Synthesis and transformations of metallacycles
37.* Cp_2ZrCl_2-Catalyzed cycloalumination of substituted methylidenecyclopropane with Et_3Al

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Cycloalumination of substituted methylidenecyclopropanes with Et_3Al catalyzed by Cp_2ZrCl_2 affords alumaspiro[2.4]heptanes in 64—92% yields.

Key words: organoaluminum compounds, metallocomplex catalysis, alumacyclopentanes, methylidenecyclopropane, cycloalumination, spiro compounds.

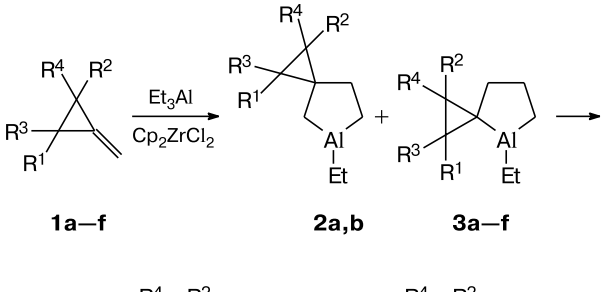
We have earlier[2,3] found that methylidenecyclobutanes enter the reaction of catalytic cycloalumination of unsaturated compounds[4—18] with Et_3Al in the presence of Cp_2ZrCl_2 to form the corresponding alumaspiro[3.4]-octanes, which are *in situ* transformed into carbo- and heterocyclic spiran compounds in high yields.

Continuing the study of this reaction, aiming at extending it to substituted methylidenecyclopropanes and synthesizing new classes of organoaluminum compounds (OAC) and developing on their basis efficient one-pot methods of synthesis of spiro[2.3]hexanes, we studied the reactions of methylidenecyclopropanes of various structures (2-alkyl-, 2-phenyl-, and 2-methyl-2-phenylmethylidenecyclopropanes, as well as 7-methylidenebicyclo-[4.1.0]heptane and 9-methylidenebicyclo[6.1.0]nonane) with Et_3Al in the presence of Cp_2ZrCl_2.

It was shown by preliminary experiments that, as in the case of methylidenecyclobutanes,[3] among the tested zirconium-based catalysts ($(MeCp)_2ZrCl_2$, $(Me_5Cp)_2ZrCl_2$, Ind_2ZrCl_2, $ZrCl_4$, $(BuO)_4Zr$, Cp_2ZrCl_2, Py_2ZrCl_6), the highest yields of spirocyclopropylalumacyclopentanes were obtained with the use of complex Cp_2ZrCl_2 in an amount of 5 mol.%. Therefore, subsequent experiments on cycloalumination of methylidenecyclopropanes were carried out with this catalyst.

We found that the cycloalumination of 2-pentyl- and 2-heptyl-1-methylidenecyclopropanes with Et_3Al in the presence of 5 mol.% Cp_2ZrCl_2 in hexane for 4 h gave mixtures of regioisomeric alumacyclopentanes with spirocyclopropane fragments in the β- (**2a,b**) and α-positions (**3a,b**) to the aluminum atom in ~70% yields. After hydrolysis or deuterolysis, compounds **2a,b** and **3a,b** are transformed into the corresponding mixtures of compounds **4a,b**, **5a,b** and **6a,b**, **7a,b** in a ratio of ~1 : 2 (Scheme 1, Table 1). Cyclopropanes **4a,b** and **7a,b** were isolated in the individual state by preparative GLC as a mixture of *cis*- and *trans*-isomers in a ratio of ~1 : 1.

Scheme 1



1—7	R^1	R^2	R^3	R^4
a	C_5H_{11}	H	H	H
b	C_7H_{15}	H	H	H
c	Ph	H	H	H
d	Ph	H	Me	H
e	$—(CH_2)_4—$		H	H
f	$—(CH_2)_6—$		H	H

X = H (**4a**,**b**, **5a**—**f**), D (**6a**,**b**, **7a**—**f**)

The study of the influence of the nature of substituents in methylidenecyclopropane showed that, under the developed conditions of synthesis (methylidenecyclopropane : Et_3Al : [Zr] = 10 : 20 : 0.5, 4 h, 20—23 °C), 2-phenyl- and 2-methyl-2-phenylmethylidenecycloprop-

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Table 1. Cycloalumination of methylidenecyclopropanes **1a—f**

Methylidenecyclopropane	Ratio* **2** : **3**	Total yield* (%)
1a	**2a** : **3a** (1 : 1)	68
1b	**2b** : **3b** (1 : 1)	74
1c	**2c** : **3c** (0 : 1)	88
1d	**2d** : **3d** (0 : 1)	90
1e	**2e** : **3e** (0 : 1)	64
1f	**2f** : **3f** (0 : 1)	92

* Determined by GLC from products of acidic hydrolysis of compounds **2** and **3**.

anes **1c**,**d**, 7-methylidenebicyclo[4.1.0]heptane (**1e**) and 9-methylidenebicyclo[6.1.0]nonane (**1f**) enter the reaction of catalytic cycloalumination to form the single regioisomer **3c—f** in which the corresponding spirocyclopropane substituent is in the α-position to the aluminum atom (see Table 1).

The structures of new OAC **2** and **3** were proved on the basis of studies of the spectra of products of their acidic hydrolysis (**4**, **5**) and deuterolysis (**6**, **7**) by 1D (^{1}H, ^{13}C, APT) and 2D (HH COSY, HSQC, and HMBC) NMR spectroscopy.

For instance, the downfield signals of the aromatic protons and the carbon atoms of the phenyl group are observed in the ^{13}C NMR spectrum of compound **5c**, whereas the signals of the alkyl substituent and cyclopropane fragment are observed in the high field. The methylene protons at the α-carbon atom of the alkenyl substituent ($\delta_{C(10)}$ 30.7) appear as two multiplets ($\delta_{H(10)}$ 0.91 and 1.18) due to diastereotopic splitting on the chiral center C(2). The 1,2-disubstituted cyclopropane fragment in the ^{1}H NMR fragment is presented by a four-spin system with two methine ($\delta_{H(1)}$ 2.13, $\delta_{H(2)}$ 1.13) and two methylene ($\delta_{H(3)}$ 0.67 and 0.99) protons.

The choice between the *cis*- and *trans*-isomers was performed on the basis of values of vicinal spin-spin coupling constants (SSCC). For example, for the most downfield signal ($\delta_{H(1)}$ 2.13), one high ($^3J_{cis} \approx 8—10$ Hz) and two medium ($^3J_{trans} \approx 4—6$ Hz) SSCC should be observed in the spectrum of the *trans*-isomer.[19] The experimental spectrum contains two high vicinal ($^3J_{cis}$ = = 8 Hz) and one medium ($^3J_{trans}$ = 5 Hz) SSCC for the signal at δ 2.13, unambiguously indicating the *cis*-configuration of the phenyl and propyl groups relative to the plane of the cyclopropane ring.

The positions of the deuterium atoms in compound **7c** formed due to deuterolysis of OAC **3c** is determined by triplet splitting of the signals of the methine and methyl atoms C(2) and C(12) (δ 18.5 and 13.7, respectively) with the upfield shift of the triplet center by $\Delta\delta_C$ = 0.3 and SSCC $^1J_{C,D}$ = 19 Hz, additionally confirming the formation of cyclic OAC **3c**.

For the α-methylene group of the propyl substituent of compound **5b**, the characteristic values of chemical shifts ($\delta_{C(11)}$ 30.9, $\delta_{H(11)}$ 1.14) are related by the cross peak in the HSQC spectrum. In the HMBC experiment, the signal of the H(11) proton at δ 1.14 correlates with the signals of the methine ($\delta_{C(2)}$ 15.5) and methylene ($\delta_{C(12)}$ 23.3) carbon atoms, which allows one to completely assign all signals in the spectrum of cyclopropane **5b**. Comparison of the chemical shifts of the α-methylene groups for compounds **5b** ($\delta_{C(11)}$ 30.9) and **5c** ($\delta_{C(10)}$ 30.7) unambiguously indicate the same *cis*-orientation of the substituents in the cyclopropane fragments. In the case of *trans*-orientation of the substituents, the chemical shifts of the α-carbon atoms would differ more than by 3 ppm. The structure of OAC **2a,b** was determined similarly.

Based on the data obtained for new OAC, we proposed structures for 5-ethyl-1-pentyl(heptyl)-5-alumaspiro-[2.4]heptanes **2a,b**, 4-ethyl-1-pentyl(heptyl, phenyl)-4-alumaspiro[2.4]heptanes **3a—c**, 4-ethyl-1-methyl-1-phenyl-4-alumaspiro[2.4]heptane (**3d**), 1-ethylspiro[bicyclo-[4.1.0]heptane-7,2´-alumacyclopentane] (**3e**), and 1-ethylspiro[bicyclo[6.1.0]octane-9,2´-alumacyclopentane] (**3f**).

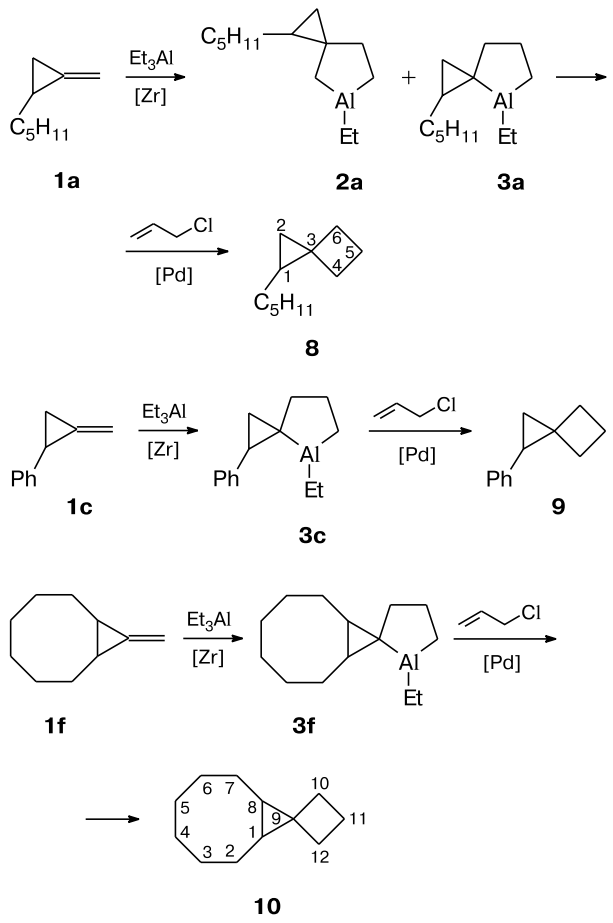
We assumed that this reaction can be used in synthesis of substituted spiro[2.3]hexanes in spite of the different regioselectivities of formation of alumacyclopentanes.

Indeed, after carbocyclization[2,3] with allyl chloride excess in the presence of the catalyst $Pd(acac)_2$—$2Ph_3P$ (2 mol.%), new alumaspiro[2.4]heptanes **2a** and **3a,c,f**, synthesized *in situ* under the conditions described above, gave 1-pentyl- (**8**), 1-phenylspiro[2.3]hexane (**9**), and spiro-[bicyclo[6.1.0]nonane-9-cyclobutane] (**10**) (Scheme 2).

The spectral characteristics of 1-phenylspiro[2.3]-hexane (**9**) turned out to be identical to those described earlier.[20] For the newly synthesized 1-pentylspiro[2.3]-hexane (**8**) and spiro[bicyclo[6.1.0]nonane-9-cyclobutane] (**10**), the full signal assignment was performed and the configuration of the molecule was established using 1D and 2D NMR experiments. So, the 1D ^{13}C NMR spectrum contains eight signals corresponding to the symmetry plane passing through the "effective" plane of the spirocyclobutane fragment and the middle of the C(4)—C(5) bond. In cyclooctane this situation takes place for *cis*-coupling of the cyclooctane and cyclopropane fragments; in addition, the *cis*-oriented C(1)—C(2) and C(7)—C(8) bonds sterically hinder the *syn*-arranged carbon atom of cyclobutane, which is manifested as the upfield shift of the signal of the C(10) atom at δ 22.4, unlike the *anti*-arranged C(12) atom ($\delta_{C(12)}$ 31.4).

Thus, for the first time we carried out cycloalumination of methylidenecyclopropanes with Et_3Al catalyzed by Cp_2ZrCl_2. The developed reaction can be successfully used in a one-pot synthesis of poorly accessible substituted spiro[2.3]hexanes.

Scheme 2



[Zr] = Cp_2ZrCl_2; [Pd] = $Pd(acac)_2$ + Ph_3P

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), helium as carried gas (30 mL min^{-1})) with temperature programming 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 (100 (^{13}C) and 400 MHz (^1H)) in $CDCl_3$ relative to Me_4Si. GC-MS analysis of the compounds was carried out on a Finnigan instrument, model 4021 (glass capillary column 50000×0.25 mm, stationary phase HP-5, helium as carried gas, temperature programming from 50 to 300 °C with a rate 5 °C min^{-1}, temperature of the evaporator 280 °C, temperature of the ion source 250 °C, 70 eV). Elemental analysis was carried out on a Karlo Erba elemental analyzer, model 1106. The yields of products were determined by GLC analysis. Reactions with organometallic compounds were carried out in a dry argon flow. Solvents were dried and used freshly distilled. Methylidenecyclopropanes were synthesized by the known procedure.[21] Cp_2ZrCl_2 was obtained from $ZrCl_4$ using the procedure described earlier.[22] Commercially available allyl chloride, Ph_3P (Acrus), and Et_3Al (98%) (joint-stock company "Redkinskii opytnyi zavod" (Redkino Experimental Plant, Moscow Region, Russia)).

Cycloalumination of methylidenecyclopropanes with Et_3Al in the presence of Cp_2ZrCl_2 (general procedure). Hexane (15 mL), methylidenecyclopropane **1a—f** (2.0 mmol), Cp_2ZrCl_2 (0.1 mmol), and Et_3Al (4 mmol) were placed with stirring in a glass reactor under dry argon at −15 °C. The temperature was brought to room temperature, and the reaction mixture was stirred for 4 h. To identify spirocyclopropylalumacyclopentanes **2a,b** and **3a—f** by the deuterolysis (**6a,b**, **7a—f**) or hydrolysis (**4a,b**, **5a—f**) products, the reaction mixture was treated with 3% DCl in D_2O or 3% HCl in H_2O. The products were extracted with ether or hexane and dried over $MgSO_4$. Low-boiling compounds were removed *in vacuo*, and the residue was passed through a small layer of neutral alumina and isolated by distillation *in vacuo*.

1-Ethyl-1-methyl-2-pentylcyclopropane (4a) (*cis* : *trans*, 1 : 1). Found (%): C, 85.49; H, 14.36. $C_{11}H_{22}$. Calculated (%): C, 85.63; H, 14.37. IR, ν/cm^{-1}: 725, 1020, 1380, 1460, 2860, 2940, 3030. ^1H NMR, δ: 1.16—1.42 (m, 10 H); 1.00 (s, 3 H); 0.96 (t, 3 H, J = 7.0 Hz); 0.92 (t, 3 H, J = 6.5 Hz); 0.17—0.43 (m, 3 H). ^{13}C NMR, δ: 34.4 (34.3), 32.6, 30.6, 28.6, 26.8, 22.6, 20.6 (20.5), 18.6 (19.0), 14.2, 11.1 (11.3). MS (EI, 70 eV), m/z: 154.

1-Ethyl-2-heptyl-1-methylcyclopropane (4b) (*cis* : *trans*, 1 : 1). Found (%): C, 85.52; H, 14.38. $C_{13}H_{26}$. Calculated (%): C, 85.63; H, 14.37. IR, ν/cm^{-1}: 724, 1020, 1378, 1465, 2845, 2930, 3045. ^1H NMR, δ: 1.15—1.48 (m, 14 H); 1.05 (s, 3 H); 0.94 (t, 3 H, J = 7.0 Hz); 0.90 (t, 3 H, J = 6.5 Hz); 0.18—0.42 (m, 3 H). ^{13}C NMR, δ: 34.6 (34.5), 32.6, 30.6, 29.7, 29.4, 28.6, 26.8, 22.7, 20.7 (20.5), 18.6 (19.0), 14.1, 11.2 (11.3). MS (EI, 70 eV), m/z: 182.

***cis*-1-Pentyl-2-propylcyclopropane (5a).** n_D^{20} 1.4363. Found (%): C, 85.54; H, 14.35. $C_{11}H_{22}$. Calculated (%): C, 85.63; H, 14.37. IR, ν/cm^{-1}: 730, 1020, 1380, 1465, 2860, 2930, 3050. ^1H NMR, δ: 1.25—1.46 (m, 10 H); 1.11—1.16 (m, 2 H); 0.94 (t, 3 H, J = 7.0 Hz); 0.91 (t, 3 H, J = 7.0 Hz); 0.66 (m, 2 H); 0.57 (m, 2 H). ^{13}C NMR, δ: 10.8 (C(3)), 14.0 (C(8)), 14.1 (C(11)), 15.5 (C(2)), 15.8 (C(1)), 22.7 (C(7)), 23.3 (C(10)), 28.9 (C(5)), 30.1 (C(4)), 30.8 (C(9)), 32.1 (C(6)). MS (EI, 70 eV), m/z: 154.

***cis*-1-Heptyl-2-propylcyclopropane (5b).** n_D^{20} 1.4409. Found (%): C, 85.49; H, 14.34. $C_{13}H_{26}$. Calculated (%): C, 85.63; H, 14.37. IR, ν/cm^{-1}: 720, 1020, 1380, 1465, 2850, 2930, 3045. ^1H NMR, δ: 1.26—1.44 (m, 14 H); 1.11—1.17 (m, 2 H); 0.94 (t, 3 H, J = 7.0 Hz); 0.90 (t, 3 H, J = 7.0 Hz); 0.67 (m, 2 H); 0.59 (m, 2 H). ^{13}C NMR, δ: 10.9 (C(3)), 14.1 (C(10), C(13)), 15.5 (C(2)), 15.7 (C(1)), 22.7 (C(9)), 23.3 (C(12)), 28.7 (C(5)), 29.4 (C(7)), 29.6 (C(6)), 30.2 (C(4)), 30.9 (C(11)), 31.9 (C(8)). MS (EI, 70 eV), m/z: 182.

***cis*-1-Phenyl-2-propylcyclopropane (5c).** B.p. 71—73 °C (3 Torr). Found (%): C, 89.81; H, 10.04. $C_{12}H_{16}$. Calculated (%): C, 89.94; H, 10.06. IR, ν/cm^{-1}: 700, 735, 780, 1050, 1380, 1450, 1590, 3040, 3070. ^1H NMR, δ: 7.29 (m, 2 H); 7.22 (m, 2 H); 7.18 (m, 1 H); 2.13 (m, 1 H); 1.32 (m, 2 H); 1.18 (m, 1 H); 1.12 (m, 1 H); 0.99 (m, 1 H); 0.91 (m, 1 H); 0.83 (t, 3 H, J = 7.0 Hz); 0.66 (m, 1 H). ^{13}C NMR, δ: 9.6 (C(3)), 14.0 (C(12)), 18.8 (C(2)), 20.9 (C(1)), 22.5 (C(11)), 30.7 (C(10)), 125.8 (C(7)), 127.8 (C(6), C(8)), 129.0 (C(5), C(9)), 139.8 (C(4)). MS (EI, 70 eV), m/z: 160.

1-Methyl-1-phenyl-2-propylcyclopropane (5d). B.p. 79—81 °C (3 Torr). Found (%): C, 89.51; H, 10.42. $C_{13}H_{18}$. Calculated (%): C, 89.59; H, 10.41. IR, ν/cm^{-1}: 700, 735, 785, 1030, 1070, 1385, 1450, 1580, 3040, 3070. ^1H NMR, δ: 7.25—7.32 (m, 5 H, Ph); 1.46 (s, 3 H); 1.07—1.31 (m, 4 H); 0.82 (t, 3 H, J = 7.0 Hz);

0.37—0.61 (m, 3 H). ^{13}C NMR, δ: 14.0 (C(12)), 18.4 (C(3)), 20.2 (C(13)), 22.8 (C(11)), 26.1 (C(1)), 28.6 (C(2)), 32.9 (C(10)), 125.8 (C(7)), 126.2 (C(6), C(8)), 128.0 (C(5), C(9)), 144.5 (C(4)). MS (EI, 70 eV), *m/z*: 174.

***endo*-7-Propylbicyclo[4.1.0]heptane (5e).** B.p. 66—68 °C (20 Torr). Found (%): C, 86.83; H, 13.14. $C_{10}H_{18}$. Calculated (%): C, 86.88; H, 13.12. IR, ν/cm^{-1}: 785, 1385, 1450, 1465, 3000. ^{1}H NMR, δ: 1.76 (d, 1 H, *J* = 10.0 Hz); 1.61—1.84 (m, 8 H); 1.05—1.29 (m, 3 H); 0.89 (t, 3 H, *J* = 7.0 Hz); 0.79 (m, 2 H); 0.58 (m, 1 H). ^{13}C NMR, δ: 10.1 (C(1), C(6)), 14.2 (C(10)), 18.5 (C(7)), 19.0 (C(2), C(5)), 22.6 (C(3), C(4)), 23.0 (C(9)), 32.5 (C(8)). MS (EI, 70 eV), *m/z*: 138.

***endo*-9-Propylbicyclo[6.1.0]nonane (5f).** B.p. 74—76 °C (5 Torr). Found (%): C, 86.53; H, 13.34. $C_{12}H_{22}$. Calculated (%): C, 86.67; H, 13.33. IR, ν/cm^{-1}: 780, 1380, 1450, 1465, 2985, 3000. ^{1}H NMR, δ: 1.23—1.69 (m, 16 H); 0.93 (t, 3 H, *J* = 7.2 Hz); 0.59—0.66 (m, 2 H); 0.29—0.37 (m, 1 H). ^{13}C NMR, δ: 14.2 (C(12)), 17.7 (C(9)), 17.9 (C(1), C(8)), 21.7 (C(3), C(6)), 23.6 (C(11)), 26.5 (C(4), C(5)), 29.7 (C(10)), 29.8 (C(2), C(7)). MS (EI, 70 eV), *m/z*: 166.

1-(2-Deuteroethyl)-1-deuteromethyl-2-pentylcyclopropane (6a) (*cis* : *trans*, 1 : 1). Found (%): C, 84.44; H + D, 14.98. $C_{11}H_{20}D_2$. Calculated (%): C, 84.53; H, 12.9; D, 2.57. IR, ν/cm^{-1}: 2160 (C—D). ^{1}H NMR, δ: 1.18—1.44 (m, 10 H); 1.03 (s, 2 H); 0.97 (t, 3 H, *J* = 7.0 Hz); 0.91 (t, 2 H, *J* = 7.0 Hz); 0.15—0.44 (m, 3 H). ^{13}C NMR, δ: 34.4 (34.2), 32.6, 30.5, 28.6, 26.6, 22.6, 20.3 (20.1) (t, $J_{C,D}$ = 19.0 Hz), 18.6 (19.0), 14.2, 10.8 (10.7) (t, $J_{C,D}$ = 19.0 Hz). MS (EI, 70 eV), *m/z*: 156.

1-(2-Deuteroethyl)-1-deuteromethyl-2-heptylcyclopropane (6b) (*cis* : *trans*, 1 : 1). Found (%): C, 84.65; H + D, 15.03. $C_{13}H_{24}D_2$. Calculated (%): C, 84.70; H, 13.12; D, 2.18. IR, ν/cm^{-1}: 2160 (C—D). ^{1}H NMR, δ: 1.10—1.45 (m, 14 H); 1.03 (s, 2 H); 0.94 (t, 3 H, *J* = 7.0 Hz); 0.91 (t, 2 H, *J* = 6.5 Hz); 0.18—0.44 (m, 3 H). ^{13}C NMR, δ: 34.6 (34.5), 32.8, 30.6, 29.7, 29.5, 28.6, 26.8, 22.6, 20.4 (20.2) (t, $J_{C,D}$ = 19.5 Hz), 18.6 (19.0), 14.1, 10.9 (11.1) (t, $J_{C,D}$ = 19.0 Hz). MS (EI, 70 eV), *m/z*: 184.

***cis*-2-Deutero-2-(3-deuteropropyl)-1-pentylcyclopropane (7a).** n_D^{20} 1.4371. Found (%): C, 84.34; H + D, 14.95. $C_{11}H_{20}D_2$. Calculated (%): C, 84.53; H, 12.90; D, 2.57. IR, ν/cm^{-1}: 2160 (C—D). ^{1}H NMR, δ: 1.25—1.44 (m, 10 H); 1.09—1.15 (m, 2 H); 0.93 (t, 2 H, *J* = 7.0 Hz); 0.90 (t, 3 H, *J* = 7.0 Hz); 0.64 (m, 1 H); 0.58 (m, 2 H). ^{13}C NMR, δ: 10.8 (C(3)), 13.8 (t, C(11), $J_{C,D}$ = = 19.0 Hz), 14.0 (C(8)), 15.3 (t, C(2), $J_{C,D}$ = 19.0 Hz), 15.8 (C(1)), 22.6 (C(7)), 23.4 (C(10)), 28.9 (C(5)), 30.1 (C(4)), 30.9 (C(9)), 32.1 (C(6)). MS (EI, 70 eV), *m/z*: 156.

***cis*-2-Deutero-2-(3-deuteropropyl)-1-heptylcyclopropane (7b).** n_D^{20} 1.4413. Found (%): C, 84.62; H + D, 15.04. $C_{13}H_{24}D_2$. Calculated (%): C, 84.70; H, 13.12; D, 2.18. IR, ν/cm^{-1}: 2165 (C—D). ^{1}H NMR, δ: 1.23—1.45 (m, 14 H); 1.10—1.18 (m, 2 H); 0.93 (t, 2 H, *J* = 7.0 Hz); 0.90 (t, 3 H, *J* = 7.0 Hz); 0.67 (m, 1 H); 0.57 (m, 2 H). ^{13}C NMR, δ: 10.8 (C(3)), 13.7 (t, C(11), $J_{C,D}$ = = 19.0 Hz), 14.0 (C(10)), 15.2 (t, C(2), $J_{C,D}$ = 19.5 Hz), 15.8 (C(1)), 22.7 (C(9)), 23.2 (C(12)), 28.7 (C(5)), 29.4 (C(7)), 29.6 (C(6)), 30.2 (C(4)), 30.9 (C(11)), 31.9 (C(8)). MS (EI, 70 eV), *m/z*: 184.

***cis*-2-Deutero-2-(3-deuteropropyl)-1-phenylcyclopropane (7c).** B.p. 71—73 °C (3 Torr). Found (%): C, 88.75; H + D, 11.23. $C_{12}H_{14}D_2$. Calculated (%): C, 88.83; H, 8.70; D, 2.48. IR, ν/cm^{-1}: 2160 (C—D). ^{1}H NMR, δ: 7.17—7.31 (m, 5 H, Ph); 2.12 (m, 1 H); 1.32 (m, 2 H); 1.19 (m, 1 H); 0.99 (m, 1 H); 0.92 (m, 1 H); 0.82 (t, 2 H, *J* = 7.0 Hz); 0.65 (m, 1 H). ^{13}C NMR, δ: 9.6 (C(3)), 13.7 (t, C(12), $J_{C,D}$ = 19.0 Hz), 18.5 (t, C(2), $J_{C,D}$ = 19.0 Hz), 20.8 (C(1)), 22.4 (C(11)), 30.5 (C(10)), 125.8 (C(7)), 127.8 (C(6), C(8)), 129.0 (C(5), C(9)), 139.8 (C(4)). MS (EI, 70 eV), *m/z*: 162.

2-Deutero-2-(3-deuteropropyl)-1-methyl-1-phenylcyclopropane (7d). B.p. 79—82 °C (3 Torr). Found (%): C, 88.48; H + D, 11.49. $C_{12}H_{14}D_2$. Calculated (%): C, 88.57; H, 9.15; D, 2.28. IR, ν/cm^{-1}: 2160 (C—D). ^{1}H NMR, δ: 7.25—7.33 (m, 5 H, Ph); 1.48 (s, 3 H); 1.09—1.30 (m, 4 H); 0.81 (t, 2 H, *J* = 7.0 Hz); 0.36—0.59 (m, 2 H). ^{13}C NMR, δ: 13.7 (t, C(12), $J_{C,D}$ = = 19.0 Hz), 18.3 (C(3)), 20.3 (C(13)), 22.8 (C(11)), 26.2 (C(1)), 28.3 (t, C(2), $J_{C,D}$ = 19.0 Hz), 32.8 (C(10)), 125.8 (C(7)), 126.2 (C(6), C(8)), 128.0 (C(5), C(9)), 144.4 (C(4)). MS (EI, 70 eV), *m/z*: 176.

***endo*-7-Deutero-7-(3-deuteropropyl)bicyclo[4.1.0]heptane (7e).** B.p. 66—68 °C (20 Torr). Found (%): C, 85.58; H + D, 14.34. $C_{10}H_{16}D_2$. Calculated (%): C, 85.64; H, 11.50; D, 2.87. IR, ν/cm^{-1}: 2160 (C—D). ^{1}H NMR, δ: 1.81 (s, 1 H); 1.60—1.84 (m, 8 H); 1.06—1.28 (m, 3 H); 0.88 (t, 2 H, *J* = 7.0 Hz); 0.78 (m, 2 H). ^{13}C NMR, δ: 10.0 (C(1), C(6)), 13.9 (t, C(10), $J_{C,D}$ = = 19.0 Hz), 18.2 (t, C(7), $J_{C,D}$ = 22.5 Hz), 19.0 (C(2), C(5)), 22.5 (C(3), C(4)), 23.0 (C(9)), 32.4 (C(8)). MS (EI, 70 eV), *m/z*: 140.

***endo*-9-Deutero-9-(3-deuteropropyl)bicyclo[6.1.0]nonane (7f).** B.p. 74—76 °C (5 Torr). Found (%): C, 85.55; H + D, 14.41. $C_{12}H_{20}D_2$. Calculated (%): C, 85.63; H, 11.98; D, 2.39. IR, ν/cm^{-1}: 2165 (C—D). ^{1}H NMR, δ: 1.22—1.67 (m, 16 H); 0.92 (t, 2 H, *J* = 7.2 Hz); 0.59—0.68 (m, 2 H). ^{13}C NMR, δ: 13.9 (t, C(12), $J_{C,D}$ = 19.0 Hz), 17.3 (t, C(9), $J_{C,D}$ = 24.0 Hz), 17.8 (C(1), C(8)), 21.7 (C(3), C(6)), 23.4 (C(11)), 26.5 (C(4), C(5)), 29.7 (C(10)), 29.8 (C(2), C(7)). MS (EI, 70 eV), *m/z*: 168.

Synthesis of spiro[2.3]hexanes (general procedure). Hexane (15 mL), methylidenecyclopropane **1a,c,f** (2.0 mmol), Cp_2ZrCl_2 (0.1 mmol), and Et_3Al (4 mmol) were placed in a glass reactor under a dry argon atmosphere at −10—15 °C with stirring. The temperature was brought to room temperature (20—21 °C), and the mixture was stirred for 4 h. Then at 0 °C Et_2O (10 mL), Ph_3P (0.2 mmol), $Pd(acac)_2$ (0.1 mmol), and allyl chloride (6 mmol) were added, the temperature was increased to room temperature, and the reaction mixture was stirred for 8 h. The reaction mixture was treated with a 7—10% aqueous solution, and the reaction products were extracted with ether, dried over $MgSO_4$, and isolated by distillation *in vacuo*.

1-Pentylspiro[2.3]hexane (8). B.p. 78—85 °C (12 Torr). The yield was 59%. Found (%): C, 87.73; H, 12.27. $C_{11}H_{20}$. Calculated (%): C, 88.76; H, 13.24. IR, ν/cm^{-1}: 3069, 2995, 1705, 1460, 1160, 760. ^{1}H NMR, δ: 2.05—2.10 (m, 4 H); 1.92—1.96 (m, 2 H); 1.12—1.36 (m, 8 H); 0.91 (t, 3 H, *J* = 6.5 Hz); 0.49—0.56 (m, 3 H). ^{13}C NMR, δ: 31.2 (C(9)), 30.9 (C(6)), 30.4 (C(7)), 29.3 (C(8)), 28.1 (C(3)), 26.4 (C(4)), 22.4 (C(10)), 22.1 (C(1)), 18.1 (C(2)), 17.4 (C(5)), 14.0 (C(11)). MS (EI, 70 eV), *m/z*: 152.

Spiro[bicyclo[6.1.0]nonane-9-cyclobutane] (10). B.p. 86—91 °C (5 Torr). The yield was 83%. Found (%): C, 87.68; H, 12.28. $C_{12}H_{20}$. Calculated (%): C, 87.73; H, 12.27. IR, ν/cm^{-1}: 3071, 2999, 1700, 1462, 1160, 760. ^{1}H NMR, δ: 2.02 (m, 4 H); 1.91 (m, 2 H); 1.73—1.85 (m, 2 H); 1.26—1.69 (m, 8 H); 0.72—0.91 (m, 2 H); 0.45 (m, 2 H). ^{13}C NMR, δ: 17.8 (C(11)), 22.4 (C(10)), 23.1 (C(3), C(6)), 24.8 (C(1), C(8)), 25.6 (C(9)), 26.6 (C(4), C(5)), 29.4 (C(2), C(7)), 31.4 (C(12)). MS (EI, 70 eV), *m/z*: 164.

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