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CHEMOSELECTIVE REMOVAL OF ALLYLIC FORMYLOXY GROUP USING SmI_2.

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Abstract: A variety of allylic formates are chemoselectively transformed into the corresponding olefins in excellent yields on treatment with SmI_2 in THF-HMPA-H_2O (20:5:1), even though allylic acetate and allylic ether groups are present in the same molecule.

Although a number of synthetic methods for deoxygenation have been reported[1], there are few methods for the chemoselective removal of allylic oxygen group under mild conditions.

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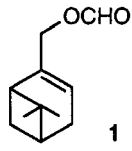
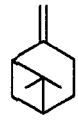
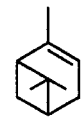
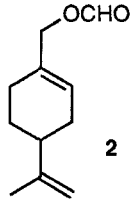
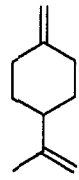
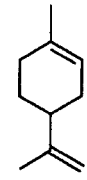
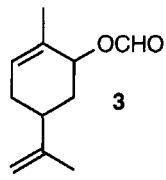
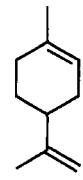
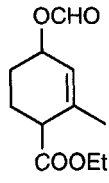
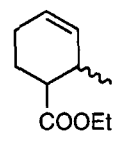
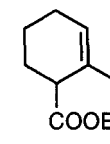
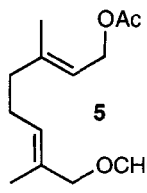
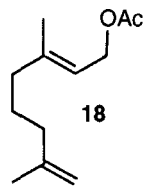
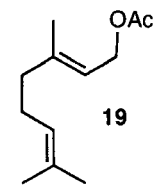
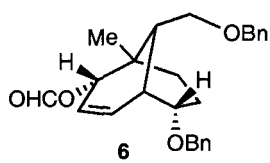
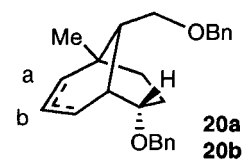
Herein, we wish to report a highly efficient method for the chemoselective transformation of allylic formates into the corresponding olefins using SmI_2. In fact, this reaction did readily take place chemoselectively at the allylic formate center leaving the other allylic ester or ether intact when the latter functionality was present in the same molecule. The reactions were simply carried out by treating the substrates with a four molar excess of SmI_2 in a mixture of THF, HMPA, and H_2O (20:5:1 v/v) at room temperature. It was found that the reaction could be terminated within a few minutes to furnish the corresponding olefins in excellent yields with some extent of double bond migration (Table 1). Myrtenyl formate and perillyl formate were smoothly converted into pinene, limonene and their corresponding isomers, respectively in excellent yield (entries 1 and 2)[2]. In order to elucidate the reaction process, we selected the optically active carvyl formate derived from (R)-(-)-carvone. While starting from (-)-carvyl formate, the value of the optical rotation of generated limonene was extremely low (entry 3)[3]. It was suggested that the generated anion was delocalized and racemized this molecule, and then trapped a proton from H_2O to produce olefins[4] as shown in Scheme 1.

Most noteworthy from the synthetic viewpoint was that the other functional groups such as allylic acetate and allylic ether in the same molecules were inert (entries 4-6). Therefore, this indicated that the present reaction was essentially different from the palladium-mediated reaction[5] in view of chemoselectivity. Interestingly, two formyloxy groups were removed from cholesten-3,4-diformate **7** to afford cholest-3,5-diene **21**[6] in 96% yield. On the other hand, cholesten-3,4-diacetate **8**

Table 1. Deoxygenation of allylic formates.

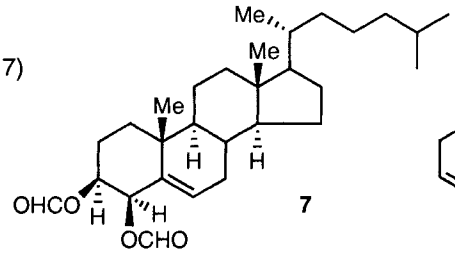
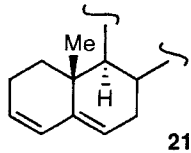
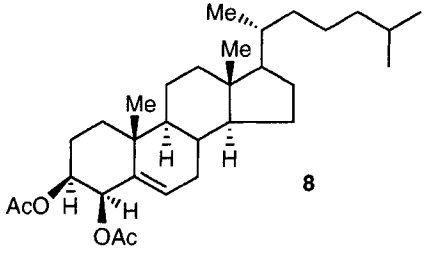
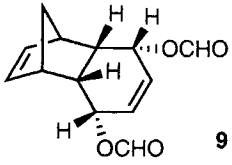
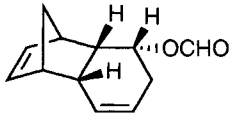
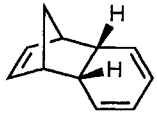
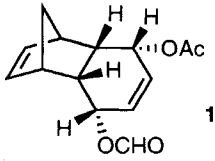
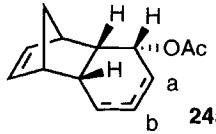
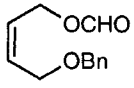
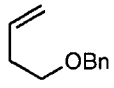
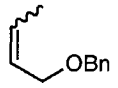
Entry	Substrate	Product	Yield, % [a] Isomeric ratio [b]
1)	 **1**	 **12**  **13**	90% **12** : **13** = 9 : 1
2)	 **2**	 **14**  **15**	93% **14** : **15** = 6 : 4
3)	 **3**	 **15**	98%
4)	 **4**	 **16**  **17**	94% **16** : **17** = 4 : 6
5)	 **5**	 **18**  **19**	71% **18** : **19** = 7 : 3
6)	 **6**	 **20a** **20b**	99% **20a** : **20b** = 3 : 7

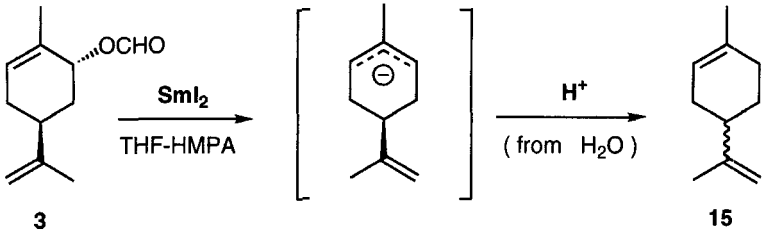
[a] Yield after purification of product by SiO_2 chromatography.

[b] Isomeric ratio was determined by ^{1}H-NMR (270 MHz).

(continued)

Table 1 (continued). Deoxygenation of allylic formates.

Entry	Substrate	Product	Yield, % [a] Isomeric ratio [b]
7)		 **7** **21**	96%
8)	 **8**		no reaction
9)	 **9**	 **22**	26%
		 **23**	(59%, Entry 9) (30%, Entry 10)
10)	 **10**	 **24a** **24b**	54% **24a** : **24b** = 1 : 1
11)	 **11**	 **25**  **26**	94% **25** : **26** = 6 : 4



3 15

Scheme 1

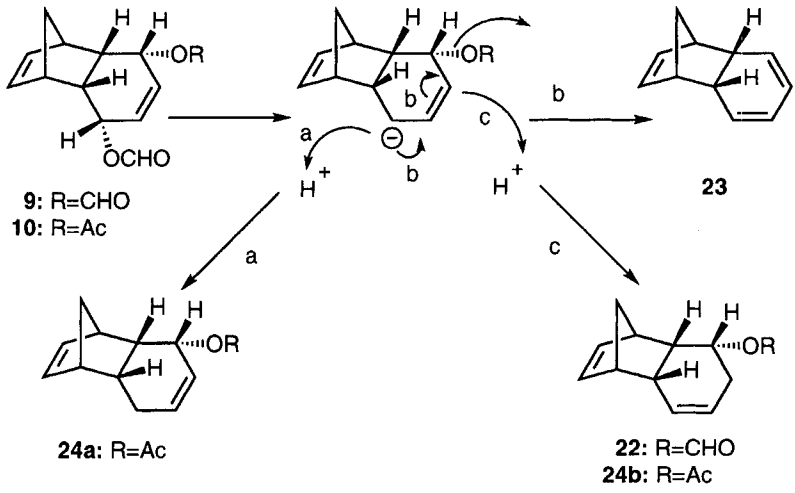
did not react at all (entries 7 and 8). Upon exposure to 1,4-methanonaphthalene-5,8-diformate **9** and 5-formyloxy-1,4-methano-naphthalene-8-acetate **10**, similar reductive eliminations were observed to give the 1,3-diene compound **23**[7] as a common product (entries 9 and 10). The pathway of the present reactions was presumed to start by the generated anion migrating to eliminate acyloxy group as a leaving group and produce the 1,3-diene compound **23** as shown in Scheme 2. In the case of diformate **9**, the reaction might predominantly proceed *via* pathway b and c.

However, even in the same substitution system, the benzyl ether group was inert under the same conditions (entry 11).

In conclusion, we found a specific and efficient removal of allylic formate functionality using SmI_2 without affecting other *O*-allylic functionalities.

Experimental Section

^{1}H-NMR spectra were recorded at 270 MHz on a JEOL GSX-270 spectrometer. ^{13}C-NMR spectra were recorded at 67.5 MHz on a JEOL



Scheme 2

GSX-270 spectrometer. IR spectra were recorded on a JASCO VALOR-III. Low resolution mass spectra (MS) and high resolution mass spectra (HRMS) were recorded on a JEOL JMS-D-300 mass spectrometer instrument. Elemental analyses were performed by Yanako MT-3. Optical rotations were measured on a JASCO DIP-370 polarimeter. Melting points were determined with a Yanagimoto micro melting point apparatus. All melting points are uncorrected. Dichloromethane (CH_2Cl_2) was distilled from P_2O_5. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use. (+)-Limonene (purity 95%) as standard sample was purchased from Tokyo Chemical Industry Co., Ltd.. Column chromatography was carried out with Merck silica gel 0.063-0.2 mm, 70-230 mesh.

Preparation of the allylic formates.

The allylic formates used in this study were prepared from the corresponding allylic alcohols following the typical procedure.

(1α, 4α, 4aα, 5β, 8β, 8aα)-1, 4, 4a, 5, 8, 8a-Hexahydro-1,4-methanonaphthalene-5, 8-diol formate (9) (Typical Procedure)

To an ice-cooled and stirred solution of 3β,7β-dihydroxy-*endo*-tricyclo[6.2.1.$0^{2,7}$]undeca-4,9-diene[7] (178 mg, 1.0 mmol) in CH_2Cl_2 (2 ml) and pyridine (0.4 ml) was added dropwise acetyl formate[8] (211 mg, 2.4 mmol). After 20 min, acetyl formate (211 mg, 2.4 mmol) and pyridine (0.4 ml) was more added. The reaction mixture was stirred at the same temperature for 30 min and dilluted with ether and water. The organic layer was sequentially washed with water, aq. 10% $KHSO_4$, sat. aq. $NaHCO_3$ and sat. aq. NaCl, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was column chromatographed on silica gel (eluted with hexane-ether=5:1) to give 232 mg (99% yield) of diformate **9** as a colorless oil. IR ($CHCl_3$) ν max (cm^{-1}): 3029, 2983, 2934, 1727, 1173; ^{1}H-NMR ($CDCl_3$) δ: 1.29 (dt, J=8.1, 1.7 Hz, 1H), 1.36 (dt, J=8.1, 1.7 Hz, 1H), 2.89 (ddd, J=5.4, 3.4, 1.7 Hz, 2H), 3.06 (dd, J=3.4, 1.7 Hz, 1H), 3.09 (dd, J=3.4, 1.7 Hz, 1H), 5.39 (s, 2H), 5.52 (brt, J=5.4 Hz, 1H), 5.55 (brt, J=5.4 Hz, 1H), 5.84 (t, J=1.7 Hz, 2H) 8.15 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ: 37.9 (d), 46.0 (d), 48.5 (t), 69.3 (d), 127.9 (d), 135.6 (d), 160.5 (d); EIMS m/z (relative intensity): 234 (M^+, 1.2), 189 (16), 66 (100); Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.69; H, 6.10.

(-)-Myrtenyl formate (1)[2]

Prepared in 95% yield as a colorless oil from (-)-myrtenol. $[\alpha]_D^{25}$= -55° (c 1.5, $CHCl_3$). Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.13; H, 8.88.

(-)-Perillyl formate (2)[2]

Prepared in 97% yield as a colorless oil from (-)-perillyl alcohol. $[\alpha]_D^{25}$= -81.3° (c 1.5, $CHCl_3$). Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.03; H,8.80.

(-) -Carvyl formate (3)

Prepared in 93% yield as a colorless oil from a 3:1 mixture of diastereomers of (-)-carveol. $[\alpha]_D^{25}$= -102.5° (c 1.0, $CHCl_3$). Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.29; H, 9.08.

4-Ethoxycarbonyl-3-methyl-2-cyclohexen-1-ol formate (4)

Prepared in 91% yield as a colorless oil from 4-ethoxycarbonyl-3-methyl-2-cyclohexen-1-ol (a 3:2 mixture of stereoisomers), which was easily obtained upon reduction of 4-ethoxycarbonyl-3-methyl-2-cyclohexanone with a combination of $NaBH_4$ and $CeCl_3$ in methanol at 0°C. IR ($CHCl_3$) ν_{max} (cm^{-1}): 3026, 2983, 2940, 1722, 1446, 1259, 1178; ^{1}H-NMR ($CDCl_3$) δ: 1.26 (t, J=7.3 Hz, 1.2H), 1.28 (t, J=7.1 Hz, 1.8H), 1.76 (d, J=1.0 Hz, 1.8H), 1.78 (d, J=1.0 Hz, 1.2H), 1.80-2.12 (m, 7H), 2.96 (m, 1H), 4.16 (q, J=7.3 Hz, 0.8H), 4.18 (q, J=7.1 Hz, 1.2H), 5.34 (m, 1H), 5.65 (m, 1H), 8.04 (d, J=1.0 Hz, 0.4H), 8.06 (d, J=1.0 Hz, 0.6H); Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.13; H, 7.60.

(*2E,6E*)-8-Acetoxy-2,6-dimethyl-2,6-octadien-1-ol formate (5)

Prepared in 75% yied as a colorless oil from (*2E,6E*)-8-acetoxy-2,6-

dimethyl-2,6-octadien-1-ol[9]. Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.19; H, 8.45.

(1*S*, 2*S*, 5*R*, 6*S*, 9*R*)-6-Benzyloxy-9-benzyloxymethyl-1-methylbicyclo[3.3.1]-3-nonen-2-ol formate (6)

Prepared in 92% yield as a colorless oil from (1*S*, 2*S*, 5*R*, 6*S*, 9*R*)-6-benzyloxy-9-benzyloxymethyl-1-methybicyclo[3.3.1]-3-nonen-2-ol, which was obtained upon exposure of (1*S*, 5*R*, 6*S*, 9*R*)-6-benzyloxy-9-benzyloxymethyl-1-methybicyclo[3.3.1]-3-nonen-2-one[10] with diisobutyl aluminum hydride (DIBAL) in CH_2Cl_2 at -78°C. $[\alpha]_D^{25}$= -45.0° (c 1.0, $CHCl_3$); IR ($CHCl_3$) ν max (cm^{-1}): 3011, 2935, 2876, 1717, 1454, 1367, 1190; ^{1}H-NMR ($CDCl_3$) δ: 0.86 (s, 3H), 1.28 (m, 1H), 1.64-1.91 (m, 3H), 2.20 (m, 1H), 3.03 (m, 1H), 3.48 (t, J=9.3 Hz, 1H), 3.58 (dd, J=9.3, 5.9 Hz, 1H), 3.64 (ddd, J=9.3, 5.9, 3.9 Hz, 1H), 4.43 (d, J=12.2 Hz, 1H), 4.48 (d, J=12.2 Hz, 1H), 4.53 (d, J=12.2 Hz, 1H), 4.55 (d, J=12.2 Hz, 1H), 5.39 (brs, 1H), 5.76 (dd, J=9.8, 1.9 Hz, 1H), 5.97 (ddd, J=9.8, 6.1, 1.9 Hz, 1H), 7.23-7.38 (m, 10H), 8.20 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ: 24.72 (t), 24.74 (q), 28.5 (t), 35.4 (s), 35.9 (d), 45.3 (d), 68.0 (t), 70.0 (t), 73.2 (t), 74.2 (d), 78.1 (d), 127.5 (d), 127.5 (d), 127.7 (d), 128.2 (d), 128.3 (d), 128.4 (d), 132.6 (d), 138.3 (s), 138.9 (s), 161.2 (d); EIMS m/z (relative intensity): 406 (M^+, 3), 360 (3), 315 (99), 91 (100); Anal. Calcd for $C_{26}H_{30}O_4$: C, 76.82; H, 7.44. Found: C, 76.81; H, 7.48.

(3*S*, 4*R*)-3,4-Diformyloxy-5-cholestene (7)

Prepared in 94% yield from (3*S*, 4*R*)-cholest-5-en-3,4-diol[11]. A sample was recrystalized from acetone-hexane to give a colorless needle (mp 138-139°C). $[\alpha]_D^{25}$= -122.7° (c 1.0, $CHCl_3$); IR ($CHCl_3$) ν max (cm^{-1}):

2962, 2935, 2870, 1716, 1467, 1171; ^{1}H-NMR ($CDCl_3$) δ: 0.68 (s, 3H), 0.85 (d, J=6.6 Hz, 3H), 0.87 (d, J=6.6 Hz, 3H), 0.91 (d, J=6.6 Hz, 3H), 0.94-1.40 (m, 14H), 1.14 (s, 3H), 1.41-1.67 (m, 6H), 1.71-2.18 (m, 6H), 4.89 (ddd, J=11.7, 4.2, 3.6 Hz, 1H), 5.64 (d, J=3.2 Hz, 1H), 5.87 (dd, J=5.1, 2.7 Hz, 1H), 8.00 (d, J=0.7 Hz, 1H), 8.12 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ: 11.9 (q), 18.7 (q), 20.4 (q), 20.5 (t), 22.5 (t), 22.6 (q), 22.8 (q), 23.8 (t), 24.2 (t), 28.0 (d), 28.2 (t), 31.6 (d), 32.0 (t), 35.8 (d), 36.2 (t), 36.1 (s), 36.6 (t), 39.5 (t), 39.6 (t), 42.3 (s), 50.2 (d), 56.1 (d), 56.8 (d), 72.4 (d), 75.7 (d), 132.8 (d), 137.7 (s), 160.1 (d), 160.3 (d); EIMS m/z (relative intensity): 458 (M^+, 0.8), 412 (100); Anal. Calcd for $C_{29}H_{46}O_4$: C, 75.94; H, 10.11. Found: C, 75.76; H, 10.10.

(3*S*, 4*R*)-3,4-Diacetoxy-5-cholestene (8)[11]

1*S*-(1α, 4α, 4aα, 5β, 8β, 8aα)-1, 4, 4a, 5, 8, 8a-Hexahydro-5-acetoxy-1,4-methanonaphthalene-8-ol formate (10)

Prepared in 97% yield as a colorless oil from (+)-1R-(1α, 4α, 4aα, 5β, 8β, 8aα)-1, 4, 4a, 5, 8, 8a-hexahydro-8-acetoxy-1,4-methanonaphthalen-5-ol[12]. IR ($CHCl_3$) ν_{max} (cm^{-1}): 3027, 2980, 2938, 1725, 1248, 1182; ^{1}H-NMR ($CDCl_3$) δ: 1.28 (dt, J=8.4, 1.4 Hz, 1H), 1.33 (dt, J=8.4, 1.7 Hz, 1H), 2.13 (s, 3H), 2.84 (td, J=3.2, 1.7 Hz, 1H), 2.88 (td, J=3.2, 1.7 Hz, 2H), 3.03 (ddd, J=8.1, 3.2, 0.9 Hz, 1H), 3.09 (ddd, J=8.1, 3.2, 0.9 Hz, 1H), 5.38 (s, 2H), 5.40 (m, 1H), 5.53 (m, 1H), 5.83 (t, J=1.7 Hz, 1H), 8.15 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ: 21.1 (q), 38.0 (d), 45.9 (d), 48.5 (t), 69.3 (d), 69.5 (d), 127.3 (d), 128.5 (d), 135.5 (d), 160.6 (d), 170.6 (s); EIMS m/z (relative intensity): 248 (M^+, 6), 203 (54), 66 (100); Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.59; H, 6.55.

(*Z*)-4-Benzyloxy-2-buten-1-ol formate (11)

Prepared in 90% yield as a colorless oil from (*Z*)-4-benzyloxy-2-buten-1-ol[13]. IR ($CHCl_3$) ν_{max} (cm^{-1}): 3031, 3012, 2935, 2861, 1724, 1169; ^{1}H-NMR ($CDCl_3$) δ: 4.14 (ddd, J=6.1, 1.5, 0.7 Hz, 2H), 4.53 (s, 2H), 4.73 (dd, J=6.1, 1.2 Hz, 2H), 5.73 (dtt, J=11.3, 6.1, 1.5Hz, 1H), 5.87 (dtt, J=11.3, 6.1, 1.2 Hz), 7.25-7.40 (m, 5H), 8.05 (t, J=0.7 Hz, 1H); EIMS m/z (relative intensity): 177 (M^+-CHO, 1.7%), 105 (100), 91 (80); Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.68; H, 6.94.

Removal of allylic formyloxy group from substrates

The removal of an allylic formyloxy group from various substrates was carried out by following the typical procedure.

Cholest-3,5-diene (21) (Typical procedure)

A 30 ml flask, equipped with a closed stopcock-controlled argon inlet, a magnetic stirrer and a vacuum adapter, was charged with HMPA (1.6 ml) and water (0.32 ml). The vacuum was replaced with argon to keep the entering system oxygen free. A solution of samarium diiodide (0.25 M solution in THF 6.4 ml, 1.6 mmol) was added. To this mixture was added in one portion a solution of diformate **7** (183 mg, 0.4 mmol) in THF (1.6 ml). After being stirred at room temperature for 5 min, the reaction mixture was diluted with sat. aq. NH_4Cl (20ml) and ether (10 ml). The organic layer was taken up and the aqueous layer was extracted with ether (2x 5ml). The combined organic layers were washed with water (3x 10 ml) and sat. aq. NaCl (10 ml), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed on silica gel (eluted with hexane) to give 140 mg

(96%) of diene **21** as a white solid (mp 79-80°C). $[\alpha]_D^{25}$= -124.9° (c 1.0, $CHCl_3$); IR ($CHCl_3$) ν_{max} (cm^{-1}): 3010, 2949, 2869, 1468, 909; ^{1}H-NMR ($CDCl_3$) δ: 0.70 (s, 3H), 0.86 (d, J=6.6 Hz, 6H), 0.92 (d, J=6.6 Hz, 3H), 0.95 (s, 3H), 0.96-2.25 (m, 26H), 5.39 (m, 1H), 5.59 (m, 1H), 5.92 (brd, J=9.8 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ: 12.0 (q), 18.7 (q), 18.8 (q), 21.0 (t), 22.6 (q), 22.8 (q), 23.1 (t), 23.8 (t), 24.2 (t), 28.0 (d), 28.3 (t), 31.8 (t), 33.8 (t), 35.2 (s), 35.8 (d), 36.2 (t), 39.5 (t), 39.8 (t), 42.5 (s), 48.4 (d), 56.2 (d), 57.0 (d), 123.2 (d), 125.0 (d), 129.0 (d), 141.5 (s); EIMS m/z (relative intensity): 368 (M^+, 100), 353 (M^+-Me, 28); HRMS Found: 368.3422, $C_{27}H_{44}$ (M^+) requires; 368.3433; Anal. Calcd for $C_{27}H_{44}$: C, 87.97; H, 12.03. Found: C, 87.95; H, 12.02.

β-Pinene (12) and α-Pinene (13)

Isolated as a 9:1 mixture of inseparable regioisomers **12** and **13** in 90% yield after column chromatography (eluted with pentane).

Limonene (14) and p-Mentha-7,8-diene (15)

Isolated as a 6:4 mixture of inseparable regioisomers **14** and **15** in 93% yield after column chromatography (eluted with pentane).

Limonene (15)

Isolated in 98% yield after column chromatography (eluted with pentane). $[\alpha]_D^{25}$= -0.9° (c 2.0, $CHCl_3$) [standard sample: (+)-limonene $[\alpha]_D^{25}$= +108.5° (c 2.0, $CHCl_3$)].

Ethyl 2-methyl-3-cyclohexen-carboxylate (16), trans-Ethyl 2-methyl-2-cyclohexen-carboxylate (17a) and cis-Ethyl 2-methyl-2-cyclohexen-carboxylate (17b)

Isolated as a 4:6 mixture of regioisomers **16** and **17** in 94% yield after

column chromatography (eluted with hexane-ether=20:1). Compound **17** was a 2:1 mixture of stereoisomers **17a** and **17b**. IR ($CHCl_3$) ν max (cm^{-1}): 3025, 2940, 2874, 1724, 1179, 1034; ^{1}H-NMR ($CDCl_3$) δ: 0.90 (d, J=6.8 Hz, 0.4H), 0.99 (d, J=7.1 Hz, 0.8H), 1.27 (t, J=7.1 Hz, 3H), 2.50 (m, 0.26H), 2.95 (m, 0.6H), 4.16 (q, J=7.1 Hz, 2H), 5.49 (dq, J=10.8, 2.2 Hz, 0.26H), ^{13}C-NMR ($CDCl_3$) major isomer **16**: δ: 14.3 (q), 19.7 (t), 22.5 (q), 25.0 (t), 26.7 (t), 45.7 (d), 60.4 (t), 125.2 (d), 130.3 (s), 174.9 (s); trans isomer **17a**: 14.3 (q), 19.2 (t), 20.3 (q), 24.5 (t), 32.6 (d), 47.9 (d), 60.2 (t), 125.5 (d), 132.0 (d), 176.1 (s); cis isomer **17b**: 14.3 (q), 16.4 (q), 19.2 (t), 25.8 (t), 31.0 (d), 43.5 (d), 60.0 (t), 125.9 (d), 131.8 (d), 176.1 (s); EIMS m/z (relative intensity): 168 (M^+, 16), 95 (100). HRMS Found: 168.1156, $C_{10}H_{16}O_2$ (M^+) requires; 168.1150.

(*2E*)-3,7-Dimethyl-2,7-octadien-1-ol acetate (18) and (*2E*)-3.7-Dimethyl-2,6-octadien-1-ol acetate (19)

Isolated as a 7:3 mixture of inseparable regioisomers **18** and **19** in 71% yield after column chromatography (eluted with hexane-ether=20:1). IR ($CHCl_3$) ν max (cm^{-1}): 2971, 2939, 2861, 1728, 1444, 1240; ^{1}H-NMR ($CDCl_3$) δ: 2.05 (s, 3H), 4.59 (d, J=7.1 Hz, 2H), 4.67 (m, 0.7 H), 4.71 (m, 0.7 H), 5.09 (m, 0.3 H), 5.35 (tdt, J=7.1, 1.5, 1.2 Hz, 2H); HRMS Found: 136.1262, $C_{10}H_{16}$ (M^+-AcOH) requires; 136.1252. (*2E, 6E*)-8-acetoxy-2,6-dimethyl-2,6-octadien-1-ol was isolated as sub-product in 17% yield (eluted with hexane-ether=1:1).

(*1R, 2S, 5S, 9R*)-2-Benzyloxy-9-benzyloxymethyl-5-methyl-bicyclo[3.3.1]-6-nonene (20a) and (*1R, 2S, 5S, 9R*)-2-

Benzyloxy-9-benzyloxymethyl-5methylbicyclo[3.3.1]-7-nonene (20b)

Isolated as a 3:7 mixture of separable regioisomers **20a** and **20b** in 99% yield after column chromatography (eluted with hexane-ether=20:1). The physical data of compound **20a** was reported in the literature[10]. Compound **20b** showed the following physical data. (a colorless oil). $[\alpha]_D^{25}$= -102.1° (c 0.9, $CHCl_3$); IR ($CHCl_3$) ν_{max} (cm^{-1}): 3010, 2950, 2874, 1454, 1095, 1072; ^{1}H-NMR ($CDCl_3$) δ: 0.87 (s, 3H), 1.31 (dddd, J=13.4, 5.4, 2.4, 1.9 Hz, 1H), 1.45 (tdd, J=13.4, 6.8, 1.4 Hz, 1H), 1.62-1.81 (m, 2H), 1.90 (ddd, J=18.6, 3.9, 1.9 Hz, 1H), 1.99-2.14 (m, 2H), 3.01(m, 1H), 3.50 (t, J=9.3 Hz, 1H), 3.59 (dd, J=10.8, 5.6 Hz, 1H), 3.61 (dd, J=10.8, 5.6 Hz, 1H), 4.43 (d, J=12.2 Hz, 1H), 4.48 (d, J=12.2 Hz, 1H), 4.53 (d, J=12.2 Hz, 1H), 4.57 (d, J=12.2 Hz, 1H), 5.78 (ddt, J=9.8, 5.8, 1.9 Hz, 1H), 5.87 (ddd, J=9.8, 3.9, 2.9 Hz, 1H), 7.20-7.38 (m, 10H); ^{13}C-NMR ($CDCl_3$) δ: 25.3 (t), 28.6 (q), 31.4 (s), 35.6 (d), 35.7 (t), 42.9 (t), 44.7 (d), 68.6 (t), 69.8 (t), 73.1 (t), 74.8 (d), 127.3 (d), 127.5 (d), 128.2 (d), 128.3 (d), 128.4 (d), 129.8 (d), 138.6 (s), 139.2 (s); EIMS m/z (relative intensity): 362 (M^+, 3), 271 (100); Anal. Calcd for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 82.84; H, 8.49.

(1α, 4α, 4aα, 5β, 8aα)-1, 4, 4a, 5, 6, 8a-Hexahydro-1,4-methanonaphthalene-5-ol formate (22)

After work-up, the residue was chromatographed on silica gel (eluted with pentane) to give **23** in 59% yield as a colorless oil and (eluted with hexane-ether=200:1) to give **22** in 26% yield as a colorless oil. Compound **22** showed the following physical data. IR ($CHCl_3$) ν_{max}

(cm^{-1}): 3028, 2972, 2931, 1712, 1190; ^{1}H-NMR ($CDCl_3$) δ: 1.34 (dt, J=8.3, 1.4 Hz, 1H), 1.47 (dt, J=8.3, 1.7 Hz, 1H), 1.90 (dddd, J=15.7, 10.0, 2.7, 1.7 Hz, 1H), 2.11 (dtd, J=15.7, 6.4, 1.4 Hz, 1H), 2.82 (m, 3H), 3.02 (brs, 1H), 5.28 (dt, J=10.0, 6.4 Hz, 1H), 5.45 (ddd, J=9.8, 6.4, 1.9 Hz, 1H), 5.73 (dddd, J=9.8, 4.3, 2.7, 0.9 Hz, 1H), 6.06 (dd, J=5.6, 2.7 Hz, 1H), 6.10 (dd, J=5.6, 2.7 Hz, 1H), 8.14 (d, J=0.9 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ: 28.3 (t), 41.6 (d), 41.6 (d), 45.8 (d), 46.0 (d), 50.3 (t), 72.8 (d), 123.3 (d), 130.7 (d), 135.0 (d), 136.0 (d), 160.9 (d); EIMS m/z (relative intensity): 191 (M^++1, 48), 144 (6), 66 (100); HRMS Found: 190.0976, $C_{12}H_{14}O_2$ (M^+) requires; 190.0994.

(1α, 4α, 4aα, 5β, 8β, 8aα)-1, 4, 4a, 8a-Tetrahydro-1,4-methanonaphthalene (23)

Compound **23** was unstable because the retro Diels-Alder reaction gradually occurred and decomposed into benzene and cyclopentadiene, which were observed by ^{1}H-NMR during measurement. IR ($CHCl_3$) ν_{max} (cm^{-1}): 3063, 3031, 3007, 2970, 2939, 2891, 2867, 1339, 1210, 908; ^{1}H-NMR ($CDCl_3$) δ: 0.99 (dddd, J=7.8, 3.4, 1.4, 0.7 Hz, 1H), 1.14 (ddd, J=7.8, 1.9, 1.4 Hz, 1H), 2.91 (dt, J=3.4, 1.4 Hz, 2H), 3.05 (ddd, J=3.4, 1.9, 1.4 Hz, 2H), 5.55 (ddd, J=9.5, 3.4, 1.9 Hz, 2H), 5.60 (dt, J=9.5, 3.4 Hz, 2H), 6.08 (t, J=1.7 Hz, 2H); ^{13}C-NMR ($CDCl_3$) δ: 39.9 (d), 44.1 (t), 48.5 (d), 121.4 (d), 128.8 (d), 135.9 (d). Triene **23** was further characterized by its Diels-Alder adduct with N-phenyltriazoline-3,5-dione[7], which was recrystalized from toluene-pentane (mp 216-217°C, Lit[14]. 214-215°C). Anal. Calcd. for $C_{19}H_{17}N_3O_2$: C, 71.46; H, 5.37. Found: C, 71.51; H,5.39.

(*1S*)-(1α, 4α, 4aα, 5β, 8aα)-1, 4, 4a, 5, 8, 8a-Hexahydro-1,4-methanonaphthalene-5-ol acetate (24a) and (*1S*)-(1α, 4α, 4aα, 5β, 8aα)-1, 4, 4a, 5, 6, 8a-Hexahydro-1,4-methanonaphthalene-5-ol acetate (24b)

After work-up, the residue was chromatographed on silica gel (eluted with pentane) to give **23** in 30% yield as a colorless oil and (eluted with hexane-ether=200:1) to give a 1:1 mixture of inseparable regioisomers **24a** and **24b** in 54% yield. IR ($CHCl_3$) ν_{max} (cm^{-1}): 3025, 2968, 2937, 1724, 1371, 1253, 1027; ^{1}H-NMR ($CDCl_3$) δ: 1.29-1.38 (m, 1.5H), 1.45 (dt, J=8.1, 1.7 Hz, 0.5H), 1.78-1.90 (m, 1H), 199-2.24 (m, 4H), 2.54 (tt, J=9.3, 3.7 Hz, 0.5H), 2.75-2.84 (m, 2.5H), 2.85-3.10 (m, 1.5H), 5.14 (dt, J=10.5, 6.3 Hz, 0.5H), 5.38-5.57 (m, 1H), 5.59-5.75 (m, 1H), 5.93 (ddd, J=5.4, 3.4, 1.0 Hz, 0.5H), 6.01 (ddd, J=5.4, 3.4, 1.0 Hz, 0.5H), 6.07 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ: 21.3 (q), 21.5 (q), 25.6 (t), 28.3 (t), 34.8 (d), 41.6 (d), 45.7 (d), 46.0 (d), 46.3 (d), 48.8 (d), 49.7 (t), 50.2 (t), 69.9 (d), 72.6 (d), 123.5 (d), 126.5 (d), 129.9 (d), 130.6 (d), 133.9 (d), 135.1 (d), 135.9 (d), 137.2 (d); EIMS m/z (relative intensity): 144 (M^+-AcOH, 75), 66 (100); HRMS Found: 144.0943, $C_{11}H_{12}$ (M^+-AcOH) requires; 144.0939.

Benzyl-3-butenyl ether (25) , Benzyl-2-(*E*)-butenyl ether (26a) and Benzyl-2-(*Z*)-butenyl ether (26b)

Isolated as a 6:2:2 mixture of inseparable regioisomers **25**, **26a** and **26b** in 94% yield after column chromatography (eluted with hexane-ether=20:1). IR ($CHCl_3$) ν_{max} (cm^{-1}): 3032, 3012, 2928, 2861, 1454, 1093, 909; ^{1}H-NMR ($CDCl_3$) major isomer **25a**: δ: 2.36 (dt, J=6.8, 1.5

Hz, 1H), 2.41 (dt, J=6.8, 1.5 Hz, 1H), 3.53 (t, J=6.8 Hz, 2H), 4.52 (s, 2H), 5.05 (ddd, J=10.8, 1.7, 1.5 Hz, 1H), 5.10 (ddt, J=16.2, 1.7, 1.5 Hz, 1H), 5.68 (dddd, J=16.2, 10.8, 6.8, 1.5 Hz, 1H), 7.24-7.38 (m, 5H); minor isomer **25b**: δ: 1.64 (brd, J=6.8 Hz, 3H), 4.09 (brd, J=6.8 Hz, 2H), 5.60 (dddd, J=12.2, 6.8, 1.5, 1.2 Hz, 1H), 5.85 (dd, J=12.2, 6.8 Hz, 1H); minor isomer **25c**: 5.79 (t, J=6.8 Hz, 1H), 5.90 (t, J=6.8 Hz, 1H); EIMS m/z (relative intensity): 162 (M^+, 33), 91 (100); HRMS Found: 162.1042, $C_{11}H_{14}O$ (M^+) requires; 162.1045.

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