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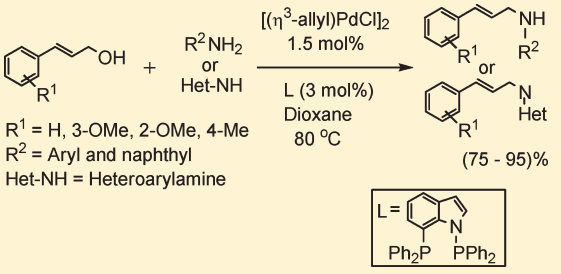
Palladium-Catalyzed Amination of Allyl Alcohols

Raju Ghosh and Amitabha Sarkar*

Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

Supporting Information

ABSTRACT: An efficient catalytic amination of aryl-substituted allylic alcohols has been developed. The complex $[(\eta^3\text{-allyl})PdCl]_2$ modified by a bis phosphine ligand, L, has been used as catalyst in the reaction that afforded a wide range of allyl amines in good to excellent yield under mild conditions.



Allyl amines are important building blocks for various biologically active compounds and advanced intermediates in total synthesis of natural products[1] and especially those involving ring-closing metathesis.[2] Therefore, their synthesis is still an important area of activity. Although catalytic C−N bond formation using nucleophilic attack on an η^3-allyl palladium complex has been widely used to this end,[3] activated derivatives of allyl alcohol (esters, carbonates, carbamates, phosphates, halides etc)[4] and allyl alcohol with activators[5] have only been chosen as substrates. Use of allyl alcohol is limited by its reactivity despite the economical and ecological advantage of this reaction that only produces water as by product.[6] Of late, a few reports have appeared where allyl alcohol has indeed been used as a substrate in Pd-catalyzed amination reactions.[7,8] The conditions, especially the ligands on palladium in such instances, are less common. It is in this context that we report a highly efficient direct catalytic amination of aryl-substituted allylic alcohols under mild condition using a combination of $[(\eta^3\text{-allyl})PdCl]_2$ and a chelating P, N−P ligand developed by us.[9]

The bidentate phosphine ligand (**L**) on treatment with $[(\eta^3\text{-allyl})PdCl]_2$ in dichloromethane followed by addition of the Ag salt afforded a 16e complex with deep magenta color (**1a**) (Scheme 1). The molecular structure of the palladium complex (**1a**) was determined by single-crystal X-ray analysis; the single crystal of the air stable complex (**1a**) was grown from acetone/hexane (see the Supporting Information).

We selected cinnamyl alcohol (**2a**) and *p*-anisidine (**3b**) as typical coupling partners during optimization study. The molar ratio of metal and ligand, the effect of different solvents, and comparison of different Pd precursors were examined. The results are summarized in Table 1. The comparative study reveals that $[(\eta^3\text{-allyl})PdCl]_2$ (entry 2) worked better as the catalyst precursor than $Pd(OAc)_2$, $Pd_2(dba)_3$, $Pd(CH_3CN)_2Cl_2$, and $PdCl_2$ (entries 6−9). The use of a phosphane/Pd molar ratio of 1:1 was found to be optimal for this catalytic system (entry 2). It was observed that the presence of excess ligand suppressed the reaction (entry 5). This reaction did not take place in absence of the bis-phosphane ligand, **L** (entry 16). We also studied the influence of different solvents on the reaction. Dioxane was found to be a superior solvent compared to toluene, DMF, and CH_3CN (entries 10−12). The temperature around 80 °C was found to be optimal for this reaction. The yield decreased with lowering the temperature (entry 14). We observed that the amount of solvent had a marked influence on the yield. Use of 0.2 mL of solvent for 1.0 mmol of cinnamyl alcohol afforded the corresponding monoallylamine (entry 2) in better yield than when the solvent volume was increased to 1.0 mL (entry 13). Also, under solvent-free conditions this catalytic system furnished *N*-cinnamylaniline in 87% yield (entry 15). We decided to retain a minimal volume of solvent dioxane to ensure even mixing of reactants, especially when one of them was a solid.

Using the optimized conditions with $[(\eta^3\text{-allyl})PdCl]_2$ (1.5 mol %) and ligand (3.0 mol %) in dioxane (0.2 mL), we conducted allylic amination reaction of a large number of electronically and structurally diverse allyl alcohols with variously substituted arylamines (Table 2). Substituted cinnamyl alcohols in combination with aniline, *p*-anisidine, *m*-acetylaniline, and 2-naphthylamine afforded the corresponding monoallylamine in good to excellent yield. Both the *trans*- and *cis*-cinnamyl alcohol afforded the allylated product as the *trans*-isomer in very good yield (entry 6), suggesting involvement of the same π-allyl complex. No product was obtained from 4-nitroaniline (entry 5) presumably due to the strong electron-withdrawing nature of nitro group, which renders the aniline less nucleophilic. 2-Methoxycinnamyl alcohol afforded the corresponding monoallylaniline in good yield (entries 14 and 15). *Ortho*-substituted anilines gave high yield of the desired products (entries 16 and 17), although sterically demanding 2,6-disubstituted aniline did not participate in the reaction. When we used benzyl amine as a nucleophile very poor yield of product was obtained (entry 19).[10]

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Scheme 1. Synthesis of Palladium Complex

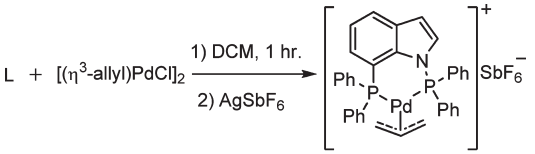
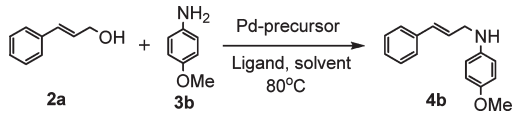


Table 1. Optimization of Amination of Cinnamyl Alcohol with *p*-Anisidine[a]



entry	Pd precursor (mol %)	ligand (mol %)	solvent	yield (%)
1	$[(\eta^3\text{-allyl})PdCl]_2$ (1.0)	2.0	dioxane	81
2	$[(\eta^3\text{-allyl})PdCl]_2$ (1.5)	3.0	dioxane	89
3	$[(\eta 3\text{-allyl})PdCl]$ (2.0)	4.0	dioxane	90
4	$[(\eta^3\text{-allyl})PdCl]_2$ (1.5)	1.5	dioxane	63
5	$[(\eta^3\text{-allyl})PdCl]_2$ (1.5)	6.0	dioxane	37
6	$Pd(OAc)_2$ (3.0)	3.0	dioxane	68
7	Pd_2dba_3 (3.0)	3.0	dioxane	57
8	$Pd(CH_3CN)_2Cl_2$ (3.0)	3.0	dioxane	31
9	$PdCl_2$ (3.0)	3.0	dioxane	5
10	$[(\eta^3\text{-allyl})PdCl]_2$ (1.5)	3.0	toluene	84
11	$[(\eta^3\text{-allyl})PdCl]_2$ (1.5)	3.0	DMF	84
12	$[(\eta^3\text{-allyl})PdCl]_2$ (1.5)	3.0	CH_3CN	85
13[b]	$[(\eta^3\text{-allyl})PdCl]_2$ (1.5)	3.0	dioxane	62
14[c]	$[(\eta^3\text{-allyl})PdCl]_2$ (1.5)	3.0	dioxane	78
15	$[(\eta^3\text{-allyl})PdCl]_2$ (1.5)	3.0	neat	87
16	$[(\eta^3\text{-allyl})PdCl]_2$ (1.5)	0	dioxane	0

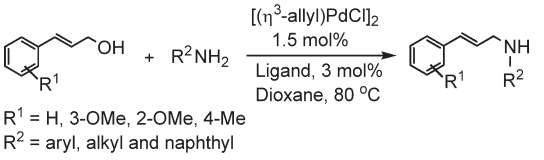
[a] Reaction conditions: cinnamyl alcohol (1.0 mmol), *p*-anisidine (1.5 mmol), solvent (0.2 mL); argon atmosphere for 6 h. [b] 1.0 mL of solvent was used. [c] At 70 °C.

Encouraged by this result, we extended allylic amination of arylallyl alcohol with heteroarylamines. Imidazole and pyrazole afforded almost quantitative yields of product with cinnamyl alcohol and its analogues (Table 3). Sterically more hindered heteroaryl amines such as carbazole and indole were unreactive under these conditions (entries 9 and 10). Allylic substitution reaction of a secondary aliphatic amine produced a relatively lower yield of the product (entry 11).

It has been reported in literature that sp^2-hybridized phosphorus with increased π-acidity is a better donor for Pd-catalyzed allylation of amines.[7d,g] The ligand (**L**) described in this paper resembles, to an extent, the ligand DPEphos featuring two phosphorus on a flexible diphenyl ether backbone. The paper,[8b] however, reports on catalysis by Pt while Pd is ineffective. In our case, the reaction is catalyzed by palladium in combination with a bidentate phosphine ligand where one of the two phosphorus atom is linked to a nitrogen. The ligand bite angle is 94° which is smaller than the angle commonly found with catalytically active complexes.[8a,b]

In summary, we have developed an efficient, direct, catalytic amination of aryl-substituted allylic alcohols with aromatic amines under mild conditions that provides an excellent yield of desired monoallylamine. The reaction proceeded without any activator

Table 2. Amination of Allyl Alcohols with Arylamine[a]



entry	allyl alcohol	amine	time(hr.)	product	yield(%)
1	2a	3a	6.0	4a	84
2		3b	6.0	4b	89
3		3c	6.0	4c	91
4		3d	6.0	4d	92
5	2a	3e	8.0	4e	0
6	2b	3b	8.0	4b	75
7[b]	2c	3a	6.0	4f	83
8		3b	4.0	4g	92
9		3c	4.0	4h	91
10		3d	5.0	4i	91
11[b]	2d	3a	6.0	4j	78
12		3b	6.0	4k	76
13		3c	6.0	4l	81
14	2e	3b	6.0	4m	78
15		3c	6.0	4n	80
16	2a	3f	8.0	4o	81
17	2a	3g	8.0	4p	79
18	2a	3h	8.0	4q	0
19	2a	3i	8.0	4r	25

[a] Reaction conditions: allyl alcohol (1.0 mmol), amine (1.5 mmol), $[(\eta^3\text{-allyl})PdCl]_2$ (1.5 mol %), **L** (3.0 mol %), dioxane (0.2 mL); argon atmosphere. [b] 0.1 mL of dioxane was used.

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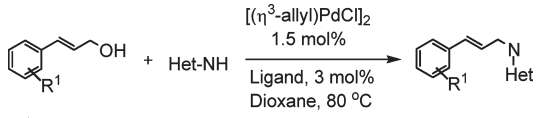
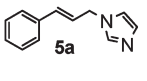
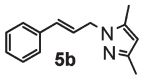
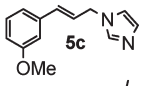
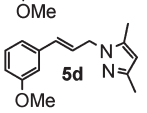
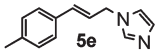
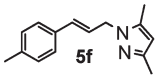
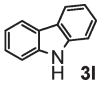
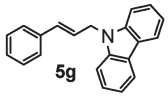
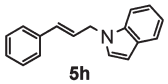
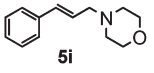
Table 3. Amination of Allyl Alcohols with Heteroarylamine[a]



R^1 = H, 3-OMe, 4-Me
Het-NH = Heteroaryl amine

entry	allyl alcohol	amine	time(hr.)	product	yield(%)
1	**2a**	 **3j**	4.0	 **5a**	93
2	**2a**	 **3k**	3.0	 **5b**	95
3	**2c**	**3j**	2.5	 **5c** OMe	94
4	**2c**	**3k**	3.5	 **5d** OMe	95
5	**2d**	**3j**	4.0	 **5e**	91
6	**2d**	**3k**	3.5	 **5f**	94
9	**2a**	 **3l**	6.0	 **5g**	0
10	**2a**	 **3m**	6.0	 **5h**	0
11	**2a**	 **3n**	8.0	 **5i**	45

[a] Reaction conditions: allyl alcohol (1.0 mmol), amine (1.5 mmol), $[(\eta^3$-allyl)PdCl$]_2$ (1.5 mol %), **L** (3.0 mol %), dioxane (0.2 mL); argon atmosphere.

and produced water as the sole coproduct, representing an inexpensive and environmentally friendly protocol for allyl amine synthesis.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all starting materials were obtained from commercial suppliers (except entries 2b, 2c, 2d, and 2e, Table 2). Organic solvents were dried and distilled as described elsewhere. All reactions were carried out in an oven-dried flask under argon atmosphere. Column chromatography was performed with silica gel 230−400 mesh. All ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 solution and are reported in ppm (δ). HRMS (ESI) spectra were recorded on micromass, Q-Tofmicro. X-ray single-crystal data were collected using Mo Kα (λ = 0.7107 Å) radiation. Data collection, data reduction, and structure solution/refinement were carried out using the software package of BRUKER APEX II. The single-crystal structure of the complex (**1a**) was solved by direct methods and refined in a routine manner.

Preparation of Ligand (L). To a stirred solution of 7-bromoindole (980.0 mg, 5 mmol) in THF (25 mL), under argon atmosphere, was added ^{n}BuLi (6.56 mL, 10.5 mmol, 1.60 M in hexane) dropwise at −78 °C. The mixture was then stirred for 2 h at −78 °C. Chlorodiphenylphosphine (1.94 mL, 10.5 mmol) in THF (5 mL) was then added dropwise and the mixture stirred for 3 h. The mixture was then warmed to rt and stirred for a further 3 h. It was then quenched with saturated NH_4Cl solution at 0 °C and extracted with diethyl ether (2 × 100 mL). The combined organic layer was washed subsequently with water and brine and dried over anhydrous Na_2SO_4. Evaporation of solvent under reduced pressure gave the crude product. Purification by flash column chromatography (silica gel, 12% dichloromethane/petroleum ether) afforded **L** as a white solid (607.0 mg, 25%).

General Procedure for Catalytic Reactions. A solution of ligand (14.6 mg, 0.03 mmol), $[(\eta^3$-allyl)PdCl$]_2$ (5.5 mg, 0.015 mmol), cinnamyl alcohol (1.0 mmol), and amine (1.5 mmol) in dioxane (0.2 mL) was stirred under argon atmosphere at 80 °C for 2.5−8.0 h (depending on substrate). The reaction mixture was then cooled to rt, diluted with DCM (5 mL), and filtered through a pad of Na_2SO_4. The filtrate was evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (230−400 mesh) using ethyl acetate/petroleum ether or methanol/dichloromethane as a eluent.

N-Cinnamylaniline (***4a***)[8b]. Light-yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43−7.21 (m, 7H), 6.80−6.64 (m, 4H), 6.37 (td, J = 15.9, 5.7 Hz, 1H), 3.97 (dd, J = 5.7, 1.2 Hz, 2H), 3.88 (bs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.6, 136.9, 132.0, 129.4, 128.7, 127.7, 126.8, 126.5, 118.2, 113.6, 46.7.

N-Cinnamyl-4-methoxyaniline (***4b***)[8a]. White-yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38−7.22 (m, 5H), 6.79 (dd, J = 6.7, 2.2 Hz, 2H), 6.63 (dd, J = 6.6, 2.3 Hz, 2H), 6.58(s, 1H), 6.33 (td, J = 15.9, 5.8 Hz, 1H), 3.88 (dd, J = 5.8, 1.3 Hz, 2H), 3.74 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.5, 142.1, 137.0, 131.7, 128.7, 127.6, 127.3, 126.4, 115.0, 114.7, 55.9, 47.4.

N-Cinnamyl-3-acetylaniline (***4c***)[11]. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39−7.24 (m, 8H), 6.87−6.84 (m, 1H), 6.63 (d, J = 15.9 Hz, 1H), 6.31 (td, J = 15.9, 5.7 Hz, 1H), 3.97 (dd, J = 5.7, 1.4 Hz, 2H), 2.57 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.7, 148.3, 138.3, 136.8, 131.9, 129.4, 128.7, 127.7, 126.5, 126.4, 118.0, 117.8, 111.9, 46.1, 26.8.

N-Cinnamyl-2-naphthylamine (***4d***). White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74−7.66 (m, 3H), 7.44−7.26 (m, 7H), 6.98−6.93 (m, 2H), 6.71 (d, J = 15.9 Hz, 1H), 6.41 (td, J = 15.9, 5.8 Hz, 1H), 4.08 (dd, J = 5.8, 1.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.7, 136.9, 135.3, 131.9, 129.1, 128.7, 127.8, 127.7, 126.7, 126.5, 126.1, 122.2, 118.1, 105.1, 46.3. HRMS (ESI): calcd for $C_{19}H_{18}N$ ($[M + H]^+$) 260.1439, found 260.1434. Mp: 45 °C.

N-(3-m-Anisylallyl)aniline (***4f***). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17−7.10 (m, 3H), 6.89 (d, J = 7.7 Hz, 1H), 6.83 (s, 1H), 6.73−6.63 (m, 4H), 6.51 (d, J = 15.9 Hz, 1H), 6.25 (td, J = 15.8, 5.8 Hz, 1H), 3.86 (dd, J = 5.8, 1.2 Hz, 2H), 3.73 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.9, 147.4, 138.4, 132.0, 129.7, 129.4, 127.0, 119.1, 118.4, 113.8, 113.4, 111.8, 55.3, 46.8. HRMS (ESI): calcd for $C_{16}H_{18}NO$ ($[M+H]^+$) 240.1388, found 240.1383.

N-(3-m-Anisylallyl)-4-methoxyaniline (***4g***). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.14 (t, J = 8.0 Hz, 1H), 6.89 (d, J = 7.7 Hz, 1H), 6.83 (s, 1H), 6.74−6.69 (m, 3H), 6.6−6.56 (m, 2H), 6.51 (d, J = 15.9 Hz, 1H), 6.25 (td, J = 15.9, 5.7 Hz, 1H), 3.81 (dd, J = 5.7, 1.1 Hz, 2H), 3.73 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.9, 152.5, 142.2, 138.5, 131.5, 129.7, 127.8, 119.1, 115.0, 114.6, 113.3, 111.8, 55.9, 55.3, 47.4. HRMS (ESI): calcd for $C_{17}H_{20}NO_2$ ($[M + H]^+$) 270.1494, found 270.1489.

N-(3-m-Anisylallyl)-3-acetylaniline (***4h***). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29−7.21 (m, 4H), 6.96 (d, J = 8.0 Hz, 1H), 6.90 (s, 1H), 6.84 (dd, J = 7.5, 2.0 Hz, 1H), 6.80 (dd, J = 8.0, 2.0 Hz, 1H), 6.60 (d, J = 15.5 Hz, 1H), 6.30 (td, J = 15.5, 5.5 Hz, 1H), 4.05 (bs, 1H), 3.98 (dd, J = 5.5, 1.1 Hz, 2H), 3.80 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.7, 160.0, 148.3, 138.3, 138.3,

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131.8, 129.7, 129.5, 126.9, 119.1, 118.1, 117.8, 113.4, 112.0, 111.9, 55.4, 46.1, 26.8. HRMS (ESI): calcd for $C_{18}H_{19}NNaO_2$ ([M + Na]$^+$) 304.1313, found 304.1314.

N-(3-m-Anisylallyl)-2-naphthylamine (***4i***). Light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63−7.55 (m, 3H), 7.30 (t, J = 7.5 Hz, 1H), 7.17−7.12 (m, 2H), 6.91−6.84 (m, 4H), 6.72 (dd, J = 8.2, 2.3 Hz, 1H), 6.56 (d, J = 15.9 Hz, 1H), 6.31 (td, J = 15.9, 5.9 Hz, 1H), 3.97 (dd, J = 5.9, 0.8 Hz, 2H), 3.72 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.9, 144.9, 138.3, 135.1, 132.2, 129.7, 129.2, 128.1, 127.8, 126.5, 126.3, 122.5, 119.2, 118.3, 113.5, 111.8, 106.1, 55.3, 46.8. HRMS (ESI): calcd for $C_{20}H_{20}NO$ ([M + H]$^+$) 290.1545, found 290.1538.

N-(3-p-Tolylallyl)aniline (***4j***)[12]. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21−7.10 (m, 4H), 7.04 (d, J = 8.0 Hz, 2H), 6.71−6.63 (m, 3H), 6.52 (d, J = 15.9 Hz, 1H), 6.21 (td, J = 15.9, 5.9 Hz, 1H), 3.85 (dd, J = 5.9, 1.2 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.6, 137.5, 134.1, 131.9, 129.4, 126.4, 125.6, 118.2, 113.7, 46.8, 21.3.

N-(3-p-Tolylallyl)-4-methoxyaniline (***4k***). Light yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19 (d, J = 8.1 Hz, 2H), 7.05 (d, J = 7.9 Hz, 2H), 6.73 (dd, J = 6.7, 2.2 Hz, 2H), 6.59−6.49 (m, 3H), 6.21 (td, J = 15.9, 5.9 Hz, 1H), 3.80 (dd, J = 5.9, 1.3 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.4, 142.4, 137.4, 134.2, 131.6, 129.4, 126.3, 115.0, 114.6, 55.9, 47.5, 21.3. HRMS (ESI): calcd for $C_{17}H_{20}NO$ ([M + H]$^+$) 254.1545, found 254.1538. Mp: 75 °C.

N-(3-p-Tolylallyl)-3-acetylaniline (***4l***). Light yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20−7.15 (m, 5H), 7.04 (d, J = 8.0 Hz, 2H), 6.79−6.75 (m, 1H), 6.51 (d, J = 15.9 Hz, 1H), 6.17 (td, J = 15.9, 5.8 Hz, 1H), 3.88 (dd, J = 5.8, 1.2 Hz, 2H), 2.48 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.7, 148.3, 138.3, 137.6, 134.0, 132.0, 129.5, 129.4, 126.4, 125.3, 118.1, 117.9, 112.0, 46.3, 26.9, 21.3. HRMS (ESI): calcd for $C_{18}H_{19}NNaO$ ([M + Na]$^+$) 288.1364, found 288.1364. Mp: 78 °C.

N-(3-o-Anisylallyl)-4-methoxyaniline (***4m***). Yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (dd, J = 7.6, 1.4 Hz, 1H), 7.28−7.22 (m, 1H), 7.01−6.89 (m, 3H), 6.86−6.80 (m, 2H), 6.71−6.66 (m, 2H), 6.39 (td, J = 15.9, 6.1 Hz, 1H), 3.93 (dd, J = 6.1, 1.4 Hz, 2H), 3.87 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.7, 152.4, 142.4, 128.7, 128.1, 127.0, 126.7, 126.1, 120.8, 115.0, 114.6, 111.0, 55.9, 55.5, 47.9. HRMS (ESI): calcd for $C_{17}H_{20}NO_2$ ([M + H]$^+$) 270.1494, found 270.1487. Mp: 69 °C.

N-(3-o-Anisylallyl)-3-acetylaniline (***4n***). Light yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (dd, J = 7.6, 1.4 Hz, 1H), 7.29−7.18 (m, 4H), 6.97−6.82 (m, 4H), 6.30 (td, J = 15.9, 6.0 Hz, 1H), 3.96 (dd, J = 6.0, 1.4 Hz, 2H), 3.82 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.8, 156.7, 148.3, 138.3, 129.4, 128.8, 127.2, 127.1, 127.1, 125.9, 120.8, 118.0, 117.9, 112.1, 111.0, 55.5, 46.7, 26.8. HRMS (ESI): calcd for $C_{18}H_{19}NNaO_2$ ([M + Na]$^+$) 304.1313, found 304.1313.

N-Cinnamyl-2-methylaniline (***4o***)[13]. Light-yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (d, J = 7.2 Hz, 2H), 7.37 (t, J = 7.0 Hz, 2H), 7.32−7.27 (m, 1H), 7.22−7.13 (m, 2H), 6.78−6.67 (m, 3H), 6.43 (td, J = 15.9, 5.8 Hz, 1H), 4.04 (dd, J = 5.8, 1.1 Hz, 2H), 2.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.0, 137.0, 131.8, 130.2, 128.7, 127.7, 127.3, 127.2, 126.5, 122.2, 117.4, 110.3, 46.3, 17.7.

N-Cinnamyl-2-methoxyaniline (***4p***)[14]. Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 (d, J = 7.1 Hz, 2H), 7.35 (t, J = 7.1 Hz, 2H), 7.29−7.24 (m, 1H), 6.92 (m, 1H), 6.84 (d, J = 7.9 Hz, 1H), 6.76−6.65 (m, 3H), 6.40 (td, J = 15.9, 5.7 Hz, 1H), 4.00 (dd, J = 5.7, 1.0 Hz, 2H), 3.9 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.1, 138.1, 137.1, 131.5, 128.7, 127.6, 127.4, 126.5, 121.4, 116.9, 110.4, 109.6, 55.5, 46.1.

N-Cinnamylbenzylamine (***4r***)[8b]. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38−7.22 (m, 10H), 6.55 (d, J = 15.9 Hz, 1H), 6.32 (td, J = 15.9, 6.2 Hz, 1H), 3.84 (s, 2H), 3.44 (dd, J = 6.2, 1.2 Hz, 2H), 1.88(bs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.3, 137.2, 131.6, 128.7, 128.6, 128.4, 128.4, 127.5, 127.2, 126.4, 53.4, 51.3.

N-Cinnamylimidazole (***5a***)[15]. Solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.38−7.26 (m, 5H), 7.10 (s, 1H), 6.96 (s, 1H), 6.52 (d, J = 15.8 Hz, 1H), 6.27 (td, J = 15.8, 6.1 Hz, 1H), 4.70 (d, J = 6.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.2, 135.8, 133.8, 129.7, 128.8, 128.4, 126.7, 123.8, 119.1, 49.1. Mp. 48.0 °C.

N-Cinnamylpyrazole (***5b***). Light yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27−7.12 (m, 5H), 6.31 (d, J = 16.0 Hz, 1H), 6.19 (td, J = 15.9, 5.4 Hz, 1H), 5.76 (s, 1H), 4.72 (d, J = 5.4 Hz, 2H), 2.17 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.4, 139.5, 136.3, 132.4, 128.6, 127.9, 126.6, 124.5, 105.6, 51.1, 13.4, 11.1. HRMS (ESI): calcd for $C_{14}H_{17}N_2$ ([M + H]$^+$) 213.1392, found 213.1385.

N-(3-m-Anisylallyl)imidazole (***5c***). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (s, 1H), 7.25 (t, J = 8.0 Hz, 1H), 7.13 (s, 1H), 6.99−6.95 (m, 2H), 6.90 (s, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.52 (d, J = 15.8 Hz, 1H), 6.28 (td, J = 15.8, 6.1 Hz, 1H), 4.74 (d, J = 6.1 Hz, 2H), 3.81(s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.0, 137.2, 137.0, 134.0, 129.8, 128.9, 123.8, 119.3, 119.2, 114.1, 112.0, 55.3, 49.2. HRMS (ESI): calcd for $C_{13}H_{15}N_2O$ ([M + H]$^+$) 215.1184, found 215.1179.

N-(3-m-Anisylallyl)pyrazole (***5d***). Light yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28−7.19 (m, 1H), 6.95 (d, J = 7.7 Hz, 1H), 6.89 (d, J = 2.0 Hz, 1H), 6.80 (dd, J = 8.2, 1.9 Hz, 1H), 6.38 (d, J = 16.0 Hz, 1H), 6.30 (td, J = 16.0, 4.9 Hz, 1H), 5.86 (s, 1H), 4.80 (d, J = 4.9 Hz, 2H), 3.83 (s, 3H), 2.27 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.9, 147.5, 139.4, 137.8, 132.2, 129.6, 124.9, 119.3, 113.7, 111.8, 105.6, 55.3, 51.1, 13.5, 11.1. HRMS (ESI): calcd for $C_{15}H_{19}N_2O$ ([M + H]$^+$) 243.1497, found 243.1492.

N-(3-p-Tolylallyl)imidazole (***5e***). Solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (d, J = 6.6 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.3 Hz, 3H), 6.99 (s, 1H), 6.54 (d, J = 15.8 Hz, 1H), 6.24 (td, J = 15.8, 6.0 Hz, 1H), 4.74 (d, J = 6.0 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.4, 137.0, 134.1, 133.0, 129.5, 128.9, 126.6, 122.3, 119.2, 49.4, 21.3. HRMS (ESI): calcd for $C_{13}H_{15}N_2$ ([M + H]$^+$) 199.1235, found 199.1230. Mp: 60.0 °C.

N-(3-p-Tolylallyl)pyrazole (***5f***). Light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.37 (d, J = 15.9 Hz, 1H), 6.22 (td, J = 15.8, 5.6 Hz, 1H), 5.84 (s, 1H), 4.78 (d, J = 5.6 Hz, 2H), 2.32 (s, 3H), 2.25 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.4, 139.3, 137.8, 133.6, 132.2, 129.3, 126.5, 123.6, 105.5, 51.2, 21.3, 13.5, 11.1. HRMS (ESI): calcd for $C_{15}H_{19}N_2$ ([M + H]$^+$) 227.1548, found 227.1543.

N-Cinnamylmorpholine (***5i***)[8b]. Oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.24 (m, 1H), 6.53 (d, J = 16.0 Hz, 1H), 6.26 (td, J = 16.0, 6.5 Hz, 1H), 3.74 (t, J = 4.5 Hz, 4H), 3.16 (d, J = 6.5 Hz, 2H), 2.51 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.9, 133.6, 128.7, 127.7, 126.5, 126.1, 67.1, 61.6, 53.8.

Typical Procedure for Synthesis of Complex 1a[16]**.** A solution of ligand **L** (87.4 mg, 0.18 mmol) and [(η^3-allyl)PdCl]$_2$ (33.0 mg, 0.09 mmol) in dichloromethane (2.0 mL) was stirred for 1 h at rt. $AgSbF_6$ (0.18 mmol, 62.0 mg) was then added, and the yellow solution became magenta. Filtration of AgCl on Celite followed by evaporation of the dichloromethane under reduced pressure affording **1a** as a deep magenta solid (125.0 mg, 80%) which was crystallized from acetone/hexane.

L−*Pd Allyl Complex* (***1a***)[16]. Deep magenta solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.98 (d, J = 7.5 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.42 (m, 3H), 7.35 (m, 5H), 7.28 (m, 2H), 7.22 (m, 4H), 7.07 (m, 5H), 6.91 (d, J = 2.0 Hz, 2H), 5.90 (m, 1H), 4.27 (m, 2H), 3.45 (m, 2H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 133.2, 133.1, 133.0, 132.9, 132.8, 132.6, 132.5, 131.8, 131.6, 131.5, 131.4, 130.8, 130.6, 130.5, 130.4, 130.1, 129.9, 129.6, 129.5, 129.4, 129.3, 129.2, 129.1, 126.1, 124.7, 124.7, 124.6, 122.8, 122.7, 109.2, 75.0. ^{31}P NMR (202.44 MHz, CD_2Cl_2): δ 62.3 (d, J = 74.9 Hz), 10.0 (d, J = 74.9 Hz). Anal. Calcd for $C_{35}H_{30}F_6NP_2PdSb$: C, 48.39; H, 3.48; N, 1.61. Found: C, 48.35; H, 3.47; N, 1.59.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Detailed experimental procedures and characterization data for all compounds and CIF file

of **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: ocas@iacs.res.in.

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REFERENCES

(1) (a) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921. (b) Johannsen, M.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689. (c) Cheikh, R. B.; Chaabouni, R.; Laurent, A.; Mison, P.; Nafti, A. *Synthesis* **1983**, 685.

(2) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4490.

(3) For reviews, see: (a) Tsuji, J. *Transition Metal Reagents and Catalysts*; Wiley: New York, 2000. (b) Godleski, S. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 3, p 585.

(4) References cited inYang, S.-C.; Hsu, Y.-C.; Gan, K.-H. *Tetrahedron* **2006**, *62*, 3949.

(5) (a) Tao, Y.; Zhou, Y.; Qu, J.; Hidai, M. *Tetrahedron Lett.* **2010**, *51*, 1982. (b) Kimura, M.; Futamata, M.; Shibata, K.; Tamaru, Y. *Chem. Commun.* **2003**, 234. (c) Yang, S.-C; Tsai, Y.-C *Organometallics* **2001**, *20*, 763. (d) Yang, S.-C; Hung, C.-W. *J. Org. Chem.* **1999**, *64*, 5000. (e) Masuyama, Y.; Kagawa, M.; Kurusu, Y. *Chem. Lett.* **1995**, 1121. (f) Yang, S.-C.; Chung, W.-H. *Tetrahedron Lett.* **1999**, *40*, 953. (g) Lu, X.; Lu, L.; Sun, J. *J. Mol. Catal.* **1987**, *41*, 245.

(6) (a) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259. (b) Trost, B. M. *Science* **1991**, *254*, 1471.

(7) (a) Tao, Y.; Wang, B.; Wang, B.; Qu, L.; Qu, J. *Org. Lett.* **2010**, *12*, 2726. (b) Usui, I.; Schmidt, S.; Keller, M.; Breit, B. *Org. Lett.* **2008**, *10*, 1207. (c) Mora, G.; Deschamps, B.; van Zutphen, S.; Le Goff, X. F.; Ricard, L.; le Floch, P. *Organometallics* **2007**, *26*, 1846. (d) Thoumazet, C.; Grützmacher, H.; Deschamps, B.; Ricard, L.; le Floch, P. *Eur. J. Inorg. Chem.* **2006**, 3911. (e) Kinoshita, H.; Shinokubo, H.; Oshima, K. *Org. Lett.* **2004**, *6*, 4085. (f) Kayaki, Y.; Koda, T.; Ikariya, T. *J. Org. Chem.* **2004**, *69*, 2595. (g) Ozawa, F.; Okamoto, H.; Kawagishi, S.; Yamamoto, S.; Minami, T.; Yoshifuji, M. *J. Am. Chem. Soc.* **2002**, *124*, 10968.

(8) Even Pt-based catalyst has been developed to use the allyl alcohol directly in catalytic amination; see: (a) Ohshima, T.; Miyamoto, Y.; Ipposhi, J.; Nakahara, Y.; Utsunomiya, M.; Mashima, K. *J. Am. Chem. Soc.* **2009**, *131*, 14317. (b) Utsunomiya, M.; Miyamoto, Y.; Ipposhi, J.; Ohshima, T.; Mashima, K. *Org. Lett.* **2007**, *9*, 3371.

(9) (a) Ghosh, R.; Adarsh, N. N.; Sarkar, A. *J. Org. Chem.* **2010**, *75*, 5320. (b) Ghosh, R.; Sarkar, A. *J. Org. Chem.* **2010**, *75*, 8283.

(10) In contrast to cinnamyl alcohol, allyl alcohol and crotyl alcohol afforded the corresponding monoallylaniline in less than 50% yield. In the case of crotyl alcohol, a regio-isomeric mixture (84:16) was obtained.

(11) Patil, N. T.; Wu, H.; Kadota, I.; Yamamoto, Y. *J. Org. Chem.* **2004**, *69*, 8745.

(12) Nishina, N.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 3314.

(13) Nishikata, T.; Lipshutz, B. H. *Org. Lett.* **2009**, *11*, 2377.

(14) Wagh, Y. S.; Sawant, D. N.; Tambade, P. J.; Dhake, K. P.; Bhanage, B. M. *Tetrahedron* **2011**, *67*, 2414.

(15) Baggaley, K. H.; Heald, M.; Hindley, R. M.; Morgan, B.; Tee, J. L.; Green, J. *J. Med. Chem.* **1975**, *18*, 833.

(16) The procedure was adopted from ref 7d.