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FULL PAPER

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Supported palladium nanoparticle-catalysed Suzuki–Miyaura cross-coupling approach for synthesis of aminoarylbenzosuberene analogues from natural precursor

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A semi-synthetic method has been developed for the synthesis of aminoarylbenzosuberenes (AABs) from naturally occurring himachalenes, an isomeric mixture of sesquiterpenes present in *Cedrus deodara* oil. Polymer-stabilized Pd(0) nanoparticle-catalysed Suzuki–Miyaura cross-coupling reaction of aminovinyl bromide-substituted benzosuberenes has been adopted for AAB synthesis. The catalyst performed well with different amine substituents, and was recycled up to five times. The synthesis of such arylated benzosuberene class of compounds from natural precursors following semi-synthetic approaches could provide an attractive alternative method with reduced number of steps.

KEYWORDS
benzosuberenes, heterogeneous catalysts, himachalenes, Suzuki–Miyaura cross-coupling

1 | INTRODUCTION

Benzosuberenes are important key structural motifs in various natural products such as terpenes,[1,2] alkaloids[3] and pharmacologically active compounds like nortriptyline which has antidepressant activity[4] and (−)colchicine which is an antitumour agent.[5] The role of arylated benzosuberene derivatives (Figure 1) is established in medicinal chemistry as anticancer agents because of their structural reminiscence to colchicine and combretastatin CA4 and CA1.[6]

Various synthetic approaches for the synthesis of arylated benzosuberene have been developed by Pinney and co-workers[7] starting from tetrahydronaphthalene following six steps with arylation being carried out using trimethoxyaryllithium, synthesized from 3,4,5-trimethoxybromobenzene, under harsh reaction conditions with poor overall yields. The developed method was further modified[8] for benzosuberene synthesis using arylaldehyde as the starting molecule following a similar approach. In another report, Jorden and co-workers synthesized metabolites of tamoxifen from benzosuberone using pyridine hydrobromide perbromide as brominating agent, followed by arylation with anhydrous zinc chloride, phenyllithium and $Pd(PPh_3)_4$.[9] All the reported methods followed multistep synthesis involving lithiation under harsh conditions, selective reductions and Grignard reagents. In this context, we envisioned that the aminovinyl bromide-substituted benzocycloheptene that was synthesized previously[10] in our laboratory could be a precursor for the synthesis of arylated benzosuberene. In addition, another synthetic route for the synthesis of arylated benzosuberene is the formation of enol triflate from benzosuberone followed by Suzuki–Miyaura (SM) cross-coupling with arylboronic acids.[11] Extensive efforts have been devoted to SM cross-coupling reactions of vinyl halides catalysed by copper[12] and palladium.[13] Recently, Li and co-workers have reported SM cross-coupling reaction of trialkylboranes with aliphatic vinyl halide in $Pd(OAc)_2$/RuPhos system.[14] Similarly, SM cross-coupling reactions of aryl and vinyl halides with aryl and aliphatic boronic acids have been reported catalysed by *trans*-PdBr(N-Succ)$(PPh_3)_2$ (a precatalyst),[15] $Pd(P(o\text{-Tol})_3)_2$,[16] $Pd_2(dba)_3/P(t\text{-Bu})_3$[17] and $Pd(PPh_3)_4$.[18] Although the handling of these

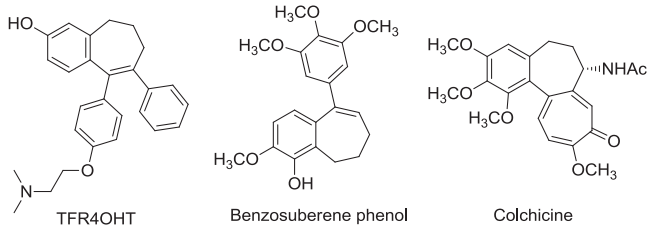


FIGURE 1 Representative biologically active molecules with benzosuberene as the central core

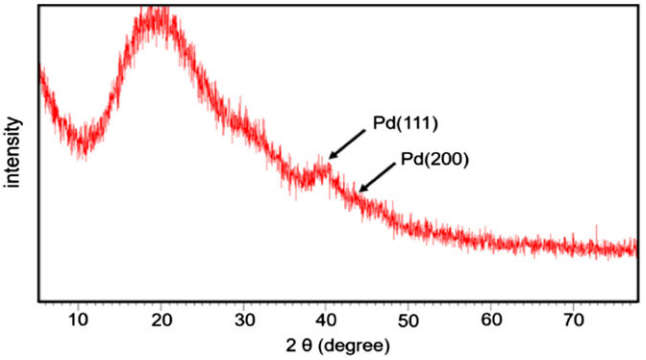
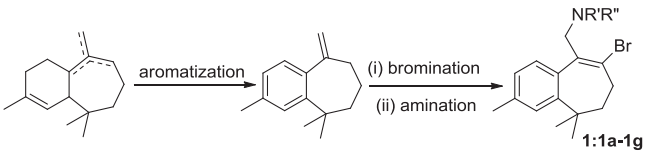


FIGURE 3 Powder XRD pattern for Pd@PS catalyst



SCHEME 1 Representative method of aminovinyl bromide-substituted benzocycloheptene synthesis from himachalene[10]

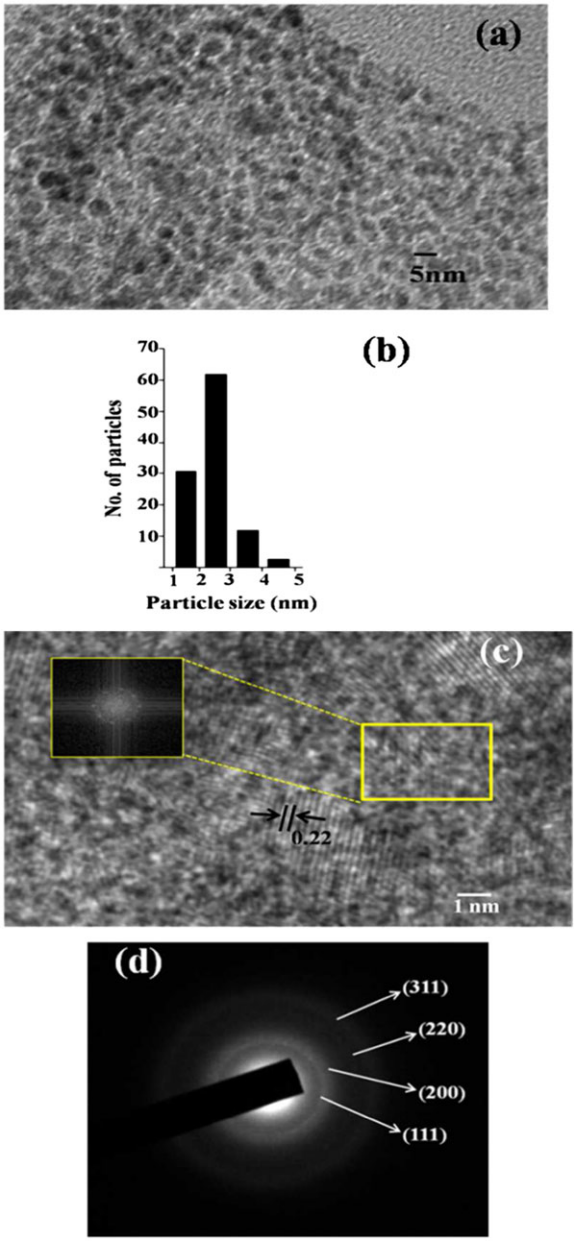


FIGURE 2 (a) TEM image at 5 nm scale. (b) histogram describing the particle size distribution. (c) high-resolution TEM image showing fast-Fourier transform of marked area. (d) SAED pattern of Pd@PS

air-sensitive ligands and catalysts is difficult, the methodologies find their value for the total synthesis of some complex molecules. The scope of this transformation has been explored for the synthesis of (+)frondosin A[19] and intramolecular β-alkyl[20] following SM cross-coupling for taxane skeleton.

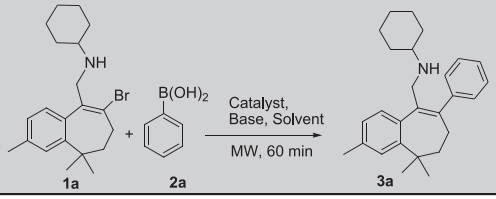
The development of supported transition metal nanoparticles (NPs) as catalysts for various organic transformations has attracted much attention in recent years.[21] Recently, our group has been working in the area of exploration of heterogeneous NPs as catalysts in various organic transformations[22] and synthetic modulation of natural products.[10] Herein, we report a semi-synthetic approach to aminoarylbenzosuberenes (AABs) from aminovinyl bromide-substituted benzosuberenes (synthesized from himachalene, an essential oil of *Cedrus deodara*) following SM cross-coupling reactions under ligand-free polymer-stabilized Pd(0) (Pd@PS)-catalysed conditions.

2 | RESULTS AND DISCUSSION

2.1 | Preparation and characterization of Pd@PS catalyst

The Pd@PS NP catalyst was prepared following a reduction deposition method[21] of partially borohydride (BH_4^-) exchanged Amberlite IRA-900 chloride from resin to influence faster reduction of Pd(II) salts to Pd(0) and simultaneous impregnation into hydrophobic pockets of the polymeric matrix. The characterization of the Pd@PS catalyst was done by scanning electron microscopy (SEM),

TABLE 1 Optimization of reaction conditions for SM cross-coupling reaction[a]



Entry	Catalyst (Mol%)	Temp. (°C)	Base	Time (min/h)	Solvent	Yield (%)[b]
1[c]	Pd@PS (4)	110	K_2CO_3	15 h	DMF	70
2	Pd@PS (4)	110	K_2CO_3	60	DMF	97
3	Pd@PS (3)	110	DABCO	60	DMF	10
4	Pd@PS (3)	110	DBU	60	DMF	Trace
5	Pd@PS (3)	110	Et_3N	60	DMF	20
6	Pd@PS (3)	110	K_2CO_3	60	1,4-Dioxane	40
7	Pd@PS (3)	110	K_2CO_3	60	EtOH	NR
8	Pd@PS (3)	110	K_2CO_3	60	THF	NR
9	Pd@PS (3)	110	K_2CO_3	60	DMA	76
10	Pd@PS (3)	110	K_2CO_3	60	PEG-400	95
11	Pd@PS (3)	110	K_2CO_3	60	DMF	98
12	Pd@PS (3)	110	Na_2CO_3	60	DMF	52
13	Pd@PS (3)	110	Cs_2CO_3	60	DMF	54
14[d]	Pd@PS (3)	110	Cs_2CO_3	90	DMF	79
15	Pd@PS (3)	110	K′OBu	60	DMF	69
16	Pd@PS (2)	110	K_2CO_3	60	DMF	80
17	$Pd(OAc)_2$ (3)	110	K_2CO_3	60	DMF	85
18	$Pd(PPh_3)_4$ (3)	110	K_2CO_3	60	DMF	73
19	Pd/C (3)	110	K_2CO_3	60	DMF	54
20	Pd@PS (3)	90	K_2CO_3	60	DMF	60
21	Pd@PS (3)	110	K_2CO_3	45	DMF	80

[a]Reaction conditions: **1a** (0.27 mmol), **2a** (0.32 mmol), Pd@PS (3 mol% of Pd), K_2CO_3 (0.54 mmol), DMF (1 ml), 110 °C, 60 min.

[b]Isolated yield of product.

[c]Conventional heating.

[d]3 equiv. of base.

transmission electron microscopy (TEM), X-ray diffraction (XRD) analysis and selected area electron diffraction (SAED) studies (Figure 2). The dispersion of the Pd NPs in the polymer matrix was analysed using SEM and SEM-EDS (supporting information, Figure S1). Further, low-field TEM images (Figure 2a) revealed the impregnation of the Pd NPs with maximum average particle size of between 1 and 3 nm (Figure 2b) as calculated from TEM image (Figure 2a). The crystal structure of Pd@PS was investigated using high-resolution TEM, showing the interplanar distance between two lattice fringes as 0.22 nm (Figure 2c) corresponding to the (111) plane of Pd. The four Debye–Scherrer rings observed in the SAED pattern of Pd@PS are assigned to (111), (200), (220) and (311) planes of Pd NPs (Figure 2 d). The fast-Fourier transform diffractogram of a selected region also shows the arrangement of Pd metal in the catalyst (Figure 2c).

Powder XRD analysis was also performed for the Pd@PS catalyst, and peaks are clearly visible at ~ 40° and ~ 45° (Figure 3) corresponding to (111) and (200) planes of Pd which also correlate with the SAED pattern (Figure 2d). The Hg(0) poisoning test was also performed to confirm the heterogeneity of the Pd@PS catalyst.

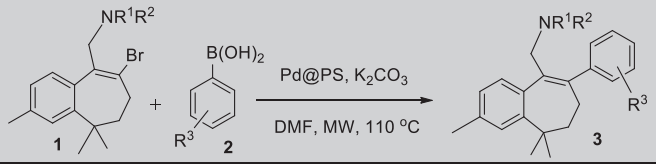
In our earlier report,[10] we described the synthesis of aminovinyl bromide-substituted benzocycloheptene (**1**) from himachalene following aromatization, bromination and

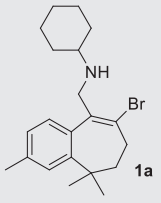
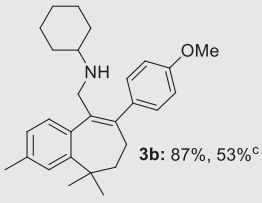
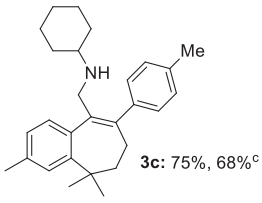
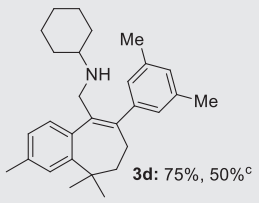
amination approaches (Scheme 1). The same strategy was employed for the synthesis of compounds **1a**–**1 g**, of which **1a**–**1e** were compared with reported data and **1f** and **1 g** were characterized using NMR spectral analysis (supporting information). These synthesized compounds were further applied for novel AAB molecule synthesis following SM cross-coupling reactions (Scheme 1).

Initially we focused on SM cross-coupling reaction of aminovinyl bromide-substituted benzocycloheptene **1a** (1 equiv.) with phenylboronic acid **2a** (1.2 equiv.) using Pd@PS (4 mol%) and K_2CO_3 (2 equiv.) under conventional heating at 120 °C for 15 h, which provided the desired product **3a** in 70% yield (Table 1, entry 1). In contrast, the same reaction under microwave irradiation (100 W) at 110 °C provided **3a** in 97% yield with a reaction time of 60 min (Table 1, entry 2). A detailed optimization study was conducted by screening some organic bases (Table 1, entries 3–5) and solvents (Table 1, entries 6–10) but no noticeable change in the product yield was observed. Further optimization studies were carried out with various inorganic bases (K_2CO_3, Na_2CO_3, Cs_2CO_3 and K^{t}OBu) (Table 1, entries 11–15) and changing the catalyst loading (Table 1, entry 16), from which K_2CO_3 was found to be a suitable base. Indeed, the reaction catalysed by homogeneous $Pd(OAc)_2$, $Pd(PPh_3)_4$ and heterogeneous Pd/C catalysts gave lower yield of desired product (Table 1, entries 17–19). The product yield dropped on reducing the temperature and reaction time (Table 1, entries 20 and 21). The optimized reaction conditions were selected to be: Pd@PS (3 mol%), K_2CO_3 (2 equiv.) in DMF solvent at 110 °C under microwave irradiation (100 W) for 60 min, giving the highest yield of product **3a** of 98% (Table 1, entry 11).

The versatility of the developed protocol was extended for SM cross-coupling reactions of various aminovinyl bromide-substituted benzocycloheptenes (**1**) with a variety of arylboronic acids (Table 2). The coupling reaction of *N*-cyclohexylaminovinyl bromide benzocycloheptene (**1a**) with electron-rich *p*-OMe-, *p*-Me- and 3,5-dimethyl-substituted phenylboronic acids as nucleophilic partners under optimized conditions gave the desired AAB products **3b–d** in 75–87% yields (Table 2, entries 1–3). *p*-Acetyl- and 3,4-dichloro-substituted phenylboronic acids also participated in

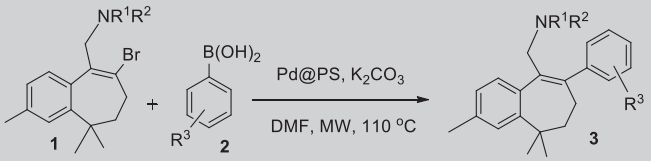
TABLE 2 Pd@PS-catalysed SM cross-coupling reaction of *N*-alkylvinyl bromide benzocycloheptenes[a]

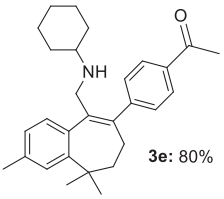
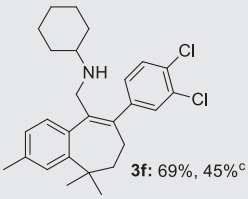
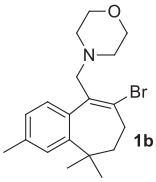
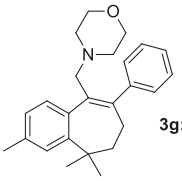
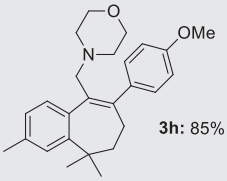
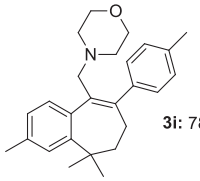
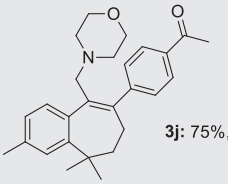
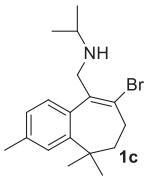
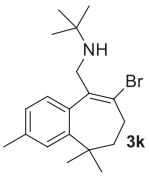


Entry	Reactant (**1**)	R^3	Product (**3**)
1		4-OMe	 **3b:** 87%, 53%[c]
2	**1a**	4-Me	 **3c:** 75%, 68%[c]
3	**1a**	3,5-dimethyl	 **3d:** 75%, 50%[c]

(*Continues*)

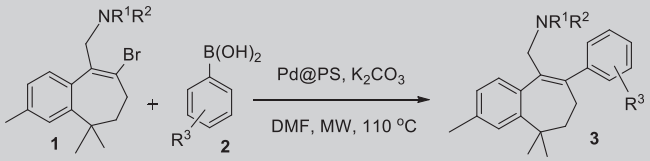
TABLE 2 (Continued)

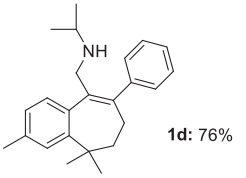
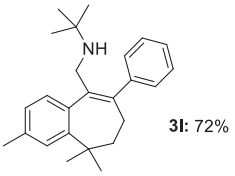


4	**1a**	4-COMe	 **3e:** 80%
5	**1a**	3,4-dichloro	 **3f:** 69%, 45%[c]
6	 **1b**	H	 **3g:** 78%, 80%[c]
7	**1b**	4-OMe	 **3h:** 85%, 60%[c]
8	**1b**	4-Me	 **3i:** 78%, 60%[c]
9	**1b**	4-COMe	 **3j:** 75%, 55%[c]
10	 **1c**	H	 **3k**

(*Continues*)

TABLE 2 (Continued)



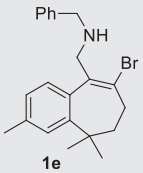
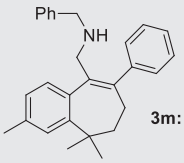
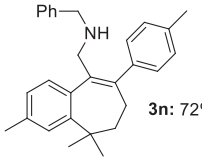
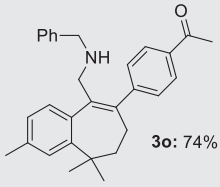
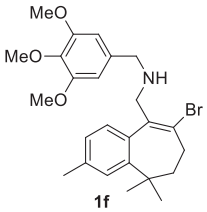
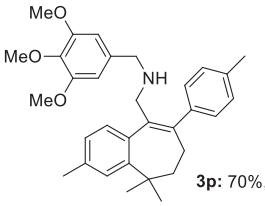
11	 **1d:** 76%	H	 **3l:** 72%

[a]Reaction conditions: **1** (1 equiv.), arylboronic acids **2** (1.2 equiv.), Pd@PS (3 mol% of Pd), K_2CO_3 (2 equiv.), DMF (1 ml), 110 °C, 60 min.

[b]Isolated yield of product.

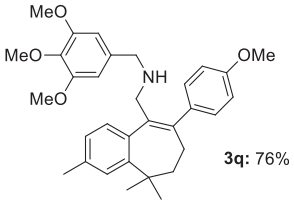
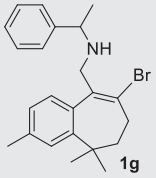
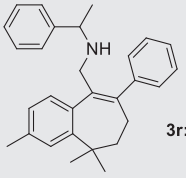
[c]Isolated yield of product in $Pd(OAc)_2$.

TABLE 3 Pd@PS-catalysed SM cross-coupling reaction of *N*-benzylvinyl bromide benzocycloheptenes[a]

Entry	Reactant (**1**)	R^2	Product (**3**)
12	 **1e**	H	 **3m:** 68%, 71%[c]
13	**1e**	4-Me	 **3n:** 72%, 68%[c]
14	**1e**	4-COMe	 **3o:** 74%, 72%[c]
15	 **1f**	4-Me	 **3p:** 70%, 60%[c]

(*Continues*)

TABLE 3 (Continued)

16	**1f**	4-OMe	 **3q:** 76%
17		H	 **3r:** 75%, 68%[c]

[a]Reaction conditions: **1** (1 equiv.), arylboronic acids **2** (1.2 equiv.), Pd@PS (3 mol%), K_2CO_3 (2 equiv.), DMF (1 ml), 110 °C, 60 min.

[b]Isolated yield of product.

[c]Isolated yield of product in $Pd(OAc)_2$.

similar reactions producing desired products **3e** and **3f** in considerably good yields of 69 and 80% (Table 2, entries 4 and 5). Gratifyingly, morpholine-substituted vinyl bromide benzocycloheptene **1b** was found to be an excellent substrate for the SM cross-coupling reaction with various electron-rich and electron-deficient arylboronic acids as nucleophilic partners and afforded the desired products **3 g–j** in good yields of 75–85% (Table 2, entries 6–9). Interestingly, no significant steric effects of highly substituted acyclic alkylamine compounds **1c** and **1d** were observed for SM cross-coupling reaction to produce the corresponding products **3 k** and **3 l** in 76 and 72% yields, respectively. *N*-benzylaminovinyl bromide benzocycloheptene **1e** (Table 3).was also found to be a good substrate for this transformation and smoothly coupled with electron-rich and electron-deficient arylboronic acids to give the desired coupled products **3 m–o** (68–74%). Most of the methoxy-substituted benzosuberenes (Figure 1) are good bioactive targets; therefore compounds **3p** and **3q** were synthesized successfully from **1f** following the same approach. Similarly, methyl substitution at α-position of benzylamine in compound **1 g** had no effect on the reaction giving the product **3r** in 75% yield (Table 3, entry 17).

The structure of compound **3i** obtained as colourless crystals from DCM–hexane (1:1) mixture was further confirmed from X-ray crystallography studies (Figure 4; supporting information).

To investigate the applicability of the present method for other bicyclic vinyl bromides, 2-bromo-1*H*-indene (**4a**) was used as a substrate under standard reaction conditions. This reacted smoothly with arylboronic acids to give the corresponding products **5a** and **5b** in 80–81% yields (Scheme 2).[23]

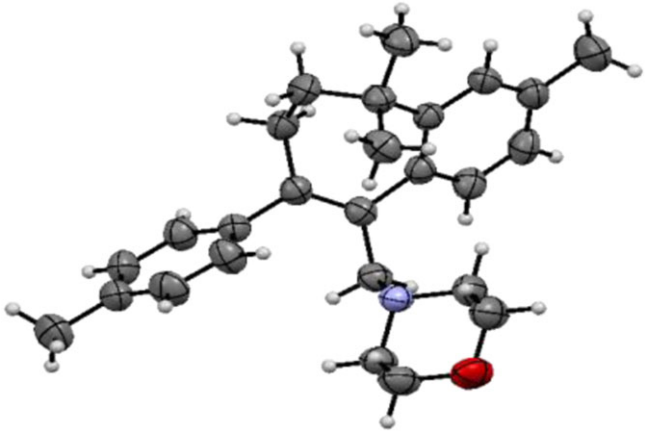
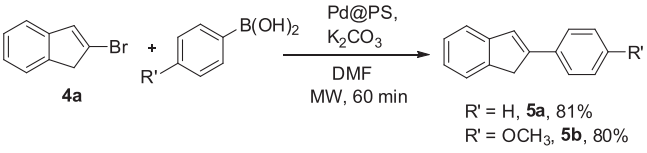


FIGURE 4 X-ray crystal structure of **3i** with an ellipsoid contour probability level of 50% (CCDC 1476591)



SCHEME 2 Pd@PS-catalysed Suzuki cross-coupling of vinyl bromides

2.2 | Recyclability experiment

The recyclability of the Pd@PS catalyst was investigated by following the SM cross-coupling reaction of **1a** and phenylboronic acid under optimized reaction conditions. After completion of the reaction the catalyst was recovered by simple filtration, washed with water and acetone and dried under reduced pressure. The catalyst was reused for subsequent reactions and found to be active for up to five runs without significant loss of activity. TEM analysis of the Pd@PS catalyst was performed after five reaction cycles to determine the morphology of the catalyst and distribution of Pd NPs at 100 nm scale with average particle size of 4–5 nm (Figure 5).

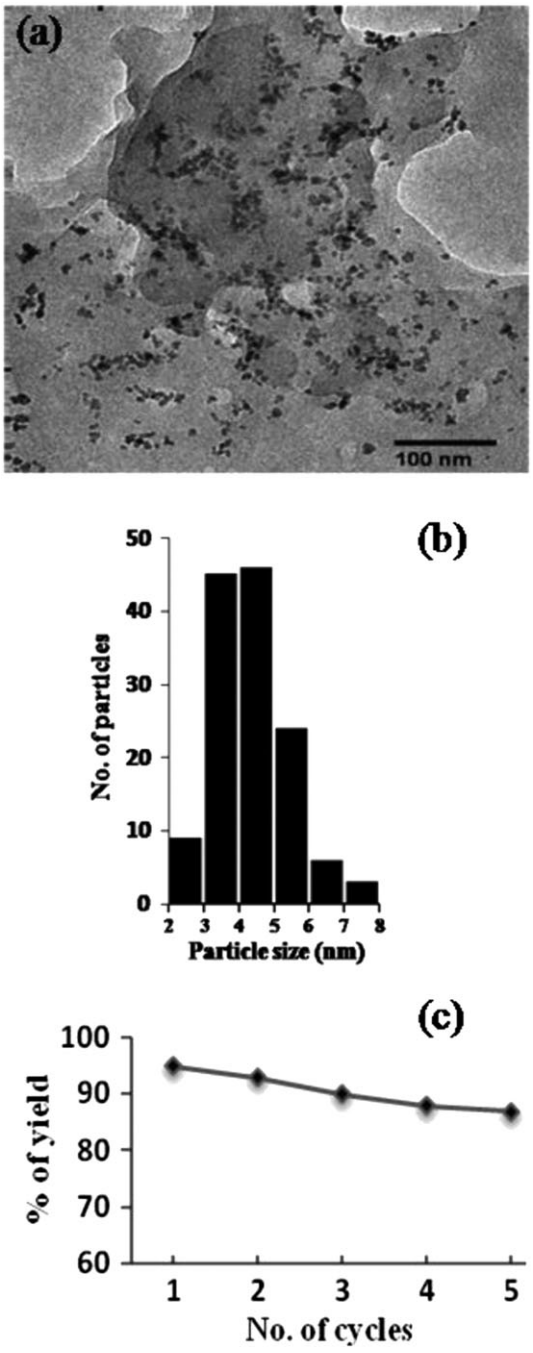


FIGURE 5 (a) TEM image of Pd@PS after five reaction cycles. (b) histogram showing particle size distribution after five cycles. (c) recyclability results for Pd@PS catalyst

2.3 | Mercury test

The mercury drop test was conducted to evaluate the catalytic active species in the reaction solution. The SM cross-coupling reaction between **1a** and phenylboronic acid was chosen as a model reaction using Pd@PS and K_2CO_3 as a base. When a drop of mercury was added to the reaction, no product formation was observed after 60 min due to amalgam formation or adsorption of Hg(0) onto the surface of the heterogeneous catalyst (Pd@PS). This indicated the catalytic participation of Pd(0) in the reaction, and the catalysis involved in the reaction is truly heterogeneous.

3 | CONCLUSIONS

In summary, a semi-synthetic approach was adopted for the synthesis of AAB classes of compounds from natural precursor with reduced number of steps. Various cyclic, acyclic and benzylamine-substituted vinyl bromide benzosuberene analogues were found to be active for SM cross-coupling reaction with electron-rich and electron-deficient phenylboronic acids. The catalyst was recycled for five runs without any observable decrease in efficiency. The present research for novel AAB compounds from himachalenes could be of interest in academia and industry for development of biological activity.

4 | EXPERIMENTAL

4.1 | General methods

All solvents and reagents were purchased from reputed commercial sources. Reactions were monitored by TLC plates coated with 0.2 mm silica gel 60 F254. TLC plates were visualized by UV irradiation (254 nm) and iodine spray. The products were purified by column chromatography employing silica gel of 60–120 mesh size. HRMS were conducted with UHR-QTOF (ultra-high resolution Q-time-of-flight). ^{1}H NMR (600 and 300 MHz) and ^{13}C NMR (150 and 75 MHz) spectra were recorded using $CDCl_3$ and tetramethylsilane as solvent and internal reference, respectively. The coupling constants (J) are reported in hertz (Hz) and the following abbreviations are used to designate signal multiplicity: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad singlet. CEM Discover™ focused microwaves (2450 MHz, 300 W) were used. The temperature on the surface of the reaction flask was measured with an inbuilt infrared temperature probe

in the microwave experiment. SEM images were recorded on E1010 ion sputter. TEM images were obtained using a carbon-coated copper grid with a JEOL 2100F and FEI Tecnoi G20 (200 kV).

4.2 | General procedure for synthesis of compounds 3

N-((6,7-dihydro-3,5,5-trimethyl-8-phenyl-5*H*-benzo[7]annulen-9-yl)methyl)cyclohexanamine (**3a**). A mixture of *N*-((8-bromo-6,7-dihydro-3,5,5-trimethyl-5*H*-benzo[7]annulen-9-yl)methyl)cyclohexanamine (**1a**; 0.26 mmol, 1.0 equiv.), phenylboronic acid (0.32 mmol, 1.2 equiv.), K_2CO_3 (0.53 mmol, 2.0 equiv.) and Pd@PS (0.007 mmol, 3 mol%) in DMF (1.5 ml) was placed in a reaction tube (8 ml) under closed vessel condition and subjected to CEM Discover microwave irradiation (110 °C, 100 W) for 60 min. After cooling to ambient temperature, water was added to the reaction mixture and extracted with ethyl acetate (3 × 10 ml). The combined organic layer was washed with water and dried over Na_2SO_4 and vacuum evaporated. The viscous liquid obtained was purified by column chromatography on silica gel (60–120 mesh) using hexane–EtOAc (99:1) to afford the desired product **3a** as a semisolid (97 mg, 98%). ^{1}H NMR ($CDCl_3$, 600 MHz, δ, ppm): 7.47–7.46 (d, J = 7.8 Hz, 1H), 7.41–7.36 (m, 4H), 7.29–7.27 (m, 2H), 7.11–7.10 (d, J = 7.7 Hz, 1H), 3.60 (s, 2H), 2.40 (s, 3H), 2.25–2.22 (m, 2H), 2.10–2.08 (m, 2H), 1.64–1.61 (m, 4H), 1.54 (m, 1H), 1.45 (s, 6H), 1.16–1.09 (s, 4H), 1.00–0.96 (m, 2H). ^{13}C NMR ($CDCl_3$, 150 MHz, δ, ppm): 147.9, 143.4, 138.4, 137.6, 136.0, 135.6, 128.1, 127.9, 127.6, 126.6, 126.5, 126.4, 57.3, 49.1, 48.8, 38.2, 34.3, 33.2, 32.5, 26.2, 24.9, 21.6. HRMS-ESI: calcd for $C_{27}H_{36}N$ $[M + H]^+$ 374.2842, found 374.2842.

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Supporting Information

Additional Supporting Information may be found online in the supporting information tab for this article.

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