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Tishchenko reactions of aldehydes promoted by diisobutylaluminum hydride and its application to the macrocyclic lactone formation

Yung-Son Hon,* Ying-Chieh Wong, Chun-Ping Chang and Cheng-Han Hsieh

Department of Chemistry and Biochemistry, National Chung Cheng University, Chia-Yi 62102, Taiwan, ROC

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Abstract—Aliphatic aldehydes react with catalytic amount of Dibal-H in *n*-pentane to give the corresponding Tishchenko products in good to excellent yields. On contrary, α-silyloxy aldehydes give α-silyloxy ketones via Oppenauer oxidation under similar condition. Tishchenko reaction of ω-alkene aldehydes followed by RCM and hydrogenation affords a convenient method to prepare the 11–37 membered macrocyclic lactones.

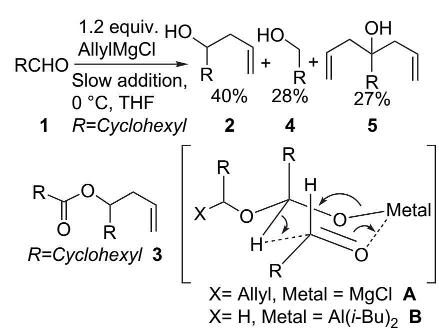
1. Introduction

Tishchenko reaction involves the aldehydes' dimerization giving the corresponding esters under the influence of aluminum alkoxides.[1] The reaction has been carried out with a number of other catalysts[2] such as alkali metal,[3] alkali earth metal oxide,[4] boric acid,[5] alumina supported KF,[6] Cp_2MH_2 (M=Zr, Hf),[7] EtLnI (Ln=Pr, Nd, Sm),[8] SmI_2,[9] $LiWO_2$,[10] $Fe(CO)_4$,[11] $RuH_2(PPh_3)_4$,[12] $RhH(CO)(PPh_3)_3$,[13] *trans*-$ROIr(CO)(PPh_3)_2$,[14] nickel complex,[15] and Cu(I).[16] Diisobutylaluminum hydride (Dibal-H) is a useful reducing agent to reduce an aldehyde to the corresponding alcohol. However, in our earlier report, we have discovered that Dibal-H is a good promoter to Tishchenko reaction of aldehydes.[17] In this article, we will describe the scope and application of this reaction in detail.

2. Results and discussion

2.1. Slow addition of Grignard reagent to aldehyde to form Tishchenko reaction intermediate

When aldehyde **1** was treated with allylmagnesium chloride in THF by a syringe pump over a period of 1 h at 0 °C, we isolated not only the desired product **2** (40%), but also primary alcohol **4** (28%) and tertiary alcohol **5** (27%) (Eq. 1). Presumably, the tertiary alcohol **5** is formed from the reaction of allylmagnesium chloride with the ester **3**, which is generated from Tishchenko reaction via intermediate **A**. Intrigued by this hypothesis, we are curious to know whether the aluminum analogue **B** is applicable to ester formation.



(1)

2.2. Tishchenko reaction of aldehydes promoted by Dibal-H

In order to avoid the possible solvation effect of the etheric solvent with the aluminum reagent, slow addition of Dibal-H to a solution of aldehyde **1** in anhydrous *n*-pentane was first tried. The typical procedure is described as follows. To a solution of aldehyde **1** (4.92 mmol) in *n*-pentane (8 mL) was added dropwise a solution of Dibal-H (0.49 mL, 1.0 M solution in hexane) in 1 mL of *n*-pentane by a syringe pump over a period of 1 h at 0 °C. After stirring at ambient temperature for 5 h, ester **7a** was isolated in 93% yield (Eq. 2; entry 1, Table 1). This reaction conditions have been applied to

Keywords: Tishchenko reaction; Oppenauer oxidation; α-Silyloxy aldehyde; α-Silyloxy ketone; Ring-closing metathesis; Macrocyclic lactones.
* Corresponding author. Tel.: +886 5 2720411x66412; fax: +886 5 2721040; e-mail: cheysh@ccu.edu.tw

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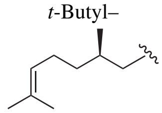
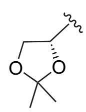
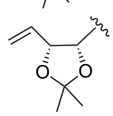
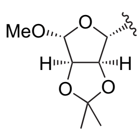
Table 1. Tishchenko reaction of aldehydes promoted by Dibal-H

Entry	RCHO, R=		Time (h)	Yield (%)	
1	Cyclohexyl–	**1**	5	93	**7a**
2	$PhCH_2CH_2$–	**6b**	5	77	**7b**
3	*n*-Hexyl–	**6c**	5	77	**7c**
4	*i*-Propyl–	**6d**	4	83	**7d**
5	*t*-Butyl–	**6e**	5	95	**7e**
6		**6f**	5	77	**7f**
7	H—≡—$(CH_2)_6$-	**6g**	14	62	**7g**
8	Ph—≡—$(CH_2)_6$-	**6h**	7	51	**7h**
9	$MeO_2C(CH_2)_6$–	**6i**	12	61	**7i**
10	$MeO_2C(CH_2)_4$–	**6j**	12	33	**7j**
11	$(MeO)_2CH(CH_2)_6$–	**6k**	12	50	**7k**
12	$(MeO)_2CH(CH_2)_4$–	**6l**	8	32	**7l**
13	$MeC(O)(CH_2)_8$–	**6m**	18	33	**7m**
14	$I(CH_2)_5$–	**6n**	12	22	**7n**
15	$Br(CH_2)_5$–	**6o**	5	70	**7o**
16	$PhOCH_2$–	**6p**	8	63	**7p**
17	$PhCH_2OCH_2$–	**6q**	8	52	**7q**
18	Ph_3COCH_2–	**6r**	6	83	**7r**
19	$PhCH_2OCH_2CH_2$–	**6s**	10	61	**7s**
20		**6t**	10	60	**7t**
21		**6u**	8	71	**7u**
22		**6v**	8	66	**7v**

aldehydes **6b–6e** in which the α-carbon contains secondary, tertiary, and even quaternary centers in excellent yields (entries 2–5, Table 1). The aldehydes tethered with olefin or alkyne moiety gave the corresponding esters **7f–7h** in good yields (entries 6–8).

$$\underset{\mathbf{6}}{\text{RCHO}} \xrightarrow[n\text{-Pentane, } 0\ ^\circ\text{C to rt}]{\text{cat. Dibal-H}} \underset{\mathbf{7}}{RCO_2CH_2R} \quad (2)$$

The proposed mechanism of this reaction is shown in Figure 1. The reaction of Dibal-H with aldehyde **1** gives aluminum alkoxide **i**, which undergoes nucleophilic addition with aldehyde **1** to give the corresponding aluminum alkoxide **ii**. The six-membered ring transition state **B'**, which is formed from the reaction of intermediate **ii** with aldehyde **1**, undergoes Tishchenko reaction to give not only the corresponding ester **7**, but also aluminum alkoxide **i**, which can undergo the second cycle of Tishchenko reaction. It is worthy to mention that the alkoxy group of intermediate **i** is the only transferable group in the reaction. Therefore, the present reaction mechanism is different from Tishchenko reaction catalyzed by aluminum trialkoxides.[1]

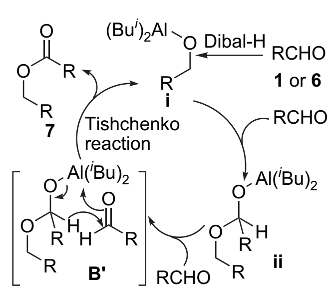


Figure 1. The possible reaction mechanism of aldehydes with Dibal-H via Tishchenko reaction.

The aldehydes **6i**, **6j** tethered with methoxycarbonyl group and **6k**, **6l** tethered with dimethyl acetal group also underwent Tishchenko reactions in modest to good yields (entries 9–12). For some unknown reason, the results indicate that the spacer group length will affect their chemical yields (entries 9 vs 10, 11 vs 12). The aldehyde **6m** tethered with methyl ketone gave the corresponding ester in 33% yield (entry 13). Dibal-H may also reduce ketone group and this side reaction will terminate the catalytic cycle shown in Figure 1. Therefore, the yield of the product **7m** is low. Both 6-iodohexanal (**6n**) and 6-bromohexanal (**6o**) react with a catalytic amount of Dibal-H to give the corresponding Tishchenko reaction products. The yield of the bromo compound is better than that of the iodo one probably due to the less tendency of the elimination for the bromo compound (entries 14 and 15). α-Alkoxyacetaldehydes **6p–6r** and β-alkoxyacetaldehyde **6s** undergo Tishchenko reactions in good yields irrelevant of their protecting groups (entries 16–19). The bulky trityl group does not retard the reaction at all (entry 18). This observation can be applied to carry out Tishchenko reaction of the optical active (*R*)-(−)-glyceraldehyde acetonide (**6t**)[18] and the acetonides **6u–6v** derived from D-ribose. All of these Tishchenko products are optically pure indicating that no epimerization occurred during the reaction (entries 20–22). Unfortunately, the α,β-unsaturated aldehydes and aryl aldehydes did not give the desired products. Small amount of reduction products was detected and most of the starting material was recovered in these cases.

2.3. Competition between Tishchenko and Oppenauer reactions of α-alkyl-α-silyloxyacetaldehydes promoted by Dibal-H

Interestingly, when α-alkyl-α-silyloxyacetaldehyde **9** was treated with a catalytic amount of Dibal-H, α-silyloxy ketone **11** was isolated instead of Tishchenko product **10** (Eq. 3, entries 1 and 2, Table 2). However, α-*tert*-butyl-α-silyloxyacetaldehyde (**9c**) did not furnish any desired product (entry 3). Presumably, the chemical reaction is a functional steric encumbrance of the α-substituent. Interestingly, Dibal-H reacts with α-phenyl-β-silyloxyacetaldehyde (**9d**) to give both Tishchenko product **10d** (37% yield) and Oppenauer oxidation product **11d** (26% yield) (entry 4). We are unable to rationalize the differences in these reactions. The proposed mechanism of the Oppenauer reaction product formation is shown in Figure 2. The reaction of Dibal-H with aldehyde **9a** (when R is $Ph(CH_2)_3$–) gives aluminum alkoxide **iii**, which undergoes 1,4-silyl group migration to give the corresponding

Table 2. Competition of Tishchenko and Oppenauer pathways in the reaction of α-silyloxy, β-silyloxy-, and α-acetoxy-aldehydes promoted by Dibal-H

Entry	R=	*n*	Σ	**8**	Time (h)	**9**	Yield (%)	Time (h)	**10**	Yield (%)	**11**	Yield (%)
1	$Ph(CH_2)_3$–	0	TBS	**8a**	8[a]	**9a**	70	12	**10a**	0	**11a**	78
2	Cyclohexyl–	0	TBS	**8b**	6[a]	**9b**	79	14	**10b**	0	**11b**	45
3	*t*-Butyl–	0	TBS	**8c**	8[a]	**9c**	68	26	**10c**	0	**11c**	0
4	Ph–	0	TBS	**8d**	6[b]	**9d**	75	8	**10d**	37	**11d**	26
5	$Ph(CH_2)_2$–	1	TBS	**8e**	6[a]	**9e**	74	6	**10e**	52	**11e**	29
6[c]	Cyclohexyl–	0	Ac	**8f**	4[a]	**9f**	64	12	**10f**	31[c]	**11f**	10

[a] Et_3N was used to workup ozonolytic reaction.
[b] Ph_3P was used to workup ozonolytic reaction.
[c] (1,2-Diacetoxyethyl)cyclohexane was isolated in 16% yield.

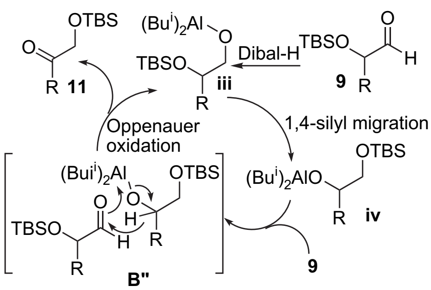
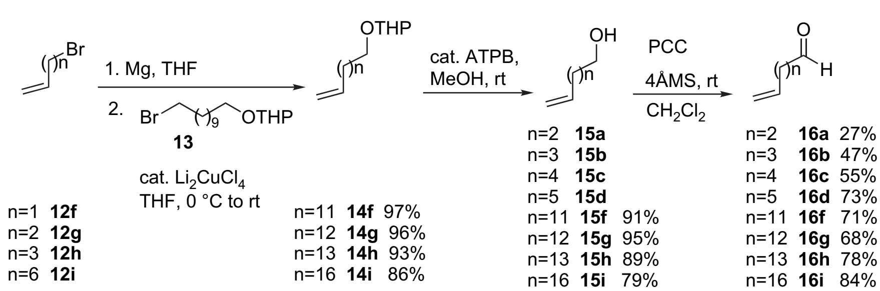


Figure 2. The possible reaction mechanism of α-silyloxy aldehyde **9** with Dibal-H via Oppenauer oxidation pathway.

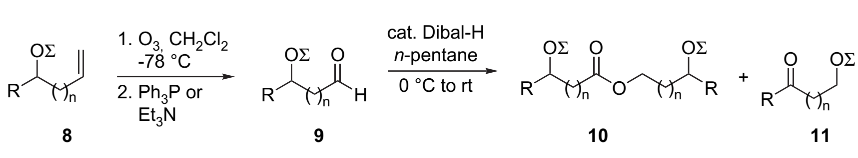
aluminum alkoxide **iv**. The six-membered ring transition state **B″**, which is formed from the reaction of intermediate **iv** with aldehyde **9a**, undergoes Oppenauer oxidation[19] to give not only the corresponding α-silyloxy ketone **11a**, but also aluminum alkoxide **iii**, which can undergo the second cycle of the reaction. The failure of secondary aluminum alkoxide **iv** to proceed via Tishchenko pathway may be due to the steric reason. In addition, the results also indicate that the migration of the silyl group from secondary alkoxysilyl ether **iii** to the primary alkoxysilyl ether **iv** is a favorable process. Similarly, Dibal-H reacts with β-silyloxyaldehyde **9e** to give both Tishchenko product **10e** (52% yield) and Oppenauer oxidation product **11e** (29% yield) (entry 5). The formation of product **11e** is resulted from the 1,5-silyl group migration, which is not a facile process, and hence Tishchenko pathway becomes predominant. On comparison of the results in entries 2 and 6, it indicates that the silyl group is better than acetyl group for the 1,4-group migration.

2.4. Tishchenko reaction of terminal alkene tethered with aldehyde promoted by Dibal-H and its application in macrolactone formation

Macrocyclic lactones are important components of naturally occurring compounds. There are several multiple-step syntheses of these compounds in moderate to high yields, which include the following: ring enlargement of smaller rings, lactonization of ω-hydroxycarboxylic acids with different reagents, C–C bond formation by intramolecular addition of enolate ion with Pd^0 catalyst, intramolecular diacetylene ester coupling, intramolecular Wittig or Horner–Emmons reactions and by olefin metathesis.[20,21] Recently, several macrocyclic natural products have been prepared by ring-closing metathesis (RCM) methodology.[22] The precursor of the RCM reaction, i.e., terminal diene ester, to prepare the macrocyclic lactone is usually made by the condensation of the corresponding ω-alkene carboxylic acid and ω-alkene alcohol. The aforementioned results indicate that the terminal diene ester should be prepared by Tishchenko reaction of the ω-alkene aldehyde. In order to demonstrate the potential of our methodology in this application, we need to prepare ω-alkene aldehyde **16**. ω-Alkene aldehydes **16a–16d** were prepared from oxidation of the readily available alcohols **15a–15d** with pyridinium chlorochromate (Scheme 1). The shorter the carbon chain, the lower the yields of the

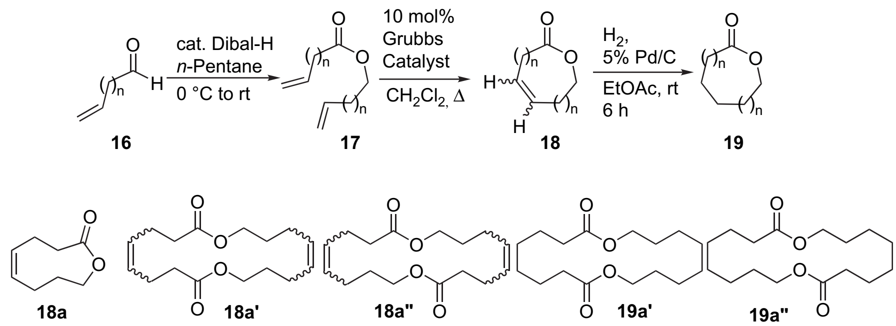


Scheme 1.

 (3)

aldehydes, probably due to their volatility. The Li_2CuCl_4 catalyzed cross-coupling[23] between bromoalkoxy-tetrahydropyran **13**[24] and Grignard reagent prepared from the corresponding olefinic bromides **12f–12i** in tetrahydrofuran gave the ω-alkenyloxytetrahydropyrans **14f–14i** in good yields. Deprotection of compounds **14f–14i** with ATPB[25] in methanol followed by pyridinium chlorochromate oxidation gave the olefinic aldehydes **16f–16i** in good yields (Scheme 1).

product isolated from seeds of *Hibiscus abelmoschus*[28] and radiata pine forest litter;[29] **19f** is a natural product isolated from *Armitermes teevani* and *Armitermes neotenicus*; **19g–19i** are natural products isolated from *A. teevani*.[30] In other words, all these natural products were successfully prepared from the corresponding ω-alkene aldehydes **16** via Tishchenko reaction, RCM reaction, and hydrogenation sequence.

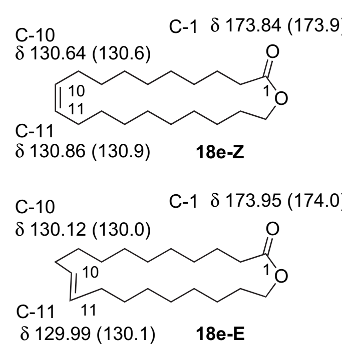


(4)

When the aldehyde **16a** was treated with Dibal-H, Tishchenko reaction product **17a** was obtained in 45% yield (entry 1, Table 3). When the 1,ω-diene ester **17a** was treated with first-generation Grubbs catalyst in dichloromethane, inseparable unsaturated diolides **18a′** and **18a″** were formed in 30% yield and no nine-membered ring lactone **18a** could be isolated. Catalytic hydrogenation of unsaturated diolides **18a′** and **18a″** afforded the inseparable diolides **19a′** and 1,10-dioxacyclooctadecane-1,11-dione (**19a″**) in 61% yield (entry 1, Table 3). The intramolecular cyclization of 8-hydroxy-octanoic acid was also known to give the diolides **19a″** in high yield,[26] because 8–11 membered ring closure is an unfavored process.[27] Therefore, intermolecular crossed metathesis of the terminal diene ester **17a** followed by ring-closing metathesis (RCM) gave compounds **18a′** and **18a″** become an overwhelming process.

Under the conditions described above, treatment of ω-alkene aldehydes **16b–16i** with Dibal-H gave Tishchenko products **17b–17i** in good yields, respectively. Furthermore, a two-step transformation of **17b–17i** via consecutive RCM reaction and catalytic hydrogenation gave the corresponding macrolactones **19b–19i**, respectively, in good yields (entries 2–9, Table 3). This RCM strategy allows synthesis of 11- up to 37-membered lactones. It is interesting to point out that macrolactone **19d** is a natural

Concerning about the *E*/*Z*-selectivity of the RCM reaction in present study, the assignment of the characteristic C-13 NMR chemical shifts of isomers **18e-*Z*** and **18e-*E*** was reported[20a] and shown in Figure 3. The C-10 and C-11 chemical shifts of compound **18e-*Z*** appear at 130.64 and 130.86 ppm, respectively. The C-10 and C-11 chemical shifts of compound **18e-*E*** are slightly shifted to upfield (Fig. 3). In general, the *E*- and *Z*-isomers of the unsaturated macrocyclic lactones are inseparable. In order to use C-13 NMR (100 MHz) peak intensity to determine the isomer



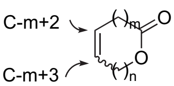
The data in the parentheses was reported in reference 20a.

Figure 3. The characteristic C-13 chemical shift of compounds **18e-Z** and **18e-*E***.

Table 3. Preparation of macrolactones (n=2–16) from aldehydes tethered with terminal olefin via three sequential catalytic steps

Entry	$H_2C{=}CH(CH_2)_nCHO$ n=	**16**	Time (h)	Yield (%)	Ester **17**	Time (h)	Yield (%)	Unsaturated lactone **18** (mixture of *Z*/*E*)	Yield (%)	Lactone **19**
1	2	**16a**	12	45	**17a**	24	30	**18a′** and **18a″**	61	**19a′** and **19a″**
2	3	**16b**	12	41	**17b**	9	58	**18b**	89	**19b**
3	4	**16c**	8	68	**17c**	11	57	**18c**	71	**19c**
4	5	**16d**	8	62	**17d**	10	59	**18d**	87	**19d**
5	8	**16e**	5	76	**17e**	6	60	**18e**	82	**19e**
6	11	**16f**	6	67	**17f**	11	75	**18f**	88	**19f**
7	12	**16g**	8	72	**17g**	14	57	**18g**	90	**19g**
8	13	**16h**	8	74	**17h**	18	57	**18h**	86	**19h**
9	16	**16i**	10	62	**17i**	29	63	**18i**	92	**19i**

Table 4. The characteristic C-13 NMR chemical shifts and the isomeric ratio of the unsaturated macrolactones **18**

	Ring size	*Z*-Isomer		*E*-Isomer		*E*/*Z* ratio
		δ (C-m+2)	δ (C-m+3)	δ (C-m+2)	δ (C-m+3)	
18b (*m*=3, *n*=4)	11	131.08	130.13	130.26	129.37	1/1
18c (*m*=4, *n*=5)	13	130.36	130.25	130.16	130.02	1/1
18d (*m*=5, *n*=6)	15	131.10	130.79	130.41	130.15	1/2.2
18e (*m*=8, *n*=9)	21	130.86	130.64	130.12	129.99	1/2.5
18f (*m*=11, *n*=12)	27	130.68	130.59	130.06	130.04	1/2.9
18g (*m*=12, *n*=13)	29	130.56	130.53	129.99	129.94	1/3.1
18h (*m*=13, *n*=14)	31	130.53	130.45	129.94	129.91	1/3.9
18i (*m*=16, *n*=17)	37	130.49	130.46	129.94	129.92	1/4.2

ratio, the inverse gated proton decoupling technique was applied to take the C-13 NMR spectrum of the unsaturated macrocyclic lactones. The chemical shifts of the *E*- and *Z*-olefinic carbon resonance peaks are listed in Table 4. The *E*/*Z*-selectivity depends on the ring strain. The larger the ring size, the lower the *E*/*Z* ratio that was observed.

3. Conclusions

In conclusion, the slow addition of the catalytic amount of Dibal-H to the aldehydes in *n*-pentane gives the corresponding Tishchenko products in good yields. The reactions work quite well for aldehydes bearing 2°-, 3°-, and 4°-α-carbon and a variety of functional groups. However, α-silyloxy aldehyde affords the Oppenauer oxidation product in good yield under similar conditions. This Dibal-H-promoted Tishchenko reaction methodology can be applied to the ω-alkene aldehydes to give 1,ω-diene esters, which can be further applied to prepare the macrocyclic lactones sequentially via RCM and hydrogenation.

4. Experimental

4.1. General

All reactions were carried out under nitrogen. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Melting points were determined by using a Thomas–Hoover melting point apparatus and were uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX400 spectrometer, and chemical shifts were given in parts per million downfield from tetramethylsilane (TMS). IR spectra were taken with a Perkin–Elmer 682 spectrophotometer and only noteworthy absorptions were listed. Mass spectra were measured on a Micromass Trio-2000 GC/MS spectrometer (National Chiao-Tung University) by electronic impact at 70 eV (unless otherwise indicated). High-Resolution Mass Spectroscopy (HRMS) was carried out on a Finnigan/Thermo Quest MAT 95XL (National Chung Hsing University) Mass Spectrometer and FAB Mass spectra were recorded with 3-nitrobenzyl alcohol matrix using argon or xenon as the target gas. Aldehydes used in this study were either commercially available or prepared by the literature method. 8-Oxooctanoic acid methyl ester (**6i**), 6-oxohexanoic acid methyl ester (**6j**), 8,8-dimethoxyoctanal (**6k**), and 6,6-dimethoxyhexanal (**6l**) were prepared according to the literature procedure from their corresponding cycloalkenes.[31] 10-Oxoundecanal (**6m**), 6-iodohexanal (**6n**), 6-bromohexanal (**6o**), pent-4-enal (**16a**), and hex-5-enal (**16b**) were prepared from their corresponding alcohols by PCC oxidation.[32] 10-Oxoundecanal (**6m**) was prepared by Wacker oxidation[33] of undec-10-en-1-ol followed by PCC oxidation. α-Benzyloxyacetaldehyde (**6q**), α-trityloxyacetaldehyde (**6r**), and β-benzyloxyacetaldehyde (**6s**) were prepared by the ozonolysis of the corresponding terminal alkene followed by treatment with triethylamine.[34] (*R*)-Glyceraldehyde dimethyl acetal (**6t**) was prepared by oxidative cleavage of the corresponding glycol.[35] Aldehydes **6u** and **6v** were prepared according to the literature procedure from D-ribose precursor.[36] Non-8-ynal (**6g**) was prepared from the zipper reaction of non-3-yn-1-ol followed by Swern oxidation.[37] 9-Phenylnon-8-ynal (**6h**) was prepared by Swern oxidation of the Sonogashira coupling product from non-3-yn-1-ol with bromobenzene.[38] Undec-10-enal (**16e**) is commercially available from Aldrich Company.

4.2. General procedure for aldehyde formation by the ozonolysis of terminal alkene followed by treatment with Ph_3P (for compounds 6p, 9a–9c, and 9f)

A 500 mL two-necked flask fitted with a glass tube to admit ozone, a $CaCl_2$ drying tube, and a magnetic stirring bar was charged with allyl phenyl ether (2.00 g, 14.93 mmol) in anhydrous CH_2Cl_2 (300 mL). The flask was cooled to −78 °C and ozone was bubbled through the solution. When the solution turned blue, ozone addition was stopped. Nitrogen was passed through the solution until the blue color was discharged. To the resulting solution was added Ph_3P (4.11 g, 15.67 mmol) and warmed slowly to rt. After stirring for 10 h, the reaction mixture was concentrated and chromatographed on a silica gel column to give aldehyde **6p** (1.10 g, 8.09 mmol, 55% yield) as a colorless oil, R_f=0.48 (hexane/EtOAc=1:1).

4.2.1. Phenoxyacetaldehyde (6p). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.55 (s, 2H), 6.89–6.94 (m, 2H), 7.00–7.03 (m, 1H), 7.29–7.33 (m, 2H), 9.85 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 72.7, 114.6, 122.0, 129.7, 157.7, 199.3; IR (thin film, NaCl plates): 3061, 3042, 2935, 2883, 1738, 1599, 1496, 1246, 754, 691 cm^{-1}; MS *m*/*z* (relative intensity): 136 (M^+, 75), 107 (72), 77 (100).

4.2.2. 2-(*tert*-Butyldimethylsilyloxy)-5-phenylpentanal (9a). Yield: 70% from 1-(3-phenylpropyl)prop-2-en-1-yl *tert*-butyldimethylsilyl ether (**8a**),[39] colorless oil, R_f=0.60 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.05 (s, 3H), 0.06 (s, 3H), 0.91 (s, 9H), 1.61–1.75 (m, 4H), 2.62 (t, *J*=7.2 Hz, 2H), 3.96–3.99 (m, 1H), 7.14–7.19 (m, 3H), 7.24–7.28 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −4.9, −4.7, 18.1, 25.7, 26.2, 32.1, 35.6, 77.5, 125.8, 128.3, 141.7, 204.0; IR (thin film, NaCl plates): 3062, 3027, 2952, 2929, 2857, 1710, 1454, 1254, 837, 747, 699 cm^{-1}; MS *m*/*z* (relative intensity): 263 (M^+−29, 12), 233 (18), 131 (100), 117 (52), 105 (18), 91 (68); HRMS calcd for $C_{16}H_{25}O_2Si$ (M^+−15) 277.1624, found 277.1624.

4.2.3. (*tert*-Butyldimethylsilyloxy)cyclohexylacetaldehyde (9b). Yield: 79% from 1-(3-phenylpropyl)prop-2-en-1-yl *tert*-butyldimethylsilyl ether (**8b**),[40] colorless oil, R_f=0.71 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.05 (s, 3H), 0.06 (s, 3H), 0.93 (s, 9H), 1.17–1.24 (m, 5H), 1.64–1.76 (m, 6H), 3.70 (dd, J=5.1 and 2.2 Hz, 1H), 9.59 (d, J=2.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −5.1, −4.6, 18.2, 25.8, 26.0, 26.1, 26.2, 27.3, 29.0, 41.2, 81.8, 204.7; IR (thin film, NaCl plates): 2930, 2856, 1735, 1451, 1126, 839, 778 cm^{-1}; MS *m/z* (relative intensity): 257 (M^++1, 4), 241 (M^+−15, 7), 199 (100), 117 (8), 55 (2); HRMS calcd for $C_{13}H_{25}O_2Si$ (M^+−15) 241.1624, found 241.1614.

4.2.4. 2-(*tert*-Butyldimethylsilyloxy)-3,3-dimethylbutyraldehyde (9c). Yield: 68% from 1-*tert*-butyl-prop-2-en-1-yl *tert*-butyldimethylsilyl ether (**8c**), colorless oil;[41] R_f=0.67 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.02 (s, 3H), 0.05 (s, 3H), 0.94 (s, 9H), 0.96 (s, 9H), 3.48 (d, J=3.2 Hz, 1H), 9.60 (d, J=3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −5.1, −4.5, 18.2, 25.7, 25.8, 35.8, 84.3, 204.6; IR (thin film, NaCl plates): 2957, 2932, 2860, 1735, 1103, 837, 777 cm^{-1}; MS *m/z* (relative intensity): 231 (M^++1, 2), 229 (M^+−1, 1), 201 (19), 189 (52), 161 (31), 103 (40), 75 (100), 57 (57); HRMS calcd for $C_{12}H_{25}O_2Si$ (M^+−1) 229.1624, found 229.1615.

4.2.5. 2-Acetoxy-2-cyclohexylacetaldehyde (9f). Yield: 64% from 1-cyclohexyl-prop-2-en-1-yl acetate (**8f**),[42] colorless oil, R_f=0.28 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.16–1.30 (m, 5H), 1.65–1.79 (m, 5H), 1.94–1.95 (br m, 1H), 2.18 (s, 3H), 4.85 (d, J=4.8 Hz, 1H), 9.54 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.4, 25.8, 25.9, 27.5, 28.9, 38.4, 81.9, 170.5, 204.7; IR (thin film, NaCl plates): 2929, 2855, 1739, 1451, 1372, 1234, 1030 cm^{-1}; MS *m/z* (relative intensity): 185 (M^++1, 3), 171 (48), 95 (45), 55 (35), 43 (100); HRMS calcd for $C_{10}H_{16}O_3$ 184.1099, found 184.1101.

4.3. General procedure for aldehyde formation from the ozonolysis of terminal alkene followed by treatment with Et_3N (for compounds 6q, 9d, and 9e)

A 250 mL two-necked flask fitted with a glass tube to admit ozone, a $CaCl_2$ drying tube, and a magnetic stirring bar was charged with allyl benzyl ether (1.00 g, 6.71 mmol) in anhydrous CH_2Cl_2 (140 mL). The flask was cooled to −78 °C and ozone was bubbled through the solution. When the solution turned blue, ozone addition was stopped. Nitrogen was passed through the solution until the blue color was discharged. To the resulting solution was added Et_3N (0.98 mL, 7.04 mmol) and warmed slowly to rt. After stirring for 7 h, the reaction mixture was concentrated and chromatographed on a silica gel column to give compound **6q** (0.61 g, 4.03 mmol, 60% yield) as a colorless oil, R_f=0.49 (hexane/EtOAc=1:1).

4.3.1. Benzyloxyacetaldehyde (6q).[34a] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.09 (s, 2H), 4.63 (s, 2H), 7.34–7.37 (m, 5H), 9.73 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 74.1, 75.7, 128.4, 128.6, 129.0, 137.4, 200.8; IR (thin film, NaCl plates): 3062, 3031, 2917, 2870, 1736, 1454, 1103, 738, 698 cm^{-1}; MS *m/z* (relative intensity): 150 (M^+, 18), 121 (16), 107 (23), 91 (100), 77 (4).

4.3.2. (*tert*-Butyldimethylsilyloxy)phenylacetaldehyde (9d). Yield: 75% from 1-phenylprop-2-en-1-yl *tert*-butyldimethylsilyl ether (**8d**),[43] colorless oil, R_f=0.43 (hexane/EtOAc=5:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.04 (s, 3H), 0.12 (s, 3H), 0.95 (s, 9H), 5.00 (d, J=2.0 Hz, 1H), 9.51 (d, J=2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −4.4, 18.7, 26.2, 80.4, 126.8, 128.8, 129.1, 137.0, 199.8; IR (thin film, NaCl plates): 3064, 2954, 2930, 2858, 1705, 1471, 1254, 838, 781, 688 cm^{-1}; MS *m/z* (relative intensity): 250 (M^+, 2), 235 (M^+−15, 5), 193 (36), 149 (66), 105 (100), 77 (48); HRMS calcd for $C_{14}H_{22}O_2Si$ 250.1389, found 250.1382.

4.3.3. 3-(*tert*-Butyldimethylsilyloxy)-5-phenylpentanal (9e). Yield: 74% from 1-(2-phenylethyl)-but-3-en-1-yl *tert*-butyldimethylsilyl ether (**8e**),[44] colorless oil, R_f=0.39 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.06 (s, 3H), 0.09 (s, 3H), 0.90 (s, 9H), 1.84–1.90 (m, 2H), 2.57–2.60 (m, 2H), 2.64–2.68 (m, 2H), 4.26 (quint, J=5.8 Hz, 1H), 7.16–7.19 (m, 3H), 7.26–7.28 (m, 2H), 9.82 (d, J=2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −4.6, −4.4, 18.0, 25.8, 31.5, 39.5, 50.8, 67.7, 125.9, 128.3, 128.4, 141.7, 201.8; IR (thin film, NaCl plates): 3027, 2953, 2929, 1713, 1471, 1255, 1098, 837, 776, 699 cm^{-1}; MS *m/z* (relative intensity): 293 (M^++1, 4), 251 (25), 233 (24), 131 (58), 117 (100), 91 (96). HRMS calcd for $C_{17}H_{28}O_2Si$ 292.1859, found 292.1856.

4.4. General procedure for aldehyde formation from the PCC oxidation of primary alcohol (for compounds 6s, 6g, 6h, and 16c–16i)

4.4.1. 3-Benzyloxypropionaldehyde (6s).[34b] To a mixture of 3-benzyloxypropanol (2.01 g, 12.11 mmol) in CH_2Cl_2 (25 mL) were added PCC (3.13 g, 14.53 mmol) and 4 Å molecular sieves (4.0 g) at 0 °C and warmed slowly to rt. After stirring for 6 h, the reaction mixture was concentrated and then added ether (10 mL). The mixture is filtered through Celite and the solid was washed twice with ether (15 mL). The combined filtrate was evaporated and the residue was chromatographed on a silica gel column to give aldehyde **6s** (1.13 g, 6.91 mmol, 56% yield) as a pale yellow oil, R_f=0.42 (hexane/EtOAc=5:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.71 (dt, J=6.0 and 1.8 Hz, 2H), 3.84 (t, J=6.0 Hz, 2H), 4.56 (s, 2H), 7.32–7.40 (m, 5H), 9.81 (t, J=1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 43.8, 63.8, 73.2, 127.6, 127.6, 128.3, 137.8, 200.9; IR (thin film, NaCl plates): 3063, 3032, 2868, 1721, 1454, 1203, 1102, 739, 699 cm^{-1}; MS *m/z* (relative intensity): 164 (M^+, 4), 163 (M^+−1, 4), 107 (81), 91 (100), 77 (24).

4.4.2. Non-8-ynal (6g). Non-8-yn-1-ol was prepared from non-3-yn-1-ol according to the literature procedure.[37a] Compound **6g** was prepared as a pale yellow oil in 69% yield from non-8-yn-1-ol by PCC oxidation, R_f=0.67 (hexane/EtOAc=5:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33–1.47 (m, 4H), 1.50–1.57 (m, 2H), 1.63–1.68 (m, 2H), 1.94 (t, J=2.6 Hz, 1H), 2.19 (td, J=6.8 and 2.6 Hz, 2H), 2.43 (td, J=7.3 and 1.8 Hz, 2H), 9.77 (t, J=1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.3, 21.9, 28.1, 28.3, 28.6, 43.8, 68.2, 84.4, 202.6; IR (thin film, NaCl plates): 3303, 3054, 2986, 2940, 2305, 2860, 2115, 1709, 1421, 1265, 742, 641 cm^{-1}; MS *m/z* (relative intensity): 137 (M^+−1, 4), 109 (19), 94 (79), 79 (65), 55 (52), 41 (100); HRMS calcd for $C_9H_{14}O$ 138.1045, found 138.1048.

4.4.3. 9-Phenylnon-8-ynal (6h). To a mixture of bromobenzene (0.22 mL, 2.07 mmol), $Pd(PPh_3)_4$ (20.8 mg, 18 μmol), and CuI (6.9 mg, 36 μmol) in Et_3N (5 mL) was added a solution of non-8-yn-1-ol (250 mg, 1.80 mmol) in MeCN (1 mL) and then stirred at rt for 8 h under an argon atomosphere.[45] After the reaction was completed, ammonium chloride solution was added and the product was extracted with ether. Then the organic phase was dried over Na_2SO_4 and concentrated. The residue was chromatographed on a silica gel column to give 9-phenyl-non-8-yn-1-ol (267 mg, 1.23 mmol, 69% yield) as a pale yellow oil, R_f=0.52 (hexane/EtOAc=5:1). The general procedure was followed to carry out the PCC oxidation of 9-phenyl-non-8-yn-1-ol to give 9-phenylnon-8-ynal (**6h**) in 83% yield as a pale yellow oil, R_f=0.57 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.36–1.42 (m, 2H), 1.45–1.51 (m, 2H), 1.57–1.68 (m, 4H), 2.41 (t, J=7.0 Hz, 2H), 2.43 (t, J=7.4 Hz, 2H), 7.26–7.27 (br s, 3H), 7.38–7.39 (br s, 2H), 9.77 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.3, 22.0, 28.5, 28.6, 28.7, 43.8, 80.8, 90.1, 124.0, 127.5, 128.2, 131.5, 202.6; IR (thin film, NaCl plates): 3057, 2933, 2858, 2719, 2231, 1724, 1490, 758, 692 cm^{-1}; MS *m/z* (relative intensity): 214 (M^+, 7), 157 (12), 143 (36), 130 (96), 115 (100), 91 (23), 77 (15); HRMS calcd for $C_{15}H_{18}O$ 214.1358, found 214.1355.

4.4.4. Hept-6-enal (16c). The general procedure of the PCC oxidation was followed to prepare aldehyde **16c** (1.36 g, 12.12 mmol, 55% yield) in 2 h from alcohol **15c** (2.94 mL, 21.89 mmol) by PCC. A pale yellow oil, R_f=0.63 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.42–1.47 (m, 2H), 1.61–1.69 (m, 2H), 2.08 (td, J=7.2 and 7.2 Hz, 2H), 2.44 (td, J=7.3 and 1.5 Hz, 2H), 4.96–5.04 (m, 2H), 5.74–5.84 (m, 1H), 9.77 (t, J=1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 28.2, 33.3, 43.6, 114.7, 138.1, 202.5; IR (thin film, NaCl plates): 3077, 2976, 2930, 2858, 2719, 1726, 1640, 996, 911, 737 cm^{-1}; MS *m/z* (relative intensity): 112 (M^+, 2), 68 (27), 55 (79), 41 (100); HRMS calcd for $C_7H_{12}O$ (M^+) 112.0887, found 112.0879.

4.4.5. Oct-7-enal (16d). The general procedure of the PCC oxidation was followed to prepare aldehyde **16d** (1.23 g, 9.75 mmol, 73% yield) in 2 h from alcohol **15d** (1.70 g, 13.26 mmol) by PCC. A pale yellow oil, R_f=0.56 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.41–1.47 (m, 2H), 1.61–1.69 (m, 2H), 2.06 (td, J=7.4 and 6.9 Hz, 2H), 2.43 (td, J=7.4 and 1.8 Hz, 2H), 4.93–5.03 (m, 2H), 5.75–5.85 (m, 1H), 9.77 (t, J=1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.8, 28.5, 33.4, 43.7, 114.4, 138.5, 202.6; IR (thin film, NaCl plates): 3077, 2930, 2858, 2719, 1726, 1640, 996, 911, 737 cm^{-1}; MS *m/z* (relative intensity): 127 (M^++1, 2), 125 (M^+−1, 2), 97 (3), 67 (35), 55 (100), 41 (79).

4.4.6. Tetradec-13-enal (16f). The general procedure of the PCC oxidation was followed to prepare aldehyde **16f** (1.34 g, 6.38 mmol, 71% yield) in 2 h from alcohol **15f** (1.91 g, 9.01 mmol) by PCC. A white solid, mp 61–62 °C, R_f=0.57 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.27–1.39 (m, 16H), 1.60–1.65 (m, 2H), 2.04 (td, J=7.6 and 6.8 Hz, 2H), 2.42 (td, J=7.4 and 1.8 Hz, 2H), 4.91–5.02 (m, 2H), 5.76–5.86 (m, 1H), 9.77 (t, J=1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.0, 28.8, 29.05, 29.07, 29.27, 29.33, 29.4, 29.5, 33.7, 43.8, 114.0, 139.1, 202.7; IR (thin film, NaCl plates): 3056, 2925, 2853, 2724, 1723, 1640, 1469, 1265, 995, 914, 741 cm^{-1}; MS *m/z* (relative intensity): 210 (M^+, 2), 209 (M^+−1, 3), 109 (29), 95 (56), 81 (68), 67 (58), 54 (100), 41 (88); HRMS calcd for $C_{14}H_{26}O$ 210.1984, found 210.1987.

4.4.7. Pentadec-14-enal (16g). The general procedure of the PCC oxidation was followed to prepare aldehyde **16g** (610 mg, 2.72 mmol, 68% yield) in 2 h from alcohol **15g** (902 mg, 3.99 mmol) by PCC. A pale yellow solid, mp 47–48 °C, R_f=0.64 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26–1.39 (m, 18H), 1.59–1.64 (m, 2H), 2.04 (td, J=7.4 and 6.8 Hz, 2H), 2.42 (td, J=7.4 and 1.8 Hz, 2H), 4.92–5.02 (m, 2H), 5.76–5.87 (m, 1H), 9.77 (t, J=1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.0, 28.9, 29.07, 29.09, 29.3, 29.35, 29.42, 29.50, 29.52, 29.54, 33.7, 43.8, 114.0, 139.1, 202.7; IR (thin film, NaCl plates): 3077, 2925, 2853, 2714, 1728, 1640, 1465, 993, 910, 736 cm^{-1}; MS *m/z* (relative intensity): 224 (M^+, 4), 206 (8), 109 (28), 95 (53), 81 (62), 67 (100), 54 (84), 41 (95); HRMS calcd for $C_{15}H_{28}O$ 224.2140, found 224.2142.

4.4.8. Hexadec-15-enal (16h). The general procedure of the PCC oxidation was followed to prepare aldehyde **16h** (610 mg, 2.56 mmol, 78% yield) in 2 h from alcohol **15h** (808 mg, 3.37 mmol) by PCC. A white solid, mp 64–65 °C, R_f=0.56 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26–1.39 (m, 20H), 1.59–1.64 (m, 2H), 2.04 (td, J=7.2 and 6.8 Hz, 2H), 2.42 (td, J=7.4 and 1.6 Hz, 2H), 4.91–5.02 (m, 2H), 5.77–5.87 (m, 1H), 9.77 (t, J=1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.9, 28.8, 29.1, 29.26, 29.33, 29.4, 29.48, 29.52, 33.7, 43.8, 114.0, 139.0, 202.5; IR (thin film, NaCl plates): 3077, 2925, 2851, 2721, 1725, 1641, 1469, 1265, 993, 912, 742 cm^{-1}; MS *m/z* (relative intensity): 237 (M^+−1, 7), 236 (M^+−2, 7), 222 (4), 95 (13), 81 (21), 69 (50), 55 (100), 41 (77); HRMS calcd for $C_{16}H_{30}O$ 238.2297, found 238.2299.

4.4.9. Nonadec-18-enal (16i). The general procedure of the PCC oxidation was followed to prepare aldehyde **16i** (330 mg, 1.18 mmol, 84% yield) in 2 h from alcohol **15i** (413 mg, 1.46 mmol) by PCC. A white solid, mp 40 °C, R_f=0.74 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.25–1.39 (m, 26H), 1.60–1.65 (m, 2H), 2.04 (td, J=7.5 and 6.9 Hz, 2H), 2.42 (td, J=7.4 and 1.8 Hz, 2H), 4.91–5.02 (m, 2H), 5.77–5.87 (m, 1H), 9.77 (t, J=1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.0, 28.9, 29.1, 29.3, 29.35, 29.4, 29.5, 29.55, 29.6, 33.7, 43.8, 114.0, 139.0, 202.4; IR (thin film, NaCl plates): 3077, 2922, 2851, 2713, 1729, 1466, 1265, 992, 905, 721 cm^{-1}; MS *m/z* (relative intensity): 281 (M^++1, 9), 280 (M^+, 11), 262 (21), 108 (23), 95 (37), 81 (38), 69 (43), 55 (100), 40 (58); HRMS calcd for $C_{19}H_{36}O$ 280.2766, found 280.2771.

4.5. General procedure for Tishchenko reaction of aldehyde promoted by Dibal-H (for compounds 7a–7v and 17a–17i)

To a solution of aldehyde **6p** (550 mg, 4.10 mmol) in *n*-pentane (10 mL) and CH_2Cl_2 (5 mL, *Note: CH_2Cl_2 is added only if the solubility of aldehyde is poor in n-pentane*) was added a solution of Dibal-H (0.41 mL, 1.0 M solution in hexane) in 1 mL of *n*-pentane dropwise by syringe pump over a period of 1 h at 0 °C. After stirring at ambient temperature for 8 h, to the reaction mixture was added 1 N HCl and extracted with CH_2Cl_2. The organic layer was dried over magnesium sulfate, filtered, and concentrated. The residue was chromatographed on a silica gel column to give ester **7p** (305 mg, 1.14 mmol, 63% yield) as a colorless oil, R_f=0.47 (hexane/EtOAc=3:1).

4.5.1. Phenoxyacetic acid 2-phenoxyethyl ester (7p). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.19 (t, *J*=4.7 Hz, 2H), 4.56 (t, *J*=4.7 Hz, 2H), 4.67 (s, 2H), 6.89–6.91 (m, 4H), 6.96–6.98 (m, 2H), 7.24–7.30 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 63.4, 65.3, 65.6, 114.6, 114.7, 121.3, 121.8, 129.5, 157.8, 158.3, 168.8; IR (thin film, NaCl plates): 3053, 2986, 1762, 1599, 1496, 1264, 1192, 737 cm^{-1}; MS *m*/*z* (relative intensity): 272 (M$^+$, 12), 179 (100), 107 (47), 77 (43); HRMS calcd for $C_{16}H_{16}O_4$ 272.1049, found 272.1056.

4.5.2. Cyclohexanecarboxylic acid cyclohexylmethyl ester (7a). Yield: 93%, colorless oil, R_f=0.65 (hexane/EtOAc=20:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.92–0.94 (m, 2H), 1.17–1.26 (m, 6H), 1.35–1.42 (m, 2H), 1.50–1.75 (m, 9H), 1.84–1.89 (m, 2H), 2.26 (tt, *J*=11.3 and 3.6 Hz, 1H), 3.83 (d, *J*=6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.4, 25.7, 25.8, 26.4, 29.1, 29.7, 37.2, 43.3, 69.2, 176.1; IR (KBr, neat): 2929, 2854, 1733, 1450, 1312, 1247, 1171, 1133, 1038 cm^{-1}; MS *m*/*z* (relative intensity): 224 (M$^+$, 100), 97 (18), 83 (21); HRMS calcd for $C_{14}H_{24}O_2$ 224.1767, found 224.1772.

4.5.3. 3-Phenylpropionic acid 3-phenylpropyl ester (7b). Yield: 77%, colorless oil, R_f=0.75 (hexane/EtOAc=5:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.90–1.97 (m, 2H), 2.62–2.66 (m, 4H), 2.96 (t, *J*=8.0 Hz, 2H), 4.09 (t, *J*=6.5 Hz, 2H), 7.14–7.31 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.1, 30.9, 32.1, 35.8, 63.7, 125.9, 126.2, 128.18, 128.29, 128.33, 128.40, 140.4, 141.1, 172.8; IR (KBr, neat): 3027, 2953, 1734, 1496, 1454, 1162, 747 cm^{-1}; MS *m*/*z* (relative intensity): 268 (M$^+$, 49), 118 (100), 116 (55), 91 (51); HRMS calcd for $C_{18}H_{20}O_2$ 268.1451, found 268.1457.

4.5.4. Heptanoic acid heptyl ester (7c). Yield: 77%, colorless oil, R_f=0.60 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.86–0.90 (m, 6H), 1.27–1.35 (m, 14H), 1.58–1.63 (m, 4H), 2.29 (t, *J*=7.7 Hz, 2H), 4.05 (t, *J*=6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.96, 14.00, 22.45, 22.54, 24.96, 25.9, 28.6, 28.8, 28.9, 31.4, 31.7, 34.4, 64.3, 173.9; IR (KBr, neat): 2930, 2857, 1739, 1467, 1378, 1354, 1170, 1103 cm^{-1}; MS *m*/*z* (relative intensity): 229 (M+1, 100), 131 (96), 113 (43), 98 (55), 70 (55); HRMS calcd for $C_{14}H_{28}O_2$ 228.2096, found 228.2093.

4.5.5. Isobutyric acid isobutyl ester (7d). Yield: 83%, colorless oil, R_f=0.63 (hexane/EtOAc=20:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.91 (d, *J*=6.7 Hz, 6H), 1.15 (d, *J*=7.0 Hz, 6H), 1.86–1.94 (m, 1H), 2.50–2.55 (m, 1H), 3.83 (d, *J*=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.97, 19.00, 27.8, 34.1, 70.3, 177.1; IR (KBr, neat): 2969, 2876, 1736, 1470, 1387, 1260, 1193, 1156, 807, 735 cm^{-1}.

4.5.6. Pivalic acid neopentyl ester (7e). Yield: 95%, colorless oil, R_f=0.88 (hexane/EtOAc=20:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.92 (s, 9H), 1.19 (s, 9H), 3.72 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.4, 27.2, 31.5, 38.9, 73.6, 178.5; IR (KBr, neat): 2961, 2873, 1733, 1480, 1394, 1366, 1285, 1158, 1039, 988, 918, 736 cm^{-1}.

4.5.7. 3,7-Dimethyloct-6-enoic acid 3,7-dimethyloct-6-enyl ester (7f). Yield: 77%, pale yellow oil, R_f=0.70 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.91 (d, *J*=6.6 Hz, 3H), 0.95 (d, *J*=6.7 Hz, 3H), 1.18–1.58 (m, 6H), 1.60 (s, 6H), 1.68 (s, 6H), 1.96–2.01 (m, 6H), 2.10 (dd, *J*=14.5 and 8.2 Hz, 1H), 2.30 (dd, *J*=14.5 and 6.0 Hz, 1H), 4.09–4.13 (m, 2H), 5.07–5.11 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.5, 19.3, 19.6, 25.3, 25.4, 25.6, 29.4, 30.0, 35.5, 36.7, 36.9, 41.8, 62.6, 124.2, 124.5, 131.2, 131.4, 173.2; $[\alpha]_D^{29.3}$ −13.95 (*c* 4.3×10^{-4}, CH_2Cl_2); IR (KBr, neat): 2967, 2918, 1736, 1457, 1384, 1195, 1152, 1078 cm^{-1}; MS *m*/*z* (relative intensity): 308 (M$^+$, 30), 138 (44), 95 (49), 81 (74), 69 (100); HRMS calcd for $C_{20}H_{36}O_2$ 308.2696, found 308.2706.

4.5.8. Non-8-ynoic acid non-8-ynyl ester (7g). Yield: 62%, colorless oil, R_f=0.49 (hexane/EtOAc=20:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.34–1.43 (m, 10H), 1.51–1.64 (m, 8H), 1.93–1.95 (m, 2H), 2.19 (td, *J*=6.9 and 2.6 Hz, 4H), 2.30 (t, *J*=7.5 Hz, 2H), 4.06 (t, *J*=6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.22, 18.26, 24.7, 25.7, 28.15, 28.23, 28.26, 28.5, 28.6, 34.2, 64.2, 68.12, 68.15, 84.37, 84.44, 173.7; IR (thin film, NaCl plates): 2935, 2860, 2115, 1734, 1461, 1176, 737, 634 cm^{-1}; MS *m*/*z* (relative intensity): 277 (M$^+$+1, 2), 107 (64), 93 (93), 79 (74), 41 (100); HRMS calcd for $C_{18}H_{28}O_2$ 276.2089, found 276.2096.

4.5.9. 9-Phenylnon-8-ynoic acid 9-phenylnon-8-ynyl ester (7h). Yield: 51%, pale yellow oil, R_f=0.41 (hexane/EtOAc=20:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.36–1.48 (m, 10H), 1.58–1.65 (m, 8H), 2.31 (t, *J*=7.5 Hz, 2H), 2.40 (t, *J*=7.0 Hz, 4H), 4.06 (t, *J*=6.7 Hz, 2H), 7.25–7.40 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.3, 19.4, 24.9, 25.8, 28.48, 28.52, 28.62, 28.63, 28.74, 34.3, 64.3, 80.66, 80.70, 90.15, 90.24, 124.06, 124.07, 127.4, 128.1, 131.5, 173.8; IR (thin film, NaCl plates): 3055, 2931, 2856, 2231, 1734, 1489, 1174, 756, 692 cm^{-1}; MS *m*/*z* (relative intensity): 428 (M$^+$, 55), 231 (30), 115 (100), 91 (55), 55 (18); HRMS calcd for $C_{30}H_{36}O_2$ 428.2715, found 428.2708.

4.5.10. Octanedioic acid 7-methoxycarbonylheptyl ester methyl ester (7i). Yield: 61%, colorless oil, R_f=0.25 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29–1.31 (m, 10H), 1.50–1.60 (m, 8H), 2.22–2.28 (m, 6H), 3.62 (s, 6H), 4.00 (t, *J*=6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.6, 24.66, 24.72, 25.6, 28.5, 28.6, 28.8, 28.9, 33.86, 33.90, 34.1, 51.3, 64.2, 173.7, 174.0, 174.1; IR (KBr, neat): 2936, 2859, 1739, 1437, 1360, 1173 cm^{-1}; MS *m*/*z* (relative intensity): 345 (M+1, 63), 313 (32), 171 (100); HRMS calcd for $C_{18}H_{33}O_6$ [M+H]$^+$ 345.2183, found 345.2180.

4.5.11. Hexanedioic acid 5-methoxycarbonylpentyl ester methyl ester (7j). Yield: 33%, colorless oil, R_f=0.60 (ethyl ether/hexane=1:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28–1.32 (m, 2H), 1.52–1.61 (m, 8H), 2.22–2.26 (m, 6H), 3.58 (s, 6H), 3.97 (t, *J*=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.2, 24.4, 25.4, 28.2, 33.5, 33.7, 51.27, 51.29, 64.0, 173.1, 173.5, 173.7; IR (KBr, neat): 2952, 2869, 1739, 1437, 1363, 1171, 1073, 1010 cm^{-1}; MS (FAB) *m/z* (relative intensity): 289 (M+1, 24), 154 (100), 136 (69), 107 (21); HRMS (FAB) calcd for $C_{14}H_{25}O_6$ $[M+H]^+$ 289.1671, found 289.1661.

4.5.12. 8,8-Dimethoxyoctanoic acid 8,8-dimethoxyoctyl ester (7k). Yield: 50%, pale yellow oil, R_f=0.50 (ethyl ether/hexane=1:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.30–1.40 (m, 12H), 1.50–1.61 (m, 10H), 2.28 (t, J=7.6 Hz, 2H), 3.30 (s, 6H), 3.31 (s, 6H), 4.05 (t, J=6.7 Hz, 2H), 4.34 (dt, J=5.7 and 2.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.3, 24.4, 24.7, 25.7, 28.5, 28.90, 28.94, 29.01, 29.2, 32.26, 32.29, 34.1, 52.4, 64.2, 104.3, 173.7; IR (KBr, neat): 2936, 2857, 2826, 1733, 1464, 1384, 1360, 1127, 1060, 730 cm^{-1}; MS *m/z* (relative intensity): 281 (82), 249 (39), 187 (M−189), 155 (33), 75 (100); HRMS calcd for $C_{10}H_{19}O_3$ (M−189) 187.1321, found 187.1328.

4.5.13. 6,6-Dimethoxyhexanoic acid 6,6-dimethoxyhexyl ester (7l). Yield: 32%, pale yellow oil, R_f=0.50 (hexane/EtOAc=1:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.30–1.34 (m, 6H), 1.52–1.61 (m, 8H), 2.25 (t, J=7.6 Hz, 2H), 3.24 (s, 6H), 3.25 (s, 6H), 4.00 (t, J=6.7 Hz, 2H), 4.30 (t, J=5.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.0, 24.1, 24.7, 25.7, 28.5, 32.0, 32.3, 34.1, 52.50, 52.53, 64.1, 104.2, 104.3, 173.5; IR (KBr, neat): 2947, 2830, 1736, 1463, 1387, 1128, 1054 cm^{-1}; MS (FAB) *m/z* (relative intensity): 320 (M^+, 2), 225 (95), 127 (100), 113 (70); HRMS (FAB) calcd for $C_{16}H_{32}O_6$ 320.2203, found 320.2201.

4.5.14. 10-Oxoundecanoic acid 10-oxoundecyl ester (7m). Yield: 33%, white solid, mp=53–54 °C, R_f=0.55 (hexane/EtOAc=3:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21–1.25 (br m, 18H), 1.50–1.58 (m, 8H), 2.09 (s, 6H), 2.24 (t, J=7.6 Hz, 2H), 2.37 (t, J=7.4 Hz, 4H), 4.00 (t, J=6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.69, 23.71, 24.9, 25.8, 28.5, 28.96, 28.99, 29.02, 29.06, 29.09, 29.2, 29.6, 29.7, 34.2, 43.6, 43.7, 64.2, 173.8, 209.0, 209.1; IR (KBr, neat): 2930, 2856, 1716, 1465, 1360, 1267, 1170, 1099, 739 cm^{-1}; MS (FAB) *m/z* (relative intensity): 369 (M+1, 85), 183 (100), 137 (25); HRMS (FAB) calcd for $C_{22}H_{41}O_4$ $[M+H]^+$ 369.3018, found 369.3011.

4.5.15. 6-Iodohexanoic acid 6-iodohexyl ester (7n). Yield: 22%, pale yellow oil, R_f=0.63 (hexane/EtOAc=5:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.37–1.43 (m, 6H), 1.61–1.66 (m, 4H), 1.81–1.85 (m, 4H), 2.31 (t, J=7.5 Hz, 2H), 3.18 (t, J=6.9 Hz, 4H), 4.06 (t, J=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 6.5, 6.8, 23.9, 24.9, 28.4, 29.9, 30.1, 33.1, 33.3, 34.0, 64.2, 173.4; IR (KBr, neat): 2933, 2858, 1732, 1458, 1427, 1351, 1265, 1207, 1182, 738 cm^{-1}; MS (FAB) *m/z* (relative intensity): 453 (M^++1, 38), 211 (35), 154 (100), 137 (81); HRMS (FAB) calcd for $C_{12}H_{22}O_2I_2$ $[M+H]^+$ 452.9782, found 452.9785.

4.5.16. 6-Bromohexanoic acid 6-bromohexyl ester (7o). Yield: 70%, pale yellow oil, R_f=0.49 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.34–1.58 (m, 6H), 1.59–1.63 (m, 4H), 1.81–1.85 (m, 4H), 2.28 (t, J=7.5 Hz, 2H), 3.37 (t, J=6.8 Hz, 4H), 4.03 (t, J=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.0, 25.0, 27.5, 27.6, 28.3, 32.3, 32.5, 33.4, 33.6, 33.9, 64.1, 173.3; IR (KBr, neat): 2937, 2860, 1733, 1460, 1253, 1185, 732 cm^{-1}; MS (FAB) *m/z* (relative intensity): 359 (M+2, 37), 357 (M+1, 21), 289 (14), 195 (15), 154 (100), 137 (90); HRMS (FAB) calcd $[M+H]^+$ for $C_{12}H_{23}O_2Br_2$ 357.0065, found 357.0073.

4.5.17. Benzyloxyacetic acid 2-benzyloxyethyl ester (7q). Yield: 52%, colorless oil, R_f=0.67 (hexane/EtOAc=2:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.69 (t, J=4.8 Hz, 2H), 4.13 (s, 2H), 4.35 (t, J=4.8 Hz, 2H), 4.45 (s, 2H), 4.63 (s, 2H), 7.27–7.37 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 63.8, 67.1, 67.7, 73.1, 73.3, 127.6, 127.7, 127.9, 128.0, 128.4, 128.4, 137.1, 137.8, 170.3; IR (thin film, NaCl plates): 3031, 2918, 2858, 1752, 1454, 1200, 1121, 736, 698 cm^{-1}; MS *m/z* (relative intensity): 301 (M^++1, 7), 299 (M^+−1, 7), 271 (12), 209 (8), 181 (12), 103 (37), 91 (100); HRMS calcd for $C_{18}H_{20}O_4$ 300.1362, found 300.1356.

4.5.18. Trityloxyacetic acid 2-trityloxyethyl ester (7r). Yield: 83%, white solid, mp 114–115 °C, R_f=0.34 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.26 (t, J=4.5 Hz, 2H), 3.83 (s, 2H), 4.27 (t, J=4.5 Hz, 2H), 7.18–7.51 (m, 30H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 61.9, 62.7, 63.9, 86.6, 87.4, 127.0, 127.2, 127.8, 128.0, 128.6, 143.3, 143.8, 169.9; IR (thin film, NaCl plates): 3058, 2924, 1758, 1734, 1491, 1448, 1265, 1098, 738, 705 cm^{-1}; MS *m/z* (relative intensity): 604 (M^+, 4), 527 (45), 243 (100), 165 (66), 105 (46); HRMS calcd for $C_{42}H_{36}O_4$ 604.2614, found 604.2615.

4.5.19. 3-Benzyloxypropionic acid 3-benzyloxypropyl ester (7s). Yield: 61%, white solid, mp 85 °C, R_f=0.69 (hexane/EtOAc=3:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.94 (quint, J=6.4 Hz, 2H), 2.59 (t, J=6.4 Hz, 2H), 3.53 (t, J=6.4 Hz, 2H), 3.73 (t, J=6.4 Hz, 2H), 4.22 (t, J=6.4 Hz, 2H), 4.48 (s, 2H), 4.52 (s, 2H), 7.25–7.35 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.0, 35.1, 61.7, 65.6, 66.6, 72.9, 73.0, 127.5, 127.5, 127.6, 128.3, 138.1, 138.3, 171.4; IR (thin film, NaCl plates): 3030, 2863, 1735, 1454, 1364, 1182, 1104, 737, 698 cm^{-1}; MS *m/z* (relative intensity): 329 (M^++1, 7), 237 (39), 131 (67), 91 (100); HRMS calcd for $C_{20}H_{24}O_4$ 328.1675, found 328.1673.

4.5.20. (4*R*)-2,2-Dimethyl-[1,3]dioxolane-4-carboxylic acid (4*R*)-2,2-dimethyl[1,3]dioxolan-4-ylmethyl ester (7t).[46] Yield: 60%, colorless oil, R_f=0.60 (hexane/EtOAc=1:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.36 (s, 3H), 1.41 (s, 3H), 1.43 (s, 3H), 1.50 (s, 3H), 3.73 (dd, J=7.5 and 5.0 Hz, 1H), 4.06–4.33 (m, 6H), 4.60 (dd, J=7.5 and 5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.20, 25.4, 25.8, 26.6, 65.2, 66.2, 67.2, 73.3, 73.9, 109.8, 111.4, 170.9; $[\alpha]_D^{24.3}$ −6.8 (c 0.012, $CHCl_3$); IR (thin film, NaCl plates): 2988, 2938, 2886, 1762, 1373, 1256, 1241, 1103 cm^{-1}; MS *m/z* (relative intensity): 261 (M^++1, 5), 245 (100), 203 (43), 101 (36), 43 (31).

4.5.21. (4*R*,5*R*)-2,2-Dimethyl-5-vinyl[1,3]dioxolane-4-carboxylic acid (4*R*,5*R*)-2,2-dimethyl-5-vinyl[1,3]dioxolan-4-ylmethyl ester (7u). Yield: 71%, pale yellow oil, R_f=0.44 (hexane/EtOAc=5:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.38 (s, 3H), 1.41 (s, 3H), 1.50 (s, 3H), 1.65 (s, 3H), 3.94 (dd, J=11.6 and 7.6 Hz, 1H), 4.21 (dd, J=11.5 and 4.8 Hz, 1H), 4.35 (ddd, J=7.3, 7.3, and 4.5 Hz, 1H), 4.66 (dd, J=6.9 and 6.8 Hz, 1H), 4.71 (d,

J=7.2 Hz, 1H), 4.82 (dd, J=7.1 and 7.0 Hz, 1H), 5.26–5.30 (m, 2H), 5.40–5.47 (m, 2H), 5.72–5.79 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.2, 25.5, 26.7, 27.7, 63.8, 75.3, 77.4, 77.9, 78.6, 109.1, 111.1, 119.0, 119.2, 131.9, 132.2, 169.2; $[\alpha]_D^{31.7}$ −25.0 (c 0.259, $CHCl_3$); IR (thin film, NaCl plates): 3083, 2987, 2938, 1760, 1380, 1218, 1093, 992, 930 cm^{-1}; MS m/z (relative intensity): 311 (M^+−1, 6), 169 (32), 98 (56), 43 (100); HRMS calcd for $C_{16}H_{24}O_6$ 312.1573, found 312.1576.

4.5.22. (4*S*,5*R*)-6-Methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole-4-carboxylic acid (4*S*,5*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-ylmethyl ester (7v). Yield: 66%, colorless oil, R_f=0.89 (hexane/EtOAc=3:2). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.32 (s, 3H), 1.33 (s, 3H), 1.48 (s, 3H), 1.49 (s, 3H), 3.32 (s, 3H), 3.40 (s, 3H), 4.20 (d, J=6.9 Hz, 2H), 4.40 (t, J=7.0 Hz, 1H), 4.55 (d, J=5.8 Hz, 1H), 4.60 (d, J=6.0 Hz, 1H), 4.65 (br d, 1H), 4.98 (s, 1H), 5.04 (s, 1H), 5.22 (d, J=5.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.8, 24.9, 26.3, 54.89, 55.4, 65.3, 81.6, 82.0, 83.5, 83.9, 84.2, 85.1, 109.3, 109.4, 112.4, 112.6, 169.59; $[\alpha]_D^{32.0}$ −59.4 (c 0.168, $CHCl_3$); IR (thin film, NaCl plates): 2988, 2938, 2836, 1732, 1374, 1208, 1096 cm^{-1}; MS m/z (relative intensity): 403 (M^+−1, 2), 389 (80), 373 (100), 271 (30), 172 (78), 126 (43), 59 (88); HRMS calcd for $C_{17}H_{25}O_{10}$ (M^+−15) 389.1448, found 389.1449.

4.5.23. Pent-4-enoic acid pent-4-enyl ester (17a). The general procedure was followed for Tishchenko reaction of aldehyde promoted by Dibal-H to prepare ester **17a** (613 mg, 3.64 mmol, 45% yield) in 12 h from aldehyde **16a** (1.37 g, 16.28 mmol). A colorless oil, R_f=0.64 (hexane/EtOAc=20:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.66–1.74 (m, 2H), 2.07–2.12 (m, 2H), 2.34–2.38 (m, 4H), 4.06 (t, J=6.4 Hz, 2H), 4.94–5.05 (m, 4H), 5.76–5.80 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.8, 28.8, 30.0, 33.5, 63.7, 115.2, 115.3, 136.6, 137.4, 172.9; IR (thin film, NaCl plates): 3080, 2979, 2925, 2851, 1737, 1642, 1447, 1173, 994, 915 cm^{-1}; MS m/z (relative intensity): 168 (M^+, 1), 141 (2), 113 (7), 83 (43), 68 (93), 55 (100); HRMS calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1156.

4.5.24. Hex-5-enoic acid hex-5-enyl ester (17b). The general procedure was followed for Tishchenko reaction of aldehyde promoted by Dibal-H to prepare ester **17b** (819 mg, 4.17 mmol, 41% yield) in 12 h from aldehyde **16b** (2.04 g, 20.78 mmol). A colorless oil, R_f=0.74 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.40–1.47 (m, 2H), 1.58–1.66 (m, 2H), 1.71 (quint, J=7.4 Hz, 2H), 2.03–2.10 (m, 4H), 4.05 (t, J=6.6 Hz, 2H), 4.93–5.03 (m, 4H), 5.72–5.98 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.1, 25.2, 28.0, 33.0, 33.2, 33.5, 64.1, 114.7, 115.2, 137.6, 138.2, 173.5; IR (thin film, NaCl plates): 3078, 2936, 2862, 1737, 1641, 1457, 1172, 994, 912 cm^{-1}; MS m/z (relative intensity): 196 (M^+, 0.2), 114 (24), 97 (44), 82 (42), 67 (64), 55 (100); HRMS calcd for $C_{12}H_{20}O_2$ 196.1463, found 196.1455.

4.5.25. Hept-6-enoic acid hept-6-enyl ester (17c). The general procedure was followed for Tishchenko reaction of aldehyde promoted by Dibal-H to prepare ester **17c** (778 mg, 3.47 mmol, 68% yield) in 8 h from aldehyde **16c** (1.14 g, 10.16 mmol). A colorless oil, R_f=0.52 (hexane/EtOAc=20:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.34–1.42 (m, 6H), 1.59–1.64 (m, 4H), 2.02–2.05 (m, 4H), 2.27 (t, J=7.6 Hz, 2H), 4.04 (t, J=6.8 Hz, 2H), 4.90–5.00 (m, 4H), 5.73–5.78 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.4, 25.3, 28.3, 28.39, 28.43, 33.3, 33.5, 34.1, 64.2, 114.4, 114.6, 138.3, 138.5, 173.5; IR (thin film, NaCl plates): 3077, 2932, 2859, 1738, 1641, 1461, 1171, 994, 911 cm^{-1}; MS m/z (relative intensity): 225 (M^++1, 100), 129 (85), 97 (34), 55 (54), 41 (45); HRMS calcd for $C_{14}H_{24}O_2$ 224.1776, found 224.1781.

4.5.26. Oct-7-enoic acid oct-7-enyl ester (17d). The general procedure was followed for Tishchenko reaction of aldehyde promoted by Dibal-H to prepare ester **17d** (733 mg, 2.90 mmol, 62% yield) in 8 h from aldehyde **16d** (1.18 g, 9.35 mmol). A colorless oil, R_f=0.78 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33–1.41 (m, 10H), 1.59–1.67 (m, 4H), 2.02–2.07 (m, 4H), 2.29 (t, J=7.5 Hz, 2H), 4.04–4.07 (t, J=6.7 Hz, 2H), 4.92–5.01 (m, 4H), 5.76–5.81 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.8, 25.7, 28.5, 28.55, 28.6, 28.7, 33.5, 33.6, 34.3, 64.3, 114.25, 114.33, 138.7, 138.8, 173.7; IR (thin film, NaCl plates): 3077, 2930, 2857, 1737, 1640, 1463, 1171, 994, 910 cm^{-1}; MS m/z (relative intensity): 253 (M^++1, 8), 252 (M^+, 2), 123 (47), 110 (65), 69 (100), 55 (80), 41 (35); HRMS calcd for $C_{16}H_{28}O_2$ 252.2089, found 252.2093.

4.5.27. Undec-10-enoic acid undec-10-enyl ester (17e). The general procedure was followed for Tishchenko reaction of aldehyde promoted by Dibal-H to prepare ester **17e** (125 mg, 0.37 mmol, 76% yield) in 5 h from aldehyde **16e** (166 mg, 0.98 mmol). A colorless oil, R_f=0.60 (hexane/EtOAc=20:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.23–1.38 (m, 22H), 1.57–1.63 (m, 4H), 2.00–2.06 (m, 4H), 2.28 (t, J=7.6 Hz, 2H), 4.05 (t, J=6.8 Hz, 2H), 4.90–5.00 (m, 4H), 5.76–5.83 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.0, 25.9, 28.7, 28.9, 29.12, 29.14, 29.2, 29.43, 29.47, 29.49, 29.55, 29.58, 29.59, 33.8, 34.4, 64.3, 114.0, 139.1, 173.9; IR (thin film, NaCl plates): 3077, 2926, 2855, 1738, 1640, 1465, 1173, 993, 909 cm^{-1}; MS m/z (relative intensity): 337 (M^++1, 4), 185 (16), 96 (100), 82 (86), 55 (82), 41 (75); HRMS calcd for $C_{22}H_{40}O_2$ 336.3036, found 336.3032.

4.5.28. Tetradec-13-enoic acid tetradec-13-enyl ester (17f). The general procedure was followed for Tishchenko reaction of aldehyde promoted by Dibal-H to prepare ester **17f** (680 mg, 1.62 mmol, 67% yield) in 6 h from aldehyde **16f** (1.05 g, 5.00 mmol). A white solid, mp 30–31 °C, R_f=0.63 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26–1.38 (m, 34H), 1.57–1.62 (m, 4H), 2.00–2.05 (m, 4H), 2.27 (t, J=7.6 Hz, 2H), 4.05 (t, J=6.8 Hz, 2H), 4.90–5.00 (m, 4H), 5.75–5.85 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.0, 25.9, 28.7, 28.9, 29.11, 29.13, 29.2, 29.42, 29.47, 29.48, 29.54, 29.56, 29.58, 33.8, 34.4, 64.3, 114.0, 139.1, 173.8; IR (thin film, NaCl plates): 3076, 2925, 2854, 1737, 1640, 1466, 1174, 993, 909 cm^{-1}; MS m/z (relative intensity): 421 (M^++1, 12), 209 (24), 96 (62), 81 (63), 55 (100), 41 (38); HRMS calcd for $C_{28}H_{52}O_2$ 420.3967, found 420.3965.

4.5.29. Pentadec-14-enoic acid pentadec-14-enyl ester (17g). The general procedure was followed for Tishchenko reaction of aldehyde promoted by Dibal-H to prepare ester **17g** (210 mg, 0.47 mmol, 72% yield) in 8 h from aldehyde **16g** (316 mg, 1.41 mmol). A white solid, mp 31–32 °C, R_f=0.67 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.20–1.39 (m, 38H), 1.57–1.62 (m, 4H), 2.00–2.06 (m, 4H), 2.28 (t, J=7.6 Hz, 2H), 4.05 (t, J=6.8 Hz, 2H), 4.90–5.00 (m, 4H), 5.75–5.85 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.9, 25.9, 28.6, 28.85, 28.88, 29.07, 29.13, 29.18, 29.19, 29.31, 29.39, 29.43, 29.49, 29.51, 29.54, 33.7, 34.3, 64.2, 113.98, 114.03, 139.0, 173.6; IR (thin film, NaCl plates): 3076, 2925, 2854, 1733, 1640, 1417, 1174, 994, 910, 742 cm^{-1}; MS m/z (relative intensity): 448 (M$^+$, 4), 208 (37), 123 (68), 109 (71), 96 (100), 82 (99), 67 (77), 54 (99), 41 (50); HRMS calcd for $C_{30}H_{56}O_2$ 448.4280, found 448.4289.

4.5.30. Hexadec-15-enoic acid hexadec-15-enyl ester (17h). The general procedure was followed for Tishchenko reaction of aldehyde promoted by Dibal-H to prepare ester **17h** (830 mg, 1.74 mmol, 74% yield) in 8 h from aldehyde **16h** (1.12 g, 4.71 mmol). A white solid, mp 37–38 °C, R_f=0.68 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26–1.39 (m, 42H), 1.59–1.63 (m, 4H), 2.01–2.06 (m, 4H), 2.28 (t, J=7.6 Hz, 2H), 4.05 (t, J=6.8 Hz, 2H), 4.90–5.01 (m, 4H), 5.77–5.84 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.0, 25.9, 28.7, 28.9, 29.1, 29.2, 29.3, 29.45, 29.49, 29.51, 29.56, 29.60, 29.62, 33.8, 34.4, 64.3, 114.1, 139.2, 173.9; IR (thin film, NaCl plates): 3077, 2925, 2854, 1732, 1640, 1466, 1265, 1176, 994, 910, 742 cm^{-1}; MS m/z (relative intensity): 476 (M$^+$, 32), 236 (21), 222 (25), 82 (9), 69 (31), 55 (100), 41 (38); HRMS calcd for $C_{32}H_{60}O_2$ 476.4593, found 476.4598.

4.5.31. Nonadec-18-enoic acid nonadec-18-enyl ester (17i). The general procedure was followed for Tishchenko reaction of aldehyde promoted by Dibal-H to prepare ester **17i** (208 mg, 0.37 mmol, 62% yield) in 10 h from aldehyde **16i** (330 mg, 1.18 mmol). A white solid, mp 55–56 °C, R_f=0.76 (hexane/EtOAc=20:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.25–1.39 (m, 54H), 1.58–1.65 (m, 4H), 2.01–2.07 (m, 4H), 2.29 (t, J=7.6 Hz, 2H), 4.05 (t, J=6.8 Hz, 2H), 4.91–5.01 (m, 4H), 5.78–5.85 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.0, 25.9, 28.7, 29.0, 29.25, 29.28, 29.48, 29.51, 29.53, 29.58, 29.61, 29.62, 29.65, 29.68, 33.8, 34.4, 64.4, 114.1, 139.2, 174.0; IR (thin film, NaCl plates): 3054, 2927, 2854, 1726, 1466, 1265, 996, 913, 741 cm^{-1}; MS m/z (relative intensity): 561 (M$^+$+1, 34), 324 (12), 83 (41), 69 (73), 54 (67), 32 (100); HRMS calcd for $C_{38}H_{72}O_2$ 560.5532, found 560.5532.

4.6. General procedure for the Oppenauer reaction of α-silyloxy aldehyde promoted by Dibal-H (for compounds 11a, 11b, 11d–11f, and 10d–10f)

To a solution of aldehyde **9a** (880 mg, 3.00 mmol) in *n*-pentane (6 mL), a solution of Dibal-H (0.41 mL, 1.0 M solution in hexane) in 1 mL of *n*-pentane was added dropwise by syringe pump over a period of 1 h at 0 °C. After stirring at ambient temperature for 12 h, to the reaction mixture was added 1 N HCl and extracted with CH_2Cl_2. The organic layer was dried over magnesium sulfate, filtered, and concentrated. The residue was chromatographed on a silica gel column to give α-silyloxy ketone **11a** (683 mg, 2.33 mmol, 78% yield) as a colorless oil, R_f=0.44 (hexane/EtOAc=20:1).

4.6.1. 1-(*tert*-Butyldimethylsilyloxy)-5-phenylpentan-2-one (11a). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.08 (s, 6H), 0.92 (s, 9H), 1.93 (quint, J=7.4 Hz, 2H), 2.51 (t, J=7.4 Hz, 2H), 2.64 (t, J=7.4 Hz, 2H), 4.41 (s, 2H), 7.17–7.28 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −5.6, 18.2, 24.7, 25.7, 35.1, 37.5, 69.2, 125.9, 128.3, 128.4, 141.5, 210.7; IR (thin film, NaCl plates): 3026, 2929, 2857, 1719, 1471, 1105, 839, 779, 699 cm^{-1}; MS m/z (relative intensity): 293 (M$^+$+1, 15), 235 (63), 143 (68), 117 (100), 105 (37), 91 (37); HRMS calcd for $C_{17}H_{28}O_2Si$ 292.1859, found 292.1858.

4.6.2. 2-(*tert*-Butyldimethylsilyloxy)-1-cyclohexylethanone (11b). Yield: 45%, colorless oil, R_f=0.51 (hexane/EtOAc=30:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.08 (s, 6H), 0.92 (s, 9H), 1.26–1.33 (m, 6H), 1.77–1.81 (m, 4H), 2.62 (tt, J=8.0 and 3.2 Hz, 1H), 4.24 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −5.6, 18.3, 25.6, 25.7, 25.8, 28.2, 46.1, 68.1, 212.9; IR (thin film, NaCl plates): 2930, 2856, 1716, 1105, 838, 778 cm^{-1}; MS m/z (relative intensity): 257 (M$^+$+1, 8), 241 (M$^+$−15, 22), 199 (100), 198 (70), 118 (18), 83 (16), 55 (24); HRMS calcd for $C_{14}H_{28}O_2Si$ 256.1859, found 256.1853.

4.6.3. (*tert*-Butyldimethylsilyloxy)phenylacetic acid 2-(*tert*-butyldimethylsilyloxy)-2-phenylethyl ester (10d) and 2-(*tert*-butyldimethylsilyloxy)-1-phenylethanone (11d). Yield: 37% of Tishchenko product **10d** as a mixture of two diastereomers; yield: 20% of Oppenauer product **11d**. *Compound* ***10d*** (a mixture of two diastereomers): a colorless oil, R_f=0.74 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.11–0.20 (m, 12H), 0.98–1.02 (m, 18H), 4.14–4.19 (m, 1H), 4.26–4.34 (m, 1H), 4.91–4.96 (m, 1H), 5.30 (s, 1.2H), 5.32 (s, 0.8H), 7.35–7.54 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −4.7, −4.7, −4.59, −4.56, −4.4, 18.6, 18.7, 26.2, 70.7, 70.9, 73.19, 73.22, 75.0, 126.7, 127.04, 127.07, 128.06, 128.12, 128.5, 128.58, 128.61, 128.7, 139.58, 139.62, 141.5, 141.6, 172.26, 172.30; IR (thin film, NaCl plates): 3064, 2955, 2929, 1757, 1733, 1472, 1256, 1124, 837, 779, 739, 699 cm^{-1}; MS m/z (relative intensity): 500 (M$^+$, 2), 443 (65), 369 (54), 235 (83), 221 (100), 179 (20), 73 (78); HRMS calcd for $C_{28}H_{43}O_4Si_2$ (M$^+$−1) 499.2700, found 499.2693. *Compound* ***11d***: a transparent solid, mp 73–74 °C, R_f=0.61 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.13 (s, 6H), 0.94 (s, 9H), 4.92 (s, 2H), 7.44–7.57 (m, 3H), 7.91–7.94 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −5.4, 18.4, 25.8, 67.4, 127.9, 128.5, 133.2, 134.9, 197.4; IR (thin film, NaCl plates): 3063, 2953, 2929, 1707, 1471, 1155, 838, 779, 690 cm^{-1}; MS m/z (relative intensity): 235 (M$^+$−15, 4), 221 (63), 193 (41), 105 (100), 77 (38); HRMS calcd for $C_{13}H_{19}O_2Si$ (M$^+$−15) 235.1151, found 235.1154.

4.6.4. 3-(*tert*-Butyldimethylsilyloxy)-5-phenylpentanoic acid 3-(*tert*-butyldimethylsilyloxy)-5-phenylpentyl ester (10e) and 1-(*tert*-butyldimethylsilyloxy)-5-phenylpentan-3-one (11e). Yield: 52% of Tishchenko product **10e** as a mixture of two diastereomers; yield: 29% of Oppenauer product **11e**. *Compound* ***10e*** (a mixture of two diastereomers): a pale yellow oil, R_f=0.93 (hexane/EtOAc=5:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.04–0.08 (ms, 12H), 0.89–0.90 (ms, 18H), 1.77–1.84 (m, 6H), 2.44–2.55 (m, 2H), 2.59–2.73 (m, 4H), 3.83–3.88 (m, 1H), 4.09–4.15 (m, 1H), 4.17–4.23 (m, 2H), 7.15–7.29 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −4.64, −4.63, −4.5, −4.4, 18.0, 18.1, 25.8, 25.9, 31.36, 31.40, 35.6, 39.2, 39.3, 39.4, 42.6, 61.5, 68.7, 68.8, 69.0, 69.1, 125.78, 125.80, 128.3, 128.4, 142.1, 142.3, 171.5, 171.6; IR (thin film, NaCl plates): 3026, 2953, 2928, 1737, 1462, 1254, 1096, 836, 775, 698 cm^{-1}; MS *m/z* (relative intensity): 585 (M^++1, 7), 277 (38), 249 (100), 145 (83), 91 (84), 73 (75); HRMS calcd for $C_{34}H_{56}O_4Si_2$ 584.3717, found 584.3715. *Compound **11e***: a pale yellow oil, R_f=0.76 (hexane/EtOAc=5:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.04 (s, 6H), 0.87 (s, 9H), 2.59 (t, *J*=6.4 Hz, 2H), 2.78 (t, *J*=7.6 Hz, 2H), 2.90 (t, *J*=7.6 Hz, 2H), 3.88 (t, *J*=6.4 Hz, 2H), 7.16–7.26 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ −5.5, 18.2, 25.8, 29.5, 45.3, 45.8, 58.9, 126.0, 128.3, 128.4, 141.1, 208.9; IR (thin film, NaCl plates): 3027, 2954, 2928, 1715, 1471, 1255, 1092, 836, 777, 699 cm^{-1}; MS *m/z* (relative intensity): 293 (M^++1, 8), 277 (8), 235 (100), 90 (97), 77 (2); HRMS calcd for $C_{17}H_{28}O_2Si$ 292.1859, found 292.1855.

4.6.5. Acetoxycyclohexylacetic acid 2-acetoxy-2-cyclohexylethyl ester (10f) and acetic acid 2-cyclohexyl-2-oxoethyl ester (11f). Yield: 31% of Tishchenko product **10f** as a mixture of two diastereomers; yield: 10% of Oppenauer product **11f**. *Compound **10f*** (a mixture of two diastereomers): a pale yellow oil, R_f=0.61 (hexane/EtOAc=4:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.02–1.26 (m, 10H), 1.58–1.72 (m, 12H), 2.04 (s, 3H), 2.10 (s, 3H), 4.15–4.19 (m, 1H), 4.23–4.31 (m, 1H), 4.78–4.81 (m, 1H), 4.86–4.94 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.4, 20.82, 20.84, 25.4, 25.6, 25.7, 25.8, 25.87, 25.93, 25.95, 26.1, 27.5, 27.6, 28.27, 28.3, 28.7, 28.86, 28.89, 38.69, 38.72, 39.35, 39.41, 63.9, 64.2, 74.7, 74.8, 76.36, 76.38, 169.46, 169.48, 170.4, 170.5, 170.6; IR (thin film, NaCl plates): 2929, 2854, 1746, 1450, 1372, 1237, 1185, 1045 cm^{-1}; MS *m/z* (relative intensity): 369 (M^++1, 74), 309 (100), 183 (93), 169 (100), 155 (63), 122 (69), 109 (73), 95 (90), 81 (30), 67 (32); HRMS calcd for $C_{20}H_{32}O_6$ 368.2199, found 368.2200. *Compound **11f***: a white solid, mp 48–49 °C, R_f=0.52 (hexane/EtOAc=4:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.23–1.31 (m, 5H), 1.78–1.86 (m, 5H), 2.16 (s, 3H), 2.42 (tt, *J*=11.2 and 3.5 Hz, 1H), 4.73 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.3, 25.3, 25.5, 28.0, 47.2, 66.5, 170.0, 206.1; IR (thin film, NaCl plates): 2930, 2855, 1753, 1725, 1449, 1229 cm^{-1}; MS *m/z* (relative intensity): 184 (M^+, 2), 124 (20), 111 (100), 83 (100), 55 (29); HRMS calcd for $C_{10}H_{16}O_3$ 184.1099, found 184.1099.

4.7. General procedure for the cross-coupling reaction of Grignard reagent with primary bromide in the presence of Li_2CuCl_4 (for compounds 14f–14i)

A solution of 3-butenyl bromide (**12g**) (0.30 mL, 2.95 mmol) in anhydrous THF (1 mL) was added to a two-necked flask containing magnesium powder (870 mg, 35.8 mmol) and a catalytic amount of iodine under nitrogen. After the reaction starts, the remaining 3-butenyl bromide (**12g**) (1.53 mL, 15.05 mmol) in 6 mL of THF was added dropwise and the reaction mixture was then refluxed for 30 min and then cooled to 0 °C. To this Grignard reagent solution was added a mixture of 2-(11-bromo-undecyloxy)-tetrahydropyran (**13**)[47] (3.08 g, 9.18 mmol) in 6 mL of THF and lithium tetrachlorocuprate (0.89 mmol, 8.9 mL, 0.1 M in THF) at 0 °C and stirred at this temperature for 2 h. The reaction was quenched with 1 N aqueous ammonium chloride solution and extracted with EtOAc. The organic layer was dried over magnesium sulfate and concentrated. The residue was chromatographed on a silica gel column to give product **14g** (2.70 g, 8.64 mmol, 96% yield) as a colorless oil, R_f=0.60 (hexane/EtOAc=10:1).

4.7.1. 2-Pentadec-14-enyloxy-tetrahydropyran (14g). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26–1.39 (m, 20H), 1.49–1.61 (m, 6H), 1.69–1.75 (m, 1H), 1.79–1.87 (m, 1H), 2.01–2.06 (m, 2H), 3.38 (dt, *J*=9.5 and 6.7 Hz, 1H, –C*H*$_2$OTHP), 3.47–3.53 (m, 1H), 3.72 (dt, *J*=9.6 and 6.9 Hz, 1H, –C*H*$_2$OTHP), 3.84–3.90 (m, 1H), 4.58 (dd, *J*=4.3 and 2.6 Hz, 1H), 4.91–5.02 (m, 2H), 5.76–5.86 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.7, 25.5, 26.2, 28.9, 29.1, 29.5, 29.59, 29.63, 29.7, 30.8, 33.8, 62.3, 67.7, 98.8, 114.1, 139.2; IR (thin film, NaCl plates): 3075, 2925, 2854, 1640, 1466, 1034, 991, 908, 734 cm^{-1}; MS *m/z* (relative intensity): 310 (M^+, 4), 309 (M^+−1, 15), 237 (22), 123 (47), 115 (91), 111 (100); HRMS calcd for $C_{20}H_{38}O_2$ 310.2872, found 310.2870.

4.7.2. 2-Tetradec-13-enyloxy-tetrahydropyran (14f). Yield: 97%, pale yellow oil, R_f=0.50 (hexane/EtOAc=20:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26–1.39 (m, 18H), 1.49–1.61 (m, 6H), 1.69–1.75 (m, 1H), 1.79–1.87 (m, 1H), 2.01–2.06 (m, 2H), 3.38 (dt, *J*=9.6 and 6.7 Hz, 1H, –C*H*$_2$OTHP), 3.47–3.53 (m, 1H), 3.73 (dt, *J*=9.6 and 6.9 Hz, 1H, –C*H*$_2$OTHP), 3.85–3.90 (m, 1H), 4.58 (dd, *J*=4.4 and 2.6 Hz, 1H), 4.91–5.02 (m, 2H), 5.76–5.87 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.6, 25.5, 26.2, 28.9, 29.1, 29.5, 29.56, 29.59, 29.7, 30.7, 33.8, 62.2, 67.6, 98.8, 114.0, 139.1; IR (thin film, NaCl plates): 3075, 2925, 2853, 1640, 1466, 1035, 991, 908 cm^{-1}; MS *m/z* (relative intensity): 296 (M^+, 4), 295 (M^+−1, 4), 223 (6), 101 (19), 85 (100), 55 (31); HRMS calcd for $C_{19}H_{36}O_2$ 296.2715, found 296.2714.

4.7.3. 2-Hexadec-15-enyloxy-tetrahydropyran (14h).[48] Yield: 93%, colorless oil, R_f=0.57 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26–1.39 (m, 22H), 1.49–1.61 (m, 6H), 1.69–1.75 (m, 1H), 1.79–1.87 (m, 1H), 2.01–2.07 (m, 2H), 3.38 (dt, *J*=9.6 and 6.7 Hz, 1H, –C*H*$_2$OTHP), 3.47–3.53 (m, 1H), 3.74 (dt, *J*=9.6 and 7.0 Hz, 1H, –C*H*$_2$OTHP), 3.85–3.90 (m, 1H), 4.58 (dd, *J*=4.4 and 2.6 Hz, 1H), 4.91–5.02 (m, 2H), 5.77–5.87 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.6, 25.5, 26.2, 28.9, 29.1, 29.45, 29.47, 29.56, 29.57, 29.6, 29.7, 30.7, 33.8, 62.2, 67.6, 98.7, 114.0, 139.1; IR (thin film, NaCl plates): 3076, 2925, 2853, 1640, 1466, 1035, 991, 908, 738 cm^{-1}; MS *m/z* (relative intensity): 325 (M^++1, 26), 100 (21), 84 (100), 54 (26), 41 (23).

4.7.4. 2-Nonadec-18-enyloxy-tetrahydropyran (14i). Yield: 88%, colorless oil, R_f=0.60 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.25–1.36 (m, 28H), 1.49–1.61 (m, 6H), 1.69–1.75 (m, 1H), 1.79–1.87 (m, 1H), 2.01–2.06 (m, 2H), 3.38 (dt, *J*=9.6 and 6.7 Hz, 1H,

–CH_2OTHP), 3.48–3.53 (m, 1H), 3.73 (dt, J=9.6 and 7.0 Hz, 1H, –CH_2OTHP), 3.85–3.90 (m, 1H), 4.58 (dd, J=4.4 and 2.6 Hz, 1H), 4.92–5.02 (m, 2H), 5.76–5.87 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.6, 25.5, 26.2, 28.9, 29.1, 29.3, 29.5, 29.6, 29.66, 29.73, 30.8, 33.8, 62.3, 67.6, 98.8, 114.0, 139.2; IR (thin film, NaCl plates): 3076, 2925, 2853, 1640, 1466, 1035, 990, 907, 739 cm^{-1}; MS m/z (relative intensity): 366 (M^+, 3), 365 (M^+-1, 6), 101 (26), 84 (100), 55 (39), 41 (22); HRMS calcd for $C_{24}H_{46}O_2$ 366.3498, found 366.3498.

4.8. General procedure for the deprotection of 2-alkoxytetrahydropyran catalyzed by acetonyltriphenylphosphonium bromide (ATPB) (for compounds 15f–15i)

To a solution of 2-alkoxytetrahydropyran **14f** (4.05 g, 13.62 mmol) in MeOH (26 mL) was added ATPB (540 mg, 1.35 mmol) and the solution was stirred at rt for 2 h. The solution was concentrated and chromatographed on a silica gel column to give alcohol **15f** (2.61 g, 12.31 mmol, 91% yield) as a colorless oil, R_f=0.41 (hexane/EtOAc=5:1).

4.8.1. Tetradec-13-en-1-ol (15f). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.20 (t, J=5.5 Hz, 1H, –OH), 1.27–1.37 (m, 18H), 1.53–1.60 (m, 2H), 2.01–2.07 (m, 2H), 3.64 (td, J=6.5 and 5.5 Hz, 2H, –CH_2OH), 4.91–5.02 (m, 2H), 5.77–5.87 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.7, 28.9, 29.1, 29.39, 29.44, 29.5, 29.6, 32.7, 33.7, 62.8, 114.0, 139.1; IR (thin film, NaCl plates): 3340, 3077, 2925, 2854, 1640, 1465, 1265, 993, 910, 742 cm^{-1}; MS m/z (relative intensity): 212 (M^+, 3), 211 (M^+-1, 3), 166 (46), 109 (21), 95 (57), 81 (82), 67 (100), 55 (74), 41 (64); HRMS calcd for $C_{14}H_{28}O$ 212.2140, found 212.2137.

4.8.2. Pentadec-14-en-1-ol (15g). Yield 95%, colorless oil, R_f=0.40 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21 (br, 1H, –OH), 1.26–1.39 (m, 20H), 1.53–1.60 (m, 2H), 2.01–2.07 (m, 2H), 3.64 (td, J=6.5 and 5.2 Hz, 2H, –CH_2OH), 4.91–5.02 (m, 2H), 5.77–5.85 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.7, 28.9, 29.1, 29.4, 29.5, 29.58, 29.61, 32.8, 33.8, 63.0, 114.0, 139.2; IR (thin film, NaCl plates): 3352, 3077, 2925, 2854, 1640, 1466, 1265, 994, 910, 742 cm^{-1}; MS m/z (relative intensity): 226 (M^+, 3), 208 (41), 180 (5), 109 (26), 95 (64), 82 (95), 67 (97), 55 (100), 41 (73); HRMS calcd for $C_{15}H_{30}O$ 226.2297, found 226.2298.

4.8.3. Hexadec-15-en-1-ol (15h). Yield: 89%, colorless oil, R_f=0.34 (hexane/EtOAc=5:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.20 (br, 1H, –OH), 1.26–1.39 (m, 22H), 1.53–1.60 (m, 2H), 2.01–2.07 (m, 2H), 3.64 (td, J=6.5 and 5.4 Hz, 2H), 4.91–5.02 (m, 2H), 5.77–5.85 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.7, 28.9, 29.1, 29.4, 29.5, 29.58, 29.62, 32.7, 33.8, 62.9, 114.0, 139.2; IR (thin film, NaCl plates): 3348, 3076, 2925, 2854, 1639, 1466, 1265, 995, 911, 742 cm^{-1}; MS m/z (relative intensity): 240 (M^+, 3), 222 (3), 194 (5), 109 (24), 95 (57), 82 (90), 67 (85), 55 (100), 41 (69); HRMS calcd for $C_{16}H_{32}O$ 240.2453, found 240.2452.

4.8.4. Nonadec-18-en-1-ol (15i). Yield: 86%, white solid, mp 50–51 °C, R_f=0.22 (hexane/EtOAc=4:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.20 (t, J=5.2 Hz, 1H, –OH), 1.25–1.39 (m, 28H), 1.53–1.60 (m, 2H), 2.01–2.07 (m, 2H), 3.64 (td, J=6.4 and 5.2 Hz, 2H, –CH_2OH), 4.91–5.02 (m, 2H), 5.77–5.87 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.7, 28.9, 29.1, 29.4, 29.5, 29.6, 29.7, 32.8, 33.8, 63.0, 114.0, 139.2; IR (thin film, NaCl plates): 3219, 3076, 2918, 2849, 1462, 1264, 1064, 912, 742 cm^{-1}; MS m/z (relative intensity): 282 (M^+, 1), 264 (46), 151(75), 109 (18), 95 (33), 82 (79), 69 (33), 54 (100), 41 (50); HRMS calcd for $C_{19}H_{38}O$ 282.2923, found 282.2921.

4.9. General procedure for the macrocyclic lactone formation from the ring-closing metathesis (for compounds 18b–18i)

First-generation Grubbs catalyst (49.38 mg, 0.06 mmol) was dissolved in a two-necked flask in CH_2Cl_2 (55 mL, degass treatment with nitrogen) in a glove bag at rt. To the resulting light orange-brown solution was added diene ester **17e** (200 mg, 0.60 mmol) in 5 mL of CH_2Cl_2 and the mixture was then heated at 50 °C (oil bath temperature) for 6 h. After cooling, the mixture was quenched by exposure to air and concentrated under reduced pressure. The residue was chromatographed on a silica gel column to give an inseparable mixture of *E*- and *Z*-unsaturated macrolactone **18e** (110 mg, 0.36 mmol, 60% yield) as a colorless oil, R_f=0.55 (hexane/EtOAc=20:1).

4.9.1. (*E*)- and (*Z*)-Oxacycloheneicos-11-en-2-one (18e).[20a] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26–1.34 (m, 22H), 1.59–1.65 (m, 4H), 1.96–1.99 (m, 4H), 2.28–2.31 (m, 2H), 4.08–4.11 (m, 2H), 5.32–5.35 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.2, 25.8, 27.7, 28.0, 28.3, 28.46, 28.51, 28.56, 28.71, 29.07, 29.1, 29.2, 29.3, 29.4, 31.7, 32.0, 34.5, 64.0, 64.2, 130.0, 130.1, 130.6, 130.9, 173.8, 174.0; IR (thin film, NaCl plates): 3074, 2925, 2854, 1737, 1462, 1351, 1251, 1235, 1172, 968, 722 cm^{-1}; MS m/z (relative intensity): 308 (M^+, 14), 290 (2), 95 (59), 81 (93), 66 (75), 54 (51), 41 (100).

4.9.2. Oxacycloundec-6-en-2-one (18b). Yield: 61%, as an inseparable mixture of *E*- and *Z*-isomer, pale yellow oil, R_f=0.31 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.41–1.45 (m, 2H), 1.60–1.72 (m, 4H), 2.00–2.07 (m, 4H), 2.27–2.31 (m, 2H), 4.06–4.11 (m, 2H), 5.33–5.43 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.5, 24.6, 25.7, 25.8, 27.6, 27.9, 31.5, 31.6, 31.9, 32.0, 33.3, 33.4, 64.0, 64.1, 129.4, 130.1, 130.3, 131.1, 173.5, 173.6; IR (thin film, NaCl plates): 3056, 2935, 2858, 1729, 1266, 970, 740 cm^{-1}; MS m/z (relative intensity): 168 (M^+, 15), 150 (61), 136 (45), 81 (41), 67 (100), 55 (74), 41 (70); HRMS calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1153.

4.9.3. Oxacyclotridec-7-en-2-one (18c). Yield: 57%, as an inseparable mixture of *E*- and *Z*-isomer; pale yellow oil, R_f=0.40 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29–1.35 (m, 6H), 1.52–1.59 (m, 4H), 1.91–1.93 (br m, 4H), 2.22 (t, J=7.1 Hz, 2H), 4.01 (t, J=6.1 Hz, 2H), 5.29–5.30 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.3, 24.5, 25.0, 25.1, 26.9, 28.3, 28.5, 28.62, 28.64, 28.7, 28.9, 31.9, 32.0, 32.1, 34.3, 34.4, 64.0, 64.1, 130.0, 130.2, 130.3, 130.4, 173.6, 173.6; IR (thin film, NaCl plates): 3055, 2932, 2857, 1728, 1266, 970, 741 cm^{-1}; MS *m*/*z* (relative intensity): 196 (M^+, 6), 107 (8), 94 (51), 81 (64), 67 (100), 55 (47), 41 (18); HRMS calcd for $C_{12}H_{20}O_2$ 196.1463, found 196.1472.

4.9.4. Oxacyclopentadec-8-en-2-one (18d). Yield: 59%, as an inseparable mixture of *E*- and *Z*-isomer, pale yellow oil, R_f=0.40 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29–1.42 (m, 10H), 1.62–1.67 (m, 4H), 2.03–2.05 (m, 4H), 2.32 (t, *J*=6.3 Hz, 2H), 4.07–4.11 (m, 2H), 5.24–5.32 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.0, 25.3, 25.4, 26.3, 26.65, 26.89, 27.3, 27.4, 28.1, 28.3, 28.36, 28.41, 28.5, 28.7, 31.9, 34.6, 64.1, 64.3, 130.2, 130.4, 130.8, 131.1, 174.1, 174.3; IR (thin film, NaCl plates): 2927, 2856, 1733, 1249, 970, 737 cm^{-1}; MS *m*/*z* (relative intensity): 224 (M^+, 13), 109 (15), 95 (30), 81 (39), 67 (41), 54 (36), 41 (100); HRMS calcd for $C_{14}H_{24}O_2$ 224.1776, found 224.1787.

4.9.5. Oxacycloheptacos-14-en-2-one (18f). Yield: 75%, as an inseparable mixture of *E*- and *Z*-isomer, pale yellow solid, 47–50 °C, R_f=0.53 (hexane/EtOAc=20:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21–1.35 (m, 34H), 1.60–1.65 (m, 4H), 2.00–2.05 (m, 4H), 2.31 (t, *J*=7.2 Hz, 2H), 4.10 (t, *J*=5.8 Hz, 2H), 5.33–5.35 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.2, 26.1, 26.2, 26.8, 270.0, 28.2, 28.4, 28.6, 28.66, 28.71, 28.9, 28.96, 29.00, 29.07, 29.1, 29.15, 29.20, 29.29, 29.3, 29.40, 29.45, 29.48, 29.52, 29.55, 29.61, 32.16, 32.19, 34.66, 34.70, 64.2, 64.3, 130.0, 130.1, 130.6, 130.7, 173.95, 173.98; IR (thin film, NaCl plates): 3075, 2925, 2853, 1737, 1465, 1259, 1167, 967, 721 cm^{-1}; MS *m*/*z* (relative intensity): 392 (M^+, 14), 374 (6), 96 (11), 82 (12), 67 (13), 55 (69), 41 (100); HRMS calcd for $C_{26}H_{48}O_2$ 392.3654, found 392.3651.

4.9.6. Oxacyclononacos-15-en-2-one (18g). Yield: 57%, as an inseparable mixture of *E*- and *Z*-isomer, colorless oil, R_f=0.69 (hexane/EtOAc=20:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21–1.35 (m, 38H), 1.60–1.65 (m, 4H), 2.00–2.05 (m, 4H), 2.31 (t, *J*=7.2 Hz, 2H), 4.10 (t, *J*=5.8 Hz, 2H), 5.33–5.35 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.92, 29.01, 29.11, 29.18, 29.20, 29.23, 29.28, 29.33, 29.35, 29.39, 29.46, 29.47, 29.49, 29.57, 29.6, 32.1, 32.2, 34.5, 64.2, 64.3, 129.9, 130.0, 130.5, 130.6, 173.91, 173.92; IR (thin film, NaCl plates): 3053, 2927, 2854, 1725, 1456, 1265, 970, 741 cm^{-1}; MS *m*/*z* (relative intensity): 420 (M^+, 8), 402 (3), 124 (9), 96 (38), 82 (55), 67 (59), 54 (100), 41 (47); HRMS calcd for $C_{28}H_{52}O_2$ 420.3967, found 420.3970.

4.9.7. Oxacyclohentriacont-16-en-2-one (18h). Yield: 51%, as an inseparable mixture of *E*- and *Z*-isomer, pale yellow oil, R_f=0.67 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21–1.46 (m, 42H), 1.59–1.65 (m, 4H), 1.95–2.05 (m, 4H), 2.31 (t, *J*=7.1 Hz, 2H), 4.09 (t, *J*=6.0 Hz, 2H), 5.32–5.39 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.1, 28.47, 28.6, 29.03, 29.06, 29.11, 29.17, 29.21, 29.23, 29.33, 29.38, 29.43, 29.47, 29.50, 29.53, 29.57, 34.5, 64.2, 64.3, 129.91, 129.94, 130.45, 130.53, 173.89, 173.92; IR (thin film, NaCl plates): 3053, 2926, 2854, 1727, 1464, 1265, 896, 741 cm^{-1}; MS *m*/*z* (relative intensity): 448 (M^+, 9), 430 (4), 110 (11), 96 (45), 82 (66), 67 (62), 54 (100), 41 (93); HRMS calcd for $C_{30}H_{56}O_2$ 448.4280, found 448.4282.

4.9.8. Oxacycloheptatriacont-19-en-2-one (18i). Yield: 63%, as an inseparable mixture of *E*- and *Z*-isomer, white solid, mp 65–68 °C, R_f=0.81 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26–1.34 (m, 54H), 1.60–1.65 (m, 4H), 1.96–2.03 (m, 4H), 2.30 (t, *J*=7.2 Hz, 2H), 4.08 (t, *J*=6.0 Hz, 2H), 5.35–5.37 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.07, 28.6, 28.9, 29.1, 29.25, 29.35, 29.38, 29.43, 29.48, 29.49, 29.51, 29.54, 29.56, 29.58, 29.63, 29.66, 34.47, 64.2, 64.3, 129.92, 129.94, 130.46, 130.49, 173.91; IR (thin film, NaCl plates): 3053, 2925, 2853, 1731, 1466, 1265, 969, 741 cm^{-1}; MS *m*/*z* (relative intensity): 532 (M^+, 16), 514 (6), 110 (14), 96 (51), 82 (76), 67 (62), 55 (100), 41 (47); HRMS calcd for $C_{36}H_{68}O_2$ 532.5219, found 532.5219.

4.10. General procedure for the hydrogenation of unsaturated macrolactone (for compounds 19a′, 19a″, and 19b–19i)

To a two-necked flask containing 5% palladium on charcoal (1.06 mg, 0.01 mmol) was added a solution of unsaturated lactone **18e** (66 mg, 0.21 mmol) in EtOAc (2 mL) and the mixture was stirred at rt for 6 h under hydrogen in the balloon. The catalyst was removed by filtration and the solvent was evaporated in vacuo. The residue was chromatographed on a silica gel column to give macrolactone **19e** (53 mg, 0.17 mmol, 82% yield) as a colorless oil, R_f=0.42 (hexane/EtOAc=20:1).

4.10.1. Oxacycloheneicosan-2-one (19e). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26–1.39 (m, 30H), 1.59–1.66 (m, 4H), 2.31 (t, *J*=7.2 Hz, 2H), 4.10 (t, *J*=6.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.1, 25.7, 27.5, 27.6, 27.7, 27.78, 27.82, 28.2, 28.4, 28.6, 28.7, 28.8, 28.9, 34.7, 64.3, 174.0; IR (thin film, NaCl plates): 2925, 2854, 1736, 1461, 1249, 1170, 738 cm^{-1}; MS *m*/*z* (relative intensity): 310 (M^+, 11), 292 (8), 95 (62), 82 (45), 54 (100), 41 (74); HRMS calcd for $C_{20}H_{38}O_2$ 310.2872, found 310.2875.

4.10.2. 1,10-Dioxacyclooctadecane-2,9-dione (19a′) and 1,10-dioxacyclooctadecane-2,11-dione (19a″). The general procedure of the RCM was followed to prepare unsaturated bislactone **18a′** and **18a″** (109 mg, 0.18 mmol, 30% yield, as an inseparable mixture of *E*- and *Z*-isomer) in 24 h from diene **17a** (280 mg, 0.44 mmol). According to the general procedure of the hydrogenation, a mixture of compounds **18a′** and **18a″** (50 mg, 0.36 mmol) was subjected to the catalytic hydrogenation to give an inseparable mixture of compounds **19a′** and **19a″** (31 mg, 0.22 mmol, 61% yield) as a white solid, mp 75–78 °C, R_f=0.35 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.32–1.37 (m, 12H), 1.59–1.67 (m, 8H), 2.32 (t, *J*=7.2 Hz, 4H), 4.11 (t, *J*=5.9 Hz, 2H), 4.10–4.12 (t, *J*=5.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.0, 25.2, 25.6, 25.7, 28.5, 28.55, 28.61, 28.64, 28.7, 34.9, 35.0, 63.8, 64.2, 173.6, 173.7; IR (thin film, NaCl plates): 2931, 2857, 1727, 1462, 1265, 739 cm^{-1}; MS *m*/*z* (relative intensity): 284 (M^+, 3), 266 (9), 138 (20), 124 (17), 82 (14), 55 (38), 41 (100).

4.10.3. Oxacycloundecan-2-one (19b).[49] Yield: 89%, a white solid, mp 83–84 °C, R_f=0.45 (hexane/EtOAc=10:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29–1.36 (m, 10H), 1.57–1.67 (m, 4H), 2.28–2.31 (m, 2H), 4.08–4.11 (m, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.2, 26.1, 28.5, 28.9, 29.1, 29.4, 34.8, 64.2, 173.8; IR (thin film, NaCl plates): 2931, 2860, 1734, 1460, 1250, 1144 cm^{-1}; MS *m/z* (relative intensity): 171 (M^++1, 3), 152 (7), 138 (11), 124 (7), 110 (9), 97 (13), 83 (11), 69 (16), 55 (72), 41 (100).

4.10.4. Oxacyclotridecan-2-one (19c). Yield: 71%, a white solid, mp 93–94 °C, R_f=0.56 (hexane/EtOAc=10:1). ^1H NMR ($CDCl_3$, 400 MHz) δ 1.28–1.59 (m, 14H), 1.60–1.71 (m, 4H), 2.31 (t, J=7.0 Hz, 2H), 4.10 (t, J=5.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.3, 26.0, 28.6, 28.9, 29.0, 29.1, 29.4, 29.5, 34.7, 64.1, 173.9; IR (thin film, NaCl plates): 2919, 2852, 1731, 1263, 740 cm^{-1}; MS *m/z* (relative intensity): 199 (M^++1, 4), 181 (2), 98 (14), 69 (14), 54 (94), 41 (100); HRMS calcd for $C_{12}H_{22}O_2$ 198.1620, found 198.1619.

4.10.5. Oxacyclopentadec-8-en-2-one (19d). Yield: 87%, a colorless oil, R_f=0.63 (hexane/EtOAc=10:1). ^1H NMR ($CDCl_3$, 400 MHz) δ 1.25–1.37 (m, 18H), 1.62–1.69 (m, 4H), 2.35 (t, J=6.3 Hz, 2H), 4.14 (t, J=5.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.7, 24.9, 25.1, 26.0, 26.36, 26.48, 26.51, 26.70, 26.72, 27.75, 28.3, 34.0, 64.0, 174.2; IR (thin film, NaCl plates): 2929, 2858, 1736, 1243, 737 cm^{-1}; MS *m/z* (relative intensity): 225 (M^+−1, 15), 207 (11), 166 (15), 95 (77), 69 (98), 54 (100), 41 (62); HRMS calcd for $C_{14}H_{26}O_2$ 226.1933, found 226.1935.

4.10.6. Oxacycloheptacosan-2-one (19f). Yield: 88%, a colorless oil, R_f=0.67 (hexane/EtOAc=10:1). ^1H NMR ($CDCl_3$, 400 MHz) δ 1.24–1.33 (m, 42H), 1.61–1.65 (m, 4H), 2.30 (t, J=7.2 Hz, 2H), 4.09 (t, J=6.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.1, 26.0, 28.4, 28.5, 28.60, 28.64, 28.7, 28.92, 28.98, 29.01, 29.08, 29.12, 29.16, 29.20, 29.3, 34.5, 64.3, 174.0; IR (thin film, NaCl plates): 2926, 2854, 1728, 1265, 742 cm^{-1}; MS *m/z* (relative intensity): 394 (M^+, 29), 376 (13), 95 (31), 69 (51), 55 (100), 41 (57); HRMS calcd for $C_{26}H_{50}O_2$ 394.3811, found 394.3811.

4.10.7. Oxacyclononacosan-2-one (19g). Yield: 90%, a white solid, mp 30–31 °C, R_f=0.56 (hexane/EtOAc=10:1). ^1H NMR ($CDCl_3$, 400 MHz) δ 1.23–1.28 (m, 46H), 1.61–1.63 (m, 4H), 2.31 (t, J=7.2 Hz, 2H), 4.08 (t, J=6.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.0, 26.0, 28.6, 28.66, 28.71, 28.74, 28.77, 28.84, 28.93, 28.94, 28.97, 29.02, 29.11, 29.13, 29.20, 29.25, 29.28, 29.30, 34.5, 64.3, 174.01; IR (thin film, NaCl plates): 2924, 2853, 1738, 1172 cm^{-1}; MS *m/z* (relative intensity): 422 (M^+, 13), 404 (6), 96 (49), 69 (47), 55 (100), 41 (61); HRMS calcd for $C_{28}H_{54}O_2$ 422.4124, found 422.4124.

4.10.8. Oxacyclohentriacontan-2-one (19h). Yield: 86%; a colorless oil, R_f=0.70 (hexane/EtOAc=10:1). ^1H NMR ($CDCl_3$, 400 MHz) δ 1.26–1.28 (m, 50H), 1.61–1.63 (m, 4H), 2.30 (t, J=7.1 Hz, 2H), 4.08 (t, J=6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.0, 25.6, 28.6, 28.7, 28.8, 28.85, 28.90, 28.93, 28.98, 29.05, 29.11, 29.15, 29.16, 29.2, 29.3, 29.46, 29.51, 29.6, 29.7, 34.5, 64.3, 174.0; IR (thin film, NaCl plates): 2924, 2853, 1738, 1171 cm^{-1}; MS *m/z* (relative intensity): 450 (M^+, 12), 432 (7), 97 (27), 69 (63), 55 (100), 41 (46); HRMS calcd for $C_{30}H_{58}O_2$ 450.4437, found 450.4435.

4.10.9. Oxacycloheptatriacontan-2-one (19i). Yield: 92%, a white solid, mp 53–54 °C, R_f=0.72 (hexane/EtOAc=20:1). ^1H NMR ($CDCl_3$, 400 MHz) δ 1.22–1.32 (m, 62H), 1.60–1.62 (m, 4H), 2.30 (t, J=7.4 Hz, 2H), 4.07 (t, J=6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.04, 28.99, 29.03, 29.09, 29.10, 29.12, 29.13, 29.18, 29.26, 29.28, 29.33, 29.38, 29.41, 29.43, 29.47, 29.69, 34.5, 64.3, 174.0; IR (thin film, NaCl plates): 2925, 2852, 1732, 1264 cm^{-1}; MS *m/z* (relative intensity): 534 (M^+, 17), 516 (6), 111 (6), 97 (14), 69 (41), 55 (100), 41 (46); HRMS calcd for $C_{36}H_{70}O_2$ 534.5376, found 534.5378.

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