Direct Platinum-Catalyzed Allylation of Anilines Using Allylic Alcohols

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A simple and efficient route for the preparation of *N*-allylanilines by the direct use of allylic alcohols has been developed. The direct activation of C−O bonds in allylic alcohols by platinum complexes has been accelerated by carrying out the reactions in the presence of titanium reagents. The platinum-catalyzed allylation of anilines using allylic alcohols directly gave allylic anilines in good yields. Anilines bearing an electron-withdrawing group gave lower chemical yields.

Introduction

A principal goal of organometallic chemistry is the catalytic synthesis of organic compounds by using the distinct reaction chemistry of organic ligands covalently bound to transition metals. Most organometallic chemistry has focused on complexes with covalent metal−carbon or metal−hydrogen bonds. The platinum group 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. Moreover, the construction of C−N bonds in amines is particularly rare.[2] In large part, routes to the necessary reactive intermediates for such catalysis and the fundamental reactions required of such intermediates are poorly developed. Considerable effort has been expended toward the development of methodologies for the synthesis of allylamines not only due to their utility as intermediates in organic synthesis[3] but also because of their physiological properties[4] and their presence in several natural products.[5] A number of synthetic methods for the preparation of allylamines from alkene derivatives have been developed, but these require severe reaction conditions or several sequential reactions.[6] 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.[7] The palladium-catalyzed allylation is an established, efficient, and highly stereo- and chemoselective method for the C−C, C−N, and C−O bond formation, which has been widely applied to organic chemistry.[8] Although halides,[9] esters,[10] carbon-

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ates,[11] carbamates,[12] phosphates,[13] and related derivatives[14] 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.[15] 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] In preliminary papers,[17] 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. However, platinum-catalyzed allylation has attracted little attraction.[18] In this paper, we wish to report a novel catalysis of platinum complex, which mediates *N*-allylation of anilines with allylic alcohols. This is, to our knowledge, the first example of platinum-catalyzed allylation of anilines by the direct use of allylic alcohols in the presence of titanium reagents.

Results and Discussion

The platinum-catalyzed allylation of 4-chloro-2-methylaniline with allyl alcohol was investigated under various conditions (Scheme 1). When a mixture of 4-chloro-2-methylaniline (**1a**, 1 mmol) and allyl alcohol (**2a**, 1.2 mmol) was heated in the presence of catalytic amounts of $Pt(acac)_2$ (0.01 mmol), PPh_3 (0.04 mmol), and $Ti(OPr^i)_4$ (0.25 mmol) in benzene (5 mL) at 50 °C for 3 h, *N*-allyl-4-chloro-2-methylaniline (**3a**) was formed in 47% yield (entry 1 in Table 1). The reaction should be accompanied by formation of water. Addition of molecular sieves (MS4A) for its removal was not necessary. The reaction, under reflux, increased the yields of products **3a** and *N*,*N*-diallyl-4-chloro-2-methylaniline (**4a**) to 81 and 16%, respectively (entry 2). It was confirmed that the yield was decreased in the absence of PPh_3 (entries 3 and 4). The absence of $Ti(OPr^i)_4$ gave only a 27% yield of **3a** (entry 5). The effect of addition of $Ti(OPr^i)_4$ to promote the platinum-catalyzed allyl−OH bond cleavage remarkably enhanced both the reaction rate and yield. Titanium reagents such as $Ti(OEt)_4$ (entry 6), $Ti(OBu^i)_4$ (entry 8), and $Ti[O(CH_2)_{17}CH_3]_4$ (entry 9) were also effective for the allylation. $Ti(OBu)_4$ (entry 7) and $TiCl_4$ (entry 10) did not so much promote the reaction. It was known that several factors, such as the solvent and nature of the nucleophile, can alter

Scheme 1

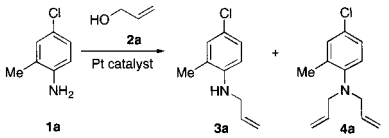

Table 1. Reaction of 4-Chloro-2-methylaniline (1a) with Allyl Alcohol (2a)[a]

entry	catalyst	titanium reagent	solvent	yield (%)[b] (3a:4a)
1	$Pt(acac)_2$-PPh_3	$Ti(OPr^i)_4$	benzene[c]	47 (100:0)
2	$Pt(acac)_2$-PPh_3	$Ti(OPr^i)_4$	benzene	97 (84:16)
3	$Pt(acac)_2$	$Ti(OPr^i)_4$	benzene[c]	17 (100:0)
4	$Pt(acac)_2$	$Ti(OPr^i)_4$	benzene	35 (100:0)
5	$Pt(acac)_2$-PPh_3	-	benzene	27 (100:0)
6	$Pt(acac)_2$-PPh_3	$Ti(OEt)_4$	benzene	92 (96:4)
7	$Pt(acac)_2$-PPh_3	$Ti(OBu)_4$	benzene	58 (82:18)
8	$Pt(acac)_2$-PPh_3	$Ti(OBu^i)_4$	benzene	97 (89:11)
9	$Pt(acac)_2$-PPh_3	$Ti[O(CH_2)_{17}CH_3]_4$	benzene	81 (98:2)
10	$Pt(acac)_2$-PPh_3	$TiCl_4$	benzene	53 (100:0)
11	$Pt(acac)_2$-PPh_3	$Ti(OPr^i)_4$	toluene[c]	31 (100:0)
12	$Pt(acac)_2$-PPh_3	$Ti(OPr^i)_4$	toluene	89 (91:9)
13	$Pt(acac)_2$-PPh_3	$Ti(OPr^i)_4$	dioxane[c]	18 (100:0)
14	$Pt(acac)_2$-PPh_3	$Ti(OPr^i)_4$	dioxane	59 (94:6)
15	$Pt(acac)_2$-PPh_3	$Ti(OPr^i)_4$	DMF	4 (100:0)
16	$Pt(acac)_2$-PPh_3	$Ti(OPr^i)_4$	CH_2Cl_2	1 (100:0)
17	$Pt(acac)_2$-PPh_3	$Ti(OPr^i)_4$	MeCN	1 (100:0)
18	*cis*-$PtCl_2(PPh_3)_2$-PPh_3	$Ti(OPr^i)_4$	benzene	52 (100:0)
19	*cis*-$PtCl_2(PPh_3)_2$	$Ti(OPr^i)_4$	benzene	33 (100:0)
20	*cis*-$PtCl_2(PhCN)_2$-PPh_3	$Ti(OPr^i)_4$	benzene	82 (98:2)
21	$Pt(CN)_2$-PPh_3	$Ti(OPr^i)_4$	benzene	4[d] (100:0)
22	$PtCl_2$-PPh_3	$Ti(OPr^i)_4$	benzene	87 (97:3)
23	$O[Si(CH_3)_2C{=}CH_2]_2Pt$-$PPh_3$	$Ti(OPr^i)_4$	benzene	95 (96:4)
24	$Pt(CH_2{=}CH_2)(PPh_3)_2$-PPh_3	$Ti(OPr^i)_4$	benzene	95 (95:5)
25	$Pt(acac)_2$-dppm	$Ti(OPr^i)_4$	benzene	29 (100:0)
26	$Pt(acac)_2$-$(2\text{-}MePh)_3P$	$Ti(OPr^i)_4$	benzene	15 (100:0)
27	$Pt(acac)_2$-$(3\text{-}MePh)_3P$	$Ti(OPr^i)_4$	benzene	86 (97:3)
28	$Pt(acac)_2$-$(4\text{-}MePh)_3P$	$Ti(OPr^i)_4$	benzene	62 (99:1)
29	$Pt(acac)_2$-$(4\text{-}ClPh)_3P$	$Ti(OPr^i)_4$	benzene	60 (99:1)
30	$Pt(acac)_2$-$(2,6\text{-}di\text{-}MeOPh)_3P$	$Ti(OPr^i)_4$	benzene	38 (100:0)
31	$Pt(acac)_2$-$(2,4,6\text{-}tri\text{-}MeOPh)_3P$	$Ti(OPr^i)_4$	benzene	28 (100:0)
32	$Pt(acac)_2$-$(2\text{-}furyl)_3P$	$Ti(OPr^i)_4$	benzene	97 (82:18)
33	$Pt(acac)_2$-$(2\text{-}pyridyl)Ph_2P$	$Ti(OPr^i)_4$	benzene	35 (100:0)
34	$Pt(acac)_2$-$(PhO)_3P$	$Ti(OPr^i)_4$	benzene	17 (100:0)

[a] Reaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), Pt catalyst (0.01 mmol), ligand (0.04 mmol), and titanium reagent (0.25 mmol) in a solvent (5 mL) were refluxed for 3 h. [b] Isolated yield. [c] Stir at 50 °C. [d] Reflux for 24 h.

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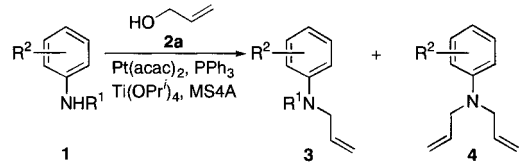
Table 2. Reaction of Anilines (1b−r) with Allyl Alcohol (2a)[a]



entry	1	R^1	R^2	products		yield (%)[b] (3:4)
1	**1b**	H	H	**3b**	**4b**	97 (83:17)
				3b	**4b**	91[c] (75:25)
2	**1c**	H	2-Br	**3c**	-	89
3	**1d**	H	2-I	**3d**	-	64
4	**1e**	H	4-Me	**3e**	**4e**	97 (65:35)
5	**1f**	H	4-Cl	**3f**	**4f**	99 (69:31)
6	**1g**	H	4-OMe	**3g**	**4g**	95 (68:32)
7	**1h**	H	4-CO_2Et	**3h**	**4h**	87 (83:17)
8	**1i**	H	4-CN	**3i**	**4i**	56 (99:1)
9	**1j**	H	4-NO_2	**3j**	-	34[d]
				3j	-	70[e]
10	**1k**	H	2,4-Me	**3k**	**4k**	99 (80:20)
11	**1l**	H	2-Cl, 4-Me	**3l**	-	98
12	**1m**	H	2-Cl, 4-Br	**3m**	**4m**	97 (99:1)
13	**1n**	H	2-OMe, 4-NO_2	**3n**	-	55
				3n	-	92[e]
14	**1o**	H	3,5-OMe	**3o**	**4o**	89 (72:28)
15	**1p**	Me	H	**3i**	-	97
16	**1q**	Et	H	**3j**	-	50
17	**1r**	Allyl	H	-	**4b**	98

[a] Reaction conditions: **1** (1 mmol), **2a** (1.2 mmol), $Pt(acac)_2$ (0.01 mmol), PPh_3 (0.04 mmol), and $Ti(OPr^i)_4$ (0.25 mmol) in benzene (5 mL) were refluxed for 3 h. [b] Isolated yield. [c] *cis*-$PtCl_2(PPh_3)_2$ was used. [d] Reflux for 6 h. [e] Reflux for 24 h.

the product pattern in metal-catalyzed allylation.[19] Six solvents were investigated, toluene, dioxane, DMF, CH_2Cl_2, and MeCN, with benzene giving the best results (entries 1, 2, and 11−17). A comparative study of different catalysts in benzene was reported. Among the platinum catalysts including $Pt(acac)_2$ (entries 1 and 2), *cis*-$PtCl_2(PPh_3)_2$ (entries 18 and 19), *cis*-$PtCl_2(PhCN)_2$ (entry 20), $Pt(CN)_2$ (entry 21), $PtCl_2$ (entry 22), $O[Si(CH_3)_2C{=}CH_2]_2Pt$ (entry 23), and $Pt(CH_2{=}CH_2)(PPh_3)_2$ (entry 24) were used. $Pt(acac)_2$, $O[Si(CH_3)_2C{=}CH_2]_2Pt$, and $Pt(CH_2{=}CH_2)(PPh_3)_2$ were found to be superior. The use of $O[Si(CH_3)_2C{=}CH_2]_2Pt$ as catalyst was cheaper than palladium reagents and could give good results. The bidentate ligand dppm (entry 25) decreased the yield of products. In the presence of various monodentate ligands including PPh_3, $(2\text{-MePh})_3P$, $(3\text{-MePh})_3P$, $(4\text{-MePh})_3P$, $(4\text{-ClPh})_3P$, $(2,6\text{-di-MeOPh})_3P$, $(2,4,6\text{-tri-MeOPh})_3P$, $(2\text{-furyl})_3P$, $(2\text{-pyridyl})Ph_2P$, and $(PhO)_3P$ (entries 1, 2, and 26−34) showed that PPh_3 (entry 1) and $(2\text{-furyl})_3P$ (entry 32) were the most effective ligands.

We also studied the influence of the substituent on aniline on the reactivity of the amination of allyl alcohol (**2a**) using $Pt(acac)_2$, PPh_3, and $Ti(OPr^i)_4$. The results collected in Table 2 showed that the nature of the substituent had a strong influence on the reaction rate and the product yield. The amination of allyl alcohol (**2a**)

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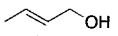
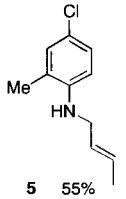
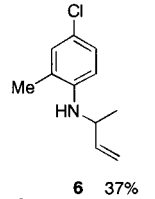
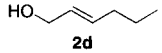
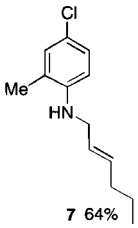
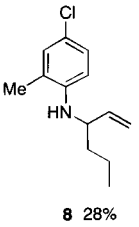
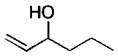
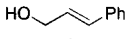
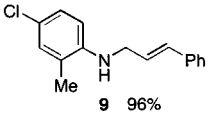
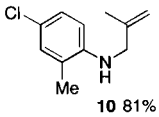
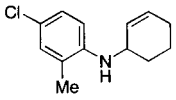
Table 3. Reaction of 4-Chloro-2-methylaniline (1a) with Allylic Alcohols (2b−h)[a]

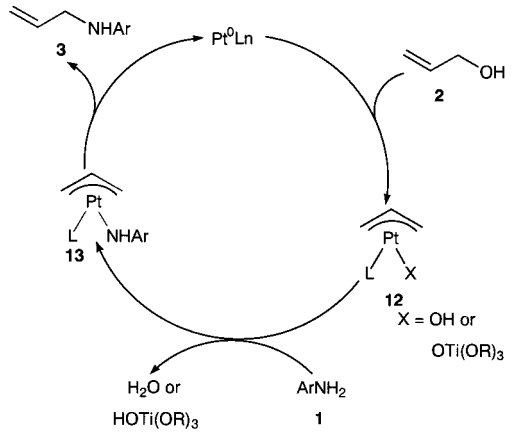
entry	2	yields[b]	
1	 **2b**	 **5** 55% (*E*/*Z*=83/17)[c]	 **6** 37%
2	 **2c**	**5** 51% (*E*/*Z*=83/17)[c]	**6** 39%
3	 **2d**	 **7** 64%	 **8** 28%
4	 **2e**	**7** 57%	**8** 30%
5	 **2f**	 **9** 96% (*E*/*Z*=98/2)[c]	
6	 **2g**	 **10** 81% (96%)[d]	
7	 **2h**	 **11** 71%	

[a] Reaction conditions: **1a** (1 mmol), **2** (1.2 mmol), $Pt(acac)_2$ (0.01 mmol), PPh_3 (0.04 mmol), and $Ti(OPr^i)_4$ (0.25 mmol) in benzene (5 mL) were refluxed for 3 h. [b] Isolated yield. [c] Determined by GC. [d] Reflux for 6 h.

worked well with anilines containing electron-donating groups, giving generally high yields of the corresponding allylic anilines. Conversely, anilines having electron-withdrawing groups, such as cyano or nitro groups (entries 8 and 9), gave lower chemical yields. These differences in reactivity could be related to the nucleophilicity of the corresponding aniline. 4-Nitroaniline (**1j**) gave 70% yield under reflux for 24 h; 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. Using $Pt(acac)_2$ as catalyst was more effective than *cis*-$PtCl_2(PPh_3)_2$ (entry 1). Anilines having the larger size of the electron-withdrawing substituents in the ortho position gave the lower yield (entries 2, 3, 11, and 12).

Results for amination of a number of allylic alcohols **2b−h** with 4-chloro-2-methylaniline (**1a**) using $Pt(acac)_2$, PPh_3, and $Ti(OPr^i)_4$ are summarized in Table 3. At 80 °C, all of the allylic alcohols examined underwent amination smoothly to give the corresponding *N*-allylanilines in overall yields ranging from 71 to 96%. Treatment of 4-chloro-2-methylaniline with crotyl alco-

Scheme 2



hol (**2b**) gave mixtures of stereo- and regioisomeric anilines **5** and **6** in yields of 55 and 37%, respectively (entry 1 in Table 3). 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 83:17 *E*/*Z* ratio of **5** 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 product *E* alkene arising from the more thermodynamically stable syn π-allyl complex. Since both regioisomeric alcohols **2b** and **2c** gave identical mixtures of the anilines **5** and **6** in similar ratios, the reaction is considered to proceed via π-allylplatinum intermediates (entry 2). The loss of the stereochemistry of the starting alcohol **2b** 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. We also noticed that the two regioisomeric **2d** and **2e** reacted with aniline to give identical mixtures of regio- and stereoisomeric anilines **7** and **8**, as expected from attack of the aniline on the two allylic termini of the π-allylplatinum species, in a similar ratio (entries 3 and 4). With the unsymmetrical allylic alcohols **2**, the major products were obtained from approach of **1** at the less sterically hindered primary site. When the allylic alcohol is unsubstituted (**2a**), the reaction is relatively fast, and high yields of the desired product are obtained. If the alcohol (and thus the π-allyl) is substituted, high chemical yields are still obtained, but the reaction proceeds more slowly, and mixtures of isomers are afforded.

A possible mechanism for the formation of *N*-allylanilines from **1** and **2** is illustrated in Scheme 2, in which the substituent on allylic alcohol is omitted. Alcohol **2** or an allyl titanate, formed by alcohol exchange reaction between **2** and isopropoxide in Ti(OPr^i)$_4$,[20] reacts with Pt(0) species generated in situ[13] to afford a π-allylplatinum intermediate (**12**). Subsequently, the reaction of **12** with aniline **1** followed by reductive elimination gives *N*-allylaniline. It would be possible that **13** is formed by ligand exchange between **12** and Ti(HNAr)$_n$(OR)$_{4-n}$ species generated in the reaction medium.

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Conclusions

We have shown that platinum(0)-catalyzed allylation of anilines using allylic alcohols directly is a simple and efficient route for the C−N bond formation. The yield was decreased in the absence of PPh_3. The effect of addition of Ti(OPr^i)$_4$ to promote the platinum-catalyzed allyl−OH bond cleavage remarkably enhanced both the reaction rate and yield. The amination of allylic alcohol worked well with anilines containing electron-donating groups, giving generally high yields of the corresponding allylic anilines. Anilines having electron-withdrawing groups gave lower chemical yields.

Experimental Section

General Considerations. General Method. 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 a Shimadzu IR-27G and Perkin-Elmer System 2000 FT-IR spectrophotometer. Proton and carbon-13 NMR were measured with a Varian Gemini-200 and Unity-400 spectrometer. HETCOR NMR 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**, **1l**, and **1m**, Pt(acac)$_2$ (acac = acetylacetonate), *cis*-$PtCl_2(PPh_3)_2$, *cis*-$PtCl_2(PhCN)_2$, $Pt(CN)_2$, $O[Si(CH_3)_2C{=}CH_2]_2Pt$, $Pt(CH_2{=}CH_2)(PPh_3)_2$, (3-MePh)$_3$P, (4-MePh)$_3$P, (2,6-di-MeOPh)$_3$P, (2,4,6-tri-MeOPh)$_3$P, and (2-pyridyl)Ph_2P were purchased from Aldrich. PPh_3 and $(PhO)_3P$ were purchased from Riedel-de Haen. 3,5-Dimethoxyaniline (**1o**), 1,1-bis(diphenylphosphino)methane (dppm), (2-MePh)$_3$P, (4-ClPh)$_3$P, and (2-furyl)$_3$P were purchased from Lancaster. 4-Methylaniline and $PtCl_2$ were purchased from Acros Organics. Anilines **1b,c**, **1e**−**k**, **1n**, and **1p**−**r**, allylic alcohols **2a**−**h**, and titanium reagents were purchased from TCI.

General Procedure for the Platinum-Catalyzed Allylation of Anilines. Reaction with 4-Chloro-2-methylaniline (1a). A mixture of 4-chloro-2-methylaniline (**1a**) (142 mg, 1 mmol), allyl alcohol (**2a**) (70 mg, 1.2 mmol), Pt(acac)$_2$ (3.9 mg, 0.01 mmol), PPh_3 (10.5 mg, 0.04 mmol), and Ti(OPr^i)$_4$ (0.075 mL, 0.25 mmol) 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 **3a** and **4a** in 81 and 16% yields, respectively.

Products **3a**,[17b] **4a**,[17b] **3b**,[17b,21] **4b**,[17b] **3e**,[17b,22] **4e**,[17b,23] **3f**,[17b,21] **4f**,[17b] **3g**,[17b,21] **4g**,[17b] **3h**,[17b] **4h**,[17b] **3i**,[17b,22] **4i**,[17b] **3j**,[17b] **3k**,[17b] **4k**,[17b] **3m**,[17b] **4m**,[17b] **3n**,[17b] **3o**,[17b] **4o**,[17b] **3p**,[17b,24] **3q**,[17b,25] **3r**,[17b] **5**,[17a] **6**,[17a] **7**,[17a] **8**,[17a] **9**,[17a] **10**,[17a] and **11**[17a] are known.

***N*-Allyl-2-bromoaniline (3c).**[26] IR (KBr): ν 3406 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.76 (dt, J = 1.6, 5.2 Hz, 2H, CH_2),

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4.40 (bs, 1H, NH), 5.15 (dq, J = 1.6, 10.4 Hz, 1H, vinyl H), 5.25 (dq, J = 2.0, 17.2 Hz, 1H, vinyl H), 5.90 (ddt, J = 5.2, 10.4, 17.2 Hz, 1H, vinyl H), 6.26 (ddd, J = 1.2, 7.2, 8.0 Hz, 1H, ArH), 6.57 (dd, J = 1.2, 8.0 Hz, 1H, ArH), 7.12 (ddd, J = 1.2, 7.2, 8.0 Hz, 1H, ArH), 7.39 (dd, J = 1.2, 8.0 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.03 (CH_2), 109.59 (C), 111.46 (CH), 116.21 (CH_2), 117.71 (CH), 128.28 (CH), 132.21 (CH), 134.53 (CH), 144.59 (C). EI-MS m/z 213 ($M^+ + 2$), 211 (M^+), 186, 184, 155, 132, 130, 117, 105, 91, 77. EI-HRMS Calcd for $C_9H_{10}BrN$: 210.9997. Found: 210.9995.

***N*-Allyl-2-iodoaniline (3d).**[27] IR (KBr): ν 3390 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80 (dt, J = 1.6, 5.2 Hz, 2H, CH_2), 4.31 (bs, 1H, NH), 5.18 (dq, J = 1.6, 10.4 Hz, 1H, vinyl H), 5.27 (dq, J = 2.0, 17.2 Hz, 1H, vinyl H), 5.93 (ddt, J = 5.2, 10.4, 17.2 Hz, 1H, vinyl H), 6.43 (ddd, J = 1.6, 7.2, 8.0 Hz, 1H, ArH), 6.54 (dd, J = 1.6, 8.0 Hz, 1H, ArH), 7.17 (ddd, J = 1.2, 7.2, 8.0 Hz, 1H, ArH), 7.64 (dd, J = 1.6, 8.0 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.47 (CH_2), 85.36 (C), 110.85 (CH), 116.36 (CH_2), 118.68 (CH), 129.28 (CH), 134.53 (CH), 138.92 (CH), 146.92 (C). EI-MS m/z 259 (M^+), 232, 203, 132, 130, 117, 105, 91, 77. EI-HRMS Calcd for $C_9H_{10}IN$: 258.9858. Found: 258.9859.

***N*-Allyl-2-chloro-4-methylaniline (3l).** IR (KBr): ν 3414 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.17 (s, 3H, CH_3), 3.73 (dt, J = 2.0, 5.2 Hz, 2H, CH_2), 4.23 (bs, 1H, NH), 5.13 (dq, J = 1.6, 10.4 Hz, 1H, vinyl H), 5.23 (dq, J = 1.6, 17.2 Hz, 1H, vinyl H), 5.89 (ddt, J = 5.2, 10.4, 17.2 Hz, 1H, vinyl H), 6.50 (d, J = 8.0 Hz, 1H, ArH), 6.87 (dd, J = 2.0, 8.0 Hz, 1H, ArH), 7.04 (d, J = 2.0 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.94 (CH_3), 46.14 (CH_2), 111.46 (CH), 116.01 (CH_2), 118.85 (C), 126.64 (C), 128.12 (CH), 129.38 (CH), 134.88 (CH), 141.39 (C). EI-MS m/z 183 ($M^+ + 2$), 181 (M^+), 156, 154, 146, 144, 140, 131, 113, 91, 77. EI-HRMS Calcd for $C_{10}H_{12}ClN$: 181.0658. Found: 181.0657.

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