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Novel ruthenium-catalyzed synthesis of 1,3-dioxolan-4-ones from α-hydroxy acids and terminal alkynes *via* enol esters *

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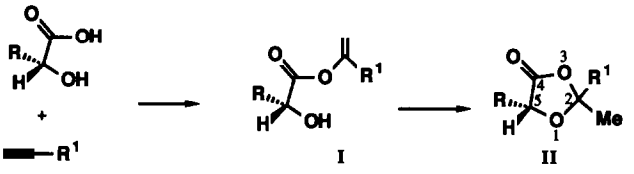
Abstract

α-Hydroxy acids react with terminal alkynes, in the presence of binuclear ruthenium complexes $[Ru(\mu\text{-}O_2CR)(CO)_2(PPh_3)]_2$ as catalyst precursors, to selectively afford either α-hydroxy enol esters or their cyclization products 1,3-dioxolan-4-ones.

1. Introduction

Chiral 5-monosubstituted 1,3-dioxolan-4-ones have become useful tools in diastereoselective synthesis to produce enolates that easily undergo aldol condensation with aldehydes or ketones [1] or alkylation by electrophiles such as alkylhalides [2,3]. They can also be opened in the presence of Lewis acids to afford enantioselectively aldols and homoallylic alcohols, by reaction with silyl enol ethers or allyl silanes [4], and ethers by addition of organotin or organoborate nucleophiles to allylic dioxolanones in the presence of nickel or palladium catalysts [5]. 1,3-Dioxolan-4-ones are usually obtained from the reaction of α-hydroxy acids with aldehydes catalyzed by acids such as *p*-toluene sulfonic acid [3], or by palladium, platinum or rhodium complexes [6] in the presence of a dehydrating reagent, or by the condensation of α-hydroxy acids with acetals [7] or enol acetates [8]. Bis(trimethylsilyl) derivatives of α-hydroxy carboxylic acids also react with ketones or aldehydes [9,10] to produce 1,3-dioxolanones. We now report a new synthesis of 1,3-dioxolan-4-ones **II** *via* enol esters **I**, directly from α-hydroxy acids and terminal alkynes using a ruthenium catalyst that allows the addition of functional carboxylic acids.



I **II**

Enol esters are useful intermediates in organic synthesis for the generation of enolates [11] or the mild acylation of amines and alcohols [12,13]. The enzymatic hydrolysis of enol acetates has recently been used for enantioselective access to chiral ketone derivatives [14]. The synthesis of enol esters by direct addition of carboxylic acids to alkynes, catalyzed by ruthenium complexes such as $[Ru_3(CO)_{12}]$ [15], [(cyclooctadienyl)$_2$Ru] [16] or [(arene)$RuCl_2(PR_3)$] [13,17] has recently been developed. As well as simple aliphatic or aromatic acids, the successful addition of functional acids to alkynes has been described, including keto acids [16], diacids [13] and *N*-protected amino acids [12b,18]. To our knowledge only one example of the addition of an α-hydroxy acid has been reported: the reaction of mandelic acid with hex-1-yne in 1,2-dimethoxyethane, catalyzed by the three component system bis(η^5-cyclooctadienyl)ruthenium–PPh_3–maleic anhydride [16].

We have now shown that $[\{Ru(\mu\text{-}O_2CH)(CO)_2(PPh_3)\}_2]$ is an efficient catalyst precursor for the mild addition of α-hydroxy acids to terminal alkynes to give enol esters **I** when the reaction is carried out in tetrahydrofuran and that the same ruthenium precursor allows the catalytic cyclization of **I** into **II** when toluene is used as a solvent.

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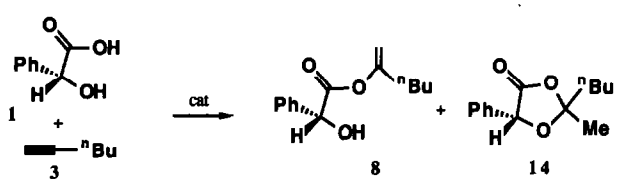
2. Results and discussion

The addition of an α-hydroxy acid to a terminal alkyne was not possible in the presence of [(arene)$RuCl_2(PR_3)$] [13], but we found that by using [{Ru(μ-O_2CH)$(CO)_2(PPh_3)$}$_2$] as catalyst precursor the formation of two addition products occurred. Ten mmol of (*R*)-mandelic acid **1** reacted with 10 mmol of hex-1-yne **3** in tetrahydrofuran at 100°C for 10 h in the presence of 0.05 mmol of [{Ru(μ-O_2CH)$(CO)_2(PPh_3)$}$_2$] to afford a 60:40 mixture of enol ester **8** and dioxolanone **14**. The relative proportions of compounds **8** and **14** depended on the reaction time and the solvent. The difference between reactivity in tetrahydrofuran and in toluene made possible the selective synthesis of either enol esters or dioxolanones, from (*R*)-mandelic and (*S*)-lactic acids with various terminal alkynes. Since the two catalytic reactions are consecutive reactions, it was impossible to obtain the enol ester alone without forming a small amount of the corresponding dioxolanone.



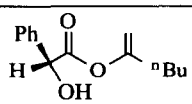
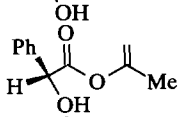
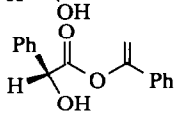
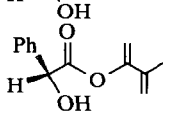
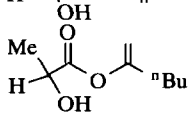
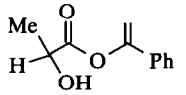
cat: [{Ru(μ-O_2CH)$(CO)_2(PPh_3)$}$_2$] (**CI**)

However, in tetrahydrofuran, optically pure enol esters **8–11** resulting from the addition of (*R*)-mandelate at the substituted carbon of the triple bond were isolated in good yield (Table 1). Their hydrolysis regenerated **1** with the same optical rotation as the starting (*R*)-mandelic acid, indicating that the reaction takes place without significant racemization. Starting from (*S*)-lactic acid, the yields in enol esters **12–13** were lower, because of the instability of the acid at 100°C and the fast cyclization of enol esters on distillation. These two enol lactates exhibited no optical activity.

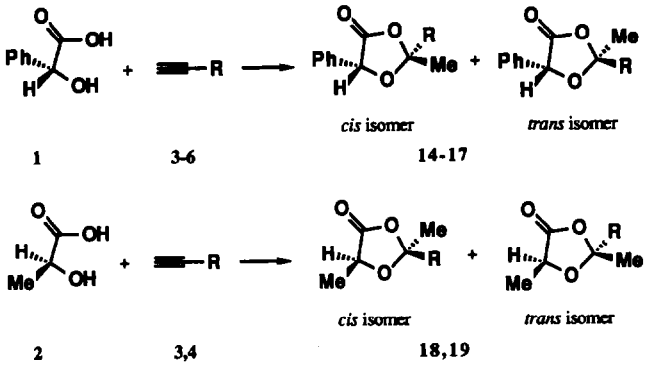
The formation of enol esters **8–13** may proceed *via* initial activation of the alkyne at one ruthenium centre, followed by external regioselective addition of the carboxylate at the substituted carbon according to a catalytic cycle similar to that suggested for mononuclear ruthenium catalysts [13].

At 100°C in toluene, the formation of the dioxolanone was favoured and a selectivity in **14** higher than 95% was found after 15 h of heating. Gas chromatographic analyses indicated that during a reaction carried out at 100°C in toluene, the **8**:**14** ratio decreased as the reaction time increased. Thus after 1, 2.5, 7.5 and 15 h of reaction, respective **8**:**14** ratios of 4, 1, 0.18 and 0.05 were observed by chromatography. This indicated that the enol ester **8** was formed first and that **14** resulted from cyclization of **8**. It was shown that the isolated ester **8** was stable in toluene at 100°C, and its quantitative conversion into **14** was observed when a catalytic amount of [{Ru(μ-O_2CH)$(CO)_2$-(PPh_3)}$_2$] was added. However, when tetrahydrofuran

TABLE 1. Synthesis of enol esters from α-hydroxy acids and alkynes [a]

Acid	Alkyne	Enol ester		Yield [b] (%)
(R)-Mandelic acid **1**	Hex-1-yne **3**		**8** [c]	42
	Propyne **4**		**9** [d]	78
	Phenylacetylene **5**		**10**	75
	Isopropenylacetylene **6**		**11** [e]	66
(S)-Lactic Acid **2**	Hex-1-yne **3**		**12**	30
	Phenylacetylene **5**		**13**	20

[a] General conditions: acid (10 mmol), alkyne (10 mmol), THF (10 mL), catalyst [{Ru(O_2CH)$(CO)_2(PPh_3)$}$_2$] (0.05 mmol), 100°C, 10 h. [b] Isolated yields based on the acid. [c] 8 h, a mixture of **8** and **14** containing 76% of **8** was isolated in 55% yield. [d] alkyne (20 mmol). [e] toluene, 90°C, 7 h (no reaction in THF).



was the solvent, the cyclization was much slower. For instance with propyne after 110 h at 100°C in THF, a 73:27 mixture of **9** and **15** (Tables 1 and 2) was obtained, whereas under similar conditions the reaction in toluene led to a 4:96 ratio of the same compounds. Thus the selective syntheses of 1,3-dioxolan-4-ones **14–17** from (*R*)-mandelic acid at 100°C were made possible (Table 2). (*S*)-Lactic acid reacted with hex-1-yne or phenylacetylene to provide 1,3-dioxolan-4-ones **18** and **19** in 60% and 50% respective yields.

Dioxolanone **14** isolated in 86% yield was optically active ($[\alpha]_D = -71°$ ($c = 1.1$ g l^{-1}, EtOH)). Its hydrolysis afforded (*R*)-mandelic acid in 97% ee, which showed that only a slight racemization occurs at C-5 during the dioxolanone formation. This cyclization was diastereoselective as shown by ^{1}H NMR: the signals of the H-5 proton and the methyl group at C-2 position of the *cis* and *trans* dioxolanone isomers were separated and showed a 90:10 ratio of the diastereoisomers **14**. From previous work [8] indicating that the presence of the phenyl group at C-5 position induces a deshielding effect on a *cis* methyl group at C-2, and data in the literature [8,19] the major compounds were identified as the *cis* isomers with the two bulky groups at C-2 and C-5 on the same side of the dioxolanone ring. From (*S*)-lactic acid, dioxolanones **18** and **19** were obtained, in each case with a diastereoselectivity of 90%.

As we have shown that the cyclization of α-hydroxy enol esters into dioxolanones was only possible in the presence of $[\{Ru(O_2CH)(CO)_2(PPh_3)\}_2]$, this reaction probably involves activation of the double bond of the enol ester by the ruthenium catalyst and intramolecular addition of the hydroxy group at the substituted carbon. Because of steric hindrance, the intermediate form **A** with the H-5 proton on the side of the double bond hindered by the ruthenium complex is probably favoured as compared to that where the phenyl substituent is close to the ligands (form **B**) (Scheme 1).

Since no racemization took place at C-5 with mandelic acid, attempts were made to improve the diastereoselectivity of the addition of hex-1-yne and phenylacetylene to (*R*)-mandelic acid. The bridging ligands of the catalyst precursor were changed to more bulky and optically active carboxylates with the aim of favouring the formation of intermediate **A** (Scheme 1). Pivalate, (*R*)- and (*S*)-mandelate binuclear complexes

TABLE 2. Synthesis of 1,3-dioxolan-4-ones from (*R*)-mandelic acid and alkynes [a]

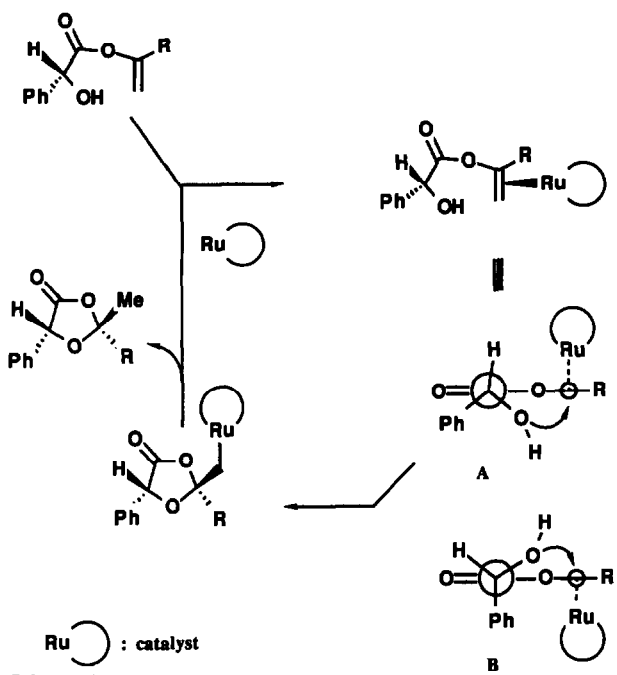
Alkyne	Dioxolanone		Yield [b] (%)	Major/minor ratio
Hex-1-yne **3**	R = ^{n}Bu	**14**	86	90:10
Propyne **4**	R = Me	**15** [c]	70	-
Phenylacetylene **5**	R = Ph	**16**	84	75:25
Isopropenylacetylene **6**	R = CH_2=C(Me)	**17** [d]	53	95:5

[a] General conditions: acid (10 mmol), alkyne (10 mmol), toluene (10 mL), catalyst $[\{Ru(O_2CH)(CO)_2(PPh_3)\}_2]$ (0.05 mmol), 100°C, 20 h. [b] Isolated yields based on the acid. [c] Alkyne (20 mmol). [d] Isolated yield 63% (dioxolanone + enol ester (83:17)).

TABLE 3. Synthesis of 1,3-dioxolan-4-ones: influence of the ruthenium catalyst on the diastereoselectivity of the reaction [a]

Ruthenium complex	Alkyne	Dioxolanone (yield [b])	ds
$[Ru(\mu\text{-}O_2CH)(CO)_2(PPh_3)]_2$ **CI**	**3**	**14** (86%)	90%
$[Ru(\mu\text{-}O_2CH)(CO)_2(PPh_3)]_2$ **CI**	**5**	**16** (84%)	75%
$[Ru(\mu\text{-}O_2C^tBu)(CO)_2(PPh_3)]_2$ **CII**	**3**	**14** (88%)	85%
$[Ru(\mu\text{-}O_2C^tBu)(CO)_2(PPh_3)]_2$ **CII**	**5**	**16** (84%)	90%
$[Ru(\mu\text{-(R)-}O_2CC^*H(OH)Ph)(CO)_2(PPh_3)]_2$ **CIII**	**3**	**14** (89%)	90%
$[Ru(\mu\text{-(R)-}O_2CC^*H(OH)Ph)(CO)_2(PPh_3)]_2$ **CIII**	**5**	**16** (32%) [c]	93%
$[Ru(\mu\text{-(S)-}O_2CC^*H(OH)Ph)(CO)_2(PPh_3)]_2$ **CIV**	**3**	**14** (39%) [d]	90%
$[Ru(\mu\text{-(S)-}O_2CC^*H(OH)Ph)(CO)_2(PPh_3)]_2$ **CIV**	**5**	**16** (82%) [e]	78%

[a] General conditions: acid (10 mmol), alkyne (10 mmol), toluene (10 mL), ruthenium complex (0.05 mmol), 100°C, 20 h, diastereoselectivity (ds) determined by ^{1}H NMR. [b] Isolated yields based on the acid. [c] Isolated yield 47% (**10**:**16** = 30:70). [d] Isolated yield 78% (**10**:**16** = 50:50). [e] 30 h.



Scheme 1.

were synthesized by literature methods [20] and used as catalyst precursors in the one-step synthesis of 1,3-dioxolan-4-ones from (*R*)-mandelic acid and hex-1-yne or phenylacetylene in toluene at 100°C. Table 3 shows that with both alkynes and under similar conditions, reactions carried out with the pivalate complex **CII** gave good yields in dioxolanones but that the diastereoselectivity of the reaction with phenylacetylene was only slightly improved. With mandelate complexes **CIII** and **CIV** the catalysts were less active, especially when phenylacetylene was used; the cyclization step seemed more difficult to achieve and large amounts of enol esters were recovered. Thus after 10 h of reaction with complex **CIII**, dioxolanone **16** was formed in 32% yield and a reaction mixture containing 70% of dioxolanone and 30% of enol ester was isolated in an overall yield of 47%.

Under similar conditions with complex **CIV**, a very small amount of dioxolanone was formed after 10 h, and a heating period of 30 h was necessary to enable the isolation of 82% of **16**. The above experiments show that with more bulky bridging carboxylate ligands it was not possible to improve the reaction and significantly increase the diastereoselectivity of the reaction above 90%.

3. Conclusion

The activation of terminal alkynes with [{Ru(μ-O_2CH)$(CO)_2(PPh_3)$}$_2$] complexes in tetrahydrofuran makes possible the preparation of α-hydroxy enol esters by addition of α-hydroxy acids without racemization of the acid moiety. A subsequent catalytic cyclization involving the activation of the double bond towards the intramolecular addition of the hydroxy group with the same catalyst precursor can be carried out in toluene. This reaction provides a novel catalytic access to optically active 1,3-dioxolan-4-ones in one step
directly from α-hydroxy acids and terminal alkynes.

4. Experimental details

4.1. Preparation of α-hydroxy enol esters

Ten mmol of α-hydroxy acid, 10 mmol of terminal alkyne and 0.05 mmol of catalyst precursor [{Ru(O_2-CH)$(CO)_2(PPh_3)$}$_2$] prepared according to [20], were stirred for 10 h at 100°C in 10 ml of tetrahydrofuran under dinitrogen. After evaporation of the solvent, enol esters **8–13** were isolated by distillation under reduced pressure or recrystallization.

4.2. Hex-1-en-2-yl (R)-mandelate (8)

From 1.52 g (10 mmol) of (*R*)-mandelic acid and 1.2 ml (10 mmol) of hex-1-yne, 1.28 g of a mixture containing 76% of the enol ester **8** (42%) was isolated as a colourless liquid after distillation under reduced pressure. ^{1}H NMR ($CDCl_3$ 300.133 MHz) δ: 0.78 (t, 3H, $^3J = 7.0$ Hz, Me); 1.17 (m, 4H, CH_2CH_2Me), 2.09 (t, 2H, $^3J = 7.0$ Hz, $=CCH_2$); 3.41 (d, 1H, $^3J = 4.0$ Hz, OH); 4.69 (d, 1H, $^2J = 1.8$ Hz, HC=C); 4.71 (m, 1H, HC=C); 5.24 (d, 1H, $^3J = 4.0$ Hz, C*H*OH), 7.30–7.46 (m, 5H, Ph). IR: 3450 (OH), 1750 (CO), 1660 (C=C) cm^{-1}.

4.3. Isopropenyl (R)-mandelate (9)

From 1.52 g (10 mmol) of (*R*)-mandelic acid and 20 mmol of propyne, 1.51 g (78%) of enol ester **9** was isolated as a white solid after distillation under reduced pressure. ^{1}H NMR (CD_2Cl_2) 80 MHz) δ: 1.76 (s, 3H, Me); 3.67 (m, 1H, OH); 4.58 (s, 2H, CH_2=C); 5.17 (s, 1H, C*H*OH); 7.32 (m, 5H, Ph). IR: 3420 (OH), 1750 (C=O), 1650 (C=C) cm^{-1}. $[\alpha]_D = -121°$ ($c = 1.05$ g l^{-1}, EtOH, 20°C).

4.4. α-Styryl (R)-mandelate (10)

From 1.52 g (10 mmol) of (*R*)-mandelic acid and 1.1 ml (10 mmol) of phenylacetylene, 1.90 g (75%) of enol mandelate **10** was isolated as white crystals after recrystallization from toluene. ^{1}H NMR (CD_2Cl_2, 80 MHz) δ: 3.34 (d, 1H, $^3J = 5.6$ Hz, O*H*); 4.97 (d, 1H, $^2J = 2.0$ Hz, CH=C); 5.29 (d, 1H, $^3J = 5.6$ Hz, C*H*OH); 5.42 (d, 1H, $^2J = 2.0$ Hz, CH=C); 7.17 (m, 5H, Ph); 7.43 (m, 5H, Ph). IR: 3460 (OH), 1745 (C=O), 1650 (C=C) cm^{-1}. $[\alpha]_D = -119°$ ($c = 1.00$ g l^{-1}, EtOH, 20°C).

4.5. 3-Methylbuta-1,3-dien-2-yl (R)-mandelate (11)

From 1.52 g (10 mmol) of (*R*)-mandelic acid and 0.95 ml (10 mmol) of isopropenylacetylene, 1.45 g (66%) of enol mandelate **11** was isolated as a white solid after recrystallization from a dichloromethane–ether–hexane mixture. ^{1}H NMR ($CDCl_3$ 300.133 MHz) δ: 1.84 (s, 3H, Me); 3.51 (s, 1H, OH); 4.51 (m, 1H, HC=C-Me); 4.78 (m, 1H, HC=C-Me); 4.84 (m, 1H, HC=C-O); 5.11 (d, 1H, ^2J = 2.2 Hz, HC=C-O); 5.34 (s, 1H, C*H*OH); 7.34–7.52 (m, 5H, Ph). IR: 3450 (OH), 1750 (CO), 1650 and 1600 (C=C) cm^{-1}. $[\alpha]_D = -121°$ (c = 1.00 g l^{-1}, EtOH, 20°C).

4.6. Hex-1-en-2-yl lactate (12)

From 0.75 ml of (*S*)-lactic acid and 1.2 ml (10 mmol) of hex-1-yne, 0.50 g (30%) of enol lactate **12** was isolated by distillation under reduced pressure. ^{1}H NMR ($CDCl_3$, 300.133 MHz) δ: 0.91 (t, 3H, ^3J = 7.2 Hz, Me); 1.43 (m, 4H, CH_2CH_2Me); 1.48 (d, 3H, ^3J = 6.9 Hz, MeCH); 2.23 (t, 2H, ^3J = 7.1 Hz, =CCH_2); 3.30 (m, 1H, OH); 4.38 (q, 1H, ^3J = 6.9 Hz, CHMe); 4.76 (s, 2H, CH_2=C). ^{13}C RMN, ($CDCl_3$, 75.469 MHz) δ: 13.6, 21.8, 22.3, 28.3, 32.7, 66.6, 101.1, 156.1, 173.7. IR: 3525 (OH), 1755 (C=O), 1670 (C=C) cm^{-1}.

4.7. α-Styryl lactate (13)

From 0.75 ml of (*S*)-lactic acid and 1.1 ml (10 mmol) of phenylacetylene, 0.37 g (20%) of enol lactate **13** was isolated after recrystallization from a dichloromethane–hexane mixture. ^{1}H NMR ($CDCl_3$, 300.133 MHz) δ: 1.59 (d, 3H, ^3J = 6.9 Hz, MeCH); 2.91 (m, 1H, OH); 4.52 (q, 1H, ^3J = 6.7 Hz, CHMe); 5.06 (d, 1H, ^2J = 2.5 Hz, C=CH); 5.50 (d, 1H, ^2J = 2.5 Hz, C=CH); 7.35 (m, 3H, Ph); 7.46 (m, 2H, Ph). ^{13}C RMN ($CDCl_3$, 75.469 MHz) δ: 20.4, 66.9, 102.4, 124.8, 128.6, 129.2, 133.7, 152.7, 176.0. IR: 3450 (OH), 1770 (C=O), 1645 (C=C) cm^{-1}.

4.8. Preparation of 1,3-dioxolan-4-ones

Ten mmol of α-hydroxy acid, 10 mmol of alkyne and 0.05 mmol of [{$Ru(O_2CH)(CO)_2(PPh_3)$}$_2$] prepared according to [20], were stirred for 20 h at 100°C in toluene under an inert atmosphere of nitrogen. After evaporation of the solvent, 1,3-dioxolan-4-ones **14–19** were isolated by distillation under reduced pressure or recrystallization.

4.9. 2-Butyl-2-methyl-5-phenyl-1,3-dioxolan-4-one (14) (cis / trans = 90 : 10)

From 1.52 g (10 mmol) of (*R*)-mandelic acid and 1.2 ml (10 mmol) of hex-1-yne, 2.09 g (89%) of dioxolanone **14** were isolated as a colourless liquid by distillation under reduced pressure. ^{1}H NMR (CD_2Cl_2, 300.133 MHz) δ: 0.95 (t, 3H, ^3J = 7.2 Hz, *Me*CH_2); 1.39 (quint., 2H, ^3J = 7.0 Hz, CH_2); 1.52 (m, 2H, CH_2); 1.62 (s, 3H, Me); 1.93 (t, 2H, ^3J = 7.6 Hz, MeCCH_2); 5.38 (s, 1H, CH); 7.40–7.50 (m, 5H, Ph); *trans* isomer 1.67 (s, 3H, Me); 5.24 (s, 1H, CH). ^{13}C NMR (CD_2Cl_2, 75.469 MHz) δ: 14.1, 23.1, 24.3, 25.8, 39.8, 76.1, 112.7, 127.4, 129.3, 129.4, 135.1, 171.9. IR: 1800 (C=O) cm^{-1}. $[\alpha]_D$ = −71° (c = 1.10 g l^{-1}, EtOH, 20°C).

4.10. 2,2-Dimethyl-5-phenyl-1,3-dioxolan-4-one (15)

From 1.52 g (10 mmol) of (*R*)-mandelic acid and 20 mmol of propyne, 1.35 g (75%) of dioxolanone **15** were isolated as a white solid after distillation. ^{1}H NMR (CD_2Cl_2, 300.133 MHz) δ: 1.66 (s, 3H, Me); 1.72 (s, 3H, Me); 5.39 (s, 1H, CH); 7.36–7.47 (m, 5H, Ph). ^{13}C NMR (CD_2Cl_2) 75.469 MHz) δ: 26.2, 27.4, 76.4, 111.4, 127.1, 129.1, 129.4, 135.2, 171.9. IR: 1800 (C=O) cm^{-1}.

4.11. 2-Methyl-2,5-diphenyl-1,3-dioxolan-4-one (16) (cis / trans = 75 : 25)

From 1.52 g (10 mmol) of (*R*)-mandelic acid and 1.1 ml (10 mmol) of phenylacetylene, 2.12 g (84%) of dioxolanone **16** were isolated as a colourless liquid by distillation under reduced pressure. ^{1}H NMR ($CDCl_3$, 300.133 MHz) δ: 1.97 (s, 3H, Me); 5.55 (s, 1H, CH); 7.30 (m, 2H, Ph); 7.47 (m, 6H, Ph); 7.56–7.60 (m, 2H, Ph); *trans* isomer 1.99 (s, 3H, Me), 5.05 (s, 1H, CH). IR: 1800 (C=O) cm^{-1}.

4.12. 2-Methyl-5-phenyl-2-(prop-1-en-2-yl)-1,3-dioxolan-4-one (17) (cis / trans = 95 : 5)

From 1.52 g (10 mmol) of (*R*)-mandelic acid and 0.95 ml (10 mmol) of isopropenylacetylene, 1.37 g (63%) of a mixture containing 83% of dioxolanone **17** (53%) was isolated as a colourless liquid after distillation under reduced pressure. ^{1}H NMR ($CDCl_3$, 300.133 MHz) δ: 1.75 (s, 3H, Me); 1.90 (dd, 3H, $^4J_{trans}$ = 1.5 Hz, $^4J_{cis}$ = 0.9 Hz, MeC=C); 5.05 (quint, 1H, $^2J = {}^4J$ = 1.5 Hz, HC=C); 5.35 (m, 1H, HC=C); 5.43 (s, 1H, C*H*OH); 7.34–7.50 (m, 5H, Ph); *trans* isomer 1.80 (s, 3H, Me). IR: 1795 (CO), 1600 (C=C) cm^{-1}.

4.13. 2-Butyl-2,5-dimethyl-1,3-dioxolan-4-one (18) (cis / trans = 90 : 10)

From 0.75 ml (10 mmol) of (*S*)-lactic acid and 1.2 ml (10 mmol) of hex-1-yne, 0.98 g (60%) of dioxolanone **18** was isolated as a colourless liquid by distillation under reduced pressure. ^{1}H NMR ($CDCl_3$, 300.133 MHz) δ: 0.85 (t, 3H, ^3J = 6.9 Hz, *Me*CH_2); 1.32 (m, 4H, CH_2CH_2Me); 1.39 (d, 3H, ^3J = 6.8 Hz, CHMe); 1.43 (s, 3H, Me); 1.74 (m, 2H, MeCCH_2); 4.42 (q, 1H, ^3J = 6.8 Hz, CHMe); *trans* isomer 1.49 (s, 3H, Me). ^{13}C NMR ($CDCl_3$, 75.469 MHz) δ: 13.9, 20.0, 22.5, 24.2, 24.9, 39.3, 70.1, 111.7, 173.9. IR: 1800 (C=O) cm^{-1}.

4.14. 2,5-Dimethyl-2-phenyl-1,3-dioxolan-4-one (19) (cis / trans = 90 : 10)

From 0.75 ml (10 mmol) of (*S*)-lactic acid and 1.1 ml (10 mmol) of phenylacetylene, 0.92 g (50%) of dioxolanone **19** was isolated as a colourless liquid after distillation under reduced pressure. ^{1}H NMR ($CDCl_3$, 300.133 MHz) δ: 1.38 (d, 3H, $^3J = 6.9$ Hz, Me-CH); 1.81 (s, 3H, Me); 4.64 (q, 1H, $^3J = 6.9$ Hz, CH); 7.25–7.53 (m, 5H, Ph); *trans* isomer 1.51 (d, 3H, $^3J = 6.9$ Hz, MeCH). ^{13}C NMR ($CDCl_3$, 75.469 MHz) δ: 16.4, 27.7, 72.5, 110.3, 125.01, 129.2, 133.2, 141.1, 173.6. IR: 1800 (C=O) cm^{-1}.

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