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Preparation of tuneable $(Ph_2P(CH_2)_nPPh_2)Ru(2\text{-methylpropenyl})_2$ catalysts and their use for the stereoselective synthesis of dienyl esters

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Summary — New $(Ph_2P(CH_2)_nPPh_2)Ru(2\text{-methylpropenyl})_2$ complexes have been prepared and their catalytic activity has made possible the regioselective anti-Markovnikov and stereoselective *trans*-addition of carboxylic acids to enynes and the straightforward access to (*Z*)-alka-1,3-dien-1-yl esters.

ruthenium catalyst / dienyl ester / activation of alkyne

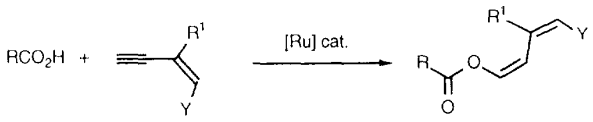
Résumé — Préparation de catalyseurs $(Ph_2P(CH_2)_nPPh_2)Ru(2\text{-méthylpropenyl})_2$ modulables et leur utilisation pour la synthèse stéréosélective d'esters de diényle. *De nouveaux complexes $(Ph_2P(CH_2)_nPPh_2)Ru(2\text{-méthylpropényl})_2$ ont été préparés et leur activité catalytique a permis l'addition régio et stéréosélective de type anti-Markovnikov d'acides carboxyliques aux énynes donnant un accès direct aux esters de (Z)-alka-1,3-diényle.*

catalyseur du ruthénium / ester de diényle / activation d'alcyne

Introduction

Ruthenium complexes containing allylic ligands have recently found useful applications in organic synthesis. Allylic ruthenium(IV) complexes have emerged as new catalysts for ring-opening polymerization of cyclic olefins [1], allylation of nitrogen and carbon nucleophiles [2], and C-C coupling of alkynes with allyl alcohol [3]. Moreover, chiral (diphosphine)Ru(2-methylpropenyl)$_2$ complexes have been used as catalyst precursors for enantioselective hydrogenation of unsaturated carbonyl and olefinic substrates [4, 5]. We have shown that (diphosphine)Ru(2-methylpropenyl)$_2$ complexes are efficient catalysts for the preparation of dienyl carbamates via the nucleophilic addition of ammonium carbamates to the triple bond of enynes [6]. The remarkable catalytic activity of these catalysts have also been exploited to selectively produce (*Z*)-alk-1-en-1-yl esters from carboxylic acids and terminal alkynes [7], whereas under closely related conditions (arene)$RuCl_2(PR_3)$ [8], (cyclooctadienyl)$_2$Ru [9] or $[Ru(O_2CH)(CO)_2(PR_3)]_2$ [10] complexes led to alk-1-en-2-yl esters according to the classical Markovnikov addition. As it is now well established that catalytic reactions involving transition metal catalyst precursors are dramatically influenced by the nature of the ancillary ligands, we have been looking for ruthenium complexes containing labile hydrocarbon ligands and a variety of closely related bidentate diphosphines able to bring slight modifications of the catalytic site and tune its reactivity.

We now describe the preparation of a series of four new $(Ph_2P(CH_2)_nPPh_2)Ru(2\text{-methylpropenyl})_2$ complexes containing diphosphine ligands differentiated only by the length of the hydrocarbon chain linking the two phosphorus atoms (n = 1, 2, 3 and 4), their evaluation towards the activation of enynes, and the utilization of $(Ph_2P(CH_2)_4PPh_2)Ru(2\text{-methylpropenyl})_2$ as an efficient catalyst for the stereoselective access to 1,3-dien-1-yl esters via highly regioselective anti-Markovnikov addition of carboxylic acids to enynes according to equation 1.



(eq 1)

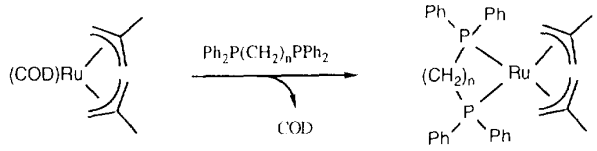
Results and discussion

Preparation of (bis(diphenylphosphino)alkane) (2-methylpropenyl)$_2$ Ru complexes

The preparation of complexes **I**–**IV** was based on the known reaction of 2-methylpropenyl Grignard reagents with the polymeric complex $[(cyclooctadiene)RuCl_2]_n$, which leads to the mononuclear (cyclooctadienyl)Ru-

* Correspondence and reprints

(2-methylpropenyl)$_2$ complex [11]. After reflux in hexane under an inert atmosphere of argon in the presence of a stoichiometric amount of bis(diphenylphosphino)-alkane, complexes **I–IV** were obtained in good yields (eq 2). This methodology is based on the displacement of cyclooctadiene by a phosphorus ligand and has already been reported for phosphites, 1,2-bis(dimethylphosphino)ethane [12], and chiral diphosphines [4, 13]. ^{1}H, ^{13}C and ^{31}P NMR were in good agreement with the expected formulas for compounds **I–IV**, and elemental analyses were satisfactory.



COD : cyclooctadiene

n= 1 (**I**), 85%
n= 2 (**II**), 82%
n= 3 (**III**), 78%
n= 4 (**IV**), 79%

(eq 2)

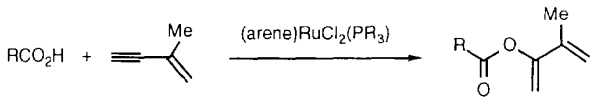
However, it is noteworthy that small modifications of the alkyl chain linking the two diphenylphosphino groups introduce significant steric and electronic effects, as shown by the variations of ^{1}H NMR chemical shifts of the allylic protons and the ^{31}P NMR of the phosphorus nuclei (^{31}P δ(ppm): 13.50 (n = 1), 84.99 (n = 2), 36.76 (n = 3), 44.58 (n = 4)). Such large variations are expected to bring significant differences in the catalytic behavior of these complexes.

Regio- and stereoselective synthesis of dienyl esters

Conjugated dienes, especially functional buta-1,3-diene derivatives, have been shown to be valuable intermediates in synthesis. Butadienyl acetates have been used as dienophiles in Diels–Alder reactions for the construction of aromatic rings [14], the preparation of alkaloids [15] or the access to cyclic aldehydes [16], ketones [17], and nitrogen heterocycles [18]. The γ, δ double bond of 1-acetoxybuta-1,3-diene reacts with chlorosulfonyl isocyanate via [2 + 2]-cycloaddition to give four-membered heterocycles [19] and with functional aryl halides via palladium-catalyzed annulation [20]. Butadien-1-yl acetate is also a reactive monomer leading to useful polymers and copolymers predominantly via 1,4-polymerization [21].

Conjugated dienyl acetates have been prepared by reaction of isopropenyl acetate with unsaturated aldehydes or ketones [22], whereas the direct addition of acetic acid to vinylacetylene catalyzed by mercuric salts or BF_3 made possible the synthesis of 2-acetoxybuta-1,3-diene in low yields [23]. Buta-1,3-dien-1-yl acetates have been obtained under catalytic conditions from butadiene or isoprene and acetic acid in the presence of oxygen in the vapor phase at high temperature (180 °C) [24]. The isomerization of propynylic esters into 1,3-dienyl esters has been carried out in the presence of silver trifluoroacetate [25]. Catalytic carbon–carbon coupling reactions have been used for the synthesis of dienyl acetates via palladium(0)-catalyzed β-vinylation of vinyl acetate with sterically hindered enol triflates [26], or Suzuki coupling of enol acetates of α-bromoketones with alkenyl boronates [27]. Recently, polyenyl esters have been prepared in high yields by O-acylation of O-trimethylsilyl dienyl ethers with acyl fluoride [28].

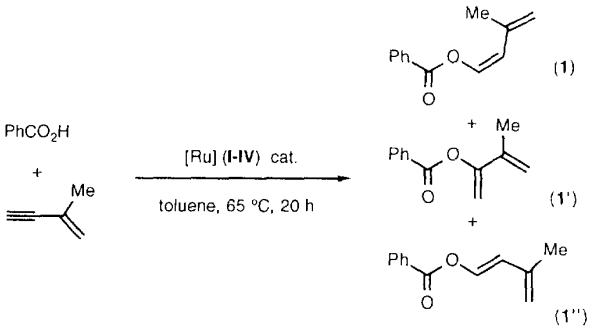
We have already shown that the direct addition of carboxylic acids to enynes catalyzed by (arene)$RuCl_2(PR_3)$ complexes constituted a general method for the access to buta-1,3-dien-2-yl esters in good yields under mild conditions [29] (eq 3).



(eq 3)

On the basis of our previous work on the regio- and stereoselective addition of carboxylic acids to terminal alkynes [7], the synthesis of 1,3-dien-1-yl esters could be considered as starting from enynes in the presence of complexes **I–IV** as catalyst precursors.

Thus, 10 mmol of benzoic acid was treated with 11 mmol of 2-methylbut-1-en-3-yne in the presence of a catalytic amount of complex **I–IV** (1 mol%) in toluene at 65 °C for 20 h to afford dienyl benzoates (eq 4).



(eq 4)

It is noteworthy that the four ruthenium complexes exhibited very different catalytic activities as almost no reaction took place at 65 °C with complex **III**, whereas complexes **I**, **II** and **IV** led to good to excellent conversions of the starting substrates into dienyl benzoates (table I). Complexes **I** and **II** were efficient catalyst precursors for the addition of benzoic acid to 2-methylbut-1-en-3-yne but **I** led to a mixture of the three dienyl esters without selectivity whilst **II** favored the formation of the (Z)-isomer but in moderate yield. By far the most efficient precursor appeared to be complex **IV**, which led to the complete conversion of the starting products via regio- and stereoselective anti-Markovnikov addition of the carboxylic acid to the terminal triple bond of the enyne to afford a 92% yield of 3-methylbuta-1,3-dien-1-yl benzoate containing 99% of the (Z)-isomer, as determined by ^{1}H NMR and gas phase chromatography. The addition to isopropenylacetylene was extended to valeric acid and N-protected phenylalanine,

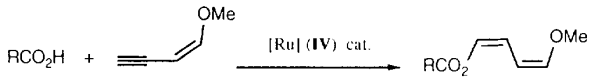
Table I. Synthesis of 3-methylbuta-1,3-dienyl benzoates[a].

Catalyst		*Yield*[b] *(%)*	*Selectivity*[c] *(%)*		
			1 *(%)*	***1′*** *(%)*	***1″*** *(%)*
$(Ph_2P(CH_2)PPh_2)Ru(2\text{-methylpropenyl})_2$	**I**	77	21	60	19
$(Ph_2P(CH_2)_2PPh_2)Ru(2\text{-methylpropenyl})_2$	**II**	69	90	1	9
$(Ph_2P(CH_2)_3PPh_2)Ru(2\text{-methylpropenyl})_2$	**III**	3	52	41	7
$(Ph_2P(CH_2)_4PPh_2)Ru(2\text{-methylpropenyl})_2$	**IV**	92	99	0	1

[a] General conditions: benzoic acid (10 mmol), isopropenylacetylene (11 mmol), complex (0.1 mmol), toluene (5 mL), 65 °C, 20 h. [b] Isolated yields. [c] Selectivity = **1**, **1′** and **1″** ester/(total dienyl esters) × 100.

and allowed the formation of the (*Z*)-dienyl esters **2** and **3** in good yields (table II). The addition of less hindered acids such as acetic or formic acid could not be achieved regioselectively even at 60 °C.

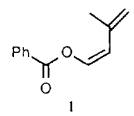
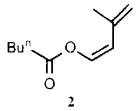
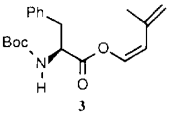
The generality of the reaction was shown by carrying out the catalytic addition of a variety of carboxylic acids to the functional (*Z*)-1-methoxybut-1-en-3-yne containing an additional ether functionality according to eq 5.



(eq 5)

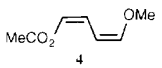
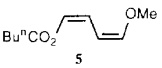
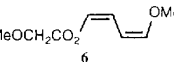
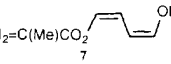
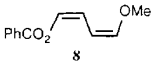
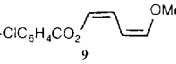
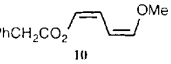
Aliphatic acids, the functional methoxyacetic and methacrylic acids, as well as aromatic acids led to the very stereoselective formation of the new (*Z*,*Z*)-(1-methoxy-4-carboxy)buta-1,3-dienes **4**–**10** under mild conditions (65 °C) with complex **IV** as catalyst (table III). Under these conditions, acetic acid was less reactive (**4**: 53%), but the stereoselectivity was very high. It is noteworthy that the addition was more difficult with an aromatic acid bearing a chloro substituent

Table II. Synthesis of (*Z*)-3-methylbuta-1,3-dien-1-yl esters[a].

Acid	*Temp* *(°C)*	*Time* *(h)*	*Ester*	*Yield*[b] *(%)*	*Selectivity*[c] *(%)*
Benzoic acid	65[d]	20	 **1**	92	99
Valeric acid	45[e]	6	 **2**	77	100
Boc-Phenyl-alanine	65[d]	20	 **3**	62	100

[a] General conditions: acid (10 mmol), isopropenylacetylene (11 mmol), complex **IV** (0.1 mmol). [b] Isolated yields. [c] Selectivity = (*Z*)-isomer/(total dienyl esters) × 100. [d] Toluene (10 mL). [e] Pentane (10 mL). Boc: $Bu^tOC(O)$.

Table III. Synthesis of (*Z*,*Z*)-4-methoxybuta-1,3-dien-1-yl esters[a].

Acid	*Time* *(h)*	*Dienyl ester*	*Yield*[b] *(%)*	*Selectivity*[c] *(%)*
$MeCO_2H$	20	 **4**	53	100
Bu^nCO_2H	19	 **5**	75	98
$MeOCH_2CO_2H$	18	 **6**	69	99
$CH_2{=}C(Me)CO_2H$	19	 **7**	60	97
$PhCO_2H$	18	 **8**	81	98
p-$ClC_6H_4CO_2H$	48	 **9**	68	99
$PhCH_2CO_2H$	20	 **10**	76	100

[a] General conditions: acid (10 mmol), (*Z*)-1-methoxybut-1-en-3-yne (10 mmol), complex **IV** (0.1 mmol), toluene (10 mL), 65 °C. [b] Isolated yields. [c] Selectivity = (*Z*,*Z*)-dienyl ester/(total dienyl esters) × 100.

in the *para* position, as only 68% yield of **9** was obtained after 48 h of reaction, but with high stereoselectivity.

These functional dienes **1**–**10** polymerize rapidly at room temperature after isolation but they can be stored in solution at 0 °C.

We have already shown that in the presence of carboxylic acid, complexes **I**–**IV** were easily converted into (diphosphine)(carboxylate)$_2$Ru complexes **V** with evolution of isobutene [7]. Under our catalytic conditions, this type of complex **V** is likely to be formed and responsible for the activation of the triple bond towards nucleophilic addition of the free carboxylate. The fact that only (*Z*)-isomers are formed shows that a formal *trans*-addition of the carboxylic acid to the triple bond takes place. Such a *trans*-addition has already been observed in the dimerization of terminal alkynes catalysed by $[(P(CH_2CH_2PPh_2)_3)Ru]$ precursors to give (*Z*)-enynes via a vinylidene–ruthenium intermediate [30]. The formation of such an unsaturated vinylidene activated species ($Ru{=}C{=}CHC(R^1){=}CH_2$) is also supported by the observation that disubstituted enynes which cannot afford such an intermediate are not reactive under our mild conditions.

Conclusion

The complex (1,4-bis(diphenylphosphino)butane)-(2-methylpropenyl)$_2$Ru appears to be a very efficient catalyst precursor for the preparation of (*Z*)-dienyl esters in one step from carboxylic acids and enynes. This catalytic reaction offers an original methodology for the general and stereoselective access to functional dienes of well-defined geometry, and presents potential for the transformation of enynes into non-conjugated unsaturated aldehydes derivatives.

Experimental section

Preparation of complexes **I–IV**

Two grams (6.26 mmol) of (cyclooctadiene)Ru(2-methylpropenyl)$_2$ and 6.10 mmol of diphosphine were refluxed for 5 h in 70 mL of hexane under argon. After cooling, a yellow powder was filtered, washed three times with 10 mL of hexane, and dried in vacuo.

• *(Bis(diphenylphosphino)methane) (2-methylpropenyl)$_2$ ruthenium* **I**

From 2.00 g of (cyclooctadiene)Ru(2-methylpropenyl)$_2$ and 2.33 g of bis(diphenylphosphino)methane, 3.18 g (85%) of complex **I** was isolated as a yellow powder.

^{1}H NMR (CD_2Cl_2, 300 MHz, ppm): δ 0.55 (m, 2H, allylic CH_2); 0.68 (m, 2H, allylic CH_2); 1.30 (m, 2H, allylic CH_2); 1.93 (s, 6H, Me); 2.65 (m, 2H, allylic CH_2); 4.76 (t, 2H, J = 9.5 Hz, PCH_2); 6.79–7.92 (m, 20H, Ph).

^{13}C NMR (CD_2Cl_2, 75 MHz, ppm): δ 25.68; 39.53; 40.39; 48.85; 87.24; 128.00–139.00.

^{31}P NMR (CD_2Cl_2, 121 MHz, ppm): δ 13.53.

Anal (%): calc for $C_{33}H_{36}P_2Ru$: C, 66.54; H, 6.09; P, 10.40. Found: C, 66.35; H, 5.89; P, 10.17.

• *(1,2-Bis(diphenylphosphino)ethane) (2-methylpropenyl)$_2$ ruthenium* **II**

From 2.00 g of (cyclooctadiene)Ru(2-methylpropenyl)$_2$ and 2.40 g of 1,2-bis(diphenylphosphino)ethane, 3.20 g (82%) of complex **II** was isolated as a grey yellow powder.

^{1}H NMR (CD_2Cl_2, 300 MHz, ppm): δ 0.81 (m, 4H, allylic CH_2); 1.42 (m, 2H, allylic CH_2); 1.69 (d, 2H, J = 2.4 Hz, allylic CH_2); 2.10 (s, 6H, Me); 2.55 (m, 2H, PCH_2); 3.48 (m, 2H, PCH_2); 6.70–7.80 (m, 20H, Ph).

^{13}C NMR (CD_2Cl_2, 75 MHz, ppm): δ 26.60; 34.72; 41.51; 42.82; 95.99; 127.90–140.40.

^{31}P NMR (CD_2Cl_2, 121 MHz, ppm): δ 84.99.

Anal (%): calc for $C_{34}H_{38}P_2Ru$: C, 66.98; H, 6.28; P, 10.16. Found: C, 66.92; H, 6.20; P, 10.09.

• *(1,3-Bis(diphenylphosphino)propane) (2-methylpropenyl)$_2$ ruthenium* **III**

From 2.00 g of (cyclooctadiene)Ru(2-methylpropenyl)$_2$ and 2.50 g of 1,3-bis(diphenylphosphino)propane, 3.10 g (78%) of complex **III** was isolated as a grey powder.

^{1}H NMR (CD_2Cl_2, 300 MHz, ppm): δ 0.79 (m, 2H, allylic CH_2); 0.95 (m, 2H, allylic CH_2); 1.19 (s, 2H, allylic CH_2); 1.98 (s, 6H, Me); 1.98–2.25 (m, 4H, PCH_2); 2.36 (dd, 2H, J = 7.1, 3.1 Hz, allylic CH_2); 2.69–2.78 (m, 2H, CH_2CH_2P); 7.00–7.50 (m, 20H, Ph).

^{13}C NMR (CD_2Cl_2, 75 MHz, ppm): δ 21.67; 26.27; 30.67; 40.22; 48.08; 96.08; 126.00–143.00.

^{31}P NMR (CD_2Cl_2, 121 MHz, ppm): δ 36.76.

Anal (%): calc for $C_{35}H_{40}P_2Ru$: C, 67.40; H, 6.46; P, 9.93. Found: C, 67.86; H, 6.44; P, 9.96.

• *(1,4-Bis(diphenylphosphino)butane) (2-methylpropenyl)$_2$ ruthenium* **IV**

From 2.00 g of (cyclooctadiene)Ru(2-methylpropenyl)$_2$ and 2.60 g of 1,3-bis(diphenylphosphino)butane, 3.07 g (79%) of complex **IV** was isolated as a yellow powder.

^{1}H NMR (CD_2Cl_2, 300 MHz, ppm): δ 0.56 (dd, 2H, J = 15.9, 4.9 Hz, allylic CH_2); 1.02 (d, 2H, J = 13.9 Hz, allylic CH_2); 1.05 (s, 2H, allylic CH_2); 1.60 (m, 2H, $P(CH_2)_4P$); 1.84 (s, 6H, Me); 2.00 (m, 2H, $P(CH_2)_4P$); 2.12 (m, 2H, allylic CH_2); 2.20–2.40 (m, 2H, $P(CH_2)_4P$); 2.70–2.90 (m, 2H, $P(CH_2)_4P$); 7.00–7.70 (m, 20H, Ph).

^{13}C NMR (CD_2Cl_2, 75 MHz, ppm): δ 24.21; 25.67; 29.26; 41.47; 47.30; 94.72; 126.00–144.00.

^{31}P NMR (CD_2Cl_2, 121 MHz, ppm): δ 44.58.

Anal (%): calc for $C_{36}H_{42}P_2Ru$: C, 67.80; H, 6.64; P, 9.71. Found: C, 66.91; H, 6.68; P, 9.72.

General procedure for the synthesis of dienyl esters

A solution of 10 mmol of carboxylic acid, 11 mmol of enyne and 0.01 mmol of (1,4-bis(diphenylphosphino)butane) (2-methylpropenyl)$_2$ ruthenium in 5 or 10 mL of solvent was stirred under an inert atmosphere of nitrogen. After treatment with $NaHCO_3$ and evaporation of the solvent, dienyl esters were isolated by distillation under reduced pressure or chromatography over silica gel.

• *(Z)-3-Methylbuta-1,3-dien-1-yl benzoate* **1**

A solution of 1.22 g (10 mmol) of benzoic acid, 0.86 g (11 mmol) of isopropenylacetylene and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene was stirred at 50 °C for 18 h. The product was purified by silica-gel chromatography to afford 1.80 g (96%) of ester **1** as a colorless liquid.

IR (cm^{-1}): 1 605, 1 660, 1 730.

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 2.18 (t, 3H, J = 1.1 Hz, Me), 4.98 and 5.11 (m, 2H, CH_2), 5.47 (dd, 1H, J = 7.3 and 0.7 Hz, =CH), 7.22 (d, 1H, J = 7.3 Hz, =CHO), 7.45–8.10 (m, 5H, Ph).

MS (m/z): 188 (M^+).

• *(Z)-3-Methylbuta-1,3-dien-1-yl valerate* **2**

A solution of 1.08 mL (10 mmol) of valeric acid, 0.86 g (11 mmol) of isopropenylacetylene and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of pentane was stirred at 45 °C for 6 h. The product was purified by silica-gel chromatography to afford 1.30 g (77%) of ester **2** as a colorless liquid.

IR (cm^{-1}): 1 610, 1 665, 1 755.

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.90 (t, 3H, J = 7.5 Hz, $MeCH_2$), 1.35 (m, 2H, $MeCH_2$), 1.65 (m, 2H, $MeCH_2CH_2$), 2.00 (s, 3H, Me), 2.45 (t, 2H, J = 7.5 Hz, CH_2CO), 4.92 (m, 1H, =CH*H*), 5.02 (m, 1H, =C*H*H), 5.30 (dd, 1H, J = 7.3 and 0.6 Hz, =CH), 7.0 (d, 1H, J = 7.3 Hz, =CHO).

MS (m/z): 168 (M^+).

• *(Z)-3-Methylbuta-1,3-dien-1-yl* N-*(tert-butoxycarbamoyl)phenylalaninate* **3**

A solution of 2.65 g (10 mmol) of Boc-phenylalanine, 0.86 g (11 mmol) of isopropenylacetylene and 64 mg (0.1 mmol) of catalyst **IV** in 10 mL of toluene was stirred at 65 °C for 20 h. The product was purified by silica-gel chromatography to afford 2.05 g (62%) of ester **3** as an oil.

IR (cm^{-1}): 1 655, 1 750, 3 375.

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 1.38 (s, 9H, Bu^t), 1.95 (s, 3H, Me), 3.12 (m, 2H, CH_2Ph), 4.66 (dt, 1H, J = 8.1

and 6.0 Hz, C*H*CH_2Ph), 4.92 (s, 1H, =C*H*H), 4.97 (d, 1H, NH), 5.00 (s, 1H, =CH*H*), 5.37 (dd, 1H, J = 7.1 and 0.5 Hz, =CH), 6.98 (d, 1H, J = 7.2 Hz, =CHO), 7.1–7.4 (m, 5H, Ph).

• *(Z)-4-Methoxybuta-1,3-dien-1-yl acetate* **4**

A solution of 0.60 mL (10 mmol) of acetic acid, 0.90 mL (11 mmol) of (*Z*)-1-methoxybut-1-en-3-yne, 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene was stirred at 65 °C for 20 h. The product was purified by distillation to afford 0.76 g (53%) of ester **4** as a colorless liquid.

IR (cm^{-1}): 1 610, 1 750.

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 2.08 (s, 3H, MeCO), 3.60 (s, 3H, MeO), 5.30 (ddd, 1H, J = 11.4, 6.2, and 1.0 Hz, =CHC*H*=), 5.76 (ddd, 1H, J = 11.4, 6.4, and 1.1 Hz, =CHC*H*=), 5.90 (ddd, 1H, J = 6.3, 1.5 and 1.2 Hz, =C*H*OMe), 6.88 (ddd, 1H, J = 6.4, 2.6 and 1.4 Hz, =CHO).

MS (m/z): 142 (M^+).

• *(Z)-4-Methoxybuta-1,3-dien-1-yl valerate* **5**

A solution of 1.08 mL (10 mmol) of valeric acid, 0.90 mL (11 mmol) of (*Z*)-1-methoxybut-1-en-3-yne and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene was stirred at 65 °C for 19 h. The product was purified by distillation to afford 1.38 g (75%) of ester **5** as a colorless liquid.

IR (cm^{-1}): 1 614, 1 660, 1 750.

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.88 (t, 3H, J = 7.0 Hz, *Me*CH_2), 1.34 (m, 2H, Me*C*H_2), 1.61 (m, 2H, $MeCH_2CH_2$), 2.37 (t, 2H, J = 6.5 Hz, CH_2CO), 3.62 (s, 3H, MeO), 5.32 (ddd, 1H, J = 11.4, 6.2 and 0.9 Hz, =CHC*H*=), 5.78 (ddd, 1H, J = 11.4, 6.4 and 0.9 Hz, =CHC*H*=), 5.91 (ddd, 1H, J = 6.2, 1.4 and 1.4 Hz, =C*H*OMe), 6.93 (ddd, 1H, J = 6.4, 2.6 and 1.4 Hz, =CHO).

MS (m/z): 100 (M^+ – *n*BuCO).

• *(Z)-4-Methoxybuta-1,3-dien-1-yl methoxyacetate* **6**

A solution of 0.90 g (10 mmol) of methoxyacetic acid, 0.90 mL (11 mmol) of (*Z*)-1-methoxybut-1-en-3-yne and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene was stirred at 65 °C for 18 h. The product was purified by distillation to afford 1.18 g (69%) of ester **6** as a colorless liquid.

IR (cm^{-1}): 1 615, 1 660, 1 750.

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 3.39 (s, 3H, *Me*OCH_2), 3.60 (s, 3H, MeO), 4.07 (s, 2H, CH_2), 5.26 (ddd, 1H, J = 11.4, 6.2 and 0.9 Hz, =CHC*H*=), 5.82 (ddd, 1H, J = 11.4, 6.4 and 0.9 Hz, =CHC*H*=), 5.90 (ddd, 1H, J = 6.9, 2.5 and 1.3 Hz, =C*H*OMe), 6.91 (ddd, 1H, J = 6.2, 2.5 and 1.4 Hz, =CHO).

• *(Z)-4-Methoxybuta-1,3-dien-1-yl methacrylate* **7**

A solution of 0.85 mL (10 mmol) of methacrylic acid, 0.90 mL (11 mmol) of (*Z*)-1-methoxybut-1-en-3-yne and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene was stirred at 65 °C for 19 h. The product was purified by distillation to afford 1.01 g (60%) of ester **7** as a colorless liquid.

IR (cm^{-1}): 1 615, 1 655, 1 735.

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 1.98 (t, 3H, J = 1.1 Hz, Me), 3.68 (s, 3H, MeO), 5.40 (ddd, 1H, J = 11.4, 6.2 and 0.9 Hz, =CHC*H*=), 5.67 (d, 1H, J = 1.5 Hz, =C*H*H), 5.89 (ddd, 1H, J = 11.4, 6.3 and 0.9 Hz, =CHC*H*=), 5.94 (ddd, 1H, J = 6.1, 2.5 and 1.3 Hz, C*H*OMe), 6.24 (d, 1H, J = 1.0 Hz, =CH*H*), 7.09 (ddd, 1H, J = 6.3, 2.6 and 1.3 Hz, =CHO).

• *(Z)-4-Methoxybuta-1,3-dien-1-yl benzoate* **8**

A solution of 1.22 g (10 mmol) of benzoic acid, 0.90 mL (11 mmol) of (*Z*)-1-methoxybut-1-en-3-yne and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene was stirred at 65 °C for 18 h. The product was purified by distillation to afford 1.64 g (81%) of ester **8** as a colorless liquid.

IR (cm^{-1}): 1 620, 1 655, 1 735.

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 3.66 (s, 3H, MeO), 5.53 (ddd, 1H, J = 11.4, 6.2 and 1.0 Hz, =CHC*H*=), 5.98 (ddd, 1H, J = 11.4, 6.3 and 0.8 Hz, =CHC*H*=), 6.01 (ddd, 1H, J = 6.6, 2.4 and 1.2 Hz, C*H*OMe), 7.20 (ddd, 1H, J = 5.9, 2.4 and 1.4 Hz, =CHO), 7.40–8.21 (m, 5H, Ph).

MS (m/z): 204 (M^+).

• *(Z)-4-Methoxybuta-1,3-dien-1-yl-4-chlorobenzoate* **9**

A solution of 1.56 g (10 mmol) of 4-chlorobenzoic acid, 0.90 mL (11 mmol) of (*Z*)-1-methoxybut-1-en-3-yne and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene was stirred at 65 °C for 48 h. The product was purified by distillation to afford 1.63 g (68%) of ester **9** as a yellow liquid.

IR (cm^{-1}): 1 615, 1 660, 1 740.

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 3.61 (s, 3H, MeO), 5.42 (ddd, 1H, J = 11.4, 6.2 and 0.8 Hz, =CHC*H*=), 5.90 (ddd, 1H, J = 11.4, 6.4 and 0.9 Hz, =CHC*H*=), 5.94 (ddd, 1H, J = 7.0, 2.5 and 0.9 Hz, =C*H*OMe), 7.09 (ddd, 1H, J = 6.4, 2.5 and 1.3 Hz, =CHO), 7.35 (dm, 2H, J = 8.7 Hz, Ph), 7.95 (dm, 2H, J = 8.7 Hz, Ph).

• *(Z)-4-Methoxybuta-1,3-dien-1-yl phenylacetate* **10**

A solution of 1.64 g (10 mmol) of phenylacetic acid, 0.90 mL (11 mmol) of (*Z*)-1-methoxybut-1-en-3-yne and 64 mg (0.1 mmol) of catalyst **IV** in 5 mL of toluene was stirred at 65 °C for 20 h. The product was purified by distillation to afford 1.66 g (76%) of ester **10** as a colorless liquid.

IR (cm^{-1}): 1 610, 1 660, 1 760.

^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 3.60 (s, 3H, MeO), 3.70 (s, 2H, $PhCH_2$), 5.35 (ddd, 1H, J = 11.4, 6.4 and 1.1 Hz, =CHC*H*=), 5.88 (ddd, 1H, J = 11.4 , 6.4 and 0.8 Hz, =CHC*H*=), 5.98 (ddd, 1H, J = 6.3, 1.6 and 1.1 Hz, =C*H*OMe), 6.97 (ddd, 1H, J = 6.4, 1.5 and 1.2 Hz, =CHO), 7.20–7.5 (m, 5H, Ph).

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