ELECTROCHEMICAL INCORPORATION OF CARBON DIOXIDE INTO ALKENES BY NICKEL COMPLEXES

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<u>Abstract</u>

Electrogenerated Ni(0) complexes from stable Ni(II) compounds are the catalysts for the electrochemical incorporation of carbon dioxide into carbon-carbon double bonds. Different kind of olefin derivatives have been carboxylated to afford mono- or dicarboxylic acid derivatives depending on the alkene structure. The electrolyses are carried out in one compartment cells fitted with a magnesium anode under mild conditions.

Introduction

The utilization and recycling of carbon dioxide as a source of organic compounds is of importance because of its unwanted accumulation in the atmosphere and the future previsible shortage of fuels.

The reactivity and fixation of CO_2 into organic substrates may contribute to the understanding of the nature of photosynthetic, bioorganic, and chemical processes ¹⁻³.

The chemical activation of CO₂ can be brought about by its coordination into transition metal compounds⁴. Among them, several electron-rich nickel(0) complexes have shown activity toward CO₂ incorporation into unsaturated substrates such as alkynes, alkenes, dienes^{1,4-6}. The development of catalytic systems for the synthesis of functionnalized compounds using CO₂ is of particular interest^{5,6}.

In contrast to alkene carbonylations, thoroughly studied⁷, the catalytic carboxylation of carbon-carbon double bonds by CO_2 has been scarcely reported⁸.

We recently developed an electrochemical method for the CO₂ incorporation into alkynes, based on the use of a catalytic amount of a Ni(II) complex as the catalyst precursor (eq. 1)⁹.



We present here our results on the carboxylation of C=C double bonds by this electrochemical method.

The method is based on the use of a Ni(0) complex generated in situ by a 2e reduction of a starting Ni(II) compound. The reactions are carried out in a single-compartment cell, fitted with a central magnesium anode and a carbon fiber cathode¹⁰, at constant intensity. A DMF solution containing tetrabutylammonium tetrafluoroborate (10^{-3} M) as supporting electrolyte is electrolyzed in the presence of the alkene and CO₂ under mild conditions : the CO₂ pressure varying from 1 to 5 atm and the temperature from 0 to 60 °C.

For the study of alkene electrocarboxylations, nickel complexes associated to several ligands, such as 2,2'-bipyridine (bipy), pentamethyldiethylene triamine (PMDTA), or triphenylphosphine were tested. Starting complexes were either Ni(bipy)₃(BF₄)₂¹¹ or commercial NiBr₂.dme (dme = 1,2-dimethoxyethane) with added ligand. Ni-bipy¹¹ and Ni-PMDTA¹² systems have shown catalytic activity in the electrocarboxylation of alkynes.

Results and discussion

Electrochemical study

The electrochemical behaviour of Ni(bipy)₃(BF₄)₂ solutions containing model olefins such as norbornene, phenylthioethylene or 1,2-undecadiene, was first examined. Figure 1 presents the cyclic voltammograms of Ni(bipy)₃(BF₄)₂ in a DMF solution in the presence of norbornene and CO₂. The N i (b i p y)₃²⁺ was reversibly reduced to Ni(bipy)₂ in a 2e process at -1.2 V vs SCE (curve a). Follows a reversible 1e reduction of the Ni(0) complex to its anion radical at -1.9 V and the reduction of free bipy at -2.1 V⁹. When 1 equiv. of norbornene per nickel was added to the solution (curve b), no apparent changes were observed. When 10 equiv. of alkene were added, the reduction wave of Ni(bipy)₂ at - 1.9 V was partially replaced by a new wave at -1.75 V vs SCE and became less reversible (curve c). This shift is interpreted as a coordination of the alkene to Ni(0) through ligand exchange, as shown in scheme 1.

Scheme 1 Ni(bipy)₃²⁺ + 2e
$$\neq$$
 Ni°(bipy)₂ + bipy
-1.2 V
Ni°(bipy)₂ + e \neq Ni(bipy)₂ⁱ
- 1.9 V
Ni°(bipy)₂ + χ \neq Ni°(bipy) (χ) + bipy
Ni°(bipy)(χ) + e \neq Ni(bipy) (χ)ⁱ
- 1.75 V

A norbornene/nickel ratio of 10 was necessary to observe a significant shift of the reduction wave of Ni^o. In contrast, in the case of alkynes, less than 1 equiv. of alkyne (4-octyne) was needed to effect the corresponding changes⁹. This is indicative of the lower affinity of alkenes toward the electrogenerated Ni(0) complex.

When CO₂ was bubbled into the solution (curve d), the cyclic voltammogram exhibited the expected irreversible reduction of Ni(II) to Ni(0) at -1.2 V followed by a catalytic wave at -1.6 V vs SCE, due to the reduction of coordinated CO₂ into its radical anion.



Figure 1. Cyclic voltammograms obtained with freshly polished gold microelectrode (3 mm^2) at 20 °C at a scan rate of 200 mV.s⁻¹ for a solution of Ni(bipy)₃(BF₄)₂ (0.3 mmol) in DMF (30 ml) containing 0.1M tetrabutylammonium terafloroborate as supporting electrolyte. a) Under argon. b) After addition of norbornene (0.3 mmol). c) After addition of norbornene (3 mmol). d) Solution as in c) saturated with CO₂.

The electrochemical behaviour of phenylvinylsulfide in the presence of Ni(bipy)₃(BF₄)₂ is shown in Figure 2. The cyclic voltammograms of the Ni²⁺ complex (curve a) appeared strongly modified after the addition of 1 equiv. of the olefin (curve b). The reduction peak of Ni(bipy)₃²⁺ at -1.2 V became non-reversible, the reoxidation of Ni(0) being shifted to - 0.6 V. The reduction peak of Ni(bipy)₂ at -1.9 V appeared at -1.7 V due to the coordination of the vinylsulfide on the Ni^o center. The better ability of phenylvinylsulfide to coordinate to the metal (either through the double bond or the sulfur), as compared to norbornene, influences the reactivity toward CO₂ incorporation (vide infra). Curve c, in the presence of CO₂ exhibited the catalytic wave of CO₂ reduction at -1.6 V vs SCE as in Figure 1.



Figure 2. See Fig.1 for general conditions. a) Under argon. b) After addition of phenylvinylsulfide (0.3 mmol). c) Solution as in b) saturated with CO₂.

The electrochemical behaviour of DMF solutions of Ni(bipy)₃(BF_4)₂ in the presence of 1,2-undecadiene and CO₂ is presented in Figure 3. Curves b and c show the cyclic voltammograms of solutions containing 0.5 and 1 equiv. of the 1,2-diene, respectively. The Ni(bipy)₃²⁺ reduction peak at -1.2 V in curve a was shifted to -1.15 V and became progressively irreversible in curves b and c. This is indicative of the rapid formation of non-electroactive Ni(0)-allene complexes under the working conditions (scan rates $v = 0.2 \text{ V.s}^{-1}$). As compared to norbornene, 1,2-undecadiene coordinates efficiently to Ni(bipy)₂ with rapid ligand exchange (see Scheme 1), important factor to facilitate the carboxylation.



Figure 3. See Fig.1 for general conditions. a) Under argon. b) After addition of 12-undecadiene (0.15 mmol). c) After addition of 1,2-undecadiene (0.3 mmol). d) Solution as in c) saturated with CO_2 .

Electrocarboxylations

The reactivity of several kind of olefin derivatives toward CO₂ was examined following the general electrolysis procedure (see experimental part) with a 10/1 molar ratio of olefin to Ni(II), unless otherwise stated.

a) Norbornene and analogs.

When Ni(bipy)₃(BF₄)₂ was used as the catalyst precursor in the preparative-scale electrocarboxylation of norbornene at $P_{CO2} = 1$ atm, monocarboxylic acid <u>1</u> was obtained as a single exo-isomer, accompanied by some dicarboxylic acid <u>2</u> (eq. 2).



At $P_{CO2} = 5$ atm, the ratio of diacid increased. The results of the carboxylations with different catalytic systems are gathered in Table 1.

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			Products ^o (%)			
Complex	Reaction Conditions	Conversion (%)	Norbornane	1	2	Dimers 3,4
Ni(bipy)3(BF4)2	1 atm 65 °C	75	60	27	7	-
n	5 atm 20 °C	15	-	67	33	-
NiBr ₂ dme + 2 PMDTA	1 atm 65 °C	90	67	22	-	-
n	5 atm 80 °C	80	100	-	-	-
NiBr ₂ (PPh ₃) ₂ + PPh ₃	1 atm 65 °C	70	7	7	-	71

<u>Table 1</u> : Norbornene electrocarboxylation^a)

a) For experimental conditions, see experimental part. A 10/2 molar ratio of norbornene/Ni(II) was used.

b) Yields of products are expressed respect to the converted alkene.

No CO₂ was incorporated into the C=C in the absence of the nickel complex or without continuous electrolysis.

In the presence of PMDTA as the ligand, the reduction of the alkene was the predominant process, although carboxylic acid $\underline{1}$ was formed in 22 % yield at 1 atm of CO₂.

The use of PPh₃ favoured the norbornene dimerization and led to a 3/1 mixture of <u>3</u> and <u>4</u>, according to eq. 3. A radical mechanism may be operating in this case.



The nature of the ligand on nickel strongly influences the kind of product of the reaction, as it has already been reported for alkyne carboxylations¹³.

Analogs of norbornene such as 3-acetylnorbornene or 3-vinylnorbornene were carboxylated with low CO₂ incorporation. In contrast, the CO₂ insertion into 2,5-norbornadiene (eq. 4, $P_{CO2} = 1$ atm, T = 20 °C, conversion 15 %) afforded carboxylic acids 5 and 6 in a 65/35 ratio.



No reaction occurred with less reactive aliphatic monoalkenes such as ethylene, 1-octene or 1,7-octadiene.

b) Arylalkenes

Arylalkenes afford monocarboxylic acids in a chemical Ni(COD)₂ mediated carboxylation¹⁴. Direct electrochemical reduction leads to mixtures of mono- and dicarboxylic acids¹⁵.

A series of 2-arylalkenes were carboxylated at $P_{CO2} = 1$ atm with Ni-PMDTA as the catalytic system, as shown in Table 2. The reactions were run at constant intensity of 50 mA for 5-7 hours.

<u>Table 2</u>: Electrocarboxylation of arylalkenes at $Pco_2 = 1$ atm, T = 20 °C with Ni-PMDTA (0.1 equiv.) as the catalytic system.

<u>Alkene</u>	conversion (%)	Products (%) ^a		
Ph	40	Ph COOH (85%)		
Ph	35	$Ph \xrightarrow{\text{COOH}} (71\%)$		
Ph	45	$Ph \longrightarrow (44\%) + Ph \longrightarrow COOH (44\%)$		
Ph Ph	25	$Ph \xrightarrow{Ph}_{Ph} COOH$ (95%)		
	70	$\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} $		
C Ph	10	(50%) + polymers (40%)		

a) Yield of major products respect to the converted alkene

A double CO_2 incorporation into the C=C was the predominant reaction. With bipy as the ligand, similar results were obtained. It is to mention that 1,2-dicarboxylation products were formed in lower yields in the absence of the catalyst, yet accompanied by polymerization of the alkene.

c) Heterosubstituted olefins

To our knowledge, no example of carboxylation of heterosubstituted olefins has been reported. RS-, R₃Si-, RO- type substituents on the double bond make it more electron rich and these olefins present in some cases an additional coordination site to the metal. The electrochemical study exhibited a strong Ni-olefin interaction in the case of phenylvinylsulfide (Fig. 2). Its electrocarboxylation in the presence of Ni-PMDTA (eq. 5) yielded mainly to diacid $\underline{7}$ as a result of a double 1,2-CO₂ incorporation on the double bond.



With bipy as the ligand, the reduction to phenyldisulfide was the main reaction, indicative of the insertion of the low-valent Ni complex into the C-S bond.

The electrocarboxylation of triethylvinylsilane (eq. 6) afforded reduced tetraethylsilane (60 %) and a mixture (40 %) of saturated and unsaturated carboxylic acids $\underline{8}$ and $\underline{9}$. A different addition-elimination mechanism must be operating in the formation of $\underline{9}$.



Butylvinylether or isoprenylacetate were poorly reactive under our conditions.

d) Electron-deficient olefins

The direct electrocarboxylation of activated olefins such as dimethylmaleate has been reported to yield mixtures of polycarboxylated products¹⁶.

We examined the reactivity of ethyl crotonate and of dimethylmaleate. Ethyl crotonate could be regioselectively monocarboxylated at the 3-position to afford <u>10</u> in 67 % yield in the presence of Ni-PMDTA system at $P_{CO2} = 1$ atm (eq. 7).

$$= \overset{\text{COOEt}}{\longrightarrow} + \text{CO}_2 \qquad \xrightarrow{1) \text{ Ni-PMDTA, e}}_{1 \text{ atm, 20 °C}} \xrightarrow{\text{COOH}}_{\text{COOEt}} \xrightarrow{\text{COOEt}}_{2) \text{ H}_3\text{O}^+} \xrightarrow{10 (67 \%)} (eq. 7)$$

Dimethylmaleate was more reactive and a mixture of mono- and dicarboxylation products was formed in a 1:2 ratio (eq.8).

e) Electrocarboxylation of 1,3-dienes

Upon reaction with CO₂, 1,3-dienes have been reported to give carboxylic acids or lactones in stoichiometric Ni(0)¹⁷ or Fe(0)¹⁸ reactions or in catalyzed Pd(0)¹⁹ or Rh²⁰ condensations under elevated CO₂ pressure. Direct electrocarboxylation of butadiene to mixtures of oligomers and carboxylic acids has also been described²¹.

The reactivity of 1,4-diphenylbutadiene with Ni-PMDTA as the catalytic system was examined (eq. 9).



A double CO₂ insertion occurred at the 1,4-positions of the diene to afford unsaturated diacid <u>11</u> in 60 % yield, as a 65/35 mixture of meso/dl diastereoisomers. The double bond in <u>11</u> had exclusively the Z-configuration, possibly due to the nickelacyclopentene intermediate. In contrast, 2,5-dimethylhexa-1,3-diene or cycloocta-1,3-diene were poorly reactive toward CO₂.

f) 1,2-dienes

Simultaneous activation of cumulenes and CO₂ has been scarcely studied. Ni(COD)₂ has been reported to react with propadiene and CO₂ to form unsaturated nickelacycles²².

1-substituted 1,2-dienes were carboxylated electrochemically in Ni-bipy or Ni-PMDTA catalyzed reactions²³. 1,2-dienes were more reactive toward CO_2 than norbornene, as already shown by cyclic

voltammetry. Aliphatic allenes such as undeca-1,2-diene, cyclohexylallene or cyclohexylidene allene yielded mainly α , β - and β , γ -unsaturated acids of type <u>12</u> and <u>13</u>, according to eq. 10.



As presented in Table 3, CO₂ was preferentially incorporated into the central position of the cumulene favouring isomer <u>12</u>, in an hydrocarboxylation-type reaction of one of the double bonds. The second double bond remained untouched.

Table 3 : Electrocarboxylation of 1,2-dienes by Ni-PMDTA at 20 °C and 5 atm CO₂.

Allene	% Conversion	<u>% Monocarboxylic</u> <u>acids^a</u>	<u>Yield of 12 + 13</u> (or 14)	<u>12</u> : <u>13</u>
C ₈ H ₁₇ .	60	80	93 %	60:40
Q	55	65	77 %	100:0
	50	70	98 %	71:29
Ph	100	50	92 %	27:73 (12:14)

a) Yield of monocarboxylic acids formed per reacted allene.

Phenylallene was preferentially carboxylated on the position α to the aromatic group, and isomer <u>14</u> (eq. 11) was the major product. This reversed regioselectivity is essentially due to the electronic effect of the aryl group.



No carboxylation of undeca-1,2-diene occurred in the absence of the nickel catalyst and the allene could be quantitatively recovered at the end of the electrolysis. A single example of direct (non-catalyzed) electrochemical carboxylation concerns the more activated tetraphenylallene²⁴.

g) 1,3-enynes

Among conjugated systems, 1,3-enynes are interesting substrates to look into the preferential site of carboxylation (double or triple bond) and to point out how the conjugation affects the CO₂ insertion. We recently examined the reactivity of a series of 1,3-enynes²⁵, but no additional example of chemical or electrochemical carboxylation of enyne systems has been reported so far. With Ni-PMDTA as the catalytic system, the results show that, independently of the enyne substitution, the carboxylation affects exclusively the triple bond, leading to two regioisomers <u>15</u> and <u>16</u> (eq. 12).



Doubly unsaturated carboxylic acids were thus obtained with controlled stereochemistry, arising from an exclusive cis-addition of H and CO₂H across the triple bond. No double bond isomerization occurred. Some results are presented in Table 4, with the ratio between 15/16, which is a function of the relative steric hindance of the substituents.

<u>Table 4</u>: Electrocarboxylation of 1,3-enynes with Ni-PMDTA as the catalytic system at $P_{CO2} = 5$ atm and T = 20 °C.

Enyne	% Conversion	<u>Yield of 15 + 16</u> ^a	<u>15:16</u>
<u> </u>	80	93 %	90:10
<>>-=-	40	76 %	50:50
<i>}</i> -≡-∕∕	70	86 %	50:50
$\int = -C_6 H_{12}$	3 30	66 %	50:50
$\int_{C_5H_{11}}^{T} C_5H_1$	¹ 20	74 %	70:30

a) Yield of carboxylic acids respect to the converted enyne.

h) α, ω -enyne

The competition between the carboxylation of double versus triple bonds was better examined with a non-conjugated enyne. The carboxylation of 1-octen-7-yne with the Ni-PMDTA system (eq. 13) affected exclusively the $C \equiv C$. Two linear regioisomers <u>17</u> and <u>18</u> were isolated in an 80:20 ratio.



A similar ratio between 17:18 was obtained when Ni(bipy)₂(BF₄)₂ was the catalyst precursor, together with some dicarboxylated compound 19, affecting exclusively the triple bond.

The terminal double bond was not functionalized with any of the catalytic systems that we tested under different reaction conditions. However, it influenced the product distribution when compared to the electrocarboxylation of 1-octyne : with Ni-PMDTA, a 98:2 ratio of the regioisomers corresponding to <u>17</u> and <u>18</u> was obtained in the case of 1-octyne¹², and this ratio was lowered to 80:20 by the presence of the ω -double bond, pointing out that the C=C is not an innocent bystander.

Mechanistic considerations

By analogy with the electrocarboxylation of alkynes⁹, the reaction may proceed via a first electrochemical reduction of Ni(II) to Ni(0). Follows the coordination of both the olefin and CO₂ to the nickel center, to form an oxanickelacyclopentanone intermediate of type <u>20</u> (Scheme 2). An analogous metallacycle was isolated from the electrochemical reaction in the case of 4-octyne⁹. Hoberg isolated and characterized such nickelacycles <u>20</u> formed by chemical reaction in the case of ethylene and norbornene²⁶. We showed that these metallacycles were opened in the presence of Lewis acids. In the electrochemical process, in the presence of a magnesium anode, Mg²⁺ ions are formed according to :

anode:
$$Mg \rightarrow Mg^{2+} + 2e$$

cathode: $Ni^{2+} + 2e \rightarrow Ni^{\circ}$

In the presence of Mg^{2+} , intermediates of type <u>20</u> and <u>21</u> form magnesium carboxylates and Ni²⁺, which can be recycled. The proposed catalytic cycle is presented in Scheme 2. The magnesium carboxylates are stable species which accumulate during the reaction.



Scheme 2. Proposed catalytic cycle for the nickel catalyzed electrocarboxylation of alkenes.

In the case of arylalkenes or of activated olefins, a second insertion of CO₂ into $\underline{20}$, e.g. $\underline{21}$ is favored, leading, after hydrolysis, to the 1,2-dicarboxylic acids.

Conclusion

The electrochemical method provides a simple and mild way to functionalize certain olefins using CO_2 as the source of carbon. An undivided cell with a magnesium anode was employed in a paired synthesis, i.e. cathodic and anodic reactions are both simultaneously interesting. The cathode generates the Ni^o active catalyst and Mg²⁺ ions are formed at the anode.

In conclusion, electrogenerated Ni(0) species complexed with ligands such as bipy or PMDTA, are, in most cases, effective for the carboxylation of C=C under mild conditions. Saturated mono- or dicarboxylic acids are generally obtained, in a ratio strongly dependent on the nature of the substrate. Activated olefins, arylalkenes and 1,3-dienes mainly afford dicarboxylic acids, in contrast to single CO₂ incorporation in less activated double bonds, tensed alkenes, allenes or enynes. The double bond is less reactive than the triple bond and, in intramolecular competition reactions, only the alkyne moiety is carboxylated.

EXPERIMENTAL PART

All the chemicals employed were of reagent grade quality. Dimethylformamide (Prolabo) was distilled under argon from calcium hydride and copper sulfate under reduced pressure and was dried over 4A molecular sieves. Tetrabutylammonium tetrafluoroborate (Fluka) was dried by heating overnight at 70 °C in vacuo. Ni(bipy)₃(BF₄)₂ was prepared according to ref 11. NiBr₂.dme was commercial (Alfa) and used directly in electrolytic solution, added to PMDTA (commercial ligand). Carbon dioxide was N45 (Alphagaz).

¹H and ¹³C NMR spectra were recorded on a Brucker AC 200 E spectrometer. IR spectra were recorded on a Perkin Elmer 577 spectrophotometer. Mass spectra were obtained on a finnigan ITD 800 spectrometer coupled to a Varian 300 chromatograph with DB-1 capillary column, either by electron impact or with CH4 or NH₃ as the ionizing agent. Gas chromatography was performed on either Intersmat IGC 120 with a SE-30 stainless steel (1/8 in-13 ft) column or a Delsi DI 200 equipped with a 25 m DB-1 capillary column.

General electrolysis procedure

For carboxylations at atmospheric CO₂ pressure, the two electrode, single-compartment electrochemical cell was similar to that described previously ¹⁰. A closed stainless-steel cell was used for carboxylations at $Pco_2 = 5$ atm. The anode is a cylindrical rod of magnesium (99.8, diameter 1 cm) surrounded by a carbon fiber cathode (apparent surface 20 cm²). A DMF (40ml) solution of nickel complex (either Ni(bipy)₃(BF₄)₂ (0.3 mmol) or NiBr₂.dme (0.3 mmol) + PMDTA (0.6 mmol)), containing n-Bu₄N⁺BF₄⁻ (0.3 mmol) and the substrate (3 mmol) was electrolyzed under carbon dioxide (1 or 5 atm), at a constant intensity of 50 mA. Faradayic yields were in the range of 50-80% for reaction times of 5-7h.

The reaction mixture was esterified directly in DMF by adding anhydrous K₂CO₃ (4 mmol) and methyl iodide (8 mmol) and stirring the mixture at 50 °C for 5h. The solution was hydrolyzed and extracted with Et₂O, and the organic layers washed with H₂O, dried over MgSO₄, and evaporated. The methyl esters corresponding to acids were isolated by column chromatography (normal or flash on silica gel) with pentane/Et₂O mixtures as eluent. The products were analyzed by NMR and IR spectrometry, mass spectroscopy, and GLC. Most carboxylated products are known compounds. For new compounds :

2-methyleneoct-7-enoic acid methyl ester (<u>17</u>).¹H NMR (CDCl₃) δ 6.06 (1H, s), 5.82-5.62 (1H, m), 5.4 (1H, s), 4.91 (1H, d, J=15.4Hz), 4.86 (1H, d, J=9.1Hz), 3.67 (3H, s), 2.23 (2H, t, J=7.2Hz), 2.04-1.93 (2H, m), 1.49-1.31 (4H, m); ¹³C NMR (CDCl₃) δ 167.59, 140.50, 138.57, 124.41, 114.30, 51.57, 33.40, 31.59, 28.31, 27.72; IR (neat, NaCl) 3070, 3015, 2990, 2970, 2920, 2850, 1720, 1635, 1625 cm⁻¹; GCMS (m/e, %) 168 (M⁺, 9.7), 137 (12.4), 109 (90.3), 67 (100); exact mass calcd for C₁₀H₁₆O₂ 168.1150, found 168.1144.

(*E*)-nona-2,8-dienoic acid methyl ester (<u>18</u>).¹H NMR (CDCl₃) δ 6.89 (1H, dt, J=15.7Hz, J=6.9Hz), 5.81-5.61 (1H, m), 5.74 (1H, d, J=15.5Hz), 4.92 (1H, d, J=15.5Hz), 4.86 (1H, d, J=8.6Hz), 3.65 (3H, s), 2.12 (2H, t, J=6.8Hz), 2.00-1.97 (2H, m), 1.41-1.33 (4H, m); ¹³C NMR (CDCl₃) δ 167.51, 149.33, 138.31, 120.82, 114.22, 51.19, 28.31, 28.18, 27.72, 27.30 ; IR (neat, NaCl) 3070, 2990, 2970, 2920, 2850, 1720, 1655, 1635 cm⁻¹; GCMS (m/e, %) 137 (M⁺-OMe, 10.3), 109 (37.4), 67 (100) ; exact mass calcd for C₁₀H₁₆O₂ 168.1150, found 168.1145.

2-(hex-5-enyl)buten-1,4-dienoic acid dimethyl ester (12).¹H NMR (CDCl₃) δ 5.74 (1H, s), 5.81-5.60 (1H, m), 4.94 (1H, d, J=14.7Hz), 4.88 (1H, d, J=9.9Hz), 3.76 (3H, s), 3.65 (3H, s), 2.29 (2H, t, J=7.0Hz), 2.04-1.95 (2H, m), 1.53-1.27 (4H, m); ¹³C NMR (CDCl₃) δ 169.24, 165.29, 150.65, 138.29, 119.10, 114.71, 52.18, 51.68, 34.10, 33.21, 27.97, 26.26 ; IR (neat, NaCl) 3070, 2990, 2970, 2930, 2850, 1735, 1720, 1655, 1640 cm⁻¹; GCMS (m/e, %) 226 (M⁺, 26.6), 195 (33.9), 167 (63.7), 107 (100) ; exact mass calcd for C₁₁H₁₅O₄ (M⁺-OMe) 211.0970, found 211.0946.

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