Synthesis and transformations of metallacycles
41.* Cyclomagnesiation of O-containing 1,2-dienes with Grignard reagents in the presence of Cp_2TiCl_2

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A Cp_2TiCl_2-catalyzed intermolecular homocyclomagnesiation of O-containing 1,2-dienes and cross-cyclomagnesiation of O-containing 1,2-dienes with aliphatic 1,2-dienes of cyclic and acyclic structure have been accomplished using Grignard reagents, which led to mono- and bicyclic organomagnesium compounds in 61—94% yields.

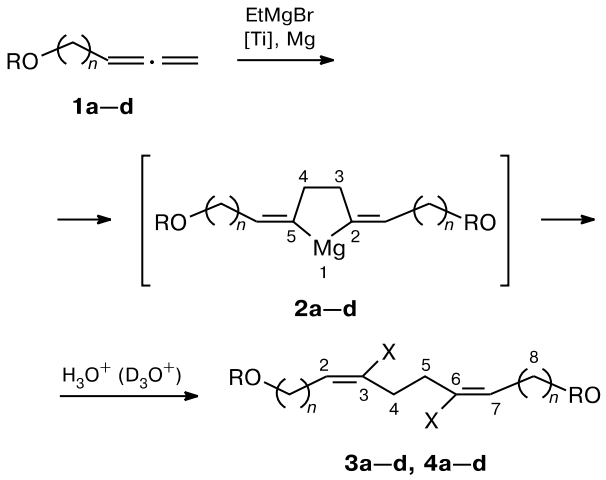
Key words: organomagnesium compounds, metal complex catalysis, magnesacyclopentane, 1,2-dienes, 1*Z*,5*Z*-dienes, cyclomagnesiation.

Earlier,[2—4] we have shown that aliphatic 1,2-dienes react with EtMgBr in the presence of Mg and Cp_2TiCl_2 with the formation of 2,5-dialkylidenemagnesacyclopentanes, which after acid hydrolysis were converted to symmetric 1*Z*,5*Z*-dienes in ~90% yields. The reaction indicated is used in the development of efficient methods for the synthesis of substituted symmetric 1*Z*,5*Z*-dienes[5] and gigantic hydrocarbon macrocycles.[6]

In continuation of these studies, as well as in order to develop efficient methods for the preparation of functionally substituted 1*Z*,5*Z*-diene compounds, which are of exclusive interest as key synthons in the synthesis of practically important insect pheromones,[7] fragrant substances,[8] and biologically active compounds of natural origin,[9,10] we have studied cyclomagnesiation of oxygen-containing 1,2-dienes using Grignard reagents in the presence of Cp_2TiCl_2.

We found that allenic and homoallenic alcohols with unprotected hydroxyl group, as well as their trimethylsilyl ethers, cannot be involved in the cyclomagnesiation reaction.[3] At the same time, allenic alcohols **1a—d** with the pyranyl or benzyl protection, in which the 1,2-diene group is separated from the oxygen atom by two or more methyl groups, react with excess EtMgBr in the presence of Cp_2TiCl_2 (5 mol.%), giving 2,5-dialkylidenemagnesacyclopentanes **2** in 68—84% yields. The latter after acid hydrolysis or deuterolysis give the corresponding symmetric O-containing 1*Z*,5*Z*-diene compounds **3** and **4** (Scheme 1).

Scheme 1



[Ti] = Cp_2TiCl_2
X = H (**3**), D (**4**)

1—4	*n*	R	**1—4**	*n*	R
a	2	THP	**c**	4	THP
b	2	Bn	**d**	6	THP

The structures of compounds **3** and **4** were reliably confirmed by modern methods of spectroscopic analysis (1D and 2D NMR spectroscopy, IR spectroscopy, mass spectrometry).

The formation of substituted 3,6-dideutero-2*Z*,6*Z*-dienes **4** as a result of deuterolysis of the reaction mixtures unambiguously indicates the presence in the starting organomagnesium compound (OMC) **2** of two Mg—C bonds. The *cis*-configuration of substituents at the double bonds in the 1,5-dienes obtained can be suggested from the presence of the upfield signals for the internal allylic carbon

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atoms δ(C(4)) = δ(C(5)) ≈ 27 in the ^{13}C NMR spectrum, indicating the presence of the *cis*-interactions with atoms C(1) and C(8).[11]

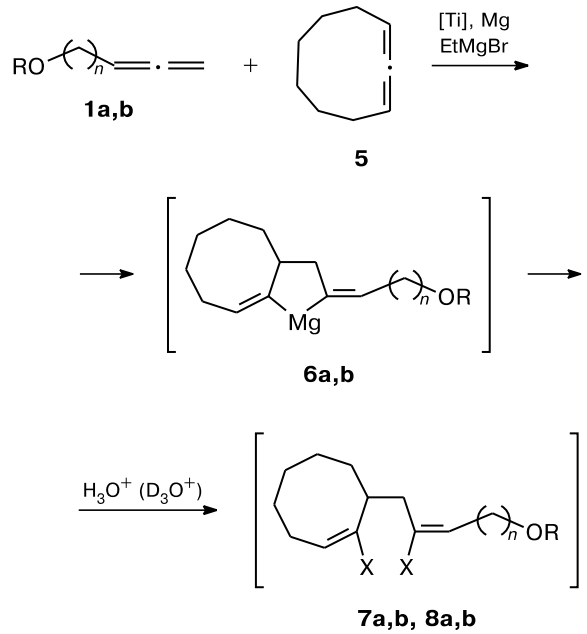
The vicinal spin-spin coupling constants of the protons at C(3) and C(6) (d, ^3J = 11 Hz; t, ^3J = 7 Hz) for the hydrolysis products **3** confirm the *cis*-arrangement of the hydrogen atoms at the double bonds.[12]

The use of other Grignard reagents instead of EtMgBr, for example, EtMgCl, Pr^{i}MgBr, BuMgBr obtained in diethyl ether, did not influence the yields and selectivity of the formation of the target OMC **2**.

These facts allowed us to suggest a possibility to synthesize unsymmetric functionally substituted magnesacyclopentanes by the cross-cyclomagnesiation of structurally different 1,2-dienes. It is necessary to note that such an approach have been earlier successfully used in the coreaction of cyclonona-1,2-diene and terminal 1,2-dienes with the formation of bicyclic OMC in up to 85% yields.[3]

In fact, the reaction of an equimolar mixture of cyclonona-1,2-diene (**5**) and 2-(penta-3,4-dien-1-yloxy)tetrahydropyran (**1a**) with EtMgBr in the presence of Mg and Cp_2TiCl_2 predominantly led to the formation of bicyclic OMC **6a**, which after hydrolysis and deuterolysis was converted to the corresponding cyclononene derivatives **7a**, **8a** in 54% yield (Scheme 2).

Scheme 2



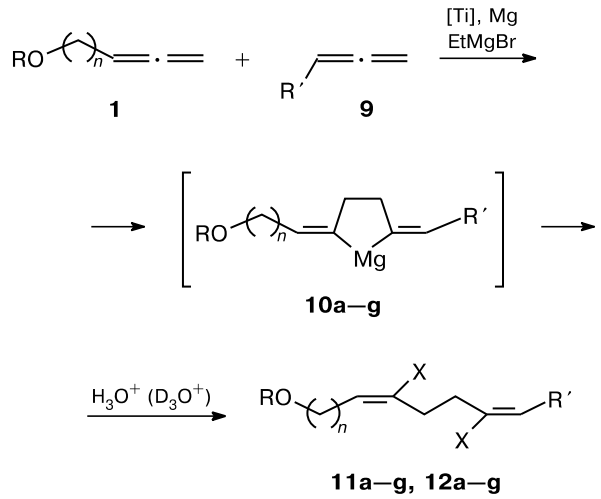
[Ti] = Cp_2TiCl_2
n = 2: R = THP (**a**), Bn (**b**)

These conditions, besides the target OMC **6a**, also gave the product of homocyclomagnesiation of cyclononadiene[3] and O-containing allene **1a** in ~20—25% yield.

The optimization of conditions for the synthesis of the target OMC **6a** by the change in the ratio of the reaction components allowed us to select such conditions (**1** : **5** : EtMgBr : Mg : [Ti] = 10 : 15 : 30 : 32 : 1; Et_2O, 6 h, 20—22 °C), in which OMC **6a** and **6b** were formed in 80 and 87% yields, respectively, with the yields of homocyclomagnesiation products totaling lower than 5—10%.

Similar investigations directed on the optimization of conditions for the cross-cyclomagnesiation of O-containing 1,2-dienes with terminal alkyl- and aryl-substituted allenes **9** in the presence of EtMgBr and Cp_2TiCl_2 (**1** : **9** : EtMgBr : Mg : [Ti] = 10 : 12 : 40 : 32 : 0.5; Et_2O, 6 h, 20—22 °C) led to the exclusive preparation of unsymmetric OMC **10** in >80% yields (Scheme 3).

Scheme 3



[Ti] = Cp_2TiCl_2
X = H (**11**), D (**12**)

	n	R	R′		*n*	R	R′
a	2	THP	C_6H_{13}	**e**	4	THP	Bu
b	2	Bn	C_6H_{13}	**f**	4	THP	C_6H_{13}
c	2	THP	Bn	**g**	6	THP	Bu
d	3	THP	$C_{12}H_{25}$				

In this case, the absence of side products of homocyclomagnesiation of aliphatic 1,2-dienes **9** was explained by the running the reaction in diethyl ether, in which, as it has been shown earlier,[2,13] no formation of 2,5-dialkylidenemagnesacyclopentanes took place.

A small excess of aliphatic 1,2-diene **9** virtually completely blocked the formation of OMC **2**, whose yields under the reaction conditions were ~2—5%.

The same pattern was observed for the cases when both the length of the alkyl substituent in the aliphatic allenes **9** and the number of the methylene units between the 1,2-diene system and the oxygen atom in the O-containing 1,2-diene **1**, were increased.

The studies performed resulted in obtaining a large series of OMC **10**, which were of interest as the starting reagents for the poorly available unsymmetric functionally substituted 1*Z*,5*Z*-dienes of a required structure.

For example, 1*Z*,5*Z*-diene **11g**, formed in 94% yield after hydrolysis of OMC **10**, is an intermediate product in the synthesis of practically important pheromone of cotton pink boll worm *Pectinophora gossypiella*, which has been obtained earlier[14] in seven steps in ~5% yield.

In conclusion, an intermolecular homocyclomagnesiation of O-containing 1,2-dienes and cross-cyclomagnesiation of O-containing allenes with aliphatic 1,2-dienes of cyclic and acyclic structure were accomplished for the first time using Grignard reagents upon the action of Cp_2TiCl_2 to furnish functionally substituted mono- and bicyclic organomagnesium compounds, possessing wide synthetic potential in the synthesis of practically important functionally substituted 1*Z*,5*Z*-dienes of a desired structure.

Experimental

Chromatographic analysis was performed on a Shimadzu GC-9A instrument, using a 2000×2-mm column with Silicon SE-30 (5%) on Chromaton N-AW-HMDS (0.125—0.160 mm) as a stationary phase, carrier gas helium (30 mL min^{-1}), the temperature was programmed from 50 to 300 °C at the speed 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 $CDCl_3$, chemical shifts were measured relative to Me_4Si. Chromato-mass spectrometric analysis of compounds was performed on a Shimadzu GCMS-QP2010 Plus instrument (SLB-5ms 60000×0.25 mm×0.25 μm glass capillary column (Supelco, USA), carrier gas helium, the temperature was programmed from 40 to 280 °C at the speed of 5 °C min^{-1}, the temperature of injector 280 °C, the temperature of the source of ions 200 °C, 70 eV). Mass spectra were recorded on a MALDI TOF/TOF Autoflex-III Bruker instrument with the matrix of 2,5-dihydroxybenzoic acids (2,5-DHB) and α-cyano-4-hydroxycinnamic acids (HCCA) in the reflective mode with recording positive ions. Elemental analysis was performed on Karlo Erba 1106 elemental analyzer. The product yields were determined using GLC analysis. Purity of the reaction products was monitored on Silufol UV-254 plates, visualizing in the iodine vapors. Reactions with organometallic compounds were performed under dry argon. Solvents were dried and distilled before use. The compound Cp_2TiCl_2 was commercially available from Aldrich. Ether solvents were distilled over $LiAlH_4$ directly before use. Solutions of RMgX in Et_2O were obtained as described earlier.[15] Penta-3,4-dien-1-ol was synthesized according to the known procedure.[16] Hexa-4,5-dien-1-ol, hepta-5,6-dien-1-ol, and nona-7,8-dien-1-ol were obtained according to a modified procedure[17] and identified by comparison with the known literature data.[18,19] Allene alcohols were protected by transformation to the corresponding ethers as described earlier.[20]

Oxygen-containing allenes (general procedure). Alkynol (2-propyn-1-ol, 3-butyn-1-ol, 4-pentyn-1-ol, 5-hexyn-1-ol, 7-octyn-1-ol) (20 mmol), dioxane (100 mL), paraformaldehyde (50 mmol), dicyclohexylamine (38 mmol) were placed in a 250-mL glass reactor equipped with a reflux condenser with stirring under dry argon at ~20 °C, followed by the addition of CuI (10 mmol). The reaction mixture was refluxed with stirring for 8 h, then cooled to 20—22 °C and filtered. The filtrate was concentrated *in vacuo*, the residue was washed with 5% solution of HCl in H_2O. The reaction products were extracted with diethyl ether, the extract was dried with $MgSO_4$, the solvent was evaporated, the residue was subjected to chromatography on a column (SiO_2, eluent light petroleum—EtOAc (10 : 1)). The yields of O-containing allenes **1** were 70—75%.

Homocyclomagnesiation of O-containing 1,2-dienes (1a—d) using RMgX (R = Et, Pr^i, Bu; X = Cl, Br) in the presence of metallic Mg and a Cp_2TiCl_2 catalyst. Diethyl ether (10 mL), 1,2-diene (10 mmol), RMgX (20 mmol, 1.5 *M* solution in Et_2O), Mg powder (24 mmol), and Cp_2TiCl_2 (0.5 mmol) were placed in a glass reactor with stirring under dry argon (~0 °C). The temperature of the reaction mixture was increased to 20—22 °C and stirring was continued for 6—8 h. To identify the substituted magnesacyclopentanes by their hydrolysis or deuterolysis products, the reaction mixture were treated with 5% solution of HCl (DCl) in H_2O (D_2O). The reaction products were extracted with diethyl ether, the extracts were dried with $MgSO_4$, the solvent was evaporated, the residue was subjected to chromatography on a column (SiO_2, eluent light petroleum—EtOAc (50 : 1)).

2,2´-[Deca-3*Z*,7*Z*-dien-1,10-diylbis(oxy)]bistetrahydro-2*H*-pyran (3a). The yield was 69%, n_D^{20} 1.4969, R_f = 0.61. Found (%): C, 70.05; H, 9.96. Calculated (%): C, 70.97; H, 10.12. MS MALDI TOF: found *m/z* 338.5. $C_{20}H_{34}O_4$. Calculated: *M* = 338.5. IR, ν/cm^{-1}: 648, 733, 909, 981, 1030, 1076, 1136, 1323, 1440, 2247, 2871, 2945. ^1H NMR, δ: 1.48—1.84 (m, 12 H, 6 CH_2); 2.10—2.11 (m, 4 H, 2 C<u>H</u>$_2$CH=C); 2.30—2.40 (m, 4 H, 2 C<u>H</u>$_2$CH=C); 3.38—3.87 (m, 8 H, 2 CH_2—O); 4.58 (t, 2 H, 2 O—CH—O, *J* = 3.6 Hz); 5.36—5.55 (m, 4 H, 4 HC=). ^{13}C NMR, δ: 19.54 (C(13), C(18)); 25.46 (C(14), C(19)); 27.32 (C(5), C(6)); 27.97 (C(2), C(9)); 30.68 (C(12), C(17)); 62.20 (C(15), C(20)); 67.00 (C(1), C(10)); 98.66 (C(11), C(16)); 126.08 (C(3), C(8)); 131.05 (C(4), C(7)).

2,2´-[4,7-Dideuterodeca-3*Z*,7*Z*-dien-1,10-diylbis(oxy)]-bistetrahydro-2*H*-pyran (4a). The yield was 68%, R_f = 0.61. Found (%): C, 70.01; H + D, 10.49. $C_{20}H_{32}D_2O_4$. Calculated (%): C, 70.55; H, 9.47; D, 1.18. MS (EI), *m/z*: 340 $[M]^+$. IR, ν/cm^{-1}: 649, 733, 908, 981, 1030, 1075, 1136, 1323, 1441, 2175 (C—D), 2247, 2870, 2945. ^1H NMR, δ: 1.50—1.88 (m, 12 H, 6 CH_2); 2.03—2.19 (m, 4 H, 2 C<u>H</u>$_2$CH=C); 2.25—2.36 (m, 4 H, 2 C<u>H</u>$_2$CH=C); 3.36—3.88 (m, 8 H, 4 CH_2—O); 4.58 (t, 2 H, 2 O—CH—O, *J* = 3.6 Hz); 5.40 (t, 2 H, 2 <u>H</u>C=CD, *J* = 6.8 Hz). ^{13}C NMR, δ: 19.56 (C(13), C(18)); 25.47 (C(14), C(19)); 27.21 (C(5), C(6)); 27.95 (C(2), C(9)), 30.69 (C(12), C(17)), 62.21 (C(15), C(20)), 67.01 (C(1), C(10)), 98.68 (C(11), C(16)), 125.95 (C(3), C(8)), 130.71 (t, C(4), C(7), $J_{C,D}$ = 24 Hz).

1,1´-[Deca-3*Z*,7*Z*-dien-1,10-diylbis(oxymethylene)]dibenzene (3b). The yield was 71%, n_D^{20} 1.5458, R_f = 0.59. Found (%): C, 81.95; H, 8.34. Calculated (%): C, 82.24; H, 8.63. MS MALDI TOF: found *m/z* 350.5. $C_{24}H_{30}O_2$. Calculated: *M* = 350.5. IR, ν/cm^{-1}: 697, 735, 1028, 1101, 1204, 1361, 1453, 1495, 2854, 2929, 3028. ^1H NMR, δ: 2.21—2.29 (m, 4 H, 2 C<u>H</u>$_2$CH=C); 2.42—2.49 (m, 4 H, 2 C<u>H</u>$_2$CH=C); 3.56 (t, 4 H, 2 CH_2—O, *J* = 6.8 Hz); 4.60 (s, 4 H, 2 C<u>H</u>$_2$Ph); 5.51—5.60 (m, 4 H, 4 HC=); 7.36—7.43 (m, 10 H, 2 Ph). ^{13}C NMR, δ: 27.46 (C(5), C(6)); 28.13 (C(2), C(9); 70.06 (C(1),C(10)); 72.94 (C(11), C(18));

126.19 (C(15), C(22)); 127.43 (C(14), C(16), C(21), C(23)); 127.58 (C(3), C(8)); 128.43 (C(13), C(17), C(20), C(24)); 131.19 (C(4), C(7)); 138.64 (C(19)).

1,1´-[4,7-Dideuterodeca-3*Z*,7*Z*-dien-1,10-diylbis(oxymethylene)]dibenzene (4b). The yield was 73%, $R_f = 0.59$. Found (%): C, 81.58; H + D, 9.02. $C_{24}H_{28}D_2O_2$. Calculated (%): C, 81.77; H, 8.01; D, 1.14. MS (EI), *m/z*: 352 $[M]^+$. IR, ν/cm^{-1}: 697, 735, 1028, 1101, 1205, 1361, 1453, 1495, 2180 (C—D), 2856, 2929, 3027. ^{1}H NMR, δ: 2.21—2.31 (m, 4 H, 2 C$\underline{H}_2$CH=C); 2.42—2.47 (m, 4 H, 2 C$\underline{H}_2$CH=C); 3.58 (t, 4 H, 2 CH_2—O, J = 6.8 Hz); 4.61 (s, 4 H, 2 C$\underline{H}_2$Ph); 5.45 (t, 2 H, 2 $\underline{H}$C=CD, J = 6.8 Hz); 7.34—7.45 (m, 10 H, 2 Ph). ^{13}C NMR, δ: 27.48 (C(5), C(6)); 28.15 (C(2), C(9)); 70.04 (C(1), C(10)); 72.96 (C(11), C(18)); 126.20 (C(15), C(22)); 127.45 (C(14), C(16), C(21), C(23)); 127.59 (C(3), C(8)); 128.42 (C(13), C(17), C(20), C(24)); 130.91 (t, C(4), C(7), $J_{C,D}$ = 22.5 Hz); 138.62 (C(19)).

2,2´-[Tetradeca-5*Z*,9*Z*-dien-1,14-diylbis(oxy)]bistetrahydro-2*H*-pyran (3c). The yield was 78%, n_D^{20} 1.4969, R_f = 0.56. Found (%): C, 72.91; H, 10.15. Calculated (%): C, 73.05; H, 10.73. MS MALDI TOF: found *m/z* 394.6. $C_{24}H_{42}O_4$. Calculated: M = 394.6. IR, ν/cm^{-1}: 647, 733, 908, 981, 1030, 1078, 1136, 1323, 1440, 2245, 2871, 2948. ^{1}H NMR, δ: 1.34—1.81 (m, 20 H, 10 CH_2); 1.99—2.11 (m, 8 H, 4 C$\underline{H}_2$CH=C); 3.30—3.84 (m, 8 H, 4 CH_2—O); 4.52 (t, 2 H, 2 O—CH—O, J = 3.6 Hz); 5.29—5.36 (m, 4 H, 4 HC=). ^{13}C NMR, δ: 19.56 (C(17), C(22)); 25.47 (C(18), C(23)); 26.33 (C(3), C(12)); 26.99 (C(7), C(8)); 27.32 (C(4), C(11)); 29.31 (C(2), C(13)); 30.70 (C(16), C(21)); 62.09 (C(19), C(24)); 67.34 (C(1), C(14)); 98.66 (C(15), C(20)); 129.34 (C(6), C(9)); 129.90 (C(5), C(10)).

2,2´-[4,7-Dideuterotetradeca-5*Z*,9*Z*-dien-1,14-diylbis(oxy)]-bistetrahydro-2*H*-pyran (4c). The yield was 77%, R_f = 0.56. Found (%): C, 72.25; H + D, 11.04. $C_{24}H_{40}D_2O_4$. Calculated (%): C, 72. 68; H, 10.17; D, 1.02. MS (EI), *m/z*: 396 $[M]^+$. IR, ν/cm^{-1}: 647, 734, 908, 980, 1030, 1078, 1136, 1323, 1441, 2170 (C—D), 2245, 2871, 2948. ^{1}H NMR, δ: 1.31—1.80 (m, 20 H, 10 CH_2); 1.99—2.12 (m, 8 H, 4 C$\underline{H}_2$CH=C); 3.28—3.80 (m, 8 H, 4 CH_2—O); 4.52 (t, 2 H, 2 O—CH—O, J = 3.6 Hz); 5.33 (t, 2 H, 2 $\underline{H}$C=CD, J = 7 Hz). ^{13}C NMR, δ: 19.54 (C(17), C(22)); 25.49 (C(18), C(23)); 26.30 (C(3), C(12)); 26.01 (C(7), C(8)); 27.30 (C(4), C(11)); 29.30 (C(2), C(13)); 30.72 (C(16), C(21)); 62.09 (C(19), C(24)); 67.36 (C(1), C(14)); 98.65 (C(15), C(20)); 129.05 (t, C(6), C(9), $J_{C,D}$ = 23.5 Hz); 129.91 (C(5), C(10)).

2,2´-[Octadeca-7*Z*,11*Z*-dien-1,18-diylbis(oxy)]bistetrahydro-2*H*-pyran (3d). The yield was 84%, n_D^{20} 1.4949, R_f = 0.53. Found (%): C, 74.28; H, 11.02. Calculated (%): C, 74.62; H, 11.18. MS MALDI TOF: found *m/z* 450.7. $C_{28}H_{50}O_4$. Calculated: M = 450.7. IR, ν/cm^{-1}: 815, 844, 869, 905, 968, 1034, 1077, 1122, 1136, 1183, 1200, 1259, 1275, 1283, 1322, 1352, 1384, 1440, 1464, 2855, 2937, 3005. ^{1}H NMR, δ: 1.25—1.31 (m, 4 H, 2 CH_2); 1.48—1.58 (m, 12 H, 6 CH_2); 1.64—1.84 (m, 12 H, 6 CH_2); 1.98—2.04 (m, 8 H, 4 C$\underline{H}_2$CH=C); 3.31—3.76 (m, 8 H, 4 CH_2—O); 4.55 (t, 2 H, 2 O—CH—O, J = 4 Hz); 5.29—5.38 (m, 4 H, 4 HC=). ^{13}C NMR, δ: 19.63 (C(21), C(26)); 25.53 (C(22), C(27)); 26.17 (C(3), C(16)); 27.15 (C(6), C(13)); 27.37 (C(9), C(10)); 29.16 (C(4), C(15)); 29.72 (C(2), C(17)); 30.60 (C(20), C(25)); 30.70 (C(5), C(14)); 62.19 (C(23), C(28)); 67.55 (C(1), C(18)); 98.73 (C(19), C(24)); 129.15 (C(8), C(11)); 130.17 (C(7), C(12)).

2,2´-[4,7-Dideuterooctadeca-7*Z*,11*Z*-dien-1,18-diylbis(oxy)]-bistetrahydro-2*H*-pyran (4d). The yield was 82%, R_f = 0.53. Found (%): C, 74.08; H + D, 11.14. $C_{28}H_{48}D_2O_4$. Calculated (%): C, 74.29; H, 10.69; D, 0.89. MS (EI), *m/z*: 452 $[M]^+$. IR, ν/cm^{-1}: 815, 844, 869, 905, 969, 1034, 1077, 1122, 1136, 1182, 1200, 1259, 1275, 1283, 1322, 1352, 1384, 1440, 1464, 2175 (C—D), 2855, 2936, 3005. ^{1}H NMR, δ: 1.24—1.32 (m, 4 H, 2 CH_2); 1.48—1.56 (m, 12 H, 6 CH_2); 1.62—1.84 (m, 12 H, 6 CH_2); 1.98—2.02 (m, 8 H, 4 C$\underline{H}_2$CH=C); 3.30—3.78 (m, 8 H, 4 CH_2—O); 4.57 (t, 2 H, 2 O—CH—O, J = 4 Hz); 5.35 (t, 2 H, 2 $\underline{H}$C=CD, J = 7 Hz). ^{13}C NMR, δ: 19.60 (C(21), C(26)); 25.54 (C(22), C(27)); 26.18 (C(3), C(16)); 27.15 (C(6), C(13)); 27.35 (C(9), C(10)); 29.18 (C(4), C(15)); 29.72 (C(2), C(17)); 30.62 (C(20), C(25)); 30.71 (C(5), C(14)); 62.18 (C(23), C(28)); 67.57 (C(1), C(18)); 98.75 (C(19), C(24)); 128.87 (t, C(8), C(11), $J_{C,D}$ = 23.5 Hz); 130.14 (C(7), C(12)).

Cross-cyclomagnesiation of O-containing 1,2-dienes with cyclonona-1,2-diene using EtMgBr in the presence of metallic Mg and a Cp_2TiCl_2 catalyst (general procedure). Diethyl ether (10 mL), O-containing 1,2-diene (10 mmol), cyclonona-1,2-diene (15 mmol), EtMgBr (30 mmol, 1.5 M solution in Et_2O), Mg powder (32 mmol), and Cp_2TiCl_2 (1 mmol) were placed in a glass reactor with stirring under dry argon (~0 °C). The temperature of the reaction mixture was increased to 20—22 °C and stirring was continued for 6—8 h. To identify the substituted unsymmetric magnesacyclopentanes by their hydrolysis or deuterolysis products, the reaction mixtures were treated with 5% solution of HCl (DCl) in H_2O (D_2O). The reaction products were extracted with diethyl ether, the extracts were dried with $MgSO_4$, the solvent was evaporated, the residue was subjected to chromatography on a column (SiO_2, eluent light petroleum—EtOAc (50 : 1)).

Cross-cyclomagnesiation of O-containing 1,2-dienes with terminal 1,2-dienes using EtMgBr in the presence of metallic Mg and a Cp_2TiCl_2 catalyst (general procedure). Diethyl ether (10 mL), O-containing 1,2-diene (10 mmol), cyclonona-1,2-diene or the corresponding aliphatic 1,2-diene (12 mmol), EtMgBr (40 mmol, 1.5 M solution in Et_2O), Mg powder (32 mmol), and Cp_2TiCl_2 (0.5 mmol) were placed in a glass reactor with stirring under dry argon (~0 °C). The temperature of the reaction mixture was increased to 20—22 °C and stirring was continued for 6—8 h. To identify the substituted unsymmetric magnesacyclopentanes by their hydrolysis or deuterolysis products, the reaction mixture were treated with 5% solution of HCl (DCl) in H_2O (D_2O). The reaction products were extracted with diethyl ether, the extracts were dried with $MgSO_4$, the solvent was evaporated, the residue was subjected to chromatography on a column (SiO_2, eluent light petroleum—EtOAc (50 : 1)).

2-[(5-Cyclonon-2-en-1-ylpent-3*Z*-en-1-yl)oxy]tetrahydro-2*H*-pyran (7a). The yield was 81%, n_D^{20} 1.4921, R_f = 0.49. Found (%): C, 77.93; H, 10.92. Calculated (%): C, 78.03; H, 11.03. MS MALDI TOF: found *m/z* 292.5. $C_{19}H_{32}O_2$. Calculated: M = 292.5. IR, ν/cm^{-1}: 740, 871, 905, 981, 1030, 1073, 1125, 1201, 1351, 1448, 2864, 2929, 3001. ^{1}H NMR, δ: 1.19—1.72 (m, 16 H, 8 CH_2); 2.00—2.20 (m, 4 H, 2 C$\underline{H}_2$CH=); 2.47—2.57 (m, 1 H, C$\underline{H}$CH$_2$); 2.94—3.03 (m, 2 H, C$\underline{H}_2$CH=); 3.33—3.87 (m, 4 H, 2 CH_2—O); 4.57 (t, 1 H, O—CH—O, J = 3.6 Hz); 5.02—5.14 (m, 1 H, CH=); 5.33—5.54 (m, 3 H, 3 CH=). ^{13}C NMR, δ: 19.52 (C(17)); 24.53 (C(10)); 25.48 (C(18)); 25.97 (C(11)); 26.02 (C(9)); 26.48 (C(13)); 26.77 (C(12)); 28.13 (C(2)); 30.73 (C(16)); 33.50 (C(5)); 34.84 (C(14)); 37.14 (C(6)); 62.09 (C(19)); 66.97 (C(1)); 98.59 (C(15)); 126.17 (C(3)); 129.45 (C(8)); 130.29 (C(4)); 134.90 (C(7)).

2-{4-Deutero-[5-(2-deuterocyclonon-2-en-1-yl)pent-3*Z*-en-1-yl]oxy}tetrahydro-*2H*-pyran (8a). The yield was 80%, R_f = 0.49.

Found (%): C, 77.23; H + D, 11.45. $C_{19}H_{30}D_2O_2$. Calculated (%): C, 77.50; H, 10.27; D, 1.37. MS (EI), *m/z*: 294 $[M]^+$. IR, ν/cm^{-1}: 740, 870, 905, 981, 1030, 1073, 1124, 1201, 1352, 1448, 2175 (C—D), 2864, 2929, 3002. ^{1}H NMR, δ: 1.18—1.70 (m, 16 H, 8 CH_2); 1.98—2.22 (m, 4 H, 2 C$\underline{H}_2$CH=); 2.47—2.56 (m, 1 H, C$\underline{H}$CH$_2$); 2.92—3.02 (m, 2 H, C$\underline{H}_2$CH=); 3.30—3.88 (m, 4 H, 2 CH_2—O); 4.58 (t, 1 H, O—CH—O, J = 3.6 Hz); 5.08 (t, 1 H, C$\underline{H}$=CD, J = 7 Hz); 5.42 (t, 1 H, C$\underline{H}$=CD, J = 6.8 Hz). ^{13}C NMR, δ: 19.53 (C(17)); 24.52 (C(10)); 25.47 (C(18)); 25.97 (C(11)); 26.04 (C(9)); 26.48 (C(13)); 26.78 (C(12)); 28.13 (C(2)); 30.75 (C(16)); 33.51 (C(5)); 34.84 (C(14)); 37.16 (C(6)); 62.08 (C(19)); 66.98 (C(1)); 98.57 (C(15)); 126.16 (C(3)); 129.48 (C(8)); 129.99 (t, C(4), $J_{C,D}$ = 23.5 Hz); 134.58 (t, C(7), $J_{C,D}$ = 23.0 Hz).

3-[5-(Benzyloxy)pent-2*Z*-en-1-yl]cyclononene (7b). The yield was 85%, n_D^{20} 1.5141, R_f = 0.47. Found (%): C, 84.26; H, 10.05. $C_{21}H_{30}O$. Calculated (%): C, 84.51; H, 10.13. MS, *m/z* (I_{rel} (%)): 298 $[M]^+$ (1), 81 (100), 67 (39), 105 (31), 55 (26), 77 (22), 69 (18), 91 (17), 82 (15), 123 (14), 53 (11), 39 (10). IR, ν/cm^{-1}: 697, 736, 1028, 1101, 1361, 1495, 2855, 2926, 3003. ^{1}H NMR, δ: 1.52 (m, 2 H, CH_2); 1.67—1.79 (m, 8 H, 4 CH_2); 2.12—2.29 (m, 2 H, CH_2); 2.44—2.49 (m, 2 H, CH_2); 2.61 (m, 1 H, C$\underline{H}$—CH_2); 3.57 (t, 2 H, CH_2—O, J = 7.2 Hz); 4.59 (s, 2 H, O—C$\underline{H}_2$—Ph); 5.22—5.25 (m, 1 H, CH=); 5.48—5.55 (m, 2 H, 2 CH=); 5.59—5.63 (m, 1 H, =CH); 7.34—7.41 (m, 5 H, Ph). ^{13}C NMR, δ: 24.64 (C(1)); 26.09 (C(10)); 26.14 (C(11)); 26.62 (C(12)); 26.87 (C(5)); 28.27 (C(2)); 33.63 (C(9)); 34.96 (C(14)); 37.26 (C(6)); 70.04 (C(1)); 72.92 (C(15)); 126.20 (C(19)); 127.54 (C(18), C(20)); 127.65 (C(17), C(21)); 128.39 (C(8)); 129.63 (C(4)); 130.51 (C(3)); 135.00 (C(7)); 138.63 (C(16)).

2-Deutero-3-[5-(benzyloxy)-2-deuteropent-2*Z*-en-1-yl]-cyclononene (8b). The yield was 87%, R_f = 0.47. Found (%): C, 83.76; H + D, 10.52. $C_{21}H_{28}D_2O$. Calculated (%): C, 83.94; H, 9.39; D, 1.34. MS (EI), *m/z*: 300 $[M]^+$. IR, ν/cm^{-1}: 697, 735, 1028, 1101, 1361, 1496, 2180 (C—D), 2855, 2926, 3004. ^{1}H NMR, δ: 1.49—1.57 (m, 2 H, CH_2); 1.66—1.77 (m, 8 H, 4 CH_2); 2.12—2.26 (m, 2 H, CH_2); 2.44—2.46 (m, 2 H, CH_2); 2.63 (m, 1 H, C$\underline{H}$—CH_2); 3.58 (t, 2 H, CH_2—O, J = 7.2 Hz); 4.58 (s, 2 H, O—C$\underline{H}_2$—Ph); 5.23 (t, 1 H, $\underline{H}$C=CD, J = 7 Hz); 5.52 (t, 1 H, $\underline{H}$C=CD, J = 7 Hz); 7.32—7.40 (m, 5 H, Ph). ^{13}C NMR, δ: 24.63 (C(1)); 26.08 (C(10)); 26.14 (C(11)); 26.64 (C(12)); 26.88 (C(5)); 28.27 (C(2)); 33.62 (C(9)); 34.96 (C(14)); 37.27 (C(6)); 70.04 (C(1)); 72.93 (C(15)); 126.22 (C(19)); 127.55 (C(18), C(20)); 127.65 (C(17), C(21)); 128.36 (C(8)); 129.31 (t, C(4), $J_{C,D}$ = 23.5 Hz); 130.52 (C(3)); 134.79 (t, C(7), $J_{C,D}$ = = 23.5 Hz); 138.62 (C(16)).

2-(Tetradeca-3*Z*,7*Z*-dien-1-yloxy)tetrahydro-2*H*-pyran (11a). The yield was 81%, n_D^{20} 1.4695, R_f = 0.45. Found (%): C, 77.36; H, 11.22. $C_{19}H_{34}O_2$. Calculated (%): C, 77.50; H, 11.64. MS, *m/z* (I_{rel} (%)): 294 $[M]^+$ (2), 85 (100), 55 (48), 105 (46), 43 (41), 57 (35), 41 (30), 207 (27), 101 (25), 131 (24), 69 (23), 77 (21), 167 (18), 73 (15), 129 (14), 70 (12). IR, ν/cm^{-1}: 814, 869, 905, 985, 1033, 1137, 1200, 1260, 1364, 1380, 1455, 1730, 2856, 2927, 3007. ^{1}H NMR, δ: 0.89 (t, 3 H, Me, J = 6.4 Hz); 1.27—1.30 (m, 8 H, 4 CH_2); 1.49—1.86 (m, 6 H, 3 CH_2); 1.94—2.13 (m, 8 H, 4 C$\underline{H}_2$CH=); 3.38—3.87 (m, 8 H, 4 CH_2—O); 4.59 (t, 1 H, O—CH—O, J = 3.6 Hz); 5.35—5.46 (m, 4 H, 4 HC=). ^{13}C NMR, δ: 14.06 (C(14)); 19.54 (C(17)); 22.63 (C(13)); 25.49 (C(18)); 27.25 (C(5), C(6)); 27.48 (C(2)); 27.98 (C(9)); 28.97 (C(10)); 29.68 (C(11)); 30.69 (C(16)); 31.77 (C(12)); 62.15 (C(19)); 67.02 (C(1)); 98.64 (C(15)); 125.97 (C(3)); 128.94 (C(7)); 130.41 (C(4)); 131.20 (C(8)).

2-(4,7-Dideuterotetradeca-3*Z*,7*Z*-dien-1-yloxy)tetrahydro-2*H*-pyran (12a). The yield was 81%, R_f = 0.45. Found (%): C, 76.77; H + D, 12.08. $C_{19}H_{32}D_2O_2$. Calculated (%): C, 76.97; H, 10.88; D, 1.36. MS (EI), *m/z*: 296 $[M]^+$. IR, ν/cm^{-1}: 815, 869, 905, 985, 1033, 1136, 1200, 1260, 1365, 1380, 1455, 1730, 2165 (C—D), 2856, 2927, 3006. ^{1}H NMR, δ: 0.90 (t, 3 H, Me, J = 6.8 Hz); 1.26—1.32 (m, 8 H, 4 CH_2); 1.49—1.84 (m, 6 H, 3 CH_2); 1.94—2.12 (m, 8 H, 4 C$\underline{H}_2$CH=); 3.36—3.86 (m, 8 H, 4 CH_2—O); 4.58 (t, 1 H, O—CH—O, J = 3.6 Hz); 5.39 (t, 1 H, $\underline{H}$C=CD, J = 7 Hz); 5.41 (t, 1 H, $\underline{H}$C=CD, J = 7 Hz). ^{13}C NMR, δ: 14.05 (C(14)); 19.54 (C(17)); 22.64 (C(13)); 25.49 (C(18)); 27.28 (C(5), C(6)); 27.46 (C(2)); 27.98 (C(9)); 28.95 (C(10)); 29.68 (C(11)); 30.68 (C(16)); 31.78 (C(12)); 62.13 (C(19)); 67.01 (C(1)); 98.64 (C(15)); 125.98 (C(3)); 128.64 (t, C(7), $J_{C,D}$ = = 23.5 Hz); 130.34 (t, C(4), $J_{C,D}$ = 23.0 Hz); 131.21 (C(8)).

[(Tetradeca-3*Z*,7*Z*-dien-1-yloxy)methyl]benzene (11b). The yield was 88%, n_D^{20} 1.5102, R_f = 0.46. Found (%): C, 83.72; H, 10.51. $C_{21}H_{32}O$. Calculated (%): C, 83.94; H, 10.73. MS, *m/z* (I_{rel} (%)): 300 $[M]^+$ (2), 105 (100), 123 (83), 77 (44), 70 (21), 122 (20), 55 (13), 51 (11), 106 (10). IR, ν/cm^{-1}: 697, 735, 1028, 1101, 1361, 1495, 2855, 2926, 3007. ^{1}H NMR, δ: 0.95 (t, 3 H, Me, J = 8 Hz); 1.21—1.50 (m, 8 H, 4 CH_2); 2.11—2.47 (m, 8 H, 4 C$\underline{H}_2$CH=C); 3.56 (t, 2 H, CH_2—O, J = 8 Hz); 4.60 (s, 2 H, C$\underline{H}_2$—Ph); 5.45—5.55 (m, 4 H, 4 HC=); 7.28—7.42 (m, 5 H, Ph). ^{13}C NMR, δ: 14.11 (C(14)); 22.74 (C(13)); 27.34 (C(5), C(6)); 27.59 (C(9)); 28.09 (C(2)); 29.07 (C(10)); 29.78 (C(11)); 31.87 (C(12)); 70.06 (C(1)); 72.92 (C(15)); 125.98 (C(19)); 127.53 (C(3)); 127.68 (C(17), C(21)); 128.38 (C(18), C(20)); 129.01 (C(7)); 130.54 (C(4)); 131.35 (C(8)); 138.61 (C(16)).

[(4,7-Dideuterotetradeca-3*Z*,7*Z*-dien-1-yloxy)methyl]benzene (12b). The yield was 87%, R_f = 0.46. Found (%): C, 83.15; H + D, 11.12. $C_{12}H_{30}D_2O$. Calculated (%): C, 83.38; H, 10.00; D, 1.33. MS (EI), *m/z*: 302 $[M]^+$. IR, ν/cm^{-1}: 696, 735, 1028, 1101, 1361, 1495, 2170 (C—D), 2856, 2926, 3007. ^{1}H NMR, δ: 0.94 (t, 3 H, Me, J = 8 Hz); 1.21—1.52 (m, 8 H, 4 CH_2); 2.12—2.46 (m, 8 H, 4 C$\underline{H}_2$CH=C); 3.58 (t, 2 H, CH_2—O, J = 8 Hz); 4.62 (s, 2 H, C$\underline{H}_2$Ph); 5.47 (t, 1 H, $\underline{H}$C=CD, J = 7 Hz); 5.52 (t, 1 H, $\underline{H}$C=CD, J = 7 Hz); 7.28—7.44 (m, 5 H, Ph). ^{13}C NMR, δ: 14.09 (C(14)); 22.72 (C(13)); 27.36 (C(5), C(6)); 27.58 (C(9)); 28.06 (C(2)); 29.07 (C(10)); 29.76 (C(11)); 31.88 (C(12)); 70.04 (C(1)); 72.91 (C(15)); 125.96 (C(19)); 127.52 (C(3)); 127.65 (C(17), C(21)); 128.36 (C(18), C(20)); 128.75 (t, C(7), $J_{C,D}$ = 23.5 Hz); 130.24 (t, C(4), $J_{C,D}$ = 24.0 Hz); 131.3 (C(8)); 138.62 (C(16)).

2-[(9-Phenylnona-3*Z*,7*Z*-dien-1-yl)oxy]tetrahydro-2*H*-pyran (11c). The yield was 84%, n_D^{20} 1.5311, R_f = 0.44. Found (%): C, 79.79; H, 10.43. $C_{20}H_{28}O_2$. Calculated (%): C, 79.96; H, 10.65. MS, *m/z* (I_{rel} (%)): 300 $[M]^+$ (2), 85 (100), 91 (80), 105 (43), 104 (37), 101 (24), 131 (21), 84 (19), 92 (18), 41 (17), 57 (15), 43 (14), 56 (13), 67 (12), 117 (11). IR, ν/cm^{-1}: 699, 747, 812, 869, 905, 983, 1032, 1075, 1120, 1200, 1261, 1352, 1453, 1762, 2870, 2938, 3390. ^{1}H NMR, δ: 1.57—1.91 (m, 6 H, 3 CH_2); 2.24—2.47 (m, 6 H, 3 C$\underline{H}_2$CH=); 3.46 (d, 2 H, C$\underline{H}_2$Ph, J = 6.4 Hz); 3.53—3.96 (m, 4 H, 2 C$\underline{H}_2$—O); 4.67 (t, 1 H, O—CH—O, J = 3.6 Hz); 5.50—5.72 (m, 4 H, 4 HC=); 7.24—7.35 (m, 5 H, Ph). ^{13}C NMR, δ: 19.63 (C(18)); 25.59 (C(19)); 27.40, 27.48 (C(5), C(6)); 28.07 (C(2)); 30.78 (C(17)); 33.61 (C(9)); 62.17 (C(20)); 67.06 (C(1)); 98.70 (C(16)); 125.92 (C(13)); 126.13 (C(3)); 128.38 (C(12), C(14)); 128.43 (C(11), C(15)); 128.62 (C(8)); 130.14 (C(7)); 131.02 (C(4)); 141.08 (C(10)).

2-[(3,6-Dideutero-9-phenylnona-3*Z*,7*Z*-dien-1-yl)oxy]tetrahydro-2*H*-pyran (12c). The yield was 83%, R_f = 0.44. Found (%): C, 79.28; H + D, 9.63. $C_{20}H_{26}D_2O_2$. Calculated (%): C, 79.42; H, 8.66; D, 1.33. MS (EI), *m/z*: 302 $[M]^+$. IR, ν/cm^{-1}: 698, 747, 812, 869, 906, 983, 1032, 1074, 1120, 1200, 1261, 1352, 1452, 1762, 2175 (C—D), 2870, 2939, 3390. ^{1}H NMR, δ: 1.56—1.90 (m, 6 H, 3 CH_2); 2.24—2.48 (m, 6 H, 3 C<u>H</u>$_2$CH=); 3.45 (d, 2 H, C<u>H</u>$_2$Ph, *J* = 6.4 Hz); 3.52—3.96 (m, 4 H, 2 CH_2—O); 4.68 (t, 1 H, O—CH—O, *J* = 3.6 Hz); 5.50—5.72 (m, 2 H, 2 <u>H</u>C=CD); 7.26—7.34 (m, 5 H, Ph). ^{13}C NMR, δ: 19.62 (C(18)); 25.59 (C(19)); 27.41, 27.47 (C(5), C(6)); 28.08 (C(2)); 30.76 (C(17)); 33.61 (C(9)); 62.18 (C(20)); 67.06 (C(1)); 98.72 (C(16)); 125.90 (C(13)); 126.15 (C(3)); 128.37 (C(12), C(14)); 128.43 (C(11), C(15)); 128.60 (C(8)); 129.87 (t, C(7), $J_{C,D}$ = 24.5 Hz); 130.72 (t, C(4), $J_{C,D}$ = 24 Hz); 141.08 (C(10)).

2-(Eucosa-4*Z*,8*Z*-dien-1-yloxy)tetrahydro-2*H*-pyran (11d). The yield was 87%, n_D^{20} 1.4801, R_f = 0.42. Found (%): C, 79.18; H, 12.69. Calculated (%): C, 79.35; H, 12.82. MS MALDI TOF: found *m/z* 392.6. $C_{26}H_{48}O_2$. Calculated: *M* = 392.6. IR, ν/cm^{-1}: 721, 905, 971, 992, 1034, 1078, 1121, 1137, 1159, 1182, 1200, 1260, 1380, 1401, 1441, 2853, 2924, 3005. ^{1}H NMR, δ: 0.89 (t, 3 H, Me, *J* = 6.7 Hz); 1.19—1.39 (m, 22 H, 11 CH_2); 1.50—1.68 (m, 6 H, 3 CH_2); 2.00—2.15 (m, 8 H, 4 C<u>H</u>$_2$CH=C); 3.38—3.87 (m, 4 H, 2 CH_2—O); 4.58 (t, 1 H, O—CH—O, *J* = 4 Hz); 5.36—5.41 (m, 4 H, 4 HC=). ^{13}C NMR, δ: 14.08 (C(21)); 19.62 (C(24)); 22.69 (C(20)); 23.91 (C(3)); 25.53 (C(25)); 27.26 (C(10)); 27.33 (C(6)); 27.37 (C(7)); 29.37 (C(2)); 29.50, 29.63, 29.74, 29.83 (C(11), C(12), C(13), C(14)); 29.67, 29.70 (2 C, C(15), C(16), C(17), C(18)); 30.76 (C(23)); 31.93 (C(19)); 62.17 (C(26)); 66.93 (C(1)); 98.77 (C(22)); 129.02 (C(9)); 129.42 (C(4)); 129.76 (C(8)); 130.37 (C(5)).

2-(5,8-Dideuteroeucosa-4*Z*,8*Z*-dien-1-yloxy)tetrahydro-2*H*-pyran (12d). The yield was 87%, R_f = 0.42. Found (%): C, 78.74; H + D, 13.09. $C_{26}H_{47}D_2O_2$. Calculated (%): C, 78.96; H, 12.27; D, 0.98. MS (EI), *m/z*: 394 $[M]^+$. IR, ν/cm^{-1}: 721, 905, 970, 992, 1034, 1078, 1121, 1137, 1159, 1181, 1200, 1260, 1380, 1401, 1440, 2160 (C—D), 2853, 2924, 3005. ^{1}H NMR, δ: 0.89 (t, 3 H, Me, *J* = 6.7 Hz); 1.19—1.38 (m, 22 H, 11 CH_2); 1.50—1.68 (m, 6 H, 3 CH_2); 2.00—2.20 (m, 8 H, 4 C<u>H</u>$_2$CH=C); 3.38—3.88 (m, 4 H, 2 CH_2—O); 4.57 (t, 1 H, O—CH—O, *J* = 4 Hz); 5.50—5.58 (m, 2 H, 2 <u>H</u>C=CD). ^{13}C NMR, δ: 14.05 (C(21)); 19.64 (C(24)); 22.68 (C(20)); 23.91 (C(3)); 25.55 (C(25)); 27.26 (C(10)); 27.34 (C(6)); 27.37 (C(7)); 29.38 (C(2)); 29.51, 29.63, 29.75, 29.84 (C(11), C(12), C(13), C(14)); 29.67, 29.71 (2 C, C(15), C(16), C(17), C(18)); 30.78 (C(23)); 31.94 (C(19)); 62.18 (C(26)); 66.94 (C(1)); 98.78 (C(22)); 129.04 (C(9)); 129.41 (C(4)); 129.48 (t, C(8), $J_{C,D}$ = 23.5 Hz); 130.07 (t, C(5), $J_{C,D}$ = 24 Hz).

2-(Tetradeca-5*Z*,9*Z*-dien-1-yloxy)tetrahydro-2*H*-pyran (11e). The yield was 84%, n_D^{20} 1.4814, R_f = 0.39. Found (%): C, 77.39; H, 11.48. Calculated (%): C, 77.50; H, 11.64. MS MALDI TOF: found *m/z* 294.5. $C_{19}H_{34}O_2$. Calculated: *M* = 294.5. IR, ν/cm^{-1}: 814, 869, 905, 970, 992, 1034, 1078, 1121, 1137, 1159, 1182, 1200, 1354, 1380, 1441, 2853, 2924, 3005. ^{1}H NMR, δ: 0.90 (t, 3 H, Me, *J* = 6.8 Hz); 1.27—1.33 (m, 14 H, 7 CH_2); 2.03—2.07 (m, 8 H, 4 C<u>H</u>$_2$CH=); 3.40—3.89 (m, 4 H, 2 CH_2—O); 4.58 (t, 1 H, O—CH—O, *J* = 3.6 Hz); 5.36—5.41 (m, 4 H, 4 HC=). ^{13}C NMR, δ: 13.97 (C(14)); 19.62 (C(17)); 22.32 (C(13)); 25.52 (C(18)); 26.39 (C(3)); 27.00 (C(4)); 27.05 (C(2)); 27.37 (C(7)); 27.42 (C(8)); 29.46 (C(11)); 30.75 (C(12)); 31.92 (C(16)); 62.18 (C(19)); 67.43 (C(1)); 98.75 (C(15)); 129.07 (C(9)); 129.61 (C(6)); 129.82 (C(5)); 129.92 (C(10)).

2-(6,9-Dideuterotetradeca-5*Z*,9*Z*-dien-1-yloxy)tetrahydro-2*H*-pyran (12e). The yield was 84%, R_f = 0.39. Found (%): C, 76.68; H + D, 12.11. $C_{19}H_{32}D_2O_2$. Calculated (%): C, 76.97; H, 10.88; D, 1.36. MS (EI), *m/z*: 296 $[M]^+$. IR, ν/cm^{-1}: 814, 868, 905, 970, 992, 1033, 1078, 1121, 1137, 1159, 1182, 1200, 1354, 1380, 1440, 2165 (C—D), 2853, 2924, 3005. ^{1}H NMR, δ: 0.91 (t, 3 H, Me, *J* = 6.8 Hz); 1.27—1.35 (m, 14 H, 7 CH_2); 2.02—2.08 (m, 8 H, 4 C<u>H</u>$_2$CH=); 3.40—3.87 (m, 4 H, 2 CH_2—O); 4.57 (t, 1 H, O—CH—O, *J* = 3.6 Hz); 5.37 (t, 1 H, <u>H</u>C=CD, *J* = 7 Hz); 5.42 (t, 1 H, <u>H</u>C=CD, *J* = 7 Hz). ^{13}C NMR, δ: 14.01 (C(14)); 19.64 (C(17)); 22.33 (C(13)); 25.54 (C(18)); 26.39 (C(3)); 27.01 (C(4)); 27.05 (C(2)); 27.38 (C(7)); 27.44 (C(8)); 29.46 (C(11)); 30.76 (C(12)); 31.92 (C(16)); 62.16 (C(19)); 67.44 (C(1)); 98.77 (C(15)); 128.84 (t, C(9), $J_{C,D}$ = 24.0 Hz); 129.31 (t, C(6), $J_{C,D}$ = 23.5 Hz); 129.84 (C(5)); 129.90 (C(10)).

2-(Hexadeca-5*Z*,9*Z*-dien-1-yloxy)tetrahydro-2*H*-pyran (11f). The yield was 89%, n_D^{20} 1.4831, R_f = 0.41. Found (%): C, 78.41; H, 11.69. Calculated (%): C, 78.20; H, 11.88. MS MALDI TOF: found *m/z* 322.5. $C_{21}H_{38}O_2$. Calculated: *M* = 322.5. IR, ν/cm^{-1}: 815, 869, 905, 971, 992, 1034, 1078, 1121, 1137, 1159, 1182, 1200, 1353, 1380, 1441, 2853, 2924, 3005. ^{1}H NMR, δ: 0.87 (t, 3 H, Me, *J* = 7.2 Hz); 1.26—1.85 (m, 18 H, 9 CH_2); 2.00—2.07 (m, 8 H, 4 C<u>H</u>$_2$CH=); 3.38—3.87 (m, 4 H, 2 CH_2—O); 4.56 (t, 1 H, O—CH—O, *J* = 3.2 Hz); 5.34—5.38 (m, 4 H, 4 HC=). ^{13}C NMR, δ: 14.04 (C(16)); 19.62 (C(19)); 22.63 (C(15)); 25.52 (C(20)); 26.38 (C(3)); 27.03 (C(4)); 27.23 (C(2)); 27.36 (C(7)); 27.40 (C(8)); 28.96 (C(11)); 29.36 (C(12)); 29.72 (C(13)); 30.73 (C(18)); 31.77 (C(14)); 62.13 (C(21)); 67.37 (C(1)); 98.68 (C(17)); 129.03 (C(9)); 129.42 (C(6)); 129.88 (C(5)); 130.30 (C(10)).

2-(6,9-Dideuterohexadeca-5*Z*,9*Z*-dien-1-yloxy)tetrahydro-2*H*-pyran (12f). The yield was 88%, R_f = 0.41. Found (%): C, 77.68; H + D, 12.28. Calculated (%): C, 77.72; H, 11.18; D, 1.24. MS MALDI TOF: found *m/z* 324.5. $C_{21}H_{36}D_2O_2$. Calculated: *M* = 324.5. IR, ν/cm^{-1}: 816, 869, 905, 971, 992, 1034, 1078, 1121, 1136, 1159, 1182, 1200, 1353, 1380, 1441, 2175 (C—D), 2853, 2924, 3005. ^{1}H NMR, δ: 0.88 (t, 3 H, Me, *J* = 7.0 Hz); 1.26—1.88 (m, 18 H, 9 CH_2); 2.00—2.12 (m, 8 H, 4 C<u>H</u>$_2$CH=); 3.38—3.85 (m, 4 H, 2 CH_2—O); 4.57 (t, 1 H, O—CH—O, *J* = 3.2 Hz); 5.34—5.37 (m, 2 H, 2 <u>H</u>C=CD). ^{13}C NMR, δ: 14.02 (C(16)); 19.64 (C(19)); 22.61 (C(15)); 25.50 (C(20)); 26.38 (C(3)); 27.04 (C(4)); 27.23 (C(2)); 27.36 (C(7)); 27.42 (C(8)); 28.96 (C(11)); 29.35 (C(12)); 29.71 (C(13)); 30.73 (C(18)); 31.78 (C(14)); 62.14 (C(21)); 67.37 (C(1)); 98.67 (C(17)); 128.75 (t, C(9), $J_{C,D}$ = 24.0 Hz); 129.12 (t, C(6), $J_{C,D}$ = 24.0 Hz); 129.87 (C(5)); 130.31 (C(10)).

2-(Hexadeca-7*Z*,11*Z*-dien-1-yloxy)tetrahydro-2*H*-pyran (11g). The yield was 94%, n_D^{20} 1.4841, R_f = 0.38. Found (%): C, 78.08; H, 11.64. Calculated (%): C, 78.20; H, 11.88. MS MALDI TOF: found *m/z* 322.5. $C_{21}H_{38}O_2$. Calculated: *M* = 322.5. IR, ν/cm^{-1}: 814, 869, 905, 971, 990, 1034, 1078, 1121, 1136, 1159, 1182, 1200, 1353, 1380, 1441, 2853, 2925, 3005. ^{1}H NMR, δ: 0.88 (t, 3 H, Me, *J* = 5.2 Hz); 1.26—1.33 (m, 12 H, 6 CH_2); 1.50—1.65 (m, 6 H, 3 CH_2); 2.02—2.16 (m, 8 H, 4 C<u>H</u>$_2$CH=); 3.38—3.88 (m, 4 H, 2 CH_2—O); 4.57 (t, 1 H, O—CH—O, *J* = 4 Hz); 5.35—5.40 (m, 4 H, 4 HC=). ^{13}C NMR, δ: 13.96 (C(16)); 19.64 (C(19)); 22.45 (C(15)); 25.52 (C(20)); 26.20 (C(3)); 26.93 (C(6)); 27.18 (C(13)); 27.39 (C(9), C(10)); 29.13 (C(14)); 29.66 (C(4)); 29.72 (C(2)); 30.80 (C(18)); 31.96 (C(5)); 62.19 (C(21)); 67.57 (C(1)); 98.75 (C(17)); 129.05 (C(11)); 129.63 (C(7)); 130.17 (C(12)); 130.60 (C(8)).

2-(8,11-Dideuterohexadeca-7*Z*,11*Z*-dien-1-yloxy)tetrahydro-2*H*-pyran (12g). The yield was 92%, R_f = 0.38. Found (%): C, 77.61; H + D, 12.24. Calculated (%): C, 77.72; H, 11.18; D, 1.24. MS MALDI TOF: found *m/z* 324.5. $C_{21}H_{36}D_2O_2$. Calculated: *M* = 324.5. IR, ν/cm^{-1}: 815, 869, 905, 971, 990, 1034, 1078, 1121, 1136, 1159, 1183, 1200, 1353, 1380, 1441, 2160 (C—D), 2853, 2925, 3005. ^{1}H NMR, δ: 0.89 (t, 3 H, Me, *J* = 6.2 Hz); 1.26—1.34 (m, 12 H, 6 CH_2); 1.51—1.63 (m, 6 H, 3 CH_2); 2.02—2.14 (m, 8 H, 4 C$\underline{H}_2$CH=); 3.38—3.86 (m, 4 H, 2 CH_2—O); 4.58 (t, 1 H, O—CH—O, *J* = 4 Hz); 5.36 (t, 1 H, $\underline{H}$C=CD, *J* = 7 Hz); 5.39 (t, 1 H, $\underline{H}$C=CD, *J* = 7 Hz). ^{13}C NMR, δ: 13.98 (C(16)); 19.62 (C(19)); 22.45 (C(15)); 25.54 (C(20)); 26.21 (C(3)); 26.94 (C(6)); 27.19 (C(13)); 27.38 (C(9), C(10)); 29.14 (C(14)); 29.68 (C(4)); 29.72 (C(2)); 30.81 (C(18)); 31.98 (C(5)); 62.18 (C(21)); 67.57 (C(1)); 98.76 (C(17)); 128.83 (t, C(11) $J_{C,D}$ = 24.5 Hz); 129.62 (C(7)); 130.18 (C(12)); 130.32 (t, C(8), $J_{C,D}$ = 24.0 Hz).

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