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# Phosphine-Free and Reusable Palladium Nanoparticles Catalyzed Domino Strategy: Synthesis of Indanone Derivatives

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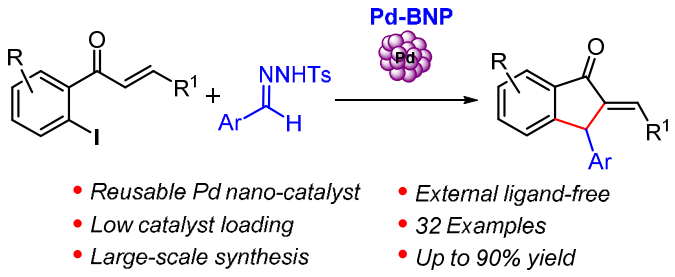



**ABSTRACT:** The carbene migratory insertion involving domino reaction by highly stable, reusable and binaphthyl stabilized Pd-nanoparticles (Pd-BNP) is disclosed. The reaction was catalyzed by 2 mol% of heterogeneous Pd-BNP catalyst under external ligand-free conditions and afforded 3-aryl-substituted indanone derivatives in up to 90% yield with exclusive *E*-selectivity. Furthermore, a one-pot reaction and derivatization of indanone derivatives were also successfully demonstrated.

***KEYWORDS:*** *Pd-nanoparticles; nano-catalyst; ligand-free; domino; N-tosylhydrazones; indanones*

## INTRODUCTION

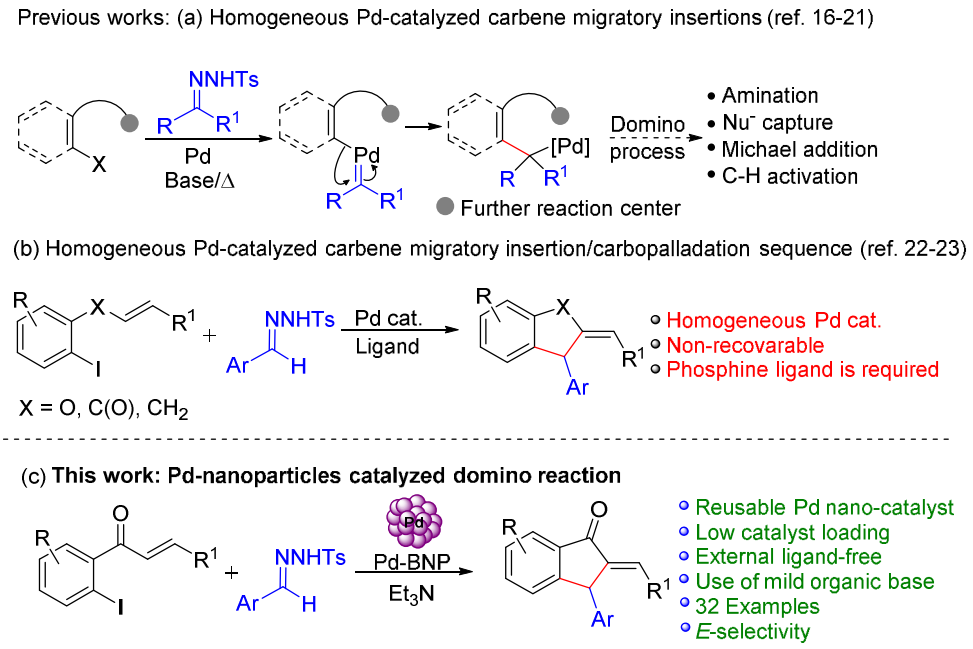
Transition-metal-catalyzed C-C bond formation reactions are well-accepted synthetic strategies for the synthesis of rich biologically active pharmaceuticals and natural products.[1-2] Recently the use of metal-carbenoid involving domino reactions holds tremendous promise to construct cyclic architectures via multiple C-C bond formation in a single step.[3-5] While diazo compounds have been primarily used as carbene precursors, they lessen synthetic strategies due to instability and explosive nature in the absence of electron withdrawing groups.[6-7] In this regard, stable and safe *N*-tosylhydrazones have been introduced as an alternative carbene precursors.[8-15] Utilizing *N*-tosylhydrazones, few Pd-catalytic cycles have been reported that converges carbene migratory insertion with other transformation for the synthesis of cyclic skeletons (Scheme 1a).[16-21]

Recently, our group and Valdés et al. have independently reported the homogeneous Pd-catalyzed carbene insertion followed by an intramolecular Heck reaction for the formation of indanone motifs (Scheme 1b).[22-23] Despite their own merits, these protocols have few shortcomings. For instance, the requirement of bulky and electron-rich external phosphine ligands to achieve smooth conversions make them less adaptable for the sustainable synthesis and it produces inevitable phosphine oxides which are tedious to remove. Moreover, the difficulties in the separation of homogeneous palladium catalyst from the final product create cost-effective and environmental barriers to broadening their scope.

These difficulties could be addressed by emergent palladium nano-catalysis which has increasing attention in both academic and industry owing to their unique reactivity, stability, recyclability and avoidance of metal residues in the products.[24-27] In this context, we have developed a binaphthyl back-bone stabilized Pd-nano catalyst (Pd-BNP) which has shown excellent activity, robustness, and recyclability for several times for many kinds of reactions

without any apparent metal leaching.[28-31] We intended to investigate the catalytic activity of Pd-BNP in domino reactions as there are very less literature reports available for nano-particle catalyzed domino reactions[32-35] and to the best of our knowledge, there is no report available for the heterogeneous Pd-catalyzed domino reaction which involves carbene migratory insertion as a key-step.

**Scheme 1.** Pd-Catalyzed Carbene Migratory Insertion Involving Domino Reactions

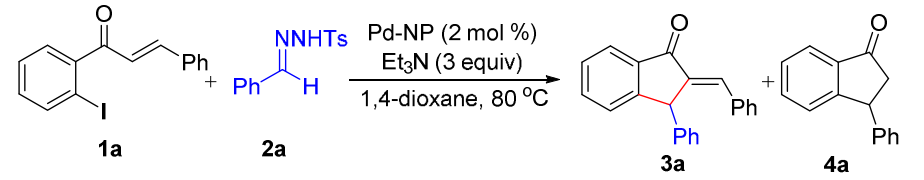


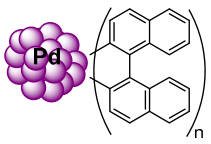

To our continuous efforts toward Pd-nanoparticles catalyzed sustainable organic transformations, we herein report the external phosphine ligand-free and reusable Pd-BNP catalyzed domino carbene migratory insertion/Heck-type cyclization strategy for the synthesis of indanone derivatives in excellent yields using mild organic base (Scheme 1c). It is noteworthy to mention that indanone containing scaffolds have been reported to show interesting biological activities.[36-42]

## RESULTS AND DISCUSSION

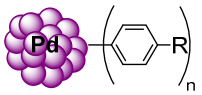
Our initial investigation was carried out by using 2'-iodochalcone **1a** and benzaldehyde derived *N*-tosylhydrazone **2a** as model substrates in the presence of Pd-BNP **5** (2.0 mol%) catalyst with $Et_3N$ (3 equiv) in 1,4-dioxane as solvent at 80 $^oC$. To our delight, the corresponding domino cyclized product 2-arylidene-3-aryl-1-indanones **3a** was detected in 71% yield with exclusive *E*-selectivity along with 8% of intramolecular reductive Heck cyclized product **4a**. Next, the reaction was studied with various nanoparticles as the catalytic activity of nano-catalyst is very much dependent on the stabilizers and results were summarized in Scheme 2.

**Scheme 2.** Domino Reaction with Various Pd-Nanoparticles




Pd-BNP **5**




R = H, **6**
= *n*-decyl, **7**
= *n*-decyloxy, **8**

| Pd-NP | yield (%)[a] 3a | 4a |
|---|---|---|
| **5** | 71 | 8 |
| **6** | 43 | 10 |
| **7** | 47 | 7 |
| **8** | 39 | 10 |
| Commercial Pd-NP | 58 | 6 |
| Pd/C | 33 | 5 |
| Pd-BNP (1:2 ratio) | 51 | 8 |

[a]Yields were determined by $^1H$ NMR using 1,3,5-trimethoxy benzene as an internal standard.

Other stabilizers such as phenyl (Pd-PNP) **6**, *n*-decyl-phenyl (Pd-DPNP) **7**, *n*-decyloxy-phenyl (Pd-DOPNP) **8** and commercially available Pd-NP have been used to improve the yield of the process. However, these stabilizers showed only low to moderate activities compared with binaphthyl stabilizer (Pd-BNP). Notably, Pd supported on carbon (10 wt% of Pd) gave **3a** in 33% yield. Additional investigation on Pd:stabilizer ratio manifested that

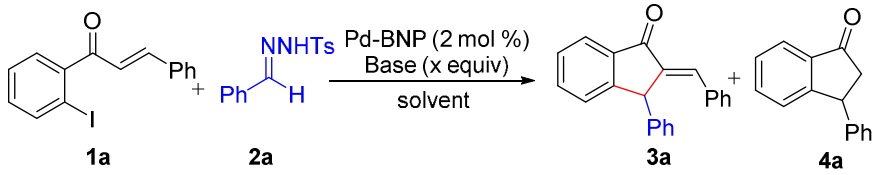
stabilizer quantity tunes the catalytic activity of nanoparticles. Pd-BNP (Pd:binaphthyl=1:2) gave less yield presumably due to decrease in active sites with excess stabilizer.

Additional investigations on catalyst loading showed that, use of 2.0 mol% was found to be optimal as 3.0 mol% and 1.0 mol% loading led to slightly decreased yield of 68% and 59% respectively (Table 1, entries 1 and 2). Except $Et_3N$ and Hünig's base (*N,N*-diisopropylethylamine), both organic and inorganic bases failed to provide the desired product **3a** (entries 3-7). Modification in the equiv of $Et_3N$ did not improve the yield (entries 8 and 9). Further screening of solvents to improve efficacy of the reaction were ineffective as 1,4-dioxane was found to be the best solvent (entries 10-12). Lowering the reaction temperature to 70 $^oC$, decreased the yield dramatically to 36% (entry 13). It can be observed that raising the temperature to 90 $^oC$ also led to slight decrease in yield (entry 14). Delightfully, we obtained the product **3a** in the best yield (94%) while adding **2a** in two portions (entry 15). However, addition of **2a** using syringe pump over 3 h resulted in slightly decreased yield (entry 16). No product **3a** was observed in the absence of the Pd-BNP catalyst. It must be noted that, domino reaction was found to be very selective towards *E*-isomer as we did not observe other isomer in the $^1H$ NMR analysis of crude mixture.

Having optimized reaction conditions (Table 1, entry 15), we then explored the scope of substrates and the results were summarized in Scheme 3. At first, various substituted *N*-tosylhydrazones **2** were employed with 2'-iodochalcone **1a**. It was observed that electron-donating group containing *N*-tosylhydrazones gave good yields of the corresponding cyclized products (**3b-3e**). Bromo-substituted hydrazones also gave the desired product **3f** in 90% yield. Electron withdrawing group such as 4-$NO_2$ and 4-CN bearing *N*-tosylhydrazones were unable to furnish the desired cyclized products (**3ah** and **3ai**) as hydrazones decomposed rapidly to give the corresponding carbonyl compounds. This may be due to unfavorable

increment in the electron deficiency of Pd-carbenoids.[43] In case of *ortho*-substituted hydrazones **2aj**, the reaction did not occur presumably due to the increased steric hindrance which may suppress the carbene migratory insertion as it situated near to $\eta^3$-benzylpalladium intermediate.

**Table 1.** Optimization of the Reaction Conditions[a]



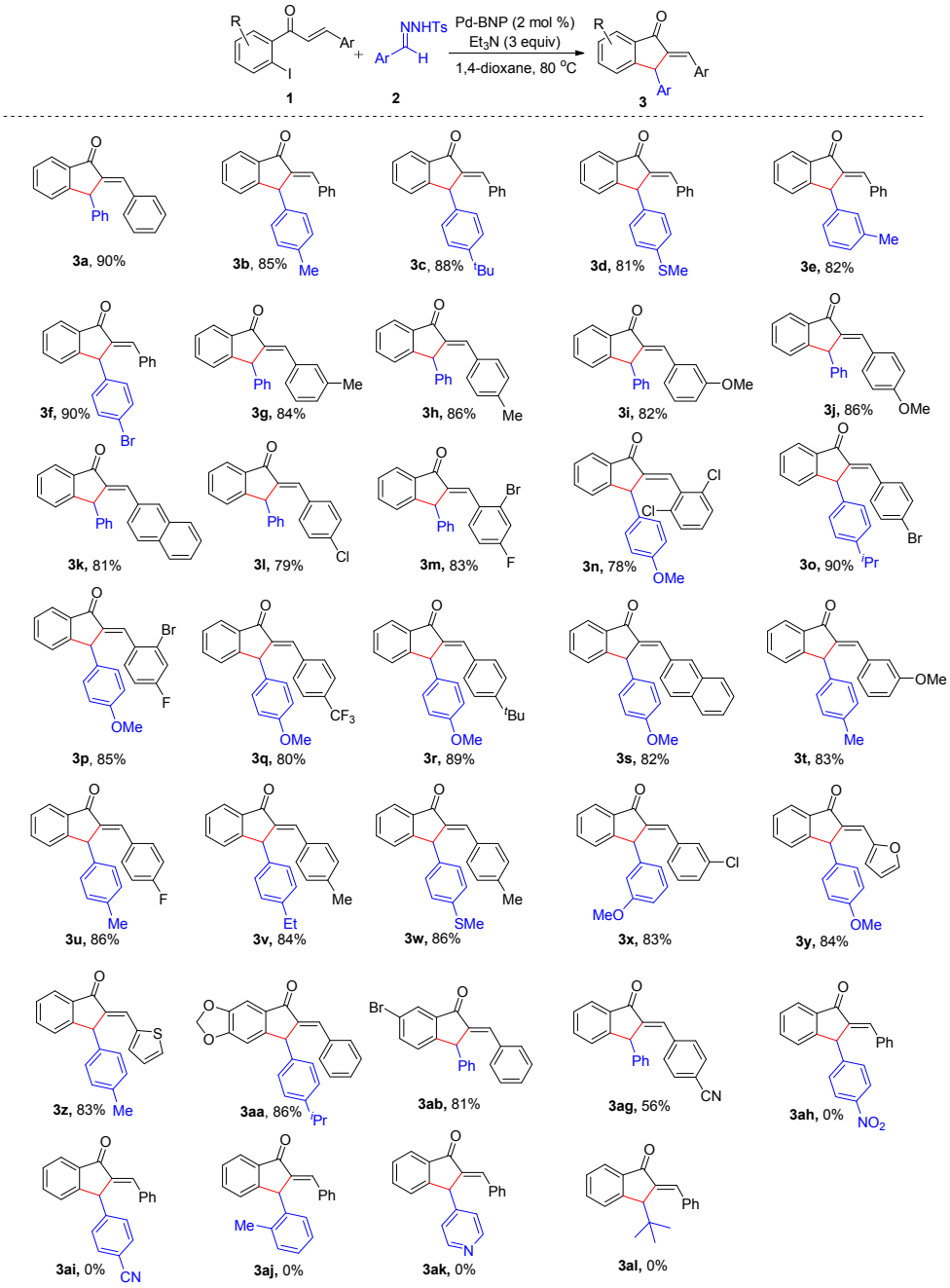

**1a** **2a** **3a** **4a**

| entry | base (equiv) | solvent | temp ($^o$C) | yield (%)[b] **3a/4a** |
|---|---|---|---|---|
| 1[c] | $Et_3N$ (3.0) | 1,4-Dioxane | 80 | 68/16 |
| 2[d] | $Et_3N$ (3.0) | 1,4-Dioxane | 80 | 59/6 |
| 3 | DIPEA (3.0) | 1,4-Dioxane | 80 | 40/48 |
| 4 | DBU (3.0) | 1,4-Dioxane | 80 | 0/0 |
| 5 | DABCO (3.0) | 1,4-Dioxane | 80 | 0/0 |
| 6 | $K_2CO_3$ (3.0) | 1,4-Dioxane | 80 | 0/0 |
| 7[e] | $LiO^tBu$ (3.0) | 1,4-Dioxane | 80 | trace/0 |
| 8 | $Et_3N$ (2.5) | 1,4-Dioxane | 80 | 57/0 |
| 9 | $Et_3N$ (4.0) | 1,4-Dioxane | 80 | 60/15 |
| 10 | $Et_3N$ (3.0) | THF | 80 | 55/12 |
| 11 | $Et_3N$ (3.0) | Diphenyl ether | 80 | 30/0 |
| 12 | $Et_3N$ (3.0) | Toluene | 80 | 49/0 |
| 13 | $Et_3N$ (3.0) | 1,4-Dioxane | 70 | 36/10 |
| 14 | $Et_3N$ (3.0) | 1,4-Dioxane | 90 | 65/15 |
| **15**[f,g] | **$Et_3N$ (3.0)** | **1,4-Dioxane** | **80** | **94 (90)/0** |
| 16[h] | $Et_3N$ (3.0) | 1,4-Dioxane | 80 | 91/0 |

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1.25 mmol), 9.6 mg of Pd-BNP (2 mol %, 11 wt% Pd by ICP-OES analysis) in 2 mL solvent for 12-15 h. [b]Yields were determined by $^1$H NMR using 1,3,5-trimethoxy benzene as an internal standard. [c]3.0mol% Pd-BNP. [d]1.0mol% Pd-BNP. [e]10.0 equiv of $H_2O$ was additionally used. [f]**2a** was added in two portions with 3 h time

interval. [g]Value in parentheses represents isolated yield. [h]**2a** was added using a syringe pump over 3 h.

**Scheme 3**. Substrate Scope of Pd-BNP Catalyzed Domino Reaction[a,b]

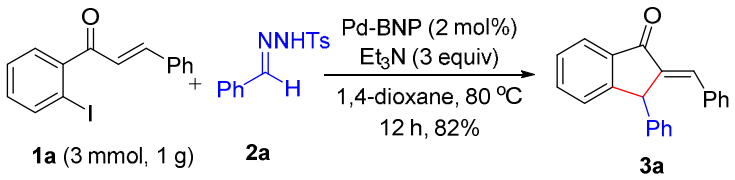



[a]Reaction conditions: **1** (0.5 mmol), **2** (1.25 mmol), 9.6 mg of Pd-BNP (2 mol %, 11 wt% by ICP-OES analysis) in 2 mL of 1,4-dioxane at 80 °C for 12-15 h. [b]**2** was added in two portions with 3 h time interval.

Next, a series of substituted 2'-iodochalcones **1** were subjected to react with benzaldehyde derived *N*-tosylhydrazones **2a** and the products were isolated in 79-86% yields (**3g-3l**). Di-halo-substituted 2'-iodochalcones also furnished corresponding products **3m** and **3p** in 83% and 85% yields respectively without affecting the halogen groups. This implies that the protocol is highly selective and the unaffected halogen groups of the resulting products can be used for further transformations. In addition, the structure of **3m** was confirmed by single crystal XRD analysis (See SI). Importantly, sterically demanding di-*ortho*-substituted system offered the product **3n** in 78% yield. This result suggests that di-*ortho* substitution did not affect the β-H elimination as substituents present away from the reaction taking place. Heterocyclic systems such as 2-furyl and 2-thienyl containing chalcones also offered the products in good yields (**3y** and **3z**). Further, we investigated the effect of substitution on the iodo-attached ring of the 2'-iodochalcone and the products were isolated in admirable yields (**3aa** and **3ab**). Electron-withdrawing group was also well tolerated as 4-CN containing chalcone gave the desired product in **3ag** in 56% yield. However, 4-pyridine containing tosylhydrazone did not deliver the product **3ak**. Less reactive 2'-bromochalcones, alkyl aldehyde **2al** and acetophenone derived tosylhydrazones also did not furnish the desired products. It must be noted that the current Pd-BNP heterogeneous catalyst displayed higher yields of many substrates than our previous homogenous $Pd(OAc)_2$ catalytic system. This is presumably due to $Pd^{2+}$ complex has to get reduced to active $Pd^0$ species to initiate the domino process via oxidative addition onto the Ar-I bond of **1** while Pd-BNP catalyst possess native $Pd^0$ form.

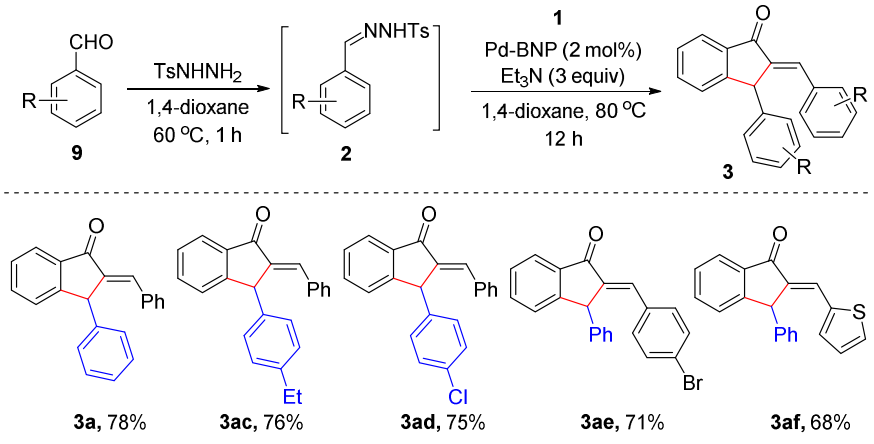
To check the scalability of our optimized reaction conditions, a gram-scale reaction was carried out by using of 1.0 g of 2'-iodochalcone **1a** and *N*-tosylhydrazones **2a**. Scale-up reaction afforded the cyclic product **3a** in 82% yield in 12 h (Scheme 4).

**Scheme 4.** Gram-Scale Synthesis using Pd-BNP Catalyst




Next, the newly developed catalytic system was tested in a one-pot condition by promoting in situ generation of *N*-tosylhydrazones from the corresponding carbonyl partner and *N*-tosylhydrazide. Pleasantly, 78% yield of **3a** was obtained in the one-pot reaction where the 2'-iodochalcone and catalyst were added after reacting the *N*-tosylhydrazide with benzaldehyde in 1,4-dioxane for 1 h (Scheme 5). 4-Et and 4-Cl substituted arylaldehydes were good substrates, giving 76% and 75% yields respectively (**3ac** and **3ad**). A thienylchalcone produced **3af** in 68% yield. However, 4-CN bearing benzaldehyde did not produce the desired product under our one-pot reaction conditions.[43]

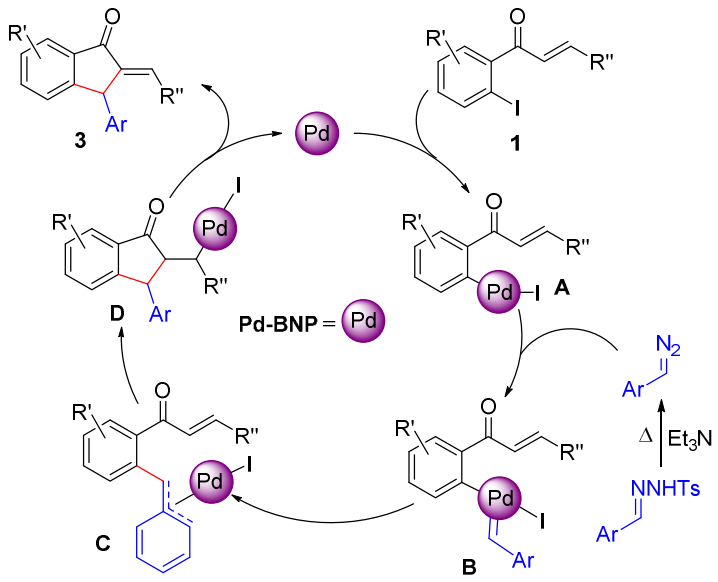
**Scheme 5.** A One-pot Reaction from Aldehyde




We suggest a possible reaction pathway based on the literature precedent (Scheme 6).[20-22] Pd-BNP nano-catalyst first reacts with the 2'-iodochalcone **1** to yield an intermediate **A** which then advances to Pd-carbenoid **B** by reacting with in situ generated diazo spices. The electrophilic carbenoid **B** subsequently undergoes migratory insertion and furnishes

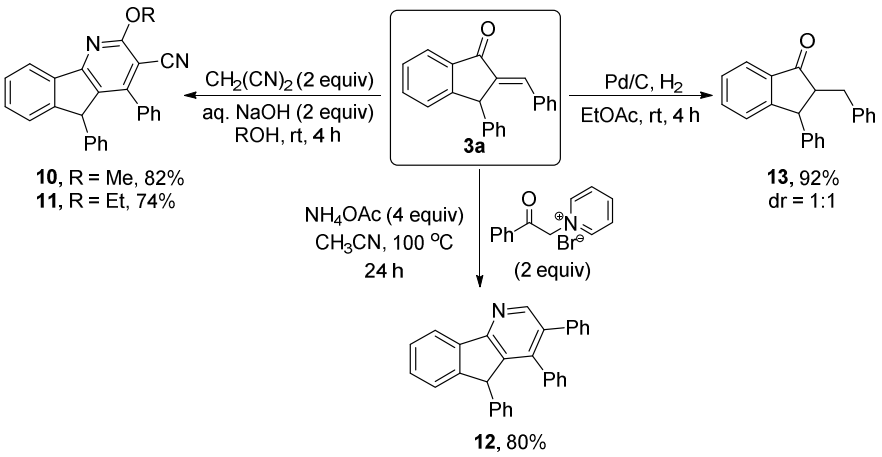
benzylpalladium intermediate **C**[44] which further undergoes intramolecular 5-*exo*-*trig* mode of carbopalladation giving rise to **D**. Upon syn-β-H elimination, **D** delivers the desired product **3** with *E*-selectivity.

**Scheme 6.** Plausible Reaction Mechanism




1-Indanone **3a** was further derivatized into useful heterocyclic compounds (Scheme 7). Densely functionalized pyridine-containing hetero-tricyclic core **10** and **11** were synthesized while treating **3a** with malononitrile in 82% and 74% yield respectively. Upon reacting with pyridinium salt, **3a** furnished 5*H*-indeno[1,2-*b*]pyridine derivative **12** in 80% yield after 24 h. Reduction of **3a** with molecular hydrogen in the presence of Pd/C gave compound **13** in 92% yield with a dr 1:1.

**Scheme 7**. Synthetic Application of the Indanones




Further efforts were made to examine the reusability and recoverability of the Pd-BNP catalyst from the viewpoint of industrial applications. The model reaction was conducted at 1 mmol scale under the standard conditions. The catalyst was recovered and reused up to five catalytic cycles and desired product **3a** was isolated in the yields of 89%, 87%, 87%, 86% and 85% in successive runs which proves the preserved activity of the catalyst (Figure 1).

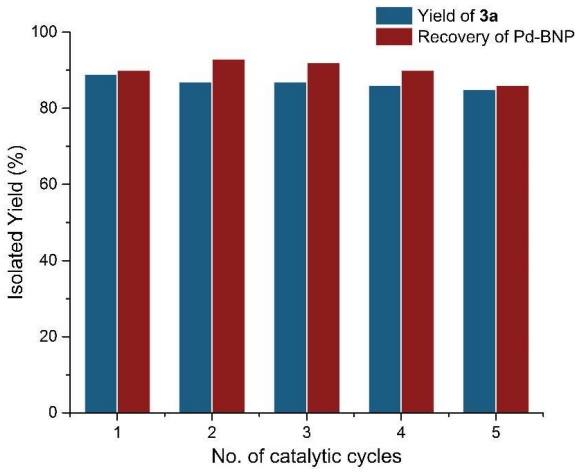



**Figure 1**. Recyclability of Pd-BNP catalyst

Moreover, HR-TEM analysis of recovered Pd-BNP catalyst after five runs showed that there was no major change in the size distribution and dispersion of the nanoparticles compared with the fresh catalyst. The average size of Pd-BNP was found to be 5-6 nm (Figure 2).

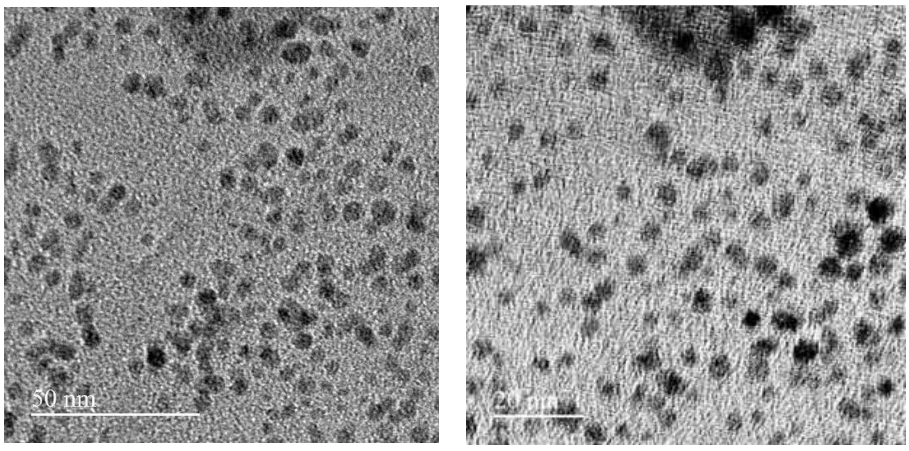



**Figure 2**. HR-TEM pictures of Pd-BNP catalyst: Fresh catalyst (left) and recycled catalyst after five runs (right)

Stability of the nano-catalyst in the solution phase is also crucial for an outstanding heterogeneous catalyst as leaching of the metal could make the catalyst to lose its activity. As our nano particles size is < 6 nm, it can pass through membrane filters. So, instead of hot filtration test, hot centrifugation test has been carried out to prove that reaction was catalyzed by the heterogeneous palladium. Pd-BNP catalyst was removed from the reaction by simple centrifugation in the middle of the reaction at two different time intervals. After centrifugation, both liquid portions were allowed to continue the reaction at 80 $^{o}$C. The reaction did not proceed in both the cases which clearly prove that no catalytically active palladium had been present in the liquid phase of the reaction (Figure 3).

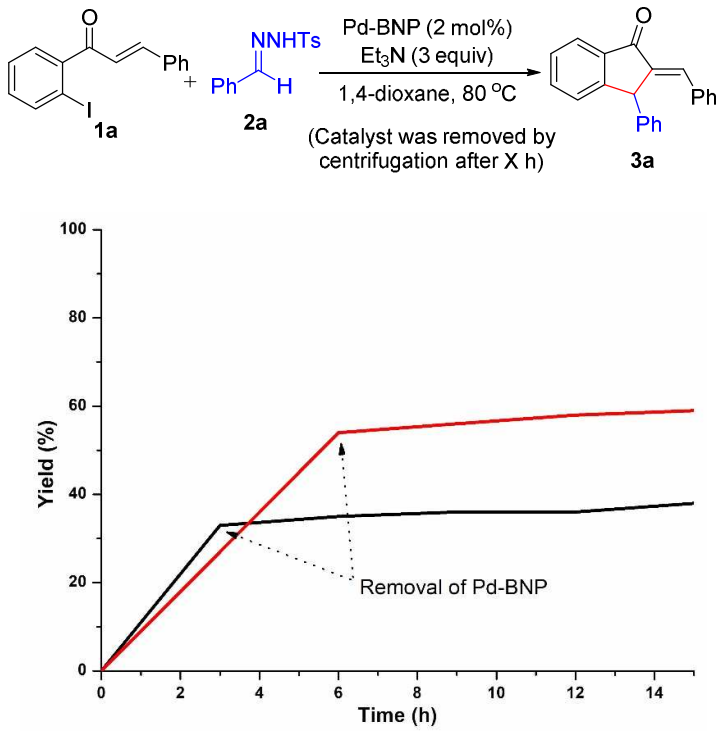



**Figure 3**. Hot centrifugation test. Black line: X = 3 h; Red line: X = 6 h.

Additionally, centrifuged residue has shown almost similar catalytic activity as compared with the fresh Pd-BNP. ICP-OES analysis of the reaction solution revealed that Pd concentration is 0.021 wt% indicating that leaching of Pd into the solution is very negligible. Mercury poisoning test also confirmed that the main catalyst to accelerate the domino reaction was the heterogeneous Pd-BNP (See SI for details). These results illustrate that Pd-BNP behaves as a sole heterogeneous catalyst for the domino process rather than leached palladium.

## CONCLUSIONS

In conclusion, an efficient and robust heterogeneous Pd-BNP catalyzed domino synthesis of indanone derivatives was developed through carbene migratory insertion strategy. This ligand-free protocol showed a broad substrate scope with respect to both the coupling partners with good to excellent yields and *E*-selectivity. Pd-BNP was easily recovered and

reused up to five times without any apparent agglomeration. However, a detailed mechanistic study and further application of Pd-BNP are under progress.

## Experimental Section

**General remarks**: All reactions were carried out in oven-dried reaction tubes. Reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 $F_{254}$ precoated plates (0.25 mm) and visualized by UV fluorescence quenching using appropriate mixture of ethyl acetate and hexanes. Silica gel (particle size: 100-200 mesh) was purchased from Avra Synthesis Pvt. Ltd. and used for column chromatography using hexanes and ethyl acetate mixture as eluent. Solvents used for extraction and column chromatography were laboratory grade and used as received. Reaction solvents used were obtained from Fischer Scientific, India Pvt. Ltd. $K_2PdCl_4$ (98%), various aldehydes and *N*-tosylhydrazide were purchased from Sigma-Aldrich, Alfa-Aesar, TCI and Spectrochem Pvt. Ltd. India. Other chemicals like $NaBH_4$, DIPEA, DBU, DABCO and triethylamine were purchased from Avra and Spectrochem Pvt. Ltd., India. (±)-BINAM was purchased from Gerchem Pvt. Ltd. Hyderabad, India. 1,1'-Binaphthyl,-2,2'-bis(diazoniumtetrafluoroborate) was prepared using literature reported procedure.[1] Nano pure water was obtained from Milli-Q Integral Water Purification System. All the reactions were carried out in temperature controlled IKA magnetic stirrers. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker 400 MHz (100 MHz for $^{13}C$) instrument. $^1H$ NMR spectra were reported relative to residual $CDCl_3$ (δ 7.26 ppm). Chemical shifts were reported in parts per million and multiplicities are as indicated: s (singlet,) d (doublet,) t (triplet,) q (quartet,) and m (multiplet). Coupling constants *J*, are reported in Hertz. Melting points were recorded on a Guna capillary melting point apparatus and are corrected. Infrared spectra were recorded on a FTIR 4000 Series Spectrometer. The

wave numbers of recorded IR signals are quoted in $cm^{-1}$. High resolution mass spectra (HRMS) were recorded on Q-Tof Micro mass spectrometer.

Inductively coupled plasma-optical emission spectrometer (ICP-OES) from Perkin Elmer Optima 5300 DV was used to find the Pd-content of the nanoparticles. Samples were prepared by digesting 5 mg of nanoparticles in 1.0 mL of $H_2SO_4$ using domestic microwave oven for 30 min. and the solutions was made up to 25 mL in standard flask. Pd emissions were detected at 340.458 nm under the flow condition.

HR-TEM analysis of samples was performed using a JEM 2010 electron microscope. TEM analysis of the samples was done using carbon coated copper grids (nanoparticles in dichloromethane solutions). The instrument was operated at 200 kV.

**Diazotization of (1,1'-binaphthalene)-2,2'-diamine (BINAM)**[28]

The binaphthyldiazonium salt **2** was synthesized by the diazotization of (1,1'-binaphthalene)-2,2'-diamine (BINAM ) **1**. The stable binaphthyldiazonium salt was prepared by the slow addition of aqueous solution of sodium nitrite ($NaNO_2$) to a stirred solution of BINAM in $HBF_4$ at 0 $^oC$ and the reaction mixture was stirred further at 0 $^oC$ for 30 min. The colour change from pale brown to yellow colour indicates the formation of diazonium salt. The resulting yellow solid was filtered and washed with cold $HBF_4$, $H_2O$ and EtOH. The diazonium salt **2** was dried under a vaccum desiccator and stored at 0 $^oC$. The reaction yielded 95% of the diazonium salt.

**General procedure for the preparation of Pd-BNP catalyst**[28]

To a 250 mL round bottom flask potassium tetrachloropalladate ($K_2PdCl_4$) (653 mg, 2.0 mmol, 1 equiv) was dissolved in nanopure water (30 mL). 1,1'-binaphthyl,-2,2'-bis(diazoniumtetrafluoroborate) **2** (964.2 mg, 2.0 mmol, 1 equiv) and toluene (30 mL) was

added to this solution and stirred vigorously for 1 h at room temperature. The orange-brown colour formation shows the complexation of Pd with diazonium salt **2**. After that a solution of $NaBH_4$ (453.8 mg, 12.0 mmol) in nanopure water (1.5 mL) was added slowly dropwise at rt and the immediate colour change to dark greenish black indicates the formation of palladium nanoparticles. The reaction mixture was further stirred at room temperature for another 2 h. The toluene layer was then separated and washed with 0.5 M aq. $H_2SO_4$ (3 × 40 mL) and 0.5 M aq. $NaHCO_3$ (3 × 40 mL) to remove unreacted metal complexes. Then the solvent was completely evaporated under rotary evaporator and the resultant solid residues were suspended in ethanol (2 × 10 mL) and sonicated for 30 minutes at room temperature. The suspension was further centrifuged (5000 rpm) for 30 min. The ethanol was decanted and dried in vacuum to obtain the Pd-binapthyl NPs (Pd-BNP) **3** (789 mg, 11 wt% Pd, ICP-OES analysis).

**Procedure for the synthesis of other diazoniumtetrafluoroborate salt**[28]

To a 100 mL round bottom flask, a solution of nanopure water (2.0 mL) and conc. HCl (2.0 mL) (1:1) was added to a mixture of aryl amine (16.0 mmol, 1.0 equiv) and conc. HCl (3.0 mL) at 0 $^oC$. To this reaction mixture, a solution of $NaNO_2$ (17.6 mmol, 1.1 equiv) in 1.5 mL of nanopure water was added slowly drop by drop and stirred for 30 min. at 0 $^oC$. After that ice cold solution of 45% aq $HBF_4$ (10 mL) was added slowly to the reaction mixture and stirred for 15 min at 0 $^oC$. The resulting solid precipitate was filtered and washed with ice cold nanopure water and dried under vacuum desiccator and stored at 0 $^oC$.

**Procedure for the preparation of Pd-nanoparticles (6, 7 and 8)**

To a stirred solution of $K_2PdCl_4$ (326.5 mg, 1.0 mmol, 1 equiv) in nanopure water (50 mL) in 250 mL round bottom flask, diazoniumtetrafluoroborate (2.0 mmol) and toluene (50 mL) was added and stirred vigorously in magnetic stirrer for 4 h. After that the toluene layer was

separated and washed twice with nanopure water. To this washed toluene layer $NaBH_4$ (226.9 mg, 6.0 mmol) in water (3.0 mL) was added dropwise at room temperature and the immediate colour change to dark greenish black indicates the formation of palladium nanoparticles. The reaction mixture was further stirred for 2 h at room temperature. The toluene layer was separated and washed with 0.5 M aq. sulphuric acid (3 × 50 mL) and 0.5 M aq. sodium bicarbonate (3 × 50 mL). The solvent was completely evaporated under rotary evaporator. The solid particles were suspended in ethanol (2 × 10 mL) and sonicated for 30 min. at room temperature and further the suspension was centrifuged. The ethanol was decanted and dried under vacuum to furnish the Pd-nanoparticles. See the SI for TEM images.

**General procedure for palladium nanoparticles catalyzed domino strategy to synthesis of indanone derivatives**

Under open atmosphere, (*E*)-2′-iodochalcone **1** (167 mg, 0.5 mmol), *N*-tosylhydrazone **2** (171 mg, 0.625 mmol), Pd-BNP (11 wt% Pd by ICP-OES analysis) (9.64 mg, 0.01 mmol), and triethylamine (0.2 mL, 1.5 mmol) were successively added to oven dried reaction tube. 1,4-Dioxane (2.5 mL) were added and closed with a glass-stopper. The reaction tube was then immersed in an 80 ºC pre-heated oil bath. After 3 h, another portion of *N*-tosylhydrazone **2** (171 mg, 0.625 mmol) was added. The reaction was heated with stirring till complete consumption of 2′-iodochalcone. Upon cooling down to room temperature, the solvent was removed under reduced pressure. Water was added to reaction mixture and extracted with ethyl acetate (3×5 mL). Brine wash (1×10 mL) was given to the combined organic extractions and dried over anhydrous $Na_2SO_4$. Removal of solvent and silica gel column separation of crude using hexanes and ethyl acetate mixture (19:1) afforded the corresponding 2-arylidene-3-aryl-1-indanone **3**.

**(*E*)-2-Benzylidene-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3a)**

133 mg, 90% yield; white solid; mp 143-145 °C (lit. 143-145 °C)[22]; $R_f$ 0.37 (10% ethyl acetate in hexanes); $^1$H NMR ($CDCl_3$, 400 MHz) δ 5.33 (s, 1H), 7.09-7.15 (m, 1H), 7.16-7.26 (m, 7H), 7.33-7.41 (m, 2H), 7.42-7.55 (m, 3H), 7.85 (d, *J* = 1.6 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100 MHz) δ 48.8, 124.3, 126.0, 127.0, 127.7, 128.0, 128.5, 129.0, 129.7, 131.4, 134.1, 135.2, 135.7, 136.1, 138.5, 141.4, 154.5, 194.7; FTIR (film) 3026, 1688, 1620, 1465, 1449, 749 cm$^{-1}$; HRMS (*m*/*z*): $[M+K]^+$ calcd for $C_{22}H_{16}OK$: 335.0833; found: 335.0829.

**(*E*)-2-Benzylidene-3-(*p*-tolyl)-2,3-dihydro-1*H*-inden-1-one (3b)**

132 mg, 85% yield; pale yellow solid; mp 149-151 °C (lit. 148-150 °C)[22]; $R_f$ 0.62 (15% ethyl acetate in hexanes); $^1$H NMR ($CDCl_3$, 400 MHz) 2.22 (s, 3H), 5.31 (s, 1H), 7.00 (d, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 7.20-7.28 (m, 3H), 7.33-7.42 (m, 2H), 7.43-7.53 (m, 3H), 7.81 (s, 1H), 7.91 (d, *J* = 7.2 Hz, 1H); $^{13}$C{$^1$H}NMR ($CDCl_3$, 100 MHz) δ 21.1, 48.5, 124.3, 126.0, 127.5, 127.9, 128.5, 129.7, 129.8, 131.6, 134.2, 135.2, 135.6, 136.1, 136.6, 138.6, 138.7, 154.8, 194.9; FTIR (film) 3025, 2917, 1698, 1623, 1292, 1093, 746 cm$^{-1}$; HRMS (*m*/*z*): $[M+K]^+$ calcd for $C_{23}H_{18}OK$: 349.0989; found: 349.0982.

**(*E*)-2-Benzylidene-3-(4-(*tert*-butyl)phenyl)-2,3-dihydro-1*H*-inden-1-one (3c)**

155 mg, 88% yield; white solid; mp 177-179 °C (lit. 176-178 °C)[22]; $R_f$ 0.42 (10% ethyl acetate in hexanes); $^1$H NMR ($CDCl_3$, 400 MHz) δ 1.22 (s, 9H), 5.31 (s, 1H), 7.11-7.29 (m, 7H), 7.36-7.55 (m, 5H), 7.83 (s, 1H), 7.92 (d, *J* = 7.6 Hz, 1H); $^{13}$C{$^1$H}NMR ($CDCl_3$, 100 MHz) δ 31.4, 34.5, 48.4, 124.3, 126.0, 126.1, 127.2, 127.9, 128.5, 129.6, 131.6, 134.3, 135.1, 135.5, 136.1, 138.4, 138.8, 149.8, 154.8, 195.0; FTIR (KBr) 2961, 2870, 1690, 1619, 1601, 1292, 1093 cm$^{-1}$; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{26}H_{24}ONa$: 375.1719; found: 375.1709.

**(*E*)-2-Benzylidene-3-(4-(methylthio)phenyl)-2,3-dihydro-1*H*-inden-1-one (3d)**

139 mg, 81% yield; pale yellow solid; mp 140-142 °C (lit. 138-140 °C)[22]; $R_f$ 0.58 (15% ethyl acetate in hexanes); $^1$H NMR ($CDCl_3$, 400 MHz) δ 2.34 (s, 3H), 5.31 (s, 1H), 7.05-7.19 (m, 4H), 7.22-7.30 (m, 3H), 7.32-7.43 (m, 2H), 7.43-7.60 (m, 3H), 7.84 (s, 1H), 7.92 (d, *J* = 7.2 Hz, 1H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100 MHz) δ 15.8, 48.3, 124.4, 126.0, 127.1, 128.1, 128.2, 128.6, 129.8, 131.5, 134.1, 135.2, 135.8, 136.1, 137.1, 138.3, 138.4, 154.4, 194.7; FTIR (film) 3029, 1698, 1622, 1491, 1292, 1092, 752 cm$^{-1}$; HRMS (*m*/*z*): $[M+K]^+$ calcd for $C_{23}H_{18}OSK$: 381.0710; found: 381.0704.

**(*E*)-2-Benzylidene-3-(*m*-tolyl)-2,3-dihydro-1*H*-inden-1-one (3e)**

127 mg, 82% yield; pale yellow solid; mp 130-132 °C (lit. 127-129 °C)[22]; $R_f$ 0.41 (10% ethyl acetate in hexanes); $^1$H NMR ($CDCl_3$, 400 MHz) δ 2.21 (s, 3H), 5.29 (s, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.98 (s, 1H), 7.09-7.16 (m, 2H), 7.20-7.29 (m, 3H), 7.33-7.42 (m, 2H), 7.43-7.52 (m, 3H), 7.83 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H); $^{13}$C{$^1$H}NMR ($CDCl_3$, 100 MHz) δ 21.5, 48.8, 124.3, 124.9, 126.1, 127.8, 128.0, 128.2, 128.5, 128.9, 129.7, 130.5, 134.3, 135.2, 135.7, 136.1, 138.7 (2C), 141.5, 154.7, 194.9; FTIR (film) 3025, 1698, 1624, 1464, 1292, 1093, 742 cm$^{-1}$; HRMS (*m*/*z*): $[M+K]^+$ calcd for $C_{23}H_{18}OK$: 349.0989; found: 349.0978.

**(*E*)-2-Benzylidene-3-(4-bromophenyl)-2,3-dihydro-1*H*-inden-1-one (3f)**

169 mg, 90% yield; pale brown solid, mp 146-148 °C (lit. 144-147 °C)[22]; $R_f$ 0.37 (10% ethyl acetate in hexanes); $^1$H NMR ($CDCl_3$, 400 MHz) δ 5.34 (s, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.23-7.30 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 3H),7.40-7.48 (m, 3H), 7.52-7.59 (m, 1H), 7.86 (s, 1H), 7.94 (d, *J* = 7.2 H , 1H); $^{13}$C{$^1$H}NMR ($CDCl_3$, 100 MHz) δ 48.2, 121.0, 124.5, 126.0, 128.3, 128.6, 129.4, 130.0, 131.4, 132.2, 134.0, 135.3, 136.1, 136.2, 138.1, 140.6, 153.9, 194.4; FTIR (film) 3029, 1698, 1624, 1292, 1092, 750 cm$^{-1}$; HRMS (*m*/*z*): $[M+Na]^+$calcd for $C_{22}H_{15}OBrNa$: 397.0198; found: 397.0183.

**(*E*)-2-(3-Methylbenzylidene)-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3g)**

130 mg, 84% yield; white solid; mp 144-146 °C (lit. 141-143 °C)[22]; $R_f$ 0.36 (10% ethyl acetate in hexanes); $^1$H NMR ($CDCl_3$, 400 MHz) δ 2.16 (s, 3H), 5.26 (s, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 7.02-7.10 (m, 2H), 7.12-7.23 (m, 6H), 7.26-7.35 (m, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.75 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100 MHz) δ 21.3, 49.0, 124.4, 126.1, 127.0, 127.8, 128.0, 128.4, 128.8, 129.0, 130.1, 132.2, 134.1, 135.1, 136.0, 136.2, 138.0, 138.4, 141.7, 154.6, 194.8; FTIR (film) 3024, 2917, 1697, 1618, 1490, 1292, 1088, 747 cm$^{-1}$; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{23}H_{18}ONa$: 333.1250; found: 333.1247.

**(*E*)-2-(4-Methylbenzylidene)-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3h)**

133 mg, 86% yield; white solid; mp 205-206 °C (lit. 202-204 °C)[22]; $R_f$ 0.42 (10% ethyl acetate in hexanes); $^1$H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 5.34 (s, 1H), 7.05 (d, *J* = 7.6 Hz, 2H), 7.12-7.17 (m, 1H), 7.20-7.28 (m, 4H), 7.34-7.43 (m, 4H), 7.49-7.56 (m, 1H), 7.83 (d, *J* = 1.6 Hz, 1H), 7.92 (d, *J* = 7.2 Hz, 1H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100 MHz) δ 21.6, 48.9, 124.4, 126.0, 127.1, 127.7, 128.0, 129.1, 129.4, 131.4, 131.7, 135.1, 135.9, 136.3, 137.4, 140.4, 141.7, 154.5, 194.9; FTIR (film) 3019, 1690, 1601, 1582, 1292, 1093, 737 cm$^{-1}$; HRMS (*m*/*z*): $[M+K]^+$ calcd for $C_{23}H_{18}OK$: 349.0989; found: 349.0976.

**(*E*)-2-(3-Methoxybenzylidene)-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3i)**

134 mg, 82% yield; pale yellow solid, mp 136-138 °C (lit. 137-1390 °C)[22]; $R_f$ 0.31 (10% ethyl acetate in hexanes); $^1$H NMR ($CDCl_3$, 400 MHz) δ 3.62 (s, 3H), 5.35 (s, 1H), 6.81(dd, *J* = 8.0, 1.6 Hz, 1H), 6.94 (s, 1H), 7.04-7.13 (m, 1H), 7.13-7.20 (m, 2H), 7.21-7.30 (m, 4H), 7.35-7.43 (m, 2H), 7.49-7.57 (m, 1H), 7.83 (d, *J* = 1.6 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100 MHz) δ 48.8, 55.4, 115.3, 116.7, 124.4, 124.8, 126.0, 127.2, 127.6, 128.1, 129.2, 129.5, 135.2, 135.5, 135.9, 136.1, 138.4, 141.7, 154.5, 159.6, 194.7; FTIR (film) 3029,

1697, 1621, 1585, 1463, 1238, 742 $cm^{-1}$; HRMS (*m*/*z*): $[M+K]^+$calcd for $C_{23}H_{18}O_2K$: 365.0938; found: 365.0932.

**(*E*)-2-(4-Methoxybenzylidene)-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3j)**

140 mg, 86% yield; pale yellow solid; mp 166-168 $^oC$ (lit. 163-165 $^oC$)[22]; $R_f$ 0.28 (10% ethyl acetate in hexanes); $^1H$ NMR ($CDCl_3$, 400 MHz,) δ 3.76 (s, 3H), 5.30 (s, 1H), 6.76 (d, *J* = 8.8 Hz, 2H), 7.10-7.19 (m, 1H), 7.20-7.29 (m, 4H), 7.34-7.41 (m, 2H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.48-7.56 (m, 1H), 7.82 (d, *J* = 1.6 Hz ,1H), 7.92 (d, *J* = 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 48.9, 55.4, 114.1, 124.3, 126.0, 126.9, 127.1, 127.7, 127.9, 129.1, 133.6, 134.9, 135.6, 135.9, 136.4, 141.6, 154.4, 161.0, 194.8; FTIR (film) 3029, 1693, 1599, 1510, 1253, 1174, 743 $cm^{-1}$; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{23}H_{18}O_2Na$: 349.1199; found: 349.1193.

**(*E*)-2-(Naphthalen-2-ylmethylene)-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3k)**

140 mg, 81% yield; pale white solid; mp 200 $^oC$; $R_f$ 0.34 (10% ethyl acetate in hexanes); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 5.46 (s, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.20-7.28 (m, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.40-7.51 (m, 4H), 7.52-7.60 (m, 2H), 7.65-7.78 (m, 3H), 7.93-8.00 (m, 2H), 8.02 (d, *J* = 1.6 Hz, 1H);$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 49.1, 124.4, 126.1, 126.6, 127.2, 127.5, 127.7, 127.8, 127.9, 128.0 (2C), 128.7, 129.2, 131.8, 132.5, 133.1, 133.6, 135.2, 135.9 ,136.3, 138.7, 141.8, 154.5, 194.7; FTIR (film) 3019, 1684, 1605, 1581, 1294, 1091, 749 $cm^{-1}$; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{26}H_{19}O$: 347.1436; found: 347.1447.

**(*E*)-2-(4-Chlorobenzylidene)-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3l)**

130 mg, 79% yield; white solid; mp 196-199 $^oC$ (lit. 198-200 $^oC$)[22]; $R_f$ 0.42 (10% ethyl acetate in hexanes); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 5.31 (s, 1H), 7.10-7.25 (m, 7H), 7.34-7.45 (m, 4H), 7.54 (td, *J* = 1.2, 7.2 Hz, 1H), 7.78 (d, *J* = 2.0 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 48.8, 124.4, 126.1, 127.3, 127.7, 128.2, 128.8, 129.2,

132.6, 132.7, 134.3, 135.4, 135.8, 136.1, 139.1, 141.2, 154.4, 194.5; FTIR (film) 3025, 1686, 1614, 1291, 1090, 736 $cm^{-1}$; HRMS (*m*/*z*): $[M+K]^+$ calcd for $C_{22}H_{15}OClK$: 369.0443; found: 369.0438.

**(*E*)-2-(2-Bromo-4-fluorobenzylidene)-3-phenyl-2,3-dihydro-1H-inden-1-one (3m)**

163 mg, 83% yield; white solid; mp 142-144 $^oC$; $R_f$ 0.36 (10% ethyl acetate in hexanes); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 5.23 (s, 1H), 6.80-6.90 (m, 1H), 7.02 (d, $J$ = 8.0 Hz, 2H), 7.08-7.19 (m, 3H), 7.20-7.29 (m, 2H), 7.31 (s, 1H), 7.45 (t, $J$ = 7.6 Hz, 1H), 7.57 (td, $J$ = 1.2, 7.6 Hz, 1H), 7.91-8.02 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 48.3, 114.2 (d, $^2J$ = 21 Hz), 120.1 (d, $^2J$ = 24 Hz), 124.4, 125.7 (d, $^3J$ = 9 Hz), 126.3, 127.1, 128.0, 128.3, 128.9, 131.2 (d, $^4J$ = 4 Hz), 131.8 (d, $^3J$ = 9 Hz), 133.4, 135.5, 136.5, 141.0, 142.0, 154.4, 162.3 (d, $^1J$ = 253 Hz), 193.8; FTIR (film) 3076, 3029, 2884, 1700, 1594, 1481, 1226 $cm^{-1}$; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{22}H_{15}OFBr$: 393.0290; found: 393.0289.

**(*E*)-2-(2,6-Dichlorobenzylidene)-3-(4-methoxyphenyl)-2,3-dihydro-1H-inden-1-one (3n)**

142 mg, 78% yield; white solid; mp 126 $^oC$; $R_f$ 0.36 (10% ethyl acetate in hexanes); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 3.67 (s, 3H), 5.08 (s, 1H), 6.50 (d, $J$ = 8.8 Hz, 2H), 6.66 (d, $J$ = 8.8 Hz, 2H), 6.99-7.06 (m, 1H), 7.10 (d, $J$ = 7.6 Hz, 2H), 7.19 (d, $J$ = 8.0 Hz, 1H), 7.44 (t, $J$ = 7.2 Hz, 1H), 7.56 (td, $J$ = 7.6 Hz, 1H), 7.61 (s, 1H), 7.95 (d, $J$ = 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 48.2, 55.4, 113.5, 124.2, 126.5, 127.6, 128.1, 129.1, 129.5, 130.1, 132.9, 133.6, 134.2, 135.7, 137.2, 145.7, 154.5, 158.3, 193.4; FTIR (film) 3004, 2957, 2903, 2834, 1705, 1509,1249 $cm^{-1}$; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{23}H_{17}O_2Cl_2$: 395.0606; found: 395.0605.

**(*E*)-2-(4-Bromobenzylidene)-3-(4-isopropylphenyl)-2,3-dihydro-1*H*-inden-1-one (3o)**

188 mg, 90% yield; white solid; mp 203-205 $^oC$; $R_f$ 0.46 (10% ethyl acetate in hexanes); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 1.16 (d, $J$ = 6.8 Hz, 6H), 2.80 (h, $J$ = 6.8 Hz, 1H), 5.25 (s, 1H),

7.07 (d, $J$ = 8.0 Hz, 2H), 7.11 (d, $J$ = 8.0 Hz, 2H), 7.30 (d, $J$ = 8.8 Hz, 2H), 7.33-7.43 (m, 4H), 7.50-7.59 (m, 1H), 7.74 (s, 1H), 7.91 (d, $J$ = 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 24.0, 33.7, 48.5, 124.1, 124.4, 126.1, 127.2, 127.5, 128.0, 131.7, 132.8, 134.1, 135.3, 136.0, 138.4, 139.5, 147.8, 154.6, 194.7; FTIR (film) 2961, 2928, 2867, 1689, 1617, 1582, 1290 $cm^{-1}$; HRMS ($m/z$): $[M+H]^+$ calcd for $C_{25}H_{22}OBr$: 417.0854; found: 417.0845.

**(*E*)-2-(2-Bromo-4-fluorobenzylidene)-3-(4-methoxyphenyl)-2,3-dihydro-1*H*-inden-1-one (3p)**

178 mg, 85% yield; white solid; mp 114 °C; $R_f$ 0.28 (10% ethyl acetate in hexanes); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 3.73 (s, 3H), 5.19 (d, $J$ = 1.6 Hz, 1H), 6.79 (d, $J$ = 8.8 Hz, 2H), 6.86 (dt, $J$ = 8.4, 2.8 Hz, 1H), 6.94 (d, $J$ = 8.8 Hz, 2H), 7.24 (dd, $J$ = 8.4, 2.8 Hz, 1H), 7.28-7.32 (m, 2H), 7.44 (d, $J$ = 7.2 Hz, 1H), 7.56 (dt, $J$ = 7.6, 1.2 Hz, 1H), 7.80-7.92 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 47.5, 55.3, 114.1, 114.2 (d, $^2J$ = 21 Hz), 120.2 (d, $^2J$ = 24 Hz), 124.4, 125.8 (d, $^3J$ = 10 Hz), 126.2, 128.2, 128.9, 131.2 (d, $^4J$ = 4 Hz), 131.9, 132.0 (d, $^3J$ = 9 Hz), 133.2, 133.3, 135.5, 136.4, 142.1, 154.7, 158.5, 162.5 (d, $^1J$ = 253 Hz), 194.0; FTIR (film) 3074, 2937, 2839, 1701, 1594, 1481, 1324, 744 $cm^{-1}$; HRMS ($m/z$): $[M+H]^+$ calcd for $C_{23}H_{17}O_2FBr$: 423.0396; found: 423.0380.

**(*E*)-3-(4-Methoxyphenyl)-2-(4-(trifluoromethyl)benzylidene)-2,3-dihydro-1*H*-inden-1-one (3q)**

158 mg, 80% yield; white solid; mp 143-145 °C; $R_f$ 0.31 (10% ethyl acetate in hexanes); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 3.72 (s, 3H), 5.29 (s, 1H), 6.75 (d, $J$ = 8.8 Hz, 2H), 7.11 (d, $J$ = 7.8 Hz, 2H), 7.36 (dd, $J$ = 7.6, 0.8 Hz, 1H), 7.41 (t, $J$ = 7.2 Hz, 1H), 7.47-7.59 (m, 5H), 7.81 (d, $J$ = 2.0 Hz, 1H), 7.93 (d, $J$ = 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 48.0, 55.3, 114.9, 122.6, 124.5, 125.4 (q, $J$ = 4 Hz), 126.1, 128.2, 128.7, 130.8 (q, $J$ = 27 Hz), 131.3, 133.2, 133.6, 135.6, 135.9, 137.7, 141.3, 154.8, 158.7, 194.5 ; FTIR (film) 2936, 1700, 1626,

1509, 1323, 1068 cm $^{-1}$; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{24}H_{17}O_2F_3Na$: 417.1078; found: 417.1053.

**(*E*)-2-(4-(*tert*-butyl)benzylidene)-3-(4-methoxyphenyl)-2,3-dihydro-1*H*-inden-1-one (3r)**

170 mg, 89% yield; pale semi solid; $R_f$ 0.37 (15% ethyl acetate in hexanes); $^1$H NMR ($CDCl_3$, 400 MHz) δ 1.27 (s, 9H), 3.72 (s, 3H), 5.27 (s, 1H), 6.78 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.34-7.41 (m, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.49-7.55 (m, 1H), 7.82 (d, *J* = 1.6 Hz, 1H), 7.89-7.94 (m, 1H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100 MHz) δ 31.2, 35.0, 48.1, 55.3, 114.6, 124.3, 125.6, 126.0, 127.9, 128.7, 131.5, 131.7, 134.0, 135.1, 135.6, 136.1, 137.9, 153.3, 154.9, 158.5, 195.0; FTIR (film) 3033, 2961, 2933, 1697, 1605, 1509, 1463 cm$^{-1}$; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{27}H_{26}O_2Na$: 405.1825; found: 405.1815.

**(*E*)-3-(4-Methoxyphenyl)-2-(naphthalen-2-ylmethylene)-2,3-dihydro-1*H*-inden-1-one (3s)**

154 mg, 82% yield; white solid; mp 150-152 $^o$C; $R_f$ 0.23 (10% ethyl acetate in hexanes); $^1$H NMR $CDCl_3$, 400 MHz) δ 3.68 (s, 3H), 5.42 (s, 1H), 6.76 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.37-7.51 (m, 4H), 7.52-7.62 (m, 2H), 7.66-7.78 (m, 3H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.98-8.03 (m, 2H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100 MHz) δ 48.2, 55.2, 114.5, 124.3, 126.0, 126.5, 127.5, 127.7, 127.9, 128.0, 128.1, 128.7, 128.8, 131.8, 132.6, 133.1, 133.6, 133.9, 135.2, 135.7, 136.1, 139.0, 154.9, 158.6, 194.8.; FTIR (film) 3054, 3004, 2932, 1696, 1614, 1509, 1464 cm$^{-1}$; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{27}H_{20}O_2Na$: 399.1361; found: 399.1391.

**(*E*)-2-(3-Methoxybenzylidene)-3-(*p*-tolyl)-2,3-dihydro-1*H*-inden-1-one (3t)**

141 mg, 83% yield; light yellow solid; mp 96-98 $^o$C; $R_f$ 0.29 (10% ethyl acetate in hexanes); $^1$H NMR ($CDCl_3$, 400 MHz) 2.25 (s, 3H), 3.64 (s, 3H), 5.32 (s, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.97 (s, 1H), 7.05 (d, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.14-7.22 (m, 3H), 7.35-7.43

(m, 2H), 7.53 (d, $J$ = 8.6 Hz, 1H), 7.82 (s, 1H), 7.91 (d, $J$= 7.2 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 21.2, 48.5, 55.4, 115.3, 116.7, 124.4, 124.9, 126.0, 127.5, 128.0, 129.5, 129.9, 135.2, 135.6, 135.7, 136.0, 136.8, 138.5, 138.7, 154.7, 159.6, 194.9; FTIR (film) 3049, 3003, 2957, 2921, 1697, 1622, 1464 $cm^{-1}$; HRMS ($m/z$): $[M+Na]^+$calcd for $C_{24}H_{20}O_2Na$: 363.1361; found: 363.1331

**(*E*)-2-(4-Fluorobenzylidene)-3-(*p*-tolyl)-2,3-dihydro-1*H*-inden-1-one (3u)**

141 mg, 86% yield; white solid; mp 155-157 $^oC$; $R_f$ 0.36 (10% ethyl acetate in hexanes); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 2.25 (s, 3H), 5.27 (s, 1H), 6.87-7.19 (m, 2H), 7.03 (d, $J$ = 7.6 Hz, 2H), 7.11 (d, $J$ = 8.0 Hz, 2H), 7.33-7.42 (m, 2H), 7.43-7.57 (m, 3H), 7.79 (d, $J$ = 1.2 Hz, 1H), 7.92 (d, $J$ = 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 21.2, 48.4, 115.7 (d, $^2J$ = 21 Hz), 124.4, 126.0, 127.5, 128.0, 129.9, 130.5 (d, $^4J$ = 3 Hz), 133.5 (d, $^3J$ = 9 Hz), 134.3, 135.3, 136.1, 136.9, 138.3, 154.7, 163.3 (d, $^1J$ = 250 Hz), 194.7; FTIR (film) 3015, 2971, 2921, 1690, 1597, 1509 $cm^{-1}$; HRMS ($m/z$): $[M+H]^+$ calcd for $C_{23}H_{18}OF$: 329.1342; found: 329.1350.

**(*E*)-3-(4-Ethylphenyl)-2-(4-methylbenzylidene)-2,3-dihydro-1*H*-inden-1-one (3v)**

142 mg, 84% yield; white solid; mp 205-207 $^oC$ ; $R_f$ 0.42 (10% ethyl acetate in hexanes); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 1.15 (t, $J$ = 7.6 Hz, 3H), 2.29 (s, 3H), 2.55 (q, $J$ = 7.6 Hz, 2H), 5.30 (s, 1H), 7.02-7.10 (m, 4H), 7.16 (d, $J$ = 8.0 Hz, 2H), 7.34-7.44 (m, 4H), 7.48-7.55 (m, 1H), 7.81 (d, $J$ = 1.6 Hz, 1H), 7.92 (d, $J$ = 7.2 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 15.4, 21.6, 28.5, 48.6, 124.3, 126.0, 127.5, 127.9, 128.6, 129.4, 131.5, 131.8, 135.1, 135.7, 136.2, 137.6, 1389, 140.3, 142.9, 154.8, 195.0; FTIR (film) 3050, 2965, 2874, 1687, 1600, 1581 $cm^{-1}$; HRMS ($m/z$): $[M+Na]^+$ calcd for $C_{25}H_{22}ONa$: 361.1568; found: 361.1545.

**(*E*)-2-(4-Methylbenzylidene)-3-(4-(methylthio)phenyl)-2,3-dihydro-1*H*-inden-1-one (3w)**

153 mg, 86% yield; light yellow solid; mp 194-196 $^{o}$C; $R_f$ 0.30 (10% ethyl acetate in hexanes); $^{1}$H NMR ($CDCl_3$, 400 MHz) δ 2.30 (s, 3H), 2.40 (s, 3H), 5.30 (s, 1H), 7.05-7.13 (m, 4H), 7.17 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.34-7.43 (m, 4H), 7.52 (td, *J* = 7.6, 0.8 Hz, 1H), 7.82 (d, *J* = 1.6 Hz, 1H), 7.92 (d, *J* = 7.2 Hz, 1H) ; $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 100 MHz) δ 15.8, 21.6, 48.4, 124.4, 126.0, 127.1, 128.0, 128.2, 129.4, 131.3, 131.7, 135.1, 135.9, 136.3, 137.0, 137.3, 138.5, 140.4, 154.4, 194.8; FTIR (film) 3055, 3024, 2919, 1695, 1621, 1604 cm$^{-1}$; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{24}H_{21}OS$: 357.1343; found: 357.1313.

**(*E*)-2-(3-Chlorobenzylidene)-3-(3-methoxyphenyl)-2,3-dihydro-1*H*-inden-1-one (3x)**

149 mg, 83% yield; white solid; mp 140-142 $^{o}$C; $R_f$ 0.27 (10% ethyl acetate in hexanes); $^{1}$H NMR ($CDCl_3$, 400 MHz) δ 3.70 (s, 3H), 5.29 (s, 1H), 6.64-6.76 (m, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 7.13-7.25 (m, 3H), 7.33 (dt, *J* = 6.8, 1.6 Hz, 1H), 7.36-7.45 (m, 2H), 7.48 (s, 1H), 7.55 (td, *J* = 8.4, 1.2 Hz, 1H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H); $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 100 MHz) δ 48.8, 55.3, 112.6, 113.4, 120.4, 124.5, 126.1, 128.2, 129.5, 129.6, 129.7, 130.2, 130.8, 134.1, 134.4, 135.5, 135.9, 136.0, 139.9, 142.7, 154.3, 160.1, 194.4; FTIR (film) 3000, 2835, 1698, 1465, 1264, 743 cm$^{-1}$; HRMS (*m*/*z*): $[M+K]^+$ calcd for $C_{23}H_{17}O_2ClK$: 399.0549; found: 399.0539.

**(*E*)-2-(Furan-2-ylmethylene)-3-(4-methoxyphenyl)-2,3-dihydro-1*H*-inden-1-one (3y)**

133 mg, 84% yield; white solid; mp 144-146 $^{o}$C; $R_f$ 0.18 (10% ethyl acetate in hexanes); $^{1}$H NMR ($CDCl_3$, 400 MHz) δ 3.72 (s, 3H), 5.27 (s, 1H), 6.39 (s, 1H), 6.57 (s, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.29-7.41 (m, 2H), 7.44 (s, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.58 (s, 1H), 7.89 (d, *J* = 7.6 Hz, 1H); $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 100 MHz) δ 48.2, 55.3, 112.8, 114.1, 117.8, 121.3, 124.3, 126.1, 127.8, 128.8, 134.8, 135.1, 136.5, 136.7, 145.6, 151.3, 154.8, 158.4, 194.5; FTIR (KBr) 3062, 3004, 2957, 1693, 1622, 1509 cm$^{-1}$; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{21}H_{17}O_3$: 317.1178; found: 317.1167.

**(*E*)-2-(Thiophen-2-ylmethylene)-3-(*p*-tolyl)-2,3-dihydro-1*H*-inden-1-one (3z)**

131 mg, 83% yield; white solid; mp 196-198 $^{o}$C; $R_f$ 0.36 (10% ethyl acetate in hexanes); $^{1}$H NMR ($CDCl_3$, 400 MHz) δ 2.27 (s, 3H), 5.18 (s, 1H), 7.01 (t, *J* = 4.0 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 2.8 Hz, 1H), 7.35-7.45 (m, 3H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.90 (t, *J* = 7.2 Hz, 1H), 8.04 (s, 1H); $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 100 MHz) δ 21.2, 48.4, 124.3, 125.9, 127.7, 127.8, 127.9, 128.0, 129.8, 132.0, 134.2, 135.1, 136.2, 136.4, 136.8, 138.1, 138.6, 154.5, 194.5; FTIR (film) 3029, 2979, 2921, 1691, 1613, 1418 cm$^{-1}$; HRMS (*m*/*z*): $[M+Na]^+$calcd for $C_{21}H_{16}ONaS$: 339.0820; found: 339.0797.

**(*E*)-6-Benzylidene-7-(4-isopropylphenyl)-6,7-dihydro-5H-indeno[5,6-d][1,3]dioxol-5-one (3aa)**

146 mg, 86% yield; white solid; mp 240-242 $^{o}$C; $R_f$ 0.28 (10% ethyl acetate in hexanes); $^{1}$H NMR ($CDCl_3$, 400 MHz) δ 1.18 (d, *J* = 7.2 Hz, 6H), 2.82 (h, *J* = 7.2 Hz, 2H), 5.19 (d, *J* = 12 Hz, 1H), 6.04 (dd, *J* = 1.2, 17.2 Hz, 2H), 6.76 (s, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.21-7.28 (m, 3H), 7.29 (s, 1H), 7.41-7.50 (m, 2H), 7.73 (d, *J* = 1.6 Hz, 1H); $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 100 MHz) δ 24.0, 33.7, 48.4, 102.3, 102.8, 105.4, 127.2, 127.5, 128.5, 129.4, 131.4, 134.0, 134.4, 138.7, 139.3, 147.7, 148.6, 152.5, 154.3, 193.1; FTIR (film) 3058, 2936, 2820, 1667, 1594, 1596, 1442 cm$^{-1}$; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{26}H_{22}O_3Na$: 405.1461; found: 405.1445.

**(*E*)-2-Benzylidene-6-bromo-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3ab)**

152 mg, 81% yield; white solid; mp 195-197 $^{o}$C (lit. 194-196 $^{o}$C)[22]; $R_f$ 0.42 (10% ethyl acetate in hexanes); $^{1}$H NMR ($CDCl_3$, 400 MHz) δ 5.32 (s, 1H), 7.18 (d, *J* = 6.8 Hz, 1H), 7.21-7.30 (m, 8H), 7.42-7.55 (m, 2H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.88 (s, 1H), 8.08 (s, 1H); $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 100 MHz) δ 48.6, 122.4, 127.3, 127.4, 127.7, 127.8, 128.6, 129.2,

130.0, 131.6, 133.9, 136.7, 137.9, 138.0, 138.1, 140.9, 153.1, 193.3; FTIR (film) 3022, 2913, 1687, 1615. 1582, 1559, 1071 $cm^{-1}$; HRMS (*m*/*z*): $[M+K]^+$ calcd for $C_{22}H_{15}OBrK$: 412.9938; found: 412.9929.

**(*E*)-2-Benzylidene-3-(4-ethylphenyl)-2,3-dihydro-1*H*-inden-1-one (3ac)**

123 mg, 76% yield; white solid; mp 145-147 °C (lit. 147-149 °C)[22]; $R_f$ 0.48 (10% ethyl acetate in hexanes); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 1.14 (t, *J* = 7.6 Hz, 3H), 2.54 (q, *J* = 7.6 Hz, 2H), 5.32 (s, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.22-7.27 (m, 3H), 7.35-7.42 (m, 2H), 7.45-7.56 (m, 3H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.89-7.95 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 15.4, 28.3, 48.5, 124.3, 126.1, 127.6, 127.9, 128.5, 128.6, 129.7, 131.6, 134.3, 135.2, 135.6, 136.1, 138.7, 138.8, 142.9, 154.8, 195.0; FTIR (film) 3022, 2965, 2870, 1698, 1624, 1292 $cm^{-1}$; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{24}H_{20}ONa$: 347.1406; found: 347.1396.

**(*E*)-2-Benzylidene-3-(4-chlorophenyl)-2,3-dihydro-1*H*-inden-1-one (3ad)**

124 mg, 75% yield; brown solid; mp 136-138 °C (lit. 136-138 °C)[22]; $R_f$ 0.40 (10% ethyl acetate in hexanes); $^1H$ NMR ($CDCl_3$, 400 MHz) 5.35 (s, 1H), 7.13-7.21 (m, 4H), 7.24-7.30 (m, 3H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.39-7.48 (m, 3H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.86 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 48.1, 124.5, 126.0, 128.3, 128.6, 129.1, 129.2, 129.9, 131.4, 132.9, 134.0, 135.3, 136.1, 136.2, 138.2, 140.1, 154.0, 194.4; FTIR (film) 3025, 1698, 1624, 1489, 1292, 1092 $cm^{-1}$; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{22}H_{15}ONaCl$: 353.0709; found: 353.0714.

**(*E*)-2-(4-Bromobenzylidene)-3-phenyl-2,3-dihydro-1*H*-inden-1-one (3ae)**

133 mg, 71% yield; light yellow solid; mp 206-208 °C (lit. 204-206 °C)[22]; $R_f$ 0.43 (10% ethyl acetate in hexanes); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 5.23 (s, 1H), 7.05-7.12 (m, 1H), 7.13-7.20

(m, 4H), 7.21-7.26 (m, 2H), 7.27-7.36 (m, 4H), 7.47 (td, $J$ = 1.2, 7.6 Hz, 1H), 7.69 (d, $J$ = 2.0 Hz, 1H), 7.86 (d, $J$ = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 48.8, 124.3, 124.5, 126.1, 127.3, 127.7, 128.2, 129.2, 131.8, 132.8, 133.1, 134.3, 135.4, 136.1, 139.2, 141.2, 154.4, 194.5; FTIR (film) 3025, 2917, 1690, 1612, 1253, 743 $cm^{-1}$; HRMS ($m/z$): $[M+H]^+$ calcd for $C_{22}H_{16}OBr$: 375.0385; found: 375.0404.

**(*E*)-3-Phenyl-2-(thiophen-2-ylmethylene)-2,3-dihydro-1*H*-inden-1-one (3af)**

103 mg, 68% yield; light brown solid; mp 184-186 $^oC$; $R_f$ 0.30 (10% ethyl acetate in hexanes); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 5.21 (s, 1H), 7.00 (dd, $J$ = 5.2, 3.6 Hz, 1H), 7.16-7.22 (m, 1H), 7.25-7.30 (m, 2H), 7.30-7.34 (m, 3H), 7.37-7.46 (m, 3H), 7.49-7.56 (m, 1H), 7.89 (d, $J$ = 7.6 Hz, 1H), 8.05 (t, $J$ = 0.8 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 48.7, 124.3, 126.0, 127.2, 127.8, 128.0, 128.1, 129.1, 132.0, 134.2, 135.1, 135.9, 136.5, 138.5, 141.1, 154.2, 194.4; FTIR (film) 3029, 2967, 1692, 1613, 1290, 1093 $cm^{-1}$; HRMS ($m/z$): $[M+Na]^+$ calcd for $C_{20}H_{14}ONaS$: 325.0663; found: 325.0661.

**(*E*)-4-((1-Oxo-3-phenyl-1,3-dihydro-2H-inden-2-ylidene)methyl)benzonitrile (3ag)**

91 mg, 56% yield; white solid; mp 217-219 $^oC$; $R_f$ 0.34 (10% ethyl acetate in hexanes); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 5.33 (s, 1H), 7.11-7.18 (m, 3H), 7.19-7.25 (m, 2H), 7.35-7.40 (m, 1H), 7.43 (t, $J$ = 7.6 Hz, 1H), 7.46-7.55 (m, 4H); 7.56 (td, $J$ = 7.6, 0.8 Hz, 1H), 7.79 (d, $J$ = 2.0 Hz, 1H), 7.94 (d, $J$ = 7.6 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 48.8, 112.6, 118.5, 124.6, 126.2, 127.5, 127.8, 128.4, 129.3, 131.3, 132.1, 133.1, 135.8, 135.9, 138.7, 140.8. 142.1, 154.4, 194.1; FTIR (film) 3024, 2220, 1684, 1625, 1292, 737 $cm^{-1}$; HRMS ($m/z$): $[M+H]^+$ calcd for $C_{23}H_{16}NO$: 322.1232; found: 322.1240.

**Experimental procedure for the preparation of 10 and 11**

In an oven-dried 25 mL round-bottomed flask, malononitrile (0.2 mmol) was taken in 1 mL solvent (MeOH for **10**; EtOH for **11**). NaOH (0.2 mmol) was dissolved in ca. 0.3 mL of water and added to the reaction at rt. (*E*)-2-Benzylidene-3-phenyl-2,3-dihydro-1*H*-inden-1-one **3a** (0.1 mmol) was added to the reaction in one portion. Reaction was allowed to stir at rt till complete consumption of **3a.** Reaction was monitored by TLC. Upon completion, the solvent was removed under reduced pressure. Water was added to reaction mixture and extracted with ethyl acetate (3×3 mL). Brine wash (1×5 mL) was given to the combined organic extractions and dried over anhydrous $Na_2SO_4$. Removal of solvent and silica gel column separation of crude using hexanes and ethyl acetate mixture (19:1) afforded the corresponding 5*H*-indeno[1,2-*b*]pyridine derivative.

**2-Methoxy-4,5-diphenyl-5*H*-indeno[1,2-*b*]pyridine-3-carbonitrile (10)**

31 mg, 82% yield; creamy white solid; mp 145-147 $^{o}$C; $R_f$ 0.61 (20% ethyl acetate in hexanes); $^{1}$H NMR ($CDCl_3$, 400 MHz) δ 4.25 (s, 3H), 5.04 (s, 1H), 6.49-6.56 (m, 2H), 6.90-6.96 (m, 2H), 6.99 (d, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 2H), 7.20-7.26 (m, 2H), 7.26-7.34 (m, 2H) 7.39 (td, *J* = 1.2, 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 8.10 (d, *J* = 7.6 Hz, 1H); $^{13}$C{$^{1}$H} NMR ($CDCl_3$, 100 MHz) δ 51.4, 54.9, 93.8, 115.8, 122.1, 125.5, 126.7, 127.9, 128.1, 128.2, 128.3, 128.5. 129.1, 130.8, 133.2, 134.7, 138.8, 138.9, 151.4, 153.3, 161.8, 166.4; FTIR (film) 3027, 2923, 2853, 2223, 1561, 1455, 1363, 1150 cm$^{-1}$; HRMS (*m*/*z*): $[M+H]^+$ calcd for $C_{26}H_{19}N_2O$: 375.1492; found: 375.1491.

**2-Ethoxy-4,5-diphenyl-5*H*-indeno[1,2-*b*]pyridine-3-carbonitrile (11)**

29 mg, 74% yield; creamy white solid; mp 151-153 $^{o}$C; $R_f$ 0.67 (20% ethyl acetate in hexanes); $^{1}$H NMR ($CDCl_3$, 400 MHz) δ 1.55 (t, *J* = 7.2 Hz, 3H), 4.72 (q, *J* = 7.2 Hz, 2H), 5.03 (s, 1H), 6.52 (d, *J* = 7.2, Hz, 2H), 6.93 (t, *J* = 7.2 Hz, 2H), 6.96-7.10 (m, 3H), 7.21-7.31 (m, 4H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 1H); $^{13}$C{$^{1}$H}

NMR ($CDCl_3$, 100 MHz) δ 14.7, 51.4, 63.6, 93.8, 115.8, 122.0, 125.5, 126.7, 127.9, 128.0, 128.1, 128.3, 128.4, 129.0, 130.7, 132.9, 134.8, 138.8, 139.0, 151.1, 153.3, 161.7, 166.1; FTIR (film) 3027, 2984, 2223, 1735, 1560, 1377, 1337 $cm^{-1}$; HRMS (*m*/*z*): $[M+K]^+$ calcd for $C_{27}H_{20}KN_2O$: 427.1212; found: 427.1201.

**Experimental procedure for the preparation 12**

A modified literature procedure was followed to synthesis **12**.Under open atmosphere, (*E*)-2-Benzylidene-3-phenyl-2,3-dihydro-1*H*-inden-1-one **3a** (0.1 mmol), ammonium acetate (0.4 mmol), pyridinium bromine salt (0.2 mmol) and acetonitrile (3 mL) were successively added to oven dried RB flask. The mixture was then refluxed at 100 $^oC$ for 24 h. Upon cooling down to room temperature, the solvent was removed under reduced pressure. Water was added to reaction mixture and extracted with ethyl acetate (3×3 mL). Brine wash (1×5 mL) was given to the combined organic extractions and dried over anhydrous $Na_2SO_4$. Removal of solvent and silica gel column separation of crude using hexanes and ethyl acetate mixture (19:1) afforded the corresponding product **12**.

**3,4,5-Triphenyl-5*H*-indeno[1,2-*b*]pyridine (12)**

32 mg, 80% yield; creamy white solid; mp 186-188 $^oC$; $R_f$ 0.75 (20% ethyl acetate in hexanes); $^1H$ NMR ($CDCl_3$, 400 MHz) δ 5.29 (s, 1H), 6.68 (dd, *J* = 1.6, 6.8 Hz, 2H), 6.90-7.02 (m, 3H), 7.17-7.30 (m, 7H), 7.36 (t, *J* = 6.8 Hz, 1H), 7.41-7.54 (m, 4H), 7.55 (s, 1H), 8.11-8.20 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 51.8, 119.5, 121.5, 125.3, 126.5, 127.3, 127.8, 128.1, 128.2, 128.3, 128.9, 129.0, 129.5, 137.9, 138.6, 138.8, 140.2, 147.9, 149.7, 157.5, 161.1; FTIR (film) 3058, 3029, 2922, 2852, 1585, 1557, 1494, 1368, 1264 $cm^{-1}$; HRMS (*m*/*z*): $[M+H]^+$calcd for $C_{30}H_{22}N$: 396.1752; found: 396.1762.

**Experimental procedure for the preparation 13**

(*E*)-2-Benzylidene-3-phenyl-2,3-dihydro-1*H*-inden-1-one **3a** (0.2 mmol) was hydrogenated in EtOAc (2 mL) using 6 mg of 10% Pd/C at rt under $H_2$ (1 atm). Reaction was monitored by TLC. Upon completion, the catalyst was removed using celite filtration using EtOAc. Solvent was removed under reduced pressure. The dr was determined by $^1$H NMR analysis of the crude reaction mixture and was subsequently purified by silica gel column separation using hexanes and ethylacetate mixture (18:2, v/v) as mobile phase afforded the corresponding product **13**.

**2-Benzyl-3-phenyl-2,3-dihydro-1*H*-inden-1-one (13)**

55 mg, 92% yield; pale yellow solid; mp 70-72 $^o$C; $R_f$ 0.73 (20% ethyl acetate in hexanes); $^1$H NMR ($CDCl_3$, 400 MHz) δ 2.26 (dd, *J* = 14.4, 10.8 Hz, 1H), 2.92-3.11 (m, 2H), 3.20-3.48 (m, 3H), 4.20 (s, 1H), 4.65 (d, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 2.8 Hz, 2H), 6.76-6.88 (m, 4H), 7.11-7.31 (m, 16H), 7.41 (q, *J* = 7.6 Hz, 2H), 7.34 (q, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H); $^{13}$C{$^1$H} NMR ($CDCl_3$, 100 MHz) δ 32.3, 35.8, 49.0, 49.8, 55.1, 59.5, 123.6, 123.7, 126.0, 126.6, 126.8, 126.9, 127.0, 127.1, 128.0, 128.1, 128.2, 128.4, 128.6, 128.7, 128.8, 129.5, 129.6, 135.3, 135.4, 136.1, 136.3, 139.0, 140.0, 140.4, 143.3, 156.5, 156.9, 207.0, 207.2; FTIR (film) 3061, 3027, 2920, 1712, 1602, 1454, 1290, 747, 700 cm$^{-1}$; HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{22}H_{18}ONa$: 321.1250; found: 321.1246.

**Experimental procedure for recovery of the Pd-BNP catalyst**

For recyclability of Pd-BNP, the reaction was repeated with *2*-iodochalcone **1a** as substrate in 1.0 mmol scale retaining the same conditions such as *N*-tosylhydrazone **2a** (2.5 equiv.), $Et_3N$ (3 equiv.), and 3 mL 1,4-dioxane at 80 $^o$C, except using the recovered Pd-BNP catalyst rather than fresh catalyst. After completion of the annulation reaction, the reaction mixture was allowed to cool to room temperature. EtOH (5 mL) was added to the reaction mixture and centrifuged. The liquid then decanted to a 50 mL conical flask. Again EtOH (5

mL) was added and centrifuged and decanted to the same conical flask, this procedure was repeated up to two to three times. After that the catalyst was washed with nano pure water (5 mL) and ethanol (5 mL) two to three times. Finally, the resulting solid black coloured particles (Pd-BNP) dried under vacuum. The dried catalyst was reused for further catalytic cycle. The collected liquid was concentrated by reduce pressure. The resulting reaction mixture was purified by column chromatography on silica gel (hexanes: ethyl acetate) to afford **3a** as desired product. The amounts of Pd nanocatalyst recovered in consecutive five catalytic cycles are 17.4 mg, 16.2 mg, 15.0 mg, 13.6 mg and 12.1 mg.

**Hot Centrifugation Test**

To determine the leaching of Pd-BNP catalyst in the Pd-BNP catalyzed carbene insertion reaction, a centrifugation test was carried out under the standard reaction condition.

2'-Iodochalcone **1a** (1.0 mmol, 1.0 equiv.),*N*-tosylhydrazone **2a** (2.5 equiv.), Pd-BNP catalyst (19.3 mg, 2 mol%), $Et_3N$ (3 equiv.) and 1,3,5-trimethoxybenzene (1 equiv.) in 3 mL 1,4-dioxane were taken in oven dried reaction tube equipped with magnetic pellet and stirred at 80 $^{o}$C. After 3 h of reaction, reaction mixture was centrifuged; decane and Pd-BNP catalyst was separated from the reaction mixture. From the mother liquid (filtrate), 0.1 mL of filtrate was taken and extracted with ethylacetate and $^{1}$H NMR showed that 31% yield of **3a** was obtained. From the remaining mother liquid *i.e.*, Pd-BNP free-reaction mixture, 0.1 mL of aliquot was withdrawn for ICP-OES analysis and rest amount of filtrate was then used for annulation reaction under the similar conditions and continued up to 12 h and 34% yield of **3a** was obtained (yield was determined by $^{1}$H NMR). Similarly, centrifugation was done at 6 h. $^{1}$H NMR analysis of mother liquor showed 54% yield of **3a**. Catalyst-free mother liquor was allowed to continue the reaction at 80 $^{o}$C. The yield of **3a** was not increased further.

**Mercury poisoning experiment**

Mercury poisoning experiment was performed to support that the carbene insertion reaction of 2'-iodochalcone and *N*-tosylhydrazonewas accelerated by Pd-BNP catalyst not by the leached Pd. Three sets of reactions were conducted:

In first set of reaction, Hg (30 equiv.) and Pd-BNP (2 mol%) in 1,4-dioxane in presence of air were stirred at room temperature for 2 h, then other reagents: **1a** (0.5 mmol, 1.0 equiv.), **2a** (2.5 equiv.), Pd-BNP (2 mol%), $Et_3N$ (3 equiv.) and 1,3,5-triamethoxylbenzene (1.0 equiv.) were added and stirred at 80 $^oC$. Even trace amount of product **3a** was not detected in the reaction; even after 24 h.

In second set of reaction, Hg (30 equiv.) was added at a time with all other reagents: **1a** (0.5 mmol, 1.0 equiv.), **2a** (2.5 equiv.), Pd-BNP (2 mol%), $Et_3N$ (3 equiv.) and 1,3, 5-trimethoxylbenzene (1.0 equiv.) in 1,4-dioxane solvent and stirred at 80 $^oC$ upto 24 h. Complete inhibition in the product **3a** formation was observed.

In third set of reaction, Hg (30 equiv.) was added after continuing the standard reaction for 4 h at 31% yield for **3a**, slight progress in the reaction was observed and 37% yield of **3a** was obtained and yield was determined by $^1H$-NMR spectra.

These results displayed that active and main catalyst in the annulation reaction is heterogeneous Pd-BNP.

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### Notes

The authors declare no competing financial interest.

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## ASSOCIATED CONTENT

### Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Copies of $^{1}H$ and $^{13}C$ NMR spectra. (PDF)

Crystallographic data for **3m** (CIF)

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