

V. Nano ceria catalyzed O, N arylation with 4-nitrochlorobenzene

5. 1 Introduction

Carbon-heteroatom bonds are found in many compounds that exhibit important biological and pharmaceutical [1-4]. Classically, the synthesis of compounds which contain these bonds involved nucleophilic aromatic substitution reactions, which required the use of electron-deficient aryl halides or N_2 as a leaving group. Several routes had been developed for their synthesis [5-7]. The transition-metal mediated reactions for the synthesis of carbon-heteroatom bonds was an important discovery for synthetic chemists. The increasing demand of coupled products in chemical and pharmaceutical industries has prompted the development of several transition metal catalysts, which aim to exert the highest turnover number and turnover frequency.

Palladium catalyzed cross-coupling reactions [6,7] and the Hartwig-Buchwald coupling [8] are the most frequently used routes for the formation of carbon heteroaromatics bonds. Although these palladium based reactions are routinely used in organic synthesis. Moreover, the high cost and air sensitivity of Pd catalyst systems commonly limit their applications to large- and industrial-scale formation of these bonds. Recently, a growing number of papers have focused on the deliberate use of additional ligands to facilitate copper-catalyzed carbon-heteroatom bond formation.

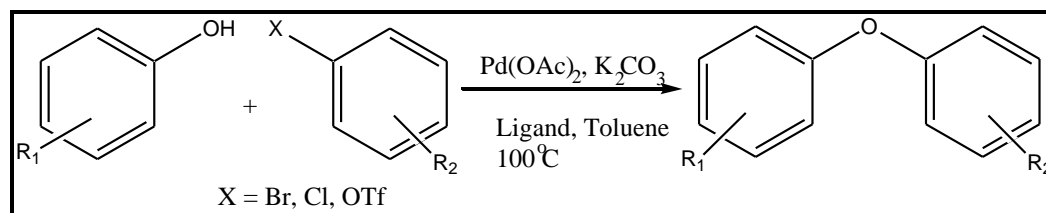
Prior to the discovery of these palladium-based reactions, copper-mediated reactions such as the Ullmann reaction,[9,11] for the Cu-mediated C–N coupling, has received a lot of attention for the formation of these carbon-heteroatom bonds [9-14]. However, the reactions are known to suffer from some drawbacks, which include high reaction temperatures ($>180\text{ }^\circ\text{C}$), the need for stoichiometric or in certain instances greater than the stoichiometric amounts of copper, low functional group tolerance and irreproducible results [15,16]. Copper-based cross coupling reactions are used in large industrial-scale reactions and have been successfully used where the palladium methods have failed [15-19].

However, despite its well known utility for the construction of carbon heteroatom linkage, the use of aryl chloride is largely restricted as compared to aryl iodides or bromides for arylation [20]. Nowadays, the use of aryl chlorides to effect such transformations is considered highly attractive due to their greatest availability and lower cost, but it is also regarded as a challenge given to their poorer tendency to undergo oxidative addition to transition metal complexes. Hence, only a few examples of copper catalyzed *N*- and *O*-arylation processes employing aryl chlorides have been reported, thus for which this field remains largely unexplored. It must be pointed out that, important applications of copper catalyzed arylation reaction can be a tool for the synthesis of biologically active heterocycles [21-26]. The development of a suitable and reusable heterogeneous catalyst for arylation reactions using aryl chlorides as starting materials would be of great interest for industry.

During the past few years, some significant modifications have been made for the ether synthesis by *O*- arylation. It has been observed that certain additives, such as 8-hydroxyquinoline [27], 1-naphthoic acid [28], 2,2,6,6-tetramethylheptane-3,5-dione [29], amino acid (L-proline, N methyl glycine, N, N dimethylglycine, [30-32], Schiff base [33], phosphazene P4-*t*-Bu base [34], β -keto ester [35], tripod [36] and some copper(I) complexes [37,38] can accelerate the rate of these reactions, and therefore, the reactions can be performed under milder conditions. In the coupling of aryl halides and aliphatic alcohols catalyzed by copper systems, Buchwald and Ma groups reported CuI as copper source with a proper ligand [39-42]. Even though most of these systems work reasonably well for aryl ethers synthesis, the use of moisture-sensitive Cs₂CO₃ is crucial to the success of the reaction.

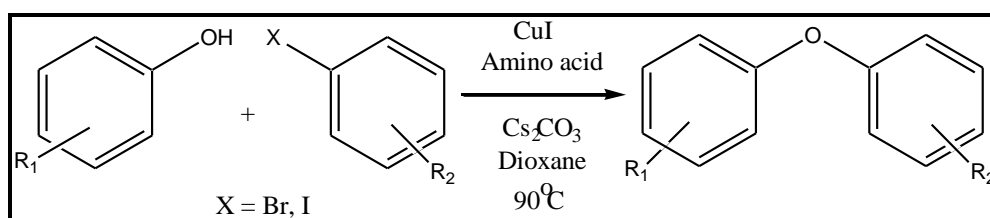
Because of the harsh reaction conditions of the classical Ullmann reaction for *O*- arylation, several modifications employing milder conditions have been developed. Hartwig [43] and Buchwald [44] employed aryl bromides and aryl

chlorides as the arylating agent (Scheme 5.1) in addition to the copper-mediated diaryl ether couplings.



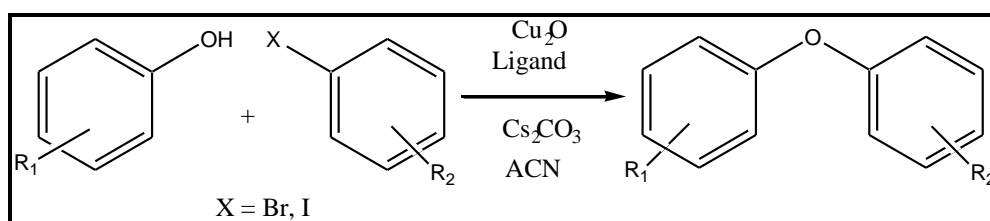
Scheme 5.1. Palladium catalyzed diaryl ether synthesis.

Ma et al. reported that Ullmann-type diaryl ether synthesis performed at 90 °C using either aryl iodides or aryl bromides as the substrates under the assistance of *N,N*-dimethyl -glycine (Scheme 5.2) [30,32].



Scheme 5.2 Ligand assisted CuI catalyzed *O*-arylation.

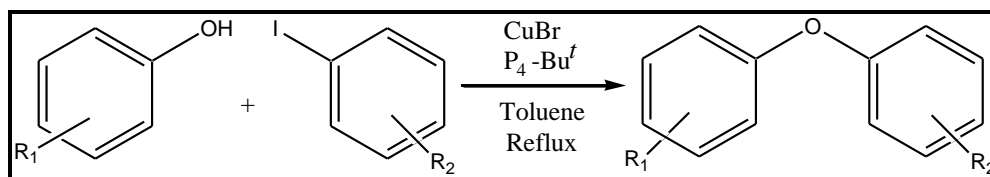
Taillefer et al. developed an efficient method for the synthesis of diaryl ethers under milder conditions (Scheme 5.3). [45] Inexpensive ligands were found to accelerate the *O*-arylation of aryl bromides or iodides with phenols. The reaction is carried out in the presence of Cs_2CO_3 and catalytic copper (I)oxide in acetonitrile.



Scheme 5.3 CuI/Ligand assisted *O*-arylation of aryl iodides and aryl bromides.

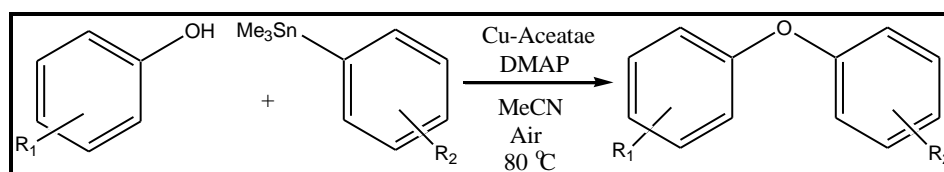
Palomo et al. described that in the presence of phosphazene P4-*But* base and CuBr, aryl halides couple with phenols to give biaryl ethers at 100 °C [46]. They found that P4-*But* base in combination with CuI salts in either dioxane or toluene

affects the Ullmann reaction of electron-rich, electron-neutral and electron-poor aryl halides with a variety of phenols (Scheme 5.4).



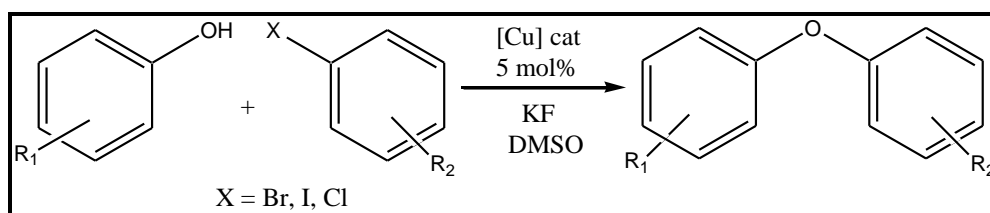
Scheme 5.4. Phosphazene base mediated diaryl ether synthesis.

A. Vakalopoulos et al. developed a novel method for the synthesis of diaryl ethers with phenols and arylstannanes under mild conditions (Scheme 5.5) [47]. This copper-mediated *O*-arylation is feasible using 4 dimethyl aminopyridine (DMAP) in acetonitrile and is complementary to the use of boronic acids as aryl donors. The reaction is tolerant to a wide range of substituents and sterically hindered coupling partners.



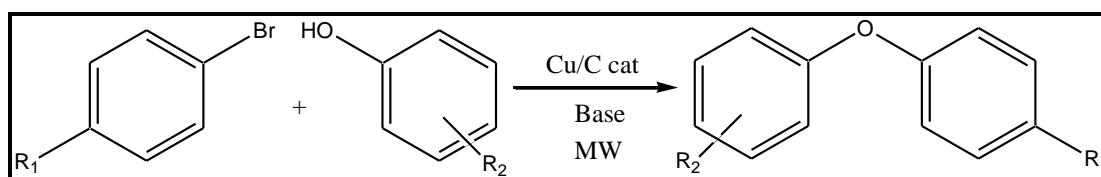
Scheme 5.5 Coupling reaction of arylstannanes and phenol with $\text{Cu}(\text{OAc})_2$ in *O*-arylation.

Wan et al. reported the immobilization of copper on silica for the Ullmann reaction. Phenols reacted with aryl iodides, aryl bromides and aryl chlorides smoothly in the presence of a 3-(2-aminoethylamino)propyl functionalized silica gel immobilized copper catalyst. The protocol involved the use of dimethyl sulfoxide (DMSO) as the solvent, and potassium fluoride as the base. (Scheme 5.6) [48]. The catalyst could be recovered and recycled by a simple filtration of the reaction solution and used for ten consecutive cycles.



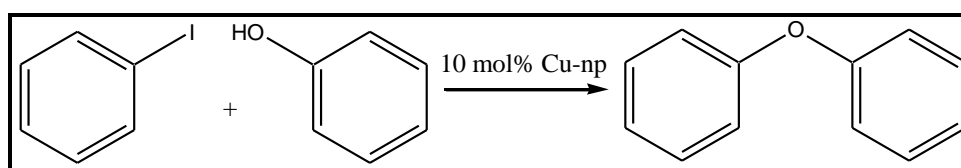
Scheme 5.6 Silica-supported copper catalyzed Ullmann diaryl etherification.

Lipshutz et al. reported impregnated copper onto charcoal for cross-coupling between aryl bromides and phenols under microwave heating (Scheme 5.7) [49].



Scheme 5.7 Copper-in-Charcoal (Cu/C) promoted diaryl ether formation.

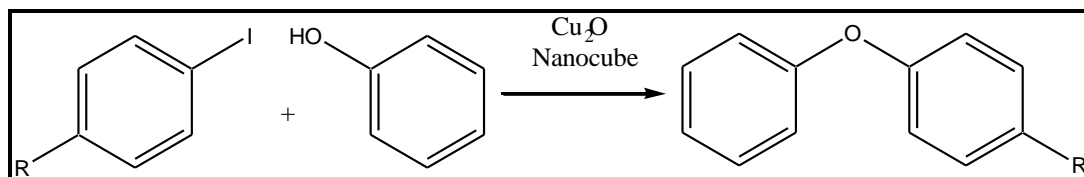
In the direction of heterogeneous catalyst development, Kiwai et al. reported recyclable Cu-nanoparticles for the synthesis of diaryl ethers via Ullmann type coupling. This method provides a wide range of substrate applicability and avoids the use of a heavy metal co-catalyst and gives diaryl ethers in satisfactory yields (Scheme 5.8) [50]. Overall, this methodology offers competitive advantages such as recyclability of the catalyst without further purification or without using additives or cofactors, low catalyst loading, broad substrate applicability, and high yields in short reaction times.



Scheme 5.8. Cu-nanoparticles catalyzed reaction of iodobenzene with phenol.

Later Song et al. developed thermal and air-stable uniform Cu₂O nanocubes for one-pot polyol synthesis by an efficient cross-coupling reaction of aryl halides

and phenols with Cs_2CO_3 as the base in tetrahydrofuran (THF) at 150 °C (Scheme 5.9) [51].



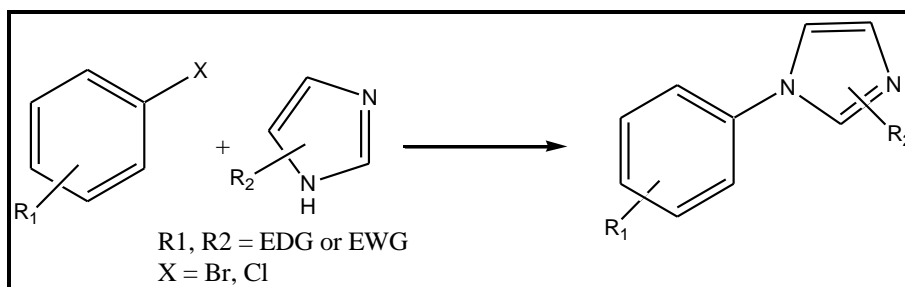
Scheme 5.9 Coupling reaction of aryl iodides and phenol with Cu_2O nanocubes.

Ma and his co-workers reported the process for preparation of *N*-Aryl α - or β -amino acids, aryl amines, *N*-arylpyrroles, *N*-arylindoles, *N*-arylimidazoles, *N*-arylpiperazines and aryl azides by CuI-catalyzed coupling reactions of aryl halides with corresponding nitrogen sources. They used amino acids as the promoters. Aryl iodides and aryl bromides in DMSO at 40-90 °C gave the corresponding *N*-arylamines or *N,N*-diarylamines in good to excellent yields by using either *N*-methylglycine or L-proline as the ligand (Scheme 5.10) [52,53].



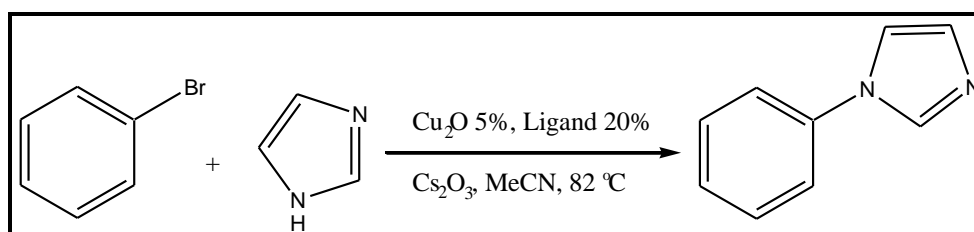
Scheme 5.10 CuI/aminoacid catalysed C-N bond formation.

The discovery and development of the catalytic path for *N*-arylation of heterocycles by Buchwald with bromo- and iodoarenes using copper complexes in the presence of basic ligands generated greater interest in industry. Initially, Buchwald used 1,10-phenanthroline as a ligand and subsequently shown that 1,2-diamines were better ligands to promote this *N*-arylation (Scheme 5.11) [54]

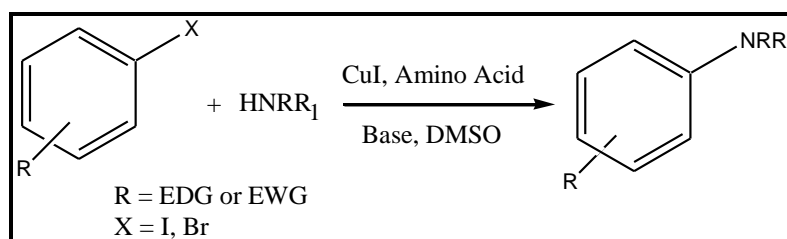


Scheme 5.11 1,10-phenanthroline/Cu₂O catalyzed N-arylation

Taillefer et al. reported oxime type and Schiff base ligands and Ma et al. reported α - and β -amino acids as ligands for effective N-arylation of N-heterocycles with aryl halides (Scheme 5.12 and 5.13) [55,56].

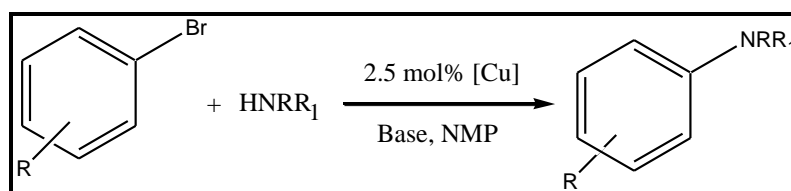


Scheme 5.12 N-arylation of aryl bromides using Schiff's base as the ligand.



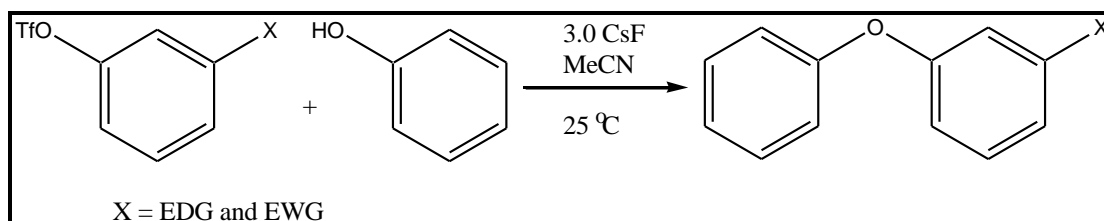
Scheme 5.13 N-arylation using amino acid as the ligands.

Koten et al. reported aminoarenethiolate-copper(I) complexes as efficient catalysts for the N-arylation of benzylamine and imidazole with bromobenzene at 160°C (Scheme 5.14) [57].



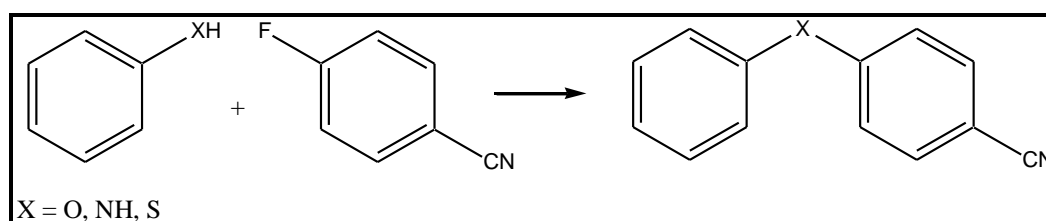
Scheme 5.14 Aminoarenethiolate-copper(I) complex for N- arylation.

Larock et al. reported a facile, transition-metal-free *O*-arylation procedure for phenols and aromatic carboxylic acids that afford good to excellent yields of arylated products under very mild reaction conditions (Scheme 5.15) [58]. A methoxy-substituted aryl triflate affords *O*-arylated products in high yields with excellent regioselectivity. This chemistry tolerates a variety of functional groups.



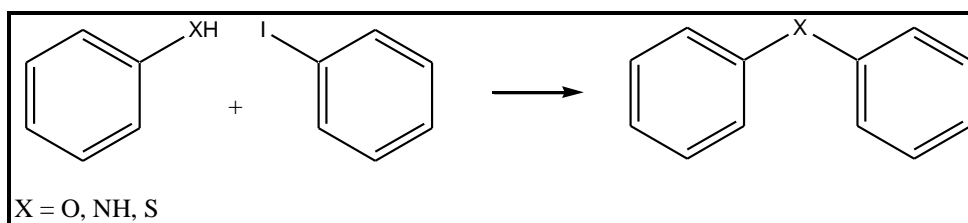
Scheme 5.15. *O*-arylation of triflates with phenols.

J. Scott Swayer and co-worker have used KF-Al₂O₃ (1-2.5 g per g of nucleophile) /18-Crown-6 for coupling of phenol, thiophenol and aniline with 4-Fluorobenzonitrile for 1-4 days. The reaction was carried out in the presence of strong electron withdrawing group at para position of fluorobenzene (Scheme 5.16) [59].



Scheme 5.16. Coupling of phenols, amines with fluorobenzene.

Deigo J. Ramon and co-worker have used only KOH (250-500 mol%) for coupling of phenol, thiophenol and aniline with iodobenzene for 1-5 days (Scheme 5.17). [60]



Scheme 5.17. Coupling of phenols, amines with iodobenzene .

Herein we have carried out various reactions of O and N-arylation by basic metal oxides by nucleophilic substitution reaction. The focus is to reduce the base concentration and time required for the nucleophilic arylation reaction than reported ones. The protocol can be applied for normal reaction condition.

5.2 Experimental

5.2.1 Materials

Cerium nitrate were purchased from M/S S.D. Fine Chemical, Mumbai, India. All the chemicals were purchased from firms of repute with their highest purity available and were used without further purification.

5.2.2 Methods

5.2.2.1 Synthesis of nano CeO₂

The nano CeO₂ was prepared as discussed in the method used chapter 4, section 4.2.2. The prepared catalyst was then characterized with various techniques such as X-ray diffractograms (XRD), EDAX, Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM).

5.2.2.2 General procedure for O arylation of phenol

A mixture of phenol/amine/thiophenol (1.2 mmol, 0.112 g), 4-nitrochlorobenzene (1 mmol, 0.157 g), base (1.2 mmol, 0.08 g) and 1 mL solvent was taken in 25 mL round bottom flask. Further 2.5 mol% catalyst (4.5 mg) is added to the reaction mixture. The reaction mixture is heated to 110° C for appropriate time. Reaction is monitored on TLC. After completion of reaction the catalyst was separated by centrifugation and subsequently washed with dichloromethane. The reaction mixture was diluted with water and the product was extracted by dichloromethane (3 × 10 cm³). The organic layer was dried over anhydrous sodium sulphate and was evaporated under reduced pressure to give the product. The product was purified by column chromatography by using pet ether and ethyl acetate solvent system (95:5). The purified product was then confirmed by its spectral analysis after analyzing by IR, ¹H NMR and mass spectra.

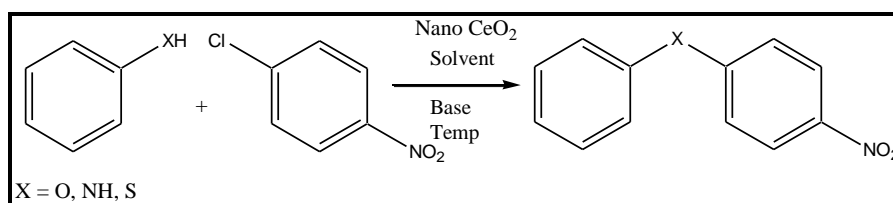
Following parameters were optimized for O-arylation of phenol

- 1) Catalyst : ZnO, TiO₂, Al₂O₃, La₂O₃, MnO₂, CeO₂
- 2) Temperature : RT to 110 °C
- 3) Effect of Solvents : DMF, DMSO, Dioxane, Toluene, Ethanol
- 4) Effect of Base : K₂CO₃, KOH, K₃PO₄, NaHCO₃, N(Et)₃
- 5) Effect of Catalyst conc. : 2.5 to 20 mol%

The optimised reaction conditions are summarised in table 5.3

5.3 Result and Discussion

The present work reports the continuation of our studies on the catalytic activity of ceria nano particles. This involve C-O, C-N and C-S bond formation by Ullmann type coupling reaction. (Scheme 5.18).



Scheme 5.18 O arylation by using nano CeO₂ as catalyst.

Various transition metal oxide catalysts such as TiO₂, ZnO, Al₂O₃, MnO₂, La₂O₃ and CeO₂ were scanned for the model reaction investigated (Table 5.1, entries 1-7). It was observed that only CeO₂ gave good yields of desired product. It was interestingly observed that after reducing the partial size of CeO₂ from bulk to nano size, CeO₂ gave 96% yield of the desired product.

Table 5.1 Influence of various catalysts on coupling of 4-nitrobenzene and phenol.^a

Sr. No	Metal Oxides	Surface Area	Size	Yield ^b (%)
1	ZnO	12.16 m ² /g	--	45
2	Al ₂ O ₃	--	150-300 mesh	51
3	TiO ₂	14.68 m ² /g	--	47
4	MnO ₂	--	22 μm	28
5	La ₂ O ₃	--	14 μm	23
6	CeO ₂	11 m ² /g	--	78
7	CeO₂ (nano)	--	4-5 nm	96

^a Reaction Condition: Phenol (1.2 mmol), 4 nitro chlorobenzene (1 mmol), potassium carbonate (1.2 mmol), 1 mL DMF and 20 mol% catalyst for 3 h at 110°C. , ^b Isolated yield.

CeO₂ has both Lewis and Bronsted basic sites [61] which are strong and widely distributed over the CeO₂ surface [62]. In addition to this it has smaller particle size and hence has high surface area due to which nano CeO₂ shows better catalytic activity for coupling reaction by nucleophilic substitution reaction.

The effect of various reaction parameters such as temperature, solvent, base and catalyst loading were studied for the model reaction (Table 5.2, entries 1-23). The reaction favoured at 110 °C temperature (Table 5.2, entries 1-4). The influence of various solvents such as DMF, DMSO, Toluene, Dioxane and ethanol on the reaction system was also investigated and it was observed that excellent yield of the product was obtained when the reaction was carried out by using DMSO as solvent (Table 5.2, entries 5-9). KOH as base gave maximum yield in comparison with bases such as K₃PO₄, N(Et)₃, NaHCO₃ and K₂CO₃ (Table 5.2, entries 14-18). The 2.5 mol% catalyst concentration was sufficient to give maximum yield of the required product (Table 5.2, entries 19-23).

Table 5.2 Influence of catalyst, solvent and Base on reaction condition^a

Entry	Catalyst loading (mol %)	Temp	Solvent	Base	Yield (%) ^b
<i>Influence of Temperature</i>					
1	20	RT	DMF	K ₂ CO ₃	--
2	20	60	DMF	K ₂ CO ₃	21
3	20	80	DMF	K ₂ CO ₃	80
4	20	110	DMF	K₂CO₃	87
<i>Influence of solvent</i>					
5	20	110	DMF	K ₂ CO ₃	87
6	20	110	Dioxane	K ₂ CO ₃	22

7	20	110	Ethanol	K ₂ CO ₃	--
8	20	110	Toluene	K ₂ CO ₃	20
9	20	110	DMSO	K₂CO₃	93
<i>Influence of Solvent and Temperature</i>					
10	20	RT	DMSO	K ₂ CO ₃	--
11	20	60	DMSO	K ₂ CO ₃	53
12	20	80	DMSO	K ₂ CO ₃	85
13	20	110	DMSO	K₂CO₃	93
<i>Effect of Base</i>					
14	20	110	DMSO	K ₂ CO ₃	93
15	20	110	DMSO	KOH	96
16	20	110	DMSO	K ₃ PO ₄	95
17	20	110	DMSO	NaHCO ₃	12
18	20	110	DMSO	N(Et) ₃	--
<i>Effect of catalyst concentration</i>					
19	20	110	DMSO	KOH	96
20	15	110	DMSO	KOH	94
21	10	110	DMSO	KOH	95
22	5	110	DMSO	KOH	96
23	2.5	110	DMSO	KOH	96

24	0	110	DMSO	KOH	50
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^a Reaction Condition: Phenol (1.2 mmol), 4 nitro chlorobenzene (1 mmol), Base (1.2 mmol) and 1 mL solvent for 3 h., ^b Isolated yield.

Table 5.3 Optimized reaction conditions for O-Arylation of phenol

Conditions	Optimized Parameters
Catalyst	Nano CeO ₂
Temperature	110 °C
Solvent	DMSO
Catalyst Concentration	2.5 mol%
Base	KOH

We have also explored different aryl chlorides for the same reaction under the optimized conditions. The results are shown in Table 5.4. It was observed that chlorobenzene with electron withdrawing groups gives the respective product. The reactivity of chloro compound decreased in the order of 4-NO₂, 4-CN and 4-CHO groups. 2-nitrochlorobenzene also gave excellent yield of product which ruled out the steric effect. The 4-chlorobenzaldehyde gave lower yield because it may oxidize aldehyde to acid at high temperature and in air. The results also show that chlorobenzene, iodobenzene and bromobenzene were ineffective for the reaction. Hence it was concluded that the cerium oxide can only work with compound which has strong electron withdrawing group to the aryl chloride.

Table 5.4 O-arylation of phenol with different chlorobenzene^a

Sr. No	Chlorobenzene	Time (h)	Yield ^b (%)
1	Chlorobenzene	10	--
2	Bromobenzene	10	--
3	Iodobenzene	10	--
4	4-Nitrochlorobenzene	3	96
5	2-Nitrochlorobenzene	3	92
6	4-Cyanochlorobenzene	4	65
7	4-Chlorobenzaldehyde	5	≤ 10
8	4-Chlorotoluene	10	--
9	4-Dichlorobenzene	10	--

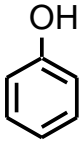
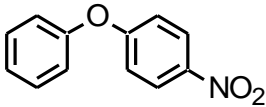
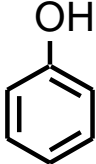
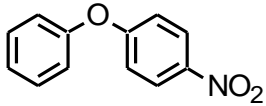
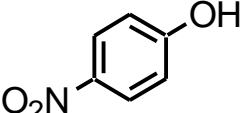
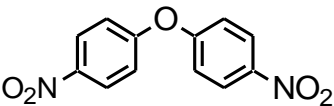
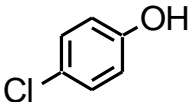
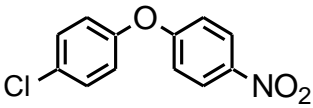
^a Reaction Condition: Phenol (1.2 mmol), chlorobenzene (1 mmol), KOH (1.2 mmol), 1 mL DMSO and 2.5 mol% catalyst at 110^oC in air.

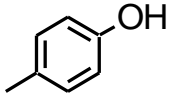
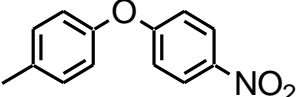
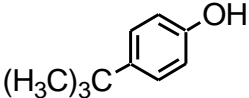
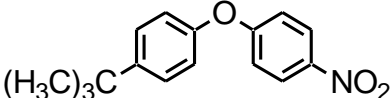
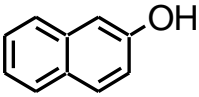
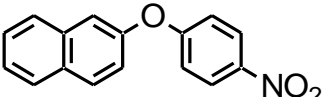
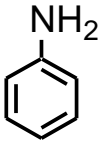
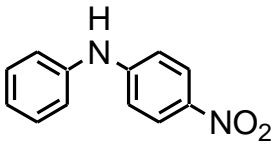
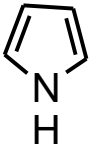
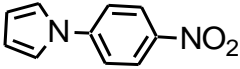
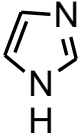
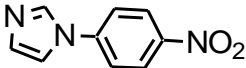
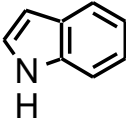
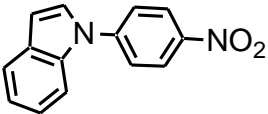
^b Isolated yield.

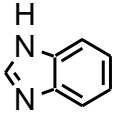
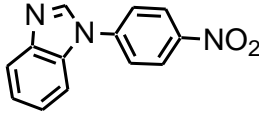
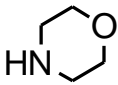
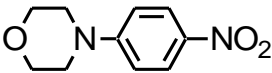
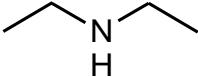
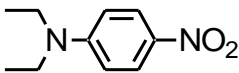
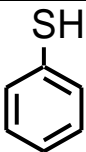
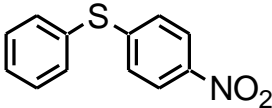
Various substituted phenols, amine, heterocyclic amines and thiophenol were also successfully coupled with 4-nitrochlorobenzene to obtain respective O, N

and S-arylated products (Table 5.5). Both the electron donating and electron withdrawing substituents on the phenol afforded the corresponding O-arylated product with good to excellent yield. Thiophenol also reacted with 4-nitrochlorobenzene and gave product with satisfactory yield.

Table 5.5 O, N and S-arylation with 4-nitrochlorobenzene^a

Sr.No.	Phenol/Amine/ Thiophenol	Product	Time (h) /Yield ^b (%)
1			3/96
2 ^c			45 min/ 98
3			6/83
4			1.5/84

5			2/72
6			2/84
7			4/75
8			6/46
9			8/80
10			8/90
11			1.5/91

12			2/93
13			10/96
14			9/42
15			2/80

^a Reaction Condition: Phenol/Amine/Thiophenol (1.2 mmol), 4-nitrochlorobenzene (1 mmol), KOH (1.2 mmol), 1 mL DMSO and 2.5 mol% catalyst at 110°C in air.

^b Isolated yield, ^c using 4-nitroiodobenzene

Catalyst Reusability

The catalyst was separated from the reaction mixture by centrifugation, washed with dichloromethane and dried. Table 5.6 indicates the reusability of the catalyst. It clearly reveals that the catalyst can be used for three cycles without much loss in the yield of desired product.

Table 5.5 Recyclability of nano CeO₂^a

Run	Fresh	Run 1	Run 2	Run 3
% Yield ^b	96	95	91	90

^a Reaction Condition: Phenol (1.2 mmol), 4-nitrochlorobenzene (1 mmol), KOH (1.2 mmol), 1 mL DMSO and 2.5 mol% catalyst at 110°C for 3 h.

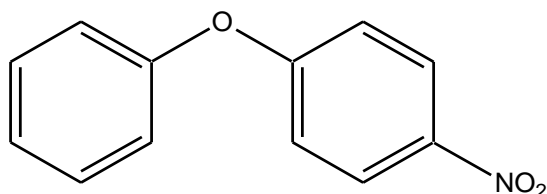
^b Isolated yield.

5.4 Conclusion

- Nano CeO₂ was found to be an efficient catalyst for Ullmann type coupling reaction.
- The present study is simple and efficient protocol for Ullmann type coupling reaction,
- The present protocol having advantages like high yields of desired products, inexpensiveness, ligand free and good selectivity.
- The present catalytic system afforded high yields of desired product within a short reaction time.
- Recyclability of the catalyst is the added advantages of the system.

5.5 Spectral Data

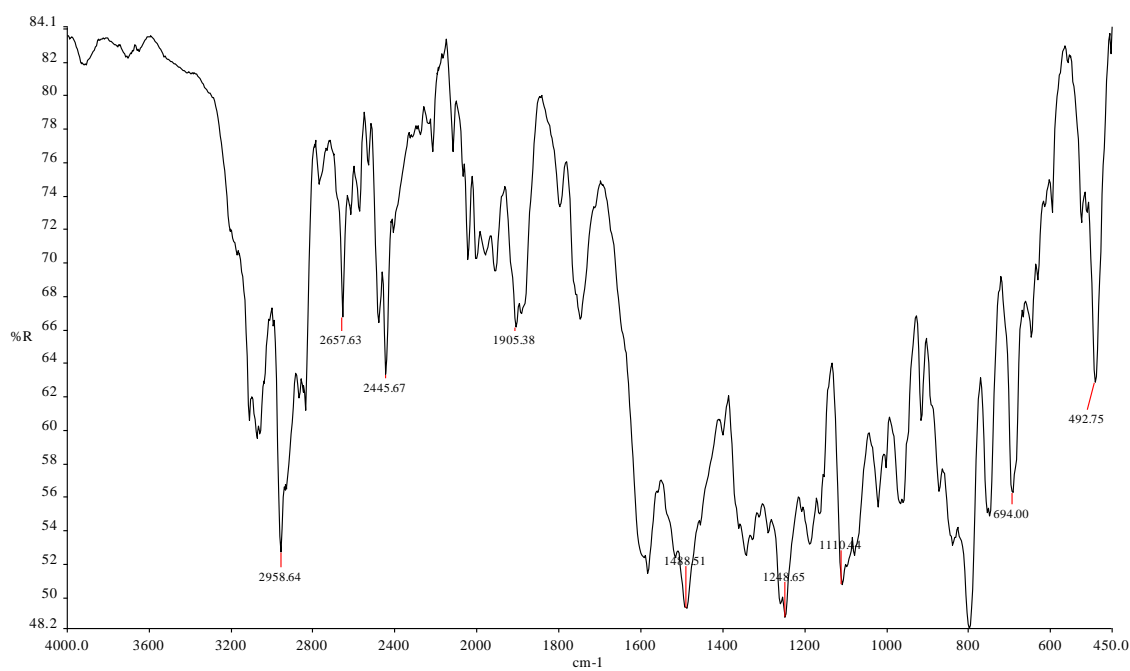
IR, Mass and ^1H -NMR of entry 1, Table 5.5



1-nitro-4-phenoxybenzene

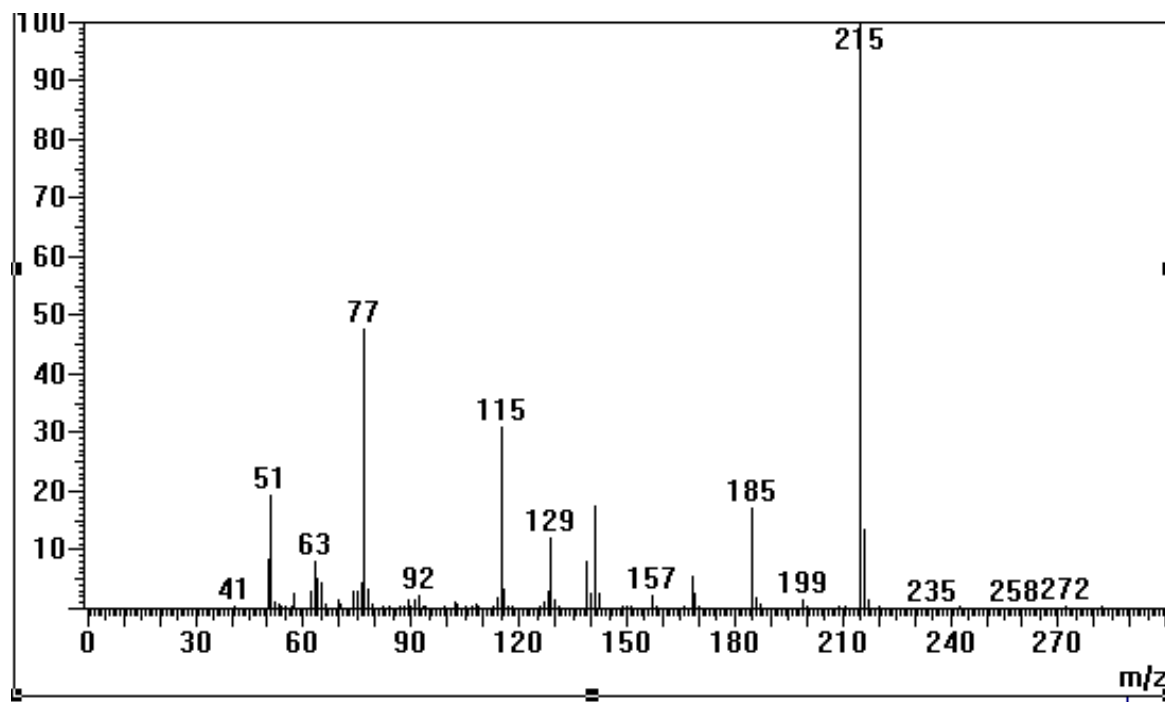
IR Spectra

IR (KBr) cm^{-1} : 2958 ($-\text{CH}$), 1580 and 1350 ($-\text{NO}_2$), 1248 ($\text{C}-\text{O}$ ether), 1110 ($-\text{CO}$ stretching).



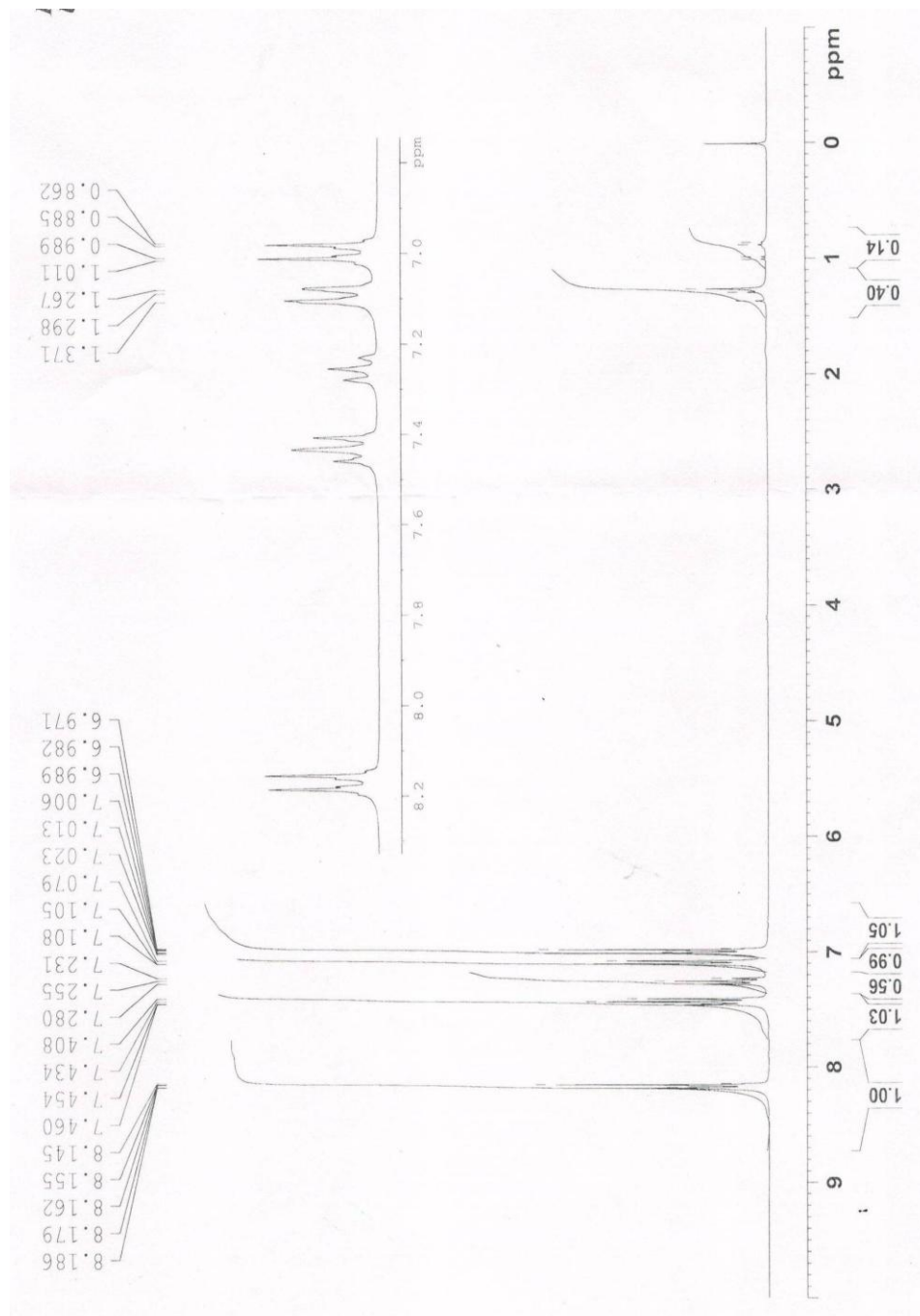
Mass Spectra

GC-MS (EI, 70 eV): m/z (%) = 51 (20%), 77(48%), 115(33%), 185 (20%), 215 (100%) $[M]^+$.



^1H -NMR Spectra (300 MHz, CDCl_3):

δ 6.95-7.05 (d, 2H, ortho H of phenyl ring), 7.05-7.15 (d, 1H, para H of phenyl ring), 7.02-7.3 (t, 2H, meta H of nitrophenyl ring), 7.4-7.5 (t, 2H, meta H of phenyl ring), 8.15-8.2 (t, 2H, ortho H of nitrophenyl ring).



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