Regio- and Stereoselectivity in Palladium(0)-Catalyzed Allylation of Anilines Using Allylic Alcohols Directly

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The direct activation of C−O bonds in allylic alcohols by palladium complexes has been accelerated by carrying out the reactions in the presence of titanium(IV) isopropoxide and 4 Å molecular sieves. The palladium(0)-catalyzed allylation of anilines using allylic alcohols directly gave regio- and stereoisomeric allylic anilines in good yields. The regioselectivity of the process was temperature dependent. Under kinetic control, the less highly substituted alkene was obtained, while under thermodynamic control the more highly substituted alkene was increased. Anilines bearing an electron-withdrawing group gave lower chemical yields. The phosphine ligand effect was very important on the regioselectivity: decreasing the size of the diphosphines or decreasing the electron-withdrawing ability of the monophosphines gave predominantly the less highly substituted alkenes.

Introduction

Palladium-catalyzed allylation is an established, efficient, and highly stereo- and chemoselective method for C−C, C−N, and C−O bond formation, which has been widely applied to organic chemistry.[1] The catalytic cycle requires the formation of the cationic η^3-allylpalladium(II) complex, an intermediate that is generated by oxidative addition of allylic compounds to a Pd(0) complex and which can be attacked by nucleophiles at both termini of the allylic system. Although halides,[2] esters,[3] carbonates,[4] carbamates,[5] phosphates,[6] and related derivatives[7] of allylic alcohols have frequently been used as substrates, 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.[8] 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.[9] In preliminary papers,[10] we have recently reported our attempts and some successful applications of a process involving C−O bond cleavage with direct use of allylic alcohols catalyzed by palladium complexes. This is, to our knowledge, the first example

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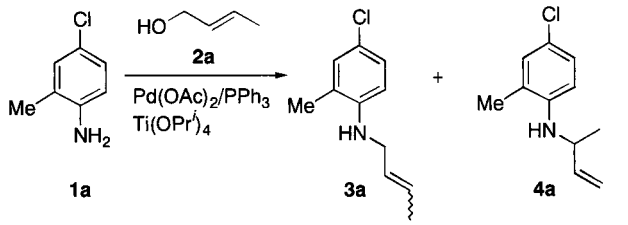
Table 1. Reaction of 4-Chloro-2-methylaniline (1a) with 2-Buten-1-ol (2a)[a]



entry	$Pd(OAc)_2$:PPh_3:$Ti(OPr^i)_4$ (in mmol)	solvent	*t* (h)	yield (%)[b] (**3a**:**4a**)	*E*/*Z* ratio of **3a**[c]
1	0.01:0.04:0.25	benzene	3	51 (43:57)	87:13
			6	63 (52:48)	88:12
2[d]	0.01:0.04:0.25	benzene	3	12 (30:70)	88:12
			12	42 (30:70)	88:12
			24	90 (29:71)	87:13
3	0.025:0.1:0	benzene	3	0	
			40	5 (100:0)	100:0
4[e]	0.01:0.04:0.25	benzene	3	10 (53:47)	88:12
5	0.0.1:0.25	benzene	12	0	
6[f]	0.01:0.04:0.25	benzene	3	94 (42:58)	87:13
7	0.025:0.1:0.25	benzene	3	80 (55:45)	86:14
8	0.01:0.04:0.25	MeCN	3	10 (15:85)	100:0
9	0.01:0.04:0.25	THF	3	12 (39:61)	100:0
10	0.01:0.04:0.25	HMPA	3	18 (34:66)	95:5
11	0.01:0.04:0.25	DMF	3	10 (26:74)	100:0
12	0.01:0.04:0.25	dioxane	3	6 (37:63)	100:0
13	0.01:0.04:0.25	toluene	3	32 (33:67)	100:0

[a] Reaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), and MS4A (200 mg) in a solvent (5 mL) at 50 °C for 3 h. [b] Isolated yield. [c] The *E*/*Z* ratio of **3a** was determined by GC. [d] Stir at room temperature. [e] Without MS4A. [f] Reflux for 3 h.

of palladium-catalyzed allylation of anilines by the direct use of allylic alcohols in the presence of $Ti(OPr^i)_4$. The effect of addition of $Ti(OPr^i)_4$ to promote the palladium-catalyzed allyl−OH bond cleavage may have potential applications to provide methodologies for using allylic alcohols directly in organic syntheses. This result prompted us to study in some detail this reaction between anilines and allylic alcohols in order to understand the main factors affecting the regio- and stereocontrol of the reaction; this is important for practical synthetic applications and also for gaining more insight into the mechanism.

Results and Discussion

The allylation process is straightforward. To evaluate the scope and limitations of the *N*-allylation of anilines with allylic alcohols, we treated a mixture of 4-chloro-2-methylaniline (**1a**, 1 mmol) and 2-buten-1-ol (**2a**, 1.2 mmol) in the presence of $Pd(OAc)_2$ (0.01 mmol), PPh_3 (0.04 mmol), $Ti(OPr^i)_4$ (0.25 mmol), and molecular sieves (MS4A) (200 mg) in benzene (5 mL) under nitrogen at 50 °C for 3 h. The mixtures of regio- and stereoisomeric anilines **3a** and **4a** were formed in 22% and 29%, respectively (entry 1 in Table 1). The more highly substituted alkene **3a** resulted from attack of the aniline on the less-substituted terminus of the π-allyl complex. The structures of compounds (*E*)-**3a** and **4a** were determined from NMR and HETCOR spectroscopy. The ^{1}H NMR spectra of the linear isomer (*E*)-**3a** was characterized by a doublet of quintets at δ 3.71 ppm for the NCH_2 group and a doublet of quartets at δ 1.73 ppm for the CH_3 group, while the branched isomer **4a** was mainly characterized by a doublet of quartets at δ 3.99 ppm for the allylic proton and a doublet at δ 1.36 ppm for the CH_3 group; we noticed signals at δ 3.80 ppm for the NCH_2 group corresponding to the isomer (*Z*)-**3a**. The ^{13}C NMR was characterized by C-1 and C-4 signals at δ 17.74 and 46.06 ppm, respectively, for the linear isomer (*E*)-**3a** and a C-3 signal at δ 51.04 ppm for the branched isomer **4a**; we also noticed signals at δ 13.14 and 40.99 ppm for C-1 and C-4, respectively, corresponding to the isomer (*Z*)-**3a**. The 87:13 *E*/*Z* ratio of **3a** was determined by GC. This stereochemistry was confirmed by the coupling constant of the vinylic protons for this major isomer (J = 15.2 Hz) being characteristic of *E*-stereochemistry. The loss of the stereochemistry of the starting alcohol **2a** is due to a rapid $\sigma \leftrightarrows \eta^3 \leftrightarrows \sigma$ interconversion of the π-allyl intermediate compared to the rate of amination of this intermediate.

A more detailed study of the influence of the temperature on the regioselectivity of the *N*-allylation showed that at room temperature for 3 h the two regioisomers **3a** and **4a** were obtained in a ratio of 30:70, and this ratio remained unchanged during the reaction course (entry 2). Conversely, performing the reaction at 50 °C for 6 h gave predominantly the more highly substituted alkene **3a** at equilibrium (52% vs 48%), the initial **3a**/**4a** ratio of 43:57 turning progressively into 52:48 (entry 1). These results showed that at 25 °C, under kinetic control, the aniline was regioselectively attacking the more substituted terminus of the π-allyl intermediate. At 50 °C, the aniline attacks the less substituted terminus of the π-allyl complex; that is, the reaction is under thermodynamic control.

In the absence of $Ti(OPr^i)_4$, the reaction gave only 5% yield (entry 3) after 40 h. The effect of addition of $Ti(OPr^i)_4$ to promote the palladium-catalyzed allyl−OH bond cleavage remarkably enhanced both the reaction rate and yield. These results suggested that the reaction should be accompanied by formation of water, which may deactivate the catalyst. Addition of molecular sieves (MS4A) for its removal showed a positive effect (entry 4). It was confirmed that the reaction did not occur in the absence of palladium species (entry 5). Note that the products could also be afforded in good yield in the reaction under reflux (entry 6) or with an increase in the amount of palladium catalyst (2.5 mol %) (entry 7). It was known that several factors, such as the solvent and nature of the nucleophile, can alter the product pattern in palladium-catalyzed allylation.[11] Seven solvents were investigated, MeCN, THF, HMPA, DMF, dioxane, and toluene, with benzene giving the best results (entries 1 and 8−13).

The results reported in Table 2 concerning the reaction of **1a** with **2a** in the presence of $Pd(OAc)_2$ and various ligands show that the **3a**/**4a** ratio depends on the ligand used. The regioselectivity is affected by decreasing the ring size of the diphosphine with selectivity in attack of the aniline on the more substituted terminus of the π-allyl complex. The **3a**/**4a** ratio increased as the size of the diphosphine increased; that

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Table 2. Palladium-Catalyzed Reaction of Aniline 1a with Alcohol 2a: Phosphine Ligand Effects

entry	ligand	pK_a[b]	*T* (°C)	yield (%)[c] (**3a**:**4a**)	*E*/*Z* ratio of **3a**[d]
1	PPh_3	2.73	50	51 (43:57)	87:13
			80	94 (42:58)	87:13
2	dppm		50	33 (37:63)	88:12
			80	93 (38:62)	87:13
3	dppe		50	9 (40:60)	88:12
			80	84 (42:58)	87:13
4	dppp		50	14 (42:58)	88:12
			80	78 (49:51)	85:15
5	dppb		50	27 (48:52)	85:15
			80	92 (50:50)	86:14
6	dpph		50	39 (51:49)	88:12
			80	54 (58:42)	88:12
7	$(PhO)_3P$	−2	50	47 (57:43)	83:17
			80	93 (91:9)	88:12
8	$(4\text{-}ClPh)_3P$	1.03	50	8 (53:47)	88:12
			80	74 (55:45)	85:15
9	$(4\text{-}FPh)_3P$	1.97	50	20 (49:51)	88:12
			80	92 (51:49)	88:12
10	$(3\text{-}MePh)_3P$	3.30	50	24 (41:59)	92:8
			80	92 (41:59)	86:14
11	$(4\text{-}MePh)_3P$	3.84	50	23 (30:70)	95:5
			80	54 (37:63)	87:13
12	$(4\text{-}MeOPh)_3P$	4.57	50	56 (27:73)	88:12
			80	85 (35:65)	86:14
13	PBu_3	8.43	50	8 (12:88)	88:12
			80	88 (32:68)	86:14
14	$(2,6\text{-di-}MeOPh)_3P$	10.7	50	0	
			80	12 (5:95)	100:0
15	$(2,4,6\text{-tri-}MeOPh)_3P$	11.2	50	3 (2:98)	100:0
			80	10 (3:97)	100:0

[a] Reaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), $Pd(OAc)_2$ (0.01 mmol), ligand (0.04 mmol), $Ti(OPr^i)_4$ (0.25 mmol), and MS4A (200 mg) in benzene (5 mL) were reacted for 3 h. [b] Taken from ref 13. [c] Isolated yield. [d] The *E*/*Z* ratio of **3a** was determined by GC.

is, **3a**/**4a** increased in the order 37:63 [dppm] < 40:60 [dppe] < 42:58 [dppp] < 48:52 [dppb] < 51:49 [dpph] (entries 2−6). From the results obtained with the monophosphines, it is obvious that steric and electronic effects direct the reaction to one or the other termini of the π-allyl complex. We observed that the **3a**/**4a** ratio increased as the electron-withdrawing ability of the ligand increased; that is, **3a**/**4a** increased in the order 2:98 [$(2,4,6\text{-tri-}MeOPh)_3P$] < 12:88 [$PBu_3$] < 27:73 [$(4\text{-}MeOPh)_3P$] < 30:70 [$(4\text{-}MePh)_3P$] < 41:59 [$(3\text{-}MePh)_3P$] < 43/57 [$PPh_3$] < 49:51 [$(4\text{-}FPh)_3P$] < 53:47 [$(4\text{-}ClPh)_3P$] < 57:43 [$(PhO)_3P$] (entries 1 and 7−15). A strong π-acceptor ligand, which increases the positive charge character of the π-allyl complex,[12] directs attack of the aniline on the less substituted terminus of the π-allyl complex. The use of basic phosphines as ligands increased the formation of **4a**. In most cases, a small amount of (*Z*)-**3a** was formed. Increasing the reaction temperature, the linear isomer (*E*)-**3a** was increased.

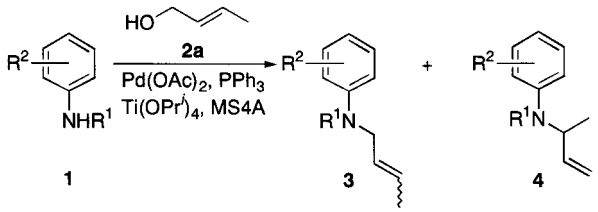
A comparative study of different palladium catalysts in benzene was reported in Table 3. Among the palladium catalysts including $Pd(OAc)_2$ (entry 1), $Pd(OCOCF_3)_2$ (entry 2), $PdCl_2$ (entry 3), $Pd(acac)_2$ (entry 4), $Pd(PPh_3)_4$ (entry 5), and $PdCl_2(MeCN)_2$ (entry 6), $Pd(OAc)_2$ was found to be the most active catalyst (entry 1). We also noticed that the ratio of **3a**/**4a** was temperature dependent.

Table 3. Palladium-Catalyzed Reaction of Aniline 1a with Alcohol 2a: Pallaium Catalyst Effects[a]

entry	catalyst	*T* (°C)	yield (%)[b] (**3a**:**4a**)	*E*/*Z* ratio of **3a**[c]
1	$Pd(OAc)_2$-PPh_3	50	51 (43:57)	87:13
		80	94 (42:58)	87:13
2	$Pd(OCOCF_3)_2$-PPh_3	50	45 (40:60)	90:10
		80	90 (60:40)	84:16
3	$PdCl_2$-PPh_3	50	3 (0:100)	
		80	38 (45:55)	75:25
4	$Pd(acac)_2$-PPh_3	50	29 (24:76)	90:10
		80	64 (37:63)	77:23
5	$Pd(PPh_3)_4$	50	22 (50:50)	89:11
		80	51 (50:50)	86:14
6	$PdCl_2(MeCN)_2$	50	39 (51:49)	94:6
		80	54 (58:42)	88:12

[a] Reaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), Pd catalyst (0.01 mmol), PPh_3 (0.04 mmol), $Ti(OPr^i)_4$ (0.25 mmol), and MS4A (200 mg) in benzene (5 mL) were reacted for 3 h. [b] Isolated yield. [c] The *E*/*Z* ratio of **3a** was determined by GC.

Table 4. Reaction of Anilines (1b−n) with 2-Buten-1-ol (2a)[a]



1	R^1	R^2	products		yield (%)[b] (**3**:**4**)	*E*/*Z* ratio of **3**[c]
1b	H	H	**3b**	**4b**	97 (83:17)	80:20
1c	H	4-Me	**3c**	**4c**	91 (83:17)	80:20
1d	H	4-Cl	**3d**	**4d**	97 (44:56)	84:16
1e	H	4-OMe	**3e**	**4e**	99 (33:67)	86:14
1f	H	$4\text{-}CO_2Et$	**3f**	**4f**	86 (58:42)	87:13
1g	H	4-CN	**3g**	**4g**	81 (24:76)	100:0
1h	H	$4\text{-}NO_2$	**3h**	**4h**	72 (37:63)	80:20
1i	H	2,4-Me	**3i**	**4i**	99 (59:41)	92:8
1j	H	2-Cl, 4-Me	**3j**	**4j**	83 (42:58)	89:11
1k	H	$2\text{-}OMe, 4\text{-}NO_2$	**3k**	**4k**	76 (43:57)	84:16
1l	H	3,5-OMe	**3l**	**4l**	98 (67:33)	84:16
1m	Me	H	**3m**	**4m**	87 (78:22)	78:22
1n	Et	H	**3n**	**4n**	82 (85:15)	81:19

[a] Reaction conditions: **1** (1 mmol), **2a** (0.8 mmol), $Pd(OAc)_2$ (0.01 mmol), PPh_3 (0.04 mmol), $Ti(OPr^i)_4$ (0.25 mmol), and MS4A (200 mg) in benzene (5 mL) were refluxed for 3 h. [b] Isolated yield. [c] Determined by GC.

The results collected in Table 4 show that the amination of 2-buten-1-ol (**2a**) worked well with anilines containing electron-donating groups, giving generally high yields of the corresponding allylic anilines. Using anilines containing electron-withdrawing groups gave lower chemical yields. These differences in reactivity could be related to the nucleophilicity of the corresponding aniline. 4-Nitroaniline (**1h**) gave 72% yield; the lower yield observed may arise from the nature of the nitro group. However, secondary anilines **1m**,**n** tend to give the more highly substituted alkene **3**.

The structures of compounds (*E*)-**3** and **4** were unambiguously determined from the NMR and HETCOR spectroscopy. The ^1H NMR spectra of the linear isomer (*E*)-**3** was characterized by a doublet of quintets at δ 3.7 ppm for the NCH_2 group and a doublet of quartets at δ 1.7 ppm for the CH_3 group, while the branched

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isomer **4** was mainly characterized by a doublet of quartets of the allylic proton at approximately δ 4.0 ppm and a doublet at δ 1.3 ppm for the CH_3 group. The ^{13}C NMR was characterized by C-1 and C-4 signals at approximately δ 17.7 and 46 ppm, respectively, for the linear isomer (*E*)-**3** and a C-3 signal at δ 51 ppm for the branched isomer **4**; we also noticed signals at δ 13 and 40 ppm for C-1 and C-4, respectively, corresponding to the isomer (*Z*)-**3**.

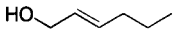
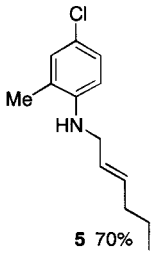
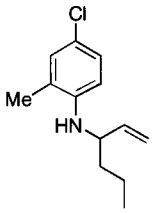
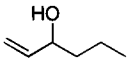
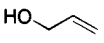
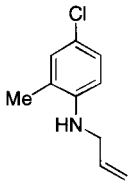
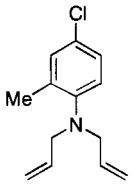
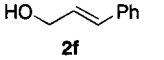
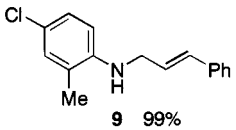
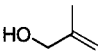
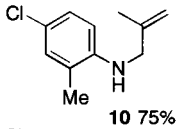
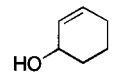
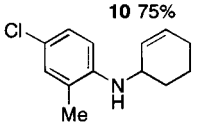
Results for amination of a number of allylic alcohols **2b**−**h** with 4-chloro-2-methylaniline (**1a**) using Pd(OAc)$_2$, PPh_3, Ti(OPr^i)$_4$, and MS4A are summarized in Table 5. At 80 °C, all of the allylic alcohols examined underwent amination smoothly to give the corresponding *N*-allylanilines in overall yields ranging from 75 to 99%. Since both regioisomeric alcohols **2a** and **2b** gave identical mixtures of the anilines **3a** and **4a** in similar ratios (entries 1, 2), the reaction is considered to proceed via π-allylpalladium intermediates. We also noticed that the regioisomeric **2c** and **2d** reacted with aniline to give identical mixtures of regio- and stereoisomeric anilines **5** and **6**, as expected from attack of the aniline on the two allylic termini of the π-allylpalldium species, in a similar ratio (entries 3, 4). When allyl alcohol (**2e**) was reacted at 50 °C, *N*-allylaniline **7** and a small amount of *N*,*N*-diallylaniline **8** were formed in yields of 78% and 8%, respectively (entry 5). The products could also be afforded in high yield in the reaction under reflux (entry 6). Decreasing the amount of **2e**, selective monoallylation product **7** was formed in 98% yield (entry 7). Increasing the amount of **2e**, diallylation product **8** was formed in 99% yield (entry 8). Depending on the ratio of **1a**/**2e** used, monoallylated **7** or diallylated product **8** was selectively produced.

A plausible reaction mechanism for this reaction is shown in Scheme 1. Alcohol **2** or an allyl titanate, formed by an alcohol exchange reaction between **2** and isopropoxide in Ti(OPr^i)$_4$,[14] reacts with Pd(0) species generated in situ[15] to afford the π-allylpalladium intermediate **12**. Intermolecular nucleophilic substitution of the amino group of **1** takes place at the π-allyl system to give intermediate **13**, followed by reductive elimination to give *N*-allylaniline.

Conclusions

We have shown that palladium(0)-catalyzed allylation of anilines using allylic alcohols directly is an efficient route for C−N bond formation. The regioselectivity of the process was temperature dependent. Under kinetic control, the less highly substituted alkene was obtained. Under thermodynamic control, the more substituted alkene was increased. The phosphine ligand effect was very important to the regioselectivity: decreasing the size of the diphosphines or decreasing the electron withdrawing ability of the monophosphines gave predominantly the less highly substituted alkenes. Depending on the amount of allylic alcohols used, mono- or diallylated aniline was selectively produced.

Table 5. Reaction of 4-Chloro-2-methylanillines (1a) with Allylic Alcohols (2b−h)[a]

entry	2	T(°C)	yields[b]	
1	 **2b**	50	**3a** 26% (*E*/*Z*=90/10)[e]	**4a** 33%
2	**2b**	80	**3a** 45% (*E*/*Z*=84/16)[e]	**4a** 53%
3	 **2c**	80	 **5** 70%	 **6** 28%
4	 **2d**	80	**5** 68%	**6** 29%
5	 **2e**	50	 **7** 78%	 **8** 8%
6	**2e**	80	**7** 94%	**8** 3%
7[c]	**2e**	80	**7** 98%[f]	
8[d]	**2e**	80		**8** 99%
9	 **2f**	80	 **9** 99%	
10	 **2g**	80	 **10** 75%	
11	 **2h**	80	 **11** 98%	

[a] Reaction conditions: **1a** (1 mmol), **2** (1.2 mmol), Pd(OAc)$_2$ (0.01 mmol), PPh_3 (0.04 mmol), Ti(OPr^i)$_4$ (0.25 mmol), and MS4A (200 mg) in benzene (5 mL) were reacted for 3 h. [b] Isolated yield. [c] 0.8 mmol of **2e** was used. [d] 4 mmol of **2e** was used. [e] Determined by GC. [f] Yields based on **2e**.

Experimental Section

General Considerations. All reactions were carried out under a nitrogen atmosphere. Solvents were dried and distilled by known methods. Column chromatography was performed on silica gel. IR absorption spectra were recorded on Shimadzu IR-27G and Perkin-Elmer System 2000 FT-IR spectrophotometers. Proton and carbon-13 NMR were measured with Varian Gemini-200 and Unity-400 spectrometers. HETCOR NMR

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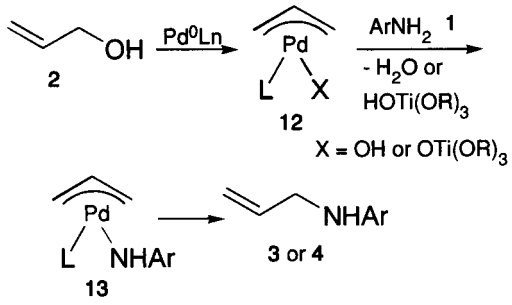
Scheme 1



spectra were recorded at 400 MHz. 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 Hewlett-Packard 5989A or JEOL JMS D-100 instrument, with a direct inlet system. All the following chemicals were commercially available and used without further purification. Anilines **1a** and **1j**, $Pd(OCOCF_3)_2$, 1,3-bis(diphenylphosphino)propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), 1,6-bis(diphenylphosphino)hexane (dpph), $(3\text{-MePh})_3P$, $(4\text{-MePh})_3P$, $(2,6\text{-di-MeOPh})_3P$, and $(2,4,6\text{-tri-MeOPh})_3P$ were purchased from Aldrich. $Pd(OAc)_2$, $PdCl_2$, MS4A, PPh_3, and $(PhO)_3P$ were purchased from Riedel-de Haen. 3,5-Dimethoxyaniline (**1l**), $Pd(acac)_2$ (acac = acetylacetonate), 1,1-bis(diphenylphosphino)methane (dppm), $(4\text{-MeOPh})_3P$, $(4\text{-ClPh})_3P$, and $(4\text{-FPh})_3P$ were purchased from Lancaster. Anilines **1b**−**i**, **1k**, and **1m**,**n**, allylic alcohols **2a**−**h**, $Pd(PPh_3)_4$, $PdCl_2(MeCN)_2$, $Ti(OPr^i)_4$, 1,2-bis(diphenylphosphino)ethane (dppe), and PBu_3 were purchased from TCI.

General Procedure for the Palladium-Catalyzed Allylation of Anilines. Reaction with 4-Chloro-2-methylaniline (1a). A mixture of 4-chloro-2-methylaniline (**1a**) (142 mg, 1 mmol), 2-buten-1-ol (**2a**) (87 mg, 1.2 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), PPh_3 (10.5 mg, 0.04 mmol), $Ti(OPr^i)_4$ (0.075 mL, 0.25 mmol), and MS4A (200 mg) in benzene (5 mL) was refluxed under nitrogen for 3 h. After cooling, the reaction mixture was poured into aqueous 10% HCl and extracted with ether. The aqueous layer was mixed with aqueous 10% NaOH and extracted with ether. The ether layers were combined, dried over Na_2SO_4, and concentrated. Column chromatography (*n*-hexane/EtOAc = 5:1) of the residue afforded 184 mg (94%) of **3a** and **4a** as a 42:58 mixture of isomers. It was not possible to obtain the (*Z*)-**3a** in isomerically pure form. Its presence was indicated by a doublet at 3.80 ppm and could be obtained as a mixture along with (*E*)-**3a**.

***N*-(But-2*E*-enyl)-4-chloro-2-methylaniline (3a):** IR (KBr) ν 3446 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.73 (dq, J = 1.2, 6.0 Hz, 3H, CH_3), 2.12 (s, 3H, CH_3), 3.56 (bs, 1H, NH), 3.71 (dquin, J = 1.2, 6.0 Hz, 2H, CH_2), 5.61 (dtq, J = 1.2, 6.0, 15.2 Hz, 1H, vinyl H), 5.73 (dtq, J = 1.2, 6.0, 15.2 Hz, 1H, vinyl H), 6.52 (d, J = 8.4 Hz, 1H, ArH), 7.02 (d, J = 2.4 Hz, 1H, ArH), 7.06 (dd, J = 2.4, 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.29 (CH_3), 17.74 (CH_3), 46.06 (CH_2), 111.00 (CH), 121.44 (C), 123.64 (C), 126.62 (CH), 127.66 (CH), 128.28 (CH), 129.66 (CH), 144.61 (C). EI-MS *m*/*z* 197 (M^++2), 195 (M^+), 182, 180, 154, 141, 125, 117, 106, 89, 77; EI-HRMS calcd for $C_{11}H_{14}ClN$ 195.0815, found 195.0814.

***N*-(2-But-3-enyl)-4-chloro-2-methylaniline (4a):** IR (KBr) ν 3436 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.36 (d, J = 6.6 Hz, 3H, CH_3), 2.13 (s, 3H, CH_3), 3.45 (bs, 1H, NH), 3.99 (dq, J = 5.8, 6.5 Hz, 1H, CH), 5.11 (dt, J = 1.3, 10.3 Hz, 1H, vinyl H), 5.19 (dt, J = 1.4, 17.2 Hz, 1H, vinyl H), 5.84 (ddd, J = 5.5, 10.3, 17.2 Hz, 1H, vinyl H), 6.52 (d, J = 9.4 Hz, 1H, ArH), 7.03−7.07 (m, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.36 (CH_3), 21.76 (CH_3), 51.04 (CH), 111.87 (CH), 114.23 (CH_2), 121.20 (C), 123.37 (C), 126.51 (CH), 129.69 (CH), 140.88 (CH), 143.80 (C); EI-MS *m*/*z* 197 (M^+ + 2), 195 (M^+), 182, 180, 168, 145, 144, 130, 117, 106, 89, 77; EI-HRMS calcd for $C_{11}H_{14}ClN$ 195.0815, found 195.0813.

***N*-(But-2*E*-enyl)aniline (3b):**[16] ^1H NMR (400 MHz, $CDCl_3$) δ 1.71 (dq, J = 1.2, 6.0 Hz, 3H, CH_3), 3.62 (bs, 1H, NH), 3.69 (dquin, J = 1.2, 6.0 Hz, 2H, CH_2), 5.61 (dtq, J = 1.2, 6.0, 15.2 Hz, 1H, vinyl H), 5.72 (dtq, J = 1.2, 6.0, 15.2 Hz, 1H, vinyl H), 6.64 (d, J = 7.6 Hz, 2H, ArH), 6.72 (t, J = 7.2 Hz, 1H, ArH), 7.18 (dd, J = 7.2, 8.4 Hz, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.73 (CH_3), 46.02 (CH_2), 112.98 (CH), 117.48 (CH), 127.90 (CH), 128.03 (CH), 129.16 (CH), 148.16 (C); EI-MS *m*/*z* 147 (M^+), 132, 106, 93, 77; EI−HRMS calcd for $C_{10}H_{13}N$ 147.1048, found 147.1047.

***N*-(2-But-3-enyl)aniline (4b):**[17] ^1H NMR (200 MHz, $CDCl_3$) δ 1.35 (d, J = 6.8 Hz, 3H, CH_3), 3.48 (bs, 1H, NH), 4.02 (dq, J = 5.6, 6.7 Hz, 1H, CH), 5.12 (dt, J = 1.4, 10.2 Hz, 1H, vinyl H), 5.25 (dt, J = 1.3, 17.2 Hz, 1H, vinyl H), 5.88 (ddd, J = 5.5, 10.3, 17.2 Hz, 1H, vinyl H), 6.65 (d, J = 7.6 Hz, 2H, ArH), 6.73 (t, J = 7.2 Hz, 1H, ArH), 7.20 (dd, J = 7.3, 8.4 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.57 (CH_3), 51.00 (CH), 113.36 (CH), 114.05 (CH_2), 117.23 (CH), 129.11 (CH), 141.24 (CH), 147.38 (C); EI-MS *m*/*z* 147 (M^+), 132, 130, 120, 117, 93, 77; EI-HRMS calcd for $C_{10}H_{13}N$ 147.1048, found 147.1049.

***N*-(But-2*E*-enyl)-4-methylaniline (3c):**[16c] ^1H NMR (400 MHz, $CDCl_3$) δ 1.77 (dq, J = 1.2, 6.4 Hz, 3H, CH_3), 2.31 (s, 3H, CH_3), 3.41 (bs, 1H, NH), 3.72 (dquin, J = 1.2, 6.0 Hz, 2H, CH_2), 5.66 (dtq, J = 1.2, 6.0, 15.2 Hz, 1H, vinyl H), 5.77 (dtq, J = 1.2, 6.0, 15.2 Hz, 1H, vinyl H), 6.61 (d, J = 8.4 Hz, 2H, ArH), 7.05 (d, J = 8.4 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.75 (CH_3), 20.36 (CH_3), 46.44 (CH_2), 113.25 (CH), 126.66 (C), 127.77 (CH), 128.26 (CH), 129.68 (CH), 145.92 (C); EI-MS *m*/*z* 161 (M^+), 146, 131, 120, 107, 106, 91, 77; EI-HRMS calcd for $C_{11}H_{15}N$ 161.1204, found 161.1203.

***N*-(2-But-3-enyl)-4-methylaniline (4c):** IR (KBr) ν 3406m^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 (d, J = 6.8 Hz, 3H, CH_3), 2.24 (s, 3H, CH_3), 3.36 (bs, 1H, NH), 3.96 (dq, J = 5.6, 6.8 Hz, 1H, CH), 5.08 (dt, J = 1.2, 10.4 Hz, 1H, vinyl H), 5.21 (dt, J = 1.2, 17.2 Hz, 1H, vinyl H), 5.84 (ddd, J = 5.6, 10.4, 17.2 Hz, 1H, vinyl H), 6.55 (d, J = 8.4 Hz, 2H, ArH), 6.98 (d, J = 8.4 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.36 (CH_3), 21.60 (CH_3), 51.43 (CH), 113.72 (CH), 114.04 (CH_2), 126.55 (C), 129.63 (CH), 141.45 (CH), 145.04 (C); EI-MS *m*/*z* 161 (M^+), 146, 131, 118, 106, 91, 77; EI-HRMS calcd for $C_{11}H_{15}N$ 161.1204, found 161.1203.

***N*-(But-2*E*-enyl)-4-chloroaniline (3d):** IR (KBr) ν 3418m^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.73 (dq, J = 1.2, 6.0 Hz, 3H, CH_3), 3.57 (bs, 1H, NH), 3.66 (dquin, J = 1.2, 6.0 Hz, 2H, CH_2), 5.58 (dtq, J = 1.2, 6.0, 15.2 Hz, 1H, vinyl H), 5.72 (dtq, J = 1.2, 6.0, 15.2 Hz, 1H, vinyl H), 6.54 (d, J = 8.8 Hz, 2H, ArH), 7.13 (d, J = 8.8 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.69 (CH_3), 46.00 (CH_2), 113.95 (CH), 121.72 (C), 127.54 (CH), 128.15 (CH), 128.92 (CH), 146.62 (C); EI-MS *m*/*z* 183 (M^+ + 2), 181 (M^+), 168, 166, 154, 140, 130, 127, 111, 99, 75; EI-HRMS calcd for $C_{10}H_{12}ClN$ 181.0658, found 181.0656.

***N*-(2-But-3-enyl)-4-chloroaniline (4d):** IR (KBr) ν 3426 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 (d, J = 6.8 Hz, 3H, CH_3), 3.67 (bs, 1H, NH), 3.93 (dq, J = 5.6, 6.8 Hz, 1H, CH), 5.10 (dt, J = 1.2, 10.4 Hz, 1H, vinyl H), 5.20 (dt, J = 1.2, 17.2 Hz, 1H, vinyl H), 5.81 (ddd, J = 5.6, 10.4, 17.2 Hz, 1H, vinyl H), 6.53 (d, J = 8.8 Hz, 2H, ArH), 7.10 (d, J = 8.8 Hz, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.53 (CH_3), 51.28 (CH), 114.34 (CH), 114.49 (CH_2), 121.81 (C), 128.91 (CH), 140.75 (CH), 145.87 (C); EI-MS *m*/*z* 183 (M^+ + 2), 181 (M^+), 168, 166, 154, 131, 130, 127, 111, 99, 75; EI-HRMS calcd for $C_{10}H_{12}ClN$ 181.0658, found 181.0657.

(16) (a) Barluenga, J.; Fananas, F. J.; Villamana, J.; Yus, M. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2685. (b) Butsugan, Y.; Nagai, K.; Nagaya, F.; Tabuchi, H.; Yamada, K.; Araki, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1707. (c) Barluenga, J.; Perez-Prieto, J.; Asensio, G. *Tetrahedron* **1990**, *46*, 2453. (d) Verardo, G.; Giumanini, A. G.; Strazzolini, P.; Poiana, M. *Synthesis* **1993**, 121. (e) Almena, J.; Foubelo, F.; Yus, M. *Tetrahedron* **1996**, *52*, 8545.

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***N*-(But-2*E*-enyl)-4-methoxyaniline (3e):**[16b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (dq, J = 1.2, 6.4 Hz, 3H, CH_3), 3.22 (bs, 1H, NH), 3.62 (dquin, J = 1.2, 5.6 Hz, 2H, CH_2), 3.72 (s, 3H, OCH_3), 5.58 (dtq, J = 1.6, 6.0, 15.2 Hz, 1H, vinyl H), 5.69 (dtq, J = 1.2, 6.4, 15.2 Hz, 1H, vinyl H), 6.57 (d, J = 8.8 Hz, 2H, ArH), 6.76 (d, J = 8.8 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.76 (CH_3), 47.00 (CH_2), 55.77 (CH_3), 114.31 (CH), 114.86 (CH), 127.71 (CH), 128.42 (CH), 142.52 (C), 152.08 (C); EI-MS *m*/*z* 177 (M^+), 162, 136, 122, 108, 95, 77; EI-HRMS calcd for $C_{11}H_{15}NO$ 177.1154, found 177.1155.

***N*-(2-But-3-enyl)-4-methoxyaniline (4e):**[18] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (d, J = 6.8 Hz, 3H, CH_3), 3.18 (bs, 1H, NH), 3.71 (s, 3H, OCH_3), 3.88 (dq, J = 6.0, 6.4 Hz, 1H, CH), 5.06 (dt, J = 1.2, 10.4 Hz, 1H, vinyl H), 5.18 (dt, J = 1.2, 17.2 Hz, 1H, vinyl H), 5.80 (ddd, J = 5.6, 10.4, 17.2 Hz, 1H, vinyl H), 6.56 (d, J = 8.8 Hz, 2H, ArH), 6.75 (d, J = 8.8 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.64 (CH_3), 52.04 (CH), 55.73 (CH_3), 114.02 (CH_2), 114.78 (CH), 114.91 (CH), 141.62 (C), 141.68 (C), 152.04 (C); EI-MS *m*/*z* 177 (M^+), 162, 147, 130, 122, 108, 95, 77; EI-HRMS calcd for $C_{11}H_{15}NO$ 177.1154, found 177.1154.

Ethyl 4-[(but-2*E*-enyl)amino]benzoate (3f): IR (KBr) ν 3385, 1701, 1616 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (t, J = 7.2 Hz, 3H, CH_2CH_3), 1.69 (dq, J = 1.2, 6.0 Hz, 3H, CH_3), 3.80 (bs, 1H, NH), 3.87 (dquin, J = 1.2, 6.0 Hz, 2H, CH_2), 4.31 (q, J = 7.1 Hz, 2H, CH_2CH_3), 5.44 (dtq, J = 1.2, 6.0, 15.2 Hz, 1H, vinyl H), 5.58 (dtq, J = 1.2, 6.0, 15.2 Hz, 1H, vinyl H), 6.64 (d, J = 8.8 Hz, 2H, ArH), 7.86 (d, J = 9.2 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.33 (CH_3), 17.59 (CH_3), 45.17 (CH_2), 60.02 (CH_2), 111.90 (CH), 118.41 (C), 126.94 (CH), 128.33 (CH), 131.31 (CH), 151.78 (C), 166.80 (C); EI-MS *m*/*z* 219 (M^+), 204, 174, 165, 137, 120; EI-HRMS calcd for $C_{13}H_{17}NO_2$ 219.1259, found 219.1259.

Ethyl 4-[(2-but-3-enyl)amino]benzoate (4f): IR (KBr) ν 3386, 1715, 1616 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (d, J = 6.4 Hz, 3H, CH_3), 1.35 (t, J = 7.2 Hz, 3H, CH_2CH_3), 4.03 (dq, J = 5.6, 6.8 Hz, 1H, CH), 4.24 (bs, 1H, NH), 4.30 (q, J = 7.2 Hz, 2H, CH_2CH_3), 5.09 (dt, J = 1.2, 10.4 Hz, 1H, vinyl H), 5.18 (dt, J = 1.2, 17.2 Hz, 1H, vinyl H), 5.79 (ddd, J = 5.6, 10.2, 17.2 Hz, 1H, vinyl H), 6.54 (d, J = 8.8 Hz, 2H, ArH), 7.85 (d, J = 8.8 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.33 (CH_3), 21.26 (CH_3), 50.52 (CH), 60.02 (CH_2), 111.43 (CH), 114.38 (CH_2), 118.41 (C), 131.26 (CH), 140.03 (CH), 151.04 (C), 166.77 (C); EI-MS *m*/*z* 219 (M^+), 204, 174, 164, 130; EI-HRMS calcd for $C_{13}H_{17}NO_2$ 219.1259, found 219.1258.

***N*-(But-2*E*-enyl)-4-cyanoaniline (3g):** IR (KBr) ν 3386 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 (dq, J = 1.2, 6.4 Hz, 3H, CH_3), 3.71 (dquin, J = 1.2, 6.0 Hz, 2H, CH_2), 4.28 (bs, 1H, NH), 5.52 (dtq, J = 1.6, 6.0, 15.2 Hz, 1H, vinyl H), 5.70 (dtq, J = 1.6, 6.0, 15.2 Hz, 1H, vinyl H), 6.55 (d, J = 8.8 Hz, 2H, ArH), 7.38 (d, J = 9.2 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.69 (CH_3), 45.03 (CH_2), 98.15 (CH), 112.25 (CH), 120.66 (C), 126.53 (CH), 128.73 (CH), 133.55 (CH), 151.42 (C), 166.80 (C); EI-MS *m*/*z* 172 (M^+), 157, 142, 131, 118, 102, 91, 90, 75; EI-HRMS calcd for $C_{11}H_{12}N_2$ 172.1000, found 172.1002.

***N*-(2-But-3-enyl)-4-cyanoaniline (4g):** IR (KBr) ν 3364 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (d, J = 6.4 Hz, 3H, CH_3), 3.99 (dq, J = 6.0, 6.4 Hz, 1H, CH), 4.45 (bs, 1H, NH), 5.11 (dt, J = 1.2, 10.4 Hz, 1H, vinyl H), 5.19 (dt, J = 1.2, 17.2 Hz, 1H, vinyl H), 5.78 (ddd, J = 5.6, 10.4, 17.2 Hz, 1H, vinyl H), 6.56 (d, J = 8.8 Hz, 2H, ArH), 7.37 (d, J = 8.8 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.31 (CH_3), 50.67 (CH), 98.14 (C), 112.76 (CH), 114.76 (CH_2), 120.64 (C), 133.50 (CH), 139.67 (CH), 150.72 (C); EI-MS *m*/*z* 172 (M^+), 157, 145, 142, 130, 118, 102, 91, 75; EI-HRMS calcd for $C_{11}H_{12}N_2$ 172.1000, found 172.1001.

***N*-(But-2*E*-enyl)-4-nitroaniline (3h):**[16d,19] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72 (dq, J = 1.2, 6.4 Hz, 3H, CH_3), 3.78 (dquin, J = 1.2, 6.0 Hz, 2H, CH_2), 4.70 (bs, 1H, NH), 5.54 (dtq, J = 1.6, 6.0, 15.2 Hz, 1H, vinyl H), 5.72 (dtq, J = 1.6, 6.4, 15.2 Hz, 1H, vinyl H), 6.53 (d, J = 9.2 Hz, 2H, ArH), 8.07 (d, J = 9.2 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.72 (CH_3), 45.29 (CH_2), 111.20 (CH), 116.07 (CH), 126.39 (CH), 129.35 (CH), 137.92 (C), 153.33 (C); EI-MS *m*/*z* 192 (M^+), 177, 164, 151, 138, 130, 105, 92, 76; EI-HRMS calcd for $C_{10}H_{12}N_2O_2$ 192.0899, found 192.0897.

***N*-(2-But-3-enyl)-4-nitroaniline (4h):** IR (KBr) ν 3369 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (d, J = 6.8 Hz, 3H, CH_3), 4.08 (dq, J = 6.0, 6.4 Hz, 1H, CH), 4.59 (bs, 1H, NH), 5.15 (dt, J = 1.2, 10.4 Hz, 1H, vinyl H), 5.21 (dt, J = 1.2, 17.2 Hz, 1H, vinyl H), 5.81 (ddd, J = 5.6, 10.4, 17.2 Hz, 1H, vinyl H), 6.53 (d, J = 8.8 Hz, 2H, ArH), 8.06 (d, J = 9.2 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.33 (CH_3), 50.96 (CH), 111.68 (CH), 115.13 (CH_2), 126.32 (C), 139.23 (CH), 139.25 (C), 152.63 (C); EI-MS *m*/*z* 192 (M^+), 177, 165, 138, 131, 130, 119, 92, 76; EI-HRMS calcd for $C_{10}H_{12}N_2O_2$ 192.0899, found 192.0898.

***N*-(But-2*E*-enyl)-2,4-dimethylaniline (3i):** IR (KBr) ν 3446 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (dq, J = 1.2, 6.0 Hz, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.13 (bs, 1H, NH), 3.69 (dquin, J = 1.2, 6.0 Hz, 2H, CH_2), 5.63 (dtq, J = 1.2, 6.0, 15.2 Hz, 1H, vinyl H), 5.71 (dtq, J = 1.2, 6.0, 15.2 Hz, 1H, vinyl H), 6.52 (d, J = 8.0 Hz, 1H, ArH), 6.87 (s, 1H, ArH), 6.91 (d, J = 8.0 Hz, 1H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.37 (CH_3), 17.73 (CH_3), 20.28 (CH_3), 46.22 (CH_2), 110.16 (CH), 122.07 (C), 126.01 (C), 127.23 (CH), 127.67 (CH), 128.32 (CH), 130.85 (CH), 143.79 (C); EI-MS *m*/*z* 175 (M^+), 160, 145, 134, 132, 121, 120, 106, 91, 77; EI−HRMS calcd for $C_{12}H_{17}N$ 175.1361, found 175.1360.

***N*-(2-But-3-enyl)-2,4-dimethylaniline (4i):** IR (KBr) ν 3420 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (d, J = 6.8 Hz, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 3.28 (bs, 1H, NH), 3.99 (dq, J = 5.6, 6.4 Hz, 1H, CH), 5.06 (dt, J = 1.2, 10.4 Hz, 1H, vinyl H), 5.19 (dt, J = 1.2, 17.2 Hz, 1H, vinyl H), 5.84 (ddd, J = 5.6, 10.4, 17.2 Hz, 1H, vinyl H), 6.52 (d, J = 8.0 Hz, 1H, ArH), 6.87 (s, 1H, ArH), 6.88 (d, J = 8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.23 (CH_3), 20.12 (CH_3), 21.55 (CH_3), 50.83 (CH), 110.97 (CH), 113.56 (CH_2), 121.54 (C), 125.52 (C), 127.03 (CH), 130.73 (CH), 141.39 (CH), 142.76 (C); EI-MS *m*/*z* 175 (M^+), 160, 145, 132, 120, 106, 91, 77; EI-HRMS calcd for $C_{12}H_{17}N$ 175.1361, found 175.1362.

***N*-(But-2*E*-enyl)-2-chloro-4-methylaniline (3j):** IR (KBr) ν 3426 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.71 (dq, J = 1.2, 6.0 Hz, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.59 (bs, 1H, NH), 3.72 (dquin, J = 1.2, 6.0 Hz, 2H, CH_2), 5.59 (dtq, J = 1.2, 6.0, 15.2 Hz, 1H, vinyl H), 5.73 (dtq, J = 1.2, 6.0, 15.2 Hz, 1H, vinyl H), 6.60 (d, J = 8.3 Hz, 1H, ArH), 6.91−6.96 (m, 1H, ArH), 7.09 (s, 1H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$)_δ 17.75 (CH_3), 20.10 (CH_3), 45.87 (CH_2), 111.59 (CH), 119.02 (C), 126.75 (C), 127.60 (CH), 128.05 (CH), 128.20 (CH), 129.49 (CH), 141.65 (C); EI-MS *m*/*z* 197 (M^+ + 2), 195 (M^+), 182, 180, 160, 154, 144, 141, 132, 113, 106, 91, 77; EI-HRMS calcd for $C_{12}H_{17}NO_2$ 195.0815, found 195.0814.

***N*-(2-But-3-enyl)-2-chloro-4-methylaniline (4j):** IR (KBr) ν 3416 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$)_δ 1.36 (d, J = 6.6 Hz, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.99 (dq, J = 5.8, 6.6 Hz, 1H, CH), 4.16 (bs, 1H, NH), 5.10 (dt, J = 1.4, 10.3 Hz, 1H, vinyl H), 5.20 (dt, J = 1.3, 17.2 Hz, 1H, vinyl H), 5.84 (ddd, J = 5.6, 10.3, 17.2 Hz, 1H, vinyl H), 6.58 (d, J = 8.3 Hz, 1H, ArH), 6.92 (dd, J = 2.0, 8.3 Hz, 1H, ArH), 7.09 (d, J = 1.8 Hz, 1H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.08 (CH_3), 21.68 (CH_3), 51.20 (CH), 112.48 (CH), 114.21 (CH_2), 122.21 (C), 126.67 (C), 128.09 (CH), 129.47 (CH), 140.84 (CH), 144.53 (C); EI-MS *m*/*z* 197 (M^+ + 2), 195 (M^+), 182, 180, 168, 145, 144, 130, 117, 106, 89, 77; EI-HRMS calcd for $C_{12}H_{17}NO_2$ 195.0815, found 195.0815.

***N*-(But-2*E*-enyl)-2-methoxy-4-nitroaniline (3k):** IR (KBr) ν 3416 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72 (dq, J = 1.2,

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6.4 Hz, 3H, CH_3), 3.80 (dquin, J = 1.2, 6.0 Hz, 2H, CH_2), 3.82 (bs, 1H, NH), 3.92 (s, 3H, OCH_3), 5.57 (dtq, J = 1.6, 6.0, 15.2 Hz, 1H, vinyl H), 5.73 (dtq, J = 1.2, 6.4, 15.2 Hz, 1H, vinyl H), 6.48 (d, J = 8.8 Hz, 1H, ArH), 7.60 (d, J = 2.4 Hz, 1H, ArH), 7.88 (dd, J = 2.4, 8.8 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.62 (CH_3), 44.78 (CH_2), 55.80 (CH_3), 104.56 (CH), 106.57 (CH), 119.79 (CH), 126.09 (CH), 129.02 (CH), 139.62 (C), 144.05 (C), 145.05 (C); EI-MS m/z 222 (M^+), 207, 181, 168, 160, 153, 121, 91, 78; EI-HRMS calcd for $C_{11}H_{14}N_2O_3$ 222.1004, found 222.1003.

***N*-(2-But-3-enyl)-2-methoxy-4-nitroaniline (4k):** IR (KBr) ν 3413 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (d, J = 6.8 Hz, 3H, CH_3), 3.93 (s, 3H, OCH_3), 3.97 (bs, 1H, NH), 4.09 (dq, J = 6.0, 6.8 Hz, 1H, CH), 5.14 (dt, J = 1.2, 10.4 Hz, 1H, vinyl H), 5.20 (dt, J = 1.2, 17.2 Hz, 1H, vinyl H), 5.81 (ddd, J = 5.6, 10.4, 17.2 Hz, 1H, vinyl H), 6.48 (d, J = 8.8 Hz, 1H, ArH), 7.61 (d, J = 2.4 Hz, 1H, ArH), 7.86 (dd, J = 2.4, 8.8 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.26 (CH_3), 50.53 (CH), 55.77 (CH_3), 104.61 (CH), 106.72 (CH), 107.56 (CH), 114.86 (CH_2), 119.63 (CH), 139.27 (C), 143.26 (C), 144.93 (C); EI-MS m/z 222 (M^+), 207, 195, 161, 160, 149, 122, 91, 78; EI-HRMS calcd for $C_{11}H_{14}N_2O_3$ 222.1004, found 222.1001.

***N*-(But-2*E*-enyl)-3,5-dimethoxyaniline (3l):** IR (KBr) ν 3412 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (dq, J = 1.2, 6.0 Hz, 3H, CH_3), 3.65 (dquin, J = 1.2, 6.0 Hz, 2H, CH_2), 3.73 (bs, 1H, NH), 3.75 (s, 6H, $OCH_3 \times 2$), 5.58 (dtq, J = 1.6, 6.0, 15.2 Hz, 1H, vinyl H), 5.71 (dtq, J = 1.2, 6.4, 15.2 Hz, 1H, vinyl H), 5.81 (d, J = 2.0 Hz, 2H, ArH), 5.88 (t, J = 2.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.70 (CH_3), 45.98 (CH_2), 55.09 (CH_3), 89.74 (CH), 91.77 (CH), 127.88 (CH), 127.95 (CH), 150.13 (C), 161.65 (C); EI-MS m/z 207 (M^+), 192, 178, 166, 153, 138, 124, 108, 79; EI-HRMS calcd for $C_{12}H_{17}NO_2$ 207.1259, found 207.1261.

***N*-(2-But-3-enyl)-3,5-dimethoxyaniline (4l):** IR (KBr) ν 3406 m^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (d, J = 6.8 Hz, 3H, CH_3), 3.63 (bs, 1H, NH), 3.74 (s, 6H, $OCH_3 \times 2$), 3.96 (dq, J = 5.6, 6.8 Hz, 1H, CH), 5.09 (dt, J = 1.2, 10.4 Hz, 1H, vinyl H), 5.22 (dt, J = 1.2, 17.2 Hz, 1H, vinyl H), 5.81 (d, J = 2.0 Hz, 2H, ArH), 5.83 (ddd, J = 5.6, 10.4, 17.2 Hz, 1H, vinyl H), 5.87 (t, J = 2.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.43 (CH_3), 51.03 (CH), 54.96 (CH_3), 89.57 (CH), 92.16 (CH), 113.97 (CH_2), 141.16 (CH), 149.24 (C), 161.52 (C); EI-MS m/z 207 (M^+), 192, 180, 178, 161, 137, 122, 107, 94, 79; EI-HRMS calcd for $C_{12}H_{17}NO_2$ 207.1259, found 207.1259.

***N*-(But-2*E*-enyl)-*N*-methylaniline (3m):**[16b,20] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.68 (dq, J = 1.2, 6.4 Hz, 3H, CH_3), 2.89 (s, 3H, CH_3), 3.84 (dquin, J = 1.2, 5.6 Hz, 2H, CH_2), 5.48 (dtq, J = 1.6, 5.6, 15.2 Hz, 1H, vinyl H), 5.60 (dtq, J = 1.2, 6.0, 15.2 Hz, 1H, vinyl H), 6.69 (t, J = 7.2 Hz, 1H, ArH), 6.73 (d, J = 8.8 Hz, 2H, ArH), 7.22 (dd, J = 7.2, 8.8 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.57 (CH_3), 37.61 (CH_3), 54.38 (CH_2), 112.49 (CH), 116.22 (CH), 126.45 (CH), 127.24 (CH), 128.98 (CH), 149.54 (C); EI-MS m/z 161 (M^+), 146, 131, 120, 107, 106, 91, 77; EI-HRMS calcd for $C_{11}H_{15}N$ 161.1204, found 161.1205.

***N*-(2-But-3-enyl)-*N*-methylaniline (4m):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (d, J = 6.8 Hz, 3H, CH_3), 4.45−4.51 (m, 1H, CH), 5.14 (dt, J = 1.6, 17.2 Hz, 1H, vinyl H), 5.16 (dt, J = 1.2, 10.8 Hz, 1H, vinyl H), 5.92 (ddd, J = 4.0, 10.8, 17.2 Hz, 1H, vinyl H), 6.71 (t, J = 7.2 Hz, 1H, ArH), 6.81 (d, J = 8.4 Hz, 2H, ArH), 7.20−7.25 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.35 (CH_3), 31.32 (CH_3), 55.03 (CH), 113.26 (CH), 114.84 (CH_2), 116.65 (CH), 129.03 (CH), 139.44 (CH), 149.91 (C); EI-MS m/z 161 (M^+), 146, 134, 131, 118, 106, 91, 77; EI-HRMS calcd for $C_{11}H_{15}N$ 161.1204, found 161.1206.

***N*-(But-2*E*-enyl)-*N*-ethylaniline (3n):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (t, J = 7.2 Hz, 3H, CH_3), 1.67 (dq, J = 1.2, 6.4 Hz, 3H, CH_3), 3.34 (q, J = 7.2 Hz, 2H, CH_2), 3.80 (dquin, J = 1.2, 6.4 Hz, 2H, CH_2), 5.47 (dtq, J = 1.6, 5.6, 15.2 Hz, 1H, vinyl H), 5.59 (dtq, J = 1.2, 6.0, 15.2 Hz, 1H, vinyl H), 6.64 (t, J = 7.2 Hz, 1H, ArH), 6.68 (d, J = 8.4 Hz, 2H, ArH), 7.19 (dd, J = 7.2, 8.8 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.18 (CH_3), 17.62 (CH_3), 44.36 (CH_2), 51.72 (CH_2), 112.09 (CH), 115.61 (CH), 126.78 (CH), 127.15 (CH), 129.09 (CH), 148.27 (C); EI-MS m/z 175 (M^+), 160, 146, 134, 121, 106, 91, 77; EI-HRMS calcd for $C_{12}H_{17}N$ 175.1361, found 175.1359.

***N*-(2-But-3-enyl)-*N*-ethylaniline (4n):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (t, J = 7.2 Hz, 3H, CH_3), 1.24 (d, J = 6.8 Hz, 3H, CH_3), 3.18 (q, J = 7.2 Hz, 2H, CH_2), 4.33−4.39 (m, 1H, CH), 5.08 (dt, J = 1.6, 17.2 Hz, 1H, vinyl H), 5.10 (dt, J = 1.6, 10.8 Hz, 1H, vinyl H), 5.88 (ddd, J = 4.4, 10.8, 17.2 Hz, 1H, vinyl H), 6.65 (t, J = 7.2 Hz, 1H, ArH), 6.73 (d, J = 8.4 Hz, 2H, ArH), 7.17 (dd, J = 7.2, 8.8 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.58 (CH_3), 17.49 (CH_3), 39.52 (CH_2), 54.86 (CH), 113.38 (CH), 114.58 (CH_2), 116.27 (CH), 129.00 (CH), 139.68 (CH), 148.13 (C); EI-MS m/z 175 (M^+), 160, 148, 132, 130, 120, 106, 91, 77; EI-HRMS calcd for $C_{12}H_{17}N$ 175.1361, found 175.1364.

***N*-(Hex-2*E*-enyl)-4-chloro-2-methylaniline (5):** IR (KBr) ν 3466 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, J = 7.2 Hz, 3H, CH_3), 1.45 (hex, J = 7.2 Hz, 2H, CH_2CH_3), 2.07 (q, J = 6.8 Hz, 2H, $CH_2CH_2CH_3$), 2.13 (s, 3H, CH_3), 3.48 (bs, 1H, NH), 3.73 (d, J = 5.6 Hz, 2H, CH_2), 5.61 (dt, J = 6.0, 15.2 Hz, 1H, vinyl H), 5.74 (dt, J = 6.8, 15.2 Hz, 1H, vinyl H), 6.54 (d, J = 8.4 Hz, 1H, ArH), 7.04 (d, J = 2.4 Hz, 1H, ArH), 7.08 (dd, J = 2.4, 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.66 (CH_3), 17.30 (CH_3), 22.35 (CH_2), 34.41 (CH_2), 46.10 (CH_2), 110.99 (CH), 121.35 (C), 123.60 (C), 126.60 (CH), 126.61 (CH), 129.65 (CH), 133.51 (CH), 144.73 (C); EI-MS m/z 225 ($M^+ + 2$), 223 (M^+), 194, 182, 180, 154, 143, 141, 125, 106, 89, 77; EI-HRMS calcd for $C_{13}H_{18}ClN$ 223.1228, found 223.1226.

***N*-(3-Hex-1-enyl)-4-chloro-2-methylaniline (6):** IR (KBr) ν 3456 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, J = 7.2 Hz, 3H, CH_3), 1.47 (hex, J = 7.2 Hz, 2H, CH_2CH_3), 1.62 (q, J = 7.2 Hz, 2H, $CH_2CH_2CH_3$), 2.13 (s, 3H, CH_3), 3.46 (bs, 1H, NH), 3.82 (q, J = 6.4 Hz, 1H, CH), 5.13 (dt, J = 1.2, 10.4 Hz, 1H, vinyl H), 5.17 (dt, J = 1.2, 17.2 Hz, 1H, vinyl H), 5.74 (ddd, J = 6.0, 10.4, 17.2 Hz, 1H, vinyl H), 6.50 (d, J = 9.6 Hz, 1H, ArH), 7.01−7.04 (m, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.95 (CH_3), 17.35 (CH_3), 19.10 (CH_2), 38.02 (CH_2), 55.69 (CH), 111.77 (CH), 115.02 (CH_2), 121.03 (C), 123.26 (C), 126.48 (CH), 129.64 (CH), 139.82 (CH), 143.97 (C); EI-MS m/z 225 ($M^+ + 2$), 223 (M^+), 196, 182, 180, 164, 145, 144, 130, 117, 89, 77; EI-HRMS calcd for $C_{13}H_{18}ClN$ 223.1228, found 223.1229.

***N*-Allyl-4-chloro-2-methylaniline (7):** IR (KBr) ν 3440 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.02 (s, 3H, CH_3), 3.53 (bs, 1H, NH), 3.69 (dt, J = 1.6, 5.2 Hz, 2H, CH_2), 5.13 (dq, J = 1.5, 10.2 Hz, 1H, vinyl H), 5.21 (dq, J = 1.5, 17.2 Hz, 1H, vinyl H), 5.89 (ddt, J = 5.2, 10.2, 17.2 Hz, 1H, vinyl H), 6.41 (d, J = 8.4 Hz, 1H, ArH), 6.94−7.02 (m, 2H, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.02 (CH_3), 46.21 (CH_2), 110.77 (CH), 116.09 (CH_2), 121.15 (C), 123.44 (C), 126.41 (CH), 129.45 (CH), 134.93 (CH), 144.35 (C); EI-MS m/z 183 ($M^+ + 2$), 181 (M^+), 156, 154, 140, 117, 104, 89, 77; EI-HRMS calcd for $C_{10}H_{12}ClN$ 181.0655, found 181.0658.

***N,N*-Diallyl-4-chloro-2-methylaniline (8)**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H, CH_3), 3.53 (dt, J = 1.6, 6.4 Hz, 4H, $CH_2 \times 2$), 5.09 (dq, J = 1.6, 10.4 Hz, 2H, vinyl H), 5.15 (dq, J = 1.6, 17.2 Hz, 2H, vinyl H), 5.75 (ddt, J = 6.0, 10.0, 17.2 Hz, 2H, vinyl H), 6.91 (d, J = 8.8 Hz, 1H, ArH), 7.06 (dd, J = 2.4, 8.4 Hz, 1H, ArH), 7.14 (d, J = 2.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.18 (CH_3), 55.71 (CH_2), 117.32 (CH_2), 123.28 (CH), 125.81 (CH), 128.14 (C), 130.76 (CH), 134.93 (CH), 135.86 (C), 148.42 (C); EI-MS m/z 223 ($M^+ + 2$), 221 (M^+), 194, 180, 152, 144, 117, 89; EI-HRMS calcd for $C_{13}H_{16}ClN$ 221.0971, found 221.0970.

***N*-(3-Phenylprop-2*E*-enyl)-4-chloro-2-methylaniline (9):** IR (KBr) ν 3446 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 3H, CH_3), 3.56 (bs, 1H, NH), 3.84 (dd, J = 1.2, 6.0 Hz, 2H,

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CH_2), 6.25 (dt, J = 6.0, 16.0 Hz, 1H, vinyl H), 6.49 (d, J = 8.4 Hz, 1H, ArH), 6.54 (d, J = 16.0 Hz, 1H, vinyl H), 6.99 (d, J = 2.4 Hz, 1H, ArH), 7.03 (dd, J = 2.4, 8.4 Hz, 1H, ArH), 7.19 (d, J = 7.2 Hz, 1H, ArH), 7.26 (d, J = 7.6 Hz, 2H, ArH), 7.32 (d, J = 7.2 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.26 (CH_3), 46.07 (CH_2), 110.98 (CH), 121.47 (C), 123.68 (C), 126.30 (CH), 126.50 (CH), 126.65 (CH), 127.58 (CH), 128.55 (CH), 129.68 (CH), 131.69 (CH), 136.64 (C), 144.47 (C); EI-MS m/z 259 ($M^+ + 2$), 257 (M^+), 242, 240, 205, 166, 152, 117, 115, 91, 77; EI-HRMS calcd for $C_{16}H_{16}ClN$ 257.0971, found 257.0970.

***N*-(2-Methylprop-2-enyl)-4-chloro-2-methylaniline (10):** IR (KBr) ν 3456 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 3.73 (s, 2H, CH_2), 3.77 (bs, 1H, NH), 4.92−4.97 (m, 2H, vinyl H), 6.49 (d, J = 8.4 Hz, 1H, ArH), 7.04−7.08 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.23 (CH_3), 20.34 (CH_3), 49.77 (CH_2), 110.91 (CH), 110.93 (CH_2), 121.24 (C), 123.33 (C), 126.55 (CH), 129.58 (CH), 142.23 (C), 144.56 (C); EI-MS m/z 197 (M^++2), 195 (M^+), 182, 180, 156, 154, 140, 125, 117, 99, 89, 77; EI-HRMS calcd for $C_{11}H_{14}ClN$ 195.0815, found 195.0813.

3-(4-Chloro-2-methylphenylamino)cyclohexene (11): IR (KBr) ν 3432 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58−1.73 (m, 3H), 1.85−1.91 (m, 1H), 2.00−2.05 (m, 2H), 2.06 (s, 3H, CH_3), 3.41 (bs, 1H, NH), 3.93−3.98 (m, 1H, CH), 5.73 (ddt, J = 2.4, 3.2, 10.4 Hz, 1H, vinyl H), 5.86 (ddt, J = 2.0, 3.6, 10.4 Hz, 1H, vinyl H), 6.54 (d, J = 8.4 Hz, 1H, ArH), 6.99 (d, J = 2.4 Hz, 1H, ArH), 7.03 (dd, J = 2.4, 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.32 (CH_3), 19.53 (CH_2), 25.11 (CH_2), 28.68 (CH_2), 47.76 (CH), 110.09 (CH), 120.89 (C), 123.55 (C), 126.55 (CH), 128.18 (CH), 129.85 (CH), 130.42 (CH), 143.59 (C); EI-MS m/z 223 (M^++2), 221 (M^+), 195, 193, 178, 165, 143, 141, 117, 106, 89, 71, 77; EI-HRMS calcd for $C_{13}H_{16}ClN$ 221.0971, found 221.0971.

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