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Ni-promoted Cyclopentenone Formation by Intramolecular Cyclocarbonylation of 1-Bromo-1,4-dienes

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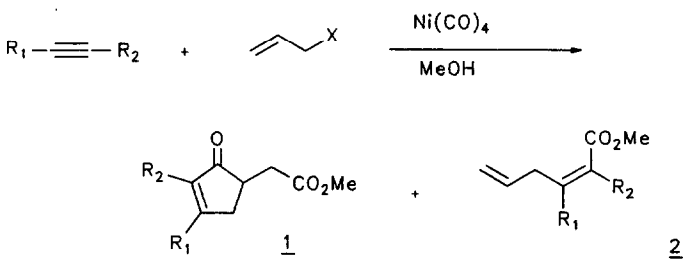
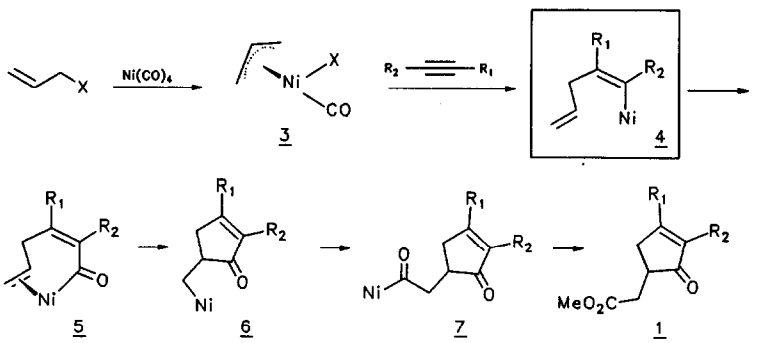
Abstract: Stereoselective *syn* addition of allyl bromide to acetylenes catalysed by palladium (II) bromide results in the formation of 1-bromo-1,4-dienes which were further converted to cyclopentenones through a $Ni(CO)_4$ promoted carbonylation-cyclization process. Four C-C bonds are formed by this two step sequence, leading to 2,3-substituted 5-methoxycarbonylmethylcyclopentenones **1**. Application of this procedure to 2-butyne affords cyclopentenone **1c**, an immediate precursor of the antibiotic methylenomicyn B.

Development of methodologies leading to formation of five membered rings is currently one of the most active fields in organic synthesis[1-3] due to their presence in natural products with outstanding biological activities. Among five member carbocyclic compounds cyclopentenones are one of the most versatile synthetic intermediates[4]. In this context, we have been studying the $Ni(CO)_4$ promoted carbonylative cycloaddition of allyl halides and acetylenes in methanol to give 2,3,5-trisubstituted cyclopent-2-en-1-ones **1** as shown in equation 1[5,6]. In this process one carbon-oxygen and four carbon-carbon bonds are formed from three separate components, under mild reaction conditions, and a variety of functional groups are tolerated including ketones, esters, alcohols, sulfones and ethers. However, the behaviour of terminal acetylenes in this reaction is not satisfactory giving allylacrylic esters **2** as the only isolable products together with a mixture of unidentified acetylene oligomerization compounds while symmetrically substituted acetylenes, or those with similar electronic characteristics in R_1 and R_2, afford the corresponding cyclic enones **1** only in low yields[5].



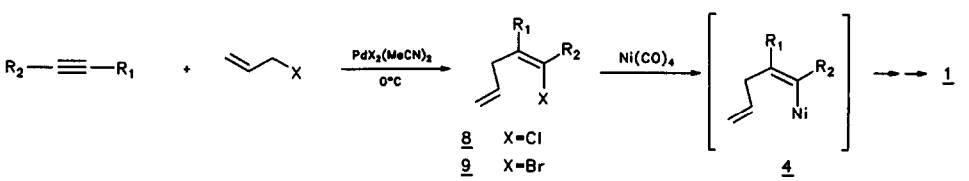
(1)

Attempts to overcome these drawbacks and to extend the scope of the carbonylative cycloaddition reaction to the aforementioned alkynes have been made and the results are described in this paper. According to the currently accepted mechanism for this reaction outlined in Scheme 1, a π-allyl nickel intermediate **3** is first formed from the allyl halide and $Ni(CO)_4$, which after a *syn* acetylene insertion gives the corresponding vinyl-nickel complex **4**. Then, CO migration would lead to an acylmetal intermediate **5** which after attack on the coordinated olefin affords the intermediate **6**. Finally, a new CO insertion and methanolysis of the resulting acyl-nickel complex **7** would give **1**. Alternatively, direct nucleophilic attack of methanol to the intermediate **5** would form allylacrylic ester **2**.



Scheme 1. Proposed mechanism for formation of **1**

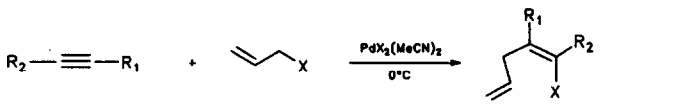
We anticipated that the problems associated with terminal or low polarized triple bond acetylenes might arise from their high reactivity towards organonickel intermediates in any of the steps leading to the products **1**. To prove this hypothesis, we planned to obtain the key intermediate **4** for formation of **1** by a different route that, obviously, should not involve the simultaneous presence of acetylenes and organometallic nickel species in the reaction flask. Thus, we decided to explore the feasibility of the approach outlined in Scheme 2. In a first step, the acetylene and the allyl halide should give halodienes **8** and **9**, which, in a second step would react with $Ni(CO)_4$ in an oxidative addition process to give the intermediate **4**[7]. This would finally lead to cyclopentenone **1** through the sequential formation of intermediates **5**, **6** and **7** as proposed to occur in the direct reaction of alkynes and allyl halides (Scheme 1).



Scheme 2. Two step synthetic alternative approach to **1**.

RESULTS and DISCUSSION

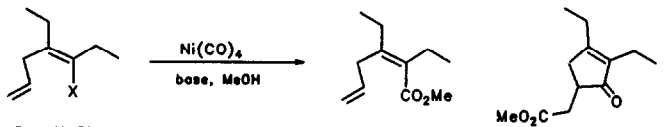
A literature survey revealed[8] that catalytic amounts of palladium (II) halides promote the *syn* addition of allyl halides to acetylenes to give the corresponding halodienes **8** and **9** (equation 2).



(2)

8a X=Cl, R_1=R_2=Et 82%
9a X=Br, R_1=R_2=Et 93%

As models for our process, we selected the halodienes **8a** and **9a** synthesised from 3-hexyne according to equation 2. The carbonylation of these compounds was attempted with an excess of $Ni(CO)_4$ **(caution!)** (3-5 eq with respect to halide) in the presence of methanol in different solvents. Additionally, a base was introduced to remove the acid formed throughout the reaction as indicated in equation 3.



(3)

8a X=Cl
9a X=Br

2a 1a

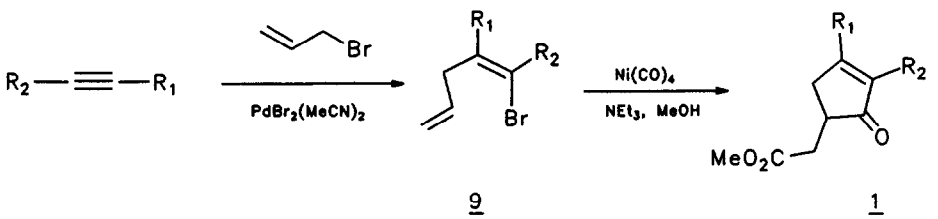
Table 1. Reactions of halodienes **8a** and **9a** with $Ni(CO)_4$ according to eq 3.

							Products[e]			
entry	halide	MeOH[b]	base (eq)[b]	Temp[c]	Solvent	Time[d]	s.m.[f]	2a	1a	other
1	8a	20	---	20	THF	24	90	-	-	-
2	8a	26	CaO (4)	30	THF	48	90	-	-	-
3	8a	20	K_2CO_3 (4)	reflux	Et_2O	24	95	-	-	-
4	8a	20	K_2CO_3 (4)	40	DMF	29	92	-	-	-
5	8a	19	NEt_3 (4)	40	MeCN	40	90	-	-	-
6	8a	18	DBN (1.5)	22	THF	30	60	-	-	29
7	8a	20	KOAc (3)	29	MeCN	30	85	-	-	-
8[a]	8a	4	NEt_3 (3)	35	MeCN	74	96	-	-	-
9	9a	20	NEt_3 (3)	30	THF	18	14	35	-	19
10	9a	20	CaO (4)	19	MeCN	24	42	30	-	15
11[a]	9a	30	NEt_3 (4)	30	MeCN	4	2	93	2	-
12[a]	9a	30	KOAc (4)	32	MeCN	8	80	10	-	3
13[a]	9a	4	NEt_3 (4)	36	MeCN	5	2	-	88	5
14[a]	9a	4	K_2CO_3 (4)	33	MeCN	6	18	3	40	15

[a] Argon was passed over the reaction mixture.
[b] Equivalents with respect to starting halide.
[c] Reaction temperature (°C).
[d] Reaction time (hours).
[e] Yields (%) determined by gas chromatography. Reactions run with 3-4 eq. of $Ni(CO)_4$.
[f] Unreacted starting halide.

Thus, different reaction conditions for the carbonylation-cyclisation reaction were tried for chlorodiene **8a**, but, unfortunately, in all cases the starting material was recovered unaltered even after prolonged reaction times (2 days). In contrast, the behaviour of bromodiene **9a** was somewhat puzzling: whereas monitoring of the reaction revealed the exclusive presence of unreacted starting material, after the usual work up procedure, in the final crude reaction mixture we observed also the presence of compound **2a**, according to the corresponding spectral data (eq. 3). We supposed that ester **2a** might be originated from a carbonylation of starting bromide **9a** induced during solvent and excess $Ni(CO)_4$ removal by passing a stream of Ar through the reaction flask. To confirm this fact we carried out a reaction while a slow stream of pure argon was passed over the reaction mixture from the beginning. We could observe a colour evolution of the mixture turning from colourless to yellow, red, purple and finally turbid dark brown and a black solid deposited on the walls of the flask, almost all starting material was converted into ester **2a** without the formation of other byproducts. In later experiments, we confirmed the fact that the reaction only took place when this slow stream of inert gas was passed through the flask. In Table I we summarise the results obtained in different attempts to induce carbonylation of halodienes **8a** and **9a**. Formation of linear ester **2a** showed the feasibility of the synthetic scheme proposed and allowed us to explore the cyclisation of **9a** to the corresponding cyclopentenone **1a**. This was achieved by decreasing the methanol/bromodiene ratio and thus favouring the intramolecular insertion process. Several other parameters influencing the reaction were optimised and in this way we found that a satisfactory 88% yield of cyclopentenone **1a** could be obtained (Table 1, *cf.* entries 11 and 13).

With this methodology optimised, next we applied this two step procedure to several acetylenes to determine the scope of the process[9]. As it can be seen in Table 2, different acetylenes were tested and in most cases good yields of the bromodienes **9** and moderate to excellent yields of the cyclopentenones **1** were obtained.



9 1 (4)

Some results deserve further comment. Thus, good yields for the intermediate bromodienes were generally found except when using volatile 2-pentyne and 2-butyne where the isolated yields of bromides **9b** and **9c** were lower. Bromodiene **9b** was isolated as a 2:1 mixture of 2-methyl and 2-ethyl regioisomers, respectively. Cyclisation of this mixture afforded the final cyclopentenones **1b** having the same regioisomeric ratio.

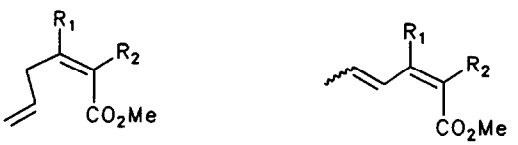
Table 2. Cyclopentenone synthesis by the two step procedure.

R_1	R_2	Bromodiene	Yield (%)[a]	Cyclopentenone	Yield (%)[a]
Et	Et	**9a**	93	**1a**	80
Et	Me	**9b**[b]	55	**1b**[b]	88
Me	Me	**9c**	67	**1c**	95
H	Ph	**9d**	87	**1d**	43
H	$SiMe_3$	**9e**	89	**1e**	65
H	*n*-pent	**9f**	87	**1f**	49
COOMe	H	**9g**	88	**1g**	27
COOMe	Me	**9h**	86	**1h**	36
CH_2OMe	Me	**9i**	92	**1i**	78
H	$C(Me)_2OH$	**9j**	98	**1j**	70
H	CH_2OMe	**9k**	72	**1k**	92

[a] Isolated yield

[b] As a 2:1 mixture of regioisomers

On the other hand, lower yields were obtained in the cyclisation step when a phenyl or methoxycarbonyl group were present in the starting alkyne. In these cases, in addition to the corresponding cyclopentenones **1d**, **1g** and **1h**, non-cyclic byproducts were formed consisting in mixtures of allylacrylic esters (**2d**, **2g** and **2h**) and the isomeric dienoates **10d**, **10g** and **10h** in 41 %, 34 % and 29 % overall yield, respectively. Esters **10** presumably originated from an isomerisation of the acrylic derivatives **2**, either during reaction or purification.



2d	R_1= H, R_2= Ph	10d
2g	R_1= CO_2Me, R_2= H	10g
2h	R_1= CO_2Me, R_2= Me	10h

It is worth mentioning that cyclic enone **1c**, obtained from 2-butyne, is an immediate precursor of the antibiotic methylenomicyn B in an efficient synthesis developed previously in our laboratory[10].

Structures of bromodienes **9a-k** and cyclopentenones **1a-k** were assigned by comparison of their spectral data with those previously described. The regioselectivity in the palladium-catalysed addition[11] of allyl bromide to terminal acetylenes was determined from consideration of the coupling constant between the vinylic hydrogen H_a and the double allylic methylene protons H_b. As shown in Figure 1, the magnitude of this coupling constant was around 7 Hz for regioisomers A whereas for the opposite regioisomer this value was 1-2 Hz.

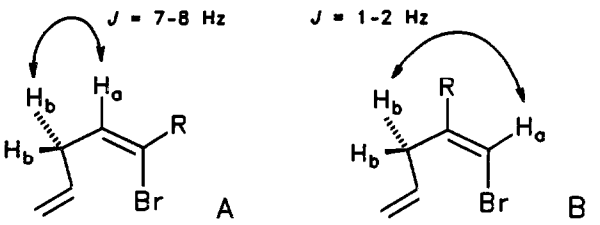


Figure 1. ^{1}-H NMR coupling constants in regioisomers **9** obtained from terminal alkynes.

For the bromodienes **9** obtained from disubstituted alkynes the regiochemistry was deduced after cyclisation to the corresponding cyclopentenones **1**. Except in the case of 2-pentyne where the two possible regioisomers were obtained, in the other cases a single regio- and stereoisomer was obtained in the palladium catalyzed reaction. Cyclopentenones **1a-k** showed characteristic spectral data: Infrared absorptions at 1725-1735 cm^{-1} of the ester C=O group, at 1690-1710 cm^{-1} of the cyclopentenone C=O group and a C=C stretching band around 1635-1645 cm^{-1}. In the ^{13}C-NMR spectra, the cyclopentenone C=O group was typically found around 207-210 ppm. The regiochemistry of the cyclopentenone formation in the case of disubstituted alkynes was deduced from the differences found in the chemical shifts of methyl groups when bonded to the 2 and 3 positions of the cyclopentenone ring. As depicted in Figure 2, 2-methyl groups were typically found at δ 1.6-1.7 ppm (^{1}H-RMN) and δ 6-7 ppm (^{13}C-RMN) while values for the 3-methyl groups were δ 2.0-2.1 (^{1}H-RMN) and δ 15-17 ppm (^{13}C-RMN). In addition, the coupling constant between H_a and H_b was significatively different in both possible regioisomers in accordance with the larger values found for homoallylic coupling constants.

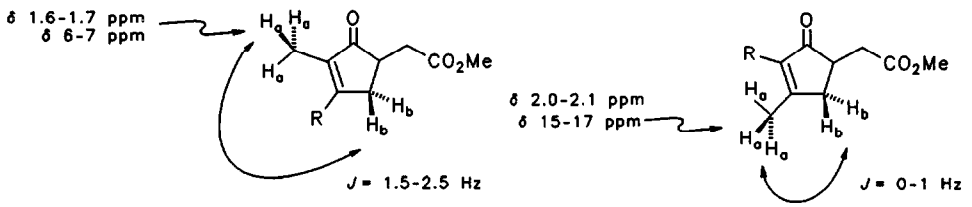
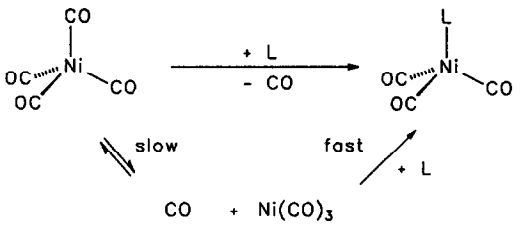


Figure 2. Regioisomeric cyclopentenones **1** obtained from internal alkynes.

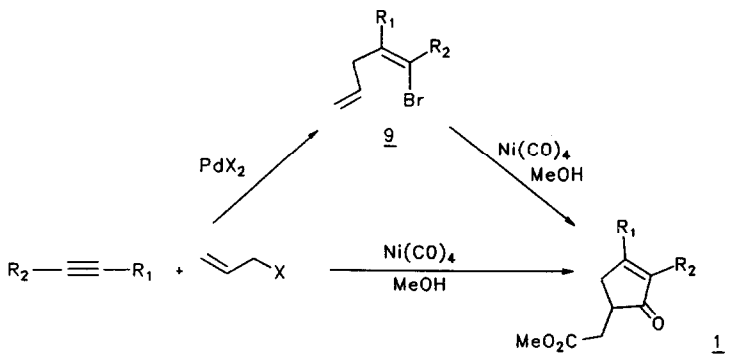
According to our observations, the reaction of bromo-1,4-dienes **9** to give the corresponding cyclopentenones **1** took place when a slight stream of an inert gas was passed over the warmed reaction mixture. This surprising activation can be explained by considering the proposed mechanism for tetracarbonylnickel reactions. Usually, this compound reacts through a dissociative mechanism[12] as depicted in Scheme 3. In the slow step, the tetrahedral nickel complex dissociates giving CO and a tricarbonylnickel species, coordinatively unsaturated, which would react rapidly with the ligand L to give again a new 18 electron species. The stream of gas could shift the equilibrium by removing the dissociated CO from the reaction mixture, so facilitating the coordination of the bromodiene and the subsequent oxidative addition.



Scheme 3. Proposed activation for $Ni(CO)_4$ ligand exchange reactions.

The cyclisation is thought to be accomplished, as described in closely related reactions[13,14], when a highly coloured species is formed in the reaction mixture. This reactive species, which has been proposed to be a carbonylnickelate anion[14], could be formed *in situ* in our case, since a method for preparing these anionic nickel clusters is simply to let tetracarbonylnickel react with alcohols or water in basic media in polar solvents[15]. To support this observation an experiment was devised involving the formation of a red-purple coloured species by mixing $Ni(CO)_4$, methanol and triethylamine in acetonitrile by passing Ar over the reaction mixture. At this point a solution of bromodiene **9a** was injected to the reaction mixture and, after few minutes, an almost quantitative yield of the cyclopentenone **1a** was obtained. In the absence of the gas stream, no colour developed and no reaction occurred for hours.

As described above, this two step procedure was planned to overcome some difficulties in the direct reaction of allyl halides, acetylenes and $Ni(CO)_4$ in methanol. Regioselectivity found on alkyne incorporation in the final cyclopentenone in both the direct and the two step methods was the same as depicted in Scheme 4. On the other hand, both methods are complementary when considering the nature of the substituents in the alkyne: whereas the one step process is favoured by electronwithdrawing substituents, in the two step process terminal or alkyl substituted alkynes gave the best results.



Scheme 4. Regioselectivity in the direct and the two step procedures for the synthesis of **1**.

CONCLUSIONS

A two step procedure complementary to the previously reported direct reaction of alkynes, allyl halides and $Ni(CO)_4$ to give cyclopentenone derivatives **1** is described. In the first step a Pd(II) catalysed reaction of

the alkyne and allyl bromide gives an intermediate bromodiene **9** which is converted in the second step to the cyclopentenone **1** by reaction with $Ni(CO)_4$.

EXPERIMENTAL SECTION

CAUTION! $Ni(CO)_4$ is an extremely harmful chemical and special precautions have to be taken when using it. All the reactions were carried out inside a glove box located in a fume cupboard and any possible unreacted nickel carbonyl was destroyed by oxidation (see below).

Unless otherwise stated IR spectra were recorded in CCl_4 with Perkin-Elmer 399B or Bonem FT-IR Spectrometers; bands are reported in cm^{-1}. ^1H NMR and ^{13}C NMR were recorded in $CDCl_3$ with WP-80-SY Bruker, Gemini 200 and Unity 300 Varian machines. Chemical shifts are reported in δ units, parts per million (ppm) downfield from tetramethysilane, or in ppm relative to the singlet at 7.26 ppm of chloroform-d_1. Splitting patterns are designated as: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. Coupling constants are reported in hertz (Hz). ^{13}C NMR are reported in ppm relative to the center line of a triplet at 77.0 ppm of chloroform-d_1. Routine ^{13}C NMR spectra were fully broad-band decoupled. Elemental analysis were performed with a Carlo Erba apparatus (1107 and 1500 Models). GC analyses were performed with a Carlo Erba 4130 instrument, fitted with a 25m x 0.25mm capillary column, type SE-54, and a Shimadzu Chromatopac C-R1B recorder and flame ionisation detector. Analytical TLC was run on Merck 60 F_{254} silica gel plates. Flash chromatography was performed on 230-400 mesh Merck 60 silica gel. Column chromatography was performed in Merck or SDS 70-230 mesh silica gel. Neutral alumina was purchased by Merck. Preparative thin layer chromatography was performed in Merck 0.2 mm thick silica 20x20 cm plates. $Ni(CO)_4$ was supplied by Merck or Strem. Acetylenes were furnished by Aldrich and Farchan and used as received. Palladium halides were obtained from Strem and Johnson Matthey. Solvents were dried and distilled under Ar prior to use.

Synthesis of halodienes[8]

(Z)-3-Chloro-4-ethylhepta-3,6-diene **8a.** To 69 mg (0.27 mmol) of bis(acetonitrile)dichloropalladium (II) in 15 mL of allyl chloride, 3-hexyne (886 mg, 10.8 mmol) was added dropwise during 2 hours. It was left 20 min at room temperature and the excess of the allylic halide evaporated. The resulting oil was filtered through alumina eluting with pentane or pentane/ether mixtures to separate the palladium salts. After concentration at reduced pressure, the resulting oil (1.709 g) was bulb to bulb distilled (60-70 °C, 9 Torr) to afford **8a** (1.403 g, 8.85 mmol, 82% yield).
IR: 3030, 2980, 2960, 2920, 1640, 1450, 1100, 995, 920. ^1H-RMN: 6.1-5.4 (m, 1H); 5.3-4.8 (m, 2H); 2.95 (d, J=9 Hz, 2H); 2.4 (q, J=10 Hz, 2H); 2.1 (q, J=10 Hz, 2H); 1.15 (t, J=10 Hz, 3H); 1.03 (t, J=10 Hz, 3H). ^{13}C-RMN: 144.6 (s); 133.2 (d); 114.9 (t); 112.6 (s); 42.4 (t); 23.2 (t); 19.7 (t); 13.6 (q); 11.7 (q).

General procedure for the synthesis of bromodienes **9.**

In a dry two necked flask, under argon, $PdBr_2(MeCN)_2$ was dissolved in allyl bromide at room temperature. The flask was immersed in an ice bath and the alkyne was slowly added dropwise (two drops per minute). When the addition was finished, the mixture was stirred at 0°C for 0.5-1 hours. The bath was removed and the reaction left at room temperature until all the alkyne had disappeared (gas chromatography). Excess of allyl bromide was evaporated at vacuum and the residue diluted with pentane or pentane/ether and filtered through an alumina (grade I) pad. Evaporation of the solvent followed by bulb to bulb distillation or flash chromatography afforded the bromodienes **10**.

(Z)-3-Bromo-4-ethylhepta-3,6-diene **9a.** 3-Hexyne (5.86 g, 71.5 mmol) was added to 42 mL of allyl bromide and 172.3

mg (0.49 mmol) of $PdBr_2(MeCN)_2$ during 3 hours. After alumina filtration 13.50 g (66.5 mmol, 93% yield) of practically pure (98% by capillary GC) **9a** was obtained.
IR: 3045, 2980, 2960, 2930, 1640, 1450, 1380, 1180, 1090, 990, 905. ^{1}H-RMN: 6.1-5.5 (m, 1H); 5.2-4.9 (m, 2H); 3.02 (d, J=7 Hz, 2H); 2.55 (q, *J*=9 Hz, 2H); 2.15 (q, *J*=9 Hz, 2H); 1.15 (t, *J*=9 Hz, 3H); 1.02 (t, *J*=9 Hz, 3H). ^{13}C-RMN: 141.7 (s); 135.6 (d); 115.7 (t); 112.8 (s); 40.2 (t); 24.8 (t); 19.9 (t); 13.7 (q); 11.7 (q). Anal. Calcd. for $C_9H_{15}Br$: C, 53.20%; H, 7.39%; Br, 39.37%. Found: C, 52.91%; H, 7.20%; Br, 38.97%.

(Z)-3-Bromo-4-methylhepta-3,5-diene and (Z)-2-bromo-3-ethylhexa-2,5-diene **9b.** 2-Pentyne (0.250 mL, 2.60 mmol) was added to a solution of 4.5 mg of $PdBr_2(MeCN)_2$ in 3 mL of allyl bromide during 40 min. at 0-5°C. After stirring for 6 hours at this temperature usual work up and bulb to bulb distillation (120-125°C, 42 Torr) afforded 270 mg (1.42 mmol, 55%) of an inseparable 2:1 mixture of regioisomeric bromodienes **9b**.
IR (film, mixture of both regioisomers): 3043, 2987, 2968, 2935, 1643, 1445, 1183, 1094, 987, 903.
(Z)-3-Bromo-4-methylhepta-3,5-diene, major regioisomer. ^{1}H-RMN: 5.9-5.6 (m, 1H); 5.0-5.2 (m, 2H), 2.97 (d, *J*= 6Hz, 2H); 2.52 (q, *J*= 7 Hz, 2H); 1.73 (s, 3H); 1.1 (t, *J*= 7Hz, 3H). ^{13}C-RMN: 134.4 (d); 124.7 (s); 117.4 (m); 115.9 (d); 43.3 (t); 31.4 (t); 18.0 (q); 13.1 (q).
(Z)-2-Bromo-3-ethylhexa-2,5-diene, minor regioisomer. ^{1}H-RMN: 5.9-5.6 (m, 1H); 5.0-5.2 (m, 2H), 2.99 (d, *J*= 6Hz, 2H); 2.31 (s, 3H); 2.12 (q, *J*= 7 Hz, 2H); 0.99 (t, *J*= 7Hz, 3H). ^{13}C-RMN: 134.8 (d); 130.7 (s); 118.3 (m); 115.9 (d); 40.9 (t); 25.3 (t); 24.9 (q); 12.6 (q).
Anal. Calcd. for $C_8H_{13}Br$ (mixture of regioisomers): C, 50.82 %; H, 6.88%. Found: C, 51.09%; H, 7.02%.

(Z)-2-Bromo-3-methylhexa-2,5-diene **9c.** Cold 2-butyne (541 mg, 10.0 mmol) was added very fast to a solution of 14.5 mg of $PdBr_2(MeCN)_2$ in 13 mL of allyl bromide 40 min. at -20°C. After stirring for 24 hours at this temperature usual work up and bulb to bulb distillation (100-105°C, 36 Torr) afforded **9c** (1.19 g, 6.71 mmol, 67% yield).
IR (film): 3045, 2988, 2965, 2954, 16433, 1467, 1389, 1173, 1048, 987, 911.
^{1}H-RMN: 5.9-5.6 (m, 1H); 5.0-5.2 (m, 2H), 2.99 (d, *J*= 6.5 Hz, 2H); 2.29 (s, 3H); 1.73 (s, 3H).
^{13}C-RMN: 134.4 (d); 131.6 (s); 116.3 (s); 115.9 (d); 43.2 (t); 25.3 (t); 18.2 (q); 13.1 (q).
Anal. Calcd. for $C_7H_{11}Br$: C, 44.85 %; H, 6.66%. Found: C, 44.51%; H, 6.89%.

(Z)-1-Bromo-1-phenyl-penta-1,4-diene **9d** [8]. To a solution of 57 mg (0.16 mmol) of $PdBr_2(MeCN)_2$ in 15 mL of allyl bromide 1.736 g (17.0 mmol) of phenylacetylene was slowly added. After the usual work up procedure, bulb to bulb distillation (95-105°C, 0.06 Torr) afforded 3.301 g (11.80 mmol, 87%) of bromodiene **9d**.
IR: 3040, 2970, 1635, 1450, 1250, 990, 690. ^{1}H-RMN: 7.6-7.2 (m, 5H); 6.20 (t, J=7 Hz, 1H); 6.2-5.6 (m, 1H); 4.9-5.3 (m, 2H); 3.1 (t, *J*=7 Hz, 2H). ^{13}C-RMN: 139.9 (s); 134.4 (d); 128.7 (d); 128.4 (d); 128.2 (d); 127.5 (d); 126.3 (s); 115.9 (t); 36.7 (t).

(Z)-1-Bromo-1-trimethylsilylpenta-1,4-diene **9e.** From trimethylsilylacetylene (2.27 g, 23.1 mmol), allyl bromide (17 mL) and $PdBr_2(MeCN)_2$ (42 mg, 0.12 mmol) the bromide **9e** (4.50 g, 20.5 mmol, 89%) was obtained.
IR: 3040, 1640, 1610, 1410, 1250, 920, 870, 850. ^{1}H-RMN: 6.24 (t, J=6 Hz, 1H); 6.2-5.8 (m, 1H); 5.25-4.9 (m, 2H); 3.05 (tt, *J*=6 Hz, *J*=1.5 Hz; 2H); 0.3 (s, 9H). ^{13}C-NMR: 140.7 (d); 136.3 (d); 123.8 (s); 112.8 (t); 42.8 (t); 1.9 (q).
Anal. Calcd. for $C_8H_{14}BrSi$: C, 43.85%; H, 6.90%; Br, 36.46%. Found: C, 43.72%; H, 6.97%; Br, 36.83%.

(Z)-5-Bromodeca-1,5-diene **9f** [8]. According to the general procedure, 1-heptyne (577 mg, 6.0 mmol), allyl bromide (6 mL) and $PdBr_2(MeCN)_2$ (10 mg, 0.038 mmol) afforded 1.13 g (5.21 mmol, 87%) of **9f**.
IR(film): 3040, 2975, 2955, 2420, 1620, 1580, 1430, 1020, 905. ^{1}H-RMN: 6.1-5.6 (m, 2H); 5.25-4.90 (m, 2H); 2.95 (t, J=7 Hz, 2H); 2.40 (t, *J*=7 Hz, 2H); 1.8-1.2 (m, 6H); 0.95 (m, 3H). ^{13}C-NMR: 135.4 (d); 133.6 (d); 122.8 (s); 115.8 (t); 42.9 (t); 33.5 (t); 27.8 (t); 25.8 (t); 21.3 (t); 13.2 (q).

Methyl (*E*)-2-bromomethylidene-4-pentenoate **9g** [8]. According to the general procedure, from 90 mg (0.34 mol) of $PdBr_2(MeCN)_2$, 10 mL of allyl bromide and 1.16 g (13.8 mmol) of methyl propiolate after 10 hours at 0°C was obtained 2.399 g (11.7 mmol, 85%) of the bromodiene **9g**.
IR: 2985, 2970, 1740, 1640, 1430, 1335, 1200, 1120, 925. ^{1}H-RMN: 6.77 (t, J=1.2 Hz, 1H); 6.2-5.7 (m, 1H); 5.5-5.1 (m, 2H); 3.87 (s, 3H); 3.15 (m, 2H). ^{13}C-RMN: 166.5 (s); 136.5 (s); 133.3 (d); 118.0 (t); 111.5 (d); 51.9 (q); 38.5 (t).

Methyl (*E*)-2-(1-bromoethylidene)-4-pentenoate **9h**. Following the procedure described, reaction of $PdBr_2(MeCN)_2$ (40 mg, 0.11 mmol), allyl bromide (6 mL) and methyl 2-butynoate (634 mg, 6.47 mmol) gave 1.38 g of crude product, which was distilled (bulb to bulb, 100-110°C/0.02 Torr) affording 1.212 g (5.53 mmol, 85%) of pure **9g**.
IR: 3040, 2980, 1730, 1620, 1450, 1305, 1210, 1120, 940. ^{1}H-RMN: 6.1-5.5 (m, 1H); 5.3-4.9 (m, 2H); 3.75 (t, 3H); 3.3 (d, J=5.5 Hz, 2H); 2.68 (s, 3H). ^{13}C-RMN: 165.7 (s); 145.2 (s); 132.0 (s); 126.7 (d); 116.6 (t); 111.6 (q); 31.6 (t); 18.8 (q). Anal. Calcd. for $C_8H_{11}O_2Br$: C, 43.86 %; H, 5.06 %; Br, 36.47 %. Found: C, 43.79 %; H, 5.06 %; Br, 36.82 %.

(*E*)-2-Bromo-3-methoxymethyl-2,5-hexadiene **9i**.

As described in the general procedure, the bromodiene **9i** (1.345 g, 6.56 mmol, 92%) was synthetised from 600 mg (7.14 mmol) of but-2-yn-1-yl methyl ether, 20 mg (0.05 mmol) of $PdBr_2(MeCN)_2$ and 5.7 mL of allyl bromide.
IR: 3040, 2970, 1640, 1630, 1300, 1210, 1130, 960. ^{1}H-RMN: 6.5-5.7 (m, 1H); 5.25-4.95 (m, 2H); 3.95 (s, 2H); 3.30 (s, 3H); 3.12 (d, J=7.5 Hz, 2H); 2.40 (s, 3H). ^{13}C-NMR: 134.1 (d); 133.0 (s); 123.7 (s); 116.2 (t); 69.7 (t); 57.7 (q); 39.4 (t); 25.3 (q). Anal. Calcd. for $C_8H_{13}OBr$: C, 46.82 %; H, 6.34 %. Found: C, 47.02 %; H, 6.33 %.

(*Z*)-2-Bromo-1-hydroxy-1-methyl-2,5-hexadiene **9j**. 2-Methyl-3-butyn-2-ol (0.72g, 8.56 mmol) was added to a solution of 40 mg (0.1 mmol) of $PdBr_2(MeCN)_2$ in 11 mL of allyl bromide. After evaporation, direct flash chromatography of the residue (hexane/*t*-BuOMe 5:1) afforded **9j** (1.77 g, 8.56 mmol, quantitative yield).
IR (film): 3380, 3066, 2979, 1637, 1363, 1168, 1137, 995, 948, 914, 811. ^{1}H-RMN: 6.05 (t, J=6.8 Hz, 1H); 5.9-5.7 (m, 1H); 5.15-5.0 (m, 2H); 2.96 (tdd, J= 6.8, 1.6, 1.2 Hz, 2H); 1.60 (bs, 1H), 1.49 (s, 9H). ^{13}C-NMR: 137.6 (s); 134.7 (d); 124.9 (d); 115.8 (t); 74.0 (s); 35.7 (t); 29.0 (q).
Anal. Calcd. for $C_8H_{13}OBr$: C, 46.82 %; H, 6.34 %. Found: C, 46.77 %; H, 6.43 %.

(*Z*)-2-Bromo-1-methoxy-2,5-hexadiene **9k**. Following the general procedure described, reaction of methyl propargyl ether (3.65 g, 0.052 mol), $PdBr_2(MeCN)_2$ (200 mg, 0.5 mmol) and allyl bromide (23 mL) gave 9.12 g (0.047 mol, 92 %) of pure **9k**.
IR: 3040, 2970, 1640, 1635, 1300, 1230, 1140, 960. ^{1}H-RMN: 6.5-5.7 (m, 2H); 5.25-4.95 (m, 2H); 3.85 (s, 2H); 3.37 (s, 3H); 3.22 (dm, J=7.5 Hz, 2H). ^{13}C-NMR: 137.6 (d); 134.3 (d); 123.7 (s); 116.2 (t); 67.4 (t); 57.8 (q); 38.4 (t). Anal. Calcd. for $C_7H_{11}BrO$: C, 43.98 %; H, 5.75 %. Found: C, 44.06 %; H, 5.81 %.

Synthesis of cyclopentenones.

General Procedure for the synthesis of cyclopentenones **1** from bromodienes **9**.

A three necked flask provided with magnetic stirring, a thermometer, a gas inlet, a graduated addition funnel and a condenser with the top outlet connected to a mercury valve, was installed in an argon filled glove box. The outlet of the mercury valve was connected, outside the glove box, to a cold trap containing a methanolic solution of iodine kept at -20-0°C. The trap outlet was directly connected to the exhaust of the fume cupboard. Prior to the reaction, the system was flushed with a stream of Ar and then a solution of the bromodiene, methanol and the base was introduced and finally the $Ni(CO)_4$ added directly from a pressure bottle to a graduated funnel and from this to the reaction flask. The reaction mixture was heated to 30-35°C while a cold fluid at -5°C was circulated through the condenser. A slow stream of pure

Ar was admitted in the flask. The reaction mixture turned gradually from colourless to yellow, orange, red and dark purple. At the end of the reaction a black precipitate was formed. The condenser was removed and the outlet of the flask directly attached to the trap cointaining iodine. Most of the solvent and any unreacted $Ni(CO)_4$ were evaporated to dryness by increasing the Ar stream passing through the flask. The dry residue was removed from the glove box and treated with CH_2Cl_2. After filtration through a celite pad, washing (NH_4Cl and NaCl saturated solutions), drying ($MgSO_4$) and evaporation, final chromatography (flash column or preparative TLC) afforded the products.

Methyl (Z)-2,3-diethylhexa-2,5-dienoate **2a**. **9a** (202.9 mg, 1.0 mmol), 1.29 mL of methanol (*ca.* 30 mmol) and triethylamine (0.55 mL, 4 mmol) in acetonitrile (20 mL) were treated with $Ni(CO)_4$ (0.5 mL, *ca.* 4 mmol). Column chromatography (hexane/AcOEt 5:1) gave 169 mg (0.93 mmol, 93%) of compound **2a**.
IR: 3010, 2960, 2920, 1720, 1645, 1605, 1430, 1320, 1200, 1110, 990, 920. ^{1}H-RMN: 6.1-5.6 (m, 1H); 5.2-4.9 (m, 2H); 3.7 (s, 3H), 3.0 (d, J=8 Hz, 2H); 2.3 (q, J=10 Hz, 2H); 2.15 (q, J=10 Hz, 2H); 1.03 (t, J=10 Hz, 6H). ^{13}C-RMN: 171.3 (s); 143.7 (s); 136.6 (d); 113.5 (t); 112.4 (s); 52.4 (q); 27.8 (t); 21.6 (t); 14.7 (q); 10.9 (q). Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49 %; H, 9.95 %. Found: C, 72.32 %; H, 9.80 %.

2,3-Diethyl-5-methoxycarbonylmethyl-2-cyclopentenone **1a**. **9a** (303 mg, 1.49 mmol), methanol (0.24 mL, *ca.* 6 mmol), NEt_3 (0.83 mL, 6 mmol) and 1.40 mL (6.2 mmol) of $Ni(CO)_4$ gave after purification (preparative TLC, hexane/*t*-BuOMe 7:1) **1a** (249 mg, 1.19 mmol, 80%).
IR (CHCl3): 2980, 2960, 1730, 1690, 1635, 1460, 1305, 1255, 1170, 1020. ^{1}H-RMN: 3.75 (s, 3H); 2.1-1.8 (m, 9H); 1.2 (t,J=9 Hz, 3H); 1.05 (t, J=9 Hz, 3H). ^{13}C-RMN: 11.7 (q); 12.9 (q); 16.1 (t); 23.9 (t); 35.3 (t); 35.6 (t); 41.1 (d); 51.6 (q); 139.9 (s); 171.5(s); 173.1 (s); 208.7 (s). Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.55 %; H, 8.63 %. Found: C, 68.47 %; H, 8.67 %.

2-Ethyl-3-methyl-5-methoxycarbonylmethyl-2-cyclopentenone and 3-ethyl-2-methyl-5-methoxycarbonylmethyl-2-cyclopentenone **1b**. A 2:1 mixture of (Z)-3-bromo-4-methylhepta-3,5-diene and (Z)-2-bromo-3-ethylhexa-2,5-diene (346 mg, 1.83 mmol), 0.24 mL of methanol (6 mmol), 0.83 mL of NEt_3 (6 mmol) and 1.40 mL (6.2 mmol) of $Ni(CO)_4$ were allowed to react as described in the general procedure. After flash chromatography (hexane/AcOEt 3:1) 316 mg (1,61 mmol, 88 %) of a 2:1 mixture of regioisomeric cyclopentenones were obtained.
IR (CHCl3, both isomers): 2985, 2960, 1728, 1694, 1635, 1462, 1325, 1305, 1255, 1170, 1020.
2-Ethyl-3-methyl regioisomer. ^{1}H-RMN: 1.03 (t, J= 8Hz, 3H); 2.05 (s, 3H); 2.22 (q, J= 8Hz, 2H); 2.0-3.0 (m, 5H); 3.72 (s, 3H). ^{13}C-RMN: 10.1 (q); 16.3 (q); 19.2 (t); 33.6 (t); 34.6 (t); 41.0 (d); 51.8 (q); 143.0 (s); 158.9 (s); 172.0 (s); 209.7 (s).
3-Ethyl-2-methyl regioisomer. ^{1}H-RMN: 1.11 (t, J= 8Hz, 3H); 1.72 (s, 3H); 2.33 (q, J= 8Hz, 2H); 1.9-3.0 (m, 5H),; 3.80 (s, 3H). ^{13}C-RMN: 8.0 (q); 11.1 (q); 24.0 (t); 36.2 (t); 37.1 (t); 41.0 (d); 52.1 (q); 134.0 (s); 172.2 (s); 173.1 (s); 209.2 (s).
Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.33 %; H 8.22 %. Found (mixture of both isomers): C, 67.16 %; H, 8.31 %.

2,3-Dimethyl-5-methoxycarbonylmethyl-2-cyclopentenone **1c**. Bromodiene **9c** (298 mg, 1.70 mmol), NEt_3 (0.69 mL, 5 mmol), MeOH (0.2 mL, 5 mmol) in acetonitrile (10 mL) were treated with $Ni(CO)_4$ (0.75 mL, 5.8 mmol). After usual work up and flash chromatography (hexane/*t*-BuOMe 1:1) afforded **1c** (287 mg, 1.57 mmol, 93%).
IR (film): 2950,2918, 2846, 1737, 1699, 1649, 1436, 1366, 1309, 1218, 1170, 1058, 983. ^{1}H-RMN: 3.66 (s 3H); 2.6-2.9 (m, 3H); 2.4-2.1 (m, 2H); 2.0 (s, 3H); 1.7 (s, 3H). ^{13}C-RMN: 209.5 (s); 172.7 (s); 168.5 (s); 135.3 (s); 51.7 (q); 41.2 (d); 38.6 (t); 35.2 (t); 17.0 (q), 8.0 (q).
Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.94 %; H 7.66 %. Found: C, 65.99 %; H, 7.42 %.

2-Phenyl-5-methoxycarbonylmethylcyclopent-2-enone **1d**. $Ni(CO)_4$ (0.80 mL, 6 mmol) was added to **9d** (252 mg, 1.13

mmol) , 0.28 mL of methanol (*ca.* 5 mmol) and 0.69 mL (5 mmol) of triethylamine in acetonitrile (13 mL). Flash chromatography of the final reaction crude afforded **1d** (111 mg, 43%) and 99 mg (0.46 mmol, 41%) of a 1:4 mixture of isomeric methyl (2*Z*)-2-phenyl-2,4-pentadienoates **10d** (9:1, 4*Z*/4*E* isomers) and methyl (2*Z*)-2-phenyl-2,5-pentanedioate.

1d. IR: 2970, 2960, 1730, 1690, 1480, 1430, 1200, 1060, 860. ^{1}H-RMN: 7.9-7.7 (m, 3H); 7.4-7.2 (m, 3H); 3.70 (s, 3H); 3.30-2.50 (m, 5H). Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.03 %; H, 6.13 %. Found: C, 72.70 %; H, 6.42 %.

5-Methoxycarbonylmethyl-2-trimethylsilylcyclopent-2-enone **1e**. (*Z*)-1-Bromo-1-trimethylsilylpenta-1,4-diene **9e** (209 mg, 0.96 mmol), triethylamine (0.56 mL, *ca.* 4 mmol) and MeOH (0.16 mL, 4 mmol) in acetonitrile (12 mL) were treated with $Ni(CO)_4$ (0.50 mL, 4 mmol). Column chromatography (AcOEt/hexane 1:12) gave **1e** (111 mg, 0.62 mmol, 65%). IR (film): 2975, 1730, 1690, 1480, 1430, 1200, 1060, 850. ^{1}H-RMN: 7.75 (t, J=1.5 Hz, 1H); 3.75 (s, 3H); 3.2-2.3 (m, 5H); 0.2 (s, 9H). ^{13}C-RMN: 212.8 (s); 172.5 (s); 170.4 (d); 146.3 (s); 51.6 (q); 42.1 (d); 37.0 (t); 34.9 (t); -1.96 (q). Anal. Calcd. for $C_{11}H_{18}O_3Si$: C, 58.37 %; H, 8.01. Found: C, 58.18%; H, 7.92 %.

2-Pentyl-5-methoxycarbonylmethylcyclopent-2-enone **1f**. **9f** (273 mg, 1.25 mmol), NEt_3 (505 mg, 5.0 mmol); MeOH (0,20 mL, 5 mmol) and $Ni(CO)_4$ (1.0 mL, 8 mmol) in 40 mL of acetonitrile gave, after preparative TLC (hexane/*t*-BuOMe 7:1), 222 mg (0.99 mmol, 79%) of enone **1f**.

IR: 2975, 1730, 1690, 1470, 1420, 1250, 1050, 890. ^{1}H-RMN: 7.25 (t, *J*=1.5 Hz,1H); 3.68 (s, 3H); 3.0-2.1 (m, 7H); 2.6-2.1 (m, 6H); 0.91 (m, 3H). ^{13}C-RMN: 208.9 (s); 172.4 (s); 155.5 (d); 145.6 (s); 51.6 (q); 41.6 (d); 35.0 (t); 33.5 (t); 31.5 (t); 27.3 (t); 24.8 (t); 22.33 (t); 13.86 (q). Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61 %; H, 8.99 %. Found: C, 69.74 %; H, 8.94 %.

3-Methoxycarbonyl-5-methoxycarbonylmethylcyclopent-2-enone **1g**. Bromodiene **9g** (265 mg, 1.29 mmol), 0.51 mL NEt_3, 0.16 mL methanol and $Ni(CO)_4$ (1.0 mL, 8mmol) were allowed to react as described above. Flash chromatography (AcOEt/hexane 1:4) afforded 74.2 mg (0.35 mmol, 27%) of the cyclopentenone **1g** and 86 mg (0.43 mmol, 34%) of a 3:1 mixture of dimethyl (1*E*,3*E*)-1,3-pentadiene-1,2-dioate **10g** and dimethyl (1*E*)-1,4-pentadiene-1,2-dioate **2g**, respectively.

1g. IR: 2980, 2970, 1730, 1685, 1440, 1240, 1200, 910. ^{1}H-RMN: 6.95 (t, *J*=2 Hz, 1H); 3.95 (s, 3H); 3.83 (s, 3H); 3.4-2.6 (m, 5H). Anal. Calcd. for $C_8H_8O_3$: C, 56.60 %; H, 5.70 %. Found: C, 56.86 %; H, 5.95 %.

2-Methyl-3-methoxycarbonyl-5-methoxycarbonylmethylcyclopent-2-enone **1h**. According to the general procedure, **9a** (329 mg, 1.51 mmol), 0.62 mL of NEt_3 (4.5 mmol); 0.36 mL of MeOH (9 mmol) and $Ni(CO)_4$ (0.95 mL, 7.5 mmol) reacted in 20 mL of acetonitrile. Flash Chromatography (hexane/AcOEt 15:1) gave 122 mg (0.54 mmol, 36%) of cyclopentenone **1h** and 91 mg (0.44 mmol, 29%) of a 9:2 mixture of (2*E*,4*E*)-2,4-hexadiene-2,3-dioate **10h** and dimethyl (2*E*)-2,5-hexadiene-2,3-dioate **2h**, respectively.

1h. IR (film): 2970, 2930, 1730, 1710, 1645, 1620, 1410, 1210, 1050, 875. ^{1}H-RMN: 3.9 (s.3H); 3.75 (s, 3H); 3.1-2.4 (m, 5H); 2.10 (t, *J*=2 Hz, 3H). ^{13}C-RMN: 209.3 (s); 172.7 (s); 167.1 (s); 153.9 (s); 146.9 (s); 52.0 (q); 51.7 (q); 10.9 (d); 34.7 (t); 33.0 (t); 9.5 (q). Anal. Calcd. for $C_{11}H_{14}O_5$: C, 58.40 %; H, 6.24 %. Found: C, 58.46 %; H, 6.43 %.

2-Methyl-5-methoxycarbonylmethyl-3-methoxymethylcyclopent-2-enone **1i**. Bromodiene **9i** (389 mg, 1.90 mmol), NEt_3 (1.04 mL, 7 mmol), methanol (0.27 mL, 6.6 mmol) and $Ni(CO)_4$ (0.90 mL, 6.9 mmol) in 17 mL of acetonitrile were allowed to react as described above. Flash chromatography (hexane/AcOEt 4:1) afforded 317 mg (1.50 mmol, 78%) of cyclopentenone **1i**.

IR: 2970, 2950, 1730, 1690, 1640, 1605, 1260, 1200, 1140, 1020, 980. ^{1}H-RMN: 4.30 (s, 2H); 3.80 (s, 3H); 3.45 (s, 3H); 2.35-2.10 (m, 5H); 1.74 (s, 3H). ^{13}C-RMN: 209.7 (s); 172.3 (s); 167.2 (s); 135.1 (s); 70.2 (t); 59.0 (q); 56.3 (q); 40.8 (d); 35.0 (t); 33.8 (t); 8.0 (q). Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.26 %; H, 7.55 %. Found: C, 62.20 %; H, 7.59

%.

2-(2-Hydroxyprop-2-yl)-5-methoxycarbonylmethylcyclopenten-2-one **1j**. Bromodiene **9j** (409 mg, 1.99 mmol), NEt_3 (0.88 mL, 6.35 mmol); MeOH (0.24 mL, 6 mmol) were treated with $Ni(CO)_4$ (0.6 mL, 4.6 mmol). Flash chromatography (hexane/*t*-BuOMe 3:1 to 1:1) gave 295 mg (1.38 mmol, 70%) of cyclopentenone **1j**.
IR (film): 2738, 2488, 2469, 1737, 1693, 1626, 1436, 1367, 1323, 1259, 1217, 1172, 997, 956. ^{1}H-RMN: 1.43 (s, 6H); 2.2-2.95 (m, 5H); 3.68 (s, 3H); 7.37 (t, J= 2.7 Hz). ^{13}C-RMN: 28.5 (q); 28.6 (q); 32.9 (t); 34.7 (t); 42.5 (d); 51.7 (q); 69.6 (s); 150.4 (s); 154.3 (d); 172.0 (s); 209.5 (s). Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.26 %; H, 7.55 %. Found: C, 61.77 %; H, 7.69 %.

5-Methoxycarbonylmethyl-3-methoxymethylcyclopent-2-enone **1k**. Following the described general procedure, bromodiene **9k** (190 mg, 0.99 mmol), triethylamine (0.32 mL, 3.5 mmol), methanol (0,13 mL, 3.3 mmol) and $Ni(CO)_4$ (0,6 mL, 4 mmol) in acetonitrile (14 mL) were allowed to react. The crude reaction product was chromatographed (flash, hexane/*t*-BuOMe 3:1) affording 182 mg (0.92 mmol, 92%) of cyclopentenone **1k**.
IR (film): 3010, 2970, 2950, 1735, 1690, 1645, 1260, 1210, 1140, 1020, 980. ^{1}H-RMN: 7.32 (t, J= 1.8 Hz, 1H); 4.10 (s, 2H); 3.74 (s, 3H); 3.45 (s, 3H); 2.35-2.00 (m, 5H). ^{13}C-RMN: 211.0 (s); 171.9 (s); 163.7 (d); 131.1 (s); 65.2 (t); 59.0 (q); 53.2 (q); 44.8 (d); 34.2 (t); 33.8 (t). Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.62 %; H, 7.05 %. Found: C, 60.37 %; H, 7.14 %.

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