Enantiopure Polycycles by Sequential Cycloadditions

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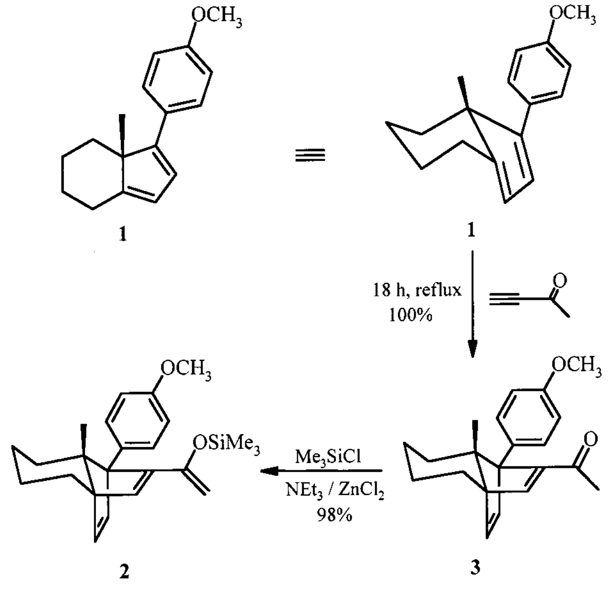
Keywords: Asymmetric synthesis / Cycloadditions / High-pressure chemistry / Polycycles / Retro reactions

The enolsilyl ether **2**, generated from butynone adduct **3**, which is easily available from the enantiomerically pure cyclopentadiene **1**, proved to be a general building block for polycyclic anellation products to cyclohexenone. After proper adjustment of functional groups in the cycloadducts by means of high pressure Diels–Alder cycloadditions, the thermal retro-process provided routes to various enantiopure alicyclic and heterocyclic target compounds in high yields.

Introduction

While selectivity studies with the chiral cyclopentadiene **1** had opened up highly efficient options for clearcut kinetic resolutions[1,2] and for the differentiation of enantiotopic double bonds in high yield,[3,4] subsequent retro-reactions producing the enantiopure target compounds proved to be quite structure-dependent.[5] Individual optimisation studies for this step were generally called for if high yields of the retro-product and good recovery of diene **1** were to be achieved.[6]

For this reason we became interested in an intermediate 4π-system **2** (Scheme 1), which would enable polycyclic compounds to be ”grown” on the butadiene moiety in subsequent cycloadditions and which would then permit reconstruction of comparable structural units in the final retro-step. Once optimized, this reaction should work reliably for a whole series of compounds, thus generating polycyclic libraries with these functional groups in common.



Scheme 1

Results and Discussion

It was therefore with quite some excitement that we observed highly diastereoselective and regioselective α-*exo* additions (see **5** and **11**), kinetic resolutions (see **9**) and differentiations of enantiotopic double bonds (see **7**) in the Diels−Alder chemistry of the electron rich diene **2**, which is easily generated from the butynone adduct **3**.

Out of quite a number of cycloadditions performed with diene **2**, we focus here on the Diels−Alder cycloadditions of dienophiles **4**, **6**, **8**, and **10**, all of which provided high yields of the corresponding cycloadducts **5**, **7**, **9**, and **11** under high pressure conditions (12−14 kbar). Additionally, they all underwent highly selective proton-catalysed enol ether hydrolysis to yield the parent ketones.

In the case of the kinetic resolution of keto ester **8**, it was possible not only to readily reisolate the pure unreacted enantiomer **12** from the reaction mixture, with an *ee* higher than 98%, but also to generate the enantiopure cyclohexenone derivative **13** from cycloadduct **9**, by means of a silyl ether hydrolysis followed by a thermal retro-reaction.

Although the α-*exo* addition configurations portrayed in Scheme 2 for all cycloadducts are fully in line with earlier observations in the field of bicycloheptanes of this type,[7] they were also explicitly proved by NMR experiments in all cases.

This was of particular importance for the quinone-monoketal adduct **11**, since this compound is clearly set up for further ring-anellating cycloadditions with electron-rich 4π-systems, thus highlighting the possibility of making polycyclic systems “grow” on the chiral template in a sterically highly predictable manner (Scheme 3).

As a simple example we picked 1-methoxybutadiene, and were pleased to isolate a quantitative yield of the single diastereomer **15**.

While the first addition is in all cases reliably directed in an α-*exo* fashion by the configuration of diene **2**, this se-

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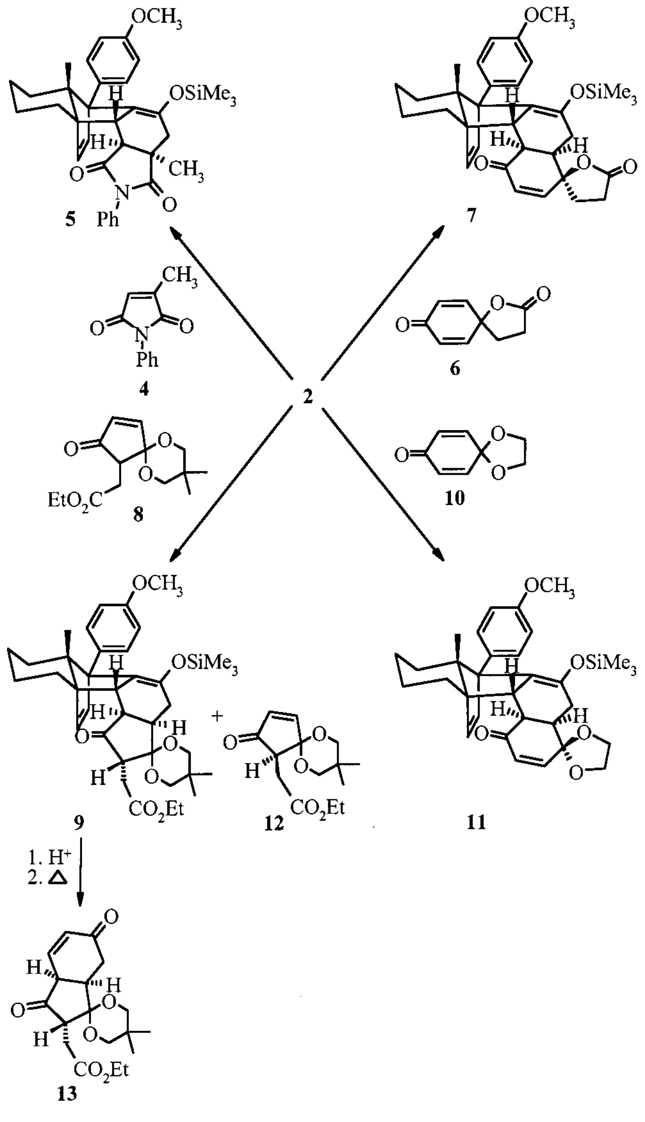
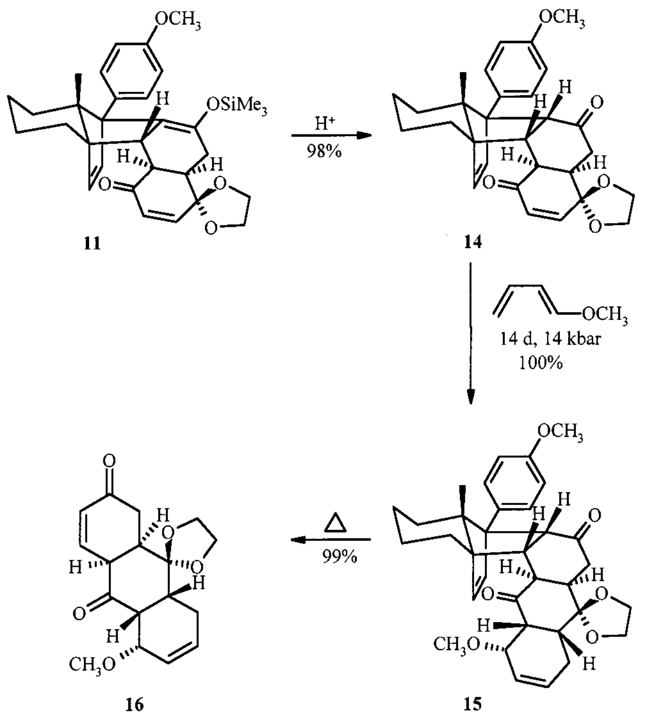
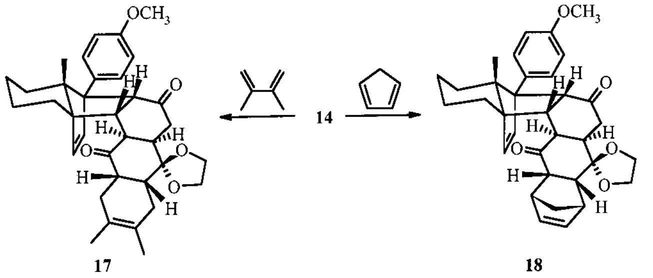


Scheme 2



Scheme 3



Scheme 4

cond one – since it takes place on a *cis*-decalone system – is expected to operate in an α-*endo* mode, which is perfectly borne out by the NMR data of cycloadduct **15**.

This compound, in the same way as already described for **9**, underwent the retro-Diels–Alder reaction as predicted, under fairly comparable conditions, to provide the cyclohexenone-anellation product **16**. While this outcome was left unoptimized in the case of **13**, the nearly quantitative yield (99%) attainable with the polyfunctionalized tricyclic compound **15** is certainly worth mentioning.

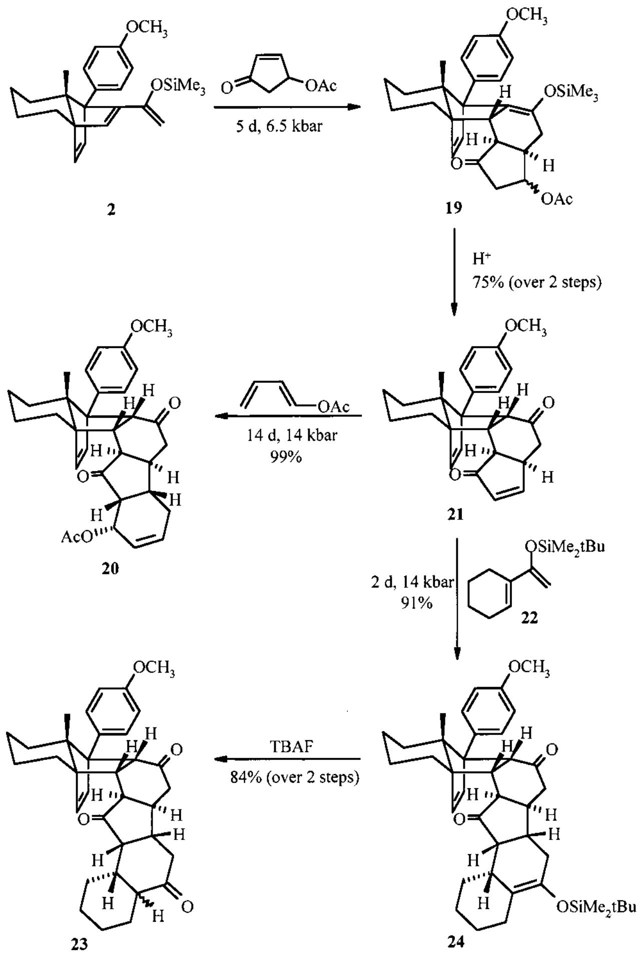
Although the outcome of the retro-process is highly satisfactory with this diketone, other cycloadducts generated from **14** clearly suffered from the fact that their retro-products represent vinylogous 1,3-dicarbonyl systems, which show a high tendency towards double bond shifts and even aromatization, owing to enolization processes.

Typical examples are the adducts with dimethylbutadiene (see **17**, Scheme 4) and with cyclopentadiene (see **18**), which both produced partially aromatic compounds (NMR evidence) on heating.

Another typical case of double bond shift was encountered with the cyclopentenone intermediate **21**. Although this material was obtained easily from the cycloaddition between 4-acetoxycyclopentenone-1 and butadiene **2**, followed by enol ether hydrolysis accompanied by a very high-yielding elimination process, the polycyclic systems produced in remarkably high yields from **21** (see Scheme 5), proved to be hard to handle.

Compound **20**, although produced in 99% yield from acetoxybutadiene and providing nice crystals for X-ray-structure determination,[8] thus once more proving the α-*endo* addition process, created difficulties in the thermal retro-process. Similarly, the tetracyclic triketone **23**, obtained in excellent yield from dienophile **22** by way of enol silyl ether **24**, gives rise to a complex mixture of retro-products.

Finally, a very similar outcome was obtained by use of β-indolylacrylate as the 4π-system (Scheme 6). This time, a high-pressure cycloaddition-isomerization sequence resulted in a 72% yield of the α-*endo* addition product **25** (X-ray data).[9] The retro-process, however, although it took place even at 200 °C, unfortunately provided a mixture of

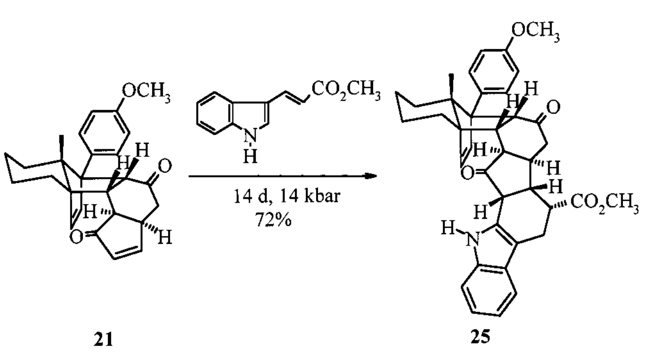


Scheme 5

retro-products containing the cyclohexenone only in a meagre 20% yield. All the rest of the retro-material proved to be the outcome of ill-defined enolisation and aromatization processes.

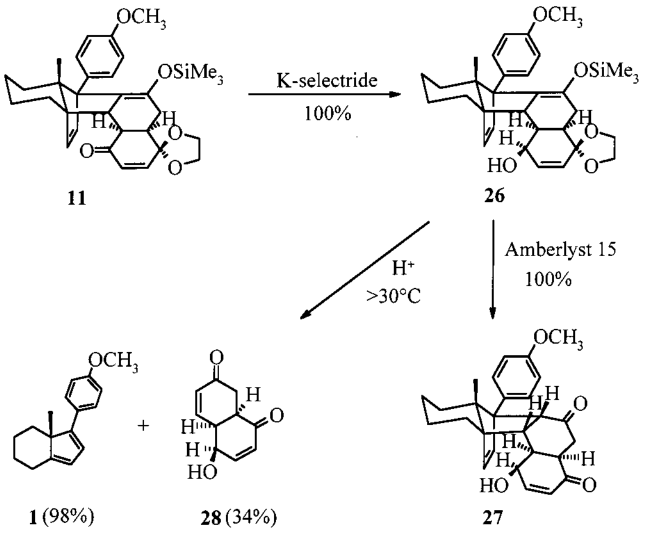
While these eclectic results certainly prove the high potential of the cycloadditions involved in the preparation of a wide range of polycyclic systems, they also point to the retro-reaction as the bottleneck of the project.

As all the information thus far collected left no doubt that the unsaturated dicarbonyl system (vinylogous 1,3-dicarbonyl) was the culprit, the simplest solution seemed to be a selective reduction of the keto group in cycloadduct **11** to abolish this functional group pattern.



Scheme 6

This indeed worked nicely with K-Selectride, which provided a quantitative yield of allylic alcohol **26**, and when this material was treated with Amberlyst 15[10] at room temperature it gave rise to the sterically well defined unsaturated ketone **27** in quantitative yield (Scheme 7).



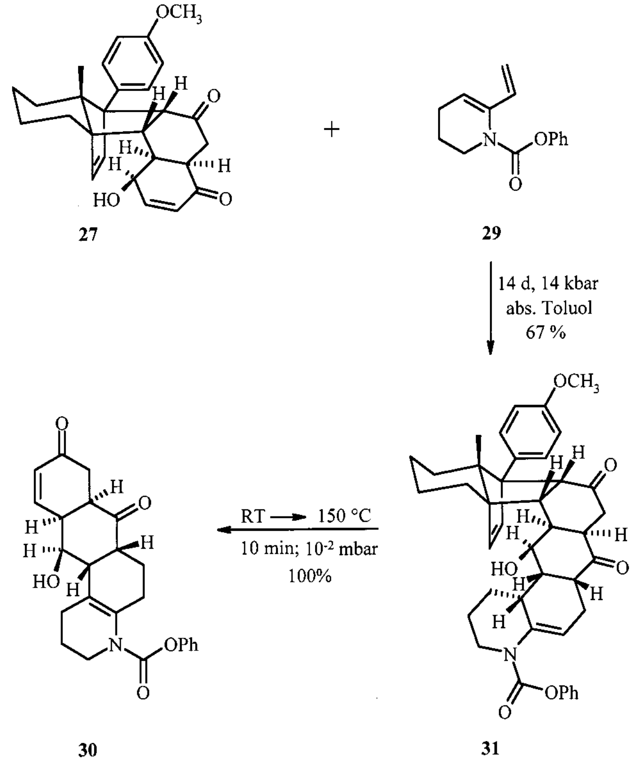
Scheme 7

Of particular interest in this case, however, was the observation of an unusually easy retro-reaction. The stable unsaturated ketone **28** was generated as soon as the reaction temperature of the subsequent silyl ether hydrolysis rose above 30 °C.

This was a very encouraging result, which called for the preparation of a more complicated ring-system starting from the unsaturated ketone **27**. To benefit from the reactivity of an electron-rich 4π-system additionally offering options for heterocyclic compounds, we selected butadiene **29**, which had been prepared[11,12] and investigated[11] by Nicolaou in connection with lactam-derived aminal-phosphates.[11]

The cycloaddition of this diene took place at 14 kbar, to provide adduct **31** as one single enantiopure reaction product (Scheme 8). This was quantitatively cleaved into diene **1** and the heterocyclic diketone **30**, even at 150 °C, without any enolization, elimination, or aromatization.

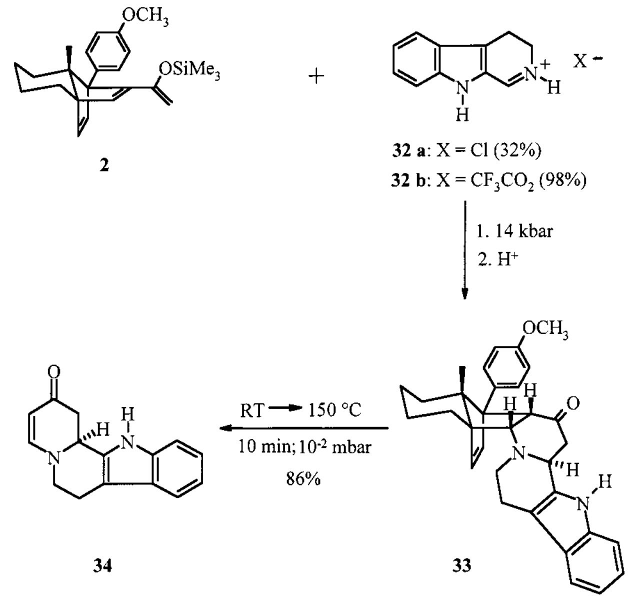
Although this convincingly establishes the advantages offered by Selectride reduction of the dienophile, one should in this particular case not overlook the ready isomerization of the enamine double bond from the trisubstituted to the thermodynamically more stable tetrasubstituted position under retro-reaction conditions. This shift can in some cases take place during the cycloaddition process itself, but was also observed under the conditions of workup or of purification of cycloaddition products. Traces of hydrochloric acid in chloroform or treatment with silica can easily trigger this reaction and, as it seems to be far more general with our system than with that documented in Nicolaou's seminal paper on these very useful dienes, we refer readers



Scheme 8

to the dissertation by one of us (M. W.)[9] for a detailed report on the behaviour of cycloadducts of this type.

Finally, to complete the list of dienophiles in the transformations with diene **2**, we chose salts of dihydro-norharmane **32**[13,14] as examples of a heterodienophile (Scheme 9).



Scheme 9

This imine, however, was not picked mainly for mechanistic reasons. We were of course also well aware of the fact that with this 2π-system our reaction sequence should provide the synthetically highly flexible indoloquinolizinone building block **34**, which has a high potential for enantioselective alkaloid synthesis.[15,16]

A close investigation of this cycloaddition proved the non-protonated imine itself to be a comparatively poor dienophile, providing only quite low yields (≈ 15%) of cycloadduct **33**. When salts were employed, however, the yield rose substantially and by far the best results were obtained with the corresponding trifluoroacetate **32b** in the presence of 10% α,α′-bis-*tert*-butylpyridine as a proton scavenger. Subsequent treatment with camphorsulfonic acid provided the sterically pure α-*exo* adduct **33** in an overall yield of 98%. In the presence of other, less hindered, bases this stereoisomer was generally accompanied by the corresponding α-*endo* product (β H_A).

With this simple and high-yielding preparation of the enantiopure cycloadduct **33** in hand, the thermal retro-process was studied. We were very pleased to note the clean (86%) formation of the versatile indoloquinolizinone **34** even at 150 °C, with an *ee* value of > 98%.

Conclusions

In conclusion, we have demonstrated that starting with the electron-rich and very efficiently directing enantiopure diene **2** one can make polycyclic systems "grow" quite easily on this chiral template.

It was also shown that the quinone monoketal adduct **7**, despite being a very attractive dienophile, has to be selectively reduced for further anellations if clean and reliable retro-reactions are to be secured.

A very simple synthesis of the enantiopure general alkaloid building block **34** illustrates the preparative value of diene **2**.

Experimental Section

General Remarks: Melting points were determined on a Gallenkamp apparatus and are uncorrected. − Optical rotations were measured on a Perkin−Elmer 241 or 341. − IR spectra were recorded in $CHCl_3$ or in KBr with a Bruker IFS 25 spectrometer or with a Bruker Vector 22 spectrometer using an attenuated total reflection (ATR) method. − UV spectra were measured on a Beckmann 3600 spectrometer. − NMR spectra were recorded on a Bruker WP 200 (200 MHz) or AM 400 (400 MHz) spectrometer; δ_H values are given relative to TMS = 0; δ_C values are given relative to $CDCl_3$ (δ = 77.05); multiplicities of ^{13}C NMR were determined by DEPT (90°/135°) or by APT. − MS assays were obtained using a Finnigan MAT 312 (MS) or a VG Autospec (MS-FAB and HRMS) with an ionization potential of 70 eV. − Elemental analysis were carried out on a Heraeus CHN rapid analyser. − For flash chromatography, Baker silica gel (30−60 μm) was used. TLC analysis were carried out on "DC aluminium foils", coated with $^{60}F_{254}$ silica gel (E. Merck); the spots were detected by UV (254 nm) and also with the aid of a dipping bath of cerium(IV) sulfate/phosphomolybdic acid reagent. − Organic solvents were purified and dried by standard procedures. Air- and moisture-sensitive reactions were performed in flame-dried reaction vessels under inert atmospheres of argon or nitrogen. High-pressure reactions were carried out in a Nova Swiss apparatus (max. 6.5 kbar) or in a Hofer apparatus (max. 14 kbar). For retro-Diels−Alder reactions, a special flash-vacuum pyrolysis apparatus was used. Cyclopentadiene **1** was prepared according to the procedure described by Winterfeldt et al.[17]

Siloxydiene 2: $ZnCl_2$ (100 mg, 747 µmol) was flame-dried under vacuum. Afterwards, NEt_3 (2 mL) was added under nitrogen atmosphere. After the suspension had been stirred at room temperature for 30 min, a solution of butynone adduct **3** (235 mg, 760 µmol) in dry toluene (2 mL) was added. After 10 min, dry TMS-Cl (116 µL, 916 µmol) was added. The solution was stirred for 1 h. Purification by fast flash chromatography on Alox N (III) afforded siloxydiene **2** (283 mg, 98%) as a bright yellow oil. $[\alpha]_D^{20} = -12.7$ ($c = 0.350$, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3055 (m), 2927 (s), 2857 (s), 1670 (m), 1614 (m), 1515 (s), 1463 (m), 1443 (m), 1250 (s), 1179 (s), 848 (s) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): $\delta = -0.19$ (m, 9 H), 0.55 (d_{br}, J = 13.0 Hz, 1 H), 1.05 (s, 3 H), 1.15−1.36 (m, 3 H), 1.58−1.76 (m, 2 H), 2.05−2.24 (m, 2 H), 3.80 (s, 3 H), 3.87 (d, J = 0.5 Hz, 1 H), 4.12 (d, J = 0.5 Hz, 1 H), 6.59 (d, J = 5.0 Hz, 1 H), 6.85 (m, 2 H), 6.97 (d, J = 5.0 Hz, 1 H), 7.17 (m, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.3 (CH_3), 17.5 (CH_3), 21.4 (CH_2), 23.8 (CH_2), 24.2 (CH_2), 30.0 (CH_2), 55.5 (CH_3), 65.9 (C), 74.7 (C), 82.5 (C), 93.8 (CH_2), 113.0 (CH), 129.8 (C), 130.1 (CH), 142.2 (CH), 144.7 (CH), 148.0 (CH), 154.2 (C), 157.0 (C), 158.4 (C). − MS (60 °C): m/z (%) = 380 (35) [M^+], 365 (16), 308 (4), 297 (12), 240 (22), 73 (78). − HRMS: $C_{24}H_{32}O_2Si$ (380.2): calcd. 380.2172; found 380.2171.

Butynone Adduct 3: A solution of cyclopentadiene **1** (3 g, 12.5 mmol) and butynone (4.2 g, 62 mmol) in dry dichloromethane (15 mL) was refluxed for 18 h under a nitrogen atmosphere with exclusion of light. Toluene (15 mL) was then added at room temperature and the mixture was concentrated. Purification of the raw material by flash chromatography (Et_2O/PE, 1:5) afforded **3** (3.85 g, 100%) as a white solid. M.p.: 73 °C. − $[\alpha]_D^{20} = -294$ (c = 1.000, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 2932 (m), 2856 (w), 1660 (s), 1612 (m), 1512 (m), 1448 (w), 1248 (w), 1180 (m), 832 (m) cm^{-1}. − UV (MeOH): λ_{max} = 206 (s), 221 (s), 260−270 (sh) nm. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.70 (d_{br}, J = 13.0 Hz, 1 H), 1.00 (s, 3 H), 1.22−1.51 (m, 3 H), 1.61−1.78 (m, 2 H), 2.03−2.30 (m, 2 H), 2.22 (s, 3 H), 3.78 (s, 3 H), 6.58 (d, J = 5.5 Hz, 1 H), 6.83 (m, 2 H), 6.97 (d, J = 5.5 Hz, 1 H), 6.98 (m, 2 H), 7.36 (s, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.8 (CH_3), 20.7 (CH_2), 23.2 (CH_2), 23.6 (CH_2), 27.3 (CH_3), 29.3 (CH_2), 55.1 (CH_3), 67.1 (C), 74.7 (C), 84.0 (C), 113.0 (CH), 128.5 (C), 128.9 (CH), 143.4 (CH), 146.8 (CH), 158.0 (C), 159.1 (CH), 160.2 (C), 196.1 (C=O). − MS (RT): m/z (%) = 308 (9) [M^+], 293 (27), 277 (11), 265 (30), 251 (26), 240 (12), 223 (21), 178 (21), 165 (27), 115 (25). − HRMS: $C_{21}H_{24}O_2$ (308.2): calcd. 308.1776; found 308.1771. − $C_{21}H_{24}O_2$ (308.2): calcd. C 81.77, H 7.85; found C 81.66, H 7.77.

Methyl-*N*-phenylmaleinimide Adduct 5: A solution of siloxydiene **2** (150 mg, 0.39 mmol) and methyl-*N*-phenylmaleinimide **4** (74 mg, 0.39 mmol) in dry THF (1 mL) was introduced into a Teflon vessel and subjected to 6.5 kbar in a high pressure autoclave for 7 days. Purification of the raw material by flash chromatography (Et_2O/PE, 3:1) afforded **5** (188 mg, 85%) as a colourless oil. − IR ($CHCl_3$): $\tilde{\nu}$ = 2932 (w), 1712 (s), 1512 (m), 1384 (m), 1252 (s), 1032 (w), 856 (m) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): $\delta = -0.09$ (m, 9 H), 0.48 (d_{br}, J = 13.0 Hz, 1 H), 0.85 (s, 3 H), 1.23 (s, 3 H), 1.26−1.57 (m, 4 H), 1.61−1.90 (m, 2 H), 2.10−2.20 (m, 2 H), 2.29 (d_{br}, J = 13.0 Hz, 1 H), 2.47−2.60 (m, 2 H), 3.81 (s, 3 H), 6.01 (d, J = 6.0 Hz, 1 H), 6.33 (d, J = 6.0 Hz, 1 H), 6.84 (d, J = 9.0 Hz, 2 H), 7.22 (d, J = 9.0 Hz, 2 H), 7.28−7.52 (m, 5 H). − MS (140 °C): m/z (%) = 567 (96) [M^+], 552 (77), 510 (15), 484 (17), 472 (56), 458 (13), 380 (15), 365 (12), 296 (12), 240 (16), 188 (42), 165 (23), 121 (50), 95 (51), 83 (57). − HRMS: $C_{35}H_{41}NO_4Si$ (567.3): calcd. 567.280488; found 567.278870.

Spirolactone Adduct 7: A solution of siloxydiene **2** (100 mg, 263 µmol) and spirolactone **6** (43 mg, 263 µmol) in dry dichloromethane (1 mL) was introduced into a Teflon vessel and subjected to 6.5 kbar in a high pressure autoclave for 14 days. Purification of the raw material by flash chromatography (Et_2O/PE, 1:1) afforded **7** (90 mg, 63%) as a white solid. $[\alpha]_D^{20} = +28.1$ (c = 0.100, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 2928 (m), 2859 (m), 1781 (vs), 1515 (s), 1463 (m), 1250 (s), 865 (m), 845 (m) cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): $\delta = -0.20$ (s, 9 H), 0.41 (d_{br}, J = 13.0 Hz, 1 H), 0.81 (s, 3 H), 1.04−1.41 (m, 4 H), 1.55 (m, 1 H), 1.74 (d_{br}, J =13 Hz, 2 H), 1.90 (ddd, J = 1/5/11 Hz, 2 H), 2.17 (m, 2 H), 2.32−2.43 (m, 1 H), 2.52 (quin, J = 4.0 Hz, 1 H), 2.72 (m, 2 H), 2.82 (d, J = 10.0 Hz, 1 H), 3.78 (s, 3 H), 5.91 (d, J = 5.5 Hz, 1 H), 6.09 (d, J = 1/10 Hz, 1 H), 6.18 (d, J = 5.5 Hz, 1 H), 6.65 (d, J = 10.0 Hz, 1 H), 6.80 (m, 2 H), 7.12−7.27 (s_{br}, 2 H). − MS (150 °C): m/z (%) = 544 (41) [M^+], 529 (4), 379 (7), 240 (100). − HRMS: $C_{33}H_{40}O_5Si$ (544.3): calcd. 544.2645; found 544.2651. − $C_{33}H_{40}O_5Si$ (544.3): calcd. C 72.76, H 7.41; found C 72.76, H 7.40.

Keto Ester Adduct 9: A solution of siloxydiene **2** (100 mg, 263 µmol) and keto ester **8** (70 mg, 263 µmol) in dry dichloromethane (1 mL) was introduced into a Teflon vessel and subjected to 6.5 kbar in a high pressure autoclave for 5 days. Purification of the raw material by flash chromatography (Et_2O/PE, 1:30) afforded **9** (85 mg, 50%) as a colourless oil. $[\alpha]_D^{20} = +42.2$ (c = 1.250, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 2960 (s), 2864 (m), 1732 (s), 1612 (m), 1512 (s), 1464 (m), 1444 (m), 1252 (s), 1156 (m), 1076 (s), 848 (s) cm^{-1}. − ^1H NMR (200 MHz, CD_2Cl_2): $\delta = -0.13$ (m, 9 H), 0.39 (d_{br}, J = 13.0 Hz, 1 H), 0.70 (s, 3 H), 0.79 (s, 3 H), 1.14 (s, 3 H), 1.25 (tr, J = 7.0 Hz, 3 H), 1.10−1.47 (m, 6 H), 1.66 (m, 1 H), 2.01−2.35 (m, 3 H), 2.57 (d, J = 6.0 Hz, 2 H), 3.12 (tr, J = 6.0 Hz, 1 H), 2.77 (m, 1 H), 3.29−3.73 (m, 5 H), 3.78 (s, 3 H), 4.15 (q, J = 7.0 Hz, 2 H), 5.90 (d, J = 5.5 Hz, 1 H), 6.25 (d, J = 5.5 Hz, 1 H), 6.82 (m, 2 H), 7.22 (m, 2 H). − MS (130 °C): m/z (%) = 648 (100) [M^+], 634 (4), 603 (9), 576 (2), 379 (16), 240 (59), 73 (50). − HRMS: $C_{38}H_{52}O_7Si$ (648.4): calcd. 648.3482; found 648.3479.

Monoketal Adduct 11: A solution of siloxydiene **2** (400 mg, 1.05 mmol) and monoketal **10** (208 mg, 1.37 mmol) in dry dichloromethane (1.5 mL) was introduced into a Teflon vessel and subjected to 14 kbar in a high pressure autoclave for 4 days. Purification of the raw material by flash chromatography (Et_2O/PE, 1:10) yielded 553 mg (1.04 mmol, 99%) of **11** as a white solid. $[\alpha]_D^{20}$ = +112.4 (c = 1.250, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3039 (w), 2919 (s), 2859 (m), 1682 (vs), 1515 (vs), 1439 (m), 1249 (s), 845 (s) cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): $\delta = -0.21$ (s, 9 H), 0.37 (d_{br}, J = 12.5 Hz, 1 H), 0.75 (s, 3 H), 1.01−1.18 (m, 2 H), 1.20−1.36 (m, 2 H), 1.50 (d_{br}, J = 13.0 Hz, 1 H), 1.70−1.82 (m, 2 H), 1.88 (ddd, J = 1/4.4/11 Hz, 1 H), 1.96 (ddd, J = 2/8.5/18 Hz, 1 H), 2.27 (d, J = 18.0 Hz, 1 H), 2.81 (dd, J = 4.5/7.7 Hz, 1 H), 2.85 (d, J = 11.0 Hz, 1 H), 3.78 (s, 3 H), 4.00−4.20 (m, 4 H), 5.90 (d, J = 6.0 Hz, 1 H), 5.95 (dd, J = 1/10 Hz, 1 H), 6.12 (d, J = 6.0 Hz, 1 H), 6.56 (d, J = 10.0 Hz, 1 H), 6.78 (d_{br}, J = 7.5 Hz, 2 H), 7.17 (m_c, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.1 (CH_3), 16.8 (CH_3), 21.7 (CH_2), 24.0 (CH_2), 25.5 (CH_2), 29.1 (CH_2), 29.7 (CH_2), 42.6 (CH), 46.1 (CH), 51.5 (CH), 55.6 (CH_3), 59.0 (C), 61.7 (C), 64.5 (CH_2), 66.3 (CH_2), 67.0 (C), 105.7 (C), 121.6 (C), 128.2 (CH), 129.1 (CH), 131.2 (C), 134.8 (CH), 135.0 (CH), 142.7 (C), 143.7 (CH), 143.8 (CH), 158.3 (C), 203.5 (C=O). − MS (130 °C): m/z

(%) = 532 (100) [M$^+$], 517 (5), 379 (6), 308 (7). − HRMS: $C_{32}H_{40}O_5Si$ (532.3): calcd. 532.2645; found 532.2637.

Cyclohexenone 13: Camphorsulfonic acid monohydrate (35 mg, 140 μmol) was added at 0 °C to a solution of keto ester adduct **9** (90 mg, 139 μmol) in dichloromethane (20 mL) for silyl ether hydrolysis. After the reaction mixture had been stirred for 90 min, it was quenched with saturated, aqueous $NaHCO_3$ and extracted with dichloromethane. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated. Chromatographic purification (Et_2O/PE, 1:3) yielded 78 mg (135 μmol, 97%) of the hydrolysis product as a white foam. This product was placed in a flash-vacuum pyrolysis apparatus and sublimed at 170 °C/10^{-3} mbar through a pyrolysis tube heated to 350 °C. Within 20 min a 1:1 mixture of **1** and cyclohexenone **13** was collected in a cold trap. Chromatographic purification (Et_2O/PE, 1:10) yielded 44 mg (130 μmol, 96%) of **13** as a bright yellow oil. $[\alpha]_D^{20}$ = +22 (*c* = 0.425, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 3000 (w), 2936 (w), 1732 (s), 1684 (s) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.80 (s, 3 H), 1.14 (s, 3 H), 1.25 (tr, *J* = 7.0 Hz, 3 H), 2.51 (d, *J* = 12.0 Hz, 1 H), 2.63 (dd, *J* = 6/12 Hz, 1 H), 3.24 (dd, *J* = 5/6 Hz, 1 H), 3.30−3.45 (m, 1 H), 3.47 (d, *J* = 7.0 Hz, 2 H), 3.55−3.75 (m, 3 H), 3.82 (m, 2 H), 4.15 (q, *J* = 7.0 Hz, 2 H), 6.06 (dd, *J* = 2/10 Hz, 1 H), 6.92 (dd, *J* = 5/10 Hz, 1 H). − MS (140 °C): *m*/*z* (%) = 336 (100) [M$^+$], 291 (72), 263 (25), 208 (31), 141 (99). − HRMS: $C_{18}H_{24}O_6$ (336.2): calcd. 336.1573; found 336.1572.

Monoketal Adduct 14: Camphorsulfonic acid monohydrate (25 mg, 100 μmol) was added at 0 °C to a solution of **11** (43 mg, 81 μmol) in dichloromethane (10 mL). After the reaction mixture had been stirred for 10 min, it was quenched with saturated, aqueous $NaHCO_3$ and extracted with dichloromethane. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated. Chromatographic purification (Et_2O/PE, 1:1) yielded 36 mg (78 μmol, 98%) of monoketal adduct **14** as a colourless oil. $[\alpha]_D^{20}$ = −0.3 (*c* = 1.75, $CHCl_3$). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.47 (d$_{br}$, *J* = 13.0 Hz, 1 H), 0.76 (s, 3 H), 1.08−1.45 (m, 4 H), 1.55−1.90 (m, 2 H), 2.04 (m, 1 H), 2.06 (dd, *J* = 6.5/17 Hz, 1 H), 2.29 (dd, *J* = 5/17 Hz, 1 H), 2.58 (dd, *J* = 5/9 Hz, 1 H), 2.78 (q$_{br}$, *J* = 5.5 Hz, 1 H), 3.01 (tr, *J* = 9.0 Hz, 1 H), 3.89 (d, *J* = 9.0 Hz, 1 H), 3.89 (s, 3 H), 3.92−4.10 (m, 4 H), 6.04 (dd, *J* = 1/10.5 Hz, 1 H), 6.13 (d, *J* = 5.5 Hz, 1 H), 6.19 (d, *J* = 5.5 Hz, 1 H), 6.54 (d, *J* = 10.5 Hz, 1 H), 6.86 (m, 2 H), 7.21 (m, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 15.4 (CH_3), 21.2 (CH_2), 23.5 (CH_2), 25.5 (CH_2), 28.7 (CH_2), 38.8 (CH_2), 42.3 (CH), 44.1 (CH), 47.6 (CH), 53.2 (CH), 55.2 (CH_3), 60.6 (C), 61.3 (C), 64.6 (CH_2), 66.0 (CH_2), 67.7 (C), 104.2 (C), 113.0 (CH, 2 ×), 128.4 (CH, 2 ×), 128.7 (CH), 130.7 (C), 138.2 (CH), 139.1 (CH), 143.0 (CH), 157.9 (C), 201.5 (C=O), 209.9 (C=O). − MS (140 °C): *m*/*z* (%) = 460 (1) [M$^+$], 240 (100), 225 (9), 197 (6), 126 (10), 98 (7). − HRMS: $C_{29}H_{32}O_5$ (460.2): calcd. 460.224974; found 460.223785.

Methoxybutadiene Adduct 15: A solution of **14** (230 mg, 0.5 mmol) and 1-methoxybutadiene (100 μL, 1 mmol) in dry dichloromethane (2 mL) was introduced into a Teflon vessel and subjected to 14 kbar in a high pressure autoclave for 14 days. Purification of the raw material by flash chromatography (Et_2O/PE, 1:1) yielded 272 mg (100%) of **15** as a colourless oil. $[\alpha]_D^{20}$ = −15.4 (*c* = 4.10, $CHCl_3$). − IR (ATR): $\tilde{\nu}$ = 2918 (m), 1714 (s), 1698 (vs), 1614 (m), 1518 (vs), 1445 (m), 1387 (m), 1258 (s), 1122 (s), 1102 (s) cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.50 (d, *J* = 13.0 Hz, 1 H), 0.82 (s, 3 H), 1.05−1.34 (m, 3 H), 1.36−1.44 (m, 1 H), 1.55−1.63 (m, 2 H), 1.76−1.88 (m, 2 H), 1.91 (dd, *J* = 7/16.3 Hz, 1 H), 1.99 (d, *J* = 13.0 Hz, 1 H), 2.15 (d$_{br}$, *J* = 19.0 Hz, 1 H), 2.32 (dd, *J* = 2/16.3 Hz, 1 H), 2.40−2.48 (m, 2 H), 2.86−2.94 (m, 1 H), 2.90 (d, *J* = 9.0 Hz, 1 H), 3.44 (s, 3 H), 3.79 (s, 3 H), 3.80 (d, *J* = 9.0 Hz, 1 H), 3.89−4.10 (m, 5 H), 5.58 (m$_c$, 1 H), 5.85 (dd$_{br}$, *J* = 1/10.4 Hz, 1 H), 6.15 (ABq, *J* = 6.0 Hz, 2 H), 6.87 (d, *J* = 9.0 Hz, 2 H), 7.26 (d, *J* = 9.0 Hz, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 15.2 (CH_3), 21.2 (CH_2), 23.3 (CH_2), 24.5 (CH_2), 25.5 (CH_2), 28.8 (CH_2), 38.8 (CH_2), 42.3 (CH), 42.8 (CH), 44.1 (CH), 46.6 (CH), 51.9 (CH), 53.1 (CH), 55.2 (CH_3), 57.1 (CH_3), 61.3 (C), 61.4 (C), 64.9 (CH_2), 65.3 (CH_2), 68.3 (C), 76.5 (CH), 109.3 (C), 113.0 (CH), 124.3 (CH), 128.0 (CH), 128.7 (CH), 130.1 (C), 137.5 (CH), 139.6 (CH), 158.0 (C), 209.0 (C=O), 210.4 (C=O). − MS-FAB: *m*/*z* (%) = 677 (49), 545 (2) [MH$^+$], 544 (6) [M$^+$], 514 (2), 305 (4), 286 (6), 273 (12), 240 (100), 154 (13), 133 (27).

Cyclohexenone 16: Compound **15** (188 mg, 0.37 mmol) was placed in a flash-vacuum pyrolysis apparatus and sublimed at 250 °C/10^{-2} mbar through a pyrolysis tube heated to 350 °C. After 15 min, all of the starting material had sublimed and a 1:1 mixture of cyclopentadiene **1** and cyclohexenone **16** was collected in a cold trap. Chromatographic purification (Et_2O/PE, 1:1) yielded 111 mg (0.37 mmol, 99%) of **16** as a yellow oil. $[\alpha]_D^{20}$ = +152.0 (*c* = 0.9, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 2900 (w), 1724 (w), 1636 (s), 1568 (w), 1408 (m), 1228 (s), 1152 (s), 1088 (s) cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.98−2.21 (m, 3 H), 2.33−2.46 (m, 3 H), 3.18−3.23 (m, 1 H), 3.41−3.49 (m, 1 H), 3.59 (s, 3 H), 3.88−3.92 (m, 2 H), 4.00−4.08 (m, 2 H), 4.29−4.32 (m, 1 H), 5.70 (d, *J* = 10.0 Hz, 1 H), 5.73−5.81 (m, 2 H), 7.64 (d, *J* = 10.0 Hz, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 24.3 (CH_2), 35.6 (CH), 36.2 (CH_2), 37.5 (CH), 38.2 (CH), 57.5 (CH_3), 64.9 (CH_2), 65.9 (CH_2), 80.3 (CH), 109.4 (C), 113.8 (CH), 121.5 (CH), 125.2 (CH), 128.8 (CH), 141.7 (CH), 155.7 (C=O), 200.1 (C=O). − MS (90 °C): *m*/*z* (%) = 304 (3) [M$^+$], 272 (2), 244 (2), 193 (7), 166 (3), 149 (4), 120 (4), 109 (16), 87 (11). − HRMS: $C_{17}H_{20}O_5$ (304.1): calcd. 304.131074; found 304.131653.

Dimethylbutadiene Adduct 17: A solution of **14** (155 mg, 0.34 mmol) and 2,3-dimethylbutadiene (75 μL, 0.68 mmol) in dry dichloromethane (1 mL) was introduced into a Teflon vessel and subjected to 14 kbar in a high pressure autoclave for 14 days. Purification of the raw material by flash chromatography (Et_2O/PE, 1:1) yielded 37 mg (0.07 mmol, 20%) of **17** as a white foam. $[\alpha]_D^{20}$ = −60.0 (*c* = 0.68, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 2924 (m), 1712 (s), 1612 (w), 1516 (m), 1444 (w), 1376 (m), 1248 (s), 1124 (m) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.50 (d$_{br}$, *J* = 14.0 Hz, 1 H), 0.80 (s, 3 H), 0.95−1.49 (m, 6 H), 1.58 (s, 3 H), 1.68 (s, 3 H), 1.61−1.75 (m, 1 H), 1.85−2.09 (m, 4 H), 2.27−2.52 (m, 4 H), 2.82 (d, *J* = 10.0 Hz, 1 H), 2.87−2.95 (m, 1 H), 3.54 (tr, *J* = 8.0 Hz, 1 H), 3.79 (d, *J* = 10.0 Hz, 1 H), 3.80 (s, 3 H), 3.90−4.10 (m, 4 H), 6.12 (d, *J* = 8.0 Hz, 1 H), 6.18 (d, *J* = 8.0 Hz, 1 H), 6.87 (d, *J* = 9.0 Hz, 2 H), 7.25 (d, *J* = 2.0 Hz, 2 H). − MS (200 °C): *m*/*z* (%) = 543 (1) [M$^+$], 317 (1), 302 (5), 275 (1), 240 (100), 225 (10), 212 (7), 197 (9), 181 (4), 165 (8), 121 (5), 107 (5), 91 (6). − HRMS: $C_{32}H_{42}O_5$ (542.3): calcd. 542.303225; found 542.303040.

Cyclopentadiene Adduct 18: A solution of **14** (400 mg, 0.87 mmol) and freshly distilled cyclopentadiene (120 μL, 1.74 mmol) in dry dichloromethane (1.5 mL) was introduced into a Teflon vessel and subjected to 14 kbar in a high pressure autoclave for 14 days. Purification of the raw material by flash chromatography (Et_2O/PE, 1:1) yielded 183 mg (0.35 mmol, 40%) of **18** as a white solid. M.p.: 206 °C. − $[\alpha]_D^{20}$ = +27.3 (*c* = 0.06, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 2928 (w), 1696 (m), 1516 (m), 1464 (w), 1336 (w), 1248 (m), 1036 (w) cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.49 (d$_{br}$, *J* = 13.0 Hz, 1 H), 0.77 (s, 3 H), 1.09−1.32 (m, 3 H), 1.34−1.44 (m, 2 H), 1.55−1.70 (m, 2 H), 1.82 (dtr, *J* = 4/13 Hz, 1 H), 1.87−2.00 (m, 2 H), 2.08−2.18 (m, 2 H), 2.28 (dd, *J* = 3/17 Hz, 1 H), 2.86

(tr, *J* = 10.0 Hz, 1 H), 2.93 (dd, *J* = 3/10 Hz, 1 H), 3.03 (s$_{br}$, 1 H), 3.13 (dd, *J* = 4/10 Hz, 1 H), 3.42 (s$_{br}$, 1 H), 3.79 (s, 3 H), 3.82 (d, *J* = 10.0 Hz, 1 H), 3.88−3.98 (m, 1 H), 4.00−4.07 (m, 2 H), 4.10−4.18 (m, 1 H), 6.05 (d, *J* = 5.0 Hz, 1 H), 6.10 (dd, *J* = 3/5 Hz, 1 H), 6.12−6.15 (m, 2 H), 6.85 (d, *J* = 9.0 Hz, 2 H), 7.18 (d, *J* = 9.0 Hz, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 15.2 (CH_3), 21.1 (CH_2), 23.3 (CH_2), 25.4 (CH_2), 26.8 (CH_2), 28.6 (CH_2), 38.3 (CH_2), 40.2 (CH), 45.3 (CH), 46.2 (CH), 46.2 (CH), 48.0 (CH_2), 48.9 (CH), 50.5 (CH), 51.1 (CH), 54.0 (CH), 55.1 (CH_3), 60.2 (C), 60.9 (C), 64.7 (CH_2), 66.5 (C), 109.1 (C), 112.9 (C), 128.1 (CH), 131.0 (C), 135.1 (CH), 137.4 (CH), 138.0 (CH), 138.5 (CH), 157.8 (C), 211.0 (C=O), 213.6 (C=O). − MS (190 °C): *m*/*z* (%) = 526 (5) [M$^+$], 460 (5), 286 (9), 258 (1), 240 (100), 225 (23), 212 (14), 197 (18), 164 (13), 126 (11), 91 (12), 66 (16). − HRMS: $C_{34}H_{38}O_5$ (526.3): calcd. 526.271925; found 526.272461.

Acetoxybutadiene Adduct 20: A solution of **21** (60 mg, 0.15 mmol) and 1-acetoxybutadiene (20 μL, 0.17 mmol) in dry dichloromethane (0.5 mL) was introduced into a Teflon vessel and subjected to 14 kbar in a high pressure autoclave for 14 days. Purification of the raw material by flash chromatography (Et_2O/PE, 1:1) yielded 74 mg (0.15 mmol, 99%) of **20** as a white solid. M.p.: 180 °C. − $[\alpha]_D^{20}$ = +17.5 (*c* = 0.40, $CHCl_3$). − IR ($CHCl_3$): ṽ = 2928 (m), 1740 (s), 1708 (m), 1516 (m), 1444 (w), 1372 (w), 1248 (s), 1180 (m), 1036 (m) cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.53 (d, *J* = 13.0 Hz, 1 H), 0.77 (s, 3 H), 1.15−1.48 (m, 6 H), 1.59−1.72 (m, 1 H), 1.76−1.87 (m, 2 H), 1.94−2.07 (m, 1 H), 2.08 (s, 3 H), 2.15−2.25 (m, 1 H), 2.26−2.39 (m, 3 H), 2.97 (dd, *J* = 8/8 Hz, 1 H), 3.06 (dd, *J* = 3/9 Hz, 1 H), 3.63 (d, *J* = 9.0 Hz, 1 H), 3.79 (s, 3 H), 5.49 (ddd, 1/4/8 Hz, 1 H), 5.94 (d, *J* = 6.0 Hz, 1 H), 5.90−5.97 (m, 1 H), 6.02−6.08 (m, 1 H), 6.23 (d, *J* = 6.0 Hz, 1 H), 6.85 (d, *J* = 9.0 Hz, 2 H), 7.14 (d, *J* = 9.0 Hz, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 15.4 (CH_3), 21.1 (CH_3), 21.5 (CH_2), 23.4 (CH_2), 25.3 (CH_2), 26.9 (CH_2), 28.4 (CH_2), 37.0 (CH), 42.0 (CH), 43.2 (CH), 44.6 (CH_2), 45.8 (CH), 48.9 (CH), 55.2 (CH_3), 55.3 (CH), 60.6 (C), 61.0 (C), 67.0 (C), 67.9 (CH), 113.2 (CH, 2 ×), 127.0 (CH), 128.0 (CH, 2 ×), 130.9 (C), 131.4 (CH), 138.1 (CH), 140.2 (CH), 158.0 (C), 170.4 (C=O), 210.0 (C=O), 215.7 (C=O). − MS (180 °C): *m*/*z* (%) = 500 (1) [M$^+$], 441 (1), 359 (1), 306 (1), 293 (1), 251 (2), 240 (100), 225 (24), 197 (21), 165 (10), 153 (8), 115 (10), 95 (21), 79 (14). − HRMS: $C_{32}H_{36}O_5$ (500.2): calcd. 500.256275; found 500.256287.

Cyclopentenone Adduct 21: A solution of **2** (405 mg, 1.06 mmol) and 1-acetoxycyclopentadiene (150 mg, 1.07 mmol) in dry THF (3 mL) was introduced into a Teflon vessel and subjected to 6.5 kbar in a high pressure autoclave for 5 days. Afterwards, camphorsulfonic acid monohydrate (265 mg, 1.06 mmol) was added at room temperature. After the reaction mixture had been stirred for 15 min, it was quenched with saturated, aqueous $NaHCO_3$ and extracted with dichloromethane. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated. Chromatographic purification (Et_2O/PE, 1:1) yielded 308 mg (0.79 mmol, 75%) of **21** as a white solid. M.p.: 178 °C. − $[\alpha]_D^{20}$ = −140.2 (*c* = 1.64, $CHCl_3$). − IR ($CHCl_3$): ṽ = 2928 (m), 1708 (s), 1516 (m), 1340 (w), 1248 (m), 1104 (w), 908 (m) cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.59 (d$_{br}$, *J* = 13.0 Hz, 1 H), 0.80 (s, 3 H), 1.16−1.52 (m, 4 H), 1.53−1.78 (m, 3 H), 1.79−1.98 (m, 2 H), 2.24 (dd, *J* = 5/6 Hz, 1 H), 2.50 (dd, *J* = 5/12 Hz, 1 H), 3.12 (dd, *J* = 5/10 Hz, 1 H), 3.71 (d, *J* = 10.0 Hz, 1 H), 3.80 (s, 3 H), 5.96 (d, *J* = 6.0 Hz, 1 H), 6.26 (dd, *J* = 2/6 Hz, 1 H), 6.34 (d, *J* = 6.0 Hz, 1 H), 6.86 (d, *J* = 9.0 Hz, 2 H), 7.14 (d, *J* = 9.0 Hz, 2 H), 7.66 (dd, *J* = 3/6 Hz, 1 H). − MS (70 °C): *m*/*z* (%) = 388 (2) [M$^+$], 264 (2), 240 (100), 225 (23), 197 (26), 165 (20), 152 (20), 120 (19), 91 (66), 83 (38). − HRMS: $C_{26}H_{28}O_3$ (388.2): calcd. 388.2038458; found 388.2039530.

Cyclohexanone Adduct 23: A solution of **21** (27 mg, 0.07 mmol) and **22** (25 mg, 0.10 mmol) in dry dichloromethane (1.5 mL) was introduced into a Teflon vessel and subjected to 14 kbar in a high pressure autoclave for 2 days. Afterwards, TBAF (1 M in THF) was added at room temperature. The reaction mixture was stirred for 10 min and concentrated. Chromatographic purification (Et_2O/PE, 1:1) yielded 30 mg (59 μmol, 84%) of **23** as a colourless oil. $[\alpha]_D^{20}$ = −58.0 (*c* = 0.10, $CHCl_3$). − IR (ATR): ṽ = 2921 (m), 2856 (m), 1726 (m), 1704 (s, br), 1613 (w), 1515 (s), 1248 (s), 1034 (s) cm^{-1}. − ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.48 (d$_{br}$, *J* = 13.0 Hz, 1 H), 0.77 (s, 3 H), 1.09−1.38 (m, 8 H), 1.39−1.49 (m, 2 H), 1.64−1.73 (m, 2 H), 1.74−1.93 (m, 4 H), 1.96−2.10 (m, 1 H), 2.11−2.21 (m, 4 H), 2.22−2.38 (m, 2 H), 2.48−2.58 (m, 2 H), 3.01 (dd, *J* = 3/9.4 Hz, 1 H), 3.67 (d, *J* = 9.4 Hz, 1 H), 3.79 (s, 3 H), 5.93 (d, *J* = 6.0 Hz, 1 H), 6.19 (d, *J* = 6.0 Hz, 1 H), 6.85 (d, *J* = 9.0 Hz, 2 H), 7.13 (d, *J* = 9.0 Hz, 2 H). − ^{13}C NMR (100 MHz, CD_2Cl_2, DEPT): δ = 15.3 (CH_3), 21.6 (CH_2), 23.5 (CH_2), 25.3 (CH_2), 25.4 (CH_2), 26.4 (CH_2), 26.5 (CH_2), 28.5 (CH_2), 29.3 (CH_2), 41.56 (CH), 41.62 (CH), 42.3 (CH), 43.4 (CH_2), 44.4 (CH_2), 45.0 (CH), 47.9 (CH), 48.5 (CH), 50.2 (CH), 55.2 (CH_3), 56.1 (CH), 60.7 (C), 60.9 (C), 67.4 (C), 113.1 (CH, 2 ×), 128.1 (CH, 2 ×), 131.4 (C), 138.0 (CH), 140.4 (CH), 158.2 (C), 209.9 (C=O), 211.1 (C=O); 218.4 (C=O). − MS (120 °C): *m*/*z* (%) = 513 (1) [MH$^+$], 512 (1) [M$^+$], 307 (6), 272 (22), 240 (100), 149 (52). − HRMS: $C_{34}H_{40}O_4$ (512.3): calcd. 512.292660; found 512.291748.

Silylenol Adduct 24: A solution of adduct **21** (90 mg, 0.23 mmol) and diene **22** (83 mg, 0.35 mmol) in dry dichloromethane (2 mL) was introduced into a Teflon vessel and subjected to 14 kbar in a high pressure autoclave for 2 days. Purification of the raw material by flash chromatography (Et_2O/PE, 1:4) yielded 130 mg (0.21 mmol, 91%) of **24** as a colourless oil. $[\alpha]_D^{20}$ = −7.6 (*c* = 1.30, $CHCl_3$). − IR (ATR): ṽ = 2925 (m), 1734 (m), 1708 (m), 1614 (w), 1515 (s), 1249 (vs), 1179 (vs) cm^{-1}. − ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.09 (s, 2 ×, 6 H), 0.48 (d$_{br}$, *J* = 13.0 Hz, 1 H), 0.74 (s, 3 H), 0.92 (s, 2 ×, 9 H), 1.10−1.46 (m, 7 H), 1.48−1.58 (m, 1 H), 1.68 (d$_{br}$, *J* = 10.5 Hz, 2 H), 1.78−1.92 (m, 5 H), 1.96−2.04 (m, 1 H), 2.13−2.21 (m, 3 H), 2.22−2.30 (m, 1 H), 2.42−2.55 (m, 3 H), 2.85 (d$_{br}$, *J* = 15.0 Hz, 1 H), 2.92 (dd, *J* = 3/9 Hz, 1 H), 3.63 (d, *J* = 9.0 Hz, 1 H), 3.78 (s, 3 H), 5.94 (d, *J* = 6.0 Hz, 1 H), 6.20 (d, *J* = 6.0 Hz, 1 H), 6.84 (d, *J* = 9.0 Hz, 2 H), 7.14 (d, *J* = 9.0 Hz, 2 H). − ^{13}C NMR (100 MHz, CD_2Cl_2, DEPT): δ = −4.1 (CH_3), −3.9 (CH_3), 15.2 (CH_3), 18.2 (C), 21.7 (CH_2), 23.54 (CH_2), 25.52 (CH_2), 25.7 (CH_3, 3 ×), 26.1 (CH_2), 26.2 (CH_2), 26.8 (CH_2), 28.6 (CH_2), 30.0 (CH_2), 32.3 (CH_2), 37.4 (CH), 38.5 (CH), 41.4 (CH), 43.9 (CH_2), 45.6 (CH), 46.5 (CH), 47.0 (CH), 55.2 (CH_3), 56.2 (CH), 60.7 (C), 61.1 (C), 67.3 (C), 113.1 (CH, 2 ×), 117.2 (C), 128.1 (CH, 2 ×), 131.4 (C), 138.1 (CH), 139.4 (C), 140.1 (CH), 158.1 (C), 210.8 (C=O), 218.3 (C=O). − MS-FAB: $C_{40}H_{54}O_4Si$ (626): *m*/*z* (%) = 627 (3) [MH$^+$], 626 (4) [M$^+$], 625 (8), 387 (13), 263 (6), 240 (100).

Methyl Indolylacrylate Adduct 25: A solution of cyclopentenone adduct **21** (135 mg, 0.35 mmol) and methyl indolylacrylate (77 mg, 0.38 mmol) in dry dichloromethane (4 mL) was introduced into a Teflon vessel and subjected to 14 kbar in a high pressure autoclave for 14 days. Purification by flash chromatography (Et_2O/PE, 1:1) yielded 146 mg (0.25 mmol, 72%) of **25** as a white solid. $[\alpha]_D^{20}$ = −34.7 (*c* = 0.30, $CHCl_3$). − IR (ATR): ṽ = 3357 (m), 2929 (m), 1740 (s), 1721 (vs), 1706 (vs), 1612 (m), 1514 (s), 1248 (vs) cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.52 (d$_{br}$, *J* = 13.0 Hz, 1 H), 0.78 (s, 3 H), 1.18−1.68 (m, 5 H), 1.79 (m$_c$, 1 H), 1.90−1.95 (m, 1

H), 2.12−2.19 (m, 1 H), 2.24 (d, J = 5.8 Hz, 1 H), 2.26−2.32 (m, 1 H), 2.57−2.67 (m, 1 H), 2.81 (dd, J = 7/9.4 Hz, 1 H), 2.84−2.93 (m, 1 H), 3.00−3.07 (m, 1 H), 3.09−3.18 (m, 2 H), 3.70 (d$_{br}$, J = 9.4 Hz, 1 H), 3.76 (s, 3 H), 3.80 (s, 3 H), 3.92 (d$_{br}$, J = 8.3 Hz, 1 H), 5.97 (d, J = 6.0 Hz, 1 H), 6.23 (d, J = 6.0 Hz, 1 H), 6.86 (d, J = 9.0 Hz, 2 H), 7.11 (dtr, J = 1/8 Hz, 1 H), 7.19 (m$_c$, 1 H), 7.19 (d, J = 9.0 Hz, 2 H), 7.33 (d, J = 8.0 Hz, 1 H), 7.51 (d, J = 8.0 Hz, 1 H), 8.22 (s$_{br}$, 1 H). − ^{1}H NMR (400 MHz, [D$_5$]pyridine): δ = 0.48 (d, J = 13.0 Hz, 1 H), 0.79 (s, 3 H), 1.02−1.21 (m, 2 H), 1.26−1.38 (m, 2 H), 1.44 (d$_{br}$, J = 10.5 Hz, 1 H), 1.78 (m$_c$, 1 H), 1.93 (d, J = 13.0 Hz, 1 H), 2.45−2.53 (m, 3 H), 2.74 (dtr, J = 16/8 Hz, 1 H), 3.08−3.21 (m, 3 H), 3.22−3.33 (m, 2 H), 3.67 (s, 3 H), 3.73 (s, 3 H), 4.03 (d, J = 9.5 Hz, 1 H), 4.11 (d, J = 8.0 Hz, 1 H), 5.96 (d, J = 6.0 Hz, 1 H), 6.34 (d, J = 6.0 Hz, 1 H), 7.04 (d, J = 9.0 Hz, 2 H), 7.27 (dtr, J = 1/7 Hz, 1 H), 7.32 (dtr, J = 1/7 Hz, 1 H), 7.39 (d, J = 9.0 Hz, 2 H), 7.66 (d, J = 7.0 Hz, 1 H), 7.74 (d, J = 7.0 Hz, 1 H), 12.19 (s, 1 H). − ^{13}C NMR (100 MHz, [D$_5$]pyridine, DEPT): δ = 15.3 (CH$_3$), 20.1 (CH$_2$), 21.6 (CH$_2$), 23.7 (CH$_2$), 26.0 (CH$_2$), 29.2 (CH$_2$), 37.6 (CH), 41.3 (CH), 42.4 (CH), 44.58 (CH), 44.63 (CH$_2$), 46.8 (CH), 47.9 (CH), 51.8 (CH$_3$), 54.9 (CH), 55.1 (CH$_3$), 61.1 (C), 61.5 (C), 68.0 (C), 109.4 (C), 111.9 (CH), 113.7 (CH, 2 ×), 118.6 (CH), 119.5 (CH), 122.1 (CH), 127.8 (C), 128.99 (CH, 2 ×), 129.02 (C), 131.4 (C), 138.4 (C), 138.8 (CH), 139.8 (CH), 158.6 (C), 174.7 (C=O), 209.8 (C=O), 214.4 (C=O). − MS-FAB: $C_{38}H_{39}NO_5$ (589): m/z (%) = 589 (41) [M$^+$], 391 (65), 350 (48), 327 (48), 307 (100), 281 (86).

Allylic Alcohol Adduct 26: In a flame-dried, two-necked flask, adduct **11** (300 mg, 564 μmol) was dissolved in dry dichloromethane (50 mL) under argon atmosphere. The solution was cooled to −78 °C and K-Selectride (1.69 mL, 1 M in THF) was added dropwise. After the reaction mixture had been stirred for 3 h at −78 °C, it was warmed up to −10 °C over 3.5 h. Afterwards it was quenched with saturated, aqueous NH$_4$Cl and extracted with EE. The combined organic layers were washed with brine, dried (MgSO$_4$), and concentrated. Chromatographic purification (Et$_2$O/PE, 1:1) yielded 301 mg (564 μmol, 100%) of adduct **26** as a colourless oil. $[\alpha]_D^{20}$ = −18.0 (c = 0.10, CHCl$_3$). − IR (ATR): $\tilde{\nu}$ = 3495 (w), 2920 (m), 1687 (m), 1613 (m), 1514 (s), 1245 (vs) cm^{-1}. − ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = −0.24 (s, 9 H), 0.30 (d$_{br}$, J = 13.0 Hz, 1 H), 0.81 (s, 3 H), 1.25−1.35 (m, 2 H), 1.36−1.44 (m, 2 H), 1.54−1.61 (m, 1 H), 1.77 (dtr, J = 4/13 Hz, 1 H), 1.92 (dd, J = 6/15 Hz, 1 H), 2.23−2.34 (m, 3 H), 2.36 (ddd, J = 1/7/15 Hz, 1 H), 2.70 (d, J = 11.0 Hz, 1 H), 3.75 (s, 3 H), 3.75 (s$_{br}$, 1 H), 3.92−4.04 (m, 4 H), 4.21−4.28 (m, 1 H), 5.81 (dd, J = 1/10 Hz, 1 H), 5.82 (d, J = 6.0 Hz, 1 H), 6.07−6.12 (m, 1 H), 6.09 (d, J = 6.0 Hz, 1 H), 6.77 (d, J = 9.0 Hz, 2 H), 7.19 (d$_{br}$, J = 8.0 Hz, 2 H). − ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = −0.03 (s, 9 H), 0.62 (d$_{br}$, J =13 Hz, 1 H), 1.12 (s, 3 H), 1.28 (trtr, J = 4/14 Hz, 1 H), 1.37 (m$_c$, 1 H), 1.42−1.56 (m, 2 H), 1.61 (dtr, J = 3/13 Hz, 1 H), 1.72 (d$_{br}$, J = 13.0 Hz, 1 H), 1.92 (d$_{br}$, J = 7.0 Hz, 1 H), 2.04 (dtr, J = 4/13 Hz, 1 H), 2.18 (dd, J = 7/16 Hz, 1 H), 2.51 (dtr, J = 7/7 Hz, 1 H), 2.63−2.74 (m, 2 H), 3.08 (d, J = 11.0 Hz, 1 H), 3.39−3.54 (m, 4 H), 3.45 (s, 3 H), 4.16 (s$_{br}$, 1 H), 5.71 (dd, J = 1/10 Hz, 1 H), 5.83 (d, J = 6.0 Hz, 1 H), 6.05 (ddd, J = 1/4/10 Hz, 1 H), 6.26 (d, J = 6.0 Hz, 1 H), 6.93 (d, J = 9.0 Hz, 2 H), 7.50 (s$_{br}$, 2 H). − ^{13}C NMR (100 MHz, C$_6$D$_6$, DEPT): δ = 0.6 (CH$_3$, 3 ×), 16.8 (CH$_3$), 21.9 (CH$_2$), 24.6 (CH$_2$), 26.9 (CH$_2$), 29.4 (CH$_2$), 31.2 (CH$_2$), 44.0 (CH), 44.1 (CH), 44.3 (CH), 54.8 (CH$_3$), 59.5 (C), 62.7 (C), 64.0 (CH$_2$), 65.7 (CH$_2$), 68.1 (C), 69.1 (CH), 107.3 (C), 123.3 (C), 128.3 (CH), 129.5 (CH), 131.0 (C), 134.1 (CH, 2 ×), 134.5 (CH, 2 ×), 136.2 (CH, 2 ×), 142.3 (C), 158.6 (C). − MS (110 °C): m/z (%) = 534 (100) [M$^+$], 516 (6), 489 (4), 403 (12), 240 (15), 105 (24). − HRMS: $C_{32}H_{42}O_5Si$ (534.3): calcd. 534.280153; found 534.278137.

Cyclohexenone Adduct 27: Amberlyst 15 was added to a solution of **26** (30 mg, 56 μmol) in acetone (3 mL). The suspension was stirred for 2 h at room temperature (max. 20 °C!). Filtration, concentration and chromatographic purification (Et$_2$O) afforded adduct **27** (23 mg, 100%) as a colourless oil. $[\alpha]_D^{20}$ = −113.2 (c = 1.60, CHCl$_3$). − IR (ATR): $\tilde{\nu}$ = 3392 (w), 2922 (m), 1671 (s), 1613 (m), 1514 (s), 1247 (vs), 1034 (s) cm^{-1}. − ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.48 (d, J = 13.0 Hz, 1 H), 0.78 (s, 3 H), 1.15−1.34 (m, 2 H), 1.42 (d$_{br}$, J = 8.0 Hz, 1 H), 1.68 (d$_{br}$, J = 5.0 Hz, 1 H), 1.82 (dtr, J = 4/13 Hz, 1 H), 1.93−2.07 (m, 3 H), 2.11 (dd, J = 5/16.5 Hz, 1 H), 2.42 (m, 1 H), 2.69−2.78 (m, 2 H), 2.82−2.89 (m, 1 H), 3.62−3.68 (m, 2 H), 3.79 (s, 3 H), 4.58 (s$_{br}$, 1 H), 6.06 (d, J = 6.0 Hz, 1 H), 6.07 (dd, J = 1/10 Hz, 1 H), 6.17 (d, J = 6.0 Hz, 1 H), 6.85 (d, J = 9.0 Hz, 2 H), 6.95 (dd, J = 4/10 Hz, 1 H), 7.23 (d, J = 9.0 Hz, 2 H). − ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 0.47 (d, J = 13.0 Hz, 1 H), 0.62 (s, 3 H), 0.89−1.40 (m, 4 H), 1.52−1.58 (m, 1 H), 1.69−1.92 (m, 4 H), 2.04 (dd, J = 5/17 Hz, 1 H), 2.46 (m$_c$, 1 H), 2.59 (dd, J = 5/9 Hz, 1 H), 2.93 (dd, J = 8/17.4 Hz, 1 H), 3.40 (s, 3 H), 3.60 (d, J = 9.0 Hz, 1 H), 3.90 (s$_{br}$, 1 H), 5.58 (d, J = 6.0 Hz, 1 H), 5.90 (dd, J = 1.5/10 Hz, 1 H), 6.07 (d, J = 6.0 Hz, 1 H), 6.31 (dd, J = 4/10 Hz, 1 H), 6.88 (d, J = 9.0 Hz, 2 H), 7.19 (d, J = 9.0 Hz, 2 H). − ^{13}C NMR (100 MHz, C$_6$D$_6$, DEPT): δ = 15.8 (CH$_3$), 21.7 (CH$_2$), 24.1 (CH$_2$), 29.0 (CH$_2$), 30.2 (CH$_2$), 30.5 (CH), 41.3 (CH$_2$), 45.0 (CH), 45.4 (CH), 54.0 (CH), 54.8 (CH$_3$), 60.9 (C), 61.5 (C), 65.9 (C), 69.6 (CH), 113.5 (CH), 128.3 (CH), 128.4 (CH), 129.2 (CH), 130.9 (C), 138.8 (CH), 139.0 (CH), 158.7 (C), 198.9 (C=O), 208.8 (C=O). − MS (190 °C): m/z (%) = 418 (0.2) [M$^+$], 240 (100), 225 (16), 197 (11), 178 (6), 84 (18). − HRMS: $C_{27}H_{30}O_4$ (418.2): calcd. 418.214410; found 418.214600.

Cyclohexenone 28: Amberlyst 15 (250 mg) was added to a solution of **26** (237 mg, 511 μmol) in acetone (30 mL) . The suspension was stirred for 6 h at around 30 °C. Filtration, concentration and chromatographic purification (1. Et$_2$O, 2. EE) afforded cyclopentadiene **1** (98%) and retro product **28** (31 mg, 34%) as a bright yellow oil. $[\alpha]_D^{20}$ = +112.5 (c = 2.60, CHCl$_3$). − IR (ATR): $\tilde{\nu}$ = 3403 (m, br), 2905 (w), 1714 (m), 1667 (vs, br), 1384 (s), 1226 (s, br) cm^{-1}. − ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 2.40 (dd, J = 5/17 Hz, 1 H), 3.04 (m$_c$, 1 H), 3.14 (ddd, J = 1/3/17 Hz, 1 H), 3.38 (d$_{br}$, J = 3.0 Hz, 1 H), 3.45 (m$_c$, 1 H), 5.03 (s$_{br}$, 1 H), 5.95 (dd, J = 2.6/10 Hz, 1 H), 6.06 (dd, J = 3/10 Hz, 1 H), 6.83 (ddd, J = 2/2/10 Hz, 1 H), 7.18 (ddd, J = 2/2/10 Hz, 1 H). − MS (110 °C): m/z (%) = 179 (18) [MH$^+$], 178 (32) [M$^+$], 160 (4), 149 (14), 95 (90), 84 (100). − HRMS: $C_{10}H_{10}O_3$ (178.1): calcd. 178.062994; found 178.063034.

Enamine Alcohol 30: Adduct **31** (12 mg, 19 μmol) was placed in a flash-vacuum pyrolysis apparatus and heated to 150 °C at 10^{-2} mbar for 10 min. Cyclopentadiene **1** was collected in a cold trap and retro-reaction product **30** was left in the heated flask. Chromatographic purification (1. Et$_2$O/PE, 4:1, 2. Et$_2$O) yielded 8 mg (19 μmol, 100%) of **30** as a colourless oil. $[\alpha]_D^{20}$ = −96.7 (c = 0.30, CHCl$_3$). − IR (ATR): $\tilde{\nu}$ = 3489 (w, br), 2921 (vs), 1694 (s, br), 1597 (w), 1494 (w), 1458 (m), 1390 (m), 1190 (s) cm^{-1}. − ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 1.57−1.65 (m, 1 H), 1.81 (d$_{br}$, J = 18.0 Hz, 1 H), 1.86−1.93 (m, 2 H), 1.94−2.02 (m, 2 H), 2.21 (d, J = 4.0 Hz, 1 H), 2.22−2.28 (m, 1 H), 2.30 (dd, J = 5/17 Hz, 1 H), 2.41 (d$_{br}$, J = 18.0 Hz, 1 H), 2.90 (dd, J = 5.5/17 Hz, 1 H), 2.94−3.05 (m, 1 H), 3.11 (dtr, J = 5.0 Hz, 1 H), 3.20 (m$_c$, 1 H), 3.26 (s$_{br}$, 1 H), 3.38 (dtr, J = 12/5.5 Hz, 1 H), 3.98 (dtr, J = 13/5 Hz, 1 H), 4.43 (dtr, J = 9.4/4.4 Hz, 1 H), 6.05 (dd, J = 2.5/10 Hz, 1 H), 6.98 (dd, J = 3/10 Hz, 1 H), 7.11 (dd, J = 1/8.5 Hz, 2 H), 7.23 (trtr, J = 1/7.5 Hz, 1 H), 7.39 (tr$_{br}$, J = 8.0 Hz, 2 H). − ^{13}C NMR (100 MHz, CD$_2$Cl$_2$, APT): δ = 23.5 (CH$_2$), 23.6 (CH$_2$), 26.2

(CH_2), 29.8 (CH_2), 30.1 (CH), 38.1 (CH_2), 39.3 (CH), 43.3 (CH), 45.3 (CH_2), 46.1 (CH), 67.5 (CH), 117.7 (C), 121.9 (CH, 2 ×), 125.5 (CH), 129.3 (CH, 2 ×), 131.5 (CH), 134.1 (C), 145.5 (CH), 151.3 (C=O), 182.7 (C), 196.9 (C=O), 210.1 (C=O). − MS-FAB: $C_{24}H_{25}NO_5$ (407): m/z (%) = 408 (52) [MH^+], 407 (93) [M^+], 307 (32), 289 (22), 279 (26), 154 (100), 136 (68).

Enamine Alcohol Adduct 31: A solution of adduct **27** (15 mg, 36 μmol) and diene **29** (10 mg, 43 μmol) in dry toluene (2 mL) was introduced into a Teflon vessel and subjected to 14 kbar in a high pressure autoclave for 14 days. Purification by flash chromatography (Et_2O/PE, 3:1) yielded 15 mg (24 μmol, 67%) of **31** as a colourless oil. $[\alpha]_D^{20} = -8.0$ (c = 0.10, $CHCl_3$). − IR (ATR): $\tilde{\nu}$ = 3449 (w), 2921 (s), 1703 (s, br), 1613 (w), 1515 (m), 1398 (m), 1248 (s), 1204 (s), 1033 (s) cm^{-1}. − ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.43 (d, J = 13.0 Hz, 1 H), 0.79 (s, 3 H), 1.18−1.38 (m, 3 H), 1.39−1.47 (m, 1 H), 1.51−1.72 (m, 3 H), 1.79−1.96 (m, 4 H), 2.03 (dd, J = 5/15 Hz, 1 H), 2.17−2.35 (m, 4 H), 2.41 (s_{br}, 1 H), 2.49−2.60 (m, 2 H), 2.72 (d, J = 9.0 Hz, 1 H), 2.98 (dd, J = 13.5/15 Hz, 1 H), 3.05 (d, J = 11.5 Hz, 1 H), 3.63 (tr, J = 4.5 Hz, 1 H), 3.79 (s, 3 H), 3.81 (d, J = 9.0 Hz, 1 H), 3.83 (s, 1 H), 4.31 (d, J = 12.5 Hz, 1 H), 5.64 (m_c, 1 H), 6.08 (ABq, J = 6.0 Hz, 2 H), 6.86 (d, J = 9.0 Hz, 2 H), 7.09 (dd, J = 1/7.4 Hz, 2 H), 7.20 (trtr, J = 1/7.4 Hz, 1 H), 7.24 (d, J = 9.0 Hz, 2 H), 7.36 (m_c, 2 H). − ^{13}C NMR (100 MHz, CD_2Cl_2, APT): δ = 15.6 (CH_3), 21.7 (CH_2), 23.5 (CH_2), 25.4 (CH_2), 25.7 (CH_2), 26.1 (CH_2), 28.2 (CH_2), 29.8 (CH_2), 36.8 (CH), 37.0 (CH), 41.4 (CH_2), 41.9 (CH), 46.1 (CH), 46.4 (CH_2), 47.4 (CH), 50.4 (CH), 54.8 (CH), 55.2 (CH_3), 61.1 (C), 61.8 (C), 69.1 (C), 75.9 (CH), 113.0 (CH, 2 ×), 116.8 (CH), 121.9 (CH, 2 ×), 125.2 (CH), 128.6 (CH, 2 ×), 129.2 (CH, 2 ×), 131.1 (C), 135.4 (C), 138.3 (CH), 138.8 (CH), 151.9 (C), 153.5 (C), 158.2 (C=O), 209.8 (C=O), 210.4 (C=O). − MS-FAB: $C_{41}H_{45}NO_6$ (647): m/z (%) = 648 (2) [MH^+], 647 (2) [M^+], 460 (15), 427 (20), 391 (39), 307 (100), 289 (53), 240 (33).

Adduct 33: A solution of siloxydiene **2** (20 mg, 53 μmol), the trifluoroacetate salt of dihydronorharmane **32b** (22 mg, 79 μmol) and 10% of α,α′-bis-*tert*-butylpyridine in a dry 1:1 mixture of CH_3CN/DMF (0.6 mL) was introduced into a Teflon vessel and subjected to 14 kbar in a high pressure autoclave for 44 h. Afterwards, camphorsulfonic acid monohydrate and Et_2O were added. After the reaction mixture had been stirred for 30 min at room temperature, it was quenched with saturated, aqueous $NaHCO_3$ and extracted with dichloromethane. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated. Chromatographic purification (Et_2O/PE, 1:1) yielded 25 mg (52 μmol, 98%) of adduct **33** as a bright yellow oil. $[\alpha]_D^{20} = +4.4$ (c = 2.30, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 3466 (vs, br), 2927 (vs), 1699 (s), 1612 (m, br), 1516 (vs), 1463 (m), 1445 (m), 1380 (m), 1290 (m), 1249 (vs), 1181 (m), 1038 (m) cm^{-1}. − ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 0.28 (d, J = 13.0 Hz, 1 H), 0.73 (s, 3 H), 1.12−1.39 (m, 3 H), 1.50 (dtr, J = 3.6/12.4 Hz, 1 H), 1.62 (d_{br}, J = 13.0 Hz, 1 H), 1.80 (dtr, J = 3.6/13 Hz, 1 H), 2.16 (d, J = 13.0 Hz, 1 H), 2.43−2.57 (m, 2 H), 2.62−2.71 (m, 1 H), 2.72−2.81 (m, 1 H), 3.05 (dtr, J = 12/6 Hz, 1 H), 3.28−3.41 (m, 1 H), 3.74 (s, 3 H), 3.90 (ABq, J = 8.3 Hz, 2 H), 4.37 (dd, J = 4.4/9.3 Hz, 1 H), 6.09 (d, J = 6.0 Hz, 1 H), 6.19 (d, J = 6.0 Hz, 1 H), 6.85 (d, J = 9.0 Hz, 2 H), 6.95 (dtr, J = 1/7 Hz, 1 H), 7.02 (dtr, J = 1/7 Hz, 1 H), 7.18−7.25 (m, 3 H), 7.38 (d, J = 7.6 Hz, 1 H), 10.72 (s, 1 H). − ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.39 (d, J = 13.0 Hz, 1 H), 0.77 (s, 3 H), 1.15−1.44 (m, 3 H), 1.51 (dtr, J = 3.5/13 Hz, 1 H), 1.68 (d, J = 13.0 Hz, 1 H), 1.87 (dtr, J = 3.7/13 Hz, 1 H), 2.22 (d, J = 11.0 Hz, 1 H), 2.51 (d, J = 6.5 Hz, 2 H), 2.77 (dtr, J = 15/5.5 Hz, 1 H), 2.87 (dtr, J = 15/5 Hz, 1 H), 3.11 (dtr, J = 12.3/5.5 Hz, 1 H), 3.42 (ddd, J = 5/5.5/12.3 Hz, 1 H), 3.67 (d, J = 8.4 Hz, 1 H), 3.76 (s, 3 H), 3.90 (d, J = 8.4 Hz, 1 H), 4.42 (tr, J = 6.5 Hz, 1 H), 6.16 (d, J = 6.0 Hz, 1 H), 6.18 (d, J = 6.0 Hz, 1 H), 6.83 (d, J = 9.0 Hz, 2 H), 7.02−7.10 (m, 3 H), 7.19 (d, J = 9.0 Hz, 2 H), 7.45 (d, J = 7.0 Hz, 1 H), 8.13 (s, 1 H). − ^{13}C NMR (100 MHz, CD_2Cl_2, DEPT): δ = 15.5 (CH_3), 21.2 (CH_2), 21.5 (CH_2), 23.6 (CH_2), 26.4 (CH_2), 28.5 (CH_2), 44.1 (CH_2), 50.6 (CH_2), 52.2 (CH), 53.6 (CH), 55.2 (CH_3), 60.7 (C), 62.5 (C), 68.1 (C), 69.3 (CH), 108.6 (C), 111.1 (CH), 113.1 (CH, 2 ×), 117.9 (CH), 119.2 (CH), 121.5 (CH), 127.1 (C), 128.5 (CH, 2 ×), 130.8 (C), 134.7 (C), 136.3 (C), 138.1 (CH), 139.9 (CH), 158.3 (C), 209.8 (C=O). − MS-FAB: $C_{32}H_{34}N_2O_2$ (478): m/z (%) = 479 (11) [MH^+], 460 (7) [M^+], 307 (60), 289 (28), 240 (30), 154 (100), 137 (66).

Indoloquinolizinone (34): Adduct **33** (66 mg, 138 μmol) was placed in a flash-vacuum pyrolysis apparatus and heated to 150 °C at 10^{-2} mbar for 5 min. Cyclopentadiene **1** was collected in a cold trap and the crude retro-reaction product **34** was left in the heated flask. Chromatographic purification (EE) yielded 28 mg (118 μmol, 86%) of indoloquinolizinone **34** as a bright yellow oil. $[\alpha]_D^{20} = +137.1$ (c = 2.3, $CHCl_3$). − IR (ATR): $\tilde{\nu}$ = 3193 (w, br), 2920 (w), 1713 (w, br), 1621 (m, br), 1564 (vs, br), 1450 (s), 1376 (s), 1242 (s), 1171 (s), 724 (s, br) cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.64 (dd, J = 15.9/15.9 Hz, 1 H), 2.92 (dd, J = 4/15 Hz, 1 H), 2.97−3.10 (m, 2 H), 3.54 (ddd, 4/12/12 Hz, 1 H), 3.74 (dd, J = 4/12.5 Hz, 1 H), 4.89 (d_{br}, J = 15.0 Hz, 1 H), 5.09 (d, J = 7.4 Hz, 1 H), 7.12 (ddd, 1/7.8/7.8 Hz, 1 H), 7.19 (dtr, J = 1/8.2 Hz, 1 H), 7.26 (d_{br}, J = 7.4 Hz, 1 H), 7.41 (d, J = 8.2 Hz, 1 H), 7.51 (d, J = 7.8 Hz, 1 H), 9.13 (s, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ = 22.1 (CH_2), 41.8 (CH_2), 50.8 (CH_2), 54.0 (CH), 98.4 (CH), 107.8 (C), 111.5 (CH), 118.1 (CH), 119.7 (CH), 122.3 (CH), 126.4 (C), 131.5 (C), 136.6 (C), 154.9 (CH), 192.2 (C=O). − MS (180 °C): m/z (%) = 238 (100) [M^+], 209 (31), 156 (54), 129 (17), 122 (31), 105 (43), 81 (21), 69 (43). − HRMS: $C_{15}H_{14}N_2O$ (238.1): calcd. 238.110613; found 238.110718.

X-ray Crystallographic Study: Single-crystal X-ray diffraction experiments were carried out with a Stoe IPDS (area detector) diffractometer, using graphite-monochromated *Mo*-K_α radiation. The data collection nominally covered a full sphere of reciprocal space within $2\theta_{max}$ of about 48°. Since the crystal was rotated only about one axis, the reflections of a small part of the reciprocal lattice were not accessible. A second measurement using another rotation axis was thought unnecessary. A few reflections with very low 2θ (< 3.6°) could not be measured, due to collision with the primary beam stop. In the case of compound **20**, three strong reflections exceeded the intensity range of the imaging plate. Repetition of the measurement using a shorter exposure time was again thought unnecessary. Intensity integration and data reduction were performed using Stoe IPDS software. The structures were solved by direct methods (SHELXS) and refined by full-matrix, least-squares against F^2 of all data (SHELXL). Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were calculated geometrically and included in the refinement as riding H's. There are two symmetrically independent molecules in the asymmetric unit of compound **20**. They differ mainly in the atomic displacement parameters of the acetoxy group at C(15). The displacement parameters of the acetoxy group in the second molecule had abnormally high values in the first refinement. A split atom model was therefore introduced and refined with application of isotropic displacement parameters and some further restraints. The Flack x parameter does not allow the determination of the absolute structures of both compounds; the configuration was chosen in agreement with earlier investigations of related sub-

Table 1. X-ray crystallography

Compound	**20**	**25**
Empirical formula	$C_{32}H_{36}O_5$	$C_{38}H_{39}NO_5$
Molecular mass	500.26	589.70
Temperature	300 K	300(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Orthorhombic
Space group	*P* 21 (No. 4)	*P* 21 21 21
Unit cell dimensions	a = 17.658(3) Å, α = 90° b = 6.354(1) Å, β = 104.48(2)° c = 25.158(4) Å, γ = 90°	a = 9.1580(10) Å, α = 90° b = 16.123(2) Å, β = 90° c = 20.245(3) Å, γ = 90°
Volume	2733.0(8) Å^3	2989.3(7) Å^3
Z	4	4
Calculated density	1.217 g/cm^3	1.310 Mg/m^3
Absorption coefficient	0.081 mm^{-1}	0.086 mm^{-1}
F(000)	1072	1256
Crystal size	0.33 × 1.0 × 0.09 mm	0.74 × 0.37 × 0.06 mm
Diffractometer	Stoe IPDS area detector	Stoe IPDS area detector
Theta range for data collection	1.79° to 24.03°	2.01° to 24.08°
Reflections collected	20990	20763
Reflections unique	8491	4601
R_{int}	0.0897	0.0886
Absorption correction	None	None
Reflections with $I > 2\sigma(I)$	2870	2213
Refined variables	660	401
$R[F^2 > 2\sigma(F^2)]$	0.0397	0.0335
Goodness-of-fit	0.64	0.72
$wR(F^2)$, all data	0.0669	0.0495
$\Delta\rho_{\mathrm{max,min}}$ [e·Å^{-3}]	0.18, −0.14	0.12, −0.13

stances. The program PLATON was used for checks and graphics. Crystal data and experimental details are listed in Table 1. [References: G. M. Sheldrick, SHELXL-93, a program for refining crystal structures, University of Göttingen, 1993. G. M. Sheldrick, SHELXS-86, a program for crystal structure determination, University of Göttingen, 1986. A. L. Spek, PLATON, an integrated tool for the analysis of the results of a single-crystal structure determination. *Acta Crystallogr. Suppl. A46*, **1990**, C-34.]

Crystallographic data (excluding structure factors) for the structures **20** and **25** reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-161439 for **20** and CCDC-161440 for **25**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Continuous support of our work by the “Fonds der chemischen Industrie” is gratefully acknowledged. We are particularly thankful to the Deutsche Forschungsgemeinschaft (DFG) for a very valuable initial grant opening the road to first exploratory studies into an exciting but by no means easily predictable field. For the experiments described here we owe particular thanks to the DFG for providing specific 14 kbar facilities.

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Received April 30, 2001
[O01213]