Fluorinated Acetylenes. Part 10.[1] Cycloadditions of α,α-Bis(3,3,3-trifluoropropynyl) benzyl Benzoate and 1,1-Bis(3,3,3-trifluoro-propynyl) ethyl Ethanoate with Furan and Cyclopentadiene[2]

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Reaction between furan and the dialkynyl ester $(CF_3C≡C)_2CPhO_2CPh$ **1a** in dichloromethane at 50 °C gave four rearranged 1:1 adducts, (Z)-5-(α-benzoyloxybenzylidene)-1,4-bis(trifluoromethyl)-8-oxa-tricyclo[4.3.0.0^{2,9}]nona-3,6-diene **11a** (major product), 4-benzoyloxy-3,8-bis(trifluoromethyl)-1,1a,-2,8c-tetrahydro-4H-1,2,8b-epoxymethenocyclopropa[c]fluorene **15**, the corresponding 3H-compound **16** and 8,9-dibenzoyl-4,7-bis(trifluoromethyl)-2-oxatetracyclo[4.3.0.0.^{3,5}0^{4,9}]non-7-ene **13a** via the common intermediate 2-benzoyloxy-2-phenyl-4,10-bis(trifluoromethyl)-7-oxapentacyclo[4.4.0.0.^{1,3}-0.^{5,9}0^{8,10}]dec-3-ene **8a** formed from the Diels–Alder adduct by intramolecular ($_π2_s + _π2_s + _π2_s$) cyclo-addition. The corresponding reaction with the ester $(CF_3C≡C)_2CMeO_2CMe$ **1b** gave analogously the diketone **13b** (major product) and a mixture of the (E)- and (Z)-isomers of the triene **11b**; a 2:1 adduct, 4-acetoxy-3-methyl-5,11-bis(trifluoromethyl)-8,15-dioxahexacyclo[10.2.1.0.^{2,11}0.^{4,9}0.^{5,7}0^{6,10}]-pentadeca-2,13-diene **10** was also isolated. A mixture of cyclopentadiene and the ester **1a** (2:1 molar ratio), heated at 50 °C, yielded mainly the bis-Diels–Alder adduct α,α-bis(3-trifluoromethyl-bicyclo[2.2.1]hepta-2,5-dien-2-yl)benzylbenzoate **7a**, together with the rearranged 1:1 adduct, diketone **13c**. Similarly, the major product from the reaction of an excess of cyclopentadiene with ester **1b** at 50 °C was the bis-Diels–Alder adduct **7b**, but a 1:1 molar ratio of reactants at 20 °C gave the mono Diels–Alder adduct 1-(3-trifluoromethylbicyclo[2.2.1]hepta-2,5-dien-2-yl)-1-(3,3,3-trifluoropropynyl)ethyl ethanoate **6d** in high yield. The bis adduct **7a** was stable at 50 °C, but the mono adduct **6d** underwent slow intramolecular ($_π2_s + _π2_s + _π2_s$) cycloaddition, cf., the furan reactions, and the intermediate **8d** so formed rearranged to a mixture of 8,9-diacetyl-4,7-bis(trifluoromethyl)-tetracyclo[4.3.0.0.^{3,5}0^{4,9}]non-7-ene **13d** and 1-acetoxy-1-[4,7-bis(trifluoromethyl)tetracyclo-[4.3.0.0.^{3,5}0^{4,9}]non-7-en-9-yl]ethene **18**. In the presence of traces of water, the ketone **13d** was only a minor product with the major products being the substituted ethene **18** and two diastereoisomers of 1-acetoxy-1-[4,7-bis(trifluoromethyl)tetracyclo[4.3.0.0.^{3,5}0^{4,9}]non-7-en-9-yl]ethanol **19**.

The Diels–Alder reaction of dienes with monoalkynes has been studied extensively[3] and has been extended to fluoroalkynes, especially those containing perfluoroalkyl groups.[4] In the present work, as part of a general study of the chemistry (especially cycloadditions) of alkynes of the type $CF_3C≡CR$,[1,5] a general route to 1,4-dialkynyl esters of type $(CF_3C≡C)_2CRO_2CR$ **1** (R = alkyl or aryl) has been established. A study of the cycloadditions of such esters with the dienes furan and cyclopentadiene (CP) has been carried out; to the best of our knowledge Diels–Alder reactions of 1,4-dialkynes have not been reported previously.

The most general route to 1,4-dialkynes involves copper(I) halide-promoted coupling of alk-1-ynyl Grignard reagents with prop-2-ynyl halides[6–8] or prop-2-ynyl tosylates,[4] or of terminal alkynes with prop-2-ynyl halides in the presence of ammonia[9] or an amine.[10] However, a report[11] that reaction of 3,3,3-trifluoropropynyllithium **2** with ethanoyl chloride gave the 1,4-dialkynyl alcohol **3** (ca. 50%) after acid work-up, attracted our attention. It was reasoned that the use of an excess of an acid chloride in such a reaction should result in the intermediate lithium 1,4-dialkynylalkoxide **4** being trapped to afford the corresponding ester **1**.

Treatment of the salt **2** with an excess of benzoyl chloride or ethanoyl chloride (ca. 1:2 molar ratio) in ether at −50 °C did indeed give the corresponding esters **1** in excellent yield, **1a** (89%) and **1b** (86%) via the ketones **5** (Scheme 1). The ketones **5** were not detected, thus confirming the observation[11] that they are more susceptible to nucleophilic attack by salt **2** than are the acid chlorides. This method has been extended[12] to the
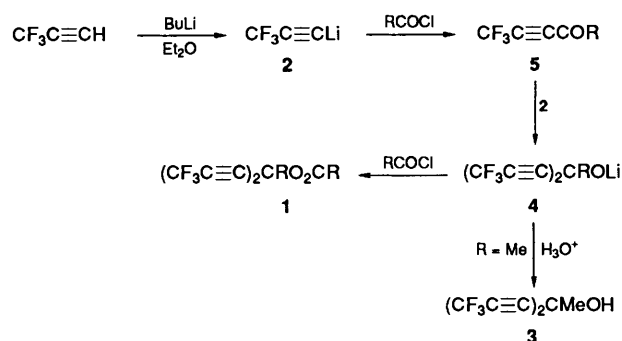
Scheme 1   a, R = Ph; b, R = Me

preparation of the 1,4-diynyl ester $(PhC≡C)_2CMeO_2CMe$, by reaction of the salt $PhC≡CLi$ with ethanoyl chloride.

The products obtained from the reactions of furan and cyclopentadiene with the esters **1a** and **1b** and the yields of isolated pure compounds are given in Table 1.
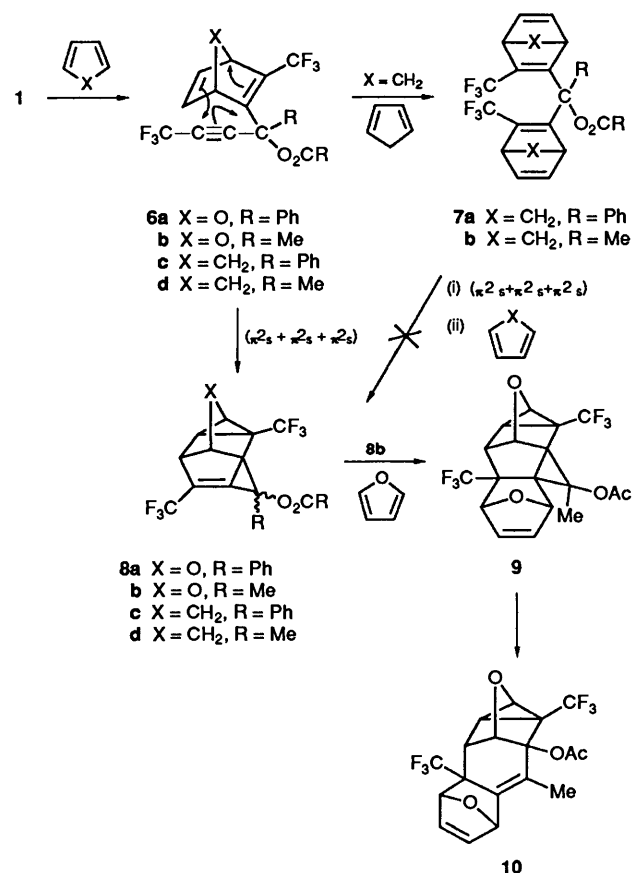
The formation of all the isolated products can be explained via initial cycloaddition ($_π4 + _π2$) of the diene to one of the triple bonds in the dialkynyl ester **1**, to give the mono Diels–Alder adducts **6**. These 1:1 adducts then react further, either by an intermolecular cycloaddition ($_π4 + _π2$) involving a second molecule of diene and the remaining triple bond in **6** to yield the bis-Diels–Alder adducts **7**, and/or by an intramolecular ($_π2_s + _π2_s + _π2_s$) cycloaddition to afford the strained, un-

Table 1 The reaction of furan and cyclopentadiene (CP) with esters 1a and 1b in dichloromethane

					Product (%)								
					1:1 Adduct						2:1 Adduct		Others
Diene	Ester	Molar ratio	Temp. (°C)	Time (days)	6	11	13	15	16	18	7	10	19
Furan	1a	2:1	50	6		44	6.5	4.5	3				
Furan	1b	2:1	50	6		20	26.5					10	
CP	1a	2:1	50	4			15				59		
CP	1b	2:1	50	4			a			12	60		5.5
CP	1b	1:1	50	5	23		a			11	14		33.5
CP	1b	1:1	20	12	88								

^{a} Present in the crude reaction product mixture (<5%) (^{19}F NMR and TLC).

stable, intermediate 1:1 adducts **8**, which contain a bridgehead double bond in fused 5- and 3-membered rings (Scheme 2).

6a X = O, R = Ph
b X = O, R = Me
c X = CH₂, R = Ph
d X = CH₂, R = Me

7a X = CH₂, R = Ph
b X = CH₂, R = Me

8a X = O, R = Ph
b X = O, R = Me
c X = CH₂, R = Ph
d X = CH₂, R = Me

Scheme 2

The possibility that the unstable adducts **8** were formed from the 2:1 adducts **7** by intramolecular $(_{\pi}2_s + _{\pi}2_s + _{\pi}2_s)$ cycloaddition followed by cleavage of diene was discounted (see later).

Only in the reactions involving the more reactive cyclopentadiene were Diels-Alder 1:1 **6d** and 2:1 adducts **7a** and **7b** isolated, and the 2:1 adducts were the major products when an excess of the diene was employed at 50 °C. The 1:1 adduct **6d** was isolated in moderate yield only from the 1:1 molar ratio reaction of cyclopentadiene was the ester **1b** at 50 °C, but at 20 °C it was isolated in excellent yield, indicating it was stable at this temperature towards $(_{\pi}2_s + _{\pi}2_s + _{\pi}2_s)$ cycloaddition to give the unstable intermediate **8d**. The use of a 1:1 molar ratio of cyclopentadiene and the ester **1a** at 20 °C would probably have enabled the isolation of the 1:1 adduct **6c**.

When the mono Diels-Alder adduct **6d** was heated at 50 °C, it underwent slow intramolecular $(_{\pi}2_s + _{\pi}2_s + _{\pi}2_s)$ cycloaddition, and after 7 days, unchanged **6d** (31% recovered) and the rearranged 1:1 adducts, the diene **18** (45%) and the diketone **13d** (21%) were isolated (Scheme 3). The bis-Diels-Alder adduct **7a** was considerably more stable, being unchanged when heated under the reaction conditions (50 °C, 4 days), and being recovered to a large extent (ca. 75% unchanged) when heated at 70 °C over 3 weeks; a complex mixture of minor products was formed, which did not contain the diketone **13c**, as shown by NMR spectroscopy. It is, therefore, considered that the rearranged 1:1 adducts **11, 13, 15, 16, 18** and 2:1 adduct **10** are formed from the mono Diels-Alder adducts **6**, and not the bis adducts (see Schemes 2 and 3).

This is in contrast to the report that, in the reaction of ethyl propynoate with 2,5-dimethylfuran, the homo Diels-Alder 2:1 adduct **20** is formed, not by reaction of the initially-formed 1:1 adduct **21** with propynoate, but by dimerisation of endoxide **21**, followed by cleavage of 2,5-dimethylfuran.[13]

Homo Diels-Alder $(_{\pi}2_s + _{\pi}2_s + _{\pi}2_s)$ cycloadditions have only been reported for reactions in which at least two of the π bonds involved are present in one reactant. Adducts of norbornadienes and electron-deficient alkenes or alkynes are the most common examples of this type of cycloaddition, e.g. reaction of norbornadiene with tetracyanoethylene[14] (TCNE) at 20 °C and with hexafluorobut-2-yne[15] at 150 °C, to afford adducts **22** (100%) and **23** (78%), respectively.

The isolated rearranged adducts **11, 13, 15, 16, 18** result from ring opening of the cyclopropane in the strained intermediates **8** (see Scheme 3).

Since the prop-2-ynyl carbon atom in each of the Diels-Alder adducts **6** is chiral, intramolecular cyclisation would afford the intermediates **8**, each as a pair of diastereoisomers **8A** and **8B**, depending on the relative stereochemistry of the R and O₂CR groups on the cyclopropane ring. Each diastereoisomer, on electrocyclic ring opening by a symmetry-allowed $(_{\pi}2_a + _{\sigma}2_s + _{\sigma}2_a)$ process, would give a different triene **11**, as far as the stereochemistry at the exocyclic double bond is concerned, i.e., diastereoisomer **8A** would give the Z-triene **11A** and the diastereoisomer **8B** would afford the E-triene **11B** (Scheme 4).

The trienes **11** were major products from the furan reactions, but they were not detected in the products from the cyclopentadiene reactions; the reason for this is not clear.

The triene **11a**, isolated from the phenyl ester **1a** reaction, was the Z-isomer, as shown by X-ray crystallography,[16] while the triene **11b**, isolated from the methyl ester **1b** reaction, was a mixture of both isomers in the ratio ca. 2:1, but it was not possible to determine whether the major product was the Z- or E-isomer. It is considered that the reasons for this are steric in origin. When R is bulky, i.e. Ph, it is in a less crowded environment in **8A** than in **8B**, where interaction with the cyclopropane CF₃ group is substantial. Furthermore, in **11B**
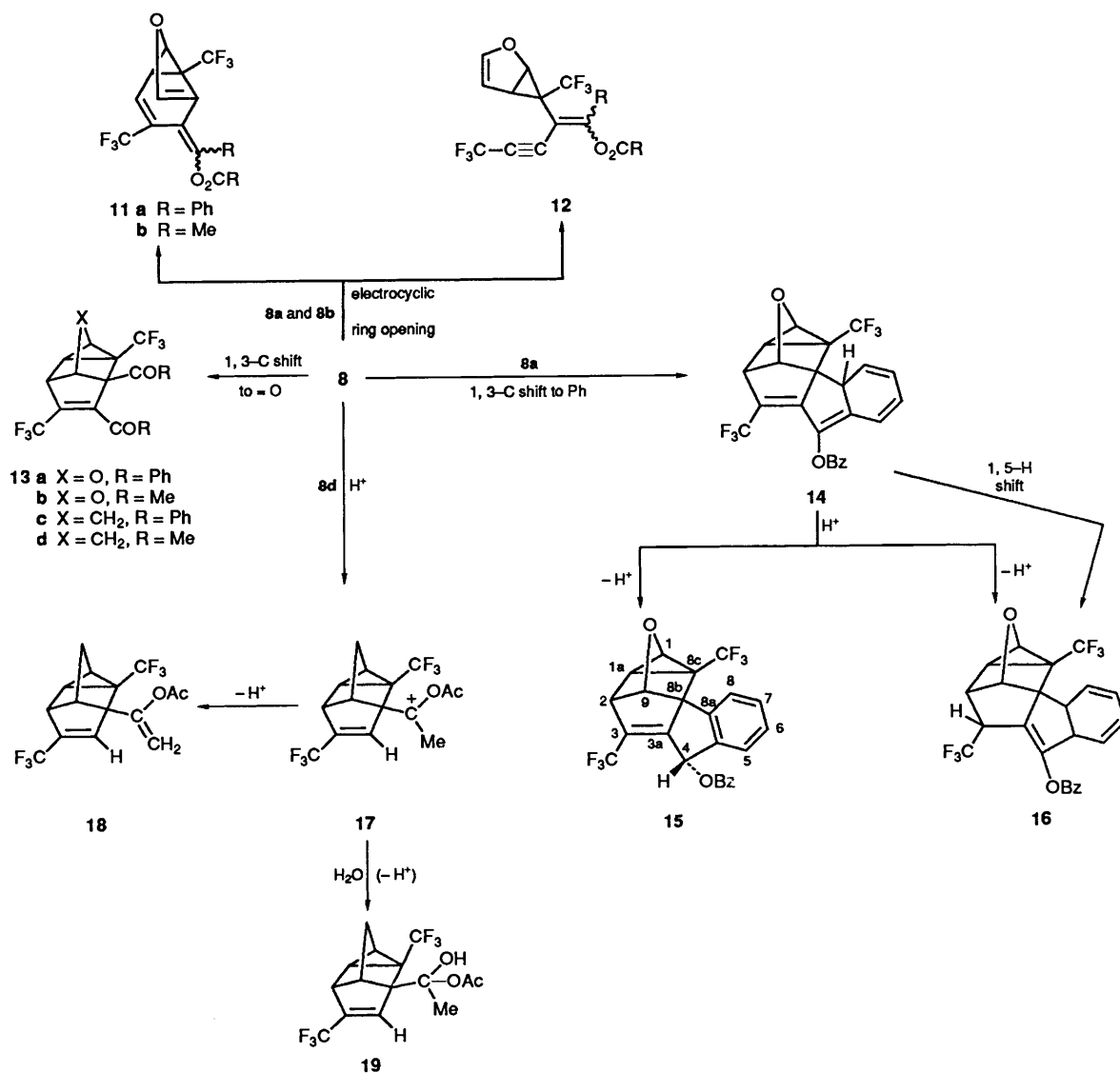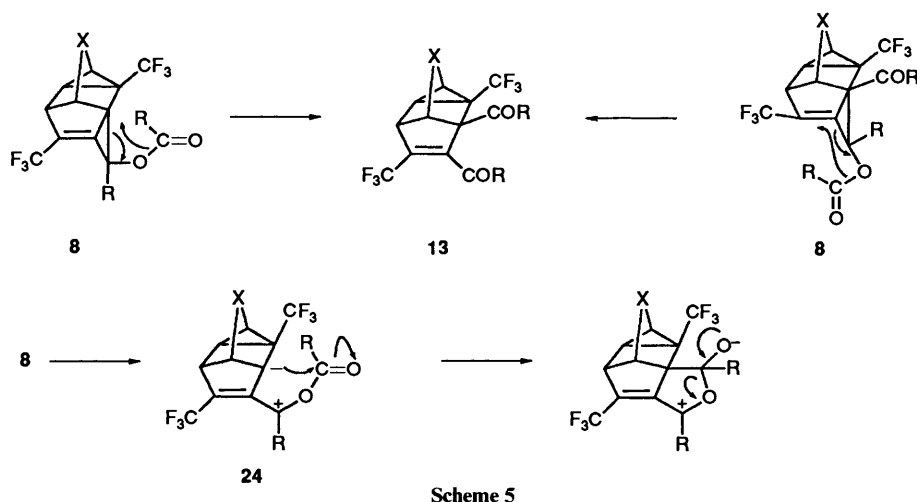
Scheme 3
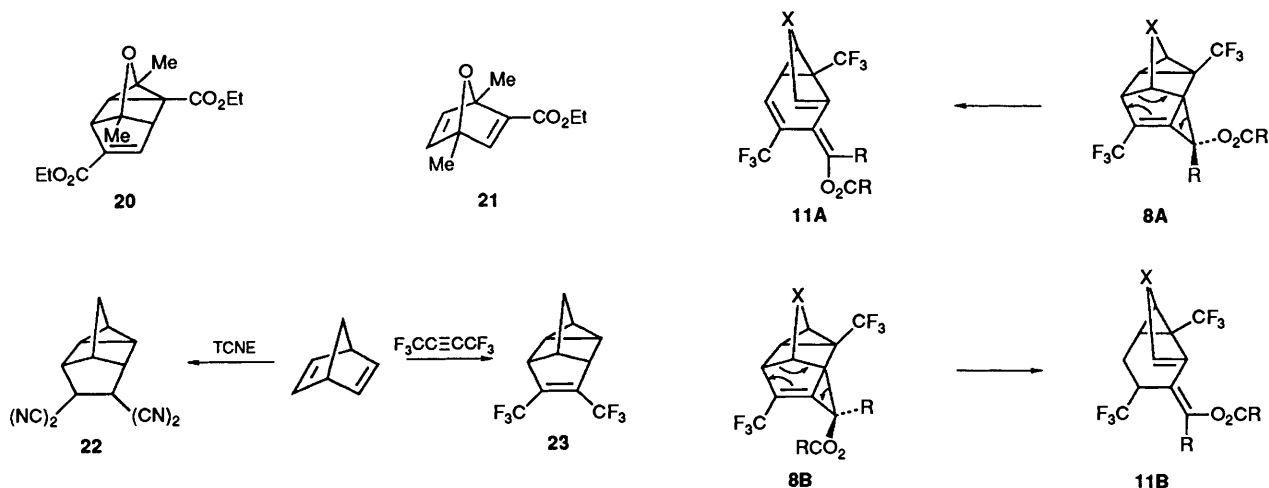
Scheme 4

there are substantial steric interactions between the R group and the vinylic CF$_3$ group, leading to further crowding in the transition state leading to **11B**. The more flexible benzoyloxy group does not suffer from this disadvantage, so both formation of **8A**, where X = O and R = Ph, and its rearrangement to **11A**, are favoured. The steric requirements of a methyl group are much less than those of a phenyl group, and so both diastereoisomers **8A** and **8B** (X = O and R = Me) can be formed and undergo

rearrangement to the triene **11b**, as a mixture of Z- and E-isomers.

Dienynes of type **12** (or products derived from them) arising from the alternative electrocyclic ring opening of intermediates **8a** and **8b** were not detected.

The diketones **13** are formed by rearrangement of the

Scheme 5

intermediates **8** by a formal 1,3-shift involving carbonyl carbon, and could arise from either of the diastereoisomers **8A** or **8B** by the breaking of either of two strained cyclopropane bonds as shown in Scheme 5. An alternative mechanistic pathway is *via* heterolytic fission of a C–C bond to afford the stabilised zwitterions **24** in which the negative charge corresponds to an orbital of high s-character, while the positive charge on a tertiary allylic carbon (which is also benzylic when R = Ph) is also stabilised by resonance involving the adjacent oxygen lone pair.

The remaining products from the reaction of furan with ester **1a**, *i.e.* the dodecenes **15** and **16**, are thought to arise *via* the tetraene **14**, the formation of which could be explained by a 1,3-carbon shift in intermediate **8a** involving an *ortho*-phenyl carbon, which is symmetry forbidden for a thermal process. A typical example of such a rearrangement is the isomerisation of allylcyclopropane to cyclopentene. This has been the subject of numerous investigations and possible alternatives for the rearrangement are a diradical mechanism[17,18] or a symmetry-allowed 1,3-sigmatropic process.[19] Few thermal uncatalysed 1,3-shifts have been reported, although it has been proposed that the conversion of compound **25** into the norbornene **26**,
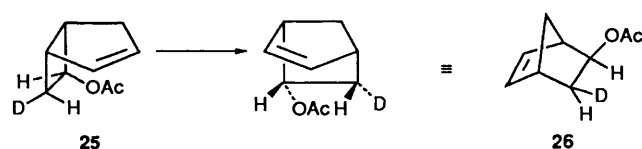

which was shown to occur with inversion of configuration at the migrating centre, involved a concerted, symmetry-allowed suprafacial 1,3-carbon shift.[20]

The rearrangement of strained intermediate **8a** to the hexacycle **14** (Scheme 6) could also occur by a suprafacial 1,3-carbon shift, or *via* the intermediacy of a resonance stabilised diradical **27**, resulting from homolytic C–C bond fission. However, it could also take place *via* heterolytic C–C bond fission to give the stabilised zwitterion **24**, (X = O and R = Ph).

Since suprafacial 1,7-hydrogen shifts are disallowed thermally, it is probable that aromatisation of the rearranged intermediate **14** to the isolated adduct **15** was catalysed by traces of protons available on the walls of the Pyrex reaction vessel. Rearrangement of **14** to adduct **16** could occur by a thermally allowed suprafacial 1,5-hydrogen shift, although it is equally possible that it arises by acid catalysis. The adduct **15**, the structure of which was established by an X-ray crystal-

Scheme 6
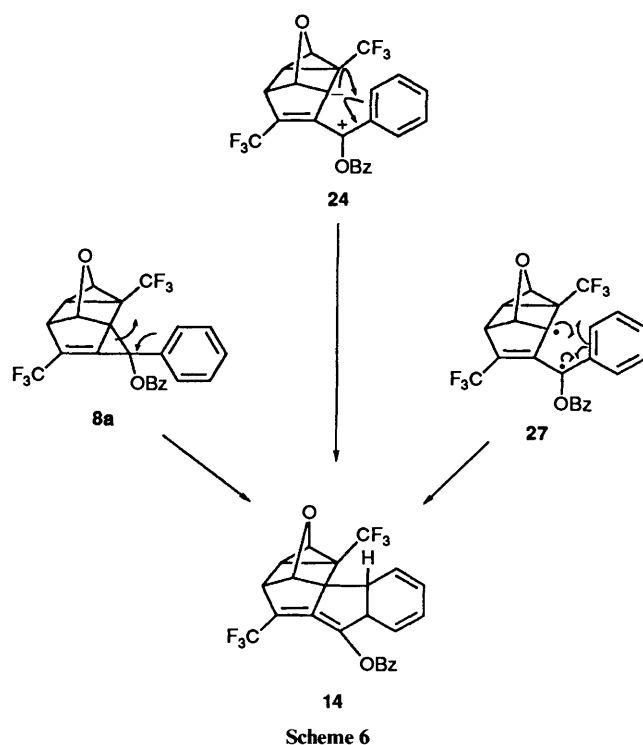
lographic study,[16] is the sterically favoured diastereoisomer with the O_2CPh group on the opposite side of the molecule to the endoxide bridge; the alternative diastereoisomer **28**, arising from protonation of C-10 on the other face was not detected. The stereochemistry of the adduct **16** was not established, but the diastereoisomer **29** would be favoured on steric grounds.
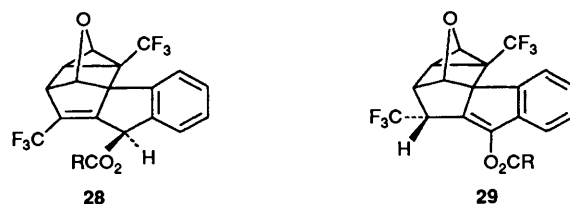
The possibility that the triene **11a** was a precursor to the other rearranged adducts **13a**, **15** and **16** was discounted, because when triene **11a** was heated in dichloromethane under the reaction conditions, the other adducts were not detected. Slow
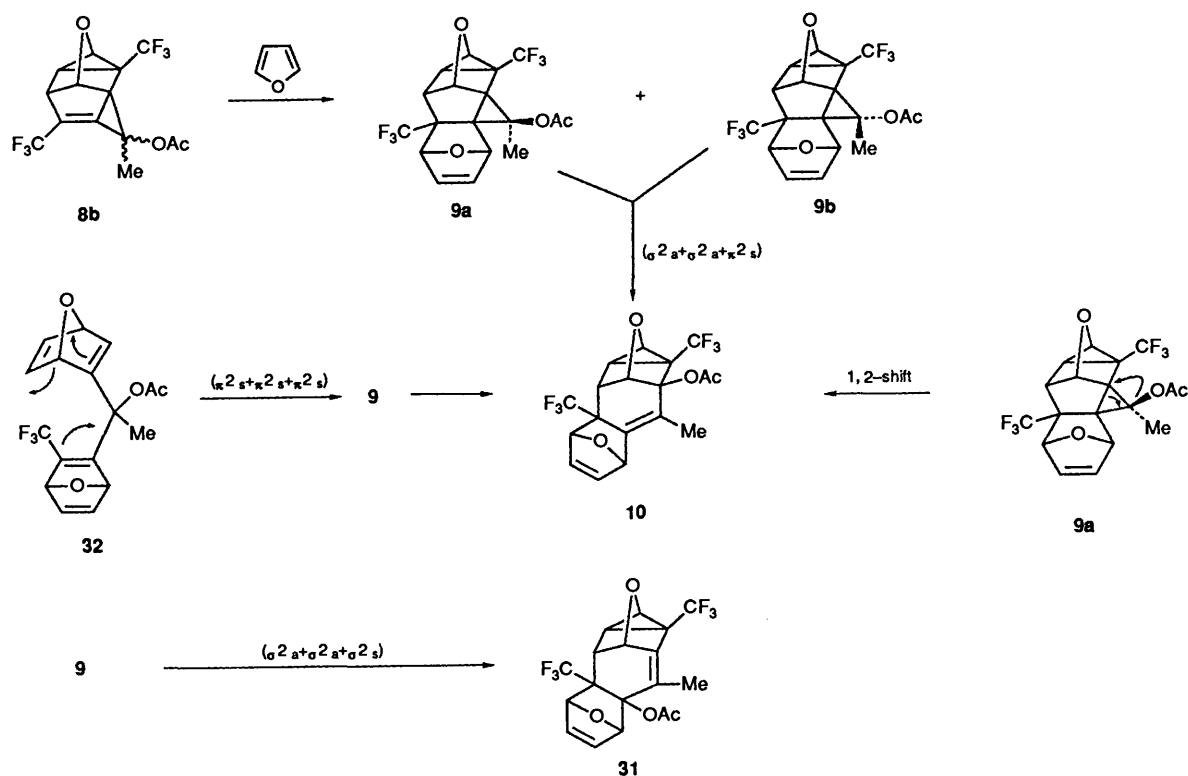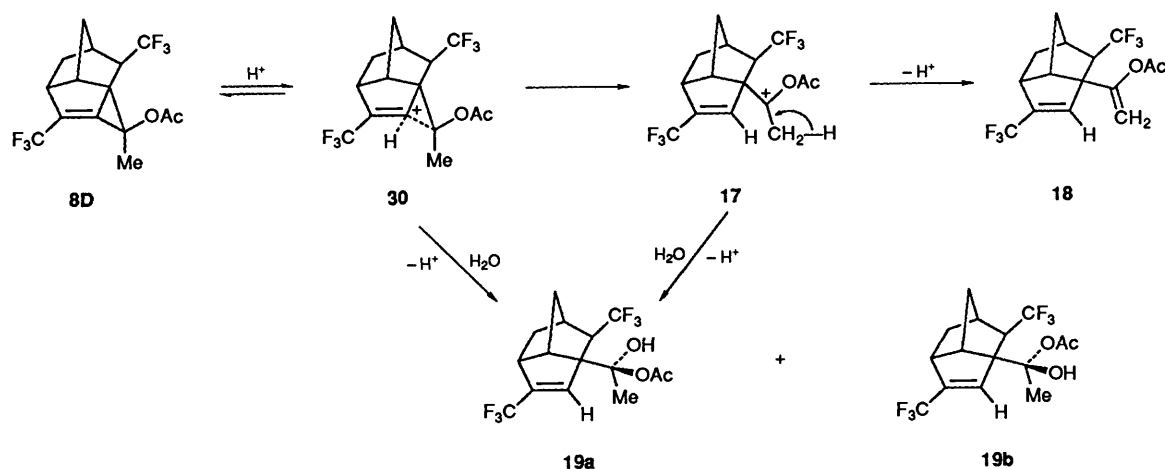
Scheme 7

Scheme 8

decomposition of the triene did occur, and a considerable number of unidentified minor products were formed.

From the reaction of cyclopentadiene with the ester **1b**, a further 1:1 adduct **18**, and its hydration product **19**, were isolated (see Scheme 3). Rearrangement of the intermediate **8d** by a 1,3-hydrogen shift would give the adduct **18**, but suprafacial 1,3-hydrogen shifts are disallowed thermally. A more likely mechanism involves acid catalysis (from traces of protons available on the walls of the tube) to give the intermediate resonance-stabilised carbocation **17**. Three mechanisms have been proposed to account for opening of a cyclopropane ring by proton attack,[21] *i.e.* corner protonation, edge protonation and direct formation of an open-chain carbocation: a corner-protonated cyclopropane is somewhat more stable than an edge-protonated cyclopropane.[22] Loss of a proton from the methyl group in the carbocation **17** would then give the alkene **18**, while the alcohol **19** could be formed from attack by water on the carbocation **17** or on the corner

protonated cyclopropane **30** (Scheme 7). The alcohol **19** was formed as a mixture of two diastereoisomers, which were separated by DCFC; the water required was found to be present in the ester **1b**.

Apart from the Diels–Alder adducts **7**, a further 2:1 adduct **10** was isolated from the reaction of furan with the ester **1b**, and its structure was determined by X-ray crystallography.[16] This was considered to be formed by reaction of the strained intermediate 1:1 adduct **8b** with furan, to afford the 2:1 adduct **9**, which underwent opening of the cyclopropane ring and migration of the O₂CMe group by a ($_\sigma 2_a$ + $_\sigma 2_a$ + $_\pi 2_s$) process involving the carbonyl carbon in both possible diastereoisomers **9a** and **9b**; a symmetry-allowed suprafacial 1,2-O₂CMe shift in the diastereoisomer **9a** would also give compound **10** but this rearrangement is much less likely. The alternative ring opening and shift of the O₂CMe group would have given the isomer **31**, but this was not detected, and models clearly show that the approach of the carbonyl oxygen to the appropriate carbon of

the cyclopropane ring necessary for this rearrangement is much more hindered because of the endoxide system than is the carbonyl carbon approach to the cyclopropane carbon leading to the observed product **10**. The apparent absence of a product analogous to **10** in the corresponding reaction involving the phenyl ester **1a** is probably due to increased steric hindrance to reaction of the intermediate **8a** with furan because of the presence of the bulkier groups, Ph and O_2CPh.

The bis Diels–Alder adduct **32** was not detected in the products and this, coupled with the observation that the bis Diels–Alder adduct **7a** was not a precursor to the other observed products formed in the reaction of the ester **1a** with cyclopentadiene, makes it unlikely that the 2:1 adduct **10b** was formed *via* cyclisation of the Diels–Alder 2:1 adduct **32** (Scheme 8).

The isolated Diels–Alder 1:1 adduct **6d** was a mixture of the two diastereoisomers **6E** and **6F**, and sufficient purification of each isomer was achieved to allow NMR spectral assignments to be made to the separated isomers, which were present in the ratio 52:48. The Diels–Alder 2:1 adducts **7a** and **7b** were mixtures of three diastereoisomers, two *meso* and one ($\pm$) pair, *i.e.* **7C**, **7D** and **7E**, as shown by NMR spectroscopy. Attempts were made to separate the three isomers of the adduct **7a**, but only one, a *meso* isomer **7C** or **7D** ($R = Ph$), was obtained in low yield (4%).

6E   **6F**   **7C**

7D   **7E**
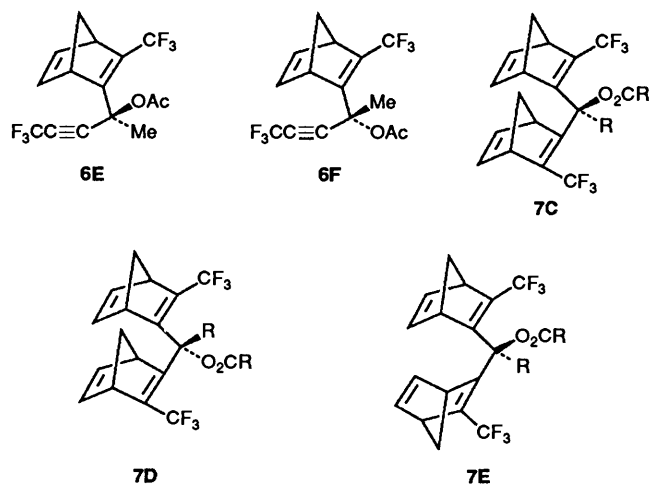
From the reactions carried out at 50 °C, the yields of isolated pure products range from 56.5 to 81.5%, and only the major or significant products could be obtained pure. Apart from the triene **11a**, which was obtained by precipitation from solvent, the other products were separated by DCFC and were present in the complex product mixtures in higher yields than the isolated yields indicated.

Experimental

Furan was a commercial sample and cyclopentadiene was made by cracking dicyclopentadiene at 200 °C. 3,3,3-Trifluoropropyne was prepared in 79% yield from 1,1,2-trichloro-3,3,3-trifluoropropene as reported [23] and its lithium salt **2** was formed by bubbling the alkyne into a stirred solution of butyllithium (1.6 mol dm^{-3} in hexane) in anhydrous diethyl ether kept at −78 °C under a nitrogen atmosphere in a flask fitted with a dropping funnel and a cold finger (−78 °C).

Crude reaction product mixtures were examined by TLC and the individual components were separated by dry column 'flash' chromatography (DCFC) (SiO_2, Merck Kieselgel 60H) and further purification, where necessary, was achieved by recrystallisation, repeated DCFC or preparative-scale TLC

(plates coated with SiO_2, Fluka 60$_{GF}$). Eluents used for chromatography are given in the text; light petroleum refers to b.p. 40–60 °C.

Products were examined by IR (Perkin-Elmer DE783 spectrometer), ^1H NMR [Bruker AC300 instrument operating at 300 MHz with tetramethylsilane (TMS) as external reference], ^{19}F NMR (Perkin-Elmer R32 spectrometer operating at 84.6 MHz with trifluoroacetic acid as external reference) and ^{13}C NMR (Bruker AC300 instrument operating at 75.0 MHz with broad band proton decoupling, D_2O as the deuterium lock signal and TMS as external reference; DEPT 135° spectra were also run on all samples) spectroscopy and mass [Kratos MS 25 or 45 instruments with an electron beam energy of 70 eV using electron impact (EI) or chemical ionisation (CI, NH_3 gas) conditions] spectrometry. NMR samples were run as solutions in $CDCl_3$ and chemical shifts to low field of reference are designated positive. *J*-Values in Hz.

Single crystal X-ray structure determinations were carried out on either a Rigaku AFC65 or CAD4 diffractometer.

B.p.s were determined by distillation and M.p.s are uncorrected.

*Reaction of 3,3,3-Trifluoropropynyllithium **2** with Acid Chlorides.*—(a) *With benzoyl chloride.* A solution of benzoyl chloride (22.50 g, 160.1 mmol) in anhydrous diethyl ether (30 cm^3) cooled to −50 °C was added in one batch to a stirred solution of the salt **2** [prepared from butyllithium (4.80 g, 75.0 mmol) in diethyl ether (200 cm^3) and 3,3,3-trifluoropropyne (7.80 g, 83.0 mmol)] at −78 °C and stirring was continued at this temperature for 1 h and then at *ca.* −55 °C for 1 h. The reaction mixture was allowed to reach room temperature when the diethyl ether was removed (rotary evaporator) and the residue was treated with aqueous sodium hydroxide (2 mol dm^{-3}; 200 cm^3) and stirred for 2 h. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 × 40 cm^3) and the extracts were added to the organic layer which was dried ($CaCl_2$) and the solvent was removed (rotary evaporator) to afford a semi-solid residue (14.51 g). This residue was purified in two portions (DCFC; eluent light petroleum) to afford α,α-*bis*(3,3,3-*trifluoropropynyl*)*benzyl benzoate* **1a** (13.22 g, 33.4 mmol, 59%) (Found: C, 60.9; H, 2.7; F, 28.9. $C_{20}H_{10}F_6O_2$ requires C, 60.6; H, 2.5; F, 28.7%); *m/z* 396 (M$^+$, 1.7%), 291 (M$^+$ − PhCO, 100), 275 (M$^+$ − PhCO$_2$, 82.3) and 105 ($C_7H_5O^+$, 53.6); v_{max}/cm^{-1} 2260 m ($C\equiv C$ str.), 1740s (ester C=O str.), 1250s (C–F str.) and 1150s (C–O str.).

(b) *With acetyl chloride.* A solution of acetyl chloride (10.20 g, 129.9 mmol) in diethyl ether (20 cm^3) cooled to −50 °C was added in one batch to a stirred solution of the salt **2** [prepared from butyllithium (3.97 g, 62.0 mmol) in diethyl ether (200 cm^3) and 3,3,3-trifluoropropyne (6.53 g, 69.5 mmol)] at −78 °C and the temperature was slowly raised to −20 °C and stirring was continued at this temperature for 0.5 h. After warming to room temperature the precipitate of lithium chloride was removed by filtration and washed with diethyl ether (3 × 20 cm^3). The combined filtrate and washings were dried ($MgSO_4$), the majority of the ether was then removed at low pressure and the residue was distilled to give 1,1-*bis*(3,3,3-*trifluoropropynyl*)*ethyl ethanoate* **1b** (14.5 g, 53.3 mmol, 86%) (Found: C, 44.0; H, 2.3; F, 42.0. $C_{10}H_6F_2O_2$ requires C, 44.1, H, 2.2; F, 41.9%); *m/z* 272 (M$^+$, 0.2%), 213 (M$^+$ − CH$_3$CO$_2$, 6.2), 209 (M$^+$ − CH$_3$CO − HF, 10.8) and 43 (CH$_3$CO$^+$, 100); v_{max}/cm^{-1} 2295m (C≡C str.), 1770s (ester C=O str.), 1255s and 1220s (C–F str.) and 1160s (C–O str.).

Reactions of the Benzoate **1a**.—(a) *With furan.* A mixture of the ester **1a** (3.99 g, 10.1 mmol), furan (1.36 g, 20.0 mmol) and dichloromethane (10 cm^3) was heated *in vacuo* in a Rotaflo tube (*ca.* 30 cm^3) at 50 °C for 6 days. The solvent was removed

(rotary evaporator) and the solid residue (4.60 g) was shown by TLC [eluent, light petroleum–dichloromethane (1:1 v/v)] to contain one major (R_f 0.90), three significant (R_f 0.82, 0.79 and 0.61) and a number of minor components. The major product was isolated from a solution of the mixture in the minimum amount of light petroleum–dichloromethane (3:1 v/v) by precipitation with an excess of light petroleum–dichloromethane (4:1 v/v) and then filtration followed by removal of the last traces of solvent *in vacuo*. It was identified by X-ray crystallography as (Z)-5(α-*benzoyloxybenzylidene*)-1,4-*bis*(*trifluoromethyl*)-8-*oxatricyclo*[4.3.0.0$^{2.9}$]*nona*-3,6-*diene* 11a (2.06 g, 4.40 mmol, 44%), colourless crystals, m.p. 122 °C (Found: C, 62.2; H, 3.0; F, 24.8. $C_{24}H_{14}F_6O_3$ requires C, 62.1; H, 3.0; F, 24.6%); *m/z* 464 (M$^+$, 0.2%), 396 (M$^+$ − C_4H_4O, 1.2), 359 (M$^+$ − PhCO, 1.3), 343 (M$^+$ − PhCO$_2$, 1.6), 242 ($C_8F_6O_2{}^+$, 2.2), 165 ($C_{10}H_7F_2{}^+$, 3.9), 105 ($C_7H_5O^+$, 100) and 77 ($C_6H_5{}^+$, 34.6); ν_{max}/cm^{-1} 1730s (ester C=O str.), 1285s and 1260s (C–F str.) and 1175s and 1165s (C–O str.).

The solvent was removed (rotary evaporator) from the filtrate and the remaining three significant components were separated from the resulting solid (2.51 g) by repeated DCFC [eluent; light petroleum–dichloromethane (1:1 v/v)] to give in order of elution: (i) a colourless, slightly impure solid (^{19}F NMR) (0.27 g), which was purified by recrystallisation from pentane and identified by X-ray crystallography as 4-*benzoyloxy*-3,8-*bis*(*trifluoromethyl*)-1,1a,2,8c-*tetrahydro*-4H-1,2,8b-*epoxymethenocyclopropa*[c]*fluorene*15 (0.21 g, 0.45 mmol, 4.5%), colourless crystals, m.p. 160 °C (Found: C, 62.2; H, 2.9; F, 24.6. $C_{24}H_{14}F_6O_3$ requires C, 62.1; H, 3.0; F, 24.6%) [*m/z* 464 (M$^+$, 3.5%), 377 (M$^+$ − C_4H_4O − F, 8.0), 359 (M$^+$ − PhCO, 78.8), 343 (M$^+$ − PhCO$_2$, 4.6) and 105 ($C_7H_5O^+$, 100); ν_{max}/cm^{-1} 1720s (ester C=O str.), 1265s (C–F str.) and 1135s and 1115s (C–O str.)]; (ii) a yellow sticky solid (0.20 g), which was further purified by preparative-scale TLC [eluent, light petroleum–dichloromethane (1:1 v/v)] to afford a colourless sticky solid, identified by NMR spectroscopy as 4-*benzoyloxy*-3,8c-*bis*(*trifluoromethyl*)-1,1a,2,8c-*tetrahydro*-3H-1,2,8b-*epoxymethenocyclopropa*[c]*fluorene* 16 (0.14 g, 0.30 mmol, 3%) (Found: C, 62.4; H, 3.3; F, 24.4. $C_{24}H_{14}F_6O_3$ requires C, 62.1; H, 3.0; F, 24.6%) [*m/z* 464 (M$^+$, 2.5%), 359 (M$^+$ − PhCO, 1.3), 105 ($C_7H_5O^+$, 100) and 77 ($C_6H_5{}^+$, 12.3); ν_{max}/cm^{-1} 1730s (ester C=O str.); 1265 and 1235s (C–F str.) and 1140s (C–O str.)]; and (iii) an impure solid (^{19}F NMR) (0.47 g) which was recrystallised from light petroleum–dichloromethane (4:1 v/v) and identified by NMR spectroscopy as 8,9-*dibenzoyl*-4,7-*bis*(*trifluoromethyl*)-2-*oxatetracyclo*[4.3.0.0.$^{3.5}$0$^{4.9}$]*non*-7-*ene* 13a (0.30 g, 0.65 mmol, 6.5%) colourless crystals, m.p. 130 °C (Found: C, 61.9; H, 3.2; F, 24.9. $C_{24}H_{14}F_6O_3$ requires C, 62.1; H, 3.0; F, 24.6%) [*m/z* 464 (M$^+$, 11.1%), 395 [M$^+$ − CF_3 (or − C_4H_4O − H), 3.2], 377 (M$^+$ − C_4H_4O − F, 4.2), 105 ($C_7H_5O^+$, 100), 77 ($C_6H_5{}^+$, 60.7) and 40 ($C_3H_4{}^+$, 49.2); ν_{max}/cm^{-1} 1670s and 1655s (ketonic C=O str.), 1335s and 1270s (C–F str.) and 1160s and 1140s (C–O str.)].

When a sample of the triene 11a (1.00 g, 2.20 mmol) in dichloromethane (5 cm^3) was heated under the reaction conditions (50 °C, 6 days) the resulting material (0.89 g) after removal of the solvent was shown (^{1}H and ^{19}F NMR) to consist of unchanged 1a and a number of minor components none of which corresponded to 1:1 adducts 13a, 15 or 16.

(b) *With cyclopentadiene.* A mixture of the ester 1a (4.00 g, 10.1 mmol), cyclopentadiene (1.50 g, 22.7 mmol) and dichloromethane (10 cm^3) was heated *in vacuo* in a Rotaflo tube (*ca.* 30 cm^3) at 50 °C for 4 days. The solvent was removed (rotary evaporator) and the yellow solid residue (5.51 g) was shown by TLC [eluent; diethyl ether–light petroleum (1:4 v/v)] to contain two major components (R_f 0.71 and 0.21) and a number of minor components. The two major components were separated by DCFC (same eluent) to give: (i) a mixture of three isomers

[two *meso* and a (±) pair] of the 2:1 adduct, α,α-bis(3-trifluoromethylbicyclo[2.2.1]hepta-2,5-dien-2-yl)benzyl benzoate 7a (3.35 g, 6.30 mmol, 59%), m.p. 115–120 °C (Found: C, 67.8; H, 4.0; F, 21.6. Calc. for $C_{30}H_{22}F_6O_2$: C, 68.2; H, 4.2; F, 21.6%) [*m/z* 528 (M$^+$, 0.9%), 462 (M$^+$ − C_5H_6, 0.9), 407 (M$^+$ − PhCO$_2$, 10.5), 105 ($C_7H_5O^+$, 100), 77 ($C_6H_5{}^+$, 14.4) and 66 ($C_5H_6{}^+$, 10.8); ν_{max}/cm^{-1} 1740s (ester C=O str.), 1320s and 1280s (C–F str.) and 1150s $_{\backslash}$C–O str.)]; and (ii) a colourless solid (1.1 g) which was recrystallised from light petroleum–dichloromethane (4:1 v/v) to afford 8,9-*dibenzoyl*-4,7-*bis*(*trifluoromethyl*)*tetracyclo*[4.3.0.0.$^{3.5}$0$^{4.9}$]*non*-7-*ene* 13c (0.70 g, 1.51 mmol, 15%), m.p. 153 °C (Found: C, 64.6; H, 3.5; F, 24.4. $C_{25}H_{16}F_6O_2$ requires C, 64.9; H, 3.8; F, 24.7%) [*m/z* (CI) 480 (M$^+$ + NH$_4$, 38.0%), 463 (M$^+$ + H, 100), 462 (M$^+$, 32.7), 443, (M$^+$ − F, 51.8), 357 (M$^+$ − PhCO, 11.0), 288 ($C_{17}H_{11}F_3O^+$, 13.5), 122 ($C_7H_6O_2{}^+$, 25.1), 106 ($C_7H_6O^+$, 42.7), 105 ($C_7H_5O^+$, 98.2), 78 ($C_6H_6{}^+$, 25.7) and 77 ($C_6H_5{}^+$, 28.1); ν_{max}/cm^{-1} 1690s and 1655s (ketonic C=O str.) and 1310s and 1275s (C–F str.)].

Attempts to separate the 2:1 adduct isomers by repeated DCFC (same eluent) were only partially successful in that one isomer was obtained pure in low yield and identified as *meso* 7C or 7D (0.20 g, 0.40 mmol, 4%), m.p. 133–135 °C (Found: C, 67.9; H, 4.1; F, 21.4. $C_{30}H_{22}F_6O_2$ requires C, 68.2; H, 4.2; F, 21.6%); *m/z* 528 (M$^+$, 5.8%), 462 (M$^+$ − C_5H_6, 3.6), 407 (M$^+$ − PhCO$_2$, 37.8), 406 (M$^+$ − PhCO$_2$ − H, 15.9), 341 ($C_{18}H_{11}F_6{}^+$, 7.3), 340 ($C_{18}H_{10}F_6{}^+$, 6.5), 337 ($C_{18}H_{10}F_5O^+$, 13.5), 105 ($C_7H_5O^+$, 100) and 77 ($C_6H_5{}^+$, 8.7); ν_{max}/cm^{-1} 1740s (ester C=O str.), 1320s and 1280s (C–F str.) and 1150s (C–O str.).

Thermolysis of the 2:1 Adduct 7a.—A solution of the adduct 7a (0.92 g, 1.70 mmol) in dichloromethane (10 cm^3) when heated *in vacuo* in a Rotaflo tube at 50 °C for 4 days was recovered unchanged. The material, resealed in the tube, was heated at 70 °C for 21 days and the solvent removed to afford a residue (0.87 g) which was shown by ^{1}H and ^{19}F NMR spectroscopy to contain unchanged adduct 7a (*ca.* 75% recovered) and a number of minor products none of which corresponded to the 1:1 adduct 13c.

Reactions of the Ethanoate 1b.—(a) *With furan.* A mixture of the ester 1b (2.94 g, 10.8 mmol), furan (1.48 g, 21.8 mmol) and dichloromethane (10 cm^3), heated *in vacuo* in a Rotaflo tube (*ca.* 30 cm^3) at 50 °C for 6 days and the solvent then removed (rotary evaporator), gave a residue (3.22 g) which was shown by TLC [eluent; light petroleum–dichloromethane (1:1 v/v)] to contain three major components (R_f, 0.53, 0.22 and 0.18) and a number of minor components. The major components were separated by DCFC (same eluent) to afford: (i) a yellow sticky oil identified as a mixture of the two isomers [ratio *ca.* 2:1 (^{19}F NMR)], (*E*)- and (*Z*)-5-(1-*acetoxyethylidene*)-1,4-*bis*(*trifluoromethyl*)-8-*oxatricyclo*[4.3.0.0$^{2.9}$]*nona*-3,6-*diene* 11b (0.74 g, 2.19 mmol, 20%) (Found: C, 49.7; H, 3.0; F, 33.6. $C_{14}H_{10}F_6O_3$ requires C, 49.4; H, 2.9; F, 33.5%) [*m/z* 340 (M$^+$, 0.8%), 285 (M$^+$ − C_3H_3O, 5.1), 281 (M$^+$ − CH_3CO_2, 5.5), 229 (M$^+$ − C_4H_4O − CH_3CO, 16.2), 69 ($CF_3{}^+$, 7.4) and 43 (CH_3CO^+, 100); ν_{max}/cm^{-1} 1770s (ester C=O str.), 1675m (C=C str.), 1320s (C–F str.) and 1180s (C–O str.)]; (ii) a solid (1.25 g), which was further purified by recrystallisation from light petroleum–dichloromethane (4:1 v/v) to give 8,9-*diacetyl*-4,7-*bis*(*trifluoromethyl*)-2-*oxatetracyclo*[4.3.0.0$^{3.5}$0.$^{4.9}$]*non*-7-*ene* 13b (0.97 g, 2.85 mmol, 26.5%), white crystals m.p. 106 °C (Found: C, 49.6; H, 2.9; F, 33.5. $C_{14}H_{10}F_6O_3$ requires C, 49.4; H, 2.9; F, 33.5%) [*m/z* 340 (M$^+$, 3.2%), 325 (M$^+$ − Me, 2.9), 271 (M$^+$ − C_4H_4O − H, 6.1) and 43 (CH_3CO^+, 34.8); ν_{max}/cm^{-1} 1710s (ketonic C=O str.), 1420m and 1405m (C=C str.), 1270s and 1225s (C–F str.) and 1140s (C–O str.)]; and (iii) a solid (0.59 g), which was further purified by preparative-scale TLC [eluent: light petroleum–dichloromethane (3:1 v/v)] to give the

2:1 adduct 4-*acetoxy*-3-*methyl*-5,11-*bis*(*trifluoromethyl*-8,15-*dioxahexacyclo*[10.2.1.0.^{2,11}0.^{4,9}0.^{5,7}0^{6,10}]*pentadeca*-2,13-*diene* **10** (0.44 g, 1.08 mmol, 10%), m.p. 154 °C (Found: C, 53.1; H, 3.6; F, 27.7. $C_{18}H_{14}F_6O_4$ requires C, 52.9; H, 3.4; F, 27.9%) [*m/z* (CI) 426 (M^+ + NH$_4$, 100%), 408 (M^+, 3.3), 365 (M^+ − CH$_3$CO, 3.0), 358 (M^+ + NH$_4$ − C$_4$H$_4$O, 9.3), 208 ($C_8H_5F_3O_3^+$, 21.8), 180 (C$_7$H$_7$F$_3$O$_2^+$, 20.7) and 43 (CH$_3$CO$^+$, 34.8); v_{max}/cm^{-1} 1765s (ester C=O str.), 1420m and 1375m (C=C str.), 1250s and 1220s (C–F str.) and 1160s and 1140s (C–O str.)]—the structure was confirmed by X-ray crystallography.

(b) *With cyclopentadiene at* 50 °C (2:1 *molar ratio*). A mixture of the ester **1b** (5.00 g, 18.4 mmol), cyclopentadiene (2.35 g, 36.4 mmol) and dichloromethane (10 cm^3), heated *in vacuo* in a Rotaflo tube (*ca.* 30 cm^3) at 50 °C for 4 days and the solvent then removed (rotary evaporator), gave a semi-solid residue (7.32 g) which was shown by TLC [eluent: light petroleum–dichloromethane (4:1 v/v)] to contain 4 major (R_f 0.72, 0.66, 0.50 and 0.44) and several minor components. The major components were separated by DCFC (same eluent) to give: (i) a liquid mixture of the three isomers [two *meso* and a (±) pair] of the 2:1 adduct 1,1-*bis*(3-*trifluoromethylbicyclo*[2.2.1]*hepta*-2,5-*dien*-2-*yl*)*ethyl ethanoate* **7b** (4.45 g, 11.0 mmol, 60%) (Found: C, 59.1; H, 4.5; F, 28.2. $C_{20}H_{18}F_6O_2$ requires C, 59.4; H, 4.5; F, 28.2%) [*m/z* 404 (M^+, 26.1%), 361 (M^+ − CH$_3$CO, 14.3), 345, (M^+ − CH$_3$CO$_2$, 100) and 344 (M^+ − CH$_3$CO$_2$ − H, 14.2), 66 (C$_5$H$_6^+$, 22.1) and 43 (CH$_3$CO$^+$, 61.6); v_{max}/cm^{-1} 1745s (ester C=O str.), 1650m (C=C str.), 1300s and 1260s (C–F str.) and 1140s (C–O str.)]; (ii) the 1:1 adduct 1-*acetoxy*-1-[4,7-*bis*(*trifluoromethyl*)*tetracyclo*[4.3.0.0.^{3,5}0^{4,9}]*non*-7-*en*-9-*yl*]-*ethene* **18** (0.75 g, 2.21 mmol, 12%), m.p. 84 °C (Found: C, 53.6; H, 3.9; F, 33.4. $C_{15}H_{12}F_6O_2$ requires C, 53.3; H, 3.6; F, 33.7%) [*m/z* 338 (M^+, 31.6%), 278 (M^+ − CH$_3$CO$_2$H, 19.0), 209 ($C_{12}H_8F_3^+$, 100) and 43 (CH$_3$CO$^+$, 49.4); v_{max}/cm^{-1} 1750s (ester C=O str.), 1660m (C=C str.), 1310s and 1285s (C–F str.) and 1130s and 1110s (C–O str.)]; (iii) 1-*acetoxy*-1-[4,7-*bis*(*trifluoromethyl*)*tetracyclo*[4.3.0.0.^{3,5}0^{4,9}]*non*-7-*en*-9-*yl*]*ethanol* (*diastereoisomer* 1) **19** (0.17 g, 0.48 mmol, 2.5%), m.p. 102 °C (Found: C, 50.7; H, 4.1; F, 31.8. $C_{15}H_{14}F_6O_2$ requires C, 50.6; H, 3.9; F, 32.0%) [*m/z*, 356 (M^+, 4.1%), 297 (M^+ − CH$_3$CO$_2$, 23.2), 296 (M^+ − CH$_3$CO$_2$ − H, 25.7), 277 (C$_{13}$H$_{10}$F$_5$O$^+$, 20.2), 228 (C$_{12}$H$_8$F$_4^+$, 26.7), 163 (C$_7$H$_3$F$_4^+$, 95.9) and 43 (CH$_3$CO$^+$, 100); v_{max}/cm^{-1} 3420br (O–H str.), 1730s (ester C=O str.), 1310s and 1280s (C–F str.) and 1140s and 1110s (C–O str.)]; and (iv) the second *diastereoisomer of* **19** (0.18 g. 0.50 mmol, 3%), m.p. 129 °C (Found: C, 50.3; H, 3.9; F, 32.1. $C_{15}H_{14}F_6O_2$ requires C, 50.6; H, 3.9; F, 32.0%) [*m/z* 356 (M^+, 2.8%), 297 (M^+ − CH$_3$CO$_2$, 25.4), 163 (C$_7$H$_3$F$_4^+$, 38.0) and 43 (CH$_3$CO$^+$, 100); v_{max}/cm^{-1} 3430br (O–H str.), 1705s (ester C=O str.), 1310s and 1290s (C–F str.) and 1190s and 1140s (C–O str.)].

In the ^{19}F NMR spectrum of the crude reaction mixture bands were present at δ_F 20.1 and 20.75 with the latter band of comparable intensity to that due to compound **19** (diastereoisomer 1) at δ_F 20.8. These bands are identical with those present in the spectrum of the diketone **13d** and a weak spot (R_f 0.42) observed on TLC examination of the mixture supports this assignment (see later).

(c) *With cyclopentadiene at* 50 °C (1:1 *molar ratio*). The preceding experiment was repeated using the ester **1b** (2.50 g, 9.19 mmol), cyclopentadiene (0.61 g, 9.20 mmol) and dichloromethane (4 cm^3) and heating at 50 °C for 5 days. Work-up gave a high-boiling residue (3.02 g) which was shown by TLC (eluent as before) to contain five major components (R_f 0.80, 0.72, 0.66, 0.50 and 0.44) and several minor components (including one with R_f 0.42). Separation of the major components by DCFC (same eluent) gave: (i) a mixture of two diastereoisomers (ratio 52:48; ^{1}H NMR) of the Diels–Alder 1:1 adduct 1-(3-*trifluoromethylbicyclo*[2.2.1]*hepta*-2,5-*dien*-2-*yl*)-1-(3,3,3-*trifluoropro*-

pynyl)*ethyl ethanoate* **6d** (0.71 g, 2.10 mmol, 23%) (Found: C, 53.6; H, 3.9; F, 33.6. $C_{15}H_{12}F_6O_2$ requires C, 53.3; H, 3.6; F, 33.7%) [*m/z* 338 (M^+, 13.2%), 319 (M^+ − F, 10.0), 295 (M^+ − CH$_3$CO, 22.4), 279 (M^+ − CH$_3$CO$_2$, 96.0), 278 (M^+ − CH$_3$CO$_2$ − H, 25.7), 259 (C$_{13}$H$_8$F$_5^+$, 66.1), 66 (C$_5$H$_6^+$, 29.6), 51 (C$_4$H$_3^+$, 74.5) and 43 (CH$_3$CO$^+$, 100); v_{max}/cm^{-1} 2280s (C≡C str.), 1760s (ester C=O str.), 1285s (C–F str.) and 1150s (C–O str.)]; (ii) 2:1 adduct **7b** (0.51 g, 1.30 mmol, 14%); (iii) the 1:1 disubstituted ethene **18** (0.33 g, 1.0 mmol, 11%); (iv) alcohol **19** (diastereoisomer 1) (0.25 g, 0.70 mmol, 8%); (v) a mixture of both diastereoisomers of alcohol **19** (0.64 g, 1.79 mmol, 19.5%); and (vi) alcohol **19** (diastereoisomer 2) (0.18 g, 0.51 mmol, 6%).

The diastereoisomers of 1:1 adduct **6d** were not separated pure by repeated DCFC (same eluent), but sufficient enhancement of purity was achieved to allow individual NMR assignments to be made.

The formation of considerable amounts of alcohol **19** in this experiment was found to be due to water present in the reactant ester **1b**. For subsequent experiments it was dried by treatment of an ethereal solution with P_2O_5.

(d) *With cyclopentadiene at* 20 °C (1:1 *molar ratio*). The reaction was repeated using a mixture of anhydrous ester **1b** (7.50 g, 27.6 mmol) and cyclopentadiene (1.82 g, 27.6 mmol) in dichloromethane (40 cm^3) at room temperature for 12 days. Work-up gave a residue (8.90 g) which was purified by DCFC [eluent, light petroleum–dichloromethane (4:1 v/v)] to give a mixture (ratio 52:48) of the two diastereoisomers of 1:1 adduct **6d** (8.16 g, 24.1 mmol, 88%).

Thermolysis of the 1:1 *Adduct* **6d**.—The adduct **6d** (1.40 g, 4.14 mmol) in dichloromethane (8 cm^3) was heated *in vacuo* in a Rotaflo tube (*ca.* 30 cm^3) at 50 °C for 7 days and the solvent removed (rotary evaporator) to give a yellow solid (1.38 g) which was shown by TLC [eluent, light petroleum–dichloromethane (4:1 v/v)] to contain unchanged ester **6d** (R_f 0.80), two major components (R_f 0.66 and 0.42) and a number of minor components. Separation of the mixture by DCFC (same eluent) gave: (i) unchanged ester **1b** (0.43 g, 1.3 mmol, 31% recovered); (ii) the 1:1 disubstituted ethene **18** (0.43 g, 1.28 mmol, 45%); and (iii) 8,9-*diacetyl*-4,7-*bis*(*trifluoromethyl*)-*tetracyclo*[4.3.0.0.^{3,5}0^{4,9}]*non*-7-*ene* **13d** (0.20 g, 0.60 mmol, 21%) (Found: C, 53.0; H, 3.6; F, 33.4; $C_{15}H_{12}F_6O_2$ requires C, 53.3; H, 3.6; F, 33.7%) [*m/z* 338 (M^+, 4.7%), 323 (M^+ − CH$_3$, 4.5), 295 (M^+ − CH$_3$CO, 0.7), 252 (M^+ − 2 × CH$_3$CO, 1.3), 207 (C$_{12}$H$_9$F$_2$O$^+$, 10.6) and 43 (CH$_3$CO$^+$, 100); v_{max}/cm^{-1} 1710br and 1680br (ketone C=O str.) and 1320s and 1265s (C–F str.)].

NMR Spectral Data.—**1a**. δ_H 8.05 (d, 2 H, 2 *o*-C$_6$H$_5$CO$_2$, *J* 8), 7.84 (m, 2 H, 2 *o*-C$_6$H$_5$) and 7.62–7.30 (m, 6 H, *m*- and *p*-C$_6$H$_5$CO$_2$ and C$_6$H$_5$); δ_F +28.7 (CF$_3$C≡C); δ_C 163.0 (s, O–C=O), 134.9 (s, *ipso*-C$_6$H$_5$CO$_2$), 133.8 (s, *ipso*-C$_6$H$_5$), 133.2, 129.7, 129.0, 128.3, 128.2 and 126.0 (6 s, *o*-, *m*- and *p*-C$_6$H$_5$CO$_2$ and C$_6$H$_5$), 114.0 (q, CF$_3$, ^1J 256), 81.2 (q, CF$_3$C≡*C*, ^3J 6), 74.8 (q, CF$_3$*C*≡C, ^2J 54) and 67.0 (s, –*C*≤).

1b. δ_H 2.60 (s, CH$_3$CO$_2$) and 2.48 (s, CH$_3$); δ_F +25.1 (CF$_3$C≡C); δ_C 167.5 (s, O–C=O), 113.9 (q, CF$_3$, ^1J 258), 81.8 (q, CF$_3$C≡*C*, ^3J 7), 72.0 (q, CF$_3$*C*≡C, ^2J 56), 61.0 (s, –*C*≤), 28.1 (s, *C*H$_3$CO$_2$) and 19.7 (s, CH$_3$).

6d. (Major diastereoisomer). δ_H 6.95–7.85 (m, 2 H, CH=CH), 3.95 and 3.84 (2 s, 2 H, 2 HC≤), 2.32 and 1.97 (AB, 2 H, CH$_A$H$_B$, J_{AB} 11), 2.09 (s, 3 H, CH$_3$CO$_2$) and 1.68 (s, 3 H, CH$_3$); δ_F + 27.5 (s, 3 F, CF$_3$C≡C) and 20.1 (s, 3 F$_3$C=C); δ_C 168.2 (s, O–C=O), 159.2 (q, CF$_3$*C*=*C*, ^3J 5), 142.7 and 141.7 (2 s, CH=CH), 137.0 (q, CF$_3$*C*=C, ^2J 35), 123.3 (q, CF$_3$C=*C*, ^1J 268), 114.0 (q, CF$_3$C≡*C*, ^1J 258), 85.3 (q, CF$_3$C≡*C*, ^3J 7), 72.9 (q, CF$_3$*C*≡C, ^2J 53), 72.1 (s, CH$_2$), 70.9 (s, –*C*≤), 55.5 and 52.2 (2 s, 2 HC≤), 25.8 (s, *C*H$_3$CO$_2$) and 20.4 (s, CH$_3$).

6d. (Minor diastereoisomer). δ_H 6.95–6.85 (m, 2 H, CH=CH),

3.86 and 3.73 (2 s, 2 H, 2HC$\leqslant$), 2.13 and 1.95 (AB, 2 H, CH$_A$H$_B$, J_{AB} 11), 2.04 (s, 3 H, CH$_3$CO$_2$) and 1.73 (s, 3 H, CH$_3$); δ_F +27.4 (s, 3 F, CF$_3$C≡C) and +20.0 (s, 3 F, CF$_3$C≡C); δ_C 168.1 (s, O–C=O), 159.2 (q, CF$_3$C=C, ^3J 5), 142.1 and 141.7 (2 s, CH=CH), 136.8 (q, CF$_3$C=C, ^2J 35), 123.3 (q, CF$_3$C=C, ^1J 268), 114.0 (q, CF$_3$C≡C, ^1J 258), 84.8 (q, CF$_3$C≡C, ^3J 7), 72.6 (q, CF$_3$C≡C, ^2J 53), 72.3 (s, CH$_2$), 70.6 (s, –C$\leqslant$), 54.9 and 52.2 (2 s, 2HC$\leqslant$), 26.2 (s, CH$_3$CO$_2$) and 20.3 (s, CH$_3$).

7a [(Z)-isomer]. δ_H 8.22 (d, 2 H, 2 o-C$_6$H$_5$CO$_2$, J 7), 8.10–7.25 (m, 8 H, m- and p-C$_6$H$_5$CO$_2$ and o-, m- and p-C$_6$H$_5$), 6.55 (s, 1 H, O–CH=), 6.31 (d, 1 H, HC=, $J_{2,3}$ 5.3), 5.02 (d, 1 H, >CH–O, $J_{2,9}$ 5.5) and 1.72 (dd, 1 H, HC$\leqslant$, $J_{9,2}$ 5.5, $J_{3,2}$ 5.3); δ_F +17.0 (s, 3 F, CF$_3$C=C) and 10.9 (s, 3 F, CF$_3$C$\leqslant$); δ_C 164.1 (s, O–C=O), 156.2 (s, =CH–O), 145.7 (s, =C–O), 139.3 (q, CF$_3$C=C, ^2J 32), 135.0 (s, ipso-C$_6$H$_5$CO$_2$), 131.4 (q, CF$_3$C=CH, ^3J 7), 133.7, 129.9, 129.3, 128.3, 128.1 and 128.0 (6 s, o-, m- and p-C$_6$H$_5$ and C$_6$H$_5$CO$_2$), 128.7 (s, ipso-C$_6$H$_5$), 123.2 (q, CF$_3$, ^1J 273), 123.1 (q, CF$_3$, ^1J 272), 116.2 (br, C-6), 111.0 (s, C-5), 75.1 (br, >CH–O), 34.6 (q, CF$_3$C$\leqslant$, ^2J 40) and 20.1 (br, –CH<).

7b. (Major isomer E or Z). δ_H 6.36 (s, 1 H, =CH–O), 6.23 (br, 1 H, =CH), 4.95 (d, 1 H, >CH–O, $J_{2,9}$ 5.3), 2.12 (s, 3 H, CH$_3$CO$_2$), 2.10 (s, 3 H, =CCH$_3$) and 1.65 (t, 1 H, HC$\leqslant$, $J_{9,2}$ ≃ $J_{3,2}$ 5.3); δ_F +18.1 (s, 3 F, CF$_3$C=C) and +10.2 (s, 3 F, CF$_3$C−); δ_C 168.3 (s, O–C=O), 155.5 (s, =CH–O), 145.7 (s, =C–O) 130.0 (q, CF$_3$C=CH, ^3J 7), 128.0 (q, CF$_3$C=C, ^2J 32), 123.3 and 123.2 (2 q, 2 CF$_3$, ^1J272), 115.6 (br, C-6), 109.2 (s, C-5, 74.8 (br, >CH–O), 34.0 (q, CF$_3$C$\leqslant$, ^2J 41), 20.6 (s, CH$_3$CO$_2$), 20.0 (q, –CH<, ^3J 2) and 19.8 (s, CH$_3$).

7b. (Minor isomer Z or E). δ_H 6.50 (s, 1 H, =CH–O), 6.13 (br, 1 H, =CH), 5.01 (d, 1 H, >CH–O, $J_{2,9}$ 5.3), 2.22 (s, 3 H, CH$_3$CO$_2$), 2.15 (s, 3 H, =CCH$_3$) and 1.65 (t, 1 H, HC$\leqslant$, $J_{9,2}$ ≃ $J_{3,2}$ 5.3); δ_F +16.0 (s, 3 F, CF$_3$C=C) and +10.5 (s, 3 F, CF$_3$C$\leqslant$); δ_C 168.6 (s, O–C=O), 154.7 (s, =CH–O), 146.5 (s, =C–O), 137.5 (q, CF$_3$C=C, ^2J 32), 130.8 (q, CF$_3$C=CH, ^3J 7), 123.4 and 123.2 (2 q, 2 CF$_3$, ^1J 272), 116.2 (br, C-6), 112.0 (s, C-5), 74.8 (br, >CH–O), 34.2 (q, CF$_3$C−, ^2J 40), 20.6 (s, CH$_3$CO$_2$), 20.4 (q, –CH<, ^3J 2) and 19.7 (s, CH$_3$).

8a. δ_H 7.90 (d, 2 H, 2 o-C$_6$H$_5$CO, J 7.3), 7.78 (d, 2 H, 2 o-C$_6$H$_5$CO, J 7.3), 7.70–7.28 (m, 6 H, m- and p-C$_6$H$_5$CO), 5.27 (d, 1 H, 3-H, $J_{5,3}$ 4.0), 4.95 (br, 1 H, 1-H), 3.42 (br, 1 H, 6-H) and 2.75 (d, 1 H, 5-H, $J_{3,5}$ 4.0); δ_F +20.1 (s, 3 F, CF$_3$C=C) and +18.1 (s, 3 F, CF$_3$C−); δ_C 193.9 (s, =C–C=O), 190.2 (s, ≥C–C=O), 145.9 (q, CF$_3$C=C, ^3J 4), 136.7 and 136.4 (2 s, 2 ipso-C$_6$H$_5$), 133.7, 132.8, 129.2, 128.4, 128.3 and 128.2 (6 s, o-, m- and p-C$_6$H$_5$), 133.2 (q, CF$_3$C=C, ^2J 36), 124.3 (q, CF$_3$, ^1J 272), 121.0 (q, CF$_3$, ^1J 271), 92.7 (br, C-1), 74.7 (s, C-9), 68.6 (q, C-3, ^3J 2), 49.1 (br, C-6), 42.4 (q, CF$_3$C$\leqslant$, ^2J 37) and 33.4 (br, C-5).

13b. δ_H 5.08 (dd, 1 H, 1-H, $J_{6,1}$ 4, $J_{3,1}$ 1), 4.46 (br, 1 H, 3-H), 3.18 (br, 1 H, 6-H), 2.65 (dd, 1 H, 5-H, $J_{3,5}$ 4, $J_{6,5}$ 1), 2.40 (s, 3 H, =CCOCH$_3$) and 2.18 (s, 3 H, ≥COCH$_3$); δ_F +19.0 (s, 3 F, CF$_3$C=C) and +17.8 (s, 3 F, CF$_3$C$\leqslant$); δ_C 201.7 (s, =C–C=O), 198.0 (s, −C–C=O), 148.4 (q, CF$_3$C=C, ^3J 4), 131.4 (q, CF$_3$C=C, ^2J 36), 125.1 (q, CF$_3$C=C, ^1J 271), 121.8 (q, CF$_3$C$\leqslant$, ^1J 270), 93.7 (s, C-1), 74.1 (s, C-9), 68.1 (q, C-3, ^3J 2), 49.1 (q, C-6, ^3J 2), 42.5 (q, CF$_3$C−, ^2J 38), 33.6 and 31.0 (2 s, 2 CH$_3$CO) and 27.6 (q, C-5, ^3J 2).

13c. δ_H 7.75 (m, 4 H, 4 o-C$_6$H$_5$CO), 7.57–7.15 (m, 6 H, 6m- and p-C$_6$H$_5$CO), 3.45 (br, 1 H, 1-H), 3.16 (d, 1 H, 3-H, $J_{5,3}$ 1), 2.68 (dd, 1 H, 6-H, $J_{5,6}$ 3.5, $J_{1,6}$ 1), 2.30 (dd, 1 H, 5-H, $J_{6,5}$ 3.5, $J_{3,5}$ 1) and 1.97 and 1.82 (AB, 2 H, CH$_A$H$_B$, $J_{A,B}$ 12); δ_F +19.4 and +19.2 (2 s, 2 CF$_3$); δ_C 194.2 (s, =C–C=O), 190.0 (s, ≥C–C=O), 147.9 (q, CF$_3$C=C, ^3J 4), 138.6 (q, CF$_3$C=C, ^2J 35), 136.9 and 136.5 (2 s. 2 ipso-C$_6$H$_5$), 133.4, 132.5, 129.9, 128.9, 128.3 and 128.1 (6 s, o-, m- and p-C$_6$H$_5$), 125.7 (q, CF$_3$C=C, ^1J 272), 121.4 (q, CF$_3$C−, ^1J 271), 74.5 (s, C-9), 62.6 (s, C-1), 51.0 (br, C-6), 41.0 (q, CF$_3$C−, ^2J 36), 33.0 (q, C-5, ^3J 2), 31.4 (br, C-3) and 30.4 (s. CH$_2$).

13d. δ_H 3.22 (br, 1 H, 1-H), 2.62 (d, 1 H, 3-H, $J_{5,3}$ 1.5), 261 (br,

6-H), 2.44 (s, 3 H, =CCOCH$_3$), 2.28 (dd, 1 H, 5-H, $J_{6,5}$ 5, $J_{3,5}$ 1.5), 2.15 (s, 3 H, ≥CCOCH$_3$) and 1.89 and 1.80 (AB, 2 H, CH$_A$H$_B$, $J_{A,B}$ 12); δ_F +20.75 and +20.1 (2 s, 2 CF$_3$); δ_C 201.8 (s, =C–C=O), 195.9 (s, ≥C–C=O), 150.3 (q, CF$_3$C=C, ^3J 4), 135.3 (q, CF$_3$C=C, ^2J 35), 125.7 (q, CF$_3$C=C, ^1J 271), 121.3 (q, CF$_3$C$\leqslant$, ^1J 271), 75.7 (s, C-9), 62.5 (s, C-1), 50.3 (br, C-6), 38.9 (q, CF$_3$C$\leqslant$, ^2J 37), 31.8 (br, C-3), 32.7 and 28.2 (2 s, 2 CH$_3$CO) and 29.8 (q, C-5, ^3J 3).

15. δ_H 8.10 (m, 2 H, 2 o-C$_6$H$_5$CO$_2$), 7.88–7.20 (m, 7 H, m- and p-C$_6$H$_5$CO$_2$ and C$_6$H$_4$), 7.14 (s, 1 H, >CH–O), 5.15 (dd, 1 H, $J_{1a,1}$ 4, $J_{9,1}$ 2), 4.38 (br, 1 H, 9-H), 3.23 (br, 1 H, 2-H) and 2.67 (dd, 1 H, 1a-H, $J_{1,1a}$ 4, $J_{2,1a}$ 2); δ_F +18.8 (s, 3 F, CF$_3$C=C) and +15.7 (s, 3 F, CF$_3$C$\leqslant$); δ_C 166.0 (s, O–C=O), 151.9 (q, CF$_3$C=C, ^3J 5), 143.6 (s, ipso-C$_6$H$_5$CO$_2$), 136.1 and 129.5 (2 s, 2 ipso-C$_6$H$_4$), 133.2, 130.4, 129.8, 129.6, 128.4, 127.6 and 125.0 (7 s, 7 aromatic =CH), 128.4 (q, CF$_3$C=C, ^2J 37), 124.9 (q, CF$_3$C=C, ^1J 271), 121.6 (q, CF$_3$C$\leqslant$, ^1J 269), 96.0 (s, C-4), 68.8 (s, C-9), 68.1 (s, C-8b), 65.9 (br, C-1), 51.0 (br, C-2), 41.1 (q, CF$_3$C$\leqslant$, ^2J 35) and 31.3 (br, C-1a).

16. δ_H 8.08 (m, 2 H, 2 o-C$_6$H$_5$CO$_2$), 7.85–7.13 (m, 7 H, m- and p-C$_6$H$_5$CO$_2$ and C$_6$H$_4$), 4.82 (dd, 1 H, 1-H, $J_{1a,1}$ 4, $J_{9,1}$ 2), 4.14 (br, 1 H, 9-H), 3.77 (qd, 1 H, CF$_3$CH<, $J_{F,3}$ 5, $J_{2,3}$ 4), 2.79 (br, 1 H, 2-H) and 2.30 (dd, 1 H, 1a-H, $J_{1,1a}$ 4, $J_{2,1a}$ 2); δ_F +17.0 (s, 3 F, CF$_3$C$\leqslant$) and +13.5 (d, CF$_3$CH<, $J_{H,F}$ 5); δ_C 163.5 (s, O–C=O), 146.8 (s, ipso-C$_6$H$_5$CO$_2$), 146.2 (q, C-3a, ^3J 5), 145.2 (s, =C–O, C-4), 137.1 and 129.1 (2 s, 2 ipso-C$_6$H$_4$), 129.9, 129.3, 129.2, 128.7, 128.6, 128.5 and 128.2 (7 s, 7 aromatic =CH), 124.8 (q, CF$_3$, ^1J 271), 121.6 (q, CF$_3$, ^1J 270), 82.6 (s, C-9), 64.7 (s, C-8b), 60.3 (br, C-1), 48.7 (br, C-2), 42.4 (q, CF$_3$CH<, ^2J 36), 40.5 (q, CF$_3$C$\leqslant$, ^2J 37) and 20.2 (br, C-1a).

18. δ_H 6.65 (s, 1 H, =CH) 5.35 and 5.24 (2 s, 2 H, =CH$_2$), 3.03 (br, 1 H, 6-H), 2.58 (br, 1 H, 1-H), 2.16 (s, 3 H, CH$_3$CO$_2$) and 2.20–1.70 (m, 4 H, CH$_2$, 3-H, 5-H); δ_F +17.5 (s, 3 F, CF$_3$C=C) and +10.1 (s, 3 F, CF$_3$C$\leqslant$); δ_C 168.6 (s, O–C=O), 138.5 (s, O–C=), 130.4 (q, CF$_3$C≡C, ^3J 6), 129.8 (q, CF$_3$C=C, ^2J 38), 125.6 (q, CF$_3$C=C, ^1J 264), 123.5 (q, CF$_3$C$\leqslant$, ^1J 264), 117.3 (s, =CH$_2$), 88.5 (s, C-9), 42.7 (br, C-6), 40.8 (br, C-1), 33.4 (q, CF$_3$C$\leqslant$, ^2J 38), 31.1 (s, CH$_2$), 28.0 (s, C-5) and 22.4 (q, C-3, ^3J 2).

7a. (Separated meso-isomer). δ_H 80.4 (d, 2 H, 2 o-C$_6$H$_5$CO$_2$, J 7), 7.63–7.10 (m, 8 H, m- and p-C$_6$H$_5$CO$_2$ and o-, m- and p-C$_6$H$_5$), 6.75 (d, 2 H, 2 =CH, J 6.5), 6.32 (d, 2 H, 2 =CH, J 6.5), 3.78 (br, 2 H, 2 HC$\leqslant$), 3.74 (br, 2 H, 2 HC$\leqslant$) and 2.46 and 1.95 (2 AB, 4 H, 2 CH$_A$H$_B$, $J_{A,B}$ 10); δ_F +19.2 (s, 2 CF$_3$C=C); δ_C 165.6 (s, O–C=O), 160.2 (q, CF$_3$C=C, ^3J 5), 141.7 and 141.5 (2 s, CH=CH), 137.3 (s, ipso-C$_6$H$_5$CO$_2$), 135.9 (q, CF$_3$C=C, ^2J 35), 132.9, 129.6, 128.3, 128.0, 127.8 and 127.1 (6 s, 6 aromatic =CH), 130.7 (s, ipso-C$_6$H$_5$), 123.3 (q, CF$_3$C=C, ^1J 269), 84.4 (s, –C$\leqslant$), 69.7 (s, CH$_2$), 56.8 (s, HC$\leqslant$) and 52.3 (q, HC$\leqslant$, ^3J 2).

7a. [(±)- and second meso-isomers]. δ_H 8.08–8.00 (2 H, o-C$_6$H$_4$CO$_2$), 7.57–7.23 (8 H, aromatic =CH), 7.17–6.30 (4 H, CH=CH), 3.85–3.50 (4 H, HC$\leqslant$), and 2.43–2.18 and 1.95–1.83 (4 H, CH$_A$H$_B$); δ_F +19.5 and +19.3 (CF$_3$); δ_C 165.0 and 164.6 (2 s, O–C=O), 158.9, 158.0 and 156.9 (3 q, CF$_3$C=C, ^3J 5), 142.2, 142.1, 141.0 and 140.2 (4 s, CH=CH), 138.5, 136.6 and 135.0 (3 q, CF$_3$C=C, ^2J 35), 137.7 and 137.3 (2 s, ipso-C$_6$H$_5$CO$_2$), 130.4 and 130.2 (2 s, ipso-C$_6$H$_5$), 129.7–127.2 (aromatic =CH), 123.7, 123.6 and 123.5 (3 q, CF$_3$C=C, ^1J 268–269), 85.4 and 85.2 (2 s, –C$\leqslant$), 71.2, 71.1 and 69.5 (3 s, CH$_2$), 56.6 and 55.9 (2 s, HC$\leqslant$) and 52.7 and 52.5 (2 q, HC$\leqslant$, ^3J 2).

7b. [(±)1- and two meso-isomers]. δ_H 6.90 (dd, =CH, J 5, 3), 6.85 (m, =CH), 6.79 (m, =CH), 6.74 (dd, =CH, J 5, 3), 6.65 (dd, =CH, J 5, 3), 4.15–3.71 (m, HC$\leqslant$), 3.51 (br, HC$\leqslant$), 3.32 (br, HC$\leqslant$) and 2.25–1.60 (complex, CH$_2$); δ_F +21.8, +21.0 and +20.1 (3 s, CF$_3$); δ_C 169.0, 168.9 and 168.8 (3 s, O–C=O), 160.9, 160.2, 159.9 and 159.3 (4 q, CF$_3$C=C, ^3J 5), 142.3, 142.1, 141.9, 141.8, 141.7, 141.4, 141.3 and 141.2 (8 s, =CH), 137.2, 137.1, 136.7 and 136.1 (4 q, CF$_3$C=C, ^2J 35), 123.7, 123.6, 123.5 and 123.4 (4 q, CF$_3$, ^1J 269–270), 79.9, 79.0 and 78.8 (3 s, –C−), 72.9, 71.9,

70.5 and 70.3 (4 s, CH_2), 54.4, 54.1, 53.9 and 53.8 (4 s, HC), 52.4, 52.1, 52.0 and 51.9 (4 q, HC $\leqslant$, ^3J 2–3), and 26.0, 24.2, 22.2, 21.0, 20.9, 20.8, 20.6 and 20.5 (8 s, CH_3CO_2 and $CH_3C=C$).

10. δ_H 6.60 (dd, 1 H, 14-H, $J_{13.14}$ 5.5, $J_{1.14}$ 1.2), 6.23 (dd, 1 H, 13-H, $J_{14.13}$ 5.5, $J_{12.13}$ 1.2), 5.38 (br, 1 H, 1-H), 5.30 (br, 1 H, 12-H), 5.13 (br, 1 H, 9-H), 4.30 (d, 1 H, 7-H, $J_{6.7}$ 4.5), 2.62 (br, 1 H, 10-H), 2.10 (s, 3 H, CH_3CO_2), 1.72 (s, 3 H, $CH_3C=$) and 1.49 (dt, 1 H, 6-H, $J_{7.6}$ 4.5, $J_{10.6}$ $\simeq$ $J_{9.6}$ 1.2); δ_F +18.8 (s, 3 F, CF_3) and +14.6 (s, 3 F, CF_3); δ_C 169.5 (s, O–C=O), 140.7 and 131.1 (2s, CH=CH), 131.8 (s, =C), 129.1 (s, =C), 126.5 (q, CF_3, ^1J 278), 124.7 (q, CF_3, ^1J 271), 87.2 (s, O–C $\leqslant$), 83.1 (q, C–12, ^3J 2), 78.6 (s, C-9), 78.2 (s, C-1), 75.2 (q, C-7, ^3J 6), 55.0 (q, C-11, ^2J 24), 42.8 (q, C-10, ^3J 2), 35.7 (q, C-5, ^2J 37), 20.8 and 19.8 (2 s, CH_3) and 14.7 (q, C-6, ^3J 2).

19. (Diastereoisomer 1). δ_H 6.95 (s, 1 H, =CH), 2.65 (br, 1 H, OH), 2.52 (br, 1 H, C-1), 2.39 (ABd, 1 H, CH_AH_B, $J_{B.A}$ 11.0, $J_{3.A}$ 1.5) and 1.55 (AB, 1 H, CH_AH_B, $J_{A.B}$ 11.0), 2.28 (br, 1 H, 3-H), 2.22 (br, 2 H, C-5, C-6), 2.15 (s, 3 H, CH_3CO_2) and 1.90 (s, 3 H, CH_3); δ_F +20.8 (s, 3 F, $CF_3C=C$) and +9.8 (s, 3 F, $CF_3C \leqslant$); δ_C 168.7 (s, O–C=O), 132.8 (q, $CF_3C=C$, ^2J 31), 130.6 (q, $CF_3C=CH$, ^3J 6), 126.0 (q, $CF_3C=C$, ^1J 272), 123.0 (q, $CF_3C \leqslant$, ^1J 271), 85.9 (s, O–C–O), 82.0 (s, C-9), 43.8 (q, C-5, ^3J 1), 40.2 (s, C-6), 30.4 (s, C-1), 29.7 (s, CH_2), 29.65 (q, $CF_3C \leqslant$ ^2J 35), 25.8 (q, C-3, ^3J 2), 22.0 (s, CH_3CO_2) and 17.9 (s, CH_3).

19. (Diastereoisomer 2). δ_H 6.55 (s, 1 H, =CH), 4.32 (s, 1 H, OH), 2.48 and 1.55 (ABt, 2 H, CH_AH_B, $J_{A.B}$ 11, $J_{1.A}$ $\simeq$ $J_{1.B}$ $\simeq$ $J_{3.A}$ $\simeq$ $J_{3.B}$ 1.5), 2.42 (br, 1 H, 6-H), 2.22 (br, 1 H, 5-H), 2.10 (s, 3 H, CH_3CO_2), 2.08 (q, 1 H, 3-H, $J_{5.3}$ $\simeq$ $J_{A.3}$ $\simeq$ $J_{B.3}$ 1.5) and 1.69 (s, 3 H, CH_3); δ_F +19.0 (s, 3 F, $CF_3C=C$) and +9.6 (s, 3 F, $CF_3C \leqslant$); δ_C 172.1 (s, O–C=O), 131.1 (q, $CF_3C=C$, ^2J 31), 130.8 (q, $CF_3C=CH$, ^3J 6), 126.5 (q, $CF_3C=C$, ^1J 270), 123.0 (q, $CF_3C \leqslant$, ^1J 272), 86.7 (s, O–C–O), 85.6 (s, C-9), 45.6 (s, C-5), 39.7 (s, C-6), 31.6 (q, $CF_3C \leqslant$, ^2J 35), 30.7 (s, CH_2), 30.7 (s, C-1), 23.9 (q, C-3. ^3J 2), 22.7 (s, CH_3CO_2) and 21.8 (s, CH_3).

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