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Bis[(2-ethoxy-2-oxoethyl)triphenyl phosphonium] di-μ-chloro-bis[bromochloro palladate (II)] and its application in Heck and Suzuki cross-coupling reactions

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ABSTRACT

In this study, the phosphonium salt $[Ph_3PCHC(O)OCH_2CH_3]Br$ undergoes a reaction with $Na_2Pd_2Cl_6$, resulting in the formation of $[Ph_3PCHC(O)OCH_2CH_3]_2[Pd_2Cl_4Br_2]$. The synthesized compound underwent thorough characterization through elemental analysis, as well as FT-IR, ^1H, ^{31}P, and ^{13}C NMR spectroscopies. The investigation revealed that this particular substance serves as an efficient catalyst for the Heck cross-coupling reaction, leading to the synthesis of diverse unsaturated products with highly favorable outcomes. Moreover, it has demonstrated effectiveness in catalyzing the Suzuki cross-coupling reaction. Notably, the catalyst exhibits sustained catalytic activity and can be conveniently recovered and reused.

1. Introduction

The utilization of phosphonium salts in organic synthesis has gained recognition due to the generation of phosphorus ylides in situ, which serve as nucleophiles in Wittig reactions [1,2]. Notably, phosphonium salts incorporating a dipalladate(II) moiety have demonstrated efficacy as versatile and sustainable heterogeneous catalysts in diverse variation reactions, encompassing amination of aryl halides, Heck and Stille and other coupling reactions, as well as oxidation and polymerization reactions [1,3-12]. As with other catalytic reactions, building upon the catalytic advancements observed in these reactions, this study explores the use of novel phosphonium salts containing hexabromodipalladate(II) as catalysts in Heck and Suzuki cross-coupling reactions. Triphenylphosphine is employed to synthesize this catalyst, chosen for its economic efficiency, ready availability, and stability in air [13-19]. Triphenylphosphine and its derivatives readily engage as nucleophiles with alkyl/aryl halides, yielding phosphonium salts characterized by high thermal stability [20]. The diverse applications of phosphonium salts underscore their significance, ranging from the preparation of phosphorus ylides crucial for Wittig reactions in alkene synthesis [21-23] to their use as anti-cancer agents for diagnosing and treating tumor cells, playing a role in biological research for targeting, and serving as pharmacological agents with antimicrobial properties against both gram-negative and gram-positive bacteria [24-26].

In this present study, a novel phosphonium compound is employed as a catalyst for facilitating carbon-carbon bond formation through the Suzuki cross-coupling reaction, aiming to achieve biphenyl derivatives. Biphenyl derivatives constitute a diverse category of compounds renowned for their wide array of biological activities, encompassing antimicrobial, antifungal, anti-proliferative, anti-diabetic, immunosuppressive, analgesic, and anti-inflammatory properties. Additionally, they serve as crucial

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precursors in the synthesis of oligo(p-phenylene)s, contributing to research on artificial ion channels [27-29].

2. Experimental

2.1. Synthesis of catalyst

2.1.1 Preparation of phosphonium salt (ligand)

A benzene solution (20 mL) containing triphenylphosphine (PPh_3) (1.30 g, 5 mmol) was introduced to a benzene solution (20 mL) of ethyl 2-bromoacetate (0.55 ml, 5 mmol) in a 250 mL round bottom flask, after stirring for two hours at room temperature resulting precipitation of the corresponding phosphonium salt, manifesting as a white solid., the mixture was filtered. Subsequent washing with diethyl ether (10 mL) and drying yielded a solid with an isolated yield of 1.50 g (70%). The melting point was recorded as 276 °C. Infrared spectroscopy (IR) (υ, cm^{-1}) exhibited peaks at 1430 (CH_2-P) and 1729 (C=O). Proton nuclear magnetic resonance (^1H NMR) analysis (400 MHz, $CDCl_3$) revealed signals at δ= 0.937 (t, 3H, CH3, J=15 Hz); 4.013 (q, 2H, CH_2O, J=27 Hz); 5.465 (d, 2H, CH_2P, J=57 Hz); and a multiplet in the range of 7.450-7.880 (m, 15H, Ph). Carbon-13{1H} NMR (75.45 MHz, DMSO) exhibited signals at δ= 13.98 (s, CH_3); 30.13 (d, CH_2P, J=89 Hz); 62.70 (s, CH_2O); 165.15 (s, C=O); and a range of 118-135 (ph). Phosphorus-31{1H} NMR (121.50 MHz, DMSO) showed a signal at δ= 20.49 ppm.

2.1.2 Synthesis of palladium complex (catalyst)

Palladium(II) chloride (0.016 g, 1 mmol) and sodium chloride (0.04 g, 1 mmol) were combined and placed in 10 ml of methanol as the solvent, stirred for 18 hours at room temperature. The resulting clear solution, $Na_2Pd_2Cl_6$, underwent treatment with ligand **1** (0.83 g, 2 mmol) at room temperature for 6 hours, yielding 2 as a brown solid. Purification of the obtained solid involved filtration, washing with methanol and diethyl ether, followed by dissolution in dichloromethane. The yield was 0.72 g (60%), with a melting point of 221 °C. IR (υ, cm^{-1}): 1436 (CH_2-P), 1739 (C=O). ^1H NMR (400 MHz, $CDCl_3$): δ= 0.950 (t, 3H, CH_3, J=25 Hz); 4.025 (q, 2H, CH_2, J=28 Hz); 5.300 (d, 2H, CH_2P, J=58 Hz); 7.465-7.891 (m, 15H, Ph). $^{13}C\{^1H\}$ NMR (75.45 MHz, DMSO): δ= 13.97 (s, CH_3); 30.31 (d, CH_2P, J=88 Hz); 62.80 (s, CH_2O); 165.10 (s, C=O); 117-135 (ph). $^{31}P\{^1H\}$ NMR (121.50 MHz, DMSO): δ= 20.47. Anal. Calc. for $C_{22}H_{22}O_2P$, $0.5(Cl_4Br_2Pd_2)$: C: 21.80; H: 1.81. Found: C: 22.06; H: 1.75.

2.1.3. General *procedure for Heck cross-coupling reaction*

A mixture of aryl halide (1 mmol), n-butyl acrylate (1.2 mmol), potassium carbonate (2 mmol), 0.005 g of catalyst compound 2, and 4 mL of PEG as the solvent was subjected to heating at 120 °C using an oil bath. The advancement of the reaction was tracked through TLC (hexane/EtOAc, 80:20). Once the reaction reached completion, the mixture was diluted with diethyl ether (10 mL) and water (10 mL), followed by catalyst regeneration. After rinsing with brine (10 mL), the organic layer underwent drying over Na_2SO_4 and concentration under reduced pressure. The residue was purified through recrystallization from water and ethanol. Ethyl acetate (3×10 mL) was employed for product extraction. The combined ethyl acetate extracts were dried over anhydrous sodium sulfate (1.5 g), filtered, and then evaporated to obtain the pure product. Characterization of the products was achieved by comparing their spectral (^1H-NMR and IR) and physical data with those of authentic samples.

2.1.4. General procedure for Suzuki cross-coupling reaction

A mixture of of phenylboronic acid (1.2 mmol), potassium carbonate (2 mmol), aryl halide (1 mmol), 4 mL of PEG as the solvent, and 0.005 g of catalyst compound 2 was subjected to heating at 80 °C using an oil bath. The progression of the reaction was monitored via TLC (n-hexane/EtOAc, 80:20). Upon completion of the reaction, the mixture was diluted with both water (10 mL) and diethyl ether (10 mL), and the catalyst was regenerated. Following washing with brine (10 mL), the organic layer underwent drying over Na_2SO_4 and concentration under reduced pressure. The residue underwent purification through recrystallization from water and ethanol. Ethyl acetate (3×10 mL) was utilized for product extraction. The combined ethyl acetate extracts were dried over anhydrous sodium sulfate (1.5 g), filtered, and then evaporated to obtain the pure product. Characterization of the products was accomplished by comparing their spectral (^1H-NMR and IR) and physical data with those of authentic samples.

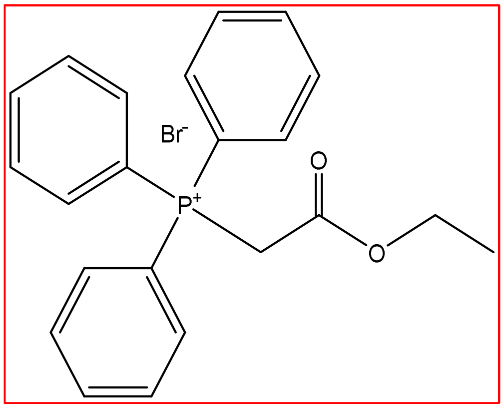
2.1.6. General procedure for recovery of the catalyst

After successfully conducting and verifying the advancement of both catalytic reactions using TLC, the reaction mixture was permitted to reach room temperature. Subsequently, water (5 mL) and the organic phase of the reaction (diethyl ether, 5 mL) were added, and the resulting mixture underwent filtration to separate the catalyst. The catalyst, after drying at 100 °C, was promptly utilized for subsequent reactions.

3.Results and discussion

3.1. Synthesis of the catalyst

Initially, the synthesis of (2-ethoxy-2-oxoethyl) triphenylphosphonium bromide (1) was carried out by treating ethyl 2-bromoacetate with PPh_3 in benzene as the solvent. The resultant product was a phosphonium salt, presenting as an exclusive white solid (Scheme 1). Subsequently, the obtained phosphonium bromide underwent a reaction with sodium hexachloropalladate(II) in a molar ratio of 2:1 in methanol at room temperature for 6 hours, resulting in the formation of (2) as a brown solid, as depicted in Scheme 2. The purity of the product was confirmed by the presence of a sharp and singular peak at δ=20.47 ppm in the ^{31}P NMR spectrum. Figure 1 shows the ^{1}H NMR of the catalyst. Based on previously reported work as well as the weaker bridging bond in $[Pd_2Cl_6]^{2-}$, reaction with phosphonium bromide leads to $[Pd_2Br_2Cl_4]^{2-}$, where the bridging bond is a bromo bridge [30-32].



Scheme 1. Synthesis of (2-ethoxy-2-oxoethyl)triphenylphosphonium bromide (**1**)

3.2. Catalytic study

3.2.1. Suzuki cross-coupling reaction

The investigation focused on the catalytic impact of the synthesized compound (2) in the cross-coupling reaction of phenylboronic acid with aryl halides. This reaction was chosen as it exhibits no progress in the absence of a catalyst. To identify optimal reaction conditions, the influence of temperature, solvent, and catalyst quantity on reaction durations and yields was systematically explored. This exploration involved studying the reaction involving potassium carbonate, phenylboronic acid, and iodobenzene in ethanol at 80˚C. The results are detailed in Table 1.

Table 1. Optimization of the amount of compound 2 for Suzuki cross-coupling reaction.

Entry	Compound 2 (mg)	Time (min)	Yield (%)
1	0.000	20	0
2	0.003	20	65
3	0.005	20	75
4	0.007	20	82
5	0.010	20	86

Reaction conditions: iodobenzene: 1 mmol, phenyl boronic acid: 1.2 mmol, K_2CO_3: 2 mmol, 4 mL PEG, at 80 ˚C

Table 1 illustrates that the catalyst-free reaction was conducted to showcase the genuine efficacy of the heterogeneous catalyst. Notably, biphenyl could not be produced in the absence of the catalyst. Before optimizing the base and temperature, the selection of an appropriate solvent took precedence. Solvents such as N,N-dimethylformamide, ethanol, polyethylene glycol (PEG), ethyl acetate, and isopropanol were assessed for this purpose, and the outcomes are presented in Table 2. Polyethylene glycol was ultimately chosen as the preferred solvent not only due to its phasetranfer property and cost-effectiveness compared to other organic solvents and its environmentally friendly nature but also due to its actions as a phase-transfer agent and support. Polar solvents such can solvate the reactants and the catalyst, leading to improved reactivity and selectivity. Additionally, polar solvents can stabilize the intermediate palladium complex formed during the reaction, leading to higher yields. However, nonpolar solvents may not be able to solvate the reactants and catalyst as effectively as polar solvents, which can lead to lower reaction rates and yields.

Subsequently, the effect of temperature on the reaction rate was explored by conducting the reaction involving potassium carbonate, phenylboronic acid, and iodobenzene in the presence of the optimal catalyst quantity (see Table 3).

Notably, the investigation revealed that, at room temperature, the reaction did not progress, but it consistently yielded the product in high abundance (98%).

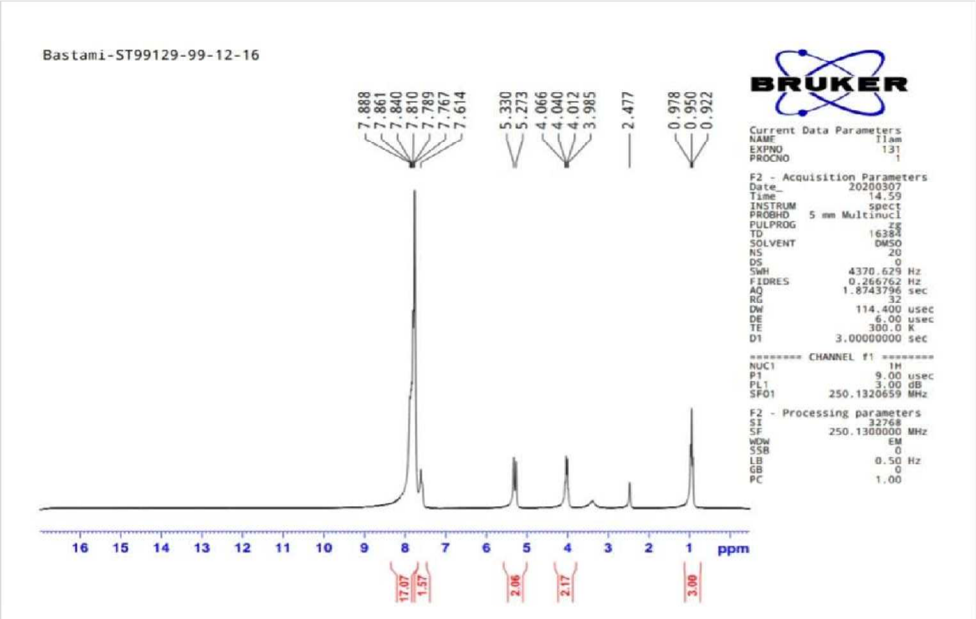
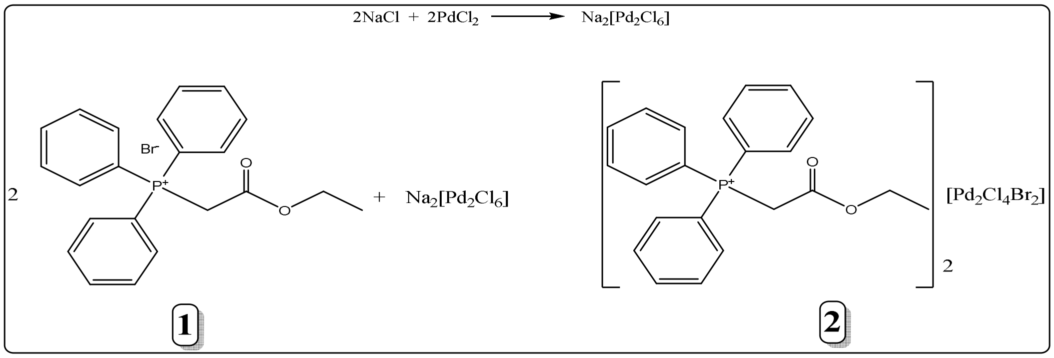


Fig. 1. ^{1}H NMR of the palladium catalyst (compound



.. **Scheme 2.** Synthesis of catalyst (**2**).

Table 2. Optimization of solvent in Suzuki cross-coupling reaction.

Entry	solvent	Time (min)	Yield (%)
1	Ethyl acetate	20	80
2	N,N-Dimethylformamide	20	70
3	PEG	20	98
4	Ethanol	20	90
5	iso-propanol	20	80
6	Dimethylsulfoxide	20	75

Reaction conditions: iodobenzene: 1 mmol, phenyl boronic acid: 1.2 mmol, K_2CO_3: 2 mmol, at 80 ˚C, catalyst: 0.006 g.

Table 3. The effect of temperature on Suzuki cross-coupling reaction.

Temperature (˚C)	Time (min)	Yield (%)
75	20	82
80	20	98
95	20	65
105	20	45

Reaction conditions: iodobenzene: 1 mmol, phenyl boronic acid: 1.2 mmol, K_2CO_3: 2 mmol, catalyst: 0.006 g.

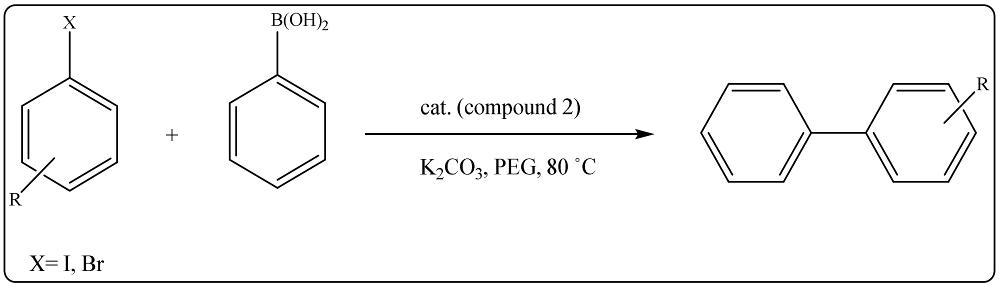
The research then proceeded to optimize the base. Table 4 (see below) suggests that potassium carbonate emerged as the most effective base among the options considered. K_2CO_3 is a mild base that can effectively deprotonate aryl halides without causing excessive side reactions. It is also relatively inexpensive and easy to handle, making it a practical choice for large-scale reactions. Additionally, K_2CO_3 is soluble in PEG-400. Na_2CO_3 is also a mild base, but it can be less effective than K_2CO_3 in this certain case. KOH and NaOH can be effective in promoting the reaction, but they can also lead to increased side reactions. In summary, K_2CO_3 is selected as the optimal base due to its mildness, effectiveness, and practicality.

Table 4. Optimization of base in Suzuki cross-coupling reaction

Base	Time (min)	Yield (%)
Potassium carbonate (K_2CO_3)	20	98
Potassium hydroxide (KOH)	20	94
Sodium carbonate (Na_2CO_3)	20	96
Sodium hydrogen carbonate ($NaHCO_3$)	20	92
Sodium hydroxide (NaOH)	20	95

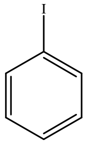
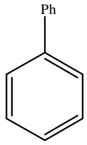
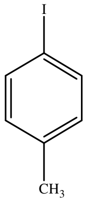
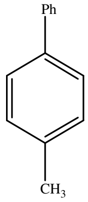
Reaction conditions: iodobenzene: 1 mmol, phenyl boronic acid: 1.2 mmol, base: 2 mmol, at 80 ˚C, catalyst: 0.006 g.

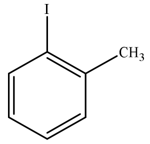
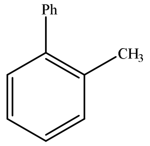
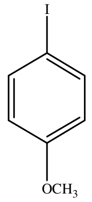
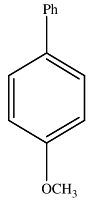
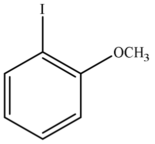
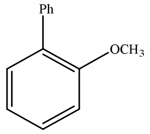
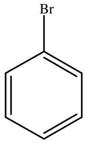
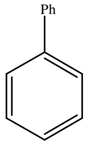
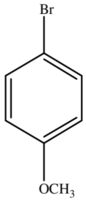
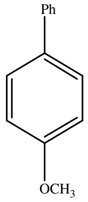
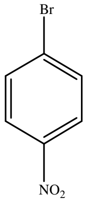
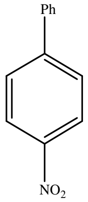
The most favorable outcome was achieved using a 1:1:2:2 ratio of aryl halides, phenylboronic acid, potassium carbonate, and 0.006 g of the catalyst at 80 ˚C. To assess the reaction's generality, various aryl halides with both electron-donating and electron-withdrawing groups were employed (Scheme 3). The corresponding products were consistently obtained in good to excellent yields across different cases (see Table 5). The effect of electron-donating and electron-drawing groups on different positions of the aryl ring on the yield and reaction time was studied. Electron-donating groups show less reactive in comparison to electron-withdrawing groups. Detailed descriptions of the products were provided through spectral methods, including ^{1}H-NMR, ^{13}C-NMR, and IR analyses.



Scheme 3. Application of the palladium catalyst (**2**) in the Suzuki reaction.

Table 5. Suzuki cross-coupling for the synthesis of biaryls from aryl halides.

Entry	Aryl halide	Product	Yield^a (%)	Time (min)	M. p. (˚C)
1			95	8	61-63 [32]
2			98	10	43-44 [33]

3			97	15	Light yellow liquid [34]
4			82	15	82-84 [33]
5			60	30	Colorless Oil [35]
6			94	15	62-64 [32]
7			94	25	82-84 [33]
8			95	10	109-111 [33]

[a] Isolated Yield.

Reaction conditions: aryl halide: 1 mmol, phenyl boronic acid: 1.2 mmol, K_2CO_3: 2 mmol, at 80 ˚C, catalyst: 0.006 g.

3.2.2. Heck cross-coupling reaction

In the current study, the Heck cross-coupling reaction underwent investigation to determine the most favourable reaction conditions and assess the catalytic effectiveness of compound 2. The impact of catalyst quantity, solvent, base, and temperature on reaction times and yields was systematically examined. To conduct this analysis, a model reaction involving iodobenzene, n-butyl acrylate, and potassium carbonate in polyethylene glycol at 120˚C was selected, and various catalyst amounts were evaluated, as outlined in Table 6.

Table 6. Optimization of the catalyst (2) amount for Heck cross-coupling reaction.

Entry	Compound 2 (mg)	Time (min)	Yield (%)
1	0.00	20	0
2	0.003	20	90
3	0005	20	96
4	0007	20	96

Reaction conditions: iodobenzene: 1 mmol, n-butyl acrylate: 1.2 mmol, K_2CO_3: 2 mmol, 4 mL PEG, at 120 ˚C.

Table 6 clearly demonstrates that the reaction does not occur in the absence of the catalyst, highlighting its crucial role. The selection of an appropriate solvent was prioritized before optimizing other variables. After investigating several solvents, polyethylene glycol was ultimately chosen, as detailed in Table 7.

Table 7. Optimization of the solvent in Heck cross-coupling reaction.

Entry	solvent	Time (min)	Yield (%)
1	Ethyl acetate	20	70
2	N,N-Dimethylformamide	20	88
3	PEG	20	95
4	Ethanol	20	80
5	Dimethylsulfoxide	20	20

Reaction conditions: iodobenzene: 1 mmol, n-butyl acrylate: 1.2 mmol, K_2CO_3: 2 mmol, catalyst: 0.005 g, at 120 ˚C.

The influence of temperature on the reaction rate was subsequently investigated, as presented in Table 8. The reaction continued effectively at 120 °C and even as the temperature increased to 105 °C, the reaction rate increased rather than decreased. Therefore, the optimal reaction temperature was maintained at 120 °C.

Table 8. The effect of temperature on Heck cross-coupling reaction.

Temperature (˚C)	Time (min)	Yield (%)
100	20	82
110	20	94
120	20	98
130	20	90
140	20	88

Reaction conditions: iodobenzene: 1 mmol, n-butyl acrylate: 1.2 mmol, K_2CO_3: 2 mmol, catalyst: 0005g, PEG.

Base optimization was then carried out, and Table 9 suggests that potassium carbonate emerged as the most suitable base among those considered.

Table 9. Optimization of the base in Heck cross-coupling reaction

Base	Time (min)	Yield (%)
Potassium carbonate (K_2CO_3)	20	98
Potassium hydroxide (KOH)	20	92
Sodium carbonate (Na_2CO_3)	20	98
Sodium hydrogen carbonate ($NaHCO_3$)	20	92
Sodium hydroxide (NaOH)	20	94

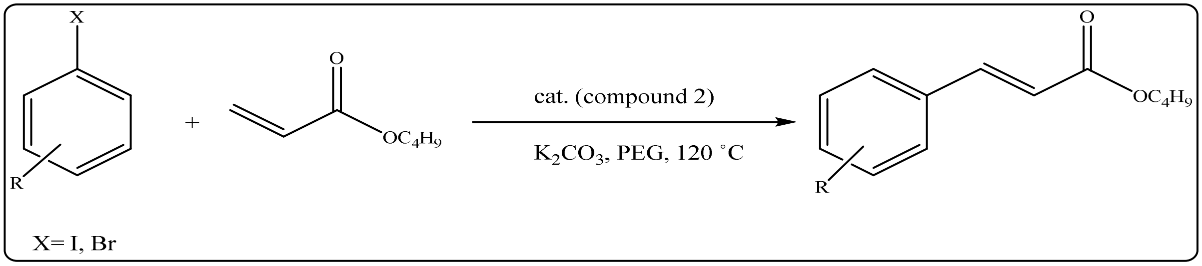
Reaction conditions: iodobenzene: 1 mmol, n-butyl acrylate: 1.2 mmol, base: 2 mmol, catalyst: 0005g, at 120 ˚C, PEG.

To assess the generality of the reaction, various aryl halide types with both electron-donating and electron-withdrawing groups were employed, as illustrated in Scheme 4. The resulting products consistently exhibited good to excellent yields in each case, as detailed in Table 10.

Tables 5 and 10 collectively demonstrate the robust performance of the employed catalytic system across different substrates when the reaction conditions were optimized.

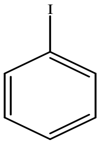
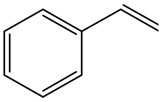
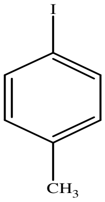
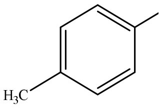
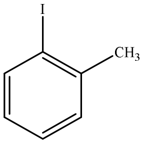
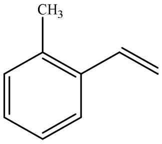
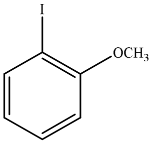
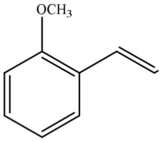
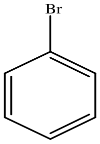
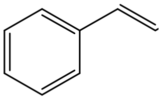
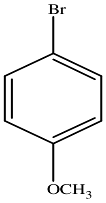
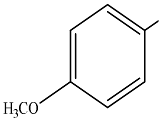
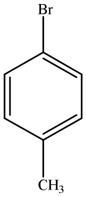
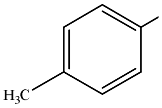
3.3.3. Recovery of the catalyst

The recyclability of catalysts is a crucial factor for their practical application in industrial and commercial settings. To assess the catalyst's reusability, its activity was tested in the Suzuki and Heck reactions over four consecutive runs. The separated catalyst demonstrated noteworthy reusability and recoverability, as illustrated in Fig. 2.



Scheme 4. Application of the palladium catalyst (**2**) in the Heck cross-coupling reactions.

Table 10. Heck cross-coupling reaction of various aryl halides with n-butyl acrylate

Entry	Aryl halide	Product	Yield[a] (%)	Time (min)	M. p. (˚C)
1			98	20	Light yellow liquid [34]
2			95	40	Light yellow liquid [34]
3			96	75	Light yellow liquid [36]
4			40	30	Light yellow liquid [36]
5			90	150	Light yellow liquid [36]
6			60	90	Light yellow liquid [36]
7			70	110	Light yellow liquid [36]

[a] Isolated Yield.

Reaction conditions: aryl halide: 1 mmol, n-butyl acrylate: 1.2 mmol, K_2CO_3: 2 mmol, catalyst: 0005g, at 120 ˚C, PEG.

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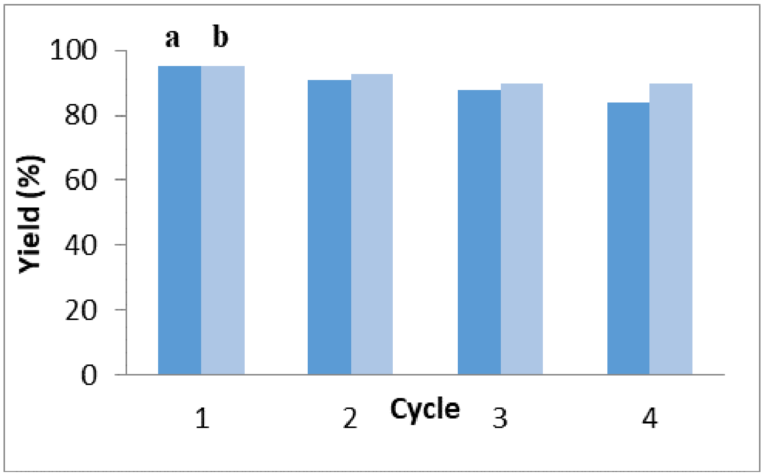

Fig. 2. Reuse of the catalyst in Heck (a) and Suzuki cross-coupling reaction (b)

٤. Conclusion

In this investigation, an innovative phosphonium salt containing the $[Pd_2Cl_4Br_2]^{2-}$ unit proved to be an exceptionally efficient catalyst for the Suzuki cross-coupling reaction. This approach enabled the direct production of numerous biaryls with consistently impressive yields, ranging from very good to excellent. Moreover, compound (2) exhibited significant catalytic prowess in facilitating the Heck cross-coupling reaction. Notably, the initiation of the reaction did not necessitate an inert or dry atmosphere. The catalyst demonstrated remarkable activity, and its capacity for reuse was validated across four consecutive cycles in both reactions.

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