

University Grants Commission under the scheme of support for Major Research Project entitled “Ultrasound Assisted Multi-Site Phase – Transfer Catalysts in Heterogeneous Organic Reactions”

Mr. V. Rajendran



UNIVERSITY GRANTS COMMISSION
BAHADURSHAH ZAFAR MARG
NEW DELHI – 110 002

Utilization Certificate

Certified that the grant of Rs.2,90,080/- (Rupees Two Lakhs Ninety Thousand and Eighty Only) received from the University Grants Commission under the Scheme of support for Major Research Project entitled “**Ultrasound assisted multi-site phase-transfer catalysts in heterogeneous organic reactions**” vide UGC Letter No.F.42-356/2013 (SR), dated 10TH June 2016 from which the sum of Rs.1,80,280/- (Rupees One Lakhs Eighty Thousand Two Hundred and Eighty Only) has been utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission.

V. Rajendran
31-01-24
PRINCIPAL INVESTIGATOR

(with seal)
Dr. V. RAJENDRAN, M.Sc., Ph.D.
Associate Professor & Head
PG Department of Chemistry
Pachaiyappa's College For Men
Kanchipuram - 631 501.

V.M. S. Sankar
STATUTORY AUDITOR
(with seal) 31/01/2024
SANKAR SREENIVASAN AND COMPANY
CHARTERED ACCOUNTANTS
NO.98, PSK STREET,
KANCHIPURAM - 631501.

UDIN: 24021196 B1CBMPF 3491



V. Rajendran
31-01-24
HEAD OF THE DEPARTMENT

(with seal)
Dr. V. RAJENDRAN, M.Sc., Ph.D.
Associate Professor & Head
PG Department of Chemistry
Pachaiyappa's College For Men
Kanchipuram - 631 501.

[Signature]
31/01/2024
PRINCIPAL
(with seal)
PRINCIPAL
PACHAIYAPPA'S COLLEGE FOR MEN,
KANCHIPURAM-631 501.

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002.

STATEMENT OF EXPENDITURE IN RESPECT OF MAJOR RESEARCH PROJECT

1. Name of the Principal Investigator : **Dr. V. RAJENDRAN, M.Sc., Ph.D.,**
2. Dept. of Principal Investigator : Chemistry
 University/College : Pachaiyappa's College for Men,
 Kanchipuram, Tamil Nadu, India – 631501.
3. UGC Approval Letter No. and Date : **F. 42-356/2013 (SR) Dated 31.03.2013**
4. Title of the research project **“Ultrasound Assisted Multi-Site
 Phase-Transfer Catalysts in
 Heterogeneous Organic Reactions”.**
5. Effective Date of Starting the Project : 10-06-2023
6. a. Period of Expenditure : From 01.12.2014 to 31.03.2017
 b. Details of Expenditure :

S.No.	Name of the Item	Amount Allocated (Rs.)	Amount Approved (2 nd Installment)	Grant already Released	Total Grant
1	Books & Journal	20,000/-	-----	20,000/-	20,000/-
2	Equipment	2,25,000/-	-----	2,25,000/-	2,25,000/-

3	Honorarium	-----	-----	-----	-----
4	Project Fellow	4,91,200/-	1,78,080/-	2,64,000/-	4,42,080/-
5	HRA	-----	-----	-----	-----
6	Chemicals	2,00,000/-	80,000/-	1,00,000/-	1,80,000/-
7	Contingency	50,000/-	20,000/-	25,000/-	45,000/-
8	Hiring Services	-----	-----	-----	-----
9	Travel/field work	30,000/-	12,000/-	15,000/-	27,000/-
10	Overhead Charges	77,800/-	-----	77,800/-	77,800/-
11	Additional Grant	-----	-----	-----	-----
12	Total	10,94,000/-	2,90,080/-	7,26,800/-	10,16,880/-

It is certified that the grant of Rs. 2,90,080/- (Rupees Two Lakh Ninety Thousand Eighty only) out received from the University Grants Commission under the scheme of support for Major Research Project entitled “Ultrasound Assisted Multi-Site Phase-Transfer Catalysts in Heterogeneous Organic Reactions” vide UGC letter No. F. No. 42-356/2013 (SR) dated 31.03.2013 from which the sum of

Rs.1,80,280/- (Rupees One Lakh Eighty Thousand and Two hundred Eighty only) has been utilized (from 2nd installment) for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission.

Principal Investigator
(Signature with Seal)

Head of the Department
(Signature with Seal)

PRINCIPAL
(Signature with Seal)



Annexure-V

**UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002**

UTILIZATION CERTIFICATE

Certified that an amount of **Rs. 2,90,080/-** (Rupees Two Lakh Ninety Thousand and Eighty only) received from the University Grants Commission under the scheme of support for Major Research Project entitled “Ultrasound Assisted Multi-Site Phase – Transfer Catalysts in Heterogeneous Organic Reactions” vide UGC letter No. F. No. 42-356/2013 (SR) dated 31.03.2013 from which the sum of **Rs.1,80,280/-** (Rupees One Lakh Eighty thousand and Two hundred Eighty only) has been paid to Mr.P.Abimannan, Project Fellow dated 10-6-2016 from 2nd installment. Herewith, we enclosed, The Utilization Certificate.

Signature of Principal Investigator

Signature of HOD of the Department

Signature of Principal



Annexure-V

**UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002**

UTILIZATION CERTIFICATE

Certified that an amount of **Rs.2,90,080/-** (Rupees Two Lakh Ninety Thousand Eighty only) received from the University Grants Commission under the scheme of support for Major Research Project entitled “Ultrasound Assisted Multi-Site Phase – Transfer Catalysts in Heterogeneous Organic Reactions” vide UGC letter No. F. No. 42-356/2013 (SR) dated 22.03.2016 **Rs.1,80,280/-** (Rupees One Lakh Eighty Thousand and Two Hundred Eighty only) has been utilized (**2nd installment**) for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission.

PRINCIPAL INVESTIGATOR
(SIGNATURE WITH SEAL)

HEAD OF THE DEPARTMENT
(SIGNATURE WITH SEAL)

PRINCIPAL
(SIGNATURE WITH SEAL)



**PROFORMA FOR SUPPLYING THE INFORMATION IN
RESPECT OF THE STAFF APPOINTED UNDER THE
SCHEME OF MAJOR RESEARCH PROJECT**

UGC FILE NO. F: 42 – 356/ 2013 (SR)

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YEAR OF COMMENCEMENT: 31-03-2013

TITLE OF THE PROJECT : “Ultrasound Assisted Multi-Site Phase-Transfer Catalysts in Heterogeneous Organic Reactions”

1	Name of Principal Investigator	Dr. V. RAJENDRAN, M.Sc., Ph. D.,
2	Name of the University /College	PACHAIYAPPA’S COLLEGE FOR MEN, KANCHIPURAM, TAMIL NADU, INDIA – 631 501.
3	Name of the Project Fellow Appointed	Mr. P.ABIMANNAN, S/O. R.PACHAIYAPPAN, Kizhandi Main Street, Sempoondi Village, L.Endathur Post, Madurathagam Taluk, Chengalpattu District, Tamil Nadu – 603 406. Mobile No. 9361148089 PAN Number: BSLPA5353C Aadhar Number: 8854 6281 1661 DOB : 01-03-1987
4	Academic Qualification of Project Fellow	M.Sc., Chemistry
5	Date of Joining	June 2013
6	Date of Birth of Research Personnel	01.03.1987
7	Amount of HRA, if drawn	Nil
8	Number of Candidate applied for the post	7 (Seven Numbers)

CERTIFICATE

This is to certify that all the rules and regulations of UGC Major Research Project outlined in the guidelines have been followed. Any lapse on the part of the University will liable to terminate of said UGC Project.

Principal Investigator

Head of the Dept.

Registrar / Principal

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002.

**PROFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF SENDING THE FINAL
REPORT OF THE WORK DONE ON THE PROJECT**

1.	Title of the Project	Ultrasound Assisted Multi-Site Phase-Transfer Catalysts in Heterogeneous Organic Reactions
2.	Name and Address of the Principal Investigator	Dr. V. RAJENDRAN, M.Sc., Ph.D., Office: Associate Professor & Head, Department of Chemistry, Pachaiyappa's College for Men, Kanchipuram, Tamil Nadu, India - 631 501. Residential: No.1, Murugu Nagar, Nasarath Pettai, Kanchipuram, (Opposite to Pachaiyappa's College for Men), Tamil Nadu, India – 631 501.
3.	Name and Address of the Institution	Department of Chemistry, Pachaiyappa's College for Men, Kanchipuram, Tamil Nadu, India – 631 501. (Affiliated to University of Madras)
4.	UGC Approval Letter No. & Date	F. No. 42-356/2013 (SR) Dated 31.03.2013
5.	Date of Implementation	10 th June 2013
6.	Tenure of the project	3 Years (2013-2016)
7.	Total Grant Allocated	Rs. 11,30,800/-
8.	Total Grant Received	1 st Installment: Rs. 7,26,800/- 2 nd Installment: Rs. 2,90,080/-
9.	Final Expenditure	Annexure IX

10.	Title of the Project	Ultrasound Assisted Multi-Site Phase-Transfer Catalysts in Heterogeneous Organic Reactions.
11.	Objectives of the Project	Synthesis of different Organic Compounds under heterogeneous condition (organic phase & aqueous phase) using different single-site, multi-site phase-transfer catalysts and also insoluble polymer supported phase-transfer catalysts under ultrasonic irradiation condition. Polymerization of vinylic monomers also carried out under heterogeneous condition in the presence of phase-transfer catalysts and ultrasonic condition using water soluble initiators viz. Potassium perdisulphate, potassium peroxomonosulphate, ammonium perdisulphate etc.,
12.	Whether Objectives were Achieved	Yes. The progress of the project work has been published in International Journals.
13.	Achievements from the Project	Yes. The progress of the project work has been published in International Journals.
14.	Summary of the Findings	We synthesized various type of new single – site phase - transfer catalysts and also multi – site phase – transfer catalysts (Onium Salts). In this work we also prepared insoluble polymer supported phase – transfer catalyst(s). Using these different type of phase – transfer catalysts, we prepared various new organic compounds along with ultrasound irradiation condition. The kinetic study of various organic reactions under heterogeneous condition also studied. The activation energy, Free energy of activation, enthalpy of activation and entropy of activation were calculated. Using these factor we proposed different type of mechanism for each reactions. The catalysts and the products are characterized by NMR, IR and elemental analysis. We published very good research articles in high impact factor Journals.

15	Contribution to the Society	Ultrasound assisted organic compounds synthesis is one of the non-conventional method which is highly useful for preparation of various pharmaceutical drugs. This method also very useful to synthesis various vinylic polymers in friendly nature. Ultrasound along with onium salts enhance the rate of the organic reactions under aqueous/organic two phase system. It is also green technology and pollution free chemical reactions.
16	Whether any Ph. D. Enrolled/Produced out of the Project	One
17	No. of Publications out of the Project	<p>The progress of the project work has been published in different International Journals.</p> <ol style="list-style-type: none"> 1. Ultrasonics Sonochemistry 7 Articles IF: 8.05. 2. Journal of Chemistry & Chemical Sciences 3 Articles. IF: 5.73. 3. Chemical Sciences Review and Letters 1 (ISSN 2278 – 6783) 4. International Journal of Science and Research: One Article ISSN: 2319 – 7064.

PRINCIPAL INVESTIGATOR
(Signature with seal)

SIGNATURE OF THE HOD (With Seal)

PRINCIPAL
(Signature with seal)



Annexure-X

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

ASSESSMENT CERTIFICATE

It is certified that the proposal entitled "Ultrasound Assisted Multi-Site Phase-Transfer Catalysts in Heterogeneous Organic Reactions" vide UGC letter No. F. No. 42-356/2013 (SR) Dated 31.03.2013, Department of Chemistry, Pachaiyappa's College for Men, Kanchipuram, has been assessed by the Expert committee consisting the following members for submission to the University Grants Commission, New Delhi for financial support under the scheme of Major Research Project:

Details of Expert Committee:

Name of Expert	Name of Department	Signature with Date
1. Prof C. VANITHA	HOD OF CHEMISTRY R.V. GOVT. ARTS COLLEGE CHENGALPATTU-603 001	 31-01-24
2. C. SEBASTIAN ANTONY SELVAN	Dr. C. SEBASTIAN ANTONY SELVAN, M.Sc, M.Phil, Ph.D, B.Ed, PGDCA, M.A(HINDI), LMISTE Associate Professor of Chemistry, R.V. GOVT. ARTS COLLEGE, Chengalpattu - 603 001. Mobile : 94440 40115.	 31-01-2024

The proposal is as per the guidelines.

(PRINCIPAL)
(Seal)

It is certified that the final report has been uploaded on UGC-MRP portal on

It is also certified that final report, Executive summary of the report, Research documents, monograph academic papers provided under Major Research Project have been posted on the website of the University/College.

(Principal)

Seal



UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

ASSESSMENT CERTIFICATE

It is certified that the proposal entitled “Ultrasound Assisted Multi-Site Phase-Transfer Catalysts in Heterogeneous Organic Reactions” vide UGC letter No. F. No. 42-356/2013 (SR) Dated 31.03.2013, Department of Chemistry, Pachaiyappa’s College for Men, Kanchipuram, has been assessed by the Expert committee consisting the following members for submission to the University Grants Commission, New Delhi for financial support under the scheme of Major Research Project:

Details of Expert Committee:

Name of Expert	Name of Department	Signature with Date
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The proposal is as per the guidelines.

(PRINCIPAL)
(Seal)



UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

Final Report Assessment / Evaluation Certificate
(Two Members Expert Committee Not Belonging to the Institute of Principal Investigator)
(to be submitted with the final report)

It is certified that the final report of Major Research Project entitled “Ultrasound Assisted Multi-Site Phase-Transfer Catalysts in Heterogeneous Organic Reactions” vide UGC letter No. F. No. 42-356/2013 (SR) dated 31.03.2013 by Dr.V.Rajendran, Department of Chemistry has been assessed by the committee consisting the following members for final submission of the report to the UGC, New Delhi under the scheme of Major Research Project.

Comments/Suggestions of the Expert Committee:-

The project was successfully completed and the findings were Published in highly reputed Journals with high impact factors.

Name & Signatures of Experts with Date:-

Name of Expert	University/College Name	Signature with Date
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1.

2.

It is certified that the final report has been uploaded on UGC-MRP portal on

It is also certified that final report, Executive summary of the report, Research documents, monograph academic papers provided under Major Research Project have been posted on the website of the University/College.

(Principal)

Seal



**UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI - 110 002**

Final Report Assessment / Evaluation Certificate
(Two Members Expert Committee Not Belonging to the Institute of Principal Investigator)
(to be submitted with the final report)

It is certified that the final report of Major Research Project entitled "Ultrasound Assisted Multi-Site Phase-Transfer Catalysts in Heterogeneous Organic Reactions" vide UGC letter No. F. No. 42-356/2013 (SR) dated 31.03.2013 by Dr.V.Rajendran, Department of Chemistry has been assessed by the committee consisting the following members for final submission of the report to the UGC, New Delhi under the scheme of Major Research Project.

Comments/Suggestions of the Expert Committee:-

The project was successfully completed and the findings were Published in highly reputed Journals with high impact factors.

Name & Signatures of Experts with Date:-

Name of Expert	University/College Name	Signature with Date
1. P. VANITHA	HOD OF CHEMISTRY R.V. GOVT. ARTS COLLEGE CHENGALPATTU-603 001	 31-01-24
2. C. SEBASTIAN ANTONY SELVAN	Dr. C. SEBASTIAN ANTONY SELVAN, M.Sc, M.Phil, Ph.D, B.Ed, PGDCA, M.A (HINDI), LMISTE Associate Professor of Chemistry, R.V. GOVT. ARTS COLLEGE, Chengalpattu - 603 001. Mobile : 94440 40115.	 31-01-2024

FINAL REPORT
OF THE
UGC MAJOR RESEARCH PROJECT
F. No. 42-356/2013 (SR) Dated 31.03.2013

**ULTRASOUND ASSISTED MULTI – SITE PHASE -TRANSFER
CATALYSTS IN HETEROGENEEOUS ORGANIC REACTIONS**

Submitted to

THE UNIVERSITY GRANTS COMMISSION

Bahadur Shah Zafar Marg New Delhi - 110 002

By

Dr. V.RAJENDRAN Principal Investigator

**DEPARTMENT OF CHEMISTRY, PACHAIYAPPA'S COLLEGE FOR
MEN, KANCHIPURAM,
TAMIL NADU, INDIA – 631 501**

INTRODUCTION

The development of new organic synthetic methods that are more environmentally benign has been propelled by the growing importance of green chemistry in organic synthesis. Green chemistry, by the design of environmentally compatible chemical reactions, offers the tools to approach pollution and sustainability concerns at the source. In order to be eco-friendly, or *green*, organic syntheses must meet, if not all, at least some of the following requirements: avoid waste, be atom efficient, avoid use and production of toxic and dangerous gases and chemicals, produce compounds which perform better or equal to already existing ones and are biodegradable, avoid auxiliary substances (e.g., solvents), reduce energy requirements, use renewable materials, use catalysts rather than stoichiometric reagents.

Chemical transformations, which produce in addition to the desired product large amounts of byproducts and waste, are less desirable. The proficient design of chemical transformations can reduce the required energy input in terms of mechanical, thermal, and other energy inputs, and the associated environmental impacts of excessive energy usage. In pharmaceutical and agrochemical industries, the need for selective transformations is even larger since delicate bioactive compounds are often not robust enough to stand the conditions used in bulk chemistry. It is important to evaluate the hazardous properties of all substances necessarily being generated from the transformation, it is important to evaluate the hazardous properties of all starting materials and reagents that are added in a synthetic transformation. Selective transformations using catalytic processes eliminate the requirement of stoichiometric auxiliary reagents in many current processes and can eventually help to reduce the amounts of waste. In addition, they are able to carry out the necessary synthetic transformation in a more environmentally benign way.

For the increasing environmental and economical concerns in recent years, it is now essential for chemists to search environmentally benign catalytic reactions as many as possible. Although the fundamental principles of catalysis are identical for the different approaches, three scientific areas viz., heterogeneous, homogeneous and biocatalysis have emerged. This historic distinction results from the different techniques and research methodologies applied in the corresponding disciplines, which provide most of the input to catalyst development and process design.

Catalysis, which has played such a vital role in the success of the industry in the 20th century, will also play a very important role in the new greener industry of the new century. Catalysis can not only help to green chemical

processes (e.g., by replacing reagents or by enabling more efficient processes) but the demonstration of their value-to reduce the environmental impact of processes and reduce the costs of the processes-will catalyze the greening of chemistry.

The term "Catalysis" coined in 1835 to characterize the phenomenon in which the addition of a small amount of a foreign substance caused a large increase in chemical change without itself getting consumed. Catalysis has been an intriguing since then and continuing efforts have been made to understand and utilize the phenomenon for practical purposes. This has resulted in numerous inventions during this century, which have been responsible in improving the quality of human life.

Transformations of starting materials into desired final products of practical applications such as pharmaceuticals, plant protection agents, photographic chemicals, dyes, monomers etc., usually require a number of chemical operations in which catalysts, additional reagents, solvents, etc. are used. For successful completion of a reaction it is necessary that the reactants collide with each other as much as possible. However it is often noticed that these reactions are immiscible in nature. To reduce the predicament of immiscibility it is necessary to ferry water soluble anionic reactant into organic soluble reactant / organic phase. Classical methods to overcome this immiscibility include use of protic/aprotic solvents, high stirring speed, high temperature etc. Nevertheless these methods have its own shortcomings viz., high energy consumption, production of byproducts and difficulty in purification together with environmental pollution. As a consequence, these techniques are industrially unattractive, constrained and polluting.

Phase Transfer Catalysis

A plausible technique now widely known as "phase transfer catalysis" (PTC) developed for overcoming the encounter problem due to the mutual insolubility of aqueous phase with organic phase appeared in the late 1970s. This key green approach, leading to waste minimization, utilizes water as the solvent and is applied and applicable to a great variety of reactions in which inorganic and organic anions and also carbenes react with organic substrates. It makes use of heterogeneous two-phase systems-one phase (water) being a reservoir of reacting anions or base for

generation of organic anions, whereas organic reactants and catalysts are located in the second, organic phase. The reacting anions are continuously introduced into the organic phase in the form of lipophilic ion-pairs with lipophilic cations supplied by the catalyst. For example the nucleophilic aliphatic substitution reaction of an aqueous sodium cyanide solution with 1-chlorooctane does not ordinarily take place because of immiscibility. By the addition of catalytic amount of the quaternary onium salts, viz., (ammonium, phosphonium etc.) cyanide ions are ferried into the organic phase from the water phase and 1-cyanooctane formed quantitatively in a matter of minutes.

Phase transfer catalytic process involves two important steps:

- (1) The transfer step in which the reactant anion is transferred from the aqueous or solid phase into the organic phase and the product anion is transferred from the organic phase into the aqueous or solid phase.
- (2) The intrinsic reaction step in which the product is formed in the organic phase. The optimization of each of these steps is a function of several variables, the most important of which is the structure of the phase transfer catalyst.

Classification of PTC

PTC reactions can be broadly classified into two main classes: soluble PTC and insoluble PTC. Each class, depending on the actual phases involved, reactions are further classified as liquid-liquid PTC (LLPTC), gas-liquid PTC (GLPTC), and solid-liquid PTC (SLPTC). In some cases, the Phase-Transfer Catalyst forms a separate liquid phase, and this variant of PTC can be grouped along with traditional insoluble PTC, where the Phase-Transfer Catalyst is immobilized on a solid support. The insoluble solid supports may be Inorganic and Organic chemical in nature. Other nontypical variants of PTC include inverse PTC (IPTC) and reverse PTC (RPTC) via a reverse transfer mechanism.

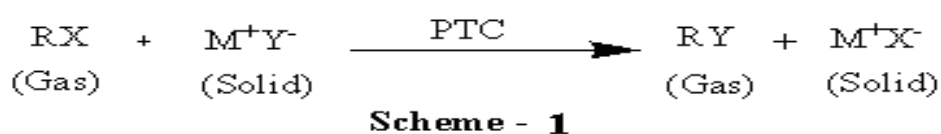
Solid-Liquid Phase Transfer Catalysis (SLPTC)

A major drawback in liquid-liquid PTC reactions involving transfer of anionic reactant from the aqueous phase into the organic phase is the coextraction of hydrated water molecules. To cope with the problem of anion deactivation caused by the water of hydration, it is reasonable to perform the PTC reactions with solid salts. This methodology is called “solid-liquid phase transfer catalysis”, which corresponds to reactions taking place with an organic reagent soluble in a solvent and a solid substrate insoluble in that solvent. However on the addition of phase

transfer agents viz., crown ether, cryptand or chelant, the solid substrate solubilized which results in successful completion of the reaction. Although, more applications of PTC have been reported in liquid-liquid systems, there is a distinct advantage in operating in the solid-liquid mode in some reactions since the elimination of the aqueous phase lowers the degree of hydration of the ion pair, leading to an increase in its reactivity. Thus, higher selectivity and yields are sometimes obtained by operating in the solid-liquid mode as compared to operation in the liquid-liquid (aqueous / organic) mode.

Gas-solid phase transfer catalysis

In Gas-solid phase transfer catalysis, a gaseous alkyl halide is passed over a catalytic column composed of a salt, a solid support and a phase transfer catalyst, resulting in substitution product. The phase transfer catalyst was either free or immobilized on a silica matrix which results in the synthesis of alkyl iodides and esters.



Gas-Liquid Phase Transfer Catalysis (GLPTC)

Gas-liquid phase transfer catalysis, offers great potential in biphasic catalysis. GLPTC involves the use of PTC in gas-liquid-solid systems, where the organic substrate is in a gaseous form and is passed over a bed consisting of the inorganic reagent or some other solid reagent/cocatalyst (commonly, solid K_2CO_3), in solid form, or an inert inorganic support both of which are coated with a phase transfer catalyst in its molten state. Although, strictly, this is a gas-liquid-solid triphase system, it has traditionally been referred to as GLPTC. Advantages of GLPTC include ease of adaptation to continuous flow operation (with the gaseous reagents flowing continuously over the solid bed), absence of organic solvent since the organic substrate is present in gaseous form, ease of recovery of the PT catalyst as it is directly loaded onto the solid bed, and better selectivity than LLPTC in some cases. A wide variety of reactions can be

carried out under GLPTC conditions including a special class of reactions using dialkyl carbonates typically dimethyl carbonate (DMC). In activated methylene compounds, DMC acts first as a carboxymethyl agent that allows protection of methylene active derivatives and permits nucleophilic displacement to occur with another molecule of DMC. This method of synthesis has been piloted for the synthesis of anti-inflammatory drugs like ketoprofen in Belgium. Similarly, methylation of aroxylacetonitriles and methyl-2-aoxyacetates using DMC gives upto 98% of the monomethylated derivatives, which are widely used in the synthesis of biologically active compounds and plant growth regulators. Other reactions carried out using GLPTC include halogen exchange, esterifications, etherifications, isomerizations, alkylations, transhalogenations, Wittig and Horner reactions, and the synthesis of primary alkyl halides from primary alcohols.

MECHANISMS OF PHASE TRANSFER CATALYSIS

Numerous two-phase catalytic reactions such as C-, O-, N-, and S-alkylations, generation of carbenes, isomerization, H/D isotope exchange etc., are carried out in the presence of strong alkali metal hydroxides. Another category of PTC methodology is hydroxide initiated reactions. Based on experimental observations two distinct mechanisms viz., extraction mechanism and the interfacial mechanism.

Classification of Phase-Transfer Catalysts

(a) Quaternary onium salts:

These are organic soluble catalysts for extracting anions into organic phase. Many quaternary ammonium, phosphonium, and arsonium salts are able to transfer anion from aqueous to organic phase. Quaternary ammonium salts are the most frequently used due to their cost and availability. The criteria for selecting a quaternary onium salt as a PTC catalyst include extraction of the catalyst and reaction species into the organic phase and anion-activating ability, accessibility, and stability of the quaternary salt.

In general, Quaternary phosphonium salts are more stable than ammonium salts. Variety of quaternary onium salts can be prepared and also are commercially available. Tetra butyl ammonium halide salts $[(n\text{-Bu})_4\text{N}^+\text{X}^-]$, are

usually stable and well partitioned into the organic phase to be good catalysts for many synthetic organic reactions. The quaternary arsonium salts ($R_4As^+X^-$), have been generally found to be poor phase transfer catalysts compared with the ammonium and phosphonium salts. Some examples of well known onium salts include Aliquat 336, tetraalkylammonium halide (TAAX, symmetrical in nature), benzyltrialkylammonium halide (unsymmetrical), triphenylbenzylphosphonium chloride, tetraphenylarsonium chloride, triphenylsulfonium chloride, 4-aminopyridinium salts, and chiral N-(4-trifluoromethyl) benzylcinchonium bromide etc.. Crown ethers and cryptands include 18-Crown-6, dibenzo-18-Crown-6, dicyclohexane-18-Crown-6, and [2.2.2]-cryptand also act as phase transfer agent.

Insoluble phase -Transfer Catalysts

Insoluble phase-transfer catalysts, also known as triphase catalysts, provide an attractive means of recycling the catalyst after the reaction. In addition to easy reparability of the catalyst, they enable reactions to be carried out in the continuous mode. Insoluble PTC catalysts can be grouped into three categories, namely, the resin bound, the inorganic solid bound, and the third-liquid-phase catalysts.

(a) Resin-Bound Phase Transfer Catalysts

The term “polymer-supported” PTC to describe the PTC reactions within the polymer phase. Resin-bound PTC catalysts include polymer - NR_3^+ , $-PPh_3^+$, $-SR_2^+$ -crown ether, -cryptand, -azacrown, -PEG (Poly Ethylene Glycol) etc. In contrast to ordinary PTC reactions using soluble catalysts, PTC reactions using resin-bound catalysts require that both reactants diffuse to active PTC sites or the resin surface or to active sites inside the resin bulk phase for the rate limited reactions.

(b) Inorganic Solid-Bound Phase Transfer Catalysts

Inorganic Solid-Bound Phase Transfer Catalysts are of two types viz., i) the “adsorption type catalysts” made by simple adsorption of quaternary salts on organophilic clays, and ii) the “chemically bonded-type catalysts” made by chemical attachment of PTC functional groups to solid inorganic supports. Adsorption of long-chain quaternary ammonium cations on particular forms of smectite clay is generally successful and commercially useful.

Selected Synthetic Applications of Phase Transfer Catalysts

Since the present work deals with C-C bond formation and dichlorocarbene addition reactions catalysed by PTC, great emphasis will be laid in application related to these types of reactions. Nevertheless, other synthetic application will be dealt very briefly.

Salient features of MPTC

In general, MPTC offers the following advantages when compared with classical single site phase transfer catalyst:

- (i) provides greater PTC activity on a PTC site per gram of PTC needed for catalytic activity basis and
- (ii) effective for a particular synthetic transformation under milder reaction conditions.

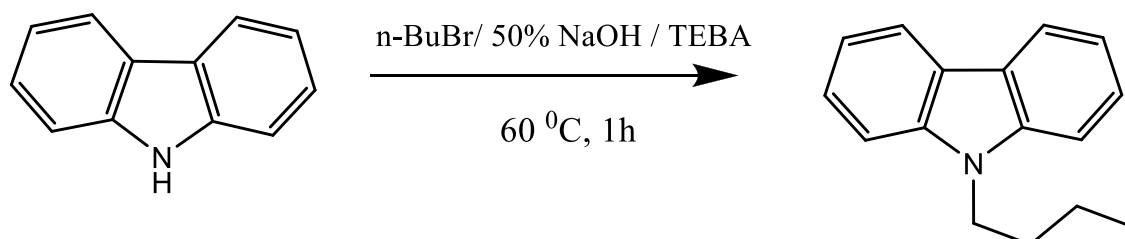
From the above mentioned facts, it is obvious that the MPTC's are more efficient and also smaller proportion of it is enough for a successful transformation.

Ultrasound in PTC systems

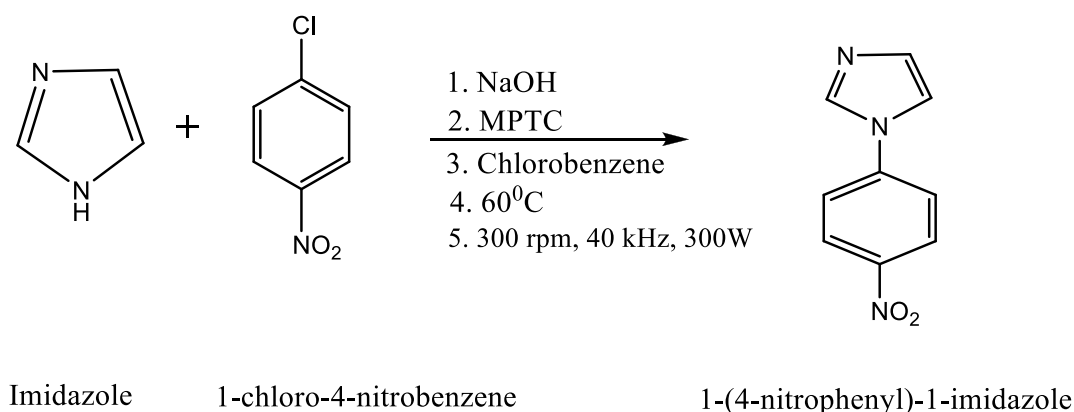
Ultrasound (in the 20-100 kHz range) has been found to enhance reactions in both liquid-liquid and solid-liquid heterogeneous systems Lindley and Mason ¹⁶. The chemical effects of ultrasound, attributed to intense local conditions generated due to cavitation, phenomena. In LLPTC systems, cavitation collapse near the liquid-liquid interface disrupts the interface and impels jets of one liquid into the other, forming fine emulsions, and leading to a dramatic increase in the interfacial contact area across which transfer of species can take place. On the other hand, in SLPTC systems the implosion of the cavitation bubbles and the concurrent phenomenon of microstreaming of solvent jets onto the solid surface can also lead to fragmentation of the solid particles, increasing the area available for mass transfer. Sonication also sweeps away reactive intermediates and products from the solid surface, renewing the surface for reaction. Ultrasound also creates a turbulent boundary layer near the solid surface, thereby reducing the film thickness and enhancing mass transport across the solid-liquid interface.

N-Alkylation

Many drugs, pesticides, natural products and synthetically precious substances are derivatives of heterocyclic compounds. It is therefore not surprising that almost immediately after the birth of PTC, this method has been used in the study of heterocyclic compounds. The N-alkylation of pyrrole, indole, imidazole, morpholine and carbazole. These heterocycles react with halides in the presence of 50 % aqueous NaOH and TEBA (Benzyltriethylammonium Chloride) affording exclusively N-alkylated products in good yield.



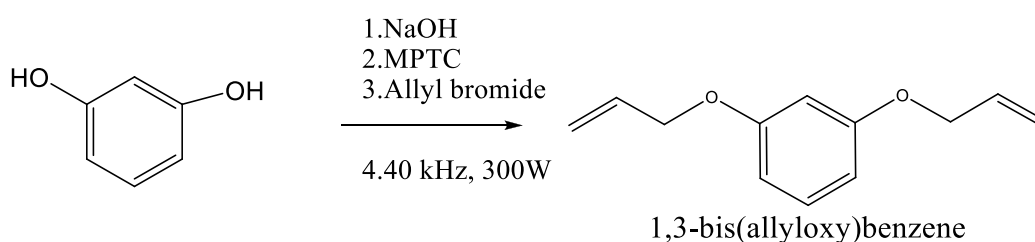
We reported the nitroarylation of imidazole catalyzed by a new novel dual-site phase-transfer catalyst (Multi-site Phase-Transfer Catalyst, MPTC) was carried out in an alkaline solution / imidazole in chlorobenzene two-phase medium with ultrasonic irradiation (40 kHz, 300W). This new synthesized phase-transfer catalyst, N¹,N⁶-diethyl-N¹,N¹,N⁶,N⁶-tetraisopropylhexane-1,6-diaminium dichloride (MPTC), which possesses two-site activity, was obtained from the reaction of 1,6-dichlorohexane and N-ethyl-N-isopropylpropane-2-amine.



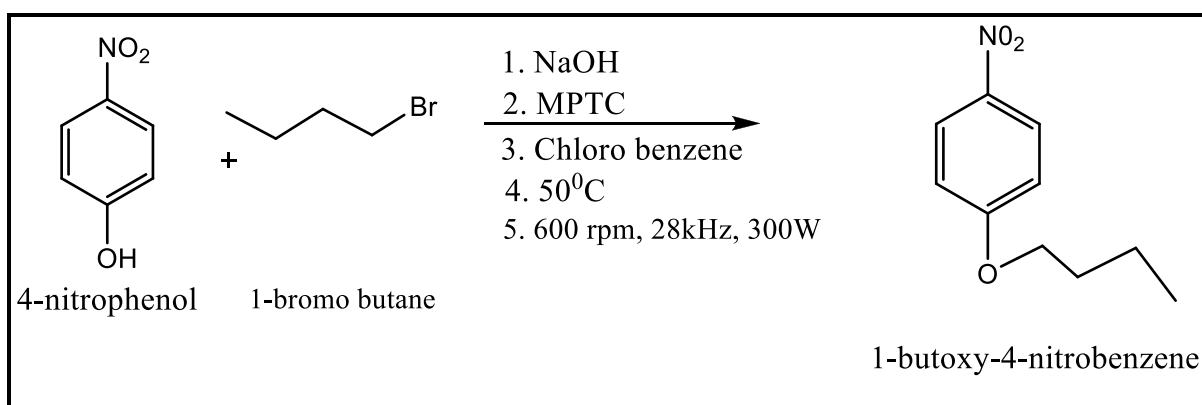
Evolution of Multi-site Phase Transfer Catalysts

Successful synthetic application of a phase transfer catalyst (in industries) mainly depends on scale of economy, efficiency, low energy requirements etc. Once its viability as efficient catalyst is demonstrated, it leads to its utilization in industrial scale preparation of organic compounds. Usually large amount of “single-site” quaternary ammonium or phosphonium salt must be used as a phase-transfer catalyst in the substitution reaction, in order to complete any transformation in an economically feasible time period. In general, utilities of commercially available single site soluble and insoluble PTC is narrow due to their low efficiency in the reaction. To circumvent these synthetic deficiencies, novel “multi-site” phase transfer catalysts have been developed which consists of poly catalytic active site i.e., more than one active site.

We also reported the preparation of 1,3-bis(allyloxy)benzene was successfully carried out by resorcinol with allylbromide using aqueous sodium hydroxide and catalyzed by a new multi-site phase-transfer catalyst (MPTC) viz., 1,3,5,7-tetrabenzylhexamethylenetetraammonium tetrachloride, under ultrasonic (40 kHz, 300 W) assisted organic solvent condition. Under ultrasound irradiation (40 kHz, 300 W) in a batch reactor, it shows that the overall reaction greatly enhanced with ultrasound irradiation than without ultrasound. It provides a method to synthesize nitro aromatic ethers by ultrasound assisted liquid–liquid multi-site phase-transfer catalysis condition.



In another research work we reported the preparation of 1-butoxy-4-nitrobenzene was successfully carried out by 4-nitrophenol with n-butyl bromide using aqueous potassium carbonate and catalyzed by a new multi-site phase-transfer catalyst (MPTC) viz., N^1,N^4 -diethyl- N^1,N^1,N^4,N^4 -tetraisopropylbutane-1,4-diammonium dibromide, under ultrasonic (40 kHz, 300 W) assisted organic solvent condition. The pseudo first-order kinetic equation was applied to describe the overall reaction. Under ultrasound irradiation (40 kHz, 300 W) in a batch reactor, it shows that the overall reaction greatly enhanced with ultrasound irradiation than without ultrasound. It provides a method to synthesize nitro aromatic ethers by ultrasound assisted liquid–liquid multi-site phase-transfer catalysis condition.



The advantages of PTC lie in the elimination of organic solvents and dangerous or expensive bases, together with simplicity of the procedure, and its high yields with purity of the products. This is particularly attractive due to the increasing number of environmental laws since PTC processes always produce much less industrial waste and consume less energy than traditional processes. With many salient features, these days PTC has been employed not only in organic chemistry but also in inorganic chemistry, photochemistry, electrochemistry, polymer chemistry, etc.,

Extensive industrial applications of phase transfer catalysis, in the manufacture of organic intermediates, fine chemicals etc., under mild conditions seem almost unlimited in scope, making it an attractive as well as a challenging field. Furthermore, the PTC were widely used to carry out the tedious reaction like alkylation, addition, etc.,

We anticipate that the higher the number of catalytic active site present in a molecule the higher the catalytic efficiency, the reaction yield and hence the economy of the reaction process. The development of novel phase transfer catalysts is an important challenge and is one of the reasons for the recent surge of interest in phase transfer catalysis.

From the literature we infer that the kinetics of C-alkylation was not widely studied. It was therefore proposed to investigate C-alkylation of isobutyraldehyde under “multi-site” phase transfer catalyst condition.

The effect of fundamental physical and chemical parameters such as stirring speed, catalyst amount, hydroxide ion concentration, substrate concentration and temperature which control the catalytic activity will be studied. The findings of the present investigation would help in designing various “multi-site” catalysts with improved activity rendering organic reaction incredibly simple employing practically desirable parameters in laboratory syntheses as well as large scale industrial process.

The conditions employed for the conventional phase transfer catalysts are drastic, and multifariously detrimental and hence it was our main aim to probe comparatively convenient parameters for our investigation thereby establishing the superiority of the multi-site phase-transfer catalyst (MPTC).

1. To synthesize phase-transfer catalysts containing one di-site onium sites (active sites).
2. To characterize newly synthesized MPTC's through various analytical techniques like ^1H NMR, ^{13}C NMR, etc.
3. We done the following organic reactions viz.,

C-Allylation of isobutyraldehyde,

O-Allylation of 4-nitrophenol, &

O-Alkylation of 4-nitrophenol

4. We examine the complete kinetics C-alkylation of isobutyraldehyde using the newly synthesized phase-transfer catalyst(s) with ultrasound irradiation condition (40 kHz, 300W). The effect of fundamental physico chemical parameters such as stirring speed, phase-transfer catalyst concentration, hydroxide ion concentration, substrate concentration and temperature, which control the catalytic activity of the organic reactions under heterogeneous condition.
5. We also evaluated pseudo first-order rate constants of the above organic reactions.
6. Based on the observed kinetic and thermodynamic results, suitable mechanisms were proposed. It was also proposed to evaluate the overall energy of activation (E_a) and other thermodynamic parameters, viz., entropy of activation (ΔS^\ddagger), enthalpy of activation (ΔH^\ddagger) and free energy of activation (ΔG^\ddagger), were also calculated.

EXPERIMENTAL METHODS

a). Gas Chromatographic analyses were performed on Varian model 3700, with flame ionization detector and Vista CDS 401 data station. The column used was 5% SE-30 Chrom WHP 80/100, 2M 1/8'' stainless steel tube.

b). The ^1H NMR and ^{13}C NMR were recorded on Bruker 300 MHz spectrometer. The chemical shifts are reported in ppm (δ) with TMS as internal standard and coupling constant (J) are expressed in Hertz.

c). Ultrasonification was carried out on ultrasonic cleaner tank is 48 cm x 28 cm 20 cm with liquid holding capacity of 5 litres (Ultrasonic water bath, Equitron, Media Instrument Manufacturing Company, Chennai, India-600

004). The reactor has an operating Frequency of 28 and 40 kHz with an output of 300 W.

d). All melting points were determined using a Tempo melting point apparatus by open capillary tube method and were uncorrected.

e). TLC was performed on silica powder on glass plate and detected under Iodine chamber.

f). Column chromatography was carried out silica gel (Merck, 100-200 mesh) as Stationary phase.

j). The organic extracts of crude products were dried over anhydrous magnesium sulphate or sodium sulphate.

Thermostat

The syntheses of various phase-transfer catalysts as well as the kinetic experiments were carried out in a cylindrical glass tank of diameter 30 cm and 20 liter capacity equipped with a overhead mechanical stirrer, a heating coil and a thermometer. The temperature of the thermostat was controlled to the precision $\pm 0.1^{\circ}\text{C}$ by means of a constant thermometer and a FHP motor control unit supplied by Raga Industries (Chennai).

RPM control mechanical stirrer

Reaction mixtures were stirred by a mechanical stirrer (Tullu F.H.P. motor, U.P.National Manufacturers Pvt. Ltd., Varanasi). Stirring speed was measured by a Tachometer (Teclock; Japan).

Reaction Vessel

The reaction vessel used for kinetic experiments was a 250 mL three-necked round-bottomed flask (Pyrex glass) fitted with a stirrer and a double-walled condenser.

Reagents

Water

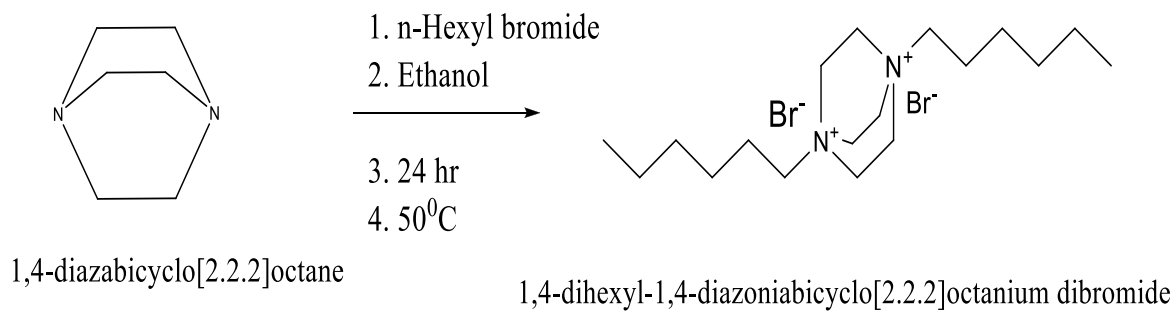
The distilled water obtained from a still was re-distilled over alkaline potassium permanganate in an all glass quick-fit Pyrex set-up. This double distilled water was used for all the kinetic experiments.

Ethanol (AR, SRL) was stirred with phosphorous pentoxide (more effective desiccant than calcium hydride). The solvent was decanted from the solid and was distilled and collected at boiling point 81- 82°C. Other reagents like sodium hydroxide (SDS), 4-Nitro Phenol (SDS), naphthalen-1-ol (CDH), Allyl bromide (SDS), drybenzene (SDS), and ether (Qualigens) were used as such without further purification

Synthesis of MPTC

Synthesis of a new dual-site phase-transfer catalyst (MPTC)

A mixture of 1,4-diazabicyclo[2.2.2]octane (DABCO, 5 g, 44.58 mmol), n-hexyl bromide (18 g, 15.3 mL, 109.04 mmol) and 80 mL of ethanol was placed in a 250 mL three-necked round-bottomed Pyrex flask. The reaction was carried out at 60 °C for 24 h and was gently refluxed in the nitrogen atmosphere. The solvent was then completely removed under vacuum and onium salt, i.e., 1,4-dihexyl-1,4-diazoniabicyclo[2.2.2]octanium dibromide, (MPTC; **Scheme 1**) was washed with n-hexane (4 x 25 mL). The Colorless jelly liquid was stored in CaCl₂ desiccators. Yield: 92%;



^1H NMR (300 MHz, D_2O): 0.878–0.926 (t, 3H $-\text{CH}_3$ in hexyl group), 1.090–1.110 (d, 6H $-\text{CH}_2$ in hexyl group), 1.708–1.811 (m, 2H, $\text{N}^+-\text{CH}_2-\text{CH}_2$ in hexyl group), 3.388–3.444 (t, 2H, N^+-CH_2 hexyl group) 3.966 (s, 6H, the cyclic N^+-CH_2).

^{13}C NMR (75 MHz, D_2O): 12.90 ($-\text{CH}_3$), 18.94 ($-\text{CH}_2-\text{CH}_3$ in hexyl carbon), 23.52 ($-\text{CH}_2-\text{CH}_2-\text{CH}_3$ in hexyl group carbon), 26.22 ($\text{N}^+-\text{CH}_2-\text{CH}_2$ in hexyl group carbon) 31.06 ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ – in hexyl group carbon), 51.16 (N^+-CH_2 in hexyl group carbon), 65.13 (N^+-CH_2 cyclic Carbon).



Current Data Parameters
NAME VB-MM-3
EXPNO 1
PROCNO 1

#2 - Acquisition Parameters

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PULPROG zg30
TD 65536
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SWH 6172.839 Hz
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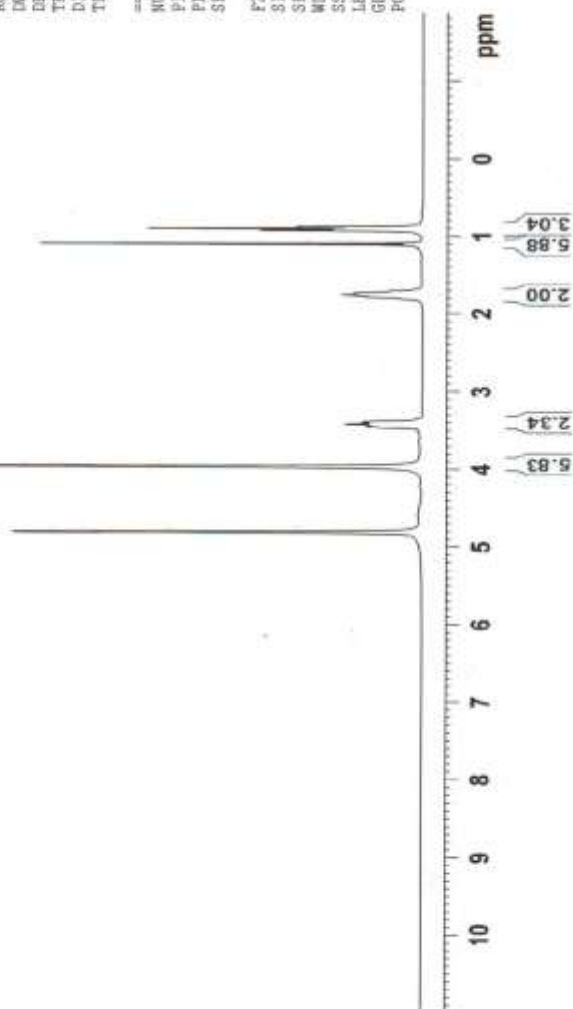
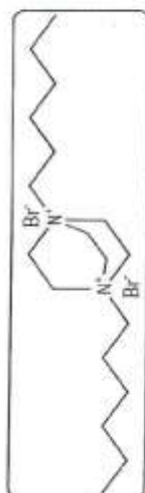
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PL1 0.00 dB
SFO1 300.1318534 MHz

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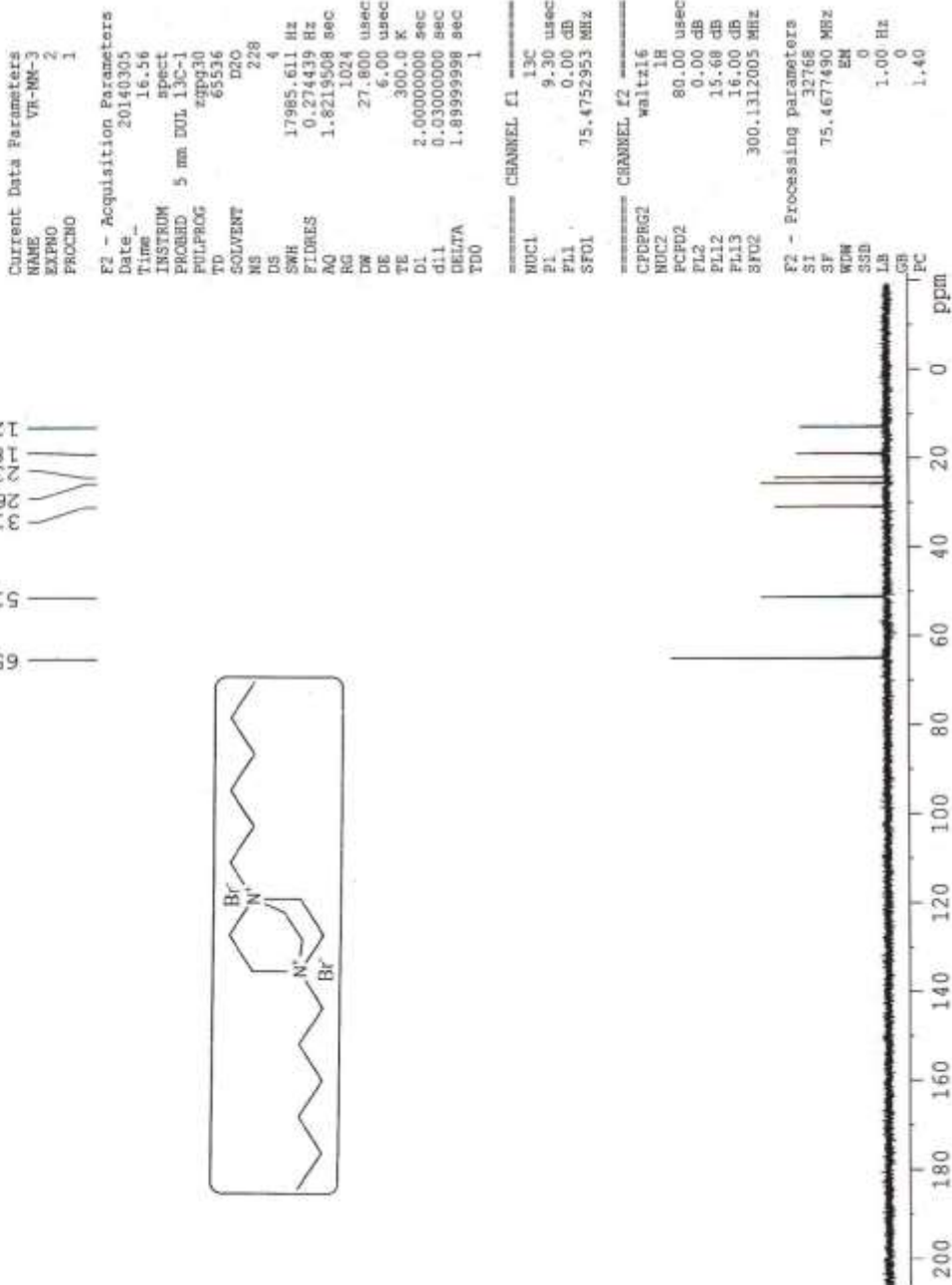
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SSB 0
LB 0.30 Hz
GB 0
PC 1.00

3.966
3.444
3.416
3.388
1.811
1.787
1.761
1.735
1.708
1.110
1.090
0.926
0.902
0.878



^1H NMR Spectra of
1,4-dihexyl-1,4-
diazoniabicyclo[2.2.
2.]octanium
dibromide

^{13}C NMR Spectra of
1,4-dihexyl-1,4-
diazoniabicyclo[2.2.
2.]octanium
dibromide



Synthesis of 2,2-dimethyloctanal

To the mixture of potassium carbonate (15 g) in water (3mL) and the newly synthesized MPTC (0.5 gm), isobutyraldehyde (13.88mmol) was added under overhead stirring to generate the anion. Then

hexylbromide (15.15mmol) in chlorobenzene (30 mL) was added slowly. The reaction mixture was heated at 50°C for 6 hours with vigorous stirring. The crude product was isolated by simple extraction with diethyl ether (3 x 25 mL). The organic layer was collected and the solvent was evaporated under reduced pressure. The crude product was

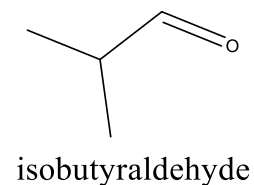
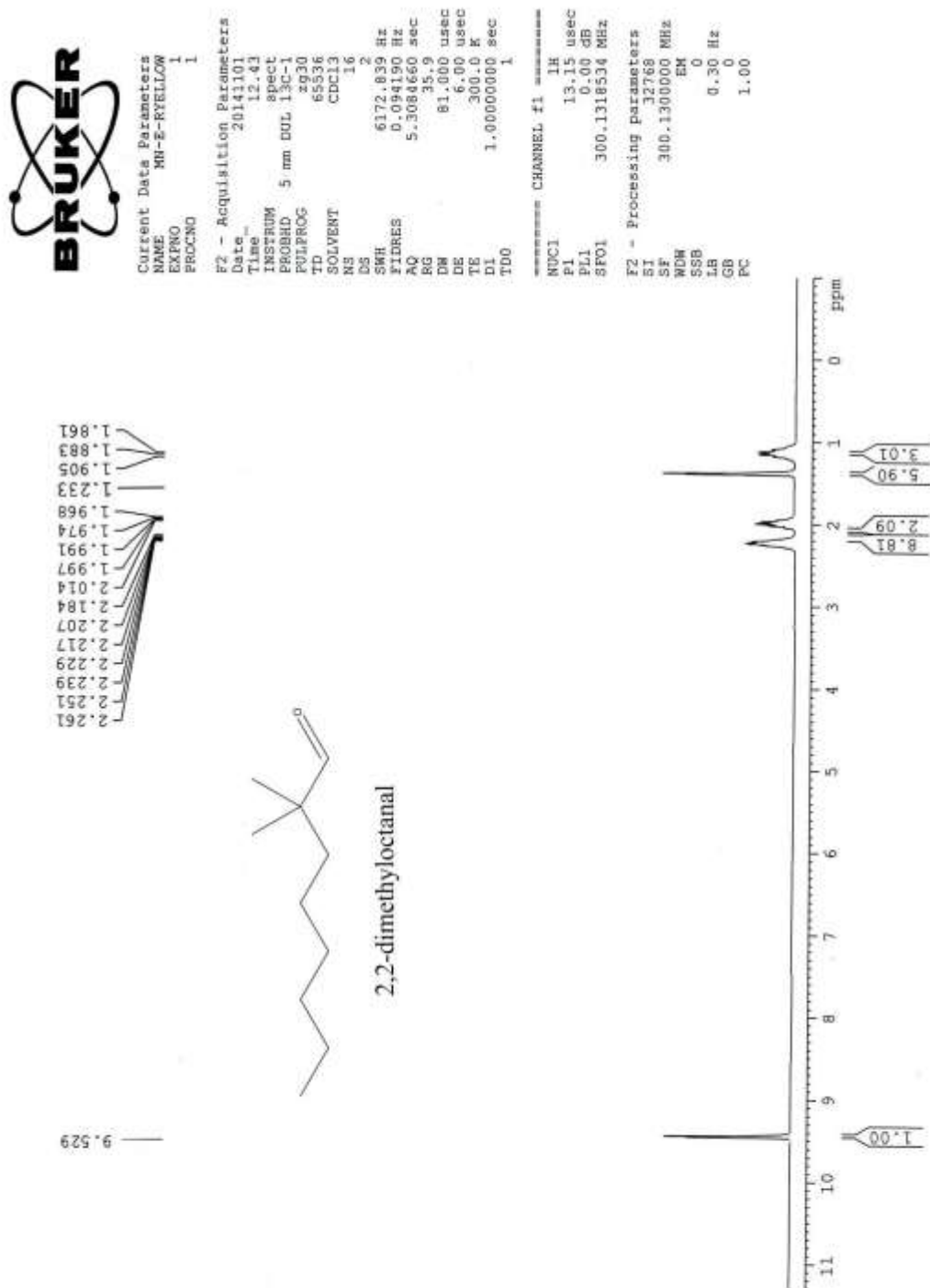
chromatographic (SiO₂) employing hexane: ethyl acetate (9:1) as an eluent to obtain a pure monoderivative. The identity of the product was confirmed by ¹H NMR and ¹³C NMR spectra of the product. Yield: 91%;

¹H NMR (300 MHz, CDCl₃):

δ 1.861-1.905 (t,3H, CH₃), 1.233 (s,6H,C-(CH₃)₂), 1.968-2.014(m,2H,-CH₂- C-(CH₃)₂-CHO), 2.184-2.261(m,8H, CH₂), 9.529(s,1H,-CHO).

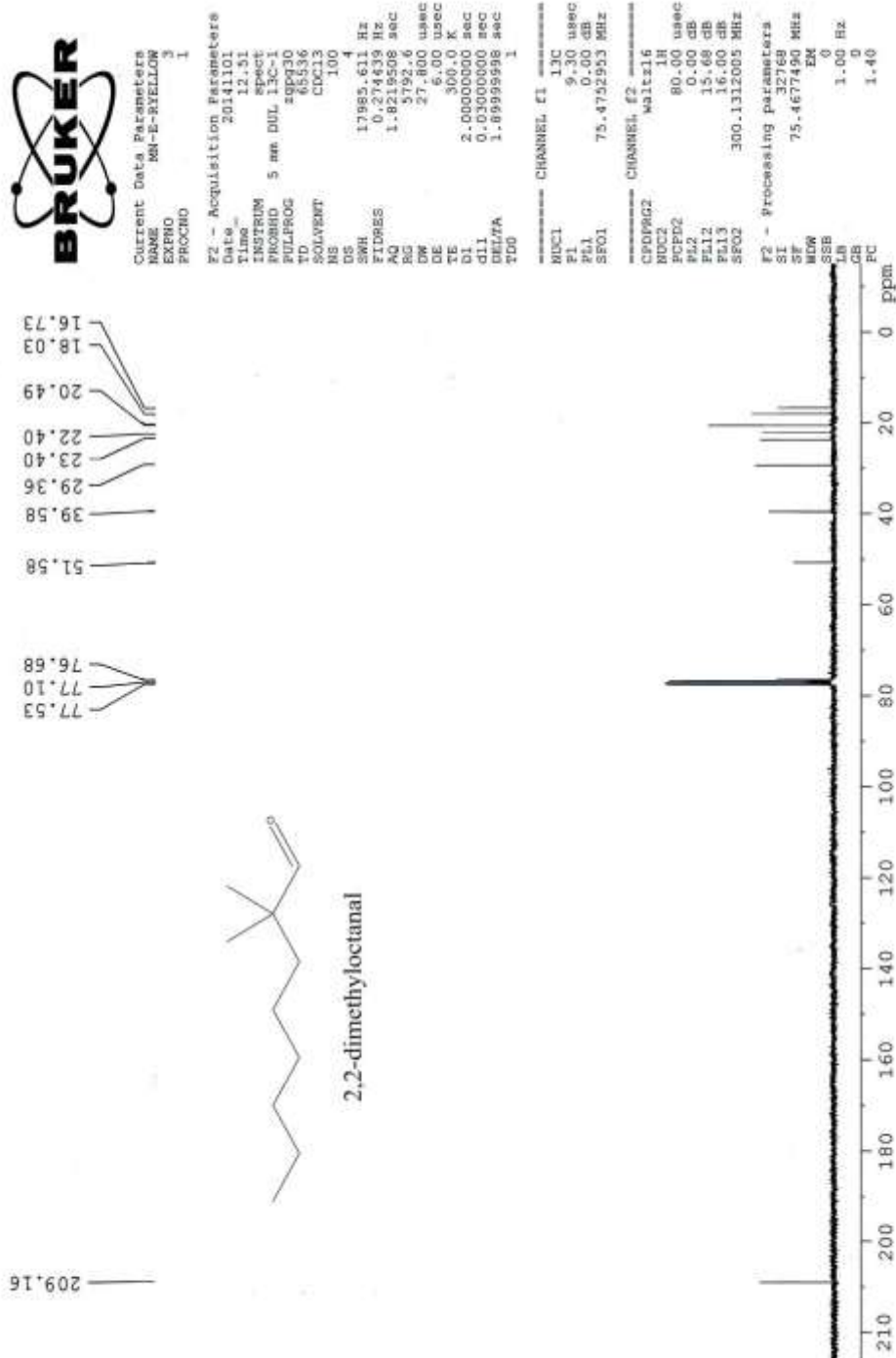
¹³C NMR (75MHz, CDCl₃):

δ.
16.73,18.03,20.49,22.40,2
3.40,29.36,39.58,51.58,20
9.16.



¹H NMR Spectra of 2,2-dimethyloctanal

¹³C NMR Spectra of 2,2-dimethyloctanal



Synthesis of 1-(allyloxy)-4-nitrobenzene

To the mixture of potassium carbonate (15 g) in water (3 mL) and the newly synthesized MPTC (3mol%), 4-Nitrophenol (0.5 g) was added under overhead stirring to generate the anion. Then allylbromide (3mL) in chlorobenzene (30 mL) was added slowly. The reaction mixture was heated at 50°C for 6 hours with vigorous stirring. The crude product was isolated by simple extraction with diethyl ether (3 x 25 mL). The organic layer was collected and the solvent was evaporated under reduced pressure. The crude product was

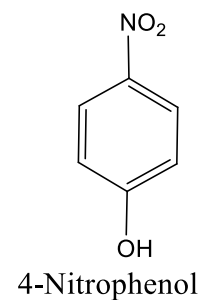
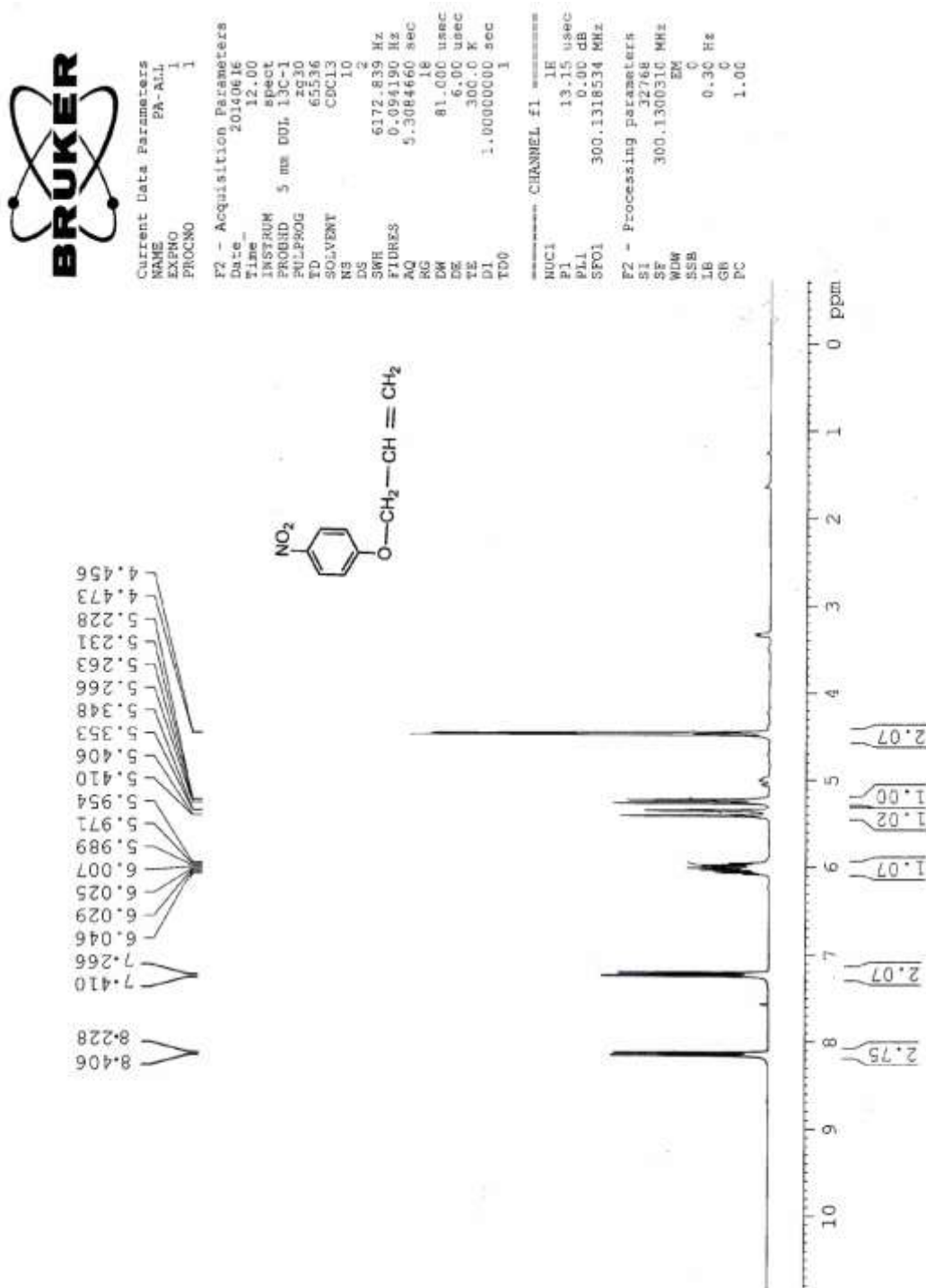
chromatographic (SiO₂) employing hexane: ethyl acetate (9:1) as an eluent to obtain a pure monoderivative. The identity of the product was confirmed by ¹H NMR and ¹³C NMR spectra of the product.

¹H NMR (300 MHz, CDCl₃):

4.456-4.473 (2H, d, -CH₂), 5.228-5.226 (1H, dd, double bond- H), 5.348-5.410 (1H, dd, double bond- H), 5.954-6.046 ((1H, m, double bond- H), 7.266-7.410 (2H, d, Ar-H), 8.288-8.406 (2H, d, Ar-H).

¹³C NMR (75MHz, CDCl₃):

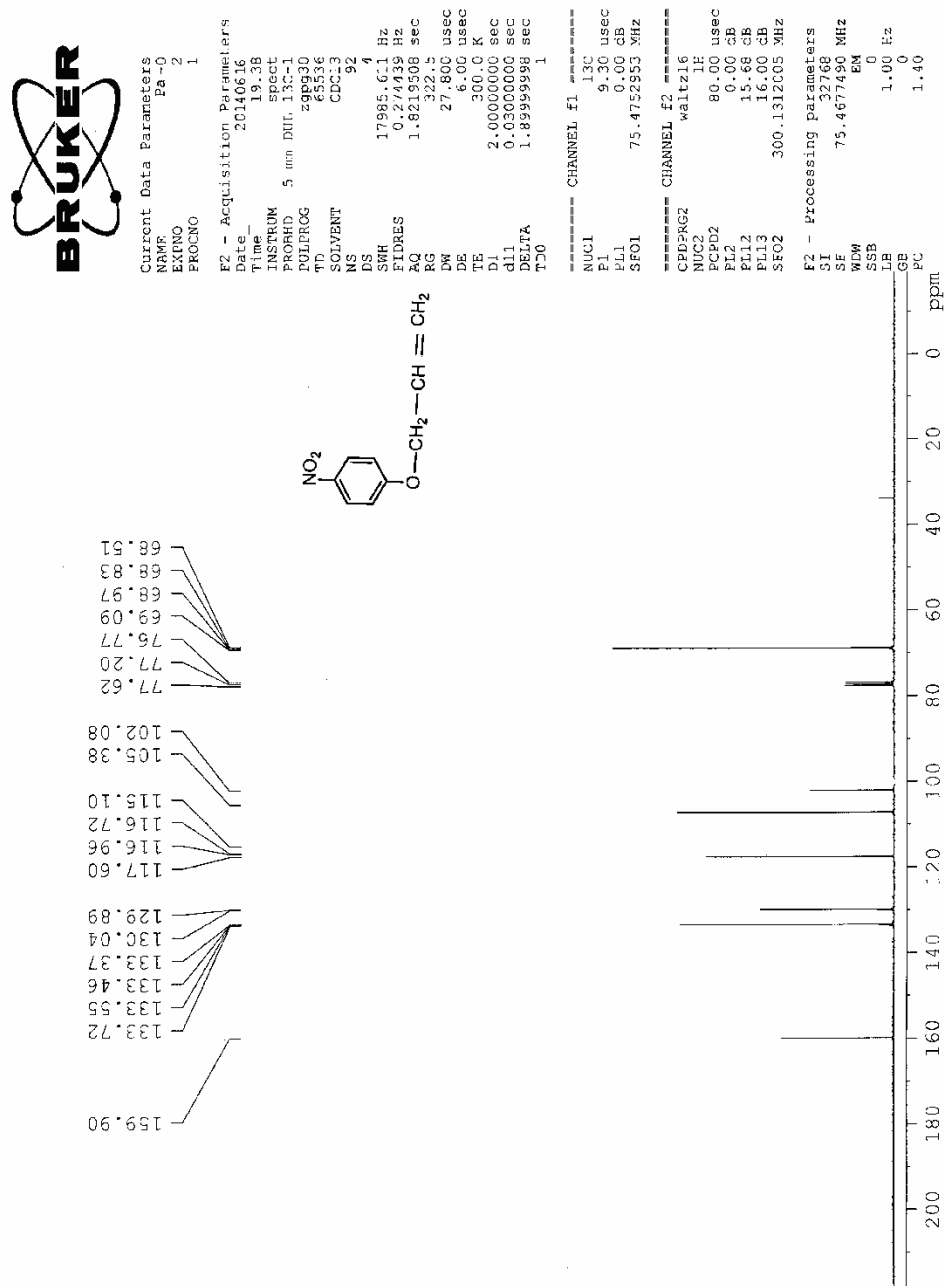
69.09 (-CH₂), 102.08 (Ar-C), 105.38 (=CH₂), 116.96 (Ar-C), 130.04 (CH=CH₂), 133.37 (Ar-C-NO₂), 159.90 (Ar-C-O)



1. Allyl bromide
2. Chlorobenzene
3. 1 hr
4. 50°C
- 5.40 kHz, (30

¹H NMR Spectra of 1-(allyloxy)-4-nitrobenzene

¹³C NMR Spectra of 1-(allyloxy)-4-nitrobenzene



Synthesis of 1-(hexyloxy)-4-nitrobenzene

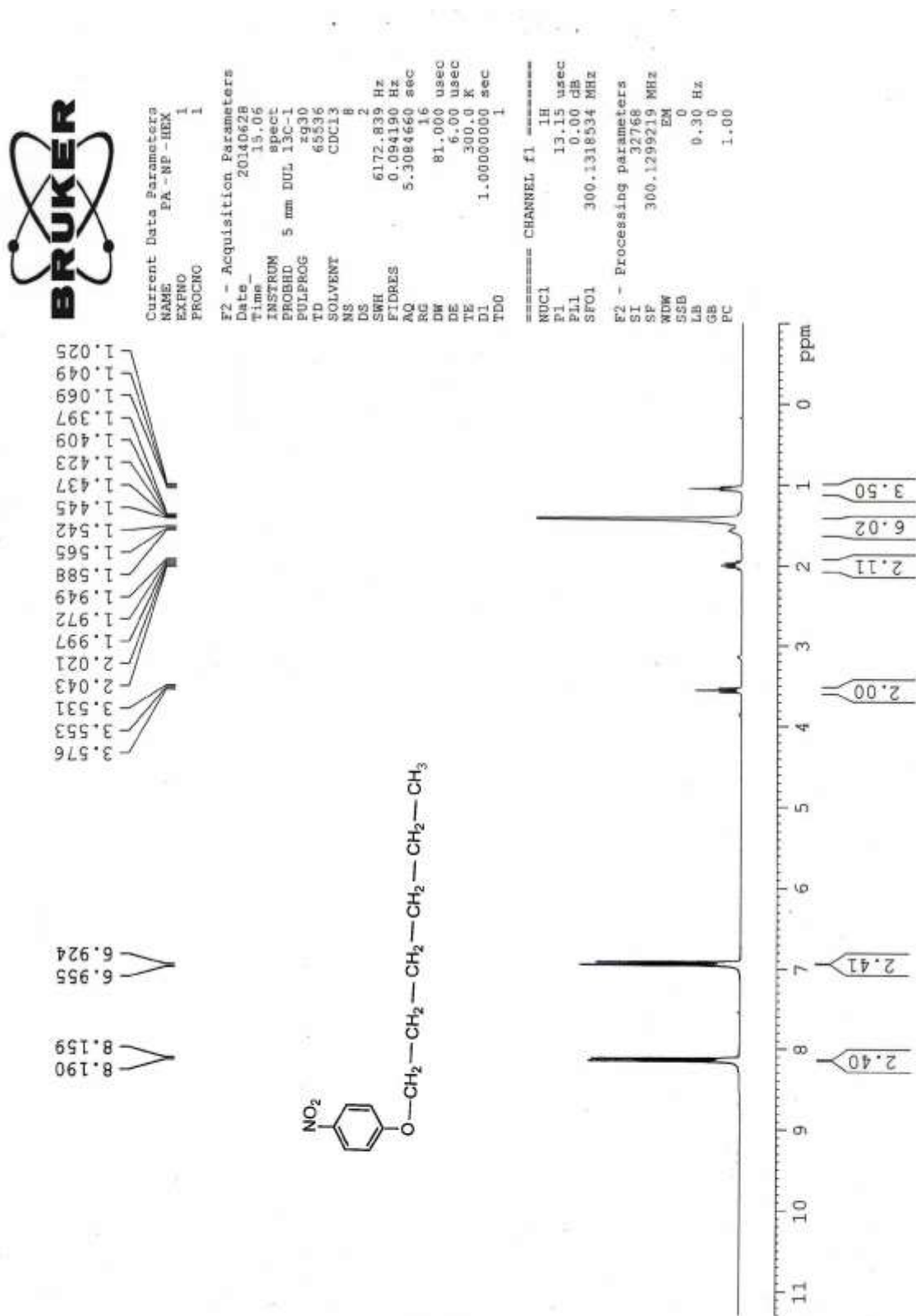
To the mixture of potassium carbonate (15 g) in water (3 mL) and the newly synthesized MPTC ($0.3 \text{ g}, 4.3859 \times 10^{-4} \text{ mol}$), 4-Nitrophenol (0.5 g) was added under overhead stirring to generate the anion. Then hexylbromide (4.30 mol) in chlorobenzene (30 mL) was added slowly. The reaction mixture was

heated at 50°C for 6 hours with vigorous stirring. The crude product was isolated by simple extraction with diethyl ether (3 x 25 mL). The organic layer was collected and the solvent was evaporated under reduced pressure. The crude

product was chromatographic(SiO_2) employing hexane: ethyl acetate (9:1) as an eluent to obtain a pure monoderivative. The identity of the product was confirmed by ^1H NMR and ^{13}C NMR spectra of the product

^1H NMR (300 MHz, CDCl_3):

δ 1.025-1.069(t,3H,- CH_3),1.397-1.588(m,6H,- CH_2),1.949-2.043(m,2H,-O- CH_2 - CH_2),3.531-3.576(t,2H,-O- CH_2),6.924-6.955(d,2H,Ar-H),8.159-8.190(d,2H,Ar-H)



^{13}C NMR (75MHz,

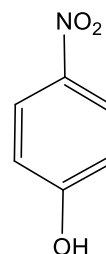
CDCl_3):

δ .

14.88,23.44,25.93,29.5

2,34.67,68.07,114.39,1

25.83,141.25,164.28



4-Nitrophenol

^1H NMR Spectra
of 1-(hexyloxy)-
4-nitrobenzene

1. n-H

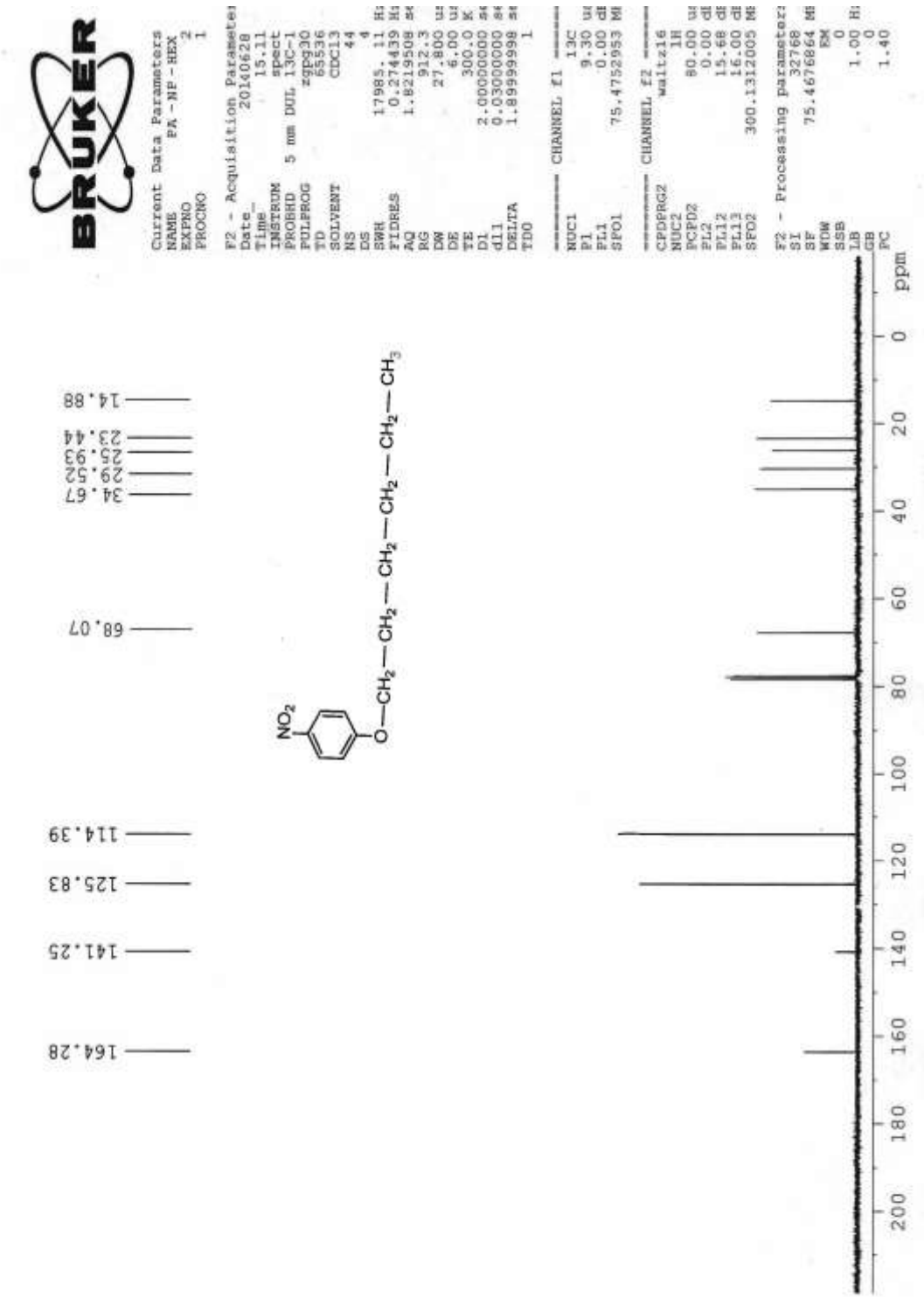
2. Chl

3. 1 hr

4. 50%

5.40K

¹³C NMR Spectra of 1-(hexyloxy)-4-nitrobenzene



EXPERIMENTAL
RESULTS

C-Alkylation of
isobutyraldehyde

Table 1

Effect of stirring

speed

0	6.40
100	12.12
200	19.16
300	28.20
400	36.43
500	36.55
600	36.70
700	36.88
800	36.95
900	37.01
1000	37.13

Effects of stirring speeds on the alkylation of isobutyraldehyde; 15 g of K_2CO_3 , in 3 mL H_2O , 0.2 g of biphenyl (internal standard), 13.88 mmol of isobutyraldehyde, 15.15 mmol of hexyl bromide, 3 mol % of MPTC, 40 mL of chlorobenzene, 318 K.

Table 2

Effect of ultrasonic frequency

Ultrasonic frequency (kHz)	$k_{app} \times 10^3, \text{ min}^{-1}$
0	10.32
28	21.12
40	36.43

Influence of ultrasonic frequencies on the rate of C-alkylation of isobutyraldehyde: 15 g of K_2CO_3 , in 3 mL H_2O , 0.2 g of biphenyl (internal standard), 13.88 mmol of isobutyraldehyde, 15.15 mmol of hexyl bromide, 3

mol % of MPTC, 40 mL of chlorobenzene, 500 rpm, 318 K.

Table 3

Effect of amount of hexyl bromide

Hexylbromide (HB), mmol	$k_{app} \times 10^3, \text{min}^{-1}$ (40 kHz, 300W)
09.10	26.68
12.12	30.52
15.15	36.43
18.18	40.30
21.21	43.78

Effect of amount of hexylbromide (HB) on the rate of C-alkylation of isobutyraldehyde under ultrasonic condition: 15 g of K_2CO_3 , in 3 mL H_2O , 0.2g of biphenyl (internal standard), 13.88 mmol of isobutyraldehyde, 3 mol % of MPTC, 40 mL of chlorobenzene, 500 rpm, 318 K.

Table 4

Effect of organic solvents

Solvent, dielectric constant	$k_{\text{app}} \times 10^3, \text{min}^{-1}$
(ϵ^a)	(40 kHz, 300W)

Chlorobenzene (5.6)	36.43
Anisole (4.3)	32.21
Toluene (2.4)	27.59
Hexane (2.2)	2.2
Cyclohexane (2.0)	2.0

Influence of organic solvents on the rate of C-alkylation of isobutyraldehyde under ultrasonic condition: 15 g of K_2CO_3 , in 3 mL H_2O , 0.2g of biphenyl (internal standard), 13.88 mmol of isobutyraldehyde, 15.15 mmol of hexylbromide, 3 mol % of MPTC, 40 mL of chlorobenzene, 500 rpm, 318 K.

Table 5

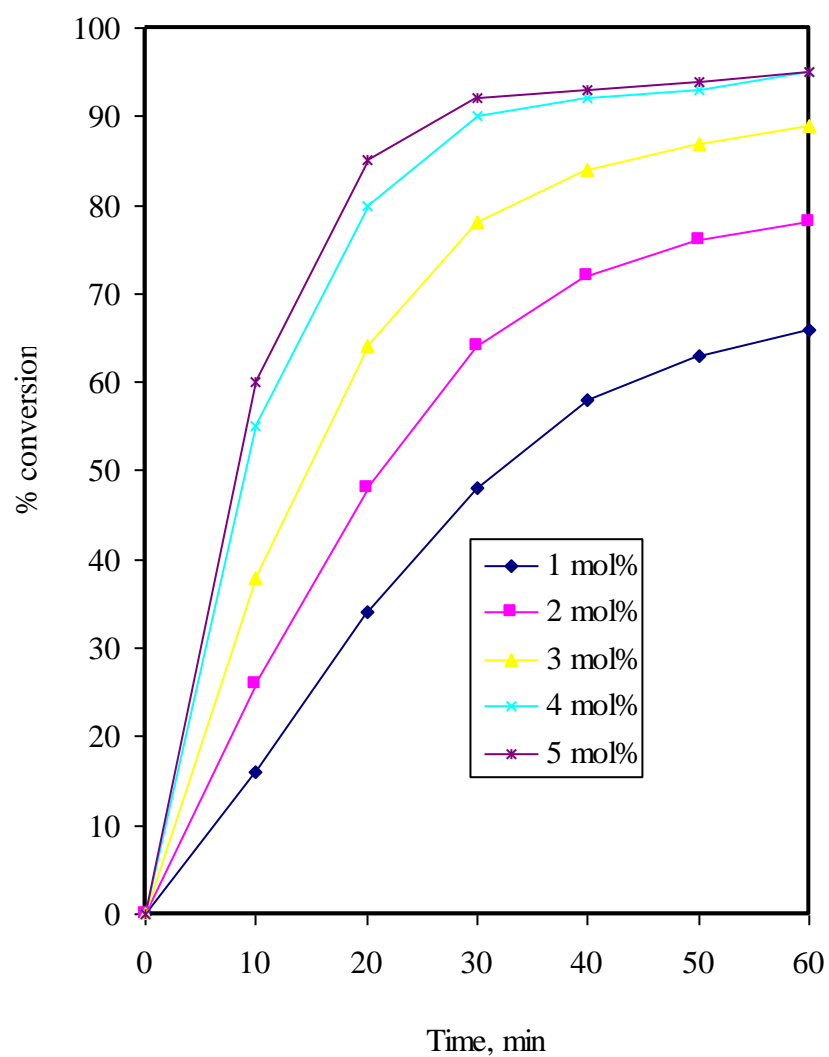
Effect of amount of potassium carbonate

Amount of potassium carbonate, (g)	$k_{app} \times 10^{-3}, \text{min}^{-1}(40 \text{ kHz}, 300\text{W})$
5	20.42
10	28.13
15	36.43
20	43.21
25	46.50

Effect of amount of potassium carbonate on the rate of C-alkylation of isobutyraldehyde: 3 mL H₂O, 0.2g of biphenyl (internal standard), 13.88 mmol of isobutyraldehyde, 15.15 mmol of hexyl bromide, 40 mL of chlorobenzene, 3 mol % of MPTC, 500 rpm, 318 K.

Figure 1

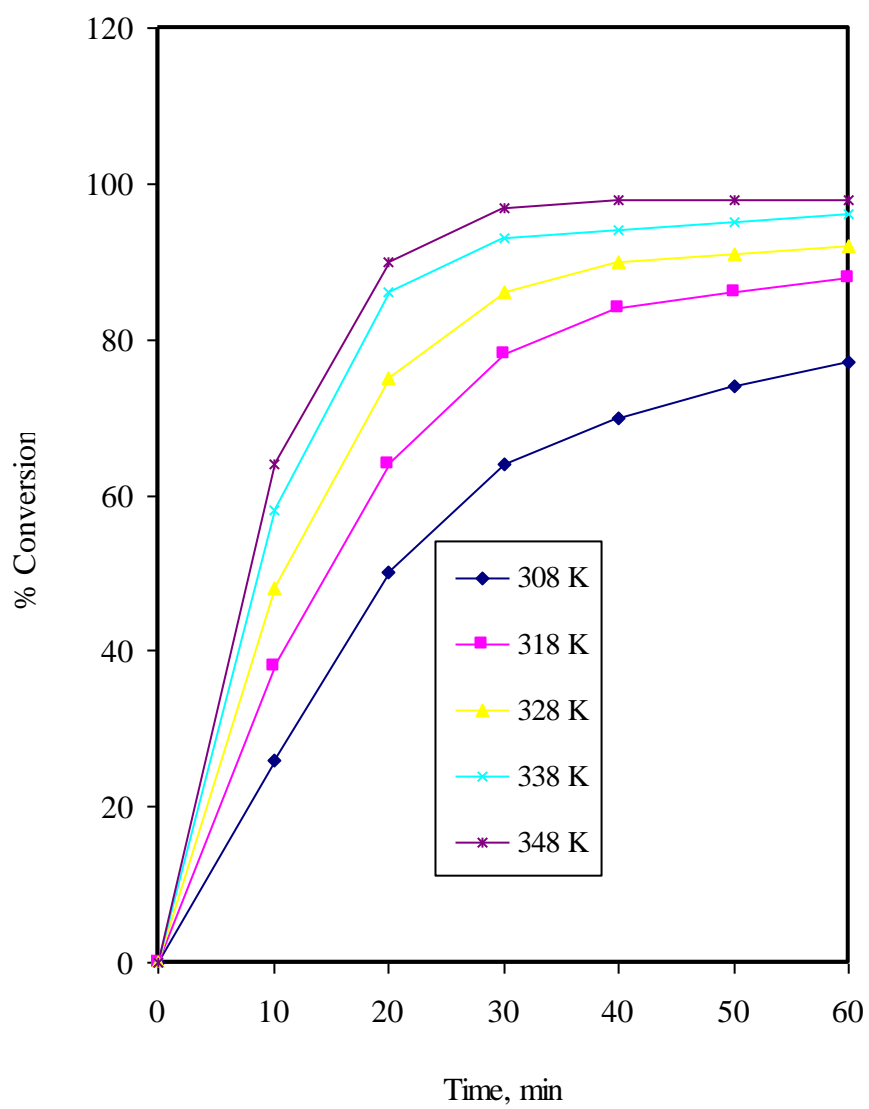
Effect of amount of MPTC



Effect of the amount of MPTC on the conversion: 15g of K_2CO_3 , 3 mL H_2O , 0.2 g of biphenyl (internal standard), 13.88 mmol mmol of isobutyraldehyde, 15.15 mmol of hexyl bromide, 40 mL of chlorobenzene, 500 rpm, 318 K; ultrasound condition (40 kHz, 300 W).

Figure 2

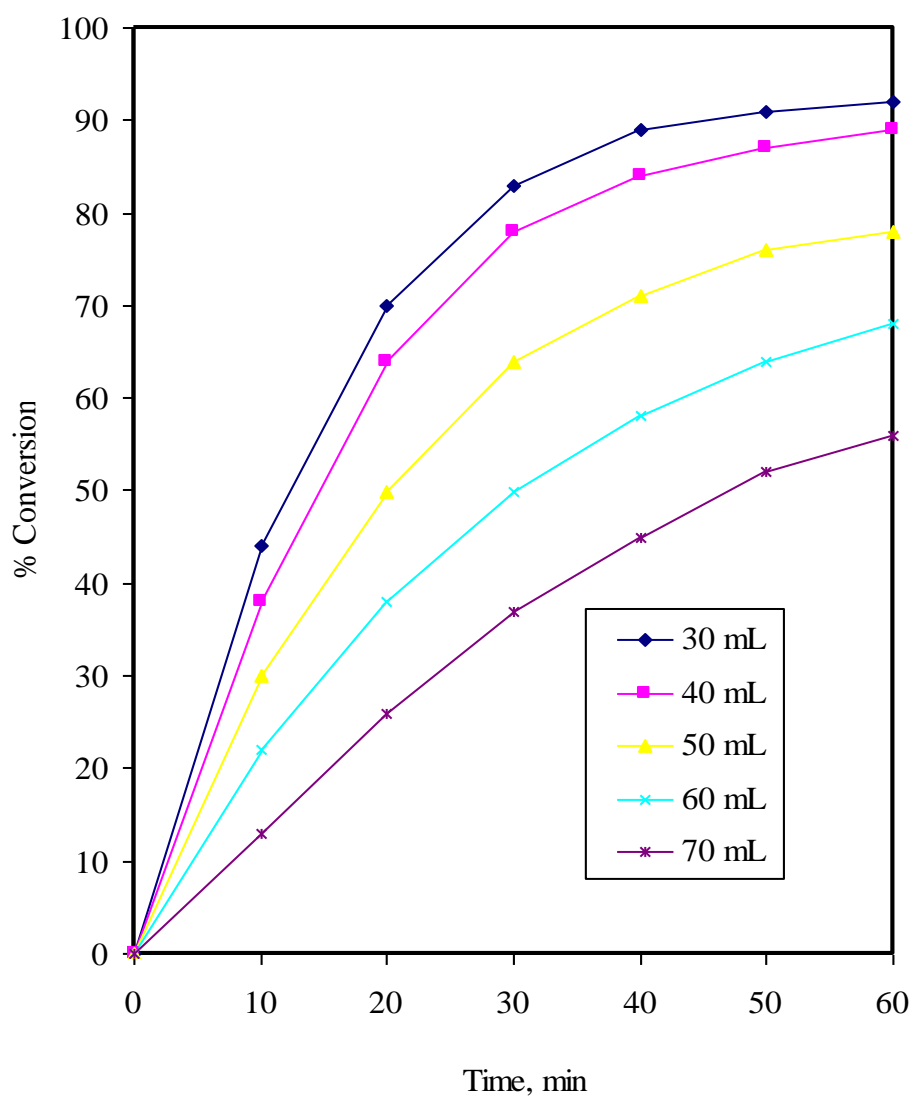
Effect of temperature



Effect of temperature on the conversion: 15 g of K_2CO_3 , 3 mL H_2O , 0.2 g of biphenyl (internal standard), 13.88 mmol of isobutyraldehyde, 15.15 mmol of hexyl bromide, 3 mol% of MPTC, 500 rpm, ultrasound condition (40 kHz, 300 W).

Figure 3

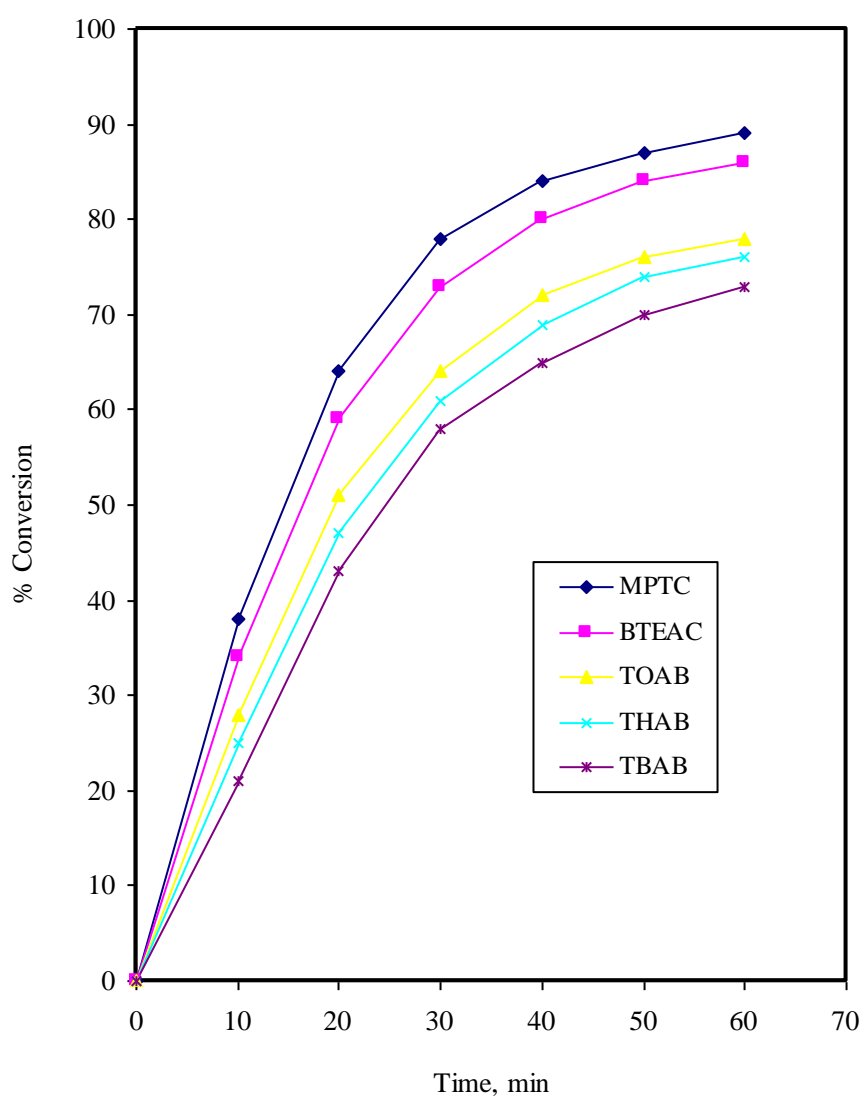
Effect of volume of chlorobenzene



Effect of volume of chlorobenzene on the conversion: 15 g of K_2CO_3 , 3 mL H_2O , 0.2 g of biphenyl (internal standard), 13.88 mmol of isobutyraldehyde, 15.15 mmol of hexyl bromide, 3 mol% of MPTC, 318 K, 500 rpm, ultrasound condition (40 kHz, 300 W).

Figure 4

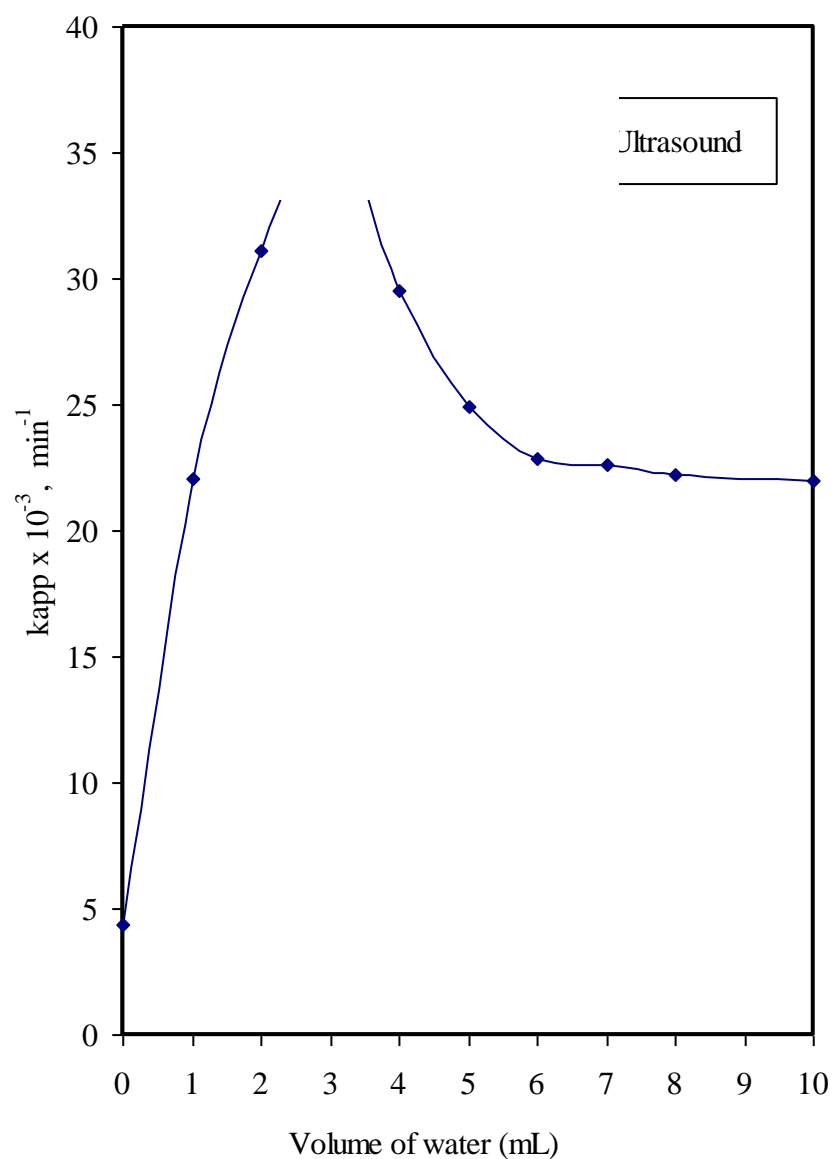
Effect of MPTC and PTCs



Effect of MPTCS and PTCs on the conversion: 15 g of K_2CO_3 , 3 mL of water, 0.2 g of biphenyl (internal standard), 13.88 mmol of isobutyraldehyde, 15.15 mmol of hexyl bromide, 3 mol% of MPTCs and PTCs, 40 mL of chlorobenzene, 500 rpm, 318 K; ultrasound condition (40 kHz, 300 W).

Figure 5

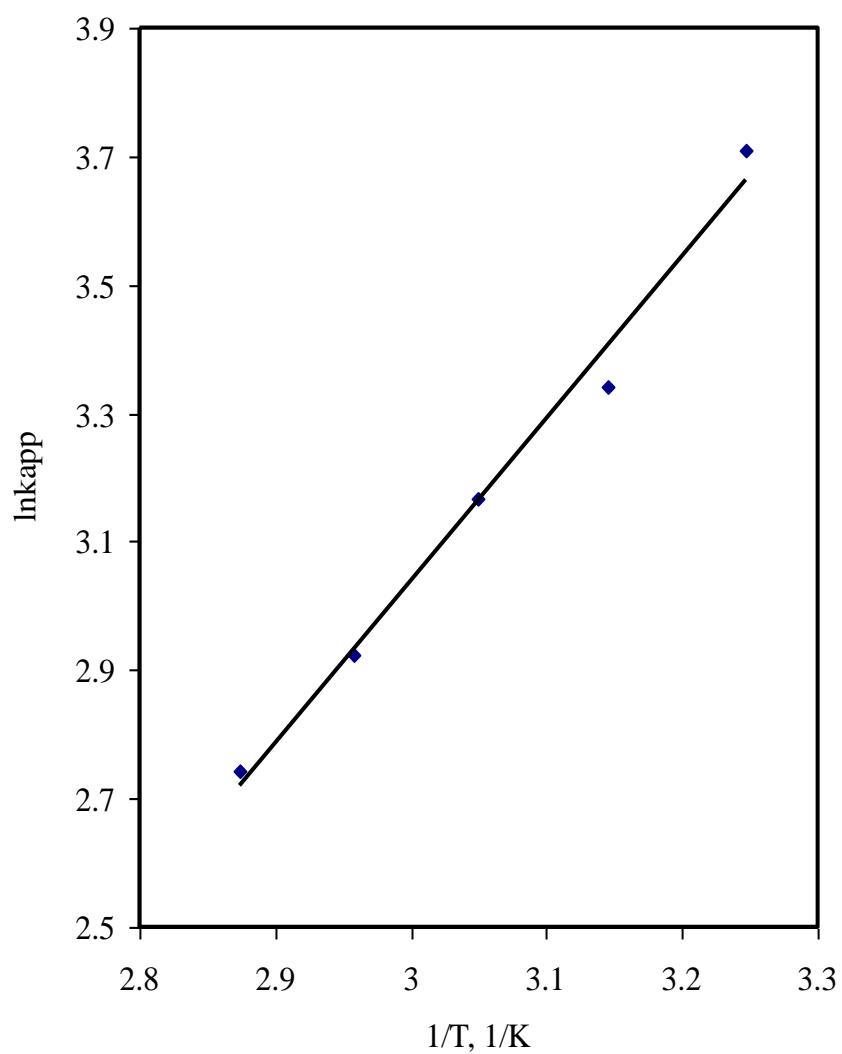
Effect of volume of water



Effect of the volume of water on the apparent rate constant: 15 g of K_2CO_3 , 0.2 g of biphenyl (internal standard), 13.88 mmol of isobutyraldehyde, 15.15 mmol of hexyl bromide, 3 mol% of MPTC, 40 mL of chlorobenzene, 500 rpm, 318 K; ultrasound condition (40 kHz, 300 W).

Figure 6

Arrhenius plot



Arrhenius plot for isobutyraldehyde; 15 g of K_2CO_3 , 3 mL H_2O , 0.2g of biphenyl (internal standard), 13.88 mmol of isobutyraldehyde, 15.15 mmol of hexyl bromide, 3 mol% of MPTC, 40 mL of chlorobenzene, 318 K, 500 rpm, ultrasound condition (40 kHz, 300 W).

DISCUSSION

Reaction mechanism and kinetic model

To overcome the small amount of product was obtained when the reaction is carried out in a liquid –liquid heterogeneous reaction due to hydration, the reaction between isobutyraldehyde and hexylbromide was carried out in a solid-liquid condition and catalyzed by multi-site phase-transfer catalyst under ultrasound irradiation (40 kHz, 300 W). A trace amount of water added to the reaction system in order to minimize the loss of reactant due to hydration and to enhance the formation of potassium salt of isobutyraldehyde.

In this work, potassium salt of isobutyraldehyde is sparingly soluble in organic solvent (chlorobenzene). First, potassium salt of isobutyraldehyde $[(CH_3)_2 - C^- - CHOK^+]$ form an active intermediate $[(CH_3)_2 - C^- - CHOQ^+]$. The inorganic salt KX precipitated as a solid form in the organic solution and then it is transported to the aqueous or solid phase. The active $[(CH_3)_2 - C^- - CHOQ^+]$ (org) then react with n-hexyl bromide (HB) to produce the desired product 2,2-dimethyloctanal, Scheme 3) and the catalyst is regenerated and the above said cyclic process take place continuously up to the disappearance of hexyl bromide in the bulk organic phase.

Definition

The conversion (X) of hexylbromide (HB) is defines as follows:

$$X = 1 - \{ [HB]_0 / [HB]_{o,i} \} \quad 1$$

where $[HB]_0$ and $[HB]_{o,i}$ represent the concentration of hexylbromide at time (t) $t=0$ and $t>0$, respectively.

Rate expression

The rate expression for this reaction may be expressed as:

$$-r_{HB} = k_{app} [HB]_0 \quad 2$$

Where k_{app} is the apparent reaction rate constant.

This reaction is carried out in a batch reactor, so the diminution rate of EBA with time (t) can be expressed as

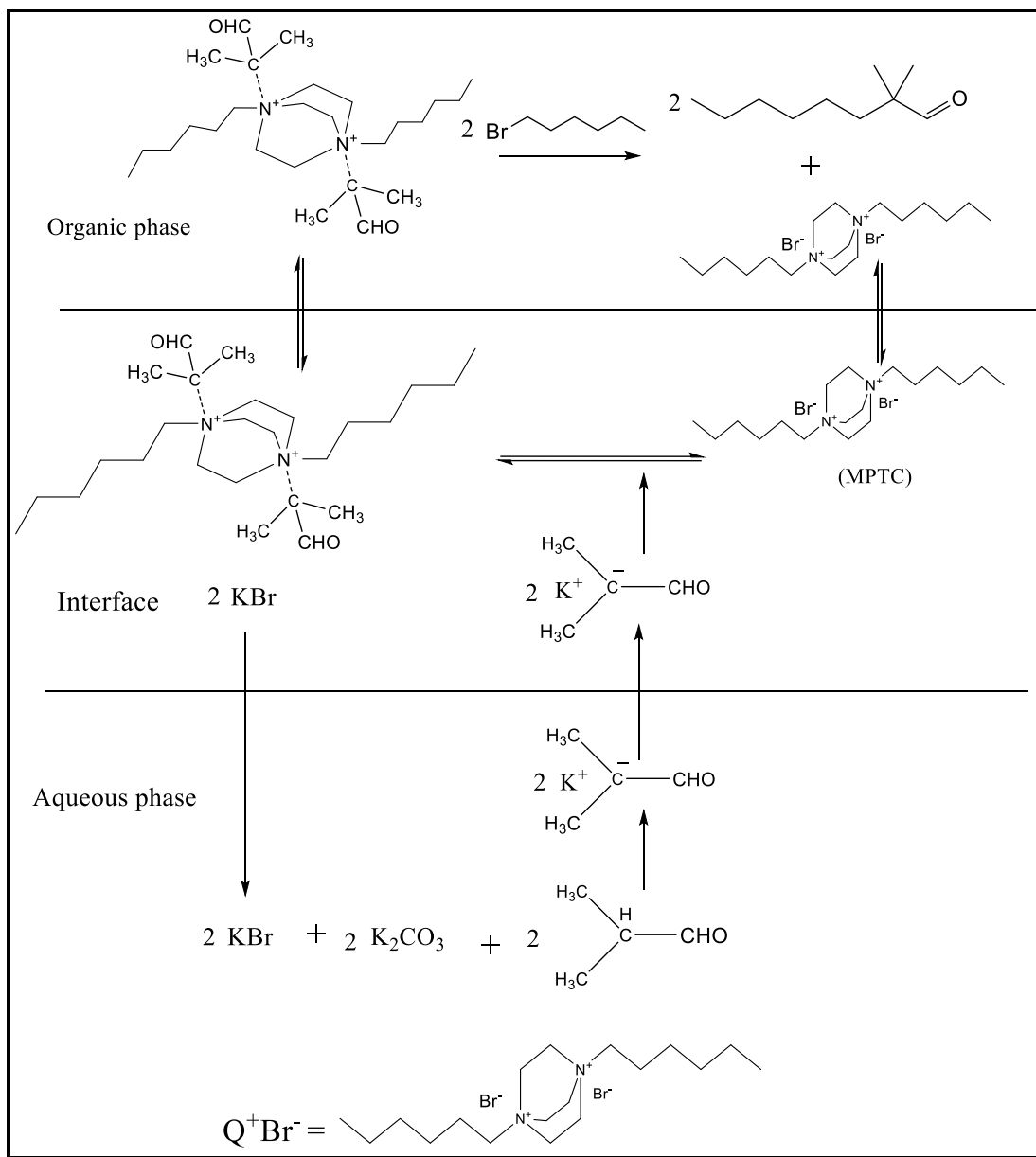
$$-d[\text{HB}]_0 / dt = -r_{\text{HB}} = k_{\text{app}} [\text{HB}]_0 \quad 3$$

on integrating the Eq. (3) yields:

$$-\ln\{[\text{HB}]_0 / [\text{HB}]_{0,i}\} = -\ln(1-X) = k_{\text{app}} \times t \quad 4$$

Using Eq. (4), we can get the k_{app} value experimentally by plotting $-\ln(1-X)$ against time, (t).

Mechanism of 2,2-dimethyloctanal formation



RESULTS AND DISCUSSION

The reactor was a 250 ml three-necked Pyrex flask, serving the purposes of agitating the solution, inserting the condenser to recover the solvent and reactant, taking samples, and feeding the feed etc. This reaction vessel was supported at the centre of the sonicator. Known quantities of chlorobenzene (30 mL, solvent), well powdered potassium carbonate (10 g in 3 mL water) and 0.2 g biphenyl (IS-internal standard) were introduced into the reactor. Then, 3 g of isobutyraldehyde (13.88mmol) and 3.3 g of hexyl bromide (15.15mmol), 3 mol % of the newly synthesized MPTC were introduced to the reactor to start the reaction. The reaction mixture was stirred at 500 rpm. The phase separation was immediate when stopping the agitation process. Samples were taken from the organic layer at regular time intervals and put it into the 10 mL vials and then 0.5 mL of chlorobenzene was added to vials to dilute the solution. The kinetics was followed by estimating the amount of hexyl bromide (limiting reagent) that disappeared and measured by a gas Chromatography (GC-Varian 3700 model). The analyzing conditions were as follows; Column, 30 m x 0.525 mm i.d. capillary column containing 100% poly(dimethyl siloxanen); injection temperature, 250°C; FID detector (300°C). Yields were determined from standard curve using biphenyl as an internal standard.

Effects of speed of agitation

The theory of mass-transfer in the phase-transfer catalyzed heterogeneous reactions is discussed in many papers by many researchers. This theory is also applicable to this S-L PTC reaction of isobutyraldehyde and n-hexyl bromide (HB) under a multi-site phase-transfer catalyst viz., 1,4-dihexyl-1,4-diazoniabicyclo[2.2.2]octanium dibromide (MPTC) along with ultrasound irradiation (40 kHz, 300 W). To ascertain the influence of external mass-transfer resistance on the transfer of the reactant to the reaction phase, the speed of agitation was varied in the range of 0-1000 rpm. As seen from Table 1, the conversion or the reaction rate increases with an increase in speed of agitation from 0 to 400 rpm. This is due to the dissolving rate of $[(CH_3)_2 - C^- - CHOK^+]$ in chlorobenzene is highly influenced by the agitation speed. In general, a high concentration of $[(CH_3)_2 - C^- - CHOK^+]$ dissolving in organic solvent is obtained at a high agitation speed up to 400 rpm. In principle, $[(CH_3)_2 - C^- - CHOK^+]$ first dissolves gradually in chlorobenzene in the

presence of MPTC to forming $[(CH_3)_2 - C^- - CHOQ^+]$ at the inter- phase. Then, the formed intermediate $[(CH_3)_2 - C^- - CHOQ^+]$ reacted with n-hexyl bromide to produce 2,2-dimethyloctanal in the organic phase. However, when the speed of agitation was increased from 400 to 1000 rpm the increase in conversion was marginal which suggests elimination of external resistance to mass transfer. Therefore all further experiments were conducted at 500 rpm.

When the reaction was carried out in ultrasound irradiation only, the k_{app} is to be $6.40 \times 10^{-3}, \text{ min}^{-1}$. The same reaction was carried out without ultrasound (having stirring speed 500 rpm only) that is, in conventional method, the observed k_{app} value ($k_{app} = 10.32 \times 10^{-3}, \text{ min}^{-1}$) almost 3.5 times lesser than in the presence of sonication (40 kHz, 300 W) and stirring ($k_{app} = 36.43 \times 10^{-3}, \text{ min}^{-1}$). The k_{app} values indicate that the mechanical effects brought up by the use of low frequency ultrasounds are responsible of the enhancement of the kinetics by harsh mixing, enhancement of mass transfer, especially in solid-liquid systems, high erosion of the solid particles occurs and the surface area is increased¹⁴ and ultrasound decreases the surface area between the two layers.

Different ultrasound frequencies

When ultrasonic wave passes through a liquid medium, a large number of micro bubbles form, grow and collapse in a very short time about a few microseconds, which is called ultrasonic cavitations. Ultrasonic cavitations creates a very extreme environment, i.e. extremely high local temperature and pressure¹⁹⁻²², as well as heating and cooling rates for chemical reaction.²³ Sonication is increased the chemical reactivity due to enhancement in mass-transfer in heterogeneous reaction. In solid-liquid system, ultrasonic frequency affects the surface morphology of the particulate phase from the impact of liquid-jet and hot-spot generated by ultrasonic wave. From the literature, it is clear that the ultrasonically promoted (having stirring) reaction proceeded somewhat faster under the same conditions than the “silent” reaction,¹⁵ The effect of increasing the ultrasound frequency only, having same output power of 300W is shown in Table. 2. In our case, two different ultrasonic frequencies (28 kHz, 40 kHz) are used to test their effect on the reaction rate or conversion in the solid-liquid biphasic reaction catalyzed by multi-site phase-transfer catalyst. When we use higher frequency (40 kHz, 300 W), it gives the higher ultrasonic energy entering the system and a consequent increase in the number of cavitation bubbles and sonochemical effect that resulted in

effective mixing of phases and, collision between the molecule increases and that resulted in the increased conversion or the apparent reaction rate. As might be expected, higher frequency of ultrasound leads to shorter reaction times as well. The reaction also conducted in conventional method as well to compare. The rate constants, $10.32 \times 10^{-3} \text{ min}^{-1}$, $25.12 \times 10^{-3} \text{ min}^{-1}$, $36.43 \times 10^{-3} \text{ min}^{-1}$ are related to 0 kHz, 28 kHz, 40 kHz respectively has shown in Table.2. Hence, the overall k_{app} value was increased by increasing the ultrasonic frequency in the order of 0 kHz (conventional method) < 28 kHz (300 W) < 40 kHz (300 W) for our system (Table 2).

Effect of MPTC concentration

The reaction of potassium salt of isobutyraldehyde and hexylbromide was carried out in a homogeneous chlorobenzene solution. The potassium salt of isobutyraldehyde in solid form first dissolves in chlorobenzene in the presence of a new MPTC (viz., 1,4-dihexyl-1,4-diazoniabicyclo[2.2.2]octanium dibromide). To find the effect of catalyst, the catalyst is varied from 1 mol% to 5 mol%. The conversion of hexylbromide is increased with the increase in the amount of catalyst. The conversion is low in the absence of any catalyst, although the reaction is greatly enhanced by adding a small amount of catalyst. As stated, potassium salt of isobutyraldehyde is insoluble in organic solvents however, it is only soluble in chlorobenzene in the presence MPTC. Figure 1 shows the effects of the amount of MPTC on the k_{app} value, which increases with the increase in the amount of MPTC along with ultrasound irradiation (40 kHz, 300 W). The increase in the k_{app} value is attributed to the synergic effect of ultrasound, i.e. induce the surface area, change the size, and morphology of phase-transfer catalyst (MPTC).^{26,27} The k_{app} value is linearly proportional to the amount of the MPTC catalyst up to 3 mol%. However, the result does not follow the linear relation between k_{app} value and the amount of the MPTC catalyst by using large amount of MPTC catalyst.

Effect of concentration of organic phase reactant

To investigate the influence of hexylbromide (HB) on the kinetics of synthesis of diethyl 2,2-dimethyloctanal under ultrasonic irradiation condition (40 kHz, 300 W), the amount of hexylbromide (HB) was varied from 9.10 mmol to 21.21 mmol. The results are shown in Table 3. The data clearly indicates that the k_{app} value increases with increase in the amount of hexylbromide (HB). This observation due to presence of more number of active sites in the MPTC and higher concentration of substrate (HB) had co-operatively influence the reaction and thus enhance the more number of contacts between active intermediate and substrate (HB), and hence it is reflected in enhanced k_{app} values. In addition ultrasound enhance the rate of the reaction, it may be due to reduces the surface area between the solid and organic phase, and hence more reactants collide to each other simultaneously we get higher k_{app} value.

Effect of various temperature

The effect of temperature on the reaction rate of hexylbromide was studied in the range of 308 to 348 K (Figure 2). The conversion of hexylbromide is increased with an increase in the temperature along with ultrasonic effect. This is due to the number of reactant molecules which possess higher activated energy at higher temperature and thus the ultrasonic wave easily passes through the reactor.³¹ The increase in the conversion is almost linear when the temperature is increased from 308 K to 338 K. For reaction temperature beyond 338 K, there was marginal difference in the final conversions (Figure 2). The use of ultrasound reduces the need of high temperature for the reaction system. Arrhenius plots were made of $-\ln k_{app}$ against T^{-1} to get activation energy of 48.44 kJ.mol⁻¹. This higher activation energy demonstrates that this ultrasound assisted solid-liquid reaction with multi-site phase-transfer catalyst (MPTC) was kinetically controlled and the mass-transfer resistance between phases was unimportant under sonication condition.

Effect of different organic phase solvents

The influence of various organic solvents on the rate of C-alkylation of isobutyraldehyde was followed under otherwise standard reaction conditions. The polarity of organic solvent affects the dissolution of solid reactant anion (i.e., potassium salt of isobutyraldehyde in organic solvent. With adding 3 mL of water, the more polar solvent induced the higher activity of phase-transfer catalyst, because a higher content of $[(CH_3)_2 - C^- - CHOQ^+]$ was acquired. From the

plot of $-\ln(1-X)$ against time, the k_{app} values are obtained. It is clear from the Table 4 chlorobenzene possesses a higher k_{app} value among the five organic solvents used.

Effect of different volume of chlorobenzene

The conversion or the reaction rate is directly proportional to the concentration of the reactants in 60 minutes of reaction. A dilute concentration of the reactant is obtained using a large amount of organic solvent. The conversion of hexylbromide is increased with the decrease in the volume of chlorobenzene. Figure 3 shows the dependence of the % conversion on the volume of chlorobenzene. The k_{app} value is inversely proportional to the volume of chlorobenzene, as we expected.

Effect of MPTC and single-site phase-transfer catalyst

In this study, the three MPTC and three single-site phase-transfer catalysts were used to check their efficacies for the C-alkylation reaction of isobutyraldehyde with hexylbromide (HB) keeping the other reaction conditions as constant under sonication (40 kHz, 300 W). The Phase-transfer catalysts are tetrabutylammonium bromide (TBAB), tetrahexylammonium bromide (THAB) and tetraoctylammonium bromide (TOAB) and the MPTCs are 1,4-dihexyl-1,4-diazoniabicyclo[2.2.2]octanium dibromide (MPTC), benzyltriethylammonium chloride (BTEAC). Figure 4 depicts the apparent rate constants for these six catalysts. Unexpectedly, the reaction rate constant estimated for the reaction in the absence of PTCs is about one-tenth of that with MPTC. It is attributed to interfacial solid–liquid reaction. In other words, the anion is generated at the surface of solid base and the intrinsic reaction occurs at the solid–liquid interface. However, the potassium salt of isobutyraldehyde can not be dissolved in chlorobenzene and contacts between molecules at the solid–liquid interface are difficult. Hence, the reaction rate is relatively low. However, the reaction rate is enhanced dramatically even with adding a small quantity of PTC or MPTC. It is attributed that the anion can be easily transferred into the bulk organic phase and the mechanism is changed. This is because, the expansion of catalytic active site of catalyst. The results suggest that the chemical reaction between the active intermediate and the hexylbromide be the sole rate-determining step. From Figure 4, it is clear that the order of catalytic reactivity of PTC and MPTCs are

MPTC > BTEAC > TOAB > THAB > TBAB. This order reveals that the lipophilic character of the phase-transfer catalysts and the MPTCs.

Effect of various potassium carbonate concentrations

The reaction rate is known to be greatly affected by a concentration of the alkaline potassium carbonate. The rate of the C-alkylation of isobutyraldehyde is strongly depends on the strength of the potassium carbonate. Kinetic experiments were carried out by employing 5 to 25 g of K_2CO_3 (keeping 3 mL water constant) under otherwise similar reaction conditions. The kinetic profile of the reaction is obtained by k_{app} against amount concentration of K_2CO_3 . The k_{app} value or conversion tremendously increased with increasing in the basicity (Table 5). The main reasons are that on increasing the alkaline concentration, (i) the base is less solvated by water molecule. (ii) The amount of production of anion (potassium salt of isobutyraldehyde) is increased. (iii) The distribution of active catalyst is increased. From the Table 5, the conversion is increased linearly with increase in the alkali concentration. The water has a subtle influence on the basicity and the hydration of the ion-pair.

Effect of dilution of solid phase

In a series of experiments, the amount of water had been varied from 0 to 15mL keeping the other conditions are constant. It was demonstrated from Figure 5 that the reaction rate first increased slightly, then decreased sharply and finally slowly decreased as the amount of water increased. The reaction rate also increases with the addition of trace water as, in the other SL-PTC reactions. The amount of the available K_2CO_3 increases, that resulting in the generation of much more anions (i.e., potassium salt of isobutyraldehyde). Nevertheless, hydration will form around the carbonate ion if the amount of water further increases. Meanwhile, a little water is extracted into the organic phase and the degree of hydration of the ion-pair increases. Accordingly, the basicity of carbonate anion considerably decreases and the reactivity of the ion-pair is lowered. In fact, the solid base will become pasty and the ion-pair in the organic phase is completely hydrated as excess water is added. Therefore, the reaction rate constant is decreased when the amount of water is increased.

SUMMARY

The present study entitled is broadly divided into six chapters.

The first chapter of the thesis Introduction outlines a brief survey of the literature on the work reported so far with various phase-transfer catalysts in sequential order with due accentuate on mechanism of PTC, applications of PTC, necessity of multi-site PTC and its origin and its various applications. Further, this chapter also highlights the necessity for the attention to be paid for the synthesis of MPTC's and literature starting with their existence period until now. Emphasis has been given to document the catalytic applications of MPTC's in the selective organic reactions like C-Alkylation of isobutyraldehyde, the kinetic criteria and mechanism operative in SPTC & MPTC system have been extensively discussed.

The second chapter deals with the scope and objectives of the present investigation. This chapter critically discusses the exploration of the recent developments in soluble of MPTC's and also their applications to different organic reactions.

Details of the chemicals employed in these studies and their corresponding purification techniques are given in detail in the third chapter viz., "Experimental methods". Also, experimental strategies adopted for the synthesis of various SSPTC & MPTC's are discussed and presented. In addition, analytical instruments used in the study for the characterization of various PTC's have been described. Finally, the kinetic procedures followed in conducting the selected organic reactions using different PTC & MPTC are described in this chapter.

The obtained experimental results in the form of tables and graphs are given coherently presented in Chapter-IV.

Chapter V presents the discussion of the comparative efficacy study of all the PTC's in organic reactions followed by thorough kinetics and mechanistic aspects of C-Alkylation of isobutyraldehyde organic reactions, summary of the present work is VI chapter,.

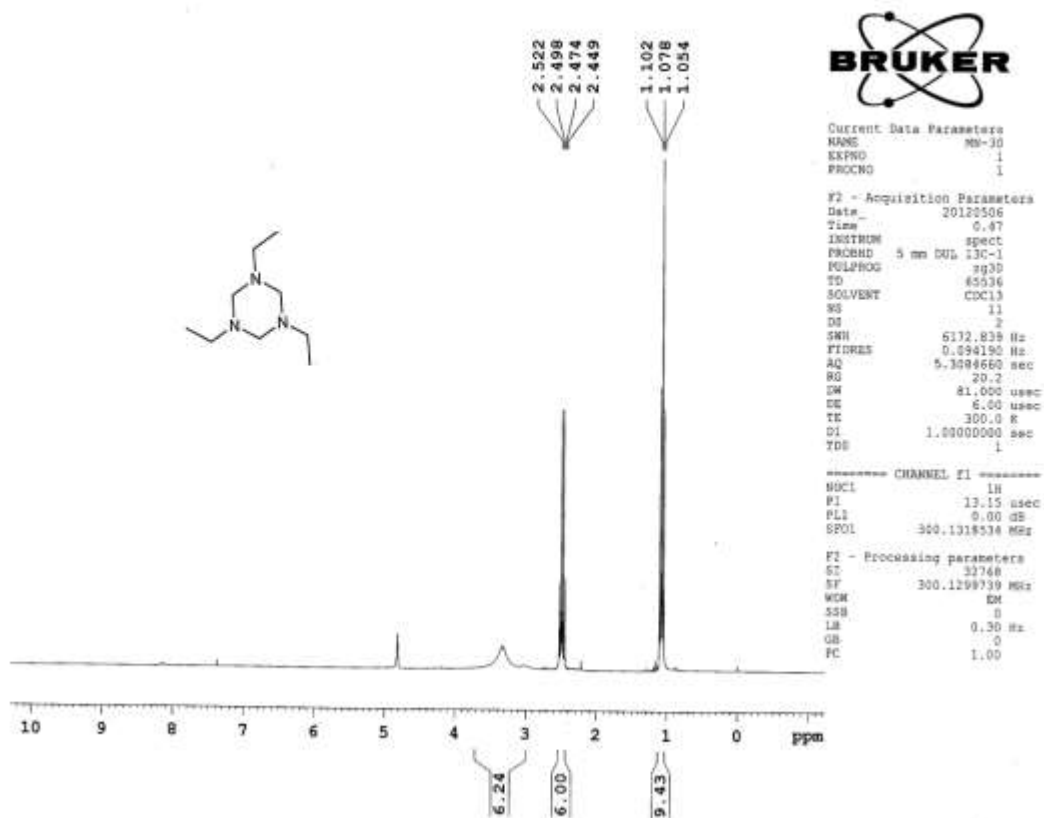
The following salient conclusion may be arrived from the present investigation:

1. For the first time, we have successfully synthesized PTC's i.e., di-site (MPTC).
2. The structures of these onium salts were confirmed through various spectral techniques viz., ^1H -NMR and ^{13}C -NMR, etc.
3. For the first time in the literature, we have examined the comparative catalytic efficiencies of all these PTC's through different organic reactions such as C-Alkylation of isobutyraldehyde under identical pseudo-first order conditions, using ultrasound irradiation (40 kHz, 300W).
4. It is established that multi-active site present in each MPTC's (a molecule) should always enhance its catalytic efficiency to the larger extent as compared with single-site PTCs and hence the new MPTC's may definitely reduced the cost of the reaction process.
5. In order to ascertain the effect of various the experimental parameters such as stirring speed, [substrate], $[\text{K}_2\text{CO}_3]$, [MPTC] and temperature on rate of the reaction, thorough kinetics for the four different organic reactions were also carried out by maintaining the identical pseudo first-order reaction conditions and varying the experimental parameters.
6. Each of the experimental parameters directly influences the rate of the reaction along with sonication.
7. Further, the E_a value and other thermodynamic parameters such as ΔS^\ddagger , ΔG^\ddagger and ΔH^\ddagger for all the four reactions are calculated and presented. Based on these kinetic results, we have proposed suitable mechanism for all these reactions.

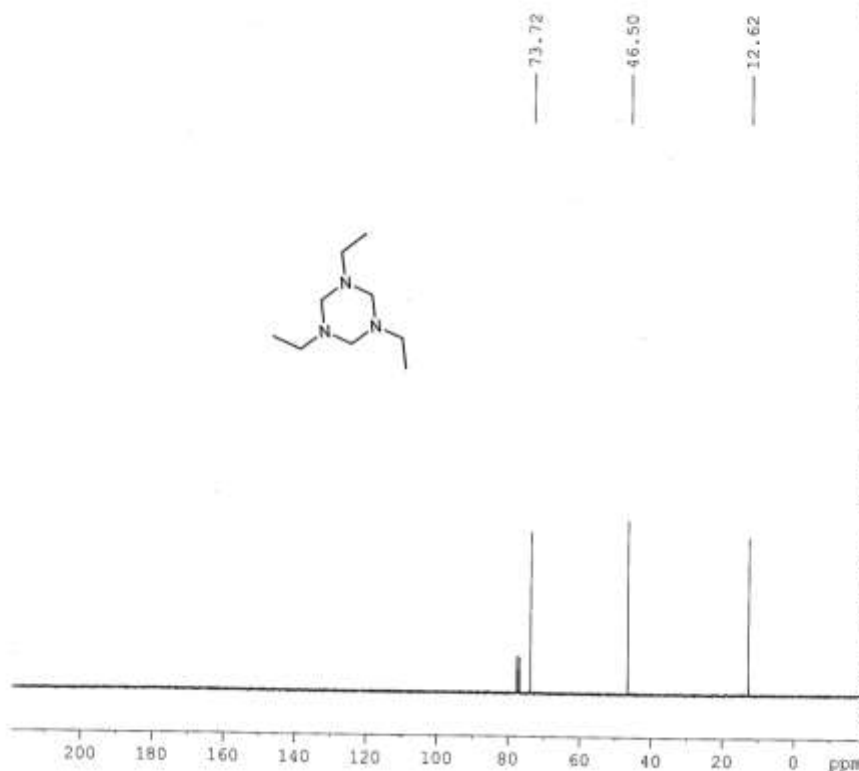
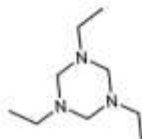
2.The Other New MPTC AND Organic Reactions

1,3,5-triethyl-1,3,5-trihexyl-1,3,5-triazinane-1,3,5-triium trichloride, (MPTC)

H¹-NMR



C^{13} - NMR



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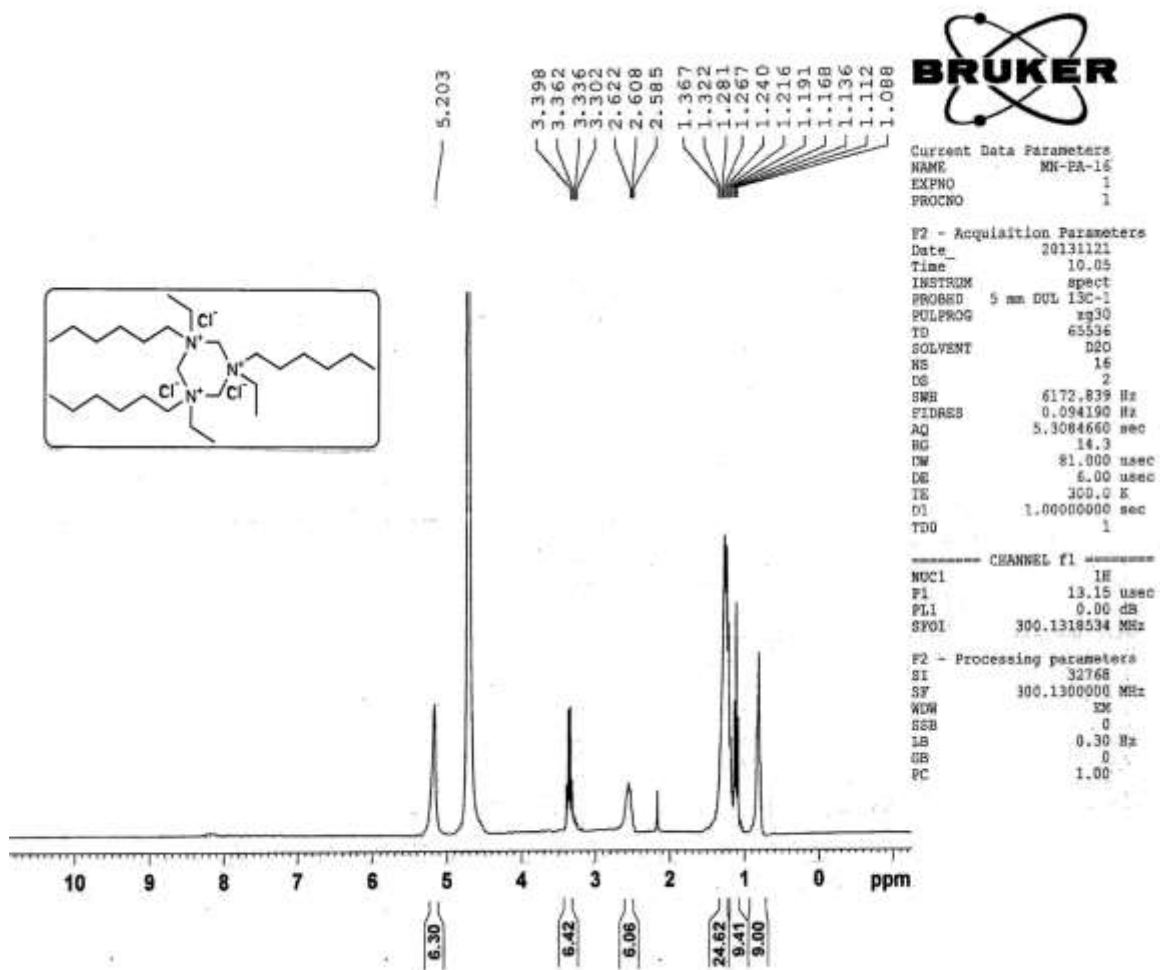
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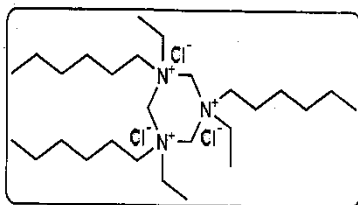
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H^1 - NMR (QX₃)



C¹³ – NMR (QX3)



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30.52
26.25
23.25
21.81
13.40
5.55



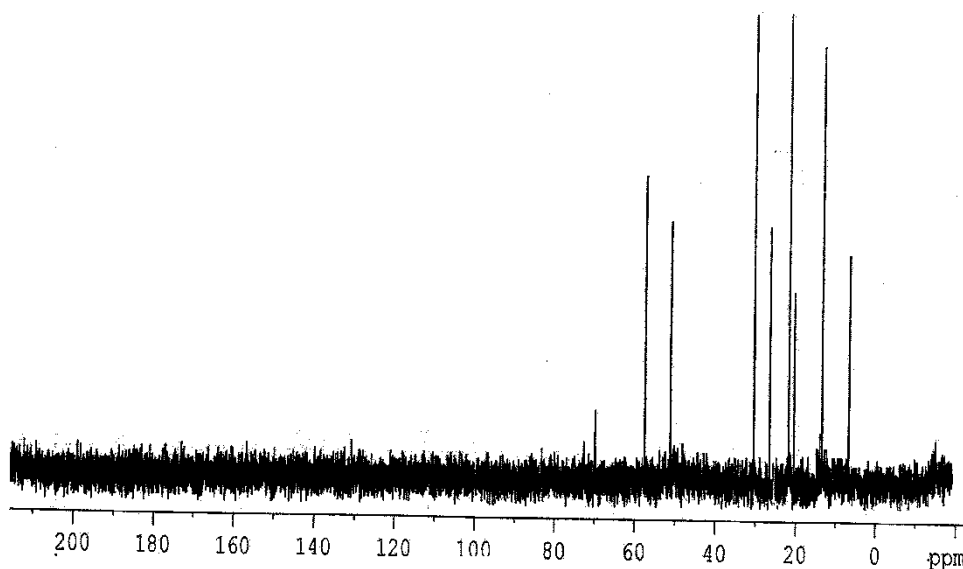
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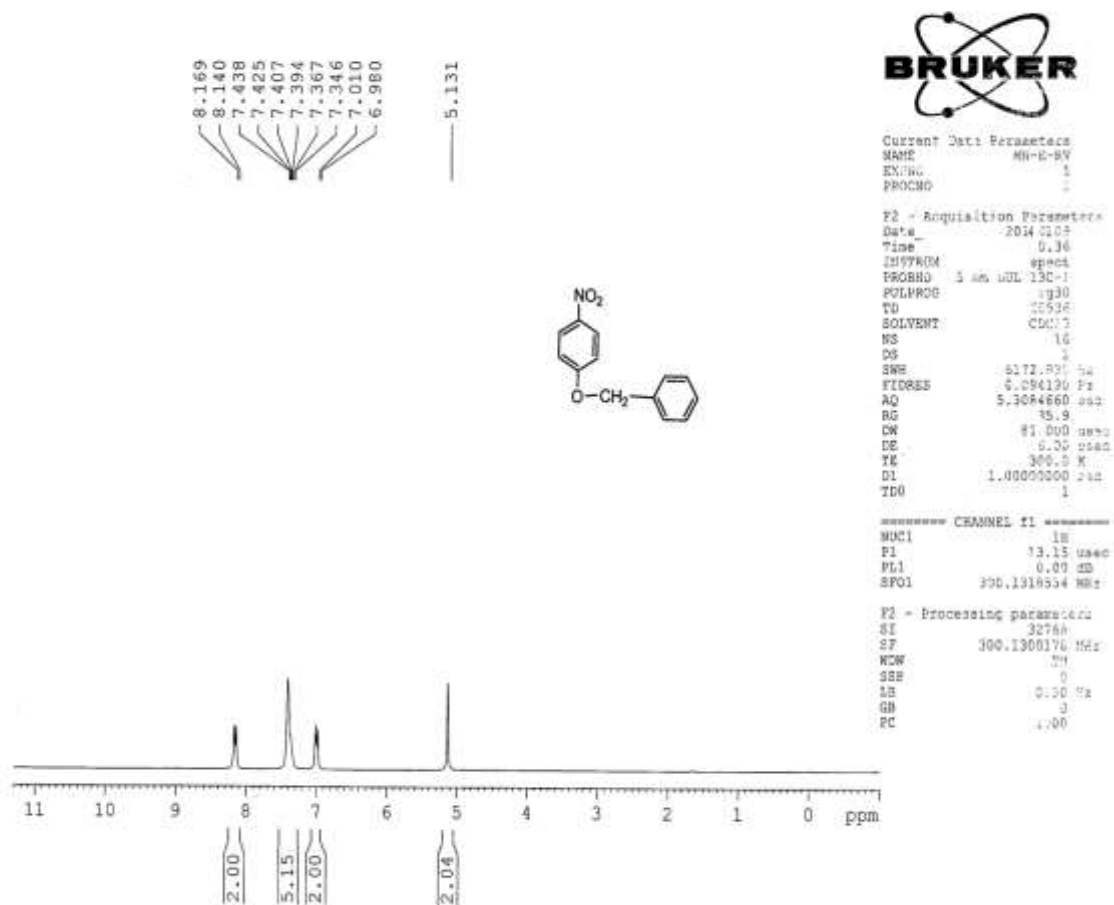
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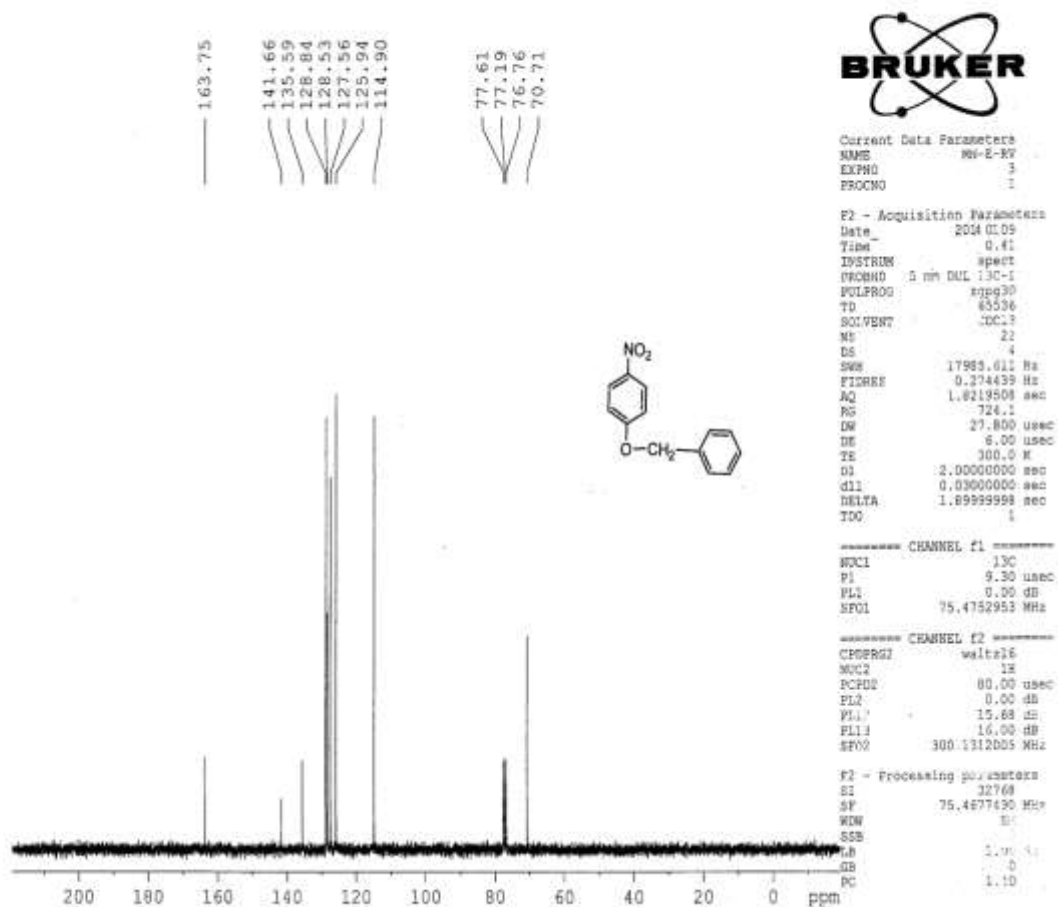
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Benzylation of 4-Nitrochlorobenzene : H¹ – NMR



Benzylation of 4-Nitrochlorobenzene : C¹³ – NMR



3. Reaction of 4-Nitrochlorobenzene with Imidazole : H^1 - NMR

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7.590
7.584
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7.283

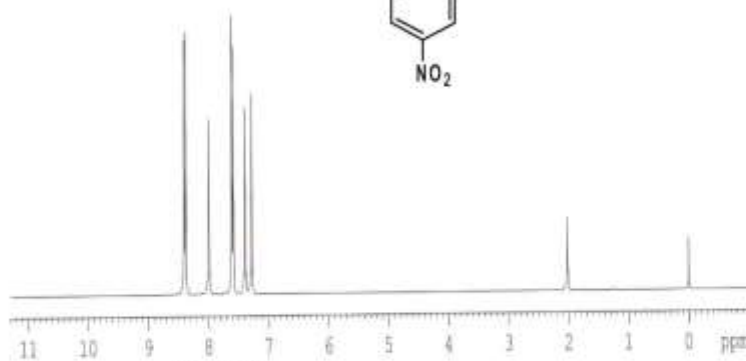
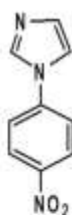


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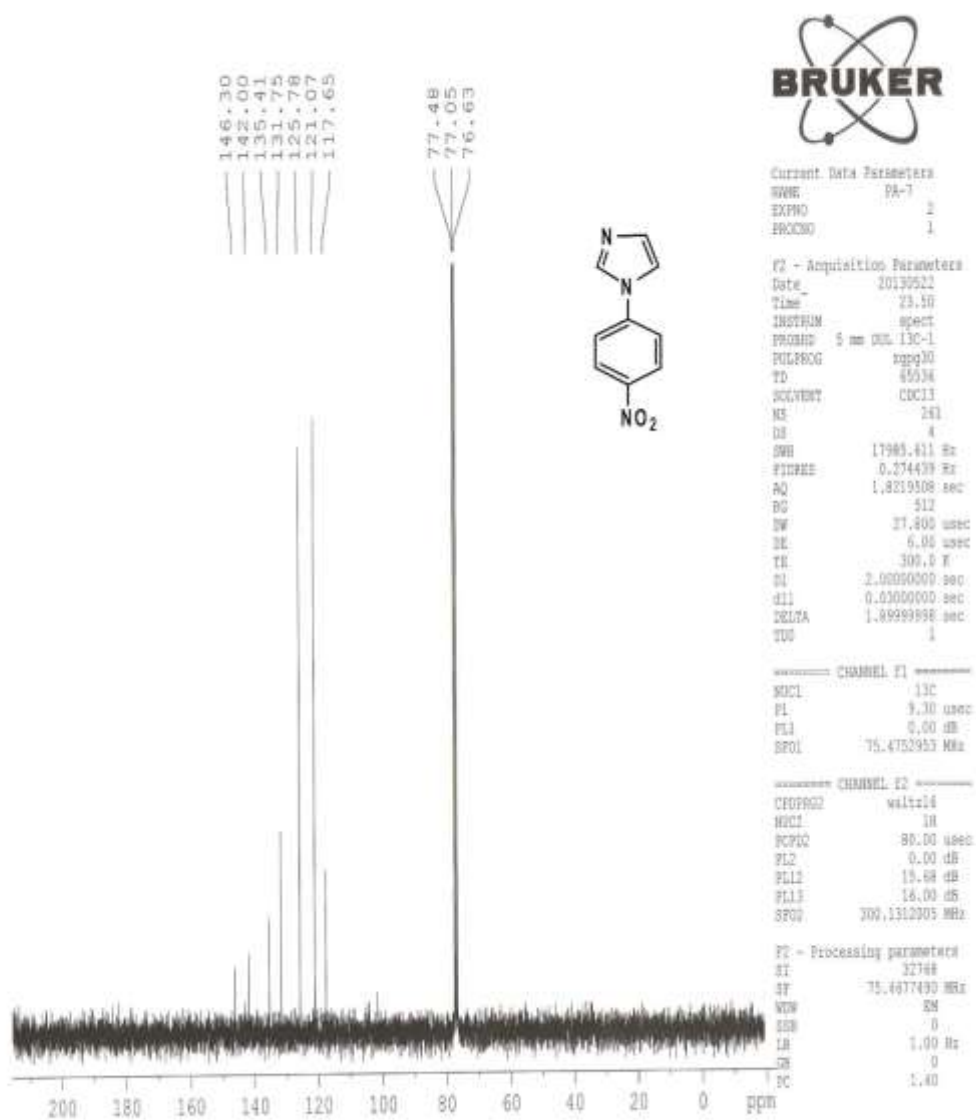
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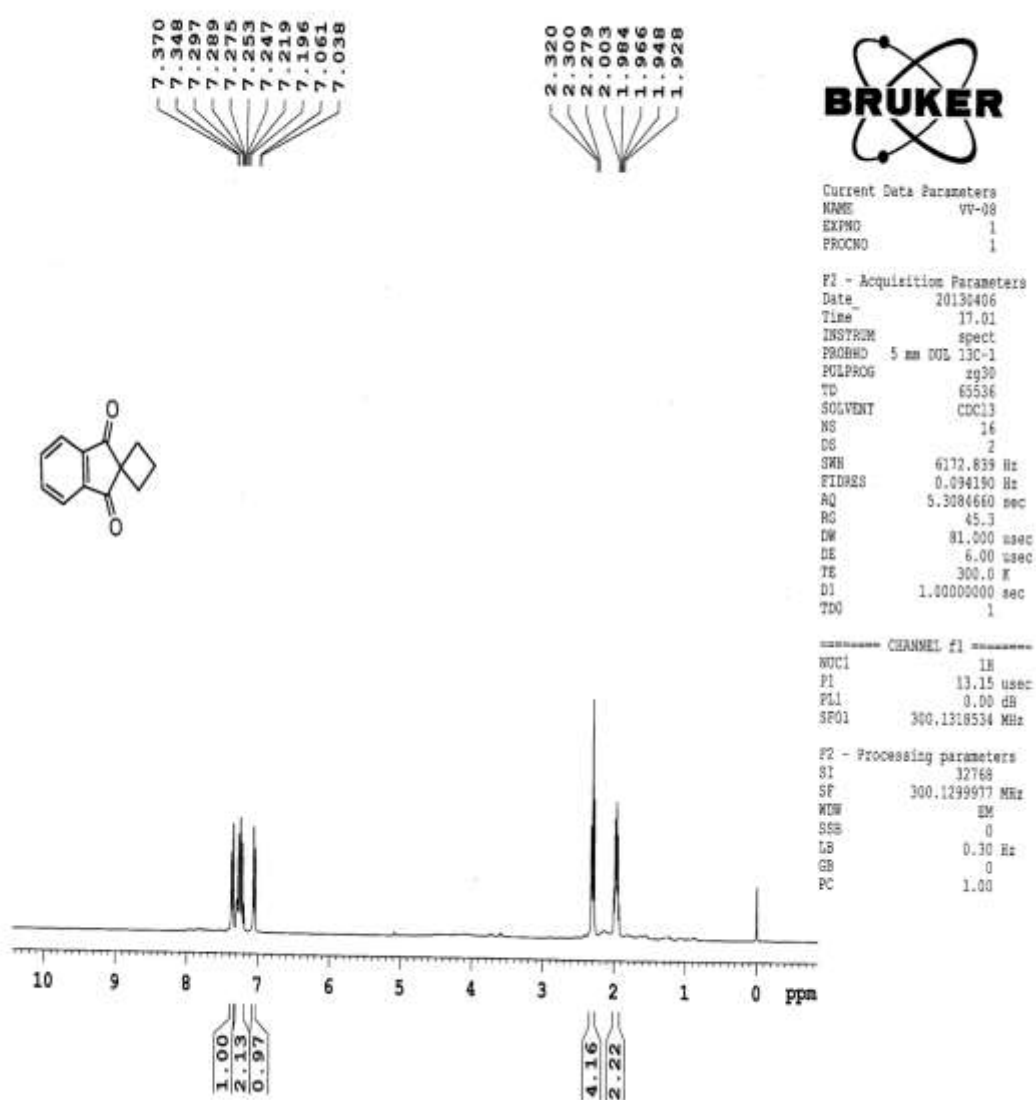


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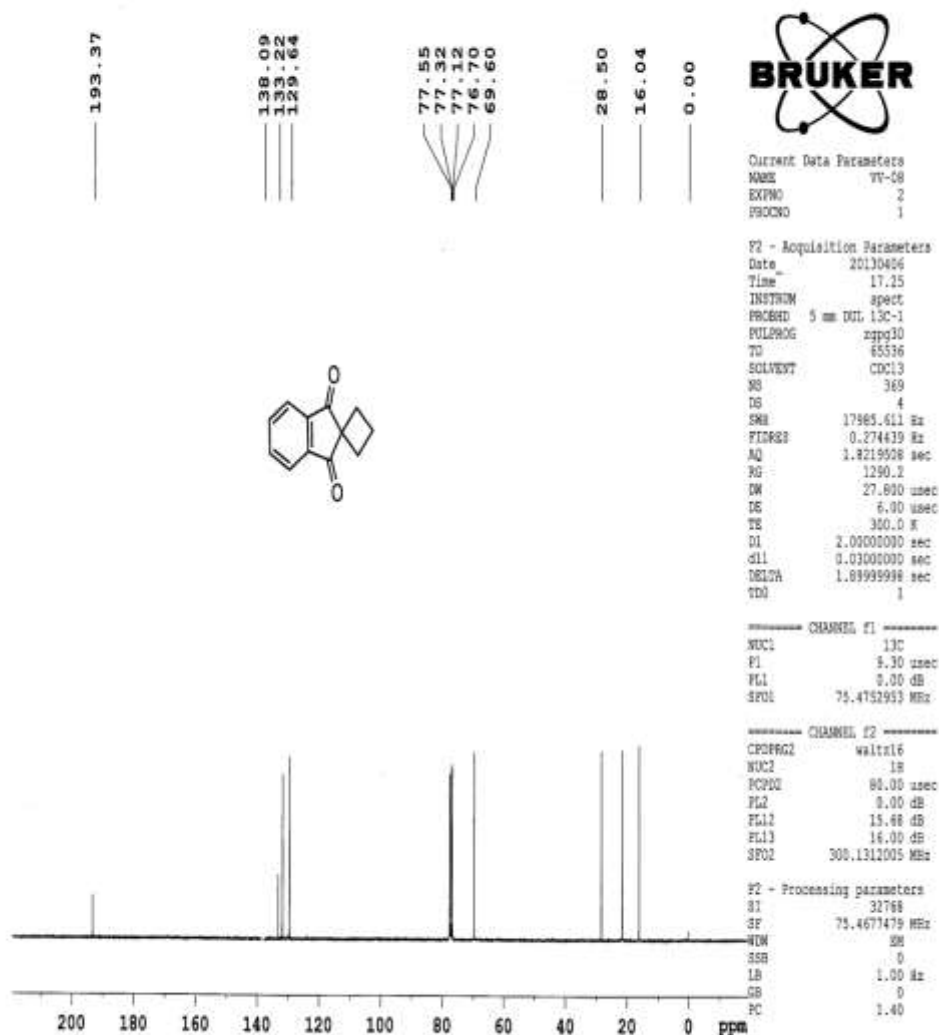
3. Reaction of 4-Nitrochlorobenzene with Imidazole : C^{13} – NMR



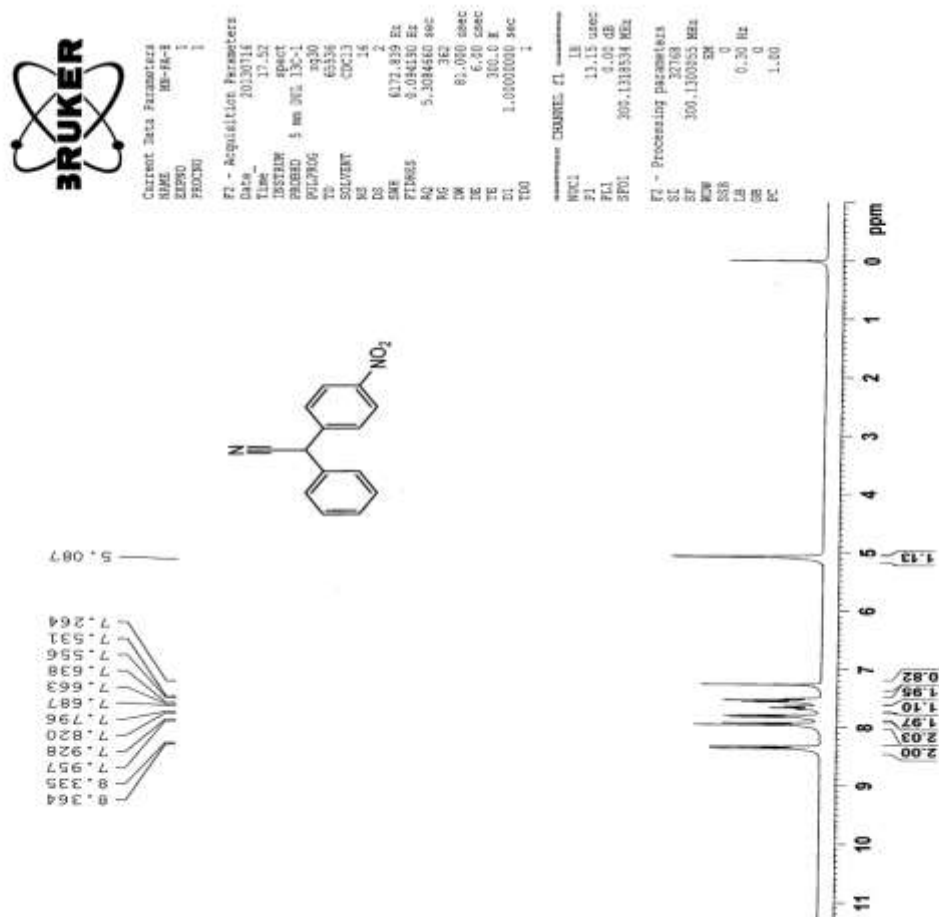
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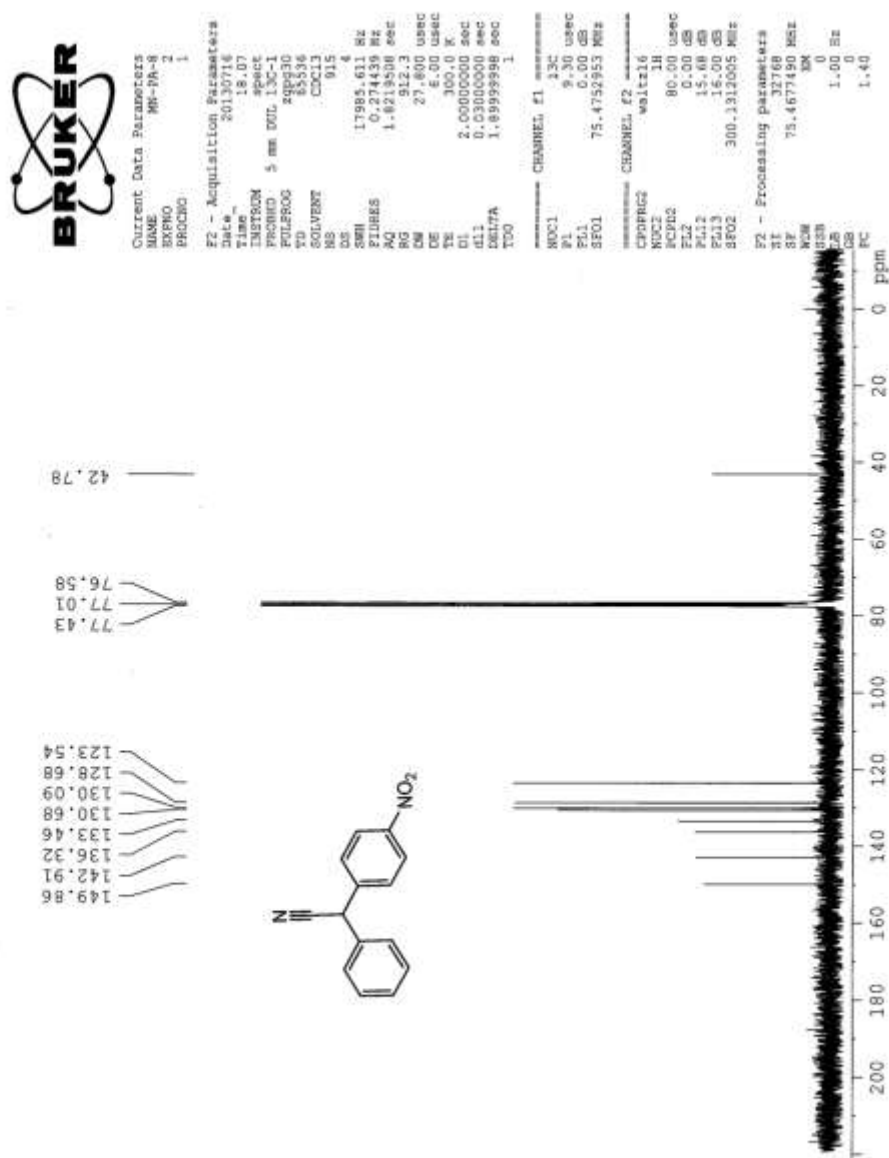
4. spiro[cyclobutane-1,2'-indene]-1',3'-dione (C^{13} -NMR) Synthesis by Ultrasound Assisted PTC Condition



5. Reaction of Phenylacetonitrile with 4-nitrochlorobenzene (C-Arylation) PTC with Ultrasonic Irradiation (H^1 -NMR)

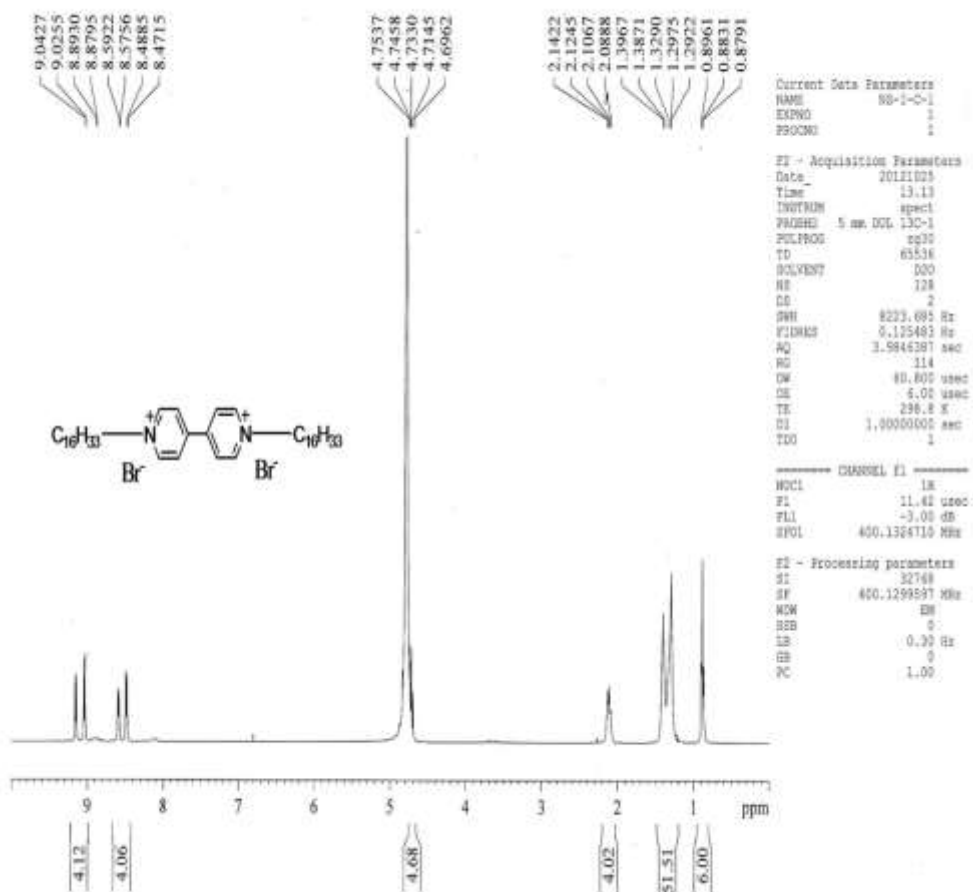


5. Reaction of Phenylacetonitrile with 4-nitrochlorobenzene (C-Arylation) PTC with Ultrasonic Irradiation (C13-NMR)



7. MPTC (H^1 -NMR)

1,1'-dihexadecyl-4,4'-bipyridine-1,1'-dium dibromide



8. MPTC (C^{13} -NMR)

1,1'-dihexadecyl-4,4'-bipyridine-1,1'-dium dibromide

PUBLICATIONS

1. Varathan Selvaraj, Pachaiyappan Abimannan and **Venugopal Rajendran**, Ultrasound assisted arylation of benzyl alcohol with 4-chloronitrobenzene under a new multi-site phase-transfer catalyst in solid liquid condition, *Ultrasonics Sonochemistry* 21 (2014) 1805 – 1814.
2. Pachaiyappan Abimannan, Varathan Selvaraj and **Venugopal Rajendran**, Sonication effect on the reaction of 4-bromo-1-methylbenzene with sodium sulphide in liquid – liquid multi-site phase-transfer catalysis condition – Kinetic study, *Ultrasonics Sonochemistry* 23 (2015) 156 – 164.
3. Pachaiyappan Abimannan and **Venugopal Rajendran**, Synthesis of 1,4-bis(benzyloxy) benzene under sonication and a multi-site phase-transfer catalyst in solid-liquid condition – kinetic aspect, *International Journal of Science and Research* 3 (2014) 1650 – 1655 (ISSN Journal).
4. Pachaiyappan Abimannan and **Venugopal Rajendran**, An Efficient Ultrasound Promoted Single spot synthesis of p-Nitrophenyl Alkyl Ethers Under Solid – Liquid Multi-Site Phase-Transfer Catalysis Condition. *International Journal of Chem. Tech. Research*, 7 (2014-2015) 2208 – 2216.
5. Pachaiyappan Abimannan and **Venugopal Rajendran**, Synthesis of Diethyl-2,2'-(1,3-phenylenebis(oxy))diacetate under a Multi-Site Phase-Transfer Catalyst and Ultrasound Irradiation in Solid-Liquid Condition, *Chem.Sci.Rev.Lett.*, 4 (2015) 474 – 488.
6. Pachaiyappan Abimannan, Varathan Selvaraj and Venugopal Rajendran, Sonication effect on the reaction of 4-bromo-1-methylbenzene with Sodium Sulphide in liquid-liquid multi-site phase-transfer catalysis condition – A kinetic study, *Ultrasonics Sonochemistry*, 23 (2015) 265 – 271.
7. Pachaiyappan Abimannan and **Venugopal Rajendran**, Kinetic study for the synthesis of 1-Nitro-4(Prop-2-ynyloxy)benzene in Solid – Liquid PTC Condition, *Current Catalysis* 5 (2016) 44 – 50.
8. Pachaiyappan Abimannan and Venugopal Rajendran, Ultrasonically Promoted Synthesis of Ethyl-2-(Naphthalene-2-yloxy)acetate in Solid – Liquid Heterogeneous Phase-Transfer Catalysis Condition, *Bulletin of Chemical Research Engineering & Catalysis* 11 (3) (2016) 273 – 283.
9. V.Selvaraj and **V.Rajendran**, Ultrasound assisted dichlorocarbene addition to 1,3-bis(allyloxy)-5-methylbenzene under biphasic condition: A kinetic study. *Iranian Chem.Comm.*, 5 (2017) 381 – 396.
10. V.Selvaraj and **V.Rajendran**, Phase – Transfer catalysed reaction disodium salt of 1,3-dihydroxybenzene with Propargyl bromide in solid-liquid biphasic condition, *Iranian Chem. Commun.*, 6 (2018) 5 – 9.
11. Pachaiyappan Abimannan and **Venugopal Rajendran**, Ultrasound Assisted Synthesis of 1-Butoxynaphthalene Under Liquid – Liquid Multi – Site Phase – Transfer Catalysis Condition and Their Kinetics, *International Journal of Science and Research (IJSR)* Volume 3 Issue 12 (2014) 1650.

