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First Comprehensive Investigation of Suzuki Couplings of Alkenyl Nonaflates with Aryl and Alkenyl Boronic Acid Derivatives by Using Classical Conditions and Microwave Heating

Jens Högermeier and Hans-Ulrich Reißig*[a]

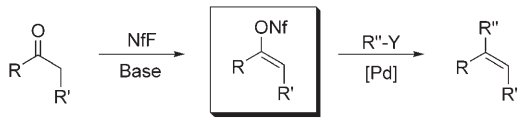
Abstract: Alkenyl nonaflates (nonafluorobutanesulfonates) are excellent substrates in a variety of palladium-catalysed coupling reactions. We herein demonstrate that bicyclic nonaflates generated from 8-heterobicyclo-[3.2.1]octan-3-one derivatives can be coupled with aryl or alkenyl boronic acids in a very efficient manner. The resulting densely functionalised bicyclic skeletons are highly suitable for further synthetic elaboration. The thermal Suzuki couplings provided the expected products in moderate to good yields. Microwave (MW) irradiation dramatically shortened reaction times and gave superior results. Bisboronic ester **19** was also coupled with bicyclic nonaflates, for example, with **14**, and double Suzuki-coupling products, such as **22**, were isolated in good yields. We demonstrated the great synthetic potential of aryl-substituted 8-heterobicyclo[3.2.1]octene derivatives, such as **15**, by the stereoselective conversion of this compound into highly substituted furanose **31** or substituted pyran derivative **33**, which were obtained in short and efficient reaction sequences.

Keywords: alkenyl nonaflates · boronic acids · catalysis · microwave · organic chemistry · palladium

Introduction

Palladium-catalysed coupling reactions have evolved over the last years as extremely powerful tools in organic synthesis. Among the many variations, one of the very widely used is the coupling of aryl or alkenyl compounds with boronic acids or boronic esters as introduced by Suzuki, Miyaura and co-workers.[1,2] Boronic acids are readily accessible and a wide variety are nowadays commercially available. In addition to their easy-to-handle and good storage abilities, boronic acids are non-toxic and their application in synthesis can therefore be regarded as "green chemistry".[3]

Over the last years, we successfully demonstrated that alkenyl nonaflates (nonafluorobutanesulfonates) are excellent coupling reagents in Heck and Sonogashira reactions (Scheme 1).[4] Relative to the widely used triflates, the use of nonaflates has several advantages: triflating reagents, such as Tf_2O or triflimides like Tf_2NPh,[5] are considerably more expensive than nonafluorobutanesulfonyl fluoride (NfF),[6] which is the most convenient precursor of nonaflates. Furthermore, NfF is air-stable, non-toxic and can be stored over a long period. The analogous reagent TfF is a poisonous gas. Alkenyl nonaflates are easily accessible by deprotonation of carbonyl compounds with bases, such as lithium diisopropylamide (LDA) and subsequent trapping of the enolate with NfF.[4] In addition to this standard method, nonaflates are also available via TMS-enol ethers which can be converted into nonaflates by using NfF and catalytic amounts of a fluoride source.[4a,c,d] This method was particularly successfully applied to alkenyl nonaflates derived from aldehydes, which are not easily accessible by conventional deprotonation and enolate trapping. The resulting alkenyl nonaflates can smoothly be purified on silica gel and can be stored for a long time without any indication of decomposition. On the other hand, aryl and alkenyl nonaflates exhibit a slightly higher reactivity in palladium-catalysed coupling reactions compared with the corresponding triflates as dem-

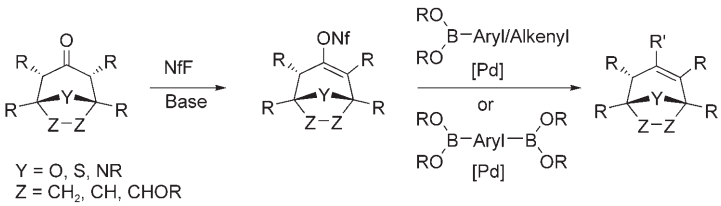


Scheme 1. Alkenyl nonaflates as intermediates for palladium-catalysed coupling reactions (NfF = $C_4F_9SO_2F$, Nf = $C_4F_9SO_2$).

[a] Dr. J. Högermeier, Prof. Dr. H.-U. Reißig
Institut für Chemie und Biochemie
Freie Universität Berlin, Takustrasse 3
14195 Berlin (Germany)
Fax: (+49) 30-8385-5367
E-mail: hans.reissig@chemie.fu-berlin.de

onstrated by Knochel[7] and also by our research group.[8] We are therefore convinced that nonaflates are not only just cheaper alternatives to triflates, but that they are superior in many applications. It is, therefore, surprising that aryl and alkenyl nonaflates are not more often employed in organic synthesis.

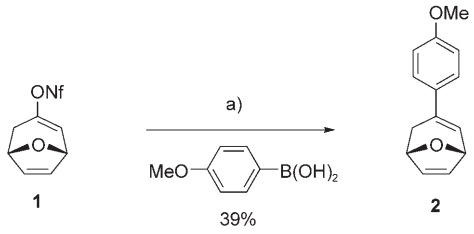
Beside our work on Heck and Sonogashira reactions, only a few examples are present in the literature describing the use of alkenyl and aryl nonaflates in palladium-catalysed couplings.[9] During our synthetic studies towards new pyridine derivatives we reported one example of a Suzuki coupling of a highly substituted pyridyl nonaflate with 4-methoxyphenyl boronic acid,[10] meanwhile it was established that this transformation is generally very efficient.[11] To the best of our knowledge, only one other example of an aryl nonaflate used in a Suzuki coupling is known, published by König et al. a couple of years ago,[12] whereas alkenyl nonaflates have not been used in Suzuki reactions as coupling partners up till now. Very recently, we reported the first coupling of bicyclic alkenyl nonaflates with bis(pinacolato)diboron and also disclosed an example for the synthesis of an epibatidine/atropine hybrid by means of Suzuki coupling.[13] Based on these promising results, we started a detailed investigation of alkenyl nonaflates in Suzuki couplings with aryl and alkenyl boronic acids as well as with boronic esters to further extend the use of alkenyl nonaflates in palladium-catalysed reactions. As in our earlier investigations, we used nonaflates prepared from 8-oxabicyclo[3.2.1]oct-6-en-3-one and its derivatives (Scheme 2).[4g] Because of their rigid bicyclic framework and their densely functionalised core, these oxabicyclic ketones have proved to be remarkably valuable building blocks in numerous syntheses.[14] We already successfully used this compound class in Heck Diels–Alder reaction sequences for diversity-oriented synthesis of new interesting polycyclic products.[4g] Based on these promising results, we envisioned to further extend the synthetic value of these bicyclic alkenyl nonaflates in Suzuki couplings.



Scheme 2. Suzuki couplings of heterobicyclic nonaflates.

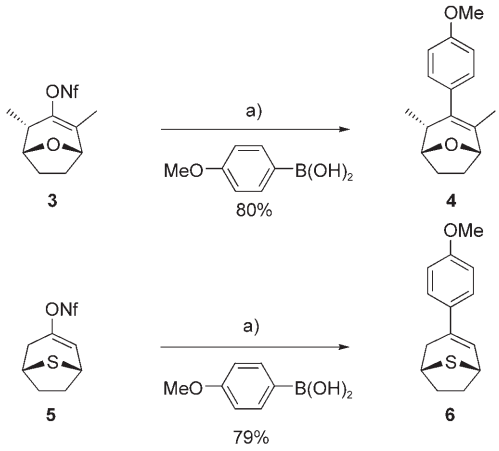
Results and Discussion

We started our investigations by exploring the coupling of alkenyl nonaflate **1**, which is available from 8-oxabicyclo-[3.2.1]oct-6-en-3-one by standard deprotonation and nonaflation.[4g] The Suzuki coupling with 4-methoxyphenyl boronic acid was carried out by using 5% $[Pd(PPh_3)_4]$ in dioxane and a mixture of potassium carbonate/potassium acetate as base,[15] which furnished the expected product **2** in only 39% yield (Scheme 3).



Scheme 3. Suzuki coupling of alkenyl nonaflate **1**: a) 5% $[Pd(PPh_3)_4]$, K_2CO_3, KOAc, dioxane, 18 h, 70 °C.

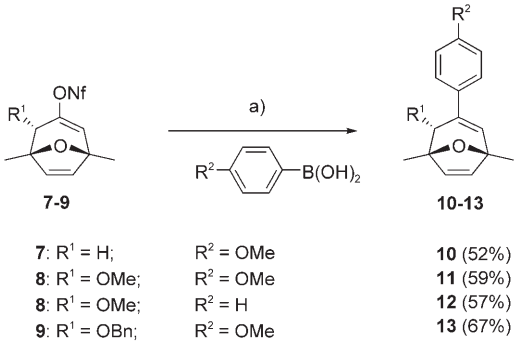
The low yield in this example may be due to a fragmentation reaction of nonaflate **1**. At higher temperatures under the influence of base these bicyclic nonaflates are cleaved by ring opening to give furan derivatives as we have found and discussed already in earlier investigations.[4f,g] For optimisation of reaction conditions we switched to nonaflate **3** as a starting material, which cannot undergo this side reaction (Scheme 4). We finally used DMF as solvent and K_2CO_3 as base, generating the Pd^0 catalyst in situ from $Pd(OAc)_2$ and PPh_3. Under these conditions we successfully coupled nonaflate **3** with the boronic acid despite the rather severe sterical hindrance and obtained **4** in 80% yield. Alkenyl nonaflate **5** which contains a bridging sulphur atom was also coupled in 79% yield, which is a remarkable result as the sulphur could obviously poison the catalyst. However, no influence on the coupling efficiency was observed in this case, which is evidence for the robust conditions and good reactivity of alkenyl nonaflates.



Scheme 4. Suzuki couplings of alkenyl nonaflates **3** and **5**: a) 5% $Pd(OAc)_2$, PPh_3, K_2CO_3, DMF, 70 °C, 18 h.

Further on, we were able to couple nonaflates, such as **7**–**9** bearing methyl groups at the bridgeheads under the same conditions in satisfying yields (Scheme 5). Coupling with 4-

methoxyphenyl boronic acid furnished the desired product **10** in 52% yield, whereas nonaflate **8**, which carries an additional α-methoxy group, was coupled with this boronic acid to give **11** in 59% yield. Alkenyl nonaflate **8** was also transformed by using phenyl boronic acid furnishing **12** in 57% yield, and the related α-benzyloxy-substituted precursor **9** furnished product **13** in 67% yield.



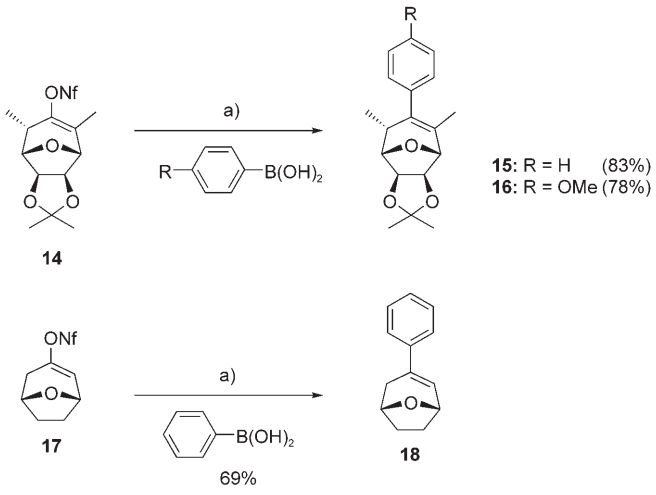
Scheme 5. Suzuki couplings of functionalised alkenyl nonaflates **7**–**9** under thermal conditions: a) 5% $Pd(OAc)_2$, PPh_3, K_2CO_3, DMF, 70°C, 18 h.

Encouraged by these successful results that were carried out by employing standard oil bath heating for 18 h, we turned our attention to the use of microwave synthesis.[16] Several examples of microwave-promoted Suzuki couplings are known.[17] The synthesis by König et al. carried out on solid support with an aryl nonaflate was also carried out by microwave heating.[12] However, alkenyl nonaflates have up to now not been used in any microwave coupling reaction.

To explore this new and powerful method, we carried out the reaction by using 100 W for 10 minutes to heat the mixture to 70°C. Alkenyl nonaflate **14** was coupled under these conditions with phenyl boronic acid furnishing compound **15** in 83% yield, and with 4-methoxyphenyl boronic acid it gave **16** in 78% yield (Scheme 6). Considering the high sterical hindrance at the reaction centre, this again demonstrates the efficacy and scope of the method. Similarly, precursor **17** was coupled with phenyl boronic acid to produce **18** in 69% yield.

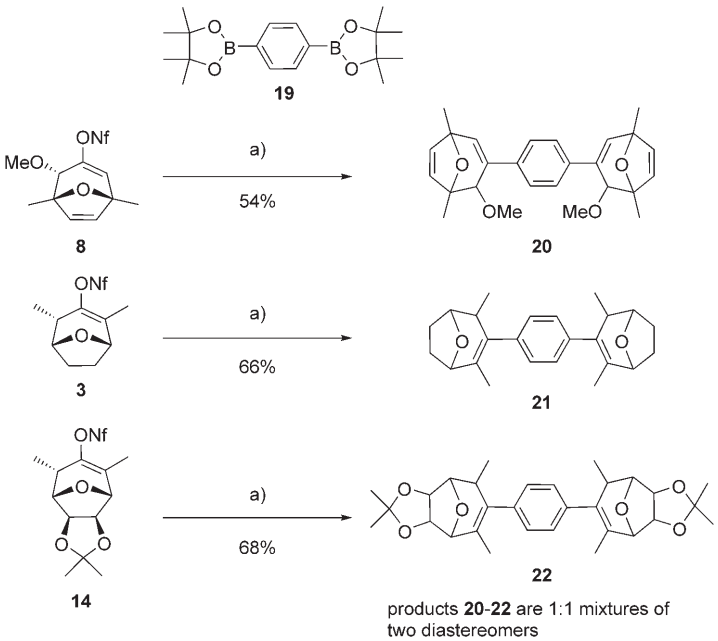
Costa et al. reported that compounds such as **15** and **16** are potent herbicides against several South American weeds. For the synthesis of these compounds, this group used a Grignard-addition/elimination sequence.[18] The method we introduce here not only gives higher yields than the Costa approach but is also highly flexible due to the broad range of commercially available boronic acids. It should also be adaptable to microwave-promoted automated synthesis, generating libraries of these compounds in a short time. These satisfying results demonstrate that microwave irradiation is suited very well as a heat source for Suzuki couplings of alkenyl nonaflates. All further coupling reactions were therefore carried out under microwave assistance.

After having successfully coupled simple aryl boronic acids, we turned our attention to difunctionalised boronic



Scheme 6. Microwave-assisted coupling reactions of alkenyl nonaflates **14** and **17**: a) 5% $Pd(OAc)_2$, PPh_3, K_2CO_3, DMF, MW, 100–250 W, 70°C, 10–40 min.

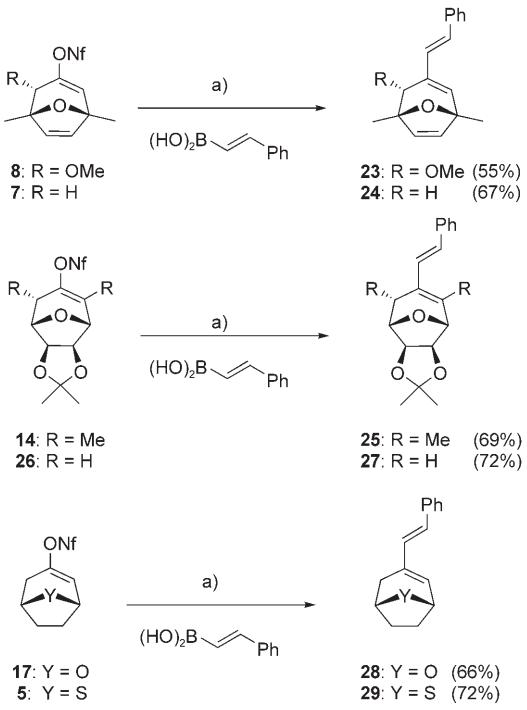
acids, such as 1,4-phenylenebisboronic acid. Carrying out the reaction of alkenyl nonaflate **8** under the microwave conditions as above by using $Pd(OAc)_2$ and PPh_3, we isolated only 19% of the desired biscoupling product **20**. This low yield is probably due to condensation of the bisboronic acid during storage delivering unreactive oligomers.[19] This problem could be overcome by transforming the boronic acid into the corresponding bispinacolic ester which also offered the chance to test pinacol boronic esters in Suzuki couplings of alkenyl nonaflates. Bisboronic ester **19** was easily synthesised by using a literature known method.[20] With this bisboronic ester in hand, we attempted the coupling reaction;



Scheme 7. Coupling of alkenyl nonaflates **8**, **3** and **14** (2.1 equiv) with bisboronic ester **19**: a) 5% $Pd(OAc)_2$, K_2CO_3, dppf, DMF, MW, 2×40 min, 150 W, 70°C.

however, yields were still poor under the standard conditions. Finally, the yields could be dramatically enhanced by changing the ligand from PPh_3 to 1,1′-bis(diphenylphosphino)ferrocene (dppf).[21] Microwave heating and dppf as ligand together with $Pd(OAc)_2$ converted alkenyl nonaflate **8** and **19** into product **20** in 54% yield. Sterically even more crowded nonaflates **3** and **14** were smoothly transformed into products **21** and **22** in 66 and 68% yield, respectively (Scheme 7). All products were obtained as mixtures of two diastereomers in a ratio of approximately 1:1 according to ^{13}C NMR spectroscopy. This is due to the fact that all chiral starting alkenyl nonaflates are racemic mixtures. We already disclosed a similar case of formation of two diastereomers (*meso* and *rac*) in an earlier communication.[13]

Coupling of alkenyl boronic acids: After having successfully tested aryl boronic acids and pinacol esters, we were then interested in the couplings of alkenyl boronic acids with bicyclic alkenyl nonaflates. Employment of *trans*-styryl boronic acid would allow a straightforward access to fairly electron-rich dienes that are highly suitable for subsequent Diels–Alder reactions. We had already investigated Heck couplings of styrene with bicyclic alkenyl nonaflates to furnish similar products; however, the efficacy was only moderate.[4g] Alkenyl nonaflates **7** and **8** were reacted with commercially available *trans*-styryl boronic acid under microwave conditions, and a reaction time of 20 minutes turned out to be necessary for complete conversion of the starting materials. Products **23** and **24** were isolated in 55 and 67% yield, respectively (Scheme 8). The sterically more demanding nonaflate **14** was smoothly converted into compound **25** in 69% yield and precursor **26** gave the desired product **27** in 72% yield. Similarly, bicyclic precursor nonaflates **17** and **5** were transformed into the desired dienes **28** and **29** in 66 and 72% yield. Again the sulphur bridge caused no problems in the latter transformation. It should be noted that all products contain an electron-rich diene moiety with styrene substructure which makes these compounds prone to polymerization or decomposition. Upon longer storage, polymerization was indicated by a change of appearance from colourless to yellow oils and by higher viscosity. Thus, the dienes have to be used shortly after their synthesis for subsequent reactions or they should be kept in the freezer for longer storage. Nevertheless, the bicyclic alkenyl nonaflates once more proved to be excellent coupling partners in this rapid approach to electron-rich dienes. Their stereoselective Diels–Alder reactions leading to new highly functionalised polycyclic skeletons have been investigated and will be reported in a future publication.[22]

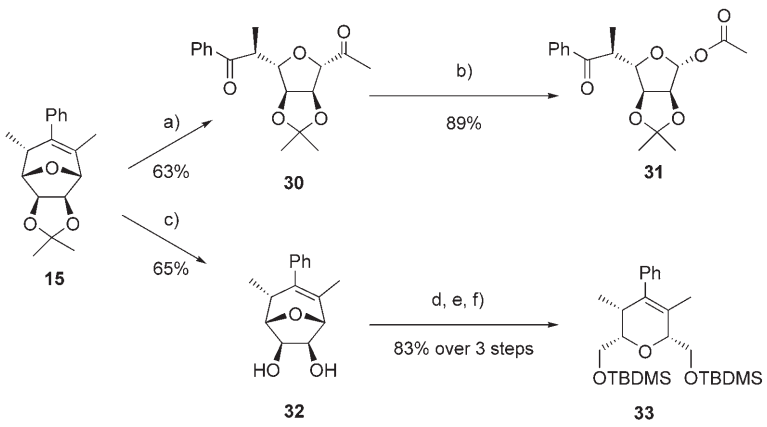


Scheme 8. Suzuki couplings of alkenyl nonaflates with *trans*-styryl boronic acid: a) 5% $Pd(OAc)_2$, PPh_3, K_2CO_3, DMF, MW, 250 W, 20 min, 70 °C.

Subsequent reactions creating diversity: Once we had demonstrated that bicyclic alkenyl nonaflates are excellent coupling partners in Suzuki reactions with aryl and alkenyl boronic acids, we preliminarily explored the synthetic potential of the 8-oxabicyclo[3.2.1]octane core as a tool for creating skeletal diversity.[23] For the first typical transformations we used compound **15** which was easily obtained from coupling nonaflate **14** with phenyl boronic acid (Scheme 6). Our results show that this product offers an easy access to highly functionalised furan and pyran derivatives.

Cleavage of the tetrasubstituted double bond of **15** by ozonolysis resulted in diketone **30** in 63% yield, which was oxidised in a very good yield of 89% to furnish ester **31** containing an anomeric centre (Scheme 9).[24] This Baeyer–Villiger reaction of **30** with *meta*-chloroperbenzoic acid (*m*CPBA) under the applied conditions was remarkably chemo-, regio- and stereoselective, generating **31** as a single isomer.[25]

Removal of the isopropylidene protective group of compound **15** yielded diol **32** in 65% yield. It subsequently underwent a sodium periodate-mediated oxidative diol cleavage followed by reduction with sodium borohydride and final protection with TBSCl (TBS = *tert*-butyldimethylsilyl). The corresponding pyran derivative **33** was obtained in an excellent yield of 83% over three steps. Both furan and pyran derivatives **31** and **33** were obtained as single diastereomers and the stereochemical information of the bicyclic starting material was completely transferred to the products. These two examples nicely demonstrate the synthetic potential of the 8-oxabicyclo[3.2.1]octane derivatives for the straightforward creation of skeletal diversity. Alkenyl nonaflates, such as **14** or **26**, and their products are actually generated from *meso* compounds. Deprotonation of the ketones with enantiopure bases provided enantiomerically highly enriched bicyclic alkenyl nonaflates (for example **14** with 79% *ee*; *ee* = enantiomeric excess).[26] Compounds such as **31** and **33** are therefore easily accessible in an enantioenriched form.



Scheme 9. Subsequent reactions of compound **15**: a) i) O_3, CH_2Cl_2, −78 °C, ii) PPh_3, −78 °C to RT, 1 h; b) *m*CPBA, $NaHCO_3$, CH_2Cl_2, 0 °C, 4 h; c) conc. HCl, 1 h, RT, MeOH/H_2O 7:1, evaporation, dissolved in MeOH, 18 h, 40 °C, 200 mbar, RT; d) $NaIO_4$, MeOH/H_2O, 10 min, RT; e) $NaBH_4$, 15 min, RT; f) TBDMSCl, THF, imidazole, 1 h, RT.

Conclusion

We successfully demonstrated that alkenyl nonaflates derived from 8-oxabicyclo[3.2.1]oct-6-en-3-ones and their derivatives are excellent coupling partners in Suzuki reactions. Aryl boronic acids and pinacolbisboronic esters were successfully coupled with different alkenyl nonaflates, which proved to be very suitable substrates for microwave-assisted Suzuki reactions. The efficient protocol developed in this publication allowed a drastic reduction of the reaction time and the products were obtained in good yields. Similarly, alkenyl boronic acids were used to prepare synthetically valuable electron-rich dienes which are not efficiently accessible by Heck reactions with styrene. These dienes are interesting precursors for subsequent Diels–Alder reactions leading to highly functionalised polycyclic compounds in a stereoselective manner. In typical examples, we demonstrated that coupling products with a bicyclo[3.2.1]octane core can be transformed in a few steps into highly functionalised furanose and pyran derivatives in excellent yields and as single diastereomers.

Our presented results together with our previous studies prove the high utility of alkenyl nonaflates in palladium-catalysed reactions. Their good availability and the economical method of their preparation makes them excellent candidates for applications in syntheses in which disadvantages with the routinely used alkenyl triflates have to be overcome.

Experimental Section

General information: NMR spectra were recorded on Bruker AC 500 and Joel Eclipse 500 (500 MHz) instruments. ^1H and ^{13}C spectroscopic chemical shifts are expressed as ppm downfield from tetramethylsilane ($\delta = 0.0$ ppm) or $CDCl_3$ ($\delta = 7.26$ and 77.0 ppm in ^{13}C NMR spectra) used as internal standards. ^{13}C NMR signals of $CF_3(CF_2)_3$ groups are not given as unambiguous assignment is not possible due to strong splitting by coupling with the ^{19}F nuclei. Mass spectra were registered with a Varian MAT 711 spectrometer. IR spectra were measured with a spectrometer 5 SXC Nicolet. TLC analysis was carried out by using Merck silica gel 60 F_{254} plates. Column chromatography was conducted on silica gel 60 (40–63 μm, Fluka). All reactions were carried out under an atmosphere of argon in heat-gun-dried reaction flasks by adding the components by means of 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. Starting materials: the precursor ketones for **14**,[18] **17**[27] and **26**[28] were synthesised according to literature procedures, nonaflates **1**, **3**, **5**, **7**, **8** and **9** were prepared according to our previously published procedure.[4g] The microwave reactions were carried out in argon-flushed microwave quartz glass vessels. The microwave oven used was a "micro-chemist" system manufactured by Milestone (2.45 GHz, Multimode, operating wavelength 12.25 cm). The temperature during the reaction was monitored by using an invasive fiber optic probe. All reactions were heated for 2 min (ramp time) to reach the hold temperature. Settings for hold temperature (in °C), time (including ramp time) and power (in W) are given in the individual experiment. The wattage given in the experiments is always the maximum wattage allowed and was not constantly applied.

General procedure 1, nonaflate synthesis (GP 1): A LDA solution in anhydrous THF was generated by adding *n*BuLi (2.5 M in hexanes) to *i*Pr_2NH at −78 °C. After 10 minutes, a solution of the bicyclic ketone in anhydrous THF was added at −78 °C, and the mixture was then stirred for 1 h at −78 °C and NfF was added. The mixture was left 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 in vacuo. The resulting crude brown oil was purified by column chromatography on silica gel.

General procedure 2, Suzuki coupling under thermal heating (GP 2, thermal): Nonaflate (1.0 equiv) and boronic acid (1.0–1.2 equiv) were dissolved in dry DMF in a heat-gun-dried and argon-flushed flask. K_2CO_3 (1.5 equiv), PPh_3 (0.2 equiv) and $Pd(OAc)_2$ (0.05 equiv) were added. The reaction mixture was heated for 18 h at 70 °C in a tightly closed flask (glass stopper and Teflon inlay). The reaction mixture was taken up in EtOAc, washed twice with water and once with brine. The organic layer was dried with $MgSO_4$, the solvent was removed in vacuo, and the resulting crude product was purified by column chromatography on silica gel.

General procedure 2, Suzuki coupling under microwave heating (GP 2, MW): Nonaflate (1.0 equiv) and boronic acid (1.0–1.2 equiv) were dissolved in dry DMF in an argon-flushed microwave vessel. K_2CO_3 (1.5 equiv), PPh_3 (0.2 equiv) and $Pd(OAc)_2$ (0.05 equiv) were added and the vessel was tightly closed. The reaction mixture was irradiated to reach 70 °C under conditions described in the individual experiment. The reaction mixture was taken up in EtOAc, washed twice with water and once with brine. The organic layer was dried with $MgSO_4$, the solvent was removed in vacuo, and the resulting crude product was purified by column chromatography on silica gel.

3-(4-Methoxyphenyl)-8-oxabicyclo[3.2.1]octa-2,6-diene (2): Nonaflate **1** (412 mg, 1.01 mmol), 4-methoxyphenyl boronic acid (170 mg, 1.12 mmol), K_2CO_3 (110 mg, 0.81 mmol) and KOAc (68 mg, 0.71 mmol) were dissolved in dioxane (4 mL). Then $[Pd(PPh_3)_4]$ (30 mg, 0.03 mmol) was added and the mixture was stirred for 18 h at 70 °C under an argon atmosphere. After this time, it was left to warm up to room temperature and was quenched with NaOH (0.5 mL, 30%) and H_2O_2 (0.5 mL, 30%).

The resulting mixture was taken up with EtOAc and was washed with water and brine. The phases were separated and the combined aqueous phases were re-extracted with EtOAc. The combined organic phases were dried with $MgSO_4$ and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (hexane/EtOAc 10:1) to afford **2** (83 mg, 39%) as a colourless solid. M.p. 140–142°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.08 (dd, J = 17.5, 1.7 Hz, 1H; 4-H), 2.95 (dddd, J = 17.5, 6.2, 1.7, 1.2 Hz, 1H; 4-H), 3.79 (s, 3H; OCH_3), 4.87–4.89 (m, 1H; 1-H), 5.07 (dd, J = 6.2, 1.9 Hz, 1H; 5-H), 6.03 (dd, J = 5.9, 1.9 Hz, 1H; 6-H), 6.42 (dt, J = 4.6, 1.7 Hz, 1H; 2-H), 6.54 ppm (dd, J = 5.9, 1.7 Hz, 1H; 7-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 28.5 (t; C-4), 55.2 (q; OCH_3), 75.8 (d; C-1), 77.3 (d; C-5), 113.6 (d; Ph), 124.5 (d; C-2), 125.7 (d; Ph), 127.4 (d; C-6), 132.0 (s; C-3), 132.9 (s; Ar), 137.4 (d; C-7), 159.1 ppm (s, Ar); IR (Film): $\tilde{\nu}$ = 3034 (=C−H), 2960–2910 (C−H), 1620, 1600, 1570 cm^{-1} (C=C); MS (EI, 80 eV, 30°C): m/z (%): 214 (14) $[M]^+$, 185 (100) $[M-CHO]^+$, 170 $[185-CH_3]^+$ (22), 153 (17I) $[185-OH]^+$, 115 (6), 77 (5) $[C_6H_5]^+$; HRMS: m/z: calcd for $C_{14}H_{14}O_2$: 214.09938; found: 214.09864.

3-(4-Methoxyphenyl)-2,4-dimethyl-8-oxabicyclo[3.2.1]oct-2-ene (4): According to GP 2 thermal, nonaflate **3** (436 mg, 1.00 mmol) and 4-methoxyphenyl boronic acid (182 mg, 1.20 mmol) were dissolved in dry DMF (3 mL). K_2CO_3 (203 mg, 1.50 mmol), PPh_3 (52 mg, 0.20 mmol) and $Pd(OAc)_2$ (11 mg, 0.05 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 90:10) to afford **4** (196 mg, 80%) as a colourless oil. According to GP 2 MW, nonaflate **3** (300 mg, 0.688 mmol) and 4-methoxyphenyl boronic acid (125 mg, 0.825 mmol) were dissolved in dry DMF (5 mL). K_2CO_3 (139 mg, 1.03 mmol), PPh_3 (36 mg, 0.14 mmol) and $Pd(OAc)_2$ (8 mg, 0.03 mmol) were added and the mixture was irradiated for 20 min at 250 W and 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 **4** (122 mg, 73%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.63 (d, J = 7.3 Hz, 3H; 4-CH_3), 1.50 (d, J = 2.3 Hz, 3H; 2-CH_3), 1.82–1.89, 1.93–2.05 (m×2, 1H, 3H; 6-H, 7-H), 3.12 (m, 1H; 4-H), 3.79 (s, 3H; OCH_3), 4.27–4.30 (m, 1H; 1-H), 4.42 (ddd, J = 7.4, 4.8, 1.5 Hz, 1H; 5-H), 6.69–6.82 (m, 2H; Ar), 6.94–6.98 ppm (m, 2H; Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (q; 4-CH_3), 16.6 (q; 2-CH_3), 23.3, 33.1 (t×2; C-6, C-7), 55.1 (q; OCH_3), 78.0 (d; C-1), 79.2 (d; C-5), 113.3, 129.7 (d×2; Ar), 131.8, 132.1, 132.8 (s×3; Ar, C-3, C-2), 157.9 ppm (s; Ar); IR (film): $\tilde{\nu}$ = 3060–3030 (=C−H), 2950–2840 (C−H), 1610 (C=C), 1510, 1470, 1440, 1360, 1290, 1270, 1180, 1160, 1130, 1040 cm^{-1}; MS (EI, 80 eV, 30°C): m/z (%): 244 (100) $[M]^+$, 229 (22), 215 (21), 202 (9), 201 (53), 200 (15), 188 (12), 187 (49), 186 (12), 173 (16), 172 (12), 159 (13), 130 (10), 121 (25), 115 (11), 108 (65), 107 (44), 91 (23), 79 (51), 78 (11), 77 (34) $[Ph]^+$, 69 (13); HRMS: m/z: calcd for $C_{16}H_{20}O_2$: 244.14575; found: 244.14633.

3-(4-Methoxyphenyl)-8-thiabicyclo[3.2.1]oct-2-ene (6): According to GP 2 thermal, nonaflate **5** (210 mg, 0.50 mmol) and 4-methoxyphenyl boronic acid (228 mg, 1.50 mmol) were dissolved in dry DMF (3 mL). K_2CO_3 (138 mg, 1.00 mmol), PPh_3 (26 mg, 0.10 mmol) and $Pd(OAc)_2$ (6 mg, 0.03 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) to afford **6** (91 mg, 79%) as a colourless solid. M.p. 92–94°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.97 (ddd, J = 13.0, 8.3, 5.3 Hz, 1H; 6-H), 2.12 (m, 1H; 7-H), 2.25–2.33 (m, 1H; 6-H), 2.40 (ddd, J = 11.5, 8.3, 2.5 Hz, 1H; 7-H), 2.49, 2.99 (dt×2, J = 17.6, 2.1 Hz, 1H each; 4-H), 3.79 (s, 3H; OCH_3), 3.80–3.84 (m, 1H; 1-H), 4.01 (m, 1H; 5-H), 6.39 (dt, J = 7.4, 2.1 Hz, 1H; 2-H), 6.81–6.85 (m, 2H; Ar), 7.24–7.28 ppm (m, 2H; Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 34.7 (t; C-6), 40.5, 40.6 (t×2; C-4, C-7), 44.2 (d; C-1), 45.9 (d; C-5), 55.3 (q; OCH_3), 113.6, 126.0 (d×2; Ar), 128.5 (d; C-2), 133.5, 134.0 (s×2; C-3, Ar), 158.9 ppm (s; Ar); IR (KBr): $\tilde{\nu}$ = 3030–3000 (=C−H), 2960–2830 (C−H), 1600 (C=C), 1510, 1470–1420, 1250, 1190, 1030 cm^{-1}; MS (EI, 80 eV, 30°C): m/z (%): 232 (100) $[M]^+$, 214 (18), 204 (60) $[M-C_2H_4]^+$, 200 (33) $[M-S]^+$, 192 (17), 188 (10), 175 (14), 121 (14), 115 (10), 43 (11) $[CH_3CO]^+$; HRMS: m/z: calcd for $C_{14}H_{16}OS$: 232.09219; found: 232.09155.

3-(4-Methoxyphenyl)-1,5-dimethyl-8-oxabicyclo[3.2.1]octa-2,6-diene (10): According to GP 2 thermal, nonaflate **7** (200 mg, 0.462 mmol) and 4-methoxyphenyl boronic acid (77 mg, 0.51 mmol) were dissolved in dry DMF (3 mL). K_2CO_3 (62 mg, 0.46 mmol), PPh_3 (24 mg, 0.09 mmol) and $Pd(OAc)_2$ (5 mg, 0.02 mmol) were added and 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 98:2 then 95:5) to afford **10** (58 mg, 52%) as a colourless solid. M.p. 69°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.53, 1.54 (s×2, 3H each; 1-CH_3, 5-CH_3), 2.15, 2.62 (dd×2, J = 17.6, 1.8 Hz, 1H each; 4-H), 3.80 (s, 3H; OCH_3), 5.72, 6.23 (d×2, J = 5.6 Hz, 1H each; 6-H, 7-H), 6.32 (t, J = 1.8 Hz, 1H; 2-H), 6.80–6.85 (m, 2H; Ar), 7.28–7.32 ppm (m, 2H; Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.9, 24.7 (q×2; 1-CH_3, 5-CH_3), 35.1 (t; C-4), 55.2 (q; OCH_3), 82.3, 83.0 (s×2; C-1, C-5), 113.7, 125.8 (d×2; Ar), 128.7, 131.3 (d×2; C-6, C-7), 132.7, 133.9 (s×2; Ar, C-3), 140.2 (d; C-2), 159.0 ppm (s; Ar); IR (KBr): $\tilde{\nu}$ = 3060–3000 (=C−H), 2970–2830 (C−H), 1600 (C=C), 1510, 1440–1260, 1380, 1370, 1290, 1270, 1250–1240, 1190–1180, 1030 cm^{-1}; MS (EI, 80 eV, 30°C): m/z (%): 242 (2) $[M]^+$, 199 (100) $[M-CH_3CO]^+$, 184 (28), 152 (12), 141 (11), 43 (28) $[CH_3CO]^+$, 41 (12); HRMS: m/z: calcd for $C_{16}H_{18}O_2$: 242.13144; found: 242.13068.

4-Methoxy-3-(4-methoxyphenyl)-1,5-dimethyl-8-oxabicyclo[3.2.1]octa-2,6-diene (11): According to GP 2 thermal, nonaflate **8** (200 mg, 0.43 mmol) and 4-methoxyphenyl boronic acid (63 mg, 0.42 mmol) were dissolved in dry DMF (3 mL). K_2CO_3 (77 mg, 0.57 mmol), PPh_3 (20 mg, 0.08 mmol) and $Pd(OAc)_2$ (4 mg, 0.02 mmol) were added and 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 **11** (69 mg, 59%) as a pale-yellow solid. M.p. 75–76°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.44, 1.67 (s×2, 3H each; 1-CH_3, 5-CH_3), 3.23 (s, 3H; OCH_3), 3.80 (s, 3H; OCH_3), 4.22 (d, J = 0.8 Hz, 1H; 4-H), 5.84, 6.41 (d×2, J = 5.7 Hz, 1H each; 6-H, 7-H), 6.23 (d, J = 0.8 Hz, 1H; 2-H), 6.83–6.87 (m, 2H; Ar), 7.25–7.29 ppm (m, 2H; Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.8, 23.3 (q×2; 1-CH_3, 5-CH_3), 55.2 (q; ArOCH_3), 59.5 (q; OCH_3), 79.6 (t; C-4), 82.9, 86.6 (s×2; C-1/C-5), 113.8, 127.9 (d×2; Ar), 131.9, 137.5 (s×2; Ar, C-3), 132.1, 142.4 (d×2; C-6, C-7), 134.2 (d; C-2), 159.0 ppm (s; Ar); IR (KBr): $\tilde{\nu}$ = 3070–3030 (=C−H), 2970–2830 (C−H), 1610 (C=C), 1510, 1460, 1440, 1370, 1270, 1250, 1180, 1100, 1040 cm^{-1}; elemental analysis calcd (%) for $C_{17}H_{20}O_3$ (272.3): C 74.97, H 7.40; found: C 74.79, H 7.29.

4-Methoxy-1,5-dimethyl-3-phenyl-8-oxabicyclo[3.2.1]octa-2,6-diene (12): According to GP 2 thermal, nonaflate **8** (276 mg, 0.59 mmol) and phenyl boronic acid (94 mg, 0.77 mmol) were dissolved in dry DMF (3 mL). K_2CO_3 (120 mg, 0.89 mmol), PPh_3 (31 mg, 0.12 mmol) and $Pd(OAc)_2$ (7 mg, 0.03 mmol) were added and 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) to afford **12** (82 mg, 57%) as a pale-yellow solid. M.p. 86–88°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.44, 1.67 (s×2, 3H each; 1-CH_3, 5-CH_3), 3.23 (s, 3H; OCH_3), 4.25 (d, J = 1.2 Hz, 1H; 4-H), 5.85, 6.43 (d×2, J = 5.7 Hz, 1H each; 6-H, 7-H), 6.30 (d, J = 1.2 Hz, 1H; 2-H), 7.23–7.26 (m, 1H; Ph), 7.28–7.35 ppm (m, 4H; Ph); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.8, 23.4 (q×2; 1-CH_3, 5-CH_3), 59.8 (q; OCH_3), 79.7 (d; C-4), 83.0, 86.7 (s×2; C-1, C-5), 126.9, 127.4, 128.3 (d×3; Ph), 132.4, 142.5 (d×2; C-6, C-7), 135.6 (d; C-2), 138.2, 139.5 ppm (s×2; Ph, C-3); IR (KBr): $\tilde{\nu}$ = 3080–3030 (=C−H), 2930–2830 (C−H), 1600 (C=C), 1500, 1450, 1370, 1340, 1190, 1100 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{18}O_2$ (242.3): C 79.31, H 7.49; found: C 79.15, H 7.59.

4-Benzyloxy-3-(4-methoxyphenyl)-1,5-dimethyl-8-oxabicyclo[3.2.1]octa-2,6-diene (13): According to GP 2 thermal, nonaflate **9** (208 mg, 0.39 mmol) and 4-methoxyphenyl boronic acid (64 mg, 0.42 mmol) were dissolved in dry DMF (3 mL). K_2CO_3 (78 mg, 0.58 mmol), PPh_3 (20 mg, 0.08 mmol) and $Pd(OAc)_2$ (4 mg, 0.02 mmol) were added and 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 **13** (91 mg, 67%) as a colourless solid. M.p. 111°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.43, 1.65 (s×2, 3H each; 1-CH_3, 5-CH_3), 3.79 (s, 3H; OCH_3), 4.32 (brs, 2H; OCH_2), 4.49 (s, 1H; 4-H), 5.64, 6.24 (d×2, J = 5.7 Hz, 1H each; 6-H, 7-H), 6.23 (s, 1H; 2-H), 6.82–6.87 (m, 2H; Ar), 6.97–7.01 (m, 2H; Ar), 7.19–7.24 (m, 3H; Ar), 7.28–7.32 ppm (m, 2H; Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.8, 23.3 (q×2; 1-CH_3, 5-CH_3), 55.3 (q; OCH_3), 73.2 (t; OCH_2), 78.4 (d; C-4), 82.9, 86.7 (s×2; C-1, C-5),

113.6, 128.1, 127.4, 127.5 (d×4; Ar), 132.0, 137.3, 137.2 (s×3; Ar, C-3), 132.4, 142.4 (d×2; C-6, C-7), 134.6 (d; C-2), 159.2 ppm (s; Ar); IR (KBr): $\tilde{\nu}$ = 3060–3020 (=C−H), 2980–2840 (C−H), 1610 (C=C), 1510, 1450, 1440, 1370, 1360, 1300, 1270, 1250, 1190, 1150, 1080, 1070, 1040 cm^{-1}; elemental analysis calcd (%) for $C_{23}H_{24}O_3$ (348.4): C 79.28, H 6.94; found: C 79.43, H 7.44.

2,2,5,7-Tetramethyl-4,5,8,8a-tetrahydro-3a*H*-4,8-epoxycyclohepta[*d*]-[1,3]dioxol-6-yl-nonaflate (14): According to GP 1, LDA was prepared by adding *n*BuLi (3.26 mL, 8.16 mmol) to a solution of *i*Pr_2NH (0.889 g, 8.79 mmol) in dry THF (20 mL). The bicyclic precursor ketone[17] (1.42 g, 6.28 mmol) was dissolved in THF (5 mL) and added. The mixture was quenched with NfF (3.03 g, 10.0 mmol) and left to warm up to room temperature overnight. The reaction was worked up as stated above and the crude product was purified on silica gel (hexane/EtOAc 98:2) to afford **14** (2.48 g, 78%) as a colourless solid. M.p. 68°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.13 (d, J = 7.3 Hz, 3H; 4-CH_3), 1.32, 1.51 (s×2, 3H each; C-$(CH_3)_2$), 1.79 (d, J = 2.6 Hz, 3H; 2-CH_3), 3.14 (m, 1H; 4-H), 4.32 (d, J = 5.8 Hz, 1H; 5-H), 4.34 (s, 1H; 1-H), 4.58, 4.78 ppm (d×2, J = 5.7 Hz, 1H each; 6-H, 7-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 11.2 (q; 4-CH_3), 13.4 (q; 2-CH_3), 24.8, 26.1 (q×2, C$(CH_3)_2$), 35.2 (d; C-4), 80.1, 84.2 (d×2; C-6, C-7), 80.9 (d; C-1), 84.5 (d; C-5), 112.5 (s; C$(CH_3)_2$), 127.2 (s; C-2), 144.1 ppm (s; C-3); IR (KBr): $\tilde{\nu}$ = 3060–2880 (=C−H, C−H), 1700 (C=C), 1470–1370, 1350–1340, 1280–1160 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{17}F_9O_6S$ (508.4): C 37.41, H 3.14; found: C 37.80, H 3.37.

2,2,5,7-Tetramethyl-6-phenyl-4,5,8,8a-tetrahydro-3a*H*-4,8-epoxycyclohepta[*d*][1,3]dioxol (15): According to GP 2 MW, nonaflate **14** (1.00 g, 1.97 mmol) and phenyl boronic acid (264 mg, 2.16 mmol) were dissolved in dry DMF (10 mL). K_2CO_3 (398 mg, 2.88 mmol), PPh_3 (103 mg, 0.39 mmol) and $Pd(OAc)_2$ (22 mg, 0.10 mmol) were added and the mixture was irradiated for 20 min at 200 W and 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 **15** (467 mg, 83%) as a colourless solid. M.p. 114–115°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.74 (d, J = 7.6 Hz, 3H; 4-CH_3), 1.37, 1.55 (s×2, 3H each; C$(CH_3)_2$), 1.56 (d, J = 2.3 Hz, 3H; 2-CH_3), 3.06 (m, 1H; 4-H), 4.26 (s, 1H; 1-H), 4.32 (d, J = 5.4 Hz, 1H; 5-H), 4.68, 4.85 (d×2, J = 5.8 Hz, 1H each; 6-H, 7-H), 7.00–7.04 (m, 2H; Ph), 7.21–7.27 (m, 1H; Ph), 7.29–7.34 ppm (m, 2H; Ph); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.9 (q; 4-CH_3), 16.7 (q; 2-CH_3), 24.9, 26.2 (q×2, C$(CH_3)_2$), 35.5 (d, C-4), 80.6, 84.7* (d×2; C-6, C-7, C-1), 81.8 (d; C-5), 112.1 (s; C$(CH_3)_2$), 126.6, 128.1, 128.4 (d×3; Ph), 129.3, 135.4 (s×2; C-2, C-3), 138.6 ppm (s; Ph), * marked signals show higher intensity; IR (KBr): $\tilde{\nu}$ = 3080–2980 (=C−H), 2950–2880, 2850 (C−H), 1600 (C=C), 1490, 1440, 1380–1370, 1270, 1210 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{22}O_3$ (286.4): C 75.50, H 7.74; found: C 75.48, H 7.49.

6-(4-Methoxyphenyl)-2,2,5,7-tetramethyl-4,5,8,8a-tetrahydro-3a*H*-4,8-epoxycyclohepta[*d*][1,3]-dioxol (16): According to GP 2 MW, nonaflate **14** (200 mg, 0.394 mmol) and 4-methoxyphenyl boronic acid (72 mg, 0.47 mmol) were dissolved in dry DMF (5 mL). K_2CO_3 (65 mg, 0.47 mmol), PPh_3 (21 mg, 0.08 mmol) and $Pd(OAc)_2$ (4 mg, 0.02 mmol) were added and the mixture was irradiated for 10 min at 100 W and 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 **16** (97 mg, 78%) as a colourless solid. M.p. 121–122°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.74 (d, J = 7.6 Hz, 3H; 4-CH_3), 1.36, 1.55 (s×2, 3H each; C$(CH_3)_2$), 1.57 (d, J = 2.5 Hz, 3H; 2-CH_3), 3.03 (m, 1H; 4-H), 3.81 (s, 3H; OCH_3), 4.25 (s, 1H; 1-H), 4.31 (d, J = 5.4 Hz, 1H; 5-H), 4.66, 4.84 (d×2, J = 5.8 Hz, 1H each; 6-H, 7-H), 6.84–6.88 (m, 2H; Ar), 6.92–6.96 ppm (m, 2H; Ar); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.0 (q; 2-CH_3), 16.7 (q; 4-CH_3), 24.9, 26.2 (q×2, C$(CH_3)_2$), 35.6 (d; C-4), 55.2 (q; OCH_3), 80.6, 84.7 (d×2; C-6, C-7), 81.8 (d; C-1), 84.8 (d; C-5), 112.0 (s; C$(CH_3)_2$), 113.5, 129.5 (d×2; Ar), 129.2, 130.9, 134.9 (s×3; Ar, C-2, C-3), 158.2 ppm (s, Ar); IR (KBr): $\tilde{\nu}$ = 3030 (=C−H), 2970–2840 (C−H), 1610 (C=C), 1511, 1460, 1450, 1440, 1370, 1370 cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{24}O_4$ (316.4): C 72.13, H 7.65; found: C 72.19, H 7.72.

8-Oxabicyclo[3.2.1]oct-2-enyl nonaflate (17): According to GP 1, LDA was prepared by adding *n*BuLi (2.19 mL, 5.48 mmol) to a solution of *i*Pr_2NH (0.351 g, 5.94 mmol) in dry THF (15 mL). The bicyclic precursor ketone[27] (0.576 g, 4.57 mmol) was dissolved in dry THF (2 mL) and added. The mixture was quenched with NfF (2.07 g, 6.85 mmol) and left to warm up to room temperature overnight. The reaction was worked up as stated above and the crude product was purified on silica gel (hexane/EtOAc 95:5) to afford **17** (1.17 g, 63%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.73–1.81 (m, 1H; 6-H), 1.92–2.02 (m, 1H; 7-H), 2.05 (d, J = 16.6 Hz, 1H; 4-H), 2.12 (m, 1H; 7-H), 2.14–2.22 (m, 1H; 6-H), 2.97 (dd, J = 16.6, 4.8 Hz, 1H; 4-H), 4.65 (br t, J ≈ 5 Hz, 1H; 1-H), 4.69 (m, 1H; 5-H), 6.00 ppm (ddd, J = 4.8, 1.8. 1.0 Hz, 1H; 2-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 29.3 (t; C-6), 35.3 (t; C-7), 37.4 (t; C-4), 71.9 (d; C-1), 76.5 (d; C-5), 122.1 (d; C-2), 146.3 ppm (s; C-3); IR (film): $\tilde{\nu}$ = 2960–2890 (C−H), 1680 (C=C), 1420, 1350, 1240–1200 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_9F_9O_4S$ (408.0): C 32.36, H 2.22; found: C 32.52, H 2.16.

3-Phenyl-8-oxabicyclo[3.2.1]oct-2-ene (18): According to GP 2 MW, nonaflate **17** (150 mg, 0.367 mmol) and phenyl boronic acid (54 mg, 0.44 mmol) were dissolved in dry DMF (10 mL). K_2CO_3 (74 mg, 0.55 mmol), PPh_3 (19 mg, 0.07 mmol) and $Pd(OAc)_2$ (4 mg, 0.02 mmol) were added and the mixture was irradiated for 40 min at 250 W at 70°C and worked up as stated above. The crude product was purified on silica gel (hexane/EtOAc 95:5) to afford **18** (47 mg, 69%) as a colourless solid. M.p. 39–41°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.71–1.80, 1.95–2.09, 2.13–2.22 (m×3, 1H, 2H, 2H; 6-H, 7-H, 4-H), 3.03 (dd, J = 16.7, 5.0 Hz, 1H; 4-H), 4.63 (t, J = 4.8 Hz, 1H; 1-H), 4.73 (br t, J ≈ 5 Hz, 1H; 5-H), 6.36 (dt, J = 4.8, 1.7 Hz, 1H; 2-H), 7.22–7.27 (m, 1H; Ph), 7.28–7.34 (m, 2H; Ph), 7.35–7.39 ppm (m, 2H; Ph); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 29.8, 35.1 (t×2; C-6, C-7), 36.2 (t; C-4), 73.0, 73.2 (d×2; C-1, C-5), 124.8 (d; C-2), 127.3, 127.8, 128.3 (d×3; Ph), 132.2 (s; Ph), 139.8 ppm (s; C-3); IR (KBr): $\tilde{\nu}$ = 3100–3020 (=C−H), 2970–2830 (C−H), 1600 (C=C), 1500, 1450, 1350, 1200, 1070, 1030 cm^{-1}; MS (EI, 80 eV, 40°C): m/z (%): 186 (17) $[M]^+$, 157 (100), 143 (18) $[M-CH_3CO]^+$, 142 (19), 141 (20), 129 (74), 128 (71), 114 (73), 103 (25), 102 (25), 91 (59), 81 (13), 77 (55) $[Ph]^+$, 65 (17), 57 (11), 55 (28), 51 (18), 43 (37) $[CH_3CO]^+$, 41 (45), 39 (26); HRMS: m/z: calcd for $C_{13}H_{14}O$: 186.10446; found: 186.10522; elemental analysis calcd (%) for $C_{13}H_{14}O$ (186.3): C 83.83, H 7.58; found: C 83.23, H 7.69.

3,3′-(1,4-Phenylene)bis(4-methoxy-1,5-dimethyl-8-oxabicyclo[3.2.1]octa-2,6-diene) (20): Nonaflate **8** (295 mg, 0.636 mmol) and bisboronic ester **19** (100 mg, 0.303 mmol) were dissolved in dry DMF (3 mL) in an argon-flushed microwave vessel. K_2CO_3 (164 mg, 1.21 mmol), dppf (33 mg, 0.06 mmol) and $Pd(OAc)_2$ (3 mg, 0.02 mmol) were added and the vessel was tightly closed. The reaction mixture was irradiated two times for 40 min at 150 W to 70°C and then taken up in EtOAc and washed with water and brine. The organic layer was dried with $MgSO_4$ and the solvent was removed afterwards in vacuo. The resulting crude product was then purified by column chromatography on silica gel (hexane/EtOAc 90:10 then 80:20) to afford **20** (66 mg, 54%) as a colourless solid. M.p. 201–203°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.44, 1.66 (s×2, 6H each; 1-CH_3, 5-CH_3), 3.22, 3.23* (s×2, 3H each; OCH_3, OCH_3'), 4.24 (br s, 2H; 4-H), 5.85, 6.42 (d×2, J = 5.6 Hz, 2H each; 6-H, 7-H), 6.323, 6.325* (d×2, J = 3.0 Hz, 1H each; 2-H, 2′-H), 7.27–7.31 ppm (m, 4H; Ar), * marked signals are doubled due to the presence of the two diastereomers; almost all ^{13}C NMR signals show splitting due to the presence of the two diastereomers. The two signals are assigned as C-X and C-X′; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.7, 23.3 (q×2; 1-CH_3, 1′-CH_3, 5-CH_3, 5′-CH_3), 59.5, 59.7 (q×2; OCH_3, OCH_3'), 79.4, 79.5 (d×2; C-4, C-4′), 82.9, 86.6 (s×2; C-1, C-1′, C-5, C-5′), 126.58, 126.59 (d×2; Ar), 132.3, 142.4 (d×2; C-6, C-6′, C-7, C-7′), 135.2, 135.3 (d×2; C-2), 137.7 (s; Ar), 138.5 ppm (s; C-3); IR (KBr): $\tilde{\nu}$ = 3080–3020 (=C−H), 2970–2830 (C−H), 1680, 1620 (C=C), 1510, 1450, 1370, 1340, 1190, 1100 cm^{-1}; MS (EI, 80 eV, 120°C): m/z (%): 406 (12) $[M]^+$, 362 (8) $[M-CH_3CO]^+$, 289 (20), 258 (14), 109 (16), 43 (100) $[CH_3CO]^+$; HRMS: m/z: calcd for $C_{26}H_{30}O_4$: 406.21442; found: 406.21375.

3,3′-(1,4-Phenylene)bis(2,4-dimethyl-8-oxabicyclo[3.2.1]oct-2-ene (21): Similar to the reaction of **8**, nonaflate **3** (165 mg, 0.379 mmol) was reacted with bisboronic ester **19** (50 mg, 0.15 mmol), K_2CO_3 (102 mg, 0.76 mmol), dppf (17 mg, 0.03 mmol) and $Pd(OAc)_2$ (2 mg, 0.01 mmol) in dry DMF (3 mL). The resulting crude product was then purified by column chromatography on silica gel (hexane/EtOAc 90:10 then 80:20)

to afford **21** (35 mg, 66%) as a colourless solid. M.p. 212–215°C; although the product was obtained as a mixture of diastereomers the ^{1}H NMR shows only one set of signals: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.62 (d, J = 7.4 Hz, 6H; 4-CH_3), 1.49, 1.50 (d×2, J = 2.3 Hz, 3H each; 2-CH_3), 1.82–1.90, 1.95–2.05 (m×2, 2H, 6H; 6-H, 7-H), 3.13 (m, 2H; 4-H), 4.29 (dd, J = 2.9, 3.5 Hz, 2H; 1-H), 4.40–4.44 (m, 2H; 5-H), 6.94–6.98 ppm (m, 4H; Ar); nearly all ^{13}C NMR signals show splitting due to the presence of the two diastereomers. The two signals are assigned as C-X and C-X′: ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.18, 14.19 (q×2; 4-CH_3, 4′-CH_3), 16.6 (q; 2-CH_3, 2′-CH_3), 23.3, 33.1 (t×2; C-6, C-7, C-6′, C-7′), 39.19, 39.21 (d×2; C-4, C-4′), 77.93, 77.95 (d×2; C-1, C-1′), 79.2 (d; C-5, C-5′), 128.2 (d; Ar), 132.47, 132.53 (s×2; Ar), 132.8 (s; C-2, C-2′), 137.35, 137.37 ppm (s×2; C-3, C-3′); IR (KBr): $\tilde{\nu}$ = 3030 (=C−H), 2980–2850 (C−H), 1510, 1460, 1450, 1440, 1360, 1290, 1230, 1150, 1050, 1010 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{30}O_2$ (350.5): C 82.24, H 8.63; found: C 82.24, H 8.51.

6,6′-(1,4-Phenylene)bis(2,2,5,7-tetramethyl-4,5,8,8a-tetrahydro-3a*H*-4,8-epoxycyclohepta[*d*][1,3]dioxol) (22): Similar to the reaction of **8**, nonaflate **14** (193 mg, 0.38 mmol) was reacted with bisboronic ester **19** (50 mg, 0.15 mmol), K_2CO_3 (102 mg, 0.76 mmol), dppf (17 mg, 0.03 mmol) and $Pd(OAc)_2$ (2 mg, 0.01 mmol) in dry DMF (3 mL). The resulting crude product was then purified by column chromatography on silica gel (hexane/EtOAc 90:10 then 80:20) to afford **22** (51 mg, 68%) as a colourless solid. M.p. 218–221°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.73 (d, J = 7.6 Hz, 6H; 4-CH_3), 1.36, 1.55 (s×2, 6H each; $C(CH_3)_2$), 1.56, 1.57* (d×2, J = 2.6 Hz, 3H each; 2-CH_3), 3.04 (m, 2H; 4-H), 4.26 (s, 2H; 1-H), 4.31 (d, J = 5.5 Hz, 2H; 5-H), 4.67, 4.84 (d×2, J = 5.8 Hz, 2H each; 6-H, 7-H), 6.96–6.99 ppm (m, 4H; Ar), * marked signals are doubled due to the presence of the two diastereomers; nearly all ^{13}C NMR signals show splitting due to the presence of the two diastereomers. The two signals are assigned as C-X and C-X′; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.0 (q; 4-CH_3, 4′-CH_3), 16.7, 16.8 (q×2; 2-CH_3, 2′-CH_3), 24.9, 26.3 (q×2; $C(CH_3)_2$), 80.6 (d; C-6/7, C-6′/7′), 81.79, 81.80 (d×2; C-1, C-1′), 84.7* (d; C-5, C-5′, C-6/7, C-6′/7′), 112.1 (s; $C(CH_3)_2$), 128.2 (d; Ar), 129.4 (s; Ar), 135.19, 135.24 (s×2; C-2, C-2′), 136.99, 137.00 ppm (s×2; C-3, C-3′), * marked signals show doubled intensity; IR (KBr): $\tilde{\nu}$ = 3030 (=C−H), 2980–2920 (C−H), 1610 (C=C), 1510, 1380, 1370, 1270, 1210, 1080, 1040 cm^{-1}; MS (EI, 80 eV, 100°C): m/z (%): 494 (49) $[M]^+$, 412 (11), 349 (12), 325 (10), 320 (12), 245 (31), 173 (41), 89 (12), 59 (11), 57 (11), 44 (20), 43 (32) $[CH_3CO]^+$, 32 (27), 28 (100); HRMS: m/z: calcd for $C_{30}H_{38}O_6$: 494.26685; found: 494.26754.

4-Methoxy-1,5-dimethyl-3-[(*E*)-2-phenylvinyl]-8-oxabicyclo[3.2.1]octa-2,6-diene (23): According to GP 2 MW, nonaflate **8** (1.08 g, 2.33 mmol) and *trans*-phenyl vinyl boronic acid (414 mg, 2.80 mmol) were dissolved in dry DMF (8 mL). K_2CO_3 (472 mg, 3.50 mmol), PPh_3 (122 mg, 0.47 mmol) and $Pd(OAc)_2$ (26 mg, 0.12 mmol) were added and the mixture was irradiated for 20 min at 250 W 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 **23** (347 mg, 55%) as a pale-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.44, 1.64 (s×2, 3H each; 1-CH_3, 5-CH_3), 3.45 (s, 3H; OCH_3), 4.07 (s, 1H; 4-H), 5.90, 6.34 (d×2, J = 5.7 Hz, 1H each; 6-H, 7-H), 6.32 (brs, 1H; 2-H), 6.58, 6.72 (d×2, J = 16.2 Hz, 1H each; CH=CH), 7.19–7.22 (m, 2H; Ph), 7.28–7.32 (m, 2H; Ph), 7.37–7.41 ppm (m, 1H; Ph); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.7, 23.4 (q×2; 1-CH_3, 5-CH_3), 58.3 (q; OCH_3), 78.6 (d; C-4), 83.1 (s; C-5), 86.5 (s; C-1), 126.3, 127.4, 128.5 (d×3; Ph), 128.2, 128.7 (d×2; CH=CH), 132.7, 141.7 (d×2; C-6, C-7), 135.2 (s; Ph), 136.8 (d; C-2), 137.6 ppm (s; C-3); IR (film): $\tilde{\nu}$ = 3030 (=C−H), 2980–2830 (C−H), 1630 (C=C), 1450, 1370, 1340, 1190 cm^{-1}; MS (EI, 80 eV, 60°C): m/z (%): 268 (16) $[M]^+$, 253 (3) $[M-CH_3]^+$, 225 (33), 195 (10), 194 (39), 193 (21), 179 (15), 178 (18), 165 $[M-C_8H_7]^+$ (12), 117 (11), 115 (11), 109 (15), 103 (8) $[C_8H_7]$, 96 (11), 95 (10), 91 (20), 77 (12), 75 (18), 43 (57), 28 (10); HRMS: m/z: calcd for $C_{18}H_{20}O_2$: 268.14633; found: 268.14599.

1,5-Dimethyl-3-[(*E*)-2-phenylvinyl]-8-oxabicyclo[3.2.1]octa-2,6-diene (24): According to GP 2 MW, nonaflate **7** (400 mg, 0.92 mmol) and *trans*-phenyl vinyl boronic acid (150 mg, 1.01 mmol) were dissolved in dry DMF (4 mL). K_2CO_3 (187 mg, 1.38 mmol), PPh_3 (48 mg, 0.18 mmol) and $Pd(OAc)_2$ (10 mg, 0.05 mmol) were added and the mixture was irradiated for 20 min at 250 W at 70°C and worked up as stated above. The crude product was purified on silica gel (hexane/EtOAc 95:5) to afford **24** (147 mg, 67%) as a pale-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.51, 1.55 (s×2, 3H each; 1-CH_3, 5-CH_3), 2.10, 2.51 (d×2, J = 17.0 Hz, 1H each; 4-H), 5.76, 6.21 (d×2, J = 5.6 Hz, 1H each; 6-H, 7-H), 6.13 (s, 1H; 2-H), 6.52, 6.69 (d×2, J = 17.1 Hz, 1H each; CH=CH), 7.20–7.24 (m, 1H; Ph), 7.29–7.34 (m, 2H; Ph), 7.36–7.41 ppm (m, 2H; Ph); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.6, 24.7 (q×2; 1-CH_3, 5-CH_3), 33.4 (t; C-4), 82.4, 83.1 (s×2; C-1, C-5), 125.8, 130.8 (d×2; CH=CH), 126.2, 127.2, 128.5 (d×3; Ph), 132.1, 140.0 (d×2; C-6, C-7), 133.9 (s; Ph), 135.4 (d; C-2), 137.3 ppm (s; C-3); IR (film): $\tilde{\nu}$ = 3060–3020 (=C−H), 2970–2890 (C−H), 1600 (C=C), 1490, 1450, 1370, 1330, 1240, 1190, 1160, 1140, 1100 cm^{-1}; MS (EI, 80 eV, 80°C): m/z (%): 238 (3) $[M]^+$, 195 (72) $[M-CH_3CO]^+$, 180 (34), 170 (42), 178 (41), 167 (18), 165 (49), 153 (13), 152 (15), 141 (11), 128 (19), 117 (55), 115 (42), 109 (24), 105 (10), 103 (53) $[C_7H_8]$, 96 (20), 91 (60), 77 (53), 65 (21), 53 (15), 43 (100) $[CH_3CO]^+$; HRMS: m/z: calcd for $C_{17}H_{18}O$: 238.13577; found: 238.13544.

2,2,5,7-Tetramethyl-6-[(*E*)-2-phenylvinyl]-4,5,8,8a-tetrahydro-3a*H*-4,8-epoxycyclohepta[*d*][1,3]dioxol (25): According to GP 2 MW, nonaflate **14** (400 mg, 0.787 mmol) and *trans*-phenyl vinyl boronic acid (128 mg, 0.866 mmol) were dissolved in dry DMF (4 mL). K_2CO_3 (159 mg, 1.18 mmol), PPh_3 (41 mg, 0.16 mmol) and $Pd(OAc)_2$ (9 mg, 0.04 mmol) were added and the mixture was irradiated for 20 min at 250 W at 70°C and worked up as stated above. The crude product was purified on silica gel (hexane/EtOAc 98:2) to afford **25** (170 mg, 69%) as a colourless solid. M.p. 110–112°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.10 (d, J = 7.3 Hz, 3H; 4-CH_3), 1.34, 1.54 (s×2, 3H each; $C(CH_3)_2$), 1.86 (d, J = 1.9 Hz, 3H; 2-CH_3), 3.09 (m, 1H; 4-H), 4.23 (s, 1H; 1-H), 4.31 (d, J = 5.9 Hz, 1H; 5-H), 4.59, 4.81 (d×2, J = 5.8 Hz, 1H each; 6-H, 7-H), 6.41, 6.79 (d×2, J = 16.7 Hz, 1H each; CH=CH), 7.20–7.25 (m, 1H; Ph), 7.30–7.35 (m, 2H; Ph), 7.37–7.40 ppm (m, 2H; Ph); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 17.8 (q; 4-CH_3), 16.3 (q; 2-CH_3), 24.9, 26.2 (q×2; $C(CH_3)_2$), 32.2 (d; C-4), 80.6 (d; C-7), 82.3 (d; C-5), 84.1 (d; C-6), 84.4 (d; C-1), 112.3 (s; $C(CH_3)_2$), 124.1 (d; CH=CH), 126.1, 127.5, 128.6 (d×3; Ph), 130.3 (d; CH=CH), 131.8, 132.0 (s×2; C-2, Ph), 137.5 ppm (s; C-3); IR (KBr): $\tilde{\nu}$ = 3080–2860 (=C−H, C−H), 1730, 1600 (C=C), 1500, 1460–1450, 1380–1370, 1280–1270, 1240–1210, 1160, 1100 cm^{-1}; MS (EI, 80 eV, 30°C): m/z (%): 312 (84) $[M]^+$, 297 (7) $[M-CH_3]^+$, 225 (23), 211 (13), 196 (28), 172 (15), 171 (100), 167 (14), 163 (14), 155 (12), 141 (13), 135 (15), 127 (19), 122 (17), 111 (12), 109 (24), 105 (24), 97 (13), 95 (16), 91 (22) $[C_7H_7]^+$, 85 (21), 83 (20), 77 (17), 71 (21), 69 (25), 60 (16), 57 (29), 55 (33), 43 (96) $[CH_3CO]^+$; HRMS: m/z: calcd for $C_{20}H_{24}O_3$: 312.17255; found: 312.17322.

2,2-Dimethyl-4,5,8,8a-tetrahydro-3a*H*-4,8-epoxycyclohepta[*d*][1,3]dioxol-6-yl-nonaflate (26): According to GP 1, LDA was prepared by adding *n*BuLi (1.91 mL, 4.78 mmol) to a solution of *i*Pr_2NH (0.520 g, 5.14 mmol) in dry THF (20 mL). The bicyclic precursor ketone[28] (0.728 g, 3.37 mmol) was dissolved in THF (5 mL) and added. The mixture was quenched with NfF (1.78 g, 5.88 mmol) and left to warm up to room temperature overnight. The reaction was worked up as stated above and the crude product was purified on silica gel (hexane/EtOAc 95:5) to afford **26** (1.43 g, 81%) as a colourless solid. M.p. 88–89°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29, 1.47 (s×2, 3H each; $C(CH_3)_2$), 2.12 (d, J = 17.6 Hz, 1H; 4-H), 2.90 (dd, J = 17.6, 6.0 Hz, 1H; 4-H), 4.48 (d, J = 6.0 Hz, 1H; 5-H), 4.58, 4.59 (AB-System, J_{AB} = 4.9 Hz, 1H each; 6-H, 7-H), 4.71 (d, J = 5.2 Hz, 1H; 1-H), 5.97 ppm (d, J = 5.2 Hz, 1H; 2-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 24.9, 26.1 (q×2; $C(CH_3)_2$), 31.9 (t; C-4), 85.2, 75.7 (d×2; C-6, C-7), 78.8 (d; C-1), 85.8 (d; C-5), 112.7 (s; $C(CH_3)_2$), 118.5 (d; C-2), 146.0 ppm (s; C-3); IR (KBr): $\tilde{\nu}$ = 2990–2940 (C−H), 1680 (C=C), 1410, 1400, 1290–1200 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{13}F_9O_6S$ (480.3): C 35.01, H 2.73; found: C 34.85, H 2.73.

2,2-Dimethyl-6-[(*E*)-2-phenylvinyl]-4,5,8,8a-tetrahydro-3a*H*-4,8-epoxycyclohepta[*d*][1,3]dioxol (27): According to GP 2 MW, nonaflate **26** (443 mg, 0.92 mmol) and *trans*-phenyl vinyl boronic acid (164 mg, 1.11 mmol) were dissolved in dry DMF (4 mL). K_2CO_3 (187 mg, 1.38 mmol), PPh_3 (48 mg, 0.18 mmol) and $Pd(OAc)_2$ (10 mg, 0.05 mmol) were added and the mixture was irradiated for 20 min at 250 W at 70°C and worked up as stated above. The crude product was purified on silica

gel (hexane/EtOAc 90:10) to afford **27** (189 mg, 72%) as a colourless solid. M.p. 149°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.32, 1.53 (s×2, 3H each; $C(CH_3)_2$), 2.08 (d, J = 17.2 Hz, 1H; 4-H), 2.82 (dd, J = 17.2, 6.1 Hz, 1H; 4-H), 4.51 (d, J = 6.1 Hz, 1H; 5-H), 4.53 (d, J = 5.0 Hz, 1H; 1-H), 4.58, 4.69 (d×2, J = 5.6 Hz, 1H each; 6-H, 7-H), 5.97 (d, J = 5.0 Hz, 1H; 2-H), 6.48, 6.66 (d×2, J = 16.2 Hz, 1H each; CH=CH), 7.21–7.25 (m, 1H; Ph), 7.29–7.34 (m, 2H; Ph), 7.36–7.44 ppm (m, 2H; Ph); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 24.9, 26.2 (q×2; $C(CH_3)_2$), 28.6 (t; C-4), 76.9, 79.0 (d×2; C-1, C-5), 85.6, 85.7 (d×2; C-6, C-7), 112.3 (s; $C(CH_3)_2$), 126.4, 127.7, 128.6 (d×3; Ph), 127.9 (d; C-2), 128.0, 129.3 (d×2; CH=CH), 133.7 (s; Ph), 136.8 ppm (s; C-3); IR (KBr): $\tilde{\nu}$ = 3030–2940 (=C–H, C–H), 1610 (C=C), 1450, 1380–1370, 1270, 1240–1210 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{20}O_3$ (284.4): C 76.03, H 7.09; found: C 75.59, H 7.14.

3-[(*E*)-2-Phenylvinyl]-8-oxabicyclo[3.2.1]oct-2-ene (28): According to GP 2 MW, nonaflate **17** (400 mg, 0.99 mmol) and *trans*-phenyl vinyl boronic acid (174 mg, 1.18 mmol) were dissolved in dry DMF (4 mL). K_2CO_3 (198 mg, 1.47 mmol), PPh_3 (51 mg, 0.20 mmol) and $Pd(OAc)_2$ (11 mg, 0.05 mmol) were added and the mixture was irradiated for 20 min at 250 W at 70°C and worked up as stated above. The crude product was purified on silica gel (hexane/EtOAc 95:5) to afford **28** (138 mg, 66%) as a colourless solid. M.p. 112–114°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.65–1.72 (m, 1H; 7-H), 1.93–2.04 (m, 3H; 6-H, 4-H), 2.11–2.20 (m, 1H; 7-H), 2.88 (dd, J = 16.6, 4.9 Hz, 1H; 4-H), 4.57 (t, J = 4.9 Hz, 1H; 5-H), 4.68 (m, 1H; 1-H), 6.05 (d, J = 4.9 Hz, 1H; 2-H), 6.43, 6.71 (d×2, J = 16.2 Hz, 1H each; CH=CH), 7.17–7.22 (m, 1H; Ph), 7.27–7.33 (m, 2H; Ph), 7.37–7.41 ppm (m, 2H; Ph); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 29.5 (t; C-7), 34.3 (t; C-4), 34.8 (t; C-6), 72.9 (d; C-5), 73.0 (d; C-1), 126.3, 127.3, 130.5 (d×3; Ph), 126.7, 128.6 (d×2; CH=CH), 131.6 (s; Ph), 132.8 (d; C-2), 137.3 ppm (s; C-3); IR (KBr): $\tilde{\nu}$ = 3060–3020 (=C–H), 2970–2860 (C–H), 1610 (C=C), 1490, 1440, 1380, 1360, 1220, 1180, 1070, 1020 cm^{-1}; MS (EI, 80 eV, 70°C): m/z (%): 212 (19) $[M]^+$, 184 (21), 182 (57), 169 (19) $[M-CH_3CO]^+$, 168 (13), 167 (16), 165 (21), 155 (52), 153 (37), 141 (95), 128 (99), 115 (79), 105 (26), 102 (27), 91 (100), 79 (28), 77 (64) $[Ph]^+$, 67 (11), 65 (25), 55 (26), 53 (18), 51 (17), 43 (13) $[CH_3CO]^+$, 39 (29), 29 (37); HRMS: m/z: calcd for $C_{15}H_{16}O$: 212.12012; found: 212.12056; elemental analysis calcd (%) for $C_{15}H_{16}O$ (212.3): C 84.87, H 7.60; found: C 84.22, H 7.49.

3-[(*E*)-2-Phenylvinyl]-8-thiabicyclo[3.2.1]oct-2-ene (29): According to GP 2 MW, nonaflate **5** (400 mg, 0.94 mmol) and *trans*-phenyl vinyl boronic acid (153 mg, 1.04 mmol) were dissolved in dry DMF (4 mL). K_2CO_3 (191 mg, 1.41 mmol), PPh_3 (49 mg, 0.19 mmol) and $Pd(OAc)_2$ (11 mg, 0.05 mmol) were added and the mixture was irradiated for 20 min at 250 W at 70°C and worked up as stated above. The crude product was purified on silica gel (hexane/EtOAc 98:2 then 95:5) to afford **29** (155 mg, 72%) as a yellow oil that quickly shows a darker colour upon storage. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.93 (ddd, J = 13.0, 8.0, 5.2 Hz, 1H; 7-H), 2.12 (m, 1H; 6-H), 2.25–2.32 (m, 1H; 7-H), 2.34–2.40 (m, 2H; 6-H, 4-H), 2.90 (dt, J = 17.2, 2.1 Hz, 1H; 4-H), 3.78 (m, 1H; 1-H), 3.99 (m, 1H; 5-H), 6.34 (br d, $J \approx$ 6.9 Hz, 1H; 2-H), 6.41, 6.64 (d×2, J = 16.1 Hz, 1H each; CH=CH), 7.17–7.21 (m, 1H; Ph), 7.26–7.31 (m, 2H; Ph), 7.34–7.38 ppm (m, 2H; Ph); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 34.6 (t; C-7), 38.1 (t; C-4), 40.1 (t; C-6), 44.2 (d; C-1), 45.5 (d; C-5), 128.9 (d; =CH), 126.2, 127.2, 128.5 (d×3; Ph), 131.6 (d; =CH), 133.7 (s; Ph), 135.3 (d; C-2), 137.4 ppm (s; C-3); IR (film): $\tilde{\nu}$ = 3050–3020 (=C–H), 2950–2820 (C–H), 1630, 1600 (C=C), 1490, 1450, 1440, 1420, 1240–1200, 1160–1140 cm^{-1}; MS (EI, 80 eV, 60°C): m/z (%): 228 (100) $[M]^+$, 199 (46), 195 (21), 194 (19), 185 (20), 181(11), 179 (18), 173 (22), 167 (17), 165 (22), 153 (13), 141 (15), 128 (19), 117 (11), 115 (26), 91 (37), 87 (60), 85 (13), 83 (11), 77 (18), 60 (14), 57 (10), 43 (20), 41 (21), 39 (13); HRMS: m/z: calcd for $C_{15}H_{16}S$: 228.09727; found: 228.09822.

3,6-Anhydro-2,8-dideoxy-4,5-*O*-isopropyliden-2-methyl-1-phenyloctos-7-ulose (30): Coupling product **15** (100 mg, 0.35 mmol) was dissolved in a round-bottomed flask in dry CH_2Cl_2 (3 mL). The solution was cooled to −78°C and ozone was bubbled through the solution until the remaining blue colour indicated the end of the reaction. The mixture was quenched with PPh_3 (458 mg, 1.75 mmol), stirred for 1 h at −78°C, left to warm up to room temperature and the solvent was removed in vacuo. The crude product was purified on silica gel (hexane/EtOAc 90:10) to afford **30** (70 mg, 63%) as a colourless solid. M.p. 72–75°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.34, 1.56 (s×2, 3H each; $C(CH_3)_2$), 1.35 (d, J = 7.3 Hz, 1H; 2-CH_3), 2.03 (s, 3H; 8-H), 3.84 (m, 1H; 2-H), 4.29 (d, J = 4.0 Hz, 1H; 6-H), 4.36 (dd, J = 6.7, 2.7 Hz, 1H; 3-H), 4.75–4.81 (m, 2H; 4-H, 5-H), 7.45–7.49 (m, 2H; Ph), 7.55–7.59 (m, 1H; Ph), 7.92–7.96 ppm (m, 2H; Ph); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.6 (q; C-8), 25.3 (q; 2-CH_3), 26.3, 27.3 (q×2; $C(CH_3)_2$), 42.7 (d; C-2), 82.2, 82.3 (d×2; C-4, C-5), 87.4 (d; C-3), 89.4 (d; C-6), 114.6 (s; $C(CH_3)_2$), 128.4, 128.7, 133.4 (d×3; Ph), 136.4 (s; Ph), 202.1, 206.6 ppm (s×3; C=O); IR (KBr): $\tilde{\nu}$ = 3110–3040 (=C–H), 2980–2870 (C–H), 1720, 1670 (C=O), 1600 (C=C), 1590, 1580, 1450, 1380–1370, 1350, 1270, 1230, 1210, 1160, 1100, 1070 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{22}O_5$ (318.4): C 67.91, H 6.97; found: C 67.67, H 6.88.

6-*O*-Acetyl-2-deoxy-4,5-*O*-isopropyliden-2-methyl-1-phenylhexodialdo-6,3-furanose (31): Diketone **30** (119 mg, 0.374 mmol) and $NaHCO_3$ (39 mg, 0.49 mmol) were suspended in dry CH_2Cl_2 (3 mL). The mixture was cooled to 0°C and *m*CPBA (138 mg, 0.561 mmol, 70% in H_2O) was added. The resulting mixture was stirred for 4 h at 0°C, quenched with aq $NaHSO_4$ solution (5 mL, 40%) and was then taken up with CH_2Cl_2. The phases were separated and the aqueous layer was extracted three times with CH_2Cl_2. The organic layers were combined, dried with $MgSO_4$ and the solvent was removed in vacuo. The crude product was purified on silica gel (hexane/EtOAc 80:20) to afford **31** (111 mg, 89%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29, 1.51 (s×2, 3H each; C-$(CH_3)_2$), 1.31 (d, J = 7.2 Hz, 1H; 2-CH_3), 1.91 (s, 3H; $OCOCH_3$), 3.66 (dq, J = 9.4, 7.2 Hz, 1H; 2-H), 4.65 (dd, J = 9.4, 0.8 Hz, 1H; 3-H), 4.67 (d, J = 5.9 Hz, 1H; 5-H), 4.71 (dd, J = 5.9, 0.8 Hz, 1H; 4-H), 6.20 (s, 1H; 6-H), 7.48–7.52 (m, 2H; Ph), 7.58–7.62 (m, 1H; Ph), 7.93–7.96 ppm (m, 2H; Ph); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 15.8 (q; 2-CH_3), 21.0 (q; $OCOCH_3$), 24.9, 26.4 (q×2, $C(CH_3)_2$), 82.5 (d; C-4), 85.0 (d; C-5), 90.3 (d; C-3), 102.6 (d; C-6), 113.0 (s; $C(CH_3)_2$), 128.4, 128.8, 133.5 (d×3; Ph), 136.2 (s; Ph), 169.3 (s; $OCOCH_3$), 202.0 ppm (s; PhC=O); IR (film): $\tilde{\nu}$ = 3030 (=C–H), 2990–2930 (C–H), 1750 (C=O), 1680 (C=O), 1600 (C=C), 1450, 1370, 1280, 1210, 1160, 1110, 1090, 1060 cm^{-1}; MS (EI, 80 eV, 120°C): m/z (%): 319 (2) $[M-CH_3]^+$, 275 (7) $[M-CH_3CO_2]^+$, 229 (3) $[M-C_7H_5O]^+$, 216 (19), 199 (60), 171 (14), 169 (114), 159 (41), 134 (27), 131 (14), 129 (11), 111 (18), 105 (100) $[C_7H_5O]^+$, 100 (11), 91 (18), 85 (29), 84 (22), 83 (27), 71 (19), 69 (15), 59 (33) $[CH_3CO_2]^+$, 51 (11), 43 (95) $[CH_3CO]^+$, 29 (14); MS (pos FAB): m/z (%): 357 (27) $[M+Na]^+$, 275 (41) $[M-CH_3CO_2]^+$, 105 (100) $[CH_3CO_2]^+$; HRMS: m/z: calcd for $C_{17}H_{19}O_6$: $[M-CH_3]^+$: 319.11816; found: 319.11786; elemental analysis calcd (%) for $C_{18}H_{22}O_6$ (334.4): C 64.66, H 6.63; found: C 65.09, H 6.41.

2,4-Dimethyl-3-phenyl-8-oxabicyclo[3.2.1]oct-2-en-6,7-diol (32): Coupling product **15** (300 mg, 1.05 mmol) was dissolved in MeOH (7 mL). Concentrated HCl (1 mL) and H_2O (1 mL) were added and the mixture was stirred for 1 h. Then the solvents were evaporated (40°C, 200 mbar). The mixture was taken up with MeOH (7 mL) again and stirred overnight at room temperature. The reaction mixture was quenched with saturated aq $NaHCO_3$ solution and taken up with CH_2Cl_2. The phases were separated and the aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were dried with $MgSO_4$, filtered and the solvent was removed in vacuo. The crude product was purified on silica gel (hexane/EtOAc 50:50, then 30:70) to afford **32** (168 mg, 65%) as a colourless solid. M.p. 193–196°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.77 (d, J = 7.6 Hz, 3H; 4-CH_3), 1.57 (d, J = 2.5 Hz, 3H; 2-CH_3), 3.11 (m, 1H; 4-H), 3.41, 3.49 (br s×2, 1H each; OH), 4.22–4.26 (m, 2H; 6-H, 7-H), 4.28 (s, 1H; 1-H), 4.50 (d, J = 6.1 Hz, 1H; 5-H), 6.98–7.05 (m, 2H; Ph), 7.23–7.27 (m, 1H; Ph), 7.30–7.35 ppm (m, 2H; Ph); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.7 (q; 4-CH_3), 16.7 (q; 2-CH_3), 36.8 (d; C-4), 72.4 (d; C-5), 75.9 (d; C-1), 84.7, 87.5 (d×2; C-6, C-7), 126.7, 128.1, 128.4 (d×3; Ph), 128.7 (s; Ph), 135.3 (s; C-2), 138.5 ppm (s; C-3); IR (KBr): $\tilde{\nu}$ = 3460 (OH), 3060–3000 (=C–H), 2950–2880, 2850 (C–H), 1600 (C=C), 1490, 1440, 1380–1370, 1270, 1210 cm^{-1}; MS (EI, 80 eV, 120°C): m/z (%): 246 (13) $[M]^+$, 185 (19), 182 (14), 171 (100), 144 (14), 129 (17), 128 (22), 115 (22), 105 (11), 91 (29), 77 (12) $[Ph]^+$, 43 (27), 41 (14); HRMS: m/z: calcd for $C_{15}H_{18}O_3$: 246.12376; found: 246.12560.

2,6-Anhydro-1,7-bis-*O*-[*tert*-butyl(dimethyl)silyl]-3,4,5-trideoxy-3,5-dimethyl-4-phenylhept-3-enitol (33): Diol **32** (83 mg, 0.34 mmol) was dis-

solved in a mixture of MeOH and H_2O (5 mL and 0.5 mL). $NaIO_4$ (108 mg, 0.51 mmol) was added and the mixture was stirred for 10 min as a white precipitate formed. After complete conversion (TLC control) $NaBH_4$ (36 mg, 1.01 mmol) was added and the mixture was stirred for additional 15 min. After complete conversion (TLC control) the reaction was quenched with aq NaOH (2 N, 2 mL). The reaction mixture was taken up with EtOAc, the phases were separated and the organic phase was washed with HCl (1 N), saturated aq $NaHCO_3$ solution and brine. The layers were separated and the organic layer was dried with $MgSO_4$, filtered and the solvent was removed in vacuo. The crude product (108 mg) was dissolved in dry CH_2Cl_2 (5 mL) in a heat-gun-dried flask under an argon atmosphere. TDBMSCl (144 mg, 0.96 mmol) and imidazole (118 mg, 1.74 mmol) were added and the mixture was stirred for 1 h at room temperature. The reaction mixture was then taken up with CH_2Cl_2 and washed with water. The organic layer was separated, dried with $MgSO_4$, filtered and the solvent was removed in vacuo. The crude product was purified on silica gel (hexane/EtOAc 99:1, then 98:2) to afford **33** (173 mg, 83 %) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.08$, 0.09 (s×2, 6H each; $(CH_3)_2Si$), 0.84 (d, $J = 6.9$ Hz, 3H; 5-CH_3), 0.90, 0.92 (s×2, 9H each; $(CH_3)_3CSi$), 1.49 (s, 3H; 3-CH_3), 2.40 (dd, $J =$ 12.9, 6.9 Hz, 1H; 5-H), 3.62 (dd, $J = 10.1$, 2.8 Hz, 1H; 6-CH_2), 3.77 (dd, $J = 10.1$, 6.8 Hz, 1H; 6-CH_2), 3.79 (dd, $J = 10.9$, 4.3 Hz, 1H; 2-CH_2), 3.82 (m, 1H; 6-H), 3.86 (dd, $J = 10.9$, 2.8 Hz, 1H; 2-CH_2), 4.11 (m, 1H; 2-H), 7.11–7.14 (m, 2H; Ph), 7.22–7.27 (m, 1H; Ph), 7.30–7.35 ppm (m, 2H; Ph); ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = -5.34$, -5.32, -5.2, -5.1 (q×4; $(CH_3)_2Si$), 12.1 (q; 5-CH_3), 15.7 (q; 3-CH_3), 18.3, 18.4 (s×2; $(CH_3)_3CSi$), 25.9, 26.0 (q×2; $(CH_3)_3CSi$), 35.8 (d; C-5), 63.7 (t; 6-CH_2), 65.0 (t; 2-CH_2), 76.7 (d; C-6), 79.9 (d; C-2), 126.4, 128.0*, 128.9 (d×3, s; Ph, C-3), 139.5, 142.0 ppm (s×2; Ph, C-4); * marked signals show higher intensity; IR (film): $\tilde{\nu} = 3020$ (=C–H), 2930–2840 (C–H), 1610 (C=C), 1480, 1430, 1380–1370, 1260, 1210, 1180, 1130 cm^{-1}; MS (EI, 80 eV, 100 °C): m/z (%): 476 (>1) $[M]^+$, 420 (10), 419 (28) $[M-C_4H_9]^+$, 332 (21), 331 (75) $[M-C_7H_{17}OSi]^+$, 195 (15), 172 (66), 143 (11), 117 (68), 115 (12), 89 (32), 75 (45), 73 (100), 59 (11), 57 (14), 43 (17), 41 (11); HRMS: m/z: calcd for $C_{27}H_{48}O_3Si_2$: 419.24377; found: 419.24477.

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