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Allylation of 1-phenyl-1-propyne with N- and O-pronucleophiles using polymer supported triphenylphosphine palladium complex as a heterogeneous and recyclable catalyst

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ABSTRACT

Simple methodology for the allylation of various N- and O-pronucleophiles with 1-phenyl-1-propyne as an allylating agent, using PS-TPP-Pd (polymer supported triphenylphosphine palladium) as a highly active heterogeneous recyclable catalyst has been developed. The protocol is applicable for a wide variety of hindered and functionalized aromatic amines, alcohols, and carboxylic acids. The catalyst exhibited remarkable catalytic activity for five consecutive recycles.

Allyl amines, allyl ethers, and allyl esters have wide applications in organic synthesis,[1,2] synthesis of biologically active compounds,[3,4] natural products synthesis,[3b] and perfumery industries.[5] These allylated products can be obtained via palladium catalyzed allylation of respective amines, alcohols, and carboxylic acids with various allylating agents such as allyl alcohols, derivatives of allyl alcohols (e.g., allyl acetate, allyl carbonates, allyl triflates, etc.), allenes, or internal alkynes.[6–10] The use of allylating agents like allylic alcohols and their derivatives is not advantageous as it produces stoichiometric amount of side products in the reaction. However, the use of allenes and internal alkynes as an allylating agent is more advantageous, as the allylated products are formed by simple addition reaction of N- and O-pronucleophiles with allenes and alkynes. Among the allenes and alkynes, alkynes are easily available and are also cost-effective. Yamamoto and coworkers[11] reported various homogeneous palladium catalyst such as $Pd(PPh_3)_4$, $Pd_2(dba)_3{\cdot}CHCl_3$ with 2-(dicyclohexylphosphanyl)-2′-(dimethylamino)biphenyl as a ligand, for the allylation of pronucleophiles. Recently, we have reported allylation of various N- and O-pronucleophiles using homogeneous $Pd(OAc)_2$/dppf as catalyst.[12] Homogeneous catalytic systems have several drawbacks like the presence of palladium based impurities in synthesized products, catalyst-product separation, and lack of catalyst reusability. It is noteworthy to mention that such toxic palladium based impurities creates considerable problems in case of pharmaceutical products as the purity of the product is of enormous importance.

Hence, suitable efforts to anchor such homogeneous complex catalyst which can overcome such limitation of catalyst-product separation and recycle are necessary. In this context, we recently reported an effective heterogeneous catalytic methodology for allylic amination of internal alkynes using polymer supported palladium catalyst.[13] The exploration of developed methodology for the allylation of weaker pronucleophiles such as hindered amines, alcohols, and carboxylic acids still remains the scope of further research. We herein report allylic amination of alkynes using polymer supported palladium catalyst for the allylation of weaker N- and O-pronucleophiles using polymer supported triphenylphosphine palladium complex (PS-TPP-Pd) as a heterogeneous and recyclable catalyst (Scheme 1).

In this work the allylation of 2-methylaniline with 1-phenyl-1-propyne (**1**) as a model reaction using $Pd(OAc)_2$ as a catalyst precursor using polymer supported triphenylphosphine as a ligand and benzoic acid as a co-catalyst was studied. Various reaction parameters such as molar ratio, solvent, temperature, time, and catalyst loading were studied to obtain the best optimized reaction conditions (Table 1).

Molar ratio has always shown a profound effect on the yield of the desired product. Hence, we have studied the effect of different molar ratios of 1-phenyl-1-propyne/2-methylaniline and found that the molar ratio 1:1.2 revealed excellent yields (90%) within 5 h (Table 1, entry 2). Various non-polar organic solvents like tolu-

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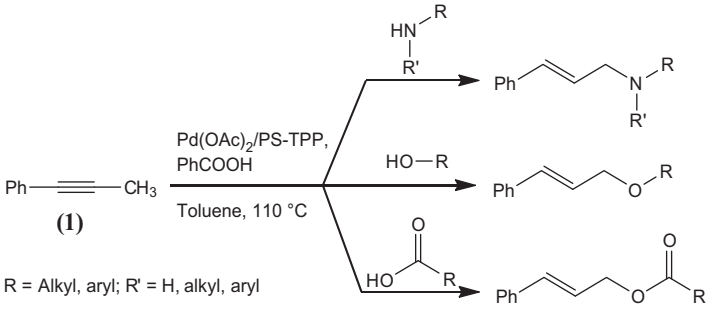

Scheme 1. PS-TPP-Pd catalyzed allylation of N- and O-pronucleophiles with 1-phenyl-1-propyne.

Table 1
Effect of reaction parameters on the allylation of 2-methyl aniline with 1-phenyl-1-propyne (**1**)[a]

Entry	Molar ratio	Solvent	Temperature (°C)	Time (h)	Catalyst loading (mol %)	Pd:P ratio	Yield[b] (%)
Influence of molar ratio							
1	1:1	Toluene	110	5	10	1:4	88
2	1:1.2	Toluene	110	5	10	1:4	90
3	1.2:1	Toluene	110	5	10	1:4	86
Influence of solvent							
4	1:1.2	Xylene	110	5	10	1:4	60
5	1:1.2	*n*-Hexane	70	5	10	1:4	05
6	1:1.2	Cyclohexane	80	5	10	1:4	—
Influence of temperature							
7	1:1.2	Toluene	100	5	10	1:4	78
8	1:1.2	Toluene	80	5	10	1:4	60
9[c]	1:1.2	Toluene	120	5	10	1:4	90
Influence of time							
10	1:1.2	Toluene	110	2	10	1:4	31
11	1:1.2	Toluene	110	4	10	1:4	76
12	1:1.2	Toluene	110	6	10	1:4	92
Influence of catalyst loading							
13	1:1.2	Toluene	110	5	5	1:4	76
14	1:1.2	Toluene	110	5	15	1:4	90
Influence of Pd:P ratio							
15	1:1.2	Toluene	110	5	10	1 : 1	40
16	1:1.2	Toluene	110	5	10	1:2	73
17	1:1.2	Toluene	110	5	10	1:3	76
18	1:1.2	Toluene	110	5	10	1:5	94

[a] Reaction condition: **1** 1-phenyl-1-propyne (5 mmol), **2** 2-methylaniline, $Pd(OAc)_2$, PS-TPP, benzoic acid (10 mol %), solvent (20 mL).
[b] GC yield.
[c] The reaction was performed in sealed vial.

ene, xylene, cyclohexane, and *n*-hexane were screened and toluene was found to be the best solvent, furnishing excellent yield (90%) (Table 1, entry 2). It was observed that with increase in the reaction temperature from 80 °C to 110 °C, the yield was increased, while further increase in temperature to 120 °C had no significant effect on the yield of the reaction (Table 1, entries 2, 7–9). We further investigated the effect of reaction time and observed that 5 h was sufficient for the reaction (Table 1, entries 2, 10–12). The catalyst loading of 10 mol % was adequate to catalyze the allylation reaction at the palladium: phosphine ratio of 1:5 (Table 1, entries 2, 13–18). We observed that excess amount of phosphine ligand was necessary to stabilize palladium complex for the allylation reaction. Hence, the final optimized reaction conditions are: 1-phenyl-1-propyne (1 equiv), 2-methylaniline (1.2 equiv), toluene at 110 °C, $Pd(OAc)_2$/PS-TPP (10 mol %), ratio of Pd:P (1:5) for 5 h.

Furthermore, the efficiency of developed methodology for the allylation of various N- and O-pronucleophiles was studied (Table 2). Several weaker N-pronucleophiles such as different aniline derivatives containing sterically hindered N-substituted compound (*N*-benzylaniline) as well as electron deficient anilines were subjected for the allylation reaction. We observed that (2-cyanoaniline) and N-sulphonated aniline (*N*-tosylaniline) were well tolerated offering good to excellent yield (82–94%) of the desired allyl amines (Table 2, entries 1–4). Encouraged with the results, we extended our protocol to much weaker pronucleophiles like alcohols and carboxylic acids (Table 2, entries 5–12). Among the O-pronucleophiles screened, the carboxylic acids were found to be much more effective for allylation reaction as compared with alcohols. Benzylalcohol and its derivatives reacted smoothly with **1** providing good yield of the desired product while the reaction of cinnamyl alcohol with **1** offered excellent yield of dicinnamyl ether (90%) as a product (Table 2, entries 5–8). Furthermore, we employed some less nucleophilic O-pronucleophiles, that is, various carboxylic acids such as acetic acid, benzoic acid, *ortho*-toluic acid, and cinnamic acid for the developed methodology. To our delight, all these substrates reacted smoothly to endow excellent yield of their respective allyl esters (Table 2, entries 9–12). In order to avoid the formation of cinnamyl benzoate as a side product in the reaction medium, the reaction of acetic acid and *ortho*-toluic acid with **1** were performed in the absence of benzoic acid (co-cat-