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MICROWAVE ASSISTED PERICYCLIC REACTIONS IN CASCADE TO CONSTRUCT DECALIN FRAMEWORKS POSSESSING QUATERNARY CENTERS. SCOPE AND LIMITATIONS†

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Abstract – The synthesis of decalin skeletons possessing quaternary carbon centers at C9 using the tandem oxy-Cope/ene/Claisen is described. The degree of substitution at the terminal olefin plays an important role in determining the pathway of the reaction. In the case of 1,2-divinylcyclohexanol having a 1,2-disubstituted allyl ether, the corresponding decalin skeletons were obtained in good yields. In the case of trisubstituted allyl ethers, decalin products resulting from a radical 1,3-shift were isolated. The microwave irradiation of 1,2-divinylcyclohexanol propargyl ethers produced tetracyclic acetal sesquiterpenes *via* an oxy-Cope/ene/Claisen/5-exo *dig* cyclization reaction in high diastereoselectivity. The scope and limitation of the method is described.

† This paper is dedicated to Professor Leo A. Paquette in occasion of his 70th birthday

INTRODUCTION

The asymmetric construction of quaternary carbons centers is a remarkable challenge. The need to prepare such C-C bonds has stimulated the development of several methods which have been recently reviewed.[1] We have reported a highly diastereoselective domino pericyclic reaction[2] to construct decalin skeletons possessing quaternary carbon centers (Figure 1).[3] This transformation is a result of series a sequence of events which start from an oxy-Cope rearrangement of the 1,2-cyclohexanols (**1**) producing the corresponding ketone (**2**).

The following stereoselective transannular ene reaction of (**2**) gives exclusively *E* enol ether (**3**) which then rearranges to the desired lactol decalin (**4**) in good yields. In most cases, this tandem reaction proved to be highly diastereoselective. Furthermore, we were able to synthesize a decalin core bearing two consecutive

quaternary carbon centers at C9 and C11 (R_1 = H, R_2 and R_3 = Me) in 76%. However, lactol (**6**) was isolated in 75% yield when the allyl ether (**5**) was employed (Scheme 1). We also observed isomerization

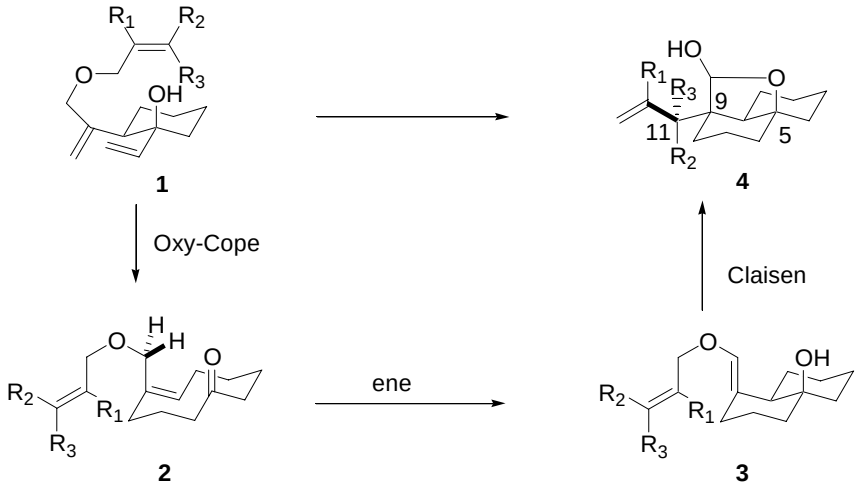
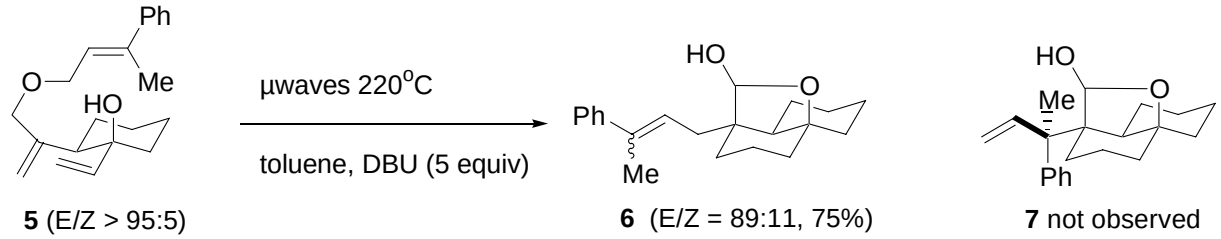


Figure 1. Tandem oxy-Cope/ene/Claisen reaction

of the trisubstituted double bond during the course of the reaction. These results suggest an alternate 1,3 shift is competing with the Claisen rearrangement. Herein, we report the scope and limitations of the tandem oxy-Cope/ene/Claisen process.



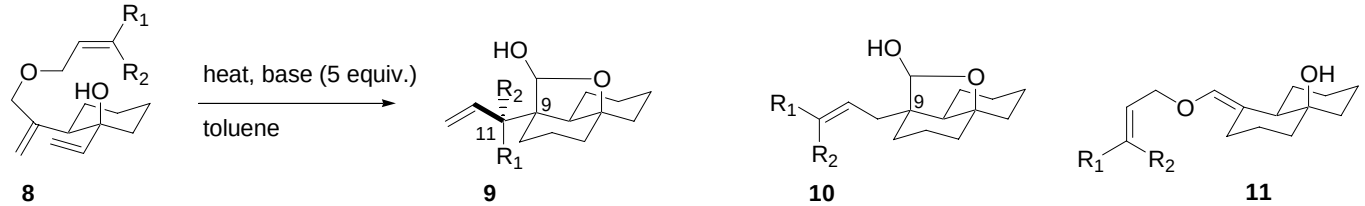
5 (E/Z > 95:5) **6** (E/Z = 89:11, 75%) **7** not observed

Scheme 1

RESULTS AND DISCUSSION

The 1,2-divinyclohexanols (**8a-h**), readily prepared from commercially available cyclohexene oxide,[3] were dissolved in toluene (0.01-0.02 M) in presence of 5 equivalents of base. The solution was carefully degassed and irradiated with microwaves in a quartz cell at 210°C for 1 h (method A)[4,5] or heated at 210°C in a sealed tube immersed in a wax bath for 18-24 h (method B). The results are summarized in Table 1.

Table 1. Tandem Oxy-Cope/Ene/Claisen Reaction of Allyl-1,2-divinylcyclohexanols



8 **9** **10** **11**

entry	substrate	R_1	R_2	method	product	yield
1	**8a**	Me	Ph	A[a]	**10a** and **11a**	34% (*E*/*Z* = 56:44) and 51%
2	**8b**	Ph	Ph	A[a]	**10b**[e]	24%
3	**8b**	Ph	Ph	B[b]	**10b** and **11b**	13% and 10%
4	**8c**	4-(CO_2Me)C_6H_4	Me	A[b] or B[b]	degradation	---
5	**8d**	Bu	Me	A[b]	**11d**	24%
6	**8d**	Bu	Me	B[b]	**11d**	51%
7	**8e**	4-(MeO)C_6H_4	H	A[b]	degradation	---
8	**8e**	4-(MeO)C_6H_4	H	B[b]	**9e**	50% (*dr* = 9:1)[f]
9	**8e**	4-(MeO)C_6H_4	H	B[c]	degradation	---
10	**8e**	4-(MeO)C_6H_4	H	B[d]	degradation	---
11	**8f**	4-(Me)C_6H_4	H	A[b]	**9f**	36% (*dr* = 4:1)[f]
12	**8f**	4-(Me)C_6H_4	H	A[d]	**9f**	63% (*dr* > 25:1)[f]
13	**8f**	4-(Me)C_6H_4	H	B[d]	degradation	---
14	**8g**	4-(CF_3)C_6H_4	H	A[b]	degradation	---
15	**8g**	4-(CF_3)C_6H_4	H	B[b]	**9g**	98% (*dr* > 25:1)[f]
16	**8h**	H	4-(CF_3)C_6H_4	A[b]	**9h**	99% (*dr* > 25:1)[f]
17	**8h**	H	4-(CF_3)C_6H_4	B[b]	**9h**	51% (*dr* > 25:1)[f]

[a] DBU. [b] Et_3N. [c] 2,6-Lutidine. [d] No base. [e] The dimer (**12b**) $(C(Ph)_2{=}CHCH_2)_2$ was isolated in 20%. [f] Diastereomeric ratios at C11 were determined by 500 MHz ^{1}H NMR spectrum of the corresponding lactone.

Microwave irradiation of **8a** afforded the 1,3-shift product (**10a**) (*E*/*Z* = 56:44) and *E*-enol ethers (**11a**) in 34% and 51% yield respectively (entry 1). This result is similar to the one depicted in Scheme 1, except, that enol ether (**11**) intermediate was not isolated and the *E*/*Z* ratio of the terminal olefin were different. Irradiation of **8b** gave 1,3-shift adduct (**10b**) along with dimer (**12b**) in 24% and 20% yield respectively. Interestingly, allyl ether (**8d**) led exclusively to *E*-enol ether (**11d**) in 24% (method A) and 51% (method B) (entries 5 and 6). In both cases, no products resulting from a subsequent 3,3- or 1,3-shift were observed in the crude reaction mixture.[6] The formation of dimer (**12b**) (entry 2) as well as the isomerization of the terminal double bond in the 1,3-rearrangement products (**10a**) and (**6**) suggest that the 1,3-shift rearrangement involves the formation of an oxaallyl-allyl radical pair (Scheme 2).[7]

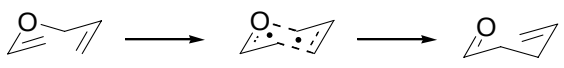
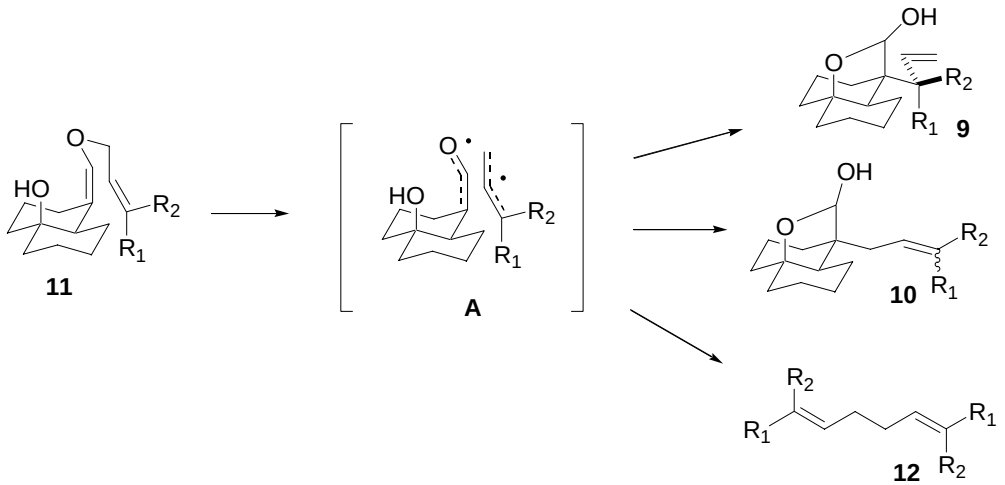


Figure 2. Gajewski'model

The proposed mechanism can also be supported with Gajewski's model, which stipulates that the chair-like transition state for the Claisen rearrangement resemble to an oxaallyl-allyl radical pair (Figure 2).[8] Thus, the homolytic cleavage of the C-O bond in **11** would produce the oxaallyl-allyl radical intermediate **A** which can recombine to form the 3,3-, 1,3- or dimer products (**9,10 and 12**) respectively *via* three energetically distinct transition state (Scheme 2). In the case of sterically demanding substitutents on the allyl ether (entries 1-6), severe steric interactions are developed between ring and substituents R1 and R2 in the transition state. This increases the energy of the Claisen rearrangement, therefore favoring other lower energetically lower 1,3-shift.

Assuming that allyl ethers (**5**) and (**8b**) produce the same radical pair intermediate **A** and the isomerization equilibrium of the allyl radical is fast, both allyl ethers should give decalins (**10a**) and (**6**) with an identical E/Z ratio according the Curtin-Hammet's principle.[9] However, the difference in the ratios indicates that the recombination rate of the oxaallyl-allyl radical pairs competes with the allyl isomerization rate.

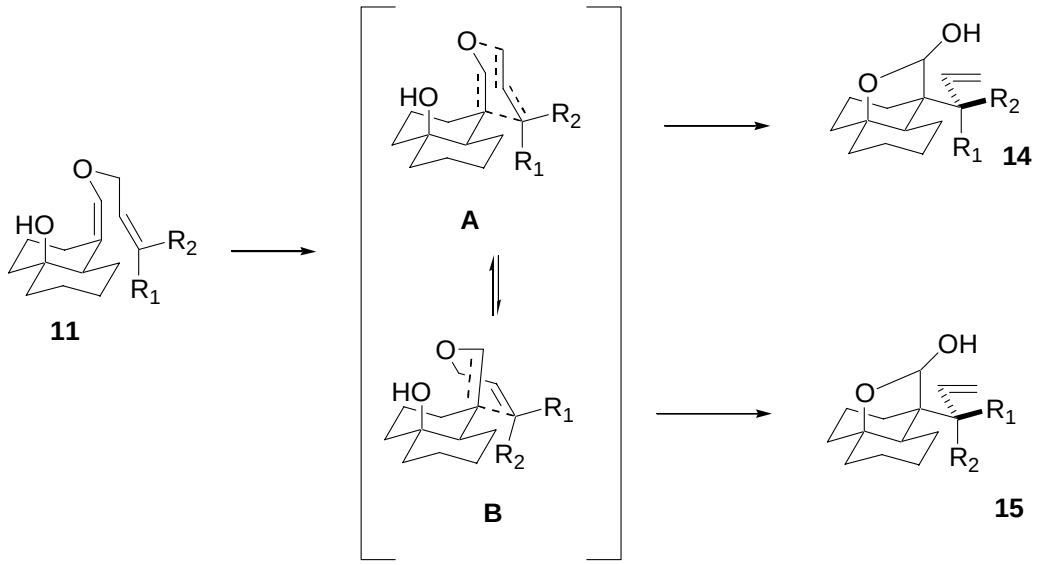


Scheme 2

In the case of disubstituted allyl ethers (**8e-h**), the corresponding decalins (**9e-h**)**,** resulting from the tandem oxy-Cope/ene/Claisen reaction, were obtained in good yields (entries 7-17). This demonstrates that the degree of substitution of the allyl ether moiety plays a decisive role in determining which reaction pathways the allyl ether (**8**) will undergo. We have noticed that the heating source greatly influences the outcome of the reaction. For example, the irradiation of **8e** with microwaves gave a complex mixture from which no decalin (**9e**) was isolated (entry 7). On the other hand, heating of **8e** in a sealed tube at 210°C gave the desired product (**9e**) in 50% yield as a mixture of diastereomer 9:1 at C11 (entry 8). Replacing triethylamine by 2,6-lutidine (entry 9) or performing the reaction without base (entry 10) led to a complete degradation of the starting material. In the case of allyl ether (**8f**), decalin (**9f**) was only obtained when using microwave irradiation (method A) (entries 11-13). Interestingly, *trans*-allyl ether (**8g**) was completely converted to desired decalin (**9g**) in 98% yield (dr > 25:1) using method B (entries 14 and 15).

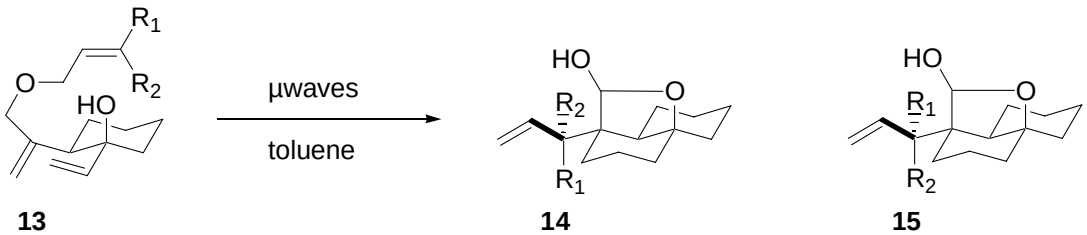
However, method A was required to convert **8h** to **9h** in quantitative yield (entry 16), since method B afforded **9h** in 51% yield (entry 17).

In some cases, a lost of selectivity at C11 was noticed (entries 8 and 11). This could be attributed to a possible epimerization with base or the involvement of a boat like transition state B in the Claisen rearrangement of the enol ether (**11**) (Scheme 3). In order to explain the formation of minor epimer at C11 (**15**), deuterium allyl ether (**13a**) was irradiated for 1 h at 220°C with and without triethylamine (entries 1 and 2, Table 2). Decalins (**14a**) and (**15a**) were isolated in a ratio of 2:1. In both cases, no exchange of deuterium at C11 was observed thereby ruling out a possible epimerization with base. On the other hand, heating allyl ether (**13b**) at different temperatures showed that the diastereoselectivity of the Claisen rearrangement is dependent on the reaction temperature. This suggests that at high temperatures transition state **B** compete with transition state **A** thus giving decalins (**15**) and (**14**) respectively.



Scheme 3

Table 2.



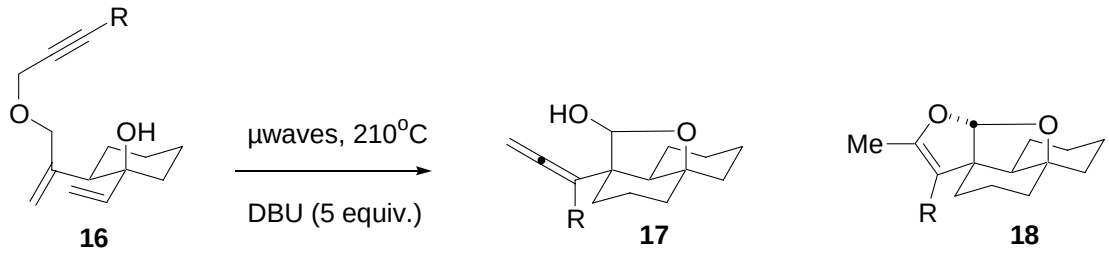
entry	substrate	R1	R2	T °C	Yield[a]	Ratio **14** : **15**
1	**13a**	Ph	D	220[b]	44%	2 : 1
2	**13a**	Ph	D	220	N.D.	2 : 1
3	**13b**	Ph	H	200	40%	11 : 1
4	**13b**	Ph	H	180	55%[c]	13 : 1
5	**13b**	Ph	H	160	N.R.	---

[a] Yield after oxidation of the lactol with TPAP. [b] 5 Equiv. of triethylamine were used.

[c] Reaction not complete, 35% of **13b** was recovered.

Propargyl ethers (**16a-e**) were exposed to microwave irradiation for 1 h to provide desired decalins (**17a-b**) and (**18c-e**) in high yield (dr > 25:1) (Table 3, entries 1 and 2). The formation of tetracyclic acetal (**18**) was observed when R was a withdrawing or an aromatic group (entries 3-5). For instance, the attack of the lactol hydroxyl on the activated allene moiety in **17c** gave the desired acetal (**18c**). The other lactol (**19c**) can not cyclize due to the formation of a highly strained 5-membered ring. As a result, the 5-exo *dig* cyclization is under thermodynamic control with the equilibrium completely shifted to acetal (**18c**). In conclusion, the tandem oxy-Cope/ene/Claisen reaction proves to be a powerful method to generate decalin structures possessing a quaternary carbon at C9. It is currently being applied toward for the synthesis of complex natural products.

Table 3. Tandem oxy-Cope/ene/Claisen reaction of propargyl ether.



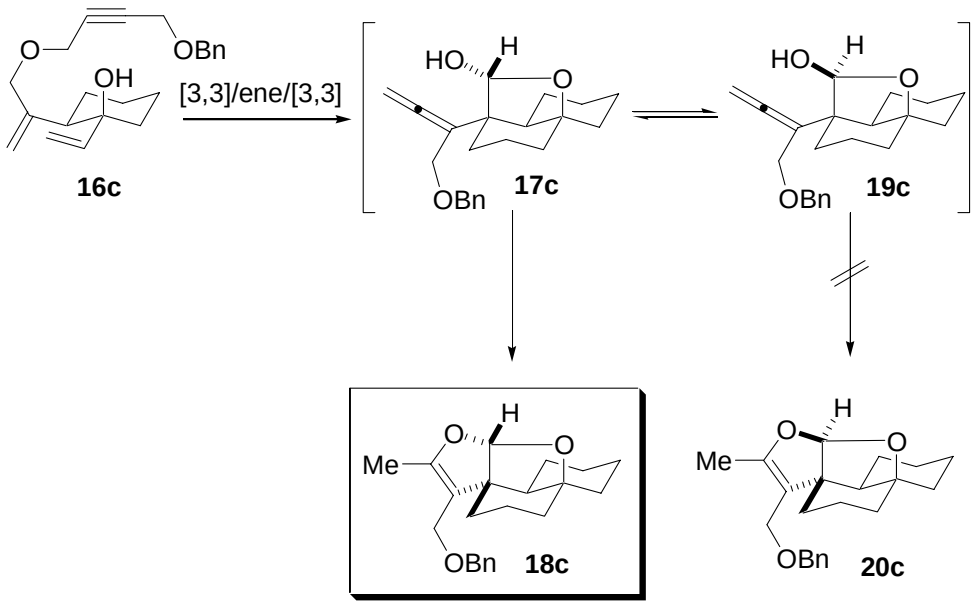
16 **17** **18**

entry	substrate	R	product	yield % (dr)
1	**16a**	H	**17a**	98 (>25:1)
2	**16b**	Me	**17b**	68 (>25:1)
3	**16c**	CH_2OBn	**18c**	81 (>25:1)
4	**16d**	Ph	**18d**	85 (>25:1)
5	**16e**	4-$(MeO)C_6H_4$	**18e**	81 (>25:1)

EXPERIMENTAL

All thermal reactions were carried out under dry argon atmosphere in a sealed or a quartz tube (previously washed with aqueous 2-propanol/NaOH solution, water and acetone). Toluene was freshly distilled from CaH_2 under dry N_2. Reactions were monitored by TLC analysis of aliquots, using aluminum sheets precoated (0.2 mm layer thickness) with silica gel 60 F_{254} (E. Merck). Flash chromatography was carried out on 230-400 mesh silica gel 60. TLC plates were viewed under UV light and stained with *p*-anisaldehyde staining solution. GC (Agilent 6890 Series) was equipped with a crosslinked 5% PH ME siloxane column (30m × 0.32 mm, 0.25 μm film). ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 300 MHz and Bruker AMX 500 MHz spectrometers. IR spectra were recorded on a FTIR spectrophotometer. HRMS spectra were obtained on a Kratos Analytical Concept instrument.

General Procedure: Method A. A solution of **8a** (133 mg, 0.43 mmol) in dry deoxygenated toluene (12 mL) and DBU (196 mg, 1.20 mmol) was heated in a quartz tube for 60 min at 210ºC. The solution was cooled to rt and concentrated *in vacuo*. The residue was purified by flash column chromatography (20% ethyl acetate in hexanes) to afford lactol (**10a**) (45 mg, 34%) and enol ether (**11a**) (66.5 mg, 51%) as colorless oils. In order to determine the diastereomeric ratios, lactols were oxidized with TPAP to afford the corresponding lactones.



Scheme 4

Method B. A solution of **8b** (119 mg, 0.32 mmol) in dry deoxygenated toluene (5 mL) and triethylamine (97.1 mg, 0.96 mmol) was heated in a sealed tube for 18 h at 210ºC. The solution was cooled to rt and concentrated *in vacuo*. The residue was purified by flash column chromatography (20% ethyl acetate in hexanes) to afford lactol (**10b**) (15.9 mg, 13%) and enol ether (**11b**) (12.4 mg, 10%) as colorless oils. In order to determine the diastereomeric ratios, lactols were oxidized with TPAP to afford the corresponding lactones.

7-(3-Phenylbut-2-enyl)-10-oxatricyclo[5.3.3.0^{1,6}]tridecan-8-one (Lactone from 10a). Prepared by following method A : Reagents and quantities for the oxidation : **10a** (13.2 mg, 0.04 mmol), 4 Å molecular sieves (21.1 mg), 4-methylmorpholine *N*-oxide (7.5 mg, 0.06 mmol), TPAP (0.7 mg, 0.002 mmol) and CH_2Cl_2 (1 mL) afforded lactone as a colorless oil (11.2 mg, 90%). IR (neat, cm^{-1}) 3053 (w), 2929 (s), 2856 (m), 1770 (s), 1444 (m), 1261 (m), 1168 (m), 1128 (m), 1025 (w), 948 (m), 915 (m). ^{1}H NMR (300 MHz, $CDCl_3$), δ_{ppm} 7.68-7.08 (m, 10H), 5.64 (t, J = 7.07 Hz, 1H), 5.40 (t, J = 7.31 Hz, 1H), 2.55-0.75 (m, 40H). ^{13}C NMR (300 MHz, $CDCl_3$) δ_{ppm} 181.0 (C_4), 180.9 (C_4), 144.2 (C_4), 141.9 (C_4), 139.9 (C_4), 138.2 (C_4), 128.6 (2 x CH), 128.2 (2 x CH), 127.3 (2 x CH), 127.1 (CH), 126.1 (2 x CH), 122.7 (CH), 121.6 (CH), 83.6 (C_4), 83.4 (C_4), 77.6 (CH), 53.5 (C_4), 53.2 (C_4), 49.5 (CH), 49.5 (CH), 36.1 (CH_2), 33.6 (CH_2), 32.5 (CH_2), 32.2 (CH_2), 30.2 (CH_2), 30.1 (CH_2), 29.7 (CH_2), 26.4 (CH_3), 24.8 (CH_2), 24.5 (CH_2), 24.2 (CH_2), 24.2 (CH_2), 21.2 (CH_2), 19.8 (CH_2), 16.7 (CH_3). LRMS (EI) *m/z* (M^+) calcd for $C_{21}H_{26}O_2$ 310, found 310.

1-(3-Phenylbut-2-enyloxymethylene)octahydronaphthalen-4a-ol (11a). Prepared by following method A. Colorless oil. IR (neat, cm^{-1}) 3554 (w), 3052, (w), 2929 (s), 2859 (m), 1674 (m), 1493 (w), 1448 (m), 1377 (w), 1255 (w), 1229 (w), 1159 (s), 1094 (m), 1030 (m), 953 (m), 830 (w), 760 (m), 708 (m). ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm} 7.36-7.14 (m, 5H), 5.66 (dt, J = 6.91, 1.32 Hz, 1H), 5.57 (s, 1H), 4.13 (d, J = 6.93 Hz, 2H), 2.85 (d, J = 10.6 Hz, 1H), 2.09 (s, 3H), 1.91-1.18 (m, 15H). ^{13}C NMR (300 MHz, $CDCl_3$) δ_{ppm} 142.1 (C_4), 141.0 (C_4), 139.9 (CH), 128.6 (2 x CH), 128.1 (2 x CH), 127.7 (CH), 123.4 (CH), 118.9 (C_4), 71.3 (C_4), 69.6 (CH_2), 47.4 (CH), 40.3 (CH_2), 38.5 (CH_2), 26.4 (CH_2), 26.4 (CH_2), 25.8 (CH_3), 23.7 (CH_2), 22.9 (CH_2), 21.7 (CH_2). LRMS (EI) *m/z* (M^+ - $C_{11}H_{17}O_2$) calcd for $C_{10}H_{11}$ 131, found 131.

7-(3,3-Diphenylallyl)-11-oxatricyclo[5.3.2.0^{1,6}]dodecan-12-ol (10b) Prepared by following method A : Reagents and quantities : **8b** (104.5 mg, 0.28 mmol), DBU (127.9 mg, 0.84 mmol) and toluene (12 mL) to give **10b** (25.0 mg, 24%) and dimer (**12b**) (20.0 mg, 20%) as colorless oils. **10b** : IR (neat, cm^{-1}) 3374 (m), 3058 (w), 2928 (s), 2852 (m), 1944 (w), 1880 (w), 1719 (w), 1667 (w), 1596 (w), 1494 (m), 1444 (m), 1444 (m), 1358 (w), 1255 (w), 1107 (m), 968 (m), 911 (m), 760 (m), 699 (s). ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm} 7.39-7.07 (m, 10H), 6.08-6.05 (t, J = 7.4 Hz, 1H), 5.28 and 5.08 (2d, J = 4.6 and 2.8 Hz, 1H), 3.04 and 2.82 (2 br s, 1H), 2.40-2.16 (m, 2H), 1.84-0.81 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$) δ_{ppm} 143.1 (C_4), 142.9 (C_4), 140.2 (C_4), 130.0 (CH), 129.9 (CH), 128.3 (C_4), 128.2 (CH), 128.1 (CH), 128.1 (CH), 127.2 (CH), 127.1 (CH), 126.9 (CH), 126.8 (CH), 126.8 (CH), 126.7 (CH), 125.9 (CH), 104.1 (CH), 101.7 (CH), 83.7 (C_4), 82.1 (C_4), 51.0 (C_4), 50.5 (CH), 49.4 (C_4), 48.9 (CH), 39.2 (CH_2), 38.6 (CH_2), 34.5 (CH_2), 34.1 (CH_2), 32.0 (CH_2), 31.6 (CH_2), 31.4 (CH_2), 30.7 (CH_2), 29.7 (CH_2), 25.8 (CH_2), 24.9 (CH_2), 24.6 (CH_2), 23.8 (CH_2), 23.6 (CH_2), 22.6 (CH_2), 21.6 (CH_2), 21.3 (CH_2), 19.5 (CH_2). HRMS (EI) *m/z* (M^+ - $C_{11}H_{17}O_2$) calcd for $C_{15}H_{13}$ 193.1017 found 193.1038. **1,1,6,6-Tetraphenylhexa-1,5–diene (12b)** : IR (neat, cm^{-1}) 3080 (w), 3062 (w), 3028 (w), 2957 (w), 2920 (w), 2853 (w), 1494 (m), 1444 (m), 762 (m), 697 (s). ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm} 7.37-7.12 (m, 20H), 6.06-6.01 (m, 2H), 2.24 (d, J = 7.2 Hz, 4H). ^{13}C NMR (75

MHz, $CDCl_3$) δ_{ppm} 142.6 (C_4), 142.0 (C_4), 140.1 (C_4), 129.9 (2 x CH), 129.0 (CH), 128.1 (2 x CH), 127.2 (2 x CH), 126.9 (CH), 126.8 (CH), 30.1 (CH_2). HRMS (EI) *m/z* (M^+- $C_{15}H_{13}$) calcd for $C_{15}H_{13}$ 193.1017, found 193.1011.

1-(3,3-Diphenylallyloxymethylene)octahydronaphthalen-4a-ol (11b). Prepared by following method B : Reagents and quantities : **8b** (119.4 mg, 0.32 mmol), triethylamine (97.1 mg, 0.96 mmol) and toluene (5 mL) to give **10b** (12.4 mg, 13%) and **11b** (15.9 mg, 10%) as colorless oils. **11b** : IR (neat, cm^{-1}) 3354 (w), 3065 (w), 3026 (w), 2923 (s), 2846 (m), 1673 (w), 1487 (w), 1435 (m), 1364 (w), 1145 (s), 1087 (m), 1029 (w), 952 (m), 843 (w). ^1H NMR (500 MHz, $CDCl_3$) δ_{ppm} 7.39-7.31 (m, 3H), 7.29-7.23 (m, 5H), 7.17-7.14 (m, 2H), 6.20 (t, J = 3.8 Hz, 1H), 5.64 (s, 1H), 4.27 (d, J = 6.8 Hz, 2H), 2.90 (ddd, J = 9.1, 8.8, 4.1 Hz, 1H), 1.92 (d, J = 11.9 Hz, 1H), 1.75-1.17 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$) δ_{ppm} 145.3 (C_4), 141.5 (C_4), 139.4 (CH), 138.9 (C_4), 129.7 (2 x CH), 128.2 (2 x CH), 128.2 (2 x CH), 127.7 (CH), 127.7 (CH), 127.6 (2 x CH), 124.5 (CH), 118.8 (C_4), 71.0 (C_4), 69.6 (CH_2), 47.0 (CH), 39.9 (CH_2), 38.1 (CH_2), 26.0 (CH_2), 26.0 (CH_2), 23.3 (CH_2), 22.5 (CH_2), 21.2 (CH_2). HRMS (EI) *m/z* M^+- ($C_{11}H_{17}O_2$) calcd for $C_{15}H_{13}$ 193.1017, found 193.0960.

1-(3-Methylhept-2-enyloxymethylene)octahydronaphthalen-4a-ol (11d). Prepared by following method A and B : Reagents and quantities for A : **8d** (19.0 mg, 0.06 mmol), triethylamine (18.2 mg, 0.18 mmol) and toluene (12 mL) to afford (**11d**) (4.5 mg, 24%) as a colorless oil. Reagents and quantities for B : **8d** (26.2 mg, 0.09 mmol), triethylamine (3 equiv.) and toluene (5 mL) to afford **11d** (13.3 mg, 51%) as a colorless oil. IR (neat, cm^{-1}) 3388 (m), 2927 (s), 2858 (m), 1723 (w), 1663 (w), 1453 (m), 1371 (w), 1242 (w), 1144 (m), 1074 (m), 1031 (m), 944 (w). ^1H NMR (500 MHz, $CDCl_3$) δ_{ppm} 5.70 (s, 1H), 5.34-5.30 (m, 1H), 4.22 (d, J = 6.8 Hz, 2H), 2.85 (dt, J = 8.9, 2.0 Hz, 1H), 2.01 (t, J = 7.4 Hz, 2H), 1.92 (dd, J = 12.6, 3.6 Hz, 1H), 1.81-1.20 (m, 19H), 0.88 (t, J = 7.3 Hz, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_{ppm} 141.3 (C_4), 139.5 (CH), 120.0 (CH), 118.5 (C_4), 70.9 (C_4), 68.4 (CH_2), 47.1 (CH), 40.0 (CH_2), 39.3 (CH_2), 38.1 (CH_2), 29.8 (CH_2), 26.1 (CH_2), 26.0 (CH_2), 23.4 (CH_2), 22.6 (CH_2), 22.3 (CH_2), 21.3 (CH_2), 16.4 (CH_3), 13.9 (CH_3). HRMS (EI) *m/z* (M^+- $C_8H_{16}O$) calcd for $C_{11}H_{16}O$ 164.1201, found 164.1184.

7-[1-(4-Methoxyphenyl)allyl]-11-oxatricyclo[5.3.2.0^{1,6}]dodecan-12-ol (9e). Prepared by following method B : Reagents and quantities : **8e** (26.5 mg, 0.08 mmol), Et_3N (24.3 mg, 0.24 mmol) and toluene (5 mL) to provide **9e** (16.4 mg, 50%) as a light yellow oil. IR (neat, cm^{-1}) 3373 (m), 3075 (w), 2928 (s), 2854 (w), 1610 (m), 1511 (s), 1449 (m), 1297 (w), 1247 (s), 1180 (m), 1107 (m), 1032 (s), 978 (m), 907 (m), 826 (m). ^1H NMR (300 MHz, $CDCl_3$) δ_{ppm} 7.22 and 7.15 (2d, J = 9.4 and 8.5 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 6.38 and 6.23-6.12 (dt and m, J = 16.9, 9.7 Hz, 1H), 5.50 and 5.24 (2d, J = 4.8 and 3.3 Hz, 1H), 5.10-4.91 (m, 2H), 3.98 and 3.56 (2d, J = 7.1 and 9.2 Hz, 1H), 3.77 (2s, 3H), 3.01 (br s, 1H), 2.31-0.81 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$) δ_{ppm} 157.9 (C_4), 139.9 (CH), 139.6 (CH), 133.6 (C_4), 133.4 (C_4), 131.5 (2 x CH), 131.5 (2 x CH), 130.1 (CH), 116.6 (CH_2), 115.3 (CH_2), 113.4 (CH), 113.2 (CH), 112.9 (CH), 103.7 (CH),

101.4 (CH), 83.9 (C_4), 82.2 (C_4), 55.1 (CH_3), 54.6 (C_4), 52.7 (C_4), 50.9 (CH), 50.1 (CH), 48.9 (CH), 47.8 (CH), 39.4 (CH_2), 38.5 (CH_2), 34.8 (CH_2), 34.5 (CH_2), 30.5 (CH_2), 28.6 (CH_2), 24.9 (CH_2), 24.8 (CH_2), 24.6 (CH_2), 23.3 (CH_2), 21.4 (CH_2), 21.4 (CH_2), 19.7 (CH_2), 19.6 (CH_2). HRMS (EI) *m/z* (M^+ - $C_{11}H_{17}O_2$) calcd for $C_{10}H_{11}O$ 147.0810, found 147.0825.

7-[1-(4-Methoxyphenyl)allyl]-11-oxatricyclo[5.3.2.0^{1,6}]dodecan-12-one (Lactone from 9e) Colorless oil. IR (neat, cm^{-1}), 3082 (w), 2933 (m), 2861 (w), 1764 (s), 1610 (m), 1512 (s), 1448 (w), 1301 (w), 1248 (s), 1182 (m), 1157 (m), 1124 (m), 1075 (w), 1035 (m), 949 (m), 925 (m). ^{1}H NMR (300 MHz, $CDCl_3$), δ_{ppm} 7.16 (d, J = 8.3 Hz, 2H), 6.82 (d, J = 8.2 Hz, 2H), 6.71-6.60 (m, 1H), 5.11 and 5.02 (2d, J = 10.4 and 10.2 Hz, 1H), 4.88 and 4.64 (2d, J = 17.4 and 17.4 Hz, 1H), 3.78 (s, 3H), 3.74 (d, J = 3.9 Hz, 1H), 52.15-0.82 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$) δ_{ppm} 179.5 (C_4), 158.1 (C_4), 139.5 (CH), 132.2 (C_4), 131.1 (2 x CH), 116.7 (CH_2), 113.5 (2 x CH), 82.5 (C_4), 55.9 (C_4), 55.2 (CH_3), 50.9 (CH), 48.6 (CH), 35.9 (CH_2), 33.5 (CH_2), 29.5 (CH_2), 24.2 (CH_2), 23.9 (CH_2), 20.7 (CH_2), 20.0 (CH_2). HRMS (EI) *m/z* (M^+) calcd for $C_{21}H_{26}O_3$ 326.1882, found 326.1843.

7-(1-*p*-Tolylallyl)-11-oxatricyclo[5.3.2.0^{1,6}]dodecan-12-ol (9f). Prepared by following method A : Reagents and quantities for A : **8f** (19.6 mg, 0.06 mmol) and toluene (12 mL) to afford **9f** (12.3 mg, 63 %) as a colorless oil. IR (neat, cm^{-1}) 3385 (m), 3078 (w), 3014 (w), 2927 (s), 2855 (m), 1635 (w), 1513 (w), 1449 (w), 1339 (w), 1262 (w), 1115 (m), 979 (m), 911 (m). ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm} 7.21-7.07 (m, 4H), 6.45-6.33 and 6.26-6.14 (2m, 1H), 5.50 and 5.23 (2d, J = 4.8 and 3.1 Hz, 1H), 5.12-4.94 (m, 2H), 3.99 and 3.57 (2d, J = 9.3 and 7.5, 1H), 2.76-2.72 (m, 1H), 2.31 and 2.30 (2s, 3H), 2.18-0.76 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$) δ_{ppm} 139.7 (CH), 139.6 (CH), 138.6 (C_4), 138.5 (C_4), 138.4 (C_4), 135.8 (C_4), 135.8 (C_4), 130.1 (2 x CH), 129.0 (2 x CH), 128.8 (2 x CH), 128.6 (2 x CH), 116.8 (CH_2), 115.4 (CH_2), 103.7 (CH), 101.5 (CH), 83.9 (C_4), 82.2 (C_4), 54.5 (C_4), 52.7 (C_4), 50.8 (CH), 50.5 (CH), 48.9 (CH), 48.3 (CH), 39.3 (CH_2), 38.4 (CH_2), 34.8 (CH_2), 34.5 (CH_2), 30.5 (CH_2), 29.7 (CH_2), 28.6 (CH_2), 24.9 (CH_2), 24.8 (CH_2), 24.6 (CH_2), 23.3 (CH_2), 21.4 (CH_2), 21.4 (CH_2), 21.0 (CH_3), 19.7 (CH_2). HRMS (EI) *m/z* (M^+ - $C_{11}H_{17}O_2$) calcd for $C_{10}H_{11}$ 131.0861, found 131.0868.

7-(1-*p*-Tolylallyl)-11-oxatricyclo[5.3.2.0^{1,6}]dodecan-12-one (Lactone from 9f) Colorless oil. IR (neat, cm^{-1}) 3084m (w), 3020 (w), 2931 (m), 2859 (m), 1766 (s), 1629 (w), 1513 (w), 1448 (w), 1352 (w), 1236 (w), 1159 (w), 1124 (m), 946 (m), 920 (w). ^{1}H NMR (500 MHz, $CDCl_3$) δ_{ppm} 7.13 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 7.8 Hz, 2H), 6.68-6.62 (m, 1H), 5.11 (d, J = 1.6 Hz, 1H), 4.66 (dd, J = 17.3, 1.6 Hz, 1H), 3.75 (d, J = 5.4 Hz, 1H), 2.31 (s, 3H), 2.15 (dd, J = 12.1, 3.9 Hz, 1H), 1.95 (d, J = 13.1 Hz, 1H), 1.86-0.05 (m, 13H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_{ppm} 179.4 (C_4), 139.4 (CH), 137.2 (C_4), 136.2 (C_4), 130.0 (2 x CH), 129.0 (2 x CH), 116.7 (CH_2), 82.5 (C_4), 55.8 (C_4), 51.0 (CH), 49.2 (CH), 36.0 (CH_2), 33.6 (CH_2), 29.6 (CH_2), 24.2 (CH_2), 23.9 (CH_2), 21.0 (CH_3), 20.7 (CH_2), 20.0 (CH_2). HRMS (EI) *m/z* (M^+) calcd for $C_{21}H_{26}O_2$ 310.1933 found 310.1949.

7-[1-(4-Trifluoromethylphenyl)allyl]-11-oxatricyclo[5.3.2.0^{1,6}]dodecan-12-ol (9g) Prepared by following method B : Reagents and quantities : **8g** (15.2 mg, 0.04 mmol), Et_3N (12.1 mg, 0.12 mmol) and toluene (5 mL) to provide **9g** (14.9 mg, 98%) as colorless crystals. mp 122.3-125.1ºC. IR (neat, cm^{-1}) 3387 (w), 2930 (m), 2859 (w), 1616 (w), 1448 (w), 1410 (w), 1326 (s), 1159 (m), 1120 (s), 1069 (m), 908 (w). ^{1}H NMR (500 MHz, $CDCl_3$) δ_{ppm} 7.53 and 7.52 (2d, J = 8.1 Hz and 8.1 Hz, 2H), 7.43 and 7.34 (2d, J = 8.2 Hz and 8.3 Hz, 2H), 6.45-6.38 and 6.21-6.14 (2m, 1H), 5.52 and 5.26 (2d, J = 4.7 Hz, and 3.2 Hz, 1H), 5.14 and 5.09 (dt and dd, J = 10.4, 1.4 Hz and 10.1, 1.7 Hz, 1H), 4.99 and 4.93 (2dt, J = 16.9, 2.88 Hz and 17.2, 1.5 Hz, 1H), 4.12 and 3.68 (2d, J = 7.1 Hz, and 9.1 Hz, 1H), 2.88 and 2.82 (2 br s, 1H), 2.31-0.79 (m, 15H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_{ppm} 145.9 (CH_4), 145.6 (C_4), 138.8 (CH), 138.5 (CH), 130.6 (2 x CH), 129.4 (2 x CH), 125.0-124.8 (q, J = 6.5 Hz, 2 x CH), 117.6 (CH_2), 116.3 (CH_2), 103.4 (CH), 101.2 (CH), 84.0 (C_4), 82.4 (C_4), 54.4 (C_4), 50.8 (CH), 48.9 (CH), 39.3 (CH_2), 38.3 (CH_2), 34.7 (CH_2), 34.4 (CH_2), 29.6 (CH_2), 29.2 (CH_2), 24.8 (CH_2), 24.8 (CH_2), 24.7 (CH_2), 23.4 (CH_2), 21.4 (CH_2), 21.3 (CH_2), 19.6 (CH_2), 19.5 (CH_2). HRMS (EI) *m/z* (M^+- $C_{11}H_{17}O_2$) calcd for $C_{10}H_8F_3$ 185.0578, found 185.0576.

7-[1-(4-Trifluoromethylphenyl)allyl]-11-oxatricyclo[5.3.2.0^{1,6}]dodecan-12-one (Lactone from 9g) Colorless oil. IR (neat, cm^{-1}) 3078 (w), 2929 (s), 2854 (m), 1760 (s), 1617 (w), 1450 (w), 1324 (s), 1164 (w), 1124 (s), 1072 (m), 1009 (w), 946 (w). ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm} 7.54 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 6.6 Hz, 2H), 6.71-6.59 (m, 1H), 5.15 (dd, J = 10.5, 1.5 Hz, 1H), 4.61 (dd, J = 17.3, 1.5 Hz, 1H), 3.86-3.85 (m, 1H), 2.18-2.11 (m, 1H), 1.97 (d, J = 13.3 Hz, 1H), 1.91-0.63 (m, 11H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_{ppm} 178.9 (C_4), 144.7 (C_4), 138.6 (CH), 130.4 (2 x CH), 125.2 (q, J = 3.5 Hz, 2 x CH), 117.5 (CH_2), 82.6 (C_4), 55.7 (C_4), 51.0 (CH), 49.7 (CH), 35.9 (CH_2), 33.5 (CH_2), 29.9 (CH_2), 24.5 (CH_2), 23.8 (CH_2), 20.6 (CH_2), 20.0 (CH_2). HRMS (EI) *m/z* (M^+) calcd for $C_{21}H_{23}O_2F_3$ 364.1650, found 364.1633.

7-[1-(4-Trifluoromethylphenyl)allyl]-11-oxatricyclo[5.3.2.0^{1,6}]dodecan-12-ol (9h)

Prepared by following method A and B : Reagents and quantities for method A : **8h** (19.6 mg, 0.05 mmol), triethylamine (15.2 mg, 0.15 mmol) and toluene (12 mL) to provide **9h** (19.4 mg, 99%) as colorless crystals. Reagents and quantities for method B : **8h** (47.8 mg, 0.13 mmol), triethylamine (3 eq) and toluene (5 mL) to provide **9h** (24.3 mg, 51%) as colorless crystals. mp 126.6-128.5°C. IR ($CDCl_3$, cm^{-1}) 3371 (w), 3073 (w), 2930 (m), 2855 (w), 1623 (w), 1451 (w), 1411 (w), 1326 (s), 1164 (m), 1124 (m), 1070 (m), 986 (w). ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm} 7.51-7.48 and 7.28 (m and d, J = 8.1 Hz, 4H), 6.34-6.16 (m, 1H), 5.53, 5.19-5.03 and 4.75 (d, m and s, J = 4.4 Hz, 3H), 4.14 and 3.64 (2d, J = 9.2 Hz and 8.5 Hz, 1H), 2.98 and 2.52 (2s (br), 1H), 2.15-0.81 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$) δ_{ppm} 146.5 (C_4), 137.5 and 136.9 (CH), 130.9 and 127.7 (2 x CH), 124.9-124.4 (q, J = 3.8 Hz, 2 x CH), 117.9 (CH_2), 102.6 and 101.0 (CH), 84.0 and 81.8 (C_4), 54.2 and 52.5 (C_4), 50.9 (CH), 49.0 (CH), 47.7 (CH), 39.3 and 38.4 (CH_2), 34.7 and 34.5 (CH), 29.7 and 28.8 (CH), 26.6 (CH), 24.9 (CH), 24.7 (CH), 23.9 (CH), 22.5 (CH), 21.6 (CH), 19.3 (CH). HRMS (EI) *m/z* (M^+) calcd for $C_{21}H_{25}O_2F_3$ 366.1807, found 366.1691.

7-[1-(4-Trifluoromethylphenyl)allyl]-11-oxatricyclo[5.3.2.0^{1,6}]dodecan-12-one (Lactone from 9h) Colorless oil. IR (neat, cm^{-1}) 3076 (w), 2932 (m), 2860 (m), 1770 (s), 1617 (w), 1454 (m), 1326 (s), 1162 (s), 1123 (s), 1068 (m), 1018 (m), 939 (m). ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm} 7.55 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 6.26-6.14 (m, 1H), 5.10 (dt, J = 10.4, 1.3 Hz, 1H), 4.93 (dt, J = 17.1, 1.4 Hz, 1H), 3.85 (d, J = 7.8 Hz, 1H), 2.07-1.92 (m, 3H), 1.79-0.81 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ_{ppm} 178.2 (C_4), 144.2 (C_4), 137.6 (CH), 130.8 (2 x CH), 124.8 (q, J = 3.5 Hz, 2 x CH), 117.6 (CH_2), 82.4 (C_4), 55.8 (C_4), 51.5 (CH), 50.7 (CH), 35.7 (CH_2), 33.6 (CH_2), 30.6 (CH_2), 25.7 (CH_2), 24.1 (CH_2), 20.8 (CH_2), 19.3 (CH_2). HRMS (EI) *m/z* (M^+) calcd for $C_{21}H_{25}O_2F_3$ 364.1650, found 364.1653.

***R*-7-(1-Phenylallyl)-11-oxatricyclo[5.3.2.0^{1,6}]dodecan-12-one (Lactone from 14b)** IR (neat, cm^{-1}) 3077 (w), 3022 (w), 2932 (m), 2858 (w), 1764 (s), 1634 (w), 1596 (w), 1448 (m). ^{1}H NMR (300 MHz, $CDCl_3$), δ_{ppm} 6.71-6.61 (m, 1H), 5.14-5.11 (d, J=9.9 Hz, 1H), 4.64 (d, J=17.3 Hz, 1H), 3.79-3.78 (d, J=4.7 Hz, 1H), 2.19-2.12 (m, 1H), 2.02-0.79 (m, 19H). ^{13}C NMR (75 MHz, $CDCl_3$), δ_{ppm} 179.0 (C_4), 140.7 (C_4), 139.6 (CH), 130.5 (CH), 130.5 (CH), 128.6 (CH), 128.6 (CH), 127.0 (CH), 117.3 (CH2), 82.9 (C4), 56.2 (C4), 51.3 (CH), 50.0 (CH), 36.3 (CH2), 33.9 (CH2), 30.0 (CH2), 24.6 (CH2), 24.3, (CH2), 21.1 (CH_2), 20.4 (CH_2). HRMS (EI) *m/z* (M^+) calcd for $C_{20}H_{24}O_2$ 296.1776, found 296.1778.

***S*-7-(1-Phenylallyl)-11-oxatricyclo[5.3.2.0^{1,6}]dodecan-12-one (Lactone from 15b)** IR (neat, cm^{-1}) 3070 (w), 3022 (w), 2934 (s), 2861 (m), 1767 (s), 1634 (w), 1602 (w), 1446 (m), 1261 (m), 1125 (m), 1002 (w), 920 (m). ^{1}H NMR (300 MHz, $CDCl_3$), δ_{ppm} 7.33-7.20 (m, 5H), 6.21 (ddd, J=7.2, 10.4 and 17.3 Hz, 1H), 5.05-5.00 (m, 1H), 4.92-4.85 (m, 1H), 3.78 (d, J=7.1 Hz, 1H), 2.09-1.95 (m, 3H), 1.74-1.11 (m , 12 H). ^{13}C NMR (75 MHz, $CDCl_3$), δ_{ppm} 179.1 (C_4), 140.2 (C_4), 139.3 (CH), 130.6 (2 x CH, 128.5 (2 x CH), 127.1 (CH), 116.9 (CH_2), 82.7 (C_4), 56.7 (C_4), 53.0 (CH), 51.4 (CH), 36.2 (CH_2), 34.0 (CH_2), 32.3 (CH_2), 26.9 (CH_2), 24.6 (CH_2), 21.3 (CH_2), 19.8 (CH_2). HRMS (EI) *m/z* (M^+) calcd for $C_{20}H_{24}O_2$ 296.1776, found 296.1782.

7-Propa-1,2-dienyl-11-oxatricyclo[5.3.2.01,6]dodecan-12-one (Lactone from 17a). IR (neat, cm^{-1}) 2934 (s), 2859 (m), 1956 (w), 1772 (s), 1445 (w), 1259 (w), 1127 (m). ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm} 5.32 (t, J=6.8 Hz, 1H), 4.89-4.78 (m, 2H), 2.04-1.98 (m, 1H), 1.92-0.83 (m, 14 H). ^{13}C NMR (75 MHz, $CDCl_3$), δ_{ppm} 209.3 (C_4), 179.1 (C_4), 89.4 (CH), 83.8 (C_4), 78.0 (CH_2), 53.3 (C_4), 51.7 (CH), 35.9 (CH_2), 33.5 (CH_2), 33.2 (CH_2), 25.5 (CH_2), 24.2 (CH_2), 21.1 (CH_2), 19.8 (CH_2). HRMS (EI) *m/z* (M^+) calcd for $C_{14}H_{18}O_2$ 218.1307, found 218.1316.

7-(1-Methylpropa-1,2-dienyl)-11-oxatricyclo[5.3.2.0^{1,6}]dodecan-12-one (Lactone from 17b). IR (neat, cm^{-1}) 2931 (s), 2858 (m), 1958 (w), 1771 (s), 1444 (m), 1258 (w), 1162 (m), 1122 (m). ^{1}H NMR (300MHz, $CDCl_3$) δ_{ppm} 4.78- 4.63 (m, 2H), 2.02-1.97 (m, 1H), 1.86-0.80 (m, 17H). ^{13}C NMR (75 MHz, $CDCl_3$) δ_{ppm} 207.8 (C_4), 177.3 (C_4), 95.8 (C_4), 82.6 (C_4), 76.0 (CH_2), 56.4 (C_4), 50.7 (CH), 36.1 (CH_2), 33.6 (CH_2), 32.8 (CH_2), 25.5 (CH_2), 24.3 (CH_2), 21.2 (CH_2), 20.0 (CH_2), 16.6 (CH_3). HRMS (EI) *m/z* (M^+) calcd for

$C_{15}H_{20}O_2$ 232.1463, found 232.1452.

Tetracyclic acetate (18c). IR (neat, cm^{-1}) 2924 (s), 2857 (m), 1679 (m), 1599 (w), 1448 (m), 1389 (w), 1356 (w), 1260 (w), 1206 (w), 1071 (s). ^{1}HMR (300 MHz, $CDCl_3$), δ_{ppm} 7.36-7.26 (m, 5H), 5.73(s, 1H), 4.50 (d, J=12.0 Hz, 1H), 4.43 (d, J=12.0 Hz, 1H), 3.99 (d, J=11.8 Hz, 1H), 3.90 (d, J=11.8 Hz, 1H), 1.95-1.90 (m, 1H), 1.77 (s, 3H), 1.71-0.83 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$) δ_{ppm} 152.4 (C_4), 139.0 (C_4), 128.7 (2 x CH), 127.9 (3 x CH), 112.8 (CH), 108.5 (C_4), 89.4 (C_4), 72.1 (CH_2), 64.6 (CH_2), 61.5 (C_4), 50.9 (CH), 39.2 (CH_2), 33.9 (CH_2), 31.4 (CH_2), 25.3 (CH_2), 24.3 (CH_2), 21.6 (CH_2), 19.7 (CH_2), 12.0 (CH_3). HRMS (EI) *m/z* (M^+-C_7H_8O) calcd for $C_{15}H_{20}O_2$ 232.1462, found 232.1443.

Tetracyclic acetal (18d). Prepared by following method A : Reagents and quantities : **16d** (76.8 mg, 0.26 mmol), DBU (118.7 mg, 0.78 mmol) and toluene (12 mL) to generate **18d** (65.3 mg, 85%) as a colorless oil. IR (neat, cm^{-1}) 3030 (w), 2927 (s), 2859 (m), 1648 (m), 1445 (w), 1237 (w), 1208 (m), 1076 (m), 977 (m), 903 (m), 757 (m), 699 (m). ^{1}H NMR (300 MHz, $CDCl_3$), δ_{ppm} 7.33-7.12 (m, 5H), 5.82 (s, 1H), 1.96 (s, 3H), 1.93-1.16 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$) δ_{ppm} 150.3 (C_4), 135.5 (C_4), 128.7 (2 x CH), 127.4 (2 x CH), 125.8 (CH), 113.8 (C_4), 112.7 (C_4), 89.3 (C_4), 62.4 (C_4), 52.1 (CH), 39.4 (CH_2), 33.9 (CH_2), 31.2 (CH_2), 25.3 (CH_2), 24.5 (CH_2), 21.7 (CH_2), 19.8 (CH_2), 13.4 (CH_3). LRMS (EI) *m/z* (M^+) calcd for $C_{20}H_{24}O_2$ 296, found 296.

Tetracyclic acetal (18e). Prepared by following method A : Reagents and quantities : **16e** (142.2 mg, 0.44 mmol), DBU (201.0 mg, 1.32 mmol) and toluene (12 mL) to afford **18e** (115.0 mg, 81%) as colorless crystals. mp 102-104°C. IR (neat, cm^{-1}) 3045 (w), 2927 (s), 2865 (m), 1655 (w), 1609 (w), 1513 (s), 1442 (w), 1346 (w), 1288 (m), 1244 (s), 1178 (m), 978 (m). ^{1}H NMR (300 MHz, $CDCl_3$), δ_{ppm} 7.04 (dd, J = 8.87, 2.10 Hz, 2H), 6.85 (dd, J = 6.83, 2.11 Hz, 2H), 5.80 (s, 1H), 3.78 (s, 3H), 1.92 (s, 3H), 1.88 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$) δ_{ppm} 157.9 (C_4), 149.1 (C_4),128.6 (2 x CH), 127.8 (C_4), 114.2 (2 x CH), 113.2 (C_4), 112.6 (CH), 89.3 (C_4), 62.4 (C_4), 55.6 (CH_3), 51.9 (CH), 39.4 (CH_2), 33.9 (CH_2), 31.3 (CH_2), 25.3 (CH_2), 24.5 (CH_2), 21.7 (CH_2), 19.8 (CH_2), 13.2 (CH_3). HRMS (EI) *m/z* (M^+) calcd for $C_{21}H_{26}O_3$ 326.1883, found 326.1884.

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