

## PAPER



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# Pd(OAc)<sub>2</sub>/[C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br: a nano palladium catalytic approach for Mizoroki–Heck and Suzuki–Miyaura coupling reactions in water†

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In this study, we have successfully used a new catalytic system comprised of Pd(OAc)<sub>2</sub> and [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br (at a ratio of 1 : 10 mol%) for various types of C–C coupling reactions, including Mizoroki–Heck and Suzuki–Miyaura, in a water-based medium. The catalyst system was analyzed using TEM, which revealed the presence of stable Pd nanoparticles (PdNPs) that were less than 5 nm in size and were protected by a “Gemini” type [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br surfactant. X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation states of Pd. Our optimization study revealed that this catalytic system was highly effective in coupling a range of aryl iodides and bromides with different olefins and aryl boronic acids. The reactions were performed at 80–100 °C with K<sub>2</sub>CO<sub>3</sub> as a base, and high yields ranging from 80–93% were obtained. The selectivity of all reactions was excellent, ranging from 92–100%, with a turnover number (TON) of 79.72–92.77 and a turnover frequency (TOF) of 0.997–2.059 min<sup>-1</sup>. Similarly, the catalytic system was highly efficient in Suzuki–Miyaura coupling of various aryl iodides and bromides with different aryl boronic acids, yielding good to excellent product yields (87–95%) with TON of 86.86–94.84 and TOF of 1.996–3.161 min<sup>-1</sup>. One of the advantages of this catalyst is that it can be recycled at least three times for Mizoroki–Heck coupling reactions with only a marginal loss in product yields.

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## Introduction

Palladium-catalyzed coupling reactions have become an important tool in organic synthesis, using various aryl and vinyl halides and nucleophiles.<sup>1</sup> Two prominent examples of these reactions are the Mizoroki–Heck olefination<sup>2</sup> and Suzuki–Miyaura coupling, which enable the construction of carbon–carbon bonds and the synthesis of new biomolecules, compounds of theoretical interest, and organic polymers.<sup>3</sup> Traditionally, these reactions have relied on the use of various phosphines,<sup>4</sup> amines,<sup>5</sup> carbenes,<sup>6</sup> and mixed ligands,<sup>7</sup> but

recent research has focused on alternative ligand systems, especially those that address issues of toxicity and sensitivity to air and moisture. These new methods rely on environmentally friendly protocols, particularly those involving water as a solvent.<sup>8</sup> Water is widely used in biological as well as many chemical processes,<sup>9</sup> but water-mediated cross-coupling reactions usually require the use of toxic and air-sensitive phosphine ligands.<sup>10,11</sup> As a result, there is a need for phosphine-free catalysts, which can require low reaction temperatures.<sup>12</sup>

Therefore, the development of a new catalytic system for use in organic reactions that is economically and environmentally viable, works at low temperatures, and is free of phosphine and ligands in aqueous media has garnered a lot of attention. Although organic reactions in water have several advantages,<sup>13</sup> the limited aqueous solubility of most neutral organic substrates and functional group reactivity are the main obstacles to water as a solvent in organic reactions. By adding common additives such as tetrabutylammonium bromide, various polymers, and ionic liquids, along with different Pd sources,<sup>14</sup> remarkable rate enhancements have been achieved in these cross-coupling reactions of aryl iodides in various solvents. The formation of colloid PdNPs under the so-called ‘Jeffery conditions’<sup>15</sup> takes place in these catalytic systems. Despite all these

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developments, many of the catalytic systems still require polar aprotic solvents. Recently, Pd catalysts in the form of Pd dispersions containing PdNPs have gained increasing scientific interest for many cross-coupling reactions.<sup>16</sup> It is generally observed that the activity and selectivity of PdNPs depend on the size and morphology of PdNPs, as they show superior catalytic properties and do not require ligands. Various strategies have been reported regarding the development of nano-catalysts in water for Mizoroki–Heck and Suzuki–Miyaura coupling reactions under environmentally sustainable conditions.<sup>17</sup>

In our previous research, we studied the development of Pd-catalyzed coupling reactions using various Pd catalysts in different reaction media, including biosurfactants and hydrotropes.<sup>18</sup> In this study, we present a new catalytic system comprising Pd(OAc)<sub>2</sub> and [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br (1:10 mol%) that demonstrates outstanding efficiency and reusability in Mizoroki–Heck and Suzuki–Miyaura coupling reactions conducted in an aqueous medium. The Gemini-type surfactant [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br<sup>19</sup> serves as a great stabilizing agent, allowing Pd(OAc)<sub>2</sub> to act as a source of Pd nanoparticles (PdNPs). This catalytic system facilitates the coupling of various aryl iodides and bromides with different nucleophiles, using K<sub>2</sub>CO<sub>3</sub> as a base and operating at 80 °C. The reactions provide the desired products in good to excellent yields, exhibiting exceptional selectivity and short reaction times. We evaluated the stereoselectivity of the catalytic system by calculating *E/Z* ratios, confirming its favorable tendency towards the formation of the *E*-isomer (92–100%) in Mizoroki–Heck coupling reactions.

## Results and discussion

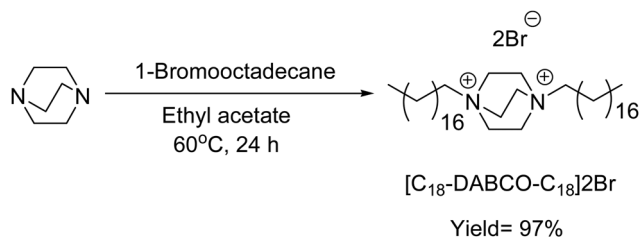
### 1. Synthesis of [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br

The diquaternization of the DABCO with 1-bromooctadecane in ethyl acetate at 60 °C provided about 97% yield of the [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br as reported in the literature procedure (Scheme 1).<sup>20</sup>

The obtained DABCO salt could be easily soluble in water and various organic solvents like MeOH, CHCl<sub>3</sub>, acetone, DMF, and DMSO, that further characterized and confirmed using <sup>1</sup>H NMR, <sup>13</sup>C NMR, and HR-MS (Fig. 1).

### 2. Study of micellization behavior of prepared [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br in aqueous solution

The micellization behavior of the pure [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br in an aqueous solution was studied using conductivity and UV-absorption measurements.



Scheme 1 Synthesis of [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br.

**(a) Conductivity measurements.** The conductivity method provides reliable information regarding the micellization behavior of the surfactants before and after the formation of micelles. The concentration above which the surfactant changes its behavior in physical and spectral properties is known as critical micelle concentration (CMC).<sup>21a</sup> In the current study, we measured the CMC of pure dimeric [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br in an aqueous solution. The graph for conductance measurements concerning the concentration of aqueous pure [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br at 298.15 K is shown in Fig. 2.

Conductance measurements based on the Onsager theory of electrolyte conductivity revealed a change in slope between the pre- and post-micellar regions, indicating the formation of micelles. The intersection point of the two straight lines representing the critical micelle concentration (CMC) of the surfactants was also observed.<sup>21b</sup> The slope after reaching the CMC decreased, suggesting the presence of micelles. The determined CMC of pure [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br at 298.15 K was found to be 0.027 mM, which is in good agreement with the CMC of the dimeric surfactant [C<sub>16</sub>-C<sub>3</sub>-C<sub>16</sub>] (0.025 mM). Notably, the CMC of the pure dimeric [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br was much lower than that of the single-chain [C<sub>18</sub>-DABCO]Br surfactant (1.15 mM).<sup>22a</sup> This significant difference in CMC values may be attributed to the increased surface activity and enhanced hydrophobic–hydrophobic interactions observed in dimeric surfactants.<sup>22b</sup>

**(b) UV-Vis absorption study.** The dye-solubilization method is used for this study which works on the principle of the solution polarity. To study the micellar behavior of [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br in an aqueous solution we used methyl orange as an anionic dye (MO) for the UV-visible measurements due to the cationic nature of the surfactant.

The absorption spectra, obtained by plotting the absorbance *versus* wavelength, were recorded for aqueous solutions of MO dye with varying concentrations of [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br surfactant, as shown in Fig. 3. The absorption peak for pure MO dye (without the addition of surfactant) was observed at a wavelength of  $\lambda_{\text{max}}$  465 nm. Upon increasing the concentration of the surfactant, a noticeable shift in the absorption peak towards shorter wavelengths (hypsochromic shift or higher frequency) was observed. This shift can be attributed to the association of dye molecules with surfactant monomers, leading to a decrease in the local polarity around the dye molecules. In the micellar pseudo-phase, the dye molecules become solubilized, resulting in a decrease in absorbance. In the presence of the surfactant, the  $\lambda_{\text{max}}$  for the methyl orange dye shifted from 465 nm to 370 nm. This shift suggests that the dye molecules are either solubilized or incorporated into the core of the surfactant molecules. Additionally, the intensity of the absorption peak decreases as the concentration of the surfactant is increased. This intensity reduction may be attributed to interactions between the surfactant and dye molecules, specifically hydrophobic–hydrophobic interactions occurring between the dye and surfactant molecules.

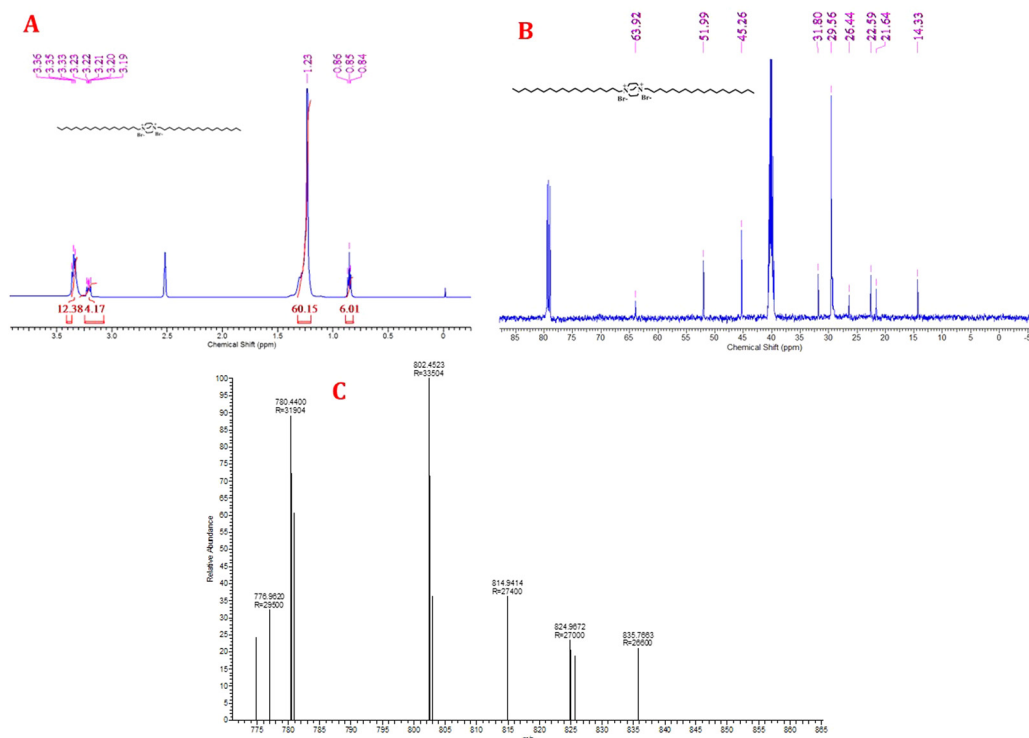


Fig. 1 Spectra of  $[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$ ; (A)  $^1\text{H}$  NMR, (B)  $^{13}\text{C}$  NMR and (C) HR-MS spectrum.

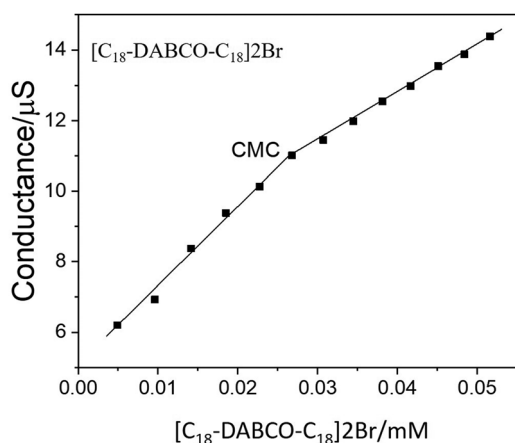


Fig. 2 Conductometric profile of pure  $[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$  in aqueous solution at 298.15 K.

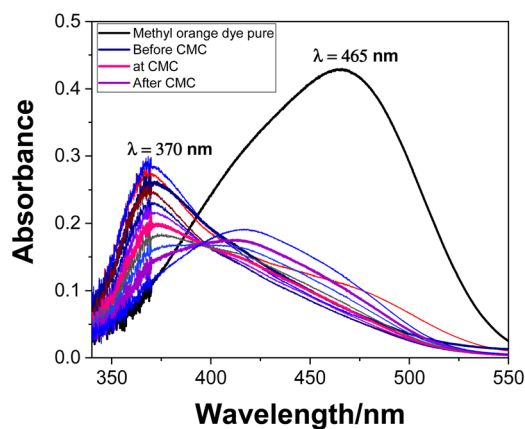


Fig. 3 The absorption spectra of methyl orange dye of pure  $[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$  in aqueous solution at 298.15 K. The  $c(\text{MO})$  is  $1.15 \times 10^{-4}$  M.

Fig. 4 illustrates the absorbance values obtained for different concentrations of pure  $[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$  in an aqueous solution at 298.15 K.

The CMC of  $[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$  was determined by identifying the intersection point of two lines. The CMC of  $[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$  was found to be 0.039 mM, which again approved with the reported literature value for the dimeric surfactant  $[C_{16}\text{-C}_3\text{-C}_{16}]$  (0.025 mM). Importantly, the CMC of the pure dimeric  $[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$  surfactant was significantly lower than that of the single-chain  $[C_{18}\text{-DABCO}]2\text{Br}$

surfactant (1.15 mM). This difference in CMC values can be attributed to the increased surface activity and enhanced hydrophobic-hydrophobic interactions observed in dimeric surfactants.<sup>23</sup>

At first, surfactant molecules are spread out in water. However, as the concentration of surfactant increases, the hydrophobic chains start interacting with each other, causing the surfactant molecules to form small clusters. These clusters are precursors to micelles, which are larger and well-defined. In micelles, the hydrophobic tails of the surfactant molecules are

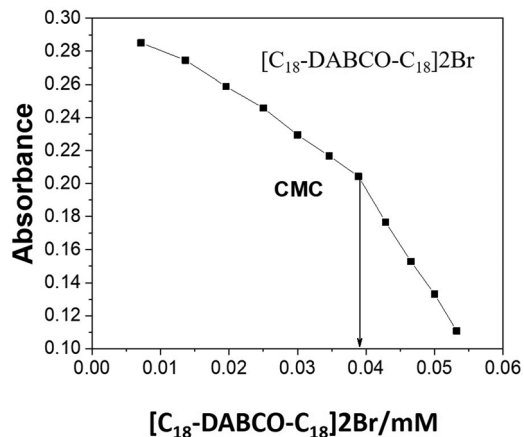


Fig. 4 Absorbance versus concentration of pure  $[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$  surfactants in aqueous solution at 298.15 K.

protected from the water, while the hydrophilic headgroups face the solvent, which makes the arrangement of surfactant molecules in the water a stable one. Micelles can effectively dissolve hydrophobic compounds, such as dye molecules, which results in a decrease in absorbance intensity. The micellization process is facilitated by the interactions between dye-surfactant and hydrophobic-hydrophobic compounds, which play significant roles in the formation and stability of micelles.

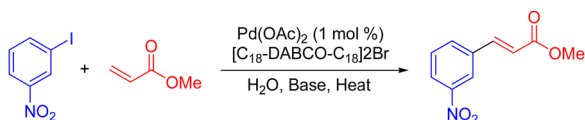
The CMC value by using the conductivity method is 0.025 mM and by UV-visible measurements is 0.039 mM. This may be due to that in UV-visible measurements we use methyl orange dye for CMC determination and due to the dye-surfactant interaction the CMC values are different by UV-visible measurements.

### 3. Applications of $\text{Pd}(\text{OAc})_2/[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$

**(a) Mizoroki-Heck coupling reactions.** The Mizoroki-Heck reaction, which was discovered in the early 1970s,<sup>24</sup> is a highly effective catalytic tool for developing carbon-carbon bonds. It has remarkable versatility in accommodating various functional groups.<sup>25</sup>

To optimize the reaction conditions, a model reaction was conducted using 3-nitro-iodobenzene and methyl acrylate in the presence of a  $\text{Pd}(\text{OAc})_2/[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$  catalytic system in water. (Scheme 2).

We used a simple *in situ* method to prepare colloidal PdNPs. First, we suspended  $\text{Pd}(\text{OAc})_2$  and  $[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$  in water and then reacted them with 3-nitro-iodobenzene and methyl acrylate in the presence of  $\text{K}_2\text{CO}_3$  as a base. Adding  $\text{Pd}(\text{OAc})_2$  directly to water caused the formation of



Scheme 2  $\text{Pd}(\text{OAc})_2/[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$  for the ligand-free Mizoroki-Heck coupling reaction.

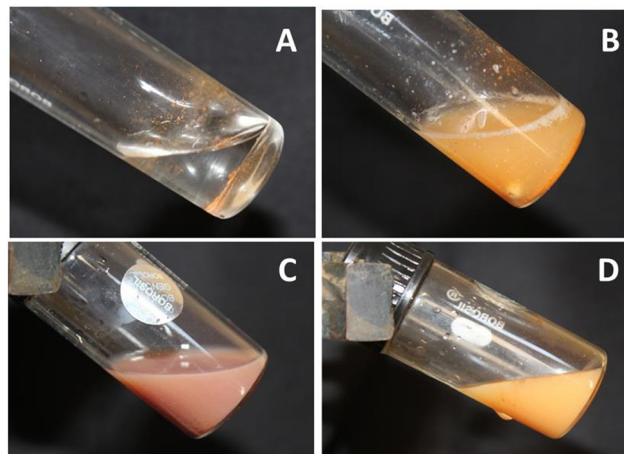


Fig. 5 Observations of reaction mixture: (A)  $\text{Pd}(\text{OAc})_2$  in neat water (heterogeneous appearance); (B)  $\text{Pd}(\text{OAc})_2/[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$  in water; (C) reaction mixture at  $t = 2$  min; and (D) aqueous phase containing catalyst after extraction of the product at  $t = 45$  min.

heterogeneous phases, making it insoluble. However, combining 1 mol%  $\text{Pd}(\text{OAc})_2$  with 10 mol%  $[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$  in water resulted in a stable dispersion with a yellow color (Fig. 5A and B). Stirring the reaction mixture at  $100^\circ\text{C}$  turned the solution into a wine-red color. This color change is likely due to the formation of colloidal PdNPs, stabilized by an excess of ammonium ions present in  $[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$ , as shown in Fig. 5C.<sup>26</sup>

The colloidal wine-red colored reaction mixture<sup>27</sup> was analyzed using TEM at various time intervals: (a) 2 minutes (Fig. 6A), (b) 30 minutes (Fig. 6B), and (c) 45 minutes (Fig. 6C) after the product was extracted. The TEM analysis clearly showed the uniform distribution of PdNPs, which had a particle size smaller than 5 nm.

The EDS spectrum of the PdNPs present in the reaction mixture after 2 min (Fig. 7) showed signals for Pd, which indicates the presence of substantial amounts of Pd in reaction mixture.

To study the change in oxidation states of Pd present in the reaction mixture the high-resolution XPS spectra (Fig. 8) of the Pd 3d were recorded after (a) 2 min, (b) 30 min, and (c) after extraction of the product (45 min) respectively. The XPS spectrum displayed two peaks with binding energies at 336.2 eV and 341.5 eV, corresponding to Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub>. The spin-orbit coupling results in a binding energy (B.E) difference of 5.2 eV between the Pd 3d<sub>5/2</sub> and 3d<sub>3/2</sub> orbitals attributed to the spin-orbit interaction. The observed binding energy (B.E) values for Pd (336.2 eV) do not precisely correspond to the B.E value for Pd<sup>0</sup> (335.1 eV), suggesting that the oxidation state of Pd falls within the range of 0 to +2 in all three samples.<sup>28,29</sup>

The impact of the quantity of  $[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$  was examined in controlled experiments. No conversion was observed when the reaction was initiated without the use of  $[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$ , even after extending the reaction time for 120 minutes (Table 1, entry 1). However, the addition of  $[C_{18}\text{-DABCO-}C_{18}]2\text{Br}$  (1 to 10 mol%) resulted in a consistent

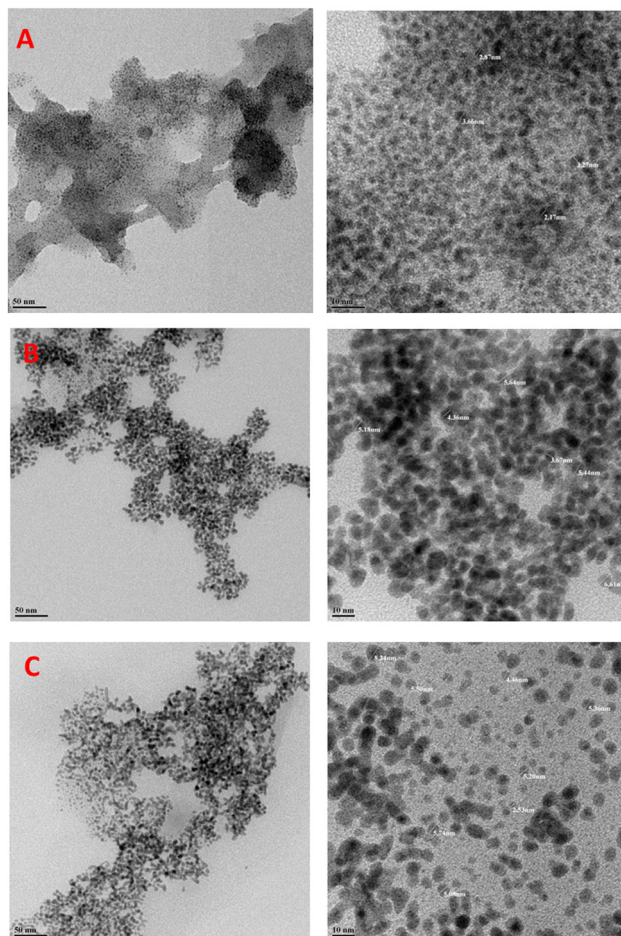


Fig. 6 TEM images of reaction mixture; (A) after 2 min, (B) after 30 min, and (C) after 45 min.

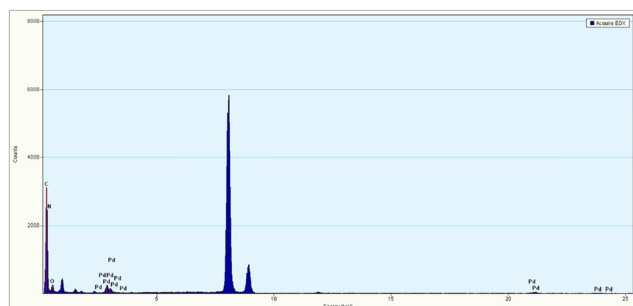


Fig. 7 EDX spectrum of reaction mixture after 2 min.

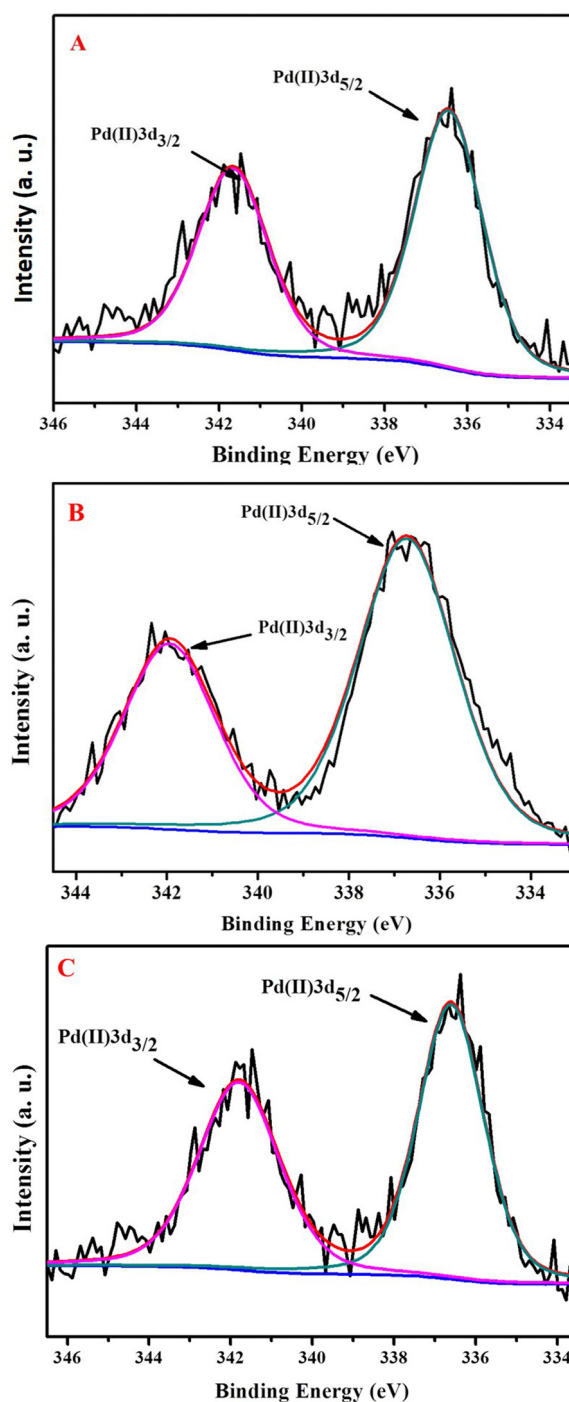


Fig. 8 XPS analysis of reaction mixture; (a) after 2 min, (b) after 30 min, and (c) after 45 min (extraction of product).

increase in the yield, up to 94% after 45 min (Table 1, entries 2–4). In general, using 10 mol% of  $[C_{18}\text{-DABCO-C}_{18}]_2\text{Br}$  in pure water was adequate to achieve satisfactory conversions, while increasing the concentration to 15 mol% did not significantly improve the yield under otherwise identical conditions (Table 1, entry 5). Interestingly, the *trans* selectivity increased from 92% to 96% as the quantity of  $[C_{18}\text{-DABCO-C}_{18}]_2\text{Br}$  increased from 1 mol% to 5 mol% (Table 1, entry 2 and 3),

but later increases in the quantity only marginally affected the selectivity (Table 1, entry 4 and 5).

Different bases and amounts of  $K_2CO_3$  were tested in a model reaction. No product was observed when no base was used (Table 1, entry 6). The use of 1 mmol of  $K_2CO_3$  gave the highest yield (Table 1, entry 4). Increasing the amount of  $K_2CO_3$  did not improve the yield or reaction time (Table 1, entry 8). Among the tested bases,  $K_2CO_3$  was the most effective in

Table 1 The effect of [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br and base in Mizoroki-Heck coupling reaction<sup>a</sup>

Entry	[C <sub>18</sub> -DABCO-C <sub>18</sub> ]2Br (mol%)	Base (mmol)	Time (min)	Yield <sup>b</sup> (%)	TON	TOF (min <sup>-1</sup> )	Selectivity <sup>c</sup> (%)	
							<i>E</i>	<i>Z</i>
1	—	K <sub>2</sub> CO <sub>3</sub> (1.0)	45	Trace	—	—	—	—
2	1	K <sub>2</sub> CO <sub>3</sub> (1.0)	45	81	80.67	1.792	92	8
3	5	K <sub>2</sub> CO <sub>3</sub> (1.0)	45	81	80.67	1.792	96	4
4	10	K <sub>2</sub> CO <sub>3</sub> (1.0)	45	94	93.71	2.082	96	4
5	15	K <sub>2</sub> CO <sub>3</sub> (1.0)	45	94	93.71	2.082	97	3
6	10	Base-free	120	—	—	—	—	—
7	10	K <sub>2</sub> CO <sub>3</sub> (0.5)	120	45	44.92	0.374	94	6
8	10	K <sub>2</sub> CO <sub>3</sub> (1.5)	45	94	93.71	2.082	97	3
9	10	NaOAc (1.0)	120	56	55.55	0.462	96	4
10	10	KOH (1.0)	120	70	69.56	0.579	99	1

<sup>a</sup> All the reactions were carried out using 3-nitro-iodobenzene (1.0 mmol), methyl acrylate (1.10 mmol), base (1–1.5 mmol), Pd(OAc)<sub>2</sub> (1 mol%), [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br (1–10 mol%) in water (5.0 mL) at 100 °C under air. <sup>b</sup> By HPLC. <sup>c</sup> By HPLC.

activating the reactant. However, NaOAc was highly inactive, resulting in only 46% conversion even after 120 minutes of reaction time (Table 1, entry 9). Although KOH showed a lower yield (70%) and longer reaction time (120 min), it exhibited the highest selectivity (99% *E*-isomer) (Table 1, entry 10). K<sub>3</sub>PO<sub>4</sub> showed good yield (85%) but the lowest selectivity (89% *E*-isomer) among the tested bases (Table 1, entry 11).

In a study on Mizoroki-Heck coupling reactions,<sup>30</sup> the impact of temperature was investigated by maintaining the ratio of Pd(OAc)<sub>2</sub>/[C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br (1 : 10 mol%) constant with K<sub>2</sub>CO<sub>3</sub> as a base in water at four different temperatures. The results showed that temperature played a crucial role in catalyst activation, as no reaction was observed at 60 and 80 °C (Table 2, entries 1 and 2). However, at 100 °C, an excellent conversion was achieved within 45 minutes (Table 2, entry 3). Further increasing the temperature to 120 °C did not result in significant improvements in yield or selectivity (Table 2, entry 4).

The impact of the amount of Pd(OAc)<sub>2</sub> was examined by maintaining the amount of [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br at 10 mol% and reaction temperature at 100 °C. The results showed that 1.0 mol% of Pd(OAc)<sub>2</sub> was highly efficient, providing almost complete conversion with consistent selectivity. Though the maximum Turnover Number (TON) 115.94 was obtained for 0.5 mol% Pd(OAc)<sub>2</sub> (Table 2, entries 5), 1 mol% Pd(OAc)<sub>2</sub> was found to be best in terms of product yield (Table 2, entries 3).

Thus, 1 mol% Pd(OAc)<sub>2</sub>, 1 mmol K<sub>2</sub>CO<sub>3</sub>, and 10 mol% [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br in water at 100 °C is considered as optimum reaction condition for exploration of next study.

To showcase the versatility and wide applicability of the developed protocol, different aryl halides were subjected to coupling reactions with various acrylates under optimized reaction conditions. The reaction conditions were as follows: aryl halides (1.0 mmol), acrylates (1.1 mmol), K<sub>2</sub>CO<sub>3</sub> (1.0 mmol), Pd(OAc)<sub>2</sub> (1 mol%), [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br (10 mol%), water (5.0 mL) at 100 °C. The desired products were obtained with good to excellent yields and showed high selectivity. Substrates that contained electron-donating groups exhibited slightly lower yields, which could be improved by extending the reaction time.<sup>31</sup> Additionally, it was observed that aryl iodides displayed higher reactivity compared to aryl bromides. Notably, the para-substituted compounds consistently yielded almost 100% of the *E*-isomer (Table 3).

**(b) Suzuki-Miyaura coupling reactions.** The successful outcomes achieved through Mizoroki-Heck coupling reactions motivated us to extend the applicability of the developed catalytic system to Suzuki-Miyaura coupling reactions. Suzuki-Miyaura coupling reaction is widely known for its efficiency in carbon-carbon bond formation and compatibility with different functional groups.<sup>32,33</sup> In this study, we explored the potential of our protocol for the Suzuki-Miyaura coupling reaction using various aryl iodides and bromides with aryl boronic acids in an aqueous environment with K<sub>2</sub>CO<sub>3</sub> as the

Table 2 The influence of temperature and amount of catalyst in the Mizoroki-Heck reaction<sup>a</sup>

Entry	Pd(OAc) <sub>2</sub> (mol%)	Temperature (°C)	Time (min)	Yield <sup>b</sup> (%)	TON	TOF	Selectivity <sup>c</sup> (%)	
							<i>E</i>	<i>Z</i>
1	1.0	60	120	—	—	—	—	—
2	1.0	80	120	—	—	—	—	—
3	1.0	100	45	94	93.71	2.082	89	97
4	1.0	120	45	94	93.71	2.082	90	96
5	0.5	100	60	58	115.94	1.932	58	98
6	1.0	100	45	89	88.88	1.975	89	96
7	2.0	100	45	95	47.34	1.052	91	95

<sup>a</sup> All the reactions were carried out using 3-nitro-iodobenzene (1.0 mmol), methyl acrylate (1.1 mmol), K<sub>2</sub>CO<sub>3</sub> (1.0 mmol), Pd(OAc)<sub>2</sub> (1 mol%), [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br (10 mol%) in water (5.0 mL) at 60–120 °C under air. <sup>b</sup> By HPLC. <sup>c</sup> By HPLC.

Table 3 A substrate scope for Mizoroki–Heck reaction using Pd(OAc)<sub>2</sub>/[C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br<sup>a</sup>

X = Br and I

Entry	Aryl halides	Products	Time (min)	Yield <sup>b</sup> (%)	TON	TOF (min <sup>-1</sup> )	E/Z <sup>c</sup>
1			50	92	91.85	1.837	100/0
2			45	93	92.67	2.059	100/0
3			65	80	79.72	1.226	100/0
4			65	82	81.63	1.255	100/0
5			50	91	90.82	1.816	100/0
6			60	83	82.63	1.377	100/0
7			50	90	89.83	1.796	100/0
8			65	85	85.00	1.307	100/0
9			60	89	88.96	1.482	100/0
10			50	93	92.77	1.855	88/12
11			90	90	89.74	0.997	88/12
12			80	88	87.61	1.095	100/0
13			80	87	86.66	1.083	100/0

<sup>a</sup> All the reactions were carried out using aryl halides (1.0 mmol), acrylates (1.1 mmol), K<sub>2</sub>CO<sub>3</sub> (1.0 mmol), Pd(OAc)<sub>2</sub> (1 mol%), [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br (10 mol%) in water (5.0 mL) at 100 °C under air. <sup>b</sup> Isolated yield. <sup>c</sup> By HPLC.

base, in Pd(OAc)<sub>2</sub>/[C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br catalyst at 80 °C. The results, presented in Table 4, demonstrate that all tested substrates could be easily converted into the expected products with yields ranging from 80% to 95%, achieved within a reaction time of 30 to 60 minutes.

### Recycling study

The lifetime and reusability of a catalyst are essential for its practical applications. To evaluate the recyclability of the Pd(OAc)<sub>2</sub>/[C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br system, consecutive Mizoroki–Heck coupling reactions were carried out using 3-nitro-

Table 4 Scope of Pd(OAc)<sub>2</sub>/[C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br catalytic system for Suzuki–Miyaura coupling reaction<sup>a</sup>

X = Br and I

Entry	Aryl halides	Arylboronic acids	Products	Time (min)	Yield <sup>b</sup> (%)	TON	TOF (min <sup>-1</sup> )
1				30	95	94.84	3.161
2				45	90	89.89	1.997
3				45	91	90.64	2.014
4				40	88	87.91	2.197
5				35	87	86.86	2.481
6				35	90	89.88	2.568
7				40	92	91.54	2.288
8				30	93	92.91	3.097
9				45	90	89.82	1.996
10				40	91	90.88	2.272

<sup>a</sup> All the reactions were carried out using aryl halides (1.0 mmol), aryl boronic acids (1.1 mmol), K<sub>2</sub>CO<sub>3</sub> (2.0 mmol), Pd(OAc)<sub>2</sub> (1 mol%), [C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br (10 mol%) in water (5.0 mL) at 80 °C under air. <sup>b</sup> Isolated yield.



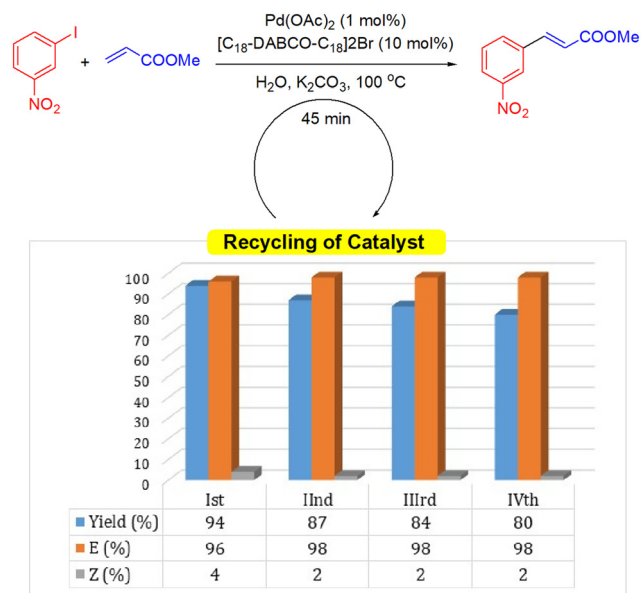


Fig. 9 Recycling of catalytic system for Mizoroki–Heck coupling reaction.

iodobenzene and methyl acrylate. After the fresh reaction product was separated from the reaction mixture with ethyl acetate extraction, the aqueous phase containing the catalyst was used for the subsequent reaction cycle without any additional treatment. The catalytic system could be effectively recovered and reused for at least three cycles, with a decrease in product yields from 94–80%, which could be attributed to the handling loss of the catalysts. However, the *E/Z* selectivity was not significantly impacted (Fig. 9).

## Conclusion

Conclusively, our study successfully demonstrated the synthesis and characterization of a novel Gemini-type diquatized DABCO surfactant which further stabilized PdNPs as depicted in TEM and XPS studies and designated as Pd(OAc)<sub>2</sub>/[C<sub>18</sub>-DABCO-C<sub>18</sub>]2Br. The catalytic system provides a straightforward and efficient approach for synthesizing diversely functionalized acrylates through ligand-free Mizoroki–Heck cross-coupling reactions in an aqueous medium at 100 °C. Additionally, we also demonstrated the effectiveness of this method for ligand-free Suzuki–Miyaura cross-coupling reactions under similar reaction conditions. The Mizoroki–Heck reactions exhibited remarkable Turnover Numbers (TON) ranging from 79.72 to 92.77, and Turnover Frequencies (TOF) ranging from 0.997 to 2.059 min<sup>-1</sup>. Similarly, the Suzuki–Miyaura reactions displayed TON values of 86.86 to 94.84 and TOF values of 1.996 to 3.161 min<sup>-1</sup>. This methodology offers notable environmental advantages, including shorter reaction times, mild reaction conditions, high product yields, excellent selectivity, and operational simplicity. Furthermore, the catalytic system showcased reusability for at least four runs, although with slightly decreased product yields while maintaining selectivity. This research contributes to the development of efficient

and sustainable catalytic systems and provides promising avenues for future applications.

## Data availability statement

The data that support the findings of this study are available in the supporting information of this article.

## Author contributions

Archana Rajmane: study conception and design, data collection, experimental work and designing of manuscript; Chunilal Pawara: data characterization and analysis; Sumit Kamble: data characterization and analysis; Utkarsh More: physical study; Suresh Patil: project co-supervisor; Arjun Kumbhar: project supervisor.

## Conflicts of interest

There are no conflicts to declare.

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