One-Pot Transformation of Silyl Enol Ethers into 1,3-Dienes: In situ Generation of Alkenyl Nonaflates and Subsequent Heck Reactions − Scope and Limitations[‡]

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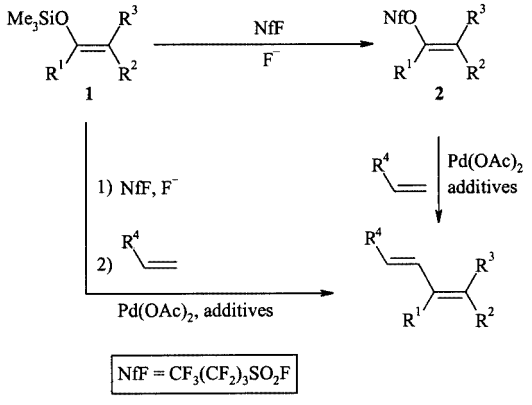
Palladium-catalysed reactions between methyl acrylate and the isolated alkenyl nonaflates **2a**, **2d** and **2e** proceed without difficulties, furnishing the desired 1,3-dienes **3**, **14** and **15** in good yields. The use of other alkenyl nonaflates and olefins in this Heck reaction was also examined. The main purpose of this study was the development of an in situ generation of the required alkenyl nonaflates **2** from the corresponding silyl enol ethers **1** and their one-pot transformation into 1,3-dienes. Thus, the previously described fluoride-promoted exchange of the trimethylsilyl substituent of typical enol ethers **1** for a nonafluorobutylsulfonyl group was directly combined with the palladium-catalysed coupling step. This sequence allowed the efficient transformation of a variety of silyl enol ethers **1** into highly substituted 1,3-dienes in a practical one-pot procedure. The scope and limitations, together with the chemo- and stereoselectivity, of this process are discussed. A particular intriguing example involves a one-pot synthesis of silyl enol ether **1j** by means of a Diels–Alder reaction, subsequent nonaflation and a Heck reaction with *tert*-butyl acrylate, furnishing the highly functionalised 1,3-diene **30** in good overall yield.

Introduction

The Heck reaction, introduced in 1968, has meanwhile become textbook knowledge.[1] This palladium-catalysed reaction between alkenes and alkenyl and aryl halides provides a variety of unsaturated systems of great importance in organic synthesis, as demonstrated in numerous applications.[2] The required alkenyl halides are very often unavailable under straightforward and mild reaction conditions, and so the corresponding alkenyl triflates, which can be prepared with good selectivity from carbonyl compounds, are extremely useful alternatives.[3] Alkenyl nonaflates (*nonafl*uorobutanesulfon*ates*) **2** behave very similarly, but their transition metal-catalysed coupling reactions have been studied in only a few cases.[4] We have recently reported that a variety of structurally rather diverse alkenyl nonaflates **2** can be prepared by fluoride-promoted conversion of silyl enol ethers **1** with nonafluorobutylsulfonyl fluoride (NfF).[5] This reagent is commercially available and presents several advantages, as described in our preceding reports.[5−9] We now wish to present our efforts aimed towards the development of one-pot conversions of silyl enol ethers **1** into the corresponding 1,3-dienes, via the intermediary stage of alkenyl nonaflates **2**, by Heck coupling, as illustrated in Scheme 1. Other palladium-catalysed one-pot reactions such as the Suzuki coupling will be described in forthcoming publications.[7,10]



Scheme 1

Heck Reactions of Isolated Alkenyl Nonaflates

We first examined Heck reactions between isolated alkenyl nonaflates **2a**−**2e** and typical olefins, in order to estab-

[‡] See ref.[7]

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lish appropriate coupling conditions for the planned one-pot transformation. For these purposes we used the phosphane-free catalytic system with palladium(II) acetate as source of palladium(0), mostly in dimethylformamide or dimethylformamide/tetrahydrofuran mixtures as solvent, and employing the following modifications:

Conditions **A** − potassium carbonate, tetra-*n*-butylammonium chloride at room temperature (Jeffery's conditions);[2e]

Conditions **B** − potassium carbonate, potassium acetate at temperatures between 60 and 85 °C;[11]

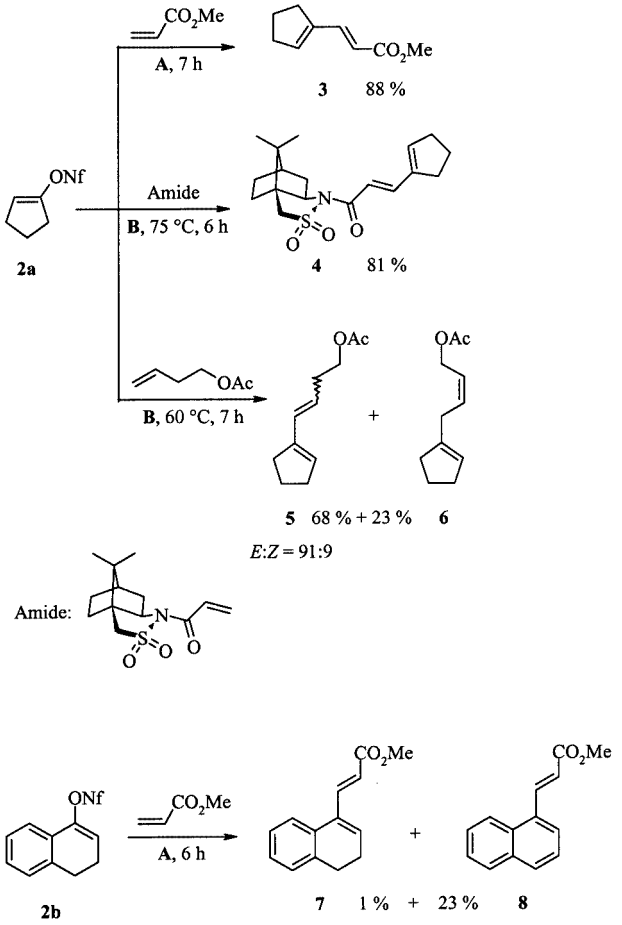
Conditions **C**− triethylamine, lithium chloride at room temperature or with heating (less expensive, modified Jeffery's conditions).

Conditions **A** and **C** were only employed with electron-deficient alkenes such as methyl acrylate, and provided better yields than conditions **B**. These last conditions were only efficient at elevated temperatures, although they are more generally applicable, including alkenes not substituted with electron-withdrawing substituents.

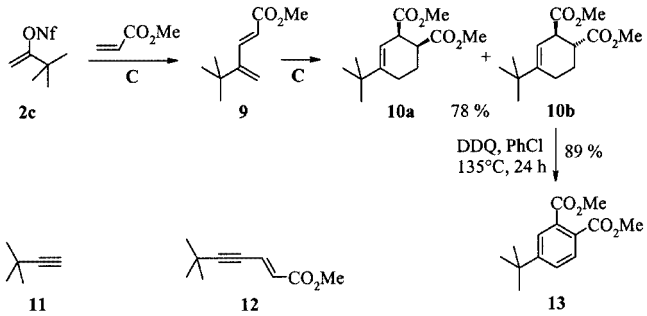
Model alkenyl nonaflate **2a** was successfully combined with methyl acrylate under conditions **A** to furnish 1,3-diene **3** in excellent yield (Scheme 2). Conditions **B** were used to couple **2a** to an acrylamide bearing a camphor-derived chiral auxiliary, which resulted in highly efficient formation of 1,3-diene **4**. Finally, **2a** and but-3-en-1-yl acetate gave the expected coupling product **5** as a mixture of *E* and *Z* isomers, together with deconjugated diene **6** as a side product. Reaction conditions **B** were highly efficient, providing a 91% yield of **5** and **6**. The formation of **6** is evidence of the expected low regioselectivity of the reductive elimination of palladium during the final step of this Heck reaction.[2a] The combination of **2a** with butyl vinyl ether under conditions **B** was less successful, and afforded (after hydrolysis of the primary coupling product) 1-acetylcyclopentene only in low yield.[7]

The coupling of the dihydronaphthalene derivative **2b** with methyl acrylate under the mild conditions **A** afforded the expected compound **7** in very small quantities, naphthalene derivative **8** instead being isolated as the major component, albeit only in moderate yield. Apparently, aromatization of the primary Heck coupling product **7** owing to a (palladium-catalysed) dehydrogenation reaction takes place under the reaction conditions (Scheme 2, last example).

The pinacolone-derived nonaflate **2c** also proved to be a special case. Whereas we later found appropriate conditions that allowed isolation of the expected diene **9** in moderate yield (see below) the palladium(II) acetate-catalysed reaction between **2c** and methyl acrylate in the presence of lithium chloride and triethylamine as base furnished Diels−Alder adducts **10**, derived from the intermediate 1,3-diene **9** and methyl acrylate, in good yields (Scheme 3). Cyclohexene derivatives **10a** and **10b** were formed in a 1:4.6 ratio and in 78% overall yield. The assumption that the two isomers were diastereomers could be confirmed by base-catalysed isomerization of pure **10a**, which again produced a mixture of the two isomers, now in a 1:7 ratio. The constitution of the Diels−Alder adducts and thus the regioselectivity of the cycloaddition could be established by oxidation of **10b** with DDQ, which afforded dimethyl 4-(*tert*-butyl)-phthalate (**13**) in 89% yield.[12] The crude product of this reaction showed the presence of a symmetrical isomer in the 3−4% range, possibly the product of a regioisomer undetectable in the primary reaction mixture.[13] The regioselectivity of the Diels−Alder reaction between 1,3-diene **9** and methyl acrylate is thus in the range of 95:5. This high selectivity and the mildness of the conditions were quite surprising,[14] although we did not further examine whether this is a result of palladium and/or lithium chloride accel-



Scheme 2. **A**: $Pd(OAc)_2$, nBu_4NCl, K_2CO_3, DMF, room temp.; **B**: $Pd(OAc)_2$, KOAc, K_2CO_3, DMF



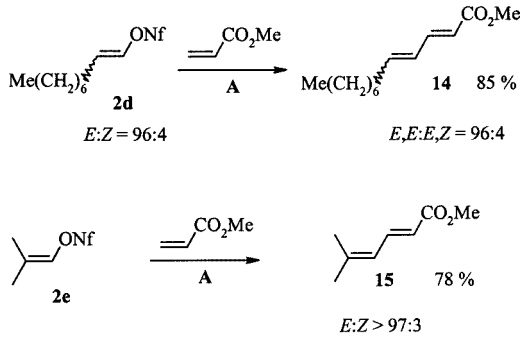
Scheme 3. **C**: $Pd(OAc)_2$, LiCl, Et_3N, THF, 58 °C, 60 h

eration or a consequence of the higher preference of the required *s-cis* conformation of **9** due to the presence of the bulky 3-*tert*-butyl group.

The coupling between **2c** and methyl acrylate provided a further side product: chromatography permitted the isolation of pure methyl (*E*)-6,6-dimethylhept-2-en-4-ynoate (**12**)[15] in 7% yield. Although mechanistically not at all clear, we assume that this compound arises from an oxidative coupling of methyl acrylate with 3,3-dimethylbutyne (**11**), which is in turn generated by base-induced elimination of nonafluorobutanesulfonic acid (NfOH) from **2c**.[16]

We also examined coupling reactions between 1,3-butadien-2-yl nonaflate and methyl acrylate or styrene, which might have produced interesting cross-conjugated trienes. However, all attempts to perform these reactions resulted only in unidentifiable product mixtures.[7]

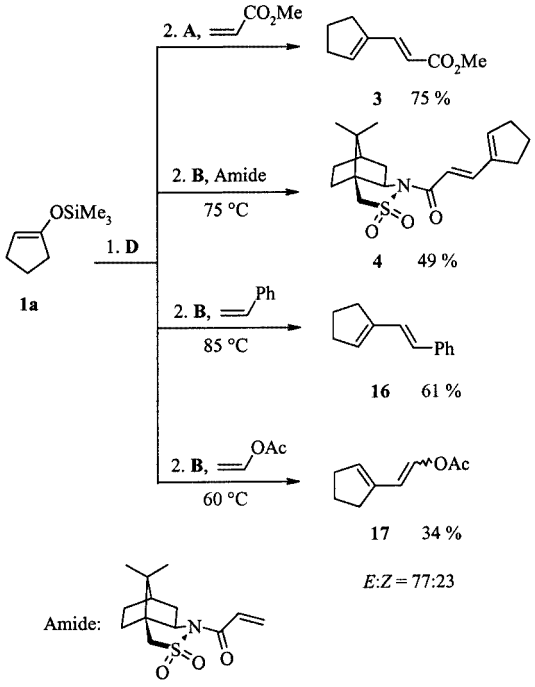
Gratifyingly, Heck reactions between aldehyde-derived alkenyl nonaflates **2d** and **2e** and methyl acrylate proceeded without any problems (Scheme 4). Conditions **A** furnished the expected 1,3-dienes **14** and **15** in very good yields. Remarkably, the *E*/*Z* ratio observed in **2d** was completely transferred to the coupling product **14**. Thus, the alkenyl nonaflates react under these mild conditions with an excellent degree of retention of configuration. The formation of the second disubstituted double bond resulting from reductive elimination of palladium proved to be exclusively *E* (with the exception of the reaction giving **5**), thereby favouring minimum steric interactions during the elimination step.[17]



Scheme 4. **A**: $Pd(OAc)_2$, nBu_4NCl, K_2CO_3, DMF, room temp., 6 h

One-pot Transformations of Silyl Enol Ethers into 1,3-Dienes

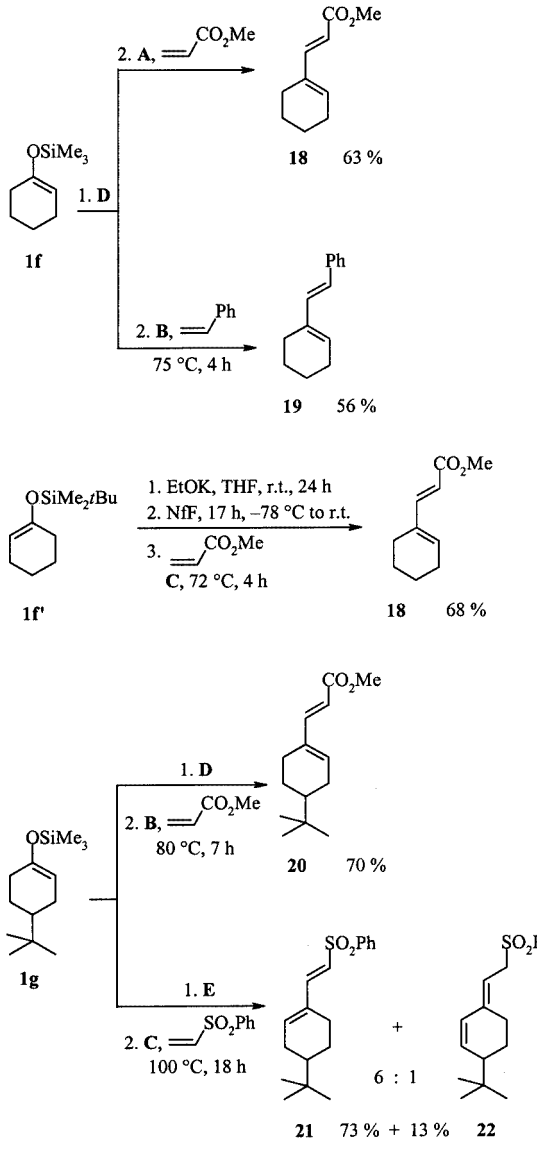
The actual purpose of this study was the development of an efficient one-pot procedure for the synthesis of synthetically valuable 1,3-dienes. Apparently, the main point of concern was the compatibility of the reagents required for the first nonaflation step − i.e., the fluoride promoters and excess of NfF − with the activity of the palladium catalysts involved in the second coupling step. The following examples demonstrate the scope and limitations of this one-pot process. We started with cyclic silyl enol ether **1a** because the intermediate nonaflate **2a** has shown particularly unproblematic behaviour in coupling reactions (see Scheme 2). An exchange of the trimethylsilyl group in **1a** for a nonafluorobutylsulfonyl substituent was achieved, as reported earlier, with nonafluorobutylsulfonyl fluoride (NfF) in the presence of substoichiometric amounts of nBu_4NF at room temperature. After 16 h, the coupling partner and the ingredients for the Heck reaction were added to the resulting solution of **2a**, and the mixture was treated as indicated in Scheme 5. This one-pot procedure furnished 1,3-dienes **3**, **4**, **16** and **17** with methyl acrylate, the chiral acrylamide, styrene or vinyl acetate as coupling partners. The yields were generally quite satisfactory, with only the coupling with vinyl acetate proceeding in low yield and resulting in an *E*/*Z* mixture.



Scheme 5. **A**: $Pd(OAc)_2$, nBu_4NCl, K_2CO_3, DMF, room temp., 6 h; **B**: $Pd(OAc)_2$, KOAc, K_2CO_3, DMF, 6 h; **D**: nBu_4NF, NfF, THF, room temp., 16 h

Not surprisingly, the coupling of the closely related trimethylsiloxycyclohexene (**1f**) with methyl acrylate and with styrene gave 1,3-dienes **18** and **19** with similar efficiency. We also examined the conversion of *tert*-butyldimethylsiloxycyclohexene (**1f′**) into a nonaflate with subsequent Heck coupling (Scheme 6). As demonstrated earlier, the standard fluoride-promoted exchange reaction only operates with *trimethyl*silyl derivatives, and not with sterically more hindered trialkylsilyl groups.[7] However, the potassium cyclohexen-1-olate generated by treatment of **1f′** with potassium ethoxide[18] could be trapped with NfF, and the intermediate nonaflate **2f** was directly coupled with methyl acrylate to provide the 1,3-diene **18** in 68% overall yield. This experiment thus demonstrates that silyl enol ethers with sterically more demanding silyl groups can also be used in a modified one-pot procedure.

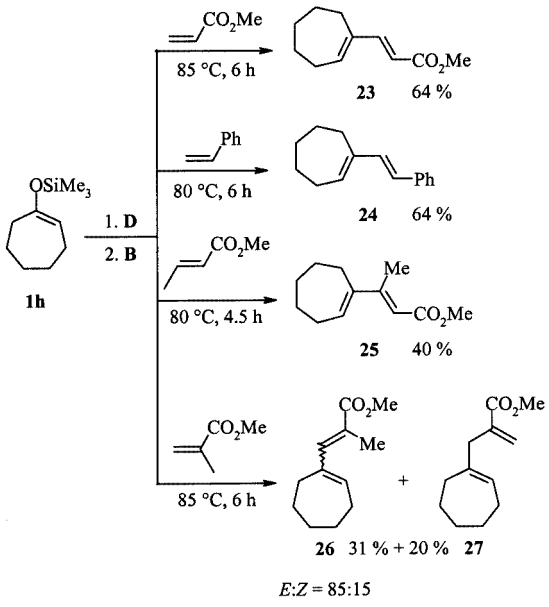
With 4-*tert*-butylcyclohexene derivative (**1g**), Heck coupling with methyl acrylate furnished the desired 1,3-diene **20**



Scheme 6. **A**: $Pd(OAc)_2$, nBu_4NCl, K_2CO_3, DMF, room temp., 6 h; **B**: $Pd(OAc)_2$, KOAc, K_2CO_3, DMF; **C**: $Pd(OAc)_2$, LiCl, Et_3N, DMF; **D**: nBu_4NF, NfF, THF, room temp., 16 h; **E**: dibenzo-18-crown-6, KF, NfF, DMF, room temp., 60 h

in good yield, whereas phenyl vinyl sulfone as the acceptor component provided the expected 1,3-diene **21** (73% yield) along with an isomeric 1,3-diene **22** (13% yield). Compound **22** was probably formed by proton migration under the reaction conditions employed. The constitution and configuration as given were unequivocally established by ^1H NMR spectroscopy by NOE.

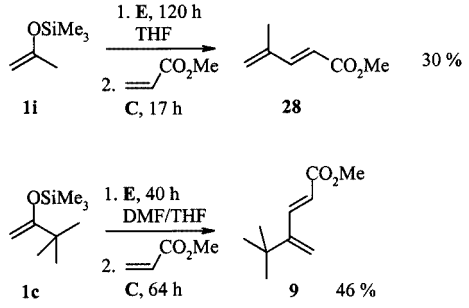
The one-pot procedure was next examined with 1-trimethylsiloxycycloheptene (**1h**) as starting material. Here, again, couplings with methyl acrylate and styrene to 1,3-dienes **23** and **24** proceeded with good overall yields (Scheme 7). We also tested disubstituted olefins as acceptors in Heck couplings with **1h**. As expected, the transformations were not very efficient. Methyl crotonate gave 1,3-diene **25** in only 40% yield, whilst methyl methacrylate afforded a mixture of the three coupling products (*E*)-**26**,



Scheme 7. **B**: $Pd(OAc)_2$, KOAc, K_2CO_3, DMF; **D**: nBu_4NF, NfF, THF, room temp., 16 h

(*Z*)-**26** and **27** in 51% yield. Both reactions proceeded less cleanly, and compounds **25** to **27** could not be isolated in analytically pure form. One-pot nonaflation/coupling reactions of **1h** were also performed with acrylonitrile and dimethyl vinyl phosphonate as acceptor olefins, but the formed 1,3-dienes were not obtained in pure form.[7]

The one-pot reactions starting with silyl enol ethers **1i** and **1c**, derived from methyl ketones, turned out to be more complex. Nonaflation of **1i**, induced by KF in the presence of dibenzo-18-crown-6, was found to be efficient,[5] and subsequent Heck reaction (conditions **C**) resulted in complete conversion of the intermediate isopropenyl nonaflate **2i** after 17 h at room temperature (^1H NMR monitoring). However, the expected coupling product **28** was isolated only in 30% yield (Scheme 8). Probably, **2i** undergoes elimination of NfOH as a competing reaction under the conditions applied (see the formation of **11** from **1c**).

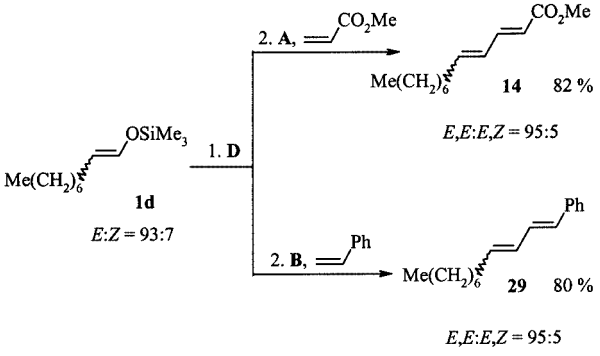


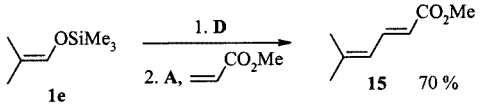
Scheme 8. **C**: $Pd(OAc)_2$, LiCl, Et_3N, DMF/THF, room temp.; **E**: dibenzo-18-crown-6, KF, NfF, room temp.

3,3-Dimethylbuten-2-yl nonaflate (**2c**), generated from silyl enol ether **1c**, required 64 h at room temperature to achieve complete conversion, probably due to steric hindrance at the reacting centre. ^1H NMR monitoring of the reaction indicated appreciable amounts of 3,3-dimethylbu-

tyne[19] **11** formed during the reaction by a base-induced elimination of NfOH from intermediate **2c**.[16] As a result, the 1,3-diene **9** was obtained in only 46% yield. Our attempts to improve the yield of **9** in experiments with isolated **2c** revealed that a highly polar solvent such as dimethylformamide favours elimination of NfOH even at room temperature.[20] When the less polar tetrahydrofuran was used as solvent, neither the Heck reaction nor the elimination took place at room temperature. At 58 °C the coupling became highly predominant over the elimination, but the subsequent Diels–Alder reaction between **9** and methyl acrylate was also accelerated under the employed conditions, producing cyclohexene derivative **10** (see Scheme 3). So far we have not performed further experiments to optimise the synthesis of 1,3-diene **9**.

Aldehyde-derived silyl enol ethers **1d** and **1e** behaved as anticipated in view of the results obtained with isolated alkenyl nonaflates already presented in Scheme 4. Heck reactions (conditions **A**) with methyl acrylate afforded the expected 1,3-diene esters **14** and **15** in good to excellent yields. Styrene could be coupled under conditions **B** to furnish **29** in 80% yield (Scheme 9). With respect to the stereoselectivity of these processes, they occur, as already stated above, with excellent retention of the double bond configuration introduced via the silyl enol ether and with high *E* selectivity with respect to the newly formed disubstituted double bond bearing the methoxycarbonyl or the phenyl group.

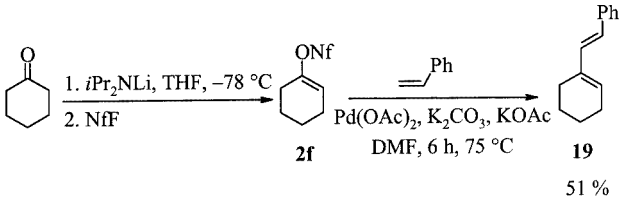




Scheme 9. **A**: $Pd(OAc)_2$, nBu_4NCl, K_2CO_3, DMF, room temp., 6 h; **B**: $Pd(OAc)_2$, KOAc, K_2CO_3, DMF, 75 °C, 6 h; **D**: nBu_4NF, NfF, THF, room temp., 16 h

Nonaflates derived from ketones may also be generated directly by deprotonation of the corresponding carbonyl compounds and trapping with a nonaflating reagent such as NfF. We were actually able to demonstrate that nonaflate **2f**, produced from cyclohexanone, LDA and quenching with NfF, can be used without isolation in a Heck reaction with styrene (Scheme 10). Under conditions **B**, the expected diene **19** was isolated in an overall yield of 51%.

What are the advantages of our "detour" via silyl enol ethers? Our method allows for the exploitation of all the

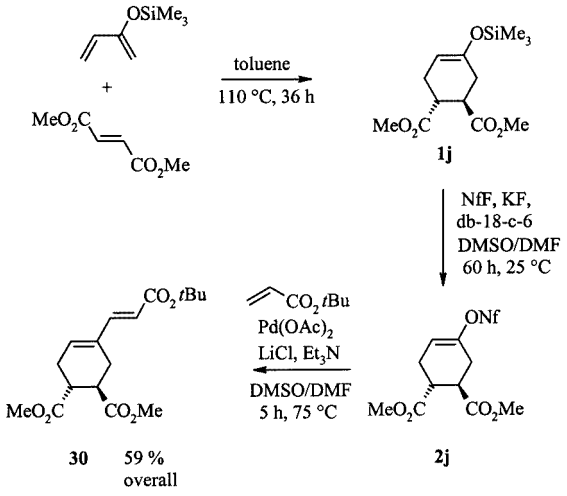


Scheme 10

beneficial properties of silyl enol ethers, in particular their regio- and stereoselective preparation combined with the possibility of purification by distillation or chromatography. Of particular value are the nonaflate intermediates produced via aldehyde-derived silyl enol ethers. Formation and trapping of aldehyde enolates is generally not very productive or even impossible.

The stereoselectivity provided by the silyl enol ethers has already been exploited for the synthesis of 1,3-dienes **14** and **29** (Scheme 9). In addition, we were recently able to demonstrate that highly enantioenriched 1,3-dienes of type **20** (Scheme 6) can be prepared by enantioselective deprotonation of ketones such as 4-*tert*-butylcyclohexanone, affording silyl enol ether **1g** in approximately 90% *ee*.[9] This enantioselectivity obtained in the deprotonation step was completely transferred to the corresponding coupling products.

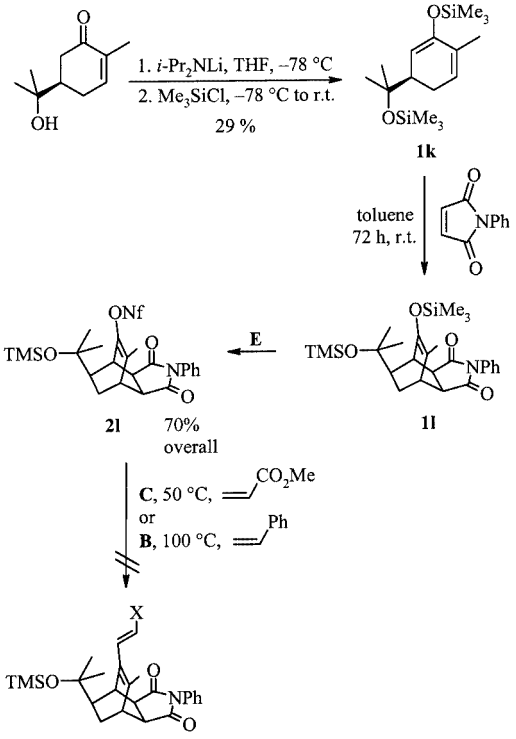
A further advantage of the use of silyl enol ethers lies in the variety of methods available for their preparation. It is not just the deprotonation of carbonyl compounds; they can also be generated by conjugate addition of nucleophiles such as cuprates to α,β-unsaturated carbonyl compounds,[21] and Diels–Alder reactions may also deliver highly substituted and functionalised silyl enol ethers. To demonstrate the potential of this approach, we performed the [4 + 2] cycloaddition between 2-trimethylsiloxy-1,3-butadiene and dimethyl fumarate, which efficiently provided the siloxycyclohexene derivative **1j** (Scheme 11).[22] Its in situ nonaflation occurred under slightly modified conditions to provide nonaflate **2j**, and the final Heck reaction



Scheme 11

was performed with *tert*-butyl acrylate under conditions **C**. These three steps were performed as a one-pot reaction and they furnished 1,3-diene **30** in a satisfactory 59% overall yield.

A similar motivation prompted us to study the siloxydiene **1k**, which was smoothly prepared from a carvone-derived α,β-unsaturated enone. The Diels−Alder reaction with *N*-phenyl maleimide gave the tricyclic *endo*-cycloadduct **1l** (Scheme 12).[23] This intermediate could be chemoselectively converted into the nonaflate **2l** without cleavage of the trimethylsilyl group of the tertiary alcohol. Unfortunately, nonaflate **2l** proved to be inert under various conditions, and all attempts to perform Heck couplings with methyl acrylate or styrene resulted only in the recovery of **2l**. We assume that this low reactivity is due to the extremely high steric shielding around the hindered tetrasubstituted alkene moiety.



Scheme 12. **B**: $Pd(OAc)_2$, KOAc, K_2CO_3, DMF, 24 h; **C**: $Pd(OAc)_2$, LiCl, Et_3N, DMF, 20 h; **E**: dibenzo-18-crown-6, KF, NfF, DMF/THF, room temp., 67 h

Conclusion

On the basis of our previously described fluoride-promoted exchange of the trimethylsilyl substituent of enol ethers for a nonafluorobutylsulfonyl group and a subsequent Heck reaction we have been able to establish an efficient one-pot procedure that converts silyl enol ethers **1** into a variety of 1,3-dienes. Most cyclic enol ethers underwent exchange reaction and couplings with monosubstituted olefins bearing electron-withdrawing substituents without problems, providing the expected 1,3-dienes in good yields. Furthermore, silyl enol ethers derived from aldehydes such as **1d** and **1e** furnished the expected products in good yield. We encountered complications in the coupling reactions of dihydronaphthalene nonaflate **2b** and of the pinacolone-derived nonaflate **2c**. The latter was convertible into diene **9**, but under conditions **C** a Diels−Alder reaction with methyl acrylate gave the cyclohexene derivative **10** as a subsequent product. However, it proved possible to establish appropriate conditions (see Scheme 8, conditions **E** combined with **C** at room temperature) under which the methyl ketone-based silyl enol ethers **1c** and **1i** were converted into the corresponding 1,3-dienes **9** and **28** in moderate to low yield. Of particular interest are reaction sequences involving Diels−Alder reactions to deliver the silyl enol ether unit. The one-pot transformation of 2-trimethylsiloxy-1,3-butadiene via the cyclohexene derivatives **1j** and **2j**, followed by coupling with *tert*-butyl acrylate, proceeded smoothly, giving the highly functionalised diene **30** in good overall yield. Without the necessity to isolate or purify the intermediate alkenyl nonaflates, our one-pot transformations make a variety of synthetically useful 1,3-dienes available in a straightforward, selective and efficient manner.

Experimental Section

General Methods: For general information see refs.[5,8]

The drying of nBu$_4$NF solution in THF (1 mmol·mL^{-1}, Aldrich or Fluka, contains 3% water) is described in our preceding publication.[8] Alkenyl nonaflates **2** are synthesised as previously described by us.[5] The nonaflation and Heck coupling reactions were routinely conducted under an atmosphere of argon in heat-gun-dried reaction flasks, although the presence of air did not appreciably affect the Heck coupling reaction results[17] in a few comparative experiments. When applicable, the addition of the components was performed by syringe.

But-3-en-1-yl acetate[24] and (1*R*,2*S*,4*S*)-(*N*-propenoyl)bornane-10,2-sultam[25] were synthesised as described in the literature. Phenyl vinyl sulfone (>98%) was used as purchased from Fluka.

Heck Coupling Reactions with Isolated Nonaflates 2 − General Procedure 1 (GP1): A mixture of the corresponding nonaflate **2**, base, additive, olefin and $Pd(OAc)_2$ (4−8 mol %) in the solvent or the solvent mixture was stirred under the conditions described in the individual experiments. After aqueous workup and extraction with EtOAc or *n*-pentane, the pure product was isolated by column chromatography (CC) or kugelrohr distillation unless stated otherwise. The bases K_2CO_3 or Et_3N and the additives KOAc, nBu$_4$NCl or LiCl were used in different combinations as described below.

Methyl (*E*)-3-(Cyclopent-1-enyl)propenoate (3): This compound was prepared by **GP1**, a mixture of nonaflate **2a** (0.366 g, 1.00 mmol), nBu$_4$NCl (0.278 g, 1.00 mmol), K_2CO_3 (0.345 g, 2.50 mmol), $Pd(OAc)_2$ (0.015 g, 0.07 mmol) and methyl acrylate (0.258 g, 3.00 mmol) in DMF (5 mL) being stirred at 25 °C for 7 h. After the usual workup and CC (hexane/EtOAc, 10:1), product **3** was furnished (0.133 g, 88% yield) as a yellowish solid, m.p. 33−34 °C (ref.[26] 36.5−37.5 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.96 (quint., J = 7.5 Hz, 2 H, CH_2), 1.88−2.58 (m, 4 H, 2 CH_2), 3.74 (s, 3 H, CO_2Me), 5.72 (d, J = 15.5 Hz, 1 H, 2-H), 6.17 (m_c, 1 H, 2′-H), 7.50 (d, J = 15.5 Hz, 1 H, 3-H) ppm.

(*E*)-3-(Cyclopent-1-enyl)-1-{(1*S*,5*R*,7*R*)-10,10-dimethyl-3,3-dioxo-3λ⁶-thia-4-azatricyclo[5.2.1.0^{1,5}]dec-4-yl}propenone (4): This compound was prepared by **GP1**, a mixture of nonaflate **2a** (0.321 g, 0.88 mmol), KOAc (0.060 g, 0.61 mmol), K_2CO_3 (0.105 g, 0.76 mmol), $Pd(OAc)_2$ (0.008 g, 0.04 mmol) and (−)-*N*-propenoyl-2,10-camphorsultam (0.237 g, 0.88 mmol) in DMF (2 mL) being stirred at 75 °C for 6 h. The usual workup and CC (hexane/EtOAc, 1:1) afforded **4** (0.239 g, 81% yield) as yellowish crystals, m.p. 145−150 °C. $[\alpha]_D = -98$ (c = 0.42, $CHCl_3$). The assignment of the NMR signals was made by COSY, NOESY, HSQC and HMBC. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.96 (s, 3 H, 12"-H), 1.16 (s, 3 H, 11"-H), 1.35−1.39 (m, 1 H, 8"-H), 1.41−1.45 (m, 1 H, 9"-H), 1.87−1.92 (m, 2 H, 8"-H, 9"-H), 1.95 (quint., J = 7.3 Hz, 2 H, 4′-H), 2.47 (br. t, J = 7.3 Hz, 2 H, 3′-H), 2.42−2.57 (m, 2 H, 5′-H), AB-system (δ_A = 3.42, δ_B = 3.47, J_{AB} = 13.8 Hz, 2 H, 2"-H), ABMX-system (δ_X = 3.93, δ_A = 2.10, δ_B = 2.08, δ_M = 1.86, J_{AB} = 13.8, J_{AM} = 7.6, J_{BM} = 5.1, J_{AX} = 3.6 Hz, 4 H, 5"-H, 6"-H, 7"-H), 6.23 (m_c, 1 H, 2′-H), 6.41 (d, J = 15.0 Hz, 1 H, 2-H), 7.57 (d, J = 15.0 Hz, 1 H, 3-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 19.9 (q, C-12"), 20.8 (q, C-11"), 23.1 (t, C-4′), 26.5 (t, C-8"), 30.7 (t, C-3′), 32.8 (t, C-9"), 33.6 (t, C-5′), 38.5 (t, C-6"), 44.7 (d, C-7"), 47.8, 48.4 (2 s, C-10′′, C-1"), 53.1 (t, C-2"), 65.1 (d, C-5"), 117.4 (d, C-2), 135.3 (s, C-1′), 141.8 (d, C-3), 142.4 (d, C-2′), 164.8 (s, C-1) ppm. IR (film): $\tilde{\nu}$ = 3500−3190 cm^{-1} (N−H), 3100−3000 (=C−H), 2960, 2890 (C−H), 1675 (C=O), 1615 (C=C), 1330 (C−N). GC/MS-data: t_r = 20.5 min (275 °C). MS (EI, 70 eV): m/z (%) = 335 (14) [M$^+$], 121 ($C_8H_9O^+$, 100), 103 (10), 91 (22), 77 (20), 55 (16), 41 (10). $C_{18}H_{25}NO_3S$ (335.5): calcd. C 64.45, H 7.51, N 4.18, S 9.56; found C 64.41, H 7.64, N 4.13, S 9.34.

4-(Cyclopent-1-enyl)but-3-enyl Acetate (5) and (*Z*)-4-(Cyclopent-1-enyl)but-2-enyl Acetate (6): These compounds were prepared by **GP1**, a mixture of nonaflate **2a** (0.366 g, 1.00 mmol), KOAc (0.068 g, 0.69 mmol), K_2CO_3 (0.120 g, 0.87 mmol), $Pd(OAc)_2$ (0.009 g, 0.04 mmol) and but-3-en-1-yl acetate (1.25 g, 1.10 mmol) in DMF (3 mL) being stirred at 60 °C for 7 h. The usual workup, CC (hexane/EtOAc, 10:1) and kugelrohr distillation furnished a 68:7:25 mixture of (*E*)-**5**, (*Z*)-**5** and **6** (0.165 g, 91% overall yield) as a colourless oil. **(*E*)-5:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.05 (s, 3 H, Me), 1.52−1.96, 2.36−2.49 (2 m, 5 H, 3 H, 4 CH_2), 4.11 (t, J = 6.8 Hz, 2 H, 1-H), 5.47 (dt, J = 15.5, 6.9 Hz, 1 H, 3-H), 5.64 (m_c, 1 H, 2′-H), 6.35 (d, J = 15.5 Hz, 1 H, 4-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.0 (q, Me), 23.0, 31.3, 32.1, 32.7 (4 t, 4 CH_2), 63.9 (t, C-1), 125.3 (d, C-2′), 129.5, 129.6 (2 d, C-4, C-3), 142.3 (s, C-1′), 171.1 (s, C=O) ppm. GC/MS-data: t_r = 22.7 min. MS (EI, 70 eV): m/z (%) = 180 (<1) [M$^+$], 120 (66) [M$^+$ − AcOH], 105 (41), 91 (100), 79 (40), 43 (72). The following signals can be assigned to compound (*Z*)-**5:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.20 (t, J = 5.8 Hz, 2 H, 1-H), 5.71 (dt*, J = 10.0, 5.8 Hz, 1 H, 3-H), 5.72 (m_c, 1 H, 2′-H), 6.12 (d, J = 10.0 Hz, 1 H, 4-H) ppm; *the signal overlaps with the 2′-H signal. GC/MS data: t_r = 22.6 min. MS (EI, 70 eV): m/z (%) = 180 (<1) [M$^+$], 120 (46) [M$^+$ − AcOH], 105 (38), 91 (100), 79 (38), 43 (65). The following signals can be assigned to compound **6:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.07 (s, 3 H, Me), 2.81 (d, J = 6.3 Hz, 1 H, 4-H), 4.53 (d, J = 6.3 Hz, 1 H, 1-H), 4.97 (br. d, J = 8.7 Hz, 1 H, 2-H), 5.36 (m_c, 1 H, 2′-H), 5.60 (br. d, J = 8.7 Hz, 1 H, 3-H) ppm. GC/MS data: t_r = 22.1 min. MS (EI, 70 eV): m/z (%) = 180 (4) [M$^+$], 120 (52) [M$^+$ − AcOH], 105 (68), 91 (100), 79 (36), 43 (88). **5/6 Mixture:** IR (film): $\tilde{\nu}$ = 3150−3000 cm^{-1} (=C−H), 2960−2850 (C−H), 1740 (C=O), 1615 (C=C), 1240 (C−O−C).

Methyl (*E*)-3-(3,4-Dihydronaphthalen-1-yl)propenoate (7) and Methyl (*E*)-3-(1-Naphthyl)propenoate (8): These compounds were prepared by **GP1**, a mixture of nonaflate **2b** (0.226 g, 0.53 mmol), nBu$_4$NCl (0.139 g, 0.50 mmol), K_2CO_3 (0.142 g, 1.03 mmol), $Pd(OAc)_2$ (0.005 g, 0.02 mmol) and methyl acrylate (0.058 g, 0.67 mmol) in DMF (3 mL) being stirred at room temperature for 6 h. The usual workup and CC (hexane/EtOAc, 10:1) furnished a 4:96 mixture of **7** and **8** (0.025 g, 24% overall yield) as a viscous oil. **Compound 7:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (td, J = 8.0, 4.9 Hz, 2 H, 3′-H), 2.75 (t, J = 8.0 Hz, 2 H, 4′-H), 3.79 (s, 3 H, CO_2Me), 6.26 (d, J = 17.0 Hz, 1 H, 2-H), 6.46 (t, J = 4.9 Hz, 1 H, 2′-H), 7.62 (d, J = 17.0 Hz, 1 H, 3-H) ppm; the signals of aromatic protons overlap with those of compound **8**. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 23.6, 27.8 (2 t, 2 CH_2), 51.6 (q, CO_2Me), 118.8, 124.1, 126.9, 127.5, 127.8, 133.2 (6 d, Ar, C-2, C-2′), 132.8, 134.6, 136.6 (3 s, C-1′, C-8a′, C-4a′), 143.7 (d, C-3), 167.7 (s, C-1) ppm. GC/MS data: t_r = 12.7 min. MS (EI, 70 eV): m/z (%) = 214 (25) [M$^+$], 181 (12), 153 (100), 76 ($C_6H_4^+$, 15). **Compound 8:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.86 (s, 3 H, CO_2Me), 6.53 (d, J = 15.8 Hz, 1 H, 2-H), 7.46−7.61 (m, 2 H, Ar), 7.75 (d, J = 6.8 Hz, 1 H, Ar), 7.86−7.91 (m, 2 H, Ar), 8.19 (d, J = 8.6 Hz, 2 H, Ar), 8.54 (d, J = 15.8 Hz, 1 H, 3-H) ppm; these data match those reported in ref.[27] ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 51.8 (q, CO_2Me), 120.4 (d, C-2), 131.4, 131.7, 133.7 (3 s, C-1′, C-8a′, C-4a′), 123.4, 125.0, 125.4, 126.2, 126.9, 128.7, 130.5 (7 d, Ar), 141.9 (d, C-3), 167.3 (s, C-1) ppm. GC/MS data: t_r = 14.2 min. MS (EI, 70 eV): m/z (%) = 212 (63) [M$^+$], 181 (65) [M$^+$ − OCH_3], 165 (12), 153 (100) [M$^+$ − $C_2H_3O_2$], 141 (16), 128 (53) [$C_{10}H_8^+$], 115 (17) [$C_9H_7^+$], 76 (22) [$C_6H_4^+$], 63 (10), 40 (14).

Dimethyl 4-*tert*-Butylcyclohex-3-ene-1,2-dicarboxylate (10): A mixture of 3,3-dimethylbuten-2-yl nonaflate (**2c**) (1.35 g, 3.53 mmol), methyl acrylate (0.91 g, 10.6 mmol), lithium chloride (0.08 g, 1.89 mmol), triethylamine (0.46 g, 4.56 mmol) and $Pd(OAc)_2$ (0.04 g, 0.18 mmol) in THF (3 mL) was heated with vigorous stirring in a tightly closed flask at 58 °C for 60 h. After 13 h heating, no starting nonaflate was any longer detectable in the reaction mixture, the degree of conversion of methyl (*E*)-4-*tert*-butylpenta-2,4-dienoate (**9**) into the cycloaddition product **10** (*cis*/*trans* ratio = 1.7:1) being 50% (^{1}H NMR). After 60 h heating, intermediate **9** had been completely consumed, resulting in cycloadduct **10** (*cis*/*trans* ratio = 1:4.6). Aqueous workup (50 mL hexane/15 mL satd. aq. $NaHCO_3$ and 15 mL water) followed by CC (gradient elution: hexane/Et_2O, 25:1 to 15:1 to 10:1 to 5:1) gave methyl (*E*)-6,6-dimethylhept-2-en-4-ynoate (**12**,[28] 40 mg, 7% yield) as a yellowish liquid, dimethyl 4-*tert*-butylcyclohex-3-ene-1,2-*trans*-dicarboxylate (**10b**, 592 mg, 66%) as a yellowish oil (slowly crystallises upon keeping in a freezer, m.p. 35−40 °C) and dimethyl 4-*tert*-butylcyclohex-3-ene-1,2-*cis*-dicarboxylate (**10a**, 103 mg, 12%) as a yellowish oil. Product **10b** was distilled after CC (b.p. 150−155 °C/0.08 mbar, kugelrohr) to obtain a correct microanalysis. **Compound 12:** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26 (s, 9 H, CMe_3), 3.74 (s, 3 H, OMe), 6.13 (d, J = 15.8 Hz, 1 H, 2-H), 6.77 (d, J = 15.8 Hz, 1 H, 3-H) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 28.3 (s, CMe$_3$), 30.5 (q, CMe_3), 51.6 (q, OMe), 76.4 (s, C-4), 108.6 (s, C-5), 126.4 (d, C-3*), 128.6 (d, C-2*), 175.4 (s, C-1) ppm; *the assignment of these signals is given as described for closely related ethyl ester.[29] **Compound 10b:** ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.03 (s, 9 H, CMe_3), 1.54−1.70, 1.98−2.24 (2 m, 1 H, 3 H, 2 CH_2), 2.86 (ddd, J = 12.0, 9.6, 3.0 Hz, 1 H, 6-H), 3.53 (d*, J = 9.6 Hz, 1 H, 1-H), 3.71 (s, 3 H, CO_2Me), 3.72 (s, 3 H, CO_2Me), 5.47−5.50 (m, 1 H, 2-H) ppm; * further splitting due to the multiple couplings. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 23.4, 25.6 (2 t, C-4, C-5), 28.7 (q, CMe_3), 35.4 (s, CMe$_3$), 41.3, 44.2 (2 d, C-1, C-6), 51.8, 52.0 (2 q, 2 CO_2Me), 114.0 (d, C-2), 147.6 (s, C-3), 174.1, 175.4 (2 s, 2 CO_2Me) ppm. IR (film): $\tilde{\nu}$ = 3060 cm^{-1} (=C−H), 2965, 2950, 2925 (C−H), 1720

(br., C=O), 1685 (C=C). $C_{14}H_{22}O_4$ (254.3): calcd. C 66.12, H 8.72; found C 65.97, H 8.67. **Compound 10a:** ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.04 (s, 9 H, C*Me*$_3$), 1.96−2.26 (m, 4 H, 2 CH_2), 2.66 (ddd, *J* = 10.4, 5.6, 3.5 Hz, 1 H, 6-H), 3.47−3.52 (m, 1 H, 1-H), 3.68 (s, 6 H, 2 CO_2Me), 5.60 (d*, *J* = 4.8 Hz, 1 H, 2-H) ppm; *further splitting due to the multiple couplings. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 22.2, 23.9 (2 t, C-4, C-5), 28.9 (q, C*Me*$_3$), 35.5 (s, *C*Me$_3$), 40.9, 42.4 (2 d, C-1, C-6), 51.6, 51.7 (2 q, 2 CO_2*Me*), 114.0 (d, C-2), 148.7 (s, C-3), 173.1, 174.0 (2 s, 2 *C*O_2Me) ppm. MS (EI, 80 eV): *m*/*z* (%) = 254 (14) [M^+], 222 (21) [$M^+ - CH_3OH$], 195 (32) [$M^+ - CO_2CH_3$], 194 (100) [$M^+ - HCO_2CH_3$], 179 (34) [$M^+ - HCO_2CH_3 - CH_3$], 138 (19) [$M^+ - CO_2CH_3 -$ *t*Bu], 135 (20) [$M^+ - HCO_2CH_3 - CO_2CH_3$], 119 (14) [*t*Bu$C_6H_6^+ - CH_4$], 57 (29) [*t*Bu$^+$].

Epimerisation of Dimethyl 4-*tert*-Butylcyclohex-3-ene-1,2-*cis*-dicarboxylate (10): DBU (19 mg) was added to the solution of **10a** (21 mg) in C_6D_6 (0.55 mL) in the NMR tube, and the sample was kept at room temp. for 15 h. The subsequent ^{1}H NMR spectrum indicated a 1:7 *cis*/*trans* ratio. In the control experiment in the absence of DBU, no changes were observed after heating at 60 °C for the same period of time.

Dimethyl 4-(*tert*-Butyl)phthalate (13): Chlorobenzene (10 mL) was added to a mixture of dimethyl 4-*tert*-butylcyclohex-3-ene-1,2-*trans*-dicarboxylate (**10b**, 127 mg, 0.50 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, 341 mg, 1.50 mmol), and the resulting mixture was heated at reflux for 24 h. After this had been cooled to ambient temperature, the solvent was removed under vacuum (0.05 mbar), and the residue was treated with CCl_4 (15 mL) and filtered. The precipitate was carefully washed with CCl_4 (3 × 5 mL), and the mother solution was evaporated under vacuum. ^{1}H NMR monitoring of the crude residue showed ≥ 98% conversion of the starting material and 3−4 mol % admixture of dimethyl 5-*tert*-butylbenzene-1,3-dicarboxylate[30] with the main product, dimethyl 4-*tert*-butylbenzene-1,2-dicarboxylate (**13**). The residue was subjected to CC (gradient elution: hexane/Et_2O, 5:1 to 3:1) to give spectroscopically and analytically pure **13**[31] (111 mg, 89% yield) as yellowish oil. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.34 (s, 9 H, C*Me*$_3$), 3.89 (s, 3 H, CO_2Me), 3.92 (s, 3 H, CO_2Me), 7.55 (dd, *J* = 8.2, 2.0 Hz, 1 H, 5-H), 7.68 (dd, *J* = 2.0, 0.4 Hz, 1 H, 3-H), 7.71 (dd, *J* = 8.2, 0.4 Hz, 1 H, 6-H) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 30.9 (q, C*Me*$_3$), 35.0 (s, *C*Me$_3$), 52.4, 52.5 (2 q, 2 CO_2*Me*), 125.6, 127.8, 129.0 (3 d, C-3, C-5, C-6), 128.4, 132.4 (2 s, C-1, C-2), 155.1 (s, C-4), 167.7, 168.8 (2 s, 2 *C*O_2Me) ppm. MS (EI, 80 eV): *m*/*z* (%) = 250 (20) [M^+], 235 (100) [$M^+ - CH_3$], 219 (23) [$M^+ - CH_3O$]. IR (film): $\tilde{\nu}$ = 2955, 2905, 2870 cm^{-1} (=C−H, C−H), 1730 (C=O). $C_{14}H_{18}O_4$ (250.3): calcd. C 67.18, H 7.25; found C 66.81, H 7.16.

Methyl (*E*,*E*)-Dodeca-2,4-dienoate (14): This compound was prepared by **GP1**, a mixture of nonaflate **2d** (0.300 g, 0.71 mmol), *n*Bu_4NCl (0.262 g, 0.94 mmol), K_2CO_3 (0.201 g, 1.45 mmol), $Pd(OAc)_2$ (0.007 g, 0.03 mmol) and methyl acrylate (0.092 g, 1.07 mmol) in DMF (15 mL) being stirred at room temperature for 6 h. The usual workup and CC (hexane/EtOAc, 10:1) provided **14**[32] (0.127 g, 85% yield, *E*,*E*/*E*,*Z* = 96:4) as a yellow oil. An assignment of the NMR signals was made by COSY and HSQC. **Compound (*E*,*E*)-14:** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.5 Hz, 3 H, Me), 1.24−1.29 (m, 8 H, CH_2), 1.40 (quint., *J* = 7.0 Hz, 2 H, 7-H), 2.13 (q, *J* = 7.0 Hz, 2 H, 6-H), 3.72 (s, 3 H, CO_2Me), 5.76 (d, *J* = 15.4 Hz, 1 H, 2-H), 6.10 (dt, *J* = 13.3, 7.0 Hz, 1 H, 5-H), 6.14* (dd, *J* = 13.3, 10.0 Hz, 1 H, 4-H), 7.25 (dd, *J* = 15.4, 10.0 Hz, 1 H, 3-H) ppm; *the signal overlaps with the 5-H signal. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.1 (q, Me), 22.6, 28.7, 29.0, 29.1, 31.7, 33.0 (6 t, CH_2), 51.4 (q, CO_2*Me*), 118.6 (d, C-2), 128.3 (d, C-4), 144.0 (d, C-5), 145.5 (d, C-3), 167.7 (s, C-1) ppm. The following signals can be assigned to compound (*E*,*Z*)-**14:** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.23−2.31 (m, 2 H, 6-H), 3.74 (s, 3 H, CO_2Me), 5.85 (d, *J* = 14.9 Hz, 1 H, 2-H), 7.55−7.66 (m, 1 H, 3-H) ppm.

Methyl (*E*)-5-Methylhexa-2,4-dienoate (15): This compound was prepared by **GP1**, a mixture of nonaflate **2e** (0.845 g, 2.50 mmol), *n*Bu_4NCl (0.695 g, 2.50 mmol), K_2CO_3 (0.690 g, 5.00 mmol), $Pd(OAc)_2$ (0.022 g, 0.10 mmol) and methyl acrylate (0.645 g, 7.50 mmol) in DMF (15 mL) being stirred at room temperature for 6 h. The usual workup and CC (hexane/EtOAc, 10:1) furnished **15**[33] (0.275 g, 78% yield, *E*/*Z* > 97:3) as a yellow oil. **Compound (*E*)-15:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.87, 1.89 (2 br. s, 3 H each, 2 Me), 3.74 (s, 3 H, CO_2Me), 5.75 (br. d, *J* = 15.2 Hz, 1 H, 2-H), 5.99 (dd, *J* = 11.6, 0.6 Hz, 1 H, 4-H), 7.56 (dd, *J* = 15.2, 11.6 Hz, 1 H, 3-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 18.9, 26.5 (2 q, 2 Me), 51.4 (q, CO_2*Me*), 118.1 (d, C-4), 123.7 (d, C-2), 141.2 (d, C-3), 146.5 (s, C-5), 168.1 (s, C-1) ppm. The following signals can be assigned to (*Z*)-**15:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.86, 1.92 (2 s, 3 H each, 2 Me), 3.72 (s, 3 H, CO_2Me), 5.56 (br. d, *J* = 11.6 Hz, 1 H, 2-H), 6.87 (dd, *J* = 11.7, 11.6 Hz, 1 H, 3-H), 7.18 (dd, *J* = 11.7, 1.2 Hz, 1 H, 4-H) ppm.

One-pot Heck-coupling Procedure Starting from Silyl Enol Ethers 1: General Procedure 2 (GP2): The corresponding nonaflate **2** was generated by treatment of silyl enol ether **1** with nonafluorobutylsulfonyl fluoride (NfF) in the presence of *n*Bu_4NF (method **D**) or dibenzo-18-crown-6 (db-18-c-6)/KF (method **E**) at room temperature (reaction time 16 h unless otherwise noted) as described earlier.[5]− Base, additive, olefin and $Pd(OAc)_2$ (4−8 mol %) were added to this mixture according to **GP1**, and the resulting solution was stirred under the conditions indicated in the individual experiments. After aqueous workup and extraction with EtOAc or *n*-pentane the pure product was isolated by CC or kugelrohr distillation.

Methyl (*E*)-3-(Cyclopent-1-enyl)propenoate (3): Nonaflation of silyl enol ether **1a** (0.390 g, 2.50 mmol) with NfF (0.906 g, 3.00 mmol) was performed according to **GP2**, with *n*Bu_4NF (0.45 mmol) in THF (0.45 mL). After addition of *n*Bu_4NCl (0.862 g, 6.25 mmol), K_2CO_3 (0.862 g, 6.25 mmol), $Pd(OAc)_2$ (0.042 g, 0.19 mmol), methyl acrylate (0.645 g, 7.50 mmol) and DMF (15 mL) the mixture was stirred at 25 °C for 6 h. Isolation and purification as described above provided product **3**[26] (0.286 g, 75% yield).

(*E*)-3-(Cyclopent-1-enyl)-1-{(1*S*,5*R*,7*R*)-10,10-dimethyl-3,3-dioxo-3λ^6-thia-4-azatricyclo[5.2.1.0^{1,5}]dec-4-yl}propenone (4): Nonaflation of **1a** (0.109 g, 0.70 mmol) with NfF (0.254 g, 0.84 mmol) was performed according to **GP2**, with *n*Bu_4NF (0.13 mmol) in THF (0.13 mL). After addition of KOAc (0.048 g, 0.49 mmol), K_2CO_3 (0.084 g, 0.61 mmol), $Pd(OAc)_2$ (0.006 g, 0.03 mmol), (−)-*N*-propenoyl-2,10-camphorsultam (0.188 g, 0.70 mmol) and DMF (2 mL), the mixture was stirred at 75 °C for 6 h. Isolation and purification as described above provided **4** (0.116 g, 49% yield).

(*E*)-2-(Cyclopent-1-enyl)styrene (16): Nonaflation of **1a** (0.780 g, 5.00 mmol) with NfF (3.02 g, 10.0 mmol) was performed with *n*Bu_4NF (0.90 mmol) in THF (0.9 mL) according to **GP2**. After addition of KOAc (0.343 g, 3.50 mmol), K_2CO_3 (0.602 g, 4.36 mmol), $Pd(OAc)_2$ (0.039 g, 0.17 mmol), styrene (0.546 g, 5.25 mmol) and DMF (6 mL), the mixture was stirred at 85 °C for 6 h followed by the usual workup and CC (hexane/EtOAc, 10:1) to afford **16** (0.522 g, 61% yield) as a yellow solid, m.p. 35−44 °C (ref.[34] 36−40 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.97 (quint.,

J = 7.5 Hz, 2 H, CH_2), 2.45−2.63 (m, 4 H, 2 CH_2), 5.86 (m_c, 1 H, 2′-H), 6.41, 7.01 (2 d, J = 16.0 Hz, 1 H each, 1-H, 2-H), 7.15−7.45 (m, 5 H, Ph) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 23.2, 31.2, 33.0 (3 t, 3 CH_2), 125.8, 128.7, 132.0 (3 d, C-2′, C-2, C-1), 126.2, 127.1, 128.5, 137.8 (3 d, s, Ph), 142.8 (s, C-1′) ppm.

2-(Cyclopent-1-enyl)ethenyl Acetate (17): Nonaflation of **1a** (0.390 g, 2.50 mmol) with NfF (0.906 g, 3.00 mmol) was performed with nBu$_4$NF (0.45 mmol) in THF (0.45 mL) according to **GP2**. After addition of KOAc (0.301 g, 3.07 mmol), K_2CO_3 (0.172 g, 1.25 mmol), $Pd(OAc)_2$ (0.020 g, 0.09 mmol), vinyl acetate (1.03 g, 12.0 mmol) and DMF (8 mL), the mixture was stirred at 60 °C for 6 h, followed by the usual workup and CC (hexane/EtOAc, 10:1) to afford **17**[35] (0.130 g, 34% yield, E:Z = 77:23) as a colourless oil. (*E*)-**17**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.94 (quint., J = 7.0 Hz, 2 H, CH_2), 2.13 (s, 3 H, Me), 2.38 (br. t, J = 7.0 Hz, 4 H, 2 CH_2), 5.70 (m_c, 1 H, 2′-H), 6.24, 7.24 (2 d, J = 12.6 Hz, 1 H each, 2-H, 1-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.7 (q, Me), 23.2, 31.6, 32.7 (3 t, CH_2), 109.5 (d, C-2), 112.6 (d, C-2′), 131.2 (d, C-1), 136.2 (s, C-1′), 168.1 (s, C=O) ppm. The following signals can be assigned to (*Z*)-**17:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.15 (s, 3 H, Me), 2.65, 2.66 (2 t, J = 7.5 Hz and 7.7 Hz, 2 H each, CH_2), 5.51 (d, J = 6.9 Hz, 1 H, 2-H), 5.79 (m_c, 1 H, 2′-H), 6.96 (d, J = 6.9 Hz, 1 H, 1-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.8 (q, Me), 23.7, 32.2, 34.4 (3 t, 3 CH_2), 132.2 (d, C-2), 132.5 (d, C-2′), 136.2 (d, C-1), 138.1 (s, C-1′), 168.1 (s, C=O) ppm.

Methyl (*E*)-3-(Cyclohex-1-enyl)propenoate (18)

Starting from 1-(Trimethylsiloxy)cyclohexene (1f): Nonaflation of silyl enol ether **1f** (0.383 g, 2.25 mmol) with NfF (0.906 g, 3.00 mmol) was performed with nBu$_4$NF (0.45 mmol) in THF (0.45 mL) according to **GP2**. After addition of nBu$_4$NCl (0.655 g, 2.36 mmol), K_2CO_3 (0.670 g, 4.85 mmol), $Pd(OAc)_2$ (0.022 g, 0.10 mmol), methyl acrylate (0.276 g, 3.21 mmol) and DMF (8 mL), the mixture was stirred at 25 °C for 6 h, followed by the usual workup and CC (hexane/EtOAc, 10:1), to furnish **18**[26] (0.236 g, 63% yield) as a yellowish oil.

Starting from 1-(*tert*-Butyldimethylsiloxy)cyclohexene (1f′): Neat 1-(*tert*-butyldimethylsiloxy)cyclohexene (**1f′**) (0.425 g, 2.00 mmol) was added dropwise to a suspension of potassium ethanolate (0.178 g, 2.00 mmol, 95% assay) in THF (3 mL), and the resulting mixture was stirred at room temperature for 24 h before cooling to −78 °C. Neat NfF (0.725 g, 2.40 mmol) was added, and the reaction mixture was allowed to warm to room temperature and stirred for 17 h. The ^{1}H NMR spectrum of the reaction mixture indicated complete conversion of the silyl enol ether into the nonaflate. Addition of LiCl (0.084 g, 2.00 mmol), methyl acrylate (0.224 g, 2.60 mmol), DMF (1 mL), Et_3N (0.263 g, 2.60 mmol) and $Pd(OAc)_2$ (0.022 g, 0.10 mmol) and stirring at 72 °C for 4 h furnished, after the usual workup (hexane) and CC (hexane/Et_2O, 10:1), pure methyl (*E*)-3-(cyclohex-1-enyl)propenoate (**18**, 0.225 g, 68% yield) as a yellowish oil. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.57−1.74, 2.11−2.26 (2 m, 4 H, 4 H, 4 CH_2), 3.75 (s, 3 H, CO_2Me), 5.77 (dd, J = 15.8, 0.7 Hz, 1 H, 2-H), 6.16 (br. t, J = 4.1 Hz, 1 H, 2′-H), 7.27 (br. d, J = 15.8 Hz, 1 H, 3-H) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 21.95, 21.98, 24.0, 26.4 (4 t, 4 CH_2), 51.3 (q, CO_2Me), 114.1 (d, C-2), 134.8 (s, C-1′), 138.8 (d, C-2′), 148.3 (d, C-3), 168.0 (s, C-1) ppm.

(*E*)-(2-Cyclohex-1-enyl)styrene (19): Nonaflation of **1f** (0.852 g, 5.00 mmol) with NfF (3.02 g, 10.0 mmol) was performed with nBu$_4$NF (1.70 mmol) in THF (1.7 mL) according to **GP2**. After addition of KOAc (0.343 g, 3.50 mmol), K_2CO_3 (0.602 g, 4.36 mmol), $Pd(OAc)_2$ (0.039 g, 0.17 mmol), styrene (0.546 g, 5.25 mmol) and DMF (6 mL), the mixture was stirred at 75 °C for 4 h, followed by the usual workup and CC (hexane/EtOAc, 20:1), to afford **19**[34] (0.569 g, 56% yield) as a yellowish solid (m.p. ca. 25 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.55−1.81, 2.15−2.38 (2 m, 4 H each, 4 CH_2), 5.90 (t, J = 4.0 Hz, 1 H, 2′-H), 6.41, 6.95 (2 d, J = 16.0 Hz, 1 H each, 2-H, 1-H), 7.10−7.45 (m, 5 H, Ph) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 22.5, 22.55, 24.5, 26.1 (4 t, CH_2), 124.6, 130.8, 132.6, (3 d, C-1, C-2, C-2′), 126.1, 126.8, 128.5, 138.0 (s, 3 d, Ph), 135.8 (s, C-1′) ppm.

Methyl (*E*)-3-(4-*tert*-Butylcyclohex-1-enyl)propenoate (20): Nonaflation of silyl enol ether **1g** (0.582 g, 2.57 mmol) with NfF (0.906 g, 3.00 mmol) was performed with nBu$_4$NF (0.45 mmol) in THF (0.45 mL) according to **GP2**. After addition of KOAc (0.172 g, 1.75 mmol), K_2CO_3 (0.301 g, 2.18 mmol), $Pd(OAc)_2$ (0.020 g, 0.09 mmol), methyl acrylate (0.230 g, 2.67 mmol) and DMF (5 mL), the mixture was stirred at 80 °C for 7 h, followed by the usual workup and CC (hexane/EtOAc, 5:1), to give **20**[6,17] (0.398 g, 70% yield) as a colourless crystalline solid, m.p. 34−36 °C (ref.[17] 37.5−39 °C).

(*E*)-2-(4-*tert*-Butylcyclohex-1-enyl)ethen-1-yl Phenyl Sulfone (21) and (*E*)-2-(4-*tert*-Butylcyclohex-2-en-1-ylidene)ethyl Phenyl Sulfone (22): Nonaflation of silyl enol ether **1g** (0.227 g, 1.00 mmol) with NfF (0.395 g, 1.30 mmol) was performed in DMF (1 mL) with KF (0.060 g, 1.03 mmol) and dibenzo-18-crown-6 (0.054 g, 0.15 mmol) at 25 °C for 60 h according to **GP2**. LiCl (0.042 g, 1.00 mmol), Et_3N (0.132 g, 1.30 mmol), phenyl vinyl sulfone (0.219 g, 1.30 mmol) and $Pd(OAc)_2$ (0.011 g, 0.05 mmol) were then added, and the mixture was stirred at 100 °C for 18 h (complete conversion of the nonaflate, 6:1 ratio of products according to ^{1}H NMR of the reaction mixture), followed by the usual workup (hexane/Et_2O, 1:1) and CC (gradient elution: hexane/Et_2O, 25:1 to 15:1 to 5:1), to provide **21** (0.222 g, 73% yield) as colourless crystals (m.p. 127−129 °C) and **22** (0.038 g, 13% yield) as a colourless, crystalline solid (m.p. 53−59 °C). **Compound 21:** ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.87 (s, 9 H, CMe_3), 1.07−1.33, 1.84−2.10, 2.13−2.35 (3 m, 2 H, 3 H, 2 H, 3′-H to 6′-H), 6.19 (d, J = 15.1 Hz, 1 H, 1-H), 6.28−6.33 (m, 1 H, 2′-H), 7.29 (d, J = 15.1 Hz, 1 H, 2-H), 7.49−7.63, 7.87−7.92 (2 m, 3 H, 2 H, Ph) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 23.1, 25.4, 28.2 (3 t, C-3′, C-5′, C-6′), 27.0 (q, CMe_3), 32.1 (s, CMe$_3$), 43.5 (d, C-4′), 123.7, 133.0, 142.0, 145.4 (4 d, C-1, C-2, C-2′, C_p), 127.3, 129.1 (2 d, C_o, C_m), 133.2, 141.3 (2 s, C-1′, $C_{Ph}SO_2$) ppm. MS (EI, 80 eV): m/z (%) = 306 (7) [M^+ + 2], 305 (21) [M^+ + 1], 304 (100) [M^+], 289 (1) [M^+ − Me], 248 (43) [M^+ − CH_2=C$(CH_3)_2$], 247 (56) [M^+ − tBu], 234 (6) [M^+ − CH_2=C$(CH_3)_2$ − CH_2], 233 (5) [M^+ − tBu − CH_2], 221 (11) [M^+ − tBu − C_2H_2], 163 (11) [M^+ − $PhSO_2$], 162 (4) [M^+ − $PhSO_2H$], 147 (9) [M^+ − $PhSO_2$ − CH_4], 143 (5) [$C_{11}H_{11}^+$] or [$PhS(OH)_2^+$], 125 (14) [$PhSO^+$], 121 (5) [M^+ − $PhSO_2$ − CH_2=$CHCH_3$], 119 (11) [$C_9H_{11}^+$], 107 (19) [M^+ − $PhSO_2$ − CH_2=C$(CH_3)_2$], 106 (15) [M^+ − $PhSO_2$ − tBu], 105 (25) [$C_8H_9^+$], 93 (14) [$C_7H_9^+$], 91 (28) [$PhCH_2^+$], 79 (27) [$C_6H_7^+$], 77 (30) [Ph^+], 57 (67) [tBu$^+$], 41 (35) [CH_2=$CHCH_2^+$]. IR (film): ṽ = 3070, 2960, 2865, 2845 cm^{-1} (=C−H, C−H), 1635 (C=C), 1315, 1150 (SO_2). $C_{18}H_{24}O_2S$ (304.45): calcd. C 71.01, H 7.95; found C 71.03, H 7.93. **Compound 22:** ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.84 (s, 9 H, CMe_3), 0.84−1.00 (m, 1 H, 5′-H_a), 1.53−1.70 (m, 2 H, 5′-H_e, 6′-H_a), 1.81−1.90 (m, 1 H, 4′-H_a), 2.14−2.25 (m, 1 H, 6′-H_e), 3.90 (d, J = 8.3 Hz, 2 H, 1-H), 5.20 (br. t, J = 8.3 Hz, 1 H, 2-H), 5.85 (br. d, J = 10.2 Hz, 1 H, 3′-H), 6.06 (dd, J = 10.2, 2.7 Hz, 1 H, 2′-H), 7.50−7.57, 7.61−7.68, 7.85−7.89 (3 m, 2 H, 1 H, 2 H, Ph) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 23.4, 25.0 (2 t, C-5′, C-6′), 27.2 (q, CMe_3), 32.6 (s, CMe$_3$), 46.3 (d, C-4′), 55.9 (t, C-1),

110.3 (d, C-2), 128.5, 128.9 (2 d, C_o, C_m), 130.0, 133.5, 134.1 (3 d, C-2′, C-3′, C_p), 138.7, 143.8 (2 s, C-1′, $C_{Ph}SO_2$) ppm. MS (EI, 80 eV): *m*/*z* (%) = 304 (6) [M^+], 247 (1) [$M^+ - t$Bu], 163 (100) [$M^+ - PhSO_2$], 148 (1) [$M^+ - PhSO_2 - CH_3$], 147 (4) [$M^+ - PhSO_2 - CH_4$], 143 (5) [$C_{11}H_{11}^+$] or [$PhS(OH)_2^+$], 141 (1) [$PhSO_2^+$], 133 (2) [$M^+ - PhSO_2 - 2\,CH_3$], 125 (2) [$PhSO^+$], 121 (2) [$M^+ - PhSO_2 - CH_2{=}CHCH_3$], 107 (33) [$M^+ - PhSO_2 - CH_2{=}C(CH_3)_2$], 106 (23) [$M^+ - PhSO_2 - t$Bu], 105 (12) [$C_8H_9^+$], 93 (12) [$C_7H_9^+$], 91 (12) [$PhCH_2^+$], 77 ($Ph^+$, 9), 57 (31) [$tBu^+$]. IR (film): $\tilde{\nu}$ = 3060, 3015, 2950, 2870, 2825 cm^{-1} (=C−H, C−H), 1640 (C=C), 1305, 1145 (SO_2). $C_{18}H_{24}O_2S$ (304.45): calcd. C 71.01, H 7.95; found C 71.14, H 7.93.

Methyl (*E*)-3-(Cyclohept-1-enyl)propenoate (23): Nonaflation of silyl enol ether **1h** (0.920 g, 5.00 mmol) with NfF (3.02 g, 10.0 mmol) was performed with nBu$_4$NF (0.90 mmol) in THF (0.9 mL) according to **GP2**. After addition of KOAc (0.343 g, 3.50 mmol), K_2CO_3 (0.602 g, 4.36 mmol), $Pd(OAc)_2$ (0.039 g, 0.17 mmol), methyl acrylate (0.452 g, 5.25 mmol) and DMF (6 mL), the mixture was stirred at 85 °C for 6 h, followed by the usual workup and CC (hexane/EtOAc, 20:1), to provide **23**[36] (0.580 g, 64% yield) as a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.47−1.58, 1.73−1.85, 2.25−2.36 (3 m, 4 H, 2 H, 4 H, 5 CH_2), 3.74 (s, 1 H, CO_2Me), 5.80 (d, *J* = 16.0 Hz, 1 H, 2-H), 6.31 (t, *J* = 7.0 Hz, 1 H, 2′-H), 7.28 (d, *J* = 16.0 Hz, 1 H, 3-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 25.8, 26.1, 27.1, 29.0, 31.8 (5 t, CH_2), 51.3 (q, CO_2*Me*), 114.1, 141.9, 143.8, 149.2 (d, s, 2 d, C-2′, C-1′, C-3, C-2), 168.1 (s, C-1) ppm. IR (film): $\tilde{\nu}$ = 3010 cm^{-1} (=C−H), 2930, 2855, 1435 (C−H), 1730 (C=O), 1620 (C=C), 1170 (C−O−C). $C_{11}H_{16}O_2$ (180.25): calcd. C 73.30, H 8.95; found C 72.79, H 8.98.

(*E*)-2-(Cyclohept-1-enyl)styrene (24): Nonaflation of **1h** (0.920 g, 5.00 mmol) with NfF (3.02 g, 10.0 mmol) was performed with nBu$_4$NF (0.90 mmol) in THF (0.9 mL) according to **GP2**. After addition of KOAc (0.343 g, 3.50 mmol), K_2CO_3 (0.602 g, 4.36 mmol), $Pd(OAc)_2$ (0.039 g, 0.17 mmol), styrene (0.546 g, 5.25 mmol) and DMF (6 mL), the mixture was stirred at 80 °C for 6 h, followed by the usual workup and CC (hexane/EtOAc, 10:1), to afford **24**[34] (0.630 g, 64% yield) as a yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.35−1.85, 2.30−2.50 (2 m, 6 H, 4 H, CH_2), 6.04 (t, *J* = 7.0 Hz, 1 H, 2′-H), 6.46, 6.76 (2 d, *J* = 16.0 Hz, 1 H each, 1-H, 2-H), 7.10−7.45 (m, 5 H, Ph) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 26.3, 26.8, 27.3, 28.8, 32.2 (5 t, CH_2), 124.7, 135.5, 136.9 (3 d, C-2′, C-2, C-1), 126.2 126.8, 128.5, 138.1 (3 d, s, Ph), 143.1 (s, C-1′) ppm.

Methyl (*E*)-3-(Cyclohept-1-enyl)but-2-enoate (25): Nonaflation of **1h** (0.920 g, 5.00 mmol) with NfF (3.02 g, 10.0 mmol) was performed with nBu$_4$NF (0.90 mmol) in THF (0.9 mL) according to **GP2**. After addition of KOAc (0.343 g, 3.50 mmol), K_2CO_3 (0.602 g, 4.36 mmol), $Pd(OAc)_2$ (0.039 g, 0.17 mmol), methyl crotonate (0.525 g, 5.25 mmol) and DMF (6 mL), the mixture was stirred at 80 °C for 4.5 h, followed by the usual workup and CC (hexane/EtOAc, 10:1), to furnish **25** (0.389 g, 40% yield) as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.27 (d, *J* = 1.0 Hz, 3 H, Me), 1.46−2.36 (m, 10 H, 5 CH_2), 3.70 (s, 1 H, CO_2Me), 5.80 (q, *J* = 1.0 Hz, 1 H, 2-H), 6.20 (t, *J* = 7.0 Hz, 1 H, 2′-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.4 (q, Me), 26.3, 26.4, 28.6, 29.9, 32.3 (5 t, CH_2), 50.8 (q, CO_2*Me*), 113.2 (d, C-2′), 133.1 (d, C-2), 146.9 (s, C-1′), 158.3 (s, C-3), 167.9 (s, C-1) ppm. IR (film): $\tilde{\nu}$ = 3010 cm^{-1} (=C−H), 2925, 2850, 1435 (CH_2), 1720 (C=O), 1690 (C=C), 1165 (C−O−C). $C_{12}H_{18}O_2$ (194.28): calcd. C 74.19, H 9.34; found C 72.99, H 9.56; no correct elemental analysis could be obtained for this compound.

Methyl 3-(Cyclohept-1-enyl)-2-methylpropenoate (26) and Methyl 2-(Cyclohept-1-enylmethyl)acrylate (27): Nonaflation of **1h** (0.920 g, 5.00 mmol) with NfF (3.02 g, 10.0 mmol) was performed with nBu$_4$NF (0.90 mmol) in THF (0.9 mL) according to **GP2**. After addition of KOAc (0.343 g, 3.50 mmol), K_2CO_3 (0.602 g, 4.36 mmol), $Pd(OAc)_2$ (0.039 g, 0.17 mmol), methyl methacrylate (0.525 g, 5.25 mmol) and DMF (6 mL), the mixture was stirred at 85 °C for 6 h, followed by the usual workup and CC (hexane/EtOAc, 10:1), to provide a 52:9:39 mixture of (*E*)-**26**, (*Z*)-**26** and **27** (0.495 g, 51% overall yield). **Compound (*E*)-26:** ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.96 (d, *J* = 1.5 Hz, 3 H, 2-Me), 1.44−1.59, 1.67−1.79, 2.03−2.34 (3 m, 4 H, 2 H, 4 H, 5 CH_2), 3.75 (s, 3 H, OMe), 5.53 (q, *J* = 1.5 Hz, 1 H, 3-H), 5.60 (t, *J* = 6.5 Hz, 1 H, 2′-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.1 (q, 2-Me), 26.4, 26.7, 28.9, 32.3, 32.5 (5 t, 5 CH_2), 51.75 (q, OMe), 136.9, 139.1, 141.1, 143.3 (d, 2 s, d, C-2′, C-1′, C-3, C-2), 169.6 (s, C-1) ppm. IR (gas phase): $\tilde{\nu}$ = 3000 cm^{-1} (=C−H), 2930 (C−H), 2855 (CH_2), 1740 (C=O), 1630 (C=C), 1145 (C−O−C). The following signals can be assigned to the compound (*Z*)-**26:** ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.72 (s, 3 H, OMe), 6.17 (t, *J* = 6.5 Hz, 1 H, 2′-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.9 (q, 2-Me), 26.45, 28.1, 32.0, 33.9, 36.8 (5 t, 5 CH_2), 51.7 (q, OMe), 127.2, 136.6, 141.0, 144.4 (s, d, s, d, C-2′, C-1′, C-3, C-2) ppm. IR (gas phase): $\tilde{\nu}$ = 3060 cm^{-1} (=C−H), 2935 (C−H), 2855 (CH_2), 1740 (C=O), 1650 (C=C), 1250 (C−O−C). **Compound 27:** ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.44−1.59, 1.67−1.79, 2.03−2.34 (3 m, 4 H, 2 H, 4 H, 5 CH_2), 2.98 (br. s, 2 H, 2-CH_2), 3.75 (s, 3 H, OMe), 6.00 (t, *J* = 6.5 Hz, 1-H, 2′-H), 6.18 (m_c, 1 H, 3-H), 7.27 (br. s, 1 H, 3-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 26.5, 27.3, 28.4, 32.4, 32.8, 41.8 (6 t, 6 CH_2), 51.75 (q, OMe), 124.8, 125.5, 129.0, 141.0 (s, t, d, s, C-2′, C-l′, C-3, C-2), 167.9 (s, C-1) ppm. IR (gas phase): $\tilde{\nu}$ = 3055 cm^{-1} (=C−H), 2930 (C−H), 2855 (CH_2), 1630 (C=C), 1740 (C=O), 1140 (C−O−C). GC/MS data: **27**, t_r = 9.0 min, (*E*)-**26**, = 10.3 min, (*Z*)-**26**, = 10.9 min. **27:** MS (EI, 70 eV): *m*/*z* (%) = 194 (41) [M^+], 180 (9), 162 (13), 152 (11), 133 (25), 119 (18), 105 (25), 95 (100), 79 (53), 67 (57), 55 (30), 41 (54), 32 (6). **(*E*)-26:** MS (EI, 70 eV): *m*/*z* (%) = 194 (100) [M^+], 179 (12), 163 (38), 151 (61), 135 (47), 125 (39), 107 (25), 91 (60), 79 (47), 67 (21), 55 (18), 41 (35), 32 (15). **(*Z*)-26:** MS (EI, 70 eV): *m*/*z* (%) = 194 (<1) [M^+], 179 (7), 165 (20), 149 (15), 133 (17), 125 (100), 111 (19), 95 (16), 79 (20), 67 (20), 55 (20), 41 (33), 32 (11).

Methyl (*E*)-4-Methylpenta-2,4-dienoate (28): Nonaflation of silyl enol ether **1i** (0.261 g, 2.00 mmol) with NfF (0.785 g, 2.60 mmol) was performed in THF (1 mL) with KF (0.120 g, 2.07 mmol) and dibenzo-18-crown-6 (0.144 g, 0.40 mmol) at 25 °C for 120 h according to **GP2**. After addition of LiCl (0.127 g, 3.00 mmol), Et_3N (0.405 g, 4.00 mmol), $Pd(OAc)_2$ (0.022 g, 0.10 mmol), methyl acrylate (0.224 g, 2.60 mmol) and DMF (1 mL), the mixture was stirred at 25 °C for 17 h, followed by the usual workup (*n*-pentane) and CC (*n*-pentane/Et_2O, 25:1), to provide **28**[37] (0.080 g, 30% yield) as a slightly yellowish oil. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.89 (dd, *J* = 1.3, 1.0 Hz, 3 H, Me), 3.76 (s, 3 H, CO_2*Me*), 5.34−5.37 (m, 2 H, 5-H), 5.88 (d, *J* = 15.8 Hz, 1 H, 2-H), 7.37 (dd, *J* = 15.8, 0.5 Hz, 1 H, 3-H) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 17.9 (q, Me), 51.5 (q, CO_2*Me*), 118.2 (t, C-5), 124.3 (d, C-2), 140.4 (s, C-4), 147.1 (d, C-3), 167.5 (s, C-1) ppm.

Methyl (*E*)-4-(*tert*-Butyl)penta-2,4-dienoate (9): Nonaflation of silyl enol ether **1c** (0.345 g, 2.00 mmol) with NfF (0.785 g, 2.60 mmol) was performed in a THF/DMF (2 mL, 1:1 v/v) mixture with KF (0.120 g, 2.07 mmol) and dibenzo-18-crown-6 (0.144 g, 0.40 mmol) at 25 °C for 40 h according to **GP2**. After addition of LiCl (0.127 g, 3.00 mmol), Et_3N (0.405 g, 4.00 mmol), methyl acrylate (0.224 g,

2.60 mmol) and $Pd(OAc)_2$ (0.022 g, 0.10 mmol), the mixture was stirred at 25 °C for 64 h, followed by the usual workup (*n*-pentane) and CC (gradient elution: *n*-pentane to *n*-pentane/Et_2O, 50:1), to provide **9** (0.146 g, 46% yield) as a slightly yellowish oil. According to ^1H NMR, the product contained 10−15% admixtures inseparable by CC. ^1H NMR (270 MHz, $CDCl_3$): δ = 1.12 (s, 9 H, C*Me*$_3$), 3.76 (s, 3 H, OMe), 5.05 (t, *J* = 0.8 Hz, 1 H, 5-H), 5.28 (t, *J* = 1.0 Hz, 1 H, 5-H), 6.13 (d, *J* = 15.6 Hz, 1 H, 2-H), 7.46 (dt, *J* = 15.6, 0.8 Hz, 1 H, 3-H) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 29.1 (q, C*Me*$_3$), 35.1 (s, *C*Me$_3$), 51.5 (q, OMe), 112.0 (t, C-5), 119.5 (d, C-2), 145.4 (d, C-3), 153.9 (s, C-4), 167.3 (s, C-1) ppm.

Methyl (*E*,*E*)-Dodeca-2,4-dienoate (14): Nonaflation of silyl enol ether **1d** (0.270 g, 1.26 mmol, *E*:*Z* = 93:7) with NfF (0.507 g, 1.68 mmol) was performed with *n*Bu_4NF (0.25 mmol) in THF (0.25 mL) according to **GP2**. After addition of *n*Bu_4NCl (0.330 g, 1.19 mmol), K_2CO_3 (0.337 g, 2.44 mmol), $Pd(OAc)_2$ (0.011 g, 0.05 mmol), methyl acrylate (0.139 g, 1.61 mmol) and DMF (6 mL), the mixture was stirred at 25 °C for 6 h, followed by the usual workup and CC (hexane/EtOAc, 10:1), to give **14**[32] (0.218 g, 82% yield, *E*,*E*/*E*,*Z* = 95:5) as a yellow oil.

1-Phenylundeca-1,3-diene (29): Nonaflation of **1d** (0.300 g, 1.40 mmol) with NfF (0.507 g, 1.68 mmol) was performed with *n*Bu_4NF (0.25 mmol) in THF (0.25 mL) according to **GP2**. After addition of KOAc (0.096 g, 0.98 mmol), K_2CO_3 (0.168 g, 1.21 mmol), $Pd(OAc)_2$ (0.011 g, 0.05 mmol), styrene (0.145 g, 1.40 mmol) and DMF (3 mL), the mixture was stirred at 75 °C for 6 h, followed by the usual workup and CC (hexane/EtOAc, 10:1), to furnish **29**[38] (0.256 g, 80% yield, *E*,*E*/*E*,*Z* = 95:5) as a slightly yellowish oil. **Compound (*E*,*E*)-29:** ^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 5.0 Hz, 3 H, Me), 1.23−1.30, 1.41 (m, 8 H, quint., *J* = 6.9 Hz, 2 H, 6-H to 10-H), 2.14 (q, *J* = 6.9 Hz, 2 H, 5-H), 5.82 (dt, *J* = 14.9, 6.9 Hz, 1 H, 4-H), 6.20 (dd, *J* = 14.9, 10.4 Hz, 1 H, 3-H), 6.43 (d, *J* = 15.6 Hz, 1 H, 1-H), 6.75 (dd, *J* = 15.6, 10.4 Hz, 1 H, 2-H), 7.15−7.42 (m, 5 H, Ph) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 14.1 (q, Me), 22.7, 22.7, 29.2*, 29.3 (4 t, CH_2), 31.8 (t, C-9), 32.9 (t, C-5), 126.2, 127.0, 128.5 (3 d, Ph), 129.5 (d, C-2), 129.9 (d, C-1), 130.4 (d, C-3), 136.1 (s, C-4), 137.7 (s, Ph) ppm; *double intensity. The following signals can be assigned to the compound (*E*,*Z*)-**29**: ^1H NMR (500 MHz, $CDCl_3$): δ = 1.54−1.58, 1.60−1.65 (2 m, 8 H, 2 H, 6-H to 10-H), 2.22−2.36 (m, 2 H, 5-H), 5.51−5.58 (m, 1 H, 4-H), 6.12−6.20 (m, 1 H, 3-H), 6.51 (d, *J* = 15.5 Hz, 1 H, 1-H), 7.05−7.12 (m, 1 H, 2-H) ppm.

Methyl (*E*)-5-Methylhexa-2,4-dienoate (15): Nonaflation of silyl enol ether **1e** (0.360 g, 2.50 mmol) with NfF (0.906 g, 3.00 mmol) was performed with *n*Bu_4NF (0.45 mmol) in THF (0.45 mL) according to **GP2**. After addition of *n*Bu_4NCl (0.695 g, 2.50 mmol), K_2CO_3 (0.690 g, 5.00 mmol), $Pd(OAc)_2$ (0.022 g, 0.10 mmol), methyl acrylate (0.645 g, 7.50 mmol) and DMF (8 mL), the mixture was stirred at 25 °C for 6 h. Isolation and purification as described above provided **15**[33] (0.245 g, 70% yield).

(*E*)-(2-Cyclohex-1-enyl)styrene (19) from Cyclohexanone by Deprotonation followed by Nonaflation and Heck Coupling: A solution of *n*-butyllithium in hexane (2.2 M, 2.32 mL, 5.10 mmol) was added at −78 °C to a solution of *i*Pr_2NH (0.516 g, 5.10 mmol) in THF (80 mL). After the mixture had been kept for 1 h at −78 °C, cyclohexanone (0.490 g, 5.00 mmol) was added and the mixture was stirred for 1 h at −78 °C. Neat NfF (3.02 g, 10.0 mmol) was added dropwise, and the reaction mixture was allowed to warm up to room temp. overnight. After all the volatile components had been removed under vacuum, DMF (6 mL) was added. KOAc (0.343 g, 3.50 mmol), K_2CO_3 (0.601 g, 4.38 mmol), $Pd(OAc)_2$ (0.039 g, 0.175 mmol) and styrene (0.545 g, 5.25 mmol) were added to the resulting solution. The resulting suspension was stirred at 75 °C for 6 h, followed by the usual workup and CC (hexane/EtOAc, 10:1), to afford **19**[34] (0.465 g, 51% yield) as a yellowish solid (m.p. ca. 25 °C).

Dimethyl 4-[(*E*)-2-*tert*-Butoxycarbonylethen-1-yl]cyclohex-4-ene-*trans*-1,2-dicarboxylate (30): Dimethyl 4-trimethylsiloxy-4-cyclohexene-*trans*-1,2-dicarboxylate (**1j**) was generated from dimethyl fumarate (0.144 g, 1.00 mmol) and 2-(trimethylsiloxy)buta-1,3-diene (0.171 g, 1.20 mmol) in toluene (1 mL) as described in the literature.[22] After the volatiles had been removed under vacuum, dibenzo-18-crown-6 (0.054 g, 0.15 mmol), DMSO (0.8 mL), DMF (0.2 mL), KF (0.060 g, 1.03 mmol) and NfF (0.453 g, 1.50 mmol) were added consecutively to the crude **1j**, and the resulting mixture was stirred at room temperature for 60 h.* LiCl (0.021 g, 0.50 mmol), Et_3N (0.132 g, 1.30 mmol), *tert*-butyl acrylate (0.170 g, 1.32 mmol) and $Pd(OAc)_2$ (0.011 g, 0.05 mmol) were then added, and the mixture was stirred at 75 °C for 5 h*, followed by the usual workup (hexane/Et_2O, 1:1) and CC (gradient elution: hexane/Et_2O, 5:1 to 3:1), to provide **30** (0.191 g, 59% overall yield) as colourless crystals (m.p. 66−68 °C); *complete conversion of the starting material was detected by ^1H NMR of the reaction mixture. ^1H NMR (270 MHz, $CDCl_3$): δ = 1.49 (s, 9 H, C*Me*$_3$), 2.20−2.49, 2.56−2.70, 2.84−3.00 (3 m, 2 H each, 6′-H, 1′-H to 3′-H), 3.71, 3.72 (2 s, 3 H, 3 H, 2 CO_2*Me*), 5.74 (d, *J* = 16.0 Hz, 1 H, 1-H), 6.09 (br. s, 1 H, 5′-H), 7.19 (d, *J* = 16.0 Hz, 1 H, 2-H) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 26.8, 28.6 (2 t, C-3′, C-6′), 28.1 (q, C*Me*$_3$), 40.8, 40.9 (2 d, C-1′, C-2′), 52.01, 52.03 (2 q, 2 CO_2*Me*), 80.2 (s, *C*Me$_3$), 118.3 (d, C-1), 133.8, 144.6 (2 d, C-2, C-5′), 132.9 (s, C-4′), 166.4 (s, *C*O_2Bu-*t*), 174.58, 174.60 (2 s, 2 *C*O_2Me) ppm. MS (EI, 80 eV): *m*/*z* (%) = 324 (4) [M^+], 293 (30) [M^+ − MeO], 268 (43) [M^+ − CH_2=CMe_2], 264 (15) [M^+ − HCO_2Me], 251 (18) [M^+ − *t*BuO], 250 (48) [M^+ − *t*BuOH], 236 (13) [M^+ − MeO − *t*Bu], 219 (23) [M^+ − *t*BuOH −MeO], 218 (47) [M^+ − *t*BuOH − MeOH], 208 (66) [M^+ − CO_2Me − *t*Bu], 191 (25) [M^+ − CO_2Me − *t*BuOH], 190 (21) [M^+ − HCO_2Me − *t*BuOH], 176 (13) [M^+ − CO_2Me − *t*BuOH − Me], 158 (15) [M^+ − HCO_2Me − *t*BuOH − MeOH], 149 (100) [M^+ − 2 CO_2Me − *t*Bu], 131 (66) [M^+ − HCO_2Me − CO_2Me − *t*BuOH], 57 (74) [*t*Bu^+]. IR (film): $\tilde{\nu}$ = 2975, 2955, 2925, 2850 cm^{-1} (=C−H, C−H), 1730, 1710 (C=O), 1640, 1620 (C=C). $C_{17}H_{24}O_6$ (324.4): calcd. C 62.95, H 7.46; found C 62.90, H 7.31.

(*R*)-2-Methyl-5-[1-methyl-1-(trimethylsiloxy)ethyl]-3-(trimethylsiloxy)cyclohexa-1,3-diene (1k): (*R*)-Carvone (25.0 g, 166 mmol) was treated with aqueous H_2SO_4 (50%, 169.5 g) as described in the literature.[39] After the reaction mixture had been poured onto ice, neutralised with 25% aqueous NH_3 solution (pH = 4−5) and extracted thoroughly with Et_2O, the organic layer was washed successively with water and brine and dried ($MgSO_4$). After removal of all volatile components under vacuum, the residue was carefully dried overnight under high vacuum. The resulting mixture of (*R*)-5-(1-hydroxy-1-methylethyl)-2-methylcyclohex-2-enone and 5-isopropyl-2-methylphenol (18.1 g, ratio = 1:0.9) was dissolved in THF (20 mL) and added dropwise at −78 °C to a solution of *i*Pr_2NLi in THF (200 mL), generated from *n*BuLi (80.0 mL, 192 mmol, 2.4 molar in hexanes) and *i*Pr_2NH (24.5 g, 242 mmol) (−78 °C to 0 °C, then down to −78 °C again). After the mixture had been stirred at −78 °C for 1 h, Me_3SiCl (32.0 g, 295 mmol) was added dropwise, and the reaction mixture was allowed to warm up to room temp. overnight. Workup (aqueous $NaHCO_3$/hexane), extraction (hexane), drying (Na_2SO_4), vacuum evaporation and fractional distillation afforded pure product **1k** (14.9 g, 29% overall yield) as a yel-

lowish oil (b.p. 99−100 °C/0.4 mbar). ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.11 (s, 9 H, $Me_2COSiMe_3$), 0.21 (s, 9 H, $SiMe_3$), 1.16, 1.18 (2 s, 3 H each, Me_2C), 1.68 (dd, *J* = 3.9, 1.7 Hz, 3 H, *Me*C=), 1.96−2.15 (m, 2 H, 6-H), 2.42 (ddd, *J* = 13.8, 8.7, 3.4 Hz, 1 H, 5-H), 4.90 (d, *J* = 3.4 Hz, 1 H, 4-H), 5.53 (m_c, 1 H, 1-H) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 0.2 (q, $SiMe_3$), 2.6 (q, $Me_2COSiMe_3$), 17.2 (q, *Me*C=), 24.9 (t, C-6), 27.1, 27.4 (2 q, Me_2C), 46.4 (d, C-5), 76.3 (s, Me_2C), 104.5 (d, C-4), 123.4 (d, C-1), 131.7 (s, C-2), 149.8 (s, C-3) ppm.

(1*R*,2*S*,6*R*,7*R*,11*R*)-9-Methyl-11-[1-methyl-1-(trimethylsiloxy)-ethyl]-3,5-dioxo-4-phenyl-4-azatricyclo[5.2.2.0^{2,6}]undec-8-en-8-yl Nonaflate (2l): *N*-Phenylmaleimide (0.246 g, 2.00 mmol) was added to a solution of the trimethylsilyl enol ether **1k** (0.625 g, 2.00 mmol) and diisopropyl ethylamine (1 drop) in toluene (1 mL), and the reaction mixture was stirred for 72 h at room temperature,[23] followed by removal of the volatiles under vacuum. The residue (single stereoisomer of **1l**, according to ^{1}H NMR) was dissolved in a DMF/THF mixture (3 mL, 1:1 v/v), and NfF (0.785 g, 2.60 mmol), KF (0.120 g, 2.07 mmol) and dibenzo-18-crown-6 (0.108 g, 0.30 mmol) were added consecutively. The resulting mixture was stirred for 67 h at room temperature. The generated nonaflate **2l** failed to react either under standard (methyl acrylate, $Pd(OAc)_2$, LiCl, Et_3N, 50 °C, 20 h) or under drastic [styrene, $Pd(OAc)_2$, KOAc, K_2CO_3, 100 °C, 24 h] Heck coupling conditions and was recovered as a single stereoisomer (0.973 g, 70% yield, colourless glassy solid) from both experiments after the usual aqueous workup (Et_2O) and CC (gradient elution: hexane/Et_2O, 5:1 to 4:1 to 5:2 to 1:1). **Compound 2l:** ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.07 (s, 9 H, $SiMe_3$), 1.14, 1.32 (2 s, 3 H, 3 H, Me_2C), 1.50, 1.67−1.85 (ddd, *J* = 11.8, 5.0, 3.0 Hz, m, 1 H, 2 H, 5-H, 6-H), 1.85 (s, 3 H, *Me*C=), 2.96−3.06, 3.26−3.30, 3.49−3.51 (3 m, 2 H, 1 H, 1 H, 3-H, 8-H, 4-H, 7-H), 7.26−7.31 7.32−7.47 (2 m, 2 H, 3 H, Ph) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 2.2 (q, $SiMe_3$), 15.1 (q, *Me*C=), 27.0 (t, C-5), 28.2, 29.2 (2 q, Me_2C), 37.4, 39.5, 43.7, 46.8, 51.3 (5 d, C-6, C-7, C-8, C-3, C-4), 74.4 (s, Me_2C), 126.5, 128.9, 128.4 (3 d, Ph), 129.2, 131.7, 140.3 (3 s, $C_{Ph}N$, C-10, C-9), 175.2, 176.7 (2 s, C-1, C-2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = −126.98 to −125.59, −121.34 to −121.17 (2 m, 2 F, 2 F, CF_2-2, CF_2-3), −110.86 (d*, *J* = 259.2 Hz, 1 F, CF_2-1), −110.14 (d*, *J* = 259.2 Hz, 1 F, CF_2-1), −81.07 (br. t, *J* = 9.7 Hz, 3 F, CF_3) ppm; *further complex splitting by ^{19}F−^{19}F couplings. MS (EI, 80 eV): *m*/*z* (%) = 696 (1) [M^+ + 1], 695 (3) [M^+], 681 (2) [M^+ + 1 − Me], 680 (6) [M^+ − Me], 638 (4) [M^+ + 1 − $SiMe_2$] or [M^+ + 1 − Me_2C=O], 637 (11) [M^+ − $SiMe_2$] or [M^+ − Me_2C=O], 412 (1) [M^+ − $CF_3(CF_2)_3SO_2$], 397 (2) [M^+ − $CF_3(CF_2)_3SO_2$ − Me], 396 (1) [M^+ − $CF_3(CF_2)_3SO_2O$], 340 (1) [M^+ − $CF_3(CF_2)_3SO_2$ − Me_2Si=CH_2], 322 (1) [M^+ − $CF_3(CF_2)_3SO_2$ − Me_3SiOH], 306 (1) [M^+ − $CF_3(CF_2)_3SO_2O$ − Me_3SiOH], 247 (3) [$C_{11}H_{19}O_4S^+$], 246 (9) [$C_{11}H_{18}O_4S^+$], 181 (1) [$C_4F_7^+$], 175 (1) [$C_{10}H_9NO_2^+$], 174 (1) [$C_{10}H_8NO_2^+$], 173 (1) [$C_{10}H_7NO_2^+$], 159 (2) [$C_{10}H_9NO^+$], 147 (3) [$PhN(CO)_2^+$], 131 (100) [CF_2=$CFCF_2^+$ or Me_3SiO=CMe_2^+], 119 (2) [$PhNCO^+$], 77 (2) [$C_6H_5^+$], 75 (6), 73 (25) [Me_3Si^+], 69 (2) [CF_3^+], 43 (2) [$HNCO^+$]. IR (film): ṽ = 2980 cm^{-1} (br., =C−H, C−H), 1715 (C=O), 1600 (C=C), 1415, 1145 (SO_2), 1240, 1200 (C−F). $C_{27}H_{30}F_9NO_6SSi$ (695.7): calcd. C 46.62, H 4.35, N 2.01; found C 46.64, H 4.24, N 1.95.

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