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Ruthenium(IV)-Catalyzed Markovnikov Addition of Carboxylic Acids to Terminal Alkynes in Aqueous Medium

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The dimeric bis(allyl)ruthenium(IV) complex [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl) (**5**) and several mononuclear species *trans*-[$RuCl_2$(η^3:η^3-$C_{10}H_{16}$)(L)] (L = two-electron-donor ligand) (**6**) derived from **5** have been checked as catalysts for the addition of carboxylic acids onto terminal alkynes using water as a green reaction medium. The best results in terms of activity and regioselectivity were obtained with the mononuclear derivative *trans*-[$RuCl_2$-(η^3:η^3-$C_{10}H_{16}$)(PPh_3)] (**6a**), which was able to promote the selective Markovnikov addition of both aromatic and aliphatic carboxylic acids to a large variety of terminal alkynes, enynes, and diynes as well as propargylic alcohols. In this way, a wide number of enol esters and β-oxo esters could be synthesized in moderate to good yields under mild conditions (60 °C) in an aqueous medium.

Introduction

Transition-metal-catalyzed addition of heteroatom−hydrogen bonds to alkynes has become one of the most powerful tools in synthetic organic chemistry, since it allows the straightforward preparation of a wide variety of functionalized unsaturated compounds of enormous interest from academic and industrial points of view.[1] In particular, the direct addition of carboxylic acids to terminal alkynes is an elegant and useful method for preparing enol esters (Scheme 1),[1,2] which are valuable intermediates for carbon−carbon and carbon−heteroatom bond formation,[3] and also have specific industrial applications as monomers for the production of several polymers and copolymers.[4]

Among the different metal sources used to promote the addition of carboxylic acids to terminal alkynes,[1,2] ruthenium catalysts have been the most widely studied, due to their high efficiency and tolerance to functional groups.[5,6] In addition, some of them allow the control of the regio- and stereoselectivity of this transformation, leading preferentially to one of the three possible enol ester isomers (see Scheme 1). Thus, while the catalytic systems bis(η^5-cyclooctadienyl)-ruthenium/PR_3,[7] [$RuCl_2$(η^6-arene)(PR_3)],[8] and [{Ru(μ-O_2CH)-$(CO)_2$(PPh_3)}$_2$][9] are known to promote the addition toward

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(4) Vinyl acetate, the monomeric precursor of poly(vinyl acetate) and poly(vinyl alcohol), is undoubtedly the most popular representative. Industrial production of vinyl acetate is presently based on the addition of acetic acid to ethylene catalyzed by Pd(II) under oxidative conditions: (a) Wittcoff, H. A.; Reuben, B. G. In *Industrial Organic Chemicals*; Wiley-Interscience: New York, 1996; p 109. For polymerization reactions of acetoxystyrenes, see: (b) Monthéard, J. P.; Camps, M.; Seytre, G.; Guillet, J.; Dubois, J. C. *Angew. Makromol. Chem.* **1978**, *72*, 45.

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(6) Specific reviews on the ruthenium-catalyzed addition of carboxylic acids to alkynes are available: (a) Bruneau, C. In *Metal Vinylidenes and Allenylidenes in Catalysis: From Reactivity to Applications in Synthesis*; Bruneau, C., Dixneuf, P. H., Eds.; Wiley-VCH: Weinheim, Germany, 2008; p 313. (b) Bruneau, C. In *Handbook of C-H Transformations: Applications in Organic Synthesis*; Dyker, G., Ed.; Wiley-VCH: Weinheim, Germany, 2005; Vol. *1*, p 72. (c) Fischmeister, C.; Bruneau, C.; Dixneuf, P. H. In *Ruthenium in Organic Synthesis*; Murahashi, S.-I., Ed.; Wiley-VCH: Weinheim, Germany, 2004; p 189.

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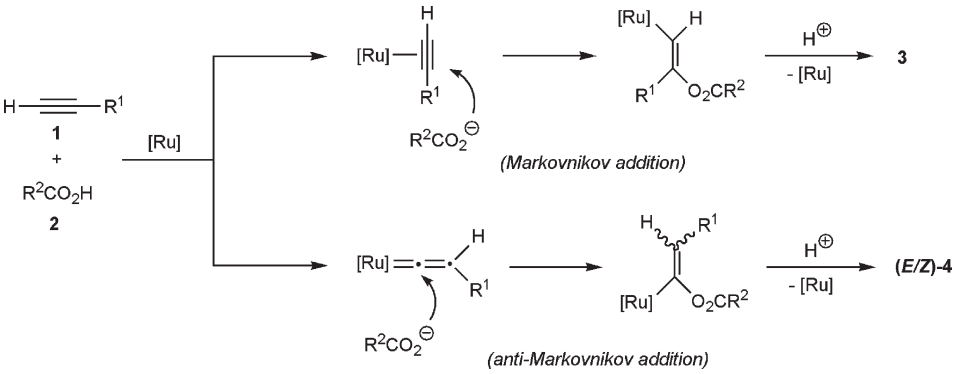
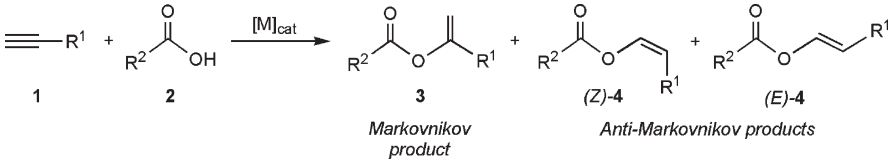


Figure 1. Proposed intermediates in the Ru-catalyzed additions of carboxylic acids to terminal alkynes.

Scheme 1. Catalytic Addition of Carboxylic Acids to Terminal Alkynes



the Markovnikov product **3**, the bis(allyl)ruthenium(II) complexes $[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)_2\{\kappa^2(P,P)\text{-}Ph_2P(CH_2)_nPPh_2\}]$ (n = 1−4), described by Dixneuf and co-workers,[10] are able to reverse the selectivity, affording almost exclusively the Z isomer of the alk-1-en-1-yl esters **4**.[11,12] It is presently well established that the different regioselectivity relies on the ability of ruthenium fragments to control the π-alkyne vs vinylidene rearrangement favoring either the Markovnikov (π-alkyne coordination) or the anti-Markovnikov (vinylidene ruthenium intermediate) addition of the carboxylate anion (see Figure 1).[6]

On the other hand, since the discoveries made by Breslow and Grieco in the early 1980s on the positive effect of water on the rate and endo/exo selectivity of Diels−Alder reactions,[13] the development of organic transformations in aqueous media has become one of the major cornerstones in modern chemistry.[14] This fact is also attributed to the increasing academic and industrial interest in fulfilling the principles of "Green Chemistry",[15] since water is the most convenient solvent that one can imagine in terms of cost, availability, safety, and environmental impact.[16,17] Although the hydrophobic character of most organic compounds has

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(11) Although other ruthenium-based catalysts able to orient the addition towards the anti-Markovnikov products **4** are known, they are in general less active and/or stereoselective than Dixneuf's catalysts. In other cases, the **3** vs **4** selectivity was found to be strongly dependent on the nature of the terminal alkyne, carboxylic acid, and/or solvent employed. See for example: (a) Gemel, C.; Trimmel, G.; Slugovc, C.; Kremel, S.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 3998. (b) Melis, K.; Samulkiewicz, P.; Rynkowski, J.; Verpoort, F. *Tetrahedron Lett.* **2002**, *43*, 2713. (c) Opstal, T.; Verpoort, F. *Tetrahedron Lett.* **2002**, *43*, 9259. (d) Melis, K.; Vos, D. D.; Jacobs, P.; Verpoort, F. *J. Organomet. Chem.* **2003**, *671*, 131. (e) Melis, K.; Verpoort, F. *J. Mol. Catal. A: Chem.* **2003**, *194*, 39. (f) Clercq, B. D.; Verpoort, F. *J. Organomet. Chem.* **2003**, *672*, 11. (g) Doherty, S.; Knight, J. G.; Rath, R. K.; Clegg, W.; Harrington, R. W.; Newman, C. R.; Campbell, R.; Amin, A. *Organometallics* **2005**, *24*, 2633. (h) Drozdzak, R.; Allaert, B.; Ledoux, N.; Dragutan, I.; Dragutan, V.; Verpoort, F. *Adv. Synth. Catal.* **2005**, *347*, 1721 and references cited therein. (i) Pelagatti, P.; Bacchi, A.; Balordi, M.; Bolaño, S.; Calbiani, F.; Elviri, L.; Gonsalvi, L.; Pelizzi, C.; Peruzzini, M.; Rogolino, D. *Eur. J. Inorg. Chem.* **2006**, 2422. (j) Ye, S.; Leong, W. K. *J. Organomet. Chem.* **2006**, *691*, 1117. (k) Yi, C. S.; Gao, R. *Organometallics* **2009**, *28*, 6585. (l) Tan, S. T.; Fan, W. Y. *Eur. J. Inorg. Chem.* **2010**, 4631. (m) Yi, C. S. *J. Organomet. Chem.* **2011**, *696*, 76.

(12) It is also interesting to note that, just by adding coordinating amines to the reaction media, the regioselectivity shown by complexes $[RuCl_2(\eta^6\text{-arene})(PR_3)]$ can be completely reversed, leading predominantly to enol esters (*Z*)-**4** instead of their expected isomers **3**: Goossen, L. J.; Paetzold, J.; Koley, D. *Chem. Commun.* **2003**, 706.

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(16) See, for example: (a) Nelson, W. M. In *Green Solvents for Chemistry: Perspectives and Practice*; Oxford University Press: New York, 2003. (b) Clark, J. H.; Taverner, S. J. *Org. Process Res. Dev.* **2007**, *11*, 149. (c) Kerton, F. M. In *Alternative Solvents for Green Chemistry*; RSC Publishing: Cambridge, U.K., 2009.

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been considered as a major drawback for a long time, it is nowadays well documented that even when the reaction medium is completely heterogeneous an enhancement of the reactivity and/or selectivity can be observed by using water as solvent.[18,19] Following this general trend, the search of metal catalysts for organic reactions in water has also attracted growing interest in recent years,[20] a wide variety of highly efficient and selective synthetic protocols conducted in aqueous media being already available for practical uses.[14,20] As far as the catalytic addition of carboxylic acids to terminal alkynes is concerned, despite the great interest of this atom-economical transformation in synthesis, up to now no general protocols have been reported in aqueous media,[21] probably owing to the competitive hydration of the alkynes in water to give carbonyl derivatives.[22,23]

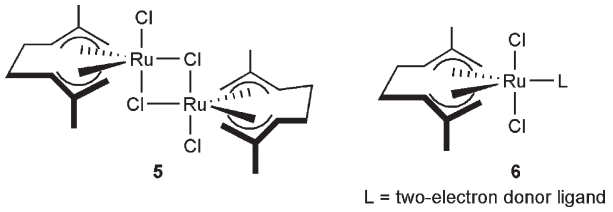

Figure 2. Structures of the bis(allyl)ruthenium(IV) complexes **5** and **6**.

In the context of our current work dealing with the catalytic applications of ruthenium complexes in aqueous media,[24] we have reported that the commercially available bis(allyl)ruthenium(IV) dimer [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] (**5**; $C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl)[25] is able to catalyze efficiently and selectively the [2 + 2 + 2] cyclotrimerization of alkynes in water without observation of hydration side reactions.[26] This fact prompted us to explore the potential of dimer **5** and its mononuclear derivatives *trans*-[$RuCl_2$(η^3:η^3-$C_{10}H_{16}$)(L)] (**6** in Figure 2), easily accessible by cleavage of the chloride bridges of **5** with two-electron-donor ligands,[27] as catalysts for the addition of carboxylic acids to terminal alkynes in aqueous media. Herein we describe the successful application of the mononuclear complex *trans*-[$RuCl_2$(η^3:η^3-$C_{10}H_{16}$)(PPh_3)] in the selective Markovnikov addition of a large variety of carboxylic acids to terminal alkynes, enynes, diynes, and propargylic alcohols. We must note that, despite the plethora of ruthenium complexes used to date to promote these catalytic transformations, high-oxidation-state Ru(IV) derivatives have been completely neglected.

Results and Discussion

Our investigations started with the evaluation of the catalytic activity of the dimer [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] (**5**) in the addition of benzoic acid (**2a**) to 1-hexyne (**1a**) (Scheme 2). Initial exploratory experiments were performed at 60 °C using equimolar amounts of the substrates (1 M in water) and a ruthenium loading of 2 mol %. Under these conditions, in the absence of any cocatalyst, the reaction proceeded to 89% overall GC yield in 24 h, producing a mixture of the three possible 1/1 adducts with low selectivity (**3aa**/(*E*)-**4aa**/(*Z*)-**4aa** ratio 3/2/4). Remarkably, neither formation of carbonyl compounds derived from the hydration of the C≡C bond of 1-hexyne nor alkyne oligomers were detected by GC/MSD of the crude reaction mixture. Although a significant rate enhancement was observed upon addition of different bases (M_2CO_3, MOH, and amines), the selectivity of the addition process remained in all cases low and formation of minor amounts of dimerization products of 1-hexyne was observed in general. As a representative example, in the presence of 4 mol % of Na_2CO_3, a conversion of 92% could be reached after only 4 h of heating, leading to a **3aa**/(*E*)-**4aa**/(*Z*)-**4aa** mixture (75% GC ield in 2/3/3 ratio)

(18) The term "on water", introduced by Sharpless and co-workers, is commonly used in the literature to refer to organic reactions proceeding in aqueous suspension: Narayan, S.; Muldoon, J.; Finn, M. G.; Fokin, V. V.; Kolb, H. C.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2005**, *44*, 3275.

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(21) The use of water-saturated organic solvents has led in some cases to a beneficial impact on the reaction rates. See ref 8i and: (a) Willem, Q.; Nicks, F.; Sauvage, X.; Delaude, L.; Demonceau, A. *J. Organomet. Chem.* **2009**, *694*, 4049. (b) In the context of a more general study, one example in water, i.e. the addition of benzoic acid to 4-ethynylanisole catalyzed by [RuHCl(CO)(PCy_3)$_2$], has been described.[11k]

(22) Catalytic transformations of alkynes in water have been recently reviewed: (a) Chen, L.; Li, C.-J. *Adv. Synth. Catal.* **2006**, *348*, 1459. (b) Li, C.-J. *Acc. Chem. Res.* **2010**, *43*, 581.

(23) The metal-catalyzed hydration of terminal alkynes to afford aldehydes (anti-Markovnikov addition) or ketones (Markovnikov addition) is a well-known and widely studied transformation of significant synthetic utility. For reviews on this topic see ref 1 and: Hintermann, L.; Labonne, A. *Synthesis* **2007**, 1121.

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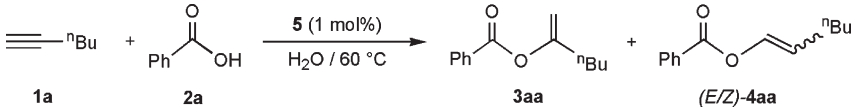
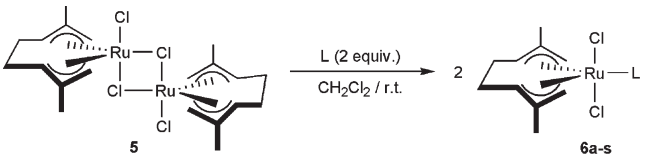
(27) For a comprehensive review on the chemistry of [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] (**5**), see: Cadierno, V.; Crochet, P.; García-Garrido, S. E.; Gimeno, J. *Curr. Org. Chem.* **2006**, *10*, 165.

Scheme 2. Catalytic Addition of Benzoic Acid (2a) to 1-Hexyne (1a)



Scheme 3. Synthesis of the Mononuclear Bis(allyl)ruthenium-(IV) Derivatives 6a−s



L = PPh_3 (**a**), TPPMS (**b**), P(*p*-Tol)$_3$ (**c**), PPh_2Me (**d**), $PPhMe_2$ (**e**), PMe_3 (**f**), P^iPr_3 (**g**), PBn_3 (**h**), $P(OMe)_3$ (**i**), $P(OEt)_3$ (**j**), $P(O^iPr)_3$ (**k**), $P(OPh)_3$ (**l**), NCMe (**m**), NCPh (**n**), NH_2Ph (**o**), py (**p**), CO (**q**), CNBn (**r**), CNCy (**s**)

and the corresponding tail-to-tail and head-to-tail dimers of 1-hexyne (17% GC yield).[28] The use of either lower temperatures or catalyst loadings did not lead to a higher selectivity for the process, also negatively affecting the reaction rate (no catalytic activity was observed below 35 °C).

In the search for a more selective catalyst, a series of mononuclear derivatives *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$(L)] (**6a−s**) was synthesized by cleavage of the chloride bridges of dimer **5** with phosphines (**6a−h**), phosphites (**6i−l**), nitriles (**6m**,**n**), amines (**6o**,**p**), carbon monoxide (**6q**), and isocyanides (**6r**,**s**) (see Scheme 3).[29] We expected that the catalytic process might be improved in terms of activity as well as regioselectivity (Markovnikov/anti-Markovnikov addition) via the influence of these ligands, featuring different electronic and steric properties.

The ability of these mononuclear species to promote the addition of benzoic acid (**2a**) to 1-hexyne (**1a**) in water was then evaluated (Scheme 2). Table 1 provides a summary of the results obtained on performing the catalytic reactions at 60 °C with a ruthenium loading of 2 mol %.

As shown in Table 1, all the mononuclear complexes checked were found to be active catalysts, providing enol esters **3aa** and **4aa** in moderate to good yields after 3−24 h of heating. In general, a higher selectivity toward the Markovnikov product was observed, as compared to that found for the dimeric precursor [{RuCl(μ-Cl)($\eta^3{:}\eta^3\text{-}C_{10}H_{16}$)}$_2$] (**5**). The anti-Markovnikov adducts (*E*/*Z*)-**4aa** were only predominatly formed from complexes **6m−p**, containing a labile nitrile or amine ligand. These results seem to indicate that the π-alkyne-to-vinylidene rearrangement is favored when the terminal alkyne coordinates in an equatorial position of the neutral [$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$] ruthenium fragment (Figure 3). In contrast, when nonlabile ligands are present, coordination of the alkyne occurs in the axial position of the cationic ruthenium(IV) complex [$RuCl(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(L)]^+$, in which such a rearrangement is disfavored.[30] The best results in terms of activity and regioselectivity were obtained with the mononuclear derivative [$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PPh_3)$] (**6a**), which was able to generate the enol ester **3aa** in 96% GC yield after only 3 h of heating (entry 1). However, from the data obtained, there is no apparent relationship between the steric and/or electronic nature of the auxiliary ligand L and the catalytic activity observed.

It is important to note that, with the exception of the water-soluble complexes *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$(TPPMS)] (**6b**; TPPMS = 3-(diphenylphosphino)benzenesulfonate sodium salt) and *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})${$P(OR)_3$}] (R = Me (**6i**), Et (**6j**), ^{i}Pr (**6k**)), all the rest of these mononuclear ruthenium-(IV) complexes are completely insoluble in water. Accordingly, a two-phase water/organic product system was formed in all cases, with the ruthenium catalyst remaining mainly in the organic phase (an emulsion is formed by stirring the catalytic reaction mixture). In light of the possibilities offered by surfactants to perform catalytic organic reactions in water, facilitating the solubility of both the metal catalyst and the reactants,[31] we decided to explore the catalytic addition of benzoic acid (**2a**) to 1-hexyne (**1a**) in aqueous micelles using the most active complex, *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PPh_3)$] (**6a**). In this regard, the commercially available sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTABr) were used as surfactants, the reactions being performed in aqueous 0.01 M solutions (Table 2, entries 2 and 3).[32] Although the reaction media were now completely homogeneous, longer reaction times were required to attain similar conversions and selectivities (entries 2 and 3 vs entry 1).[33] Interestingly, the use of organic solvents, regardless of their

(28) (a) Competitive dimerization of the alkyne has been previously observed in related ruthenium-catalyzed addition processes. See, for example, refs 8i, 11d, and 21a. Formation of dienyl esters (alkyne/carboxylic acid 2/1 adducts) was not detected by GC/MSD: (b) Le Paih, J.; Monnier, F.; Dérien, S.; Dixneuf, P. H.; Clot, E.; Eisenstein, O. *J. Am. Chem. Soc.* **2003**, *125*, 11964.

(29) With the exception of **6h** (see the Experimental Section), the preparation of these mononuclear complexes has been previously described in the literature. In all cases equatorial adducts are exclusively formed: (a) Head, R. A.; Nixon, J. F.; Swain, J. R.; Woodard, C. M. *J. Organomet. Chem.* **1974**, *76*, 393. (b) Cox, D. N.; Roulet, R. *J. Chem. Soc., Chem. Commun.* **1988**, 951. (c) Cox, D. N.; Roulet, R. *Inorg. Chem.* **1990**, *29*, 1360. (d) Cox, D. N.; Small, R. W. H.; Roulet, R. *J. Chem. Soc., Dalton Trans.* **1991**, 2013. (e) Steed, J. W.; Tocher, D. A. *J. Organomet. Chem.* **1994**, *471*, 221. (f) Wache, S.; Herrmann, W. A.; Artus, G.; Nuyken, O.; Wolf, D. *J. Organomet. Chem.* **1995**, *491*, 181. (g) Glander, S. C.; Nuyken, O.; Schattenmann, W. C.; Herrmann, W. A. *Macromol. Symp.* **1998**, *127*, 67. (h) Werner, H.; Stüer, W.; Jung, S.; Weberndörfer, B.; Wolf, J. *Eur. J. Inorg. Chem.* **2002**, 1076. (i) See also refs 24d, 24o, and 24q.

(30) One reviewer suggested that anti-Markovnikov addition of the carboxylic acid to the vinylidene ligand can proceed in an intramolecular fashion. Although this reaction pathway cannot be totally discarded, we must note that the use of the benzoate complex [RuCl{$\kappa^2(O,O)$-O_2CPh)}($\eta^3{:}\eta^3\text{-}C_{10}H_{16}$)] (its preparation and characterization are described in the Experimental Section) as catalyst resulted in remarkably lower yields, without improving the selectivity toward the anti-Markovnikov product **4aa**. Thus, under the same reaction conditions, only 33% conversion was observed after 24 h of heating, giving to a **3aa**/(*E*)-**4aa**/(*Z*)-**4aa** mixture in ca. 1/1/1 ratio. This fact suggests that coordination of the benzoate anion to ruthenium does not occur during the catalytic event.

(31) See, for example: (a) Dwards, T.; Paetzold, E.; Oehme, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 7174. (b) Zhang, J.; Meng, X.-G.; Zheng, X.-C.; Yu, X.-Q. *Coord. Chem. Rev.* **2009**, *253*, 2166. (c) Cavarzan, A.; Scarso, A.; Strukul, G. *Green Chem.* **2010**, *12*, 790.

(32) The critical micelle concentrations of CTABr and SDS are 9×10^{-4} and 8×10^{-3} M, respectively. The use of 0.01 M solutions of these surfactants assures the correct formation of micelles: (a) Fendler, J. H.; Fendler, E. J. In *Catalysis in Micellar and Macromolecular Systems*; Academic Press: New York, 1975. (b) Furton, K.; Norelus, A. *J. Chem. Educ.* **1993**, *70*, 254. Under these reaction conditions both the organometallic catalyst **6a** and the organic substrates are completely soluble in the aqueous phase.

Table 1. Addition of Benzoic Acid (2a) to 1-Hexyne (1a) Catalyzed by the Mononuclear Ruthenium(IV) Complexes *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(L)$] (6a−s) in Water[a]

entry	cat.	time (h)	conversn (%)[b]	yield of **3aa** (%)[b]	yield of **4aa** (%)[b,c]
1	**6a** (L = PPh_3)	3	99	96	3 (2:3)
2	**6b** (L = TPPMS)	4	99	92	7 (3:2)
3	**6c** (L = $P(p\text{-Tol})_3$)	3	98	94	4 (2:3)
4	**6d** (L = PPh_2Me)	4	96	94	2 (1:1)
5	**6e** (L = $PPhMe_2$)	5	97	79	18 (1:8)
6	**6f** (L = PMe_3)	24	94	79	18 (5:4)
7	**6g** (L = P^iPr_3)	6	99	95	4 (1:3)
8	**6h** (L = PBn_3)	9	87	81	6 (1:2)
9	**6i** (L = $P(OMe)_3$)	3	92	88	4 (1:1)
10	**6j** (L = $P(OEt)_3$)	3	97	95	2 (1:1)
11	**6k** (L = $P(O^iPr)_3$)	3	85	83	2 (1:1)
12	**6l** (L = $P(OPh)_3$)	24	78	63	15 (1:1)
13	**6m** (L = NCMe)	24	76	23	53 (3:2)
14	**6n** (L = NCPh)	24	65	21	44 (3:2)
15	**6o** (L = NH_2Ph)	24	37	12	25 (1:1)
16	**6p** (L = py)	24	81	22	59 (1:1)
17	**6q** (L = CO)	24	75	64	11 (3:2)
18	**6r** (L = CNBn)	24	89	63	26 (1:1)
19	**6s** (L = CNCy)	24	91	68	23 (1:1)

[a] Reactions performed under a N_2 atmosphere at 60 °C using 1 mmol of 1-hexyne, 1 mmol of benzoic acid, 0.02 mmol of the corresponding ruthenium complex, and 1 mL of water. [b] Conversion and yields determined by GC (uncorrected GC areas). [c] *E*/*Z* ratios are given in brackets (GC determined).

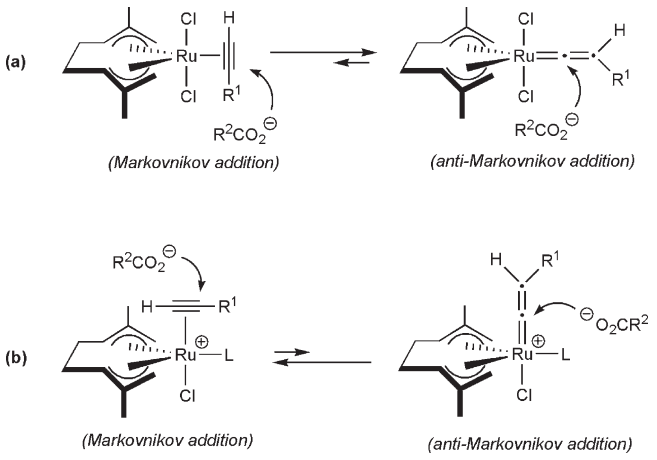


Figure 3. π-Alkyne-to-vinylidene equilibrium: (a) coordination in the equatorial position; (b) coordination in the axial position.

polarity or hydrogen-bonding capacity (entries 4−11), also reduced considerably the catalytic activity of **6a** (a homogeneous reaction medium was in all cases observed). A similar behavior was observed in the absence of solvent (entry 12). All these results clearly indicate that the "on-water" effect (trans-phase H-bonding interactions of water with transition states and reactants) plays a key role in this catalytic transformation.[19b]

In order to evaluate the scope of the catalytic activity of *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PPh_3)$] (**6a**) in water, the addition of a number of other carboxylic acids to 1-hexyne (**1a**) was explored. Thus, as shown in Table 3, using the same reaction conditions employed in the preparation of **3aa** (entry 1), related enol esters **3ab**−**3ap** could prepared in good to excellent yields (83−98% GC yields; 70−90% isolated yields) by addition of other aromatic (**2b**−**j**; entries 2−10), aliphatic (**2k**−**o**; entries 11−15) and α,β-unsaturated carboxylic acids (**2p**; entry 16) to **1a**. Remarkably, several common functional groups were tolerated and remained unaffected using this aqueous procedure: i.e., halide, ether, cyanide, alkene, and alcohol. Concerning the aromatic substrates (entries 1−10), no influence of the electronic properties of the aryl rings on the efficiency of the process was observed. The generality of this addition process was also confirmed by using a variety of other aliphatic (**1b**−**l**; entries 17−27) and aromatic terminal alkynes (**1m**,**n**; entries 28 and 29), as well as 1,3-enynes (**1o**,**p**; entries 30 and 31), the addition of benzoic acid (**2a**) to these substrates leading to the high-yield formation of enol esters **3ba**−**3pa** (73−97% GC yields; 60−88% isolated yields). As a general trend, faster reactions and higher yields were reached with aliphatic alkynes in comparison to the aromatic alkynes. In the case of methyl propargyl ether (**1j**; entry 25) a long reaction time (24 h) and a higher ruthenium loading (3 mol %) was also required to attain a high conversion. We must note that, in all the reactions given in Table 3, the formation of minor amounts of the corresponding anti-Markovnikov addition products was detected by GC. Although the content of these products in the crude reaction mixtures was in general less than 10%, this amount was significantly higher when the aromatic alkynes phenylacetylene and 4-methoxyphenylacetylene were used as substrates (17−23%; entries 28 and 29).[34] Solvent removal and chromatographic workup on silica gel provided analytically pure samples of all enol esters **3aa**−**3pa**, whose identity was assessed by comparison of their ^1H and $^{13}C\{^1H\}$ NMR data with those previously described in the literature and by their fragmentation in GC/MSD (characterization data for new compounds are included in the Experimental Section).

To further demonstrate the synthetic utility of the complex *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PPh_3)$] (**6a**), we next examined the coupling reactions of benzoic acid (**2a**) with diynes

(33) This negative effect is particularly marked for CTABr, probably due to the presence of an excess of bromide anions in the reaction medium that compete with the alkyne for coordination to the metal center.

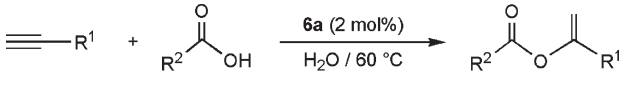
(34) This fact is in accord with the higher tendency of aromatic alkynes to undergo the π-alkyne-to-vinylidene rearrangement. For reviews on the chemistry of transition-metal vinylidene complexes, see: (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193*−*195*, 977. (c) Wakatsuki, Y. *J. Organomet. Chem.* **2004**, *689*, 4092. (d) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Coord. Chem. Rev.* **2004**, *248*, 1627. (e) Lynnam, J. M. *Chem. Eur. J.* **2010**, *16*, 8238.

Table 2. Addition of Benzoic Acid (2a) to 1-Hexyne (1a) Catalyzed by the Mononuclear Ruthenium(IV) Complex *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PPh_3)$] (6a) in Different Solvent Media[a]

entry	solvent	time (h)	conversn (%)[b]	yield of **3aa** (%)[b]	yield of **4aa** (%)[b,c]
1	H_2O	3	99	96	3 (2:3)
2	SDS(aq) (0.01 M)	5	99	93	6 (2:4)
3	CTABr(aq) (0.01 M)	24	88	82	6 (2:4)
4	CH_2Cl_2	24	90	83	7 (2:5)
5	THF	24	10	7	3 (1:2)
6	MeOH	24	43	37	6 (1:5)
7	EtOH	24	56	48	8 (2:6)
8	MeCN	24	15	12	3 (1:2)
9	dioxane	24	88	82	6 (2:4)
10	toluene	24	57	53	4 (1:3)
11	*n*-hexane	24	92	87	5 (1:4)
12	None	24	80	74	6 (1:5)

[a] Reactions performed under an N_2 atmosphere at 60 °C using 1 mmol of 1-hexyne, 1 mmol of benzoic acid, 0.02 mmol of complex **6a**, and 1 mL of the appropriate solvent. [b] Conversion and yields determined by GC (uncorrected GC areas). [c] *E*/*Z* ratios are given in brackets (GC determined).

Table 3. Addition of Carboxylic Acids to Terminal Alkynes Catalyzed by the Mononuclear Ruthenium(IV) Complex *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PPh_3)$] (6a) in Water[a]



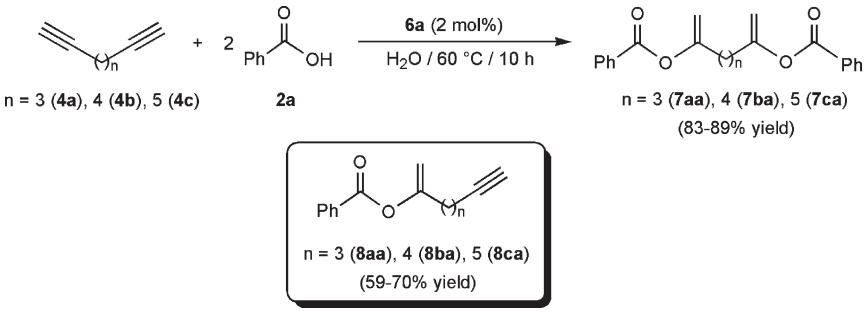
1a-p **2a-p** **3aa-3pa**

entry	alkyne **1** (R^1)	acid **2** (R^2)	time (h)	conversn (%)[b]	product **3**; yield (%)[c]
1	^{n}Bu (**1a**)	Ph (**2a**)	3	99	**3aa**; 96 (82)
2	^{n}Bu (**1a**)	2-C_6H_4F (**2b**)	2	99	**3ab**; 92 (80)
3	^{n}Bu (**1a**)	2-C_6H_4Cl (**2c**)	2	99	**3ac**; 95 (85)
4	^{n}Bu (**1a**)	3-C_6H_4Cl (**2d**)	3	99	**3ad**; 98 (90)
5	^{n}Bu (**1a**)	3-C_6H_4Br (**2e**)	3	99	**3ae**; 94 (83)
6	^{n}Bu (**1a**)	3-C_6H_4OMe (**2f**)	3	99	**3af**; 95 (81)
7	^{n}Bu (**1a**)	4-C_6H_4Cl (**2g**)	3	99	**3ag**; 84 (73)
8	^{n}Bu (**1a**)	4-C_6H_4CN (**2h**)	6	99	**3ah**; 96 (87)
9	^{n}Bu (**1a**)	4-$C_6H_4CH{=}CH_2$ (**2i**)	6	99	**3ai**; 96 (85)
10	^{n}Bu (**1a**)	C_6F_5 (**2j**)	1	99	**3aj**; 83 (70)
11	^{n}Bu (**1a**)	*n*-C_6H_{13} (**2k**)	6	98	**3ak**; 90 (80)
12	^{n}Bu (**1a**)	*n*-C_7H_{15} (**2l**)	7	99	**3al**; 96 (84)
13	^{n}Bu (**1a**)	CH_2Cy (**2m**)	7	94	**3am**; 84 (72)
14	^{n}Bu (**1a**)	CH_2CH_2Ph (**2n**)	5	99	**3an**; 91 (82)
15	^{n}Bu (**1a**)	(*S*)-CH(OH)Ph (**2o**)	6	99	**3ao**; 92 (83)
16	^{n}Bu (**1a**)	(*E*)-CH=CHPh (**2p**)	5	99	**3ap**; 91 (80)
17	^{n}Pr (**1b**)	Ph (**2a**)	6	99	**3ba**; 94 (86)
18	*n*-C_6H_{13} (**1c**)	Ph (**2a**)	5	99	**3ca**; 97 (85)
19	*n*-C_8H_{17} (**1d**)	Ph (**2a**)	3	99	**3da**; 95 (83)
20	*n*-$C_{10}H_{21}$ (**1e**)	Ph (**2a**)	3	99	**3ea**; 94 (86)
21	$CH_2{}^i$Pr (**1f**)	Ph (**2a**)	6	99	**3fa**; 86 (78)
22	CH_2Cy (**1g**)	Ph (**2a**)	4	99	**3ga**; 96 (85)
23	CH_2-c-C_5H_9 (**1h**)	Ph (**2a**)	3	99	**3ha**; 94 (85)
24	CH_2Ph (**1i**)	Ph (**2a**)	5	99	**3ia**; 94 (86)
25[d]	CH_2OMe (**1j**)	Ph (**2a**)	24	95	**3ja**; 89 (77)
26	^{t}Bu (**1k**)	Ph (**2a**)	5	99	**3ka**; 91 (79)
27	Cy (**1l**)	Ph (**2a**)	3	99	**3la**; 96 (88)
28	Ph (**1m**)	Ph (**2a**)	24	90	**3ma**; 73 (60)
29	4-C_6H_4OMe (**1n**)	Ph (**2a**)	24	99	**3na**; 76 (61)
30	$C(Me){=}CH_2$ (**1o**)	Ph (**2a**)	7	99	**3oa**; 90 (81)
31	c-C_6H_9 (**1p**)[e]	Ph (**2a**)	7	99	**3pa**; 98 (87)

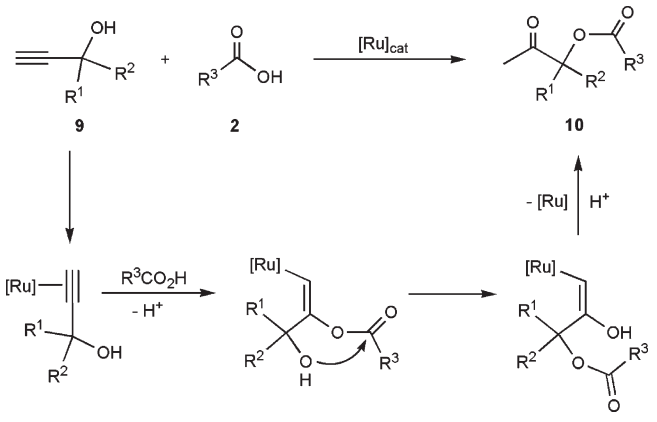
[a] Reactions performed under an N_2 atmosphere at 60 °C using 1 mmol of the corresponding alkyne and carboxylic acid, 0.02 mmol of complex **6a**, and 1 mL of water. [b] Determined by GC. [c] Determined by GC (uncorrected GC areas; isolated yields are given in parentheses). The differences between conversions and yields correspond to the anti-Markovnikov products present in the reaction media. [d] Reaction performed with a ruthenium loading of 3 mol %. [e] c-C_6H_9 = 1-cyclohexenyl.

(Scheme 4). Thus, when commercially available 1,6-heptadiyne (**4a**), 1,7-octadiyne (**4b**), and 1,8-nonadiyne (**4c**) were used as starting materials and the catalytic reactions were performed in the presence of 2 equiv of **2a**, the corresponding *gem*-dienol diesters **7aa**−**7ca** were regioselectively formed (91−95% GC yields; 83−89% isolated yields) after 10 h of heating at 60 °C in the presence of 2 mol % of complex **6a**. Albeit in lower yields due to the competitive formation of **7aa**−**7ca**, the monoaddition products **8aa**−**8ca** could also be synthesized using **6a** just by performing the catalytic reactions with a diyne/benzoic acid ratio of 1.3/1 (details are given in the Experimental Section). All these results clearly demonstrate the extraordinary synthetic potential of *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PPh_3)$] (**6a**). However, we must note that all attempts made to promote the addition of benzoic acid to alkynes bearing an internal C≡C bond (i.e., 3-hexyne

Scheme 4. Catalytic Addition of Benzoic Acid to Terminal Diynes



Scheme 5. β-Oxo Ester Formation by Addition of Carboxylic Acids to Terminal Propargylic Alcohols



and 4-octyne) using **6a** were unsuccessful.[35] In all cases, the starting materials were recovered unchanged ever after prolonged heating at 100 °C (24 h) in the presence of 5 mol % of **6a**.

The catalytic addition of carboxylic acids **2** to terminal propargylic alcohols **9** promoted by ruthenium complexes is a well-known process that provides a straightforward and atom-economical route of access to synthetically useful β-oxo esters **10** (Scheme 5).[7a,11k,m,24m,36] The generally accepted mechanism for this transformation involves the initial Markovnikov addition of the carboxylic acid to the alkynol C≡C bond,[37] followed by an intramolecular transesterification step.[38] The high selectivity shown by *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PPh_3)$] (**6a**) toward the formation of Markovnikov adducts starting from terminal alkynes prompted us to study the suitability of this catalyst to generate β-oxo esters in water. In this context, we should note that the compatibility of this coupling process with the use of an aqueous medium has been recently demonstrated by us, employing the hydrophilic ruthenium(II) complex [$RuCl_2(\eta^6\text{-}C_6H_6)$(TPPMS)] as catalyst.[24m]

We were pleased to find that treatment of several terminal propargylic alcohols **9a**−**s** with 1 equiv of benzoic acid (**2a**), in water at 60 °C and in the presence of **6a** (2 mol %), resulted in the formation of the desired β-oxo esters **10aa**−**10sa**, which were isolated in 52−88% yield after appropriate chromatographic workup (see Table 4; details are given in the Experimental Section). The wide scope of this aqueous transformation was assessed by using both aliphatic and aromatic secondary (**9b**−**l**; entries 2−12) and tertiary alkynols (**9m**−**s**; entries 13−19), as well as propargylic alcohol itself (**9a**; entry 1). Furthermore, as shown in Figure 4, the process was not restricted to benzoic acid, since the catalytic addition of 2-chlorobenzoic acid (**2c**), pentafluorobenzoic acid (**2j**), heptanoic acid (**2k**), and 3-cyclopentylpropionic acid (**2r**) to 1-phenyl-2-propyn-1-ol (**9d**) also took place, affording the β-oxo esters **10dc**, **10dj**, **10dk**, and **10dr**, respectively, in moderate to good yields (47−90%).

In general, the catalytic activity of *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PPh_3)$] (**6a**) turned out to be somewhat lower than that shown by the hydrophilic complex [$RuCl_2(\eta^6\text{-}C_6H_6)$(TPPMS)].[24m] However, it is worth noting that the addition of benzoic acid to tertiary aromatic alkynols HC≡CC(OH)Ar_2 (Ar = 4-C_6H_4F (**9m**), 4-C_6H_4Cl (**9n**)) gave rise to the β-oxo esters **10ma** and **10na** as the major reaction products (entries 13 and 14 of Table 4), in contrast with the catalytic activity of [$RuCl_2(\eta^6\text{-}C_6H_6)$(TPPMS)],[24m] which resulted in the almost exclusive formation of the alkene products $H_2C{=}CAr_2$ via hydrolysis of the highly reactive allenylidene intermediate [Ru]=C=C=CAr_2 generated by dehydration of the alkynol.[39] However, we must note that formation of minor amounts of

(35) Although rare, ruthenium-catalyzed additions of carboxylic acids to internal alkynes are known. See, ref 5 and: (a) Rotem, M.; Shvo, Y. *J. Organomet. Chem.* **1993**, *448*, 189. (b) Kabouche, A.; Kabouche, Z.; Bruneau, C.; Dixneuf, P. H. *J. Soc. Alger. Chim.* **1999**, *9*, 141. (c) Karabulut, S.; Öztürk, B. Ö; Imamoğlu, Y. *J. Organomet. Chem.* **2010**, *695*, 2161. We assume that in our case the greater steric hindrance between the internal-alkyne substituents and the ancillary triphenylphosphine ligand prevent the coordination of the C≡C bond to the metal center.

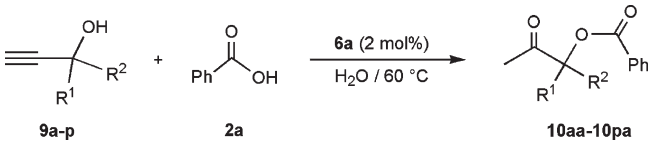
(36) (a) Devanne, D.; Ruppin, C.; Dixneuf, P. H. *J. Org. Chem.* **1988**, *53*, 925. (b) Bruneau, C.; Kabouche, Z.; Neveux, M.; Seiller, B.; Dixneuf, P. H. *Inorg. Chim. Acta* **1994**, *222*, 154. (c) Darcel, C.; Bruneau, C.; Dixneuf, P. H.; Neef, G. *J. Chem. Soc., Chem. Commun.* **1994**, 333. (d) Costin, S.; Rath, N. P.; Bauer, E. B. *Adv. Synth. Catal.* **2008**, *350*, 2414. (e) Heitt, N. P.; Lynam, J. M.; Welby, C. E.; Whitwood, A. C. *J. Organomet. Chem.* **2011**, *696*, 378.

(37) Ruthenium-catalyzed anti-Markovnikov additions of carboxylic acids to terminal propargylic alcohols are rare: (a) Picquet, M.; Fernández, A.; Bruneau, C.; Dixneuf, P. H. *Eur. J. Org. Chem.* **2000**, 2361. (b) Berger, S.; Haak, E. *Tetrahedron Lett.* **2010**, *51*, 6630.

(38) One reviewer suggested that an alternative mechanism involving an initial ruthenium-catalyzed propargylic substitution of the hydroxyl group of the alkynol by carboxylate, followed by intramolecular attack of carboxylate C=O to C-2 and hydrolysis, could be operative in these transformations. This reaction pathway has been discarded, since the independently synthesized propagylic benzoate HC≡CCHPh(O_2CPh) remained unchanged after 12 h of heating in water at 60 °C in the presence of **6a** (2 mol %): Huang, X.; de Haro, T.; Nevado, C. *Chem. Eur. J.* **2009**, *15*, 5904.

(39) For reviews on the chemistry of transition-metal allenylidene complexes, see: (a) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797. (b) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Eur. J. Inorg. Chem.* **2001**, 571. (c) Cadierno, V.; Crochet, P.; Gimeno, J. In *Metal Vinylidenes and Allenylidenes in Catalysis: From Reactivity to Applications in Synthesis*; Bruneau, C., Dixneuf, P. H., Eds.; Wiley-VCH: Weinheim, Germany, 2008; p 61. (d) Cadierno, V.; Gimeno, J. *Chem. Rev.* **2009**, *109*, 3512. (e) Cadierno, V.; Garcḳa-Garrido, S. E. *Top. Organomet. Chem.* **2010**, *30*, 151.

Table 4. Addition of Carboxylic Acids to Terminal Propargylic Alcohols Catalyzed by the Mononuclear Ruthenium(IV) Complex *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PPh_3)$] (6a) in Water[a]



9a-p 2a 10aa-10pa

entry	propargylic alcohol **9**	time (h)	conversn (%)[b]	product **10**; yield (%)[b]
1	$R^1 = R^2 = H$ (**9a**)	24	74	**10aa**; 74 (67)
2	$R^1 = H$, $R^2 = Me$ (**9b**)	21	87	**10ba**; 87 (78)
3	$R^1 = H$, $R^2 = Bn$ (**9c**)	24	99	**10ca**; 99 (83)
4	$R^1 = H$, $R^2 = Ph$ (**9d**)	24	99	**10da**; 93 (80)
5	$R^1 = H$, $R^2 = 2\text{-}C_6H_4Cl$ (**9e**)	20	99	**10ea**; 94 (83)
6	$R^1 = H$, $R^2 = 3\text{-}C_6H_4Cl$ (**9f**)	22	97	**10fa**; 94 (81)
7	$R^1 = H$, $R^2 = 4\text{-}C_6H_4Cl$ (**9g**)	15	98	**10ga**; 94 (86)
8	$R^1 = H$, $R^2 = 2\text{-}C_6H_4OMe$ (**9h**)	20	80	**10ha**; 72 (60)
9	$R^1 = H$, $R^2 = 3\text{-}C_6H_4OMe$ (**9i**)	22	99	**10ia**; 87 (79)
10	$R^1 = H$, $R^2 = 4\text{-}C_6H_4OMe$ (**9j**)	22	99	**10ja**; 84 (71)
11	$R^1 = H$, $R^2 =$ 1-Napht (**9k**)	22	99	**10ka**; 76 (62)
12	$R^1 = H$, $R^2 =$ 2-Napht (**9l**)	20	99	**10la**; 82 (73)
13	$R^1 = R^2 = 4\text{-}C_6H_4F$ (**9m**)	24	77	**10ma**; 62 (56)
14	$R^1 = R^2 = 4\text{-}C_6H_4Cl$ (**9n**)	24	83	**10na**; 68 (61)
15	$R^1 = Me$, $R^2 = Ph$ (**9o**)	24	88	**10oa**; 72 (64)
16	$R^1R^2 = -(CH_2)_4-$ (**9p**)	7	99	**10pa**; 99 (88)
17	$R^1R^2 = -(CH_2)_5-$ (**9q**)	22	72	**10qa**; 72 (65)
18	$R^1R^2 = -(CH_2)_6-$ (**9r**)	24	80	**10ra**; 74 (63)
19	$R^1R^2 = -(CH_2)_7-$ (**9s**)	24	74	**10sa**; 65 (52)

[a] Reactions performed under an N_2 atmosphere at 60 °C using 1 mmol of the corresponding propargylic alcohol, 1 mmol of benzoic acid, 0.02 mmol of complex **6a**, and 1 mL of water. [b] Yields determined by GC (uncorrected GC areas; isolated yields are given in parenthses). The differences between conversions and yields correspond to the olefinic side products $CH_2{=}CR^1R^2$ present in the reaction media.

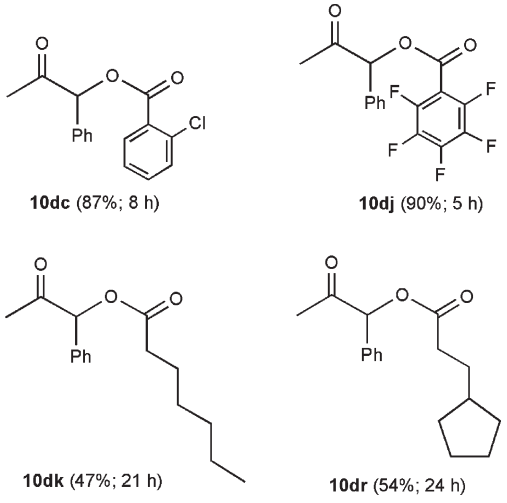


Figure 4. Structure of β-oxo esters **10dc**, **10dj**, **10dk**, and **10dr**.

olefinic side products was observed in many of the reactions given in Table 4.

Conclusion

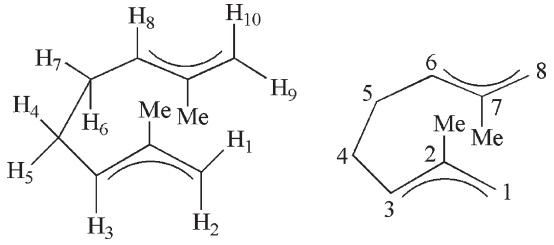
In brief, we have reported the catalytic addition of carboxylic acids onto terminal alkynes, enynes, and diynes by using the readily available mononuclear bis(allyl)ruthenium(IV) complex *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PPh_3)$] (**6a**) under mild thermal conditions (60 °C). This is the first efficient synthetic protocol of enol esters performed in water as a green reaction medium.[40] The process is based on the selective Markovnikov addition of both aromatic and aliphatic carboxylic acids to the alkynes. The synthetic methodology is also feasible for propargylic alcohols and compares well with the catalytic activity of [$RuCl_2(\eta^6\text{-}C_6H_6)$(TPPMS)] previously reported by us.[24m]

Experimental Section

Reactions were performed under an atmosphere of nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification with the exception of the compounds [{RuCl-(μ-Cl)($\eta^3{:}\eta^3\text{-}C_{10}H_{16}$)}$_2$] (**5**),[25] *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PPh_3)$] (**6a**),[29a] *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$(TPPMS)] (**6b**),[24o] *trans*-[$RuCl_2$-($\eta^3{:}\eta^3\text{-}C_{10}H_{16}$){P(*p*-Tol)$_3$}] (**6c**),[24d] *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$-($PPh_2Me$)] (**6d**),[24d] *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PPhMe_2)$] (**6e**),[24d] *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PMe_3)$] (**6f**),[24d] *trans*-[$RuCl_2(\eta^3{:}\eta^3$-$C_{10}H_{16})(P^iPr_3)$] (**6g**),[29h] *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})${P(OMe)$_3$}] (**6i**),[29b,d] *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})${P(OEt)$_3$}] (**6j**),[29g] *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})${P(O^{i}Pr)$_3$}] (**6k**),[29g] *trans*-[$RuCl_2(\eta^3{:}\eta^3$-$C_{10}H_{16})${P(OPh)$_3$}] (**6l**),[29f] *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$(NCMe)] (**6m**),[29c] *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$(NCPh)] (**6n**),[29g] *trans*-[$RuCl_2$-($\eta^3{:}\eta^3\text{-}C_{10}H_{16}$)($NH_2Ph$)] (**6o**),[29e] *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$-(py)] (**6p**),[29c] *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$(CO)] (**6q**),[29a] *trans*-[$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$(CNBn)] (**6r**),[24q] and *trans*-[$RuCl_2(\eta^3{:}\eta^3$-$C_{10}H_{16})$(CNCy)] (**6s**),[24q] which were prepared by following the methods reported in the literature. Flash chromatography was performed using Merck silica gel 60 (230−400 mesh). Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. GC (FID detection) measurements

(40) Preliminary studies indicate that more classical areneruthenium(II) complexes are also operative catalysts for this transformation in aqueous media. As an example, under the same reaction conditions employed in this work, the complex [$RuCl_2(\eta^6$-*p*-cymene)(PPh_3)] (2 mol %) is able to generate the enol ester **3aa**, by selective Markovnikov addition of benzoic acid (**2a**) to 1-hexyne (**1a**), in 94% GC yield after 4 h of heating (to be compared with entry 1 in Table 1). Full details will be presented in due course.

were made on Hewlett-Packard HP6890 equipment using a Supelco Beta-Dex column (30 m length; 250 μm diameter). GC/MSD measurements were performed on Agilent 6890N equipment coupled to a 5973 mass detector (70 eV electron impact ionization) using a HP-1MS column. NMR spectra were recorded on a Bruker DPX300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standard. DEPT experiments have been carried out for all the compounds reported in this paper. The numbering for protons and carbons of the 2,7-dimethylocta-2,6-diene-1,8-diyl skeleton is as follows:



Synthesis of *trans*-[RuCl$_2$(η^3:η^3-C$_{10}$H$_{16}$)(PBn$_3$)] (6h). Tribenzylphosphine (0.609 g; 2 mmol) was added, at room temperature, to a solution of [{RuCl(μ-Cl)(η^3:η^3-C$_{10}$H$_{16}$)}$_2$] (**5**) (0.616 g; 1 mmol) in 20 mL of dichloromethane. After the mixture was stirred for 10 min, the solvent was removed under vacuum and the resulting yellow solid residue washed with hexanes (3 × 10 mL) and dried in vacuo. Yield: 84% (1.029 g). Anal. Calcd for $RuC_{31}H_{37}Cl_2P$: C, 60.78; H, 6.09. Found: C, 60.89; H, 6.13. IR (KBr, cm^{-1}): ν 480 (w), 706 (s), 723 (m), 764 (m), 786 (m), 842 (s), 919 (w), 1029 (w), 1070 (w), 1238 (w), 1383 (m), 1450 (s), 1494 (s), 1600 (m), 2854 (w), 2917 (m), 2970 (w), 2998 (w), 3057 (w). ^{31}P{^{1}H} NMR (C_6D_6): δ 10.3 (s) ppm. ^{1}H NMR (CD_2Cl_2): δ 2.28 (s, 6H, CH_3), 2.31 (m, 2H, H_4 and H_6), 3.23 (m, 2H, H_5 and H_7), 3.50 (d, 2H, $^3J_{HP}$ = 3.5 Hz, H_2 and H_{10}), 3.67 (d, 6H, $^2J_{HP}$ = 8.7 Hz, PCH_2), 4.54 (d, 2H, $^3J_{HP}$ = 9.3 Hz, H_1 and H_9), 5.43 (m, 2H, H_3 and H_8), 7.11 (m, 15H, Ph) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 20.2 (s, CH_3), 32.3 (d, $^1J_{CP}$ = 20.0 Hz, PCH_2), 36.1 (s, C_4 and C_5), 64.0 (d, $^2J_{CP}$ = 5.9 Hz, C_1 and C_8), 107.1 (d, $^2J_{CP}$ = 9.6 Hz, C_3 and C_6), 122.9 (s, C_2 and C_7), 126.4, 128.5, and 130.8 (s, CH of Ph), 135.6 (d, $^2J_{CP}$ = 16.8 Hz, C of Ph) ppm.

Synthesis of [RuCl{κ^2(*O*,*O*)-O$_2$CPh}(η^3:η^3-C$_{10}$H$_{16}$)]. Sodium benzoate (0.050 g; 0.324 mmol) was added, at room temperature, to a solution of [{RuCl(μ-Cl)(η^3:η^3-C$_{10}$H$_{16}$)}$_2$] (**5**) (0.100 g; 0.162 mmol) in 10 mL of acetone. After the mixture was stirred for 24 h, the solvent was removed under vacuum, the resulting purple solid residue was extracted with dichloromethane (ca. 20 mL), and the extract was filtered over Kieselguhr. Concentration of the resulting solution (ca. 2 mL) followed by the addition of hexanes (ca. 30 mL) precipitated a purple solid, which was washed with hexanes (5 × 5 mL) and vacuum-dried. Yield: 72% (0.092 g). Anal. Calcd for $RuC_{17}H_{21}O_2Cl$: C, 51.84; H, 5.37. Found: C, 51.98; H, 5.46. IR (KBr, cm^{-1}): ν 482 (w), 686 (m), 715 (m), 801 (m), 841 (w), 863 (s), 936 (w), 1023 (s), 1096 (m), 1261 (m), 1420 (s), 1444 (s), 1491 (m), 1507 (m), 1601 (m), 2854 (w), 2920 (m), 2962 (w). ^{1}H NMR (C_6D_6): δ 1.78 and 2.12 (s, 3H each, CH_3), 2.00 (m, 4H, H_4, H_5, H_6 and H_7), 3.37 and 4.33 (m, 1H each, H_3 and H_8), 3.57 and 4.50 (s, 1H each, H_2 and H_{10}), 4.88 and 5.65 (s, 1H each, H_1 and H_9), 7.03 (m, 3H, Ph), 8.89 (d, 2H, $^3J_{HH}$ = 7.6 Hz, Ph) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 18.1 and 18.6 (s, CH_3), 31.5 and 33.4 (s, C_4 and C_5), 85.6 and 85.9 (s, C_1 and C_8), 91.7 and 93.0 (s, C_3 and C_6), 118.0 and 123.7 (s, C_2 and C_7), 129.5 and 134.1 (s, CH of Ph), 132.2 (s, C of Ph), 182.7 (s, O_2CPh) ppm.

General Procedure for the Addition of Carboxylic Acids to Terminal Alkynes Catalyzed by *trans*-[RuCl$_2$(η^3:η^3-C$_{10}$H$_{16}$)-(PPh$_3$)] (6a). Under a nitrogen atmosphere, water (1 mL), the corresponding terminal alkyne (1 mmol) and carboxylic acid (1 mmol), and the ruthenium catalyst **6a** (11 mg, 0.02 mmol) were introduced into a sealed tube and the resulting reaction mixture was stirred at 60 °C for the time indicated in Table 3. The course of the reaction was monitored by regular sampling and analysis by GC (FID detection). After elimination of the solvent under reduced pressure, chromatographic workup of the crude reaction mixtures over silica gel, using an ethyl acetate−hexane mixture (1/100 v/v) as eluent, provided pure samples of enol esters **3aa**−**3pa**. The identities of known compounds were assessed by comparison of their ^{1}H and ^{13}C{^{1}H} NMR data with those previously described in the literature[5,7−9,11] and by their fragmentation in GC/MS. Characterization data for the novel enol esters synthesized in this work are as follows.

1-Hexen-2-yl 2-Fluorobenzoate (3ab). Orange oil. Yield: 80% (0.177 g). IR (neat, cm^{-1}): ν 1664 (m, C=C), 1740 (s, C=O). ^{1}H NMR ($CDCl_3$): δ 0.90 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH_3), 1.36 and 1.52 (m, 2H each, CH_2), 2.33 (t, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2), 4.82 and 4.87 (d, 1H each, $^2J_{HH}$ = 1.3 Hz, =CH_2), 7.18 (m, 2H, CH_{arom}), 7.52 and 7.97 (m, 1H each, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 13.8 (s, CH_3), 21.9, 28.5, and 33.0 (s, CH_2), 101.4 (s, =CH_2), 117.0 (d, $^2J_{CF}$ = 22.2 Hz, CH_{arom}), 118.2 (d, $^2J_{CF}$ = 9.5 Hz, C_{arom}), 123.9 (d, $^3J_{CF}$ = 3.8 Hz, CH_{arom}), 132.2 (s, CH_{arom}), 134.8 (d, $^3J_{CF}$ = 8.9 Hz, CH_{arom}), 156.5 (s, =C), 162.0 (d, $^1J_{CF}$ = 260.7 Hz, C_{arom}), 162.3 (d, $^3J_{CF}$ = 3.5 Hz, C=O) ppm. MS (EI 70 eV): *m*/*z* 222 (M$^+$, 1%), 165 (2), 123 (100), 95 (20).

1-Hexen-2-yl 2-Chlorobenzoate (3ac). Yellow solid. Yield: 85% (0.203 g). IR (Nujol, cm^{-1}): ν 1666 (m, C=C), 1744 (s, C=O). ^{1}H NMR ($CDCl_3$): δ 0.91 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH_3), 1.37 and 1.52 (m, 2H each, CH_2), 2.35 (t, 2H, $^3J_{HH}$ = 7.1 Hz, CH_2), 4.83 and 4.88 (s, 1H each, =CH_2), 7.32 (m, 1H, CH_{arom}), 7.43 (m, 2H, CH_{arom}), 7.87 (d, 1H, $^3J_{HH}$ = 7.7 Hz, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 13.8 (s, CH_3), 22.0, 28.5, and 32.9 (s, CH_2), 101.5 (s, =CH_2), 126.6, 131.1, 131.5, and 132.8 (s, CH_{arom}), 129.6 and 133.9 (s, C_{arom}), 156.6 (s, =C), 163.7 (s, C=O) ppm. MS (EI 70 eV): *m*/*z* 238 (M$^+$, 1%), 139 (100), 111 (20), 75 (10).

1-Hexen-2-yl 3-Chlorobenzoate (3ad). Yellow oil. Yield: 90% (0.214 g). IR (neat, cm^{-1}): ν 1667 (m, C=C), 1737 (s, C=O). ^{1}H NMR ($CDCl_3$): δ 0.90 (m, 3H, CH_3), 1.35 and 1.47 (m, 2H each, CH_2), 2.32 (t, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2), 4.83 and 4.85 (s, 1H each, =CH_2), 7.38, 7.52, and 7.94 (m, 1H each, CH_{arom}), 8.03 (d, 1H, $^4J_{HH}$ = 1.4 Hz, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 13.8 (s, CH_3), 22.0, 28.5, and 32.9 (s, CH_2), 101.4 (s, =CH_2), 127.9, 129.7, 129.8, and 133.2 (s, CH_{arom}), 131.5 and 134.5 (s, C_{arom}), 156.5 (s, =C), 163.4 (s, C=O) ppm. MS (EI 70 eV): *m*/*z* 238 (M$^+$, 1%), 139 (100), 111 (25), 75 (10).

1-Hexen-2-yl 3-Bromobenzoate (3ae). Yellow oil. Yield: 83% (0.235 g). IR (neat, cm^{-1}): ν 1667 (m, C=C), 1732 (s, C=O). ^{1}H NMR ($CDCl_3$): δ 0.91 (t, 3H, $^3J_{HH}$ = 7.4 Hz, CH_3), 1.36 and 1.50 (m, 2H each, CH_2), 2.32 (t, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2), 4.84 and 4.85 (s, 1H each, =CH_2), 7.33, 7.68, and 7.71 (m, 1H each, CH_{arom}), 8.20 (d, 1H, $^4J_{HH}$ = 2.0 Hz, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 13.7 (s, CH_3), 22.0, 28.5, and 33.0 (s, CH_2), 101.4 (s, =CH_2), 122.5 and 131.8 (s, C_{arom}), 128.4, 129.9, 132.8, and 136.1 (s, CH_{arom}), 156.6 (s, =C), 163.3 (s, C=O) ppm. MS (EI 70 eV): *m*/*z* 284 (M$^+$, 1%), 183 (100), 155 (25), 76 (20).

1-Hexen-2-yl 3-Methoxybenzoate (3af). Orange oil. Yield: 81% (0.190 g). IR (neat, cm^{-1}): ν 1666 (m, C=C), 1732 (s, C=O). ^{1}H NMR ($CDCl_3$): δ 0.91 (t, 3H, $^3J_{HH}$ = 7.3 Hz, CH_3), 1.37 and 1.52 (m, 2H each, CH_2), 2.34 (t, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2), 3.85 (s, 3H, OCH_3), 4.83 and 4.85 (s, 1H each, =CH_2), 7.12 and 7.67 (d, 1H each, $^3J_{HH}$ = 7.5 Hz, CH_{arom}), 7.36 (dd, 1H, $^3J_{HH}$ = 7.5 and 7.5 Hz, CH_{arom}), 7.59 (s, 1H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 13.8 (s, CH_3), 22.1, 28.7, and 33.1 (s, CH_2), 55.4 (s, OCH_3), 101.3 (s, =CH_2), 114.3, 119.8, 122.3, and 129.5 (s, CH_{arom}), 131.2 and 159.6 (s, C_{arom}), 156.8 (s, =C), 164.6 (s, C=O) ppm. MS (EI 70 eV): *m*/*z* 234 (M$^+$, 5%), 178 (5), 135 (100), 107 (20), 92 (10), 77 (10).

1-Hexen-2-yl 4-Cyanobenzoate (3ah). Yellow oil. Yield: 87% (0.199 g). IR (neat, cm^{-1}): ν 1667 (m, C=C), 1738 (s, C=O), 2232 (m, C≡N). ^{1}H NMR ($CDCl_3$): δ 0.89 (t, 3H, $^3J_{HH}$ = 7.4 Hz, CH_3),

1.32−1.49 (m, 4H, CH_2), 2.32 (t, 2H, $^3J_{HH}$ = 7.1 Hz, CH_2), 4.85 (s, 2H, =CH_2), 7.76 and 8.17 (d, 2H each, $^3J_{HH}$ = 8.5 Hz, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.7 (s, CH_3), 22.0, 28.5, and 32.9 (s, CH_2), 101.7 (s, =CH_2), 116.6 and 117.8 (s, C≡N and C_{arom}), 130.3 and 132.2 (s, CH_{arom}), 133.6 (s, C_{arom}), 156.4 (s, =C), 163.0 (s, C=O) ppm. MS (EI 70 eV): *m*/*z* 229 (M^+, 10%), 172 (5), 130 (100), 102 (30), 83 (10).

1-Hexen-2-yl 4-Vinylbenzoate (3ai). Orange solid. Yield: 85% (0.195 g). IR (Nujol, cm^{-1}): ν 1630 and 1666 (m, C=C), 1731 (s, C=O). ^1H NMR ($CDCl_3$): δ 0.92 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH_3), 1.39 and 1.50 (m, 2H each, CH_2), 2.34 (t, 2H, $^3J_{HH}$ = 7.1 Hz, CH_2), 4.83 and 4.86 (s, 1H each, =CH_2), 5.40 (d, 1H, $^3J_{HH}$ = 11.1 Hz, CH=CH_2), 5.87 (d, 1H, $^3J_{HH}$ = 17.6 Hz, CH=CH_2), 6.75 (dd, 1H, $^3J_{HH}$ = 17.6 and 11.1 Hz, C*H*=CH_2), 7.48 and 8.04 (d, 2H each, $^3J_{HH}$ = 8.5 Hz, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.8 (s, CH_3), 22.0, 28.6, and 33.1 (s, CH_2), 101.2 (s, =CH_2), 116.6 (s, CH=*C*H_2), 126.1 and 130.2 (s, CH_{arom}), 128.9 and 142.2 (s, C_{arom}), 135.9 (s, *C*H=CH_2), 156.7 (s, =C), 164.4 (s, C=O) ppm. MS (EI 70 eV): *m*/*z* 230 (M^+, 5%), 131 (100), 103 (20), 77 (15).

1-Hexen-2-yl Pentafluorobenzoate (3aj). Orange oil. Yield: 70% (0.206 g). IR (neat, cm^{-1}): ν 1670 (m, C=C), 1753 (s, C=O). ^1H NMR ($CDCl_3$): δ 0.91 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH_3), 1.37 and 1.50 (m, 2H each, CH_2), 2.32 (t, 2H, $^3J_{HH}$ = 7.1 Hz, CH_2), 4.87 and 4.91 (br, 1H each, =CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.6 (s, CH_3), 21.9, 28.2, and 32.7 (s, CH_2), 102.0 (s, =CH_2), 116.9 (s, C_{arom}), 133.4 (s, =C), 135.9−147.0 (m, CF_{arom}), 156.2 (s, C=O) ppm. MS (EI 70 eV): *m*/*z* 294 (M^+, 1%), 276 (5), 224 (5), 195 (100), 167 (20), 117 (10).

1-Hexen-2-yl Heptanoate (3ak). Yellow oil. Yield: 80% (0.170 g). IR (neat, cm^{-1}): ν 1665 (m, C=C), 1755 (s, C=O). ^1H NMR ($CDCl_3$): δ 0.85 and 0.87 (t, 3H each, $^3J_{HH}$ = 7.1 Hz, CH_3), 1.28−1.46 (m, 10H, CH_2), 1.60 (m, 2H, CH_2), 2.17 (t, 2H, $^3J_{HH}$ = 6.9 Hz, CH_2), 2.35 (t, 2H, $^3J_{HH}$ = 7.7 Hz, CH_2), 4.66 and 4.68 (d, 1H each, $^2J_{HH}$ = 1.3 Hz, =CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.7 and 13.8 (s, CH_3), 21.9, 22.3, 24.8, 28.5, 28.6, 31.3, 32.9, and 34.3 (s, CH_2), 100.8 (s, =CH_2), 156.5 (s, =C), 171.9 (s, C=O) ppm. MS (EI 70 eV): *m*/*z* 212 (M^+, 1%), 142 (5), 113 (100), 85 (40), 55 (20), 43 (60).

1-Hexen-2-yl Octanoate (3al). Yellow oil. Yield: 84% (0.190 g). IR (neat, cm^{-1}): ν 1665 (m, C=C), 1757 (s, C=O). ^1H NMR ($CDCl_3$): δ 0.86 and 0.88 (t, 3H each, $^3J_{HH}$ = 7.1 Hz, CH_3), 1.26−1.48 (m, 12H, CH_2), 1.65 (m, 2H, CH_2), 2.18 (t, 2H, $^3J_{HH}$ = 7.7 Hz, CH_2), 2.36 (t, 2H, $^3J_{HH}$ = 7.3 Hz, CH_2), 4.67 and 4.69 (s, 1H each, =CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.7 and 13.9 (s, CH_3), 22.0, 22.5, 24.9, 28.5, 28.8, 28.9, 31.5, 32.9, and 34.3 (s, CH_2), 100.8 (s, =CH_2), 156.5 (s, =C), 171.9 (s, C=O) ppm. MS (EI 70 eV): *m*/*z* 226 (M^+, 1%), 142 (5), 127 (90), 109 (10), 98 (10), 57 (100), 43 (40).

1-Hexen-2-yl Cyclohexylacetate (3am). Orange oil. Yield: 72% (0.161 g). IR (neat, cm^{-1}): ν 1665 (m, C=C), 1755 (s, C=O). ^1H NMR ($CDCl_3$): δ 0.87 (t, 3H, $^3J_{HH}$ = 7.3 Hz, CH_3), 1.08 (m, 2H, CH_2), 1.27−1.74 (m, 13H, CH_2 and CH), 2.16 (t, 2H, $^3J_{HH}$ = 6.9 Hz, CH_2), 2.36 (t, 2H, $^3J_{HH}$ = 7.5 Hz, CH_2), 4.65 and 4.66 (s, 1H each, =CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.7 (s, CH_3), 21.9, 25.0, 28.5, 31.0, 32.3, 32.9, and 33.6 (s, CH_2), 39.5 (s, CH), 100.7 (s, =CH_2), 156.5 (s, =C), 171.9 (s, C=O) ppm. MS (EI 70 eV): *m*/*z* 226 (M^+, 1%), 142 (10), 125 (100), 107 (100), 97 (20), 79 (50), 69 (20), 55 (90).

1-Hexen-2-yl (*E*)-3-Phenylacrylate (3ap). Yellow oil. Yield: 80% (0.184 g). IR (neat, cm^{-1}): ν 1636 and 1666 (m, C=C), 1732 (s, C=O). ^1H NMR ($CDCl_3$): δ 0.94 (t, 3H, $^3J_{HH}$ = 7.2 Hz, CH_3), 1.39 and 1.51 (m, 2H each, CH_2), 2.31 (t, 2H, $^3J_{HH}$ = 7.2 Hz, CH_2), 4.80 and 4.83 (s, 1H each, =CH_2), 6.50 and 7.76 (d, 1H each, $^3J_{HH}$ = 16.0 Hz, =CH), 7.40 (br, 3H, CH_{arom}), 7.55 (br, 2H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.9 (s, CH_3), 22.2, 28.7, and 33.2 (s, CH_2), 101.1 (s, =CH_2), 117.7 and 145.9 (s, =CH), 128.1, 128.9, and 130.5 (s, CH_{arom}), 134.2 (s, C_{arom}), 156.7 (s, =C), 165.1 (s, C=O) ppm. MS (EI 70 eV): *m*/*z* 202 (M^+ - Et, 5%), 131 (100), 103 (30), 77 (20).

1-Decen-2-yl Benzoate (3da). Yellow oil. Yield: 83% (0.216 g). IR (neat, cm^{-1}): ν 1667 (m, C=C), 1733 (s, C=O). ^1H NMR ($CDCl_3$): δ 0.87 (br, 3H, CH_3), 1.27−1.54 (m, 14H, CH_2), 2.34 (t, 2H, $^3J_{HH}$ = 7.1 Hz, CH_2), 4.84 and 4.86 (s, 1H each, =CH_2), 7.44−7.59 (m, 3H, CH_{arom}), 8.09 (d, 2H, $^3J_{HH}$ = 7.4 Hz, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.0 (s, CH_3), 22.6, 26.5, 28.9, 29.1, 29.3, 31.7, and 33.4 (s, CH_2), 101.2 (s, =CH_2), 128.4, 129.8, and 133.2 (s, CH_{arom}), 156.8 (s, =C), 164.7 (s, C=O) ppm; C_{arom} not observed. MS (EI 70 eV): *m*/*z* 260 (M^+, 1%), 105 (100), 77 (20).

1-Dodecen-2-yl Benzoate (3ea). Yellow oil. Yield: 86% (0.248 g). IR (neat, cm^{-1}): ν 1666 (m, C=C), 1733 (s, C=O). ^1H NMR ($CDCl_3$): δ 0.88 (t, 3H, $^3J_{HH}$ = 6.2 Hz, CH_3), 1.26 (m, 14H, CH_2), 1.52 (m, 2H, CH_2), 2.35 (t, 2H, $^3J_{HH}$ = 7.4 Hz, CH_2), 4.84 and 4.86 (s, 1H each, =CH_2), 7.44−7.58 (m, 3H, CH_{arom}), 8.08 (d, 2H, $^3J_{HH}$ = 8.4 Hz, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.0 (s, CH_3), 22.6, 26.5, 29.0, 29.2, 29.3, 29.5 (2C), 31.8 and 33.4 (s, CH_2), 101.2 (s, =CH_2), 128.4, 129.8, and 133.2 (s, CH_{arom}), 156.8 (s, =C), 164.6 (s, C=O) ppm; C_{arom} not observed. MS (EI 70 eV): *m*/*z* 288 (M^+, 1%), 105 (100), 77 (15).

4-Methyl-1-penten-2-yl Benzoate (3fa). Yellow oil. Yield: 78% (0.159 g). IR (neat, cm^{-1}): ν 1666 (m, C=C), 1732 (s, C=O). ^1H NMR ($CDCl_3$): δ 0.97 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH_3), 1.85 (m, 1H, CH), 2.23 (d, 2H, $^3J_{HH}$ = 7.1 Hz, CH_2), 4.83 and 4.90 (s, 1H each, =CH_2), 7.44−7.59 (m, 3H, CH_{arom}), 8.07 (d, 2H, $^3J_{HH}$ = 7.7 Hz, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.2 (s, CH_3), 25.8 (s, CH), 42.8 (s, CH_2), 102.5 (s, =CH_2), 128.4, 129.8, and 133.2 (s, CH_{arom}), 155.5 (s, =C), 164.6 (s, C=O) ppm; C_{arom} not observed. MS (EI 70 eV): *m*/*z* 204 (M^+, 1%), 105 (100), 77 (30).

3-Cyclohexyl-1-propen-2-yl Benzoate (3ga). Yellow oil. Yield: 85% (0.207 g). IR (neat, cm^{-1}): ν 1666 (m, C=C), 1734 (s, C=O). ^1H NMR ($CDCl_3$): δ 0.94 (m, 2H, CH_2), 1.21 (m, 3H, CH_2), 1.52 (m, 1H, CH), 1.65−1.85 (m, 5H, CH_2), 2.26 (d, 2H, $^3J_{HH}$ = 7.1 Hz, CH_2), 4.82 and 4.92 (s, 1H each, =CH_2), 7.45−7.60 (m, 3H, CH_{arom}), 8.10 (d, 2H, $^3J_{HH}$ = 7.6 Hz, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.2, 26.4, 33.0, and 41.5 (s, CH_2), 35.3 (s, CH), 102.5 (s, =CH_2), 128.5, 129.9, and 133.2 (s, CH_{arom}), 130.0 (s, C_{arom}), 155.2 (s, =C), 164.6 (s, C=O) ppm. MS (EI 70 eV): *m*/*z* 244 (M^+, 1%), 187 (10), 105 (100), 77 (30).

3-Cyclopentyl-1-propen-2-yl Benzoate (3ha). Yellow oil. Yield: 85% (0.196 g). IR (neat, cm^{-1}): ν 1664 (m, C=C), 1732 (s, C=O). ^1H NMR ($CDCl_3$): δ 1.20 and 1.80 (m, 2H each, CH_2), 1.55 (m, 4H, CH_2), 2.05 (m, 1H, CH), 2.34 (d, 2H, $^3J_{HH}$ = 7.1 Hz, CH_2), 4.84 and 4.87 (s, 1H each, =CH_2), 7.42−7.59 (m, 3H, CH_{arom}), 8.09 (d, 2H, $^3J_{HH}$ = 8.3 Hz, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.0, 32.3, and 39.7 (s, CH_2), 37.2 (s, CH), 101.9 (s, =CH_2), 128.4, 129.8, and 133.2 (s, CH_{arom}), 156.3 (s, =C), 164.6 (s, C=O) ppm; C_{arom} not observed. MS (EI 70 eV): *m*/*z* 230 (M^+, 1%), 173 (5), 105 (100), 77 (20).

1-Cyclohexylvinyl Benzoate (3la). Yellow oil. Yield: 88% (0.203 g). IR (neat, cm^{-1}): ν 1660 (m, C=C), 1732 (s, C=O). ^1H NMR ($CDCl_3$): δ 1.24 (br, 6H, CH_2), 1.69−1.96 (m, 4H, CH_2), 2.44 (br, 1H, CH), 4.83 (br, 2H, =CH_2), 7.43−7.58 (m, 3H, CH_{arom}), 8.10 (d, 2H, $^3J_{HH}$ = 7.4 Hz, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.9, 26.0, and 30.6 (s, CH_2), 41.7 (s, CH), 99.6 (s, =CH_2), 128.4, 129.9, and 133.2 (s, CH_{arom}), 160.6 (s, =C), 164.8 (s, C=O) ppm; C_{arom} not observed. MS (EI 70 eV): *m*/*z* 230 (M^+, 1%), 105 (100), 77 (20).

1-Cyclohexenylvinyl Benzoate (3pa). Yellow oil. Yield: 87% (0.198 g). IR (neat, cm^{-1}): ν 1626 and 1651 (m, C=C), 1740 (s, C=O). ^1H NMR ($CDCl_3$): δ 1.59, 1.73, 2.10, and 2.26 (m, 2H each, CH_2), 4.84 and 5.08 (d, 1H each, $^2J_{HH}$ = 1.0 Hz, =CH_2), 5.99 (br, 1H, =CH), 7.45−7.60 (m, 3H, CH_{arom}), 8.15 (m, 2H, CH_{arom}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.7, 22.2, 24.6, and 25.2 (s, CH_2), 100.1 (s, =CH_2), 125.9 (s, =CH), 128.5, 129.9, and 133.3 (s, CH_{arom}), 129.6 and 130.2 (s, *C*=CH and C_{arom}), 153.9 (s, =C), 164.8 (s, C=O) ppm. MS (EI 70 eV): *m*/*z* 228 (M^+, 10%), 210 (5), 105 (100), 77 (30).

Catalytic Synthesis of Dienol Diesters 7aa−7ca. Under a nitrogen atmosphere, water (1 mL), the corresponding diyne (1 mmol), benzoic acid (0.244 g, 2 mmol), and the ruthenium catalyst **6a** (11 mg, 0.02 mmol) were introduced into a sealed tube and the resulting reaction mixture was stirred at 60 °C for 10 h. After elimination of the solvent under reduced pressure, chromatographic workup of the crude reaction mixtures over silica gel, using an ethyl acetate−hexane mixture (1/100 v/v) as eluent, provided pure samples of dienol diesters **7aa−7ca** in 83−89% yield. The identity of **7aa** and **7ba** was assessed by comparison of their ^{1}H and ^{13}C{^{1}H} NMR data with those previously described in the literature[11k,41] and by their fragmentation in GC/MS. Characterization data for the novel dienol diester **7ca** are as follows. Yellow oil. Yield: 86% (0.313 g). IR (neat, cm^{-1}): ν 1667 (m, C=C), 1732 (s, C=O). ^{1}H NMR ($CDCl_3$): δ 1.45−1.61 (m, 6H, CH_2), 2.35 (t, 4H, $^3J_{HH}$ = 7.1 Hz, CH_2), 4.83 and 4.87 (d, 2H each, $^2J_{HH}$ = 1.4 Hz, $=CH_2$), 7.43−7.61 (m, 6H, CH_{arom}), 8.07 (m, 4H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 26.2, 28.3, and 33.3 (s, CH_2), 100.5 (s, $=CH_2$), 128.4, 129.8, and 133.2 (s, CH_{arom}), 156.4 (s, =C), 164.7 (s, C=O) ppm; C_{arom} not observed. MS (EI 70 eV): *m*/*z* 259 (M^+ - PhCO, 5%), 120 (5), 105 (100), 77 (20).

Catalytic Synthesis of Enol Esters 8aa−8ca. Under a nitrogen atmosphere, water (1 mL), the corresponding diyne (1.3 mmol), benzoic acid (0.122 g, 1 mmol), and the ruthenium catalyst **6a** (11 mg, 0.02 mmol) were introduced into a sealed tube and the resulting reaction mixture was stirred at 60 °C for 6 h. After elimination of the solvent under reduced pressure, chromatographic workup of the crude reaction mixtures over silica gel, using an ethyl acetate−hexane mixture (1/100 v/v) as eluent, provided pure samples of the novel enol esters **8aa−8ca**. Characterization data are as follows.

1-Hepten-6-yn-2-yl Benzoate (8aa). Yellow oil. Yield: 59% (0.126 g). IR (neat, cm^{-1}): ν 1667 (m, C=C), 1733 (s, C=O), 2118 (w, C≡C), 3302 (m, ≡CH). ^{1}H NMR ($CDCl_3$): δ 1.77, 2.27, and 2.48 (m, 2H each, CH_2), 1.97 (br, 1H, ≡CH), 4.88 and 4.91 (s, 1H each, $=CH_2$), 7.44−7.61 (m, 3H, CH_{arom}), 8.08 (d, 2H, $^3J_{HH}$ = 8.1 Hz, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 17.6, 25.3, and 32.3 (s, CH_2), 68.9 (s, ≡CH), 83.5 (s, ≡C), 102.2 (s, $=CH_2$), 128.4, 129.9, and 133.3 (s, CH_{arom}), 155.4 (s, =C), 164.6 (s, C=O) ppm; C_{arom} not observed. MS (EI 70 eV): *m*/*z* 214 (M^+, 1%), 105 (100), 77 (30).

1-Octen-7-yn-2-yl Benzoate (8ba). Yellow oil. Yield: 63% (0.144 g). IR (neat, cm^{-1}): ν 1666 (m, C=C), 1732 (s, C=O), 2117 (w, C≡C), 3301 (m, ≡CH). ^{1}H NMR ($CDCl_3$): δ 1.63 (m, 4H, CH_2), 1.94 (t, 1H, $^4J_{HH}$ = 2.6 Hz, ≡CH), 2.20 and 2.37 (m, 2H each, CH_2), 4.86 and 4.88 (s, 1H each, $=CH_2$), 7.44−7.61 (m, 3H, CH_{arom}), 8.07 (d, 2H, $^3J_{HH}$ = 8.5 Hz, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 18.1, 25.4, 27.6, and 32.8 (s, CH_2), 68.5 (s, ≡CH), 84.0 (s, ≡C), 101.7 (s, $=CH_2$), 128.4, 129.9, and 133.3 (s, CH_{arom}), 129.7 (s, C_{arom}), 156.1 (s, =C), 164.7 (s, C=O) ppm. MS (EI 70 eV): *m*/*z* 228 (M^+, 1%), 105 (100), 77 (20).

1-Nonen-8-yn-2-yl Benzoate (8ca). Yellow oil. Yield: 70% (0.169 g). IR (neat, cm^{-1}): ν 1662 (m, C=C), 1730 (s, C=O), 2116 (w, C≡C), 3303 (m, ≡CH). ^{1}H NMR ($CDCl_3$): δ 1.53 (m, 6H, CH_2), 1.93 (t, 1H, $^4J_{HH}$ = 2.5 Hz, ≡CH), 2.18 and 2.35 (m, 2H each, CH_2), 4.84 and 4.86 (s, 1H each, $=CH_2$), 7.44−7.61 (m, 3H, CH_{arom}), 8.08 (d, 2H, $^3J_{HH}$ = 8.4 Hz, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 18.2, 25.9, 27.9, 28.1, and 33.2 (s, CH_2), 68.3 (s, ≡CH), 84.3 (s, ≡C), 101.5 (s, $=CH_2$), 128.4, 129.8, and 133.3 (s, CH_{arom}), 156.4 (s, =C), 164.7 (s, C=O) ppm; C_{arom} not observed. MS (EI 70 eV): *m*/*z* 242 (M^+, 1%), 120 (5), 105 (100), 77 (20).

General Procedure for the Addition of Carboxylic Acids to Terminal Propargylic Alcohols Catalyzed by *trans*-[$RuCl_2(\eta^3{:}\eta^3$-$C_{10}H_{16}$)(PPh_3)] (6a). Under a nitrogen atmosphere, water (1 mL), the corresponding propargylic alcohol (1 mmol) and carboxylic acid (1 mmol), and the ruthenium catalyst **6a** (11 mg, 0.02 mmol) were introduced into a sealed tube and the resulting reaction mixture was stirred at 60 °C for the time indicated in Table 4 and Figure 3. The course of the reaction was monitored by regular sampling and analysis by GC (FID detection). After elimination of the solvent under reduced pressure, chromatographic workup of the crude reaction mixtures over silica gel, using an ethyl acetate−hexane mixture (1/10 v/v) as eluent, provided pure samples of the β-oxo-esters **10aa−10dr**. The identity of known compounds was assessed by comparison of their ^{1}H and ^{13}C{^{1}H} NMR data with those previously described in the literature[24m,36a,36d,42] and by their fragmentation in GC/MS. Characterization data for the novel β-oxo esters synthesized in this work are as follows.

1,1-Bis(4-fluorophenyl)-2-oxopropyl Benzoate (10ma). Yellow oil. Yield: 56% (0.205 g). IR (neat, cm^{-1}): ν 1716 (s, C=O). ^{1}H NMR ($CDCl_3$): δ 2.18 (s, 3H, CH_3), 7.06 (m, 4H, CH_{arom}), 7.51−7.66 (m, 7H, CH_{arom}), 8.16 (d, 2H, $^3J_{HH}$ = 7.2 Hz, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 25.0 (s, CH_3), 89.4 (s, C), 115.6 (d, $^3J_{CF}$ = 21.9 Hz, CH_{arom}), 129.2, 130.4, and 134.4 (s, CH_{arom}), 129.7 (s, C_{arom}), 130.7 (d, $^2J_{CF}$ = 8.7 Hz, CH_{arom}), 135.1 (br, C_{arom}), 162.9 (d, $^1J_{CF}$ = 248.5 Hz, CH_{arom}), 165.6 (s, OC=O), 202.4 (s, C=O) ppm. MS (EI 70 eV): *m*/*z* 323 (M^+ − COMe, 1%), 201 (10), 123 (10), 105 (40), 77 (50), 43 (100).

1,1-Bis(4-chlorophenyl)-2-oxopropyl Benzoate (10na). Yellow oil. Yield: 61% (0.243 g). IR (neat, cm^{-1}): ν 1714 (s, C=O). ^{1}H NMR ($CDCl_3$): δ 2.16 (s, 3H, CH_3), 7.33 (m, 4H, CH_{arom}), 7.51−7.67 (m, 7H, CH_{arom}), 8.13 (d, 2H, $^3J_{HH}$ = 8.5 Hz, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 24.7 (s, CH_3), 88.7 (s, C), 128.4, 128.7, 129.6, 129.8, and 133.9 (s, CH_{arom}), 129.1, 134.5, and 137.2 (s, C_{arom}), 165.0 (s, OC=O), 201.5 (s, C=O) ppm. MS (EI 70 eV): *m*/*z* 355 (M^+ − COMe, 5%), 199 (5), 139 (10), 105 (100), 77 (20).

1-Acetylcyclooctyl Benzoate (10sa). Colorless oil. Yield: 52% (0.143 g). IR (neat, cm^{-1}): ν 1716 (s, C=O). ^{1}H NMR ($CDCl_3$): δ 1.58−1.63 (m, 10H, CH_2), 2.11−2.31 (m, 4H, CH_2), 2.12 (s, 3H, CH_3), 7.44−7.62 (m, 3H, CH_{arom}), 8.06 (m, 2H, CH_{arom}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.3, 24.8, 27.7, and 29.3 (s, CH_2), 23.6 (s, CH_3), 89.2 (s, C), 128.4, 129.7, and 133.3 (s, CH_{arom}), 165.5 (s, OC=O), 206.9 (s, C=O) ppm; C_{arom} not observed. MS (EI 70 eV): *m*/*z* 231 (M^+ − COMe, 19%), 105 (100), 77 (30).

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Supporting Information Available: Figures giving the ^{1}H and ^{13}C{^{1}H} NMR spectra of all new enol esters and β-oxo esters synthesized in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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