Organometallic Chemistry

A new route of the reaction of $EtAlCl_2$ with α-olefins catalyzed by Ti complexes

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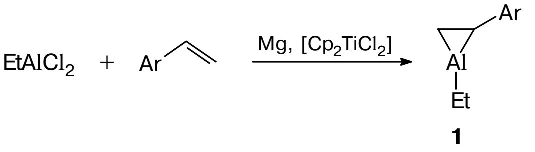
A new method for the synthesis of dialkyl(ethyl)alanes by the reaction of $EtAlCl_2$ with α-olefins in the presence of Mg and a catalytic amount of Cp_2TiCl_2 ($Ti(OPr^i)_4$, $Ti(OBu^n)_4$) in THF was developed.

Key words: organoaluminum compounds, catalysis, hydrometallation, dehydrogenation, Ti complexes, olefins.

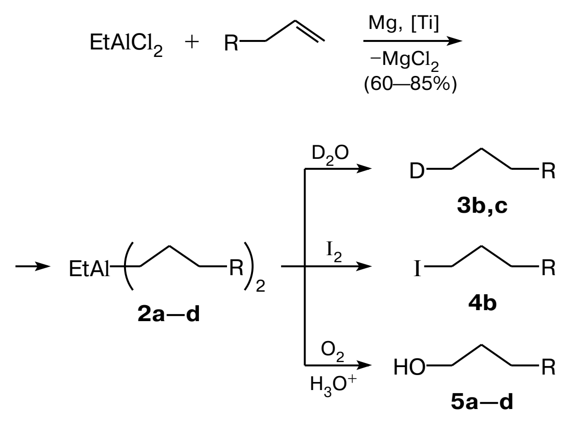
Recently[1], we have proposed an approach to the synthesis of a new series of organoaluminum compounds (OAC), *viz.*, substituted aluminacyclopropanes (**1**), by cyclometallation of arylethenes with $EtAlCl_2$ in the presence of metallic Mg in THF and a catalytic amount of Cp_2TiCl_2.



(1)

To extend the area of application of this method, to obtain new types of small metallacycles, and to determine the possibility of cyclometallation of aliphatic α-olefins, we studied the interaction of α-olefins containing H atoms at the allylic C atom (aliphatic C_6—C_{11} α-olefins, allylbenzene, and allylnaphthalene) with $EtAlCl_2$ under the conditions described previously[1] (5 mol.% Cp_2TiCl_2, THF, ~20 °C).

However, dialkyl(ethyl)alanes **2a—d** were formed instead of the corresponding aluminacyclopropanes.



(2)

R = Pr^n (**a**), n-C_5H_{11} (**b**), n-C_7H_{15} (**c**), n-C_8H_{17} (**d**)

The OAC obtained were transformed into the corresponding partially deuterated alkanes **3b,c**, 1-iodoalkane

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4b, and alcohols **5a—d**. These results allowed us to suggest the formulae **2a—d** for the OAC synthesized. The presence of the broadened high-field signals in the ^{13}C NMR spectra of **2a,b** at δ 0.29 and 9.77 assigned to the α-C atoms of the ethyl and alkyl groups, respectively, confirmed their structures.[2]

In this reaction, acyclic OAC **2** can be obtained only by catalytic hydrometallation *via* intermediate titanium hydride complexes (Ti—H). The idea on the key role of the Ti—H complexes in the reaction under discussion is confirmed by the results of the study reported previously[3], which have demonstrated that the low-valent Ti complexes obtained by the reduction of $TiCl_4$ with metallic Mg split tetrahydrofuran yielding Ti hydrides and a mixture of gaseous products.

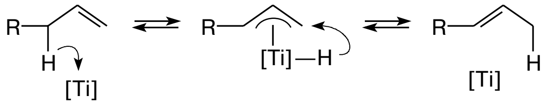
Unlike aliphatic α-olefins, arylethenes give aryl-substituted aluminacyclopropanes **1** under the same conditions.[1]

The known[4—7] schemes of hydrometallation of α-olefins with "hydride-free" reagents, *e.g.*, Bu^i_3Al,[4] Bu^i_2AlCl,[5,6] or Et_3Al, involving Ti and Zr complexes do not explain the mechanism of the transformations observed and do not answer the question why $EtAlCl_2$ reacts with arylethenes according to the cyclometallation route and with aliphatic α-olefins according to the hydrometallation route under the same conditions.

Experimental and literature data[8,9] allow us to assume that arylethenes behave like conjugated dienes and form stable titanacyclopropane intermediates with "Cp_2Ti" (analogously to phenyl-substituted titanacyclopropenes[10]), which are inert with respect to tetrahydrofuran. Aliphatic α-olefins or allylarenes probably give labile low-valent titanium complexes **6**, which split tetrahydrofuran yielding Ti hydrides,[3] which reduce α-olefins.

Based on the results obtained, we suggested a scheme of the reaction of α-olefins with $EtAlCl_2$. Its first stage includes reduction of Cp_2TiCl_2 with Mg to "Cp_2Ti", which coordinates α-olefin and tetrahydrofuran molecules resulting in the formation of complex **6**. Dehydrogenation[3] of the tetrahydrofuran molecule by low-valent Ti complexes **6** affords titanium hydrides[7], which hydrometallate olefin molecules to give Ti alkyl derivatives **8**. Transmetallation of alkyl complexes **8** by the starting $EtAlCl_2$ resulting in the formation of OAC **2** and regeneration of the catalyst Cp_2TiCl_2 (see Scheme 1) is the terminal stage.

Depending on duration of the reaction and the ratio of the starting reagents and the catalyst, the reaction mixture contains 15—30% of disubstituted (*Z*/*E*)-olefins **9a—d**, which are likely generated by isomerisation of the starting α-olefins upon treatment with Ti complexes.[11]



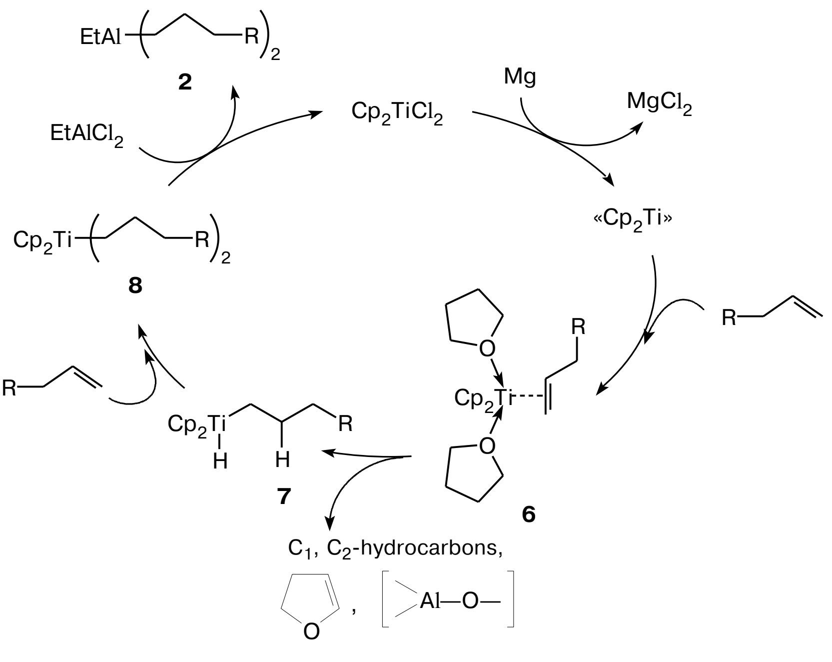
9a—d

(3)

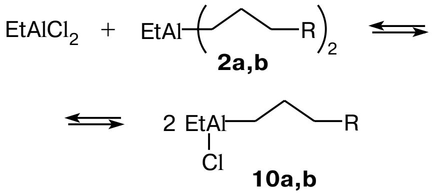
The reactions performed in Et_2O result in a decrease in the yield of OAC **2** to 25—40% and at the same time increase the content of (*Z*/*E*)-olefins **9a—d**. The reaction does not proceed in aliphatic solvents. When using benzene as a solvent, the reported[12] reaction of cyclometallation of α-olefins yielding regioisomeric alkyl-substituted aluminacyclopentanes is observed. The yield of alkylalanes **2** is 45—50% in the presence of 3—5 mol.% of titanium alkoxides ($Ti(OPr^i)_4$, $Ti(OBu^n)_4$).

Using ^{13}C NMR spectra, we have established that the reaction mixture contains alkyl(chloro)ethylalanes **10a,b** along with dialkyl(ethyl)alanes, *e.g.*, **2a,b**. The

Scheme 1



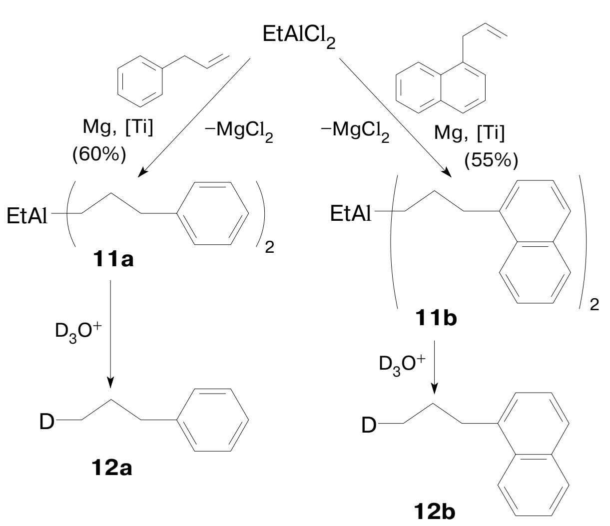
former compounds can be generated[13] by the exchange reaction of OAC **2** with the starting $EtAlCl_2$.



(4)

Allylbenzene and allylnaphthalene were found to react with $EtAlCl_2$ in the presence of Cp_2TiCl_2 as the catalyst resulting in the corresponding higher OAC **11a,b** (Scheme 2) in the same way as alkyl-substituted α-olefins.

Scheme 2

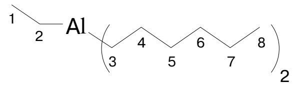


The results obtained attest that we have found a new direction of the reaction of $EtAlCl_2$ with α-olefins containing H atoms at the allylic C atom in the presence of the catalysts based on Ti complexes, which permits one to obtain acyclic OAC in the ether-type solvents.

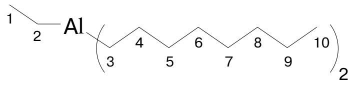
Experimental

The reactions with organometallic compounds were carried out in the atmosphere of dry argon. Solvents were distilled from $LiAlH_4$ immediately before use. GLC analysis of the products of hydrolysis, deuterolysis, or iodinolysis was performed on a Chrom-5 instrument with He as the carrier gas, using a 1200×3-mm column with 5% SE-30 or 15% PEG-6000 on Chromaton N-AW. IR spectra were recorded on a UR-20 spectrometer (film). Mass spectra were measured on an MKh-1306 spectrometer (70 eV, 200 °C). ^1H and ^{13}C NMR spectra were registered in $CDCl_3$ on JEOL. FX-90 Q (90 and 22.5 MHz) and Bruker AM-300 (300 and 75 MHz) spectrometers, respectively, with Me_4Si as the internal standard. The ^{13}C NMR spectra of OAC were taken on a JEOL. FX-90Q spectrometer (22.5 MHz) in complete and partial proton decoupling modes. Dilute solutions of OAC in THF were used with the addition of C_6D_{12} for the internal field stabilization. The OAC solutions were placed in sealed ampoules under dry argon. The yields of OAC were determined by GLC analysis of the hydrolysis products. Alcohols **5a—d** were identified by comparison with the authentic samples.[14]

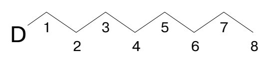
Reactions of α-olefins with $EtAlCl_2$—Mg—[Ti] (general procedure). An α-olefin (10 mmol), Cp_2TiCl_2 ($Ti(OBu^n)_4$, $Ti(OPr^i)_4$) (0.5 mmol), Mg powder (10 mg-at.), THF (10 mL), and $EtAlCl_2$ (12 mmol) were placed into a glass reactor at −5 °C under dry argon. The solution was heated to 21—22 °C and stirred for 8 h. The reaction mixture was oxidized with atmospheric oxygen at ~50 °C or treated with 15% DCl in D_2O or with I_2. The products were extracted with ether and isolated by distillation. Below is shown the numbering of the atoms of the resulting OAC and the products of their hydrolysis, deuterolysis, oxidation, and iodinolysis:



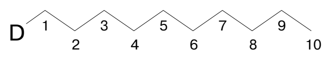
2a



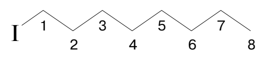
2b



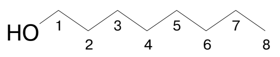
3b



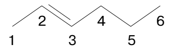
3c



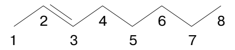
4b



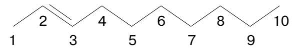
5b



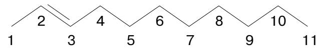
E-**9a**



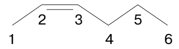
E-**9b**



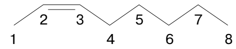
E-**9c**



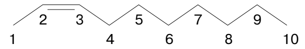
E-**9d**



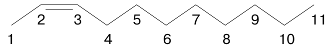
Z-**9a**



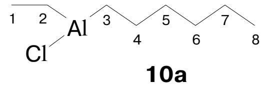
Z-**9b**



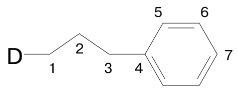
Z-**9c**



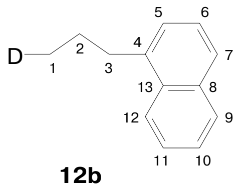
Z-**9d**

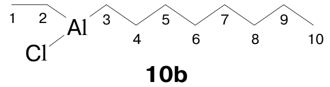


10a



12a





10b

12b

Di(*n*-hexyl)ethylalane (2a). ^{13}C NMR (C_6D_{12}, δ): 0.29 (br.t, C(2)); 8.15 (q, C(1)); 9.77 (br.t, C(3)); 14.07 (q, C(8)); 23.04 (t, C(7)); 27.79 (t, C(4)); 32.08 (t, C(6)); 35.46 (t, C(5)).

Di(*n*-octyl)ethylalane (2b). ^{13}C NMR (C_6D_{12}, δ): 0.29 (br.t, C(2)); 8.15 (q, C(1)); 9.77 (br.t, C(3)); 13.94 (q, C(10)); 22.91 (t, C(9)); 27.79 (t, C(4)); 28.64 (t, C(6)); 29.61 (t, C(7)); 32.21 (t, C(8)); 35.85 (t, C(5)).

1-Deuteriohexane (3a), b.p. 68—69 °C, n_D^{20} 1.3756. IR, ν/cm^{-1}: 3000, 2160 (C—D), 1460, 1380, 950, 700. ^{1}H NMR, δ: 0.79—0.90 (m, 5 H, CH_2D, CH_3); 1.10—1.25 (m, 8 H, CH_2). MS, *m/z*: 87 [M]$^+$. Found (%): C, 82.68; H, 17.15. $C_6H_{13}D$. Calculated (%): C, 82.76; H, 14.94; D, 2.30.

1-Deuteriooctane (3b), b.p. 124—125 °C, n_D^{20} 1.3973. IR, ν/cm^{-1}: 3000, 2165 (C—D), 1455, 1390, 1075, 960, 700. ^{1}H NMR, δ: 0.80—0.94 (m, 5 H, CH_2D, CH_3); 1.20—1.42 (m, 12 H, CH_2). ^{13}C NMR ($CDCl_3$, δ): 13.83 (t, C(1), $^1J_{CD}$ = 19.1 Hz); 14.09 (q, C(8)); 22.80 (t, C(2), C(7)); 29.56 (t, C(4), C(5)); 31.64 (t, C(3), C(6)). MS, *m/z*: 115 [M]$^+$. Found (%): C, 83.39; H, 16.43. $C_8H_{17}D$. Calculated (%): C, 83.48; H, 14.78; D, 1.74.

1-Deuteriodecane (3c), b.p. 57—58 °C (10 Torr), n_D^{20} 1.4112. IR, ν/cm^{-1}: 2160 (C—D). ^{1}H NMR, δ: 0.81—0.93 (m, 5 H, CH_2D, CH_3); 1.12—1.40 (m, 16 H, CH_2). ^{13}C NMR ($CDCl_3$, δ): 13.83 (t, C(1), $^1J_{CD}$ = 19.1 Hz); 14.15 (q, C(10)); 22.80 (t, C(2), C(9)); 29.50 (t, C(4), C(7)); 29.76 (t, C(5), C(6)); 32.04 (t, C(3), C(8)). MS, *m/z*: 143 [M]$^+$. Found (%): C, 83.82; H, 15.99. $C_{10}H_{21}D$. Calculated (%): C, 83.91; H, 14.69; D, 1.40.

1-Deuterioundecane (3d), b.p. 75—76 °C (10 Torr), n_D^{20} 1.4168. IR, ν/cm^{-1}: 2160 (C—D).^{1}H NMR δ: 0.81—0.94 (m, 5 H, CH_2D, CH_3); 1.13—1.39 (m, 16 H, CH_2). MS, *m/z*: 157 [M]$^+$. Found (%): C, 83.99; H, 15.84. $C_{11}H_{23}D$. Calculated (%): C, 84.08; H, 14.65; D, 1.27.

1-Iodoctane (4b), b.p. 100 °C (10 Torr), n_D^{20} 1.4875. IR, ν/cm^{-1}: 510, 585, 720, 1160, 1465, 2860, 2965. ^{1}H NMR, δ: 0.78—0.94 (m, 3 H, CH_3); 1.25 (m, 10 H, CH_2); 1.69—1.86 (m, 2 H, $C\underline{H_2}CH_2I$); 3.02—3.22 (m, 2 H, CH_2I). ^{13}C NMR ($CDCl_3$, δ): 6.93 (t, C(1)); 14.09 (q, C(8)); 22.67 (t, C(7)); 28.12 (t, C(5)); 29.11 (t, C(4)); 30.54 (t, C(3)); 31.77 (t, C(6)); 33.60 (t, C(2)). MS, *m/z*: 240 [M]$^+$. Found (%): C, 40.25; H, 7.05. $C_8H_{17}I$. Calculated (%): C, 40.00; H, 7.08; I, 52.92.

Hex-2-ene (9a) (*Z* : *E* ≈ 1 : 9), b.p. 68—69 °C, n_D^{20} 1.3966. ^{1}H NMR, δ: 0.88 (t, 3 H, CH_3, *J* = 7.1 Hz); 1.20—1.35 (m, 2 H, $\underline{CH_2}CH_3$); 1.97—2.05 (m, 2 H, $\underline{CH_2}CH_2CH_3$); 1.59—1.70 (m, 3 H, $\underline{CH_3}CH$); 5.36—5.42 (m, 2 H, CH=CH). MS, *m/z*: 84 [M]$^+$. Found (%): C, 85.62; H, 14.19. C_6H_{12}. Calculated (%): C, 85.71; H, 14.29.

Oct-2-ene (9b), b.p. 123 °C, n_D^{20} 1.4129. ^{1}H NMR, δ: 0.90 (t, 3 H, CH_3, *J* = 7.1 Hz); 1.20—1.31 (m, 6 H, CH_2); 1.86—2.12 (m, 2 H, $\underline{CH_2}CH$); 1.58—1.67 (m, 3 H, $\underline{CH_3}CH$); 5.33—5.45 (m, 2 H, CH=CH). MS, *m/z*: 112 [M]$^+$. Found (%): C, 85.63; H, 14.19. C_8H_{16}. Calculated (%): C, 85.71; H, 14.29.

Dec-2-ene (9c), b.p. 78—80 °C (30 Torr). ^{1}H NMR, δ: 0.88 (t, 3 H, CH_3, *J* = 7.0 Hz); 1.12—1.40 (m, 10 H, CH_2); 1.93—2.05 (m, 2 H, $\underline{CH_2}CH$); 1.61—1.65 (m, 3 H, $\underline{CH_3}CH$); 5.33—5.45 (m, 2 H, CH=CH). MS, *m/z*: 140 [M]$^+$. Found (%): C, 85.62; H, 14.20. $C_{10}H_{20}$. Calculated (%): C, 85.71; H, 14.29.

Undec-2-ene (9d), b.p. 70—72 °C (10 Torr). ^{1}H NMR, δ: 0.88 (t, 3 H, CH_3, *J* = 7.1 Hz); 1.26—1.40 (m, 12 H, CH_2); 1.85—2.05 (m, 2 H, $\underline{CH_2}CH$); 1.57—1.67 (m, 3 H, $\underline{CH_3}CH$); 5.34—5.45 (m, 2 H, CH=CH). MS, *m/z*: 154 [M]$^+$. Found (%): C, 85.60; H, 14.19. $C_{11}H_{22}$. Calculated (%): C, 85.71; H, 14.29.

***trans*-Hex-2-ene (*E*-9a).** ^{13}C NMR ($CDCl_3$), δ: 14.11 (q, C(6)); 17.95 (q, C(1)); 22.80 (t, C(5)); 32.80 (t, C(4)); 125.02 (d, C(2)); 132.22 (d, C(3)).

***cis*-Hex-2-ene (*Z*-9a).** ^{13}C NMR ($CDCl_3$), δ: 12.92 (q, C(1)); 14.11 (q, C(6)); 22.80 (t, C(5)); 27.00 (t, C(4)); 123.62 (d, C(2)); 130.94 (d, C(3)).

***trans*-Oct-2-ene (*E*-9b).** ^{13}C NMR ($CDCl_3$), δ: 14.09 (q, C(8)); 17.92 (q, C(1)); 22.79 (t, C(7)); 29.50 (t, C(5)); 32.75 (t, C(4)); 32.10 (t, C(6)); 124.57 (d, C(2)); 131.79 (d, C(3)).

***cis*-Oct-2-ene (*Z*-9b).** ^{13}C NMR ($CDCl_3$), δ: 12.72 (q, C(1)); 14.09 (q, C(8)); 22.79 (t, C(7)); 26.96 (t, C(4)); 28.98 (t, C(5)); 32.10 (t, C(6)); 123.60 (d, C(2)); 130.94 (d, C(3)).

***trans*-Dec-2-ene (*E*-9c).** ^{13}C NMR ($CDCl_3$), δ: 14.15 (q, C(10)); 17.92 (q, C(1)); 22.80 (t, C(9)); 29.50 (t, C(7)); 29.76 (t, C(5), C(6)); 32.04 (t, C(8)); 32.69 (t, C(4)); 124.57 (d, C(2)); 131.73 (d, C(3)).

***cis*-Dec-2-ene (*Z*-9c).** ^{13}C NMR ($CDCl_3$), δ: 12.72 (q, C(1)); 14.15 (q, C(10)); 22.80 (t, C(9)); 26.96 (t, C(4)); 29.50 (t, C(7)); 29.76 (t, C(5), C(6)); 32.04 (t, C(8)); 123.60 (d, C(2)); 130.95 (d, C(3)).

***trans*-Undec-2-ene (*E*-9d).** ^{13}C NMR ($CDCl_3$), δ: 14.18 (q, C(11)); 17.97 (q, C(1)); 22.82 (t, C(10)); 29.50 (t, C(7)); 29.68 (t, C(5), C(6)); 29.82 (t, C(8)); 32.06 (t, C(9)); 32.71 (t, C(4)); 124.75 (d, C(2)); 131.90 (d, C(3)).

***cis*-Undec-2-ene (*Z*-9d).** ^{13}C NMR ($CDCl_3$), δ: 12.74 (q, C(1)); 14.18 (q, C(11)); 22.82 (t, C(10)); 26.98 (t, C(4)); 29.50 (t, C(7)); 29.68 (t, C(5), C(6)); 29.82 (t, C(8)); 32.06 (t, C(9)); 123.62 (d, C(2)); 130.96 (d, C(3)).

Ethyl(*n*-hexyl)aluminum chloride (10a). ^{13}C NMR (C_6D_{12}), δ: 0.29 (br.t, C(2)); 8.67 (q, C(1)); 9.56 (br.t, C(3)); 13.94 (q, C(8)); 22.91 (t, C(7)); 27.07 (t, C(4)); 31.82 (t, C(6)); 34.86 (t, C(5)).

Ethyl(*n*-octyl)aluminum chloride (10b). ^{13}C NMR (C_6D_{12}), δ: 0.29 (br.t, C(2)); 8.73 (q, C(1)); 9.77 (br.t, C(3)); 14.20 (q, C(10)); 22.91 (t, C(9)); 27.07 (t, C(4)); 28.12 (t, C(6)); 29.61 (t, C(7)); 32.21 (t, C(8)); 35.27 (t, C(5)).

(3-Deuteriopropyl)benzene (12a), b.p. 65 °C (30 Torr), n_D^{20} 1.4921. IR, ν/cm^{-1}: 3020, 3010, 2960, 2850, 2160 (C—D), 1500, 1450, 1020, 730, 690. ^{1}H NMR, δ: 0.90 (t, 2 H, CH_2D, *J* = 7.1 Hz); 1.35—1.70 (m, 2 H, CH_2); 2.58 (t, 2 H, $\underline{CH_2}$—Ph, *J* = 7.1 Hz); 7.10—7.35 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 13.66 (t, C(1), $^1J_{CD}$ = 19.1 Hz); 22.30 (t, C(2)); 35.27 (t, C(3)); 142.54 (s, C(4)); 126.83 (d, C(5)); 126.42 (d, C(6)); 125.57 (d, C(7)). MS, *m/z*: 121 [M]$^+$. Found (%): C, 89.14; H, 10.66. $C_9H_{11}D$. Calculated (%): C, 89.26; H, 9.09; D, 1.65.

1-(3-Deuteriopropyl)naphthalene (12b), b.p. 116 °C (1 Torr), n_D^{20} 1.5307. IR, ν/cm^{-1}: 3000, 2160 (C—D), 1940, 1800, 1600, 1500, 1450, 980, 730, 690. ^{1}H NMR, δ: 1.10 (t, 2 H, CH_2D, *J* = 7.0 Hz); 1.80—1.90 (m, 2 H, CH_2); 2.98 (t, 2 H, $\underline{CH_2}$—Ph, *J* = 7.0 Hz); 7.25—8.02 (m, 7 H, H arom.). ^{13}C NMR ($CDCl_3$), δ: 13.96 (t, C(1), $^1J_{CD}$ = 19.1 Hz); 23.78 (t, C(2)); 35.09 (t, C(3)); 123.53 (d, C(6), C(12)); 125.68 (d, C(10)); 127.24 (d, C(11)); 128.34 (d, C(7)); 128.47 (d, C(5)); 128.80 (d, C(9)); 131.20 (s, C(13)); 132.12 (s, C(8)); 138.62 (s, C(4)). MS, *m/z*: 171 [M]$^+$. Found (%): C, 91.14; H, 8.68. $C_{13}H_{13}D$. Calculated (%): C, 91.23; H, 7.60; D, 1.17.

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