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Powerful control by organoruthenium catalysts of the regioselective addition to C(1) or C(2) of the prop-2-ynyl ethers C≡C triple bond [1]

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Abstract

The catalytic activation of pro-2-ynylic ethers $HC{\equiv}CCR_2OMe$ towards carboxylic acids is controlled to regioselectively afford the functional enol esters $R^1CO_2C(=CH_2)CR_2OMe$ or $R^1CO_2CH=CHCR_2OMe$ corresponding to the addition of the carboxylate to either C(2) or C(1) of the terminal triple bond, depending on the nature of the ruthenium catalyst precursor $RuCl_2(PPh_3)$(*p*-cymene) or Ru(η^3-2-methylpropenyl)$_2$(dppe), respectively. © 1997 Elsevier Science S.A.

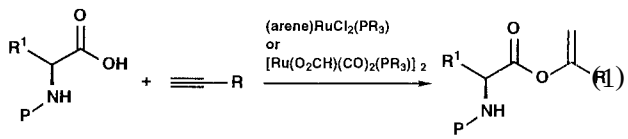
Keywords: Organoruthenium catalyst; Carboxylic acid; Triple bond

1. Introduction

Acetylenic compounds have found a considerable interest in organic synthesis due to the development of new selective metal-catalysed transformations [1–3]. They have been involved in a variety of catalysed carbon–carbon bond formation reactions including dimerization [4–10] and cyclotrimerization [11–13], coupling with alkenes [14–21], allenes [22–26], carbenes [27,28], carbonucleophiles [29–31], cross-coupling with halogenated olefins and arenes [32–34], and carbonylation [35–39].

The formation of carbon–heteroatom bonds from alkynes to produce functional alkenes is less documented and besides the direct addition of methanol [40] or water [41–43] to triple bonds, the most useful examples concern intramolecular cyclizations which generate oxygenated and nitrogen heterocycles [44–51].

We have shown that especially ruthenium(II) complexes were able to provide electrophilic activation of the triple bond of terminal aryl and alkyl acetylenes towards the addition of ammonium carbamates [52,53] and carboxylic acids [54–58]. (Arene)$RuCl_2(PR_3)$ (**I**) and even the ruthenium(I) derivative [Ru(η^2-O_2CH)$(CO)_2(PR_3)$]$_2$ appeared to be the best catalysts to promote the regioselective addition of the carboxylate to the internal C(2) carbon of the alkyne and make possible the preparation of a variety of enol esters, even from functional and optically active carboxylic acids that have been used for acylation under mild conditions [59–61] (Eq. (1)).



(1)

More recently, the regioselectivity of the addition was reversed by using a new class of ruthenium(II) catalysts containing a chelating diphosphine and two allylic groups as ligands. (1,4-Bis(diphenylphosphino)butane)Ru(η^3-CH_2CMeCH_2)$_2$ **II** led to the selective anti-Markovnikov and *trans*-ad-

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[1] Dedicated to Professor Peter M. Maitlis for his innovative contribution to catalysis during 45 yr of research and his initiative to develop exchange between the Universities of Rennes and Sheffield.

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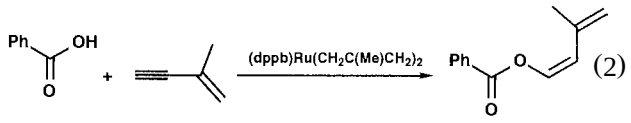
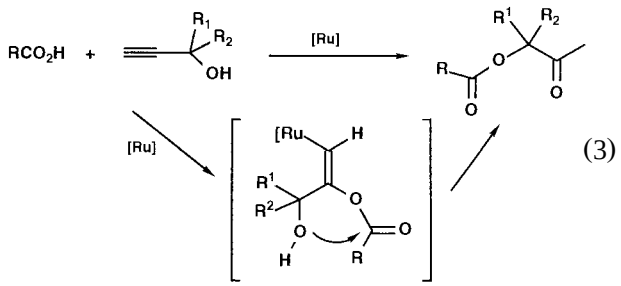
dition of carboxylates to terminal alkynes to afford (*Z*)-alk-1-en-1-yl esters in high yields [62–64].



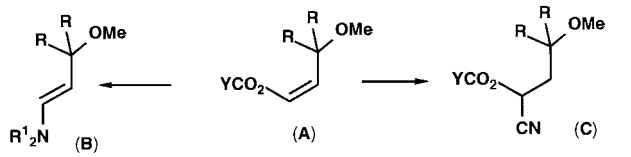
(2)

The utilization of the functional propargyl alcohol revealed that the presence of the hydroxy group had a strong influence on the reaction as it orientated the addition of the carboxylate to the internal C(2) carbon of the triple bond and allowed the formation of β-keto-esters via an intramolecular transesterification whatever the type of catalyst, (arene)$RuCl_2(PR_3)$ (**I**), $[Ru(O_2CH)(CO)_2(PR_3)]_2$ or (dppb)$Ru(CH_2CMeCH_2)_2$ **II** (Eq. (3)) [65–67].

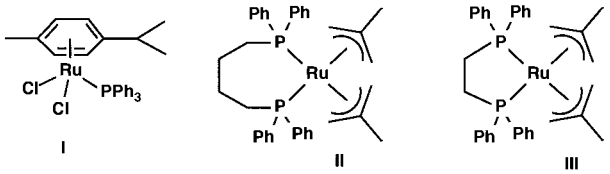


(3)

To elucidate the influence of the functional group at the α-position of the C≡C triple bond on the regioselectivity of the addition, the catalytic activation was performed with *O*-protected propargylic derivatives in the presence of various ruthenium catalysts in an attempt to selectively produce the functional allyl ethers $R^1CO_2CH{=}CHCR_2OMe$ (**A**), which have potential for the synthesis of enamines (**B**) [68] and α-cyanoesters (**C**) [69].



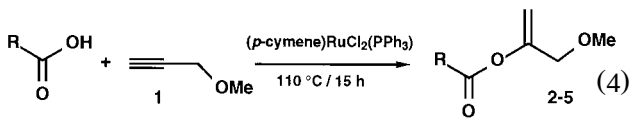
We now report the study of the catalytic activation of propargylic ethers promoted by ruthenium catalysts in the series (arene)$RuCl_2(PR_3)$ (**I**) and (diphosphine)Ru(bis(2-methylpropenyl) (**II** and **III**) complexes. We show that the protection of prop-2-yn-1-ols as ether derivatives makes possible the regioselective addition of carboxylates to either the terminal or the internal carbon atom of the triple bond, depending on the nature of the catalyst, and offers a selective access to the functionalised olefins $RCO_2C(=CH_2)CR^1R^2OMe$ (Eq. (4)) or $RCO_2CH{=}CHCR^1R^2OMe$ (Eq. (6)).



2. Results and discussion

2.1. Regioselective synthesis of 1-methoxyprop-2-en-2-yl esters

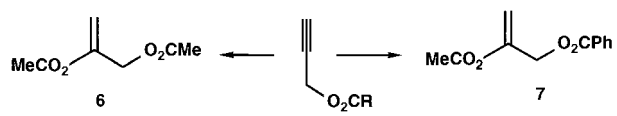
The addition of carboxylic acids to methyl prop-2-ynyl ether **1** in toluene at 110°C for 15 h in the presence of $RuCl_2(PPh_3)$(*p*-cymene) **I** as catalyst led to the formation of the esters **2–5** in 73–90% yields (Eq. (4)). The reaction appeared to be general and could be applied to *N*-protected amino acids for the preparation of optically pure enol ester as exemplified by the obtention of compound **5** from the natural (L)-alanine derivative.



(4)

R= Ph (**2**) 73% ; iPr (**3**) 80% ; $PhCH_2OC(O)NHCH_2$ (**4**) 90% ; (L)-^{t}BuOC(O)NHCHMe (**5**) 87%

The protection of the hydroxy group of the alkynol via an ether group does not change the regioselectivity of the addition of the carboxylate to the triple bond with catalyst **I** which is specific of the addition to the C(2) carbon atom of terminal triple bonds. However, the reaction requires a higher temperature (110°C) than from prop-2-yn-1-ols (65°C). It is noteworthy that the addition of carboxylic acids to the triple bond to give a functional enol ester is also possible when the hydroxy group is protected by an ester group. Thus, the addition of acetic acid to propargyl acetate and propargyl benzoate at 100°C for 15 h in the presence of 1 mol% of (*p*-cymene)$RuCl_2(PMe_3)$ led to the corresponding 1-acetoxyprop-2-en-2-yl (**6**) and 1-benzoylprop-2-en-2-yl (**7**) acetates in 93 and 60% yield, respectively.

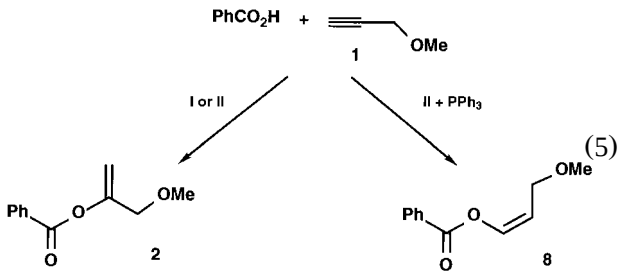


The efficiency of another catalytic system based on bis(η^5-cyclooctadienyl)Ru/maleic anhydride/trial-

kylphosphine for the Markovnikov addition of carboxylic acids to propynyl ethers, acetates and carbonates has also been demonstrated [70,71].

2.2. Regio- and stereoselective synthesis of 3-methoxyprop-1-en-1-yl esters

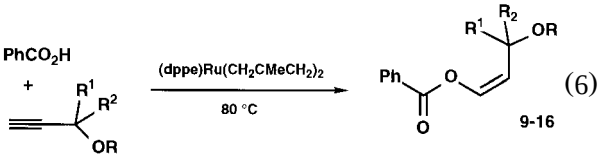
We had previously shown that (dppb)Ru(2-methylpropenyl)$_2$ **II** was the catalyst precursor of choice to promote the regioselective addition of carboxylic acids to the C(1) carbon atom of the triple bond of terminal alkynes such as phenylacetylene or hex-1-yne and conjugated enynes [62–64]. This catalyst was evaluated in the activation of HC≡CCH$_2$OMe towards the addition of carboxylic acids. Benzoic acid reacted with **1** in toluene at 65°C for 20 h in the presence of 1 mol% of **II** to give the enol ester **2** as the main product in 73% isolated yield and 96% selectivity (Eq. (5)). The regioselectivity of this reaction could be completely reversed by adding 1 mol% of PPh_3 to the catalytic system and 96% yield of (*Z*)-3-methoxyprop-1-en-1-yl benzoate **8** was obtained after 2.5 h at 80°C (Eq. (5)).



(5)

The influence of the addition of PPh_3 has an effect on both the regioselectivity and the rate of the reaction. The utilization of this catalytic system based on the association of (dppb)Ru(2-methylpropenyl)$_2$ **II** and PPh_3 (1–1 mol%) **2** with aliphatic carboxylic acids did not lead to alk-1-en-1-yl esters **8** but selectively to alk-1-en-2-yl esters, and was not efficient enough to make possible the addition of benzoic acid to more bulky propargylic ethers. For instance, the addition of benzoic acid to 4-ethyl-3-methoxyoct-1-yne in the presence of **II**/PPh_3 (1–1 mol%) led to the (*Z*)-benzoate **9** (Table 1), but with a poor yield of 22% after 22 h at 80°C.

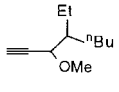
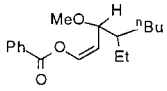
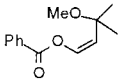
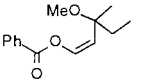
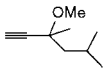
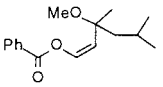
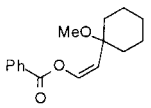
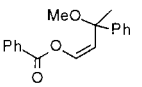
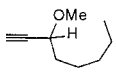
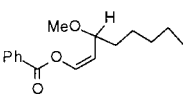
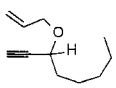
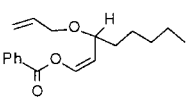
A drastic improvement of this reaction resulted from the use of (1,2-bis(diphenylphosphino)ethane)Ru(2-methylpropenyl)$_2$ **III** as catalyst precursor without any additional phosphine. Thus, the reaction carried out at 80°C for 4 h in the presence of 1 mol% of **III**, led to a complete conversion of the starting reagents and the isolation of the sole (*Z*)-benzoate **9** in 81% yield (Eq. (6), Table 1).



(6)

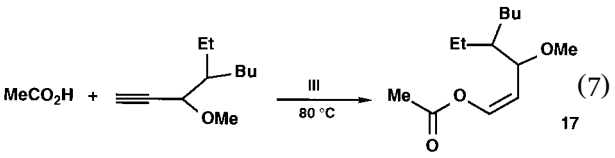
The activity of catalyst **III** for the addition of benzoic acid to a variety of propargylic ethers was studied. Propargyl ethers were converted into (*Z*)-3-methoxyalk-1-en-1-yl benzoates **9–15** and the (*Z*)-3-allyloxyalk-1-en-1-yl benzoate **16** in good yields and high regio- and stereoselectivities (Table 1). The use of the catalyst precursor **III** also made possible the addition of the less reactive acetic acid to selectively give **17** in 50% yield (Eq. (7)). These compounds could find applications in organic synthesis as they bear a leaving allylic ether group, which is known to be easily activated by palladium(0) complexes, and an enol ester group which can

Table 1
Synthesis of (*Z*)-enol benzoates from propargylic ethers and benzoic acid[a]

Propynyl ether	Time h	Product		Yield[b] %	Selectivity[c] %
	4		**9**	81	99
	21		**10**	86	94
	5		**11**	73	99
	19		**12**	74	98
	21		**13**	58	99
	5		**14**	95	98
	2		**15**	98	95
	3		**16**	96	99

[a] Reactions were carried out by using 10 mmol of benzoic acid, 10 mmol of propargylic ether and 0.1 mmol of complex **III** at 80°C in toluene under dinitrogen.
[b] Isolated yield.
[c] Selectivity is ((*Z*)-isomer/total enol esters)×100.

react with secondary amines to give functionalised enamines [68] or nitriles [69].



(7)

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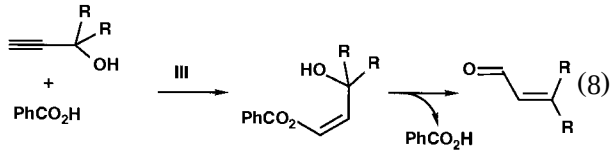
We have recently shown that the anti-Markovnikov addition could even take place in the case of free alkynols as 3-hydroxyprop-1-en-1-yl esters could be generated by the reaction of benzoic acid with propargylic alcohols in the presence of the same ruthenium catalyst precursor **III**. However, in this case, the hydroxylated enol esters were very reactive and they easily released the acid and an enal either upon thermal treatment or elution over silicagel, and the overall reaction constitutes an excellent method to isomerise prop-2-yn-1-ols into conjugated unsaturated aldehydes (Eq. (8)) [72].



(8)

3. Conclusion

The activation of the triple bond of propargylic ethers by ruthenium complexes towards the addition of carboxylic acids has been achieved and both regioselectivities have been controlled by changing the nature of the catalyst precursor. This catalytic regioselective reaction gives access to allylic ethers bearing an ester functionality: Either $RCO_2C(=CH_2)CR^1R^2OR^3$ with (*p*-cymene)$RuCl_2(PR_3)$ (**I**) or $RCO_2CH=CHCR^1R^2OR^3$ with (dppe)Ru(methallyl)$_2$ (**III**) catalyst precursor. It represents a new example of a reaction which satisfies the atom economy criteria [73]. The presence of the oxygen atom at the propargylic position does not force the Markovnikov addition of the carboxylate to the C(2) carbon atom of the terminal triple bond, as suggested by the first experiments with catalysts **I** and **II**. Indeed, we have shown that the addition to C(1) always requires the presence of a bidentate diphosphine ligand coordinated to the ruthenium(II) centre but its nature depends on that of the substrate: The anti-Markovnikov addition to simple alkynes and enynes can be performed with dppb as ligand [62–64], but the above results show that the use of dppe becomes compulsory for the activation of propargylic alcohols [72] and their ether derivatives. At this stage, the mechanism is not established and only suggestions can be made. In previous reactions with non-oxygenated alkynes [57,63], we have made clear that the formation of enol esters does not take place via insertion of the C≡C bond into a (carboxylate) O–Ru bond. We can postulate that an external addition of the carboxylate occurs at the C≡C bond activated by coordination to the ruthenium centre. The $(Ph_2PCH_2CH_2PPh_2)$Ru moiety might allow an interaction of the metal with both the triple bond and the oxygen atom of the ether functionality in $HC\equiv CCR_2OMe$ or $HC\equiv CCR_2OH$ [72] so that the approach of the carboxylate at the carbon (1) of the triple bond is favoured. On the other hand, the $(Ph_2P(CH_2)_4PPh_2)$Ru moiety is distorted from planarity and this might have an effect on the coordination of $HC\equiv CCR_2OMe$ which prevents the addition at carbon (1) and preferentially orientates the addition to carbon (2) of the terminal alkyne.

4. Experimental section

*4.1. Preparation of 1-methoxyprop-2-en-2-yl esters **2–5***

20 mmol of carboxylic acid, 24 mmol of methyl prop-2-ynyl ether and 0.2 mmol of (*p*-cymene)$RuCl_2(PPh_3)$ were stirred for 15 h at 110°C in 10 ml of toluene under dinitrogen. After evaporation of the solvent, the esters **2–5** were isolated by Kugelrohr distillation under reduced pressure or chromatography over silicagel with diethylether as eluent.

*4.2. 1-methoxyprop-2-en-2-yl benzoate (**2**)*

2.8 g (73%) of the ester **2** were isolated as a colourless liquid by Kugelrohr distillation (100°C/2.5 mm Hg). ^{1}H NMR ($CDCl_3$), 300.133 MHz) δ: 3.39 (s, 3H, Me); 4.09 (s, 2H, CH_2O); 5.10 (d, 1H, $^2J = 1.7$ Hz, $=CHH$); 5.12 (d, 1H, $^2J = 1.7$ Hz, $=CHH$); 7.33 (m, 2H, Ph); 7.59 (m, 1H, Ph); 8.08 (m, 2H, Ph). IR: 1735 (C=O), 1675 (C=C) cm^{-1}. Anal. calcd. for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.79; H, 6.31. MS (*m*/*z*) 192 (M^+).

*4.3. 1-methoxyprop-2-en-2-yl isobutanoate (**3**)*

2.25 g (80%) of the ester **3** were isolated as a colourless liquid by Kugelrohr distillation (70°C/2.5 mm Hg). ^{1}H NMR ($CDCl_3$), 300.133 MHz) δ: 1.15 (d, 3H, $^3J = 7.0$ Hz, *Me*CH); 1.45 (d, 3H, $^3J = 7.0$ Hz, *Me*CH); 2.70 (m, 1H, Me_2CH); 3.28 (s, 3H, MeO); 3.92 (s, 2H, CH_2O); 4.95 (s, 2H, $=CH_2$). IR: 1735 (C=O), 1672 (C=C) cm^{-1}. Anal. calcd. for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.79; H, 8.93. MS (*m*/*z*) 158 (M^+).

*4.4. 1-methoxyprop-2-en-2-yl N-(benzyloxycarbonyl)glycinate (**4**)*

5.02 g (90%) of the ester **4** were isolated as a yellow oil after purification over silicagel. ^{1}H NMR ($CDCl_3$), 300.133 MHz) δ: 3.34 (s, 3H, MeO); 3.90 (s, 2H, CH_2OMe); 3.98 (d, 2H, $^3J = 5.2$ Hz, CH_2N); 4.96 (s, 2H, $=CH_2$); 5.08 (s, 2H, CH_2Ph); 5.64 (t, 1H, $^3J = 5.2$ Hz, NH); 7.30 (s, 5H, Ph). IR: 1765 (C=O), 1725 (C=O), 1675 (C=C) cm^{-1}. Anal. calcd. for $C_{14}H_{17}NO_5$: C, 60.21; H, 6.14; N, 5.02. Found: C, 60.24; H, 6.17; N, 5.07. MS (m/z) 279 (M^+).

*4.5. 1-methoxyprop-2-en-2-yl N-(tert-butoxycarbonyl)-L-alaninate (**5**)*

4.52 g (87%) of the ester **5** were isolated as a yellow oil after purification over silicagel. ^{1}H NMR ($CDCl_3$), 300.133 MHz) δ: 1.42 (s, 9H, Me_3C); 1.49 (d, 3H, $^3J = 7.1$ Hz, *Me*CH); 3.28 (s, 3H, MeO); 3.90 and 3.91 (2s, 2H, CH_2OMe); 4.32 (m, 1H, C*H*Me); 4.93 (d, 1H, $^2J = 2.4$ Hz, =C*H*H); 4.98 (m, 1H, =CH*H*); 5.12 (br s, 1H, NH). IR: 1770 (C=O), 1715 (C=O), 1675 (C=C) cm^{-1}. Anal. calcd. for $C_{12}H_{21}NO_5$: C, 55.58; H, 8.16; N, 5.40. Found: C, 55.78; H, 8.20; N, 5.37. MS (m/z) 203 (M–CH_2=CMe_2^+).

*4.6. (Z)-3-methoxyprop-1-en-1-yl benzoate (**8**)*

From 1.22 g (10 mmol) of benzoic acid, 1.1 ml of methyl prop-2-ynyl ether, 64 mg (0.1 mmol) of bis(2-methylpropenyl)(dppb)Ru and 26 mg (0.1 mmol) of triphenylphosphine at 80°C for 2.5 h, 1.4 g (73%) of the ester **8** was isolated after purification over silicagel. ^{1}H NMR ($CDCl_3$), 300.133 MHz δ: 3.30 (s, 3H, MeO); 4.22 (dd, 2H, $^3J = 6.7$ Hz, $^4J = 1.5$ Hz, CH_2O); 5.12 (dt, 1H, $^3J = 6.5$ and 6.7 Hz, =C*H*CH_2); 7.3–7.6 (m, 4H, Ph + =CHO); 8.00 (m, 2H, Ph). IR: 1735 (C=O), 1670 (C=C) cm^{-1}. Anal. calcd. for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.79; H, 6.31. MS (m/z) 192 (M^+).

*4.7. Preparation of (Z)-3-methylprop-1-en-1-yl esters **9–17***

10 mmol of carboxylic acid, 10 mmol of propynyl ether and 0.1 mmol of (dppe)Ru(CH_2CMeCH_2)$_2$ were stirred at 80°C in toluene under dinitrogen. After evaporation of the solvent, the esters **9–17** were isolated by Kugelrohr distillation under reduced pressure or chromatography over silicagel.

*4.8. (Z)-4-ethyl-3-methoxyoct-1-en-1-yl benzoate (**9**)*

2.59 g (81%) of the ester **9** were isolated as a colourless liquid by Kugelrohr distillation (177°C/3 mm Hg). ^{1}H NMR ($CDCl_3$), 300.133 MHz) δ: 0.83–0.96 (m, 6H, 2 Me); 1.23–1.53 (m, 9H, 4 CH_2 + C*H*CH_2); 3.32 (s, 3H, OMe); 4.32 (dd, 0.5H, $^3J = 8.9$ and 4.6 Hz, MeOC*H*); 4.34 (dd, 0.5H, $^3J = 8.9$ and 4.6 Hz, MeOC*H*); 4.95 (ddd, 1H, $^3J = 9.5$ and 6.5 Hz, $^4J = 0.5$ Hz, =C*H*CH(OMe)); 7.45–8.11 (m, 6H, Ph + =CHO). IR: 1735 (C=O), 1670 (C=C) cm^{-1}. MS (m/z) 191 (M–CH(Et)$C_4H_9^+$).

*4.9. (Z)-3-methoxy-3-methylbut-1-en-1-yl benzoate (**10**)*

1.80 g (86%) of the ester **10** was isolated as a colourless liquid by Kugelrohr distillation (145°C/3 mm Hg). ^{1}H NMR ($CDCl_3$), 300.133 MHz) δ: 1.50 (s, 6H, Me_2C); 3.25 (s, 3H, OMe); 4.94 (d, 1H, $^3J = 7.3$ Hz, =CH); 7.33 (d, 1H, $^3J = 7.3$ Hz, OCH=); 7.44–8.12 (m, 5H, Ph). IR: 1765 (C=O), 1670 (C=C) cm^{-1}. MS (m/z) 205 (M–Me^+).

*4.10. (Z)-3-methoxy-3-methylpent-1-en-1-yl benzoate (**11**)*

1.71 g (73%) of the ester **11** was isolated as a colourless liquid by Kugelrohr distillation (145°C/3 mm Hg). ^{1}H NMR ($CDCl_3$), 300.133 MHz) δ: 0.91 (t, 3H, $^3J = 7.5$ Hz, *Me*CH_2); 1.46 (s, 3H, MeC); 1.74 (qd, 2H, $^3J = 5.7$ Hz, $^4J = 1.7$ Hz, CH_2); 3.21 (s, 3H, OMe), 4.84 (d, 1H, $^3J = 7.3$ Hz, =CH); 7.34 (d, 1H, $^3J = 7.3$ Hz, OCH=); 7.43–8.10 (m, 5H, Ph). IR: 1735 (C=O), 1668 (C=C) cm^{-1}. MS (m/z) 202 (M–$MeOH^+$).

*4.11. (Z)-3,5-dimethyl-3-methoxyhex-1-en-1-yl benzoate (**12**)*

2.52 g (74%) of the ester **12** were isolated as a colourless liquid by Kugelrohr distillation (140°C/3 mm Hg). ^{1}H NMR ($CDCl_3$), 300.133 MHz) δ: 0.95 (d, 3H, $^3J = 6.6$ Hz, MeCH*Me*); 0.97 (d, 3H, $^3J = 6.6$ Hz, *Me*CHMe); 1.52 (s, 3H, MeC); 1.64 (dd, 1H, $^2J = 14.1$ Hz, $^3J = 6.4$ Hz, C*H*HCHMe_2); 1.72 (dd, 1H, $^2J = 14.1$ Hz, $^3J = 6.4$ Hz, CH*H*CHMe_2); 1.83 (m, 1H, Me_2CH); 3.22 (s, 3H, OMe); 4.92 (d, 1H, $^3J = 7.4$ Hz, =CH); 7.33 (d, 1H, $^3J = 7.4$ Hz, OCH=); 7.46–8.12 (m, 5H, Ph). IR: 1738 (C=O), 1667 (C=C) cm^{-1}.

*4.12. (Z)-2-(1-methoxycyclohexyl)ethen-1-yl benzoate (**13**)*

1.50 g (58%) of the ester **13** was isolated as a colourless liquid by Kugelrohr distillation (170°C/3 mm Hg). ^{1}H NMR ($CDCl_3$), 300.133 MHz) δ: 1.40–1.87 (m, 10H, C_5H_{10}); 3.23 (s, 3H, OMe); 4.77 (d, 1H, $^3J = 7.3$ Hz, =CH); 7.38 (d, 1H, $^3J = 7.3$ Hz, OCH=); 7.44–8.13 (m, 5H, Ph). IR: 1735 (C=O), 1672 (C=C) cm^{-1}.

*4.13. (Z)-3-methoxy-3-phenylbut-1-en-1-yl benzoate (**14**)*

2.67 g (95%) of the ester **14** were isolated as a colourless liquid by chromatography over silicagel (hexane–ether). ^{1}H NMR ($CDCl_3$), 300.133 MHz) δ: 1.79 (s, 3H, Me); 3.21 (s, 3H, OMe); 5.27 (d, 1H, $^3J = 7.2$ Hz, =CH); 7.22–7.73 (m, 11H, 2 Ph + OCH=). IR: 1736 (C=O), 1668 (C=C) cm^{-1}. MS (m/z) 161 (M–$PhCO_2^+$)

*4.14. (Z)-3-methoxyoct-1-en-1-yl benzoate (**15**)*

1.29 g (98%) of the ester **15** was isolated as a colourless liquid by Kugelrohr distillation (190°/3 mm Hg). ^{1}H NMR ($CDCl_3$), 300.133 MHz) δ: 0.84 (t, 3H, $^3J = 6.9$ Hz, *Me*CH_2); 1.27–1.57 (m, 6H, (CH_2)$_3$Me); 1.67 (m, 2H, C(OMe)CH_2); 3.31 (s, 3H, OMe); 4.31 (dt, 1H, $^3J = 9.1$ and 6.2 Hz, HC(OMe); 4.88 (dd, 1H, $^3J = 9.2$ and 6.5 Hz, =CH); 7.42–8.08 (m, 6H, Ph + OCH=). IR: 1738 (C=O), 1665 (C=C) cm^{-1}. MS (m/z) 191 (M–$(CH_2)_4Me^+$).

*4.15. (Z)-3-allyloxyoct-1-en-1-yl benzoate (**16**)*

3.16 g (96%) of the ester **16** were isolated as a colourless liquid by Kugelrohr distillation (180°C/3 mm Hg.) ^{1}H NMR ($CDCl_3$), 300.133 MHz) δ: 0.85 (t, 3H, $^3J = 6.8$ Hz, Me); 1.17–1.32 (m, 4H, $(CH_2)_2$); 1.40–1.50 (m, 2H, CH_2); 1.56–1.75 (m, 2H, CH_2); 3.88 (ddt, 1H, $^2J = 12.8$ Hz, $^3J = 6.1$ Hz, $^4J = 1.3$ Hz, *H*HCCH=CH_2); 4.08 (ddt, 1H, $^2J = 12.8$ Hz, $^3J = 5.1$ Hz, $^4J = 1.3$ Hz, H*H*CCH=CH_2); 4.50 (dtd, 1H, $^3J =$ 9.3 and 6.4 Hz, $^4J = 0.8$ Hz, =CH–C*H*O); 4.93 (dd, 1H, $^3J = 9.3$ and 6.4 Hz, =CH); 5.12 (ddt, 1H, $^2J = 1.3$ Hz, $^3J = 10.3$ Hz, $^4J = 1.8$ Hz, CH=C*H*H); 5.22 (ddt, 1H, $^2J = 1.3$ Hz, $^3J = 17.2$ Hz, $^4J = 1.8$ Hz, CH=CH*H*); 5.91 (dddd, 1H, $^3J = 5.1$, 6.1, 10.3 and 17.2 Hz, CH_2C*H*=CH_2); 7.43–8.08 (m, 6H, Ph + OCH=). IR: 1735 (C=O), 1672 and 1684 (C=C) cm^{-1}. MS (m/z) 217 (M–$(CH_2)_4Me^+$).

*4.16. (Z)-4-ethyl-3-methoxyoct-1-en-1-yl acetate (**17**)*

1.14 g (50%) of the ester **17** was isolated as a colourless liquid by Kugelrohr distillation (125°C/3 mm Hg). ^{1}H NMR ($CDCl_3$), 300.133 MHz) δ: 0.82–0.94 (m, 6H, 2 Me); 1.03–1.47 (m, 9H, 4 CH_2 + C*H*CH_2); 2.01 (s, 3H, MeCO); 3.18 (s, 3H, OMe); 4.06 (dd, 1H, $^3J = 5.2$ and 9.3 Hz, MeOCH); 4.73 (dd, 1H, $^3J = 6.4$ and 9.3 Hz, =CH); 7.18 (d, 1H, $^3J = 6.4$ Hz, OCH=). IR: 1736 (C=O), 1666 (C=C) cm^{-1}.

References

[1] B.M. Trost, Chem. Ber. 129 (1996) 1313.
[2] M. Furber, In: Comprehensive Organic Functional Group Transformations, A.R. Katritzky, O. Meth-Cohn, C.W. Rees (Eds.), Pergamon, Cambridge, Vol. 1, p. 997.
[3] C. Bruneau, P.H. Dixneuf, In: Comprehensive Organic Functional Group Transformations, A.R. Katritzky, O. Meth-Cohn, C.W. Rees (Eds.), Pergamon, Cambridge, Vol. 1, p. 953.
[4] C. Bianchini, P. Frediani, D. Masi, M. Peruzzini, F. Zanobini, Organometallics 13 (1994) 4616.
[5] C. Slugovc, K. Mereiter, E. Zobetz, R. Schmid, K. Kirchner, Organometallics 15 (1996) 5275.
[6] C.S. Yi, N. Liu, Organometallics 15 (1996) 3968.
[7] B.M. Trost, C. Chan, G. Rühter, J. Am. Chem. Soc. 109 (1987) 3486.
[8] H.J. Heeres, J. Nijhoff, J.H. Teuben, Organometallics 12 (1993) 2609.
[9] Y. Wakatsuki, N. Yamazaki, N. Kumegawa, P.S. Johar, Bull. Chem. Soc. Jpn. 66 (1993) 987.
[10] B.M. Trost, M.T. Sorum, C. Chan, A.E. Harms, G. Rühter, J. Am. Chem. Soc. 119 (1997) 698.
[11] K.P.C. Vollhardt, Angew. Chem. Int. Ed. Engl. 23 (1984) 539.
[12] A.T. McNichols, P.J. Stang, Synlett (1992) p. 971.
[13] G.P. Chiusoli, M. Costa, Z. Zhou, Gazz. Chim. Ital. 122 (1992) 441.
[14] B.M. Trost, A.F. Indolese, T.J.J. Müller, B. Treptow, J. Am. Chem. Soc. 117 (1995) 615.
[15] T.A. Mitsudo, H. Naruse, T. Kondo, Y. Ozaki, Y. Watanabe, Angew. Chem. Int. Ed. Engl. 33 (1994) 580.
[16] B.M. Trost, R.J. Kulawiec, J. Am. Chem. Soc. 114 (1992) 5579.
[17] S. Dérien, D. Jan, P.H. Dixneuf, Tetrahedron 52 (1996) 5511.
[18] B.M. Trost, G.T. Tanoury, M. Lautens, C. Chan, D.T. MacPherson, J. Am. Chem. Soc. 116 (1994) 4255.
[19] N. Chatani, T. Morimoto, T. Muto, S. Murai, J. Am. Chem. Soc. 116 (1994) 6049.
[20] A. Kinoshita, M. Mori, Synlett (1994) p. 1020.
[21] S.-I. Ikeda, K. Kondo, Y. Sato, J. Org. Chem. 61 (1996) 8248.
[22] B.M. Trost, G. Kottirsch, J. Am. Chem. Soc. 112 (1990) 2816.
[23] M. Yamaguchi, K. Omata, M. Hirama, Tetrahedron Lett. 35 (1994) 5689.
[24] M. Yamaguchi, Y. Kido, K. Omata, M. Hirama, Synlett (1995) p. 1181.
[25] C. Stephan, C. Munz, H. tom Dieck, J. Organomet. Chem. 468 (1994) 273.
[26] D. Llerena, C. Aubert, M. Malacria, Tetrahedron Lett. 37 (1996) 7027.
[27] A. Padwa, K.E. Krumpe, K.M. Kassir, J. Org. Chem. 57 (1992) 4940.
[28] M.P. Doyle, M. Protopova, P. Müller, D. Ene, E.A. Shapiro, J. Am. Chem. Soc. 116 (1994) 8492.
[29] N. Monteiro, J. Goré, B. Van Hemelryck, G. Balme, Synlett (1994) p. 447.
[30] R. Stammler, M. Malacria, Synlett (1994) p. 92.
[31] J. Tsuji, T. Mandai, Angew. Chem. Int. Ed. Engl. 34 (1995) 2589.
[32] D. Chemin, G. Linstrumelle, Tetrahedron 48 (1992) 1943.
[33] M. Alami, F. Ferri, G. Linstrumelle, Tetrahedron Lett. 34 (1993) 6403.
[34] O. Lavastre, L. Ollivier, P.H. Dixneuf, Tetrahedron 52 (1996) 5495.
[35] J. Tsuji, M. Takahashi, T. Takahashi, Tetrahedron Lett. 21 (1980) 849.
[36] L. Delaude, A.M. Masdeu, H. Alper, Synthesis (1994) p. 1149.
[37] E. Drent, P. Arnoldy, P.H.M. Budzelaar, J. Organomet. Chem. 475 (1994) 57.
[38] E. Negishi, C. Copéret, S. Ma, S.-Y. Liou, F. Liu, Chem. Rev. 96 (1996) 365.
[39] B. Gabriele, G. Salerno, F. De Pascali, M. Costa, G.P. Chiusoli, J. Chem. Soc. 1 (1997) 147.
[40] T. Murat, Y. Mizobe, H. Gao, Y. Ishii, T. Wakabayashi, F. Nakano, T. Tanase, S. Yano, M. Hidai, I. Echizen, H. Nanikawa, S. Motomura, J. Am. Chem. Soc. 116 (1994) 3389.

[41] W. Baidossi, M. Lahav, J. Blum, J. Org. Chem. 62 (1997) 669.
[42] N. Menashe, Y. Shvo, J. Org. Chem. 58 (1993) 7434.
[43] Y. Fukuda, K. Utimoto, J. Org. Chem. 56 (1991) 3729.
[44] A. Arcadi, S. Cacchi, R.C. Larock, F. Marinelli, Tetrahedron Lett. 34 (1993) 2813.
[45] B. Seiller, C. Bruneau, P.H. Dixneuf, Tetrahedron 51 (1995) 13089.
[46] F.T. Luo, I. Schreuder, R.T. Wang, J. Org. Chem. 57 (1992) 2213.
[47] R.C. Larock, E.K. Yum, J. Am. Chem. Soc. 113 (1991) 6689.
[48] Y. Li, P.F. Fu, T.J. Marks, Organometallics 13 (1994) 439.
[49] M. Cavicchioli, D. Bouyssi, J. Goré, G. Balme, Tetrahedron Lett. 37 (1996) 1429.
[50] V. Dalla, P. Pale, Tetrahedron Lett. 35 (1994) 3525.
[51] D.M.T. Chan, T.B. Marder, D. Milstein, N.J. Taylor, J. Am. Chem. Soc. 109 (1987) 6385.
[52] R. Mahé, Y. Sasaki, C. Bruneau, P.H. Dixneuf, J. Org. Chem. 54 (1989) 1518.
[53] C. Bruneau, P.H. Dixneuf, J. Mol. Catal. 74 (1992) 97.
[54] C. Ruppin, P.H. Dixneuf, Tetrahedron Lett. 27 (1986) 6323.
[55] C. Ruppin, P.H. Dixneuf, S. Lécolier, Tetrahedron Lett. 29 (1988) 5365.
[56] K. Philippot, D. Devanne, P.H. Dixneuf, J. Chem. Soc., Chem. Commun. (1990) p. 1199.
[57] C. Bruneau, M. Neveux, Z. Kabouche, P.H. Dixneuf, Synlett (1991) p. 755.
[58] C. Bruneau, P.H. Dixneuf, J. Chem. Soc., Chem. Commun. (1997) p. 507.
[59] Z. Kabouche, C. Bruneau, P.H. Dixneuf, Tetrahedron Lett. 32 (1991) 5359.
[60] M. Neveux, C. Bruneau, S. Lécolier, P.H. Dixneuf, Tetrahedron 49 (1993) 2629.
[61] M. Neveux, B. Seiller, F. Hagedorn, C. Bruneau, P.H. Dixneuf, J. Organomet. Chem. 451 (1993) 133.
[62] H. Doucet, J. Höfer, C. Bruneau, P.H. Dixneuf, J. Chem. Soc. Chem. Commun. (1993) p. 850.
[63] H. Doucet, B. Martin-Vaca, C. Bruneau, P.H. Dixneuf, J. Org. Chem. 60 (1995) 7247.
[64] H. Doucet, J. Höfer, N. Derrien, C. Bruneau, P.H. Dixneuf, Bull. Soc. Chim. Fr. 133 (1996) 939.
[65] D. Devanne, C. Ruppin, P.H. Dixneuf, J. Org. Chem. 53 (1988) 925.
[66] C. Bruneau, Z. Kabouche, M. Neveux, B. Seiller, P.H. Dixneuf, Inorg. Chim. Acta 222 (1994) 155.
[67] C. Darcel, C. Bruneau, P.H. Dixneuf, G. Neef, J. Chem. Soc. Chem. Commun. (1994) p. 333.
[68] H. Doucet, C. Bruneau, P.H. Dixneuf, Synlett (1997) p. 807.
[69] H. Doucet, C. Bruneau, P.H. Dixneuf, unpublished results.
[70] T.A. Mitsudo, Y. Hori, Y. Yamakawa, Y. Watanabe, J. Org. Chem. 52 (1987) 2230.
[71] Y. Hori, T.A. Mitsudo, Y. Watanabe, Tetrahedron Lett. 27 (1986) 5389.
[72] M. Picquet, C. Bruneau, P.H. Dixneuf, J. Chem. Soc. Chem. Commun. (1997) p. 1201.
[73] B.M. Trost, Angew. Chem. Int. Ed. Engl. 34 (1995) 259.