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Pentamethylcyclopentadienyl ruthenium: an efficient catalyst for the redox isomerization of functionalized allylic alcohols into carbonyl compounds

Asmae Bouziane [a], Bertrand Carboni [a], Christian Bruneau [b], François Carreaux [a,*], Jean-Luc Renaud [c,d,*]

[a] Sciences Chimiques de Rennes, Ingéniérie Chimique et Molécules pour le Vivant, UMR 6226: CNRS-Université de Rennes 1, Campus de Beaulieu-35042 Rennes Cedex, France
[b] Sciences Chimiques de Rennes, Catalyse et Organométalliques, UMR 6226: CNRS-Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France
[c] Sciences Chimiques de Rennes, Chimie Organique et Supramoléculaire, UMR 6226: Ecole Nationale Supérieure de Chimie de Rennes, Campus de Beaulieu-35700 Rennes, France
[d] Laboratoire de Chimie Moléculaire et Thioorganique, UMR 6507, INC3M, FR 3038, ENSICAEN-Université de Caen, 14050 Caen, France

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ABSTRACT

The catalytic activity of the ruthenium(II) complex $[RuCp^*(CH_3CN)_3][PF_6]$ **1** in the transposition of allylic alcohols into carbonyl compounds, in acetonitrile, is reported. This catalyst has proven to be able to catalyze the transformation of poorly reactive and/or functionalized substrates under smooth conditions.

1. Introduction

The concept of atom economy, that is, all atoms of the reactant end up in the final product, has emerged as an important tool and a desirable goal in chemistry.[1] Among the catalytic reactions dealing with this concept, considerable effort was devoted to the redox isomerization.[2] This catalytic reaction formally corresponds to the conversion, in a one-step process, of an allylic alcohol into a carbonyl compound via the oxidation of the alcohol and reduction of the alkene. Several metal complexes, mainly from the group 8, 9, and 10, were reported to perform this transformation.

Among a variety of ruthenium complexes used for this internal redox process,[2c] ruthenium(II) complexes with a cyclopentadienyl type ligand and ruthenium(IV) complexes featuring an allylic ligand have emerged as very efficient catalytic systems. The mononuclear $RuCpCl(PPh_3)_2$, $Ru(indenyl)Cl(PPh_3)_2$, $[RuCp(MeCN)_2(PR_3)]PF_6$, $[RuCp(MeCN)_3]PF_6$, RuCpCl(diphosphine) complexes have revealed good catalytic activities for the isomerization of aliphatic and aromatic allylic alcohols into ketones or aldehydes at 65–100 °C.[3] The binuclear ruthenium catalyst $[(Ru(CO)_2)_2(H)(C_5Ph_4OHOC_5Ph_4)]$,[4] $RuCp^*Cl(Ph_2PCH_2CH_2NH_2\text{-}\eta^2\text{-}P,N)$,[5] and $Ru(C_5MePh_4)X(CO)_2$ (X=Br, Cl)[6] complexes were shown also to be active Cp-containing ruthenium catalysts. Ruthenium(IV) complexes bearing the bis(allyl) dodeca-2,6,10-triene-1,12-diyl (**L1**)[7a] or 2,7-dimethylocta-2,6-dien-1,8-diyl (**L2**)[7b] ligand in $RuCl_2$(**L1**) and $[RuCl_2(\mathbf{L2})]_2$, $RuCl_2(L)(\mathbf{L2})$ (L=CO, phosphine, ^{t}BuNC, MeCN, $PhNH_2$), and $[RuCl(\mathbf{L2})(MeCN)_2]SbF_6$ have also shown very high turnover frequencies in the redox isomerization of allylic alcohols into carbonyl compounds, both in organic solvent and in water at 75 °C.

In conjunction with our work on η^3-allyl-ruthenium(IV) species as catalyst in allylic transformation,[8,9] we discovered that, starting from cinnamyl chloride derivatives and phenylboronic acid in the presence of $[RuCp^*(MeCN)_3]^+$ as catalyst precursor, the reaction gives rise to the branched allylic alcohols, as the major isomer.[9] From electron-rich cinnamyl chloride derivatives, this process led, directly at room temperature, to propiophenones via a subsequent redox isomerization of the branched allylic alcohol intermediates.[10] In light of these results and encouraged by the mild conditions required for this redox isomerization, we decided to study this process with our catalyst system. Here we report our preliminary results showing the good activity of the stable $[RuCp^*(MeCN)_3][PF_6]$ **1** in the isomerization of allylic alcohols to saturated carbonyl compounds. A large variety of substrates can be isomerized very efficiently using these conditions and the regioselectivity of this new process was also demonstrated. Finally, a mechanistic study using a labeled compound was also carried out.

* Corresponding authors. Fax: +33 (0) 223236227 (F.C.); fax: +33 (0) 223238102, +33 (0) 231452877 (J.-L.R.).
E-mail addresses: francois.carreaux@univ-rennes1.fr (F. Carreaux), jean-luc.renaud@univ-rennes1.fr, jean-luc.renaud@ensicaen.fr (J.-L. Renaud).

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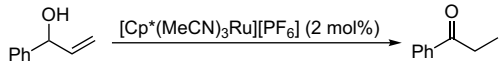
2. Results and discussion

Initially, we used the same reaction conditions that those described for the synthesis of propiophenones from electron-rich cinnamyl chloride:[10] acetonitrile as solvent, potassium carbonate (1.2 equiv) as base, and [RuCp*(MeCN)$_3$][PF$_6$] **1** (2 mol %) as catalyst. Then, from 1-phenylprop-2-en-1-ol **2a** (a less reactive substrate than the corresponding α-vinyl-alkyl alcohol[7]), the propiophenone was isolated in 88% yield after 7 h at room temperature (entry 1, Table 1). The importance of the base was clearly evidenced when the reaction was carried out only in presence of the catalyst with **2a** (entry 2, Table 1). Without any base, the starting material was mainly recovered accompanied with 5% of the expected ketone. We therefore sought to optimize the isomerization reaction conditions of **2a** in the presence of a catalytic amount of [RuCp*(MeCN)$_3$][PF$_6$] (Table 1). A decrease of the amount of base led to a drop of the yield and no improvement occurred when THF was the solvent (entries 3 and 4). However, the reaction rate was improved by increasing the reaction temperature (reflux of solvent), and the propiophenone **3a** was isolated with an almost quantitative yield (95%) in only 1 h (entry 5). Under these experimental conditions (temperature), the amount of K_2CO_3 can be reduced to 50 mol % without alteration of the yield (compare entries 5 and 6). In the presence of 10 mol % of base, the isomerization reaction still occurred but, then, the reaction time had to be increased to reach high yields (Table 1, entry 7). This decreasing reactivity might be due to the heterogeneous conditions. *More interestingly, it is to pointed out that [RuCp* (MeCN)$_3$][PF$_6$], unlike the less stable [RuCp(MeCN)$_3$][PF$_6$], is still an efficient catalyst in presence of water. The reaction can be run in an aqueous solution of K_2CO_3 (2 M) in opened flask without any deleterious effect to furnish* ***3a*** *in 80% yield within 1 h* (entry 8). Then, distilled solvents are not required. Finally, stronger base such as potassium *tert*-butoxide, or organic base such as triethylamine, could also be used in this isomerization and provided comparable yields (entries 9–10). Given that potassium carbonate is not expensive, easy to handle, and to remove from the reaction medium, all the other catalytic reactions have been carried out with this base in refluxing acetonitrile.

To evaluate the scope and limitation of **1**, the study has been extended to a variety of α-arylallylic alcohols. The results are summarized in Table 2. Except for the phenyl ring bearing a nitro function in *ortho* position (**3b**), all the ketones were isolated in nearly quantitative yields. Neither the steric hindrance nor the electronic effect of the substituent has an influence on the efficiency of this redox isomerization. The lowest reactivity of **2b** might be explained either by an intramolecular hydrogen bond, which renders the hydrogen less acidic, or by a coordination of the nitro group on the ruthenium center, which decreases its activity.

Having in hand an efficient process for the synthesis of aromatic ketones, the reactivity of complex [RuCp*(MeCN)$_3$][PF$_6$] **1** was evaluated with other substituted allylic alcohols (Table 3). Isomerization of aliphatic allylic alcohols bearing an unsubstituted vinyl group under previous experimental conditions was

Table 1
Optimization of the reaction conditions

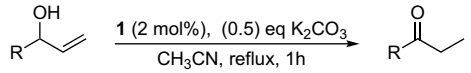


2a **3a**

Entry[a]	Base (equiv)	Temp (°C)	Solvent	Time (h)	Yield[c] (%)
1	K_2CO_3 (1.2)	rt	CH_3CN	7	88
2	—	rt	CH_3CN	7	5
3	K_2CO_3 (0.5)	rt	CH_3CN	7	50
4	K_2CO_3 (0.5)	rt	THF	7	52
5	K_2CO_3 (1.2)	Reflux	CH_3CN	1	95
6	K_2CO_3 (0.5)	Reflux	CH_3CN	1	95
7	K_2CO_3 (0.1)	Reflux	CH_3CN	1	60
8[b]	aq K_2CO_3 (1.2, 2 M)	Reflux	CH_3CN	1	80
9	*t*-BuOK (0.5)	Reflux	CH_3CN	1	95
10	Et_3N (0.5)	Reflux	CH_3CN	1	94

[a] Conditions: 0.5 mmol of allylic alcohol, 0.25 mmol of potassium carbonate, 0.01 mmol of catalyst (2 mol %) in 1.3 mL of solvent.
[b] Conditions: 0.5 mmol of allylic alcohol, 0.01 mmol of catalyst (2 mol %), 0.5 mL of aqueous solution of K_2CO_3 (2 M) in 1 mL of solvent.
[c] Isolated yields after purification on silica gel.

Table 2
Redox isomerization of various 1-arylprop-2-en-1-ols

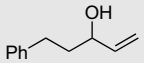
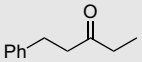
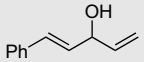
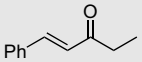
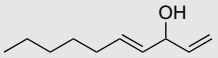
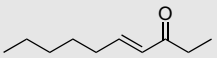
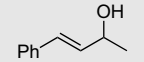
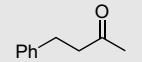
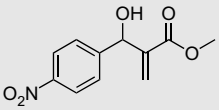
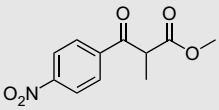


2 **3**

Entry[a]	Products	R	Yield[b] (%)
1	**3a**	Ph	95
2	**3b**	2-NO_2-C_6H_4	33
3	**3c**	4-NO_2-C_6H_4	96
4	**3d**	Br-C_6H_4	99
5	**3e**	4-MeO-C_6H_4	99
6	**3f**	4-F-C_6H_4	98
7	**3g**	2,4,6-$(Me)_3$-C_6H_2	97
8	**3h**	2,4,6-$(MeO)_3$-C_6H_2	98
9	**3i**	2-Naphthyl	99
10	**3j**	1-Naphthyl	99

[a] Conditions: 0.5 mmol of allylic alcohol, 0.25 mmol of potassium carbonate, 0.01 mmol of catalyst (2 mol %) in 1.3 mL of solvent.
[b] Isolated yields after purification on silica gel.

Table 3
Isomerization of a variety of allylic alcohols catalyzed by [RuCp*(MeCN)$_3$][PF$_6$][a]

Entry[a]	Substrate	Product	Yield[b] (%)
1	 **2k**	 **3k**	94
2	 **2l**	 **3l**	82
3	 **2m**	 **3m**	77
4	 **2n**	 **3n**	85
5	 **2o**	 **3o**	96
6	 **2p**	 **3p**	84

[a] Conditions: 0.5 mmol of allylic alcohol, 0.25 mmol of potassium carbonate, 0.01 mmol of catalyst (2 mol %) in 1.3 mL of acetonitrile, reflux, 1 h.
[b] Isolated yields after purification on silica gel.

thus investigated. Substrate **2k** was readily converted into the corresponding ketone **3k** in high yield (94%) (entry 1).

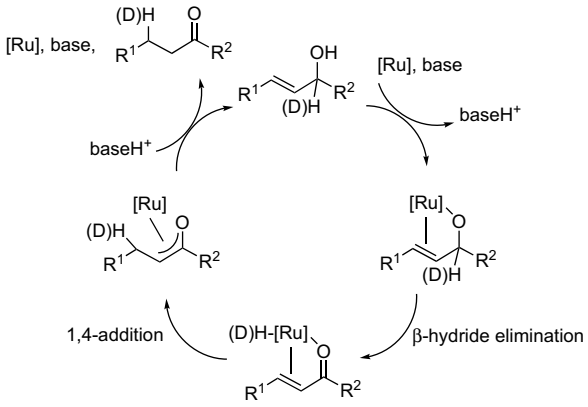
More substituted allylic or more challenging alcohols can be also engaged in this catalytic transformation.[11] Particularly, the chemoselectivity of this redox isomerization was never tackled up to now in previous works using other catalysts. Due to this lack of information, we tried to isomerize different substituted 1,4-dien-3-ols. Whatever the substituent, the redox isomerization occurs chemoselectively from the less substituted double bond. Substrates **2l**–**m**, in the presence of 2 mol % of **1**, led exclusively to the formation of the α,β-unsaturated ketones **3l**–**m** in 82% and 77% yield, respectively (entries 2 and 3).

E- and *Z*-disubstituted allylic alcohols are also prone to isomerization, even if they are known to be less reactive.[2,11] Then compounds **2n**,**o** led to the ketones **3n**,**o** in high yields within 1 h reaction (entries 4 and 5). The last result is definitely important and demonstrated the good activity of catalyst **1** as previously reported catalysts either did not furnish the cyclohexanone $RuCpCl(PPh_3)_2$, $Ru(indenyl)Cl(PPh_3)_2$, $[RuCp(MeCN)_2(PR_3)]PF_6$, $[RuCp(MeCN)_3]PF_6$, RuCpCl(diphosphine)[3] or provided it in low yields, even after long reaction times.[7]

Baylis–Hillman adducts can also be isomerized in the presence of $RuCl_2(Ph_3)_3$.[12] However, relative harsh reaction conditions were required (12 h in refluxing toluene) to provide the corresponding saturated carbonyl in moderate yields. With our catalytic process, the ketone **3p** was isolated in 84% yield after only 1 h (entry 6), showing that the complex $[RuCp^*(MeCN)_3][PF_6]$ kept an excellent activity even with electron-poor allylic alcohols and can be used with functionalized derivatives.

The efficiency of our catalyst was also evaluated with substrates containing an additional free hydroxy group. To the best of our knowledge, such substrates have never been studied in the known reported isomerization reactions. For this purpose, the 1,5-dihydrohept-6-ene **2q** was prepared from 2,3-dihydropyran,[13] via an acidic treatment followed by addition of vinyl magnesium bromide, in a 65% overall yield (Scheme 1). The desired ketone **3q** arising from the isomerization was successfully obtained in 50% yield. It is worth noting that this isomerization opens an access to a compound, which could not easily be prepared without any laborious protection/deprotection steps.

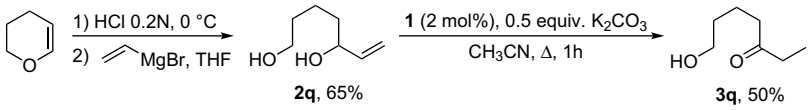
Due to the fact that deuterium is exclusively present at the β-position of the ketone function, we may propose a mechanism involving two key steps: (i) a β-hydride elimination to form the α,β-unsaturated ketone, (ii) followed by the 1,4-addition of the ruthenium monohydride species as depicted in Scheme 3.[16]



Scheme 3.

3. Conclusion

In conclusion, we have demonstrated that $[RuCp^*(MeCN)_3][PF_6]$ **1** is an efficient catalyst for the redox isomerization of allylic alcohols, an atom economical and powerful transformation. This catalyst tolerates substitution patterns and functionalities on the substrates, moreover it allows the transformation of less reactive derivatives and functionalized allylic alcohols. The reactions can be run in opened flask (that is impossible with the less stable $[CpRu(CH_3CN)_3][PF_6]$) in the presence of water (so distilled solvents are not required). Even if $[RuCp^*(MeCN)_3][PF_6]$ **1** is not the best catalyst in term of TON and TOF, its activity represents an important improvement in catalysis and provides a new tool for organic chemists. The asymmetric version of this reaction is under active progress in our group.



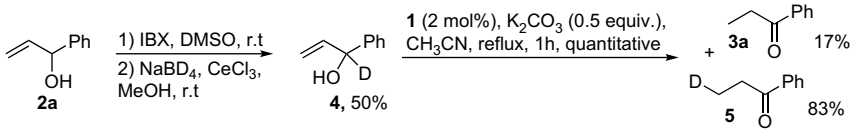
Scheme 1. Straightforward synthesis of **3q** using a redox isomerization step.

In order to have information concerning the mechanism of this isomerization reaction, we synthesized a deuterated allylic alcohol. The compound **4**, namely 1-deuterio-1-phenylprop-2-en-1-ol, was obtained by reduction of the enone with $NaBD_4$ according to a described procedure.[14] Under the optimized reaction conditions, the isomerization of **4** led to the formation of two products of which mainly a monodeuterated saturated ketone **5** (Scheme 2).[15]

4. Experimental section

4.1. General remarks

Catalyst $[Cp^*Ru(MeCN)_3]PF_6$ was prepared according to our previously reported procedure.[17] Reactions were performed in oven-dried glassware under an argon atmosphere. Tetrahydrofuran



Scheme 2.

(THF) was distilled from deep blue solutions of sodium/benzophenone ketyl prior to use. Unless otherwise stated, all reagents were used as received. Most of reactions were monitored by TLC on pre-coated silica plates (Merck 60 F_{254} 0.25 mm). Silica gel 60 F_{254} was used for column flash chromatography. Melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ on a 300 or 200 MHz spectrometer operating in the Fourier transform mode. ^1H NMR data are presented as follows: chemical shift, multiplicity, coupling constant, integration. The following abbreviation are used in reporting data: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; dt, doublet of triplets; dq, doublet of quartets; dd, doublet of doublets; ddd, doublet of doublets of doublets; m, multiplet. ^{13}C NMR spectra were obtained with broadband proton decoupling. Chemical shifts were recorded relative to the internal tetramethylsilane (TMS) reference signal. Coupling constants (J) are given in hertz. High resolution mass spectrum (HRMS) were performed by Centre Régional de Mesures Physiques de l'Ouest. 1-Phenylpropan-1-one **3a**, 1-(4-fluorophenyl)propan-1-one **3f**, 4-phenylbutan-2-one **3n**, cyclohexanone **3o** are also commercially available, and these compounds obtained by using our procedure were confirmed to be identical with those authentic samples.

4.2. General procedure for the preparation of allylic alcohols

In an oven-dried Schlenk flask, a solution of aldehyde (1.3 mmol, 1 equiv) in THF (1.8 mL) was prepared under an inert atmosphere at 0 °C. To the solution, the Grignard reagent (1.4 mmol, 1.1 equiv) was added and the reaction was stirred for 2 h. The reaction was allowed to warm up to room temperature, quenched with a saturated aqueous NH_4Cl solution, and extracted with diethyl ether. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and evaporated to give the crude allylic alcohol that was purified by flash chromatography on silica gel (cyclohexane/AcOEt, 8:2 v/v).

4.2.1. 1-Phenylprop-2-en-1-ol (**2a**)[18]

Colorless oil (95%). ^1H NMR ($CDCl_3$, 200 MHz) δ 3.10 (br s, 1H), 5.10–5.20 (m, 2H), 5.40 (m, 1H), 6.10 (ddd, 1H, J=6.0, 10.2, 16.4 Hz), 7.25–7.50 (m, 5H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 76.8, 116.2, 126.2, 127.4, 128.3, 138.5, 141.4.

4.2.2. 1-(2-Nitrophenyl)prop-2-en-1-ol (**2b**)[18]

Colorless oil (70%). ^1H NMR ($CDCl_3$, 300 MHz) δ 3.20 (br s, 1H), 5.22 (ddd, 1H, J=1.1, 1.1, 10.4 Hz), 5.35 (ddd, 1H, J=1.1, 1.1, 17.1 Hz), 5.71 (d, 1H, J=5.3 Hz), 6.05 (ddd, 1H, J=5.3, 10.4, 17.1 Hz), 7.40 (m, 1H), 7.63 (m, 1H), 7.77 (m, 1H), 7.95 (dd, 1H, J=0.9, 8.1 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 69.8, 116.1, 124.5, 128.4, 128.8, 133.6, 137.6, 138.1, 148.2.

4.2.3. 1-(4-Nitrophenyl)prop-2-en-1-ol (**2c**)[18]

Colorless oil (68%). ^1H NMR ($CDCl_3$, 200 MHz) δ 2.20 (br s, 1H), 5.22 (ddd, 1H, J=1.1, 1.1, 10.4 Hz), 5.30 (d, 1H, J=6.7 Hz), 5.40 (ddd, 1H, J=1.1, 1.1, 17.4 Hz), 6.00 (ddd, 1H, J=6.5, 10.4, 17.4 Hz), 7.60 (d, 2H, J=8.6 Hz), 8.20 (d, 2H, J=8.6 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 74.7, 116.4, 123.7, 127.1, 139.5, 147.3, 149.5.

4.2.4. 1-(4-Bromophenyl)prop-2-en-1-ol (**2d**)[19]

Colorless oil (96%). ^1H NMR ($CDCl_3$, 300 MHz) δ 3.05 (br s, 1H), 5.08 (d, 1H, J=6.1 Hz), 5.20 (ddd, 1H, J=1.3, 1.3, 10.3 Hz), 5.35 (ddd, 1H, J=1.3, 1.3, 17.1 Hz), 5.96 (ddd, 1H, J=6.1, 10.3, 17.1 Hz), 7.25 (d, 2H, J=8.4 Hz), 7.50 (d, 2H, J=8.4 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 74.6, 115.6, 121.5, 128.6, 131.5, 139.7, 141.5.

4.2.5. 1-(4-Methoxyphenyl)prop-2-en-1-ol (**2e**)[20]

Colorless oil (98%). ^1H NMR ($CDCl_3$, 300 MHz) δ 3.05 (br s, 1H), 3.80 (s, 3H), 5.09–5.21 (m, 2H), 5.35 (ddd, 1H, J=1.4, 1.4, 17.2 Hz), 6.04 (ddd, 1H, J=5.9, 10.3, 17.2 Hz), 6.87 (dd, 2H, J=1.8, 8.7 Hz), 7.30 (dd, 2H, J=2.1, 8.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.3, 74.8, 113.9, 114.7, 127.7, 134.9, 140.5, 159.1.

4.2.6. 1-(4-Fluorophenyl)prop-2-en-1-ol (**2f**)[18]

Colorless oil (94%). ^1H NMR ($CDCl_3$, 300 MHz) δ 2.22 (br s, 1H), 5.18–5.24 (m, 2H), 5.34 (ddd, 1H, J=1.2, 1.2, 17.1 Hz), 6.01 (ddd, 1H, J=6.0, 10.3, 17.1 Hz), 7.02–7.08 (m, 2H), 7.31–7.37 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 74.6, 115.2, 115.3 (d, J=21.7 Hz), 128.1 (d, J=7.5 Hz), 138.2 (d, J=3.1 Hz), 140.1, 162.2 (d, J=244.3 Hz, C–F).

4.2.7. 1-(2,4,6-Trimethylphenyl)prop-2-en-1-ol (**2g**)

White solid (95%), mp 52–54 °C. ^1H NMR ($CDCl_3$, 300 MHz) δ 2.30 (s, 3H), 2.39 (s, 6H), 3.05 (br s, 1H), 5.18 (ddd, 1H, J=1.8, 1.8, 10.5 Hz), 5.22 (ddd, 1H, J=1.7, 1.7, 17.3 Hz), 5.72 (m, 1H), 6.15 (ddd, 1H, J=4.5, 10.5, 17.3 Hz), 6.90 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.5, 20.7, 71.5, 114.3, 130.0, 134.9, 136.5, 137.1, 138.6. HRMS (EI): m/z calcd for $C_{12}H_{16}O$: 176.1201; found: 176.1204.

4.2.8. 1-(2,4,6-Trimethoxyphenyl)prop-2-en-1-ol (**2h**)

Colorless oil (98%). ^1H NMR ($CDCl_3$, 300 MHz) δ 2.34 (br s, 1H), 3.80 (s, 3H), 3.83 (s, 6H), 5.02 (ddd, 1H, J=1.6, 1.6, 10.2 Hz), 5.12 (ddd, 1H, J=1.6, 1.6, 17.1 Hz), 5.19 (m, 1H), 5.59 (ddd, 1H, J=5.5, 10.2, 17.1 Hz), 6.16 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.3, 55.7, 68.1, 91.1, 111.1, 112.9, 140.5, 158.3, 160.6. HRMS (EI): m/z calcd for $C_{12}H_{16}O_4$: 224.1048; found: 224.1051.

4.2.9. 1-(Naphthalen-2-yl)prop-2-en-1-ol (**2i**)[21]

Colorless oil (90%). ^1H NMR ($CDCl_3$, 200 MHz) δ 2.20 (br s, 1H), 5.20 (m, 1H), 5.35–5.45 (m, 2H), 6.25 (m, 1H), 7.40–7.50 (m, 3H), 7.80–8.10 (m, 4H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 75.5, 115.4, 124.4, 124.8, 125.8, 126.0, 127.5, 127.9, 128.1, 132.8, 133.1, 139.6, 140.0.

4.2.10. 1-(Naphthalen-1-yl)prop-2-en-1-ol (**2j**)[19]

Colorless oil (95%). ^1H NMR ($CDCl_3$, 300 MHz) δ 2.18 (br s, 1H), 5.30 (ddd, 1H, J=1.2, 1.2, 10.3 Hz), 5.48 (ddd, 1H, J=1.3, 1.3, 17.3 Hz), 5.97 (d, 1H, J=5.3 Hz), 6.27 (ddd, 1H, J=5.3, 10.3, 17.3 Hz), 7.50–7.66 (m, 4H), 7.80–7.90 (m, 2H), 8.23 (d, 1H, J=9.1 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 72.3, 115.6, 123.7, 123.9, 125.4, 125.6, 126.0, 128.5, 128.8, 130.6, 133.9, 138.0, 139.6.

4.2.11. 5-Phenylpent-1-en-3-ol (**2k**)[22]

Colorless oil (59%). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.85–1.91 (m, 3H), 2.67–2.81 (m, 2H), 4.14 (m, 1H), 5.15 (ddd, 1H, J=1.3, 1.3, 10.4 Hz), 5.26 (ddd, 1H, J=1.3, 1.3, 17.2 Hz), 5.95 (ddd, 1H, J=6.1, 10.4, 17.2 Hz), 7.17–7.42 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.6, 38.5, 72.4, 114.9, 125.8, 128.4, 128.5, 141.0, 141.9.

4.2.12. (4E)-1-Phenylpenta-1,4-dien-3-ol (**2l**)[23]

Colorless oil (96%). ^1H NMR ($CDCl_3$, 300 MHz) δ 2.86 (br s, 1H), 4.81 (m, 1H), 5.23 (dd, 1H, J=1.5, 10.4 Hz), 5.35 (ddd, 1H, J=1.5, 1.5, 17.2 Hz), 5.98 (ddd, 1H, J=6.0, 10.4, 17.2 Hz), 6.25 (dd, 1H, J=6.4, 15.9 Hz), 6.61 (d, 1H, J=15.9 Hz), 7.28–7.44 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 73.7, 115.4, 126.6, 127.8, 128.6, 130.5, 130.7, 136.7, 139.4.

4.2.13. (4E)-Deca-1,4-dien-3-ol (**2m**)

Colorless oil (74%). ^1H NMR ($CDCl_3$, 300 MHz) δ 2.78 (br s, 1H), 0.85 (t, 3H, J=7.5 Hz), 1.09–1.40 (m, 6H), 2.00 (dt, 2H, J=6.7, 6.7 Hz), 4.52 (dd, 1H, J=6.0, 6.0 Hz), 5.05 (ddd, 1H, J=1.4, 1.4, 10.5 Hz), 5.19 (ddd, 1H, J=1.4, 1.4, 17.3 Hz), 5.44 (dd, 1H, J=6.7, 16.5 Hz), 5.64 (dt, 1H, J=7.5, 16.5 Hz), 5.82 (ddd, 1H, J=6.0, 10.5, 17.3 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.9, 22.4, 28.7, 31.1, 32.1, 73.6, 114.3, 131.0, 132.4, 140.0. HRMS (EI): m/z calcd for $C_{10}H_{18}O$: 154.1357; found: 154.1361.

*4.2.14. (3E)-4-Phenylbut-3-en-2-ol (**2n**)*[24]

Yellow oil (94%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.40 (d, 3H, J=6.3 Hz), 3.50 (br s, 1H), 4.51 (m, 1H), 6.28 (dd, 1H, J=6.3, 15.9 Hz), 6.62 (d, 1H, J=15.9 Hz), 7.24–7.42 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.4, 68.9, 126.4, 127.6, 128.6, 129.3, 133.5, 136.7.

*4.2.15. Methyl 2-[(4-nitrophenyl)(hydroxy)methyl]acrylate (**2p**)*

To a stirred solution of 4-nitrobenzaldehyde (151 mg, 1 mmol), DMAP (61 mg, 0.5 equiv), and 0.5 mL of H_2O in 1,4-dioxane (2 mL) was added methyl acrylate (260 mg, 3 mmol). The resulting mixture was stirred at room temperature for 4 h. Then chloroform (20 mL) and water (5 mL) were added, and the organic phase was separated. The water phase was extracted with chloroform (2×10 mL) and the combined organic layers were dried over $MgSO_4$. After filtration and evaporation of the solvent, the crude product was purified by column chromatography on silica gel (cyclohexane/AcOEt, 9:1 v/v) to afford **2p** as a yellow solid (62%). Mp 70–72 °C [lit.[25] 71–73 °C]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.93 (br s, 1H), 3.73 (s, 3H), 5.61 (s, 1H), 5.85 (s, 1H), 6.38 (s, 1H), 7.55 (d, 2H, J=8.6 Hz), 8.18 (d, 2H, J=8.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.9, 72.4, 123.5, 127.1, 127.3, 141.0, 147.3, 148.7, 166.3.

*4.2.16. 1,5-Dihydroxyhept-6-ene (**2q**)*[14]

Colorless oil (65%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.40–1.50 (m, 6H), 2.80 (br s, 2H), 3.65 (q, 2H, J=5.3 Hz), 4.10 (m, 1H), 5.10 (dd, 1H, J=3.5, 10.4 Hz), 5.23 (dd, 1H, J=3.5, 17.1 Hz), 5.84 (ddd, 1H, J=6.2, 10.4, 17.1 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 32.2, 36.5, 62.0, 72.8, 114.4, 141.1.

4.3. General procedure for the isomerization of allylic alcohols

In a Schlenk tube, under an inert atmosphere, the ruthenium catalyst (0.014 mmol, 2 mol%) was added to a solution of allylic alcohol **2** (0.75 mmol) and K_2CO_3 (0.372 mmol, 0.5 equiv) in acetonitrile (2 mL). Then, the mixture was heated at reflux for 1 h. After evaporation of the solvent, the crude product was purified by flash chromatography on silica gel (cyclohexane/AcOEt, 9.5:0.5 v/v) to afford the desired ketones.

*4.3.1. 1-Phenylpropan-1-one (**3a**)*

Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.24 (t, 3H, J=7.2 Hz), 3.02 (q, 2H, J=7.2 Hz), 7.44–7.59 (m, 3H), 7.99 (dd, 2H, J=0.9, 6.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.1, 31.6, 127.9, 128.5, 132.8, 136.8, 200.6.

*4.3.2. 1-(2-Nitrophenyl)propan-1-one (**3b**)*[26]

Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.23 (t, 3H, J=7.2 Hz), 2.82 (q, 2H, J=7.2 Hz), 7.42 (m, 1H), 7.56–7.85 (m, 3H), 8.15 (dd, 1H, J=1.1, 8.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.7, 33.5, 123.2, 126.5, 132.2, 132.9, 135.8, 145.1, 199.7.

*4.3.3. 1-(4-Nitrophenyl)propan-1-one (**3c**)*

Yellow solid, mp 89–91 °C [lit.[27] 86–88 °C]. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.27 (t, 3H, J=7.2 Hz), 3.06 (q, 2H, J=7.2 Hz), 8.14 (d, 2H, J=8.8 Hz), 8.34 (d, 2H, J=8.8 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 7.9, 32.4, 123.8, 128.9, 141.3, 199.1.

*4.3.4. 1-(4-Bromophenyl)propan-1-one (**3d**)*

White solid, mp 46–48 °C [lit.[28] 47–48 °C]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.22 (t, 3H, J=7.2 Hz), 2.97 (q, 2H, J=7.2 Hz), 7.60 (d, 2H, J=8.5 Hz), 7.83 (d, 2H, J=8.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.1, 30.1, 128.0, 129.5, 131.8, 135.6, 199.7.

*4.3.5. 1-(4-Methoxyphenyl)propan-1-one (**3e**)*[27]

Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.24 (t, 3H, J=7.2 Hz), 2.95 (q, 2H, J=7.2 Hz), 3.88 (s, 3H), 6.93 (d, 2H, J=8.8 Hz), 7.95 (d, 2H, J=8.8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.4, 31.4, 55.4, 113.6, 130.0, 130.2, 163.3, 199.5.

*4.3.6. 1-(4-Fluorophenyl)propan-1-one (**3f**)*

Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.24 (t, 3H, J=7.2 Hz), 3.00 (q, 2H, J=7.2 Hz), 7.14 (m, 2H), 8.02 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.2, 31.7, 115.5, 115.8, 130.5, 130.6, 199.2.

*4.3.7. 1-(2,4,6-Trimethylphenyl)propan-1-one (**3g**)*[29]

Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.21 (t, 3H, J=7.2 Hz), 2.20 (s, 6H), 2.30 (s, 3H), 2.73 (q, 2H, J=7.2 Hz), 6.86 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.6, 19.0, 21.0, 37.9, 128.4, 132.4, 138.1, 139.9, 211.5.

*4.3.8. 1-(2,4,6-Trimethoxyphenyl)propan-1-one (**3h**)*

Yellow solid, mp 94–96 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.20 (t, 3H, J=7.3 Hz), 2.95 (q, 2H, J=7.3 Hz), 3.85 (s, 9H), 6.10 (s, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.9, 38.0, 55.4, 55.5, 90.5, 113.5, 158.0, 162.1, 205.3. HRMS (EI): m/z calcd for $C_{12}H_{16}O_4$: 224.1048; found: 224.1053.

*4.3.9. 1-(Naphthalen-2-yl)propan-1-one (**3i**)*

White solid, mp 62–64 °C [lit.[27] 64–65 °C]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.28 (t, 3H, J=7.3 Hz), 3.11 (q, 2H, J=7.3 Hz), 7.48–7.62 (m, 3H), 7.85–7.88 (m, 2H), 8.00 (d, 1H, J=8.3 Hz), 8.60 (d, 1H, J=8.3 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.6, 35.3, 124.4, 125.8, 126.4, 127.1, 127.8, 128.4, 130.1, 132.3, 133.9, 136.2, 205.3.

*4.3.10. 1-(Naphthalen-1-yl)propan-1-one (**3j**)*

Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.32 (t, 3H, J=7.2 Hz), 3.09 (q, 2H, J=7.2 Hz), 7.50–7.61 (m, 3H), 7.85–7.90 (m, 2H), 8.01 (d, 1H, J=8.3 Hz), 8.60 (d, 1H, J=8.3 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.7, 35.4, 124.4, 125.8, 126.4, 127.1, 127.9, 128.4, 130.1, 132.3, 133.9, 136.2, 205.3. HRMS (EI): m/z calcd for $C_{13}H_{12}O$: 184.0888; found 184.0889.

*4.3.11. 1-Phenylpentan-3-one (**3k**)*[30]

Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.06 (t, 3H, J=7.3 Hz), 2.44 (q, 2H, J=7.3 Hz), 2.75 (t, 2H, J=7.8 Hz), 2.93 (t, 2H, J=7.8 Hz), 7.20–7.33 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.8, 29.9, 36.1, 43.9, 126.1, 128.3, 128.5, 141.2, 210.6.

*4.3.12. (1E)-1-Phenylpent-1-en-3-one (**3l**)*

Yellow solid, mp 36–38 °C [lit.[31] 35–36 °C]. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.18 (t, 3H, J=7.3 Hz), 2.71 (q, 2H, J=7.3 Hz), 6.80 (d, 1H, J=16.2 Hz), 7.39–7.60 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.2, 34.0, 126.0, 128.2, 128.9, 130.4, 134.6, 142.2, 200.9.

*4.3.13. (4E)-Deca-4-en-3-one (**3m**)*[32]

Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, 3H, J=7.0 Hz), 1.09 (t, 3H, J=7.4 Hz), 1.28–1.35 (m, 4H), 1.42–1.52 (m, 2H), 2.20 (m, 2H), 2.56 (q, 2H, J=7.4 Hz), 6.10 (d, 1H, J=15.1 Hz), 6.83 (dt, 1H, J=6.9, 15.1 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.1, 13.9, 22.4, 27.8, 31.3, 32.4, 33.1, 130.0, 147.2, 201.2. HRMS (EI): m/z calcd for $C_{10}H_{18}O$: 154.1357; found: 154.1362.

*4.3.14. 4-Phenylbutan-2-one (**3n**)*

Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.16 (s, 3H), 2.78 (t, 2H, J=7.4 Hz), 2.92 (t, 2H, J=7.4 Hz), 7.20–7.34 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.7, 30.0, 45.2, 126.1, 128.3, 128.5, 141.0, 207.9.

*4.3.15. Cyclohexanone (**3o**)*

Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.65–1.72 (m, 2H), 1.79–1.84 (m, 4H), 2.28–2.32 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.9, 26.9, 41.9, 212.1.

*4.3.16. Methyl 3-(4-nitrophenyl)-2-methyl-3-oxopropanoate (**3p**)*

Yellow solid, mp 70–72 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.52 (d, 3H, J=7.1 Hz), 3.70 (s, 3H), 4.42 (q, 1H, J=7.1 Hz), 8.13 (d, 2H, J=8.8 Hz), 8.32 (d, 2H, J=8.8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.4, 26.8, 48.5, 123.9, 129.6, 140.3, 150.4, 170.5, 194.2. HRMS (EI): m/z calcd for $C_{11}H_{12}O_5N$: 237.0637; found 237.0641.

*4.3.17. 7-Hydroxyheptan-3-one (**3q**)*

Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.06 (t, 3H, J=7.3 Hz), 1.48–1.77 (m, 4H), 2.4–2.54 (m, 4H), 3.65 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.8, 19.7, 32.1, 35.9, 41.8, 62.3, 211.8. HRMS (EI): m/z calcd for $C_7H_{14}O_2$: 130.0994; found: 130.0991.

*4.3.18. 3-Deuterio-1-phenylpropanone (**5**)*[33]

The ratio between the two compounds **5** and **3a** (83:17) was determined by comparison of the integration of the ^{13}C NMR signals of the CH_2D signal (at δ=7.95 ppm, t, J_{C-D}=19.4 Hz) with the signal of CH_3 group (at δ=8.21 ppm, s). ^{13}C NMR ($CDCl_3$, 125 MHz) of **5**: δ=7.95 ppm (t, J_{C-D}=19.4 Hz), 31.57, 128.21, 128,54, 132.88, 136.85, 200.79.

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