Synthesis and transformations of metallacycles
39.* Zr-Catalyzed cyclomagnesiation of N-containing allenes

V. A. D´yakonov, A. A. Makarov, E. Kh. Makarova, T. V. Tyumkina, and U. M. Dzhemilev*

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences,
141 prosp. Oktyabrya, 450075 Ufa, Bashkortostan, Russian Federation.
Fax: +7 (347) 284 2750. E-mail: ink@anrb.ru

Catalytic cyclomagnesiation of N-containing 1,2-dienes with Et_2Mg in the presence of the Zr-based complexes affords 2-(aminoalkylidene)magnesacyclopentanes in 68—84% yields.

Key words: organomagnesium compounds, metallocomplex catalysis, magnesacyclopentane, 1,2-dienes, cyclomagnesiation.

The catalytic cyclomagnesiation of olefins with RMgR´ in the presence of Cp_2ZrCl_2 gives magnesacyclopentanes in high regio- and stereoselectivity.[2—5] The study of this reaction using as examples compounds of the norbornene structure, acetylenes, and 1,2-dienes made it possible to synthesize mono-, bi-, tri-, and polycyclic magnesacarbocycles and to develop many preparative one-pot methods for the synthesis of practically important and earlier poorly accessible carbo- and heterocyclic compounds.[6—12]

In spite of a great variety of unsaturated compounds used as objects of the study in the catalytic cyclomagnesiation reaction, there are only few published examples for the use of functionally substituted olefins and data on this reaction involving 1,2-dienes containing the heteroatom in the structure are entirely lacking.[13—17]

In this work, we present for the first time the results of studying the cyclomagnesiation of N-containing 1,2-dienes with RMgR´ in the presence of the Zr-containing catalysts exhibiting the highest activity in the cyclometallation of olefins, allenes, and acetylenes.[18—25]

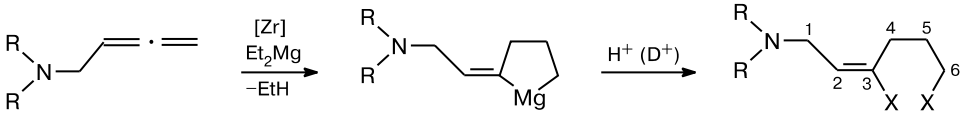
It was established for the reaction of 1-buta-2,3-dien-1-ylmorpholine (**1d**) with twofold excess of Et_2Mg that in the presence of 5 mol.% Cp_2ZrCl_2 in Et_2O magnesacyclopentane **2d** was selectively formed within 8 h at 20—22 °C, which follows from an analysis of its acidic hydrolysis and deuterolysis. For instance, the hydrolysis and deuterolysis of the reaction mixture gave 4-[(2*Z*)-hex-2-en-1-yl]-morpholine (**3d**) and 4-[(2*Z*)-3,6-dideuteriohex-2-en-1-yl]morpholine (**4d**) in ~80% yields (Scheme 1).

The structures of synthesized magnesacyclopentanes **2** were determined by the study of the 1D and 2D NMR spectra of hydrolysis product **3** and deuterolysis product **4**.

For instance, the hydrolysis of compound **2a** afforded *N*,*N*-diethylhex-2-ene-1-amine (**3a**) exclusively with the *Z*-configuration of the double bond, which is unambiguously determined by the presence of the NOE effect between the allylic protons (δH(1) = 3.09 and δH(4) = 2.06) and also by the values of vicinal spin-spin coupling constants δH(3) = 5.43 (d, ^3J = 11 Hz, t, ^3J = 7 Hz).[26]

After the deuterolysis of organomagnesium compound (OMC) **2a**, we obtained partially deuterated amine including deuterium at C(3) and C(6) >98 and ~95%, respectively, which is confirmed by two Mg—C bonds in initial compound **2a**. Similar results were achieved by the cyclomagnesiation of allenes **1b—d**, which suggests the formation of N-containing 2-alkylidenemagnesacyclopentanes **2** during the reaction.

Scheme 1



1a—d **2a—d** **3a—d, 4a—d**

[Zr] = Cp_2ZrCl_2; X = H (**3**), D (**4**); R = Et (**a**), Pr^i (**b**); R—R = $(CH_2)_4$ (**c**), $C_2H_4OC_2H_4$ (**d**)

* For Part 38, see Ref. 1.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 156—162, January, 2012.

The substituent at the allene group exerts a noticeable effect on stereoselectivity of the reaction. Under the developed conditions, 1,1-disubstituted N-containing 1,2-dienes **5** react with Et_2Mg in the presence of 10 mol.% Cp_2ZrCl_2 (Scheme 2), giving (after the hydrolysis of the reaction mixture) the corresponding unsaturated amines as *cis*- (**8**) and *trans*-isomers (**10**). *cis*-Isomers ($Z : E = 10 : 1$) predominate in the case of 2-methyl-1-buta-2,3-dien-1-yl(diethyl)amine (**5a**) or 2-methyl-1-buta-2,3-dien-1-ylmorpholine (**5b**) containing the methyl substituent at the allene group. The configuration of the substituents at the double bond of the main isomer was unambiguously proved by the presence of the intense cross-peak of the hydrogen atoms of the methyl group δH(7) = 1.74 with the proton at the double bond δH(3) = 5.34 in the NOESY experiment and by the appearance of the signal from the methyl group at δC(7) = 23.09 and 14.96 for the *cis*- and *trans*-isomer, respectively. An increase in the content of the *trans*-isomers over the *cis*-isomers is observed with the elongation of the chain of the alkyl substituent at the allene group, for instance, 2-ethyl-1-buta-2,3-dien-1-ylmorpholine (**5c**) or 2-butyl-1-buta-2,3-dien-1-ylmorpholine (**5d**) (Table 1, see Scheme 2).

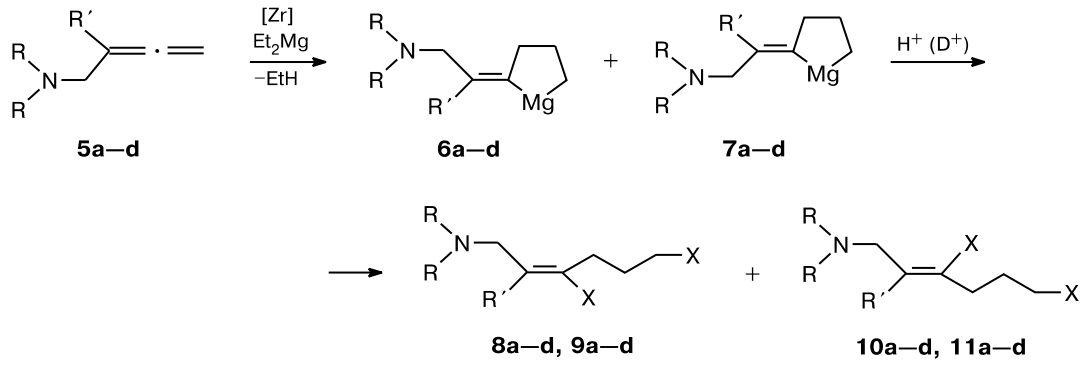
The structures of the synthesized cyclic OMC were identified by the spectra of the hydrolysis and deuterolysis products and, in some cases, by the 1D and 2D ^1H and ^{13}C NMR spectra detected directly for the magnesacarbocycles.

For instance, for the major product of cyclomagnesiation of compound **5a**, the spectrum corresponding to the sp^2-hybridized carbon atoms exhibits signals with δ 168.86 and 136.34, the latter being broadened because of the influence of the adjacent metal atom (the spin of the magnesium nucleus is 5/2). The HMBC spectrum with these characteristic signals (Fig. 1) include three cross-peaks, due to which the signals from the methylenic protons of the NCH_2 group at δ 2.74 and the $C(2)H_2$ group of the cycle at δ 2.01 were assigned, as well as the protons of the methyl substituent at δ 1.56. According to the HSQC correlation spectral data, the chemical shifts of the carbon atoms bonded to these protons are 54.15, 39.93, and 28.50 ppm, respectively. Having unambiguously determined the ^1H and ^{13}C NMR parameters of the atoms in position 3 of magnesacyclopentane, we also determined the chemical shifts of the whole cyclic framework using COSYHH (see Fig. 1).

Thus, the new *N*-alkylidenemagnesacyclopentanes acting, as a rule, as intermediate synthones were identified for the first time by the NMR spectra.

Of the tested Zr-based complexes, the highest activity in the cycloalumination of 1,2-diene **1d** belongs to Cp_2ZrCl_2

Scheme 2



[Zr] = Cp_2ZrCl_2; X = H (**8**, **10**), D (**9**, **11**); R = Et, R′ = Me (**a**); R—R = $C_2H_4OC_2H_4$, R′ = Me (**b**), Et (**c**), Bu (**d**)

Table 1. Cyclomagnesiation of N-containing 1,2-dienes **1** and **5** with Et_2Mg using the Cp_2ZrCl_2 catalyst

1,2-Diene	R or R—R	R′	*Z*/*E* (product)	Yield (%)
1-Buta-2,3-dien-1-yl(diethyl)amine (**1a**)	Et	H	1 : 0 (**3a**)	68
1-Buta-2,3-dien-1-yl(di-*iso*-propyl)amine (**1b**)	Pr^i	H	1 : 0 (**3b**)	72
1-Buta-2,3-dien-1-ylpiperidine (**1c**)	$-(CH_2)_4-$	H	1 : 0 (**3c**)	75
1-Buta-2,3-dien-1-ylmorpholine (**1d**)	$-C_2H_4OC_2H_4-$	H	1 : 0 (**3d**)	79
2-Methyl-1-buta-2,3-dien-1-yl(diethyl)amine (**5a**)	Et	Me	10 : 1 (**8a** : **10a**)	77
2-Methyl-1-buta-2,3-dien-1-ylmorpholine (**5b**)	$-C_2H_4OC_2H_4-$	Me	10 : 1 (**8b** : **10b**)	82
2-Ethyl-1-buta-2,3-dien-1-ylmorpholine (**5c**)	$-C_2H_4OC_2H_4-$	Et	3 : 1 (**8c** : **10c**)	84
2-Butyl-1-buta-2,3-dien-1-ylmorpholine (**5d**)	$-C_2H_4OC_2H_4-$	Bu	1 : 1 (**8d** : **10d**)	81

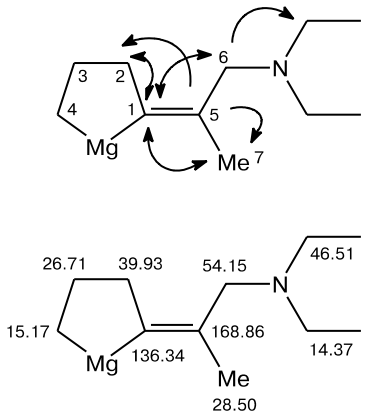


Fig. 1. Proof of the structure of magnesacyclopentane **6a**.

(79%, **3d**) and $(CpMe)_2ZrCl_2$ (51%, **3d**). When using other compounds (Ind_2ZrCl_2, $Zr(acac)_2$, $ZrCl_4$, or Py_2ZrCl_2), the yield of the target metallacycles did not exceed 10%.

Under the conditions developed above, the reaction of 1,2-dienes with EtMgBr affords a mixture of cyclo- and carbomagnesiation products in a ratio of ~1 : 1 and the yield of OMC decreases to 40%.

Only the carbomagnesiation products are formed when THF is used as a solvent, which is well consistent with the earlier[7,13] obtained data on the cyclomagnesiation of 1,2-dienes and α-olefins.

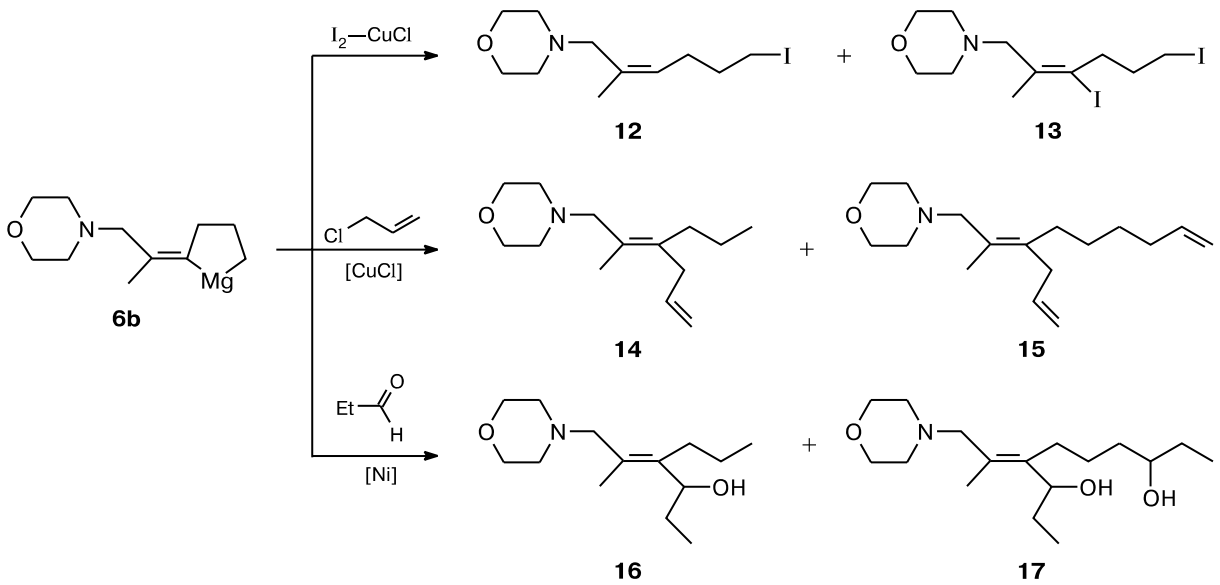
The reactivity of the Mg—C bonds in magnesacyclopentane **6b** synthesized from 1,2-diene **5b** was studied in the reactions with I_2, allyl chloride, and propanal. The reaction of cyclic OMC **6b** obtained *in situ* with the reactants indicated (Scheme 3) afforded the corresponding monofunctionalized derivatives **12**, **14**, and **16** exclusively at the vinylic Mg—C bond. The use of the Cu- or Ni-based catalysts made it possible to involve the second Mg—C bond and to isolate bifunctional compounds **13**, **15**, and **17** in high yields (~80%, see Scheme 3).

Thus, we carried out for the first time the catalytic cyclomagnesiation of N-containing terminal allenes with Et_2Mg in the presence of the Zr-based complexes and obtained N-containing alkylidenemagnesacyclopentanes, which can be used in the synthesis of poorly accessible heterocyclic and acyclic bifunctional compounds of specified structure.

Experimental

Chromatographic analysis was carried out on a Shimadzu GC-9A instrument (column 2000×2 mm, stationary phase Silicon SE-30 (5%) on Chromaton N-AW-HMDS (0.125—0.160 mm), carrier gas helium (30 mL min^{-1}), temperature-programmed regime from 50 to 300 °C with a rate of 8 °C min^{-1}). ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer (^{13}C, 100 MHz; ^1H, 400 MHz) in $CDCl_3$, and chemical shifts are given relative to Me_4Si. The GC/MS analysis was carried out on a Finigan instrument, model 4021 (glass capillary column 50 000×0.25 mm, stationary phase HP-5, carrier gas helium, temperature-programmed regime from 50 to 300 °C with a rate of 5 °C min^{-1}, evaporator temperature 280 °C, ion source temperature 250 °C, 70 eV). Elemental analyses were carried out on a Karlo Erba elemental analyzer, model 1106. The yields of the products were determined by GLC. The purity of the reaction products were monitored on Silufol UV-254 plates in diiodine vapors. The reactions with the organometallic compounds

Scheme 3



[Ni] = $Ni(acac)_2$—$2Ph_3P$

were carried out in a dry argon flow. Solvents were dried and used freshly distilled. Allenes were synthesized according to a known procedure.[27] A Cp_2ZrCl_2 sample was prepared from $ZrCl_4$ using an earlier described procedure.[28] The ether solvents were distilled prior to use over $LiAlH_4$. Solutions of RMgHlg in Et_2O and THF were prepared as described previously.[29]

Cyclomagnesiation of N-containing 1,2-dienes 1a—d and 5a—d with Et_2Mg in the presence of the Cp_2ZrCl_2 catalyst (general procedure). A glass reactor was loaded with Cp_2ZrCl_2 (0.5 mmol), 1,2-diene (10 mmol), and Et_2Mg (20 mmol) in Et_2O in a dry argon flow (~0 °C) with stirring. The temperature was increased to ambient (20—22 °C), and the reaction mixture was stirred for 8 h. To identify substituted magnesacyclopentanes **6a** and **6c** using the ^{13}C NMR spectra, the solvent was distilled off from the reaction mixture *in vacuo* and the residue was transferred under argon to a tube of the NMR spectrometer with several droplets of THF-d_8. The reaction mixture was treated with 10% NH_4Cl in H_2O (ND_4Cl in D_2O) to identify substituted magnesacyclopentadienes by the hydrolysis or deuterolysis products. The reaction product was extracted with ether, the extract was dried with $MgSO_4$, and the residue was fractionated *in vacuo* (amines **3a,b—4a,b** and compounds **8a**, **10a**) or chromatographed on a column (SiO_2, eluent petroleum ether—EtOAc (5 : 1)).

(2*Z*)-*N*,*N*-Diethylhex-2-ene-1-amine (3a). B.p. 69—72 °C (15 Torr). ^1H NMR, δ: 0.91 (t, 3 H, Me, J = 6.5 Hz); 1.04 (t, 6 H, 2 Me, J = 7 Hz); 1.28—1.41 (m, 2 H, C$\underline{H}_2$Me); 2.04—2.10 (m, 2 H, C$\underline{H}_2$H=); 2.51 (q, 4 H, 2 CH_2N, J = 7 Hz); 3.09 (s, 2 H, CH_2C=, J = 5.5 Hz); 5.39—5.51 (m, 2 H, 2 CH=). ^{13}C NMR, δ: 11.79 (C(9), C(11)); 13.87 (C(6)); 22.79 (C(5)); 23.21 (C(7)); 29.74 (C(4)); 46.62 (C(8), C(10)); 53.66 (C(1)); 128.26 (C(3)); 133.76 (C(2)). Found (%): C, 77.98; H, 13.54. $C_{11}H_{23}N$. Calculated (%): C, 78.03; H, 13.69. MS (EI), m/z: 155 $[M]^+$.

3,6-Dideuterio-(2*Z*)-*N*,*N*-diethylhex-2-ene-1-amine (4a). B.p. 69—71 °C (15 Torr). ^1H NMR, δ: 0.93 (t, 2 H, CD$\underline{H}_2$, J = 7 Hz); 1.05 (t, 6 H, 2 Me, J = 7 Hz); 1.29—1.43 (m, 2 H, C$\underline{H}_2$Me); 2.03—2.09 (m, 2 H, C$\underline{H}_2$CH=); 2.52 (q, 4 H, 2 CH_2N, J = 7 Hz); 3.08 (s, 2 H, CH_2C=, J = 6 Hz); 5.49 (t, 1 H, CD=C$\underline{H}$, J = 6 Hz). ^{13}C NMR, δ: 11.78 (C(9), C(11)); 13.63 (C(6), J = 19 Hz, Δ = 0.24 ppm); 22.79 (C(5)); 23.23 (C(7)); 29.74 (C(4)); 46.61 (C(8), C(10)); 53.67 (C(1)); 128.04 (C(3), J = 24 Hz, Δ = 0.22 ppm); 133.78 (C(2)). Found (%): C, 76.29; H + D, 14.61. $C_{10}H_{19}ND_2$. Calculated (%): C, 76.36; H, 12.18; D, 2.56. MS (EI), m/z: 157 $[M]^+$.

(2*Z*)-*N*,*N*-Di-*iso*-propylhex-2-ene-1-amine (3b). B.p. 91—93 °C (10 Torr). ^1H NMR, δ: 0.92 (t, 3 H, Me, J = 7 Hz); 1.03 (d, 12 H, 4 Me, J = 6.8 Hz); 1.22—1.39 (m, 2 H, C$\underline{H}_2$Me); 2.01—2.09 (m, 2 H, C$\underline{H}_2$CH=); 3.03—3.13 (m, 2 H, 2 CHN, J = 6.8 Hz); 3.14 (d, 2 H, CH_2C=, J = 6.4 Hz); 5.21—5.48 (m, 2 H, 2 CH=). ^{13}C NMR, δ: 13.44 (C(6)); 20.58 (C(8), C(9), C(11), C(12)); 23.12 (C(5)); 30.65 (C(4)); 42.15 (C(1)); 48.34 (C(7), C(10)); 128.84 (C(2)); 132.17 (C(3)). Found (%): C, 78.48; H, 13.68. $C_{12}H_{25}N$. Calculated (%): C, 78.62; H, 13.74. MS (EI), m/z: 183 $[M]^+$.

3,6-Dideuterio-(2*Z*)-*N*,*N*-di-*iso*-propylhex-2-ene-1-amine (4b). B.p. 91—93 °C (10 Torr). ^1H NMR, δ: 0.91 (t, 2 H, CD$\underline{H}_2$, J = 7 Hz); 1.04 (d, 12 H, 4 Me, J = 6.8 Hz); 1.22—1.38 (m, 2 H, C$\underline{H}_2$Me); 2.04—2.10 (m, 2 H, C$\underline{H}_2$CH=); 3.01—3.12 (m, 2 H, 2 CHN, J = 6.8 Hz); 3.14 (d, 2 H, CH_2C=, J = 6.4 Hz); 5.35 (t, 1 H, C$\underline{H}$=CD, J = 6.5 Hz). ^{13}C NMR, δ: 13.18 (C(6), J = 19 Hz, Δ = 0.26 ppm); 20.55 (C(8), C(9), C(11), C(12)); 23.10 (C(5)); 30.64 (C(4)); 42.15 (C(1)); 48.33 (C(7), C(10)); 128.81 (C(2)); 131.95 (C(3), J = 23 Hz, Δ = 0.22 ppm). Found (%): C, 77.65; H + D, 14.58. $C_{12}H_{23}ND_2$. Calculated (%): C, 77.76; H, 12.51; D, 2.17. MS (EI), m/z: 185 $[M]^+$.

4-[(2*Z*)-Hex-2-en-1-yl]piperidine (3c), R_f = 0.63, n_D^{20} 1.4695. ^1H NMR, δ: 0.92 (t, 3 H, Me, J = 7 Hz); 1.30—1.36 (m, 2 H, C$\underline{H}_2$Me); 1.38—1.69 (m, 6 H, 3 CH_2); 2.01—2.07 (m, 2 H, C$\underline{H}_2$CH=); 2.35—2.44 (m, 4 H, 2 CH_2N); 2.97 (d, 2 H, C$\underline{H}_2$CH=, J = 5 Hz); 5.48—5.58 (m, 2 H, 2 CH=). ^{13}C NMR, δ: 13.73 (C(6)); 22.81 (C(5)); 24.16 (C(9)); 25.89 (C(8), C(10)); 29.47 (C(4)); 55.74 (C(1)); 126.17 (C(2)); 133.05 (C(3)). Found (%): C, 78.89; H, 12.28. $C_{11}H_{21}N$. Calculated (%): C, 78.98; H, 12.65. MS (EI), m/z: 167 $[M]^+$.

3,6-Dideuterio-4-[(2*Z*)-hex-2-en-1-yl]piperidine (4c), R_f = 0.63, n_D^{20} 1.4709. ^1H NMR, δ: 0.94 (t, 2 H, CD$\underline{H}_2$, J = 7 Hz); 1.31—1.38 (m, 2 H, C$\underline{H}_2$Me); 1.40—1.68 (m, 6 H, 3 CH_2); 2.02—2.08 (m, 2 H, C$\underline{H}_2$CH=); 2.35—2.46 (m, 4 H, 2 CH_2N); 2.98 (d, 2 H, C$\underline{H}_2$CH=, J = 5 Hz); 5.51 (t, 1 H, C$\underline{H}$=CD, J = 7 Hz). ^{13}C NMR, δ: 13.42 (C(6), J = 19 Hz, Δ = 0.31 ppm); 22.83 (C(5)); 24.17 (C(9)); 25.89 (C(8), C(10)); 29.49 (C(4)); 55.74 (C(1)); 126.18 (C(2)); 132.79 (C(3), J = 24 Hz, Δ = 0.26 ppm). Found (%): C, 77.96; H + D, 13.59. $C_{11}H_{19}ND_2$. Calculated (%): C, 78.04; H, 11.31; D, 2.38. MS (EI), m/z: 169 $[M]^+$.

4-[(2*Z*)-Hex-2-en-1-yl]morpholine (3d), R_f = 0.58, n_D^{20} 1.4661. ^1H NMR, δ: 0.92 (t, 3 H, Me, J = 6 Hz); 1.33—1.39 (m, 2 H, C$\underline{H}_2$Me); 2.01—2.09 (m, 2 H, C$\underline{H}_2$CH=); 2.44 (br.s, 4 H, 2 CH_2N); 3.00 (d, 2 H, CH_2C=, J = 7 Hz); 3.71 (t, 4 H, 2 CH_2O, J = 4.5 Hz); 5.42—5.57 (m, 2 H, 2 CH=). ^{13}C NMR, δ: 13.73 (C(6)); 22.66 (C(5)); 29.54 (C(4)); 53.63 (C(7), C(10)); 55.49 (C(1)); 67.00 (C(8), C(9)); 125.58 (C(2)); 133.47 (C(3)). Found (%): C, 70.89; H, 11.28. $C_{10}H_{19}NO$. Calculated (%): C, 70.96; H, 11.31. MS (EI), m/z: 169 $[M]^+$.

3,6-Dideuterio-4-[(2*Z*)-hex-2-en-1-yl]morpholine (4d), R_f = 0.58, n_D^{20} 1.4657. ^1H NMR, δ: 0.93 (t, 2 H, CD$\underline{H}_2$, J = 7 Hz); 1.33—1.37 (m, 2 H, C$\underline{H}_2$Me); 2.02—2.07 (m, 2 H, C$\underline{H}_2$CH=); 2.44 (br.s, 4 H, 2 CH_2N); 3.01 (d, 2 H, CH_2C=, J = 7 Hz); 3.73 (t, 4 H, 2 CH_2O, J = 4.5 Hz); 5.49 (t, 1 H, C$\underline{H}$=CD, J = 7 Hz). ^{13}C NMR, δ: 13.42 (C(6), J = 19 Hz, Δ = 0.21 ppm); 22.54 (C(5)); 29.38 (C(4)); 53.61 (C(7), C(10)); 55.44 (C(1)); 66.99 (C(8), C(9)); 125.43 (C(2)); 133.1 (C(3), J = 23 Hz, Δ = 0.35 ppm). Found (%): C, 70.09; H + D, 12.21. $C_{10}H_{17}NOD_2$. Calculated (%): C, 70.13; H, 10.00; D, 2.35. MS (EI), m/z: 171 $[M]^+$.

***N*,*N*-Diethyl-2-magnesacyclopentan-2-ylidenepropane-1-amine (6a).** ^1H NMR, δ: 0.65 (m, 2 H, CH_2); 0.76 (m, 6 H, 3 CH_2); 1.05 (m, 2 H, CH_2); 1.55 (s, 3 H, Me); 2.01 (m, 2 H, CH_2); 2.20 (m, 4 H, CH_2); 2.72 (br.s, 2 H, CH_2). ^{13}C NMR, δ: 14.37 (C(9), C(11)); 15.17 (C(4)); 26.71 (C(3)); 28.50 (C(6)); 39.93 (C(2)); 46.51 (C(8), C(10)); 54.15 (C(7)); 136.34 (C(1)); 168.86 (C(5)).

4-[2-Magnesacyclopentan-2-ylidenebutyl]morpholine (6c). ^1H NMR, δ: 0.60—0.70 (m, 5 H, Me, CH_2); 1.25 (m, 2 H, CH_2); 1.90 (m, 2 H, CH_2); 2.00 (m, 2 H, CH_2); 2.17 (m, 4 H, CH_2); 2.79 (m, 2 H, CH_2); 3.44 (m, 4 H, C(10)H_2, C(12)H_2). ^{13}C NMR, δ: 14.96 (C(8)); 15.40 (C(4)); 24.80 (C(7)); 27.77 (C(3)); 38.24 (C(2)); 55.20 (C(9), C(11)); 68.17 (C(10), C(12)); 68.26 (C(6)); 138.78 (C(1)); 171.1 (C(5)).

(2*Z*)-*N*,*N*-Diethyl-2-methylhex-2-ene-1-amine (8a). B.p. 84—86 °C (10 Torr). ^1H NMR, δ: 0.91 (t, 3 H, Me, J = 7 Hz); 1.03 (t, 6 H, 2 Me, J = 7.2 Hz); 1.34—1.46 (m, 2 H, C$\underline{H}_2$Me); 1.90 (s, 3 H, Me); 2.01—2.09 (m, 2 H, C$\underline{H}_2$CH=); 2.45 (q, 4 H,

2 CH_2N, J = 7 Hz); 2.97 (s, 2 H, CH_2C=); 5.31 (t, 1 H, CH=, J = 7.2 Hz). ^{13}C NMR, δ: 11.79 (C(9), C(11)); 13.87 (C(6)); 22.79 (C(5)); 23.21 (15.03) (C(7)); 29.74 (C(4)); 46.62 (C(8), C(10)); 53.66 (C(1)); 128.26 (C(3)); 133.76 (C(2)). Found (%): C, 77.98; H, 13.54. $C_{11}H_{23}N$. Calculated (%): C, 78.03; H, 13.69. MS (EI), m/z: 169 $[M]^+$.

(2*Z*)-3,6-Dideuterio-*N*,*N*-diethyl-2-methylhex-2-ene-1-amine (9a). B.p. 84—86 °C (10 Torr). ^1H NMR, δ: 0.92 (t, 2 H, $CD\underline{H}_2$, J = 7 Hz); 1.02 (t, 6 H, 2 Me, J = 7.2 Hz); 1.32—1.44 (m, 2 H, $C\underline{H}_2Me$); 1.91 (s, 3 H, Me); 2.05 (t, 2 H, =$CDC\underline{H}_2$, J = 7.2 Hz); 2.46 (q, 4 H, 2 CH_2N, J = 6.8 Hz); 2.97 (s, 2 H, CH_2C=). ^{13}C NMR, δ: 11.78 (C(9), C(11)); 13.62 (C(6), $J_{C,D}$ = = 19 Hz, Δ = 0.25 ppm); 22.79 (C(5)); 23.22 (C(7)); 29.74 (C(4)); 46.61 (C(8), C(10)); 53.65 (C(1)); 128.04 (C(3), $J_{C,D}$ = 24 Hz, Δ = 0.22 ppm); 133.75 (C(2)). Found (%): C, 77.08; H + D, 14.63. $C_{11}H_{21}ND_2$. Calculated (%): C, 77.12; H, 12.36; D, 2.35. MS (EI), m/z: 171 $[M]^+$.

4-[(2*Z*)-2-Methylhex-2-en-1-yl]morpholine (8b), R_f = 0.60. ^1H NMR, δ: 0.89 (t, 3 H, Me, J = 7.2 Hz); 1.33 (m, 2 H, $C\underline{H}_2Me$); 1.74 (s, 3 H, Me); 2.01—2.04 (m, 2 H, $C\underline{H}_2CH$=); 2.36 (br.s, 4 H, 2 CH_2N); 2.91 (s, 2 H, CH_2C=); 3.69 (t, 4 H, 2 CH_2O, J = 9 Hz); 5.34 (t, 1 H, CH=, J = 7.2 Hz). ^{13}C NMR, δ: 13.82 (C(6)); 22.78 (C(5)); 23.09 (C(7)); 29.72 (C(4)); 53.57 (C(8), C(11)); 59.0 (C(1)); 67.11 (C(9), C(10)); 129.5 (C(3)); 131.81 (C(2)). Found (%): C, 71.99; H, 11.43. $C_{11}H_{21}NO$. Calculated (%): C, 72.08; H, 11.55. MS (EI), m/z: 183 $[M]^+$.

3,6-Dideuterio-4-[(2*Z*)-2-methylhex-2-en-1-yl]morpholine (9b), R_f = 0.60. ^1H NMR, δ: 0.88 (t, 2 H, $CD\underline{H}_2$, J = 7.2 Hz); 1.33 (m, 2 H, $C\underline{H}_2Me$); 1.74 (s, 3 H, Me); 2.02—2.05 (m, 2 H, $C\underline{H}_2CH$=); 2.36 (br.s, 4 H, 2 CH_2N); 2.93 (s, 2 H, CH_2C=); 3.68 (t, 4 H, 2 CH_2O, J = 9 Hz). ^{13}C NMR, δ: 13.51 (C(6), $J_{C,D}$ = 19 Hz, Δ = 0.31 ppm); 22.77 (C(5)); 23.09 (C(7)); 29.73 (C(4)); 53.57 (C(8), C(11)); 59.04 (C(1)); 67.11 (C(9), C(10)); 129.27 (C(3), $J_{C,D}$ = 24.5 Hz, Δ = 0.24 ppm); 131.82 (C(2)). Found (%): C, 71.21; H + D, 12.41. $C_{11}H_{19}NOD_2$. Calculated (%): C, 71.30; H, 10.33; D, 2.17. MS (EI), m/z: 185 $[M]^+$.

4-(2-Ethylhex-2-en-1-yl)morpholine (8c, 10c), R_f = 0.59. ^1H NMR, δ: (*Z*): 0.72, (*E*): 0.71 (t, 3 H, Me, J = 7 Hz); (*Z*): 0.82, (*E*): 0.81 (t, 3 H, Me, J = 7 Hz); 1.13—1.24 (m, 2 H, $C\underline{H}_2Me$); 1.81—1.91 (m, 4 H, 2 $C\underline{H}_2CH$=); 2.14 (br.s, 4 H, 2 CH_2N); 2.72—2.73 (m, 2 H, CH_2C=); 3.46 (br.s, 4 H, 2 CH_2O); (*Z*): 5.07, (*E*): 5.13 (t, 1 H, HC=C, J = 6.8 Hz). ^{13}C NMR, δ: 12.88 (12.76) (C(8)); 13.62 (13.58) (C(6)); 21.63 (28.50) (C(7)); 22.81 (22.75) (C(5)); 29.30 (29.41) (C(4)); 53.50 (C(9), C(12)); 65.29 (57.19) (C(1)); 66.77 (C(10), C(11)); 127.86 (127.36) (C(3)); 137.42 (137.11) (C(2)). Found (%): C, 72.89; H, 11.56. $C_{12}H_{23}NO$. Calculated (%): C, 73.04; H, 11.75. MS (EI), m/z: 197 $[M]^+$.

3,6-Dideuterio-4-(2-ethylhex-2-en-1-yl)morpholine (9c, 11c), R_f = 0.59. ^1H NMR, δ: (*Z*): 0.73, (*E*): 0.72 (t, 2 H, $CD\underline{H}_2$, J = 7 Hz); (*Z*): 0.82, (*E*): 0.82 (t, 3 H, Me, J = 7 Hz); 1.14—1.26 (m, 2 H, $C\underline{H}_2Me$); 1.82—1.90 (m, 4 H, 2 $C\underline{H}_2CH$=); 2.15 (br.s, 4 H, 2 CH_2N); 2.72—2.74 (m, 2 H, CH_2C=); 3.46 (br.s, 4 H, 2 CH_2O). ^{13}C NMR, δ: 12.86 (12.77) (C(8)); 13.36 (13.20) (C(6), J = 19 Hz); 21.64 (28.50) (C(7)); 22.82 (22.74) (C(5)); 29.30 (29.42) (C(4)); 53.50 (C(9), C(12)); 65.28 (57.19) (C(1)); 66.77 (C(10), C(11), *(C(3)); 137.44 (137.11) (C(2)). Found (%): C, 72.24; H + D, 12.53. $C_{12}H_{21}NOD_2$. Calculated (%): C, 72.31; H, 10.62. MS (EI), m/z: 199 $[M]^+$.

* The signal is not observed.

4-(2-Butylhex-2-en-1-yl)morpholine (8d, 10d), R_f = 0.55. ^1H NMR, δ: 0.83—0.85 (m, 6 H, 2 Me); 1.22—1.36 (m, 6 H, 3 CH_2); 1.94—2.01 (m, 4 H, 2 $C\underline{H}_2CH$=); 2.28 (br.s, 4 H, 2 CH_2N); 2.83 (2.78) (s, 2 H, CH_2C=); 3.6 (br.s, 4 H, 2 CH_2O); (*Z*): 5.22, (*E*): 5.27 (t, 1 H, CH=C, J =7 Hz). ^{13}C NMR, δ: 13.71 (13.78) (C(6)); 13.96 (13.86) (C(10)); 22.94 (22.76) (C(5)); 23.08 (22.32) (C(9)); 28.50 (35.55) (C(4)); 29.58 (29.57) (C(8)); 30.57 (30.54) (C(7)); 53.60 (C(11), C(14)); 65.62 (57.24) (C(1)); 67.00 (C(12), C(13)); 128.69 (128.55) (C(3)); 136.00 (135.67) (C(2)). Found (%): C, 74.54; H, 11.99. $C_{14}H_{27}NO$. Calculated (%): C, 74.61; H, 12.08. MS (EI), m/z: 225 $[M]^+$.

3,6-Dideuterio-4-(2-butylhex-2-en-1-yl)morpholine (9d, 11d), R_f = 0.55. ^1H NMR, δ: 0.82—0.86 (m, 5 H, $CD\underline{H}_2$, Me); 1.22—1.36 (m, 6 H, 3 CH_2); 1.94—2.04 (m, 4 H, 2 $C\underline{H}_2CH$=); 2.27 (br.s, 4 H, 2 CH_2N); 2.84 (2.78) (s, 2 H, CH_2C=); 3.62 (br.s, 4 H, 2 CH_2O). ^{13}C NMR, δ: 13.50 (13.54) (C(6), J = 19 Hz); 13.96 (13.88) (C(10)); 22.95 (22.77) (C(5)); 23.08 (22.33) (C(9)); 28.52 (35.57) (C(4)); 29.58 (29.59) (C(8)); 30.57 (30.55) (C(7)); 53.60 (C(11), C(14)); 65.62 (57.25) (C(1)); 67.01 (C(12), C(13), *(C(3)); 136.03 (135.68) (C(2)). Found (%): C, 73.84; H + D, 12.76. $C_{14}H_{25}NOD_2$. Calculated (%): C, 73.95; H, 11.08; D, 1.77. MS (EI), m/z: 227 $[M]^+$.

Synthesis of 4-[(2*E*)-3-iodo-2-methylhex-2-en-1-yl]morpholine (12) and 4-[(2*E*)-3,6-diiodo-2-methylhex-2-en-1-yl]-morpholine (13). A glass reactor was loaded with Cp_2ZrCl_2 (0.5 mmol), 2-methyl-1-buta-2,3-dien-1-ylmorpholine (10 mmol), and Et_2Mg (20 mmol) in Et_2O (13.4 mL, 1.5 mmol mL^{-1}) under dry argon (~0 °C) with stirring, the temperature was increased to ~20 °C, and the reaction mixture was stirred for 8 h. The reaction mixture was cooled to 0 °C, CuCl (1 mmol) was added, and an ethereal solution of I_2 (22 mmol) was added dropwise. The temperature was brought to ambient, and the reaction mixture was stirred for 10 h and then treated with 10% NH_4Cl in H_2O. The reaction products were extracted with ether and treated with a saturated solution of $Na_2S_2O_3$, the extracts were dried with $MgSO_4$, and the residue was chromatographed on a column (SiO_2, eluent petroleum ether—EtOAc (5 : 1)).

4-[(2*E*)-3-Iodo-2-methylhex-2-en-1-yl]morpholine (12), R_f = 0.58. ^1H NMR, δ: 0.87 (t, 3 H, Me, J = 6.8 Hz); 1.48—1.52 (m, 2 H, $C\underline{H}_2Me$); 1.95 (s, 3 H, CH_3); 2.55—2.61 (m, 2 H, $C\underline{H}_2CH$=); 2.33 (br.s, 4 H, 2 CH_2N); 2.97 (s, 2 H, CH_2C=); 3.63 (br.s, 4 H, 2 CH_2O). ^{13}C NMR, δ: 13.04 (C(6)); 29.13 (C(5)); 42.93 (C(4)); 53.29 (C(8), C(11)); 59.37 (C(1)); 66.96 (C(9), C(10)); 109.16 (C(3)); 137.11 (C(2)). Found (%): C, 42.65; H, 6.44. $C_{11}H_{20}INO$. Calculated (%): C, 42.73; H, 6.52.

4-[(2*E*)-3,6-Diiodo-2-methylhex-2-en-1-yl]morpholine (13), R_f = 0.45. ^1H NMR, δ: 1.78—1.80 (m, 2 H, $C\underline{H}_2Me$); 1.41 (t, 2 H, CH_2I, J = 7.2 Hz); 1.90 (s, 3 H, Me); 2.39 (br.s, 4 H, 2 CH_2N); 2.54—2.58 (m, 2 H, $C\underline{H}_2CH$=); 3.11 (s, 2 H, CH_2C=); 3.63 (t, 4 H, 2 CH_2O, J = 9 Hz). ^{13}C NMR, δ: 5.16 (C(6)); 19.58 (C(7)); 33.43 (C(5)); 43.79 (C(4)); 53.20 (C(8), C(11)); 59.70 (C(1)); 67.33 (C(9), C(10)); 106.25 (C(3)); 138.74 (C(2)). Found (%): C, 30.28; H, 4.33. $C_{11}H_{19}I_2NO$. Calculated (%): C, 30.37; H, 4.40.

Synthesis of 4-[(2*E*)-2-methyl-3-propylhexa-2,5-dien-1-yl]morpholine (14) and 4-[(2*E*)-3-allyl-2-methylnona-2,8-dien-1-yl]morpholine (15). A glass reactor was loaded with Cp_2ZrCl_2 (0.5 mmol), 2-methyl-1-buta-2,3-dien-1-ylmorpholine (10 mmol), and Et_2Mg (20 mmol) in Et_2O (13.4 mL, 1.5 mmol mL^{-1}) under dry argon (~0 °C) with stirring. The temperature was increased to 20—22 °C, and the reaction mixture was stirred for 8 h, then

CuCl (1 mmol) was added at –20 °C, and allyl chloride (26 mmol) was slowly added dropwise. The temperature was increases to ~20 °C, and the reaction mixture was stirred for 6 h. The reaction mixture was treated with 10% NH_4Cl in H_2O. The reaction products were extracted with ether, the extracts were dried with $MgSO_4$, and the residue was chromatographed on a column (SiO_2, eluent petroleum ether—EtOAc (5 : 1)).

Compound 14, R_f = 0.57. ^{1}H NMR, δ: 0.88 (t, 3 H, Me, J = 6 Hz); 1.34—1.39 (m, 2 H, C<u>H</u>$_2$Me); 1.69 (t, 3 H, Me, J = 6 Hz); 2.04 (t, 2 H, C<u>H</u>$_2$CH$_2$, J = 7.6 Hz); 2.35 (br.s, 4 H, 2 CH_2N); 2.78 (d, 2 H, CH_2C=, J = 6 Hz); 2.91 (s, 2 H, CH_2C=); 3.66 (t, 4 H, 2 CH_2O, J = 4.4 Hz); 4.94—4.99 (m, 1 H, CH=); 5.69—5.76 (m, 2 H, H_2C=). ^{13}C NMR, δ: 14.25 (C(9)); 16.97 (C(10)); 22.08 (C(8)); 34.14 (C(7)); 37.18 (C(4)); 53.49 (C(11), C(14)); 60.93 (C(1)); 67.15 (C(12), C(13)); 114.59 (C(6)); 127.00 (C(2)); 134.91 (C(3)); 136.17 (C(5)). Found (%): C, 75.19; H, 11.17. $C_{14}H_{25}NO$. Calculated (%): C, 75.28; H, 11.28. MS (EI), m/z: 223 $[M]^+$.

Compound 15, R_f = 0.54. ^{1}H NMR, δ: 1.36—1.43 (m, 4 H, 2 CH_2); 1.71 (s, 3 H, Me); 2.04—2.11 (m, 4 H, 2 CH_2); 2.80 (d, 2 H, CH_2, J = 6 Hz); 2.37 (br.s, 4 H, 2 CH_2N); 2.93 (s, 2 H, CH_2C=); 3.69 (t, 4 H, 2 CH_2O, J = 4.4 Hz); 4.94—5.03 (m, 2 H, H_2C=); 5.69—5.84 (m, 4 H, 2 <u>H</u>$_2$C=CH$_2$). ^{13}C NMR, δ: 17.05 (C(13)); 28.35 (C(5)); 29.05 (C(6)); 31.84 (C(4)); 33.66 (C(7)); 37.21 (C(10)); 53.52 (C(14), C(17)); 60.97 (C(1)); 67.18 (C(15), C(16)); 114.36 (C(12)); 114.68 (C(9)); 126.93 (C(2)); 134.98 (C(3)); 136.17 (C(11)); 138.90 (C(8)). Found (%): C, 77.45; H, 11.01. $C_{17}H_{29}NO$. Calculated (%): C, 77.51; H, 11.10. MS (EI), m/z: 263 $[M]^+$.

Synthesis of (2*E*)-2-methyl-1-morpholin-4-yl-3-propylhept-2-en-4-ol (16) and (5*E*)-5-(1-methyl-2-morpholin-4-ylethylidene)dodecane-4,9-diol (17). A glass reactor was loaded with Cp_2ZrCl_2 (0.5 mmol), 2-methyl-1-buta-2,3-dien-1-ylmorpholine (10 mmol), and Et_2Mg (20 mmol) in Et_2O (13.4 mL, 1.5 mmol mL^{-1}) under dry argon (~0 °C) with stirring. The mixture was increased to ~20 °C, and the reaction mixture was stirred for 8 h. Then Ph_3P (2 mmol) and Ni(acac)$_2$ (1 mmol) were added at –20 °C. Propanal (26 mmol) was slowly added dropwise, the temperature was increased to ~20 °C, and the mixture was stirred for 6 h and treated with 10% NH_4Cl in H_2O. The reaction products were extracted with ether, the extracts were dried with $MgSO_4$, and the residue was chromatographed on a column (SiO_2, eluent petroleum ether—EtOAc (5 : 1)).

Compound 16, R_f = 0.51. ^{1}H NMR, δ: 0.91 (t, 3 H, Me, J = 7 Hz); 0.93 (t, 3 H, Me, J = 7 Hz); 1.15—1.54 (m, 6 H, 3 CH_2); 1.71 (s, 3 H, Me); 1.91—2.04 (m, 2 H, CH_2); 2.24 (s, 2 H, CH_2C=); 2.37 (br.s, 4 H, 2 CH_2N); 3.67 (t, 4 H, 2 CH_2O, J = 4.4 Hz); 4.49 (t, 1 H, C<u>H</u>OH, J = 7.2 Hz); 5.69—5.84 (m, 4 H, 2 C<u>H</u>$_2$=CH$_2$). ^{13}C NMR, δ: 10.41 (C(7)); 14.72 (C(10)); 16.39 (C(11)); 24.79 (C(9)); 28.14 (C(6)); 28.63 (C(8)); 29.32 (C(5)); 53.35 (C(12), C(15)); 61.23 (C(1)); 66.92 (C(13), C(14)); 73.22 (C(4)); 114.36 (C(12)); 127.84 (C(2)); 139.82 (C(3)). Found (%): C, 70.49; H, 10.95. $C_{15}H_{29}NO_2$. Calculated (%): C, 70.54; H, 11.45.

Compound 17, R_f = 0.43. ^{1}H NMR, δ: 0.87 (t, 3 H, Me, J = 7.6 Hz); 0.93 (t, 3 H, Me, J = 7.2 Hz); 1.41—1.49 (m, 8 H, 4 CH_2); 1.57—1.68 (m, 4 H, 2 CH_2); 1.71 (s, 3 H, Me); 2.02—2.09 (m, 2 H, CH_2C=); 2.34 (br.s, 4 H, 2 CH_2N); 2.85—2.99 (m, 2 H, CH_2C=); 3.45—3.59 (t, 1 H, C<u>H</u>OH); 3.66 (t, 4 H, 2 CH_2O, J = 4.4 Hz); 4.48—4.57 (m, 1 H, C<u>H</u>OH). ^{13}C NMR, δ: 9.97 (10.07) (C(12)); 10.46 (10.51) (C(1)); 16.62 (16.67) (C(19)); 27.05 (C(2)); 27.11 (C(11)); 26.33 (C(6)); 27.51 (C(7)); 28.81 (28.82) (C(10)); 30.23 (30.33) (C(3)); 37.10 (36.79) (C(8)); 53.47 (C(15), C(18)); 61.44 (C(14)); 67.08 (C(16), C(17)); 72.12 (72.94) (C(9)); 73.33 (72.94) (C(4)); 127.93 (127.99) (C(13)); 139.38 (139.49) (C(5)). Found (%): C, 69.59; H, 11.27. $C_{19}H_{37}NO_3$. Calculated (%): C, 69.68; H, 11.39.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 10-03-00046, 11-03-00105, and 11-03-97001).

References

1. V. A. D´yakonov, R. A. Tuktarova, U. M. Dzhemilev, *Izv. Akad. Nauk, Ser. Khim.*, 2011, 1607 [*Russ. Chem. Bull., Int. Ed.*, 2011, **60**, 1633].
2. U. M. Dzhemilev, *Tetrahedron*, 1995, **51**, 4333; U. M. Dzhemilev, P. M. Sultanov, R. G. Gaimaldinov, R. R. Muslukhov, *Materialy Vseros. konf. "Primenenie metallokompleksnogo kataliza v organicheskom sinteze"* [*Abstrs of the All-Russia Conf. "The Use of Metallocomplex Catalysis in Organic Synthesis"*], Ufa, 1989, p. 40 (in Russian).
3. U. M. Dzhemilev, R. M. Sultanov, R. G. Gaimaldinov, *J. Organomet. Chem.*, 1995, **491**, 1.
4. V. A. D´yakonov, in *Dzhemilev Reactions in Organic and Organometallic Synthesis*, NOVA Sci. Publ., New York, 2010, p. 96.
5. V. A. D´yakonov, in *Organometallic Compounds: Preparation, Structure and Properties*, Ed. H. F. Chin, NOVA Sci. Publ., New York, 2010, p. 51.
6. U. M. Dzhemilev, A. G. Ibragimov, *J. Organomet. Chem.*, 2010, **695**, 1085.
7. U. M. Dzhemilev, V. A. D´yakonov, L. O. Khafizova, A. G. Ibragimov, *Tetrahedron*, 2004, **60**, 1287.
8. U. M. Dzhemilev, V. A. D´yakonov, L. O. Khafizova, A. G. Ibragimov, *Zh. Org. Khim.*, 2005, **41**, 363 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2005, **41**, 352].
9. V. A. D´yakonov, A. A. Makarov, A. G. Ibragimov, L. M. Khalilov, U. M. Dzhemilev, *Tetrahedron*, 2008, **64**, 10188.
10. U. M. Dzhemilev, A. G. Ibragimov, V. A. D´yakonov, M. Pudas, U. Bergmann, L. O. Khafizova, T. V. Tyumkina, *Zh. Org. Khim.*, 2007, **43**, 686 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2007, **43**, 681].
11. V. A. D´yakonov, A. A. Makarov, U. M. Dzhemilev, *Tetrahedron*, 2010, **66**, 6685.
12. V. A. D´yakonov, R. A. Zinnurova, A. G. Ibragimov, U. M. Dzhemilev, *Zh. Org. Khim.*, 2007, **43**, 962 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2007, **43**, 176].
13. D. P. Lewis, R. J. Whitby, R. V. H. Jones, *Tetrahedron*, 1995, **51**, 4541.
14. K. S. Knight, D. Wang, R. M. Waymouth, J. Ziller, *J. Am. Chem. Soc.*, 1994, **116**, 1845.
15. N. Uesaka, M. Mori, K. Okamura, T. Date, *J. Org. Chem.*, 1994, **59**, 4542.
16. Y. Yamaura, M. Hyakutake, M. Mori, *J. Am. Chem. Soc.*, 1997, **119**, 7615.
17. U. Wischmeyer, K. S. Knight, R. M. Waymouth, *Tetrahedron Lett.*, 1992, **33**, 7735.
18. V. A. D´yakonov, R. K. Timerkhanov, T. V. Tumkina, A. G. Ibragimov, U. M. Dzhemilev, *Tetrahedron Lett.*, 2009, **50**, 1270.

19. V. A. D´yakonov, R. K. Timerkhanov, O. A. Trapeznikova, A. A. Makarov, L. M. Khalilov, R. A. Zinnurova, A. G. Ibragimov, L. F. Galimova, *Chem. Heterocycl. Compd.*, 2009, **45**, 317.
20. V. A. D´yakonov, R. A. Tuktarova, U. M. Dzhemilev, *Tetrahedron Lett.*, 2010, **51**, 5886.
21. D. Y. Kondakov, E. Negishi, *J. Am. Chem. Soc.*, 1996, **118**, 1577.
22. V. A. D´yakonov, R. K. Timerkhanov, T. V. Tyumkina, U. M. Dzhemilev, *Izv. Akad. Nauk*, *Ser. Khim.*, 2009, 2378 [*Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 2456].
23. V. A. D´yakonov, R. K. Timerkhanov, U. M. Dzhemilev, *Zh. Org. Khim.*, 2010, **46**, 816 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2010, **46**, 807].
24. E. Negishi, D. Y. Kondakov, *Chem. Soc. Rev.*, 1996, **26**, 417.
25. V. A. D´yakonov, E. Sh. Finkelshtein, A. G. Ibragimov, *Tetrahedron Lett.*, 2007, **48**, 8583.
26. G. Levi, G. Nelson, *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, John Wiley and Sons, New York, 1972, 292 pp.
27. *Best Synthetic Methods: Acetylenes, Allenes and Cumulenes*, Ed. L. Brandsma, Academic Press, New York, 2003, 502 pp.
28. R. Kh. Freidlina, E. M. Brainina, A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, 1969, **138**, 1369 [*Dokl. Chem.* (*Engl. Transl.*), 1969].
29. S. T. Ioffe, A. N. Nesmeyanov, *Metody elementoorganicheskoi khimii. Podgruppa magniya, berilliya, kal´tsiya, strontsiya, bariya* [*Methods of Organoelement Chemistry. Subgroup of Magnesium, Beryllium, Calcium, Strontium, and Barium*], Akad. Nauk USSR, Moscow, 1963, 561 pp. (in Russian).

Received March 29, 2011;
in revised form July 7, 2011