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Platinum-catalyzed allylation of aminonaphthalenes with allylic acetates

Shyh-Chyun Yang,* Wei-Hao Feng and Kim-Hong Gan

Graduate Institute of Pharmaceutical Sciences, Kaohsiung Medical University, Kaohsiung 807, Taiwan, ROC

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Abstract—The activation of C–O bonds in allylic acetates has been accelerated by carrying out the reactions in the presence of platinum complexes associated with ligands. Platinum-catalyzed allylation of aminonaphthalenes with allylic acetates leads to *N*-allylic aminonaphthalenes 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. Aromatic amines have not been used commonly in allylic amination, presumably because they are less nucleophilic than the more commonly used benzylamine or stabilized anionic nitrogen nucleophiles.[10] 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.[11] The reactions should be promoted in the presence of titanium reagent. However, platinum-catalyzed allylation has attracted little attraction.[12] In this paper, we wish to report a novel catalysis of platinum complex, which mediates N-allylation of aminonaphthalenes with allylic acetates.

2. Results and discussion

To evaluate the scope and limitations of the N-allylation of aminonaphthalenes with allylic acetates, we treated a mixture of 1-aminonaphthalene (**1a**, 2 mmol) and allyl acetate (**2a**, 1.6 mmol) in the presence of $Pt(acac)_2$ (1 mol%) and PPh_3 (4 mol%) in benzene under nitrogen, at 50 °C for 3 h, *N*-allyl-1-naphthylamine (**3a**) was formed in only 9% yield (entry 1 in Table 1). The reaction, under reflux, increased the yields of products **3a** and *N*,*N*-diallyl-1-naphthylamine (**4a**) to 75 and 6%, respectively (entry 2). The reaction gave 91% yield under reflux for 6 h (entry 3). It was confirmed that the yield was only 3% in the absence of PPh_3 (entry 4). The reaction did not occur in the absence of the platinum species (entry 5). Among the platinum catalysts including $Pt(acac)_2$ (entry 2), *cis*-$PtCl_2(PhCN)_2$ (entry 6), *cis*-$PtCl_2(PPh_3)_2$ (entry 7), $PtCl_2$ (entry 8), PtI_2 (entry 9), $O[Si(CH_3)_2C{=}CH_2]_2Pt$ (entry 10), $Pt(CH_2{=}CH_2)(PPh_3)_2$ (entries 11 and 12), and $Pt(PPh_3)_4$ (entries 13 and 14) 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

Keywords: Platinum-catalyzed; Allylation; Aminonaphthalenes.
* Corresponding author. Tel.: +886 7 3121101; fax: +886 7 3210683; e-mail: scyang@kmu.edu.tw

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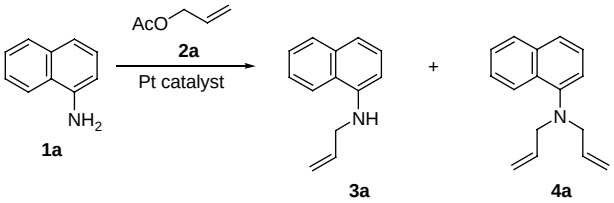
Table 1. Reaction of 1-aminonaphthalene (**1a**) with allyl acetate (**2a**)[a]



Entry	Platinum catalyst	Ligand	Solvent	Yield (%) (**3a**:**4a**)[b]
1	$Pt(acac)_2$	PPh_3	Benzene[c]	9 (100:0)
2	$Pt(acac)_2$	PPh_3	Benzene	81 (93:7)
3	$Pt(acac)_2$	PPh_3	Benzene[d]	91 (93:7)
4	$Pt(acac)_2$	—	Benzene	3 (100:0)
5	—	PPh_3	Benzene	0
6	*cis*-$PtCl_2(PhCN)_2$	PPh_3	Benzene	57 (99:1)
7	*cis*-$PtCl_2(PPh_3)_2$	PPh_3	Benzene	2 (100:0)
8	$PtCl_2$	PPh_3	Benzene	8 (100:0)
9	PtI_2	PPh_3	Benzene	1 (100:0)
10	$O[Si(CH_3)_2C{=}CH_2]_2Pt$	PPh_3	Benzene	88 (86:14)
11	$Pt(CH_2{=}CH_2)(PPh_3)_2$	—	Benzene	66 (99:1)
12	$Pt(CH_2{=}CH_2)(PPh_3)_2$	PPh_3	Benzene	90 (96:4)
13	$Pt(PPh_3)_4$	—	Benzene	5 (100:0)
14	$Pt(PPh_3)_4$	PPh_3	Benzene	68 (87:13)
15	$Pt(acac)_2$	Bu_3P	Benzene	32 (100:0)
16	$Pt(acac)_2$	$(2\text{-}MeC_6H_4)_3P$	Benzene	3 (100:0)
17	$Pt(acac)_2$	$(3\text{-}MeC_6H_4)_3P$	Benzene	82 (97:3)
18	$Pt(acac)_2$	$(4\text{-}MeC_6H_4)_3P$	Benzene	71 (96:4)
19	$Pt(acac)_2$	$(4\text{-}FC_6H_4)_3P$	Benzene	96 (96:4)
20	$Pt(acac)_2$	$(4\text{-}ClC_6H_4)_3P$	Benzene	99 (92:8)
21	$Pt(acac)_2$	$(4\text{-}MeOC_6H_4)_3P$	Benzene	90 (96:4)
22	$Pt(acac)_2$	$[2,6\text{-}(MeO)_2C_6H_3]_3P$	Benzene	1 (100:0)
23	$Pt(acac)_2$	$(2\text{-Furyl})_3P$	Benzene	95 (96:4)
24	$Pt(acac)_2$	$(2\text{-Pyridyl})Ph_2P$	Benzene	91 (97:3)
25	$Pt(acac)_2$	Dppp[e]	Benzene	25 (99:1)
26	$Pt(acac)_2$	Dppb[f]	Benzene	73 (98:2)
27	$Pt(acac)_2$	Dpph[g]	Benzene	69 (98:2)
28	$Pt(acac)_2$	$(4\text{-}ClC_6H_4)_3P$	Benzene[c]	87 (78:22)
29	$Pt(acac)_2$	$(4\text{-}ClC_6H_4)_3P$	Benzene	99 (92:8)
30	$Pt(acac)_2$	$(4\text{-}ClC_6H_4)_3P$	Toluene[c]	82 (87:13)
31	$Pt(acac)_2$	$(4\text{-}ClC_6H_4)_3P$	Toluene	98 (97:3)
32	$Pt(acac)_2$	$(4\text{-}ClC_6H_4)_3P$	CH_2Cl_2[c]	5 (100:0)
33	$Pt(acac)_2$	$(4\text{-}ClC_6H_4)_3P$	THF[c]	85 (81:19)
34	$Pt(acac)_2$	$(4\text{-}ClC_6H_4)_3P$	THF	89 (90:10)
35	$Pt(acac)_2$	$(4\text{-}ClC_6H_4)_3P$	Dioxane[c]	39 (93:7)
36	$Pt(acac)_2$	$(4\text{-}ClC_6H_4)_3P$	Dioxane	85 (95:5)
37	$Pt(acac)_2$	$(4\text{-}ClC_6H_4)_3P$	MeCN[c]	52 (83:17)
38	$Pt(acac)_2$	$(4\text{-}ClC_6H_4)_3P$	MeCN	76 (89:11)
39	$Pt(acac)_2$	$(4\text{-}ClC_6H_4)_3P$	DMF[c]	58 (85:15)
40	$Pt(acac)_2$	$(4\text{-}ClC_6H_4)_3P$	DMF	66 (94:6)
41	$Pt(acac)_2$	$(4\text{-}ClC_6H_4)_3P$	HMPA[c]	38 (93:7)
42	$Pt(acac)_2$	$(4\text{-}ClC_6H_4)_3P$	HMPA	4 (100:0)

[a] Reaction conditions: **1a** (2 mmol), **2a** (1.6 mmol), Pt catalyst (0.02 mmol), ligand (0.08 mmol), and MS 4 Å in a solvent (5 mL) were refluxed for 3 h.
[b] Isolated yield.
[c] Stirred at 50 °C.
[d] Reflux for 6 h.
[e] 1,3-Bis(diphenylphosphino)propane.
[f] 1,4-Bis(diphenylphosphino)butane.
[g] 1,6-Bis(diphenylphosphino)hexane.

superior. The use of $O[Si(CH_3)_2C{=}CH_2]_2Pt$ as catalyst was cheaper than palladium reagents and could give good results. However, using $Pt(CH_2{=}CH_2)(PPh_3)_2$ or $Pt(PPh_3)_4$ with extra PPh_3 as catalyst increased the yield of products (entries 12 and 14). 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, $(2\text{-}MeC_6H_4)_3P$, $(3\text{-}MeC_6H_4)_3P$, $(4\text{-}MeC_6H_4)_3P$, $(4\text{-}FC_6H_4)_3P$, $(4\text{-}ClC_6H_4)_3P$, $(4\text{-}MeOC_6H_4)_3P$, $[2,6\text{-}(MeO)_2C_6H_3]_3P$, $(2\text{-furyl})_3P$, and $(2\text{-pyridyl})Ph_2P$ (entries 2, and 15–24) showed that $(4\text{-}FC_6H_4)_3P$ (entry 19), $(4\text{-}ClC_6H_4)_3P$ (entry 20), $(4\text{-}MeOC_6H_4)_3P$ (entry 21), $(2\text{-furyl})_3P$ (entry 23), and $(2\text{-pyridyl})Ph_2P$ (entry 24) were the most effective ligands. The bidentate ligand dppp (entry 25) decreased the yield of products. Dppb (entry 26) and dpph (entry 27) gave moderate yields of products. It was known that several factors, such as the solvent and nature of the nucleophile, can alter the product pattern in metal-catalyzed allylation.[13] At 50 °C, in the presence of $Pt(acac)_2$ and $(4\text{-}ClC_6H_4)_3P$, eight solvents were investigated, CH_2Cl_2, dioxane, and

Table 2. Reaction of aromatic amines (**1b–k**) with allyl acetate (**2a**)[a]

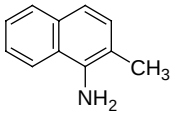
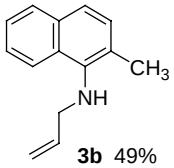
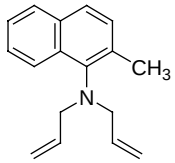
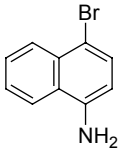
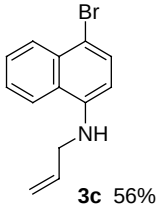
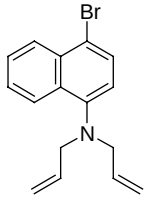
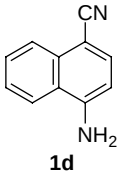
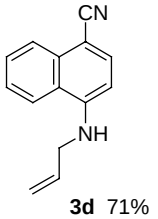
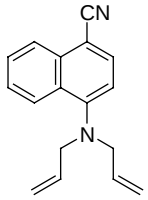
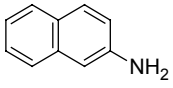
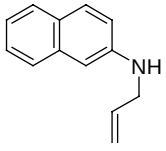
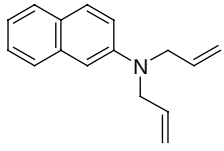
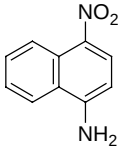
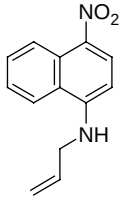
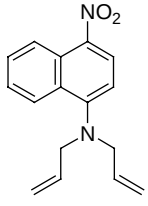
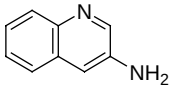
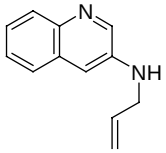
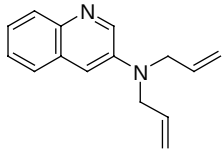
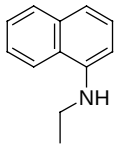
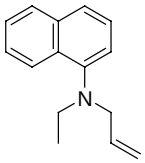
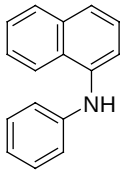
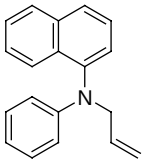
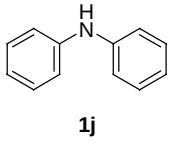
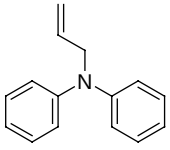
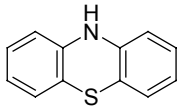
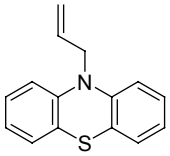
Entry	1	Yields[b]	
1	 **1b**	 **3b** 49%	 **4b** 19%
2[c]	**1b**	**3b** 48%	**4b** 18%
3[d]	**1b**	**3b** 41%	**4b** 42%
4	 **1c**	 **3c** 56%	 **4c** 7%
5[c]	**1c**	**3c** 72%	**4c** 14%
6	 **1d**	 **3d** 71%	 **4d** 5%
7	 **1e**	 **3e** 70%	 **4e** 18%
8	 **1f**	 **3f** 18%	
9[e]	**1f**	**3f** 51%	 **4f** 2%
10	 **1g**	 **3g** 81%	 **4g** 14%

Table 2 (*continued*)

Entry	1	Yields[b]
11	 **1h**	 **3h** 42%
12	 **1i**	 **3i** 30%
13	 **1j**	 **3j** 53%
14	 **1k**	 **3k** 32%

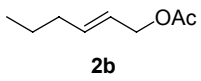
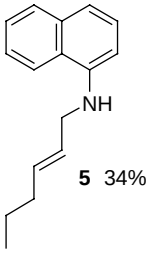
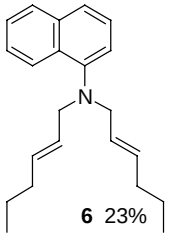
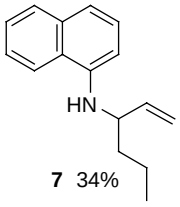
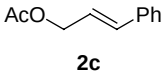
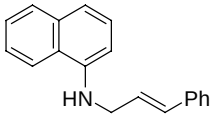
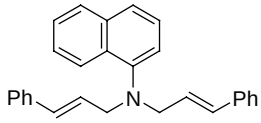
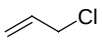
[a] Reaction conditions: **1** (2 mmol), **2a** (1.6 mmol), $Pt(acac)_2$ (0.02 mmol), $(4\text{-}ClC_6H_4)_3P$ (0.08 mmol), and MS 4 Å in benzene (5 mL) were refluxed for 3 h.
[b] Isolated yield.
[c] Compound **2a** (4.0 mmol) was used.
[d] Compound **2a** (8.0 mmol) was used.
[e] Reflux for 24 h.

HMPA gave worst results. The reaction, under reflux, benzene, toluene, and THF gave the best results (entries 28–42).

The results collected in Table 2 show that the amination of allyl acetate (**2a**) with aminonaphthalenes using $Pt(acac)_2$ and $(4\text{-}ClC_6H_4)_3P$, giving general good yields of the corresponding allylic aminonaphthalenes (entries 1–7). As expected, increasing the relative amount of the allyl alcohol favored the formation of the diallylated compound (entries 1–3). Using aminonaphthalenes having strong electron-withdrawing groups, such as the nitro group, gave only 18% lower chemical yields (entry 8). These differences in reactivity could be related to the nucleophilicity of the corresponding aminonaphthalene. 1-Amino-4-nitronaphthalene (**1f**) gave 53% yield under reflux for 24 h (entry 9); the lower yield observed may arise from the nature of the nitro group. The more acidic 1-amino-4-nitronaphthalene (**1f**) is probably less reactive in attack on the π-allyl complex. 3-Aminoquinoline (**1g**) reacted to give the *N*-allylated products in excellent yields (entry 10). The sterically more demanding secondary aminonaphthalenes (**1h** and **1i**) gave lower yields (entries 11 and 12). Secondary aromatic amines, such as diphenylamine (**1j**) and phenothiazine (**1k**), also reacted to give the *N*-allylamine in moderate yield (entries 13 and 14).

The results for amination of a number of derivatives of allylic alcohols **2b–e** with 1-aminonaphthalene (**1a**) using $Pt(acac)_2$ and $(4\text{-}ClC_6H_4)_3P$ are summarized in Table 3. Amination of *trans*-2-hexen-1-yl acetate (**2b**) gave mixtures of monoallylated, diallylated and regioisomeric aminonaphthalenes **5**, **6**, and **7** in yields of 34, 23, and 38%, respectively (entry 1 in Table 1). 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 reaction is considered to proceed via π-allylplatinum intermediates. The loss of the stereochemistry of the starting acetate **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. Reaction of aromatic allylic acetate **2c**, the corresponding monoallylated and diallylated products were formed in overall 97% yields (entry 2). Increasing the amount of **2c**, favored the formation of the diallylated compound **9** and gave the products in quantitatively yields (entry 3). With the allyl chloride (**2d**), produces only **3a** in 9% yield (entry 4). Allyl carbonate (**2e**) gave products in moderate yields (entry 5).

Table 3. Reaction of 1-aminonaphthalene (**1a**) with allylic compounds (**2b–e**)[a]

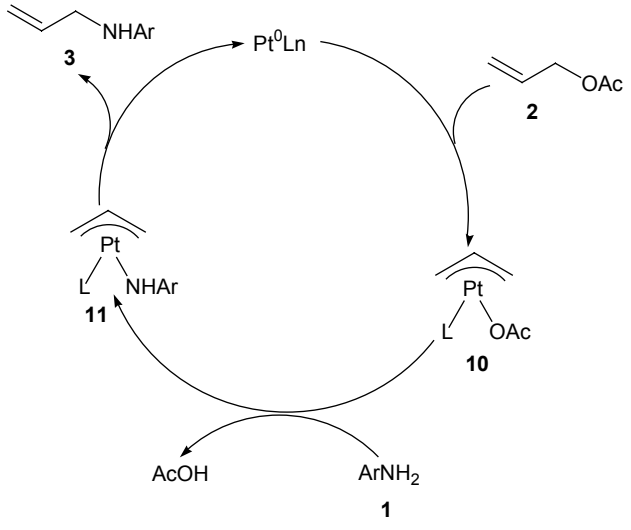
Entry	2	Yields[b]		
1	 **2b**	 **5** 34%	 **6** 23%	 **7** 34%
2	 **2c**	 **8** 89%		 **9** 8%
3[c]	**2c**	**8** 46% **3a** 9%		**9** 54%
4	 **2d**			
5	 **2e**	**3a** 57%		**4a** 4%

[a] Reaction conditions: **1a** (2 mmol), **2** (1.6 mmol), $Pt(acac)_2$ (0.02 mmol), $(4\text{-}ClC_6H_4)_3P$ (0.08 mmol), and MS 4 Å in benzene (5 mL) were refluxed for 3 h.
[b] Isolated yield.
[c] Compound **2a** (4.0 mmol) was used.

A possible mechanism for the formation of *N*-allylanilines from **1** and **2** is illustrated in Scheme 1, in which the substituent on allylic acetate is omitted. Acetate **2** reacts with Pt(0) species generated in situ to afford a π-allylplatinum intermediate (**10**). Subsequently, the reaction of **10** with aminonaphthalene **1** followed by reductive elimination gives *N*-allylaminonaphthalene.

3. Conclusion

In summary, we have shown that platinum-catalyzed allylation of aminonaphthalenes using allylic acetates is a simple and efficient route for C–N bond formation. The reaction did not occur in the absence of the platinum catalyst. The amination of allylic acetates worked well with aminonaphthalenes, giving generally good yields of the corresponding allylic aminonaphthalenes. Aminonaphthalenes with steric constraints gave lower chemical yields.



Scheme 1.

4. Experimental

4.1. 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. 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.

4.2. General procedure for the platinum-catalyzed allylation of aminonaphthalenes. Reaction with 1-aminonaphthalene (1a)

A mixture of 1-aminonaphthalene (**1a**) (283 mg, 2 mmol), allyl acetate (**2a**) (160 mg, 1.6 mmol), $Pt(acac)_2$ (7.8 mg, 0.02 mmol), PPh_3 (21 mg, 0.08 mmol) and MS 4 Å in benzene (5 mL) was refluxed under nitrogen for 3 h. After cooling, the reaction mixture was filtered through Celite and the solvent was distilled under reduced pressure. Column

chromatography (*n*-hexane/chloroform 2:1) of the residue afforded **3a** and **4a** in 75 and 6% yields, respectively.

Products **3j**[11d] and **3k**[11d] are known.

4.2.1. *N*-Allyl-1-naphthylamine (3a). Light yellow thick oil. IR (KBr): ν 3442 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.75 (ddd, J=1.6, 1.6, 5.6 Hz, 2H, CH_2), 4.25 (br s, 1H, NH), 5.12 (ddt, J=1.6, 1.6, 10.0 Hz, 1H, vinyl H), 5.24 (ddt, J=1.6, 1.6, 17.2 Hz, 1H, vinyl H), 5.92 (ddt, J=5.6, 10.0, 17.2 Hz, 1H, vinyl H), 6.50 (d, J=7.6 Hz, 1H, ArH), 7.18 (d, J=8.0 Hz, 1H, ArH), 7.26 (d, J=7.6 Hz, 1H, ArH), 7.30 (ddd, J=1.6, 6.8, 8.4 Hz, 1H, ArH), 7.35 (ddd, J=1.6, 6.8, 8.0 Hz, 1H, ArH), 7.63 (d, J=8.4 Hz, 1H, ArH), 7.71 (d, J=8.0 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.5 (CH_2), 104.6 (CH), 116.3 (CH_2), 117.4 (CH), 119.8 (CH), 123.3 (C), 124.5 (CH), 125.5 (CH), 126.4 (CH), 128.5 (CH), 134.1 (C), 134.9 (CH), 142.9 (C). EI-MS: *m*/*z* 183 (M^+), 168, 154, 142, 127, 115, 89, 77. EI-HRMS calcd for $C_{13}H_{13}N$: 183.1048. Found: 183.1049.

4.2.2. *N*,*N*-Diallyl-1-naphthylamine (4a). Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 3.79 (d, J=5.6 Hz, 4H, $CH_2\times2$), 5.13 (ddt, J=1.6, 1.6, 10.4 Hz, 2H, vinyl H), 5.23 (ddt, J=1.6, 1.6, 17.2 Hz, 2H, vinyl H), 5.86 (ddt, J=6.0, 10.4, 17.2 Hz, 2H, vinyl H), 7.08 (d, J=7.2 Hz, 1H, ArH), 7.36 (dd, J=7.6, 8.0 Hz, 1H, ArH), 7.42–7.47 (m, 2H, ArH), 7.53 (d, J=8.0 Hz, 1H, ArH), 7.81 (dd, J=2.0, 7.2 Hz, 1H, ArH), 8.29 (d, J=7.2 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.1 (CH_2), 117.2 (CH_2), 117.6 (CH), 123.3 (CH), 123.9 (CH), 125.2 (CH), 125.3 (CH), 125.7 (CH), 128.3 (CH), 130.0 (C), 134.8 (C), 135.0 (CH), 147.6 (C). EI-MS: *m*/*z* 223 (M^+), 208, 198, 182, 180, 167, 155, 141, 127, 115, 101, 77. EI-HRMS calcd for $C_{16}H_{17}N$: 223.1361. Found: 223.1362.

4.2.3. *N*-Allyl-1-(2-methylnaphthyl)amine (3b). Red thick oil. IR (KBr): ν 3370 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H, CH_3), 3.27 (br s, 1H, NH), 3.72 (ddd, J=1.2, 1.6, 6.0 Hz, 2H, CH_2), 5.11 (ddt, J=1.2, 1.6, 10.0 Hz, 1H, vinyl H), 5.30 (ddt, J=1.6, 1.6, 17.2 Hz, 1H, vinyl H), 6.03 (ddt, J=6.0, 10.0, 17.2 Hz, 1H, vinyl H), 7.23 (d, J=8.4 Hz, 1H, ArH), 7.35 (ddd, J=1.2, 6.8, 8.0 Hz, 1H, ArH), 7.41 (ddd, J=1.6, 6.8, 8.4 Hz, 2H, ArH), 7.73 (d, J=8.0 Hz, 1H, ArH), 8.04 (d, J=8.4 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.8 (CH_3), 52.7 (CH_2), 115.8 (CH_2), 122.6 (CH), 122.7 (CH), 124.8 (CH), 125.3 (CH), 125.4 (C), 128.2 (CH), 128.5 (C), 129.2 (CH), 133.5 (C), 136.6 (CH), 142.2 (C). EI-MS: *m*/*z* 197 (M^+), 182, 180, 168, 156, 141, 129, 115, 102, 89, 77. EI-HRMS calcd for $C_{14}H_{15}N$: 197.1204. Found: 197.1207.

4.2.4. *N*,*N*-Diallyl-1-(2-methylnaphthyl)amine (4b). Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H, CH_3), 3.79 (m, 4H, $CH_2\times2$), 4.98 (ddt, J=1.2, 1.6, 10.0 Hz, 2H, vinyl H), 5.08 (ddt, J=1.6, 1.6, 17.2 Hz, 2H, vinyl H), 5.87 (ddt, J=6.8, 10.0, 17.2 Hz, 2H, vinyl H), 7.19 (d, J=8.4 Hz, 1H, ArH), 7.32 (ddd, J=1.2, 6.8, 8.0 Hz, 1H, ArH), 7.41 (ddd, J=1.6, 6.8, 8.4 Hz, 1H, ArH), 7.48 (d, J=8.4 Hz, 1H, ArH), 7.71 (d, J=8.0 Hz, 1H, ArH), 8.17 (d, J=8.8 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.7 (CH_3), 56.5 (CH_2), 116.2 (CH_2), 124.6 (CH), 124.7 (CH), 125.3 (CH), 125.5 (CH), 128.1 (CH), 129.7 (CH), 133.3 (C), 133.6 (C), 133.8 (C), 136.7 (CH), 144.7 (C). EI-MS: *m*/*z* 237 (M^+), 222, 210, 196, 180, 168, 154, 141, 115, 89. EI-HRMS calcd for $C_{17}H_{19}N$: 237.1517. Found: 237.1520.

4.2.5. *N*-Allyl-1-(4-bromonaphthyl)amine (3c). Claret thick oil. IR (KBr): ν 3445 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.71 (ddd, J=1.2, 1.6, 5.2 Hz, 2H, CH_2), 4.27 (br s, 1H, NH), 5.14 (ddt, J=1.2, 1.6, 10.4 Hz, 1H, vinyl H), 5.24 (ddt, J=1.6, 1.6, 17.2 Hz, 1H, vinyl H), 5.90 (ddt, J=5.2, 10.4, 17.2 Hz, 1H, vinyl H), 6.28 (d, J=8.0 Hz, 1H, ArH), 7.32 (ddd, J=1.2, 6.8, 8.4 Hz, 1H, ArH), 7.45 (ddd, J=1.2, 6.8, 8.4 Hz, 1H, ArH), 7.50 (d, J=8.0 Hz, 1H, ArH), 7.61 (d, J=8.4 Hz, 1H, ArH), 8.18 (dd, J=0.8, 8.0 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.4 (CH_2), 105.3 (CH), 109.9 (C), 116.7 (CH_2), 120.1 (CH), 124.5 (C), 125.2 (CH), 126.9 (CH), 127.6 (CH), 130.2 (CH), 131.9 (C), 134.4 (CH), 142.8 (C). EI-MS: *m*/*z* 263 (M^++2), 261 (M^+), 248, 246, 222, 220, 195, 193, 180, 167, 155, 140, 126, 114, 77. EI-HRMS calcd for $C_{13}H_{12}BrN$: 261.0153. Found: 261.0155.

4.2.6. *N*,*N*-Diallyl-1-(4-bromonaphthyl)amine (4c). Amber thick oil. ^1H NMR (400 MHz, $CDCl_3$): δ 3.76 (d, J=6.0 Hz, 4H, $CH_2\times2$), 5.14 (ddt, J=0.8, 1.2, 10.4 Hz, 2H, vinyl H), 5.22 (ddt, J=1.6, 1.6, 17.2 Hz, 2H, vinyl H), 5.84 (ddt, J=6.0, 10.4, 17.2 Hz, 2H, vinyl H), 6.93 (d, J=8.0 Hz, 1H, ArH), 7.55 (ddd, J=1.6, 6.8, 8.0 Hz, 2H, ArH), 7.65 (d, J=8.0 Hz, 1H, ArH), 8.20 (d, J=8.0 Hz, 1H, ArH), 8.32 (d, J=8.4 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.3 (CH_2), 117.0 (C), 117.6 (CH_2), 118.5 (CH), 124.3 (CH), 126.1 (CH), 127.2 (CH), 127.6 (CH), 129.3 (CH), 131.4 (C), 132.9 (C), 134.5 (CH), 147.8 (C). EI-MS: *m*/*z* 303 (M^++2), 301 (M^+), 288, 286, 260, 245, 234, 232, 222, 207, 195, 180, 167, 153, 126, 113, 82. EI-HRMS calcd for $C_{16}H_{16}BrN$: 301.0466. Found: 301.0466.

4.2.7. *N*-Allyl-1-(4-cyanonaphthyl)amine (3d). Light yellow crystal. Mp: 129–131 °C ($CHCl_3$/*n*-hexane). IR (KBr): ν 3393 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.00 (ddd, J=1.6, 1.6, 5.2 Hz, 2H, CH_2), 5.21 (br s, 1H, NH), 5.27 (ddt, J=1.6, 1.6, 10.4 Hz, 1H, vinyl H), 5.36 (ddt, J=1.6, 1.6, 17.2 Hz, 1H, vinyl H), 6.02 (ddt, J=5.2, 10.4, 17.2 Hz, 1H, vinyl H), 6.52 (d, J=8.0 Hz, 1H, ArH), 7.52 (ddd, J=1.2, 6.8, 8.4 Hz, 1H, ArH), 7.62 (ddd, J=1.2, 6.8, 8.4 Hz, 1H, ArH), 7.74 (d, J=8.4 Hz, 1H, ArH), 7.83 (d, J=8.4 Hz, 1H, ArH), 8.15 (dd, J=0.8, 8.4 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.1 (CH_2), 96.9 (C), 103.2 (CH), 117.5 (CH_2), 119.6 (C), 120.2 (CH), 122.0 (C), 125.9 (CH), 126.0 (CH), 128.2 (CH), 133.4 (CH), 133.5 (C), 134.6 (CH), 147.1 (C). EI-MS: *m*/*z* 208 (M^+), 193, 181, 167, 154, 140, 125, 113, 90, 77. EI-HRMS calcd for $C_{14}H_{12}N_2$: 208.1000. Found: 208.1003.

4.2.8. *N*,*N*-Diallyl-1-(4-cyanonaphthyl)amine (4d). Light yellow thick oil. ^1H NMR (400 MHz, $CDCl_3$): δ 3.88 (ddd, J=1.6, 1.6, 5.6 Hz, 4H, $CH_2\times2$), 5.21 (ddt, J=1.2, 1.6, 10.4 Hz, 2H, vinyl H), 5.28 (ddt, J=1.6, 1.6, 17.2 Hz, 2H, vinyl H), 5.84 (ddt, J=5.6, 10.4, 17.2 Hz, 2H, vinyl H), 7.01 (d, J=8.0 Hz, 1H, ArH), 7.56 (ddd, J=1.2, 6.8, 8.4 Hz, 1H, ArH), 7.63 (ddd, J=1.2, 6.8, 8.0 Hz, 1H, ArH), 7.78 (d, J=8.0 Hz, 1H, ArH), 8.19 (ddd, J=0.4, 0.8, 8.4 Hz, 1H, ArH), 8.26 (ddd, J=0.4, 0.8, 8.4 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.7 (CH_2), 103.3 (C), 115.5 (CH),

118.0 (CH_2), 118.6 (C), 124.7 (CH), 125.7 (CH), 126.4 (CH), 128.2 (CH), 128.6 (C), 132.7 (CH), 133.7 (CH), 134.0 (C), 152.7 (C). EI-MS: *m/z* 248 (M^+), 233, 221, 205, 192, 179, 166, 152, 140, 125, 99, 82. EI-HRMS calcd for $C_{17}H_{16}N_2$: 248.1313. Found: 248.1312.

4.2.9. *N*-Allyl-2-naphthylamine (3e). Brown thick oil. IR (KBr): ν 3417 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.64 (br s, 1H, NH), 3.67 (ddd, J=1.6, 1.6, 5.6 Hz, 2H, CH_2), 5.10 (ddt, J=1.6, 1.6, 10.4 Hz, 1H, vinyl H), 5.21 (ddt, J=1.6, 1.6, 17.2 Hz, 1H, vinyl H), 5.85 (ddt, J=5.6, 10.4, 17.2 Hz, 1H, vinyl H), 6.69 (d, J=2.8 Hz, 1H, ArH), 6.71 (d, J=2.4 Hz, 1H, ArH), 7.14 (ddd, J=1.2, 6.8, 8.0 Hz, 1H, ArH), 7.30 (ddd, J=1.2, 6.8, 8.0 Hz, 1H, ArH), 7.54 (m, 2H, ArH), 7.60 (d, J=8.0 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.3 (CH_2), 104.6 (CH), 116.1 (CH_2), 117.8 (CH), 121.8 (CH), 125.8 (CH), 126.1 (CH), 127.4 (C), 127.5 (CH), 128.7 (CH), 134.9 (CH), 135.0 (C), 145.5 (C). EI-MS: *m/z* 183 (M^+), 168, 156, 141, 129, 115, 89, 77. EI-HRMS calcd for $C_{13}H_{13}N$: 183.1048. Found: 183.1046.

4.2.10. *N*,*N*-Diallyl-2-naphthylamine (4e). Light yellow thick oil. ^1H NMR (400 MHz, $CDCl_3$): δ 4.02 (ddd, J=1.6, 2.0, 4.8 Hz, 4H, $CH_2\times2$), 5.18 (ddt, J=1.6, 2.0, 10.0 Hz, 2H, vinyl H), 5.24 (ddt, J=1.6, 1.6, 17.2 Hz, 2H, vinyl H), 5.91 (ddt, J=4.8, 10.0, 17.2 Hz, 2H, vinyl H),6.92 (s, 1H, ArH), 7.08 (d, J=8.0 Hz, 1H, ArH), 7.18 (ddd, J=2.0, 6.8, 8.0 Hz, 1H, ArH), 7.31–7.36 (m, 1H, ArH), 7.61 (d, J=8.4 Hz, 1H, ArH), 7.65 (s, 1H, ArH), 7.67 (d, J=2.4 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.9 (CH_2), 106.0 (CH), 116.1 (CH_2), 116.2 (CH), 121.8 (CH), 126.1 (CH), 126.2 (CH), 126.2 (C), 127.4 (CH), 128.7 (CH), 133.9 (CH), 135.5 (C), 146.5 (C). EI-MS: *m/z* 223 (M^+), 208, 196, 180, 167, 155, 141, 127, 115, 101, 89, 77. EI-HRMS calcd for $C_{16}H_{17}N$: 223.1361. Found: 223.1361.

4.2.11. *N*-Allyl-1-(4-nitronaphthyl)amine (3f). Orange-red crystal. Mp: 142–143.5 °C (EtOAc/*n*-hexane). IR (KBr): ν 3391 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 4.06 (ddd, J=1.6, 1.6, 5.2 Hz, 2H, CH_2), 5.20 (br s, 1H, NH), 5.30 (ddt, J=1.2, 1.6, 10.4 Hz, 1H, vinyl H), 5.37 (ddt, J=1.2, 1.6, 17.2 Hz, 1H, vinyl H), 6.02 (ddt, J=5.2, 10.4, 17.2 Hz, 1H, vinyl H), 6.49 (d, J=8.8 Hz, 1H, ArH), 7.53 (ddd, J=1.2, 6.8, 8.4 Hz, 1H, ArH), 7.69 (ddd, J=1.2, 6.8, 8.8 Hz, 1H, ArH), 7.84 (dd, J=0.8, 8.4 Hz, 1H, ArH), 8.43 (d, J=8.8 Hz, 1H, ArH), 9.02 (dd, J=0.8, 8.8 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.2 (CH_2), 101.8 (CH), 117.9 (CH_2), 120.0 (CH), 121.8 (C), 124.9 (CH), 125.8 (CH), 127.6 (C), 129.3 (CH), 129.6 (CH), 132.9 (CH), 135.1 (C), 149.3 (C). EI-MS: *m/z* 228 (M^+), 193, 180, 167, 154, 140, 129, 114, 102, 88, 77. EI-HRMS calcd for $C_{13}N_{12}N_2O_2$: 228.0899. Found: 228.0898.

4.2.12. *N*,*N*-Diallyl-1-(4-nitronaphthyl)amine (4f). Orange-red thick oil. ^1H NMR (400 MHz, $CDCl_3$): δ 3.93 (ddd, J=1.2, 1.6, 6.0 Hz, 4H, $CH_2\times2$), 5.24 (ddt, J=1.2, 1.6, 10.0 Hz, 2H, vinyl H), 5.30 (ddt, J=1.6, 1.6, 17.2 Hz, 2H, vinyl H), 5.86 (ddt, J=5.6, 10.4, 17.2 Hz, 2H, vinyl H), 6.99 (d, J=8.8 Hz, 1H, ArH), 7.56 (ddd, J=1.6, 7.2, 8.4 Hz, 1H, ArH), 7.68 (ddd, J=1.6, 7.2, 8.4 Hz, 1H, ArH), 8.27 (d, J=8.4 Hz, 1H, ArH), 8.29 (dd, J=0.8, 8.0 Hz, 1H, ArH), 8.75 (dd, J=0.8, 8.8 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.8 (CH_2), 114.0 (CH), 118.2 (CH_2), 123.9 (CH), 124.8 (CH), 125.6 (CH), 126.1 (CH), 127.4 (C), 128.8 (C), 129.3 (CH), 133.5 (CH), 141.8 (C), 154.6 (C). EI-MS: *m/z* 268 (M^+), 253, 238, 224, 222, 210, 207, 194, 180, 167, 153, 140, 127, 115, 82, 77. EI-HRMS calcd for $C_{16}N_{16}N_2O_2$: 268.1212. Found: 268.1215.

4.2.13. *N*-Allyl-3-quinolylamine (3g). Pale yellow thick oil. IR (KBr): 3410 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.72 (ddd, J=1.6, 1.6, 5.2 Hz, 2H, CH_2), 4.64 (br s, 1H, NH), 5.13 (ddt, J=1.6, 1.6, 10.4 Hz, 1H, vinyl H), 5.24 (ddt, J=1.6, 1.6, 17.2 Hz, 1H, vinyl H), 5.86 (ddt, J=5.6, 10.0, 17.2 Hz, 1H, vinyl H), 6.90 (d, J=2.8 Hz, 1H, ArH), 7.32–7.38 (m, 2H, ArH), 7.52–7.56 (m, 1H, ArH), 7.92–7.97 (m, 1H, ArH), 8.43 (d, J=2.8 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.6 (CH_2), 110.0 (CH), 116.3 (CH_2), 124.5 (CH), 125.7 (CH), 126.6 (CH), 128.3 (CH), 129.3 (C), 133.9 (CH), 141.3 (CH), 141.3 (C), 141.4 (C), 142.9 (CH). EI-MS: *m/z* 185 (M^+), 169, 157, 143, 128, 116, 101, 89, 75, 63. EI-HRMS calcd for $C_{12}H_{12}N_2$: 184.1000. Found: 184.0996.

4.2.14. *N*,*N*-Diallyl-3-quinolinylamine (4g). Yellow thick oil. ^1H NMR (400 MHz, $CDCl_3$): δ 4.05 (ddd, J=1.6, 1.6, 4.8 Hz, 4H, $CH_2\times2$), 5.22 (ddt, J=1.6, 1.6, 10.0 Hz, 2H, vinyl H), 5.24 (ddt, J=1.6, 1.6, 17.6 Hz, 2H, vinyl H), 5.90 (ddt, J=4.8, 10.0, 17.6 Hz, 2H, vinyl H), 7.14 (d, J=2.8 Hz, 1H, ArH), 7.37–7.43 (m, 2H, ArH), 7.58–7.62 (m, 1H, ArH), 7.91–7.95 (m, 1H, ArH), 8.62 (d, J=2.8 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.9 (CH_2), 112.6 (CH), 116.8 (CH_2), 125.0 (CH), 126.0 (CH), 126.8 (CH), 128.7 (CH), 129.2 (C), 133.0 (CH), 141.1 (CH), 141.3 (C), 142.1 (C). EI-MS: *m/z* 224 (M^+), 209, 197, 183, 168, 156, 142, 128, 115, 101, 89, 75, 63. EI-HRMS calcd for $C_{15}H_{16}N_2$: 224.1313. Found: 224.1314.

4.2.15. *N*-Allyl-*N*-ethyl-1-naphthylamine (3h). Light green thick oil. ^1H NMR (400 MHz, $CDCl_3$): δ 1.01 (t, J=7.2 Hz, 3H, CH_3), 3.18 (q, J=7.2 Hz, 2H, CH_2), 3.70 (ddd, J=1.2, 1.6, 6.0 Hz, 2H, CH_2), 5.09 (ddt, J=1.2, 2.0, 10.4 Hz, 1H, vinyl H), 5.22 (ddt, J=1.6, 2.0, 17.2 Hz, 1H, vinyl H), 5.88 (ddt, J=6.0, 10.4, 17.2 Hz, 1H, vinyl H), 7.06 (dd, J=1.2, 7.6 Hz, 1H, ArH), 7.34 (dd, J=7.6, 8.0 Hz, 1H, ArH), 7.38–7.46 (m, 2H, ArH), 7.50 (d, J=8.4 Hz, 1H, ArH), 7.76 (dd, J=2.0, 7.6 Hz, 1H, ArH), 8.30 (dd, J=1.2, 8.0 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.0 (CH_3), 46.7 (CH_2), 57.3 (CH_2), 116.7 (CH_2), 117.6 (CH), 123.3 (CH), 124.0 (CH), 125.1 (CH), 125.4 (CH), 125.6 (CH), 128.2 (CH), 130.6 (C), 134.9 (C), 135.6 (CH), 147.7 (C). EI-MS: *m/z* 211 (M^+), 196, 184, 168, 155, 141, 127, 115, 89, 77, 63. EI-HRMS calcd for $C_{15}H_{17}N$: 211.1361. Found: 211.1360.

4.2.16. *N*-Allyl-*N*-phenyl-1-naphthylamine (3i). Pale yellow thick oil. ^1H NMR (400 MHz, $CDCl_3$): δ 4.38 (ddd, J=1.6, 1.6, 5.2 Hz, 2H, CH_2), 5.18 (ddt, J=1.6, 1.6, 10.4 Hz, 1H, vinyl H), 5.30 (ddt, J=1.6, 1.6, 17.2 Hz, 1H, vinyl H), 6.04 (ddt, J=5.2, 10.4, 17.2 Hz, 1H, vinyl H), 6.58 (dd, J=0.8, 8.0 Hz, 2H, ArH), 6.70 (ddd, J=0.8, 6.8, 7.6 Hz, 1H, ArH), 7.12 (ddd, J=2.0, 7.2, 8.4 Hz, 2H, ArH), 7.39–7.51 (m, 4H, ArH), 7.79 (d, J=8.0 Hz, 1H, ArH), 7.86 (d, J=8.4 Hz, 1H, ArH), 7.90 (d, J=8.0 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2 (CH_2), 113.7 (CH), 116.8

(CH_2), 117.1 (CH), 123.8 (CH), 126.2 (CH), 126.3 (CH), 126.4 (CH), 126.5 (CH), 126.9 (CH), 128.5 (CH), 128.9 (CH), 131.4 (C), 134.5 (CH), 135.2 (C), 143.7 (C), 149.2 (C). EI-MS: *m/z* 259 (M^+), 244, 218, 189, 167, 154, 127, 104, 89, 77. EI-HRMS calcd for $C_{19}H_{17}N$: 259.1361. Found: 259.1359.

4.2.17. *N*-(Hex-2*E*-enyl)-1-naphthylamine (5). Grass-green thick oil. IR (KBr): ν 3432 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, J=7.2 Hz, 3H, CH_3), 1.39 (hext, J=7.2 Hz, 2H, CH_2), 2.01 (dt, J=6.4, 7.2 Hz, 2H, CH_2), 3.77 (dd, J=0.8, 6.0 Hz, 2H, CH_2), 4.22 (br s, 1H, NH), 5.63 (dt, J=5.6, 15.2 Hz, 1H, vinyl H), 5.72 (dt, J=6.4, 15.2 Hz, 1H, vinyl H), 6.57 (d, J=7.2 Hz, 1H, ArH), 7.20 (d, J=8.4 Hz, 1H, ArH), 7.30 (dd, J=7.6, 8.0 Hz, 1H, ArH), 7.34–7.40 (m, 2H, ArH), 7.73 (ddd, J=1.2, 8.0, 8.0 Hz, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7 (CH_3), 22.3 (CH_2), 34.4 (CH_2), 46.2 (CH_2), 104.6 (CH), 117.3 (CH), 119.9 (CH), 123.4 (C), 124.5 (CH), 125.6 (CH), 126.5 (CH), 126.5 (CH), 128.5 (CH), 133.6 (CH), 134.2 (C), 143.2 (C). EI-MS: *m/z* 225 (M^+), 196, 182, 168, 165, 143, 127, 115, 89, 77. EI-HRMS calcd for $C_{16}H_{19}N$: 225.1517. Found: 225.1513.

4.2.18. *N*,*N*-Di(hex-2*E*-enyl)-1-naphthylamine (6). Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 0.84 (t, J=7.2 Hz, 6H, $CH_3\times2$), 1.34 (hext, J=7.2 Hz, 4H, $CH_2\times2$), 1.96 (dt, J=6.8, 7.2 Hz, 4H, $CH_2\times2$), 3.72 (d, J=6.4 Hz, 4H, $CH_2\times2$), 5.46 (dt, J=6.4, 15.2 Hz, 2H, vinyl H), 5.58 (dt, J=6.8, 15.2 Hz, 2H, vinyl H), 7.03 (d, J=7.2 Hz, 1H, ArH), 7.35 (dd, J=7.6, 8.0 Hz, 1H, ArH), 7.40–7.47 (m, 2H, ArH), 7.49 (d, J=8.4 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6 (CH_3), 22.5 (CH_2), 34.5 (CH_2), 55.2 (CH_2), 117.7 (CH), 122.9 (CH), 124.1 (CH), 125.0 (CH), 125.3 (CH), 125.5 (CH), 126.6 (CH), 128.2 (CH), 130.1 (C), 133.6 (CH), 134.8 (C), 148.1 (C). EI-MS: *m/z* 307 (M^+), 278, 264, 250, 225, 194, 182, 165, 154, 143, 127, 115, 77. EI-HRMS calcd for $C_{22}H_{29}N$: 307.2300. Found: 307.2303.

4.2.19. *N*-(1-Propylallyl)-1-naphthylamine (7). Dark brown thick oil. IR (KBr): ν 3446 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.97 (t, J=7.2 Hz, 3H, CH_3), 1.45–1.56 (m, 2H, CH_2), 1.73 (dt, J=6.8, 14.4 Hz, 2H, CH_2), 4.01 (dt, J=6.4, 6.4 Hz, 1H, CH), 4.38 (br s, 1H, NH), 5.15 (ddd, J=1.2, 1.2, 10.0 Hz, 1H, vinyl H), 5.25 (d, J=17.2 Hz, 1H, vinyl H), 5.83 (ddd, J=6.0, 10.0, 17.2 Hz, 1H, vinyl H), 6.63 (d, J=6.4 Hz, 1H, ArH), 7.20–7.24 (m, 1H, ArH), 7.31 (dd, J=7.6, 8.0 Hz, 1H, ArH), 7.41–7.46 (m, 2H, ArH), 7.76–7.84 (m, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0 (CH_3), 19.2 (CH_2), 38.0 (CH_2), 55.8 (CH), 105.4 (CH), 115.3 (CH_2), 117.1 (CH), 119.7 (CH), 123.3 (C), 124.6 (CH), 125.6 (CH), 126.5 (CH), 128.7 (CH), 134.3 (C), 139.7 (CH), 142.3 (C). EI-MS: *m/z* 225 (M^+), 182, 165, 154, 143, 127, 115, 89, 77. EI-HRMS calcd for $C_{16}H_{19}N$: 225.1517. Found: 225.1513.

4.2.20. *N*-(3-Phenylallyl)-1-naphthylamine (8). Brown crystal. Mp: 78–80 °C. IR (KBr): ν 3431 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.95 (dd, J=1.6, 6.0 Hz, 2H, CH_2), 4.42 (br s, 1H, NH), 6.32 (dt, J=6.0, 16.0 Hz, 1H, vinyl H), 6.56–6.61 (m, 2H, vinyl H and ArH), 7.16–7.42 (m, 9H, ArH), 7.71–7.76 (m, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.2 (CH_2), 104.8 (CH), 117.6 (CH), 119.9 (CH), 123.4 (C), 126.6 (CH), 125.7 (CH), 126.3 (CH), 126.5 (CH), 126.5 (CH), 127.5 (CH), 128.5 (CH), 128.6 (CH), 131.7 (CH), 134.2 (C), 136.7 (C), 143.0 (C). EI-MS: *m/z* 259 (M^+), 242, 215, 181, 168, 154, 143, 127, 117, 91, 77. EI-HRMS calcd for $C_{19}H_{17}N$: 259.1361. Found: 259.1361.

4.2.21. *N*,*N*-Di(3-phenylallyl)-1-naphthylamine (9). Amber thick oil. ^1H NMR (400 MHz, $CDCl_3$): δ 3.95 (d, J=6.0 Hz, 4H, $CH_2\times2$), 6.25 (dt, J=1.6, 16.0 Hz, 2H, vinyl H), 6.54 (d, J=16.0 Hz, 2H, vinyl H), 7.09–7.14 (m, 1H, ArH), 7.16 (dd, J=1.2, 7.2 Hz, 2H, ArH), 7.23 (t, J=7.6 Hz, 4H, ArH), 7.29 (dd, J=1.6, 7.2 Hz, 4H, ArH), 7.34 (dd, J=7.6, 8.0 Hz, 1H, ArH), 7.43 (ddd, J=1.2, 1.6, 8.0 Hz, 1H, ArH), 7.48 (dd, J=1.2, 8.0 Hz, 1H, ArH), 7.51 (d, J=8.0 Hz, 1H, ArH), 7.79 (d, J=8.0 Hz, 1H, ArH), 8.38 (d, J=8.0 Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6 (CH_2), 117.7 (CH), 123.4 (CH), 123.9 (CH), 125.3 (CH), 125.4 (CH), 125.7 (CH), 126.3 (C), 126.7 (CH), 127.3 (CH), 128.3 (CH), 128.5 (CH), 129.8 (C), 132.4 (CH), 134.9 (C), 137.0 (C), 147.7 (CH). EI-MS: *m/z* 375 (M^+), 284, 270, 258, 256, 241, 229, 217, 194, 180, 169, 154, 141, 127, 117, 115, 91, 77, 65, 51. EI-HRMS calcd for $C_{28}H_{25}N$: 375.1987. Found: 375.1987.

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