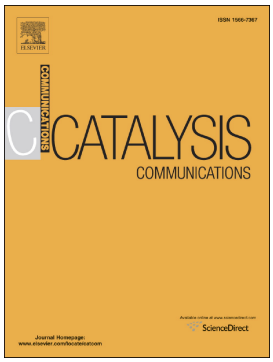

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Oxidative mono- and di- vinylation of 1-phenylpyrazole: Aqueous Rh(III)-catalyzed cross dehydrogenative coupling reactions

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ABSTRACT

A water-mediated, green strategy for carbon-carbon dehydrogenative coupling between phenylpyrazole and alkene was developed using a Rh(III) catalyst under aerobic and very mild reaction conditions. The reaction offers temperature controlled selectivity for mono and di-vinylations products as well as the chemoselective formation of both the products. Moreover, an excellent functional group tolerance with high yields of vinylated products for symmetric as well as asymmetric di-vinylated products was observed. In contrast to previously published reports, our Rh-catalyst works efficiently at low mol% and in a comparable reaction time. This represents the first account of this reaction using an environmentally benign solvent.

In the last decade, a plethora of efficient C-C bond synthetic strategies have been explored. One such predominant technique is the use of cross-coupling methods, which has been reviewed extensively.[1-5] This method has evolved from being a niche strategy to one of the most versatile tools in synthetic chemistry and further demonstrates the vast potential of this reaction.[6] The ubiquitous nature of C-H bonds in organic molecules motivates for the innovative development of this synthetic strategy, as it allows for the incorporation of various functional groups. These moieties can be effectively tuned for the construction of important organic synthons with relevance in the fine chemical, natural product, polymer and molecular sensing fields.[1, 6, 8-12]

With the importance of these scaffolds noted, it is vitally important to provide efficient and sustainable pathways for the formation of these compounds. One such approach is the use of transition-metal catalysts.[1] Classical transition metal cross coupling methodologies, such as the Mizoroki-Heck reaction, often makes use of pre-functionalized starting materials, which inherently contain leaving groups in an effort to control the regio-selectivity of the reaction.[13,14] The use of pre-functionalized starting materials are costly and are synthesized via tedious synthetic procedures. The incorporation of leaving groups may result in the formation of various undesired by-products and inevitably results in the formation of stoichiometric amounts of waste.[1,2,15,16] With most organic molecules containing C-H bonds which characteristically have comparable dissociation energies, the advancement of regioselective methods still remains a major challenge for cross-coupling reactions.[1]

To combat the challenges outlined above the cross dehydrogenative coupling (CDC) reaction, the Fujiwara-Moritani reaction in particular, is an environmentally and economically elegant reaction for the formation of C-C bonds.[14] The reaction is defined as the oxidative coupling of two different C-H bonds and further circumvents the use of pre-functionalized starting material.[5,17] More importantly, in combination with transition metal catalysts, this reaction is in line with Green Chemistry principles.[6] To combat the challenge of regio-selectivity, Lewis-basic directing groups are frequently employed to act as metal chelators, and selected examples are reported in various publications and reviews.[1,18-20] A relevant example includes 1H-pyrazoles, which is of particular importance to biological and materials chemistry and further warrants the extensive study of these molecular scaffolds.[21] Various CDC coupling reactions have been reported using Platinum Group Metals (PGMs) such as Ru,[18, 21, 22] Pd[5, 15, 16, 19] or Rh[1, 2, 6, 7, 9, 11, 14, 20, 23-25] catalyst precursors. Notably Rh has heralded success in these reactions and is often utilized due to the increased activity, lower catalyst loading and stability. A pertinent example is the work by Umeda et al. which reported the use of the

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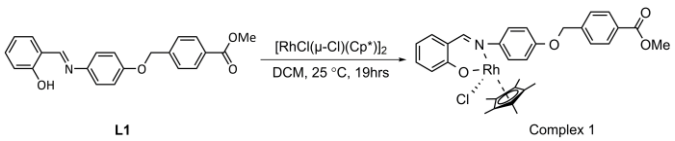
$[Cp^*RhCl_2]_2$ dimer as the catalyst precursor in the mono- and di-vinylation of 1-phenylpyrazole with various alkenes.[20] Moreover, Zhang et al. have also reported this reaction using $[Ru(p\text{-cymene})Cl_2]$.[21] As an extension of this work, herein we report the synthesis and characterization of a Rh(III)-N,O-salicylaldimine catalyst precursor (1) and its evaluation in the oxidative mono- and di-vinylation of 1-phenylpyrazole with various olefins.

Synthesis and Characterization of Rh(III)-N,O-salicylaldimine catalyst precursor (1)

A Rh(III) half-sandwich organometallic complex was prepared using a modified literature procedure.[26,27] Known N,O-salicylaldimine ligands[28] (L1) was reacted with the $[RhCl(\mu\text{-}Cl)(Cp^*)]_2$ dimer via a bridge splitting reaction to afford the desired complex 1 (Scheme 1). Complex 1 was isolated in good yield as a deep red/orange powder.



Scheme 1 Synthesis of Rh(III)-N,O-salicylaldimine Complex 1

Evidence of successful complexation was obtained from ^{1}H NMR spectroscopy. An upfield shift of the imine proton was observed from

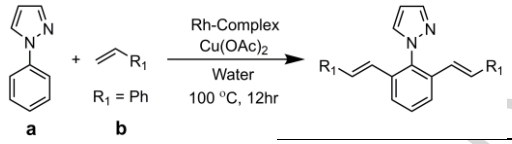
8.88 to 8.07 ppm (1) from the ligand to the complex. The upfield shift is attributed to the increased electron density around the nitrogen center, which emanates from the back bonding of electrons from the metal center to the imine nitrogen. The ^{1}H NMR spectrum of the ligand displays a distinct broad phenolic signal at 13.25 ppm ($CDCl_3$). This signal is absent in the ^{1}H NMR spectrum of the complex, which strongly suggests the deprotonation and resulting bidentate coordination of the N,O-salicylaldimine ligand to the Rh(III) metal. Furthermore, the absence of the salicylaldimine phenolic proton indicates the metal has coordinated in a bidentate manner, which is supported by the published work of Smith and co-workers.[29-33] Further evidence of successful complexation is the presence of the Cp* methyl groups which further motivates for the successful formation of the N,O-salicylaldimine Rh(III) complex (1). The ^{13}C{1H} NMR spectrum shows the expected number of ^{13}C{1H} signals. In the IR spectra, a shift to lower wavenumbers was observed for the C=N stretching vibration on going from the ligand to the Rh(III) organometallic complex, which further confirms the co-ordination to the imine nitrogen. The MS spectra displays a $[M-Cl]^+$ fragment at m/z 598.1519 for 1, commonly observed for structurally analogous complexes.[34, 35]

Catalytic evaluation of 1 for the oxidative di-vinylation of 1-phenylpyrazole

Experimental investigations to evaluate the catalytic activity of the Rh(III) catalyst was initiated by the reaction of phenylpyrazole with styrene in the presence of $Cu(OAc)_2$ in DMSO at 140 °C. Upon characterization, the isolated product was identified as the di-alkenylated CDC coupled product in 65% yield. To increase the yield of the product, solvent optimization was conducted, but the high temperature was found to be impractical and restricted the use of various solvents. Hence, further trials of solvent optimization were carried out at 100 °C. The polar aprotic solvents i.e. DMSO, NMP and dioxane, produce mediocre yields of the desired coupling product. Using DMF and water as solvent for the present reaction produces the desired product in good yield (Table 1). The non-polar solvent, toluene, was not suitable for this reaction.

After solvent optimizations were completed, water was found to be the ideal solvent, notwithstanding its green nature and environmentally benign properties in comparison with DMF. Other salient features that impel us to use water in this reaction are its natural abundance, ease of separation of organics and reusability (Table 1 Entry 1-6). The quantity of styrene in the reaction is one of the key factors that directly affects the nature of product formation. The 1.5 equivalent of styrene, produces the moderate yields; continual increase of styrene up to 2.5 mol% increases the yield up to 90%. However, further increments of styrene do not bring any significant changes in yield of the desired product (Table 1 Entry 7-11). Furthermore, the catalyst optimizations was also performed, most of reactions performed using 0.5 mol% of the Rh catalyst. The 0.5 mol% of the catalyst was found to be highly significant as it produces almost 90% transformation of the desired product. Further trials of increasing the catalyst up to 1 mol% does not produced a sizeable increase in the product yield (Table 1 Entry 12-19). Similarly, the absence of the $Cu(OAC)_2$ produces traces of the desired product. While, the gradual increase in the quantity of $Cu(OAC)_2$ up to 1mmol increases the yield, further increment does not bring any additional increase in the yield of the desired product (Table 1 Entry 20-24). While comparing the results with the previously known catalyst $(Cp^*RhCl_2)_2$ at the present optimized reaction parameters, a considerably low yield (30-35%) of the di-vinylated product was obtained.

Table 1 Reaction Optimizations with Phenyl pyrazole



S.No.	mmol (A)	mmol (B)	Solvent	Catalyst mol%	$Cu(OAc)_2$ mmol	% Yield[a]
1.	1	2.5	Toluene	0.5	1	18
2.	1	2.5	Dioxane	0.5	1	52
3.	1	2.5	NMP	0.5	1	60
4.	1	2.5	DMF	0.5	1	84
5.	1	2.5	DMSO	0.5	1	58
6.	1	2.5	Water	0.5	1	90
7.	1	1.0	Water	0.5	1	37
8.	1	1.5	Water	0.5	1	56
9.	1	2.0	Water	0.5	1	78
10.	1	2.5	Water	0.5	1	90
11.	1	3.0	Water	0.5	1	91
12.	1	2.5	Water	-	1	-
13.	1	2.5	Water	0.2	1	71
14.	1	2.5	Water	0.4	1	82
15.	1	2.5	Water	0.5	1	90
16.	1	2.5	Water	0.6	1	90
17.	1	2.5	Water	0.7	1	90
18.	1	2.5	Water	0.8	1	91
19.	1	2.5	Water	1.0	1	92
20.	1	2.5	Water	0.5	-	12
21.	1	2.5	Water	0.5	0.5	67
22.	1	2.5	Water	0.5	1.0	90
23.	1	2.5	Water	0.5	1.5	89
24.	1	2.5	Water	0.5	2.0	90

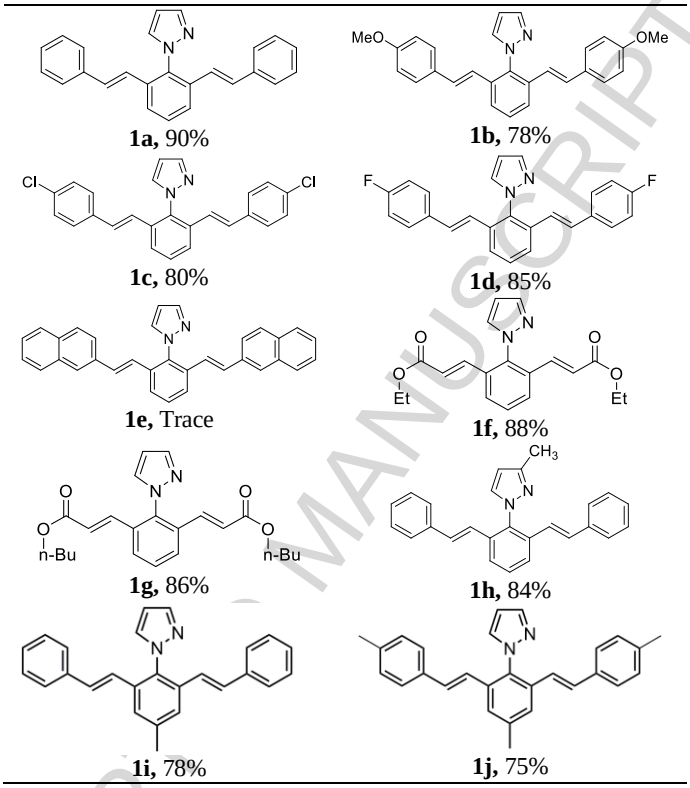
[a]Isolated Yield, Temperature 100 °C, Time 12hr

To expand the general scope of the reaction, various derivatives of styrene as well as phenylpyrazole were explored and are listed in Table 2. All the synthesized products were isolated and characterized using spectroscopic techniques. The Rh-catalyst using the established

methodology catalyses the reaction using all the substituents. Initial reactions of phenylstyrene with phenylpyrazole produces compound 1a, in 90% yield. In comparison to phenylstyrene, slightly lower yields of the 4-methoxy, 4-chloro and 4-flouro substituted styrenes (1b, 1c and 1d) 78, 80, and 85 % respectively of the CDC product was obtained. Due to the bulk structure of naphthalene, the di-vinylations of napthyl styrene (1e) did not work and results in trace amounts of CDC product. Aliphatic groups such as ethylacrylate and n-butyl acrylate (1f and 1g) were also explored for the vinylation, and the excellent formation of the CDC product was noted in significant yields of 86 and 88% respectively. Moreover, alkyl derivatives of phenylpyrazole, i.e. 3-methyl and 3,5-di-methylphenylpyrazole were also screened for the present reaction, the 3-methylphenylpyrazole produces a sizeable yield of the corresponding CDC coupling product in 1h, but 3,5-di-methylphenylpyrazole failed to form the desired CDC product. This might be due to the steric hindrance imparted by the methyl group present on the adjacent carbon restricting the activation of the C-H bond. Reaction was further explored for phenyl substituted phenylpyrazole derivatives, the p-tolyl-1H-pyrazole smoothly react with styrene and p-methylstryene to yield the 1i and 1j in excellent amount 78% and 75% respectively. This further support the strong feasibility of the reaction with various phenyl as well as pyrazole substituted derivatives of phenylpyrazole.

The reported literature of the CDC coupling reactions shows the formation of mono-alkenylated products along with di-alkenylated products. Gratifyingly the formation of mono-alkenylated product was also observed in our work, when reactions were performed at low temperatures.

Table 2 Substrate Scope for di-vinylation of substituted styrene and phenylpyrazole



Isolated yields of di-alkenylated CDC coupled product, Temperature 100 °C. Phenyl Pyrazole (1 Equiv), Styrene (2.5 Equiv), Rh Catalyst: 0.5 mol%, $Cu(OAc)_2$: 1 mmol, Solvent: Water, Time: 12hr

Here, Table 3 shows the various temperature conditions in which optimizations reactions were performed. Low reaction temperature favors the formation of the mono-alkenylated CDC coupled product. Di-alkenylation does occur at room temperature, but the mono-alkenylated product was also found in trace amounts. Increasing the temperature to 50 °C, selectively increases the formations of the mono-alkenylated product and a small quantity of the di-alkenyalation product was also observed. Furthermore, at 100 °C, the di-alkenyalted product became dominant and mono-alkenylated product was not detected, even in trace quantities. Further increasing the reaction temperature does not affect the product composition.

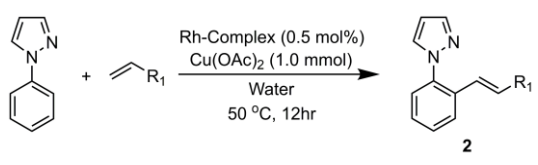
Table 3 Temperature Optimization and Selectivity

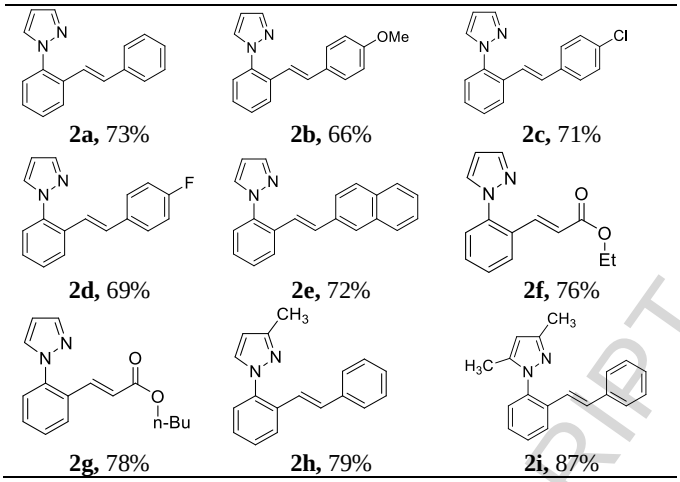
Entry	Temp (°C)	Mono-alkylation (Yield %)	Bi-alkylation (Yield %)
1.	RT	10	-
2.	50	73	14
3.	75	24	65
4.	100	-	90
5.	110	-	90

Isolated yield of product, Phenyl Pyrazole (1 Equiv), Styrene (2.5 Equiv), Catalyst: 0.5 mol%, $Cu(OAC)_2$: 1 mmol, Solvent: Water, Time: 12hr

To study the effect of time with respect to product selectivity at low temperature for longer durations, the reaction of phenylpyrazole and styrene was conducted at 50 °C and the progress of the reaction were continuously monitored. Mono-alkenylation was observed during the initial 12 h of reaction, while a gradual increase in reaction time improves the yield of di-alkenylation but not to a great extent. Hence, this experiment supports the selectivity of the reaction towards the mono-alkenylation or di-alkenylation depending upon the reaction temperature.

Table 4 Substrate Scope for mono-vinylation of substituted styrene and phenylpyrazole





2a, 73% **2b,** 66% **2c,** 71%

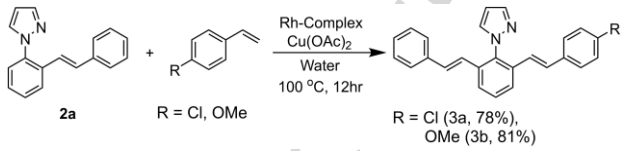
2d, 69% **2e,** 72% **2f,** 76%

2g, 78% **2h,** 79% **2i,** 87%

Reaction condition: Temperature 50 °C, Phenyl Pyrazole (1 Equiv), Styrene (2.5 Equiv), Rh Catalyst: 0.5 mol%, $Cu(OAc)_2$: 1 mmol, Solvent: Water, Time: 12hr, all are isolated yield

The reaction of various substituted styrene was screened with different phenylpyrazoles. Mono-alkenylations of phenylpyrazole was also performed with all the substituents. A slight modification in the reaction methodology leads to the increased yield of the mono-alkenylated product. Table 4, represents the substrate scope for the mono-alkenylation reaction at optimised conditions. Phenylpyrazole with styrene produces a good yield of 73%. (2a, Table 4), while para-substituted methoxy-, chloro- and flouro- styrene yielded the 66%, 71% and 69% yield of the corresponding product (2b, 2c and 2d, Table 4). Aromatic functionality, like naphthalene produce excellent results contrary to di-alkenylation; 72% yield was obtained (2e, Table 4). The ethylacrylate and n-butylacrylate yields good results and produces 76% and 78% yield of mono-alkenylated products (2f and 2g, Table 4). The 3-methyl phenylpyrazole and styrene produces the corresponding mono-alkenylated product (2h, Table 4) in good yields of 79% and 3,5-dimethylphenylpyrazole also produced a 87% yield of the mono-vinylated product (2i, Table 4).

For the formation of unsymmetrical di-alkenylated product, a reaction of phenylpyrazole with equimolar mixture of styrene and 4-methoxy styrene was performed with following the optimized reaction parameters (SI, Scheme 1). The formation of five different coupling products 1a, 1b, 2a, 2b and 3a were obtained in the reaction mixture, however, due to the close proximity of these spots on TLC, it was almost impossible to separate these products through column chromatography. Hence, the formation of these all CDC products was confirmed by the high resolution mass spectra (HRMS). Since, the reaction was conducted at 100 °C which favours the formation of di-alkenylated products, hence, the low yield of mono-alkenylated CDC product, 2a and 2b, in comparison to di-alkenyalated CDC products was observed. Moreover, HRMS also confirms the formation of unsymmetrical di-alkenylated product, which was formed in very insignificant amount. Hence, a different strategy was adopted to scale up the yield of unsymmetrical di-alkenylated product 3a. When the reaction of 4-methoxy styrene and compound 2a was attempted using the optimized reaction parameters, the selective formation of desired unsymmetrical CDC product was obtained in 81% yield (Scheme 2). Hence, the presented method is highly suitable for the synthesis of unsymmetrical di-vinylated compounds, as per literature concern, the high yield synthesis of unsymmetrical phenylpyrazole is quite rare and not observed frequently.

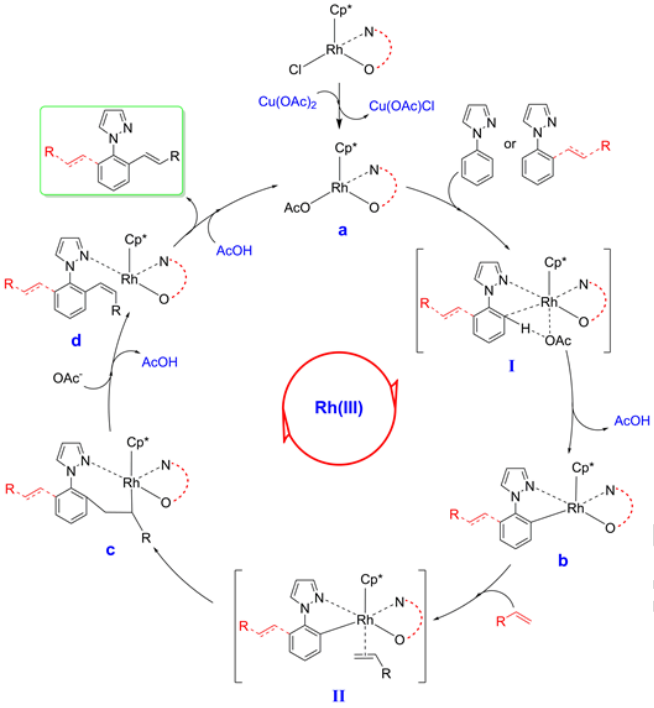


Scheme 2 Direct method for the synthesis of unsymmetrical di-vinylated phenylpyrazole

Plausible reaction mechanism for mono and di-vineylation of phenylpyrazole: A plausible hypothesis for the reaction mechanism of Rh(III) catalyzed CDC coupling reaction is depicted in scheme 3. The exchange of Cl ligand with OAc of Complex 1 via the ligand exchange reaction produces the more activated complex **a**. Through a concerted step, the Rh metal coordinates with nitrogen atom of pyrazole and simultaneously shows metalation–deprotonation at ortho-position of the phenyl ring with the assistance of OAc ligand (Intermediate I).[18] The intermediate **I**, produces a rhodacycle **b**, which directly undergoes to alkene insertion. The oxidative addition of aryl alkene produces complex **c**, through intermediate **II**.[20,21] Furthermore, in the final step, reductive elimination and the action of Cu, produces the vinylated product and regenerates the catalyst back in to the reaction for simultaneous di-vinylation.

Scheme 3 Schematic representation of plausible mechanism

In conclusion, we had successfully employed a N,O-salicylaldimine Rh(III) catalyst for the well-known cross dehydrogenative coupling (CDC) reaction. Various phenylpyrazoles and functionalized phenyl styrene were used in the reaction. The presented Rh(III) catalyst works exceptionally well with all the substituents in excellent yields. The present method offers a temperature dependent selective formation of mono- and di-vinylation. The method is highly efficient for the synthesis of unsymmetrical di-vinylated CDC products. Moreover, we are the first to report the CDC coupling in green solvent, water.



Experimental

Catalyst Synthesis: Triethylamine (35 mg, 0.347 mmol, 1.1 eq.) dissolved in DCM (5 mL) was added dropwise to a stirring solution of the G0-COOMe-N,O-salicyladimine ligand (114 mg, 0.316 mmol, 1 eq.) in DCM (10 mL). After 1hr, a solution of $[RhCp^*Cl_2]_2$ (98 mg, 0.158 mmol, 0.5 eq.) dissolved in DCM (10 mL) was added dropwise to the yellow solution. The solution was allowed to stir at 25 °C for 18 hrs. The mixture was allowed to cool to room temperature and evaporated to dryness under reduced pressure. The residue was partitioned between water (20 mL) and DCM (20 mL), and the aqueous layer was extracted with DCM (3 x 20 mL). The combined organic extracts were washed with sat. brine solution, and consequently dried using anhydrous $MgSO_4$. The organic layer was concentrated to a residue under reduced pressure and dried in vacuo. The crude product was purified by flash chromatography eluting with DCM (100 mL) and then with $CHCl_3$. The fractions containing the product were combined and dried over anhydrous $MgSO_4$. The filtrate was collected, solvent removed under reduced pressure and the residue was dried in vacuo to yield the product as an orange powder.

General Procedure for catalytic transformation: A clean and oven dry sealed tube was charged with 1-phenylpyrazole (0.5 mmol, 1 equiv.), and styrene (1.25 mmol, 2.5 equiv.), to this added (Rh-Complex 0.4 mol%, 4mg) and $Cu(OAc)_2.H_2O$ (100 mg, 0.5 mmol), of water (1 ml) as a reaction medium. Thereafter, the reaction mixture was heated at 90-100 °C under sealed conditions for 12 h. The gain in product formation was examined by periodic monitoring through TLC. Then the reaction mixture was cool to room temperature, added water (50 ml) and EtOAc (75 mL) were added, and the organic layer was extracted thrice, and dried with anhydrous Na_2SO_4. The final crude product was obtained by evaporating the solvent under reduced pressure. Finally, the product was purified through column chromatography (EtOAc/hexane).

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Highlights

- A carbon-carbon dehydrogenative coupling was establish with Rh(III) catalyst.
- Catalyst works in green solvent water and coupled the phenylpyrazoles and alkenes.
- Reaction is chemo-selective and can be easily tuned for mono- and di- vinylations.
- High yield of unsymmetrical di-vinylated phenylpyrazole derivatives obtained.