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Pd-grafted periodic mesoporous organosilica: an efficient heterogeneous catalyst for Hiyama and Sonogashira couplings, and cyanation reactions[†]

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The high surface area of 2D-hexagonal periodic mesoporous organosilica (PMO) containing a phloroglucinol-diimine moiety inside the pore wall has been utilized for grafting Pd(II) at the surface of the mesopores. This Pd-containing PMO material (Pd-LHMS-3) shows excellent catalytic activity in fluoride-free Hiyama cross-coupling reactions in water at alkaline pH conditions. Sonogashira cross-couplings between terminal alkynes and aryl halides take place in the presence of water and hexamine as base in the absence of any Cu co-catalyst. Cyanation of aryl halides is equally promoted with K_4 [Fe(CN)₆] as the cyanide source (in the absence of poisonous KCN, NaCN or Zn(CN)₂) over Pd-LHMS-3. Excellent yield of the products, reusability and the facile work-up could make this Pd-grafted PMO material a unique catalyst for the synthesis of substituted benzonitriles, unsymmetrical biphenyls and di-substituted alkynes under environmentally benign reaction conditions. Further good yield of products and no evidence of leached Pd from the catalyst surface during the reaction and its smooth recovery confirm the true heterogeneity in these catalytic reactions.

Introduction

Since the discovery of MCM-41,¹ ordered mesoporous materials synthesized through supramolecular-templating pathways have attracted widespread applications in gas adsorption and storage, ion exchange, sensing, catalysis and so on. Organic-inorganic hybrid periodic mesoporous organosilica $(PMO)^2$ is such a class of organically functionalized mesoporous material, where the covalent attachment of organic functional groups with the silica matrix constitute the pore wall of the material. Among several properties explored so far, in heterogeneous catalysis PMO based materials have a huge potential to be explored through judicial choice of the covalently embedded organic functional groups at the mesopore wall.³ The high surface areas of the PMO materials together with strong covalent attachment of the catalytic active metal centres at the mesopore surface can make them promising candidates for heterogeneous catalysis together with good reusability and a minimum possibility for leaching of the grafted metals. Further, the heterogeneous catalyst that can work under eco-friendly conditions is very challenging from an environmental perspective. Growing ecological concern has motivated researchers to focus on the synthetic strategies which have no adverse effect on humans and the environment. Several attempts in terms of immobilization of homogeneous metal complexes on different solid supports,⁴ grafting of active metals on organic and inorganic supports or the synthesis of 2D-hexagonal

ordered mesoporous materials containing active Pd-sites have been reported recently.⁵ However, to meet the ever growing demand for the synthesis of functionalized materials having good catalytic efficiency and selectivity, high metal loadings, stability of the catalyst, use of environmentally benign reaction media and the design of a leach-proof catalytic system, with more intensive research on functionalized PMOs⁶ in catalysis is necessary.

The Hiyama cross-coupling reaction⁷ is an efficient tool in organic chemistry for the synthesis of unsymmetrical biphenyl derivatives, which have wide-scale applications in materials science, drug discovery and the production of several bioactive natural products. This C-C bond formation technique uses aryl halides, aryl-trialkoxysilane, base and a fluoride source, such as tetrabutylammonium fluoride, along with a Pd-containing catalyst. Due to the low toxicity and easy availability of aryl-silanes compared to aryl-zinc used in Negishi couplings⁸ or arylboronic acid used in Suzuki coupling reactions,9 the Hiyama coupling reaction over a solid supported heterogeneous catalyst is very demanding. Several attempts have been made for designing an efficient Pd-catalyst using complex phosphine ligands, DABCO, XPhos or K₂PdCl₂ in PEG-600, etc., in the presence of an expensive fluoride source for the activation of the silica precursor in environmentally hazardous organic solvents like DMSO or DMF.10 Using Pd-LHMS-3 as a heterogeneous catalyst, the Hiyama cross-coupling of aryl iodides and bromides proceeds well, yielding considerable amounts of cross-coupling products in water as a green reaction medium without the addition of any external fluoride source. On the other hand benzonitriles are of considerable interest in organic chemistry as they are an integral part for the synthesis of dyes, herbicides, agrochemicals,

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pharmaceuticals and natural products. Numerous synthetic strategies, with multistep challenging phosphine ligands, have been developed so far for a facile benzonitrile synthesis.¹¹ But only few catalytic systems in this context can meet the requirements of discarding of the lethal cyanide source and production of heavy metal waste, together with good reusability.

Herein, we report a Pd-grafted PMO material Pd-LHMS-3 as a unique catalytic system, which produces arylnitriles in quantitative amounts from aryl iodides and also from most challenging aryl bromides. Apart from Hiyama and the cyanation reaction, Sonogashira cross-couplings between aryl halides and terminal alkynes for the generation of di-substituted alkynes is also very promising from the perspective of the synthesis of natural products and heterocyclic compounds. Since its discovery, degassed organic solvents under an inert atmosphere using either an expensive gold(I) catalyst or phosphine containing Pd-catalyst along with CuI as co-catalyst has been used for performing facile Sonogashira reactions.¹² However, while using copper salt as a co-catalyst, the system actually suffers from a huge drawback due to the formation of homo-coupling products as a byproduct in the presence of an oxidizing agent. Use of Zn, Sn, B, Al, AgOTf, Ag₂O, etc., instead of Cu, had no significant effect on the amount of the cross-coupling products.¹³ Thus several attempts have been made in the design and synthesis of bulky palladium containing catalysts to minimize any possibility for the homo-coupling products. This tempted us to develop a mild protocol for facile Sonogashira cross-coupling reactions in the absence of any copper salts. Our Pd-LHMS-3 material has shown significant catalytic activity in water (without any organic solvent) and has easily available hexamine as a base under ambient air in this reaction. To the best of our knowledge these cross-coupling reactions under environmentally benign reaction conditions have not been explored to date utilizing a Pd-containing periodic mesoporous organosilane material as a solid support. Due to the presence of a silica backbone, the mechanical stability of the PMO material is quite high compared to that of pure organic polymers or other microporous organic polymers.¹⁴ This has prompted us to choose the PMO material as a unique scaffold for these Pd-mediated organic transformations.

Results and discussions

The Schiff base organosilane precursor (I, Scheme 1) was allowed to polymerize in a basic medium ($pH \sim 12$) in the presence of a cationic surfactant as the structure directing agent with stirring at room temperature for 12 h. This was followed by hydrothermal treatment of the resulting gel for 3 days under static conditions. This helps for complete polymerization of the organosilica gel. The resulting hexagonally ordered PMO



Scheme 1 Synthetic pathway for the formation of Pd-LHMS-3.

material was further grafted by $Pd(\pi)$ to obtain Pd-LHMS-3.¹⁵ The small angle powder X-ray diffraction pattern of the Pd-LHMS-3 catalyst and the reusable catalyst are shown in Fig. 1. As seen from this figure, the Pd-LHMS-3 material before any catalytic reaction and after its first reaction cycle exhibit good ordering, which corresponds to the 100, 110, 200 planes of the 2D-hexagonal mesophase. However, the ordering is partially disturbed after repeated catalytic cycles, as observed by a decrease in the XRD peak intensity (Fig. 1b and c). A decrease in ordering could be attributed to the strongly alkaline reaction conditions, which could hydrolyze the silicas.

The N₂ adsorption/desorption isotherms of Pd-LHMS-3 is shown in Fig. 2. This isotherm can be classified as a type IV isotherm, corresponding to the presence of ordered mesopores. The BET surface area for this Pd-LHMS-3 was 370 m² g⁻¹. Pore size distribution (as calculated by employing NLDFT method) shows the existence of uniformly distributed 3.38 nm mesopores throughout the specimen, together with a calculated pore volume of 0.234 cc g^{-1} . Sorption isotherms of the reused catalysts are shown in Fig. S1 and S2 (ESI⁺). Those isotherms provide some useful information regarding the surface area, pore volume and reusability of the catalyst for successive chemical reactions. Fig. S1[†] shows the N₂ sorption isotherm of the Pd-LHMS-3 catalyst after its second catalytic cycle. The BET surface area of this catalyst (after the second run) was found to be 170 m² g⁻¹, which is considerably lower compared to that after first catalytic cycle. The pore size distribution plot shown in the inset of Fig. S1[†] exhibits a sharp distribution with a 5.25 nm size uniform mesopore. Sorption isotherms of Pd-LHMS-3, after its



Fig. 1 Powder X-ray diffraction patterns of Pd-LHMS-3 catalyst after first (a), third (b), and fifth catalytic cycle (c). In all cases is cyanation reaction was used as reference reaction.



Fig. 2 N_2 sorption isotherms of Pd-LHMS-3 at 77 K. Adsorption and desorption points are marked by filled and empty circles respectively. Pore size distribution (determined by NLDFT method based on silica cylindrical pore at 77 K) is shown in the inset.

fourth catalytic cycle have been shown in Fig. S2.† The BET surface area calculated from this isotherm was 135 m² g⁻¹ together with a broad pore size distribution. A decrease in the surface area in successive Hiyama cross-coupling reactions could be attributed to the presence of the alkaline reaction conditions, which could partly hydrolyze the surface, thereby reducing the surface area. However, the catalytic efficiency is still quite high as evidenced from Fig. S3 (ESI†), which shows the reusability data for the Sonogashira coupling reaction. More than 70% yield of the coupling product was observed after the fourth catalytic cycle (Scheme 2).

HR TEM images of the resulting Pd-LHMS-3 are shown in Fig. 3(a), where presence of 2D-hexagonal mesophase and hexagonal arrangement of the pore channels are clearly observed. Low electron density spots (pores) are present throughout the specimen and they are arranged in a honeycomb-like hexagonal array where dimension of pores are ca. 2.6 nm. FFT pattern shown in the inset of Fig. 3(a) further confirmed the hexagonal arrangement of the pores. This result suggests that the ordered arrangement of the porous framework of Pd-LHMS-3 remains unperturbed after rigorous step of palladium loading on LHMS-3. The loading of phloroglucinol-diimine moiety per gram of the solid support was found to be 1.17 mmol g^{-1} as determined from CHN chemical analysis (N content was found to be 3.3 wt%). Further, atomic absorption spectroscopy (AAS) analysis revealed loading of 2.78 wt% Pd in Pd-LHMS-3. Presence of phloroglucinol-diimine moiety at the PMO surface has been evidenced from the corresponding ¹³C and ²⁹Si MAS NMR spectra, where presence of 9.6, 13.9, 22.8, 52.2, 99.6, 104.8, 158.2 and 160 ppm resembles different carbon atoms in bis(propyliminomethyl-silyl)-phloroglucinol fraction and chemical shifts corresponding to -57.3, -51.9 and -103.8, -95.0 ppm suggests the presence of different Si states (T²/T¹).



Scheme 2 Anchoring procedure of *p*-iodo benzoyl chloride to aminopropyl functionalized mesoporous silica.



Fig. 3 High resolution transmission electron microscopic images of Pd-LHMS-3 (a), reused Pd-LHMS-3 after first (b), second (c), third (d) cycles.

 Q^3/Q^2) of the organosilane moiety present in the Pd-LHMS-3 framework.¹⁵ Further, TGA analysis of Pd-LHMS-3 catalyst has been shown in Fig. S4 (ESI[†]). The initial sharp weight loss of about 15% up to 150 °C may be due to the pore occupancy by solvent molecules and moistures. A maximum weight loss of about 25 wt% has been observed from 280 °C to 700 °C and this could be attributed to the loss of the organic fragments from Pd-LHMS-3 material.

Catalysis

We have carried out several C–C cross-coupling reactions such as the Hiyama, Sonogashira and cyanation reactions of aryl halides under liquid phase conditions over a Pd-LHMS-3 catalyst. After completion of these reactions, the catalyst was simply filtered and the filtrate was subjected to further work-up for collection of biphenyls, alkynes and benzonitriles in good yields. The fluoride-free Hiyama coupling reaction over a Pd-LHMS-3 catalyst in water at 100 °C proceeds within a short period of time and produces good yields of substituted biphenyls. The results of the Hiyama coupling reactions are summarized in Table 1. As

seen from the table, our Pd-grafted PMO catalytic system tolerates a wide range of substrates bearing electron-donating to electron-withdrawing groups, and also *ortho*-substituted aryl halides and heteroaryl iodides. Both aryl bromides and iodides exhibit



Table 1 Hiyama cross couplings of aryl halides with aryl trimethoxysilane promoted by Pd-LHMS-3 in basic aqueous media^a



^{*a*} Reactions were carried out using 1 mmol aryl halide, 2 mmol aryl trimethoxysilane, 2 M NaOH, 0.03 g Pd-LHMS-3 catalyst at 100 °C. ^{*b*} Yields refer to those purified products based on (¹H, ¹³C NMR) and GC analysis.

coupling products along with phenyltrimethoxysilane and vinyltrimethoxysilane with good conversion. This result suggests that our present catalytic system is equally efficient for catalyzing both aromatic as well as aliphatic alkoxysilanes. The

Sonogashira cross-coupling reaction of aryl halides with terminal alkynes is also quite efficient when using water as the reaction medium in the presence of hexamine as base under copper-free conditions (Tables 2 and 3). This reaction produces different disubstituted aryl alkynes which are dependent upon the aryl halides, which range from electron-donating to electron-

Table 2 Cu-free Sonogashira cross-coupling reactions of aryl-iodides over the Pd-LHMS-3 catalyst in water^a



^{*a*} Reactions were carried out using 1 mmol aryl halide, 1.5 mmol terminal alkyne, 5 equivalents hexamine with 0.03 g Pd-LHMS-3 catalyst at 120 °C under an inert atmosphere. ^{*b*} Yields refer to the purified products based on (1 H, 13 C NMR) and GC analysis.





^{*a*} Reactions were carried out using 1 mmol aryl halide, 1.5 mmol terminal alkyne, 5 equivalents hexamine with 0.03 g Pd-LHMS-3 catalyst at 120 °C under an inert atmosphere. ^{*b*} Yields refer to the purified products based on (1 H, 13 C NMR) and GC analysis.

withdrawing groups and also to sterically hindered *ortho*-substituted aryl iodides and heteroaryl iodides. Both aryl iodides and bromides couple with phenyl acetylene, producing good to moderate yields of the coupling products. However, the coupling of aryl bromides is difficult in water and in the presence of hexamine. Although, after several attempts it has been found that aryl bromides react with phenyl acetylene in DMF under a N₂ atmosphere. It is pertinent to mention that aryl halides couple with aryl alkynes with much difficulty in water and in the absence of any copper source under aerobic conditions, which has hardly been reported in literature.¹⁶ The novelty in our Pd-LHMS-3 catalyst is that it is effective under mild reaction conditions with water alone as solvent (for iodides).

On the other hand, cyanation reactions of aryl iodides to form corresponding benzonitriles proceed very efficiently in the presence of non-toxic potassium ferrocyanide over our Pd-LHMS-3 catalyst (Tables 4 and 5). As seen from the table, aryl iodides and bromides give their respective benzonitriles under the reaction conditions. Depending upon the substituents present in the aryl halides, the corresponding benzonitriles obtained were produced in moderate to good yield. These C–C coupling reactions fail in the absence of Pd-loading in the catalyst, suggesting the possible role of the active Pd-centre during these reactions. Again the catalytic potential of Pd-LHMS-3 has been checked by loading Pd(II) on a precursor Schiff base, organosilane bis(propyliminomethyl-triethoxysilyl)-phloroglucinol(I). The

Table 4 KCN free cyanation of aryl iodides with Pd-LHMS-3^a



R= NO₂, CH₃, OCH₃, NH₂ etc.



^{*a*} Reactions were carried out using 1 mmol aryl halide along with 0.66 mmol potassium ferrocyanide, 1.33 mmol triethylamine in a 1:1 mixture of DMF and water at 100 °C. ^{*b*} Yields refer to the purified products based on (1 H, 13 C NMR) and GC analysis.

resulting catalytic system was employed for the reaction between iodobenzene and phenyltrimethoxysilane, and produces a moderate yield of biphenyl (40% in 6 h). However, the main drawback of this catalytic system is the separation, as there is leaching of the active site into the solution, and a non-porous Schiff base gelatinous catalyst forms in the reaction mixture due to hydrolysis of silica fragments, which actually makes the work-up procedure much more tedious and so often impossible.

The catalytic potential of Pd-LHMS-3 has also been checked while comparing the catalytic activity of the material with the one obtained after grafting of the organic group with the silica framework. To achieve this, we at first synthesized aminopropyl functionalized mesoporous silica by reacting 3-aminopropyltriethoxysilane with MCM-41 under refluxing conditions in toluene.¹⁷ The amino functionalized mesoporous silica matrix was later anchored with phloroglucinol-dialdehyde by refluxing in acetonitrile. In this way the LHMS-3 material has been synthesized by means of a post-synthetic grafting strategy and is then loaded with Pd(II) upon refluxing with Pd(OAc)₂ in acetic acid. Thus, the Pd-LHMS-3-P synthesized from the post-synthetic strategy was tested in the Hiyama cross-coupling reaction with aryl halides and the outcome of the catalysis is not satisfactory compared to our catalyst Pd-LHMS-3. This may be due to the fact that the post-synthetic method of Schiff base chemistry cannot incorporate too much organic group with the silica

framework, as a result, much more free -OH sites are available, which coordinate with palladium, which is in addition to there being a lower number of imine sites present in the framework. However, from CHN analysis, the post-synthetic grafting of organic groups in Pd-LHMS-3 was found to be 0.05 mmol g^{-1} with a N content of ~ 1.5 wt%. Now, to investigate the role of Schiff base (I) in Pd-LHMS-3, we have prepared a MCM-41 supported Pd catalyst through direct impregnation of palladium acetate with MCM-41. All reactions are carried out over this material, maintaining similar reaction conditions. We observed that the non-Schiff base supported Pd catalyst (Pd/MCM-41) produces biphenyl from iodobenzene in 68% yield after 6 h in the first cycle. However, the major problem encountered in this reaction is that the non-Schiff base anchored Pd-catalyst produced heavy metal waste due to possible leaching of Pd from the support. Thus in the second cycle, the yield of biphenyl was drastically reduced to 37% and the coupling reaction could not be continued further.

The catalytic activity of Pd-LHMS-3 is highly temperature dependent and we found that the yield of the cross-coupling products decreased considerably when the Hiyama coupling was performed at room temperature (25% yield of biphenyl *vis-à-vis* 90% at 80 °C), cyanation of aryl iodides (20% yield of benzonitrile *vis-à-vis* 90% at 100 °C) and Sonogashira of aryl iodides (30% yield of diphenyl-acetylene *vis-à-vis* 85% at 90 °C). Catalytic cycles of all the catalytic reactions have been shown. A
 Table 5
 Cyanation of aryl bromides with Pd-LHMS-3^a



^a Reactions were carried out using 1 mmol aryl bromide, 0.22 mmol potassium ferrocyanide, 1 mmol sodium carbonate, DMAC (2 ml) and the Pd-LHMS-3 catalyst (0.03 g).



Fig. 4 Proposed catalytic cycle for the cyanation reaction catalyzed by Pd-LHMS-3 in the presence of non-toxic potassium ferrocyanide.

possible catalytic reaction cycle for the cyanation reaction has been shown in Fig. 4. At first, oxidative addition of Ar–I with the catalyst takes place, followed by ligand exchange from the inner coordination sphere of K_4 [Fe(CN)₆] to the Pd site of the



Fig. 5 Catalytic cycle of Hiyama cross-coupling reaction over Pd-LHMS-3 under fluoride-free conditions in water.

catalyst, and lastly, reductive elimination of Ar–CN to form aryl nitrile. Similarly probable catalytic cycles of Hiyama coupling and Sonogashira reactions have also been illustrated in Fig. 5 and 6, respectively over active Pd-sites present in Pd-LHMS-3.



Fig. 6 Catalytic cycle of Cu-free Sonogashira coupling reaction over Pd-LHMS-3 in water.

Reusability of the catalyst

For heterogeneous catalysis, the most crucial issue is the reusability of the catalyst, which is largely dependent on keeping the active sites of the catalyst intact. To address this issue we have performed several tests to understand the morphological changes of the catalyst after the completion of several catalytic cycles. Changes in the X-ray diffraction pattern of the catalyst and its surface area have been discussed previously. Regarding morphological changes of the catalyst, we have performed HR TEM (Fig. 3) and FE SEM (Fig. 7) analysis of the fresh and reused catalysts. This electron microscopic image analysis suggest partial distortion of the hexagonal porous arrangement of the mesoporous framework from the fresh catalyst to the reused ones, as evidenced from the partial decrease in the BET surface area of the reused catalysts. Fig. 3a and 3b revels that the ordered porous framework has been retained upto the first catalytic cycle. On the other hand, the particle size of the catalyst after the second and third catalytic cycles became much smaller and uniformly distributed (Fig. 3c and 3d). Here mesopores are observed as white spots along with palladium species being confined as black spots within the white spots (Fig. 3c and 3d). Thus, the TEM analysis suggests that palladium is stabilized within the porous cavity bearing a bis(propyliminomethyl



Fig. 7 Scanning electron microscopic images of Pd-LHMS-3 (a) and Pd-LHMS-3 catalysts after first (b), second (c), third (d) cycles.

phloroglucinol) moiety and is not aggregated at the surface of the mesopores. 18

Further, the scanning electron microscopic results of the fresh catalyst (Fig. 7a) as well as the reused catalysts (Fig. 7b-d) shows the retention of the individual spherical nature of the particles. As seen from these images, the observed dimension of the fresh catalyst (ca. 80 nm) has been reduced to ca. 25 nm after the third reaction cycle. After the reaction was over, the catalyst was simply filtered and washed successively with acetone, THF, and DCM until TLC confirmation or GC analysis of the filtrate shows no detectable amount of reactant or products. The catalyst was then dried under vacuum overnight before doing reusability tests. It can be stated that the presence of many donor sites, *i.e.*, imine-N, as well as phenolic-OH groups of phloroglucinol serve as better chelators for the Pd-sites and thereby minimizes its possible leaching into solution.¹⁹ In Fig. S3 (ESI[†]) we have plotted the conversion profile of the Sonogashira coupling reaction between iodobenzene with phenyl acetylene, which shows that the conversion level decreases from 90% to 75% after the fourth catalytic cycle. Three experiments, hot filtration, solid phase poisoning and three phase text reactions were carried out to prove the true heterogeneity of the Pd-LHMS-3 catalyst. In the hot filtration test no increase in the yield of the coupling product was observed after 4 h, which suggests the true heterogeneity of the catalyst. Again any possibility of the leaching of Pd in the reaction mixture during the reaction has been ruled out from the chemical analysis of the filtrate (via AAS analysis). Thus, the retention of morphology and Pd-loading of the catalyst before and after the catalytic reactions clearly demonstrates the potential of Pd-LHMS-3 for C-C cross-coupling reactions using water as solvent or dispersion medium.

In the solid phase poisoning test, after completion of the reaction (TLC has been employed for monitoring the progress of the reaction) and usual work-up of the reaction mixture, we found almost no change in the product yield, as was observed previously in the absence of poisoning. Taking into consideration the HSAB principle, since the –SH group is a good soft donor and Pd^{2+} is a soft acid, the Pd-sites should better coordinate with a soft base²⁰ than a hard donor like imine-N or OH-sites from phloroglucinol. So if any palladium is being leached out from the solid support to the solution, it hardly gets a chance to redeposit in the solid framework after the reaction and thus results in poor conversion. However, no change in product yield takes place, suggesting that Pd remains in the solid framework during catalysis.

For the three phase test experiment, the solid phase reactant attached to MCM-41 has been assigned as IPhCONH@SiO₃ (Scheme 3). Formation of the amide linkage of the aromatic halide part with the solid silica surface has been confirmed from FTIR spectroscopy due to the presence of bands around 1680–1700 cm⁻¹. Now this solid reactant (IPhCONH@SiO₃) was allowed to react with phenyltrimethoxysilane in water, in the presence of 2 M NaOH, along with 0.02 g Pd-LHMS-3 catalyst. After 14 h of the reaction, the solid phases were separated by filtration and after usual work-up of the liquid phase, no product was obtained. This result suggested that Pd remains in the solid catalyst during the course of any leaching of Pd from the solid surface is further confirmed by digesting the solid residue part



Scheme 3 Three phase test of the Hiyama coupling of 4-iodoanisole with phenyltrimethoxysilane in water and 2 M NaOH under refluxing conditions in the presence of Pd-LHMS-3 as the catalyst and IPh-CONH@SiO₃ as the solid reactant.

with strongly alkaline conditions. After hydrolysis, the amide bond breaks and the corresponding 4-iodobenzoic acid is obtained, but no coupling product, *i.e.*, biphenyl-4-carboxylic acid, was detected (evidenced from the TLC and NMR spectra).

In another experiment, the solid supported reactant (IPh-CONH@SiO₃) was allowed to react with 4-iodoanisole and phenyltrimethoxysilane in presence of 2 M NaOH and the Pd-LHMS-3 catalyst in water. The reaction has been continued for 12 h under refluxing conditions and at the end of the reaction, both solids were separated and the filtrate thus obtained was further extracted with ethylacetate, which produces 4-methoxybiphenyl. Solids are further digested in a strong alkaline solution, which breaks amide bonds and forms 4-iodobenzoic acid. This result clearly suggests that no product formation is due to leached palladium from the solid support Pd-LHMS-3 to the solution. Had the palladium from Pd-LHMS-3 being leached to the solution, the product that could have been obtained would be 4-carboxy biphenyl instead of 4-methoxybiphenyl.

Conclusions

In summary, we have synthesized a Pd-grafted ordered periodic mesoporous organosilica material and it has been utilized as an efficient heterogeneous catalyst for a series of C–C cross-coupling reactions, namely Hiyama and Sonogashira couplings, and cyanation reactions. The synthetic conditions maintained here are environmentally benign, giving very high yields for the respective coupling products, while the catalyst can be recycled a number of times. Hiyama cross-couplings of aryl halides with aqueous NaOH, copper-free Sonogashira couplings with hexamine, and cyanide-free cyanations of aryl iodides and even more adamant aryl bromides with potassium ferrocyanide, easily gave the respective coupling products over the Pd-LHMS-3 catalyst. The reactions described herein can contribute significantly to the development of eco-friendly catalytic processes for the synthesis of value added biaryl derivatives.

Experimental section

Materials and instrumentation

All the reagents used for catalysis purposes were obtained from either Sigma-Aldrich, USA or from Avra chemicals, India. Elemental analysis was carried out using a Perkin Elmer 2400 Series II CHN analyzer. FTIR spectra were recorded using a Nicolet MAGNA-FT IR 750 Spectrometer Series II. ¹H and ¹³C NMR experiments (liquid state) were carried out on a Bruker DPX-300 NMR spectrometer. Mass spectrometric data were acquired by the electron spray ionization (ESI) technique at 25-70 eV in a Micromass Q-tof-Micro Quadruple mass spectrophotometer. X-Ray diffraction patterns of the powder samples were obtained with a Bruker AXS D8 Advanced SWAX diffractometer using Cu K α ($\lambda = 0.15406$ nm) radiation. Nitrogen sorption experiments and micropore analysis were conducted at -195.8 °C using a Beckman Coulter, SA 3100 instrument. Prior to adsorption measurements the samples were degassed in a vacuum at 120 °C for about 4 h. The pore-size distribution of the material was determined from the sorption isotherms by using a NLDFT model on the carbon/slit-cylindrical pore model. The ¹³C cross-polarization magic angle spinning (CP-MAS) NMR spectrum was obtained on a Bruker Avance 500 MHz NMR spectrometer using a 4 mm MAS probe under static conditions. Thermogravimetry (TGA) and differential thermal analyses (DTA) of the samples are carried out in a TGA Instruments thermal analyzer TA-SDT Q-600. Atomic absorption spectroscopic (AAS) measurements were carried-out using a Shimadzu AA-6300 AAS spectrometer fitted with a double beam monochromator. Transmittance electron microscopic images of the samples were recorded on a UHR-FEG-TEM, JEM 2100F operated at 200 KV. Scanning electron microscopic analysis was performed with a JEOL JEM 6700F field-emission scanning electron microscope (FE SEM).

Synthesis of LHMS-3 and post synthetic Pd-grafting

LHMS-3 and its further Pd grafting was synthesized according to the literature procedure.¹⁵ Phloroglucinol-dialdehyde (synthesized via the Vilsmeier-Hacck formylation of phloroglucinol) was allowed to react with 3-aminopropyltriethoxysilane (APTES) and the resulting Schiff base organosilica was then hydrolysed in alkaline pH conditions using a cationic structure directing agent (CTAB) and tetraethyl orthosilicate followed by hydrothermal treatment at 75 °C for about 2 days. The yelloworange material thus obtained was extracted thrice with ethanol/ dilute HCl at room temperature for the removal of the template from its porous architecture. The template-free material was allowed to react with palladium acetate in glacial acetic acid under an inert N2 atmosphere. After refluxing for about 14 h, the orange-yellow colour of the material changed to black. Prior to catalysis, Pd-LHMS-3 was filtered and repeatedly washed with methanol, acetone and THF to remove all Pd-salts present at the surface of the material, it was then vacuum dried at 90 °C for

2 days. Pd-grafting onto the mesoporous surface was later confirmed by atomic absorption spectroscopic analysis (AAS) of the filtrate.

Catalytic reactions

The catalytic activity of Pd-LHMS-3 was evaluated for a series of useful C–C cross-coupling reactions such as Hiyama and Sonogashira couplings, and cyanation reactions.

General procedure for the Hiyama coupling reaction

In a typical procedure, 1 mmol aryl bromide was allowed to react with 1.5 mmol phenyltrimethoxysilane, 2 M NaOH in a 50 ml round bottom flask. To the mixture, 2 ml water and 0.03 g Pd-LHMS-3 were added and was refluxed at 80 °C in an oil bath for the appropriate amount of time (monitored by TLC). The reaction mixture was cooled and the catalyst was separated by filtration, washed thoroughly by ethyl acetate. The filtrate portion was extracted with ethyl acetate thrice $(3 \times 20 \text{ ml})$ and the combined organic portions were washed with saturated brine solution, then dried in sodium sulphate and solvent removed under reduced pressure to leave the crude product, which was re-crystallized from (3-5) % ethyl acetate in petroleum ether (boiling point range 60-80 °C) to furnish aryl substituted biphenyl as white crystalline compound. This procedure was followed for the synthesis of all the products listed in Table 1. Known compounds were identified by comparison of their spectral data with those reported earlier. The same procedure has been repeated for the coupling of aryl halides with vinyltrimethoxysilane for the production of substituted styrenes.

General procedure for the Sonogashira coupling reactions

To a 50 ml round bottom flask, aryl iodide (1 mmol), phenyl acetylene (1.5 equivalent), hexamine (5 equivalents) were mixed with 3 ml water, along with 0.02 g Pd-LHMS-3 catalyst. The resulting mixture was subjected to reflux conditions under an air atmosphere with vigorous stirring at 90 °C. In the case of aryl bromides, coupling with alkynes does not take place in water alone as solvent, however, in DMF under an inert atmosphere, aryl bromides undergo facile Sonogashira coupling with phenyl acetylene. The progress of the reaction was monitored by TLC. After the reaction was over, the catalyst was separated by simple filtration, with extensive washing with ethyl acetate. The filtrate was then extracted with ethyl acetate followed by washing with brine solution. The organic part thus obtained was dried by sodium sulphate and the solvent was then removed by rotary evaporation under reduced pressure. The product thus obtained was further purified before spectroscopic analysis.

Procedure for the cyanation reactions

In a typical procedure, a mixture of aryl iodide (1 mmol), K_4 [Fe-(CN)₆] (0.66 mmol), catalyst Pd-LHMS-3 (0.02 g, 0.00524 mmol Pd) and triethylamine (1.33 mmol) was mixed in a round bottom flask. Then a mixture of DMF–water (6 ml, 2 : 1) was added and stirred under reflux at 100 °C under atmospheric

conditions. The progress of the reaction was monitored by TLC. After the reaction was over, the solution was quenched by water and filtered to remove the catalyst. The filtrate was extracted thrice with ethyl acetate and washed with brine repeatedly. The organic layer was dried in sodium sulphate and then removed by rotary evaporation to produce the pure product, which was further re-crystallized before spectroscopic analyses (given below). All products are known and compared with authentic samples. For the cyanation reactions of aryl bromides, a sealed tube reaction has been performed. In this case, a 18 cm \times 4 cm sized glass tube was charged with aryl bromide (1 mmol), potassium ferrocyanide (0.22 mmol), sodium carbonate (1 mmol), DMAC (2 ml) and the catalyst Pd-LHMS-3 (0.03 g). The tube was flash frozen with liquid nitrogen and evacuated to create a vacuum inside which was immediately sealed with a Bunsen flame burner. The sealed tube was immersed in an oil bath at 110 °C and heated until completion of the reaction. At the end of the reaction, the tube was allowed to cool at room temperature. The progress of the reaction was successfully monitored by TLC and at the end of the reaction the tube was allowed to come at room temperature. The reaction mixture was diluted and extracted with diethyl ether. The combined organic parts were washed thoroughly with water and brine and dried over sodium sulphate. Removal of organic part yielded the final product, which was further purified by either re-crystallization or using column chromatography for characterization purposes.

Hot filtration test

To check whether Pd was being leached from the solid support to the solution, the cyanation reaction with our supported Pd-LHMS-3 catalyst has been carried out. Thus, in a typical hot filtration,²¹ 1 mmol of aryl iodide was allowed to react with K_4 [Fe(CN)₆] and triethylamine in DMF–water along with 0.02 g catalyst. The reaction was performed at 100 °C and after 4 h, during hot conditions, the reaction mixture was immediately filtered so that if any Pd was being leached out from the solid to the solution, it may not be re-deposited to the solid support while the solution cooled. After removing the catalyst, the filtrate was taken in a round bottom flask and the reaction was allowed to continue in the absence of catalyst for another 4 h.

Solid phase poisoning test

To prove the heterogeneity of the Pd-LHMS-3 catalyst we have used a 3-mercaptopropyl functionalized mesoporous silica material as a reference in the solid phase poisoning experiment.²² 3-Mercaptopropyl functionalized mesoporous silica was synthesized through anchoring –SH groups on the surface of mesoporous silica by means of a post-synthetic grafting technique. MCM-41 was allowed to react with (3-mercaptopropyl)-triethoxysilane in refluxing toluene and the product thus obtained was filtered and thoroughly washed with organic solvents. Next Hiyama coupling of iodobenzene with phenyltrimethoxysilane was performed in the presence of a mixture of Pd-LHMS-3 and 3-mercaptopropyl functionalized MCM-41 under refluxing conditions.

Three phase test

To check the true heterogeneity of our catalytic system we have carried out a three phase test experiment.²³ Here one of the reactants is tethered onto a solid support, which constitutes one of the three phases among which the other phases include the solid catalyst Pd-LHMS-3 and liquid phase reactant, and the other coupling partner. The experiment was continued by grafting 3-aminopropyltriethoxysilane (APTES) to –OH functionalized mesoporous silica in dry toluene under refluxing conditions for about 12–14 h. The amino functionalized mesoporous material then washed well with THF, acetonitrile and dried at 80 °C. Finally, 4-iodoacetylchloride was anchored with amino functionalized mesoporous material *via* a post-synthetic process by refluxing in dry THF with pyridine for 14 h.

Spectroscopic data of ¹H and ¹³C NMR of Hiyama crosscoupling products

Biphenyl (Table 1, entries 1, 2; S1). Colourless crystalline solid, m.p. = 64-65 °C.

¹H NMR (300 MHz, CDCl₃): δ = 7.53 (d, 4H, *J* = 8.7 Hz, ArH), δ = 7.38 (t, 4H, *J* = 7.77 Hz, ArH), δ = 7.26 (t, 2H, *J* = 7.32 Hz) ppm.

¹³C (75 MHz, CDCl₃): δ = 141, 128, 127, 127.3 ppm.

4-Nitro-biphenyl (Table 1, entries 3, 4; S2). Yellow crystalline solid, m.p. = 114–115 °C.

¹H NMR (300 MHz, CDCl₃): δ = 8.31 (d, 2H, *J* = 8.84 Hz, ArH), 7.76 (d, 2H, *J* = 8.85 Hz, ArH), 7.64 (d, 2H, *J* = 7.85), 7.53 (m, 3H, ArH) ppm.

¹³C (75 MHz, CDCl₃): δ = 147.7, 147.2, 138.8, 129.5, 129, 127.9, 127.5, 124 ppm.

4-Acetyl-biphenyl (Table 1, entries 5, 6; S3). White powder, m.p. = 115-117 °C.

¹H NMR (300 MHz, CDCl₃): δ = 2.64 (s, 3H, -CH₃), 8.05 (d, 2H, *J* = 8.30 Hz, ArH), 7.70 (d, 2H, *J* = 8.30 Hz, ArH), 7.64 (d, *J* = 7.13 Hz, 2H, ArH), 7.47 (m, 3H, ArH) ppm.

¹³C (75 MHz, CDCl₃): δ = 27, 197.9, 145, 140, 136, 129, 128.37, 127.42, 127.3 ppm.

4-Methoxy-biphenyl (Table 1, entries 7, 8; S4). White powder, m.p. = 90 °C.

¹H NMR (300 MHz, CDCl₃): δ = 3.77 (s, 3H, -CH₃), 6.92 (d, 2H, *J* = 8.76 Hz, ArH), 7.25 (t, 2H, *J* = 7.24 Hz, ArH), 7.36 (t, 1H, *J* = 7.29 Hz, ArH), 7.49 (m, 4H, ArH) ppm.

¹³C (75 MHz, CDCl₃): δ = 159.3, 140.9, 133.9, 128.8, 128.3, 126.8, 126.7, 114.3, 55.48 ppm.

4-Methyl-biphenyl (Table 1, entries 9, 10; S5). White crystalline solid, m.p. = 52 °C.

¹H NMR (300 MHz, CDCl₃): δ = 2.40 (s, 3H, –CH₃), 7.60 (d, 2H, *J* = 7.10 Hz, ArH), 7.51 (d, 2H, *J* = 8.13 Hz), 7.45 (t, 2H, *J* = 7.19 Hz), 7.35 (t, 1H, *J* = 7.23 Hz), 7.27 (d, 2H, *J* = 7.8 Hz). ¹³C (75 MHz, CDCl₃): δ = 141.3, 138, 137, 135, 133.5, 129.6, 128.8, 128.14, 127.12 ppm.

4-Cyano-biphenyl (Table 1, entry 11, S6). Pale yellow solid, m.p. = 85-87 °C.

¹H NMR (300 MHz, CDCl₃): δ = 7.74 (d, 4H, *J* = 8.62 Hz, ArH), 7.61 (d, 2H, *J* = 7.82 Hz, ArH), 7.57 (m, 3H, ArH).

¹³C (75 MHz, CDCl₃): δ = 145.8, 139, 132, 129.3, 128.8, 127.9, 127.4, 119, 111 ppm.

Biphenyl-4-carboxylic acid (Table 1, entry 12, S7). White solid powder, m.p. = 224-228 °C.

¹H NMR (300 MHz, DMSO-d₆): δ = 7.77 (d, 2H, J = 8.49 Hz, ArH), 7.61 (d, 2H, J = 8.46 Hz, ArH), 7.68 (d, 2H, J = 6.44 Hz), 7.23 (m, 3H, ArH).

¹³C (75 MHz, DMSO-d₆): δ = 167, 134.6, 132.25, 131.8, 130.5, 127.8, 127.4 ppm.

p-Terphenyl (Table 1, entry 13, S8). White powder, m.p. = $214 \, ^{\circ}$ C.

¹H NMR (300 MHz, CDCl₃): δ = 7.46 (m, 8H, ArH), 7.56 (m, 6H, ArH) ppm.

 13 C (75 MHz, CDCl₃): δ = 129, 127.4, 135.5, 137 ppm.

Styrene (Table 1, entries 14, 15, S9). Viscous oil.

¹H NMR (500 MHz, CDCl₃): δ = 7.51 (d, 2H, *J* = 7.5 Hz), 7.42 (t, 2H, *J* = 7.5 Hz), 7.35 (t, 1H, *J* = 7 Hz), 6.85 (m, 1H, vinyl-H), 5.87 (d, 1H, *J* = 17.5 Hz), 5.35 (d, 1H, *J* = 11 Hz) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 137, 128, 127, 126, 113 ppm.

p-Nitrostyrene (Table 1, entries 16, 17; S10). Pale yellow viscous oil.

¹H NMR (500 MHz, DMSO-d₆): δ = 8.20 (d, 2H, ArH, J = 14.8 Hz), 7.76 (d, 2H, ArH, J = 14.3 Hz), 6.93 (m, vinyl H), 6.12 (d, 1H, J = 29.42 Hz, vinyl H), 5.55 (d, 1H, J = 18.22 Hz, vinyl H) ppm.

¹³C (125 MHz, DMSO-d₆) δ = 143.6, 134.8, 127.2, 123.8, 119.3 ppm.

p-Methyl styrene (Table 1, entries 18, 19; S11). Colourless oil, slightly viscous.

¹H NMR (500 MHz, CDCl₃): δ = 7.35 (d, 2H, ArH, J = 8 Hz), 7.17 (d, 2H, ArH, J = 7.5 Hz), 6.75 (m, 1H, vinyl-H), 5.75 (d, 1H, J = 17.5 Hz), 5.23 (d, 1H, J = 11 Hz) ppm.

¹³C (125 MHz, CDCl₃): δ = 137, 136, 134, 129, 126, 112, 21 ppm.

1-Phenyl benzoic acid (Table 1, entry 20, S12). ¹H NMR (500 MHz, CDCl₃): δ = 7.99 (1H, d, J = 7 Hz, ArH), 7.61 (1H, t, J = 7.5 Hz, ArH), 7.47 (t, 1H, J = 7.5Hz, ArH), 7.428 (d, 1H, J = 7Hz, ArH), 7.3 (m, 5H, ArH) ppm.

¹³C (125 MHz, CDCl₃): δ = 172, 130.6, 127, 129, 134, 136 ppm.

3-Phenyl thiophene (Table 1, entry 21, S13). ¹H NMR (500 MHz, CDCl₃): δ = 7.62 (d, J = 7.5 Hz, 2H, thiophene), 7.46 (s, 1H, thiophene), 7.41 (m, 4H, ArH), 7.31 (t, 1H, J = 7 Hz, ArH) ppm.

¹³C (125 MHz, CDCl₃): δ = 128, 124, 122, 142, 138, 127, 129, 128 ppm.

5-Phenylsalicylaldehyde (Table 1, entry 22, S14). ¹H NMR (300 MHz, CDCl₃): δ = 10.9 (s, 1H, –CHO), 7.49 (d, 2H, J = 7.23 Hz, ArH), 7.38 (m, 2H, ArH), 7.3 (m, 1H, ArH), 7.02 (1H,

d, *J* = 9.45 Hz, ArH), 7.71 (m, 1H, ArH), 7.68 (s, 1H, ArH), 9.9 (s, 1H, -OH) ppm.

¹³C (125 MHz, CDCl₃): δ = 196, 161, 139, 136, 135, 133, 131, 129, 127, 126, 120, 118 ppm.

Product, diphenyl acetylene (Table 2, entry 1; S15). ¹H NMR (300 MHz, CDCl₃) δ = 7.60 (d, 4H, J = 6.4 Hz, ArH), δ = 7.45 (m, 6H, ArH) ppm.

¹³C (75 MHz, CDCl₃): δ = 132.6, 129.3, 128.58, 121.96, 81.7 ppm.

Product, 4-nitro-diphenylacetylene (Table 2, entry 2, 10; S16). ¹H NMR (300 MHz, CDCl₃) δ = 8.25 (d, 2H, J = 8.88 Hz, ArH), δ = 7.69 (d, 2H, J = 8.88 Hz, ArH), δ = 7.59 (d, 2H, J = 6.14 Hz, ArH), δ = 7.42 (m, 3H, ArH) ppm.

¹³C (75 MHz, CDCl₃): δ = 147.1, 132.6, 131.9, 130.4, 129.4, 128.68, 128.58, 123.77, 122.25, 94.8 ppm.

Product, 4-acetyl-diphenylacetylene (Table 2, entry 3; S17). ¹H NMR (300 MHz, CDCl₃) δ = 2.61 (s, 3H, COCH₃), δ = 7.937 (d, 2H, *J* = 8.6 Hz, ArH) δ = 7.356 (m,3H, ArH), δ = 7.543 (m, 4H, ArH) ppm.

¹³C (75 MHz, CDCl₃): δ = 196.5, 137.1, 128, 94, 132.2, 121, 125, 128.4, 132.3, 26.7 ppm.

Product, 4-methyl-diphenylacetylene (Table 2, entry 6, S₂₀). ¹H NMR (500 MHz, CDCl₃) δ = 2.61 (s, 3H, -CH₃), δ = 7.36 (m, 4H, ArH), δ = 7.84 (d, 2H, *J* = 9 Hz, ArH), δ = 7.65 (d, 2H, *J* = 8.5 Hz, ArH), 7.54 (m, 1H, ArH) ppm.

¹³C (125 MHz, CDCl₃): δ = 128.8, 139.5, 132.1, 119, 94, 125.3, 132.1, 129.3, 128.2, ppm.

Product, 1-carboxy-diphenylacetylene (Table 2, entry 4, S18). ¹H NMR (500 MHz, CDCl₃) δ = 8.14 (d, 1H, J = 8 Hz, ArH), 8.07 (d, 2H, J = 8 Hz, ArH), 7.20 (1H, t, J = 7.5 Hz, ArH), 7.54 (4H, m, ArH), 7.35 (1H, d, J = 7.5, ArH) ppm.

¹³C (125 MHz, CDCl₃): δ = 172, 134, 133, 128, 94, 125, 132, 133, 122 ppm.

Product, 4-methoxy-diphenylacetylene (Table 2, entry 5, S19). ¹H NMR (500 MHz, CDCl₃) δ = 3.8 (s, 3H, -OCH₃), 7.3 (m, 3H, ArH), 7.46 (d, *J* = 9Hz, 2H, ArH), 7.3 (m, 2H, ArH), 6.9 (d, *J* = 9 Hz, ArH, 2H) ppm.

¹³C (125 MHz, CDCl₃): *δ* = 55, 161, 134, 128, 123, 131, 122, 92 ppm.

Benzonitrile (Table 4, S30, Table 5, S35). Colourless liquid with sweet almond odour.

¹H NMR (500 MHz, CDCl₃): δ = 7.42 (t, 2H, Ar-H, J = 7.5 Hz), 7.56 (m, 3H, Ar-H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 132.6, 131.8, 128.9, 118.6, 112 ppm.

4-Cyano-toluene (Table 4, S31, Table 5, S42). Solid, m.p. = 25–26 °C.

¹H NMR (500 MHz, CDCl₃): δ = 7.57 (d, 2H, Ar-H, J = 8.5 Hz), 6.94 (d, 2H, Ar-H, J = 8 Hz), 2.29 (s, 3H, -CH₃) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 137, 132, 131, 129, 90, 21 ppm.

4-Cyano-nitrobenzene (Table 4, S32, Table 5, S36). Yellow solid, m.p. = 148-150 °C.

¹H NMR (500 MHz, CDCl₃): δ = 8.36 (d, 2H, Ar-H, J = 9 Hz), 7.95 (d, 2H, Ar-H, J = 9 Hz) ppm.

¹³C NMR (125 MHz, CDCl₃): 116, 118, 124, 133, 150 ppm.

4-Cyano-anisole (Table 4, S33, Table 5, S37). Solid, m.p. = 60 °C.

¹H NMR (500 MHz, CDCl₃): δ = 7.59 (d, 2H, Ar-H, *J* = 9 Hz), 6.69 (d, 2H, Ar-H, *J* = 9 Hz), 3.77 (s, 3H, -OCH₃) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 159, 138, 134, 116, 114, 82, 56 ppm.

4-Amino-benzonitrile (Table 4, S34). Pale yellow solid, m.p. = 84 °C.

¹H NMR (500 MHz, CDCl₃): δ = 7.41 (d, 2H, Ar-H, J = 8.5 Hz), 6.65 (d, 2H, Ar-H, J = 9 Hz), 4.16 (s, 2H, NH) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 150.5, 133.9, 120, 114, 100.38 ppm.

4-Cyano acetophenone (Table 5, S38). ¹H NMR (500 MHz, CDCl₃): δ = 7.78 (d, 2H, ArH, J = 8.5 Hz), 8.07 (d, 2H, ArH, J = 8 Hz), 2.67 (–CH₃, 3H) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 196, 140, 132, 129, 128, 127, 116.9, 116.5, 26.8 ppm.

5-Cyano indole (Table 5, S40). ¹H NMR (500MHz, CDCl₃): $\delta = 6.5$ (m, 1H, ArH), 7.77 (s, 1H, ArH), 7.27 (d, ArH, 2H, J = 7Hz), 7.21 (m, 1H, ArH), 8.22 (s, 1H, NH) ppm.

¹³C NMR (125 MHz, CDCl₃): δ = 134, 129, 125, 124.9, 123.3, 114, 112, 102, 91.6 ppm.

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