Nonaflates from 8-Oxabicyclo[3.2.1]oct-6-en-3-ones as Building Blocks for Diversity-Orientated Synthesis: Preparation, Heck-Couplings and Subsequent Diels–Alder Reactions

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Dedicated to Prof. H. M. R. Hoffmann on the occasion of his 70th birthday.

Abstract: A series of bicyclic alkenyl nonaflates was prepared in good yields by deprotonation of the corresponding 8-oxabicyclo[3.2.1]oct-6-en-3-ones and a sulfur relative with LDA followed by trapping with nonafluorobutanesulfonyl fluoride (NfF). The resulting compounds undergo Heck couplings to methyl acrylate under standard conditions, generally providing bicyclic dienes in satisfactory yields. For nonaflates **2** and **12** a novel base-promoted fragmentation reaction to substituted furan derivatives was observed. Several Diels–Alder reactions of the bicyclic dienes were conducted leading to polycyclic compounds. Whereas the diastereofacial selectivity with respect to the oxygen or sulfur bridge of the dienes is excellent, the *exo*/*endo* selectivity strongly depends on the substitution patterns of the bicyclic diene and the dienophile. The results presented demonstrate the potential of bicyclic nonaflates to serve as versatile building blocks in diversity-orientated synthesis.

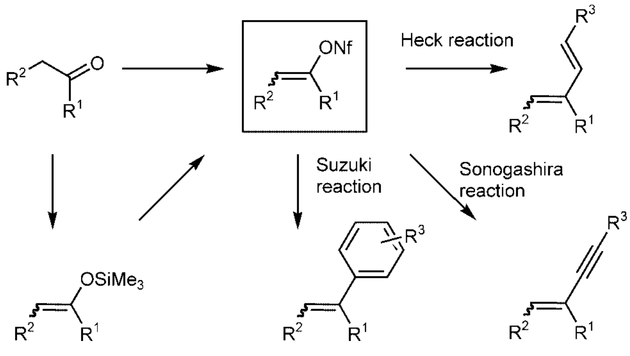
Keywords: alkenyl nonaflates; Diels–Alder reaction; Heck coupling; 8-oxabicyclo[3.2.1]oct-6-en-3-one; palladium catalysis

Introduction

8-Oxabicyclo[3.2.1]oct-6-en-3-ones are highly versatile building blocks for natural product synthesis.[1,2] The bicyclo[3.2.1]octane core of these molecules is densely functionalized and is accessible with a wide variety of substituents at the C-2 and C-4 positions. Further functionalizations, cleavage of the oxygen bridge,[3,4] or ring annulations[5] at the double bond are possible. Beside their potential as a building block in synthesis, 8-oxabicyclo[3.2.1]octane derivatives also resemble compounds with tropane substructure (e.g., cocaine) and hence they have been investigated as analogues of monoamine transport inhibitors, in particular of dopamine transport inhibitors (DAT).[6]

So far the carbonyl group of 8-oxabicyclo[3.2.1]oct-6-en-3-ones has not been transformed into reactive moieties able to undergo transition metal-catalyzed coupling reactions. This is partly due to the fact that a carbonyl group cannot be converted into alkenyl bromides or iodides under mild conditions. Surprisingly, triflates derived from 8-oxabicyclo[3.2.1]oct-6-en-3-ones are not known although they should offer a broad scope of synthetically useful transformations. In general, alkenyl triflates are widely employed in palladium-catalyzed C–C couplings although several problems are involved in their reactions. Alkenyl triflates are often only moderately stable and the reagents for their preparation are moisture sensitive and relatively expensive (generally, 50% of the triflating unit is lost as leaving group).

We recently demonstrated that alkenyl nonaflates[7] are excellent coupling partners for palladium-catalyzed C–C coupling reactions,[8] in particular Heck,[9] Suzuki,[10] and Sonogashira couplings.[11] Alkenyl nonaflates are either directly accessible by simple deprotonation of ketones and subsequent quenching with a slight excess of nonafluorobutanesulfonyl fluoride (NfF)[12] or,



Scheme 1. Synthesis and coupling reactions of alkenyl nonaflates.

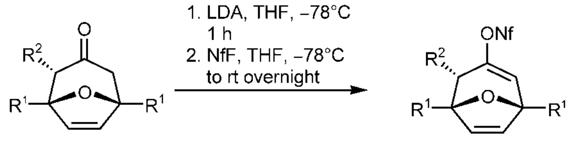
alternatively, *via* the corresponding trimethylsilyl enol ethers by employing NfF together with catalytic amounts of fluoride (Scheme 1). The later method is of particular advantage if aldehydes are starting materials, which cannot be cleanly transformed into the corresponding enolates.

These methods have been recently used to prepare nonaflates derived from 8-azabicyclo[3.2.1]octan-3-ones which underwent several palladium-catalyzed reactions.[13] In this report we describe our results with the related 8-oxabicyclo[3.2.1]oct-6-en-3-ones which, *via* nonaflates, allow the preparation of functionalized bicyclic dienes. Their subsequent Diels–Alder reactions should easily lead to relatively complex polycyclic compounds in a highly flexible manner.

Results and Discussion

Synthesis of Bicyclic Alkenyl Nonaflates

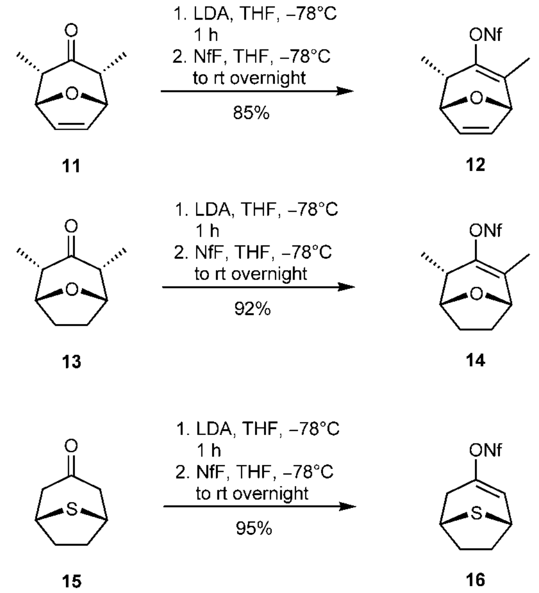
The direct method employing deprotonation of 8-oxabicyclo[3.2.1]oct-6-en-3-ones with LDA followed by NfF quenching proved to be suitable for the synthesis of the corresponding nonaflates. Deprotonation of ketones **1**, **3**, **7** and **9** with LDA under kinetic conditions (–78 °C) and reaction of the generated bicyclic enolates with the electrophile NfF under slow warm up to room temperature afforded the expected alkenyl nonaflates **2**, **4**, **8** and **10** in 60 to 80% yield (Scheme 2). For reasons so far unclear, the transformation of 4-benzyloxy-substituted bicyclic ketone **5** furnished only 27% of nonaflate **6**. Despite many attempts to optimize the conditions no better yield could be obtained. The enolate derived from **5** seems to be particularly sensitive.



1	R^1 = H,	R^2 = H	**2**	73%
3	R^1 = Me,	R^2 = H	**4**	79%
5	R^1 = H,	R^2 = OBn	**6**	27%
7	R^1 = Me,	R^2 = OBn	**8**	70%
9	R^1 = Me,	R^2 = OMe	**10**	62%

Scheme 2. Nonaflations of 8-oxabicyclo[3.2.1]oct-6-en-3-ones **1**, **3**, **5**, **7** and **9**.

Excellent results were obtained with the 2,4-dimethyl-substituted ketone **11** and its saturated derivative **13** which is quantitatively accessible from **11** by hydrogenation of the double bond with Pd/C.[14] Deprotonation and subsequent reaction with NfF converted **11** into **12** in 85% yield and **13** gave **14** even in 92% yield (Scheme 3). Compound **12** was also prepared *via* the corresponding trimethylsilyl enol ether of **11** in good overall yield,[15] however, since the direct nonaflation proceeds without problems there is no need to follow this detour. Having prepared bicyclic alkenyl nonaflates with an oxygen bridge (and earlier those with a nitrogen bridge)[13] we were now interested to include a sulfur-containing compound into our collections of bicyclo[3.2.1]octane derivatives containing hetero atoms in position 8. This motivated us to prepare ketone **15** according to a literature procedure[16] and to convert it into the corresponding nonaflate **16**. This compound could easily be isolated in excellent 95% yield.

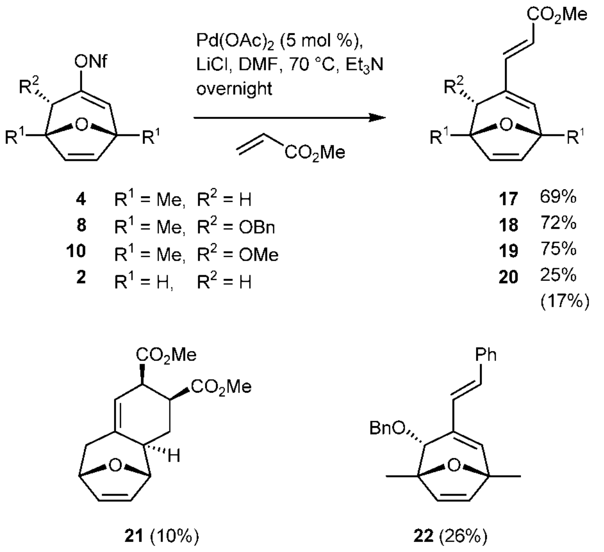


Scheme 3. Nonaflations of bicyclic ketones **11**, **13** and **15**.

Our results depicted in Schemes 2 and 3 prove that it is not necessary to go *via* silyl enol ethers. The desired alkenyl nonaflates are directly available from the ketone enolates by deprotonation with LDA and subsequent quenching with NfF. With the exception of compound **6** the yields are good to excellent.

Heck Reactions

The smooth entry into these bicyclic alkenyl nonaflates allowed us to investigate their palladium-catalyzed reactions. Methyl acrylate is known to be a good substrate in Heck reactions and therefore we first studied the behavior of the bicyclic nonaflates with this olefin. We generally employed 5 mol % of palladium acetate together with triethylamine as base and LiCl as additive in DMF as solvent. Nonaflates **4**, **8** and **10** and methyl acrylate provided the expected coupling products in good yields, affording the conjugated dienes **17**, **18** and **19** in



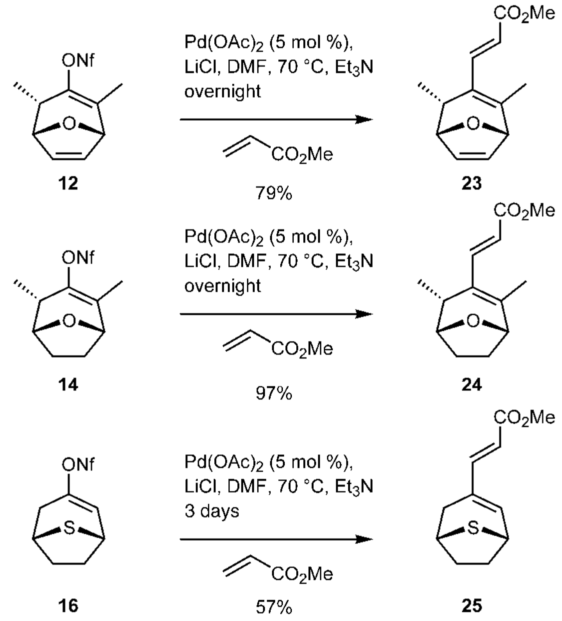
Scheme 4. Heck-coupling reactions with methyl acrylate leading to diene esters **17**–**20**.

69% to 78% yield, respectively (Scheme 4). All these compounds contain methyl groups in the two bridge-head positions.

In contrast to these very encouraging results, alkenyl nonaflate **2** without bridge-head substituents coupled to methyl acrylate under standard conditions less cleanly, providing a yield of only 17% for diene **20**. As a side product the tricyclic compound **21** was isolated in 10% yield. The unexpected product **21** could be identified as the product of a subsequent Diels–Alder reaction of diene **20** with a second equivalent of methyl acrylate serving as dienophile. Based on the coupling constants of 4-H with 5-H ($J \approx 10$ Hz) we conclude that the dienophile underwent an *endo*-attack leading to *cis*-positioned methoxycarbonyl groups in **21**. We assume that the transformation of **2** (*via* **20**) into cycloadduct **21** proceeds by a "top-side" attack of the dienophile, which contradicts our experience with a related compound bearing a more bulky N-CO_2Et group instead of the bridging oxygen.[13] The sequence **10** *via* **19** to Diels–Alder products **32** shows a similar stereochemical outcome (see Scheme 7). The *endo*-approach *syn* to the sterically less demanding bridge-head oxygen is most favorable in these bicyclic diene systems. The low mass balance of the sequence **2** to **20** to **21** does not rigorously exclude formation of isomers, however, it should also be mentioned here that **2** is able to undergo a fragmentation reaction which can diminish the amount of starting material available for the coupling step (see Scheme 6).

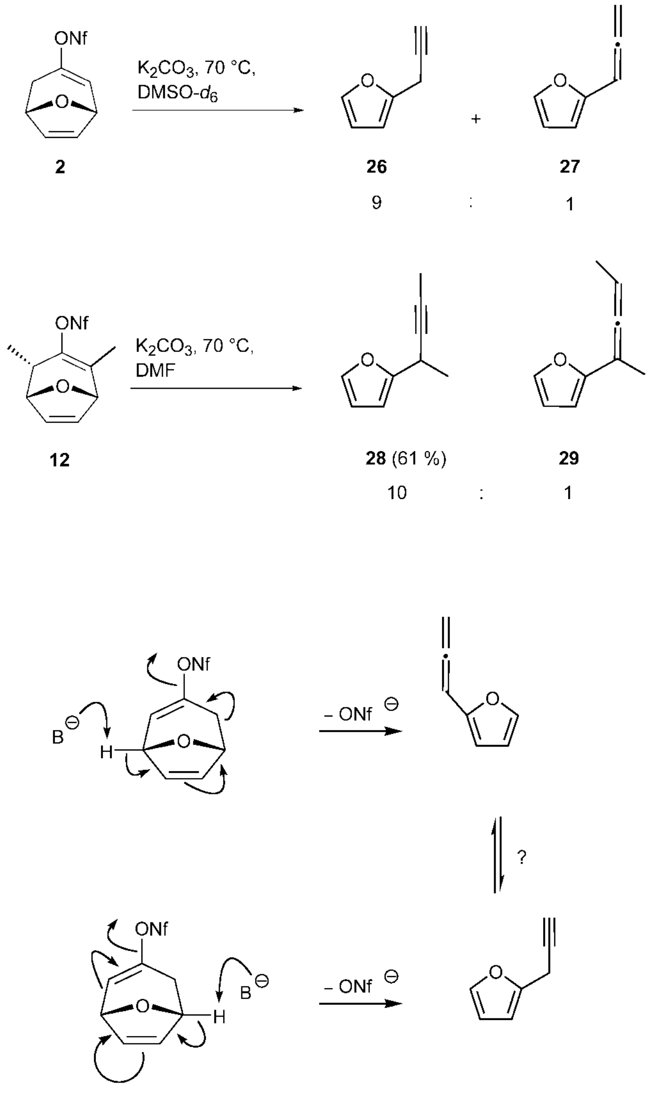
The elevated temperature (70 °C) of the Heck reaction led in the case of **20** to the formation of the Diels–Alder product **21**. Although sequential reactions of this type are synthetically very valuable, we were nevertheless interested to improve the yield of **20**. Therefore, the considerably milder reaction conditions introduced by Jeffery for the Heck reaction were applied to **2**.[17] However, use of *n*-Bu_4NCl, K_2CO_3 in DMF and 5 mol % palladium acetate at room temperature did not dramatically improve the situation: although formation of **21** was not observed only 25% of **20** and 5% of starting material **2** were isolated.

Encouraged by the results obtained with bicyclic alkenyl nonaflates such as **10** we also tried to extend the Heck reaction to other olefins. Interestingly, only relatively few examples of alkenyl triflate couplings with styrene are known.[18] We employed standard conditions but used PPh_3 as additive, since Stille[18a] had found that phosphane ligands are superior for triflate couplings to styrene. So far bicyclic alkenyl nonaflates **10** could be converted into **22** in 26% yield only (Scheme 4). Although the starting material was consumed in this experiment no other defined products could be identified. The couplings with olefins such as styrenes therefore require more careful optimization to avoid oligomerizations or other side reactions.



Scheme 5. Heck-coupling reactions with methyl acrylate leading to diene esters **23**–**25**.

Gratifyingly, methyl acrylate and 2,4-dimethyl-substituted alkenyl nonaflates **12** and **14** were converted into the expected dienes **23** and **24** under standard conditions in good to excellent yields (Scheme 5). It was particularly interesting to examine whether the sulfur-containing nonaflate **16** is able to undergo the palladium-catalyzed reaction without problems. Coupling of **16** with methyl acrylate also proceeded satisfactorily yielding 57% of diene **25**. Nevertheless, the reaction time was much longer in this case (3 days) and additional 5 mol % of the palladium source was required to drive the reaction to completion. Apparently, interaction of the palla-



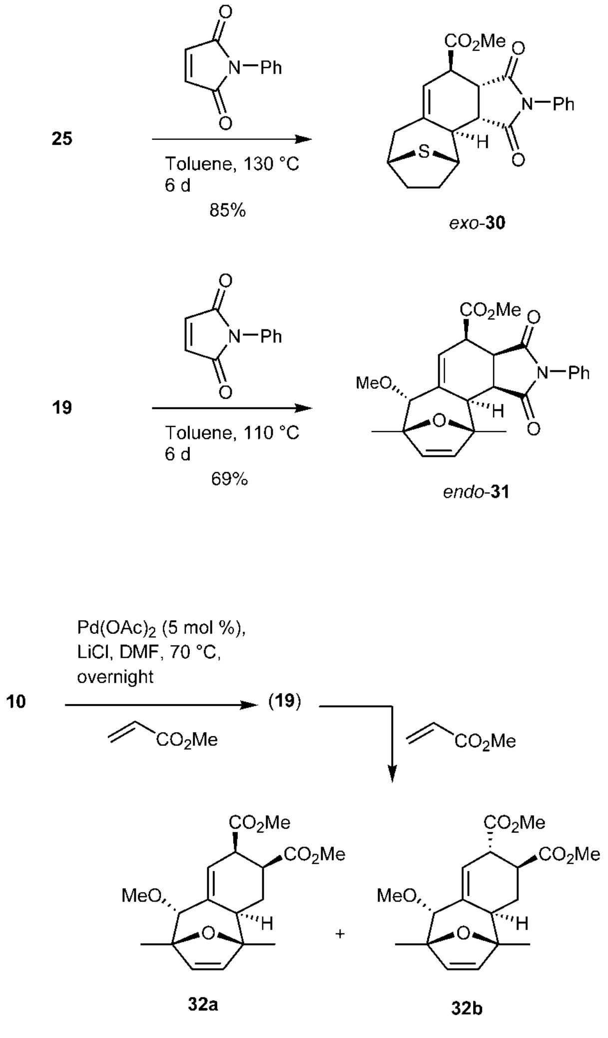
Scheme 6. Fragmentations of bicyclic alkenyl nonaflates **2** and **12**.

dium with the sulfur bridge decreases the rate of the reaction.

The unusually low yield of **20** motivated us to investigate the reactivity of **2** in more detail. In an NMR-experiment bicyclic alkenyl nonaflate **2** was heated in DMSO-d_6 with K_2CO_3 to 70 °C for 2 days. The proton and carbon spectra showed full conversion of **2** into furan derivatives **26** and **27** (ratio 9:1, Scheme 6). A similar result was obtained with triethylamine as base. This type of fragmentation has already been observed in the case of the 8-azabicyclo[3.2.1]oct-6-en-3-one derived nonaflate leading to analogous pyrrole derivatives.[13] It was assumed that nonaflate **12** should also be fragmented under basic conditions in a polar solvent. Nonaflate **12** was therefore treated with K_2CO_3 in DMF for 2 d at 70 °C and after careful work-up with pentane followed by column chromatography the pentynyl-substituted furan derivative **28** was isolated in 61% yield. The corresponding allenyl furan derivative **29** could not be isolated in this case, but an NMR experiment clearly showed the signals of this compound (ratio **28**:**29** = 10:1). The mechanism of the fragmentation involves deprotonation at one of the bridge-head positions and ring opening under expulsion of nonafluorobutanesulfonate as an excellent leaving group. Both possible pathways are depicted in Scheme 6. It should be mentioned that a polar solvent such as DMF or DMSO is required for this base-promoted fragmentation.

Diels–Alder Reactions

The Heck coupling products depicted in Schemes 4 and 5 should be excellent substrates for a variety of addition reactions (e.g., Michael additions, cycloadditions, reactions with electrophiles and radicals) or other synthetically useful transformations leading to highly functionalized compounds. To demonstrate this potential we studied a few typical Diels–Alder reactions as first ex-



Scheme 7. Diels–Alder reactions of dienes **25** and **19**.

amples. *N*-Phenylmaleimide was the dienophile of choice, which was first heated with the sulfur-containing bicyclic diene **25** in toluene at 130 °C for 6 days. The tetracyclic product *exo*-**30** was obtained as single compound in a very good 85% yield (Scheme 7). The coupling constants of 2-H with 3-H and 7-H with 8-H were found to be 10 Hz suggesting *trans*-arrangements of these protons. Therefore an *exo*-product has been obtained, an assignment which was confirmed by NOESY experiments showing interactions of the phenyl protons with 2-H and 9-H. Again the dienophile attacks the less hindered "top-side" of the bicyclic diene (*syn* to the sulfur bridge).

In a second example the Diels–Alder reaction of *N*-phenylmaleimide was conducted with oxgygen-bridged diene **19**, which provided after 6 days at 110 °C as single product *endo*-**31** in 69% yield. In this case the coupling constants of 2-H with 3-H and 7-H with 8-H are in the range of 5 Hz indicating that **31** is result of an *endo*-"top-side" attack. The methoxy group of **19** additionally shields the "bottom-side". The switch from *exo*- to *endo*-selectivity can be interpreted as follows: in the case of the sulfur-containing bicyclic system **25** the repulsion caused by the heteroatom and the bulky phenyl group prevents an *endo*-attack of the dienophile, whereas in case of bicyclic diene **19** the bridging oxygen is less bulky and the 1-methyl group additionally disfavors the *exo*-attack.

When the Heck coupling of alkenyl nonaflate **10** to methyl acrylate (1.4 equivalents) was conducted under standard conditions for an extended reaction time (2 days) 20% of **19** and two Diels–Alder products **32a** (12%) and **32b** (30%) were isolated (Scheme 7). After analysis of the NMR data (coupling constants and NOESY experiments) compound **32a** was assigned to be the *endo*-"top-side" Diels–Alder product. The second cycloadduct **32b** could be crystallized (Figure 1) and an X-ray analysis revealed the configuration as depicted, showing that bridge-head 2-H is pointing *trans* to the oxygen bridge. Again a "top-side" attack had occurred, but 5-H and 2-H are *trans*-positioned which cannot be the direct result of the Diels–Alder reaction. We have to assume that under the influence of the base triethylamine primary adduct **32a** equilibrates at C-5 forming the thermodynamically more stable *trans*-product **32b**. In the sequential reaction illustrated in Scheme 7 the stereofacial selectivity again is very high, leading to products resulting from an *exo*-"top-side" attack of the dienophile. Reactions of this type clearly show the potential to perform Heck coupling and Diels–Alder reaction as one-pot reactions. They will be further optimized and explored in our group since they open a very straightforward and flexible route to polycyclic skeletons.

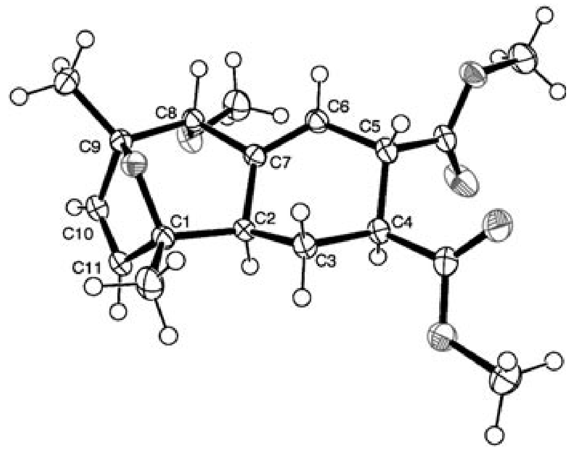


Figure 1. ORTEP[19] plot of the isomerized Diels–Alder product **32b**.

Conclusion

We have demonstrated that alkenyl nonaflates are smoothly available from 8-oxabicyclo[3.2.1]octan-3-ones. They undergo Heck couplings to methyl acrylate generally in good yields and the resulting bicyclic dienes are suitable for highly stereoselective Diels–Alder reactions. Thus, a straightforward and potentially very flexible route to novel polycyclic skeletons has been established. The cycloadducts are just the first examples of advanced products derived from the bicyclic dienes. Alternative transition metal-catalyzed reactions of the nonaflates are possible as well as functionalizations of the double bonds and/or ring cleavage reactions opening the oxygen bridge. All these transformations should lead to interesting, configurationally defined compounds with or without the 8-oxabicyclo[3.2.1]octane core. The alkenyl nonaflates introduced in this report are therefore expected to serve as versatile building blocks for diversity-orientated chemistry.[20]

Experimental Section

General Information

NMR spectra were recorded on Bruker WH 270, Bruker AC 500 and Joel Eclipse 500 (500 MHz) instruments. ^1H and ^{13}C chemical shifts are expressed as ppm downfield from tetramethylsilane ($\delta = 0$) used as an internal standard. ^{13}C NMR signals of $CF_3(CF_2)_3$ groups are not given since unambiguous assignment is not possible due to strong splitting by coupling with the ^{19}F nuclei. Mass spectra were registered with Varian MAT 711 spectrometer. IR spectra were measured with a spectrometer 5 SXC Nicolet. TLC analysis was performed using Merck silica gel 60 F_{254} plates. Column chromatography was conducted on silica gel 60 (40–63 μm, Fluka). The deprotonation and nonaflation reactions were carried out under an atmosphere of argon in heat gun-dried reaction flasks by adding the components *via* syringes. Solvents for reactions were dried by standard procedures. Nonafluorobutane-1-sulfonyl fluoride was obtained from Bayer AG; it can also be purchased from Aldrich. Commercially available 2.5 M *n*-BuLi solution (Acros) was used.

The following bicyclic ketones were synthesized according to literature procedures: 8-oxabicyclo[3.2.1]oct-6-en-3-one (**1**),[21] 1,5-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**3**),[22] 2-benzyloxy-8-oxabicyclo[3.2.1]oct-6-en-3-one (**5**),[23] 2-benzyloxy-1,5-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**7**),[24] 2-methoxy-1,5-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**9**),[25] 2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**11**),[26] 2,4-dimethyl-8-oxabicyclo[3.2.1]octan-3-one (**13**),[14] 8-thiabicyclo[3.2.1]octan-3-one (**15**).[16]

General Procedure for the Nonaflation of 8-Oxabicyclo[3.2.1]oct-6-en-3-ones (GP 1)

An LDA solution in anhydrous THF was generated by adding *n*-butyllithium (2.5 M in hexane, 1.4 equivs.) to diisopropylamine (1.5 equivs.) at −78 °C. After 10 minutes a solution of the bicyclic ketone (1 equiv.) in anhydrous THF was added at −78 °C, the mixture was then stirred for 1 h at −78 °C and NfF (1.6 equivs.) was added. The mixture was allowed to warm up to room temperature overnight. The resulting brown solution was taken up with Et_2O and washed twice with water and once with brine. The organic layer was then dried with $MgSO_4$ and the solvent was removed under vacuum. The resulting crude brown oil was purified by column chromatography on silica gel.

General Procedure for Heck Reactions with Nonaflates (GP 2)

A mixture of the bicyclic nonaflate (1 equiv.), triethylamine (1.2 equivs.), LiCl (3 equivs.), olefin (1.2 equivs.) and $Pd(OAc)_2$ (5 mol %) was stirred in anhydrous DMF for 17 h under the conditions described in the individual experiments. The reaction mixture was taken up in EtOAc, washed twice with water and once with brine. The organic layer was dried with $MgSO_4$ and the solvent was then removed under vacuum. The resulting crude product was purified by column chromatography on silica gel.

8-Oxabicyclo[3.2.1]octa-2,6-dien-3-yl Nonaflate (2)

According to GP 1, LDA was prepared using $(i\text{-}Pr)_2NH$ (0.53 mL, 386 mg, 3.75 mmol) and *n*-BuLi (1.20 mL, 3.00 mmol) in THF (5 mL). Ketone **1** (310 mg, 2.50 mmol) was dissolved in THF (2 mL) and added to the solution. The mixture was quenched with NfF (0.59 mL, 996 mg, 3.30 mmol) and allowed to warm up to room temperature overnight. It was worked up as stated above and the crude product was purified on silica gel (hexane, then hexane : EtOAc 95 : 5) to afford **2** as a light yellow solid; yield: 737 mg (73%); mp 47–49 °C; ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 2.05$ (dd, $J = 17.5$, 1.2 Hz, 1H, 4-H_{eq}), 2.98 (ddt, $J = 17.5$, 6.3, 1.5 Hz, 1H, 4-H_{ax}), 4.95–4.98 (m, 1H, 1-H), 5.08 (dd, $J = 6.3$, 1.9 Hz, 1H, 5-H), 6.05 (dd, $J = 6.0$, 1.9 Hz, 1H, 6-H), 6.23 (dt, $J = 4.8$, 1.5 Hz, 1H, 2-H), 6.55 (dd, $J = 6.0$, 1.9 Hz, 1H, 7-H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 31.1$ (t, C-4), 74.5 (d, C-1), 76.8 (d, C-5), 122.1 (d, C-2), 127.6 (d, C-6), 137.4 (d, C-7), 145.2 (s, C-3); IR (film): $\nu = 3080$ (=C–H), 2980–2920 (C–H), 1670 (C=C), 1410 cm^{-1} (C–O); MS (EI, 80 eV): *m/z* (%) = 406 (M^+, < 1), 377 ($M^+ - CHO$, 87), 131 (12), 77 (100), 69 (37); anal. calcd. for $C_{11}H_7F_9O_4S$ (406.2): C 32.69, H 1.25; found: C 32.33, H 1.60%.

1,5-Dimethyl-8-oxabicyclo[3.2.1]octa-2,6-dien-3-yl Nonaflate (4)

According to GP 1, LDA was prepared using $(i\text{-}Pr)_2NH$ (0.31 mL, 225 mg, 2.23 mmol) and *n*-BuLi (0.82 mL, 2.06 mmol) in THF (10 mL). Ketone **3** (261 mg, 1.71 mmol) was dissolved in THF (2 mL) and added to the solution. The mixture was quenched with NfF (0.60 mL, 1.00 g, 3.32 mmol) and allowed to warm up to room temperature overnight. It was worked up as stated above and the crude product was purified on silica gel (hexane : EtOAc 98 : 2) to afford **4** as a colorless oil; yield: 585 mg (79%). ^1H NMR ($CDCl_3$, 500 MHz): $\delta =$ 1.52 (s, 6H, 1-CH_3, 5-CH_3), 2.11 (d, $J = 17.7$ Hz, 1H, 4-H), 2.62 (dd, $J = 17.7$, 0.9 Hz, 1H, 4-H), 5.76, 6.24 (2d, $J = 5.4$ Hz, 1H each, 6-H, 7-H), 6.11 (s, 1H, 2-H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 21.4$, 24.0 (2q, 1-CH_3, 5-CH_3), 37.1 (t, C-4), 81.8, 83.4 (2 s, C-1, C-5), 125.6 (d, C-2), 131.5, 140.3 (2d, C-6, C-7), 147.3 (s, C-3); IR (film): $\nu = 3080$ (=C–H), 2980–2875 (C–H), 1660, 1425, 1380 cm^{-1}; anal. calcd. for $C_{13}H_{11}F_9O_5S$ (434.2): C 35.95, H 2.55; found: C 35.46, H 2.46%.

4-Benzyloxy-8-oxabicyclo[3.2.1]octa-2,6-dien-3-yl Nonaflate (6)

According to GP 1, LDA was prepared using $(i\text{-}Pr)_2NH$ (0.28 mL, 197 mg, 1.95 mmol) and *n*-BuLi (0.62 mL, 1.56 mmol) in THF (10 mL). Ketone **5** (300 mg, 1.30 mmol) was dissolved in THF (2 mL) and added to the solution. The mixture was quenched with NfF (0.397 mL, 668 mg, 2.21 mmol) and allowed to warm up to room temperature overnight. It was worked up as stated above and the crude product was purified on silica gel (hexane + 5% Et_3N, then hexane : EtOAc 95 : 5 + 5% Et_3N) to afford **6** as a colorless oil; yield: 177 mg (27%). ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 4.49$ (d, $J =$ 6.0 Hz, 1H, 4-H), 4.58, 4.80 (AB system, $J_{AB} = 11.8$ Hz, 1H each, OCH_2), 4.84 (dd, $J = 4.6$, 1.7 Hz, 1H, 1-H), 4.99 (dd, $J =$ 6.0, 1.9 Hz, 1H, 5-H), 6.09 (dd, $J = 6.0$, 1.9 Hz, 1H, 7-H), 6.37 (d, $J = 4.6$ Hz, 1H, 2-H), 6.69 (dd, $J = 6.0$, 1.7 Hz, 1H, 6-H), 7.29–7.42 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 73.0$ (d, C-4), 73.9 (t, OCH_2), 75.8 (d, C-1), 80.0 (d, C-5), 125.4 (d, C-2), 128.2, 128.4, 128.6, 137.3 (3d, s, Ph), 128.6 (d, C-6), 139.8 (d, C-7), 145.2 (s, C-3); MS (EI, 80 eV): *m/z* (%) = 512 (M^+, 1), 421 ($M^+ - C_7H_7$, < 1), 229 (3), 138 (3), 109 (2), 91 (Bn^+, 100), 81 (4), 69 (5), 65 (6); IR (film): $\nu = 3090–3030$ (=C–H), 2970–2870 (C–H), 1720, 1660, 1460–1420 (C=C), 1350 cm^{-1} (C–O); anal. calcd. for $C_{18}H_{13}F_9O_5S$ (512.0): C 42.20, H 2.56; found: C 41.77, H 2.43%.

4-Benzyloxy-1,5-dimethyl-8-oxabicyclo[3.2.1]octa-2,6-dien-3-yl Nonaflate (8)

According to GP 1, LDA was prepared using $(i\text{-}Pr)_2NH$ (0.42 mL, 303 mg, 3.00 mmol) and *n*-BuLi (1.04 mL, 2.60 mmol) in THF (15 mL). Ketone **7** (517 mg, 2.00 mmol) was dissolved in THF (2 mL) and added to the solution. The mixture was quenched with NfF (0.60 mL, 1.00 g, 3.32 mmol) and allowed to warm up to room temperature overnight. It was worked up as stated above and the crude product was purified on silica gel (hexane:EtOAc 98:2) to afford **8** as a light yellow oil; yield: 750 mg (70%). ^{1}H NMR (CDCl$_3$, 500 MHz): $\delta=1.45$, 1.47 (2 s, 3H each, 1-CH$_3$, 5-CH$_3$), 4.12, (s, 1H, 4-H), 4.56, 4.86 (2d, $J=11.1$ Hz, 1H each, OCH$_2$), 5.85, 6.40 (2d, $J=5.7$ Hz, 1H each, 6-H, 7-H), 6.24 (s, 1H, 2-H), 7.27–7.28 (m, 5H, Ph); ^{13}C NMR (CDCl$_3$, 125 MHz): $\delta=21.4$, 22.1 (2q, 1-CH$_3$, 5-CH$_3$), 75.6 (t, OCH$_2$), 79.0 (d, C-4), 82.9, 87.2 (2s, C-1, C-5), 128.1, 128.2, 128.4, 128.5, 137.2 (4d, s, Ph), 132.9, 142.4 (2d, C-6, C-7), 147.4 (s, C-3); MS (EI, 80 eV): *m/z* (%) = 540 (M$^+$, 2), 449 (M$^+$ – Bn, 100), 434 (M$^+$107, 32), 393 (10), 391 (71), 166 (20), 151 (90), 137 (24), 109 (42), 92 (43), 91 (Bn$^+$, 100), 65 (13); IR (film): $\nu=3090$–3030 (=C–H), 2980–2870 (C–H), 1660 (C=C), 1450, 1450, 1420, 1370 cm^{-1}; anal. calcd. for C$_{20}$H$_{17}$F$_9$O$_5$S (540.4): C 44.45, H 3.17; found: C 44.77, H 2.92%.

4-Methoxy-1,5-dimethyl-8-oxabicyclo[3.2.1]octa-2,6-dien-3-yl Nonaflate (10)

According to GP 1, LDA was prepared using (i-Pr)$_2$NH (0.53 mL, 388 mg, 3.84 mmol) and n-BuLi (1.42 mL, 3.56 mmol) in THF (10 mL). Ketone **9** (500 mg, 2.74 mmol) was dissolved in THF (5 mL) and added to the solution. The mixture was quenched with NfF (0.74 mL, 1.24 g, 4.12 mmol) and allowed to warm up to room temperature overnight. It was worked up as stated above and the crude product was purified on silica gel (hexane:EtOAc 98:2) to afford **10** as a colorless oil; yield: 791 mg (62%). ^{1}H NMR (CDCl$_3$, 500 MHz): $\delta=1.46$, 1.63 (2s, 3H each, 1-CH$_3$, 5-CH$_3$), 3.58 (s, 3H, OCH$_3$), 3.85 (s, 1H, 4-H), 5.86, 6.42 (2d, $J=5.8$ Hz, 1H each, 6-H, 7-H), 6.22 (s, 1H, 2-H); ^{13}C NMR (CDCl$_3$, 125 MHz) $\delta=21.4$, 22.2 (2q, 1-CH$_3$, 5-CH$_3$), 61.6 (q, OCH$_3$), 81.3 (d, C-4), 82.9, 87.2 (2 s, C-1, C-5), 128.4 (d, C-2), 132.7, 142.6 (2d, C-6, C-7), 147.2 (s, C-3); MS (EI, 80 eV): *m/z* (%) = 464 (M$^+$, 100), 219 (C$_4$F$_9$$^+$, 23), 182 (M$^+$ – SO$_2$C$_4$F$_9$, 23), 153 (51), 123 (13), 109 (17), 107 (21), 79 (14), 69 (21); IR (film): $\nu=3085$ (=C–H), 2990, 2870–2830 (C–H), 1660, 1420 cm^{-1}; anal. calcd. for C$_{14}$H$_{13}$F$_9$O$_5$S (464.0): C 36.22, H, 2.82; found: C 36.17, H 2.68%.

2,4-Dimethyl-8-oxabicyclo[3.2.1]octa-2,6-dien-3-yl Nonaflate (12)

According to GP 1, LDA was prepared using (i-Pr)$_2$NH (0.21 mL, 152 mg, 1.50 mmol) and n-BuLi (0.48 mL, 1.20 mmol) in THF (5 mL). Ketone **11** (152 mg, 1.00 mmol) was dissolved in THF (2 mL) and added. The mixture was quenched with NfF (0.25 mL, 421 mg, 1.32 mmol) and allowed to warm up to room temperature overnight. It was worked up as stated above and the crude product was purified on silica gel (hexane:EtOAc 95:5) to afford **12** as a light yellow oil; 371 mg (85%). ^{1}H NMR (CDCl$_3$, 270 MHz): $\delta=0.96$ (d, $J=7.4$ Hz, 3H, 4-CH$_3$), 1.82 (d, $J=2.4$ Hz, 3H, 2-CH$_3$), 3.07–3.20 (m, 1H, 4-H), 4.68 (br d, $J\approx1.5$ Hz, 1H, 1-H), 4.99 (dd, $J=6.2$, 1.8 Hz, 1H, 5-H), 6.06 (dd, $J=6.0$, 1.8 Hz, 1H, 6-H), 6.69 (dd, $J=6.0$, 1.7 Hz, 1H, 7-H); ^{13}C NMR (CDCl$_3$, 68 MHz): $\delta=9.9$ (q, 4-CH$_3$), 13.4 (q, 2-CH$_3$), 35.7 (d, C-4), 79.8 (d, C-1), 82.4 (d, C-5), 128.1 (d, C-6), 132.4 (s, C-2), 138.4 (d, C-7), 143.0 (s, C-3); IR (film) $\nu=3050$ (=C–H), 2970–2830 (C–H), 1680 (C=C), 1420, 1350 cm^{-1} (R-SO$_2$-OR); MS (EI, 80 eV). *m/z* (%) = 434 (M$^+$, 3), 419 (M$^+$ – CH$_3$, 3), 405 (M$^+$ – CHO, 26), 326 (20), 219 (C$_4$F$_9$$^+$, 4), 151 (C$_9H_{10}O_2$$^+$, 7), 134 (21), 121 (23), 106 (15), 105 (100), 95 (70), 91 (11), 79 (12), 69 (CF$_3$$^+$, 35), 67 (16), 55 (14), 43 (39); anal. calcd. for C$_{13}$H$_{11}$F$_9$O$_4$S (434.1): C 35.95, H 2.55; found: C 35.95, H 2.39%.

2,4-Dimethyl-8-oxabicyclo[3.2.1]oct-2-en-3-yl Nonaflate (14)

According to GP 1, LDA was prepared using (i-Pr)$_2$NH (1.36 mL, 981 mg, 9.72 mmol) and n-BuLi (3.12 mL, 7.80 mmol) in THF (5 mL). Ketone **13** (1.00 g, 6.50 mmol) was dissolved in THF (2 mL) and added. The mixture was quenched with NfF (1.56 mL, 2.59 g, 8.58 mmol) and allowed to warm up to room temperature overnight. It was worked up as stated above and the crude product was purified on silica gel (hexane + 5% Et$_3$N, then hexane:EtOAc 95:5 + 5% Et$_3$N) to afford **14** as a light yellow solid; yield: 2.60 g (92%); mp 35–37 °C. ^{1}H NMR (CDCl$_3$, 500 MHz): $\delta=1.02$ (d, $J=7.1$ Hz, 3H, 4-CH$_3$), 1.73 (d, $J=2.5$ Hz, 3H, 2-CH$_3$), 1.86–2.01 (m, 4H, 6-H, 7-H), 3.22 (m$_c$, 1H, 4-H), 4.40 (d, $J=5.2$ Hz, 1H, 1-H), 4.44–4.49 (m, 1H, 5-H); ^{13}C NMR (CDCl$_3$, 125 MHz): $\delta=11.3$ (q, 4-CH$_3$), 13.2 (q, 2-CH$_3$), 22.9 (t, C-6), 32.7 (t, C-7), 38.4 (d, C-4), 77.1 (d, C-1), 79.3 (d, C-5), 130.3 (s, C-2), 143.9 (s, C-3); IR (KBr): $\nu=3005$ (=C–H), 2990–2890 (C–H), 1705 (C=C), 1410 cm^{-1} (C–O); MS (EI, 80 eV): *m/z* (%) = 436 (M$^+$, 2), 329 (M$^+$ – 77, 2), 219 (4), 153 (48), 125 (15), 109 (13), 97 (100), 95 (11), 85 (16), 69 (19), 55 (11); anal. calcd. for C$_{13}$H$_{13}$F$_9$O$_4$S (436.0): C 35.79, H 3.00; found: C 35.81, H 2.85%.

8-Thiabicyclo[3.2.1]oct-2-en-3-yl Nonaflate (16)

According to GP 1, LDA was prepared using (i-Pr)$_2$NH (0.74 mL, 534 mg, 5.25 mmol) and n-BuLi (1.68 mL, 4.20 mmol) in THF (5 mL). Ketone **15** (500 mg, 3.50 mmol) was dissolved in THF (2 mL) and added. The mixture was quenched with NfF (0.83 mL, 1.40 g, 4.62 mmol) and allowed to warm up to room temperature overnight. It was worked up as stated above and the crude product was purified on silica gel (hexane:EtOAc 95:5) to afford **16** as a light yellow oil; yield: 1.41 g (95%). ^{1}H NMR (CDCl$_3$, 500 MHz) $\delta=1.93$–2.20 (m, 2H, 6-H, 7-H), 2.23–2.55 (m, 3H, 4-H$_{eq}$, 6-H, 7-H), 2.93 (br d, $J\approx17$ Hz, 1H, 4-H$_{ax}$), 3.76–3.85 (m 1H, 1-H), 3.96–4.02 (m, 1H, 5-H), 6.29 (d, $J=7.4$ Hz, 1H, 2-H); ^{13}C NMR (CDCl$_3$, 125 MHz): $\delta=34.3$ (t, C-6), 40.5 (t, C-7), 41.2 (t, C-4), 42.7 (d, C-1), 45.2 (d, C-5), 125.3 (d, C-2), 149.2 (s, C-3); IR (film): $\nu=2970$–2830 (C–H), 1680 (C=C), 1420, 1350 cm^{-1} (R-SO$_2$-OR); MS (EI, 80 eV): *m/z* (%) = 424 (M$^+$, 26), 326 (M$^+$ – C$_2$F$_4$, 14), 219 [C$_4$F$_9$$^+$, 5], 141 (C$_7H_9OS^+$, 100), 113 (24), 69 (CF$_3$$^+$, 19); anal. calcd. for C$_{11}$H$_9$F$_9$O$_3$S$_2$ (424.3): C 31.13, H 2.11; found: C 31.11, H 2.02%.

Methyl (*E*)-3-[1,5-Dimethyl-8-oxabicyclo[3.2.1]octa-2,6-dien-3-yl]propenoate (17)

According to GP 2, nonaflate **4** (160 mg, 0.37 mmol) was dissolved in DMF (2 mL). LiCl (47 mg, 1.11 mmol), Et$_3$N (0.04 mL, 0.37 mmol), methyl acrylate (0.03 mL, 32 mg, 0.37 mmol) and Pd(OAc)$_2$ (4 mg, 0.02 mmol) were added. The mixture was stirred for 18 h at 70 °C and worked up as stated above. The crude product was purified on silica gel (hexane:EtOAc 95:5, then 90:10) to afford **17** as a light yellow oil; yield: 56 mg (69%). ^{1}H NMR (CDCl$_3$, 500 MHz): $\delta = 1.45$, 1.47 (2 s, 3H each, 1-CH$_3$, 5-CH$_3$), 1.19, 2.35 (2d, $J = 17.4$ Hz, 1H each, 4-H), 3.70 (s, 3H, OCH$_3$), 5.72, 6.14 (2d, $J = 5.5$ Hz, 1H each, 6-H, 7-H), 5.80, 7.18 (2d, $J = 15.9$ Hz, 1H each, CH=CH), 6.34 (s, 1H, 2-H); ^{13}C NMR (CDCl$_3$, 125 MHz): $\delta = 21.2$, 24.5 (2q, 1-CH$_3$, 5-CH$_3$), 32.8 (t, C-4), 51.4 (q, OCH$_3$), 82.4, 83.0 (2s, C-1, C-5), 115.3, 146.5 (2d, CH=CH), 132.5 (s, C-3), 132.6, 142.9 (2d, C-6, C-7), 139.5 (d, C-2), 167.4 (s, CO); MS (pos. FAB): *m/z* (%) = 221 (MH$^+$, 16), 205 (12), 203 (11), 177 (21), 165 (14), 163 (11), 161 (100), 147 (14), 145 (23); IR (film): $\nu = 3070$–3020 (=C–H), 2970–2870 (C–H), 1719 (C=O), 1625 (C=C), 1450, 1440, 1380 cm^{-1}.

Methyl (*E*)-3-[4-Benzyloxy-1,5-dimethyl-8-oxabicyclo[3.2.1]octa-2,6-dien-3-yl]propenoate (18)

According to GP 2, nonaflate **8** (200 mg, 0.37 mmol) was dissolved in DMF (2 mL). LiCl (47 mg, 1.11 mmol), Et$_3$N (0.05 mL, 0.37 mmol), methyl acrylate (0.03 mL, 38 mg, 0.44 mmol) and Pd(OAc)$_2$ (5 mg, 0.02 mmol) were added. The mixture was stirred for 18 h at 70 °C and worked up as stated above. The crude product was purified on silica gel (hexane:EtOAc 95:5, then 90:10) to afford **18** as a light yellow oil; yield: 87 mg (72%). ^{1}H NMR (CDCl$_3$, 500 MHz): $\delta = 1.44$, 1.65 (2s, 6H, 1-CH$_3$, 5-CH$_3$), 3.72 (s, 3H, OCH$_3$), 4.24 (s, 1H, 4-H), 4.57, 4.62 (2d, $J = 11.3$ Hz, 1H each, OCH$_2$), 5.90, 6.33 (2d, $J = 5.7$ Hz, 1H each, 6-H, 7-H), 6.07, 7.17 (2d, $J = 16.0$ Hz, 1H each, CH=CH), 6.57 (s, 1H, 2-H), 7.26–7.36 (m, 5H, Ph); ^{13}C NMR (CDCl$_3$, 125 MHz): $\delta = 21.3$, 23.5 (2q, 1-CH$_3$, 5-CH$_3$), 51.5 (q, OCH$_3$), 72.6 (t, OCH$_2$), 77.1 (d, C-4), 83.1, 86.6 (2 s, C-1, C-5), 118.2 (d, CH=CH), 127.4, 127.6, 128.4 (3d, Ph), 133.5, 141.3 (2d, C-6, C-7), 133.9, 137.9 (2s, C-3, Ph), 144.0, 144.1 (2d, C-2, CH=CH), 167.4 (s, CO); MS (EI, 80 eV): *m/z* (%) = 326 (M$^+$, <1), 161 (11), 109 (11), 96 (C$_6$H$_8$O$^+$, 27), 91 (C$_7$H$_7^+$, 100), 43 (35); IR (film): $\nu = 3070$, 3030 (=C–H), 2980, 2930, 2870 (C–H), 1720 (C=O), 1630 (C=C), 1450, 1440, 1380 cm^{-1}; HRMS (80 eV): calcd. for (C$_{20}$H$_{22}$O$_4$) M$^+$: 326.15322; found: 326.15179.

Methyl (*E*)-3-[4-Methoxy-1,5-dimethyl-8-oxabicyclo[3.2.1]octa-2,6-dien-3-yl]propenoate (19)

According to GP 2, nonaflate **10** (200 mg, 0.43 mmol) was dissolved in DMF (2 mL). LiCl (54 mg, 1.29 mmol), Et$_3$N (0.06 mL, 0.43 mmol), methyl acrylate (0.03 mL, 37 mg, 0.43 mmol) and Pd(OAc)$_2$ (5 mg, 0.02 mmol) were added. The mixture was stirred for 18 h at 70 °C and worked up as stated above. The crude product was purified on silica gel (hexane:EtOAc 95:5, then 90:10) to afford **19** as a light yellow oil; yield: 81 mg (75%). ^{1}H NMR (CDCl$_3$, 500 MHz): $\delta = 1.43$, 1.63 (2 s, 3H each, 1-CH$_3$, 5-CH$_3$), 3.43, 3.74 (2 s, 3H each, OCH$_3$), 3.97 (s, 1H, 4-H), 5.90, 6.31 (2d, $J = 5.7$ Hz, 1H each, 6-H, 7-H), 6.00, 7.14 (2d, $J = 15.9$ Hz, 1H each, CH=CH), 6.55 (s, 1H, 2-H); ^{13}C NMR (CDCl$_3$, 125 MHz): $\delta = 21.3$, 23.4 (2q, 1-CH$_3$, 5-CH$_3$), 51.5, 58.6 (2q, OCH$_3$), 78.2 (d, C-4), 83.1, 86.5 (2s, C-1, C-5), 117.8, 141.1 (2d, C-6, C-7), 133.4, 144.3 (2d, CH=CH), 133.9 (s, C-3), 144.7 (d, C-2), 167.5 (s, CO); MS (EI, 80 eV): *m/z* (%) = 250 (M$^+$, 2), 145 (14), 109 (25), 96 (C$_6$H$_8$O$^+$, 100), 43 (40); IR (film) $\nu = 3080$ (=C–H), 2980, 2950, 2940, 2830 (C–H), 1720 (C=O), 1630 (C=C), 1440 cm^{-1}; HRMS (80 eV): calcd. for M$^+$: 250.12051; found: 250.12166.

Methyl (*E*)-3-[8-Oxabicyclo[3.2.1]octa-2,6-dien-3-yl]propenoate (20)

According to GP 2, nonaflate **2** (300 mg, 0.74 mmol) was dissolved in DMF (2 mL). LiCl (47 mg, 1.11 mmol), Et$_3$N (0.15 mL, 1.04 mmol), methyl acrylate (0.09 mL, 89 mg, 1.04 mmol) and Pd(OAc)$_2$ (8 mg, 0.04 mmol) were added. The mixture was stirred for 17 h at 60 °C and worked up as stated above. The crude product was purified on silica gel (hexane:EtOAc 95:5, 90:10, and finally 80:20) to afford **20** (24 mg, 17%) and **21** (21 mg, 10%).

Alternative procedure: Nonaflate **2** (200 mg, 0.50 mmol), (*n*-Bu)$_4$NCl (139 mg, 0.50 mmol) and K$_2$CO$_3$ (173 mg, 1.25 mmol) were dissolved in DMF (2 mL). Methyl acrylate (0.18 mL, 129 mg, 1.50 mmol) and Pd(OAc)$_2$ (8 mg, 0.04 mmol) were added and the mixture was stirred at room temperature for 3 d. Additional Pd(OAc)$_2$ (8 mg, 0.04 mmol) was added and the mixture was stirred for further 24 h. The reaction mixture was taken up in EtOAc and washed three times with water and once with brine. The aqueous phases were reextracted with EtOAc once. The combined organic phases were dried with MgSO$_4$ and the solvent was removed under vacuum. The crude product was purified on silica gel (hexane:EtOAc 95:5, 90:10, and finally 80:20) to afford **20** (24 mg, 25%) and starting material **2** (20 mg, 5%) as light yellow oils. ^{1}H NMR (CDCl$_3$, 500 MHz): $\delta = 1.84$–1.90 (m, 1H, 4-H$_{eq}$), 2.71–2.77 (m, 1H, 4-H$_{ax}$), 3.74 (s, 3H, OCH$_3$), 4.85–4.87 (m, 1H, 1-H), 5.04 (dd, $J = 6.2$, 1.9 Hz, 1H, 5-H), 5.80, 7.18 (2d, $J = 15.8$ Hz, 1H each, CH=CH), 6.05 (dd, $J = 6.0$, 1.9 Hz, 1H, 6-H), 6.48–6.51 (m, 2H, 2-H, 7-H); ^{13}C NMR (CDCl$_3$, 125 MHz): $\delta = 26.4$ (t, C-4), 51.5 (q, OCH$_3$), 75.7 (d, C-1), 77.1 (d, C-5), 115.3 (d, CH=CH), 128.8 (d, C-6), 130.7 (s, C-3), 136.6 (d, C-2), 138.9 (d, C-7), 146.8 (d, CH=CH), 167.5 (s, CO); IR (film): $\nu = 3090$ (=C–H), 2950–2850 (C–H), 1730 (C=O), 1650, 1630 (C=C), 1440 cm^{-1}; anal. calcd. for C$_{11}$H$_{12}$O$_3$ (192.2): C 68.74, H 6.29; found: C, 66.30; H, 6.38%. A satisfactory elemental analysis and mass spectrum could not be obtained due to the small amount of product and its fast decomposition/polymerization.

Dimethyl 12-Oxatricyclo[7.2.1.0^{2,7}]dodeca-6,10-diene-4,5-dicarboxylate (21)

^{1}H NMR (CDCl$_3$, 500 MHz): $\delta = 1.73$ (q, $J \approx 12.5$ Hz, 1H, 3-H), 2.13 (ddd, $J = 12.3$, 4.5, 3.2 Hz, 1H, 3-H), 2.20 (dd, $J = 15.6$, 1.0 Hz, 1H, 8-H$_{ax}$), 2.24–2.30 (m, 1H, 2-H), 2.58 (ddd, $J = 15.6$, 8.0, 1.0 Hz, 1H, 8-H$_{eq}$), 2.99 (ddd, $J = 13.2$, 10.2, 3.1 Hz, 1H, 4-H), 3.61 (ddd, $J = 10.2$, 6.5, 3.5 Hz, 1H, 5-H), 3.69, 3.71 (2s, 3H each, OCH$_3$), 4.40 (br s, 1H, 1-H), 4.81 (d,

$J = 8.0$ Hz, 1H, 9-H), 5.40–5.43 (m, 1H, 6-H), 6.28 (br s, 2H, 10-H, 11-H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 32.3 (t, C-3), 33.2 (t, C-8), 38.9 (d, C-2), 41.7 (d, C-4), 44.2 (d, C-5), 52.0, 52.1 (2q, OCH_3), 76.7 (d, C-9), 81.4 (d, C-1), 121.7 (d, C-6), 134.2, 136.0 (2d, C-10, C-11), 138.2 (s, C-7), 173.4, 174.5 (2 s, CO); MS (EI, 80 eV): *m/z* (%) = 278 (M^+, 13), 247 ($M^+ - CH_3O$, 11), 246 (38), 219 ($M^+ - C_2H_3O_2$, 35), 218 (79), 159 (44), 150 (28), 91 (100), 81 (45), 59 (23); IR (film): ν = 3020 (=C–H), 2950 (C–H), 1740 (C=O), 1440 cm^{-1}; HRMS (80 eV): calcd. for M^+: 278.11543; found: 278.11494.

(*E*)-4-Benzyloxy-1,5-dimethyl-3-(2-phenylethenyl)-8-oxabicyclo[3.2.1]octa-2,6-diene (22)

Nonaflate **8** (224 mg, 0.41 mmol) was dissolved in DMF (3 mL). Et_3N (0.20 mL, 1.45 mmol), styrene (0.04 mL, 55 mg, 0.53 mmol), and $Pd(PPh_3)_4$ (27 mg, 0.02 mmol) were added. The mixture was stirred in a closed flask for 18 h at 60 °C. The mixture was taken up with EtOAc and the organic layer was washed three times with water and once with brine. The solvent was removed under vacuum and the crude product was purified on silica gel (hexane:EtOAc 95:5, then 90:10) to afford **22** as a yellow oil; yield: 37 mg (26%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.46, 1.69, (2s, 3H each, 1-CH_3, 5-CH_3), 4.35 (s, 1H, 4-H), 4.59, 4.69 (2d, $J = 11.5$ Hz, 1H each, OCH_2) 5.93 (d, $J = 5.6$ Hz, 1H, 6/7-H), 6.36–6.39 (m, 2H, 6/7-H, 2-H), 6.58, 6.78 (2d, $J = 16.2$ Hz, 1H each, CH=CH), 7.25–7.35 (m, 10H, Bn, Ph); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.7, 23.5 (2q, 1-CH_3, 5-CH_3), 72.3 (t, OCH_2), 77.7 (d, C-4), 83.1, 86.6 (2s, C-1, C-5), 126.3, 127.4, 127.5, 127.6, 128.4, 128.5 (6d, Ph), 128.0, 129.0 (2d, CH=CH), 128.8, 141.9 (2d, C-6, C-7), 135.3, 137.5, 138.4 (3s, Ph, C-3), 136.7 (d, C-2); MS (EI, 80 eV): *m/z* (%) = 344 (M^+, <1), 105 (15), 91 ($C_7H_7^+$, 100), 78 (22), 65 (10), 51 (14), 43 (58); IR (film): ν = 3060, 3030 cm (=C–H), 2980, 2930, 2870 (C–H), 1720, 1690 (C=C), 1630, 1490, 1450 cm^{-1}; HRMS (80 eV): calcd. for $(C_{24}H_{24}O_2)_n$ M^+: 344.17764; found: 344.17844.

Methyl (*E*)-3-[2,4-Dimethyl-8-oxabicyclo[3.2.1]octa-2,6-dien-3-yl]propenoate (23)

According to GP 2, nonaflate **12** (434 mg, 1.00 mmol) was dissolved in DMF (2 mL). LiCl (64 mg, 1.50 mmol), Et_3N (0.20 mL, 1.40 mmol), methyl acrylate (0.13 mL, 129 mg, 1.50 mmol) and $Pd(OAc)_2$ (11 mg, 0.05 mmol) were added. The mixture was stirred for 17 h at 60 °C and worked up as stated above. The crude product was purified on silica gel (hexane:EtOAc 95:5, 90:10) to afford **23** as a colorless solid; yield: 176 mg (79%); mp 82–84 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.88 (d, $J = 7.3$ Hz, 3H, 4-CH_3), 1.94 (d, $J = 1.7$ Hz, 3H, 2-CH_3), 2.76–2.89 (m, 1H, 4-H), 3.75 (s, 3H, OCH_3), 4.57 (d, $J = 1.7$ Hz, 1H, 1-H), 4.89 (dd, $J = 6.2$, 1.6 Hz, 1H, 5-H), 5.73, 7.57 (2d, $J = 16.1$ Hz, 1H each, CH=CH), 6.14 (dd, $J = 6.0$, 1.6 Hz, 1H, 6-H), 6.58 (dd, $J = 6.0$, 1.7 Hz, 1H, 7-H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 12.3 (q, 4-CH_3), 16.5 (q, 2-CH_3), 29.7 (d, C-4), 51.5 (q, OCH_3), 81.4 (d, C-1), 81.9 (d, C-5), 116.6 (d, CH=CH), 128.3 (s, C-3), 129.4 (d, C-6), 136.3 (d, C-7), 141.1 (s, C-2), 144.8 (d, CH=CH), 167.9 (s, CO); MS (EI, 80 eV): *m/z* (%) = 220 (M^+, 5), 205 ($M^+ - CH_3$, 4), 192 (19), 191 ($M^+ - CHO$, 100), 189 ($M^+ - CH_3O$, 6), 177 (5), 161 (189 – CO, 6), 159 (11), 121 (64), 117 (16), 103 (15), 89 (16), 87 (11), 67 (38), 63 (20); IR (KBr): ν = 3070–3015 (=C–H), 2970–2880 (C–H), 1710 (C=O), 1710–1610 cm^{-1} (C=C); HRMS (80 eV): calcd. for $(C_{13}H_{16}O_3)$ M^+: 220.10755; found: 220.10995.

Methyl (*E*)-3-[2,4-Dimethyl-8-oxabicyclo[3.2.1]oct-2-en-3-yl]propenoate (24)

According to GP 2, nonaflate **14** (436 mg, 1.00 mmol) was dissolved in DMF (2 mL). LiCl (64 mg, 1.50 mmol), Et_3N (0.21 mL, 1.50 mmol), methyl acrylate (0.13 mL, 129 mg, 1.50 mmol) and $Pd(OAc)_2$ (15 mg, 0.07 mmol) were added. The mixture was stirred for 17 h at 60 °C and worked up as stated above. The crude product was purified on silica gel (hexane then hexane:EtOAc 95:5) to afford **24** as a colorless solid; yield: 215 mg (97%); mp 45–47 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.94 (d, $J = 7.1$ Hz, 3H, 4-CH_3), 1.85 (d, $J = 1.9$ Hz, 3H, 2-CH_3), 1.93–2.04 (m, 4H, 6-H, 7-H), 3.07 (m_c, 1H, 4-H), 3.75 (s, 3H, OCH_3), 4.28 (d, $J = 5.7$ Hz, 1H, 1-H), 4.41 (t, $J = 5.7$ Hz, 1H, 5-H), 5.75, 7.55 (2d, $J = 16.1$ Hz, 1H each, CH=CH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.5 (q, 4-CH_3), 16.2 (q, 2-CH_3), 23.3 (t, C-6), 32.1 (t, C-7), 34.9 (d, C-4), 51.4 (q, OCH_3), 77.9 (d, C-1), 78.5 (d, C-5), 117.7 (d, CH=CH), 128.4 (s, C-2), 140.8 (d, CH=CH), 144.7 (s, C-3), 167.8 (s, CO); MS (EI, 80 eV): *m/z* (%) = 222 (M^+, 100), 207 ($M^+ - CH_3$, 8), 191 ($M^+ - OCH_3$, 27), 179 (207 – CO, 46), 163 (191 – CO, 26), 151 (11), 147 (40), 145 (37), 135 (24), 133 (34), 125 (56), 121 (18), 119 (60), 107 (25), 105 (34), 95 (16), 93 (21), 91 (39), 79 (23), 77 (23), 74 (13); IR (KBr): ν = 3080 (=C–H), 2990–2850 (C–H), 1720 (C=O), 1620 (C=C), 1440 cm^{-1}; HRMS (80 eV): calcd. for $(C_{13}H_{18}O_3)$ M^+: 222.12559; found: 222.12733.

Methyl (*E*)-3-[8-Thiabicyclo[3.2.1]oct-2-en-3-yl]propenoate (25)

According to GP 2, nonaflate **16** (423 mg, 1.00 mmol) was dissolved in DMF (2 mL). LiCl (64 mg, 1.50 mmol), Et_3N (0.21 mL, 1.50 mmol), methyl acrylate (0.13 mL, 129 mg, 1.50 mmol) and $Pd(OAc)_2$ (11 mg, 0.05 mmol) were added. The mixture was stirred for 17 h at 70 °C. Another 5 mol % of $Pd(OAc)_2$ were added and the mixture was stirred for 2 d. The mixture was worked up as stated above. The crude product was purified on silica gel (hexane:EtOAc 95:5) to afford **25** as a light yellow solid; yield: 121 mg (58%); mp 47–49 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.89, 2.12 (2 m_c, 1H each, 6-H, 7-H), 2.22 (ddd, $J = 17.3$, 2.3, 1.8 Hz, 1H, 4-H), 2.25–2.32, 2.32–2.37 (2 m, 1H each, 6-H, 7-H), 2.78 (dd, $J = 17.3$, 1.9 Hz, 1H, 4-H), 3.73 (s, 3H, OCH_3), 3.78 (dd, $J = 7.3$, 5.5 Hz, 1H, 1-H), 3.92–4.00 (m, 1H, 5-H), 5.75, 7.18 (2d, $J = 15.9$ Hz, 1H each, CH=CH), 6.60 (d, $J = 7.3$ Hz, 1H, 2-H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 34.6 (t, C-6), 37.5 (t, C-4), 39.6 (t, C-7), 43.9 (d, C-1), 45.1 (d, C-5), 51.5 (q, OCH_3), 115.4 (d, CH=CH), 132.5 (s, C-3), 142.9 (d, C-2), 147.3 (d, CH=CH), 167.5 (s, CO); MS (EI, 80 eV): *m/z* (%) = 210 (M^+, 100), 181 (18), 177 ($M^+ - SH$, 19), 167 (19), 151 ($M^+ - CO_2CH_3$, 26), 145 (19), 137 (12), 123 (13), 117 (151 – H_2S, 27), 115 (11), 111 ($M^+ - C_5H_7S$, 95), 91 (22), 85 (20), 59 ($CO_2CH_3^+$, 13), 45 (13), 41 (12), 39 (16); IR (KBr): ν = 3060–3020 (=C–H), 2990–2820 (C–H), 1720 (C=O), 1620, 1610 cm^{-1} (C=C); anal. calcd. for $C_9H_{14}O_2S$ (210.1): C 62.83, H 6.71; found: C 63.09, H 6.52%.

2-(2-Propynyl)furan (26) and 2-(1,2-Propadienyl)furan (27)

NMR Experiment: Nonaflate **2** (32 mg, 0.08 mmol) and K_2CO_3 (11 mg, 0.08 mmol) were dissolved in DMSO-d_6 (0.8 mL). The mixture was heated in an NMR tube for 2 d to 70 °C. Signals for **26** as the major component and **27** as the minor component were observed (ratio 9:1).

26: ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 2.99 (t, J = 2.7 Hz, 1H, 3′-H), 3.63–3.65 (m, 2H, 1′-H), 6.21–6.23, 6.37–6.39, 7.54–7.56 (3m, 1H each, 3-H, 4-H, 5-H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 18.1 (t, C-1′), 72.8 (d, C-3′), 80.2 (s, C-2′), 106.8, 111.1, 142.7, 150.2 (3d, s, C-3, C-4, C-5, C-2).

27: ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 5.30 (d, J = 6.9 Hz, 2H, 3′-H), 6.31–6.33 (m, 1H, 3-H), 6.36 (d, J = 6.9 Hz, 1H, 1′-H), 6.49 (dd, J = 3.2, 1.9 Hz, 1H, 4-H), 7.58–7.59 (m, 1H, 5-H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 80.4 (t, C-3′), 85.1 (d, C-1′), 112.2, 142.7, 143.2 (3d, C-3, C-4, C-5); the signals of C-2′ and C-2 are missing.

2-(1-Methyl-2-butynyl)furan (28) and 2-(1-Methyl-1,2-butadienyl)furan (29)

Nonaflate **12** (423 mg, 0.97 mmol) was dissolved in DMF (1 mL). Et_3N (0.21 mL, 1.50 mmol) and LiCl (64 mg, 1.50 mmol) were added. The mixture was stirred for 4 d at 60 °C. The reaction mixture was taken up in Et_2O and extracted with water and brine. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under vacuum (60 mbar/40 °C). After column chromatography on silica gel (hexane) **28** was obtained as a colorless liquid that changed color to yellow after a few days at 6 °C; yield: 121 mg (61%).

28: ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 1.68 (d, J = 7.0 Hz, 3H, 1′-CH$_3$), 1.83 (d, J = 2.5 Hz, 3H, 4′-H), 3.77 (m$_c$, 1H, 1′-H), 6.14–6.16 (m, 1H, 3-H), 6.29 (dd, J = 3.2, 1.8 Hz, 1H, 4-H), 7.32–7.34 (m, 1H, 5-H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ = 3.6 (q, C-4′), 20.7 (q, 1′-CH$_3$), 25.8 (d, C-1′), 76.8, 79.5 (2s, C-2′, C-3′), 104.5, 110.2, 141.5, 156.3 (3d, s, C-3, C-4, C-5, C-2); MS (EI, 80 eV): m/z (%) = 134 (M$^+$, 65), 119 (M$^+$ – CH$_3$, 100), 91 (119 – CO, 38), 65 (91 – C_2H_2, 24), 43 (31), 28 ($C_2H_4^+$, 27); IR (film): ν = 3120 (=C–H), 2980–2880 (C–H), 2250 (C≡C), 1720, 1600 cm^{-1} (C=C); HRMS (80 eV): calcd. for ($C_9H_{10}O$) M$^+$: 134.07317; found: 134.07563.

NMR-Experiment: Nonaflate **12** (50 mg, 0.11 mmol) and K_2CO_3 (18 mg, 0.13 mmol) were dissolved in DMSO-d_6 (0.8 mL). The mixture was heated in an NMR tube for 2 d to 70 °C. Signals for **28** as the major component and **29** as the minor component were observed (ratio 10:1).

29: ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 1.76 (d, J = 7 Hz, 3H, 4′-H), 1.98 (d, J = 0.8 Hz, 3H, 1′-CH$_3$), 5.48 (m$_c$, 1H, 3′-H), 6.15 (m$_c$, 1H, 3-H), 6.37 (dd, J = 3.3, 1.8 Hz 1H, 4-H), 7.34–7.36 (m, 1H, 5-H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 14.1 (q, C-4′), 22.6 (q, 1′-CH$_3$), 88.8 (d, C-3′), 105.7, 105.8, 111.2, 141.4 (d, s, 2d, C-3, C-1′, C-4, C-5), 141.7 (s, C-2), 209.7 (s, C-2′).

Methyl 4,6-Dioxo-5-phenyl-15-thia-5-azatetracyclo[10.2.1.0.^{2,10}0^{3,7}]pentadec-9-ene-8-carboxylate (*exo*-30)

Diene **25** (138 mg, 0.66 mmol) and N-phenylmaleimide (137 mg, 0.79 mmol) were dissolved in toluene (5 mL) and the mixture was heated in a closed flask for 6 d to 130 °C. The solvent was removed under vacuum and the resulting crude product was purified on silica gel (hexane:EtOAc 90:10) to afford *exo*-**30** as a colorless solid; yield: 215 mg (85%); mp 187–190 °C; ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 1.91–2.01, 2.10–2.20, 2.30–2.38 (3m, 2H, 1H, 2H, 13-H, 14-H, 2-H), 2.59, 2.99 (2br d, J ≈ 17 Hz, 1H each, 11-H), 3.10 (t, J = 10.0 Hz, 1H, 3-H), 3.11–3.16 (m, 1H, 8-H), 3.57 (t, J = 10.0 Hz, 1H, 7-H), 3.62 (t, J = 6.1 Hz, 1H, 12-H), 3.82 (s, 3H, OCH$_3$), 4.46 (d, J = 7.1 Hz, 1H, 1-H), 5.68 (br s, 1H, 9-H), 7.30–7.50 (m, 5H, Ph); ^{13}C NMR (CDCl$_3$, 125 MHz): δ = 34.4 (t, C-14), 36.7 (t, C-13), 39.7 (t, C-11), 41.6 (d, C-8), 42.8 (d, C-7), 43.6 (d, C-12), 43.7 (d, C-3), 46.7 (d, C-1), 47.2 (d, C-2), 52.7 (q, OCH$_3$), 124.3 (d, C-9), 126.3, 128.2, 129.0, 129.1 (2d, s, d, Ph), 137.3 (s, C-3), 173.4, 176.4, 177.1 (3s, CO); MS (EI, 80 eV): m/z (%) = 383 (M$^+$, 98), 351 (M$^+$ – S, 23), 324 (M$^+$ – $C_2H_3O_2$, 12), 299 (M$^+$ – $C_5H_{10}N$, 100), 267 (33), 239 (22), 92 (33), 85 (31); IR (KBr): ν = 2940–2900, 2830 (C–H), 1780, 1745, 1740 (C=O), 1710 (C=C), 1590, 1500, 1490, 1450, 1440, 1380 cm^{-1}; HRMS (80 eV): calcd. for ($C_{21}H_{23}NO_4S$) M$^+$: 383.11913; found: 383.11786.

Methyl 11-Methoxy-1,12-dimethyl-4,6-dioxo-5-phenyl-15-oxa-5-azatetracyclo[10.2.1.0.^{2,10}0^{3,7}]pentadeca-9,13-diene-8-carboxylate (*endo*-31)

Compound **19** (78 mg, 0.31 mmol) and N-phenylmaleimide (54 mg, 0.31 mmol) were dissolved in toluene (3 mL) and the mixture was heated in a closed flask for 6 d to 110 °C. The solvent was removed under vacuum and the resulting crude product was purified on silica gel (hexane:EtOAc 90:10, then 80:20) to afford *endo*-**31** as a colorless solid; yield: 91 mg (69%); mp 235–237 °C. ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 1.47, 1.83 (2s, 3H each, 1-CH$_3$, 12-CH$_3$), 2.23 (m$_c$, 1H, 2-H), 3.16 (m$_c$, 1H, 8-H), 3.53 (dd, J = 8.6, 5.6 Hz, 1H, 3-H), 3.62, 3.83 (2s, 3H each, OCH$_3$), 3.68 (dd, J = 5.1, 2.1 Hz, 1H, 11-H), 3.92 (dd, J = 8.6, 5.2 Hz, 1H, 7-H), 6.02, 6.03 (AB system, J_{AB} = 5.8 Hz, 2H, 13-H, 14-H), 6.66 (dt, J = 4.1, 2.0 Hz, 1H, 9-H), 7.18–7.22, 7.31–7.35, 7.38–7.43 (3m, 2H, 1H, 2 H, Ph); ^{13}C NMR (CDCl$_3$, 125 MHz): δ = 20.7, 21.9 (2q, 1-CH$_3$, 12-CH$_3$), 40.4 (d, C-3), 41.3 (d, C-8), 43.9 (d, C-2), 44.9 (d, C-7), 52.4, 61.9 (2q, OCH$_3$), 84.3, 86.3 (2s, C-1, C-12), 126.1, 128.4, 128.9 (3d, Ph), 126.3 (d, C-9), 131.7, 141.0 (2s, C-10, Ph), 134.1, 140.4 (2d, C-13, C-14), 170.7, 174.6, 175.4 (3s, CO); MS (EI, 80 eV): m/z (%) = 423 (M$^+$, 5), 327 (M$^+$ – C_6H_8O, 42), 299 (62), 284 (33), 180 (14), 175 (15), 165 (16), 142 (11), 128 (10), 121 (100), 105 (119), 96 ($C_6H_8O^+$, 15), 77 (22); IR (KBr): ν = 3070 (=C–H), 2980–2840 (C–H), 1740, 1720 (C=O), 1590, 1490, 1450, 1440 cm^{-1} (C=C); HRMS (80 eV): calcd. for ($C_{24}H_{25}NO_6$) M$^+$: 423.16818; found: 423.16733.

Dimethyl 8-Methoxy-1,9-dimethyl-12-oxatricyclo[7.2.1.0^{2,7}]dodeca-6,10-diene-4,5-dicarboxylates (32a) and (32b)

Nonaflate **10** (700 mg, 1.51 mmol) was dissolved in DMF (4 mL). LiCl (192 mg, 4.52 mmol), Et_3N (0.30 mL, 2.11 mmol), methyl acrylate (0.19 mL, 181 mg, 2.11 mmol) and $Pd(OAc)_2$ (17 mg, 0.08 mmol) were added. The mixture was stirred for 2 d at 70 °C. The mixture was taken up in EtOAc and washed with water and brine. The organic layer was dried with $MgSO_4$ and the solvent removed under vacuum. The crude product was purified on silica gel (hexane:EtOAc 95:5, then 90:10) to afford **19** (76 mg, 20%) as a light yellow oil, **32a** (63 mg, 12%) as a colorless oil and **32b** (152 mg, 30%) as a colorless solid.

32a: ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 1.41$, 1.44 (2 s, 3H each, 1-CH_3, 9-CH_3), 1.80 (m$_c$, 1H, 3-H), 2.27 (m$_c$, 1H, 3-H), 2.31 (ddd, $J = 12.4$, 4.7, 2.3 Hz, 1H, 2-H), 2.58 (ddd, $J = 12.7$, 5.8, 2.6 Hz, 1H, 4-H), 3.33 (s, 3H, OCH_3), 3.53 (s, 1H, 8-H), 3.62–3.64 (m, 1H, 5-H), 3.69 (s, 6H, OCH_3), 5.74 (dd, $J = 4.7$, 2.6 Hz, 1H, 6-H), 5.97, 6.04 (2 d, $J = 5.7$ Hz, 1H each, 10-H, 11-H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 20.7$, 23.3 (2q, 1-CH_3, 9-CH_3), 24.3 (t, C-3), 39.4 (d, C-2), 41.2 (d, C-4), 43.0 (d, C-5), 51.8, 52.1, 57.3 (3q, OCH_3), 85.4, 85.5 (2s, C-1, C-9), 86.9 (d, C-8), 127.7 (d, C-6), 134.1, 139.7 (2d, C-10, C-11), 139.9 (s, C-7), 171.7, 173.5 (2s, CO); MS (EI, 80 eV): *m/z* (%) = 336 (M^+, 3), 240 (50), 181 (50), 142 (11), 121 (100), 96 ($C_6H_8O^+$, 11), 91 ($C_7H_7^+$, 17), 78 (10), 59 (13), 45 (18), 43 (29); IR (KBr) $\nu = 2980$, 2950 (C–H), 1740 (C=O), 1650, 1440 cm^{-1} (C=C); HRMS (80 eV): calcd. for ($C_{18}H_{24}O_6$) M^+: 336.15729; found: 336.15844.

32b: mp 112–114 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 1.35$, 1.45 (2s, 3H each, 1-CH_3, 9-CH_3), 1.53 (m$_c$, 1H, 3-H), 2.12 (ddd, $J = 12.0$, 4.4, 2.8 Hz, 1H, 3-H), 2.39 (ddd, $J = 12.0$, 6.9, 3.8 Hz, 1H, 2-H), 2.91 (ddd, $J = 13.1$, 10.5, 2.6 Hz, 1H, 4-H), 3.26 (s, 3H, OCH_3), 3.53 (s, 1H, 8-H), 3.66 (dt, $J = 10.5$, 3.0 Hz, 1H, 5-H), 3.71, 3.73 (2s, 3H each, OCH_3), 5.72 (t, $J \approx 3.0$ Hz, 1H, 6-H), 5.99, 6.01(AB system, $J_{AB} = 5.7$ Hz, 2H, 10-H, 11-H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 20.6$, 23.1 (2q, 1-CH_3, 9-CH_3), 28.9 (t, C-3), 38.3 (d, C-2), 41.9 (d, C-4), 44.5 (d, C-5), 52.1, 52.2, 56.9 (3q, OCH_3), 85.3, 85.5 (2s, C-1, C-9), 86.8 (d, C-8), 127.9 (d, C-6), 134.4, 139.1 (2d, C-10, C-11), 138.0 (s, C-7), 172.8, 174.7 (2s, CO); IR (KBr) $\nu = 3100$, 3070, 3030 (=C–H), 2980–2870 (C–H), 1735 (C=O), 1450 (C=C), 1430 cm^{-1}; anal. calcd. for $C_{18}H_{24}O_6$ (336.4): C 64.27, H 7.19; found: C 64.16, H 7.00%.

Crystals of **32b** suitable for X-ray analysis were obtained by recrystallization from 2-propanol/hexane. $C_{18}H_{24}O_6$, $M_r = 336.37$, $T = 173$ K; crystal size: 0.7 × 0.5 × 0.4 mm; orthorhombic; space group *Pbcn*, $a = 24.625(5)$, $b = 7.863(5)$, $c = 17.905(5)$ Å, $\alpha = 90.000°$, $\beta = 90.000°$, $\gamma = 90.000°$; $V = 3467(3)$ Å^3, $Z = 8$; $\rho_{calcd} = 1.289$ Mg/m^3; $F(000) = 1440$; $\mu(Mo_{K\alpha}) = 0.096$ mm^{-1}; Φ range for data collection: 2.27–30.52°; index range: $-35 = h = 30$, $-11 = k = 11$, $-24 = l = 25$; reflections collected/unique: 40124/5286 ($R_{int} = 0.0222$); final R [$I > 2\sigma(I)$]: $R_1 = 0.0422$, $wR_2 = 0.1101$; R (all data): $R_1 = 0.0517$, $wR_2 = 0.1191$.

For structure solution and refinement the programs SHELXS97 and SHELCL97 were used.[27]

X-Ray Crystallographic Study

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-243432. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: int. code +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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