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Background

Dye sensitizer solar cells (DSSCs) are cells that harvest solar energy and convert it into electrical energy using chemical complexes called sensitizers. Metal-free organic sensitizers have been widely used in DSSCs because they possess high molar extinction coefficients, easy synthetic processability as well as tunable photo and electrochemical properties apart from the desired flexibility. The molecular design of the sensitizers is among the several indispensable aspects for achieving superior power conversion efficiency.¹

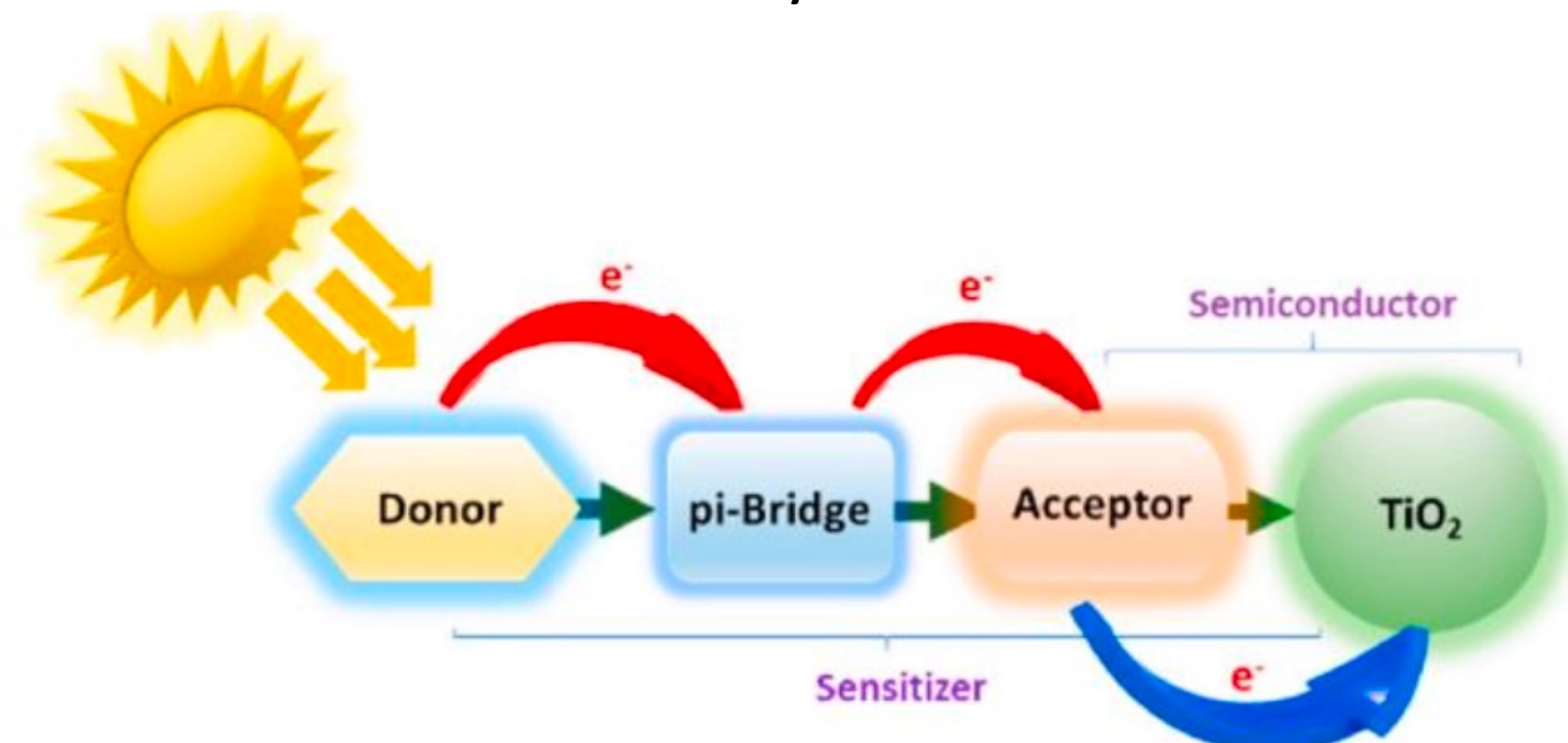


Figure 1. Schematic diagram for intramolecular charge transfer (ICT) process in sensitizers for DSSC

Upon light absorption by the sensitizer, electrons in the molecule are promoted to the excited state. Electron-rich attachment to the sensitizers helps in pushing the electrons towards the other end of the molecule containing electron-accepting groups. This process leads to an electron injection into the semiconductor's conduction band via the anchoring group attached to the acceptor.³

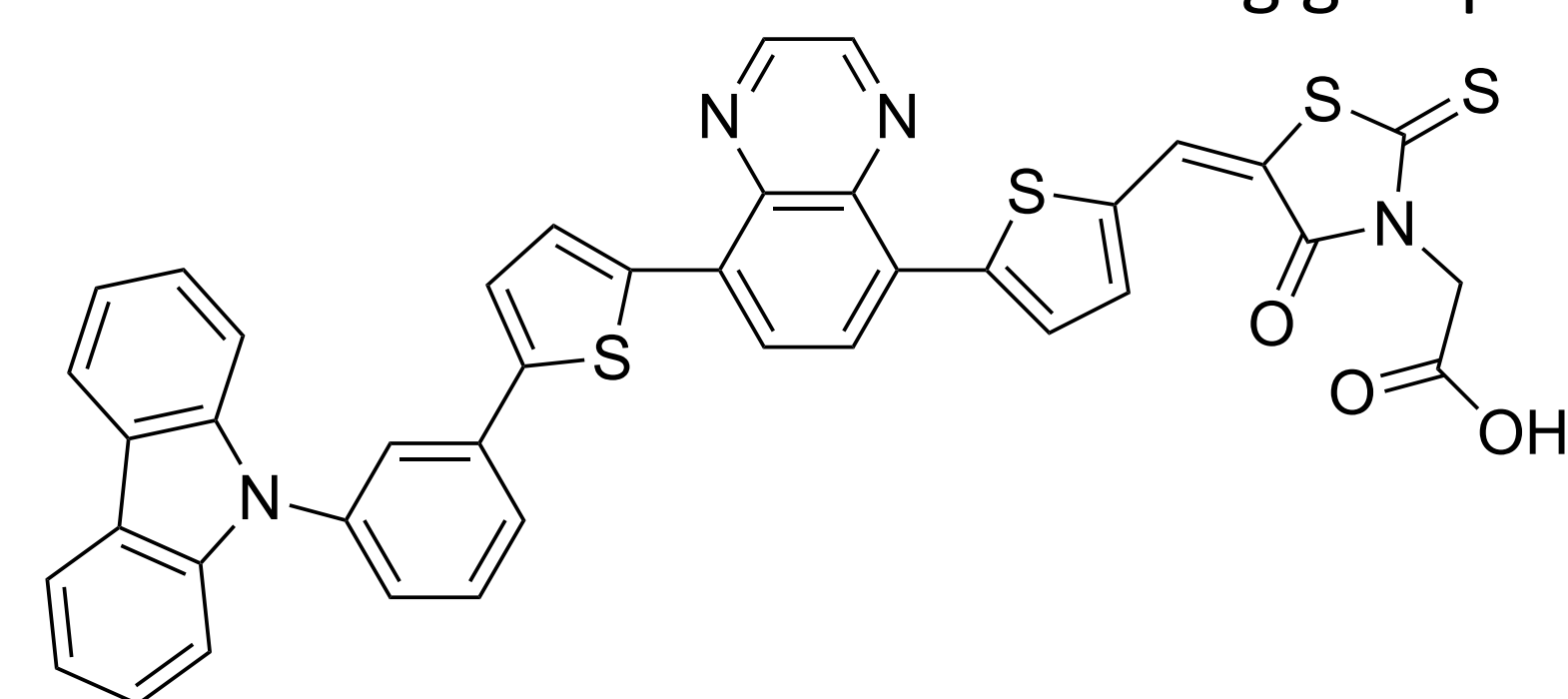
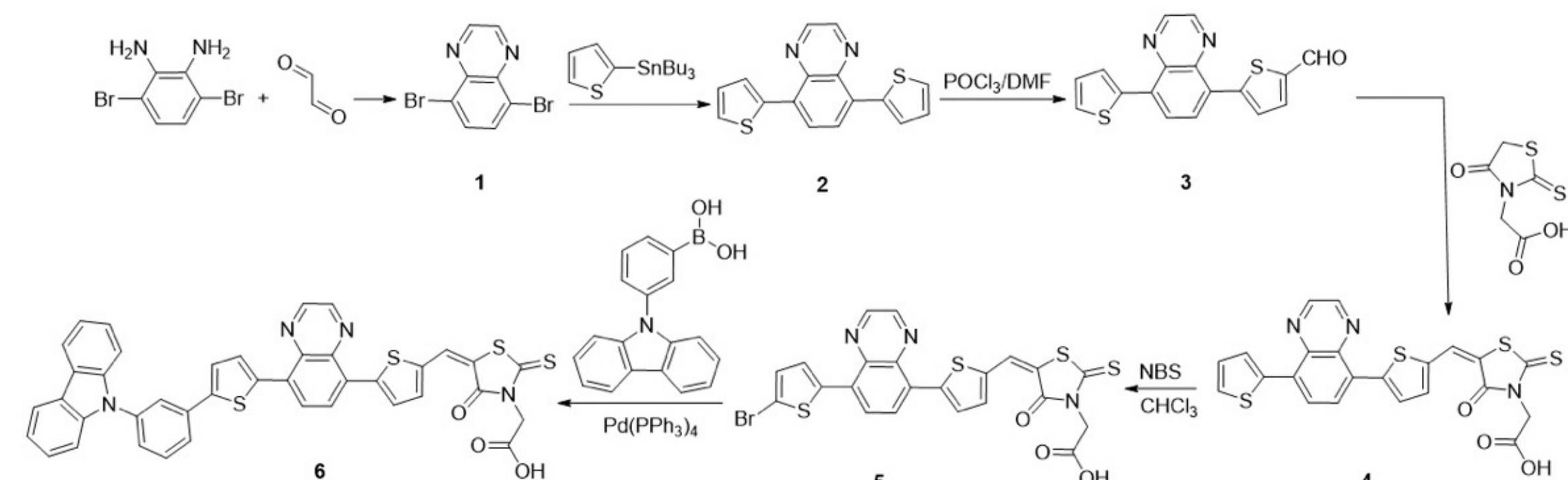


Figure 1. Target Sensitizer for DSSCs

Motivation

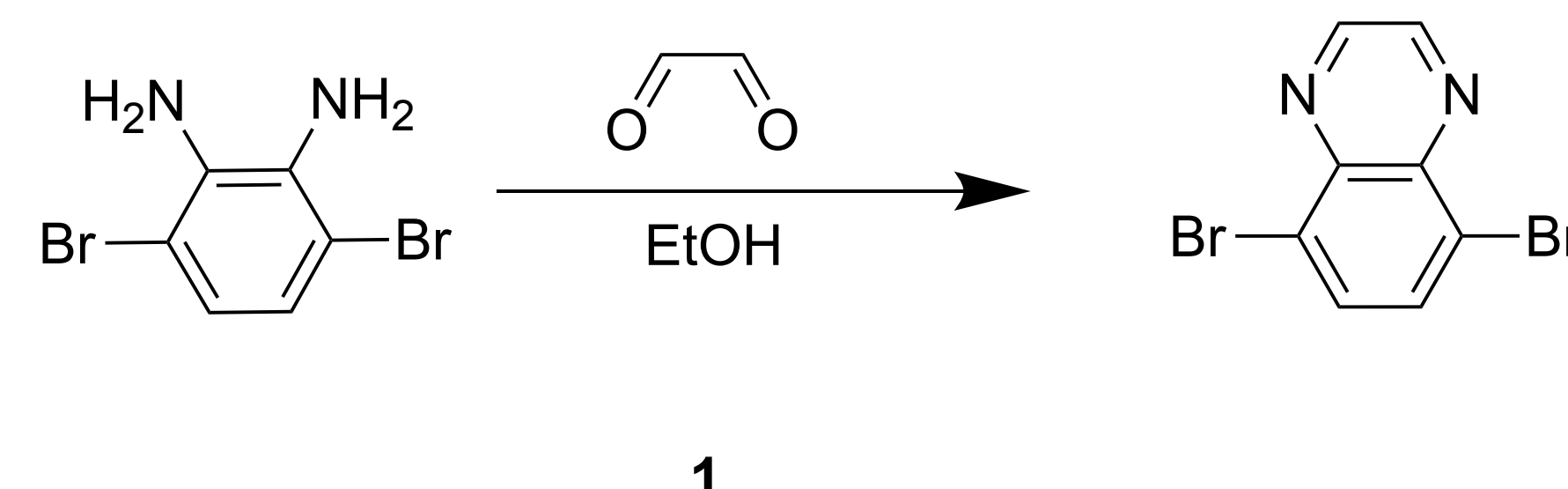


Scheme 1. Reaction Mechanism for DSSCs

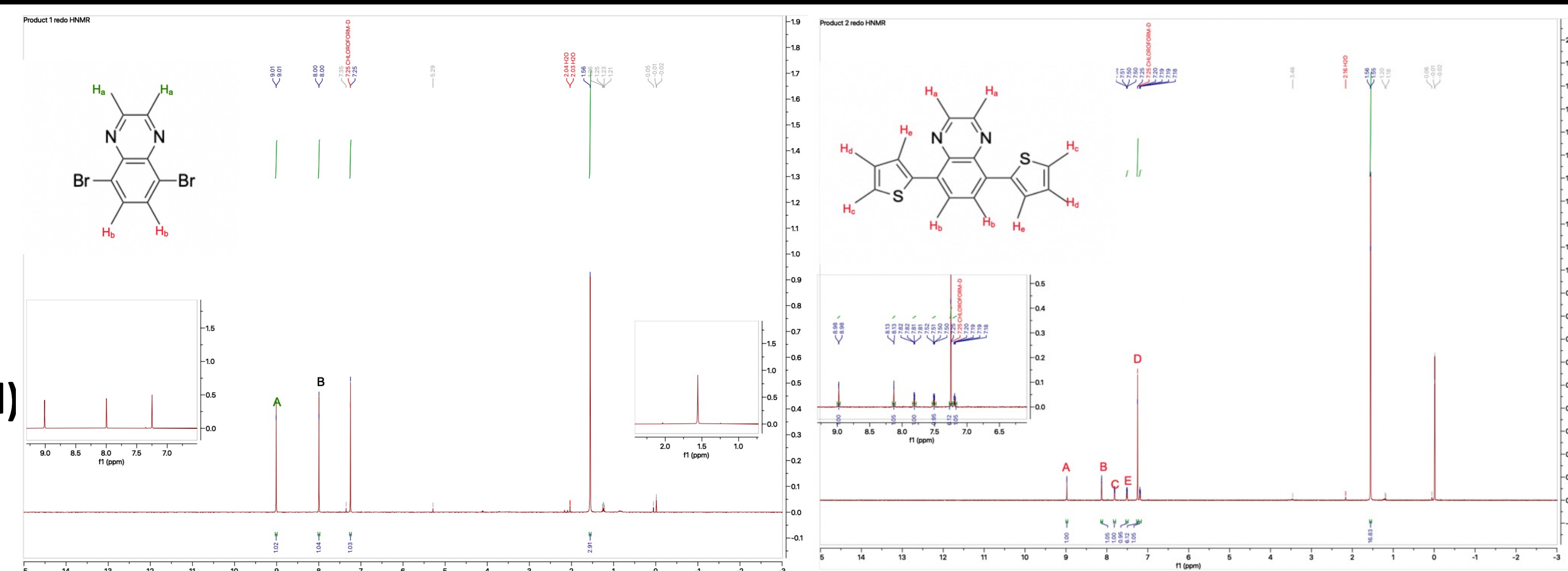
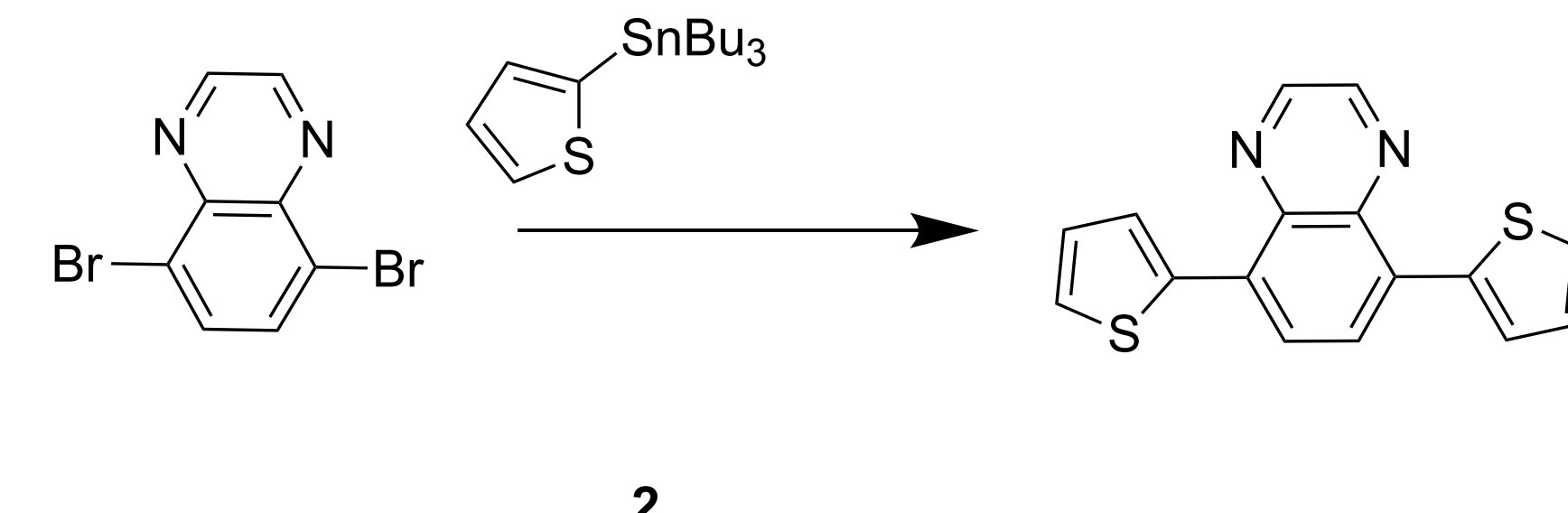
Our project focuses on the synthesis of the target sensitizer, as shown in Figure 2. The synthetic plan for the target sensitizer is depicted in Scheme 1. The target sensitizer has a D- π -AA- π -A architecture, using arylcarbazole as a donor, thiophene moieties as π -spacers, diphenylquinoxaline as an auxiliary acceptor, and rhodamine-3-acetic acid as an electron acceptor.

Step 1: Synthesis and Characterization

Synthesis of 5,8-Dibromoquinoxaline



Synthesis of 2,3-Di(2-furyl)-5,8-bis(2-thienyl)quinoxaline



5,8-Dibromoquinoxaline
 δ - 9.01 (s, 2H), 8.00 (s, 2H)

2,3-Di(2-furyl)-5,8-bis(2-thienyl) quinoxaline
 δ - 8.10 (s, 2H, ArH), 8.13 (d, 2H, $J = 8.0$ Hz), 7.82 (d, 2H, $J = 7.6$ Hz), 7.51 (d, 2H, $J = 7.6$ Hz), 7.35 (q, 2H), 7.25 (d, 2H, $J = 7.6$ Hz), 6.63 (q, 2H)

Step 2: Frontier Molecular Orbitals

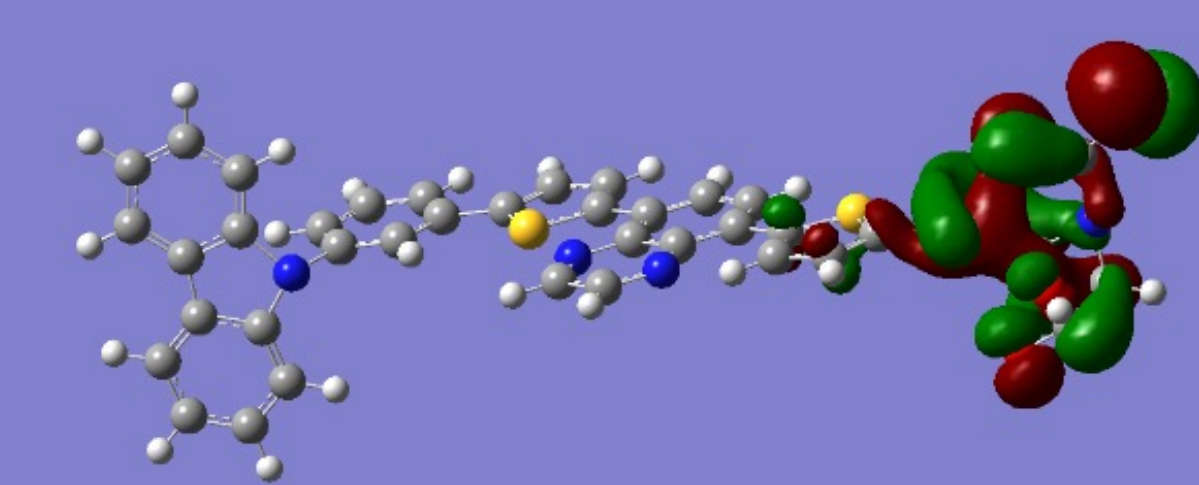


Figure 4. HOMO Orbital

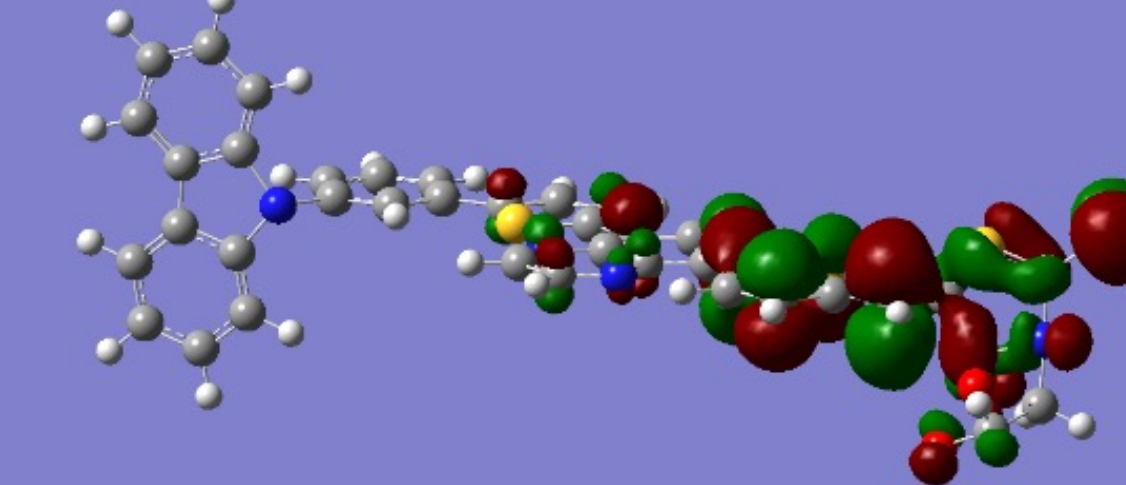


Figure 5. LUMO Orbital

1. The HOMO (-4.93 eV) and LUMO (-4.05 eV) energies fall near typical D- π -A dye ranges and meet DSSC energy level requirements.
2. The HOMO-LUMO gap of 0.88 eV indicates efficient charge transfer, with energies suitable for dye regeneration and electron injection

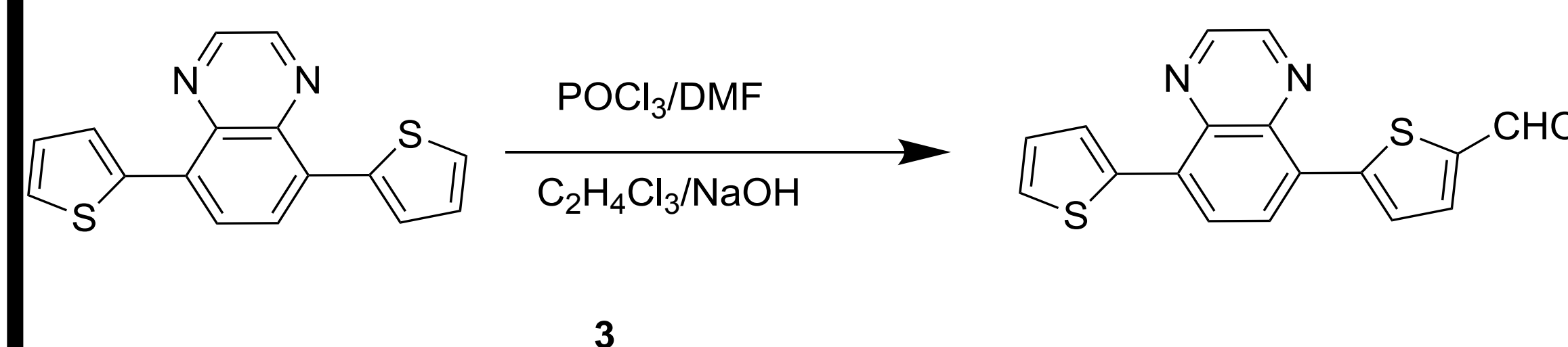
Conclusion & Future Works

Compounds **1** and **2** were successfully synthesized and confirmed by proton nuclear magnetic resonance (¹H NMR) spectroscopy. Attempts to synthesize compound **3** were unsuccessful, with only partial evidence observed via infrared spectroscopy, leading to a plan to increase reaction scale for improved yield and detection. Density Functional Theory calculations showed the target sensitizer (compound **6**) has a small HOMO-LUMO gap (0.88 eV), indicating efficient charge transfer potential. However, orbital localization on the acceptor suggests loss of coplanarity, which may limit electron transfer efficiency.

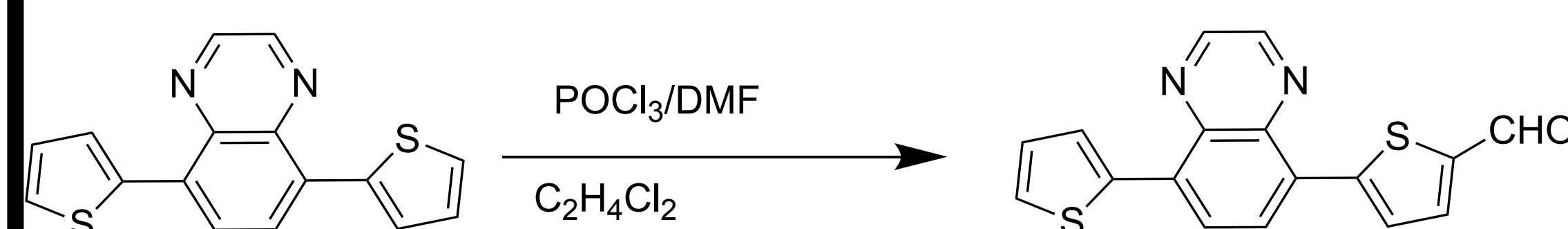
Future work

1. Structural modifications to restore coplanarity between donor and acceptor are also necessary to improve conjugation and charge transfer efficiency.²
2. Improved control methods, such as sealed systems or reflux, are recommended to prevent solvent loss and enhance yields

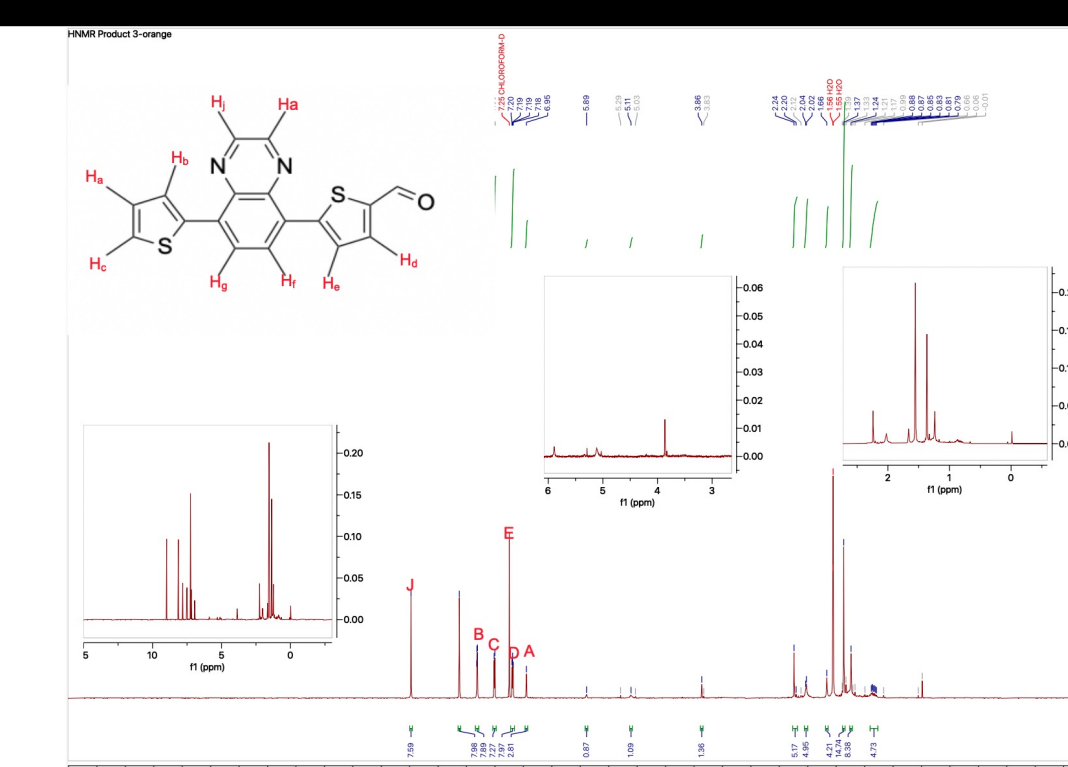
Key Challenges/Limitations



Trial 1: Synthesis of product 3



Trial 2: Synthesis of product 3



References

1. O'Regan, B. & Grätzel, M. A low-cost, high efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *1991 Nature* 353, 737–740.
2. Pandey, L.; Risko, C.; Norton, J. E.; Brédas, J.-L. Donor-Acceptor Copolymers of Relevance for Organic Photovoltaics: A Theoretical Investigation of the Impact of Chemical Structure Modifications on the Electronic and Optical Properties. *Macromolecules* **2012**, 45 (16), 6405–6414. <https://doi.org/10.1021/ma301164e>.
3. Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-Sensitized Solar Cells. *Chem. Rev.* **2010**, 110 (11), 6595–6663. <https://doi.org/10.1021/cr900356p>.