Highly Chemical and Regio-selective Catalytic Oxidation with a Novel Manganese Catalyst†

LIU, Bin(刘斌) CHEN, Yi#(陈怡) YU, Cheng-Zhi(余成志) SHEN, Zheng-Wu#*(沈征武)
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

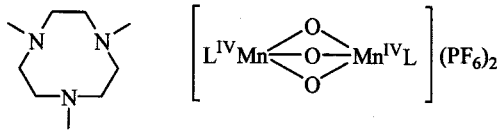
The chemical selectivity of a novel active manganese compound $[Mn_2^{IV}\mu\text{-}O)_3(TMTACN)_2](PF_6)_2$ (1) in catalytic oxidation reactions depended on the structure of substrates and 1 was able to catalyze the oxidation of toluene into benzaldehyde and/or benzoic acid under very mild conditions. The following results were obtained: (1) The selectivity of the oxidation depended on the electronic density of double bonds. Reactivity was absent when strong electron-witherawing groups were conjugated with double bonds. (2) Allylic oxidation reactions mostly take place when double bond is present inside a ring system, whilst epoxidation reactions occur when the alkene moiety is part of linear chain. (3) In ring systems, the methylene group was more likely to be oxidized than the methyl group on allylic position. As expected, the C—H bonds at the bridgeheads were unreactive. The secondary hydroxyl groups are more easily to be oxidized than the primary hydroxyl groups.

Keywords TACN, catalytic oxidation, maganese, benzaldehyde

Introduction

Over the past two decades, a number of biomimetic manganese complexes have been synthesized in order to understand the nature of metalloproteins which make use of the redox capabilities of the manganese ions to catalyze a variety of important biological processes.[1] Metal catalytic oxidation of various organic substrates is of interest to synthetic organic chemists as well as to biochemists.[2-8] Nature has developed many enzymes to achieve selective oxidation using either dioxygen or hydrogen peroxide as the electron-acceptor. Examples of such enzymes include methane monooxygenase, cytochrome P450, various peroxidases and oxidases.[9] It is of great interest for chemists to mimic these systems and use them to achieve selective oxidation under very mild conditions.

Manganese complexes containing the tricapping ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (TMTACN, L) have been described as model for biologically active system, such as the poly-nuclear manganese cluster in the oxygen evolving center of the water oxidation catalyst of photosystem II.[1f,10,11] Subsequently, it was found that manganese compounds containing TMTACN are highly active oxidation catalysts for low-temperature bleaching with hydrogen peroxide as oxidant.[12] Furthermore, complex 1 could also catalyze the epoxidation of styrene and 4-vinyl benzoic acid in aqueous solutions or in water/methanol mixtures. De Vos and Bein reported a similar catalytic system that was used for the epoxidation of alkene and styrene in pure organic solvents with hydrogen peroxide as oxidant.[5] It was also reported that 1 gave selective oxidation of benzyl alcohol into benzaldehyde with relatively high turnovers (up to 1000).[13] More recently, the compound 1 was reported to have an ability of oxidizing phenolic substrate in aqueous media.[14] From the various reports on oxidation catalysis with 1, it is clear that this compound does exhibit unusual catalytic properties, which prompted us to investigate the capability of this agent in organic synthesis.



L (Ligand) 1

The initial scouting started from the oxidation of pregn-5,16-diene-3-acetoxyl-20-ketone, and the results indicated that only 25% of epoxide product was formed, which suggested 50 turnovers without the exist of co-catalyst. The main products were allylic oxidation products (Table 1). The result also indicated that the system was not able to oxidize the α,β-unsaturated ketone. This phenomenon led us to a further investigation of the chemical selectivity of 1.

In contrast with the reaction in water solution, the addition of trace of organic acid such as acetic acid into the reaction system did not affect reaction speed and selectivity. However, when triethyl amine was added, the rate of oxidation decreased significantly, although the yield did

* E-mail: jeff_shen_1999@yahoo.com; Fax: 021-64177337

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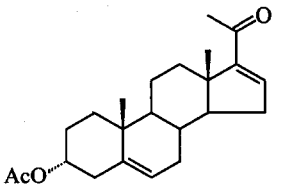
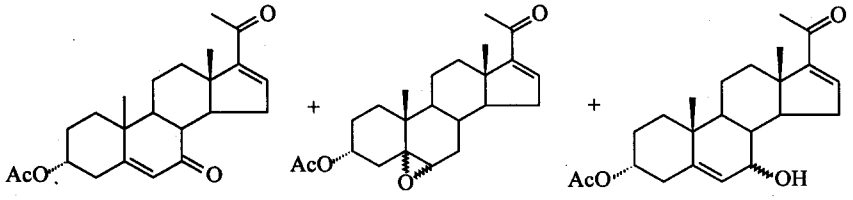
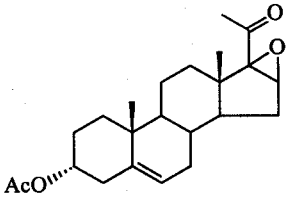
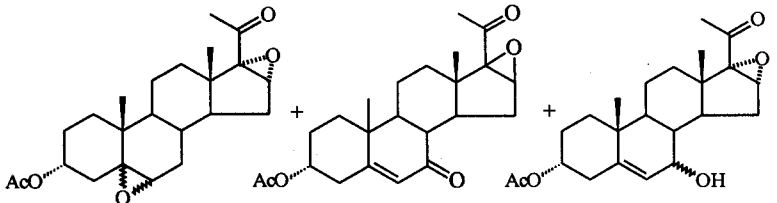
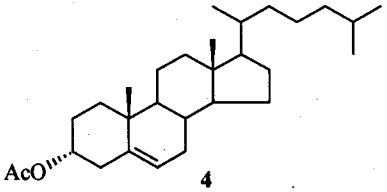
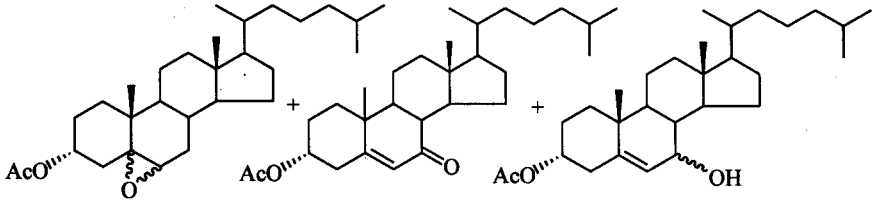
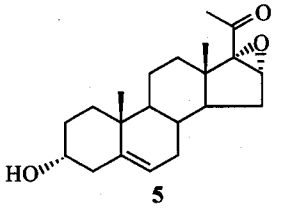
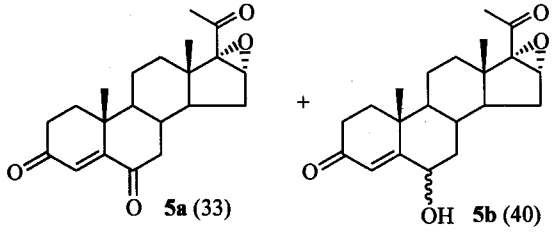
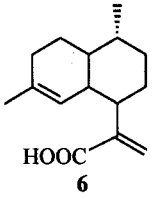
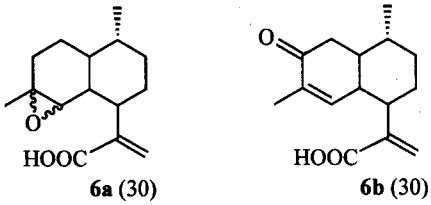
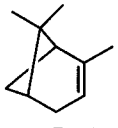
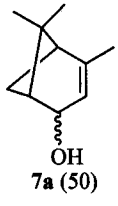
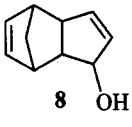
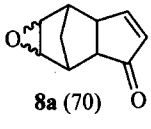
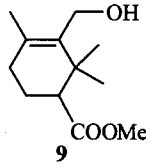
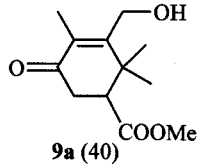
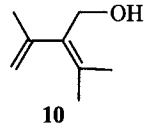
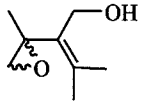
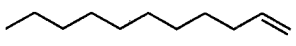
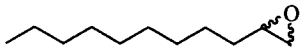
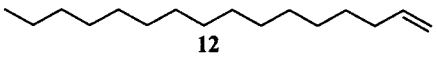
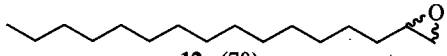
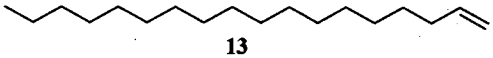
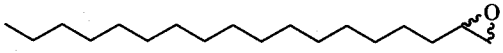
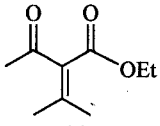
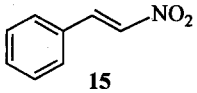
#The present address of the authors: Shanghai University of Traditional Chinese Medicine, 530 Lingling Lu, Shanghai 200032, China.

Table 1 Substrate conversions by **1** and 30% H_2O_2[a]

Entry	Substrate	Product (yield[b], %)
1	 **2**	 **2a** (25) + **2b** (40) + **2c** (21)
2	 **3**	 **3a** (18) + **3b** (50) + **3c** (30)
3	 **4**	 **4a** (23) + **4b** (46) + **4c** (31)
4	 **5**	 **5a** (33) + **5b** (40)
5	 **6**	 **6a** (30) **6b** (30)
6	 **7**	 **7a** (50)
7	 **8**	 **8a** (70)

Continued

Entry	Substrate	Product (yield[b], %)
8	 **9**	 **9a** (40)
9	 **10**	 **10a** (30)
10	 **11**	 **11a** (50)
11	 **12**	 **12a** (70)
12	 **13**	 **13a** (50)
13	 **14**	No reaction
14	 **15**	No reaction

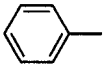
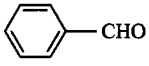
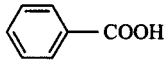
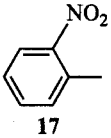
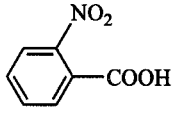
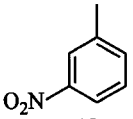
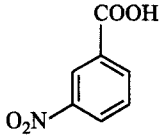
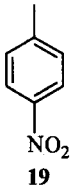
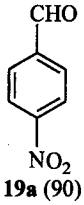
[a] Substrate : catalyst : rose bengal = 360 : 1 : 0.1 (molar ratio), H_2O_2 (0.5 mL, 30%)/substrate (1 mmol). [b] All of the yields were separated yields and the reaction conditions were not optimized.

not drop when we prolonged the reaction time. A very interesting observation was made that photosensitiser, such as rose bengal or methylene blue, could tremendously accelerate the reaction and increase the yield. In order to determine whether light has any effects on above observation, *e.g.* via producing singlet oxygen, a light expelled reaction was performed. It was proved that light did not have any observable influence on the oxidation either in the speed or in the yield. Therefore, a small amount of rose bengal (0.1% of substrate) was added into the reaction mixture as co-catalyst which not only reduced the reaction time and the consumption of oxidants, but also increased the turnover number of these reactions. The catalytic reactions were carried out by gradual addition of aqueous H_2O_2 (30%), diluted in acetone, to a mixture of starting material, rose bengal and **1** in acetone. After stirring at 4 ℃ for 6 h, the products were isolated and the results are shown in Table 1. From the data listed in Table 1, the following conclusions were obtained: (1) The selectivity of the oxidation depended on the electronic density of double bonds. Reactivity was absent when strong electron-withdrawing groups were conjugated with double bonds. (2) Allylic oxidation reactions mostly take place when double bond is present inside a ring system, whilst epoxidation reactions appear to occur when the alkene moiety is part of linear chain. (3) In ring systems, the methylene group was more likely to be oxidized than the methyl group at allylic position (Entries 6 and 8). As expected, the C—H bonds at the bridgeheads were unreactive. (Entry 7). The secondary hydroxyl groups were more easily to be oxidized than the primary hydroxyl groups. (4) In the case of arteannuric acid **6** (Entry 5), we separated same amounts of epoxide product **6a** and allylic oxidized product **6b**. Possibly, a peracid functional group was formed during the reaction. From stereochemistry point of view, the peracid at this position favors to oxidize the double bond into epox-

ide.

From above experiments, It was found that **1** was able to catalyze allylic oxidation. Thus it became more interesting to find out whether it could oxidize toluene into benzaldehyde. As shown in Table 2, oxidation of toluene into benzaldehyde and benzoic acid has been realized under very mild conditions. By controlling the reaction time, the amounts of catalyst **1** and oxidant, benzaldehyde or benzoic acid could be selectively obtained.

Table 2 Oxidation of toluene and its derivatives into benzaldehydes

Entry	Reactant	Reaction time (h)	Reaction condition[a]	Product (yield[b], %)
15	 **16**	24	A	 **16a** (90)
		48	B	 **16b** (78)
16	 **17**	48	A	 **17a** (90)
17	 **18**	48	A	 **18a** (80)
18	 **19**	18	A	 **19a** (90)

[a] A, substrate : catalyst : rose bengal = 360 : 1 : 0.1 (molar ratio), 0.5 mL of 30% H_2O_2/1 mmol of substrate; B, substrate : catalyst : Rose bengal = 100 : 1 : 0.1 (molar ratio), 0.5 mL of 30% H_2O_2/1 mmol substrate. [b] Yields were determined by GC and calculated as yield = product/starting material converted.

In conclusion, catalyst **1** has the capability of catalytic oxidize of a variety of substrates under very mild conditions. The electric density on the double bond decides the chemical selectivity of the oxidation. How to control and improve the selectivity of these reactions will be a challenge for the next stage of investigation. More importantly, **1** has the capability of catalyzing oxidize toluene into benzaldehyde under very mild conditions. This approach may lead to more environmental friendly production of benzaldehyde and benzoic acid derivatives. This method will also have potential applications in multi-step organic syntheses.

Experimental

Melting points were measured on a Buchi Melting point B-545 instrument. IR spectra were measured on Shimadazu-440, Perkin-Elmer 983 and Digilab FT-IR instruments. ^{1}H NMR spectra were measured on Varian EM 360A, Varian EM390L and Bruker AMX-300 NMR spectrometers. ^{13}C NMR spectra were measured on a Bruker DPX-300 NMR spectrometer. Mass spectra were measured on a Finnigan MAT instrument. GC analyses were measured on a SE-54102 gas chromatography. Elemental analyses were performed by analytic department of Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Manganese catalyst was provided by Dr. Ronald Hage in Unilever Research Valaardingen, Holland. The steric chemistry of products was not determined because this work was mainly focused on chemical and regio-selectivity of the reaction. All products in this work were known compounds.

Method 1

1 mmol of substrate, 4 mg (0.005 mmol) of catalyst **1** and 1 mg (0.001 mmol) of rose bengal were dissolved into 5 mL of acetone. A mixture of 1.5 mL of 30% H_2O_2 and 3 mL of acetone was slowly added into the solution at 0 ℃. The reaction mixture was kept stirring at 20 ℃, and monitored by TLC until the starting material disappeared. The solvent was removed by evaporation. The residue was purified by silica gel chromatography.

Method 2

1 mmol of substrate, 8 mg (0.01 mmol) of catalyst **1** and 2 mg (0.002 mmol) of rose bengal were dissolved into 5 mL of acetone. A mixture of 1.5 mL of 30% H_2O_2 and 3 mL of acetone was slowly added into the solution at 0 ℃. The reaction mixture was kept stirring at 50 ℃, and monitored by TLC until the starting material disappeared. The solvent was removed by evaporation. The residue was purified by silica gel chromatography.

3-Acetoxy-5,6-epoxy-pregn-16-en-20-one (**2a**) m.p. 146—148 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.88 (s, 3H), 1.40 (s, 3H), 2.05 (s, 3H), 2.36 (s, 3H), 0.88—2.50 (m, 17H), 3.10 (d, J = 1.9 Hz, 1H), 4.70—4.80 (m, 1H), 6.70 (dd, J = 1.7, 3.0 Hz, 1H); IR (KBr) ν: 2850, 1720, 1650, 1360, 1230, 1020 cm^{-1}; MS (70 eV) m/z (%): 372 (M^+, 8), 375 (43), 312 (53). Anal. calcd for $C_{23}H_{32}O_4$: C 74.16, H 8.66; found C 73.88, H 8.39.

3-Acetoxy-pregn-5,16-dien-7,20-dione (**2b**) m.p. 220—222 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.90 (s, 3H), 1.25 (s, 3H), 2.05 (s, 3H), 2.30 (s, 3H), 3.05—3.15 (m, 1H), 4.65—4.80 (m, 1H), 5.75 (d, J = 1.5 Hz, 1H), 6.80 (dd, J_1 = 1.8 Hz, J_2 = 3.3 Hz,

1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ: 0—50 (15C), 72, 126, 145, 153, 165, 170, 196, 201; IR (KBr) ν: 2494, 2877, 1730, 1670, 1660, 1241, 1037 cm^{-1}; MS (70 eV) *m/z* (%): 370 (M^+, 11), 310 (19).

3-Acetoxy-7-hydoxy-pregn-5, 16-dien-20-one (**2c**) ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.90 (s, 3H), 1.00 (s, 3H), 2.05 (s, 3H), 2.25 (s, 3H), 0.90—2.50 (m, 16H), 3.85 (dd, J_1 = 4.9 Hz, J_2 = 7.0 Hz, 1H), 4.55—4.65 (m, 1H), 5.32 (d, J = 4.9 Hz, 1H), 6.75 (s, 1H); IR (KBr) ν: 3411, 2947, 1733, 1677, 1375, 1245, 1035 cm^{-1}; MS (70 eV) *m/z* (%): 328 (M^+, 19), 312 (28), 283 (35). HRMS calcd for $C_{23}H_{32}O_4C_2H_4O_2$-HOAc 312.2089, found 312.2103.

3-Acetoxy-5, 6, 16, 17-diepoxy-pregn-20-one (**3a**) m.p. 195—197 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.00 (s, 3H), 1.01 (s, 3H), 2.02 (s, 3H), 2.03 (s, 3H), 3.06 (d, J = 2.4 Hz, 1H), 3.66 (s, 1H), 4.70—4.80 (m, 1H); IR (KBr) ν: 2971, 2927, 1726, 1701, 1370, 1261, 1035 cm^{-1}; MS (70 eV) *m/z* (%): 388 (M^+, 13), 371 (53), 328 (78). Anal. calcd for $C_{23}H_{32}O_5$: C 71.09, H 8.31; found C 70.83, H 8.53.

3-Acetoxy-16, 17-epoxy-pregn-5-en-7, 20-dione (**3b**) m.p. 196—198 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.05 (s, 3H), 1.25 (s, 3H), 2.02(s, 3H), 2.05 (s, 3H), 2.28—2.32 (m, 1H), 2.40—2.60 (m, 1H), 2.50—2.65 (m, 1H), 2.82 (dd, J_1 = 5.5 Hz, J_2 = 13.5 Hz, 1H), 3.70 (t, J = 5.5 Hz, 1H), 4.65—4.75 (m, 1H), 5.70 (s, 1H); IR (KBr) ν: 2850, 1720, 1650, 1370, 1230, 1200 cm^{-1}; MS (70 eV) *m/z* (%): 386 (M^+, 11), 342 (23), 328 (62). Anal. calcd for $C_{23}H_{30}O_5$: C 71.48, H 7.82; found C 71.90, H 8.28.

3-Acetoxy-5, 6-epoxy-cholestane (**4a**) m.p. 67—69 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.68 (s, 3H), 0.92 (d, J = 6.8 Hz, 9H), 1.05 (s, 3H), 2.05 (s, 3H), 0.90—2.20 (m, 28H), 3.14 (s, 1H), 4.75—4.85 (m, 1H); IR (KBr) ν: 2850, 1720, 1440, 1360, 1240, 1200 cm^{-1}; MS (70 eV) *m/z* (%): 444 (M^+, 5), 400 (10), 384 (55).

3-Acetoxy-cholest-5-en-7-one (**4b**) m.p. 158—159 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.72 (s, 3H), 0.90 (d, J = 1.3 Hz, 6H), 0.95 (d, J = 6.5 Hz, 3H), 1.25 (s, 3H), 2.05 (s, 3H), 2.20—2.25 (m, 1H), 2.45—2.60 (m, 3H), 4.68—4.80 (m, 1H), 5.75 (s, 1H); IR (KBr) ν: 2950, 2872, 1735, 1672, 1241, 1037 cm^{-1}; MS (70 eV) *m/z* (%): 424 (7), 400 (23), 382 (44). Anal. calcd for $C_{29}H_{46}O_3$: C 78.68, H 10.47; found C 78.59, H 10.78.

3-Acetoxy-7-hydroxy-cholest-5-en (**4c**) ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.75 (s, 3H), 0.90 (d, J = 6.46 Hz, 6H), 0.95 (d, J = 6.38 Hz, 3H), 1.05 (s, 3H), 2.05 (s, 3H), 2.38—2.42 (m, 2H), 3.88—2.92 (m, 1H), 4.60—4.75 (m, 1H), 5.36 (s, 1H), 5.50 (d, J = 5.0 Hz, 1H); IR (KBr) ν: 3458, 2950, 2870, 1736, 1467, 1375, 1244, 1034 cm^{-1}; MS (70 eV) *m/z* (%): 443 (M^+, 15), 384 (100). HRMS calcd for $C_{29}H_{48}O_3C_2H_4O_2$-HOAc 384.3394, found 384.3396.

16, 17-Epoxy-pregn-4-en-3, 6, 20-trione (**5a**) m.p. 178—180 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.10 (s, 3H), 1.20 (s, 3H), 1.30—2.20 (m, 12H), 2.05 (s, 3H), 2.20—2.25 (m, 2H), 2.45—2.70 (m, 3H), 3.75 (s, 1H), 6.18 (s, 1H); IR (KBr) ν: 2941, 2863, 1698, 1678, 1243, 1220 cm^{-1}; MS (70 eV) *m/z* (%): 342 (M^+, 9), 327 (4), 281 (15), 137 (48). Anal. calcd for $C_{21}H_{26}O_4$: C 73.66, H 7.65; found C 73.58, H 7.83.

16, 17-Epoxy-6-hydroxy-pregn-4-en-3, 20-dione (**5b**) ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.10 (s, 3H), 1.40 (s, 3H), 2.05 (s, 3H), 2.35—2.55 (m, 2H), 3.70 (s, 1H), 4.35 (t, J = 2.7 Hz, 1H), 5.80 (s, 1H); IR (KBr) ν: 3431, 2865, 1708, 1654, 1377, 1276, 1035, 885 cm^{-1}; MS (70 eV) *m/z* (%): 344 (M^+, 39), 329 (13), 283 (12).

7, 8-Epoxy-arteannuinic acid (**6a**) m.p. 85—87 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.88 (d, J = 1.9 Hz, 3H), 1.45—1.52 (m, 12H), 1.35 (s, 3H), 2.58 (s, 1H), 2.78 (d, J = 4.25 Hz, 1H), 5.70 (s, 1H), 6.50 (s, 1H); IR (KBr) ν: 2923, 2874, 1682, 1621, 1285, 874 cm^{-1}; MS (70 eV) *m/z* (%): 250 (M^+, 16), 233 (84), 217 (28), 187 (59). Anal. calcd for $C_{15}H_{22}O_3$: C 71.97, H 8.86; found C 72.09, H 9.06.

9-Oxo-arteannuinic acid (**6b**) ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.88 (d, J = 1.48 Hz, 3H), 1.00—2.00 (m, 10H), 2.50 (dd, J_1 = 1.53 Hz, J_2 = 5.49 Hz, 1H), 2.76—2.78 (m, 2H), 3.06 (s, 1H), 5.70 (s, 1H), 6.32 (d, J = 4.5 Hz, 1H), 6.60 (s, 1H); IR (KBr) ν: 3424, 2928, 1717, 1674, 1626, 1180 cm^{-1}; MS (70 eV) *m/z* (%): 248 (M^+, 27), 230 (13), 149 (70), 135 (84). HRMS calcd for $C_{15}H_{20}O_3$ 248.1213, found 248.1394.

4-Hydroxy-α-pinene (**7a**) ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.20 (s, 6H), 1.8 (s, 3H), 1.70—2.51 (m, 4H), 4.05 (dd, J_1 = 2.30 Hz, J_2 = 3.40 Hz, 1H), 5.58 (d, J = 3.0 Hz, 1H); IR (KBr) ν: 3300, 2900, 1430, 1370, 1150, 1140 cm^{-1}; MS (70 eV) *m/z* (%): 169 (M^+ + 1, 2), 152 (26), 137 (42). HRMS calcd for $C_{10}H_{16}O$ 152.1201, found 152.1250.

3, 4-Epoxy-7-oxo-tricyclo [4, 3, 0, 1]-*8-decadene* (**8a**) m.p. 90—92 ℃; ^{1}H NMR (90 MHz, CCl_4) δ: 1.00—1.70 (m, 2H), 2.50—3.50 (m, 4H), 2.70 (dd, J_1 = 5.7 Hz, J_2 = 2.4 Hz, 2H), 6.05 (dd, J_1 = 6.6 Hz, J_2 = 4.3 Hz, 1H), 7.45 (d, J = 6.6 Hz, 1H); IR (KBr) ν: 3047, 2976, 1697, 1573, 1351, 1232, 880, 850 cm^{-1}; MS (70 eV) *m/z* (%): 162 (M^+, 6), 147 (4), 133 (16), 81 (100). Anal. calcd for $C_{10}H_{10}O_2$: C 74.06, H 6.21; found C 73.78, H 6.15.

Methyl 3-hydroxylmethylene-5-oxo-2, 2, 4-trimethyl-3-cyclohexene carboxylate (**9a**) ^{1}H NMR (CCl_4, 90 MHZ) δ: 1.20 (s, 3H), 1.35 (s, 3H), 1.5 (s, 3H), 2.50—2.90 (m, 3H), 3.70 (s, 3H), 4.30 (s, 2H); IR (KBr) ν: 3448, 2955, 1734, 1673, 1437, 1369, 1212, 1162 cm^{-1}; MS (70 eV) *m/z* (%): 226 (M^+, 21), 209 (100), 197 (75), 165 (44). HRMS calcd for $C_{12}H_{18}O_4$ 226.1205, found 226.1190.

1, 2-*Epoxy*-3-*hydroxylmethylene*-2, 4-*dimethyl*-3-*pentadene* (**10a**) ^{1}H NMR (CCl_4, 90 MHz) δ: 1.64 (s, 3H), 1.77 (s, 3H), 2.40 (s, 3H), 3.15 (d, J = 14.7 Hz, 2H), 4.10 (d, J = 9.0 Hz, 2H); IR (KBr) ν: 3432, 2976, 2933, 1656, 1381, 1276, 783 cm^{-1}; MS (70 eV) m/z (%): 142 (M^+, 6), 126 (13), 125 (12), 111 (18), 83 (100). HRMS calcd for $C_8H_{14}O_2$ + 1 143.1073 (M^+ + 1), found 143.1096.

1,2-*Epoxyundecane* (**11a**) ^{1}H NMR (CCl_4, 90 MHz) δ: 0.90—1.80 (m, 19H), 2.45 (d, J = 8.2 Hz, 1H), 2.75 (d, J = 8.2 Hz, 1H), 2.80—3.00 (m, 1H); MS (70 eV) m/z (%): 169 (M^+ - 1, 1), 151 (3), 109 (6), 81 (28), 71 (91).

1,2-*Epoxyhexadecane* (**12a**) m.p. 25—26 ℃; ^{1}H NMR (CCl_4, 60 MHz) δ: 0.90—1.70 (m, 29H), 2.45 (d, J = 7.8 Hz, 1H), 2.70 ~ 2.90 (m, 2H); IR (KBr) ν: 2926, 2855, 1467, 836 cm^{-1}; MS (70 eV) m/z (%): 241 (M^+ - 1, 4), 213 (2), 149 (8), 111 (23), 71 (87).

1,2-*Epoxyoctadecane* (**13a**) m.p. 35—37 ℃; ^{1}H NMR (CCl_4, 90 MHz) δ: 1.00—1.80 (m, 33H), 2.2 (d, J = 6.9 Hz, 1H), 2.50 (d, J = 6.9 Hz, 1H), 2.60—3.00 (m, 1H); IR (KBr) ν: 2919, 2851, 1467, 914, 849, 721 cm^{-1}; MS (70 eV) m/z (%): 267 (M^+ - 1, 1), 220 (2), 149 (14), 109 (28), 71 (100).

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