

Dr. S. Muhamad Rafiq - Curriculum Vitae

PROFILE (As on 29.08.2024)



Dr. S. Muhamad Rafiq

Assistant Professor of Chemistry
National College (Autonomous) (Nationally Re-Accredited with 'A+' Grade by NAAC)
(Collège with Potential for Excellence)
Tiruchirappalli - 620 001., Tamil Nadu, India.

Web site : <http://www.nct.ac.in>

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Mobile : +91-9444842991

Education

- **Doctor of Philosophy (Ph. D) in Organic Chemistry Jun 2011-Sep 2016**
University : University of Madras, Chennai, Tamil Nadu, India
Thesis title : "*Synthesis of n -conjugated arenes and heteroarenes involving Lewis acid/Brønsted acid-mediated domino reactions*"
Ph. D Advisor : Prof. A. K. Mohanakrishnan
- **Master of Science (M. Sc) in Physical Chemistry Jun 2007-Apr 2009**
University : University of Madras, Chennai, Tamil Nadu, India
Dissertation Title: "*Glassy carbon electrode Surface pretreatment effects on its redox behavior*"
Advisor : Prof. K. Chandrasekara pillai
Grade : First Class with distinction (75%)
- **Bachelor of Science (B. Sc) in Chemistry June 2004-April 2007**
University : The New College, University of Madras, Chennai, Tamil Nadu, India
Grade : First Class (70%)
- **Higher Secondary School (HSC) June 2003-April 2004**
Institution : Anderson Higher Secondary School, Kanchipuram, Tamil Nadu.
Grade : First Class with distinction (83.5%)
- **Secondary School (SSLC) June 2001-April 2002**
Institution : Govt. High School, Govindavadi, Kanchipuram, Tamil Nadu, India
Grade : First Class (82.4%)

Research Experiences:

- **SERB-National Post Doctoral Research Fellow Apr 2017-Sep 2017**
Institute : Indian Institute of Technology-Madras, Chennai, Tamil Nadu, India
Project title : "*Unified Synthetic Approach Towards Polycyclic Polyprenylated Acylphloroglucinols (PPAPs) Natural Products: Doitunggarcinones A-C*"
Mentor : Dr. P. Anbarasan
- **CSIR-Research Associateship (RA) in Organic Chemistry Jan 2017-Mar 2017**
University : University of Madras, Chennai, Tamil Nadu, India
Mentor : Prof. A. K. Mohanakrishnan

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Awards/Scholarships:

- Awarded CAS President's International Fellowship Initiative (**PIFI-2017**) Chinese Academy of Sciences, China (**January, 2018**).
- Secured University **1st Rank (Gold Medal)** in Master degree (M.Sc. Physical Chemistry, University of Madras, Chennai, Tamil Nadu, India).
- Awarded Inspire Fellowship, Department of Science and Technology (DST), New Delhi, India (**December 2010**).
- Awarded Royal Society of Chemistry (RSC) Fellowship to participate in the 9th CRSI-RSC Symposium and the 17th CRSI National Symposium in Chemistry by RSC and National Chemical Laboratory, Pune, India (**February 4-8, 2015**).
- Awarded Senior Research Fellowship (SRF) by Department of Science and Technology (DST), New Delhi, India (**June 2013-Present**).
- Awarded Junior Research Fellowship (JRF) Department of Science and Technology (DST), New Delhi, India (**June 2011-June 2013**).
- Received various Endowment Award for having secured highest marks in Master degree at University of Madras, Chennai, Tamil Nadu, India.

Experiences:

Sl. No	Positions held	Name of the Institute	From	To
1.	Lecturer	Aalim Muhammad Salegh College of Engineering, Avadi, Chennai-600 055, Tamil Nadu, India.	Mar-2010	May-2011
2.	Ph.D., Research Scholar	Department of Organic Chemistry, University of Madras, Chennai-600 025, Tamil Nadu, India.	Jun-2011	Sep-2016
3.	CSIR Research Associate	Department of Organic Chemistry, University of Madras, Chennai-600 025, Tamil Nadu, India.	Jan-2017	Mar-2017
4.	SERB-National Post Doctoral Fellow	Indian Institute of Technology-Madras, Chennai-600 025, Tamil Nadu, India.	Apr-2017	Sep-2017
5.	Assistant Professor	National College (Autonomous), Tiruchirappalli-620001, Tamil Nadu, India.	Sep-2017	Till Date
6.	Assistant Professor (SS)	National College (Autonomous), Tiruchirappalli-620001, Tamil Nadu, India.	Sep-2021	Till Date

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Research Interest:

- Design and synthesis of materials for opto-electronic applications.
- One pot annulation protocol for π -conjugated poly aromatics and heteroaromatics.
- Lewis/Brønsted acid-mediated organic synthesis.
- Synthesis of new materials for applications in day-to-day life.
- New synthetic methodologies for synthetically challenging organic molecules.
- Π -Conjugated organic materials.
- Multi-Step organic synthesis.

Field of Interest–TEACHING:

- Organic Chemistry
- Physical Chemistry
- Analytical Chemistry & Inorganic Chemistry

Experimental and Instrumentation Skills

- Conversant with the multi step organic synthesis, purification and characterization of various organic compounds in milligram and multigram scale.
- Engaged in domino-type reactions to synthesize variety of annulated aromatics and heteroaromatics.
- Familiar in the preparation of Grignard reagents.
- Skilled in Lewis acid-mediated organic synthesis.
- Good experience in handling of Alkyl lithium (RLi), Lithium Aluminium Hydride (LAH), Grignard Reagents (RMgX) and Sodium cyanide (NaCN) reactions.
- Expertise in handling highly air and moisture sensitive compounds.
- Familiar with all conventional spectroscopy techniques (NMR, FT-IR, UV-vis) and other instrumentations.
- Proficient in carrying out independent and collaborative research.
- Experienced in Quantum Yield measurement using UV and Emission instruments.
- Well-versed with chemistry computer packages, Chem Draw, Orgin and Endnote, SciFinder Scholar and etc.
- Good communication, management and inter-personal skills.

Research Identity:

Google Scholar: <https://scholar.google.com/citations?hl=en&authuser=1&user=SJDedDkAAAAJ>

Scopus ID: <https://www.scopus.com/authid/detail.uri?authorId=56166451700>

Orcid ID: <http://www.orcid.org/0000-0002-7455-0772>

Research ID: <https://www.researchid.co/rid12460>

Vidwan Profile: <https://vidwan.inflibnet.ac.in/profile/164618>

Research Guidance

- ❖ Recognized Research Supervisor for M.Phil., and Ph.D., Programmes in Bharathidasan University, Tiruchirappalli-620 024.

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❖ Details of Ph.D., Research Scholars:

Sl.No	Name	Reg. No.	Date of registration
1	Mr. KUMARAVEL R [BDU/PhD/20/0129-5454]	BDU2020192778429	03.07.2020
2.	D. Suresh Kumar [BDU/PhD/21/0694]	BDU2220192780004	23.05.2022

Professional Recognition/ Award/ Prize/ Certificate, Fellowship received:

Sl. No	Name of Award	Awarding Agency	Year
1.	DST-INSPIRE-JRF/SRF	DST, India	2011-2016
2.	Royal Society of Chemistry (RSC) Fellowship	RSC and National Chemical Laboratory, Pune	2015
3.	CAS President's International Fellowship Initiative (PIFI-2017)	Chinese Academy of Sciences, China	2018

Orientation/Refresher/FDP/Workshop Programme attended:

- ❖ Participated in the 28 Days UGC Sponsored Orientation Programme in Staff Academic College, UGC-HRDC Bharathidasan University, Tiruchirappalli-620020, Tamil Nadu, India from **08.11.2018 to 05.12.2018**.
- ❖ Completed a Sixteen weeks Online Refresher Course in Chemistry For Higher Education designed and developed by National Resource Centre of MHRD through SWAYAM portal of Govt. of India from **01.09.2019 to 31.12.2019**.
- ❖ Participated in the 14 Days UGC Sponsored Refresher Course in "Recent Advances in Chemical Sciences" at HRDC, Dr. Harisingh Gour University, Sagar University, Madhya Pradesh-470003 from **17.08.2020 to 29.08.2020**.
- ❖ Participated in the 14 Days UGC Sponsored Online Refresher Course in Chemistry at Staff Academic College, UGC-HRDC, North Eastern Hill University, Shillong-793022 from **01.11.2022 to 15.11.2022**.

Additional Responsibilities

- ❖ Serving/Working as a Coordinator for the Study in India (SII) Programme from **January 2018 to till date**.
- ❖ Department representative for NIRF from **July 2019 to till date**.
- ❖ Department representative for the IQAC internal body from **Jul-2018 onwards**.
- ❖ Acted as an Organizing Committee Member in Workshop, Conference, State level Intercollegiate and Intra-Department collegiate organized by PG and Research Department of Chemistry, National College (Autonomous), Tiruchirappalli, from **2017 to 2023**.
- ❖ Member of Organizing Committee in National level Intercollegiate chemistry **quiz competition-2k19**.

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- ❖ Serving/Working as In-Charge for maintaining Network/Internet in the whole college campus from **June 2020-May 2022**.
- ❖ Acted as Tutor In-charge for students in the Chemistry Department, National College (Autonomous), Tiruchirappalli-620 001, from **2017 to Till Date**.
- ❖ In-charge in the preparation of Department Academic Audit Report.
- ❖ In-charge in the preparation of AQAR and NIRF reports.
- ❖ Member of Question setting and Valuation board in various colleges.
- ❖ Acting as Doctoral Committee member for Ph.D Research Scholars.

Online Activities:

Number of National Webinars Participated	35
Number of International Webinars Participated	7
Online FDP Attended	15
MOOC Courses Completed	2

Project Students Guided:

M.Sc., Students : 08

M.Phil., Students: 02

Industries Visited

- Visited to CSIR-Central Electrochemical Research Institute (CSIR-CECRI)", Karaikudi, Tamil Nadu India on **25-09-2019**.
- Visited to Pioneer Institute "Indian Institute of Food Processing Technology (IIFPT)", Thanjavur, Tamil Nadu on **28-02-2020**.
- Visited to the Naga, Limited (Food Processing Company), Dindigul, Tamil Nadu-624005, India on **18-05-2022**.

Details of Chairing as Resource Person:

- Served as a Resource Person in Young Student Scientists Program supported by Tamil Nadu State Council for Science and Technology, Department of Higher Education, Government of Tamil Nadu held between **6th to 11th August 2018** at National College, Tiruchirappalli-620 001.
- Served as a Resource person and delivered a special lecture and hands on Training in Young Student Scientist Programme – YSSP 2018 organized by National College (Autonomous), Tiruchirappalli – 620 001 and supported by TNSCST, Dept. of Higher Education, Govt. of Tamil Nadu, during **24.12.2018** to **07.01.2019**.
- Served as Chairperson in the Royal Society of Chemistry Sponsored "**State Level Symposium on Energy, Environment, and Employment**" (RSC-SLSEEE **2019**) held by National College (Autonomous), Tiruchirappalli, Tamil Nadu, India on **22.03.2019**.
- Acted as a judge in an intercollegiate science competition for the student of Botany titled Botany Utsav '20 on **14th February 2020**.

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- Served as resource person in a one-day national webinar on **"Emerging Trends in Material Chemistry"** and delivered lecture on **" π -Conjugated Materials in Organic Solar Cells"** at Department of Chemistry, The New College, Royapettah, Chennai-600 014, Tamil Nadu on **21.06.2021**.
- Served as resource person in the Chemistry Association and delivered lecture on **"Stereochemistry and its Importance"** at PG and Research Department of Chemistry, Government Arts College, Tiruchirapalli-620 022, Tamil Nadu, India on **05.04.2022**.
- Served as a chief guest for inaugurating Maths, Science, Social science clubs and delivered a lecture at Arockia Matha Matriculation Higher secondary School, Tiruchirappalli-620 001 on **19.07.2022**.
- Served as Chairperson for in the **International Conference on Microbiome and Synthetic Biology (ICMSB-22)**, Bharathidasan University, Tiruchirappalli, Tamil Nadu, India on **September 22-23, 2022**.
- Served as resource person in a one-day national seminar on **"Future direction of Stereo Chem, Pharma, Ayurveda Research"** and delivered lecture on **"Importance of Stereochemistry Day-to-Day Life"** at Department of Chemistry, Lakshmi Bangaru Arts & Science College, Melmaruvathur, Tamil Nadu on **06.10.2022**.
- Served as resource person in a Faculty Development Programme and delivered lecture on **"Research Methodology"** at Shri Indira Ganesan College of Pharmacy, Manikandam, Tiruchirappalli-620 012, Tamil Nadu on **21.01.2023**.
- Served as resource person in the Chemistry Association and delivered lecture on **"The Role of Chemistry in Day-to-Day Life"** at Thanthai Periyar Government Arts & Science College, Tiruchirappalli-620 023, Tamil Nadu on **02.03.2023**.
- Served as resource person in the Department of Chemistry and delivered lecture on **"Career opportunities available for chemistry graduates"** and **"Importance of stereochemistry in our daily life"** at Thaivanai Ammal College for women (autonomous), Villupuram-605 401, Tamil Nadu, India on **03.04.2023**.
- Served as resource person in the Chemistry Association and delivered lecture on **"Nuclear Magnetic Resonance Spectroscopy"** At Kunthavai Naachiyaar Govt. Arts College For Women (A), Tanjavur-7, Tamil Nadu on **10.04.2023**.
- Served as resource person in the six days Faculty Development Programme on **"Organic-inorganic hybrid layered materials supported by green chemistry"** and delivered lecture on **" π -Conjugated Materials. A Smooth entry into their Organic Solar Cell Applications"** at Nehru Institute of Technology (Autonomous), Jawahar Gardens, Kaliapuram, Thirumalayampalayam, Coimbatore – 641 105, Tamil Nadu, India on **14.07.2023**.
- Served as resource person in the Five days Faculty Development Programme on **"Recent Trends in chemical Sciences"** and delivered lecture on **" π -**

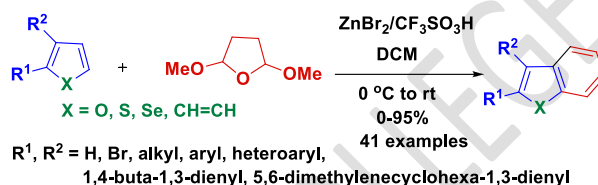
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Conjugated Materials for Organic Solar Cell Applications” at Thaivanai Ammal College for women (autonomous), Villupuram-605 401, Tamil Nadu, India on **24.01.2024**.

- Served as resource person in the Five days Faculty Development Programme on **“Recent Innovative Approaches to Achieve Sustainability”** and delivered lecture on **“ π -Conjugated Materials. A Sustainable Platform for High Performance Organic Solar Cells Applications”** at Kongunadu College of Engineering & Technology (Autonomous), Namakkal-Trichy Main Road, Tholurpatti Post, Thottiam Taluk, Trichy Dt, Tamil Nadu, India - 621215., Tamil Nadu, India on **29.08.2024**.

List of Publications (*papers published in SCI Journals, in year wise descending order*).

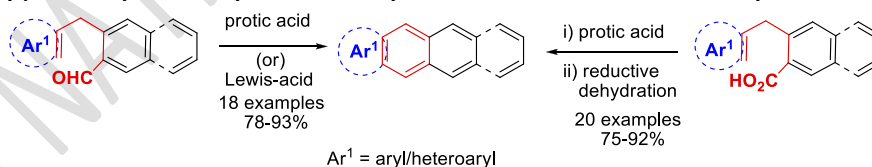
1. *“Lewis Acid/Brønsted Acid-Mediated Benz-Annulation of Thiophenes and Electron Rich Arenes”*



A facile preparation of benz-annulated heterocycles were achieved at room temperature involving a Lewis acid/Brønsted acid-mediated annulation of heterocycles using 2,5-dimethoxytetrahydrofuran as a four carbon synthon. The benz/naphth-annulation was found to be successful with electron rich arenes as well.

Rafiq, S. M.; Sivasakthikumar, R.; Mohanakrishnan, A. K. *Org. Lett.* **2014**, *16*, 2720-2723. (<http://pubs.acs.org/doi/pdf/10.1021/ol501006t>). **Impact factor 6.7**

2. *“Synthesis of Annulated Anthracenes, Carbazoles and Thiophenes Involving Bradsher Type Cyclodehydration/Cyclization-Reductive Dehydration Reactions”*



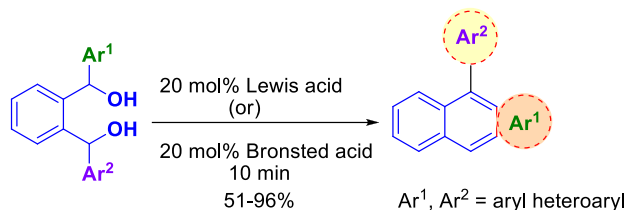
A conventional boron $\text{BF}_3 \cdot \text{OEt}_2$ -mediated Bradsher type cyclodehydration of 2-aryl/heteroaryl methyl benzaldehydes in DCM at room temperature furnished annulated arenes and heteroarenes in good yields. Alternatively, these anthracene analogues could be successfully synthesized in relatively better yields from 2-arylmethylbenzoic acids *via* Brønsted acid-mediated cyclization followed by reductive dehydration protocol.

Rafiq, S. M.; Sivasakthikumar, R.; Karunakaran, J. Mohanakrishnan, A. K. *Eur. J. Org. Chem.* **2015**, 5099-5114.

(<http://onlinelibrary.wiley.com/doi/10.1002/ejoc.201500493/epdf>). **IF: 3.26**

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3. "Regioselective Annulation of Unsymmetrical 1, 2-Phenylenebis(diaryl/diheteroarylmethanol): A Facile Synthesis of Anthracene, Tetracene and Naphtho[b]thiophene Analogues"

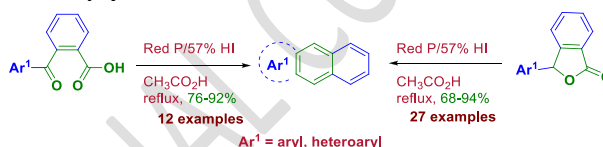


The Lewis acid/Brønsted acid-mediated regioselective annulation of unsymmetrical 1,2- diaryl/diheteroarylmethanol in DCM at room temperature led to the formation of annulated arenes and heteroarenes. A regioselective cyclization of benzene as well as naphthalene based unsymmetrical diols using 33% HBr in acetic acid at room temperature led to the formation of anthracene as well as naphtho[b]thiophene analogues in good to excellent yields.

Sivasakthikumar, R.; **Rafiq, S. M.**; Sankar, E.; Mohanakrishnan, A. K. *Eur. J. Org. Chem.* **2015**, 7816-7835.

(<http://onlinelibrary.wiley.com/doi/10.1002/ejoc.201501087/epdf>). **IF: 3.26**

4. "Synthesis of Annulated Arenes and Heteroarenes Involving Hydriodic Acid and Red Phosphorus (HI/P)-Mediated Reductive Cyclization of 2-(Aroyl/Heteroaryl)Benzoic Acids or 3-(Aryl/Heteroaryl)Phthalides"



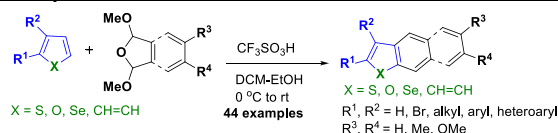
A facile preparation of annulated arenes and heteroarenes was achieved in good to excellent yields involving hydriodic acid and red phosphorus (HI/P)-mediated reductive cyclization of 3-(aryl/heteroaryl)phthalides. The reductive cyclization was found to be successful with 2-arylbobenzoic acids and 2-arylnaphthoic acids.

Rafiq, S. M.; Mohanakrishnan, A. K. *Synlett.* **2017**, 28, 362-370.

(<https://www.thieme-connect.com/products/ejournals/abstract/10.1055/s-0036-1588337>. DOI: 10.1055/s-0036-1588337). **Impact factor 2.4**

5. "Synthesis of Annulated Heterocycles Using Benzo-DMTHF Involving Triflic acid-mediated Domino Reactions" *ChemistrySelect* **2017**, 2, 2578-2582.

(<http://onlinelibrary.wiley.com/doi/10.1002/slct.201700002/pdf>). **IF: 2.31**



A facile preparation of naphth-annulated heterocycles was achieved at room temperature involving a triflic acid-mediated annulation of heterocycles using benzo-DMTHF. The naphth-annulation was found to be successful with electron rich arenes as well.

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6. "Crystal structure of 6-(*p*-tolyl)benzo[*b*]naphtho[2,3-*d*]thiophene and of an orthorhombic polymorph of 7-phenylanthra[2,3-*b*]benzo[*d*]thiophene" Gopinath, S.; K. Sethusankar, K.; Evans, H. S.; **Rafiq, S. M.**; Mohanakrishnan, A. K. *Acta Cryst.* **2016**, E72, 1310–1314.
7. "5,13-Bis(4-methoxyphenyl)dinaphtho[2,3-*b*:20,30-*d*]-thiophene *S,S*-dioxide dichloromethane hemisolvate" R. Manickam, R.; Jagadeesan, G.; **Rafiq, S. M.**; Mohanakrishnan, A. K.; Srinivasan, G. *IUCrData* (2019). 4, x191394.

Conferences/Workshops Participation:

- Royal Society of Chemistry Sponsored One Day workshop on Solar Energy Materials.
 - *Jointly organised by* Royal Society of Chemistry and University of Madras on **10th September, 2014**.
- Transcending Frontiers in Organic Chemistry (**TFOC-2014**) National Symposium in Organic Chemistry
 - *Organised by* National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Trivandrum, India on **October 9-11, 2014**.
- Recent Advances on Luminescent Materials (**RALM-2015**) UGC-FIST & UGC-SAP Sponsored National Seminar
 - *Organised by* Annamalai University, Chidambaram, India on **January 23-24, 2015**
- 17th CRSI-National Symposium in Chemistry
 - *Organised by* Chemical Research Society of India held at National Chemical Laboratory Pune on **February 6-8, 2015**.
- Springer & Anna University sponsored Author Workshop
 - *Jointly organised by* Springer & Anna University, Chennai on **17th March, 2015**.
- Presented my research proposal to get the INSPIRE Faculty Award-2017 under AORC Scheme of DST-Material Sciences on **16 November, 2017** at National Science Academy (INSA), New Delhi.
- Participated in One Day Workshop on "**X-ray Diffraction studies**" held at National College (Autonomous), Tiruchirappalli- 620 001 on **16.12.2017**.
- Participated in DST-Inspire Internship Science Camp which is held at National College during **6th to 11th August 2018**.
- Participated in Royal Society of Chemistry Sponsored "**State Level Symposium on Energy, Environment, and Employment**" (**RSC-SLSEEE 2019**) was organized by Department of Chemistry, National College (Autonomous), Tiruchirappalli-620001 during **21.03.2019-22.03.2019**.
- Participated in International level seminar "**DST & ACS Workshop**" held at Bharathidasan University, Tiruchirappalli- 620 024 on **09.12.2019**.

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- Participated in One Day Workshop on "**Analytical Techniques**" held at National College (Autonomous), Tiruchirappalli- 620 001 on **20.12.2019**.
- Participated in One Day Seminar on "**Assembled Advanced Organic Materials**" organized by Department of Chemistry, National College (Autonomous), Tiruchirappalli- 620 001 on **03.06.2020**.
- Participated in One-day Orientation Programme on "Introduction on Chemistry and Analytical Chemistry" held at Department of Chemistry, National College (Autonomous), Tiruchirappalli- 620 001 on **09-09-2021**.
- Participated in One Day Workshop on "**Save Energy**" held at National College (Autonomous), Tiruchirappalli- 620 001 on **25.10.2021**.
- Participated in One day State level workshop on "Entrepreneurial Development" - Hands-on Training in "**CLEANSING PRODUCTS**" Under the auspices of DBT - STAR College Scheme on **25.08.2022**.
- Participated in One-day Orientation Programme on "**Food – Adulterants, Analysis & Auditing**" Organized by National College Instrumentation Facility (NCIF), National College (Autonomous), Tiruchirappalli- 620 001 on **09-04-2022**.
- Participated in One Day Workshop on "**Ornamental Fish Culture Technology**" held at National College (Autonomous), Tiruchirappalli- 620 001 on **28.04.2022**.
- Participated in DST-SERB Sponsored Two Days Workshop for College Teachers on "**Fostering Research Culture**" held at Bharathidasan University, Tiruchirappalli- 620 024 from **18.08.2023-19.08.2023**.

Any other Information:

- (i) Secured University 1st Rank (**Gold Medal**) in Master degree (M.Sc. Physical Chemistry, University of Madras, Chennai, Tamil Nadu)
- (ii) Awarded **Inspire Fellowship**, Department of Science and Technology (DST), New Delhi (**December 2010**).
- (iii) Selected for **Royal Society of Chemistry (RSC) Fellowship** to participate in the 9th CRSI-RSC Symposium and the 17th CRSI National Symposium in Chemistry by RSC and National Chemical Laboratory, Pune (**February 4-8, 2015**).
- (iv) Received various Endowment Award for having secured highest marks in Master degree (M.Sc. Physical Chemistry) University of Madras, Chennai, Tamil Nadu).

(V) Organizing seminars, conferences, workshops and other college activities

- Serving/Working as a Coordinator for the Study in India (SII) Programme from **January 2018 onwards**.
- Serving/Working as In-Charge for maintaining Network/Internet in the whole campus, Network in-charge, National College from **June 2020-May-2022**.
- Serving/Working as a liaison Officer for Chemistry Department for the IQAC internal body, National College from **June 2018 onwards**.

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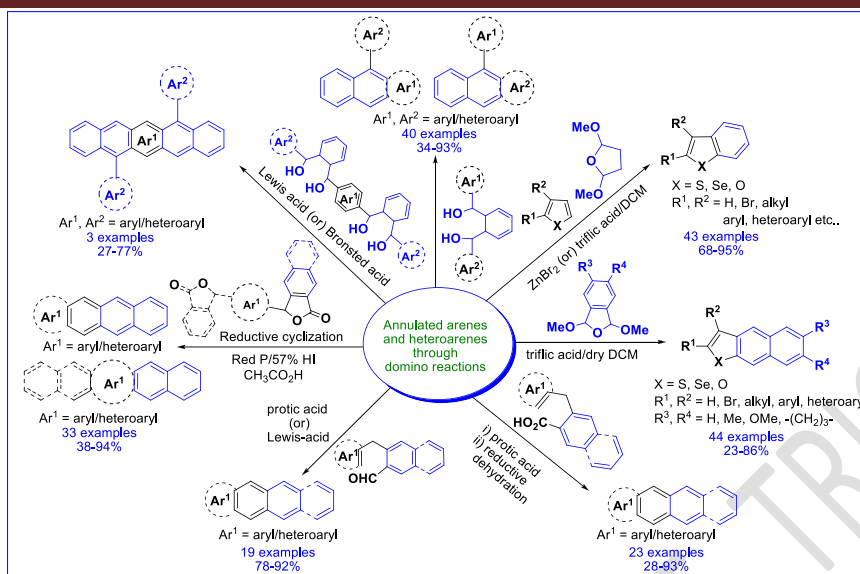
Personal Details

Father's Name	:	N. Settu
Date of Birth	:	30 th May 1987
Gender	:	Male
Marital Status	:	Married
Language Proficiency	:	Tamil (Native), English
Nationality	:	Indian
Address	:	Plot No. 290, Cauvery Nagar, Mahatma Gandhi Road, Pirattiyur West, Tiruchirappalli-620 009, Tamil Nadu, India
Mobile No.	:	+91-9444842991
Email id.	:	rafiq@nct.ac.in & drsmdrafiq@gmail.com

(Dr. S. MUHAMAD RAFIQ)

Work Summary

Organic synthesis of π -conjugated thiophene-based materials is one of the most challenging tasks; it requires meticulous planning and execution. My doctoral work interest relates to synthesis of organic π -conjugated thiophene-based heteroarenes and development of new annulations methodologies for annulations of thiophenes and electron-rich arenes. The Bradsher type cyclodehydration reaction of 2-(aryl/heteroaryl)methyl benzaldehydes for the synthesis of π -conjugated arenes and heteroarenes, alternatively, the synthesis of similar types of arenes and heterocycles were achieved *via* cyclization followed by reductive dehydration protocol. Next, the synthesis of π -conjugated arenes and heteroarenes involving hydriodic acid-mediated reductive cyclization reaction commencing from 2-(aryl/ heteroaryl)benzoic acids/3-(aryl/heteroaryl) phthalides. Finally, Lewis/Brønsted acid-mediated regioselective cyclization of unsymmetrical 1,2-diaryl/1,2-diheteroarylmethinediols for the synthesis of substituted naphtho[*b*]thiophenes and anthracene analogues. The figures below represent the molecules synthesized and methodologies developed during course of my Ph.D work.



Research Summary

Title of thesis: "Synthesis of *n*-conjugated arenes and heteroarenes involving Lewis acid/Brønsted acid-mediated domino reactions"

The term acenes describes a family of polycyclic aromatic hydrocarbons (PAHs) consisting of linearly fused benzene rings introduced by Clar,¹ are among the most widely studied small-molecule organic semiconductors with potential applications in organic electronics.² In order to enhance the further performance of organic *n*-conjugated materials, their modification by attaching functionalized substitution groups or increasing the number of linearly fused benzene rings have been literally exploded and the tremendous amount of investigations carried out.

These PAHs molecules have become popular synthetic targets due to their small but challenging structures. The reported synthesis of these higher acenes suffers from disadvantages such as insolubility and high reactivity, making their processing difficult. Stabilizing these acenes through bulky substituents that kinetically protect them from possible reactions, which makes their devices more stable under ambient conditions, enhancing the practical use of the larger polyacenes-based OFETs.³ In order to avoid such instability of simple hydrocarbon-based large acenes, thiophene are incorporated into the acene structures, affording thienoacenes, which in many cases realizes good stability and enables high carrier mobility simultaneously.⁴

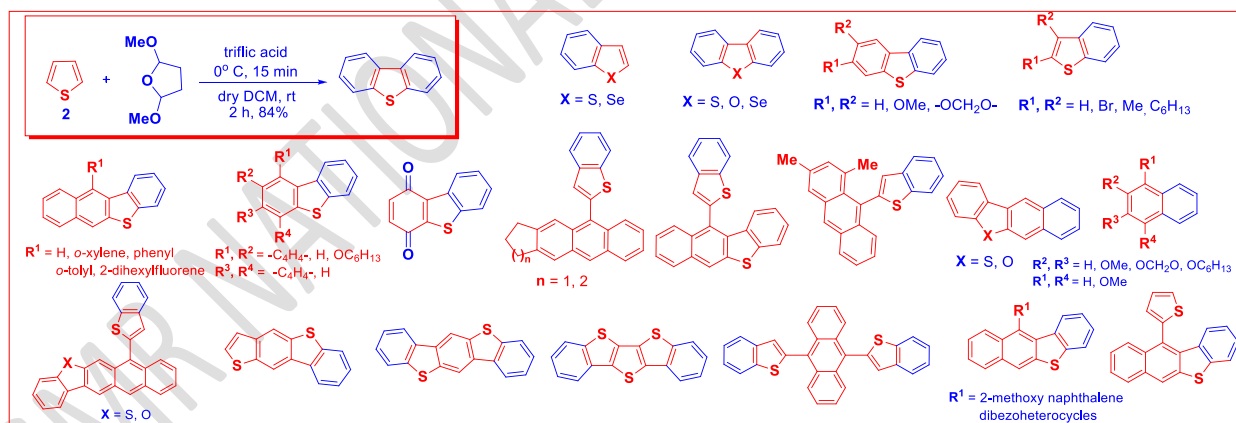
Hence, the need for the synthesis of annulated arenes and heteroarenes as well as thiophenes based acenes from commercially available simple starting materials is of current interest. The thesis is divided into four chapters. The title of the thesis clearly reflects the objective, which is to utilize the Lewis acid as well as Brønsted acid for the synthesis of annulated arenes and heteroarenes. **Chapter I** deals with Lewis acid/Brønsted acid catalyzed benz and naphth-annulation of thiophenes and electron-rich arenes. **Chapter II** describes a classical route for the synthesis of thiophene, bithiophene, dihexylfluorene, pyrene, *N*-alkylcarbazole, triphenyl amine,

benzo[*b*]heterocycle and dibenzoheterocycle fused anthracenes and tetracenes *via* 2-arylmethyl benzaldehydes or 2-arylmethylbenzoic acids. **Chapter III** deals with the synthesis of π -conjugated arenes and heteroarenes involving hydriodic acid-mediated reductive cyclization of 2-(aryl/heteroaryl)benzoic acids/3-(aryl/heteroaryl) phthalides. **Chapter IV** describes a regioselective synthesis of anthracene and naphtho[*b*]thiophene analogues *via* Lewis/Brønsted acid-mediated cyclization of unsymmetrical 1,2-diaryl/1,2-diheteroaryl methinediols.

1. Synthesis of benz-annelated heteroarenes and arenes involving Lewis/Brønsted acid-mediated annulation of thiophenes and electron-rich arenes with 2,5-dimethoxy tetrahydrofurans (DMTHFs)

The 2,5-dimethoxytetrahydrofuran (DMTHF) has been sporadically utilized for the synthesis of heterocycles such as pyrrole, indole and carbazole.⁵ The DMTHF was also utilized for the synthesis of benzo[*b*]thiophene-5,6-dicarboxaldehyde. Development of elegant strategies using annulation has allowed the synthesis of polycyclic aromatic hydrocarbon (PAH) arenes and heteroarenes. Still there is a plenty of scope for the development of reactions using DMTHF. We have effectively utilized the DMTHF as well as benzo-DMTHF for the synthesis of interesting and useful molecular frameworks from readily available starting materials under mild reaction conditions.

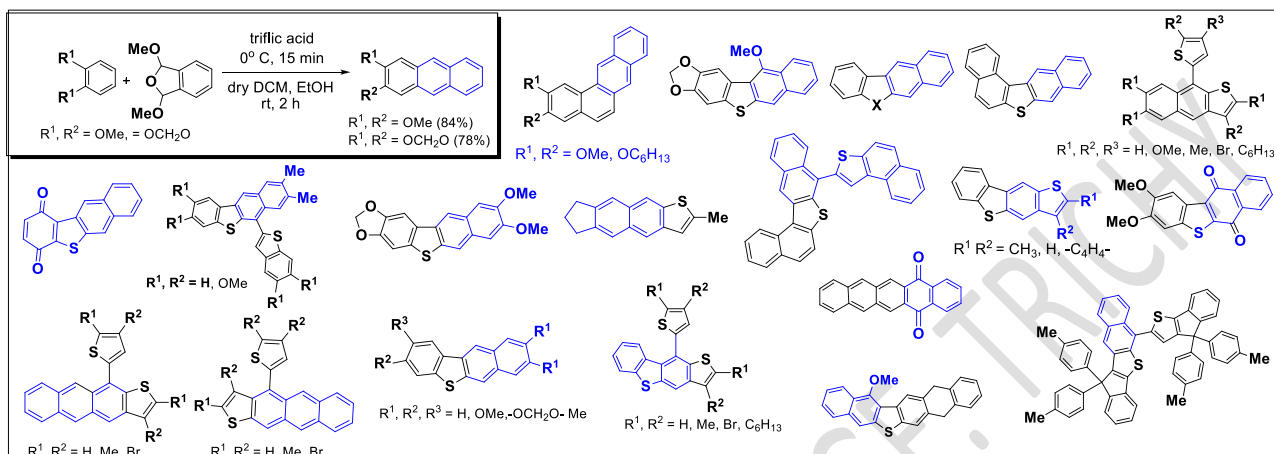
This chapter describes the synthesis of various annulated thienyl heterocycles and naphthalenes using Lewis/Brønsted acid catalyzed reaction of 2,5-dimethoxytetrahydrofuran (DMTHF) with thiophenes and electron-rich arenes. This strategy has been applied to the synthesis of various benzo[*b*]thiophenes in a single step starting from the corresponding thiophenes (**Scheme 1**).



Scheme 1: Lewis/Brønsted acid-mediated annulation of heteroarenes: A facile preparation of benz-annelated heteroarenes.

This strategy has also been applied for the naphth-annulation of electron rich arenes, substituted thiophenes and benzo[*b*]heterocycles with benzo-DMTHF also afforded respective annulated products in good yields. The methodology could be successfully extended with substituted benzo-DMTHF to afford the respective annulated products in good yields (**Scheme 2**). This transformation shows significant substrate

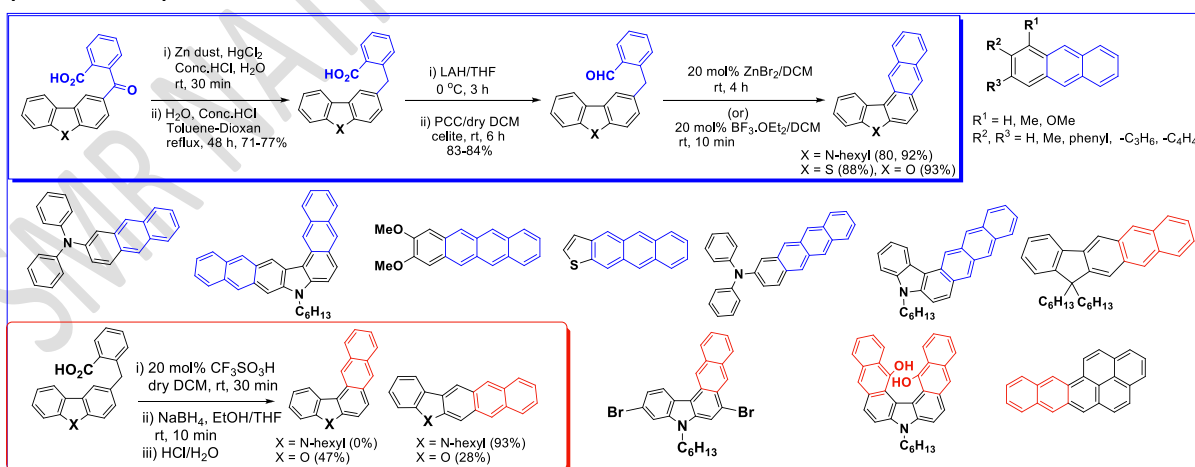
scope. The substituted benzo-DMTHFs were prepared from corresponding dialdehyde and methanol in the presence of acid. Substrate scope was studied substituted benzo-DMTHFs. Several benz-annulated thiophenes derivatives with different functional groups have been prepared using this method.



Scheme 2: Triflic acid-mediated annulation of heteroarenes: A facile preparation of naphth-annulated heteroarenes

2. Synthesis of π -conjugated arenes and heteroarenes involving Bradsher type cyclodehydration/cyclization-reductive dehydration reactions

Fused polycyclic aromatic compounds played stellar role in material chemistry.⁶ More specifically, the anthracene and its derivatives are the family of carbon-rich compounds of current interest and attracting considerable attention because of the light-emitting function leading to potential application as optoelectronic materials. Recently, the plenty of anthracene and hetero-annulated anthracene analogues have been synthesized and used in electronic applications. Hence, considering the optical applications of π -conjugated arenes and heteroarenes,⁷ the synthesis of these compounds is planned.



Scheme 3: Synthesis of annulated arenes and heteroarenes involving Bradsher cyclodehydration reactions

In our effort to develop transformations from 3-aryl/heteroaryl (methyl)benzaldehyde to annulated as well as heteroannulated anthracene derivatives in the presence of Lewis or Brønsted acid catalyst, we have found that the formation of annulated arenes and heteroarenes from 2-aryl/heteroaryl methyl benzaldehydes in the presence of Lewis acid/Brønsted acid as a catalyst. The cyclodehydration reaction was successfully extended with 2-arylmethyl/2-heteroarylmethyl naphthaldehydes as well. Alternatively, the triflic acid-mediated cyclization of 2-arylmethylbenzoic acids as well as 2-arylmethylnaphthoic acids followed by reductive dehydration protocol furnished annulated anthracenes in relatively better yields (**Scheme 3**).

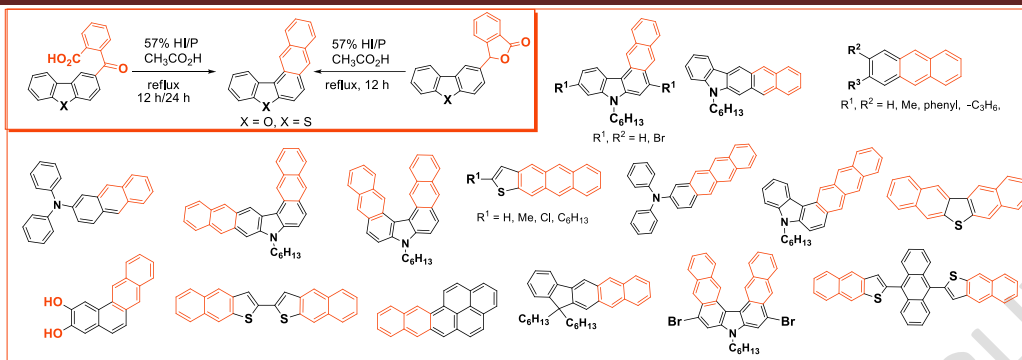
The thiophene, bithiophene, dihexylfluorene, pyrene, *N*-alkylcarbazole, triphenyl amine, benzo[*b*]heterocycle and dibenzoheterocycle fused anthracenes and tetracenes have also been prepared in good-excellent yields. The various types of benzo[*b*]heterocycle fused anthracenes and triphenylamino derivatives syntheses herein may find applications in field-effect transistors and also in organic solar cells (OSCs). The optical properties of selected annulated anthracenes and π -conjugated heteroarenes are also studied.

3. Synthesis of π -conjugated arenes and heteroarenes involving hydriodic acid-mediated reductive cyclization of 2-(aryl/heteroaryl)benzoic acids/3-(aryl/heteroaryl) phthalides

As outlined in the second chapter, transformation of 2-aryl/2-heteroaryl benzoic acids into the corresponding π -conjugated arenes and heterocycles could be achieved through Bradsher type cyclodehydration as well as cyclization followed by reductive dehydration in good yields. Despite these synthetic protocols, there remains a need for a straight forward reductive cyclization of 2-aryl/2-(heteroaryl)methyl benzoic acids. Hence, an alternative method which will provide complex π -conjugated heterocycles from corresponding 2-aryl/heteroaryl benzoic acids as well as 3-aryl/heteroaryl phthalides was planned.

In this chapter, the utility of hydriodic acid and red phosphorus (HI/P) catalysis is further extended on the synthesis of π -conjugated arenes and heterocycles under refluxing acetic acid conditions. **Chapter III** describes a one-pot procedure to synthesis the π -conjugated arenes and heterocycles from 2-aryl/heteroaryl benzoic acids or 3-aryl/heteroaryl phthalides. Additionally, using HI/P-mediated reductive cyclization strategy, a facile approach has been developed to synthesize π -conjugated arenes and heterocycles from bis-heteroaryl phthalides (**Scheme 4**).

The synthesis of naphthodibenzoheterocycles, naphtho[*b*]thiophenes, substituted anthracenes and tetracenes were achieved in good to excellent yields involving hydroiodic acid and red phosphorus (HI/P)-mediated reductive cyclization of 3-aryl/heteroaryl phthalides. Additionally, the 2-arylbenzoic acids as well as 2-arylnaphthoic acids upon HI/P-mediated reductive cyclization also furnished the above mentioned annulated arenes and heteroarenes in relatively better yields.

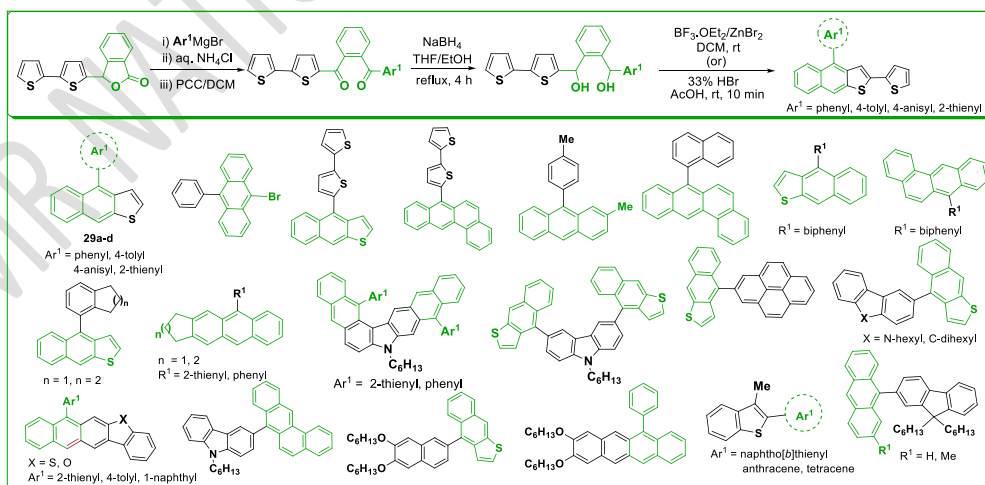


Scheme 4: HI/P-mediated reductive cyclization of keto-acid/phthalides. A facile preparation of annulated heterocycles

The methodology was successfully applied for the synthesis of dinaphtho[*b*]thiophene, 2,2'-binnaphtho[*b*]thiophene, 9,10-di(naphtho[*b*]thiophenyl)anthracene and dinaphthocarbazoles from corresponding bis-phthalides in good to excellent yields. Compared to the existing methods available for the synthesis of PAHs, the present protocol using HI/P is simple, widely applicable, and also the number of steps involved to synthesis of annulated arenes and heteroarenes are less. In the case of complex π -conjugated heterocycles, the HI/P protocol was found to be better than that of Bradsher as well as acid cyclization followed by reductive dehydration.

4. Synthesis of anthracene and naphtho[*b*]thiophene analogues via Lewis/Brønsted acid-mediated regioselective cyclization of unsymmetrical 1,2-diaryl/1,2-diheteroarylmethinediols

Chapter IV outlines the synthesis of substituted naphtho[*b*]thiophenes and anthracene analogues from the lactone. Ring opening of lactone with aryl magnesium bromide followed by oxidation and subsequent reduction of the resulting diketone may lead to diol. Annulation of the diol using Lewis/Brønsted acid-mediated cyclization may furnish benz-annulated naphtho[*b*]thiophenes and anthracenes (**Scheme 5**).



Scheme 5: Lewis/Brønsted acid-mediated regioselective cyclization of unsymmetrical 1,2-diaryl/diheteroarylmethinediols

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The annulation of the diol proceeds through the intermediacy of benzylic carbocations followed by intramolecular cyclization and subsequent aromatization to give the annulated products. The annulation methodology is highly efficient for the syntheses of anthracene as well as naphtho[*b*]thiophene analogues.

The naphtho[*b*]thiophene analogues and anthracenes were prepared in good yields involving Lewis-acid/HBr-acetic acid-mediated regioselective cyclization of unsymmetrical diols. Under identical condition, synthesis of various cyclopenta[*b*]/cyclohexa[*b*]anthracenes were achieved in excellent yields. Also biphenyl, dihexylfluorene, pyrene based annulated arenes and pentacene analogues containing dibenzoheterocycles have been synthesized in good to excellent yields. The wide variety of anthracenes, tetracenes, pentacenes and annulated thiophene derivatives syntheses herein may find application in OLEDs.

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