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Tandem olefin metathesis/hydrogenation at ambient temperature: activation of ruthenium carbene complexes by addition of hydrides

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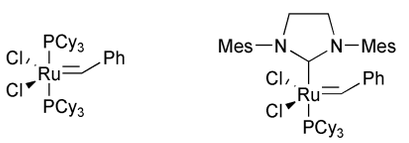
Sodium hydride activates ruthenium carbene complexes to catalyze hydrogenation reactions subsequent to ring closing olefin metathesis. Under these conditions, hydrogenation of cyclopentenols proceeds smoothly at ambient temperature and under 1 atm of hydrogen in toluene. An alternative protocol was developed that involves the formation of hydrogen *in situ* by reaction of excess sodium hydride with protic functional groups and water.

Introduction

Hydrogenation of C–C-double bonds resulting from olefin metathesis reactions[1] is an important issue in organic synthesis directed towards target molecules. While this transformation is normally achieved in a two-step procedure using palladium on charcoal as a hydrogenation catalyst,[2] some attempts have recently been made to improve the overall efficiency of these transformations by using tandem catalysis. One approach involves the use of two distinct catalysts. In the field of olefin metathesis this approach has been investigated by Grigg *et al.* for metathesis/Heck-reaction sequences[3] and very recently by Cossy *et al.* for metathesis/PtO_2-catalyzed hydrogenation reactions.[4] Alternatively, olefin metathesis catalysts **A** or **B** (Fig. 1) can be activated to mediate a non-metathesis transformation by changing the reaction conditions upon completion of the metathesis reaction.



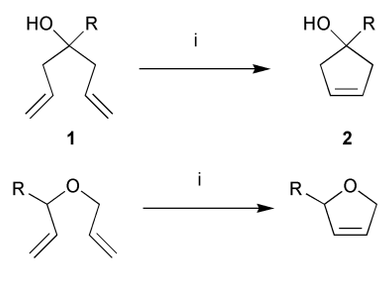
A **B**

Fig. 1 First (**A**) and second (**B**) generation Grubbs' catalyst.

Thus, it was demonstrated by Grubbs and co-workers that exposure of olefin metathesis reactions to a hydrogen atmosphere at elevated temperatures induces the conversion of the ruthenium carbene species to $RuHCl(H_2)(PCy_3)_2$,[5] which is an effective hydrogenation catalyst.[6] Tandem ring closing metathesis/double bond migration reactions *via* an *in situ* generated ruthenium hydride species have recently been published by Snapper and co-workers[7] and by one of us.[8] While Snapper and co-workers achieved activation of the metathesis catalyst for double bond migration reactions using an atmosphere of hydrogen diluted with nitrogen, we were able to demonstrate that ruthenium carbene complexes can be efficiently activated to promote double bond migration reactions by addition of hydride donor reagents in an aprotic solvent such as toluene. To the best of our knowledge, this method of activation was hitherto unknown for ruthenium carbene complexes.[9] In this contribution we describe that our method of activation also allows ring closing metathesis and ruthenium-catalyzed hydrogenation to be coupled in 'tandem'. In contrast to previously described RCM-hydrogenation tandem reactions our method does not require elevated temperatures.

Results and discussion

We have chosen diallyl carbinols **1** and diallyl ethers **4** as metathesis precursors for the project described in this contribution. Both give five-membered rings **2** and **5**, respectively, by ring closing metathesis (Scheme 1).



Scheme 1 *Reagents and conditions*: i, **B** (1.1–2.9 mol%), CH_2Cl_2, 20 °C (68%–92%) (*cf.* Table 1); ii, **A** (2.0 mol%), CH_2Cl_2, 20 °C, *cf.* ref. 8,10.

Five-membered carba- or oxacycles are normally hydrogenated at relatively low pressures of 1 atm[6b] While ring closing metathesis of diallyl ethers **4** is smoothly catalyzed by the first generation Grubbs' catalyst **A** (Fig. 1),[10] we experienced serious difficulties for the ring closing metathesis of diallyl carbinols **1** with catalyst **A**: comparatively high catalyst loadings of 5 to 8 mol% and elevated temperatures (refluxing toluene) over a relatively long period of time are required. Unidentified by-products, probably resulting from competing double bond isomerization reactions, were often observed under these conditions.[11] Diallyl carbinol **1a** turned out to be particularly unreactive, as no ring closing metathesis (RCM) product **2a** could be isolated from the reaction mixture when 5 mol% of **A** was used. In contrast, complete conversion was observed with 1.1 mol% of second generation catalyst **B** within two hours at 20 °C (Table 1). Generally, quantitative conversion and good isolated yields of cyclopentenols **2a**–**e** were obtained using 1.1 to 2.9 mol% of **B** at ambient temperature (Scheme 1 and Table 1). After we found conditions that allow smooth and rapid conversion of diallyl carbinols to the corresponding cyclopentenols, different additives were screened for their potential to activate the metathesis catalyst for hydrogenation reactions. To this end, **1a** was converted to the metathesis product **2a** in the presence of approximately 1.5 mol% of **B** under an argon atmosphere. After TLC indicated complete consumption of the starting material, additives as indicated in Table 2 were added to the reaction mixture which was then exposed to an atmosphere of hydrogen (1 atm) for 16 hours.

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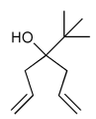
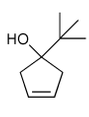
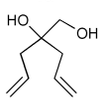
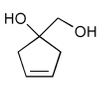
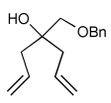
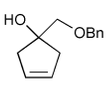
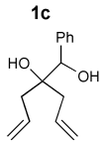
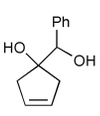
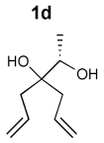
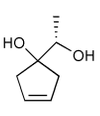
Table 1 RCM of diallyl carbinols with catalyst **B**[a]

Entry	Starting material	RCM product	**B** (mol%)	Yield
1	 **1a**	 **2a**	1.1 mol%	92%
2	 **1b**	 **2b**	2.0 mol%	68%
3	 **1c**	 **2c**	2.7 mol%	89%
4	 **1d**	 **2d**	2.9 mol%	74%
5	 **1e**	 **2e**	1.9 mol%	78%

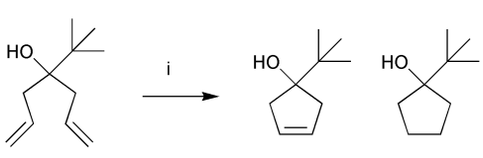
[a] For reaction conditions see legend to Scheme 1.

Table 2 Screening of hydride additives[a]

Entry	**B** (mol%)	Additive	Amount of additive (mol%)	Ratio **2a** : **3a**
1	1.7	None	—	>95 : 5
2	1.7	NaH	14	<5 : 95
3	1.5	$LiAlH_4$	13	1 : 2
4	1.6	CaH_2	13	>95 : 5

[a] See Scheme 2.

After this time the ratio of hydrogenated product **3a** and primary metathesis product **2a** was determined by NMR-spectroscopy of the crude reaction mixture. The results are summarized in Scheme 2 and Table 2.



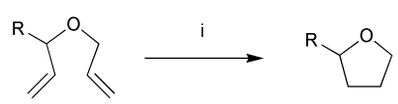
1a **2a** **3a**

Scheme 2 *Reagents and conditions*: i, **B** (1.5–1.7 mol%), toluene, 20 °C, 2 hours, then add additive, H_2, 20 °C, 16 hours (*cf.* Table 1).

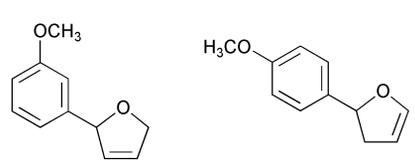
The result described in entry 1 clearly demonstrates that exposure of an olefin metathesis reaction mixture to an atmosphere of hydrogen at ambient temperature does not activate the ruthenium carbene species for hydrogenation reactions. Under these conditions, the primary RCM product **2a** is exclusively formed. The hydrogenated product **3a** could not be detected by H-NMR-spectroscopy of the crude reaction mixture. In sharp contrast, under otherwise identical conditions, the addition of 14 mol% of NaH (used as a dispersion in mineral oil) prior to exposure of the reaction mixture to hydrogen leads to complete conversion of the metathesis product **2a** to the cyclopentanol **3a** (entry 2, Table 2). Other inorganic hydrides proved to be significantly less effective: while addition of $LiAlH_4$ gives a ratio of hydrogenated and non-hydrogenated product of 2 : 1 after 16 hours (entry 3, Table 2), less than 5% of **3a** was obtained using CaH_2 as an additive (entry 4, Table 2). We applied the optimum protocol found for the conversion of **1a** to **3a** to a variety of other diallyl carbinols. The results are summarized in Table 3.

Remarkably, the protocol works well with substoichiometric amounts of NaH for all substrates containing only a tertiary alcohol, which is not readily deprotonated at ambient temperature.[12] For substrates **1d** and **1e** containing secondary alcohol groups, a large excess of NaH is required to achieve hydrogenation, presumably because the secondary hydroxy function is deprotonated faster than reaction of the ruthenium species with the hydride occurs.

Application of our protocol to diallyl ethers **4** gives tetrahydrofurans **6** in good overall yield. We examined three examples **4a**, **b** and **c**. Surprisingly, for the 3-methoxy derivative **4b** the hydrogenation step fails. In this case, the corresponding dihydrofuran **5b** was isolated. The reasons for this result are unclear. In the case of 4-methoxy substituted derivative **6c** a trace (approximately 5%) of the corresponding double bond migration product **7c** could be detected from the ^1H NMR spectrum of the crude reaction product (Scheme 3).



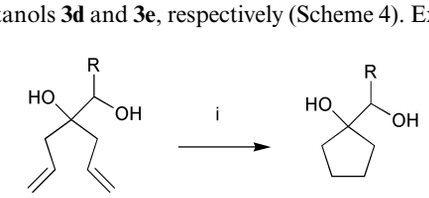
R = 2-$H_3COC_6H_4$-: **4a** — **6a** (74%)
R = 3-$H_3COC_6H_4$-: **4b** — **6b** (--)
R = 4-$H_3COC_6H_4$-: **4c** — **6c** (78%)



5b **7c**

Scheme 3 *Reagents and conditions*: **B** (2.0 mol%), toluene, 20 °C until **4** is completely consumed, then add NaH (13 mol%), H_2 (3 bar), 20 °C, 16 hours.

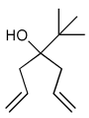
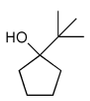
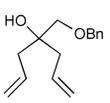
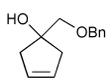
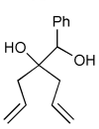
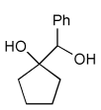
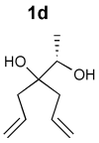
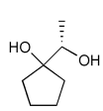
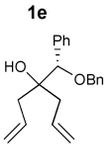
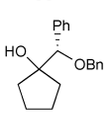
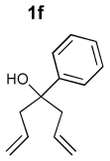
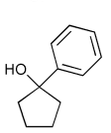
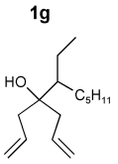
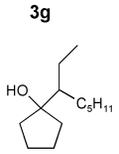
Finally, we investigated the possibility of using an excess of sodium hydride not only to activate the catalyst for hydrogenation reactions, but also as a source for hydrogen. Thus, the hydrogen required for the C–C-double bond hydrogenation step was generated *in situ* by the reaction of excess NaH with protic functional groups or with water. After completion of the olefin metathesis step (normally two hours), three to four equivalents of NaH were added to the reaction mixture and the vessel was stoppered tightly. During this period, the catalyst was activated for the hydrogenation step and molecular hydrogen was formed by deprotonation of the secondary alcohol functions. To make sure that enough hydrogen was present to achieve complete conversion, additional water was added after one hour. Using this protocol, substrates **1d** and **1e** were smoothly converted to cyclopentanols **3d** and **3e**, respectively (Scheme 4). Extension of



1d (R = Ph) — **3d** (78%)
1e (R = Me) — **3e** (75%)

Scheme 4 *Reagents and conditions*: i, **B** (2.0 mol%), toluene, 20 °C; then add NaH (4.0 eq.), 1 h, 20 °C; then add water (30 eq.), 16 hours.

Table 3 Sequential RCM/hydrogenation of diallyl carbinols[a]

Entry	Diallyl carbinol	**B** (mol%)	Cylopentanol	NaH (mol%)	Yield of **3**
1	 **1a**	1.7	 **3a**	14	92%
2	 **1c**	2.7	 **3c**	28	81%
3	 **1d**	2.0	 **3d**	300	81%
4	 **1e**	2.5	 **3e**	300	55%
5	 **1f**	2.0	 **3f**	38	61%
6	 **1g**	2.0	 **3g**	17	81%
7	 **1h**	2.0	 **3h**	42	78%

[a] *Reagents and conditions*: **B**, toluene, 20 °C until **1** is completely consumed, then add indicated amount of NaH, H_2 (1 bar), 20 °C, 16 hours.

this protocol to other substrates without secondary hydroxy functions will be investigated in due course.

In conclusion, we describe a method to activate ruthenium carbene complexes to catalyze hydrogenation reactions subsequent to the olefin metathesis step. In contrast to previous reports in the literature, we achieved formation of a ruthenium hydride species by treatment of the reaction mixture with catalytic amounts of inorganic hydrides, with NaH giving the best results. Products resulting from double bond migration reactions could only be detected in one example in trace amounts. This finding is quite remarkable, because we used toluene as a solvent in all experiments. Aromatic solvents have previously been described in the literature to facilitate ruthenium-catalyzed double bond migration reactions.[6b] A possible explanation why competing double bond migration is not a problem in our studies might be that our protocol does not require elevated temperatures.

Experimental

General

All experiments were conducted in dry reaction vessels under an atmosphere of dry argon. Solvents were purified by standard procedures. ^{1}H NMR spectra were recorded at 400 MHz, 500 MHz or 600 MHz in $CDCl_3$ with $CHCl_3$ (δ = 7.24 ppm) as an internal standard. Coupling constants are given in Hz. ^{13}C NMR spectra were recorded at 100 MHz or at 125 MHz in $CDCl_3$ with $CDCl_3$ (δ = 77.0 ppm) as an internal standard. The number of coupled protons was analyzed by APT experiments and is denoted by a number in parentheses following the chemical shift value. IR spectra were recorded as films on NaCl or KBr plates. The peak intensities are defined as strong (s), medium (m) or weak (w). Mass spectra were obtained at 70 eV. The ruthenium catalyst **B** was prepared following a literature procedure.[13] Preparation and ring closing metathesis of diallyl ethers **4** have been described previously.[10]

General procedure for the preparation of diallyl carbinols 1

A solution of allyl magnesium bromide (2.5 eq., *c* 1.0) in ether was added to a solution of the corresponding ester (1.0 eq.) in ether (*c* 0.5) at 0 °C. The reaction mixture was poured onto aqueous NH_4Cl solution, the organic layer was separated and the aqueous layer was extracted with ether. The combined organic extracts were dried with $MgSO_4$, filtered, and evaporated. The residue was purified by distillation or flash chromatography on silica. For the preparation of **1b**, **1d** and **1e**, 4.0 eq. of the allyl Grignard solution were required.

4-*tert*-Butyl-hepta-1,6-dien-4-ol (1a)

Obtained from ethyl pivaloate (5.00 g, 38.4 mmol) as a colour-

less liquid that was purified by flash chromatography (TLC: cyclohexane–MTBE 5 : 1 (v/v), R_f = 0.6). Yield 5.30 g, 82%. Analytical data are identical with those reported in the literature.[14a]

2-Allyl-pent-4-ene-1,2-diol (1b)

Obtained from butyl glycolate (3.96 g, 30.0 mmol) as a colourless liquid that was purified by flash chromatography (TLC: cyclohexane–MTBE 1 : 1 (v/v), R_f = 0.2). Yield 2.20 g, 52%. Analytical data are identical with those reported in the literature.[14b]

4-Benzyloxymethyl-hepta-1,6-dien-4-ol (1c)

Obtained from diallyl carbinol **1b** (1.00 g, 7.0 mmol) by treatment with NaH (0.38 g of a 60% dispersion in mineral oil, 9.4 mmol) and benzyl bromide (0.50 mL, 7.5 mmol) in THF (20 mL) as a colourless liquid that was purified by flash chromatography (TLC: cyclohexane–MTBE 2 : 1 (v/v), R_f = 0.8). Yield 0.80 g, 50%.[14c] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.28 (5H, Ph), 5.86 (dddd, 2H, J = 17.0, 10.5, 7.3, 7.3, –C*H*=CH$_2$), 5.12 (d, 2H, J = 10.5, –CH=C*H*$_2$), 5.10 (d, 2H, J = 17.0, –CH=C*H*$_2$), 4.56 (s, 2H, –OC*H*$_2$Ph), 3.35 (s, 2H, –C*H*$_2$OBn), 2.37–2.27 (5H, –C*H*$_2$CH=, –O*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0 (0), 133.5 (1), 128.3 (1), 127.7 (1), 127.6, (1), 118.4 (2), 74.9 (2), 73.4 (2), 73.2 (0), 41.3 (2).

2-Allyl-1-phenyl-pent-4-ene-1,2-diol (1d)

Obtained from *rac*-methyl mandelate (2.00 g, 12.0 mmol) as a colourless solid, mp 52 °C, that was purified by flash chromatography (TLC: cyclohexane–MTBE 1 : 1 (v/v), R_f = 0.5). Yield 2.30 g, 89%.[14d] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.28 (5H, Ph), 5.92 (dddd, 1H, J = 17.0, 10.2, 7.5, 7.5, –C*H*=CH$_2$), 5.81 (dddd, 1H, J = 17.2, 10.0, 7.3, 7.3, –C*H*=CH$_2$), 5.18 (d, 1H, J = 10.0, –CH=C*H*$_2$), 5.15 (d, 1H, J = 17.0, –CH=C*H*$_2$), 5.10 (d, 1H, J = 10.2, –CH=C*H*$_2$), 5.03 (d, 1H, J = 17.2, –CH=C*H*$_2$), 4.61 (s, 1H, –OC*H*Ph), 2.65 (br s, 1H, –O*H*), 2.42 (dd, 1H, J = 14.2, 7.5, –CH*H*CH=), 2.30–2.20 (3H, –O*H*, –CH*H*CH=), 1.98 (dd, 1H, J = 14.2, 7.4, –CH*H*CH=). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.9 (0), 133.6 (1), 133.5 (1), 128.0 (1), 127.9 (1), 127.7 (1), 119.0 (2), 118.9 (2), 77.5 (1), 75.7 (0), 40.4 (2), 39.4 (2). IR (disc, KBr) ν/cm^{-1} 3443s, 3074m, 1639m, 1027s, 915s, 703s. MS (EI) m/z (%) 115 (25, M$^+$ − CH$_2$CH=CH$_2$), 69 (87), 41 (100). Found: C, 76.5%; H, 8.4%. $C_{14}H_{18}O_2$ requires C, 77.0%; H, 8.3%.

(*S*)-3-Allyl-hex-5-ene-2,3-diol (1e)

Obtained from (*S*)-ethyl lactate (10.0 g, 84.7 mmol) as a colourless liquid that was purified by flash chromatography (TLC: cyclohexane–MTBE 1 : 1 (v/v), R_f = 0.3). Yield 11.4 g, 86%.[14e] $[\alpha]_D^{20}$ +23.6° (*c* 2.0 in CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.93–5.83 (2H, –C*H*=CH$_2$), 5.18–5.08 (4H, –CH=C*H*$_2$), 3.71 (q, 1H, J = 6.4, –OC*H*CH$_3$), 2.39 (dd, 1H, J = 14.2, 7.3, –CH*H*–), 2.34 (dd, 1H, J = 14.2, 7.3, –CH*H*–), 2.25 (dd, 1H, J = 14.2, 7.3, –CH*H*–), 2.15 (dd, 1H, J = 14.2, 7.3, –CH*H*–), 2.04 (br s, 2H, –O*H*), 1.17 (d, 3H, J = 6.4, –C*H*$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.6 (1), 133.5 (1), 118.8 (2), 118.5 (2), 75.4 (0), 71.6 (1), 40.9 (2), 38.9 (2), 16.9 (3). IR (disc, KBr) ν/cm^{-1} 3473s, 3076s, 2979s, 1640s, 1047s, 914s. MS (EI) m/z (%) 218 (M$^+$, 2), 131 (35), 108 (74), 69 (100). Found: C, 68.8%; H, 10.5%. $C_9H_{16}O_2$ requires C, 69.2%; H, 10.3%.

4-(Benzyloxy-phenyl-methyl)-hepta-1,6-dien-4-ol (1f)

Obtained from diallyl carbinol **1d** (1.10 g, 5.0 mmol) by treatment with NaH (0.40 g of a 60% dispersion in mineral oil, 10.0 mmol) and benzyl bromide (0.70 mL, 6.0 mmol) in THF (30 mL) as a colourless liquid that was purified by flash chromatography (TLC: cyclohexane–MTBE 2 : 1 (v/v), R_f = 0.6). Yield 1.00 g, 69%. $[\alpha]_D^{20}$ +39.9° (*c* 0.9 in CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.43 (10H, Ph), 5.82–5.92 (2H, C*H*=CH$_2$), 5.11 (dm, 1H, J = 10.2, –CH=C*H*$_2$), 5.07 (dm, 1H, J = 9.2, –CH=C*H*$_2$), 5.06 (dm, 1H, J = 17.2, –CH=C*H*$_2$), 5.02 (dm, 1H, J = 17.2, –CH=C*H*$_2$), 4.46 (d, 1H, J = 11.5, –OCH*H*Ph), 4.36 (s, 1H, –C*H*OBn), 4.26 (d, 1H, J = 11.5, –OC*H*HPh), 2.48 (dd, 1H, J = 14.2, 7.5, –C*H*HCH=), 2.34 (s, 1H, O*H*), 2.23–2.29 (2H, –C*H*$_2$–CH=), 2.04 (dd, 1H, J = 14.2, 8.0, –C*H*HCH=). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0 (0), 137.5 (0), 134.1 (1), 133.8 (1), 128.8 (1), 128.4 (1), 128.1 (1), 128.0 (1), 127.9 (1), 127.7 (1), 118.2 (2), 118.1 (2), 84.6 (1), 75.7 (0), 71.0 (2), 40.5 (2), 40.0 (2). IR (neat, NaCl) ν/cm^{-1} 3546w, 3028s, 1066s, 914m. MS (EI) m/z (%) 223 (M$^+$ −1, 1), 207 (6), 141 (44), 71 (100), 57 (69). Found: C, 81.1%; H, 7.9%. $C_{21}H_{24}O_2$ requires C, 81.8%; H, 7.8%.

4-Phenyl-hepta-1,6-dien-4-ol (1g)

Obtained from ethyl benzoate (2.90 g, 18.5 mmol) as a colourless liquid that was purified by flash chromatography (TLC: cyclohexane–MTBE 5 : 1 (v/v), R_f = 0.7). Yield 2.60 g, 75%. Analytical data are identical with those reported in the literature.[14f]

4-(1-Ethyl-hexyl)-hepta-1,6-dien-4-ol (1h)

Obtained from 2-ethyl-heptanoic acid methyl ester (0.72 g, 4.2 mmol) as a colourless liquid that was purified by flash chromatography (TLC: cyclohexane–MTBE 5 : 1 (v/v), R_f = 0.7). Yield 0.67 g, 70%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85 (dddd, 2H, J = 17.4, 10.2, 7.3, 7.3, –C*H*=CH$_2$), 5.11 (dm, 2H, J = 10.3, –CH=C*H*$_2$), 5.09 (dm, 2H, J = 17.6, –CH=C*H*$_2$), 2.29 (ddm, 2H, J = 14.1, 7.5, –C*H*HCH=), 2.19 (ddm, 2H, J = 14.1, 7.5, –CH*H*CH=), 1.60 (m, 1H, CH), 1.52 (m, 1H, CH*H*), 1.47 (s, 1H, O*H*), 1.38 (m, 1H, CH*H*), 1.12–1.31 (8H, CH*H*), 0.93 (t, 3H, J = 7.5, –CH$_3$), 0.86 (t, 3H, J = 7.2, –CH$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.3 (1), 118.4 (2), 76.3 (0), 47.5 (1), 41.5 (2), 41.4 (2), 32.6 (2), 30.1 (2), 29.3 (2), 23.1 (2), 22.6 (2), 14.1 (3), 13.9 (3). IR (neat, NaCl) ν/cm^{-1} 3535m, 2965s, 2926s, 1456m, 909m. MS (EI) m/z (%) 223 (M$^+$ −1, < 5), 141 (45), 71 (100). Found: C, 80.3%; H, 12.7%. $C_{15}H_{28}O$ requires C, 80.3%; H, 12.6%.

General procedure for the preparation of cyclopentenols 2

The corresponding metathesis precursor **1** was dissolved in dry CH_2Cl_2 (*c* 0.3–0.5) and ruthenium complex **B** (1.1 mol%–2.9 mol%) was added. The mixture was stirred until the starting material was fully consumed as indicated by TLC. The solvent was evaporated, and the residue was purified by flash chromatography or by Kugelrohr distillation.

1-*tert*-Butyl-cyclopent-3-enol (2a)

Obtained from **1a** (1.00 g, 5.9 mmol) and **B** (54 mg, 1.1 mol%) as a colourless liquid after Kugelrohr distillation (25 °C, 0.5 mbar). TLC: cyclohexane–MTBE 5 : 1 (v/v), R_f = 0.4). Yield 0.77 g (92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67 (s, 2H, –C*H*=), 2.67 (d, 2H, J = 16.5, –CH*H*–), 2.13 (d, 2H, J = 16.5, –C*H*H–), 1.51 (s, 1H, –O*H*), 0.92 (s, 9H, ^{t}Bu). ^{13}C NMR (125 MHz, $CDCl_3$) δ 128.6 (1), 86.5 (0), 43.1 (2), 36.4 (0), 25.7 (3). IR (neat, NaCl) ν/cm^{-1} 3476w, 2918m, 1439w, 1063w. MS (EI) m/z (%) 139 (M$^+$ −1, < 5), 123 (95), 83 (70), 57 (100). Found: C, 76.8%; H, 11.5%. $C_9H_{16}O$ requires C, 77.1%; H, 11.5%.

1-Hydroxymethyl-cyclopent-3-enol 2b

Obtained from **1b** (1.97 g, 13.9 mmol) and **B** (236 mg, 2.0 mol%) as a colourless liquid after flash chromatography on silica (TLC: cyclohexane–MTBE 1 : 1 (v/v), R_f = 0.1). Yield 1.07 g (68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 (s, 2H, –C*H*=), 3.81 (br s, 1H, –O*H*), 3.64 (br s, 1H, –O*H*), 3.51 (s, 2H, –C*H*$_2$OH), 2.42 (d, 2H, J = 16.1, –CH*H*–), 2.31 (d, 2H, J = 16.1, –CH*H*–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.2 (1), 81.5 (0),

69.0 (2), 43.7 (2). IR (neat, NaCl) ν/cm^{-1} 3385m, 2927m, 1432w, 1107m. MS (EI) *m*/*z* (%) 114 (M^+, < 5), 96 (20), 83 (95), 79 (30), 55 (100). Found: C, 62.8%; H, 8.8%. $C_6H_{10}O_2$ requires C, 63.1%; H, 8.8%.

1-Benzyloxymethyl-cyclopent-3-enol 2c

Obtained from **1c** (0.40 g, 1.7 mmol) and **B** (40 mg, 2.7 mol%) as a colourless liquid after flash chromatography on silica (TLC: cyclohexane–MTBE 2 : 1 (v/v), R_f = 0.6). Yield 0.31 g (89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.38 (5H, Ph), 5.65 (s, 2H, –C*H*=), 4.58 (s, 2H, –OCH_2Ph), 3.47 (s, 2H, –CH_2OBn), 2.70 (s, 1H, –O*H*), 2.49 (d, 2H, *J* = 16.2, –CH*H*–), 2.42 (d, 2H, *J* = 16.2, –CH*H*–). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0 (0), 128.4 (1), 128.2 (1), 127.7 (1), 127.6 (1), 80.3 (0), 76.7 (2), 73.4 (2), 44.3 (2). IR (neat, NaCl) ν/cm^{-1} 3441w, 2856m, 1453w, 1098s. MS (EI) *m*/*z* (%) 204 (M^+, 3), 91 (100), 83 (55). Found: C, 76.3%; H, 8.0%. $C_{13}H_{16}O_2$ requires C, 76.4%; H, 7.9%.

1-(Hydroxy-phenyl-methyl)-cyclopent-3-enol 2d

Obtained from **1d** (0.16 g, 0.7 mmol) and **B** (18 mg, 2.9 mol%) as a colourless solid after flash chromatography on silica (TLC: cyclohexane–MTBE 1 : 1 (v/v), R_f = 0.3). Yield 0.14 g (89%). Mp 91 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.41 (5H, Ph), 5.67 (m, 1H, –C*H*=), 5.61 (m, 1H, –C*H*=), 4.68 (s, 1H, –CHPh), 2.80 (ddd, 1H, *J* = 17.0, 2.0, 1.8, –CH*H*–), 2.59 (ddd, 1H, *J* = 17.2, 2.0, 1.8, –CH*H*–), 2.51 (s, 1H, –OH), 2.40 (dd, 1H, *J* = 17.0, 1.8, –C*H*H–), 2.05 (dm, 1H, *J* = 17.2, –CH*H*–), 1.60 (s, 1H, –O*H*). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.6 (0), 128.4 (1), 128.2 (1), 128.2 (1), 128.0 (1), 127.5 (1), 86.8 (0), 79.1 (1), 45.0 (2), 43.5 (2). IR (disc, KBr) ν/cm^{-1} 3436s, 3289m, 3059w, 2901w, 1281m, 1019s. MS (EI) *m*/*z* (%) 173 (M^+ − 17, 100), 156 (25), 108 (85), 79 (50). Found: C, 75.5%; H, 7.3%. $C_{12}H_{14}O_2$ requires C, 75.8%; H, 7.4%.

(*S*)-1-(1-Hydroxy-ethyl)-cyclopent-3-enol 2e

Obtained from **1e** (0.50 g, 3.2 mmol) and **B** (51 mg, 1.9 mol%) as a colourless liquid after Kugelrohr distillation (75 °C oven temperature, 0.3 mbar). TLC: cyclohexane–MTBE 1 : 1 (v/v), R_f = 0.2. Yield 0.32 g (78%). $[\alpha]_D^{20}$ −3.4° (*c* 2.7 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68–5.63 (2H, –C*H*=), 3.71 (q, 1H, *J* = 6.3, –C*H*OH), 2.85 (br s, 2H, –O*H*), 2.50 (d, 1H, *J* = 16.0, –C*H*H–), 2.47 (d, 1H, *J* = 16.0, –C*H*H–), 2.33 (d, 1H, *J* = 16.0, –C*H*H–), 2.19 (d, 1H, *J* = 16.0, –C*H*H–), 1.12 (d, 3H, *J* = 6.3, –CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 128.5 (1), 128.3 (1), 83.5 (0), 73.1 (1), 45.2 (2), 42.4 (2), 17.8 (3). IR (neat, NaCl) ν/cm^{-1} 3408s, 2939m, 1454w, 1058w. MS (EI) *m*/*z* (%) 128 (M^+, < 5), 83 (100), 82 (60), 55 (50). Found: C, 65.3%; H, 9.2%. $C_7H_{12}O_2$ requires C, 65.6%; H, 9.4%.

General procedure for the sequential RCM-hydrogenation reaction with hydrogen

The corresponding metathesis precursor **1** was dissolved in dry toluene (*c* 0.3–0.5) and ruthenium complex **B** (1.7 mol%–2.7 mol%) was added. The mixture was stirred until the starting material was fully consumed as indicated by TLC. NaH (14 mol%–300 mol%, 60%-dispersion in mineral oil) was added and the argon atmosphere was replaced by an atmosphere of hydrogen. Stirring was continued under an atmosphere of hydrogen for 16 hours. After this time, the reaction mixture was diluted with ether, washed with water, dried with $MgSO_4$, filtered and the solvents were evaporated. The dark residue was purified by flash chromatography on silica or Kugelrohr distillation.

1-*tert*-Butyl-cyclopentanol 3a

Obtained from **1a** (0.59 g, 3.5 mmol) and **B** (50 mg, 1.7 mol%) as a colourless liquid after Kugelrohr distillation (25 °C, 0.3 mbar). TLC: cyclohexane–MTBE 5 : 1 (v/v), R_f = 0.4. Yield 0.46 g (92%). Analytical data are identical with those reported in the literature.[15a]

1-Benzyloxymethyl-cyclopentanol 3c

Obtained from **1c** (0.40 g, 1.7 mmol) and **B** (40 mg, 2.7 mol%) as a colourless liquid after flash chromatography on silica (TLC: cyclohexane–MTBE 2 : 1 (v/v), R_f = 0.6). Yield 0.29 g (81%). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2 (0), 128.3 (1), 127.6 (1), 127.5 (1), 81.5 (0), 77.1 (2), 73.4 (2), 37.2 (2), 24.1 (2). Other analytical data are identical with those reported in the literature.[15b]

1-(Hydroxy-phenyl-methyl)-cyclopentanol 3d

Obtained from **1d** (0.57 g, 2.6 mmol) and **B** (44 mg, 2.0 mol%) as a colourless solid, mp = 75 °C, after flash chromatography on silica (TLC: cyclohexane–MTBE 1 : 1 (v/v), R_f = 0.3). Yield 0.29 g (81%).[15c] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, 2H, *J* = 7.3, Ph), 7.34 (dd, 2H, *J* = 7.3, 7.3, Ph), 7.30 (t, 1H, *J* = 7.3, Ph), 4.61 (s, 1H, –C*H*OH–), 2.20 (br s, 2H, –O*H*), 1.88–1.71 (4H, –CH*H*), 1.68–1.52 (3H, –CH*H*–), 1.30 (m, 1H, –CH*H*–). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.0 (0), 128.0 (1), 127.8 (1), 127.3 (1), 84.8 (0), 79.6 (2), 37.5 (2), 36.0 (2), 23.6 (2), 23.6 (2). IR (neat, NaCl) ν/cm^{-1} 3417s, 3317s, 2965m, 2869m, 1452m, 1041m, 702m. MS (EI) *m*/*z* (%) 192 (M^+, 2), 108 (100), 85 (48). Found: C, 74.6%; H, 8.2%. $C_{12}H_{16}O_2$ requires C, 75.0%; H, 8.4%.

(*S*)-1-(1-Hydroxy-ethyl)-cyclopentanol 3e

Obtained from **1e** (0.53 g, 3.4 mmol) and **B** (72 mg, 2.5 mol%) as a colourless liquid after Kugelrohr distillation (0.4 mbar, 40 °C). TLC: cyclohexane–MTBE 1 : 1 (v/v), R_f = 0.2. Yield 0.24 g (55%). $[\alpha]_D^{20}$ −2.3° (*c* 1.5 in CH_2Cl_2). Other analytical data are identical with those reported in the literature.[15d]

(*S*)-1-(Benzyloxy-phenyl-methyl)-cyclopentanol 3f

Obtained from **1f** (0.40 g, 1.3 mmol) and **B** (23 mg, 2.0 mol%) as a colourless liquid after flash chromatography on silica (TLC: cyclohexane–MTBE 2 : 1 (v/v), R_f = 0.4). Yield 0.22 g (61%). $[\alpha]_D^{20}$ +65.5° (*c* 2.0 in CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.43 (10H, Ph), 4.54 (d, 1H, *J* = 11.7, CH*H*–Ph), 4.31 (s, 1H, C*H*–OH), 4.28 (d, 1H, *J* = 11.7, CH*H*–Ph), 2.16 (s, 1H, O*H*), 1.50–1.80 (8H, –CH_2–CH_2–). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4 (0), 138.2 (0), 128.4 (0), 128.3 (0), 128.0 (0), 127.8 (0), 127.8 (0), 127.6 (1), 86.2 (1), 84.2 (0), 70.7 (2), 37.4 (2), 35.7 (2), 23.5 (2). IR (neat, NaCl) ν/cm^{-1} 2961m, 2869m, 1495w, 1453m, 1066s. MS (EI) *m*/*z* (%) 282 (M^+, < 5), 198 (20), 107 (85), 91 (100), 79 (45), 77(25). Found: C, 80.4%; H, 7.5%. $C_{19}H_{22}O_2$ requires C, 80.8%; H, 7.8%.

1-Phenyl-cyclopentanol 3g

Obtained from **1g** (0.55 g, 2.9 mmol) and **B** (50 mg, 2.0 mol%) as a colourless liquid after flash chromatography on silica (TLC: cyclohexane–MTBE 5 : 1 (v/v), R_f = 0.5). Yield 0.38 g (81%). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0 (0), 128.1 (1), 126.7 (1), 125.0 (1), 83.4 (0), 41.7 (2), 23.8 (2). Other analytical data are identical with those reported in the literature.[15e]

1-(1-Ethyl-pentyl)-cyclopentanol 3h

Obtained from **1h** (0.20 g, 1.2 mmol) and **B** (15 mg, 2.0 mol%) as a colourless liquid after flash chromatography on silica (TLC: cyclohexane–MTBE 5 : 1 (v/v), R_f = 0.5). Yield 0.14 g (78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.76 (2H), 1.50–1.62 (7H), 1.40 (2H), 1.15–1.30 (8H), 1.16 (s, 1H, OH), 0.91 (t, 3H, *J* = 7.3, –CH_3), 0.84 (t, 3H, *J* = 6.9, –CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 86.2 (0), 49.3 (1), 38.7 (2), 38.7 (2), 32.5 (2), 30.6 (2), 28.8 (2), 23.8 (2), 23.8 (2), 23.6 (2), 22.6 (2), 14.1 (3), 13.4 (3). IR

(neat, NaCl) ν/cm^{-1} 3463w, 2959s, 2872m, 1465w. MS (EI, 70 eV) *m*/*z* (%) 198 (M^+, 1), 181 (1), 141 (11), 85 (100), 57 (18). HREI-MS [M^+] for $C_{13}H_{26}O$ calc. 198.1984 found 198.1984.

2-(2-Methoxy-phenyl)-tetrahydro-furan 6a

Obtained from **4a** (0.60 g, 3.0 mmol) and **B** (50 mg, 2.0 mol%) as a colourless liquid after Kugelrohr distillation (140 °C, 0.2 mbar). TLC: cyclohexane–MTBE 10 : 1 (v/v), R_f = 0.5. A hydrogen pressure of 3 bar was applied in this case. Yield 0.41 g (74%).[15f] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, 1H, J = 7.5, Ar), 7.23 (ddd, 1H, J = 8.0, 7.5, 1.5, Ar), 6.96 (dd, 1H, J = 7.5, 7.5, Ar), 6.86 (d, 1H, J = 7.5, Ar), 5.18 (dd, 1H, J = 7.0, 7.0, –OC*H*Ar), 4.11 (ddd, 1H, J = 7.5, 6.7, 6.7, –OCH*H*–), 3.92 (ddd, 1H, J = 7.5, 7.5, 7.5, –OCH*H*–), 3.83 (s, 3H, –OCH_3), 2.38 (m, 1H, –CH*H*–), 2.00–1.92 (2H, –CH*H*–), 1.71 (m, 1H, –CH*H*–). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6 (0), 133.7 (0), 129.2 (1), 127.0 (1), 121.9 (1), 111.5 (1), 77.3 (1), 70.0 (2), 56.7 (3), 34.6 (2), 27.4 (2).

2-(4-Methoxy-phenyl)-tetrahydro-furan 6c

Obtained from **4c** (0.99 g, 4.9 mmol) and **B** (103 mg, 2.0 mol%) as a colourless liquid after Kugelrohr distillation (140 °C, 0.2 mbar). TLC: cyclohexane–MTBE 10 : 1 (v/v), R_f = 0.5. A hydrogen pressure of 3 bar was applied in this case. Yield 0.41 g (78%). The product contains approximately 10% of dihydrofuran **7c**. TLC: cyclohexane–MTBE 10 : 1 (v/v), R_f = 0.8. Analytical data of **6c** are identical with those reported in the literature.[15f] ^{1}H NMR data of **7c** were obtained from the mixture: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, 2H, J = 8.5, Ar), 6.85 (d, 2H, J = 8.5, Ar), 6.40 (ddd, 1H, J = 2.5, 2.5, 2.5, –OC*H*=CH–), 5.45 (dd, 1H, J = 10.5, 8.5, –OC*H*(Ar)–), 4.94 (ddd, 1H, J = 2.5, 2.5, 2.5, –OCH=C*H*–), 3.72 (s, 3H, –OCH_3), 3.01 (dddd, 1H, J = 15.1, 10.5, 2.5, 2.5, –OCH(Ar)C*H*H–), 2.59 (dddd, 1H, J = 15.1, 8.5, 2.5, 2.5, –OCH(Ar)C*H*H–).

General procedure for the sequential RCM-hydrogenation reaction with *in situ* generated hydrogen

The corresponding metathesis precursor **1** was dissolved in dry toluene (*c* 0.3–0.5) and ruthenium complex **B** (2.0 mol%) was added. The mixture was stirred until the starting material was fully consumed as indicated by TLC. NaH (4 eq.) was added and the reaction vessel was stoppered immediately (Caution: gas evolution !). Stirring at ambient temperature was continued for 1 hour. After this time water (30 eq.) was added rapidly (Caution: vigorous gas evolution!) and the reaction vessel was stoppered immediately. Stirring was continued for 16 hours at ambient temperature. The mixture was diluted with water, extracted with ethyl acetate (in the case of diols) or MTBE. The combined organic layers were dried with $MgSO_4$, filtered and the solvents were evaporated. The residue was purified by flash chromatography.

1-(Hydroxy-phenyl-methyl)-cyclopentanol 3d

Obtained from **1d** (0.21 g, 0.9 mmol) and **B** (29 mg, 3.6 mol%) as a colourless solid, mp = 75 °C, after flash chromatography on silica (eluent cyclohexane–ethyl acetate 3 : 1 (v/v)). Yield 0.14 g (78%).

(*S*)-1-(1-Hydroxy-ethyl)-cyclopentanol 3e

Obtained from **1e** (0.38 g, 2.5 mmol) and **B** (51 mg, 2.4 mol%) as a colourless liquid after Kugelrohr distillation (0.4 mbar, 40 °C). Yield 0.24 g (74%).

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