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Exclusive γ-Regio Functionalization of Crotonaldehyde Using γ-Trimethylsilyl Crotonaldimine. Application to the One Pot Synthesis of Conjugated dienals.

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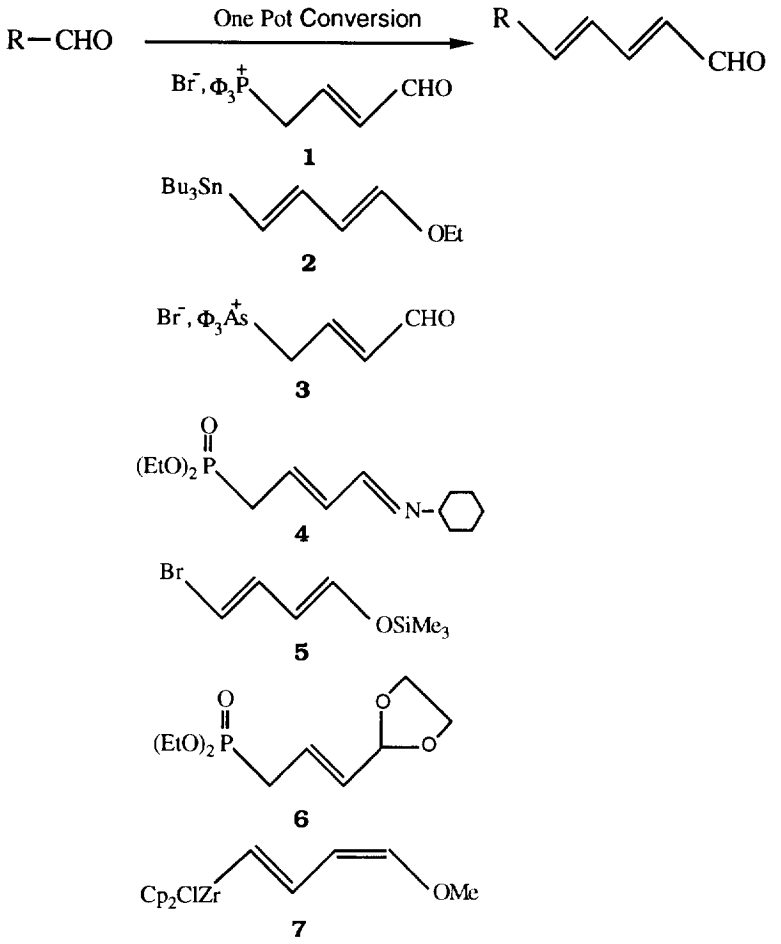
Abstract: Cesium fluoride mediated reaction of γ-trimethylsilyl N-tert-butyl crotonaldimine **9** with a wide range of aldehydes takes place in DMSO at room temperature and affords exclusive γ-regio functionalized products. Heating (rt to 100°C) the δ-silyloxy imines **11** thus obtained leads, after very mild hydrolysis of the tert-butylimine function, to the conjugated dienals **1 4** in good yields and with excellent (*E,E*)-selectivities.

INTRODUCTION AND BACKGROUND

The direct conversion of an aldehyde into an elongated conjugated dienal by four-carbon unit introduction is a very attractive reaction since polyethylenic aldehydes are useful intermediates in organic synthesis. They can be used for the construction of many important classes of natural products such as Amphotericin[1] and Fuligorubine A[2]. Moreover, some dienals are themselves biologically active[3]. To our knowledge, seven reagents can be used for the direct four-carbon homologation of aldehydes(Scheme 1). Phosphonium salt[4] **1** is the first reagent used for this conversion; however, the corresponding "ylidal" is unstable and the yield of the obtained dienal is very low. The 1-tributylstannyl 4-ethoxybutadiene **2** was described in 1978 by Wollenberg[5]; this is a true efficient reagent for this four-carbon homologation; the only difficulty concerns its preparation. Arsonium salt[6] **3** is easy to prepare and stable at room temperature; unfortunately, it suffers from a lack of stereoselectivity. The synthesis of 4-(diethylphosphono) crotonyl-cyclohexylimine **4** is laborious and very long since the direct phosphorylation of the unsaturated imine failed[7]. 1-Bromo 4-trimethylsiloxybutadiene **5** and the masked carbonyl phosphonate **6** were described by L. Duhamel[8]; the preparation of these two reagents requires several steps. Recently, δ-alkoxy dienyl-zirconocene chloride[9] **7** was used for this one pot conversion; this reagent, which was not isolated, was prepared from Schwartz's reagent and methoxy enyne.



Scheme 1

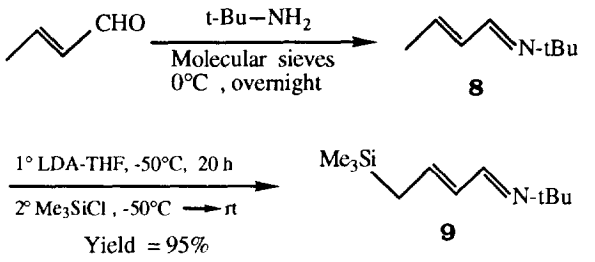
In a preliminary work[10], we proposed a new synthetic method of (2*E*,4*E*)-dienals by four-carbon homologation of aldehydes using γ-trimethylsilyl crotonaldimine **9**. In this paper, we describe in details our study of the preparation and the condensation reactions of this organosilicon reagent with carbonyl compounds.

RESULTS AND DISCUSSION

Preparation of γ-trimethylsilyl crotonaldimine 9

The desired organosilicon reagent **9** required for the present study was prepared for the first time in 1975 by Takabe et al[11]. However, no data have been reported for the products obtained and the authors used two equivalents of trimethylsilyl chloride at -15°C in ether for the silylation of the lithiated crotonaldimine.

We have reexamined the deprotonation and the silylation of the N-tert-butyl crotonaldimine **8** through the reaction sequence shown in Scheme 2.

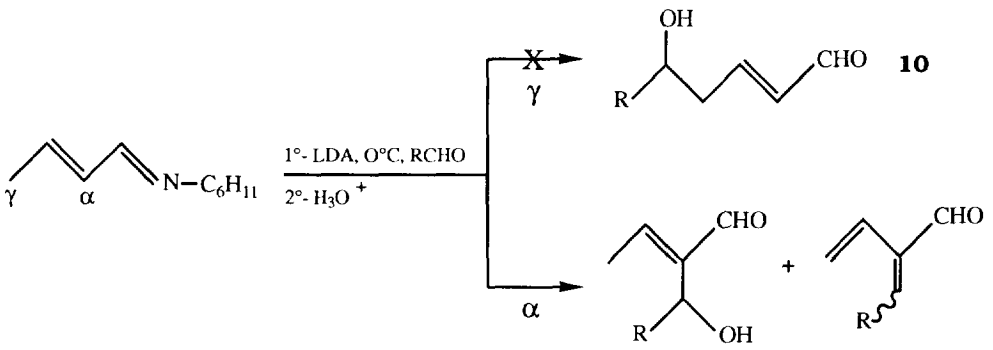


Scheme 2

The best yield (95 %) is obtained when the reactions are carried out at -50°C in the tetrahydrofuran (THF). In this case, the trapping of the lithiated intermediate requires only one equivalent of trimethylsilyl chloride. The crotonaldimine **8** is prepared from crotonaldehyde and N-tert-butylamine in pentane[12] and then used directly for deprotonation without any purification. As judged by ^{1}H-NMR, this transformation proceeds quantitatively. The silylation of **8** affords exclusively the γ-trimethylsilylated aldimine **9** and no product of α-silylation is isolated from this reaction. Moreover, the ^{1}H-NMR spectrum of **9** excluded an enamine structure. Once obtained in pure form, the silyl crotonaldimine is stable if stored under nitrogen at -20°C. Nevertheless, use of the colourless freshly distilled reagent is recommended to avoid the formation of by-products.

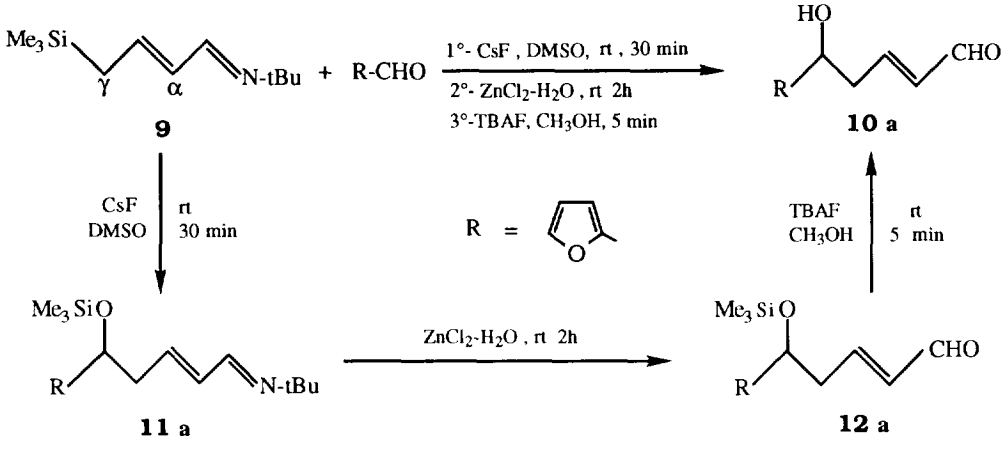
Reaction with aldehydes

Vedejs[13] has reported that lithiocrotonaldimine reacts with aldehydes to afford only α-attack products (Scheme 3). Then, attempts to prepare the desired δ-hydroxy aldehydes **10** have been largely unsuccessful. Furthermore, when the crotonaldimine adduct is submitted, before imine hydrolysis, to equilibrating conditions (heating at reflux in THF) which might cause α to γ migration[14], no identifiable product is obtained.



Scheme 3

Interestingly, nucleophilic addition of **9** to furaldehyde in the presence of catalytic amounts of CsF(10%) in THF at reflux for 4 hours leads to the δ-siloxy imine **11a** (82%), the single reaction product (Scheme 4). This result is of interest since it shows the exclusive γ-regioselective condensation of the silicon reagent **9** unlike the α attack obtained from the lithium derivative of cyclohexyl crotonaldimine.



Scheme 4

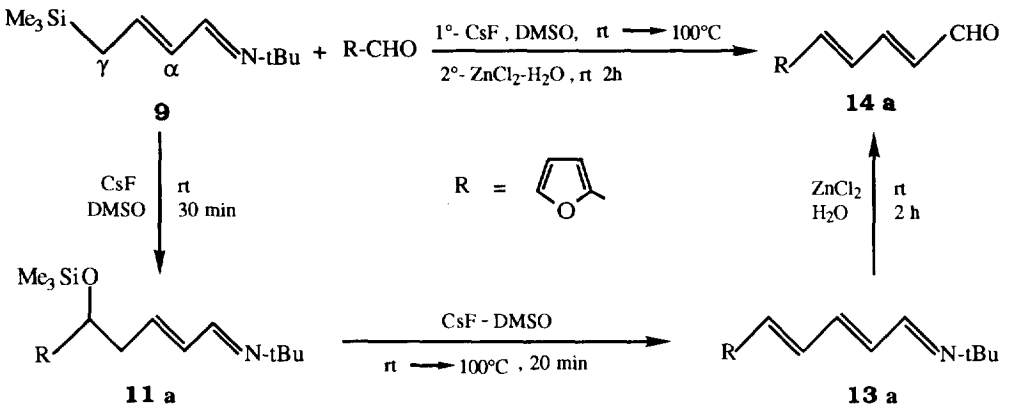
Subsequent hydrolysis of the tert-butylimine function under very mild conditions ($ZnCl_2$-H_2O) gives the corresponding aldehyde **12a**. In ether or dichloromethane, 24 hours are necessary to achieve the condensation reaction. We therefore decided to look for more efficient solvents that could simultaneously affect both reaction time and the temperature of the condensation. Among others, dimethylsulfoxide was found to be remarkably efficient since almost quantitative yield (95 %) of **11a** is obtained after 30 min at room temperature.

It is noteworthy that the source of the fluoride is also essential for this condensation reaction. Thus for example, no product is formed in DMSO at 20°C with LiF, MgF_2 or ZnF_2 even after several hours. In sharp contrast to those latter results, the reaction is very rapid (5 min) and exothermic (25 to 65°C) with tetrabutylammonium fluoride (TBAF) in DMSO. In this case, a mixture of **11a** and hydroxyimine is obtained. The solution of TBAF (1.0 M in THF, available from Aldrich Chemical Co Ltd.) contains water, which probably accounts for the formation of the hydroxyimine. On the basis of these results, CsF is selected as the representative catalyst and employed throughout our work. All reactions are carried out in anhydrous DMSO as solvent.

Prompted by the excellent results obtained with furaldehyde, we have examined the generalization of this γ-regio functionalization reaction to other aldehydes. The results are summarized in Table 1.

One Pot Synthesis of Conjugated Dienals

When the adduct **11a** is heated at 100°C in DMSO with a catalytic amount of cesium fluoride present, TLC-monitoring reveals the total conversion of the silyloxyimine to the dienimine **13a** in 20 min. The latter product was smoothly hydrolyzed by an aqueous solution of zinc chloride to afford the corresponding conjugated (2*E*, 4*E*)-dienal **14a** (Scheme 5).



Scheme 5

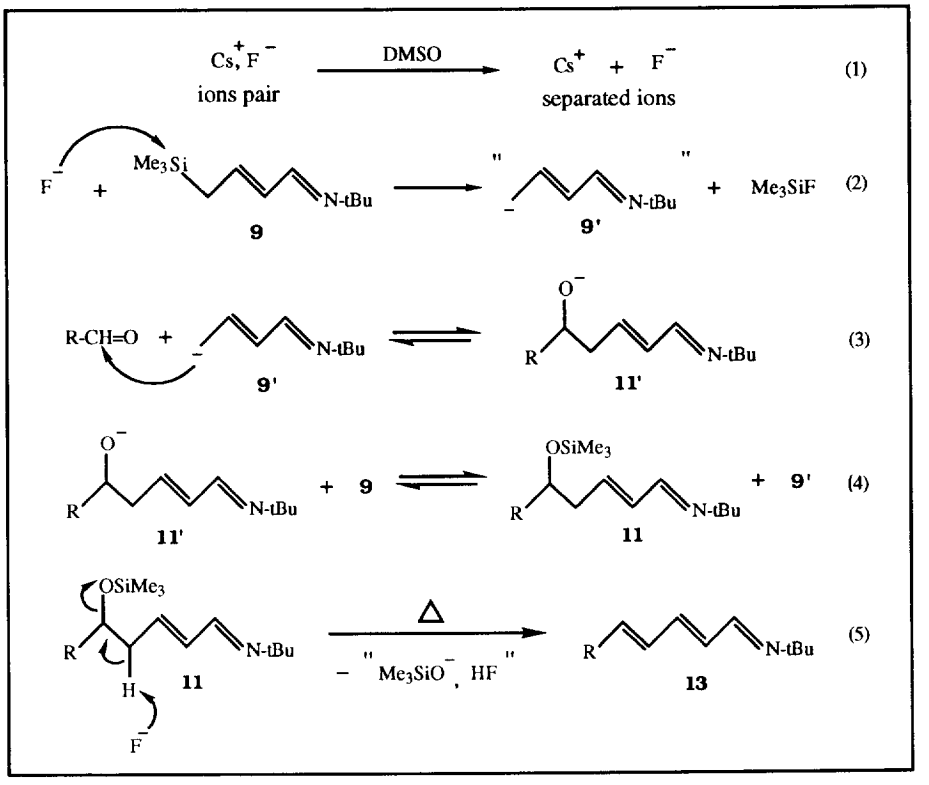
Still a one pot preparation of the unsaturated aldehyde **14a** turned out to be more advantageous since the intermediate hydroxy imine **11a** was not isolated. In a typical experiment, a mixture of reagent **9** and furaldehyde was added to a catalytic amount of CsF (10%) in DMSO at room temperature. After 30 minutes, the red solution was heated at 100°C for 20 min. Hydrolysis of the tert-butylimine function gave the four-carbon homologated starting aldehyde **14a** in excellent yield (94%). To determine the scope and limitation of this new route to dienals, the reaction has been performed with several carbonyl compouds. As can be seen from the results (Table 2), formylenylolefination of aromatic (entries a, b, c, d, e, o), 4-substituted aromatic (entries f, g, h) and unsaturated (entries i, j) aldehydes is achieved efficiently.The *E* stereoselectivity of each addition is confirmed by the 400 MHz ^{1}H-NMR spectrum of the crude product. Aliphatic aldehydes (entries k, l,) afford also the corresponding dienals in good yields. Starting from the available sorbic aldehyde, this methodology is successfully applied to the one pot synthesis of 2,4,6,8-decatetraenal (entry j), an intermediate in the total synthesis of Fuligorubin A[2].

We next examined the behavior of the organosilicon reagent **9** with ketones. Cyclohexanone gave the desired dienal in low yield (entry m) accompanied with the corresponding trimethylsilylenol ether. In the case of benzophenone (entry n), the reaction was sluggish and only moderate yield could be obtained.

Reaction mechanism

Although the exact role of the fluoride ion in this condensation-elimination reaction is not very clear at present, the mechanism shown in the Scheme 6 is postulated.

It is very likely that the reaction is initiated by fluoride ion to generate the silyl carbanion **9'** (eq. 2) which then reacts with the aldehyde to afford the alcolate **11'** (eq. 3). Subsequent reaction of the latter with **9** gives the corresponding δ-silyloxy imine **11** with regeneration of the silyl carbanion (eq. 4). The fact that the condensation is more rapid in DMSO (30 min at rt) than in THF (4 h at reflux) could be explained by the dissociated power of the former (eq. 1). Similar results are obtained with dimethyl formamide (DMF). While the question of the relative basicity of the alkali metal fluorides may remain a matter of speculation, there is no doubt about their ability to generate carbanions from weak carbon acids[15]. The formation of the dienimine **13** is proposed to illustrate the basic behavior of the fluoride ion in DMSO (eq. 5).

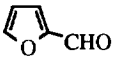
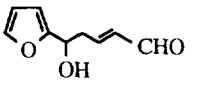
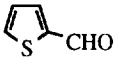
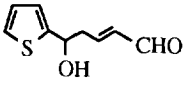
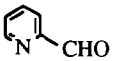
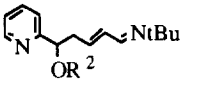
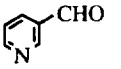
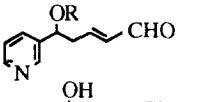
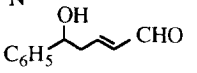
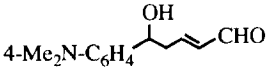
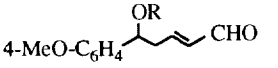
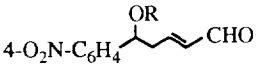
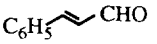
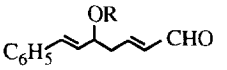
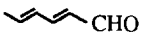
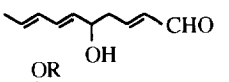
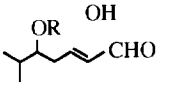
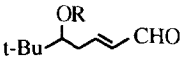
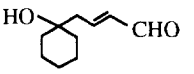
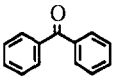
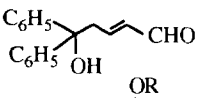
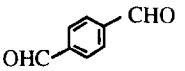
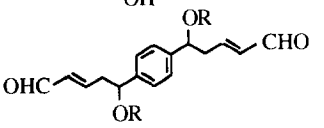
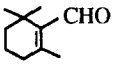
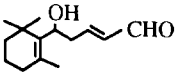


Scheme 6

Conclusion

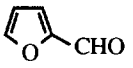
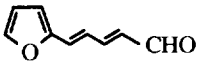
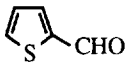
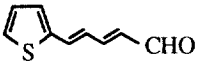
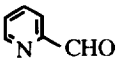
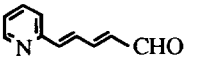
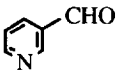
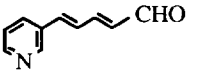
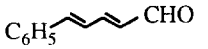
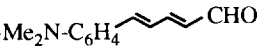
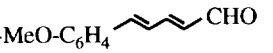
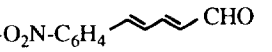
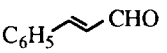
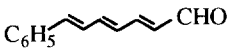
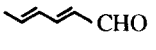
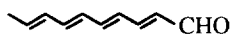
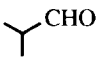
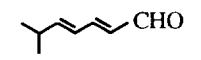
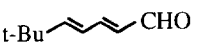
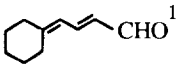
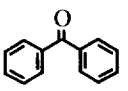
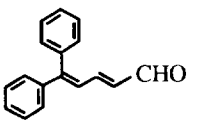
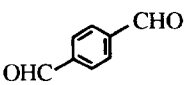
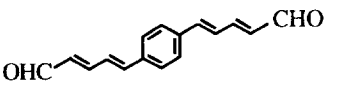
From the results reported in Table 1, it is clear that γ-trimethylsilyl N-tert-butyl crotonaldimine **9** is a versatile reagent for exclusive γ-regio functionalization of crotonaldehyde. This finding led us to develop a facile one pot synthesis of (2*E*,4*E*)-dienals. Easy access to starting **9**, as well as wide scope and preparative simplicity make this new procedure especially convenient for the synthesis of polyenals.

Table 1 : Reaction of the Organosilicon Reagent **9** With Some Carbonyl Compounds.

Entry	Starting Carbonyl Compounds	δ-Hydroxy **10** (or Siloxy **12**) Enals Obtained	Yield (%)
a			91
b			70
c			92[1]
d			67
e	C_6H_5-CHO		70
f	4-Me_2N-C_6H_4-CHO		81
g	4-MeO-C_6H_4-CHO		89
h	4-O_2N-C_6H_4-CHO		95
i			97
j			60
k			60
l	t-Bu-CHO		70
m			20
n			20
o			64
p			15

1-Yield of the corresponding imine. 2-R=$SiMe_3$

Table 2 : One Pot Synthesis of (2*E*,4*E*)-Dienals **14** Using Reagent **9**

Entry	Starting Carbonyl Compounds	Heating Time	(2*E*,4*E*)-Dienals **14**	Yield (%)
a		20 min		94
b		30 min		86
c		30 min		94
d		30 min		86
e	C_6H_5-CHO	2 h		70
f	4-Me_2N-C_6H_4-CHO	45 min		93
g	4-MeO-C_6H_4-CHO	30 min		78
h	4-O_2N-C_6H_4-CHO	30 min		73
i		30 min		92
j		30 min		68
k		30 min		62
l	t-Bu-CHO	30 min		82
m		1h 30 min	 [1]	19
n		18 h		40
o		30 min		86

1 : The corresponding trimethylsilylenol ether was also isolated.

EXPERIMENTAL SECTION

All commercially available compounds used in this work are purchased from Aldrich and used without further purification unless otherwise specified. Trimethylchlorosilane is distilled over magnesium. Diisopropylamine is distilled from CaH_2 and stored over molecular sieves. Tetrahydrofuran and diethylether are distilled over sodium and benzophenone. Lithium diisopropylamide (LDA) is prepared in situ from diisopropylamine and n-butyllithium (1.6 M solution in hexane) at - 50°C.

N-tert-butylcrotonaldimine is easily prepared from crotonaldehyde and tert-butylamine in pentane following the usual way[12]. Reactions requiring anhydrous conditions are performed in flame-dried glassware under a nitrogen atmosphere.

Proton nuclear magnetic resonance spectra are recorded at 200 MHz (Bruker AC 200), 400 MHz (Bruker ARX 400) or 500 MHz (Bruker AM 500). All chemical shifts are reported as δ values (ppm) relative to internal tetramethylsilane. Infrared spectra are recorded on an IR-FT UNICAM spectrophotometer. Melting points are determined on a Thomas Hoover apparatus. Flash column chromatography is performed as described by Still et al[16] (Merck silica gel, 230-400 mesh). TLC analyses are performed on Merck F254 silica gel plates, using UV light or iodine (for non conjugated compounds) as revelator. Mass spectral data with electron ionization (EI) at 70 eV and high resolution (HRMS) are obtained on a Fisons Instruments ZAB HSQ spectrometer.

N-tert-butylcrotonaldimine 8. The starting imine is prepared from the crotonaldehyde and the tert-butylamine in pentane[12]. A solution of tert-butylamine (0.11 mol, 8.03 g) in pentane (10 mL) is added, dropwise to a mixture of crotonaldehyde (0.1 mol, 7 g) and molecular sieves (10 g, 4 Å) in pentane (10 mL). The mixture is cooled with a water-ice bath during 5 hours. Then, the solution is filtered and the solvent is removed in vacuo. The product is distilled to lead to the expected imine as a colourless liquid. **8** : bp : 39-40°C (12 mmHg); yield : 11.38 g (91%) ; IR : 2963; 1685; 1660; 1468; 1371; 1226; 1178; 985 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, 1H, J = 8.43 Hz, C<u>H</u>=N); 6.26 (dd, 1H, J = 15.43, 8.43 Hz, C<u>H</u>-CH=N); 6.18 (dq, 1H, J = 15.43, 6.21 Hz, C<u>H</u>=CH-CH=N); 1.80 (d, 3H, J = 6.21 Hz, C<u>H</u>$_3$); 1.19 (s, 9H, tBu). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.95 (<u>C</u>H=N); 139.18 (<u>C</u>H=CH-CH=N); 132.89 (<u>C</u>H-CH=N); 56.86 (N-<u>C</u>); 29.41 (3 Me); 18.06 (<u>C</u>H$_3$-CH). m/z (%) : 126 (M+1, 23); 110 (15); 100 (23); 84 (17); 69 (18); 57 (100); 44 (34); 41 (50); 29 (24).

Preparation of γ-trimethylsilyl-N-tert-butylcrotonaldimine 9. A solution of **8** (0.1 mol, 12.5 g) in THF (10 mL) is added dropwise to LDA (0.1 mol) at - 50°C. After stirring the solution for 20 hours at this temperature, chlorotrimethylsilane (0.1 mol, 13 mL) is added to the reaction mixture. The resulting solution is stirred for another 2 hours at - 50°C, then gradually warmed to room temperature and finally filtered through a pad of Celite. The solvent is removed and the product distilled. **9** : bp : 47-50°C (0.05 mmHg); yield : 18.72 g (95%); colourless liquid; IR : 2987; 2866; 1685; 1660; 1492; 1371; 1251; 1178; 1101; 1046; 985; 889 cm^{-1}. ^1H NMR (400 MHz, C_6D_6) δ ppm 7.96 (d, 1H, J = 8.56 Hz, C<u>H</u>=N); 6.49 (dd, 1H, J = 15.30, 8.63 Hz, C<u>H</u>-CH=N); 6.01 (dt, 1H, J = 15.34, 8.58 Hz, C<u>H</u>=CH-CH=N); 1.55 (d, 2H, J = 8.52 Hz, C<u>H</u>$_2$); 1.31 (s, 9H, tBu); 0.01 (s, 9H, $SiMe_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.40 (<u>C</u>H=N); 144.35 (<u>C</u>H=CH-CH=N); 132.22 (<u>C</u>H-CH=N); 58.21 (N-<u>C</u>); 31.60 (3 Me); 26.43 (<u>C</u>H$_2$); 0.00 ($SiMe_3$). m/z (%) : 198 (M+1, 4); 179 (24); 148 (24); 147 (100); 123 (28); 82 (15); 75 (42); 73 (24); 57 (68); 41 (28).

Preparation of δ-hydroxyenals 10 and δ-trimethylsiloxyenals 12 (Table 1).

a) Trimethylsiloxyenals 12. To a stirred solution of CsF (10%) in DMSO (2 mL) is added dropwise a mixture of the carbonyl compound (8.5 mmol) and **9** (10 mmol) in DMSO (2 mL) at room temperature. The reaction is exothermic (25° to 45° C). When the temperature comes back to rt, the solution is hydrolyzed with an aqueous solution of $ZnCl_2$ in Et_2O (as described in the general procedure for the preparation of dienals **14**).

b) γ-Hydroxyenals 10. To a mixture of trimethylsiloxyenal **12** (8.5 mmol) in CH_3OH (5 mL) and THF (5 mL), is added dropwise a solution of TBAF in THF (1 mL). After being stirred for 30 minutes, the reaction mixture is extracted with ether (20 mL) , washed with water (2 x 10 mL), dried over magnesium sulphate and the solvent removed in vacuo.

10a : The corresponding δ-hydroenimine has been isolated as a light yellow oil and characterized : bp : 200°C (0.05 mmHg; Büchi); . ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, 1H, J = 8.80 Hz, C<u>H</u>=N); 7.24 (d, 1H, J = 1.65 Hz, H5 ar); 6.21 (dd, 1H, J = 15.39, 8.79 Hz, C<u>H</u>-CH=N); 6.19 (dd, 1H, J = 3.30, 1.65 Hz, H4 ar); 6.12 (d, 1H, J = 3.30 Hz, H3 ar); 6.03 (dt, 1H, J = 15.39, 7.15 Hz, C<u>H</u>=CH-CH=N); 4.67 (t, 1H, J = 6.60 Hz, C<u>H</u>-CH_2); 2.62 (dd, 2H, J = 7.15, 6.59 Hz, <u>C</u>H_2); 1.04 (s, 9H, tBu). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.36 (<u>C</u>H=N); 156.37 (<u>C</u>H=CH-CH=N); 141.24 (C5 ar); 140.50 (C2 ar); 132.83 (<u>C</u>H-CH=N); 109.72 (C4 ar); 105.60 (C3 ar); 65.79 (<u>C</u>H-CH_2); 56.46 (<u>C</u>H_2); 38.78 (N-<u>C</u>); 29.16 (3 Me). m/z (%) : 221 (M^+); 203; 188; 164; 142; 125; 118; 110; 97; 84; 69; 57; 41; 29. HRMS : calcd : 221.1415. Found : 221.1415. After mild hydrolysis, the crude product is purified by flash chromatography (cyclohexane/acetone : 2/1) to lead to **10a** as a bright brown oil; yield : 1.28 g (91%); IR : 3435; 2963; 1710; 1630; 1251; 1082 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.45 (d, 1H, J = 8.25 Hz, C<u>H</u>O); 8.33 (d, 1H, J = 4.95 Hz, H5 ar); 6.81 (dt, 1H, J = 15.94, 7.14 Hz, C<u>H</u>=CH-CHO); 6.28 (dd, 1H, J = 4.95, 3.30 Hz, H4 ar); 6.22 (d, 1H, J = 3.30 Hz, H3 ar); 6.14 (dd, 1H, J = 15.95, 8.25 Hz, C<u>H</u>-CHO); 4.84 (t, 1H, J = 6.60 Hz, C<u>H</u>-CH_2); 2.84 (dd, 2H, J = 7.14, 6.60 Hz, C<u>H</u>$_2$); 2.55 (m, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.93 (<u>C</u>HO); 155.47 (C2 ar); 153.97 (<u>C</u>H=CH-CHO); 142.10 (<u>C</u>H-CHO); 135.04 (C5 ar); 110.33 (C3 ar); 106.76 (C4 ar); 67.03 (<u>C</u>H-CH_2); 39.98 (<u>C</u>H_2). m/z (%) : 166 (M^+,weak); 148 (M-18, 6); 120 (4); 110 (4); 97 (100); 91 (10); 81 (7); 70 (11); 41 (28). HRMS : calcd : 166.0629. Found : 166.0630.

10b : Flash column chromatography is done using cyclohexane/ethyl acetate (4/1) as eluent; an orange oil; yield : 1.08 g (70%); IR : 3420; 1685; 1635; 1600; 1375; 1120; 970; 900 cm-1. ^1H NMR (400 MHz, $CDCl_3$) δ 9.39 (d, 1H, J = 7.70 Hz, C<u>H</u>O); 7.24 (dd, 1H, J = 3.30, 1.65 Hz, H4 ar); 6.96 (d, 1H, J = 1.65 Hz, H5 ar); 6.94 (d, 1H, J = 3.30 Hz, H3 ar); 6.84 (dt, 1H, J = 15.94, 7.15 Hz, C<u>H</u>=CH-CHO); 6.12 (dd, 1H, J = 15.95, 7.69 Hz, C<u>H</u>-CHO); 5.07 (m, 1H, C<u>H</u>-CH_2); 3.44 (m, 1H, OH); 2.82 (dd, 2H, J = 7.14, 6.60 Hz, C<u>H</u>$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.21 (<u>C</u>HO); 153.86 (<u>C</u>H=CH-CHO); 147.02 (C2 ar); 134.73 (<u>C</u>H-CHO); 126.69 (C4 ar); 124.86 (C5 ar); 123.89 (C3 ar); 68.41 (<u>C</u>H-CH_2); 42.00 (<u>C</u>H_2). m/z (%) : 182 (M^+, 8); 165 (21); 135 (11); 113 (100); 85 (62); 70 (12); 45 (22). HRMS : calcd : 182.0401. Found : 182.0401.

10c : Only the δ-trimethylsiloxyenimine **11c** has been isolated as a brown oil and characterized : yield : 2.38 g (92%); IR($CHCl_3$) : 2920; 1645; 1615; 1590; 1575; 1400; 1360; 1145; 1060; 890 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, 1H, J = 3.85 Hz, H6 ar); 7.73 (d, 1H, J = 8.25 Hz, C<u>H</u>=N); 7.60 (td, 1H, J = 7.70, 1.65 Hz, H4 ar); 7.39 (d, 1H, J = 7.70 Hz, H3 ar); 7.09 (dd, 1H, J = 7.70, 3.95 Hz, H5 ar); 6.19-6.12 (m, 1H, C<u>H</u>=CH-CH=N); 6.04 (dd, 1H, J = 15.40, 8.24, C<u>H</u>-CH=N); 4.80 (dd, 1H, J = 7.15, 4.40 Hz, C<u>H</u>-CH_2); 2.70-2.63 (m, 1H, C<u>H</u>$_2$); 2.60-2.54 (m, 1H, C<u>H</u>$_2$); 1.11 (s, 9H, tBu); 0,00 (s, 9H, $SiMe_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.71 (C2 ar); 157.63 (<u>C</u>H=N); 148.67 (<u>C</u>H=CH-CH=N); 140.44 (C6 ar); 137.20 (C4

ar); 134.40 (CH-CH=N); 122.85 (C3 ar); 120.77 (C5 ar); 72.50 (CH-CH_2); 57.19 (C-N); 42.03; (CH_2) 29.95 (3 Me); 0.00 ($SiMe_3$). m/z (%) : 304 (M^+, 45); 289 (29); 247 (30); 199 (42); 180 (80); 157 (68); 147 (70); 130 (30); 105 (49); 84 (49); 73 (100); 57 (64). HRMS : calcd : 304.1970. Found : 304.1969. Anal.calcd. for $C_{17}H_{28}N_2OSi$: C, 67.06; H, 9.27; N, 9.20. Found : C, 67.17; H, 9.17; N, 9.28.

12d : Flash column chromatography is done using cyclohexane/acetone (3/1) as eluent. We obtain a yellow-orange oil; yield : 1.42 g (67%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.44 (d, 1H, J = 7.70 Hz, CHO); 8.52 (s, 1H, H2 ar); 8.46 (d, 1H, J = 4.95 Hz, H6 ar); 7.68 (d, 1H, J = 7.70 Hz, H4 ar); 7.25 (dd, 1H, J = 7.69, 4.95 Hz, H5 ar); 6.81 (dt, 1H, J = 15.39, 7.15 Hz, CH=CH-CHO); 6.12 (dd, 1H, J = 15.39, 7.70 Hz, CH-CHO); 4.90 (dd, 1H, J = 7.70, 4.95 Hz, CH-CH_2); 2.76-2.70 (m, 2H, CH_2); 0.00 (s, 9H, $SiMe_3$). m/z (%) : 250 (M+1; weak); 159 (20); 149 (33); 108 (90); 80 (20); 69 (32); 57 (40); 41 (41). HRMS : calcd : 249.1185. Found : 249.1183.

10e : The product is obtained after flash column chromatography (eluent : cyclohexane/ethyl acetate : 2/1) : a light brown oil; yield : 1.05 g (70%); IR : 3420; 3030; 2960; 1685; 1640; 1498; 1454 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.43 (d, 1H, J = 7.70 Hz, CHO); 7.34-7.19 (m, 5H ar); 6.79 (dt, 1H, J = 15.40, 7.15 Hz, CH=CH-CHO); 6.11 (dd, 1H, J = 15.95, 7.70 Hz, CH-CHO); 4.83 (dd, 1H, J = 7.70, 4.95 Hz, CH-CH_2); 2.78-2.67 (m, 2H, CH_2); 2.00 (m, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.04 (CHO); 154.39 (CH=CH-CHO); 143.64 (C1 ar); 134.64 (CH-CHO); 128.50, 127.84 & 125.59 (5 Car); 72.59 (CH-CH_2); 41.94 (CH_2). m/z (%) : 176 (M^+, weak); 158 (20); 129 (27); 115 (18); 107 (100); 91 (19); 70 (38); 51 (35); 41 (29). HRMS : calcd : 176.0837. Found : 176.0838.

10f : Flash column chromatography is done using cyclohexane/acetone (2/1) as eluent. Dark red crystals; mp : 110°C; yield : 1.51 g (81%); IR($CHCl_3$) : 3420; 1685; 1660; 1580; 1360; 1145; 1120 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.42 (d, 1H, J = 8.24 Hz, CHO); 7.16 (d, 2H, J = 8.80 Hz, H2 ar); 6.78 (dt, 1H, J = 15.95, 7.15 Hz, CH=CH-CHO); 6.51 (d, 2H, J = 8.80 Hz, H3 ar); 6.11 (dd, 1H, J = 15.94, 8.25 Hz, CH-CHO); 4.71 (t, 1H, J = 6.60 Hz, CH-CH_2); 2.87-2.74 (m, 1H, CH_2); 2.70-2.64 (m, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.92 (CHO); 155.37 (CH=CH-CHO); 149.98 (C4 ar); 134.46 (CH-CHO); 131.37 (C1 ar); 126.59 (2 C2ar); 112.16 (2 C3ar); 75.39 (CH-CH_2); 43.63 (CH_2); 40.46 (2 Me). m/z (%) : 219 (M^+, 20); 201 (62); 172 (39); 157 (18); 150 (100); 134 (11); 120 (18); 107 (15); 91 (8); 77 (15). HRMS : calcd : 219.1259. Found : 219.1259.

12g : Flash column chromatography is done using cyclohexane/ethyl acetate (3/1) as eluent; orange oil; 2.10 g (89%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.44 (d, 1H, J = 8.25 Hz, CHO); 7.19 (d, 2H, J = 8.80 Hz, H2 ar); 6.83 (d, 2H, J = 8.79 Hz, H3 ar); 6.76 (dt, 1H, J = 15.40, 7.15 Hz, CH=CH-CHO); 6.73 (dd, 1H, J = 15.40, 8.25 Hz, CH-CHO); 4.73 (dd, 1H, J = 7.70, 4.95 Hz, CH-CH_2); 3,77 (s, 3H, OMe); 2.72-2.62 (m, 2H, CH_2); 0.00 (s, 9H, $SiMe_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.83 (CHO); 158.90 (C1 ar); 154.90 (CH-CH_2); 135.81 (C4 ar); 134.62 (CH-CHO); 126.81 (2 C2ar); 113.62 (2 C3ar); 73.12 (CH-CH_2); 55.10 (CH_2); 43.64 (OMe); 0.00 ($SiMe_3$). m/z (%) : 278 (M^+, weak); 209 (90); 147 (100); 137 (27); 127 (10); 73 (52). HRMS : calcd : 278.1338. Found : 278.1337.

12h : Flash chromatography is done using cyclohexane/acetone (3/1) as eluent; light brown crystals; mp : 70-71°C; yield : 2.36 g (95%); IR($CHCl_3$) : 3150; 1685; 1595; 1550; 1460; 1375; 1340; 1090 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.42 (d, 1H, J = 8.24 Hz, CHO); 8.14 (d, 2H, J = 8.80 Hz, H3 ar); 7.42 (d, 2H, J = 8.80 Hz, H2 ar); 6.70 (dt, 1H, J = 15.95, 7.14 Hz, CH=CH-CHO); 6.03 (dd, 1H, J = 15.94, 8.24 Hz, CH-CHO); 4.87 (t, 1H, J = 6.05 Hz, CH-CH_2); 2.62 (dd, 2H, J = 7.14, 6.05 Hz, CH_2); 0.00 (s, 9H, $SiMe_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 193.51 (CHO); 152.83 (CH=CH-CHO); 151.17 (C1 ar); 147.44 (C4 ar); 135.44 (CH-CHO); 126.48 (2 C3ar); 123.46 (2 C2ar); 72.62 (CH-CH_2); 43.25 (CH_2); 0.00 ($SiMe_3$). m/z (%) : 292 (M-1, weak); 224 (79); 147 (21); 127 (19); 73 (100). HRMS : calcd : 293.1083. Found : 293.1084.

12i : Flash column chromatography is done using cyclohexane/acetone (2/1) as eluent; light brown oil; yield : 1.66 g (97%); IR : 3035; 2963; 1685; 1588; 1516; 1468 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.46 (d, 1H, J = 7.70 Hz, CHO); 7.38-7.19 (m, 5H ar); 6.85 (dt, 1H, J = 15.94, 7.15 Hz, CH=CH-CHO); 6.57 (d, 1H, J = 15.95 Hz, Ar-CH); 6.20-6.13 (m, 2H, CH-CHO & Ar-CH=CH); 4.44 (t, 1H, J = 6.05 Hz, CH-CH_2); 2.61 (t, 2H, J = 6.04 Hz, CH_2); 0.00 (s, 9H, $SiMe_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.95 (CHO); 153.94 (CH=CH-CHO); 136.05 (C1 ar); 134.95 (CH-CHO); 131.26 (Ar-CH); 130.66 (Ar-CH=CH); 128.77, 128.61, 128.50, 127.99 & 126.51 (5C ar); 71.26 (CH-CH_2); 40.30 (CH_2). m/z (%) : 274 (M^+, weak); 247 (5); 221 (20); 184 (25); 155 (20); 147 (100); 133 (88); 115 (41); 105 (27); 91 (36); 73 (30); 55 (28). HRMS : calcd : 274.1389. Found : 274.1388.

10j : Flash column chromatography is done using cyclohexane/ethyl acetate (2/1) as eluent; orange oil; yield : 0.85 g (60%); IR : 3421; 2939; 1685; 1638; 1583; 1275 cm^{-1}. ^1H NMR (400 MHz, C_6D_6) δ 8.98 (d, 1H, J = 7.70 Hz, CHO); 5.95 (dt, 1H, J = 14.30, 7.15 Hz, CH=CH-CHO); 5.73 (dd, 1H, J = 14.85, 10.45 Hz, CH=CH-CH(OH)); 5.68-5.61 (m, 2H, CH=CH-CH(OH) & H_3C-CH); 5.25 (dq, 1H, J = 14.85, 7.70 Hz, H_3C-CH); 4.97 (dd, 1H, J = 14.30, 7.15 Hz, CH-CHO); 3.48 (dt, 1H, J = 6.60, 6.05 Hz, CH-CH_2); 1.77-1.65 (m, 2H, CH_2); 1.28 (d, 3H, J = 7.14 Hz, Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.01 (CHO); 154.23 (CH=CH-CHO); 134.83 (CH-CHO); 131.79, 131.33, 131.04 & 130.29 (H_3C-CH=CH-CH=CH); 71.06 (CH-CH_2); 40.31 (CH_2); 18.06 (Me). m/z (%) : 166 (M^+, weak); 149 (29); 133 (10); 121 (16); 105 (16); 97 (100); 91 (24); 79 (39); 69 (39); 55 (29); 43 (68); 41 (94). HRMS : calcd : 166.0993. Found : 166.0993.

12k : Flash column chromatography is done using cyclohexane/ethyl acetate (4/1) as eluent; we have isolated a yellow oil; yield : 1.09 g (60%); IR : 2972; 1700; 1648; 1480; 1058; 850 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 9.49 (d, 1H, J = 7.88 Hz, CHO); 6.88 (dt, 1H, J = 15.75, 7.80 Hz, CH=CH-CHO); 6.11 (dd, 1H, J = 15.75, 7.88 Hz, CH-CHO); 3.55 (q, 1H, J = 7.80 Hz, CH-CH_2); 2.43 (t, 2H, J = 7.80 Hz, CH_2); 1.55 (m, 1H, H6); 0.85 (d, 6H, J = 7.80 Hz, 2 Me); 0.07 (s, 9H, $SiMe_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.78 (CHO); 155.54 (CH=CH-CHO); 134.20 (CH-CHO); 75.00 (CH-CH_2); 37.07 ($(Me)_2CH$); 33.27 (CH_2); 18.23 (Me); 18.16 (Me); 1.50 ($SiMe_3$). m/z (%) : 215 (M+1, 12); 171 (17); 145 (70); 125 (27); 98 (18); 83 (20); 73 (100); 70 (76); 55 (46); 43 (39). HRMS : calcd : 214.1388. Found : 214.1389.

12l : Flash column chromatography is done using cyclohexane/ethyl acetate (4/1) as eluent; yellow oil; yield : 1.36 g (70%); IR : 2939; 2870; 1685; 1630; 1492; 1371; 1251; 889; 843 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.51 (d, 1H, J = 7.92 Hz, CHO); 6.88 (dt, 1H, J = 14.90, 7.73 Hz, CH=CH-CHO); 6.11 (dd, 1H, J = 15.55, 7.96 Hz, CH-CHO); 3.44 (dd, 1H, J = 8.02, 3.59 Hz, CH-CH_2); 2.51-2.38 (m, 2H, CH_2); 0.87 (s, 9H, 3 Me); 0.07 (s, 9H, $SiMe_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.08 (CHO); 157.14 (CH=CH-CHO); 134.33 (CH-CHO); 78.46 (CH-CH_2); 35.12 (CH_2); 28.88 ($(Me_3)C$); 25.50 (3 Me); 1.89 ($SiMe_3$). m/z (%) : 227 (M-1, 8); 211 (8); 187 (17); 171 (13); 159 (100); 149 (46); 139 (82); 121 (20); 109 (10); 95 (18); 87 (25); 73 (39); 57 (42); 41 (31). HRMS : calcd : 228.1545. Found : 228.1545.

10m: Flash column chromatography is done using cyclohexane/ethyl acetate (10/1) as eluent; orange oil; yield : 0.29 g (20%); IR : 3600; 3405; 3150; 2915; 1685; 1630; 1445; 1375; 1090 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.47 (d, 1H, J = 7.70 Hz, CHO); 6.92 (dt, 1H, J = 15.39, 7.70 Hz, CH=CH-CHO); 6.06 (dd, 1H,

J = 15.40, 7.70 Hz, CH-CHO); 2.43 (d, 2H, J = 7.70 Hz, CH_2); 1.52-1.40 (m, 10H cycle). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.10 (CHO); 154.64 (CH=CH-CHO); 135.51 (CH-CHO); 71.67 (C(OH)); 45.52 (CH_2); 37.77 , 25.47 & 22.08 (5C cycle). m/z (%) : 169 (M+1, weak); 151 (11); 133 (5); 99 (100); 81 (49); 70 (16); 55 (18); 41 (16). HRMS : calcd : 168.1150. Found : 168.1149. Anal.calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found : C, 71.39; H, 9.51.

10n: To a solution of benzophenone (8.5 mmol, 1.55 g) and TBAF (2 mL) in DMSO (2 mL), is added, dropwise a mixture of **9** (10 mmol, 1.97 g) in DMSO (2 mL) at rt. After being stirred 30 minutes, the reaction mixture is hydrolyzed (aqueous solution of $ZnCl_2$) during 3 hours. After purification on silica gel (eluent : cyclohexane/acetone (20/1)), we have isolated the expected compound as orange crystals; mp : 85-87°C; yield : 0.43 g (20%); IR($CHCl_3$) : 3670; 3590; 3400; 2920; 2820; 1685; 1635; 1600; 1485; 1440; 1125; 1000; 970 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.31 (d, 1H, J = 7.69 Hz, CHO); 7.35-7.25 (m, 10H ar); 6.70 (dt, 1H, J = 15.94, 7.14 Hz, CH=CH-CHO); 6.08 (dd, 1H, J = 15.95, 7.70 Hz, CH-CHO); 3.27 (d, 1H, J = 7.15 Hz, CH_2); 2.30 (m, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.88 (CHO); 153.90 (CH=CH-CHO); 145.76 (2 C1ar); 135.52 (CH-CHO); 128.30, 127.26, 125.85 (10C ar); 77.00 (CH-CH_2); 45.23 (CH_2). m/z (%) : 234 (M-18, weak); 205 (5); 183 (100); 167 (7); 149 (14); 122 (4); 105 (89); 91 (5); 77 (49); 51 (11). HRMS (M-18) : calcd : 234.1044. Found : 234.1043. Anal.calcd. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found : C, 81.12; H, 6.30.

12o : Flash column chromatography is done using cyclohexane/acetone (6/1) as eluent ; yellow oil; yield : 3.20 g (90%); IR($CHCl_3$) : 2920; 2840; 1685; 1620; 1600; 1270; 1140; 1040; 970 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.45 (d, 2H, J = 7.70 Hz, CHO); 7.25 (s, 4H ar); 6.77 (dt, 2H, J = 15.95, 7.70 Hz, CH=CH-CHO); 6.08 (dd, 2H, J = 15.95, 7.69 Hz, CH-CHO); 4.78 (dd, 2H, J = 7.69, 4.95 Hz, CH-CH_2); 2.72-2.65 (m, 4H, CH_2); 0.00 (s, 18H, $SiMe_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.85 (2 CHO); 154.57 (2 CH=CH-CHO); 143.10 (2 C1ar); 134.80 (2 CH-CHO); 125.77 (4 C2ar); 73.30 (2 CH-CH_2); 43.47 (CH_2); 0.00 ($SiMe_3$). m/z (%) : 403 (M-15, weak); 349 (45); 334 (9); 280 (63); 259 (16); 207 (37); 174 (17); 149 (35); 127 (20); 91 (15); 57 (22); 41 (48). HRMS (M-15) : calcd : 403.1760. Found : 403.1761.

10p: The starting β-cyclocitral is prepared following the Gedye[17] procedure. Column Flash chromatography is done using cyclohexane/ethyl acetate (10/1) as eluent ; orange solid; mp : 48-49°C; yield : 0.28 g (15%); IR($CHCl_3$) :3410; 2920; 2860; 1685; 1635; 1600; 1375; 1125; 970 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, 1H, J = 7.70 Hz, CHO); 6.90 (dt, 1H, J = 15.40, 7.15 Hz, CH=CH-CHO); 6.14 (dd, 1H, J = 15.40, 7.70 Hz, CH-CHO); 4.38 (dd, 1H, J = 7.14, 3.30 Hz, CH-CH_2); 2.94-2.86 (m, 1H, CH_2); 2.48-2.42 (m, 1H, CH_2); 1.91-1.87 (m, 2H, CH_2-C(Me_2)); 1.80 (s, 3H, Me); 1.51-1.46 (m, 2H, CH_2-CH_2); 1.38-1.34 (m, 2H, CH_2-(Me)C=); 1.19 (s, 3H, Me); 1.03 (s, 3H, Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.10 (CHO); 156.22 (CH=CH-CHO); 139.47 (C=C(Me)); 134.09 (CH-CHO); 132.58 ((Me_2)C-C); 69.77 (CH-CH_2); 39.98 (CH_2); 39.71 (Me); 34.63 (C cycle); 33.99 (Me); 28.54 (Me); 27.97, 21.00 & 19.12 (3C cycle). m/z (%) : 222 (M^+, weak); 204 (4); 189 (4); 153 (100); 135 (13); 123 (16); 109 (72); 95 (45); 81 (23); 69 (39); 55 (29); 41 (48). HRMS : calcd : 222.1619. Found : 222.1620. Anal.calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found : C, 75.99; H, 10.00.

Preparation of dienals 14a-o. General procedure.

A detailed procedure for the reaction of **9** with carbonyl compounds is given below. All reactions are carried out under nitrogen and conducted in a similar manner, unless otherwise specified. Reaction times and

yields are reported in Table 2. Physical, spectral and analytical data follow. To a solution of the carbonyl compound (8.5 mmol) and CsF (1 mmol, 0.15g) in DMSO (2 mL) was added a solution of **9** (10 mmol, 1.97 g) in DMSO (2 mL), dropwise at room temperature. After being stirred for 30 minutes, the resulting mixture is heated at 100°C during 20 minutes to 2 hours (depending on the structure of the starting aldehyde). Then, the solution is hydrolyzed at rt with an aqueous solution of $ZnCl_2$ (2 g in 25 mL of water) and ether (25 mL) and stirred for 2-3 hours. The precipitate is filtered on a pad of Celite. The aqueous layer is extracted with ether (2 x 25 mL) and the combined organic extracts are washed with water (2 x 20 mL) and dried over $MgSO_4$. The solvent is removed in vacuo. The reaction crude product is purified by flash chromatography on silica gel to give the dienals **14a-o**.

14a[6] : Prepared from 2-furfural (8.5 mmol, 0.82 g) and **9** (10 mmol, 1.97 g). The corresponding imine **13a** has been isolated as a bright brown solid and characterized : mp : 50-52°C; IR(KBr) : 2987; 1685; 1635; 1610; 1492; 1371; 1275; 1226; 1154 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, 1H, J = 8.79 Hz, C<u>H</u>=N); 7.33 (d, 1H, J = 1.65 Hz, H5 ar); 6.74 (dd, 1H, J = 15.39, 11.00 Hz, C<u>H</u>=CH-CH=N); 6.63 (dd, 1H, J = 15.40, 11.00 Hz, Ar-CH=C<u>H</u>); 6,43 (d, 1H, J = 15.40 Hz, Ar-C<u>H</u>); 6.39 (dd, 1H, 15.40, 8.80 Hz, C<u>H</u>-CH=N); 6.34 (dd, 1H, J = 3.30, 1.65 Hz, H4 ar); 6.29 (d, 1H, J =3.30 Hz, H3 ar); 1.16 (s, 9H, tBu). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.00 (<u>C</u>H=N); 152.51 (C2 ar); 142.79 (<u>C</u>H=CH-CH=N); 140.40 (Ar-<u>C</u>H); 132.85 (<u>C</u>H-CH=N); 126.23 (C5 ar); 122.96 (Ar-CH=<u>C</u>H); 111.78 (C3 ar); 110.06 (C4 ar); 57.05 (N-<u>C</u>$(CH_3)_3$); 29.55 (3 Me). m/z (%) : 203 (M^+, 88); 188 (37); 173 (13); 146 (100); 131 (25); 118 (67); 103 (16). Anal.calcd. for $C_{13}H_{17}NO$: C, 76.81; H, 8.43 and N, 6.89. Found : C, 76.60; H, 8.24 and N, 6.62. After hydrolysis and purification by flash chromatography (cyclohexane/acetone (3/1) as eluent), we have isolated **14a** as a brown solid; mp : 60-62°C; yield : 1.18 g (94%); IR(KBr) : 1685; 1612; 1492; 1395; 1275; 1178; 1106 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.52 (d, 1H, J = 8.25 Hz, CHO); 7.41 (d, 1H, J = 1.65 Hz, H5 ar); 7.12 (dd, 1H, J = 14.84, 11.00 Hz, C<u>H</u>=CH-CHO); 6.82 (dd, 1H, J = 15.39, 10.99 Hz, Ar-CH=C<u>H</u>); 6.71 (d, 1H, J = 15.40 Hz, Ar-C<u>H</u>); 6.47 (d, 1H, J = 3.30 Hz, H3 ar); 6.40 (dd, 1H, J = 3.30, 1.65 Hz, H4 ar); 6.18 (dd, 1H, J = 14.85, 8.25 Hz, C<u>H</u>-CHO). ^{13}C NMR (50 MHz, $CDCl_3$) δ 193.18 (<u>C</u>HO); 152.00 (C2 ar); 151.25 (<u>C</u>H=CH-CHO); 144.29 (Ar-<u>C</u>H); 131.41 (<u>C</u>H-CHO); 128.46 (C5 ar); 124.44 (Ar-CH=<u>C</u>H); 113.07 (C3 ar); 112.36 (C4 ar). m/z (%) : 148 (M^+, 97); 120 (48); 119 (30); 105 (8); 94 (29); 91 (100). Anal.calcd. for $C_9H_8O_2$: C, 72.96; H, 5.44. Found : C, 72.50; H, 5.52.

14b[18] : Prepared from 2-thiophenecarbaldehyde (8.5 mmol, 0.95 g) and **9** (10 mmol, 1.97 g). Flash column chromatography is done using cyclohexane/ethyl acetate (4/1) as eluent. After purification, we obtain brown crystals; mp : 32°C (lit : 45-46°C); yield : 1.20 g (86%); IR(KBr) : 1685; 1612; 1443; 1154; 1130 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.53 (d, 1H, J = 7.68 Hz, C<u>H</u>O); 7.29 (d, 1H, J = 4.96 Hz, H5 ar); 7.13 (dd, 1H, J = 14.88, 11.00 Hz, Ar-CH=C<u>H</u>); 7.12 (d, 1H, J = 3.85 Hz, H3 ar); 7.07 (d, 1H, J = 14.88 Hz, Ar-C<u>H</u>); 6.98 (dd, 1H, J = 4.96, 3.85 Hz, H4 ar); 6.72 (dd, 1H, J = 15.40, 11.00 Hz, C<u>H</u>=CH-CHO); 6.16 (dd, 1H, J = 15.40, 7.68 Hz, C<u>H</u>-CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.20 (<u>C</u>HO); 151.41 (<u>C</u>H=CH-CHO); 140.86 (C2 ar); 134.55 (Ar-<u>C</u>H); 130.88 (<u>C</u>H-CHO); 129.39 (Ar-CH=<u>C</u>H); 128.00 (C5 ar); 127.67 (C3 ar); 125.33 (C4 ar). m/z (%) : 164 (M^+, 82); 135 (100); 121 (12); 110 (33); 91 (63). Anal.calcd. for C_9H_8OS : C, 65.82; H, 4.91. Found : C, 65.41; H, 4.88.

14c : Prepared from 2-pyridinecarbaldehyde (8.5 mmol, 0.91 g) and **9** (10 mmol, 1.97 g). The crude imine is hydrolyzed with a pH=4.5 buffer (CH_3CO_2H (2.4 g), CH_3CO_2Na (2.07 g), water (50 mL), Et_2O (25 mL) and THF (25 mL)), during 2 hours at 25°C. After routine aqueous-organic workup, the product has been

isolated by flash chromatography using cyclohexane/acetone (2/1) as eluent. A bright dark solid; mp : 61.5°C; yield : 1.27 g (94%); IR(KBr) : 1685; 1620; 1170; 1135; 1030 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 9.65 (d, 1H, J = 7.72 Hz, CHO); 8.63 (d, 1H, J = 4.26 Hz, H6 ar); 7.70 (td, 1H, J = 7.82, 1.85 Hz, H4 ar); 7.50 (dd, 1H, J = 15.25, 11.23 Hz, CH=CH-CHO); 7.39 (d, 1H, J = 7.82 Hz, H3 ar); 7.30 (dd, 1H, J = 15.28, 11.23 Hz, Ar-CH=CH); 7.23 (dd,1H, J = 7.82, 4.26 Hz, H5 ar); 7.05 (d, 1H, J = 15.28 Hz, Ar-CH); 6.35 (dd, 1H, J = 15.27, 7.72 Hz, CH-CHO). ^{13}C NMR (100 MHz, CDCl3) δ 193.30 (CHO); 155.00 (C2 ar); 150.65 (CH=CH-CHO); 150.01 (C6 ar); 140.73 (Ar-CH); 136.66 (C4 ar); 133.36 (CH-CHO); 129.63 (Ar-CH=CH); 123.51 (C3 & C5 ar). m/z (%) : 159 (M^+, 62); 130 (100); 117 (6); 103 (16); 81 (18); 78 (30). Anal.calcd. for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80. Found : C, 75.35; H, 5.77; N, 8.64.

14d[6] : Prepared from 3-pyridinecarbaldehyde (8.5 mmol, 0.91 g) and **9** (10 mmol, 1.97 g). The crude imine is hydrolyzed with a pH=4.5 buffer (CH_3CO_2H (2.4 g),CH_3CO_2Na (2.07 g), water (50 mL), Et_2O (25 mL) and THF (25 mL)), during 2 hours at 25°C. After routine aqueous-organic workup, the product has been isolated by flash chromatography using cyclohexane/acetone (2/1) as eluent. We obtain bright brown crystals; mp : 85-86°C; yield : 1.16 g (86%); IR(KBr) : 1685; 1636; 1178; 1130; 1034 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 9.65 (d, 1H, J = 7.58 Hz, CHO); 8.72 (s, 1H, H2 ar); 8.57 (dd, 1H, J = 4.94, 1.19 Hz, H6 ar); 7.86 (d, 1H, J = 8.02 Hz, H4 ar); 7.35 (dd, 1H, J = 7.96, 4.87 Hz, H5 ar); 7.27 (dd, 1H, J = 15.34, 10.35 Hz, CH=CH-CHO); 7.07 (dd, 1H, J =15.62, 10.35 Hz, Ar-CH=CH); 7.00 (d, 1H, J = 15.71 Hz, Ar-CH); 6.32 (dd, 1H, J = 15.26, 7.81 Hz, CH-CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.18 (CHO); 150.70 (CH=CH-CHO); 149.93 (C6 ar); 149.02 (C2 ar); 137.95 (Ar-CH); 133.31 (CH-CHO); 132.25 (C4 ar); 131.13 (C3 ar); 127.86 (Ar-CH=CH); 123.54 (C5 ar). m/z (%) : 159 (M^+, 61); 130 (100); 116 (6); 103 (21); 81 (20); 77 (30). Anal.calcd. for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80. Found : C, 75.09; H, 6.01; N, 8.18.

14e[8] : Prepared from benzaldehyde (8.5 mmol, 0.901 g) and **9** (10 mmol, 1.97 g) using the general procedure. After flash chromatography (eluent : cyclohexane/acetone : 3/1), we obtain a yellow solid; mp : 39°C; yield : 0.94 g (70%); IR(KBr) : 1690 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 9.65 (d, 1H, J = 8.00 Hz, CHO); 7.50-7.32 (m, 5H ar); 7.21 (dd, 1H, J = 16.00; 7.80 Hz, CH=CH-CHO); 6.98 (d, 1H, J = 16.10 Hz, Ar-CH); 6.96 (dd, 1H, J = 16.10, 7.80 Hz, Ar-CH=CH); 6.23 (dd, 1H, J = 16.00, 8.00 Hz, CH-CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.42 (CHO); 151.93 (CH=CH-CHO); 142.29 (Ar-CH); 135.43 (2C ar); 131.41 (CH-CHO); 129.54 (Ar-CH=CH); 128.79, 127.40 & 126.01 (3C ar). m/z (%) : 158 (M^+, 92); 129 (100); 115 (45); 105 (62); 91 (16); 77 (82). Anal.calcd. for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found : C, 83.45; H, 6.35.

14f[19] : Prepared from 4-dimethylaminobenzaldehyde (8.5 mmol, 1.38 g) and **9** (10 mmol, 1.97 g). The corresponding imine is hydrolyzed with wet silica gel (silica gel : 3 g, benzene : 3 mL, water : 0.5 mL) during 3 hours. Flash column chromatography is done using cyclohexane/ethyl acetate (4/1) as eluent. Purple crystals; mp : 137.5°C; yield : 1.59 g (93%); IR(KBr) : 1684 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.49 (d, 1H, J= 8.25 Hz, CHO); 7.33 (d, 2H, J = 9.35 Hz, H2 ar); 7.18 (dd, 1H, J = 14.85, 11.00 Hz, CH=CH-CHO); 6.87 (d, 1H, J = 15.40 Hz, Ar-CH); 6.75 (dd, 1H, J = 15.40, 11.00 Hz, Ar-CH=CH); 6.62 (d, 2H, J = 9.35 Hz, H3 ar); 6.11 (dd, 1H, J = 14.85, 8.25 Hz, CH-CHO); 2.96 (s, 6H, NMe_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.55 (CHO); 153.83 (CH=CH-CHO); 151.23 (Ar-CH); 143.55 (C ar); 129.19 (2C ar); 129.14 (C ar); 123.36 (CH-CHO); 121.33 (Ar-CH=CH); 111.76 (2C3 ar); 40.06 & 40.01 (2 Me). m/z (%) : 201 (M^+, 25); 172 (18); 157 (10); 149 (87); 148 (100). Anal.calcd. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found : C, 77.61; H, 7.50; N, 7.00.

14g[7] : Prepared from 4-methoxybenzaldehyde (8.5 mmol, 1.156 g) and **9** (10 mmol, 1.97 g). Flash column chromatography is done using cyclohexane/ethyl acetate (4/1) as eluent; yellow crystals; mp : 72-73°C; yield : 1.42 g (89%); IR(KBr) : 1685; 1620; 1588; 1516; 1323; 1251; 1178; 1106 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.53 (d, 1H, J = 8.25 Hz, CHO); 7.38 (d, 2H, J = 8.80 Hz, H2 ar); 7.18 (dd, 1H, J = 15.40, 10.45 Hz, CH=CH-CHO); 6.87 (d, 1H, 15.40 Hz, Ar-CH); 6.83 (d, 2H, J = 8.79 Hz, H3 ar); 6.81 (dd, 1H, J = 15.40, 10.45 Hz, Ar-CH=CH); 6.16 (dd, 1H, J = 15.40, 8.25 Hz, CH-CHO); 3.77 (s, 3H, OMe). ^{13}C NMR (50 MHz, $CDCl_3$) δ 193.23 (CHO); 160.90 (C4 ar) 152.38; (CH=CH-CHO); 142.13 (Ar-CH); 130.45 (CH-CHO); 129.04 (2 C2ar); 128.38 (C1 ar); 123.99 (Ar-CH=CH); 114.37 (2 C3ar); 55.25 (OMe). m/z (%) : 188 (M^+, 100); 174 (19); 159 (52); 149 (25); 144 (39); 134 (35); 129 (30); 115 (50). Anal.calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found : C, 76.55; H, 6.52.

14h[20] : A solution of TBAF (2 mL) is added dropwise to a mixture of 4-nitrobenzaldehyde (8.5 mmol, 1.28 g) and **9** (10 mmol, 1.97 g) in DMSO (4 mL). After 30 minutes of stirring, TMSCl (10 mmol, 1.5 mL) is added dropwise to the reaction mixture. Then, the resulting mixture is hydrolyzed with an aqueous solution of $ZnCl_2$ (2 g in 20 mL of water) and ether (25 mL). After stirring for 2 hours, the precipitate is filtered through a pad of Celite. The aqueous layer is extracted with ether (2 x 25 mL) and the combined organic layers are washed with water (2 x 20 mL) and the solvent removed in vacuo. The crude product is then purified by flash chromatography (eluent : cyclohexane/acetone : 2/1). We isolate a red solid ; mp : 106-107.4°C; yield : 1.26 g (73%); IR($CHCl_3$) : 2910; 2850; 1675; 1620; 1600; 1340; 1150; 1100 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.61 (d, 1H, J = 8.25 Hz, CHO); 8.18 (d, 2H, J = 8.79 Hz, H3 ar); 7.58 (d, 2H, J = 8.80 Hz, H2 ar); 7.21 (dd, 1H, J = 15.40, 10.45 Hz, CH=CH-CHO); 7.07 (dd, 1H, J = 15.40, 10.44 Hz, Ar-CH=CH); 6.98 (d, 1H, J = 15.40 Hz, Ar-CH); 6.30 (dd, 1H, J = 15.40, 8.24 Hz, CH-CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.29 (CHO); 150.24 (CH=CH-CHO); 147.55 (C1 ar); 141.61 (Ar-CH); 138.90 (C4 ar); 133.35 (2 C3ar); 130.05 (CH-CHO); 127.82 (Ar-CH=CH); 123.96 (2 C2ar). m/z (%) : 203 (M^+, 73); 173 (10); 157 (15); 149 (53); 128 (100); 115 (18). Anal.calcd. for $C_{11}H_9NO_3$: C, 64.97; H, 4.46; N, 6.89. Found : C, 62.97; H, 4.47; N, 6.91.

14i[7] : Prepared from E-cinnamaldehyde (8.5 mmol, 1.17 g) and **9** (10 mmol, 1.97 g). Flash column chromatography is done using cyclohexane/acetone (6/1) as eluent. We obtain an orange solid; mp : 113.6°C; yield : 1.44 g (92%); IR(KBr) : 1686 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 9.57 (d, 1H, J = 8.00 Hz, CHO); 7.48-7.28 (m, 5H ar); 7.15 (dd, 1H, J = 16.00, 12.00 Hz, CH=CH-CHO); 6.87 (dd, 1H, J = 15.30, 10.90 Hz, Ar-CH=CH); 6.81 (dd, 1H, J = 14.60, 10.90 Hz, Ar-CH=CH-CH); 6.79 (d, 1H, J = 15.30 Hz, Ar-CH); 6.53 (dd, 1H, J = 14.60, 12.00 Hz, CH-CH=CH-CHO); 5.80 (dd, 1H, J = 16.00, 8.00 Hz, CH-CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.53 (CHO); 151.85 (CH=CH-CHO); 142.73 (Ar-CH=CH-CH); 138.23 (Ar-CH); 136.11 (C1 ar); 130.88 (CH-CHO); 129.99 (CH-CH=CH-CHO); 128.68 (C3, C4 & C5 ar); 127.51 (Ar-CH=CH); 126.87 (C2 & C6 ar). m/z (%) : 184 (M^+, 100); 155 (89); 141 (33); 128 (50); 115 (59); 105 (34); 91 (85); 77 (70). Anal.calcd. for $C_{13}H_{12}O$: C, 84.75; H, 6.56. Found : C, 84.86; H, 6.55.

14j[2] : Prepared from sorbic aldehyde (8.5 mmol, 0.82 g) and **9** (10 mmol, 1.97 g). Flash column chromatography is done using cyclohexane/acetone (5/1) as eluent. We isolate unstable orange crystals; mp : 105.8°C; yield : 0.86 g (68%); IR(KBr) : 1680 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 9.51 (d, 1H, J = 7.50 Hz, CHO); 7.35 (dd, 1H, J = 15.00, 11.20 Hz, CH=CH-CHO); 6.84 (dd, 1H, J = 15.00, 11.20 Hz, Me-$(CH=CH)_2$-CH); 6.55 (dd, 1H, J = 15.00, 11.20 Hz, CH-CH=CH-CHO); 6.35 (dd, 1H, J = 15.00, 10.00 Hz, Me-CH=CH-CH); 6.31 (dd, 1H, J = 15.00, 11.20, Me-CH=CH-CH=CH); 6.21 (dd, 1H, J = 15.00,

10.00 Hz, Me-CH=CH); 6.14 (dd, 1H, J = 15.00, 7.50 Hz, CH-CHO); 5.95 (m, 1H, Me-CH); 1.78 (d, 3H, J = 7.50 Hz, Me). m/z (%) : 148 (M^+, 32); 133 (18); 105 (27); 91 (40); 71 (58); 57 (100); 43 (71). HRMS : calcd : 148.0888. Found : 148.0887. Anal.calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found : C, 80.99; H, 8.18.

14k[7] : The mixture of isobutyraldehyde (8.5 mmol, 0.61 g) and **9** (10 mmol, 1.97 g) in DMSO (1 mL) is added dropwise to the solution of CsF (0.15g, 10%) in DMSO (2 mL). After being stirred and heated 30 minutes at 100°C, the reaction mixture is hydrolyzed (as described in the general procedure). After flash chromatography (eluent : cyclohexane/ethyl acetate: 5/1), we obtain a light yellow oil; yield : 0.66 g (62%); IR(KBr) : 2940; 1685; 1635 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.46 (d, 1H, J = 8.25 Hz, CHO); 7.02 (dd, 1H, J = 15.39, 7.89 Hz, CH=CH-CHO); 6.21-6.18 (m, 2H, CH-CH=CH-CHO, Me_2CH-CH); 6.03 (dd, 1H, J = 15.39, 8.24 Hz, CH-CHO); 2.41 (m, 1H, Me_2CH); 1.00 (d, 6H, J = 7.15 Hz, 2 Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.85 (CHO); 153.62 (CH=CH-CHO); 153.12 (Me_2CH-CH); 130.01(CH-CHO); 125.64 (CH-CH=CH-CHO); 32.39 (Me_2CH); 21.47 (2 Me). m/z (%) : 123 (M-1, 50); 109 (24); 95 (26); 91 (63); 83 (50); 73 (41); 69 (45); 57 (80); 55 (65); 43 (94); 41 (100).

14l[21] : Prepared from trimethylacetaldehyde (8.5 mmol, 0.73 g) and **9** (10 mmol, 1.97 g). Flash column chromatography is done using cyclohexane/ethyl acetate (5/1) as eluent. We obtain a yellow oil; yield : 0.96 g (82%); IR($CHCl_3$) : 2970; 2930; 1675; 1635; 1600; 1405; 1360; 1280; 1090; 990 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.46 (d, 1H, J = 8.25 Hz, CHO); 7.03 (dd, 1H, J = 15.39, 8.80 Hz, CH=CH-CHO); 6.21-6.17 (m, 2H, Me_3C-CH, CH-CH=CH-CHO); 6.04 (dd, 1H, J = 15.40, 8.25 Hz, CH-CHO); 1.02 (s, 9H, 3 Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.91 (CHO); 157.54 (CH=CH-CHO); 153.59 (Me_3C-CH); 130.20 (CH-CHO); 123.63 (CH-CH=CH-CHO); 34.15 (Me_3C); 28.88, 28.85 & 25.74 (3 Me). m/z (%) : 138 (M^+, 12); 123 (20); 109 (9); 95 (100); 81 (16); 73 (20); 67 (30); 55 (28); 41 (33).

14m[2] : Prepared from cyclohexanone (8.5 mmol, 0.83 g) and **9** (10 mmol, 1.97 g). The purification by flash chromatography (pentane/ether : (5/1)) leads to the expected dienal as a colourless oil; yield : 0.24 g (19%); IR : 2930, 2860, 1685; 1630 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.49 (d, 1H, J = 8.25 Hz, CHO); 7.39 (dd, 1H, J = 14.85, 11.55 Hz, CH=CH-CHO); 6.03 (d, 1H, J = 11.54 Hz, CH-CH=CH-CHO); 6.02 (dd, 1H, J = 15.84, 8.25 Hz, CH-CHO); 2.40-2.34 (m, 2H, H2 cycle); 2.22-2.16 (m, 2H, H6 cycle); 1.60-1.52 (m, 6H, H3, H4 & H5 cycle). ^{13}C NMR (400 MHz, $CDCl_3$) δ 194.05 (CHO); 157.44 (Cq cycle); 147.95 (CH=CH-CHO); 129.89 (CH-CHO); 121.04 (CH-CH=CH-CHO); 37.98, 29.97, 28.49, 27.94 & 26.38 (5C cycle).

14n[8] : Prepared from benzophenone (8.5 mmol, 1.55 g) and **9** (10 mmol, 1.97 g). Flash column chromatography is done using cyclohexane/ethyl acetate (20/1) as eluent. We obtain yellow crystals; mp : 57-58°C; yield : 0.80 g (40%); IR($CHCl_3$): 2920; 2810; 1670; 1605; 1140; 1105; 1070; 1005; 970; 890 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 9.56 (d, 1H, J = 8.25 Hz, CHO); 7.55-7.54 (m, 3H ar); 7.43 (s, 4H ar); 7.35-7.33 (m, 3H ar); 7.30 (dd, 1H, J = 15.40, 11.00 Hz, CH=CH-CHO); 7.04 (d, 1H, J = 10.99 Hz, CH-CH=CH-CHO); 6.40 (dd, 1H, J = 15.39, 8.25 Hz, CH-CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.61 (CHO); 152.86 (CH=CH-CHO); 149.55 (2 C1ar); 140.63 (Ph_2C=CH); 132.30 (CH-CHO); 130.22 (2C ar); 129.09 (CH-CH=CH-CHO); 128.52, 128.32, 128.13 & 125.08 (6C ar). m/z (%) : 234 (M^+, 30); 205 (32); 141 (33); 191 (20); 182 (60); 165 (12); 157 (14); 105 (100). Anal.calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found : C, 87.58; H, 6.09.

14o : Prepared from terephthaldicarbaldehyde (8.5 mmol, 1.14 g) and **9** (20 mmol, 3.94 g). Flash column chromatography is done using cyclohexane/ethyl acetate (2/1) as eluent. We obtain the expected dienal as orange crystals ; mp : 160-162°C; yield : 1.74 g (86%); IR($CHCl_3$) : 2920; 2850; 1675; 1620; 1145; 1110; 980 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, 2H, J = 8.25 Hz, C<u>H</u>O); 6.94 (s, 4H ar); 6.49 (dd, 2H, J = 15.40, 10.45 Hz, C<u>H</u>=CH-CHO); 6.38 (dd, 2H, J = 15.40, 10.44 Hz, Ar-CH=C<u>H</u>); 6.29 (d, 2H, J = 15.41 Hz, Ar-C<u>H</u>); 5.87 (dd, 2H, J = 15.39, 8.24 Hz, C<u>H</u>-CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.49 (2 <u>C</u>HO); 151.32 (2 <u>C</u>H=CH-CHO); 141.25 (2 Ar-<u>C</u>H); 136.75 (2 C1ar); 132.10 (2 <u>C</u>H-CHO); 128.04 (4C ar); 127.13 (2 Ar-CH=<u>C</u>H). m/z (%) : 238 (M^+, 35); 214 (13); 191 (20); 167 (22); 149 (78); 131 (38); 91 (45); 69 (53); 59 (70); 41 (40); 28 (100). Anal.calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found : C, 80.82; H, 6.01.

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