

Chemical consequences of fluorine substitution. Part 1. Experimental and theoretical results on Diels–Alder reactions of α - and β -fluorostyrenes †

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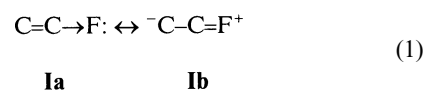
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Vinyl fluorides such as α - and β -fluorostyrenes **2** and **3** are poor dienophiles for Diels–Alder reactions. Under thermal conditions these compounds do not react with usual dienes, but with the highly reactive 1,3-diphenylisobenzofuran (**4**) to give mixtures of the corresponding *endo*- and *exo*-products. Kinetic measurements show that the fluorostyrenes **2** and **3** are less reactive than the parent styrene (**1a**). Additional electron withdrawing as well as electron donating substituents (*p*-Cl, *p*-F, *m*-Me) on the phenyl ring of **2** and **3** slightly accelerate the reaction rate by a maximum factor of 4. DFT calculations (UB3LYP/6-31G(d)) of activation energies for furan and isobenzofuran as model dienes reflect the order of the reaction rates of the kinetic measurements. The charge difference in the double bond carbon atoms of the different dienophiles pre-determines the activation energies for the *endo*- and *exo*-transition states. The optimised structures of the transition states show that the reactions are concerted but asynchronous without biradical character. This asynchrony is determined by the differences in the p_z orbital coefficients of the double bond carbon atoms of the fluorostyrenes. The frontier molecular orbitals reveal that all the reactions are cycloadditions with normal electron demand. The calculated small *endolexo* preferences are in qualitative agreement with the experimental values. In the transition states of the reactions of **2a** and (*E*)-**3a** where the fluorine atom and the oxygen atom of furan are *syn*-orientated with respect to the reaction center, electrostatic repulsion determines the *endolexo* selectivity. Semiempirical calculations show that the reactions of **4** are more exothermic with respect to the parent furan and more endothermic with respect to isobenzofuran. However, regarding relative reactivity and diastereoselectivity, the semiempirical methods are less reliable in comparison to either experiment or DFT.

Introduction

Interest in fluorinated compounds has increased greatly in the last decades due to the strong influence of the fluorine substituent on the chemical, physical and physiological properties of these compounds.¹ Diels–Alder reactions of monofluorinated olefins are an attractive approach toward selectively fluorinated cyclohexenes, many of which are biologically active. In a preliminary communication, we reported on the [4 + 2]-cycloaddition of α - and β -fluorostyrenes with diphenylisobenzofuran.² Only a few more reactions of this type, solely with strongly activated dienophiles like 2-fluoroacroleins,^{3a,3b} α,β -unsaturated α -fluoro-carboxylic acid derivatives,^{3b,3d–3f} polyfluorinated cyclohexa-2,4-dienones^{3g} or fluorinated vinyl sulfones⁴ have been published until now. No simple non-activated monofluoro alkenes have been used so far.⁵ In fact, there is little information concerning the effect of a single fluorine substituent on the electronic properties, the stability and the reactivity of the π -system of simple vinyl fluorides.^{1,6,7} Only fluoroethylene itself and several of its halogenated derivatives have been investigated in more detail by experimental and theoretical methods,⁸ which showed a single fluorine substituent that has only a weak influence. Although the atomic charges on carbon atoms are quite different for ethylene and vinyl fluoride, the HOMO and LUMO levels are almost unaffected.^{8d} Qualitatively, the ground state of a monofluoro alkene can be described as illustrated in **Ia** and **Ib**, where the electron withdrawing effect of the fluorine atom may be offset by p – π -interaction, which increases π -electron density.⁹



The ionisation energy, determined by photoelectron spectroscopy, of vinyl fluoride is only 0.14 eV higher than that of ethylene showing a weak interaction of the π -bond with the 2p-orbital of the fluorine atom.¹⁰

In contrast, many investigations have dealt with the electronic properties and reactions of higher fluorinated olefins^{4a,11,12} or fluorinated allenes.⁷ It has been shown that under thermal conditions polyfluorinated olefins rarely react in a [4 $_{\pi}$ + 2 $_{\pi}$]-manner to give cyclohexenes but mainly in a [2 $_{\pi}$ + 2 $_{\pi}$]-cycloaddition to give fluorinated cyclobutanes.^{11a–11c} These reactions are not concerted but proceed by a two-step mechanism *via* biradical intermediates.¹³ Only the reactions of trifluoroethylene and substituted 1,2-difluoroethylenes with cyclopentadiene and furans gave Diels–Alder products predominantly.^{11d–11f} On the other hand, partially fluorinated allenes react faster in Diels–Alder reactions than their non-fluorinated parent compounds, leading selectively to the cycloadducts of the less fluorinated double bond.^{7a}

In general, [4 + 2]-cycloaddition is one of the most fundamental and useful synthetic processes in organic chemistry.¹⁴ Recently, a review on synthetic applications of furan in Diels–Alder chemistry showed the profit of the formed 7-oxa-norbornenes ‡ as starting compounds for phenols and other aromatic targets.¹⁵

In addition, numerous papers have focused on theoretical investigations of the Diels–Alder reaction utilising MO calcu-

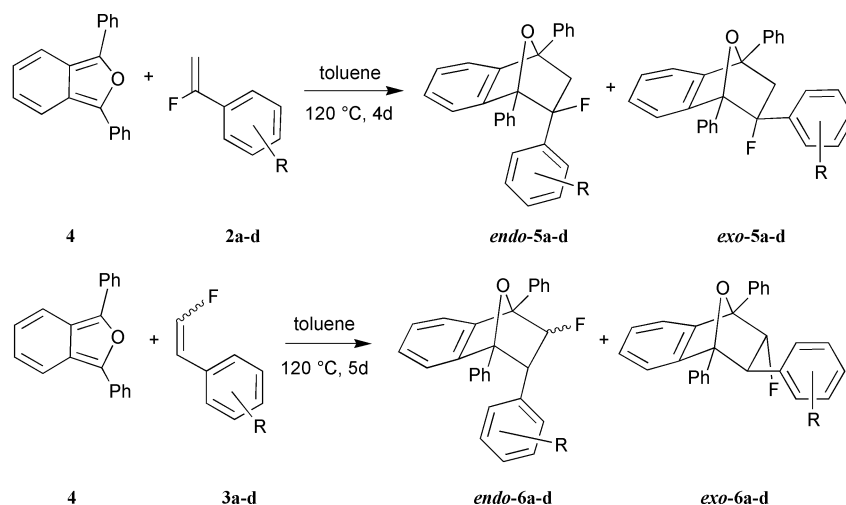
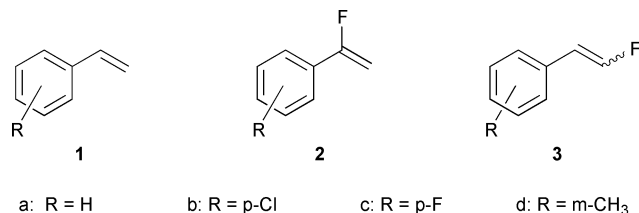
† Electronic supplementary information (ESI) available: details of the quantum chemical calculations (HOMO and LUMO energies, Gaussian94 archive entries). See <http://www.rsc.org/suppdata/p1/b1/b102684b/>

‡ The IUPAC name for norbornene is bicyclo[2.2.1]hept-2-ene.

lations, *i.e.*, semiempirical and/or *ab initio* methods.¹⁶ Despite the detailed experimental insight into selected transition states by femtosecond spectroscopy,¹⁷ quantum chemical calculations are currently the only approach to explore the cycloaddition transition state structures. Different semiempirical methods such as AM1¹⁸ or PM3¹⁹ or the use of larger basis sets for *ab initio* calculations including electron correlation, have shown the one-step, *i.e.* concerted, mechanism to be lower in energy²⁰ by 2–7 kcal mol⁻¹ compared to the stepwise mechanism. Only a few reactions have been found to proceed *via* a diradical intermediate.²¹ Furthermore, solvent effects can significantly influence the activation energy²² and may even favour a two-step mechanism.²³

The question as to whether the bond forming process is synchronous or concerted is still open. At first glance, one might expect that symmetrically substituted reactants will lead to transition structures of a synchronous reaction as is true for the parent system butadiene and ethylene,²⁴ and other reactants leading to C_s symmetric products,²⁵ but there are exceptions to this generalization.²⁶ Experimentally and theoretically determined kinetic isotope effects have been used for the discussion of the asynchrony of several Diels–Alder transition state structures.^{20,27} To the best of our knowledge systematic theoretical evidence for secondary orbital interaction as the origin for *endolexo* selectivity has been reported in only two cases. Apeloig and Matzner^{28a} and others^{28b–28d} carried out theoretical studies on the stereochemistry of the reaction of cyclopropene with various substituted butadienes and cyclopentadienes, and Jursic showed by calculation that *exo*-cycloadducts should be preferred in reactions of cyclopropene and benzo[*c*]-fused furan, thiophene and pyrrole.^{28b,29} However, these results as well as most of the other “evidence” of secondary orbital interactions can also be interpreted in terms of classical concepts such as solvent effects, steric interactions, hydrogen bonds, electrostatic forces, *etc.*³⁰

In the present paper we report our experimental and theoretical investigations on the Diels–Alder reactions of α - and β -fluorostyrenes (**2** and **3**, respectively). The reactivity of these species is compared to styrene (**1a**) and the kinetics and the observed *endolexo*-selectivities are rationalised.



Scheme 1

Results and discussion

Syntheses

The substituted α -fluorostyrenes **2** were easily accessible in two steps from the corresponding styrenes **1** by regioselective bromofluorination³¹ and subsequent dehydrobromination.³² The β -fluorostyrenes **3** were prepared by a Wittig-type olefination of the benzaldehydes with tributylphosphine and trichlorofluoromethane according to a procedure described by Burton *et al.*³³ These reactions gave mixtures of isomers (*E*–*Z* about 85 : 15) which were not separated for the following investigations.

Surprisingly, the fluoroolefins did not react under thermal conditions (toluene, 120 °C, sealed tube) with common dienes such as cyclopentadiene, 2,3-dimethylbutadiene, cyclohexa-1,3-diene or Danishefsky's diene³⁴ to form [4 + 2]-cycloadducts. Likewise, under thermal conditions they do not undergo [2 + 2]-cycloadditions either with the diene or with the fluorostyrenes themselves. Moreover, all attempts failed to catalyse the Diels–Alder reaction with the usual Lewis acids, and no reaction occurred in polar solvents (5 M LiClO₄-ether³⁵), under high pressure (9 kbar) or under the influence of radical cation inducers.³⁶ Also, Diels–Alder reactions with reverse electron demand using hexachlorocyclopentadiene did not succeed. In none of these reactions could any polymerisation products be detected. Only the very reactive 1,3-diphenylisobenzofuran (**4**), which is, in fact, a stabilised *o*-quinodimethane,³⁷ reacted smoothly with all of the fluorostyrenes investigated (**2** and **3**, respectively; Scheme 1) to give the expected Diels–Alder adducts, isolated as analytically pure products in 38–63% yield (Table 1).² The *endolexo*-selectivity depends strongly on the

Table 1 Yields and *endo* : *exo* ratios of the reactions of α -fluorostyrenes **2** and β -fluorostyrenes **3** with 1,3-diphenylisobenzofuran (**4**)

Olefin	R	Yield %	<i>endo</i> : <i>exo</i> ratio
1a	H	70	72 : 28 ^{41,42}
2a	H	63	60 : 40
2b	<i>p</i> -Cl	58	65 : 35
2c	<i>p</i> -F	52	60 : 40
2d	<i>m</i> -Me	42	62 : 38
3a	H	41 ^a	40 : 60 ^b
3b	<i>p</i> -Cl	38 ^a	40 : 60 ^b
3c	<i>p</i> -F	40 ^a	42 : 58 ^b
3d	<i>m</i> -Me	45 ^a	43 : 57 ^b

^a The yields are given for an 87 : 13 mixture of (*E*)- and (*Z*)-isomers of the β -fluorostyrenes. ^b *endo* : *exo* ratio for (*E*)- β -fluorostyrene; the (*Z*)-isomers always gave pure *endo*-isomers.

Table 2 Second order rate constants^a $10^5 k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ of the Diels–Alder reactions of *p*-fluorostyrene (**1c**) and α -fluorostyrenes (**2**) with 1,3-diphenylisobenzofuran (**4**)

<i>T</i> /°C	α -Fluorostyrenes				Styrene ^b
	H (2a)	<i>p</i> -Cl (2b)	<i>p</i> -F (2c)	<i>m</i> -Me (2d)	<i>p</i> -F (1c)
63	—	—	—	—	25.0 ± 1.7
72	1.5 ± 0.1	5.5 ± 0.4	1.9 ± 0.2	2.1 ± 0.1	58.0 ± 2.7
84	3.3 ± 0.2	9.3 ± 0.4	3.9 ± 0.3	3.5 ± 0.1	103.0 ± 6.3
92	4.1 ± 0.1	12.0 ± 0.9	6.6 ± 0.2	5.3 ± 0.2	—
107	6.3 ± 0.6	28.0 ± 1.8	10.0 ± 0.5	11.0 ± 1.6	—

^a The weighting error (2%) is disregarded in the given deviations of rate constants. ^b In order to follow the progress of the reaction by ¹⁹F NMR spectroscopy *p*-fluorostyrene (**1c**) was used as a styrene that is nonfluorinated in the vinylic position.

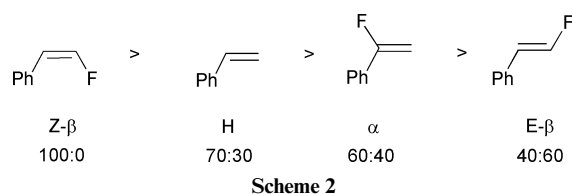
Table 3 Second order rate constants^a $10^5 k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ of the Diels–Alder reactions of β -fluorostyrenes **3** with 1,3-diphenylisobenzofuran (**4**)

<i>T</i> /°C	β -Fluorostyrenes				Styrene ^b
	H (3a)	<i>p</i> -Cl (3b)	<i>p</i> -F (3c)	<i>m</i> -Me (3d)	<i>p</i> -F (1c)
63	—	—	—	—	25.0 ± 1.7
72	2.8 ± 0.3	5.9 ± 0.1	3.5 ± 0.2	3.2 ± 0.2	58.0 ± 2.7
84	5.4 ± 0.2	14.0 ± 0.6	6.1 ± 0.4	6.3 ± 0.3	103.0 ± 6.3
92	11.0 ± 0.8	17.0 ± 0.2	12.0 ± 0.9	12.0 ± 0.7	—
102	16.0 ± 0.6	34.0 ± 2.2	19.0 ± 2.3	20.0 ± 1.1	—

^a The weighting error (2%) is disregarded in the given deviations of rate constants. ^b In order to follow the progress of the reaction by ¹⁹F NMR spectroscopy *p*-fluorostyrene (**1c**) was used as a styrene that is nonfluorinated in the vinylic position.

position of the fluorine substituent at the double bond, but is almost independent of the ring substituents (Table 1).

While (*Z*)- β -fluorostyrene (**Z-3a**) gave the *endo*-phenyl product exclusively, the selectivity decreased from styrene (**1a**) (72 : 28) to α -fluorostyrene (**2a**) (60 : 40) whereas (*E*)- β -fluorostyrene (**E-3a**) reacted *exo*-selectively (40 : 60) with respect to the phenyl ring (Scheme 2). The structures were



confirmed by NMR experiments and X-ray crystallography of *endo*-**5a** and *exo*-**6a**.³⁸

The *endo*/*exo*-selectivity of the Diels–Alder reaction has been rationalised by evaluating the calculated transition structures of the reactions for secondary orbital interaction.^{14a,39} However, in the case of the reactions of **4** with fluorostyrenes **2** and **3** lone pair repulsion of the furan oxygen and fluorine seems to determine the *endo*/*exo*-selectivity (*vide infra*).

Kinetic measurements

Our interest in the influence of the fluorine substituent on the kinetics of the Diels–Alder reaction prompted us to determine the rate constants of the reactions of the fluorostyrenes **2** and **3**, respectively, with 1,3-diphenylisobenzofuran (**4**) and to compare them to those of the reaction of *p*-fluorostyrene (**1c**). Consequently, we measured the time dependence of the dienophile concentration using ¹⁹F NMR spectroscopy. Because of the low concentration of the (*Z*)- β -fluorostyrenes **Z-3** in the isomeric mixture only the values for (*E*)- β -fluorostyrenes **E-3** were evaluated. The results summarised in Tables 2 and 3 show that the differences in the second order rate constants are quite small. The corresponding Arrhenius plots are shown in Fig. 1 and 2.

All substituents in the aryl ring of the vinyl fluorides **2** and **3**—either electron withdrawing or electron donating—slightly

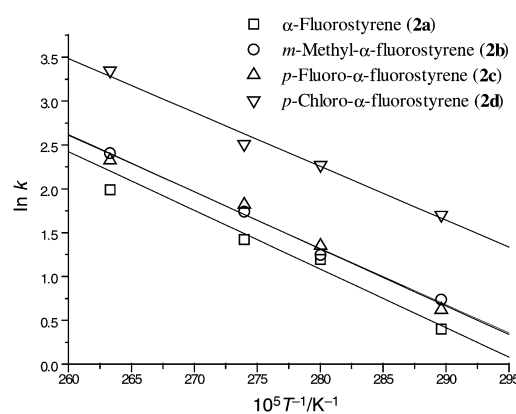


Fig. 1 Arrhenius plot of substituted α -fluorostyrenes **2a–d**.

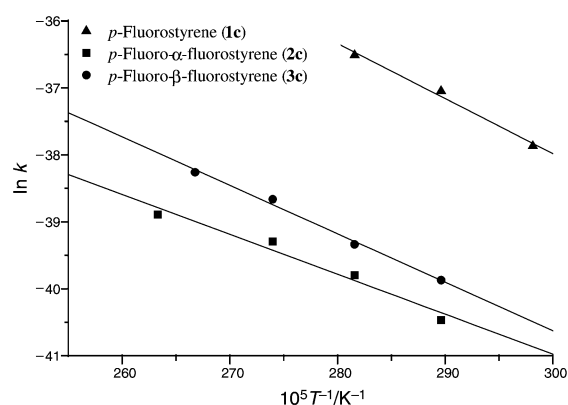


Fig. 2 Arrhenius plot of *p*-fluorostyrene (**1c**), *p*-fluoro- α -fluorostyrene (**2c**) and *p*-fluoro- β -fluorostyrene (**3c**).

increase the reaction rate compared to the parent α - or β -fluorostyrenes. On this basis, the reaction of α -fluorostyrene (**2a**) and β -fluorostyrene (**3a**) with 1,3-diphenylisobenzofuran (**4**) can be considered as a “neutral”⁴⁰ Diels–Alder reaction, whereas that of styrene (**1a**) with **4** is a “normal” one⁴¹ (see MO calculations). Considering the reactions under investigation, the fluorine substituent has an electron donating effect rather

Table 4 Activation enthalpies, entropies and free activation enthalpies for the Diels–Alder reactions based on the experimentally determined data

Olefin	$\Delta H^\ddagger/\text{kcal mol}^{-1}$	$\Delta S^\ddagger/\text{cal mol}^{-1} \text{K}^{-1}$	$\Delta G^\ddagger/\text{kcal mol}^{-1}$ (373 K)	k_{rel} (345 K)
1c	16.3 ± 1.7	−26.4 ± 5.0	26.2 ± 3.6	39
2a	12.3 ± 1.7	−44.9 ± 6.0	29.0 ± 3.9	1.0
2b	11.3 ± 1.1	−45.4 ± 3.0	28.3 ± 2.2	3.7
2c	11.8 ± 0.7	−45.8 ± 2.7	28.9 ± 1.7	1.3
2d	11.7 ± 0.2	−46.2 ± 1.0	28.9 ± 0.6	1.4
3a	14.8 ± 1.2	−36.7 ± 3.2	28.5 ± 2.4	1.9
3b	13.6 ± 0.4	−38.5 ± 0.8	27.9 ± 0.7	3.9
3c	14.3 ± 1.9	−37.6 ± 3.5	28.4 ± 3.2	2.3
3d	15.3 ± 2.0	−34.9 ± 3.4	28.3 ± 3.3	2.1

Table 5 Calculated activation energies E_A and reaction enthalpies ΔH_R of selected reactions at the UB3LYP/6-31G(d) level of theory leading to *endo*- and *exo*-products

Compound	Furan				Isobenzofuran			
	$E_A/\text{kcal mol}^{-1}$		$\Delta H_R/\text{kcal mol}^{-1}$		$E_A/\text{kcal mol}^{-1}$		$\Delta H_R/\text{kcal mol}^{-1}$	
	<i>endo</i>	<i>exo</i>	<i>endo</i>	<i>exo</i>	<i>endo</i>	<i>exo</i>	<i>endo</i>	<i>exo</i>
Styrene (1a)	27.7	27.9	2.8	1.2	17.5	17.5	−17.9	−19.7
α -Fluorostyrene (2a)	30.3	28.8	3.1	1.2	19.3	18.6	−17.6	−19.3
(<i>E</i>)- β -Fluorostyrene (E-3a)	29.6	28.2	2.4	0.5	18.9	18.1	−17.1	−20.0
(<i>Z</i>)- β -Fluorostyrene (Z-3a)	29.2	30.8	3.5	2.9	18.8	19.8	−16.7	−18.1

than a weak electron withdrawing one, although the HOMO and LUMO energies of α -fluorostyrene (**2a**) are slightly lower than the corresponding MO energies of styrene (**1a**) (see ESI). This is also supported by the fact that the bromofluorinations of α -fluorostyrene (**2a**) and β -fluorostyrene (**3a**) proceed faster than that of styrene.⁴²

From the measured rate constants at different temperatures we determined the activation enthalpies assuming simple second order kinetics. The values are given in Table 4. It is surprising that the activation enthalpy of *p*-fluoro- α -fluorostyrene (**2c**) is 4.5 kcal mol^{−1} lower than that of *p*-fluorostyrene (**1c**), although *p*-fluorostyrene (**1c**) reacts about 30 times faster. With β -fluorostyrene (**3c**) the results are similar, as the activation enthalpy at 373 K of *p*-fluoro-(*E*)- β -fluorostyrene (**E-3c**) is 2.0 kcal mol^{−1} lower compared to **1c** but it reacts about 17 times slower than *p*-fluorostyrene (**1c**).

The phenomenon that a faster reacting dienophile in Diels–Alder reaction has a higher activation enthalpy compared to a slower reacting one is known in the literature.⁴³ One reason for this behaviour could be that such reactions are not of simple second order, but include a fast pre-equilibrium.^{14a,44} A molecular complex (MC) between the diene and the dienophile was suggested to give the products *via* the transition state.

MO calculations

Computational procedures. All *ab initio* calculations were carried out utilising the Gaussian 94⁴⁵ and Gaussian 98⁴⁶ programs employing the basis set 6-31G(d). Since calculations on Diels–Alder reactions with diphenylisobenzofuran (**4**) are prohibitive because of the necessary resources, we used furan and isobenzofuran as model dienophiles for the *ab initio* calculations of structures and energies. With regard to the necessity to include correlation effects and on account of published work on similar systems^{24,47} we decided to apply an unrestricted hybrid density functional method, namely Becke's three parameter exchange functional, along with the correlation functional of Lee, Yang and Parr (UB3LYP),⁴⁸ which includes both local and non-local terms. The guess = mix option was used throughout; all calculations came out with restricted solutions without spin contamination. All energies are corrected by zero point vibrational energies (UB3LYP/6-31G(d) + ZPVE).

Based on the DFT results (see below), the semiempirical calculations were carried out with the MOPAC 93⁴⁹ program using

the PM3 and AM1 Hamiltonian at the RHF level of theory.³⁶ UHF/PM3 calculations are not reported here because the calculated cycloaddition transition structures using this method are extremely asymmetric, erroneously indicating a highly asynchronous reaction. The optimisations were performed utilising the eigenvector following algorithm with a threshold for the gradient norm of 0.01 or 0.05. All stationary points have been characterised by frequency calculations.

In order to examine the [4_π + 2_π]-cycloadditions of furan and isobenzofuran and the dienophiles styrene (**1a**), α -fluorostyrene (**2a**), (*E*)- β -fluorostyrene (**E-3a**) and (*Z*)- β -fluorostyrene (**Z-3a**) theoretically, we optimised all reactants, transition states and products at the UB3LYP/6-31G(d) level of theory for both, the *endo*- and the *exo*-reaction channels. For comparison, semiempirical calculations using the AM1 and PM3 methods including the experimentally studied diphenylisobenzofuran (**4**) were also performed. The corresponding activation energies E_A and the reaction enthalpies ΔH_R are given in Table 5 (DFT UB3LYP/6-31G(d) and Table 7 (AM1 and PM3).

DFT calculations. All of the Diels–Alder reactions studied proceeded *via* a concerted mechanism without intermediates. Although the possibility of biradical transition states was admitted by use of the UB3LYP method, all of the calculations came out with restricted solutions without spin contamination. Thus, all the reactions studied involve closed shell transition states without biradical character. The reactions of furan as a diene are predicted to be slightly endothermic by 0.5–3.5 kcal mol^{−1}, whereas isobenzofuran cycloadditions proceed, as expected, very exothermically (−16.7 to −20 kcal mol^{−1}). As anticipated, in both series the *exo*-products are thermodynamically favoured by 1–3 kcal mol^{−1} over the *endo*-products.

For furan as a diene the calculated activation energies of the cycloadditions lay in the order of 28–31 kcal mol^{−1}; for isobenzofuran activation barriers of about 10 kcal mol^{−1} fewer are predicted. For (*Z*)- β -fluorostyrene a pronounced kinetic preference for the formation of the *endo*-products is calculated. However, for α -fluorostyrene and (*E*)- β -fluorostyrene, significantly lower transition state energies for the *exo*-cycloadditions are obtained. The calculations for styrene show no *exo/endo*-selectivity (see below).

The calculated activation energies of the *endo*-cycloadditions reflect the order of the reaction rates observed in the kinetic

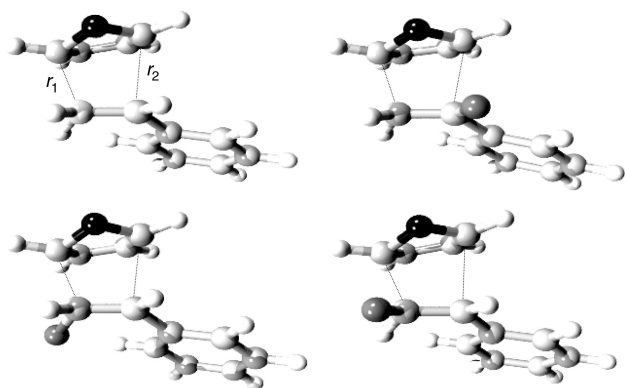


Fig. 3 Calculated Diels–Alder *endo* transition state structures of furan with styrene (**1a**) (upper left), α -fluorostyrene (**2a**) (upper right), (*E*)- β -fluorostyrene (**E-3a**) (lower left) and (*Z*)- β -fluorostyrene (**Z-3a**) (lower right) at the UB3LYP/6-31G(d) level of theory.

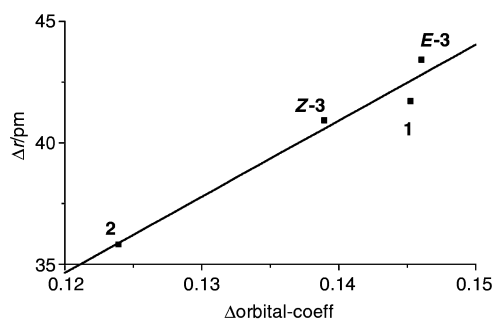


Fig. 4 Plot of the difference in the bond lengths (pm) of the forming bonds in the *endo* transition states vs. the difference in the absolute orbital coefficients for the double bond carbon atoms of the dienophiles **1–3**.

measurements (k_{rel} in Table 4) revealing the sequence: styrene (**1a**) < β -fluorostyrenes (**3a**) < α -fluorostyrene (**2a**).

The calculated transition state structures for the *endo*-reaction channels (Fig. 3) show that the degree of the bond formation is not synchronous but significantly asynchronous. The distance between the furan carbon atom and the α -carbon atom of the dienophile (r_1) is always shorter compared to the one to the β -carbon atom (r_2) (Table 6). The calculated differences ($\Delta = r_2 - r_1$) in the lengths of the forming bonds are: $\Delta = 41.7$ pm [styrene (**1a**)], $\Delta = 35.8$ pm [α -fluorostyrene (**2a**)], $\Delta = 43.4$ pm [(*E*)- β -fluorostyrene (**E-3a**)] and $\Delta = 40.9$ pm [(*Z*)- β -fluorostyrene (**Z-3a**)]. Similar differences in bond lengths were also found for the isobenzofuran reactions.

In order to shed light on the origin of the asymmetry of the transition state structures, we analysed the atomic charges and the orbital coefficients of reactants and transition states of the furan cycloadditions based on the *natural population analysis* (NPA).⁵⁰ Comparison of the atomic charges of the reactants with those of the transition state do not reveal any significant differences. However, there is a correlation between the charge difference in the double bond carbon atoms of the different dienophiles and the calculated activation energies for the *endo* transition states. The calculated linear regression results in a correlation coefficient of 0.98. Although this result is based on only four data points, *i.e.* the four different dienophiles, it seems to imply that the difference in the charges of the two double bond carbon atoms predetermines the activation energy of the cycloaddition.

Similarly the differences in the bond lengths of the forming bonds (Δ values in Table 6) correlate with the differences of the corresponding absolute p_z orbital coefficients of the double bond carbon atoms. This supports the interpretation that the asynchrony of the reactions has an electronic rather than a steric origin (Fig. 4).

The calculated energies of the frontier molecular orbitals

Table 6 Calculated bond lengths of the forming bonds (r_1/r_2)/pm in the *endo* transition states of cycloadditions of **1–3** with different dienes and methods. The differences between the two bonds is given in parentheses

	Furan r_1/r_2 (Δ)/pm		Isobenzofuran r_1/r_2 (Δ)/pm		Diphenylisobenzofuran r_1/r_2 (Δ)/pm	
	UB3LYP/6-31G(d)	RHF/AM1	RHF/PM3	RHF/AM1	RHF/PM3	RHF/AM1
Styrene (1a)	195.1/236.8 (41.7)	195.7/224.0 (28.3)	206.1/219.5 (13.4)	206.8/225.3 (18.5)	210.4/229.3 (18.9)	202.1/229.6 (27.5)
α -Fluorostyrene (2a)	197.0/232.8 (35.8)	192.4/234.4 (42.0)	207.1/247.9 (40.8)	204.0/232.6 (28.6)	208.2/236.6 (28.4)	198.6/243.8 (45.2)
(<i>E</i>)- β -Fluorostyrene (E-3a)	193.7/237.1 (43.4)	206.1/211.6 (5.5)	205.8/251.2 (45.4)	213.3/219.2 (5.9)	215.7/226.7 (11.0)	211.3/219.8 (5.3)
(<i>Z</i>)- β -Fluorostyrene (Z-3a)	194.4/235.3 (40.9)	205.6/210.5 (4.9)	206.1/248.5 (42.4)	212.7/217.8 (5.1)	214.6/226.0 (11.4)	209.3/219.8 (10.5)

Table 7 PM3 and AM1 calculated activation energies E_A and reaction enthalpies ΔH_R /kcal mol⁻¹ of reactions of furan and diphenylisobenzofuran (**4**) with different dienophiles leading to *endo*- or *exo*-products, respectively

Compound	Method	Furan				Isobenzofuran				Diphenylisobenzofuran			
		E_A /kcal mol ⁻¹		ΔH_R /kcal mol ⁻¹		E_A /kcal mol ⁻¹		ΔH_R /kcal mol ⁻¹		E_A /kcal mol ⁻¹		ΔH_R /kcal mol ⁻¹	
		<i>endo</i>	<i>exo</i>	<i>endo</i>	<i>exo</i>	<i>endo</i>	<i>exo</i>	<i>endo</i>	<i>exo</i>	<i>endo</i>	<i>exo</i>	<i>endo</i>	<i>exo</i>
Styrene (1a)	PM3	34.8	34.3	-9.0	-9.6	28.5	27.2	-25.5	-26.3	31.0	31.1	-14.2	-14.5
	AM1	28.3	31.0	-9.2	-11.7	24.6	23.0	-26.1	-28.5	29.7	30.0	-14.8	-15.6
α -Fluorostyrene (2a)	PM3	34.7	34.9	-7.4	-7.2	27.9	28.3	-24.4	-23.9	32.3	32.6	-11.5	-11.2
	AM1	33.4	32.3	-5.0	-6.4	26.6	26.0	-20.9	-22.5	32.8	32.9	-7.5	-9.5
<i>(E)</i> - β -Fluorostyrene (E-3a)	PM3	35.7	35.4	-6.0	-6.7	29.3	29.1	-22.3	-23.1	33.5	33.6	-10.5	-10.6
	AM1	35.5	34.7	-5.0	-6.1	27.9	27.1	-21.2	-22.4	35.6	35.0	-7.5	-9.1
<i>(Z)</i> - β -Fluorostyrene (Z-3a)	PM3	36.1	35.3	-4.6	-4.9	30.5	27.9	-20.4	-23.8	33.6	34.6	-9.8	-10.7
	AM1	35.3	34.5	-2.8	-4.9	28.1	25.7	-18.2	-21.6	33.2	35.1	-6.5	-6.3

(FMOs) of all of the reactants reveal that the HOMO of the dienes, furan and isobenzofuran, are energetically closer to the LUMOs of the dienophiles than the inverse combination, supporting the view of a Diels–Alder reaction with normal electron demand (see ESI).

The calculated *endolexo* preferences which can be extracted from the E_A values given in Table 5 are in agreement with the experimentally observed tendencies given in Table 1. The calculated data show a significant preference for the *endo*-reaction channel of furan with (*Z*)- β -fluorostyrene (**Z-3a**). All the other reactions reveal a smaller *endolexo*-selectivity. In the case of the reaction of furan with α -fluorostyrene (**2a**) and (*E*)- β -fluorostyrene (**E-3a**), respectively, a preference for the reaction channels leading to the *exo*-products is predicted. This is in disagreement with experimental results for **2a** where an *endo* preference is obtained. However, the selectivity is low and the calculated activation energies do have the correct order, *i.e.*, they show the same trend as the experimental data. The calculated data imply that there is a significant destabilisation in the cases where the fluorine atom is orientated on the same side of the furan oxygen atoms in the transition states, such as in the *endo*-transition state structures of α -fluorostyrene (**2a**) and (*E*)- β -fluorostyrene (**E-3a**) (Fig. 3). In these transition state structures, the O...F distances (274–287 pm) are smaller than the sum of the van der Waals radii (299 pm).⁵¹ The same consideration holds for the calculated and experimentally observed high *endo* preference in the reaction with (*Z*)- β -fluorostyrene (**Z-3a**) (Table 5 and Scheme 2). Here, the fluorine atom is on the “other side” of the dienophile double bond compared to **2a** and **E-3a** (Fig. 3) and therefore, the *endo* selectivity is observed. Thus, the *endolexo* selectivity obtained has its origin in a repulsive lone pair interaction of the negatively charged oxygen atoms (NBO charges: -0.45 to -0.48) and fluorine atoms (NBO charges -0.36 to -0.37) rather than in attractive secondary π -orbital interaction.

Semiempirical calculations. In order to extend the theoretical study from furan and isobenzofuran also to diphenylisobenzofuran (**4**), which has been used in the experiments, we carried out semiempirical RHF/PM3 and RHF/AM1 calculations of all the starting materials, transition states and products. The resulting activation energies and reaction enthalpies are given in Table 7. In the following discussion we concentrate on the PM3 data, which give a more consistent picture relative to the DFT results for the model systems. In general, the activation energies and the heats of reaction for diphenylisobenzofuran (**4**) are 3–4 kcal mol⁻¹ and up to 6 kcal mol⁻¹, respectively, lower compared to furan, which is very much in line with the experimental results. However, the parent dienophile isobenzofuran is significantly more reactive as seen from the calculated barriers (6–7 kcal mol⁻¹ lower) than furan; its reactions are more exothermic by 10–20 kcal mol⁻¹.

For furan, the semiempirically calculated activation barriers

are 5–7 kcal mol⁻¹ higher compared to the DFT data (Table 7 vs. Table 5), for isobenzofuran up to 12 kcal mol⁻¹. More importantly, the sequence of the diene reactivity is different. Whereas the DFT calculated activation energies predict—in accordance with experiment—the transition states of the β -fluorostyrenes to be lower than that of α -fluorostyrene, the semiempirical E_A values show the reverse order.

The PM3 and AM1 transition state structures are more symmetrical with respect to the two forming bonds compared to the DFT data. The corresponding bond lengths are given in Table 7. A comparison of the transition states shows that the PM3 calculated bond lengths of bonds to be formed in the reactions of the styrenes with diphenylisobenzofuran (**4**) are elongated by 3–5 pm for r_1 and 10–13 pm for r_2 with respect to the corresponding bond lengths in the reactions with furan (Table 6). Therefore, it is reasonable to assume that the *ab initio* calculated transition state structures of the reactions with diphenylisobenzofuran (**4**) would be even more asynchronous than the corresponding ones calculated with furan as diene. RHF/AM1 calculations indicate a more asymmetric transition state for **1** and **2a** while for **E-3a** (and **Z-3a**) a more symmetric transition state is calculated, compared to the PM3 results.

Inspection of the energies of the frontier molecular orbitals (FMOs) reveals that the electron demand does not alter by changing the diene from furan to isobenzofuran and diphenylisobenzofuran (**4**) although the HOMO_{diene}–LUMO_{dienophile} difference is much closer to the LUMO_{diene}–HOMO_{dienophile} difference in the latter case (see ESI).

The PM3 calculated *endolexo* selectivities, *i.e.*, the difference in the activation energies for the *endo* and *exo* transition states $\Delta_{sel} = E_{a,endo} - E_{a,exo}$ for the reactions of furan, isobenzofuran and **4**, respectively, are very small (-0.3 to +0.5 kcal mol⁻¹), except for the reaction of (**Z-3a**). Here the value of Δ_{sel} of +0.8 kcal mol⁻¹ for the reaction with furan, 2.6 kcal mol⁻¹ and -1.0 kcal mol⁻¹ for the reaction with diphenylisobenzofuran (Table 7) were obtained. Interestingly, PM3 indicates for the reactions with furan and isobenzofuran a preference for the *exo* reaction channels, whereas for the reactions with diphenylisobenzofuran (**4**) a kinetic preference for the *endo* products is predicted. Compared to the *ab initio* data, which are in qualitative agreement with experiment, neither PM3 calculated selectivities for furan and isobenzofuran nor those for **4** have the correct order.

Experimental

General

Unless noted otherwise, all starting materials were obtained from commercial suppliers and were used without further purification. Toluene was distilled over a 40 cm Vigreux column. CH₂Cl₂ was dried with P₂O₅, distilled and stored over 3 Å molecular sieves.

NMR spectra were recorded with a Bruker WM 300 (¹H, 300 MHz; ¹³C, 75 MHz; ¹⁹F, 282 MHz) or a Varian U 600 spec-

trometer (^{13}C , 150 MHz) using about 5% solutions in CDCl_3 . Chemical shifts δ (ppm), refer to tetramethylsilane (^1H , 0.0 ppm), CDCl_3 (^{13}C , 77.0 ppm) or CFCl_3 (^{19}F , 0.0 ppm). Coupling constants J are given in Hz. Mass spectra were recorded using a combination of Varian GC 3400 gas chromatograph and a Finnigan MAT 8230 mass spectrometer (70 eV, EI).

Procedures

Synthesis of fluorostyrenes. The α -fluorostyrenes **2a–d** were prepared by bromofluorination³⁰ of the corresponding styrenes and subsequent dehydrobromination³¹ with potassium *tert*-butyl alcoholate in pentane. The spectroscopic data agree with those given in the literature.⁵² The β -fluorostyrenes **3a–d** were prepared by a Wittig-type olefination of corresponding benzaldehydes with tri-*n*-butylphosphine and trichlorofluoromethane.³² The spectroscopic data of **3a** agree with published ones.⁵³

Diels–Alder reactions. The fluorostyrene (2 mmol) and 1,3-diphenylisobenzofuran (**4**) (540 mg, 2 mmol) in toluene (3 cm^3) were heated in a sealed glass tube at 120 °C for 4 days. Then the solvent was removed under reduced pressure. After taking a ^{19}F NMR spectrum of the crude product, in order to determine the ratio of diastereomers, the residue was dissolved in cyclohexane–ethyl acetate (20 : 1) and crystallised to give a white product. By recrystallisation the *endo* isomers were separated whereas the *exo* isomers were enriched in the mother liquor.

Kinetic measurements. Fluorostyrenes **1c**, **2a–d**, **3a–d** (2 mmol) and 1,3-diphenylisobenzofuran (**4**) (270 mg, 1 mmol) in toluene (3 cm^3) were heated in a sealed glass tube at the required temperature. The toluene contained *m*-fluorotoluene (0.15 mol dm^{-3}) as an internal standard. From time to time a sample (0.4 cm^3) was taken and the concentration of the fluorostyrene relative to *m*-fluorotoluene was measured by ^{19}F NMR spectroscopy.

p-Chloro- β -fluorostyrenes **3b**

Colourless liquid (1.9 g, 50%) of *E*- and *Z*-**3b** (78 : 22); bp 72 °C (25 hPa).

Compound E-3b. δ_{H} 6.34 (1 H, dd, $^3J_{\text{H,H}}$ 11.4, $^3J_{\text{H,F}}$ 19.0, 1-H), 7.0–7.5 (4 H, m, arom. H); δ_{C} (75 MHz) 112.9 (1 C, dd, $^2J_{\text{C,F}}$ 17.8, 1-C), 127.4 (2 C, d, arom. C), 128.7 (1 C, s, arom. C), 129.0 (2 C, d, arom. C), 130.1 (1 C, d, $^3J_{\text{C,F}}$ 7.6, arom. C), 150.4 (1 C, dd, $^1J_{\text{C,F}}$ 259.4, 2-C); δ_{F} –129.1 (dd, $^3J_{\text{F,H}}$ 19.0, $^2J_{\text{F,H}}$ 82.0); m/z 156/158 (100%, M^+), 136/138 (4, M – HF), 121 (38, M – Cl), 120 (11, M – HCl), 101 (48, 121 – HF), 78 (12, C_6H_6^+).

Compound Z-3b. δ_{H} 5.51 (1 H, dd, $^3J_{\text{H,H}}$ 5.5, $^3J_{\text{H,F}}$ 44.1, 1-H), 6.78 (1 H, dd, $^3J_{\text{H,H}}$ 5.5, $^2J_{\text{H,F}}$ 82.5, 2-H), 7.1–7.5 (4 H, m, arom. H); δ_{C} (75 MHz) 148.6 (1 C, dd, $^1J_{\text{C,F}}$ 269.6, 2-C); δ_{F} –121.9 (dd, $^3J_{\text{F,H}}$ 44.1, $^2J_{\text{F,H}}$ 82.5).

p-Fluoro- β -fluorostyrenes **3c**

Colourless liquid (1.8 g, 55%) of *E*- and *Z*-**3c** (75 : 25); bp 60 °C (30 hPa).

Compound E-3c. δ_{H} 6.35 (1 H, dd, $^3J_{\text{H,H}}$ 19.3, $^3J_{\text{H,F}}$ 11.5, 1-H), 7.0 (3 H, m, arom. H and 2-H), 7.2 (2 H, m, arom. H); δ_{C} (75 MHz) 112.9 (1 C, dd, $^2J_{\text{C,F}}$ 15.3, 1-C), 115.7 (2 C, dd, $^2J_{\text{C,F}}$ 20.3, 3'-C), 127.7 (2 C, dd, $^3J_{\text{C,F}}$ 7.6, 2'-C), 130.5 (1-C, dd, $^3J_{\text{C,F}}$ 7.6, $^4J_{\text{C,F}}$ 7.6, 1'-C), 149.9 (1 C, dd, $^1J_{\text{C,F}}$ 259.4, 2-C), 162.2 (1 C, d, $^1J_{\text{C,F}}$ 246.7, 4'-C); δ_{F} –115.1 (m, 4'-F), –130.5 (dd, $^3J_{\text{F,H}}$ 19.3, $^2J_{\text{F,H}}$ 83.9, 2-F); m/z 140 (100%, M^+), 139 (22, M – H), 120 (10, M – HF), 119 (24, 139 – HF), 114 (24), 96 (8, M – $\text{C}_2\text{H}_2\text{F}$).

Compound Z-3c. δ_{H} 5.56 (1 H, dd, $^3J_{\text{H,H}}$ 5.3, $^3J_{\text{H,F}}$ 44.1, 1-H), 6.62 (1 H, dd, $^3J_{\text{H,H}}$ 5.3, $^2J_{\text{H,F}}$ 82.7, 2-H), 7.0 (2 H, m, arom. H), 7.2 (2 H, m, arom. H); δ_{C} (75 MHz) 147.8 (1 C, d, $^1J_{\text{C,F}}$ 272.0, 4'-C); δ_{F} –115.1 (m, 4'-F), –124.1 (dd, $^3J_{\text{F,H}}$ 44.1, $^2J_{\text{F,H}}$ 82.7, 2'-F).

m-Methyl- β -fluorostyrenes **3d**

Colourless liquid (1.6 g, 50%) of *E*- and *Z*-**3d** (89 : 11); bp 65 °C (40 hPa).

Compound E-3d. δ_{H} 2.30 (3 H, s, CH_3), 6.32 (1 H, dd, $^3J_{\text{H,H}}$ 11.4, $^3J_{\text{H,F}}$ 19.5, 1-H), 7.11 (1 H, dd, $^3J_{\text{H,H}}$ 11.4, $^2J_{\text{H,F}}$ 83.4, 2-H), 7.1–7.3 (4 H, m, arom. H); δ_{C} (75 MHz) 21.2 (s, CH_3), 113.8 (dd, $^2J_{\text{C,F}}$ 15.3, 1-C), 123.2 (d, arom. C), 126.9 (d, $^4J_{\text{C,F}}$ 5.1, 2'-C), 128.2 (d, arom. C), 128.6 (d, arom. C), 132.5 (d, $^3J_{\text{C,F}}$ 12.7, 1'-C), 138.3 (s, 3'-C), 150.2 (dd, $^1J_{\text{C,F}}$ 220.5, 2-C); δ_{F} –129.7 (dd, $^3J_{\text{F,H}}$ 19.5, $^2J_{\text{F,H}}$ 83.4); m/z 136 (100%, M^+), 135 (56, M – H), 116 (12, M – HF), 115 (28, 135 – HF), 91 (8, M – $\text{C}_2\text{H}_2\text{F}$).

Compound Z-3d. δ_{H} 2.31 (3 H, s, CH_3), 5.51 (1 H, dd, $^3J_{\text{H,H}}$ 5.5, $^3J_{\text{H,F}}$ 45.1, 1-H), 6.52 (1 H, dd, $^3J_{\text{H,H}}$ 5.5, $^2J_{\text{H,F}}$ 83.0, 2-H), 7.1–7.3 (4 H, m, arom. H); δ_{F} –121.7 (dd, $^3J_{\text{F,H}}$ 45.1, $^2J_{\text{F,H}}$ 83.0).

9-Fluoro-1,8,9-triphenyl-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-triene **5a**

Colourless crystals (597 mg, 64%) of *endo*- and *exo*-**5a** (60 : 40) (Found: C, 85.43; H, 5.38. $\text{C}_{28}\text{H}_{21}\text{FO}$ (392.5) requires C, 85.68, H, 5.40%); mp 131 °C.

Compound endo-5a. Mp 142 °C. δ_{H} 2.86 (1 H, dd, $^2J_{\text{H,H}}$ 13.0, $^3J_{\text{H,F}}$ 17.8, *endo*-H), 3.20 (1 H, dd, $^2J_{\text{H,H}}$ 13.0, $^3J_{\text{H,F}}$ 32.8, *exo*-H), 6.72 (2 H, d, $^3J_{\text{H,H}}$ 7.4, 3-H and 6-H), 7.2–7.7 (15 H, m, arom. H), 7.92 (2 H, d, $^3J_{\text{H,H}}$ 7.4, 4-H and 5-H); δ_{C} (150 MHz) 52.4 (dt, $^2J_{\text{C,F}}$ 22.6, 10-C), 87.9 (s, 1-C), 94.5 (d, $^2J_{\text{C,F}}$ 26.4, 8-C), 104.0 (d, $^1J_{\text{C,F}}$ 197.0, 9-C), 119.0 (d, arom. C), 122.7 (dd, $^4J_{\text{C,F}}$ 1.0, arom. C), 125.9 (dd, $^3J_{\text{C,F}}$ 10.3, arom. C), 126.2, 126.50, 126.55 (d, arom. C), 127.2 (dd, $^4J_{\text{C,F}}$ 2.0, arom. C), 127.6 (d, arom. C), 127.82 (dd, $^4J_{\text{C,F}}$ 1.1, arom. C), 127.85, 128.1, 128.3, 128.6 (d, arom. C), 134.2 (d, $^3J_{\text{C,F}}$ 1.2, arom. C), 137.6 (s, arom. C), 138.4 (d, $^2J_{\text{C,F}}$ 24.1, arom. C), 142.6 (d, $^3J_{\text{C,F}}$ 4.2, 7-C), 149.8 (d, $^4J_{\text{C,F}}$ 2.4, 2-C); δ_{F} –148.1 (dd, $^3J_{\text{F,H}_{\text{cis}}}$ 17.8, $^3J_{\text{F,H}_{\text{trans}}}$ 32.8); m/z 372 (25%, M^+ – HF), 295 (10, 372 – C_6H_5), 270 (100, M – $\text{C}_8\text{H}_7\text{F}$, retro Diels–Alder), 193 (60, 270 – C_6H_5).

Compound exo-5a. δ_{H} 2.85 (1 H, dd, $^2J_{\text{H,H}}$ 13.0, $^3J_{\text{H,F}}$ 21.8, *endo*-H), 3.20 (1 H, dd, $^2J_{\text{H,H}}$ 13.0, $^3J_{\text{H,F}}$ 14.8, *exo*-H), 6.72 (2 H, d, $^3J_{\text{H,H}}$ 7.4, 3-H and 6-H), 7.2–7.7 (15 H, m, arom. H), 7.92 (2 H, d, $^3J_{\text{H,H}}$ 7.4, 4-H and 5-H); δ_{C} (150 MHz) 52.9 (dt, $^2J_{\text{C,F}}$ 22.0, 10-C), 88.2 (d, $^3J_{\text{C,F}}$ 3.6, 1-C), 93.0 (d, $^2J_{\text{C,F}}$ 26.9, 8-C), 102.6 (d, $^1J_{\text{C,F}}$ 198.4, 9-C), 118.7 (d, arom. C), 122.0 (dd, $^4J_{\text{C,F}}$ 1.8, 3-C), 125.7 (dd, $^3J_{\text{C,F}}$ 1.0, arom. C), 126.3 (d, arom. C), 126.87 (dd, $^4J_{\text{C,F}}$ 0.5, arom. C), 126.90 (dd, $^4J_{\text{C,F}}$ 1.0, arom. C), 127.46, 127.54, 127.55, 127.8, 128.3, 128.6 (d, arom. C), 135.4 (d, $J_{\text{C,F}}$ 1.2, arom. C), 138.1 (d, $J_{\text{C,F}}$ 1.2, arom. C), 141.6 (d, $^2J_{\text{C,F}}$ 24.7, arom. C), 144.9 (d, $^3J_{\text{C,F}}$ 2.6, 7-C), 148.8 (d, $J_{\text{C,F}}$ 1.4, arom. C); δ_{F} –151.12 (dd, $^3J_{\text{F,H}_{\text{trans}}}$ 14.8, $^3J_{\text{F,H}_{\text{cis}}}$ 21.8).

9-Fluoro-1,8-diphenyl-9-(4-chlorophenyl)-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-triene **5b**

Colourless crystals (251 mg, 59%) of *endo*- and *exo*-**5b** (65 : 35) (Found: C, 78.90; H, 4.76. $\text{C}_{28}\text{H}_{20}\text{ClFO}$ (426.9) requires C, 78.77; H, 4.73%); mp 144 °C.

Compound endo-5b. δ_{H} 2.75 (1 H, dd, $^2J_{\text{H,H}}$ 13.1, $^3J_{\text{H,F}}$ 17.6, *endo*-H), 3.15 (1 H, dd, $^2J_{\text{H,H}}$ 13.1, $^3J_{\text{H,F}}$ 32.7, *exo*-H), 6.37 (2 H, d, $^3J_{\text{H,H}}$ 6.7, 3-H and 6-H), 7.0–7.4 (16 H, m, arom. H); δ_{C} (150 MHz) 52.3 (dt, $^2J_{\text{C,F}}$ 22.4, 10-C), 87.9 (s, 1-C), 94.4 (d, $^2J_{\text{C,F}}$ 26.4, 8-C), 103.9 (d, $^1J_{\text{C,F}}$ 197.9, 9-C), 119.0 (s, arom. C), 122.7 (dd, $^4J_{\text{C,F}}$ 1.2, arom. C), 126.1, 126.5, 126.6 (d, arom. C), 127.4 (dd,

$^3J_{C,F}$ 10.5, arom. C), 127.4 (dd, $^4J_{C,F}$ 1.8, arom. C), 127.8, 127.9, 128.3 (d, arom. C), 128.3 (dd, $^4J_{C,F}$ 5.8, arom. C), 128.6, 129.6, 129.8, 130.3, 132.9 (d, arom. C), 133.9 (d, $^4J_{C,F}$ 1.5, arom. C), 134.0 (d, $^4J_{C,F}$ 1.3, arom. C), 137.3 (d, $^2J_{C,F}$ 40.3, arom. C), 140.0 (s, arom. C-Cl), 142.4 (d, $^3J_{C,F}$ 4.1, arom. C), 149.8 (d, $^3J_{C,F}$ 2.4, 7-C); δ_F -147.6 (dd, $^3J_{F,Hendo}$ 17.6, $^3J_{F,Hexo}$ 32.7); m/z 426 (2%, M^+), 406/408 (30, $M - HF$), 270 (100, $M - C_8H_7FCl$, retro Diels–Alder), 193 (45, 270 - C_6H_5), 139 (50, 165 - C_2H_2).

Compound *exo*-5b. δ_H 2.80 (1 H dd, $^2J_{H,H}$ 12.9, $^3J_{H,F}$ 21.6, *endo*-H), 3.00 (1 H, dd, $^2J_{H,H}$ 12.9, $^3J_{H,F}$ 14.3, *exo*-H), 6.37 (2 H, d, $^3J_{H,H}$ 6.7, 3-H and 6-H), 7.0–7.4 (16 H, m, arom. H); δ_C (150 MHz) 53.0 (dt, $^2J_{C,F}$ 22.0, 10-C), 88.3 (d, $^3J_{C,F}$ 3.6, 1-C), 92.9 (d, $^2J_{C,F}$ 26.4, 8-C), 102.6 (d, $^1J_{C,F}$ 199.0, 9-C), 118.7 (s, arom. C), 122.1 (dd, $^4J_{C,F}$ 2.0, arom. C), 125.6 (dd, $^4J_{C,F}$ 0.9, arom. C), 126.3 (d, arom. C), 126.6 (dd, $^3J_{C,F}$ 10.7, arom. C), 127.0 (d, arom. C), 127.6 (d, arom. C), 127.8 (dd, $^4J_{C,F}$ 2.3, arom. C), 128.7 (d, arom. C), 132.8 (d, $^4J_{C,F}$ 1.6, arom. C), 135.2 (d, $^4J_{C,F}$ 1.0, arom. C), 137.9 (s, arom. C-Cl), 140.4 (d, $^2J_{C,F}$ 25.2, arom. C), 144.6 (d, $^3J_{C,F}$ 2.5, arom. C), 148.8 (d, $^3J_{C,F}$ 1.4, 7-C); δ_F -150.9 (dd, $^3J_{F,Hexo}$ 14.3, $^3J_{F,Hendo}$ 21.6).

9-Fluoro-1,8-diphenyl-9-(4-fluorophenyl)-11-oxatricyclo-[6.2.1.0^{2,7}]undeca-2(7),3,5-triene 5c

Colourless crystals (452 mg, 55%) of *endo*- and *exo*-5c (60 : 40) (Found: C, 81.58; H, 5.03. $C_{28}H_{20}F_2O$ (410.5) requires C, 81.93; H, 4.91%); mp 165 °C.

Compound *endo*-5c. δ_H 2.88 (1 H, dd, $^2J_{H,H}$ 13.1, $^3J_{H,F}$ 17.6, *endo*-H), 3.15 (1 H dd, $^2J_{H,H}$ 13.1, $^3J_{H,F}$ 32.9, *exo*-H), 6.4 (2 H, m, arom. H), 6.8 (2 H, m, arom. H), 7.0–7.5 (14 H, m, arom. H); δ_C (150 MHz) 52.4 (dt, $^2J_{C,F}$ 22.8, 10-C), 87.8 (s, 1-C), 94.4 (d, $^2J_{C,F}$ 26.4, 8-C), 104.0 (d, $^1J_{C,F}$ 197.5, 9-C), 114.2 (dd, $^2J_{C,F}$ 23.2, arom. C), 119.0 (d, arom. C), 122.7 (dd, $^4J_{C,F}$ 1.2, arom. C), 126.2, 126.5, 126.6, 127.8 (d, arom. C), 127.8 (ddd, $^3J_{C,F}$ 8.1, $^3J_{C,F}$ 10.2, arom. C), 127.9, 128.28, 128.34, 128.6, 129.6, 129.8, 130.1 (d, arom. C), 132.9 (s, arom. C), 134.2 (dd, $^2J_{C,F}$ 24.9, $^4J_{C,F}$ 3.0, arom. C), 137.5 (s, arom. C), 142.5 (d, $^3J_{C,F}$ 4.4, arom. C), 149.9 (d, $^3J_{C,F}$ 2.7, 7-C), 162.4 (d, $^2J_{C,F}$ 247.3, arom. C); δ_F -147.5 (1 F, dd, $^3J_{F,Hendo}$ 17.6, $^3J_{F,Hexo}$ 32.9, 9-F), -113.2 (1 F, m, arom. F); m/z 390 (24%, $M^+ - HF$), 313 (18, 390 - C_6H_5), 270 (100, $M - C_8H_7F$, retro Diels–Alder), 193 (43, 270 - C_6H_5), 139 (56, 165 - C_2H_2).

Compound *exo*-5c. δ_H 2.78 (1 H, dd, $^2J_{H,H}$ 12.9, $^3J_{H,F}$ 12.9, *endo*-H), 2.98 (1 H, dd, $^2J_{H,H}$ 12.9, $^3J_{H,F}$ 21.0, *exo*-H), 6.40 (2 H, m, arom. H), 6.80 (2 H, m, arom. H), 7.0–7.5 (14 H, m, arom. H); δ_C (150 MHz) 52.8 (dt, $^2J_{C,F}$ 22.2, 10-C), 88.2 (d, $^3J_{C,F}$ 3.5, 1-C), 92.8 (d, $^2J_{C,F}$ 23.9, 8-C), 102.5 (d, $^1J_{C,F}$ 193.9, 9-C), 114.4, 118.6 (d, arom. C), 122.0 (dd, $^4J_{C,F}$ 2.0, arom. C), 125.5 (dd, $^4J_{C,F}$ 1.1, arom. C), 126.2 (d, arom. C), 126.7 (ddd, $^3J_{C,F}$ 8.3, $^3J_{C,F}$ 10.8, arom. C), 127.2, 127.5, 127.8, 128.2, 128.6, 129.6, 129.7, 130.4, 132.9 (d, arom. C), 137.1 (s, arom. C), 137.4 (d, $^2J_{C,F}$ 22.0, arom. C), 137.9 (d, $^4J_{C,F}$ 1.2, arom. C), 139.9 (s, arom. C), 144.5 (d, $^4J_{C,F}$ 2.4, arom. C), 148.7 (d, $^4J_{C,F}$ 1.2, arom. C); δ_F -152.8 (1 F, dd, $^3J_{F,Hendo}$ 12.9, $^3J_{F,Hexo}$ 21.0, 9-F), -115.8 (1 F, m, arom. F).

9-Fluoro-1,8-diphenyl-9-(3-methylphenyl)-11-oxatricyclo-[6.2.1.0^{2,7}]undeca-2(7),3,5-triene 5d

Colourless crystals (431 mg, 53%) of *endo*- and *exo*-5d (62 : 38) (Found: C, 85.59; H, 5.80. $C_{29}H_{23}FO$ (406.5) requires C, 85.68; H, 5.71%); mp 170 °C.

Compound *endo*-5d. δ_H 2.15 (3 H, s, CH_3), 2.83 (1 H, dd, $^2J_{H,H}$ 13.1, $^3J_{H,F}$ 17.7, *endo*-H), 3.15 (1 H, dd, $^2J_{H,H}$ 13.1, $^3J_{H,F}$ 32.9, *exo*-H), 6.9–7.5 (18 H, m, arom. H); δ_C (150 MHz) 21.3 (q, CH_3), 52.5 (dt, $^2J_{C,F}$ 22.5, 10-C), 87.9 (s, 1-C), 94.6 (d, $^2J_{C,F}$ 26.7, 8-C), 104.2 (d, $^1J_{C,F}$ 197.3, 9-C), 118.9 (d, arom. C), 122.8 (dd,

$^4J_{C,F}$ 1.0, 3-C), 123.0 (dd, $^3J_{C,F}$ 10.4, arom. C), 126.3, 126.4, 126.5 (d, arom. C), 126.7 (dd, $^3J_{C,F}$ 10.0, arom. C), 127.1 (dd, $^4J_{C,F}$ 2.0, arom. C), 127.6, 127.8, 128.0, 128.2, 128.3 (d, arom. C), 128.4 (dd, $^4J_{C,F}$ 1.0, arom. C), 128.5, 129.6, 129.8, 130.3 (d, arom. C), 132.9 (s, arom. C), 134.3 (d, $^4J_{C,F}$ 1.2, arom. C), 136.7 (d, $^4J_{C,F}$ 1.9, arom. C), 137.7 (s, arom. C), 138.3 (d, $^2J_{C,F}$ 24.0, arom. C), 139.9 (s, arom. C), 142.8 (d, $^3J_{C,F}$ 4.2, arom. C), 149.9 (d, $^4J_{C,F}$ 2.5, 7-C); δ_F -147.8 (dd, $^3J_{F,Hendo}$ 17.7, $^3J_{F,Hexo}$ 32.9); m/z 406 (2%, M^+), 386 (30, $M - HF$), 309 (10, 386 - C_6H_5), 293 (27, 356 - C_6H_5), 270 (100, $M - C_8H_7F$, retro Diels–Alder), 193 (49, 270 - C_6H_5).

Compound *exo*-5d. δ_H 2.31 (3 H, s, CH_3), 2.92 (1 H, dd, $^2J_{H,H}$ 12.9, $^3J_{H,F}$ 21.2, *endo*-H), 3.17 (1 H, dd, $^2J_{H,H}$ 12.9, $^3J_{H,F}$ 14.3, *exo*-H), 6.90–7.90 (18 H, m, arom. H); δ_C (150 MHz) 21.4 (q, CH_3), 52.9 (dt, $^2J_{C,F}$ 22.3, 10-C), 88.2 (d, $^3J_{C,F}$ 3.6, 1-C), 93.1 (d, $^2J_{C,F}$ 26.9, 8-C), 102.7 (d, $^1J_{C,F}$ 198.2, 9-C), 118.7 (d, arom. C), 122.0 (dd, $^4J_{C,F}$ 2.1, arom. C), 122.2 (dd, $^3J_{C,F}$ 10.5, arom. C), 125.6 (dd, $^3J_{C,F}$ 10.7, arom. C), 125.7 (dd, $^4J_{C,F}$ 0.9, arom. C), 126.4, 126.8, 127.1, 127.4, (d, arom. C), 127.5 (dd, $^4J_{C,F}$ 2.2, arom. C), 127.6, 127.7, 128.3, 128.6 (4d, arom. C), 135.5 (d, $^4J_{C,F}$ 1.2, arom. C), 137.0 (d, $^4J_{C,F}$ 2.3 arom. C), 138.2 (d, $^4J_{C,F}$ 1.0, arom. C), 141.6 (d, $^2J_{C,F}$ 24.4, arom. C), 145.0 (d, $^4J_{C,F}$ 1.3, arom. C), 148.8 (d, $^4J_{C,F}$ 1.4, arom. C); δ_F -151.0 (dd, $^3J_{F,Hexo}$ 14.3, $^3J_{F,Hendo}$ 21.2).

9-Fluoro-1,8,10-triphenyl-11-oxatricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-triene 6a

Colourless crystals (452 mg, 57%) of *endo*- and *exo*-6a (40 : 60) (Found: C, 85.37; H, 5.41. $C_{28}H_{21}FO$ (392.5) requires C, 85.68; H, 5.40%); mp 141 °C.

Compound *endo,trans*-6a. δ_H 3.85 (1 H, dd, $^3J_{H,H}$ 2.1, $^3J_{H,F}$ 34.1, 10-H), 5.31 (1 H, dd, $^3J_{H,H}$ 2.1, $^2J_{H,F}$ 55.8, 9-H), 6.30 (2 H, d, $^4J_{H,H}$ 6.7, arom. H), 7.00–7.90 (19 H, m, arom. H); δ_C (150 MHz) 61.6 (dd, $^2J_{C,F}$ 21.4, 10-C), 91.0 (d, $^3J_{C,F}$ 2.3, 1-C), 91.4 (d, $^2J_{C,F}$ 22.9, 8-C), 102.0 (dd, $^1J_{C,F}$ 201.9, 9-C), 120.7, 126.4, 127.3, 127.6, 127.8, 128.2, 128.3, 128.5, 129.2, 129.6, 129.7, 130.3 (d, arom. C), 127.9 (dd, $^4J_{C,F}$ 8.4, arom. C), 132.9 (s, arom. C), 134.7 (s, arom. C), 136.8 (d, $^3J_{C,F}$ 2.3, arom. C), 144.0 (d, $^3J_{C,F}$ 4.7, 2-C), 145.6 (d, $^3J_{C,F}$ 1.7, arom. C); δ_F -174.9 (dd, $^3J_{F,H}$ 34.1, $^2J_{F,H}$ 55.8); m/z 372 ($M^+ - HF$ 18%), 270 (100, $M - C_8H_7F$, retro Diels–Alder), 193 (58, 270 - C_6H_5).

Compound *exo,trans*-6a. δ_H 3.48 (1 H, dd, $^3J_{H,H}$ 2.4, $^3J_{H,F}$ 23.1, 10-H), 5.51 (1 H, dd, $^3J_{H,H}$ 2.3, $^2J_{H,F}$ 55.7, 9-H), 7.20–8.20 (19 H, m, arom. H); δ_C (150 MHz) 59.4 (dd, $^2J_{C,F}$ 19.8, 10-C), 91.4 (d, $^3J_{C,F}$ 2.6, 1-C), 92.5 (s, 8-C), 102.8 (dd, $^1J_{C,F}$ 201.1, 9-C), 118.5, 122.5, 126.1, 126.6, 127.0, 127.2, 127.7, 127.9, 128.1, 128.4, 128.6, 128.9, 129.3 (d, arom. C), 131.6 (d, $^3J_{C,F}$ 2.7, arom. C), 136.3 (s, arom. C), 139.9 (d, $^3J_{C,F}$ 1.7, arom. C), 143.9 (d, $^3J_{C,F}$ 1.8, 2-C), 148.7 (s, 7-C); δ_F -175.9 (dd, $^3J_{F,H}$ 23.1, $^2J_{F,H}$ 55.7).

Compound *endo,cis*-6a. δ_H 3.98 (1 H, dd, $^3J_{H,H}$ 9.0, $^3J_{H,F}$ 14.8, 10-H), 5.61 (1 H, dd, $^3J_{H,H}$ 9.0, $^2J_{H,F}$ 58.2, 9-H), 7.00–7.9 (19 H, m, arom. H); δ_C (150 MHz) 58.0 (dd, $^2J_{C,F}$ 18.0, 9-C), 88.6 (d, $^2J_{C,F}$ 21.6, 1-C), 91.5 (s, 8-C), 94.3 (dd, $^1J_{C,F}$ 202.4, 10-C), 122.2 (d, arom. C), 126.0–130.0 (d, arom. C), 131.7 (d, $^3J_{C,F}$ 3.0, arom. C), 133.7 (d, $^3J_{C,F}$ 3.1, arom. C), 137.5 (s, 7-C), 144.6 (d, $^3J_{C,F}$ 1.5, 2-C), 144.9 (d, $^3J_{C,F}$ 1.5, 6-C); δ_F -183.7 (dd, $^3J_{F,H}$ 14.8, $^2J_{F,H}$ 58.2).

9-Fluoro-1,8-diphenyl-10-(4-chlorophenyl)-11-oxatricyclo-[6.2.1.0^{2,7}]undeca-2(7),3,5-triene 6b

Colourless crystals (480 mg, 56%) of *endo*- and *exo*-6b (40 : 60) (Found: C, 78.67; H, 4.83. $C_{28}H_{20}ClFO$ (426.9) requires C, 78.77; H, 4.73%); mp 177 °C.

Compound *endo,trans*-6b. δ_{H} 3.81 (1 H, dd, $^3J_{\text{H,H}}$ 2.2, $^3J_{\text{C,F}}$ 33.6, 10-H), 5.27 (1 H, dd, $^3J_{\text{H,H}}$ 2.2, $^2J_{\text{H,F}}$ 55.8, 9-H), 6.9–7.9 (18 H, m, arom. H); δ_{C} (150 MHz) 61.0 (dd, $^2J_{\text{C,F}}$ 20.4, 10-C), 91.1 (d, $^2J_{\text{C,F}}$ 15.4, 8-C), 91.8 (s, 1-C), 101.8 (dd, $^1J_{\text{C,F}}$ 203.5, 9-C), 118.4, 121.0, 126.0–131.0 (d, arom. C), 132.5 (s, arom. C), 133.5 (s, arom. C), 134.5 (s, arom. C), 135.3 (s, arom. C), 144.0 (d, $^3J_{\text{C,F}}$ 5.1, arom. C), 148.3 (s, arom. C); δ_{F} –174.8 (dd, $^3J_{\text{F,H}}$ 33.6, $^2J_{\text{F,H}}$ 55.8); *m/z* 406 (0.1%, M^+ – HF), 391 (0.1, M – Cl), 270 (100, M – $\text{C}_8\text{H}_6\text{FCl}$, retro Diels–Alder), 193 (4, 270 – C_6H_5).

Compound *exo,trans*-6b. δ_{H} 3.46 (1 H, dd, $^3J_{\text{H,H}}$ 2.4, $^3J_{\text{H,F}}$ 22.7, 10-H), 5.42 (1 H, dd, $^3J_{\text{H,H}}$ 2.4, $^2J_{\text{H,F}}$ 55.6, 9-H), 6.90–7.90 (18 H, m, arom. H); δ_{C} (150 MHz) 58.8 (dd, $^2J_{\text{C,F}}$ 20.3, 9-C), 88.2 (d, $^2J_{\text{C,F}}$ 12.9, 1-C), 92.3 (d, $^3J_{\text{C,F}}$ 5.1, 8-C), 102.4 (dd, $^1J_{\text{C,F}}$ 200.9, 10-C), 122.5, 126.0–131.0 (d, arom. C), 133.0 (s, arom. C), 136.0 (s, arom. C), 136.6 (s, arom. C), 138.7 (s, arom. C), 143.9 (s, arom. C), 148.6 (s, arom. C); δ_{F} –175.6 (dd, $^2J_{\text{F,H}}$ 55.6, $^3J_{\text{F,H}}$ 22.7).

Compound *endo,cis*-6b. δ_{H} 3.94 (1 H, dd, $^3J_{\text{H,H}}$ 8.3, $^2J_{\text{H,F}}$ 14.5, 10-H), 5.60 (1 H, dd, $^3J_{\text{H,H}}$ 8.3, $^2J_{\text{H,F}}$ 57.5, 9-H), 6.90–7.90 (18 H, m, arom. H); δ_{F} –183.9 (dd, $^3J_{\text{F,H}}$ 14.5, $^2J_{\text{F,H}}$ 57.5).

9-Fluoro-1,8-diphenyl-10-(4-fluorophenyl)-11-oxatricyclo-[6.2.1.0^{2,7}]undeca-2(7),3,5-triene 6c

Colourless crystals (498 mg, 61%) of *endo*- and *exo*-6c (42 : 58) (Found: C, 82.00; H, 4.90. $\text{C}_{28}\text{H}_{20}\text{F}_2\text{O}$ (410.5) requires C, 81.93; H, 4.91%); mp 167 °C.

Compound *endo,trans*-6c. δ_{H} 3.84 (1 H, dd, $^3J_{\text{H,H}}$ 2.2, $^3J_{\text{H,F}}$ 34.3, 10-H), 5.26 (1 H, dd, $^3J_{\text{H,H}}$ 2.2, $^2J_{\text{H,F}}$ 55.3, 9-H), 7.20–7.60 (18 H, m, arom. H); δ_{C} (150 MHz) 61.5 (dd, $^2J_{\text{C,F}}$ 22.0, 10-C), 90.9 (s, 1-C), 91.4 (d, $^2J_{\text{C,F}}$ 23.1, 8-C), 102.0 (dd, $^1J_{\text{C,F}}$ 201.8, 9-C), 114.8 (dd, $^2J_{\text{C,F}}$ 21.3, arom. C), 120.9, 125.9, 126.4, 127.4, 127.8, 128.1, 128.3, 128.4, 128.6, (d, arom. C), 132.7 (d, $J_{\text{C,F}}$ 7.4, arom. C), 133.0 (s, arom. C), 136.6 (s, arom. C), 143.9 (d, $^3J_{\text{C,F}}$ 4.5, arom. C), 145.5 (s, arom. C), 162.6 (d, $^1J_{\text{C,F}}$ 246.8, arom. C); δ_{F} –175.3 (dd, $^3J_{\text{F,H}}$ 34.3, $^2J_{\text{F,H}}$ 55.3, 9-F), –115.0 (m, arom. F); *m/z* 410 (1%, M^+), 390 (2, M – HF), 270 (100, M – $\text{C}_8\text{H}_6\text{F}_2$, retro Diels–Alder), 193 (28, 270 – C_6H_5), 140 (12, $\text{C}_8\text{H}_6\text{F}_2$).

Compound *exo,trans*-6c. δ_{H} 3.48 (1 H, dd, $^3J_{\text{H,H}}$ 2.4, $^3J_{\text{H,F}}$ 22.9, 10-H), 5.44 (1 H, dd, $^3J_{\text{H,H}}$ 2.4, $^2J_{\text{H,F}}$ 55.3, 9-H), 7.20–7.60 (18 H, m, arom. H); δ_{F} –176.1 (dd, $^3J_{\text{F,H}}$ 22.9, $^2J_{\text{F,H}}$ 55.3, 5-F), –116.4 (m, arom. F).

Compound *endo,cis*-6c. δ_{H} 3.96 (1 H, dd, $^3J_{\text{H,H}}$ 8.3, $^3J_{\text{H,F}}$ 14.5, 6-H), 5.59 (dd, $^3J_{\text{H,H}}$ 8.3, $^2J_{\text{H,F}}$ 57.2, 9-H), 7.20–7.60 (18 H, m, arom. H); δ_{C} (150 MHz) 57.3 (1 H, dd, $^2J_{\text{C,F}}$ 17.3, 10-C), 88.6 (d, $^2J_{\text{C,F}}$ 21.1, 8-C), 90.4 (s, 1-C), 94.1 (dd, $^1J_{\text{C,F}}$ 203.6, 9-C), 114.4 (dd, $^2J_{\text{C,F}}$ 21.3, arom. C), 122.1, 122.6, 125.6, 126.1, 127.1, 127.7, 127.9, 128.4, 128.6, (d, arom. C), 133.06 (d, $^3J_{\text{C,F}}$ 2.7, arom. C), 133.12 (d, $^3J_{\text{C,F}}$ 2.7, arom. C), 136.8 (s, arom. C), 137.7 (s, arom. C), 144.6 (d, $^3J_{\text{C,F}}$ 17.5, 7-C), 162.3 (d, $^1J_{\text{C,F}}$ 247.0, arom. C); δ_{F} –184.2 (1 F, dd, $^3J_{\text{F,H}}$ 14.5, $^2J_{\text{F,H}}$ 57.2, 5-F), –115.4 (m, arom. F).

9-Fluoro-1,8-diphenyl-10-(3-methylphenyl)-11-oxatricyclo-[6.2.1.0^{2,7}]undeca-2(7),3,5-triene 6d

Colourless crystals (602 mg, 75%) of *endo*- and *exo*-6d (43 : 57) (Found: C, 85.53; H, 5.76. $\text{C}_{29}\text{H}_{23}\text{FO}$ (406.5) requires C, 85.68; H, 5.71%); mp 175 °C.

Compound *endo,trans*-6d. δ_{H} 2.15 (3 H, s, CH_3), 3.81 (1 H, dd, $^3J_{\text{H,H}}$ 2.1, $^3J_{\text{H,F}}$ 34.4, 10-H), 5.30 (1 H, dd, $^3J_{\text{H,H}}$ 2.1, $^2J_{\text{H,F}}$ 57.2, 9-H), 7.20–7.60 (18 H, m, arom. H); δ_{C} (150 MHz) 21.3 (q, CH_3), 61.5 (dd, $^2J_{\text{C,F}}$ 23.4, 10-C), 91.1 (s, 1-C or 8-C), 91.6 (s, 8-C or 1-C), 102.1 (dd, $^1J_{\text{C,F}}$ 200.9, 9-C), 120.8, 122.6, 126.1, 126.4, 127.1, 127.6, 127.7, 127.9, 128.0, 128.1, 128.2, 128.5

(d, arom. C), 130.0 (s, arom. C), 134.8 (s, arom. C), 136.8 (s, arom. C), 137.4 (s, arom. C), 144.1 (d, $^3J_{\text{C,F}}$ 5.1, arom. C), 145.9 (s, arom. C); δ_{F} –175.3 (dd, $^3J_{\text{F,H}}$ 34.4, $^2J_{\text{F,H}}$ 57.2); *m/z* 406 (0.2%, M^+), 386 (1.5, M – HF), 270 (100, M – $\text{C}_9\text{H}_9\text{F}$, retro Diels–Alder), 193 (18, 270 – C_6H_5), 136 (16, $\text{C}_9\text{H}_9\text{F}$).

Compound *exo,trans*-6d. δ_{H} 2.16 (3 H, s, CH_3), 3.43 (1 H, dd, $^3J_{\text{H,H}}$ 2.4, $^3J_{\text{H,F}}$ 22.9, 9-H), 5.50 (1 H, dd, $^3J_{\text{H,H}}$ 2.4, $^2J_{\text{H,F}}$ 55.3, 10-H), 7.20–7.60 (18 H, m, arom. H); δ_{C} (150 MHz) 29.7 (q, CH_3), 59.3 (dd, $^3J_{\text{C,F}}$ 17.8, 10-C), 88.0 (s, 1-C or 8-C), 92.5 (s, 8-C or 1-C), 102.7 (dd, $^1J_{\text{C,F}}$ 200.9, 9-C), 118.4, 122.5, 126–129 (arom. C), 136.4 (s, arom. C), 136.7 (s, arom. C), 137.6 (s, arom. C), 139.8 (s, arom. C), 144.0 (s, arom. C), 148.8 (s, arom. C); δ_{F} –176.4 (dd, $^3J_{\text{F,H}}$ 22.9, $^2J_{\text{F,H}}$ 55.3).

Compound *endo,cis*-6d. δ_{H} 2.31 (3 H, s, CH_3), 3.94 (1 H, dd, $^3J_{\text{H,H}}$ 8.3, $^3J_{\text{H,F}}$ 14.8, 10-H), 5.62 (1 H, dd, $^3J_{\text{H,H}}$ 8.3, $^2J_{\text{H,F}}$ 57.2, 9-H), 7.20–7.60 (18 H, m, arom. H); δ_{F} –184.2 (dd, $^3J_{\text{F,H}}$ 14.8, $^2J_{\text{F,H}}$ 57.2).

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