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Novel organomagnesium reagents in synthesis. Catalytic cyclomagnesiation of allenes in the synthesis of N-, O-, and Si-substituted 1*Z*,5*Z*-dienes

Vladimir A. D'yakonov *, Aleksey A. Makarov, Elina Kh. Makarova, Usein M. Dzhemilev

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 450075 Ufa, 141 Prospekt Oktyabrya, Russian Federation

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An efficient method for the synthesis of valuable N-, O-, and Si-containing 1*Z*,5*Z*-diene compounds was developed. The method comprises Cp_2TiCl_2-catalyzed homo- and cross-cyclomagnesiation of 1,2-dienes by Grignard reagents (RMgR′) to give 2,5-dialkylidenemagnesacyclopentanes in up to 96% yield. This approach was successfully used in the synthesis of 5*Z*,9*Z*-dienoic acids, precursors of acetogenins and insect pheromones.

1. Introduction

The development of new methods for the synthesis of functionally substituted hydrocarbons containing a 1*Z*,5*Z*-diene group is stimulated by the abundance of these compounds as parts of numerous insect pheromones,[1] some biologically active natural products[2] and acetogenin precursors exhibiting antiviral, antibacterial, and antitumor properties.[3] There are no general versatile methods for the synthesis of stereochemically pure 1*Z*,5*Z*-diene compounds; in addition, the known methods for the synthesis of 1*Z*,5*Z*-dienes are multistep and the yields of the final compounds vary from 5 to 15%.[4] The intermolecular cyclomagnesiation of aliphatic 1,2-dienes that we developed previously[5] affords high yields of 1*Z*,5*Z*-dienes difficult to prepare by other methods and could serve, as an efficient tool in the synthesis of 1*Z*,5*Z*-dienes of specified structure (Scheme 1).

There are two key drawbacks of the above method, namely, the synthesis of only symmetric hydrocarbons containing a 1*Z*,5*Z*-diene group and the lack of any information on the possibility of cyclomagnesiation of functionally substituted 1,2-dienes. These markedly reduce the value of this approach for the targeted synthesis of 1,5-diene compounds of a specified structure. In this paper, we describe the targeted design of 1*Z*,5*Z*-dienes, and demonstrate the potential of catalytic cyclomagnesiation of 1,2-dienes in the synthesis of O-, N-, and Si-containing 1*Z*,5*Z*-dienes, in particular, as applied to the synthesis of biologically active compounds existing in nature.

2. Homocyclomagnesiation of O-, N-, and Si-containing 1,2-dienes

As the investigation objects, we chose O-, N-, and Si-containing allenes with different distances separating the functional group from the 1,2-diene group. First, it was found that *O*-containing 1,2-dienes with a non-protected hydroxyl group and their trimethylsilyl ethers cannot be involved in Cp_2TiCl_2-catalyzed cyclomagnesiation.[5] Meanwhile, pyranyl-, ethoxyethyl-, or benzyl-protected allene alcohols **1a**–**e** in which the 1,2-diene group is separated from oxygen by two or more methylene groups react with an excess of EtMgBr (**1**/EtMgBr/Mg/[Ti]=10:20:24:0.5, Et_2O, 6 h, 20–22°C) to give 2,5-dialkylidenemagnesacyclopentanes **2** in 69–84% yield. After acid hydrolysis or deuterolysis, these products furnish the corresponding symmetric O-containing 1*Z*,5*Z*-diene compounds **3**,**4** (Scheme 2, Table 1).

As a continuation of these studies, we demonstrated that under the developed conditions, N- and Si-containing 1,2-dienes can undergo catalytic cyclomagnesiation with EtMgBr in the presence of Cp_2TiCl_2. Hydrolysis and deuterolysis of magnesacyclopentanes **2**

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* Corresponding author. Tel./fax: +7 347 2842750; e-mail address: DyakonovVA@rambler.ru (V.A. D'yakonov).

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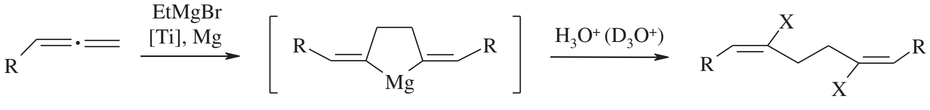
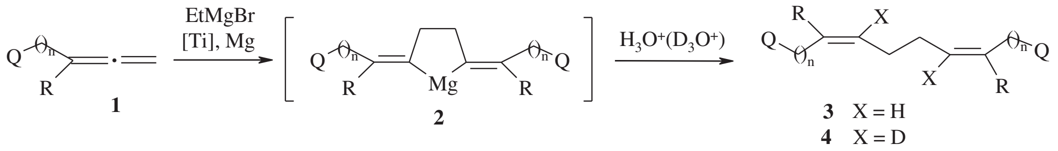


[Ti] = Cp_2TiCl_2, R = alkyl, aryl, X = H, D

Scheme 1. Ti-catalyzed cyclomagnesiation of alkyl allenes.

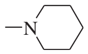
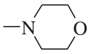


[Ti] = Cp_2TiCl_2

Q = OTHP, R = H: n = 2, (**a**), 4 (**b**), 6 (**c**); Q = OBn, R = H: n = 2 (**d**); Q = OEE, R = H: n = 4 (**e**); Q = OEE, R = H: n = 4 (**f**); Q = Et_2N, R = H: n = 1 (**g**); Q = Pr^i_2N, R = H: n = 1 (**h**); Q = Piperidyl, R = H: n = 1 (**i**); Q = Morpholyl: R = H, n = 1 (**k**); R = Me, n = 1 (**l**); R = Et, n = 1 (**m**); R = Bu, n = 1 (**n**); R = H, n = 2 (**o**); R = H, n = 3 (**p**); Q = TMS, n = 1: R = H (**q**), R = Et (**r**), R = Bu (**s**).

Scheme 2. Ti-Catalyzed homocyclomagnesiation of O-, N-, and Si-containing 1,2-dienes.

Table 1
Effect of the substituent on the yield of magnesacyclopentanes **2**

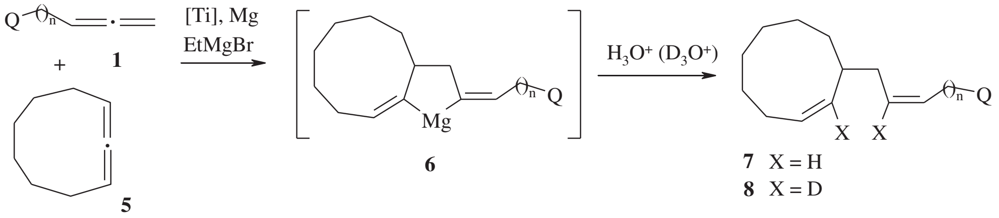
Entry	Q	R	*n*	Yield, %
1	OTHP	H	2	69 (**2a**)
2		H	4	78 (**2b**)
3		H	6	84 (**2c**)
4	OBn	H	2	71 (**2d**)
5	OEE	H	4	88 (**2e**)
6	OTHF	H	4	80 (**2f**)
7	NEt_2	H	1	68 (**2g**)
8	N*i*-Pr_2	H	1	72 (**2h**)
9		H	1	75 (**2i**)
10		H	1	79 (**2k**)
11		Me	1	82 (**2l**)
12		Et	1	84 (**2m**)
13		Bu	1	82 (**2n**)
14		H	2	85 (**2o**)
15		H	3	81 (**2p**)
16	TMS	H	1	92 (**2q**)
17		Et	1	89 (**2r**)
18		Bu	1	87 (**2s**)

result in the formation of unsaturated α,ω-diamines and α,ω-disilanes in 68–92% yield (Scheme 2, Table 1).

The formation of substituted 3,6-dideutero-2*Z*,6*Z*-dienes **4** upon deuterolysis of the reaction mixture unambiguously indicates that the initial organomagnesium compounds (OMCs) **2** contain two Mg–C bonds. The cis-configuration of the substituents at the double bonds in the obtained 1,5-dienes can be derived from the presence of high-field signals in the ^{13}C NMR spectrum caused by the internal allylic carbon atoms, $\delta C(4)=\delta C(5) \sim 27$ ppm, indicating the presence of cis-interaction with C(1) and C(8).[6] The vicinal spin–spin coupling constants for C(3) and C(6) protons (d, ^3J=11 Hz; t, ^3J=7 Hz) of hydrolysis products **3** additionally confirms the cis-arrangement of the hydrogen atoms at double bonds.[7] The replacement of EtMgBr by other Grignard reagents, for example, EtMgCl, *i*-PrMgBr, BuMgBr does not affect the yield or the selectivity of formation of the target OMCs **2**.

3. Cross-cyclomagnesiation of O-, N-, and Si-containing 1,2-dienes with cyclic and acyclic allenes

The results we obtained suggested the possibility of synthesis of unsymmetric functionally substituted magnesacyclopentanes by cross-cyclomagnesiation of various 1,2-dienes. Previously, we successfully implemented a similar approach for the joint reaction of cyclonona-1,2-diene and terminal 1,2-dienes to give bicyclic OMCs in up to 85% yield.[5b] For implementation of this idea, we first studied the reaction of an equimolar mixture of cyclonona-1,2-diene **5** and 2-(3,4-pentadien-1-yloxy)tetrahydropyran **1a** with EtMgBr in the presence of Mg and Cp_2TiCl_2 catalyst (**1**/**5**/EtMgBr/Mg/[Ti]=10:10:24:20:1, Et_2O, 6 h, 20–22 °C). This resulted in the predominant formation of bicyclic OMC **6a**, which was converted upon hydrolysis or deuterolysis in to the corresponding derivatives of cyclononene **7a** and **8a** in an 81% yield (Scheme 3).



[Ti] = Cp_2TiCl_2; Q = OTHP, n = 2 (**a**); Q = OBn, n = 2 (**b**); Q = Morpholyl: n = 1 (**c**), 2 (**d**); Q = TMS, n = 1 (**e**).

Scheme 3. Ti-catalyzed cross-cyclomagnesiation of O-, N-, and Si-containing 1,2-dienes with acyclic allenes.

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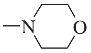
Under the conditions used, the formation of target OMC **6a** is accompanied by the formation of cyclononadiene homo-cyclomagnesiation products[5b] or the corresponding functionally substituted allene **1a** in a ~15% yield.

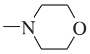
Optimization of the synthesis conditions in order to maximize the yield of the target organomagnesium compound **6a** by varying the ratios of the reaction components resulted in conditions (**1**/**5**/EtMgBr/Mg/[Ti]=10:15:30:32:1, Et_2O, 6 h, 20–22 °C) under which cross-cyclomagnesiation of functionally substituted allenes **1** with cyclonona-1,2-diene **5** gave OMC **6a** in 81–86% yield and the total yield of homocyclomagnesiation products did not exceed 5–10% (Table 2).

Table 2
Effect of the substituent on the yield of magnesacyclopentanes **6**

Entry	Q	n	Yield, %		
			Cross-product (**6**)	Homo-product (**2**)	Homo-product (cyclona-1,2-diene)
1	OTHP	2	81 (**6a**)	3 (**2a**)	4
2	OBn	2	85 (**6b**)	2 (**2d**)	4
3		1	80 (**6c**)	3 (**2h**)	3
4		2	86 (**6d**)	4 (**2n**)	4
5	TMS	1	85 (**6e**)	3 (**2p**)	2

Having obtained encouraging results in the intermolecular cyclomagnesiation of cyclonona-1,2-diene with functionally substituted allenes, we subsequently developed the optimal conditions for cross-cyclomagnesiation of O-, N-, and Si-containing 1,2-dienes with terminal alkyl- and aryl-substituted allenes **9** in the presence of EtMgBr and the Cp_2TiCl_2 catalyst (**1**/**9**/EtMgBr/Mg/[Ti]=10:12:40:32:0.5; Et_2O, 6 h, 20–22 °C) for the preparation of only unsymmetrical OMC **10** of high stereochemical purity (>99%) in yield of >80% (Scheme 4, Table 3).

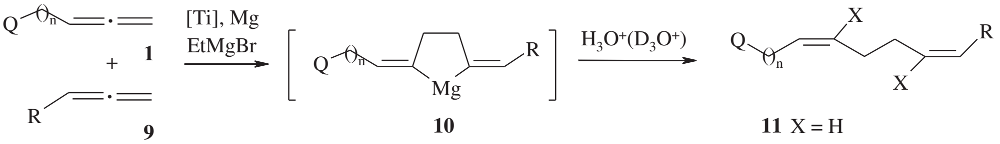
Table 3
Effect of the substituent on the yield of magnesacyclopentanes **10**

Entry	R	Q	n	Yields, %		
				Cross-product (**10**)	Homo-product (**2**)	Homo-product (terminal 1, 2-diene)
1	Hex	OBn	2	88 (**10a**)	2	7
2	Hex	OTHP	2	81 (**10b**)	1	6
3	Bn		2	84 (**10c**)	1	5
4	Dodec		3	87 (**10d**)	—	5
5	Bu		4	84 (**10e**)	—	6
6	Hex		4	90 (**10f**)	1	5
7	Bu		6	94 (**10g**)	2	6
8	Bn		2	87 (**10h**)	—	6
9	Hex		2	89 (**10i**)	—	7
10	Bn	TMS	1	91 (**10k**)	2	8
11	Hex		1	89 (**10l**)	1	7

4. Synthetic applications of the developed reactions and reagents

The intermolecular cross-cyclomagnesiation of 1,2-dienes can underlie the development of methods for the synthesis of diene insect pheromones and attractants.[1] For example, acylation of diene **11g** with acetyl bromide[8] gave hexadeca-7*Z*,11*Z*-dien-1-yl acetate **12**, the pink bollworm *Pectinophora gossypiella* attractant,[1c] in a final yield of 89% (Scheme 5).

The same approach was used to obtain the key synthons in the preparation of some acetogenins exhibiting high antitumor, antimalarial, and immunosuppressive activities that are isolated from the plants *Annonacea*.[3] Cross-cyclomagnesiation of 1,2-hexadecane and 2-(4,5-hexadiene-1-yloxy)tetrahydropyran followed by hydrolysis furnished 2-(hexacosa-4*Z*,8*Z*-dien-1-yloxy)tetrahydropyran **11h** (yield 84%), which is the key intermediate in the preparation of the acetogenin *cis*-Solamin **14** (Scheme 6).[3c]



[Ti] = Cp_2TiCl_2; n = 1, Q = TMS: R = Bn (**k**), Hex (**l**); n = 2: Q = OBn, R = Hex (**a**); Q = OTHP, R = Hex (**b**); Q = OTHP, R = Bn (**c**); Q = Morph, R = Bn (**h**); Q = Morph, R = Hex (**i**) n = 3: Q = THP, R = $C_{12}H_{25}$ (**d**); n = 4: Q = THP, R = Bu (**e**); Q = THP, R = Hex (**f**); n = 6: Q = THP, R = Bu (**g**).

Scheme 4. Ti-Catalyzed cross-cyclomagnesiation of O-, N-, and Si-containing 1,2-dienes with acyclic allenes.

The absence of by-products resulting from homocyclomagnesiation of aliphatic 1,2-dienes **9** under conditions we chose is a consequence of conducting the reaction in diethyl ether in which, as shown previously,[5a] no 2,5-dialkylidenemagnesacyclopentanes are formed. A slight excess of aliphatic 1,2-diene **9** precludes almost entirely the formation of OMC **2**, which is formed in ~5–8% yield under the reaction conditions (Table 3). The regularities we elucidated hold both upon increase in the length of the alkyl group in the initial aliphatic allene **9** and upon increase in the number of methylene units that separate the 1,2-diene system from the heteroatom in functionally substituted 1,2-dienes **1** (Table 3). The performed studies resulted in the synthesis of a series of OMC **10**, which are of interest as the starting reactants for the targeted synthesis of unsymmetrical functionally substituted 1*Z*,5*Z*-dienes difficult to obtain by other methods.

In addition, we developed an efficient approach to the synthesis of valuable natural 5*Z*,9*Z*-dienoic acids, which possess antiviral, antibacterial, and antitumor properties and which had been isolated previously from natural sources. 5*Z*,9*Z*-Hexadecadienoic acid **15** was prepared in 46% yield upon oxidation of alcohol **14** with pyridinium dichromate (PDC[9]) according to Scheme 7. It should be noted that the synthetic routes to 5*Z*,9*Z*-dienoic acids, in particular, 5*Z*,9*Z*-hexadecadienoic acid, reported in the literature are multistep (5–20 steps) and the yields of the target compounds vary from 0.5 to 15%.[4]

5. Conclusion

We have reported for the first time intermolecular homo-cyclomagnesiation of O-, N-, and Si-containing 1,2-dienes and

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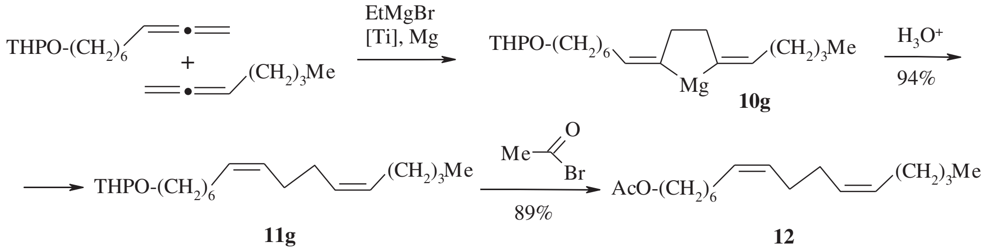
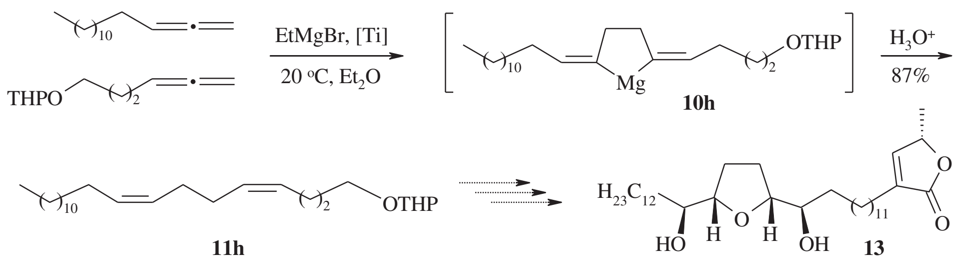
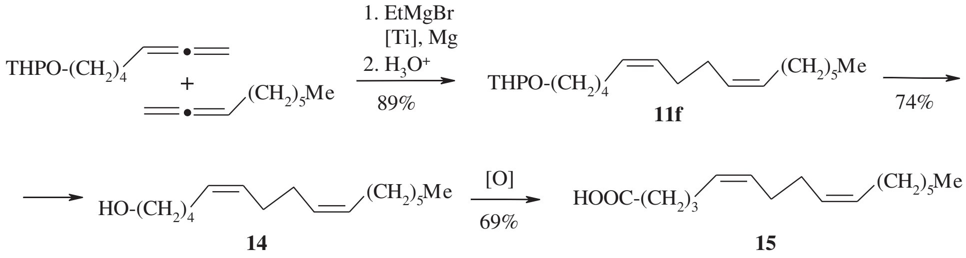


Scheme 5. The synthesis of the pink bollworm *Pectinophora gossypiella* attractant.



Scheme 6. The synthesis of the key intermediate in the preparation of *cis*-Solamin.



Scheme 7. New approach to the synthesis of 5*Z*,9*Z*-dienoic acids.

cross-cyclomagnesiation of O-, N-, and Si-containing allenes with cyclic and acyclic aliphatic 1,2-dienes by means of Grignard reagents and Cp_2TiCl_2 catalysts, resulting in the preparation of functionally substituted mono- and bicyclic organomagnesium compounds having an extensive potential in the synthesis of valuable natural and synthetic functionally substituted 1*Z*,5*Z*-dienes of a specified structure.

6. Experimental section

6.1. General

All solvents were dried (hexane, THF, benzene over Na) and freshly distilled before use. All reactions were carried out under a dry argon atmosphere. ^1H and ^{13}C NMR spectra were obtained using a Bruker AVANCE 400 spectrometer in $CDCl_3$ operating at 400 MHz for ^1H and 100 MHz for ^{13}C. Optical rotations were measured on a Perkin–Elmer 341 polarimeter. IR spectra were recorded on Bruker VERTEX 70V using KBr discs over the range of 400–4000 cm^{-1}. Elemental analyses were measured on a 1106 Carlo Erba apparatus. Mass spectra were obtained on MALDI TOF/TOF spectrometer in a 2,5-dihydroxybenzoic acid matrix and Shimadzu GCMS-QP2010 Plus spectrometer at 70 eV and working temperature 200 °C. Individuality and purity of the synthesized compounds were controlled using of TLC on Silufol UV-254 plates; anisic aldehyde in acetic acid was used as a developer. Column chromatography was carried out on Acrus silica gel (0.060–0.200 mm).

6.2. Homocyclomagnesiation O-, N-, and Si-containing 1,2-dienes with RMgX (R=Et, *i*-Pr, Bu; X=Cl, Br) in the presence of Mg metal and Cp_2TiCl_2 catalyst

Diethyl ether (10 mL), 1,2-diene (10 mmol), RMgX (20 mmol) (as a 1.5 M solution in Et_2O), Mg powder (24 mmol), and Cp_2TiCl_2 (0.5 mmol) were charged into a glass reactor with stirring under argon (∼0 °C). The reaction mixture was warmed-up to room temperature (20–22°C) and stirred for 6–8 h. For identification of substituted magnesacyclopentanes based on hydrolysis or deuterolysis products, the reaction mixture was treated with a 5% solution of NH_4Cl (ND_4Cl) in H_2O (D_2O). The products were extracted with diethyl ether, the extracts were dried with $MgSO_4$, the solvent was evaporated, and the residue was chromatographed on a column (SiO_2, elution with petroleum ether/EtOAc (50:1)).

*6.2.1. 2,2′-[Deca-3Z,7Z-diene-1,10-diylbis(oxy)]bistetrahydro-2H-pyran (**3a**).* Yield=69% (1.17 g), as a colorless oil. n_d^{20}=1.4969. R_f=0.61 (hexane/EtOAc 5:1). IR: 2945, 2871, 2247, 1440, 1323, 1136, 1076, 1030, 981, 909, 733, 648 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.48 to 1.84 (m, 12H, C(12,13,14,17,18,19)H_2), 2.10–2.11 (m 4H, C(5,6)H_2), 2.30–2.40 (m, 4H, C(2,9)H_2), 3.38–3.87 (m, 8H, C(1,10,15,20)H_2), 4.58 (t, 2H, C(11,16)H, *J*=3.6 Hz), 5.36–5.55 (m, 4H, C(3,4,7,8)

H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 19.5 (C(13,18)), 25.5 (C(14,19)), 27.3 (C(5,6)), 28.0 (C(2,9)), 30.7 (C(12,17)), 62.2 (C(15,20)), 67.0 (C(1,10)), 98.7 (C(11,16)), 126.1 (C(3,8)), 131.1 (C(4,7)) ppm. MALDI TOF: 338.5. Anal. Calcd for C$_{20}$H$_{34}$O$_4$: C, 70.97; H, 10.12. Found: C, 70.05; H, 9.96.

*6.2.2. 2,2′-[4,7-Dideuterodeca-3Z,7Z-diene-1,10-diylbis(oxy)]bistetrahydro-2H-pyran (**4a**).* Yield=68% (1.15 g), as a colorless oil. R_f=0.61 (hexane/EtOAc 5:1). IR: 2945, 2870, 2247, 2175 (C–D), 1441, 1323, 1136, 1075, 1030, 981, 908, 733, 649 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −1.50 to 1.88 (m, 12H, C(12,13,14,17,18,19)H$_2$), 2.03–2.19 (m 4H, C(5,6)H$_2$), 2.25–2.36 (m, 4H, C(2,9)H$_2$), 3.36–3.88 (m, 8H, C(1,10,15,20)H$_2$), 4.58 (t, 2H, C(11,16)H, J=3.6 Hz), 5.40 (t, 2H, C(3,8)H, J=6.8 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 19.6 (C(13,18)), 25.5 (C(14,19)), 27.2 (C(5,6)), 27.9 (C(2,9)), 30.7 (C(12,17)), 62.2 (C(15,20)), 67.0 (C(1,10)), 98.7 (C(11,16)), 125.9 (C(3,8)), 130.7 (t, C(4,7), $J_{C,D}$=24 Hz) ppm. Anal. Calcd for C$_{20}$H$_{32}$D$_2$O$_4$: C, 70.55; H, 9.47; D, 1.18. Found: C, 70.01; H+D, 10.49.

*6.2.3. 2,2′-[Tetradeca-5Z,9Z-diene-1,14-diylbis(oxy)]bistetrahydro-2H-pyran (**3b**).* Yield=78% (1.54 g), as a colorless oil. n_d^{20}=1.4969. R_f=0.56 (hexane/EtOAc 5:1). IR: 2948, 2871, 2245, 1440, 1323, 1136, 1078, 1030, 981, 908, 733, 647 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −1.34 to 1.81 (m, 20H, C(2,3,12,13,16,17,18,21,22,23)H$_2$), 1.99–2.11 (m, 8H, C(4,7,8,11)H$_2$), 3.30–3.84 (m, 8H, C(1,14,19,24)H$_2$), 4.52 (t, 2H, C(15,20)H, J=3.6 Hz), 5.29–5.36 (m, 4H, C(5,6,9,10)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 19.6 (C(17,22)), 25.5 (C(18,23)), 26.3 (C(3,12)), 27.0 (C(7,8)), 27.3 (C(4,11)), 29.3 (C(2,13)), 30.7 (C(16,21)), 62.1 (C(19,24)), 67.3 (C(1,14)), 98.7 (C(15,20)), 129.3 (C(6,9)), 129.9 (C(5,10)) ppm. MALDI TOF: 394.6. Anal. Calcd for C$_{24}$H$_{42}$O$_4$: C, 73.05; H, 10.73. Found: C, 72.91; H, 10.15.

*6.2.4. 2,2′-[6,9-Dideuterotetradeca-5Z,9Z-diene-1,14-diylbis(oxy)]bistetrahydro-2H-pyran (**4b**).* Yield=77% (1.52 g), as a colorless oil. R_f=0.56 (hexane/EtOAc 5:1). IR: 2948, 2871, 2245, 2170 (C–D), 1441, 1323, 1136, 1078, 1030, 980, 908, 734, 647 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −1.31 to 1.80 (m, 20H, C(2,3,12,13,16,17,18,21,22,23)H$_2$), 1.99–2.12 (m, 8H, C(4,7,8,11)H$_2$), 3.28–3.80 (m, 8H, C(1,14,19,24) H$_2$), 4.52 (t, 2H, C(15,20)H, J=3.6 Hz), 5.33 (t, 2H, C(5,10)H, J=7 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 19.5 (C(17,22)), 25.5 (C(18,23)), 26.3 (C(3,12)), 26.0 (C(7,8)), 27.3 (C(4,11)), 29.3 (C(2,13)), 30.7 (C(16,21)), 62.1 (C(19,24)), 67.4 (C(1,14)), 98.6 (C(15,20)), 129.1 (t, C(6,9), $J_{C,D}$=23.5 Hz), 129.9 (C(5,10)) ppm. Anal. Calcd for C$_{24}$H$_{40}$D$_2$O$_4$: C, 72.68; H, 10.17; D, 1.02. Found: C, 72.25; H+D, 11.04.

*6.2.5. 2,2′-[Octadeca-7Z,11Z-diene-1,18-diylbis(oxy)]bistetrahydro-2H-pyran (**3c**).* Yield=84% (1.89 g), as a colorless oil. n_d^{20}=1.4949. R_f=0.53 (hexane/EtOAc 5:1). IR: 3005, 2937, 2855, 1464, 1440, 1384, 1352, 1322, 1283, 1275, 1259, 1200, 1183, 1136, 1122, 1077, 1034, 968, 905, 869, 844, 815 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −1.25 to 1.31 (m, 4H, C(2,17)H$_2$), 1.48–1.58 (m, 12H, C(2,17)H$_2$), 1.64–1.84 (m, 12H, C(20,21,22,25,26,27)H$_2$), 1.98–2.04 (m, 8H, C(6,9,10,13)H$_2$), 3.31–3.76 (m, 8H, C(1,18,23,28)H$_2$), 4.55 (t, 2H, (19,24)H, J=4 Hz), 5.29–5.38 (m, 4H, C(7,8,11,12)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 19.6 (C(21,26)), 25.5 (C(22,27)), 26.2 (C(3,16)), 27.2 (C(6,13)), 27.4 (C(9,10)), 29.2 (C(4,15)), 29.7 (C(2,17)), 30.6 (C(20,25)), 30.7 (C(5,14)), 62.2 (C(23,28)), 67.6 (C(1,18)), 98.7 (C(19,24)), 129.2 (C(8,11)), 130.2 (C(7,12)) ppm. MALDI TOF: 450.7. Anal. Calcd for C$_{28}$H$_{50}$O$_4$: C, 74.62; H, 11.18. Found: C, 74.28; H, 11.02.

*6.2.6. 2,2′-[8,11-Dideuterooctadeca-7Z,11Z-diene-1,18-diylbis(oxy)]bistetrahydro-2H-pyran (**4c**).* Yield=82% (1.85 g), as a colorless oil. R_f=0.53 (hexane/EtOAc 5:1). IR: 3005, 2936, 2855, 2175 (C–D), 1464, 1440, 1384, 1352, 1322, 1283, 1275, 1259, 1200, 1182, 1136, 1122, 1077, 1034, 969, 905, 869, 844, 815 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −1.24 to 1.32 (m, 4H, C(2,17)H$_2$), 1.48–1.56 (m, 12H, C(2,17)H$_2$), 1.64–1.84 (m, 12H, C(20,21,22,25,26,27)H$_2$), 1.98–2.02 (m, 8H, C(6,9,10,13)H$_2$), 3.30–3.78 (m, 8H, C(1,18,23,28)H$_2$), 4.57 (t, 2H, (19,24)H, J=4 Hz), 5.35 (t, 4H, C(7,12)H, J=4 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 19.6 (C(21,26)), 25.5 (C(22,27)), 26.2 (C(3,16)), 27.2 (C(6,13)), 27.4 (C(9,10)), 29.2 (C(4,15)), 29.7 (C(2,17)), 30.6 (C(20,25)), 30.7 (C(5,14)), 62.2 (C(23,28)), 67.6 (C(1,18)), 98.7 (C(19,24)), 128.9 (t, C(8,11), $J_{C,D}$=23.5 Hz), 130.1 (C(7,12)) ppm. Anal. Calcd for C$_{28}$H$_{48}$D$_2$O$_4$: C, 74.29; H, 10.69; D, 0.89. Found: C, 74.08; H+D, 11.14.

*6.2.7. 1,1′-[Deca-3Z,7Z-diene-1,10-diylbis(oxymethylene)]dibenzene (**3d**).* Yield=71% (1.24 g), as a colorless oil. n_d^{20}=1.5458. R_f=0.59 (hexane/EtOAc 5:1). IR: 3028, 2929, 2854, 2180, 1495, 1453, 1361, 1204, 1101, 1028, 735, 697 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −2.21 to 2.29 (m, 4H, C(5,6)H$_2$), 2.42–2.49 (m, 4H, C(2,9)H$_2$), 3.56 (t, 4H, C(1,10)H$_2$, J=6.8 Hz), 4.60 (s, 2H, C(11,18)H$_2$), 5.51–5.60 (m, 4H, C(3,4,7,8)H), 7.36–7.43 (m, 10H, C(13–17,20–24)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 27.5 (C(5,6)), 28.1 (C(2,9)), 70.1 (C(1,10)), 72.9 (C(11,18)), 126.2 (C(15,22)), 127.4 (C(14,16,21,23)), 127.6 (C(3,8)), 128.4 (C(13,17,20,24)), 131.2 (C(4,7)), 138.6 (C(19)) ppm. MALDI TOF: 350.5. Anal. Calcd for C$_{24}$H$_{30}$O$_2$: C, 82.24; H, 8.63. Found: C, 81.95; H, 8.34.

*6.2.8. 1,1′-[4,7-Dideuterodeca-3Z,7Z-diene-1,10-diylbis(oxymethylene)] dibenzene (**4d**).* Yield=73% (1.28 g), as a colorless oil. R_f=0.59 (hexane/EtOAc 5:1). IR: 3027, 2929, 2856, 2180 (C–D), 2180, 1495, 1453, 1361, 1205, 1101, 1028, 735, 697 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −2.21 to 2.31 (m, 4H, C(5,6)H$_2$), 2.42–2.47 (m, 4H, C(2,9)H$_2$), 3.58 (t, 4H, C(1,10)H$_2$, J=6.8 Hz), 4.61 (s, 2H, C(11,18)H$_2$), 5.45 (t, 4H, C(3,8)H, J=6.8 Hz), 7.34–7.45 (m, 10H, C(13–17,20–24)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 27.5 (C(5,6)), 28.2 (C(2,9)), 70.0 (C(1,10)), 73.0 (C(11,18)), 126.2 (C(15,22)), 127.4 (C(14,16,21,23)), 127.6 (C(3,8)), 128.4 (C(13,17,20,24)), 130.9 (t, C(4,7), $J_{C,D}$=22.5 Hz), 138.6 (C(19)) ppm. Anal. Calcd for C$_{24}$H$_{28}$D$_2$O$_2$: C, 81.77; H, 8.01; D, 1.14. Found: C, 81.58; H+D, 9.02.

*6.2.9. (10Z,14Z)-4,21-Dimethyl-3,5,20,22-tetraoxatetracosa-10,14-diene (**3e**).* Yield=88% (1.63 g), as a colorless oil. n_d^{20}=1.5659. R_f=0.56 (hexane/EtOAc 5:1). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.09 (d, 6H, C(25,26)H$_3$, J=7.2 Hz), 1.29–1.48 (m, 8H, C(7,8,17,18)H$_2$), 1.84 (t, 6H, C(1,24)H$_3$, J=8.4 Hz), 1.93–2.12 (m, 8H, C(9,12,13,16)H$_2$), 3.33–3.57 (m, 8H, C(2,6,19,23)H$_2$), 4.56 (q, 2H, C(4,21)H, J=5.2 Hz), 5.25–5.30 (m, 4H, C(10,11,14,15)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 15.2 (C(1,24)), 19.7 (C(25,26)), 26.3 (C(8,17)), 26.9 (C(9,16)), 27.3 (C(8,17)), 29.4 (C(12,13)), 60.4 (C(2,23)), 64.9 (C(6,19)), 99.3 (C(4,21)), 129.3 (C(11,14)), 129.8 (C(10,15)) ppm. MALDI TOF: 370.6. Anal. Calcd for C$_{24}$H$_{42}$O$_4$: C, 71.31; H, 11.42. Found: C, 71.18; H, 11.30.

*6.2.10. (10Z,14Z)-4,21-Dimethyl-3,5,20,22-tetraoxatetracosa-10,14-diene (**4e**).* Yield=87% (1.62 g), as a colorless oil. R_f=0.56 (hexane/EtOAc 5:1). IR: 2175 (C–D) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.09 (d, 6H, C(25,26)H$_3$, J=7.2 Hz), 1.29–-1.49 (m, 8H, C(7,8,17,18)H$_2$), 1.85 (t, 6H, C(1,24)H$_3$, J=8.4 Hz), 1.93–2.14 (m, 8H, C(9,12,13,16)H$_2$), 3.33–3.57 (m, 8H, C(2,6,19,23)H$_2$), 4.57(q, 2H, C(4,21)H, J=5.2 Hz), 5.28 (t, 2H, C(10,15)H, J=6.8 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 15.19 (C(1,24)), 19.7 (C(25,26)), 26.3 (C(8,17)), 26.9 (C(9,16)), 27.3 (C(8,17)), 29.4 (C(12,13)), 60.4 (C(2,23)), 64.9 (C(6,19)), 99.3 (C(4,21)), 129.3 (t, C(11,14), $J_{C,D}$=23.5 Hz), 129.8 (C(10,15)) ppm. Anal. Calcd for C$_{22}$H$_{40}$O$_4$D$_2$: C, 70.92; H, 10.82; D 1.08. Found: C, 70.81; H+D, 11.84.

*6.2.11. 2,2′-[(5Z,9Z)-Tetradeca-5,9-diene-1,14-diylbis(oxy)]ditetrahydrofuran (**3f**).* Yield=78% (1.43 g), as a colorless oil. n_d^{20}=1.5167. R_f=0.60 (hexane/EtOAc 5:1). IR: 2948, 2871, 2248, 1440, 1325, 1136, 1078, 1031, 981, 910, 733, 648 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz):

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δ 1.24–1.58 (m, 16H, C(2,3,12,13,17,18,21,22)H$_2$), 1.79–2.05 (m, 12H, C(4,7,8,11,16,20)H$_2$), 3.31–3.89 (m, 8H, C(1,14,18,22)H$_2$), 5.08 (t, 2H, C(15,19)H, J=2.8 Hz), 5.33–5.38 (m, 4H, C(5,6,9,10)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 23.5 (C(17,21)), 26.3 (C(3,12)), 26.9 (C(4,11)), 27.3 (C(2,13)), 29.3 (C(7,8)), 32.3 (C(16,20)), 66.7 (C(1,14)), 67.0 (C(18,22)), 103.7 (C(15,19)), 129.4 (C(6,9)), 129.9 (C(5,10)) ppm. MALDI TOF: 366.5. Anal. Calcd for $C_{22}H_{38}O_4$: C, 72.09; H, 10.45. Found: C, 71.91; H, 10.30.

*6.2.12. 2,2′-[6,9-Dideutero-(5Z,9Z)-tetradeca-5,9-diene-1,14-diylbis (oxy)]ditetrahydrofuran (**4f**).* Yield=78% (1.43 g), as a colorless oil. n_d^{20}=1.5169. R_f=0.60 (hexane/EtOAc 5:1). IR: 2175 (C–D) cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.25–1.58 (m, 16H, C(2,3,12,13,17,18, 21,22)H$_2$), 1.79–2.07 (m, 12H, C(4,7,8,11,16,20)H$_2$), 3.30–3.89 (m, 8H, C(1,14,18,22)H$_2$), 5.06 (t, 2H, C(15,19)H, J=2.8 Hz), 5.35 (t, 2H, C(5,10)H, J=6.8 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 23.5 (C(17,21)), 26.3 (C(3,12)), 26.9 (C(4,11)), 27.3 (C(2,13)), 29.3 (C(7,8)), 32.3 (C(16,20)), 66.7 (C(1,14)), 67.0 (C(18,22)), 103.7 (C(15,19)), 129.1 (t, C(6,9), $J_{C,D}$=23.5 Hz), 129.9 (C(5,10)) ppm. Anal. Calcd for $C_{22}H_{36}D_2O_4$: C, 71.70; H, 9.85; D, 1.09. Found: C, 71.59; H+D, 10.88.

*6.2.13. (2Z,6Z)-N,N,N′,N′-Tetraethylocta-2,6-diene-1,8-diamine (**3g**).* Yield=68% (0.86 g), as a pale yellow oil. R_f=0.61 (hexane/EtOAc 5:1). IR: 3011, 2966, 2933, 2871, 1464, 1381, 1363, 1202, 1179, 908, 736 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –1.06 (t, 12H, C(10,12,14,16)H$_3$, J=7.2 Hz), 2.14–2.16 (m, 4H, C(4,5)H$_2$), 2.56 (q, 8H, C(9,11,13,15)H$_2$, J=14.4 Hz, J=7.2 Hz), 3.14 (d, 4H, C(1,8)H$_2$, J=5.2 Hz), 5.5–5.6 (t, 4H, C(2,3,6,7)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 11.6 (C(10,12,14,16)), 27.5 (C(4,5)), 46.6 (C(9,11,13,15)), 49.5 (C(1,8)), 127.1 (C(2,7)), 131.7 (C(3,6)) ppm. Anal. Calcd for $C_{16}H_{32}N_2$: C, 76.13; H, 12.78. Found: C, 76.00; H, 12.75.

*6.2.14. (2Z,6Z)-3,6-Dideutero-N,N,N′,N′-tetraethylocta-2,6-diene-1,8-diamine (**4g**).* Yield=67% (0.85 g), as a pale yellow oil. R_f=0.60 (hexane/EtOAc 5:1). IR: 3012, 2964, 2932, 2872, 2175 (C–D), 1463, 1380, 1364, 1203, 1178, 907, 735 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –1.05 (t, 12H, C(10,12,14,16)H$_3$, J=7.2 Hz), 2.14–2.16 (m, 4H, C(4,5) H$_2$), 2.55 (q, 8H, C(9,11,13,15)H$_2$, J=14.4 Hz, J=7.2 Hz), 3.14 (d, 4H, C(1,8)H$_2$, J=5.2 Hz), 5.48 (t, 2H, C(2,7)H, J=7.2 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 11.6 (C(10,12,14,16)), 27.5 (C(4,5)), 46.6 (C(9,11,13,15)), 49.4 (C(1,8)), 127.1 (C(2,7)), 131.4 (t, C(3,6), $J_{C,D}$=22.5 Hz) ppm. Anal. Calcd for $C_{16}H_{30}D_2N_2$: C, 75.53; H, 11.88; D, 1.58. Found: C, 75.31; H+D, 12.98.

*6.2.15. (2Z,6Z)-N,N,N′,N′-Tetra-iso-propylocta-2,6-diene-1,8-diamine (**3h**).* Yield=72% (1.11 g), as a pale yellow oil. R_f=0.59 (hexane/EtOAc 5:1). IR: 3012, 2965, 2932, 2872, 1463, 1380, 1362, 1203, 1178, 909, 735 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –1.05 (d, 24H, C(9,11,12,14,15,17,18,20)H$_3$, J=6.8 Hz), 2.12–2.14 (m, 4H, C(4,5)H$_2$), 3.03–3.09 (m, 4H,C(10,13,16,19)H), 3.13 (d, 4H, C(1,8)H$_2$, J=6.4 Hz), 5.39–5.49 (m, 4H, C(2,3,6,7)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 20.6 (C(9,11,12,14,15,17,18,20)), 27.6 (C(4,5)), 47.9 (C(1,8)), 48.2 (CC(10,13,16,19)), 129.1 (C(3,6)), 131.7 (C(2,7)) ppm. MS m/z (EI, 70 eV) m/z (%): 308 [M]$^+$ (1.14), 114 (100), 79 (68), 86 (67), 43 (60), 70 (58), 192 (55), 153 (51), 166 (45), 265 (42), 180 (41), 208 (39), 194 (35), 41 (34), 138 (33), 100 (29), 140 (28), 72 (25), 44 (24), 97 (22), 126 (20), 91 (18), 107 (16). Anal. Calcd for $C_{20}H_{40}N_2$: C, 77.85; H, 13.07. Found: C, 77.69; H, 13.04.

*6.2.16. (2Z,6Z)-3,6-Dideutero-N,N,N′,N′-tetra-iso-propylocta-2,6-diene-1,8-diamine (**4h**).* Yield=70% (1.09 g), as a pale yellow oil. R_f=0.59 (hexane/EtOAc 5:1). IR: 3010, 2964, 2934, 2870, 2170 (C–D), 1465, 1382, 1364, 1202, 1177, 908, 734 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –1.03 (d, 24H, C(9,11,12,14,15,17,18,20)H$_3$, J=6.8 Hz), 2.12–2.14 (m, 4H, C(4,5)H$_2$), 3.04–3.09 (m, 4H,C(10,13,16,19)H), 3.14 (d, 4H, C(1,8)H$_2$, J=6.4 Hz), 5.46 (m, 4H, C(2,7)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 20.6 (C(9,11,12,14,15,17,18,20)), 27.5 (C(4,5)), 41.9 (C(1,8)), 48.2 (C(10,13,16,19)), 129.2 (C(3,6)), 131.2 (t, C(2,7), $J_{C,D}$=22.5 Hz) ppm. Anal. Calcd for $C_{20}H_{38}D_2N_2$: C, 77.35; H, 12.33; D, 1.29. Found: C, 77.21; H+D, 13.08.

*6.2.17. 1,1′-(2Z,6Z)-Octa-2,6-diene-1,8-diylpiperidine (**3i**).* Yield=75% (1.04 g), as a pale yellow oil. R_f=0.57 (hexane/EtOAc 5:1). IR: 2936, 2797, 2750, 1443, 1115, 908, 733, 641 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –1.44 to 1.46 (m, 4H, C(11,15)H$_2$), 1.59–1.60 (m, 8H, C(10,15,15,17)H$_2$), 2.13–2.15 (m, 4H, C(4,5)H$_2$), 2.38–2.41 (m, 8H, C(9,13,14,18)H$_2$), 2.99 (d, 4H, C(1,8)H$_2$, J=5.8 Hz), 5.52–5.61 (m, 4H, C(2,3,6,7)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 24.3 (C(11,16)), 25.9 (C(10,12,15,17)), 27.4 (C(4,5)), 54.4 (C(1,8)), 54.6 (C(9,13,14,18)), 126.9 (C(2,7)), 131.9 (C(3,6)) ppm. Anal. Calcd for $C_{18}H_{32}N_2$: C, 78.20; H, 11.67. Found: C, 78.02; H, 11.64.

*6.2.18. 1,1′-(2Z,6Z)-3,6-Dideuteroocta-2,6-diene-1,8-diylpiperidine (**4i**).* Yield=74% (1.02 g), as a pale yellow oil. R_f=0.57 (hexane/EtOAc 5:1). IR: 2935, 2796, 2751, 2175 (C–D), 1444, 1116, 907, 732, 642 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –1.43 to 1.45 (m, 4H, C(11,15)H$_2$), 1.59–1.61 (m, 8H, C(10,15,15,17)H$_2$), 2.13–2.15 (m, 4H, C(4,5)H$_2$), 2.39–2.41 (m, 8H, C(9,13,14,18)H$_2$), 3.01 (d, 4H, C(1,8)H$_2$, J=5.8 Hz), 5.54 (m, 2H, C(2,7)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 24.3 (C(11,16)), 25.9 (C(10,12,15,17)), 27.4 (C(4,5)), 54.4 (C(1,8)), 54.6 (C(9,13,14,18)), 126.9 (C(2,7)), 131.9 (C(3,6)) ppm. Anal. Calcd for $C_{18}H_{30}D_2N_2$: C, 77.64; H, 10.86; D, 1.44. Found: C, 77.38; H+D, 12.24.

*6.2.19. 1,1′-(2Z,6Z)-Octa-2,6-diene-1,8-diylmorpholine (**3k**).* Yield=79% (1.01 g), as a pale yellow oil. R_f=0.51 (hexane/EtOAc 5:1). IR: 2961, 2898, 2806, 1116, 1454, 1292, 909, 865, 732 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –2.12 to 2.14 (m, 4H, C(4,5)H$_2$), 2.43 (t, 8H, C(9,12,13,16)H$_2$, J=4.8 Hz), 2.98 (d, 4H, C(1,8)H$_2$, J=6.8 Hz), 3.69 (t, 8H, C(10,11,14,15)H$_2$, J=4.8 Hz), 5.43–5.56 (m, 4H, C(2,3,6,7) H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 27.4 (C(4,5)), 53.6 (C(9,12,15,16)), 55.5 (C(1,8)), 66.9 (C(10,11,13,14)), 126.2 (C(2,7)), 132.5 (C(3,6)) ppm. MS m/z (EI, 70 eV) m/z (%): 280 [M]$^+$ (7.61), 87 (100), 139 (89), 100 (62), 126 (56), 110 (44), 86 (40), 106 (36), 124 (33), 79 (32), 140 (28), 42 (24), 194 (22), 51 (21), 81 (19), 67 (17), 113 (16), 96 (15). Anal. Calcd for $C_{16}H_{28}N_2O_2$: C, 68.53; H, 10.06. Found: C, 68.41; H, 10.04.

*6.2.20. 1,1′-(2Z,6Z)-3,6-Dideuteroocta-2,6-diene-1,8-diylmorpholine (**4k**).* Yield=77% (0.99 mg), as a pale yellow oil. R_f=0.51 (hexane/EtOAc 5:1). IR: 2960, 2899, 2807, 2173 (C–D), 1117, 1455, 1293, 908, 864, 733 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –2.12 to 2.15 (m, 4H, C(4,5)H$_2$), 2.41 (t, 8H, C(9,12,13,16)H$_2$, J=4.8 Hz), 2.96 (d, 4H, C(1,8) H$_2$, J=6.8 Hz), 3.67 (t, 8H, C(10,11,14,15)H$_2$, J=4.8 Hz), 5.44 (t, 4H, C(2,7)H, J=6.8 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 27.2 (C(4,5)), 53.5 (C(9,12,15,16)), 55.4 (C(1,8)), 66.9 (C(10,11,13,14)), 126.0 (C(2,7)), 132.2 (t, C(3,6), $J_{C,D}$=22.5 Hz) ppm. Anal. Calcd for $C_{16}H_{26}D_2N_2O_2$: C, 68.05; H, 9.28; D, 1.42. Found: C, 67.89; H+D, 10.65.

*6.2.21. 1,1′-(2Z,6Z)-2,7-Dimethylocta-2,6-diene-1,8-diyldimorpholine (**3l**).* Yield=82% (1.26 g), as a pale yellow oil. R_f=0.50 (hexane/EtOAc 5:1). IR: 2958, 2892, 2852, 1453, 1292, 1118, 1007, 867 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –1.71 (s, 6H, C(1,8)H$_3$), 2.05–2.06 (m, 4H, C(4,5) H$_2$), 2.34 (t, 8H, C(10,13,15,18)H$_2$, J=4.8 Hz), 2.88 (s, 4H, C(9,14)H$_2$), 3.67 (t, 8H, C(11,12,16,17)H$_2$, J=4.8 Hz), 5.31 (t, 2H, C(3,6) H, J=7 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 22.81 (C(1,8)), 28.0 (C(4,5)), 53.6 (C(10,13,15,18)), 59.0 (C(9,14)), 67.1 (C(11,12,16,17)), 129.0 (C(3,6)), 132.0 (C(2,7)) ppm. MS m/z (EI, 70 eV) m/z (%): 308 [M]$^+$(12), 100 (100), 140 (60), 119 (57), 134 (46), 86 (45), 87 (39), 182 (27), 56 (25), 93 (24), 57 (22), 105 (20), 138 (18), 67 (16), 87 (100), 139 (89), 100 (62), 126 (56), 110 (44), 86 (40), 106 (36), 124 (33), 79 (32), 140 (28), 42 (24), 194 (22), 51 (21), 81 (19), 67 (17), 113 (16), 96

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(15). Anal. Calcd for $C_{18}H_{32}N_2O_2$: C, 70.09; H, 10.46. Found: C, 69.91; H, 10.44.

*6.2.22. 1,1′-(2Z,6Z)-2,7-Dimethyl-3,6-dideuteroocta-2,6-diene-1,8-diyldimorpholine (**4l**).* Yield=80% (1.24 g), as a pale yellow oil. R_f=0.50 (hexane/EtOAc 5:1). IR: 2957, 2893, 2851, 2175 (C–D), 1454, 1291, 1117, 1008, 866 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –1.72 (s, 6H, C(1,8)H$_3$), 2.08 (m, 4H, C(4,5) H$_2$), 2.34 (t, 8H, C(10,13,15,18)H$_2$, J=4.8 Hz), 2.89 (s, 4H, C(9,14)H$_2$), 3.68 (t, 8H, C(11,12,16,17)H$_2$, J=4.8 Hz), 5.33 (t, 2H, C(3,6)H, J=7 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 22.8 (C(1,8)), 28.0 (C(4,5)), 53.6 (C(10,13,15,18)), 59.0 (C(9,14)), 67.1 (C(11,12,16,17)), 128.6 (t, C(3,6), $J_{C,D}$=22.5 Hz), 132.0 (C(2,7)) ppm. Anal. Calcd for $C_{18}H_{30}D_2N_2O_2$: C, 69.64; H, 9.74; D, 1.29. Found: C, 69.49; H+D, 10.98.

*6.2.23. 1,1′-(3Z,7Z)-3,8-Dimethyldeca-3,7-diene-1,10-diyldimorpholine (**3m**).* Yield=84% (1.41 g), as a pale yellow oil. R_f=0.51 (hexane/EtOAc 5:1). IR: 2961, 2931, 2857, 2807, 1726, 1454, 1345, 1290, 1117, 1006, 909, 865, 734 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –0.99 (t, 6H, C(1,10)H$_3$, J=4.8 Hz), 2.08 (t, 4H, C(5,6)H$_2$, J=7.2 Hz), 2.35 (t, 8H, C(12,15,17,20)H$_2$, J=4.8 Hz), 2.91 (s, 4H, C(11,16)H$_2$), 3.68 (t, 8H, C(13,14,18,19)H$_2$, J=16 Hz), 5.33 (t, 2H, C(4,7)H, J=6.4 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 12.8, 12.9, 13.2 (C(1,10)), 21.9 (C(2,9)), 28.6 (C(5,6)), 53.6 (C(12,15,17,20)), 57.5 (C(11,16)), 67.1 (C(13,14,18,19)), 127.1, 127.20 (C(4,7)), 137.5, 134.5 (C(3,8)) ppm. MS m/z (EI, 70 eV) m/z (%): 336 [M]$^+$ (26), 133 (100), 162 (69), 100 (65), 87 (40), 152 (29), 86 (28), 55 (27), 147 (24), 167 (23), 154 (22), 56 (21), 67 (19), 41 (18), 57 (17), 93 (16), 250 (15), 134 (14), 120 (11). Anal. Calcd for $C_{20}H_{36}N_2O_2$: C, 71.38; H, 10.78. Found: C, 71.09; H, 10.57.

*6.2.24. 1,1′-(3Z,7Z)-3,8-Dimethyl-3,6-dideuterodeca-3,7-diene-1,10-diyldimorpholine (**4m**).* Yield=82% (1.39 g), as a pale yellow oil. R_f=0.51 (hexane/EtOAc 5:1). IR: 2961, 2931, 2857, 2808, 2170 (C–D), 1726, 1454, 1345, 1290, 1116, 1006, 909, 866, 734 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –0.98 (t, 6H, C(1,10)H$_3$, J=4.8 Hz), 2.07 (t, 4H, C(5,6)H$_2$, J=7.2 Hz), 2.34 (t, 8H, C(12,15,17,20)H$_2$, J=4.8 Hz), 2.91 (s, 4H, C(11,16)H$_2$), 3.67 (t, 8H, C(13,14,18,19)H$_2$, J=16 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 12.8, 12.9, 13.2 (C(1,10)), 22.0 (C(2,9)), 28.7 (C(5,6)), 53.7 (C(12,15,17,20)), 57.5, 57.6 (C(11,16)), 67.1 (C(13,14,18,19)), 127.2, 126.9 (t, C(3,6), $J_{C,D}$=22.5 Hz), 137.5, 134.5 (C(3,8)) ppm. Anal. Calcd for $C_{20}H_{34}\ D_2N_2O_2$: C, 70.96; H, 10.12; D, 1.19. Found: C, 70.80; H+D, 11.19.

*6.2.25. 1,1′-(3Z,7Z)-1,5-Dimethyltetradeca-5,9-diene-1,14-diyldimorpholine (**3n**).* Yield=82% (1.61 g), as a pale yellow oil. R_f=0.51 (hexane/EtOAc 5:1). IR: 2956, 2929, 2856, 2806, 2763, 1678, 1454, 1396, 1378, 1345, 1290, 1269, 1240, 1118, 1005, 911, 867, 798, 733 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –0.91 (t, 3H, C(1,14)H$_3$, J=7 Hz), 0.92 (t, 3H, C(1,14)H$_3$, J=7 Hz), 1.29–1.38 (m, 8H, C(2,3,12,13)H$_2$), 2.00–2.17 (m, 8H, C(4,7,8,11)H$_2$), 2.36 (t, 8H, C(16,19,21,24)H$_2$), 2.81 (s, 2H, C(15,20) H$_2$), 2.91 (s, 2H, C(15,20)H$_2$), 3.69 (t, 8H, C(17,18,22,23)H$_2$, J=4 Hz), 5.28 (t, 2H, C(6,9)H, J=7 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 14.1 (C(1,14)), 22.5, 22.9 (C(2,13)), 27.9, 28.0, 28.7, 35.6 (C(4,7,8,11)), 53.7 (C(16,19,21,24)), 57.4, 65.6 (C(15,20)), 67.2 (C(17,18,22,23)), 128.1, 128.3 (C(6,9)), 136.1, 136.4 (C(5,10)) ppm. MS m/z (EI, 70 eV) m/z (%): 392 [M]$^+$ (63), 100 (100), 87 (54), 166 (40), 196 (37), 86 (35), 152 (34), 55 (24), 67 (22), 195 (21), 69 (19), 58 (16), 180 (15), 89 (14), 68 (12), 197 (11). Anal. Calcd for $C_{24}H_{44}N_2O_2$: C, 73.42; H, 11.30. Found: C, 73.28; H, 11.21.

*6.2.26. 1,1′-(3Z,7Z)-1,5-Dimethyl-3,6-dideuterotetradeca-5,9-diene-1,14-diyldimorpholine (**4n**).* Yield=82% (1.61 g), as a pale yellow oil. R_f=0.51 (hexane/EtOAc 5:1). IR: 2956, 2929, 2856, 2806, 2764, 2175 (C–D), 1678, 1454, 1396, 1378, 1345, 1290, 1269, 1240, 1117, 1005, 911, 868, 798, 734 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –0.91 (t, 3H, C(1,14)H$_3$, J=7 Hz), 0.92 (t, 3H, C(1,14)H$_3$, J=7 Hz), 1.29–1.39 (m, 8H, C(2,3,12,13)H$_2$), 2.01–2.17 (m, 8H, C(4,7,8,11)H$_2$), 2.38 (t, 8H, C(16,19,21,24)H$_2$), 2.81 (s, 2H, C(15,20)H$_2$), 2.92 (s, 2H, C(15,20)H$_2$), 3.69 (t, 8H, C(17,18,22,23)H$_2$, J=4 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 14.1 (C(1,14)), 22.5, 22.9 (C(2,13)), 27.9, 28.0, 28.7, 35.6 (C(4,7,8,11)), 53.7 (C(16,19,21,24)), 57.4, 65.6 (C(15,20)), 67.2 (C(17,18,22,23)), 128.1, 128.0 (t, C(6,9), $J_{C,D}$=22.5 Hz), 136.1, 136.4 (C(5,10)) ppm. Anal. Calcd for $C_{24}H_{42}D_2N_2O_2$: C, 73.05; H, 10.73; D, 1.02. Found: C, 72.91; H+D, 11.69.

*6.2.27. 1,1′-(3Z,7Z)-Deca-3,7-diene-1,10-diyldimorpholine (**3o**).* Yield=85% (1.31 g), as a pale yellow oil. R_f=0.50 (hexane/EtOAc 5:1). IR: 3016, 2834, 2862, 1384, 1218, 1115, 1066, 923, 754, 667, 628 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –2.11 to 2.13 (m, 4H, C(5,6)H$_2$), 2.37 (t, 4H, C(1,10) H$_2$, J=7.2 Hz), 2.47 (t, 8H, C(11,14,15,18)H$_2$, br s), 3.73 (t, 8H, C(12,13,16,17)H$_2$, J=4.4 Hz), 5.37–5.45 (m, 2H, C(3,4,7,8)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 24.6 (C(2,9)), 27.3 (C(5,6)), 53.6 (C(11,14,15,18)), 58.7 (C(1,10)), 66.8 (C(12,13,16,17)), 127.3 (C(3,8)), 130.4 (C(4,7)) ppm. MS m/z (EI, 70 eV): 308 [M]$^+$ (3), 100 (100), 56 (11), 101 (10), 70 (5), 102 (4). Anal. Calcd for $C_{18}H_{32}N_2O_2$: C, 70.09; H, 10.46. Found: C, 68.08; H, 9.25.

*6.2.28. 1,1′-(3Z,7Z)-4,7-Dideuterodeca-3,7-diene-1,10-diyldimorpholine (**4o**).* Yield=83% (1.29 g), as a pale yellow oil. R_f=0.50 (hexane/EtOAc 5:1). IR: 3016, 2833, 2862, 2175 (C–D), 1385, 1216, 1116, 1065, 922, 755, 669, 627 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –2.16 (t, 4H, C(5,6)H$_2$, J=7.6 Hz), 2.30 (t, 4H, C(1,10)H$_2$, J=7.2 Hz), 2.39 (t, 8H, C(11,14,15,18)H$_2$, br s), 3.65 (t, 8H, C(12,13,16,17)H$_2$, J=4.4 Hz), 5.31 (t, 2H, C(3,8)H, J=6.4 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 24.6 (C(2,9)), 27.1 (C(5,6)), 53.6 (C(11,14,15,18)), 58.7 (C(1,10)), 66.8 (C(12,13,16,17)), 127.1 (C(3,8)), 130.0 (t, C(4,7), $J_{C,D}$=23 Hz) ppm. Anal. Calcd for $C_{18}H_{30}D_2N_2O_2$: C, 69.63; H, 9.74; D, 1.30. Found: C, 69.04; H+D, 10.94.

*6.2.29. 1,1′-(4Z,8Z)-Dodeca-4,8-diene-1,12-diyldimorpholine (**3p**).* Yield=81% (1.36 g), as a pale yellow oil. R_f=0.50 (hexane/EtOAc 5:1). IR: 3019, 2831, 2865, 1382, 1215, 1116, 1067, 927, 756, 669, 627 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –1.45 to 1.56 (m, 4H, C(2,11)H$_2$), 2.01–2.11 (m, 8H, C(3,10)H$_2$), 2.31 (t, 4H, C(1,12)H$_2$, J=7 Hz), 2.41 (t, 8H, C(13,16,17,20)H$_2$, J=7 Hz), 3.68 (t, 8H, C(14,15,18,19)H$_2$, J=5 Hz), 5.29–5.34 (m, 4H, C(4,5,8,9)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 25.0 (C(2,11)), 26.3 (C(3,10)), 27.3 (C(6,7)), 53.6 (C(13,16,17,20)), 58.5 (C(1,12)), 66.8 (C(14,15,18,19)), 129.5 (C(4,9)), 129.7 (C(5,8)) ppm. MS m/z (EI, 70 eV) m/z (%): 336 [M]$^+$ (15), 100 (100), 138 (14), 72 (12), 56 (11), 168 (10). Anal. Calcd for $C_{20}H_{36}N_2O_2$: C, 71.38; H, 10.78. Found: C, 70.02; H, 9.65.

*6.2.30. 1,1′-(4Z,8Z)-5,8-Dideuterododeca-4,8-diene-1,12-diyldimorpholine (**4p**).* Yield=79% (1.34 mg), as a pale yellow oil. R_f=0.50 (hexane/EtOAc 5:1). IR: 3018, 2831, 2864, 2170 (C–D), 1382, 1216, 1116, 1067, 926, 756, 669, 628 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –1.43 to 1.55 (m, 4H, C(2,11)H$_2$), 2.01–2.14 (m, 8H, C(3,10)H$_2$), 2.30 (t, 4H, C(1,12)H$_2$, J=7 Hz), 2.42 (t, 8H, C(13,16,17,20)H$_2$, J=7 Hz), 3.66 (t, 8H, C(14,15,18,19)H$_2$, J=5 Hz), 5.32 (t, 2H, C(4,9)H, J=6.4 Hz) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 25.1 (C(2,11)), 26.3 (C(3,10)), 27.3 (C(6,7)), 53.6 (C(13,16,17,20)), 58.4 (C(1,12)), 66.8 (C(14,15,18,19)), 129.4 (C(4,9)), 129.5 (t, C(5,8), $J_{C,D}$=23 Hz) ppm. Anal. Calcd for $C_{16}H_{26}D_2N_2O_2$: C, 70.96; H, 10.12; D, 1.19. Found: C, 70.02; H+D, 11.31.

*6.2.31. (2Z,6Z)-Octa-2,6-diene-1,8-diylbis(trimethylsilane) (**3q**).* Yield=92% (1.17 g), as a colorless oil. R_f=0.72 (hexane). IR: 3019, 2955, 1249, 1216, 853, 758 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ –0.049 (s, 18H, C(9–14)H$_3$), 1.51 (d, 4H, C(1,8)H$_2$, J=8.4 Hz), 2.07–2.08 (m, 4H, C(4,5)H$_2$), 5.32–5.34 (m, 2H, C(3,6)H, J=4.8 Hz), 5.41–5.48 (m, 2H, C(2,7)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ –1.7 (C(9,10,11,12,13,14)), 18.5 (C(1,8)), 27.3 (C(4,5)), 125.6 (C(2,7)), 127.2

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(C(3,6)) ppm. MS *m*/*z* (EI, 70 eV) *m*/*z* (%): 254 [M]$^+$ (1), 73 (100), 127 (31), 74 (14), 45 (11), 97 (8). Anal. Calcd for $C_{14}H_{30}Si_2$: C, 67.04; H, 13.36. Found: C, 66.85; H, 13.21.

*6.2.32. (2Z,6Z)-3,6-Dideuteroocta-2,6-diene-1,8-diylbis(trimethylsilane) (**4q**).* Yield=90% (1.15 g), as a colorless oil. R_f=0.71 (hexane). IR: 3018, 2956, 2175 (C–D), 1249, 1216, 854, 758 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ −0.048 (s, 18H, C(9–14)H_3), 1.52 (d, 4H, C(1,8) H_2, *J*=8.4 Hz), 2.06–2.09 (m, 4H, C(4,5)H_2), 5.41–5.46 (m, 2H, C(2,7) H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ −1.7 (C(9,10,11,12,13,14)), 18.5 (C(1,8)), 27.3 (C(4,5)), 125.6 (C(2,7)), 126.9 (t, C(3,6), $J_{C,D}$=23 Hz) ppm. Anal. Calcd for $C_{14}H_{28}D_2Si_2$: C, 66.57; H, 12.57; D, 1.40. Found: C, 65.81; H+D, 13.69.

*6.2.33. (2Z,6Z)-2-Ethyl-3,6-dideutero-7-[(trimethylsilyl)methyl] nona-2,6-diene-1-yl(trimethyl)silane (**3r**).* Yield=89% (1.38 g), as a colorless oil. R_f=0.70 (hexane). IR: 3019, 2955, 1248, 1216, 853, 757 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ −0.082 (s, 18H, C(13–15,16–18)H_3), 1.07 (t, 6H, C(9,12)H_3, *J*=7 Hz), 1.59 (s, 4H, C(1,10) H_2), 1.97–2.11 (m, 8H, C(4,5,8,11)H_2), 5.07 (t, 2H, C(3,6)H, *J*=6.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ −0.6 (C(11,12,13,16,17,18)), 12.9 (C(9,15)), 21.4 (C(1,10)), 28.9 (C(8,14)), 31.8 (C(4,5)), 120.3 (C(3,6)), 138.5 (C(2,7)) ppm. MS *m*/*z* (EI, 70 eV): 310 [M]$^+$. Anal. Calcd for $C_{18}H_{38}Si_2$: C, 70.08; H, 13.53. Found: C, 69.82; H, 13.14.

*6.2.34. (2Z,6Z)-2-Butyl-7-[(trimethylsilyl)methyl]undeca-2,6-diene-1-yl(trimethyl)silane (**3s**).* Yield=87% (1.36 g), as a colorless oil. R_f=0.70 (hexane). IR: 2956, 2926, 2856, 1292, 1247, 967, 856, 735 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ −0.06 (c, 18H, C(17–19,20–22)H_3), 0.94 (t, 6H, C(11,16)H_3, *J*=3.6 Hz), 1.55 (c, 4H, C(1,12)H_2), 1.94–2.19 (m, 16H, C(4,5,8–10,13–15)H_2), 5.05 (t, 2H, C(3,6)H, *J*=6.4 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ −0.6 (C(13,14,15,20,21,22)), 14.1 (C(11,19)), 21.2 (C(1,12)), 22.5 (C(10,18)), 28.9 (C(8,16)), 30.5 (C(9,17)), 32.0 (C(4,5)), 121.4 (C(3,6)), 137.0 (C(2,7)) ppm. MS *m*/*z* (EI, 70 eV): 366 [M]$^+$. Anal. Calcd for $C_{22}H_{46}Si_2$: C, 72.27; H, 13.65. Found: C, 72.01; H, 13.21.

6.3. Cross-cyclomagnesiation of O-, N-, and Si-containing 1,2-dienes with cyclonona-1,2-diene by EtMgBr in the presence of Mg metal and Cp_2TiCl_2 catalyst (general procedure)

Diethyl ether (10 mL), O-, N-, and Si-containing 1,2-diene (10 mmol), cyclonona-1,2-diene (15 mmol), EtMgBr (30 mmol) (as 1.5 M solution in Et_2O), Mg powder (32 mmol), and Cp_2TiCl_2 (1 mmol) were charged into a glass reactor with stirring under argon (~0 °C). The reaction mixture was warmed-up to room temperature (20–22 °C) and stirred for 6–8 h. For identification of unsymmetrical substituted magnesacyclopentanes based on hydrolysis or deuterolysis products, the reaction mixture was treated with a 5% solution of NH_4Cl (ND_4Cl) in H_2O(D_2O). The products were extracted with diethyl ether, the extracts were dried with $MgSO_4$, the solvent was evaporated, and the residue was chromatographed on a column (SiO_2, elution with petroleum ether/EtOAc (50:1)).

*6.3.1. 2-[(5-Cyclonon-2-en-1-ylpent-3Z-en-1-yl)oxy]tetrahydro-2H-pyran (**7a**).* Yield=81% (2.36 g), as a colorless oil. n_d^{20}=1.4921. R_f=0.49, (hexane/EtOAc 5:1). IR: 3001, 2929, 2864, 1448, 1351, 1201, 1125, 1073, 1030, 981, 905, 871, 740 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ −1.19 to 1.72 (m, 16H, C(4–8,16–18)H_2), 2.00–2.20 (m, 4H, C(10,13)H_2), 2.47–2.57 (m, 1H, C(3)H), 2.94–3.03 (m, 2H, C(9) H_2), 3.33–3.87 (m, 4H, C(14,19)H_2), 4.57 (t, 1H, C(15)H, *J*=3.6 Hz), 5.02–5.14 (m, 1H, C(2)H), 5.33–5.54 (m, 3H, C(9,11,12)H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.52 (C(17)), 24.5 (C(8)), 25.5 (C(18)), 25.9 (C(7)), 26.0 (C(9)), 26.5 (C(5)), 26.8 (C(6)), 28.1 (C(13)), 30.7 (C(16)), 33.5 (C(10)), 34.8 (C(4)), 37.1 (C(3)), 62.1 (C(19)), 67.0 (C(14)), 98.6 (C(15)), 126.2 (C(12)), 129.5 (C(1)), 130.3 (C(11)), 134.9 (C(2)) ppm. MALDI TOF: 292.5. Anal. Calcd for $C_{19}H_{32}O_2$: C, 78.03; H, 11.03. Found: C, 77.93; H, 10.92.

*6.3.2. 2-[(4-Deutero-(5-(2-deuterocyclonon-2-en-1-ylpent-3Z-en-1-yl))oxy)]tetrahydro-2H-pyran (**8a**).* Yield=80% (2.34 g), as a colorless oil. R_f=0.50 (hexane/EtOAc 5:1). IR: 3002, 2929, 2864, 2175 (C–D), 1448, 1352, 1201, 1124, 1073, 1030, 981, 905, 870, 740 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ −1.18 to 1.70 (m, 16H, C(4–8,16–18)H_2), 1.98–2.22 (m, 4H, C(10,13)H_2), 2.47–2.56 (m, 1H, C(3)HCH_2), 2.92–3.02 (m, 2H, C(9)H_2), 3.30–3.88 (m, 4H, C(14,19)H_2), 4.58 (t, 1H, C(15)H, *J*=3.6 Hz), 5.08 (t, 1H, C(1)H, *J*=7 Hz), 5.42 (m, 3H, C(12) H, *J*=6.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.5 (C(17)), 24.5 (C(8)), 25.5 (C(18)), 25.9 (C(7)), 26.0 (C(9)), 26.5 (C(5)), 26.8 (C(6)), 28.1 (C(13)), 30.7 (C(16)), 33.5 (C(10)), 34.8 (C(4)), 37.2 (C(3)), 62.1 (C(19)), 67.0 (C(14)), 98.6 (C(15)), 126.2 (C(12)), 129.5 (C(1)), 130.0 (t, C(11), $J_{C,D}$=23.5 Hz), 134.9 (C(2)) ppm. Anal. Calcd for $C_{19}H_{30}D_2O_2$: C, 77.50; H, 10.27; D, 1.37. Found: C, 77.23; H+D, 11.45.

*6.3.3. 3-[5-(Benzyloxy)pent-2Z-en-1-yl]cyclononene (**7b**).* Yield=85% (2.54 g), as a colorless oil. n_d^{20}=1.5141. R_f=0.47 (hexane/EtOAc 5:1). IR: 3003, 2926, 2855, 1495, 1361, 1101, 1028, 736, 697 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ −1.52 (m, 2H, C(4)H_2), 1.67–1.79 (m, 8H, C(5–8) H_2), 2.12–2.29 (m, 4H, C(10,13)H_2), 2.44–2.49 (m, 2H, C(9)H_2), 2.61 (m, 1H, C(3)H), 3.54 (t, 2H, C(14)H_2, *J*=6.8 Hz), 4.59 (s, 2H, C(15)H_2), 5.22–5.25 (m, 1H, C(2)H), 5.48–5.55 (m, 2H, C(1,11)H), 5.59–5.63 (m, 1H, C(12)H), 7.34–7.41 (m, 5H, C(17–21)H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.6 (C(8)), 26.1 (C(5)), 26.1 (C(7)), 26.6 (C(6)), 26.9 (C(10)), 28.3 (C(13)), 33.6 (C(9)), 35.0 (C(4)), 37.3 (C(3)), 70.0 (C(14)), 72.9 (C(15)), 126.2 (C(19)), 127.5 (C(18, 20)), 127.6 (C(17, 21)), 128.4 (C(1)), 129.6 (C(11)), 130.5 (C(12)), 135.0 (C(2)), 138.6 (C(16)) ppm. MS *m*/*z* (EI, 70 eV) *m*/*z* (%): 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). Anal. Calcd for $C_{21}H_{30}O$: C, 84.51; H, 10.13. Found: C, 84.26; H, 10.05.

*6.3.4. 2-Deutero-3-[5-(benzyloxy)-2-deutero-pent-2Z-en-1-yl]cyclononene (**8b**).* Yield=87% (2.62 g), as a colorless oil. R_f=0.47 (hexane/EtOAc 5:1). IR: 3004, 2926, 2855, 2175 (C–D), 1496, 1361, 1101, 1028, 735, 697 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ −1.49 to 1.57 (m, 2H, C(4)H_2), 1.66–1.77 (m, 8H, C(5–8)H_2), 2.12–2.26 (m, 4H, C(10,13) H_2), 2.44–2.46 (m, 2H, C(9)H_2), 2.63 (m, 1H, C(3)H), 3.58 (t, 2H, C(14)H_2, *J*=6.8 Hz), 4.58 (s, 2H, C(15)H_2), 5.23 (t, 1H, C(1)H, *J*=7 Hz), 5.52 (t, 2H, C(12)H, *J*=7 Hz), 7.32–7.40 (m, 5H, C(17–21)H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.6 (C(8)), 26.1 (C(5)), 26.1 (C(7)), 26.6 (C(6)), 26.8 (C(10)), 28.3 (C(13)), 33.6 (C(9)), 35.0 (C(4)), 37.3 (C(3)), 70.0 (C(14)), 72.9 (C(15)), 126.2 (C(19)), 127.5 (C(18, 20)), 127.6 (C(17, 21)), 128.4 (C(1)), 129.6 (C(11)), 130.5 (C(12)), 135.0 (C(2)), 138.6 (C(16)) ppm. Anal. Calcd for $C_{21}H_{28}D_2O$: C, 83.94; H, 9.39; D, 1.34. Found: C, 83.76; H+D, 10.52.

*6.3.5. 1-[(2Z)-4-Cyclonon-2-en-1-ylbut-2-en-1-yl]morpholine (**7c**).* Yield=80% (2.1 g), as a pale yellow oil. R_f=0.50 (hexane/EtOAc 5:1). IR: 2926, 2853, 2806, 1447, 1274, 1137, 1119, 1034, 867, 739 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ −1.16 to 1.72 (m, 12H, C(4–9)H_2), 2.00–2.20 (m, 2H, C(10)H_2), 2.47 (t, 4H, C(14,17)H_2, br s), 2.53–2.57 (m, 1H, C(3)H), 3.02 (d, 2H, C(13)H_2), 3.72 (t, 4H, C(15,16) H_2, *J*=4.4 Hz), 5.10–5.15 (m, 1H, C(2)H), 5.45–5.53 (m, 1H, C(11)H), 5.54–5.61 (m, 2H, C(1,12)H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.5 (C(8)), 26.0 (C(7)), 26.6 (C(5)), 26.8 (C(6)), 33.6 (C(9)), 34.4 (C(4)), 35.0 (C(10)), 37.2 (C(3)), 53.6 (C(14,17)), 55.6 (C(13)), 67.0 (C(15,16)), 126.0 (C(12)), 129.8 (C(1)), 132.3 (C(11)), 134.6 (C(2)) ppm. MS *m*/*z* (EI, 70 eV): 263 [M]$^+$. Anal. Calcd for $C_{17}H_{29}NO$: C, 77.51; H, 11.10. Found: C, 77.40; H, 11.01.

*6.3.6. 1-[(2Z)-4-Cyclonon-2-en-1-ylpent-2-en-1-yl]morpholine (**7d**).* Yield=86% (2.38 g), as a pale yellow oil. R_f=0.51 (hexane/EtOAc 5:1). IR: 2926, 2853, 2806, 1446, 1274, 1137, 1118, 1034, 867, 738 cm^{-1}. ^{1}H

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NMR ($CDCl_3$, 400 MHz): δ −1.45 to 1.57 (m, 12H, C(4–9)H_2), 2.01–2.28 (m, 2H, C(10)H_2), 2.48 (t, 4H, C(15,18)H_2, *J*=4.4 Hz), 2.35–2.39 (m, 1H, C(3)H), 3.00 (d, 2H, C(14)H_2, *J*=6 Hz), 3.73 (t, 4H, C(16,17)H_2, *J*=4.8 Hz), 5.11–5.16 (m, 1H, C(2)H), 5.35–5.46 (m, 2H, C(1,12)H), 5.52–5.58 (m, 1H, C(11)H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.9 (C(8)), 26.9 (C(7)), 26.0 (C(5)), 26.5 (C(6)), 26.8 (C(10)), 33.6 (C(9)), 34.9 (C(4)), 37.2 (C(3)), 53.7 (C(15,18)), 58.8 (C(14)), 66.9 (C(16,17)), 127.4 (C(12)), 129.6 (C(11)), 129.8 (C(1)), 134.9 (C(2)) ppm. MS *m*/*z* (EI, 70 eV) *m*/*z* (%): 277 [M]$^+$ (3), 100 (100), 126 (11), 113 (7), 101 (6), 56 (5). Anal. Calcd for $C_{18}H_{31}NO$: C, 77.92; H, 11.26. Found: C, 77.79; H, 11.07.

*6.3.7. [(2Z)-4-Cyclonon-2-en-1-ylbut-2-en-1-yl](trimethyl)silane (**7e**).* Yield=85% (2.12 g), as a pale yellow oil. R_f=0.74 (hexane). IR: 3005, 2953, 1248, 1020, 908, 856, 735 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ −0.034 (s, 9H, C(14–16)H_3), 1.49 (d, 2H, C(13)H_2, *J*=8 Hz), 1.97–2.02 (m, 10H, C(4–8)H_2), 2.05–2.07 (m, 2H, C(9)H_2), 2.19–2.23 (m, 2H, C(10)H_2), 2.54–2.56 (m, 2H, C(3)H_2), 5.16–5.21 (m, 1H, C(2)H), 5.29–5.32 (m, 1H, C(12)H), 5.40–5.46 (m, 1H, C(1)H), 5.53–5.55 (m, 1H, C(11)H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ −1.7 (C(14,15,16)), 18.5 (C(13)), 24.7 (C(8)), 26.0 (C(5)), 26.1 (C(7)), 26.5 (C(6)), 27.3 (C(10)), 33.6 (C(9)), 34.7 (C(4)), 37.3 (C(3)), 126.1 (C(12)), 127.2 (C(11)), 129.4 (C(1)), 135.4 (C(2)) ppm. MS *m*/*z* (EI, 70 eV): 250 [M]$^+$. Anal. Calcd for $C_{16}H_{30}Si$: C, 76.72; H, 12.07. Found: C, 76.41; H, 11.95.

6.4. Cross-cyclomagnesiation of O-, N-, and Si-containing 1,2-dienes with terminal 1,2-dienes by EtMgBr in the presence of Mg metal and Cp_2TiCl_2 catalyst (general procedure)

Diethyl ether (10 mL), O-, N-, and Si-containing 1,2-diene (10 mmol), corresponding 1,2-diene (12 mmol), EtMgBr (40 mmol) (as 1.5 M solution in Et_2O), Mg powder (32 mmol), and Cp_2TiCl_2 (0.5 mmol) were charged into a glass reactor with stirring under argon (∼0 °C). The reaction mixture was warmed-up to room temperature (20–22 °C) and stirred for 6–8 h. For identification of unsymmetrical substituted magnesacyclopentanes based on hydrolysis or deuterolysis products, the reaction mixture was treated with a 5% solution of NH_4Cl (ND_4Cl) in H_2O(D_2O). The products were extracted with diethyl ether, the extracts were dried with $MgSO_4$, the solvent was evaporated, and the residue was chromatographed on a column (SiO_2, elution with petroleum ether/EtOAc (50:1)).

*6.4.1. [(Tetradeca-3Z,7Z-dien-1-yloxy)methyl]benzene (**11a**).* Yield =88% (2.64 g), as a colorless oil. n_d^{20}=1.5102. R_f=0.56 (hexane/EtOAc 5:1). IR: 3007, 2926, 2855, 1495, 1361, 1101, 1028, 735, 697 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ −0.95 (t, 3H, C(14)H_3, *J*=8 Hz), 1.21–1.50 (m, 8H, C(10–13)H_2), 2.11–2.47 (m, 8H, C(2,5,6,9)H_2), 3.56 (t, 2H, C(1)H_2, *J*=8 Hz), 4.60 (s, 2H, C(15)H_2), 5.45–5.55 (m, 4H, C(3,4,7,8)H), 7.28–7.42 (m, 5H, C(17–21)H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.1 (C(14)), 22.7 (C(13)), 27.3 (C(5,6)), 27.6 (C(9)), 28.1 (C(2)), 29.1 (C(10)), 29.8 (C(11)), 31.9 (C(12)), 70.1 (C(1)), 72.9 (C(15)), 125.9 (C(19)), 127.5 (C(3)), 127.7 (C(17,21)), 128.4 (C(18,20)), 129.0 (C(7)), 130.5 (C(4)), 131.3 (C(8)), 138.6 (C(16)) ppm. MS *m*/*z* (EI, 70 eV) *m*/*z* (%): 300 [M]$^+$ (2), 105 (100), 123 (83), 77 (44), 70 (21), 122 (20), 55 (13), 51 (11), 106 (10). Anal. Calcd for $C_{21}H_{32}O$: C, 83.94; H, 10.73. Found: C, 83.72; H, 10.51.

*6.4.2. 2-(Tetradeca-3Z,7Z-dien-1-yloxy)tetrahydro-2H-pyrane (**11b**).* Yield=81% (2.38 g), as a colorless oil. n_d^{20}=1.4695. R_f=0.55 (hexane/EtOAc 5:1). IR: 3007, 2927, 2856, 1730, 1455, 1380, 1364, 1260, 1200, 1137, 1033, 985, 905, 869, 814 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ −0.89 (t, 3H, C(14)H_3, *J*=6.4 Hz), 1.27–1.30 (m, 8H, C(10–13)H_2), 1.49–1.86 (m, 6H, C(16–18)H_2), 1.94–2.13 (m, 8H, C(2,5,6,9)H_2), 3.38–3.87 (m, 4H, C(1,19)H_2), 4.59 (t, 1H, C(15)H, *J*=3.6 Hz), 5.35–5.46 (m, 4H, C(2)H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.1 (C(14)), 19.5 (C(17)), 22.6 (C(13)), 25.5 (C(18)), 27.2 (C(5,6)(2C)), 27.5 (C(2)), 28.0 (C(9)), 29.0 (C(10)), 29.7 (C(11)), 30.7 (C(16)), 31.8 (C(12)), 62.2 (C(19)), 67.0 (C(1)), 98.6 (C(15)), 125.9 (C(3)), 128.9 (C(7)), 130.4 (C(4)), 131.2 (C(8)) ppm. MS *m*/*z* (EI, 70 eV) *m*/*z* (%): 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). Anal. Calcd for $C_{19}H_{34}O_2$: C, 77.50; H, 11.64. Found: C, 77.36; H, 11.22.

*6.4.3. 2-[(9-Phenylnona-3Z,7Z–dien-1-yl)oxy]tetrahydro-2H-pyrane (**11c**).* Yield=84% (2.52 g), as a colorless oil. n_d^{20}=1.5311. R_f=0.54 (hexane/EtOAc 5:1). IR: 3390, 2938, 2870, 1762, 1453, 1352, 1261, 1200, 1120, 1075, 1032, 983, 905, 869, 812, 747, 699 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ −1.57 to 1.91 (m, 6H, C(17–19)H_2), 2.24–2.47 (m, 6H, C(2,5,6)H_2), 3.46 (d, 2H, C(9)H_2, *J*=6.4 Hz), 3.53–3.96 (m, 4H, C(1,20)H_2), 4.67 (t, 1H, C(16)H, *J*=3.6 Hz), 5.50–5.72 (m, 4H, C(3,4,7,8)H), 7.24–7.35 (m, 5H, C(11–15)H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.6 (C(18)), 25.6 (C(19)), 27.4, 27.5 (C(5), C(6)), 28.1 (C(2)), 30.8 (C(17)), 33.6 (C(9)), 62.2 (C(20)), 67.1 (C(1)), 98.7 (C(16)), 125.9 (C(13)), 126.1 (C(3)), 128.4 (C(14)), 128.4 (C(15)), 128.6 (C(8)), 130.1 (C(7)), 131.0 (C(4)), 141.1 (C(10)) ppm. MALDI TOF: 300.4 [M]$^+$. Anal. Calcd for $C_{20}H_{28}O_2$: C, 79.96; H, 10.65. Found: C, 79.79; H, 10.43.

*6.4.4. 2-(Henicosa-4Z,8Z–dien-1-yloxy)tetrahydro-2H-pyrane (**11d**).* Yield=87% (3.41 g), as a colorless oil. n_d^{20}=1.4801. R_f=0.52 (hexane/EtOAc 5:1). IR: 3005, 2924, 2853, 1441, 1401, 1380, 1260, 1200, 1182, 1159, 1137, 1121, 1078, 1034, 992, 971, 905, 721 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ −0.89 (t, 3H, C(21)H_3, *J*=6.7 Hz), 1.19–1.39 (m, 22H, C(2,11–20)H_2), 1.50–1.68 (m, 6H, C(23–25)H_2), 2.00–2.15 (m, 8H, C(3,6,7,10)H_2), 3.38–3.87 (m, 4H, C(1,26)H_2), 4.58 (t, 1H, C(22)H, *J*=4 Hz), 5.36–5.41 (m, 4H, C(4,5,8,9)H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.1 (C(21)), 19.6 (C(24)), 22.7 (C(20)), 23.9 (C(3)), 25.5 (C(25)), 27.3 (C(10)), 27.3 (C(6)), 27.4 (C(7)), 29.4 (C(2)), 29.5, 29.6, 29.7, 29.8 (C(11,12,13,14)), 29.6, 29.7 (C(15,16,17,18) (2C)), 30.8 (C(23)), 31.9 (C(19)), 62.2 (C(26)), 66.9 (C(1)), 98.8 (C(22)), 129.0 (C(9)), 129.4 (C(4)), 129.8 (C(9)), 130.4 (C(5)) ppm. MALDI TOF: 392.6. Anal. Calcd for $C_{26}H_{48}O_2$: C, 79.35; H, 12.82. Found: C, 79.18; H, 12.69.

*6.4.5. 2-(Tetradeca-5Z,9Z-dien-1-yloxy)tetrahydro-2H-pyrane (**11e**).* Yield=84% (2.47 g), as a colorless oil. n_d^{20}=1.4814. R_f=0.51 (hexane/EtOAc 5:1). IR: 2924, 2853, 1441, 1380, 1354, 1200, 1182, 1159, 1137, 1121, 1078, 1034, 992, 970, 905, 3005, 869, 814 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ −0.90 (t, 3H, C(14)H_3, *J*=6.8 Hz), 1.27–1.33 (m, 14H, C(2,3,12,13,16–18)H_2), 2.03–2.07 (m, 8H, C(4,7,8,11)H_2), 3.40–3.89 (m, 4H, C(1,19)H_2), 4.58 (t, 1H, C(15)H, *J*=3.6 Hz), 5.36–5.41 (m, 4H, C(5,6,9,10)H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.9 (C(14)), 19.6 (C(17)), 22.3 (C(13)), 25.5 (C(18)), 26.4 (C(3)), 27.0 (C(4)), 27.1 (C(2)), 27.4 (C(7)), 27.4 (C(8)), 29.5 (C(11)), 30.8 (C(12)), 31.9 (C(16)), 62.2 (C(19)), 67.4 (C(1)), 98.7 (C(15)), 129.1 (C(9)), 129.6 (C(6)), 129.8 (C(5)), 129.9 (C(10)) ppm. MALDI TOF: 294.5 [M]$^+$. Anal. Calcd for $C_{19}H_{34}O_2$: C, 77.50; H, 11.64. Found: C, 77.38; H, 11.48.

*6.4.6. 2-(Hexadeca-5Z,9Z-dien-1-yloxy)tetrahydro-2H-pyrane (**11f**).* Yield=89% (2.87 g), as a colorless oil. n_d^{20}=1.4831. R_f=0.51 (hexane/EtOAc 5:1). IR: 3005, 2924, 2853, 1441, 1380, 1353, 1200, 1182, 1159, 1137, 1121, 1078, 1034, 992, 971, 905, 869, 815 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ −0.87 (t, 3H, C(16)H_3, *J*=7.2 Hz), 1.26–1.85 (m, 18H, C(2,3,12–15,18–20)H_2), 2.00–2.07 (m, 8H, C(4,7,8,11)H_2), 3.38–3.87 (m, 4H, C(1,21)H_2), 4.56 (t, 1H, C(17)H, *J*=3.2 Hz), 5.34–5.38 (m, 4H, C(5,6,9,10)H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.0 (C(16)), 19.6 (C(19)), 22.6 (C(15)), 25.5 (C(20)), 26.4 (C(3)), 27.0 (C(4)), 27.2 (C(2)), 27.3 (C(7)), 27.4 (C(8)), 29.4 (C(11)), 29.7 (C(13)), 30.7 (C(18)), 31.8 (C(14)), 62.1 (C(21)), 67.4 (C(1)), 98.7 (C(17)), 129.0 (C(9)), 129.4 (C(6)), 129.9 (C(5)), 130.3 (C(10)) ppm.

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MALDI TOF: 322.5 $[M]^+$. Anal. Calcd for $C_{21}H_{38}O_2$: C, 84.51; H, 11.88. Found: C, 78.41; H, 11.69.

*6.4.7. 2-(Hexadeca-7Z,11Z-dien-1-yloxy)tetrahydro-2H-pyrane (**11g**).* Yield=94% (3.03 g), as a colorless oil. n_d^{20}=1.4841. R_f=0.58 (hexane/EtOAc 5:1). IR: 3005, 2925, 2853, 1441, 1380, 1353, 1200, 1182, 1159, 1136, 1121, 1078, 1034, 990, 971, 905, 869, 814 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −0.88 (t, 3H, C(16)H$_3$, *J*=5.2 Hz), 1.26–1.33 (m, 12H, C(2–5,14,15)H$_2$), 1.50–1.65 (m, 6H, C(20–22)H$_2$), 2.02–2.16 (m, 8H, C(6,9,10,13)H$_2$), 3.38–3.88 (m, 4H, C(1,23)H$_2$), 4.57 (t, 1H, C(19)H, *J*=4 Hz), 5.35–5.40 (m, 4H, C(7,8,11,12)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 13.96 (C(16)), 19.64 (C(19)), 22.45 (C(15)), 25.52 (C(20)), 26.20 (C(3)), 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)) ppm. MALDI TOF: 322.5 $[M]^+$. Anal. Calcd for $C_{21}H_{38}O_2$: C, 78.20; H, 11.88. Found: C, 78.08; H, 11.64.

*6.4.8. 4-[(7Z)-9-Phenylnona-3,7-diene-1-yl]morpholine (**11h**).* Yield =87% (2.48 g), as a pale yellow oil. R_f=0.50 (hexane/EtOAc 5:1). IR: 2956, 2931, 2854, 2807, 1494, 1454, 1274, 1118, 1071, 1007, 867, 740, 698 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −2.17 to 2.30 (m, 2H, C(2)H$_2$), 2.37 (t, 4H, C(16,19)H$_2$, *J*=6.8 Hz), 2.41 (t, 2H, C(1)H$_2$, br s), 3.42 (t, 2H, C(9)H$_2$), 3.73 (t, 4H, C(17,18)H$_2$, *J*=4.4 Hz), 5.40–5.63 (m, 4H, C(3,4,7,8)H), 7.19–7.34 (m, 5H, C(11–15)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 24.72 (C(2)), 27.27 (C(5)), 27.42 (C(6)), 33.54 (C(9)), 53.66 (C(16,19)), 58.75 (C(1)), 66.92 (C(17,18)), 127.16 (C(13)), 127.45 (C(8)), 128.33 (C(12,14)), 128.41 (C(11,15)), 128.70 (C(3)), 130.88 (C(7)), 141.01 (C(10)) ppm. MS *m/z* (EI, 70 eV) *m/z* (%): 285 $[M]^+$ (7), 31 (100), 100 (76), 206 (29), 43 (16), 39 (6). Anal. Calcd for $C_{19}H_{27}NO$: C, 79.95; H, 9.53. Found: C, 79.76; H, 9.19.

*6.4.9. 4-Tetradeca-3,7-diene-1-ylmorpholine (**11i**).* Yield=89% (2.48 g), as a pale yellow oil. R_f=0.50 (hexane/EtOAc 5:1). IR: 2956, 2926, 2854, 2807, 1456, 1274, 1137, 1007, 867 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −0.85 (t, 3H, C(14)H$_3$, *J*=6 Hz), 1.23–1.30 (m, 8H, C(10–13)H$_2$), 1.94–2.04 (m, 8H, C(2,5,6,9)H$_2$), 2.39 (t, 2H, C(1)H$_2$, *J*=4.4 Hz), 2.94 (t, 4H, C(15,18)H$_2$), 3.66 (t, 4H, C(16,17)H$_2$, *J*=4.4 Hz), 5.30–5.40 (m, 4H, C(3,4,7,89)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 14.05 (C(14)), 22.59 (C(13)), 24.66 (C(2)), 27.22 (C(5,6) (2C)), 27.44 (C(9)), 28.93 (C(10)), 29.64 (C(11)), 53.62 (C(15,18)), 58.72 (C(1)), 66.87 (C(16,17)), 127.13 (C(3)), 128.84 (C(7)), 130.43 (C(4)), 130.55 (C(8)) ppm. MS *m/z* (EI, 70 eV) *m/z* (%): 279 $[M]^+$ (18), 149 (100), 167 (47), 57 (25), 71 (22), 70 (16), 43 (15), 113 (13), 150 (12), 41 (11). Anal. Calcd for $C_{18}H_{39}NO$: C, 77.01; H, 11.65. Found: C, 77.01; H, 11.65.

*6.4.10. Trimethyl[(2Z,6Z)-8-phenylocta-2,6-diene-1-yl]silane (**11k**).* Yield=91% (2.35 g), as a colorless oil. R_f=0.72 (hexane). IR: 2958, 2892, 2852, 1453, 1292, 1118, 1007, 867 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −0.08 (s, 9H, C(15–17)H$_3$), 1.54 (d, 2H, C(1)H$_2$, *J*=8 Hz), 2.14–2.28 (m, 4H, C(4,5)H$_2$), 3.48 (d, 2H, C(8)H$_2$, *J*=6 Hz), 5.37–5.40 (m, 1H, C(2)H), 5.44–5.52 (m, 2H, C(3)H), 5.59–5.66 (m, 1H, C(6,7)H), 7.24–7.34 (m, 5H, C(10–14)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ −1.66 (C(15,16,17)), 18.62 (C(1)), 27.25 (C(5)), 27.54 (C(4)), 33.62 (C(8)), 125.40 (C(2)), 125.88 (C(12)), 126.07 (C(7)), 126.82 (C(3)), 128.41 (C(11,13)), 128.45 (C(10,14)), 130.50 (C(6)), 141.22 (C(9)) ppm. MS *m/z* (EI, 70 eV): 258 $[M]^+$. Anal. Calcd for $C_{17}H_{26}Si$: C, 70.09; H, 10.46. Found: C, 69.91; H, 10.44.

*6.4.11. Trimethyl[(2Z,6Z)-trideca-2,6-diene-1-yl]silane (**11l**).* Yield= 89% (2.24 g), as a colorless oil. R_f=0.74 (hexane). IR: 2955, 2926, 2856, 1292, 1248, 967, 856, 735 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −0.05 (s, 9H, C(14–16)H$_3$), 0.93 (t, 3H, C(13)H$_3$, *J*=7 Hz), 1.28–1.43 (m, 8H, C(9–12)H$_2$), 1.52 (d, 2H, C(1)H$_2$Si, *J*=8 Hz), 2.07–2.19 (m, 6H, C(4,5,8)H$_2$), 5.31–5.48 (m, 4H, C(2,3,6,7)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ −1.74 (C(14,15,16)), 14.11 (C(13)), 18.51 (C(1)), 22.70 (C(12)), 27.33 (C(4)), 27.48 (C(5)), 29.04 (C(9)), 29.78 (C(10)), 125.69 (C(2)), 127.03 (C(3)), 129.33 (C(6)), 137.26 (C(7)) ppm. MS *m/z* (EI, 70 eV): 252 $[M]^+$. Anal. Calcd for $C_{16}H_{32}Si$: C, 76.03; H, 13.51. Found: C, 75.85; H, 13.04.

6.5. Hexadeca-7*Z*,11*Z*-dien-1-yl acetate (12)

Yield=89% (2.34 g), as a colorless oil. R_f=0.64 (hexane/EtOAc 5:1). IR: 3006, 2928, 2856, 1743, 1464, 1385, 1365, 1238, 1038, 969, 727 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −0.84 (t, 3H, C(16)H$_3$, *J*=6.8 Hz), 1.21–1.28 (m, 10H, C(3,4,5,14,15)H$_2$), 1.54–1.58 (m, 2H, C(2)H$_2$), 1.97 (s, 3H, C(18)H$_3$), 2.01–2.10 (m, 8H, C(6,9,10,13)H$_2$), 3.99 (t, 2H, C(1)H$_2$, *J*=8 Hz), 5.31 (m, 4H, C(7,8,11,12)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 13.77 (C(16)), 20.67 (C(18)), 22.16 (C(15)), 25.68 (C(2)), 26.95 (C(13)), 27.26 (C(10)), 28.45 (C(3)), 28.71 (C(14)), 29.11 (C(4)), 29.41 (C(9)), 31.77 (C(5)), 32.55 (C(6)), 64.32 (C(1)), 128.91 (C(8)), 129.17 (C(11)), 129.82 (C(7)), 130.09 (C(12)), 170.73 (C(17)) ppm. MS *m/z* (EI, 70 eV) *m/z* (%): 280 $[M]^+$(6), 43 (100), 55 (68), 67 (49), 61 (48), 41 (43), 54 (28), 96 (22), 78 (18). Anal. Calcd for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 76.91; H, 11.26.

6.6. 5*Z*,9*Z*-Hexadecadienoic alcohol (14)

Yield=74% (1.56 g), as a colorless oil. R_f=0.51 (hexane/EtOAc 5:1). IR: 3006, 2928, 2856, 1743, 1464, 1385, 1365, 1238, 1038, 969, 727 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −0.88 (t, 3H, C(16)H$_3$, *J*=6.8 Hz), 1.26–1.62 (m, 12H, C(2,3,12,13,14,15)H$_2$), 2.01–2.07 (m, 8H, C(4,7,8,11)H$_2$), 3.60 (t, 2H, C(1)H$_2$, *J*=6.4 Hz), 5.32–5.40 (m, 4H, C(5,6,9,10)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 14.05 (C(16)), 22.64 (C(15)), 25.85 (C(3)), 26.96 (C(4)), 27.24 (C(7)), 27.33 (C(8)), 27.41 (C(11)), 28.97 (C(12)), 29.68 (C(13)), 31.77 (C(14)), 32.29 (C(2)), 62.58 (C(1)), 129.02 (C(9)), 129.55 (C(6)) ppm. MALDI TOF: 238.4. Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.50; H, 12.49.

6.7. 5*Z*,9*Z*-Hexadecadienoic acid (15)

Yield=69% (1.15 g), as a colorless oil. R_f=0.45 (hexane/EtOAc 5:1). IR: 3006, 2928, 2856, 1743, 1464, 1385, 1365, 1238, 1038, 969, 727 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −0.90 (t, 3H, C(16)H$_3$, *J*=7.2 Hz), 1.30–1.32 (m, 8H, C(4,5,14,15)H$_2$); 1.70 (q, 2H, C(3)H$_2$, *J*=7.6 Hz); 2.01–2.14 (m, 8H, C(4,7,8,11)H$_2$); 2.37 (t, 2H, C(2)H$_2$, *J*=7.2 Hz); 5.33–5.46 (m, 4H, C(5,6,9,10)H) ppm. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −0.88 (t, 3H, C(16)H$_3$, *J*=6.8 Hz), 1.26–1.62 (m, 12H, C(2,3,12,13,14,15)H$_2$), 2.01–2.07 (m, 8H, C(4,7,8,11)H$_2$), 3.60 (t, 2H, C(1)H$_2$, *J*=6.4 Hz), 5.32–5.40 (m, 4H, C(5,6,9,10)H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 14.08 (C(16)), 22.65 (C(15)), 24.63 (C(3)), 26.51 (C(11)), 27.27 (C(7,8)), 27.40 (C(4)), 28.99 (C(12)), 29.69 (C(13)), 31.78 (C(14)), 33.60 (C(2)), 128.63 (C(10)), 128.92 (C(9)), 130.53 (C(5)), 130.57 (C(6)), 180.27 (C(1)) ppm. MALDI TOF: 252.4. Anal. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 76.01; H, 11.05.

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