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Short Communication

Copper(II) catalyzed allylic amination of terpenic chlorides in water

Brahim Boualy [a], Mohamed Anouar Harrad [a], Soufiane El Houssame [b], Larbi El Firdoussi [a,*], Mustapha Ait Ali [a], Abdallah Karim [a]

[a] Equipe de Chimie de Coordination et Catalyse, Département de Chimie, Faculté des Sciences Semlalia, BP 2390, 40001 Marrakech, Morocco
[b] Université Hassan 1er, Faculté Polydisciplinaire de Khouribga, BP: 145-25000 Khouribga, Morocco

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ABSTRACT

A highly efficient method for the synthesis of allylic amines from terpenic chlorides by cheap copper (II) as catalyst in water has been developed. Allylic chlorides react with high regioselectivity in the presence of secondary amines, under mild conditions to give N-allylic amines in excellent yields.

1. Introduction

Allylic amines are important products found in many naturally occurring compounds such as gabaculin [1], oryzoxymicin [2], and cytosinine [3]. The development of easier and selective methods for the synthesis of allylic amines merits thorough investigation [4], since direct reaction require rather drastic conditions [5]. Transition metal-promoted allylic amination of alkenes offers an attractive route to prepare amines via C–N bond formation [6]. However, complexes of palladium are found to be most effective for selective processes, although complexes of iron, nickel, and copper are also used for allylic amination [7–9].

The catalytic activity of a number of copper complexes and salts toward allylic amination of alkenes using phenylhydroxylamine as the nitrogen fragment donor has been investigated [10]. The copper (I) complex $[Cu(CH_3CN)_4]PF_6$ catalyzes the allylic amination of alkenes by aryl hydroxylamine in fair to moderate yields [6].

Recently Clark et al. reported that asymmetric allylic amination can be achieved by reaction of an alkene with a peroxycarbamate catalyzed by a chiral copper bis-oxazoline complex [11].

An efficient method to perform the allylic substitution in water has been reported [12–14]. It should be noted that, Sinou et al. and Kobayashi et al. have reported that palladium-catalyzed alkylation also occurred in water in the presence of non-water-soluble ligands, but the addition of surfactants such as cetyltrimethylammonium bromide was required [15,16]. Moreover, Feuerstein et al. showed that Tedicyp–palladium complex provides a convenient catalyst for the allylic amination reaction in water [17].

A large number of biologically active natural compounds consist of a nitrogen-containing heterocycle and occupy a leading position in medicinal therapy [18,19]. In particular, allylic aminated terpenoids because of their effects of inhibiting tumor cell growth in vivo and vitro [20–22] and it serves as a tool for the synthesis of new enantiomerically pure compounds [23–25].

Baruah et al. have developed a new method for the conversion of allylic halides to allylic amines by using a mixture of copper (II) perchlorate and copper metal [26]. They found significant differences in the product ratios of the isomeric corresponding allylic amines formed.

In the course of our studies on monoterpenes and their derivatives, we have recently reported an extremely efficient method for the preparation of various allylic terpenic chlorides [23]. Following our catalysis objective on the coupling of various amines and natural allylic compounds [27], we herein, with a view to extend the potential use of these terpenic chlorides, focused our efforts on the allylic amination reaction using copper complexes. Our results show that monoterpenic chlorides react to give the corresponding allylic amines with a good to excellent yields. The optical purity of the reaction products has been also discussed. The use of water as solvent for this reaction is of interest in sustainable chemistry. It provides in addition noticeable advantages in terms of economical, environmental and safety reasons.

* Corresponding author. Tel.: +212 524 434649; fax: +212 524 437408.
E-mail address: elfirdoussi@ucam.ac.ma (L. El Firdoussi).

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2. Experimental section

2.1. General

Optical rotations were measured on a Perkin Elmer 241 polarimeter. NMR studies were performed on a Bruker Avance 300 spectrometer in $CDCl_3$. Chemicals shifts are given in ppm relative to external TMS and coupling constant (J) in Hz. Mass spectra were recorded on a GC–MS Varian Polaris-Q mass spectrometer. The reaction mixtures were analyzed on a Trace GC TheromFinnigan chromatograph equipped with an FID detector. GC parameters for capillary columns BP (25 m × 0.25 mm, SGE): injector 250 °C; detector 250 °C; oven 70 °C for 5 min then 3 °C min^{-1} until 250 °C for 30 min; column pressure 20 kPa, column flow 6.3 mL min^{-1}; linear velocity 53.1 cm s^{-1}; and total flow 138 mL min^{-1}. Liquid chromatography was performed on silica gel (Merk 60, 220–440 mesh; eluent: hexane/ethylacetate). EI mass spectra were recorded on an AMD 402 spectrometer (70 eV, AMD Intectra GmbH). Analytical thin-layer chromatography (TLC) was conducted on Merck aluminum plates with 0.2 mm of silica gel 60F-254. All the reagents and solvents used in the experiments were purchased from commercial sources as received without further purification (Aldrich, Acros).

2.2. Catalytic allylic amination of allylic chlorides

In a typical experiment, to a stirred solution of allylic chloride (0.5 mmol), triethylamine (0.25 mmol) and Cu(II) (0.005 mmol) in 25 mL of water was added secondary amine (1 mmol) at room temperature, and the reaction mixture was stirred for 12 h. After diluting with H_2O (25 mL) and CH_2Cl_2 (25 mL), the two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. Pure allylic amines were obtained by column chromatography over silica gel using a mixture of hexane/ethylacetate (8/2) as eluent.

2.3. 4-(2-Phenylallyl)morpholine 2a

^{1}H NMR: δ 7.6 (2H, m), 7.4 (3H, m), 5.6 (1H, s), 5.5 (1H, s), 3.2 (2H, s), 2.1 (4H, m), 1.6 (4H, m); ^{13}C NMR: δ 143.6 (Cq), 140.0 (C═), 128.4 (CH ar), 126.6 (CH), 125.0 (CH), 115.3 (CH_2═), 63.8 (CH_2–O), 60.5 (CH_2–N), 53.2 (CH_2–N); MS, m/z: 203 (M+, 100).

2.4. 1-(2-Phenylallyl)pyrrolidine 2b

^{1}H NMR: δ 7.6 (2H, m); 7.4 (3H, m); 5.6 (1H, s); 5.5 (1H, s); 3.4 (2H, s); 3.6 (4H, m); 2.4 (4H, m); ^{13}C NMR: δ 143.4 (Cq), 139.7 (Cq) 127.8 (CH), 125.6 (CH), 124.0 (CH), 115.3 (CH_2═), 66.8 (CH_2–N), 60.4 (CH_2–N), 24.2 (CH_2); MS, m/z: 187 (M+, 100).

2.5. N,N-diethyl-2-phenylprop-2-en-1-amine 2c

^{1}H NMR: δ 7.4 (2H, m), 7.3 (3H, m), 5.7 (1H, s), 5.6 (1H, s), 3.0 (2H, s), 2.4 (4H, q, J = 7.11), 0.9 (6H, t, J = 7.11); ^{13}C NMR: δ 145.2 (Cq), 140.1 (Cq), 127.2 (CH), 125.2 (CH), 124.0 (CH), 114.3 (CH_2═), 60.8 (CH_2–N), 54.4 (CH_2–N), 15.2 (–CH_3); MS, m/z: 189 (M+, 100).

2.6. 1-(4-Isopropenylcyclohex-1-enylmethyl)pyrrolidine 4a

$[\alpha]_D^{20} = -13.3$ (c = 2.1, $CHCl_3$); ^{1}H NMR: δ 5.7 (1H, m), 5.1 (2H, m), 3.1 (2H, s), 2.6 (4H, m), 1.8 (3H, s), 1.6 (4H, m); ^{13}C NMR: δ 148.6 (Cq), 137.7 (CH═), 122.3 (Cq), 109.1 (CH_2═), 64.1 (CH_2–N), 62.2 (CH_2–N), 41.3 (–CH–), 31.4 (–CH_2–), 28.3 (–CH_2–), 28.2 (–CH_2–), 22.9 (–CH_2–), 20.5 (–CH_3); MS, m/z: 205 (M+, 100).

2.7. 4-(4-Isopropenylcyclohex-1-enylmethyl)morpholine 4b

$[\alpha]_D^{20} = -21.1$ (c = 1.5, $CHCl_3$); ^{1}H NMR: δ 5.6 (1H, m), 4.7 (2H, m), 3.6 (4H, m), 2.8 (2H, s), 2.3 (4H, m), 1.6 (3H, s); ^{13}C NMR: δ 149.3 (Cq), 134.5 (CH═), 124.3 (Cq), 108.5 (CH_2═), 66.8 (O–CH_2–), 65.8 (CH_2–N), 53.5 (CH_2–N), 41.1 (CH–), 31.4 (–CH_2–), 27.3 (–CH_2–), 27.3 (–CH_2–), 21.1 (–CH_3); MS, m/z: 221 (M+, 100).

2.8. N-ethyl-N-((4-(prop-1-en-2-yl)cyclohex-1-enyl)methyl)ethanamine 4c

$[\alpha]_D^{20} = -9.3$ (c = 1.5, $CHCl_3$). ^{1}H NMR: δ 5.6 (1H, m), 4.9 (2H, m), 3.1 (2H, s), 2.6 (4H, q, J = 7.18), 1.7 (3H, s), 1.1 (6H, t, J = 7.18); ^{13}C NMR: δ 149.1 (Cq), 134.7 (CH═), 124.3 (Cq), 109.1 (CH_2═), 63.8 (CH_2–N), 53.1 (CH_2–N), 41.2 (–CH–), 31.3 (–CH_2–), 27.3 (–CH_2–), 27.2 (–CH_2–), 20.2 (–CH_3), 15.1 (–CH_3); MS, m/z: 207 (M+, 100).

2.9. 2-Methyl-5-(1-pyrrolidin-1-ylmethylvinyl)cyclohex-2-enone 6a

$[\alpha]_D^{20} = -57.4$ (c = 2.1, $CHCl_3$); ^{1}H NMR: δ 6.55 (1H, m), 5.20 (1H, s), 5.10 (1H, s), 3.12 (2H, m), 2.92 (2H, s), 2.61 (4H, m), 2.38 (3H, s), 1.6 (4H, m); ^{13}C NMR: δ 199.5 (C═O), 146.5 (Cq), 144.2 (CH═), 132.8 (Cq), 112.7 (CH_2═), 63.4; 62.1 (CH_2–N), 44.2 (CH_2–N), 39.7 (–CH–), 31.2 (–CH_2–), 23.4 (–CH_2–), 16.5 (–CH_3); MS, m/z: 219 (M+, 100).

2.10. 2-Methyl-5-(1-morpholin-4-ylmethylvinyl)cyclohex-2-enone 6b

$[\alpha]_D^{20} = -53.9$ (c = 2.5, $CHCl_3$); ^{1}H NMR: δ 6.35 (1H, m), 5.22 (1H, s), 5.13 (1H, s), 3.82 (4H, m), 3.10 (2H, s), 2.84 (2H, m), 2.58 (4H, m), 2.38 (3H, s); ^{13}C NMR: δ 198.6 (C═O), 146.5 (Cq), 143.2 (CH═), 132.9 (Cq), 112.2 (CH_2–), 66.8 (CH_2–O), 62.1 (CH_2–N), 59.2 (CH_2–N), 44.2 (–CH–) 40.7 (–CH_2–), 32.2 (–CH_2–), 17.5 (–CH_3); MS, m/z: 235 (M+, 100).

2.11. 5-(3-(diethylamino)prop-1-en-2-yl)-2-methylcyclohex-2-enone 6c

$[\alpha]_D^{20} = -55.2$ (c = 2.5, $CHCl_3$); ^{1}H NMR: δ 6.45 (1H, m), 5.32 (1H, s), 5.22 (1H, s), 3.02 (2H, m), 2.88 (2H, m), 2.61 (4H, q, J = 7.23), 2.31 (3H, s), 1.08 (6H, t, J = 7.23); ^{13}C NMR: δ 199.7 (C═O), 146.4 (Cq), 145.0 (–CH═), 132.1 (Cq), 110.9 (CH_2═), 63.1 (CH_2–N), 53.3 (CH_2–N), 44.3 (–CH–), 38.7 (–CH_2–), 31.2 (–CH_2–), 17.4 (–CH_3), 14.8 (–CH_3); MS, m/z: 221 (M+, 100).

2.12. 1-(3,7-Dimethylocta-2,6-dienyl)pyrrolidine 8a

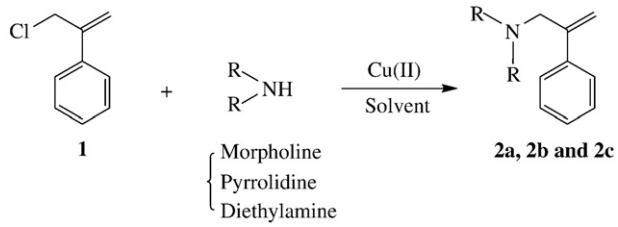
^{1}H NMR: δ 5.32 (1H, t, J = 6.8 Hz), 5.12 (1H, t, J = 6.7 Hz), 2.79 (2H, d, J = 6.7 Hz), 2.53 (4H, m), 2 (2H, m), 1.94 (2H, m), 1.75 (4H, m), 1.68 (3H, s), 1.62 (3H, s), 1.50 (3H, s); ^{13}C NMR: δ 139.7 (Cq), 133.9 (Cq), 124.2 (CH═), 121.9 (CH═), 62.3 (CH_2–N), 58.0 (CH_2–N), 39.7 (–CH_2–), 26.4 (–CH_2–), 25.7 (–CH_2–), 23.7 (–CH_3), 17.3 (–CH_3), 15.7 (–CH_3); MS, m/z: 207 (M+, 100).

2.13. 4-(3,7-Dimethylocta-2,6-dienyl)morpholine 8b

^{1}H NMR: δ 5.32 (1H, t, J = 6.8 Hz), 5.12 (1H, t, J = 6.7 Hz), 3.6 (4H, m), 2.87 (2H, d, J = 6.7 Hz), 2.53 (4H, m), 2 (2H, m), 1.94 (2H, m), 1.68 (3H, s), 1.62 (3H, s), 1.50 (3H, s); ^{13}C NMR: δ 139.7 (Cq), 133.9 (Cq), 124.2 (CH═), 121.9 (CH═), 66.8 (O–CH_2), 62.3 (CH_2–N), 54.0 (CH_2–N), 41.1 (–CH_2–), 26.4 (–CH_2–), 25.7 (–CH_3), 22.7 (–CH_3), 17.3 (–CH_3); MS, m/z: 223 (M+, 100).

2.14. N,N-diethyl-3,7-dimethylocta-2,6-dien-1-amine 8c

^{1}H NMR: δ 5.32 (1H, t, J = 6.8 Hz), 5.12 (1H, t, J = 6.7 Hz), 2.83 (2H, d, J = 6.7 Hz), 2.61 (4H, q, J = 7.13), 2 (2H, m), 1.94 (2H, m), 1.68 (3H, s),



Scheme 1. Allylic amination of styrene chloride **1**.

1.62 (3H, s), 1.50 (3H, s), 0.92 (6H, t, J = 7.13); ^{13}C NMR: δ 139.7 (Cq), 133.9 (Cq), 124.2 (CH=), 121.9 (CH=), 52.3 (CH_2–N), 48.0 (CH_2–N), 26.4 (–CH_2–); 23.7 (–CH_2–), 19.3 (–CH_3), 16.7 (–CH_3), 15.3 (–CH_3); MS, m/z: 209 (M+, 100).

2.15. 1-(5-Isopropenyl-2-methylcyclohex-2-enyl)pyrrolidine 10a

$[\alpha]_D^{20} = 0$ (c = 1.5, $CHCl_3$); ^{1}H NMR: δ 5.6 (1H, m), 4.8 (2H, m), 2.9 (1H, m), 2.6 (4H, m), 2.15 (1H, m), 2.05 (2H, m), 1.9 (2H, m), 1.8 (4H, m), 1.6 (3H, s), 1.5 (3H, s); ^{13}C NMR: δ 150.2 (Cq), 143.2 (CH=), 124.4 (Cq), 109.5 (CH_2=), 62.5 (CH–N), 54.8 (CH_2–N), 37.8 (–CH–), 31.2 (–CH_2–), 30.6 (–CH_2–), 23.7 (–CH_2–), 22.3 (–CH_3), 20.8 (–CH_3); MS, m/z: 205 (M+, 100).

2.16. 4-(5-Isopropenyl-2-methylcyclohex-2-enyl)morpholine 10b

$[\alpha]_D^{20} = 0$ (c = 1.7, $CHCl_3$); ^{1}H NMR: δ 5.5 (1H, m), 4.8 (2H, m), 3.4 (4H, m), 3.1 (1H, m), 2.6 (4H, m), 2.15 (1H, m), 2.05 (2H, m), 1.9 (2H, m), 1.6 (3H, s), 1.5 (3H, s); ^{13}C NMR: δ 150.2 (Cq), 143.2 (CH=), 124.4 (Cq), 110.5 (CH_2=), 66.7 (O–CH_2–), 63.5 (–CH–N), 56.8 (N–CH_2–), 37.8 (–CH–), 31.2 (–CH_2–), 30.6 (–CH_2–), 22.3 (–CH_3), 20.8 (–CH_3); MS, m/z: 221 (M+, 100).

2.17. N,N-diethyl-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enamine 10c

$[\alpha]_D^{20} = 0$ (c = 1.5, $CHCl_3$); ^{1}H NMR: δ 5.4 (1H, m), 4.8 (2H, m), 2.9 (1H, m), 2.4 (4H, q, J = 7.2), 2.15 (1H, m), 2.05 (2H, m), 1.9 (2H, m), 1.6 (3H, s), 1.5 (3H, s), 1.1 (6H, t, J = 7.2); ^{13}C NMR: δ 149.2 (Cq), 142.2 (CH=), 124.4 (Cq), 109.5 (CH_2=), 62.5 (CH–N), 49.8 (CH_2–N), 37.8 (–CH–), 31.2 (–CH_2–), 30.6 (–CH_2–), 22.7 (–CH_3), 22.3 (–CH_3), 14.8 (–CH_3); MS, m/z: 207 (M+, 100).

Table 1
Effect of catalyst and solvent on the allylic amination of **1**.[a]

Entry	Solvent	Catalyst	Time (h)	Conversion[b] (%)	Yield[c] (%)
1	H_2O	None	72	0	0
2	THF	$CuCl_2$	48	49	35
3	THF	$Cu(Otf)_2$	24	66	63
4	H_2O	$CuCl_2$	48	96	93
5	H_2O	$Cu(Otf)_2$	24	100	97
6	Dioxane	$CuCl_2$	48	72	70
7	Dioxane	$Cu(Otf)_2$	24	77	75
8	MeOH	$CuCl_2$	48	63	53
9	MeOH	$Cu(Otf)_2$	24	71	68
10	MeCN	$CuCl_2$	48	47	42
11	MeCN	$Cu(Otf)_2$	24	64	59

[a] Conditions: Allylic chloride (0.5 mmol), catalyst (0.005 mmol), morpholine (1 mmol), solvent (25 mL), room temperature.
[b] Determined by GC.
[c] Isolated yield.

Table 2
Effect of base on the allylic amination of **1**.[a]

Entry	Catalyst/base	Time (h)	Conversion[b] (%)	Yield[c] (%)
12	$CuCl_2/K_2CO_3$	24	100	94
13	$CuCl_2/NEt_3$	18	100	93
14	$Cu(OTf)_2/K_2CO_3$	16	100	96
15	$Cu(OTf)_2/NEt_3$	12	100	97

[a] Conditions: Allylic chloride (0.5 mmol), catalyst (0.005 mmol), morpholine (1 mmol), water (25 mL), K_2CO_3 or NEt_3 (0.25 mmol), room temperature.
[b] Determined by GC.
[c] Isolated yield.

3. Results and discussion

Initially attempted was the allylic amination of (1-Chloromethyl-vinyl)-benzene (styrene chloride) **1** chosen as model substrate under conventional thermal conditions (Scheme 1). Systematic investigations of its reactivity with morpholine as secondary amine, in the presence of various copper based catalytic systems and solvents were undertaken to define the best reaction conditions. The results are summarized in Table 1.

In THF the reaction occurs either with $CuCl_2$ or $Cu(OTf)_2$, resulted in a moderate yields of the allylic amine **2a** (entries 2 and 3). Among the other solvent studied, water was found to be the solvent of choice (entries 4 and 5). All attempts to convert **1** into allylic amine **2a** in the absence of catalyst were unsuccessful even after prolonged reaction times (entry 1). As shown in Table 1, $Cu(OTf)_2$ seems to be more reactive than $CuCl_2$.

Next we investigate the effect of the addition of acceptor bases. With 0.5 equivalent of K_2CO_3 or triethylamine, the reaction time was reduced and the total conversion was obtained both with $CuCl_2$ or $Cu(OTf)_2$ (Table 2).

The extension of the allylic amination of **1** in water in the presence of copper (II) complexes using pyrrolidine and diethylamine lead to the allylated amines **2b** and **2c** in excellent yield 94%, 98% respectively (Fig. 1).

Under identical mild reaction conditions, allylic amination was carried out starting from terpenic chlorides (**3**, **5**, **7** and **9**) in the presence of $Cu(OTf)_2$ as catalyst using pyrrolidine, morpholine and diethylamine as a nitrogen-fragment donor. The reaction proceeds smoothly at room temperature for 12 h in the presence of 0.5 equivalent of triethylamine as the acceptor base. All the substrates are converted regioselectively to the corresponding allylic amines in excellent yields. The results are depicted in Table 3.

Perillyl chloride **3**, **5** and geranyl chloride **7** show a total conversion even with pyrrolidine, morpholine and diethylamine. The best yields were obtained with pyrrolidine. Carvyl chloride **9**, prepared according to the literature [28], as a secondary chloride was less efficient than **3**, **5** and **7** (entries 10–12). Comparing to the regiochemistry of the attack by various amines with allylic system in the presence of nickel [29] and palladium [27] catalysts leads always to terminal attack, the copper promoted amination of terpenic chlorides is found to give the same results.

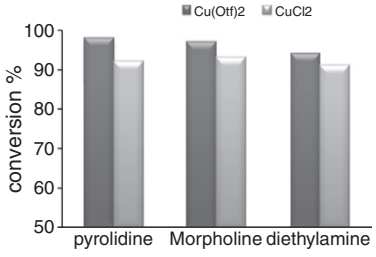
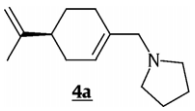
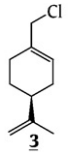
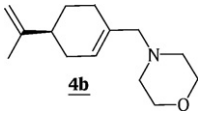
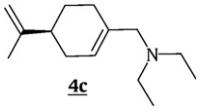
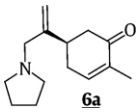
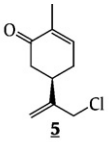
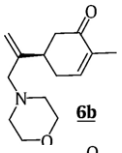
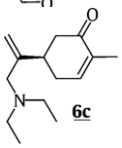
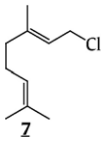
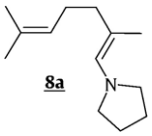
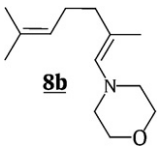
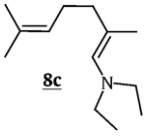
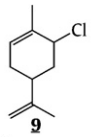
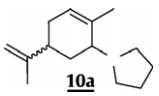
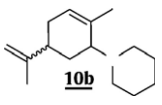
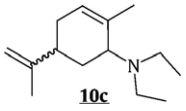


Fig. 1. Effect of secondary amine on the allylic amination of **1**.

Table 3
Allylic amination of terpenic allylic chlorides.[a]

Entry	Allylic chloride	Secondary amine	Allylic amine	$[\alpha]_D^{20}$ (concentration)	Conversion[b]/Yield[c]	Ref
1			 **4a**	−13.3 (2.03)	100/98	[25]
2	 **3** $[\alpha]_D^{20}$= −67(1.95)		 **4b**	−21.1 (1.78)	100/96	[25]
3			 **4c**	−9.3 (1.85)	100/92	–
4			 **6a**	−57.4 (1.93)	100/98	[32]
5	 **5** $[\alpha]_D^{20}$= −56 (2.13)		 **6b**	−53.9 (1.82)	100/96	–
6			 **6c**	−55.2 (1.97)	100/97	–
7	 **7**		 **8a**	–	100/93	[25]
8			 **8b**	–	100/91	[25]
9			 **8c**	–	100/91	–
10	 **9** $[\alpha]_D^{20}$= −32 (2.01)		 **10a**	0	87/83	[25]
11			 **10b**	0	88/81	[25]
12			 **10c**	0	82/76	–

[a] Conditions: Allylic chloride 0.5 mmol; $Cu(OTf)_2$ 0.05 mmol; secondary amine 1 mmol; K_2CO_3 0.25 mmol; water 15 ml; room temperature for 12 h.
[b] Determined by GC.
[c] Isolated yield.

It is also noteworthy that the β, γ-unsaturated amines synthesized from optically active allylic chlorides **3** and **5** preserved an optical activity as indicated in Table 3 (entries 1–6). In contrast allylic amines derived from the optically active carvyl chloride **9** (Table 3, entries 10–12), was found optically inactive. As the mechanism of the reaction is not yet perfectly clear, we can reasonably propose that the amines **10a–10c** derive from a symmetrical intermediate unlike the **4a–4c** and **6a–6c** compounds [30]. Hence, the reaction proceeds probably via an intermediate in which copper is linked to olefins through a π-olefin bond [31], which can be converted to a symmetrical intermediate as we have previously shown with palladium complexes [30].

4. Conclusion

An efficient method for the preparation of monoterpenic allylamines using copper (II) complex has been described. This preparative method, carried out in water under mild conditions satisfies the requirement of sustainable chemistry and atom economy. Moreover, it opens the way to a variety of valuable compounds since terpenic chlorides have been successfully coupled with secondary amines to afford terpenic amines in excellent yields. The use of optically active monoterpenes as starting materials allowed preparing natural asymmetric amines compounds.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.12.019.

References

[1] R.R. Rando, F. Bangerter, Journal of the American Chemical Society 98 (1976) 6762–6764.
[2] C.Y.P. Teng, B. Ganem, Tetrahedron Letters 23 (1982) 313–316.
[3] T. Kondo, H. Nakai, T. Goto, Tetrahedron 29 (1973) 1801–1806.
[4] R.B. Cheikh, R. Chaabouni, A. Laurent, P. Mison, A. Nafti, Synthesis 685 (1983) 691–696.
[5] W.G. Young, I.D. Webb, H.L. Goering, Journal of the American Chemical Society 73 (1951) 1076–1083.
[6] G.A. Hogan, A.A. Gallo, K.M. Nicholas, R.S. Srivastava, Tetrahedron Letters 43 (2002) 9505–9508.
[7] G.S. Silverman, S. Strickland, K.M. Nicholas, Organometallics 5 (1986) 2117–2124.
[8] J. Kiji, E. Sasakawa, K. Yamamoto, J. Furukawa, Journal of Organometallic Chemistry 77 (1974) 125–130.
[9] T. Sturm, B. Abad, W. Weissensteiner, K. Mereiter, B.R. Manzano, F.A. Jalón, Journal of Molecular Catalysis.A 255 (2006) 209–219.
[10] C.-M. Ho, T.-C. Lau, New Journal of Chemistry 24 (2000) 859–863.
[11] J.S. Clark, C. Roche, Chemical Communications 41 (2005) 5175–5177.
[12] For review on allylic amination:. M. Johannsen, K. Jorgensen, Chemical Reviews 98 (1998) 1689–1708.
[13] For review on palladium catalyzed reactions in aqueous medium: J.P. Genet, M. Savignac, J. Organomet. Chem. 576 (1999) 305–317.
[14] J.-P. Genet, E. Blart, M. Savignac, Synlett 9 (1992) 715–717.
[15] C. Rabeyrin, C. Nguefack, D. Sinou, Tetrahedron Letters 41 (2000) 7461–7464.
[16] S. Kobayashi, W. Lam, K. Manabe, Tetrahedron Letters 41 (2000) 6115–6119.
[17] M. Feuerstein, D. Laurenti, H. Doucet, M. Santelli, Tetrahedron Letters 42 (2001) 2313–2315.
[18] K.C. Nicolaou, E.J. Sorensen, Classics in Total Synthesis, first ed Wiley, Weinheim, 1996.
[19] M. Beller, C. Bolm, Transition Metals for Organic Synthesis, Building Blocks and Fine Chemicals, Vol. 1 and 2, Wiley, Weinheim, 1998.
[20] J.J. Mills, R.S. Chri, I.J. Boyer, M.N. Gould, R.I. Jirtele, Cancer Research 55 (1995) 979–983.
[21] J.D. Haag, M.N. Gould, Cancer Chemotherapy and Pharmacology 34 (1994) 477–483.
[22] P.L. Crowell, Z. Ren, S. Lin, E. Vedejs, M.N. Gould, Biochemical Pharmacology 47 (1994) 1405–1415.
[23] B. Boualy, L. El Firdoussi, M. Ait Ali, A. Karim, Journal of the Brazilian Chemical Society 22 (2011) 1259–1262.
[24] B. Ait Allal, L. El Firdoussi, S. Allaoud, A. Karim, Y. Castanet, A. Mortreux, Journal of Molecular Catalysis. A 200 (2003) 177–184.
[25] S. El Houssame, L. El Firdoussi, S. Allaoud, A. Karim, Y. Castanet, A. Mortreux, Journal of Molecular Catalysis. A 168 (2001) 15–23.
[26] J.B. Baruah, A.G. Samuelson, Tetrahedron 47 (1991) 9449–9454.
[27] S. El Houssame, H. Anane, L. El Firdoussi, A. Karim, Central European Journal of Chemistry 6 (2008) 470–476.
[28] H.J. Liu, J.M. Nyangulu, Tetrahedron Letters 30 (1988) 5097–5098.
[29] G.S. Silverman, S. Strickland, K.M. Nicholas, Organometallics 5 (1986) 2117–2124.
[30] L. El Firdoussi, A. Baqqa, S. Allaoud, B. Ait Allal, A. Karim, Y. Castanet, A. Mortreux, Journal of Molecular Catalysis. A 135 (1998) 11–22.
[31] Ya.E. Filinchuk, D. Schollmeyer, V.V. Oliinik, M.G. Mys'kiv, E.A. Goreshnik, Russian Journal of Coordination Chemistry 22 (1996) 815–820.
[32] J. Chen, M. Lu, Y. Jing, J. Dong, Bioorganic & Medicinal Chemistry 14 (2006) 6539–6547.