Synthesis, structure, and (chir)optical features of hetero[7]helicenes and hetero[7]dehydrohelicenes," focuses on double oxaza[7]dehydrohelicene **1**, dithiaza[7]helicenes **2**, and dithiaza[7]dehydrohelicenes **3**, aiming to develop efficient synthetic pathways using advanced optimization techniques to study the effects of structural modifications on the photophysical and chiroptical properties of these compounds.

In **Chapter 2**, I developed an efficient electrochemical synthesis of a new double hetero dehydrohelicene molecule, notable for its high epimerization barrier (33.8 kcal mol^{-1}) and strong chiroptical response with $|g_{lum}| = 1.5 \times 10^{-3}$ at 430 nm, among the highest for heterocyclic nanographenes with dehydrohelicene core scaffolds, using Bayesian Optimization with LCB and EI acquisition functions to achieve the highest global yield.[2]





In **Chapter 3**, I discuss the synthesis of various new dithiaza[7]helicenes **2** and dithiaza[7]dehydrohelicenes **3**, assess the oxidation of dithiaza[7]helicene to the corresponding sulfone **2-SO2**, and explore the enantioselective synthesis of dehydrohelicene **3**. The study revealed significant CPL values (up to 4×10^{-3}) and provided insights into how structural modifications influence the photophysical, chiroptical features, and chiral stability of the synthesized compounds. To further unravel the structural properties, I also conducted in-depth DFT calculations, including NICS and AICD plots to understand aromaticity, and analyzed the photophysical properties using TD-DFT calculations. This work contributes to the advancement of synthetic methodologies and the understanding of structure-property relationships in heterohelicenes, paving the way for their application in various advanced materials and technologies.

References:

1) Borissov, A.; Maurya, Y. K.; Moshniaha, L.; Wong, W.-S.; Zyła-Karwowska, M.; Stepien, M. Recent advances in heterocyclic nanographenes and other polycyclic heteroaromatic compounds. *Chemical Reviews* **2021**, *122* (1), 565-788.

(2) Salem, M. S. H.; Sharma, R.; Khalid, Md. I.; Sasi, M.; Amasaki, R.; Imai, Y.; Arisawa, M.; Takizawa, S. Data-driven electrochemical one-pot synthesis of double hetero[7]dehydrohelicene. *Electrochemistry* **2023**, *91*(11), 112015.

様式 7

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

多環芳香族複素環化合物であるヘテロヘリセン並びにヘリセン末端の芳香環同士がσ結合で連結したデヒドロヘリセン及びその誘導体は、ヘリシティーを有し新しい機能性光学材料としての応用が期待されている。学位申請者の Meghna Sasi 氏は、七環式芳香族複素環化合物の直截的構築法を検討し、新規な[7]デヒドロヘリセン二量体並びに含窒素・硫黄[7]ヘリセンの電解酸化合成に成功した。機械学習による最適合成反応条件探索と連続電解酸化反応を積極的に導入することで、効率的な合成反応プロセスを確立している。得られた新規化合物の物性評価や、円偏光発光等のキロプティカル特性についても詳細に解析し、解析データと DFT 計算からさらに高い円偏光発光特性を示す高機能な関連化合物構造をデザインしている。

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。