High-Pressure Selectivity Studies—A Simple Route to a Homochiral Wistarin Precursor

Costanze Knappwost-Gieseke,*[a] Frank Nerenz,[b] Rudolf Wartchow,[c] and Ekkehard Winterfeldt*[d]

Abstract: The cycloaddition of spirobutenolide **3** to the homochiral cyclopentadiene **1** at 6.5 kbar leads exclusively to cycloadduct **5**. Subsequent Diels–Alder or Michael additions again favour the cyclohexenone double bond; this perfect chemo- regio- and face selectivity was employed for a short and efficient approach to the wistarin framework.

Keywords: cycloaddition · diastereoselectivity · Diels–Alder reactions · high-pressure chemistry

Introduction

High pressure Diels–Alder cycloadditions to the homochiral cyclopentadiene **1** have been shown to result in perfect kinetic resolution with various chiral dienophiles.[1] The differentiation of enantiotopic double bonds in prochiral dienophiles—such as spirolactone **2**—provided only one homochiral cycloadduct in high yield, thus transforming all the material into one single enantiomer.[2, 3]

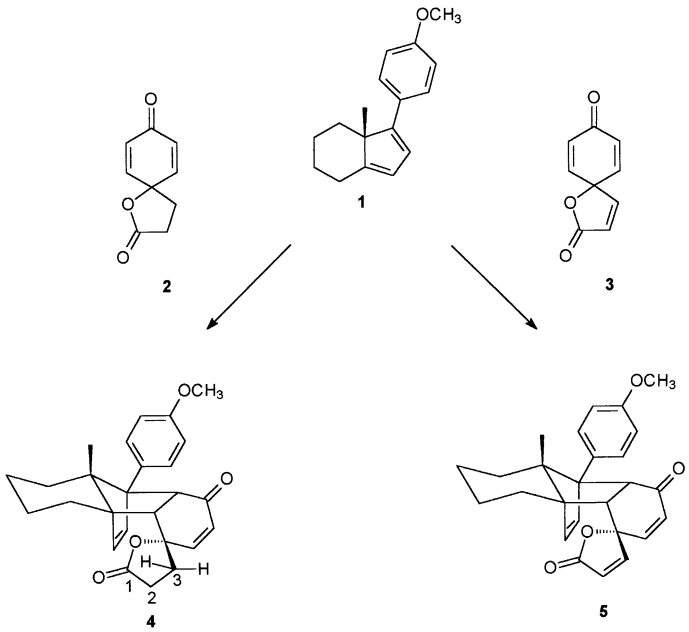
In all other similar cases studied thus far, the oxygen atom in the five-membered ring always proved to be less sterically demanding than the corresponding CH_2 group (see C3 in **3**); this predictably and reliably led to the exclusive formation of only one cycloadduct which secures the β orientation for the carbon atom in position 3.[4]

The leading role of the steric hindrance over any electronic contributions was clearly shown by theoretical calculations of these cycloadditions.[5]

Although the model compounds indicated that the same outcome should be expected for an sp^2 carbon atom located at the spirocenter (C_3)—as for example present in spirobutenolide **3**—no experimental data are available at this stage to support this expectation.

Our preceding cycloaddition experiments, which had proven that rather small differences in the steric hinderance can lead to the exclusive population of only one transition state,[6] and the fact that lactones and butenolides are frequently found as substructures in the framework of natural products[7] (see also below) prompted us to further investigate the cycloaddition reactions of spirobutenolide **3**.

Furthermore a closer look at adduct **5** (Scheme 1) clearly indicated that **3** in contrast to **2** would not only pose a face-selectivity but more of a chemoselectivity problem, as the butenolide double bond can also serve as a dienophile.



Scheme 1.

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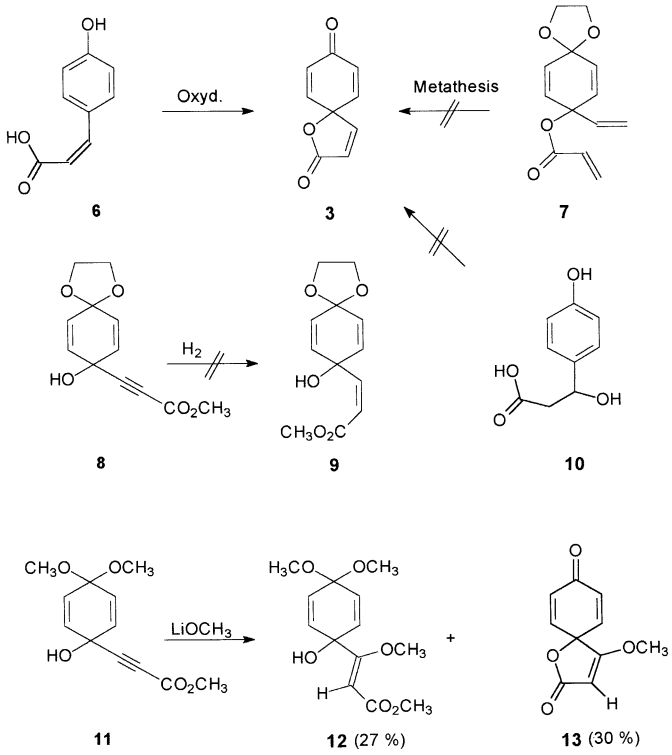
The preparation of spirobutenolide 3: Since spirolactone **2** is very easily available by oxidative cyclisation (using phenyliodoso-bistrifluoroacetate, PIFA) of the corresponding *p*-hydroxydihydrocinnamic acid[8] the very low yield of **3** (1%) reported for the anodic oxidation of the very similar *Z*-cinnamic acid **6** came as a great surprise.[9]

However, our efforts to prepare the butenolide moiety by metathesis[10] or by spirocyclisation of β-hydroxy acid **10**[11–13] failed at an early stage. The selective hydrogenation of the triple bond in **8** and **10** was also unsuccessful.

For the benefit of chemistry aiming at substituted spirobutenolides we also report the result of the conjugate addition of methanol which along with the corresponding *Z* ester **12** (27%) provided spirobutenolide **13** directly in 30% yield (Scheme 2).

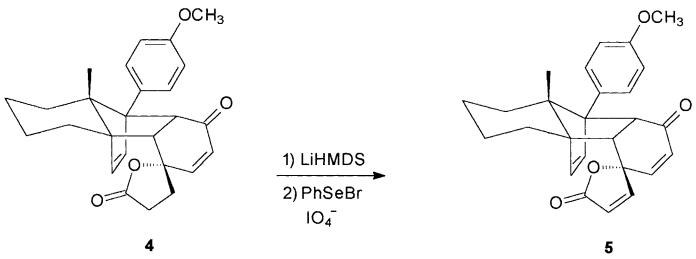


Scheme 2.

The selective *Z* additions to triple bonds, which are well documented in the literature, appear to be an excellent option for substituted compounds of this type.[14, 15]

At this stage we returned to the optimisation of the PIFA oxidation.[8] We finally succeeded using lower temperatures (see Experimental Section). The reaction provided spirobutenolide **3** in 80% yield, related to the pure *Z* acid present in the starting material (similar NMR data). This represented a reliable basis for the preparation of our starting material and the investigation of its cycloaddition chemistry.

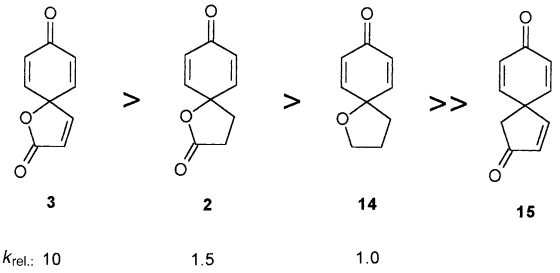
Diels–Alder chemistry: Surprisingly cycloaddition of spirobutenolide **3** to the enantiomerically pure cyclopentadiene **1** the 6.5 kbar provided one single adduct after 4 d at room temperature in 93% yield. Although the NMR data (typical butenolide pattern) did agree with structure **5** (Scheme 3), we



Scheme 3.

corroborated this result by an independent preparation of this compound.

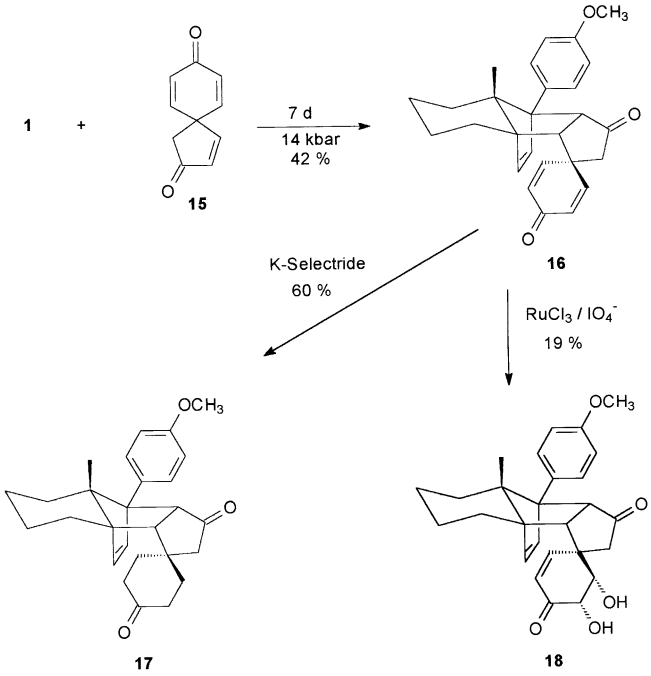
Thus, the lithium enolate of spirolactone **4** was treated with phenylselenyl bromide and the resulting phenylselenide gave rise to spirobutenolide **5** in an oxidative elimination.[16] As the constitution and configuration of lactone **4** had been proved by X-ray structure determination,[3] this transformation constitutes unequivocal proof that we are dealing with a perfect chemo-, face- and regioselective Diels–Alder cycloaddition; this reaction discriminates between three electron-poor double bonds in which again the oxygen atom is recognized as the less sterically demanding centre. Although this is in agreement with the observations made with the spirolactone **2** and spiroether **14**, the higher reaction rate of **3** compared with **2** and **14** (see Scheme 4) indicates that there are additionally electronic contributions to the rate of this transformation.



Scheme 4.

This triggered a detailed investigation, which should define the balance between steric and electronic effects in cycloadditions of this type by comparing experimental data with the results of FMO analysis.[17] To document the crucial role of the oxygen atom in the one possible transition state of these spirodienophiles we extended the investigations to spirocyclopentenone **15** (Schem 5). As the "small" oxygen atom present in **3**, **2** and **14** is replaced by a CH_2 group, a severe drawback for the cycloaddition reaction can be predicted, which was also observed experimentally.

Compound **15**, which can easily be prepared by an improved literature procedure (see Experimental Section) from *p*-methoxyphenylacetic chloride and acetylene in the presence of aluminiumchloride,[18] could not be added to diene **1** using our standard reaction conditions (6.5 kbar, room temperature). However, when the pressure was increased to 14 kbar the main reaction product could be isolated after 7 d in 42% yield.



Scheme 5.

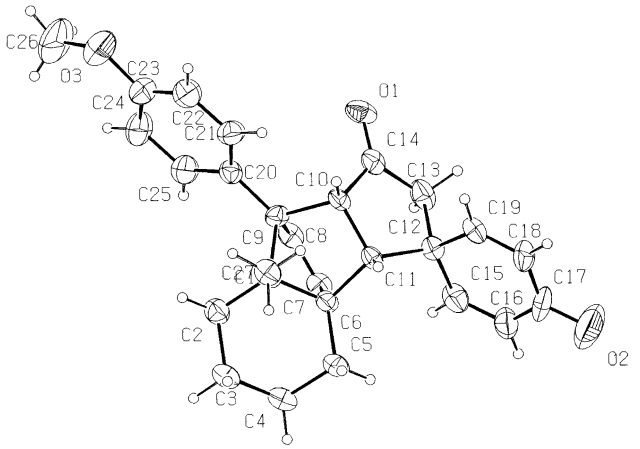


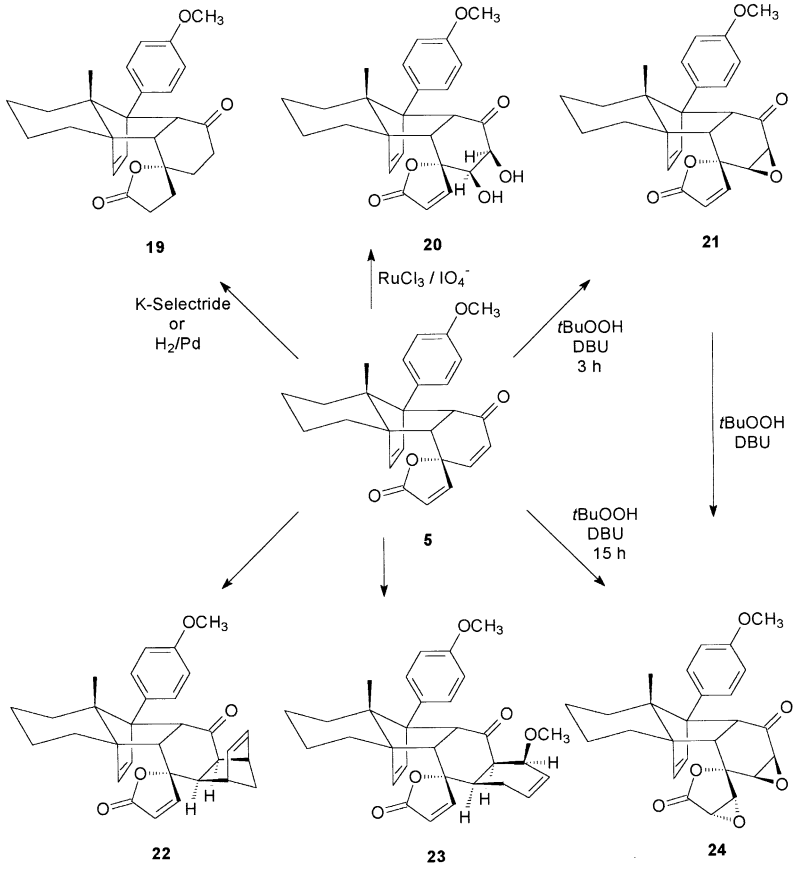
Figure 1.

IR and NMR spectroscopical data of this 1:1 cycloadduct (ratio determined by MS) indicated addition to the cyclopentenone double bond. Structure **16** was obtained from an X-ray structure investigation (Figure 1).

This constitutes a further proof for the dominating role of the oxgen atom in the five-membered ring in directing the selectivity of the cycloadditions.

Diastereoselective transformations of Diels–Alder adducts: In spite of the moderate yield of **16** we performed several reactions to compare the similar chemistry of spirobutenolide **5** (see Scheme 6). However, the conjugate addition or epoxidation of diketone **16** were unsuccessful.

Even the so called "flash hydroxylation"[19] which had been routinely and highly reliably applied to other cyclohexenones in this series took at least two hours in this case and still provided only a mere 19% of the corresponding α-diol **18** (Scheme 5).[3, 6] The only satisfactory reaction so far turned out to be the conjugate hydride addition with potassium selectride which gave rise to the saturated diketone **17** in 60% yield in 10 minutes at $-78\,^{\circ}C$. While this special reduction is similar to the corresponding reaction with spirobutenolide **5** (see **19**), this spirolactone differs completely in all the other transformations which generally show a strong preference for reactions at the cyclohexenone double bond (see Scheme 6). This started with the fast and selective "flash hydroxylation" to form diol **20** exclusively, followed by epoxidation which after 3 h provided mono-epoxide **21** as the sole reaction product; it took more than 15 h to generate the corresponding bis-epoxide **24**, which was also finally observed in the Diels–Alder cycloadditions.



Scheme 6.

Cyclopenta-1,3-diene and 1-methoxybuta-1,3-diene both added exclusively to the cyclohexenone double bond of **5** and provided *endo*-adducts **22** and **23**, respectively.

While the configuration, which demonstrates the *endo*-attack in the formation of **22**, was confirmed by the X-ray data (see Figure 2) of the very rigid, polycyclic cycloadduct itself. The configuration of **23** was obtained by an X-ray structure determination of the corresponding nicely crystalline retro-Diels–Alder product **36** (see Scheme 11 and Figure 3).

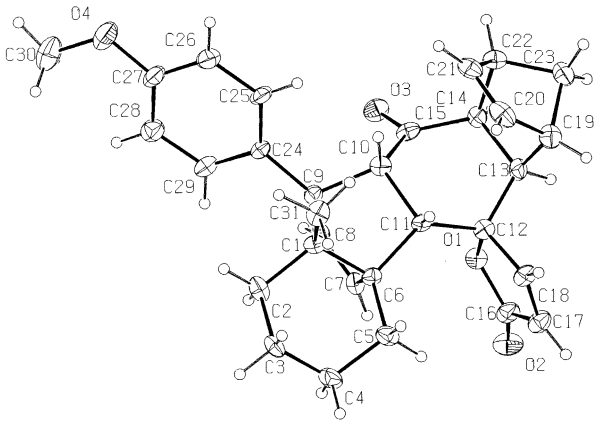
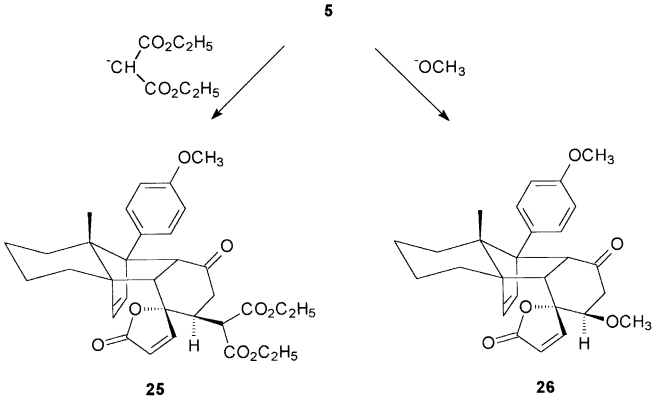


Figure 2.

These two examples prove that **5** holds numerous options for selective annulation reactions at the cyclohexenone double bond and to probe the scope of this chemistry we focussed next on conjugate additions which under high-pressure conditions proved to be of excellent chemo-, regio- and diastereoselectivity. Two typical examples demonstrating the efficiency of this process are the addition of sodium malonate giving rise to a quantitative yield of diester **25** and the formation of methanol adduct **26** in 96% yield (see Scheme 7).

It has to be mentioned at this stage, however, that more sterically demanding nucleophiles such as isopropylate and pyrrolidine did not undergo the Michael addition under comparable conditions.

The ease of malonate addition on the other hand called for a closer investigation of β-dicarbonyl systems and so we turned to double donors with the intention to annulate further rings to the spiro moiety.

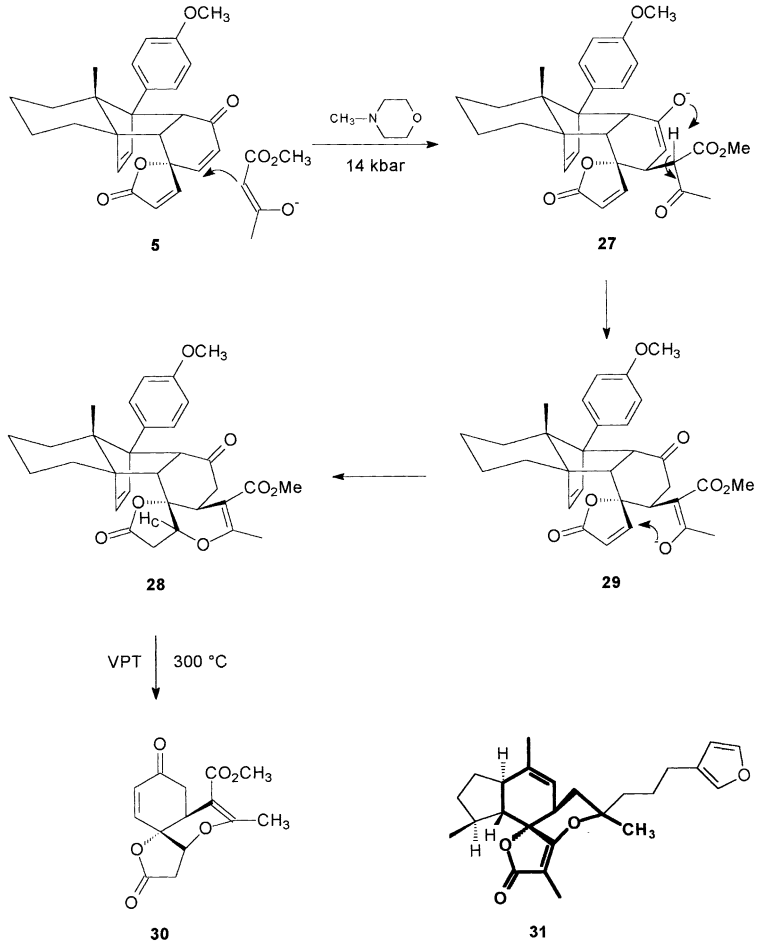


Scheme 7.

First, the anion of methyl acetoacetate was checked as double addition of this potential bisnucleophile could lead to the tricylic core of the quite unusual and certainly easily accessible wistarin framework (see **31** Scheme 8).[20, 21]

To shift the Michael equilibrium completely toward the side of products we ran this reaction at 14 kbar in the presence of *N*-methylmorpholine and were pleased to obtain the 1:1 annulation product **28** in 93% yield.

The structure in Scheme 8 is based on MS and NMR data including NOE experiments (see Experimental Section). The most revealing features are the following: the complete



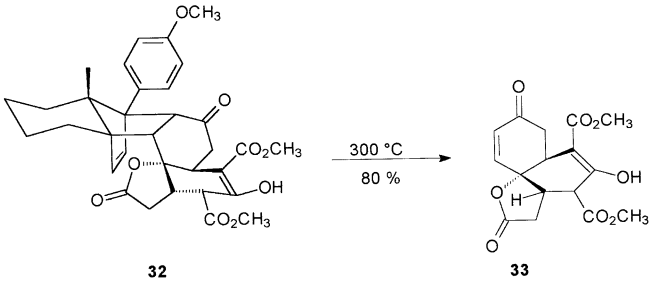
Scheme 8.

absence of any olefinic proton resonances connected to a cyclohexenone or butenolide double bond, the appearance of a three-proton singlet at $\delta = 2.21$ for a methyl group bound to an sp^2 carbon atom and of a one-proton doublett at $\delta = 4.70$ for H_C which proves enolate addition to the butenolide.

Although these data support also primary attack at the cyclohexenone double bond for this addition, a very convincing proof of this outcome resulted from an investigation of the chemical behaviour of the retro Diels–Alder product **30** which is discussed below.

With the intention to investigate the regioselectivity of the cyclisation step we finally treated **5** with dimethyl acetonedicarboxylate under high-pressure conditions. Again a 1:1 annulation product (**32**) was isolated but as contrary to **28** the $\delta = 4.7$ proton resonance was lacking as well as in the corresponding retro-product **33**, the formation of a carbon–carbon bond was indicated.

Although complete enolisation could be concluded from NMR data, the regioselectivity of this process remained unclear. The direction of enolisation given in **32** and **33** (Scheme 9) is therefore arbitrary and merely based on simple ring-strain considerations.



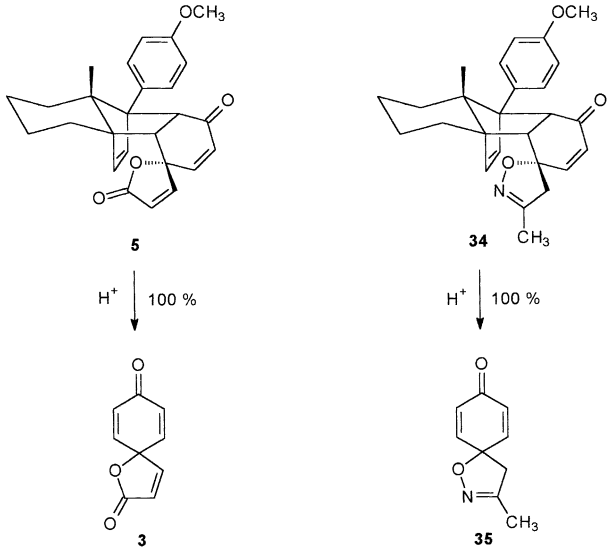
Scheme 9.

Retro Diels–Alder chemistry: Since in all the reactions the reported diene **1** is operating as a chiral template, which secures the enantioselectivity via chiral recognition in the first cycloaddition and induces high diastereoselectivity in subsequent transformations, one is of course particularly interested in the outcome of the retro process to yield the desired homochiral compounds.

There are in principle always two options available to enforce retro-splitting.[22] It can either be achieved by acid or Lewis acid catalysis or one can rely on a purely thermal procedure. For the latter microwave treatment or vapour-phase thermolysis (VPT) are certainly the most popular versions.[23, 24]

A very efficient trifluoroacetic-acid catalysis was encountered with cyclohexadienone adducts such as **5** and **34** (Scheme 10).

Upon treatment with dilute trifluoroacetic acid in dichloromethane at 0 °C both compounds **5** and **34** provided a quantitative yield of the corresponding cyclohexadienones **3** and **35**. Unfortunately this technique could not be applied to the more complicated reaction products prepared from **5**.

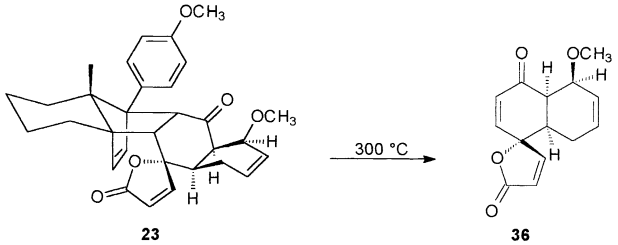


Scheme 10.

Although in every case the appearance of diene **1** in the crude reaction mixtures (TLC) indicated retro-splitting, none of the desired spiro compounds could be isolated.

We then turned to thermolysis and were pleased to note that the methoxy-butadiene adduct **23** was indeed cleaved at 300 °C to yield spirocyclohexenone **36** (38 %) in the first run without any optimisation (Scheme 11); compound **36** provided nice crystals for X-ray strucure determination after chromatography (Figure 3).

Even more exciting and of considerable synthetic value was the result with wistarin-precursor **28**. Despite its complexity and the fact that product **30** shows a high tendency to



Scheme 11.

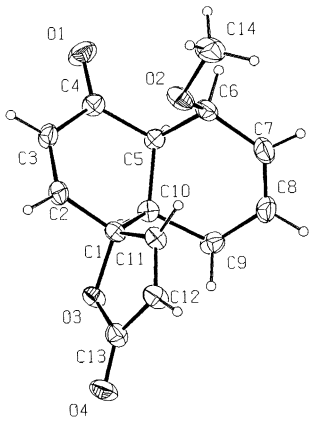


Figure 3.

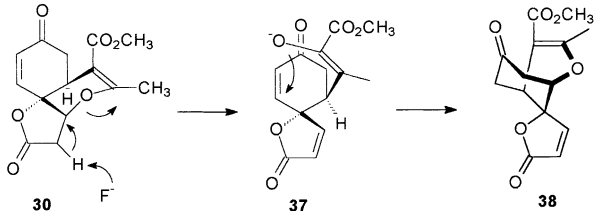
rearrange (see below, Scheme 12) the retro product was generated in quantitive yield and very high optical purity (>95% *ee*) (see Scheme 8).

The functional groups present in **30** offer a number of synthetic options for this wistarin intermediate (cf. **31**, Scheme 8, bold lines indicate wistarin core). The cyclohexenone double bond allows cycloadditions for annulation of five- or six-membered rings; the corresponding carbonyl group give easy access to many variations of the trisubstituted double bond[25] present in wistarin.

While first orientating experiments led to quite encouraging results they also revealed a high tendency for **30** to rearrange under even mild basic conditions.[26]

Even at 0 °C treatment with tetraalkylammonium fluoride led to a very fast and clean spot to spot transformation to generate spirobutenolide **38** in quantitative yield (see Schem 12).

For a quite obvious rationalisation of this outcome we assume that the retro-Michael process (see arrows) forms **37** (Scheme 12) which collapses in a conjugate addition to the unsaturated ketone thus giving rise to **38**.



Scheme 12.

As the most convincing argument in favour of this structure we noticed the disappearance of the two cyclohexenone protons ($\delta = 6.22$, 6.70; $J = 10$ Hz) which are replaced by the very characteristic butenolide pattern ($\delta = 6.27$, 7.62; $J =$ 6 Hz).

Since the cyclohexenone moiety as well as the 1,3-dicarbonyl system are still present in **38** in a mutually protected manner it allows further cyclisations and rearrangements.

Conclusion

In summary it has been demonstrated that spirobutenolide **3** in spite of the availability of three electron-poor double bonds at 6.5 kbar adds to the homochiral diene **1** with perfect chemo-, regio-, endo- and face selectivity leading to cycloadduct **5** exclusively. Subsequent conjugate additions or cycloadditions to this Diels–Alder adduct showed absolute preference for the cyclohexenone double bond.

In the case of acetoacetate the reaction gave rise to the polycyclic adduct **28** in a predictable sequence of high-pressure Michael additions; the adduct then underwent a very clean retro-Diels–Alder fission to provide a quantitative yield of the potential wistarin precursor **30** showing high synthetic flexibility.

Experimental Section

General techniques: Dry solvents were freshly distilled, and if necessary, dried according to usual procedures. Reactions with dry solvents were carried out under Ar atmosphere. All reactions were monitored by thin-layer chromatography (Merck silica gel glass plates 60F-254) using UV light and acidic phosphomolybdic acid/cerium(IV) sulfate. Silica gel from Baker (30–60 μm) was used for flash column chromatography. High-pressure was applied in a 14 kbar high-pressure apparatus from the Hofer company.

NMR spectra were recorded on Bruker WP 200 and AM 400 instruments. δ_H values are given relative to tetramethylsilane = 0; J values in Hz; δ_C values are given relative to $CDCl_3 = 77.05$; multiplicities of ^{13}C NMR were determined by DEPT (90°/135°). IR spectra were recorded on Bruker FS 25 (PtBr) and Vector 22 ($CHCl_3$ and Golden Gate). Mass spectra were recorded on a MAT 312 Finigan by 70 eV. FAB spectra were recorded on a VG-Autospec in a *m*-nitrobenzylalcohol matrix. The high resolution mass spectra (HRMA) were recorded on a VG-Autospec. Melting points are uncorrected and were recorded on a Gallenkamp melting point apparatus.

Specific rotation α were recorded with a Perkin–Elmer 241 with the sodium D line.

Cyclopentadiene **1** was prepared according to the procedure described by Winterfeldt et al.[27]

Spirobutenolide 3: 4-Hydroxy-*Z*-dihydrocinnamic acid[28] (243 mg, ≈1.48 mmol, 1 equiv) was dissolved in CH_2Cl_2 (3 mL) and a few drops of dry acetonitrile. The mixture was slowly added to a solution of PIFA (828 mg, 1.93 mmol; 1.3 equiv) in dry CH_2Cl_2 (10 mL) at 0 °C. After 30 min stirring at 0 °C and 4.5 h at RT the reaction mixture was quenched with sat. aq. $NaHCO_3$. The aqueous layer was extracted with ethyl acetate, dried ($MgSO_4$) and purified by chromatography to yield as a yellow solid (137 mg, 0.85 mmol, 57%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.37$ (d, $J =$ 5.5 Hz, 1H), 6.42 (d, $J = 10$ Hz, 2H), 6.56 (d, $J = 10$ Hz, 2H), 7.17 (d, $J =$ 5.5 Hz, 1H); UV (MeOH): $\lambda = 214$ nm; IR (KBr): $\tilde{\nu} = 3092$ (w), 1766 (vs), 1664 (s), 1628 (m), 1200 (m), 1060 (m), 832 cm^{-1}(s); MS: *m*/*z* (%): 162 (41) [M^+], 134 (100), 121 (25), 106 (51), 82 (47), 78 (59); HRMS: *m*/*z*: calcd for $C_9H_6O_3$: 162.0317; found: 162.0320.

Spirobutenolide 5

a) A solution of diene **1** (160 mg, 0.667 mmol) and spirobutenolide **3** (108 mg, 0.667 mmol, 1 equiv) in dry $CHCl_3$ (3.5 mL) was introduced into a Teflon hose and submitted to 6.5 kbar for 2 d. Purification of the raw material by flash chromatography (PE/Et_2O 1:1) yielded a white solid (244 mg, 91%).

b) Spirolactone-adduct **4** (500 mg, 1.24 mmol) in dry THF (15 mL) was slowly added at −78 °C to a solution of LiHMDS (2.72 mL, 1M, 2.72 mmol, 2.2 equiv) in dry THF (3 mL) After 1 h at this temperature a solution of phenylselenylbromide (351 mg, 1.49 mmol; 1.2 equiv) in dry THF (3 mL) was added, and the mixture was stirred for 30 min. The reaction mixture was poured into sat. aq. NH_4Cl and extracted with CH_2Cl_2. The combined organic layers were washed with water and brine and dried over $MgSO_4$. Chromatography yielded (PE/Et_2O 2:1) the seleno intermediate, which was dissolved in acetone (10 mL) at RT. To this solution was added a solution of $NaIO_4$ (256 mg, 1.24 mmol; 1 equiv) in acetone (10 mL) and water (0.5 mL). After 12 h at RT the reaction was quenched with sat. aq. $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2, dried ($MgSO_4$) and concentrated. Chromatographic purification (PE/Et_2O 1:1) yielded a white solid (204 mg, 41%). $[\alpha]_D^{20} = -230.9°$ ($c = 1.03$, $CHCl_3$); UV (MeOH): $\lambda = 227$ nm; IR ($CHCl_3$): $\tilde{\nu} = 3028$ (w), 1776 (vs), 1680 (s), 1192 (m), 1068 (m), 820 cm^{-1}(s); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.46$ (br d, $J =$ 13 Hz, 1H), 0.79 (s, 3H), 1.10–1.45 (m, 4H), 1.64 (br d, $J = 13$ Hz, 1H), 1.84 (br dt, $J = 13$, 4 Hz, 1H), 2.39 (d, $J = 12$ Hz, 1H), 2.77 (d, $J = 8$ Hz, 1H), 3.81 (s, 3H), 3.89 (d, $J = 8$ Hz, 1H), 5.90 (d, $J = 5.5$ Hz, 1H), 5.91 (d, $J = 10$ Hz, 1H), 6.10 (d, $J = 5$ Hz, 1H), 6.13 (d, $J = 10$ Hz, 1H), 6.23 (d, $J = 5.5$ Hz, 1H), 6.89 (d, $J = 9$ Hz, 2H), 7.24 (d, $J = 5.5$ Hz, 1H), 7.32 (d, $J = 9$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 15.15$ (q), 20.97 (t), 23.80 (t), 27.37 (t), 28.43(t), 46.31 (d), 49.64 (d), 55.18 (q), 61.65 (s), 63.00 (s), 71.85 (s), 86.64(s), 113.12 (d), 118.96(d), 128.29(s), 129.13 (d), 132.77 (d), 136.28 (d), 138.68 (d), 144.05 (d), 158.43 (s), 160.12 (d), 171.97 (s), 197.63 (s); MS: *m*/*z* (%): 402 (3) [M^+], 344 (2), 312 (2), 241 (20), 240 (100), 225 (25), 197 (22), 181 (9), 165 (10), 134 (22), 106 (12), 91 (10), 78 (15); HRMS: *m*/*z*: calcd for $C_{26}H_{26}O_9$: 402.1831; found: 402.1829.

***Z*-ester 12**: *n*BuLi (15.3 mL, 1.6 M, 22.24 mmol, 1.65 equiv) was added at −120 °C to a solution of methyl propiolate (2 mL, 22.2 mmol, 1.5 equiv) in Trapp mixture (40 mL).[29] After stirring for 5 min (2.205 g, 13.14 mmol, 1 equiv) quinone dimethylketal was added. After 5 min the reaction mixture was raised to room temperature and the reaction was quenched with sat.aq. NH_4Cl. The aqueous layer was extracted with Et_2O, dried ($MgSO_4$) and concentrated. Chromatographic purification (PE/MTBE 1:1) led to ketal splitting and yielded cream-coloured solid propargyl ester **11** (2.011 g, 10.47 mmol, 73 %).

Lithium methanolate (0.032 g, 0.84 mmol, 2 equiv) was added to a solution of propargylester **11** (0.100 g, 0.42 mmol, 1 equiv) in dry MeOH (9 mL) under Ar. After 3 h at RT the reaction was quenched with water and extracted with CH_2Cl_2 and ethyl acetate. The combined organic layers were dried (Na_2SO_4) and concentrated. Chromatographic purification (PE/MTBE 1:1 to ethyl acetate) yielded a yellow solid (0.025 g, 0.112 mmol, 27 %). IR ($CHCl_3$): $\tilde{\nu}$ = 3580 (w), 3000(w), 2856(w), 1716 (s), 1672 (s), 1640 (s), 1454 (m), 1388 (w), 1268 (w), 1184 (m), 1092 (w), 1048 (w), 1004 cm^{-1} (w); ^1H NMR (400 MHz, $CDCl_3$): δ = 3.68 (s, 3H), 3.94 (s, 3H), 5.68 (s, 1H), 6.25 (d, J = 10 Hz, 2H), 6.73 (d, J = 10 Hz, 2H); MS (FAB): *m*/*z* (%): 224 (15) [M^+], 206 (26), 192 (98), 178 (6), 165 (24), 149 (31), 137 (38), 115 (25), 110 (51), 101 (27), 81 (23), 69 (100); HRMS: *m*/*z*: calcd for $C_{11}H_{12}O_5$: 224.0685; found: 224.0688.

Spirobutenolide **13**: Lithium methanolate (0.096 mg) was added under Ar to a solution of propargylester **11** (0.300 g, 1.26 mmol, 1 equiv) in dry MeOH (25 mL). After 72 h at RT the reaction was quenched with water and extracted with CH_2Cl_2 and ethyl acetate. The combined organic layers were dried (Na_2SO_4) and concentrated. Chromatographic purification (PE/MTBE 1:1 to ethyl acetate) yielded an orange solid (0.138 g, 0.72 mmol, 57 %). IR ($CHCl_3$): $\tilde{\nu}$ = 3304 (w), 3040 (w), 2944 (w), 1760 (s), 1640 (s), 1452 (w), 1440 (w), 1318 (m), 1284 (m), 1252 (m), 1192 (m), 1168 (m), 1064 (m), 956 cm^{-1}(m); ^1H NMR (400 MHz, $CDCl_3$): δ = 3.92 (s, 3H), 5.32 (s, 1H), 6.44 (d, J = 10 Hz, 2H), 6.63 (d, J = 10 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.2 (q), 60.2 (s), 78.6 (s), 89.7 (d), 132.0 (d), 141.9 (d), 179.2 (s), 183.9 (s); MS: *m*/*z* (%): 192 (64) [M^+], 164 (17), 149 (23), 136 (9), 123 (18), 97 (11), 83 (13), 69 (100); HRMS: *m*/*z*: calcd for $C_{10}H_8O_4$: 192.0423; found: 192.0417.

Spirocyclopentenone 15: A solution of 4-methoxyphenyl-acetic chloride (0.52 mL, 3.4 mmol, 1 equiv) in dry CH_2Cl_2 (8 mL) was 15 min saturated with acetylene. Aluminiumchloride (1.342 g, 9.2 mmol, 2.7 equiv) was added in portions in a acytelene stream. The solution turned red and was quenched after 10 min stirring at 0 °C the reaction by solid Na_2CO_3, ice and few mL of sat. aq. Na_2CO_3. Immediate chromatography with florisile (Et_2O/PE 1:1) yielded a yellow solid (246 mg, 1.54 mmol, 45 %). For characterization see [17].

Spirocyclopentenone adduct 16: A solution of spirocyclopentenone **15** (246 mg, 1.54 mmol, 1 equiv) and diene **1** (406 mg, 1.69 mmol, 1.1 equiv) in dry CH_2Cl_2 (2 mL) was introduced into a Teflon hose and submitted to 14 kbar for one week. Purification of the raw material by flash chromatography (PE/Et_2O 1:1) yielded a yellow crystalline solid (256 mg, 42 %, 0.64 mmol). $[\alpha]_D^{20}$ = −39.7° (c = 0.93, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}$ = 2928 (s), 2856 (m), 1720 (s), 1664 (s), 1612 (w), 1588 (w), 1516 (m), 1404 (m), 1288 (w), 1252 (m), 1180 (m), 1036 cm^{-1} (w); ^1H NMR (400 MHz, $CDCl_3$): δ = 0.64 (d, J = 13 Hz, 1H), 0.75 (s, 3H), 1.14–1.39 (m, 3H), 1.54–1.69 (m, 2H), 1.94–2.06 (m, 2H), 2.08 (d, J = 18.4 Hz, 1H), 2.56 (d, J = 18.4 Hz, 1H), 2.75 (d, J = 8 Hz, 1H), 3.82 (s, 3H), 3.92 (d, J = 8 Hz, 1H), 6.17 (d, J = 5.8 Hz, 1H), 6.21 (dd, J = 2, 10 Hz, 1H), 6.37 (d, J = 5.6 Hz, 1H), 6.39 (dd, J = 10, 2 Hz, 1H), 6.80 (dd, J = 3, 10 Hz, 1H), 6.91 (d, J = 9 Hz, 2H), 6.97 (dd, J = 3, 10 Hz, 1H), 7.30 (d, J = 9 Hz, 2H). NOE experiment:

0.75 ⇒ 2.75 (3.9 %), 3.92 (2.1 %), 6.91 (0.3 %), 7.30 (0.8 %);

2.75 ⇒ 0.77 (11.3 %), 3.92 (8.6 %), 6.39 (0.5 %);

3.92 ⇒ 0.77 (6.3 %), 2.75 (10.3 %), 6.80 (4.6 %), 6.97 (0.5 %), 7.30 (27.2 %);

MS: *m*/*z* (%): 400 (3) [M^+], 279 (4), 266 (3), 240 (99), 225 (15), 205 (19, 160 (16), 149 (57), 132 (29), 121 (10), 104 (19), 86 (100), 78 (23); HRMS: *m*/*z*: calcd for $C_{27}H_{28}O_3$: 400.2039; found: 400.2040.

Adduct 17: K-selectride(0.1 mL, 1 M in THF) was added at −78 °C to a solution of spirocyclopentenone adduct **16** (20 mg, 0.05 mmol, 1 equiv) in dry THF (2 mL). After 1 h at −78 °C and 10 min at RT H_2O_2(1 mL, 30 %) and NaOH (0.5 mL, 10 %) were added. The aqueous layer was extracted with ethyl acetate. The combined organic layers were dried ($MgSO_4$) and concentrated. Chromatographic purification (Et_2O/PE 1:2) yielded a light yellow oil (12 mg, 0.03 mmol, 60 %). $[\alpha]_D^{20}$ = −75.5° (c = 0.90, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}$ = 2928 (s), 2856 (m), 1739 (m), 1613 (w), 1516 (m), 1464 (m), 1264 (s), 1181 (m), 1036 (m), 909 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 0.55 (br d, J = 12 Hz, 1H), 0.77 (s, 3H), 0.80–2.36 (m, 13H), 2.89 (m, 1H), 2.96 (d, J = 6.9 Hz, 1H), 3.59 (dd, J = 1.6, 4.5 Hz, 1H), 3.75 (d, J = 6.9 Hz, 1H), 3.81 (d, J = 6.1 Hz, 1H), 3.81 (s, 3H), 4.04 (d, J = 4.4 Hz, 1H), 5.89 (d, J = 5.9 Hz, 1H), 5.95 (d, J = 5.9 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H).

Diol 18: $RuCl_3 \cdot x\,H_2O$ (1.3 mg, 0.006 mmol) and $NaIO_4$ (8 mg, 0.04 mmol) in water (0.08 mL) were added to vigorously stirred solution of spirocyclopentenone adduct **16** (10 mg, 0.025 mmol, 1 equiv) in ethyl acetate (0.25 mL) and acetonitrile (0.3 mL). After 2 h at 0 °C the reaction mixture was quenched with sat. aq. $NaHSO_3$ and extracted with ethyl acetate. The combined organic layers were dried ($MgSO_4$) and purified by chromatography (PE/Et_2O 1:1) to yield a yellow oil (2 mg, 0.005 mmol; 19 %). $[\alpha]_D^{20}$ = 6.42° (c = 0.72, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}$ = 3582 (w), 2957 (w), 2927 (s), 2855 (m), 1725 (s), 1697 (m), 1667 (w), 1613 (w), 1516 (m), 1464 (m), 1289 (s), 1120 cm^{-1} (m); ^1H NMR ($CDCl_3$): δ = 0.63 (br d, J = 12 Hz, 2H), 0.75 (s, 3H), 0.83–1.75 (m, 6H), 1.90–2.70 (m, 2H), 2.23 (d, J = 19.4 Hz, 1H), 2.59 (d, J = 19.2 Hz, 1H), 2.73 (d, J = 7.8 Hz, 1H), 3.81 (s, 3H), 3.87 (d, J = 7.9 Hz, 1H), 4.42 (t, J = 2.4 Hz, 1H), 4.50 (d, J = 2.4 Hz, 1H), 6.06 (d, J = 10 Hz, 1H), 6.14 (d, J = 5.4 Hz, 1H), 6.35 (d, J = 5.8 Hz, 1H), 6.47 (dd, J = 2.4, 10 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.9 Hz, 2H).

Spirolactone adduct 19

a) K-Selectride (0.05 mL, 1 M in THF) was added dropwise to a solution of spirobutenolide **5** (10 mg, 0.025 mmol, 1 equiv) in dry THF (2 mL) at −78 °C. After 1 h at at −78 °C and another hour at RT the reaction was quenched with NaOH (0.1 mL, 10 % ig) and H_2O_2 (0.5 mL, 30 %). After stirring for 3 h, the aqueous layer was extracted with ethyl acetate and the combined organic layers were dried ($MgSO_4$). Chromatographic purification (PE/Et_2O 1:1) yielded a white solid (13 mg, 0.025 mmol; 100 %).

b) Pd/C (3 mg, 10 % ig) was added to a solution of spirobutenolide **5** (25 mg, 0.06 mmol) in dry THF (0.5 mL). After 2 h under a H_2 atmosphere the catalyst was removed by filtration through silica gel. Chromatographic purification (PE/Et_2O 1:1) yielded **19** (22 mg, 0.05 mmol; 87 %). For characterization see [3].

Diol 20: A mixture of $RuCl_3 \cdot x\,H_2O$ (3 mg, 0.015 mmol, 0.25 equiv) and $NaIO_4$ (19 mg, 0.11 mmol, 1.8 equiv) in water (0.2 mL) was added at 0 °C under vigorous stirring to a solution of spirobutenolide **5** (25 mg, 0.06 mmol) in ethyl acetate (0.6 mL) and acetonitrile (0.7 mL). After 50 min at 0 °C the reaction was quenched with sat. aq. $NaHSO_3$ and extracted with ethyl acetate. The combined organic layers were dried ($MgSO_4$)and purified by chromatography (Et_2O) to yield a white foam (15 mg, 0.034 mmol, 56 %). $[\alpha]_D^{20}$ = −32.5° (c = 1.12, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}$ = 3588 (w), 3496 (w), 3000 (w), 2932 (s), 2856 (m), 1768 (s), 1708 (s), 1676 (m), 1604 (m), 1511 (s), 1252 (s), 1180 (s), 1128 (m), 1096 (s), 1064 (m), 1036 cm^{-1}(m); ^1H NMR (400 MHz, $CDCl_3$): δ = 0.49 (br d, J = 13 Hz, 1H), 0.86–1.43 (m, 9H), 1.62 (m, 2H), 1.87 (dt, J = 4, 13 Hz, 1H), 3.10 (d, J = 9 Hz, 1H), 3.66 (d, J = 2 Hz, 1H), 3.81 (s, 3H), 3.97 (d, J = 9 Hz, 1H), 4.24 (d, J = 2 Hz, 1H), 6.02 (d, J = 6 Hz, 1H), 6.14 (d, J = 5.5 Hz, 1H), 6.42 (d, J = 6 Hz, 1H), 6.88 (d, J = 9 Hz, 2H), 7.30 (d, J = 9 Hz, 2H), 7.84 (d, J = 5.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.27 (q), 21.10 (t), 23.74 (t), 26.89 (t), 28.56 (t), 47.11 (d), 52.66 (d), 55.38 (q), 62.06 (s), 63.38 (s), 68.81 (s), 76.58 (d), 78.81 (d), 88.01 (s), 113.40 (d), 120.59 (d), 128.65 (s), 129.13 (d), 131.43 (d), 133.13 (d), 142.49 (d), 143.06 (d), 158.66 (s), 162.28 (d), 172.12 (s), 210.80 (s).

Monoepoxide 21: *t*BuOOH (0.08 mL, 5.5 equiv, 80 %) and 1,8-diazabicyclo[5.4.0]undec-7-en (DBU) (0.2 mL) were added to a solution of spirobutenolide **5** (40 mg, 0.1 mmol) in dry CH_2Cl_2 (3 mL). After 3 h stirring at RT the reaction was quenched with sat. aq. $NaHSO_3$ and the reaction mixture extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$), concentrated and purified by chromatography (PE/Et_2O 4:1) to yield a white foam (29 mg, 0.07 mmol; 69 %). $[\alpha]_D^{20}$ = 37.3° (c = 0.85, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}$ = 2933 (m), 2856 (w),1767 (s), 1722 (m), 1613 (w), 1516 (m), 1086 (m), 1039 (w), 920 (w), 819 (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 0.54 (br d, J = 13 Hz, 1H), 0.75 (s, 3H), 0.84–1.58 (m, 6H), 1.93 (m, 1H), 3.09 (d, J = 4 Hz, 1H), 3.12 (d, J = 10 Hz, 1H), 3.37 (d, J = 4 Hz, 1H), 3.79 (s, 3H), 4.62 (d, J = 10 Hz, 1H), 5.95 (d, J = 6 Hz, 1H), 6.18 (d, J = 6 Hz, 1H), 6.24 (d, J = 5.5 Hz, 1H), 6.85 (d, J = 9 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 7.74 (d, J = 5.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =

15.76 (q), 20.99 (t), 23.31 (t), 27.39 (t), 28.08 (t), 49.05 (d), 52.45 (d), 55.04 (d), 55.31 (q), 60.13 (d), 60.14 (s), 61.68 8s), 63.54 (s), 87.21 (s), 113.64 (d), 122.43 (d), 127.84 (d), 130.19 (s), 135.82 (d), 139.02 (d), 15832 (d), 159.24 (d), 171.06 (s), 203.23 (s); MS: *m/z* (%): 418 (5) [M^+], 338 (4), 323 (11), 267 (7), 241 (100), 240 (4), 197 (9), 165 (5), 121 (5); HRMS: *m/z*: calcd for $C_{26}H_{26}O_5$: 418.1780; found: 418.1780.

Bisepoxide 24: *t*BuOOH (0.02 mL, 5.5 equiv, 80%)and 1,8-diazabicyclo[5.4.0]undec-7-en (DBU) (0.2 mL) were added to a solution of spirobutenolide **5** (10 mg, 0.025 mmol) in dry CH_2Cl_2 (1 mL). After 15 h of stirring at RT the reaction was quenched with sat. aq. $NaHSO_3$ and the reaction mixture extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$), concentrated, purified by chromatography (PE/Et_2O 4:1) and yielded a white foam (5 mg, 0.012 mmol, 46%). $[\alpha]_D^{20} = 4.0^\circ$ ($c = 0.33$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 2927$ (vs), 2854 (m), 1790 (m), 1780 (m), 1723 (s), 1252 (s), 1181 (m), 1058 (m), 910 (w); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.59$ (br d, $J = 13$ Hz, 1H), 0.80 (s, 3H), 0.80 – 1.64 (m, 6H), 1.97 (m, 1H), 2.98 (d, $J = 10$ Hz, 1H), 3.39 (d, $J = 4$ Hz, 1H), 3.70 (d, $J = 4$ Hz; 1H), 3.79 (s, 3H), 3.95 (d, $J = 2$ Hz, 1H), 4.07 (d, $J = 10$ Hz, 1H), 4.21 (d, $J = 2$ Hz, 1H), 5.85 (d, $J = 6$ Hz, 1H), 6.19 (d, $J = 6$ Hz, 1H), 6.86 (d, $J = 9$ Hz, 2H), 7.11 (d, $J = 9$ Hz, 2H).

NOE experiment

2.98 ⇒ 0.80 (0.12%),4.07 (0.13%), 4.21 (0.19%);

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.21$ (q), 27.79 (t), 29.79 (t), 30.76 (t), 30.49 (t), 32.03 (t), 50.67 (d), 51.78 (d), 52.61 (d), 54.63 (d), 55.30 (q), 56.27 (d), 59.31 (s), 60.01 (d), 61.86 (s), 63.66 (s), 83.04 8s), 113.68 (d), 129.89 (s), 136.52 (d), 138.06 (d), 158.39 (s), 168.14 (s), 203.23 (s); MS: *m/z* (%): 434 (3) [M^+], 402 (2), 266 (3), 240 (100), 219 (82), 197 (7), 71 (9); HRMS: *m/z*: calcd for $C_{26}H_{26}O_6$: 434.1729; found: 434.1728.

Cyclopentadiene adduct 22: A solution of spirobutenolide **5** (10 mg, 0.03 mmol, 1 equiv) and cyclopentadiene (3 mg, 0.04 mmol, 1.3 equiv) in dry CH_2Cl_2 (1 mL) was introduced into a Teflon hose and submitted to 14 kbar for one week. Purification of the raw material by flash chromatography (PE/Et_2O 1:2) yielded a white solid (14 mg, 0.03 mmol; 100%). $[\alpha]_D^{20} = 38.7^\circ$ ($c = 0.99$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 2932$ (m),2864 (w), 1757 (s), 1694 (m), 1613 (w), 1516 (m), 1464 (w), 1287 (w), 1252 (m), 1182 (m), 1089 (m), 1038 (m), 928 (w), 829 cm^{-1}(m); ^{1}H NMR (400 MHz; $CDCl_3$): $\delta = 0.58$ (br d, $J = 13$ Hz, 1H), 0.66 (s, 3H), 2.00 (dt, 1H, $J = 4$, 12 Hz, 1H), 2.16 (br d, $J = 13$ Hz, 1H), 2.40 (d, $J = 10$ Hz, 1H), 2.79 (dd, $J = 3$, 11 Hz, 1H), 2.89 (br s, 1H), 2.99 (dd, $J = 3$, 11 Hz, 1H), 3.06 (br s, 1H), 3.79 (s, 3H), 5.92 (d, $J = 6$ Hz, 1H), 6.03 (dd, $J = 3$, 5 Hz, 1H), 6.22 (d, $J = 6$ Hz, 1H), 6.26 (d, $J = 6$ Hz, 1H), 6.31 (dd, $J = 3$, 5 Hz, 1H), 6.86 (d, $J = 9$ Hz, 2H), 7.19 (d, $J = 9$ Hz, 2H), 7.38 (d, $J = 6$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 15.69$ (q), 21.23 (t), 23.50 (t), 26.97 (t), 27.58 (t), 28.91 (t), 45.06 (d), 45.39 (d), 51.31 (d), 53.16 (d), 54.27 (d), 55.26 (q), 55.44 (d), 61.83 (s), 64.71 (s), 66.98 (s), 91.48 (s), 113.49 (d), 118.04 (d), 128.44 (d), 129.40 (s), 135.69 (d), 136.29 (d), 136.35 (d), 139.01(d), 158.43 (s), 161.92 (d), 171.92 (s), 211.51 (s); MS: *m/z* (%): 468 (2) [M^+], 402 (2), 280 (1), 266 (1), 240 (100), 197 (14), 149 (8); HRMS: *m/z*: calcd for $C_{31}H_{32}O_4$: 468.2301; found: 468.2303.

Methoxybutadiene adduct 23: A solution of spirobutenolide **5** (30 mg, 0.08 mmol, 1 equiv) and catalytic amounts of TEMPO and methoxybutadiene (2 mg, 0.016 mmol, 2 equiv) in dry CH_2Cl_2 (2 mL) was introduced into a Teflon hose and submitted to 14 kbar for 6 d. Purification of the raw material by flash chromatography (PE/Et_2O 1:1) yielded a white solid (38 mg, 0.08 mmol, 100%). $[\alpha]_D^{20} = 5.6^\circ$ ($c = 0.56$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} =$ 2929 (s), 2856 (w), 1759 (s), 1612 (w), 1516 (m), 1464 (m), 1253 (m), 1230 (w), 1082 (s), 909 (m), 860 cm^{-1}(s); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.45$ (br d, $J = 13$ Hz, 1H), 0.74 (s, 3H), 0.79 – 1.75 (m, 6H), 1.84 (m, 1H), 2.05 (br m, 2H), 2.41 (br s, 1H), 2.78 (br s, 1H), 2.87 (d, $J = 9$ Hz, 1H), 3.34 (s, 3H), 3.79 (s, 3H), 3.79 (m, 1H), 3.85 (m, 1H), 5.73 (m, 1H), 5.91 (m, 1H),5.98 (br d, $J = 5$ Hz, 1H), 6.16 (br d, $J = 6$ Hz, 1H), 6.30 (d, $J = 6$ Hz, 1H), 6.85 (d, $J = 9$ Hz, 2H), 7.23 (d, $J = 9$ Hz, 2H), 7.95 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 16.13$ (q), 19.30 (t), 23.89 (t), 27.02 (t), 27.34 (t), 28.44 (t), 30.43 (t), 30.69 (d), 48.67 (d), 55.30 (s), 57.24 (s), 62.15 (t), 91.18 (s), 113.18 (d), 125.62 (d), 128.95 (d), 128.97 (d), 130.26 (s), 131.01 (d), 136.23 (d), 158.14 (s), because of the width of the peaks, it was not possible to identify more signals; MS: *m/z* (%): 486 (20) [M^+], 473 (47), 472 (100), 434 (22), 410 (21), 402 (35), 358 (55), 296 (48); HRMS: *m/z*: calcd for $C_{31}H_{34}O_5$: 486.2406; found: 486.2403.

Diester 25: Malonic diethylester (0.01 mL, 0.05 mmol, 2 equiv) was added at 0 °C to a solution of NaH (3 mg, 0.05 mmol, 2 equiv) in dry THF (2 mL). After 20 min stirring at 0 °C a solution of spirobutenolide **5** (10 mg, 0.025 mmol, 1 equiv) in dry THF (1 mL) was added. The reaction was quenched after 2.5 h with sat. aq. NH_4Cl. The reaction mixture was extracted with ethyl acetate and the combined organic layers were dried ($MgSO_4$). Purification of the raw material by flash chromatography (PE/Et_2O 2:1) yielded a yellow foam (14 mg, 0.025 mmol, 100%). $[\alpha]_D^{20} = -38.2^\circ$ ($c = 1.06$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 2982$ (m), 2932 (m), 2865 (w), 1767 (s), 1730 (s), 1614 (w), 1516 (m), 1250 (m), 1181 (m), 1089 (m), 1028 (m); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.49$ (br d, $J = 13$ Hz, 1H), 0.73 (s, 3H), 0.85 – 1.61 (m, 2H), 1.23 (m, 2H), 1.28 (t, $J = 7$ Hz, 6H), 1.90 (m, 1H), 2.22 (d, $J = 12$ Hz, 1H), 2.41 (dd, $J = 9$, 19 Hz, 1H), 2.56 (m, 2H), 3.30 (d, $J = 8$ Hz, 1H), 3.45 (t, $J = 9$ Hz, 1H), 3.78 (d, 1H), 3.79 (s, 3H), 4.21 (q, $J =$ 7 Hz, 4H), 6.15 (d, $J = 6$ Hz, 1H), 6.38 (d, $J = 6$ Hz, 1H), 6.86 (d, $J = 9$ Hz, 2H), 7.23 (d, $J = 9$ Hz, 2H), 7.43 (d, $J = 6$ Hz, 1H); MS: *m/z* (%): 562 (11) [M^+], 517/17), 402 (28), 322 (48), 304 (100), 278 (62), 254 (34); HRMS: *m/z*: calcd for $C_{33}H_{38}O_8$: 562.2567; found: 562.2568.

Methanol adduct 26: NaOMe (10 mg, 0.019 mmol, 3 equiv) was added to a solution of spirobutenolide **5** (25 mg, 0.06 mmol, 1 equiv) in dry MeOH (3 mL). After stirring for 1 day at RT the reaction mixture was extracted with CH_2Cl_2. The combined organic layers were washed with sat. aq. NH_4Cl, dried ($MgSO_4$) and concentrated. Chromatographic purification (PE/Et_2O 2:1) yielded a white foam (25 mg, 0.06 mmol, 96%). $[\alpha]_D^{20} = -97.8^\circ$ ($c = 1.50$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 2984$ (w), 2932 (w), 2856 (w), 1764 (m), 1708 (w), 1600 (w), 1516 (m), 1464 (w), 1264 (s), 1096 (w); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.50$ (br d, $J = 13$ Hz, 1H), 0.78 (s, 3H), 0.79 – 1.63 (m, 5H), 1.92 (m, 1H), 2.48 (dd, $J = 4$, 19 Hz, 1H), 2.63 (dd, $J = 2$, 19 Hz, 1H), 3.20 (d, $J = 10$ Hz, 1H), 3.25 (dd, $J = 2$, 4 Hz, 1H), 3.35 (s, 3H), 3.76 (d, $J = 10$ Hz, 1H), 3.80 (s, 3H), 6.04 (d, $J = 6$ Hz, 1H), 6.10 (d, $J =$ 6 Hz, 1H), 6.13 (d, $J = 5.5$ Hz, 1H), 6.86 (d, $J = 9$ Hz, 2H), 7.20 (d, $J = 9$ Hz, 2H), 7.81 (d, $J = 5.5$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 16.23$ (q), 21.08 (t), 23.50 (t), 27.29 (t), 28.35 (t), 40.74 (t), 47.28 (d), 53.87 (d), 55.29 (q), 47.21 (q), 59.74 (s), 61.89 (s), 66.22 (s), 82.85 (d), 88.31 (s), 113.32 (d), 121.19 (d), 128.25 (d), 130.76 (s), 135.57 (d), 139.87 (d), 158.11 (s), 161.68 (d), 171.75 (s), 207.80 (s); MS: *m/z* (%): 434 (1) [M^+], 402 (3), 310 (81), 280 (5), 240 (60), 220 (16), 205 (57), 167 (10), 149 (100), 97 (15), 84 (33); HRMS: *m/z*: calcd for $C_{27}H_{30}O_5$: 434.2093; found: 434.2102.

Methyl acetoacetate adduct (wistarin precursor) 28: A solution of spirobutenolide **5** (100 mg, 0.25 mmol, 1 equiv). *N*-Methylmorpholine (0.4 mL) and methyl acetoacetate (0.1 mL, 87 mg, 0.75 mmol, 3 equiv) in dry CH_2Cl_2 (4 mL) was introduced into a Teflon hose and submitted to 14 kbar for one week. Purification of the raw material by flash chromatography (PE/Et_2O 1:1) yielded **28** (121 mg, 0.23 mmol, 93%) as a white foam. $[\alpha]_D^{20} = -101.0^\circ$ ($c = 0.92$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 2928$ (s), 2858 (w), 1785 (s), 1708 (s), 1639 (m), 1614 (w), 1516 (s), 1439 (m), 1381 (w), 1253 (s), 1183 (w), 1153 (w), 1104 (w), 1074 (m), 909 (m), 792 (s); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.46$ (br d, $J = 12$ Hz, 1H), 0.77 (s, 3H), 0.79 – 1.71 (m, 5H), 1.85 (m, 1H), 2.08 (dd, $J = 12$, 18 Hz, 1H), 2.21 (s, 3H), 2.42 (br d, $J = 12$ Hz, 1H), 2.52 (dd, $J = 7$, 17 Hz, 1H), 2.57 (d, $J = 9$ Hz, 1H), 2.70 (d, $J = 18$ Hz, 1H), 3.17 (dd, $J = 5$, 18 Hz, 1H), 3.64 (dd, $J = 7$, 12 Hz, 1H), 3.70 (s, 3H), 3.79 (d, $J = 8$ Hz, 1H), 3.80 (s, 3H), 4.70 (d, $J = 5$ Hz, 1H), 6.30 (d, $J = 6$ Hz, 1H), 6.42 (d, $J = 6$ Hz, 1H), 6.87 (d, $J = 9$ Hz, 2H), 7.23 (d, $J = 9$ Hz, 2H).

NOE experiment:

3.64 ⇒ 2.52 (7.8%), 6.30 (2.2%), 6.42 (13.5%);

4.70 ⇒ 2.08 (3.0%), 2.57 (5.1%), 3.17 (2.3%);

^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 16.05$ (q), 20.29 (q), 20.90 (t), 23.85 (t), 27.42 (t), 28.23 (t), 30.43 (s), 31.84 (d), 37.37 (t), 43.79 (t), 50.35 (d), 51.69 (q), 54.70 (d), 55.30 (q), 62.71 (s), 63.21 (s), 69.83 (s), 77.98 (d), 87.91 (s), 104.97 (s), 113.35 (d), 128.70 (d), 129.08 (d), 137.20 (d), 139.49 (d), 158.41 (s), 164.04 (s), 167.03 (s), 173.49 (s), 208.19 (s); MS: *m/z* (%): 519 ($M^+ + 1$, 6), 473 (5), 391 (12), 307 (37), 240 (43), 154 (100); HRMS: *m/z*: calcd for $C_{31}H_{34}O_7$: 518.2306; found: 518.2308.

Retro-Diels – Alder product 30: Methyl acetoacetate adduct **28** (45 mg, 0.09 mmol) was sublimed at 2×10^{-2} mbar into a pyrolysis tube heated to 300 °C. Diene **1** was trapped on a cooling finger. Purification of the raw material by flash chromatography (PE/Et_2O 1:1) yielded a white foam (25 mg, 0.09 mmol, 100%). $[\alpha]_D^{20} = -198.6^\circ$ ($c = 1.03$, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu} = 2927$ (m), 2855 (w), 1798 (s), 1695 (s), 1636 (m), 1437 (w), 1384 (m), 1285 (w), 1198 (m), 1107 (s), 1042 (m), 860 (w); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.25$ (m, 1H), 2.31 (s + dd, $J = 13.5/17$ Hz, 3H), 2.63 (d, $J =$ 18 Hz, 1H), 2.90 (dd, $J = 4/17$ Hz, 1H), 3.02 (dd, $J = 4.5/18$ Hz, 1H), 3.68

(dd, $J = 4.5/13.5$ Hz, 1H), 3.73 (s, 3H), 4.84 (d, $J = 4.5$ Hz, 1H), 6.22 (d, $J =$ 10 Hz, 1H), 6.70 (d, $J = 10$ Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 20.18$ (q), 34.44 (d), 38.33 (t), 41.70 (t), 51.71 (q), 75.23 (d), 81.88 (s), 101.42 (s), 132.71 (d), 146.38 (d), 163.67 (s), 166.69 (s), 172.75 (s), 195.11 (s); MS: *m*/*z* (%): 278 (2) [M^+], 240 (2), 219 (29), 176 (3), 149 (100), 131 (10), 109 (50), 91 (12), 72 (11); HRMS: *m*/*z*: calcd for $C_{14}H_{14}O_6$: 278.0790; found: 278.0793.

Acetone dicarboxylate adduct 32: A solution of spirobutenolide **5** (100 mg, 0.25 mmol, 1 equiv). *N*-Methylmorpholine (0.5 mL) and acetone dicarboxylate (0.044 mL, 0.3 mmol, 1.2 equiv) in dry CH_2Cl_2 (3 mL) was introduced into a Teflon hose and submitted to 14 kbar for one week. Purification of the raw material by flash chromatography (PE/Et_2O 1:1) yielded a white foam (95 mg, 0.17 mmol, 66%). $[\alpha]_D^{20} = -82.2^\circ$ ($c = 4.19$, $CHCl_3$); IR (Golden Gate): $\tilde{\nu} = 2923$ (w), 2852 8w), 1773 (m), 1741 (m), 1704 (m), 1663 (m), 1616 (m), 1516 (m), 1440 (m), 1249 (s), 1222 (s), 1180 (s), 1160 (m), 823 (m); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.43$ (br d, $J = 13$ Hz, 1H), 0.74 (s, 3H), 1.11–1.45 (m, 5H), 1.37 (m, 1H), 1.62 (m, 1H), 1.89 (m, 1H), 2.05 (dd, $J = 6$, 19 Hz, 2H), 2.40 (dd, $J = 6$, 19 Hz, 1H), 2.50 (dd, $J = 8$, 18 Hz, 1H), 2.75 (d, $J = 9$ Hz, 1H), 3.08 (dd, $J = 9$, 18 Hz, 1H), 3.36 (m, 1H), 3.69 (d, $J = 9$ Hz, 1H), 3.72 (s, 3H), 3.79 (s, 3H), 3.84 (s, 3H), 6.07 (d, $J = 6$ Hz, 1H), 6.23 (d, $J = 6$ Hz, 1H), 6.86 (d, $J = 9$ Hz, 2H), 7.21 (d, $J =$ 9 Hz, 2H), 12.37 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 16.20$ (q), 21.03 (t), 23.73 (t), 27.66 (t), 27.83 (t), 28.47 (t), 30.15 (d), 35.95 (t), 37.32 (d), 39.86 (d), 49.51 (d), 52.45 (q), 52.88 (q), 53.73 (d), 55.23 (q), 84.40 (s), 98.99 (s), 113.12 (d), 128.52 (d), 130.02 (s), 135.20 (d), 140.54 (d), 158.38 (s), 166.27 (s), 169.55 (s), 171.96 (s), 173.77 (s), 207.74 (s), because of the width of the peaks, it was not possible to identify more; MS (FAB): *m*/*z* (%): 577 (100) [M^++H], 576 (50), 566 (38), 550 (42), 535 (26).

Retro Diels–Alder product 33: Acetone dicarboxylat adduct **32** (38 mg, 0.066 mmol) was sublimed at 2×10^{-2} mbar into a pyrolysis tube heated to 300 °C. The diene **1** was trapped on a cooling finger. Purification of the raw material by flash chromatography (PE/Et_2O 2:1) yielded a white foam (18 mg, 0.05 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.46$ (dd, $J =$ 11, 17 Hz, 1H), 2.58 (dd, $J = 5$, 18 Hz, 1H), 2.77 (dd, $J = 5$, 17 Hz, 1H), 3.10 (dd, $J = 9$, 18 Hz, 1H), 3.19 (d, $J = 5$ Hz, 1H), 3.32 (dt, $J = 11$, 5 Hz, 1H), 3.43 (dd, $J = 5$, 9 Hz, 1H), 3.76 (s, 3H), 3.85 (s, 3H), 6.09 (d, $J = 10$ Hz, 1H), 6.80 (d, $J = 10$ Hz, 1H), 12.34 (s, 1H).

Spirobutenolide 3: TFA (0.3 mL) was added at 0 °C to a solution of spirobutenolide **5** (40 mg, 0.1 mmol) in dry CH_2Cl_2 (8 mL). The reaction was quenched with sat. aq. Na_2CO_3 after 15 min stirring at 0 °C and 30 min at RT. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated. Chromatographic purification (PE/Et_2O 1:1) yielded a yellow solid (16 mg, 0.099 mmol, 100%).

Spiroisoxazoline 35: TFA (0.2 mL) was added at 0 °C to a solution of spiroisoxazoline adducst **34** (20 mg, 0.05 mmol) in dry CH_2Cl_2 (3 mL). The reaction was quenched with sat. aq. Na_2CO_3 after 15 min stirring at 0 °C and 30 min at RT. The aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated. Chromatographic purification (PE/Et_2O 1:1) yielded a cream-coloured solid (9 mg, 0.05 mmol, 100%). For characterization see [30].

Retro Diels–Alder product 36: Methoxybutadiene adduct **23** (31 mg, 0.06 mmol) was sublimed at 2×10^{-2} mbar into a pyrolysis tube heated to 300 °C. The diene **1** was trapped on a cooling finger. Purification of the raw material by flash chromatography (PE/Et_2O 4:1) yielded **36** as a light

Table 1. Crystal data for **16**, **22**, **36**.[a]

	16[b]	**22**[c]	**36**[d]
empirical formula	$C_{27}H_{28}O_3 \times C_6H_{12}$	$C_{31}H_{32}O_4$	$C_{14}H_{14}O_4$
F_w	484.6	468.59	246.26
crystal system	orthorhombic	orthorhombic	orthorhombic
space group	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)
a [Å]	6.486(1)	10.074(1)	7.760(1)
b [Å]	20.332(2)	11.089(1)	12.210(2)
c [Å]	21.374(2)	21.698(3)	13.028(2)
α, β, γ [°]	90, 90, 90	90, 90, 90	90, 90, 90
V [Å^3]	2818.7(6)	2423.9(5)	1234.4(3)
Z	4	4	4
ρ_{obs}, ρ_{calcd} [g cm^{-3}]	0.000, 1.142	0.000, 1.284	0.000, 1.325
$F(000)$ [electrons]	1048	1000	520
μ ($Mo_{K\alpha}$) [cm^{-1}]	0.7	0.8	1.0
crystal	colorless needle	colorless plate	colorless plate
size [mm]	$2.6 \times 0.06 \times 0.07$	$0.48 \times 0.59 \times 0.06$	$0.56 \times 0.06 \times 0.37$
T [K]	300	173	300
$2\theta_{min,max}$ [°]	3.8, 41.7	3.8, 48.1	4.6, 52.2
scan type/exposures	150	150	222
$\Delta\phi$ [°]	1.2	1.1	1.5
data set *hkl* limits	−6:6; −20:20; −21:20	−11:11; −10:12; −24:24	−9:9; −15:15; −16:16
total data	10914	12555	16444
unique data	2868	3788	2427 (Friedel pairs kept separate)
$R(I)$	0.057	0.185	0.070
completeness of data set but [%]	96.8	100	100
absorption correction	none	none	none
extinction correction	none	none	none
observed data [$I > 2.0\sigma(I)$]	1890	1039	1999
N_{ref}, N_{par}	2868, 319	3877, 316	2427, 163
$R1, wR2, S$	0.0502, 0.1052, 1.17	0.0407, 0.0806, 0.46	0.0300, 0.0417, 0.88
min/max resd. dens. [e Å^{-3}]	−0.11, 0.20	−0.14, 0.15	−0.15, 0.11

[a] λ $Mo_{K\alpha} = 0.71073$ Å (fine-focus sealed tube, graphite monochromator); diffractometer: Stoe IPDS (imaging plate), for technical details see refs. [31] and [32]; structure solution: Direct methods, program used: SHELXS-86;[33] program used: Stoe IPDS software and SHELXL;[34] refinement, program used: SHELXL-93;[34] Programs used for plots = PLATON.[35] Program used for checks and tables = PLATON (**16**, **36**)[35] and MOPLO (**22**);[36] hydrogen atoms in geometrically calculated positions. [b] R1 is based on F of 1890 reflections with $F_o > 4\sigma(F_o)$. *wR*2 is based on F^2 of all 2868 unique reflections. A disordered solvent molecule (C_6H_{12}) was not resolved. [c] *R*1 is based on *F* of 1039 reflections with $F_o > 4\sigma(F_o)$. *wR*2 is based on F^2 of all 3788 unique reflections. $\omega = 1/(\sigma^2(F_o^2) + (0.03*P)2)$, where $P = (\max(F_o^{2,0}) + 2F_c^2)/3$. [d] *R*1 is based on *F* of 1199 reflections with $F_o > 4\sigma(F_o)$. *wR*2 is based on F^2 of all 2427 unique reflections. $\omega = 1/\sigma^2 F_o^2$.

cream-coloured solid (6 mg, 0.024 mmol, 38 %). $[\alpha]_D^{20} = 88.6^\circ$ ($c = 0.54$, $CHCl_3$); m.p. 168 °C; IR ($CHCl_3$): $\tilde{\nu} = 2925$ (w), 1754 (s), 1678 (m), 1392 (w), 1267 (m), 1189 (m), 1069 (s), 1013 (w), 928 (m), 817 (m), 725 (m); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.90$ (dd, $J = 5.3$, 19.6 Hz, 1H), 2.03 (ddd, $J = 2$, 7, 19.4 Hz, 1H), 3.00 (t, $J = 6$ Hz, 1H), 3.08 (t, $J = 7$ Hz, 1H), 3.31 (s, 3H), 3.99 (br t, $J = 4$ Hz, 1H), 5.78 (m, 1H), 6.01 (br d, $J = 10$ Hz, 1H), 6.08 (d, $J = 6$ Hz, 1H), 6.20 (d, $J = 10$ Hz, 1H), 6.39 (d, $J = 10$ Hz, 1H), 8.04 (d, $J = 6$ Hz, 1H).

Spirobutenolide 38: Tetra-*n*-butylammoniumfluoride (0.4 mL, 1.25 M) was added dropwise at 0 °C to a solution of retro-Diels–Alder-product **30** (17 mg, 0.06 mmol) in dry CH_2Cl_2 (2 mL). The reaction was quenched after 5 min stirring at 0 °C with sat. aq. K_2CO_3. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and concentrated. Chromatographic purification (PE/Et_2O 1:1) yielded a yellow oil (17 mg, 0.06 mmol, 100 %). $[\alpha]_D^{20} = -4.2^\circ$ ($c = 0.50$, $CHCl_3$); IR (Golden Gate): $\tilde{\nu} = 2952$ (w), 2253 (w), 1772 (m), 1713 (s), 1617 (m), 1435 (w), 1327 (m), 1218 (m), 1118 (w), 1075 (s), 1020 (w), 911 (m), 818 (m), 730 (m); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.29$ (s, 3H), 2.71 (t, $J = 19$ Hz, 2H), 2.98 (dd, $J = 4$, 16 Hz, 1H), 3.07 (dd, $J = 4$, 16 Hz, 1H), 3.14 (m, 1H), 3.71 (s, 3H), 4.40 (m, 1H), 6.27 (d, $J = 6$ Hz, 1H), 7.62 (d, $J = 6$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.68$ (q), 37.01 (d), 43.16 (t), 45.34 (t), 51.84 (q), 76.60 (d), 82.79 (s), 102.88 (s), 122.55 (d), 156.55 (d), 163.35 (s), 166.08 (s), 170.48 (s), 205.69 (s); MS: *m*/*z* (%): 279 (67) [M^++H], 246 (47), 192 (22), 169 (68), 137 (100); HRMS: *m*/*z*: calcd for $C_{14}H_{14}O_6$: 278.0790; found: 278.0788.

X-ray data are collected in Table 1.

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