# Metal Mediated One-Pot Synthesis of Cyclopentanones from Allyl Vinyl Ethers or Diallyl Ethers via Tandem Claisen Rearrangement and Hydroacylation

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Cyclopentanones **3** and **7** are generated in a one-pot procedure from allyl vinyl ethers **1** and diallyl ethers **4**, respectively. The conversion is carried out in the presence of RhCl(cod)(dppe) or $RuCl_2(PPh_3)_3$ at elevated temperatures and involves a sequence of aliphatic Claisen rearrangement and intramolecular hydroacylation of the pent-4-enals generated as intermediates. The diallyl ethers **4** undergo an additional double-bond isomerization prior to the Claisen rearrangement.

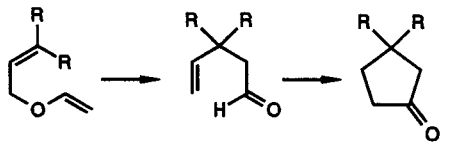
Cyclopentanones can be prepared from unsaturated aldehydes, especially pent-4-enals, via intramolecular hydroacylation.[1] This addition reaction is catalyzed by various rhodium systems, such as "Wilkinson's catalyst" $[RhCl(PPh_3)_3]$[1,2] or, more efficiently, by cationic complexes of type [Rh(diphosphine)(solvent)]$^+$.[3] With chiral substrates the procedure can be used in diastereoselective asymmetric syntheses of cyclopentanoid natural products.[4] Effective enantioselective transformations of prochiral pentenals are achieved with optically active catalyst ligands as chiral auxiliaries.[5,6,7]

Pent-4-enals are required as starting materials. They are easily obtained from allyl vinyl ethers via aliphatic Claisen rearrangement.[2,8] Like other thermal [3,3] sigmatropic rearrangements this conversion can be promoted by transition metal catalysts.[9] With a suitable catalyst both steps might be combined in a sequential transformation[10] or tandem reaction,[11] thus offering a more convenient experimental procedure which avoids the isolation of labile aldehyde intermediates.

We report here reaction conditions allowing the conversion of allyl vinyl ethers directly to cyclopentanones via thermal Claisen rearrangement followed by metal catalyzed hydroacylation in the presence of RhCl(cod)(dppe) or $RuCl_2(PPh_3)_3$ as catalyst precursors. In contrast to other hydroacylation catalysts of rhodium (see above) these systems are not decomposed at higher reaction temperatures (150–200 °C). Thus they are still active to catalyze the hydroacylation step. To some extent, these catalysts also accelerate the sigmatropic rearrangement. Under the conditions applied here, even diallyl ethers can be converted to cyclopentanones. This conversion requires an additional olefin isomerization step prior to the Claisen rearrangement.

Allyl vinyl ethers **1** with alkyl or aryl substituents in the terminal position of the allylic double bond were chosen as model compounds for the reaction sequence investigated. After Claisen rearrangement, these yield pent-4-enals **2** containing a quaternary center at C-3. This blocks double-bond isomerization within the unsaturated aldehyde, as observed under hydroacylation conditions with other compounds.[3a]

In the presence of hydroacylation catalyst precursors such as $RhCl(PPh_3)_3$ or $[Rh(dppe)]_2(ClO_4)_2$ (1–5 mol%) the allyl vinyl ethers **1** are not converted at room temperature. At elevated temperatures (140 °C) these complexes decompose and only the pent-4-enals **2** as products of the thermal Claisen rearrangement are observed. However, using the more stable complex RhCl(cod)(dppe) the conversion of allyl vinyl ethers **1** in benzonitrile or dimethyl formamide (DMF) at 140–190 °C leads to cyclopentanones **3** in up to 74% yield (see Table 1). Other donor solvents can also be used, while hydrocarbon solvents (decane, toluene) lead to much lower yields.




| | R | R |
|---|---|---|
| a | Me | Me |
| b | Ph | Ph |
| c | Me | Ph |

**Scheme 1**

**Table 1.** Conversion of Allyl Vinyl Ethers **1** to Cyclopentanones **3** in the Presence of Rhodium or Ruthenium Catalysts

| 1 | R, R | Catalyst | Method[a] | Temp (°C) | time (h) | Yield of 3 (%) |
|---|---|---|---|---|---|---|
| **1a** | Me, Me | RhCl(cod)(dppe) | A | 140 | 20 | 35 |
| | | $RuCl_2(PPh_3)_3$ | C | 200 | 16 | 73 |
| **1b** | Ph, Ph | RhCl(cod)(dppe) | B | 190 | 20 | 74 |
| | | $RuCl_2(PPh_3)_3$ | A | 190 | 72 | 45 |
| **1c** | Ph, Me | RhCl(cod)(dppe) | A(DMF) | 152 | 20 | 74 |
| | | $RuCl_2(PPh_3)_3$ | C | 200 | 16 | 66 |

[a] Method A: benzonitrile/Ar or DMF/Ar
Method B: benzonitrile/CO
Method C: octane/50 bar CO

Other rhodium catalysts, such as $RhH(CO)(PPh_3)_3$, $[Rh(cod)(dppe)BF_4$ or $[RhCl(cod)]_2$ are clearly less effective in the conversion described above and enhance side reactions e.g. decarbonylation or competitive [1,3] rearrangement. Similarly, complexes of palladium $[Pd_2(dba)_3 \cdot CHCl_3$, $PdCl_2(CH_3CN)_2$, $Pd(OAc)_2]$, nickel $[NiCl_2(dppe)]$, iridium $[IrCl(CO)(PPh_3)_2]$, or cobalt $[Co_2(CO)_8]$ turned out to be inactive as catalysts for the tandem reaction of allyl vinyl ethers **1** to cyclopentanones **3**. While in some cases (e.g. palladium) Claisen rearrangement is observed at low temperatures, the same catalysts fail to initiate the hydroacylation step.

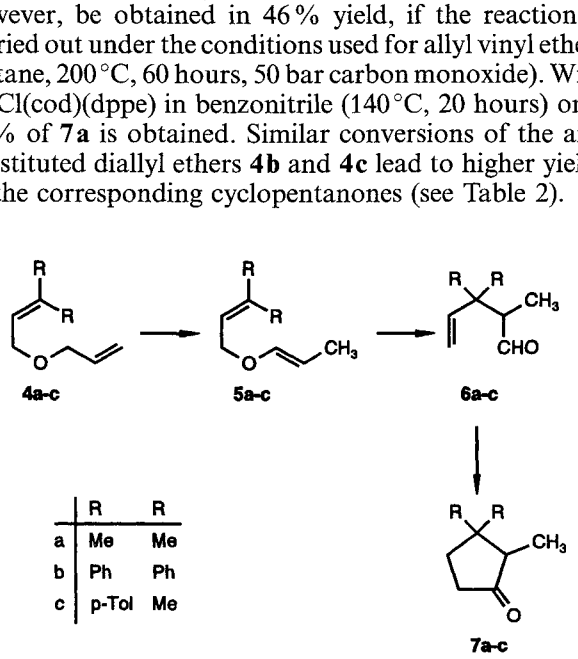
The catalyst $RuCl_2(PPh_3)_3$ (1–5 mol%), however, is an active catalyst precursor for reactions carried out in oc-

tane at 200 °C under 50 bar carbon monoxide pressure. The cyclopentanones **3** are obtained in up to 73% yield. The ruthenium catalyst can be recovered (80–100%) as $RuCl_2(CO)_2(PPh_3)_2$[12] and this compound also converts ethers **1** to the cyclopentanones **3** in comparable yields. Thus the catalytic ruthenium system is not deactivated by carbon monoxide or aldehyde decarbonylation as observed with $RhCl(PPh_3)_3$.[2] Other ruthenium complexes, such as $Ru_3(CO)_{12}$ or $Ru(CO)_3(PPh_3)_2$ also catalyse the reaction sequence discussed above, mostly, however, with lower yields.

At lower temperatures (140–150 °C) $RuCl_2(PPh_3)_3$ clearly accelerates the Claisen rearrangement (5–10 fold), even with only 0.1 mol% present in the reaction mixture. Under these conditions the intramolecular hydroacylation is slow and mainly the aldehydes **2** result as reaction products.

These results prove that direct conversion of allyl vinyl ethers **1** to cyclopentanones of type **3** can be achieved at elevated temperatures in the presence of RhCl(cod)(dppe) or $RuCl_2(PPh_3)_3$. The yields are comparable to the two step route involving isolation of the pent-4-enals **2**. Both catalysts can easily be prepared. While rhodium complexes are known to be active hydroacylation catalysts, the use of less expensive ruthenium complexes was hitherto limited to rare cases of intermolecular hydroacylation.[14,15]

Ruthenium catalysts have been reported to promote the conversion of diallyl ethers to yield pent-4-enals.[13] Reaction of diallyl ether **4a** to the aldehyde **6a** was carried out neat in a sealed tube at 200 °C (3 hours) in the presence of $RuCl_2(PPh_3)_3$. No further conversion to the cyclopentanone **7a** was reported.[13a] This latter product can, however, be obtained in 46% yield, if the reaction is carried out under the conditions used for allyl vinyl ethers (octane, 200 °C, 60 hours, 50 bar carbon monoxide). With RhCl(cod)(dppe) in benzonitrile (140 °C, 20 hours) only 22% of **7a** is obtained. Similar conversions of the aryl substituted diallyl ethers **4b** and **4c** lead to higher yields of the corresponding cyclopentanones (see Table 2).




Scheme 2

As shown above, unsymmetrically substituted diallyl ethers **4** undergo a reaction sequence with regioselective isomerization of the less substituted double bond prior to Claisen rearrangement and hydroacylation. Compared to the conversion of the allyl vinyl ethers **1**, the lower yields of 50–60% possibly are due to the fact that intramolecular hydroacylation of pent-4-enals is hindered by substituents in the α-position to the aldehyde function.[2,3] Up to now the procedure appears to have been limited to substrates which generate a quaternary center at C-3 of the intermediate pentenal. According to preliminary results, systems leading to pentenals with a monosubstituted or unsubstituted C-3 position only give moderate yields of the resulting cyclopentanones.

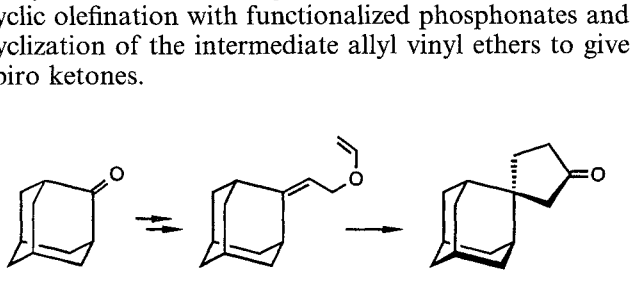
**Table 2.** Conversion of Diallyl Ethers **4** to Cyclopentanones **7** in the Presence of Rhodium or Ruthenium Catalysts

| 4 | R,R | Catalyst | Method[a] | Temp (°C) | Time (h) | Yield of 7 (%) |
|---|---|---|---|---|---|---|
| **4a** | Me, Me | $RuCl_2(PPh_3)_3$ | C | 200 | 60 | 46 |
| | | RhCl(cod(dppe) | A | 140 | 20 | 22 |
| **4b** | Ph, Ph | $RuCl_2(PPh_3)_3$ | C | 220 | 72 | 50 |
| | | RhCl(cod)(dppe) | B | 190 | 24 | 57 |
| **4c** | tolyl, Me | $RuCl_2(PPh_3)_3$ | C | 200 | 16 | 48 |

[a] See Table 1 footnote.

If the substituted double bond bears different substituents (e.g. in **1c** and **4c**) a stereogenic center at C-3 of the pent-4-enals and the cyclopentanones is created. Further experiments, presently under investigation with appropriate substrates, will have to demonstrate whether the olefin configuration (*E*/*Z*), stereogenic centers within the substrate, or chiral ligands in the catalyst can determine the stereochemical outcome of the cyclization method.

The procedure reported here offers wide application and can also be incorporated as an elementary step in polycyclic ring syntheses and spiro anellation: The latter is easily achieved if starting from cyclic ketones via exocyclic olefination with functionalized phosphonates and cyclization of the intermediate allyl vinyl ethers to give spiro ketones.




Scheme 3

Thus, in a four-step procedure adamantanone **(8)** after conversion to the allyl vinyl ether **9** yields the spirocyclopentanone **10**.

NMR spectra were recorded with TMS as internal standard. Chromatography was carried out with silica gel 60 (70–230 mesh) from Merck, Darmstadt. Gas chromatography with 25 m or 50 m CP sil-5 or CP 19 (CB) capillaries, FID. RhCl(cod)(dppe)[16a] and $RuCl_2(PPh_3)_3$[16b] were prepared according to the described procedures. Satisfactory microanalyses were obtained for compounds **1b, 3c, 4b,c, 10**: C ± 0.16, H ± 0.21.

**3-Methyl-1-vinyloxybut-2-ene (1a):**[17,18]
Preparation was as described[18] from 3-methylbut-2-en-1-ol with ethyl vinyl ether in the presence of catalytic amounts of mercuric acetate.

**1,1-Diphenyl-3-vinyloxyprop-1-ene (1b):**[17a]
Benzophenone was olefinated with diethyl(ethoxycarbonylmethyl)phosphonate to give ethyl 3,3-diphenylprop-2-enoate[19] which was reduced with $LiAlH_4$ to 3,3-diphenylprop-2-en-1-ol.[20] **1b**[17a] was obtained analogously to **1a**, $n_D^{20} = 1.5909$.

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 4.01$ (dd, $^2J = 2.1$, $^3J_{cis} = 6.8$ Hz, 1H, O–CH=CH$_2$), 4.15 (dd, $^2J = 2.1$, $^3J_{trans} = 14.3$ Hz, 1H, O–CH–CH$_2$), 4.33 [d, $^3J = 6.7$ Hz, 2H, O–CH$_2$–CH=C($C_6H_5$)$_2$], 6.26 [t, $^3J = 6.7$ Hz, 1H, O–CH$_2$–CH=C($C_6H_5$)$_2$], 6.47 (dd, $^3J_{cis} = 6.8$, $^3J_{trans} = 14.3$ Hz, O–CH=CH$_2$), 7.2–7.4 (m, 10H, arom.).

$^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 65.9$ (=CH–CH$_2$–O), 87.0 (–CH=CH$_2$), 123.7 (=CH–CH$_2$O), 126.8–130.0 (CH arom.), 138.8 (Cq), 141.6 (Cq), 145.3 (Cq), 151.2 (=CHOR).

IR (film, NaCl): $\nu$ = 3100–3000 (w), 2920 (vw), 1630 (s), 1610 (vs), 1490 (s), 1445 (s), 1320 (s), 1190 (vs), 820 (s), 760 (s), 700 (vs) cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) = 236 (2, $M^+$), 44 (100).

**3-Phenyl-1-vinyloxybut-2-ene (1c):**[17a]
Preparation was from methyl crotonate and bromobenzene via Heck arylation[21] according to the described procedure to give methyl 3-phenylbut-2-enoate,[22] which was reduced to 3-phenylbut-2-en-1-ol[23] with $LiAlH_4$ and converted to **1c**[17a] analogously to the procedure for **1a**.

**1-Allyloxy-3-methylbut-2-ene (4a):**[13a]
Preparation was from 3-methylbut-2-en-1-ol and allyl bromide/NaH according to the described procedure.[13a]

**3-Allyloxy-1,1-diphenylpropene (4b):**
Under Ar 3,3-diphenylprop-2-en-1-ol[20] (15.0 g, 0.071 mol) was slowly added to a suspension of NaH (3.28 g, 0.1 mol) in abs. THF (200 mL). The mixture was heated to reflux (2 h) and then cooled to −30 °C. Within 30 min allyl bromide (12.1 g, 0.1 mol) was added dropwise. After 2 h heating to reflux temperature the reaction mixture was cooled in an ice bath and hydrolysed with 10% HCl (100 mL). The organic layer was separated and the aqueous phase extracted with hexane (5 × 30 mL). The combined organic layers were washed twice with 10% HCl (2 × 20 mL) sat. $NaHCO_3$ (30 mL) and sat. NaCl (30 mL). After evaporation of the solvent the organic residue was separated on silica gel with hexane/methyl *t*-butyl ether (MTBE) (10:1). The main fraction after distillation at 90 °C/0.02 mbar gave **4b**; yield: 14.24 g (80%).

$^1$H NMR (200 MHz, $CDCl_3$): $\delta = 3.93$ (d, $J = 5.5$. Hz, 2H, O–CH$_2$–CH=CH$_2$), 4.04 (d, $J = 6.9$ Hz, 2H, O–CH$_2$–CH=CPh$_2$), 5.13 (dd, 1H, $^3J_{cis} = 10.3$, $^2J = 2$ Hz, CH=CH$_2$), 5.22 (dd, 1H, $^3J_{trans} = 17.2$, $^2J = 2$ Hz, CH=CH$_2$), 5.87 (ddt, 1H, $^3J = 5.5$, $^3J_{trans} = 17.2$, $^3J_{cis} = 10.3$ Hz, CH$_2$–CH=CH$_2$), 6.24 (t, $J = 6.9$ Hz, 1H, CH=CPh$_2$), 7.22 (m, 10H, arom.).

$^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 67.9$ (CH$_2$–CH=CPh$_2$), 71.2 (CH$_2$–CH=CH$_2$), 117.0 (CH$_2$=CH), 125.5 (CH=CPh$_2$), 127.0–129.0 (CH arom.), 134.7 (CH=CH$_2$), 139.2 (Cq), 141.8 (Cq), 144.6 (Cq).

IR (film, NaCl): $\nu$ = 3065 (m), 3030 (m), 2930 (m), 2855 (m) 1494 (s), 1447 (s), 1362 (w), 1342 (w), 1276 (w), 1106 (s), 1074 (vs), 1029 (m), 994 (m), 923 (s), 759 (vs), 700 (vs) cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) = 250 (33, $M^+$), 103 (100).

**3-(4-Methylphenyl)but-2-en-1-ol:**
A solution of ethyl 3-(4-methylphenyl)but-2-enoate[24] (28.6 g, 0.14 mol) in abs. $Et_2O$ (100 mL) was added dropwise within 1 h under Ar to a −20 °C cooled suspension of $LiAlH_4$ (10.06 g, 0.28 mol) in abs. $Et_2O$ (500 mL). After warming up to r.t. the mixture was stirred for 15 h, cooled to −10 °C and hydrolysed with ice water (200 mL). The white precipitate was dissolved with 10% $H_2SO_4$. The organic layer was separated and the aqueous phase extracted several times with $Et_2O$ after saturating with NaCl. The combined organic phases were washed with $NaHCO_3$ and dried ($MgSO_4$). After evaporating the organic solvent the crude product was distilled at 112 °C/1.0 mbar to give 3-(4-methylphenyl)but-2-en-1-ol;[23] yield: 21.5 g (95%).

$^1$H NMR (60 MHz, $CDCl_3$): $\delta = 2.0$ (s, 3H, –CH=CR–CH$_3$), 2.3 (s, 3H, –$C_6H_4$–CH$_3$), 3.6 (s, OH), 4.3 (d, 2H, $^3J = 7$ Hz, –O–CH$_2$–CH=CR$_2$), 6.0 (t, 1H, $^3J = 7$ Hz, –O–CH$_2$–CH=CR$_2$), 7.0–7.4 (m, 4H, arom.).

IR (film, NaCl): $\nu$ = 3320 (s), 3080 (m), 3020 (m), 2980 (m), 2920 (s), 2860 (s), 1640 (w), 1510 (s), 1440 (m), 1380 (m), 1000 (s), 820 (s) cm$^{-1}$.

**1-Allyloxy-3-(4-methylphenyl)but-2-ene (4c):**
Under Ar 3-(4-methylphenyl)but-2-en-1-ol (34.0 g, 0.207 mol) was added to a suspension of NaH (80% in oil, 9.7 g, 0.322 mol) in abs. THF (600 mL). After 2 h heating to reflux the mixture was kept at 35 °C and allyl bromide (38.1 g, 0.315 mol) was added dropwise. After 2 h at reflux temperature the mixture was cooled to r.t. and hydrolysed with 10% HCl. The organic layer was separated and the aqueous phase extracted with hexane. The combined organic phases were washed with saturated solutions of $NaHCO_3$ and NaCl and dried ($MgSO_4$). Evaporation of the solvent and distillation of the crude product at 100 °C/0.09 mbar gave **4c**; yield: 34.7 g (83%).

$^1$H NMR (300 MHz, $CDCl_3$): $\delta = 2.13$–$2.14$ (m, 3H, —HC=CR–CH$_3$), 2.41 (s, 3H, –$C_6H_4$–CH$_3$), 4.11 (d, 2H, $^3J = 5.7$ Hz, –O–CH$_2$–CH=CH$_2$), 4.27 (d, 2H, $^3J = 6.6$ Hz, R$_2$C=CH–CH$_2$–O–), 5.28 (ddt, 1H, $^3J_{cis} = 10.3$, $^2J = 1.7$, $^4J = 1.2$ Hz, –O–CH$_2$–CH=CH), 5.38 (dd, 1H, $^3J_{trans} = 17.2$, $^2J = 1.7$ Hz, –OCH$_2$–CH=CH), 5.99–6.04 (m, 1H, R$_2$C=CH–CH$_2$–O–), 6.04 (ddt, 1H, $^3J_{trans} = 17.2$, $^3J_{cis} = 10.3$, $^3J = 5.7$ Hz, –O–CH$_2$–CH=CH$_2$), 7.17–7.22 (m, 2H, arom.), 7.37–7.42 (m, 2H, arom.).

$^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 16.0$ (–C=CR–CH$_3$), 20.9 (–$C_6H_4$–CH$_3$), 67.0 (–O–CH$_2$–CH=CH$_2$), 71.1 (–O–CH$_2$–CH=CR$_2$), 116.9 (–O–CH$_2$–CH=CH$_2$), 123.3 (–O–CH$_2$–CH=CR$_2$), 125.5 (–$C_6H_4$–, arom.), 128.8 (CH, arom.), 134.8 (–O–CH$_2$–CH=CH$_2$), 136.7 (Cq, arom.), 138.0 (Cq, –O–CH$_2$–CH=CR$_2$), 139.9 (Cq, arom.).

IR (film, NaCl): $\nu$ = 3070 (m), 3050 (m), 3018 (m), 2975 (m), 2910 (m), 2845 (s), 1642 (m), 1595 (w), 1572 (w), 1492 (s), 1442 (s), 1378 (m), 1358 (m), 1120 (s), 1090 (s), 1055 (s), 1025 (s), 930 (s) cm$^{-1}$.

MS (EI, 70 eV): $m/z$ (%) = 202 (5, $M^+$), 161 (30), 145 (39), 133 (61), 131 (32), 129 (31), 119 (33), 115 (25), 105 (65), 91 (47), 57 (100), 41 (57).

**Cyclopentanones 3 and 7 via Tandem Claisen Rearrangement and Hydroacylation:**

*3,3-Dimethylcyclopentanone* **(3a)**:

Method A: Under Ar a solution of **1a** (1.12 g, 10 mmol) and RhCl(cod)(dppe) (0.193 g, 0.30 mol, 3 mol%) in abs. benzonitrile (3 mL) was heated 20 h to 140 °C. Evaporation of the solvent and Kugelrohr distillation gave a crude product containing **3a**,[3a] crude yield: 0.392 g (35%) (GC, NMR). Further purification was achieved by column chromatography on silica gel with hexane/MTBE (10:1).

Method C: Under Ar a solution of **1a** (0.95 g, 8.47 mmol) and $RuCl_2(PPh_3)_3$ (406 mg, 0.42 mmol, 5 mol%) in abs. octane (30 mL) was placed in an autoclave and pressurized with CO (50 bar). After heating for 16 h at 200 °C, the cooled reaction mixture was decanted from colorless crystalline needles of $RuCl_2(CO)_2(PPh_3)_2$[12] (270 mg, 86% dried after washing with pentane, IR). The decanted solution and the pentane washing were combined, evaporated and chromatographed on silica with hexane/MTBE (10:1). The main fraction upon distillation at 70 °C/0.08 bar (Kugelrohr) gave **3a**;[3a] yield: 0.69 g (73%) (NMR, IR).

*3,3-Diphenylcyclopentanone* **(3b)**:

Method B: A solution of **1b** (1.00 g, 4.23 mmol) and RhCl(cod)(dppe) (0.13 g, 0.21 mmol, 5 mol%) in benzonitrile (3 mL) under an atmosphere of CO was heated to 190 °C for 20 h. Evaporation of the solvent, column chromatography on silica gel with hexane/MTBE (10:1) and recrystallization of the main fraction

from MTBE gave **3b**[25] as colorless needles; yield: 0.74 g (74%), mp 86°C (NMR, IR).

Method A: Conversion of **1b** (1.00 g, 4.23 mmol) and $RuCl_2(PPh_3)_3$ (0.2 g, 0.21 mmol, 5 mol%) in benzonitrile (2 mL) (72 h, 190°C) after similar workup gave **3b**,[25] 0.45 g (45%) (NMR, IR).

*3-Methyl-3-phenylcyclopentanone* (**3c**):

Method A: Conversion of **1c** (1.05 g, 6 mmol) and RhCl(cod)(dppe) (0.116 g, 0.19 mmol, 3 mol%) in abs. DMF (3 mL) (152°C, 20 h) after workup and chromatography [silica gel, petroleum ether (bp 30–60°C)/MTBE, 5:1] gave **3c**;[26] 0.77 g (74%) (NMR, IR).

Method C: Conversion of **1c** (1.00 g, 5.74 mmol) and $RuCl_2(PPh_3)_3$ (0.275 g, 0.287 mmol, 5 mol%) in abs. octane (25 mL) (50 bar CO, 16 h, 200°C) after workup and chromatography on silica gel (hexane/MTBE, 10:1) gave **3c**,[26] as colorless oil; yield: 0.655 g (66%).

$^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.39 (s, 3H, $-CH_3$), 2.24–2.30 (m, 2H, $CH_2$), 2.34–2.50 (m, 2H, $CH_2$), 2.47 (d, 1H, $^2J$ = 17.6 Hz, CH), 2.65 (d, 1H, $^2J$ = 17.6 Hz, CH), 7.20–7.37 (m, 5H, arom.).

IR (film): $\nu$ = 3055 (w), 3020 (w), 2955 (m), 2922 (m), 2865 (m), 1740 (vs), 1495 (m), 1595 (w), 1442 (m), 1405 (m), 1160 (s), 818 (s), 700 (s) $cm^{-1}$.

MS (EI, 70 eV): *m/z* (%) = 174 (72, $M^+$), 159 (26), 131 (25), 118 (100), 117 (66), 115 (27), 103 (20), 91 (42), 78 (17), 77 (21), 41 (16).

*2,3,3-Trimethylcyclopentanone* (**7a**):

Method C: Conversion of **4a** (0.50 g, 3.96 mmol) and $RuCl_2(PPh_3)_3$ (0.19 g, 0.198 mmol, 5 mol%) in abs. octane (20 mL) (50 bar CO, 60 h, 200°C) after workup (chromatography on silica gel and distillation, 70°C/0.08 bar, Kugelrohr) gave **7a**;[27] yield: 0.23 g (46%) (NMR, IR).

Method A: Conversion of **4a** (0.76 g, 6.0 mmol) and RhCl(cod)(dppe) (0.116 g, 0.18 mmol, 3 mol%) in benzonitrile (3 mL, 140°C, 20 h under Ar) after workup as above gave **7a**;[27] yield: 0.167 g (22%).

*2-Methyl-3,3-diphenylcyclopentanone* (**7b**):

Method B: Conversion of **4b** (1.00 g, 0.399 mmol) and RhCl(cod)(dppe) (0.13 g, 0.199 mmol, 5 mol%) in benzonitrile (3 mL) (190°C, 72 h, under CO atmosphere) after workup (filtration over $Al_2O_3$ and column chromatography on silica gel, hexane/MTBE, 10:1) gave **7b**;[28] 0.57 g (57%) (NMR, IR).

Method C: Conversion of **4b** (1.00 g, 0.399 mmol) and $RuCl_2(PPh_3)_3$ (0.19 g, 0.2 mmol, 5 mol%) in octane (10 mL) (50 bar CO, 220°C, 72 h) after the usual workup gave **7b**;[28] yield: 0.50 g (50%).

*2,3-Dimethyl-3-(4-methylphenyl)cyclopentanone* (**7c**):

Method C: Conversion of **4c** (1.00 g, 4.95 mmol) and $RuCl_2(PPh_3)_3$ (0.474 g, 0.495 mmol, 10 mol%) in abs. octane (30 mL) (50 bar CO, 200°C, 16 h) after workup as described above (decanting, distillation of the crude material at 130°C/0.1 bar, column chromatography on silica gel, hexane/MTBE, 10:1) gave a 3:1 mixture of ***E***- and ***Z***-**7c**;[28,29] yield: 0.48 g (48%) (NMR, IR).

*2-(2-Vinyloxyethylidene)adamantane* (**9**):

The allyl vinyl ether **9** was prepared starting from adamantanone **(8)** which was converted to ethyl adamant-2-ylideneacetate[30] with ethyl (diethoxyphosphono)acetate. The ester was reduced with $LiAlH_4$ to give 2-adamant-2-ylideneethanol[31,32] which was converted to the allyl vinyl ether **9**[32] with ethyl vinyl ether in the presence of mercuric acetate.

*2-(Spirocyclopentan-3'-one)adamantane* (**10**):

A solution of 2-(2-vinyloxyethylidene)adamantane (**9**, 1.00 g, 49 mmol) and RhCl(cod)(dppe) (0.079 g, 0.12 mmol, 2.5 mol%) in abs. benzonitrile (3 mL) was heated under Ar for 20 h at reflux. Chromatography of the crude reaction mixture on silica gel with hexane/MTBE (10:1) gave low boiling products (0.32 g) and 2-(spirocyclopentan-3'-one)adamantane **(10)**;[33] yield: 0.49 g (49%).

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 1.56–1.86 (m, 12H), 1.99–2.06 (m, 4H), 2.21–2.29 (m, 2H, $CH_2$), 2.31 (s, 2H, $CH_2$).

$^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 27.3 (CH), 27.7 (CH), 32.6 ($CH_2$), 33.2 ($2CH_2$), 34.4 ($2CH_2$), 35.9 (2CH), 36.5 ($CH_2$), 38.5 ($CH_2$), 45.8 ($C_q$), 50.6 ($CH_2$), 220.2 (C=O).

IR (KBr): $\nu$ = 2190 (vs), 1738 (vs), 1451 (w, br), 1404 (w, br), 1165 (m), $cm^{-1}$.

MS (70 eV, EI): *m/z* (%) = 204 (100, $M^+$), 161 (65).

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