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Niobium- and zirconium-catalyzed reactions of substituted 2 alkynylamines with Et_2Zn†

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The $NbCl_5$–EtMgBr-catalyzed reaction of *N*,*N*-disubstituted 2-alkynylamines with Et_2Zn followed by hydrolysis or deuterolysis affords (2*Z*)-alkenylamines (reduction products of alkyne) in high yields. The reaction of *N*,*N*-disubstituted 2-alkynylamines with Et_2Zn catalyzed by the Cp_2ZrCl_2–EtMgBr system occurs as 2-zincoethylzincation, resulting, after deuterolysis or iodinolysis, in the regio- and stereoselective formation of the corresponding dideuterated and diiodinated 2-alkenylamine derivatives with a trisubstituted double bond. This study demonstrates the difference between the catalytic effects of $NbCl_5$ and Cp_2ZrCl_2 on the pathway of reaction of tertiary 2-alkynylamines with Et_2Zn in the presence of catalytic amounts of EtMgBr.

Introduction

Metal alkyne complexes of Ti,[1–10] Zr,[11–15] Ta,[16–22] and Nb[23–30] have a high value for organic synthesis, as they are efficient precursors for the preparation of a broad range of organic compounds. A considerable contribution to the chemistry of zirconocene–alkyne derivatives was made by Buchwald[31–33] and Negishi.[34,35] It is known that halides of low-valent transition metals such as Mo[36,37] and W[36] also readily react with acetylene substrates to give low-valent metal complexes of the alkyne molecule. Considering low-valent niobium complexes with acetylene substrates, the first synthetic application of niobium complexes was demonstrated in relation to the reaction of a niobium cyclopropene complex with phthalaldehyde to give 2,3-disubstituted 1-naphthols.[38] The chemistry of low-valent niobium complexes with unsaturated substrates is poorly developed; no methods for the preparation of niobium cyclopropene complexes based on functionally substituted acetylene compounds are available from the literature. Studies into the chemistry of low-valent niobium are often coupled with studies of analogous tantalum complexes, which is due to the similarity of their electronic and chemical properties. The first studies of niobium[16] and tantalum[23,24] complexes with acetylene derivatives were performed by Cotton and co-workers. They demonstrated that reactions of niobium(III) or tantalum(III) compounds with acetylene derivatives such as diphenylacetylene and *tert*-butylmethylacetylene are accompanied by generation of chloride-bridged bimetallic complexes of the pentavalent metal. From analysis of the published data, it follows that Zn,[39] Mg, Al,[40–43] and Na/Hg amalgam[44–49] are the most popular reducing agents suitable for efficient generation of low-valent niobium and tantalum in the presence of alkyne molecules. Oshima and co-workers reported for the first time that the reaction of non-functionalized disubstituted acetylenes with low-valent niobium, generated by reduction of $NbC1_5$ with $NaAlH_4$, results in the selective formation of monodeuterated *Z*-olefins.[50] An interesting approach to generation of highly reactive low-valent niobium was demonstrated in the cyclotrimerization of isocyanates using $Nb(OEt)_5$ and organomagnesium reagents such as i-PrMgCl and EtMgCl.[51] However, there are no examples of preparation of low-valent niobium or tantalum by reduction of niobium or tantalum compounds with zinc or aluminum organic derivatives. Currently, we have demonstrated that 2-zincoethylzincation of nitrogen- and phosphorus-containing acetylene derivatives with Et_2Zn is accompanied by generation of low-valent titanium diisopropoxide complex.[52–54] Meanwhile, it follows from analysis of the literature that reduction of five-coordinate niobium compounds in the presence of acetylene substrates is accompanied by the formation of metal alkyne complexes. We were interested in studying the behavior of $NbC1_5$ in the Ti–Mg-catalyzed reaction of functionally substituted alkynes with Et_2Zn, which we currently study. We were faced with the following questions: (1) can the replacement of titanium tetraisopropoxide by niobium(V) chloride promote the catalytic carbometallation of alkyne molecules with Et_2Zn? (2) Are niobium cyclopropene intermediates, which are hydrolyzed to give 1,2-disubstituted olefins (reduction products of alkyne molecules), generated during the organozinc synthesis? The reduction of acetylene compound with $NbC1_5$ in the presence of diethylzinc would attest to generation of low-valent niobium under the action of dialkylzinc and to

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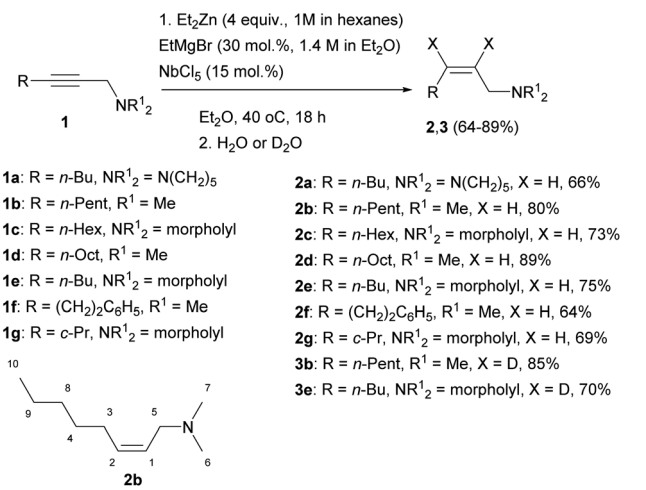
formation of niobium cyclopropene intermediates. Previously, 1-alkynylamines demonstrated high reactivity in Ti–Mg-catalyzed reaction with Et_2Zn.[54,55] Therefore, first of all, we studied the reaction of substituted 2-alkynylamines with Et_2Zn in the presence of catalytic amounts of $NbC1_5$ and EtMgBr.

Results and discussion

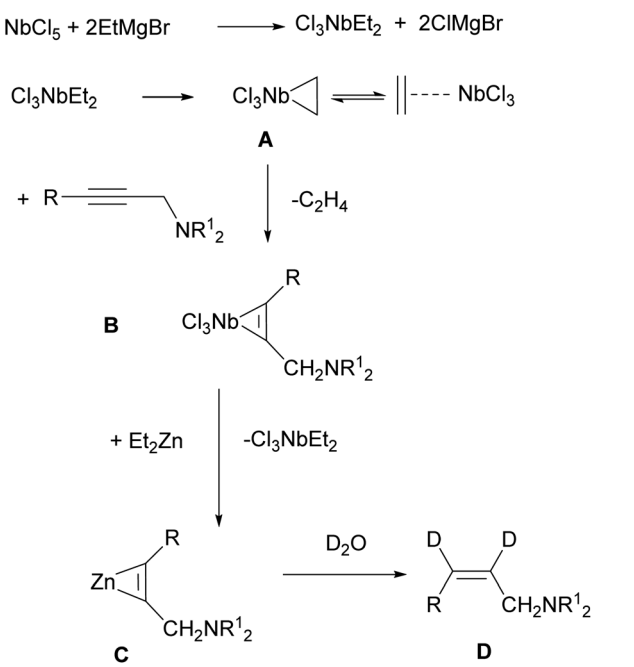
The reaction of 2-alkynylamines **1a–g** with 4 equivalents of Et_2Zn (1 M in hexane) in the presence of 30 mol% EtMgBr (1.4 M in diethyl ether) and 15 mol% $NbCl_5$ in diethyl ether at 40 °C for 18 h resulted in the selective formation of reduction products **2a–g**, **3b**, **e** in 64–89% yields (Scheme 1). When *N*,*N*-dimethyl-3-phenylprop-2-yn-1-amine was used as an alkyne substrate, the reduction product yield after 48 h was 27%. In this case, the amount of the original unreacted propargylamine was 77% (GC/MS data). The reaction of *N*,*N*-dimethyl-5-phenylpent-2-yn-1-amine **1f** with Et_2Zn catalyzed by the $NbCl_5$–EtMgBr system for 18 h resulted in the selective formation of reduction product **2f** in 64% yield. The structural identification of the products was carried out by ^{1}D and ^{2}D NMR spectroscopy techniques. The stereochemistry of the resulting allylamine molecules was studied by analyzing coupling of HC-1 and HC-2 ethylene protons ($\delta \sim 5.44$–5.49 ppm and $\delta \sim 5.53$–5.58 ppm) and H_2C-3 ($\delta \sim 2.05$–2.07 ppm) and H_2C-5 ($\delta \sim 2.05$–2.07 ppm) methylene protons. The Overhauser effects detected in the NOESY spectra between the H_2C-3 ($\delta \sim 2.05$–2.07 ppm) and H_2C-5 ($\delta \sim 2.94$–2.96 ppm) methylene protons attest to the *Z*-configuration of the double bond of compound **2b** (Scheme 1). The positions of deuterium atoms in the dideuterated alkenylamines were also established on the basis of NMR spectra. In the ^{13}C NMR spectra of the compounds **3b**, **e**, no signals were presented for the sp^2-hybridized carbon atoms that is typical of deuterated alkenes. Also, a signal of double bond hydrogen atom is absent in the ^{1}H NMR spectra of the compounds **3b**, **e**. Thus, replacement of titanium tetraisopropoxide in the 2-zincoethylzincation of 2-alkynylamines, which we reported previously,[54] by $NbCl_5$ changes the reaction pathway and leads to generation of organometallic cyclopropene intermediates instead of metallacyclopentenes.

Gas chromatography and gas chromatography/mass spectrometry analysis of the reaction mixture demonstrated that the reduction of the substituted propargylamines in the organozinc synthesis is accompanied by side formation of compounds that can be described as carbozincation products (9–15% yield) and products of 2-alkynylamine homocoupling catalyzed by low-valent niobium (2–5% yield).

In our opinion, allylamines **2** and **3** with *Z*-configuration of the double bond are formed in the following way. Previously, Negishi,[55] who studied the Ti–Mg-catalyzed carbocyclization of non-functionalized and oxygenated enynes with Et_2Zn, suggested that diisopropoxytitanium ethylene complex or diisopropoxytitanacyclopropane is the key intermediate of this reaction. The EtMgBr–$Ti(OiPr)_4$-catalyzed 2-zincoethylzincation of 2-alkynylamines with Et_2Zn is also presumably initiated by the generation of diisopropoxytitanacyclopropane intermediate.[54] Urabe and Sato *et al.*[10,56] previously reported that the use of $Ti(OiPr)_4$ in conjunction with i-PrMgCl led to the formation of the corresponding low-valent alkoxytitanium species. Relying on these results, we assumed that the exchange reaction between $NbCl_5$ and EtMgBr leads to generation of diethylniobium complex Cl_3NbEt_2 (Scheme 2). Upon disproportionation, this unstable complex is rapidly converted to niobium ethylene complex or niobacyclopropane intermediate **A**. According to literature,[57–59] we assumed intermediate formation the structure **A**. For example, $TaCl_5$-catalyzed carbomagnesiation of alkenes with *n*-alkyl Grignard reagents is initiated by the generation of alkene complex of tantalum(III) chloride. It was



Scheme 1 Nb–Mg-catalyzed reaction of *N*,*N*-disubstituted 2-alkynylamines with Et_2Zn.

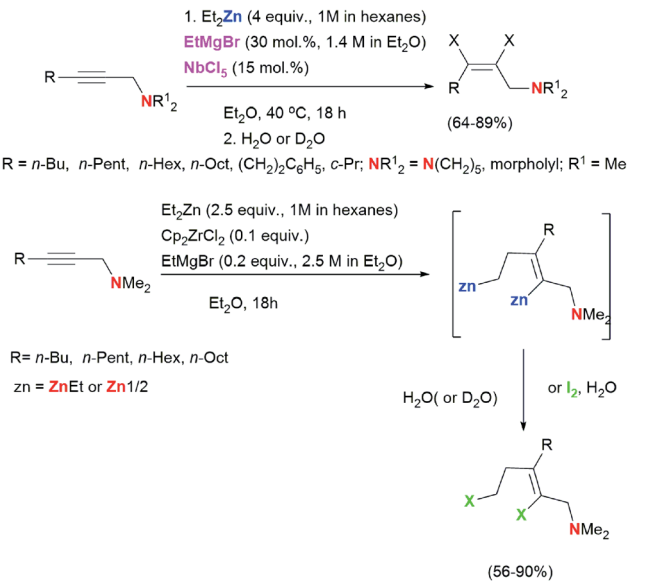


Scheme 2 Putative mechanism of Nb–Mg-catalyzed reaction of *N*,*N*-disubstituted 2-alkynylamines with Et_2Zn.

proposed that this complex is formed from the dialkyltantalum complex [$TaCl_3R_2$] (R is an alkyl group) as a result of beta-hydride transfer and elimination of alkane. Since niobium and tantalum are metals of close nature, we assumed a similar route for the formation of niobacyclopropane intermediate **A**. Subsequently, propargylamine, being a stronger nucleophile, displaces ethylene from the niobium coordination sphere to give niobacyclopropene complex **B**. The generated niobacyclopropene intermediate undergoes transmetallation under the action of Et_2Zn to give zincacyclopropene intermediate **C**, the deuterolysis of which affords dideuterated allylamine **D**. The formation of low-valent niobium under the action of magnesium alkyl halides is additionally supported by the cyclotrimerization reaction of isocyanates induced by low-valent niobium generated upon the reaction of $Nb(OEt)_5$ with Grignard reagents such as i-PrMgCl or EtMgCl.[51]

The use of EtMgBr in this reaction is important. We found that, without EtMgBr, the reaction of *N*,*N*-dimethyloct-2-yn-1-amine with 4 equivalents of Et_2Zn carried out in the presence of 15 mol% $NbCl_5$ in diethyl ether for 18 h at 40 °C affords a mixture of reduction, 2-zincoethylzincation, and dimerization products in 40 : 40 : 10 ratio. This indicates that low-valent niobium is also generated in the reaction of $NbCl_5$ with Et_2Zn. However, in the absence of EtMgBr, the selectivity of reduction of 2-alkynylamines decreases. Since it was ascertained that $NbCl_5$ reacts with Et_2Zn giving intermediates that show reactivity towards 2-alkynylamines, it was of interest to study this reaction using stoichiometric amounts of $NbCl_5$ and Et_2Zn with respect to functionally substituted alkyne. In the reaction of *N*,*N*-dimethyloct-2-yn-1-amine with 2 equivalents of $NbCl_5$ and 3 equivalents of Et_2Zn in the absence of EtMgBr, the proportion of the carbozincation product increased to 60%. We believe that the selectivity observed in the reduction of 2-alkynylamines in the presence of catalytic amounts of EtMgBr may be attributable to different compositions of low-valent niobium complexes formed upon reduction of $NbCl_5$ with EtMgBr and Et_2Zn. Meanwhile, the use of stoichiometric amount of EtMgBr without Et_2Zn also produces unsatisfactory results. Indeed, the reaction of *N*,*N*-dimethylundec-2-yn-1-amine with 4 equivalents of EtMgBr in the presence of 15 mol% $NbCl_5$ in diethyl ether at 40 °C is accompanied by complete conversion to give, after 2 days, a mixture of reduction and carbometallation products in 1 : 1 ratio. Thus, the optimal conditions for the reduction of 2-alkynylamines to *Z*-allylamines *via* organozinc synthesis imply the presence of catalytic amounts of $NbCl_5$ and EtMgBr.

In order to study the effect of various transition metals on the reduction of 2-alkynylamines *via* organozinc synthesis, we carried out a number of experiments with various metals. It was found that the replacement of $NbCl_5$ in the Nb–Mg-catalyzed reaction of 2-alkynylamines with Et_2Zn (entry 1, Table 1) by $ZrCl_4$ (entry 2, Table 1) inhibited the conversion of *N*,*N*-dimethyloct-2-yn-1-amine (Table 1). According to GLC analysis of the reaction mixture, no reduction product was formed in this case. The low conversion of *N*,*N*-dimethyloct-2-yn-1-amine is associated with the formation of carbometallation product (according to GC/MS data) in minor amounts (2%) (entry 2). In the case of using $TaCl_5$, apart from the trace amount of compound **2b** (5%), the reaction gave a hard-to-separate mixture of macromolecular olefins (25%) (entry 3). When $NbCl_5$ was replaced by $TiCl_4$, the reaction was no longer chemoselective, and the conversion of the starting propargylamine after 24 h was 27%. The reduction product **2b** was formed in 13% yield, while the contents of compounds that can be



Scheme 3 Zr–Mg-catalyzed reaction of *N*,*N*-disubstituted 2-alkynylamines with Et_2Zn.

Table 1 Optimization of the catalytic system

Entry	Catalyst precursor	Reducing agent	Conv. (%)	Yield of **2b** (%)	Yield of product of carbometallation (%)
1	$NbCl_5$	EtMgBr	>99	80	10
2	$ZrCl_4$	EtMgBr	2	n.d.[a]	2
3	$TaCl_5$	EtMgBr	30	5	n.d.[a]
4	$TiCl_4$	EtMgBr	25	13	8
5	Cp_2ZrCl_2	EtMgBr	>99	n.d.[a]	84

[a] Not detected by GC.

described as carbometallation and dimerization products were 8% and 4%, respectively (GC/MS data) (entry 4). To our surprise, when Cp_2ZrCl_2 was used as the catalyst, the reaction pathway crucially changed (entry 5).

We found that the reaction of 2-alkynylamines **1** with 2.5 equivalents of Et_2Zn (1 M in hexane) in the presence of 10 mol% Cp_2ZrCl_2 and 20 mol% EtMgBr (2.5 M in Et_2O) carried out in diethyl ether at room temperature for 18 hours and followed by deuterolysis, hydrolysis, or iodinolysis furnished substituted allylamines **5**, **6**, or **7** with *Z*-configuration of the double bond (Scheme 3). The reactions were regio- and stereoselective. The structures of the substituted 2-alkenylamines were established using ^{1}D and ^{2}D NMR spectroscopy of the products of their hydrolysis **5a–d**, deuterolysis **6d**, and iodinolysis **7b**. We believe that in this case, the reaction follows the 2-zincoethylzincation pathway due to similar natures of zirconium and titanium atoms. As noted above, the use of titanium tetraisopropoxide as a catalyst in the reaction of substituted alkynes with Et_2Zn also results in the formation of 2-zincoethylzincation products.[54] Thus, the nature of the transition metal of the organometallic catalyst affects the conversion pathway of acetylene substrates in the reaction with Et_2Zn.

It is noteworthy that no examples of Zr-catalyzed 2-zincoethylzincation of functionally substituted alkynes were reported in the literature. At the same time, it should be noted that addition of alkynylboronates to the reagent Cp_2ZrCl_2/2EtMgBr leads to selective formation of the zirconacyclopentenes which, upon hydrolysis, afforded (*Z*)-2-(2-ethylhex-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes in high yield.[60] In this study, we demonstrated for the first time that the Zr-catalyzed reaction of 2-alkynylamines with Et_2Zn leads to regio- and stereoselective formation of 2-zincoethylzincation products. Regarding carbozincation of non-functionalized alkynes during the organozinc synthesis, the only relevant example reported in the literature[61] is Cp_2ZrCl_2-catalyzed 2-zincoethylzincation of dec-5-yne, which selectively gives the dideuterated product. Meanwhile, the conversion of dec-5-yne under conditions we developed in the presence of 4 equivalents of Et_2Zn (1 M in hexane), 30 mol% EtMgBr (1.4 M in diethyl ether), and 15 mol% $NbCl_5$ in diethyl ether is not selective and gives, together with the reduction product (10–15%), a hard-to-analyze product mixture, apparently, composed of oligo- and polymerization products of dialkyl-substituted acetylene induced by low-valent niobium complexes. Thus, we showed for the first time that the reaction of 2-alkynylamines with Et_2Zn in the presence of catalytic amounts of EtMgBr and $NbCl_5$ results in stereoselective conversion of 2-alkynylamines to (2*Z*)-alkenylamines. A regio- and stereoselective method was developed for the synthesis of 2-alkenylamines with a trisubstituted double bond by the reaction of 2-alkynylamines with Et_2Zn catalyzed by the Cp_2ZrCl_2–EtMgBr system.

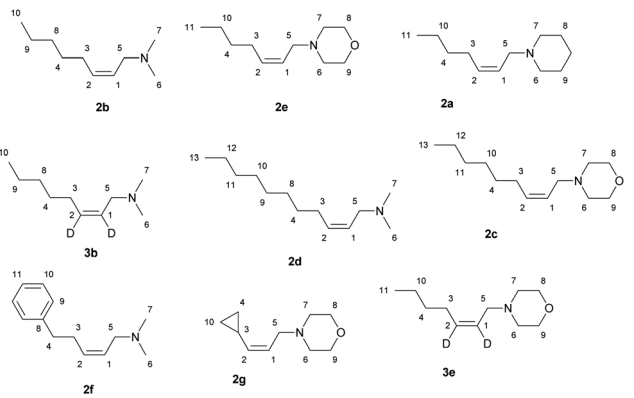


Fig. 1 The numbering of atoms in the ^{13}C- and ^{1}H-NMR spectra of the compounds **2a–g**, **3b**, **e**.

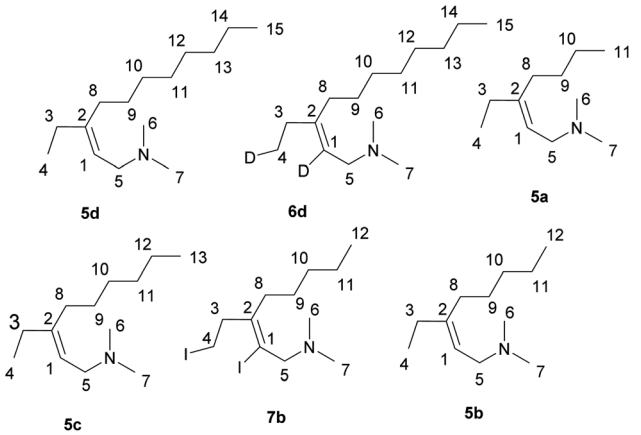


Fig. 2 The numbering of atoms in the ^{13}C- and ^{1}H-NMR spectra of the compounds **5a–d**, **6d**, **7b**.

Conclusions

Thus, the $NbCl_5$–EtMgBr-catalyzed reaction of *N*,*N*-disubstituted 2-alkynylamines with Et_2Zn followed by hydrolysis or deuterolysis affords (2*Z*)-alkenylamines in high yields. On other hand, the reaction of *N*,*N*-disubstituted 2-alkynylamines with Et_2Zn catalyzed by the Cp_2ZrCl_2–EtMgBr system occurs as 2-zincoethylzincation, resulting, after deuterolysis or iodinolysis, in the regio- and stereoselective formation of the corresponding dideuterated and diiodinated 2-alkenylamine derivatives with a trisubstituted double bond. The study demonstrates that the pathway of the reaction of tertiary 2-alkynylamines with Et_2Zn depends on transition metal in the catalytic system.

Experimental section

General information

The reagents were obtained from Sigma-Aldrich or Acros. Hexane were distilled over P_2O_5. Diethyl ether, benzene and 1,2-dimethoxyethane were dried over sodium. 2-Alkynylamines **1b**, **d**, **f** were prepared by aminomethylation of terminal alkynes by bisamine.[62] Alkynylamines **1a**, **e**, **c**, **g** were prepared by aminomethylation of terminal alkynes with aqueous formaldehyde and secondary amines under CuI catalysis.[63] Nuclear magnetic resonance spectroscopy was performed on a Brucker Avance 500. The ^{1}H NMR spectra were recorded at 500 MHz and ^{13}C-{1H} NMR spectra at 100 MHz in $CDCl_3$. The chemical shifts are

reported in ppm relative to tetramethylsilane (TMS) as the internal standard. The numbering of atoms in the ^{13}C-{1H} and ^{1}H NMR spectra of the compounds **2a–g**, **3b**, **e**, **5a–d**, **6d**, **7b** is shown in Fig. 1 and 2. Elemental analysis was performed using a Carlo-Erba CHN 1106 elemental analyser. Mass spectra were obtained on a Finnigan 4021 instrument. The yields were calculated from the isolated amount of allylamines obtained from starting 2-alkynylamines.

Preparation of allylamines **2a–g**, **3e**, **b** *via* Nb–Mg-catalyzed reaction of substituted propargylamines with Et_2Zn.

(*Z*)-*N*,*N*-Dimethyloct-2-en-1-amine; typical procedure

To a solution of *N*,*N*-dimethyloct-2-yn-1-amine (306 mg, 2 mmol) and Et_2Zn (1 M in hexanes, 8 mL, 8 mmol) in Et_2O (6 mL) was added $NbCl_5$ (0.081 g, 0.30 mmol). Ethylmagnesiurn bromide (1.4 M in Et_2O, 0.428 mL, 0.6 mmol) was then added and the reaction mixture rapidly turned black. After 18 h at 40 °C, the reaction mixture was diluted with Et_2O (5 mL), and 25 wt% KOH solution (3 mL) was added dropwise while the reaction flask was cooled in an ice bath. The aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous $MgSO_4$. The reaction mixture was filtered through a filter paper and concentrated *in vacuo* to give crude product as a yellow oil. The residue was distilled through a micro column at 20 mmHg to give **2b** (248 mg, 80%) as a colourless oil. b.p. 77–79 °C (20 mmHg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (s, 3H, C(10)H_3), 1.31 (s, 4H, C(9,8)H_2), 1.36–1.41 (m, 2H, C(4)H_2), 2.05–2.09 (m, 2H, C(3)H_2), 2.25 (s, 6H, C(6,7)H_3), 2.95 (d, J = 6 Hz, 2H, C(5)H_2), 5.44–5.49 (m, 1H, C(1)H), 5.53–5.61 (m, 1H, C(2)H).

^{13}C NMR (500 MHz, $CDCl_3$): δ = 14.04 (C(10)), 22.54 (C(9)), 27.43 (C(3)), 29.24 (C(4)), 31.48 (C(8)), 45.22 (C(6,7)), 56.13 (C(5)), 126.59 (C(1)), 132.97 (C(2)).

MS (EI): *m*/*z*, % = 155 (18) [M^+], 98 (29), 84 (53), 58 (89), 45 (100).

Anal. calcd for $C_{10}H_{21}N$, (%): C, 77.35; H, 13.63; N, 9.02. Found, %: C, 77.58; H, 13.58; N, 8.71.

(*Z*)-1-(Hept-2-en-1-yl)piperidine (2a). Using the procedure described above 358 mg of 1-(hept-2-yn-1-yl)piperidine (2 mmol) gave crude product that was distilled through a micro column at 3,4 mmHg to afford **2a** (239 mg, 66%) as a colourless oil. b.p. 107–110 °C (3,4 mmHg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 7 Hz, 3H, C(11)H_3), 1.31 (s, 4H, C(4,10)H_2), 1.41 (m, 2H, C(12)H_2), 1.55–1.59 (m, 4H, C(8,9)H_2), 2.03 (q, J = 6 Hz, 2H, C(3)H_2), 2.36 (s, 4H, C(6,7)H_2), 2.95 (d, J = 6 Hz, 2H, C(5)H_2), 5.43–5.53 (m, 1H, C(1,2)H).

^{13}C NMR (500 MHz, $CDCl_3$): δ = 13.93 (C(11)), 22.68 (C(10)), 24.37 (C(12)), 25.99 (C(8,9)), 27.16 (C(3)), 31.73 (C(4)), 54.51 (C(6,7)), 55.88 (C(5)), 126.43 (C(1)), 132.71 (C(2)).

MS (EI): *m*/*z*, % = 181 (7) [M^+], 138 (4), 124 (10), 98 (29), 84 (100), 55 (30), 41 (15).

Anal. calcd for $C_{12}H_{23}N$, (%): C, 79.49; H, 12.79; N, 7.72; found, %: C, 79.45; H, 12.92; N, 7.52.

(*Z*)-4-(Non-2-en-1-yl)morpholine (2c). Using the procedure described above 418 mg of 4-(non-2-yn-1-yl)morpholine (2 mmol) gave crude product that was distilled through a micro column at 2,4 mmHg to afford **2c** (308 mg, 73%) as a colourless oil. b.p. 127–129 °C (2,4 mmHg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83 (t, J = 6 Hz, 3H, C(13)H_3), 1.22–1.25 (m, 6H, C(10–12)H_2), 1.26–1.30 (m, 2H, C(4)H_2), 1.98–2.02 (q, J = 7 Hz, 2H, C(3)H_2), 2.39 (s, 4H, C(6,7)H_2), 2.94 (d, J = 7 Hz, 2H, C(5)H_2), 3.64–3.66 (m, 4H, C(8,9)H_2), 5.36–5.40 (m, 1H, C(1)H), 5.49–5.53 (m, 1H, C(2)H).

^{13}C NMR (500 MHz, $CDCl_3$): δ = 13.99 (C(13)), 22.55 (C(12)), 27.45 (C(3)), 28.87 (C(10)), 29.43 (C(4)), 31.65 (C(11)), 55.43 (C(5)), 53.59 (C(6,7)), 66.94 (C(8,9)), 125.33 (C(1)), 133.67 (C(2)).

MS (EI): *m*/*z*, % = 211 (3) [M^+], 126 (5), 87 (100), 86 (40), 57 (30), 40 (15).

Anal. calcd for $C_{13}H_{25}NO$, (%): C, 73.88; H, 11.92; N, 6.63; found, %: C, 74.03; H, 12.08; N, 6.77.

(*Z*)-*N*,*N*-Dimethylundec-2-en-1-amine (2d). Using the procedure described above 390 mg of *N*,*N*-dimethylundec-2-yn-1-amine (2 mmol) gave crude product that was distilled through a micro column at 5 mmHg to afford **2d** (351 mg, 89%) as a colourless oil. b.p. 107–109 °C (5 mmHg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, J = 7 Hz, 3H, C(13)H_3), 1.29 (s, 8H, C(9–12)H_2), 1.35–1.38 (m, 4H, C(4,8)H_2), 2.04–2.09 (m, 2H, C(3)H_2), 2.25 (s, 6H, C(6,7)H_3), 2.95 (d, J = 6 Hz, 2H, C(5)H_2), 5.44–5.49 (m, 1H, C(1)H), 5.52–5.57 (m, 1H, C(2)H).

^{13}C NMR (500 MHz, $CDCl_3$): δ = 14.11 (C(13)), 22.68 (C(12)), 27.47 (C(3)), 29.29 (C(9,10)), 29.49 (C(8)), 29.57 (C(4)), 31.89 (C(11)), 45.26 (C(6,7)), 56.16 (C(5)), 126.66 (C(1)), 132.93 (C(2)).

MS (EI): *m*/*z*, % = 197 (9) [M^+], 110 (4), 98 (24), 84 (52), 58 (89), 45 (100).

Anal. calcd for $C_{13}H_{27}N$, (%): C, 79.11; H, 13.79; N, 7.10; found, %: C, 79.16; H, 13.65; N, 6.95.

(*Z*)-4-(Hept-2-en-1-yl)morpholine (2e). Using the procedure described above 362 mg of 4-(hept-2-yn-1-yl)morpholine (2 mmol) gave crude product that was distilled through a micro column at 5 mmHg to afford **2e** (275 mg, 75%) as a colourless oil. b.p. 110–112 °C (5 mmHg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (s, 3H, C(11)H_3), 1.21–1.25 (m, 4H, C(4,10)H_2), 2.04–2.07 (m, 2H, C(3)H_2), 2.45 (s, 4H, C(6,7)H_2), 3.01 (d, J = 6 Hz, 2H, C(5)H_2), 3.72 (s, 4H, C(8,9)H_2), 5.42–5.46 (m, 1H, C(1)H), 5.55–5.59 (m, 1H, C(2)H).

^{13}C NMR (500 MHz, $CDCl_3$): δ = 13.94 (C(11)), 22.29 (C(10)), 27.20 (C(3)), 31.68 (C(4)), 53.46 (C(5)), 53.59 (C(6,7)), 66.98 (C(8,9)), 125.26 (C(1)), 133.79 (C(2)).

MS (EI): *m*/*z*, % = 183 (10) [M^+], 140 (4), 110 (28), 87 (100), 57 (70), 41 (21).

Anal. calcd for $C_{11}H_{21}NO$, (%): C, 72.08; H, 11.55; N, 7.64; found, %: C, 72.22; H, 11.56; N, 7.37.

(*Z*)-*N*,*N*-Dimethyl-5-phenylpent-2-en-1-amine (2f). Using the procedure described above 374 mg of *N*,*N*-dimethyl-5-phenylpent-2-yn-1-amine (2 mmol) gave crude product that was distilled through a micro column at 2,2 mmHg to afford **2f** (242 mg, 64%) as a colourless oil. b.p. 118–120 °C (2,2 mmHg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.24 (s, 6H, C(6,7)H_3), 2.43 (q, J = 7 Hz, 2H, C(3)H_2), 2.71 (t, J = 7 Hz, 2H, C(4)), 2.94 (s, 2H, C(5)H_2), 5.51–5.55 (m, 1H, C(1)H), 5.59–5.64 (m, 1H, C(2)H), 7.30 (t, J = 7 Hz, 2H, C(9)H), 7.21 (d, J = 7 Hz, 3H, C(10,11)H).

^{13}C NMR (500 MHz, $CDCl_3$): δ = 29.46 (C(3)), 35.80 (C(4)), 45.01 (C(6,7)), 55.93 (C(5)), 125.89 (C(11)), 127.38 (C(1)), 128.33 (C(9)), 128.49 (C(10)), 131.73 (C(2)), 141.74 (C(8)).

MS (EI): *m*/*z*, % = 189 (16) [M^+], 144 (11), 143 (11), 129 (59), 98 (45), 91 (64), 58 (100), 45 (90).

Anal. calcd for $C_{13}H_{19}N$, (%): C, 82.48; H, 10.12; N, 7.40; found, %: C, 82.44; H, 9.97; N, 7.27.

(*Z*)-4-(3-Cyclopropylallyl)morpholine (2g). Using the procedure described above 330 mg of 4-(3-cyclopropylprop-2-yn-1-yl) morpholine (2 mmol) gave crude product that was distilled through a micro column at 4 mmHg to afford **2g** (230 mg, 69%) as a colourless oil. b.p. 90–92 °C (4 mmHg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.26–0.28 (m, 2H(A), C(4,10)H_2), 0.68–0.71 (m, 2H(B), C(4,10)H_2), 1.26–1.30 (m, 2H, C(4)H_2), 1.49–1.57 (m, 1H, C(3)H), 2.44 (s, 4H, C(6,7)H_2), 3.08 (d, J = 7 Hz, 2H, C(5)H_2), 3.66–3.67 (m, 4H, C(8,9)H_2), 5.29–5.34 (m, 1H, C(1)H), 4.87 (t, J = 10 Hz, 1H, C(2)H).

^{13}C NMR (500 MHz, $CDCl_3$): δ = 6.46 (C(4,10)), 9.76 (C(3)), 53.61 (C(6,7)), 55.84 (C(5)), 66.98 (C(8,9)), 123.39 (C(1)), 137.76 (C(2)).

MS (EI): *m*/*z*, % = 167 (10) [M^+], 138 (33), 87 (70), 79 (87), 56 (69), 40 (100).

Anal. calcd for $C_{10}H_{17}NO$, (%): C, 71.81; H, 10.25; N, 8.37; found, %: C, 71.98; H, 10.35; N, 8.35.

(*Z*)-*N*,*N*-Dimethyloct-2-en-1-amine-2,3-d_2 (3b). Using the procedure described above 306 mg of *N*,*N*-dimethyloct-2-yn-1-amine (2 mmol) and D_2O gave crude product that was distilled through a micro column at 5 mmHg to afford **3b** (267 mg, 85%) as a colourless oil. b.p. 107–109 °C (5 mmHg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (s, 3H, C(10)H_3), 1.27–1.30 (m, 4H, C(8,9)H_2), 1.35–1.39 (m, 2H, C(4)H_2), 2.03–2.07 (m, 2H, C(3)H_2), 2.24 (s, 6H, C(6,7)H_3), 2.94 (d, J = 6 Hz, 2H, C(5)H_2).

^{13}C NMR (500 MHz, $CDCl_3$): δ = 14.04 (C(10)), 22.54 (C(9)), 27.28–27.42 (C(3)), 29.23 (C(4)), 31.48 (C(8)), 45.25 (C(6,7)), 56.09 (d, J = 11 Hz, C(5)), 126.57 (d, J = 17 Hz, C(1)), 132.85 (d, J = 15 Hz, C(2)).

MS (EI): *m*/*z*, % = 157 (26) [M^+], 100 (21), 86 (36).

Anal. calcd for $C_{10}H_{19}D_2N$, (%): C, 76.36; N, 8.90; found, %: C, 76.39; N, 9.02.

(*Z*)-4-(Hept-2-en-1-yl-2,3-d_2)morpholine (3e). Using the procedure described above 362 mg of 4-(hept-2-yn-1-yl) morpholine (2 mmol) and D_2O gave crude product that was distilled through a micro column at 2,4 mmHg to afford **3e** (259 mg, 70%) as a colourless oil. b.p. 119–121 °C (2,4 mmHg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, J = 6 Hz, 3H, C(11)H_3), 1.23–1.28 (m, 4H, C(4,10)H_2), 2.07 (t, J = 6 Hz, 2H, C(3)H_2), 2.47 (s, 4H, C(6,7)H_2), 3.03 (s, 2H, C(5)H_2), 3.73 (s, 4H, C(8,9)H_2).

^{13}C NMR (500 MHz, $CDCl_3$): δ = 13.96 (C(11)), 22.32 (C(10)), 27.07 (C(3)), 31.68 (C(4)), 53.59 (C(6,7)), 55.34 (C(5)), 66.99 (C(8,9)).

MS (EI): *m*/*z*, % = 185 (7) [M^+], 156 (1), 128 (6), 112 (19), 87 (100), 57 (70), 57 (70), 42 (13).

Anal. calcd for $C_{11}H_{19}D_2NO$, (%): C, 71.30; N, 7.56; found, %: C, 71.46; N, 7.42.

Preparation of allylamines **5a–d**, **6d**, **7b** *via* Zr–Mg-catalyzed reaction of substituted propargylamines with Et_2Zn.

(*Z*)-3-Ethyl-*N*,*N*-dimethylundec-2-en-1-amine; typical procedure

To a solution of *N*,*N*-dimethylundec-2-yn-1-amine (390 mg, 2 mmol) and Et_2Zn (1 M in hexanes, 5 mL, 5 mmol) in Et_2O (6 mL) was added Cp_2ZrCl_2 (0.058 g, 0.20 mmol). Ethylmagnesiurn bromide (1.6 M in Et_2O, 0.25 mL, 0.4 mmol) was then added and the reaction mixture rapidly turned black. After 18 h at r.t. °C, the reaction mixture was diluted with Et_2O (5 mL), and 25 wt% KOH solution (3 mL) was added dropwise while the reaction flask was cooled in an ice bath. The aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous $MgSO_4$. The reaction mixture was filtered through a filter paper and concentrated *in vacuo* to give crude product as a yellow oil. The residue was distilled through a micro column at 1 mmHg to give **5d** (401 mg, 89%) as a colourless oil. b.p. 104–107 °C (1 mmHg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, J = 6 Hz, 3H, C(15)H_3), 1.01 (t, J = 7 Hz, 3H, C(4)H_3), 1.29 (s, 8H, C(10–13)H_2), 1.32–1.38 (m, 4H, C(9,14)H_2), 2.03–2.06 (m, 4H, C(3,8)H_2), 2.23 (s, 6H, C(6,7)H_3), 2.91 (d, J = 6 Hz, 2H, C(5)H_2), 5.22 (t, J = 6 Hz, 1H, C(1)H).

^{13}C NMR (500 MHz, $CDCl_3$): δ = 12.74 (C(4)), 14.10 (C(15)), 22.07 (C(14)), 28.49 (C(9)), 29.29 (C(10)), 29.52 (C(12)), 29.57 (C(11)), 29.79 (C(3)), 30.58 (C(8)), 31.89 (C(13)), 45.26 (C(6,7)), 56.86 (C(5)), 120.48 (C(1)), 144.41 (C(2)).

MS (EI): *m*/*z*, % = 225 (32) [M^+], 210 (15), 196 (17), 180 (14), 151 (19), 112 (47), 95 (100), 82 (81), 67 (74), 58 (79), 46 (96).

Anal. calcd for $C_{15}H_{31}N$, (%): C, 79.92; H, 13.86; N, 6.21. Found, %: C, 79.80; H, 13.82; N, 6.01.

(*Z*)-3-Ethyl-*N*,*N*-dimethylhept-2-en-1-amine (5a). Using the procedure described above 390 mg of *N*,*N*-dimethylhept-2-yn-1-amine (278 mg, 2 mmol) gave crude product that was distilled through a micro column at 10 mmHg to afford **5c** (294 mg, 87%) as a colourless oil. b.p. 88–91 °C (10 mmHg). The spectral properties (^{1}H NMR, ^{13}C NMR, MS) were in good agreement with those that were reported in the literature.[54]

(*Z*)-3-Ethyl-*N*,*N*-dimethylnon-2-en-1-amine (5c). Using the procedure described above 334 mg of *N*,*N*-dimethylnon-2-yn-1-amine (2 mmol) gave crude product that was distilled through a micro column at 5 mmHg to afford **5c** (311 mg, 79%) as a colourless oil. b.p. 103–106 °C (5 mmHg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, J = 6 Hz, 3H, C(13)H_3), 1.03 (t, J = 8 Hz, 3H, C(4)H_3), 1.28–1.31 (m, 6H, C(10–12)H_2), 1.33–1.39 (m, 2H, C(9)H_2), 2.03–2.07 (m, 4H, C(3,8)H_2), 2.25 (s, 6H, C(6,7)H_3), 2.93 (d, J = 6 Hz, 2H, C(5)H_2), 5.23 (t, J = 7 Hz, 1H, C(1)H).

^{13}C NMR (500 MHz, $CDCl_3$): δ = 12.75 (C(4)), 14.09 (C(13)), 22.65 (C(12)), 28.47 (C(9)), 29.59 (C(10)), 29.70 (C(3)), 31.79 (C(11)), 45.24 (C(6,7)), 56.84 (C(5)), 120.41 (C(1)), 144.51 (C(2)).

MS (EI): *m*/*z*, % = 197 (32) [M^+], 182 (17), 168 (20), 152 (22), 123 (55), 112 (49), 95 (82), 82 (93), 67 (74), 58 (88), 46 (100).

Anal. calcd for $C_{13}H_{27}N$, (%): C, 79.11; H, 13.79; N, 7.10. Found, %: C, 79.10; H, 13.74; N, 6.89.

(*Z*)-3-Ethyl-*N*,*N*-dimethyloct-2-en-1-amine (5b). Using the procedure described above 306 mg of *N*,*N*-dimethyloct-2-yn-1-amine (2 mmol) gave crude product that was distilled through

a micro column at 5 mmHg to afford **5b** (307 mg, 84%) as a colourless oil. b.p. 91–93 °C (5 mmHg). The spectral properties (^{1}H NMR, ^{13}C NMR, MS) were in good agreement with those that were reported in the literature.[54]

(*Z*)-3-(Ethyl-2-*d*)-*N*,*N*-dimethylundec-2-en-1-amine-2-*d* (6d). Using the procedure described above 390 mg of *N*,*N*-dimethylundec-2-yn-1-amine (2 mmol) gave crude product that was distilled through a micro column at 1 mmHg to afford **6d** (409 mg, 90%) as a colourless oil. b.p. 103–106 °C (1 mmHg).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, J = 6 Hz, 3H, C(15)H_3), 1.02 (qv, J = 7 Hz, 2H, C(4)H_2D), 1.29 (s, 8H, C(10–13)H_2), 1.31–1.35 (m, 4H, C(9,14)H_2), 2.06–2.11 (m, 4H, C(3, 8)H_2), 2.19 (s, 6H, C(6,7)H_3), 2.87 (s, 2H, C(5)H_2).

^{13}C NMR (500 MHz, $CDCl_3$): δ = 12.57 (t, J = 19 Hz, C(4)), 14.12 (C(15)), 22.69 (C(14)), 27.45 (C(8)), 28.28 (C(3)), 29.30 (C(10)), 29.37 (C(12)), 29.54 (C(11)), 30.03 (C(9)), 31.91 (C(13)), 45.47 (C(6,7)), 58.31 (C(5)).

MS (EI): m/z, % = 227 (12) [M^+], 212 (20), 210 (11), 198 (23).

Anal. calcd for $C_{15}H_{29}D_2N$, (%): C, 79.22; N, 6.16. Found, %: C, 79.36; N, 6.12.

(*Z*)-2-Iodo-3-(2-iodoethyl)-*N*,*N*-dimethylnon-2-en-1-amine (7b). To a solution of *N*,*N*-dimethyloct-2-yn-1-amine (306 mg, 2 mmol) and Et_2Zn (1 M in hexanes, 5 mL, 5 mmol) in ether (6 mL) was added Cp_2ZrCl_2 (0.058 g, 0.20 mmol). Ethylmagnesiurn bromide (1.6 M in Et_2O, 0.25 mL, 0.4 mmol) was then added and the reaction mixture rapidly turned black. After 18 h at 23C, the reaction mixture was cooled to −78 °C, and a solution of I_2 (1575 mg, 12.5 mmol) in THF (12.5 mL) was added *via* cannula. The reaction mixture was warmed to 23 °C, and stirred overnight. The mixture was then partitioned between 25% aqueous KOH and ether. The organic layer was washed with water and aqueous $Na_2S_2O_3$, drying over $MgSO_4$. Evaporation of solvent and purification of the residue by column chromatography (hexane/ethyl acetate, 5 : 1) gave a yellow oil; yield: 487 mg, (56%); R_f = 0.68 (hexane/ethyl acetate, 5 : 1). The spectral properties (^{1}H NMR, ^{13}C NMR, MS) were in good agreement with those that were reported in the literature.[54] Anal. calcd for $C_{13}H_{25}I_2N$, (%): C, 33.12; H, 5.33; N, 3.22. Found, %: C, 32.91; H, 5.30; N, 3.21.

Conflicts of interest

The authors declare no competing financial interest.

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