Pathways of the reaction between *N,N*-disubstituted propargylic amines and cationic zirconium complexes*

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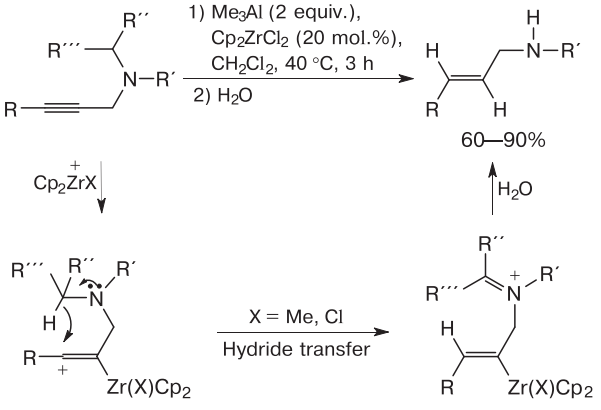
The reaction of *N*-*tert*-alkyl-substituted propargylic amines with trialkylalanes in the presence of 20 mol.% Cp_2ZrCl_2 was studied. The pattern of the products depended on the nature of substituents at the nitrogen atom. *N*-*tert*-Alkyl-*N*-arylmethyl-substituted propargylic amines when reacted in CH_2Cl_2 afford a mixture of *N*-*tert*-alkyl-*N*-(arylmethyl)alkylamines and *N*-*tert*-alkyl-*N*-(arylmethyl)amines at ratios from ~2 : 3 to ~3 : 2 in total yield of 70—95%. In hexane, *N*-*tert*-alkyl-*N*-(arylmethyl)amines are produced selectively. *N*-Alkyl-*N*-*tert*-alkyl-substituted propargylic amines similar to *N*-isoalkyl-substituted ones underwent a Zr-promoted hydride transfer to afford (2*E*)-alkenylamines in good yield (58—69%).

Key words: organoaluminum compounds, hydride transfer, cationic zirconium complexes, propargylic amines, trialkylalanes, zirconocene catalysis.

Zirconium-catalyzed carbo-[1] and cycloaluminations[2] of alkynes are convenient tools for the synthesis of trisubstituted olefins.[3] These reactions are also efficient for the formation of small, medium, large, and giant carba- and metallacarbacycles, spirocarbacycles, oxygen-, nitrogen-, sulfur-, and phosphorus-containing heterocycles, which include new classes of bioactive compounds with terpenoid and steroid structure, lembehynes, and pheromones.[4]

At the same time, the presence of heterofunctional group in the acetylenic substrate can complicate the course of the reaction to favor its inhibition and occurrence of side reactions. For example, despite our success in involving O-, S-, and Cl-containing arylacetylenes[5] and propargylic alcohols[6] into the methylalumination, at the time of initiation of our studies the carboalumination of substituted propargylic amines has almost not been studied. There was only one example[7] of the methylalumination of *N*-benzylpent-2-yn-1-amine; however, the yield of corresponding iodoalkene after iodinolysis was only 26%. Moreover, all our attempts to carry out the Zr-catalyzed methylalumination of *N*-alk-2-ynyl-*N,N*-dimethylamines and *N*-alk-2-ynylpiperidines failed: these compounds underwent no reaction. We assumed that cationic zirconium intermediates bind to the nitrogen atom of propargylic amines to prevent the reaction. At the same time, bulky substituents at the nitrogen atom can hinder donor-acceptor bonding between the nitrogen and zirconium atoms. Thus, the bulkiness of substituents at the nitrogen atom can play a significant role in the reaction. Indeed, *N*-isoalkyl-substituted propargylic amines readily react with Me_3Al in the presence of catalytic amounts of Cp_2ZrCl_2 (Scheme 1);[8] however, the reaction resulted in the reduction product rather than the methylalumination one. This new reaction is a unique example of the hydride transfer from the isoalkyl group to the acetylenic bond in *N*-isoalkyl-substituted propargylic amines mediated by cationic zirconium complexes.

Scheme 1



R = alkyl, Ph
R′ = Pr^i, $ArCH_2$, *c*-C_6H_{11}
R″R‴CH = Pr^i, *c*-C_6H_{11}, Ph(Me)CH

* Based on the materials of the Russian National Conference "Interplay between Ionic and Covalent Interactions in Design of Molecular and Nano Chemical Systems" (ChemSci-2019) (May 13—17, 2019, Moscow, Russia).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 0061—0067, January, 2020.

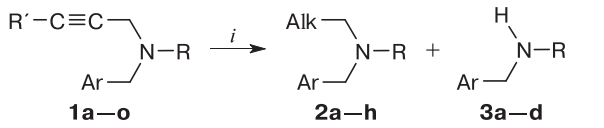
1066-5285/20/6901-061

Continuing these researches, we interested how *N-tert*-alkyl-substituted propargylic amines behave in this reaction. The bulky *tert*-alkyl group also should prevent donor-acceptor bonding between the nitrogen and zirconium atoms; however, the hydride transfer in the case of these propargylic amines is excluded. In the present work, we aimed to carry out the Zr-catalyzed methylalumination of substituted propargylic amines and to stereoselectively prepare nitrogen-containing trisubstituted olefins. The catalyst was chosen to be Cp_2ZrCl_2, since this compound is known[9,10] to catalyze the methylalumination of mono- and disubstituted acetylenes with Me_3Al.

The reaction of *N-tert*-alkyl-*N*-arylmethyl-substituted propargylic amines **1a—o** with 2 equiv. of Me_3Al in the presence of 20 mol.% Cp_2ZrCl_2 in dichloromethane at 40 °C for 6 h afforded a mixture of *N-tert*-alkyl-*N*-(arylmethyl)ethylamines **2** and *N-tert*-alkyl-*N*-(arylmethyl)-amines **3** in the ratios from ~2 : 3 to ~3 : 2 (Scheme 2, Table 1, Runs *1—9*) in total yield of 70—95%. Similar transformations have not been described previously. When 6 equiv. of Me_3Al and 1 equiv. of Cp_2ZrCl_2 were used, the course of the reaction remained almost unchanged. *N-tert*-Alkyl-*N*-arylmethyl-substituted propargylic amines react similarly with Et_3Al in the presence of 20 mol.% Cp_2ZrCl_2 in dichloromethane (see Table 1, Runs *10—13*). Upon the reaction in hexane, only *N-tert*-alkyl-*N*-(arylmethyl)-amine **3** was isolated from the reaction mixture in yield of 63—82% (Runs *14—21*). No compounds, which could correspond to the products of the transformation of the acetylenic fragment, were detected. This can be due to the formation of allene hydrocarbons followed by their oligomerization and polymerization. Earlier,[11] we have observed cycloalumination products of substituted propargylic alcohols to be produced in a very low yield in the presence of Et_3Al and Cp_2ZrCl_2: in the course of the reaction the hydroxy group was eliminated with a probable formation of allene, which completely oligomerized and polymerized under the reaction conditions.

In contrast to the *N*-benzyl analogs, *N*-alkyl-*N-tert*-alkyl-substituted propargylic amines **4a,b** react with Me_3Al in an unexpected manner. Upon the reaction of compounds **4a,b** with 2 equiv. of Me_3Al in the presence of 20 mol.% Cp_2ZrCl_2 in dichloromethane at 40 °C for 1 h, (2*E*)-alkenylamines **5a—c** were produced in high yields (Scheme 3). The reaction products were identified after hydrolysis or deuterolysis of the reaction mixture, since the organometallic compounds that formed readily oxidized in air. The presence of the deuterium atom in the deuterolysis product suggests the presence of a metal—carbon bond in the organometallic intermediate. Thus, the replacement of the *N*-benzyl substituent with the *n*-alkyl one dramatically changes the reaction pathway. *N*-Alkyl-*N-tert*-alkyl- and *N,N*-diisopropyl-substituted propargylic amines behave in the studied reaction similarly. In general, the pattern of products in the Zr-catalyzed reaction of *N,N*-disubstituted propargylic amines with trialkylalanes depends on the nature of the substituents at the nitrogen atom.

Scheme 2



1a—o **2a—h** **3a—d**

Compounds **1a—o**	Ar	R	R′
a	4-$MeOC_6H_4$	Oct^t	Hex
b	4-$MeOC_6H_4$	Oct^t	Bu
c	4-$MeOC_6H_4$	Oct^t	C_8H_{17}
d	4-MeC_6H_4	Oct^t	Bu
e	4-MeC_6H_4	Oct^t	Ph
f	4-$MeOC_6H_4$	Bu^t	C_8H_{17}
g	4-$MeOC_6H_4$	Bu^t	Hex
h	4-MeC_6H_4	Bu^t	Bu
i	4-MeC_6H_4	Bu^t	C_5H_{11}
j	4-MeC_6H_4	Oct^t	C_8H_{17}
k	4-MeC_6H_4	Bu^t	C_8H_{17}
l	4-MeC_6H_4	Oct^t	Hex
m	4-$MeOC_6H_4$	Bu^t	Bu
n	4-MeC_6H_4	Bu^t	Ph
o	4-MeC_6H_4	Bu^t	Hex

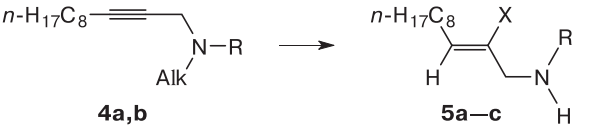
Compounds **2a—h**	Ar	R	Alk
a	4-$MeOC_6H_4$	Oct^t	Me
b	4-MeC_6H_4	Oct^t	Me
c	4-$MeOC_6H_4$	Bu^t	Me
d	4-MeC_6H_4	Bu^t	Me
e	4-$MeOC_6H_4$	Oct^t	Et
f	4-MeC_6H_4	Oct^t	Et
g	4-$MeOC_6H_4$	Bu^t	Et
h	4-MeC_6H_4	Bu^t	Et

Compounds **3a—d**	Ar	R
a	4-$MeOC_6H_4$	Oct^t
b	4-MeC_6H_4	Oct^t
c	4-$MeOC_6H_4$	Bu^t
d	4-MeC_6H_4	Bu^t

Note. Here and in Scheme 3, Oct^t (*tert*-octyl) is 2,4,4-trimethylpent-2-yl ($—CMe_2CH_2CMe_3$).

Reagents and conditions: *i*. 1) Alk_3Al (2 equiv.), Cp_2ZrCl_2 (20 mol.%), solvent, 40 °C, 6 h, 2) H_2O.

Scheme 3



4a,b **5a—c**

4: R = Bu^t, Alk = Bu (**a**), R = Oct^t, Alk = C_8H_{17} (**b**)

Compounds **5a—c**	R	X	Yield (%)
a	Bu^t	H	69
b	Oct^t	D	58
c	Oct^t	H	64

Reagents and conditions: 1) Me_3Al (2 equiv.), Cp_2ZrCl_2 (20 mol.%), CH_2Cl_2, 40 °C, 1 h; 2) H_2O or D_2O.

Table 1. Zirconium-catalyzed reaction of *N-tert*-alkyl-*N*-(arylmethyl)-substituted propargylic amines **1a—o** with trialkylalanes Alk_3Al (see Scheme 2)

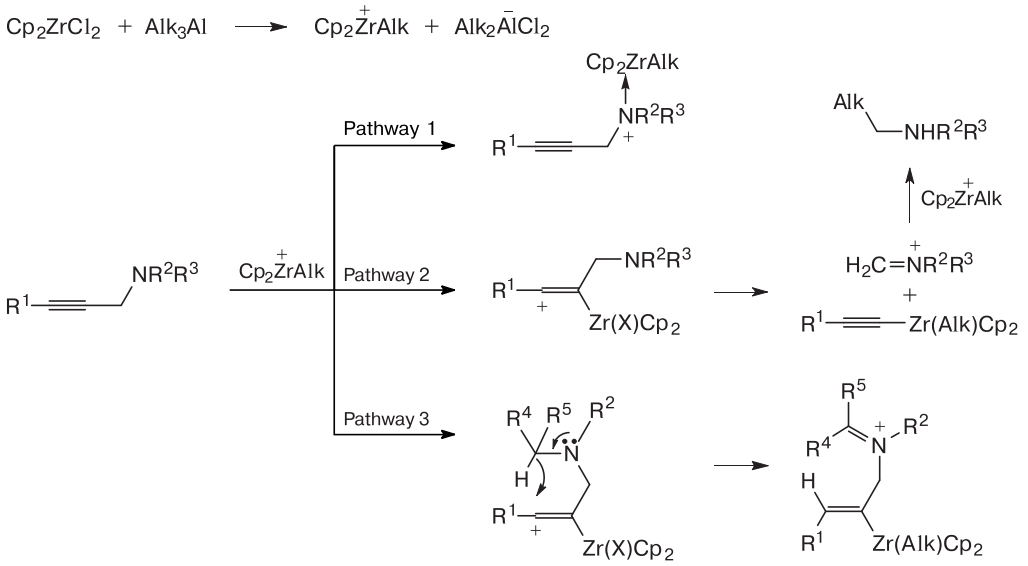
Run	Propargylic amine **1**	Alk_3Al	Solvent	Products (yield (%))	
				2	**3**
1	**1a**	Me_3Al	CH_2Cl_2	**2a** (32)	**3a** (47)
2	**1b**	Me_3Al	CH_2Cl_2	**2a** (42)	**3a** (50)
3	**1c**	Me_3Al	CH_2Cl_2	**2a** (39)	**3a** (48)
4	**1d**	Me_3Al	CH_2Cl_2	**2b** (44)	**3b** (51)
5	**1e**	Me_3Al	CH_2Cl_2	**2b** (56)	**3b** (35)
6	**1f**	Me_3Al	CH_2Cl_2	**2c** (48)	**3c** (34)
7	**1g**	Me_3Al	CH_2Cl_2	**2c** (35)	**3c** (41)
8	**1h**	Me_3Al	CH_2Cl_2	**2d** (31)	**3d** (39)
9	**1i**	Me_3Al	CH_2Cl_2	**2d** (47)	**3d** (35)
10	**1c**	Et_3Al	CH_2Cl_2	**2e** (41)	**3a** (29)
11	**1j**	Et_3Al	CH_2Cl_2	**2f** (34)	**3b** (45)
12	**1f**	Et_3Al	CH_2Cl_2	**2g** (44)	**3c** (30)
13	**1k**	Et_3Al	CH_2Cl_2	**2h** (51)	**3d** (35)
14	**1c**	Me_3Al	Hexane	—*	**3a** (63)
15	**1b**	Me_3Al	Hexane	—*	**3a** (71)
16	**1e**	Me_3Al	Hexane	—*	**3b** (82)
17	**1l**	Me_3Al	Hexane	—*	**3b** (65)
18	**1f**	Me_3Al	Hexane	—*	**3c** (63)
19	**1m**	Me_3Al	Hexane	—*	**3c** (71)
20	**1n**	Me_3Al	Hexane	—*	**3d** (82)
21	**1o**	Me_3Al	Hexane	—*	**3d** (65)

* Not detected.

Contrary to our expectations, the Zr-catalyzed reaction of *N-tert*-alkyl-*N*-(arylmethyl)- (**1**) and *N*-alkyl-*N-tert*-alkyl-substituted (**4**) propargylic amines with trialkylalanes gave no expected carboalumination products. In order to get insight into the mechanism of the reaction with *tert*-alkyl-substituted propargylic amines, we performed quantum-chemical simulation of the *N*-benzyl-*N*-(*tert*-butyl)-but-2-yn-1-amine complex with the methylzirconocene cation Cp_2Zr^+Me generated in the reaction of Cp_2ZrCl_2 with Me_3Al. Since it was assumed that bulky substituents hinder the reaction of cationic intermediates with the nitrogen atom, only such configuration of reagents where the zirconium atom reacts with a triple carbon—carbon bond were considered. Several stationary points corresponding to complexes where the methylzirconocene cation is linked with the *sp*-hybridized carbon atom at the aminomethyl group were localized on the potential energy surface by the B3LYP/6-31G(d)/LanL2DZ method. According to calculations, such a configuration favors stronger polarization of the triple bond. During localization of the transition states, which would correspond to the assumed steps of C—C and C—N bond activation, we detected a transition state where the aminomethyl group undergoes elimination. The energy of activation of this transformation is 6.6 kcal mol^{-1} and the Gibbs energy change is equal to −4.4 kcal mol^{-1}. Elimination of the aminomethyl group results in zirconocene alkynyl derivative and iminium salt. The deuterolysis of the latter affords *N*-benzyl-2-methylpropan-2-amine. The described transformation of *N,N*-disubstituted propargylic amine mediated by cationic zirconium complex correspond to pathway 2 in Scheme 4. This pathway results in the formation of type **3** secondary amine after hydrolysis (see Table 1). Side formation of type **2** tertiary amine is likely due to the alkylation of the iminium salt with alkylzirconocene cation Cp_2Zr^+Alk. One can assume that, upon the reaction in hexane, the rate of iminium salt alkylation decreases, which favors selective formation of secondary amines of type **3**. Usually, the Zr-catalyzed methylalumination is carried out in chlorine-containing solvents (dichloromethane, dichloroethane, and chlorobenzene), which favors an increase in the concentration of methylzirconocene cation Cp_2Zr^+Me.[12,13] The use of hexane as a solvent prevents the Zr-catalyzed methylalumination.

Another transformation pathway of *N,N*-disubstituted propargylic amines is associated with the Zr-promoted hydride transfer from the isoalkyl group earlier discovered by us. In general, the reaction of *N*-alkyl-*N-tert*-alkyl-substituted propargylic amines with cationic zirconium complexes agrees with the scheme that we have proposed earlier for *N*-isoalkyl-substituted propargylic amines.[8] The B3LYP/6-31G(d)/LanL2DZ calculated energy of activation of hydride transfer for *N*-(*tert*-butyl)-*N*-ethylbut-2-yn-1-amine according to pathway 3 (see Scheme 4) is 6.7 kcal mol^{-1} and the Gibbs energy change for this transformation is equal to−9.9 kcal mol^{-1}. Note that corre-

Scheme 4



sponding values for *N,N*-diisopropylbut-2-yn-1-amine are 4.7 and −15.9 kcal mol^{-1}.[8] As noted above, *N*-butyl-*N*-isopropyl-substituted propargylic amines, in contrast to *N*-alkyl-*N*-*tert*-alkyl-substituted ones, are unreactive under the studied reaction conditions. This can be due to smaller steric hindrances at the nitrogen atoms to result in pathway 1 shown in Scheme 4.

In conclusion, substituted propargylic amines in the presence of cationic zirconium complex can transform *via* several pathways depending on the nature of the substituents at the nitrogen atom. Since alkylzirconocene cation is a Lewis acid and propargylic amine is a Lewis base, propargylic amine can complex with alkylzirconocene cation in the absence of steric hindrances. We assumed that this scenario occurs in the case of *N,N*-dialkyl-substituted propargylic amines. Bulkier substituents, such as isoalkyl and *tert*-alkyl groups, prevent such coordination and favor the electrophilic attack of alkylzirconocene cation at the acetylenic bond. However, due to unique electronic properties of the nitrogen atom (high electronegativity and capability of negative hyperconjugation), other reactions, instead of expected carboalumnation, proceed at higher rates. Of great interest is the earlier undetected Zr-promoted hydride transfer resulting in unusual organoaluminum and organozirconium iminium salts which can possess nontrivial reactivity.

Experimental

Commercially available reagents were used. Reactions with organoaluminum compounds were carried out under a dry argon atmosphere. Hexane was distilled over Bu^i_3Al. Propargylic amines were obtained by the reaction of terminal acetylenes with formaldehyde and secondary amines in dioxane.[14] Secondary amines were obtained by the reduction of Schiff bases with sodium borohydride.[15] Reaction products were analyzed on a Carlo Erba chromatograph (Ultra-1 glass capillary column (Hewlett Packard), 25 m×0.2 mm, flame ionization detector, the thermostate temperature was 50—170 °C, the carrier gas was helium). Mass spectra were recorded using a Finnigan 4021 instrument at an ionizing electron energy of 70 eV; the ionization chamber temperature was 200 °C. Elemental analysis was carried out on a Carlo Erba model 1106 analyzer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C) relative to $SiMe_4$ and carbon signals of $CDCl_3$ (the internal standards). Atomic numbering used in the description of ^{1}H and ^{13}C NMR spectra for compounds **2a—h**, **3a—d,** and **5a—c** is shown in Fig. 1. Thin-layer chromatography was carried out on Silufol UV-254 plates.

Caution! *Organoaluminum compounds are pyrophoric and can flame upon contact with air, water, and any oxidizer.*

Zirconium-catalyzed reaction of *N*-*tert*-alkyl-*N*-(arylmethyl)-substituted propargylic amines 1 with trialkylalanes (general procedure). A Teflon-coated magnetic stir bar and Cp_2ZrCl_2 (0.117 g, 0.4 mmol) were placed in a 25-mL one-necked round-bottom flask mounted on a magnetic stirrer. The flask was tightly sealed with a septum and purged with argon. Dichloromethane or hexane (5 mL), Me_3Al (0.4 mL) or Et_3Al (0.6 mL, 4 mmol), and *N*-*tert*-alkyl-*N*-(arylmethyl)-substituted propargylic amine **1a—o** (2 mmol) were syringed at room temperature. The mixture was stirred at 40 °C for 6 h, cooled to room temperature and the same solvent (5 mL) was added. The mixture was cooled using an ice bath and then water (3 mL) was added dropwise. The precipitate that formed was filtered off and the aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic layers were dried over anhydrous KOH. Pure compounds were isolated by column chromatography using hexane—ethyl acetate (5 : 1) as the eluent.

***N*-Ethyl-*N*-(4-methoxybenzyl)-2,4,4-trimethylpentan-2-amine (2a).** Transparent oil. R_f 0.5 (ethyl acetate—hexane, 1 : 5).

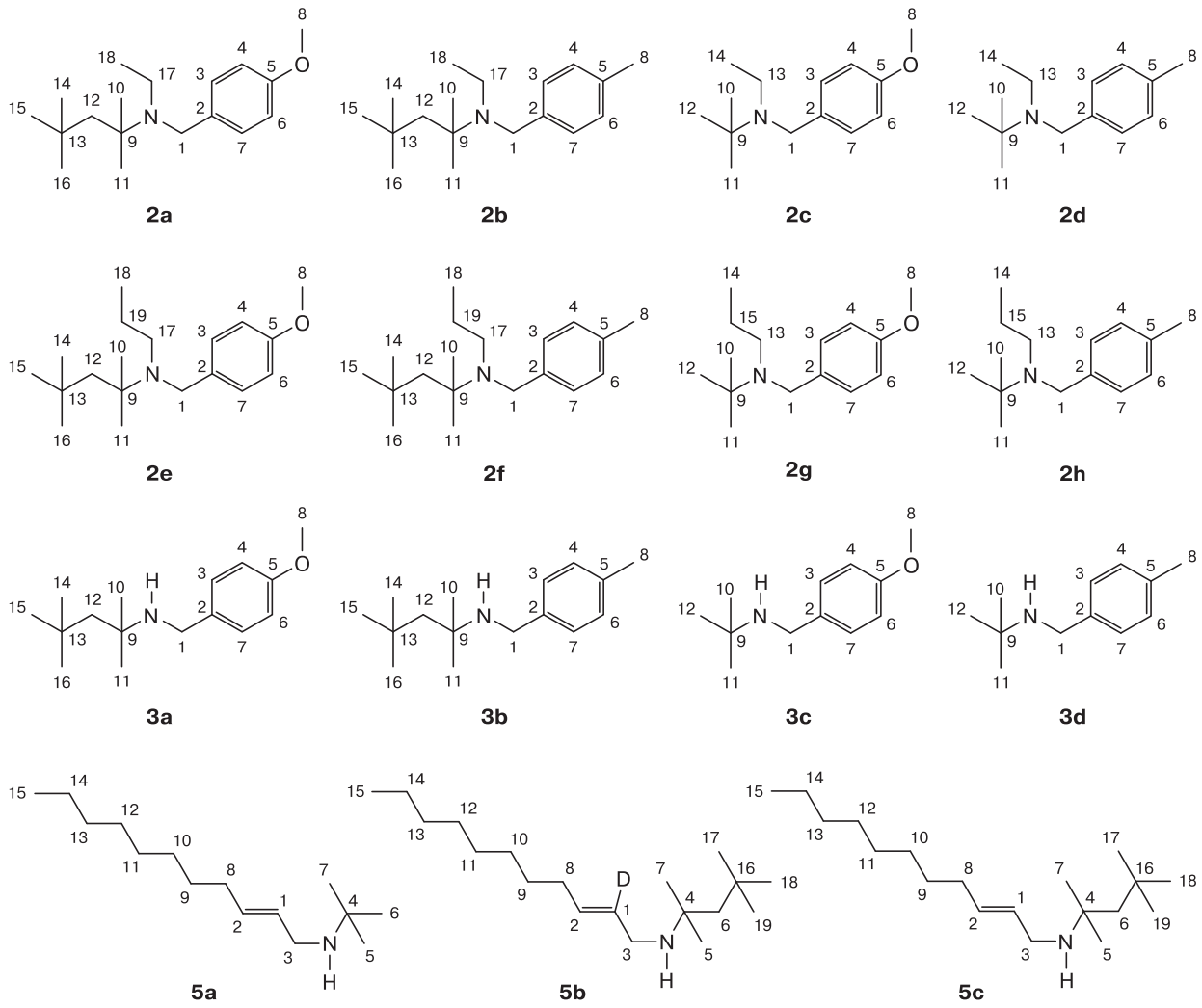


Fig. 1. Numbering of carbon atoms in compounds **2a—h**, **3a—d**, and **5a—c** used for interpretation of their ^{1}H and ^{13}C NMR spectra.

Found (%): C, 77.86; H, 11.29; N, 4.91. $C_{18}H_{31}NO$. Calculated (%): C, 77.92; H, 11.26; N, 5.05. ^{1}H NMR, δ: 0.89 (t, 3 H, C(18)H_3, J = 7.1 Hz); 1.05 (s, 9 H, C(14)H_3, C(15)H_3, C(16)H_3); 1.19 (s, 6 H, C(10)H_3, C(11)H_3); 1.54 (s, 2 H, C(12)H_2); 2.64 (q, 2 H, C(17)H_2, J = 7.1); 3.67 (s, 2 H, C(1)H_2); 3.82 (s, 3 H, C(8)H_3); 6.86 (d, 2 H, C(3)H, C(7)H, J = 8.6); 7.34 (d, 2 H, C(4)H, C(6)H, J = 8.4). ^{13}C NMR, δ: 16.03 (C(18)); 27.81 (2 C, C(10), C(11)); 31.41 (C(13)); 32.05 (3 C, C(14), C(15), C(16)); 44.06 (C(17)); 50.15 (C(12)); 52.80 (C(1)); 55.23 (C(8)); 59.04 (C(9)); 113.27 (2 C, C(4), C(6)); 128.70 (2 C, C(3), C(7)); 136.31 (C(2)); 157.93 (C(5)). MS, *m/z*: 262 (1) $[M - Me]^+$, 206 (16), 121 (100), 57 (5).

***N*-Ethyl-2,4,4-trimethyl-*N*-(4-methylbenzyl)pentan-2-amine (2b).** Transparent oil. R_f 0.7 (ethyl acetate—hexane, 1 : 5). Found (%): C, 82.70; H, 11.88; N, 5.20. $C_{18}H_{31}N$. Calculated (%): C, 82.69; H, 11.95; N, 5.36. ^{1}H NMR, δ: 0.92 (t, 3 H, C(18)H_3, J = 7.0 Hz); 1.07 (s, 9 H, C(14)H_3, C(15)H_3, C(16)H_3); 1.21 (s, 6 H, C(10)H_3, C(11)H_3); 1.56 (s, 2 H, C(12)H_2); 2.37 (s, 3 H, C(8)H_3); 2.65 (q, 2 H, C(17)H_2, J = 7.1 Hz); 3.71 (s, 2 H, C(1)H_2); 7.13 (d, 2 H, C(3)H, C(7)H, J = 7.7 Hz); 7.34 (d, 2 H, C(4)H, C(6)H, J = 7.6 Hz). ^{13}C NMR, δ: 15.99 (C(18)); 21.06 (C(8)); 27.79 (2 C, C(10), C(11)); 31.42 (C(13)); 32.06 (3 C, C(14), C(15), C(16)); 44.19 (C(17)); 50.19 (C(12)); 53.21 (C(1)); 59.08 (C(9)); 127.64 (2 C, C(4), C(6)); 128.58 (2 C, C(3), C(7)); 135.30 (C(2)); 141.34 (C(5)). MS, *m/z*: 261 (<1) $[M]^+$, 246 (3), 190 (45), 105 (100), 57 (8).

***N*-Ethyl-*N*-(4-methoxybenzyl)-2-methylpropan-2-amine (2c).** Transparent oil. R_f 0.5 (ethyl acetate—hexane, 1 : 5). Found (%): C, 75.81; H, 10.35; N, 6.36. $C_{14}H_{23}NO$. Calculated (%): C, 75.97; H, 10.47; N, 6.33. ^{1}H NMR, δ: 0.89 (t, 3 H, C(14)H_3, J = 7.1 Hz); 1.15 (s, 9 H, C(10)H_3, C(11)H_3, C(12)H_3); 2.63 (q, 2 H, C(13)H_2, J = 7.1 Hz); 3.64 (s, 2 H, C(1)H_2); 3.82 (s, 3 H, C(8)H_3); 6.86 (d, 2 H, C(3)H, C(7)H, J = 8.5 Hz); 7.33 (d, 2 H, C(4)H, C(6)H, J = 8.4 Hz). ^{13}C NMR, δ: 15.79 (C(14)); 27.57 (3 C, C(10), C(11), C(12)); 43.73 (C(13)); 52.55 (C(1)); 54.87 (C(9)); 55.24 (C(8)); 113.31 (2 C, C(4), C(6)); 128.88 (2 C, C(3), C(7)); 135.76 (C(2)); 157.03 (C(5)). MS, *m/z*: 221 (5) $[M]^+$, 206 (20), 121 (100), 77 (8).

***N*-Ethyl-2-methyl-*N*-(4-methylbenzyl)propan-2-amine (2d).** Transparent oil. R_f 0.8 (ethyl acetate—hexane, 1 : 5). Found (%): C, 81.99; H, 11.30; N, 6.69. $C_{14}H_{23}N$. Calculated (%): C, 81.89; H, 11.29; N, 6.82. ^{1}H NMR, δ: 0.95 (t, 3 H, C(14)H_3, J = 7.1 Hz);

1.19 (s, 9 H, C(10)H_3, C(11)H_3, C(12)H_3); 2.93 (s, 2 H, C(1)H_2); 2.68 (q, 2 H, C(13)H_2, J = 7.1 Hz); 3.71 (s, 3 H, C(8)H_3); 7.16 (d, 2 H, C(3)H, C(7)H, J = 7.7 Hz); 7.36 (d, 2 H, C(4)H, C(6)H, J = 7.7 Hz). ^{13}C NMR, δ: 15.83 (C(14)); 21.09 (C(1)); 27.59 (3 C, C(10), C(11), C(12)); 43.91 (C(13)); 53.00 (C(8)); 54.92 (C(9)); 127.81 (2 C, C(3), C(7)); 128.64 (2 C, C(4), C(6)); 135.46 (C(2)); 140.81 (C(5)). MS, *m/z*: 205 (7) $[M]^+$, 190 (65), 134 (8), 105 (100), 41 (15).

***N*-(4-Methoxybenzyl)-2,4,4-trimethyl-*N*-propylpentan-2-amine (2e).** Transparent oil. R_f 0.5 (ethyl acetate—hexane, 1 : 5). Found (%): C, 78.17; H, 11.48; N, 4.90. $C_{19}H_{33}NO$. Calculated (%): C, 78.29; H, 11.41; N, 4.81. ^{1}H NMR, δ: 1.03 (t, 3 H, C(18)H_3, J = 7.2 Hz); 1.06 (s, 9 H, C(14)H_3, C(15)H_3, C(16)H_3); 1.21 (s, 6 H, C(10)H_3, C(11)H_3); 1.20—1.45 (m, 4 H, C(17)H_2, C(19)H_2); 1.55 (s, 2 H, C(12)H_2); 3.68 (s, 2 H, C(1)H_2); 3.82 (s, 3 H, C(8)H_3); 7.15—7.48 (m, 4 H, Ar). ^{13}C NMR, δ: 14.12 (C(18)); 22.70 (C(19)); 27.99 (2 C, C(10), C(11)); 32.04 (3 C, C(14), C(15), C(16)); 49.66 (C(12)); 53.16 (C(8)); 53.38 (C(1)); 55.17 (C(17)); 113.24 (2 C, C(4), C(6)); 128.63 (2 C, C(3), C(7)); 136.32 (C(2)); 157.95 (C(5)). MS, *m/z*: 291 (<1) $[M]^+$, 276 (<1) $[M - Me]^+$, 220 (16), 121 (100), 41 (6).

2,4,4-Trimethyl-*N*-(4-methylbenzyl)-*N*-propylpentan-2-amine (2f). Transparent oil. R_f 0.6 (ethyl acetate—hexane, 1 : 5). Found (%): C, 82.69; H, 12.13; N, 4.88. $C_{19}H_{33}N$. Calculated (%): C, 82.84; H, 12.07; N, 5.08. ^{1}H NMR, δ: 1.04 (t, 3 H, C(18)H_3, J = 7.2 Hz); 1.08 (s, 9 H, C(14)H_3, C(15)H_3, C(16)H_3), 1.25 (s, 6 H, C(10)H_3, C(11)H_3); 1.25—1.50 (m, 4 H, C(17)H_2, C(19)H_2); 1.54 (s, 2 H, C(12)H_2); 2.36 (s, 3 H, C(8)H_3); 3.73 (s, 2 H, C(1)H_2); 7.15—7.48 (m, 4 H, Ar). ^{13}C NMR, δ: 14.14 (C(18)); 21.08 (C(8)); 22.71 (C(19)); 29.16 (2 C, C(10), C(11)); 31.77 (3 C, C(14), C(15), C(16)); 46.38 (C(1)); 53.10 (C(12)); 54.52 (C(17)); 128.13 (2 C, C(4), C(6)); 129.03 (2 C, C(3), C(7)); 136.14 (C(2)); 138.65 (C(5)). MS, *m/z*: 275 (<1) $[M]^+$, 260 (3), 204 (76), 134 (6), 105 (100), 41 (23).

***N*-(*tert*-Butyl)-*N*-(4-methoxybenzyl)propan-1-amine (2g).** Transparent oil. R_f 0.5 (ethyl acetate—hexane, 1 : 5). Found (%): C, 76.78; H, 10.87; N, 5.97. $C_{15}H_{25}NO$. Calculated (%): C, 76.55; H, 10.71; N, 5.95. ^{1}H NMR, δ: 0.79 (d, 3 H, C(14)H_3, J = 7.3); 1.28 (s, 9 H, C(10)H_3, C(11)H_3, C(12)H_3); 1.22—1.46 (m, 2 H, C(15)H_2); 2.52 (t, 2 H, C(13)H_2, J = 7.6); 3.67 (s, 2 H, C(1)H_2); 3.84 (s, 3 H, C(8)H_3); 6.88 (d, 2 H, C(3)H, C(7)H, J = 8.5); 7.34 (d, 2 H, C(4)H, C(6)H, J = 8.4). ^{13}C NMR, δ: 15.79 (C(14)); 23.67 (C(15)); 27.46 (3 C, C(10), C(11), C(12)); 52.83, 53.63, 55.19 (C(1), C(8), C(13)); 54.85 (C(9)); 113.29 (2 C, C(4), C(6)); 126.77 (2 C, C(3), C(7)); 135.95 (C(2)); 158.03 (C(5)).

***N*-(*tert*-Butyl)-*N*-(4-methylbenzyl)propan-1-amine (2h).** Transparent oil. R_f 0.7 (ethyl acetate—hexane, 1 : 5). Found (%): C, 82.20; H, 11.37; N, 6.42. $C_{15}H_{25}N$. Calculated (%): C, 82.13; H, 11.49; N, 6.39. ^{1}H NMR, δ: 0.80 (d, 3 H, C(14)H_3, J = 7.3 Hz); 1.30 (s, 9 H, C(10)H_3, C(11)H_3, C(12)H_3); 1.20—1.46 (m, 2 H, C(15)H_2); 2.38 (s, 3 H, C(8)H_3); 2.54 (t, 2 H, C(13)H_2, J = 7.6 Hz); 3.70 (s, 2 H, C(1)H_2); 7.14 (d, 2 H, C(3)H, C(7)H, J = 7.6 Hz); 7.33 (d, 2 H, C(4)H, C(6)H, J = 7.6 Hz). ^{13}C NMR, δ: 11.89 (C(14)); 21.08, 23.61 (C(8), C(15)); 27.45 (3 C, C(10), C(11), C(12)); 52.98, 53.42 (C(1), C(13)); 54.08 (C(9)); 127.66 (2 C, C(4), C(6)); 128.59 (2 C, C(3), C(7)); 135.37 (C(2)); 141.02 (C(5)). MS, *m/z*: 219 (3) $[M]^+$, 204 (17), 134 (17), 105 (100), 41 (6).

***N*-(4-Methoxybenzyl)-2,4,4-trimethylpentan-2-amine (3a).** Transparent oil. R_f 0.5 (ethyl acetate—hexane, 1 : 5). Found (%): C, 77.26; H, 10.80; N, 5.79. $C_{16}H_{27}NO$. Calculated (%): C, 77.06; H, 10.91; N, 5.62. ^{1}H NMR, δ: 0.89 (t, 3 H, C(18)H_3, J = 7.1 Hz); 1.05 (s, 9 H, C(14)H_3, C(15)H_3, C(16)H_3); 1.19 (s, 6 H, C(10)H_3, C(11)H_3); 1.54 (s, 2 H, C(12)H_2); 2.64 (q, 2 H, C(17)H_2, J = 7.1 Hz); 3.67 (s, 2 H, C(1)H_2); 3.82 (s, 3 H, C(8)H_3); 6.86 (d, 2 H, C(3)H, C(7)H, J = 8.6 Hz); 7.34 (d, 2 H, C(4)H, C(6)H, J = 8.4 Hz). ^{13}C NMR, δ: 27.99 (2 C, C(10), C(11)); 31.94 (C(13)); 32.04 (3 C, C(14), C(15), C(16)); 49.66 (C(12)); 53.16 (C(1)); 55.17 (C(1)); 55.23 (C(8)); 59.04 (C(9)); 113.27 (2 C, C(4), C(6)); 128.70 (2 C, C(3), C(7)); 136.31 (C(2)); 157.93 (C(5)). MS, *m/z*: 249 (<1) $[M]^+$, 232 (87), 176 (100), 135 (94), 77 (26), 57 (57), 41 (61).

2,4,4-Trimethyl-*N*-(4-methylbenzyl)pentan-2-amine (3b). Transparent oil. R_f 0.6 (ethyl acetate—hexane, 1 : 5). Found (%): C, 82.38; H, 11.53; N, 6.11. $C_{16}H_{27}N$. Calculated (%): C, 82.34; H, 11.66; N, 6.00. ^{1}H NMR, δ: 1.12 (s, 9 H, C(14)H_3, C(15)H_3, C(16)H_3); 1.28 (s, 6 H, C(10)H_3, C(11)H_3); 1.57 (s, 2 H, C(12)H_2); 2.39 (s, 3 H, C(8)H_3); 3.76 (s, 2 H, C(1)H_2); 7.15—7.35 (m, 4 H, Ar). ^{13}C NMR, δ: 21.13 (C(8)); 29.22 (2 C, C(10), C(11)); 31.88 (3 C, C(14), C(15), C(16)); 46.42, 53.13 (C(1), C(12)); 54.51 (C(9)); 128.16 (2 C, C(4), C(6)); 129.06 (2 C, C(3), C(7)); 136.14 (C(2)); 138.72 (C(5)). MS, *m/z*: 233 (<1) $[M]^+$, 216 (99), 174 (14), 160 (98), 91 (40), 41 (100).

***N*-(4-Methoxybenzyl)-2-methylpropan-2-amine (3c).** Transparent oil. R_f 0.6 (ethyl acetate—hexane, 1 : 5). Found (%): C, 74.70; H, 9.77; N, 7.29. $C_{12}H_{19}NO$. Calculated (%): C, 74.57; H, 9.91; N, 7.25. ^{1}H NMR, δ: 1.20 (s, 9 H, C(10)H_3, C(11)H_3, C(12)H_3); 3.69 (s, 2 H, C(1)H_2); 3.81 (s, 3 H, C(8)H_3); 6.87 (d, 2 H, C(3)H, C(7)H, J = 8.4 Hz); 7.28 (d, 2 H, C(4), C(6)H, J = 8.1 Hz). ^{13}C NMR, δ: 29.05 (3 C, C(10), C(11), C(12)); 46.59 (C(1)); 50.83 (C(9)); 55.28 (C(8)); 113.84 (2 C, C(4), C(6)); 129.47 (2 C, C(3), C(7)); 133.29 (C(2)); 158.54 (C(5)). MS, *m/z*: 193 (<1) $[M]^+$, 178 (4), 121 (46), 40 (100).

2-Methyl-*N*-(4-methylbenzyl)propan-2-amine (3d). Transparent oil. R_f 0.8 (ethyl acetate—hexane, 1 : 5). Found (%): C, 81.50; H, 10.71; N, 7.73. $C_{12}H_{19}N$. Calculated (%): C, 81.30; H, 10.80; N, 7.90. ^{1}H NMR, δ: 1.16 (s, 9 H, C(10)H_3, C(11)H_3, C(12)H_3); 3.67 (s, 2 H, C(1)H_2); 3.84 (s, 3 H, C(8)H_3); 6.88 (d, 2 H, C(3)H, C(7)H, J = 8.5 Hz); 7.34 (d, 2 H, C(4)H, C(6)H, J = 8.4 Hz). ^{13}C NMR, δ: 23.67 (C(1)); 27.46 (3 C, C(10), C(11), C(12)); 52.83 (C(8)); 54.85 (C(9)); 113.29 (2 C, C(4), C(6)); 128.77 (2 C, C(3), C(7)); 135.95 (C(2)); 158.03 (C(5)). MS, *m/z*: 177 (<1) $[M]^+$, 160 (100), 118 (60), 91 (23), 57 (41), 41 (34).

Zirconium-catalyzed reaction of *N*-alkyl-*N*-*tert*-alkyl-substituted propargylic amines 4a,b with trimethylaluminum (general procedure). A Teflon-coated magnetic stir bar and Cp_2ZrCl_2 (0.117 g, 0.4 mmol) were placed in a 25-mL one-necked round-bottom flask mounted on a magnetic stirrer, sealed with a septum and purged with dry argon. Dichloromethane (5 mL), Me_3Al (0.38 mL, 4 mmol), and *N*-alkyl-*N*-*tert*-alkyl-substituted propargylic amine **4a,b** (2 mmol) were sequentially syringed through the septum at room temperature. The reaction mixture was stirred at 40 °C for 1 h and cooled to room temperature. Additional portion of CH_2Cl_2 (5 mL) was added. The mixture was cooled using an ice bath and water (3 mL) or D_2O (3 mL) was added dropwise. The precipitate that formed was filtered off and the aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic layers were dried over anhydrous KOH. Pure compounds were isolated by column chromatography using hexane—ethyl acetate (5 : 1) as the eluent.

(*E*)-*N*-(*tert*-Butyl)undec-2-en-1-amine (5a). Transparent oil. R_f 0.7 (ethyl acetate—hexane, 1 : 5). Found (%): C, 80.11; H, 13.76; N, 6.03. $C_{15}H_{31}N$. Calculated (%): C, 79.92; H, 13.86; N, 6.21. ^{1}H NMR, δ: 0.89 (t, 3 H, C(15)H_3, J = 6.8 Hz); 1.13 (s, 9 H, C(5)H_3, C(6)H_3, C(7)H_3); 1.20—1.35 (m, 10 H, C(10)H_2, C(11)H_2, C(12)H_2, C(13)H_2, C(14)H_2); 1.35—1.50 (m, 2 H, C(9)H_2); 2.01 (dd, 2 H, C(8)H_2, J = 13.6 Hz, J = 6.5 Hz); 3.15 (d, 2 H, C(3)H_2, J = 5.5 Hz); 5.50—5.50 (m, 2 H, C(1)H, C(2)H). ^{13}C NMR, δ: 14.10 (C(15)); 22.67 (C(14)); 29.06 (3 C, C(5), C(6), C(7)); 29.22, 29.28, 29.47, 31.89 (5 C, C(9), C(10), C(11), C(12), C(13)); 32.40 (C(8)); 128.97 (C(1)); 132.33 (C(2)). MS, m/z: 225 (10) $[M]^+$, 210 (100), 135 (7), 57 (81), 41 (18).

(*E*)-*N*-(2,4,4-Trimethylpent-2-yl)undec-2-en-1-amine-2-*d* (5b). Transparent oil. R_f 0.6 (ethyl acetate—hexane, 1 : 5). Found (%): C, 80.70; N, 4.89. $C_{19}H_{38}DN$. Calculated (%): C, 80.77; N, 4.96. ^{1}H NMR, δ: 0.88 (t, 3 H, C(15)H_3 , J = 6.9 Hz); 1.01 (s, 9 H, C(17)H_3, C(18)H_3, C(19)H_3); 1.15 (s, 6 H, C(5)H_3, C(7)H_3); 1.20—1.60 (m, 12 H, C(9)H_2, C(10)H_2, C(11)H_2, C(12)H_2, C(13)H_2, C(14)H_2); 1.44 (s, 2 H, C(6)H_2); 2.00 (dd, 2 H, C(8)H_2, J = 14.3 Hz, J = 7.0 Hz); 3.12 (s, 2 H, C(3)H_2); 5.56 (t, 1 H, C(2)H, J = 6.5 Hz). ^{13}C NMR, δ: 14.08 (C(15)); 22.66 (C(14)); 29.07 (2 C, C(5), C(7)); 29.19, 29.28, 29.30, 31.88, 31.91 (5 C, C(9), C(10), C(11), C(12), C(13)); 31.63 (C(16)); 32.36 (C(8)); 44.25 (C(3)); 52.65 (C(6)); 54.12 (C(4)); 128.70 (t, C(1), $^1J_{CD}$ = 23.15 Hz); 131.95 (C(2)).

(*E*)-*N*-(2,4,4-Trimethylpent-2-yl)undec-2-en-1-amine (5c). Transparent oil. R_f 0.6 (ethyl acetate—hexane, 1 : 5). Found (%): C, 81.16; H, 13.88; N, 5.03. $C_{19}H_{39}N$. Calculated (%): C, 81.06; H, 13.96; N, 4.98. ^{1}H NMR, δ: 0.89 (t, 3 H, C(15)H_3, J = 6.8 Hz); 1.02 (s, 9 H, C(17)H_3, C(18)H_3, C(19)H_3); 1.16 (s, 6 H, C(5)H_3, C(7)H_3); 1.20—1.60 (m, 12 H, C(9)H_2, C(10)H_2, C(11)H_2, C(12)H_2, C(13)H_2, C(14)H_2); 1.46 (s, 2 H, C(6)H_2); 2.00 (dd, 2 H, C(8)H_2, J = 13.5 Hz, J = 6.4 Hz); 3.14 (d, 2 H, C(3)H_2, J = 5.3 Hz); 5.44—5.67 (m, 2 H, C(1)H, C(2)H). ^{13}C NMR, δ: 14.10 (C(15)); 22.67 (C(14)); 29.08 (2 C, C(5), C(7)); 29.20, 29.28, 29.31, 29.47, 31.89 (5 C, C(9), C(10), C(11), C(12), C(13)); 31.64 (C(16)); 32.42 (C(8)); 44.37 (C(3)); 52.66 (C(6)); 54.15 (C(4)); 129.04 (C(1)); 132.10 (C(2)). MS, m/z: 266 (12) $[M - Me]^+$, 210 (100), 58 (49), 41 (27).

This work was financially supported by the Russian Science Foundation (Project No. 19-73-20128).

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Received July 15, 2019;
in revised form September 27, 2019;
accepted October 22, 2019