



Titanium(IV) isopropoxide-mediated dimerization of 2-(ferrocenylmethylidene)-1,3-dicarbonyl compounds

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ARTICLE INFO

Article history:

Received 26 February 2010

Received in revised form

15 June 2010

Accepted 16 June 2010

Available online 30 July 2010

Keywords:

Ferrocene

2-(Ferrocenylmethylidene)-1,3-dicarbonyl compounds

Reductive dimerization

Titanium(IV) isopropoxide

Electrochemistry

ABSTRACT

Diethyl 2-(ferrocenylmethylidene)malonate undergoes linear dimerization with formation of tetraethyl 2,3-diferrocenylbutane-1,1,4,4-tetracarboxylate when treated with EtMgBr in the presence of Ti(OⁱPr)₄. Under similar conditions, ethyl (*E*)-2-(ferrocenylmethylidene)benzoylacetate and ethyl (*E,Z*)-2-(ferrocenylmethylidene)acetoacetate afford linear dimerization products (3,4-diferrocenyladipic acid derivatives) and intramolecular cyclization products of the latter (3,4-diferrocenylcyclopentanol derivatives). No products of the Kulinkovich reaction (hydroxycyclopropanation of the ester groups) were observed. The structures of the compounds obtained were established based on data from IR, ¹H and ¹³C NMR spectroscopy, mass spectrometry and X-ray diffraction analysis. The mechanistic aspects of these reactions are discussed. Electrochemical properties of the compounds **7a**, **10** and **12** were investigated using cyclic voltammetry, one step potential chronoamperometry and square wave voltammetry. Two electrochemical processes (I–II), attributed to the oxidations of the ferrocenes moieties, *E*⁰(I), *E*⁰(II), Δ*E*⁰(II–I) and comproportionation constant *K*_{com} are reported.

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1. Introduction

Organometallic derivatives of the main group metals (organolithium, organomagnesium, organozinc, organoaluminum compounds) are widely used in synthetic organic chemistry as monocarbanionic nucleophiles in reactions with electrophiles [1,2]. In the presence of stoichiometric or catalytic amounts of transition metal complexes, structural transformations of monocarbanionic equivalents can occur leading to new, e.g., bis-anionic intermediates [3,4]. The transformations pertaining to this type of reactions include hydroxycyclopropanation of ester groups (the Kulinkovich reaction) under the action of, formally, ethylene bis-anion derived from ethylmagnesium bromide (ethyl monoanion) in the presence of Ti(OⁱPr)₄ [5–7] (Scheme 1).

In recent years, the Kulinkovich reaction in its diverse versions has widely been used for the construction of the hydroxycyclopropane ring in different types of organic compounds,

mainly, starting from esters of saturated acids or unsaturated nonconjugated acids [8].

As to esters of α,β-unsaturated acids, they have not virtually been studied. The only publication known [9] is devoted to the introduction of the hydroxycyclopropane ring into acrylates, cyclohex-1-enecarboxylates, and cyclopent-1-enecarboxylates. No studies on the behaviour of metallocene derivatives under the conditions of the Kulinkovich reaction have been carried out so far.

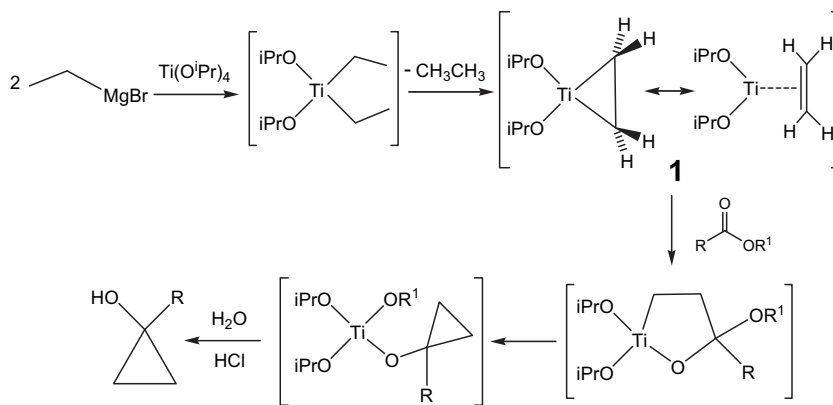
As a continuation of our research into ferrocenylcyclopropanes and ferrocenylcyclopropenes, it was of interest to investigate the Kulinkovich reaction as a feasible route for the conversion of alkoxy carbonyl derivatives of the ferrocene series into the hydroxycyclopropane-containing compounds. In the present work, we report the results of studies of reactions of 2-(ferrocenylmethylidene)-1,3-dicarbonyl compounds with EtMgBr/Ti(OⁱPr)₄.

2. Results and discussion

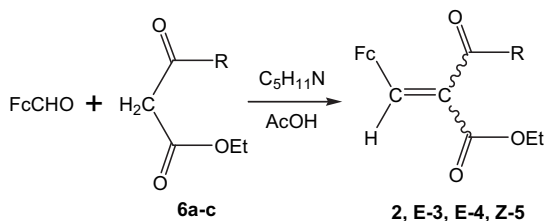
Diethyl 2-(ferrocenylmethylidene)malonate (**2**), ethyl (*E*)-2-(ferrocenylmethylidene)benzoylacetate (**E-3**), and ethyl (*E,Z*)-2-(ferrocenylmethylidene)acetoacetates (**E-4** and **Z-5**) were used as

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Scheme 1.



R = OEt (2, 6a); R = Ph (E-3, 6b); R = CH₃ (E-4, Z-5, 6c); Fc = C₅H₅FeC₅H₄

Scheme 2.

the starting compounds. They were prepared by coupling ferrocene-carbaldehyde (**1**) with diethyl malonate (**6a**), ethyl benzoylacetate (**6b**), and ethyl acetoacetate (**6c**), respectively, in the presence of piperidinium acetate [10,11] (Scheme 2).

We found that the reaction of diethyl 2-(ferrocenylmethylidene)malonate **2** with EtMgBr in the presence of Ti(OⁱPr)₄ afforded 68% of linear dimer (**7a,b**) as a ca. 2:1 mixture of two diastereomers **7a** and **7b** (¹H NMR data). In addition, the reduction product of the starting compound, viz., diethyl 2-(ferrocenylmethyl)malonate (**8**), and the 1,4-adduct of EtMgBr to the conjugated system, viz., diethyl 2-(1-ferrocenylpropyl)malonate (**9**), were also isolated (Scheme 3).

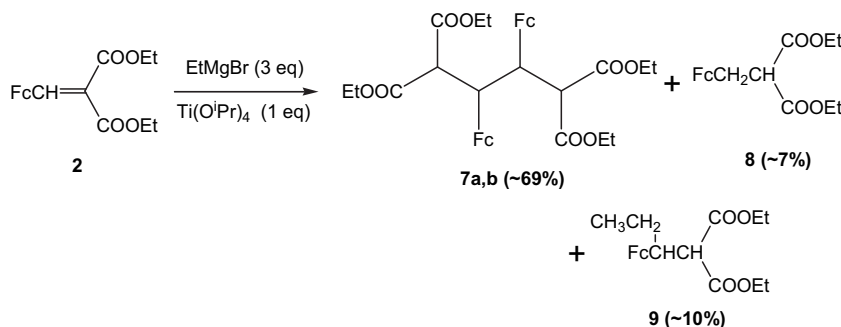
The structures of compounds **7a**, **7b**, **8**, and **9** isolated by column chromatography on alumina were established based on the data from IR and NMR spectroscopy, mass spectrometry, and elemental analysis. The dimeric nature of compounds **7a** and **7b** followed from their mass spectra, which contain peaks (*m/z* = 714) corresponding to the doubled molecular weight of the starting ester **2** [*2* × *M_r*(**2**) + 2].

The diastereomers **7a** and **7b** differ in physical parameters (m.p., *R_f*), and exhibit similar NMR spectral characteristics, which suggest their symmetrical structures (Fig. 1a, b, respectively). Thus the ¹H NMR spectra of the dimers **7a** and **7b** contain each two characteristic triplets and two quadruplets for the protons of four CH₃ and four CH₂ groups of the four –COOEt groups, one singlet for the protons of two unsubstituted cyclopentadienyl rings of two ferrocene substituents, one doublet for the protons of two methyne groups and one multiplet for the protons of two FcCH-fragments.

The spatial structure of the major diastereomer **7a** (yield ca. 40%) was elucidated by X-ray diffraction analysis of a single crystal obtained by crystallization from dichloromethane. The general view of the molecule **7a** is shown in Fig. 2. It follows from these data that compound **7a** is tetraethyl 2*S*^{*},3*R*^{*}-2,3-diferrocenylbutane-1,1,4,4-tetracarboxylate. The structure of tetraethyl 2*R*^{*},3*R*^{*}-2,3-diferrocenylbutane-1,1,4,4-tetracarboxylate was assigned to diastereomer **7b**.

We found further that the reactions of ethyl (*E*)-2-(ferrocenylmethylidene)benzoylacetate (*E*-3) and ethyl (*E,Z*)-2-(ferrocenylmethylidene)acetoacetates (*E*-4 and Z-5) with EtMgBr in the presence of Ti(OⁱPr)₄ afford, in addition to linear (**10**, **11**) dimers, the corresponding cyclic products (**12**, **13**) (ca. 1:2, ¹H NMR data) in a total yield of 65–71%. The stereochemistry of acetoacetates (*E*- or *Z*-) did not virtually influence the ratio of cyclic and linear dimers. As in the case of reaction with malonate **2**, the reduction products of the starting compounds (**14**, **15**) and the 1,4-adducts of EtMgBr to the system of conjugated double bonds (**16a,b**, **17a,b**) (Scheme 4) also represented minor components.

The structures of compounds **10**–**17** were established by spectroscopy. The ¹H NMR spectra of dimers **10** and **12** are shown in Fig. 1c, d. The spectroscopic data (¹H NMR) suggest that compounds



Scheme 3.

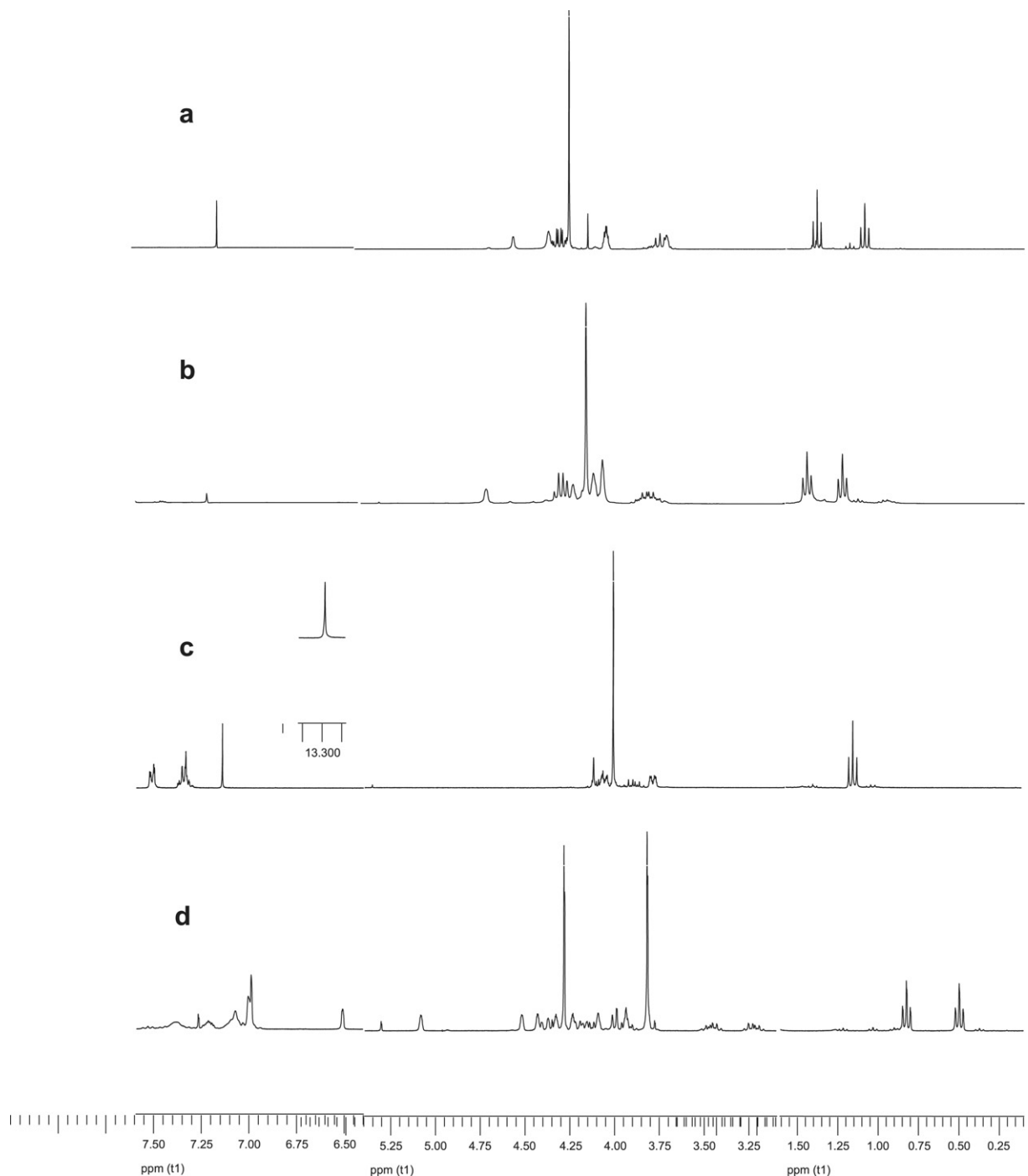


Fig. 1. ^1H NMR spectra: (a) of **7a**; (b) of **7b**; (c) of **10**; (d) of **12**.

10–13 represent each single diastereomer and compounds **16, 17** represent two diastereomers (**16a,b** and **17a,b**).

The dimeric nature of compounds **10–13** followed from their mass spectra, which contain peaks ($m/z = 778$ for **10** and **12**, 654 for **11** and **13**) corresponding to the doubled molecular weight of the starting esters **E-3**, **E-4** and **Z-5**.

The ^1H NMR spectrum of the linear dimer **10** contains characteristic signals for two protons of the enolic hydroxyl groups (δ 13.24), one triplet for six protons of two methyl groups ($-\text{COOEt}$), one singlet for the protons of unsubstituted C_5H_5 rings of two ferrocenes, and a multiplet for the protons of two Ph groups

(Fig. 1c). The presence in the ^{13}C NMR spectrum of compound **10** of one signal for two methyl groups, two ferrocenyl fragments, two C_{ipso} Fc carbon atoms, two C_{ipso} carbon atoms, two $\text{C}=\text{O}$ groups, and presence of two signals for two $\text{Ph}(\text{OH})=\text{C}-$ fragments [δ 106.40 (2C) and 171.75 (2C–OH) ppm] corroborates completely the suggested symmetric structure.

The ^1H NMR spectrum of the cyclodimer **12** contains signals for the protons of two methyl groups ($-\text{COOEt}$), two C_5H_5 fragments of two ferrocenyl substituents, two doublets and one doublet of doublets for the methine protons of the cyclopentane ring (Fig. 1d).

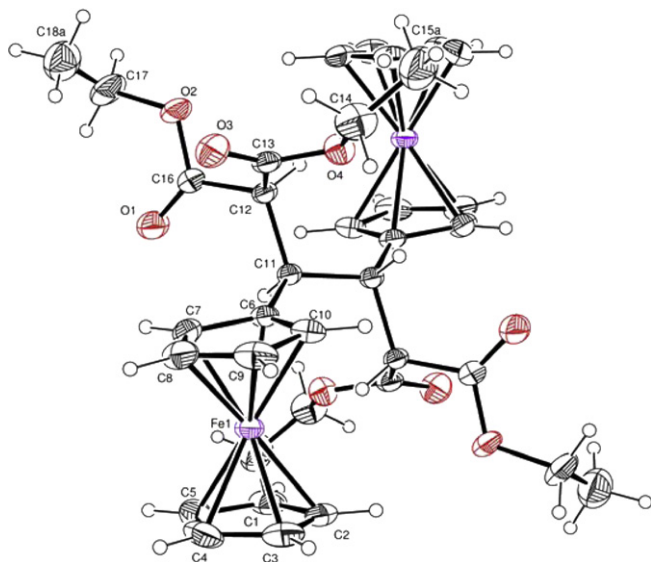


Fig. 2. Molecular structure of **7a**. Selected bond lengths (Å): C(11)–C(12) = 1.567(3), C(13)–O(4) = 1.333(3), C(11)–C(11a) = 1.544(4), C(12)–C(13) = 1.515(3), C(16)–O(1) = 1.193(3), C(16)–O(2) = 1.326(3), C(13)–O(3) = 1.187(2). Selected bond angles (°): C(12)–C(11)–C(11a) = 109.85(19), C(6)–C(11)–C(11a) = 114.4(2), O(1)–C(16)–O(2) = 123.6(2), O(1)–C(16)–C(12) = 126.3(2), O(2)–C(16)–C(12) = 110.01(18), C(7)–C(6)–C(10) = 106.91(18), C(7)–C(6)–C(11) = 123.85(19), C(7)–C(6)–Fe(1) = 68.19(12).

The spatial structure of cyclodimer **12** could be elucidated by X-ray diffraction analysis of a single crystal obtained by crystallization from chloroform. The general view of the molecule **12** is shown in Fig. 3.

The key element of the structure is the central cyclopentane ring in the envelope conformation. The ferrocenyl substituents are *trans* oriented to each other as are the hydrogen atoms at C(15), C(16), and C(17). The lengths of the bonds C(14)–C(18), C(14)–C(15), and C(17)–C(18) of the cyclopentadiene ring are equal to 1.605(4), 1.574(4), and 1.573(4) Å, respectively, which exceed somewhat the standard C–C σ -bonds (*cf.* literature data [12,13]: $d(\text{C}–\text{C}) = 1.54$ Å). The data from the X-ray diffraction analysis show that compound **12** is 2*R**-benzoyl-2,5*S**-diethoxycarbonyl-3*R**,4*S**-difero-cenyl-1*R**-phenylcyclopentanol. An analogous structure was assigned to

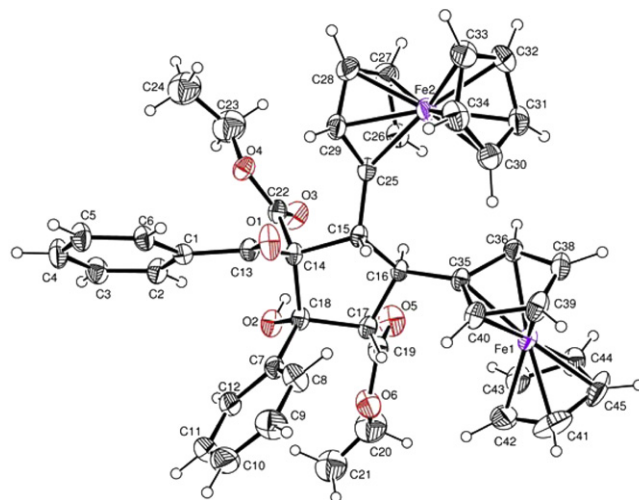
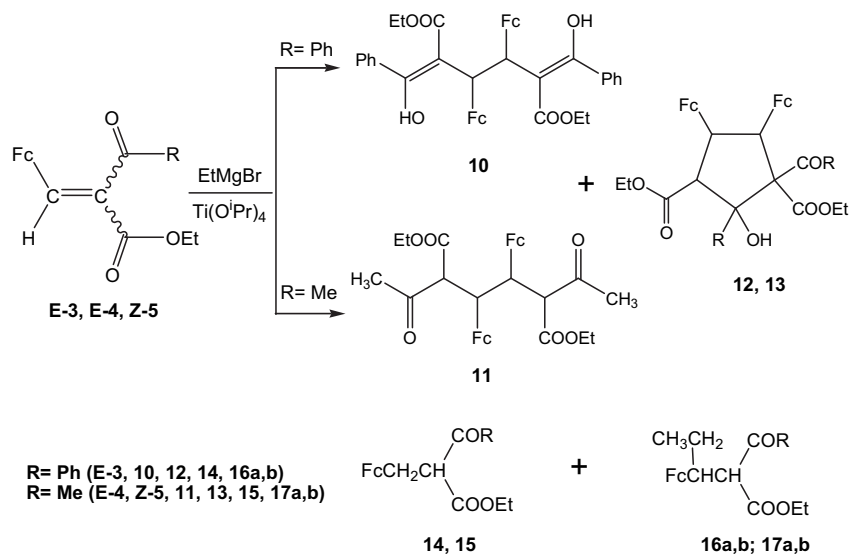


Fig. 3. Molecular structure of **12**. Selected bond lengths (Å): C(14)–C(15) = 1.577(4), C(15)–C(16) = 1.545(4), C(16)–C(17) = 1.525(4), C(17)–C(18) = 1.573(4), C(14)–C(13) = 1.558(4), C(14)–C(22) = 1.526(4), C(13)–O(1) = 1.213(3), C(22)–O(3) = 1.203(4). Selected bond angles (°): C(14)–C(15)–C(16) = 105.5(2), C(15)–C(14)–C(18) = 105.4(2), C(22)–C(14)–C(13) = 111.0(3), O(3)–C(22)–O(4) = 123.8(3), O(2)–C(18)–C(7) = 106.0(2), C(22)–C(14)–C(15) = 106.0(2), O(2)–C(18)–C(17) = 111.4(2), C(14)–C(15)–C(25) = 112.0(2).

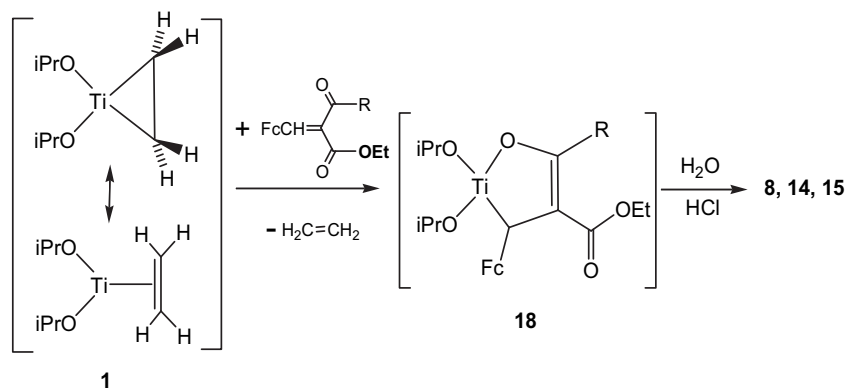
cyclodimer **13**. Our attempts to obtain crystals of compounds **10** and **11** suitable for X-ray diffraction analysis failed, therefore we could not unambiguously establish the spatial structures of these linear dimers.

The formation of dimers with linear (**7a,b**, **10**, **11**) and cyclic structures (**12**, **13**) and reduction products (**8**, **14**, **15**) of 2-(ferrocenylmethylidene)-1,3-dicarbonyl compounds (**2**–**5**) upon treatment with EtMgBr in the presence of Ti(O^{*i*}Pr)₄ proceeds, in our opinion, *via* dialkoxytitanate **1** as in the Kulinkovich reaction [5–7]. This intermediate generated in the first step plays the role of ethylene bis-anion in the reaction with α,β -unsaturated carbonyl compounds, but then adds, unlike the Kulinkovich reaction, at positions 1,4 of the C=C–C=O system of multiple bonds (Scheme 5).

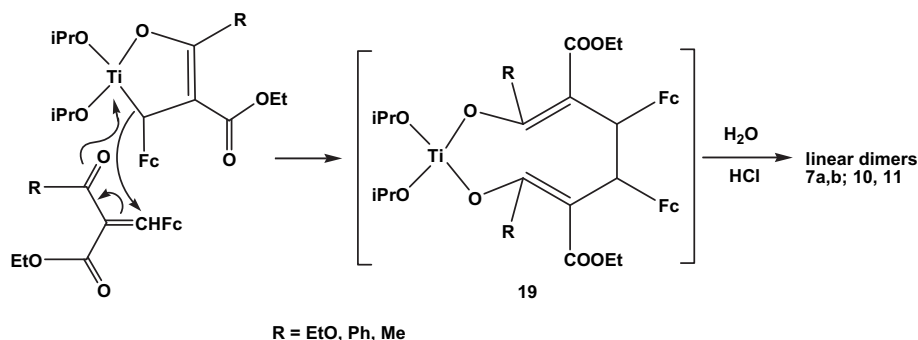
The intermediate 5-membered oxatitanacycle **18** with a 4,5-double bond is converted to the reduction product (**8**, **14**, **15**) or



Scheme 4.



Scheme 5.



Scheme 6.

serves as a monoanionic equivalent in subsequent reactions with 2-(ferrocenylmethylidene)-1,3-dicarbonyl compounds according to Schemes 6 and 7:

These dimerization schemes are supported by the following experimental facts: (1) the absence of hydroxycyclopropanation products of the ethoxycarbonyl groups in neither of reactions studied; (2) isolation of the reduction products of the starting 2-(ferrocenylmethylidene)-1,3-dicarbonyl compounds; (3) identification of linear dimers in the enol **10**, ketone **7a,b, 11** and cyclic **12, 13** forms.

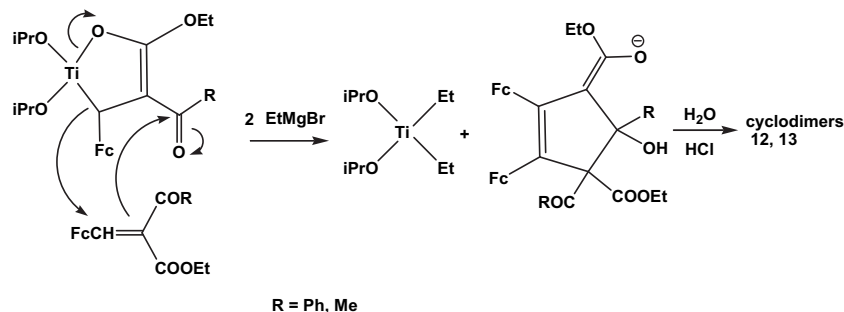
Particular attention should be paid to the diastereoselectivity of the dimerization processes, i.e., the formation of two linear diastereomers **7a** and **7b** (*ca.* 2:1) or linear (**10, 11**) and cyclic (**12, 13**) products (*ca.* 1.5:1).

3. Electrochemistry

Fig. 4 shows cyclic voltammetric response of compound **7a** in acetonitrile containing 0.1 M tetra-*N*-butylammonium tetrafluoroborate (TBABF₄).

When the potential scan was initiated to a positive direction, two oxidation signals (**I_a** and **II_a**) were observed. When the cycle was completed, two complementary reduction signals (**I_c** and **II_c**) were also detected. The anodic peak current values for signals **I_a** and **II_a** were independent of scan rate, which indicates that both responses are diffusion-controlled. In order to obtain the number of exchanged electrons in each process, one-step potential chronoamperometry experiments were performed at a potential step corresponding to the potential peak values, $E_{pa}(I)$ and $E_{pa}(II)$ (Fig. 5).

For two consecutive electron transfer reactions controlled by diffusion, the currents are established by the Cottrell equations (1) and (2) [14]. These relationships indicate that when a potential is held at the electrode surface with a constant value that promotes either the first (Eq. (1)) or the second electrochemical reaction (Eq. (2)), the current depends on the diffusion of the electroactive species from a solution to the electrode surface and the number of exchanged electrons. Under these conditions, the current $I(t)$ is a function of $t^{-1/2}$, due to the growth of a diffusion layer caused by the electrolysis near the electrode.



Scheme 7.

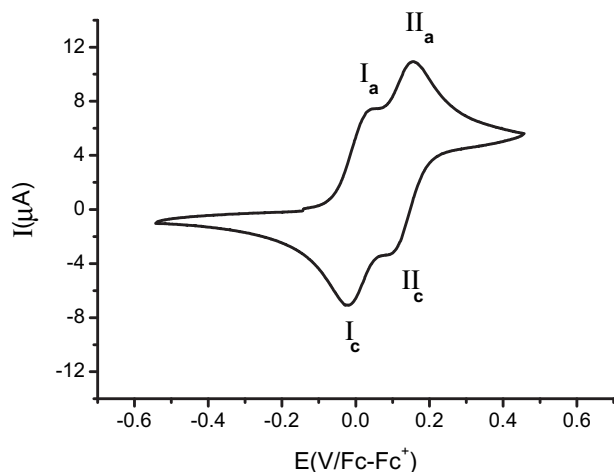


Fig. 4. Cyclic voltammograms obtained for **7a** in the presence of 0.1 M TBABF₄ in acetonitrile. The scan potential was initiated from E_{ocp} to positive direction. The scan rate 0.1 V s⁻¹. The working electrode used was platinum.

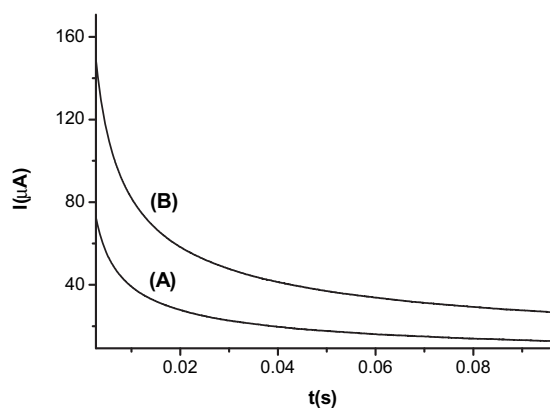


Fig. 5. One-step potential chronoamperometric experiments for **7a** in the presence of 0.1 M TBABF₄ in acetonitrile. The initial potential was the open circuit potential value E_{ocp} . The potential step (E_1) was (A) $E_{pa}(I)$ and (B) $E_{pa}(II)$. Pulse width time of 0.1 s.

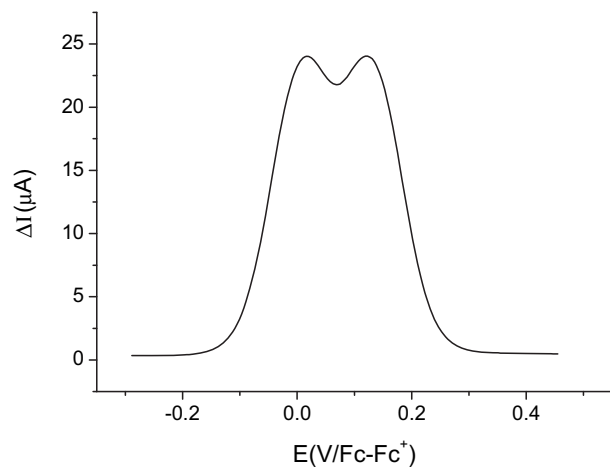


Fig. 6. Square wave voltammetry obtained for **7a** in the presence of 0.1 M TBABF₄ in acetonitrile. The amplitude was 50 mV with a frequency of 10 Hz. The working electrode used was platinum.

Table 1

Formal electrode potential $E^0(I)$, $E^0(II)$ and $\Delta E^0(II-I)$, and constant K_{com} for compounds **7a**, **10** and **12**.^a

Compound	$E^0(I)$	$E^0(II)$	$\Delta E^0(II-I)$	K_{com}
7a	0.015	0.120	0.105	60
10	0.019	0.073	0.054	8
12	-0.017	0.093	0.110	73

^a Formal electrode potential (E^0) vs ferrocene/ferrocenium in the presence of 0.1 M TBABF₄-acetonitrile. Obtained by square wave voltammetry.

$$I(t) = n_1 F \times A \times D_0^{1/2} \times \pi^{-1/2} \times Co^* t^{-1/2} \quad (1)$$

$$I(t) = (n_1 + n_2) F \times A \times D_0^{1/2} \times \pi^{-1/2} \times Co^* t^{-1/2} \quad (2)$$

For processes **I** and **II**, two linear relationships of current $I(t)$ and $t^{-1/2}$ were obtained, with the equations $I_I(t) = 3.9t^{-1/2} + 0.36$ ($r = 0.999$) and $I_{II}(t) = 8.1t^{-1/2} + 0.8$ ($r = 0.999$). Considering the same values of diffusion coefficient, the ratio of the slopes from the obtained relationships, allows us to estimate $n_1 = 1$ and $n_2 = 1$. This evidence indicates that processes **I** and **II** are attributed to the two consecutive one-electron transfers for ferrocene moieties. To obtain the formal electrode potential for both processes, square wave voltammetry experiments were carried out (Fig. 6).

The obtained values for processes **I** and **II**, were $E^0(I) = 0.015$ V/Fc-Fc⁺ and $E^0(II) = 0.120$ V/Fc-Fc⁺. The value of $\Delta E^0(II-I)$ for processes **I** and **II** was 0.105 V and the corresponding value of comproportionation constant K_{com} was 60 [14,15]. The electrochemical response of compounds **10** and **12** is very similar than the presented in compound **7a**. Table 1 shows a summary of the obtained values of $E^0(I)$, $E^0(II)$, and K_{com} for the compounds **7a**, **10**, and **12**. The estimated values of K_{com} for all compounds suggest that the electronic charge is slightly delocalized in the mixed valence state generated electrochemically according to the Robin-Day

Table 2

Crystal data and structure refinement parameters for compounds **7a** and **12**.

Data	7a	12
Molecular formula	C ₃₆ H ₄₂ Fe ₂ O ₈	C ₄₄ H ₄₂ Fe ₂ O ₆
Formula weight (g mol ⁻¹)	714.40	778.48
Temperature (K)	298 (2)	293 (2)
Crystal system	Monoclinic	Triclinic
Space group	P21/n	P-1
<i>a</i> (Å)	10.0544 (6)	8.2180 (2)
<i>b</i> (Å)	18.9430 (6)	12.5620 (5)
<i>c</i> (Å)	10.0633 (5)	17.6610 (6)
α (°)	90	87.120 (3)
β (°)	118.258 (7)	78.448 (3)
γ (°)	90	86.795 (3)
<i>V</i> (Å ³)	1688.24 (18)	1782.08 (10)
<i>Z</i>	2	2
<i>D</i> calc. (mg mm ⁻³)	1.405	1.451
Absorption coefficient (mm ⁻¹)	0.910	0.865
<i>F</i> (000)	748	812
Radiation, λ (Å)	Mo-K α , 0.71073	Mo-K α , 0.71073
Monochromator	Graphite	Graphite
θ range (°)	3.15–29.48	3.38–26.73
Reflections collected	6259	16187
Reflections independent	3460	7511
<i>R</i> _{int}	0.0180	0.0238
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0357, <i>wR</i> ₂ = 0.0905	<i>R</i> ₁ = 0.0506, <i>wR</i> ₂ = 0.1425
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0566, <i>wR</i> ₂ = 0.0963	<i>R</i> ₁ = 0.0788, <i>wR</i> ₂ = 0.1563
Refinable parameters	232	453
Goodness-of-fit	0.985	1.086
Refinement method	Full-matrix-least-squares on <i>F</i> ²	Full-matrix-least-squares on <i>F</i> ²
Minimum/maximum residual electron density (e Å ⁻³)	-0.287/0.303	-0.930/1.246

classification [15,16]. These values are in agreement with the presence of ethylene group between the ferrocene moieties [17]. It can be noticed that the presence of four COOEt groups in compound **7a** enhances the electronic charge delocalization ($K_{\text{com}} = 60$) compared with its analogue, compound **10** ($K_{\text{com}} = 8$), where there are only two COOEt groups.

4. Conclusion

Thus, diethyl 2-(ferrocenylmethylidene)malonate (**2**), ethyl (*E*)-2-(ferrocenylmethylidene)benzoylacetate (**E-3**) and ethyl (*E,Z*)-2-(ferrocenylmethylidene)acetoacetate (**E-4** and **Z-5**) produce no hydroxycyclopropyl derivatives in reactions with EtMgBr in the presence of $\text{Ti}(\text{O}^i\text{Pr})_4$ but rather undergo stereoselective dimerization into linear and cyclic polyfunctional products.

5. Experimental

All the solvents were dried according to the standard procedures and were freshly distilled before use. The ^1H and ^{13}C NMR spectra of compounds **2–17** were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz for ^1H and ^{13}C , respectively) of solutions in CDCl_3 with Me_4Si as the internal standard. Chemical shifts are given in ppm and J values in Hz. The IR spectra of samples prepared as KBr pellets were measured with an FTIR spectrophotometer (Spectrum RXI Perkin–Elmer instruments). The mass spectra were obtained on a Varian–MAT CH-6 instrument (EI, 70 eV). Elemental Analysensysteme LECO CHNS-900 was used for elemental analyses. Column chromatography was carried out on alumina (Brockmann activity III).

The unit cell parameters and the X-ray diffraction intensities were recorded on a Siemens P4 diffractometer. The crystallographic data, the experimental conditions, and corrections are given in Table 2. The structures of compounds **7a** and **12** were solved by the direct method (SHELXS-97 [18]) and refined using full-matrix least-squares on F^2 .

All electrochemical studies were performed at sample concentrations of ca. 1 mM in acetonitrile containing 0.1 M tetra-*N*-butylammonium tetrafluoroborate (TBABF₄) using an Epsilon-BAS potentiostat/galvanostat. A typical three-electrode array was employed. The working electrode was a platinum disk ($\varphi = 2$ mm). A platinum wire served as a counter-electrode. A silver wire immersed in acetonitrile solution with 0.1 M tetra-*N*-butylammonium chloride (TBACl), in a separate compartment connected to the working cell through a BAS vycor™ tip, was used as a pseudo reference electrode. All solutions were bubbled with nitrogen prior each measurement. Cyclic voltammetry experiments were initiated from open circuit potential (E_{ocp}) to a positive direction using a range of scan rate from 0.1 to 0.5 V s^{-1} . One step potential chronoamperometry experiments with a pulse width time of 1 s were acquired from open circuit potential (E_{ocp}) to different potential values (E_2) which correspond to anodic peak potential values. Square wave voltammetry experiments with amplitude of 50 mV and a frequency of 10 Hz were also performed. All potentials were reported versus the couple Fc/Fc^+ according to IUPAC convention [19].

The following reagents were purchased from Aldrich: ferrocenecarbaldehyde, 99%; diethyl malonate, 99%; ethyl acetoacetate, 99+%; ethyl benzoylacetate, 90%; ethylmagnesium bromide, 3.0 M solution in diethyl ether; titanium (IV) isopropoxide, 97%.

Diethyl 2-(ferrocenylmethylidene)malonate **2**, ethyl 2-(ferrocenylmethylidene)benzoylacetate **E-3** and ethyl 2-(ferrocenylmethylidene)acetoacetates **E-4** and **Z-5** were prepared by condensation of ferrocenecarbaldehyde with diethyl malonate, ethyl benzoylacetate and ethyl acetoacetate, respectively, in benzene in the presence of

piperidinium acetate [10,11]. The physical and ^1H NMR spectroscopic characteristics of compounds **2**, **E-3**, **E-4** and **Z-5** were in accord with the literature data [20–22].

5.1. Reactions of diethyl 2-(ferrocenylmethylidene)malonate (**2**) with EtMgBr in the presence of $\text{Ti}(\text{O}^i\text{Pr})_4$

- (a) A solution of EtMgBr in THF (1.0 M, 20 ml) was added dropwise with stirring at 10–15 °C to a solution of compound **2** (3.56 g, 10 mmol) and $\text{Ti}(\text{O}^i\text{Pr})_4$ (2.84 g, 10 mmol) in anhydrous THF (50 ml) and ether (100 ml) in an inert dry atmosphere. The mixture was stirred at this temperature for 2 h and quenched with 10% HCl (100 ml). The organic layer was separated, washed with water and 5% aqueous NaHCO_3 , and dried with MgSO_4 . The solvent was evaporated *in vacuo* and the residue was chromatographed on a column with Al_2O_3 (activity III) to afford the following reaction products: diethyl 2-(ferrocenylmethyl)malonate (**8**) (0.29 g, 8%, eluted with hexane); diethyl 2-(1-ferrocenylpropyl)malonate (**9**) (0.35 g, 9%, eluted with hexane); dimer **7b** (0.82 g, 23%, eluted with hexane–ethyl acetate, 1:10) and dimer **7a** (1.64 g, 46%, eluted with hexane–ethyl acetate, 1:2).
- (b) A solution of $\text{Ti}(\text{O}^i\text{Pr})_4$ (2.84 g, 10 mmol) in anhydrous THF (50 ml) was added dropwise to a 1.0 M solution of EtMgBr in THF (20 ml) in an inert dry atmosphere at 0–5 °C. The resulting dark-blue solution was stirred for an additional 30 min at 20 °C and a solution of **2** (3.56 g, 10 mmol) in THF (30 ml) was added dropwise and 100 ml of ether. After 1 h, the reaction mixture was quenched with HCl and worked up as described above. The following products were isolated by column chromatography: **8** (0.25 g, 7%), **9** (0.39 g, 10%), **7b** (0.75 g, 21%) and **7a** (1.6 g, 45%).

Tetraethyl 2*S**,3*R**-2,3-diferrocenylbutane-1,1,4,4-tetracarboxylate (**7a**), yellow crystals, m.p. 168–169 °C. IR (KBr): ν 486, 574, 661, 730, 818, 948, 1001, 1027, 1057, 1105, 1171, 1268, 1291, 1331, 1356, 1392, 1452, 1479, 1510, 1549, 1594, 1649, 1709, 1851, 2920, 2955, 3086 cm^{-1} . ^1H NMR: δ 1.07 (6H, t, 2CH₃, $J = 7.2$ Hz), 1.35 (6H, t, 2CH₃, $J = 7.11$ Hz), 3.77 (4H, m, 2CH₂), 4.09 (2H, m, C₅H₄), 4.14 (2H, m, 2CH-Fc), 4.27 (10H, s, 2C₅H₅), 4.37 (4H, m, 2CH₂), 4.39 (4H, m, C₅H₄), 4.59 (2H, m, C₅H₄), 4.33 (2H, d, 2CH, $J = 7.2$ Hz). ^{13}C NMR: δ 13.69, 14.18 (4CH₃), 42.42, 54.16 (4CH), 61.21, 61.45 (4CH₂), 68.88 (2C₅H₅), 66.36, 67.40, 69.05, 70.46 (2C₅H₄), 91.13 (2C_{ipso} Fc), 168.64, 170.06 (4C=O). Anal. Calc. for C₃₆H₄₂Fe₂O₈: C, 60.52; H, 5.93; Fe, 15.64. Found: C, 60.41; H, 6.09; Fe, 15.59%. MS: m/z 714 [M]⁺.

Tetraethyl 2*R**,3*R**-2,3-diferrocenylbutane-1,1,4,4-tetracarboxylate (**7b**), yellow powder, m.p. 149–151 °C. IR (KBr): ν 416, 477, 531, 587, 632, 698, 724, 754, 813, 946, 999, 1025, 1080, 1226, 1325, 1381, 1417, 1460, 1480, 1527, 1549, 1594, 1652, 1712, 1839, 2991, 3057 cm^{-1} . ^1H NMR: δ 1.15 (6H, t, 2CH₃, $J = 7.2$ Hz), 1.36 (6H, t, 2CH₃, $J = 7.11$ Hz), 3.75–3.93 (4H, m, 2CH₂), 4.08 (4H, m, C₅H₄), 4.11 (2H, m, 2CH-Fc), 4.17 (10H, s, 2C₅H₅), 4.15 (2H, m, 2CH₂), 4.73 (2H, m, C₅H₄), 4.31 (4H, q, 2CH₂, $J = 7.2$ Hz), 4.25 (2H, d, 2CH, $J = 6.0$ Hz). ^{13}C NMR: δ 13.81, 14.13 (4CH₃), 40.71, 56.72 (4CH), 61.06, 61.20 (4CH₂), 69.02 (2C₅H₅), 66.55, 66.98, 68.59, 69.47 (2C₅H₄), 90.66 (2C_{ipso} Fc), 168.22, 169.52 (4C=O). Anal. Calc. for C₃₆H₄₂Fe₂O₈: C, 60.52; H, 5.93; Fe, 15.64. Found: C, 60.68; H, 5.88; Fe, 15.55%. MS: m/z 714 [M]⁺.

Diethyl 2-ferrocenylmethylmalonate (**8**), yellow oil. ^1H NMR: δ 0.80 (6H, t, 2CH₃, $J = 7.2$ Hz), 3.02 (1H, dd, CH₂, $J = 6.3, 10.2$ Hz), 3.12 (1H, dd, CH₂, $J = 4.2, 10.2$ Hz), 3.47 (1H, dd, CH, $J = 4.2, 6.3$ Hz), 4.04 (4H, q, 2CH₂, $J = 7.2$ Hz), 4.05 (1H, m, C₅H₄), 4.09 (2H, m, C₅H₄), 4.12 (5H, s, C₅H₅), 4.16 (1H, m, C₅H₄). Anal. Calc. for C₁₈H₂₂FeO₄: C, 60.35; H, 6.19; Fe, 15.60. Found: C, 60.41; H, 6.23; Fe, 15.50%. MS: m/z 358 [M]⁺.

66.83, 67.64, 67.91, 68.27 (C₅H₄), 89.96 (C_{ipso} Fc), 168.11 (COOEt), 189.93 (MeC=O). Anal. Calc. for C₁₇H₂₀FeO₃: C, 62.21; H, 6.14; Fe, 17.02. Found: C, 62.17; H, 6.21; Fe, 16.99%. MS: *m/z* 328 [M]⁺.

Ethyl 2-(1-ferrocenylpropyl)acetoacetate (**17a,b**) (~1:1), yield 0.25 g (7% from **E-4**) and 0.21 g (6% from **Z-4**) (hexane), yellow oil. ¹H NMR: δ 1.05 (3H, t, CH₃, *J* = 7.2 Hz), 1.11 (3H, t, CH₃, *J* = 7.2 Hz), 1.21 (3H, t, CH₃, *J* = 6.9 Hz), 1.25 (3H, t, CH₃, *J* = 6.9 Hz), 1.95–2.18 (4H, m, 2CH₂, 2Et), 2.31 (3H, s, CH₃), 2.40 (3H, s, CH₃), 3.59 (2H, m, 2CH–Fc), 4.03 (4H, q, 2CH₂, *J* = 6.9 Hz), 4.07 (5H, s, C₅H₅), 4.10 (5H, s, C₅H₅), 4.12 (2H, m, C₅H₄), 4.15 (2H, m, C₅H₄), 4.21 (2H, m, C₅H₄), 4.29 (2H, m, C₅H₄), 4.49 (1H, d, CH, *J* = 6.9 Hz), 4.68 (1H, d, CH, *J* = 6.9 Hz). ¹³C NMR: δ 12.13, 12.23, 13.79, 13.97, 20.23, 20.64 (6CH₃), 26.69, 26.98 (2CH₂), 41.42, 43.87 (2FcCH), 59.85, 60.06 (2CH), 61.29, 61.71 (OCH₂), 68.52, 68.61 (2C₅H₅), 66.97, 67.09, 67.34, 67.58, 67.88, 68.37, 68.75, 68.89 (2C₅H₄), 90.03, 90.79 (2C_{ipso} Fc), 167.81, 168.03 (2COOEt), 189.12, 189.26 (2MeC=O). Anal. Calc. for C₁₉H₂₄FeO₃: C, 64.06; H, 6.79; Fe, 15.68. Found: C, 64.12; H, 6.67; Fe, 15.74%. MS: *m/z* 356 [M]⁺.

Acknowledgements

This work was supported by the CONAyT (Mexico, grant 100970). Thanks are due to E.A. Vázquez López for his technical assistance.

Appendix A. Supplementary material

CCDC-761352 (for **7a**) and CCDC-761353 (for **12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/const/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk].

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