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# Cerium-containing MCM-41 catalyst for selective oxidative arene cross-dehydrogenative coupling reactions

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ABSTRACT

Cerium (IV)-mediated intermolecular direct biaryl coupling of aromatic tertiary amines and naphthol via dual C—H bond activation has been reported. The new C—C bond is formed regioselectively *ortho* to the amino and hydroxyl substituents under oxidative conditions to give substituted bifunctional amino naphthols. We report here the use of Ce-MCM-41 catalyst for the synthesis of these unsymmetrical biaryls via oxidative cross coupling under mild conditions. The catalyst was recovered by simple filtration and reused for several cycles with consistent activity.



## 1. Introduction

The constructions of C—C bonds, especially aryl–aryl linkages, are among the most important reactions in organic synthesis [1]. Biaryl structures are a ubiquitous motif in biological, pharmaceutical, and material sciences [2]. Numerous economically important pharmaceuticals and agrochemicals such as valsartan, boscalid, and liquid-crystalline NCB 807 have biaryl units as indispensable substructures [3]. A vast majority of biaryl linkages are constructed via metal-mediated cross coupling of two pre-functionalized arene building blocks [4]. However, the required organometallic nucleophilic reagents are relatively expensive and rarely commercially available. With the emergence of the concepts of atom economy and green chemistry, metal-catalyzed C—H bond activation as well as direct use of unactivated C—H bonds for C—C bond formation has attracted much interest in recent years [5]. Moreover, it has been reported that biaryls containing amino naphthols functionalities act as organo catalysts and ligand precursors in asymmetric catalysis [6]. Although several reports have been published on homo-coupling of either naphthols or aniline derivatives, the regioselective cross-coupling of unactivated moieties is often challenging [7]. An efficient approach for the formation of new C—C bonds involves the direct oxidative coupling of two arene C—H substrates under mild conditions [8].

In recent years, several groups have reported cross dehydrogenative coupling reactions [9]. In particular, the C—H activation of aromatic tertiary amines and subsequent C—C bond formation with nucleophiles has gained much attraction [10]. These oxidative coupling reactions require the presence of metal ions together with a one-electron oxidant [11]. A majority of these coupling reactions are catalyzed by salts of transition metals (such as copper, iron, nickel palladium, ruthenium and rhodium), under appropriate conditions [12]. There is a growing demand for the development of new catalyst systems based on readily available and relatively cheap non-noble metals. In this regard, cerium salts are particularly appealing, since they have low toxicity, reasonable solubility in many organic media, air stable, easily handled, and are inexpensive [13].

The propensity of Ce(IV) to efficiently participate in one-electron transfer reactions while existing in stable oxidation states +3 and +4, and its high reduction potential (1.61 V vs. normal hydrogen electrode), makes it a very efficient oxidizing agent compared to many other metal cations. Its salts, such as the commercially available cerium ammonium nitrate (CAN), have found wide spread use as one-electron oxidants [14]. The dual role of CAN as an oxidant and a Lewis acid facilitates its catalytic role in cross-dehydrogenative coupling (CDC) reactions [15]. Various oxidative reactions involving CAN in homogeneous media have

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been reported by several groups [16]; however, they suffer from serious limitations such as high catalyst loading, difficulty in recovery and reusability of the catalyst and tedious work-up procedures. The development of highly active and reusable heterogeneous catalysts for C—C cross dehydrogenative coupling reactions is an open challenge [17].

In the last few decades, mesoporous materials have received much attention in the field of catalysis, especially for their use as solid supports [18]. These porous supports have uniform pore size and large surface area and are ideal materials for heterogenization of various metal salts. The most widely used mesoporous silica, MCM-41, exhibits a highly ordered hexagonal array of one dimensional mesopores with diameters varying from 15 to 100 Å [19]. In Ce-MCM-41, cerium (IV) ions are covalently anchored to silica. It is well known that cerium, coordinated with tetrahedral silicon via oxygen bridges, acts as a Lewis acid catalyst for selective oxidations in the presence of peroxides [20]. Therefore, it was conceptualized that the use of Ce-MCM-41 as catalyst should result in good yields of biaryls under mild conditions as compared to homogenous system. Herein, we report a facile and reusable heterogeneous catalyst, namely Ce-MCM-41 for the synthesis of unsymmetrical biaryls through C—H activation [21].

## 2. Experimental

### 2.1. Chemicals and reagents

Sodium silicate ($NaSiO_3 \cdot 9H_2O$), cetyl trimethyl ammonium bromide (CTAB), ceric ammonium nitrate (CAN), tertiary butyl hydrogen peroxide (TBHP, 70 wt% in water), ditertiary butyl peroxide (DTBP), $H_2O_2$ (30 wt% in water), and all other starting materials and reagents were purchased from Sigma–Aldrich and are used as received. All the solvents used are of analytical grade and were purchased from Merck India Ltd. Deionized water was used to prepare the aqueous solutions. Sulfuric acid and sodium hydroxide were used to control the pH of the aqueous solutions.

### 2.2. Instrumentation

The Thin Layer Chromatography (TLC) was performed on Merck silica gel 60 $F_{254}$ plates using ethyl acetate and hexane as eluting agents. Thin layer chromatography plates were visualized by exposure to UV-light/iodine and/or by immersion in an acidic staining solution of phosphomolybdic acid followed by heating on a hot plate. Purification of products was carried out by column chromatography using silica gel (100–200 mesh) and a mixture of ethyl acetate and hexane as eluting agent. All the products were characterized by Mass, $^1H$ and $^{13}C$ NMR spectroscopy. The NMR spectra of samples were acquired on a Varian Unity Inova 500 MHz, Inova 400 MHz, and Bruker Avance 300 MHz spectrometer using TMS as an internal standard in $CDCl_3$. Mass spectra were acquired on a Thermo LCQ fleet ion trap mass spectrometer. High-resolution mass spectra were acquired on a Q STAR XL Hybrid LC/MS/MS system, Applied Biosystems, USA. FT-IR data were acquired on a Thermo Nicolet Nexus 670 FT-IR spectrometer with DTGS KBr detector. XPS spectra were recorded on a Kratos AXIS 165 with a dual anode apparatus using the Mg Kα anode. X-ray powder diffraction data were collected on a Siemens/D-5000 diffractometer using Cu Kα radiation. The particle size and external morphology of the samples were observed on a Philips TECNAI F12 FEI transmission electron microscopy (TEM). SEM-EDX was performed on a Hitachi SEM S-520, EDX-Oxford Link ISIS-300 instrument. Diffuse reflectance UV/vis spectra for samples as KBr pellets were recorded on a GBC Cintra 10e UV–vis spectrometer in the range 200–800 nm with a scan speed 400 nm/min.

### 2.3. Synthesis of catalyst (Ce-MCM-41)

MCM-41 was prepared by the direct hydrothermal method described in the literature [22] and dried at 80 °C for 10 h prior to use. The cerium-loaded MCM-41 mesoporous material was prepared by a wet impregnation method using 10% and 15% ceric ammonium nitrate solution respectively [23]. All the characterization studies were carried out with Ce-MCM-41 loaded with 15 wt% of cerium. The calcined template-free MCM-41 (0.21 g) was added to 10 mL of an aqueous solution of ceric ammonium nitrate (0.12 g, 0.02 M) and stirred vigorously for 24 h at room temperature. The solid was isolated by evaporation of the solvent, dried overnight at 100 °C and then calcined at 500 °C in air for 5 h to obtain Ce-MCM-41 containing 15 wt% of cerium.

### 2.4. Experimental procedure for the synthesis of N,N-dialkyl aniline derivatives

To a solution of aniline (1 mmol) in glacial acetic acid (7 mL) under argon was added paraformaldehyde (10 mmol) and sodium cyanoborohydride (5 mmol). After stirring overnight, the reaction mixture was poured into ice cooled water (~100 mL) containing NaOH (7 g). This mixture (pH 14) was extracted thrice with $CH_2Cl_2$ (3 × 350 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to obtain the crude product. Flash chromatographic purification of the crude product using silica gel and a mixture of hexane and ethyl acetate as the eluent provided the pure product.

### 2.5. General procedure for the synthesis of 1-(5-R-2-(piperidin-1-yl)phenyl)naphthalen-2-ol (R = alkyl, alkoxy, halide)

A suspension of phenyl boronic acid (2.0 mmol), $Cu(OAc)_2 \cdot H_2O$ (10 mol%) and powdered 4 Å molecular sieves (0.75 g) in dichloromethane (8 mL) was stirred for 5 min at room temperature. To this mixture was added the amine (1.0 mmol). The reaction vessel was sealed with a rubber septum and stirred at 40 °C under oxygen for 24 h. The reaction mixture was then filtered through a plug of Celite and the product was purified by column chromatography using silica gel and a mixture of hexane and ethyl acetate as the eluent.

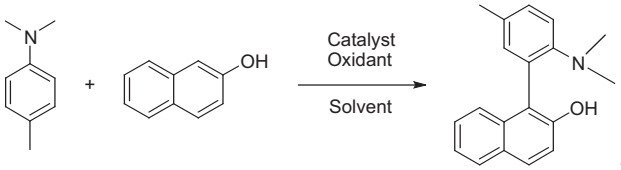
### 2.6. General procedure for the synthesis of unsymmetrical biaryls

A 25 mL round bottomed flask was charged with N,N-dialkylaniline (0.5 mmol), 2-naphthol (0.5 mmol) and acetonitrile (3 mL), followed by 10 mg of Ce-MCM-41 and TBHP (2 equiv.) via syringe. The mixture was heated to 60 °C and stirred for 3 h in open air. After completion of the reaction, as judged by TLC, the solution was cooled and the catalyst was removed by filtration. The resulting crude mixture was gently evaporated under reduced pressure and purified by column chromatography using silica gel and a mixture of hexane and ethyl acetate as the eluent.

## 3. Results and discussion

The optimization studies for cross-dehydrogenative coupling reaction were performed in a 0.5 mmol scale using *N,N*,4-trimethylaniline and 2-naphthol as the model substrates in acetonitrile at 60 °C. Employing 2 equiv. of TBHP as the oxidant, various cerium salts such as $CeCl_3$, $Ce(SO_4)_2$, CAN, 5% Ce-MCM-41,10% Ce-MCM-41,15% Ce-MCM-1and 20% Ce-MCM-41, were examined for their catalytic activity. Among cerium salts screened, CAN was found superior to other salts such as $CeCl_3$ and $Ce(SO_4)_2$, and furnished the corresponding cross coupled product in moderate to

**Table 1**
Optimization of reaction conditions for cross-dehydrogenative coupling reaction[a,b].




| Entry | Catalyst | Oxidant | Solvent | Temperature (°C) | Time (h) | Yield[c] (%) |
|---|---|---|---|---|---|---|
| 1 | $CeCl_3$ | TBHP | $CH_3CN$ | 80 | 12 | Traces |
| 2 | $Ce(SO_4)_2$ | TBHP | $CH_3CN$ | 60 | 12 | 30 |
| 3 | CAN | – | $CH_3CN$ | 30 | 3 | 40 |
| 4 | MCM-41 | TBHP | $CH_3CN$ | 80 | 10 | 0 |
| 5 | 5% Ce-MCM-41 | TBHP | $CH_3CN$ | 80 | 12 | Traces |
| 6 | 10% Ce-MCM-41 | TBHP | $CH_3CN$ | 80 | 6 | 20 |
| 7 | 15%Ce-MCM-41 | TBHP | $CH_3CN$ | 60 | 3 | 66 |
| 8 | 15%Ce-MCM-41 | $H_2O_2$ | $CH_3CN$ | 80 | 6 | 30 |
| 9 | 15%Ce-MCM-41 | DTHP | $CH_3CN$ | 80 | 6 | 25 |
| 10 | 15%Ce-MCM-41 | $O_2$ | $CH_3CN$ | 80 | 10 | 20 |
| 11 | 15%Ce-MCM-41 | TBHP | MeOH | 100 | 8 | 10 |
| 12 | 15%Ce-MCM-41 | TBHP | DCM | 80 | 8 | 20 |
| 13 | 20%Ce-MCM-41 | TBHP | $CH_3CN$ | 100 | 12 | 65 |
| 14 | 15%Ce-MCM-41 | TBHP | Toluene | 100 | 8 | 40 |
| 15 | 15%Ce-MCM-41 | $K_2S_2O_8$ | $CH_3CN$ | 80 | 10 | 0 |
| 16 | 15%Ce-MCM-41 | m-CPBA | $CH_3CN$ | 80 | 10 | 0 |

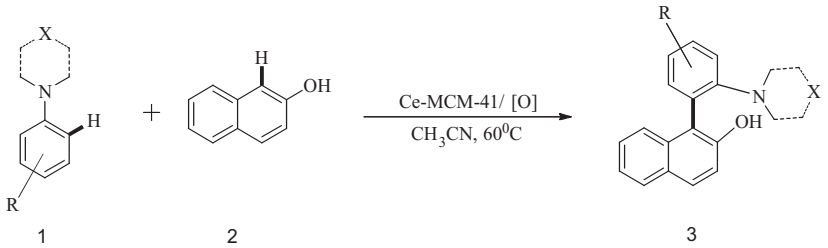
DTHP - ditertiary butyl hydro peroxide, TBHP - tertiary butyl hydrogen peroxide, mCPBA - meta chloro per benzoic acid.
[a] Reactions (entries 1–3) were carried out with *N*,*N*,4-trimethylaniline (0.5 mmol), 2-naphthol (0.5 mmol), oxidant (2 equiv.) and catalyst (20 mol%) in acetonitrile (3 mL).
[b] Reactions (entries 4–16) performed in a 0.5 mmol scale (with respect to amine) using 10 mg (0.9 mol% for entries 7–12, 14–16) of catalyst.
[c] Isolated yields (based on amine) after column chromatography.

good yield in a short reaction time (Table 1, entries 1–3). Notably, it was observed that the use of 10 mg (0.9 mol%) of Ce-MCM-41 containing 15 wt% of ceria increased the product yield to 66% (Table 1, entry 7). Thereafter, optimization studies for solvents revealed acetonitrile as the best solvent compared to DCM, methanol and toluene (Table 1, entries 7, 11, 12, and 14). Later, different oxidants like $H_2O_2$, mCPBA, $K_2S_2O_8$, DTHP and oxygen were examined; however, all these were found to be least effective as compared to TBHP (Table 1, entries 7–10, 15, and 16). Thus, among the various optimization studies listed in the Table 1, the most promising result was obtained using Ce-MCM-41 (containing 15 wt% of ceria) as catalyst employing TBHP and acetonitrile as the oxidant and solvent respectively (Table 1, entry 7).

The catalytic cerium species was anchored on the inner surface of the mesopore of MCM-41 to exhibit high activity and good reusability. The surface acidity of the catalyst calculated by using $NH_3$-TPD analysis was 0.6330 mmol/g. The enhanced efficacy of Ce-MCM-41 in the catalytic C—C coupling reaction is attributed to the high internal surface area of the mesoporous catalyst that provides enough space for organic substrate to interact with active acidic sites present on the solid surface inside the ordered mesopore [19a,20]. It was observed that the yields for this reaction were not encouraging with $\leq$5% loading of ceria whereas, the yields obtained with 15% Ce-MCM-41 loading was higher than that for 10% Ce-MCM-41. This implied that a higher amount of cerium in the frame work was favorable for an increased catalytic activity of Ce-MCM-41. However, further increase in the metal loading (20–25%) did not change the reactivity of the catalyst and percentage of conversion even at elevated temperature. This is probably due to a relatively disordered mesostructure arising from the excessive ceria loading, as evidenced by the decreasing intensities of the low angle peaks in powder XRD pattern and gradual change in the structural morphology of catalyst confirmed by SEM and TEM [19a]. Notably, cerium doped commercially available silica remained virtually inactive in this reaction.

Using the above optimized conditions, the scope of this method was explored for different amine substrates. As depicted in Table 2, this reaction is general for various *N*,*N*-disubstituted anilines containing electron donating substituents in *meta*- and *para*- position of the aromatic ring. For example, the reaction proceeded smoothly for substituted *N*,*N*-dimethylanilines such as, 4-ethyl-*N*,*N*-dimethylaniline, 4-methoxy-*N*,*N*-dimethylaniline, 4-isopropyl-*N*,*N*-dimethylaniline, and 4-halo-*N*,*N*-dimethylaniline, with 2-naphthol to furnish the corresponding cross dehydrogenative coupling products in good yields (Table 2). The reaction of amines containing two substituents; namely, 3-bromo-N,N,4-trimethylaniline and N,N,3,4-tetramethylaniline, proceeded smoothly to yield the respective products (Table 2, entries 11 and 12). It is noteworthy that for these substrates the reactions occurs regioselectively at the less hindered 6th position of the phenyl ring. Similarly, cyclic amines also reacted smoothly to afford the respective products in good yields (Table 2, entries 14–20). In contrast, the reaction failed to yield the desired products for *ortho*- substituted anilines as well as amine containing strong electron withdrawing groups (Table 2, entries 5, 10 and 13). The ortho regioselectivity of the oxidative cross coupling presumably arise from the hydrogen bonding between amino and hydroxyl groups (geometrical proximity between *ortho* C—H bonds) [7a], and the unsymmetrical coupling pattern (through NMR analysis) observed in the coupled product of unsubstituted N,N-dimethyl aniline and 2-naphthol confirmed the ortho regioselectivity of C—C bond (Table 2, entry 21). Furthermore, this protocol is not applicable for mono alkylated anilines as well as simple anilines as their reaction failed to proceed [24]. In the present work, use of only 0.9 mol% of catalyst gave comparative yields to the homogeneous system [7a]. Moreover, the unacceptable metal contamination in the desired isolated product observed with homogeneous iron catalyst was not observed in the present system. We also extended the scope of reaction in the cross-coupling of N-phenyl (substituted) piperidine and morpholine derivatives with 2-naphthol (Table 2, entries 14–20). The catalytic efficacy of mesoporous catalyst Ce-MCM-41 was found to be much higher than the corresponding homogeneous catalysts. Hence this system provides greener synthetic pathways for organic transformations.

**Table 2**
Oxidative cross-coupling of substituted N,N dialkyl anilines and 2-naphthol in the presence of Ce-MCM-41 and TBHP[a,b].




1 2 3

R = alkyl, alkoxy, halide; X =carbon, oxygen

45-66% yield

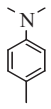
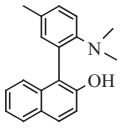
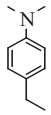
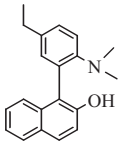
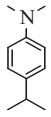
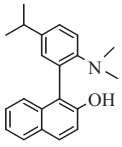
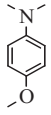
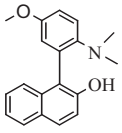
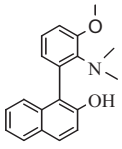
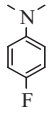
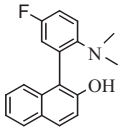
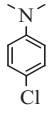
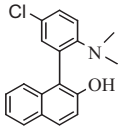
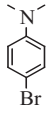
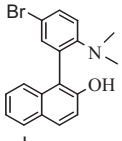
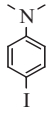
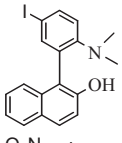
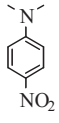
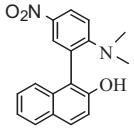
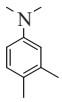
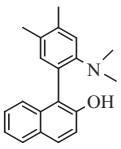
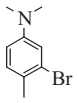
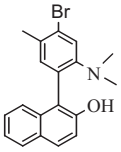
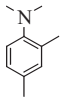
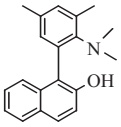
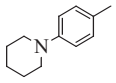
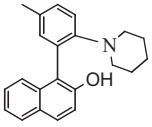
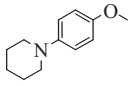
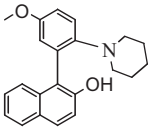
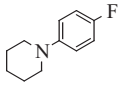
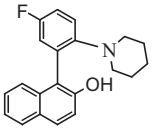
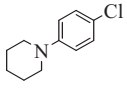
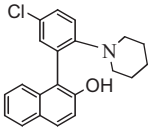
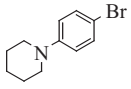
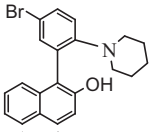
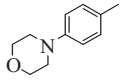
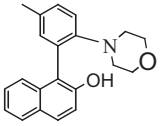
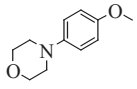
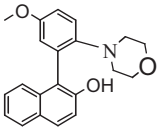
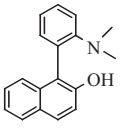
| Entry | 1 | Product[b] | | Yield[c] |
|---|---|---|---|---|
| 1. |  |  | 3a | 66, 63[d] |
| 2. |  |  | 3b | 63 |
| 3. |  |  | 3c | 61 |
| 4. |  |  | 3d | 62 |
| 5. |  |  | 3e | 0 |
| 6. |  |  | 3f | 58 |
| 7. |  |  | 3g | 54 |
| 8. |  |  | 3h | 45 |
| 9. |  |  | 3i | 48 |
| 10. |  |  | 3j | 0 |

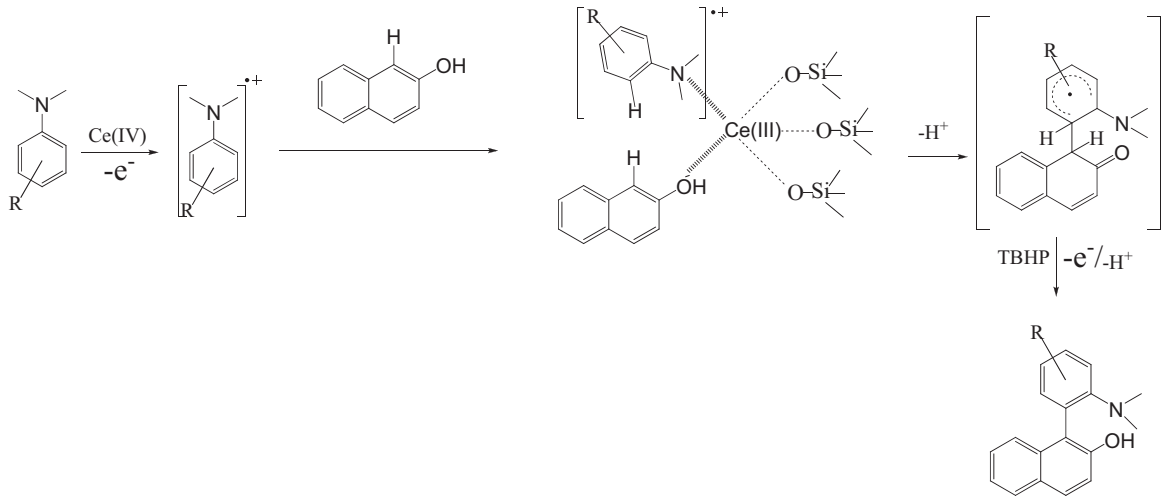
Table 2 (*Continued*)

| Entry | 1 | Product[b] | | Yield[c] |
|---|---|---|---|---|
| 11. |  |  | 3k | 65 |
| 12. |  |  | 3l | 60 |
| 13. |  |  | 3m | 0 |
| 14. |  |  | 3n | 62 |
| 15. |  |  | 3o | 60 |
| 16. |  |  | 3p | 48 |
| 17. |  |  | 3q | 45 |
| 18. |  |  | 3r | 50 |
| 19. |  |  | 3s | 64, 61[d] |
| 20. |  |  | 3t | 62 |
| 21. |  |  | 3u | 61 |

[a] Reaction conditions: amine (0.5 mmol), 2-naphthol (0.5 mmol), Ce-MCM-41 (0.9 mol%) and TBHP (2 equiv.), 60–80 °C, 3 h.
[b] All products are characterized by NMR and mass spectroscopy.
[c] Isolated yields after column chromatography.
[d] Yield after fifth cycle.

### 3.1. Proposed mechanism

The plausible mechanism for the Ce-MCM-41 catalyzed cross-dehydrogenative coupling reaction is described as follows (Scheme 1). N,N-dialkylaniline, having higher reduction potential as compared to 2-naphthol, is more susceptible to oxidation by Ce(IV) to form a radical cation and in turn yielding a Ce(III) species. This should be followed by the concurrent partial coordination of nitrogen and oxygen of amine and naphthol respectively to the Ce-MCM-41. A sequential




**Scheme 1.** Proposed reaction pathway for the oxidative cross-coupling with Ce-MCM-41.

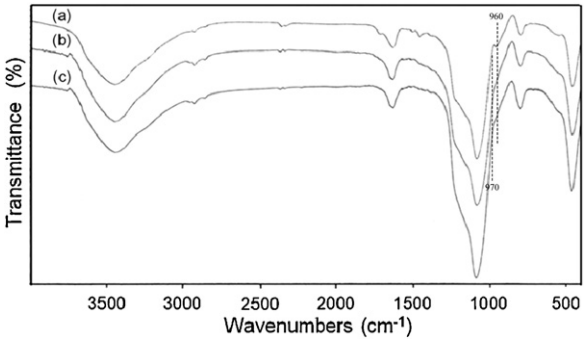



**Fig. 1.** FT-IR spectra of (a) MCM-41 (b) fresh Ce-MCM-41 and (c) used Ce-MCM-41 (after 1st recycle).

deprotonation and oxidation (by TBHP) step provides the final product. Later, Ce(IV) is regenerated via the oxidation of Ce(III) by TBHP, and hence the catalytic cycle continues [25].

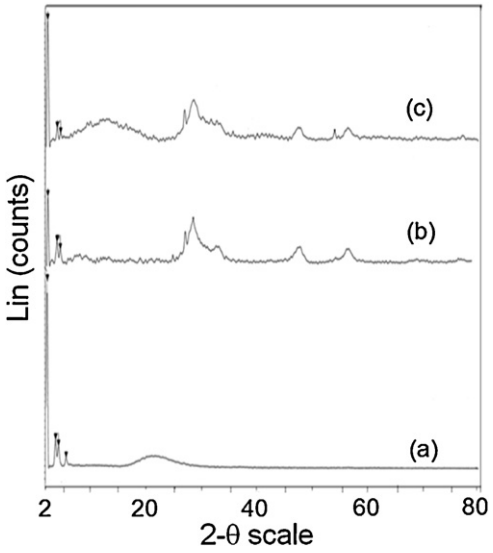



**Fig. 2.** X-ray diffraction patterns of (a) MCM-41, (b) fresh Ce-MCM-41 and (c) used Ce-MCM-41 (after 1st recycle).

### 3.2. Characterization of the Ce-MCM-41 catalyst

#### 3.2.1. FT-IR analysis

From the Fig. 1 (IR spectra), it has been observed that the band around 960 $cm^{-1}$ (in MCM-41 Fig. 1a) is shifted toward the higher wave number side (shown by dotted lines in the Fig. 1) in the case of Ce impregnated MCM-41samples (Fig. 1a and b) and thus can be assigned to asymmetric stretching vibration of Si—O—Ce bond [26]. This is in accordance with a similar higher wave number shift

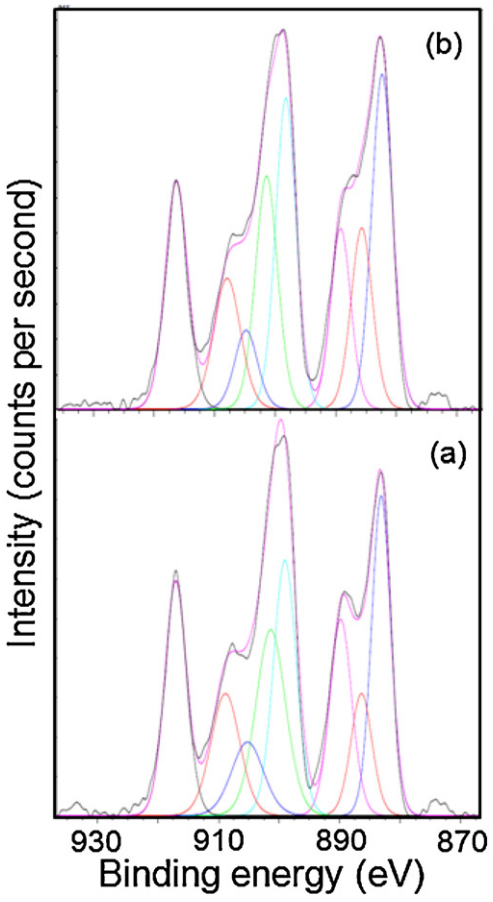



**Fig. 3.** XPS spectra of (a) fresh Ce-MCM-41 and (b) used Ce-MCM-41 (after 3rd recycle).

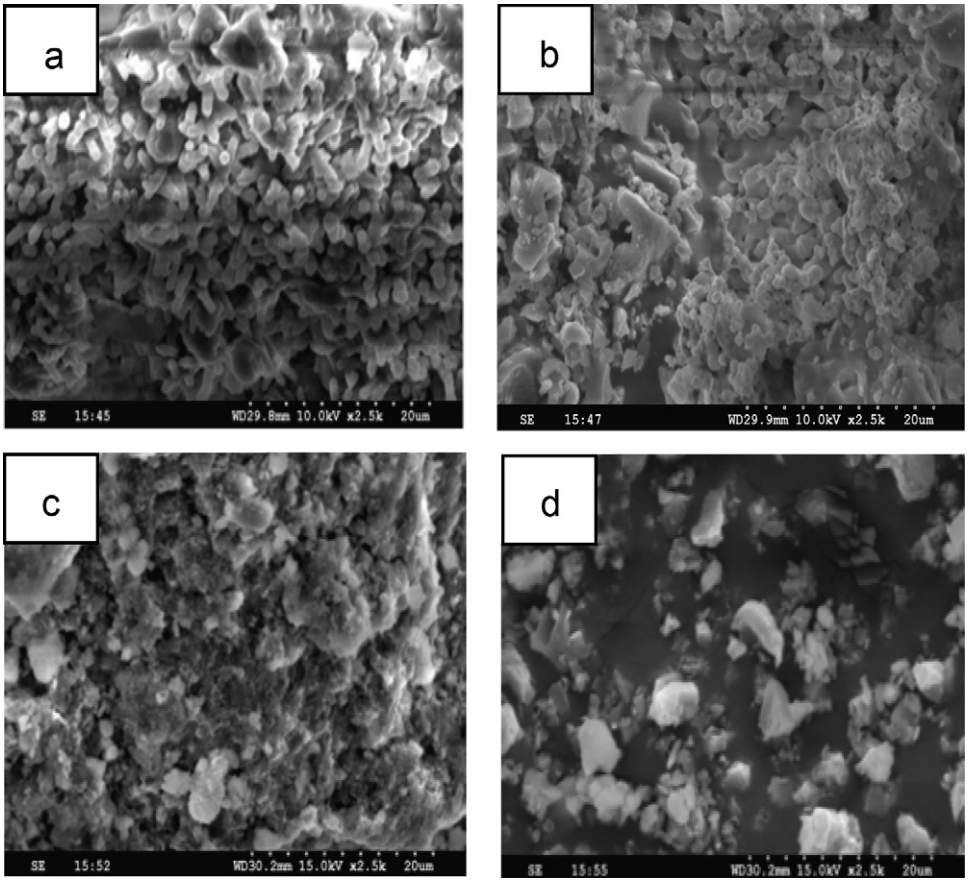



**Fig. 4.** SEM images of (a) MCM-41 (b) fresh Ce-MCM-41 (c) used Ce-MCM-41 (1st cycle) and (d) Ce-MCM-41 (5th cycle).

observed by Kumar and co-workers for the Si—O—Ce absorption band [19a]. Notably, IR spectra of both the fresh Ce-MCM-41 and used Ce-MCM-41 (after 1st recycle) were rather identical to that of MCM-41, suggesting the framework of MCM-41 is retained after incorporation of cerium.

### 3.2.2. XRD analysis

Fig. 2 shows the powder X-ray diffraction patterns of the MCM-41, Ce-MCM-41 (fresh), and Ce-MCM-41 (after 1st recycle). The most intense diffraction peak of MCM-41 appears at $2\theta = 2^\circ$–$3^\circ$. Other low intensity diffraction peaks of higher order appear at $2\theta = 4^\circ$–$5^\circ$. This diffraction pattern is observed in Ce-MCM-41 (fresh), and Ce-MCM-41 (after 1st recycle) samples suggesting that there mesoporous frameworks are similar. In addition, the diffraction peaks observed at $2\theta = 28.5^\circ$, $47.4^\circ$ and $56.3^\circ$ in the high angle XRD patterns of Ce-MCM-41 and Ce-MCM-41 (after 1st recycle) confirms the presence of ceria [27].

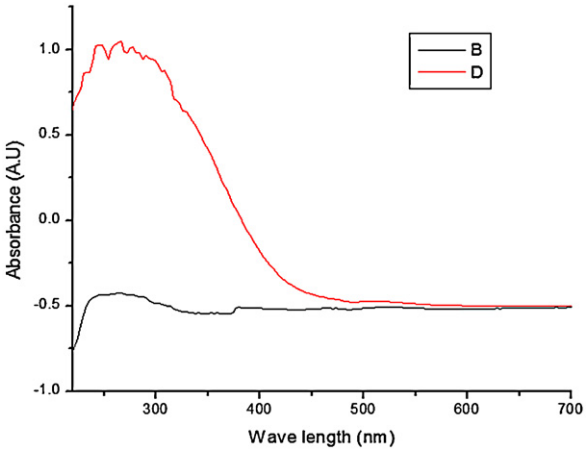



**Fig. 5.** The diffuse reflectance UV–vis spectra of (B) MCM-41 and (D) Ce-MCM-41.

### 3.2.3. XPS analysis

Fig. 3 displays the XPS spectra of fresh Ce-MCM-41 (Fig. 3a) and used Ce-MCM-41 (after 3rd recycle, Fig. 3b). The peak located at 883.1and 899.0 eV can be assigned to the Ce $3d_{5/2}$, while the peaks located at 901.3 and 917.1 eV can be assigned to the Ce $3d_{3/2}$. These values are consistent with $CeO_2$. It is also observed that a peak located at about 530.4 eV, corresponds to the O 1s and can be attributed to the oxygen in Ce—O linkages. The intense peak at ca. 532.4 eV can be assigned to the Si—O bond [22,28]. Similar results were also obtained for the used catalyst. Therefore, it can be concluded that the cerium cations in both the fresh and used catalysts are retained in the pore wall of the mesoporous molecular sieves through Ce—O—Si bond. On quantification it is observed that the ratio of $SiO_2$:$CeO_2$ is 2:1 in both the fresh and used catalyst, which also confirms that the homogeneity of the catalyst remains unaltered even after five catalytic cycles.

### 3.2.4. SEM and EDX

Fig. 4 shows the SEM micrographs of MCM-41, fresh Ce-MCM-41, used Ce-MCM-41 (after 1st cycle) and Ce-MCM-41 (after 5th cycle). The SEM micrographs for the fresh and used Ce-MCM-41 (after 1st cycle) showed similar particle morphology and the Si/Ce ratios of these samples do not differ significantly as demonstrated by EDX analysis, indicating the incorporation of well-dispersed cerium into the framework of the MCM-41 [19a]. However, there

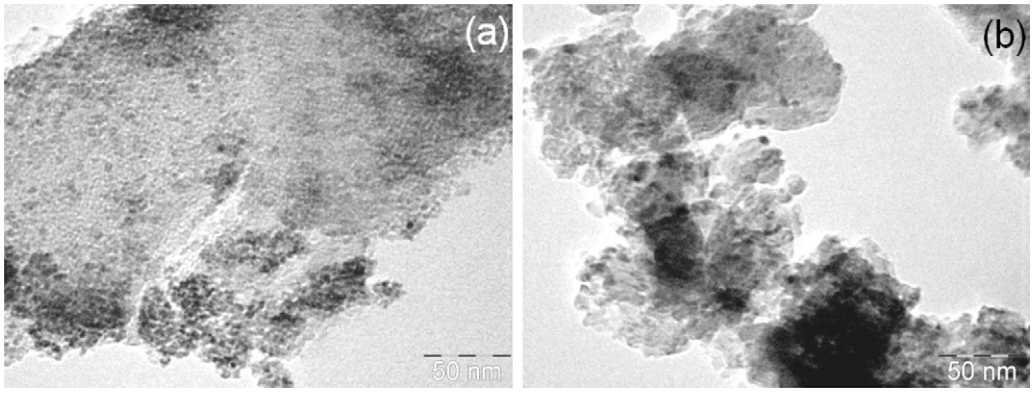



**Fig. 6.** TEM images of (a) fresh catalyst, and (b) used catalyst (after 5th cycle).

was a gradual change in the catalyst morphologies with the increasing number of recycles.

### 3.2.5. Diffuse reflectance UV–visible spectroscopy

Fig. 5 shows the overlay of the diffuse reflectance UV–vis spectra of the MCM-41 and Ce-MCM-41. The UV–vis spectrum of Ce-MCM-41 clearly displays a high intensity band with a maximum around 250, 265 and 280 nm attributed to the presence of Ceria, and two types of well dispersed $Ce^{+4}$ species (higher energy tetra-coordinated, lower energy hexa-coordinated) [29]. This is also evident by the high reactivity of the catalyst. Hence, we predict that the synthesized Ce-MCM-41 sample is mixture of ceria along with some $Ce^{+4}$ species [19a,22].

### 3.3. Reusability of the catalyst

After completion of the reaction, the catalyst was removed from the reaction mixture by simple filtration and washed sequentially with dichloromethane and methanol to remove organic material. Finally, it was oven dried and reused without any further treatment. However, there was a slight decrease in the catalytic activities with the increasing number of recycles (Table 2, entries 1, 19). This was evident from the SEM (Fig. 5) as well as from TEM analysis (Fig. 6) of the used catalyst, wherein these analyses reveal a gradual change in the catalyst morphologies with increasing number of recycles. In addition, no quantifiable amount of leached cerium was detected in the filtrate by ICP-AES analysis, hence it can be concluded that the catalytic process is truly heterogeneous.

## 4. Conclusions

In conclusion, we have prepared a heterogeneous Ce-MCM-41 catalyst and successfully used it for the oxidative arylation of N,N-dialkyl anilines. The catalyst showed notable activity for the carbon–carbon coupling of a variety of substituted anilines with 2-naphthol under mild conditions. Thus, the Ce-MCM-41 offers an effective and facile catalytic method for the synthesis of a wide variety of bifunctional amino naphthols.

## Acknowledgments

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## Appendix A.

### A.1. Spectral information

1-(2-(Dimethylamino)-5-methylphenyl)naphthalene-2-ol[1] [3a]: colorless solid, isolated by column chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.7), mp 158–159 °C; $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 7.82–7.71 (m, 3H), 7.38–7.30 (m, 3H), 7.21 (m, 3H), 2.71 (s, 6H), 2.34 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ 152.1, 147.6, 135.8, 130.6, 130.2, 129.9, 129.6, 129.2, 128.9, 128.1, 126.0, 125.3, 123.0, 120.6, 117.9, 112.5, 43.7, 20.7; FTIR ($cm^{-1}$): 2924, 2860, 1724, 1620, 1509, 1462, 1342, 1234, 1177, 1090, 1041, 963, 932, 816, 751, 511, 433; MS (ESI) *m/z*: 278 $[M+H]^+$; HRMS (ESI) calcd. for $C_{19}H_{20}NO$ $[M+H]^+$: 278.1544; found: 278.1535.

1-(2-(Dimethyl amino)-5-ethyl phenyl) naphthalene-2-ol[1] [3b]: brownish solid, isolated by column chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.6), mp 186–187 °C; $^1$H NMR (500 MHz, $CDCl_3$, ppm): $\delta$ 7.76–7.70 (m, 3H), 7.32–7.26 (m, 2H), 7.21–7.12 (m, 4H), 2.67 (s, 6H), 2.64–2.60 (q, 2H, J = 8.0 Hz), 1.24–1.21 (t, 3H, J = 8.0 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ 152.2, 147.2, 139.2, 134.8, 133.5, 130.6, 129.9, 129.3, 128.2, 127.8, 126.1, 125.2, 123, 122.4, 120.6, 118.2, 44, 28.2, 15.8; FTIR ($cm^{-1}$): 3391, 3059, 2963, 1718, 1662, 1621, 1503, 1457, 1348, 1274, 1219, 1119, 969, 896, 822, 752, 622, 548; MS (ESI) *m/z*: 292 $[M+H]^+$; HRMS (ESI) calcd. for $C_{20}H_{22}NO$ $[M+H]^+$: 292.1701; found: 292.1711.

1-(2-(Dimethyl amino)-5-isopropyl phenyl) naphthalene-2-ol[1] [3c]: reddish brown solid, isolated by column chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.5), mp 98–100 °C; $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 7.84–7.77 (m, 3H), 7.37–7.29 (m, 4H), 7.20–7.13 (m, 2H), 2.82 (m, 1H), 2.66 (s, 6H), 1.24–1.21 (m, 6H);$^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ 152.1, 147.5, 143.3, 133.4, 130.4, 129.8, 129.5, 129.1, 128.1, 126.2, 125.9, 125.3, 124.9, 122.9, 120.6, 117.9, 43.6, 33.4, 23.9; FTIR ($cm^{-1}$): 3446, 2959, 2870, 1716, 1672, 1621, 1595, 1498, 1461, 1363, 1232, 1095, 955, 819, 753, 625; MS (ESI) *m/z*: 306.2 $[M+H]^+$; HRMS (ESI) calcd. for $C_{20}H_{24}NO$ $[M+H]^+$: 306.1852; found: 306.1857.

1-(2-(Dimethyl amino)-5-methoxy phenyl) naphthalene-2-ol[1] [3d]: brownish solid, isolated by column chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.4), mp 136–137 °C; $^1$H NMR (500 MHz, $CDCl_3$, ppm): $\delta$ 7.80–7.71 (m, 3H), 7.33–7.27 (m, 2H), 7.20 (d, 1H, J = 8.9 Hz), 7.14 (d, 1H, J = 8.9 Hz), 6.92–6.88 (m, 2H), 3.73 (s, 3H), 2.65(s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ 155.4, 152.1, 142.7, 133.3, 132.1, 129.8, 129.5, 128.1, 127.6, 126.1, 125.0, 123.0, 120.6, 119.8, 119.2, 114.1, 55.5, 44.1; FTIR ($cm^{-1}$): 2924, 2854, 1732, 1623, 1503, 1461, 1342, 1239, 1171, 1092, 1035, 957, 929, 813, 752, 475; MS (ESI) *m/z*: 294 $[M+H]^+$; HRMS (ESI) calcd. for $C_{19}H_{20}NO_2$ $(M+H)^+$: 294.1494; found: 294.1491.

1-(2-(Dimethyl amino)-5-fluoro phenyl) naphthalene-2-ol[1] [3f]: brownish yellow sticky solid, isolated by column

chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.3), mp 64–65 °C; $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 7.78–7.72 (m, 3H), 7.38–7.27 (m, 2H), 7.22–7.0 (m, 4H), 2.68 (s, 6H);$^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ 152.2, 146.0, 133.0, 129.8, 129.0, 128.2, 126.4, 124.8, 123.2, 121.6, 121.3, 120.7, 119.4, 119.3, 114.9, 114.6, 43.8; FTIR ($cm^{-1}$): 3061, 2955, 2926, 2858, 1725, 1665, 1619, 1592, 1497, 1462, 1341, 1271, 1231, 1171, 929, 889, 818; MS (ESI) *m/z*: 282 $[M+H]^+$; HRMS (ESI) calcd. for $C_{18}H_{17}NOF$ $[M+H]^+$: 282.1294; found: 282.1302.

1-(5-chloro-2-(dimethyl amino) phenyl) naphthalene-2-ol[1] [3 g]: brownish yellow solid, isolated by column chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.4), mp 135–136 °C; $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 7.80–7.70 (m, 3H), 7.41–7.30 (m, 4H), 7.21–7.17 (m, 2H), 2.68 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ 152.0, 148.6, 134.6, 132.9, 132.3, 131.6, 129.8, 128.2, 128.0, 126.5, 124.8, 123.3, 120.5, 119.7, 119.4, 116.3, 43.5; FTIR ($cm^{-1}$): 3048, 2925, 2740, 1730, 1663, 1622, 1591, 1482, 1400, 1339, 1270, 1234, 1149, 1038, 991, 952. MS (ESI) *m/z*: 298 $[M+H]^+$; HRMS (ESI) calcd. for $C_{18}H_{17}NOCl$ $[M+H]^+$: 298.0998; found: 298.0995.

1-(5-Bromo-2-(dimethyl amino) phenyl) naphthalene-2-ol[1] [3h]: brownish solid, isolated by column chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.5), mp 90 °C; $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 7.78–7.70 (m, 3H), 7.51–7.27 (m, 4H), 7.21–7.18 (m, 1H), 7.10–7.0 (m, 1H), 2.67 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ 152.0, 147.1, 137.4, 132.9, 132.8, 131.1, 129.9, 129.8, 128.2, 126.5, 124.7, 123.3, 120.4, 119.8, 117.4, 112.0, 43.4; FTIR ($cm^{-1}$): 3448, 2934, 2908, 1621, 1485, 1468, 1374, 1308, 1259, 1156, 1080, 1024, 885, 846, 635.; MS (ESI) *m/z*: 342 $[M+H]^+$; HRMS (ESI) calcd. for $C_{18}H_{17}NOBr$ $[M+H]^+$: 342.0493; found: 342.0485.

1-(2-(Dimethyl amino)-5-iodo phenyl) naphthalene-2-ol[1] [3i]: brownish solid, isolated by column chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.6), mp 160–162 °C; $^1$H NMR (500 MHz, $CDCl_3$, ppm): δ 7.77–7.64 (m, 5H), 7.40–7.36 (m, 1H), 7.31–7.28 (m, 1H), 7.19–7.18 (m, 1H), 6.95–6.94 (m, 1H), 2.65 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): δ 152.0, 149.9, 143.3, 137.1, 132.9, 132.7, 129.8, 128.2, 126.5, 124.7, 123.3, 120.4, 120.1, 119.6, 113.4, 86.1, 43.3; FTIR ($cm^{-1}$): 3416, 2922, 2852, 1729, 1591, 1501, 1467, 1351, 1304, 1232, 1098, 926, 815, 751; MS (ESI) *m/z*: 390 $[M+H]^+$; HRMS (ESI) calcd. for $C_{18}H_{17}NOI$ $[M+H]^+$: 390.0354; found: 390.0367.

1-(2-(Dimethyl amino)-4, 5 dimethyl phenyl) naphthalene-2-ol[1] [3k]: pale yellow solid, isolated by column chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.6), mp 130 °C; $^1$H NMR (500 MHz, $CDCl_3$, ppm): $\delta$ 7.77–7.70 (m, 3H), 7.33–7.26 (m, 2H), 7.22 (m, 1H), 7.14 (s, 1H), 7.05 (m, 1H), 2.70 (s, 6H), 2.35 (s, 3H), 2.24 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ 152.0, 147.2, 136.8, 136, 133.3, 131.5, 129.8, 129.0, 128.0, 127.7, 125.9, 125.3, 124.9, 122.9, 120.5, 119.4, 43.8, 19.8, 18.9; FTIR ($cm^{-1}$): 3434, 2924, 2851, 1621, 1596, 1459, 1383, 1121, 817, 667; MS (ESI) *m/z*: 292 $[M+H]^+$; HRMS (ESI) calcd. for $C_{20}H_{22}NO$ $[M+H]^+$: 292.1701; found: 292.1706.

1-(4-Bromo-2-(dimethyl amino)-5-methyl phenyl) naphthalene-2-ol [3l]: pale yellow solid, isolated by column chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.5), mp 105–107 °C; $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 7.84–7.73 (m, 3H), 7.42–7.27 (m, 4H), 7.24 (m, 1H), 2.65 (s, 6H), 2.35 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ 151.9, 148.9, 136.7, 133.0, 129.8, 129.5, 128.1, 127.3, 126.2, 124.9, 123.2, 122.1, 120.4, 120.0, 113.0, 111.9, 43.5, 21.9; FTIR ($cm^{-1}$): 3431, 2923, 2851, 1733, 1623, 1457, 1262, 1171, 1037, 814, 721; MS (ESI) *m/z*: 356 $[M+H]^+$; HRMS (ESI) calcd. for $C_{19}H_{19}NOBr$ $[M+H]^+$: 356.0644; found: 356.0647.

1-(5-methyl-2-(piperidin-1-yl) phenyl) naphthalen-2-ol [3n]: colorless solid, isolated by column chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.7), mp 132–134 °C; $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.77–7.70 (m, 3H), 7.33–7.30 (m, 1H), 7.25–7.0 (m, 5H), 3.0–2.87 (m, 4H), 2.32 (s, 3H), 1.58–1.50 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ 151.9, 147.7, 135.7, 133.4, 132.4, 131.1, 129.9, 129.1, 128.9, 128.0, 125.8, 125.4, 122.9, 121.0, 120.9, 118.5, 53.5, 26.0, 23.7, 20.6; FTIR ($cm^{-1}$): 3433, 2962, 2933,2854, 1618, 1497, 1261, 1234, 1097, 1026, 864, 807, 749; MS (ESI) *m/z*: 318 $[M+H]^+$; HRMS (ESI) calcd. for $C_{22}H_{24}NO$ $[M+H]^+$: 318.1852; found: 318.1856.

1-(5-Methoxy-2-(piperidin-1-yl) phenyl) naphthalen-2-ol [3o]: brownish solid, isolated by column chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.5), mp 87–89 °C; $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 7.85–7.77 (m, 3H), 7.39–7.29 (m, 3H), 7.19–7.16 (m, 1H), 6.97–6.94 (m, 2H), 3.74 (s, 3H), 2.92 (m, 4H), 1.58 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ 155.2, 152.0, 133.9, 133.5, 132.6, 129.9, 129.4, 128.1, 126.0, 125.2, 122.9, 122.5, 121.0, 120.0, 119.6, 114.1, 55.6, 53.9, 26.0, 23.6; FTIR ($cm^{-1}$): 3445, 2926, 2853, 1740, 1598, 1496, 1461, 1410, 1339, 1287, 1263, 1236, 1148, 1099, 1047, 912, 815; MS (ESI) *m/z*: 334 $[M+H]^+$; HRMS (ESI) calcd. for $C_{22}H_{24}NO_2$ $[M+H]^+$: 334.1801; found: 334.1803.

1-(5-Fluoro-2-(piperidin-1-yl) phenyl) naphthalen-2-ol [3p]: yellow viscous liquid, isolated by column chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.4); $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 7.85–7.78 (m, 3H), 7.43–7.28 (m, 3H), 7.21–7.07 (m, 3H), 2.94 (m, 4H), 1.58 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ 152.0, 146.3, 133.2, 129.9, 129.8, 128.2, 126.3, 124.8, 123.2, 121.6, 121.4, 121.0, 119.9, 119.8, 114.9, 114.7, 53.7, 26.0, 23.6; FTIR ($cm^{-1}$): 3438, 2928, 2854, 1737, 1619, 1596, 1493, 1466, 1260, 1235, 1098, 1026, 816; MS (ESI) *m/z*: 322 $[M+H]^+$; HRMS (ESI) calcd. for $C_{21}H_{21}NOF$ $[M+H]^+$: 322.1601; found: 322.1601.

1-(5-Chloro-2-(piperidin-1-yl) phenyl) naphthalen-2-ol [3q]: colorless solid, isolated by column chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.5), mp 118–119 °C; $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 7.85–7.75 (m, 3H), 7.44–7.28 (m, 5H), 7.17–7.15 (m, 1H), 2.94 (m, 4H), 1.58 (m, 6H).; $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ 151.9, 148.8, 134.6, 133.17, 133.12, 129.9, 129.8, 128.3, 128.24, 128.21, 126.4, 124.8, 123.2, 120.8, 120.0, 119.7, 53.4, 25.9, 23.6; FTIR ($cm^{-1}$): 3432, 2923, 2851, 1731, 1626, 1459, 1256, 1028, 798, 600; MS (ESI) *m/z*: 338 $[M+H]^+$; HRMS (ESI) calcd. for $C_{21}H_{21}NOCl$ $[M+H]^+$: 338.1306; found: 338.1308.

1-(5-Bromo-2-(piperidin-1-yl) phenyl) naphthalen-2-ol [3r]: pale yellow solid, isolated by column chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.6), mp 80–82 °C; $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 7.85–7.75 (m, 3H), 7.53–7.27 (m, 5H), 7.12–7.09 (m, 1H), 2.94 (m, 4H), 1.57 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ 152.0, 149.3, 137.5, 133.5, 133.1, 131.1, 129.9, 129.8, 128.2, 126.4, 124.8, 123.2, 120.8, 120.4, 119.6, 115.9, 53.3, 25.9, 23.6; FTIR ($cm^{-1}$): 3436, 2929, 2853, 1618, 1595, 1479, 1466, 1358, 1261, 1234, 1096, 1026, 906, 749; MS (ESI) *m/z*: 382 $[M+H]^+$; HRMS (ESI) calcd. for $C_{21}H_{21}NOBr$ $[M+H]^+$: 384.0797; found: 384.0784.

1-(5-Methyl-2-morpholino phenyl) naphthalen-2-ol [3s]: colorless solid, isolated by column chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.5), mp 105–106 °C; $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 7.83–7.74 (m, 2H), 7.40–7.28 (m, 4H), 7.22 (m, 1H), 7.12–7.0 (m, 2H), 3.67–3.54 (m, 4H), 3.0–2.9 (m, 4H), 2.33 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ 151.2, 146.5, 142.1, 135.7, 133.0, 130.2, 130.0, 129.4, 129.3, 128.1, 126.1, 125.2, 124.0, 123.2, 120.5, 118.0, 66.8, 52.1, 20.6; FTIR ($cm^{-1}$): 3443, 2922, 2854, 1666, 1608, 1500, 1451, 1393, 1266, 1222, 1114, 1058, 923, 818, 756, 672; MS (ESI) *m/z*: 319 $[M+H]^+$; HRMS (ESI) calcd. for $C_{21}H_{22}NO_2$ $[M+H]^+$: 320.1645; found: 320.1642.

1-(5-Methoxy-2-morpholino phenyl) naphthalen-2-ol [3t]: reddish brown solid, isolated by column chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.3), mp 91–92 °C; $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 7.83–7.78 (m, 2H), 7.40–7.28 (m, 3H), 7.16–7.14 (m, 1H), 7.0–6.95 (m, 2H), 6.87–6.86 (m, 1H), 3.75 (s, 3H), 3.66 (m, 4H), 3.1–2.87 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ 151.3, 148.8, 142.4, 129.9, 129.7, 128.1, 126.2, 125.1, 123.2, 120.6, 120.1, 119.1, 118.3, 117.2, 114.7, 114.3, 66.8, 55.6, 52.4; FTIR ($cm^{-1}$): 3444, 2924, 2853, 1737, 1622, 1596, 1512, 1459, 1261, 1235, 1116, 1036, 926,

818; MS (ESI) $m/z$: 336 $[M+H]^+$; HRMS (ESI) calcd. for $C_{21}H_{22}NO_3$ $[M+H]^+$: 336.1594; found: 336.1600.

1-(2-(Dimethylamino)phenyl)naphthalen-2-ol[1] [3u]: yellow sticky solid, isolated by column chromatography (ethyl acetate:hexane = 1:9, $R_f$ = 0.7) mp 73–74 °C; $^1$H NMR (300 MHz, $CDCl_3$, ppm): $\delta$ 7.78–7.72 (m, 3H), 7.39–7.26 (m, 4H), 7.23–7.20 (m, 2H), 7.14–7.09 (m, 1H), 2.70 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$, ppm): $\delta$ 152.0, 149.9, 135.2, 133.2, 130.6, 129.8, 129.3, 128.3, 128.0, 126.0, 125.2, 123.0, 122.9, 120.9, 120.5, 118, 43.5; FTIR ($cm^{-1}$): 3441, 2924, 2857, 1615, 1595, 1486, 1459, 1335, 1232, 1155, 1045, 927, 817, 749, 672; MS (ESI) $m/z$: 264 $[M+H]^+$; HRMS (ESI) calcd. for $C_{19}H_{20}NO$ $[M+H]^+$: 264.1388; found: 264.1376.

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