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Rhodium Catalysed Carbonylation of Homoallylic Alcohols to Spiropyrans bearing Quaternary Centres

Beate Kitsos-Rzychon, Peter Eilbracht *

Organische Chemie I (FB 3), Universität Dortmund, Otto-Hahn-Str.6, D-44221 Dortmund, Germany

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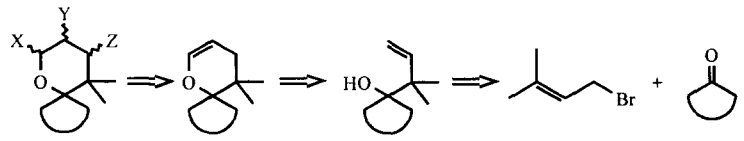
Abstract

A convenient preparation of substituted spiropyrans via rhodium catalysed hydroformylation of homoallylic alcohols, followed by a condensation sequence to form hemiacetals and 2,2,3,3-tetraalkyl-4[H]-pyrans, is described.

Keywords: Alcohols; Pyrans; Rhodium catalysis, Spiro compounds

Spiropyrans, including spiroketals and other systems bearing quaternary centres, are important subunits of a large variety of naturally occuring products with biological and pharmacological activities, such as pheromones and antibiotics.[1] Among many others the 1-oxaspiro[n.5]alkane skeleton is of current interest[2] and various synthetic pathways towards its preparation have been developed.[3] Following our interest in tandem hydroformylations[4] we here present a short access to 1-oxaspiro[n.5]alkanes **2** containing a pyran subunit bearing one or two quaternary centres, by using a one-pot hydroformylation/hemiacetal/elimination sequence starting from homoallylic alcohols. These are easily accessible from cyclic ketones **5** and prenyl bromide **4** as outlined in the retro synthetic scheme **1**.



1 **2** **3** **4** **5**

Scheme 1

The hydroformylation of unsaturated alcohols is intensively studied.[5] Various allylic or homoallylic alcohols can be hydroformylated in good yields to form heterocyclic furan or pyran systems using rhodium carbonyl triphenylphosphine or chiral phosphine-phosphite complexes.[5f,g]

Fax (+49)(0)231/7555363; e-mail: eilbrach@citrin.chemie.uni-dortmund.de

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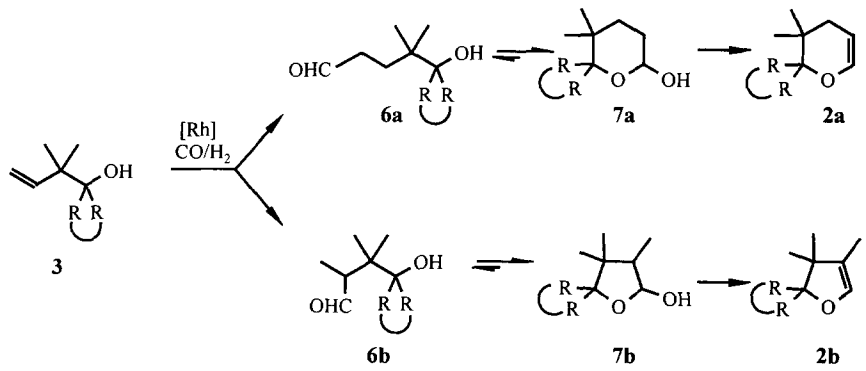
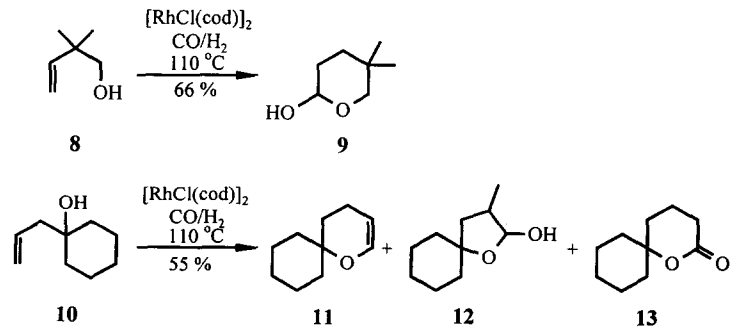
The products of the hydroformylation and cyclisation sequence of allylic alcohols are usually identified as lactols or after oxidation as the corresponding lactones.[5g,6] Cyclic enol ethers have also been observed previously, but only a few examples are described for the preparation of substituted pyran derivatives by this method.[7] These products, on the other hand after elimination of the hydroxy function, offer access to wide range of substituted pyran derivatives via dihydroxylation, epoxidation or other addition and allylic substitution of the dihydropyran.

Selective formation of pyran products **2** from homoallylic alcohols as outlined above requires regioselective *n*-hydroformylation, while the *iso*-products lead to furan derivatives **7b**, **2b**.



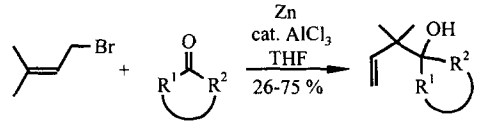
Scheme 2

According to model investigations, as shown with the homoallylic alcohols **8** and **10** this regioselectivity is effectively controlled by a quaternary centre in the allylic position of the double bond. While **8** solely gives **9** in 66 % yield, treatment of **10** under identical conditions (dioxane, 30/20 bar CO/H_2, 1 mol-% $[Rh(cod)Cl]_2$, 20 h) nonselectively gives a mixture of **11** (37 %), **12** (15 %) and traces of **13**.



Scheme 3

Likewise substrates with quaternary centres both in allylic and homoallylic position again selectively give the *n*-hydroformylation and the pyran products derived thereof. This is demonstrated with the homoallylic alcohols **3 a-g** (Scheme 5, Table 1) prepared by a Grignard-type allylation of the cyclic ketones **5a-g** with prenyl bromide **4** and zinc powder in the presence of catalytic amounts of $AlCl_3$ in anhydrous THF.[8]



4 **5a-g** **3a-g**

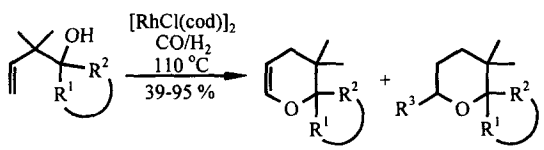
Scheme 4:

Table 1. Synthesis of homoallylic alcohols

Entry	Allylbromide	Ketone	$R^1—R^2$	Time [h]	Product 3	Yield[a] [%]
1	**4**	**5a**	$-(CH_2)_4-$	4	**3a**	75
2		**5b**	$-(CH_2)_5-$	4	**3b**	54
3		**5c**	$-(CH_2)_6-$	16	**3c**	52
4		**5d**	$-(CH_2)_7-$	22	**3d**	26
5		**5e**	$-CH_2(CMe_2)-CH_2-CH(Me)-$	16	**3e**	62
6		**5f**	$-(CH_2)_3-CH(COOEt)-$	16	**3f**	50
7		**5g**	$-(CH_2)_2-O-(CH_2)_2-$	2	**3g**	54

[a]isolated yields

These substrates under hydroformylation conditions selectively form pyranosidic derivatives in good to excellent yields. In the most cases the elimination to the spiroanellated pyran derivatives **14a-g** is achieved under the conditions applied.



3a-g **14a-g** **15a-h**

Scheme 5

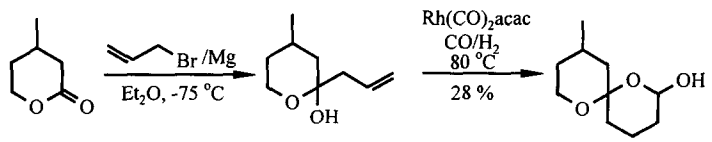
Table 2. One-Pot hydroformylation/hemiacetal/elimination sequence of homoallylic alcohols

Entry	Alcohol	Solvent	Pressure CO/H_2	Time [h]	Product **14**	Yield [%]	R^3	Product **15**	Yield [%]
8	**3a**	A	90/20	65	**14a**	39	OH	**15a**	15
9	**3a**	A	30/20	65	**14a**	43	OH	-	-
10	**3b**	A	30/20	65	**14b**	39	OH	**15b**	48
11	**3b**	A	30/20	20	**14b**	64	OH	-	-
12	**3b**	B	30/20	20	-	-	OCH_3	**15h**	50
13	**3c**	A	30/20	65	**14c**	95	OH	-	-
14	**3d**	A	30/20	20	**14d**	70	OH	**15d**	9
15	**3e**	A	30/20	65	**14e**	69	OH	-	-
16	**3f**	A	30/20	20	**14f**	21	OH	**15f**	26
17	**3g**	A	30/20	20	**14g**	61	OH	-	-

A = dioxane B = methanol

Selective formation of the pyran products **14a-g** and **15a-h** obviously is supported by the "geminal dialkyl (Thorpe-Ingold) effect"[9] and the "blocking" of double bond isomerisation to the allylic alcohols **3a-g** all showing high *n*-selectivity in the hydroformylation step. Evidently the reaction conditions can be widely varied in reaction time and pressure (50 (CO/H_2 : 30/20) to 110 bar (CO/H_2 : 90/20)) . The ratio of **14** to **15** depends on the homoallylic alcohol used (compare entry 10 and 13), but in most cases the enol ether **14** is the major product. If methanol is used as solvent the corresponding acetal is formed (entry 12).

In conclusion we have shown that the methodology presented is successfully applied to the preparation of pyran derivatives with high *n*-regioselectivity. This one-pot reaction offers an attractive method for the synthesis of pyrans with different substitution patterns in good to excellent yields. A similar procedure can be used to generate spiroketals via a one-pot hydroformylation/hemiacetal condensation sequence. Hemiacetal **17** was prepared by addition of allyl magnesium bromide to lactone **16**[10] and exclusively leads to one diastereoisomer.[11] The intramolecular ring closure reaction gives the spiroketal **18** as a 6:1 mixture of diastereoisomers reflecting the ratio of diastereoisomers of the allyl lactol **17**. The relative configuration of **17** and **18** could not yet be determined and is currently under investigation together with experiments towards an effective control of stereoselectivity. Further investigations towards an extension of the synthetic potential of this reaction are in progress.



16 **17** **18**

Scheme 6

EXPERIMENTAL

NMR spectra were recorded on Bruker spectrometer DRX 400 using TMS as internal standard. IR spectra were obtained with a Shimadzu 470, mass spectra on a Finnigan CA 5 and elementary analysis with a Leco CHNS-932. Column chromatography was carried out with aluminum oxide N (act. 1) from ICN Biomedicals, Eschwege, by using diethyl ether/ethanol as eluent. Gas chromatography was carried out on a Fisons GC 9130 with 15m CP sil-19 capillaries. GC-MS spectra were obtained by using comparable capillaries and a Finnigan MAT 8320. The $[RhCl(cod)]_2$ catalyst was prepared according to literature procedures[12]. Pressure reaction have been carried out in autoclaves (type A, 250 ml, PTFE-insert) from Berghof , Eningen, Germany.

General procedure for the preparation of homoallylic alcohols 3a-g:

To a suspension of zinc (3.12 g, 48 mmol) and $AlCl_3$ (2.4 mmol) in anhydrous THF (64 ml) a solution of prenyl bromide (7.1 g, 48 mmol) in THF (16 ml) was added dropwise at room temperature under inert gas atmosphere. The resulting mixture was stirred for 5 min and the cyclic ketone 5**a-g** was added. The reaction mixture was stirred at room temperature for 4 h or 16 h (compare table 1). The reaction mixture was diluted with 10 % HCl (100 ml) and extracted with diethyl ether (50 ml x 3). The combined organic phases were washed with brine and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the residue was chromatographed on silica gel (PE:MTBE, 10:1) to afford the pure homoallylic alcohols **3a-g**.

2,2-Dimethyl-1-cyclopentane-3-buten-1-ol (3a)[13]. Obtained from **5a** and prenyl bromide **(4)** as a colourless liquid in 75 % yield.

2,2-Dimethyl-1-cyclohexane-3-buten-1-ol (3b)[13,14]. Obtained from **5b** and prenyl bromide **(4)** as a colourless liquid in 54 % yield.

2,2-Dimethyl-1-cycloheptane-3-buten-1-ol (3c). Obtained from **5c** and prenyl bromide **(4)** as a colourless liquid in 52 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.04 (s, 6 H, 2xCH_3, $Cq(CH_3)_2$), 1.45-1.80 (m, 13 H, 6xCH_2, 1xOH), 5.02 (d, *J* = 17.8 Hz, 1 H, CHH, CHH=CH), 5.06 (d, *J* = 10.9 Hz, 1 H, CHH, CHH=CH), 6.03 (d, *J* = 17.8 Hz, 1H, 10.9 Hz, CHH=CH), ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 22.2 (2xCH_3, $Cq(CH_3)_2$), 23.1 (2xCH_2), 29.9 (2xCH_2), 36.2 (2xCH_2), 45.2 (Cq), 78.0 (Cq-OH), 113.0 (CH_2, $CH{=}CH_2$), 145.7 (CH, $CH{=}CH_2$). IR(KBr/film) $\tilde{\nu}$ = 3484 (s), 3080 (m), 2925 (vs), 2852 (vs), 1700 (m), 1635 (s), 1458 (s), 1446 (s), 1414 (s), 1377 (s), 1345 (m), 1324 (m), 1045 (s), 10184 (s), 910 (vs) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 165 (M^+-17, 41%), 109 (90), 95 (100), 81 (15), 69 (7), 55 (2).

2,2-Dimethyl-1-cyclooctane-3-buten-1-ol (3d). Obtained from **5d** and prenyl bromide **(4)** as a colourless liquid in 26 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.07 (s, 6 H, 2xCH_3, $Cq(CH_3)_2$), 1.42-1.45 (m, 4 H, 2xCH_2), 1.55-1.60 (m, 4 H, 2xCH_2), 1.71-1.74 (m, 6 H, 3x CH_2), 5.02 (dd, *J* = 17.5 Hz, 1.5 Hz, 1 H, CHH, CHH=CH), 5.05 (dd, *J* = 10.8 Hz, 1.5 Hz, 1 H, CHH, CHH=CH), 6.06 (dd, *J* = 17.5 Hz, 10.8 Hz, 1 H, CH, CHH=CH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 22.2 (CH_2), 22.7 (2xCH_3, $Cq(CH_3)_2$), 24.6 (CH_2), 28.1 (2xCH_2), 31.9 (2xCH_2), 45.3

(Cq), 76.7 (Cq-OH), 112.7 (CH_2, $CH=CH_2$), 146.2 (CH, $CH=CH_2$). IR(KBr/film) $\tilde{\nu}$ = 3490 (s), 3080 (m), 2964 (vs), 2922 (vs), 2851 (vs), 1634 (m), 1471 (vs), 1447 (s), 1414 (s), 1379 (s), 1345 (w), 1328 (w), 1227 (w), 1126 (s), 1103 (m), 1085 (m), 1063 (w), 1041 (w), 1013 (vs), 986 (s), 909 (vs) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 179 (M^+-1; 21 %), 127 (21), 123 (68), 109 (100), 97 (71), 81 (50), 67 (21), 55(15). $C_{13}H_{24}O$ (196.33): Calc. C, 79.5; H, 12.3. Found C, 79.0; H, 12.4.

1-(1,1-Dimethylallyl)-2,4,4-trimethylcyclopentanol (3e). Obtained from **5e** and prenyl bromide **(4)** as a colourless liquid in 62 % yield. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.92 (d, *J* = 6.7 Hz, 3 H, CH_3, CH-CH_3), 0.97 (s, 3 H, CH_3, $Cq(CH_3)_2$), 1.04 (s, 3 H, CH_3, $Cq(CH_3)_2$), 1.06 (s, 3 H, CH_3, $Cq(CH_3)_2$), 1.09 (s, 3 H, CH_3, $Cq(CH_3)_2$), 1.42-1.83 (5 H, 2xCH_2, 1 H, OH), 2.20 (qt, *J* = 6.7 Hz, 2.3 Hz, 1 H, CH-CH_3), 5.04 (dd, *J* = 15.6 Hz, 1.4 Hz, 1 H, 1xCHH, CHH=CH), 5.08 (dd, *J* = 9.7 Hz, 1.4 Hz, 1 H, 1xCHH, CHH=CH), 6.00 (dd, *J* = 15.6 Hz, 9.7 Hz, 1 H, 1xCH, CH_2=CH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 14.7 (CH_3), 22.8 (CH_3), 23.4 (CH_3), 31.0 (CH_3), 31.6 (CH_3), 34.3 (Cq), 38.4 (CH), 43.8 (Cq), 49.8 (CH_2), 51.8 (CH_2), 85.7 (C-OH), 113.3 (CH_2, $CH=CH_2$), 145.8 (CH, $CH=CH_2$). IR(KBr/film) $\tilde{\nu}$ = 3490 (s), 3080 (m), 2964 (vs), 2922 (vs), 2851 (vs), 1634 (m), 1471 (vs), 1447 (s), 1414 (s), 1379 (s), 1345 (w), 1328 (w), 1227 (w), 1126 (s), 1103 (m), 1085 (m), 1063 (w), 1041 (w), 1013 (vs), 986 (s), 909 (vs) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 179 (M^+-1; 21 %), 127 (21), 123 (68), 109 (100), 97 (71), 81 (50), 67 (21), 55(15). $C_{13}H_{24}O$ (196.3): Calc. C, 79.5; H, 12.3; Found C, 79.1; H, 12.3.

2-(1,1-Dimethyl-allyl)-2-hydroxycyclopentane-ethylcarboxylate (3f). Obtained from **5f** and prenyl bromide **(4)** as a colourless liquid in 50 % yield. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.03 (s, 3 H, 1xCH_3, $Cq(CH_3)_2$), 1.06 (s, 3 H, 1xCH_3, $Cq(CH_3)_2$), 1.28 (t, *J* = 7.2 Hz, 1 H), 2.71 (t, *J* = 9.3 Hz, 1 H, 1xCH, CH-CO_2Et), 4.14 (q, *J* = 7.2 Hz, 2 H, CH_2, $CO_2CH_2CH_3$), 4.34 (d, *J* = 1.4 Hz, 1 H, Cq-OH), 5.01 (dd, *J* = 10.9 Hz, 1.4 Hz, 1 H, 1xCHH, $CH=CH_2$), 5.03 (dd, *J* = 17.5 Hz, 1.4 Hz, 1 H, 1xCHH, $CH=CH_2$), 5.98 (dd, *J* = 17.5 Hz, 10.9 Hz, 1H, $CH=CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 14.0 (CH_3,CH_2CH_3), 22.1 (CH_2), 22.66 (1xCH_3, $Cq(CH_3)_2$), 22.71 (1xCH_3, $Cq(CH_3)_2$), 30.6 (CH_2), 35.4 (CH_2), 43.6 (Cq), 47.0 (CH, $CHCO_2Et$), 60.7 (CH_2, OCH_2CH_3), 87.0 (Cq-OH), 112.88 (1xCH_2, $CH=CH_2$), 144.9 (1xCH, $CH=CH_2$), 177.6 (C=O). IR(KBr/film) $\tilde{\nu}$ = 3471 (s), 3083 (w), 2978, 2876 (vs), 1708 (vs), 1637 (w), 1468 (s), 1449 (s), 1416 (m), 1394 (s),1377 (s), 1360 (vs), 1348 (s), 1305 (s), 1261 (m),1245 (m), 1178 (vs), 1158 (vs), 1098 (s), 1075 (s), 1039 (s), 1015 (s) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 210 (M^+-16, 100 %), 135 (15), 111(3). $C_{13}H_{22}O_3$ (226.31): Calc. C, 69.0; H, 9.8; Found C, 68.8; H, 9.5.

4-(1,1-Dimethyl-allyl)-tetrahydropyran-4-ol (3g). Obtained from **5g** and prenyl bromide **(4)** as white crystals in 54 % yield.^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.05 (s, 6 H, 2xCH_3, $Cq(CH_3)_2$), 1.38 (br *d*, *J* = 13.6 Hz, 2 H, 2xCHH), 1.61 (brs, 1 H, OH), 1.87 (ddd, *J* = 12.9 Hz, 5.5 Hz, 2 H, 2xCHH), 3.77 (ddd, *J* = 12.2 Hz, 5.5 Hz, 2.1 Hz, 4 H, 2xCH_2, CH_2-O), 5.10 (dd, *J* = 17.6 Hz, 1.3 Hz, 1 H, 1xCHH, $CH=CH_2$), 5.16 (dd, *J* = 10.8 Hz, 1.3 Hz, 1 H, 1xCHH, $CH=CH_2$), 5.95 (dd, *J* = 17.6 Hz, 10.8 Hz, 1 H, 1xCHH, $CH=CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 21.3 (2xCH_3, $Cq(CH_3)_2$), 32.0 (2xCH_2), 43.9 (Cq), 63.9 (2xCH_2), 72.2 (Cq-OH), 114.8 (CH_2, $CH=CH_2$), 144.2 (CH, $CH=CH_2$). IR(KBr) $\tilde{\nu}$ = 3422 (vs), 3082 (w), 3007

(w), 2978 (s), 2966 (s), 2954 (s), 2932 (s), 2883 (s), 1637 (w), 1475 (m), 1464 (w), 1416 (w), 1392 (m), 1385 (m), 1358 (s), 1307 (m), 1266 (w), 1244 (m), 1203 (w), 1136 (s), 1113 (m), 1094 (vs), 1070 (s), 1015 (s), 955 (s), 909 (s), 847 (vs) cm^{-1}. MS (EI, 70 eV): m/z (%) = 153 (M^+-17, 7), 109 (8), 101 (60), 83 (53). HR-MS: $C_{10}H_{18}O_2$ (170.25, M^+-17): calc. 153.1279; found: 153.1280. Calc. C, 70.6; H, 10.7; Found C, 70.0; H, 10.5.

General procedure for the carbonylation/cyclization reaction of homoallylic alcohols 3a-g:

The reaction were carried out in an autoclave. A solution of the homoallylic alcohol (4.8 mmol) and $[Rh(cod)Cl]_2$ (1 mol%) or $Rh(CO)_2acac$ in 10 ml anhydrous dioxane (in case of product **15c** methanol as solvent) was heated for 20 h or 65 h to 110 °C under 30 or 90 bar carbon monoxide and 20 bar hydrogen atmosphere. The crude product obtained after rotary evaporation of the solvent was filtered through neutral alumina (eluated with diethyl ether and further with ethanol). After evaporation of the solvent we obtained the pure product unless otherwise noted.

5,5-Dimethyl-tetrahydro-pyran-2-ol (9) Obtained from **8**[15] as a colourless liquid in 66 % yield. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.91 (s, 3 H, 1xCH_3, Cq(CH_3)$_2$), 0.96 (s, 3 H, 1xCH_3, Cq(CH_3)$_2$), 1.27-1.77 (m, 4 H, CH_2, cyclic), 2.51 (br s, OH), 3.17 (d, J = 11.0 Hz, 1 H, CHH-O), 3.59 (d, J = 11.0 Hz, 1 H, CHH-O), 4.88 (dd, J = 5.4 Hz, 2.7 Hz, 1 H, CH-OH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 24.6 (1xCH_3, Cq(CH_3)$_2$), 24.9 (1xCH_3, Cq(CH_3)$_2$), 27.7 (CH_2), 29.2 (Cq), 32.9 (CH_2), 72.3 (CH_2, CH_2O), 93.5(CH, CH-OH). IR(KBr/film) $\tilde{\nu}$ = 3383 (s), 2950 (vs), 2867 (s), 1450 (m), 1367 (m), 1133 (m), 1050 (vs) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 129 (3%), 113 (100), 95 (41), 84 (9), 69 (26), 56 (59). $C_7H_{14}O_2$ (130.19): Calc. C, 64.6; H, 10.8; Found C, 64.4; H, 10.5.

1-Oxa-spiro[5.5]undec-2-ene (11). Obtained from **10**[16] as a colourless liquid in 37 % yield after chromatography on silica, eluent petrolether/MTBE mixtures with increasing polarity. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.51 (m, 14 H, 7xCH_2, cyclic), 1.96 (ddd, J = 6.3 Hz, 3.6 Hz, 1.9 Hz, 2 H, CH_2-CH=CH), 4.60 (dt, J = 5.2 Hz, 3.6 Hz, 1 H, O-CH=CH), 6.29 (dt, J = 5.2 Hz, 1.7 Hz, 1 H, O-CH=CH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 17.1 (CH_2), 21.7 (CH_2), 26.0 (CH_2), 31.9 (CH_2), 34.7 (CH_2), 73.9 (Cq, spiro), 99.1 (CH, O-CH=CH), 142.0 (CH, O-CH=CH), GC-FTIR: $\tilde{\nu}$ = 3069 (w), 2942 (vs), 2865 (m), 1649 (m), 1453 (w), 1249 (m), 1073 (s) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 152 (M^+, 67 %), 135 (57), 121 (24), 108 (10), 95 (33), 81 (100), 67 (43), 55 (19). $C_{10}H_{16}O$ (152.24): Calc. C, 78.9; H, 10.6; Found C, 78.7; H, 10.6.

3-Methyl-1-oxa-spiro[4.5]decan-2-ol (12) [17]. Obtained from **10** as a colourless liquid in 15 % yield as a 1:1 mixture of diastereomers after chromatography on silica, eluent petrolether/MTBE mixtures with increasing polarity. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): δ =1.06 (d, J = 6.6 Hz, 3 H, 1xCH_3, CH-CH_3), 1.08 (d, J = 6.9 Hz, 3 H, 1xCH_3, CH-CH_3), 1.29-1.68 (m, 22 H, CH_2, cyclic), 1.92 (dd, J = 11.9 Hz, 7.7 Hz, 1 H), 2.12 (dd, J = 12.4 Hz, 8.0 Hz, 1 H), 2.23-2.28 (m, 2 H), 3.57 (br s, 1 H), 4.07 (d, J = 3.1 Hz, 1 H), 5.09 (m, 1 H, CH-OH), 5.24 (m, 1 H, CH-OH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 12.9 (CH_3), 17.8 (CH_3), 23.7

(CH_2), 23.8 (CH_2), 23.9 (CH_2), 24.0 (CH_2), 25.3 (CH_2), 25.4 (CH_2), 37.6 (CH_2), 38.1 (CH), 39.4 (CH_2), 39.5 (CH_2), 40.7 (CH), 41.0 (CH_2), 84.3 (Cq, spiro), 84.4 (Cq, spiro), 98.9 (CH, CHOH), 104.3 (CH, CH-OH). IR(KBr/film) $\tilde{\nu}$ = 3405 (s), 3396 (s), 2932 (vs), 2857 (vs), 1449 (s), 1360 (w), 1338 (w), 1329 (w), 1291 (w), 1260 (w), 1167 (m), 1155 (m), 1142 (m), 1109 (m), 1080 (m), 1022 (vs), 988 (vs), 931.6 (s) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 153 (M^+-17, 100%), 135 (9), 127 (21), 109 (18), 99 (18), 86 (15), 81 (56), 71 (21), 67 (35), 55 (82). $C_{10}H_{18}O_2$ (170.25): Calc. C, 70.6; H, 10.7; Found C, 70.6; H, 10.6.

1-Oxa-spiro[5.5]undecan-2-one (13)[3a,3b, 18]. Obtained from **10** as a colourless liquid in traces after chromatography on silica, eluent petrolether/MTBE mixtures with increasing polarity.

10,10-Dimethyl-6-oxa-spiro[4.5]dec-7-ene (14a). Obtained from **3a** as a colourless liquid in 39 %-43 % yield after chromatography on silica, eluent hexane/ether 2 : 1. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.93 (s, 6 H, 2xCH_3,Cq(CH_3)$_2$), 1.54-1.80 (m, 10 H, 5xCH_2), 4.62 (dt, *J* = 6.1 Hz, 3.1 Hz, 1 H, CH, CH=CH-O), 6.15 (dt, *J* = 6.1 Hz, 1.8 Hz, 1 H, CH, CH=CH-O). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 24.5 (2xCH_3, Cq(CH_3)$_2$,), 25.0 (2xCH_2), 32.82 (Cq), 32.85 (2xCH_2), 34.5 (CH_2), 91.7 (Cq), 99.9 (CH, CH=CH-O), 141.4 (CH, CH=CH-O). IR(KBr/film) $\tilde{\nu}$ = 3058 (m), 2963 (s), 2908 (s), 2873 (s), 2837 (m), 1653 (m), 1466 (m), 1451 (m), 1386 (m), 1368 (m), 1257 (s), 1233 (m), 1167 (m), 1136 (m), 1072 (vs), 1031 (s), 977 (m), 959 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 166 (M^+, 46%), 149 (43), 133 (5), 109 (100), 95 (32), 81 (34), 67 (52), 55 (11). $C_{10}H_{18}O$ (166.26)

10,10-Dimethyl-6-oxa-spiro[4.5]decan-7-ol (15a). Obtained from **3a** as white crystals in 15 % yield after chromatography on silica, eluent hexane/ether 2 : 1. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.85 (s, 3 H, 1xCH_3,Cq(CH_3)$_2$), 1.04 (s, 3 H, 1xCH_3,Cq(CH_3)$_2$), 1.41-1.54 (m, 2 H, CH_2, cyclic), 1.57-1.66 (m, 6 H, CH_2, cyclic), 1.72-1.82 (m, 1 H, OH, CH_2, cyclic), 2.91 (dd, *J* = 6.4 Hz, 1 H, CH_2, cyclic), 4.89 (m, 1 H, CH-OH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 22.9 (1xCH_3, Cq(CH_3)$_2$), 23.7 (CH_2), 25.1 (CH_2), 25.5 (1xCH_3, Cq(CH_3)$_2$), 30.0 (CH_2), 30.4 (CH_2), 33.6 (Cq), 35.0 (CH_2), 91.2 (CH-OH), 91.5 (CH-OH). IR(KBr) $\tilde{\nu}$ = 3290 (s), 2961 (vs), 2908 (s), 2868 (s), 2852 (m), 1461 (s), 1383 (s), 1364 (s), 1354 (m), 1330 (w), 1308 (w), 1138 (s), 1105 (m), 1056 (vs), 1013 (vs), 988 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 167 (M^+-17, 41 %), 149 (100), 109 (18), 95 (12), 85 (44) 81 (18), 67 (35), 55 (15). $C_{11}H_{20}O_2$ (184.28)

5,5-Dimethyl-1-oxa-spiro[5.5]undec-2-ene (14b). Obtained from **3b** as a colourless liquid in 39-64% yield (depend on the used conditions see table 2) after chromatography on silica, eluent hexene/ether mixtures with increasing polarity. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.92 (s, 3 H, 2xCH_3,Cq(CH_3)$_2$), 1.28 (ddd, *J* = 12.9 Hz, 4.7 Hz, 3 H, 1xCH_2, 1xCHH), 1.51-1.83 (m, 9 H, 4xCH_2, 1xCHH), 4.58 (dt, *J* = 6.1 Hz, 3.1 Hz, 1 H, CH=CH-O), 6.24 (dt, *J* = 6.1 Hz, 1.8 Hz, 1 H, CH=CH-O). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 21.5 (2xCH_2, CH_2), 24.1 (2xCH_3, Cq(CH_3)$_2$), 25.7 (CH_2), 28.1 (CH_2), 33.9 (Cq), 34.1 (2xCH_2, CH_2), 79.1 (Cq), 99.4 (CH=CH-CH_2),140.9 (O-CH=). IR(KBr/film) $\tilde{\nu}$ = 3058 (m), 2959 (vs), 2937 (vs), 2862 (s), 2851 (s), 1731 (w), 1653 (s), 1464 (m), 1447 (s), 1387 (s), 1368 (m), 1256 (s), 1231 (s), 1151 (m), 1127 (m), 1037 (m), 1014 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 180 (M^+-1, 13%), 163 (69), 123 (62), 109 (15), 95 (21), 81 (69), 67 (31), 55 (15). $C_{12}H_{20}O$ (180.29): Calc. C, 79.9; H, 11.2; Found C, 79.6; H, 11.5.

5,5-Dimethyl-1-oxa-spiro[5.5]undecan-2-ol (15b). Obtained from **3b** as white crystals in 48 % yield after chromatography on silica, eluent hexene/ether mixtures with increasing polarity. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.83 (s, 3 H, 1xCH_3, Cq(CH_3)$_2$), 1.02 (s, 3 H, 1xCH_3, Cq(CH_3)$_2$), 1.21-1.35 (m, 4 H, CH_2, cyclic), 1.46-1.58 (m, 4 H, CH_2, cyclic), 1.65-1.77 (m, 5 H, CH_2, cyclic), 2.08 (d, J = 13.8 Hz, 1 H, CHH, cyclic), 2.80 (d, J = 5.6 Hz, 1 H, CHH-cyclic), 4.93 (m, J = 5.6 Hz,1 H, CH, CH-OH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 20.9 (CH_2), 21.3 (CH_2), 22.9 (1xCH_3, Cq(CH_3)$_2$), 25.5 (1xCH_3, Cq(CH_3)$_2$), 25.8 (CH_2), 27.1 (CH_2), 30.0 (CH_2), 31.2 (CH_2), 33.7 (CH_2), 34.3 (Cq), 79.1 (Cq), 90.3 (CH, CH-OH). IR(KBr) $\tilde{\nu}$ = 3397 (s), 2943 (vs), 2862 (s), 1465 (m), 1453 (s), 1385 (m), 1366 (m), 1262 (m), 1173 (w), 1153 (m), 1137 (m), 1119 (s), 1075 (s), 1058 (vs), 1037 (s), 1016 (vs), 995 (w), 967 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 181 (M^+-17, 12%), 163 (100), 123 (3), 107 (3), 81 (44), 67 (6), 55 (9). $C_{12}H_{22}O_2$ (198.30): Calc. C, 72.7; H, 11.2; Found C, 72.3; H, 11.3.

2-Methoxy-5,5-dimethyl-1-oxa-spiro[5.5]undecane (15h). Obtained from **3b** as a colourless liquid in 50 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.82 (s, 3 H, 1xCH_3,Cq(CH_3)$_2$), 1.02 (s, 3 H, 1xCH_3,Cq(CH_3)$_2$), 1.12-1.31 (m, 4 H, CH_2, cyclic), 1.48-1.54 (m, 4 H, CH_2, cyclic), 1.56-1.62 (m, 1 H, CH_2, cyclic), 1.66-1.80 (m, 4 H, CH_2, cyclic), 2.12 (d, J = 13.9 Hz, 1 H, CH_2, cyclic), 3.50 (s, 3 H, CH_3, OCH_3), 4.48 (dd, J = 8.5 Hz, 4.0 Hz, 1 H, CH, O-CH-O). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 20.7 (CH_2), 20.9 (CH_2), 22.3 (1xCH_3, Cq(CH_3)$_2$), 25.3 (1xCH_3, Cq(CH_3)$_2$), 25.5 (CH_2), 26.4 (CH_2), 27.6 (CH_2), 31.1 (CH_2), 33.5 (CH_2), 34.0 (Cq, Cq(CH_3)$_2$), 55.7 (CH_3, O-CH_3), 77.8 (Cq), 96.5 (CH, CH-OCH_3). IR(KBr/film) $\tilde{\nu}$ = 2939 (vs), 2860 (s), 2833 (m), 1477 (m), 1463 (m), 1454 (m), 1392 (m), 1384 (s), 1365 (m) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 211 (M^+-1, 10 %), 195 (5), 181 (18), 163 (100), 124 (5), 114 (5), 86 (72), 81 (8), 71 (8), 58 (31). $C_{13}H_{24}O_2$ (212.33): Calc. C, 73.5; H, 11.4; Found C, 73.3; H, 11.7.

5,5-Dimethyl-1-oxa-spiro[5.6]dodec-2-ene (14c). Obtained from **3c** as a colourless liquid in 95 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.93 (s, 6 H, 2xCH_3,Cq(CH_3)$_2$), 1.44-1.56 (m, 4 H, CH_2, cyclic), 1.57-1.71 (m, 6 H, CH_2, cyclic), 1.75-1.79 (m, 4 H, CH_2, cyclic), 4.56 (dt, J = 6.1 Hz, 3.0 Hz, 1 H, CH, CH=CH-O), 6.20 (dt, J = 6.1 Hz, 1.8 Hz, 1 H, CH, CH=CH-O).^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 23.1 (2xCH_2), 24.5 (2xCH_3, Cq(CH_3)$_2$), 29.1 (2xCH_2, CH_2), 32.9 (CH_2), 34.6 (CH_2), 35.0 (Cq), 83.0 (Cq), 99.2 (CH, CH=CH-O), 141.4 (CH, CH=CH-O). IR(KBr/film) $\tilde{\nu}$ = 3057 (w), 2957 (vs), 2925 (vs), 2852 (s), 1467 (m), 1456 (m), 1387 (m), 1368 (w), 1250 (s), 1124 (m), 1074 (vs)1064 (s) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 193 (M^+-1, 6%), 175 (18), 162 (9), 137 (38), 123 (9), 109 (12), 95 (82), 81 (100), 67 (35), 55 (35). $C_{13}H_{22}O$ (194.32): Calc. C, 80.4; H, 11.4; Found C, 80.0; H, 11.4.

5,5-Dimethyl-1,9-oxa-spiro[5.7]tridec-2-ene (14d). Obtained from **3d** as a colourless liquid in 70 % yield after chromatography on silica, eluent Petrolether/MTBE mixtures with increasing polarity. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.95 (s, 6 H, 2xCH_3,Cq(CH_3)$_2$), 1.43-1.89 (m, 16 H, 8xCH_2), 4.55 (dt, J = 6.3 Hz, 3.4 Hz, 1 H, CH=CH-O), 6.19 (dd, J = 4.4 Hz, 1.7 Hz, 1 H, CH=CH-O). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 22.2 (2xCH_2), 24.8 (2xCH_3), 25.1 (2xCH_2), 28.1 (2xCH_2), 28.8 (CH_2), 35.1 (CH_2), 35.2 (Cq), 82.0 (Cq, spiro), 98.9 (CH, CH=CH-O), 141.21 (CH, CH=CH-O). IR(KBr/film) $\tilde{\nu}$ = 3057 (m), 2963 (vs), 2921 (vs), 2850 (vs), 1653 (vs), 1471 (s), 1387 (m), 1369 (m), 1321 (m), 1249 (s), 1069 (vs) cm^{-1}.

GC-MS (EI, 70 eV): m/z (%) = 209 (M^++1, 4 %), 191 (53), 177 (16), 162 (12), 151 (31), 135 (8), 123 (8), 109 (49), 95 (100), 81 (63), 67 (55), 55 (29). $C_{14}H_{24}O$ (208.35): Calc. C, 80.7; H, 11.6; Found C, 80.4; H, 11.4.

5,5-Dimethyl-1-oxa-spiro[5.7]tridecan-2-ol (15d). Obtained from **3d** as a colourless oil in 9 % yield after chromatography on silica, eluent petrolether/MTBE mixtures with increasing polarity. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.87 (s, 3 H, 1xCH_3, Cq-CH_3), 1.06 (3 H, 1xCH_3, Cq-CH_3), 1.29-1.84 (m, 18 H, CH_2, cyclic), 3.71 (s, 1 H, OH), 4.87 (dd, *J*= 9.2 Hz, 2.2 Hz, 1H, CH, CH-OH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 20.4 (CH_2), 21.7 (CH_2), 24.1 (CH_3), 25.0 (CH_2), 25.7 (CH_3), 27.0 (CH_2), 27.7 (CH_2), 28.4 (CH_2), 29.7 (CH_2), 32.0 (CH_2), 34.9 (CH_2), 35.3 (Cq), 81.6 (Cq, Spiro), 90.8 (CH, CH-OH). IR(KBr/film) $\tilde{\nu}$ = 3409 (s), 2954 (vs), 2918 (vs), 2871 (s), 1476 (s), 1452 (s), 1385 (s), 1368 (s), 1169 (m), 1157 (m), 1121 (s), 1099 (s), 1059 (vs), 1040 (s), 1017 (s) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 226 (M^+, 4 %), 209 (7), 191 (26), 127 (100), 109 (63), 95 (33), 81 (33), 67 (89), 55 (59). HR-MS:$C_{14}H_{26}O_2$ (226.36): Calc. 226.1933; Found. 226.1933

1,3,3,10,10-Pentamethyl-6-oxa-spiro[4.5]dec-7-ene (14e). Obtained from **3e** as a colourless liquid in 69 % yield after chromatography on silica, eluent hexene/ether mixtures with increasing polarity. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.87 (s, 3 H, 1xCH_3,Cq(CH_3)$_2$), 0.91 (s, 6 H, 2xCH_3, Cq(CH_3)$_2$), 0.96 (d, *J* = 6.5 Hz, 3 H, 1xCH_3, CH-CH_3), 0.98 (s, 3 H, CH_3), 1.42-1.78 (m, 6 H, CH_2, cyclic, OH), 2.19 (m, 1 H, CH, CH-CH_3), 4.49(m_c, 1 H, *J* = 6.0 Hz, 4.8 Hz, 2.5 Hz, 1.26 Hz, CH, CH=CH-O), 6.10 (d, *J* = 6.0 Hz, 1 H, CH, CH=CH-O). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 15.0 (CH_3), 24.3 (CH_3), 25.6 (CH_3), 30.8 (CH_3), 31.2 (CH_3), 33.2 (Cq), 34.6 (Cq), 35.6 (CH_2), 37.8 (CH), 49.0 (CH_2), 50.1 (CH_2), 90.8 (Cq), 99.1 (CH, CH=CH-O), 141.4 (CH, CH=CH-O). IR(KBr/film) $\tilde{\nu}$ = 3059 (m), 2955 (vs), 2878 (s), 2865 (s), 2842 (m), 1738 (m), 1653 (s), 1462 (s), 1386 (s), 1376 (m), 1366 (m), 1254 (s), 1232 (s), 1067 (vs), 1044 (w) cm^{-1}. MS (EI, 70 eV): m/z (%) = 207 (M^+-1, 12 %), 190 (35), 175 (4), 164 (4), 151 (54), 136 (31), 121 (4), 109 (31), 95 (46), 81 (27), 67 (8), 55(12). $C_{14}H_{24}O$ (208.34): Calc. C, 80.7; H, 11.6; Found C, 80.6; H, 11.7.

Ethyl 10,10-Dimethyl-6-oxa-spiro[4.5]dec-7-ene-1-carboxylate (14f). Obtained from **3f** as a colourless liquid in 21 % yield after chromatography on silica, eluent petrolether/MTBE mixtures with increasing polarity. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.96 (s, 3 H, 1xCH_3, Cq(CH_3)$_2$), 1.06 (s, 3 H, 1xCH_3,Cq(CH_3)$_2$), 1.24 (t, 3 H, CH_3, $CO_2CH_2CH_3$) 1.57-2.02 (m, 7 H, cyclic), 2.94 (dd, *J* = 8.1 Hz, 5.3 Hz, 1 H, CH), 4.04-4.19 (m, 2 H, CH_2, $CO_2CH_2CH_3$), 4.61 (dt, *J* = 6.1 Hz, 3.1 Hz, 1 H, CH, CH=CH-O), 6.14 (dt, *J* = 6.1 Hz, 1. 8 Hz, 1 H, CH, CH=CH-O). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 13.9 (CH_3, $CO_2CH_2CH_3$), 23.7 (CH), 24.5 (CH_2), 24.9 (2xCH_3, Cq(CH_3)$_2$), 30.9 (CH_2), 33.8 (CH_2), 34.1 (CH_2), 34.5 (Cq), 48.8 (CH), 59.9 (CH_2, $CO_2CH_2CH_3$), 92.0 (Cq), 99.7 (CH, CH=CH-O), 141.45 (CH, CH=CH-O), 173.19 (C=O, $CO_2CH_2CH_3$). IR(KBr/film) $\tilde{\nu}$ = 3061 (w), 2969 (vs), 2902 (s), 2877 (s), 2842 (m), 1738 (vs), 1652 (s), 1466 (m), 1452 (m), 1391 (m), 1368 (m), 1341 (m), 1310 (w), 1250 (vs), 1221 (m), 1193 (s), 1175 (s), 1150 (s), 1116 (w) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 239 (M^++1, 100 %), 221 (29), 193 (8), 165 (8), 147 (29), 135 (8), 121 (8), 109 (50), 100 (13), 93 (4), 81 (4), 67 (8), 55 (8). $C_{14}H_{22}O_3$ (238.32): Calc. C, 70.6; H, 9.3; Found C, 70.3; H, 9.0.

Ethyl 7-hydroxy-10,10-dimethyl-6-oxa-spiro[4.5]decane-1-carboxylate (15f). Obtained from **3f** as a colourless liquid in 26 % yield after chromatography on silica, eluent petrolether/MTBE mixtures with increasing polarity. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.84 (s, 3 H, 1xCH_3,Cq(CH_3)$_2$), 1.17 (s, 3 H, 1xCH_3,Cq(CH_3)$_2$), 1.25 (t, J = 7.0 Hz, 3 H, CH_3, $CO_2CH_2CH_3$) 1.38-2.18 (m, 7 H, CH_2, cyclic), 2.89 (t, J = 8.3 Hz, 1 H), 3.70 (s, 1 H, OH), 4.06-4.20 (m, 2 H, CH_2, $CO_2CH_2CH_3$), 4.85 (dd, J = 9.4 Hz, 2.6 Hz, 1 H, CH-OH). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 14.1 (CH_3, $CO_2CH_2CH_3$), 22.9 (1xCH_3, Cq(CH_3)$_2$), 25.2 (CH_2), 25.6 (1xCH_3, Cq(CH_3)$_2$), 29.1 (CH_2), 29.7 (CH_2), 33.6 (CH_2), 35.0 (CH_2), 35.1 (Cq), 50.1 (CH), 60.1 (CH_2, $CO_2CH_2CH_3$), 91.0 (Cq, spiro), 92.1 (CH, CH-OH), 173.5 (C=O, $CO_2CH_2CH_3$). IR(KBr/film) $\tilde{\nu}$ = 3450 (s), 2972 (vs), 2874 (s), 1732 (vs), 1468 (s), 1447 (s), 1388 (s), 1369 (s), 1343 (s), 1298 (s), 1260 (s), 1202 (s), 1174 (vs), 1150 (vs), 1120 (vs), 1100 (vs), 1055 (vs), 1011 (vs) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 255 (M^+-1, 53 %), 237 (100), 209 (12), 154 (12), 126 (12), 111 (29), 70 (35), 55 (59). $C_{14}H_{24}O_4$ (256.34): Calc. C, 65.6; H, 9.4; Found C, 65.5; H, 9.1.

5,5-Dimethyl-1,9-dioxa-spiro[5.5]undec-2-ene (14g). Obtained from **3g** as a colourless liquid in 61 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 0.93 (s, 6 H, 2xCH_3,Cq(CH_3)$_2$), 1.61 (dd, J = 12.8 Hz, 1.0 Hz, 2 H, CqCHH, cyclic), 1.70-1.78 (m, 4 H, CH_2, cyclic), 3.70 (ddd, J = 11.5 Hz, 2.1 Hz, 2 H, 2xCHH, O-CH_2, cyclic), 3.78 (dd, J = 11.5 Hz, 5.5 Hz, 2 H, 2xCHH, O-CH_2, cyclic), 4.63 (dt, J = 6.1 Hz, 3.1 Hz,1 H, CH, CH=CH-O), 6.25 (dt, J = 6.1 Hz, 1.8 Hz, 1 H, CH, CH=CH-O). ^{13}C NMR (100 MHz, $CDCl_3$, 20 °C): δ = 23.4 (2xCH_3, Cq(CH_3)$_2$), 28.5 (CH_2), 33.2 (2xCH_2, CH_2), 33.4 (Cq), 63.3, (2xCH_2, CH_2O), 76.6 (Cq), 99.5 (CH, CH=CH-O), 140.4 (CH, CH=CH-O). IR(KBr) $\tilde{\nu}$ = 3059 (m), 2964 (vs), 2936 (vs), 2910 (s), 2866 (vs), 2843 (s), 1651 (vs), 1470 (s), 1419 (w), 1389 (s), 1368 (m), 1359 (m), 1306 (m), 1257 (vs), 1244 (vs), 1227 (vs), 1159 (s), 1131 (vs), 1108 (vs), 1072 (vs), 1021 (vs), 976 (w), 960 (s), 897 (m), 844 (vs), 797 (w), 737 (s), 677 (m) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 182 (M^+, 16 %), 165 (3), 147 (8), 125 (59), 121 (14), 111 (19), 97 (11), 83 (100), 67 (32), 55 (45). $C_{11}H_{18}O_2$ (182.26): Calc. C, 72.5; H, 10.0; Found C, 72.5; H, 9.9.

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