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α,α'-Dioxothiones Part 2.[1] Asymmetric Diels-Alder Reactions of Chiral Non-Racemic α,α'-Dioxothiones

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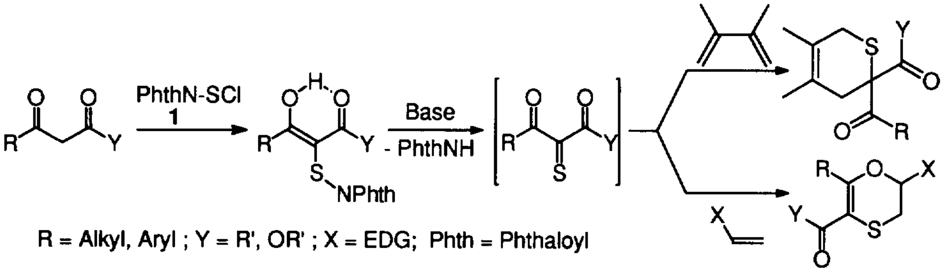
Abstract: Chiral non-racemic α,α'-dioxothiones **2a-g** and **17** are obtained from chiral β-ketoesters using the phthalimidesulfenyl chloride **1** as key reagent. The ability of these thiones to discriminate between the enantiotopic faces of several dienophiles has been evaluated. The best diastereoisomeric excesses (67-80%) were obtained when the α-acyl thiones were involved as electron-poor dienes in inverse electron demand Diels-Alder reactions with electron-rich styrenes as dienophiles. The possibility to obtain thiones bearing two chiral groups as well as the reactions where the α-acyl thiones **2** participate as dienophiles are also shown. © 1997 Elsevier Science Ltd.

The asymmetric Diels-Alder reaction represents one of the topics of growing interest of contemporary organic synthesis since it allows the simultaneous formation of two new bonds in a stereocontrolled fashion.[2] Many efforts to set up efficient chiral dienes[3], dienophiles[4] and catalysts[5] useful for the synthesis of cycloadducts with high enantioselectivity have been made.

We have recently reported a simple strategy for obtaining α,α'-dioxothiones, a new class of thiones which behave as electron-poor *bis*-hetero dienes[1] as well as dienophiles.[1,6] This strategy utilises the reaction of the phthalimidesulfenyl chloride **1** (PhthN-SCl) with β-dicarbonyl compounds to give the corresponding α,α'-*N*-thiophthalimides which generate the α-acylthiones by tertiary base mediated elimination of phthalimide. The oxothiones can be trapped by dienes or by electron-rich dienophiles to give dihydrothiopyrans or 1,4-oxathiins respectively (Scheme 1).



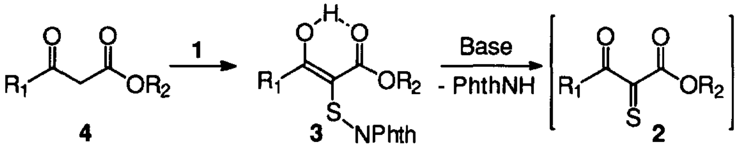
SCHEME 1

The formation of oxathiin derivatives "via" inverse electron-demand Diels-Alder reaction of α-acylthiones occurs with interesting stereochemical features. In any case we observe retention of the dienophile geometry and formation of a single regioisomeric oxathiin. Moreover only the ketonic carbonyl participates to the heterodiene system in the cycloadditions of α,α'-dioxothiones deriving from β-ketoesters.[1]

In this paper we report our studies on asymmetric cycloaddition reactions by means of chiral α,α'-dioxothiones generated following the above described procedure.

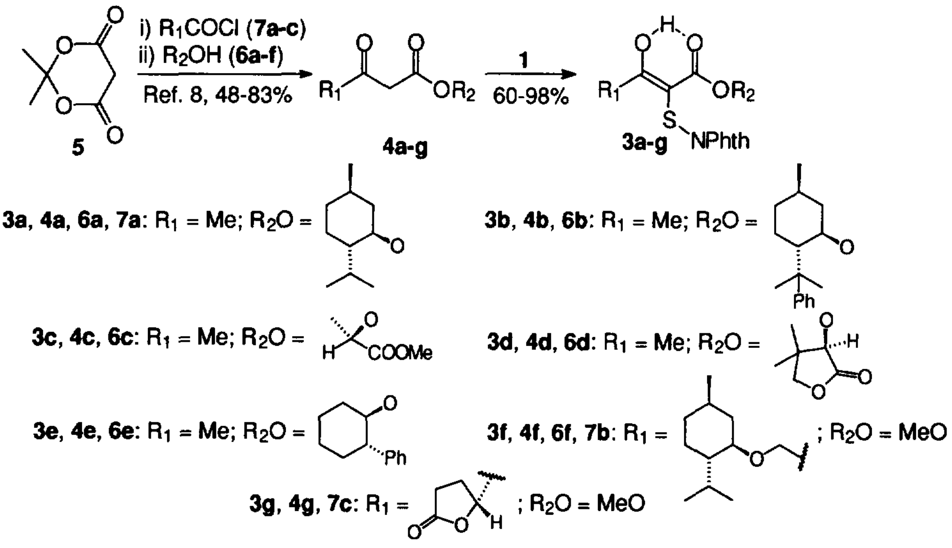
RESULTS AND DISCUSSION

We focused our attention on thiones of type **2** (R_1 or R_2 chiral non-racemic) which can be obtained from the thiophthalimide precursors **3**, which in turn can be synthesised by the reaction of phthalimidesulfenyl chloride **1** with β-ketoesters **4** (Scheme 2). Thus the first problem was to synthesise chiral β-ketoesters.



SCHEME 2

Among the various approaches available for the synthesis of β-ketoesters[7] we choose the Yonemitsu method[8] which uses the Meldrum acid **5** as key reagent. Following this strategy and using chiral alcohols **6a-e** and chiral acyl chlorides **7a-b**, we prepared chiral β-ketoesters **4a-g** as reported in Scheme 3.

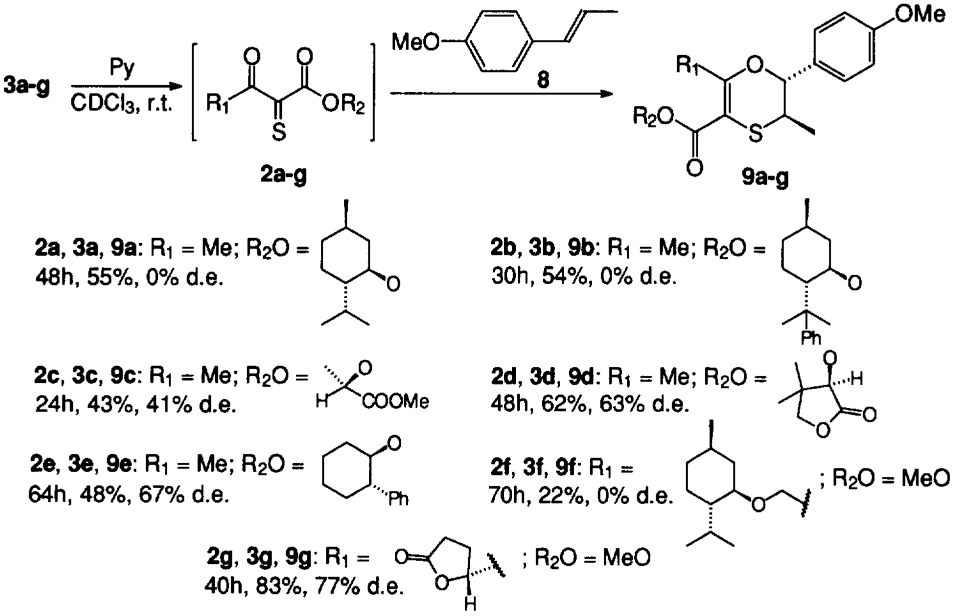


SCHEME 3

Scheme 3 also illustrates the transformation of ketoesters **4** into the corresponding thiophthalimides **3** using the phthalimidesulfenyl chloride **1**. The optical rotations ($[\alpha]^{D}_{20}$) measured for ketoesters **4** and thiophthalimides **3**[9] ensured that no racemization had occurred during the overall process.

The formation of derivatives **4** offers the possibility of generating in solution chiral non-racemic acylthiones **2**, thus we could evaluate their ability to discriminate between the two enantiotopic faces of an electron-rich dienophile in an asymmetric inverse electron demand Diels-Alder reaction.

In a first set of reactions thiophthalimides **3a-g** were allowed to react in $CDCl_3$ with pyridine (1 equivalent) at room temperature, and the thiones **2a-g** obtained were trapped by β-*trans*-methyl-4-methoxystyrene (**8**) (anethole, 1 equivalent). In each case we could isolate the expected 1,4-oxathiins **9a-g** as a mixture of diastereoisomers. Reaction times, yields and diastereoisomeric excesses are reported in Scheme 4.



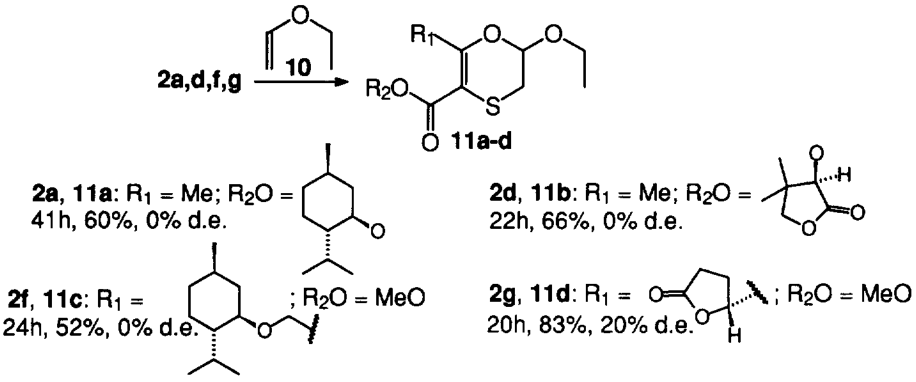
SCHEME 4

The diastereoisomer ratio of derivatives **9a-g** can be measured in the crude reaction mixtures by integration of the ^1H NMR signals of the benzylic protons which appear as doublets at an appreciably different frequency when the spectra are recorded in benzene-d_6.

As indicated in Scheme 4 cycloadducts **9a**, **9b** and **9f** were obtained as equimolecular mixtures of diastereoisomers, a low distereoselectivity was obtained for **9c**, while appreciable diastereoisomeric excesses were measured for derivatives **9d**, **9e** and **9g**. In the case of cycloadduct **9g** the major isomer was obtained pure compound by flash-chromatography.

The analysis of the diastereoisomeric excess clearly indicates that the distance between the chiral auxiliary and the reactive diene is crucial for good facial selectivity in the cycloaddition. In fact the best results were obtained when the auxiliary was directly linked to the ketonic carbonyl which participates in the reaction as in **2g**, or when a phenyl ring could "cover" one of the faces of the diene as in **2e**. However relatively small groups, as in **2c** and **2d**, are able to discriminate between the enantiotopic faces of the dienophile better than relatively bigger groups as in **2a** or **2b**. Thus other effects, probably secondary electronic effects, are able to increase the proximity of particular chiral auxiliaries to one of the faces of the diene in the transition state, giving rise to better diastereoselectivity.

To some extent we evaluated the role of the substitution of the dienophile on the diastereoselectivity of these cycloadditions. The reaction of thiones **2a**, **2d**, **2f** and **2g** with ethyl vinyl ether (**10**) as dienophile afforded the corresponding cycloadducts **11a-d**. While derivative **11a-c** were obtained as equimolecular mixtures of diastereoisomers, the reaction of **2g** with **10** afforded oxathiin **11d** as a 60:40 mixture of diastereoisomers (Scheme 5).

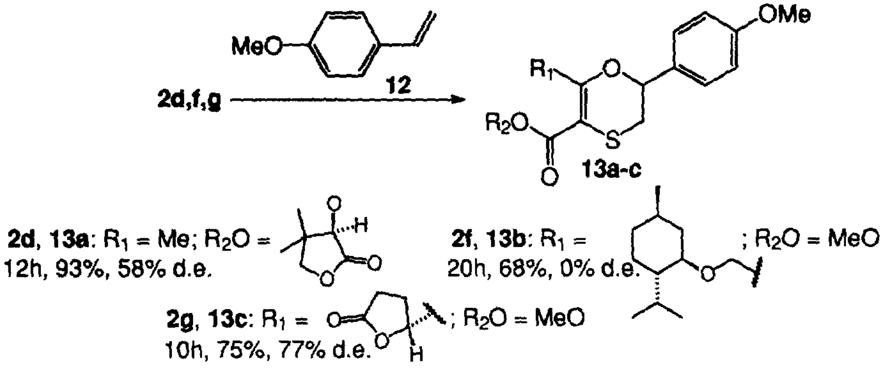


SCHEME 5

Also in this case the 5-oxo-tetrafurancarboxylic moiety of **2g** is the more efficient chiral auxiliary tested, moreover the dramatic decreasing of diastereoisomeric excesses indicates that styrenes are more efficient dienophilic partners for these asymmetric Diels-Alder reactions suggesting that an aromatic ring linked to the electron rich alkene is required for good discrimination.

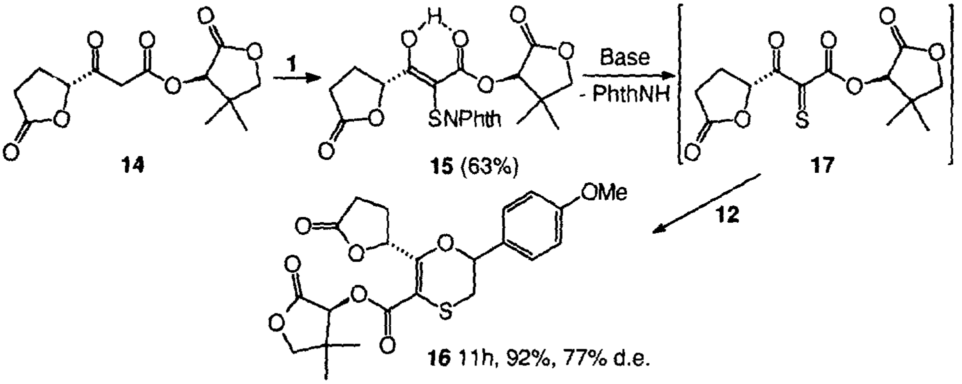
The results obtained in a different set of experiments using 4-methoxystyrene (**12**) as dienophile were in perfect agreement with these observations. We could isolate the oxathiins **13a-c** with distereoisomeric excesses very similar to those observed when anethole **8** was used as dienophile (Scheme 6).

Thus thione **2f** gave no facial discrimination while thiones **2d** and **2g** afforded cycloadducts **13b-c** as 79:21 and 89:11 mixtures of diastereoisomers respectively (Scheme 6). Clearly the phenyl ring conjugated to the reactive double bond plays an important role in the face discrimination of the thione, while the methyl group in β position of the styrene seems to have a minor effect.[10] Carrying out the reaction of **2g** and **12** at 2 °C we obtained, after six days, cycloadduct **13c** with 80% d.e. This result represents, up to now, the highest diastereoselectivity in asymmetric Diels-Alder reaction of α,α'-dioxothiones.[11]



SCHEME 6

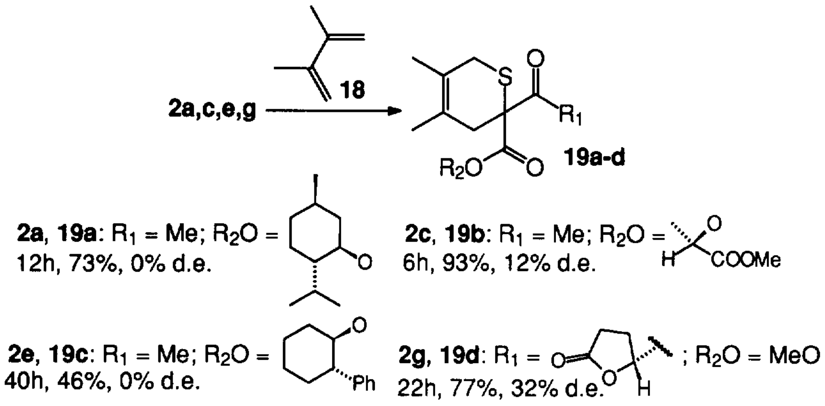
Eventually we decided to verify whether the simultaneous presence of two chiral groups on the same thione could improve the diastereoselectivity. With this in mind we prepared ketoester **14** which was then transformed into the thiophthalimide **15**, following the previously described strategy (Scheme 7). The reaction of **15** with 1 equivalent of lutidine in the presence of styrene **12** afforded the cycloadduct **16**, "via" the intermediate thione **17**. Despite **17** had two groups able to discriminate between the faces of **12**, the d.e. (77%) measured for **16** was identical to that observed in cycloadduct **13** (see Scheme 6).



SCHEME 7

Such a result can be tentatively explained considering the possibility of two different reactive "cisoid" conformations for α,α'-dioxothiones **2d** and **17** both bearing the pantolacton moiety at the ester group. The good stereoselectivity observed in the reactions of **2d** with styrenes **8** and **12** (see Schemes 4 and 6) might indicate that in the transition state the chiral group lies close to one of the faces of the diene causing the diastereoselectivity. Probably in the case of heterodiene **17**, due to the presence of the 5-oxo-furancarboxylic group, the reactive "cisoid" conformation has the pantolacton ester group "far" from the reactive centre, thus the overall result in the reaction of **17** with **12** is the same as observed for thione **2g** (Scheme 6) where the ester group is simply replaced by a methyl.

The dual nature of α,α'-dioxothiones, which can act as electron-poor dienes as well as efficient electron-poor dienophiles, allowed us to verify the potential of their asymmetric Diels-Alder reaction with electron-rich dienes. Thus thiones **2a**, **2c**, **2e** and **2g** were generated in the presence of 2,3-dimethyl-1,3-butadiene **18**. In any case we isolated the expected dihydrothiopyrans **19a-d** as mixtures of diastereoisomers (Scheme 8).[12] Although thione **2g** is again the best in discriminating between the enantiotopic faces of the diene, the lower diastereoselectivity observed seems to indicate that these thiones are less suitable for asymmetric Diels-Alder reactions when acting as dienophiles, probably because of the increasing of the distance between the reactive carbon-sulfur double bond and the chiral auxiliaries.



SCHEME 8

CONCLUSIONS

In conclusion we have shown a simple approach to the synthesis of chiral non-racemic α,α'-dioxothiones based on the reactivity of phthalimidesulfenyl chloride **1**. The ability of thiones **2a-g** to discriminate the faces of various dienophiles and of dimethylbutadiene **18**, has been evaluated and in some instances good diastereoselectivity has been obtained. We have also demonstrated that for these thiones the best results (d.e. 75-80%) are obtained in inverse electron-demand Diels-Alder reaction with electron-rich dienophiles bearing a phenyl ring conjugated to the reactive double bond. Although not exhaustive this work describes the first example of non-racemic α-acylthiones involved in asymmetric Diels-Alder reactions. Further aspects of the chemistry of α,α'-dioxothiones are under investigation in this laboratory.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded (when not specified) in $CDCl_3$ or C_6D_6 at 200 and 50 MHz respectively. Mass spectra and GC-MS analysis were obtained using a gaschromatograph, equipped with a OV101 30 m. capillary column, interfaced with a mass spectrometer. Melting points are uncorrected. $CHCl_3$, and CH_2Cl_2, and pyridine were dried following standard procedures, all commercial reagents were used without further purification as obtained from freshly opened containers. Phthalimidesulfenyl chloride **1** was obtain from the corresponding disulfide[13] and sulfuryl chloride at

40 °C for 48 hours. Acyl chlorides 7 were obtained from the corresponding commercial acids using oxalyl chloride and catalytic DMF.[14] β-Ketoesters 4 were prepared according to a reported procedure[8] and used for the synthesis of thiophthalimides 3 as obtained from flash chromatography. Derivatives **4** occur in solution as mixture of keto and enol forms, when easily identifiable the signals of the minor enolic form are indicated by an asterisk.

β-*Ketoester* **4a.** Oil, (petroleum ether/ethyl acetate = 7/1), 69%, (Keto/Enol* = 78/22). $[\alpha]_D^{20}$ -22° (c = 0.66, CH_2Cl_2); ^{1}H-NMR: 12.20 (s, 1H, OH)*; 4.95 (s, 1H)*; 4.73 (dt, 1H, J = 10.6 and 4.4 Hz); 3.42 (s, 2H); 2.25 (s, 3H)*; 1.94 (s, 3H); 2.1-0.92 (m, 8H); 0.90 (d, 3H, J = 8.0 Hz); 0.88 (d, 3H J = 8.0 Hz); 0.76 (d, 3H, J = 8.0 Hz) δ. ^{13}C-NMR: 200.5 (s); 175.0 (s)*; 172.0 (s)*; 166.6 (s); 90.0 (d)*; 75.2 (d); 72.9 (d)*; 50.4 (t); 46.7 (d); 40.5 (t); 34.0 (t); 31.2 (d); 30.0 (q); 25.9 (d); 23.1 (t); 21.8 (q); 20.6 (q); 16.0 (q) δ. MS *m/z* (rel. int.): 240 ($M^{+\cdot}$, 0.04); 138 (49); 95 (100); 81 (79). $C_{14}H_{24}O_3$. C, 69.97; H, 10.06. Found: C, 69.67; H, 10.35

β-*Ketoester* **4b.** Oil, (petroleum ether/ethyl acetate = 5/1), 56%, (Keto/Enol* = 85/15). $[\alpha]_D^{20}$ -71° (c = 0.20, CH_2Cl_2); ^{1}H-NMR: 12.10 (s, 1H)*; 7.30-7.09 (m, 5H); 4.82 (dt, 1H, J = 10.4 and = 4.0 Hz); 4.45 (s, 1H)*; 2.70 (AB system, 2H, J = 15.8 Hz); 2.10 (s, 3H); 2.05-1.00 (m, 8H, Cicloesano); 1.30 (s, 3H); 1.20 (s); 0.88 (d, 3H, J = 6.4 Hz) δ. ^{13}C-NMR: 200.7 (s); 166.3 (s); 151.7 (s); 127.8 (d, 2C Arom.); 125.6 (d, 2C Arom.); 124.9 (d); 74.9 (d); 50.0 (d); 49.6 (t); 41.3 (s); 39.4 (t); 34.8 (t); 31.2 (d); 30.0 (q); 29.1 (q); 26.1 (t); 23.2 (q); 21.7 (q) δ. MS *m/z* (rel. int.): 316 ($M^{+\cdot}$, 1); 214 (90); 197 (20); 91 (100). Anal. Calcd. for $C_{20}H_{28}O_3$ C, 75.91; H, 8.91. Found: C, 75.76; H, 8.96.

β-*Ketoester* **4c.** Pale yellow oil, (petroleum ether/ethyl acetate = 3/1), 50%, (Keto/Enol* = 80/20). $[\alpha]_D^{20}$ -37° (c = 0.88, CH_2Cl_2); ^{1}H-NMR (C_6D_6): 12.50 (s, 1H)*; 5.25 (q, 1H, J = 6.9 Hz)*; 5.11 (q, 1H, J = 7.0 Hz); 5.08 (s, 1H)*; 3.38 (s, 3H)*; 3.34 (s, 3H); 3.12 (s, 2H); 1.86 (s); 1.56 (s, 3H)*; 1.35 (d, 3H J = 6.9 Hz)*; 1.27 (d, 3H, J = 7.0 Hz) δ. ^{13}C-NMR (C_6D_6): 199.4 (s); 170.8 (s); 166.6 (s); 89.4 (d)*; 69.4 (d); 68.5 (d)*; 51.9 (q); 49.5 (t); 29.5 (q); 20.8 (q)*; 16.8 (q)*; 16.6 (q) δ. MS *m/z* (rel. int.): 189 ($M^{+\cdot}$, 31); 173 (65); 105 (100). Anal. Calcd. for $C_8H_{12}O$ C, 51.05; H, 6.43. Found: C, 50.87; H, 6.38.

β-*Ketoester* **4d.** Yellow oil, (petroleum ether/ethyl acetate = 3/2), 70%, (Keto/Enol* = 87/13). $[\alpha]_D^{20}$ -12° (c = 0.85, CH_2Cl_2); ^{1}H-NMR: 11.60 (s, 1H)*; 5.39 (s, 1H); 5.10 (s, 1H)*; 4.02 (s, 2H); 3.60 (AB system, 2H, J = 16 Hz); 2.47 (s, 3H)*; 2.27 (s, 3H); 1.96 (s, 3H)*; 1.68 (s, 3H)*; 1.21 (s, 3H); 1.07 (s, 3H) δ. ^{13}C-NMR: 199.7 (s); 171.9 (s); 165.9 (s); 103.38 (d)*; 88.7 (t); 75.5 (d); 49.4 (t); 40.1 (s); 30.0 (q); 26.9 (q)*; 22.6 (q); 19.6 (q) δ. MS *m/z* (rel. int.): 214 ($M^{+\cdot}$, 1); 172 (46); 85 (100). Anal. Calcd. for $C_{10}H_{14}O_5$: C, 56.06; H, 6.58. Found: C, 56.37; H, 7.10.

β-*Ketoester* **4e.** Oil, (petroleum ether/ethyl acetate = 5/1), 83%, (Keto/Enol* = 96/4). $[\alpha]_D^{20}$ +15° (c = 0.19, CH_2Cl_2); ^{1}H-NMR: 12.00 (s, 1H)*; 7.40-7.10 (m, 5H); 5.1 (dt, 1H, J = 10.0 and J = 4.4 Hz); 4.8 (s, 1H)*; 3.19 (s, 2H); 2.80-2.63 (m, 1H); 2.2-1.2 (m, 8H); 1.83 (s, 3H) δ. ^{13}C-NMR: 200.3 (s); 166.2 (s); 142.7 (s); 128.29 (d, 2C Arom.); 127.37 (d, 2C Arom.); 126.47 (d); 77.1 (d); 50.34 (t); 49.54 (d); 33.8 (t); 32.0 (t); 28.9 (q); 25.6 (t); 24.5 (t) δ. Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.71; H, 7.87.

β-*Ketoester* **4f.** Oil, (petroleum ether/ethyl acetate = 20/1), 48%, (Keto/Enol* = 89/11). $[\alpha]_D^{20}$ -62° (c = 0.34, CH_2Cl_2); ^{1}H-NMR: 11.83 (s, 1H)*; 5.26 (bs, 1H)*; 4.09 (AB system, 2H, J = 16.8 Hz); 4.05 (AB, 2H, J = 14.0 Hz)*; 3.74 (s, 3H)*; 3.73 (s, 3H); 3.57 (s, 2H); 3.15 (dt, 1H, J = 9.6 and 4.0 Hz); 2.3-0.92 (m, 8H); 0.92 (d, 3H, J = 6.0 Hz); 0.89 (d, 3H, J = 6.4 Hz); 0.76 (d, 3H, J = 7.0 Hz) δ. ^{13}C-NMR: 202.4 (s); 175.0 (s); 167.4 (s)*; 88.0 (d)*; 80.0 (t); 73.2 (d)*; 66.9 (d); 52.0 (q); 47.9 (t); 45.7 (d); 39.6 (t); 34.2 (t);31.2 (d); 25.4 (d); 23.1 (t); 22.1 (q); 20.8 (q); 15.95 (q) δ. MS *m/z* (rel. int.): 270 ($M^{+\cdot}$, 0.8); 139 (28); 101 (17); 95 (43); 43 (100). Anal. Calcd. for $C_{15}H_{26}O_4$: C, 66.64; H, 9.69. Found: C, 66.60; H, 9.53.

β-*Ketoester* **4f.** Oil, (petroleum ether/ethyl acetate = 2/1), 65%, (Keto/Enol* = 80/20). $[\alpha]_D^{20}$ +11° (c = 0.76, CH_2Cl_2); ^{1}H-NMR: 11.97 (s, 1H)*; 5.30 (s, 1H)*; 5.00-4.85 (m, 1H); 3.76 (s, 3H)*; 3.73 (s, 3H); 3.70-3.65 (m, 2H); 2.65-2.25 (m,4H) δ. ^{13}C-NMR: 201.6 (s); 176.6 (s); 173.0 (s); 167.7 (s)*; 89.2 (d)*; 82.1 (d); 53.0 (q); 45.8 (t); 27.6 (t); 24.7 (t) δ. MS *m/z* (rel. int.): 186 ($M^{+\cdot}$, 2); 155 (11); 101 (39); 85 (100). Anal. Calcd. for $C_8H_{10}O_5$: C, 51.61;H ,5.41. Found: C, 51.50; H, 5.30

β-*Ketoester* **14.** Oil, (petroleum ether/ethyl acetate = 1/1), 76%, (Keto/Enol* = 66/34). $[\alpha]_D^{20}$ -1° (c = 0.82, CH_2Cl_2); ^{1}H-NMR: 11.3 (bs, 1H)*; 5.46-5.29 (m, 3H); 4.98-4.88 (m, 1H); 4.05-3.98 (m, 2H); 3.81(AB system, 2H, J = 16.4 Hz); 2.75-2.20 (m, 2H); 1.95 (s, 3H)*; 1.87 (s, 3H); 1.76 (s, 3H); 1.68 (s, 3H)* δ. ^{13}C-NMR: 200.0 (s); 175.7, 171.8, 165.5 (s), 88.1 (d)*; 81.3, 75.8 (d); 45.0 (t); 40.1 (s); 26.9, 25.6, 22.0 (t); 22.4 (q); 19.5 (q) δ. MS *m/z* (rel. int.): 285 (M^{+}., 2); 172 (44); 85 (100). Anal. Calcd. for $C_{13}H_{16}O_7$: C, 54.93; H, 5.67. Found: C, 54.65; H, 5.70

Thiophthalimides **3** and **15** have been obtained following the general procedure described elsewhere[1,5] and usually in $CDCl_3$ solution are completely in enolic form.

N-Thiophthalimide **3a.** White solid, (m.p. 97-99 °C) 93%. $[\alpha]_D^{20}$ -91° (c = 0.16, CH_2Cl_2); ^{1}H-NMR: 14.06 (s, 1H); 7.90-7.70 (m, 4H); 4.8 (dt, 1H, J = 10.6 and 4.4 Hz); 2.77 (s, 3H); 1.09-0.9 (m, 9H); 0.86 (d, 3H, J = 6.2 Hz); 0.66 (d, 3H, J = 6.6 Hz); 0.63 (d, J = 6.6 Hz) δ. ^{13}C-NMR: 188.0 (s); 171.7 (s); 167.51 (s, 2C); 134.3 (d, 2C); 132.1 (s, 2C); 123.5 (d, 2C); 96.5 (d); 75.7 (d); 46.2 (d); 40.8 (t); 33.9 (t); 31.4 (d); 25.9 (d); 22.8 (t); 21.9 (q); 21.6 (q); 20.6 (q); 15.7 (q) δ. Anal. Calcd. for $C_{22}H_{27}O_5NS$: C, 63.28; H, 6.51; N, 3.35. Found: C, 63.05; H, 6.36; N, 3.42.

N-Thiophthalimide **3b.** White solid, (m.p. 56-57 °C) 98%. $[\alpha]_D^{20}$ -13° (c = 0.29, CH_2Cl_2); ^{1}H-NMR: 14.00 (s, 1H); 7.86-7.70 (m); 7.24-7.02 (m, 5H); 4.82 (dt, 1H, J = 10 and 4.0 Hz); 2.73 (s, 3H); 2.42 (s, 3H); 1.34 (s, 3H); 1.20 (s, 3H); 0.89 (s, 3H); 2.00-0.85 (m, 8H) δ. ^{13}C-NMR 187.9 (s); 171.3 (s); 167.6 (s, 2C); 150.5 (s); 134.3 (d, 2C); 132.3 (s, 2C); 128.0 (d, 2C); 125.3 (d, 2C); 124.30 (d); 123.5 (d, 2C); 97.4 (s); 75.8 (d); 47.7 (d); 41.4 (s); 40.2 (t); 34.2 (t); 31.3; 28.3 (q); 26.9 (q); 26.5 (t); 25.0 (q); 21.6 (q) δ. Anal. Calcd. for $C_{28}H_{31}O_5NS$: C, 68.13; H, 6.32; N, 2.83. Found: C, 68.19: H, 6.26; N, 2.78.

N-Thiophthalimide **3c.** White solid, (m.p. 121-124 °C) 83%. $[\alpha]_D^{20}$ -36° (c = 0.50, CH_2Cl_2); ^{1}H-NMR: 13.56 (s, 1H); 7.79-7.71 (m, 4H); 5.13 (q, 1H, J = 7.4 Hz); 3.48 (s, 3H); 2.79 (s, 3H); 1.63 (d, 3H, J = 7.4 Hz) δ. ^{13}C-NMR: 189 1 (s); 171.4 (s); 170.5 (s); 167.5 (s, 2C); 134.3 (d, 2C); 132.2 (s, 2C); 123.4 (d, 2C); 96.2 (s); 69.8 (d); 52.2 (q); 21.7 (q); 16.6 (q) δ. MS *m/z* (rel. int.): 365 ($M^{+\cdot}$, 2); 219 (9), 148 (46), 147 (100). Anal. Calcd. for $C_{16}H_{15}O_7NS$: C, 52.60; H, 4.14; N, 3.83. Found: C, 52.36; H, 4.15; N, 3.98.

N-Thiophthalimide **3d.** White solid, (m.p. 80 °C dec.) 94%. $[\alpha]_D^{20}$ -73° (c = 0.65, CH_2Cl_2); ^{1}H-NMR: 13.45 (s, 1H); 7.96-7.68 (m, 4H); 5.27 (s, 1H); 4.22- 3.92 (m, 2H); 1.34 (s, 3H); 1.23 (s, 3H) δ. Anal. Calcd. for $C_{18}H_{17}O_7NS$: C, 55.24; H, 4.38; N, 3.58. Found: C, 55.46; H, 4.25; N, 3.81.

N-Thiophthalimide **3e.** Glassy solid, 89%. $[\alpha]_D^{20}$ -27° (c = 0.17, CH_2Cl_2); ^{1}H-NMR: 13.83 (s, 1H); 8.00-7.70 (m, 4H); 7.20-6.90 (m, 5H); 5.08 (dt, 1H, J = 10.0 and = 4.0 Hz); 2.68 (s, 3H); 2.20-1.20 (m, 9H) δ. ^{13}C-NMR 188.0 (s); 171.0 (s); 167.4 (s, 2C); 142.49 (s); 134.1 (d, 2C); 132.1 (s, 2C); 127.7 (d, 2C); 127.3 (d, 2C); 126.0 (d); 123.4 (d, 2C); 96.2 (s); 77.3 (d); 48.6 (d); 33.6 (t); 31.9 (t); 25.5 (t); 24.6 (t); 21.5 (q) δ. Anal. Calcd. for $C_{24}H_{24}O_5NS$: C, 65.73; H, 5.51; N, 3.19. Found: C, 65.43; H, 5.22; N, 3.50.

N-Thiophthalimide **3f.** Glassy solid, 86%. $[\alpha]_D^{20}$ -44° (c = 0.55, CH_2Cl_2). In this case a ketonic/enolic equilibrium between an enolic form and two diastereoisomeric ketonic forms [indicated by a diamond (♦)] was visible: (Keto♦/Enol = 35/65). ^{1}H-NMR: 13.81 (s, 1H); 8.00-7.60 (m, 4H); 5.05 (AB system, 2H, J = 12.0 Hz); 4.86 - 4.00 (m, 3H)♦; 3.79 (s, 3H); 3.66 (s, 3H)♦; 3.35-3.00 (m, 1H); 2.10-0.92 (m, 17H) δ. Anal. Calcd. for $C_{23}H_{29}O_6NS$: C, 61.73; H, 6.53; N, 3.13. Found: C, 61.48; H, 6.42; N, 3.18.

N-Thiophthalimide **3g.** White solid, (m.p. 111-115 °C) 60%. $[\alpha]_D^{20}$ +9° (c = 0.40, CH_2Cl_2); ^{1}H-NMR: 13.9 (s, 1H); 7.95-7.65 (m, 4H); 7.00 (bs, 1H); 3.87 (s, 3H); 2.80-2.20 (m, 4H) δ. Anal. Calcd. for $C_{16}H_{13}O_7NS$: C, 52.87; H, 3.61;N, 3.85. Found: C, 52.42; H, 3.83; N, 3.58

N-Thiophthalimide **15.** Glassy solid, 63%. $[\alpha]_D^{20}$ -20° (c = 0.80, CH_2Cl_2); ^{1}H-NMR: 13.4 (s, 1H); 8.00-7.60 (m, 4H); 7.00 (bs, 1H); 5.4 (s, 1H); 4.15 (AB system, 2H, J = 9.2 Hz); 2.85-2.40 (m, 4H); 1.41 (s, 3H); 1.28 (s, 3H) δ. Anal. Calcd. for $C_{21}H_{19}O_9NS$: C, 54.66; H, 4.15; N, 3.04. Found: C, 54.52; H, 3.98; N, 2.88.

Oxathiin cycloadducts **9**, **11**, **13**, **16** and dihydrothiopyrans **19** have been obtained following the general procedure described elsewhere,[1,5] diastereoisomeric excesses were measured by integration of two well separated signals of the diastereoisomers (indicated as ***M*** and ***m***) in the ^{1}H-NMR recorded on the crude reaction mixtures in C_6D_6.

1,4-oxathiin **9a.** Oil, (petroleum ether/ethyl acetate = 30/1), 55%, (d.e. 0%). ^{1}H-NMR: 7.20-6.90 (m, 4H); 4.77 (td, 1H, J = 10.6 and 4.4 Hz); 4.66- 4.58 (m, 1H); 3.82 (s, 3H); 3.20-3.06 (m, 1H); 2.36 (s, 3H, ***M***); 2.35 (s, 3H, ***m***); 2.10-1.05 (m, 9H); 1.00 (d, 3H, J = 8.5 Hz); 0.93 (d, 3H, J = 7.2 Hz); 0.90 (d, 3H, J = 6.2 Hz); 0.79 (d, 3H, J = 7.2 Hz) δ. MS *m/z* (rel. int.): 418 ($M^{+\cdot}$, 5); 263 (1); 148 (100). Anal. Calcd. for $C_{24}H_{34}O_4S$: C, 68.86; H, 8.18. Found: C, 68.69, H, 8.40.

1,4-oxathiin **9b.** White solid, m.p. 47-50 °C (petroleum ether/ethyl acetate = 30/1), 54%, (d.e. 0%). ^{1}H-NMR: 7.35-7.22 (m, 5H); 7.10-6.95 (m, 4H); 5.00 (td, 1H, J = 11.0 and J = 4.8 Hz); 4.65 (d, 1H, J = 8.4 Hz, ***M***); 4.54 (d, 1H, J = 8.4 Hz, ***m***); 3.83 (s, 3H); 3.16-2.98 (m, 1H); 2.28 (s, 3H, ***M***); 2.20 (s, 3H, ***m***); 2.00-0.80 (m, 8H); 1.40 (s, 3H, ***M***); 1.39 (s, 3H, ***m***); 1.31 (s, 3H, ***M***); 1.30 (s, 3H, ***m***); 1.02 (d, 3H, J = 6.0 Hz ***M***); 0.86 (d, 3H, J = 6.1 Hz ***m***) δ. MS *m/z* (rel. int.): 494 ($M^{+\cdot}$, 3); 148 (100); 105 (57); 77 (98). Anal. Calcd. for $C_{30}H_{38}O_4S$: C, 72.83; H, 7.74. Found: C, 72.60; H, 7.69.

1,4-oxathiin **9c.** Oil, (petroleum ether/ethyl acetate = 6/1), 43%, (d.e. 41%). ^{1}H-NMR: 6.99-6.80 (m, 4H); 5.32 (m, 1H); 4.55 (bd, 1H, J = 8.4 Hz, ***M***); 4.44-D_2 (bd, 1H, J = 8.8 Hz, ***m***); 3.4 (s, 3H); 3.38 (s, 3H); 3.10-2.81 (m, 1H); 2.62 (s, 3H,

m); 2.56 (s, 3H, ***M***); 1.44 (d, 3H, J = 7.4 Hz, ***m***); 1.43 (d, 3H, J = 6.8 Hz, ***M***); 0.93 (d, 3H, J = 6.6 Hz) δ. MS *m/z* (rel. int.): 366 ($M^{+\cdot}$, 2); 263 (3); 148 (100). Anal. Calcd. for $C_{18}H_{22}O_6S$: C, 59.00; H, 6.05. Found: C, 59.03; H, 6.20.

1,4-oxathiin **9d.** Oil, (petroleum ether/ethyl acetate = 3/1), 62%, (d.e. 63%). ^{1}H-NMR: 7.10-6.90 (m, 4H); 5.61 (s, 2H, ***m***); 5.60 (s, 2H, ***M***); 4.62 (d, 1H, J = 8.4 Hz, ***M***); 4.54 (d, 2H, J = 8.4 Hz, ***m***); 3.48 (s, 3H); 3.40 (q, 2H, J = 8.4 Hz) 3.00 (dq, 1H, J = 8.4 and 7.0 Hz); 2.68 (s, 3H); 1.11 (s, 3H); 1.01 (d, 3H, J = 7.0 Hz); 0.85 (s, 3H) δ. MS *m/z* (rel. int.): 392 ($M^{+\cdot}$, 1); 148 (100). Anal. Calcd. for $C_{20}H_{24}O_6S$: C, 61.21; H, 6.16. Found: C, 61.23; H, 6.12.

1,4-oxathiin **9e.** Oil, (petroleum ether/ethyl acetate = 7.5/1), 48%, (d.e. 67%). ^{1}H-NMR: 7.30-7.00 (m, 5H); 6.80-6.60 (m, 4H); 5.35 (td, 1H, J = 10.0 and 4.0 Hz); 4.25 (d, 1H, J = 8.4 Hz, ***M***); 4.18 (d, 1H, J = 8.4 Hz ***m***); 3.24 (s, 3H); 2.74 (m, 2H); 2.33 (s, 3H); 2.31-2.25 (m, 1H); 1.80-1.00 (m, 7H); 0.75 (d, 3H, J = 6.6 Hz) δ. MS *m/z* (rel. int.): 438 ($M^{+\cdot}$, 2); 176 (3); 148 (100). Anal. Calcd. for $C_{26}H_{30}O_4S$: C, 71.20; H, 6.89. Found: C, 71.37; H, 7.00.

1,4-oxathiin **9f.** Oil, (petroleum ether/ethyl acetate = 6/1), 22%, (d.e. 0%). ^{1}H-NMR: 7.21-6.87 (m, 4H); 4.65-4.42 (m, 3H); 3.82 (s, 3H); 3.78 (s, 3H); 3.21-3.02 (m, 2H); 2.25-1.02 (m, 8H); 1.06 (d, 3H, J = 6.6 Hz, ***M***); 1.05 (d, 3H, J = 7.0 Hz, ***m***); 0.87 (d, 6H, J = 6.6 Hz, ***M***); 0.82 (d, 6H, J = 7.2 Hz, ***m***); 0.68 (d, 3H, J = 7.0 Hz, ***M***); 0.66 (d, 3H, J = 7.0 Hz, ***m***) δ. MS *m/z* (rel. int.): 448 ($M^{+\cdot}$, 0.5); 148 (100). Anal. Calcd. for $C_{25}H_{36}O_5S$: C, 66.93; H, 8.09. Found: C, 67.18; H, 8.28.

1,4-oxathiin **9g.** Oil, (petroleum ether/ethyl acetate = 2/1), 83%, (d.e. 77%). The column chromatography allowed the isolation of the pure major stereoisomer. ^{1}H-NMR: 7.04-6.85 (m, 4H); 6.40 (bs, 1H); 4.70 (d, 1H, J = 8.2 Hz); 3.81 (s, 3H); 3.80 (s, 3H); 3.18-3.00 (m, 1H); 2.50-2.20 (m, 4H); 1.07 (d, 3H, J = 6.6 Hz) δ. Anal. Calcd. for $C_{18}H_{20}O_6S$: C, 59.33; H, 5.53. Found: C, 59.28; H, 5.42.

1,4-oxathiin **11a.** Oil, (petroleum ether/ethyl acetate = 2/1), 60%, (d.e. 0%). ^{1}H-NMR: 5,20 (td, 1H, J= 10.6 and 4.8 Hz); 4.86 (dd, X part of an ABX system, 1H, J = 2.6 and 5.0 Hz, ***M***); 4.82 (dd, X part of an ABX system, 1H, J = 2.2 and 4.4 Hz, ***m***); 3.5 (m, 2H); 2.62 (s, 3H, ***M***); 2.61 (s, 3H, ***m***) 2.60-2.53 (m, 2H); 1.20-0.81 (m, 18H) δ. MS *m/z* (rel. int.): 342 ($M^{+\cdot}$, 18); 297 (4); 204 (100); 159 (31). Anal. Calcd. for $C_{18}H_{30}O_4S$: C, 63.12; H, 8.82. Found: C, 63.20; H, 8.95.

1,4-oxathiin **11b.** Oil, (petroleum ether/ethyl acetate = 4/1), 66%, (d.e. 0%). ^{1}H-NMR: 5.41 (s, 1H); 5.33-5.25 (m, 1H); 4.05 (s, 2H); 3.80-3.60 (m, 2H); 3.92-2.84 (m, 2H); 2.37 (s, 3H); 1.28 (s, 3H); 1.21 (t, 3H, J = 6.9 Hz); 1.17 (s, 3H, ***M***); 1.16 (s, 3H, ***m***) δ. MS *m/z* (rel. int.): 316 ($M^{+\cdot}$, 24); 186 (100). Anal. Calcd. for $C_{14}H_{20}O_6S$: C, 53.15; H, 6.37. Found: C, 53.20; H, 6.47.

1,4-oxathiin **11c.** Oil, (petroleum ether/ethyl acetate = 5/1), 52%, (d.e. 0%). ^{1}H-NMR: 5.29-5.21 (m, 1H); 4.55 (AB system, 2H, J = 11.6 Hz, ***m***); 4.54 (AB system, 2H, J = 11.0 Hz, ***M***); 4.01-3.6 (m, 4H); 3.76 (s, 3H); 3.15 (dt, 1H, J = 11.1 and 5.5 Hz); 3.00-2.80 (m, 2H); 2.25-1.40 (m, 8H); 1.27 (t, 3H, J = 6.4 Hz, ***m***); 1.26 (t, 3H, J = 7.2 Hz, ***M***); 0.90 (bt, 3H, J = 7.4 Hz); 0.77 (d, 3H, J = 7.0 Hz); 0.76 (d, 3H, J = 6.8 Hz) δ. MS *m/z* (rel. int.): 372 ($M^{+\cdot}$, 0.1); 234 (2); 202 (3); 95 (18); 84 (100). Anal. Calcd. for $C_{19}H_{32}O_5S$: C, 61.26; H, 8.66. Found: C, 61.38; H, 8.58.

1,4-oxathiin **11d.** Oil, (petroleum ether/ethyl acetate = 1/1), 83%, (d.e. 20%). ^{1}H-NMR: 6.64 (bs, 1H); 4.84 (bt, 1H, J = 4.5 Hz, ***M***); 4.77 (dd, 1H, J = 2.2 and 5.2 Hz, ***m***); 4.20-3.61 (m, 2H); 3.51-3.20 (m, 2H); 3.45 (s, 3H, ***M***); 3.42 (s, 3H, ***m***); 2.55-2.20 (m, 3H); 2.20-2.10 (m, 3H); 1.19 (t, 3H, J = 6.9 Hz, ***M***); 1.10 (t, 3H, J = 7.0 Hz, ***m***) δ. Anal. Calcd. for $C_{12}H_{16}O_6S$: C, 49.99; H, 5.60. Found: C, 50.13; H, 5.65.

1,4-oxathiin **13a.** Oil, (petroleum ether/ethyl acetate = 3/1), 93%, (d.e. 58%). ^{1}H-NMR: 7.28-6.90 (m, 4H); 5.44 (s, 1H); 4.80-4.76 (m, 1H, ***M***); 4.74-4-69 (m, 1H, ***m***); 4.06 (bs, 2H); 3.82 (s, 3H); 3.01-2.92 (m, 2H); 2.42 (s, 3H); 1.23 (s, 3H); 1.17 (s, 3H) δ. MS *m/z* (rel. int.): 378 (M$^{+\cdot}$, 100); 249 (46). Anal. Calcd. for $C_{19}H_{22}O_6S$: C, 60.30; H, 5.86. Found: C, 60.32; H, 5.71.

1,4-oxathiin **13b.** Oil, (petroleum ether/ethyl acetate = 6/1), 68%, (d.e. 0%). ^{1}H-NMR: 7.27-6.88 (m, 4H); 5.15-5.05 (m, 1H); 4.60 (AB system, 2H, J = 11.0 Hz, ***M***); 4.58 (AB system, 2H, J = 12.8 Hz, ***m***); 3.81 (s, 3H); 3.78 (s, 3H); 3.17 (dt, 1H, J = 10.9 and 3.6 Hz); 3.04-3.00 (m, 2H); 2.30-0.70 (m, 8H); 0.90 (d, 6H, J = 6.6 Hz, ***M***); 0.84 (d, 6H, J = 6.2 Hz, ***m***); 0.71 (d, 3H, J = 6.6 Hz, ***M***); 0.70 (d, 3H, J = 7.0 Hz, ***m***) δ. MS *m/z* (rel. int.): 434 (M$^{+\cdot}$, 3); 148 (4); 134 (100). Anal. Calcd. for $C_{24}H_{34}O_5S$: C, 66.33; H, 7.89. Found: C, 66.50; H, 7.87

1,4-oxathiin **13c.** White solid, m.p. 98-101 °C, (petroleum ether/ethyl acetate = 2/1), 75%, (d.e. 77%). The column chromatography allowed the isolation of the pure major stereoisomer $[\alpha]_D^{20}$ -53° (c = 0.63, CH_2Cl_2); ^{1}H-NMR: 7.20-6.88 (m, 4H); 6.65-6.60 (m, 1H); 4.89 (dd, 1H, J = 8.8 and 2.2 Hz); 3.53 (s, 3H), 3.40 (s, 3H), 2.65 (dd, 1H, J = 14.0 and 8.8 Hz); 2.50 (dd, 1H, J = 14.0 and 2.2 Hz); 2.30-1.80 (m, 4H) δ. ^{13}C-NMR: 177.0 (s); 164.8 (s); 159.9 (s); 158.4 (s); 130.6 (s); 126.7 (d, 2C); 114.3 (d, 2C); 97.30 (s); 78.2 (d); 76.0 (d); 55.3 (q); 52.6 (q); 31.7 (t); 27.9 (t); 26.2 (t) δ. MS *m/z* (rel. int.): 350 (M$^{+\cdot}$, 4); 134 (100). Anal. Calcd. for $C_{17}H_{18}O_6S$: C, 58.27; H, 5.18. Found: C, 58.12; H, 4.97

1,4-oxathiin **16.** Glassy solid, (petroleum ether/ethyl acetate = 2/1), 92%, (d.e. 77%). The column chromatography allowed the isolation of the pure major stereoisomer $[\alpha]_D^{20}$ -13° (c = 0.54, CH_2Cl_2); ^{1}H-NMR: 7.21-6.98 (m, 4H); 6.58-6.45 (m, 1H); 5.51 (s, 1H); 4.87 (dd, 1H, J = 8.4 and 3.0 Hz); 3.34 (AB system, 2H, J = 9.0 Hz); 2.60-2.36 (m, 2H); 2.30-1.80 (m, 4H); 1.04 (s, 3H); 0.77 (s, 3H) δ. Anal. Calcd. for $C_{22}H_{24}O_8S$; C, 58.92; H, 5.39. Found: C, 58.81; H, 5.24.

Dihydrothiopyran **19a.** Oil, (petroleum ether/ethyl acetate = 30/1), 73%, (d.e. 0%). ^{1}H-NMR: 4.93 (td, 1H, J= 11.0 and 4.4 Hz), 3.04-2.69 (m, 2H); 2.81 (bs, 2H); 2.38 (s, 3H, ***M***); 2.37 (s, 3H, ***m***); 1.67 (bs, 3H); 1.50 (bs, 3H); 1.04-0.80 (m, 18H) δ. MS *m/z* (rel. int.): 352 (M$^{+\cdot}$, 6); 215 (81); 154 (100). Anal. Calcd. for $C_{20}H_{32}O_3S$: C, 68.14; H, 9.15. Found: C, 68.12; H, 9.22.

Dihydrothiopyran **19b.** Oil, (petroleum ether/ethyl acetate = 3/1), 93%, (d.e. 12%). ^{1}H-NMR: 5.13 (q, 1H, J = 7.0 Hz, ***m***); 5.12 (q, 1H, J = 7.0 Hz, ***M***); 3.74 (s, 3H); 2.95 (bs, 2H); 2.80-2.43 (m, 2H); 2.40 (s, 3H); 1.60 (s, 3H); 1.5 (d, 3H, J = 7.2 Hz) δ. Anal. Calcd. for $C_{14}H_{20}O_5S$: C, 55.98; H, 6.71. Found: C, 55.75; H,6.64

Dihydrothiopyran **19c.** Oil, (petroleum ether/ethyl acetate = 30/1), 46%, (d.e. 0%). ^{1}H-NMR: 7.20-7.00 (m, 5H); 5.18 (td, 1H, J = 10.0 and 4.0 Hz); 2.90-2.64 (m, 2H); 2.60-2.40 (m, 2H); 2.07 (s, 3H, ***M***); 1.83 (s, 3H, ***m***); 1.66 (bs, 3H); 1.57 (bs, 3H); 1.41-0.89 (m, 8H) δ. MS *m/z* (rel. int.): 372 (M$^{+\cdot}$, 4); 195 (11); 159 (100); 91 (98). Anal. Calcd. for $C_{22}H_{28}O_3S$: C, 70.93; H, 7.57. Found: C, 70.84; H, 7.77.

Dihydrothiopyran **19d.** Oil, (petroleum ether/ethyl acetate = 3/1), 77%, (d.e. 32%). The column chromatography allowed the isolation of the pure major stereoisomer; ^{1}H-NMR: 5.22-5.20 (m, 1H); 3.82 (s, 3H); 3.84 (bs, 2H); 2.78-2.20 (m, 6H); 1.72 (bs, 6H) δ. MS *m/z* (rel. int.): 298 ($M^{+\cdot}$, 3); 186 (15); 125 (100); 85 (60). Anal. Calcd. for $C_{14}H_{18}O_5S$: C, 56.36; H, 6.08. Found: C, 56.48; H, 6.17.

REFERENCES AND NOTES

1. For part 1 see: Capozzi, G.; Franck, R. W.; Mattioli, M.; Menichetti, S.; Nativi, C.; Valle, G., *J. Org. Chem.* **1995**, *60*, 6416-6426
2. a) Waldmann, H., *Synthesis*, **1994**, 535-552, and references cited therein. b) Borm, C.; Meibom, D.; Winterfeldt, E. *Chem. Commun.*, **1996**, 887-894.
3. Adams, H.; Jones, D. N.; Aversa, M. C.; Bonaccorsi, P.; Giannetto, P. *Tetrahedron Lett.*, **1993**, *34*, 6481-6484.
4. a) Ohfune, Y.; Tomita, M. *J. Am. Chem. Soc.*, **1982**, *104*, 3511-3513. b) Saito, T.; Karakasa, T.; Fujii, H.; Furuno, E.; Suda, H.; Kobayashi, K. *J. Chem. Soc., Perkin Trans. 1*, **1994**, 1359-1362. c) Dujardin, G.; Rossignol, S.; Molato, S.; Brown, E. *Tetrahedron*, **1994**, *50*, 9037-9050. d) Boa, N. A.; Dawkins, A. D.; Hergueta, R. A.; Jenkins, R. P. . *J. Chem. Soc., Perkin Trans. 1*, **1994**, 953-960. e) Saito, T.; Fujii, H.; Hayashibe, S.; Matsushita, T.; Kato, H.; Kobayashi, K. *J. Chem. Soc., Perkin Trans. 1*, **1996**, 1897-1903. f) Fraile, J. M.; Garcia, J. I.; Gracia, D.; Mayoral, J. A.; Pires, E. *J. Org. Chem.*, **1996**, *61*, 9479-9482.
5. a) Posner, G.; Eydoux, F.; Lee, K. J.; Scott Bull, D. *Tetrahedron Lett.*, **1994**, *35*, 7541-7544. b) Posner, G.; Ishihara, Y. *Tetrahedron Lett.*, **1994**, *35*, 7545-7548. c) Marko, I.; Evans, R. G.; Declercq, J-P. *Tetrahedron*, **1994**, *50*, 4557-4574. d) Kobayashi, S.; Ishitani, H.; Hachiya, I.; Araki, M. *Tetrahedron*, **1994**, *50*, 11623-11636.
6. Capozzi, G.; Nativi, C.; Menichetti, S.; Rosi, A.; Valle, G. *Tetrahedron*, **1992**, *48*, 9023-9032.
7. a) Breslow, D.; Baumgarten, E.; Hauser, R. C. *J. Am. Chem. Soc.*, **1944**, *66*, 1286-1288. b) Ratke, M. W.; Sullivan, D. F. *Tetrahedron Lett.*, **1973**, *14*, 1297-1300. c) Wierenga, W.; Skulnick, I. H. *J. Org. Chem.* **1979**, *44*, 310-311. d) Clay, J. R.; Collom, A. T.; Karrick, L. G.; Wemple, J. *Synthesis*, **1993**, 290-293. e) Wang, X.; Monte, T. W.; Napier, J. J.; Ghannam, A. *Tetrahedron Lett.*, **1994**, *35*, 9323-9326.
8. Oikawa, Y.; Sugano, K.; Yonemitsu, O. *J. Org. Chem.* **1978**, *43*, 2087-2088.
9. Attempts to measure the enantiopurity of thiophthalimides **3** by ^{1}H NMR using Eu(hcf)$_3$ as chiral shift reagent were unsuccessful.
10. Using **12** as dienophile and lutidine as base we had faster reactions with increasing of the chemical yields of the cycloadducts since prolonged reaction times lead to the formation of thione oligomers as byproducts.[6]
11. The reaction of thiophthalimide **3g** with styrene **12** and lutidine was also performed in the presence of several Lewis acids as catalysts (20% mol.) [$BF_3{\cdot}OEt_2$, $ZnCl_2{\cdot}OEt_2$, $TiCl_4$ and Eu(hcf)$_3$] without increasing of the diastereoselectivity and/or the reaction time.
12. Also for these compounds the distereoisomeric excesses were measured by ^{1}H NMR of the crude mixtures recorded in benzene-d_6
13. Bombala, M. U.; Ley, S. V. *J. Chem. Soc., Perkin Trans. 1*, **1979**, 3013-3016.
14. Wissner, A.; Grudzinskas, C. *J. Org. Chem.* **1978**, *43*, 3972-3973.

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