^1H and ^{13}C NMR spectroscopic studies of half-esters from monohydrolysis of dialkyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylates

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Abstract. The structures of the half-esters from the monohydrolysis of (*exo,exo*)-, (*endo,endo*)-, and (*endo,exo*)-dialkyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylates were determined by ^1H and ^{13}C NMR as well as 2D NMR spectra, and the complete spectral assignment has been made. After conversion of one of the carboalkoxy groups to a carboxyl group, different tendencies were observed for the differences in ^1H and ^{13}C NMR chemical shifts between half-esters and the corresponding diesters.

1. Introduction

Bicyclo[2.2.1]heptene (norbornene) derivatives have been known for their characteristic chemical and structural properties due to their uniquely strained rigid structures [1]. The characteristic chemical properties associated with the strained skeleton are particularly susceptible to small changes in the structure as exemplified by pyramidalization or π -orbital tilting [2]. Such distortions can sometimes be monitored by spectroscopic methods. For example, we reported earlier that a series of half-esters that possess a norbornene skeleton shows characteristic large differences in the ^{13}C -NMR chemical shifts on the two olefinic carbons bearing a carboalkoxy group and a carboxyl group. We explained these characteristic differences by conformational effects from the two carbonyl groups based on thorough NMR and X-ray crystal studies [3]. Similarly, several more complete structure determinations of the bicyclo[2.2.1]heptene derivatives have been reported, taking advantage of additional advanced NMR techniques [4]. Such studies are important for more thoroughly understanding structural properties of bicyclo[2.2.1]heptene derivatives.

Here we report ^1H and ^{13}C NMR studies of several half-esters of bicyclo[2.2.1]hept-5-ene derivatives with *exo*- and/or *endo*-carboalkoxy or carboxyl groups at the C-2 and C-3 positions, **4a**, **4b**, **5a**, **5b**, **6a**, **6b**, **7a**, **7b**, as little has been reported about spectroscopic differences induced by two different

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Scheme 1.

Scheme 2. Carbon and proton numbering of the half-esters. Numbering of the protons is made from the carbon bearing the proton(s).

functional groups, *exo*- and/or *endo*-carboalkoxy and carboxyl groups, on the bicyclo[2.2.1]hept-5-ene skeleton.

These half-esters were obtained by selective monohydrolysis of the corresponding symmetric diesters, which Niwayama reported earlier [5,6]. Here we describe the ^1H and ^{13}C NMR assignments and spectral variations of these half-esters from the corresponding diesters.

2. Experimental

2.1. General

^1H and ^{13}C NMR spectra were measured and recorded on a JEOL ECP-500 spectrometer in CDCl_3 . The resonances of CDCl_3 at δ_{H} 7.24 ppm and δ_{C} 77.0 ppm were used as internal standards for NMR spectra. Mass spectra (EIMS) were recorded at 70 eV on a JEOL SX-102A spectrometer. High-performance liquid chromatography (HPLC) was performed using a system composed of a JASCO PU-980 pump and a JASCO UV-970 detector.

2.2. General procedure for monohydrolysis of diesters

All dimethyl and diethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylates **1a**, **1b**, **2a**, **2b**, **3a**, and **3b** were readily obtained in high yields by following reported procedures [7]. A diester (0.3 mmol) was dissolved in 0.5 mL of THF, and 5 mL of water was added. The reaction mixture was immersed in an ice-water bath and cooled to 0°C. To this reaction mixture, 2.5 mL of 0.25 M NaOH was added. The reaction mixture was stirred at the same temperature. Consumption of the starting material was monitored by thin-layer chromatography. To quench the reaction, the reaction mixture was acidified with 1 M HCl at 0°C, saturated with NaCl, and extracted with ethyl acetate three times. This extract was evaporated *in vacuo* and purified by silica gel column chromatography. In the monohydrolysis of **3a** and **3b**, the further separation of half esters **6a** and **7a** as well as **6b** and **7b** from the mixtures was carried out repeatedly on an analytical HPLC column [Inertsil SIL-100 (GL Science, 4.6 mm i.d. $\times$ 250 mm), flow rate 2.0 ml/min; solvent hexane–2-propanol (98 : 2); detection UV (215 nm)].

IR and mass data for these products are as follows: **4a**; colorless oil, IR (neat, cm^{-1}): 1707, 1735, 2950–3000; HR-EIMS calcd for $\text{C}_{10}\text{H}_{12}\text{O}_4$: 196.0736, found 196.0736. **4b**; colorless oil, IR (neat, cm^{-1}): 1708, 1735, 2950–3000; HR-EIMS calcd for $\text{C}_{11}\text{H}_{14}\text{O}_4$: 210.0892, found 210.0891. **5a**; white solid (m.p. 71–72°C), IR (neat, cm^{-1}): 1711, 1739, 2950–3000; HR-EIMS calcd for $\text{C}_{10}\text{H}_{12}\text{O}_4$: 196.0736, found 196.0735. **5b**; colorless oil, IR (neat, cm^{-1}): 1711, 1737, 2950–3000; HR-EIMS calcd for $\text{C}_{11}\text{H}_{14}\text{O}_4$: 210.0892, found 210.0892. **6a**; white solid (m.p. 121–122°C), IR (neat, cm^{-1}): 1696, 1724, 2950–3000; HR-EIMS calcd for $\text{C}_{10}\text{H}_{12}\text{O}_4$: 196.0736, found 196.0735. **6b**; colorless oil, IR (neat, cm^{-1}): 1704, 1732, 2950–3000; HR-EIMS calcd for $\text{C}_{11}\text{H}_{14}\text{O}_4$: 210.0892, found 210.0892. **7a**; colorless oil, IR (neat, cm^{-1}): 1696, 1724, 2950–3000; HR-EIMS calcd for $\text{C}_{10}\text{H}_{12}\text{O}_4$: 196.0736, found 196.0735. **7b**; colorless oil, IR (neat, cm^{-1}): 1704, 1732, 2950–3000; HR-EIMS calcd for $\text{C}_{11}\text{H}_{14}\text{O}_4$: 210.0892, found 210.0892.

3. Results and discussion

3.1. Monohydrolysis of diesters **1a**, **b**, **2a**, **b**, and **3a**, **b**

Earlier, Niwayama reported a highly efficient selective monohydrolysis reaction of symmetric diesters, employing THF and aqueous NaOH solution at 0°C [5]. In contrast to classical saponification, this reaction produces the corresponding half-esters from a series of symmetric diesters in near-quantitative to modestly high yields. We reported recently that when this reaction is applied to norbornene diesters that possess ester groups at *exo*- and/or *endo*-positions, **1a**, **b**–**3a**, **b**, the reaction predominantly monohydrolyzes the *exo*-carbomethoxy or carboethoxy groups [6]. In the monohydrolysis of **3a** and **3b**, the product ratios of **6a** and **7a** as well as **6b** and **7b** were determined to be 87 : 13 from the relative intensities of integral curves corresponding to the olefinic protons in the ^1H NMR spectrum of the mixture of these half-esters (*vide infra*). The *exo*-facial selectivities in the reaction of **3a**, **b** may be attributed to the steric bulkiness of the C_5 – C_6 ethylene versus C_7 methylene bridges.

3.2. NMR spectral assignments of (*exo*,*exo*)-half-esters **4a**, **b** from (*exo*,*exo*)-diesters **1a**, **b**

The ^1H NMR spectra of (*exo*,*exo*)-half-esters **4a**, **b** from (*exo*,*exo*)-diesters **1a**, **b** are shown in Fig. 1. The assignments of ^1H and ^{13}C signals of the half-esters were achieved by ^1H – ^1H COSY, HMBC, and

Fig. 1. The ^1H NMR spectra of (*exo,exo*)-half-esters **4a** (upper) and **4b** (lower).

HMBC spectra and differential NOE experiments. The ^1H and ^{13}C NMR assignments of diesters **1a, b** and half-esters **4a, b** are presented in Tables 1 and 2.

As can be seen in Fig. 1 and Table 1, although the symmetry of the compounds was destroyed by the reaction, the ^1H NMR signals of H-1/H-4, H-2/H-3, and H-5/H-6 of the half-esters **4a, b** were observed at about the same chemical shifts. On the other hand, the ^{13}C NMR signals of half-esters at C-1/C-4, C-2/C-3, and C-5/C-6 appeared at different chemical shifts by desymmetrization of the molecules, although these pairs of carbons have identical chemical shifts in the starting symmetric diesters, **1a, b**. However, the differences in the ^{13}C -NMR chemical shifts for each pair of half-esters **4a, b** were small (<0.2 ppm). The assignments of geminal protons at H-7a and H-7b were made with the aid of the NOE interaction observed between H-7a and the olefin protons H-5/H-6 (0.5%), rather than analysis of the ^1H - ^1H COSY, HMQC, and HMBC spectra.

Table 1

^1H NMR chemical shifts^a (ppm) of diesters (*exo,exo*)-**1a**, **b** and half-esters (*exo,exo*)-**4a**, **b** (500 MHz, CDCl_3) (coupling constants in parentheses)

Proton	1a	1b	4a	4b
1	3.05 (brs)	3.04 (brs)	3.08 (m) ^b	3.09 (m) ^b
2	2.58 (brs)	2.56 (brs)	2.61 (m) ^c	2.61 (m) ^c
3	2.58 (brs)	2.56 (brs)	2.61 (m) ^c	2.61 (m) ^c
4	3.05 (brs)	3.04 (brs)	3.08 (m) ^b	3.09 (m) ^b
5	6.16 (brs)	6.17 (brs)	6.18 (m) ^d	6.20 (m) ^d
6	6.16 (brs)	6.17 (brs)	6.18 (m) ^d	6.20 (m) ^d
7a	1.45 (brd, 8.7)	1.44 (brd, 8.7)	1.47 (brd, 9.2)	1.47 (brd, 9.2)
7b	2.07 (brd, 8.7)	2.10 (brd, 8.7)	2.06 (brd, 9.2)	2.09 (brd, 9.2)
Ester				
CH_3	3.61 (s)	1.20 (t, 7.1)	3.62 (s)	1.21 (t, 7.1)
CH_2		4.06 (m)		4.09 (q, 7.1)

^a δ 7.26 was used as the internal standard.

^b Signal patterns with the same superscript (b–d) are unclear due to overlapping.

In order to examine the differences in ^1H and ^{13}C NMR chemical shifts between (*exo,exo*)-diesters **1a**, **b** and (*exo,exo*)-half-esters **4a**, **b** more thoroughly, we analyzed the chemical shift differences, $\Delta\delta\text{H}$ ($= \delta\text{H}_{(\text{Half-ester})} - \delta\text{H}_{(\text{Diester})}$) and $\Delta\delta\text{C}$ ($= \delta\text{C}_{(\text{Half-ester})} - \delta\text{C}_{(\text{Diester})}$) for each proton and carbon on the bicyclo[2.2.1]hept-5-ene skeleton. In particular, we focused on the differences in these $\Delta\delta\text{H}$ and $\Delta\delta\text{C}$ values for each proton and carbon and those for the carbon (C-7) located at the symmetry center of the bicyclo[2.2.1]hept-5-ene skeleton and the proton (H-7a) attached to this C-7 more remotely from the reaction site. Therefore, $\Delta\Delta\delta\text{H}$ values (defined $\Delta\Delta\delta\text{H} = 0.00$ for H-7a) and $\Delta\Delta\delta\text{C}$ values (defined $\Delta\Delta\delta\text{C} = 0.0$ for C-7) between (*exo,exo*)-diesters **1a**, **b** and (*exo,exo*)-half-esters **4a**, **b** were calculated and the results are summarized in Scheme 3. Positive and negative values mean relative up-

Table 2

^{13}C NMR chemical shifts^a (ppm) of diesters (*exo,exo*)-**1a, b** and half-esters (*exo,exo*)-**4a, b** (125 MHz, CDCl_3)

Carbon	1a	1b	4a	4b
1	45.5	45.6	45.7 ^b	45.8 ^b
2	47.2	47.3	47.4 ^c	47.5 ^c
3	47.2	47.3	47.3 ^c	47.2 ^c
4	45.5	45.6	45.4 ^b	45.5 ^b
5	137.9	138.0	137.9 ^d	137.9 ^d
6	137.9	138.0	138.0 ^d	138.1 ^d
7	45.2	45.4	45.3	45.4
Ester				
C=O	173.9	173.5	173.8	173.3
CH_3	51.7	14.1	51.8	14.0
CH_2		60.5		60.8
Carboxylic acid				
C=O			179.8	179.1

^a δ 77.0 was used as the internal standard.

^b Assignments with the same superscript (b–d) may be reversed.

field and downfield shifts of the chemical shifts of the half-esters from those of the starting diesters, respectively.

As seen in Scheme 3, most of the ^1H NMR signals of half-esters shifted downfield, while distinct tendencies were not observed by conversion of the carboalkoxy group to the carboxyl group at the C-3 position. On the other hand, probably due to the change in the electron density or conformational changes by conversion to the carboxyl group at C-3, $\Delta\Delta\delta\text{C}$ values at C-1/C-2/C-6 and C-3/C-4/C-5 were observed to have opposite signs to a small extent.

3.3. NMR spectral assignments of (*endo,endo*)-half-esters **5a, b** from (*endo,endo*)-diesters **2a, b**

The ^1H NMR spectra of (*endo,endo*)-half-esters **5a, b** from (*endo,endo*)-diesters **2a, b** are shown in Fig. 2. In contrast to (*exo,exo*)-half-esters **4a, b**, the ^1H and ^{13}C NMR signals of (*endo,endo*)-half-esters **5a, b** exhibit different chemical shifts. With the assistance of ^1H – ^1H COSY, HMQC, and HMBC spectra and differential NOE experiments, all of ^1H and ^{13}C NMR signals of **2a, b** and **5a, b** were able to be assigned as listed in Tables 3 and 4.

Scheme 3. The relative $\Delta\delta H$ values ($\Delta\delta H = \delta H_{(\text{Half-ester})} - \delta H_{(\text{Diester})}$; $\Delta\delta H = 0.00$ for H-7a) and $\Delta\delta C$ values ($\Delta\delta C = \delta C_{(\text{Half-ester})} - \delta C_{(\text{Diester})}$; $\Delta\delta C = 0.00$ for C-7) of the half-esters. The $\Delta\delta C$ values are given in parentheses. Plus and minus signs mean upfield and downfield shifts of the chemical shift of the half-esters from those of the starting diesters, respectively. The values with the same superscript (a-c) in 4a, b may be reversed.

Fig. 2. The ^1H NMR spectra of (*endo,endo*)-half-esters **5a** (upper) and **5b** (lower).

In particular, the ^1H signals of the H-2/H-3 and H-5/H-6, which were located at the same chemical shifts as broad singlets in diesters **2a, b**, showed a double doublet pattern at different chemical shifts. Moreover, in diethyl ester **2b** and half-ester **5b**, the coupling pattern of the methylene protons of the carboethoxy group was a more complicated, probably due to the anisotropic effect from the carbonyl group of the *endo*-carboethoxy group. The assignments of the geminal protons H-7a/H-7b were achieved by the NOE interaction observed between H-7a and the protons H-2/H-3 (4.8%).

As shown in Scheme 3, the $\Delta\Delta\delta$ values in ^1H and ^{13}C NMR chemical shifts for (*endo,endo*)-half-esters **5a, b** showed different tendencies from those of (*exo,exo*)-half-esters **4a, b**. After conversion of the carboalkoxy group at C-3 to a carboxyl group, the $\Delta\Delta\delta\text{H}$ values for protons at H-2/H-4/H-5 were positive, while the value of the proton at H-3 was negative. Notably, the $\Delta\Delta\delta\text{H}$ value at H-5 was the largest positive value. Moreover, the $\Delta\Delta\delta\text{C}$ values for carbons at C-3/C-4/C-5 were positive, while that for the carbon at C-6 was negative.

Table 3

^1H NMR chemical shifts^a (ppm) of diesters (*endo,endo*)-**2a**, **b** and half-esters (*endo,endo*)-**5a**, **b** (500 MHz, CDCl_3) (coupling constants in parentheses)

Proton	2a	2b	5a	5b
1	3.11 (brs)	3.12 (brs)	3.15 (m)	3.16 (m)
2	3.24 (brs)	3.23 (brs)	3.25 (dd, 3.2, 10.3)	3.25 (dd, 3.2, 10.3)
3	3.24 (brs)	3.23 (brs)	3.29 (dd, 3.2, 10.3)	3.30 (dd, 3.2, 10.3)
4	3.11 (brs)	3.12 (brs)	3.12 (m)	3.14 (m)
5	6.21 (brs)	6.22 (brs)	6.17 (dd, 3.0, 5.5)	6.20 (dd, 3.0, 5.5)
6	6.21 (brs)	6.22 (brs)	6.27 (dd, 3.0, 5.5)	6.28 (dd, 3.0, 5.5)
7a	1.42 (brd, 8.9)	1.42 (brd, 8.7)	1.45 (brd, 8.7)	1.46 (brd, 8.7)
7b	1.28 (brd, 8.9)	1.28 (brd, 8.7)	1.30 (brd, 8.7)	1.31 (brd, 8.7)
Ester				
CH ₃	3.56 (s)	1.20 (t, 7.1)	3.55 (s)	1.19 (t, 7.1)
CH ₂		4.02 (m)		4.03 (q, 7.1)

^a δ 7.26 was used as the internal standard.

3.4. NMR spectral assignments of (*endo,exo*)-half-esters **6a**, **b** and **7a**, **b** from (*endo,exo*)-diesters **3a**, **b**

The ^1H NMR spectra of the mixture of half-esters **6a** and **7a** as well as the mixture of **6b** and **7b** from (*endo,exo*)-diesters **3a**, **b** are shown in Fig. 3. We have reported that the product ratios of **6a** and **7a** as well as **6b** and **7b** in the monohydrolysis of **3a**, **b** were determined to be 87 : 13 by the relative intensities of the integral curves corresponding to the olefinic protons [6]. The mixtures of **6a** and **7a** as well as **6b** and **7b** were separated into each half-ester by HPLC. All of the ^1H and ^{13}C NMR signals of (*endo,exo*)-diesters **3a**, **b** and (*endo,exo*)-half-esters **6a**, **b** and **7a**, **b** were assigned with the assistance of 2D NMR spectra and differential 1D-NOE experiments (Tables 5 and 6).

Table 4

^{13}C NMR chemical shifts^a (ppm) of diesters (*endo,endo*)-**2a**, **b** and half-esters (*endo,endo*)-**5a**, **b** (125 MHz, CDCl_3)

Carbon	2a	2b	5a	5b
1	46.2	46.3	46.5	46.6
2	48.0	48.3	48.2	48.5
3	48.0	48.3	48.0	48.0
4	46.2	46.3	46.0	46.2
5	134.8	134.8	134.3	134.4
6	134.8	134.8	135.5	135.4
7	48.6	45.4	48.7	48.7
Ester				
C=O	172.8	172.4	172.8	172.3
CH_3	51.4	14.1	51.4	14.0
CH_2		60.2		60.4
Carboxylic acid				
C=O			178.5	177.9

^a δ 77.0 was used as the internal standard.

In the ^1H - ^1H COSY spectra of the major half-ester **6a** as shown in Fig. 4, the signal of H-1 (δ 3.26) showed cross peaks with H-2 (δ 3.36) and the geminal protons H-7a/H-7b (δ 1.45 and 1.59). However, the signal of H-4 (δ 3.19) showed cross peaks with the geminal protons of H-7, while a cross peak with H-3 (δ 2.71) was not observed. According to the cross peaks of the ^1H - ^1H COSY and the H-C-C-H dihedral angles of H(1)-C-C-H(2) and H(4)-C-C-H(3) [8], the signals of H-2 and H-3 of major half-ester **6a** could be assigned to *exo* and *endo* positions, respectively. Furthermore, the assignment of H-2 was confirmed by the observed NOE interaction between H-7b and H-2 (3.8%). By similar methods, the signals of H-2 (δ 3.41) and H-3 (δ 2.64) of minor half-ester **7a** were assigned to *exo* and *endo* positions, respectively. In major half-ester **6b**, the ^1H NMR signals of methylene protons of the carboethoxy group showed a more complicated coupling pattern, as in the case of half-ester **5b**.

The ^1H and ^{13}C NMR data of minor half-ester **7b** were identical to those reported except for the ^{13}C assignment of the carbonyl carbon of the carboxyl group [9]. The small difference in the ^{13}C NMR chemical shift for the carbonyl carbon of the carboxyl group (1.5 ppm) is probably due to the difference in the concentration [10].

As can be seen from Scheme 3, the $\Delta\Delta\delta\text{H}$ and $\Delta\Delta\delta\text{C}$ values of major half-esters **6a**, **b** and minor half-esters **7a**, **b** showed different tendencies. In the case of major half-esters **6a**, **b**, the protons at H-3/H-4 showed negative $\Delta\Delta\delta\text{H}$ values after conversion of the carboalkoxy group at C-3 to the carboxyl

Fig. 3. The ^1H NMR spectra of the product mixture of (*endo,exo*)-half-esters **6a** and **7a** (upper) and the product mixture of **6b** and **7b** (lower).

group, while the proton at H-2 showed a positive $\Delta\Delta\delta\text{H}$ value. However, the variation in $\Delta\Delta\delta\text{C}$ values of major half-esters **6a, b** was small. On the other hand, in the case of minor half-esters **7a, b**, the protons at H-1/H-2/H-4/H-6 showed negative $\Delta\Delta\delta\text{H}$ values after conversion of the carboalkoxy group at C-2 to the carboxyl group, while the proton at H-3 showed a positive $\Delta\Delta\delta\text{H}$ value. Also, the carbons at C-1/C-2/C-4 were observed to have positive $\Delta\Delta\delta\text{C}$ values. The differences in these variations of the $\Delta\Delta\delta\text{C}$ values between major half-esters **6a, b** and minor half-esters **7a, b** may be attributed to several factors induced by conversion of the *endo* and *exo* carboalkoxy groups to the carboxyl groups, such as the difference in electron densities on the carbon skeleton or differences in the conformation of these functional groups.

Fig. 4. The two-dimensional ^1H - ^1H correlation diagram of the product mixture of half-esters **6a** and **7a**. Peak lines show the correlation cross peaks of selected ^1H signals.

Table 5

^1H NMR chemical shifts^a (ppm) of diesters (*endo,exo*)-**3a, b** and half-esters (*endo,exo*)-**6a, b, 7a, b** (500 MHz, CDCl_3) (coupling constants in parentheses)

Proton	3a	3b	6a	6b	7a	7b
1	3.21 (m)	3.23 (m)	3.26 (m)	3.25 (m)	3.28 (m)	3.27 (m)
2 (<i>exo</i>)	3.32 (dd, 3.7, 4.6)	3.34 (dd, 3.7, 4.4)	3.36 (dd, 3.7, 4.6)	3.34 (dd, 3.7, 4.6)	3.41 (dd, 3.7, 4.6)	3.42 (dd, 3.7, 4.6)
3 (<i>endo</i>)	2.63 (dd, 1.6, 4.6)	2.64 (dd, 1.6, 4.6)	2.71 (dd, 1.6, 4.6)	2.71 (dd, 1.6, 4.6)	2.64 (dd, 1.6, 4.6)	2.62 (dd, 1.6, 4.6)
4	3.07 (m)	3.08 (m)	3.19 (m)	3.18 (m)	3.13 (m)	3.12 (m)
5	6.22 (dd, 3.2, 5.5)	6.25 (dd, 3.2, 5.5)	6.28 (dd, 3.2, 5.5)	6.27 (dd, 3.2, 5.5)	6.28 (dd, 3.2, 5.5)	6.28 (dd, 3.2, 5.5)
6	6.02 (dd, 2.8, 5.5)	6.04 (dd, 2.8, 5.5)	6.07 (dd, 2.8, 5.5)	6.06 (dd, 2.6, 5.5)	6.12 (dd, 2.8, 5.5)	6.11 (dd, 2.8, 5.5)
7a	1.41 (dq, 1.6, 8.9)	1.42 (dq, 1.6, 2.9)	1.47 (dq, 1.6, 8.9)	1.46 (dq, 1.6, 8.9)	1.47 (dq, 1.6, 8.7)	1.45 (dq, 1.6, 8.7)
7b	1.56 (brd, 8.9)	1.59 (brd, 8.9)	1.60 (brd, 8.9)	1.60 (brd, 8.9)	1.59 (brd, 8.7)	1.59 (brd, 8.7)
<i>exo</i> -Ester						
CH ₃	3.66 (s)	1.25 (t, 7.1)			3.71 (s)	1.25 (t, 7.1)
CH ₂		4.13 (q, 7.1)				4.15 (q, 7.1)
<i>endo</i> -Ester						
CH ₃	3.59 (s)	1.20 (t, 7.1)	3.64 (s)	1.22 (t, 7.1)		
CH ₂		4.07 (m)		4.08 (m)		

^a δ 7.26 was used as the internal standard.

Table 6

^{13}C NMR chemical shifts^a (ppm) of diesters (*endo,exo*)-**3a, b** and half-esters (*endo,exo*)-**6a, b**, **7a, b** (125 MHz, CDCl_3)

Carbon	3a	3b	6a	6b	7a	7b
1	45.5	45.6	45.6	45.7	45.6	45.6
2	47.8	47.8	47.8	47.9	47.6	47.7
3	47.0	47.1	47.1	47.2	47.1	47.3
4	47.5	47.7	47.6	47.7	47.6	47.6
5	137.5	137.5	137.5	137.5	137.8	137.8
6	135.1	135.0	135.3	135.2	135.2	135.2
7	47.2	47.2	47.4	47.3	47.5	47.4
<i>exo</i> -Ester or carboxylic acid						
C=O	174.8	174.4	179.0	180.0	174.7	174.2
CH_3	52.0	14.2 ^b			52.2	14.2
CH_2		60.7				61.0
<i>endo</i> -Ester or carboxylic acid						
C=O	173.6	173.2	173.6	173.1	177.2	177.9
CH_3	51.7	14.2 ^b	51.9	14.2		
CH_2		60.4		60.7		

^a δ 77.0 was used as the internal standard.

^b Assignments with the same superscript may be reversed.

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