

Sustainable Synthesis of Novel Small Molecules with D- π -(A or D)- π -D Architectures for Organic Photovoltaics



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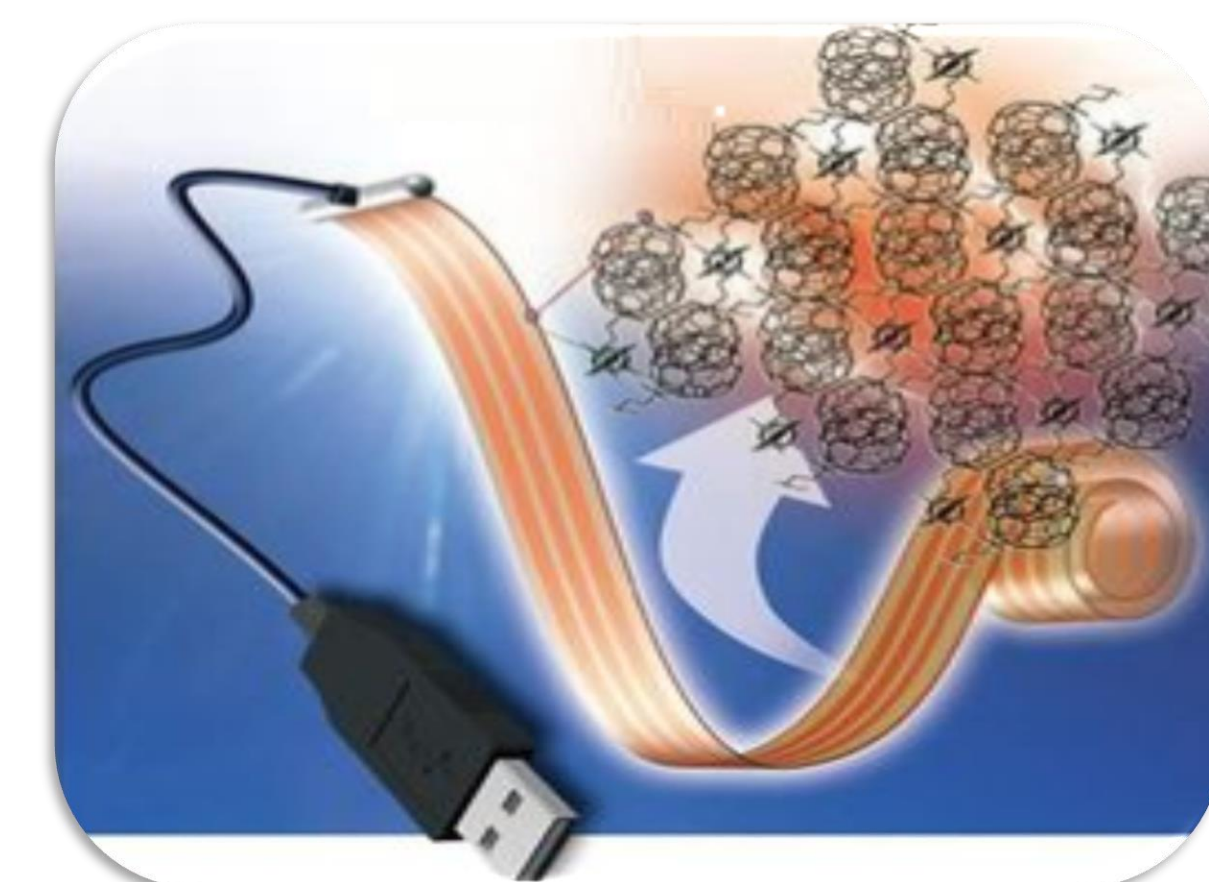
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Introduction

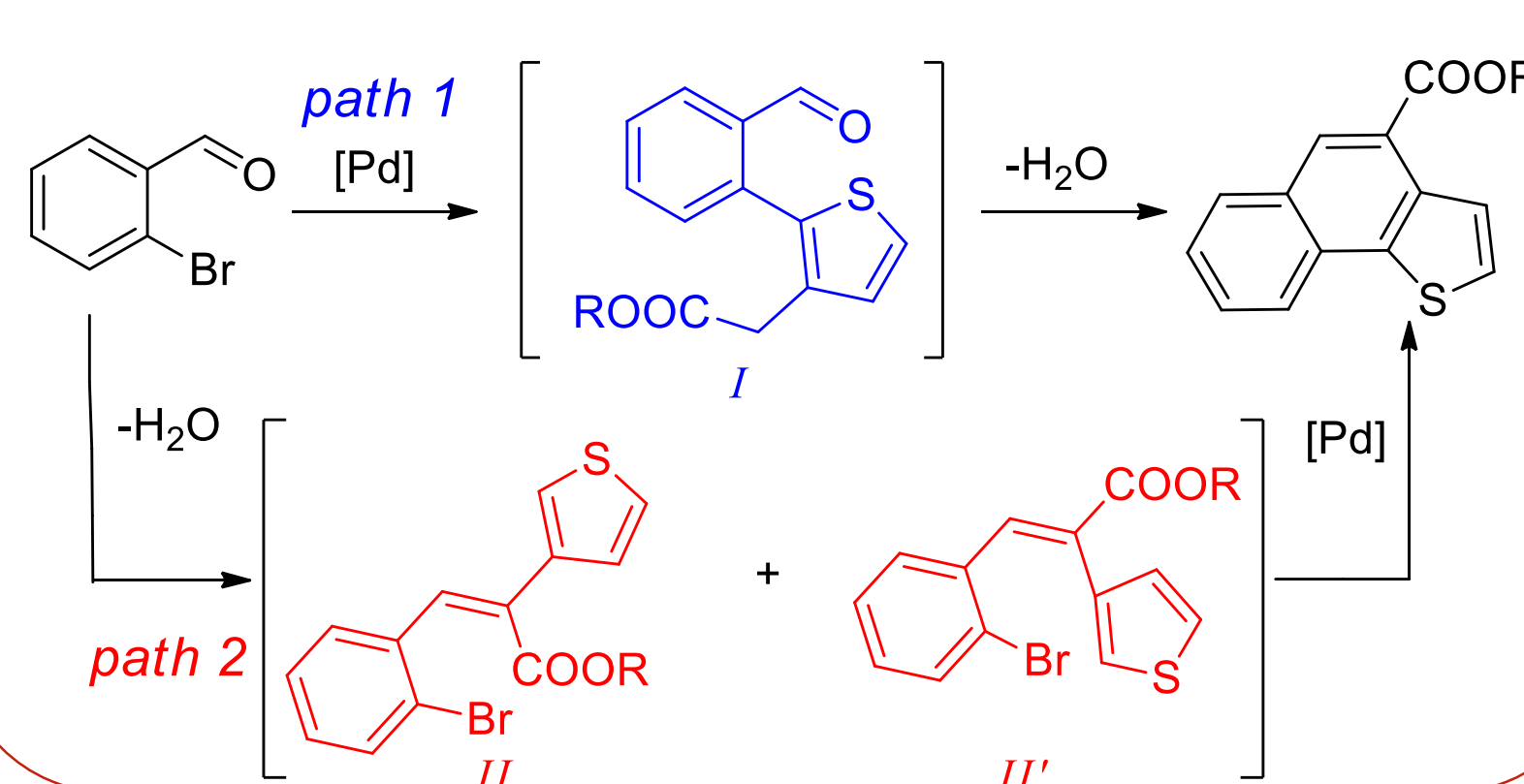
Organic semiconductors are crucial component in organic photovoltaics (OPV) since they serve as both light harvesting unit and charge transporting material in the energy conversion process. To effectively convert solar energy into electrical current, the organic semiconductors should have broad and intense absorption to harvest photon flux from the solar spectrum, proper HOMO and LUMO energy levels and sufficient charge carrier mobility to facilitate charge collection.^[1,2] Typically, organic semiconductors consist of π -conjugated system and are polymer-based. Small π -conjugated molecules may provide benefit as they can be made with high purity, with well-defined chemical structures, precise molecular weights and synthetic reproducibility is never an issue.^[3] As such, they are gaining increasing attention in the OPV field.



Previous Work

We have recently developed a low cost and sustainable synthetic strategy that use domino/cascade reaction for the rapid construction of π -extended compounds used as monomers for high performance photovoltaic materials. The starting materials are commercially available at low cost or obtained with short, easy and scalable synthetic sequences.^[4,5] The proposed mechanism takes advantage of a correct timing of the direct arylation/aldol reaction cascade (blue path) to give high yields of annulated products.

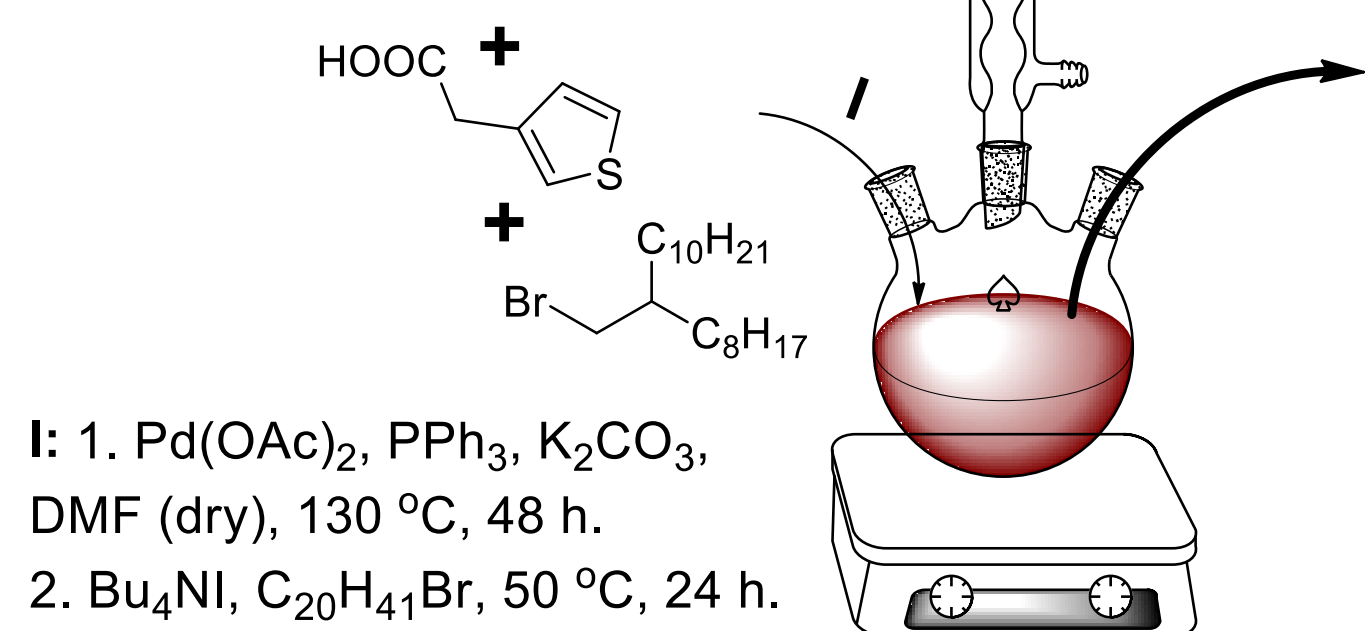
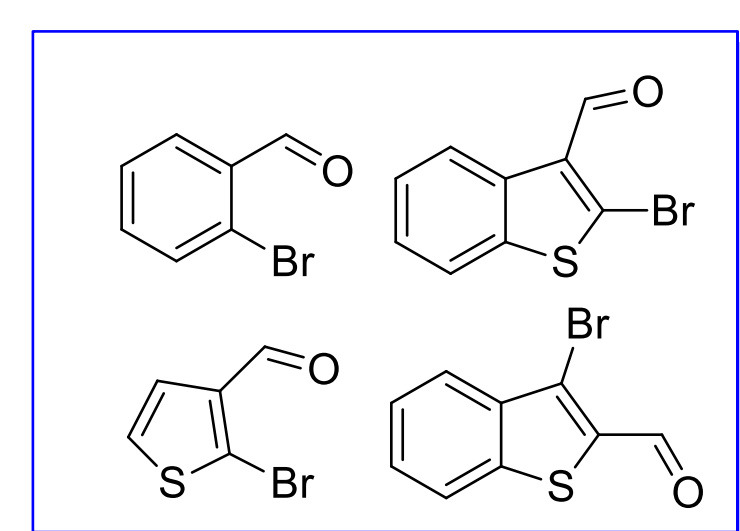
Proposed mechanism



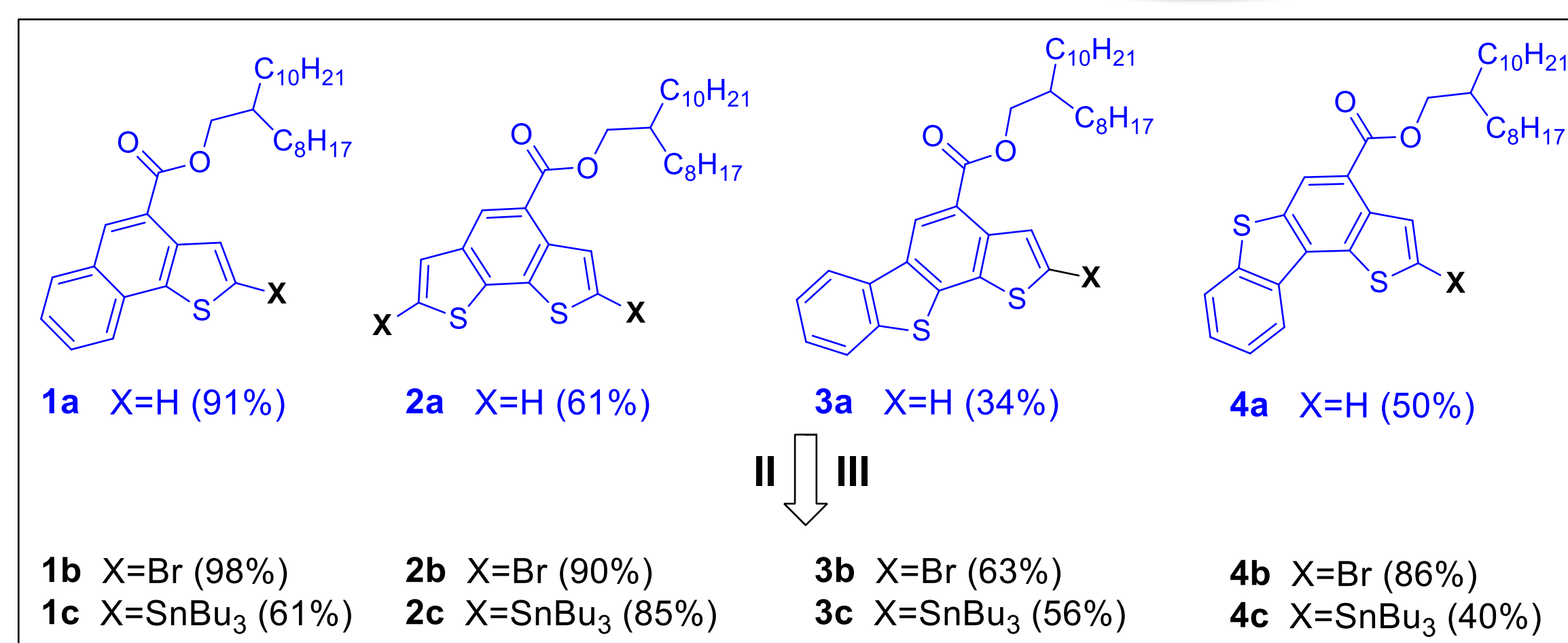
Aim of the Project

Our approach makes use of the described regiospecific annulation methodology for the synthesis of endcapping donor compounds (D) **1a-4a**, with increasing degree of complexity. **4a** contains thiophene residues with inverted positions, with consequences on the conjugation profile of the molecule. Further functionalization into compounds **1b,c-4b,c** affords suitable synthons for coupling with an either electron-donating (D) or accepting (A) π -core, using both Stille and DHA reactions.^[6]

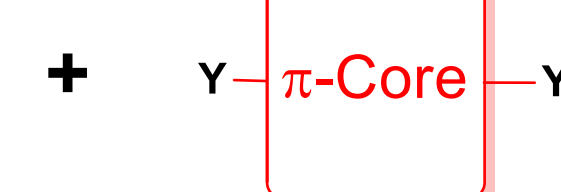
Results



Step 1: Cascade Direct Arylation-Cross Aldol

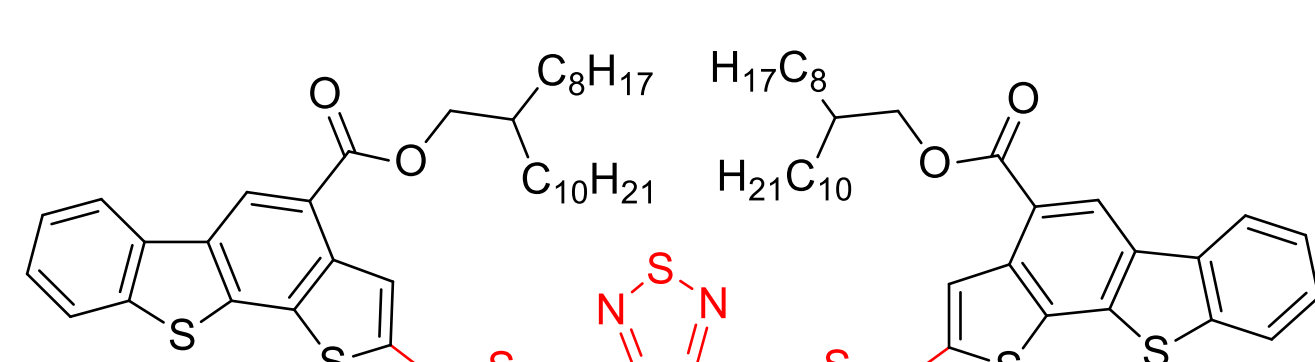
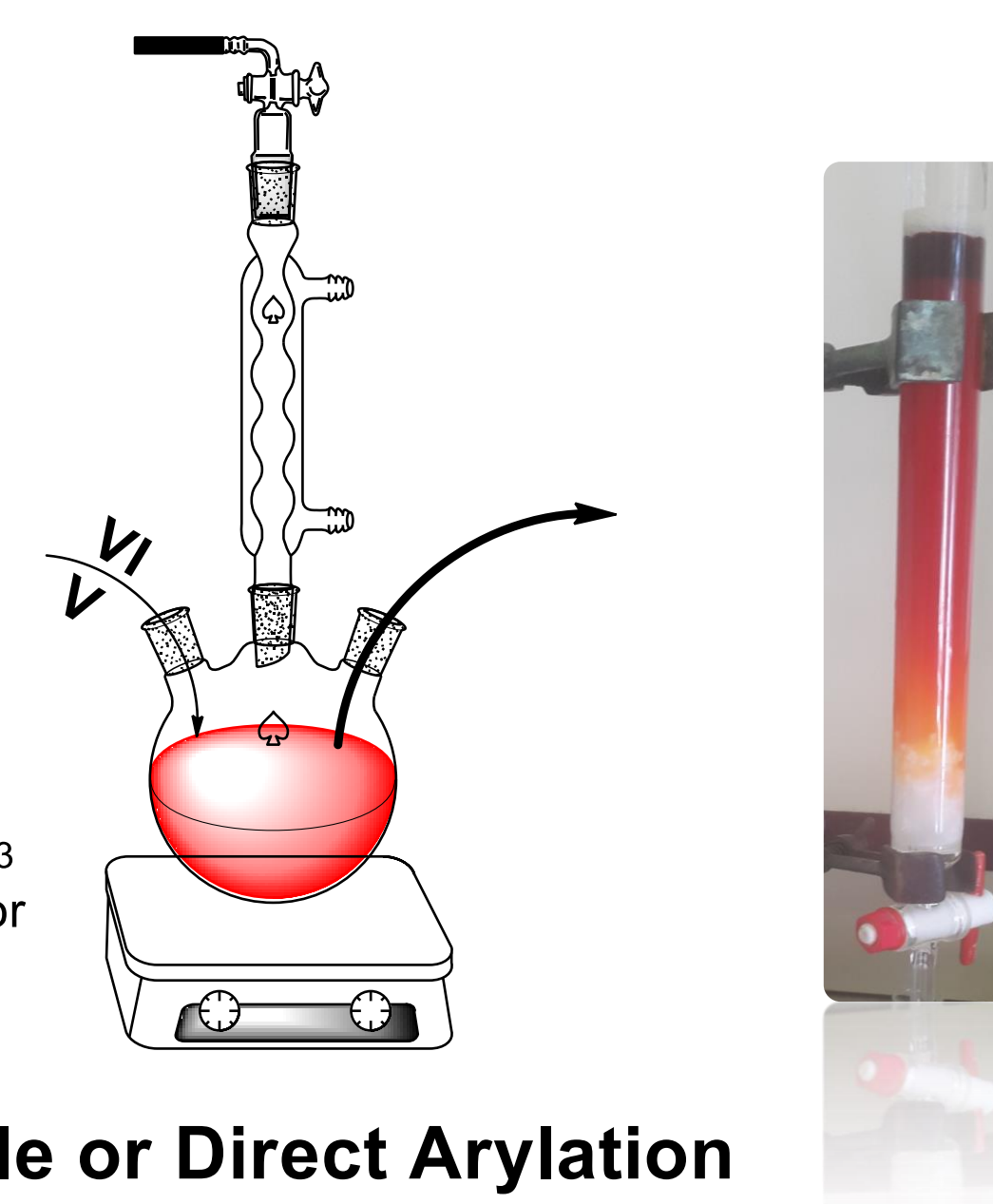


II (Bromination): NBS, CHCl₃, r.t., 24 h.
III (Stannylation): 1. LDA, THF (dry), -78 °C, 2 h.
2. SnBu₃Cl, -78 °C to r.t. overnight.

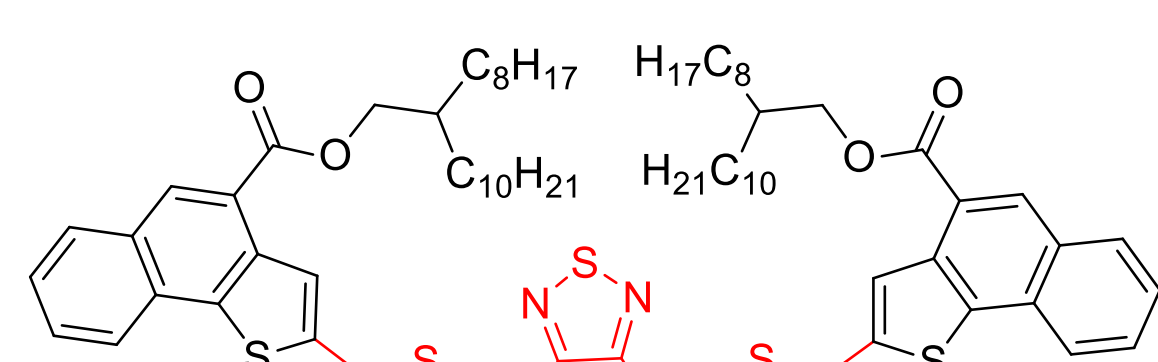


VI (Stille): Pd(PPh₃)₄, Toluene (dry), 110 °C, 48 h.
V (Direct Arylation): Pd(OAc)₂, PPh₃ (or PtBu₂Me.HBF₄), PivOH, K₂CO₃ (or KOAc), dry DMAc (or dry Toluene), 130 °C, 48 h.

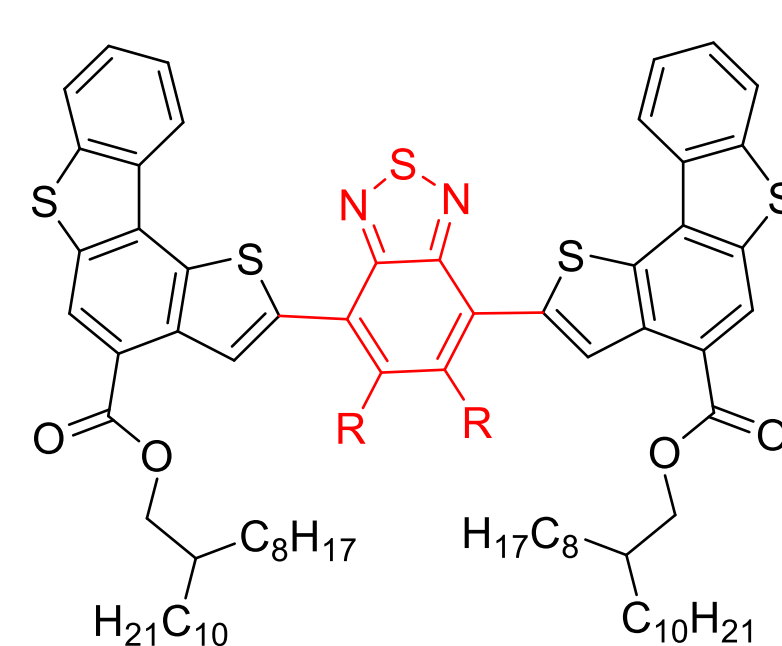
Step 2: Stille or Direct Arylation



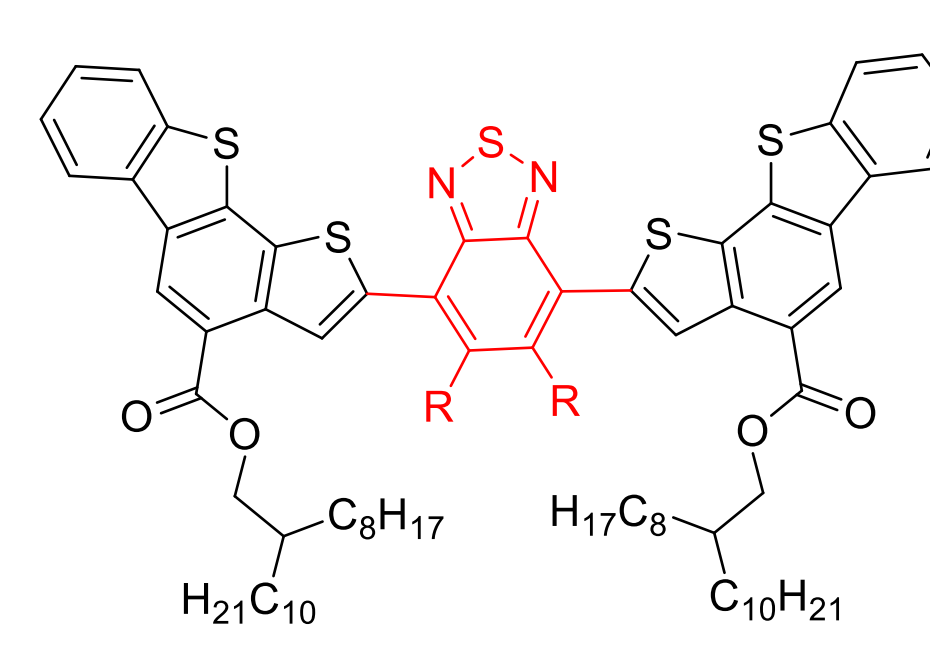
13 R=H (9%) DHA from **3a**
14 R=F (60%) Stille from **3c**



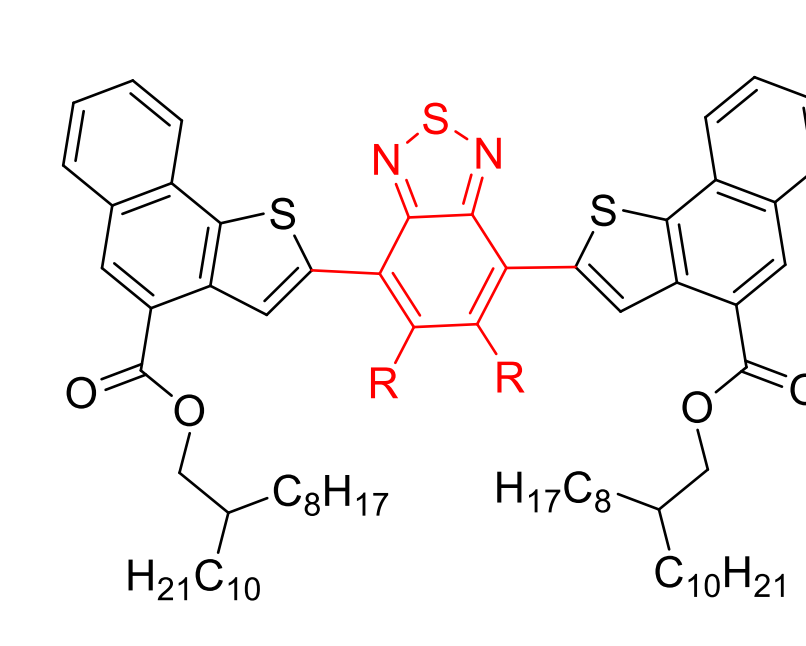
11 R=H (33%) DHA from **1b**
12 R=F (77%) Stille from **1c**



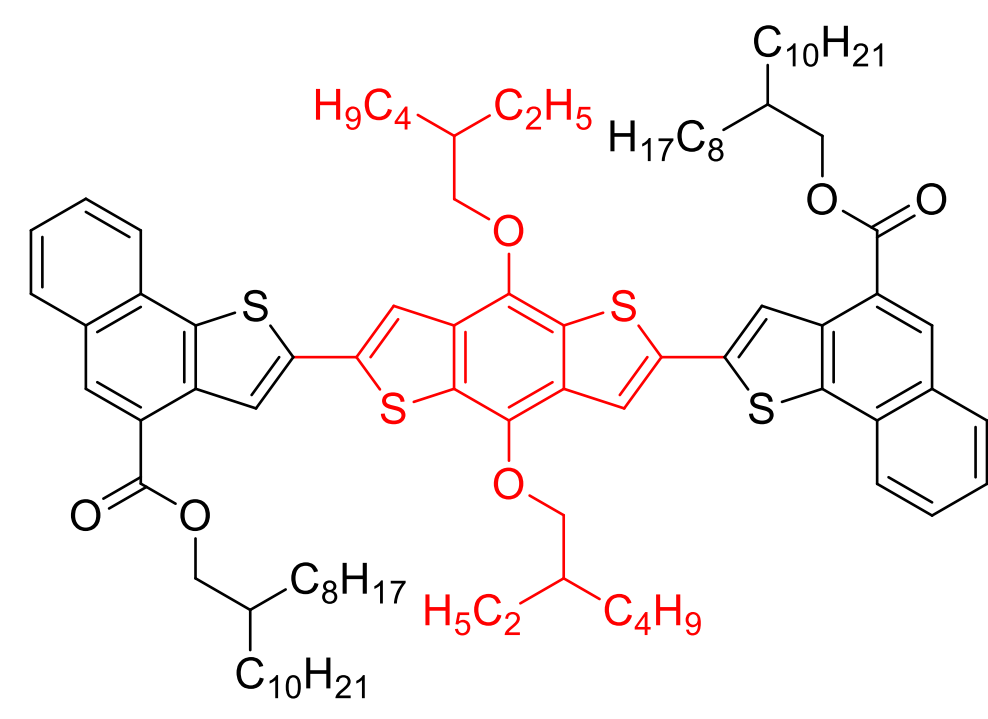
9 R=H (36%) DHA from **4a**
10 R=F (75%) Stille from **4c**



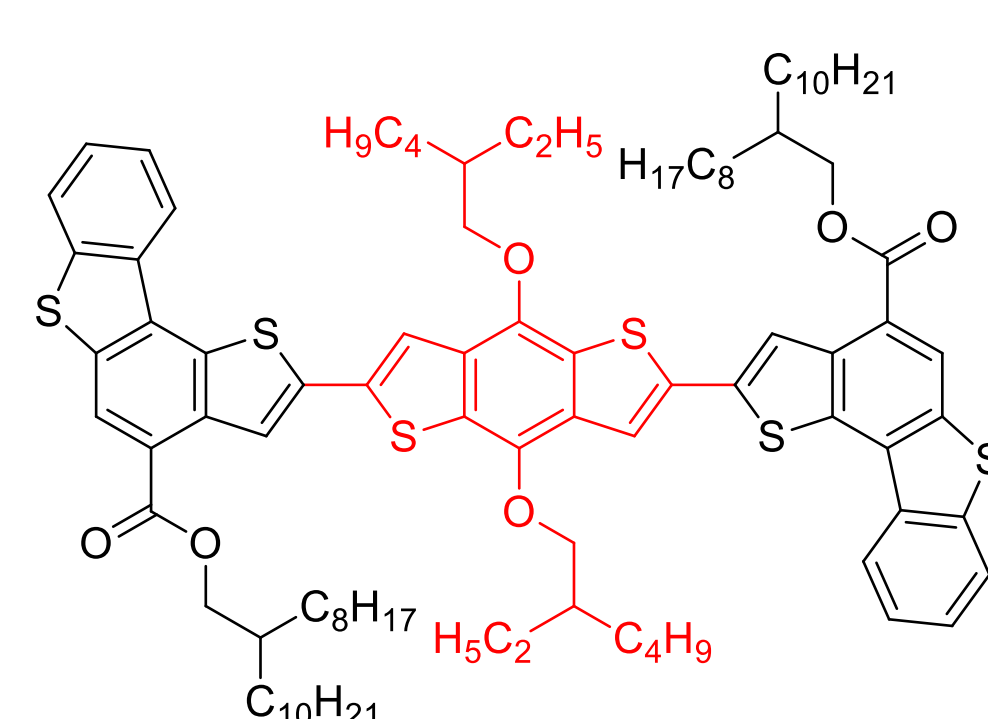
7 R=H (16%) DHA from **3a**
8 R=F (80%) Stille from **3c**



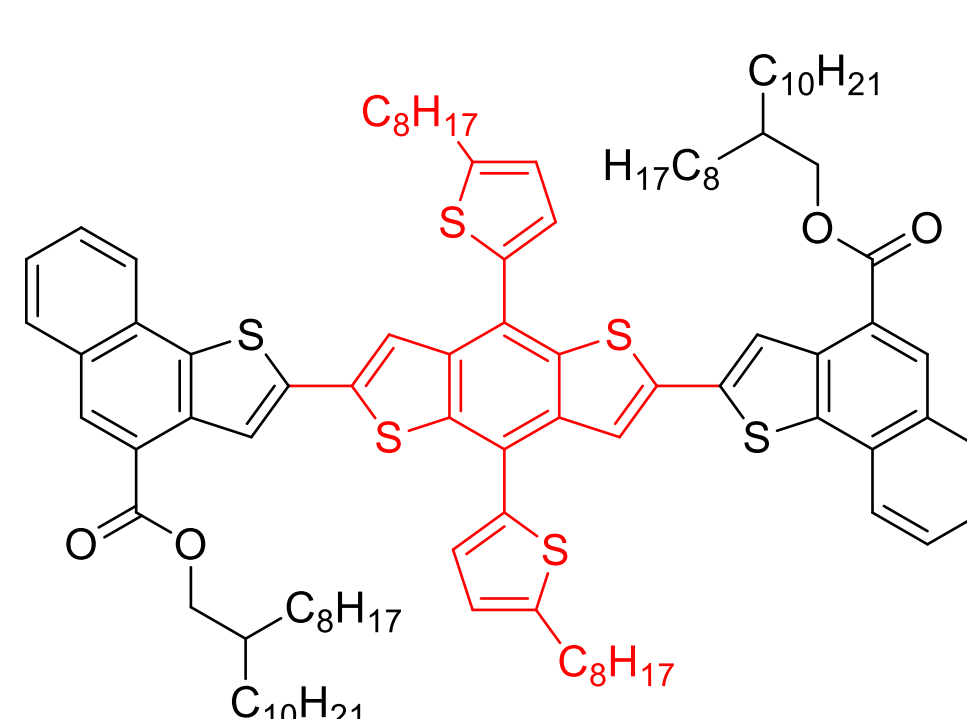
5 R=H (71%) DHA from **1a**
6 R=F (87%) Stille from **1c**



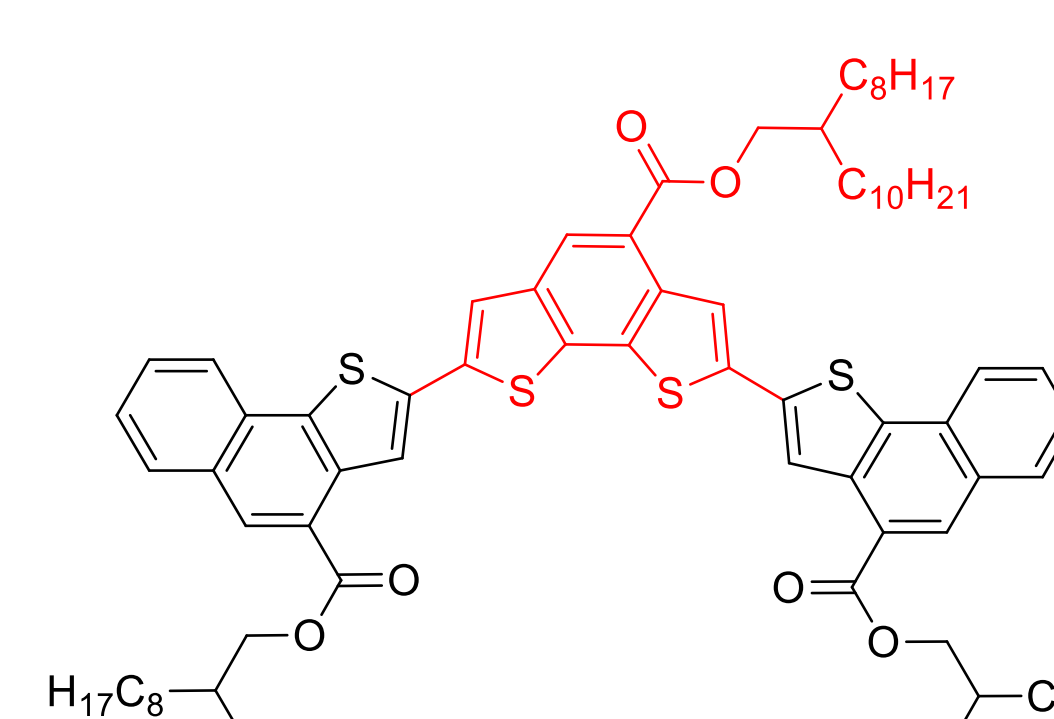
15 (80%) Stille from **1b**
(48%) DHA from **1b**



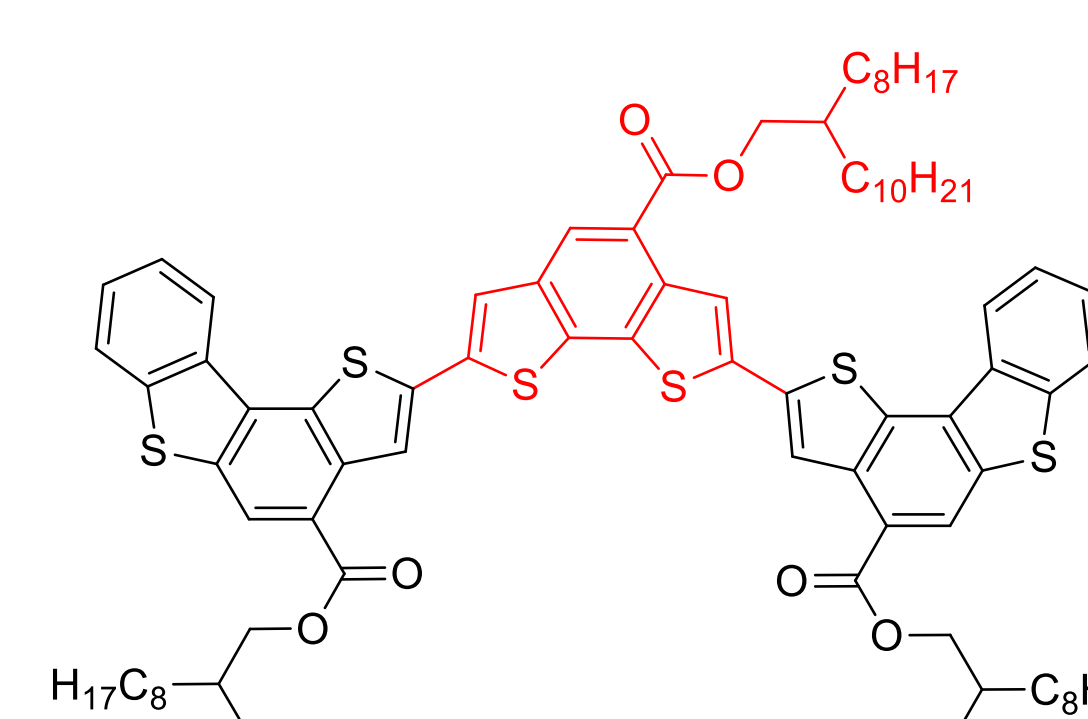
16 (17%) DHA from **4a**



17 (32%) Stille from **1b**



18 (87%) DHA from **1b** and **2a**



19 (22%) DHA from **2a** and **4b**

Future Work

The obtained compounds will be characterized in terms of optical and electrochemical, thermal, structural properties, and their potential in an organic photovoltaic application.

References

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- [3] A. Mishra, P. Bauerle, *Angew Chem Int Ed.* **2012**, *51*, 2020–2067.
- [4] A. Nitti, G. Bianchi, R. Po, T.M. Swager, D. Pasini, *J. Am. Chem. Soc.* **2017**, *139*, 8788–8791.
- [5] A. Nitti, G. Bianchi, R. Po, D. Pasini, *Synthesis.* **2019**, *51*, 677–682.
- [6] A. Nitti, P. Osw, M. Abdullah, A. Galbiati, D. Pasini, *Synlett.* **2018**, *29*, 2577–2581.

Acknowledgments

We gratefully acknowledge the Salahaddin University and Pavia University for financial support.

OMCOS 20
20th IUPAC International Symposium on Organometallic
Chemistry Directed Towards Organic Synthesis
July 21–25, 2019 in Heidelberg, Germany

