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Allylmanganation and Diallylation of Acetylenic Compounds

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Abstract: Treatment of homopropargylic alcohol and its derivatives or propargylic alcohols with tetraallylmanganate or triallylmanganate provided monoallylated products in good yields with high regio- and stereoselectivities. The intermediary alkenylmanganese compounds were trapped by various electrophiles. The reaction was clearly oxygen-assisted since 6-dodecyne was completely recovered unchanged. Diallylation products were obtained in the presence of air. Allylmagnesation and diallylation of these acetylenic compounds catalyzed by manganese salts are also disclosed.

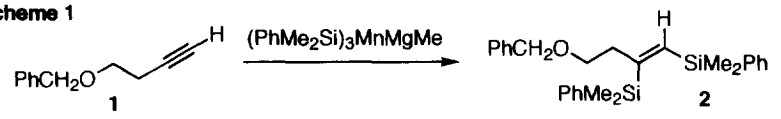
Allylic organometallic compounds have been studied extensively and widely used for highly stereoselective synthesis of homoallylic alcohols.[1] In contrast, only a few reports regarding the addition of allylic metals to triple bonds are found in the literature,[2] although allylmetalation of the carbon-carbon triple bond by allylmetals is useful for the synthesis of 1,4-dienes that widely exist in naturally occurring compounds. An allyl Grignard reagent adds to propargylic alcohols or homopropargylic alcohols by an *anti* addition process to give both regioisomers in the absence[3] or in the presence of a CuI catalyst.[4] Allylzincation of terminal alkynes is generally complicated by competitive zincation of alkynes and double allylzincation.[5,6] Bis-addition is sometimes observed and becomes the main reaction if the alkyne is metalated with an organomagnesium or organolithium reagent prior to the addition of allylzinc halides. Here we wish to report the preparation of tetraallylmanganate and triallylmanganate and their reaction with acetylenes, and the addition of allylmagnesium halide to the triple bond in the presence of a catalytic amount of a manganese salt.[7]

(1) Stoichiometric Reaction of Acetylenic Compounds with Triallyl- and Tetraallylmanganate

We have reported[8] on the preparation of tris(trialkylsilyl)manganate $(R_3Si)_3MnMgMe$ and its reaction with acetylenes. The treatment of 4-benzyloxy-1-butyne (**1**) with $(PhMe_2Si)_3MnMgMe$, derived from three equivalents of $PhMe_2SiMgMe$ and one equivalent of $MnCl_2$, afforded a disilylated product, 4-benzyloxy-1,2-bis(dimethylphenylsilyl)-1-butene (**2**) in 51% yield as a stereoisomeric mixture (*Z*/*E*=42/58) (Scheme 1). The use of Me_3MnMgI or $Et_3MnMgBr$ in place of $(PhMe_2Si)_3MnMgMe$ resulted in formation of complex mixtures and only small amounts of the desired dimethylated or diethylated products could be obtained (<10% yield). Fortunately, we have found that triallylmanganate or tetraallylmanganate added to the triple bond of

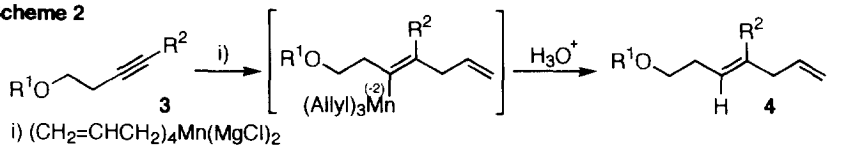
propargylic alcohols or homopropargylic alcohol and its derivatives to give monoallylated products or diallylated products.

Scheme 1



We chose several stoichiometric reagents such as allylmanganese chloride [(Allyl)MnCl],[9] diallylmanganese [(Allyl)$_2$Mn], triallylmanganate [(Allyl)$_3$MnMgCl], and tetraallylmanganate [(Allyl)$_4$Mn(MgCl)$_2$][10] and examined the reaction of these reagents with the methyl ether of 3-decyn-1-ol (**3a**). Among them, tetraallylmanganate, derived from four equivalents of allylmagnesium chloride and one equivalent of manganese(II) chloride, proved to be the best reagent in terms of the yield of the allylated product. Thus, treatment of **3a** with tetraallylmanganate at 0 °C for 1 h and 25 °C for 12 h gave (*E*)-4-hexyl-7-methoxy-1,4-heptadiene (**4a**) in 80% yield after aqueous workup (Scheme 2). The reaction of **3a** with triallylmanganate provided **4a** in only 35–40% yield accompanied by unidentified complex side products and the starting ether **3a** was recovered completely in the reaction with diallylmanganese or allylmanganese chloride. 3-Decyn-1-ol (**3b**), benzyl ether of 3-decyn-1-ol (**3c**) and tetrahydropyranyl ether of 3-decyn-1-ol (**3d**) also provided the corresponding allylated products **4b**, **4c**, **4d** in 60%, 30%, and 40% yields, respectively, upon treatment with tetraallylmanganate. The reaction was clearly oxygen-assisted since 6-dodecyne was completely recovered even after heating the mixture at reflux in THF for 10 h.

Scheme 2

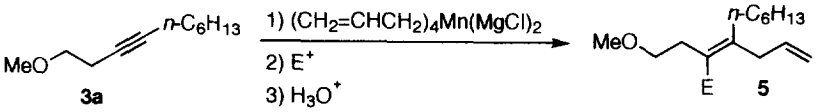


i) $(CH_2{=}CHCH_2)_4Mn(MgCl)_2$

a : R^1 = Me, R^2 = *n*-C_6H_{13} b : R^1 = H, R^2 = *n*-C_6H_{13}
c : R^1 = $PhCH_2$, R^2 = *n*-C_6H_{13} d : R^1 = THP, R^2 = *n*-C_6H_{13}

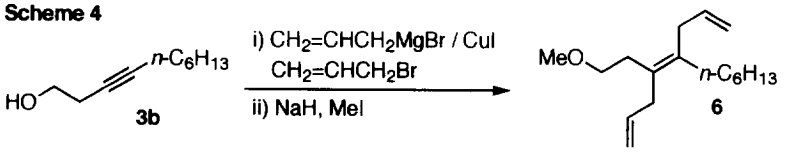
The intermediary alkenylmanganate could be trapped by electrophiles. An addition of deuterium oxide or allyl bromide afforded the corresponding adducts **5a** or **5b** in 70% or 65% yield, respectively (Scheme 3). An attempt to trap the intermediary alkenylmanganese species by benzaldehyde resulted in formation of a complex mixture. The reaction proceeded with high regio- and stereoselectivities. The *syn*-addition of an allyl-manganese component was confirmed by comparison of **5b** with an authentic sample of the *trans*-diallylated product, (4*Z*)-4-hexyl-5-(2-methoxyethyl)-1,4,7-octatriene (**6**) derived from 3-decyn-1-ol according to the reported procedure (Scheme 4).[3]

Scheme 3



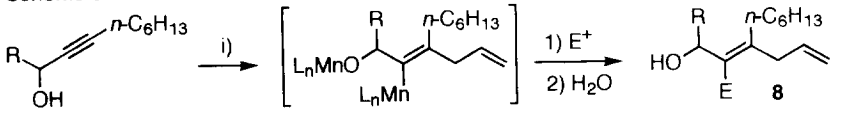
5a : E = D **5b** : E = $CH_2CH{=}CH_2$

Scheme 4



The use of propargylic alcohol alkyl ether (n-$C_6H_{13}C{\equiv}C$-CH_2OMe) instead of homopropargylic ether afforded a complex mixture containing an allenyl product, [n-$C_6H_{13}(CH_2{=}CHCH_2)C{=}C{=}CH_2$], generated by S_N2' displacement of methoxide by the allyl anion. However, the reaction of propargylic alcohol, 2-nonyn-1-ol (**7a**) with triallylmanganate in THF gave allylated product **8a** in 55% yield. The presence of HMPA increased the yield of **8a** up to 90%.[11] The use of triallylmanganate was also essential for the successful reaction in this case, and the yield of **8a** dropped to 30–40% upon treatment with tetraallylmanganate because of the formation of an allenyl product.[12] The intermediary alkenylmanganese compound could be trapped by various electrophiles. The addition of D_2O, allyl bromide, iodine, and benzoyl chloride provided the corresponding adducts **8b**, **8c**, **8d**, **8e** in 90%, 65%, 50%, and 50%, respectively. Trapping with benzaldehyde or iodomethane was not successful and **8a** was obtained as the main product. Secondary propargylic alcohol such as 6-tridecyn-5-ol (**7b**) was less reactive than primary propargylic alcohol **7a** and afforded 4-hexyl-1,4-decadien-6-ol (**8f**) in only 45% yield (Scheme 5). The *syn*-addition of the reaction was confirmed by comparison of **8c** with an authentic sample of the *trans*-diallylated product, (4*Z*)-4-hexyl-5-hydroxymethyl-1,4,7-octatriene (**9**) which was prepared from **7a** with allylmagnesium bromide as **6**.

Scheme 5



7a : R = H, **7b** R = *n*-Bu

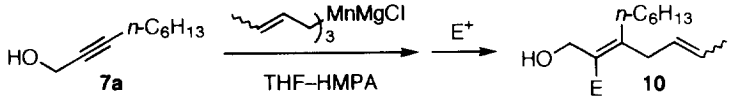
i) $(CH_2{=}CHCH_2)_3MnMgCl$ / THF–HMPA

8a : R = H, E = H **8b** : R = H, E = D **8c** : R = H, E = $CH_2CH{=}CH_2$

8d : R = H, E = I **8e** : R = H, E = C(O)Ph **8f** R = *n*-Bu, E = H

Other allylic Grignard reagents were studied on the reaction with **7a**. The tricrotylmanganate reagent provided 3-hexyl-2,5-heptadien-1-ol (**10a**) exclusively in 90% yield upon treatment with **7a** in THF-HMPA (Scheme 6). The regioisomeric product, 3-hexyl-4-methyl-2,5-hexadien-1-ol could not be detected in the reaction mixture. An addition of allyl bromide gave the corresponding allylated product **10b** in 65% yield. Triprenylmanganate did not react with **7a** and the starting alcohol **7a** was recovered unchanged.[13]

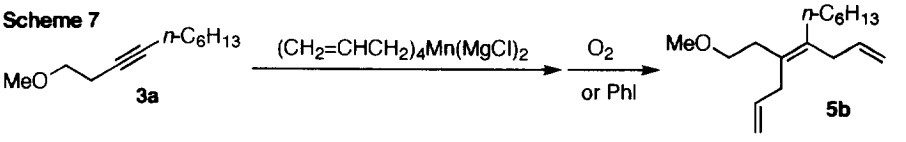
Scheme 6



10a : E = H, **10b** : E = $CH_2CH{=}CH_2$

A diallylation product was obtained after standing the reaction mixture overnight at 25 °C in a flask equipped with a balloon filled with argon. Atmospheric oxygen could diffuse into the balloon to equilibrate the partial pressure and the concentration of oxygen reached 10% (volume %) after 12 h. Thus, treatment of **3a** with tetraallylmanganate in a flask equipped with a balloon filled with argon for 12 h afforded (4*E*)-4-hexyl-5-(2-methoxyethyl)-1,4,7-octatriene (**5b**) in 75% yield. The addition of iodobenzene was also effective for the formation of the diallylated product. An addition of iodobenzene to the reaction mixture, derived from **3a** and tetraallylmanganate under argon atmosphere, gave **5b** in 80% yield (Scheme 7).

Scheme 7



We can summarize the stoichiometric reactions as follows:

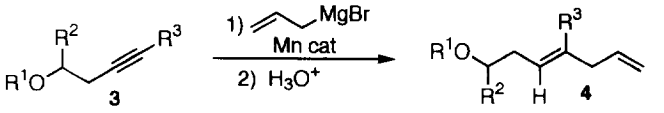
(1) Tetraallylmanganate is the choice for the allylmanganation of homopropargylic alcohols and their ethers. (2) The use of triallylmanganate and HMPA as a cosolvent is recommendable for the allylmanganation of propargylic alcohols. (3) Oxidative conditions (O_2 or PhI) are necessary to obtain diallylation products.

(2) Allylmagnesation and Diallylation of Acetylenic Compounds Catalyzed by Manganese Salts

We report here that allylmagnesium bromide adds to the triple bond of the alkyl ethers of homopropargylic alcohols to give monoallylated products with high regio- and stereoselectivities in the presence of a catalytic amount of a manganese salt such as MnI_2, $Mn(acac)_3$, or $Mn_2(CO)_{10}$. The formation of diallylation products under an oxygen atmosphere is also disclosed.

Treatment of an ethereal solution of homopropargylic alcohol methyl ether (**3a**, 1.0 mmol) with allylmagnesium bromide (1.5 mmol) in the presence of an MnI_2 catalyst (3 mol %) at 25 °C for 3 h provided monoallylated product **4a** in 83% yield (Scheme 8). Other manganese catalysts such as $Mn(acac)_3$, $MeC_5H_4Mn(CO)_3$, and $Mn_2(CO)_{10}$ were also effective for the reaction. The yields of **4a** with these catalysts were 93%, 89%, and 80%, respectively, under the same reaction conditions.[14] Benzyl ether of 3-decyn-1-ol (**3c**), THP ether of 3-decyn-1-ol (**3d**), methyl ether of 5-nonyn-3-ol (**3e**), or methyl ether of 4-phenyl-3-butyn-1-ol (**3f**) also gave the corresponding allylated product **4c**, **4d**, **4e**, or **4f** in 77%, 74%, 72%, or 74% yield, respectively, upon treatment with allylmagnesium bromide in the presence of $Mn(acac)_3$ (3 mol %) in toluene at 25 °C for 3 h.[15] Other metallic catalysts such as $PdCl_2(CH_3CN)_2$, $NiCl_2(PPh_3)_2$, $CrCl_3$, and $RuCl_3$ were ineffective, and the starting acetylenic compound **3a** was recovered unchanged.

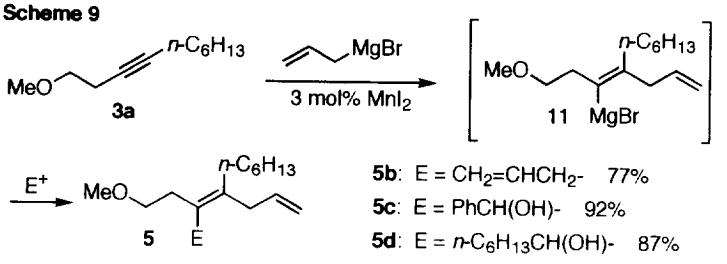
Scheme 8



a : R^1 = Me, R^2 = H, R^3 = *n*-C_6H_{13} b : R^1 = R^2 = H, R^3 = *n*-C_6H_{13}
c : R^1 = $PhCH_2$, R^2 = H, R^3 = *n*-C_6H_{13} d : R^1 = THP, R^2 = H, R^3 = *n*-C_6H_{13}
e : R^1 = Me, R^2 = Et, R^3 = *n*-C_3H_7 f : R^1 = Me, R^2 = H, R^3 = Ph

The intermediary alkenylmagnesium compound **11** could be trapped by electrophiles such as allyl bromide, PhCHO, or *n*-$C_6H_{13}CHO$ (Scheme 9). The *syn* addition of an allyl-metal component was confirmed by comparison of **5b** with the sample derived from the stoichiometric reaction described in Schemes 3 and 4.

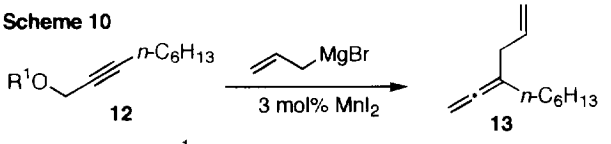
Scheme 9



5b: E = CH_2=$CHCH_2$- 77%
5c: E = PhCH(OH)- 92%
5d: E = *n*-$C_6H_{13}CH(OH)$- 87%

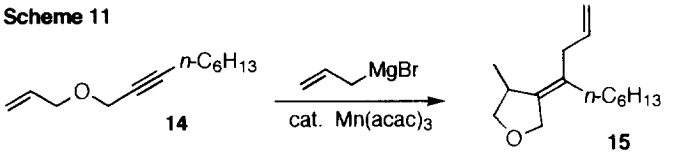
The reaction was clearly oxygen-assisted as in the case of the stoichiometric reaction since the yield dropped to 42% in the case of benzyl ether of 4-hexyn-1-ol, and 6-dodecyne was completely recovered even after heating the mixture at reflux in ether for 10 h. The use of propargylic alcohol alkyl ether **12** instead of homopropargylic substrate afforded allenyl product **13** which was generated by S_N2' type displacement of the alkoxy group by the allylic anion (Scheme 10).[16] Treatment of allyl propargyl ether **14** with allylmagnesium bromide under the same reaction conditions gave furan derivative **15** in only 27% yield in addition to allenic product **13** (15%) (Scheme 11).[17]

Scheme 10



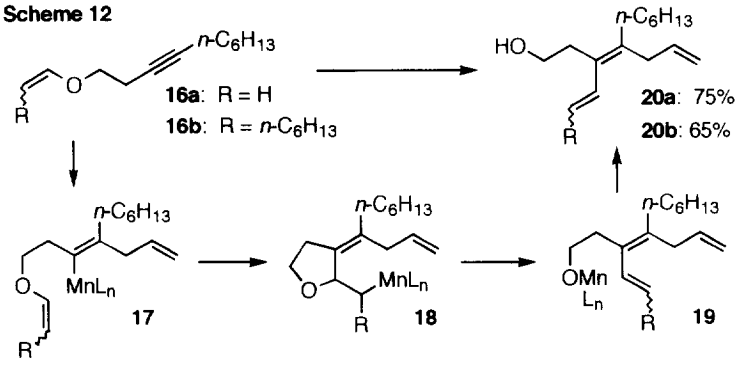
a : R^1 = Me_2C=$CHCH_2$: 56%
b : R^1 = Me : 56%

Scheme 11



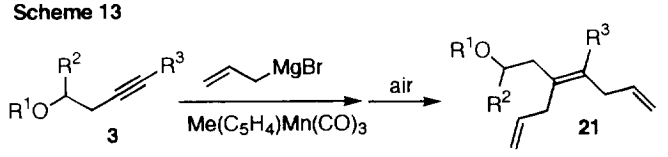
Next, the reaction of homopropargylic ether having an olefinic moiety was examined. An addition of allylmagnesium bromide to a THF solution of homopropargyl alkenyl ether **16a** and **16b** (*Z*/*E* = 90/10) in the presence of a catalytic amount of $Mn(acac)_3$ afforded tetrasubstituted alkene **20a** (75%) and **20b** (*Z*/*E* = 10/90, 65%)[18] with high stereoselectivity. We are tempted to assume the following reaction mechanism: (1) allylmanganation of **16** gives alkenylmanganese intermediate **17**, (2) intramolecular carbomanganation provides furan derivative **18**, and (3) deoxymanganation followed by transmetallation and aqueous workup affords tetrasubstituted alkene **20** (Scheme 12).

Scheme 12



Diallylation products could be formed along with the monoallylated product in the presence of oxygen. The nature of the manganese catalysts and the solvent have played a critical role in the successful formation of diallylation products. The manganese salt $MeC_5H_4Mn(CO)_3$ was our choice. Thus, treatment of a THF solution of **3a** (1.0 mmol) with allylmagnesium bromide (4.0 mmol) in the presence of $MeC_5H_4Mn(CO)_3$ (10 mol%) under argon atmosphere for 2 h at 25 °C followed by exposure of the reaction mixture to air for 12 h gave diallylated product **21a** = **5b** in 80% yield without contamination of monoallylated product **4a** (Scheme 13).[19] Starting from **3c**, **3d**, and **3e**, the corresponding diallylated product **21c**, **21d**, and **21e** were obtained in 78%, 35%, and 78% yields, respectively under the same reaction conditions. The use of $Mn(acac)_3$ instead of $MeC_5H_4Mn(CO)_3$ decreased the yield of diallylated product **21a** to 66% and the MnI_2-catalyzed reaction afforded a mixture of **4a** (42%) and **21a** (22%).

Scheme 13



a : R^1 = Me, R^2 = H, R^3 = *n*-C_6H_{13} c : R^1 = $PhCH_2$, R^2 = H, R^3 = *n*-C_6H_{13}
d : R^1 = THP, R^2 = H, R^3 = *n*-C_6H_{13} e : R^1 = Me, R^2 = Et, R^3 = *n*-C_3H_7

Summary of the catalytic reaction: (1) Treatment of homopropargylic alcohol methyl ether with allylmagnesium bromide in the presence of a manganese salt catalyst provided the monoallylated product in good yields with high regio- and stereoselectivities. (2) The intermediary alkenylmagnesium compound was trapped by various electrophiles such as carbonyl compounds and allyl bromide. (3) The $MeC_5H_4Mn(CO)_3$ catalyzed reaction with excess allylmagnesium bromide in the presence of oxygen gave the diallylated product exclusively.

Experimental

Distillation of the products was performed by the use of Kugelrohr (Büchi), and boiling points are indicated by air-bath temperature without correction. ^1H NMR and ^{13}C NMR spectra were taken on a Varian GEMINI 300 spectrometer, $CDCl_3$ was used as a solvent, and chemical shifts are given in δ with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Diethyl ether and toluene was dried over a slice of sodium. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use. Allylmagnesium bromide was purchased from Tokyo Kasei

Kogyo Co. and allylmagnesium chloride, crotylmagnesium chloride, and prenylmagnesium chloride were prepared according to the literature by Lipshutz.[4]

General Procedure for the Reaction of Homopropargylic Alcohol and its Alkyl Ether with Tetraallylmanganate. Manganese(II) chloride (188 mg, 1.5 mmol) was sonicated in tetrahydrofuran (THF, 5.0 mL) under argon atmosphere for 10 min. Allylmagnesium chloride (0.77*M* THF solution, 7.8 mL, 6.0 mmol) was added to the suspension of $MnCl_2$ in THF at 0 °C. The mixture turned into a clear brown solution and then, after being stirred for 30 min at 0 °C, a solution of 1-methoxy-3-dodecyne (**3a**, 0.17 g, 1.0 mmol) in THF (2 mL) was added at 0 °C. The whole was stirred at 0 °C for 1 h and then at 25 °C for 12 h. The mixture was poured into 1*M* HCl and extracted with ethyl acetate (3 X 20 mL). Purification of the products by silica-gel column chromatography gave (4*E*)-4-hexyl-7-methoxy-1,4-heptadiene (**4a**, 0.15 g) in 70% yield: Bp 85 °C (0.3 Torr); IR (neat) 3750, 3074, 2954, 2924, 2856, 2824, 1637, 1459, 1431, 1380, 1191, 1120, 1062, 995, 962, 910, 859 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.6 Hz, 3H), 1.21–1.41 (m, 8H), 2.02 (t, *J* = 7.2 Hz, 2H), 2.31 (dt, *J* = 7.2, 7.2 Hz, 2H), 2.74 (d, *J* = 6.9 Hz, 2H), 3.35 (s, 3H), 3.37 (t, *J* = 7.2 Hz, 2H), 4.98–5.07 (m, 2H), 5.15 (t, *J* = 7.2 Hz, 1H), 5.78 (ddt, *J* = 9.9, 16.7, 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.97, 22.54, 28.14, 28.30, 29.28, 30.18, 31.68, 41.45, 58.54, 72.72, 115.71, 121.38, 137.31, 140.34. Found: C, 79.91; H, 12.44%. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.46%.

(4E)-4-Hexyl-3,6-heptadien-1-ol (4b): Bp 125 °C (0.5 Torr); IR (neat) 3270, 2924, 2854, 1467, 1048, 994, 911 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, *J* = 7.2 Hz, 3H), 1.25–1.35 (m, 9H), 2.20 (t, *J* = 7.8 Hz, 2H), 2.29 (dt, *J* = 7.2, 6.6 Hz, 2H), 2.73 (d, J = 6.9 Hz, 2H), 3.61 (t, *J* = 6.6 Hz, 2H), 5.00 (m, 2H), 5.12 (t, *J* = 7.2 Hz, 1H), 5.75 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.97, 22.52, 28.23, 29.29, 30.21, 31.30, 31.65, 41.47, 62.57, 115.91, 121.00, 137.11, 141.91. Found: C, 79.25; H, 12.48%. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32%.

(4E)-4-Hexyl-7-benzyloxy-1,4-heptadiene (4c): Bp 140 °C (0.3 Torr); IR (neat) 3062, 3028, 2952, 2924, 2852, 1456, 1361, 1101, 1028, 994, 910, 731, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.6 Hz, 3H), 1.21–1.41 (m, 8H), 2.02 (t, *J* = 7.5 Hz, 2H), 2.36 (dt, *J* = 6.9, 7.5 Hz, 2H), 2.73 (d, *J* = 6.9 Hz, 2H), 3.46 (t, *J* = 7.5 Hz, 2H), 4.52 (s, 2H), 4.97–5.07 (m, 2H), 5.16 (t, *J* = 6.9 Hz, 1H), 5.78 (ddt, *J* = 9.9, 18.6, 6.9 Hz, 1H), 7.25–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.99, 22.54, 28.15, 28.45, 29.28, 30.20, 31.69, 41.43, 70.25, 72.83, 115.70, 121.39, 127.71, 128.43, 137.30, 138.66, 140.30. Found: C, 83.56; H, 10.75%. Calcd for $C_{20}H_{30}O$: C, 83.86; H, 10.56%.

(4E)-4-Hexyl-7-tetrahydropyranyloxy-1,4-heptadiene (4d): Bp 128 °C (0.3 Torr); IR (neat) 2924, 2854, 1640, 1466, 1458, 1201, 1138, 1121, 1070, 1033, 990, 909 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.6 Hz, 3H), 1.20–1.41 (m, 8H), 1.44–1.64 (m, 4H), 1.65–1.90 (m, 2H), 2.03 (t, *J* = 7.4 Hz, 2H), 2.33 (dt, *J* = 7.5, 6.9 Hz, 2H), 2.73 (d, *J* = 6.9 Hz, 2H), 3.39 (dt, *J* = 9.6, 7.2 Hz, 1H), 3.45–3.55 (m, 1H), 3.71 (dt, *J* = 9.6, 7.2 Hz, 1H), 3.83–3.93 (m, 1H), 4.60 (t, *J* = 3.5 Hz) 4.96–5.07 (m, 2H), 5.16 (t, *J* = 7.5 Hz, 1H), 5.77 (ddt, *J* = 9.9, 17.1, 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.98, 19.49, 22.54, 25.39, 28.16, 28.45, 29.29, 30.16, 30.63, 31.70, 41.45, 62.25, 67.33, 98.77, 115.65, 121.54, 137.34, 140.21. Found: C, 77.30; H, 11.75%. Calcd for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50%.

General procedure for the reaction of intermediate alkenylmanganese species with electrophiles. A solution of **3a** in THF was added at 0 °C to tetraallylmanganate reagent generated as described above. The mixture was stirred at 0 °C for 1 h and at 25 °C for 12 h. Then electrophiles such as D_2O and allyl bromide were added and the resulting mixture was stirred for another 1 h at 25 °C and then poured into 1.0 *M* HCl.

(4E)-4-Hexyl-5-deuterio-7-methoxy-1,4-heptadiene (5a) : IR (neat) 2922, 2854, 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, *J* = 6.9 Hz, 3H), 1.20–1.40 (m, 8H), 1.99 (t, *J* = 6.6 Hz, 2H), 2.28 (t, *J* = 6.9 Hz, 2H), 2.71 (d, *J* = 6.9 Hz, 2H), 3.32 (s, 3H), 3.34 (t, *J* = 6.9 Hz, 2H), 5.00 (m, 2H), 5.76 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.97, 22.53, 28.12, 28.19, 29.27, 30.14, 31.68, 41.37, 58.54, 72.69, 115.70, 121.00 (t, *J* = 22.4 Hz), 137.29, 140.23.

(4E)-4-Hexyl-5-(2-methoxyethyl)-1,4,7-octatriene (5b): Bp 100 °C (0.3 Torr); IR (neat) 3074, 2952,

2924, 2854, 1636, 1458, 1381, 1194, 1116, 994, 909 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3H), 1.22–1.41 (m, 8H), 2.02 (t, J = 7.7 Hz, 2H), 2.34 (t, J = 7.8 Hz, 2H), 2.74–2.80 (m, 4H), 3.34 (s, 3H), 3.37 (t, J = 7.8 Hz, 2H), 4.93–5.06 (m, 4H), 5.67–5.82 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.97, 22.55, 28.84, 29.50, 31.73, 31.97, 32.13, 36.08, 36.61, 58.48, 71.78, 114.82, 114.98, 127.95, 135.01, 136.75, 136.90. Found: C, 81.26; H, 12.14%. Calcd for $C_{17}H_{30}O$: C, 81.54; H, 12.08%.

General Procedure for the Reaction of 2-Nonyn-1-ol (7) with Triallylmanganate. Manganese(II) chloride (313 mg, 2.5 mmol) was sonicated in THF under argon atmosphere for 10 min. Allylmagnesium chloride (0.77*M* THF solution, 9.74 mL, 7.5 mmol) was added to the suspension of $MnCl_2$ at 0 °C. The mixture turned into a clear brown solution. After being stirred for 30 min, HMPA (3.0 mmol) was added and the resulting mixture was stirred for another 10 min. A solution of 2-nonyn-1-ol (**7a**, 0.14 g, 1.0 mmol) in THF (2 mL) was added at 0 °C and the mixture was stirred at 0 °C for 1 h and then at 25 °C for 10 h. Allyl bromide (1.21 g, 10 mmol) was added and the whole was stirred for 1 h at 25 °C and poured into 1*M* HCl. Extraction with ethyl acetate (20 mL X 3) followed by silica gel column chromatography purification afforded (4*E*)-4-hexyl-5-hydroxymethyl-1,4,7-octatriene (**8c**, 144 mg) in 65% yield: Bp 120 °C (0.5 Torr); IR (neat) 3270, 3074, 2998, 2952, 2924, 2854, 1637, 1459, 993, 909 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, J = 7.2 Hz, 3H), 1.16 (s, 1H), 1.20–1.40 (m, 8H), 2.08 (t, J = 6.6 Hz, 2H), 2.78 (d, J = 6.3 Hz, 2H), 2.91 (d, J = 6.0 Hz, 2H), 4.11 (s, 2H), 5.00 (m, 4H), 5.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.96, 22.51, 29.35, 29.37, 31.62, 31.73, 34.45, 36.54, 61.81, 115.24, 115.49, 131.36, 136.26, 136.92, 137.71. Found: C, 80.96; H, 11.81%. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79%.

(2E)-3-Hexyl-2,5-hexadien-1-ol (8a): Bp 103 °C (0.5 Torr); IR (neat) 3254, 3072, 2924, 2854, 1638, 1459, 1431, 995, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 7.2 Hz, 3H), 1.20–1.40 (m, 9H), 2.04 (t, J = 6.9 Hz, 2H), 2.74 (d, J = 6.6 Hz, 2H), 4.14 (d, J = 6.9 Hz, 2H), 5.03 (m, 2H), 5.40 (t, J = 6.9 Hz, 1H), 5.77 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.94, 22.48, 28.44, 29.15, 30.31, 31.58, 41.22, 59.15, 116.38, 124.56, 136.44, 142.64. Found: C, 78.78; H, 12.24%. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16%.

(2E)-2-Deuterio-3-hexyl-2,5-hexadien-1-ol (8b): Bp 105 °C (0.5 Torr); IR (neat) 3294, 3074, 2924, 2856, 1637, 1467, 1459, 1431, 994 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 6.9 Hz, 3H), 1.18–1.40 (m, 9H), 2.03 (t, J = 6.9 Hz, 2H), 2.74 (d, J = 6.9 Hz, 2H), 4.13 (s, 2H), 5.03 (m, 2H), 5.77 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.95, 22.49, 28.44, 29.16, 30.29, 31.59, 41.17, 59.08, 116.38, 124.20 (t, J = 23, 6 Hz), 136.45, 142.60. Found: C, 78.73; H, 11.40%. Calcd for $C_{12}H_{21}DO$: C, 78.63; H, 11.55%.

(2Z)-2-Iodo-3-hexyl-2,5-hexadien-1-ol (8d): IR (neat) 3304, 2954, 2924, 2856, 1468, 1458, 1060, 994, 914 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 6.9 Hz, 3H), 1.20–1.42 (m, 8H), 1.90 (t, J = 6.3 Hz, 1H), 2.24 (t, J = 7.2 Hz, 2H), 3.02 (d, J = 6.6 Hz, 2H), 4.32 (d, J = 6.3 Hz, 2H), 5.09 (m, 2H), 5.71 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.92, 22.43, 28.92, 28.99, 31.43, 32.15, 46.91, 67.39, 105.40, 116.87, 133.81, 146.09. We could not have a sample for elemental analysis because of its thermal instability.

(6E)-7-Hexyl-6,9-decadien-5-ol (8f): Bp 130 °C (0.5 Torr); IR (neat) 3308, 2956, 2920, 2856, 1468, 996, 912 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (m, 6H), 1.20–1.70 (m, 15H), 2.05 (m, 2H), 2.72 (d, J = 6.9 Hz, 2H), 4.34 (m, 1H), 5.01 (m, 2H), 5.16 (d, J = 9.0 Hz, 1H), 5.75 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.94, 22.50, 22.59, 27.64, 28.50, 29.30, 30.54, 31.61, 37.38, 41.12, 68.26, 116.28, 129.15, 136.61, 141.63. Found: C, 80.47; H, 12.58%. Calcd for $C_{16}H_{30}O$: C, 80.60; H, 12.68%.

(4Z)-4-Hexyl-5-hydroxymethyl-1,4,7-octatriene (9). The title compound was prepared according to the literature.[3] The spectral data of **9** is as follows. ^1H NMR ($CDCl_3$) δ 0.86 (t, J = 6.9 Hz, 3H), 1.16–1.38 (m, 9H), 2.02 (t, J = 6.3 Hz, 2H), 2.87 (d, J = 6.0 Hz, 2H), 2.92 (d, J = 6.6 Hz, 2H), 4.08 (s, 2H), 5.01 (m, 4H), 5.78 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.96, 22.52, 28.49, 29.51, 31.65, 32.46, 34.80, 36.17, 61.92, 115.10, 115.37, 131.77, 137.00, 137.35, 137.60.

(2E)-3-Hexyl-2,5-heptadien-1-ol (5E :5Z = 1 : 1) (10a): Bp 115 °C (0.5 Torr); IR (neat) 3284, 3016,

2952, 2926, 2854, 1453, 1438, 1378, 1048, 1003, 967 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, J = 7.2 Hz, 3H), 1.18 (s, 1H), 1.20–1.40 (m, 8H), 1.65 (d, J = 6.0 Hz, 3H), 2.02 (t, J = 6.9 Hz, 2H), 2.66 (d, J = 5.7 Hz, 2H), 4.13 (d, J = 6.9 Hz, 2H), 5.39 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 13.96, 17.80, 22.49, 28.49, 29.17, 30.32, 31.59, 39.98, 59.22, 123.99, 126.98, 128.83, 143.59. Found: C, 79.25; H, 12.18%. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32%.

(2E)-2-Allyl-3-hexyl-2,5-heptadien-1-ol (5E :5Z = 1 : 1) (10b): Bp 135 °C (0.5 Torr); IR (neat) 3300, 2954, 2924, 2854, 1456, 992, 966, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, J = 6.6 Hz, 3H), 1.14 (s, 1H), 1.20–1.38 (m, 8H), 1.62 (d, J = 6.0 Hz, 1.5H), 1.63 (d, J = 6.0 Hz, 1.5H), 2.07 (t, J = 7.2 Hz, 2H), 2.70 (d, J = 6.3 Hz, 2H), 2.91 (d, J = 6.3 Hz, 2H), 4.10 (s, 2H), 5.00 (m, 2H), 5.36 (m, 2H), 5.79 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.95, 17.78, 22.51, 29.35, 29.38, 31.62, 34.45, 35.30, 61.88, 115.15, 126.04, 128.71, 130.69, 137.07, 138.67. Found: C, 80.75; H, 11.95%. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94%.

Diallylation of 1-Methoxy-3-Decyne (3a) with tetrallylmanganate. In a flask equipped with a balloon filled with argon, allylmagnesium chloride (0.77*M* THF solution, 7.8 mL, 6.0 mmol) was added at 0 °C to a suspension of $MnCl_2$ (188 mg, 1.5 mmol, sonicated for 10 min). After being stirred for 30 min, a solution of 1-methoxy-3-decyne (**3a**, 0.17 g, 1.0 mmol) in THF (2 ml) was added and the resulting mixture was stirred at 0 °C for 1 h and then 25 °C for 12 h. Atmospheric oxygen could diffuse into the balloon to equilibrate the partial pressures and the concentration of oxygen reached 10% (volume %) after 12 h. The mixture was poured into 1*M* HCl and extracted with ethyl acetate (20 mL X 3). Purification by silica gel column chromatography afforded diallylated product **5b** in 75% yield. welcome datacomplodobenzene was also effective for the formation of diallylation diallylation product. A mixture of **3a** and tetraallylmanganate was stirred in a flask which is sealed by stopcock for 8 h at 25 °C. Then iodobenzene (8.0 mmol) was added and the whole was stirred for another 1 h. Extractive workup followed by purification gave **5b** in 80% yield.

General procedure for allylmagnesation of homopropargylic alcohol derivatives catalyzed by manganese salts. Manganese(II) iodide (9.1 mg, 0.03 mmol) and allylmagnesium bromide (1.0 *M* ether solution, 1.5 mL, 1.5 mmol) were added to a solution of 1-methoxy-3-decyne (**3a**, 0.17 g, 1.0 mmol) in ether (7 mL) at 25 °C under argon atmosphere. The reaction mixture was stirred for 2 h and poured into water. Extraction with ether (20 mL X 3) followed by purification by silica gel column chromatography provided (4*E*)-4-hexyl-7-methoxy-1,4-heptadiene (**4a**, 174 mg) in 83% yield

(4E)-7-Methoxy-4-propyl-1,4-nonadiene (4e): Bp 85 °C (2 Torr); IR (neat) 3074, 2960, 2924, 2872, 2820, 1638, 1464, 1434, 1377, 1354, 1100, 995, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (dt, J = 2.4, 7.5 Hz, 6H), 1.33–1.58 (m, 4H), 2.01 (t, J = 7.5 Hz, 2H), 2.12–2.32 (m, 2H), 2.74 (d, J = 6.9 Hz, 2H), 3.10 (tt, J = 6.9, 7.2 Hz, 1H), 3.35 (s, 3H), 4.97–5.07 (m, 2H), 5.19 (t, J = 7.2 Hz, 1H), 5.79 (ddt, J = 10.5, 17.1, 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 9.44, 14.03, 21.20, 25.97, 31.21, 32.23, 41.49, 56.60, 82.40, 115.60, 121.89, 137.42, 139.48. Found: C, 79.37; H, 12.53%. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32%.

(4Z)-7-Methoxy-4-phenyl-1,4-heptadiene (4f): Bp 108 °C (0.3 Torr); IR (neat) 3074, 3054, 2954, 2922, 2856, 2822, 1638, 1493, 1459, 1443, 1431, 1382, 1193, 1118, 993, 911, 763, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.26 (dt, J = 7.5, 6.6 Hz, 2H), 3.09 (d, J = 6.6 Hz, 2H), 3.29 (s, 3H), 3.36 (t, J = 6.6 Hz, 2H), 4.95–5.06 (m, 2H), 5.51 (t, J = 7.5 Hz, 1H), 5.72–5.88 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 29.35, 43.41, 58.45, 72.53, 116.08, 124.09, 126.71, 128.12, 128.43. Found: C, 83.04; H, 8.75%. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

General procedure for the reaction of intermediate alkenylmagnesium species with electrophiles. Allylmagnesium bromide (1.0 *M* ether solution, 1.5 mL, 1.5 mmol) was added to a solution of 1-methoxy-3-decyne (**3a**, 0.17 g, 1.0 mmol) and manganese(II) iodide (9.1 mg, 0.03 mmol) in ether (7 mL) at 25°C under argon atmosphere. After being stirred for 2 h, benzaldehyde (0.16 g, 1.5 mmol) was added. The resulting mixture was stirred for another 1.5 h at 25 °C and poured into 0.5 *M* HCl. Extraction with ether (20 mL X 2) followed by silica gel column purification afforded (4Z)-4-hexyl-5-(1-hydroxybenzyl)-7-methoxy-(1,4)-heptadiene (**5c**, 0.31 g) in 92% yield: Bp 148 °C (0.2 Torr); IR (neat) 3406, 3058, 3022, 2952, 2924, 2856,

2732, 1654, 1635, 1602, 1492, 1450, 1410, 1379, 1256, 1188, 1155, 1109, 1025, 995, 966, 912, 725, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3H), 1.21–1.50 (m, 8H), 1.97–2.19 (m, 3H), 2.32 (dt, J = 15.0, 3.6 Hz, 1H), 2.95–3.13 (m, 2H), 3.32 (s, 3H), 3.37 (t, J = 3.6 Hz, 2H), 4.32 (d, J = 6.0, Hz, 1H), 5.02–5.15 (m, 2H), 5.69 (d, J = 6.0 Hz, 1H), 5.87 (ddt, J = 10.5, 15.0, 6.0 Hz, 1H), 7.16–7.39 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.94, 22.53, 27.74, 28.32, 29.57, 31.67, 32.46, 36.05, 58.72, 71.07, 72.90, 115.60, 125.86, 126.45, 128.09, 134.01, 136.81, 137.61, 144.52. Found: C, 79.58; H, 10.34%. Calcd for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19%.

(4Z)-4-Hexyl-5-(1-hydroxyheptyl)-7-methoxy-1,4-heptadiene (5d): Bp 180 °C (0.3 Torr); IR (neat) 3380, 3074, 2952, 2924, 2854, 1637, 1459, 1380, 1177, 1112, 994, 909 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.82–0.93 (m, 6H), 1.20–1.42 (m, 18H), 1.90–2.15 (m, 2H), 2.31–2.48 (m, 2H), 2.74–2.94 (m, 2H), 3.35 (s, 3H), 3.36–3.43 (m, 2H), 3.49–3.56 (m, 1H), 4.43–4.51 (m, 1H), 4.96–5.07 (m, 2H), 5.76 (ddt, J = 10.2, 17.0, 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.97, 22.52, 25.88, 26.76, 28.41, 29.31, 29.50, 31.70, 31.78, 32.40, 35.45, 36.53, 58.72, 70.09, 73.32, 115.07, 134.54, 135.43, 136.91. Found: C, 77.49; H, 12.65%. Calcd for $C_{21}H_{40}O_2$: C, 77.72; H, 12.42%.

(4E)-8-Benzyloxy-4-methyl-1,4-octadiene (generated from benzyl ether of 4-hexyn-1-ol): Bp 118 °C (0.3 Torr); IR (neat) 3062, 3026, 2928, 2852, 2790, 1637, 1497, 1477, 1454, 1433, 1411, 1383, 1364, 1204, 1103, 1028, 994, 911, 733, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.55 (s, 3H), 1.67 (tt, J = 6.6, 7.2 Hz, 2H), 2.10 (dt, J = 7.2, 7.2 Hz, 2H), 2.70 (d, J = 6.6 Hz, 2H), 3.47 (t, J = 6.6, Hz, 2H), 4.50 (s, 2H), 4.96–5.06 (m, 2H), 5.16 (t, J = 7.2 Hz, 1H), 5.78 (ddt, J = 9.9, 16.8, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 15.87, 24.46, 29.67, 44.05, 69.87, 72.87, 115.57, 124.98, 127.55, 127.71, 128.42, 134.15, 137.20, 138.80. Found: C, 83.33; H, 9.65%. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.62%.

3-Hexyl-1,2,5-hexatriene (13): Bp 115 °C (8 Torr); IR (neat) 3074, 2954, 2922, 2854, 1958, 1638, 1466, 1458, 1449, 992, 912, 844 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3H), 1.20–1.50 (m, 8H), 1.88–1.98 (m, 2H), 2.66–2.74 (m, 2H), 4.63–4.69 (m, 2H), 5.00–5.11 (m, 2H), 5.82 (ddt, J = 10.2, 17.1, 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.96, 22.53, 27.29, 28.89, 31.55, 31.64, 37.08, 75.41, 101.85, 115.75, 136.13, 206.20. Found: C, 86.73; H, 12.63%. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27%.

3-(1-Hexyl-3-butenylidene)-4-methyl-1-oxacyclopentane (15): Bp 114 °C (0.3 Torr); IR (neat) 3074, 2954, 2924, 2852, 1638, 1459, 1377, 1091, 1047, 992, 953, 923, 912 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3H), 1.10 (d, J = 6.9 Hz, 3H), 1.21–1.40 (m, 8H), 1.86 (t, J = 6.9 Hz, 2H), 2.75–2.90 (m, 3H), 3.65 (dd, J = 1.8, 8.4, Hz, 1H), 3.82 (dd, J = 5.7, 8.4 Hz, 1H), 4.24 (d, J = 12.9 Hz, 1H), 4.42 (d, J = 12.9 Hz, 1H), 4.98–5.09 (m, 2H), 5.76 (ddt, J = 6.6, 10.2, 17.0 Hz); ^{13}C NMR ($CDCl_3$) δ 13.95, 19.35, 22.52, 27.50, 29.16, 31.67, 32.43, 36.29, 36.87, 69.39, 75.80, 115.60, 127.81, 136.55, 139.29. Found: C, 80.77; H, 11.96%. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79%.

General procedure for the formation of tetrasubstituted alkene. Allylmagnesium bromide (1.0 *M* ether solution, 2.5 mL, 2.5 mmol) was added to a solution of homopropargyl ethenyl ether **16a** (0.18 g, 1.0 mmol) and $Mn(acac)_3$ (10.5 mg, 0.03 mmol) in THF (7 mL) at 25 °C under argon atmosphere. The resulting mixture was stirred for 9 h and poured into 0.5 *M* HCl. Extraction followed by purification by silica gel column chromatography provided (*3Z*)-4-hexyl-3-(2-hydroxyethyl)-1,3,6-heptatriene (**20a**, 0.17 g) in 75% yield: Bp 65 °C (0.2 Torr); IR (neat) 3296, 3082, 2952, 2924, 2854, 1637, 1625, 1467, 1041, 989, 909, 898, 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J = 7.2 Hz, 3H), 1.20–1.45 (m, 8H), 2.15 (t, J = 6.6 Hz, 2H), 2.61 (t, J = 7.4 Hz, 2H), 2.96 (d, J = 6.0 Hz, 2H), 3.67 (dt, J = 5.4, 7.4 Hz, 2H), 5.00 (m, 2H), 5.05 (dd, J = 10.8, 0.9 Hz, 1H), 5.22 (dd, J = 17.4, 0.9 Hz, 1H), 5.76 (ddt, J = 17.7, 9.6, 6.0 Hz, 1H), 6.67 (dd, J = 17.4, 10.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.95, 22.51, 28.59, 29.57, 30.75, 31.66, 33.44, 36.16, 61.95, 112.48, 115.30, 128.50, 134.62, 136.25, 140.29.

(4Z)-4-Hexyl-5-(2-hydroxyethyl)-1,4,6-tridecatriene (20b, 6Z/6E = 10/90): Bp 125 °C (0.2 Torr); IR (neat) 3256, 2954, 2922, 2852, 1640, 1459, 1040, 962, 909 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.6

Hz, 6H), 1.21–1.43 (m, 16H), 2.06–2.16 (m, 4H), 2.42 (t, J = 7.2 Hz, 0.2H), 2.58 (t, J = 7.2 Hz, 1.8H), 2.80 (d, J = 6.9, Hz, 0.2H), 2.93 (d, J = 6.3 Hz, 1.8H), 3.59–3.70 (m, 2H), 4.94–5.04 (m, 2H), 5.35–5.55 (m, 0.1H), 5.60–5.85 (m, 2H), 6.30 (d, J = 15.6 Hz, 0.9H); ^{13}C NMR ($CDCl_3$) δ 13.97, 22.53, 28.73, 28.80, 29.54, 29.60, 31.59, 31.64, 31.70, 33.28, 33.34, 36.31, 62.13, 115.09, 127.90, 128.06, 129.91, 136.61, 137.47. Found: C, 82.19; H, 12.44%. Calcd for $C_{21}H_{38}O$: C, 82.29; H, 12.49%.

General procedure for diallylation of homopropargylic alcohol derivatives in the presence of a catalytic amount of manganese salt. Allylmagnesium bromide (1.0 *M* ether solution, 4.0 mL, 4.0 mmol) was added to a solution of 1-benzyloxy-3-decyne (**3c**, 0.17 g 1.0 mmol) and $MeC_5H_4Mn(CO)_3$ (21.8 mg, 0.10 mmol) in THF (10 mL) at 25 °C under argon atmosphere. After being stirred for 2 h under argon atmosphere, the resulting mixture was exposed to air and stirring was continued for another 12 h. The mixture was poured into 0.5 *M* HCl. Extractive workup followed by purification gave diallylated product, (4*E*)-4-hexyl-5-(2-benzyloxyethyl)-1,4,7-octatriene (**21c**, 0.25 g) in 78% yield: Bp 155 °C (0.3 Torr); IR (neat) 3066, 3030, 2952, 2926, 2858, 1721, 1639, 1454, 1364, 1316, 1276, 1204, 1176, 1100, 1072, 1028, 996, 915, 747, 712, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3H), 1.22–1.40 (m, 8H), 2.02 (t, J = 7.8 Hz, 2H), 2.40 (t, J = 7.8 Hz, 2H), 2.77 (m, 4H), 3.48 (t, J = 7.8, Hz, 2H), 4.51 (s, 2H), 4.93–5.04 (m, 4H), 5.66–5.80 (m, 2H), 7.24–7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.99, 22.56, 28.84, 29.51, 31.74, 31.98, 32.28, 36.09, 36.62, 36.37, 72.77, 114.83, 114.96, 127.55, 127.61, 128.03, 128.42, 135.01, 136.76, 136.89, 138.69. Found: C, 84.36; H, 10.47%. Calcd for $C_{23}H_{34}O$: C, 84.60; H, 10.50%.

(4E)-4-Hexyl-5-(2-tetrahydropyranyloxyethyl)-1,4,7-octatriene (21d): Bp 143 °C (0.3 Torr); IR (neat) 3074, 2928, 2854, 1637, 1466, 1456, 1442, 1352, 1201, 1183, 1160, 1137, 1120, 1077, 1064, 1032, 908 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3H), 1.22–1.40 (m, 8H), 1.46–1.62 (m, 4H), 1.64–1.90 (m, 2H), 2.04 (t, J = 7.8 Hz, 2H), 2.37 (t, J = 7.8 Hz, 2H), 2.78 (m, 4H), 3.36–3.54 (m, 2H), 3.68–3.91 (m, 2H), 4.60 (t, J = 3.5 Hz, 1H), 4.92–5.05 (m, 4H), 5.66–5.82 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.99, 19.45, 22.56, 25.39, 28.81, 29.52, 30.63, 31.75, 31.93, 32.19, 36.03, 36.52, 62.16, 66.32, 98.73, 114.77, 114.91, 128.15, 134.96, 136.78, 136.89. Found: C, 78.90; H, 11.60%. Calcd for $C_{21}H_{36}O_2$: C, 78.70; H, 11.32%.

(4E)-4-Propyl-5-(2-methoxybutyl)-1,4,7-octatriene (21e): Bp 65 °C (0.3 Torr); IR (neat) 3074, 2958, 2868, 2818, 1637, 1459, 1378, 1364, 1201, 1190, 1090, 993, 909 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86–0.96 (m, 6H), 1.32–1.56 (m, 4H), 2.04 (t, J = 7.8 Hz, 2H), 2.09–2.35 (m, 2H), 2.75–2.85 (m, 4H), 3.13–3.23 (m, 1H), 3.33 (s, 3H), 4.94–5.06 (m, 4H), 5.68–5.83 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 9.80, 14.19, 21.74, 26.78, 34.03, 35.62, 36.02, 36.47, 57.10, 82.21, 114.71, 114.77, 129.32, 134.46, 136.96. Found: C, 81.14; H, 12.08%. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94%.

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11. In the absence of HMPA, displacement of the metaloxy (OMtl) group by the allylic anion proceeded to give an allenyl compound as by-product. The addition of HMPA could suppress the formation of the allenic product.
12. Treatment of propargylic alcohol **7a** with diallylmanganese could also give the desired product **8a** in 80% yield. Because the dialkylmanganese is less stable than trialkylmanganate according to the report by Normant,[10] the reaction of propargylic alcohols was performed with triallylmanganate.
13. The reaction of propargyl alcohol **7a** with allylmagnesium chloride in the presence of $MnCl_2$ catalyst gave allylated product in 48% yield along with recovered starting alcohol **7a** (36%).
14. Toluene was used as a solvent instead of ether. In the case of MnI_2, ether was used because of its solubility.
15. 3-Decyn-1-ol (**3b**) and 2-nonyn-1-ol (**7a**) provided only small amounts of the corresponding allylated products **4a** and **8a** (<5% yield) upon treatment with allylmagnesium bromide in the presence of MnI_2 (3 mol%) in ether at 25 °C for 3 h. After heating at reflex for 10 h, **4a** was obtained in 48% yield, but **8a** was obtained in only <5% yield.
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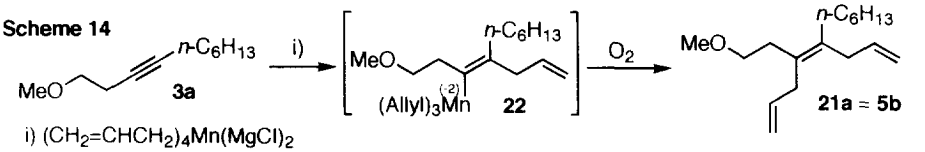
17. The reaction of **14** with $(allyl)_4Mn(MgCl)_2$ provided **15** in only 10% yield along with unidentified complex mixture.
18. The formation of **20b** as a mixture of *Z*/*E* = 10/90 starting from **16b** (*Z*/*E* = 90/10) might suggest that both intramolecular carbomanganation and deoxymanganation proceed in *syn* fashion.
19. We are tempted to assume that reductive elimination from alkenylmanganese intermediate **22** affords the diallylated product in the presence of air. Oxygen would facilitate the reductive elimination but the role of oxygen and precise mechanism of the reaction are not clear at this stage. (Scheme 14).

Scheme 14



i) $(CH_2{=}CHCH_2)_4Mn(MgCl)_2$

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