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Stereoselective Synthesis of Allylamines by Iron-Catalyzed Cross-Coupling of 3-Chloroprop-2-en-1-amines with Grignard Reagents. Synthesis of Naftifine

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Abstract—A general procedure for the synthesis of *trans*- and *cis*-allylamines has been developed on the basis of iron-catalyzed cross-coupling of Grignard reagents with stereochemically pure 3-chloroprop-2-en-1-amines prepared by allylation of amines with commercially available 1,3-dichloropropene isomers.

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Persistent interest in the development of new and optimization of existing methods of synthesis of allylamines is determined by their occurrence in nature and wide application in medicine. Allylamine fragment is a structural unit of many alkaloids, such as strychnine, brucine, diaboline [1], tabersonine [2], and aloperine [3], cytosinine [4], gabaculine [5], valienamine [6], and other natural compounds. Allylamines are used in the synthesis of amino acids [7], alkaloids [8], amino sugars [9], and other biologically active compounds. Commercial allylamine-based medicines, in particular terbinafine [10] and naftifine [11] are of great practical importance as antifungal drugs used in the treatment of various mycoses.

Among a wide variety of known methods of synthesis of allylamines, the main ones are based on nucleophilic allylic substitution, electrophilic amination of alkenes, sigmatropic rearrangements, and CH-activation methods (for detailed reviews, see [12]). However, procedures ensuring stereoselective synthesis of allylamines with a required double bond configuration are very few in number. Multicomponent Petasis reaction [13] of (*E*)-vinylboronic acids or esters with amines and aldehydes is stereospecific, but its application is limited because of low accessibility of (*E*)-vinylboronic acids and their esters; furthermore, this reaction yields only *trans*-allylamines.

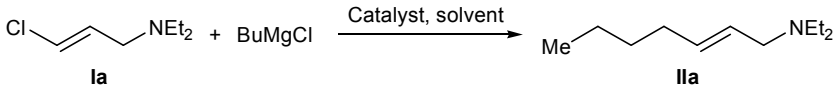
trans-Allylamines were also synthesized with high stereoselectivity by coupling of zirconocene imine complexes with alkynes [14] or of (*E*)-alkenylzirconocene chlorides (prepared by hydrozirconation of alkynes with the Schwartz reagent) with imines in the presence of a catalytic amount of Ru(I) [15], as well as by reactions of organozinc [16] and organoaluminum derivatives [17] of alkenylzirconocene chlorides with imines.

Heck arylation of allylamines under conventional conditions generally yields mixture of regioisomers [18]; if the reaction is carried out with aryl trifluoromethanesulfonates in the presence of bidentate ligands, the β-position of allylamine is typically involved [19]. Examples of coupling of arenediazonium salts with protected allylamines with formation of γ-substituted products with fairly high regioselectivity and (*E*)-stereoselectivity have recently been reported [20]. Xie et al. [21] recently described a novel synthetic approach to (*E*)-allylamines, based on Pd-catalyzed vinylation of aminals with alkenes.

The main drawbacks of the above methods are the use of difficultly accessible reagents and expensive and toxic catalysts, as well as impossibility to obtain (*Z*)-allylamines.

In the present study we made an attempt to synthesize stereochemically pure (*E*)- and (*Z*)-allylamines by cross-coupling of (*E*)- and (*Z*)-3-chloroprop-2-en-1-amines with Grignard reagents. Initial (*E*)- and (*Z*)-3-chloroprop-2-en-1-amines were prepared by nucleophilic substitution of the allylic chlorine atom in the corresponding individual 1,3-dichloropropene isomers by the action of primary and secondary amines;

Scheme 1.



Ia **IIa**

these reactions occurred with complete retention of the double bond configuration [22]. The *trans*- and *cis*-stereoisomers of 1,3-dichloropropene (large-scale by-product in the manufacture of allyl chloride) are characterized by strongly different boiling points, so that the isomers can be effectively separated by fractional distillation. Individual 1,3-dichloropropene isomers possess allylic and vinylic chlorine atoms exhibiting different reactivities and thus offer the unique synthetic potential. The strategy involving functionalization of 1,3-dichloropropene isomers at the allylic position with, e.g. N- and C-centered nucleophiles and subsequent stereoselective cross-coupling at the vinylic position seems to be quite promising for the synthesis of stereochemically pure unsaturated compounds [23].

The well-known Kumada–Tamao–Corriu reaction [24], i.e., cross-coupling of aryl(vinyl) halides with Grignard reagents catalyzed by Pd and Ni complexes, has found limited synthetic applications, due mainly to high sensitivity of many functional groups to highly reactive organomagnesium compounds. In 1971, Tamura and Kochi [25] reported on successful $FeCl_3$-catalyzed vinylation of Grignard reagents with vinyl bromide. In 1998, Cahiez and Avedissian [26] essentially improved the procedure for Fe-catalyzed cross-coupling of vinyl halides with aliphatic Grignard compounds by adding *N*-methylpyrrolidin-2-one (NMP) as co-solvent. In recent years, various iron catalytic systems have been proposed, which ensured successful cross-coupling of alkylmagnesium halides with aryl halides, *p*-toluenesulfonates, and trifluoromethanesulfonates [27, 28], of aromatic Grignard reagents with alkyl halides [29], heteroaromatic halides [28, 30], and vinyl halides [31], of alkenylmagnesium halides with alkyl halides [32], and of alkynylmagnesium bromides with vinyl bromides and trifluoromethanesulfonates [33]. Undoubted advantages of Fe-catalyzed cross-

Table 1. Cross-coupling of (2*E*)-3-chloro-*N*,*N*-diethylprop-2-en-1-amine (**Ia**) with butylmagnesium chloride[a]

Run no.	Solvent	Amount of NMP, equiv	Catalyst	Amount, mol %	Reaction time, min	Yield of **IIa**,[b] %
1	THF	–	$Fe(acac)_3$	3	90	60
2	Diglyme	–	$Fe(acac)_3$	3	90	62
3	THF	0.5	$Fe(acac)_3$	3	90	76
4	THF	1	$Fe(acac)_3$	3	90	80
5	THF	2	$Fe(acac)_3$	3	90	86
6	THF	4	$Fe(acac)_3$	3	90	92
7	THF	6	$Fe(acac)_3$	3	90	94
8	THF	8	$Fe(acac)_3$	3	90	91
9	THF	16	$Fe(acac)_3$	3	90	82
10	NMP	–	$Fe(acac)_3$	3	90	63
11	THF	6	$Fe(acac)_3$	1	90	93[c]
12	THF	6	–	–	90	3
13	THF	6	$Fe(acac)_3$	1	15	84
14	THF	6	$Fe(acac)_3$	1	45	90
15	THF	–	$Pd(OAc)_2$	1	90	3
16	THF	–	$Pd(PPh_3)_4$	1	90	16

[a] Reaction conditions: **Ia**, 0.5 mmol; BuMgCl, 0.75 mmol (1 M solution in THF, 0.75 mL); solvent, 1 mL; the Grignard reagent was added to a solution of **Ia** at 0°C, and the mixture was then stirred at room temperature for a required time.

[b] According to the GLC data.

[c] A similar yield was obtained with 0.65 mmol of BuMgCl.

Table 2. Iron-catalyzed cross-coupling of 3-chloroprop-2-en-1-amines **I** with Grignard reagents[a]

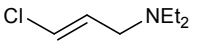
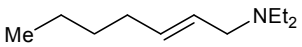
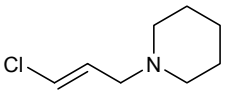
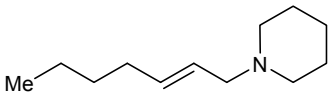
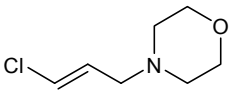
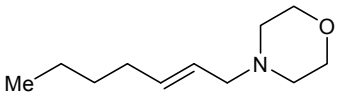
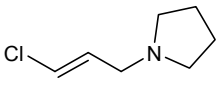
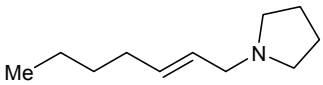
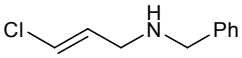
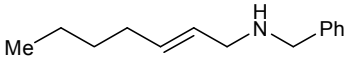
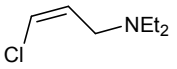
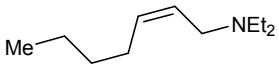
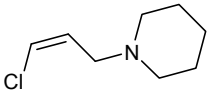
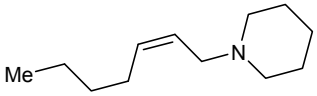
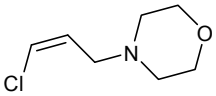
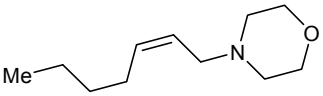
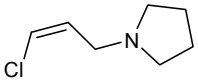
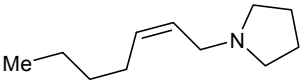
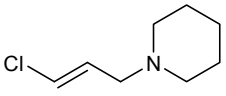
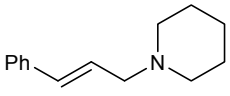
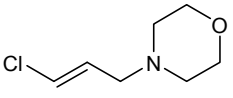
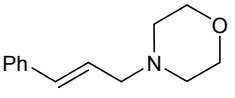
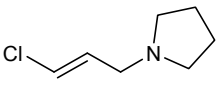
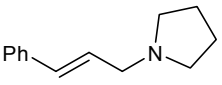
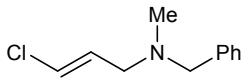
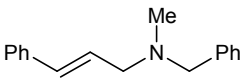
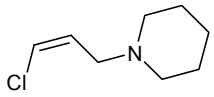
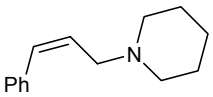
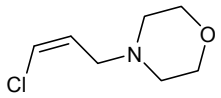
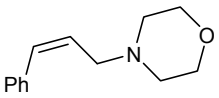
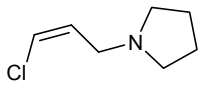
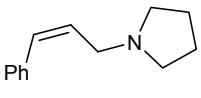
RMgHlg	3-Chloroprop-2-en-1-amines **I**[b]	Allylamines **II**	Yield of **II**,[c] %	*E*/*Z*-Isomer ratio
BuMgCl[d]	 **Ia**	 **IIa**	83	99:1
	 **Ib**	 **IIb**	80	99:1
	 **Ic**	 **IIc**	84	99:1
	 **Id**	 **IId**	82	99:1
	 **Ie**	 **IIe**	89	99:1
	 **If**	 **IIf**	76	5:95
	 **Ig**	 **IIg**	78	5:95
	 **Ih**	 **IIh**	80	5:95
	 **Ii**	 **IIi**	74	5:95
PhMgBr[e]	 **Ib**	 **IIj**	89	97:3
	 **Ic**	 **IIk**	92	98:2
	 **Id**	 **III**	90	95:5

Table 2 (Contd.).

RMgHlg	3-Chloroprop-2-en-1-amines **I**[b]	Allylamines **II**	Yield of **II**,[c] %	*E*/*Z*-Isomer ratio
PhMgBr[e]	 **Ij**	 **IIm**	92	97:3
	 **Ig**	 **IIn**	80	23:77
	 **Ih**	 **IIo**	82	18:82
	 **Ii**	 **IIp**	87	14:86

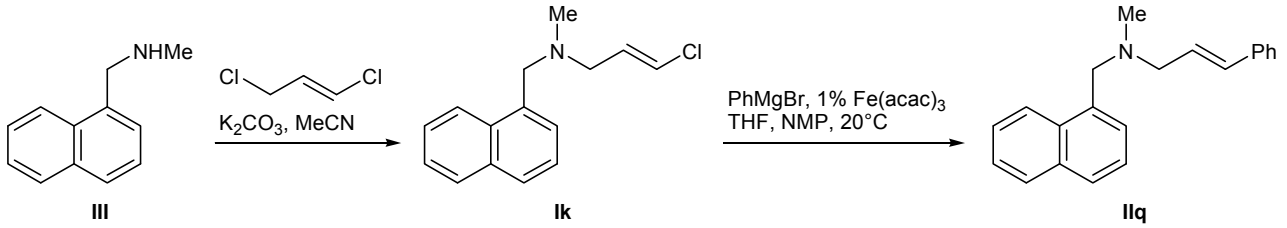
[a] Reaction conditions: 3-chloroprop-2-en-1-amine **I**, 1.3 mmol; THF, 2 mL; 20–25°C, 1.5 h.
[b] Initial amines **I** contained 99% of the major isomer.
[c] Yield of isolated product.
[d] $Fe(acac)_3$, 2%; NMP, 0.8 mL; BuMgCl, 1.7 mmol (1 M solution in THF, 1.7 mL).
[e] $Fe(acac)_3$, 1%; NMP, 0.1 mL; PhMgBr, 2.1 mmol (1 M solution in THF, 2.1 mL).

couplings are high reaction rates and low toxicity and low cost of the catalyst.

The present study was aimed at searching for optimal catalytic system for the cross-coupling reaction of 3-chloroprop-2-en-1-amines with Grignard compounds. As model reaction we used cross-coupling of (2*E*)-3-chloro-*N*,*N*-diethylprop-2-en-1-amine (**Ia**) with butylmagnesium chloride (Scheme 1, Table 1). The reaction catalyzed by 3 mol % of $Fe(acac)_3$ in conventional ether solvents (tetrahydrofuran or diglyme) gave the corresponding cross-coupling product, (2*E*)-*N*,*N*-diethylhept-2-en-1-amine (**IIa**) in 60–62% yield (Table 1, run nos. 1, 2). When the reaction of the same compounds was carried out in THF–NMP mixtures, the yield of amine **IIa** increased as the concentration of NMP rose, and it attained its maximum value in the presence of 6 equiv of NMP. Further raising the NMP concentration led to reduction of the yield of **IIa** (63% in pure NMP; Table 1, run nos. 3–10). The lower yield of **IIa** at low NMP concentrations was determined by incomplete conversion of the substrate, whereas high NMP concentration favored formation of by-products in addition to incomplete conversion. Reduction of the amount of $Fe(acac)_3$ to 1 mol % almost did not affect the yield of allylic amine **IIa** within the experimental error (Table 1, run no. 11). The process is characterized by a high rate, and the yield of **IIa** reaches 84% in the first 15 min (Table 1, run nos. 13, 14). The yield of (2*E*)-*N*,*N*-diethylhept-2-en-1-amine (**IIa**) in the absence of a catalyst was as poor as 3% (Table 1, run no. 12). The use of palladium catalysts (Kumada reaction) gave much worse results (Table 1, run nos. 15, 16), presumably due to low reactivity of vinyl chloride **Ia** in the rate-determining step (oxidative addition to zero-valent palladium).

Under the optimal conditions thus determined butylmagnesium chloride was brought into reactions with various stereochemically pure *E*- and *Z*-isomeric tertiary and secondary 3-chloroprop-2-en-1-amines **Ia**–**Ii** (Table 2). The reactions with *E* isomers were stereospecific, and the corresponding *trans*-allylamines **IIa**–**IIe** were formed in high yields; the yields of (*Z*)-allylamines **IIf**–**IIi** were lower, and the stereoselectivity was also lower (*Z*/*E* 95:5). In order to attain the maximum yield of 3-phenylprop-2-en-1-amines **IIj**–**IIp** in the cross-couplings of 3-chloroprop-2-en-1-amines **Ib**–**Id** and **Ig**–**Ij** with phenylmagnesium bromide, somewhat increased amount of PhMgBr was necessary, and

Scheme 2.



III **Ik** **IIq**

the amount of NMP was reduced to 1 equiv, though these reactions afforded high yields even in the presence of a catalytic amount of NMP (0.02 equiv). In all cases, the reaction mixtures contained a small amount of biphenyl (product of Fe-catalyzed homocoupling of PhMgBr) which can be readily separated by chromatography. (*E*)-3-Phenylprop-2-en-1-amines **IIj**–**IIm** were formed with an appreciably higher stereoselectivity (*E*/*Z* 95:5 to 98:2), as compared to the corresponding *Z* isomers (*Z*/*E* 77:23 to 86:14). The stereoselectivity in the reactions with (*Z*)-allylamines **Ig**–**Ii**, leading to amines **IIn**–**IIp**, also decreased with increase in the steric size of the amine fragment. Cross-coupling of a secondary amine, (2*E*)-*N*-benzyl-3-chloroprop-2-en-1-amine (**Ie**), with butylmagnesium chloride smoothly produced secondary allylamine **IIe** in high yield.

On the basis of the described approach we have developed an efficient procedure for the synthesis of naftifine, (2*E*)-*N*-methyl-*N*-(naphthalen-1-ylmethyl)-3-phenylprop-2-en-1-amine. Naftifine (commercial name Exoderil) is a widely known antifungal drug which is used for the treatment of various mycoses. The cross-coupling of phenylmagnesium bromide with (2*E*)-3-chloro-*N*-methyl-*N*-(naphthalen-1-ylmethyl)-prop-2-en-1-amine (**Ik**) [prepared by allylation of *N*-methyl(naphthalen-1-yl)methanamine (**III**) with (*E*)-1,3-dichloropropene] in the presence of 1 mol % of $Fe(acac)_3$ in a mixture of THF with NMP gave naftifine (**IIq**) in 89% yield with 98% stereoselectivity (Scheme 2).

The structure, stereochemical purity, and double bond configuration of the cross-coupling products were confirmed by GLC analyses and IR, NMR, and mass spectra. The only difference between the IR spectra of the (*E*)- and (*Z*)-allylamines was the presence in the former of a strong absorption band in the region 966–976 cm^{-1}, which is typical of out-of-plane bending vibrations of C–H bonds in disubstituted *trans*-alkenes. The coupling constant for the vinylic protons in (*E*)-3-phenylprop-2-en-1-amines **IIj**–**IIm** was 15.8–15.9 Hz against 11.6–11.8 Hz for *Z* isomers **IIn**–**IIp**. A reliable proof of steric configuration of the synthesized allylamines is the downfield shift of the allylic carbon signal of *trans* isomers by 4–5 ppm relative to the corresponding signal of their *cis* isomers.

In summary, we have developed a general procedure for the synthesis of *trans*- and *cis*-allylamines via iron-catalyzed cross-coupling of Grignard reagents with stereochemically pure 3-chloroprop-2-en-1-amines prepared by allylation of amines with commercially available isomeric 1,3-dichloropropenes.

EXPERIMENTAL

The IR spectra were recorded from thin films on a Shimadzu IR Prestige-21 spectrometer with Fourier transform (10 most intense absorption bands are given). The NMR spectra were measured from solutions in $CDCl_3$ on Bruker AM-300 (300.13 MHz for ^1H and 75.47 MHz for ^{13}C) and AV-500 instruments (500.13 MHz for ^1H and 125.76 MHz for ^{13}C); the chemical shifts were determined relative to TMS (^1H) or solvent signal ($CDCl_3$, δ_C 77.0 ppm).

GC/MS analysis was performed on a Shimadzu GCMS-QP2010S instrument (electron impact, 70 eV; a.m.u. range 33–350; HP-1MS capillary column, 30 m×0.25 mm, film thickness 0.25 μm; injector temperature 280°C, ion source temperature 200°C; oven temperature programming from 50 to 300°C at a rate of 10 deg/min; carrier gas helium, flow rate 1.1 mL/min); given are the molecular ion peak and 10 most abundant fragment ion peaks. The elemental compositions were determined from the high-resolution mass spectra which were recorded on a Finnigan MAT 95XP instrument.

Solutions of Grignard compounds in THF were prepared as described in [34], and their concentration was determined by acid–base titration [35] or by titration with salicylaldehyde phenylhydrazone [36]. (*E*)- and (*Z*)-3-Chloroprop-2-en-1-amines **Ia**–**Ij** were synthesized according to the procedures reported in

[22]. *N*-Methyl(naphthalen-1-yl)methanamine hydrochloride was commercial product (Sigma–Aldrich).

(2*E*)-*N*,*N*-Diethylhept-2-en-1-amine (IIa). A solution of 0.192 g (1.3 mmol) of (2*E*)-3-chloro-*N*,*N*-diethylprop-2-en-1-amine (**Ia**) and 9.2 mg (2 mol %) of $Fe(acac)_3$ in a mixture of 2 mL of THF and 0.8 mL of NMP was cooled to 0°C, 1.7 mL of a 1 M solution of BuMgCl in THF was slowly added dropwise under argon, and the mixture was stirred for 1.5 h at room temperature. The mixture was treated with 1 mL of water and 5 mL of diethyl ether, the organic layer was separated, the aqueous layer was extracted with diethyl ether (2×3 mL), and the extracts were combined with the organic phase, washed with brine, dried over Na_2SO_4, and concentrated. The product was isolated by silica gel column chromatography using hexane–ethyl acetate (9:1 to 3:1) as eluent. Yield 0.183 g (83%), oily substance. IR spectrum, ν, cm^{-1}: 2963, 2926, 2872, 2795, 1703, 1456, 1381, 1292, 1200, 970. ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, 7-H, *J* = 7 Hz), 1.02 t (6H, C**H**$_3$CH$_2$N, *J* = 7.2 Hz), 1.30–1.36 m (4H, 5-H, 6-H), 2.03 q (2H, 4-H, *J* = 6.8 Hz), 2.52 q (4H, CH_2N, *J* = 7.2 Hz), 3.04 d (2H, 1-H, *J* = 6.3 Hz), 5.43–5.62 m (2H, 2-H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 11.57 (**C**H$_3$CH$_2$N), 13.87 (C^7), 22.14 (C^6), 31.43 and 32.03 (C^4, C^5), 46.35 (CH_2N), 55.13 (C^1), 126.73 (C^2), 133.95 (C^3). Mass spectrum, *m*/*z* (I_{rel}, %): 169 (7) $[M]^+$, 154 (31), 97 (14), 86 (33), 73 (21), 72 (14), 58 (100), 56 (17), 55 (82), 42 (12), 41 (18). Found: *m*/*z* 169.1822 $[M]^+$. $C_{11}H_{23}N$. Calculated: *M* 169.1830.

Compounds **IIb**–**IIi** were synthesized in a similar way.

1-[(2*E*)-Hept-2-en-1-yl]piperidine (IIb) was synthesized from amine **Ib**. Yield 0.189 g (80%), oily substance. IR spectrum, ν, cm^{-1}: 2932, 2853, 2793, 2752, 1466, 1454, 1155, 1119, 1107, 972. ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, 7-H, *J* = 7 Hz), 1.23–1.65 m (10H, 5-H, 6-H, 3′-H, 4′-H, 5′-H), 2.03 q (2H, 4-H, *J* = 6.7 Hz), 2.35 br.s (4H, 2′-H, 6′-H), 2.89 d (2H, 1-H, *J* = 6.6 Hz), 5.44–5.61 m (2H, 2-H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 13.80 (C^7), 22.12 (C^6), 24.34 (C$^{4'}$), 25.87 (C$^{3'}$, C$^{5'}$), 31.32 and 31.95 (C^4, C^5), 54.30 (C$^{2'}$, C$^{6'}$), 61.69 (C^1), 126.54 (C^2), 134.09 (C^3). Mass spectrum, *m*/*z* (I_{rel}, %): 181 (11) $[M]^+$, 180 (20), 138 (15), 124 (33), 110 (14), 98 (67), 85 (90), 84 (100), 55 (50), 42 (20), 41 (32). Found: *m*/*z* 181.1835 $[M]^+$. $C_{12}H_{23}N$. Calculated: *M* 181.1830.

4-[(2*E*)-Hept-2-en-1-yl]morpholine (IIc) was synthesized from amine **Ic**. Yield 0.201 g (84%), oily substance. IR spectrum, ν, cm^{-1}: 2958, 2927, 2855, 2806, 1683, 1454, 1121, 1005, 974, 867. ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, 7-H, *J* = 6.9 Hz), 1.23–1.41 m (4H, 5-H, 6-H), 2.04 q (2H, 4-H, *J* = 6.6 Hz), 2.44 t (4H, CH_2N, *J* = 4.5 Hz), 2.94 d (2H, 1-H, *J* = 6.3 Hz), 3.72 t (4H, CH_2O, *J* = 4.5 Hz), 5.41–5.66 m (2H, 2-H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 13.79 (C^7), 22.09 (C^6), 31.24 and 31.93 (C^4, C^5), 53.28 (CH_2N), 61.18 (C^1), 66.76 (CH_2O), 125.26 (C^2), 135.32 (C^3). Mass spectrum, *m*/*z* (I_{rel}, %): 183 (6) $[M]^+$, 126 (18), 110 (30), 100 (25), 96 (22), 87 (100), 86 (42), 56 (23), 55 (62), 42 (17), 41 (31). Found: *m*/*z* 183.1633 $[M]^+$. $C_{11}H_{21}NO$. Calculated: *M* 183.1623.

1-[(2*E*)-Hept-2-en-1-yl]pyrrolidine (IId) was synthesized from amine **Id**. Yield 0.178 g (82%), oily substance. IR spectrum, ν, cm^{-1}: 2958, 2926, 2872, 2783, 1699, 1458, 1377, 1346, 1144, 970. ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, 7-H, *J* = 7 Hz), 1.26–1.39 m (4H, 5-H, 6-H), 1.72–1.80 m (4H, 3′-H, 4′-H), 2.02 q (2H, 4-H, *J* = 6.7 Hz), 2.44–2.54 m (4H, 2′-H, 5′-H), 3.02 d (2H, 1-H, *J* = 6.6 Hz), 5.46–5.59 m (2H, 2-H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 13.82 (C^7), 22.09 (C^6), 23.29 (C$^{3'}$, C$^{4'}$), 31.32 and 31.92 (C^4, C^5), 53.75 (C$^{2'}$, C$^{5'}$), 58.22 (C^1), 127.27 (C^2), 133.32 (C^3). Mass spectrum, *m*/*z* (I_{rel}, %): 167 (14) $[M]^+$, 166 (25), 124 (27), 110 (62), 84 (90), 71 (76), 70 (100), 55 (46), 43 (19), 42 (33), 41 (32). Found: *m*/*z* 167.1663 $[M]^+$. $C_{11}H_{21}N$. Calculated: *M* 167.1674.

(2*E*)-*N*-Benzylhept-2-en-1-amine (IIe) was synthesized from amine **Ie**. Yield 0.234 g (89%), oily substance. IR spectrum, ν, cm^{-1}: 2957, 2926, 2872, 2857, 1480, 1454, 1120, 970, 733, 698. ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, 7-H, *J* = 7 Hz), 1.25–1.38 m (4H, 5-H, 6-H), 1.46 br.s (1H, NH), 2.03 q (2H, 4-H, *J* = 6.5 Hz), 3.21 d (2H, 1-H, *J* = 6.4 Hz), 3.77 s (2H, PhC**H**$_2$), 5.48–5.63 m (2H, 2-H, 3-H), 7.21–7.35 m (5H, H$_{arom}$). ^{13}C NMR spectrum, δ_C, ppm: 13.84 (C^7), 22.11 (C^6), 31.37 and 31.97 (C^4, C^5), 51.08 (C^1), 53.18 (Ph**C**H$_2$), 126.79 (C^2), 127.99 (CH$_{arom}$), 128.11 (2C, CH$_{arom}$), 128.29 (2C, CH$_{arom}$), 132.94 (C^3), 140.31 (C$_{arom}$). Mass spectrum, *m*/*z* (I_{rel}, %): 203 (3) $[M]^+$, 146 (12), 108 (23), 106 (24), 92 (11), 91 (100), 81 (8), 65 (10), 55 (12), 54 (9), 41 (10).

(2*Z*)-*N*,*N*-Diethylhept-2-en-1-amine (IIf) was synthesized from amine **If**. Yield 0.167 g (76%), oily substance. IR spectrum, ν, cm^{-1}: 2960, 2930, 2873, 2797, 1685, 1466, 1382, 1200, 1168, 1068. ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, 7-H, *J* = 7 Hz), 1.04 t (6H, C**H**$_3$CH$_2$N, *J* = 7.1 Hz), 1.31–1.36 m (4H, 5-H, 6-H), 2.07 q (2H, 4-H, *J* = 6.8 Hz), 2.52 q (4H, CH_2N, *J* = 7.1 Hz), 3.11 d (2H, 1-H, *J* = 6.4 Hz), 5.44–5.55 m

(2H, 2-H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 11.71 (**C**H_3CH_2N), 13.93 (C^7), 22.29 (C^6), 27.18 (C^4), 31.80 (C^5), 46.62 (CH_2N), 49.51 (C^1), 126.59 (C^2), 132.50 (C^3). Mass spectrum, *m*/*z* (I_{rel}, %): 169 (4) $[M]^+$, 154 (14), 86 (19), 73 (25), 72 (13), 58 (100), 56 (10), 55 (45), 43 (5), 42 (8), 41 (12). Found: *m*/*z* 169.1825 $[M]^+$. $C_{11}H_{23}N$. Calculated: *M* 169.1830.

1-[(2*Z*)-Hept-2-en-1-yl]piperidine (IIg) was synthesized from amine **Ig**. Yield 0.183 g (78%), oily substance. IR spectrum, ν, cm^{-1}: 2931, 2855, 2778, 2745, 1466, 1452, 1298, 1153, 1117, 1107. ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, 7-H, *J* = 7 Hz), 1.24–1.65 m (10H, 5-H, 6-H, 3′-H, 4′-H, 5′-H), 2.05 q (2H, 4-H, *J* = 6.7 Hz), 2.38 br.s (4H, 2′-H, 6′-H), 2.97 d (2H, 1-H, *J* = 6.6 Hz), 5.43–5.60 m (2H, 2-H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 13.91 (C^7), 22.27 (C^6), 24.31 ($C^{4'}$), 25.92 ($C^{3'}$, $C^{5'}$), 27.12 (C^4), 31.71 (C^5), 54.47 ($C^{2'}$, $C^{6'}$), 55.85 (C^1), 126.34 (C^2), 132.75 (C^3). Mass spectrum, *m*/*z* (I_{rel}, %): 181 (5) $[M]^+$, 124 (9), 98 (22), 86 (8), 85 (67), 84 (100), 55 (22), 44 (10), 43 (7), 42 (12), 41 (19).

4-[(2*Z*)-Hept-2-en-1-yl]morpholine (IIh) was synthesized from amine **Ih**. Yield 0.191 g (80%), oily substance. IR spectrum, ν, cm^{-1}: 2958, 2929, 2856, 2802, 1685, 1455, 1292, 1119, 1008, 866. ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, 7-H, *J* = 7 Hz), 1.25–1.41 m (4H, 5-H, 6-H), 2.07 q (2H, 4-H, *J* = 6.7 Hz), 2.46 t (4H, CH_2N, *J* = 4.5 Hz), 3.01 d (2H, 1-H, *J* = 6.4 Hz), 3.72 t (4H, CH_2O, *J* = 4.5 Hz) 5.40–5.62 m (2H, 2-H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 13.87 (C^7), 22.22 (C^6), 27.13 (C^4), 31.61 (C^5), 53.51 (CH_2N), 55.38 (C^1), 66.90 (CH_2O), 125.13 (C^2), 133.79 (C^3). Mass spectrum, *m*/*z* (I_{rel}, %): 183 (4) $[M]^+$, 110 (13), 100 (12), 87 (100), 86 (48), 57 (40), 56 (15), 55 (34), 54 (17), 42 (12), 41 (22).

1-[(2*Z*)-Hept-2-en-1-yl]pyrrolidine (IIi) was synthesized from amine **Ii**. Yield 0.162 g (74%), oily substance. IR spectrum, ν, cm^{-1}: 2959, 2927, 2873, 2782, 1696, 1460, 1378, 1345, 1199, 1141. ^{1}H NMR spectrum, δ, ppm: 0.90 t (3H, 7-H, *J* = 7 Hz), 1.26–1.37 m (4H, 5-H, 6-H), 1.73–1.80 m (4H, 3′-H, 4′-H), 2.07 q (2H, 4-H, *J* = 6.6 Hz), 2.45–2.54 m (4H, 2′-H, 5′-H), 3.12 d (2H, 1-H, *J* = 6.6 Hz), 5.43–5.59 m (2H, 2-H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 13.88 (C^7), 22.24 (C^6), 23.38 ($C^{3'}$, $C^{4'}$), 27.09 (C^4), 31.68 (C^5), 52.47 (C^1), 53.96 ($C^{2'}$, $C^{5'}$), 126.88 (C^2), 131.82 (C^3). Mass spectrum, *m*/*z* (I_{rel}, %): 167 (6) $[M]^+$, 110 (16), 84 (30), 72 (10), 71 (67), 70 (100), 55 (21), 54 (8), 43 (18), 42 (16), 41 (19).

1-[(2*E*)-3-Phenylprop-2-en-1-yl]piperidine (IIj). A solution of 0.207 g (1.3 mmol) of 1-[(2*E*)-3-chloroprop-2-en-1-yl]piperidine (**Ib**) and 4.6 mg (1 mol %) of $Fe(acac)_3$ in a mixture of 2 mL THF and 0.1 mL of NMP was cooled to 0°C, 2.1 mL of a 1 M solution of PhMgBr in THF was slowly added dropwise under argon, and the mixture was stirred for 1.5 h at room temperature. The mixture was treated with 1 mL of water and 5 mL of diethyl ether, the organic layer was separated, and the aqueous layer was extracted with diethyl ether (2×3 mL). The extracts were combined with the organic phase, washed with brine, dried over Na_2SO_4, and concentrated, and the residue was subjected to silica gel column chromatography using hexane–ethyl acetate (9 : 1 to 3 : 1) as eluent. Yield 0.232 g (89%), oily substance. IR spectrum, ν, cm^{-1}: 2934, 2853, 2794, 2755, 1443, 1154, 1111, 966, 738, 692. ^{1}H NMR spectrum, δ, ppm: 1.37–1.70 m (6H, 3′-H, 4′-H, 5′-H), 2.43 br.s (4H, 2′-H, 6′-H), 3.11 d (2H, 1-H, *J* = 6.6 Hz), 6.30 d.t (1H, 2-H, J_{trans} = 15.9, 6.6 Hz), 6.49 d (1H, 3-H, J_{trans} = 15.9 Hz), 7.18–7.45 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 24.21 ($C^{4'}$), 25.86 ($C^{3'}$, $C^{5'}$), 54.47 ($C^{2'}$, $C^{6'}$), 61.75 (C^1), 126.16 (2C, CH_{arom}), 127.12 (C^2), 127.24 (CH_{arom}), 128.41 (2C, CH_{arom}), 132.52 (C^3), 136.98 (C_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 201 (14) $[M]^+$, 200 (14), 117 (44), 115 (31), 110 (100), 98 (21), 91 (16), 84 (13), 55 (9), 42 (12), 41 (12). Found: *m*/*z* 201.1524 $[M]^+$. $C_{14}H_{19}N$. Calculated: *M* 201.1517.

Compounds **IIk**–**IIq** were synthesized in a similar way.

4-[(2*E*)-3-Phenylprop-2-en-1-yl]morpholine (IIk) was synthesized from amine **Ic**. Yield 0.243 g (92%), oily substance. IR spectrum, ν, cm^{-1}: 2957, 2854, 2806, 1452, 1118, 1007, 968, 869, 740, 693. ^{1}H NMR spectrum, δ, ppm: 2.49 t (4H, CH_2N, *J* = 4.6 Hz), 3.14 d (2H, 1-H, *J* = 6.8 Hz), 3.73 t (4H, CH_2O, *J* = 4.6 Hz), 6.25 d.t (1H, 2-H, J_{trans} = 15.8, 6.8 Hz), 6.53 d (1H, 3-H, J_{trans} = 15.8 Hz), 7.19–7.45 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 53.54 (CH_2N), 61.30 (C^1), 66.81 (CH_2O), 125.92 (C^2), 126.19 (2C, CH_{arom}), 127.42 (CH_{arom}), 128.44 (2C, CH_{arom}), 133.23 (C^3), 136.68 (C_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 203 (23) $[M]^+$, 144 (12), 118 (13), 117 (67), 116 (11), 115 (45), 112 (100), 104 (11), 91 (23), 86 (16), 56 (34). Found: *m*/*z* 203.1321 $[M]^+$. $C_{13}H_{17}NO$. Calculated: *M* 203.1310.

1-[(2*E*)-3-Phenylprop-2-en-1-yl]pyrrolidine (IIl) was synthesized from amine **Id**. Yield 0.218 g (90%), oily substance. IR spectrum, ν, cm^{-1}: 2965, 2874, 2785, 1690, 1497, 1346, 1140, 966, 739, 692. ^{1}H NMR spectrum, δ, ppm: 1.74–1.86 m (4H, 3′-H, 4′-H), 2.49–2.60 m (4H, 2′-H, 5′-H), 3.26 d (2H, 1-H, *J* = 6.6 Hz),

6.33 d.t (1H, 2-H, J_{trans} = 15.8, 6.6 Hz), 6.53 d (1H, 3-H, J_{trans} = 15.8 Hz), 7.18–7.46 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 23.38 ($C^{3'}$, $C^{4'}$), 54.00 ($C^{2'}$, $C^{5'}$), 58.33 (C^1), 126.20 (2C, CH_{arom}), 127.24 (C^2), 127.70 (CH_{arom}), 128.43 (2C, CH_{arom}), 131.71 (C^3), 137.05 (C_{arom}). Mass spectrum, *m/z* (I_{rel}, %): 187 (10) $[M]^+$, 186 (13), 117 (38), 115 (36), 110 (11), 96 (100), 91 (18), 84 (23), 44 (62), 42 (17), 40 (21).

(2*E*)-*N*-Benzyl-*N*-methyl-3-phenylprop-2-en-1-amine (IIm) was synthesized from amine **Ij**. Yield 0.283 g (92%), oily substance. IR spectrum, ν, cm^{-1}: 3026, 2785, 1495, 1451, 1365, 1024, 968, 736, 698, 693. ^1H NMR spectrum, δ, ppm: 2.24 s (3H, CH_3N), 3.19 d (2H, 1-H, J = 6.6 Hz), 3.55 s (2H, Ph**C**$\mathbf{H}_2$), 6.31 d.t (1H, 2-H, J_{trans} = 15.9, 6.6 Hz), 6.54 d (1H, 3-H, J_{trans} = 15.9 Hz), 7.17–7.44 m (10H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 42.16 (CH_3N), 59.81 (C^1), 61.81 (Ph**C**H_2), 126.25 (2C, CH_{arom}), 126.97 (C^2), 127.33 (CH_{arom}), 127.48 (CH_{arom}), 128.23 (2C, CH_{arom}), 128.49 (2C, CH_{arom}), 129.09 (2C, CH_{arom}), 132.57 (C^3), 137.03 (C_{arom}), 138.83 (C_{arom}). Mass spectrum, *m/z* (I_{rel}, %): 237 (12) $[M]^+$, 236 (8), 147 (10), 146 (88), 118 (9), 117 (43), 115 (29), 92 (11), 91 (100), 65 (14), 42 (68).

1-[(2*Z*)-3-Phenylprop-2-en-1-yl]piperidine (IIn) was synthesized from amine **Ig**. Yield 0.209 g (80%), oily substance. IR spectrum, ν, cm^{-1}: 2933, 2853, 2781, 2745, 1443, 1298, 1153, 1113, 770, 698. ^1H NMR spectrum, δ, ppm: 1.36–1.69 m (6H, 3′-H, 4′-H, 5′-H), 2.40 br.s (4H, 2′-H, 6′-H), 3.25 d (2H, 1-H, J = 6.4 Hz), 5.82 d.t (1H, 2-H, J_{cis} = 11.6, 6.4 Hz), 6.55 d (1H, 3-H, J_{cis} = 11.6 Hz), 7.20–7.43 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 24.21 ($C^{4'}$), 25.91 ($C^{3'}$, $C^{5'}$), 54.61 ($C^{2'}$, $C^{6'}$), 57.02 (C^1), 126.67 (CH_{arom}), 128.02 (2C, CH_{arom}), 128.83 (2C, CH_{arom}), 130.18 (C^2), 130.70 (C^3), 137.19 (C_{arom}). Mass spectrum, *m/z* (I_{rel}, %): 201 (11) $[M]^+$, 200 (16), 118 (9), 117 (41), 115 (32), 110 (100), 98 (25), 91 (17), 84 (17), 42 (14), 41 (14).

4-[(2*Z*)-3-Phenylprop-2-en-1-yl]morpholine (IIo) was synthesized from amine **Ih**. Yield 0.217 g (82%), oily substance. IR spectrum, ν, cm^{-1}: 2956, 2857, 2803, 1452, 1119, 1076, 1007, 783, 739, 700. ^1H NMR spectrum, δ, ppm: 2.45 t (4H, CH_2N, J = 4.5 Hz), 3.27 d (2H, 1-H, J = 6.4 Hz), 3.71 t (4H, CH_2O, J = 4.5 Hz), 5.77 d.t (1H, 2-H, J_{cis} = 11.8, 6.4 Hz), 6.59 d (1H, 3-H, J_{cis} = 11.8 Hz), 7.18–7.45 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 53.57 (CH_2N), 56.48 (C^1), 66.87 (OCH_2), 126.85 (CH_{arom}), 128.05 (2C, CH_{arom}), 128.77 (2C, CH_{arom}), 128.86 (C^2), 131.59 (C^3), 136.86 (C_{arom}). Mass spectrum, *m/z* (I_{rel}, %): 203 (17) $[M]^+$, 202 (12), 144 (14), 118 (13), 117 (65), 115 (43), 112 (100), 100 (14), 91 (24), 86 (16), 56 (25).

1-[(2*Z*)-3-Phenylprop-2-en-1-yl]pyrrolidine (IIp) was synthesized from amine **Ii**. Yield 0.211 g (87%), oily substance. IR spectrum, ν, cm^{-1}: 2965, 2874, 2785, 1695, 1495, 1344, 1142, 773, 739, 700. ^1H NMR spectrum, δ, ppm: 1.73–1.86 m (4H, 3′-H, 4′-H), 2.47–2.59 m (4H, 2′-H, 5′-H), 3.40 d (2H, 1-H, J = 6.4 Hz), 5.85 d.t (1H, 2-H, J_{cis} = 11.8, 6.4 Hz), 6.51 d (1H, 3-H, J_{cis} = 11.8 Hz), 7.20–7.46 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 23.40 ($C^{3'}$, $C^{4'}$), 53.89 (C^1), 54.00 ($C^{2'}$, $C^{5'}$), 126.66 (CH_{arom}), 127.99 (2C, CH_{arom}), 128.82 (2C, CH_{arom}), 129.97 (C^2), 130.37 (C^3), 137.13 (C_{arom}). Mass spectrum, *m/z* (I_{rel}, %): 187 (8) $[M]^+$, 186 (16), 117 (39), 115 (34), 110 (10), 96 (100), 91 (18), 84 (28), 70 (11), 44 (14), 42 (18).

(2*E*)-*N*-Methyl-*N*-(naphthalen-1-ylmethyl)-3-phenylprop-2-en-1-amine (IIq, naftifine) was synthesized from amine **Ik**. Yield 0.332 g (89%), oily substance. IR spectrum, ν, cm^{-1}: 2786, 1495, 1450, 1363, 967, 798, 792, 775, 744, 692. ^1H NMR spectrum, δ, ppm: 2.27 s (3H, CH_3N), 3.28 d (2H, 1-H, J = 6.6 Hz), 3.94 s (2H, CH_2N), 6.36 d.t (1H, 2-H, J = 15.8, 6.6 Hz), 6.58 d (1H, 3-H, J = 15.8 Hz), 7.21–7.55 m (9H, H_{arom}), 7.77 d (1H, H_{arom}, J = 7.7 Hz), 7.84 d (1H, H_{arom}, J = 7.7 Hz), 8.30 d (1H, H_{arom}, J = 7.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 42.46 (CH_3N), 60.05 (C^1), 60.38 (CH_2N), 124.60 (CH_{arom}), 125.11 (CH_{arom}), 125.55 (CH_{arom}), 125.88 (CH_{arom}), 126.30 (2C, CH_{arom}), 127.35 (C^2), 127.44 (CH_{arom}), 127.53 (CH_{arom}), 127.92 (CH_{arom}), 128.43 (CH_{arom}), 128.52 (2C, CH_{arom}), 132.47 (C_{arom}), 132.68 (C^3), 133.88 (C_{arom}), 134.81 (C_{arom}), 137.12 (C_{arom}). Mass spectrum, *m/z* (I_{rel}, %): 287 (18) $[M]^+$, 196 (29), 182 (13), 146 (34), 142 (25), 141 (100), 117 (38), 116 (8), 115 (49), 91 (14), 42 (60). Found: *m/z* 287.1686 $[M]^+$. $C_{21}H_{21}N$. Calculated: *M* 287.1674.

(2*E*)-3-Chloro-*N*-methyl-*N*-(naphthalen-1-ylmethyl)prop-2-en-1-amine (Ik). *N*-Methyl(naphthalen-1-yl)methanamine (**III**), 1.71 g (0.01 mol), was added to a suspension of 1.22 g (0.011 mol) of (*E*)-1,3-dichloropropene and 2.07 g (0.015 mol) of K_2CO_3 in 20 mL of anhydrous acetonitrile, and the mixture was stirred for 1 h at room temperature and was then heated for 4 h under reflux until complete conversion of amine **III** (GLC). The mixture was cooled and filtered, the precipitate was washed with ethyl acetate, the filtrate was combined with the washings and concentrated, and the product was isolated by silica gel column chromatography using

hexane–ethyl acetate (9:1 to 3:1) as eluent. Yield 1.97 g (80%), oily substance. IR spectrum, ν, cm^{-1}: 2838, 2790, 1635, 1495, 1452, 1366, 1018, 934, 791, 775. ^1H NMR spectrum, δ, ppm: 2.21 s (3H, CH_3N), 3.06 d (2H, 1-H, J = 6.3 Hz), 3.86 s (2H, CH_2N), 6.04 d.t (1H, 2-H, J_{trans} = 13.3, 6.3 Hz), 6.13 d (1H, 3-H, J_{trans} = 13.3 Hz), 7.37–7.53 m (4H, H_{arom}), 7.73–7.84 m (2H, H_{arom}), 8.23 d (1H, H_{arom}, J = 7.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 42.07 (CH_3N), 57.23 (C^1), 59.81 (CH_2N), 120.14 (C^3), 124.48 (CH_{arom}), 125.05 (CH_{arom}), 125.62 (CH_{arom}), 125.86 (CH_{arom}), 127.33 (CH_{arom}), 128.05 (CH_{arom}), 128.40 (CH_{arom}), 130.83 (C^2), 132.36 (C_{arom}), 133.83 (C_{arom}), 134.40 (C_{arom}). Mass spectrum, m/z (I_{rel}, %): 247 (1) and 245 (3.5) $[M]^+$, 142 (32), 141 (98), 118 (26), 115 (69), 106 (30), 104 (100), 82 (27), 77 (24), 75 (61), 42 (79).

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