

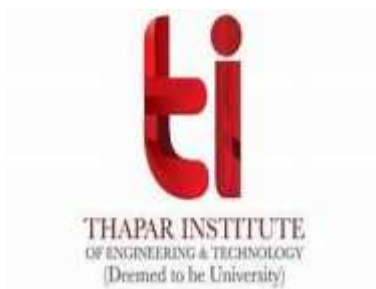
Towards Alkylation of Aromatic Phenol Assisted by 2,4-Dinitrophenyl Substituent

Thesis submitted in the partial fulfilment of
the requirements for the degree of

Master of Science in Chemistry

by

ANISHA
301702006



Under the supervision of

Dr. Manmohan Chhibber
Associate Professor

**School of Chemistry and Biochemistry
Thapar Institute of Engineering and Technology
Patiala**

July 2019

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All these thanks are however only fraction of what is due to almighty for granting me an opportunity and strength to successfully accomplish this project.

Anisha

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Candidate Declaration

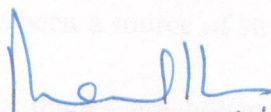
I, hereby declare that the work presented in the dissertation entitled "*Towards Alkylolation of Aromatic Phenol Assisted by 2,4-Dinitrophenyl Substituent*" in partial fulfillment of the requirement for the award of degree of Master of Science (Chemistry), School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala, in my own during the period January 2019 to July 2019, under the supervision of Dr. Manmohan Chhibber, Associate Professor, School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala. No part of the work has been submitted anywhere else for any degree.

Place: Patiala

Date: 15th July 2019


ANISHA

I hereby acknowledge above statement made by Ms. Anisha (Reg. No.3017020060) and certify that the above M.Sc (Chemistry) thesis has been supervised under my guidance.



Dr. Manmohan Chhibber

Supervisor
Associate Professor
School of Chemistry and Biochemistry
Thapar Institute of Engineering and Technology, Patiala

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Abstract

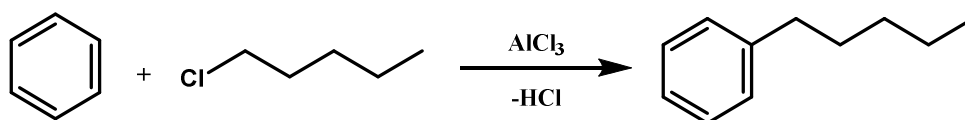
Alkylation on aromatic ring is an important reaction both from industry and synthesis point of view. Ever since the discovery of Friedel-Crafts Alkylation reactions a number of reactions have been reported for in literature. Despite such an important reaction most of the reported procedures use transition metal based reagents. However from environmental point of view metal based reagents need to be replaced with organic reagents. The work presented in this thesis describes the concept and attempt to carry out alkylation of phenol, namely resorcinol, using 2,4-dinitrophenol as a substituent. Two alkylating agents ethyl bromide and benzyl bromide gave spots different from starting materials in TLC. However, purification of the alkylated product could not be achieved due to multiple product formation.

Key Words: 2,4-Dinitrofluorobenzene, m-Methoxyphenol, Nucleophilic Aromatic Substitution, Non-Aromatic Intermediate

CHAPTER-1

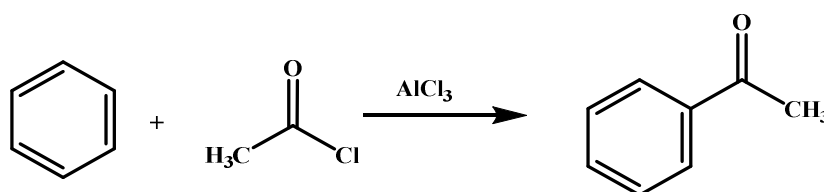
Introduction

Alkylation is basically the addition of an alkyl group in an organic compound by substitution or addition (**Scheme-1.1**). Doing alkylation in aromatic compounds have always been a challenging job for the researchers. Numerous attempts have been made towards the synthesis of alkylated aromatic compounds using different reaction conditions and different catalysts. One most common route of doing it is via Friedel-Crafts reactions. The reaction removes hydrogen atom of an aromatic compound and introduces an alkyl group of an alkylating agent. The position of the substitution depends upon the substituents attached to the aromatic ring



Scheme-1.1 AlCl₃ mediated friedal craft alkylation

Besides alkylation, another important class of reaction is Friedel-Crafts acylation reaction where acyl group adds to the organic compound as shown in **scheme-1.2**. Both acylation and alkylation require use of a lewis acid such as AlCl₃ which polarizes the electron density on electron rich aromatic ring to facilitate the substitution of a nucleophile.



Scheme- 1.2 AlCl₃ mediated friedel craft acylation

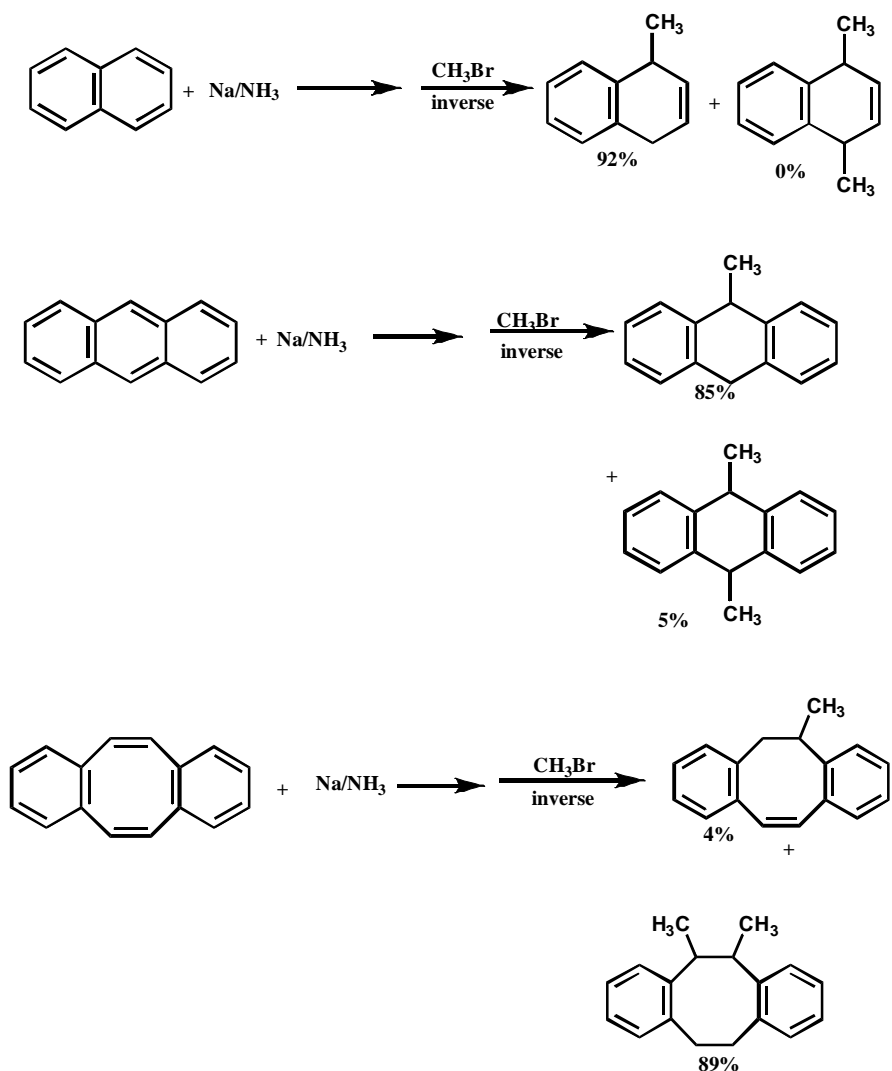
Despite being an important class of reactions the use of metal based lewis acid has demerits like release of harmful gasses like HCl, metal contamination of soil and water resource and their cascade environmental effects. Considering the green approach requirement of present times many alternative reactions have been reported to minimize the harmful materials to carry out the reaction^[1]. Some of them have been discussed in next section. Present work is an attempt to carry out alkylation reaction without use of metal ions by polarizing the aromatic ring with organic substituents.

CHAPTER-2

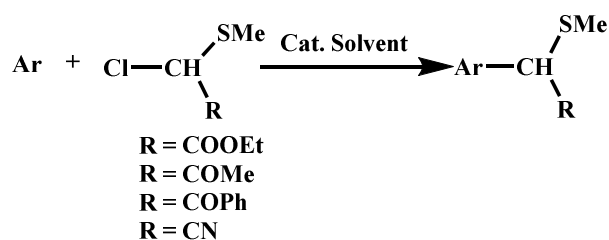
Literature Review

Peter W. Rabideau did the alkylation of naphthalene and anthracene using ammonia. Metals that he included were lithium or sodium but potassium and calcium can also be used. The most important thing about this reaction is that the reaction has to be done with utmost care because the selection of reaction conditions can lead to a wide range of products.

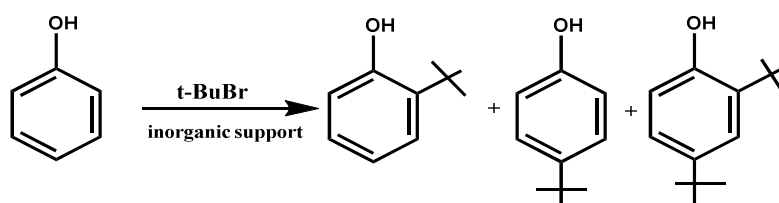
Naphthalene and anthracene gives mono alkylation as the major product while sym –dibenzocyclo octatetraene gives dialkylation as the major product. [2]



In another review α - (acyl) methyl thiomethyl group was introduced in the aromatic ring. The product thus formed can be easily converted into acyl methylated aromatics like phenyl acetate and phenyl acetone. The maximum yield for this reaction was obtained when the reaction was done using COOEt group in place of R. The catalyst used for the reaction was SnCl₄ and the reaction was done for about 20 min at room temperature and yield obtained was 90 %^[3].



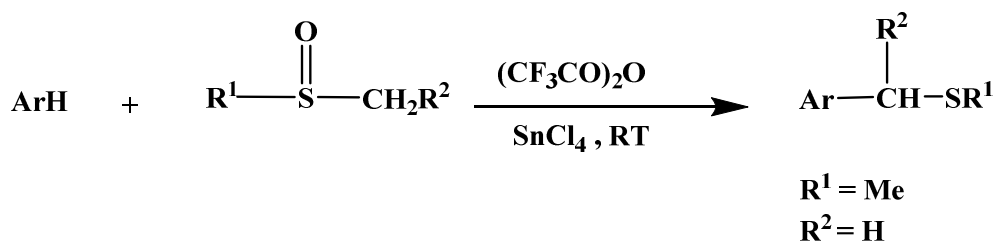
Another important method proposed by Yasuhiro Kamitori^[4] is appreciable as he used the readily available silica gel for doing alkylation. Recently many chemists have adopted his method of doing alkylation with the help of an inorganic support and moreover various heterocyclic compounds were also synthesized by this process. He was successful in making 2-tert-butyl, 2, 6-di-tert-butyl and 2, 4, 6-tri-tert-butyl phenols.



The ortho product formed in this reaction was in major amount and can be separated from the rest by column chromatography.

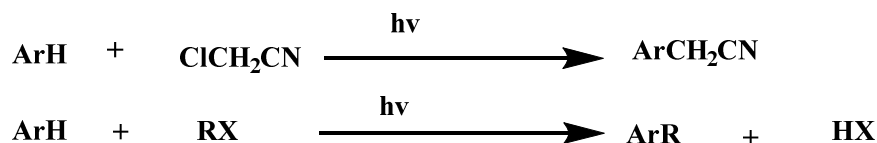
In addition to these catalysts using alcohols to substitute alkyl chloride would be quite beneficial as the side product in that case will be water. Good ideas always take time so it's not surprising that it took 100 years to come out from the classical method of making alkylated products and still so much is left unexplored.

Another interesting synthesis that was proposed used pummerer rearrangement mechanism. They used aromatic compound and dry DMSO and to this (CF₃CO)₂O was added drop wise with the help of syringe. After about an hour SnCl₄ was added through syringe^[5]. So in this way they synthesized methyl aryl compounds. The reaction is as follows

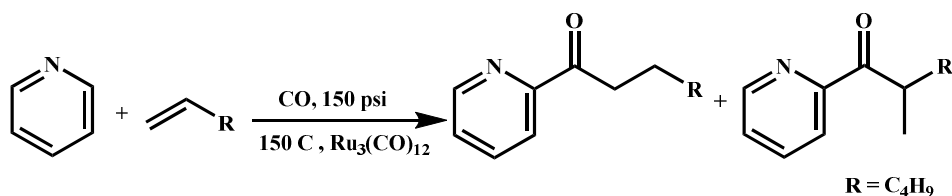


Another very interesting way of doing alkylation is via using photochemistry i.e. by photochemical activation. This mechanism involves the reaction of n-alkyl iodides in neat aromatic compounds. Here the reaction mixtures were analyzed by using GCMS whereas in some cases the iodine produced was quantitatively determined by sodium thiosulphate. First they did it with the help of chloroaceto nitrile. The mechanism involved in this reaction is basically an electron transfer occurs from aromatic compound to the halide. Subsequently they tried it with bromo and iodo acetonitrile and then also they got the cyano methylated product.

After that they tried the alkylation using simple alkyl chlorides and alkylated product was obtained^[6].



Another review by Eric J. Moore depicted the regioselective acylation of heteroaromatic compounds with the help of olefins and carbon monoxide. The main goal for this reaction was to increase the rate of reaction by not compromising with the selectivity of the product^[7].

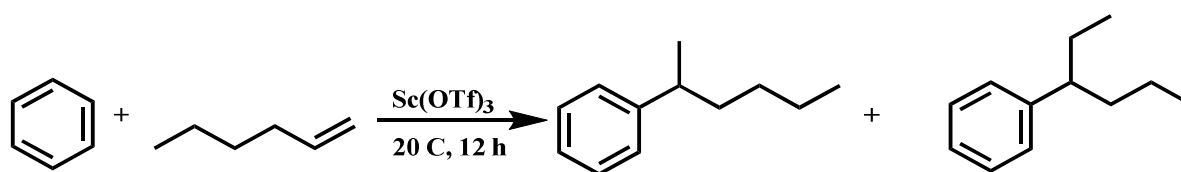


They only got the ortho products in this reaction as checked by ¹H NMR and GC-MS spectroscopy techniques. The reaction follows first order reaction with respect to pyridine. Another alkylation in aromatic compounds was done by Choong Eui Song in the year 2000. They used scandium triflate which were immobilized in ionic liquids for their reaction and this scandium triflate acts as a

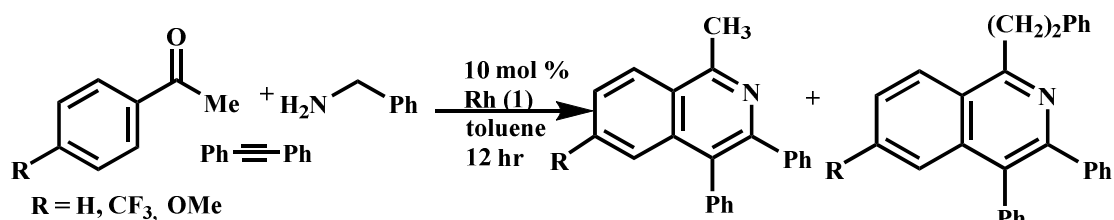
catalyst. The interesting thing about this reaction was that the catalyst used can be recycled. The major problem with the catalysts AlCl_3 , HF and H_2SO_4 was that they can't be reused after the aqueous work up. They tried the reaction with different solvent system but the reaction didn't go with water, CH_2Cl_2 , CH_3CN and the solvents which showed up alkylation reaction were emim $[\text{SbF}_6]$ and bmim $[\text{PF}_6]$. Emim here is 1-ethyl-3-methylimidazolium cation whereas the bmim here is 1-butyl-3-methylimidazolium cation.

Catalytic activities in these reactions are strongly influenced by the nature of anion.

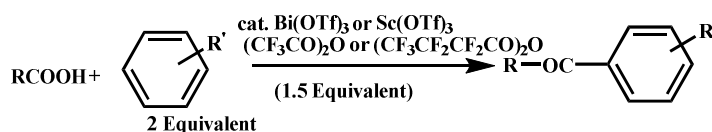
For the reaction hex-1-ene reacted with benzene in presence of $\text{Sc}(\text{OTf})_3$ and solvent for about 12 hr. The conversion was checked using GC^[8].



Another report from 2003 reported the alkenylation of aromatic ketimines with the help of Rhodium which act as a catalyst for the reaction. Here aromatic ketone react with alkyne and the product so formed has an application in making isoquinoline derivatives.^[9]



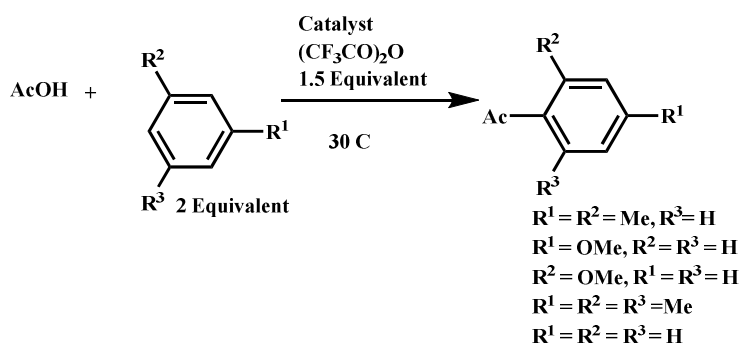
Yoh-ichi Matsushita reported the acylation of aromatic compounds by using carboxylic acids and perfluoroalkanoic anhydride and bismuth or scandium triflate. In this reaction aromatic ketones were synthesised by friedal craft acylation reaction. The catalyst used in this reaction was easy to recover and recycle.



Here aromatic ketones were made by dehydrative acylation reaction in presence of perfluoroalkanoic anhydride and Bi (OTf)₃ or Sc (OTf)₃ act as the catalyst for the reaction and the reaction was carried out at 30 degree celcius.

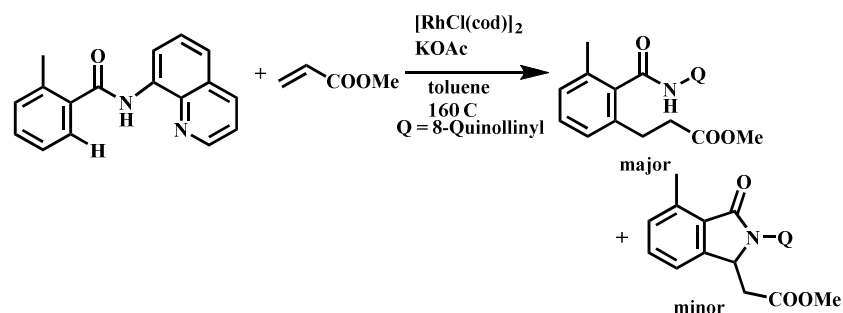
Another important reaction that was reported in that paper was the reaction of acetic acid with that of benzene and the acylated product was formed.

These reactions were carried out without using solvent and mild conditions and here less reactive substrates can be converted into benzophenones.^[10]

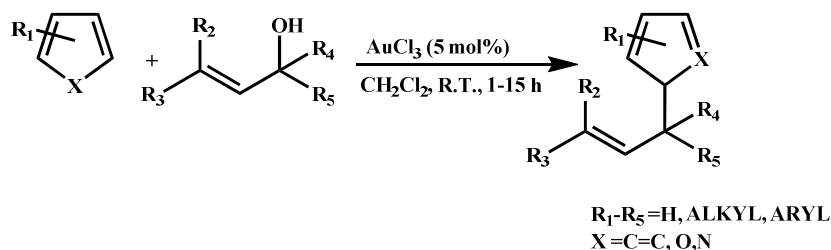


Another Rh catalyzed reaction was done in aromatic amides with α , β -unsaturated esters. The reaction was done using 8 amino quinoline moiety. The reaction showed high regioselectivity. Here the alkylation of C-H bond was done with the help of an alkene. The reaction occurs at the ortho position and the β position of acyclic unsaturated carbonyl compound.

In this reaction amide group reacts with methyl acrylate in the presence of Rh which act as a catalyst and KOAc acts as a base in toluene at 160 degree celcius for about 12 hrs gave the alkylated product. The byproduct also formed along with the alkylated products and various attempts were made to remove that byproduct but all failed. However both the products were easily separated by column chromatography^[11].

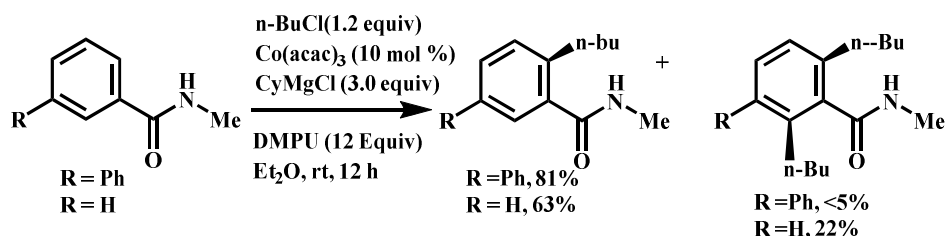


Another transition metal which can help in alkylation is Gold and was published in the year 2008. They did the allylic alkylation of aromatic and heteroaromatic compounds with the help of allylic alcohol^[12]. Here they did some modification in Friedel-Crafts allylating reagents like allylic acetates, carbonates with allylic alcohols and the best part of doing all this that the yield they obtained was **99%** with high regioselectivity and the reaction was performed at room temperature.

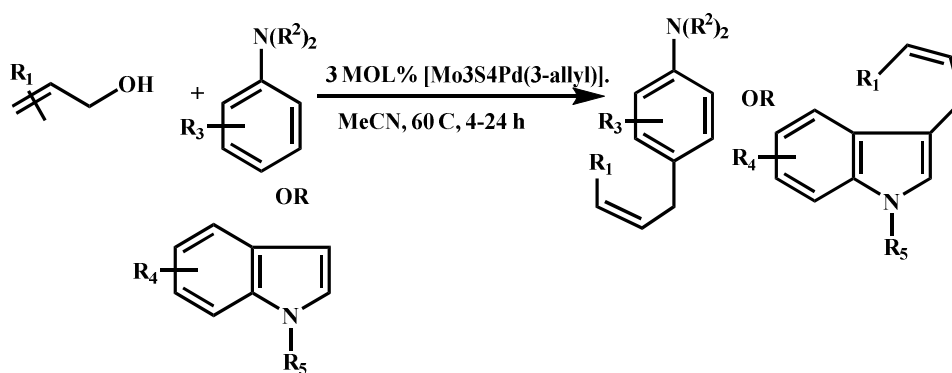


On seeing the above reviews this can be concluded that the transition metal compounds act as the best source for making alkylated products.

Nakamura et al. demonstrated alkyl aromatic ring using Cobalt catalyst and DMPU at room temperature in 63 to 81% yield. In this case a minor amount of dialkylated product was also obtained. In case of an aromatic ring being not substituted by another aromatic ring the quantity of dialkylated product increased^[13].



With the passage of time more such methods had been developed and that too by taking care of the principles of green chemistry. Yinsong Tao discovered another method and he used the molybdenum catalyst for the reaction $[\text{Mo}_3\text{S}_4\text{Pd}(\eta^3\text{-allyl})]$. He also used allylic alcohol for the reaction because using allylic alcohol gives water as the byproduct. They even tried it using bronsted acids but they failed because of the scavenging of proton by the basic N, N-dimethylaniline ^[14].



From the above literature it can be seen that although many alkylated products have been synthesised but alkylation on aromatic phenol assisted by 2, 4-dinitro phenyl substituent has not been tried till yet. Present work attempts to concentrate this reaction.

CHAPTER-3

Materials and Method

General: The chemicals and solvents used were from M/s AVRA Chemicals, Hyderabad, India and were of LR grade. Silica gel (60-120 mesh) was used for doing purification of compounds. Silica coated aluminum sheets (60 F254; 0.2mm thickness, Merck, India) were used for TLC monitoring. Characterisation was done using ^1H NMR and ^{13}C NMR.

Synthesis of 1-(2-methoxyphenoxy)-2, 4-dinitrobenzene (4.8): Meta-methoxy phenol (400 mg, 1.6 mmol), K_2CO_3 (660 mg, 3.18 mmol) and 18-crown-6 in DMF (6 ml) were taken in a round bottom flask. The reaction mixture was stirred for five minutes to make its phenoxy ions. After adequate stirring 1-fluoro-2, 4-dinitrobenzene (600 mg, 3.22 mmol) was added in the reaction mixture and stirred for 12 hours at room temperature TLC was monitored and on the completion of reaction, the mixture was extracted with DCM and water and dried over anhydrous sodium sulphate. The solvent was evaporated and then column was done for purification of compound using hexane and ethyl acetate (%). (**Compound-4.8**) Yield= 43%. ^1H NMR (400 MHz; CdCl_2): 8.829 (d, J= 2.4 hz, 1H), 8.316-8.285 (dd, J= 6.8 hz, 1H), 7.378 (t, J=8, 1H), 7.068 (d, J= 9.6, 1H), 6.869 to 6.841 (dd, J=6, 1H), 6.707 to 6.664 (multiplet, 2H), 3.808 (s, 3H). ^{13}C NMR (CdCl_2): 161.591, 156.230, 154.510, 141.415, 139.432, 131.222, 128.905, 122.183, 118.619, 112.485, 112.383, 106.681, 55.706.

Synthesis of (2,4-dinitrophenyl)(3-hydroxyphenyl) methanone (4.9) : Above synthesised compound 2.8 (400 mg, 1.886 mmol) taken in a 250 ml round bottom flask and solvent acetic acid (6ml) added. The contents were placed over oil bath at a temperature of about 100 degree and stirred for 5 minutes. After that HBr (5 ml) was added to the mixture with the help of syringe and was further heated as well as stirred for 8 hours. TLC was monitored and showed the formation of product. The product was extracted using DCM and water and dried using sodium sulphate. The solvent was evaporated and the product extracted (Compound-4.1) was finally purified. Yield=52.63% ^1H NMR: (400 MHz; CdCl_2) 8.825 (d, J= 2.8 hz, 1H), 8.317 to 8.287 (dd, J=0.537, 2H), 7.318 to 7.246 (multiplet, 2H), 7.080 (d, J=9.2, 1H), 6.795 to 6.769 (dd, J=6, 1H), 6.677 to 6.620 (multiplet, 2H). ^{13}C NMR: (CdCl_2) 157.793, 156.144, 154.542, 141.438, 139.420, 131.457, 128.981, 122.207, 118.768, 113.841, 112.478, 108.136.

Synthesis of (2,4-dinitrophenyl)(4-hydroxy-[1,1'-biphenyl]-2-yl)methanone (4.10): The compound **4.1** (200 mg, 0.760 mmol), NaOH (1 equivalents, 0.077g) were taken in a 100 ml round bottom flask and to which THF (3 ml) was added and stirred for about 5 min. Finally electrophile benzyl bromide (20 micro litre) was added dropwise to the mixture and the reaction was completed in 5 hours and that was confirmed with the help of TLC. The product thus formed was extracted using DCM and water.

Synthesis of (2,4-dinitrophenyl)(2-ethyl-5-hydroxyphenyl)methanone (4.11): The compound **4.1** (200 mg, 0.760 mmol), NaOH (1 equivalents, 0.077g) were taken in a 100 ml round bottom flask to which THF (3 ml) was added and stirred for about 5 min. Finally electrophile ethyl bromide (40 micro litre) was added dropwise to the mixture and the reaction was completed in 5 hours and that was confirmed with the help of TLC. The product thus formed was extracted using DCM and water. The purification of the product extracted was done with the help of column.

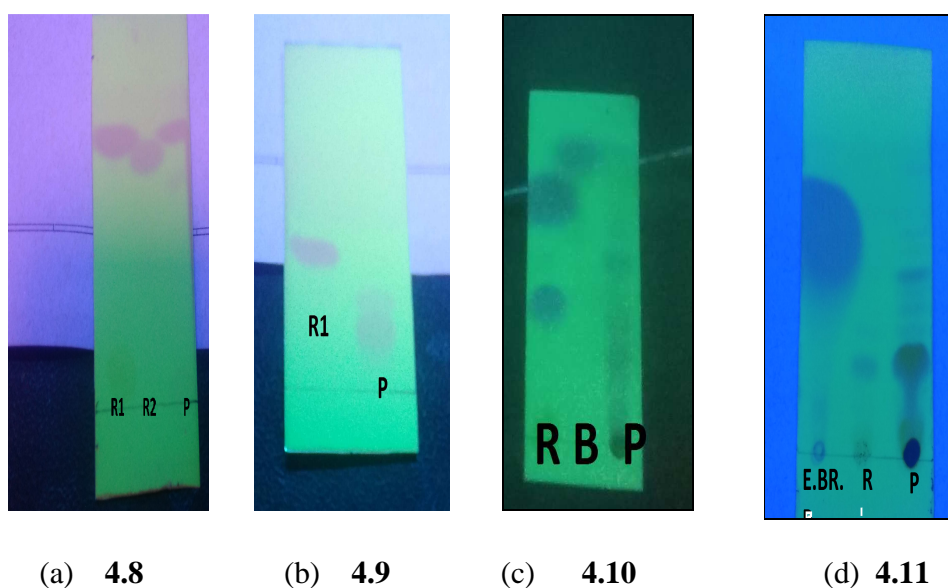
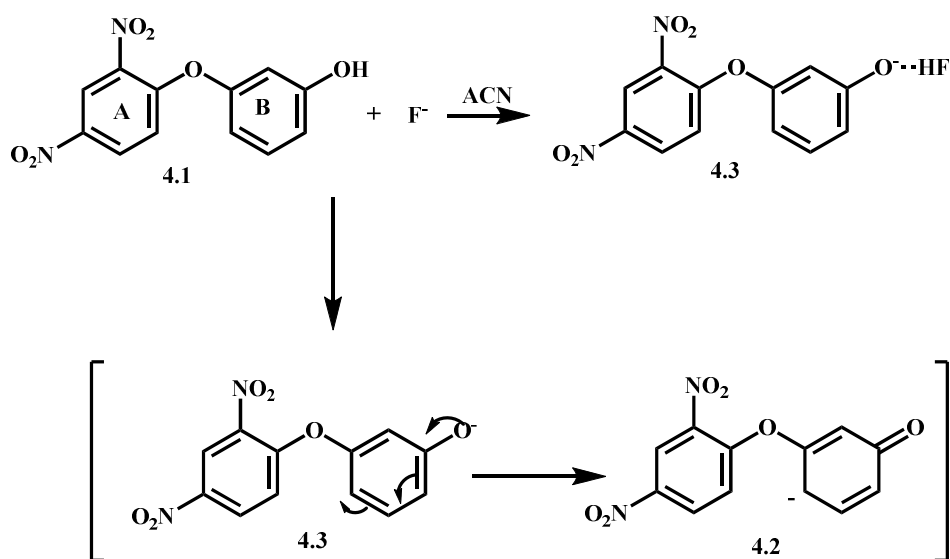


Fig. 3.1 Reaction monitoring by TLC using ethyl acetate and hexane solvent system for products.

CHAPTER-4

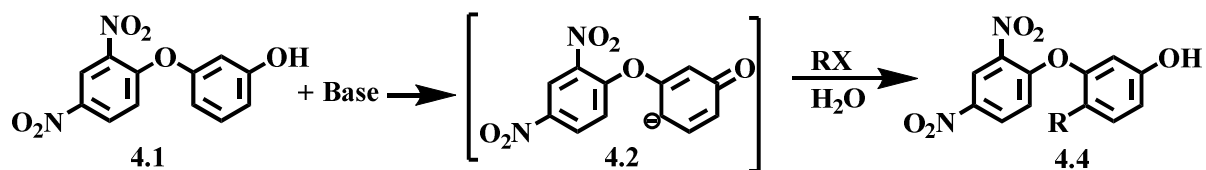
Result and Discussion:

It has been reported that compound **4.1** shown below selectively detects fluoride ion in acetonitrile medium giving change in colour from yellow to green over a period of time¹⁵. It was reasoned that the change in colour is due to the formation of carbanion species **4.2** formed as a result of resonance after abstraction of phenolic proton from ring B.



Scheme 4.1 Formation of Carbanion species **4.2** due to abstraction of phenolic proton from DPF **4.3**

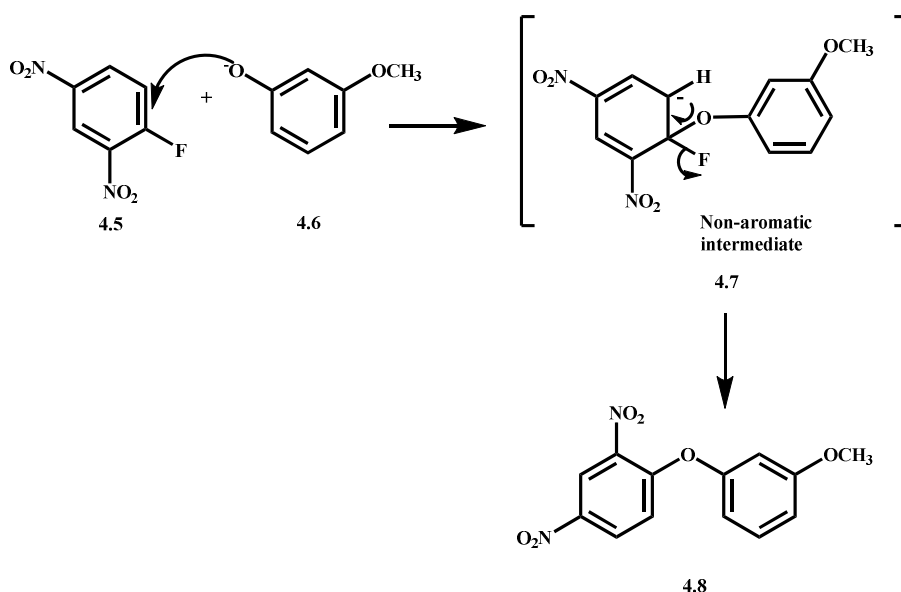
It was envisaged to use the carbanion species **4.2** for the alkylation of aromatic ring with an alkyl halide as shown in **Scheme-4.2** below.



Scheme 4.2 Proposed Scheme to alkylate the aromatic ring using the carbanion **4.2**

With above mentioned objectives the two step synthesis of compound **4.1** was taken up starting 2,4-dinitro fluoro benzene (**4.5**) and meta methoxy phenol (**4.6**). Nucleophilic aromatic substitution of compounds **4.5** and **4.6** in presence of potassium carbonate, 18-crown-6 in aprotic solvent gave compound **4.8** as shown in **Scheme-4.5**. Fluorine in compound **4.5** act as a good leaving group

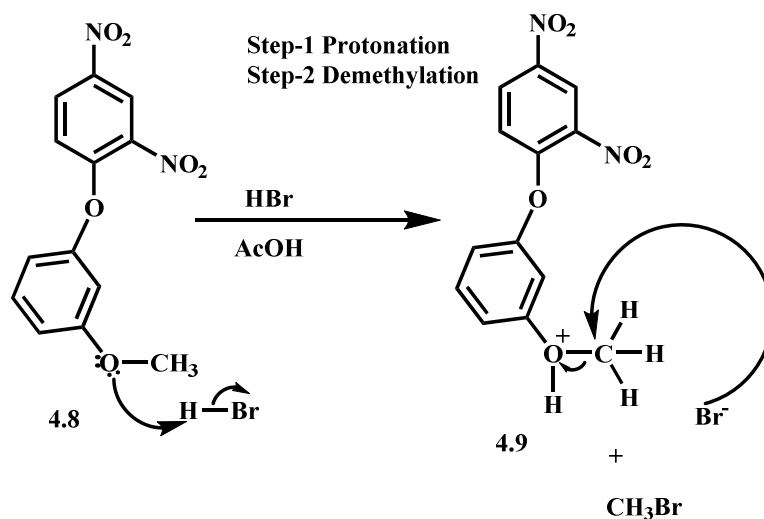
from the non-aromatic intermediate **4.7** to impart aromaticity to final compound **4.8**. The non-aromatic intermediate (**4.7**) is formed as a result of nucleophile attacking positive carbon centre of compound **4.5** after abstraction of proton by base as shown in **Scheme- 4.3** from compound **4.6**. Crown ether function here is to increase the basicity of potassium carbonate after trapping its cation. Crown ether function here is to increase the basicity of potassium carbonate after trapping its cation.



Scheme-4.3 Mechanism of the formation of diphenyl ether.

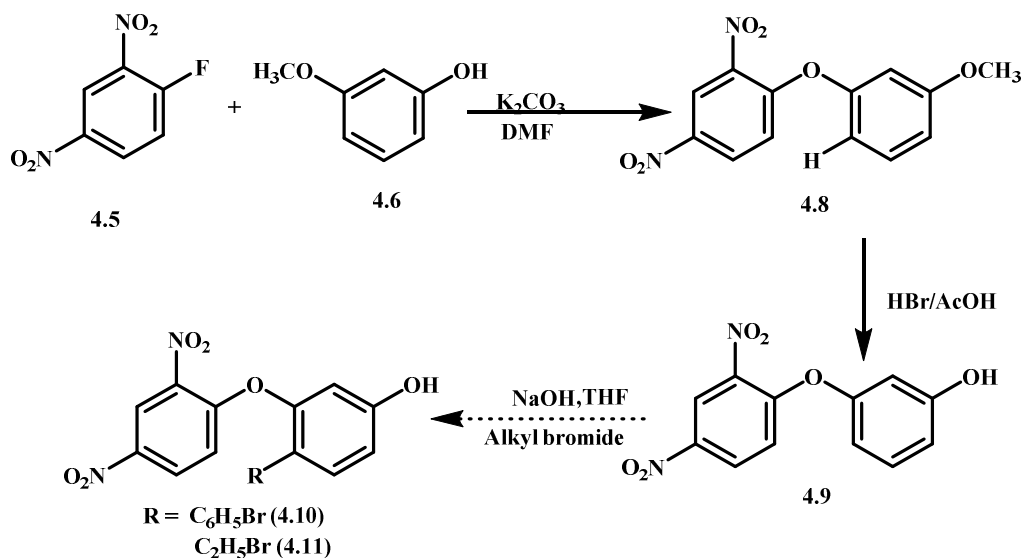
Compound-**4.8** formed was characterized using ^1H NMR and ^{13}C NMR spectroscopy where presence of three methoxy protons at δ 3.8 (^1H) and carbon at δ 55.7 (^{13}C) along with seven aromatic protons and carbon in the respective region confirmed its formation.

Next step involved demethylation of the methoxy group to obtain corresponding phenolic compound **4.1**. This was accomplished by refluxing the compound **4.8** in 48% hydrobromic acid using acetic acid as the solvent. The proton of hydrobromic acid as shown in **Scheme-4.4** protonates oxygen of the methoxy followed by its corresponding nucleophile (Br^-) attacking the carbon of methoxy to yield corresponding phenol and methyl bromide. This reaction is regioselective because despite presence of two ether linkages only one involving methoxy linkage gets selectively hydrolyzed due to presence of electron rich phenyl ring on other ether's either side



Scheme-4.4 Mechanism for demethylation (D)

Absence of methoxy protons and carbon and presence of seven aromatic protons and carbon in ^1H and ^{13}C NMR respectively at the desired δ value confirmed the synthesis of the product **4.1**. Further ^{13}C NMR displayed desired five quaternary carbons that were not attached to any hydrogens.



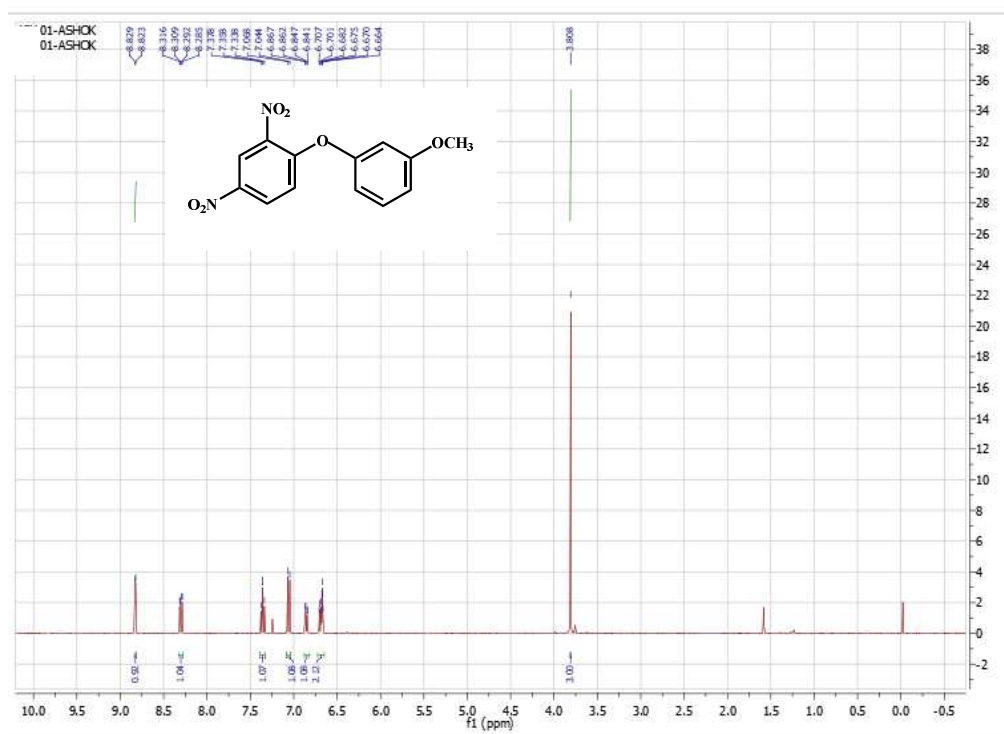
Scheme 4.5-Synthesis of alkylated product

Alkylation at the aromatic B ring of the compound **4.1** was tried using a strong base “sodium hydroxide”, in a protic solvent THF. The electrophiles tried were benzyl bromide and ethyl bromide. On addition of base there was a clear change in colour of the solution from transparent to red due to the formation of anionic species. Subsequent to this electrophile was added drop wise

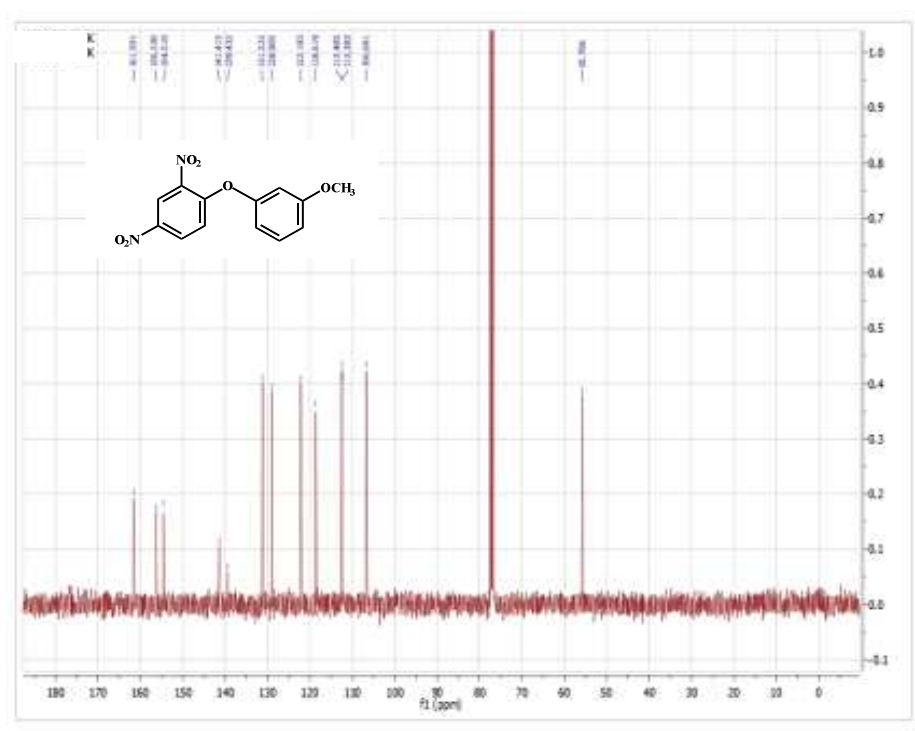
with a syringe. The reaction after half an hour was quenched with water and its TLC run in ethyl acetate and hexane. A spot distinct from reactants appeared both in case of benzyl bromide and ethyl bromide as shown in **Fig 3.1 (c) and (d)**. Isolation of the product using column chromatography did not yield sufficient material for column chromatography in case of benzyl bromide. ^1H NMR in case of alkylation product of ethyl bromide displayed multiple products. However peaks corresponding to desired product were also present in the respective regions.

In conclusion, alkylation of aromatic ring substituted to 2, 4-dinitrobenzene moiety was attempted using a strong base and aprotic solvent. Although there are indications of the product being formed in TLC and ^1H NMR but conditions still need to be optimized for higher yields and purification of the products from the reaction mixture.

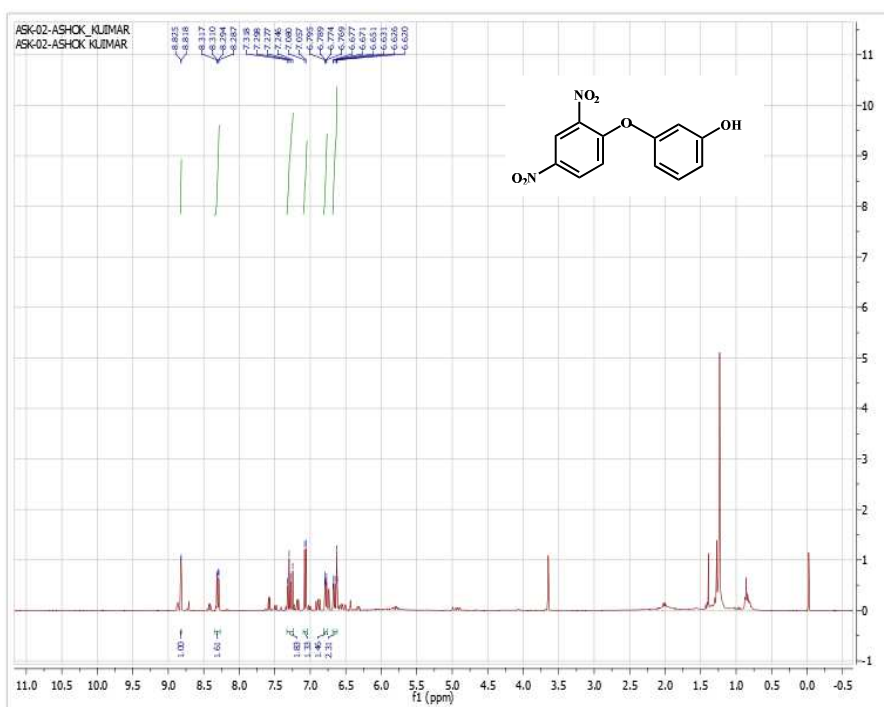
PROTON NMR:



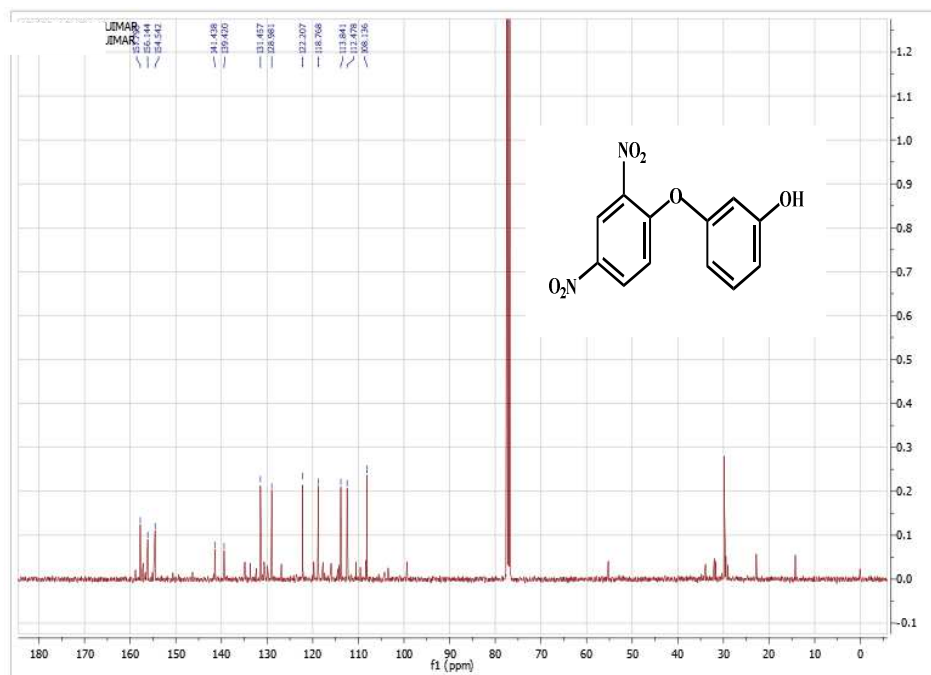
CARBON NMR:



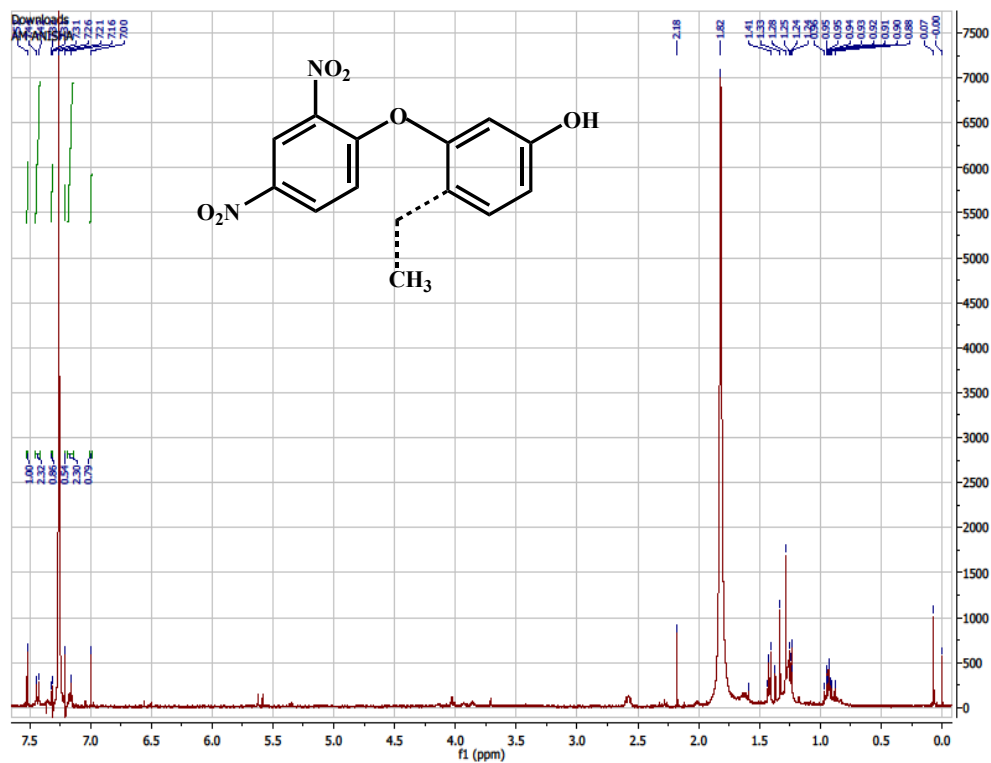
PROTON NMR:



CARBON NMR:



PROTON NMR:



References:

1. Clayden, Jonathan; Greeves, Nick; Warren, S. *Org. Chem.*, **2001**, 1st edition, Oxford University Press
2. Rabideau, W.P.; Burkholder, G.E. Metal ammonia reduction and reductive alkylation of polycyclic aromatic compounds: nature of the anionic intermediates *J. Org. Chem.* **1978**, 43, 4283-4287.
3. Tamura, Y.; Shindo, H.; Uenishi, J.; Ishibashi, H. Introduction of α -acyl methylthiomethyl group into the aromatic ring by Friedel-Craft reaction *Tetrahedron Lett.* **1980**, 21, 2547-2548.
4. Kamitori, Y.; Hojo, M.; Masuda, R.; Izumi, T.; Tsukamoto, S. Silica gel as an effective catalyst for the alkylation of phenols and some heterocyclic aromatic compounds *J. Org. Chem.* **1984**, 49, 4161-4165.
5. Ioannis, K.S.; Ave, K. Alkylation of aromatic compounds with pummerer rearrangement intermediates. Application to the preparation of methyl aryl compounds *Tetrahedron Lett.* **1985**, 26, 2787-2788.
6. Kurj, E.M. Photochemical aromatic alkylation *Org. Chem.* **1988**, 53, 172-177
7. Moore, J.E.; Pretzer, R.W.; Harris, J. Catalytic regioselective acylation of aromatic heterocycles using carbon monoxide and olefins. *J. Am. Chem. Soc.* **1992**, 114, 5888-5890.
8. Song, E.C.; Shim, H.W.; Roh, J.E.; Choi, H.J., Scandium (III) triflate immobilized in ionic liquids: a novel and recyclable catalytic system for Friedel-Craft alkylation of aromatic compounds with alkenes *Chem Commun.* **2000**, 1695-1696.
9. Lim, G.S.; Lee, H.J.; Moon, W.C.; Hong, B.J.; Jun, H.C. Rh (I) catalysed direct ortho-Alkenylation of aromatic ketimines with alkynes and its application to the synthesis of Isoquinoline derivatives *Org. Lett.* **2003**, 5, 2759-2761
10. Matsushita, Y.; Sugamoto, K.; Matsui, T. The Friedel-Craft acylation of aromatic compounds with carboxylic acids by the combined use of perfluoroalkanoic anhydride and bismuth or scandium triflate. *Tetrahedron Lett.* **2004**, 45, 4723-4727.

11. Shibata, K.; Chatani, N.; Rhodium catalysed alkylation of C-H bonds in aromatic amides with esters, **2007**
12. Rao, W.; Chan, W.P. Gold catalysed allylic alkylation of aromatic and hetero aromatic compounds with allylic alcohols *Org. Biomol. Chem.* **2008**, 6, 2426-2433.
13. Chen, Q.; Ilies, L.; Nakamura, E. Cobalt catalysed ortho alkylation of secondary benzamide with alkyl chloride through directed C-H bond activation *J. Am. Chem. Soc.*, **2011**, 133, 428-429
14. Tao, Y.; Wang, B.; Zhao, J.; Qu, J. Friedal craft type allylation of Nitrogen containing Aromatic compounds with allylic alcohols catalysed by a [Mo₃S₄Pd(η³-allyl)] cluster *J. Org. Chem.* **2012**, 77, 2942-2946
15. Sharma, R.; Mittal, S.K.; and Chhibber, M., Voltammetric Sensor for Fluoride Ions Using Diphenylether Derivatives Supported by NMR and Theoretical Studies, *J. Electrochem. Soc.*, **2015**, 162, B1-B8.

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