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Ruthenium Catalyzed Selective Regio-and-Mono-Allylation of Cyclic 1,3-Diketones Using Allyl Alcohols as Substrates

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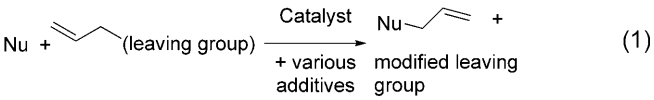
Abstract: The new ruthenium-sulfonate catalyst $Ru(Cp^*)(\eta^3\text{-}C_3H_5)(p\text{-}CH_3C_6H_4SO_3)_2$, ($Cp^*$ = pentamethylcyclopentadienyl), rapidly and regioselectively mono-allylates dimedone to the branched products using substituted allyl alcohols as substrates, without acid, base or other additives, under relatively mild conditions. We consider the ruthenium sulfonate to be a "green" alternative in that it uses allyl alcohols as substrate, (rather than carbonates, acetates, etc.) and therefore does not waste the leaving group. The catalyst induces rapid double allylation of various 1,3-diketones in high yield using allylic alcohol.

Keywords: allylation; catalysis; diketones; regioselectivity; ruthenium

Introduction

The use of transition metal catalysts to facilitate the allylation of a variety of organic nucleophiles now represents an established methodology with examples from Pd,[1] Ir,[2] Cu[3] and Ru[4–10] chemistry all well documented [see Eq. (1)]. The nucleophile, Nu, can be C-, O-, N- or S-based.

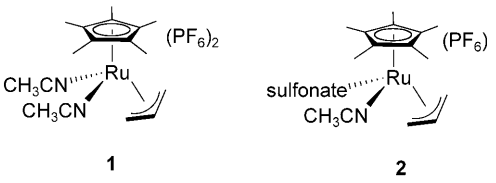


(1)

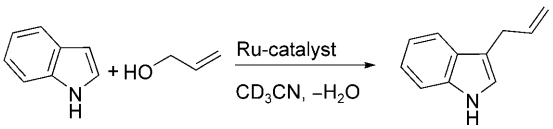
Unfortunately, many of these allylation reactions are not very "atom economical" in that they waste the leaving group that may contain a substantial number of atoms.[5–10] Furthermore, additives, such as a base, in stoichiometric quantities are often necessary in order to generate an anionic nucleophile to ensure that the chemistry proceeds in good yield.[11–14] Even under such conditions, the reactions are often observed to be relatively slow, requiring 10–20 h[7,15a] and/or increased reaction temperatures[11,12] to go to completion.

The recent literature has recorded some few examples of an improvement that involves the use of allyl alcohols as substrates.[15] (rather than acetates, carbonates or halogen derivatives); nevertheless, these reports often state that additives, such as a boron or other derivatives, are required to facilitate the reaction.[16–18] Presumably these additives help to turn the OH moiety into a better leaving group during the oxidative addition step.

We have recently suggested that Ru(IV) salts,[19] **1** and **2**, are excellent, rapid catalysts under mild conditions for the allylation of various nucleophiles using allyl alcohols as substrates [e.g., see Eq. (2)]. The

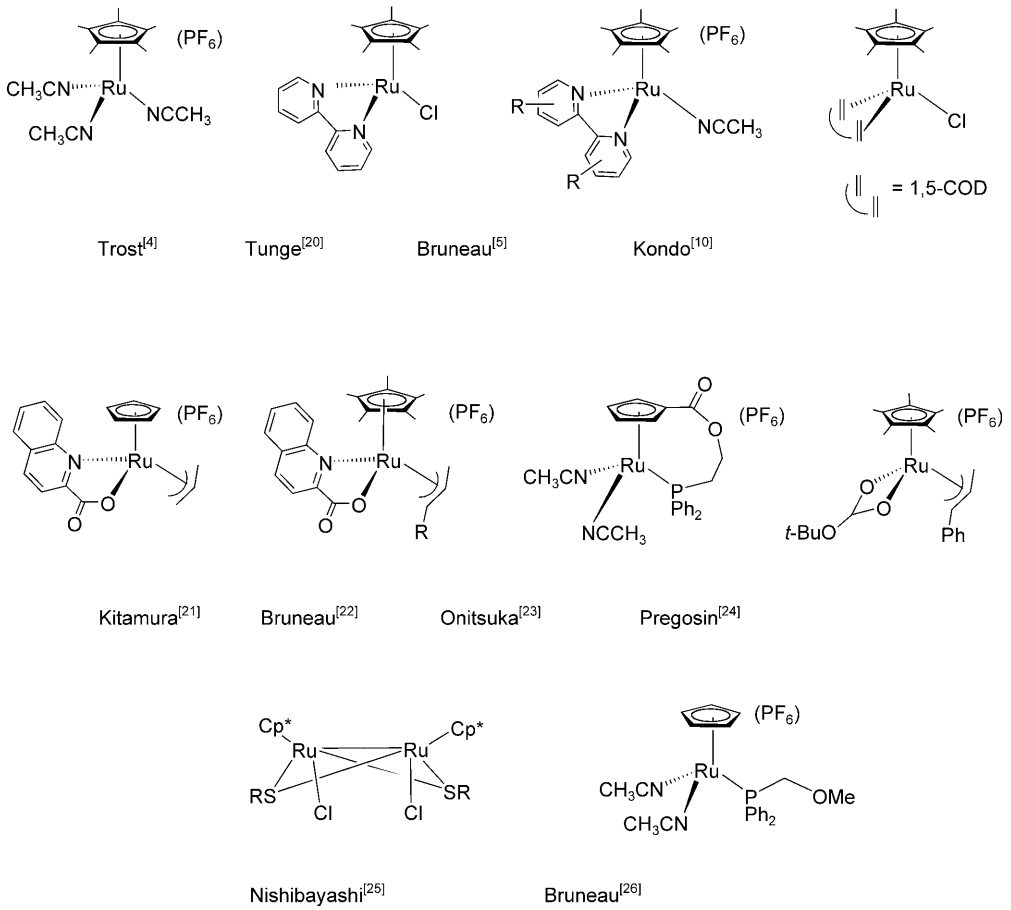


1 **2**



(2)

leaving group in the oxidative addition step is H_2O and the necessary proton is generated *via* the attack of the nucleophile on the coordinated allyl in an intermediate related to **1**. Alternatively, we have shown that one can use a catalyst comprised of Trost's catalyst, $[Ru(Cp^*)(CH_3CN)_3](PF_6)$, as the ruthenium source, plus a catalytic amount of a sulfonic acid (that serves both as the source of a proton and the sulfo-

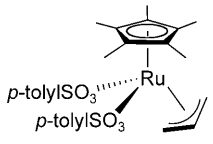


Scheme 1. A selection of literature-known Ru allylation catalysts.

nate anion) to achieve the same end.[19e] Sulfonic acids appear to be the reagents of choice in that more conventional organic and inorganic acids do not perform as well.[19g]

There are now a number of Ru complexes capable of catalyzing allylation reactions[20–26] and Scheme 1 shows a selection of these.

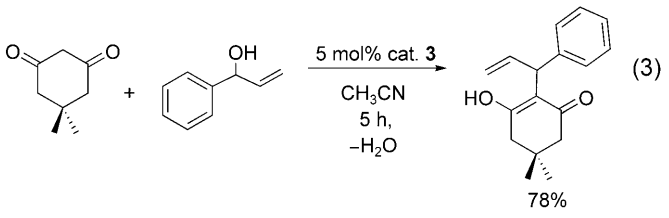
We show here that the neutral Ru sulfonate catalyst precursor **3**[19d] (which affords an analogue of **2** in acetonitrile solution) *rapidly and regioselectively monoallylates 1,3-diketone substrates using a substituted allyl alcohol as substrate, without acid, base or other additives*, under relatively mild conditions.



3

Results and Discussion

The reaction of commercially available dimedone (5,5-dimethylcyclohexane-1,3-dione) with 1-arylallyl alcohols affords the new products in good yield, see Eq. (3) and Eq. (4) and Table 1 for additional examples. Related reactions on similar diketone compounds using palladium catalysts[15b,27] afford either mixtures of mono-and bis-allylated products or only double allylation[13,27b] and exclusively the linear rather than the branched product. The yields shown in Table 1 are for isolated products, after recrystalliza-



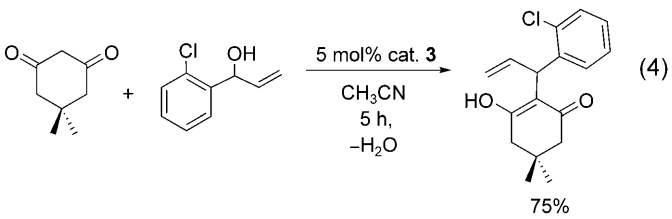
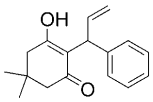
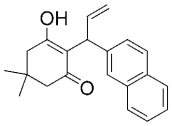
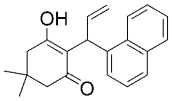
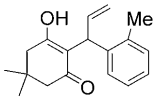
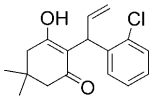
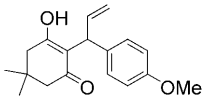
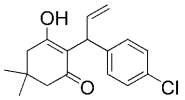
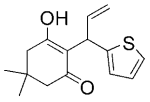


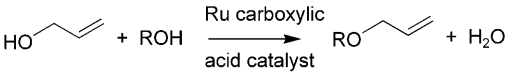
Table 1. Mono-allylation of dimedone with ArCH(OH)CH=CH_2 catalyzed by **3**.

Entry[a]	Ar	Product	Yield [%]
1	Ph		78
2	2-naphthyl		79
3	1-naphthyl		70
4	*o*-Me-C_6H_4-		77
5	*o*-Cl-C_6H_4-		75
6	*p*-MeO-C_6H_4-		73
7	*p*-Cl-C_6H_4-		62
8	1-thiophenyl		77

[a] *Reaction conditions:* CH_3CN (1.6 mL), H_2O (1.6 mL), diketone (0.65 mmol), ArCH(OH)CH=CH_2 (0.68 mmol), **3** (0.03 mmol = 5 mol%), room temperature, 5 h.

tion. These reactions proceed smoothly even in the presence of bulky aryl groups at the tertiary carbon.

We have monitored all of these reactions as a function of time *via* ^{1}H NMR spectroscopy, and find that the conversion to the desired product is of the order of 90%, with the losses arising from the purification step. The reactions proceed smoothly at room temperature and are complete in a few hours. In chloroform solution the organic products exist as a mixture of the enol and diketone forms.[28] We have measured their NMR spectra in DMF in which the enol form dominates (see Figure 1) and therefore show this product in the equations.[29] The OH resonance of the enol form is clearly visible at $\delta = 10.73$. For this type of 1,3-diketone substrate, we know of no other catalyst that is completely regioselective or even specific for the mono-allyl product. Both of these characteristics are unique. Further, we note that, as indicated in Eq. (5), although Pd[15g] and Ru catalysts[15e] are known to



(5)

be capable of converting allyl alcohols into allyl ethers, there is essentially no diallyl ether side product formed in our reactions although acid is generated.

This is yet another form of selectivity that, presumably, arises from the relatively mild reaction conditions. We have previously offered an explanation for the generally observed regioselectivity in Ru-catalyzed allyl chemistry, based on orbital control of the reaction.[19d,30] The LUMO of the Ru(IV) allyl inter-

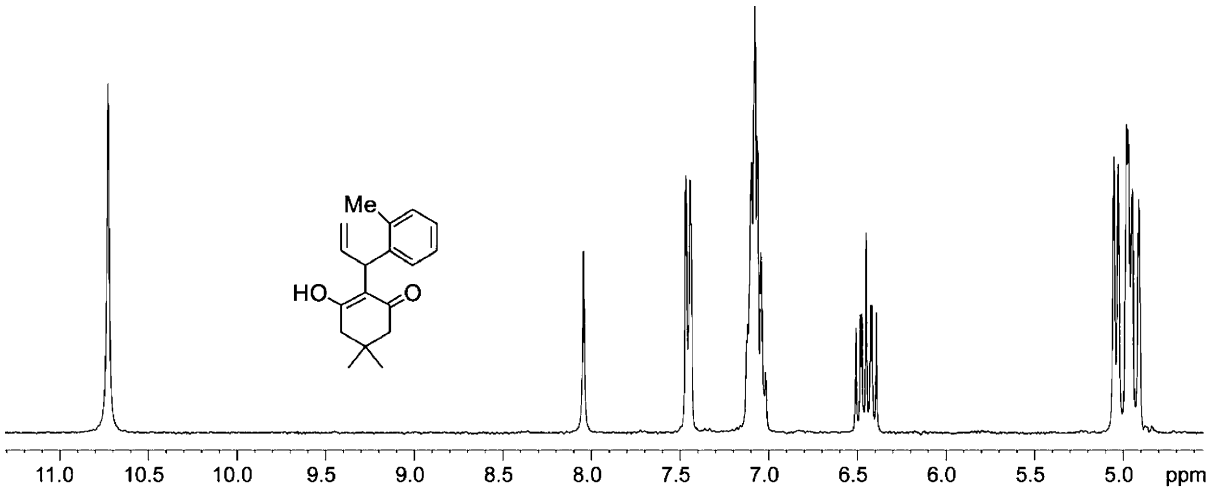
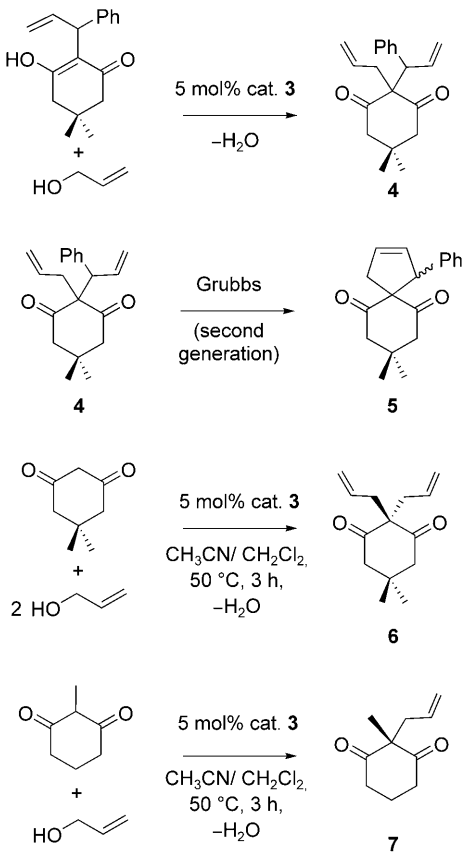


Figure 1. Section of the ^{1}H NMR spectrum of the product derived from dimedone and the allyl alcohol, (*o*-tolyl)-CH(OH)CH=CH_2. The resonance at $\delta = 10.73$ stems from the OH group of the enol. There are three signals (two from the vinyl group CH=CH_2 and the aliphatic CH) in the region around $\delta = 5.0$. The residual CHO of the solvent appears at *ca* $\delta =$ 8.04 (300 MHz, DMF-d_7).



Scheme 2. Allylation reactions.

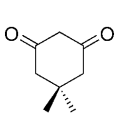
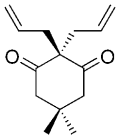
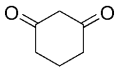
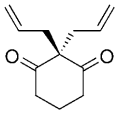
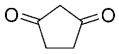
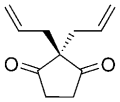
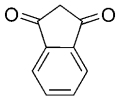
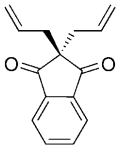
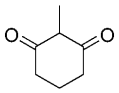
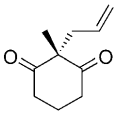
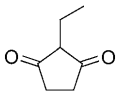
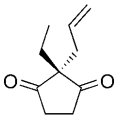
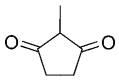
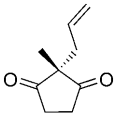
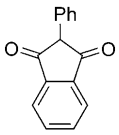
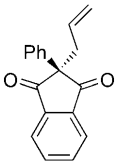
mediate has relatively large coefficients on the substituted allyl carbon.

In a second catalyzed step, the mono-allylated product can then be treated with, e.g., allyl alcohol, to afford a mixed bis-allyl product such as **4**, in 60% yield (see Scheme 2). Compound **4** can then be ring-closed[27a] in 96% yield to give an asymmetric spirane derivative, **5** (and this is also indicated in Scheme 2).

Continuing, Scheme 2 also shows that sulfonate catalyst **3** easily affords the products of the double allylation of a variety of 1,3-diketones using CH_2=$CHCH_2OH$ as substrate in greater than 90% yield (see **6** and entries 1–4 of Table 2). Furthermore, one can smoothly add an allyl function to an existing tertiary carbon centre, as shown by compound **7** in Scheme 2 and entries 5–8 in Table 2. The yields are essentially quantitative and the values shown are, once again, for isolated yields, after column chromatography.

Figure 2 gives an overview of the development of the double-allylation compound, **6**, as a function of time using CH_2=$CHCH_2OH$ as substrate. From this figure, one can deduce that the rate of the second allylation for this relatively small alcohol is similar to that of the rate for the first allylation so that a high yield of the mono-allyl product would be difficult to obtain. Scheme 3 shows a proposed mechanism for the regioselective mono-allylation of dimedone to the branched product using a substituted allyl alcohol as substrate.

Table 2. Allylation of 1,3-diketones with CH_2=$CHCH_2OH$ using **3**.

Entry[a]	Nucleophile	Product	Yield [%]
1			97
2			92
3			88
4[b]			89
5			96
6			92
7			98
8			96

[a] *Reaction conditions:* CH_3CN (0.8 mL), CH_2Cl_2 (3.3 mL), diketone (0.80 mmol), CH_2=$CHCH_2OH$ (0.85 mmol or 1.65 mmol), **3** (0.04 mmol = 5 mol%), 50 °C, 3 h.

[b] 16 h at 50 °C.

Several points should be noted: a) the sulfonate is not always coordinated in acetonitrile solution,[19e] b) perhaps the nucleophile looses a proton, to form an anion, before it attacks the Ru(IV) allyl complex and c) based on stoichiometric reactions [see, for example, Eq (6)], we believe the oxidative addition reaction to be relatively fast and the nucleophilic attack on the allyl complex to be rate-determining. In the stoichiometric oxidative addition chemistry of Eq. (6), where the ratio Ru/alcohol is 1:1, the reaction goes to com-

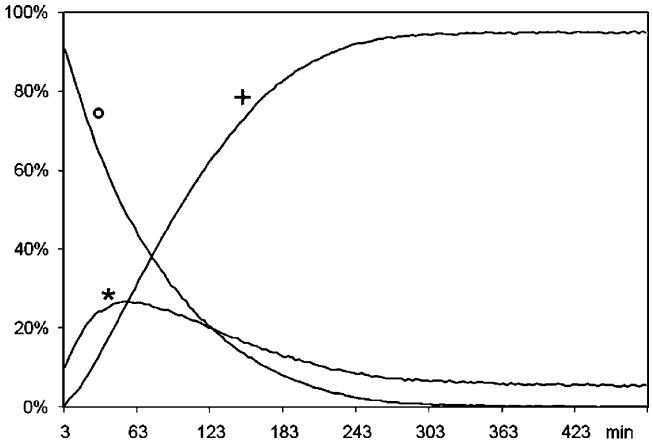
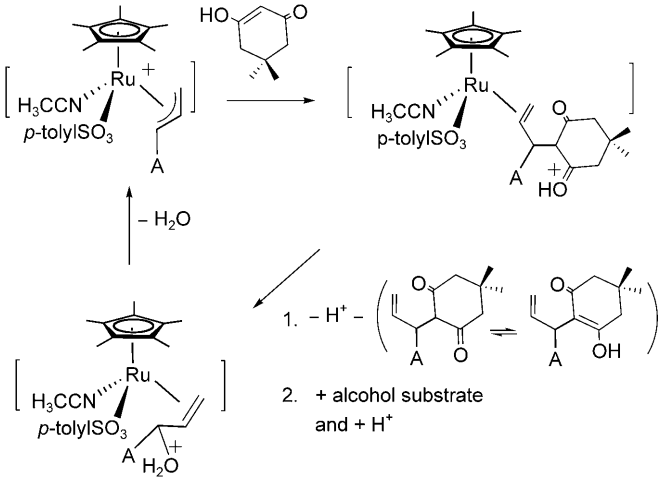
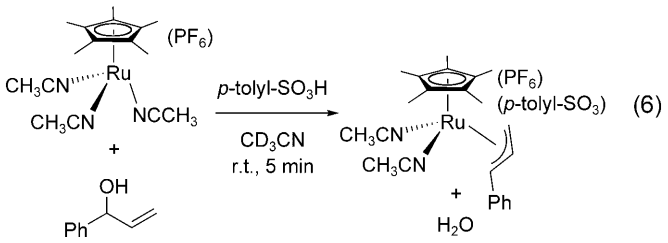


Figure 2. An overview of the development of the double-allylation, giving **6**, (+) and the mono-allylation (*) products as a function of time at room temperature. The double-allylation and mono-allylation compounds grow at similar rates. The curve marked (o) represents the concentration of allyl alcohol as a function of time.



Scheme 3. Proposed mechanism. In the first cycle, A = H. After this cycle, A = the aryl substituents of the alcohol.



pletion within 5 min. In the catalytic reaction, where the alcohol is in excess (and thus the oxidative addition should be even faster) the reaction requires several hours. This observation, and others, supports the view that oxidative addition is fairly facile.

Conclusions

Summarizing, because it readily accommodates allyl alcohols as substrate, Ru sulfonate catalyst **3** represents an efficient "green" alternative to existing allylation catalysts in that it does not waste the leaving group. Furthermore, the reactions take place under mild conditions and no additives of any kind are required. In contrast to Pd-catalyzed reactions of 1,3-diketones with substituted allyl alcohols that afford mixtures of mono- and di-allyl products, catalyst **3** is capable of *both* regioselectivity and controlled mono-allylation of these compounds. The catalyst is sufficiently fast such that the desired products are formed before the alcohol can react with acid to form diallyl ether. The regioselectivity, specificity (for the mono-allyl product) and ability to use alcohols make complex **3** a very attractive reagent.

Experimental Section

General Information

All air-sensitive manipulations were carried out under a nitrogen atmosphere. DMF-d_7 was dried over molecular sieves and stored under nitrogen. Readily available starting materials were purchased from commercial sources and used as received. $[Ru(Cp^*)(\eta^3\text{-}C_3H_5)(p\text{-}CH_3C_6H_4SO_3)_2]$[19d] was synthesized according to a known literature procedure. ^1H, ^{13}C, and 2D NMR spectra were recorded with Bruker DPX-300 and 700 MHz spectrometers at room temperature. ^1H and ^{13}C chemical shifts are given in ppm and referenced relative to TMS. Mass spectroscopic studies were performed at the ETHZ.

Synthesis of Allyl Alcohols

The allyl alcohols used in the allylation reaction were synthesized according to a modified literature procedure.[31] The modification consisted of performing the addition of vinylmagnesium bromide (1 M in THF, 1.2 equivalents) at −78 °C within 15 min with subsequent stirring at room temperature for 15 min. The alcohols were isolated by distillation under vacuum.

Typical Preparative Procedure for Allylation of the Diketones with $ArCH(OH)CH{=}CH_2$

Dimedone (0.65 mmol) was added to an acetonitrile solution (1.6 mL) of $ArCH(OH)CH{=}CH_2$ (0.68 mmol) and $[Ru(Cp^*)(\eta^3\text{-}C_3H_5)(p\text{-}CH_3C_6H_4SO_3)_2]$, (**3**) (0.020 g, 0.03 mmol). After addition of H_2O (1.6 mL) the reaction mixture was stirred for 5 h at room temperature and then evaporated under vacuum. Addition of an excess EtOAc followed by filtration through silica gel removed the Ru catalyst. The crude material was crystallized from either EtOAc, Et_2O, hexane or mixtures of these solutions at −30 °C. At ambient temperature the ^{13}C NMR spectra in DMF-d_7 of all of the enol forms show only an average of the C–O and C=O signals.

Preliminary tests on acyclic 1,3-diketones, and a few 1,3-diesters, were not successful under our very mild conditions, in the absence of base.

3-Hydroxy-5,5-dimethyl-2-(1-phenylallyl)cyclohex-2-enone: Crystallized from EtOAc at −30 °C; yield: 78%; white solid; mp 129–130 °C; ^{1}H NMR (DMF-d_7, 300 MHz): δ = 11.0 (brs, 1H) 7.47–7.28 (m, 5H), 6.83–6.71 (m, 1H), 5.28–5.14 (m, 3H), 2.54 (brs, 4H), 1.23 (s, 6H); ^{13}C NMR (DMF-d_7, 75 MHz): δ = 184.0, 144.6, 140.4, 127.9, 127.7, 125.4, 116.2, 114.4, 47.2, 43.9, 32.0, 27.9; HR-EI-MS: m/z = 256.1463, calcd. for $[C_{17}H_{20}O_2^+]$: 256.1458.

2-[1-(*o*-Chlorophenyl)allyl]-3-hydroxy-5,5-dimethylcyclohex-2-enone: Crystallized from EtOAc at −30 °C; yield: 75%; white solid; mp 169–170 °C; ^{1}H NMR (DMF-d_7, 300 MHz): δ = 10.8 (brs, 1H), 7.56 (d, 1H, J = 8 Hz), 7.36–7.17 (m, 3H), 6.40–6.31 (m, 1H), 5.22 (d, 1H, J = 7 Hz), 5.06–4.98 (m, 2H), 2.34 (brs, 4H), 1.05 (s, 6H); ^{13}C NMR (DMF-d_7, 75 MHz): δ = 141.9, 139.1, 133.5, 131.3, 129.1, 127.4, 126.4, 114.5, 114.1, 47.3, 41.7, 31.8, 27.9, C−O not observed; HR-EI-MS: m/z = 290.1057, calcd. for $[C_{17}H_{19}ClO_2^+]$: 290.1068

3-Hydroxy-5,5-dimethyl-2-(1-(naphthalen-1-yl)allyl)cyclohex-2-enone: Crystallized from EtOAc at −30 °C; yield: 70%; white solid; mp 165–166 °C; ^{1}H NMR (DMF-d_7, 300 MHz): δ = 11.0 (brs, 1H), 8.37–7.58 (m, 7H), 6.81–6.70 (m, 1H), 5.82 (d, 1H, J = 7 Hz), 5.32–5.26 (m, 2H), 2.56–2.43 (m, 4H), 1.15 (s, 6H); ^{13}C NMR (DMF-d_7, 75 MHz): δ = 140.2, 139.9, 133.9, 132.2, 128.6, 126.6, 126.2, 125.5, 125.2, 125.1, 124.4, 115.8, 113.8, 47.1, 40.3, 31.7, 27.7, C−O not observed; HR-EI-MS: m/z = 306.1618,calcd. for $[C_{21}H_{22}O_2^+]$: 306.1614.

3-Hydroxy-5,5-dimethyl-2-(1-*o*-tolylallyl)cyclohex-2-enone: Crystallized from EtOAc at −30 °C; yield: 77%; white solid; mp 151–152 °C; ^{1}H NMR (DMF-d_7, 300 MHz): δ = 10.7 (brs, 1H), 7.46 (d, 1H, J = 7 Hz), 7.12–7.04 (m, 3H), 6.51–6.39 (m, 1H), 5.05–4.91 (m, 3H), 2.35–2.32 (m, 7H), 1.04 (s, 6H); ^{13}C NMR (DMF-d_7, 75 MHz): δ = 142.6, 140.8, 136.2, 129.9, 129.2, 125.6, 125.4, 115.6, 112.9, 47.6, 41.5, 31.8, 27.9, 19.3, C−O not observed; HR-EI-MS: m/z = 270.1612, calcd. for $[C_{18}H_{22}O_2^+]$: 270.1614.

3-Hydroxy-2-[1-(*p*-methoxyphenyl)allyl]-5,5-dimethylcyclohex-2-enone: Crystallized from EtOAc at −30 °C; yield: 73%; white solid; mp 126–127; ^{1}H NMR (DMF-d_7, 300 MHz): δ = 10.8 (brs, 1H), 7.19 (d, 2H, J = 8 Hz), 6.83 (d, 2H, J = 8 Hz), 6.63–6.51 (m, 1H), 5.07–4.89 (m, 3H), 3.77 (s, 3H), 2.35 (brs, 4H), 1.05 (s, 6H); ^{13}C NMR (DMF-d_7, 75 MHz): δ = 157.6, 140.7, 136.3, 128.5, 116.2, 113.8, 113.2, 54.8, 47.1, 43.1, 31.8, 27.8, C−O not observed; HR-EI-MS: m/z = 286.1563, calcd. for $[C_{18}H_{22}O_3^+]$: 286.1563.

3-Hydroxy-5,5-dimethyl-2-(1-(naphthalene-2-yl)allyl)cyclohex-2-enone: Crystallized from EtOAc at −30 °C; yield: 79%; white solid; mp 121–123 °C; ^{1}H NMR (DMF-d_7, 300 MHz): δ = 10.9 (brs, 1H), 7.86–7.44 (m, 7H), 6.80–6.68 (m, 1H), 5.22–5.15 (m, 3H), 2.42 (brs, 4H), 1.10 (s, 6H); ^{13}CNMR (DMF-d_7, 75 MHz): δ = 143.0, 140.0, 133.6, 132.0, 127.6, 127.5, 127.2, 126.8, 125.8, 125.3, 125.1, 115.9, 114.6, 47.0, 43.9, 31.8, 27.8, C−O not observed; HR-EI-MS: m/z = 306.1613, calcd. for $[C_{21}H_{22}O_2^+]$: 306.1614.

2-[1-(*p*-chlorophenyl)allyl]-3-hydroxy-5,5-dimethylcyclohex-2-enone: Crystallized from Et_2O/hexane at −30 °C; yield: 62%; white solid; mp 135–137 °C; ^{1}H NMR (DMF-d_7, 300 MHz): δ = 10.9 (brs, 1H), 7.33–7.26 (m, 4H), 6.56–6.47 (m, 1H), 5.121–4.93 (m, 3H), 2.36 (brs, 4H), 1.05 (s, 6H); ^{13}C NMR (DMF-d_7, 75 MHz): δ = 183.3, 143.6, 139.6, 130.3, 129.3, 127.7, 115.5, 114.6, 47.0, 43.1, 31.8, 27.7; HR-EI-MS: m/z = 290.1068, calcd. for $[C_{17}H_{19}ClO_2^+]$: 290.1068.

3-Hydroxy-5,5-dimethyl-2-[1-(thiophen-2-yl)allyl]cyclohex-2-enone: Crystallized from Et_2O at −30 °C; yield: 77%; white solid; mp 131–132 °C; ^{1}H NMR (DMF-d_7, 300 MHz): δ = 11.2 (brs, 1H), 7.42 (d, 1H, J = 5 Hz), 7.09–7.07 (m, 1H), 6.96–6.94 (m, 1H), 6.96–6.94 (m, 1H), 6.80–6.68 (m, 1H), 5.31–5.17 (m, 3H), 2.53 (brs, 4H), 1.24 (s, 6H); ^{13}C NMR (DMF-d_7, 75 MHz): δ = 82.6, 148.7, 140.0, 126.4, 123.3, 123.0, 116.0, 114.3, 47.0, 39.9, 31.8, 27.8; HR-EI-MS: m/z = 262.1022, calcd. for $[C_{15}H_{18}O_2S^+]$: 262.1022.

2-Allyl-5,5-dimethyl-2-(1-phenylallyl)cyclohexane-1,3-dione

3-Hydroxy-5,5-dimethyl-2-(1-phenylallyl)cyclohex-2-enone (0.80 mmol) was added to a CH_3CN solution (0.8 mL) of allyl alcohol (0.88 mmol) and [Ru(Cp*)(η^3-C_3H_5)(*p*-$MeC_6H_4SO_3$)$_2$], (**3**) (0.025 g, 0.04 mmol). After addition of CH_2Cl_2 (3.4 mL) the reaction mixture was refluxed for 16 h at 70°, then evaporated under vacuum and separated by column chromatography on silica gel (hexane/EtOAc gradient from 8:1 to 6:1). The product was dried under vacuum to afford a very viscous oil; yield: 140 mg (60%); ^{1}H NMR ($CDCl_3$, 700 MHz): δ = 7.29 (t, 2H, J_1 = 8 Hz, J_2 = 7 Hz), 7.24 (t, 1H, J_1 = 8 Hz, J_2 = 7 Hz), 7.08 (d, 2H, J_1 = 8 Hz), 6.32 (dt, 1H, J_1 = 17 Hz, J_2 = 11 Hz), 5.58–5.54 (m, 1H), 5.21 (dd, 1H, J_1 = 1 Hz, J_1 = 11 Hz), 5.13 (d, 1H, J = 17 Hz), 5.07 (dd, 1H, J_1 = 18 Hz, J_2 = 1 Hz), 5.00 (dd, 1H, J_1 = 11 Hz, J_2 = 1 Hz), 3.77 (d, 1H, J = 11 Hz), 2.66 (dd, 1H, J_1 = 13 Hz, J_1 = 7 Hz), 2.58 (dd, 1H, J_1 = 13 Hz, J_1 = 7 Hz), 2.42 (dd, 1H, J_1 = 15 Hz, J_1 = 2 Hz), 2.38–2.36 (m, 2H), 2.06 (d, 1H, J = 15 Hz), 0.85 (s, 3H), 0.77 (s, 3H); ^{13}C NMR ($CDCl_3$ 176 MHz): δ = 209.7, 209.3, 139.2, 135.5, 133.4, 129.2, 128.5, 127.5, 119.5, 118.5, 71.3, 57.8, 54.3, 54.0, 37.5, 30.4, 30.1, 28.1; HR-EI-MS: m/z = 296.1773, calcd. for $[C_{20}H_{24}O_2^+]$: 296.1771.

8,8-Dimethyl-1-phenylspiro[4.5]dec-2-ene-6,10-dione

A mixture of 2-allyl-5,5-dimethyl-2-(1-phenylallyl)-cyclohexane-1,3-dione (0.11 mmol) and Grubb's catalyst [bis(tricylohexylphosphine)benzylideneruthenium(IV) dichloride] (5 mg, 0.006 mmol) in dry CH_2Cl_2 (4 mL) was stirred at room temperature for 14 h under N_2 atmosphere. The reaction mixture was evaporated under vacuum and separated by column chromatography on silica gel (hexane/EtOAc = 6:1). The product was dried under vacuum to afford a white solid; yield: 29 mg (96%); mp 135–136 °C; ^{1}H NMR ($CDCl_3$, 700 MHz): δ = 7.30–7.27 (m, 3H), 7.13 (d, 2H, J_1 = 7 Hz), 6.02–6.00 (m, 1H,), 5.38–5.36 (m, 1H), 4.14 (d, 1H, J = 1 Hz), 3.25 (dd, 1H, J_1 = 17 Hz, J_1 = 3 Hz), 3.05–3.01 (m, 2H), 2.51 (dd, 1H, J_1 = 15 Hz, J_1 = 3 Hz), 2.02 (dd, 1H, J_1 = 15 Hz, J_1 = 3 Hz), 1.74 (d, 1H, J = 15 Hz), 1.04 (s, 3H), 0.76 (s, 3H); ^{13}C NMR ($CDCl_3$ 176 MHz): δ = 207.0, 206.1, 138.8, 131.6, 129.2, 128.6, 128.4, 128.0, 75.8, 63.1, 53.8, 51.6, 34.0, 30.6, 30.1, 26.7; HR-EI-MS: m/z = 268.1456, calcd. for $[C_{18}H_{20}O_2^+]$: 268.1458.

Typical Preparative Procedure for Allylation of 1,3-Diketones with CH_2=$CHCH_2OH$

The 1,3-diketone (0.80 mmol) was added to an acetonitrile solution (0.8 mL) of allyl alcohol (0.85 mmol or 1.65 mmol) and $[Ru(Cp^*)(\eta^3\text{-}C_3H_5)(p\text{-}CH_3C_6H_4SO_3)_2]$, (**3**) (0.025 g, 0.04 mmol). After addition of CH_2Cl_2 (3.3 mL) the reaction mixture was stirred for 3 h at 50 °C. The reaction mixture was then evaporated under vacuum and the product separated by column chromatography on silica gel. These products are all known compounds and were identified by comparison of their spectroscopic data (^{1}H and ^{13}C NMR) and HR-EI-MS with those from the literature.

2,2-Diallyl-5,5-dimethylcyclohexane-1,3-dione:[32] Hexane/EtOAc = 6:1; yield: 97%; viscous oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.67–5.55 (m, 2H), 5.14–5.07 (m, 4H), 2.56 (s, 4H), 2.52 (d, 4H, J = 8 Hz), 1.00 (s, 6H); ^{13}C NMR ($CDCl_3$ 75 MHz): δ = 208.7, 132.4, 119.4, 68.0, 52.1, 38.9, 30.7, 28.8; HR-EI-MS: m/z = 220.1459, calcd. for $[C_{14}H_{20}O_2^+]$: 220.1458.

2,2-Diallylcyclohexane-1,3-dione:[33] Hexane/EtOAc = 6:1; yield: 92%; viscous oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.61–5.50 (m, 2H), 5.08–5.03 (m, 4H), 2.58 –2.52 (m, 8H), 1.98–1.91 (m, 2H); ^{13}C NMR ($CDCl_3$ 75 MHz): δ = 210.3, 132.4, 119.4, 68.3, 40.9, 40.0, 16.4; HR-EI-MS: m/z = 192.1147, calcd. for $[C_{12}H_{16}O_2^+]$: 192.1145.

2-Allyl-2-ethylcyclopentane-1,3-dione:[34] Hexane/EtOAc = 6:1; yield:92%; viscous oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.64–5.50 (m, 1H), 5.08–5.03 (m, 2H), 2.67 (brs, 4H), 2.36 (d, 2H, J = 8 Hz), 1.71 (q, 2H, J = 8 Hz), 0.79 (t, 3H, J = 8 Hz); ^{13}C NMR ($CDCl_3$ 75 MHz): δ = 216.9, 131.6, 119.7, 61.8, 39.2, 36.4, 28.2, 9.1; HR-EI-MS: m/z = 166.0990, calcd. for $[C_{10}H_{14}O_2^+]$: 166.0988.

2,2-Diallylcyclopentane-1,3-dione:[35] Hexane/EtOAc = 6:1; yield: 88%; viscous oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.64–5.50 (m, 2H), 5.09–5.04 (m, 4H), 2.63 (brs, 4H), 2.38 (d, 4H, J = 8 Hz); ^{13}C NMR ($CDCl_3$ 75 MHz): δ = 216.4, 131.3, 120.0, 61.2, 39.4, 36.4; HR-EI-MS: m/z = 178.0989, calcd. for $[C_{11}H_{14}O_2^+]$: 178.0988.

2-Allyl-2-methylcyclopentane-1,3-dione:[34] Hexane/EtOAc = 6:1; yield: 98%; viscous oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.64–5.53 (m, 1H), 5.09–5.04 (m, 2H), 2.82–2.63 (m, 4H), 2.35 (d, 2H, J = 8 Hz), 1.12 (s, 3H); ^{13}C NMR ($CDCl_3$ 75 MHz): δ = 216.2, 131.5, 119.8, 56.7, 40.0, 35.4, 18.8; HR-EI-MS: m/z = 152.0830, calcd. for $[C_9H_{12}O_2^+]$: 152.0832.

2-Allyl-2-phenyl-indene-1,3-dione:[36] Hexane/EtOAc = 6:1; yield: 98%; viscous oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.05–8.03 (m, 2H), 7.88–7.86 (m, 2H), 7.45 (d, 2H, J = 5 Hz), 7.35–7.26 (m, 3H), 5.62–5.56 (m, 1H), 5.15 (d, 1H, J = 10 Hz), 4.96 (d, 1H, J = 6 Hz), 3.06 (d, 2H, J = 4 Hz); ^{13}C NMR ($CDCl_3$ 75 MHz): δ = 201.5, 142.5, 137.0, 136.3, 132.2, 129.2, 128.2, 127.3, 123.9, 124.0, 120.4, 62.6, 40.5; HR-EI-MS: m/z = 262.0992, calcd. for $[C_{18}H_{14}O_2^+]$: 262.0988.

2-Allyl-2-methylcyclohexane-1,3-dione:[37] Hexane/EtOAc = 6:1; yield: 96%; viscous oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.63–5.54 (m, 1H), 5.10–5.05 (m, 2H), 2.68 –2.64 (m, 4H), 2.54 (d, 2H, J = 8 Hz), 2.05–1.87 (m, 2H), 1.25 (s, 3H); ^{13}C NMR ($CDCl_3$ 75 MHz): δ = 209.8, 132.2, 119.2, 65.2, 41.3, 38.2, 19.5, 17.5; HR-EI-MS: m/z = 166.0989, calcd. for $[C_{10}H_{14}O_2^+]$: 166.0988.

2,2-Diallyl-1-indene-1,3(2*H*)-dione:[36] Hexane/EtOAc = 6:1; yield: 89%; viscous oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.97–7.93 (m, 2H), 7.86–7.82 (m, 2H), 5.54–5.40 (m, 1H), 5.03 (d, 2H, J = 17 Hz), 4.89 (d, 2H, J = 10 Hz), 2.55 (d, 4H, J = 8 Hz); ^{13}C NMR ($CDCl_3$ 75 MHz): δ = 203.3, 142.23, 135.7, 131.4, 123.0, 119.5, 58.3, 38.8; HR-EI-MS: m/z = 226.0983, calcd. for $[C_{15}H_{14}O_2^{\cdot+}]$ 226.0988.

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References

[1] B. M. Trost, D. L. van Vranken, *Chem. Rev.* **1996**, *96*, 395.

[2] A. Leitner, C. T. Shu, J. F. Hartwig, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5830; C. García-Yebra, J. P. Janssen, F. Rominger, G. Helmchen, *Organometallics* **2004**, *23*, 545; G. Helmchen, A. Dahnz, P. Dubon, M. Schelwies, R. Weihofen, *Chem. Commun.* **2007**, 675.

[3] L. Palais, I. S. Mikhel, C. Bournaud, L. Micouin, C. A. Falciola, M. Vuagnoux-d'Augustin, S. Rosset, G. Bernardinelli, A. Alexakis, *Angew. Chem.* **2007**, *119*, 7606; *Angew. Chem. Int. Ed.* **2007**, *46*, 7462; D. Polet, A. Alexakis, K. Tissot-Croset, C. Corminboeuf, K. Ditrich, *Chem. Eur. J.* **2006**, *12*, 3596.

[4] B. M. Trost, P. L. Fraisse, Z. T. Ball, *Angew. Chem.* **2002**, *114*, 1101; *Angew. Chem. Int. Ed.* **2002**, *41*, 1059.

[5] C. Bruneau, J. L. Renaud, B. Demerseman, *Chem. Eur. J.* **2006**, *12*, 5178, J. L. Renaud, B. Demerseman, M. D. Mbaye, C. Bruneau, *Curr. Org. Chem.* **2006**, *10*, 115.

[6] Y. Tsuji, T. Mukai, T. Kondo, Y. Watanabe, *J. Organomet. Chem.* **1989**, *369*, C51; S. Zhang, T. Mitsudo, T. Kondo, Y. Watanabe, *J. Organomet. Chem.* **1993**, *450*, 197; Y. Morisaki, T. Kondo, T. A. Mitsudo, *Organometallics* **1999**, *18*, 4742.

[7] Y. Yamamoto, Y. Nakagai, K. Itoh, *Chem. Eur. J.* **2004**, *10*, 231.

[8] S. Tanaka, H. Saburi, M. Kitamura, *Adv. Synth. Catal.* **2006**, *348*, 375; S. Tanaka, H. Saburi, T. Hirakawa, T. Seki, M. Kitamura, *Chem. Lett.* **2009**, *38*, 188; J. A. van Rijn, M. Lutz, L S. von Chrzanowski, A. L. Spek, E. Bouwman, E. Drent, *Adv. Synth. Catal.* **2009**, *351*, 1637.

[9] S. Oi, Y. Tanaka, Y. Inoue, *Organometallics* **2006**, *25*, 2773.

[10] T. Kondo, H. Ono, N. Satake, T. Mitsudo, Y. Watanabe, *Organometallics* **1995**, *14*, 1945.

[11] R. Grigg, N. Kongathip, B. Kongathip, S. Luangkamin, H. Donda, A. , *Tetrahedron* **2001**, *57*, 9187.

[12] L. Renaud, C. Bruneau, B. Demerseman, *Synlett* **2003**, 408.

[13] B. Ranu, K. Chattopdhyay, L. Adak, *Org. Lett.* **2007**, *9*, 4595.

[14] A. Bouziane, M. Helou, B. Carboni, F. Carreaux, B. Demerseman, C. Bruneau, J. Renaud, *Chem. Eur. J.* **2008**, *14*, 5630.

[15] a) I. Usui, S. Schmidt, B. Breit, *Org. Lett.* **2009**, *11*, 1453; b) K. Gan, C. Jhong, S. Yang, *Tetrahedron* **2008**,

64, 1204; c) Y. Tamaru, *Eur. J. Org. Chem.* **2005**, 2647; d) M. Kimura, M. Shimizu, S. Tanaka, Y. Tamaru, *Tetrahedron* **2005**, *61*, 3709; e) H. Saburi, S. Tanaka, M. Kitamura, *Angew. Chem.* **2005**, *117*, 1758; *Angew. Chem. Int. Ed.* **2005**, *44*, 1730; f) G. Onodera, H. Imajima, M. Yamanashi, Y. Nishibayashi, M. Hidai, S. Uemura, *Organometallics* **2004**, *23*, 5841; g) Y. Kayaki, T. Koda, T. Ikariya, *J. Org. Chem.* **2004**, *69*, 2595; h) S. Yang, Y. Tsai, *Organometallics* **2001**, *20*, 763; i) T. Kondo, T. Mukai, Y. Watanabe, *J. Org. Chem.* **1991**, *56*, 487.

[16] B. M. Trost, J. Quancard, *J. Am. Chem. Soc.* **2006**, *128*, 6314.

[17] M. Kimura, M. Futamata, R. Mukai, Y. Tamaru, *J. Am. Chem. Soc.* **2005**, *127*, 4592; M. Kimura, M. Fukasaka, Y. Tamaru, *Synthesis* **2006**, 3611.

[18] I. Usui, S. Schmidt, M. Keller, B. Breit, *Org. Lett.* **2008**, *10*, 1207–1210.

[19] a) A. B. Zaitsev, S. Gruber, P. S. Pregosin, *Chem. Commun.* **2007**, 4692; b) I. F. Nieves, D. Schott, S. Gruber, P. S. Pregosin, *Helv. Chim. Acta* **2007**, *90*, 271; c) S. Gruber , A. B. Zaitsev, M. Wörle, P. S. Pregosin, L. F. Veiros, *Organometallics* **2008**, *27*, 3796; d) A. B. Zaitsev, S. Gruber, P. A. Pluss, P. S. Pregosin, L. F. Veiros, M. Worle, *J. Am. Chem. Soc.* **2008**, *130*, 11604; e) S. Gruber, A. B. Zaitsev, M. Worle, P. S. Pregosin, L. F. Veiros, *Organometallics* **2009**, *28*, 3437; f) A. B. Zaitsev, H. F. Caldwell, P. S. Pregosin, L. F. Veiros, *Chem. Eur. J.* **2009**, *15*, 6468.

[20] E. C. Burger, J. A. Tunge, *Org. Lett.* **2004**, *6*, 2603.

[21] S. Tanaka, H. Saburi, M. Kitamura, *Adv. Synth. Catal.* **2006**, *348*, 375.

[22] H. J. Zhang, B. Demersernan, L. Toupet, Z. F. Xi, C. Bruneau, *Adv. Synth. Catal.* **2008**, *350*, 1601.

[23] K. Onitsuka, Y. Ajioka, Y. Matsushima, S. Takahashi, *Organometallics* **2001**, *20*, 3274.

[24] R. Hermatschweiler, I. Fernandez, F. Breher, P. S. Pregosin, L. F. Veiros, M. J. Calhorda, *Angew. Chem.* **2005**, *117*, 4471; *Angew. Chem. Int. Ed.* **2005**, *44*, 4397.

[25] Y. Nishibayashi, H. Imajima, G. Onodera, M. Hidai, S. Uemura, *Organometallics* **2004**, *23*, 26; Y. Nishibayashi, H. Imajima, G. Onodera, Y. Inada, M. Hidai, S. Uemura, *Organometallics* **2004**, *23*, 5100; Y. Nishibayashi, G. Onodera, Y. Inada, M. Hidai, S. Uemura, *Organometallics* **2003**, *22*, 873.

[26] B. Demerseman, J. L. Renaud, L. Toupet, C. Hubert, C. Bruneau, *Eur. J. Inorg. Chem.* **2006**, 1371.

[27] a) B. Ranu, K. Chattopdhyay, L. Adak, *Org. Lett.* **2007**, *9*, 4595; b) S. Sigismondi, D. Sinou, *J. Mol. Catal. A* **1997**, *116*, 289.

[28] J. Clayden, N. Greeves, S. Warren, P. Wothers, *Organic Chemistry*, Oxford University Press, **2001**, pp 534–534.

[29] For product **7** (entry 1 of Table 1.) at 223 K, the enol OH proton is found at 11.67 ppm. The ^{13}C NMR signals for C–OH and C=O are observed at 171.0 and 196.4 ppm, respectively.

[30] R. Hermatschweiler, I. Fernandez, P. S. Pregosin, E. J. Watson, A. Albinati, S. Rizzato, L. F. Veiros, M. J. Calhorda, *Organometallics* **2005**, *24*, 1809; R. Hermatschweiler, I. Fernandez, P. S. Pregosin, E. J. Watson, A. Albinati, S. Rizzato, L. F. Veiros, M. J. Calhorda, *Organometallics* **2008**, *27*, 3796.

[31] A. Briot, C. Baehr, R. Brouillard, A. Wagner, C. Mioskowski, *J. Org. Chem.* **2004**, *69*, 1374.

[32] M. A. Lapitskaya, K. K. Pivnitskii, *Zhur. Org. Khim.* **1990**, *26*, 1926.

[33] S. Kotha, E. Manivannan, T. Ganesh, N. Sreenivasachary, A. Deb, *Synlett* **1999**, 1618.

[34] H. Schick, H. Schwarz, A. Finger, S. Schwarz, *Tetrahedron* **1982**, *38*, 1279.

[35] C. E. Schwartz, D. P. Curran, *J. Am. Chem. Soc.* **1990**, *112*, 9272.

[36] M. Braun, R. Veith, *Tetrahedron Lett.* **1986**, *27*, 179.

[37] R. Thennati, P. Namasivayam, *Synth. Commun.* **1993**, *23*, 3095.

