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Palladium Catalyzed Coupling of Tosylhydrazones with Aryl & Heteroaryl Halides in the Absence of External ligands: Synthesis of Substituted Olefins

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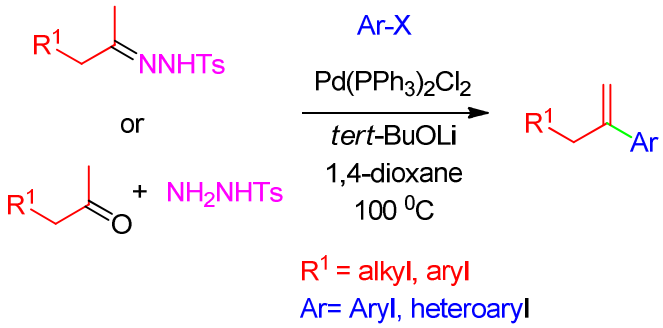


Abstract

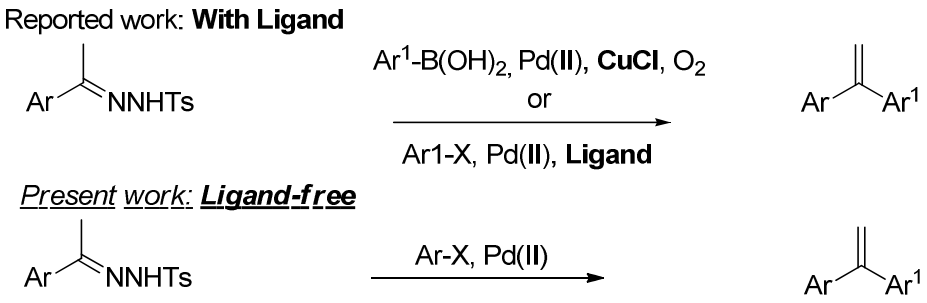
Palladium catalyzed cross coupling reaction of hydrazones with aryl halides in the absence of external ligand is reported. The versatility of this coupling reaction is demonstrated in showcasing the selectivity of coupling reaction in the presence of hydroxyl and amine functional groups. This method allows synthesizing a variety of heterocyclic compounds, which are difficult to access from other traditional methods and are not synthesized by employing similar coupling reactions. Application of the present methodology is validated in tandem reaction of ketones to the corresponding substituted olefins in a single pot experiment.

Introduction

Amongst the several approaches for C-C bond formation, oxidative cross-coupling reactions with a variety of organometallic compounds are both attractive as well as useful.[1] A variety of organometallic reagents such as organocopper, magnesium, zinc, tin, silicon, and boron have been subject of intensive research to furnish C-C bonds.[2] In this respect, the metal mediated C-H functionalization provides a potentially more efficient methodology to construct aromatic as well as heteroaromatic compounds.[3] Palladium catalyzed cross-coupling reactions to provide $C(sp^2)$-$C(sp^2)$ bonds are emerging as most prominent methods for accomplishing complex organic scaffolds.[4] In this context, palladium catalyzed cross-coupling reactions of tosylhydrazone with aryl halides was first conceived by Barluenga and Valdés.[5] This intriguing discovery was extended to variety nucleophiles such as heteroaromatics, aryl boronic acids, phenyl acetylenes, etc. to form C-C bonds to accomplish carbocyclic as well as heterocyclic compounds.[6] An extensive research has led to establish reaction of several hydrazones such as tosylhydrazones, aliphatic chiral hydrazones, *in situ* generated hydrazones, with a variety of coupling partners such as aromatic halides, aromatic boronic acids derivatives, and vinyl halides, alcohols and thiols.[7] For all these transformations, a catalytic amount of $[Pd_2(dba)_3]$ or $PdCl_2(MeCN)_2$ has been used in the presence of catalytic amount of ligands such as Xphos or dppp. It is Wang and coworkers,[8] who developed Pd chemistry in the presence of Cu additives for these cross-coupling reactions. The reaction

of hydrazones with aryl halides in the presence of $[Pd_2(dba)_3]$ resulted in the formation of substituted olefins,[5] whereas the similar reaction of arylhydrazones with arylboronic acid resulted in the alkylation or arylation of hydrazones to furnish corresponding biarylmethanes.[6a] Although $[Pd_2(dba)_3]$ catalyzes the cross coupling of aryl halides with unhindered hydrazones to form diarylethylenes, it is not effective with sterically hindered hydrazones, which resulted in the formation of trisubstituted olefins as major products, without any coupling of the aryl halide. [9] However, it was revealed that $PdCl_2(MeCN)_2$ is efficient in furnishing the tetrasubstituted olefins in good yields. [9] Aryl sulfonates, triflates, nonaflates are also employed as coupling partners with hydrazones in the presence of $Pd(OAc)_2$ and $Pd_2(dba)_3$.[10] Further, C-C bond formation was accomplished using benzyl halides, hydrazones in the presence of $[Pd_2(dba)_3]$ employing P(2-furyl)$_3$ as a ligand (Scheme 1).[11]

Scheme 1.



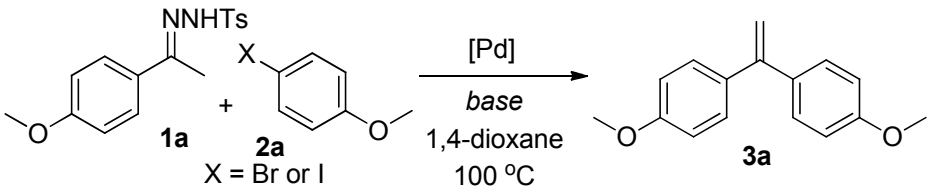
Generally, the coupling reactions require additional ligands like xphos[12a] or dppp[12b] etc,[12c] which are expensive. Moreover, the reactions are not suitable in the presence of sensitive functional groups such as hydroxyl, amino etc.[7c, 14] Further, 1,3-azole-heteroaryl halides have not been explored as coupling partners. In this context, herein we present our new findings on the reactions of aryl hydrazones with aryl/heteroaryl halides in the presence of catalytic amount of $Pd(PPh_3)_2Cl_2$ (bis(triphenylphosphine)palladium dichloride) in the absence of any activating ligands to furnish the corresponding substituted olefins.

Results and discussion

The preliminary studies were carried out with *N*-tosylhydrazone **1a** and 4-methoxyhalobenzenes **2a** and **2b**. Reaction of **1a** with arylbromide (**2a**) in the presence of $Pd_2(dba)_3$ (2.5 mol%) and *tert*-BuOLi at 100 °C for 1 h resulted in the formation of **3a** in 7% (entry 1, Table 1). In the absence of Pd catalyst, the reaction of **1a** did not proceed with arylbromide **2a** (entry 2, Table 1). Further, it was found that Cs_2CO_3 was a better base for this reaction as the reaction provided the expected product in 70% with aryliodide (**2b**), whereas similar reaction with arylbromide (**2a**) was not successful (entries 3 and 4, Table 1). Increasing the amount of hydrazone resulted in the formation of the corresponding olefin in almost quantitative yield with iodobenzene, whereas arylbromide **2a** found to yield trace amount of product (entries 5 and 6, Table 1). Similar reaction with *tert*-BuOLi resulted in the formation of **3a** in almost quantitative yield with aryliodide **2b** and 7% with arylbromide **2a** (entries 7 and 8, Table 1). Interestingly, the reaction of hydrazone **1a** with arylbromide **2a** in the presence of $Pd(PPh_3)_2Cl_2$ and CuCl as an additive with *tert*-BuOLi resulted in the formation of **3a** in 66% yield (entry 9, Table 1).However, the reaction in the absence of CuCl failed to produce the expected product (entry 10, Table 1).[15] It was pleasing to find that the reaction of **1a** in the presence of $Pd(PPh_3)_2Cl_2$ (2.5 mol%), *tert*-BuOLi afforded **3a** in almost quantitative yields both with **2a** as well as **2b** (entries 11 and 12, Table 1). It is remarkable to see that this cross-coupling reaction between hydrazone **1a** and **2a** or **2b** catalyzed by *trans*-$Pd(PPh_3)_2Cl_2$ works very effectively in the absence of additives and noteworthy to mention that most of the reactions with other catalysts require expensive additives such as xphos (entries 11 and 12, Table 1). Further screening studies indicated that the reaction is compatible with MeOH as the reaction of **1a** and **2a** in MeOH furnished the product **3a** in almost quantitative yield (entry 13, Table 1). As this result suggests that there is a possibility of the formation of MeOLi in the reaction, few more controls were performed (entries 14 and 15). The reaction of **1a** and **2a** in the presence of NaOMe in 1,4-dioxane resulted in the formation of **3a** in quantitative yield (entry 14, Table 1). Next, control reaction of 1a and 2a in the presence of *tert*-BuONa in methanol did not afford the product (entry 15). These two control reactions suggest that the reaction of *tert*-BuOLi in methanol is not generating MeOLi intermediate. However, attempts to perform reaction in H_2O were not encouraging, as this reaction of **1a** and **2a** in

water resulted in the formation of **3a** in poor yield (entry 16, Table 1). Subsequent screening studies indicated that the similar reaction using lesser amount of hydrazone (1.3 equiv) decreased the yield of **3a** (entry 17, Table 1). In an optimal reaction procedure, hydrazone (1.5 equiv) and halobenzene (1 equiv) were heated at reflux in the presence of $Pd(PPh_3)_2Cl_2$ (2.5 mol%) with *tert*-BuOLi (4 equiv) in 1,4-dioxane for 1 h. However, using PPh_3 as an external ligand failed to furnish expected product under optimized reaction conditions (entry 18, Table 1). This control experiment clearly indicates that the presence of external ligand does not promote the reaction under the optimal reaction conditions.

Table 1. Screening of Pd catalysts



entry	**1a** (mmol)	**2a** (mmol)	[Pd] (2.5 mol%)	additive	base (4 equiv)	conversion[a] (%)
1	1	1.5	$Pd_2(dba)_3$	none	*tert*-BuOLi	7
2	1	1.5	none	CuCl	*tert*-BuOLi	ND
3	1	1.5	$Pd(OAc)_2$	CuCl	Cs_2CO_3	ND
4	1	1.5	$Pd(OAc)_2$	CuCl	Cs_2CO_3	70[b]
5	1.5	1	$Pd(OAc)_2$	CuCl	Cs_2CO_3	trace
6	1.5	1	$Pd(OAc)_2$	CuCl	Cs_2CO_3	100[b]
7	1.5	1	$Pd(OAc)_2$	CuCl	*tert*-BuOLi	7
8	1.5	1	$Pd(OAc)_2$	CuCl	*tert*-BuOLi	100[b]
9	1.5	1	$Pd(PPh_3)_2Cl_2$	CuCl	*tert*-BuOLi	66
10	1.5	1	$Pd(OAc)_2$	none	*tert*-BuOLi	ND
11	1.5	1	$Pd(PPh_3)_2Cl_2$	none	*tert*-BuOLi	100
12	1.5	1	$Pd(PPh_3)_2Cl_2$	none	*tert*-BuOLi	100[b]
13	1.5	1	$Pd(PPh_3)_2Cl_2$	none	*tert*-BuOLi	100[c]
14	1.5	1	$Pd(PPh_3)_2Cl_2$	none	NaOMe	100
15	1.5	1	$Pd(PPh_3)_2Cl_2$	none	*tert*-BuONa	ND[c]
16	1.5	1	$Pd(PPh_3)_2Cl_2$	none	*tert*-BuOLi	27[d]
17	1.3	1	$Pd(PPh_3)_2Cl_2$	none	*tert*-BuOLi	93
18	1.5	1	$PdCl_2$	PPh_3	*tert*-BuOLi	ND[e]

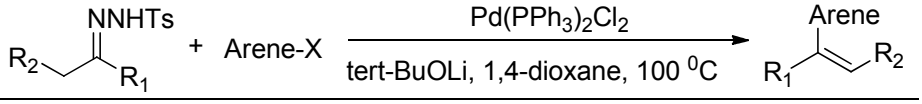
[a] By 1H NMR analysis with respect to starting material. [b]4-iodoanisole. [c] Reaction was performed in MeOH as solvent at 60 °C. [d] Reaction was performed in H_2O as solvent at 100 °C. [e] Reaction was carried out with $PdCl_2$ (5 mol%), PPh_3 (10 mol%). ND=Not detected

After successfully achieving the optimal conditions for cross-coupling reaction, we focused our attention to study the scope of the reaction (Table 2). Tosylhydrazone **1a** reacted well with 4-methoxybromobenzene **2a** or and 4- methoxyiodobenzene **2b** in 1h to furnish the product **3a** in excellent yields (95% and 93%, entries 1 and 2, Table 2). Similarly, 4-methyliodobenzene and 4-methylbromobenzene (**2c** and **2d**) underwent smooth coupling with hydrazone **1a** and furnished the product **3b** (90% and 88%, entries 3 and 4, Table 2). 3-Methoxybromobenzene **2e** underwent a smooth

coupling with tosylhydrazone **1b** in 1h to afford **3c** in good yield (87%, entry 5, Table 2). Hydrazone **1c** reacted with a variety of substituted aromatic bromides and aromatic iodides. As can be seen in Table 2, coupling reaction of hydrazone **1c** proceeded smoothly with 4-bromoacetophenone, 4-bromoanisole, 4-iodoanisole, 4-bromotoluene and 4-iodotoluene to furnish the products **3d**, **3e**, and **3f** in good to excellent yields (entries 6-10).[13] It is interesting to see that carbonyl group does not interfere in the reaction (entry 6). It is known that substrates that contain hydroxyl and amine groups are not good substrates for coupling as they have tendency of forming the corresponding ethers and substituted amines. [7c, 14] To test this hypothesis, 4-bromophenol (**2g**) was reacted with hydrazone **1b** using $Pd_2(dba)_3$ (1 mol%) in the presence of xphos (4 mol%) under the standard reaction conditions that have been employed earlier.[5] But this reaction resulted in the formation of a complex mixture with trace amount of starting material. Interestingly, the similar reaction of 4-bromophenol (**2g**) and hydrazone **1b** under the present reaction conditions produced a remarkable result as it furnished the corresponding olefin **3g** in good yield (72%, entry 11, Table 2). This observation was substantiated by the reaction of hydrazone **1d** derived from 1-(3-hydroxyphenyl)ethanone, which contains OH group, with 1-bromo-3,5-bis(trifluoromethyl)benzene (**2h)** and 1-bromo-4-chlorobenzene (**2i**) to furnish the coupled products **3h** and **3i** in 92% and 90% respectively (entries 12 and 13, Table 2). Similarly, the reaction of hydrazone **1a** with 2-bromoaniline (**2j**) and 2-iodoaniline (**2k**) furnished the coupled product **3j** in 88% and 92% (entries 13, 14, Table 2). As observed in the reaction of 4-bromophenol (entry 11), 2-bromoaniline in a reaction with hydrazone **1b** in the presence of $Pd_2(dba)_3$ (1 mol%) and xphos (4 mol%) resulted in the formation of dimer of haloaniline 5,10-dihydrophenazine in almost quantitative yield.[16] Whereas the similar reaction of 2-bromoaniline (**2j**) and hydrazones **1a** or **1b** under the present reaction conditions furnished the olefins **3j** and **3k** in good to excellent yields (entries 15 and 16, Table 2). In these examples (entries 11-16), phenolic OH group as well as NH_2 groups were intact during the reaction conditions, and hydrazone **1a** underwent a facile coupling with halides containing amine and phenolic OH groups. More importantly, formation of corresponding ethers or substituted amines was not observed. It was found that the coupling reaction tolerates nitrile and chloro functionalities as 4-

bromobenzonitrile (**2l**) and 4-chlorobromobenzene (**2i**) underwent a smooth coupling reaction with hydrazone **1e** to form the products **3l** and **3m** respectively in excellent yields (entries 17-18, Table 2). Importantly, these examples demonstrate that heterocyclic compound such as **1e** is a good precursor for the coupling reaction. Aliphatic hydrazones such as **1f** and **1g** were found to be good precursors as they underwent coupling reaction with aromatic bromides and iodides. Accordingly, **1f** in a reaction with **2a** and **2b** furnished the coupled product **3n** in good to excellent yields (entries 19-20, Table 2). However, reaction of **1g** with **2a** furnished a mixture of **3o** (as *E:Z* mixtures in 94:6 ratio) and **3p** in 91% (88:12 ratio)(entry 21, Table 2). It was further found that the reaction of **1f** with **2a** did not proceed in water. This result is on agreement with our observation that the reaction of **1a** with **2a** under the present reaction conditions forms the product **3a** in poor yield (entry 13, Table 1).

Table 2. Palladium catalyzed coupling reactions[a]



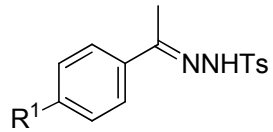
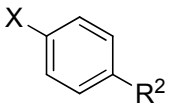
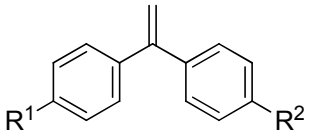
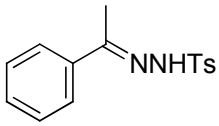
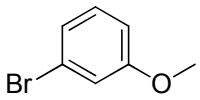
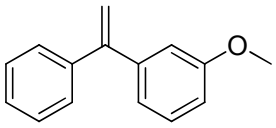
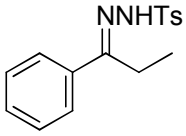
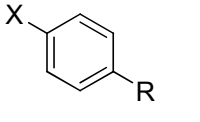
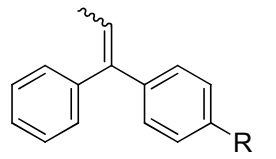
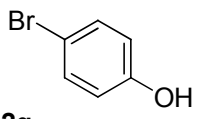
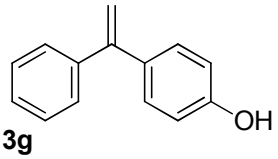
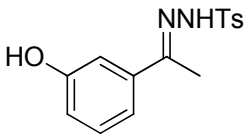
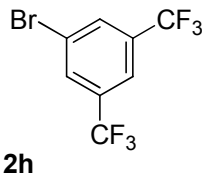
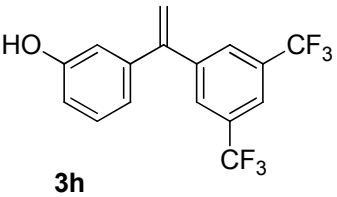
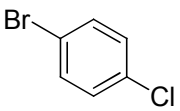
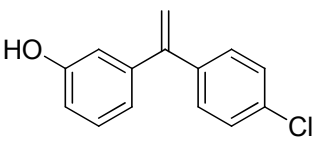
entry	hydrazone	halo-arenes	product	time (h)	yield (%)[b]
					
1	**1a**: R^1 = -OMe	**2a** : X=Br, R^2 = -OMe	**3a:** R^1 = R^2 = -OMe	1	95
2	**1a:** R^1 = -OMe	**2b**: X=I, R^2 = -OMe	**3a:** R^1 = R^2 = -OMe	1	93
3	**1a**: R^1 = -OMe	**2c:**X=I, R^2 = -Me	**3b:** R^1 = -OMe, R^2 = -Me	1	90
4	**1a:** R^1 = -OMe	**2d:**X=Br, R^2 = -Me	**3b:**R^1 = -OMe, R^2 = -Me	1	88
					
5	**1b**	**2e**	**3c**	1	87
					
6	**1c**	**2f:** X = Br, R = -C(O)Me	**3d:** R = -C(O)Me	2	91
7	**1c**	**2a:** X = Br, R = -OMe	**3e:** R = -OMe	2	93
8	**1c**	**2b:** X = I, R = -OMe	**3e**	2	85
9	**1c**	**2d:** X = Br, R = -Me	**3f:** R = -Me	2	90
10	**1c**	**2c:** X = I, R = -Me	**3f**	2	90
					
11	**1b**	**2g**	**3g**	6	72[c]
					
12	**1d**	**2h**	**3h**	2	92[c]
					
13	**1d**	**2i**	**3i**	2	90[c]

Table 2 continued….

entry	hydrazone	halo-arenes	product	time (h)	yield (%)[b]
14	**1a**	**2j:** X = Br	**3j**	2	88[d]
15	**1a**	**2k:** X = I	**3j**	2	92[d]
16	**1b**	**2j**	**3k**	6	92
17	**1e**	**2l:** X = Br, R = -CN	**3l:** R = -CN	2	93
18	**1e**	**2i:** X = Br, R = -Cl	**3m:** R = -Cl	3	91
19	**1f**	**2a**: X=Br, R = -OMe	**3n**	6	91
20	**1f**	**2b**: X=I, R = -OMe	**3n**	5	93
21	**1g**	**2a**: X=Br	**3o** E:Z (94:6) **3p**	4	91[e]

[a] Reactions conditions: **1a** (1.5 equiv.), **2a** (1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (2.5 mol%), *tert*-BuOLi (4.0 equiv.) in 1,4-dioxane . [b] isolatd yields. [c] Cs_2CO_3 (4 equiv.), [d] 90 ^{0}C. [e] **3o:3p** are formed in 88:12 ratio.

Synthesis of heteroaromatics is an important area of research which provides an access for biologically and pharmaceutically activity compounds. Surprisingly, the cross-coupling reactions are not used to accomplish heterocyclic derivatives that are compiled in Table 3. As the present strategy presents an opportunity to accomplish corresponding heterocyclic derivatives, 2-halo-benzo[d]thiazoles **2m** and **2n** were subjected for coupling reaction with hydrazones **1f** and **1g** to obtain corresponding coupled products **3q** and **3r** in excellent yields (entries 1-3, Table 3). It is noteworthy that it is not easy

to synthesize these classes of benzothiazoles using traditional methods, which require multistep sequences using ketones precursors.[17] Similarly, hydrazones **1f** and **1a** coupled smoothly with 3-bromopyridine (**2o**) and 2-bromopyridine (**2p**) to furnish products **3s** and **3t** (entries 4 and 5, Table 3).

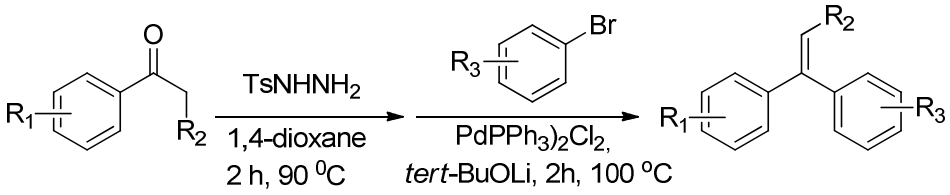
Table 3. Palladium catalyzed coupling reactions with heterocyclic compounds[a]

entry	hydrazone	halo-arene	product	time (h)	yield (%)[b]
1	**1f**	**2m:** X = Cl	**3q**	6	94
2	**1f**	**2n**: X = Br	**3q**	7	86
3	**1g**	**2n**	**3r**	6	80
4	**1f**	**2o**	**3s**	6	86
5	**1a**	**2p**	**3t**	6	68[c]

[a] reaction conditions: hydrazone (1.5 equiv), heteroarylhalides (1 equiv), Pd catalyst (2.5 mol%), *tert*-BuOLi (4 equiv), dioxane, 100 °C. [b] isolatd yields. c Yield based on ^{1}H NMR

The application and usefulness of this methodology is further demonstrated by employing ketones as the precursors (Table 3). In this one-pot tandem reaction, the hydrazone was generated *in situ* by treating corresponding ketones with tosylhydrazine, and hydrazones thus generated were subjected for coupling reaction with aryl halides in the presence of $Pd(PPh_3)_2Cl_2$ (2.5 mol%) with *tert*-BuOLi (4 equiv) (Scheme 2). As can be seen in Scheme 2, ketones **4a**, **5a**, and **6a** underwent a smooth tandem reaction with **2a**, **2e**, and **2f** respectively in dioxane to furnish the expected couple products **3a**, **3c**, and **3d** in good yields (entries 1-3, Scheme 2).[18]

Scheme 2. Tandem reaction of *in situ* generated ketones with aryl halides[a]

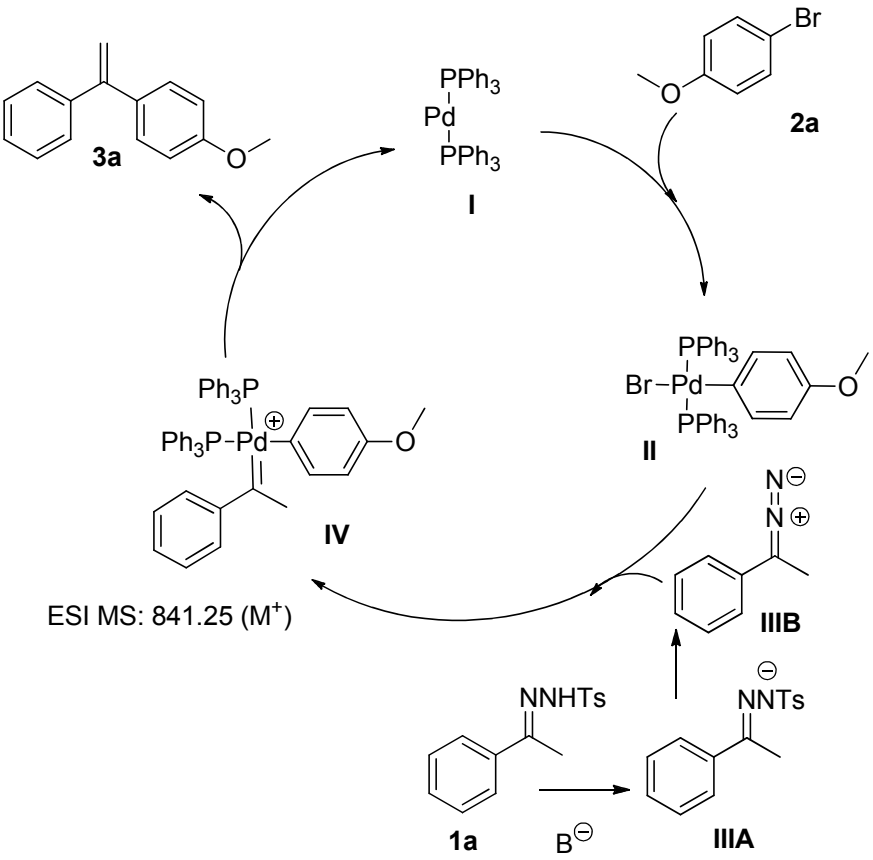


4a: R_1 = 4-OMe, R_2 = -H	**2a**:R_3 = 4-OMe	**3a**(74%)[b]
5a: R_1 = -H, R_2 = -H	**2e**:R_3 = 3-OMe	**3c**(70%)[b]
6a: R_1 = -H, R_2 = -CH_3	**2f**:R_3 = 4-C(O)CH_3	**3d** (73%)[b, c]

[a] reaction conditions: ketone (1.5 equiv), $TsNHNH_2$ (1.5 equiv), arylbromide (1 equiv), Pd catalyst (2.5 mol%), *tert*-BuOLi (4 equiv), dioxane, 100 °C. [b] isolatd yields.
[c] isloated as a mixtyre of *E*:*Z* isomer in 50:50 ratio

A tentative mechanism of this transformation is presented in Scheme 3, based on the literature precedence.[7,8,11,19] Pd^0 (**I**), undergoes an oxidative insertion with aromatic halide (**2a**) to form Pd complex **II**. Azo-compound **IIIB** generated by hydrazone (**1a**) via **IIIA** in the presence of base inserts into Pd complex (**II)** to form the palladium complex **IV**.[19c] Migration of aryl group from intermediate **IV** leads to product **3a**, and regenerates Pd catalyst.

Scheme 3. Tentative mechanism



In conclusion, we have demonstrated a Pd catalyzed, ligand-free cross coupling reaction of aryl halides with hydrazones to furnish corresponding substituted olefins. The salient feature of this methodology is, the coupling reaction is performed in the absence of ligand. The coupling reaction exhibits an excellent selectivity in the presence of hydroxyl and amine functionalities. Additionally, the method provides excellent avenue to accomplish a variety of heterocyclic derivatives, which are difficult

to access from other traditional methods and hitherto are not synthesized by employing similar coupling reactions. Application of the present methodology is demonstrated in tandem reaction of ketones to the corresponding substituted olefins in a single pot experiment.

Experimental Section

General procedures for the preparation of tosylhydrazones: A mixture of ketone (20 mmol) and methanolic solution (30 mL) of *p*-toluenesulfonylhydrazide (20 mmol) was refluxed for 0.5-2 h. Then the mixture was allowed to cool to room temperature, the precipitated product was filtered, which was washed thoroughly with hexane to get corresponding tosylhydrazone as a crystalline product.

Typical experimental procedure for coupling reaction of hydrazone with arylbromide: A well stirred mixture of tosylhydrazone (**1a**, 130 mg, 0.4 mmol), 4-bromoanisole (**2a**, 50 mg, 0.267 mmol), $Pd(PPh_3)_2Cl_2$ (5 mg, 0.0067 mmol) in 1,4-dioxane (3 mL) under nitrogen atmosphere was heated at 100 °C. To this hot clear solution was added *tert*-BuOLi (84 mg, 1 mmol), and the reaction was stirred at 100 °C for 1h (monitored by TLC). Then the reaction mixture was cooled to room temperature and diluted with EtOAc (10 mL) and passed through a short Celite pad, the solvent was evaporated under reduced pressure, and purified on a silica gel column (hexane/EtOAc, 99:1) to obtain the product **3a** as a white solid, yield: 61 mg (94%).

Typical experimental procedure for one-pot tandem reaction of ketone, tosylhydarzine with arylbromide: A well stirred mixture of 4-methoxyacetophenone (60 mg, 0.4 mmol), tosylhydrazide (74 mg, 0.4 mmol), in dioxane (3 mL) was heated at 90 °C for 2h. To this reaction mixture was added 4-bromoanisole (**2a**, 50 mg, 0.267 mmol), $Pd(PPh_3)_2Cl_2$ (5 mg, 0.0067 mmol), *tert*-BuOLi (84 mg, 1 mmol) under nitrogen atmosphere at 100 °C and reaction was further stirred at 100 °C for 2h (monitored by TLC). Then the reaction mixture was cooled to room temperature and diluted with EtOAc (10 mL) and passed through a short Celite pad, the solvent was evaporated under reduced pressure, and purified on a silica gel column (hexane/EtOAc, 99:1) to obtain the product **3a** as a white solid, yield: 48 mg (74%).

N'-(1-(3-hydroxyphenyl)ethylidene)-4-methylbenzenesulfonohydrazide (1d); Prepared according to the above procedure, the precipitated product was filtered as White solid: Yield: 1.88 g (84%), *mp* 126-127 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.21-7.13 (m, 3H), 6.85-6.83 (m, 1H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.7, 152.1, 144.3, 138.7, 135.2, 129.7, 129.5, 128.1, 118.8, 116.9, 112.96; **IR** (neat, cm^{-1}): 3325, **HRMS (ESI):** Calculated for $C_{15}H_{16}N_2O_3S$ (M+Na): 327.0779, found (M+H): 327.0777.

General procedure for coupling reaction of tosylhydrazones with aryl halides:

A well stirred mixture of tosylhydrazone (0.4 mmol), aryl halide (0.267 mmol), $Pd(PPh_3)_2Cl_2$ (0.0067 mmol) in 1,4-dioxane (3 mL) under nitrogen atmosphere was heated at 100 °C. To this hot clear solution was added *tert*-BuOLi (1 mmol) at 100 °C till the completion of the reaction (monitored by TLC). Then the reaction mixture was cooled to room temperature and diluted with EtOAc and passed through a short Celite pad, the solvent was evaporated under reduced pressure, and purified on a silica gel column.

Typical experimental procedure for one-pot tandem reaction of ketone, tosylhydarzine with arylbromide: A well stirred mixture of ketone (60 mg, 0.4 mmol), tosylhydrazide (0.4 mmol), in dioxane (3 mL) was heated at 90 °C for 2h. To this reaction mixture was added arylbromide (0.267 mmol), $Pd(PPh_3)_2Cl_2$ (5 mg, 0.0067 mmol), *tert*-BuOLi (84 mg, 1 mmol) under nitrogen atmosphere at 100 °C and reaction was further stirred at 100 °C for 2h (monitored by TLC). Then the reaction mixture was cooled to room temperature and diluted with EtOAc (10 mL) and passed through a short Celite pad, the solvent was evaporated under reduced pressure, and purified on a silica gel column.

4,4'-(ethene-1,1-diyl)bis(methoxybenzene) (3a);[8] Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column (hexane/EtOAc, 99:1) to obtain the product as White solid: Yield: 0.048g (94%) from 4-iodoanisole and 0.061g (95%) from 4-bromoanisole ; *mp* 135-137 ºC (lit. [8] m.p. 136-138 ºC). R_f = 0.9 (hexane/EtOAc, 20 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.4 Hz, 4H), 6.86 (d, *J* = 8.4 Hz, 4H), 5.29 (s, 2H), 3.82 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ

159.3, 148.9, 134.3, 129.1, 113.5, 111.6, 55.3; **IR** (neat, cm^{-1}): 2935, 2837, 1607, 1508, 1252, 841, 738; **HRMS (ESI):** Calculated for $C_{16}H_{16}O$ (M+H): 225.1279, found (M+H): 225.1278.

1-methoxy-4-(1-(p-tolyl)vinyl)benzene (3b);[8] Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column (hexane/EtOAc, 99:1) to obtain the product as White solid: Yield: 0.058g (88%) from 4-bromotoluene and 0.046g (90%) from 4-iodotoluene. *mp* 72-74 ºC (lit.[8] *mp* 73-74 ºC). R_f = 0.95 (hexane/EtOAc, 20 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28-7.23 (m, 4H), 7.01 (d, *J* = 7.7 Hz, 2H), 6.86 (d, *J* = 8.24 Hz, 2H), 5.33 (d, *J* = 5.56 Hz, 2H), 3.82 (s, 3H), 2.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.3, 149.3, 138.91, 137.4, 134.2, 129.4, 128.8, 128.2, 113.5, 112.3, 55.3, 21.3; **IR** (neat, cm^{-1}): 2918, 2850, 1607, 1508, 1250, 832; **HRMS (ESI):** Calculated for $C_{16}H_{16}O$ (M+H): 225.1279, found (M+H): 225.1278.

1-methoxy-3-(1-phenylvinyl)benzene (3c);[20] Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column (hexane/EtOAc, 99:1) to obtain the product as Colorless oil: Yield: 0.049g (87%). R_f = 0.95 (hexane/EtOAc, 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31-7.33 (m, 5H), 7.22-7.24 (m, 1H), 6.93 (m, 3H), 5.46 (s, 2H), 3.78 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.4, 149.9, 142.9, 141.3, 129.1, 128.1, 127.7, 120.8, 114.4, 113.9, 113.1, 55.2; **IR** (neat, cm^{-1}): 2920, 2850, 1597, 1578, 143, 1239, 777, 698. **HRMS (ESI):** Calculated for $C_{15}H_{15}O$ (M+H): 211.1123, found (M+H): 211.1123.

1-(4-(1-phenylprop-1-en-1-yl)phenyl)ethanone (3d); Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column (hexane/EtOAc, 98:2) to obtain the product as Light yellow oil: Yield: 0.054g (91%), R_f= 0.85 (hexane/EtOAc, 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.15-7.71 (m, 7H), 6.31 (q, *J* = 7.0 Hz, 0.4H), 6.23 (q, *J* = 7.0 Hz, 0.6H), 2.63 (s, 1.7H), 2.57 (s, 1.2H), 1.78 (t, *J* = 7.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.8, 197.7, 147.5, 145.3, 142.2, 141.7, 139.1, 135.6, 130.3, 129.9, 128.2, 128.2, 127.1, 127.0, 126.6,

125.2, 26.6, 26.5, 15.8, 15.7; **IR** (neat, cm^{-1}): 2914, 1682, 1603, 1356, 1267, 760, 701; **HRMS (ESI):** Calculated for $C_{17}H_{16}O$ (M+Na): 259.1099, found (M+Na): 259.1099.

1-methoxy-4-(1-phenylprop-1-en-1-yl)benzene 3e);[21] Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column (hexane/EtOAc, 99:1) to obtain the product as Colourless oil: Yield: 0.056g (93%), R_f = 0.95 (hexane/EtOAc, 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 (t, *J* = 7.2 Hz, 1H), 7.09-7.3 (m, 7H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.05-6.014 (m, 1H), 3.83 (s, 1.6H), 3.83 (s, 1.4H), 1.77 (d, *J* = 6.9 Hz, 1.5H), 1.73 (d, *J* = 7.0 Hz, 1.6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.6, 158.4, 143.4, 141.97, 141.8, 140.3, 135.7, 132.3, 131.2, 128.2, 128.1, 128.0, 127.3, 126.7, 126.6, 123.8, 122.4, 113.4, 55.2, 55.2, 15.8, 15.6; **IR** (neat, cm^{-1}): 3361, 2925, 1645, 1508, 1245, 702; **HRMS (ESI):** Calculated for $C_{16}H_{16}O$ (M+H): 225.1279, found (M+H): 225.1279.

1-methyl-4-(1-phenylprop-1-en-1-yl)benzene (3f); Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column (hexane) to obtain the product as Colorless oil: Yield: 0.058g (90%) from 4-bromotoluene and 0.043g (90%) from 4-Iodotoluene. R_f = 0.9 (hexane/EtOAc, 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 (t, *J* = 7.0, 1H), 7.17-7.30 (m, 5H), 7.05-7.11 (m, 3H), 6.13 (q, *J* = 7.0 Hz, 1H), 2.38 (s, 1.5H), 2.23 (s, 1.6H), 1.75 (t, *J* = 8.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.2, 142.22, 142.2, 140.2, 136.9, 136.4, 130.0, 129.9, 128.8, 128.7, 128.0, 127.9, 127.2, 127.0, 126.7, 126.6, 123.9, 123.2, 21.2, 21.0, 15.7, 15.6; **IR** (neat, cm^{-1}): 3023, 2922, 2855, 1510, 1441, 810, 759, 701.

4-(1-phenylvinyl)phenol (3g); Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column (PE:EA, 20:1) to obtain the product as Colourless oil: Yield: 0.041g (72%) from 4-bromophenol. R_f = 0.6 (hexane/EtOAc, 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.306-7.332 (m, 5H), 7.203-7.245 (m, 4H), 6.7865 (d, *J* = 8.76 Hz, 2H), 5.38 (d, *J* = 1.28 Hz, 1H), 5.34 (d, *J* = 1.28 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.4, 149.4, 132.4, 129.6, 128.3, 128.1, 127.6, 117.2,

114.99, 112.9; **IR** (neat, cm^{-1}): 3399, 2926, 1984, 1509, 1223, 851, 699; **HRMS (ESI):** Calculated for $C_{14}H_{12}O$ (M+H): 197.0966, found (M+H): 197.0961

3-(1-(3,5-bis(trifluoromethyl)phenyl)vinyl)phenol (3h); Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column (hexane/EtOAc, 90:10) to obtain the product as Colourless oil: Yield: 0.052g (92%), R_f = 0.39 (hexane/EtOAc, 10:1) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.77 (s, 2H), 7.25 (t, *J* = 8 Hz, 1H), 6.86-6.76 (dd, J_1 = 9.2 Hz, J_2 = 2.5 Hz, 2H), 5.64 (s, 1H), 5.54 (s, 1H), 4.9 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.7, 147.4, 143.5, 141.4, 131.67 (q, *J* = 33 Hz), 129.9, 128.24 (d, *J* = 3.6 Hz), 123.3 (q, *J* = 271.1), 121.5 (m), 117.3, 115.5, 114.9 ; **IR** (neat, cm^{-1}): 2926, 2854, 1713, 1279, 1181, 1138, 900. **HRMS (ESI):** Calculated for $C_{16}H_{10}F_6O$ (M-H): 331.0558, found (M-H): 331.0559.

3-(1-(4-chlorophenyl)vinyl)phenol (3i): Prepared as shown in general procedure A. Crude reaction mixture was purified on a silica gel column (hexane/EtOAc, 99:1) to obtain the product as colourless oil: Yield: 0.054g (90%), R_f = 0.55 (hexane/EtOAc, 80:20) , **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.25-7.31 (m, 4H), 7.21(t, J = 8 Hz, 1H), 6.88 (m, 1H), 6.79 (m, 2H), 5.458 (d, *J* = 1 Hz, 1H), 5.4257 (d, J = 1 Hz, 1 Hz), 4.83 (br s, 1H) ; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.4, 148.5, 142.7, 139.7, 133.6, 129.56, 129.5, 128.3, 120.8, 115.1, 114.9, 114.8; **IR** (neat, cm^{-1}): 3320, 2943, 1450, 624 ; **HRMS (ESI):** Calculated for $C_{14}H_{11}ClO$ (M-H): 229.0420, found (M+H): 226.0394.

2-(1-(4-methoxyphenyl)vinyl)aniline (3j) : Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column (hexane/EtOAc, 80:20) to obtain the product as waxy solid : Yield: 0.057g (88%) from 2-bromoaniline and 0.047 (92%) from 2-iodoaniline, R_f = 0.5 (hexane/EtOAc, 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.303 (dt, J_1 = 9 Hz, J_2 = 2 Hz, 2H), 7.13 (m, 2H), 6.84 (dt, J_1 = 8.8 Hz, J_2 = 2.5 Hz, 2H), 6.78 (td, J_1 = 7.5 Hz, J_2 = 1 Hz, 1H), 6.69 (dd, J_1 = 8 Hz, J_2 = 0.9 Hz, 1H), 5.69 (d, *J* = 1.5 Hz, 1H), 5.24 (d, *J* = 1.5 Hz, 1H) 3.79 (s, 3H), 3.57 (br s, 2H); **^{13}C NMR**

(100 MHz, $CDCl_3$): δ 159.6, 146.5, 143.9, 132.1, 130.7, 128.6, 127.8, 127.6, 118.3, 115.5, 114.2, 113.9; **IR** (neat, cm^{-1}): 3320, 2943, 1450, 624 ; **HRMS (ESI):** Calculated for $C_{15}H_{15}NO$ (M+H): 226.1232, found (M+H): 226.1237.

2-(1-phenylvinyl)aniline (3k); Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column (hexane/EtOAc, 20:1) to obtain the product as colourless crystalline solid : Yield: 0.052g (92%) from 2-bromoaniline, *mp* 61-64 ºC; R_f = 0.6 (hexane/EtOAc, 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38-7.37 (m, 2H), 7.34-7.28 (m, 3H), 7.18-7.1 (m, 2H), 6.78 (td, J_1 = 7.5 Hz, J_2 = 1 Hz, 1H), 6.69 (dd, J_1 = 8 Hz, J_2 = 0.9 Hz, 1H), 5.79 (d, J = 1.5 Hz, 1H), 5.35 (d, J = 1.5 Hz, 1H) 3.55 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.2, 143.9, 139.6, 130.8, 128.7, 128.5, 128.1, 127.3, 126.6, 118.3, 116.1, 115.5; **IR** (neat, cm^{-1}): 3376, 3052, 1613, 752 ; **HRMS (ESI):** Calculated for $C_{14}H_{13}N$ (M+H): 196.1126, found (M+H): 196.1121.

4-(1-(pyridin-3-yl)vinyl)benzonitrile (3l); Prepared as shown in general procedure A. Crude reaction mixture was purified on a silica gel column (hexane/EtOAc, 70:30) to obtain the product as Brown oil: Yield: 0.051g (93%), R_f = 0.4 (hexane/EtOAc, 80:20) , **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.59-8.42 (m, 2H), 7.64-7.67 (m, 2H), 7.56-7.59 (m, 1H), 7.41-7.44(m, 2H), 7.291-7.32 (m, 1H), 5.66 (d, J = 7.64 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.4, 149.1, 145.5, 144.8, 135.9, 135.4, 132.3, 128.6, 123.3, 118.6, 118.4, 111.9; **IR** (neat, cm^{-1}): 2923, 2852, 2228, 1606, 1406, 850, 716 ; **HRMS (ESI):** Calculated for $C_{14}H_{10}N_2$ (M+H): 207.0922, found (M+H): 207.0921.

3-(1-(4-chlorophenyl)vinyl)pyridine (3m); Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column (hexane/EtOAc, 70:30) to obtain the product as brown oil; Yield: 0.051g (93%), R_f = 0.4 (hexane/EtOAc, 80:20). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.61-8.57 (m, 2H), 7.59-7.58 (m, 1H), 7.34-7.24 (m, 5H), 5.54 (d, J = 18.9 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$)**:** δ 149.1, 149.1, 145.8, 138.8, 136.6, 135.4, 134.1, 129.3, 128.6, 123.1, 116.2; **IR** (neat, cm^{-1}): 2956, 2924, 2852, 1490, 1402, 1013, 906, 835, 714 ; **HRMS (ESI):** Calculated for $C_{13}H_{10}ClN$ (M+H): 216.058, found (M+H): 216.058.

4'-methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl (3n);[10b] Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column (hexane/EtOAc, 99:1) to obtain the product as Colourless oil: Yield: 0.046g (91%) from 4-bromoanisole and 0.047 (93%) from 4-Iodoanisole. R_f = 0.9 (hexane/EtOAc, 20:1) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32-7.29 (m, 2H), 6.86-6.83 (m, 2H), 6.04-6.01 (m, 1H), 3.8 (s, 3H), 2.4-2.35 (m, 2H), 2.21-2.16 (m, 2H), 1.8-1.74 (m, 2H), 1.68-1.61 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.4, 135.9, 135.3, 125.9, 123.1, 113.5, 55.3, 27.5, 25.8, 23.1, 22.2; **IR** (neat, cm^{-1}): 2933, 2858, 1602, 1512, 1249, 1178, 829 **HRMS (ESI):** Calculated for $C_{13}H_{16}O$ (M+H): 189.1279, found (M+H): 189.1279.

1-(but-2-en-2-yl)-4-methoxybenzene (3o);[22] Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column (hexane/EtOAc, 99:1) to obtain the product as colourless oil; Yield: 0.039g. (91%), R_f = 0.95 (hexane/EtOAc, 20:1) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32-7.28 (m, 2H), 6.09-6.08 (m, 2H), 5.81-5.75 (qq, J_1 = 6.8 Hz, J_2 = 1.2 Hz, 1H), 3.8 (s, 3H), 2.00-1.99 (t, J = 1.2 Hz, 3H), 1.79-1.71 (dd, J_1 = 6.8 Hz, J_2 = 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.3, 136.7, 134.8, 126.8, 120.8, 113.5.

2-(cyclohex-1-en-1-yl)benzo[d]thiazole (3q);[23] Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column (hexane/EtOAc, 99:1) to obtain the product as colorless oil; Yield: .048g (96%) from 2-bromobenzothiazole and 0.053g (86%) from 2-chlorobenzothiazole. R_f = 0.4 (hexane/EtOAc, 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$)**:** δ 7.97 (dq, J_1 = 8.2 Hz, J_2 = 0.56 Hz, 1H), 7.81 (dq, J_1 = 7.92 Hz, J_2 = 0.44 Hz, 1H), 7.42 (m, 1H), 7.32 (m, 1H), 6.81 (m, 1H), 2.68 (m, 2H), 2.31 (m, 2H), 1.82 (m, 2H), 1.72(m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.3, 153.7, 134.1, 134.1, 133.4, 125.9, 124.8, 122.8, 121.3, 26.4, 26.1, 22.3, 21.9; (neat, cm^{-1}): 2943, 2832, 1777, 1716, 1526, 1496, 983, 757 ; **HRMS (ESI):** Calculated for $C_{13}H_{13}NS$ (M+H): 216.0847, found (M+H): 216.0845.

(Z)-2-(but-2-en-2-yl)benzo[d]thiazole (3r);[24] Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column (hexane/EtOAc, 99:1). Yield: 0.035g (80 %), R_f = 0.4

(hexane/EtOAc, 5:1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.0-7.96 (m, 1H), 7.98-7.96 (m, 1H), 7.57-7.32 (m, 2H), 6.65-6.63 (m, 1H), 2.28 (s, 3H), 2.23 (dd, J_1 = 6.8 Hz, J_2 = 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 171.5, 153.8, 131.5, 129.5, 124.8, 122.8, 121.2, 36.2, 24.01, 14.5; **IR** (neat, cm^{-1}); 2923, 1433, 906, 726; **HRMS (ESI):** Calculated for $C_{11}H_{12}NS$ (M+H): 190.069, found (M+H): 190.0694.

3-(cyclohex-1-en-1-yl)pyridine (3s); Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column (hexane/EtOAc, 70:30) to obtain the product as colourless liquid; Yield: 0.043g (86%), R_f = 0.5 (hexane/EtOAc, 80:20). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.64-8.63 (d, J = 1.96 Hz, 1H), 8.48-8.43 (dd, J_1 = 4.7 Hz, J_2 =1.28 Hz, 1H), 7.66-7.62 (dt, J_1 = 7.96 Hz, J_2 = 2 Hz, 1H), 7.234-7.21 (dd, J_1 = 7.9 Hz, J_2 = 4.1 Hz, 1H), 6.18-6.16 (m, 1H), 2.42-2.38 (m, 2H), 2.248-2.08 (m, 2H), 1.83-1.77 (m, 2H), 1.71-1.65 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.6, 146.7, 137.9, 133.9, 132.1, 126.6, 123.0, 27.1, 25.8, 22.8, 21.9 ; **IR** (neat, cm^{-1}): 2925, 2854, 1465, 1112, 964, 752 ; **HRMS (ESI):** Calculated for $C_{11}H_{13}N$ (M+H): 160.1126, found (M+H): 160.1122.

2-(1-(4-methoxyphenyl)vinyl)pyridine (3t); Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column (90: 1); Yield: 0.040g (60%), followed by preparatory TLC to obtain the product as a colourless liquid; R_f = 0.4 (hexane/EtOAc, 85:15). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.64 (d, J = 5 Hz, 1H), 7.64 (t, J = 7.5 Hz, 1H), 7.31-7.28 (m, 3H), 7.23-7.19 (m, 1H), 6.89 (d, J = 8.6 Hz, 2H), 5.86 (s, 1H), 5.55 (s, 1H), 3.83 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 159.3, 158.9, 149.3, 148.6, 136.2, 132.8, 129.5, 122.8, 122.3, 116.4, 113.6, 55.3, **IR** (neat, cm^{-1}): 2929, 1599, 1248, 1167, 1019, 835; **HRMS (ESI):** Calculated for $C_{14}H_{14}NO$ (M+H): 212.1075, found (M+H): 212.1074.

Reaction of hydrazone (1a) and 2-bromoaniline (2j) with $Pd_2(dba)_3$ in the presence of xphos: A well stirred mixture of tosylhydrazone (**1b**, 220 mg, 0.75 mmol), 4-bromoanilene (**2m,** 100 mg, 0.58 mmol), $Pd_2(dba)_3$ (9 mg, 0.01 mmol) and xphos (28 mg, 0.06 mmol) in 1,4-dioxane (4 mL) under nitrogen atmosphere was heated at 90 °C. To this hot clear solution was added tert-BuOLi (186 mg, 2.3 mmol), and the reaction was stirred at 90 °C for 6h (monitored by TLC). Then the reaction mixture was

cooled to room temperature and diluted with EtOAc (10 mL) and passed through a short Celite pad, the solvent was evaporated under reduced pressure, and purified on a silica gel column (hexane/EtOAc, 20:1) to obtain the product 5,10-dihydrophenazine **7** as a white solid, yield: 74 mg (70%); mp 278 °C (lit.[25] mp 280 °C). R_f = 0.4 (hexane/EtOAc, 10 : 1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.29-8.24 (4, 4H), 7.88-7.84 (m, 4H),; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.5, 130.5, 129.7,; **IR** (neat, cm^{-1}); 2925, 2854, 1465, 1112, 964, 752 ; **IR** (neat, cm^{-1}); 3328, 2948, 2832, 1118, 1023, 639; **HRMS (ESI):** Calculated for $C_{12}H_{10}N_2$ (M^+): 182.0844, found (M^+): 182.0840.

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Supporting Information Available

^{1}H and ^{13}C spectra, spectral data of all compounds and ESI-MS of **IV**. This material is available free of charge via the Internet at http://pubs.acs.org

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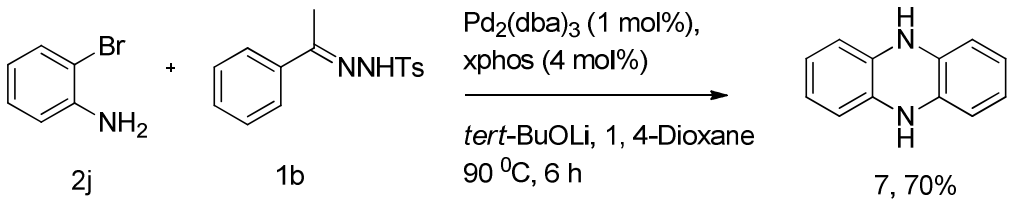

2j 1b 7, 70%

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