Cascade radical cyclization of polyolefinic vinyl iodides: comparison between 5-*exo* and 6-*endo* cyclization of vinyl radicals

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Dedicated to Professor S. V. Kessar on the occasion of his 70th birthday
(received 18 Jul 02; accepted 11 Sep 02; published on the web 19 Sep 02)

Abstract
We herein describe sequential radical cyclization of acyclic polyenes having a vinyliodide moiety that can act as both of a radical donor and an acceptor during the same reaction. The regioselectivity is extremely dependent on the substrate structure. Tricyclo[8.4.0.$0^{2,7}$]tetradecene and tricyclo[6.3.0.$0^{2,6}$]undecane were obtained by cascade radical cyclization from the well-designed substrates, 1-iodo-1,5,9,14-tetraene and 1-iodo-1,5,10-triene, in a single operation.

Keywords: Cascade reaction, radical reaction, regioselectivity, vinyl radicals, polycyclic systems

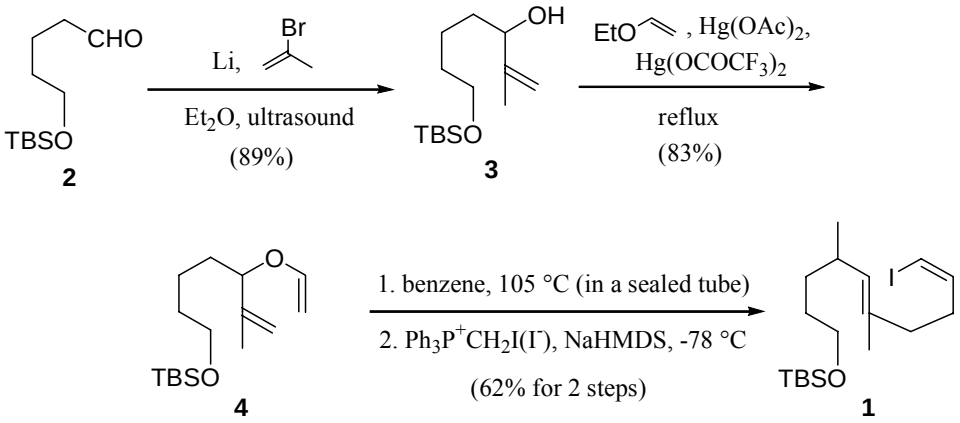
Introduction

Radical reactions have become valuable tools for the construction of complex molecules and have solved various fundamental problems associated with ionic reactions.[1] Out of various types of radical reaction, the cascade (tandem) reaction is one of the most powerful methods to construct a polycyclic ring system in one step from unsaturated acyclic precursors.[2] It is well documented that 5-alkenyl radicals (alkyl radicals) predominantly undergo 5-*exo* cyclization to give 5-membered products over the 6-*endo* mode.[3] The cascade 5-*exo* radical cyclization reactions based on the above feature have been developed to synthesize polycyclic 5-membered compounds.[4] Although the examples were limited, cascade 6-*endo* radical cyclizations were investigated and utilized in the syntheses of steroidal skeletons. It was made clear that ketyl radicals are effective for consecutive 6-*endo* cyclization.[5] On the other hand, in 1980s Beckwith and Stork have independently reported that the use of vinyl radicals for a ring closure has shown unique behavior indicating an equilibrium between 5-*exo* and 6-*endo* cyclizations.[6,7] In this paper

we try to focus on the cascade radical cyclization of vinyl radicals to assemble terpenoid frameworks from simple polyolefinic materials.[8]

Results and Discussion

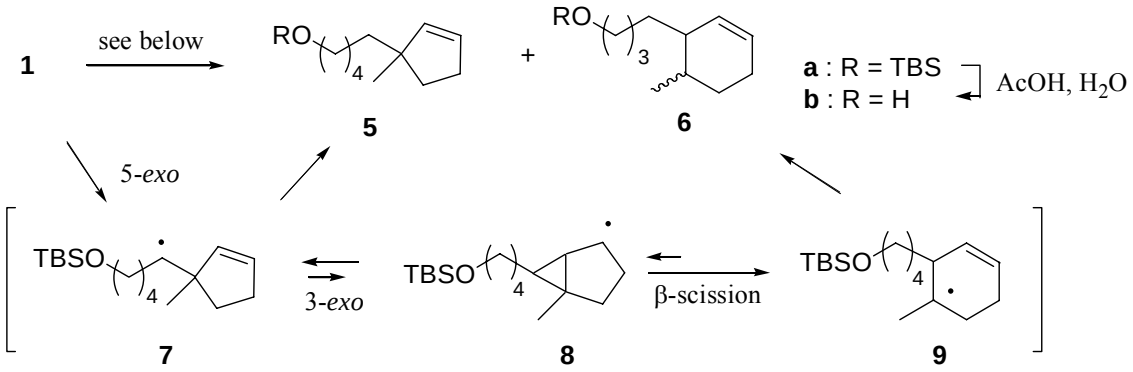
As a preliminary experiment, we examined the intramolecular radical cyclization of a vinyl iodide with a trisubstituted olefin moiety. The iodo olefinic substrate **1** was readily prepared from 1-(*tert*-butyldimethylsiloxy)pentanal (**2**)[9] in four steps (Scheme 1). Allylic alcohol **3** was prepared by Barbier reaction of **2** in 89% yield under the ultrasonic circumstance. After *O*-vinylation of **3**, the corresponding ether **4** was transformed into vinyl iodide **1** by Claisen rearrangement, followed by *Z*-selective Wittig olefination.[10]



Scheme 1. Preparation of 1-iodo-1,5-diene **1**.

The radical reactions were performed by using Bu_3SnH (TBTH) in the presence of a catalytic amount of AIBN or $Et_3B–O_2$ as a radical initiator (Table 1). Under refluxing conditions in benzene at 80 °C, **1** was transformed into the cyclohexene **6a**, which was isolated as **6b**, after deprotection of the silyl group, as a diastereomeric mixture in the ratio of 1 : 3.5 (entry 1). On the other hand, the treatment of **1** at low temperature (–40 °C), followed by desilylation, provided the cyclopentene **5b** as a major product along with **6b** (entry 2). The formation of the 6-*endo* adduct under thermodynamic conditions can be explained as follows based on homoallyl–homoallyl radical rearrangement.[11] The radical reaction initially proceeds through 5-*exo* cyclization in accordance with Baldwin's rule[12] to give the secondary radical species **7**. At higher temperature the 5-*exo* adduct **7** further cyclizes by 3-*exo* manner to give the unstable intermediate **8**. Cyclopropylcarbinyl radical **8** is rapidly transformed by β-scission into the thermodynamically stable tertiary radical **9**, which was consequently transformed into the 6-*endo* product **6a**. Thus, 5-*exo* or 6-*endo* adducts could be synthesized from the vinyl radical precursor by changing the reaction temperature.

Table 1. Radical cyclization of 1-iodo-1,5-diene **1**

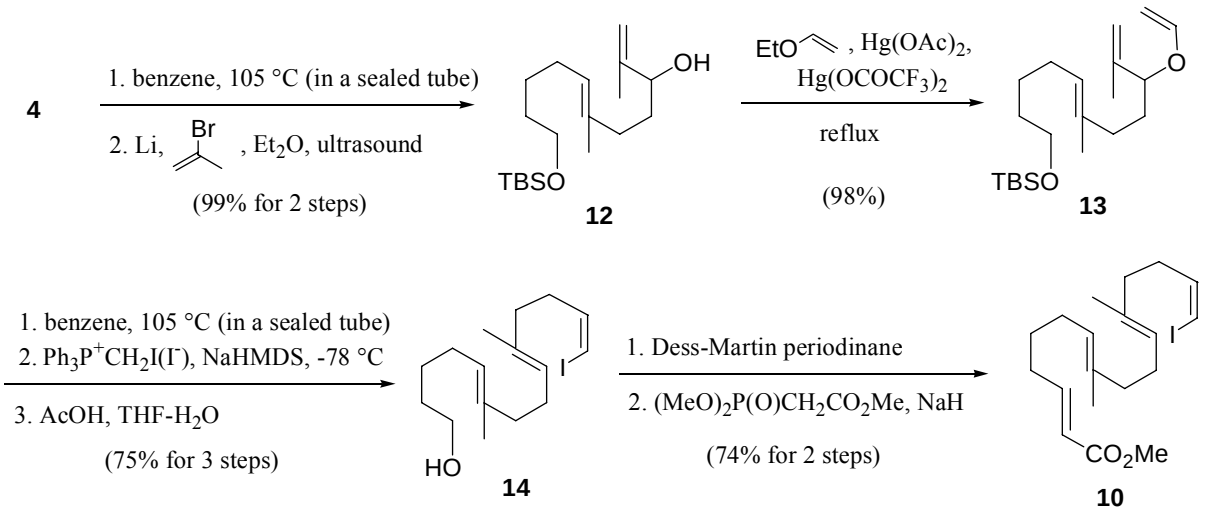


entry	conditions	cyclized yield (%)[a]	ratio[b] (**5b** : **6b**[c])
1	Bu_3SnH, AIBN, benzene (1 mM), reflux	70	0 : 1
2	Bu_3SnH, Et_3B, O_2, toluene (1 mM), –40 °C	85	2 : 1

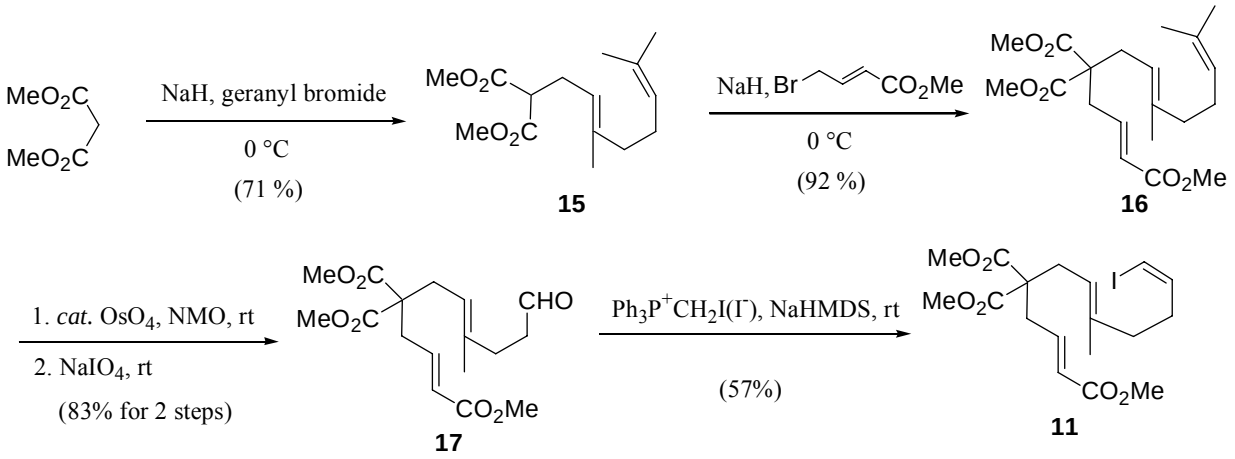
[a] Overall yield in 2 steps. [b] The ratio was determined by ^{1}H-NMR.
[c] **6b** was obtained as a 3.5:1 diastereomeric mixture.

Next, we planned the sequential radical cyclization of suitably functionalized acyclic substrates to construct polycyclic skeletons. We rationally designed vinyl iodides **10** and **11** as geranylgeranyl and farnesyl motifs, respectively. The terminal unsaturated ester moiety was anticipated to act as a good acceptor to accelerate the radical addition.[13] 1-Iodo-1,5,9,14-tetraenoate **10** was prepared from **4** in 8 steps (Scheme 2). Allyl alcohol **12** was prepared by Claisen rearrangement of **4**, followed by Barbier reaction with 2-bromopropene. *O*-Vinylation of **12** provided vinyl ether **13** in 98% yield. Vinyl iodide **14** was prepared by Claisen rearrangement of **13**, followed by Wittig olefination and desilylation. **14** was obtained as a single isomer having *Z* configuration with respect to the iodo olefine double bond. Oxidation of hydroxyl group of **14** with Dess-Martin periodinane,[14] followed by HWE reaction, afforded the key substrate **10**.

1-Iodo-1,5,10-trienoate **11** was prepared by a short sequence of reactions as shown in Scheme 3. Dimethyl malonate was mono-alkylated with geranyl bromide to afford diene **15** in 71% yield, and further alkylation of **15** with methyl 4-bromocrotonate gave trienoate **16** in 92% yield. The treatment of **16** with a catalytic amount of osmium tetroxide in the presence of *N*-methylmorpholine oxide (NMO), followed by oxidative cleavage of the corresponding diol by sodium periodate, provided the desired aldehyde **17** (83% overall yield in two step). (*Z*)-Vinyl iodide **11** was prepared by Wittig reaction of **17** in 57% yield as a single isomer.



Scheme 2. Preparation of 1-iodo-1,5,9,14-tetraene **10**.

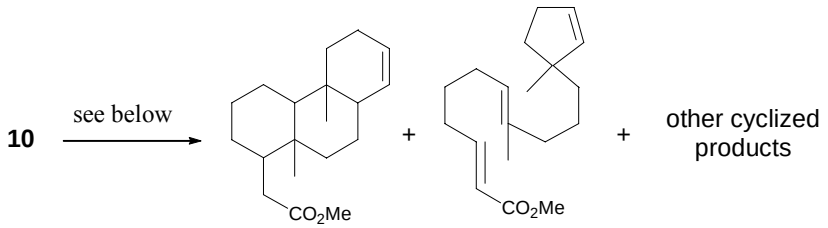


Scheme 3. Preparation of 1-iodo-1,5,10-triene **11**.

The radical reaction of tetraene **10** was examined under various conditions; reductive electrolysis,[15] TBTH method, and tris(trimethylsilyl)silane (TTMSH) method (Table 2). The electrolysis, mediated by $Ni(cyclam)^{2+}$ of **10** at room temperature, yielded the dodecahydrophenanthrene derivative **18**, the cyclopentene derivative **19**, and other cyclized products with a 5 : 2 : 3 ratio in low yield (entry 1). The formation of **18** results from the 6-*endo*, 6-*endo*, 6-*exo* cascade cyclization. When the reaction was performed at 100 °C, the ratio of **18** increased considerably but the yield was still low (entry 2). On the other hand, when **10** was exposed to thermal conditions by using TBTH or TTMSH, the desired cascade cyclization proceeded in high yield to give **18** as a major product (entries 3 and 4). Especially, the treatment with TTMSH–AIBN at 80 °C exclusively afforded **18** in 77% yield. The structure of **18** was

established by the spectral analysis after conversion of the olefin moiety into the carbonyl function,[16] although the stereochemistry was not determined owing to difficulty of separation of each diastereomer. The free radical reaction at –40 °C using TBTH–Et_3B in the presence of O_2 gas gave only **19** in very high yield (entry 5).

Table 2. Radical cyclization of 1-iodo-1,5,9,14-tetraene **10**



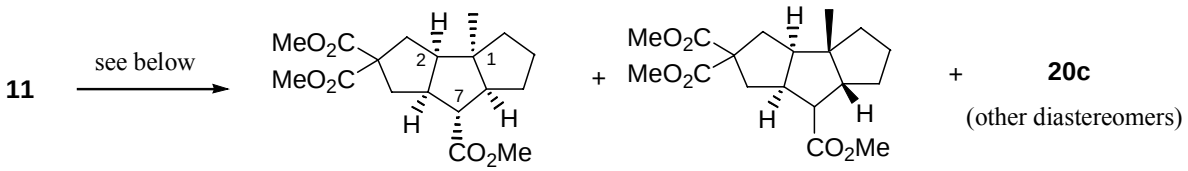
18 **19**

Entry	Conditions	% Yield	Ratio[a] (**18**[b]:**19**:others[c])
1	Ni(cyclam)$(ClO_4)_2$, NH_4ClO_4, DMF, –1.5 V, rt	22	5 : 2 : 3
2	Ni(cyclam)$(ClO_4)_2$, NH_4ClO_4, DMF, –1.5 V, 100 °C	39	8 : 0 : 2
3	Bu_3SnH, AIBN, benzene (1 mM), reflux	76	8.5 : 0 : 1.5
4	$(TMS)_3SiH$, AIBN, benzene (1 mM), reflux	77	10 : 0 : 0
5	Bu_3SnH, Et_3B, O_2, toluene (1 mM), –40 °C	94	0 : 10 : 0

[a] Ratio was determined by ^{1}H-NMR. [b] **18** was obtained as a 4:4:1:1 diastereomeric mixture.
[c] The structures were not determined.

In contrast, the radical reaction of 1-iodo-1,5,10-trienoate **11**, which lacks one isoprene unit compared with **10**, gives quite different results.[17] The radical cyclization reaction of **11** was conducted under similar conditions as above (Table 3). The reaction with TBTH–AIBN under refluxing conditions afforded tricyclo[6.3.0.$0^{2,6}$]undecanes **20** in 80% yield as a mixture of more than four isomers (entry 1). The cascade reaction proceeded to give a linear-triquinane framework, but unselective formation of several diastereomers was observed. At room temperature the number of stereoisomers was reduced; treatment with TBTH–Et_3B at room temperature afforded only two isomers, **20a** and **20b**, in 83% yield with a ratio of 4 : 3 (entry 2). However, when the temperature was further lowered (–40 °C), the yields of mono and double-cyclized products were increased (entry 3). The TTMSH method gave almost similar results to the TBTH method (entries 4 and 5). On the contrary, the cathodic electrolysis, mediated by $Ni(cyclam)^{2+}$, afforded poor production of **20** (entries 6 and 7).

Table 3. Radical cyclization of 1-iodo-1,5,10-triene **11**



20a **20b**

Entry	Conditions	Total yield of **20** (%)	Ratio[a] (**20a**:**20b**:**20c**)
1	Bu_3SnH, AIBN, benzene (2 mM), reflux	80	4 : 3 : 4
2	Bu_3SnH, Et_3B, O_2, benzene (2 mM), rt	83	4 : 3 : 0
3	Bu_3SnH, Et_3B, O_2, toluene (2 mM), –40 °C	54	nd[b]
4	$(TMS)_3SiH$, AIBN, benzene (2 mM), reflux	80	4 : 3 : 7
5	$(TMS)_3SiH$, Et_3B, O_2, benzene (2 mM), rt	74	4 : 3 : 0
6	$Ni(cyclam)(ClO_4)_2$, NH_4ClO_4, DMF, –1.5 V, 100 °C	54	nd[b]
7	$Ni(cyclam)(ClO_4)_2$, NH_4ClO_4, DMF, –1.5 V, rt	29	nd[b]

[a] Ratio of **20a**, **20b** and **20c** was determined by ^{1}H-NMR . [b] "nd" means "not determined".

After a careful purification by column chromatography on silica gel, only **20a** was separated from the mixture of **20a** and **20b** (from entry 2 in Table 3). The structural assignment of **20a** was achieved on the basis of detailed 2D NMR experiments (NOE correlation was shown in Figure 1). Its framework was determined as a *cis*-*syn*-*cis* linear-triquinane and the methoxycarbonyl group at C (7) was located on the convex side of the skeleton. On the contrary, isolation of **20b** could not be achieved by any efforts. No epimerization of **20a** occurred by treatment with DBU under thermodynamic conditions or by LDA under kinetic conditions. It indicates that the acidic proton at C (7) of **20a** stands on the sterically hindered position. When a mixture of **20a** and **20b** was subjected to kinetic deprotonation conditions (LDA, then aqueous work up), a new epimer was obtained along with **20a** and **20b**. This suggests that the new epimer is the diastereomer of **20b** and, moreover, **20b** has a different stereochemistry of a linear-triquinane skeleton from **20a**. Based on the mechanistic aspect and Curran's previous results,[17] the framework of **20b** might be *cis*-*anti*-*cis* configuration.

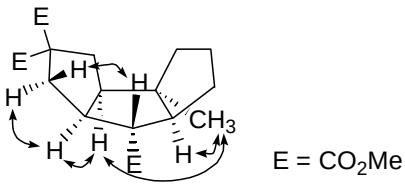
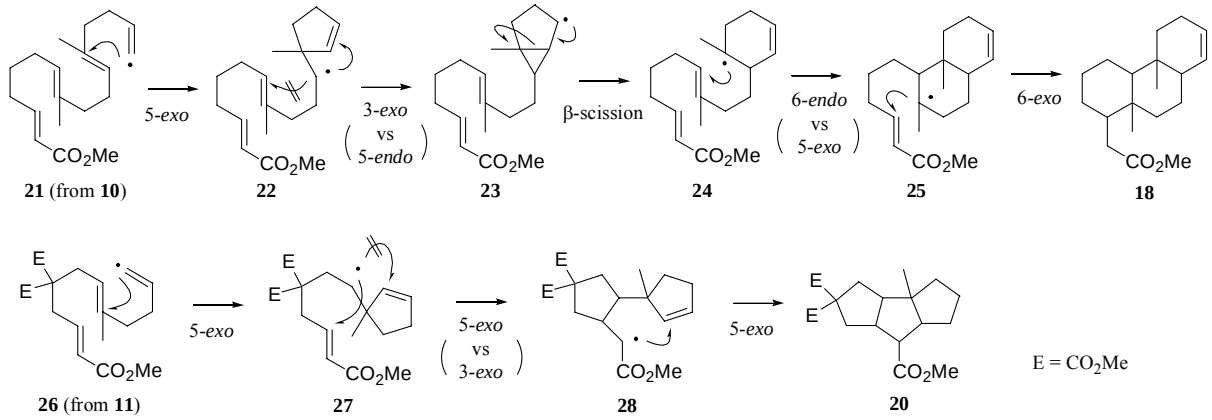


Figure 1. Characteristic NOEs for **20a**.

It is interesting to observe that the radical reactions of acyclic isoprenoid analogs **10** and **11** proceed in different cyclization manners. The reaction of geranylgeranyl analog **10** produces tricyclo[8.4.0.$0^{2,7}$]tetradecene **18**, which is a linear fused six-membered ring carbocycle, through a sequential 6-*endo*, 6-*endo*, 6-*exo* cyclization. Whereas a 5-*exo*, 5-*exo*, 5-*exo* cyclization proceeds in the case of farnesyl analog **11** to give tricylo[6.3.0.$0^{2,6}$]undacane **20**, which is a linear fused five-membered ring carbocycle. The reaction pathways of tetraene **10** and triene **11** can be rationally explained as shown in Scheme 4. In both case, the first radical cyclizations of corresponding **21** and **26** proceed through the kinetically favored 5-*exo* cyclization to form cyclopentenyl intermediates **22** and **27**, respectively. But the cascade sequences may be firmly dependent on the regioselectivity at the second stage of the radical addition. In the former case, 3-*exo*-*trig* cyclization undergoes to give intermediate **23** under the thermodynamic conditions, whereas 5-*endo*-*trig* cyclization with another olefin moiety can be ruled out by Baldwin's rule. Unstable intermediate **23** is rearranged into thermodynamically stable tertiary alkyl radical **24**, which is consistent with the formal 6-*endo*-*trig* cyclized intermediate from vinyl radical **21**. In the third radical cyclization stage, due to the steric effect, the 6-*endo* cyclization may be predominant over 5-*exo* to afford bicyclic radical **25**.[18] Finally, the radical reaction completes by the sequential 6-*exo*-trig cyclization to give the decahydrophenanthrene adduct **18**. On the contrary, in the reaction of **11**, cyclized radical intermediate **27** will be converted into **28** by means of the 5-*exo*-trig cyclization. 5-*Exo* cyclization should be much preferred to 3-*exo*-*trig* one owing to the stereoelectronic effect.[19] Final 5-*exo*-trig radical cyclization of **28**, followed by hydride abstraction, furnishes the linear-triquinane adduct **20**. The complementary results of radical reactions of **10** and **11** will be attributed to the characteristic features of radical cascades.



Scheme 4. Proposal mechanisms of cascade radical reaction of tetraene **10** and triene **11**.

In summary, tricyclo[8.4.0.$0^{2,7}$]tetradecene **18** and tricyclo[6.3.0.$0^{2,6}$]undecane **20** were obtained by cascade radical cyclization from 1-iodo-1,5,9,14-tetraene **10** and 1-iodo-1,5,10-triene **11**, respectively, in a single operation. The reactivity and selectivity of the cascade reaction can be controlled by the rational design of the substrate, such as incorporation of an

isoprene unit or the introduction of terminal ester function. Further studies will pave way for the facile total syntheses of various natural products.

Experimental Section

General. **Procedures.** All reactions were carried out under an inert atmosphere. Anhydrous THF, Et_2O, MeCN, and CH_2Cl_2 were purchased from the Kanto Chemical Co., Inc. Toluene, DME and benzene were distilled from CaH_2 under atmospheric. Unless otherwise described, the materials were obtained from commercial suppliers and used without further purification. Organic extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure using an evaporator. Unless otherwise described, the ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, and were reported in ppm downfield from TMS ($\delta = 0$) for the ^1H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.00$) for the ^{13}C NMR.

7-*tert*-Butyldimethylsiloxy-2-methyl-1-hepten-3-ol (3). To a suspension of Li (321 mg, 46.3 mmol) in Et_2O (50 mL) was added a solution of 2-bromopropene (1.23 mL, 13.9 mmol) in Et_2O (3 mL) at 0 °C, and then the mixture was irradiated of an ultrasonic cleaner (30 W) at 0 °C for 2 h. After the slow addition of a solution of the aldehyde **2** (2.00 g, 9.25 mmol) in Et_2O (10 mL) at 0 °C, the resulting mixture was continued to be irradiated at the same temperature for 10 min. The mixture was quenched with sat. NH_4Cl at 0 °C, and then the resulting mixture was extracted with Et_2O. The organic extracts were washed with brine, dried, filtered, and evaporated to give a crude product. Chromatography of the residue on silica gel (19: 1 hexane/EtOAc) furnished **3** (2.13 g, 89%) as colorless oil. IR (neat) ν 3670–3100, 2950, 2860, 1470, 1460, 1260, 1100, 840, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.89 (s, 1H), 4.79 (s, 1H), 4.05–3.99 (m, 1H), 3.57 (t, *J* = 6.6 Hz, 2H), 1.68 (s, 3H), 1.65–1.42 (m, 5H), 1.41–1.23 (m, 2H), 0.85 (s, 9H), 0.00 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 147.8, 111.1, 76.0, 63.2, 34.6, 32.6, 25.9, 21.9, 18.3, 17.4, –5.4; LRMS *m/z* (rel intensity) 201 (1, M^+–^{t}Bu), 109 (100). *Anal*. Calcd for $C_{14}H_{30}O_2Si$: C, 65.06; H, 11.70. Found: C, 65.04; H, 11.40.

7-*tert*-Butyldimethylsiloxy-2-methyl-3-vinyloxy-1-heptene (4). To a stirred solution of the alcohol **3** (5.70 g, 22.1 mmol) in ethyl vinyl ether (200 mL) were added $Hg(OAc)_2$ (94.0 mg, 221 μmol) and $Hg(OCOCF_3)_2$ (70.0 mg, 221 μmol) at rt, and then the mixture was stirred at 50 °C for 48 h. After cooled to rt, the mixture was evaporated to furnish a crude product, which was chromatographed on silica gel (49: 1 hexane/EtOAc) affording **4** (5.22 g, 83%) as colorless oil. IR (neat) ν 2950, 2850, 1640, 1610, 1470, 1460, 1260, 1200, 1100, 840, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.24 (dd, *J* = 14.0, 6.6 Hz, 1H), 4.89–4.86 (m, 2H), 4.25 (dd, *J* = 14.0, 1.4 Hz, 1H), 4.03 (t, *J* = 6.6 Hz, 1H), 3.93 (dd, *J* = 6.6, 1.4 Hz, 1H), 3.56 (t, *J* = 6.6 Hz, 2H), 1.62 (s, 3H), 1.58–1.43 (m, 4H), 1.21–1.41 (m, 2H), 0.85 (s, 9H), 0.00 (s, 6H); ^{13}C NMR ($CDCl_3$) δ150.8, 144.4, 113.4, 88.7, 83.9, 63.1, 33.0, 32.6, 25.9, 21.8, 18.3, 16.8, –5.4; LRMS *m/z* (rel intensity)

241 (6, $M^+–C_2H_3O$), 227 (10, $M^+–{}^tBu$), 109 (100). *Anal*. Calcd for $C_{16}H_{32}O_2Si$: C, 67.54; H, 11.33. Found: C, 67.65; H, 11.35.

(1*Z*,5*E*)-10-*tert*-Butyldimethylsiloxy-1-iodo-5-methyl-1,5-decadiene (1). A solution of the vinyl ether **4** (1.56 g, 5.50 mmol) in degassed benzene (8 mL) in a sealed tube was allowed to warm at 105 °C for 48 h. After being cooled to rt, the mixture was evaporated to give the crude oil, which was used in the next step without purification. To a solution of $Ph_3P^+CH_2I(I^-)$ (4.10 g, 7.70 mmol) in THF (45 mL) at –78 °C was dropwise added NaHMDS (1.0 M in THF; 6.60 mL, 5.66 mmol), and then the resulting solution was stirred at –78 °C for 30 min. After the slow addition of the solution of the above aldehyde in THF (5 mL), the mixture was stirred at –78 °C for 1 h, and allowed to warn to rt. The mixture was diluted with hexane and filtered through Celite, and the residue was washed with hexane. The filtrate was washed with H_2O, brine, dried, filtered, and evaporated. Chromatography of the resulting oil on silica gel (49: 1 hexane/EtOAc) afforded **1** (1.45 g, 62%) as colorless oil. IR (neat) ν 2920, 2850, 1460, 1250, 1100, 830, 770 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.19–6.13 (m, 2H), 5.15 (m, 1H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.26–1.97 (m, 6H), 1.62(s, 3H), 1.58-1.34 (m, 4H), 0.90 (s, 9H), 0.05 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 141.2, 134.0, 125.7, 82.3, 63.2, 37.7, 33.2, 32.5, 27.6, 26.0, 18.4, 15.9, –5.3; LRMS *m/z* (rel intensity) 351 (51, $M^+–{}^tBu$), 75 (100). HRMS calcd for $C_{13}H_{24}IOSi$ ($M^+–{}^tBu$) 351.0639, found 351.0639.

(6*E*)-11-*tert*-Butyldimethylsiloxy-2,6-dimethyl-1,6-undecadien-3-ol (12). A solution of the vinyl ether **4** (1.96 g, 6.88 mmol) in degassed benzene (5 mL) in a sealed tube was allowed to warm at 105 °C for 48 h. After being cooled to rt, the solution was concentrated under reduced pressure to furnish the residue, which was used in the next step without purification. To a suspension of Li (239 mg, 34.4 mmol) in Et_2O (70 mL) was added 2-bromopropene (0.92 mL, 10.3 mmol) in Et_2O (3 mL) at 0 °C, and then the mixture was irradiated of an ultrasonic cleaner at 0 °C for 1 h. After the slow addition of the above aldehyde in Et_2O (10 mL) at 0 °C, the resulting mixture was irradiated at the same temperature for 10 min. The reaction solution was quenched with *sat.* NH_4Cl at 0 °C, and then extracted with Et_2O. The organic extracts were washed with brine, dried, filtered, and evaporated to give crude residue, which was chromatographed on silica gel (19: 1 hexane/EtOAc) to provide **12** (2.22 g, 99% from **4**) as colorless oil. IR (neat) ν 3650–3150, 2950, 2860, 1480, 1470, 1390, 1260, 1100, 840, 780 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.13 (t, *J* = 7.0 Hz, 1H), 4.90 (m, 1H), 4.80 (s, 1H), 4.01 (s, 1H), 3.56 (t, *J* = 6.3 Hz, 2H), 2.05–1.90 (m, 4H), 1.69 (s, 3H), 1.57 (s, 3H), 1.65–1.43 (m, 5H), 1.37–1.29 (m, 2H), 0.85 (s, 9H), 0.00 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 147.7, 134.9, 125.2, 111.2, 75.8, 63.2, 35.7, 33.2, 32.5, 27.7, 26.0, 18.4, 17.6, 16.0, –5.32; LRMS *m/z* (rel intensity) 269 (3, $M^+–{}^tBu$), 75 (100). *Anal*. Calcd for $C_{19}H_{38}O_2Si$: C, 69.88; H, 11.73. Found: C, 70.07; H, 11.55.

(6*E*)-11-*tert*-Butyldimethylsiloxy-2,6-dimethyl-3-vinyloxy-1,6-undecadiene (13). To a stirred solution of the alcohol **12** (5.00 g, 15.3 mmol) in ethyl vinyl ether (115 mL) were added $Hg(OAc)_2$ (49.0 mg, 150 μmol) and $Hg(OCOCF_3)_2$ (65.0 mg, 150 μmol) at rt, and then the mixture was stirred at 50 °C for 48 h. After being cooled to rt, the mixture was evaporated to give an oily residue, which was purified by chromatography on silica gel (49: 1 hexane/EtOAc)

giving **13** (5.27 g, 98%) as colorless oil. IR (neat) ν 2940, 2860, 1640, 1480, 1460, 1260, 1200, 1170, 1100, 840, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.27 (dd, *J* = 14.0, 6.6 Hz, 1H), 5.14 (t, *J* = 6.0 Hz, 1H), 4.93–4.90 (m, 2H), 4.29 (dd, *J* = 14.0, 1.4 Hz, 1H), 4.05 (t, *J* = 6.6 Hz, 1H), 3.97 (dd, *J* = 6.6, 1.4 Hz, 1H), 3.60 (t, *J* = 6.3 Hz, 2H), 2.06–1.94 (m, 5H), 1.83–1.71 (m, 1H), 1.67 (s, 3H), 1.59 (s, 3H), 1.57–1.47 (m, 2H), 1.40–1.31 (m, 2H), 0.89 (s, 9H), 0.00 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 150.8, 144.5, 134.3, 125.4, 113.4, 88.7, 83.3, 63.2, 35.4, 32.5, 31.7, 27.7, 26.0, 26.0, 26.0, 18.4, 16.9, 16.0, –5.3; LRMS *m/z* (rel intensity) 309 (1, M^+–C_2H_3O), 295 (2, M^+–^{t}Bu), 43 (100). *Anal*. Calcd for $C_{21}H_{40}O_2Si$: C, 71.53; H, 11.43. Found: C, 71.50; H, 11.28.

(5*E*,9*E*,13*Z*)-14-Iodo-6,10-dimethyl-5,9,13-tetradecatrien-1-ol (14). A solution of the vinyl ether **13** (1.66 g, 4.72 mmol) in degassed benzene (2 mL) in a sealed tube was allowed to warm at 105 °C for 24 h. After being cooled to rt, the mixture was evaporated to give crude residue, which was used in the next step without purification. To a solution of $Ph_3P^+CH_2I(I^-)$ (3.50 g, 6.61 mmol) in THF (70 mL) at –78°C was added dropwise NaHMDS (1.0 M in THF; 5.66 mL, 5.66 mmol), and then the resulting solution was stirred at –78 °C for 0.5 h. After the slow addition of the solution of the above aldehyde in THF (8 mL), the mixture was stirred at –78 °C for 1 h, and allowed to warm to rt. The mixture was diluted with hexane and filtered through Celite. The filtrate was washed with H_2O, brine, dried, filtered, and evaporated to give oily residue, which was used in the next step without purification. To a solution of the above *Z*-olefin in THF (5 mL) was added a mixture of AcOH and H_2O (3 : 1 v/v, 20 mL) at 0 °C, and the resulting mixture was stirred at 0 °C for 48 h. The mixture was quenched with *sat.* $NaHCO_3$, and then extracted with EtOAc. The organic layers were washed with brine, dried, filtered. Removal of the solvent under reduced pressure followed by chromatography on silica gel (4: 1 hexane/EtOAc) afforded **14** (1.28 g, 75% from **13**) as colorless oil. IR (neat) ν 3600–3100, 2930, 2850, 1450, 1300, 1280, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.19–6.10 (m, 2H), 5.13 (t, *J* = 6.9 Hz, 2H), 3.64 (t, *J* = 6.3 Hz, 2H), 2.27–2.20 (m, 2H), 2.15–2.00 (m, 9H), 1.62 (s, 3H), 1.60 (s, 3H), 1.58–1.53 (m, 2H), 1.45–1.35 (m, 2H); LRMS *m/z* (rel intensity) 362 (4), 71 (100). HRMS calcd for $C_{16}H_{27}IO$ (M^+) 362.1104, found 362.1109.

Methyl (2*E*,7*E*,11*E*,15*Z*)-16-iodo-8,12-dimethyl-2,7,11,15-hexadecatetraenoate (10). To a stirred suspension of Dess–Martin periodinane (8.17 g, 19.3 mmol) in CH_2Cl_2 (50 mL) was added **14** (1.99 g, 5.5 mmol) in CH_2Cl_2 (10 mL) at rt for 2 h. The resulting mixture was diluted with Et_2O, and then quenched with sat. $NaHCO_3$ and 0.1 N $Na_2S_2O_3$, and stirred for an additional hour. The solution was extracted with Et_2O, and the ethereal layers were washed with *sat.* $NaHCO_3$ and brine, dried, filtered, and evaporated to furnish the crude aldehyde, which was used in the next step without further purification. To a stirred suspension of NaH (60% w/w in oil; 441 mg, 11.0 mmol) in DME (100 mL) was added trimethylphosphonoacetate (2.23 ml, 13.8 mmol) at rt and stirred for 30 min. After the slow addition of the above aldehyde in DME (10 mL), the resulting mixture was stirred at the same temperature for 3 h. The mixture was quenched with H_2O, and the solution was extracted with Et_2O. The ethereal layers were washed with H_2O, brine, dried, filtered, and evaporated. Chromatography of the resultant oil on silica gel (97: 3 hexane/EtOAc) afforded **10** (1.70 g, 74% from **14**) as colorless oil. IR (neat) ν 2930, 2850,

1720, 1660, 1440, 1280, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.98 (dt, *J* = 15.7, 7.0 Hz, 1H), 6.19–6.10 (m, 2H), 5.82 (d, *J* = 15.7 Hz, 1H), 5.15–5.10 (m, 2H), 3.73 (s, 3H), 2.27–1.98 (m, 12H), 1.63 (s, 3H), 1.59 (s, 3H), 1.55–1.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 167.3, 149.8, 141.1, 135.8, 133.9,125.2, 123.9, 121.0, 82.2, 51.3, 39.5, 37.6, 33.2, 31.6, 28.0, 27.2, 26.4, 15.9, 15.8; LRMS *m/z* (rel intensity) 416 (1), 108 (100). HRMS calcd for $C_{19}H_{29}IO_2$ (M^+) 416.1210, found 416.1224.

Dimethyl (6*E*)-2,6-dimethylnona-2,6-diene-9,9-dicarboxylate (15). To a stirred suspension of NaH (1.15 g, 60% in oil, 28.8 mmol) in dry THF (150 mL) was added dimethyl malonate (3.47 g, 26.3 mmol) in dry THF (30 mL) dropwise at 0 °C. After being stirred for 15 min, a solution of geranyl bromide (5.70 g, 26.3 mmol) in dry THF (20 mL) was added to the reaction mixture at the same temperature. The reaction mixture was stirred for additional 45 min. The mixture was quenched with H_2O, and then extracted with Et_2O. The organic layer was washed with 10% HCl, $NaHCO_3$ solution and brine, dried ($MgSO_4$), evaporated to give oily residue. The crude oil was purified by column chromatography on silica gel (9: 1 hexane/EtOAc) to afforded **15** (5.00 g, 71%) as colorless oil. IR (neat) ν 2948, 2928, 1735, 1429, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.07 (br s, 2H), 3.73 (s, 6 H), 3.38 (t, *J* = 7.7 Hz, 1H), 2.61 (t, *J* = 7.7 Hz, 2H), 2.06–1.94 (m, 4H), 1.67 (s, 3H), 1.63 (s, 3H), 1.59 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 169.7, 138.8, 131.5, 124.1, 119.5, 52.3, 51.8, 39.6, 27.4, 26.4, 25.5, 17.5, 15.8; LRMS *m/z* 268 (M^+), 225, 199, 167, 136, 107, 69; Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01%. Found: C, 66.72; H, 9.04%.

Trimethyl (6*E*,11*E*)-2,6-dimethyldodeca-2,6,11-triene-9,9,12-tricarboxylate (16). To a suspension of NaH (0.48 g, 60% in oil, 12.1 mmol) in dry THF (100 mL), was added diester **15** (3.00 g, 11.19 mmol) in dry THF (15 mL) dropwise at 0 °C, and stirred for 20 min. To the reaction mixture was added a solution of methyl 4-bromocrotonate (1.5 mL, 12.8 mmol) in dry THF (10 mL) at the same temperature. After being stirred for 1 h, H_2O was added into the reaction mixture. The mixture was extracted with Et_2O, washed with 10% HCl, $NaHCO_3$ solution and brine, dried and concentrated. The crude oil was purified by column chromatography on silica gel (4: 1 hexane/EtOAc) to afford **16** (3.77 g, 92%) as colorless. IR (neat) ν 2950, 2851, 1735, 1721, 1649, 1436 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.79 (dt, *J* = 15.5, 7.7 Hz, 1H), 5.84 (dt, *J* = 15.5, 1.4 Hz, 1H), 5.01–4.90 (m, 2H), 3.76 (s, 9 H), 2.75 (dd, *J* = 7.7, 1.4 Hz, 2H), 2.63 (d, *J* = 7.7 Hz, 2H), 2.16–1.98 (m, 4H), 1.68 (s, 3H), 1.60 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 171.2, 166.5, 143.4, 140.1, 131.8, 124.7, 124.1, 117.2, 57.6, 52.6, 51.5, 39.9, 35.3, 31.4, 26.4, 25.6, 17.7, 16.2; LRMS *m/z* 366 (M^+), 334, 306, 237, 205, 145, 69; HRMS calcd for $C_{20}H_{30}O_6$: 366.2042. Found: 366.2036.

Trimethyl (3*E*,8*E*)-1-formyl-3-methylnona-3,8-diene-6,6,9-tricarboxylate (17). To a solution of the triester **16** (3.00 g, 8.2 mmol) in CH_3CN–H_2O (2: 1; 75 mL) was added *N*-methylmorpholine oxide (1.92 g, 16.4 mmol) and catalytic amount of OsO_4 (1 mL, 1% w/v in THF) at 0 °C. The mixture was stirred for 8 h at room temperature. A saturated solution of Na_2SO_3 was added into the reaction mixture. After being stirred for 2 h, the reaction mixture was diluted with EtOAc. The mixture was extracted with EtOAc, washed with 10% HCl, $NaHCO_3$ solution and brine, dried and concentrated. The crude oil was purified by column

chromatography on silica gel (1: 1 hexane/EtOAc) to afford the corresponding diol (2.79 g, 85%) as colorless oil. Diol; IR (neat) ν 3448, 2951, 1735,1722,1650, 1435 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.80 (dt, *J* = 15.4, 7.7 Hz, 1H), 5.86 (dt, *J* = 15.4, 1.4 Hz, 1H), 5.05 (t, *J* = 7.1 Hz, 1H), 3.73 (s, 6H), 3.72 (s, 3H), 3.30 (br d, *J* = 10.4 Hz, 1H), 2.77 (d, *J* = 7.7 Hz, 2H), 2.63 (d, *J* = 7.7 Hz, 2H), 2.36 (br s, 1H), 2.29–2.05 (m, 3H), 1.79 (br s, 1H), 1.61 (s, 3H), 1.46–1.33 (m, 1H), 1.20 (s, 3H), 1.16 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 171.2, 166.5, 143.2, 139.8, 124.6, 117.6, 77.7, 72.9, 57.5, 52.6, 51.5, 36.8, 35.3, 31.4, 29.4, 26.2, 23.2, 16.0; LRMS *m/z* 382 (M^+–H_2O), 351, 341, 299, 251, 237, 198, 166, 59.

To a solution of the above diol (3.60 g, 9.00 mmol) in Et_2O–H_2O (2 : 1) (100 mL) was added $NaIO_4$ (2.30 g, 10.8 mmol) at room temperature. After being stirred for 2 h, the reaction mixture was diluted with Et_2O, and then extracted with Et_2O. The mixture was washed with brine, dried and evaporated. The crude oil was purified by column chromatography on silica gel (4: 1 hexane/EtOAc) to afford **17** (3.00 g, 98%) as colorless oil. IR (neat) ν 2936, 1735, 1720, 1648, 1426 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.75 (t, *J* = 1.8 H, 1H), 6.77 (dt, *J* = 15.4, 7.7 Hz, 1H), 5.85 (dt, *J* = 15.4, 1.4 Hz, 1H), 5.04–4.99 (m, 1H), 3.73 (s, 6 H), 3.72 (s, 3H), 2.74 (dd, *J* = 7.7, 1.4 Hz, 2H), 2.62 (d, *J* = 7.4 Hz, 2H), 2.54–2.49 (m, 2H), 2.33 (t, *J* = 7.7 Hz, 2H), 1.62 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 202.2, 171.1, 166.5, 143.0, 138.2, 124.8, 118.4, 57.5, 52.7, 51.6, 42.1, 35.5, 32.0, 31.4, 16.3; LRMS *m/z* 341 (M^++1), 308, 277, 258, 226, 198, 177, 166; Anal. Calcd for $C_{17}H_{24}O_7$: C, 59.99; H, 7.11%. Found: C, 59.65; H, 7.01%.

Trimethyl (1*Z*,5*E*,10*E*)-1-Iodo-5-methylundeca-1,5-10-triene-8,8,11-tricarboxylate (11). To a solution of (iodomethyl)triphenylphosphonium iodide [$Ph_3P^+CH_2I(I^-)$] (7.03 g, 13.3 mmol) in THF (60 mL) was added 1.5 M hexane–solution of sodium hexamethyldisilazide (NaHMDS; 10 mL, 15 mmol) at room temperature, and then the mixture was stirred for 2 h at the same temperature. To the resulting mixture was added a solution of **17** (2.25 g, 6.62 mmol) in THF (5 mL) at –78 °C. The mixture was stirred for 20 min at –78 °C, and then diluted with hexane. After filtration through Celite and rinse with hexane, the organic layer was washed with brine, and then dried. The residue was purified with column chromatography on silica gel (1: 9 EtOAc/hexane) to give **11** (1.70 g, 57%) as colorless oil. IR (neat) ν 2950, 1735, 1725, 1649, 1437 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.79 (dt, *J* = 15.4, 7.7 Hz, 1H), 6.21 (dt, *J* = 7.4, 1.3 Hz, 1H), 6.11 (q, *J* = 6.3 Hz, 1H), 5.86 (dt, *J* = 15.4, 1.4 Hz, 1H), 5.00–4.95 (m, 1H), 3.76 (dd, *J* = 7.7, 1.3 Hz, 2H), 3.73 (s, 6H), 2.63 (d, *J* = 7.4 Hz, 2H), 2.27–2.20 (m, 2H), 2.21 (t, *J* = 7.1 Hz, 2H), 1.63 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 171.0, 166.3, 143.1, 140.6, 138.9, 124.7, 118.0, 82.7, 57.4, 52.6, 51.5, 37.8, 35.3, 33.0, 31.3, 16.1; MS *m/z* 465 (M^++1); HRMS *m/z* calcd for $C_{19}H_{26}IO_6$ (M^++1) 465.0774, found 465.0797.

General procedure of radical reaction. (for TBTH and TTMSH methods)

To a stirred solution of the vinyl iodide (0.10 mmol) in degassed benzene or toluene (1~2 mM) was added a 1 M solution of Et_3B in hexane (50 μL, 0.05 mmol) or AIBN (8.5 mg, 0.05 mmol) at room temperature. To the mixture was slowly added a solution of Bu_3SnH (30 μL, 0.12 mmol) or $(TMS)_3SiH$ (40 μL, 0.12 mmol) in degassed benzene (5 mL) over 3 h using a syringe pump.

After being stirred, the solution was concentrated. The resulting residue was chromatographed on silica gel.

(for indirected electrolysis) The radical cyclization of the iodides (1.0 equiv.) by electroreductively generated nickel(I) species was carried out in DMF (13 mL) containing supporting electrolyte (Et_4NClO_4; 0.1 M in DMF), proton source (NH_4ClO_4, 2 equiv. based onthe iodide), and catalytic amount of the nickel(II) complex (0.1 equiv based on the iodide) potentiostatically at the reductive peak potential of the nickel(II) complex using a graphite electrode as the cathode in an H-shaped divided cell under inert gas with mechanical stirring. Electrolysis of the iodides was carried out at –1.50 V *vs*. SCE. After all the iodide was consumed by electrolysis, the catholyte was subjected to the usual extractive work up followed by purification on silica gel column chromatography.

1-(5-Hydroxypentyl)-1-methyl-2-cyclopentene (5b) and 1-(4-Hydroxybutyl)-6-methyl-2-cyclohexene (6b). (Table 1, entry 1) Radical reaction was carried out by TBTH method at –40 °C to give crude mixture of silyl ethers **5a** and **6a**. To a solution of the above silyl ethers in THF (1 mL) was added a mixture of AcOH and H_2O (3 : 1 v/v, 4 mL) at 0 °C, and the resulting mixture was stirred at 0 °C for 24 h. The mixture was quenched with sat. $NaHCO_3$ and the resulting solution was extracted with EtOAc. The organic extracts were washed with brine, dried, and filtered. Removal of the solvent under reduced pressure followed by chromatography on silica gel (4: 1 hexane/EtOAc) provided alcohols **5b** and **6b** (22.0 mg, 70% from **1**) as an inseparable 2 : 1 mixture. As a 2: 1 mixture; IR (neat) ν 3600–3100, 2900, 2850, 1450, 1050, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.61–5.47 (m, 2H), 3.68–3.61 (m, 2H), 2.35–2.28 (m, 1H), 2.09–1.99 (m, 2H), 1.75–1.26 (m, 10H), 1.01 (s, 2H), 0.96 (d, *J* = 6.6 Hz, 0.3H), 0.85 (d, *J* = 6.9 Hz, 0.7H); LRMS *m/z* (rel intensity) 168 (8), 81 (100). HRMS calcd for $C_{11}H_{20}O$ (M^+) 168.1513, found 168.1505.

1-(4-Hydroxybutyl)-6-methyl-2-cyclohexene (6b). (Table1, entry 2) As a 2 : 1 diastereomeric mixture; Colorless oil, IR (neat) ν 3330, 2920, 2850, 1450, 1370, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.65–5.51 (m, 2H), 3.66 (t, *J* = 6.6 Hz, 2H), 2.00–1.97 (m, 3H), 1.61–1.26 (m, 10H), 0.96 (d, *J* = 6.6 Hz, 0.66H), 0.85 (d, *J* = 6.9 Hz, 2.34H); LRMS *m/z* (rel intensity) 168 (19), 95 (100). HRMS calcd for $C_{11}H_{20}O$ (M^+) 168.1513, found 168.1513.

11-Methoxycarbonylmethyl-2,10-dimethyltricyclo[8.4.0.0^{2,7}]tetradec-5-ene (18). Purified by Chromatography on silica gel (49: 1 hexane/EtOAc). As a 4: 4: 1: 1 diastereomeric mixture; Colorless oil, IR (neat) ν 2950, 2870, 1720, 1600, 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.72–5.68 (m, 0.6H), 5.57–5.55 (m, 0.8H), 5.36–5.32 (m, 0.6H), 3.67 (s, 0.3H), 3.66 (s, 0.3H), 3.65 (s, 1.2H), 3.65 (s, 1.2H), 2.46–0.82 (m, 25H); LRMS *m/z* (rel intensity) 290 (94), 108 (100). HRMS calcd for $C_{19}H_{30}O_2$ (M^+) 290.2244, found 290.2242.

Methyl (2*E*,7*E*)-8-Methyl-11-(1-methyl-2-cyclopentenyl)-2,7-undecadienoate (19). Purified by Chromatography on silica gel (97: 3 hexane/EtOAc). Colorless oil. IR (neat) ν 2920, 2850, 1720, 1650, 1450, 1430, 1260, 1200, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.98 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.82 (dt, *J* = 15.7, 1.5 Hz, 1H), 5.59 (dt, *J* = 5.5, 2.2 Hz, 1H), 5.49 (dt, *J* = 5.5, 2.2 Hz, 1H), 5.08 (m, 1H), 3.73 (s, 3H), 2.35–2.29 (m, 2H), 2.37–2.16 (m, 2H), 2.05–1.92 (m, 4H), 1.72–1.61

(m, 2H), 1.60 (s, 3H), 1.57–1.26 (m, 6H), 1.01 (s, 3H); LRMS *m/z* (rel intensity) 290 (3), 81 (100). HRMS calcd for $C_{19}H_{30}O_2$ (M^+) 290.2244, found 290.2241.

Trimethyl (1R*,2R*,6S*,7S*,8S*)-1-methyltricyclo[6.3.0.0^{2,6}]undecane-4,4,7-tricarboxylate (20[a]). Colorless oil, IR (neat) ν 2952, 2867, 1732, 1435, 1265, 1199 cm^{-1}; 1H NMR (500 MHz, $CDCl_3$) δ 3.66 (s, 3H), 3.65 (s, 3H), 3.60 (s, 3H), 2.84–2.76 (m, 1H), 2.51 (dd, *J* = 14.2, 8.2 Hz, 1H), 2.34 (t, *J* = 8.0 Hz, 1H), 2.30 (t, *J* = 8.0 Hz, 1H), 2.27–2.24 (m, 1H), 2.20 (t, *J* = 10.3 Hz, 1H), 1.97 (dd, *J* = 14.2, 5.3 Hz, 1H), 1.96–1.90 (m, 1H), 1.69–1.58 (m, 4H), 1.51–1.46 (m, 1H), 1.15 (dt, *J* = 13.3, 6.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$)δ 175.7, 172.51, 172.50, 62.7, 59.8, 56.7, 54.9, 52.73, 52.65, 51.7, 51.6, 48.4, 38.8, 36.3, 36.1, 30.0, 29.9, 26.0; LRMS *m/z* 339 (M^++1); HRMS *m/z* calcd for $C_{19}H_{27}O_6$ (M^++1) 339.1808, found 339.1790.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Encouragement of Young Scientists, JSPS Postdoctoral Fellowship (for S.M.) and a Grant-in-Aid for Scientific Research on Priority Areas (A) "Exploration of Multi Element Cyclic Molecules" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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17. Previously, Curran depicted the radical reaction of analogous 1-iodo-1,5,10-triene. However, the reaction was unsatisfactory resulted in the production of tricyclo[6.3.0.$0^{2,6}$]undecane as an inseparable mixture of four diastereomers and another isomers. Curran, D. P.; Sun, S. *Aust. J. Chem.* **1995**, *48*, 261.
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