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Synthesis of Cross-conjugated Dienic Alcohols

Patrick Gamez, Cécile Ariente, Jacques Goré and Bernard Cazes*

Laboratoire de Chimie Organique I, associé au CNRS, Université Claude Bernard-LYON, CPE-Lyon, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne, France.

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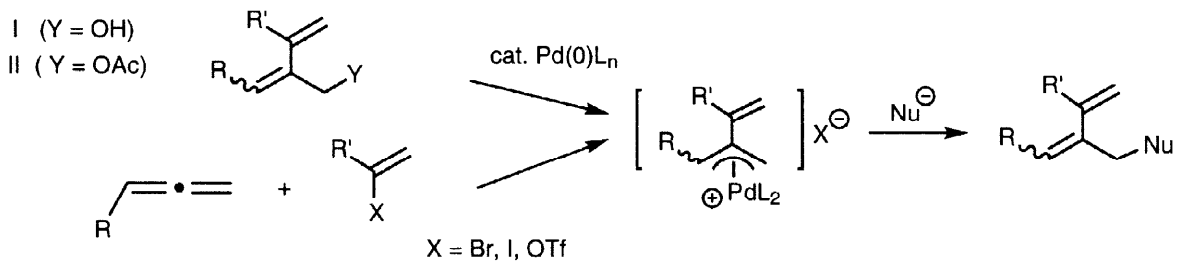
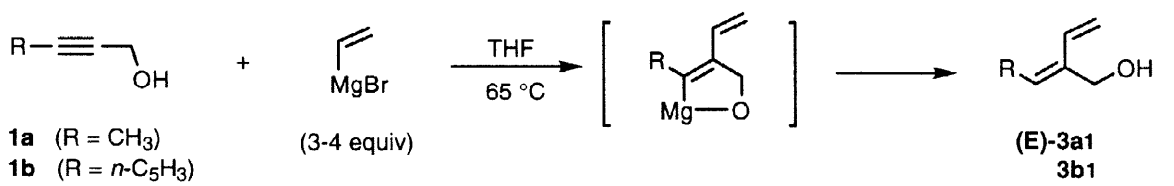
Abstract : Cross-conjugated dienols **3** were satisfactorily obtained *via* the palladium-catalyzed coupling reaction of 2-iodo-2-alken-1-ol **6** with vinyl Grignard reagents.

In connection with our ongoing studies directed to the stereoselective synthesis of functionalized dienes via the catalytic carbopalladation of allenic compounds,[1-3] we required several cross-conjugated dienic alcohols I (Y = OH) for mechanistic studies.[4] Indeed, the palladium-catalyzed substitution of dienic acetates II (Y = OAc) should involve the same π-allylpalladium intermediate as in the aforementioned carbopalladation process (scheme 1).



<scheme 1>

To the best of our knowledge, a general synthesis of these dienic alcohols I with defined E or Z stereochemistry is not available. A straightforward route to these compounds lies in the addition of vinylmetal species to metallated propargylalcohols.[5] Indeed, reports by Richey and Von Rein[6,7] described the addition of vinylmagnesium chloride to but-2-ynol **1a** in refluxing tetrahydrofurane to lead to (E)-2-vinylbut-2-en-1-ol **3a1** (scheme 2). However, this reaction turned out to be of low reproductibility as we could not obtain this alcohol (E)-**3a1** with a yield higher than 19 %.[8]



1a (R = CH_3)
1b (R = *n*-C_5H_3)

(E)-3a1
3b1

<scheme 2>

* Fax : +33 (0)4.72.43.12.14 E-mail : cazes@univ-lyon1.fr

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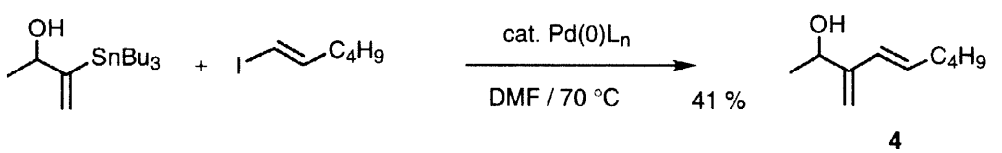
Furthermore it did not seem to be of general applicability with more hindered propargyl alcohols or vinyl halides. For example, reaction of vinylmagnesium bromide with oct-2-yn-1-ol **1b** did not give alcohol **3b1**. We report herein on an alternative route to the desired dienols **3** through the palladium-catalyzed cross-coupling of vinylmetals with 2-iodo-2-alken-1-ol **6**.

Palladium-catalyzed coupling of vinylmetals with 2-iodo-2-alken-1-ols.

We envisioned that the preparation of cross-conjugated dienic alcohols **3** could be provided by the palladium-catalyzed cross-coupling of hydroxy vinylstannanes with electrophiles as described by Stille's group[9,10]. This coupling reaction has been widely used for the synthesis of linear dienic systems[11] ; in particular, linear dienic alcohols have been obtained from 3-(tributylstannyl)allyl alcohols.[12] To our knowledge, there is only one report on the use of a 2-stannyl-2-alkenol in such coupling reaction : the coupling of 3-tributylstannylbut-3-en-2-ol with a terminal vinyliodide, (E)-1-iodohex-1-ene, afforded the dienic alcohol **4** with a 41 % yield[13] (scheme 3).



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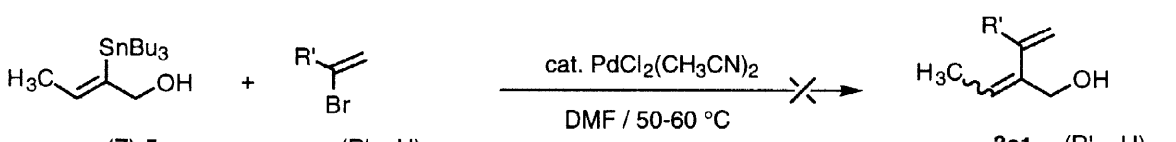
<scheme 3>

In our hands, several attempts in coupling 2-tributylstannylbut-2-en-1-ol **5a** with vinylbromide and 2-bromopropene in DMF met little success and only trace amounts of dienic alcohol **3a1** were obtained in the reaction of the less bulky vinylbromide (scheme 4).



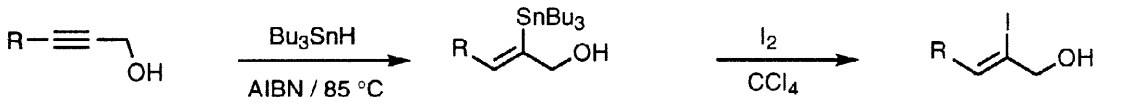
(Z)-**5a** **2** (R' = H) (R' = CH_3)

3a1 (R' = H) **3a2** (R' = CH_3)

<scheme 4>

This lack of reactivity might be ascribed to the steric hindrance of the two sp^2 carbon centers and led us to look to the coupling reaction of vinyl iodides **6** with vinyl Grignard reagents[14] (scheme 6 and 7).

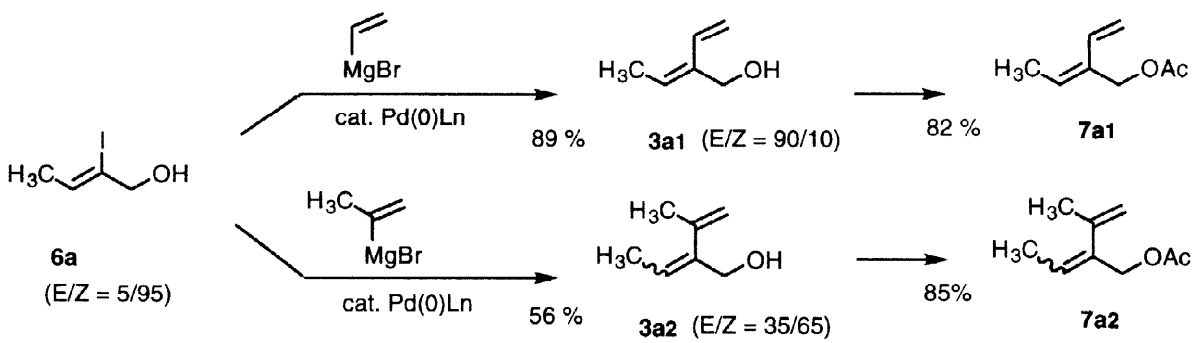
2-Stannyl allyl alcohols **5** were obtained as described by Ensley *et al*[15] by the *trans*-addition of tributyltin hydride to propargyl alcohols **1** in the presence of AIBN. The stereoselectivity favoring the (Z)-**5** stereoisomers was higher than 95 %. Clean iododestannylation of these vinylstannanes **5** with iodine gave the corresponding 2-iodo-2-alkyn-1-ols **6** with practically no change of the E/Z ratio[15] (scheme 5).



1a (R = CH_3) 71 % **5a** (E/Z = 5/95) 95 % **6a** (E/Z = 5/95)
1b (R = *n*-C_5H_9) 75 % (Z)-**5b** 77 % **6b** (E/Z = 3/97)

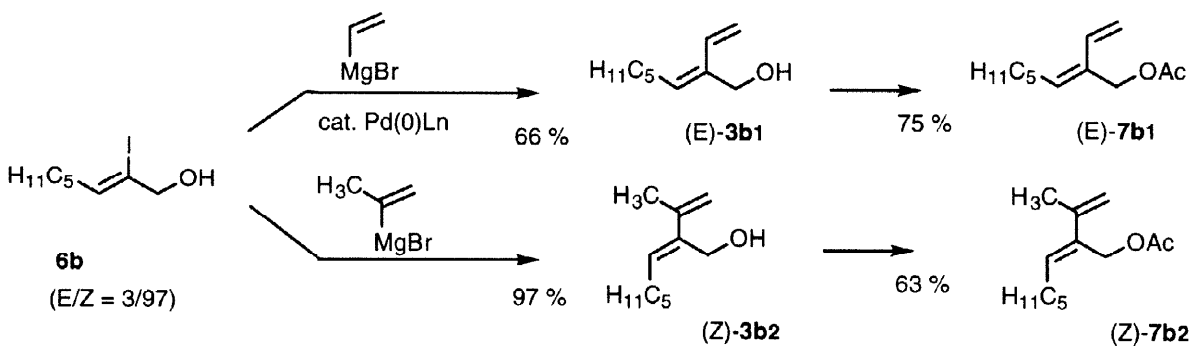
<scheme 5>

The cross-coupling reaction of these iodoalcohols **6** were then carried out in tetrahydrofurane by adding 2.5 equivalents of the vinyl Grignard reagents in the presence of the $Pd(dba)_2$-PPh_3 catalytic system (5 % molar). The reaction of iodoalcohol **6a** (E/Z = 5/95) with vinylmagnesium bromide gave dienol **3a1** with a 89 % yield and practically no change of the configuration of the trisubstituted double bond (**3a1**, E/Z = 90/10). On the contrary, the reaction with isopropenylmagnesium bromide led to an important change of this stereochemistry (**3a2**, E/Z = 35/65) (scheme 6).



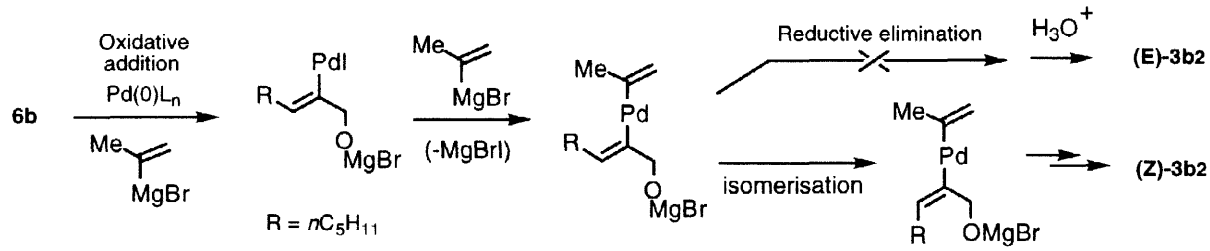
<scheme 6>

Similar results were obtained for iodoalcohol **6b** (E/Z = 3/97) (scheme 7). Reaction with vinylmagnesium bromide gave pure (E)-**3b1** (yield 66 %), while the reaction with isopropenylmagnesium bromide led to a complete inversion of configuration of the trisubstituted double bond.



<scheme 7>

Thus the cross-coupling of iodoalcohols **6a** and **6b** with vinylmagnesium bromide occured with a nearly total retention of configuration as previously observed with terminal alkenylmagnesium halides.[14] In the case of a more bulky alkenyl metal such as isopropenylmagnesium bromide, the stereochemistry is altered and depends on the steric hindrance around the new σ C(sp^2)-C(sp^2) bond (synthesis of **3a2** and **3b2**). The complete configuration change of the double bond derived from iodoalcohol **6b** could be explained by a fast isomerisation of the double bond before reductive elimination to dienol (Z)-**3b2**, rather than by an acid-catalyzed isomerisation of the dienol (scheme 8).



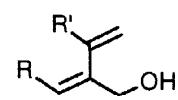
<scheme 8>

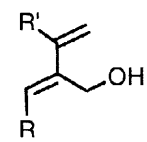
Finally, classical DMAP-catalyzed acetylation[16] of dienic alcohols **3a,b** afforded the corresponding acetates **7a,b** (60-85 %).

Stereochemical assignement of dienols 3a,b.

The stereochemistry of cross-conjugated dienols **3a,b** was assigned by comparaison of the chemical shift in ^{13}C NMR spectroscopy of the carbon of their $\underline{C}H_2$-OH group : this allylic carbon atom was upshielded (51-66 ppm) in the (Z)-**3** stereoisomers [64-71 ppm for the (E)-**3** stereoisomers] because of a positive cis γ-effect from the allylic carbon atom of the R group[3a] (Table 1).

Table 1 Chemical shift in ^{13}C NMR of $\underline{C}H_2$-OH group

(E)-**3** 

(Z)-**3** 

			δ_E	δ_Z
3a1	R = CH_3	R' = H	64.6 ppm	58.2 ppm
3a2		R' = CH_3	71.6 -	66.3 -
3b1	R = C_5H_{11}	R' = H	64.6 -	51.3 -
3b2		R' = CH_3	–	66.3 -

In summary, we have shown that cross-conjugated dienols **3** are easily obtained *via* the palladium-catalyzed coupling reaction of 2-iodo-2-alkenols **6** with vinyl Grignard reagents. This cross-coupling reaction occured with total retention of configuration with vinylmagnesium bromide while the use of a substituted vinyl metal such as isopropenylmagnesium bromide led to partial to complete inversion of the configuration of the double-bond of the starting iodoalcohol.

EXPERIMENTAL SECTION

General remarks. All reactions were conducted in oven-dried glassware under nitrogen. Tetrahydrofuran was distilled under nitrogen from sodium-benzophenone ketyl. Dimethylsulfoxide, dimethylformamide and triethylamine were distilled from calcium hydride. Analytical TLC analyses were performed on Merck precoated Kieselgel 60-F_{254} (aluminum-backed sheets) with visualisation by UV light and/or anisaldehyde dip. Flash chromatography using Merck silica gel 60 (230-400 mesh) refers to the procedure of Still *et al.*[17] Capillary GLC analyses were performed on a Varian 3300 gas-chromatograph (column DB1 or DB5, 25m) equipped with a flame ionization detector. IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer. ^{1}H NMR spectra were measured at 200 MHz on a Bruker AC 200 spectrometer. Data, reported using the residual solvent proton resonance of $CDCl_3$ (δ_H = 7.25 ppm) as the internal reference, are as follows in the order : chemical shift (δ in ppm relative to TMS), multiplicity (s, d, t, q, m, br for singulet, doublet, triplet, quartet, multiplet, broad), coupling constants (*J*, in Hz), number of protons.^{13}C NMR were measured at 50 MHz on the same instrument, using $CDCl_3$ solvent peak at δ_C = 77.0 ppm as the reference. Mass Spectra (m/z, relative intensity) were obtained (electron impact mode, at 70 eV) with a Nermag R10-10S quadrupole mass spectrometer coupled with a Delsi-DI 700 gas chromatograph fitted with a OV1 capillary column (25m x 0.32 mm i.d). Microanalyses were performed by the "Service Central d'Analyse" of the CNRS in Vernaison.

Materials. But-2-yn-1-ol **1a** was prepared by a literature method[18]. Oct-2-yn-1-ol **1b** was purchased from Lancaster. 2-Tributylstannyl-2-alkenols **5a** (E/Z = 5/95), (Z)-**5b** and (Z)-2-iodooct-2-en-1-ol **6b** were prepared as described by Ensley *et al*[15]. Vinylmagnesium bromide (1M in tetrahydrofurane) was commercial from Aldrich. Isopropenylmagnesium bromide[19] was prepared in THF according to a literature procedure as well as bis(dibenzylidene)palladium[20] and tetrakis(triphenylphosphine)palladium[21].

Addition of vinylmagnesium bromide to but-2-yn-1-ol 1a.

To a stirred suspension of but-2-yn-1-ol **1a** (280 mg, 4 mmol, 1 eq) in THF (20 mL) at 0 °C under nitrogen a 1 M THF solution of vinylmagnesium bromide (16 mL, 16 mmol, 4 eq) was added dropwise with a syringe. The reaction mixture was stirred at 65 °C for 18 h. After cooling, hydrolysis with saturated NH_4Cl, extraction with ether (3 x 100 mL), washing and drying over $MgSO_4$, evaporation of solvents gave a crude oil (480 mg). Purification by flash chromatography (140 g SiO_2, 50:50 PE/Et_2O) gave dienol (E)-**3a1** (76 mg, 19 %).

(E)-2-Ethenylbut-2-en-1-ol 3a1.

TLC analysis (SiO_2 , 60:40 PE/EtOAc) Rf = 0.37.

IR (film) = 3350, 3080, 3020, 1650, 1600, 970, 910, 835 cm^{-1}

^{1}H NMR (200 MHz, $CDCl_3$) δ 6.67 (dd, *J* = 11.1 Hz and *J* = 17.7 Hz, 1H, C<u>H</u>=CH_2), 5.75 (q, *J* = 7.1 Hz, 1H, CH_3-C<u>H</u>=C), 5.36 (d, *J* = 17.7 Hz, 1H, HC=C<u>H</u>H), 5.19 (d, *J* = 11.1 Hz, 1H, CH=C<u>H</u>H), 4.28 (s, 2H, C<u>H$_2$</u>-OH), 1.78 (d, *J* = 7.1 Hz, 3H, C<u>H$_3$</u>-CH=C), 1.42 (s, 1H, OH).

^{13}C NMR (50 MHz, $CDCl_3$) δ 136.6 (vinyl C_2), 130.9 (vinyl C_3), 126.6 (<u>C</u>H=CH_2), 114.1 (CH=<u>C</u>H_2), 64.6 (C_1, <u>C</u>H_2-OH), 13.0 (C_4, <u>C</u>H_3-CH=C).

MS (m/z, %) : 98 ($M^{+\bullet}$, 17), 80 (16), 79 (21), 69 (18), 55 (37), 53 (20), 43 (47), 41 (100), 39 (62), 29 (29), 27 (36).

Anal. Calcd for $C_6H_{10}O$: C, 73.43 ; H, 10.27. Found : C, 73.22 ; H, 9.95.

Cross-coupling reactions of vinylmagnesium bromides with iodoalcohols 6a,b.

2-Iodobut-2-en-1-ol 6a.

According to Ensley *et al*[15], iodine (10.15 g, 40 mmol) was added at 0 °C to a solution of stannyl alcohol **5a**[17] (E/Z = 5/95) (6 g, 17 mmol) in CCl_4 (100 mL) ; the mixture was stirred for 10 min at 0 °C. Decolorization occured on treatment with an excess of 10 % aqueous sodium bisulfite $Na_2S_2O_3$ solution. Extraction with ether (4 x 25 mL), drying with Na_2SO_4 and evaporation of solvents gave a crude oil which was filtered through a short column of silica gel (50:50 PE/EtOAc) to give 3.22 g (95 %) of iodoalcohol **6a** (E/Z = 5/95).

TLC analysis (SiO_2 ; 90:10 PE/EtOAc) $Rf = 0.11$.

Major isomer (Z)-**6a** : ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.98 (q, J = 6.5 Hz, 1H, CH_3-C<u>H</u>=C), 4.26 (d, J = 6 Hz, 2H, C<u>H</u>$_2$OH), 2.12 (t, J = 6 Hz, 1H, OH), 1.8 (d, J = 6.5 Hz, 3H, C<u>H</u>$_3$-CH=C). ^{13}C NMR (50 MHz, $CDCl_3$) δ 131.1 (C_2), 109.5 (C_3), 71.4 (C_1), 21.4 (C_4).

Minor isomer (E)-**6a** : ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.78 (q, J = 6.5 Hz, 1H), 4.2 (s, 2H), 2 (s, 1H), 1.74 (d, J = 6.5 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 134.1 (C_2), 101.9 (C_3), 67.3 (C_1), 13.6 (C_4).

2-Ethenylbut-2-en-1-ol 3a1.

A solution of iodoalcohol **6a** (E/Z = 5/95) (2.9 g, 14.6 mmol), $Pd(dba)_2$ (403 mg, 0.7 mmol), triphenylphosphine (367 mg, 1.4 mmol) in dry THF (10 mL) was prepared under a nitrogen gas atmosphere and cooled at 0 °C. To this solution, a 1 M THF solution of vinylmagnesium bromide (36.6 mL, 36.6 mmol, 2.5 eq) was added with a syringe. The reaction mixture was stirred at 0 °C for 3 h, and then hydrolyzed with saturated NH_4Cl. Extraction with ether, washing with water followed by drying over $MgSO_4$ and evaporation of solvents gave a crude oil (1.7 g ; GLC analysis : alcohol **3a1**, E/Z = 90/10). Purification through flash chromatography (240 g SiO_2 ; 90:10 to 50:50 PE/EtOAc) gave 1.18 g (83 %) of the two unseparable (E) and (Z)-stereoisomers **3a1**

Minor stereoisomer (Z)-**3a1**:

^{1}H NMR (200 MHz, $CDCl_3$) : a distinctive signal from (E)-**3a1** stereoisomer arises from the vinylic proton (CH_3-C<u>H</u>=C) at 5.97 ppm (q, J = 6.9 Hz, 1H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 132.9 (CH=<u>C</u>-CH_2OH), 130.9 (CH_3-<u>C</u>H=C), 128.8 (<u>C</u>H=CH_2), 115.5 (CH=<u>C</u>H_2), 58.2 (<u>C</u>H_2-OH), 19.7 (<u>C</u>H_3).

2-(Propen-2'-yl)but-2-en-1-ol 3a2.

To a solution of iodo alcohol **6a** (E/Z = 5/95) (220 mg, 1.10 mmol), $Pd(dba)_2$ (31 mg, 0.05 mmol), PPh_3 (27.8 mg, 0.11 mmol) in THF (5 mL) at 0 °C, a 0.83 M THF solution of isopropenylmagnesium bromide (3.4 mL, 2.78 mmol, 2.5 eq) was added with a syringe. The mixture was stirred at room temperature during 3 h, hydrolyzed and extracted as above. Purification through flash chromatograhy (45 g SiO_2 ; 90:10 to 70:30 PE/EtOAc) gave 70 mg (56 %) of a mixture of the two (E) and (Z)-stereoisomers **3a2** (GLC analysis : E/Z = 35/65).

TLC analysis (SiO_2, 50:50 Et_2O/EtOAc) $Rf = 0.66$.

Major isomer **(Z)-3a2** : ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.8 (C=<u>C</u>-C=C), 141.9 (CH_3-<u>C</u>=C), 122.1 (CH_3-<u>C</u>H=C), 115.4 (C=<u>C</u>H_2), 66.3 (<u>C</u>H_2-OH), 22.2 (<u>C</u>H_3-C=C), 14.2 (<u>C</u>H_3-CH=C).

Pure minor isomer **(E)-3a2** could be obtained after a second flash-chromatography :
TLC analysis (SiO_2, 50:50 Et_2O/EtOAc) Rf = 0.64.
IR (film) : 3330, 3080, 1630, 900, 835 cm^{-1}
^1H NMR (200 MHz, $CDCl_3$) δ 5.53 (q, J = 6.8 Hz, 1H, CH_3-C<u>H</u>=C), 5.11 (s, 1H, C=C<u>H</u>H), 4.78 (s, 1H, C=CH<u>H</u>), 4.09 (s, 2H, C<u>H</u>$_2$-OH), 1.85 (s, 3H, C<u>H</u>$_3$-C=CH_2), 1.68 (d, J = 6.8 Hz, 3H, C<u>H</u>$_3$-CH=C).
^{13}C NMR (50 MHz, $CDCl_3$) δ 142.8 (C=<u>C</u>-C=C), 141.9 (CH_3-<u>C</u>=C), 131.1 (CH_3-<u>C</u>H=C), 109.8 (C=<u>C</u>H_2), 71.6 (<u>C</u>H_2-OH), 22.4 (<u>C</u>H_3-C=C), 21.6 (<u>C</u>H_3-CH=C).
MS (m/z, %) : 112 ($M^{+\bullet}$, 15), 94 (34), 79 (100), 77(20), 67 (12), 55 (27), 53 (12), 43 (19).
Anal. Calcd for $C_7H_{12}O$: C, 73.33 ; H, 10.38. Found : C, 73.15 ; H, 10.59.

(E)-2-Ethenyloct-2-en-1-ol 3b1.
To a solution of catalyst $Pd(PPh_3)_4$ (391.2 mg, 0.34 mmol, 5 % molar) and iodoalcohol **6b** (1.72 g, 6.8 mmol) in THF (15 mL) at 0 °C under nitrogen, a 1 M solution of vinylmagnesium bromide (20.3 mL, 20.3 mmol, 3 eq) was added slowly. The reaction mixture was stirred at room temperature for 24 h. Workup included hydrolysis with saturated aqueous NH_4Cl, extraction with ether (3 x 50 mL), washing with brine and drying over $MgSO_4$. After removal of solvents, flash chromatography (90:10 CH_2Cl_2/EtOAc) gave 680 mg (66 %) of pure alcohol (E)-**3b1**.
TLC analysis (SiO_2 , 90:10 PE/EtOAc) Rf = 0.62
IR (film) : 3300, 3080, 2950, 2850, 1645, 1595, 1455, 1365, 990,955, 850 cm^{-1}.
^1H NMR (200 MHz, $CDCl_3$) δ 6.64 (dd, J_{cis} = 11.2 Hz and J_{trans} = 17.7 Hz, 1H, C<u>H</u>=CH_2), 5.66 (t, J = 7.4 Hz, 1H, CH_2-C<u>H</u>=C), 5.34 (d, J_{trans} = 17.7 Hz, 1H, CH=CH<u>H</u>), 5.16 (d, J_{cis} = 11.2 Hz, 1H, CH=CH<u>H</u>), 4.28 (s, 2H, C<u>H</u>$_2$-OH), 2.21 (m, 2H, C<u>H</u>$_2$-CH=C), 1.65 (s, 1H, O<u>H</u>), 1.15-1.40 (m, 6H, (C<u>H</u>$_2$)$_3$), 0.88 (t, J = 6.4 Hz, 3H, C<u>H</u>$_3$).
^{13}C NMR (50 MHz, $CDCl_3$) δ 135.7 (CH=<u>C</u>-CH_2OH), 131.3 (<u>C</u>H=CH_2), 132.8 (CH_2-<u>C</u>H=C), 114.1 (C=<u>C</u>H_2), 64.6 (<u>C</u>H_2-OH), 31.5 (<u>C</u>H_2), 29.2 (<u>C</u>H_2), 27.3 (<u>C</u>H_2-CH=C), 22.5 (<u>C</u>H_2), 14.0 (<u>C</u>H_3).
Anal. Calcd for $C_6H_{10}O$: C, 77.87 ; H, 11.76. Found : C, 77.45 ; H, 11.50.

(Z)-2-(Propen-2'-yl)oct-2-en-1-ol 3b2.
To a solution iodoalcohol **6b** (E/Z = 3 / 97) (2.5 g, 9.84 mmol) and complex $Pd(PPh_3)_4$ (568.5 mg, 0.49 mmol, 5 %) in THF (15 mL) at 0 °C, a 1.05 M THF solution of isopropenylmagnesium bromide (23.4 mL, 24.6 mmol, 2.5 eq) was added with a syringe. After stirring at room temperature for 3 h, similar workup gave a crude oil. Purification by short column chromatography gave dienol (Z)-**3b2** (1.61 g, 97 %).
TLC analysis (SiO_2, 90:10 PE/EtOAc) Rf = 0.20.
IR (film) : 3320, 3080, 2950, 2920, 2850, 1615, 1460, 1360, 960, 895 cm^{-1}
^1H NMR (200 MHz, $CDCl_3$) δ 5.43 (t, J = 7.4 Hz, 1H, CH_2-C<u>H</u>=C), 5.07 (q, J = 0.7 Hz, 1H, C=C<u>H</u>H), 4.76 (s, 1H, C=CH<u>H</u>) ; 4.10 (s, 2H, C<u>H</u>$_2$OH), 2.10 (dt, J = 7.4 and 6.8 Hz, 2H, C<u>H</u>$_2$-CH=C), 1.84 (d, J = 0.7 Hz, C<u>H</u>$_3$-C=C), 1.62 (s, 1H, OH), 1.1-1.5 (m, 6H, (C<u>H</u>$_2$)$_3$), 0.88 (d, J = 6.8 Hz, 3H, CH_3).
^{13}C NMR (50 MHz, $CDCl_3$) δ 142.2 (-<u>C</u>=C), 141.9 (-<u>C</u>=C), 128.0 (CH_2-<u>C</u>H=C), 115.2 (C=<u>C</u>H_2), 66.3 (<u>C</u>H_2-OH), 31.5 (<u>C</u>H_2), 29.6 (<u>C</u>H_2), 28.5 (<u>C</u>H_2-CH=C), 22.6 (<u>C</u>H_2), 22.5 (<u>C</u>H_3-C=C), 14.0 (<u>C</u>H_3).
MS (m/z,%) = 168 ($M^{+\bullet}$), 107 (44), 93 (100), 81 (44), 79 (78), 77 (46), 69 (67), 67 (57), 55 (83), 41 (69).
Anal. Calcd for $C_{11}H_{20}O$: C, 78.51 ; H, 11.98. Found : C, 78.10 ; H, 11.50.

Dienic acetates 7.

(E+Z)-2-Ethenylbut-2-enyl acetate 7a1.

To a solution of dienic alcohol **3a1** (E/Z= 90/10) (1.3 g, 13.2 mmol) pyridine (79 mg, 0.65 mmol), and DMAP[16] (79 mg, 13.2 mmol) in CH_2Cl_2 (30 mL) at 0 °C, acetic anhydride (5.5 mL, 58 mmol) was added slowly. The reaction mixture was stirred at room temperature for 6 h and then hydrolyzed with ice-water. After extraction with ether (2 x 50 mL), successive washings with 2 N HCl solution, saturated aqueous $NaHSO_4$. After evaporation of solvents, purification by chromatography on silica gel (PE) afforded 1.52 g (82 %) of acetate **7a1** (GLC analysis : ratio E/Z = 90/10).

TLC analysis (SiO_2, 50:50 Et_2O/EtOAc) Rf = 0.71.

IR (E+Z) : 3080, 3020, 1740, 1650, 1600, 1230, 990, 910 cm^{-1}

^1H NMR (200 MHz, $CDCl_3$) δ :

(E)-**7a1** (major isomer) δ 6.68 (dd, J_{cis} = 11 Hz and J_{trans} = 18 Hz, 1H, C<u>H</u>=CH_2), 5.80 (q, J = 7.1 Hz, 1H, CH_3-C<u>H</u>=C), 5.28 (d, J_{trans} = 18 Hz, 1H, C=C<u>H</u>$_{trans}$), 5.19 (d, J_{cis} = 11 Hz, 1H, C=C<u>H</u>$_{cis}$), 4.71 (s, 2H, C<u>H</u>$_2$-OAc), 2.08 (s, 3H, CO-C<u>H</u>$_3$), 1.81 (d, J = 6.9 Hz, 3H, C<u>H</u>$_3$-CH=C).

(Z)-**7a1** (minor isomer) δ 6.68 (dd, J_{cis} = 11 Hz and J_{trans} = 18 Hz, 1H, C<u>H</u>=CH_2), 6.03 (q, J = 6.4 Hz, 1H, CH_3-C<u>H</u>=C), 5.28 (d, J_{trans} = 18 Hz, 1H, C=C<u>H</u>$_{trans}$), 5.19 (d, J_{cis} = 11 Hz, 1H, C=C<u>H</u>$_{cis}$), 4.78 (s, 2H, C<u>H</u>$_2$-OAc), 2.12 (s, 3H, CO-C<u>H</u>$_3$), 1.81 (d, J = 6.9 Hz, 3H, C<u>H</u>$_3$-CH=C).

MS (m/z, %) : 140 ($M^{+\cdot}$, 15), 98 (9), 83 (10), 81 (12), 80 (82), 79 (100),77 (12), 55 (12), 53 (26), 43 (81).

(E)-2-(Propen-2'-yl)but-2-enyl acetate 7a2.

The same procedure[16] as above was used from alcohol (E)-**3a2** (170 mg, 1.52 mmol), pyridine (918 mg, 11.6 mmol), DMAP (9.2 mg, 0.075 mmol) and acetic anhydride (676 mg, 6.63 mmol) in CH_2Cl_2 (10 mL) at 0 °C. Short silica gel column chromatography gave 202 mg (85 %) of acetate (E)-**7a2**.

TLC analysis (SiO_2, 90:10 PE/EtOAc) Rf = 0.48.

IR (film) : 3030, 2920, 1740, 1650, 1450, 1230, 1025, 890 cm^{-1}

^1H NMR (200 MHz, $CDCl_3$) δ 5.62 (q, J = 6.8 Hz, H_3C-C<u>H</u>=C), 5.80 (s, 1H, C=C<u>H</u>H) ; 4.77 (s, 1H, C=CH<u>H</u>), 4.57 (s, 2H, C<u>H</u>$_2$-OAc), 2.06 (s, 3H, CO-C<u>H</u>$_3$), 1.71 (s, 3H, C<u>H</u>$_3$-C=CH_2), 1.70 (d, J = 6.7 Hz, 3H, C<u>H</u>$_3$-CH=C).

MS (m/z, %) : 154 ($M^{+\cdot}$, <1), 139 (1), 112 (6), 94 ([M-AcOH]$^{+\cdot}$, 34), 79 (100), 77 (20), 67 (12), 55 (27), 53 (12), 43 (19).

(E)-2-Ethenyloct-2-enyl acetate 7b1.

Esterification was carried out via the same procedure from alcohol (E)-**3b1** (650 mg, 4.24 mmol), pyridine (2.51 g, 31.8 mmol), DMAP (26 mg, 0.21 mmol) and acetic anhydride (1.95 g, 19.08 mmol) in CH_2Cl_2 (15 mL). Purification by silica gel (PE to 90:10 PE/EtOAc) gave 625 mg (75 %) of pure acetate (E)-**7b1**.

TLC analysis (SiO_2, 90:10 PE/EtOAc) Rf = 0.51.

IR (film) : 3080, 3010, 2950, 2850, 1745, 1645, 1595, 1455, 1365, 1220, 1020, 990, 955, 905, 855 cm^{-1}

^1H NMR (200 MHz, $CDCl_3$) δ 6.64 (dd, J = 11.2 and 17.7 Hz, 1H, C<u>H</u>=CH_2), 5.70 (t, J = 7.5 Hz, 1H, CH_2-C<u>H</u>=C), 5.25 (d, J = 11.2 Hz, 1H, CH=C<u>H</u>H), 5.15 (d, J = 17.7 Hz, 1H, CH=CH<u>H</u>), 4.70 (s, 2H,

$C\underline{H}_2$-O), 2.20 (q, J = 7.2 Hz, 2H, $C\underline{H}_2$-CH=C), 2.07 (s, 3H, CO-$C\underline{H}_3$), 1.30 (m, 6H, $(CH_2)_3$), 0.89 (t, J = 6.6 Hz, 3H, $C\underline{H}_3$).

^{13}C NMR (50 MHz, $CDCl_3$) δ 171.0 (C=O), 136.0 (CH_2-$\underline{C}$H=C), 131.3 (C=$\underline{C}$-C=C), 131.0 ($\underline{C}$H=CH_2), 114.5 (CH=$\underline{C}H_2$), 66.1 ($\underline{C}H_2$-OAc), 31.5 ($\underline{C}H_2$), 29.0 ($\underline{C}H_2$), 27.5 ($\underline{C}H_2$-CH=C), 22.5 ($\underline{C}H_2$), 21.1 ($\underline{C}H_3$-CO).

MS (m/z, %) : 196 ($M^{+\cdot}$, < 1), 136 ([M-AcOH]$^{+\cdot}$, 4), 94 (27), 93 (27), 80 (31), 79 (100), 67 (12), 55 (12), 43 (83).

(Z)-2-(Propen-2'-yl)oct-2-enyl acetate 7b2.

Same procedure from alcohol (Z)-**3b2** (1.61 g, 9.6 mmol), triethylamine (7.26 g, 72 mmol), DMAP (58.5 mg, 0.48 mmol) and acetic anhydride (4.4 g, 43 mmol) in CH_2Cl_2 (30 mL). Purification by silica gel (65 g) chromatography (PE to 95:5 PE/EtOAc) gave 1.1 g (63 %) of acetate (Z)-**7b2**.

TLC analysis (SiO_2, 90:10 PE/EtOAc) Rf = 0.48.

IR (film) : 3080, 2950, 2920, 2850, 1745, 1615, 1460, 1360, 1220, 1020, 960, 895 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$) δ 5.50 (t, J = 7.4 Hz, 1H, CH_2-C$\underline{H}$=C), 5.03 (s, 1H, C=C$\underline{H}$H), 4.75 (s, C=C$\underline{H}$H), 4.56 (s, 2H, $C\underline{H}_2$-OAc), 2.09 (dt, J = 6.5 and 7.2 Hz, 2H, $C\underline{H}_2$-CH=C), 2.04 (s, CO-$C\underline{H}_3$), 1.82 (s, 3H, $C\underline{H}_3$-C=C), 1.35 (m, 6H, $(C\underline{H}_2)_3$), 0.88 (t, J = 6.4 Hz, 3H, $C\underline{H}_3$).

^{13}C NMR (50 MHz, $CDCl_3$) δ 170.8 (C=O), 141.7 (CH_3-$\underline{C}$=C), 137.3 (C=$\underline{C}$-CH_2-OAc), 131.3 (CH_2-$\underline{C}$H=C), 115.2 (C=$\underline{C}H_2$), 67.8 ($\underline{C}H_2$-OAc), 31.5 ($\underline{C}H_2$), 29.5 ($\underline{C}H_2$), 28.7 ($\underline{C}H_2$-CH=C), 22.6 ($\underline{C}H_2$), 22.4 ($\underline{C}H_3$-C=C), 21.0 ($\underline{C}H_3$-CO), 14.0 ($\underline{C}H_3$).

MS (m/z, %) : 210 ($M^{+\cdot}$, < 1), 150 ([M-AcOH]$^{+\cdot}$, 3), 107 (13), 93 (100), 79 (34), 77 (22), 67 (9), 55 (14), 43 (72), 41 (23).

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