

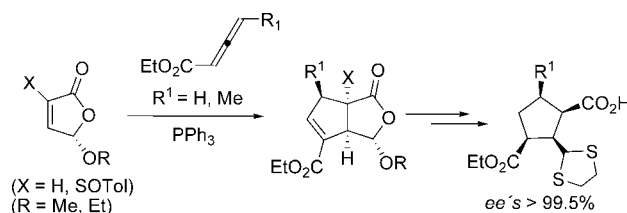
Totally Regio- and Stereoselective Behavior of Mono- and Diactivated Cyclic Alkenes in the Lu Reaction: Synthesis of Enantiopure Functionalized Cyclopentanes

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Received August 27, 2008



5-Alkoxyfuran-2(5H)-ones and their optically pure 3-*p*-tolylsulfinyl derivatives, synthetic equivalents of the acyclic esters, react with dipoles generated from allenoates and PPh₃ (Lu reaction), in a completely regioselective, π -facial selective and *endo*-selective manner, yielding bicyclic adducts, which are easily converted into optically pure highly substituted cyclopentane derivatives.

Introduction

Nucleophilic catalysis by phosphines has emerged as a good synthetic tool in organic chemistry.¹ In 1995 Lu reported the first [3+2] cycloaddition of electron-deficient olefins with the 1,3-dipoles generated by conjugate addition of phosphines to 2-butynoates or 2,3-butadienoates² to afford cyclopentenes. Since this disclosure, allene cycloadditions to a wide range of electron-poor C=C bonds^{3–5} and polarized C=X bonds (X = N,⁶ O⁷) have been studied. Intramolecular processes work in a

highly regio- and stereoselective manner⁸ but the efficiency of the intermolecular ones, mainly studied on acyclic and exocyclic alkenes, is usually lower and clearly dependent on the structure of the dipolarophile. Moreover, only dual activated or terminal alkenes can be used as the two-carbon partner (except for intramolecular processes) due to reactivity and regioselectivity problems.^{1a,2} The asymmetric version of the intermolecular Lu reaction has been reported by using chiral phosphines,⁹ chiral 1,3-dipoles derived from butynoic acid derivatives,^{5b,c} and chiral dipolarophiles.^{4d,5b,10} Antecedents in this field are scarce and most of the cases are enones with exocyclic double bonds. Concerning acyclic unsaturated esters, only unsubstituted acrylates and diethyl maleate react with the allene with high enantiomeric excess in the presence of some chiral phosphines.^{9a} On the other hand, although it could be expected that electron-poor endocyclic olefins exhibited better dipolarophilic features (higher reactivity, and better regio- and stereoselectivity) than their corresponding acyclic ones, they have also been scarcely used in the Lu reaction.¹¹ Consequently, reactions with unsaturated esters have not been widely exploited in the synthesis of

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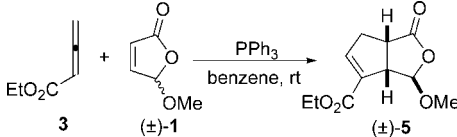
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TABLE 1. Reaction of (±)-1 with 3



entry	equiv of (±)-1	equiv of PPh ₃	time (h)	isolated yield (%)
1	1.5	0.15	14	61
2	1.5	0.30	14	68
3	2.0	0.30	14	75
4	2.0	0.40	6.5	69

optically pure cyclopentane carboxylic derivatives, despite their wide occurrence in natural products.

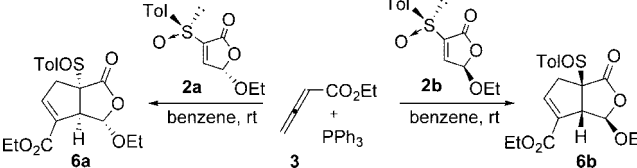
The excellent features as dipolarophiles exhibited by 5-methoxyfuran-2(5H)-one (**1**) and its 3-*p*-tolylsulfinyl derivatives (**2a** and **2b**) in many [3+2] dipolar cycloadditions,¹² and the scarce knowledge about the dipolarophilic behavior of endocyclic double bonds in Lu reactions, prompted us to study the behavior of these compounds in their reactions with the allenyl esters **3** and **4** in the presence of PPh₃. Furanones **1** and **2** can be considered as synthetic equivalents of 3-formylacrylate, leading to adducts that can be easily transformed into highly functionalized cyclopentanes. In this paper we report the results obtained in the reactions of ethyl allenates **3** and **4** with furanones **1** or **2**, which provide a new entry to optically pure highly substituted cyclopentanes.

Results and Discussions

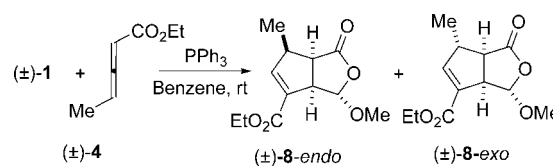
We first studied the reaction of racemic furanone **1** with commercially available ethyl 2,3-butadienoate (**3**) in the presence of catalytic amounts of PPh₃ (Table 1). The reaction evolved in benzene at room temperature. The ¹H NMR spectra of the crude reaction revealed the presence of a sole adduct [(±)-5], easily isolated by flash column chromatography, along with the signals corresponding to the unreacted furanone **1**. The ratios allene/catalyst and allene/furanone slightly modified the reaction rate (it seems to be faster on increasing the amount of catalyst, entry 4) and the yields (see Table 1), with the conditions of entry 3 being the most efficient.

The complete regioselectivity observed in reactions from (±)-**1** is worth mentioning, in contrast with the mixture of regioisomers usually obtained from acyclic dipolarophiles, which suggests that the endocyclic character of the double bond improves the dipolarophilic features of the olefins. The stereoselectivity is also completely controlled by the orientation of the OMe group at C-5, which hinders the approach of the dipole, only affording the *anti* adduct. Moreover, as the reaction of **3** with ethyl crotonate does not work,² the formation of adduct **5** from (±)-**1** indicates that the cyclic compound is much more reactive than the acyclic analogues.

We then studied the reactions of the allenolate **3** with the optically pure sulfinylfuranones **2a** and **2b**. The obtained results

TABLE 2. Reactions of 5-Ethoxy-3-*p*-tolylsulfinylfuran-2(5H)-ones **2a** and **2b** with Ethyl 2,3-Butadienoate (**3**) under PPh₃ Catalysis


entry	furanone	equiv of 3	equiv of PPh ₃	time (h)	cycloadduct (isolated yield, %)
1	2a	1.5	0.15	12	6a (84)
2	2a	1.5	0.30	3.3	6a (91)
3	2a	2.0	0.20	6.5	6a (75)
4	2a	2.0	0.30	3	6a (96)
5	2b	1.5	0.30	3.5	6b (47)
6	2b	1.5	0.20	5.5	6b (33)
7	2b	2.0	0.30	2.5	6b (75)

SCHEME 1. Reaction of Furanone **1** with Allenolate (±)-4

are collected in Table 2. The regio- and stereoselectivity of these reactions were also complete and compounds **6a** and **6b** were isolated as the sole adducts of their respective reactions. They are the result of the *anti* approach of the dipole to the 5-ethoxy group, regardless of the configuration at sulfur,¹³ which indicates that C-5 is the controller of the facial selectivity.

Under the optimal conditions, the isolated yield for **6a** was excellent (96%, entry 4, Table 2), whereas it was high but lower for **6b** (75%, entry 7, Table 2). It could be presumably due to the different stability of the starting furanones and/or adducts (lower for **b** isomers) in the presence of PPh₃.¹⁴

The role of the sulfinyl group in these reactions is limited to an enhancement of the reactivity of the dipolarophile (compare reaction times in Tables 1 and 2), which was confirmed by a competitive experiment. Thus, the reaction of a 1:1 mixture of **1** and **2a** (2 equiv) with allenolate **3** (1 equiv) and PPh₃ (0.3 equiv), at room temperature for 1 h, afforded a 1:8 mixture of adducts **5/6a**.

Finally, we have studied the reactions of the cyclic dipolarophiles with ethyl pent-2,3-dienoate [(±)-4] in the presence of PPh₃. Reactions of **4** with (±)-**1** (Scheme 1) also evolved in a completely regioselective and π -facial selective manner but with a moderate *endo/exo* selectivity,¹⁵ thus yielding a 2:1 mixture of two *anti* adducts, **8-endo** being the major one. Under the best conditions (1.5 equiv of **4** and 0.3 equiv of PPh₃, for 14 h) isolated yields were 45% (**8-endo**) and 24% (**8-exo**). The influence of the methyl group on the reactivity of the allene was scarce as it could be established by competitive experiments.¹⁶

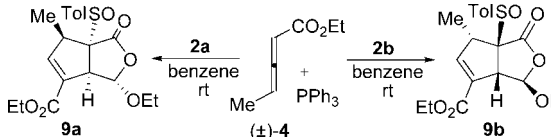
(13) Though we have used only the sulfoxide of *S* configuration, we can say "regardless of the configuration at sulfur", because **2b** [(*S,S*,5*R*)-isomer] is the enantiomer of (*S*),*R*,5*S*-isomer, and the (*S*),*R*,5*R*-stereoisomer is the enantiomer of **2a** [(*S*),*S*,5*S*-isomer].

(14) It is noteworthy that a small amount (5%) of ethyl 3-(*p*-tolylsulfinyl)but-3-enoate **7** could be isolated in the reaction from epimer **2b**, which could be the result of the addition of sulfenic acid (resulting from the *syn*-pyrolytic elimination from **6b**) to the allene **3**. See: (a) Grainger, R. S.; Tisselli, P.; Steed, J. W. *Org. Biomol. Chem.* **2004**, *2*, 151. (b) Aversa, M. C.; Barattucci, A.; Bonaccorsi, P.; Giannetto, P. *Curr. Org. Chem.* **2007**, *11*, 1034.

(15) *Endo/exo* selectivity refers to the orientation of the methyl group on the bicyclic structure.

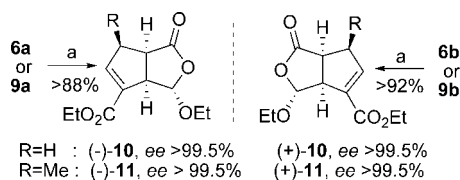
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TABLE 3. Reactions of **2a** and **2b** with (\pm)-**4** under PPh_3 Catalysis


entry	furanone	equiv of 4	equiv of PPh_3	<i>endo/exo</i> ratio ^a	time (h)	yield (%)
1	2a	3	0.30	97:<3	1	9a (44)
2	2a	2	0.30	97:<3	2	9a (34)
3	2a	1.5	0.30	97:<3	1.5	9a (47)
4 ^b	2b	1.5	0.30	97:<3	3.5	9b (29)
5	2b	2	0.20	97:<3	1	9b (24)

^a Ratio determined by ^1H NMR. ^b $\text{P}(p\text{-ClC}_6\text{H}_4)_3$ was used instead of PPh_3 .

SCHEME 2. Desulfinylation of Adducts **6** and **9** with $\text{Al}(\text{Hg})^a$ 

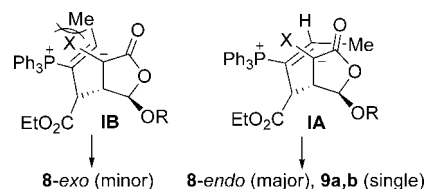
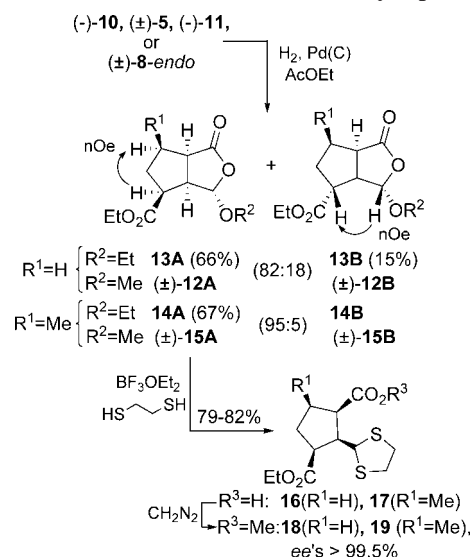
^a a = $\text{Al}(\text{Hg})$, THF/ H_2O , rt.

Only one adduct (**9a** or **9b**) was isolated in the reactions of **4** with furanones **2a** and **2b** (Table 3). This means that the *endo/exo* selectivity was completely controlled by the sulfinyl group, which also increased the reactivity. Under the best conditions (entries 3 and 4, respectively) the isolated yields are moderate (47% for **9a**, entry 3) or low (29% for **9b**, entry 4), but no other adduct could be isolated from the reaction mixture.

The adducts **6** and **9** were efficiently desulfinylated with Al/Hg . Thus, **6a** and **6b** afforded enantiomers (–)-**10** and (+)-**10**, respectively, both in optically pure form (Scheme 2). 6-Methyl derivatives **9a** and **9b** also were efficiently desulfinylated into (–)-**11** and (+)-**11**, respectively.¹⁷ Therefore, compounds **2a** and **2b** can be considered as the enantiomerically pure synthetic equivalents of furanone (\pm)-**1**.

Although many stereochemical features of these compounds could be established from NMR studies, their unequivocal configurational assignment required the X-ray diffraction studies of compounds **6b** and **9b**.¹⁸ The chemical correlation of these compounds with **6a** and **9a**, through their desulfinylated products **10** and **11**, allowed the stereochemical assignment of the adducts derived from furanones **2a** and **2b**. The comparison of the NMR spectra of compounds **10** and **11** with (\pm)-**5** and (\pm)-**8-endo**, respectively, revealed their structural similarities.

The complete regioselectivity¹⁹ observed in reactions of the furanones with **3** and **4** contrasts with the modest regioselectivity

**FIGURE 1.** Rationalization of the *endo*-selectivity.**SCHEME 3.** Transformations toward Cyclopentanes

reported for ethyl acrylate (75:25 mixture),² acrylonitrile (83:17 mixture),² and methyl vinyl ketone (63:37 mixture),² which reveals the positive influence of the furanone moiety.²⁰

The complete π -facial selectivity observed in reactions from **1** and **2** can be easily explained by assuming that the *syn*-approach is strongly destabilized with respect to the *anti*-approach by steric and stereoelectronic interactions of the dipole with the 5-alkoxy group. Moreover, the exclusive formation of *anti*-adducts both from **2a** and **2b** indicates that the orientating character of the alkoxy group at C-5 is higher than that of the sulfinyl function at C-3. However, the sulfinyl group completely controls the *endo*-selectivity, which is very low in reactions from **1**. This control can be explained taking into account the higher stability of intermediate **IA** with respect to that of **IB**, destabilized by the Me/SOTol interaction (Figure 1).

The presence of the α,β -unsaturated ester moiety in the obtained adducts offers multiple synthetic possibilities to obtain polysubstituted rings. Additionally, their bicyclic structure suggests an efficient control of the stereoselectivity, which opens interesting possibilities in the synthesis of optically pure cyclopentanes. Our initial studies in this field concern the hydrogenation focused on the preparation of all-*cis* tri- and tetrasubstituted cyclopentanes. Hydrogenation of (\pm)-**5** or (–)-**10** catalyzed by Pd/C yielded 82:18 mixtures of two stereoisomers (**A** and **B**) of **12** and **13**, respectively (Scheme 3). The **A** isomers can be epimerized into **B** isomers with NaH. The major **A** isomer results from the approach of the hydrogen to the less hindered face, as has been demonstrated by NOESY experiments. Under similar conditions, (–)-**11** or (\pm)-**8-endo** evolved with higher selectivity (95:5) to afford adducts **14A** (Scheme 3) and **15A**. The major compounds, (\pm)-**12A**, **13A**,

(16) Reaction of a 1:1:1 mixture of **1**, **3**, and **4** yielded a 3:2 mixture of **5** and **8** (determined by ^1H NMR analysis of the crude reaction mixture).

(17) The ee values were determined by HPLC employing a Daicel Chiralpack AD column and with hexane and isopropyl alcohol as eluent.

(18) Crystallographic data (excluding structure factors) for **6b** and **9b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 695572 and 695573. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax +44(0)-1223-366033 or e-mail deposit@ccdc.cam.ac.uk].

(19) Regioselectivity of these reactions with acrylate esters has been explained by theoretical calculations at the B3LYP/6-31G(d) level. See: Dudding, T.; Kwon, O.; Mercier, E. *Org. Lett.* **2006**, *8*, 3643.

(20) Other examples of regioselective Lu reactions are reported, see refs 5b and 11.

14A, and (\pm)-**15A**, were transformed into the *all-cis* trisubstituted and tetrasubstituted methyl cyclopentanecarboxylates (**18** and **19**), by reaction with ethanodithiol catalyzed by $\text{BF}_3 \cdot \text{OEt}_2$,²¹ and further reaction with diazomethane.

In summary 5-alkoxyfuran-2(5*H*)-ones react efficiently with allenates with complete regioselectivity and *anti*-selectivity. The incorporation of the sulfinyl group to the furanones increases the reactivity and controls the *endo*-selectivity thus affording optically pure bicyclic adducts, which have been selectively transformed into *all-cis* functionalized cyclopentane carboxylic acids. Application of adducts obtained from furanones and allenes in the stereoselective synthesis of cyclopentanes with great functional diversity will be reported in due course.

Experimental Section

a. Cycloaddition of Ethyl 2,3-Butadienoate (3) to Furanones Catalyzed by Triphenylphosphine. To a stirred solution of 0.2 M furanone **1**,²² **2a**,²³ or **2b**²³ in benzene, under positive pressure of argon, was added at room temperature allene **3** (2 equiv) and finally 0.3 equiv of triphenylphosphine (solution 0.6 M) in benzene. The reaction was monitored by TLC. The solvent was removed in vacuo and the crude reaction was analyzed by ^1H NMR and immediately purified by column chromatography.

Ethyl (\pm)-(R₃,S_{3a},S_{6a})-3-Methoxy-1-oxo-3,3a,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-carboxylate (5). **5** was obtained by reaction of 5-methoxyfuran-2(5*H*)-one (**1**) (0.53 mmol), commercial ethyl 2,3-butadienoate (1.05 mmol), and PPh_3 (0.13 mmol) after 14 h. It was isolated by column chromatography (hexane–ethyl acetate, 4:1) as a colorless oil. Yield 75%. IR (neat) 1780, 1716, 1632, 1270, 1201, 1102, 948 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 6.82 (q, 1H, $J = 2.3$ Hz), 5.49 (s, 1H), 4.23 (m, 2H), 3.66 (m, 1H), 3.53 (s, 3H), 3.35 (dt, 1H, $J = 2.8$ and 7.7 Hz), 2.91 (m, 2H), 1.31 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ 179.4 (C), 163.4 (C), 144.7 (CH), 133.6 (C), 106.6 (CH), 60.8 (CH₂), 56.8 (CH₃), 53.1 (CH), 41.0 (CH), 36.6 (CH₂), 14.2 (CH₃). Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_5$: C, 58.40; H, 6.24. Found: C, 58.69; H, 6.07.

Ethyl (S₃,R_{3a},S_{6a},S₈)-3-Ethoxy-6a-[(4-methylphenyl)sulfinyl]-1-oxo-3,3a,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-carboxylate (6a). **6a** was obtained from furanone **2a** (0.20 mmol), ethyl 2,3-butadienoate (0.38 mmol), and PPh_3 (0.06 mmol) after 3.3 h. It was isolated by column chromatography (hexane–ethyl acetate, 3:1) as a colorless oil. Yield 91%. $[\alpha]_D^{20} +93.3$ (c 0.60, CHCl_3). IR (neat) 1772, 1714, 1635, 1208, 1157, 1115, 944 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 7.56 and 7.33 (AA'BB' system, 4H), 6.71 (m, 1H), 5.69 (s, 1H), 4.23 (m, 2H), 4.16 (m, 1H), 3.92 (m, 1H), 3.74 (m, 1H), 3.22 (dt, 1H, $J = 2.3$ and 19.1 Hz), 2.45 (dt, 1H, $J = 2.5$ and 19.1 Hz), 2.43 (s, 3H), 1.31 (t, 3H, $J = 7.1$ Hz), 1.30 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ 173.1 (C), 162.8 (C), 143.0 (C), 142.9 (CH), 135.7 (C), 132.6 (C), 129.4 (CH), 125.9 (CH), 104.8 (CH), 72.3 (C), 65.8 (CH₂), 61.0 (CH₂), 55.4 (CH), 34.9 (CH₂), 21.6 (CH₃), 14.9 (CH₃), 14.2 (CH₃). Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_6\text{S}$: C, 60.30; H, 5.86; S, 8.47. Found: C, 59.96; H, 6.03; S, 8.41.

Ethyl (R₃,S_{3a},R_{6a},S₈)-3-Ethoxy-1-oxo-6a-[(4-methylphenyl)sulfinyl]-3,3a,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-carboxylate (6b). **6b** was obtained from furanone **2b** (0.20 mmol), ethyl 2,3-butadienoate (0.40 mmol), and PPh_3 (0.06 mmol) after 2.5 h. It was isolated by column chromatography (hexane–ethyl acetate, 3:1) as a white yellow solid: mp 130–131 $^{\circ}\text{C}$. $[\alpha]_D^{20} +91.5$ (c 0.82, CHCl_3). Yield 75%. IR (KBr) 1765, 1710, 1631, 1597, 1340, 1236, 1115, 1084, 944 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 7.54

and 7.31 (AA'BB' system, 4H), 6.74 (m, 1H), 5.23 (d, 1H, $J = 1.3$ Hz), 4.20 (m, 2H), 3.82 (m, 1H), 3.55 (ddd, 1H, $J = 1.7$, 2.5 and 19.8 Hz), 3.36 (dt, 1H, $J = 2.5$ and 19.8 Hz), 3.28 (m, 2H), 2.41 (s, 3H), 1.28 (t, 3H, $J = 7.1$ Hz), 0.85 (t, 3H, $J = 7.1$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ 173.6 (C), 162.7 (C), 142.6 (C), 141.9 (CH), 135.2 (C), 134.0 (C), 129.7 (CH), 125.8 (CH), 107.0 (CH), 75.7 (C), 65.6 (CH₂), 61.0 (CH₂), 51.1 (CH), 41.5 (CH₂), 21.5 (CH₃), 14.4 (CH₃), 14.1 (CH₃). Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_6\text{S}$: C, 60.30; H, 5.86; S, 8.47. Found: C, 60.08; H, 5.90; S, 8.50.

Ethyl (\pm)-3-[(4-Methylphenyl)sulfinyl]but-3-enoate (7). This product was obtained as a byproduct from ethyl 2,3-butadienoate (**3**), sulfinylfuranones **2**, and triphenylphosphine. ^1H NMR (CDCl_3 , 300 MHz) δ 7.51 and 7.29 (AA'BB' system, 4H), 6.22 (s, 1H), 5.88 (s, 1H), 4.01 (q, 2H, $J = 7.2$ Hz), 3.13 and 2.93 (AB system, 2H, $J = 16.8$ Hz), 2.40 (s, 3H), 1.17 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ 169.0 (C), 147.5 (C), 142.0 (C), 138.6 (C), 129.9 (CH), 125.4 (CH), 120.8 (CH₂), 61.2 (CH₂), 32.9 (CH₂), 21.4 (CH₃), 14.0 (CH₃). MS (FAB⁺) (m/z) 253 ($\text{M}^+ + 1$) 100%.

b. Cycloaddition of Ethyl 2,3-Pentadienoate (4) to Furanones Catalyzed by Triphenylphosphine. To a stirred solution of 0.2 M furanone **1**, **2a**, or **2b** in benzene, under positive pressure of argon, was added at room temperature allene **4**²⁴ and finally a benzene solution of triphenylphosphine. The reaction was monitored by TLC. The amounts of reactants and catalyst are indicated in each case. The solvent was removed in vacuo and the crude reaction was analyzed by ^1H NMR and immediately purified by column chromatography.

Ethyl (\pm)-3-Methoxy-6-methyl-1-oxo-3,3a,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-carboxylates (8). These compounds were obtained as a mixture 60:40 *endo:exo*, from 5-methoxyfuran-2(5*H*)-one (**1**) (0.79 mmol), **4** (1.19 mmol), and PPh_3 (0.24 mmol in 4 mL), after 14 h. These isomers were separated by column chromatography (hexane–ethyl acetate, 9:1). Overall yield 69%.

(\pm)-(R₃,S_{3a},R_{6a},S₈)-8-*exo*: Colorless oil. TLC R_f (hexane–ethyl acetate, 6:1) 0.26. Yield 24%. IR (neat) 1780, 1714, 1630, 1454, 1266, 1217, 1102, 956 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 6.78 (t, 1H, $J = 2.3$ Hz), 5.47 (s, 1H), 4.23 (m, 2H), 3.71 (dt, 1H, $J = 2.3$ and 7.5 Hz), 3.52 (s, 3H), 3.25 (m, 1H), 2.97 (dd, 1H, $J = 1.1$ and 7.5 Hz), 1.31 (t, 3H, $J = 7.1$ Hz), 1.19 (d, 3H, $J = 7.3$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ 178.9 (C), 163.7 (C), 149.9 (CH), 132.0 (C), 106.5 (CH), 60.8 (CH₂), 56.7 (CH₃), 52.0 (CH), 48.5 (CH), 44.4 (CH), 20.1 (CH₃), 14.2 (CH₃). Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_5$: C, 59.99; H, 6.71. Found: C, 60.10; H, 6.78.

(\pm)-(R₃,S_{3a},S_{6a},S₈)-8-*endo*: Colorless oil. TLC R_f (hexane–ethyl acetate, 6:1) 0.21. Yield 45%. IR (neat) 1779, 1713, 1638, 1343, 1264, 1166, 1121, 941 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 6.68 (t, 1H, $J = 1.9$ Hz), 5.39 (s, 1H), 4.23 (m, 2H), 3.69 (m, 1H), 3.51 (s, 3H), 3.39–3.25 (m, 2H), 1.31 (t, 3H, $J = 6.9$ Hz), 1.30 (d, 3H, $J = 6.8$ Hz). ^1H NMR (C_6D_6 , 300 MHz) δ 6.28 (t, 1H, $J = 2.1$ Hz), 5.26 (d, 1H, $J = 0.9$ Hz), 3.96 (m, 2H), 3.44 (dtd, 1H, $J = 0.9$, 2.1 and 8.2 Hz), 3.18 (s, 3H), 2.82 (dd, 1H, $J = 8.2$ and 9.3 Hz), 2.62 (m, 1H), 1.06 (d, 3H, $J = 7.5$ Hz), 0.99 (t, 3H, $J = 7.1$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ 175.6 (C), 163.7 (C), 150.1 (CH), 132.0 (C), 106.0 (CH), 60.8 (CH₂), 56.7 (CH₃), 53.8 (CH), 44.1 (CH), 42.3 (CH), 15.1 (CH₃), 14.2 (CH₃). HRMS (FAB⁺) calcd for $\text{C}_{12}\text{H}_{17}\text{O}_5$ [$\text{M} + \text{H}$] 241.1076, found 241.1077.

Ethyl (S₃,R_{3a},R_{6a},S₈)-3-Ethoxy-6-methyl-1-oxo-6a-[(4-methylphenyl)sulfinyl]-3,3a,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-carboxylate (9a). **9a** was obtained from sulfinylfuranone **2a** (0.40 mmol), ethyl 2,3-pentadienoate (**4**) (0.60 mmol), and PPh_3 (0.12 mmol in 2 mL), after 1 h. It was isolated by column chromatography (hexane–ethyl acetate, 3:1) as a colorless oil. Yield 47%. $[\alpha]_D^{20} +100.1$ (c 1.40, CHCl_3). IR (neat) 1771, 1721, 1644, 1179, 1055 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 7.64 and 7.33 (AA'BB' system, 4H), 6.54 (t, 1H, $J = 2.1$ Hz), 5.52 (d, 1H, $J = 1.1$ Hz), 4.23 (m, 2H), 4.18 (m, 1H), 3.88 (m, 1H), 3.68 (m, 1H), 3.56 (tq, 1H, $J = 1.9$ and 7.5 Hz), 2.43 (s, 3H), 1.30 (t, 3H, $J = 7.2$ Hz),

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1.27 (t, 3H, $J = 7.1$ Hz), 0.74 (d, 3H, $J = 7.5$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ 169.9 (C), 162.9 (C), 148.7 (CH), 143.1 (C), 135.0 (C), 130.6 (C), 129.3 (CH), 126.4 (CH), 104.2 (CH), 74.3 (C), 65.7 (CH₂), 61.0 (CH₂), 56.5 (CH), 41.7 (CH), 21.1 (CH₃), 15.8 (CH₃), 14.9 (CH₃), 14.2 (CH₃). Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_6\text{S}$: C, 61.21; H, 6.16; S, 8.17. Found: C, 61.53; H, 6.30; S, 8.17.

Ethyl ($R_{3a}, S_{3a}, S_{6a}, R_{6a}, S_8$)-3-Ethoxy-6-methyl-1-oxo-6a-[(4-methylphenyl)sulfinyl]-3,3a,6,6a-tetrahydro-1H-cyclopenta[c]furan-4-carboxylate (9b). 9b was obtained from sulfinylfuranone 2b (0.20 mmol), ethyl 2,3-pentadienoate (4) (0.30 mmol), and PPh_3 (0.06 mmol in 1 mL), after 1 h. It was isolated by column chromatography (hexane–ethyl acetate, 3:1) as a yellow pale solid, mp 103–105 °C. Yield 24%. $[\alpha]_D^{20} +128.9$ (c 0.46, CHCl_3). IR (neat) 1761, 1715, 1644, 1263, 1084, 938 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 7.56 and 7.32 (AA'BB' system, 4H), 6.66 (t, 1H, $J = 2.1$ Hz), 5.17 (d, 1H, $J = 1.7$ Hz), 4.21 (m, 2H), 3.90 (m, 1H), 3.84 (m, 1H), 3.28 (q, 2H, $J = 7.1$ Hz), 2.41 (s, 3H), 1.41 (d, 3H, $J = 7.6$ Hz), 1.29 (t, 3H, $J = 7.1$ Hz), 0.83 (t, 3H, $J = 7.0$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ 170.6 (C), 163.0 (C), 147.6 (CH), 142.6 (C), 135.0 (C), 131.9 (C), 129.7 (CH), 126.2 (2CH), 106.0 (CH), 79.0 (C), 65.4 (CH₂), 61.0 (CH₂), 51.8 (CH), 46.9 (CH), 21.5 (CH₃), 15.7 (CH₃), 14.5 (CH₃), 14.2 (CH₃). HRMS (FAB⁺) calcd for $\text{C}_{20}\text{H}_{25}\text{O}_6\text{S}$ [M + H] 393.1372, found 393.1385. Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_6\text{S}$: C, 61.21; H, 6.16; S, 8.17. Found: C, 61.47; H, 6.06.

c. Desulfinylation of Primary Adducts with Aluminum Amalgam: General Procedure. To a vigorously stirred 0.01 M solution of sulfinylcycloadduct in a 9:1 mixture of THF–water was added aluminum amalgam (obtained from aluminum kitchen foil)²⁵ in small portions. Reaction is monitored by TLC and when the starting material was not observed the reaction mixture was filtered through celite and the solid was washed with dichloromethane. The solution was evaporated at reduced pressure to dryness. The product was isolated as indicated in each case.

All desulfinylated adducts were analyzed by HPLC with a Daicel Chiralpack AD column and with hexane and isopropyl alcohol as eluents with a continuous flow of 1 mL/min. Conditions and retention times are indicated in each case.

Ethyl (S_3, R_{3a}, R_{6a})-3-Ethoxy-1-oxo-3,3a,6,6a-tetrahydro-1H-cyclopenta[c]furan-4-carboxylate [(–)-10]. (–)-10 was obtained following the general procedure from cycloadduct 6a and was isolated by column chromatography (hexane–ethyl acetate, 5:1). Yield 88%. White solid, mp 70–72 °C. $[\alpha]_D^{20} -33.2$ (c 0.72, CHCl_3), ee >99.5% (hexane–isopropyl alcohol, 90/10, $R_t = 7.6$ min). IR (KBr) 1793, 1711, 1621, 1271, 1099, 1043, 948 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 6.83 (q, 1H, $J = 2.4$ Hz), 5.61 (s, 1H), 4.24 (m, 2H), 3.88 (m, 1H), 3.73–3.62 (m, 3H), 3.38 (td, 1H, $J = 2.6$ and 7.9 Hz), 2.92 (m, 2H), 1.31 (t, 3H, $J = 7.1$ Hz), 1.26 (t, 3H, $J = 7.1$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ 179.6 (C), 163.5 (C), 144.7 (CH), 133.7 (C), 105.4 (CH), 65.2 (CH₂), 60.8 (CH₂), 53.2 (CH), 41.1 (CH), 36.6 (CH₂), 14.9 (CH₃), 14.2 (CH₃). Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_5$: C, 59.99; H, 6.71. Found: C, 59.73; H, 6.32.

Ethyl (R_3, S_{3a}, S_{6a})-3-Ethoxy-1-oxo-3,3a,6,6a-tetrahydro-1H-cyclopenta[c]furan-4-carboxylate [(+)-10]. (+)-10 was obtained following the general procedure from furanone 2b and ethyl 2,3-butadienoate and subsequent desulfinylation with aluminum amalgam. It was isolated by column chromatography (hexane–ethyl acetate, 5:1) and crystallized from diethyl ether and hexane. Overall yield 60%. White solid, mp 71–73 °C. $[\alpha]_D^{20} +34.0$ (c 0.25, CHCl_3), ee >99.5% (hexane–isopropyl alcohol, 90/10, $R_t = 6.5$ min).

Ethyl (R_3, S_{3a}, S_{6a})-3-Ethoxy-6-methyl-1-oxo-3,3a,6,6a-tetrahydro-1H-cyclopenta[c]furan-4-carboxylate [(+)-11]. (+)-11 was obtained following the general procedure from cycloadduct 9b and was isolated by column chromatography (hexane–diethyl ether, 5:2) as a colorless oil. Yield 92%. $[\alpha]_D^{20} +93.5$ (c 0.80, CHCl_3), ee >99.5% (hexane–isopropyl alcohol, 95/5, $R_t = 7.3$ min). IR (neat) 1782, 1714, 1638, 1373, 1340, 941 cm^{-1} . ^1H NMR

(CDCl_3 , 300 MHz) δ 6.69 (t, 1H, $J = 2.0$ Hz), 5.50 (d, 1H, $J = 0.9$ Hz), 4.23 (m, 2H), 3.88 (m, 1H), 3.65 (m, 2H), 3.34 (m, 2H), 1.31 (t, 3H, $J = 7.0$ Hz), 1.30 (d, 3H, $J = 6.8$ Hz), 1.25 (t, 3H, $J = 7.1$ Hz). ^{13}C NMR (CDCl_3 , 300 MHz) δ 6.27 (t, 1H, $J = 2.1$ Hz), 5.49 (d, 1H, $J = 0.8$ Hz), 3.95 (m, 2H), 3.67 (m, 1H), 3.52 (dtd, 1H, $J = 0.8, 2.2$ and 8.3 Hz), 3.32 (m, 2H), 2.81 (dd, 1H, $J = 8.3$ and 9.3 Hz), 2.48 (m, 1H), 1.09 (d, 3H, $J = 7.4$ Hz), 1.00 (t, 3H, $J = 7.1$ Hz), 0.94 (t, 3H, $J = 7.1$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ 175.5 (C), 164.2 (C), 150.5 (CH), 133.0 (C), 105.1 (CH), 65.6 (CH₂), 61.0 (CH₂), 54.8 (CH), 44.6 (CH), 42.8 (CH), 15.8 (CH₃), 15.6 (CH₃), 14.7 (CH₃). HRMS (EI) calcd for $\text{C}_{13}\text{H}_{18}\text{O}_5$ [M] 254.1154, found 254.1167.

Ethyl (S_3, R_{3a}, R_{6a})-3-Ethoxy-6-methyl-1-oxo-3,3a,6,6a-tetrahydro-1H-cyclopenta[c]furan-4-carboxylate [(–)-11]. (–)-11 was obtained following the general procedure from cycloadduct 9a and isolated by column chromatography (pentane–diethyl ether, 4:1). Yield 93%. $[\alpha]_D^{20} -95.8$ (c 0.50, CHCl_3), ee >99.5% (hexane–isopropyl alcohol, 95/5, $R_t = 8.7$ min). HRMS (FAB⁺) calcd for $\text{C}_{13}\text{H}_{19}\text{O}_5$ [M + H] 255.1232, found 255.1229.

d. Catalytic Hydrogenation of Cyclopentenenes. A solution of (±)-5 or (–)-10 (0.28 mmol) in ethyl acetate (4.2 mL) containing 10% Pd(C) (25.3 mg) was stirred under positive pressure of hydrogen at room temperature. After 14 h the suspension was filtered through celite, the solid residue was washed with ethyl acetate, and the solvent was removed in vacuo. The residue analyzed by ^1H NMR contains a mixture 82:18 of A and B isomers, which were isolated diastereoisomerically pure by column chromatography (hexane–ethyl acetate, 6:1).

Ethyl 3-Methoxy-1-oxo-hexahydro-1H-cyclopenta[c]furan-4-carboxylates (12). Compounds 12 were obtained from (±)-5.

(±)-($3R, 3aR, 4R, 6aS$)-12A: Colorless oil. TLC R_f (hexane–ethyl acetate, 6:1) 0.18. Yield 60%. IR (neat) 1780, 1731, 1190, 1116 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 5.16 (d, 1H, $J = 1.6$ Hz), 4.19 (m, 2H), 3.46 (s, 3H), 3.19 (m, 1H), 2.97 (m, 2H), 2.20 (m, 1H), 1.93 (m, 2H), 1.69 (m, 1H), 1.28 (t, 3H, $J = 7.1$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ 178.7 (C), 172.0 (C), 106.2 (CH), 60.9 (CH₂), 56.9 (CH₃), 47.9 (CH), 47.7 (CH), 44.1 (CH), 29.9 (CH₂), 27.8 (CH₂), 14.2 (CH₃). Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_5$: C, 57.88; H, 7.07. Found: C, 57.62; H, 7.06.

(±)-($3R, 3aR, 4S, 6aS$)-12B: Colorless oil. TLC R_f (hexane–ethyl acetate, 6:1) 0.25. Yield 15%. IR (neat) 1781, 1730, 1184, 1115, 946, 928 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 5.21 (s, 1H), 4.17 (q, 2H, $J = 7.2$ Hz), 3.49 (s, 3H), 3.22 (dt, 1H, $J = 3.3$ and 8.6 Hz), 3.02 (dd, 1H, $J = 6.4$ and 8.6 Hz), 2.72 (dd, 1H, $J = 6.4$ and 13.8 Hz), 2.01 (m, 4H), 1.27 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ 179.5 (C), 173.4 (C), 107.8 (CH), 61.1 (CH₂), 56.6 (CH₃), 50.1 (CH), 48.1 (CH), 43.8 (CH), 29.7 (CH₂), 28.7 (CH₂), 14.2 (CH₃).

Ethyl 3-Ethoxy-1-oxo-hexahydro-1H-cyclopenta[c]furan-4-carboxylate (13). Compounds 13 were obtained from (–)-10.

($3S, 3aS, 4S, 6aR$)-13A: Colorless oil. TLC R_f (hexane–ethyl acetate, 6:1) 0.18. Yield 66%. $[\alpha]_D^{20} +32.4$ (c 1.9, CHCl_3). IR (neat) 1775, 1734, 1191, 1159, 1118, 959 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 5.26 (d, 1H, $J = 1.8$ Hz), 4.18 (m, 2H), 3.83 (qd, 1H, $J = 7.1$ and 9.6 Hz), 3.56 (qd, 1H, $J = 7.1$ and 9.6 Hz), 3.20 (m, 1H), 2.97 (m, 2H), 2.21 (m, 1H), 1.91 (m, 2H), 1.67 (m, 1H), 1.28 (t, 3H, $J = 7.1$ Hz), 1.20 (t, 3H, $J = 7.1$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ 178.8 (C), 172.0 (C), 104.9 (CH), 65.4 (CH₂), 60.8 (CH₂), 48.1 (CH), 47.8 (CH), 44.2 (CH), 29.9 (CH₂), 27.8 (CH₂), 14.9 (CH₃), 14.2 (CH₃).

($3S, 3aS, 4S, 6aR$)-13B: Colorless oil. TLC R_f (hexane–ethyl acetate, 6:1) 0.25. Yield 15%. $[\alpha]_D^{20} +10.0$ (c 0.5, CHCl_3). IR (neat) 1782, 1731, 1191, 1114, 1045, 926 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 5.31 (s, 1H), 4.17 (q, 2H, $J = 7.1$ Hz), 3.86 (qd, 1H, $J = 7.1$ and 9.5 Hz), 3.69 (qd, 1H, $J = 7.1$ and 9.5 Hz), 3.24 (dt, 1H, $J = 3.2$ and 8.6 Hz), 3.02 (dd, 1H, $J = 6.5$ and 8.6 Hz), 2.72 (dd, 1H, $J = 6.5$ and 13.8 Hz), 2.01 (m, 4H), 1.27 (t, 3H, $J = 7.1$ Hz), 1.24 (t, 3H, $J = 7.1$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ 179.6 (C),

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173.4 (C), 106.6 (CH), 65.1 (CH₂), 61.1 (CH₂), 50.3 (CH), 48.2 (CH), 43.9 (CH), 29.7 (CH₂), 28.7 (CH₂), 14.9 (CH₃), 14.2 (CH₃).

(3S,3aS,4S,6R,6aR)-Ethyl 3-Ethoxy-6-methyl-1-oxohexahydro-1H-cyclopenta[c]furan-4-carboxylate (14). **14** was obtained from (–)-**11** after 14 h. The residue analyzed by ¹H NMR contains a mixture of (+)-**14** and the other stereoisomer in 95:5 ratio. (+)-**14** was isolated by column chromatography (hexane–ethyl acetate, 6:1) in 67% yield as a colorless oil. [α]_D²⁰ +37.5 (*c* 1.2, CHCl₃). IR (neat) 1778, 1731, 1186, 1121, 961 cm^{–1}. ¹H NMR (CDCl₃, 300 MHz) δ 5.26 (d, 1H, *J* = 2.7 Hz), 4.18 (m, 2H), 3.84 (qd, 1H, *J* = 7.1 and 9.5 Hz), 3.55 (qd, 1H, *J* = 7.1 and 9.5 Hz), 3.06 (m, 2H), 2.96 (m, 1H), 2.30 (m, 1H), 2.05 (m, 1H), 1.44 (q, 1H, *J* = 12.9 Hz), 1.28 (t, 3H, *J* = 7.2 Hz), 1.20 (t, 3H, *J* = 7.1 Hz), 1.18 (d, 1H, *J* = 7.0 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ 175.4 (C), 172.0 (C), 105.0 (CH), 65.6 (CH₂), 60.8 (CH₂), 49.3 (CH), 47.5 (CH), 46.5 (CH), 36.9 (CH), 35.8 (CH₂), 15.5 (CH₃), 14.9 (CH₃), 14.2 (CH₃).

(±)-(3R,3aR,4R,6S,6aS)-Ethyl 3-Methoxy-6-methyl-1-oxohexahydro-1H-cyclopenta[c]furan-4-carboxylate (15A). **15A** was obtained from (±)-**8-endo** after 14 h. The residue analyzed by ¹H NMR contains a mixture of (±)-**15A** and the other stereoisomer in 95:5. It was isolated by column chromatography (hexane–ethyl acetate, 6:1) in 65% yield. White solid, mp 38–40 °C. IR (neat) 1780, 1731, 1189, 1123, 965 cm^{–1}. ¹H NMR (CDCl₃, 300 MHz) δ 5.14 (d, 1H, *J* = 2.3 Hz), 4.18 (m, 2H), 3.45 (s, 3H), 3.09–2.90 (m, 2H), 2.29 (m, 1H), 2.05 (td, 1H, *J* = 5.6 and 12.8 Hz), 1.42 (q, 1H, *J* = 12.8 Hz), 1.26 (t, 3H, *J* = 7.1 Hz), 1.17 (d, 3H, *J* = 7.0 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ 175.3 (C), 171.9 (C), 106.3 (CH), 60.8 (CH₂), 57.1 (CH₃), 49.1 (CH), 47.4 (CH), 46.5 (CH), 36.9 (CH), 35.8 (CH₂), 14.3 (CH₃), 14.2 (CH₃). Anal. Calcd for C₁₂H₁₈O₅: C, 59.49; H, 7.49. Found: C, 59.13; H, 7.49.

e. Furanone Ring-Opening. A solution 0.2 M of (±)-**12A**, (+)-**13A**, (+)-**14**, or (±)-**15** and ethane-1,2-dithiol (5 equiv) in dry dichloromethane was added dropwise to a 0.1 M solution of boron trifluoride–diethyl ether (2 equiv) in the same solvent, kept under stirring at 0 °C. The solution was stirred at 0 °C over 6 h (monitored by TLC). Water was added to the reaction mixture, and the aqueous layer was extracted several times with ethyl acetate. The combined organic layer was washed with brine then dried over MgSO₄ and the solvent was removed in vacuo. The crude material was analyzed by ¹H NMR and the cyclopentanes was purified by column chromatography (hexane–acetone, 4:1).

(1R,2R,3S)-2-(1,3-Dithiolan-2-yl)-3-(ethoxycarbonyl)cyclopentanecarboxylic Acid (16). **16** was obtained in optically pure form from **13A** and ethane-1,2-dithiol. Yield 79%, colorless oil. [α]_D²⁰ +11.3 (*c* 1.7, CHCl₃). IR (neat) 3400–2600, 1725, 1702, 1184 cm^{–1}. ¹H NMR (CDCl₃, 300 MHz) δ 5.16 (d, 1H, *J* = 11.8 Hz), 4.14 (m, 2H), 3.22 (s, 4H), 3.28–3.06 (m, 2H), 2.51 (td, 1H, *J* = 7.8 and 11.8 Hz), 2.33–2.17 (m, 2H), 2.04–1.84 (m, 2H), 1.27 (t, 3H, *J* = 7.2 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ 178.6 (C), 174.1 (C), 60.8 (CH₂), 56.8 (CH), 52.1 (CH), 46.5 (CH), 46.2 (CH), 38.5 (CH₂), 38.4 (CH₂), 28.4 (2CH₂), 14.1 (CH₃). Anal. Calcd for C₁₂H₁₈O₄S₂: C, 49.63; H, 6.25; S, 22.08. Found: C, 49.83; H, 6.42; S, 21.39.

The racemic compound was obtained from (±)-**12A**.

(1R,2S,3S,5R)-2-(1,3-Dithiolan-2-yl)-3-(ethoxycarbonyl)-5-methylcyclopentanecarboxylic Acid (17). **17** was obtained in optically

pure form from **14A** and ethane-1,2-dithiol. Yield. 82%. [α]_D²⁰ +26.2 (*c* 1.3, CHCl₃). IR (neat) 3500–2500, 1727, 1705, 1184 cm^{–1}. ¹H NMR (CDCl₃, 300 MHz) δ 5.11 (d, 1H, *J* = 11.8 Hz), 4.15 (q, 2H, *J* = 7.1 Hz), 3.30–3.10 (m, 5H), 3.07 (m, 1H), 2.62 (ddd, 1H, *J* = 6.3, 9.9 and 11.8 Hz), 2.32–2.03 (m, 3H), 1.27 (t, 3H, *J* = 7.2 Hz), 1.10 (d, 3H, *J* = 6.4 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ 176.2 (C), 174.8 (C), 61.0 (CH₂), 56.2 (CH), 53.4 (CH), 52.6 (CH), 45.3 (CH), 38.8 (CH₂), 38.1 (CH₂), 37.4 (CH), 36.8 (CH₂), 15.8 (CH₃), 14.1 (CH₃).

The racemic compound was obtained from (±)-**15**.

f. Methylation of Acids with Diazomethane. Carboxylic acids **16** and **17** were treated with an excess of diazomethane at 0 °C in diethyl ether giving the corresponding methyl esters in quantitative yield. They were analyzed by HPLC with a Daicel Chiralcell OD column with hexane and isopropyl alcohol as eluents (97/3) with a continuous flow of 1 mL/min. Retention times are indicated in each case.

Ethyl 3-Methyl-(1S,2R,3R)-2-(1,3-dithiolan-2-yl)cyclopentane-1,3-dicarboxylate (18). **18** was obtained in optically pure form from **16**. Quantitative yield. [α]_D²⁰ +1.8 (*c* 1.0, CHCl₃), ee >99.5% (*R*_t = 13.4 min). IR (neat) 1726, 1175, 933 cm^{–1}. ¹H NMR (CDCl₃, 300 MHz) δ 5.13 (d, 1H, *J* = 11.8 Hz), 4.13 (m, 2H), 3.67 (s, 3H), 3.21 (m, 4H), 3.07 (m, 2H), 2.47 (td, 1H, *J* = 7.7 and 11.8 Hz), 2.22 (m, 2H), 1.90 (m, 2H), 1.28 (t, 3H, *J* = 7.2 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ 174.1 (C), 173.7 (C), 60.5 (CH₂), 57.1 (CH), 52.4 (CH), 51.6 (CH), 46.2 (CH), 46.1 (CH), 38.4 (2CH₂), 28.3 (CH₂), 28.2 (CH₂), 14.2 (CH₃). HRMS (FAB⁺) calcd for C₁₃H₂₁O₄S₂ [M + H] 305.0881, found 305.0880.

The racemic compound was obtained from (±)-**16** (*R*_t = 13.5 and 14.5 min).

1-Ethyl 3-Methyl-(1S,2S,3R,4R)-2-(1,3-dithiolan-2-yl)-4-methylcyclopentane-1,3-dicarboxylate (19). **19** was obtained from **17** in quantitative yield and optically pure form. [α]_D²⁰ +40.4 (*c* 0.8, CHCl₃), ee >99.5% (*R*_t = 11.5 min). IR (neat) 1730, 1171, 1029 cm^{–1}. ¹H NMR (CDCl₃, 300 MHz) δ 5.09 (d, 1H, *J* = 11.7 Hz), 4.17 (q, 2H, *J* = 7.1 Hz), 3.67 (s, 3H), 3.31–3.07 (m, 5H), 3.03 (m, 1H), 2.59 (ddd, 1H, *J* = 6.2, 9.9 and 11.8 Hz), 2.28–2.12 (m, 3H), 1.29 (t, 3H, *J* = 7.2 Hz), 1.03 (d, 3H, *J* = 6.3 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ 173.7 (C), 172.6 (C), 60.5 (CH₂), 56.5 (CH), 53.1 (CH), 52.9 (CH), 51.1 (CH₃), 45.2 (CH), 38.9 (CH₂), 37.9 (CH₂), 37.3 (CH), 36.4 (CH₂), 15.9 (CH₃), 14.2 (CH₃). HRMS (FAB⁺) calcd for C₁₄H₂₃O₄S₂ [M + H] 319.1038, found 319.1033.

The racemic compound was obtained from (±)-**17** (*R*_t = 11.6 and 14.2 min).

Acknowledgment. We thank DGICYT (Grant CTQ2006-06741/BQU) and Comunidad Autónoma de Madrid (CCG07-UAM/PPQ-1849) for financial support. We thank Universidad Autónoma de Madrid for a Predoctoral Fellowship to Alberto Núñez.

Supporting Information Available: NMR spectra of all new compounds and crystallographic data for compounds **6b** and **9b** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO801896A