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Direct palladium/carboxylic acid-catalyzed allylation of anilines with allylic alcohols in water

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Abstract—The direct activation of C–O bonds in allylic alcohols in water as a suspension medium by palladium complexes has been accelerated by carrying out the reactions in the presence of a carboxylic acid. The palladium-catalyzed allylation of anilines using allylic alcohols directly gave allylic anilines in good yields.

1. Introduction

A principal goal of organometallic chemistry is the catalytic synthesis of organic compounds by using the chemistry of organic ligands covalently bound to transition metals. Most organometallic chemistry has focused on complexes with covalent metal–carbon or metal–hydrogen bonds. Transition metals, in particular palladium and rhodium, have been workhorse elements in many commercialized catalytic processes that include hydrogenations, hydroformylations, acetic acid production, and other C–C and C–H bond forming processes.[1] Although carbon–oxygen, carbon–nitrogen, or carbon–sulfur bonds are found in the majority of important organic molecules, catalytic organometallic reaction chemistry that leads to the formation of carbon-heteroatom bonds is less common than that forming carbon–carbon and carbon–hydrogen bonds. Transition metal η^3-allyl complexes, as well as transition metal σ-alkyl complexes, play important roles as active species and key intermediates in many reactions catalyzed by transition metal complexes.[2] The palladium-catalyzed allylation is a powerful tool for C–C, C–N, and C–O bond formation, which has been widely applied to organic chemistry.[3] The processes have been shown to proceed by attack of nucleophiles on intermediate η^3-allylpalladium(II) complexes generated by oxidative addition of allylic compounds including halides,[4] esters,[5] carbonates,[6] carbamates,[7] phosphates,[8] and related derivatives[9] to a Pd(0) complex. Because these substrates are synthesized from the corresponding allylic alcohols, palladium-catalyzed conversion of allylic alcohols directly into allylation products are highly desirable, especially from the viewpoint of the atom economy.[10] For achieving the palladium-catalyzed C–O bond cleavage of allylic alcohols, various other processes to facilitate the bond cleavage have been reported.[11] These processes include conversion of allylic alcohols into the esters of inorganic acids (e.g., As_2O_3,[12] B_2O_3,[13] CO_2[3b]) or employment of a Lewis acid (e.g., BEt_3,[14] BF_3,[15] BPh_3,[16] $SnCl_2$[17]). However, there have been only limited and sporadic reports dealing with the direct cleavage of the C–O bond in allylic alcohols on interaction with a transition metal complex.[18] Successful applications using allylic alcohols directly in catalytic processes are even more limited. This apparently stems from the poor capability of a nonactivated hydroxyl to serve as a leaving group.[16] Ozawa reported that (π-allyl)palladium complexes bearing diphosphinidenecyclobutene ligands effectively catalyze the direct conversion of allylic alcohols in the absence of activating agents.[19] Manabe[20] in 2003 and Patil[21] in 2004 disclosed the direct palladium-catalyzed allylic substitution of allylic alcohols by carbon nucleophiles. We have recently reported our attempts and some successful applications of a process involving the C–O bond cleavage with direct use of allylic alcohols catalyzed by palladium complexes in the presence of $Ti(OPr^i)_4$ in benzene.[22] However, reactions in water have recently attracted much attention, not only because unique reactivity is often observed in water but also because water is a safe and economical solvent.[23] Thus, development of atom-economical reactions in water is one of the most important goals of synthetic chemistry. Due to our continuing interest in the palladium-catalyzed allylation of anilines, we disclose a new catalytic system for palladium-catalyzed allylation of anilines with allylic alcohols in water as a suspension

Keywords: Palladium-catalyzed; Allylation; Water; Anilines; Allylic alcohols.
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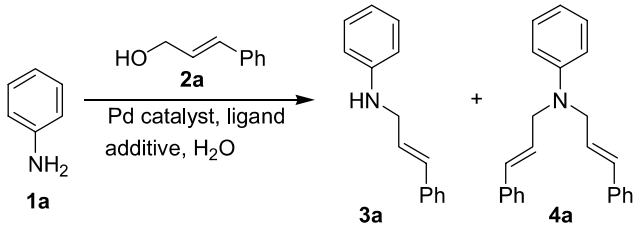
medium.[24] This is, to our knowledge, the first example of palladium/carboxylic acid-catalyzed allylation of anilines by the direct use of allylic alcohols in water.

2. Results and discussion

To evaluate the scope and limitations of the N-allylation of anilines with allylic alcohols, we treated a mixture of aniline (**1a**, 1 mmol) and cinnamyl alcohol (**2a**, 0.8 mmol) in the presence of $Pd(acac)_2$ (0.02 mmol), PPh_3 (0.08 mmol), and 1-adamantanecarboxylic acid (1-$AdCO_2H$) (0.1 mmol) in water at 50 °C for 30 min. The mixtures of *N*-cinnamylaniline (**3a**) and *N*,*N*-dicinnamylaniline (**4a**) were formed in 35 and 7%, respectively (entry 1 in Table 1). The reaction, under reflux, increased the yields of products **3a** and **4a** to 54 and 42%, respectively (entry 2). It was confirmed that the yield was decreased in the absence of PPh_3 (entry 3). The reaction did not occur in the absence of the palladium species as a catalyst or without water solvent (entries 4 and 5). The effect of water may activate allyl alcohol via hydration of the hydroxyl group for the smooth generation of the π-allylpalladium intermediate.[25] The absence of a carboxylic acid gave only a 10% yield of **3a** (entry 6). The effect of addition of 1-$AdCO_2H$ to promote the palladium-catalyzed allyl–OH bond cleavage remarkably enhanced both the reaction rate and yield. Other carboxylic acids such as $PhSCH_2CO_2H$ (entry 7), $PhOCH_2CO_2H$ (entry 8), and lauric acid (entry 9) were also effective for the allylation. (*S*)-(−)-2-bromopropionic acid (entry 10) and $PhCO_2H$ (entry 11) gave moderate yields of products. CH_3CO_2H (entry 12), 4-octylbenzoic acid (entry 13), and Ph_2CHCO_2H (entry 14) retarded the allylation. Strong acids such as C_6F_5OH (entry 15) and dodecylbenzenesulfonic acid (DBSA) (entry 16) also enhanced the substitution reaction.

Table 1. Allylation of aniline (**1a**) with cinnamyl alcohol (**2a**): temperature and acid effects[a]



Entry	Additive	Yield (%) (**3a**+**4a**)[b]	Yield (%) of **3a**[b]	Yield (%) of **4a**[b]
1[c]	1-$AdCO_2H$	42	35	7
2	1-$AdCO_2H$	96	54	42
3[d]	1-$AdCO_2H$	6	6	
4[e]	1-$AdCO_2H$	0		
5[f]	1-$AdCO_2H$	0		
6[g]	—	10	10	
7	$PhSCH_2CO_2H$	91	55	36
8	$PhOCH_2CO_2H$	86	49	37
9	$CH_3(CH_2)_{10}CO_2H$	84	50	34
10	$CH_3CH(Br)CO_2H$	59	21	38
11	$PhCO_2H$	56	41	15
12	CH_3CO_2H	14	9	5
13	4-Oct$C_6H_4CO_2H$	11	11	
14	Ph_2CHCO_2H	11	11	
15	C_6F_5OH	80	62	18
16	DBSA	78	55	23

[a] Reaction conditions: **1a** (1 mmol), **2a** (0.8 mmol), $Pd(acac)_2$ (0.02 mmol), PPh_3 (0.08 mmol), and additive (0.1 mmol) in water (5 mL) were refluxed for 30 min.
[b] Isolated yield was based on **2a**.
[c] Stirred at 50 °C for 30 min.
[d] Without PPh_3.
[e] Without $Pd(acac)_2$.
[f] Without water.
[g] Without acid.

A comparative study of different palladium catalysts and phosphine ligands in water was reported (Table 2). Among the palladium catalysts including $Pd(acac)_2$ (entry 1), $PdCl_2$(1,10-phen) (entry 2), $Pd(OAc)_2$ (entry 3), $Pd(OCOCF_3)_2$ (entry 4), $PdCl_2(MeCN)_2$ (entry 5), $PdCl_2(PhCN)_2$ (entry 6), $PdCl_2$ (entry 7), Pd(propionate)$_2$ (entry 8), Pd(hfacac)$_2$ (entry 9), $Pd_2(dba)_3$ (entries 10 and 11), and $Pd(PPh_3)_4$ (entries 12 and 13) were used. $Pd(acac)_2$, $PdCl_2$(1,10-phen), $PdCl_2$, $Pd(PPh_3)_4$, and Pd(propionate)$_2$ were found to be superior. However, using $Pd_2(dba)_3$ or $Pd(PPh_3)_4$ with extra PPh_3 as catalyst increased the yield of products (entries 11 and 13). The catalytic reactivity of the phosphine ligands is likely due to improved catalyst stability. In the presence of various monodentate ligands including PPh_3, Bu_3P, $(PhO)_3P$, $(2\text{-}MeC_6H_4)_3P$, $(2\text{-furyl})_3P$, $(2\text{-pyridyl})Ph_2P$, $(3\text{-}MeC_6H_4)_3P$, $(4\text{-}MeC_6H_4)_3P$, $(4\text{-}MeOC_6H_4)_3P$, $(4\text{-}FC_6H_4)_3P$, $(4\text{-}ClC_6H_4)_3P$, and $[2,4,6\text{-}(MeO)_3C_6H_2]_3P$ (entries 1 and 14–24) showed that PPh_3 (entry 1), $(PhO)_3P$ (entry 15), $(3\text{-}MeC_6H_4)_3P$ (entry 19), and $(4\text{-}MeOC_6H_4)_3P$ (entry 21) were the most effective ligands. The bidentate ligand dppp, dppb, and dpph gave moderate yields of products (entries 25–29). (±)-BINAP afforded high yields of products (entry 30).

We also studied the influence of the substituent on aniline on the reactivity of the amination of cinnamyl alcohol (**2a**) using $Pd(acac)_2$, PPh_3, and 1-$AdCO_2H$. Allylation of 4-substituted anilines containing both electron-withdrawing and electron-donating groups **1b–g** worked well with cinnamyl alcohol (**2a**) under reflux giving the corresponding *N*-allylanilines and *N*,*N*-diallylanilines in overall yields ranging from 65 to 96% (entries 1–6 in Table 3). These differences in reactivity could be related to the nucleophilicity of the corresponding aniline. 4-Nitroaniline (**1g**) gave 65% yield; the lower yield observed may arise from the nature of the nitro group. The more acidic nitroaniline is probably less reactive in attack on the π-allyl complex than the methoxyaniline, for example. The sterically more demanding 2-substituted anilines **1h–n** gave lower yields (entries 7–13). The reaction of 2-nitroaniline (**1i**), because of its strong electron-withdrawing and sterically group, gave only 27% yields. Conversely, anilines having groups on the 3-position, such as 3-OCH_2Ph (**1o**), 3-NO_2 (**1p**), and 3,5-di-OMe (**1q**), also gave the products in the high yields of 81, 92 and 77%, respectively (entries 14–16). Secondary aromatic amine, such as diphenylamine (**1r**) and phenothiazine (**1s**), also reacted to give the *N*-allylamine in excellent yields (entries 17 and 18).

Results for amination of both aromatic and aliphatic allylic alcohols **2b–j** with aniline (**1a**) using $Pd(acac)_2$, PPh_3, and 1-$AdCO_2H$ are summarized in Table 4. In addition to the parent cinnamyl alcohol (**2a**), *trans*-1,3-diphenyl-2-propen-1-ol (**2b**) reacted to give the allylating product **5** in excellent yields (entry 1). In contrast to the previous systems for

Table 2. Allylation of aniline (**1a**) with cinnamyl alcohol (**2a**): palladium and phosphine ligand effects[a]

Entry	Palladium	Ligand	Yield (%) (**3a**+**4a**)[b]	Yield (%) of **3a**[b]	Yield (%) of **4a**[b]
1	$Pd(acac)_2$	PPh_3	96	54	42
2	$PdCl_2$(1,10-phen)	PPh_3	99	43	56
3	$Pd(OAc)_2$	PPh_3	70	34	36
4	$Pd(OCOCF_3)_2$	PPh_3	86	63	23
5	$PdCl_2(MeCN)_2$	PPh_3	78	41	37
6	$PdCl_2(PhCN)_2$	PPh_3	66	41	25
7	$PdCl_2$	PPh_3	95	44	51
8	Pd(propionate)$_2$	PPh_3	91	56	35
9	Pd(hfacac)$_2$[c]	PPh_3	37	34	3
10	$Pd_2(dba)_3$	—	22	22	
11	$Pd_2(dba)_3$	PPh_3	69	42	27
12	$Pd(PPh_3)_4$	—	75	49	26
13	$Pd(PPh_3)_4$	PPh_3	98	59	39
14	$Pd(acac)_2$	Bu_3P	67	34	33
15	$Pd(acac)_2$	$(PhO)_3P$	89	51	38
16	$Pd(acac)_2$	$(2\text{-}MeC_6H_4)_3P$	39	26	13
17	$Pd(acac)_2$	$(2\text{-Furyl})_3P$	55	29	26
18	$Pd(acac)_2$	$(2\text{-Pyridyl})Ph_2P$	39	21	18
19	$Pd(acac)_2$	$(3\text{-}MeC_6H_4)_3P$	89	51	38
20	$Pd(acac)_2$	$(4\text{-}MeC_6H_4)_3P$	63	38	25
21	$Pd(acac)_2$	$(4\text{-}MeOC_6H_4)_3P$	86	37	49
22	$Pd(acac)_2$	$(4\text{-}FC_6H_4)_3P$	54	31	23
23	$Pd(acac)_2$	$(4\text{-}ClC_6H_4)_3P$	37	25	12
24	$Pd(acac)_2$	$[2,4,6\text{-}(MeO)_3C_6H_2]_3P$	28	28	
25	$Pd(acac)_2$	Dppm[d]	2	2	
26	$Pd(acac)_2$	Dppe[e]	1	1	
27	$Pd(acac)_2$	Dppp[f]	41	34	7
28	$Pd(acac)_2$	Dppb[g]	59	43	16
29	$Pd(acac)_2$	Dpph[h]	45	35	12
30	$Pd(acac)_2$	(±)-BINAP[i]	92	46	46

[a] Reaction conditions: **1a** (1 mmol), **2a** (0.8 mmol), Pd catalyst (0.02 mmol), ligand (0.08 mmol), and 1-AdCO_2H (0.1 mmol) in water (5 mL) were refluxed for 30 min.
[b] Isolated yield was based on **2a**.
[c] Palladium hexafluoroacetylacetonate.
[d] Bis(diphenylphosphino)methane.
[e] 1,2-Bis(diphenylphosphino)ethane.
[f] 1,3-Bis(diphenylphosphino)propane.
[g] 1,4-Bis(diphenylphosphino)butane.
[h] 1,6-Bis(diphenylphosphino)hexane.
[i] (±)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl.

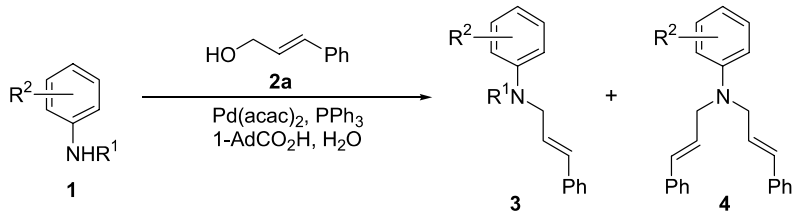
allylic substitution, reactions of aliphatic allylic alcohols occurred only moderate yields (entries 2–9). Allylation of aniline with allyl alcohol (**2c**) and methallyl alcohol (**2d**), the corresponding monoallylated and diallylated products were formed in overall 45 and 62% yields, respectively (entries 2 and 3). Using 2-chloro-2-propen-1-ol (**2e**) as allylating reagent gave only monoallylated product *N*-(2-chloroallyl)aniline (**10**) in 40% yield (entry 4). The sterically more demanding secondary alcohol **2f** gave lower yields (entry 5). Treatment of aniline (**1a**) with crotyl alcohol (**2g**) gave mixtures of stereo- and regioisomeric anilines **12** and **13** in the yield of 41 and 9%, respectively (entry 6). These products may all be derived from the same π-allyl intermediate, which can be attacked at either the C-1 or C-3 position. The 80:20 *E*/*Z* ratio of **12** was determined by GC. The product *E* alkene arising from the more thermodynamically stable *syn* π-allyl complex. Since both regioisomeric alcohols **2g** and **2h** gave identical mixtures of the anilines **12** and **13** in similar ratios, the reaction is considered to proceed via π-allylpalladium intermediates (entry 7). The loss of the stereochemistry of the starting alcohol **2g** is due to a rapid $\sigma \rightleftarrows \eta^3 \rightleftarrows \sigma$ interconversion of the π-allyl intermediate compared to the rate of amination of this intermediate. With the unsymmetrical allylic alcohols **2**, the major products were obtained from approach of **1** at the less sterically hindered primary site. Similarly, both regioisomeric alcohols **2i** and **2j** reacted with aniline to give identical mixtures of **14** and regioisomeric aniline **15**, as expected from attack of the aniline on the two allylic termini of the π-allylpalladium species, in similar ratios (entries 8 and 9).

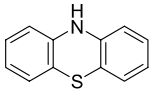
A possible mechanism for the formation of *N*-allylanilines from **1** and **2** is illustrated in Scheme 1, in which the substituent on allylic alcohol is omitted. Oxidative addition of alcohol **2** or protonated alcohol, formed by the acid, to Pd(0) species affords the π-allylpalladium intermediate (**16**). The formation of the π-allylpalladium may be accelerated by the acid, possibly by protonation to increase the leaving group ability of the OH group of the allyl alcohol.[26] Formation of a π-allylpalladium with the carboxylic acid could be the key for the rate enhancement by the acid.[27] Intermolecular nucleophilic substitution of the amino group of **1** takes place at the π-allyl system to give intermediate **17**, followed by reductive elimination gives *N*-allylaniline. In the presence of anilines, which may be relatively reactive toward the palladium center, **16** should be predominantly transformed to **17** to afford aryl amine.

3. Conclusions

In summary, we have developed a catalytic system that enables reactions of aromatic amines with allylic alcohols as

Table 3. Allylic amination of cinnamyl alcohol (**2a**) with anilines (**1b–s**)[a]



Entry	1	R^1	R^2	Yield (%) (3+4)[b]	Yield of 3[b]	Yield of 4[b]
1	**1b**	H	4-Me	81	**3b** 41%	**4b** 40%
2	**1c**	H	4-Cl	78	**3c** 63%	**4c** 15%
3	**1d**	H	4-OMe	96	**3d** 69%	**4d** 27%
4	**1e**	H	4-CO_2Et	91	**3e** 81%	**4e** 10%
5	**1f**	H	4-CN	87	**3f** 70%	**4f** 17%
6	**1g**	H	4-NO_2	65	**3g** 51%	**4g** 14%
7	**1h**	H	2-Br	30	**3h** 30%	
8	**1i**	H	2-CN	78	**3i** 78%	
9	**1j**	H	2-NO_2	27	**3j** 27%	
10	**1k**	H	2,4-Di-Me	60	**3k** 55%	**4k** 5%
11	**1l**	H	2-Cl, 4-Me	73	**3l** 73%	
12	**1m**	H	2-Me, 4-OMe	65	**3m** 59%	**4m** 6%
13	**1n**	H	2-OMe, 4-NO_2	73	**3n** 73%	
14	**1o**	H	3-OCH_2Ph	81	**3o** 65%	**4o** 16%
15	**1p**	H	3-NO_2	92	**3p** 76%	**4p** 16%
16	**1q**	H	3,5-Di-OMe	77	**3q** 56%	**4q** 21%
17	**1r**	Ph	H	92	**3r** 92%	
18	**1s**			95	**3s** 95%	

[a] Reaction conditions: **1** (1 mmol), **2a** (0.8 mmol), $Pd(acac)_2$ (0.02 mmol), PPh_3 (0.08 mmol), and 1-$AdCO_2H$ (0.1 mmol) in water (5 mL) were refluxed for 30 min.
[b] Isolated yield was based on **2a**.

Table 4. Reaction of aniline (**1a**) with allylic alcohols (**2b–j**)[a]

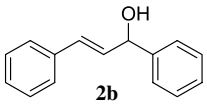
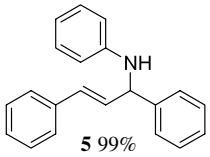
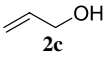
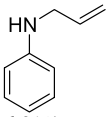
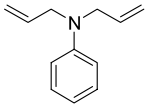
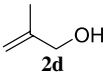
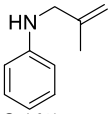
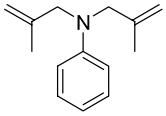
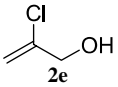
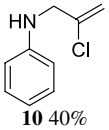
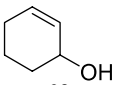
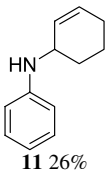
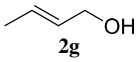
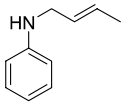
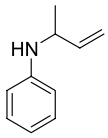
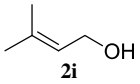
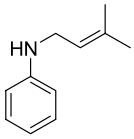
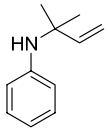
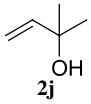
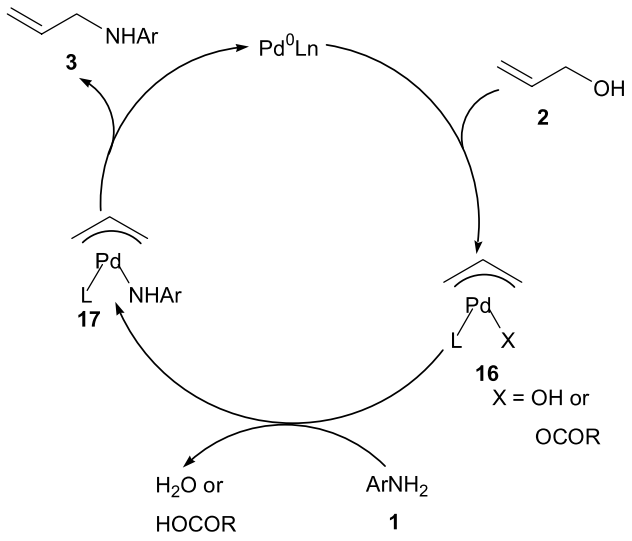
Entry	2	Yields[b]		
1	 **2b**	 **5** 99%		
2	 **2c**	 **6** 31%	 **7** 14%	
3	 **2d**	 **8** 46%	 **9** 16%	
4	 **2e**	 **10** 40%		
5	 **2f**	 **11** 26%		

Table 4 (*continued*)

Entry	2	Yields[b]	
6	 **2g**	 **12** 41% (*E*/*Z*=80/20)[c]	 **13** 9%
7	 **2h**	**12** 40% (*E*/*Z*=78/22)[c]	**13** 11%
8	 **2i**	 **14** 35%	 **15** 8%
9	 **2j**	**14** 38%	**15** 7%

[a] Reaction conditions: **1a** (1 mmol), **2** (0.8 mmol), $Pd(acac)_2$ (0.02 mmol), PPh_3 (0.08 mmol), 1-$AdCO_2H$ (0.1 mmol) and water (5 mL) were refluxed for 30 min.
[b] Isolated yield was based on **2**.
[c] Determined by GC.



Scheme 1.

allylating agents in water. This is a simple and efficient route for C–N bond formation. The effect of addition of a carboxylic acid to promote the palladium-catalyzed allyl–OH bond cleavage remarkably enhanced both the reaction rate and yield. The amination of aromatic and aliphatic allylic alcohol worked well with anilines, giving generally good to high yields of the corresponding allylic anilines. Anilines with steric constraints gave lower chemical yields.

4. Experimental

4.1. General considerations. General method

All melting points were uncorrected. IR absorption spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrophotometer. Proton and carbon-13 NMR were measured with a Unity-400 or Mercury Plus-400 spectrometer. Carbon multiplicities were obtained from DEPT experiments. Chemical shifts (δ) and coupling constants (Hz) were measured with respect to TMS or chloroform-d_1. MS and high-resolution mass spectra (HRMS) were taken on a Thermo-Finnigan trace GC or Finnigan MAT-95XL instrument, with a direct inlet system. Elemental analyses were carried out on a Heraeus CHN-O-Rapid elemental analyzer. All the following chemicals were commercially available and used without further purification. $Pd(acac)_2$ (acac=acetylacetonate), $Pd_2(dba)_3$ (dba=dibenzylideneacetone), $(2\text{-}MeC_6H_4)_3P$, $(2\text{-furyl})_3P$, $(4\text{-}MeOC_6H_4)_3P$, $(4\text{-}FC_6H_4)_3P$, dppm, 1-adamantanecarboxylic acid, C_6F_5OH, 3,5-dimethoxyaniline, and diphenylamine were purchased from Lancaster. $PdCl_2$(1,10-phen) (phen=phenanthroline), $Pd(OCOCF_3)_2$, $PdCl_2(MeCN)_2$, $PdCl_2(PhCN)_2$, Pd(propionate)$_2$, Pd(hfacac)$_2$, (2-pyridyl)Ph_2P, $(3\text{-}MeC_6H_4)_3P$, $(4\text{-}MeC_6H_4)_3P$, $[2,4,6\text{-}(MeO)_3C_6H_2]_3P$, dppp, dppb, dpph, phenoxyacetic acid, diphenylacetic acid, 2-chloro-4-methylaniline, 4-methoxy-2-methylaniline, 3-benzyloxyaniline, and 2-chloro-2-propen-1-ol were purchased from Aldrich. $Pd(OAc)_2$, PPh_3, $(PhO)_3P$, and allyl alcohol were purchased from Riedel-de Haen. $PdCl_2$, $(4\text{-}ClC_6H_4)_3P$, (±)BINAP, lauric acid, 4-octylbenzoic acid, 4-chloroaniline, 2-cyanoaniline, 2-nitroaniline, and phenothiazine were purchased from Acros Organics. $Pd(PPh_3)_4$, Bu_3P, dppe, (phenylthio)acetic acid, (*S*)-(−)-2-bromopropionic acid, sodium dodecylbenzenesulfonate, aniline, *p*-tolulidine, *p*-anisidine, 4-aminobenzoic acid ethyl ester, 4-cyanoaniline, 4-nitroaniline, 2-bromoaniline, 2,4-dimethylaniline, 2-methoxy-4-nitroaniline, 3-nitroaniline, cinnamyl alcohol, 2-buten-1-ol, 3-buten-2-ol, 2-cyclohexen-1-ol, methallyl alcohol, 2-methyl-3-buten-2-ol, 3-methyl-2-buten-1-ol, and 2-methyl-3-buten-2-ol were purchased from TCI. *trans*-1,3-Diphenyl-2-propen-1-ol was purchased from Fluka. Benzoic acid and acetic acid were purchased from Showa.

4.2. General procedure for the palladium-catalyzed allylation of anilines. Reaction with aniline (1a)

Cinnamyl alcohol (**2a**) (107 mg, 0.8 mmol) and 1-adamantanecarboxylic acid (18 mg, 0.1 mmol) were suspended in water (5 mL) at rt, and then $Pd(acac)_2$ (6 mg, 0.02 mmol), PPh_3 (21 mg, 0.08 mmol) and aniline (93 mg, 1 mmol) were added. The whole was heated under reflux conditions for 30 min. After the mixture was cooled to rt, water and brine were added. The organic materials were extracted with dichloromethane, dried over magnesium sulfate, and concentrated under vacuum. Column chromatography (chloroform/*n*-hexane 1:2) of the residue afforded **3a** and **4a** in 54 and 42% yields, respectively.

Products **3f**,[22e] **4f**,[22e] **3g**,[22e] **4g**,[22e] **3j**,[22e] **3p**,[22e] **4p**,[22e] **3r**,[22e] **3s**,[22e] **6**,[22a] **7**,[22a] **12**,[22b] and **13**,[22b] are known.

4.2.1. *N*-Cinnamylaniline (3a).[28] Light brown oil. IR (KBr) ν: 3421 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 3.58 (br s, 1H, NH), 3.89 (dd, $J=1.6$, 5.6 Hz, 2H, CH_2), 6.29 (dt, $J=5.6$, 16.0 Hz, 1H, vinyl H), 6.59 (dt, $J=1.6$, 16.0 Hz, 1H, vinyl H), 6.63–6.66 (m, 2H, ArH), 6.72 (ddt, $J=0.8$, 1.2, 7.2 Hz, 1H, ArH), 7.17–7.23 (m, 3H, ArH), 7.28 (dd, $J=7.6$, 7.6 Hz, 2H, ArH), 7.34 (dd, $J=1.6$, 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 46.1 (CH_2), 113.0 (CH), 117.6 (CH), 126.3 (CH), 126.9 (CH), 127.5 (CH), 128.5 (CH), 129.2 (CH), 131.4 (CH), 136.8 (C), 147.9 (C). EI-MS *m/z*: 209 (M^+), 132, 117, 115, 91. HR-MS calcd for $C_{15}H_{15}N$ 209.1204, found 209.1204.

4.2.2. *N,N*-Dicinnamylaniline (4a).[29] Light yellow crystals. Mp 81–83 °C (chloroform/hexane). ^1H NMR ($CDCl_3$) δ: 4.13 (d, $J=5.2$ Hz, 4H, $CH_2\times2$), 6.28 (dt, $J=5.2$, 16.0 Hz, 2H, vinyl H), 6.54 (d, $J=16.0$ Hz, 2H, vinyl H), 6.72 (dd, $J=6.8$, 7.2 Hz, 1H, ArH), 6.82 (d, $J=8.0$ Hz, 2H, ArH), 7.19–7.25 (m, 4H, ArH), 7.29 (dd, $J=7.2$, 8.0 Hz, 4H, ArH), 7.36 (dd, $J=1.2$, 7.2 Hz, 4H, ArH). ^{13}C NMR ($CDCl_3$) δ: 52.2 (CH_2), 112.6 (CH), 116.6 (CH), 125.8 (CH), 126.3 (CH), 127.4 (CH), 128.5 (CH), 129.2 (CH), 131.2 (CH), 136.8 (C), 148.8 (C). EI-MS *m/z*: 325 (M^+), 234, 220, 206, 144, 117, 115, 91, 77. HR-MS calcd for $C_{24}H_{23}N$ 325.1830, found 325.1832. Anal. Calcd for $C_{24}H_{23}N$: C, 88.57; H, 7.12; N, 4.30. Found: C, 88.18; H, 7.16; N, 4.19.

4.2.3. *N*-Cinnamyl-4-methylaniline (3b). Deep yellow oil. IR (KBr) ν: 3406 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.23 (s, 3H, CH_3), 3.43 (br s, 1H, NH), 3.87 (dd, $J=1.6$, 6.0 Hz, 2H, CH_2), 6.30 (dt, $J=6.0$, 16.0 Hz, 1H, vinyl H), 6.58 (dt, $J=1.6$, 16.0 Hz, 1H, vinyl H), 6.58 (d, $J=8.4$ Hz, 2H, ArH), 6.99 (d, $J=8.0$ Hz, 2H, ArH), 7.18–7.22 (m, 1H, ArH), 7.28 (dd, $J=7.2$, 7.6 Hz, 2H, ArH), 7.34 (dd, $J=1.6$, 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 20.4 (CH_3), 46.5 (CH_2), 113.2 (CH), 126.3 (CH), 126.8 (C), 127.2 (CH), 127.4 (CH), 128.5 (CH), 129.7 (CH), 131.3 (CH), 136.8 (C), 145.7 (C). EI-MS *m/z*: 223 (M^+), 208, 196, 181, 165, 146, 131, 117, 115, 91, 77. HR-MS calcd for $C_{16}H_{17}N$ 223.1361, found 223.1361.

4.2.4. *N,N*-Dicinnamyl-4-methylaniline (4b). Light yellow crystals. Mp 66–68 °C (chloroform/hexane). ^1H NMR ($CDCl_3$) δ: 2.24 (s, 3H, CH_3), 4.07 (dd, $J=1.6$, 5.2 Hz, 4H, $CH_2\times2$), 6.25 (dt, $J=5.2$, 16.0 Hz, 2H, vinyl H), 6.51 (d, $J=16.0$ Hz, 2H, vinyl H), 6.74 (d, $J=8.8$ Hz, 2H, ArH), 7.03 (d, $J=8.0$ Hz, 2H, ArH), 7.17–7.21 (m, 2H, ArH), 7.27 (dd, $J=7.2$, 7.6 Hz, 4H, ArH), 7.33 (dd, $J=1.6$, 8.0 Hz, 4H, ArH). ^{13}C NMR ($CDCl_3$) δ: 20.2 (CH_3), 52.4 (CH_2), 112.9 (CH), 125.8 (C), 126.1 (CH), 126.3 (CH), 127.3 (CH), 128.5 (CH), 129.7 (CH), 131.1 (CH), 136.9 (C), 146.7 (C). EI-MS *m/z*: 339 (M^+), 327, 320, 299, 281, 267, 250, 234, 207, 171, 158, 128, 115, 91, 73. HR-MS calcd for $C_{25}H_{25}N$ 339.1987, found 339.1988. Anal. Calcd for $C_{25}H_{25}N$: C, 88.45; H, 7.42; N, 4.13. Found: C, 88.44; H, 7.64; N, 3.98.

4.2.5. *N*-Cinnamyl-4-chloroaniline (3c). White crystals. Mp 77–79 °C (chloroform/hexane). IR (KBr) ν: 3421 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 3.71 (br s, 1H, NH), 3.86 (dd, $J=1.6$, 6.0 Hz, 2H, CH_2), 6.26 (dt, $J=6.0$, 16.0 Hz, 1H, vinyl H), 6.55 (d, $J=8.8$ Hz, 2H, ArH), 6.58 (d, $J=16.0$ Hz, 1H, vinyl H), 7.11 (d, $J=8.8$ Hz, 2H, ArH), 7.19–7.24 (m, 1H, ArH), 7.29 (dd, $J=7.2$, 8.0 Hz, 2H, ArH), 7.34 (dd, $J=1.6$, 7.2 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 46.2 (CH_2), 114.1 (CH), 122.1 (C), 126.2 (CH), 126.3 (CH), 127.6 (CH), 128.5 (CH), 129.0 (CH), 131.7 (CH), 136.6 (C), 146.4 (C). EI-MS *m/z*: 245 ($M^+ + 2$), 243 (M^+), 226, 208, 191, 166, 140, 130, 117, 115, 91, 77. HR-MS calcd for $C_{15}H_{14}ClN$ 243.0814, found 243.0815. Anal. Calcd for $C_{15}H_{14}ClN$: C, 73.92; H, 5.79; N, 5.75. Found: C, 73.95; H, 5.80; N, 5.75.

4.2.6. *N,N*-Dicinnamyl-4-chloroaniline (4c). Light yellow crystals. Mp 79–81 °C (chloroform/hexane). ^1H NMR ($CDCl_3$) δ: 4.11 (dd, $J=1.6$, 5.2 Hz, 4H, $CH_2\times2$), 6.24 (dt, $J=5.2$, 16.0 Hz, 2H, vinyl H), 6.51 (d, $J=16.0$ Hz, 2H, vinyl H), 6.72 (d, $J=8.4$ Hz, 2H, ArH), 7.16 (d, $J=9.2$ Hz, 2H, ArH), 7.20–7.25 (m, 2H, ArH), 7.30 (dd, $J=7.2$, 7.6 Hz, 4H, ArH), 7.35 (dd, $J=1.6$, 7.2 Hz, 4H, ArH). ^{13}C NMR ($CDCl_3$) δ: 52.4 (CH_2), 113.7 (CH), 121.3 (C), 125.2 (CH), 126.3 (CH), 127.6 (CH), 128.6 (CH), 129.0 (CH), 131.4 (CH), 136.7 (C), 147.3 (C). EI-MS *m/z*: 361 ($M^+ + 2$), 359 (M^+), 327, 299, 281, 268, 254, 240, 225, 217, 207, 204, 192, 190, 178, 166, 154, 142, 140, 127, 125, 115, 111, 91, 77. HR-MS calcd for $C_{24}H_{22}ClN$ 359.1440, found 359.1441. Anal. Calcd for $C_{24}H_{22}ClN$: C, 80.10; H, 6.16; N, 3.89. Found: C, 79.96; H, 6.19; N, 3.77.

4.2.7. *N*-Cinnamyl-4-methoxyaniline (3d). Light yellow crystals. Mp 63–64 °C (chloroform/hexane). IR (KBr) ν: 3400 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 3.42 (br s, 1H, NH), 3.72 (s, 3H, OCH_3), 3.85 (dd, $J=1.6$, 6.0 Hz, 2H, CH_2), 6.31 (dt, $J=6.0$, 16.0 Hz, 1H, vinyl H), 6.59 (d, $J=16.0$ Hz, 1H, vinyl H), 6.62 (d, $J=8.8$ Hz, 2H, ArH), 6.78 (d, $J=8.8$ Hz, 2H, ArH), 7.18–7.22 (m, 1H, ArH), 7.29 (dd, $J=7.2$, 8.0 Hz, 2H, ArH), 7.35 (dd, $J=1.2$, 7.2 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 47.1 (CH_2), 55.6 (CH_3), 114.3 (CH), 114.8 (CH), 126.2 (CH), 127.3 (CH), 127.4 (CH), 128.5 (CH), 131.3 (CH), 136.8 (C), 142.1 (C), 152.2 (C). EI-MS *m/z*: 239 (M^+), 222, 208, 197, 162, 147, 122, 117, 115, 91, 77. HR-MS calcd for $C_{16}H_{17}NO$ 239.1310, found 239.1312. Anal. Calcd for $C_{16}H_{17}NO$: C, 80.32; H, 7.16; N, 5.85. Found: C, 80.29; H, 7.17; N, 5.79.

4.2.8. *N,N*-Dicinnamyl-4-methoxyaniline (4d). Light brown oil. ^1H NMR ($CDCl_3$) δ: 3.75 (s, 3H, OCH_3), 4.06 (dd, $J=1.6$, 5.6 Hz, 4H, $CH_2\times2$), 6.26 (dt, $J=5.6$, 16.0 Hz, 2H, vinyl H), 6.53 (d, $J=16.0$ Hz, 2H, vinyl H), 6.76–6.84 (m, 4H, ArH), 7.18–7.23 (m, 2H, ArH), 7.29 (dd, $J=7.2$,

8.0 Hz, 4H, ArH), 7.35 (dd, J=1.2, 7.2 Hz, 4H, ArH). ^{13}C NMR ($CDCl_3$) δ: 53.2 (CH_2), 55.7 (CH_3), 114.7 (CH), 115.0 (CH), 126.2 (CH), 126.3 (CH), 127.4 (CH), 128.5 (CH), 131.4 (CH), 136.9 (C), 143.4 (C), 151.9 (C). EI-MS *m/z*: 355 (M^+), 327, 315, 281, 264, 250, 238, 221, 207, 174, 160, 149, 134, 121, 117, 115, 91, 77. HR-MS calcd for $C_{25}H_{25}NO$ 355.1936, found 355.1937.

4.2.9. Ethyl 4-(cinnamylamino)benzoate (3e). White crystals. Mp 132–133 °C (chloroform/hexane). IR (KBr) ν: 3429 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.34 (t, J=7.2 Hz, 3H, CH_3), 3.96 (dd, J=1.6, 5.6 Hz, 2H, CH_2), 4.30 (dd, J=7.2, 7.2 Hz, 2H, CH_2), 4.49 (br s, 1H, NH), 6.26 (dt, J=5.6, 15.6 Hz, 1H, vinyl H), 6.59 (dt, J=1.2, 16.0 Hz, 1H, vinyl H), 7.20–7.25 (m, 1H, ArH), 7.30 (dd, J=7.2, 7.6 Hz, 2H, ArH), 7.35 (dd, J=1.6, 7.2 Hz, 2H, ArH), 7.88 (d, J=9.2 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 14.4 (CH_3), 45.5 (CH_2), 60.2(CH_2), 111.7 (CH), 119.0 (C), 125.6 (CH), 126.3 (CH), 127.7 (CH), 128.5 (CH), 131.4 (CH), 132.0 (CH), 136.5 (C), 151.5 (C), 166.8 (C). EI-MS *m/z*: 281 (M^+), 252, 236, 208, 191, 150, 130, 117, 115, 91. HR-MS calcd for $C_{18}H_{19}NO_2$ 281.1416, found 281.1415. Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.77; H, 6.81; N, 4.90.

4.2.10. Ethyl 4-(dicinnamylamino)benzoate (4e). White crystals. Mp 120–122 °C (chloroform/hexane). ^{1}H NMR ($CDCl_3$) δ: 1.35 (t, J=7.2 Hz, 3H, CH_3), 4.20 (dd, J=1.2, 5.2 Hz, 2H, $CH_2\times2$), 4.32 (dd, J=7.2 Hz, 2H, CH_2), 6.25 (dt, J=5.2, 16.0 Hz, 2H, vinyl H), 6.51 (d, J=16.0 Hz, 2H, vinyl H), 6.79 (d, J=9.2 Hz, 2H, ArH), 7.21–7.25 (m, 2H, ArH), 7.30 (dd, J=7.2, 7.6 Hz, 4H, ArH), 7.35 (dd, J=1.6, 7.2 Hz, 4H, ArH), 7.92 (d, J=8.8 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 14.4 (CH_3), 52.2 (CH_2), 60.1 (CH_2), 108.1 (C), 111.3 (CH), 124.2 (CH), 126.3 (CH), 127.6 (CH), 128.5 (CH), 131.3 (CH), 131.7 (CH), 136.4 (C), 151.7 (C), 166.7 (C). EI-MS *m/z*: 397 (M^+), 368, 352, 341, 327, 319, 306, 292, 281, 267, 253, 230, 207, 192, 178, 163, 150, 135, 117, 91, 77. HR-MS calcd for $C_{27}H_{27}NO_2$ 397.2041, found 397.2043. Anal. Calcd for $C_{27}H_{27}NO_2$: C, 81.58; H, 6.85; N, 3.52. Found: C, 81.75; H, 6.90; N, 3.45.

4.2.11. *N*-Cinnamyl-2-bromoaniline (3h). Light brown oil. IR (KBr) ν: 3422 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 3.99 (dd, J=1.6, 5.6 Hz, 2H, CH_2), 4.68 (br s, 1H, NH), 6.31 (dt, J=5.6, 16.0 Hz, 1H, vinyl H), 6.59 (ddd, J=1.2, 7.2, 7.6 Hz, 1H, ArH), 6.62 (dd, J=1.6, 16.0 Hz, 1H, vinyl H), 6.70 (dd, J=1.6, 8.4 Hz, 1H, ArH), 7.17 (ddd, J=1.6, 7.2, 7.6 Hz, 1H, ArH), 7.20–7.25 (m, 1H, ArH), 7.28–7.33 (m, 2H, ArH), 7.35–7.39 (m, 2H, ArH), 7.44 (dd, J=1.6, 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$) δ: 46.0 (CH_2), 109.8 (C), 117.8 (CH), 118.1 (CH), 126.1 (CH), 126.4 (CH), 127.6 (CH), 128.5 (CH), 128.6 (CH), 131.8 (CH), 132.4 (CH), 136.6 (C), 144.6 (C). EI-MS *m/z*: 290 (M^++2), 288 (M^+), 208, 191, 130, 117, 115, 91. HR-MS calcd for $C_{15}H_{14}BrN$ 287.0310, found 287.0309.

4.2.12. *N*-Cinnamyl-2-cyanoaniline (3i). Colorless crystals. Mp 70–72 °C (chloroform/hexane). IR (KBr) ν: 3431, 2212 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 4.00 (dd, J=1.6, 5.6 Hz, 2H, CH_2), 4.85 (br s, 1H, NH), 6.24 (dt, J=5.6, 16.0 Hz, 1H, vinyl H), 6.60 (dt, J=1.6, 16.0 Hz, 1H, vinyl H), 6.67 (ddd, J=0.8, 7.2, 7.6 Hz, 1H, ArH), 6.69 (d, J=8.4 Hz, 1H, ArH), 7.21–7.25 (m, 1H, ArH), 7.31 (dd, J=7.2, 7.6 Hz, 2H, ArH), 7.33–7.40 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$) δ: 45.1 (CH_2), 95.7 (C), 110.8 (CH), 116.5 (CH), 117.8 (C), 125.1 (CH), 126.2 (CH), 127.6 (CH), 128.4 (CH), 131.9 (CH), 132.6 (CH), 134.1 (CH), 136.2 (C), 149.9 (C). EI-MS *m/z*: 234 (M^+), 217, 207, 155, 131, 117, 115, 102, 91. HR-MS calcd for $C_{16}H_{14}N_2$ 234.1157, found 234.1159. Anal. Calcd for $C_{15}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 82.18; H, 6.00; N, 11.94.

4.2.13. *N*-Cinnamyl-2,4-dimethylaniline (3k). Brown oil. IR (KBr) ν: 3431 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.12 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.40 (br s, 1H, NH), 3.90 (dd, J=1.6, 6.0 Hz, 2H, CH_2), 6.33 (dt, J=6.0, 16.0 Hz, 1H, vinyl H), 6.57 (d, J=8.0 Hz, 1H, ArH), 6.59 (dt, J=1.6, 16.0 Hz, 1H, vinyl H), 6.89 (s, 1H, ArH), 6.92 (dd, J=1.6, 8.0 Hz, 1H, ArH), 7.17–7.23 (m, 1H, ArH), 7.27 (dd, J=7.2, 7.6 Hz, 2H, ArH), 7.34 (dd, J=1.6, 7.2 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 17.4 (CH_3), 20.3 (CH_3), 46.4 (CH_2), 110.3 (CH), 122.2 (C), 126.2 (CH), 127.1 (C), 127.2 (CH), 127.3 (CH), 127.4 (CH), 128.5 (CH), 130.9 (CH), 131.2 (C), 131.4 (CH), 136.8 (C). EI-MS *m/z*: 237 (M^+), 144, 132, 117, 115, 91. HR-MS calcd for $C_{17}H_{19}N$ 237.1518, found 237.1517.

4.2.14. *N,N*-Dicinnamyl-2,4-dimethylaniline (4k). Light brown oil. ^{1}H NMR ($CDCl_3$) δ: 2.27 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 3.74 (d, J=6.4 Hz, 4H, $CH_2\times2$), 6.21 (dt, J=6.4, 16.0 Hz, 2H, vinyl H), 6.51 (d, J=16.0 Hz, 2H, vinyl H), 6.93–7.01 (m, 3H, ArH), 7.18–7.25 (m, 2H, ArH), 7.28 (dd, J=7.2, 7.6 Hz, 4H, ArH), 7.34 (d, J=7.2 Hz, 4H, ArH). ^{13}C NMR ($CDCl_3$) δ: 18.3 (CH_3), 20.7 (CH_3), 55.3 (CH_2), 121.9 (CH), 126.3 (CH), 126.6 (CH), 127.3 (CH), 128.1 (CH), 128.5 (CH), 131.8 (CH), 132.1 (CH), 132.6 (C), 133.7 (C), 137.2 (C), 147.5 (C). EI-MS *m/z*: 353 (M^+), 262, 248, 237, 220, 172, 158, 147, 132, 117, 115, 103, 91, 77. HR-MS calcd for $C_{26}H_{27}N$ 353.2144, found 353.2144.

4.2.15. *N*-Cinnamyl-2-chloro-4-methylaniline (3l). Yellow oil. IR (KBr) ν: 3418 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.20 (s, 3H, CH_3), 3.93 (dd, J=1.6, 5.6 Hz, 2H, CH_2), 4.36 (br s, 1H, NH), 6.29 (dt, J=5.6, 16.0 Hz, 1H, vinyl H), 6.59 (d, J=15.6 Hz, 1H, vinyl H), 6.60 (d, J=8.4 Hz, 1H, ArH), 6.92 (dd, J=2.0, 8.4 Hz, 1H, ArH), 7.09 (d, J=2.0 Hz, 1H, ArH), 7.18–7.23 (m, 1H, ArH), 7.30 (dd, J=7.2, 7.6 Hz, 2H, ArH), 7.35 (dd, J=1.2, 7.2 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 20.1 (CH_3), 46.0 (CH_2), 111.6 (CH), 119.0 (C), 126.3 (CH), 126.5 (CH), 127.5 (CH), 128.3 (CH), 128.5 (CH), 129.5 (CH), 131.5 (CH), 136.7 (C), 141.5 (C). EI-MS *m/z*: 259 (M^++2), 257 (M^+), 222, 205, 178, 154, 144, 117, 115, 91, 77. HR-MS calcd for $C_{16}H_{16}ClN$ 257.0971, found 257.0970.

4.2.16. *N*-Cinnamyl-4-methoxy-2-methylaniline (3m). Deep brown oil. IR (KBr) ν: 3422 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.14 (s, 3H, CH_3), 3.20 (br s, 1H, NH), 3.71 (s, 3H, OCH_3), 3.89 (dd, J=1.2, 5.6 Hz, 2H, CH_2), 6.34 (dt, J=6.0, 16.0 Hz, 1H, vinyl H), 6.59 (d, J=16.0 Hz, 1H, vinyl H), 6.60 (d, J=8.4 Hz, 1H, ArH), 6.67–6.71 (m, 2H, ArH), 7.18–7.22 (m, 1H, ArH), 7.28 (dd, J=7.2, 7.6 Hz, 2H, ArH), 7.35 (dd, J=1.6, 7.2 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 17.7 (CH_3), 46.9 (CH_2), 55.6 (CH_3), 111.2 (CH), 111.4 (CH), 116.9 (CH), 123.9 (C), 126.2 (CH), 127.3 (CH), 127.4 (CH), 128.5 (CH), 131.4 (CH), 136.8 (C), 140.1 (C),

151.7 (C). EI-MS *m/z*: 253 (M^+), 136, 117, 115, 93, 91. HR-MS calcd for $C_{17}H_{19}NO$ 253.1467, found 253.1468.

4.2.17. *N*,*N*-Dicinnamyl-4-methoxy-2-methylaniline (4m). Yellow oil. ^1H NMR ($CDCl_3$) δ: 2.37 (s, 3H, CH_3), 3.70 (d, $J=6.4$ Hz, 4H, $CH_2\times2$), 3.74 (s, 3H, OCH_3), 6.20 (dt, $J=6.4$, 16.0 Hz, 2H, vinyl H), 6.49 (d, $J=16.0$ Hz, 2H, vinyl H), 6.68 (dd, $J=2.8$, 8.8 Hz, 1H, ArH), 6.75 (d, $J=2.8$ Hz, 1H, ArH), 7.02 (d, $J=8.8$ Hz, 1H, ArH), 7.19–7.23 (m, 2H, ArH), 7.29 (dd, $J=7.2$, 7.6 Hz, 4H, ArH), 7.32 (dd, $J=1.6$, 7.6 Hz, 4H, ArH). ^{13}C NMR ($CDCl_3$) δ: 18.4 (CH_3), 55.2 (CH_3), 55.9 (CH_2), 111.0 (CH), 116.2 (CH), 123.3 (CH), 126.2 (CH), 127.2 (CH), 127.3 (CH), 128.4 (CH), 132.1 (CH), 135.8 (C), 137.2 (C), 143.2 (C), 155.6 (C). EI-MS *m/z*: 369 (M^+), 278, 264, 252, 207, 188, 148, 135, 133, 117, 115, 91. HR-MS calcd for $C_{26}H_{27}NO$ 369.2093, found 369.2089.

4.2.18. *N*-Cinnamyl-2-methoxy-4-nitroaniline (3n). Light yellow crystals. Mp 129–131 °C (chloroform/hexane). IR (KBr) ν: 3429 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 3.91 (s, 3H, OCH_3), 4.04 (dd, $J=1.6$, 5.6 Hz, 2H, CH_2), 5.28 (br s, 1H, NH), 6.26 (dt, $J=5.6$, 15.6 Hz, 1H, vinyl H), 6.52 (d, $J=8.8$ Hz, 1H, ArH), 6.60 (d, $J=15.6$ Hz, 1H, vinyl H), 7.21–7.26 (m, 1H, ArH), 7.31 (dd, $J=7.2$, 7.6 Hz, 2H, ArH), 7.36 (dd, $J=1.6$, 7.2 Hz, 2H, ArH), 7.61 (d, $J=2.4$ Hz, 1H, ArH), 7.88 (dd, $J=2.4$, 8.8 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$) δ: 44.9 (CH_2), 55.8 (CH_3), 104.6 (CH), 106.9 (CH), 119.7 (CH), 124.7 (CH), 126.3 (CH), 127.8 (CH), 128.5 (CH), 132.4 (CH), 136.2 (C), 137.2 (C), 143.9 (C), 145.1 (C). EI-MS *m/z*: 284 (M^+), 253, 237, 207, 193, 165, 147, 117, 115, 91. HR-MS calcd for $C_{16}H_{16}N_2O_3$ 284.1161, found 284.1162. Anal. Calcd for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.56; H, 5.64; N, 9.72.

4.2.19. *N*-Cinnamyl-3-benzyloxyaniline (3o). Brown oil. IR (KBr) ν: 3411 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 3.75 (br s, 1H, NH), 3.82 (dd, $J=1.2$, 6.0 Hz, 2H, CH_2), 4.97 (s, 2H, CH_2), 6.24 (dt, $J=6.0$, 15.6 Hz, 1H, vinyl H), 6.24–6.28 (m, 2H, ArH), 6.34 (ddd, $J=0.8$, 2.4, 8.0 Hz, 1H, ArH), 6.54 (d, $J=16.0$ Hz, 1H, vinyl H), 7.06 (t, $J=8.0$ Hz, 1H, ArH), 7.17–7.21 (m, 1H, ArH), 7.27 (d, $J=7.2$ Hz, 2H, ArH), 7.28–7.35 (m, 5H, ArH), 7.38 (dd, $J=1.6$, 6.8 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 46.0 (CH_2), 69.7 (CH_2), 99.8 (CH), 103.5 (CH), 106.4 (CH), 126.2 (CH), 126.8 (CH), 127.4 (CH), 127.4 (CH), 127.7 (CH), 128.4 (CH), 128.5 (CH), 129.9 (CH), 131.4 (CH), 136.7 (C), 137.2 (C), 149.3 (C), 160.0 (C). EI-MS *m/z*: 315 (M^+), 288, 271, 239, 224, 207, 196, 182, 146, 117, 115, 91, 77. HR-MS calcd for $C_{22}H_{21}NO$ 315.1623, found 315.1625.

4.2.20. *N*,*N*-Dicinnamyl-3-benzyloxyaniline (4o). Brown crystals. Mp 73–74 °C (chloroform/hexane). ^1H NMR ($CDCl_3$) δ: 4.10 (dd, $J=1.2$, 5.6 Hz, 4H, $CH_2\times2$), 5.03 (s, 2H, CH_2), 6.25 (dt, $J=5.6$, 16.0 Hz, 2H, vinyl H), 6.37 (d, $J=8.0$ Hz, 1H, ArH), 6.42–6.49 (m, 2H, ArH), 6.52 (d, $J=16.0$ Hz, 2H, vinyl H), 7.11–7.24 (m, 4H, ArH), 7.28–7.33 (m, 2H, ArH), 7.29 (dd, $J=6.8$, 8.0 Hz, 4H, ArH), 7.35 (dd, $J=1.6$, 7.2 Hz, 4H, ArH), 7.41 (dd, $J=1.6$, 6.8 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 52.2 (CH_2), 69.9 (CH_2), 100.0 (CH), 102.4 (CH), 105.9 (CH), 125.7 (CH), 126.4 (CH), 127.4 (CH), 127.5 (CH), 127.8 (CH), 128.3 (CH), 128.5 (CH), 129.9 (CH), 131.3 (CH), 136.8 (C), 137.3 (C), 150.2 (C), 160.1 (C). EI-MS *m/z*: 431 (M^+), 401, 355, 340, 327, 281, 250, 207, 179, 166, 150, 131, 117, 91. HR-MS calcd for $C_{31}H_{29}NO$ 431.2249, found 431.2250. Anal. Calcd for $C_{31}H_{29}NO$: C, 86.27; H, 6.77; N, 3.25. Found: C, 86.16; H, 6.83; N, 3.20.

4.2.21. *N*-Cinnamyl-3,5-dimethoxyaniline (3q). Light green oil. IR (KBr) ν: 3408 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 3.70 (s, 6H, $CH_3\times2$), 3.82 (br s, 1H, NH), 3.83 (dd, $J=1.6$, 5.6 Hz, 2H, CH_2), 5.83 (d, $J=2.4$ Hz, 2H, ArH), 5.89 (dd, $J=2.0$, 2.4 Hz, 1H, ArH), 6.25 (dt, $J=5.6$, 16.0 Hz, 1H, vinyl H), 6.55 (d, $J=16.0$ Hz, 1H, vinyl H), 7.16–7.21 (m, 1H, ArH), 7.27 (dd, $J=7.6$, 7.6 Hz, 2H, ArH), 7.33 (dd, $J=1.6$, 7.2 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 46.0 (CH_2), 54.9 (CH_3), 54.9 (CH_3), 89.7 (CH), 91.7 (CH), 126.2 (CH), 126.7 (CH), 127.4 (CH), 128.4 (CH), 131.3 (CH), 136.7 (C), 149.9 (C), 161.6 (C). EI-MS *m/z*: 269 (M^+), 252, 238, 223, 190, 178, 166, 147, 117, 115, 91. HR-MS calcd for $C_{17}H_{19}NO_2$ 269.1416, found 269.1416.

4.2.22. *N*,*N*-Dicinnamyl-3,5-dimethoxyaniline (4q). Brown oil. ^1H NMR ($CDCl_3$) δ: 3.75 (s, 6H, $OCH_3\times2$), 4.10 (dd, $J=1.2$, 5.2 Hz, 4H, $CH_2\times2$), 5.92 (dd, $J=2.0$, 2.0 Hz, 1H, ArH), 6.01 (d, $J=2.0$ Hz, 2H, ArH), 6.26 (dt, $J=5.2$, 16.0 Hz, 2H, vinyl H), 6.53 (d, $J=16.0$ Hz, 2H, vinyl H), 7.19–7.23 (m, 2H, ArH), 7.29 (dd, $J=7.2$, 7.6 Hz, 4H, ArH), 7.35 (dd, $J=1.6$, 7.2 Hz, 4H, ArH). ^{13}C NMR ($CDCl_3$) δ: 52.3 (CH_2), 55.1 (CH_3), 88.6 (CH), 91.9 (CH), 125.7 (CH), 126.3 (CH), 127.4 (CH), 128.5 (CH), 131.2 (CH), 136.8 (C), 150.7 (C), 161.7 (C). EI-MS *m/z*: 385 (M^+), 356, 318, 307, 294, 268, 253, 238, 222, 210, 190, 177, 166, 153, 117, 115, 91. HR-MS calcd for $C_{26}H_{27}NO_2$ 385.2041, found 385.2038.

4.2.23. (1,3-Diphenylallyl)phenylamine (5). Brown oil. IR (KBr) ν: 3414 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 4.08 (br s, 1H, NH), 5.04 (d, $J=6.0$ Hz, 1H, CH), 6.34 (dd, $J=6.0$, 15.6 Hz, 1H, CH), 6.58 (d, $J=15.6$ Hz, 1H, ArH), 6.59 (dd, $J=0.8$, 8.8 Hz, 2H, CH, ArH), 6.67 (ddt, $J=0.8$, 1.2, 7.2 Hz, 1H, ArH), 7.07–7.40 (m, 12H, ArH). ^{13}C NMR ($CDCl_3$) δ: 60.5 (CH), 113.5 (CH), 117.6 (CH), 126.4 (CH), 127.1 (CH), 127.4 (CH), 127.6 (CH), 128.5 (CH), 128.7 (CH), 129.1 (CH), 130.6 (CH), 131.0 (CH), 136.6 (C), 142.0 (C), 147.1 (C). EI-MS *m/z*: 285 (M^+), 270, 206, 193, 178, 165, 152, 115, 91, 77, 65. HR-MS calcd for $C_{21}H_{19}N$ 285.1517, found 285.1514.

4.2.24. *N*-(2-Methylprop-2-enyl)aniline (8).[30] Deep brown oil. IR (KBr) ν: 3419 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.77 (s, 3H, CH_3), 3.66 (s, 2H, CH_2), 3.80 (br s, 1H, NH), 4.86–4.89 (m, 1H, vinyl H), 4.95–4.98 (m, 1H, vinyl H), 6.60 (d, $J=8.0$ Hz, 2H, ArH), 6.69 (t, $J=7.2$ Hz, 1H, ArH), 7.16 (dd, $J=7.2$, 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 20.4 (CH_3), 49.9 (CH_2), 110.9 (CH_2), 112.8 (CH), 117.3 (CH), 129.1 (CH), 142.7 (C), 148.2 (C). EI-MS *m/z*: 147 (M^+), 132, 118, 106, 91, 77. HR-MS calcd for $C_{10}H_{13}N$ 147.1048, found 147.1045.

4.2.25. *N*,*N*-Bis(2-methylprop-2-enyl)aniline (9). Deep blue oil. ^1H NMR ($CDCl_3$) δ: 1.74 (s, 6H, $CH_3\times2$), 3.80 (s, 4H, $CH_2\times2$), 4.81 (d, $J=24.8$ Hz, 4H, $CH_2\times2$), 6.62 (d, $J=8.8$ Hz, 2H, ArH), 6.66 (d, $J=7.2$ Hz, 1H, ArH), 7.17 (dd, $J=7.6$, 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 20.0 (CH_3), 56.3 (CH_2), 110.2 (CH_2), 111.9 (CH), 115.9 (CH), 128.8 (CH), 140.5 (C), 148.7 (C). EI-MS *m/z*: 201 (M^+),

186, 160, 145, 130, 118, 104, 91, 77. HR-MS calcd for $C_{14}H_{19}N$ 201.1518, found 201.1517.

4.2.26. *N*-(2-Chloroallyl)aniline (10). Deep brown oil. IR (KBr) ν: 3418 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 3.88 (dd, $J=1.2$, 1.2 Hz, 2H, CH_2), 4.03 (br s, 1H, NH), 5.29 (dt, $J=1.2$, 2.8 Hz, 1H, vinyl H), 5.39 (dt, $J=1.6$, 2.8 Hz, 1H, vinyl H), 6.58 (dd, $J=0.8$, 8.4 Hz, 2H, ArH), 6.73 (ddt, $J=0.8$, 1.2, 7.6 Hz, 1H, ArH), 7.17 (dd, $J=7.6$, 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 50.0 (CH_2), 112.4 (CH_2), 112.9 (CH), 118.1 (CH), 129.2 (CH), 139.2 (C), 146.7 (C). EI-MS *m/z*: 169 ($M^+ +2$), 167 (M^+), 132, 118, 106, 92, 77. HR-MS calcd for $C_9H_{10}ClN$ 167.0502, found 167.0503.

4.2.27. *N*-(2-Cyclohexenyl)aniline (11). Light brown oil. IR (KBr) ν: 3407 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.57–1.74 (m, 3H, CH_2), 1.86–1.92 (m, 1H, CH_2), 1.99–2.05 (m, 2H, CH_2), 3.57 (br s, 1H, NH), 3.94–4.01 (m, 1H, CH), 5.74 (ddt, $J=2.4$, 2.4, 10.0 Hz, 1H, vinyl H), 5.83 (ddt, $J=1.6$, 3.6, 10.0 Hz, 1H, vinyl H), 6.60 (d, $J=8.4$ Hz, 2H, ArH), 6.67 (dt, $J=0.8$, 7.2 Hz, 1H, ArH), 7.12–7.18 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 19.6 (CH_2), 25.1 (CH_2), 28.8 (CH_2), 47.8 (CH), 113.2 (CH), 117.1 (CH), 128.5 (CH), 129.2 (CH), 130.0 (CH), 147.1 (C). EI-MS *m/z*: 173 (M^+), 145, 144, 130, 96. HR-MS calcd for $C_{12}H_{15}N$ 173.1205, found 173.1203.

4.2.28. *N*-(3-Methylbut-2-enyl)aniline (14). Brown oil. IR (KBr) ν: 3408 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.71 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 3.60 (br s, 1H, NH), 3.68 (d, $J=$ 6.8 Hz, 2H, CH_2), 5.30–5.35 (m, 1H, vinyl H), 6.61 (dd, $J=$ 1.2, 8.4 Hz, 2H, ArH), 6.70 (ddd, $J=0.8$, 1.2, 7.2 Hz, 1H, ArH), 7.17 (dd, $J=7.2$, 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 17.9 (CH_3), 25.7 (CH_3), 42.0 (CH_2), 112.9 (CH), 117.3 (CH), 121.6 (C), 129.1 (C), 135.6 (C), 148.4 (C). EI-MS *m/z*: 161 (M^+), 146, 144, 130, 118, 106, 93, 77. HR-MS calcd for $C_{11}H_{15}N$ 161.1205, found 161.1204.

4.2.29. *N*-(1,1-Dimethylprop-2-enyl)aniline (15). Brown oil. IR (KBr) ν: 3421 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.38 (s, 6H, $CH_3\times2$), 3.52 (br s, 1H, NH), 5.10 (dd, $J=1.2$, 10.8 Hz, 1H, vinyl H), 5.18 (dd, $J=1.2$, 17.6 Hz, 1H, vinyl H), 6.01 (dd, $J=10.8$, 17.6 Hz, 1H, vinylH), 6.66–6.70 (m, 1H, ArH), 6.69 (dd, $J=1.2$, 7.6 Hz, 2H, ArH), 7.10 (dd, $J=$ 7.6, 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ: 28.3 (CH_3), 54.6 (CH), 112.7 (CH_2), 115.7 (CH), 117.4 (CH), 128.7 (CH), 146.1 (CH), 146.6 (C). EI-MS *m/z*: 161 (M^+), 146, 131, 130, 120, 118, 103, 93, 91, 77. HR-MS calcd For $C_{11}H_{15}N$ 161.1205, found 161.1207.

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