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Ruthenium(II) Complexes with η^6-Coordinated 3-Phenylpropanol and 2-Phenylethanol as Catalysts for the Tandem Isomerization/Claisen Rearrangement of Diallyl Ethers in Water

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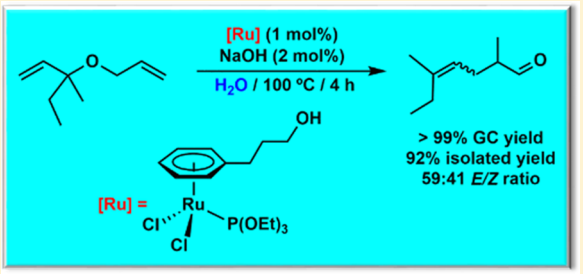
Supporting Information

ABSTRACT: A series of half-sandwich ruthenium(II) complexes containing η^6-coordinated 2-phenylethanol and 3-phenylpropanol ligands, namely $[RuCl_2\{\eta^6\text{-}C_6H_5CH_2(CH_2)_nCH_2OH\}(PR_3)]$ (PR_3 = PMe_3, PPh_3, $P(OMe)_3$, $P(OEt)_3$, $P(O^iPr)_3$, $P(OPh)_3$; n = 0 (**1a–f**), 1 (**2a–f**)), have been investigated as catalysts for the tandem isomerization/Claisen rearrangement of diallyl ethers into γ,δ-unsaturated aldehydes using, for the first time, water as solvent. The best results in terms of activity and regioselectivity were obtained with the 3-phenylpropanol derivative $[RuCl_2(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)\{P(OEt)_3\}]$ (**2d**). Thus, using only 1 mol % of this complex, in combination with NaOH (2 mol %), different diallyl ethers could be conveniently converted into the corresponding aldehydes in high yields and short times under relatively mild thermal conditions (100 °C).



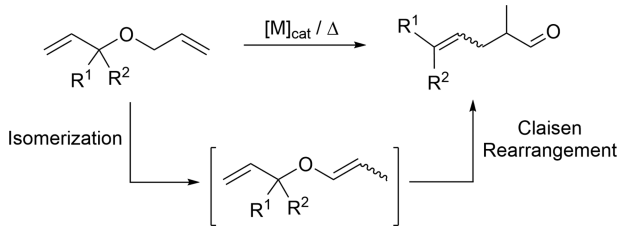
INTRODUCTION

Since its discovery in 1912,[1] the Claisen rearrangement has become one of the most widely used synthetic tools for the selective formation of new C–C bonds.[2] In particular, its aliphatic version starting from allyl vinyl ethers is one of the most effective methods currently available for the preparation of γ,δ-unsaturated carbonyl compounds in an atom-economical manner (Scheme 1). Although these transformations have been traditionally performed under strong thermal activation (ca. 200 °C), a wide number of transition-metal complexes/salts, Lewis acids, and organocatalysts are now known to promote the process, allowing the use of milder reaction conditions compatible with a greater variety of substrates, as well as the development of asymmetric versions leading to enantioenriched products.[2] Worth noting is also the rate-acceleration effect exerted by water in these [3,3]-sigmatropic reactions, a fact that has been associated with the hydrophobic destabilization of the reactants relative to the polar transition state, and the stabilization of the latter by hydrogen bonding.[3]

In addition to stereoselectivity issues,[2] the most problematic aspect associated with this reaction is the access to the starting materials, since the classical methods for preparing allyl vinyl ethers, such as the acid- or base-promoted cleavage of allyl ketals[4] or the Hg-catalyzed transfer of a vinyl group from vinyl ethers to allylic alcohols,[5] usually proceed in low yields.[6] An emerging strategy for simplifying the introduction of the vinyl ether unit is the in situ generation of the allyl vinyl ether substrates from diallyl ethers, compounds that are much easier to synthesize, via a metal-catalyzed isomerization of one of the allyl units (Scheme 2). To avoid the formation of regioisomeric mixtures of products (or the formation of the corresponding divinyl ethers), in these tandem isomerization/Claisen rearrangement (ICR) reactions, diallyl ethers featuring a substituted carbon atom adjacent to one of the C=C bonds

Scheme 1. Claisen Rearrangement of the Model Allyl Vinyl Ether

Scheme 2. Tandem Isomerization/Claisen Rearrangement (ICR) of Diallyl Ethers



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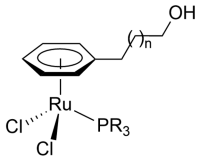
are employed as substrates to ensure the selective isomerization of only one of the two allylic units. To date, catalytic systems based on ruthenium,[7] iridium,[8] and to a lesser extent palladium[9] and rhodium[10] complexes, have been described for these ICR processes.[11−13] However, it is somewhat surprising that, despite the growing interest in developing metal catalysis in environmentally friendly aqueous media[14] and the benefits exerted by water in Claisen rearrangements,[3] the feasibility of ICR reactions in water has not been yet demonstrated, with all of the examples described in the literature making use of anhydrous organic solvents as the reaction medium.

Our group has been interested for a long time in aqueous catalysis, describing different ruthenium(II) and ruthenium(IV) complexes able to promote the migration of allylic C=C bonds in aqueous environments. Substrates covered in our previous works include allyl alcohols,[15] ethers,[16] amines[17] and benzenes.[18] As a continuation, we report herein the successful application of a series of hydrophilic half-sandwich ruthenium(II) complexes, containing η^6-coordinated 2-phenylethanol and 3-phenylpropanol ligands (compounds **1a−f** and **2a−f** in Figure 1), in the tandem isomerization/Claisen rearrangement of diallyl ethers in water.[19,20]



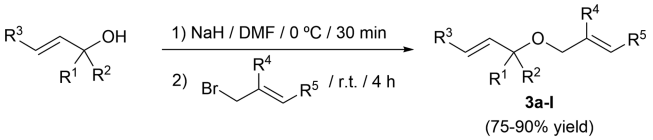
n = 0; PR_3 = PMe_3 (**1a**), PPh_3 (**1b**), $P(OMe)_3$ (**1c**), $P(OEt)_3$ (**1d**), $P(O^iPr)_3$ (**1e**), $P(OPh)_3$ (**1f**)
n = 1; PR_3 = PMe_3 (**2a**), PPh_3 (**2b**), $P(OMe)_3$ (**2c**), $P(OEt)_3$ (**2d**), $P(O^iPr)_3$ (**2e**), $P(OPh)_3$ (**2f**)

Figure 1. Structure of the Ru(II) catalysts employed in this work.

RESULTS AND DISCUSSION

As the starting point of our investigation, we synthesized the required diallyl ethers starting from the corresponding allylic alcohols and bromides, through the general *O*-alkylation route outlined in Scheme 3. The substrates covered include diallyl ethers containing a quaternary (**3a−i**), tertiary (**3j,k**), and secondary (**3l**) carbon atom adjacent to one of the C=C bonds, and different substitution patterns on the olefinic units. Details on the preparation and characterization of all these compounds are given in the Supporting Information.[21]

Scheme 3. Procedure Employed for the Synthesis of the Diallyl Ethers 3a−l

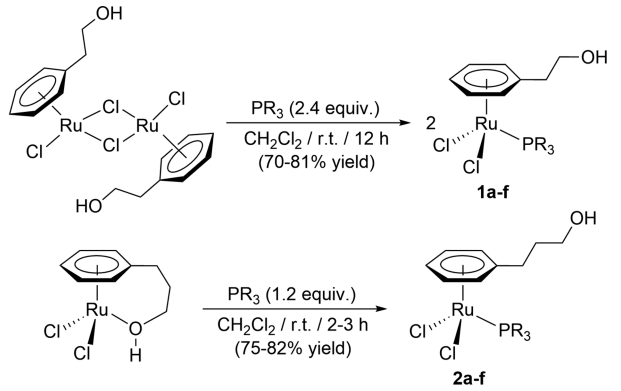


3a-l
(75-90% yield)

R^1 = Me; R^2 = Et; R^3 = R^4 = R^5 = H (**3a**)
R^1 = R^2 = Me; R^3 = R^4 = R^5 = H (**3b**)
R^1 = Me; R^2 = ^{n}Hex; R^3 = R^4 = R^5 = H (**3c**)
R^1/R^2 = -$(CH_2)_5$-; R^3 = R^4 = R^5 = H (**3d**)
R^1 = Me; R^2 = Ph; R^3 = R^4 = R^5 = H (**3e**)
R^1 = Me; R^2 = $CH_2CH_2CH{=}CMe_2$; R^3 = R^4 = R^5 = H (**3f**)
R^1 = R^2 = Me; R^3 = Ph; R^4 = R^5 = H (**3g**)
R^1 = R^2 = R^4 = Me; R^3 = R^5 = H (**3h**)
R^1 = R^2 = R^5 = Me; R^3 = R^4 = H (**3i**)
R^1 = ^{n}Pr; R^2 = R^3 = R^4 = R^5 = H (**3j**)
R^1 = R^3 = Me; R^2 = R^4 = R^5 = H (**3k**)
R^1 = R^2 = R^3 = R^4 = H; R^5 = ^{n}Pr (**3l**)

Concerning the preparation of the arene-ruthenium(II) complexes $[RuCl_2(\eta^6\text{-}C_6H_5CH_2CH_2OH)(PR_3)]$ (**1a−f**) and $[RuCl_2(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)(PR_3)]$ (**2a−f**), they were obtained in 70−82% yield by reacting the dimeric $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_5CH_2CH_2OH)\}_2]$ or monomeric $[RuCl_2\{\eta^6{:}\kappa^1(O)\text{-}C_6H_5CH_2CH_2CH_2OH\}]$ precursor, respectively, with the appropriate P-donor ligand in dichloromethane at room temperature (Scheme 4). As a consequence of the lower solubility of $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_5CH_2CH_2OH)\}_2]$ with respect to $[RuCl_2\{\eta^6{:}\kappa^1(O)\text{-}C_6H_5CH_2CH_2CH_2OH\}]$, longer reaction times were required in the syntheses of the 2-phenylethanol derivatives **1a−f** (12 h vs 2−3 h in the case of **2a−f**). As expected, the formation of all these complexes could be conveniently monitored by $^{31}P\{^1H\}$ NMR spectroscopy, the spectra showing a shift of the phosphorus signal to low fields in the case of the phosphine derivatives **1a,b** and **2a,b** ($\Delta\delta$ 25−68 ppm), and to high fields in the case of the phosphite ones **1c−f** amd **2c−f** ($\Delta\delta$ −16 to −26 ppm), in comparison to the corresponding uncoordinated PR_3 ligand. The preparation and characterization of compounds $[RuCl_2(\eta^6\text{-}C_6H_5CH_2CH_2OH)(PPh_3)]$ (**1b**)[19b] and $[RuCl_2(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)(PR_3)]$ (PR_3 = PPh_3 (**2b**),[19a] $P(OEt)_3$ (**2d**),[19c] $P(OPh)_3$ (**2f**)[19c]) were previously described by us and others. The rest of the complexes synthesized in the present work were fully characterized by means of elemental analysis and IR and multinuclear NMR spectroscopy, the data obtained being in complete agreement with the proposed formulations (details are given in the Experimental Section). In particular, in their ^1H and $^{13}C\{^1H\}$ NMR spectra the aromatic CH_{ortho} and CH_{meta} protons and carbon atoms of the η^6-coordinated 2-phenylethanol and 3-phenylpropanol units were shown to be equivalent, thus confirming the presence of a symmetry plane in the complexes. The IR and ^1H NMR spectra also confirmed that the OH groups of these functionalized arenes are maintained untouched in the final products, showing the characteristic ν(OH) stretching vibration at 3389−3478 cm^{-1} and the proton signal of this functionality at δ_H 1.82−2.87 ppm (as a

Scheme 4. Synthesis of the Arene-Ruthenium(II) Complexes 1a−f and 2a−f



PR_3 = PMe_3 (**a**), PPh_3 (**b**), $P(OMe)_3$ (**c**), $P(OEt)_3$ (**d**), $P(O^iPr)_3$ (**e**), $P(OPh)_3$ (**f**)

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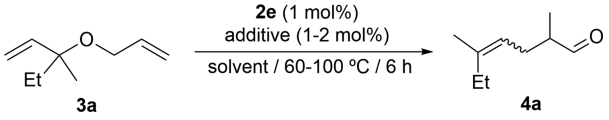
triplet for compounds **1a,c–f** with $^3J_{HH}$ = 5.4–6.9 Hz or as a broad singlet for **2a,c,e**), respectively.

In order to evaluate the feasibility of the tandem isomerization/Claisen rearrangement (ICR) reactions of compounds **3** in water and establish the optimal reaction conditions, we focused on the transformation of 3-(allyloxy)-3-methylpent-1-ene (**3a**) into 2,5-dimethylhept-4-enal (**4a**) employing complex [$RuCl_2(\eta^6$-$C_6H_5CH_2CH_2CH_2OH$){P($O^iPr)_3$}] (**2e**) as a model catalyst. The results of this initial screening are shown in Table 1.

Table 1. Catalytic ICR of 3-(Allyloxy)-3-methylpent-1-ene (3a) Using the Ru(II) Complex [$RuCl_2(\eta^6$-$C_6H_5CH_2CH_2CH_2OH$){$P(O^iPr)_3$}] (2e) as Catalyst[a]



3a **4a**

entry	solvent	additive	T (°C)	conversion (%)[b]	yield of **4a** (%)[b]	E:Z ratio[c]
1	H_2O	none	60	18	17	57:43
2	H_2O	none	80	65	62	57:43
3	H_2O	none	100	91	91	57:43
4	toluene	none	100	28	24	57:43
5	THF	none	100	31	27	58:42
6[d]	toluene/H_2O	none	100	46	43	58:42
7[d]	THF/H_2O	none	100	60	40	58:42
8[e]	H_2O	$AgSbF_6$	100	90	90	57:43
9[e]	H_2O	HCl	100	>99	62	57:43
10[e,f]	H_2O	NaOH	100	>99	93	57:43
11[g]	H_2O	NaOH	100	>99	98	58:42

[a]Reactions performed under an argon atmosphere using 2 mmol of **3a**, 0.02 mmol of **2e**, and 1 mL of the corresponding solvent. [b]Conversions and yields determined by GC. The differences between conversions and yields correspond to the intermediate allyl vinyl ether present in the reaction media. [c]E:Z ratios determined by ^{1}H NMR spectroscopy after evaporation of the solvent. [d]A 1/1 v/v mixture of solvents was employed. [e]Reaction performed with 1 mol % of the additive. [f]Propanal and 3-methylpent-1-en-3-ol were in this case the major byproducts detected by GC. [g]Reaction performed with 2 mol % of the additive.

Thus, a first experiment carried out directly in water with 1 mol % of **2e**, at 60 °C and in the absence of additives, led to a poor conversion of the diallyl ether **3a** (18% by GC) after 6 h (Table 1, entry 1). However, we were delighted to find that this initial result could be significantly improved by increasing the working temperature (entries 2 and 3). In particular, when the reaction was performed at 100 °C, 91% conversion of **3a** was observed by GC after the same time and, more importantly, under these conditions only 2,5-dimethylhept-4-enal (**4a**) was formed (entry 3). At lower temperatures, in addition to the desired aldehyde, minor amounts of a secondary product were present in the chromatograms (entries 1 and 2), which correspond to the nonrearranged allyl vinyl ether intermediate resulting from the initial migration of the C=C bond of the $-OCH_2CH{=}CH_2$ unit of **3a** (see Scheme 2). Also of note is the null effect that the temperature exerts on the stereoselectivity of the reaction, the aldehyde **4a** being in all cases formed as a mixture of E and Z isomers in a 57:43 ratio (entries 1–3).[22] On the other hand, we would like also to remark at this point that, when the same reaction was carried out in toluene or THF, the desired 2,5-dimethylhept-4-enal (**4a**) was generated in much lower yield (≤43% by GC), thus evidencing for the first time the beneficial effect of water on ICR reactions (entries 4 and 5). Although the use of biphasic toluene/H_2O and THF/H_2O mixtures (1/1 v/v) improved the results obtained in the pure organic solvents, the effectiveness of the process was far from that observed in water (entries 6 and 7).

The ability of complex [$RuCl_2(\eta^6$-$C_6H_5CH_2CH_2CH_2OH$)-{$P(O^iPr)_3$}] (**2e**) to promote the ICR reaction of **3a** in the absence of additives is certainly remarkable, since most ruthenium-based catalysts previously described in the literature require the addition of an acid or a base to be active.[7] On this basis, and with the aim of improving the effectiveness shown by **2e**, we decided to explore its behavior in the presence of different additives. Thus, as shown in entry 8, we found that the catalytic activity of **2e** is not affected by the addition of the chloride abstractor $AgSbF_6$ (1 mol %). This result indicates that cleavage of the Ru–Cl bonds, required to generate vacant sites on the metal for substrate binding, is not the rate-limiting step of the process. On the other hand, although in the presence of acid, i.e. 1 mol % of HCl, quantitative conversion of the diallyl ether **3a** was observed after 6 h, the yield in the aldehyde **4a** was in this case much lower (62%; Table 1, entry 9). This is because the acid favors the hydrolysis of the allyl vinyl ether intermediate, thus leading, as assessed by GC, to the formation of propanal and 3-methylpent-1-en-3-ol as byproducts. Finally, we observed that the addition of a base (1 or 2 mol % of NaOH) accelerates the process, leading also to the quantitative conversion of the diallyl ether **3a** (entries 10 and 11). In terms of **4a** yield the best result was obtained with 2 mol % of NaOH, an experiment that led to the formation of the aldehyde in 98% GC yield (E:Z ratio 58:42), with only 2% of allyl vinyl ether intermediate being detected in the chromatogram. Concerning the stereoselectivity of the reaction, no major changes were observed in any of these experiments.

From this initial screening with complex **2e**, we decided to use NaOH (2 mol %) in the rest of the catalytic experiments. At this point we wish to emphasize that the use of a low metal loading (1 mol %), in combination with a low temperature (100 °C), is a novelty in ICR reactions promoted by ruthenium. In fact, in most of the examples described to date, catalysts loadings of 5–8 mol % of Ru were employed (with temperatures in the range 80–120 °C),[7c–j] and those that operate with lower metal loadings do so at temperatures above 150 °C.[7a,b]

With the optimized experimental conditions in hand, i.e. 1 mol % of Ru, 2 mol % of NaOH, pure water, and 100 °C, the catalytic activity of the rest of the ruthenium(II) complexes synthesized was subsequently evaluated, employing again the diallyl ether **3a** as a model substrate. As shown in Table 2, the nature of the η^6-arene ligand, i.e. 2-phenylethanol (**1a–f**) or 3-phenylpropanol (**2a–f**), practically does not exert any effect on the catalytic activity of the complexes or on the stereoselectivity of the process (even vs odd entries). In contrast, the outcome of the reaction was strongly dependent on the auxiliary P-donor ligand coordinated to ruthenium. Thus, while all those complexes containing aliphatic phosphite ligands, i.e. compounds **1c–e** and **2c–e**, gave rise to the quantitative conversion of the starting material after 6 h (entries 5–10), incomplete conversions were observed with the corresponding

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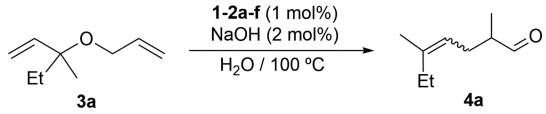
Table 2. ICR of the Diallyl Ether 3a Catalyzed by Complexes $[RuCl_2\{\eta^6\text{-}C_6H_5CH_2(CH_2)_nCH_2OH\}(PR_3)]$ (1a–f and 2a–f) in Water[a]



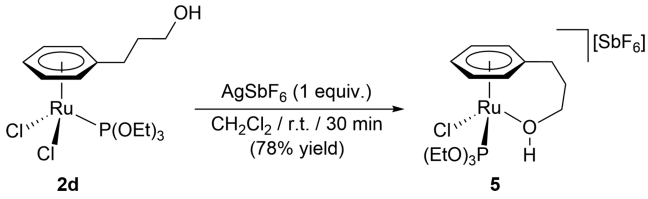
entry	catalyst	time (h)	conversion (%)[b]	yield (%)[b]	E:Z ratio[c]
1	**1a** (n = 0; PR_3 = PMe_3)	6	73	69	57:43
2	**2a** (n = 1; PR_3 = PMe_3)	6	75	70	58:42
3	**1b** (n = 0; PR_3 = PPh_3)	6	47	45	57:43
4	**2b** (n = 1; PR_3 = PPh_3)	6	45	41	58:42
5	**1c** (n = 0; PR_3 = $P(OMe)_3$)	6	>99	96	55:45
6	**2c** (n = 1; PR_3 = $P(OMe)_3$)	6	>99	94	55:45
7	**1d** (n = 0; PR_3 = $P(OEt)_3$)	6 (4)	>99 (>99)	>99 (97)	58:42
8	**2d** (n = 1; PR_3 = $P(OEt)_3$)	6 (4)	>99 (>99)	>99 (>99)	59:41
9	**1e** (n = 0; PR_3 = $P(O^iPr)_3$)	6	>99	98	58:42
10	**2e** (n = 1; PR_3 = $P(O^iPr)_3$)	6	>99	97	58:42
11	**1f** (n = 0; PR_3 = $P(OPh)_3$)	6	37	29	58:42
12	**2f** (n = 1; PR_3 = $P(OPh)_3$)	6	35	25	58:42

[a]Reactions performed under an argon atmosphere using 2 mmol of **3a**, 0.02 mmol of the corresponding Ru(II) complex **1a–f** and **2a–f**, 0.04 mmol of NaOH, and 1 mL of water. [b]Conversions and yields determined by GC. The differences between conversions and yields correspond to the intermediate allyl vinyl ether present in the reaction media. [c]E:Z ratios determined by ^{1}H NMR spectroscopy after evaporation of the solvent.

phosphine derivatives **1a,b** and **2a,b** (entries 1–4) and compounds **1f** and **2f** containing an aromatic phosphite (entries 11 and 12). These observations are consistent with our previous results in the isomerization of allylic alcohols and allylbenzenes in water with the related arene-ruthenium(II) complexes $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)(PR_3)]$,[15g,18a,c] for which the highest catalytic activities were observed with aliphatic phosphites due to the high solubility in water that these types of ligands give to their complexes.[23] According to the water solubility measurements carried out with complexes **1a–f** and **2a–f**, the same explanation can also be given in the present case (30–120 mg/mL for **1c–e** and **2c–e** vs <0.5 mg/mL for **1a,b,f** and **2a,b,f** at room temperature). Among the aliphatic phosphite complexes **1c–e** and **2c–e**, the best results were obtained with $[RuCl_2\{\eta^6\text{-}C_6H_5CH_2(CH_2)_nCH_2OH\}\{P(OEt)_3\}]$ (n = 0 (**1d**), 1 (**2d**)), which were able to generate the γ,δ-unsaturated aldehyde **4a** in quantitative GC yield (entries 7 and 8). Additional experiments at a shorter time (4 h instead of 6 h) allowed us to identify the 3-phenylpropanol derivative **2d** as the most effective catalyst of the series. Finally, with regard to the stereoselectivity of the reaction, it was little affected by the nature of the catalyst employed (E:Z ratios from 55:45 to 59:41).

On the other hand, it is known that 3-phenylpropanol derivatives $[RuCl_2(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)(PR_3)]$ readily generate cationic tethered species $[RuCl\{\eta^6\text{:}\kappa^1(O)\text{-}C_6H_5CH_2CH_2CH_2OH\}(PR_3)]^+$ by abstraction of one of the chloride ligands.[19a,c,24] This fact prompted us to investigate the catalytic behavior of the known complex $[RuCl\{\eta^6\text{:}\kappa^1(O)\text{-}C_6H_5CH_2CH_2CH_2OH\}\{P(OEt)_3\}][SbF_6]$ (**5**) in order to determine if a change in the coordination mode of the arene ligand has any effect on the catalytic reaction. As shown in Scheme 5, complex **5** is accessible by treatment of a dichloromethane solution of **2d** with silver hexafluoroantimonate.[19c] Although a higher catalytic activity of **5** vs **2d** could be anticipated on the basis of on easier dissociation of the alcohol group, the experimental result was just the opposite. Thus, under reaction conditions identical with those employed in Table 2, incomplete transformation of the diallyl ether **3a** was

Scheme 5. Synthesis of the Tethered Ruthenium(II) Complex 5



observed after 6 h (93% conversion with a selectivity toward aldehyde **4a** of 87%, in comparison with entry 8). Solubility issues could be behind of this inferior performance again since, despite its ionic nature, **5** is very poorly soluble in water (2.3 mg/mL vs 101.5 mg/mL in the case of **2d**).[25]

In addition, to get insight into the mechanism, we studied the behavior of complexes $[RuCl_2(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)(PR_3)]$ (**2a–f**) in pure water as well as in aqueous NaOH solutions, the conditions employed for the catalytic experiments. As a general trend, three species, which coexist in equilibrium,[26] were observed by NMR spectroscopy in pure water: the dichloride precursor $[RuCl_2(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)(PR_3)]$, detected as the major compound in all of the cases, the aquo derivative $[RuCl(H_2O)(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)(PR_3)][Cl]$, and the tethered complex $[RuCl(\eta^6\text{:}\kappa^1(O)\text{-}C_6H_5CH_2CH_2CH_2OH)(PR_3)][Cl]$. Upon addition of NaOH to these aqueous solutions, different chemical processes take place, the outcome of the reactions depending on the nature of the phosphorated ligand. As an example, the phosphine complex $[RuCl_2(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)(PMe_3)]$ (**2a**) gave rise to the formation of two new organometallic products, tentatively assigned to the hydroxo species $[Ru(H_2O)(OH)(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)(PMe_3)][Cl]$ and $[Ru(OH)(\eta^6\text{:}\kappa^1(O)\text{-}C_6H_5CH_2CH_2CH_2OH)(PMe_3)][Cl]$.[27,28] However, when the $P(OMe)_3$-containing derivative $[RuCl_2(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)\{P(OMe)_3\}]$ (**2c**) was involved in the reaction, formation of the dimethyl phosphite compounds $[RuCl_2(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)\{P(OMe)_2(OH)\}]$ and $[RuCl(\eta^6\text{:}\kappa^1(O)\text{-}$

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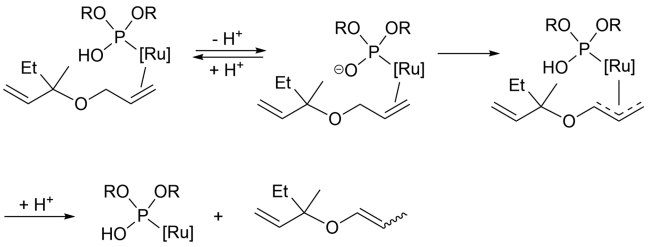
$C_6H_5CH_2CH_2CH_2OH\{P(OMe)_2(OH)\}][Cl]$ was observed,[29] along with methanol, as the result of the attack of OH^- anions to the coordinated phosphite ligand. Therefore, the superior activity of the phosphite catalysts, respective to the phosphine species, is probably related not only to solubility issues but also to their ability to generate species with a coordinated $P(OR)_2(OH)$ ligand. In summary, the main role of NaOH during the catalytic reactions is to promote the formation of a $P(OR)_2(OH)$ ligand, which could cooperate with the metal in the initial allyl unit isomerization step (see Scheme 6).[30]

Scheme 6. Tentative Role of the in Situ Formed $P(OR)_2(OH)$ Ligands



The scope of the process was subsequently evaluated employing the whole family of diallyl ethers **3a–l** (Scheme 3) and the most active catalyst **2d**. In all of the cases, the reactions were carried out in water at 100 °C, with a ruthenium loading of 1 mol %, and in the presence of 2 mol % of NaOH. The results obtained are shown in Table 3. As observed for **3a** (entry 1), the diallyl ethers **3b–f**, also containing a quaternary carbon atom in a position α to oxygen and featuring nonsubstituted olefinic $CH{=}CH_2$ units, could be completely and chemoselectively transformed into the corresponding γ,δ-unsaturated aldehydes **4b–f**, which were isolated after chromatographic workup in 85–94% yield (entries 2–6). At the end of the reactions, which required short times in general (1.5–9 h), the intermediate allyl vinyl ethers or other byproducts were not detected by GC in the crude products, even in the case of compound **3f**, where an extra C=C bond is present (entry 6). For diallyl ethers **3c,e,f**, which contain two different substituents on the α-carbon atom, the corresponding aldehydes were generated as mixtures of *E* and *Z* isomers (entries 3, 5, and 6). When these substituents are aliphatic groups, the *E*:*Z* ratios in the aldehydes (**4c,f**) are very similar to those observed for **4a**, i.e. ca. 60:40 (entries 3 and 6). In contrast, the stereoselectivity achieved in the case of aldehyde **4e** was much higher (*E*:*Z* ratio 72:28; entry 5) as a consequence of the stronger electronic and steric differences between the methyl and phenyl substituents.[31]

More disparate results were obtained when substrates containing nonterminal olefinic units were employed. Thus, when substituents were present in the allyl group that has to be isomerized, the catalytic activity of complex **2d** decreased drastically, with conversions of up to 17% after 24 h of heating (Table 3, entries 8 and 9). This behavior, observed regardless of whether the substituent is located on the internal (diallyl ether **3h**; entry 8) or external olefinic carbon (diallyl ether **3i**; entry 9), stems from the sterically disfavored coordination of the C=C bond to ruthenium, which results in a drastic rate decrease in the initial isomerization step (Scheme 2).[32] Conversely, the effectiveness of the ICR process was not affected by the introduction of a substituent on the olefin group that is not isomerized in the first step. Thus, starting from diallyl ether **3g**, the novel γ,δ-unsaturated aldehyde **4g** could be synthesized in 94% yield after only 1.5 h of reaction (entry 7). As a consequence of the Claisen rearrangement, two stereogenic centers are generated in this case, and **4g** was isolated as a nonseparable mixture of the corresponding syn and anti diastereoisomers in a ca. 1:1 ratio.

To our delight, despite the diallyl ethers **3j,k** bear two potentially isomerizable allyl units due to the presence of only one substituent in a position α to oxygen, a high regiocontrol was observed in their reactions, which afforded selectively the aldehydes **4j,k**, respectively, resulting from the exclusive isomerization of the $CH_2CH{=}CH_2$ unit (Table 3, entries 10 and 11). In addition, the stereoselectivity of the ICR process was very high in these cases, delivering the products as the *E* isomers. Nonetheless, as observed for **4g**, in the case of **4k** a mixture of syn and anti diastereoisomers in a ca. 1:1 ratio was formed. Finally, concerning the diallyl ether **3l** (entry 12), in which no substituents adjacent to the C=C bonds are present, the reaction led after a short time to a complex mixture of products that, due to the signals overlapping in the ^1H NMR spectrum, could not be identified (we do not rule out that in addition to the expected aldehydes **4l** and **4l′** the intermediate allyl vinyl ethers were also present in the mixture).

CONCLUSION

In summary, we have demonstrated that hydrophilic arene-ruthenium(II) complexes of general composition $[RuCl_2\{\eta^6\text{-}C_6H_5CH_2(CH_2)_nCH_2OH\}(PR_3)]$ (n = 0, 1; PR_3 = phosphine, phosphite) are able to catalyze, in combination with NaOH, tandem isomerization/Claisen rearrangement (ICR) reactions of diallyl ethers in water. In particular, the 3-phenylpropanol derivative $[RuCl_2(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)\{P(OEt)_3\}]$ (**2d**) proved to be the most efficient, allowing the high-yield formation of different γ,δ-unsaturated aldehydes starting from diallyl ethers featuring a quaternary or tertiary carbon atom adjacent to one of the C=C bonds. Remarkably, in comparison to other ruthenium catalysts previously described in the literature, complex **2d** stands out for its high activity at a low metal loading (1 mol %) and under relatively mild temperature conditions (100 °C). Its efficiency seems to be related to its ability to generate $P(OEt)_2(OH)$-containing species under the basic conditions employed. In addition, it is the first metal catalyst able to promote ICR processes in water, an environmentally friendly reaction medium whose use has also been demonstrated to be beneficial in these types of tandem transformations of olefins.

EXPERIMENTAL SECTION

Synthetic procedures were performed under an atmosphere of dry argon using vacuum-line and standard Schlenk or sealed-tube techniques. Solvents were dried by standard methods and distilled under argon before use.[33] The ruthenium complexes $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_5CH_2CH_2OH)\}_2]$,[34] $[RuCl_2\{\eta^6:\kappa^1(O)\text{-}C_6H_5CH_2CH_2CH_2OH\}]$,[19a,35] $[RuCl_2(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)(PPh_3)]$ (**1b**),[19b] $[RuCl_2(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)(PR_3)]$ (PR_3 = PPh_3 (**2b**),[19a] $P(OEt)_3$ (**2d**),[19c] $P(OPh)_3$ (**2f**)[19c]), and $[RuCl\{\eta^6:\kappa^1(O)\text{-}C_6H_5CH_2CH_2CH_2OH\}\{P(OEt)_3\}][SbF_6]$ (**5**),[19c] were prepared by following the methods reported in the literature. The diallyl ethers **3a–l** were synthesized by allylation of the corresponding allylic alcohol as detailed in the Supporting Information. Infrared spectra were recorded on a PerkinElmer 1720-XFT spectrometer. NMR spectra were recorded at 25 °C on Bruker DPX-300 and AV400 instruments. The chemical shift values (δ) are given in parts per

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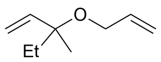
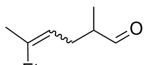
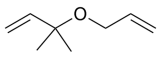
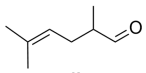
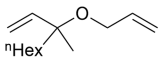
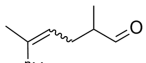
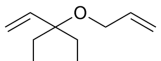
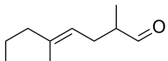
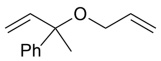
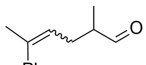
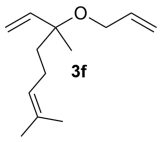
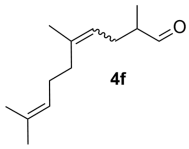
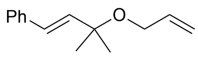
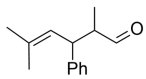
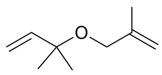
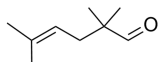
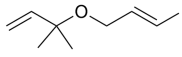
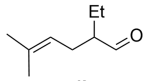
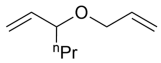
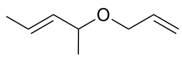
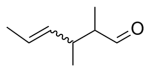
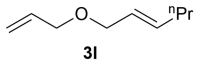
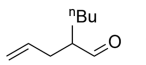
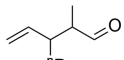
Table 3. ICR of the Diallyl Ethers 3a–l Catalyzed by Complex $[RuCl_2(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)\{P(OEt)_3\}]$ (2d) in Water[a]

Entry	Substrate	Product	Time (h)	Conv. (%)[b]	Yield (%)[c]	*E*/*Z* ratio[d]
1	 3a	 4a	4	> 99	> 99 (92)	59:41
2	 3b	 4b	1.5	> 99	> 99 (90)	-----
3	 3c	 4c	6	> 99	> 99 (94)	58:42
4	 3d	 4d	4	> 99	> 99 (87)	----
5	 3e	 4e	9	> 99	> 99 (85)	72:28
6	 3f	 4f	4	> 99	> 99 (89)	57:43
7[e]	 3g	 4g	1.5	> 99	> 99 (94)	----
8	 3h	 4h	24	12	n.d.	----
9	 3i	 4i	24	17	n.d.	----
10	 3j	 4j	8	> 99	> 99 (91)	99:1
11[e]	 3k	 4k	6	> 99	> 99 (85)	99:1
12	 3l	 4l  4l′	2	> 99	n.d.	----

[a]Reactions performed under an argon atmosphere using 2 mmol of the corresponding diallyl ether **3**, 0.02 mmol of the Ru(II) complex **2d**, 0.04 mmol of NaOH, and 1 mL of water. [b]Conversions determined by GC. [c]Yields determined by GC. Isolated yields after chromatographic workup are given in parentheses. [d]*E*:*Z* ratios determined by ^{1}H NMR spectroscopy. [e]The corresponding aldehyde is generated as a mixture of syn and anti diastereoisomers in a ca. 1:1 ratio.

million and are referenced to the residual peak of the deuterated solvent employed (^{1}H and ^{13}C). DEPT experiments have been carried out for all of the compounds reported in this paper. GC measurements were made on a Hewlett-Packard HP6890 apparatus (Supelco Beta-Dex 120 column, 30 m length, 250 μm diameter). Elemental analyses were provided by the Analytical Service of the Instituto de Investigaciones Químicas (IIQ-CSIC) of Seville. HRMS data were obtained on a QTOF Bruker Impact II mass spectrometer in the General Services of the University of Oviedo. For column chromatography, Merck silica gel 60 (230–400 mesh) was employed.

General Procedure for the Preparation of Complexes $[RuCl_2(\eta^6\text{-}C_6H_5CH_2CH_2OH)(PR_3)]$ (PR_3 = PMe_3 (1a), $P(OMe)_3$

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(1c), P(OEt)$_3$ (1d), P(O^{i}Pr)$_3$ (1e), P(OPh)$_3$ (1f)). A suspension of the dimer [{RuCl(μ-Cl)(η^6-$C_6H_5CH_2CH_2OH$)}$_2$] (0.300 g, 0.510 mmol) and the corresponding phosphite or phosphine ligand (1.22 mmol) in CH_2Cl_2 (50 mL) was stirred, at room temperature, overnight. The reaction mixture was then filtered through Kieselguhr to eliminate small quantities of the undissolved starting material, and the filtrate was evaporated to dryness. The residue was washed with diethyl ether (3 × 5 mL) and the resulting reddish orange solid dried in vacuo. Data for **1a** are as follows. Yield: 0.306 g (81%). IR (KBr): ν 3389 (br, O−H) cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 6.6 (s) ppm. ^1H NMR (CD_2Cl_2): δ 5.61 (d, $^3J_{HH}$ = 6.0 Hz, 2H, CH_{ortho}), 5.41 (ddd, $^3J_{HH}$ = 6.0 and 5.4 Hz, $^3J_{PH}$ = 1.5 Hz, 2H, CH_{meta}), 5.24 (td, $^3J_{HH}$ = 5.4 Hz, $^3J_{PH}$ = 2.4 Hz, 1H, CH_{para}), 4.03 (m, 2H, CH_2OH), 2.87 (t, $^3J_{HH}$ = 6.9 Hz, 1H, OH), 2.78 (t, $^3J_{HH}$ = 5.1 Hz, 2H, CH_2Ph), 1.64 (d, $^2J_{PH}$ = 11.4 Hz, 9H, Me) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 106.6 (s, C_{ipso}), 89.2 and 84.9 (s, CH_{ortho} and CH_{meta}), 79.9 (s, CH_{para}), 60.4 (s, CH_2OH), 35.7 (s, CH_2Ph), 16.2 (d, $^1J_{PC}$ = 33.9 Hz, Me) ppm. Anal. Calcd for $C_{11}H_{19}Cl_2OPRu$: C, 35.69; H, 5.17. Found: C, 35.60; H, 5.25. Data for **1c** are as follows. Yield: 0.311 g (73%). IR (KBr): ν 3421 (br, O−H) cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 119.0 (s) ppm. ^1H NMR (CD_2Cl_2): δ 5.70 (d, $^3J_{HH}$ = 5.7 Hz, 2H, CH_{ortho}), 5.59 (ddd, $^3J_{HH}$ = 5.7 and 5.4 Hz, $^3J_{PH}$ = 1.5 Hz, 2H, CH_{meta}), 5.48 (td, $^3J_{HH}$ = 5.4 Hz, $^3J_{PH}$ = 2.4 Hz, 1H, CH_{para}), 4.05 (m, 2H, CH_2OH), 3.79 (d, $^3J_{PH}$ = 11.1 Hz, 9H, OMe), 2.82 (td, $^3J_{HH}$ = 6.0 Hz, $^3J_{PH}$ = 2.1 Hz, 2H, CH_2Ph), 2.57 (t, $^3J_{HH}$ = 6.0 Hz, 1H, OH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 111.6 (d, $^2J_{PC}$ = 10.2 Hz, C_{ipso}), 92.0 (d, $^2J_{PC}$ = 6.9 Hz, CH_{ortho} or CH_{meta}), 87.5 (s, CH_{ortho} or CH_{meta}), 81.9 (s, CH_{para}), 60.6 (s, CH_2OH), 54.3 (d, $^2J_{PC}$ = 5.6 Hz, OMe), 35.7 (s, CH_2Ph) ppm. Anal. Calcd for $C_{11}H_{19}O_4Cl_2PRu$: C, 31.59; H, 4.58. Found: C, 31.44; H, 4.67. Data for **1d** are as follows. Yield: 0.347 g (74%). IR (KBr): ν 3445 (br, O−H) cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 113.7 (s) ppm. ^1H NMR (CD_2Cl_2): δ 5.68 (d, $^3J_{HH}$ = 6.0 Hz, 2H, CH_{ortho}), 5.54 (dd, $^3J_{HH}$ = 6.0 and 5.4 Hz, 2H, CH_{meta}), 5.45 (td, $^3J_{HH}$ = 5.4 Hz, $^3J_{PH}$ = 2.4 Hz, 1H, CH_{para}), 4.16 (quint, $^3J_{PH}$ = $^3J_{HH}$ = 7.2 Hz, OCH_2CH$_3$), 4.04 (m, 2H, CH_2OH), 2.81 (td, $^3J_{HH}$ = 5.7 Hz, $^3J_{PH}$ = 1.5 Hz, 2H, CH_2Ph), 2.66 (t, $^3J_{HH}$ = 5.7 Hz, 1H, OH), 1.32 (t, $^3J_{HH}$ = 7.2 Hz, 9H, OCH$_2$CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 110.9 (d, $^2J_{PC}$ = 12.5 Hz, C_{ipso}), 92.1 (d, $^2J_{PC}$ = 7.4 Hz, CH_{ortho} or CH_{meta}), 87.0 (s, CH_{ortho} or CH_{meta}), 82.3 (s, CH_{para}), 63.2 (d, $^2J_{PC}$ = 4.0 Hz, OCH$_2$CH$_3$), 60.6 (s, CH_2OH), 35.7 (s, CH_2Ph), 16.2 (d, $^3J_{PC}$ = 7.0 Hz, OCH$_2$CH_3) ppm. Anal. Calcd for $C_{14}H_{25}O_4Cl_2PRu$: C, 36.53; H, 5.47. Found: C, 36.62; H, 5.56. Data for **1e** are as follows. Yield: 0.359 g (70%). IR (KBr): ν 3403 (br, O−H) cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 106.9 (s) ppm. ^1H NMR (CD_2Cl_2): δ 5.64 (d, $^3J_{HH}$ = 5.4 Hz, 2H, CH_{ortho}), 5.49−5.43 (m, 3H, CH_{meta} and CH_{para}), 4.88 (m, 3H, OCH(CH$_3$)$_2$), 4.05 (m, 2H, CH_2OH), 2.81 (td, $^3J_{HH}$ = 5.7 Hz, $^3J_{PH}$ = 1.8 Hz, 2H, CH_2Ph), 2.74 (t, $^3J_{HH}$ = 5.7 Hz, 1H, OH), 1.32 (d, $^3J_{HH}$ = 6.0 Hz, 18H, OCH(CH_3)$_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 110.1 (d, $^2J_{PC}$ = 12.1 Hz, C_{ipso}), 92.5 (d, $^2J_{PC}$ = 7.9 Hz, CH_{ortho} or CH_{meta}), 86.4 (s, CH_{ortho} or CH_{meta}), 82.9 (s, CH_{para}), 71.7 (d, $^2J_{PC}$ = 7.6 Hz, OCH(CH$_3$)$_2$), 60.5 (s, CH_2OH), 35.4 (s, CH_2Ph), 24.0 (d, $^3J_{PC}$ = 2.9 Hz, OCH(CH$_3$)$_2$) ppm. Anal. Calcd for $C_{17}H_{31}O_4Cl_2PRu$: C, 40.64; H, 6.22. Found: C, 40.77; H, 6.35. Data for **1f** are as follows. Yield: 0.475 g (77%). IR (KBr): ν 3412 (br, O−H) cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 111.0 (s) ppm. ^1H NMR (CD_2Cl_2): δ 7.46−7.39 (m, 11H, OPh), 7.30−7.25 (m, 4H, OPh), 5.33 (d, $^3J_{HH}$ = 6.3 Hz, 2H, CH_{ortho}), 5.01 (ddd, $^3J_{HH}$ = 6.3 and 5.7 Hz, $^3J_{PH}$ = 1.5 Hz, 2H, CH_{meta}), 4.51 (td, $^3J_{HH}$ = 5.7 Hz, $^3J_{PH}$ = 2.1 Hz, 1H, CH_{para}), 3.95 (m, 2H, CH_2OH), 2.66 (td, $^3J_{HH}$ = 5.4 Hz, $^3J_{PH}$ = 2.1 Hz, 2H, CH_2Ph), 2.31 (t, $^3J_{HH}$ = 5.4 Hz, 1H, OH) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 151.1 (d, $^2J_{PC}$ = 9.2 Hz, C_{ipso} of OPh), 129.7 (s, C_{meta} of OPh), 125.4 (s, C_{para} of OPh), 121.6 (d, $^3J_{PC}$ = 4.3 Hz, (s, C_{ortho} of OPh), 113.0 (d, $^2J_{PC}$ = 9.6 Hz, C_{ipso}), 91.8 (d, $^2J_{PC}$ = 8.1 Hz, CH_{ortho} or CH_{meta}), 87.9 (s, CH_{ortho} or CH_{meta}), 80.3 (s, CH_{para}), 60.2 (s, CH_2OH), 35.6 (s, CH_2Ph) ppm. Anal. Calcd for $C_{26}H_{25}O_4Cl_2PRu$: C, 51.67; H, 4.17. Found: C, 51.77; H, 4.21.

General Procedure for the Preparation of Complexes [RuCl$_2$(η^6-$C_6H_5CH_2CH_2CH_2OH$)(PR$_3$)] (PR$_3$ = PMe$_3$ (2a), P(OMe)$_3$ (2c), P(O^{i}Pr)$_3$ (2e)). A suspension of the complex [RuCl$_2${η^6:κ^1(O)-$C_6H_5CH_2CH_2CH_2OH$}] (0.308 g, 1 mmol) and the corresponding phosphite or phosphine ligand (1.2 mmol) in CH_2Cl_2 (50 mL) was stirred, at room temperature, until complete dissolution of the starting Ru complex (ca. 2−3 h). The reaction mixture was then evaporated to dryness, and the residue was washed with diethyl ether (3 × 5 mL) to give a reddish orange solid which was dried in vacuo. Data for **2a** are as follows. Yield: 0.288 g (75%). IR (KBr): ν 3391 (br, O−H) cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 6.3 (s) ppm. ^1H NMR (CD_2Cl_2): δ 5.52 (td, $^3J_{HH}$ = 4.8 Hz, $^3J_{PH}$ = 2.1 Hz, 2H, CH_{meta}), 5.43 (d, $^3J_{HH}$ = 4.8 Hz, 2H, CH_{ortho}), 5.11 (t, $^3J_{HH}$ = 4.8 Hz, 1H, CH_{para}), 3.76 (m, 2H, CH_2OH), 2.64 (t, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2Ph), 2.15 (br s, 1H, OH), 1.98−1.89 (m, 2H, CH_2CH$_2$Ph), 1.63 (d, $^2J_{PH}$ = 11.1 Hz, 9H, Me) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 110.7 (d, $^2J_{PC}$ = 6.0 Hz, C_{ipso}), 86.9 (d, $^2J_{PC}$ = 5.7 Hz, CH_{ortho} or CH_{meta}), 86.6 (s, CH_{ortho} or CH_{meta}), 78.3 (s, CH_{para}), 61.3 (s, CH_2OH), 31.2 and 28.9 (s, CH_2CH_2Ph), 16.7 (d, $^1J_{PC}$ = 34.8 Hz, Me) ppm. Anal. Calcd for $C_{12}H_{21}Cl_2OPRu$: C, 37.51; H, 5.51. Found: C, 37.62; H, 5.48. Data for **2c** are as follows. Yield: 0.337 g (78%). IR (KBr): ν 3478 (br, O−H) cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 119.7 (s) ppm. ^1H NMR (CD_2Cl_2): δ 5.64 (t, $^3J_{HH}$ = 5.4 Hz, 2H, CH_{meta}), 5.53 (d, $^3J_{HH}$ = 5.4 Hz, 2H, CH_{ortho}), 5.38 (t, $^3J_{HH}$ = 5.4 Hz, 1H, CH_{para}), 3.81−3.77 (m, 2H, CH_2OH), 3.79 (d, $^3J_{PH}$ = 11.1 Hz, 9H, OMe), 2.71 (t, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2Ph), 2.05 (br s, 1H, OH), 1.99−1.90 (m, 2H, CH_2CH$_2$Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 114.7 (d, $^2J_{PC}$ = 6.3 Hz, C_{ipso}), 90.0 and 88.7 (s, CH_{ortho} and CH_{meta}), 81.0 (s, CH_{para}), 61.0 (s, CH_2OH), 54.2 (d, $^2J_{PC}$ = 5.6 Hz, OMe), 31.2 and 28.9 (s, CH_2CH_2Ph) ppm. Anal. Calcd for $C_{12}H_{21}O_4Cl_2PRu$: C, 33.35; H, 4.90. Found: C, 33.57; H, 4.95. Data for **2e** are as follows. Yield: 0.423 g (82%). IR (KBr): ν 3452 (br, O−H) cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 107.5 (s) ppm. ^1H NMR (CD_2Cl_2): δ 5.55 (t, $^3J_{HH}$ = 5.4 Hz, 2H, CH_{meta}), 5.43 (d, $^3J_{HH}$ = 5.4 Hz, 2H, CH_{ortho}), 5.29 (t, $^3J_{HH}$ = 5.4 Hz, 1H, CH_{para}), 4.94−4.83 (m, 3H, OCH(CH$_3$)$_2$), 3.78 (t, $^3J_{HH}$ = 5.7 Hz, 2H, CH_2OH), 2.70 (t, $^3J_{HH}$ = 6.9 Hz, 2H, CH_2Ph), 1.99−1.91 (m, 2H, CH_2CH$_2$Ph), 1.82 (br s, 1H, OH), 1.32 (d, $^3J_{HH}$ = 6.0 Hz, 18H, OCH(CH_3)$_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 114.7 (d, $^2J_{PC}$ = 8.9 Hz, C_{ipso}), 89.8 (d, $^2J_{PC}$ = 7.9 Hz, CH_{ortho} or CH_{meta}), 88.6 (s, CH_{ortho} or CH_{meta}), 81.5 (s, CH_{para}), 72.0 (d, $^2J_{PC}$ = 7.2 Hz, OCH(CH$_3$)$_2$), 61.5 (s, CH_2OH), 30.9 and 28.6 (s, CH_2CH_2Ph), 24.4 (d, $^3J_{PC}$ = 3.8 Hz, OCH(CH_3)$_2$) ppm. Anal. Calcd for $C_{18}H_{33}O_4Cl_2PRu$: C, 41.87; H, 6.44. Found: C, 41.82; H, 6.51.

General Procedure for ICR Reactions Catalyzed by Complex [RuCl$_2$(η^6-$C_6H_5CH_2CH_2CH_2OH$){P(OEt)$_3$}] (2d). Under an argon atmosphere, the corresponding diallyl ether **3** (2 mmol), water (1 mL), the ruthenium(II) complex **2d** (0.009 g, 0.02 mmol; 1 mol %), and NaOH (0.0016 g, 0.04 mmol; 2 mol %) were introduced into a Teflon-capped sealed tube, and the reaction mixture was stirred at 100 °C for the indicated time (see Table 3). The course of the reaction was monitored by regularly taking samples of ca. 10 μL which, after extraction with CH_2Cl_2 (3 mL), were analyzed by GC. Once the maximum conversion of the starting substrate was reached, the solvent was removed under vacuum and the crude reaction mixture purified by column chromatography (silica gel) employing a EtOAc/hexanes mixture (1/10) as eluent. Characterization data for the isolated γ,δ-unsaturated aldehydes **4** are as follows.

2,5-Dimethylhept-4-enal (4a).[36] Isolated as a nonseparable mixture of *E* and *Z* isomers in 59:41 ratio. Colorless oil. Yield: 0.258 g (92%). HRMS (ESI): *m*/*z* 141.1275, [M + H$^+$] (calcd for $C_9H_{17}O$: 141.1279). NMR data for the *E* isomer are as follows. ^1H NMR ($CDCl_3$): δ 9.65 (s, 1H, CHO), 5.13−5.04 (m, 1H, =CH), 2.42−2.38 (m, 2H, CH_2), 2.06−1.99 (m, 3H, CH and CH_2), 1.63 (s, 3H, =CCH_3), 1.02−0.95 (m, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 205.1 (s, CHO), 139.5 (s, = C), 119.0 (s, =CH), 46.8 (s, CH), 32.3 and 28.9 (s, CH_2), 22.8 (s, =CCH_3), 12.9 and 12.7 (s, CH_3) ppm. NMR data for the *Z* isomer are as follows. ^1H NMR ($CDCl_3$): δ 9.66 (s, 1H, CHO), 5.13−5.04 (m, 1H, =CH), 2.42−2.38 (m, 2H, CH_2), 2.06−1.99 (m, 3H, CH and CH_2), 1.11 (s, 3H, =CCH_3), 1.02−0.95 (m, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 205.1 (s, CHO), 139.5 (s, =C), 120.1 (s, =CH), 46.8 (s, CH), 28.6 and 24.7 (s, CH_2), 15.9 (s, =CCH_3), 13.0 and 12.5 (s, CH_3) ppm.

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*2,5-Dimethylhex-4-enal (**4b**).*[7a] Colorless oil. Yield: 0.227 g (90%). ^{1}H NMR (C_6D_6): δ 9.46 (s, 1H, CHO), 5.06 (t, 1H, $^3J_{HH}$ = 6.2 Hz, =CH), 2.25−2.19 (m, 1H, CH), 2.10−1.92 (m, 2H, CH_2), 1.66 and 1.62 (s, 3H each, =CCH_3), 0.92 (d, 3H, $^3J_{HH}$ = 7.2 Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 203.3 (s, CHO), 146.6 (s, =C), 121.1 (s, =CH), 46.5 (s, CH), 29.0 (s, CH_2), 25.6 and 25.5 (s, =CCH_3), 12.7 (s, CH_3) ppm.

*2,5-Dimethylundec-4-enal (**4c**).* Isolated as a nonseparable mixture of *E* and *Z* isomers in 58:42 ratio. Colorless oil. Yield: 0.369 g (94%). HRMS (ESI): *m*/*z* 197.1903, [M + H$^+$] (calcd for $C_{13}H_{25}O$: 197.1905). NMR data for the *E* isomer are as follows. ^{1}H NMR (C_6D_6): δ 9.50 (s, 1H, CHO), 5.13−5.06 (m, 1H, =CH), 2.31−2.26 (m, 1H, CH), 2.17−1.97 (m, 4H, CH_2), 1.56 (br, 3H, =CCH_3), 1.44−1.27 (m, 8H, CH_2), 0.99−0.94 (m, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 202.8 (s, CHO), 137.3 (s, = C), 120.8 (s, =CH), 46.5 (s, CH), 39.7, 31.9, 29.3, 29.0, 27.9, and 22.7 (s, CH_2), 23.1 (s, =CCH_3), 13.9 and 12.7 (s, CH_3) ppm. NMR data for the *Z* isomer are as follows. ^{1}H NMR (C_6D_6): δ 9.51 (s, 1H, CHO), 5.13−5.06 (m, 1H, =CH), 2.31−2.26 (m, 1H, CH), 2.17−1.97 (m, 4H, CH_2), 1.70 (br, 3H, =CCH_3), 1.44−1.27 (m, 8H, CH_2), 0.99−0.94 (m, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 202.8 (s, CHO), 137.5 (s, = C), 121.4 (s, =CH), 46.5 (s, CH), 31.8, 31.7, 28.9, 28.7, 27.9, and 22.7 (s, CH_2), 15.7 (s, =CCH_3), 13.9 and 12.8 (s, CH_3) ppm.

*4-Cyclohexylidene-2-methylbutanal (**4d**).*[7a] Colorless oil. Yield: 0.289 g (87%). ^{1}H NMR (C_6D_6): δ 9.48 (d, 1H, $^3J_{HH}$ = 1.2 Hz, CHO), 5.03 (t, 1H, $^3J_{HH}$ = 7.4 Hz, =CH), 2.30−2.22 (m, 1H, CH), 2.14−1.94 (m, 6H, CH_2), 1.57−1.43 (m, 6H, CH_2), 0.94 (d, 3H, $^3J_{HH}$ = 8.1 Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 202.9 (s, CHO), 141.5 (s, =C), 117.7 (s, =CH), 46.6 (s, CH), 37.2, 28.7 (2C), 28.1, 27.7, and 26.9 (s, CH_2), 12.7 (s, CH_3) ppm.

*2-Methyl-5-phenylhex-4-enal (**4e**).* Isolated as a nonseparable mixture of *E* and *Z* isomers in 72:28 ratio. Colorless oil. Yield: 0.320 g (85%). HRMS (ESI): *m*/*z* 189.1278, [M + H$^+$] (calcd for $C_{13}H_{17}O$: 189.1279). NMR data for the *E* isomer are as follows. ^{1}H NMR (C_6D_6): δ 9.46 (s, 1H, CHO), 7.38−7.14 (m, 5H, Ph), 5.70−5.66 (m, 1H, =CH), 2.40−2.33 (m, 1H, CH), 2.10−2.08 (m, 2H, CH_2), 1.91 (s, 3H, =CCH_3), 0.93 (d, 3H, $^3J_{HH}$ = 7.2 Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 203.0 (s, CHO), 143.7 (s, C_{ipso}), 137.0 (s, =C), 128.3 (s, CH_{meta}), 127.9 (s, CH_{para}), 125.9 (s, CH_{ortho}), 124.5 (s, =CH), 46.4 (s, CH), 29.6 (s, CH_2), 15.8 (s, =CCH_3), 12.7 (s, CH_3) ppm. NMR data for the *E* isomer are as follows. ^{1}H NMR (C_6D_6): δ 9.32 (s, 1H, CHO), 7.38−7.14 (m, 5H, Ph), 5.36−5.33 (m, 1H, =CH), 2.28−2.22 (m, 1H, CH), 2.05−1.97 (m, 2H, CH_2), 1.99 (s, 3H, =CCH_3), 0.82 (d, 3H, $^3J_{HH}$ = 7.2 Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 203.1 (s, CHO), 141.8 (s, C_{ipso}), 138.7 (s, =C), 128.3 (s, CH_{meta}), 126.9 (s, CH_{para}), 126.8 (s, CH_{ortho}), 123.8 (s, =CH), 46.5 (s, CH), 29.9 (s, CH_2), 25.6 (s, =CCH_3), 12.8 (s, CH_3) ppm.

*2,5,9-Trimethyldeca-4,8-dienal (**4f**).*[7g] Isolated as a nonseparable mixture of *E* and *Z* isomers in 57:43 ratio. Colorless oil. Yield: 0.346 g (89%). NMR data for the *E* isomer are as follows. ^{1}H NMR (C_6D_6): δ 9.48 (d, 1H, $^3J_{HH}$ = 1.5 Hz, CHO), 5.25−5.19 and 5.15−5.07 (m, 1H each, =CH), 2.28−2.00 (m, 7H, CH and CH_2), 1.80−1.71 (m, 6H, =CCH_3), 1.63 (br, 3H, =CCH_3), 0.93 (d, 3H, $^3J_{HH}$ = 7.6 Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 203.0 (s, CHO), 136.9 and 131.0 (s, =C), 124.4 and 121.1 (s, =CH), 46.5 (s, CH), 39.8, 28.9, and 26.7 (s, CH_2), 25.5, 23.2, and 17.4 (s, =CCH_3), 12.7 (s, CH_3) ppm. NMR data for the *Z* isomer are as follows. ^{1}H NMR (C_6D_6): δ 9.48 (d, 1H, $^3J_{HH}$ = 1.5 Hz, CHO), 5.25−5.19 and 5.15−5.07 (m, 1H each, =CH), 2.28−2.00 (m, 7H, CH and CH_2), 1.80−1.71 (m, 6H, =CCH_3), 1.56 (br, 3H, =CCH_3), 0.94 (d, 3H, $^3J_{HH}$ = 7.6 Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 203.0 (s, CHO), 137.1 and 131.3 (s, =C), 124.3 and 121.9 (s, =CH), 46.5 (s, CH), 31.9, 28.8, and 26.5 (s, CH_2), 25.5, 17.3, and 15.8 (s, =CCH_3), 12.8 (s, CH_3) ppm.

*2,3-Dimethyl-3-phenylhex-4-enal (**4g**).* Isolated as a nonseparable mixture of syn and anti diastereoisomers in ca. 1:1 ratio. Colorless oil. Yield: 0.380 g (94%). HRMS (ESI): *m*/*z* 203.1434, [M + H$^+$] (calcd for $C_{14}H_{19}O$: 203.1436). ^{1}H NMR (C_6D_6): δ 9.63 and 9.49 (d, 1H, $^3J_{HH}$ = 2.1 or 2.7 Hz, CHO, syn and anti), 7.23−7.08 (m, 5H, Ph), 5.41 and 5.30 (d, 1H, $^3J_{HH}$ = 9.6 Hz, =CH, syn and anti), 3.80 and 3.61 (dd, 1H, $^3J_{HH}$ = $^3J_{HH}$ = 9.6 Hz, C*H*, syn and anti), 2.59−2.53 (m, 1H, C*H*CH_3, syn and anti), 1.64 and 1.61 (d, 3H, $^3J_{HH}$ = 1.2 Hz, =CHC*H*$_3$, syn and anti), 1.54 (br, 3H, =CHC*H*$_3$, syn and anti), 1.01 and 0.85 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH_3, syn and anti) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 203.2 and 202.9 (s, CHO, syn and anti), 143.0 and 142.7 (s, C_{ipso}, syn and anti), 133.3 and 133.0 (s, = C, syn and anti), 128.6 (s, CH_{meta}, syn and anti), 127.9 and 127.8 (s, CH_{ortho}, syn and anti), 126.3 (s, CH_{para}, syn and anti), 126.0 and 124.8 (s, =CH, syn and anti), 51.7 and 51.6 (s, *C*HCH$_3$, syn and anti), 46.2 and 45.3 (s, *C*HPh, syn and anti), 25.6, 25.5, and 17.9 (2C) (s, =CHCH$_3$, syn and anti), 12.3 and 11.2 (s, CH_3, syn and anti) ppm.

*(E)-2-Methyloct-4-enal (**4j**).*[37] Colorless oil. Yield: 0.255 g (91%). ^{1}H NMR (C_6D_6): δ 9.45 (d, 1H, $^3J_{HH}$ = 1.5 Hz, CHO), 5.46−5.26 (m, 2H, =CH), 2.27−2.20 (m, 1H, CH), 2.09−1.90 (m, 4H, =C*H*$_2$), 1.43−1.31 (m, 2H, CH_2), 0.94−0.90 (m, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 202.9 (s, CHO), 132.9 and 126.7 (s, =CH), 46.0 (s, CH), 34.6 and 33.6 (s, =CCH_2), 22.6 (s, CH_2), 13.4 and 12.6 (s, CH_3) ppm.

*(E)-2,3-Dimethylhex-4-enal (**4k**).*[13] Isolated as a nonseparable mixture of syn and anti diastereoisomers in ca. 1:1 ratio. Colorless oil. Yield: 0.214 g (85%). ^{1}H NMR (C_6D_6): δ 9.50 and 9.47 (d, 1H, $^3J_{HH}$ = 1.8 or 2.1 Hz, CHO, syn and anti), 5.44−5.14 (m, 2H, =CH, syn and anti), 2.36−2.30 and 2.10−1.98 (m, 1H, CH, syn and anti), 1.51−1.62 (m, 3H, =CC*H*$_3$, syn and anti), 1.00−0.86 (m, 6H, CH_3, syn and anti) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 203.4 (s, CHO, syn and anti), 134.1, 133.0, 125.4, and 124.9 (s, =CH, syn and anti), 51.2, 50.9, 37.3, and 37.2 (s, CH, syn and anti), 18.1 and 17.6 (s, =CHC*H*$_3$, syn and anti), 16.4 (s, CH_3, syn and anti), 10.2 and 9.7 (s, CH_3, syn and anti) ppm.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00187.

Details of the synthesis and characterization of the diallyl ethers **3a−l** and NMR spectra of the novel diallyl ethers **3a,c,i,k** and γ,δ-unsaturated aldehydes **4a,c,e,g** (PDF)

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Notes

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(21) Within the series, compounds **3a**,**c**,**i**,**k** have not been previously described in the literature.

(22) All attempts to separate the *E* and *Z* isomers of aldehyde **4a** by column chromatography failed; therefore, they were jointly characterized. Unfortunately, most signals in the ^{1}H NMR spectrum were overlapped, thus preventing the carrying out of conclusive NOESY experiments to unambiguously determine the stereochemistry of the major isomer. However, given the stereoselectivity usually found in aliphatic Claisen rearrangements (see ref 2), we assumed that the *E* stereoisomer is the major species.

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(25) (a) The low solubility in water of complex **5** is most likely related to the SbF_6^- counteranion. Unfortunately, all attempts made

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to synthesize analogous species with more solubilizing counteranions (AcO^- or TfO^-) in a pure manner failed. (b) On the other hand, the catalytic behavior of the precursor complexes $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)\}_2]$ and $[RuCl_2\{\eta^6:\kappa^1(O)\text{-}C_6H_5CH_2CH_2CH_2OH\}]$ was also evaluated, leading to very low conversions after 6 h (up to 31%).

(26) The equilibrium could be shifted toward the formation of cationic complexes $[RuCl(H_2O)(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)(PR_3)][Cl]$ and $[RuCl(\eta^6{:}\kappa^1(O)\text{-}C_6H_5CH_2CH_2CH_2OH)(PR_3)][Cl]$ by addition of a silver salt (e.g., $AgNO_3$). On the other hand, the dichloride derivative $[RuCl_2(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)(PR_3)]$ is the only product observed by NMR in aqueous NaCl solutions.

(27) All attempts to isolate and fully characterize these species failed.

(28) The complex $[Ru(H_2O)(OH)(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)(PMe_3)][Cl]$ is probably in rapid equilibrium (on the NMR time scale) with $[Ru(OH)_2(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)(PMe_3)]$ and $[Ru(H_2O)_2(\eta^6\text{-}C_6H_5CH_2CH_2CH_2OH)(PMe_3)][Cl]_2$. Similarly, $[Ru(OH)(\eta^6{:}\kappa^1(O)\text{-}C_6H_5CH_2CH_2CH_2OH)(PMe_3)][Cl]$ should be in equilibrium with $[Ru(H_2O)(\eta^6{:}\kappa^1(O)\text{-}C_6H_5CH_2CH_2CH_2O)(PMe_3)][Cl]$, $[Ru(OH)(\eta^6{:}\kappa^1(O)\text{-}C_6H_5CH_2CH_2CH_2O)(PMe_3)]$, and $[Ru(H_2O)(\eta^6{:}\kappa^1(O)\text{-}C_6H_5CH_2CH_2CH_2OH)(PMe_3)][Cl]_2$. For similar processes see, for example: Gossens, C.; Dorcier, A.; Dyson, P. J.; Rothlisberger, U. *Organometallics* **2007**, *26*, 3969−3975.

(29) The transformation of $P(OMe)_3$ into $P(OMe)_2OH$ was evidenced by NMR spectroscopy by a change of the chemical shift of the phosphorus nucleus from ca. 121 ppm to ca. 100 ppm, as well as by the decrease of the relative integration for the Me units in the ^1H NMR spectrum (from 9H to 6H).

(30) Ruthenium complexes containing ligands functionalized with basic groups are known to favor C═C bond migrations through bifunctional catalysis mechanisms related to that proposed in Scheme 6. See, for example: Grotjahn, D. D.; Larsen, C. R.; Gustafson, J. L.; Nair, R.; Sharma, A. *J. Am. Chem. Soc.* **2007**, *129*, 9592−9593.

(31) As in the case of **4a**, the overlapping of signals in the ^1H NMR of **4c**,**f** did not allow us to carry out conclusive NOESY experiments to confirm in an unequivocal manner the *E* stereochemistry proposed for the major isomer. Fortunately, this was possible for **4e**, the NOESY spectrum showing for the major stereoisomer a positive NOE effect between the olefinic and aromatic protons in agreement with the *E* stereochemistry proposed (for the minor isomer the expected spatial proximity between the olefinic proton and the methyl group was also evidenced by the NOESY experiments).

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