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A Novel Propargylation/Cycloisomerization Tandem Process Catalyzed by a Ruthenium(II)/Trifluoroacetic Acid System: One-Pot Entry to Fully Substituted Furans from Readily Available Secondary Propargylic Alcohols and 1,3-Dicarbonyl Compounds

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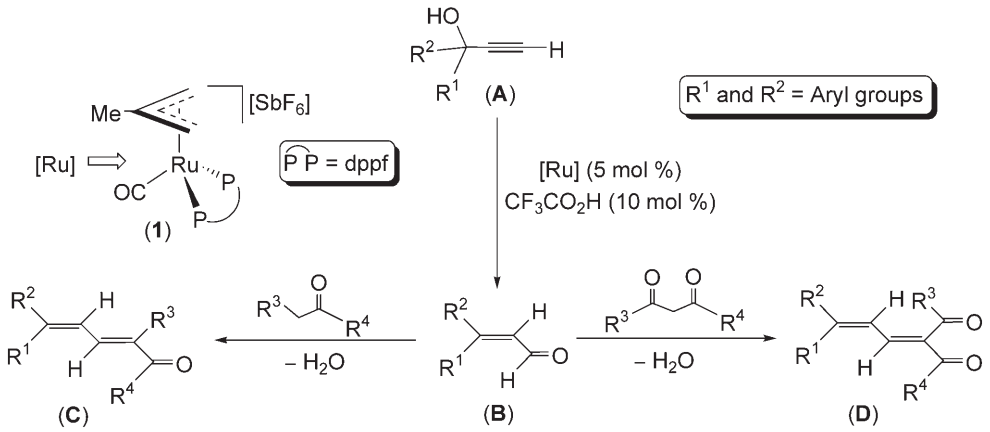
Abstract: A simple and highly efficient method for the preparation of tetrasubstituted furans starting from readily accessible propargylic alcohols and commercially available 1,3-dicarbonyl compounds has been developed. The process, which proceeds in a *one-pot* manner, involves the initial propargylation of the 1,3-dicarbonyl compound promoted by trifluoroacetic acid, and subsequent cycloisomerization of the resulting γ-ketoalkyne catalyzed by the 16-electron allyl-ruthenium(II) complex $[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)(CO)(dppf)][SbF_6]$.

Keywords: cycloisomerization; 1,3-dicarbonyl compounds; furans; propargylic alcohols; propargylic substitution reactions; ruthenium

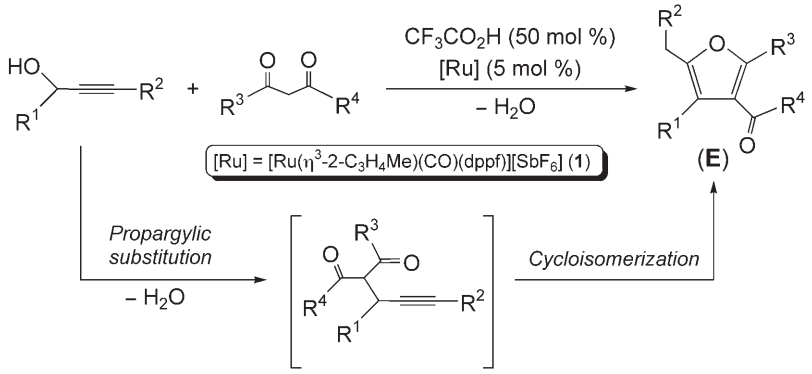
Introduction

In the course of our current studies directed to the application of ruthenium complexes as catalysts in organic synthesis,[1,2] we have recently reported the preparation, in excellent yields and with total *E*-stereoselectivity,[3] of conjugated dienones **C** and dienediones **D** *via* a tandem process involving the catalytic isomerization of diaryl-substituted terminal propargylic alcohols **A** into enals **B** (Meyer–Schuster-type rearrangement)[4] which further undergo aldol-type condensations with enolizable ketones or 1,3-dicarbonyl compounds (see Scheme 1).[5]

While extending these initial studies to the coupling of secondary alkynols with 1,3-dicarbonyl compounds we have now discovered that the corresponding dienones **D** are not formed, the reactions giving instead keto- or ester-functionalized furans **E** which are gen-



Scheme 1. Catalytic transformations of diaryl-substituted propargylic alcohols promoted by complex **1**.



Scheme 2. Synthesis of furans from propargylic alcohols and 1,3-dicarbonyl compounds.

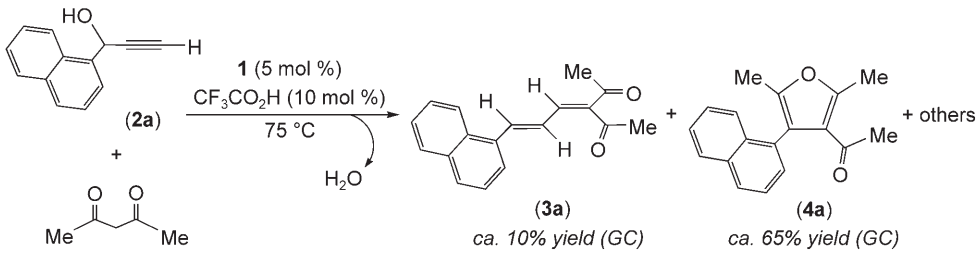
erated through an unexpected C–C coupling process (Scheme 2).[6]

The furan ring represents a key structural subunit in many natural and pharmaceutically important substances, being also found in the molecular skeleton of several flavor and fragrance compounds.[7] Furthermore, substituted furans are useful and versatile intermediates in synthetic organic chemistry.[7] As a consequence, much attention has been paid to the synthesis of furan derivatives in the last decades, the most innovative and efficient strategies involving transition metal-catalyzed heteroannulation reactions of suitable acyclic precursors such as (*Z*)-enynols, α-epoxyalkynes, β-ketoalkynes or α-ketoallenes, among others.[8] Nevertheless, by following these cycloisomerization-based methodologies, the construction of furan rings with the desired substitution pattern is sometimes a problematic task due to the difficult access to the corresponding functionalized starting materials.[8] Thereby, the development of novel synthetic routes allowing the facile assembly of polysubstituted furans from readily available and inexpensive precursors still remains an important objective for synthetic organic chemists. Herein, a novel and highly efficient catalytic method for the preparation of fully substituted furans, in which easily accessible secondary propargylic alcohols and commercially available 1,3-dicarbonyl compounds are used as starting materials, is reported. The process outlined in Scheme 2, which proceeds in a *one-pot* manner, involves two different steps based on: (*i*) an initial CF_3CO_2H-promoted propargylic substitution of the secondary alkynol by the 1,3-dicarbonyl compound, and (*ii*) subsequent ruthenium-catalyzed cyclosiomerization of the resulting γ-ketoalkyne.

Results and Discussion

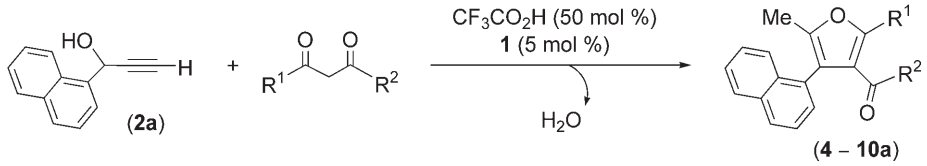
Access to Fully Substituted Furans from Secondary Propargylic Alcohols and 1,3-Dicarbonyl Compounds: Optimization of the Reaction Conditions and Scope

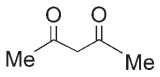
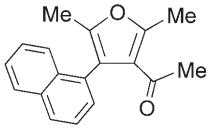
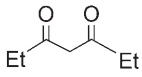
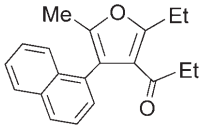
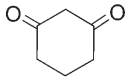
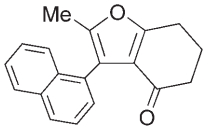
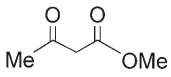
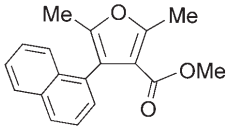
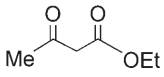
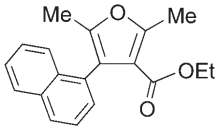
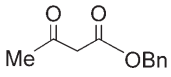
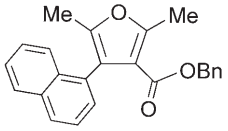
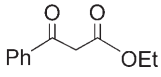
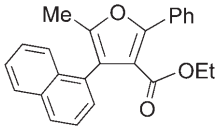
Following the optimal experimental conditions to promote the catalytic C–C coupling of diaryl-substituted propargylic alcohols **A** with 1,3-dicarbonyl compounds (Scheme 1) using the 16e$^-$ Ru(II) complex $[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)(CO)(dppf)][SbF_6]$ (**1**) {i.e., [**A**]:[1,3-dicarbonyl]:[CF_3CO_2H]:[**1**] ratio = 20:200:2:1; 75 °C; sealed tube; without solvent},[3] we have found that the secondary terminal propargylic alcohol 1-(1-naphthyl)-2-propyn-1-ol (**2a**) reacts with 2,4-pentanedione to afford, after 8 h, a mixture containing the expected diene-dione **3a** (*ca.* 10% yield; GC determined) and 2,5-dimethyl-3-acetyl-4-(1-naphthyl)furan (**4a**; *ca.* 65% yield; GC determined) along with minor amounts of other uncharacterized by-products (see Scheme 3).[9] The tetrasubtituted furan **4a** formally results from an intermolecular condensation between the propargylic alcohol **2a** and the 1,3-diketone through an unprecedented cycloaddition reaction.[10,11]



Scheme 3. The reaction of alkynol **2a** with 2,4-pentanedione catalyzed by **1**/CF_3CO_2H.

Table 1. Synthesis of furans **4–10a** from alkynol **2a** and 1,3-dicarbonyl compounds.[a]



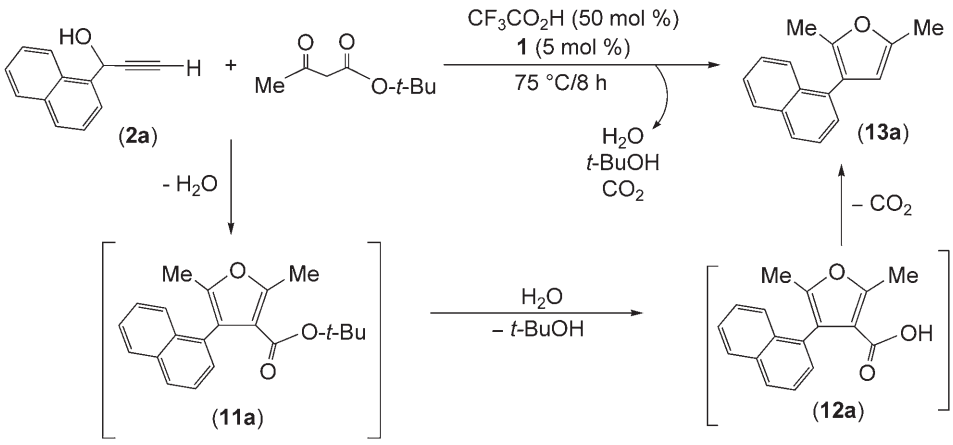
Entry	1,3-Dicarbonyl	Product		Time	Yield[b]
1			**4a**	4 h	81 %
2			**5a**	3 h	76 %
3			**6a**	3 h	79 %
4			**7a**	3 h	92 %
5			**8a**	4 h	93 %
6			**9a**	2 h	91 %
7			**10a**	22 h	62 %

[a] Reactions performed under N_2 atmosphere at 75 °C using 1 mmol of **2a** and 10 mmol of the corresponding 1,3-dicarbonyl compound. [**2a**]:[1,3-dicarbonyl]:[CF_3CO_2H]:[Ru] ratio = 20:200:10:1.

[b] Isolated yield.

By increasing the quantity of trifluoroacetic acid in the reaction media, both the selectivity and the rate of this cyclocondensation process could be easily improved. Thus, when 50 mol % of CF_3CO_2H was used, i.e., [**2a**]:[2,4-pentanedione]:[CF_3CO_2H]:[**1**] ratio = 20:200:10:1, furan **4a** was formed in > 92 % yield (GC determined) after 4 h, the presence of **3a** being in this case not detected by GC. This result indicates that the ability of complex **1** to perform the Meyer–Schuster isomerization of alkynols is completely inhibited under these reaction conditions.[4] The identity of furan **4a**, isolated in pure form in 81 % yield after chromatographic work-up (entry 1 in Table 1), was readily assigned by its MS, IR and NMR spectroscopic data (see the Experimental Section).

The generality of this transformation has been studied by using other 1,3-dicarbonyl compounds (see Table 1). Thus, under the optimized reaction conditions {[**2a**]:[1,3-dicarbonyl]:[CF_3CO_2H]:[**1**] ratio = 20:200:10:1}, other 1,3-diketones, such as 3,5-heptanedione (entry 2) or 1,3-cyclohexanedione (entry 3), as well as a variety of β-keto esters (entries 4–7) also reacted with alkynol **2a** to afford the corresponding furans **5–10a** (62–93 % isolated yields) regardless the



Scheme 4. Synthesis of the trisubstituted furan **13a**.

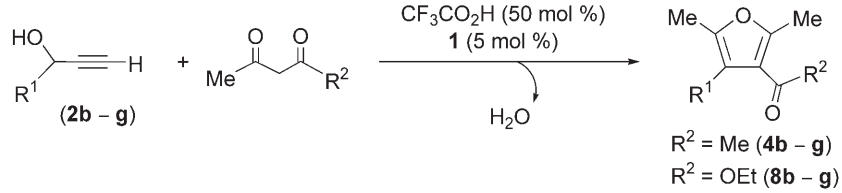
presence of aliphatic (entries 1–5) or aromatic (entries 6 and 7) substituents. Remarkably, when β-keto esters are used as substrates (entries 4–7) the reactions proceed in all cases in a regioselective manner since only the keto group participates in the cyclization process, the ester function behaving as a simple spectator. It should be also noted that, although the starting propargylic alcohol **2a** is completely consumed, no furan formation was observed in the reaction **2a** with dimethyl malonate [$CH_2(CO_2Me)$], the precipitation of a highly insoluble material being in this case observed. This result suggests that the presence of at least one keto function is indispensable to promote this coupling process. The characterization of compounds **5–10a** was achieved by means of standard spectroscopic techniques (MS, IR as well as ^1H and $^{13}C\{^1H\}$ NMR) and, in the case of solid samples, by elemental analyses, all data being fully consistent with the proposed formulations (see the Experimental Section).

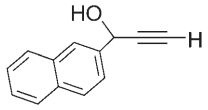
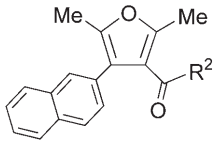
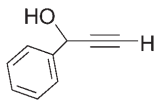
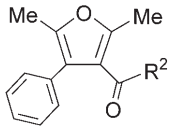
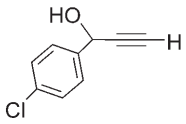
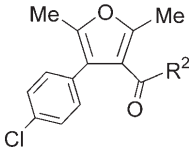
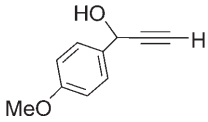
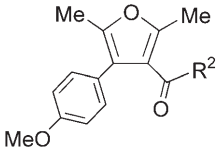
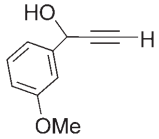
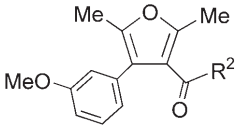
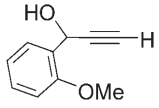
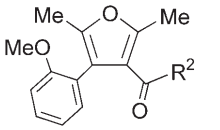
The high-yield formation of furans **4–10a** demonstrates the wide scope of this cycloaddition process. Nevertheless, it should be noted that a disappointing result was encountered in the reaction of **2a** with the β-keto ester *tert*-butyl acetoacetate. Thus, under the standard reaction conditions, the trisubstituted furan **13a**, instead of the expected tetrasubstituted one **11a**, is obtained (79% yield after 8 h; see Scheme 4). Apparently, furan **11a** is initially formed[12] but the hydrolysis of the *tert*-butyl ester (Boc) function (probably mediated by CF_3CO_2H)[13] leads to carboxylic acid **12a** which undergoes a ruthenium-catalyzed decarboxylation to give **13a**.[14,15] Although in both individual steps well-known reactions are involved, the overall **11a**→**13a** transformation can be considered as rather unusual.[16]

We have also found that this cyclization reaction can be successfully applied to other aryl-monosubstituted alkynols, independent of the substitution pattern and electronic properties of the aromatic ring. Thus, as shown in Table 2, terminal propargylic alcohols **2b–g** readily and cleanly react with 2,4-pentanedione or ethyl acetoacetate to afford in good yields (66–94%), after only 2–5 h, the tetrasubstituted furans **4b–g** (odd entries) and **8b–g** (even entries), respectively. In contrast, starting from alkyl-monosubstituted alkynols such as 1-octyn-3-ol or 3-butyn-2-ol, mixtures containing the expected tetrasubstituted furans, albeit in very low yields (15–28% yield; GC determined), are obtained. The major formation of several uncharacterized by-products prevented the isolation of the furans.

Interestingly, internal aryl-monosubstituted alkynols can also participate in this cycloaddition process. Nevertheless, the furan ring formation requires in these cases longer reaction times. As an example, treatment of 1-phenyl-3-butyn-1-ol (**2h**) with ethyl acetoacetate in the presence of CF_3CO_2H/**1** generates the tetrasubstituted furan **15h** in only a moderate yield (43%) after 72 h at 75 °C (see Scheme 5). Remarkably, the GC/MS monitoring of this reaction showed after 3 h the almost quantitative formation of an intermediate species which could be isolated in 93% yield after chromatographic work-up. Spectroscopic IR, MS and NMR (^1H and $^{13}C\{^1H\}$) data allowed the identification of this intermediate as the γ-ketoalkyne **14h** (details are given in the Experimental Section), resulting from a formal propargylic substitution process of the alkynol **2h** by the β-keto ester. Since this C–C coupling process involves the formation of two stereogenic centers, compound **14h** is formed as a *ca.* 1.2:1 mixture of two non-separable diastereoisomers. Under the standard reaction conditions, both isomers slowly and cleanly evolve into the final furan **15h** without detection of any other intermediate species.

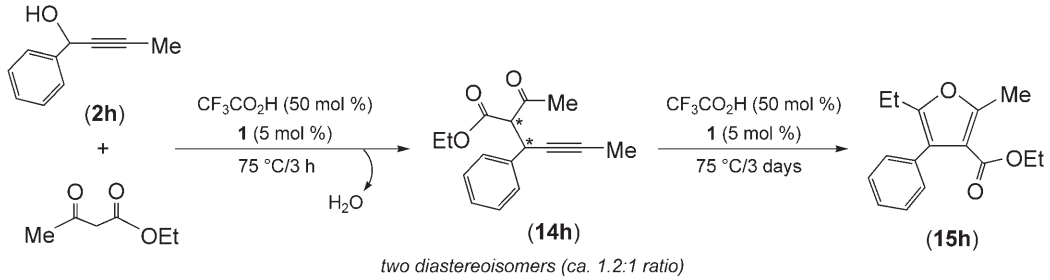
Table 2. Synthesis of furans **4b–g** and **8b–g** from propargylic alcohols **2b–g** and 1,3-dicarbonyl compounds.[a]



Entry	Alkynol		Product		Time	Yield[b]
1		**2b**		R^2 = Me **4b**	4 h	80 %
2				R^2 = OEt **8b**	3 h	87 %
3		**2c**		R^2 = Me **4c**	5 h	83 %
4				R^2 = OEt **8c**	4 h	86 %
5		**2d**		R^2 = Me **4d**	5 h	66 %
6				R^2 = OEt **8d**	4 h	80 %
7		**2e**		R^2 = Me **4e**	5 h	86 %
8				R^2 = OEt **8e**	4 h	94 %
9		**2f**		R^2 = Me **4f**	5 h	73 %
10				R^2 = OEt **8f**	5 h	85 %
11		**2g**		R^2 = Me **4g**	3 h	90 %
12				R^2 = OEt **8g**	2 h	94 %

[a] Reactions performed under N_2 atmosphere at 75 °C using 1 mmol of the corresponding propargylic alcohol **2** and 10 mmol of the appropriate 1,3-dicarbonyl compound. [**2**]:[1,3-dicarbonyl]:[CF_3CO_2H]:[Ru] ratio = 20:200:10:1.

[b] Isolated yield.

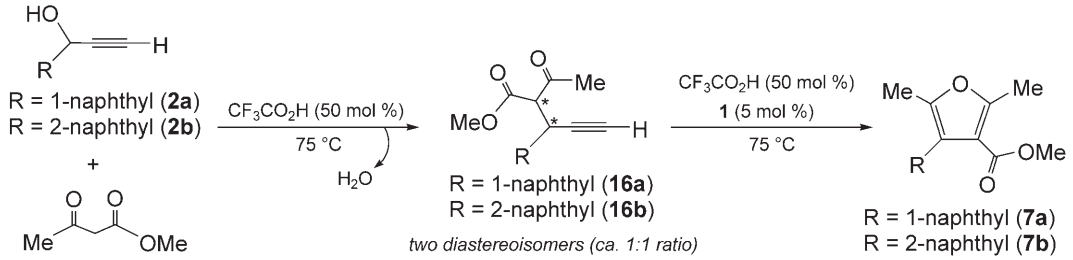


Scheme 5. Coupling of the internal propargylic alcohol **2h** with ethyl acetoacetate.

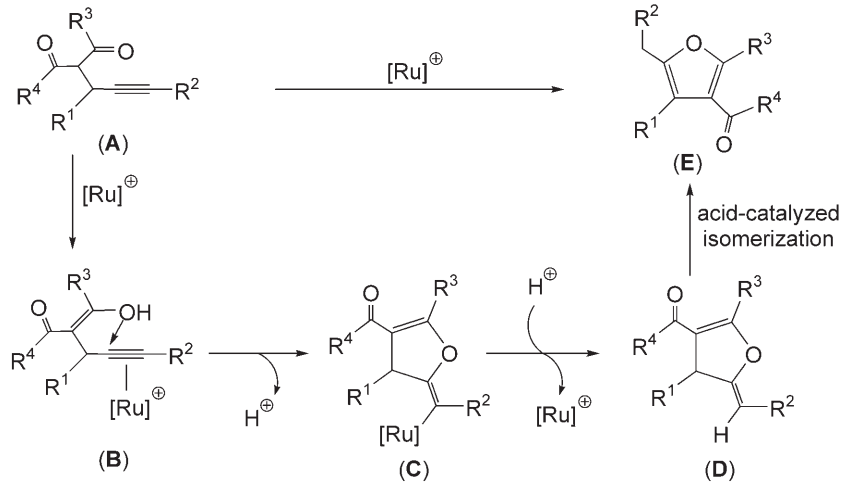
Mechanistic Proposal for the Cycloaddition Reaction of Propargylic Alcohols with 1,3-Dicarbonyl Compounds

It is well-established that a series of transition-metal complexes are able to catalyze substitution reactions of alkynols.[17] In particular, allenylidene-ruthenium(II) species formed from terminal alkynol substrates are prone to catalyze propargylic substitutions using a wide variety of carbon- and heteroatom-centered nucleophiles.[17a] The results shown in Scheme 5, along with a recent report showing the catalytic activity of Brønsted acids when internal propargylic alcohols are used,[18] raises the question whether complex **1** is the actual catalytic species of the initial propargylation process.[19] To this regard, the reactivity of alkynols **2a,b** towards methyl acetoacetate using only CF_3CO_2H (50 mol%) in the absence of complex **1** was studied (Scheme 6). The reaction affords the corresponding γ-ketoalkynes **16a** and **16b** which are selectively formed after 1.5 or 4 h, respectively.[20] Chromatographic work-up allowed the isolation (81–90%) and spectroscopic characterization of these functionalized alkynes (see the Experimental Section), which are generated in both cases as a non-separable mixture of two diastereoisomers in ca. 1:1 ratio. Remarkably, in the absence of ruthenium, γ-ketoalkynes **16a, b** are stable and do not evolve into the final furans **7a,b** even when heated at 75 °C for 24 h in the presence of CF_3CO_2H (50 mol%), the formation of **7a,b** being only observed when complex **1** was added to the reaction media. This fact strongly suggests that the generation of the furan ring is the result of a ruthenium-catalyzed cycloisomerization of the intermediate γ-ketoalkyne. As far as we are aware, this is the first ruthenium-catalyzed cycloisomerization of γ-ketoalkynes to afford furans reported to date.[21,22]

In accordance with these particular features, a mechanistic proposal accounting for the catalytic cycloisomerization of γ-ketoalkynes **A** into furans **E** is shown in Scheme 7. We assume that the initial step involves the activation of the C≡C triple bond of the alkyne, *via* coordination to the metal, to give the π-alkyne ruthenium intermediate **B**. Subsequent intramolecular nucleophilic attack of the enolic form of the keto group at the C_2 position of the coordinated alkyne (*endo* addition) generates the alkenyl-ruthenium derivative **C**, which after protonolysis liberates the heterocycle **D** regenerating the catalytically active ruthenium species. Final acid-promoted aromatization of the five-membered ring of **D** leads to the tetrasubstituted furan **E**. We note that, although it is well-



Scheme 6. Formation and cycloisomerization of γ-ketoalkynes **16a,b**.



Scheme 7. Reaction pathway for the Ru-catalyzed cycloisomerization reaction.

known that terminal π-alkyne ruthenium complexes [$L_nRu(\eta^2$-HC≡CR)] show a great tendency to tautomerize into η^1-vinylidene species [L_nRu{=C=C(H)R}],[23] such an isomerization reaction seems to be completely inhibited when terminal alkynols **2a–g** are used as substrates since cyclization of the corresponding intermediates should give rise to the formation of six-membered pyranic rings (*exo* addition).[10]

Conclusions

In this work a novel and highly efficient catalytic approach of tetrasubstituted furans has been developed using as starting materials readily accessible secondary aryl-substituted propargylic alcohols and an excess (10 equivalents) of commercially available 1,3-dicarbonyl compounds. The process, which takes place in a *one-pot* manner and under *solvent-free* conditions (the 1,3-dicarbonyl compound itself acts as solvent), is shown to proceed through two different steps involving: (*i*) an initial CF_3CO_2H-promoted propargylic substitution of the secondary alkynol by the 1,3-dicarbonyl compound, leading to an intermediate γ-ketoalkyne, and (*ii*) a subsequent ruthenium-catalyzed cycloisomerization reaction to give the final tetrasubstituted furans.[24] This unprecedented cyclization reaction is quite general being applicable both to terminal and internal monosubstituted alkynols, as well as to a variety of β-dicarbonyl compounds.

At present, the most innovative and efficient synthetic approaches of substituted furans involve transition metal-catalyzed heteroannulation reactions of acyclic precursors such as (*Z*)-enynols, α-epoxyalkynes, β-ketoalkynes or α-ketoallenes, among others.[8] Nevertheless, a major drawback of these methodologies is the difficult access of suitable precursors containing preloaded functional groups at the desired positions. The methodology herein described, which allows the introduction of carbonyl functionalities in the furanic skeleton, represents a very competitive and more desirable synthetic approach since it stems from readily available and inexpensive precursors.

In summary, selectivity, time/cost saving and experimental simplicity, concepts to be assembled by modern academic and industrial synthetic chemists to reach the maximum of efficiency, are clearly represented in this *one-pot* catalytic transformation making it appealing for a wide range of synthetic organic chemists.

Experimental Section

All reagents were obtained from commercial suppliers and used without further purification with the exception of complex [$Ru(\eta^3$-2-$C_3H_4Me)(CO)(dppf)][SbF_6$] (**1**),[4a] the terminal propargylic alcohols **2a**, **b**, **d–g**[25] and the internal one **2h**[26] which were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin–Elmer 1720-XFT spectrometer. Elemental C and H analyses were carried out with a Perkin–Elmer 2400 microanalyzer. NMR spectra were recorded on a Bruker DPX-300 instrument at 300 MHz (^{1}H), or 75.4 MHz (^{13}C) or a Bruker AC-400 instrument at 400.1 MHz (^{1}H), or 100.6 MHz (^{13}C). Chemical shifts are referred to the residual peak of the deuterated solvent used ($CDCl_3$). DEPT experiments have been carried out for all the compounds reported. Gas chromatographic (GC) measurements were made on a Hewlett–Packard HP6890 equipment using a HP-INNOWAX cross-linked polyethyleneglycol (30 m, 250 μm) or a Supelco Beta-Dex™ 120 (30 m, 250 μm) column. GC/MS measurements were performed on a Agilent 6890N equipment coupled to a 5973 mass detector (70 eV electron impact ionization) using a HP-1 MS column. High-resolution mass spectra were recorded on a Finnigan-Mat 95 spectrometer.

General Procedure for the Synthesis of Furans 4–13

Complex [$Ru(\eta^3$-2-$C_3H_4Me)(CO)(dppf)][SbF_6$] (**1**) (0.049 g, 0.05 mmol), the corresponding propargylic alcohol **2a–g** (1 mmol), the appropriate 1,3-dicarbonyl compound (10 mmol) and CF_3CO_2H (37 μL, 0.5 mmol) were introduced into a sealed tube under nitrogen atmosphere. The reaction mixture was then heated at 75 °C for the indicated time (see Table 1, Table 2 and Scheme 4; the course of the reaction was monitored by regular sampling and analysis by GC or GC/MS). After removal of volatiles under vacuum, the residue was purified by column chromatography (silica gel) using a mixture EtOAc/hexane (1:50) as eluent.

The following furans obtained in this paper are known compounds: 2,5-dimethyl-3-acetyl-4-phenylfuran (**4c**),[27] 2,5-dimethyl-3-acetyl-4-(4-methoxyphenyl)furan (**4e**),[28] 2,5-dimethyl-3-acetyl-4-(2-methoxyphenyl)furan (**4g**)[29] and 2,5-dimethyl-4-phenylfuran-3-carboxylic acid ethyl ester (**8c**).[29]

Analytical and spectroscopic data for the new compounds are as follows:

2,5-Dimethyl-3-acetyl-4-(1-naphthyl)furan (4a): Colourless oil; yield: 0.214 g (81%); IR (Nujol): ν = 1564 (s, C=C), 1668 cm^{-1} (s, C=O); ^{1}H NMR ($CDCl_3$): δ = 1.65 (s, 3H, $COCH_3$), 2.09 and 2.68 (s, 3H each, CH_3), 7.41–7.58 (m, 4H, $C_{10}H_7$), 7.72 (m, 1H, $C_{10}H_7$), 7.90–7.94 (m, 2H, $C_{10}H_7$); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 11.6 and 14.5 (s, CH_3), 29.8 (s, $COCH_3$), 118.4 and 123.5 (s, =C), 125.4, 125.5, 126.0, 126.5, 128.2, 128.3 and 128.4 (s, CH of $C_{10}H_7$), 131.4, 133.0 and 133.6 (s, C of $C_{10}H_7$), 147.7 and 157.0 (s, =C-O), 195.8 (s, C=O); MS (EI 70 eV): *m/z* = 264 (100%) [M^+], 249 (92%) [M^+–Me], 221 (12%) [M^+–COMe], 178 (22%) [$C_{10}H_7CCCO$], 152 (10%) [$C_{10}H_7CC$]; HR-MS: *m/z* = 264.11418, calcd. for $C_{18}H_{16}O_2$: 264.11448.

2,5-Dimethyl-3-acetyl-4-(2-naphthyl)furan (4b): Yellow solid; yield: 0.211 g (80%); IR (Nujol): ν = 1564 and 1597 (m, C=C), 1681 cm^{-1} (s, C=O); ^{1}H NMR ($CDCl_3$): δ = 1.96 (s, 3H, $COCH_3$), 2.22 and 2.60 (s, 3H each, CH_3), 7.37 (d, *J* = 8.5 Hz, 1H, $C_{10}H_7$), 7.51 (m, 2H, $C_{10}H_7$), 7.74 (br, 1H, $C_{10}H_7$), 7.84–7.90 (m, 3H, $C_{10}H_7$); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 11.6 and 14.3 (s, CH_3), 30.8 (s, $COCH_3$), 120.8 and 123.1

(s, =C), 126.1, 126.3, 127.7, 127.8, 128.0, (2 C) and 128.4 (s, CH of $C_{10}H_7$), 131.2, 132.5 and 133.3 (s, C of $C_{10}H_7$), 147.3 and 156.3 (s, =C-O), 196.1 (s, C=O); MS (EI 70 eV): *m/z* = 264 (100%) [M^+], 249 (87%) [M^+−Me], 221 (17%) [M^+−COMe], 193 (7%) [M^+−2Me−COMe], 178 (30%) [$C_{10}H_7CCCO$], 152 (10%) [$C_{10}H_7CC$]; anal. calcd. for $C_{18}H_{16}O_2$: C 81.79, H 6.10%; found: C 82.13, H 6.25%.

2,5-Dimethyl-3-acetyl-4-(4-chlorophenyl)furan (4d): Yellow oil; yield: 0.164 g (66%); IR (Nujol): ν = 1568 (s, C=C), 1674 cm^{-1} (s, C=O); ^1H NMR ($CDCl_3$): δ = 2.00 (s, 3H, $COCH_3$), 2.17 and 2.55 (s, 3H each, CH_3), 7.20 and 7.40 (m, 2H each, C_6H_4Cl); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.5 and 14.3 (s, CH_3), 30.7 (s, CO*C*H_3), 119.7 and 122.8 (s, =C), 128.6 and 131.1 (s, CH of C_6H_4Cl), 132.2 and 133.3 (s, C of C_6H_4Cl), 147.1 and 156.3 (s, =C-O), 195.4 (s, C=O); MS (EI 70 eV): *m/z* = 248 (85%) [M^+], 233 (100%) [M^+−Me], 213 (1%) [M^+−Cl], 205 (20%) [M^+−COMe], 191 (2%) [M^+−Me−COMe], 177 (5%) [M^+−2Me−COMe], 162 (8%) [$C_6H_4ClCCCO$], 141 (5%) [M^+−2Me−COMe−Cl]; HR-MS: *m/z* = 248.05943, calcd. for $C_{14}H_{13}O_2Cl$: 248.05985.

2,5-Dimethyl-3-acetyl-4-(3-methoxyphenyl)furan (4f): Colourless oil; yield: 0.178 g (73%); IR (Nujol): ν = 1575 and 1598 (m, C=C), 1674 cm^{-1} (s, C=O); ^1H NMR ($CDCl_3$): δ = 1.95 (s, 3H, $COCH_3$), 2.16 and 2.51 (s, 3H each, CH_3), 3.81 (s, 3H, OCH_3), 6.77–6.89 (m, 3H, C_6H_4OMe), 7.31 (m, 1H, C_6H_4OMe); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.6 and 14.2 (s, CH_3), 30.6 (s, CO*C*H_3), 55.2 (s, OCH_3), 112.7, 115.6, 122.4 and 129.5 (s, CH of C_6H_4OMe), 120.7 and 123.0 (s, =C), 135.1 (s, C of C_6H_4OMe), 147.0, 156.1 and 159.5 (s, =C-O and C of C_6H_4OMe), 196.2 (s, C=O); MS (EI 70 eV): *m/z* = 244 (95%) [M^+], 229 (100%) [M^+−Me], 201 (20%) [M^+−COMe], 187 (7%) [M^+−Me−COMe], 171 (10%) [M^+−2Me−COMe], 159 (12%) [C_6H_4OMeCCCO]; HR-MS: *m/z* = 244.10911, calcd. for $C_{15}H_{16}O_3$: 244.10939.

2-Ethyl-3-ethylcarbonyl-5-methyl-4-(1-naphthyl)furan (5a): Colourless oil; yield: 0.222 g (76%); IR (Nujol): ν = 1557 (s, C=C), 1673 cm^{-1} (s, C=O); ^1H NMR ($CDCl_3$): δ = 0.72 (t, *J* = 7.3 Hz, 3H, $COCH_2CH_3$), 1.38 (t, *J* = 7.6 Hz, 3H, CH_2CH_3), 1.79 and 2.01 (m, 1H each, CH_2CH_3), 2.09 (s, 3H, CH_3), 3.09 (m, 2H, $COCH_2CH_3$), 7.41–7.58 (m, 4H, $C_{10}H_7$), 7.72 (m, 1H, $C_{10}H_7$), 7.90–7.95 (m, 2H, $C_{10}H_7$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 7.7, 11.7 and 12.3 (s, CH_3), 21.8 (s, CH_2), 34.8 (s, $COCH_2$), 118.0 and 122.5 (s, =C), 125.4, 125.6, 126.0, 126.5, 128.1, 128.2 and 128.3 (s, CH of $C_{10}H_7$), 131.6, 132.9 and 133.6 (s, C of $C_{10}H_7$), 147.7 and 161.5 (s, =C-O), 199.0 (s, C=O); MS (EI 70 eV): *m/z* = 292 (60%) [M^+], 277 (2%) [M^+−Me], 263 (100%) [M^+−Et], 248 (22%) [M^+−Me−Et], 233 (2%) [M^+−2Et], 219 (7%) [M^+−Me−COEt], 205 (10%) [M^+−Et−COEt], 190 (9%) [M^+−Me−Et−COEt], 179 (5%) [$C_{10}H_7CCCO$], 152 (2%) [$C_{10}H_7CC$]; HR-MS: *m/z* = 292.14574, calcd. for $C_{20}H_{20}O_2$: 292.14578.

2-Methyl-3-(1-naphthyl)-6,7-dihydro-5*H*-benzofuran-4-one (6a): Colourless oil; yield: 0.218 g (79%); IR (Nujol): ν = 1577 (s, C=C), 1681 cm^{-1} (s, C=O); ^1H NMR ($CDCl_3$): δ = 2.20 (s, 3H, CH_3), 2.25, 2.53 and 2.99 (m, 2H each, CH_2), 7.43–7.58 (m, 4H, $C_{10}H_7$), 7.71 (d, *J* = 7.9 Hz, 1H, $C_{10}H_7$), 7.91–7.95 (m, 2H, $C_{10}H_7$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.8 (s, CH_3), 22.5, 23.6 and 38.1 (s, CH_2), 116.7 and 121.3 (s, =C), 125.2, 125.6, 125.8, 125.9, 128.0, 128.1 and 128.3 (s, CH of $C_{10}H_7$), 129.6, 132.4 and 133.6 (s, C of $C_{10}H_7$), 150.0 and 166.4 (s, =C-O), 194.8 (s, C=O); MS (EI 70 eV): *m/z* = 276 (100%) [M^+], 261 (5%) [M^+−Me], 248 (36%) [M^+−2CH_2], 233 (7%) [M^+−Me−2CH_2], 205 (30%) [M^+−$CH_2CH_2CH_2CO$], 152 (7%) [$C_{10}H_7CC$]; HR-MS: *m/z* = 276.11445, calcd. for $C_{19}H_{16}O_2$: 276.11448.

2,5-Dimethyl-4-(1-naphthyl)furan-3-carboxylic acid methyl ester (7a): White solid; yield: 0.258 g (92%); IR (Nujol): ν = 1593 (s, C=C), 1720 cm^{-1} (s, C=O); ^1H NMR ($CDCl_3$): δ = 2.13 and 2.71 (s, 3H each, CH_3), 3.42 (s, 3H, OCH_3), 7.37–7.56 (m, 4H, $C_{10}H_7$), 7.71 (d, *J* = 8.2 Hz, 1H, $C_{10}H_7$), 7.87–7.93 (m, 2H, $C_{10}H_7$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.7 and 14.1 (s, CH_3), 50.8 (s, OCH_3), 114.6 and 119.1 (s, =C), 125.1, 125.5, 125.7, 125.8, 127.7 (2C) and 128.1 (s, CH of $C_{10}H_7$), 131.2, 132.9 and 133.4 (s, C of $C_{10}H_7$), 148.0 and 157.7 (s, =C-O), 164.6 (s, C=O); MS (EI 70 eV): *m/z* = 280 (100%) [M^+], 265 (1%) [M^+−Me], 248 (46%) [M^+−OMe], 233 (9%) [M^+−Me−OMe], 220 (25%) [M^+−CO_2Me], 205 (29%) [M^+−Me−CO_2Me], 191 (7%) [M^+−2Me−CO_2Me], 178 (22%) [$C_{10}H_7CCCO$], 152 (7%) [$C_{10}H_7CC$]; anal. calcd. for $C_{18}H_{16}O_3$: C 77.12, H 5.75%; found: C 76.99, H 5.83%.

2,5-Dimethyl-4-(2-naphthyl)furan-3-carboxylic acid methyl ester (7b): Reaction time: 4 h; yellow oil; yield: 0.246 g (88%); IR (Nujol): ν = 1584 and 1597 (m, C=C), 1717 cm^{-1} (s, C=O); ^1H NMR ($CDCl_3$): δ = 2.29 and 2.65 (s, 3H each, CH_3), 3.67 (s, 3H, OCH_3), 7.42–7.53 (m, 3H, $C_{10}H_7$), 7.73 (br, 1H, $C_{10}H_7$), 7.86–7.91 (m, 3H, $C_{10}H_7$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.8 and 14.1 (s, CH_3), 50.9 (s, OCH_3), 113.3 and 121.3 (s, =C), 125.7, 125.8, 126.9, 127.6, 127.8, 128.2 and 128.6 (s, CH of $C_{10}H_7$), 130.8, 132.3 and 133.1 (s, C of $C_{10}H_7$), 147.5 and 157.7 (s, =C-O), 164.7 (s, C=O); MS (EI 70 eV): *m/z* = 280 (100%) [M^+], 265 (2%) [M^+−Me], 248 (51%) [M^+−OMe], 233 (5%) [M^+−Me−OMe], 220 (22%) [M^+−CO_2Me], 205 (20%) [M^+−Me−CO_2Me], 191 (5%) [M^+−2Me−CO_2Me], 178 (26%) [$C_{10}H_7CCCO$], 152 (10%) [$C_{10}H_7CC$]; HR-MS: *m/z* = 280.10956, calcd. for $C_{18}H_{16}O_3$: 280.10939.

2,5-Dimethyl-4-(1-naphthyl)furan-3-carboxylic acid ethyl ester (8a): Yellow oil; yield: 0.274 g (93%); IR (Nujol): ν = 1595 (s, C=C), 1708 cm^{-1} (s, C=O); ^1H NMR ($CDCl_3$): δ = 0.57 (t, *J* = 7.1 Hz, 3H, CH_2CH_3), 2.17 and 2.73 (s, 3H each, CH_3), 3.85 (m, 2H, CH_2CH_3), 7.37–7.56 (m, 4H, $C_{10}H_7$), 7.73 (m, 1H, $C_{10}H_7$), 7.87–7.93 (m, 2H, $C_{10}H_7$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.7, 13.1 and 13.9 (s, CH_3), 59.3 (s, CH_2), 114.9 and 119.1 (s, =C), 125.1, 125.5, 125.6, 126.0, 127.6 (2C) and 128.0 (s, CH of $C_{10}H_7$), 131.6, 133.2 and 133.4 (s, C of $C_{10}H_7$), 147.8 and 157.7 (s, =C-O), 164.2 (s, C=O); MS (EI 70 eV): *m/z* = 294 (100%) [M^+], 279 (1%) [M^+−Me], 265 (17%) [M^+−Et], 248 (47%) [M^+−OEt], 233 (7%) [M^+−Me−OEt], 220 (20%) [M^+−CO_2Et], 205 (20%) [M^+−Me−CO_2Et], 191 (7%) [M^+−2Me−CO_2Et], 178 (22%) [$C_{10}H_7CCCO$], 152 (10%) [$C_{10}H_7CC$]; HR-MS: *m/z* = 294.12509, calcd. for $C_{19}H_{18}O_3$: 294.12504.

2,5-Dimethyl-4-(2-naphthyl)furan-3-carboxylic acid ethyl ester (8b): Yellow oil; yield: 0.256 g (87%); IR (Nujol): ν = 1582 and 1601 (m, C=C), 1710 cm^{-1} (s, C=O); ^1H NMR ($CDCl_3$): δ = 1.09 (t, *J* = 7.1 Hz, 3H, CH_2CH_3), 2.29 and 2.66 (s, 3H each, CH_3), 4.15 (q, *J* = 7.1 Hz, 2H, CH_2CH_3), 7.44–7.55 (m, 3H, $C_{10}H_7$), 7.74 (br, 1H, $C_{10}H_7$), 7.86–7.91 (m, 3H, $C_{10}H_7$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 11.8, 13.9 and 14.1 (s, CH_3), 59.8 (s, CH_2), 113.6 and 121.3 (s, =C), 125.7, 125.8, 126.8, 127.6, 127.8, 128.3 and 128.8 (s, CH of $C_{10}H_7$), 130.9, 132.3 and 133.1 (s, C of $C_{10}H_7$), 147.4 and 157.6 (s, =C-O), 164.3 (s, C=O); MS (EI 70 eV): *m/z* = 294 (100%) [M^+], 279 (2%) [M^+−Me], 265 (25%) [M^+−Et], 248 (58%)

[M^+−OEt], 233 (5%) [M^+−Me−OEt], 220 (15%) [M^+−CO_2Et], 205 (15%) [M^+−Me−CO_2Et], 191 (5%) [M^+−2Me−CO_2Et], 178 (25%) [$C_{10}H_7CCCO$], 152 (10%) [$C_{10}H_7CC$]; HR-MS: m/z = 294.12498, calcd. for $C_{19}H_{18}O_3$: 294.12504.

2,5-Dimethyl-4-(4-chlorophenyl)furan-3-carboxylic acid ethyl ester (8d): Yellow oil; yield: 0.223 g (80%); IR (Nujol): ν = 1584 and 1599 (m, C=C), 1712 cm^{-1} (s, C=O); ^{1}H NMR ($CDCl_3$): δ = 1.16 (t, J = 7.3 Hz, 3H, CH_2CH_3), 2.20 and 2.60 (s, 3H each, CH_3), 4.16 (q, J = 7.3 Hz, 2H, CH_2CH_3), 7.21 and 7.36 (m, 2H each, C_6H_4Cl); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 11.6, 13.9 and 14.0 (s, CH_3), 59.8 (s, CH_2), 113.2 and 120.3 (s, =C), 127.8 and 131.3 (s, CH of C_6H_4Cl), 131.7 and 132.7 (s, C of C_6H_4Cl), 147.2 and 157.6 (s, =C-O), 164.1 (s, C=O); MS (EI 70 eV): m/z = 278 (100%) [M^+], 263 (1%) [M^+−Me], 249 (95%) [M^+−Et], 233 (37%) [M^+−OEt], 214 (2%) [M^+−Et−Cl], 204 (7%) [M^+−CO_2Et], 189 (5%) [M^+−Me−CO_2Et], 162 (8%) [$C_6H_4ClCCCO$], 141 (5%) [M^+−2Me−CO_2Et−Cl]; HR-MS: m/z = 278.07052, calcd. for $C_{15}H_{15}O_3Cl$: 278.07042.

2,5-Dimethyl-4-(4-methoxyphenyl)furan-3-carboxylic acid ethyl ester (8e): Yellow solid; yield: 0.258 g (94%); IR (Nujol): ν = 1584 and 1606 (m, C=C), 1709 cm^{-1} (s, C=O); ^{1}H NMR ($CDCl_3$): δ = 1.17 (t, J = 7.1 Hz, 3H, CH_2CH_3), 2.21 and 2.60 (s, 3H each, CH_3), 3.85 (s, 3H, OCH_3), 4.17 (q, J = 7.1 Hz, 2H, CH_2CH_3), 6.94 and 7.21 (m, 2H each, C_6H_4OMe); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 11.6, 14.0 and 14.1 (s, CH_3), 55.1 (s, OCH_3), 59.6 (s, CH_2), 113.0 and 131.1 (s, CH of C_6H_4OMe), 113.5 and 120.9 (s, =C), 125.4 (s, C of C_6H_4OMe), 146.9, 157.2 and 158.5 (s, =C-O and C of C_6H_4OMe), 164.3 (s, C=O); MS (EI 70 eV): m/z = 274 (100%) [M^+], 259 (1%) [M^+−Me], 245 (34%) [M^+−Et], 227 (41%) [M^+−Me−OMe], 213 (2%) [M^+−Et−OMe], 200 (12%) [M^+−CO_2Et], 185 (7%) [M^+−Me−CO_2Et], 172 (3%) [M^+−2Me−CO_2Et], 159 (10%) [$C_6H_4OMeCCCO$]; anal. calcd. for $C_{16}H_{18}O_4$: C 70.06, H 6.61%; found: C 69.88, H 6.69%.

2,5-Dimethyl-4-(3-methoxyphenyl)furan-3-carboxylic acid ethyl ester (8f): Yellow oil; yield: 0.233 g (85%); IR (Nujol): ν = 1589 and 1602 (m, C=C), 1711 cm^{-1} (s, C=O); ^{1}H NMR ($CDCl_3$): δ = 1.11 (t, J = 7.0 Hz, 3H, CH_2CH_3), 2.20 and 2.57 (s, 3H each, CH_3), 3.81 (s, 3H, OCH_3), 4.12 (q, J = 7.0 Hz, 2H, CH_2CH_3), 6.79–6.86 (m, 3H, C_6H_4OMe), 7.26 (m, 1H, C_6H_4OMe); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 11.8, 13.9 and 14.0 (s, CH_3), 55.2 (s, OCH_3), 59.8 (s, CH_2), 112.2, 115.8, 122.6 and 128.5 (s, CH of C_6H_4OMe), 113.5 and 121.2 (s, =C), 134.6 (s, C of C_6H_4OMe), 147.1, 157.4 and 158.9 (s, =C-O and C of C_6H_4OMe), 164.3 (s, C=O); MS (EI 70 eV): m/z = 274 (78%) [M^+], 245 (25%) [M^+−Et], 228 (100%) [M^+−Me−OMe], 213 (5%) [M^+−Et−OMe], 200 (32%) [M^+−CO_2Et], 185 (24%) [M^+−Me−CO_2Et]; HR-MS: m/z = 274.11982, calcd. for $C_{16}H_{18}O_4$: 274.11996.

2,5-Dimethyl-4-(2-methoxyphenyl)furan-3-carboxylic acid ethyl ester (8g): Yellow oil; yield: 0.258 g (94%); IR (Nujol): ν = 1579 and 1602 (m, C=C), cm^{-1} 1712 (s, C=O); ^{1}H NMR ($CDCl_3$): δ = 1.04 (t, J = 7.0 Hz, 3H, CH_2CH_3), 2.18 and 2.56 (s, 3H each, CH_3), 3.76 (s, 3H, OCH_3), 4.07 (q, J = 7.0 Hz, 2H, CH_2CH_3), 6.89–6.99 (m, 2H, C_6H_4OMe), 7.15 (m, 1H, C_6H_4OMe), 7.30 (m, 1H, C_6H_4OMe); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 11.8, 13.8 and 13.9 (s, CH_3), 55.3 (s, OCH_3), 59.5 (s, CH_2), 110.3, 120.1, 128.5 and 131.1 (s, CH of C_6H_4OMe), 114.5, 117.3 and 122.5 (s, =C and C of C_6H_4OMe), 147.2, 156.6 and 157.4 (s, =C-O and C of C_6H_4OMe), 164.6 (s, C=O); MS (EI 70 eV): m/z = 274 (80%) [M^+], 259 (1%) [M^+−Me], 245 (5%) [M^+−Et], 228 (17%) [M^+−Me−OMe], 213 (100%) [M^+−Et−OMe], 201 (15%) [M^+−CO_2Et], 185 (34%) [M^+−Me−CO_2Et], 172 (10%) [M^+−2Me−CO_2Et]; HR-MS: m/z = 274.11969, calcd. for $C_{16}H_{18}O_4$: 274.11996.

2,5-Dimethyl-4-(1-naphthyl)furan-3-carboxylic acid benzyl ester (9a): Yellow solid; yield: 0.324 g (91%); IR (Nujol): ν = 1586 (s, C=C), 1713 cm^{-1} (s, C=O); ^{1}H NMR ($CDCl_3$): δ = 2.15 and 2.75 (s, 3H each, CH_3), 4.90 (m, 2H, CH_2), 6.59 (d, J = 7.6 Hz, 2H, Ph), 7.09–7.22 (m, 3H, Ph), 7.36–7.52 (m, 4H, $C_{10}H_7$), 7.73 (d, J = 8.2 Hz, 1H, $C_{10}H_7$), 7.86–7.93 (m, 2H, $C_{10}H_7$); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 11.7 and 14.1 (s, CH_3), 65.5 (s, CH_2), 114.7 and 118.9 (s, =C), 125.2, 125.6, 125.8 (2C), 127.3, 127.4, 127.6, 127.7, 128.0 and 128.1 (s, CH of $C_{10}H_7$ and Ph), 131.4, 133.1, 133.5 and 135.5 (s, C of $C_{10}H_7$ and Ph), 148.0 and 158.3 (s, =C-O), 164.1 (s, C=O); MS (EI 70 eV): m/z = 356 (100%) [M^+], 265 (83%) [M^+−Bn], 249 (51%) [M^+−OBn], 234 (8%) [M^+−Me−OBn], 219 (17%) [M^+−CO_2Bn], 178 (18%) [$C_{10}H_7CCCO$], 152 (5%) [$C_{10}H_7CC$]; anal. calcd. for $C_{24}H_{20}O_3$: C 80.88, H 5.66%; found: C 80.71, H 5.45%.

5-Methyl-4-(1-naphthyl)-2-phenylfuran-3-carboxylic acid ethyl ester (10a): Yellow solid; yield: 0.221 g (62%); IR (Nujol): ν = 1582 and 1592 (m, C=C), 1716 cm^{-1} (s, C=O); ^{1}H NMR ($CDCl_3$): δ = 0.47 (t, J = 7.1 Hz, 3H, CH_2CH_3), 2.28 (s, 3H, CH_3), 3.80 (q, J = 7.1 Hz, 2H, CH_2CH_3), 7.44–7.59 (m, 7H, $C_{10}H_7$ and Ph), 7.81–8.04 (m, 5H, $C_{10}H_7$ and Ph); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 12.0 and 12.8 (s, CH_3), 60.0 (s, CH_2), 116.0 and 121.0 (s, =C), 125.2, 125.6, 125.8, 125.9, 127.6, 127.7, 127.9, 128.2 (2C) and 128.9 (s, CH of Ph and $C_{10}H_7$), 130.0, 131.2, 133.0 and 133.4 (s, C of Ph and $C_{10}H_7$), 149.2 and 155.0 (s, =C-O), 164.1 (s, C=O); MS (EI 70 eV): m/z = 356 (100%) [M^+], 328 (5%) [M^+−Et], 309 (20%) [M^+−OEt], 295 (2%) [M^+−Me−OEt], 282 (10%) [M^+−CO_2Et], 268 (4%) [M^+−Me−CO_2Et], 252 (7%) [M^+−Ph−Et], 239 (20%) [$C_{10}H_7CCCPh$], 205 (3%) [M^+−Ph−CO_2Et], 176 (3%) [$C_{10}H_7CCCC$]; anal. calcd. for $C_{24}H_{20}O_3$: C 80.88, H 5.66%; found: C 80.59, H 5.72%.

2,5-Dimethyl-4-(1-naphthyl)furan (13a): Colourless oil; yield: 0.176 g (79%); IR (Nujol): ν = 1592 cm^{-1} (s, C=C); ^{1}H NMR ($CDCl_3$): δ = 2.25 and 2.40 (s, 3H each, CH_3), 6.15 (s, 1H, =CH), 7.38–7.55 (m, 4H, $C_{10}H_7$), 7.83–8.01 (m, 3H, $C_{10}H_7$); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 12.3 and 13.5 (s, CH_3), 109.3 (s, =CH), 120.0 (s, =C), 125.4, 125.6, 125.7, 126.1, 127.2 (2C) and 128.2 (s, CH of $C_{10}H_7$), 132.2, 132.4 and 133.7 (s, C of $C_{10}H_7$), 147.0 and 149.4 (s, =C-O); MS (EI 70 eV): m/z = 222 (100%) [M^+], 207 (9%) [M^+−Me], 192 (5%) [M^+−2Me], 179 (64%) [$C_{10}H_7CCCO$], 165 (12%) [$C_{10}H_7CCC$], 152 (15%) [$C_{10}H_7CC$]; HR-MS: m/z = 222.10392, calcd. for $C_{16}H_{14}O$: 222.10391.

Synthesis of 2-Acetyl-3-phenylhex-4-ynoic Acid Ethyl Ester (14h)

Complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**1**) (0.049 g, 0.05 mmol), 1-phenyl-2-butyn-1-ol (**2h**) (0.146 g, 1 mmol), ethyl acetoacetate (1.32 mL, 10 mmol) and CF_3CO_2H (37 μL, 0.5 mmol) were introduced into a sealed tube under a nitrogen atmosphere. The reaction mixture was then heated at 75 °C for 3 h. After removal of volatiles under

vacuum, the residue was purified by column chromatography (silica gel) using a mixture EtOAc/hexane (1:10) as eluent. The resulting γ-ketoalkyne **14h** was isolated as a mixture of two diastereoisomers in *ca.* 1.2:1 ratio; yellow oil; yield: 0.240 g (93%); IR (Nujol): ν = 1723 and 1749 (s, C=O), 2237 cm^{-1} (w, C≡C); MS (EI 70 eV): *m/z* = 258 (1%) [M^+], 229 (3%) [M^+−Et], 215 (50%) [M^+−COMe], 185 (100%) [M^+−CO_2Et], 170 (50%) [M^+−Me−CO_2Et], 142 (20%) [M^+−COMe−CO_2Et], 129 (80%) [PhCHCCMe]; HR-MS: *m/z* = 258.12555, calcd. for $C_{16}H_{18}O_3$: 258.12504.

NMR data for the major diastereoisomer: ^{1}H NMR ($CDCl_3$): δ = 1.01 (t, *J* = 7.1 Hz, 3H, CH_2CH_3), 1.79 (d, *J* = 2.5 Hz, 3H, C≡CCH_3), 2.38 (s, 3H, $COCH_3$), 3.87 (d, *J* = 10.7 Hz, 1H, *CH*CHC≡CCH_3), 3.94 (q, *J* = 7.1 Hz, 2H, CH_2), 4.35 (m, 1H, *CH*C≡CCH_3), 7.20–7.35 (m, 5H, Ph); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 3.5 (s, C≡*C*CH_3), 13.7 (s, CH_2CH_3), 29.5 (s, CO*C*H_3), 37.4 (s, *C*HC≡CCH_3), 61.4 (s, CH_2), 66.9 (s, *C*HCHC≡CCH_3), 77.7 and 80.3 (s, C≡C), 127.4, 128.0 and 128.4 (s, CH of Ph), 138.8 (s, C of Ph), 166.9 [s, *C*(=O)OEt], 201.1 [s, *C*(=O)Me].

NMR data for the minor diastereoisomer: ^{1}H NMR ($CDCl_3$): δ = 1.30 (t, *J* = 7.1 Hz, 3H, CH_2CH_3), 1.80 (d, *J* = 2.6 Hz, 3H, C≡CCH_3), 1.95 (s, 3H, $COCH_3$), 3.95 (d, *J* = 10.0 Hz, 1H, *CH*CHC≡CCH_3), 4.25 (q, *J* = 7.1 Hz, 2H, CH_2), 4.35 (m, 1H, *CH*C≡CCH_3), 7.20–7.35 (m, 5H, Ph); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 3.5 (s, C≡*C*CH_3), 14.0 (s, CH_2CH_3), 30.5 (s, CO*C*H_3), 37.3 (s, *C*HC≡CCH_3), 61.6 (s, CH_2), 66.5 (s, *C*HCHC≡CCH_3), 78.0 and 79.6 (s, C≡C), 127.4, 128.1 and 128.6 (s, CH of Ph), 138.8 (s, C of Ph), 167.2 [s, *C*(=O)OEt], 200.6 [s, *C*(=O)Me].

Synthesis of 5-Ethyl-2-methyl-4-phenylfuran-3-carboxylic Acid Ethyl Ester (15h)[30]

Complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**1**) (0.049 g, 0.05 mmol), 1-phenyl-2-butyn-1-ol (**2h**) (0.146 g, 1 mmol), ethyl acetoacetate (1.32 mL, 10 mmol) and CF_3CO_2H (37 μL, 0.5 mmol) were introduced into a sealed tube under a nitrogen atmosphere. The reaction mixture was then heated at 75 °C for 72 h (the reaction was monitored by regular sampling and analysis by GC or GC/MS). After removal of volatiles under vacuum, the residue was purified by column chromatography (silica gel) using a mixture EtOAc/hexane (1:50) as eluent. The resulting furan **15h** was isolated as a yellow oil; yield: 0.111 g (43%).

General Procedure for the Synthesis of γ-Ketoalkynes 16

The corresponding propargylic alcohol **2a–b** (0.182 g, 1 mmol), methyl acetoacetate (1.08 mL, 10 mmol) and CF_3CO_2H (37 μL, 0.5 mmol) were introduced into a sealed tube under nitrogen atmosphere. The reaction mixture was then heated at 75 °C for 1.5 h (**16a**) or 4 h (**16b**) (the course of the reaction was monitored by regular sampling and analysis by GC or GC/MS). After removal of volatiles under vacuum, the residue was purified by column chromatography (silica gel) using a mixture EtOAc/hexane (1:10) as eluent.

2-Acetyl-3-(1-naphthyl)pent-4-ynoic acid methyl ester (16a): Yellow oil; yield: 0.252 g (90%); IR (Nujol): ν = 1719 and 1750 (s, C=O), 2117 (w, C≡C), 3290 cm^{-1} (m, ≡C-H); ^{1}H NMR ($CDCl_3$): δ = 2.00 and 2.45 (s, 3H each, CH_3), 2.36 and 2.37 (d, *J* = 2.6 Hz, 1H each, C≡CH), 3.42 and 3.83 (s, 3H each, OCH_3), 4.40 (d, *J* = 9.7 Hz, 2H, *CH*CHC≡CH), 5.25 (m, 2H, *CH*C≡CH), 7.43–7.65 (m, 8H, $C_{10}H_7$), 7.80–7.91 (m, 4H, $C_{10}H_7$), 8.27–8.30 (m, 2H, $C_{10}H_7$); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 30.1 and 30.4 (s, CH_3), 33.2 and 33.4 (s, *C*HC≡CH), 52.5 and 52.7 (s, OCH_3), 64.2 and 64.3 (s, *C*HCHC≡CH), 72.4 and 72.8 (s, C≡*C*H), 82.8 (2C) (s, *C*≡CH), 123.2, 123.3, 125.3 (2C), 125.8, 125.9, 126.1, 126.4, 126.6 (2C), 128.6, 128.7, 129.0 and 129.1 (s, CH of $C_{10}H_7$), 130.4, 130.6, 133.1, 133.2 and 134.1 (2C) (s, C of $C_{10}H_7$), 167.2 and 167.8 [s, *C*(=O)OMe], 200.1 and 200.6 [s, *C*(=O)Me]; MS (EI 70 eV): *m/z* = 280 (5%) [M^+], 262 (5%) [M^+−Me−2H], 248 (2%) [M^+−OMe], 237 (9%) [M^+−COMe], 221 (41%) [M^+−CO_2Me], 205 (30%) [M^+−Me−CO_2Me], 178 (17%) [M^+−COMe−CO_2Me], 165 (100%) [$C_{10}H_7$CHCCH], 152 (9%) [$C_{10}H_7$CHC]; HR-MS: *m/z* = 280.10932, calcd. for $C_{18}H_{16}O_3$: 280.10939.

2-Acetyl-3-(2-naphthyl)pent-4-ynoic acid methyl ester (16b): Yellow oil; yield: 0.227 g (81%); IR (Nujol): ν = 1720 and 1749 (s, C=O), 2118 (w, C≡C), 3286 cm^{-1} (m, ≡C-H); ^{1}H NMR ($CDCl_3$): δ = 1.97 and 2.42 (s, 3H each, CH_3), 2.36 (d, *J* = 2.7 Hz, 1H, C≡CH), 2.37 (d, *J* = 2.5 Hz, 1H, C≡CH), 3.48 and 3.81 (s, 3H each, OCH_3), 4.09 (d, *J* = 10.8 Hz, 1H, *CH*CHC≡CH), 4.15 (d, *J* = 10.4 Hz, 1H, *CH*CHC≡CH), 4.63 (m, 2H, *CH*C≡CH), 7.47–7.53 (m, 6H, $C_{10}H_7$), 7.81–7.84 (m, 8H, $C_{10}H_7$); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 29.7 and 30.4 (s, CH_3), 36.7 (2C) (s, *C*HC≡CH), 52.2 and 52.5 (s, OCH_3), 65.5 and 65.9 (s, *C*HCHC≡CH), 72.0 and 72.7 (s, C≡*C*H), 82.4 and 82.7 (s, *C*≡CH), 125.4 (2C), 125.8, 125.9, 126.0, 126.1, 126.9, 127.1, 127.3 (2C), 127.5, 127.6, 128.2 and 128.3 (s, CH of $C_{10}H_7$), 132.4, 132.5, 132.9, 133.0, 134.5 and 134.6 (s, C of $C_{10}H_7$), 166.7 and 167.1 [s, *C*(=O)OMe], 199.7 and 200.0 [s, *C*(=O)Me]; MS (EI 70 eV): *m/z* = 280 (5%) [M^+], 262 (26%) [M^+−Me−2H], 248 (2%) [M^+−OMe], 237 (68%) [M^+−COMe], 221 (90%) [M^+−CO_2Me], 205 (46%) [M^+−Me−CO_2Me], 178 (29%) [M^+−COMe−CO_2Me], 165 (100%) [$C_{10}H_7$CHCCH], 152 (10%) [$C_{10}H_7$CHC]; HR-MS: *m/z* = 280.10950, calcd. for $C_{18}H_{16}O_3$: 280.10939.

Supporting Information Available

Copies of the ^{13}C{^{1}H} NMR spectra of all compounds synthesized in this work.

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[4] The 16e$^-$ (η^3-allyl)-ruthenium(II)complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] [**1**; dppf = 1,1'-bis(diphenylphosphino)ferrocene], associated with CF_3CO_2H, is a highly efficient catalyst for the isomerization of diarylsubstituted terminal propargylic alcohols **A** into enals **B** (Meyer–Schuster-type rearrangement): a) V. Cadierno, J. Díez, S. E. García-Garrido, J. Gimeno, *Chem. Commun.* **2004**, 2716–2717; b) V. Cadierno, S. E. García-Garrido, J. Gimeno, *Adv. Synth. Catal.* **2006**, *348*, 101–110.

[5] We note that the dinuclear Ru(III) species [Cp*Ru(μ^2-XMe)$_2$RuCp*(OH_2)][OTf]$_2$ (X = S, Se, Te) are also able to catalyze related C–C coupling reactions between propargylic alcohols and acetone: G. Onodera, H. Matsumoto, Y. Nishibayashi, S. Uemura, *Organometallics* **2005**, *24*, 5799–5801.

[6] We note that, although monosubstituted alkynols HC≡CC(OH)HR (R = aryl group) also undergo the Meyer–Schuster isomerization into enals in the presence of complex **1** (see ref.[4]), attempts to promote its *one-pot* coupling with acetone resulted in the formation of the corresponding (*EE*)-dienones RCH=CHCH=C(H)C(=O)Me (**C**) in remarkably low yields (see ref.[3]). The monitoring of these reactions by GC showed, in addition to the complete consumption of the starting propargylic alcohol, that some uncharacterized by-products are also formed pointing out the existence of competitive processes in solution involving probably furan ring formation.

[7] For general reviews on its occurrence and applications see: a) B. H. Lipshutz, *Chem. Rev.* **1986**, *86*, 795–820; b) R. Benassi, in: *Comprehensive Heterocyclic Chemistry II*, (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon Press, Oxford, **1996**, vol. 2, pp. 259–295; c) H. Heaney, J. S. Ahn, in: *Comprehensive Heterocyclic Chemistry II*, (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon Press, Oxford, **1996**, vol. 2, pp. 297–350; d) W. Friedrichsen, in: *Comprehensive Heterocyclic Chemistry II*, (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon Press, Oxford, **1996**, vol. 2, pp. 351–393; e) B. A. Keay, P. W. Dibble, in: *Comprehensive Heterocyclic Chemistry II*, (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon Press, Oxford, **1996**, vol. 2, pp. 395–436; f) X. L. Hou, Z. Yang, H. N. C. Wong, in: *Progress in Heterocyclic Chemistry*, (Eds.: C. W. Gribble, T. L. Gilchrist), Pergamon Press, Oxford, **2003**, vol. 15, pp. 167–205.

[8] For recent reviews on the synthesis of furans see: a) X. L. Hou, H. Y. Cheung, T. Y. Hon, P. L. Kwan, T. H. Lo, S. Y. Tong, H. N. C. Wong, *Tetrahedron* **1998**, *54*, 1955–2020; b) B. A. Keay, *Chem. Soc., Rev.* **1999**, *28*, 209–215; c) A. Jeevanandam, A. Ghule, Y.-C. Ling, *Curr. Org. Chem.* **2002**, *6*, 841–864; d) R. C. D. Brown, *Angew. Chem. Int. Ed.* **2005**, *44*, 850–852; e) S. F. Kirsch, *Org. Biomol. Chem.* **2006**, *4*, 2076–2080.

[9] Attempts to isolate diene-dione **3a** in pure form from this crude reaction mixture failed, being characterized only by MS (EI 70 eV): *m/z* = 264 (100%) [M$^+$], 249 (12%) [M$^+$–Me], 234 (10%) [M$^+$–2Me], 221 (50%) [M$^+$–COMe], 205 (40%) [M$^+$–Me–COMe], 178 (60%) [M$^+$–2COMe], 165 (34%) [M$^+$–C(COMe)$_2$], 152 (15%) [M$^+$–CHC(COMe)$_2$], 140 (10%) [M$^+$–CHCHC(COMe)$_2$], 128 (5%) [M$^+$–CHCHCHC(COMe)$_2$].

[10] A closely related cycloaddition reaction of terminal secondary alkynols and cyclic 1,3-dicarbonyl compounds to give 4,6,7,8-tetrahydrochromen-5-ones or 4*H*-cyclopenta[*b*]pyran-5-ones, catalyzed by the thiolate-bridged diruthenium(III)complexes [Cp*RuCl(μ^2-SR)$_2$RuCp*Cl] (R = Me, *n*-Pr, *i*-Pr) (5 mol%) in the presence of NH_4BF_4 (10 mol%), has been recently reported: Y. Nishibayashi, M. Yoshikawa, Y. Inada, M. Hidai, S. Uemura, *J. Org. Chem.* **2004**, *69*, 3408–3412.

[11] Formation of tri- and tetrasubstituted furans from secondary propargylic alcohols and enolizable ketones, in the presence of catalytic amounts of [Cp*RuCl(μ^2-SMe)$_2$RuCp*Cl] (10 mol%), NH_4BF_4 (20 mol%) and $PtCl_2$ (20 mol%), has been reported. This process involves also the initial formation of a γ-ketoalkyne, *via* Ru-catalyzed propargylic substitution of the alkynol with the ketone, which undergoes a Pt-catalyzed Markovnikov hydration of the alkyne moiety to give a 1,4-diketone. Subsequent cyclization of this diketone, also catalyzed by Pt, generates the final furans. We note that (*i*) no 1,3-dicarbonyl compounds were used as substrates in this catalytic reaction, and (*ii*) the process is only operative with terminal alkynols HC≡CC(OH)HAr (Ar = aryl group): Y. Nishibayashi, M. Yoshikawa, Y. Inada, M. D. Milton, M. Hidai, S. Uemura, *Angew. Chem. Int. Ed.* **2003**, *42*, 2681–2684.

[12] Formation of the intermediate tetrasubstituted furan **11a** was confirmed by monitoring the catalytic reaction by GC/MS. MS (EI 70 eV) data of **11a** are as follows: *m/z* = 322 (48%) [M$^+$], 266 (100%) [M$^+$–*t*-Bu], 249

(44%) [M^+−O-*t*-Bu], 234 (5%) [M^+−Me−O-*t*-Bu], 219 (20%) [M^+−2Me−O-*t*-Bu], 206 (25%) [M^+−Me−CO_2-*t*-Bu], 191 (5%) [M^+−2Me−CO_2-*t*-Bu], 178 (20%) [$C_{10}H_7CCCO$].

[13] The Boc group is known to be a versatile and widely used protecting group for carboxylic acids. Several methods have been reported for its removal, most of them involving the use of Brønsted (HCl, H_2SO_4, HNO_3 or CF_3CO_2H) or Lewis (I_2, $TiCl_4$, $ZnBr_2$, $CeCl_3$, SiO_2 or silyl triflates) acids. Representative references are the following: a) J. S. Yadav, E. Balanarsaiah, S. Raghavendra, M. Satyanarayana, *Tetrahedron Lett.* **2006**, *47*, 4921–4924; b) P. Strazzolini, N. Misuri, P. Polese, *Tetrahedron Lett.* **2005**, *46*, 2075–2078; c) R. Kaul, Y. Brouillette, Z. Sajjadi, K. A. Hansford, W. D. Lubell, *J. Org. Chem.* **2004**, *69*, 6131–6133; d) E. Marcantoni, M. Massaccesi, E. Torregiani, G. Bartoli, M. Bosco, L. Sambri, *J. Org. Chem.* **2001**, *66*, 4430–4432; e) R. W. Jackson, *Tetrahedron Lett.* **2001**, *42*, 5163–5165; f) P. Strazzolini, M. Scuccato, A. G. Giumanini, *Tetrahedron* **2000**, *56*, 3625–3633; g) Y.-Q. Wu, D. L. Limburg, D. E. Wilkinson, M. J. Vaal, G. S. Hamilton, *Tetrahedron Lett.* **2000**, *41*, 2847–2849; h) M. Valencic, T. van der Does, E. de Vroom, *Tetrahedron Lett.* **1998**, *39*, 1625–1628; i) A. B. Jones, A. Villalobos, R. G. Linde II, S. J. Danishefsky, *J. Org. Chem.* **1990**, *55*, 2786–2797.

[14] The carboxylic acid **12a** could not be detected by GC/MS pointing out that its decarboxylation is a highly favoured process.

[15] Transition metal-catalyzed decarboxylation of carboxylic acids is a well-documented process. Representative examples can be found in: a) S. Matsubara, Y. Yokota, K. Oshima, *Org. Lett.* **2004**, *6*, 2071–2073; b) D. Tanaka, A. G. Myers, *Org. Lett.* **2004**, *6*, 433–436; c) E. M. O'Brien, E. A. Bercot, T. Rovis, *J. Am. Chem. Soc.* **2003**, *125*, 10498–10499; d) A. G. Myers, D. Tanaka, M. R. Mannion, *J. Am. Chem. Soc.* **2002**, *124*, 11250–11251; e) L. J. Gooβen, L. Winkel, A. Döhring, K. Ghosh, J. Paetzold, *Synlett* **2002**, 1237–1240; f) D. J. Darensbourg, E. M. Longridge, M. W. Holtcamp, K. K. Klausmeyer, J. H. Reibenspies, *J. Am. Chem. Soc.* **1993**, *115*, 8839–8840; g) D. J. Darensbourg, E. M. Longridge, E. V. Atnip, J. H. Reibenspies, *Inorg. Chem.* **1992**, *31*, 3951–3955.

[16] Although very rare, some metal-catalyzed reductive decarboxylation of esters RCO_2R' to form the corresponding hydrocarbons RH are known: a) N. Chatani, H. Tatamidani, Y. Ie, F. Kakiuchi, S. Murai, *J. Am. Chem. Soc.* **2001**, *123*, 4849–4850; b) H. Tatamidani, K. Yokota, F. Kakiuchi, N. Chatani, *J. Org. Chem.* **2004**, *69*, 5615–5621, and references cited therein.

[17] See, for example: a) Y. Nishibayashi, S. Uemura, *Curr. Org. Chem.* **2006**, *10*, 135–150, and references cited therein; b) E. Bustelo, P. H. Dixneuf, *Adv. Synth. Catal.* **2005**, *347*, 393–397; c) C. Fischmeister, L. Toupet, P. H. Dixneuf, *New J. Chem.* **2005**, *29*, 765–768; d) M. Georgy, V. Boucard, J.-M. Campagne, *J. Am. Chem. Soc.* **2005**, *127*, 14180–14181; e) J. J. Kennedy-Smith, L. A. Young, F. D. Toste, *Org. Lett.* **2004**, *6*, 1325–1327; f) M. R. Luzung, F. D. Toste, *J. Am. Chem. Soc.* **2003**, *125*, 15760–15761; g) B. D. Sherry, A. T. Radosevich, F. D. Toste, *J. Am. Chem. Soc.* **2003**, *125*, 6076–6077.

[18] a) Propargylic substitution reactions of alkynols $R^1C{\equiv}CC(OH)R^2R^3$ with a variety of carbon- and heteroatom-centered nucleophiles (NuH) to afford $R^1C{\equiv}CC(Nu)R^2R^3$ catalyzed by Brønsted acids (PTS, CSA, HCl, etc.) have been recently described. These reactions are believed to proceed through the intermediate formation of a propargylic cation $R^1C{\equiv}CC^+R^2R^3$ which undergoes the addition of the nucleophile (in our case the enolic form of the 1,3-dicarbonyl compound acts as a carbon-centered nucleophile): R. Sanz, A. Martínez, J. M. Álvarez-Gutiérrez, F. Rodríguez, *Eur. J. Org. Chem.* **2006**, 1383–1386; b) it should be also noted that very recently two general and highly efficient procedures for the propargylic substitution of alkynols catalyzed by the Lewis acids $BiCl_3$ and $FeCl_3$ have been reported: Z.-P. Zhan, W.-Z. Yang, R.-F. Yang, J.-L. Yu, J.-P. Li, H.-J. Liu, *Chem. Commun.* **2006**, 3352–3354; Z.-P. Zhan, J.-L. Yu, H.-J. Liu, Y.-Y. Cui, R.-F. Yang, W.-Z. Yang, J.-P. Li, *J. Org. Chem.* **2006**, *71*, 8298–8301.

[19] Although complex **1** is known to be an active catalyst in propargylic substitution processes of alkynols with alcohols (see ref.[4a]), it is not active at all when carbon-centered nucleophiles, such as enolizable ketones, are used as substrates (see ref.[3]).

[20] In accord with previous results, the treatment of **2a** with methyl acetoacetate and complex **1** (5 mol%), at 75 °C and in the absence of CF_3CO_2H, results in the exclusive formation of enal (*E*)-RHC=CHCHO (R = 1-naphthyl) as the result of the Meyer–Schuster isomerization of the alkynol (see ref.[4b]).

[21] Pd(0)-, Pd(II)- and Au(III)-catalyzed cycloisomerizations of internal β-ketoalkynes $R^1C{\equiv}CCH(R^2)C(=O)R^3$ into furans are known. Similarly, α-ketoalkynes $R^1CH_2C{\equiv}CC(=O)R^2$ can be cycloisomerized into furans in the presence of copper(I) salts. All these reactions are believed to proceed through the intermediate formation of allenyl isomers that undergo metal-mediated cyclization: a) H. Sheng, S. Lin, Y. Huang, *Synthesis* **1987**, 1022–1023; b) Y. Fukuda, H. Shiragami, K. Utimoto, H. Nozaki, *J. Org. Chem.* **1991**, *56*, 5816–5819; c) A. S. K. Hashmi, L. Schwarz, J.-H. Choi, T. M. Frost, *Angew. Chem. Int. Ed.* **2000**, *39*, 2285–2288; d) A. S. K. Hashmi, T. M. Frost, J. W. Bats, *J. Am. Chem. Soc.* **2000**, *122*, 11553–11554; e) A. V. Kel'in, V. Gevorgyan, *J. Org. Chem.* **2002**, *67*, 95–98; f) J. T. Kim, A. V. Kel'in, V. Gevorgyan, *Angew. Chem. Int. Ed.* **2003**, *42*, 98–101; g) A. W. Sromek, A. V. Kel'in, V. Gevorgyan, *Angew. Chem. Int. Ed.* **2004**, *43*, 2280–2282.

[22] Ru(II)-catalyzed cycloisomerizations of (*Z*)-2-en-4-yn-1-ols and α-epoxyalkynes into furans are well-known processes. Representative examples can be found in ref.[1f] and: a) B. Seiller, C. Bruneau, P. H. Dixneuf, *Tetrahedron* **1995**, *51*, 13089–13102; b) H. Kücükbay, B. Cetinkaya, S. Guesmi, P. H. Dixneuf, *Organometallics* **1996**, *15*, 2434–2439; c) B. Çetinkaya, I. Özdemir, C. Bruneau, P. H. Dixneuf, *Eur. J. Inorg. Chem.* **2000**, 29–32; d) C.-Y. Lo, H. Guo, J.-J. Lian, F.-M. Shen, R. S. Liu, *J. Org. Chem.* **2002**, *67*, 3930–3932; e) B. Çetinkaya, N. Gürbüz, T. Seçkin, I. Özdemir, *J. Mol. Catal. A: Chem.* **2002**, 184, 31–38.

[23] For reviews on this topic see: a) M. I. Bruce, *Chem. Rev.* **1991**, *91*, 197–257; b) C. Bruneau, P. H. Dixneuf,

Acc. Chem. Res. **1999**, *32*, 311–323; c) M. C. Puerta, P. Valerga, *Coord. Chem. Rev.* **1999**, *193–195*, 977–1025; d) V. Cadierno, M. P. Gamasa, J. Gimeno, *Coord. Chem. Rev.* **2004**, *248*, 1627–1657.

[24] It should be noted that other ruthenium(II) sources, such as $[RuCl_2(PPh_3)_3]$, $[RuCl_2(DMSO)_4]$, $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}p\text{-cymene})\}_2]$, $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$, $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$ and $[Ru(\eta^3\text{–}2\text{-}C_3H_4Me)_2(COD)]$, were also found to be operative in this furan-ring formation reaction. Nevertheless, their efficiency is by far lower than that shown by complex **1**. Thus, using the coupling of alkynol **2c** with ethyl acetoacetate as a model reaction ([**2c**]:[ethyl acetoacetate]:$[CF_3CO_2H]$:[Ru] ratio = 20:200:10:1), the best results were obtained using $[RuCl_2(DMSO)_4]$ and $[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)_2(COD)]$ which give furan **8c** in 60% and 64% yield (GC determined), respectively, after 8 h (to be compared with entry 4 in Table 2).

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[26] J. Suffert, D. Toussaint, *J. Org. Chem.* **1995**, *60*, 3550–3553.

[27] T. S. Balaban, M. Hiegemann, *Tetrahedron* **1992**, *48*, 9827–9840.

[28] M. S. Akhtar, M. Seth, A. P. Bhaduri, *J. Heterocycl. Chem.* **1985**, *22*, 1323–1324.

[29] M. H. Suhre, M. Reif, S. F. Kirsch, *Org. Lett.* **2005**, *7*, 3925–3927.

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