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# Pd-Colloids catalyzed/$Ag_2O$ Oxidized General and Selective Esterification of Benzylic Alcohols

Vaibhav Sable[a]+,Jagrut Shah[a]+,Anuja Sharma[a], Anant R. Kapdi[a],*

**Abstract:**.Palladium colloids obtained from the degradation of Hermann-Beller palladacycle proved to be an efficient catalytic system in combination with silver oxide as a selective oxidant for the oxidative esterification of differently substituted benzyl alcohols in MeOH as solvent. Excellent reactivity exhibited by the catalytic system also allowed the alcoholic coupling partner to be changed from MeOH to a wide range of alcohols having diverse functionalities. The mildness of the developed protocol also made it possible to employ propargyl alcohol as the coupling partner without any observation of any interference of the terminal alkyne. Selective oxidative coupling of a primary alcoholic functional group over secondary in the case of glycols and glycerols was also made possible using the developed catalyst system. To test the relevancy of Pd/Ag combined catalysis mixed Pd/Ag colloids were synthesized, characterized by TEM, XRD and XPS and applied to oxidative-esterification successfully.

Aromatic esters are important synthetic substrates with applications ranging from flavourants, fragrants, solvents, cosmetics, intermediates as well as medicinal compounds.[1,2]Some of the representative examples of commercially relevant aromatic esters have been provided in **Figure 1**, exhibiting marzipan smell (methyl benzoate), strawberry flavor (methyl cinnamate), rose flavor (geranyl 4-nitrobenzoate), banana flavour (butyl benzoate) and the famous Iodex smell (oil of winter green- methyl 2-salicylate). Traditional methods of synthesis of esters have long been replaced by the more efficient and selective processes involving the use of coupling reagents[3], organo-catalysts[4,5], lewis-acid catalysts[6,7], ionic liquids[8]as well as transition metal catalysts. Amongst these methods, transition metal-catalyzed oxidative esterification has played a pivotal role in providing an efficient and mild synthetic strategy for obtaining these diverse structural motifs.[9–24] Earliest example for the oxidative esterification of primary alcohols was reported by Milstein and co-workers using ruthenium-based catalytic system,[25] thus providing the required impetus to the research community for further exploration. This was followed by a series of reports involving transition metal catalyzed oxidative esterification of alcohols to give dimeric esters.[26–29] Oxidation of benzylic alcohols was difficult since they tend to oxidize to benzaldehydes and the aliphatic alcohols to dimeric esters. Lei and co-workers achieved dimeric esterification of benzyl alcohols using Pd in the absence of other aliphatic alcohol.[30] Earlier, oxidative esterification of two different alcohols was obscure as both the alcohols could oxidize. Methanol is difficult to get oxidized and hence, researchers started reporting methyl ester synthesis from benzyl alcohols by transition metal catalyzed hydrogen transfer approach.[31]In 2011, Beller and Lei concurrently and independently reported Pd-catalyzed oxygen mediated oxidative esterification of benzyl alcohols[32,33] (using a few long-chain aliphatic alcohols too). Based on these early results, many groups reported similar oxidative esterification of benzylic alcohols. However, the reports had drawbacks, which majorly included, limited substrate scope, use of bulky ligands, harsh reaction conditions, etc. Recently, Stahl and co-workers, in 2018, have reported mechanistic insights on heterogeneous oxidative esterification of benzyl alcohols and methanol[34]. Aerobic alcohol oxidation reactions that use heterogeneous Pd[35] and Pt[36]catalysts containing promoters have been the subject of considerable investigation, commonly focusing on the oxidation of sugars and other primary alcohols to carboxylic acids under aqueous conditions.[37–39] Most of the reports have reported the use of air or oxygen as an oxidant.[35] Herein, we show a heterobimetallic system featuring Pd and Ag working synergistically in oxidation of benzyl alcohols as well as promoting final esterification step.

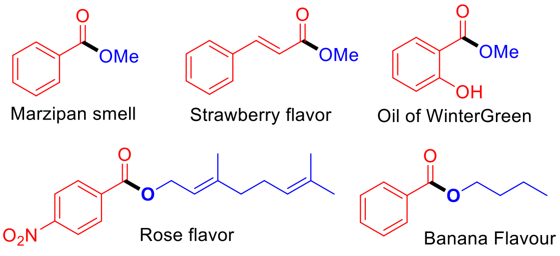

**Figure 1**: Aromatic esters of commercial importance.

The importance of developing an efficient synthetic procedure for esterification beyond conventional methods is a challenging task for researchers, however, it also allows them to explore different and unique substrate combinations. The success related to these types of explorations necessarily depends on the nature of the catalyst employed and the selectivity exhibited towards the respective process. In comparison to commonly employed homogeneous or heterogeneous catalysts, nano or colloidal metal catalysts are ever more clearly evidencing enhanced reactivity and selectivity.[40–42]

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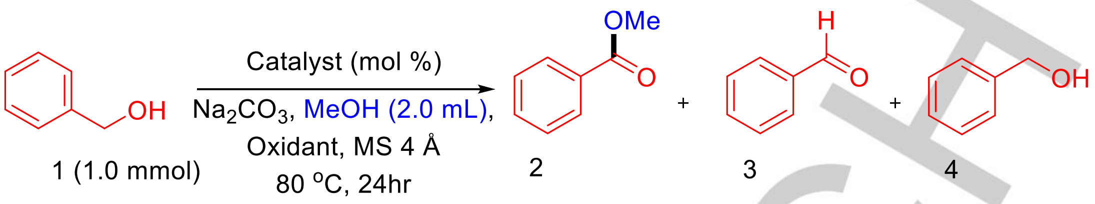
**Table 1**: Screening studies for the oxidative esterification of benzyl alcohols.



| No. | Catalyst/Ligand | Cat/Lig(mol %) | Oxidant | Base | Temp °C | Time | Conversion | 2 (%)[a] | 3 (%)[a] | 4(%)[a] |
|---|---|---|---|---|---|---|---|---|---|---|
| **Catalyst Screening** | | | | | | | | | | |
| 1 | $Pd(OAc)_2$ | 0.0 | $O_2$ | $Na_2CO_3$ | 80 | 24 | 10 | 0 | 10 | 90 |
| 2 | $Pd(OAc)_2$ | 2.5 | $O_2$ | $Na_2CO_3$ | 80 | 24 | 35 | 10 | 25 | 65 |
| 3 | $Pd(OAc)_2$ | 5.0 | $O_2$ | $Na_2CO_3$ | 80 | 24 | 35 | 10 | 25 | 65 |
| **Catalyst Study** | | | | | | | | | | |
| 4 | $Pd(OAc)_2$/ $PPh_3$ | 2.5/5.0 | $O_2$ | $Na_2CO_3$ | 80 | 24 | 25 | 10 | 15 | 75 |
| 5 | $Pd(OAc)_2$/ P(o-Tol)$_3$ | 2.5/5.0 | $O_2$ | $Na_2CO_3$ | 80 | 24 | 45 | 25 | 15 | 60 |
| 6 | $Pd(OAc)_2$/[BMIM]HCl | 2.5/5.0 | $O_2$ | $Na_2CO_3$ | 80 | 24 | 10 | 0 | 10 | 90 |
| 7 | $Pd(OAc)_2$/1,10-phenanthroline | 2.5/5.0 | $O_2$ | $Na_2CO_3$ | 80 | 24 | 0 | 0 | 0 | 100 |
| 8 | $Pd(OAc)_2$/ IMes.HCl | 2.5/2.5 | $O_2$ | $Na_2CO_3$ | 80 | 24 | 0 | 0 | 0 | 100 |
| 9 | $Pd(OAc)_2$/ Ipr.HCl | 2.5/2.5 | $O_2$ | $Na_2CO_3$ | 80 | 24 | 0 | 0 | 0 | 100 |
| 10 | H-B complex | 2.5 | $O_2$ | $Na_2CO_3$ | 80 | 24 | 45 | 25 | 15 | 60 |
| 11 | Pd/C | 5.0 | $O_2$ | $Na_2CO_3$ | 80 | 24 | 5 | 5 | 0 | 95 |
| **12** | **Pd colloids** | **0.32 (10 mg)**[43] | $O_2$ | **$Na_2CO_3$** | **80** | **24** | **50** | **30** | **20** | **50** |
| 13 | Nano $Fe_2O_3$ | 5.0 | $O_2$ | $Na_2CO_3$ | 80 | 24 | 30 | 10 | 20 | 70 |
| **Base Study** | | | | | | | | | | |
| **14** | **Pd colloids** | **0.32** | $O_2$ | **$Na_2CO_3$** | **80** | **24** | **50** | **30** | **20** | **50** |
| 15 | Pd colloids | 0.32 | $O_2$ | $K_2CO_3$ | 80 | 24 | 35 | 10 | 25 | 65 |
| 16 | Pd colloids | 0.32 | $O_2$ | $Cs_2CO_3$ | 80 | 24 | 10 | 0 | 10 | 90 |
| 17 | Pd colloids | 0.32 | $O_2$ | NaOMe | 80 | 24 | 45 | 25 | 20 | 55 |
| 18 | Pd colloids | 0.32 | $O_2$ | DMAP | 80 | 24 | 35 | 20 | 15 | 65 |
| 19 | Pd colloids | 0.32 | $O_2$ | NaOtBu | 80 | 24 | 0 | 0 | 0 | 100 |
| 20 | Pd colloids | 0.32 | $O_2$ | $N(C_2H_5)_3$ | 80 | 24 | 0 | 0 | 0 | 100 |
| **Temperature Study** | | | | | | | | | | |
| 21 | Pd colloids | 0.32 | $O_2$ | $Na_2CO_3$ | 30 | 24 | 0 | 0 | 0 | 100 |
| 22 | Pd colloids | 0.32 | $O_2$ | $Na_2CO_3$ | 50 | 24 | 25 | 10 | 15 | 75 |
| **23** | **Pd colloids** | **0.32** | $O_2$ | **$Na_2CO_3$** | **80** | **24** | **50** | **30** | **20** | **50** |
| 24 | Pd colloids | 0.32 | $O_2$ | $Na_2CO_3$ | 100 | 24 | 35 | 0 | 35 | 65 |
| 25 | Pd colloids | 0.32 | $O_2$ | $Na_2CO_3$ | 140 | 24 | 0 | 0 | 0 | 100 |
| **Reaction Duration Study** | | | | | | | | | | |
| 26 | Pd colloids | 0.32 | $O_2$ | $Na_2CO_3$ | 80 | 12 | 30 | 10 | 20 | 70 |
| 27 | Pd colloids | 0.32 | $O_2$ | $Na_2CO_3$ | 80 | 24 | 50 | 30 | 20 | 50 |
| 28 | Pd colloids | 0.32 | $O_2$ | $Na_2CO_3$ | 80 | 36 | 80 | 45 | 35 | 20 |
| **29** | **Pd colloids** | **0.32** | $O_2$ | **$Na_2CO_3$** | **80** | **48** | **90** | **50** | **40** | **10** |
| **Oxidant** | | | | | | | | | | |
| 30 | Pd colloids | 0.32 | $N_2$ | $Na_2CO_3$ | 80 | 48 | 0 | 0 | 0 | 100 |
| 31 | Pd colloids | 0.32 | $O_2$ | $Na_2CO_3$ | 80 | 48 | 90 | 50 | 40 | 10 |
| 32 | Pd colloids | 0.32 | TBHP | $Na_2CO_3$ | 80 | 48 | 85 | 55 | 30 | 15 |
| 33 | Pd colloids | 0.32 | $MnO_2$ | $Na_2CO_3$ | 80 | 48 | 50 | 5 | 45 | 50 |
| **34** | **Pd colloids** | **0.32** | **$Ag_2O$** | **$Na_2CO_3$** | **80** | **48** | **100** | **<99** | **0** | **0** |
| 35 | Pd colloids | 0.32 | Air | $Na_2CO_3$ | 80 | 48 | 15 | 0 | 15 | 85 |
| 36 | Pd colloids | 0.32 | NBS | $Na_2CO_3$ | 80 | 48 | 0 | 0 | 0 | 100 |
| 37 | Pd colloids | 0.32 | $H_2O_2$ | $Na_2CO_3$ | 80 | 48 | 100 | 0 | 65 | 0 |

[a] GCMS yields

Several factors such as surface composition and surface stabilization of the nanoparticles/colloidal particles, morphology of the nanoparticles as well as their sizes are key contributors to their unparalleled reactivity.[44–46] Fine tuning these factors should allow the development of superior, more efficient catalytic technologies for C–C bond formation processes. One contribution to the development of novel C–C bond forming technologies using active palladium colloidal catalysts from our

10.1002/asia.201900566

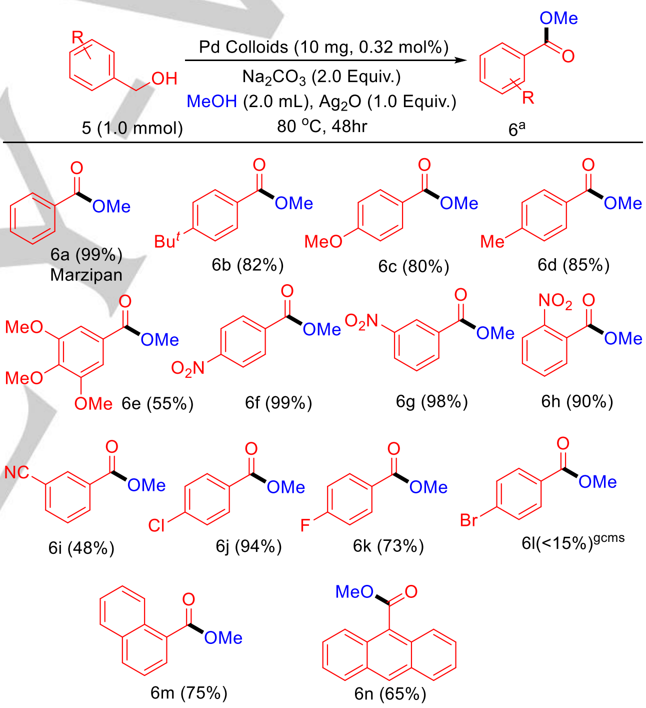
group was published covering the efficient homocoupling and heterocoupling of arylboronic acids. The isolation and the complete characterization of the synthesized palladium colloidal catalyst was possible by utilizing techniques such as TEM, HRTEM, XRD, XPS, EDS and EXAFS.[43,47]

Oxidative esterification of benzyl alcohols employing metal nanoparticles (MNPs) has been well-known for the past several years[48].Although the MNPs employed were usually expensive such as Au[18,49–52] and Ag,[53] they were also supported on certain frameworks[54,55] thereby leading to a tedious synthetic route for the preparation of these catalystsand making the reproducibility of protocol relatively difficult for other researchers. These protocols also usually faced shortcomings in terms of the limited substrate scopeexhibited in such reports as most of them dealt only with the synthesis of methyl benzoates. Hence, with a deliberate attempt to expand the substrate scope to esters beyond methyl counterparts as well as showing unprecedented chemoselectivity, we report herein a much-improvedprotocol forthe oxidative esterification of benzyl alcohols.

At the outset of our studies, conditions for the esterification of benzyl alcohol were optimized by varying the respective parameters including the screening of different catalyst systems for comparison (Table 1). The optimization studies were performed with benzyl alcohol and methanol (2.0 mL of MeOH for 1.0 mmol of benzyl alcohol) as model substrates with $O_2$ balloon, as abundantly available oxidant, and with twice the amount of base ($Na_2CO_3$) at 80 ºC for 24h and added molecular sieves 4 Å for mopping-up the water formed.GC-MS was used to calculate yields in optimization studies. Without the addition of any metal catalyst or catalyst precursor the reaction failed to proceed (**Entry 1, Table 1**). $Pd(OAc)_2$ with increasing mol% (2.5 mol% and 5.0 mol%) as a ligand-free system[56–60] yielded low conversions of the desired products (**Entries 2 & 3, Table 1**). Meanwhile, the detection of benzaldehyde (by GC-MS) provides us vital evidence about the possibility of the catalytic reaction proceeding *via* theoxidation of benzyl alcohol to aldehyde eventually formingthe esterification product. Addition of phosphines as activating ligands, especially $P(o\text{-}Tol)_3$, accelerated the formation of the desired product upto a certain extent, although still in poor yield (**Entries 4 & 5, Table 1**). Poor results were obtained when other commercially available ligands such as 1,10-phenanthroline, IMes.HCl or IPr.HCl were employed (**Entries 6-9, Table 1**). Hermann-Beller Pd-dimer complex further enhanced the formation of the ester product (**Entry 10, Table1**). However, employing the synthesized palladium colloids resulted in an improved selectivity for the formation of ester. Nonetheless, the starting material was still unreacted to a large extent, but, the formation of aldehyde was decreased (**Entry 11, Table1**).

Next, we turned our attention to analyze the effect of base employed as the optimization studiesrevealedthat the use of $Na_2CO_3$ was necessary for providing an optimum yield of the product(**Entry 14, Table 1**) in comparison to other bases (**Entry 15-20, Table 1**).Any change in temperature failed to increase the yield of the ester product as 80 ºC was found to be the most suitable (**Entry 23, Table 1**). Improvement in yield was observed with an increase in reaction time to 36 h (**Entry 28, Table 1**) and further to 48 h (**Entry 29, Table 1**).

All the above results provide an important insight into the role of an efficient oxidant that could bring about smooth conversion of benzyl alcohol to benzaldehydethat is helpful in providing the desired ester. This further was confirmed by performing the catalytic oxidative esterification without an oxidant under inert conditions with nitrogen gas as the complete receovery of benzyl alcohol was observed (**Entry 30, Table 1**). Keeping this in mind, we evaulated the influence of different oxidants on the catalytic esterification. Out of many oxiadants used, only TBHP and $MnO_2$ furnished the desired product (**Entries 32 & 33, Table 1**). Finally, employing silver oxide ($Ag_2O$)as an oxidant providedexcellent yield of the desired ester, which is based on the efficient oxidation of the benzyl alcohol to benzaldehyde (**Entry 34, Table 1**). Improved reactivity brought about by the intrroduction of $Ag_2O$ in the presence of palladium colloids could be due to the synergistic effect exerted by the two metals.



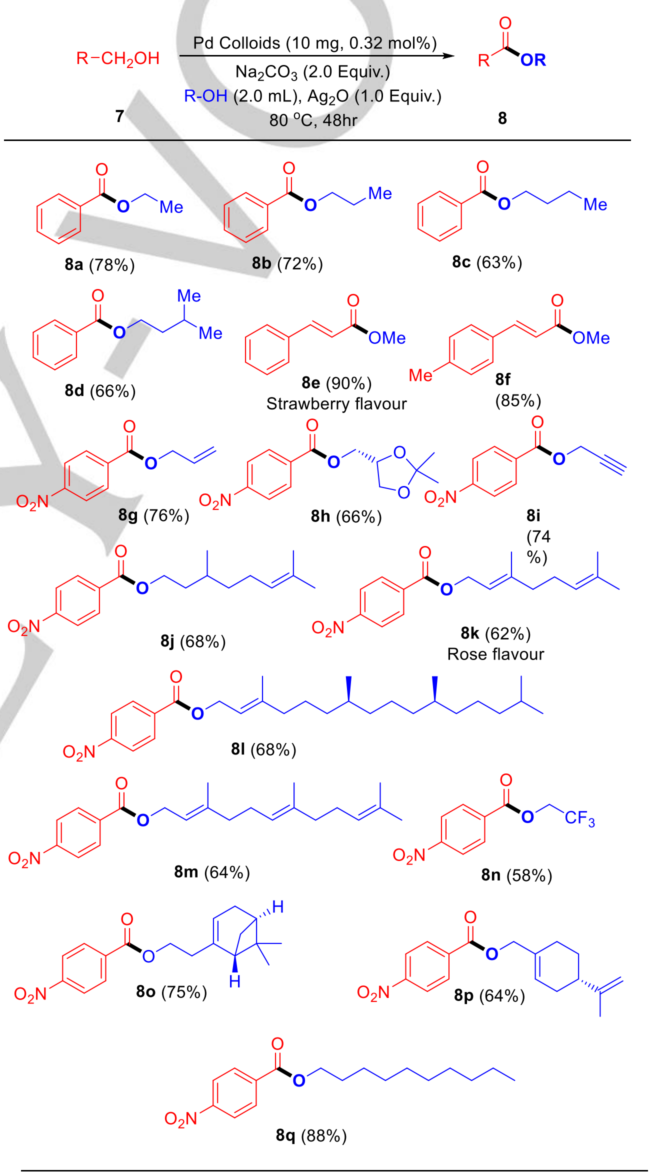
a Isolated Yields except 6l

**Scheme 1: Substrate Scope For Methyl Esters.**

With the establishment of an efficient protocol for oxidative esterification of benzyl alcohols using palladium colloids, we decided to investigate the generality of the reaction by carrying out esterification reactions using methanol and varying the substituents on the benzyl alcohol (**Scheme 1**). Electronically poor or rich benzyl alcohols, when added to the catalyst system followed by addition of methanol, provides good yields of the ester product suggesting a negligible influence on the reactivity.

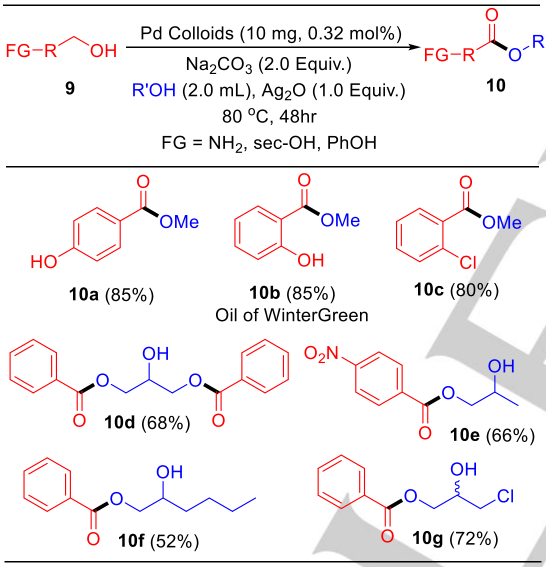
The employment of 3- or 4- nitrophenyl, 4-chlorobenzyl,and 4-fluoro benzyl alcohols as the electron-poor benzyl alcohol coupling partners were effective in providing the desired ester products. Also, a variety of electron-rich benzyl alcohols were employed to provide in most cases good to high yields of the desired products, thus highlighting the potential of the developed esterification protocol. Oxidative esterification of trimethoxy benzyl alchol gave corresponding product, which has aflatoxin production inhibitory activities[61] (**entry 6e**) Esterification of naphthalen-1-ylmethanol, as well as anthracen-1-ylmethanol, was also carried out without much difference in reactivity. These substrates are generally less reactive than simpler benzyl alcohols as well as provide steric hindrance but the developed catalytic protocol provides no such limitations.

As shown in **Scheme 1**, it was established that there is ample scope for the oxidative esterification of benzyl alcohols with methanol using the developed catalytic system. Next the attention was turned to the non-methanolic aliphatic alcohols (**Scheme 2**). These substrates in most cases are less reactive for oxidative esterification as they promote self esterification of the benzyl alcohol (benzyl benzoate), while long chain alcohols as substrates are also prone to undergo cyclization[62–64]. However, in spite of these limitations, it was our endevourtotest oxidative esterification of aliphatic alcohols other than methanol. To investigate such a possibility, we first replaced methanol with ethanol as the coupling partner in combination with benzyl alcohol. Successful conversion to the desired ethyl benzoate (**entry 8a**), which is a pharmaceutically relevant as well as is a flavorant, we further carried out reactions with other simple medium chain-length aliphatic alcohols like butanol (corresponding product being banana flavour food additive – **8c**) as well as isoamyl alcohol (**8d**) giving good to high yields of the esterification products. The catalytic esterification protocol was further extended to vinyl alcohol such as cinnamyl alcohol giving high yields with one of the product, methyl cinnamate useful commercially as a component of strawberry flavour (**8e-8f,Scheme 2**).
Next, to exhibit proficiency of the developed protocol for complex structures, we employed the protocol for the oxidative esterification of 4-nitrobenzyl alcohol. Presence of reactive functional groups that could interfere with the esterficiation reaction providing undesired byproducts were next to be tested.Ally alcohol, as well as propagyl alcohol both providing good yields of the esterification product under the developed conditions, reiterate the mild and selective nature of the palladium colloid/$Ag_2O$ systemas the terminal alkene or alkyne functionality did not interfere[65,66] with the ester formation process. We also employed a hetero-alicyclic alcohol which furnished moderate yield of the corresponding ester (**8h**) Naturally occurring long chain aliphatic unsaturated alcohols such as citronellol, geraniol, phytol and farnesol were next to be introduced to further enhance the appeal of the catalytic process. The corresponding esters, which were obtained in decent yields had pleasant odour with one particularly (**geranyl ester 8k, Scheme 2**)exhibiting rose-like flavour that has found commercial application is flavour and food industry.
Furthermore,alicyclic chiral alcohols were employed. The reaction furnished desired products in good yields (**8o-p**) without racemization owing to the mild reaction conditions under which catalytic esterification is conducted.We also employs fluorinated alcohol(trifluoro ethanol)also provided the corresponding ester in moderated yield (**8n**).Such a synthetic strategy could prove to be highly useful as trifluoroethanol esters (TFE) are known to undergo facile trans-amidation with a variety of amines.[67,68] We finally employed a long chain aliphatic alcohol – decanol and the subsequent product was obtained in good yield (**8q**).Thus, a robust, selective, as well as a sensitive protocol that is tolerant to a wide range of functional groups, has been established where one could employ a variety of alcohols other than methanol and get moderate to high yields.



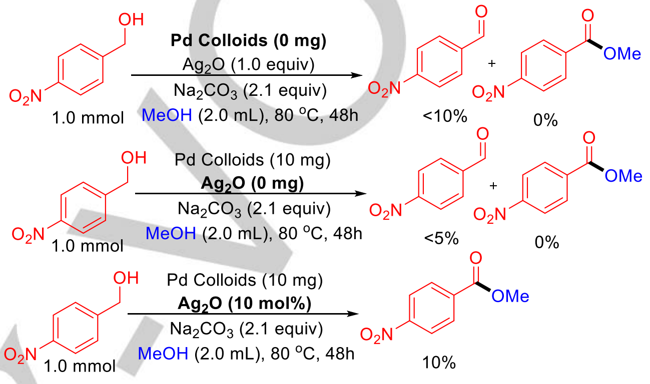
**Scheme 2**: **Oxidative esterification with different alcoholic partners.**

Higher order alcohols such as isopropyl alcohol, *tert* butyl alcohol as well as complex long chain unsaturated secondary alcohol – Linalool were also employed, but these failed to furnish any product due to steric hindrance. It is to be mentioned that, previous reports showed no selectivity exclusively forprimaryalcoholic group and esterify secondary and tertiary alcohols in similar manner as they do for primary[69–71]. However, Pd colloids/$Ag_2O$ was observed to be selective towards the conversion of primary alcohols. Harnessing this catalytic ability of the Pd colloid/$Ag_2O$ system it was decided to further explorethechemoselectivity between primary and secondary alcoholic groups (**Scheme 3**) present in the same molecule. For this purpose, propylene glycol, as well as 1,2-hexane diol, were selected to check the aforementioned chemoselectivity. Excellent reactivity was observed for the selective esterification of the primary alcoholic functional group over the secondary alcoholic group. On similar lines, we tried di-esterification reaction using glycerol and benzyl alcohol subsequently providing moderate yields of di-ester with secondary alcohol remaining intact. Likewise, the tolerance of the protocol towards other functional groups was next undertakenwithoxidative esterification of 4-hydroxy benzyl alcohol and 2-hydroxy benzyl alcohol (oil of winter green – **10b**) as well as 2-chloro benzyl alcohol possessing interfering groups like -OH and –Cl at *ortho* and *para* positions. All thesereaction gave excellent yields for all the 3 products rendering this protocol as very efficient and possessing excellent functional group tolerance.



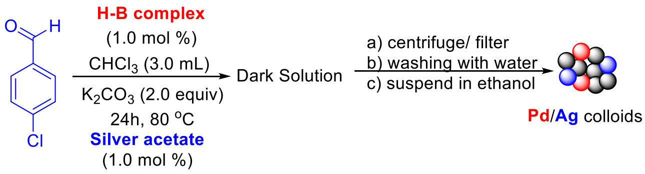
**Scheme 3: Chemo- and regio-selective oxidative esterification.**

The above results re-confirm the usefulness of the developed oxidative esterification strategy and to further ascertain the role of oxidant in synergy with the palladium colloids,certain set of experiments were undertaken (**Scheme 4**). Under the optimized set of conditions, the first reaction was carried out without employing Pd colloids, while the oxidant $Ag_2O$ was added to assess its effect on the catalytic activity. Although, it was expcted that the absence of Pd colloids could hamper the catalytic activity, negligible formation of benzaldehyde (oxidized product of benzyl alcohol) in the presence of $Ag_2O$ was unexpected. Likewise, we carried out another reaction involving Pd colloids with no added $Ag_2O$ (or any other oxidant) under the optimized conditions. The reaction failed to provide the desired product as no change in the starting material was observed.Similar result was obtained with the addition of a catalytic amount of $Ag_2O$ as compared to stoichiometric suggesting the requirement of an equivalent amount for benzyl alcohol oxidation. The above results also point towards some type of synergy to be existent between the Pd colloids and $Ag_2O$ in efficiently catalyzing the oxidative esterification. In literature, several reports have discussed about the synergistic effect of two different metals in catalytic reactions performing under distinctly different catalytic mechanisms[72–76].



**Scheme 4: Analysis of synergistic effect of Pd colloids and $Ag_2O$.**

Realizing these synergistic effects of metals on the catalytic activity of one another and also the fact that the employment of stoichiometric amounts of $Ag_2O$ (expensive oxidant) is detrimental for any commercial exploitation of the pprocess, we decided to synthesize a mixed heterobimetallic colloidal catalyst containing Pd and Ag. Synthesis of the Pd/Ag colloidal catalyst was undertaken by following a similar procedure used for obtaining Pd colloids involving the combination of Hermann-Beller palladacycle, with 4-chlorobenzaldehyde in $CHCl_3$ and added $K_2CO_3$ as base as well as AgOAcas Ag source at 80 ºC, thus resulting in the formation of black powder (**Scheme 5**). The resultant powder was subjected to centrifugal separation from the supernatant solution and was further washed several times with deionized water. The powder was subsequently suspended into dry ethanol, collected and dried to obtain the heterobimetallic colloidal catalyst.



**Scheme 5**:**Synthetic procedure for obtaining Pd/Ag heterobimetallic colloids.**

The synthesized heterobi-metallic colloidal catalyst was subjected to rigorous characterization using techniques such as XRD, HRTEM and XPS analysis. The black powder obtained was first submitted to High resolution transmission electron

10.1002/asia.201900566

microscopic studies (HR-TEM) for the assessment of the size and morphology of the synthesized colloids (**Figure 2**). It was observed that rather than having a nanoparticular morphology wherein the particles could be well separated, a clustered arrangement (colloids) of Pd and Ag was observed with an overall size ranging from 2-5 nm. Presence of such fine colloids would certainly provide large surface area for the catalytic oxidative esterification, although the exact composition of the colloids could not be ascertained using TEM analysis. Further characterization using powder XRD and XPS was therefore performed to provide detailed information about the nature of the colloids.

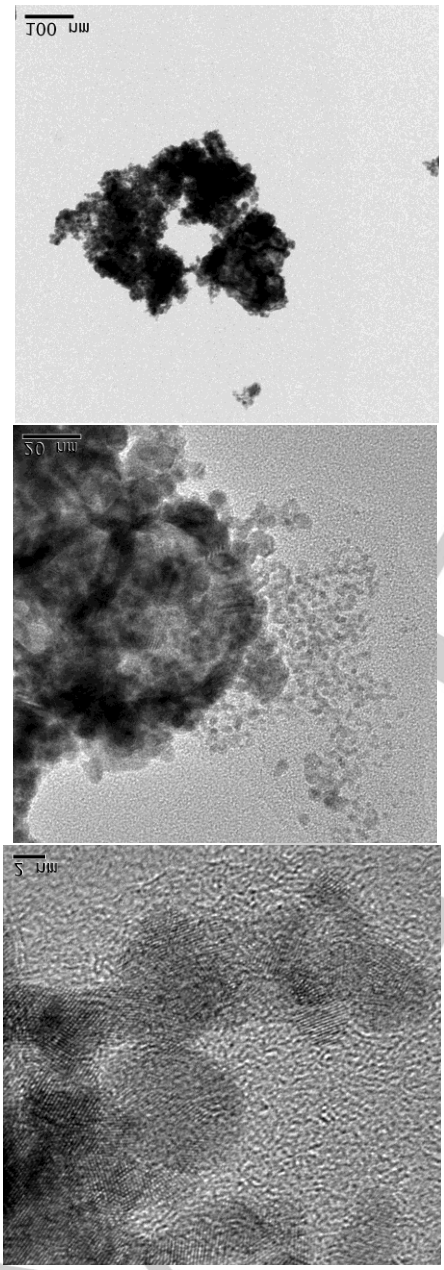


**Figure 2: HRTEM analysis of heterobi-metallicPd/Ag colloids.**

The structural features of the synthesized heterobi-metallicPd/Ag colloids were characterized by subjecting the powder to XRD studies with the XRD profiles of the synthesized Pd/Ag overlayed onto the native Pd colloidal catalyst (**Figure 3**). Commonly, typical diffraction peaks related to Pd could be observed i.e. at 39.7°, 45.2°, 67.3° and 80.8° corresponding to the (111), (200), (220) and (311) lattice planes.[77,78] Although, in case of the native Pd colloidal catalyst the (111) could be observed prominently while (200), (220) and (311) are less prominent. However, with the synthesized heterobimetallicPd/Ag colloid system a definite shift in the diffraction peaks could be observed with the (111) lattice showing maximum shift. Contraction in lattice planes of Pd could therefore be made possible by the addition of Ag as it is visible from **Figure 3**.

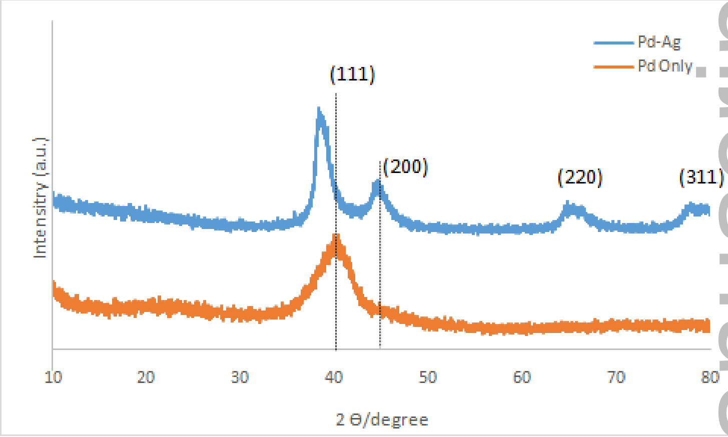


**Figure 3**: **Powder XRD analysis of heterobi-metallicPd/Ag colloids**.

The presence of Pdas well as Ag in the synthesized heterobimetallic colloidal catalyst was ascertained by subjecting the colloids to X-ray photoelectron spectroscopy (XPS). The XPS spectral analysis conclusively revealed the presence of palladium, carbon and silver (presence of oxygen cannot be ruled out) as the main elements, while phosphorus that was a part of the Hermann-Beller complex used as the precursor for heterobimetallic colloid synthesis could not be observed. Closer inspection of the obtained data and comparison to the Pd colloids reveals a significant decrease in the $Pd^{2+}$ species in the mixed metal colloids (Figure 4).

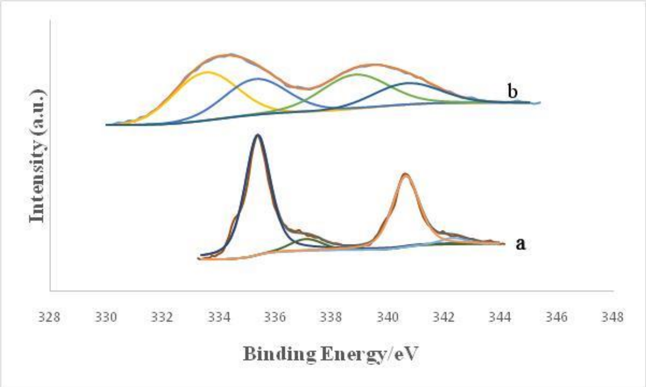


**Figure 4:Palladium oxidation state in a)Pd-Ag Species,**

### b) Pd Colloid species

This could be further understood from the Table 2 which details the comparison of the binding energy values for $Pd^{2+}$ and $Pd^0$ in both the heterobi-metallic colloidal catalyst and native Pd colloid catalyst.

| *Catalyst* | *Binding Energy (eV)* | | |
|---|---|---|---|
| | $Pd^0$ | $Pd^{2+}$ | $Pd^{+2}/Pd^0$ |
| Pd/Ag mixed species | 335.359 | 337.079 | 0.09005 |
| | 342.319 | 340.629 | |
| Pd colloids | 333.5 | 335.28 | 0.707014 |
| | 338.81 | 340.66 | |

**Table 2**: **XPS interpretation of $Pd^{2+}/Pd^0$ concentration in Pd/Ag heterobimetallic colloids and native Pd colloids.**

Similarly, Ag present in the Pd/Ag heterobi-metallic colloidal catalyst was also assessed based on the obtained data (Figure 5) revealing the presence of metallic Ag species rather than $Ag^I$ or higher oxidation states of silver. This would mean that the presence of $Ag^0$ as the main species in the heterobi-metallic colloids need to be oxidized to $Ag^I$ in solution using a sacrificial oxidant (possibly pure $O_2$) for efficiently catalyzing the oxidative esterification of benzyl alcohols in the synergistic presence of Pd.

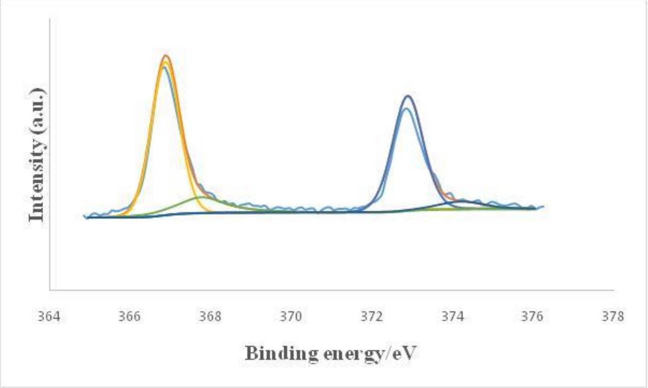
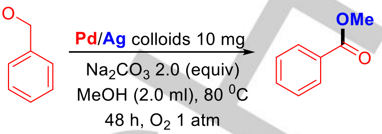


**Figure5; Representation of $Ag^0$ in Pd/Ag heterobimetallic colloids**.

The heterobi-metallicPd/Ag colloidal catalyst was next tested for the oxidative esterification of benzyl alcohol with methanol under the developed reactions conditions, although without the addition of $Ag_2O$ as oxidant, however pure oxygen (that had performed poorly) was used. Different parameters such as temperature, catalyst amount, reaction time and recyclability were varied to obtain the most optimum conditions for esterification (Scheme 6). Optimum results were obtained with a catalyst amount of 10 mg at 80 ˚Ctemperature and the reaction continued for 48 h. This result points strongly towards synergistic involvement of Pd and Ag for the efficient oxidative esterification of benzyl alcohols.An unimpressive recyclability can be attributed to difficulty in retrieving the catalyst due to its increased depressiveness. However such results keep the scope open for further investigation..



*Temperature Study*

| Entry | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Temperature | 30 °C | 50 °C | 80 °C | 100 °C |
| Yield (%)$^a$ | 10 | 80 | 100 | 100 |

*Catalyst Loading*

| Entry | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Amount | 1 mg | 2.5mg | 5 mg | 10 mg |
| Yield (%)$^a$ | 30 | 50 | 70 | 100 |

*Time Study*

| Entry | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Time | 12 h | 24 h | 36 h | 48 h |
| Yield (%)$^a$ | 10 | 30 | 75 | 100 |

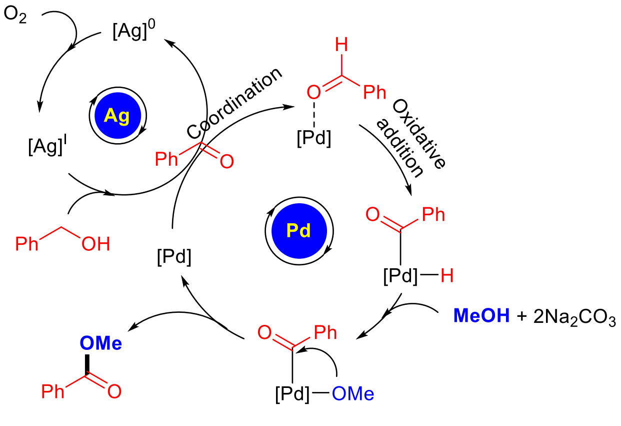
*Recyclability*

| Entry | 1st Cycle | 2nd Cycle | 3rd Cycle | 4th Cycle |
|---|---|---|---|---|
| Yield (%)$^a$ | 100 | 85 | 35 | 0 |

$^a$ *GC-MS yields*

**Scheme 6**: **Oxidative esterification of benzyl alcohol using heterobi-metallicPd/Ag colloids.**

A mechanistic pathway involving both Pd as well as Ag, in mixed colloidal species, in a synergistic manner could therefore be proposed on the basis of the results obtained so far with Ag efficiently involved in the selective oxidation of benzyl alcohol to benzaldehyde, which further undergoes oxidative addition reaction with Pd and on interaction with methanol in presence of base provides the desired ester (**Scheme 7**).



**Scheme 7: Plausible mechanism for Pd/Ag synergistic oxidative Esterification of benzyl alcohols.**

Recycling studies were performed by the isolation of the catalytic material after the first catalytic reaction, however after the first reaction the catalytic activity was observed to be reduced suggesting lower stability of the colloids under the catalytic conditions.

In conclusion, we present a highly efficient protocol for oxidative esterification of benzyl alcohol with a vast substrate scope. Although, one cannot overlook the fact that the oxidant used is expensive and protocols with cheaper metals like Co[79] as well with expensive metals like Pd[32] which use oxygen as oxidant exist, the protocol presented here is mild, straightforward and catalyst is easy to prepare. Other heterobimetallic catalytic systems are also know involving Pd with noble metals such as Ag, Au etc. but the selectivity obtained in the protocol presented in this manuscript is more convenient given the broad substrate scope presented herein.[80] We not only show traditional methyl esterification of benzyl alcohols but also show unprecedented transition metal catalysed oxidative esterification of benzyl alcohol with a variety of complex primary aliphatic alcohols with long chains, unsaturation, bridged and chiral carbons. We also characterize the mixed species of heterobi-metallic system of Pd and Ag with HR-TEM, XRD and XPS. We can suggest presence of synergism between two metals involved as well as presence of a probable true hetero bi-metallic system.

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**Keywords:** oxidative esterification • Palladium colloids • bi-metallic system • Hermann-Beller Complex • palladacycle

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