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$Pd(OAc)_2$/dppf as an efficient and highly active catalyst for the allylation of amines, alcohols and carboxylic acids with 1-phenyl-1-propyne

Yogesh S. Wagh, Dinesh N. Sawant, Pawan J. Tambade, Kishor P. Dhake, Bhalchandra M. Bhanage *

Department of Chemistry, Institute of Chemical Technology (Autonomous), N. Parekh Marg, Matunga, Mumbai 400019, Maharashtra, India

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ABSTRACT

$Pd(OAc)_2$/1,1′-bis(diphenylphosphino)ferrocene as an efficient, highly active catalyst for the allylation of amines, alcohols and carboxylic acids with 1-phenyl-1-propyne has been developed. The effect of various reaction parameters, such as ligand, time, solvent, temperature, metal: ligand ratio and catalyst concentration on yields of the product were investigated. The optimized procedure works well under mild operating conditions and permits rapid generation of a library for various allylated products.

1. Introduction

Allylation of *N*- and *O*-pronucleophiles is one of the most important protocol for synthesis of allyl amines, allyl ethers and allyl esters rendering their applications in organic synthesis,[1,2] biological systems,[3] natural products[4] and perfumery industry.[5] These allylated products can be synthesized by palladium catalyzed allylation of *N*- and *O*-pronucleophiles with allenes,[6] allylic alcohols[7] and their derivatives such as ether,[8] acetate[9] and carbonate[10] by substitution reaction. Among the various reported methodologies, allylation using internal alkynes is considerably important from synthetic point of view. Yamamoto and co-workers reported intermolecular allylic amination of internal alkynes with amines using palladium/carboxylic acid catalyst using monophosphine ligands.[11] However, very few reports can be found on allylic alkoxylation and allylic carboxylation reactions.[12] The major drawback of allylation reactions with *O*-pronucleophiles is that it requires longer reaction time (1–3 days) and high catalyst concentration. A partial solution to decrease reaction time, Yamamoto and co-workers reported allylation of some pronucleophiles with alkynes under microwave irradiation condition in the absence of solvent.[13] Many of these reports on the allylation using alkynes have drawbacks like requirement of high catalyst concentration, longer reaction time and lower substrate compatibility, which limits their applications. Also, generality of the protocol has not been explored with respect to the structural and electronic variation in pronucleophiles. To the best of our knowledge till date, the various bisphosphine ligands are not yet explored for the present methodology and no report exist on a single catalytic system, which can effectively catalyze variety of allylation reactions of amines or alcohols or carboxylic acids. Therefore, there is need to develop a truly catalytic, active and viable protocol for the allylation of amines, alcohols and carboxylic acids, which can operate under milder reaction conditions.

As part of our interest in amination reactions,[14] we herein report a facile protocol for the allylation of amines or alcohols or carboxylic acids with 1-phenyl-1-propyne using $Pd(OAc)_2$/1,1′-bis(diphenylphosphino)ferrocene [$Pd(OAc)_2$/dppf] as a highly active catalytic system, which functions under mild reaction conditions (Scheme 1). Excellent yield of desired allylated products was obtained by using only 2.5 mol % of the catalyst under optimized reaction conditions.

2. Result and discussion

2.1. Allylation of aromatic and aliphatic amines

The reaction of *N*-methyl aniline (**1**) with 1-phenyl-1-propyne (**2**) in the presence of $Pd(OAc)_2$/dppf as a catalyst was selected as a model reaction (Scheme 2) and influence of various reaction parameters, such as type of ligand, time, solvent, temperature and catalyst concentration were examined (Tables 1 and 2).

* Corresponding author. Tel.: +91 22 2414 5616; fax: +91 22 2414 5614; e-mail address: bhalchandra_bhanage@yahoo.com (B.M. Bhanage).

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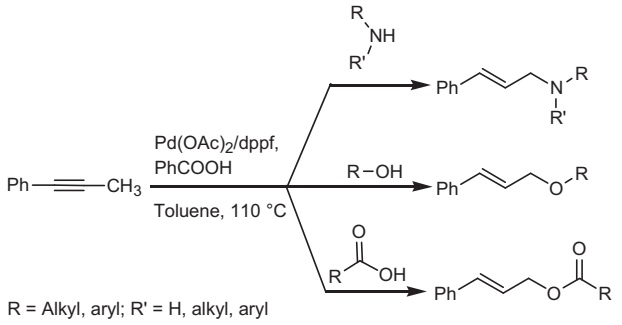
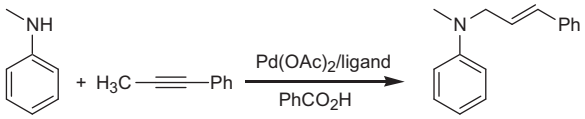


Scheme 1. $Pd(OAc)_2$/dppf catalyzed allylation of amines/alcohols/carboxylic acids with internal alkynes.



Scheme 2. $Pd(OAc)_2$/dppf catalyzed allylic amination of 1-phenyl-1-propyne with *N*-methyl aniline.

Table 1
Effect of phosphine ligands on allylic amination of 1-phenyl-1-propyne with *N*-methyl aniline[a]

Entry	Time (h)	Yield[b] (%)							
		L_1[c]	L_1*[d]	L_2	L_3	L_4	L_5	L_6	L_7
1	1.0	80	53	02	37	14	75	99	39
2	2.0	88	68	21	77	18	81	99	48
3	4.0	95	84	46	88	30	85	99	53
4	8.0	96	92	52	90	42	85	99	59
5	12.0	96	92	65	90	73	88	99	65

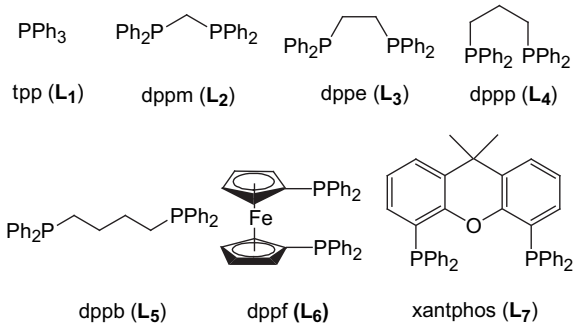
[a] Reaction conditions: **1** (1 mmol), **2** (1 mmol), $Pd(OAc)_2$ (5 mol %), ligand (10 mol %), PhCOOH (10 mol %), toluene (10 mL), temperature (110 °C).
[b] GC yield.
[c] $Pd(OAc)_2$/L_1 (1:4).
[d] L_1*= Preformed $Pd(PPh_3)_4$.

Table 2
Effect of reaction parameters on the allylic amination of 1-phenyl-1-propyne with *N*-methyl aniline[a]

No.	Solvent	$Pd(OAc)_2$	dppf	Temp (°C)	Yield[b] (%)
Effect of solvent					
1	Toluene	5.0	10	110	99
2	Hexane	5.0	10	70	00
3	Cyclohexane	5.0	10	80	00
4	Xylene	5.0	10	140	64
5	1,4-Dioxane	5.0	10	100	40
6	THF	5.0	10	70	80
7	DMF	5.0	10	140	24
8	Acetonitrile	5.0	10	80	62
Effect of temperature					
9	Toluene	5.0	10	80	84
10	Toluene	5.0	10	90	90
11[c]	Toluene	5.0	10	120	99
Effect of catalyst concentration					
12	Toluene	2.5	5	110	99
13	Toluene	1.0	2.0	110	40
14	Toluene	2.5	2.5	110	66
15	Toluene	2.5	7.5	110	99

[a] Reaction conditions: **1** (1 mmol), **2** (1 mmol), PhCOOH (10 mol %), toluene (4 mL), 1 h.
[b] GC yield.
[c] Reaction was performed in sealed vial.

The nature of ligand plays a key role on activity and selectivity of reaction and hence, various phosphine ligands were screened (see Table 1). In order to investigate the influence of ligand on allylation of amine, the reaction of **1** with **2** in the presence of $Pd(OAc)_2$ (5 mol %) as a catalyst precursor and toluene as a solvent under reflux conditions was carried out with different phosphine ligands.



The activity of each ligand was investigated with respect to time by continuous monitoring of reaction progress on GC up to 12 h. The results were also compared with preformed $Pd(PPh_3)_4$ complex (Table 1, L_1'). The catalyst was prepared by interaction of palladium precursor $Pd(OAc)_2$ and the ligand (PPh_3) in the ratio of 1:4 (Table 1, L_1) and can be compared to preformed catalyst. In comparison to preformed $Pd(PPh_3)_4$ complex, the catalyst prepared in situ was found to be much more active providing good yield of desired product. The study was further continued with catalyst prepared in situ using various bisphosphine ligands. Initially, the ligand 1,1-bis (diphenylphosphino) methane (dppm) was studied with very low rate of reaction at earlier stage. However, after 12 h it yielded 65% of desired product. The results obtained using dppm as a ligand encouraged us to examine the effect of other bisphosphine ligands on the product yield. Then we tried various bisphosphine ligands, such as dppe, dppp, dppb, dppf and xantphos for allylation of amine. The results revealed that rate of reaction are much faster when dppe, dppb and dppf were used as ligands, whereas other ligands showed poor activity (Table 1). It was observed that dppf (L_6) showed excellent activity with 99% yield of **3** in just 1 h. Thus, $Pd(OAc)_2$/dppf was chosen as a optimized catalyst for further study.

The effect of various polar and non-polar solvents on allylic amination was studied to find out the optimum solvent for present reaction (Table 2, entries 1–8). The non-polar solvents like toluene, hexane, cyclohexane and xylene were screened. It was observed that reaction does not proceed in the case of low boiling solvents like hexane and cyclohexane while high boiling non-polar solvents like toluene and xylene provides good yield of the product. The polar solvents like dioxane, THF, DMF and acetonitrile were also studied, however, they provide comparatively lower yield of the product (Table 2, entries 5–8). Among all the solvents screened, toluene was found to furnish excellent yield of product (99%) (Table 2, entry 1). Subsequently, we examined the effect of temperature ranging from 80 °C to 120 °C on formation of the product (Table 2, entries 1 and 9–11). It was observed increase in temperature upto 110 °C, increases the yield of product (**3**) up to 99%. However, further increase in temperature to 120 °C has no significant effect on catalytic activity (Table 2, entry 11).

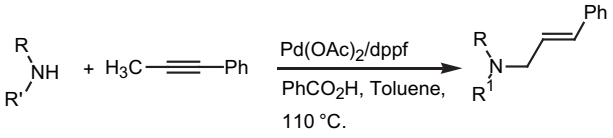
The effect of catalyst concentration from 1 mol % to 5 mol % of substrate on allylic amination reaction was examined (Table 2 entries 1, 12 and 13). Initially, the reaction was carried out using 5 mol % of catalyst which offers 99% yield of the desired product **3** (Table 2, entry 1). Hence, we tried to decrease the catalyst concentration to make the protocol more economical and performed the reaction at 2.5 mol % of catalyst and observed 99% yield of

product **3** (Table 2, entry 12). It was observed that further decrease in catalyst concentration (1 mol %), decreases the yield of desired product (Table 2, entry 13). The reaction was also performed at different metal: ligand ratio, i.e., 1:1, 1:2 and 1:3 with 2.5 mol % of the $Pd(OAc)_2$ (Table 2, entries 12, 14 and 15) where metal: ligand ratio of 1:2 was found to be best for catalyzing the present allylation reaction offering 99% yield of desired product **3** (Table 2, entry 12).

Thus, using $Pd(OAc)_2$/dppf as a preferred catalyst, PhCOOH as a co-catalyst and toluene as a solvent at 110 °C, the allylic amination of various functionalized aromatic and aliphatic amines with 1-phenyl-1-propyne (**2**) was studied (Table 3). The reaction of **2** with sterically hindered *N*-substituted, *N*-phenyl aniline requires comparatively more time, providing good yield of the desired product in 6 h (Table 3, entry 2). Aniline on reaction with **2** gives two products, i.e., mono and diallylated anilines with the selectivity ratio of 90:10 in just 1 h (Table 3, entry 3). The reaction of **2** with aniline having electron donating and withdrawing group, such as $-CH_3$, $-OCH_3$, $-F$, $-Cl$, $-NO_2$, $-CF_3$ and $-CN$ at *ortho* position provides selectivity towards monoallylated product with excellent yield (88–98%) within short period of time (Table 3, entry 4–10). Treatment of 2,4-difluroaniline with **2** under optimized conditions gives corresponding monoallylated product in 98% yield (Table 3, entry 11).

Anilines having ring activating as well as ring deactivating groups at *meta* and *para* position endows mixture of mono and diallylated products with excellent selectivity towards monoallylated product. In case of *ortho* substituted anilines only monoallylated products were obtained owing to the steric hindrance of *ortho* substituent for diallylation reaction, which is not the case in *meta* and *para* substituted aniline. Reaction of **2** with *meta*-trifluoromethyl aniline provides mixture of mono and diallylated products with the ratio of 90:10 (Table 3, entry 12). Treatment of **2** with *para*-toluedine furnishes excellent yield of corresponding products with 98% yield of mixture of products in the ratio of 88:12 (Table 3, entry 13). *para*-Anisidine also reacts effectively with **2** providing mixture of mono and diallylated product with the ratio of 85:15 (Table 3, entry 14). The reaction of *para*-nitro aniline with **2** preceded 90% yield with 80:20 ratio for mono: diallylated products (Table 3, entry 15). Reaction of **2** with bulky α-naphthylamine under optimized reaction conditions gave 96% yield of desired product with excellent selectivity (Table 3, entry 16). Encouraged with the results obtained, we

Table 3
Allylation of aromatic and aliphatic amines with 1-phenyl-1-propyne[a]



R = aryl, alkyl; R' = H, alkyl, aryl

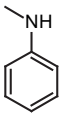
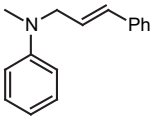
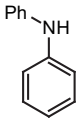
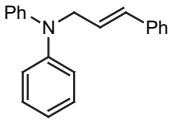
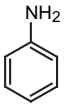
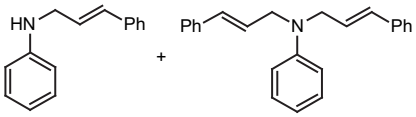
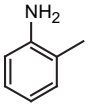
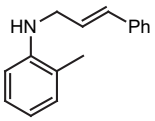
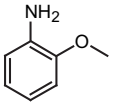
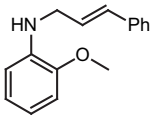
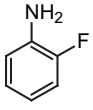
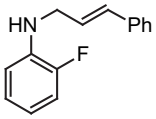
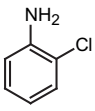
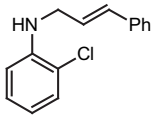
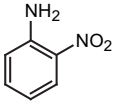
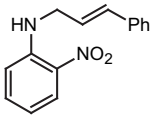
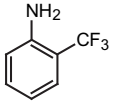
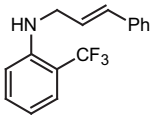
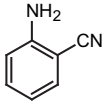
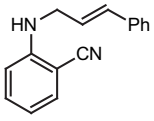
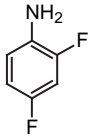
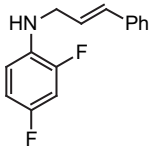
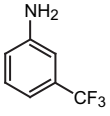
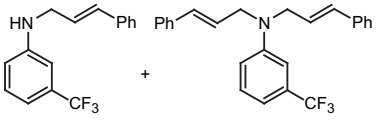
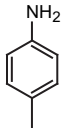
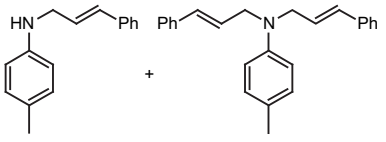
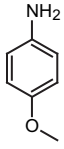
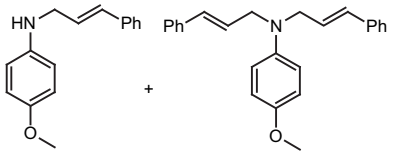
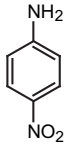
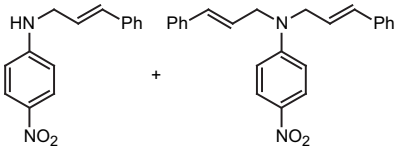
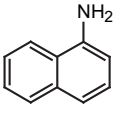
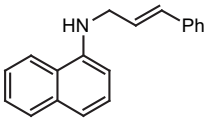
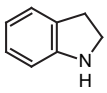
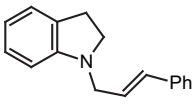
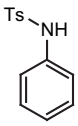
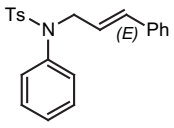
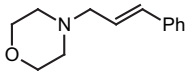
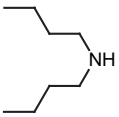
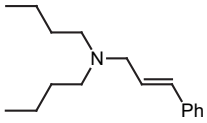
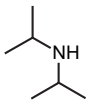
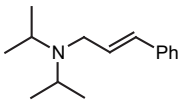
No.	Amine (**1**)	Products (**3**)	Time (**h**)	Yield[b] (%)
1			1	99[c]
2			6	80
3			1	98 (90:10)[c]
4			1	96
5			1	98[c]
6			1	97[c]
7			1	96

Table 3 (*continued*)

No.	Amine (**1**)	Products (**3**)	Time (**h**)	Yield[b] (%)
8			4	88[c]
9			1	98[c]
10			4	97
11			1	98[c]
12			1	98 (90:10)[c]
13			1	98 (88:12)[c]
14			1	95 (85:15)[c]
15			6	90 (80:20)[c]
16			1	96[c]
17			1	98
18			4	95[c]
19			1	96

(*continued on next page*)

Table 3 (*continued*)

No.	Amine (**1**)	Products (**3**)	Time (**h**)	Yield[b] (%)
20			1	98
21			2	80

[a] Reaction conditions: 1-Phenyl-1-propyne (1 mmol), amine (1 mmol), $Pd(OAc)_2$ (2.5 mol %), dppf (5 mol %), PhCOOH (10 mol %), toluene (4 mL), temperature (110 °C).
[b] Yield on the basis of GC and GC–MS analysis.
[c] Isolated yields.

tried the reaction of indoline with **2**, which endowed remarkable yield of 98% for monoallylated product in just 1 h (Table 3, entry 17). The sulfonyl protected aniline, such as *N*-tosyl-aniline effectively reacts with **2** providing 95% yield (Table 3, entry 18).

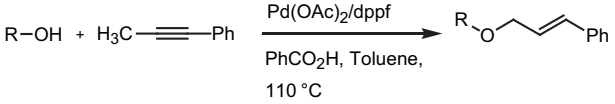
Furthermore, the efficiency of present catalytic system for allylic amination of aliphatic amines, such as morpholine, di-butyl amine and di-isopropyl amine with **2** was studied (Table 3, entries 19–21). Morpholine and di-butyl amine react productively with **2** providing selectively monoallylated products in 1 h, however, sterically hindered aliphatic amine, such as di-isopropyl amine reacts moderately with **2** providing 80% yield of desired product in 2 h.

2.2. Allylation of alcohols and carboxylic acids

Present protocol was extended to the allylation of less nucleophilic substrates, such as alcohols and carboxylic acids with 1-phenyl-1-propyne (**2**) (Table 4, entries 1–10). Although there are some reports on such transformations, no single catalytic system exists, which can effectively catalyze all these mentioned reactions. In order to illustrate the efficiency of present catalytic system for allylation of less nucleophilic substrate, initially reaction of benzyl alcohol (1.2 mmol) and **2** (1 mmol) in the presence of $Pd(OAc)_2$ (2.5 mol %), dppf (5.0 mol %) and benzoic acid (10 mol %) in toluene was carried out at 110 °C. It was observed that reaction requires longer time as compared to allylation of amines and provides 96% of desired product in 12 h (Table 4, entry 1). Substituted benzyl alcohol, such as 4-methoxy benzyl alcohol was treated with **2** (Table 4, entry 2), which reacts smoothly and gave 85% yield of expected product. The reaction of secondary alcohols, such as 1-phenyl ethanol, benzhydrol and menthol was carried out with **2**. It was observed that 1-phenyl ethanol reacts efficiently and provided 84% yield of desired product (Table 4, entry 3). However, sterically hindered and less nucleophilic alcohols, such as benzhydrol and menthol offered good yields of allylated product with extended reaction time (Table 4, entries 4–5). The dramatic result was observed when cinnamyl alcohol was allowed to react with **2**, the reaction ensued 98% yield of dicinnamyl ether (Table 4, entry 6), however, GC and GC–MS analysis of reaction shows complete consumption of cinnamyl alcohol and only 80% conversion of **2** (which is a limiting reagent), this might be because of homocoupling reaction of cinnamyl alcohol. In order to untie this ambiguity, we attempted the reaction of cinnamyl alcohol in the absence of **2**, which furnishes excellent yield of 96% of homocoupled product of cinnamyl alcohol within 4 h.

Furthermore, we investigated the effect of aliphatic and aromatic carboxylic acids to the present methodology, as normally they require longer reaction time.[12a] However, in our case all the carboxylic acids screened react smoothly with comparatively lower reaction time. The reaction of acetic acid with 1-phenyl-1-propyne furnishes 95% yield of cinnamyl acetate within 4 h (Table 4, entry 7). The allylation of acetic acid and *ortho*-tolueic acid are studied in the absence of benzoic acid, to avoid the formation of cinnamyl benzoate as a side product. The reaction of benzoic acid and *ortho*-tolueic acid with **2** provided desired products with excellent yield in 5 h (Table 4, entries 8 and 9). The α,β-unsaturated carboxylic acid such as cinnamic acid on treatment with **2** gave cinnamyl cinnamate as a sole product (Table 4, entry 10).

Table 4
Allylation of alcohols and carboxylic acids with 1-phenyl-1-propyne[a]



R = alkyl, aryl,
alkyl/ aryl carbonyl

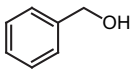
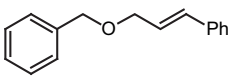
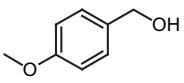
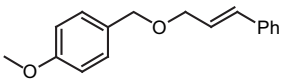
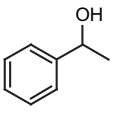
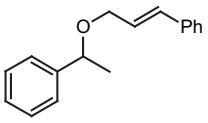
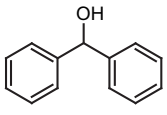
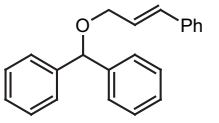
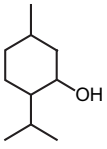
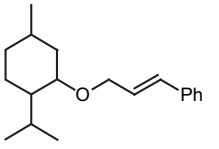
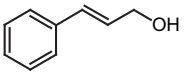
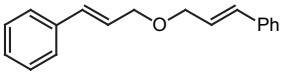
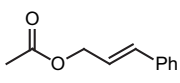
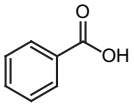
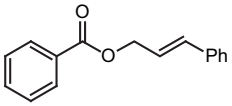
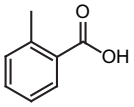
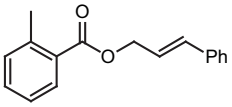
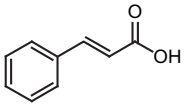
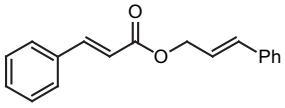
No.	Alcohol/acid	Products	Time (h)	Yield[b] (%)
1			12	96[c]
2			12	85
3			4	84
4			12	84[c]
5			12	88
6			4	98[c]
7			4	95[c,d]

Table 4 (*continued*)

No.	Alcohol/acid	Products	Time (h)	Yield[b] (%)
8			5	95[c,d]
9			5	94[d]
10			5	85

[a] Reaction conditions: 1-Phenyl-1-propyne (1 mmol), alcohol/acid (1.2 mmol), Pd $(OAc)_2$ (2.5 mol %), dppf (5 mol %), PhCOOH (10 mol %), toluene (4 mL). temperature (110 °C).
[b] Yield on the basis of GC and GC–MS analysis.
[c] Isolated yields.
[d] Reaction without PhCOOH.

3. Conclusion

In conclusion, we have developed a facile and efficient protocol for the allylation of various amines, alcohols and carboxylic acids with internal alkyne using $Pd(OAc)_2$/dppf as a highly active catalytic system. The reaction was optimized with respect to various reaction parameters and enabled allylation of various electron rich, electron deficient and sterically hindered amines, alcohols and carboxylic acids affording excellent yield of desired products at low catalyst concentration.

4. Experimental section

4.1. Materials and methods

Palladium acetate, 1,1-bis(diphenylphosphino) ferrocene, 1-phenyl-1-propyne, amines and benzoic acid were purchased from Sigma–Aldrich Ltd. with their highest purity available and were used without further purification. Optimized yields were based on GC (Perkin–Elmer, Clarus 400) and GC–MS (Shimadzu QP 2010) analysis. All the products were known and representative products were characterized by FTIR (Perkin–Elmer), ^{1}H NMR (Varian 300 MHz) or (Varian 400 MHz), ^{13}C NMR (Varian 75 MHz), GC–MS (Shimadzu QP 2010) analysis and HRMS (Bruker daltonics, ESI micrOTOF-Q). Purity of compounds was determined with the help GC–MS analysis.

4.2. General procedure for allylation of amines

In a typical experimental procedure, 2.5 mol % of Pd $(OAc)_2$ (5.6 mg), 5 mol % of 1,1-bis(diphenylphosphino) ferrocene (dppf) (27.8 mg) and 4 mL toluene were taken in 25 mL round bottom flask and stirred under nitrogen for 5 min at room temperature. Then, 1 mmol 1-phenyl-1-propyne (116 mg), 1 mmol amine and 10 mol % of benzoic acid (12 mg) were added. The resulting mixture was then stirred at 110 °C till the consumption of starting material. The reaction was monitored using GC. After completion of reaction, the reaction mixture was cooled to room temperature and filtered through Celite bed. Filtrate obtained was removed under reduced pressure and product was purified by column chromatography (silica gel, 60–120 mesh; ethyl acetate/petroleum ether, 05/95) to afford the desired products. The products are well characterized with GC–MS, ^{1}H and ^{13}C NMR analysis.

4.3. General procedure for allylation of alcohol/acid

In a typical experimental procedure, 2.5 mol % of Pd $(OAc)_2$ (5.6 mg), 5 mol % of 1,1-bis(diphenylphosphino) ferrocene (dppf) (27.8 mg) and 4 mL toluene were taken in a 25 mL round bottom flask and stirred under nitrogen for 5 min at room temperature. Then, 1 mmol 1-phenyl-1-propyne (116 mg), 1.2 mmol alcohol/carboxylic acid and 10 mol % of benzoic acid (12 mg) were added. The resulting mixture was then stirred at 110 °C till the consumption of starting material. The progress of reaction was monitored on GC. The reaction mixture was then cooled to room temperature and filtered through Celite bed. Filtrate obtained was removed under reduced pressure and product was purified by column chromatography (silica gel, 60–120 mesh; ethyl acetate/petroleum ether, 05/95) to afford the desired products. All the prepared compounds were confirmed by GC–MS, ^{1}H and ^{13}C NMR analysis.

4.4. Spectral data for selected products

4.4.1. N-Cinnamyl-N-methyl aniline (Table 3, entry 1). Yield: 99% (220 mg). R_f (5% EtOAc/pet. ether) 0.54, IR (liquid film) 3063, 3011, 2928, 1599, 1356, 1216, 965. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ=7.16–7.34 (m, 7H, Ar), 6.76 (d, J=7.69 Hz, 2H, Ar), 6.71 (t, J=7.33 Hz, 1H, Ar), 6.49 (d, J=16.13 Hz, 1H, CH=*CH*–Ph), 6.21 (td, J=16.13, 5.49 Hz, 1H, CH_2–*CH*=CH), 4.03 (dd, J=5.49, 1.46 Hz, 2H, N–CH2–CH), 2.94 (s, 3H, N–*CH*$_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=149.75 (N–*C*q, Ar), 137.08 (*C*q, Ar), 131.44 (CH_2–*C*H=CH), 129.37 (2*C*H, Ar), 128.70 (2*C*H, Ar), 127.57 (*C*H, Ar), 126.50 (2*C*H, Ar), 125.93 (CH=*C*H–Ar), 116.78 (*C*H, Ar), 112.81 (2*C*H, Ar), 55.05 (N–CH_2–CH), 38.17 (N–*C*H$_3$) ppm. GC–MS (EI, 70 eV): m/z (%)=223 (40) [M^+], 118 (12), 117 (100), 115 (45), 91 (25), 51 (8.9), 44 (15.2). HRMS (ESI^+) calcd for $C_{16}H_{17}N$ (MH^+): 224.1441, found 224.1444.

4.4.2. N-Cinnamyl-2-methoxyaniline (Table 3, entry 5). Yield: 98% (234 mg). R_f (5% EtOAc/pet. ether) 0.42. IR (liquid film) 3425, 2927, 2854, 1602, 1356, 1216, 967, 750. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=7.22–7.39 (m, 5H, Ar), 6.6–6.89 (m, 5H, (4H, Ar and 1H, CH=*CH*–Ph)), 6.35 (td, J=15.76, 5.86 Hz, 1H, CH_2–*CH*=CH), 4.42 (br s, 1H, N*H*), 3.95 (dd, J=5.5, 1.46 Hz, 2H, HN–*CH*$_2$–CH), 3.85=(s, 3H, –O*CH*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=146.92 (*C*q, Ar), 138.02 (N–*C*q, Ar), 136.99 (*C*q, Ar), 131.35 (CH_2–*C*H=CH), 128.56 (2*C*H, Ar), 127.46 (*C*H, Ar), 127.27 (CH=*C*H–Ph), 126.36 (2*C*H, Ar), 121.34 (*C*H, Ar), 116.71 (*C*H, Ar), 110.24 (*C*H, Ar), 109.45 (*C*H, Ar), 55.41 (–O*C*H$_3$), 45.94 (HN–CH_2–CH) ppm. GC–MS (EI, 70 eV): m/z (%)=239 (43) [M^+], 117 (100), 115 (41), 91 (31), 77 (10), 45 (46), 44 (38). HRMS (ESI^+) calcd for $C_{16}C_{17}NO$(MH^+): 240.1388, found 240.1387.

4.4.3. N-Cinnamyl-2-fluoroaniline (Table 3, entry 6). Yield: 97% (220 mg). R_f (5% EtOAc/pet. ether) 0.62. IR (liquid film) 3432, 3027, 2850, 1620, 1516, 1447, 1335, 1114, 966, 743, 693. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=7.18–7.36 (m, 5H, Ar), 6.94–7.0 (m, 2H, Ar), 6.73 (t, J=8.8 Hz, 1H, Ar), 6.63 (m, 1H, Ar), 6.6 (d, J=15.76, 1H, CH=*CH*–Ph), 6.28 (td, J=15.76, 5.5 Hz, 1H, CH_2–*CH*=CH), 4.1 (br s, 1H, N*H*), 3.93 (d, J=5.5, 2H, HN–*CH*$_2$–CH), ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=151.93 (F–*C*q, Ar), 136.77 (*C*q, Ar), 136.6 (N–*C*q, Ar), 131.70 (CH_2–*C*H=CH), 128.61 (2*C*H, Ar), 127.64 (*C*H, Ar), 126.56 (CH=*C*H–Ph), 126.40 (2*C*H, Ar), 124.64 (*C*H, Ar), 116.84 (*C*H, Ar), 114.45 (*C*H, Ar), 112.44 (*C*H, Ar), 45.74 (HN–*C*H$_2$–CH) ppm. GC–MS (EI, 70 eV): m/z (%)=227(33.7) [M^+], 117 (100), 115 (44), 91 (20), 77 (10). HRMS (ESI^+) calcd for $C_{15}H_{14}NF$ (MH^+)=228.1189, found: 228.1183.

4.4.4. N-Cinnamyl-2-(trifluoromethyl)aniline (Table 3, entry 9). Yield: 98% (218 mg). R_f (5% EtOAc/pet. ether) 0.64. IR (liquid film) 3482, 2926, 2855, 1615, 1521, 1332, 1125, 967, 755. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ=7.23–7.45 (m, 7 H, Ar), 6.61–6.79 (m, 2H, Ar), 6.63 (d, J=16, 1H, CH=*CH*–Ph), 6.31 (td, J=16, 5.6 Hz, 1H,

CH_2–CH=CH), 4.59 (br s, 1H, N*H*), 4.02 (d, *J*=4.8 Hz, 2H, HN–CH_2–CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): *δ*=145.74 (N–*C*q, Ar), 136.67 (*C*q, Ar), 133.17 (*C*H, Ar), 131.94 (CH_2–*C*H=CH), 128.65 (2*C*H, Ar), 127.75 (*C*H, Ar), 127.15 (*C*H, Ar), 126.67 (*C*F_3), 126.46 (2*C*H, Ar), 125.94 (CH=*C*H–Ph), 116.21 (*C*H, Ar), 113.56 (*C*q, Ar), 112.24 (*C*H, Ar), 45.63 (N–CH_2–CH) ppm. GC–MS (EI, 70 eV): *m*/*z* (%)=277 (29) [M^+], 117 (100), 115 (38), 91 (19), 77 (5.5).

4.4.5. N-Cinnamyl-2,4-difluoroaniline (Table 3, entry 11). Yield: 98% (244 mg). R_f (5% EtOAc/pet. ether) 0.46. IR (liquid film) 3418, 3027, 2850, 1602, 1517, 1266, 1202, 1102, 960, 746. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): *δ*=7.22–7.38 (m, 7 H, Ar), 6.66–6.83(m, 2H, Ar), 6.63 (d, *J*=16 Hz, 1H, CH=*C*H–Ph), 6.26 (d, *J*=16 Hz, 1H, CH_2–*C*H=CH), 3.95 (d, *J*=3.7 Hz, 2H, HN–CH_2–CH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): *δ*=154.51 (F–*C*q, Ar), 150.58 (F–*C*q, Ar), 136.77 (*C*q, Ar), 133.07 (N–*C*q, Ar), 131.92 (CH_2–*C*H=CH), 128.73 (2*C*H, Ar), 127.80 (*C*H, Ar), 126.49 (3*C*H, CH=*C*H–Ph, Ar), 112.42 (*C*H, Ar), 110.74 (*C*H, Ar), 103.53 (*C*H, Ar), 46.27 (N–CH_2–CH) ppm. GC–MS (EI, 70 eV): *m*/*z* (%)=245(24) [M^+], 117 (100), 115 (43), 91 (19). HRMS (ESI^+) calcd for $C_{15}H_{13}NF_2$ (MH^+): 246.1094, found 246.1089.

4.4.6. N-Cinnamyl-3-(trifluoromethyl)aniline (Table 3, entry 12). Yield: 88% (244 mg). R_f (5% EtOAc/pet. ether) 0.38. IR (liquid film) 3445, 3020, 2926, 1617, 1495, 1340, 1216, 967, 755. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): *δ*=7.2–7.38 (m, 6H, Ar), 6.94 (d, *J*=7.3 Hz, 1H, Ar), 6.84 (s, 1H, Ar), 6.76 (d, *J*=8 Hz, 1H, Ar), 6.62 (d, *J*=15.76 Hz, 1H, CH=*C*H–Ph), 6.27 (td, *J*=15.76, 5.5 Hz, 1H, CH_2–*C*H=CH), 4.01 (br s, 1H, N*H*), 3.39 (d, *J*=4.8, 2H, HN–CH_2–CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): *δ*=148.21 (N–*C*q, Ar), 136.7 (*C*q, Ar), 132.1 (2C, CH_2–*C*H=CH, *C*q–CF_3), 129.72 (*C*H, Ar), 128.69 (2*C*H, Ar), 127.77 (*C*H, Ar), 126.43 (2*C*H, Ar), 126.11 (CH=*C*H–Ph), 115.96 (*C*H, Ar), 114.0 (*C*H, Ar), 109.25 (*C*H, Ar), 45.97 (N–CH_2–CH) ppm. GC–MS (EI, 70 eV): *m*/*z* (%)=277 (29) [M^+], 117 (100), 115 (38), 91 (19), 77 (6). HRMS (ESI^+) calcd for $C_{16}H_{14}NF_3$ (MNa^+): 300.0976, found 300.0971.

4.4.7. N,N-Dicinnamyl-3-(trifluoromethyl)aniline (Table 3, entry 12). Yield: 10% (39 mg). R_f (5% EtOAc/pet. ether) 0.58. IR (liquid film) 3020, 2927, 2855, 1614, 1495, 1456, 1323, 1167, 1128, 1072, 967. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): *δ*=7.21–7.55 (m, 11H, Ar), 7.00 (s, 1H, Ar), 6.92–6.98 (m, 2H, Ar), 6.54 (d, *J*=16.12 Hz, 2H, CH=*C*H–Ph), 6.24 (td, *J*=16.12, 5.5 Hz, 2H, CH_2–*C*H=CH), 4.17 (d, *J*=4.40, 4H, HN–CH_2–CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): *δ*=148.02 (N–*C*q, Ar), 136.73 (2*C*q, Ar), 131.81 (2CH_2–*C*H=CH), 129.74 (*C*q–CF_3), 128.67 (4*C*H, Ar), 127.70 (2*C*H, Ar), 126.45 (4*C*H, Ar), 124.93 (*C*H, Ar), 115.53 (*C*H, Ar), 113.07 (*C*H, Ar), 108.80 (*C*H, Ar), 52.31 (HN–CH_2–CH) ppm. MS–MS (ESI^+): *m*/*z* calcd for (M+1): 394.17; found (M+1): 394.33. HRMS (ESI^+) calcd for $C_{25}H_{22}NF_3$ (M+H^+): 394.1783, found 394.1777.

4.4.8. N-Cinnamyl-naphthylamine (Table 3, entry 16). Yield: 96% (248 mg). R_f (5% EtOAc/pet. ether) 0.45. IR (liquid film) 3425, 3028, 2860, 1612, 1581, 1524, 966, 756. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): *δ*=7.77–7.84 (m, 2H, Ar), 7.2–7.4 (m, 9H, Ar), 6.7 (m, 1H, Ar), 6.66 (m, 1H, CH=*C*H–Ph), 6.43 (td, *J*=15.76, 5.87 Hz, 1H, CH_2–*C*H=CH), 4.5 (br s, 1H), 4.08 (d, *J*=5.5 Hz, 2H, HN–CH_2–CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): *δ*=143.25 (N–*C*q, Ar), 136.93 (*C*q, Ar), 134.44 (*C*q, Ar), 132.06 (CH=*C*H–Ph), 128.81(*C*H, Ar), 128.72 (2*C*H, Ar), 127.72 (*C*H, Ar), 126.75 (2*C*H, Ar), 126.49 (2*C*H, Ar), 125.85 (*C*H, Ar), 124.87 (*C*H, Ar), 123.63 (*C*q, Ar), 120.02 (*C*H, Ar), 117.79 (*C*H, Ar), 104.98 (*C*H, Ar), 46.51 (HN–CH_2–CH) ppm. GC–MS (EI, 70 eV): *m*/*z* (%)=339 (21) [M^+], 234 (12), 227 (74), 223 (2), 117 (46), 115 (19), 91 (28), 44 (100). HRMS (ESI^+) calcd for $C_{19}H_{17}N$ (MH^+) 260.1439, found 260.1434.

4.4.9. N-Cinnamyl-N-tosyl-aniline (Table 3, entry 18). Yield: 95% (334 mg). R_f (10% EtOAc/pet. ether) 0.43. IR (liquid film) 3055, 2923, 1616, 1595, 1493, 1347, 1166, 967, 867, 750. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): *δ*=7.42 (d, *J*=7.7 Hz, 2H, Ar), 6.98–7.15 (m, 12H, Ar), 6.27 (d, *J*=15.76 Hz, 1H, CH=*C*H–Ph), 6.0 (m, 1H, CH_2–*C*H=CH), 4.48 (d, *J*=6.14 Hz, 2H, HN–CH_2–CH), 2.3 (s, 3H, CH_3–Ar), ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): *δ*=143.45 (*C*q–NH, Ar), 139.28 (*C*q–CH_3, Ar), 136.36 (*C*q-SO_2, Ar), 135.7 (Cq–CH=CH, Ar), 133.76 (CH=*C*H–Ph), 129.44 (2*C*H, Ar), 128.93 (4*C*H, Ar), 128.48 (2*C*H, Ar), 127.74 (*C*H, Ar), 127.74 (CH_2–*C*H=CH), 126.42 (2*C*H, Ar), 124.12 (*C*H, Ar), 53.31 (HN–CH_2–CH), 21.52 (CH_3) ppm. MS–MS (ESI): *m*/*z* calcd for (M+Na): 386.13, found (M+Na): 386.2.

4.4.10. Cinnamyl-(1,1-diphenyl)-methylether (Table 4, entry 4). Yield: 84% (252 mg). R_f (5% EtOAc/pet. ether) 0.57. IR (liquid film) 3010, 2927, 1600, 1216, 1071, 967, 755. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): *δ*=7.2–7.4 (m, 15H, Ar), 6.6 (d, *J*=16.13 Hz, 1H, CH=*C*H–Ph), 6.34 (td, *J*=15.76, 5.86 Hz, 1H, CH_2–*C*H=CH), 5.48 (s, 1H, *C*HPh_2), 4.17 (dd, *J*=5.86, 1.1 Hz, 2H, O–CH_2–CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): *δ*=142.28 (2*C*q, Ar), 136.88 (*C*q–CH, Ar), 132.39 (CH=*C*H–Ph, Ar), 128.63 (2*C*H, Ar), 128.52 (4*C*H, Ar), 127.72 (*C*H, Ar), 127.57 (2*C*H, Ar), 127.16 (4*C*H, Ar), 126.59 (2*C*H, Ar), 126.29 (CH_2–*C*H=CH), 82.75 (Ph_2*C*H–O), 69.46 (O–CH_2–CH) ppm. GC–MS (EI, 70 eV): *m*/*z* (%)=168 (17), 167 (100), 152 (14), 118 (44), 117 (16), 77(11).

4.4.11. Dicinnamylether (Table 4, entry 6). Yield: 98% (245 mg). R_f (5% EtOAc/pet. ether) 0.47. IR (liquid film) 3020, 1602, 1495, 1452, 1216, 968, 759. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): *δ*=7.2–7.4 (m, 10H, Ar), 6.63 (d, *J*=16.13 Hz, 2H, CH=*C*H–Ph), 6.32 (td, *J*=15.76, 6.23 Hz, 2H, CH_2–*C*H=CH), 4.2 (dd, *J*=6.23, 1.1 Hz, 2H, O–CH_2–CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): *δ*=136.75 (2*C*q–CH, Ar), 132.62 (2CH=*C*H–Ph), 128.59 (4*C*H, Ar), 127.73 (2*C*H, Ar), 126.55 (4CH, Ar), 126.07 (2CH_2–CH=CH), 70.77 (2 O–CH_2–CH) ppm. GC–MS (EI, 70 eV): *m*/*z* (%)=250 (1) [M^+], 118 (32), 117 (100), 115 (34), 77 (9).

4.4.12. Cinnamyl acetate: (Table 4, entry 7). Yield: 95% (167 mg). R_f (5% EtOAc/pet. ether) 0.38. IR (liquid film) 3026, 2933, 1736, 1597, 1236, 966, 752. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): *δ*=7.2–7.4 (m, 5H, Ph), 6.65 (d, *J*=15.76 Hz, 1H, CH=*C*H–Ph), 6.28 (td, *J*=15.76, 6.23 Hz, 1H, CH_2–*C*H=CH), 4.72 (dd, *J*=6.23, 1.1 Hz, 2H, O–CH_2–CH), 2.1 (s, CH_3–CO_2, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): *δ*=170 (CH_3–CO_2–CH_2), 136.26 (*C*q, Ar), 134.25 (CH=*C*H–Ph), 128.65 (2*C*H, Ar), 128.11 (*C*H, Ar), 126.66 (2*C*H, Ar), 123.23 (CH_2–*C*H=CH), 65.11 (O–CH_2), 21 (CH_3) ppm. GC–MS (EI, 70 eV): *m*/*z* (%)=176 (28) [M^+], 134 (40), 133 (39), 117 (29), 115 (86), 92 (35), 77 (20), 43 (100).

4.4.13. Cinnamyl benzoate (Table 4, entry 8). Yield: 95% (226 mg). R_f (5% EtOAc/pet. ether) 0.5. IR (liquid film) 3020, 2930, 1717, 1602, 1271, 1216, 967, 759. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): *δ*=8.1 (d, *J*=8.43 Hz, 2H, Ar), 7.2–5.9 (m, 8H, Ar), 6.75 (d, *J*=15.76, 1H, CH=*C*H–Ph), 6.4 (td, *J*=15.76, 6.23 Hz, 1H, CH_2–*C*H=CH), 5.0 (dd, *J*=6.23, 1.1 Hz, 2H, O–CH_2–CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): *δ*=166.37 (CO_2), 136.25 (*C*q–CH, Ar), 134.27 (*C*q–CO_2, Ar), 133 (*C*H, Ar), 129.67 (2*C*H, Ar), 128.63 (2*C*H, Ar), 128.39 (2*C*H, Ar), 128.1 (CH=*C*H–Ph, Ar), 126.67 (2*C*H, Ar), 123.29 (CH_2–*C*H=CH), 65.23 (O–CH_2–CH) ppm. GC–MS (EI, 70 eV): *m*/*z* (%)=238 (4) [M^+], 133 (11), 117 (12), 115 (28), 105 (100), 77 (28), 45 (27).

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