Synthesis of Allyl Acetals and Their Catalytic Claisen–Cope Rearrangement

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We have synthesized various types of acetals using 3-methyl-3-butenal and 2-alkenyl, furfuryl, benzyl, *p*-substituted benzyl, and 2-pentynyl alcohols. These acetals have given corresponding aldehydes after an acid catalytic reaction. Trifluoroacetic acid (CF_3COOH) was the best catalyst. The best yield attained was 79% when 3-methyl-3-butenal di(*trans*-2-pentenyl) acetal was used as a substrate. We also demonstrated that this reaction proceeded via a Claisen–Cope rearrangement.

After 1970, the demand for synthetic organic products has increased in accordance with the need for natural organic compounds. The use of synthetic organic perfumes and fragrances has also multiplied very much recently. With this movement, many methods for the synthesis of organic perfumes and fragrances have been investigated.[1–6]

For instance, citral has been synthesized from pinene via geraniol, as shown by reaction (1) in Fig. 1.[5] It has also been synthesized from 6-methyl-5-hepten-2-one, as shown by reaction (2).[5] The synthesis of terpene perfume aldehydes has been carried out by Ichikawa and Yamaji.[7,8] This reaction is shown in reaction (3).

This reaction can be called a Claisen–Cope rearrangement reaction; it is very interesting to execute the two rearrangements in one step. It would be useful to investigate this reaction more in order to increase the conversion and selectivity, and to solve the reaction mechanism to develop an industrial process for perfumes and fragrances. We have synthesized various kinds of acetals, and conducted further experiments to clarify this reaction. Here, we report on the details of the results.

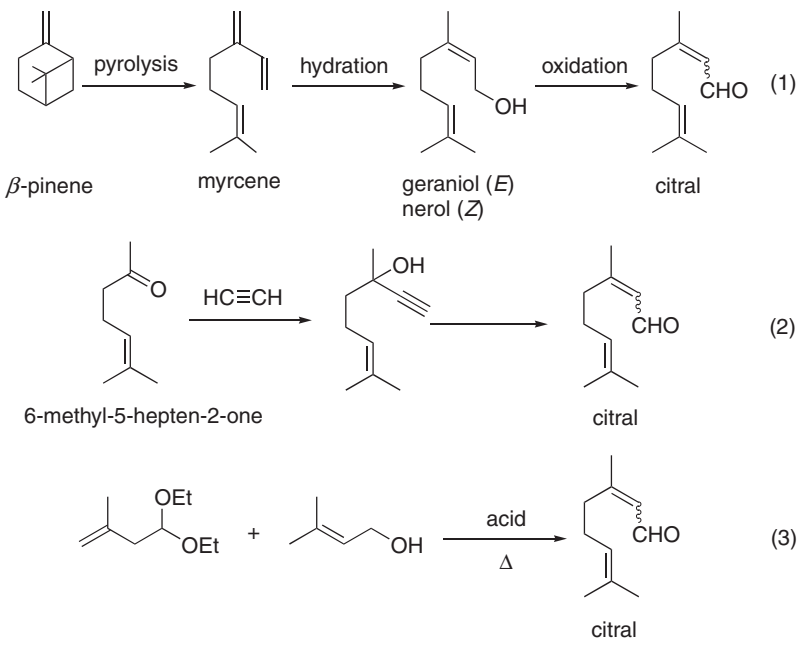

Fig. 1. Synthesis of citral.

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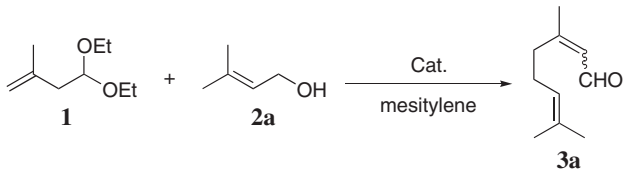
Table 1. Effect of Catalysts in Synthesis of Citral[a)]



Entry	Cat.	pK_{a_1}	Time/h	Conv./%[b)]	Selectivity/%	Yield/%[b)]	E:Z[b)]
1	H_2SO_4	−3	0.5	100	1.7	1.7	48:52
2	CH_3SO_3H	−1.2	0.5	100	3.7	3.7	57:43
			0.25	100	9.3	9.3[c)]	58:42
3	CF_3COOH	0.25	0.5	22	2.7	0.6	63:37
			4	85	13.6	11.7	53:47
			4	83	33.9	28.0[c)]	60:40
4	*p*-TsOH	0.9	1	100	5.9	5.9	32:68
5	$(COOH)_2$	1.27	0.5	14	4.5	0.6[c)]	58:42
6	H_3PO_4	2.15	4	59	2.2	1.3	55:45
7	Isophthalic acid	3.6	4	0	—	0	—
			4	37	5.9	2.2[c)]	59:41
8	CH_3COOH	4.8	1	0	—	0	—
			0.5	1	0	0	—

a) Reaction conditions: Glass tube (6 mm × 13 cm), a catalyst (7.9×10^{-4} mmol), **1** (0.63 mmol), **2a** (1.27 mmol), 150 °C. b) Determined by GC. c) 190 °C.

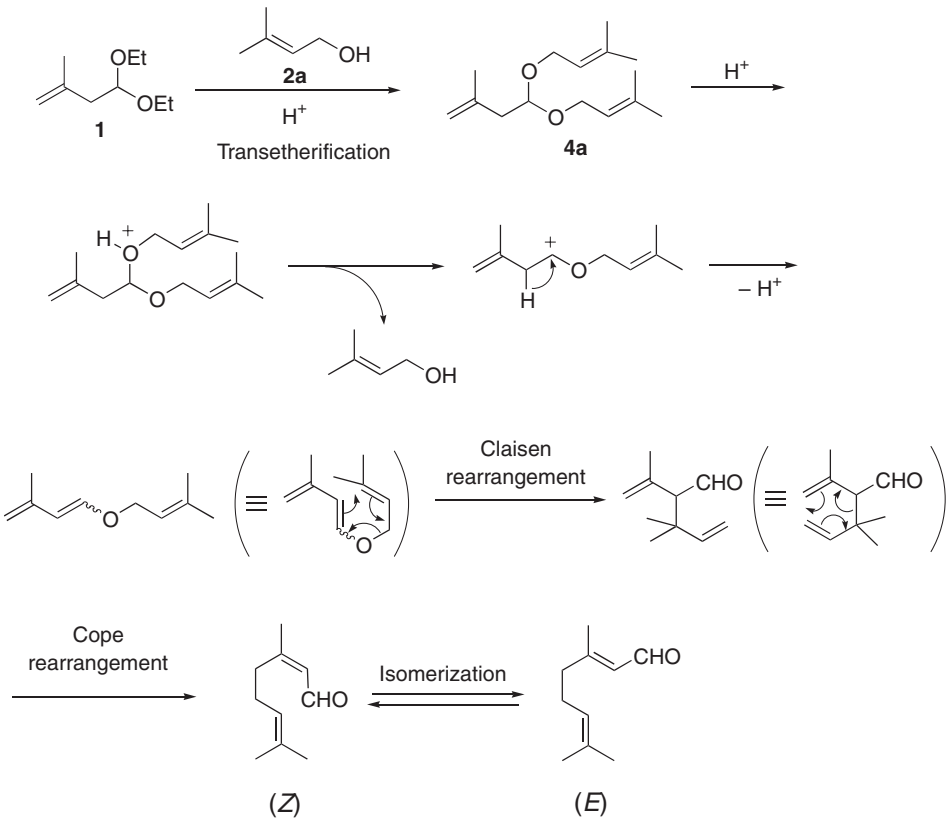


Fig. 2. Possible mechanism.

Results and Discussion

Effect of Catalysts in the Synthesis of Citral. In order to understand the formation of citral, we first examined of all of the best acidic catalyst in a direct synthesis of citral. We carried out a reaction of 3-methyl-3-butenal diethyl acetal (**1**) and 3-methyl-2-butenyl alcohol (**2a**) in an acidic solution, giving citral, 3,7-dimethylocta-2,6-dienal (**3a**). Table 1 gives the results. By changing pK_a of the acids from −3 to 4.8, we could selected CF_3COOH as the best catalyst for this rearrangement reaction (entry 3). Other catalysts showed poor catalytic properties. A high conversion was attained by using acids with a low pK_a (en-

tries 1, 2, 4). On the contrary, those acids with a high pK_a showed a low conversion (entries 5, 7, 8). The *E*:*Z* ratio remained almost constant 60% in the case of CF_3COOH. However, *p*-TsOH showed a unique ratio (entry 4). This is presently under investigation. The low yield of an aldehyde by using an acid catalyst with a low pK_a may be caused by further reactions of the aldehydes, as observed in the rather complex gas chromatograph of the products.

Possible Reaction Mechanism. We may be able to induce a reaction mechanism in the following way, as shown in Fig. 2.

Acetal **1** undergoes a transetherification readily to give a new acetal, 3-methyl-3-butenal bis(3-methyl-2-butenyl) acetal (**4a**). Acetal **4a** demonstrates a departure of 3-methy-2-butenyl alcohol by an acid catalyst. This process produces a particularly stabilized carbocation, in which deprotonation affords an allyl dienyl ether. This allyl dienyl ether undergoes a Claisen rearrangement, and a Cope rearrangement then occurs to give the intended aldehyde. If the allyl dienyl ether is formed, the reaction proceeds mainly with heat. Because we could not isolate the ally dienyl ether, we prepared acetal **4a** and examined the reaction conditions for successive rearrangements.

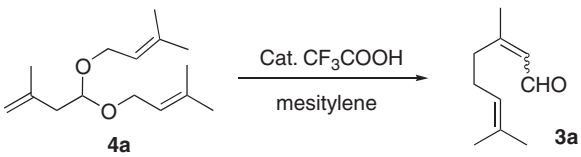
Effect of Temperature. In order to improve the yield of citral **3a**, we examined the reaction conditions of the successive rearrangement of acetal **4a**. In order to find the effect of temperature, we investigated the rearrangement of **4a** from 150 °C to 210 °C. The results are given in Table 2. It shows that citral was prepared in 60% yield at 190 °C (entry 3). However, by highering or lowering the temperature, the reaction gave inferior results (entries 1, 2, 4). The *E*:*Z* ratio increased slightly with higher temperatures from 54% (150 °C) to 63% (210 °C). This means that *cis–trans* isomerization occurred after the rearrangement reaction.

Effect of a Solvent without a Catalyst. In order to investigate the effect of solvents, we heated **4a** without a catalyst. The results are given in Table 3. Only aromatic solvents gave the aldehyde practically (entries 1–3, 7, 8). It was observed that the reaction without a solvent did not proceed effectively.

Effect of a Solvent with an Acidic Catalyst. An aromatic solvent exhibited a good result. We proceeded the reaction in various aromatic solvents. The results are given in Table 4. The best result, 60% of citral **3a**, was obtained from the corresponding acetal **4a** in mesitylene with an *E* ratio of 57% (entry 3). Toluene and mesitylene gave rather good results (entries 2, 3). When we extended the reaction time to 4 h, the yield and *E* ratio did not change at all. This means that the produced aldehydes are stable in these aromatic solvents within this range of time.

Effect of Various Lewis Acid Catalysts. We could not ob-

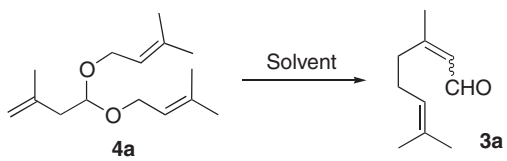
Table 2. Effect of Temperature[a)]



Entry	Temp./°C	Conv./%[b)]	Selectivity/%	Yield/%[b)]	*E*:*Z*[b)]
1	150	25	14	4	54:46
2	170	39	50	19	55:45
3	190	97	62	60	57:43
4	210	>99	44	44	63:37

a) Reaction conditions: Glass tube (6 mm × 13 cm), CF_3COOH (7.9×10^{-4} mmol), **4a** (0.63 mmol), mesitylene (1 mL), 190 °C, 2 h. b) Determined by GC.

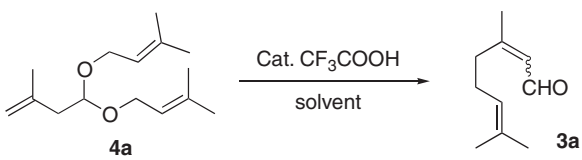
Table 3. Effect of Solvents without the Catalyst[a)]



Entry	Solvent	Yield/%[b)]	*E*:*Z*[b)]
1	mesitylene	8	53:47
2	benzene	13	56:44
3	benzonitrile	8	61:39
4	THF	—	—
5	DMF	—	—
6	CH_3CN	6	56:44
7	methoxybenzene	16	53:47
8	chlorobenzene	17	53:47
9	none	5	61:39

a) Reaction conditions: Glass tube (6 mm × 13 cm), **4a** (0.63 mmol), solvent (1 mL), 190 °C, 2 h. b) Determined by GC.

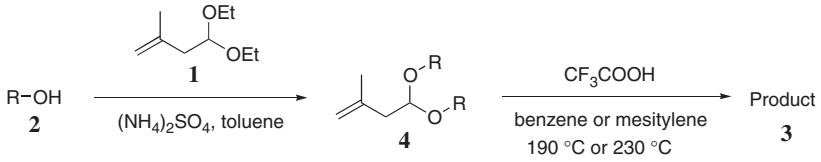
Table 4. Effect of Solvents with CF_3COOH Catalyst[a)]

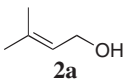
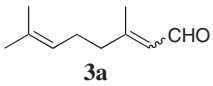
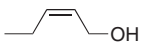
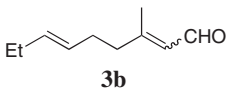
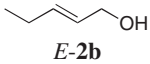
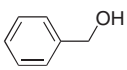
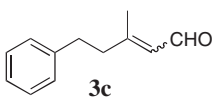
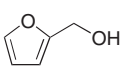
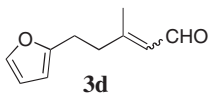
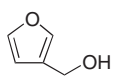
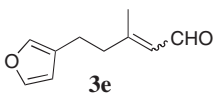
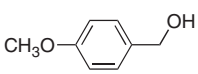
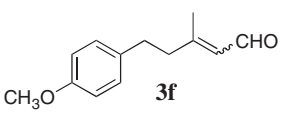
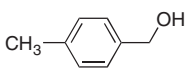
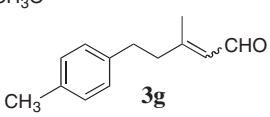
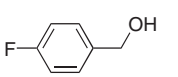
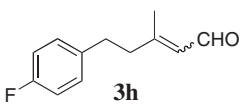


Entry	Solvent	Yield/%[b)]	*E*:*Z*[b)]
1	hexane	21	57:43
2	toluene	48	61:39
3	mesitylene	60	57:43
4	benzene	50	61:39
5	chlorobenzene	41	61:39
6	anisole	33	61:39

a) Reaction conditions: Glass tube (6 mm × 13 cm), CF_3COOH (7.9×10^{-4} mmol), **4a** (0.63 mmol), a solvent (2 mL), 190 °C, 2 h. b) Determined by GC.

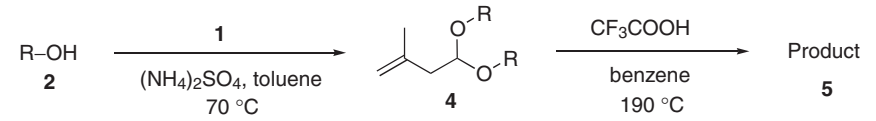
Table 5. Preparation and Reaction of 2-Alkenyl and Arylmethyl Acetals **4**

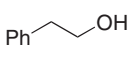
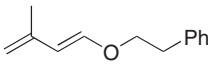
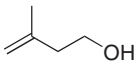
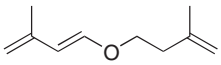
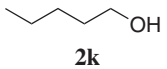
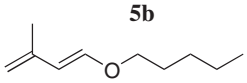
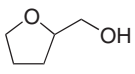
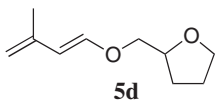
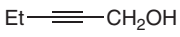


Entry	Formation of **4**[a]				Formation of **3**[b]			
	R–OH	Temp./°C	Time/h	Yield/%[c]	Time/ h	Product	Yield/%[c]	E : Z[d]
1	 **2a**	70	24	72	2[e]	 **3a**	43	63 : 37
2					2[e,f]	**3a**	54[g]	60 : 40
3	 *Z*-**2b**	70	24	52	2[e,f]	 **3b**	71[g]	52 : 48
4					5[e]	**3b**	54	59 : 41
5	 *E*-**2b**	70	24	39	2[e,f]	**3b**	71[g]	54 : 46
6					5[e]	**3b**	79	57 : 43
7	 **2c**	70	24	50	4[h]	 **3c**	46	63 : 37
8	 **2d**	70	24	36	4[h]	 **3d**	59	58 : 42
9	 **2e**	70	24	62	4[h,i]	 **3e**	50	61 : 39
10	 **2f**	90	24	78	4[h,j]	 **3f**	6	58 : 42
11	 **2g**	90	28	82	4[h]	 **3g**	27	62 : 38
12	 **2h**	90[k]	54	77	4[h]	 **3h**	44	59 : 41

a) Reaction conditions: a flask (50 mL), $(NH_4)_2SO_4$ (1.0 mmol), **1** (23 mmol), ROH (69 mmol), toluene (150 mmol). b) Reaction conditions: a glass tube (6 mm × 13 cm), CF_3COOH (7.9×10^{-4} mmol), **4** (0.63 mmol), benzene (1 mL). c) Isolated yield. d) Determined by ^1H NMR. e) 190 °C. f) Mesitylene (2 mL) was used as solvent. g) GC yield. h) 230 °C. i) CF_3COOH (3.15×10^{-3} mmol). j) CF_3COOH (7.9×10^{-5} mmol). k) Mesitylene was used as solvent.

Table 6. Preparation and Reaction of Other Acetals **4**



Entry	Formation of **4**[a]		Formation of **5**[b]			
	R–OH	Yield/%[c]	Time/h	Product	Yield/%[c]	E : Z[d]
1	 **2i**	77	4	 **5a**	23	82 : 18
2	 **2j**	18	5	 **5b**	14	100 : 0
3	 **2k**	48	5	 **5c**	—[e]	—
4	 **2l**	78	4	 **5d**	36	73 : 37
5	 **2m**	50	4[f]	No reaction	—	—

a) Reaction conditions: a flask (50 mL), $(NH_4)_2SO_4$ (1.0 mmol), **1** (23 mmol), ROH (69 mmol), toluene (150 mmol), 70 °C, 24 h. b) Reaction conditions: a glass tube (6 mm × 13 cm), CF_3COOH (7.9×10^{-4} mmol), **4** (0.63 mmol), benzene (1 mL), 190 °C. c) Isolated yield. d) Determined by ^{1}H NMR. e) Vinyl ether was observed by ^{1}H NMR. f) 230 °C.

tain any aldehyde products from **4a** by using various Lewis acid catalysts ($TiCl_4$, $Ti(OEt)_4$, $Ti(Oi\text{-}Pr)_4$, $FeCl_3$, and Et_2AlCl), even in a polar or nonpolar solvent (CH_2Cl_2 or benzene) at low temperatures. After the reactions, substrate **4a** decomposed and did not give any products, or recover.

As we chose the reaction conditions for the rearrangement of **4a** to **3a**, we furthermore examined the synthesis of various acetals **4** and the rearrangement.

Synthesis of Acetals 4. More various acetals were prepared by changing the substrate alcohols. The results are given in Table 5. Mainly, five types of acetals were prepared. Allyl alcohols, alkyl alcohols, furfuryl alcohols, and benzyl alcohols were reacted with 3-methyl-3-butenal diethyl acetal (**1**) at 70 °C for 24 h. *para*-Substituted benzyl alcohols did not give the corresponding acetals at 70 °C. They reacted at 90 °C for a longer time. From these data, we can state the followings. The yield of acetals by 4-substituted benzyl alcohols was best, 82% (entry 11). Good yields of over 70% were also obtained in the case of 4-methoxybenzyl, 4-fluorobenzyl, and 3-methyl-2-butenyl alcohols (entries 10, 12, 16, and 1).

Rearrangement of 2-Alkenyl and Arylmethyl Acetals 4. The conditions for the synthesis of terpene aldehydes have become clear. Various 2-alkenyl acetals were allowed to rearrange with CF_3COOH as a catalyst in benzene or mesitylene at 190 °C. The data for 2-alkenyl acetals are given in Table 5. The data for arylmethyl acetals are also given in Table 5. 2-Pentenyl alcohol gave the best yield of 79% (entry 6). Moderate yields were obtained for *cis*- and *trans*-2-pentenyl acetals (entries 3, 5). Furylmethyl acetal required a rather higher reaction temperature (entries 8, 9) compared to that used for 2-alkenyl acetals to obtain the same grade of yield. Arylmethyl acetals also required the same range of temperature for the reaction (Table 5, entries 7, 10–12). These may be caused by the difficulty of a Claisen rearrangement via double bonding in the ring. A Claisen rearrangement may be easier in the furfuryl ring than in the benzene ring based on these results.

Rearrangement of 3-Alkenyl and Alkyl Acetals 4. In connection with the reaction mechanism, we used 3-alkenyl and alkyl alcohols for the acetal. The preparation and rearrangement results are given in Table 6. However, aldehydes were not produced in these rearrangement reactions. Dienyl compounds were obtained instead. These results suggest that dealcohol occurs first to form the dienyl ether by the action of an acid catalyst, followed by first a Claisen rearrangement and then a Cope rearrangement. The dienyl ether formed without a proper double bonding does not execute a Claisen rearrangement. The reaction stops instantly. The substrate can not proceed eventually to a Cope rearrangement. In these cases, no aldehydes were formed. It is appropriate to call this reaction a Claisen–Cope reaction. When the rearrangement of 2-pentynyl acetal (entry 5) was performed at 230 °C, no reaction occurred. The substrate was recovered. The formation of dienyl ether was difficult at this temperature.

Conclusion

We have synthesized various types of acetals using 3-methyl-3-butenal and alkyl-2,3-olefinic, 2-furylmethyl, benzylic, and para-substituted benzylic, and pentylic alcohols. These acetals gave corresponding aldehydes after the acid catalytic reaction. CF_3COOH was the best catalyst. The best yield attained was 79% when 3-methyl-3-butenal di(*trans*-2-pentenyl)acetal was used as a substrate. We also have demonstrated that this reaction proceeds via a Claisen–Cope rearrangement.

Experimental

General. GC analyses were performed on a Shimadzu GC-8A system equipped with a 3.0 m × 3.2 mm i.d. glass column packed with a [Unisole Thermon-3000 (5%)] on 80/100 Chromosorb for a certain injection/detector temperature (250 °C), column temperature (70–230 °C, 4 °C/min) and N_2 pressure (70 kPa), and a Shimadzu GC-14B system equipped with a 60 m × 0.25 mm i.d. capillary column [SPB™-OCTYL] for a certain injection/detector temperature (250 °C), column temperature (50–230 °C, 4 °C/min), and He pressure (200 kPa).

^{1}H NMR spectra were recorded on a JEOL JNM-AL300 (300 MHz) spectrometer and ^{13}C NMR spectra were recorded with a JEOL JNM-AL300 (75 MHz) spectrometer. The chemical shifts were expressed in parts per million downfield from tetramethylsilane. The IR spectra were recorded on an FT-IR HORIBA 200 spectrophotometer. Elemental analyses were performed by the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University. GC-MS analyses were performed on a Shimadzu GCMS-QP5050A system equipped with an electron ionization detector using a 60 m × 0.25 mm i.d. capillary column [SPB™-OCTYL] under the conditions of an injection temperature of 280 °C, a detector temperature of 280 °C, a column temperature of 70–230 °C, 4 °C/min and He pressure of 200 kPa. HRMS analyses were performed on a JMS-HX110A-type MS system.

Material. All reagents were obtained from commercial sources and used as received. Benzene, benzonitrile, acetonitrile, anisole, *N*,*N*-dimethylformamide (DMF), toluene, hexane, 3-methyl-2-buten-1-ol were distilled. Tetrahydrofuran (THF) was distilled from sodium diphenylketyl. Chloroform and dichloromethane were distilled from P_2O_5.

3-Methyl-3-butenal Diethyl Acetal (1).[9] The synthesis of 3-methyl-3-butenal diethyl acetal was based on the literature.[9] Yield (44%), colorless liquid, bp 75–76 °C (2.7×10^3 Pa). ^{1}H NMR (300 Hz, $CDCl_3$) δ 1.20 (t, $J = 4.0$ Hz, 3H, CH_3), 1.77 (s, 3H, CH_3), 2.28 (d, $J = 5.85$ Hz, 2H, CH_2), 2.34 (d, $J = 5.7$, 2H, CH_2), 3.43 (m, 2H, CH_2), 3.68 (m, 2H, CH_2), 4.81 (s, 1H, CH_2=), 4.79 (s, 1H, CH_2=), 4.63 (t, $J = 5.9$ Hz, 1H, CH). ^{13}C NMR (75 Hz, $CDCl_3$) δ 15.2, 23.0, 41.8, 60.9, 101.8, 112.7, 141.5. IR (neat): 1050, 1133 (C–O), 1650 cm^{-1}.

Preparation of Various Acetals (4). 3-Methyl-3-butenal diethyl acetal, alcohols (3 molar amounts), $(NH_4)_2SO_4$ (0.044 mol. amt.), and toluene were placed in a 50 mL flask. The flask was connected to a packed fractionating column, and the solution was stirred at a stated temperature for a stated time. The mixture was then stirred at a stated temperature for a stated time under reduced pressure to remove ethanol. At last, it was distilled under reduced pressure until an azeotropic mixture of toluene and ethanol was completely removed. The reaction mixture was washed with H_2O (20 mL × 2) and saturated aqueous NaCl. A water layer was extracted with ether (20 mL × 3). Then, the combined organic layer was dried by anhydrous Na_2SO_4. After removal of Na_2SO_4, the mixture was separated by distillation under reduced pressure or column chromatography on silica gel with a mixed solvent.

3-Methyl-3-butenal Bis(3-methyl-2-butenyl) Acetal (4a): Yield (72%), colorless liquid, bp 94–96 °C (120 Pa). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.72 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 1.78 (s, 3H, CH_3), 2.40 (d, 2H, $J = 6.0$ Hz), 4.05 (m, 2H, CH_2), 4.72 (t, 1H, $J = 6.0$ Hz), 4.79 (s, 1H, CH_2=) 4.81 (s, 1H, CH_2=), 5.35 (m, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.9, 22.9, 26.7, 41.7, 61.5, 100.5, 112.7, 120.9, 136.7, 141.4.

3-Methyl-3-butenal Di[(*Z*)-2-pentenyl] Acetal (4b-Z): Yield (52%), colorless liquid, bp 71–72 °C (20 Pa). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (t, $J = 7.5$ Hz, 6H, CH_3), 1.77 (s, 3H, CH_3), 2.08 (d, $J = 7.5$ Hz, 4H, CH_2), 2.39 (d, $J = 5.7$ Hz, 2H, CH_2), 4.11 (m, 4H, OCH_2), 4.73 (t, $J = 5.7$ Hz, 1H, CH), 4.79 (s, 1H, CH_2=), 4.82 (s, 1H, CH_2=), 5.54 (m, 4H, CH=CH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 20.8, 22.9, 41.7, 60.6, 100.6, 112.9, 125.1, 135.1, 141.3.

3-Methyl-3-butenal Di[(*E*)-2-pentenyl] Acetal (4b-E): Yield (39%), colorless liquid, bp 85–86 °C (67 Pa). ^{1}H NMR (300 Hz, $CDCl_3$) δ 1.00 (t, $J = 7.2$ Hz, 6H, CH_3), 1.76 (s, 1H, CH_3), 2.38 (d, $J = 5.7$ Hz, 2H, CH_2), 4.01 (m, 4H, OCH_2), 4.72 (t, $J = 5.7$ Hz, 1H, CH), 4.78 (s, 1H, CH_2=), 4.81 (s, 1H, CH_2=), 5.65 (m, 4H, CH=CH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.2, 23.0, 25.2, 41.8, 66.1, 100.5, 112.8, 125.0, 136.1, 141.3.

3-Methyl-3-butenal Dibenzyl Acetal (4c): Yield (50%), yellow oil, bp 115–117 °C (27 Pa). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14 (t, $J = 7.5$ Hz, 6H, CH_3), 1.79 (s, 3H, CH_3), 2.23 (q, 4H, CH_2), 2.41 (d, $J = 5.7$ Hz, 2H, CH_2), 4.24 (s, 4H, OCH_2), 4.83 (s, 1H, CH_2=), 4.90 (t, $J = 5.7$ Hz, 1H, CH), 7.28–7.37 (m, ArH, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.0, 41.6, 67.1, 100.8, 113.2, 127.5, 127.7, 128.3, 138.1, 141.0.

3-Methyl-3-butenal Difurfuryl Acetal (4d): Yield (36%), yellow oil, bp 108–110 °C (37 Pa). ^{1}H NMR (300 Hz, $CDCl_3$) δ 1.77 (s, 3H, CH_3), 2.34 (d, $J = 5.9$ Hz, 2H, CH_2), 3.43 (m, 2H, CH_2), 3.68 (m, 2H, CH_2), 4.63 (t, $J = 5.9$ Hz, 1H, CH), 4.79 (s, 1H, CH_2=), 4.81 (s, 1H, CH_2=), 6.17 (dd, $J = 1.9$, 1.5 Hz, 2H, ArH), 6.35 (dd, $J = 0.9$, 1.9 Hz, 2H, ArH), 7.41 (dd, $J = 1.5$, 0.9 Hz, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.7, 41.4, 59.0, 100.2, 109.1, 110.2, 113.0, 140.8, 142.7, 151.6. IR (neat) 1147 (C–O), 2919 (C–H), 3122 cm^{-1} (C–H). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92%. Found: C 68.42; H 6.85%.

3-Methyl-3-butenal Bis(3-furylmethyl) Acetal (4e): Yield (62%), yellow oil, bp 102–103 °C (37 Pa). ^{1}H NMR (300 Hz, $CDCl_3$) δ 1.75 (s, 3H, CH_3), 2.44 (d, $J = 5.7$ Hz, 2H, CH_2), 4.49 (m, 4H, CH_2), 4.80 (t, $J = 5.7$ Hz, 1H, CH), 4.83 (m, 2H, CH_2), 6.40 (s, 2H, ArH), 7.40 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.9, 41.6, 58.6, 100.3, 110.2, 113.2, 122.2, 140.5, 141.0, 143.3. IR (neat) 1106 (C–O), 2871 (C–H), 3122 cm^{-1} (C–H).

3-Methyl-3-butenal Bis(4-methoxybenzyl) Acetal (4f): Yield (78%), colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.74 (s, 3H, CH_3), 2.47 (d, $J = 5.7$ Hz, 2H, CH_2CH), 3.80 (s, 3H, OCH_3), 4.50 (d, $J = 11.4$ Hz, 2H, OCH_2), 4.60 (d, $J = 10.8$ Hz, 2H, OCH_2), 4.80 (m, 1H, CH_2=), 4.83 (m, 1H, CH_2=), 4.85 (t, $J = 5.9$ Hz, 1H, CH), 6.87 (m, 4H, ArH), 7.26 (m, 4H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.1, 41.9, 55.0, 66.9, 71.5, 100.7, 113.1, 113.8, 129.3, 130.4, 141.3, 159.3.

3-Methyl-3-butenal Bis(4-methylbenzyl) Acetal (4g): Yield (82%), yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.74 (s, 3H, CH_3), 2.31 (s, 3H, $ArCH_3$), 2.48 (d, $J = 2.9$ Hz, 2H, CH_2), 4.51 (d, $J = 5.9$ Hz, 2H, OCH_2), 4.61 (d, $J = 5.9$ Hz, 2H, OCH_2),

4.82 (s, 1H, CH_2=), 4.86 (s, 1H, CH_2=), 4.86 (t, J = 2.9 Hz, 1H, CH), 7.11 (d, J = 3.9 Hz, 5H, ArH), 7.21 (d, J = 3.9 Hz, 5H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.1, 22.9, 41.6, 66.9, 100.6, 113.0, 127.8, 128.9, 135.1, 137.0, 141.0.

3-Methyl-3-butenal Bis(4-fluorobenzyl) Acetal (4h): Yield (77%), yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.68 (s, 3H, CH_3), 2.41 (d, J = 2.9 Hz, 2H, CH_2CH), 4.44 (d, J = 5.9 Hz, 2H, OCH_2), 4.55 (d, J = 5.9 Hz, 2H, OCH_2), 4.74 (s, 1H, CH_2=), 4.78 (s, 1H, CH_2=), 4.80 (t, J = 5.9 Hz, 1H, CH), 7.16–7.29 (m, 10H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.0, 31.6, 66.5, 100.9, 113.3, 115.1, 115.4, 129.4, 129.5, 133.8, 133.9, 140.9, 160.7, 163.9.

3-Methyl-3-butenal Diphenethyl Acetal (4i): Yield (77%), colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.69 (s, 3H, CH_3), 2.32 (d, J = 5.7 Hz, 2H, CH_2CH), 2.82 (t, J = 7.2 Hz, 4H, CH_2Ph), 3.61 (t, J = 7.2 Hz, 2H, OCH_2), 3.71 (m, J = 7.2 Hz, 2H, OCH_2), 4.61 (t, J = 5.7 Hz, 1H, CH), 4.75 (s, 1H, CH_2=), 4.79 (s, 1H, CH_2=), 7.16–7.29 (m, 10H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.0, 36.4, 41.7, 66.3, 102.1, 112.8, 126.1, 128.2, 128.9, 139.0, 141.3, 141.4.

3-Methyl-3-butenal Bis(3-methyl-3-butenyl) Acetal (4j): Yield (18%), colorless liquid, bp 70–72 °C (13.3 Pa). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75 (s, 6H, CH_3), 1.76 (s, 3H, CH_3), 2.29 (t, J = 6.6 Hz, 4H, CH_2), 2.36 (d, J = 5.7 Hz, 2H, CH_2), 4.66 (t, J = 5.7 Hz, 1H, CH), 4.73 (s, 1H, CH_2=), 4.78 (s, 1H, CH_2=), 4.78 (s, 1H, CH_2=), 4.81 (s, 1H, CH_2=). ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.7, 23.0, 37.8, 41.6, 63.7, 101.9, 111.4, 112.8, 141.4, 142.8.

3-Methyl-3-butenal Dipentyl Acetal (4k): Yield (48%), colorless liquid, bp 61–63 °C (60 Pa). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 7.2 Hz, 6H, CH_3), 1.33 (m, 8H, CH_2), 1.55 (m, 4H, CH_2), 1.77 (s, 3H, CH_3), 2.34 (d, J = 5.7 Hz, 2H, CH_2), 3.42 (m, 2H, OCH_2), 3.58 (m, 2H, OCH_2), 4.60 (t, J = 5.7 Hz, 1H, CH), 4.77 (s, 1H, CH_2=), 4.80 (s, 1H, CH_2=). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.5, 23.1, 28.4, 29.5, 41.8, 65.6, 102.1, 112.6, 141.6. Anal. Calcd for $C_{15}H_{30}O_2$: C, 74.32; H, 12.47%. Found C, 74.23; H, 12.43%.

3-Methyl-3-butenal Bis(tetrahydrofurfuryl) Acetal (4l): Yield (78%), yellow oil, bp 120–122 °C (53 Pa). ^{1}H NMR (300 Hz, $CDCl_3$) δ 1.63 (m, 2H, CH_2) 1.77 (s, 3H, CH_3) 1.90 (m, 5H, CH_2), 2.38 (m, 2H, CH_2), 3.50 (m, 2H, OCH_2), 3.75 (m, 4H, OCH_2), 4.07 (m, 2H, CH), 4.75 (m, 2H, CH_2=). ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.9, 25.5, 25.6, 28.1, 28.2, 41.3, 41.4, 67.6, 68.1, 68.2, 77.7, 77.8, 101.9, 102.1, 102.2, 112.8, 141.2. IR (neat) 1130 (C–O), 2927 (C–H), 3078 cm^{-1} (C–H). Anal. Calcd for $C_{15}H_{24}O_4$: C, 66.64; H, 9.69%. Found: C, 66.26; H, 9.63%.

3-Methyl-3-butenal Di(2-pentynyl) Acetal (4m): Yield (50%), colorless oil, bp 95–96 °C (47 Pa). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.76 (s, 3H, CH_3), 2.23 (q, J = 7.5 Hz, 4H, CH_2), 2.14 (d, J = 5.7 Hz, 2H, CH_2), 4.24 (s, 4H, CH_2), 4.83 (s, 2H, CH_2=), 4.97 (t, J = 5.7 Hz, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4, 13.7, 22.8, 41.6, 53.8, 75.1, 88.0, 99.6, 113.1, 140.8.

Effect of Catalysts on the Synthesis of Citral. 3-Methyl-3-butenal diethyl acetal, 3-methyl-2-buten-1-ol, and a catalyst solution in mesitylene (1 mL) were placed in a glass tube (6 mm ϕ × 8 cm). The sealed tube was stirred at 150–230 °C for 0.5–4 h. After the reaction, the sealed tube was cooled in an ice bath. The reaction mixture was analyzed by GC using biphenyl as an internal standard. These results are listed in Table 1.

General Procedure for the Reaction of 3-Methyl-3-butenal Bis(3-methyl-2-butenyl) Acetal. 3-Methyl-3-buenal bis(3-methyl-2-butenyl) acetal (0.150 g, 0.63 mmol) and a solution of the acid catalyst in the solvent were placed in a glass tube (6 mm × 13 cm). The sealed tube was stirred at the stated temperature for the stated time. After the reaction, the sealed tube was cooled in an ice bath. The mixture was analyzed by the GC-8A and GC-14B system. The products in Tables 1–5 were analyzed by GC-8A system.

General Procedure for the Reaction of 3-Methyl-3-butenal Bis(3-methyl-2-butenyl) Acetal in the Presence of Lewis Acid. Method A: To a solution of 3-methyl-3-butenal bis(3-methyl-2-butenyl) acetal in a solvent, a Lewis acid was slowly added. The mixture was stirred for a stated time and at a stated temperature under an Ar atmosphere. The reaction mixture was quenched by the addition of 2 M (1 M = 1 mol dm^{-3}) aq. NaOH and extracted. The organic layer was washed with water and dried over anhydrous Na_2SO_4. The resultant residue was analyzed by GC.

Method B: To the solution of a Lewis acid in the solvent, 3-methyl-3-butenal bis(3-methyl-2-butenyl) acetal was added slowly. The mixture was stirred for a stated time and at a stated temperature under an Ar atmosphere. The reaction mixture was quenched by the addition of 2 M aq. NaOH and extracted. The organic layer was washed with water and dried over anhydrous Na_2SO_4. The resultant residue was analyzed by GC.

General Procedure for the Reaction of Various Acetals (3a–h). A solution of an acetal (0.63 mmol) and trifluoroacetic acid (7.9×10^{-4} mmol) in benzene or mesitylene (1 mL) was placed in a glass tube (6 mm × 13 cm). The sealed tube was stirred at 190 °C for the stated time. After the reaction, the sealed tube was cooled in an ice bath. The mixture was concentrated and separated by column chromatography on silica gel with a mixed solvent.

Citral (3a): Yield (43%), yellow oil. (*E*)-3,7-dimethyl-2,6-octadienal: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.59 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 2.17 (d, J = 1.0 Hz, 3H, CH_3), 2.21–2.24 (m, 4H, CH_2), 5.04–5.13 (m, 1H, $(CH_3)_2$=CH), 5.87 (dd, J = 8.0, 1.0 Hz, 1H, CH), 9.99 (d, J = 8.0 Hz, 1H, CHO). (*Z*)-3,7-Dimethyl-2,6-octadienal: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 1.98 (d, J = 1.2 Hz, 3H, CH_3), 2.17–2.24 (m, 2H, CH_2), 2.58 (t, J = 7.8 Hz, 2H, CH_2), 5.04–5.13 (m, 1H, $(CH_3)_2$=CH), 5.87 (dd, J = 8.0, 1.0 Hz, 1H, CH), 9.89 (d, J = 8.0 Hz, 1H, CHO).

(6*E*)-3-Methyl-2,6-nonadienal (3b): Yield (54 and 79%), colorless oil. (2*E*, 6*E*)-3-Methyl-2,6-nonadienal: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, J = 7.2 Hz, 3H, CH_3), 1.99 (m, 2H, CH_2), 2.16 (d, J = 0.9 Hz, 3H, CH_3), 2.19–2.30 (m, 4H, CH_2), 5.30–5.55 (m, 2H, –CH=CH–), 5.88 (dd, J = 8.1, 0.9 Hz, 1H, CH), 9.99 (d, J = 8.1 Hz, 1H, CHO). (2*Z*,6*E*)-3-Methyl-2,6-nonadienal: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, J = 7.2 Hz, 3H, CH_3), 1.97 (d, J = 0.9 Hz, 3H, CH_3), 1.99 (m, 2H, CH_2), 2.25 (m, 2H, CH_2), 2.62 (t, J = 7.3 Hz, 2H, CH_2), 5.31–5.55 (m, 2H, –CH=CH–), 5.88 (dd, J = 8.1, 0.9 Hz, 1H, CH), 9.91 (d, J = 8.1 Hz, 1H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 13.7, 17.5, 25.0, 25.4, 25.5, 30.0, 31.4, 32.6, 40.5, 126.7, 127.0, 127.4, 128.5, 133.4, 134.1, 163.6, 163.7, 190.9, 191.3. IR (neat) 970, 1673 cm^{-1} (C=O). HRMS (EI) Found: m/z 151.1129. Calcd for $C_{10}H_{16}O$ [M − 1]$^+$: 151.1123.

3-Methyl-5-phenyl-2-pentenal (3c): Yield (46%), yellow oil. (*E*)-3-Methyl-5-phenyl-2-pentenal: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (s, 3H, CH_3), 2.52 (m, 2H, CH_2), 2.85 (m, 2H, CH_2), 5.89 (d, J = 7.8 Hz, 1H, CH), 7.15–7.31 (m, 5H, ArH), 9.99 (d, J = 7.8 Hz, 1H, CHO). (*Z*)-3-Methyl-5-phenyl-2-pentenal: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.96 (s, 3H, CH_3), 2.82 (m, 2H, CH_2), 2.85 (m, 2H, CH_2), 5.88 (d, J = 7.8 Hz, 1H, CH), 7.15–7.31 (m, 5H, ArH), 9.71 (d, J = 7.8, 1.5 Hz, 1H, CHO). ^{13}C NMR (75 MHz,

$CDCl_3$) δ 17.7, 25.0, 33.5, 34.6, 34.9, 42.1, 126.2, 126.5, 127.6, 128.2, 128.3, 128.5, 128.6, 128.8, 140.1, 140.5, 162.6, 162.8, 190.4, 191.1. IR (neat) 702, 746, 1670 (C=O), 3027 cm^{-1}. HRMS (EI) Found: m/z 173.0998. Calcd for $C_{12}H_{14}O$ $[M - 1]^+$: 173.0966.

5-(2-Furyl)-3-methyl-2-pentenal (3d): Yield (59%), yellow oil. (*E*)-5-(2-Furyl)-3-methyl-2-pentenal: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.18 (d, $J = 1.2$ Hz, 3H, CH_3) 2.80–2.95 (m, 4H, CH_2), 5.88 (m, 1H, CH), 6.01 (dd, $J = 3.3$, 0.9 Hz, 1H, ArH), 6.24 (dd, $J = 3.3$, 1.8 Hz, 1H, ArH), 7.04 (dd, $J = 1.8$, 0.9 Hz, 1H, ArH), 9.99 (d, $J = 7.2$ Hz, 1H, CHO). (*Z*)-5-(2-Furyl)-3-methyl-2-pentenal: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.97 (d, $J = 1.2$ Hz, 3H, CH_3) 2.56 (t, $J = 9.0$ Hz, 2H, CH_2), 2.86 (t, $J = 9.0$ Hz, 2H, CH_2), 5.88 (m, 1H, CH), 6.01 (dd, $J = 3.3$, 0.9 Hz, 1H, ArH), 6.24 (dd, $J = 3.3$, 1.8 Hz, 1H, ArH), 7.04 (dd, $J = 1.8$, 0.9 Hz, 1H, ArH), 9.76 (d, $J = 8.4$ Hz, 1H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.5, 24.7, 25.7, 26.9, 31.2, 38.7, 105.5, 106.1, 110.2, 127.6, 129.1, 141.2, 141.4, 153.5, 154.0, 162.2, 190.5, 191.1. IR (neat) 1670 cm^{-1} (C=O). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37%. Found: C, 72.18; H, 7.26%.

5-(3-Furyl)-3-methyl-2-pentenal (3e): Yield (50%), yellow oil. (*E*)-5-(3-Furyl)-3-methyl-2-pentenal: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.19 (d, $J = 1.2$ Hz, 3H, CH_3) 2.66 (t, $J = 7.5$ Hz, 2H, CH_2), 2.81 (t, $J = 7.5$ Hz, 2H, CH_2), 5.89 (m, 1H, CH), 6.27 (s, 1H, ArH), 7.20–7.40 (m, 2H, ArH), 10.0 (d, $J = 7.8$ Hz, 1H, CHO). (*Z*)-5-(3-Furyl)-3-methyl-2-pentenal: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (d, $J = 1.5$ Hz, 3H, CH_3) 2.48 (t, $J = 7.4$ Hz, 2H, CH_2), 2.68 (t, $J = 7.1$ Hz, 2H, CH_2), 5.89 (m, 1H, CH), 6.27 (s, 1H, ArH), 7.20–7.40 (m, 2H, ArH), 9.82 (d, $J = 8.1$ Hz, 1H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.5, 22.5, 23.9, 24.8, 33.1, 40.6, 110.6, 123.1, 123.4, 127.6, 128.8, 138.9, 139.1, 142.9, 143.1, 162.6, 190.4, 191.1.

5-(4-Methoxyphenyl)-3-methyl-2-pentenal (3f): Yield (6%), yellow oil. (*E*)-5-(4-Methoxyphenyl)-3-methyl-2-pentenal: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.19 (d, $J = 0.6$ Hz, 3H, CH_3), 2.49 (m, 2H, CH_2), 2.81 (m, 2H, $ArCH_2$), 3.79 (s, 3H, OCH_3), 5.88 (m, 1H, CH), 6.83 (m, 2H, ArH), 7.09 (m, 4H, ArH), 9.99 (d, $J = 4.1$ Hz, 1H, CHO). (*Z*)-5-(4-Methylphenyl)-3-methyl-2-pentenal: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (d, $J = 0.6$ Hz, 3H, CH_3), 2.78 (m, 2H, CH_2), 2.81 (m, 2H, $ArCH_2$), 3.79 (s, 3H, OCH_3), 5.88 (m, 1H, CH), 6.83 (m, 4H, ArH), 7.09 (m, 4H, ArH), 9.72 (d, $J = 4.1$ Hz, 1H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.7, 25.1, 32.7, 34.1, 34.9, 42.5, 55.2, 113.9, 127.6, 128.8, 129.2, 129.3, 132.6, 158.0, 163.0, 163.1, 190.6, 191.3.

5-(4-Methylphenyl)-3-methyl-2-pentenal (3g): Yield (27%), yellow oil. (*E*)-5-(4-Methylphenyl)-3-methyl-2-pentenal: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.19 (d, $J = 0.6$ Hz, 3H, CH_3), 2.32 (s, 3H, $ArCH_3$), 2.51 (m, 2H, CH_2), 2.83 (m, 2H, $ArCH_2$), 5.89 (dd, $J = 8.3$, 0.8 Hz, 1H, CH), 7.07 (m, 4H, ArH), 9.99 (d, $J = 4.1$ Hz, 1H, CHO). (*Z*)-5-(4-Methylphenyl)-3-methyl-2-pentenal: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (d, $J = 0.6$ Hz, 3H, CH_3), 2.32 (s, 3H, $ArCH_3$), 2.78 (m, 2H, CH_2), 2.83 (m, 2H, $ArCH_2$), 5.89 (dd, $J = 9.9$, 0.6 Hz, 1H, CH), 7.07 (m, 4H, ArH), 9.72 (d, $J = 4.1$ Hz, 1H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.7, 21.0, 25.1, 33.1, 34.5, 34.7, 42.4, 127.6, 128.1, 128.2, 128.8, 129.2, 129.3, 135.8, 137.4, 163.1, 190.6, 191.3.

5-(4-Fluorophenyl)-3-methyl-2-pentenal (3h): Yield (44%), yellow oil. (*E*)-5-(4-Fluorophenyl)-3-methyl-2-pentenal: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.19 (d, $J = 0.6$ Hz, 3H, CH_3), 2.50 (m, 2H, CH_2), 2.84 (m, 2H, $ArCH_2$), 5.88 (dd, $J = 8.3$, 0.5 Hz, 1H, CH), 6.98 (m, 2H, ArH), 7.13 (m, 2H, ArH), 9.99 (d, $J = 3.9$ Hz, 1H, CHO). (*Z*)-5-(4-Fluorophenyl)-3-methyl-2-pentenal: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (d, $J = 0.8$ Hz, 3H, CH_3), 2.80 (m, 2H, CH_2), 2.84 (m, 2H, $ArCH_2$), 5.88 (dd, $J = 8.3$, 0.5 Hz, 1H, CH), 6.98 (m, 2H, ArH), 7.13 (m, 2H, ArH), 9.71 (d, $J = 4.1$ Hz, 1H, CHO). ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.1, 25.1, 32.6, 34.1, 34.6, 42.2, 115.1, 115.2, 115.4, 115.5, 127.6, 128.8, 129.5, 129.6, 129.7, 129.8, 136.1, 136.1, 159.8, 162.4, 162.6, 163.0, 190.4, 191.2.

3-Methyl-1-phenethyloxy-1,3-butadiene (5a): Yield (23%). yellow oil. (*E*)-3-Methyl-1-phenethyloxy-1,3-butadiene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.79 (s, 3H, CH_3), 2.98 (t, $J = 7.2$ Hz, 2H, CH_2), 3.96 (t, $J = 7.2$ Hz, 2H, OCH_2), 5.67 (d, $J = 12.9$ Hz, 1H, vinyl H), 6.52 (d, $J = 12.9$ Hz, 1H, vinyl H), 7.20–7.33 (m, 5H, ArH). (*Z*)-3-Methyl-1-phenethyloxy-1,3-butadiene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.79 (s, 3H, CH_3), 2.98 (t, $J = 7.2$ Hz, 2H, CH_2), 3.96 (t, $J = 7.2$ Hz, 2H, OCH_2), 4.82 (d, $J = 7.2$ Hz, 1H, vinyl H), 5.93 (d, $J = 7.2$ Hz, 1H, vinyl H), 7.20–7.33 (m, 5H, ArH).

3-Methyl-1-(3-methyl-3-butenyloxy)-1,3-butadiene (5b): Yield (14%), colorless liquid. (*E*)-3-Methyl-1-(3-methyl-3-butenyloxy)-1,3-butadiene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.77 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 2.38 (t, $J = 7.2$ Hz, 2H, CH_2), 3.86 (t, $J = 6.6$ Hz, 2H, OCH_2), 4.68 (s, 1H, CH_2=), 4.76 (s, 1H, CH_2=), 4.76 (s, 1H, CH_2=), 4.82 (s, 1H, CH_2=), 5.68 (d, $J = 13.2$ Hz, 1H, vinyl H), 6.54 (d, $J = 13.2$ Hz, 1H, vinyl H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.6, 37.2, 67.9, 109.2, 111.5, 112.0, 139.7, 142.0, 147.9.

3-Methyl-1-(tetrahydrofurfuryloxy)-1,3-butadiene (5d): Yield (36%), yellow oil. (*E*)-3-Methyl-1-(tetrahydrofurfuryloxy)-1,3-butadiene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.81 (s, 3H, CH_3) 1.85–2.05 (m, 4H, CH_2), 3.70–3.94 (m, 4H, ArH), 4.06–4.18 (m, 1H, OCH), 4.73 (m, 2H, CH_2), 5.68 (d, $J = 12.8$ Hz, 1H, CH=CH), 6.57 (d, $J = 12.8$ Hz, 1H, CH=CH). (*Z*)-3-Methyl-1-(tetrahydrofurfuryloxy)-1,3-butadiene: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.81 (s, 3H, CH_3) 1.85–2.05 (m, 4H, CH_2), 3.70–3.94 (m, 4H, ArH), 4.06–4.18 (m, 1H, OCH), 4.73 (m, 2H, CH_2), 4.82 (d, $J = 7.1$ Hz, 1H, CH=CH), 5.98 (d, $J = 7.1$ Hz, 1H, CH=CH). IR (neat) 1128 (C–H), 2872 cm^{-1} (C–H).

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