Chemical consequences of fluorine substitution. Part 4.† Diels–Alder reactions of fluorinated *p*-benzoquinones with Dane's diene. Synthesis of fluorinated D-homosteroids

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Four fluorinated *p*-benzoquinones (**2**) have been reacted with Dane's diene (**1**) in Diels–Alder reactions and the formed fluorinated D-homosteroids were characterized. The number of products, their stereochemistry and stability depends on the fluorine substitution pattern of the corresponding fluorinated *p*-benzoquinones. If the *p*-benzoquinone (**2**) contains an unfluorinated double bond, this bond reacts faster with diene **1** yielding *endo*-products selectively. In contrast, [4+2]cycloadditions with 2,6-difluoro (**2c**) and 2,3,5,6-tetrafluorobenzoquinone (**2d**) gave the products with *exo*-orientation of the carbonyl part preferably.

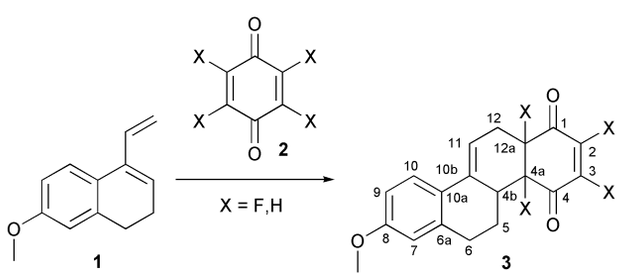
Introduction

There is increasing interest in organofluorine compounds due to the strong influence of the fluorine substituent on the chemical, physical and physiological properties of these compounds.[1,2] For example, in 1970 the share of fluorinated agrochemicals was 3%. Thirty years later, in 2000, 55% of the agrochemicals contained at least one carbon fluorine bond.[3] In the same time period, the share of fluorinated pharmaceuticals on the world market rose from 2% to 18%.[3] Diels–Alder reactions of fluorinated olefins are an attractive approach towards a range of selectively fluorinated cyclohexenes, many of which have potential biological activity. There are two contributions to the effect of a single fluorine at a double bond, the strong electron withdrawing effect (−I-effect) and the mesomeric p-π-interaction (+M-effect).[4,5] Generally, the latter effect is dominating.[5–7]

Regarding simple vinyl fluorides, just the reactions of some fluorostyrenes with the highly reactive diphenylisobenzofuran[6] and with some fluorinated dienes[8] are known. Several more reactions of this type, which solely take place with strongly activated dienophiles such as 2-fluoroacroleins,[9] α,β-unsaturated α-fluoroketones,[5,10] α,β-unsaturated α-fluorocarboxylic acid derivatives,[5,7,11] fluorinated vinylsulfones[12] or a fluorinated electron-poor vinyl sulfoxide[13] have been published.[14]

A second fluorine substituent attached to the double bond seems to increase the reactivity of the corresponding alkenes in Diels–Alder reactions. Several reactions of perfluoroalkenyl ketones with various dienes,[15] of cyclopentadiene with enol derivatives of difluoroacetaldehyde,[16] of furan with perfluoropropene or a corresponding sulfonyl fluoride,[17] and of trifluoroethylene with several substituted furans[18] have been published recently. Furthermore, Diels–Alder reactions of tetrafluoro-*p*-benzoquinone (**2d**) with buta-1,3-diene,[19,20] 1-acetoxybuta-1,3-diene,[20] and cyclopentadiene[20,21] are known.

As part of our efforts directed toward the synthesis of fluorinated steroids, a substance class representing well known pharmaceuticals,[22] the synthesis of fluorinated chrysenediones (**3**) *via* Diels–Alder reaction of various fluorinated *p*-benzoquinones (**2**) with Dane's diene (**1**) (Scheme 1)[23] was investigated, especially regarding the effect of the fluorine substitution pattern of the *p*-benzoquinones (**2**) on the outcome of the cycloadditions. The results of this study are reported in the present paper.



Scheme 1

Results and discussion

Syntheses of the reactants

Dane's diene[24] (**1**) was synthesised according to the literature procedure.[25] In our hands, the Grignard reaction of vinylmagnesium bromide with 6-methoxy-α-tetralone‡ always yielded mixtures of the expected allylic alcohol 1,2,3,4-tetrahydro-6-methoxy-1-vinyl-1-naphthol (**4**) and Dane's diene (**1**) in ratios varying from 4 : 1 to 1 : 2 (**4** : **1**, ^{1}H NMR). A similar partial dehydration was already reported for the reaction of 6-methoxy-α-tetralone with ethynylmagnesium bromide.[26] The diene **1** is described to possess low stability[26–28] and our investigations are in accordance with these reports. Due to this instability, some literature procedures used a solution of **1** in benzene for subsequent reactions.[26,29] As the dehydration of **4** can result in polymerisation,[26] in our study the mixture of **4** and **1** was used as, under the conditions of thermal Diels–Alder reactions, the tertiary allylic alcohol **4** could be expected to dehydrate.

For the syntheses of fluorinated *p*-benzoquinones, some drastic conditions are described in the literature, *e.g.* reaction of

† For Part 3 *cf*. G Haufe, O. G. J. Meyer, C. Mück-Lichtenfeld, *Coll. Czech. Chem. Commun.* 2002, in the press.

‡ The IUPAC name for α-tetralone is 3,4-dihydro-1(2*H*)-naphthone.

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Table 1 Yields and reaction times for the Elbs oxidation of the fluorophenols (**5**) to the fluorohydroquinones (**6**), and CAN oxidation of the fluorohydroquinones (**6**) to the fluoro-*p*-benzoquinones (**2**)

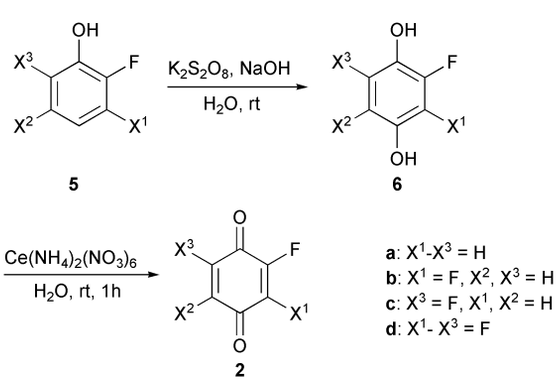
Entry	Fluorophenol	Reisolated **5** (%)	Time/h	Fluorohydroquinone	Yield[a] (%)	Fluoro-*p*-benzoquinone	Yield[a] (%)
1	**5a**	23	14	**6a**	47 (41)[b]	**2a**	94 (78)[b]
2	**5b**	41	14	**6b**	37	**2b**	93
3	**5b**	39	37	**6b**	33		
4	**5c**	45	14	**6c**	26 (22)[c]	**2c**	98
5				**6d**		**2d**	99

[a] Yields obtained in the literature are given in brackets. [b] Ref. 39. [c] Ref. 40.

a fluorinated aniline with a mixture of sulfuric acid and nitric acid[30] or substitution of appropriate chloro- derivatives with potassium fluoride at 350 °C.[31] Furthermore, partly difficult to handle reagents like hydrogen fluoride or xenon difluoride have been employed.[32] Several of the reactions mentioned also exhibit low selectivity.

Initially, an alternative approach to the fluoro-*p*-benzoquinones (**2**) was envisaged, whereby unfluorinated or monofluorinated hydroquinones are directly fluorinated with electrophilic fluorinating agents. Such agents have attracted much interest in recent years[33,34] and emphasis in the literature has been on fluorinations in the α-position to the carbonyl group and on fluorination of aromatic compounds.[35,36] For our investigations we chose the cheap and readily available Selectfluor™ [1-chloromethyl-4-fluoro-1,4-diazabicyclo[2.2.2]-octan-1,4-diylium bis(tetrafluoroborate)]. However, reacting fluorohydroquinone (**6a**) with 1.2 to 2.0 equivalents of Selectfluor™ in dry acetonitrile or dry methanol in a closed vessel at temperatures between 20 °C and 100 °C afforded, apart from fluoro-*p*-benzoquinone (**2a**) (95%), only a maximum of 5% of 2,5-difluoro-*p*-benzoquinone (^{19}F NMR). Thus, oxidation of the hydroquinone **6a** is obviously faster compared to the desired fluorination. Accordingly, an attempted electrophilic fluorination of hydroquinone using Selectfluor™ furnished almost pure *p*-benzoquinone. The oxidative properties of electrophilic fluorinating agents have already been reported.[37] In order to avoid oxidation to the corresponding benzoquinones, the reaction of 1,4-dimethoxybenzene with Selectfluor™ (2.2 equivalents, acetonitrile, 75 °C, 1 h) was investigated. Unfortunately, a complex product mixture was observed.

In contrast to this, Feiring and Sheppard presented a method which converts *o*-fluorophenol (**5a**) into fluorohydroquinone (**6a**) in 41% yield (crude product) *via* an Elbs oxidation.[38,39] The subsequent oxidation with ceric ammonium nitrate (CAN) yielded fluoro-*p*-benzoquinone (**2a**) (78%)[39] (Scheme 2, Table 1).



Scheme 2

An Elbs oxidation as mentioned above was also used by King and Cohen for the oxidation of 2,6-difluorophenol (**5c**) to 2,6-difluorohydroquinone (**6c**) (22%).[40] Generalizing the two-step reaction sequence of Elbs and CAN oxidation was envisaged as a means of easily accessing differently substituted fluoro-*p*-benzoquinones for use in the subsequent [4+2]cycloadditions. The results of application of this strategy for the synthesis of fluoro-*p*-benzoquinone (**2a**), 2,3-difluoro-*p*-benzoquinone (**2b**), 2,6-difluoro-*p*-benzoquinone (**2c**), and tetrafluoro-*p*-benzoquinone (**2d**, fluoranil), are shown in Scheme 2 and Table 1, starting from the corresponding fluorophenols **5**, where for the synthesis of **2d** commercially available tetrafluorohydroquinone (**6d**) was employed. The literature procedures[39] were slightly modified in order to improve the yields: omitting the yield-diminishing recrystallisation,[39] after chromatography the products of the Elbs oxidation did not result in diminished purity of the hydroquinones (**6**), which were obtained in an analytically pure form, except for fluorohydroquinone (**6a**) (94% (GC)). According to gas chromatographic analysis, the corresponding unreacted fluorophenols (**5**) were reisolated cleanly. Prolonged reaction time led, at least in the case of **5b**, to slightly diminished yields (Table 1, entries 2 and 3). After the fast and easy CAN oxidation, the crude product was purified by column filtration instead of sublimation[39] giving the fluoro-*p*-benzoquinones **2a**–**d** in an analytically pure form and in almost quantitative yields (Scheme 2, Table 1).

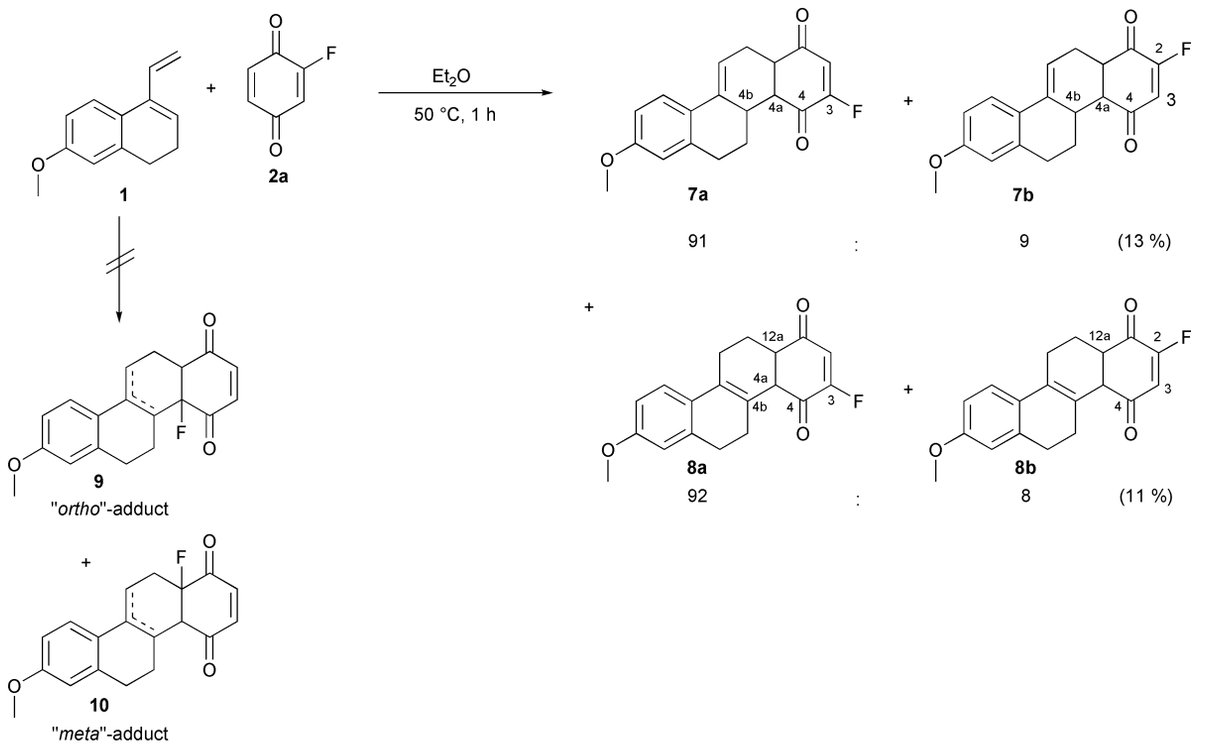
Diels–Alder reactions

Diels–Alder reaction with fluoro-*p*-benzoquinone

We began our study with the Diels–Alder reaction of fluoro-*p*-benzoquinone (**2a**) with Dane's diene (**1**, mixture with **4**).[41] After heating the dienophile **2a** with a slight excess of **1** in diethyl ether at 50 °C in a sealed tube, the formation of a bright-yellow precipitate was observed which corresponded to the regioisomeric mixtures **7a/b** and **8a/b** (Scheme 3). The solubilities of **7a/b** and **8a/b** differ significantly in different solvents. Compounds **7a/b** are only sparingly soluble in chloroform, whereas **8a/b** are poorly soluble in acetone. These differing characteristics were exploited for separation in order to furnish the double bond isomers **7a/b** and **8a/b** as regioisomeric mixtures with respect to the position of the fluorine substituent.

Due to the Diels–Alder adducts being just partly stable under gas chromatographic conditions, quantitative information on regio- and diastereomeric ratios in the crude products cannot be obtained by this method. Such information could not be obtained by means of NMR, either, as owing to the great differences in solubility of **7a/b** and **8a/b**, no sufficiently concentrated solution for ^{19}F NMR analysis could be obtained. However, no products were detected, which would hint at participation of the fluorinated double bond of **2a** in cycloaddition, resulting in "*ortho*"-**9** or "*meta*"-adduct[42] **10** (Scheme 3).

The regioisomeric mixture **7a/b**, bearing an olefinic proton in the C-ring, was furnished after crystallisation from acetone (13%). In this solid, the regioisomeric ratio was 91 : 9 (**7a** : **7b**, ^{1}H NMR). Thus, fluoro-*p*-benzoquinone (**2a**) reacted preferentially to the chrysenediones with the fluorine substituent in position 3 (Scheme 3). Compounds **8a/b** (11%), which evolve from the primary cycloadducts **7a/b** *via* double bond migration, bearing the higher substituted double bond, were obtained in a regioisomeric ratio of 92 : 8 (**8a** : **8b**, ^{1}H NMR). Such isomerisations have already been observed under acid catalysis



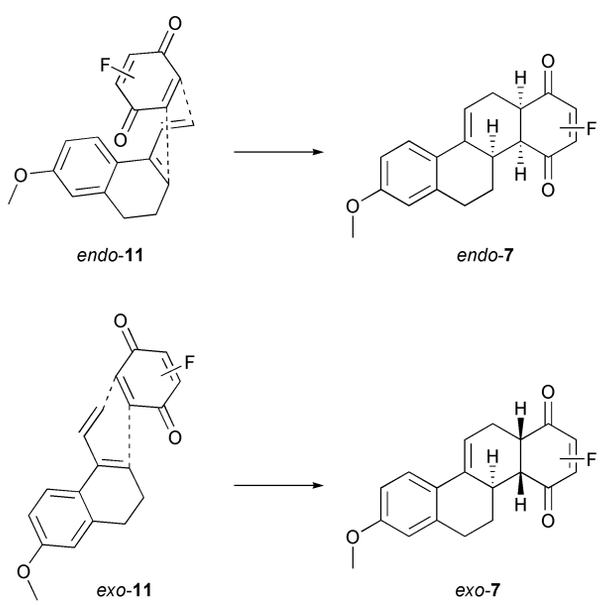
Scheme 3

in similar, unfluorinated compounds.[26–28,43] The structures of **7a/b** and **8a/b** were confirmed by two-dimensional NMR experiments (^{1}H,^{1}H- and ^{1}H,^{13}C). For preparative purposes, the conversion of reactants can presumably be enhanced by prolonged reaction times as the mother liquor still contained 32% **2a** and 11% fluorohydroquinone (**6a**) (GC). Furthermore, a greater excess of Dane's diene (**1**) could be helpful, too, as **1** might, especially in slowly proceeding Diels–Alder reactions where the fast "trapping" of the diene does not take place, decompose to some extent. The formation of fluorohydroquinone (**6a**) can be explained by a redox reaction in the course of which **2a** may be reduced to **6a** by **1**.

Additionally, the Diels–Alder reaction described above was conducted in toluene at 100 °C (65 min). Nevertheless, fluoro-*p*-benzoquinone (**2a**, 41%) and fluorohydroquinone (**6a**, 8%) were found in the crude product mixture as judged by gas chromatography. The higher reaction temperature promoted the double bond migration: Chrysenediones **8a/b** (26%) were isolated in a regioisomeric ratio of 76 : 24 (**8a** : **8b**, ^{19}F NMR). Compounds **7a/b** had a regiosisomeric ratio of 63 : 37. Thus, regioselectivity decreases with increasing reaction temperature. Under the reaction conditions just described, some addition of fluoro-*p*-benzoquinone (**2a**) *via* the fluorinated double bond cannot be ruled out as by mass spectrometry (GC-MS coupling) a peak with *m*/*z* = 292 was observed in the crude product mixture, which may have evolved from HF-elimination from "*ortho*"-adduct **9** or "*meta*"-adduct **10** (Scheme 3). Such an elimination is unlikely in the case of **7a/b** and **8a/b** and was not observed for these compounds.

Assignment of the position of the fluorine substituent in the fluorinated cycloadducts (Scheme 3) shall be demonstrated on the regioisomeric compounds **8a/b**: In **8a**, the fluorine atom couples to carbons 4a ($^3J_{C,F}$ = 3.9 Hz) and 4b ($^4J_{C,F}$ = 1.8 Hz), but not to carbon 12a. Consequently, the fluorine substituent must be in position 3 in **8a**. In the ^{13}C NMR spectrum of **8b**, no coupling of fluorine to carbon 4a is observed; instead the signal arising from carbon 12a is split ($^3J_{C,F}$ = 3.3 Hz).

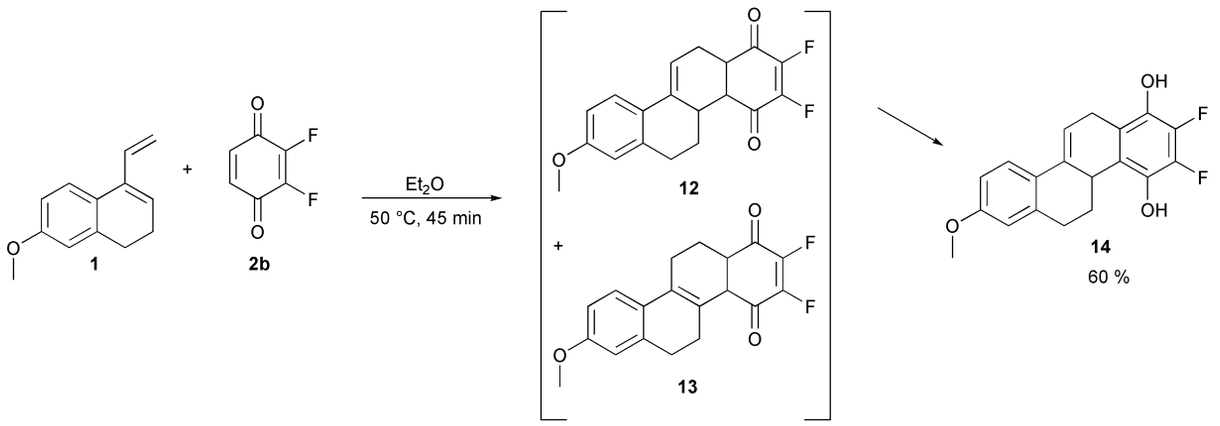
The relative configuration (*endo*/*exo*) of **7a/b** could not be assigned due to multiplets in the ^{1}H NMR spectrum for protons 4a and 4b from which no coupling constants could be deducted. As chrysenediones **7a/b** as well as **8a/b** crystallise as fine needles, no crystals suitable for X-ray analysis could be obtained yet. Nevertheless, it is reasonable to assign *endo*-configuration for **7a/b**, as solely *endo*-adducts were observed in related studies with other *p*-benzoquinones,[26,43*b*,44–47] the "*endo*-rule"[48] not being violated. Consequently, the π-electrons of the reactants approach each other in a manner enabling the best possible orbital overlap, *i.e.*, they lie directly on top of one another in the transition state *endo*-**11**, leading to the *endo*-adduct as shown for **7** in Scheme 4. Secondary orbital interactions might



Scheme 4

also play a role.[49] Also for the reaction of fluorobenzoquinone (**2a**) with cyclopentadiene, the formation of the *endo*-adduct has been proven.[50]

The [4+2]cycloaddition of **2a** with Dane's diene (**1**) showed the significantly lowered reactivity of monofluorinated compared to unfluorinated double bonds once more.[5–7]



Scheme 5

Diels–Alder reaction with 2,3-difluoro-*p*-benzoquinone

Subsequently the Diels–Alder reaction of **1** with 2,3-difluoro-*p*-benzoquinone (**2b**) was investigated. Dienophile **2b** was reacted with 2.5 equivalents of Dane's diene (**1**) in diethyl ether (45 min at 50 °C). A yellow solid was formed in 76% crude product yield comprising of two isomers, presumably **12** and **13** (Scheme 5), in a 73 : 27 ratio (^{19}F NMR).[58] On attempted separation by column chromatography, a drastic colour change to red occurred and hexahydrochrysene-1,4-diol **14** was obtained as a red solid (60%) (Scheme 5). As the primary adducts described above were not expected to be *endo*/*exo*-isomers of **12** (*cf.* formation of **15**, *vide infra* and ref. 50), we assume the regioisomers **12** and **13** were formed, whereat **12** tautomerized to the D-ring hydroquinone **14** on silica gel. This consideration is supported by the ^{19}F NMR spectrum of the yellow crude product before subjection to column chromatography: The signals of two compounds in the ratio 73 : 27, each bearing two fluorine atoms, were observed. In the major isomer (−136.4 ppm, d, $^3J_{F,F}$ = 5.7 Hz; −139.2 ppm, dd, $^4J_{F,H}$ = 5.7, $^3J_{F,F}$ = 5.7 Hz) as well as in the minor isomer (−136.7 ppm, d, $^3J_{F,F}$ = 5.7 Hz; −137.9 ppm dd, $^4J_{F,H}$ = 5.7, $^3J_{F,F}$ = 5.7 Hz), due to the $^4J_{F,H}$-coupling both fluorine atoms are obviously not bound to an aromatic ring, but taking a vinylic position (Fig. 1). Also the small vicinal

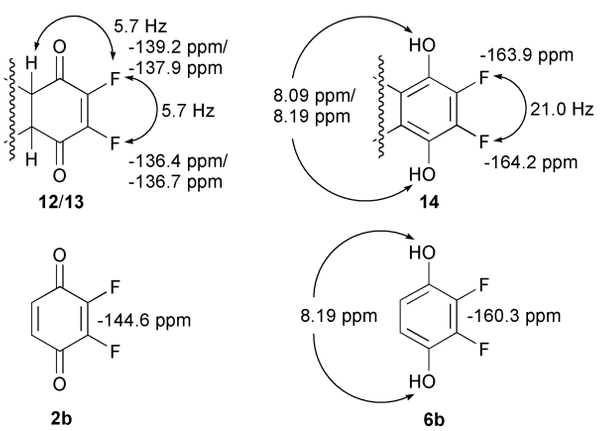


Fig. 1 Comparison of the chemical shifts and coupling constants of compounds **12**, **13** and **14** with the "model compounds" **2b** and **6b**.

coupling constant $^3J_{F,F}$ of 5.7 Hz, which in the case of the aromatic secondary product **14** is 21.0 Hz, rules out an aromatic D-ring for the primary products **12** and **13**. Additionally, the comparison with the chemical shifts of ^{19}F NMR-signals of 2,3-difluoro-*p*-benzoquinone (**2b**), δ = −144.6, and 2,3-difluorohydroquinone (**6b**), δ = −160.3, confirm these assignments (Fig. 1).

Finally, the identical coupling constants for isomers **12/13** (Fig. 1) strongly support the assumption of formation of double bond isomers (also *cf.* **7**/**8**). For *endo*/*exo*-isomers significantly different coupling constants are expected (*cf. endo*/*exo*-**18**, *vide infra*).

Isolation of **14**, but not of the sequential product of **13**, is probably due to the purification method: compound **14** (or the corresponding tautomer) was probably not eluted by the eluents (pentane–diethyl ether mixtures) used. Very different solubility of similar double bond isomers was alrerady observed for **7** and **8**.

As aromatisation of the D-ring was not observed for the Diels–Alder adducts of **1** with fluoro-*p*-benzoquinone (**2a**), despite migration of a double bond, this phenomenon can probably be accounted to the stronger influence of two fluorine substituents on the acidity of the tertiary protons.

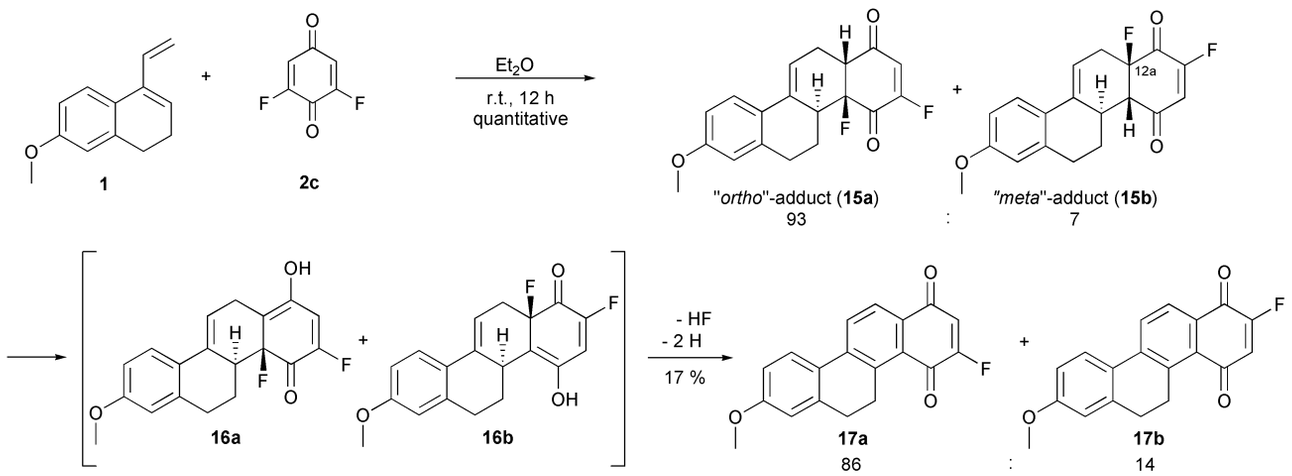
Thus, also in the [4+2]-cycloaddition of 2,3-difluoro-*p*-benzoquinone (**2b**) with Dane's diene (**1**), the unfluorinated double bond reacted preferably.

Diels–Alder reaction with 2,6-difluoro-*p*-benzoquinone

Subsequently, the corresponding reaction of 2,6-difluoro-*p*-benzoquinone (**2c**) was envisaged in order to force one of the two monofluorinated double bonds of this dienophile into the desired cycloaddition. Initially, diene **1** was heated with an equimolar amount of 2,6-difluoro-*p*-benzoquinone (**2c**) in dry toluene at 110 °C (2 h). In the ^{19}F NMR spectrum of the crude product mixture two main signals (−109.4 ppm, d, $^3J_{F,H}$ = 10.0 Hz and −134.4 ppm, d, $^3J_{F,H}$ = 7.6 Hz) were observed in a 1 : 1 ratio, which represent two compounds and do not result from the primary adducts **15a** or **15b** (Scheme 6). The first signal is assigned to benzoquinone **17a** (*vide infra* and Scheme 6). This assumption is further supported by comparison with the ^{19}F NMR spectrum of the related chrysenedione **7a** (−109.1 ppm d, $^3J_{F,H}$ = 11.2 Hz) and the mass spectrum, which shows the expected molecular ion peak *m*/*z* = 308 as the base peak. The formation of **17a** can be rationalized by a tandem Diels–Alder reaction–HF-elimination, followed by an oxidative aromatisation (Scheme 6).

The dienophile 2,6-difluoro-*p*-benzoquinone (**2c**) might serve as an oxidant for this process. This is confirmed by the above-mentioned second ^{19}F NMR signal of the crude product mixture at δ = −134.4 (in $CDCl_3$), which, taking recording of the spectra in different solvents into account, correlates well with the signal at δ = −133.1(in acetone-d_6) of 2,6-difluorohydroquinone (**6c**). On attempted chromatographic separation of the crude product mixture, some decomposition occurred and only product mixtures were obtained containing considerable amounts of **6c**.

In order to avoid the HF-elimination, which is favoured by the enolizable ketone functionality in **15a/b**, the above-mentioned reaction was repeated under very mild conditions (rt, diethyl ether, 12.5 h). According to ^{19}F NMR spectroscopy, the crude product isolated in quantitative yield contained 95%



Scheme 6

3,4a-difluoro-8-methoxy-4a,4b,5,6,12,12a-hexahydrochrysene-1,4-dione (**15a/b**, Scheme 6); also the ^{1}H NMR spectrum indicated minor impurities only. The observed regioisomeric ratio *ortho* (**15a**) : *meta* (**15b**) was 93 : 7. The regioisomeric outcome of this reaction was assigned unambiguously *via* the coupling constants in the ^{1}H and ^{19}F NMR spectra as shown exemplarily for **15a** (Fig. 2).

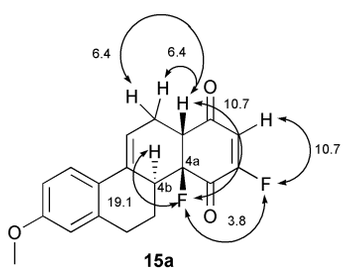


Fig. 2 Couplings from the ^{1}H- and ^{19}F NMR spectra of compound **15a** as proof for the assigned regiochemistry.

The assignment of an *exo*-configuration for adduct **15a** is reasonable due to the $^{3}J_{\text{F-4a,H-4b}}$-coupling of 19.1 Hz. For the *endo*-isomer a significantly smaller H,F-coupling constant should be found (*cf.* Fig. 3 and discussion for compounds *exo*-

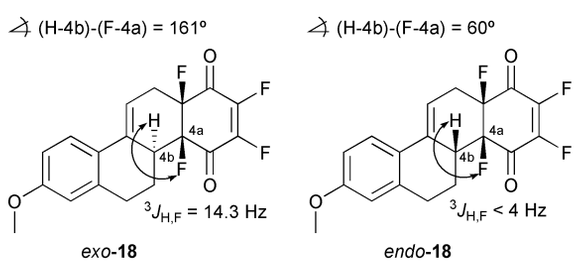


Fig. 3 Assignment of the configuration of the diastereomeric 2,3,4a,12a-tetrafluoro-8-methoxy-4a,4b,5,6,12,12a-hexahydrochrysene-1,4-diones **18**.

and *endo*-**18**). For the regioisomer **15b**, the position of the fluorine substituents is easily confirmed by the fact that the fluorine atom in position 12a (Scheme 6) shows three $^{3}J_{\text{F,H}}$-couplings consistent solely with this position.

Immediately after attempted separation of the regioisomeric mixture **15a/b** by column chromatography, a regioisomeric mixture of **17a/b** (Scheme 6) started to precipitate (17%, **17a/17b** 86 : 14 (GC)), which astonishingly was almost insoluble in all common organic solvents. ^{19}F NMR spectroscopic and mass spectrometric data of **17a** are consistent with those of the presumed naphthoquinone **17a**, which was observed in the above-mentioned reaction in toluene at 110 °C. Difluoro-chrysenediones **15a**,**b** could only be isolated again as partially decomposed material.

An analogous Diels–Alder reaction of Dane's diene (**1**) with 2,6-dimethyl-*p*-benzoquinone was reported earlier by Valenta and coworkers: for the thermal reaction in refluxing benzene they observed complete *ortho*-selectivity.[46,47]

A tandem Diels–Alder reaction–elimination process with subsequent aromatisation was already observed by Carreño *et al.* for a similar system. On converting a sulfinyl-*p*-benzoquinone with Dane's diene (**1**), these authors found a tandem-Diels–Alder reaction–sulfoxide-elimination, followed by aromatisation on subjection of the crude product to column chromatography.[44,45]

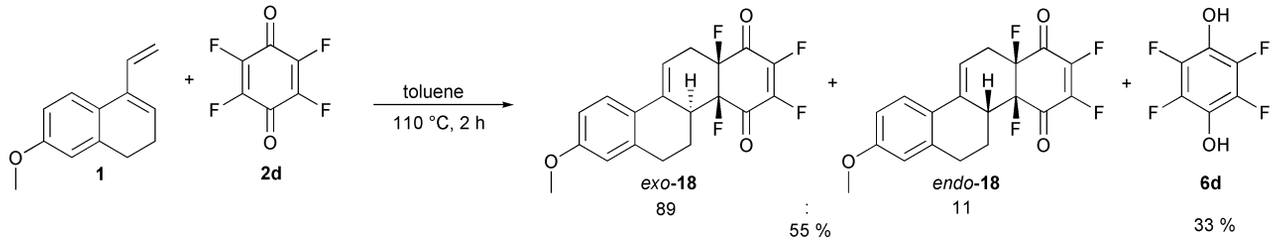
Diels–Alder reaction with tetrafluoro-*p*-benzoquinone

Due to the labile nature of the primary cycloadducts **15a/b**, we next considered the thermal Diels–Alder reaction of tetrafluoro-*p*-benzoquinone (**2d**) with Dane's diene (**1**). The thermal reaction of **2d** with buta-1,3-diene,[19,20] 1-acetoxybuta-1,3-diene,[20] and cyclopentadiene[20,21] has already been successfully investigated. Consequently, equimolar amounts of compounds **2d** and **1** were heated in toluene at 110 °C. Subsequent column chromatography afforded the diastereomeric tetrafluoro-chrysenediones *exo*/*endo*-**18** (55%) in 89 : 11 ratio (Scheme 7). Furthermore, tetrafluorohydroquinone (**6d**) was isolated (33%).

Additionally, the reaction was conducted in a polar medium (diethyl ether–dichloromethane 4 : 7) at 75 °C in a sealed tube. The yield was slightly lower (49%) compared to the reaction in toluene and a nearly unchanged diastereomeric ratio of 86 : 14 (*exo*/*endo*) was found for **18**. Furthermore, an attempt was made to perform the cycloadditon with 1.3 equivalents of boron trifluoride at −20 °C in analogy to a procedure[47] using 2,6-dimethyl-*p*-benzoquinone instead of **2d**. Unfortunately, only complete decomposition of diene **1** was observed.

The structure of *endo*-**18** was additionally confirmed by two-dimensional NMR experiments (^{1}H,^{1}H- and ^{1}H,^{13}C). The configuration of *exo*/*endo*-**18** was assigned *via* the vicinal coupling constant $^{3}J_{\text{H-4b,F-4a}}$, which should differ considerably for *exo*-**18** and *endo*-**18** due to the different dihedral angles.[51] After optimisation of the two structures on AM1 level (closed shell), the dihedral angles depicted in Fig. 3 were calculated.

Due to the angles calculated and taking the Karplus equation[51] into account, a small coupling constant $^{3}J_{\text{H-4b,F-4a}}$ (Fig. 3) for *endo*-**18** and a significantly greater one in case of *exo*-**18** can be expected. The ^{1}H NMR spectrum for *exo*-**18** shows a coupling constant $^{3}J_{\text{H-4b,F-4a}}$ of 14.3 Hz, while for *endo*-**18** no resolved $^{3}J_{\text{H,F}}$-coupling could be found in the ^{19}F NMR spectrum and therefore $^{3}J_{\text{H-4b,F-4a}}$ is obviously less than *ca.* 4 Hz. The ^{1}H NMR spectrum for *endo*-**18** displays a multiplet for H-4b, from which no H,F-coupling could be extracted. As the



Scheme 7

$^3J_{H,F}$-coupling is the only criterion so far to assign the configuration, we tried to obtain single crystals of **18** suitable for X-ray analysis, but so far only very fine needles have been grown. Interestingly, *exo*-**18** is stable under gas chromatographic conditions, while *endo*-**18** probably suffers a retro-Diels–Alder reaction as a signal is observed which shows a retention time very similar to that of Dane's diene (**1**).

According to AM-1 calculations, *exo*-**18** ($\Delta H_f = -211.5$ kcal mol^{-1}) is 2.1 kcal mol^{-1} more stable than *endo*-**18** ($\Delta H_f = -209.4$ kcal mol^{-1}). Thus, in the Diels–Alder reaction of tetrafluoro-*p*-benzoquinone (**2d**) with diene **1** at 75 and 110 °C, the thermodynamically more stable product has been formed preferentially. This means that the dienophiles **2c** and **2d** show a reverse diastereoselectivity compared to the unfluorinated *p*-benzoquinones[26,43*b*,44–47] investigated to date and to fluoro-*p*-benzoquinone (**2a**) and 2,3-difluoro-*p*-benzoquinone (**2b**). All these dienophiles reacted in an *endo*-selective fashion as expected (*vide supra* and refs. 48,50). *Exo*-selectivity has already been reported for Diels–Alder reactions of other monofluorinated or *cis*-1,2-difluorinated vinylic compounds.[5,7,10,11*d*,11*e*,13,18,52] Due to quantum chemical calculations done for related fluorinated dienophiles, kinetic effects of fluorine substituents should be responsible for the reverse diastereoselectivity rather than higher thermodynamic stability of the *exo*-products.[5,6*b*]

Compared to **15a/b**, the cycloadduct resulting from 2,6-difluoro-*p*-benzoquinone (**2c**) and Dane's diene (**1**), it should be pointed out that HF-elimininationwas successfully prevented for compounds **18a/b** under identical reaction conditions due to the lack of an enolizable ketone functionality.

Conclusion

We presented a general, concise and practical method for the synthesis of fluorinated *p*-benzoquinones. The differently fluorinated *p*-benzoquinones have been reacted with Dane's diene (**1**) in Diels–Alder reactions and the observed cycloadducts were characterised. An unfluorinated double bond in the benzoquinone leads, as deduced from literature precedents,[26,43*b*,44–48,50] to selective formation of the *endo*-cycloadducts, which evolve from [4+2]addition of the unfluorinated double bond of the benzoquinone. Benzoquinones with fluorinated, less reactive double bonds, form the corresponding *exo*-adducts. The number of cycloadducts and their stability depends on the fluorine substitution pattern of the corresponding fluorinated benzoquinones. The primary Diels–Alder products, except **18**, were observed to stabilise themselves *via* tautomerisation, HF-elimination and/or oxidative aromatisation.

Experimental

General

NMR spectra of solutions in $CDCl_3$ or acetone-d_6 were recorded at 300 or 400 MHz (^{1}H), at 75, 100, or 150 MHz (^{13}C) and at 282 MHz (^{19}F) and are reported in ppm downfield from TMS (^{1}H and ^{13}C) or $CFCl_3$ (^{19}F). The multiplicity of ^{13}C NMR signals was determined by DEPT experiments. Coupling constants *J* are given in Hz. Mass spectra were recorded by GC/MS coupling (EI, 70 eV) or by ESI-MS (Nanospray). Gas chromatographic analyses were performed using a column HP-5 (30 m, Ø 0.32 mm, film 0.25 μm, carrier gas N_2). Thin-layer chromatography was carried out on a coated plate 60 F_{254}. Column chromatography was carried out with silica gel 60 (0.063–0.2 mm). Elemental analyses: Microanalytical laboratory, Organic Chemistry Institute, University of Münster. All reactions involving air-sensitive agents were conducted under an argon atmosphere applying Schlenk-techniques. All reagents purchased from suppliers were used without further purification. Solvents for chromatography were distilled prior to use.

General procedure A: oxidation of phenols to the corresponding 1,4-hydroquinones (Elbs oxidation)[38,39]

To the fluorophenol (100 mmol) dissolved in 6% aqueous NaOH (400 cm^3) was added solid potassium persulfate (27.0 g, 100 mmol) with stirring, in several portions, over 10 min, resulting in a dark solution. This was stirred overnight at rt, then concentrated to *ca.* one third of its original volume under reduced pressure. The solution was cooled to 0 °C, neutralised with concentrated HCl and extracted once with diethyl ether (200 cm^3). This organic phase was dried ($MgSO_4$) and concentrated under reduced pressure to reisolate unreacted substrate. The aqueous solution was acidified with concentrated HCl (100 cm^3), refluxed for 1 h, then concentrated to *ca.* 50 cm^3 under reduced pressure. Addition of acetone (200 cm^3) precipitated the inorganic salts, which were removed by filtration. The filtrate was taken to dryness on the rotary evaporator and the dark residue, dissolved in acetone, was coated on silica gel (12 g). The dry material was subjected to column chromatography (pentane–diethyl ether 2 : 1 (**6b**, **6c**) or cyclohexane–ethyl acetate 3 : 1 (**6a**)).

General procedure B: oxidation of 1,4-hydroquinones to the corresponding *p*-benzoquinones with ceric ammonium nitrate (CAN oxidation)[39]

The fluorohydroquinone (23.0 mmol) was added to a solution of ceric ammonium nitrate (26.6 g, 48.5 mmol) in water (150 cm^3) and stirred for 1 h at rt. The reddish solution was extracted with diethyl ether (3 × 100 cm^3) and the combined organic phases dried ($MgSO_4$). The filtrate was passed through a silica gel column (2 × 9 cm) and eluted (diethyl ether). After concentration of the obtained filtrate on the rotary evaporator, the corresponding benzoquinone was furnished as bright-yellow to bright-orange crystals which were stored protected from light.

6-Methoxy-1,2,3,4-tetrahydro-1-vinyl-1-naphthol (4) and 3,4-dihydro-6-methoxy-1-vinylnaphthalene (Dane's diene, 1)

6-Methoxy-1,2,3,4-tetrahydro-1-vinyl-1-naphthol (**4**) was prepared according to the literature method.[25] In our hands, the Grignard reaction of vinyl magnesium bromide (97 cm^3 of a 1 M solution in THF) with 6-methoxy-α-tetralone (9.0 g, 51.1 mmol) in dry THF (60 cm^3) yielded a mixture (13.66 g, 99.8%) of the expected allylic alcohol (**4**) and Dane's diene (**1**) (ratios of **4** and **1** varying from 4 : 1 to 1 : 2 (^{1}H NMR)). This mixture,

which decomposes with attempted column chromatography on silica gel or distillation,[26–28] was used as is for the subsequent cycloadditions. Spectroscopic data of **1** and **4** agree with published ones.[25]

o-Fluorohydroquinone (6a)

Following the general procedure A, *o*-fluorophenol (**5a**) (10.08 g, 90.0 mmol) was reacted. Compound **5a** (2.30 g, 23%) was reisolated and *o*-fluorohydroquinone (**6a**) was obtained as beige crystals (5.40 g, 47%, 94% purity (GC)). Recrystallisation from chloroform yielded analytically pure **6a** (2.54 g, 27%); mp 121–122 °C (lit.,[39] 122–123 °C); ^{1}H NMR (acetone-d_6) δ 6.50 (ddd, $^5J_{H,F}$ 1.4, $^4J_{H,H}$ 2.9, $^3J_{H,H}$ 8.7, 1 H, 5-H), 6.59 (dd, $^4J_{H,H}$ 2.9, $^3J_{H,F}$ 12.4, 1 H, 3-H), 6.81 (dd, $^4J_{H,F}$ 9.9, $^3J_{H,H}$ 8.7, 1 H, 6-H), 7.78 (s, 1 H, OH), 7.99 (s, 1 H, OH); ^{13}C NMR (acetone-d_6) δ 103.9 (dd, $^2J_{C,F}$ 20.3, C-3), 111.2 (dd, $^4J_{C,F}$ 3.8, C-5), 118.4 (dd, $^3J_{C,F}$ 3.8, C-6), 137.9 (d, $^2J_{C,F}$ 12.7, C-1), 151.0 (d, $^2J_{C,F}$ 8.9, C-4), 151.9 (d, $^1J_{C,F}$ 239.1, C-2); ^{19}F NMR (acetone-d_6) δ −135.6 (pseudo t, $^4J_{F,H}$ 9.9, $^3J_{F,H}$ 12.4 Hz); *m*/*z* [as bis(TMS-ether)] 272 (100%, M^+), 257 (37, $M^+ - CH_3$), 242 (75, 257 − CH_3), 213 (14), 199 (2, M^+ − TMS), 197 (3), 185 (3), 183 (2, 199 − O), 165 (7, 183 − F + H), 137 (9), 77 (13), 73 (61, TMS^+), 45 (9). ^{1}H and ^{19}F NMR data agree with published data.[39]

2,3-Difluorohydroquinone (6b)

Following the general procedure A, 2,3-difluorophenol (**5b**) (2.061 g, 15.8 mmol) was reacted. Phenol **5b** (0.814 g, 41%) was reisolated and 2,3-difluorohydroquinone (**6b**) (0.843 g, 37%) was obtained as colourless crystals (Found: C, 49.38; H, 2.80%. $C_6H_4F_2O_2$ (146.1) requires C, 49.33; H, 2.76%); mp 124–126 °C (pentane–diethyl ether); ^{1}H NMR (acetone-d_6) δ 6.56–6.63 (m, 2 H, 5-H, 6-H), 8.19 (br s, 2 H, OH); ^{13}C NMR (acetone-d_6) δ 111.9 (d, 2 C, C-5, C-6), 139.1 (pseudo t, $^2J_{C,F} = {}^3J_{C,F}$ 5.1, 2 C, C-1, C-4), 141.6 (dd, $^2J_{C,F}$ 12.7, $^1J_{C,F}$ 242.9, 2 C, C-2, C-3); ^{19}F NMR (acetone-d_6) δ −160.3 (s); *m*/*z* 146 (100%, M^+), 126 (5, $M^+ - F - H$), 117 (3, $M^+ - COH$), 98 (26, 117 − F), 70 (24), 69 (8), 62 (3, $C_2F_2^+$), 53 (3), 39 (6, $C_3H_3^+$]. Found (HRMS): M^+, 146.0209. $C_6H_4F_2O_2$ (146.1) requires 146.0179.

2,6-Difluorohydroquinone (6c)

Following the general procedure A, 2,6-difluorophenol (**5c**) (4.00 g, 30.75 mmol) was reacted. Phenol **5c** (1.78 g, 45%) was reisolated and 2,6-difluorohydroquinone (**6c**) (1.16 g, 26%) was obtained as colourless crystals (Found: C, 49.32; H, 2.78%. $C_6H_4F_2O_2$ (146.1) requires C, 49.33; H, 2.76%); mp 151–152 °C (dichloromethane) (lit.,[40] 150.5–152 °C); ^{1}H NMR (acetone-d_6) δ 6.41–6.53 (m, 2 H, 5-H, 6-H), 8.02 (s, 1 H, OH), 8.41 (s, 1 H, OH); ^{13}C NMR (acetone-d_6) δ 99.6 (dd, $^2J_{C,F}$ 25.4, 2 C, C-3, C-5), 126.9 (t, $^2J_{C,F}$ 16.5, 1 C, C-1), 150.3 (t, $^3J_{C,F}$ 12.7, 1 C, C-4), 153.3 (dd, $^3J_{C,F}$ 7.6, $^1J_{C,F}$ 240.3, 2 C, C-2, C-6); ^{19}F NMR (acetone-d_6) δ −133.1 (d, $^3J_{H,F}$ 7.6); *m*/*z* 146 (100%, M^+), 126 (1, $M^+ - F - H$), 125 (4), 117 (5, $M^+ - COH$), 98 (25, 117 − F), 73 (10), 70 (33), 69 (8), 63 (3, $C_2F_2H^+$), 53 (6), 39 (9, $C_3H_3^+$].^{1}H NMR data can be found in ref. 40 which agree with those obtained in this study.

2-Fluoro-*p*-benzoquinone (2a)

Following the general procedure B, 2-fluorohydroquinone (**6a**) (2.50 g, 19.5 mmol) was reacted and 2-fluoro-*p*-benzoquinone (**2a**) (2.32 g, 94%) was obtained; mp 77–78 °C (diethyl ether) (lit.,[39] 78–79 °C); ^{1}H NMR (acetone-d_6) δ 6.58 (dd, $^3J_{H,F}$ 10.7, $^4J_{H,H}$ 2.2, 1 H, 3-H), 6.83–6.96 (m, 2 H, 5-H, 6-H); ^{13}C NMR (acetone-d_6) δ 115.4 (dd, $^2J_{C,F}$ 7.6, C-3), 135.1 (dd, $^3J_{C,F}$ 3.8, C-6), 137.2 (d, C-5), 159.7 (d, $^1J_{C,F}$ 293.6, C-2), 179.8 (d, $^2J_{C,F}$ 24.2, C-1), 187.8 (d, $^3J_{C,F}$ 15.3, C-4); ^{19}F NMR (acetone-d_6) δ −114.4 (m); *m*/*z* 128 (18%, $M^+ + 2$ H), 126 (100, M^+), 108 (3, $M^+ - F + H$), 100 (7, $M^+ - C_2H_2$), 98 (40, $M^+ - CO$), 82 (7), 80 (7, 100 − HF), 72 (99, 98 − C_2H_4), 70 (39), 54 (30), 53 (25, 72 − F), 44 (44, 72 − CO). ^{1}H and ^{19}F NMR data can be found in ref. 39 which agree with those obtained in this study.

2,3-Difluoro-*p*-benzoquinone (2b)

Following the general procedure B, hydroquinone **6b** (613 mg, 4.20 mmol) was reacted and 2,3-difluoro-*p*-benzoquinone **2b** (560 mg, 93%) was obtained (Found: C, 49.70; H, 1.43%. $C_6H_2F_2O_2$ (144.1) requires C, 50.02; H, 1.40%); mp 79–81 °C (diethyl ether); ^{1}H NMR (acetone-d_6) δ 6.95 (ddd, $^5J_{H,F}$ 2.2, $^4J_{H,F}$ 6.4, $^3J_{H,H}$ 4.8, 2 H, 5-H, 6-H); ^{13}C NMR (acetone-d_6) δ 134.7 (d, 2 C, C-5, C-6), 145.2 (dd, $^2J_{C,F}$ 6.4, $^1J_{C,F}$ 284.8, 2 C, C-2, C-3), 180.2 (dd, $^2J_{C,F}$ 15.3, $^3J_{C,F}$ 10.2, 2 C, C-1, C-4); ^{19}F NMR (acetone-d_6) δ −144.6 (d, $^4J_{F,H}$ 6.4); *m*/*z* 146 (15%, $M^+ + 2$ H), 144 (100, M^+), 118 (3, $M^+ - C_2H_2$), 116 (20, $M^+ - CO$), 98 (5), 97 (3, 116 − F), 90 (45), 88 (47), 71 (8, C_3FO^+), 62 (26, $C_2F_2^+$), 53 (11). Found (HRMS): M^+, 144.0039. $C_6H_2F_2O_2$ (144.1) requires 144.0023.

2,6-Difluoro-*p*-benzoquinone (2c)

Following the general procedure B, 2,6-difluorohydroquinone (**6c**) (429 mg, 2.94 mmol) was reacted and the 2,6-difluoro-*p*-benzoquinone **2c** (416 mg, 98%) was obtained (Found: C, 49.66; H, 1.42%. $C_6H_2F_2O_2$ (144.1) requires C, 50.02; H, 1.40%); mp 81–82 °C (diethyl ether) (lit.,[30] 83–85 °C); ^{1}H NMR (acetone-d_6) δ 6.64 (dm, $^3J_{H,F}$ 9.3, 2 H, 3-H, 5-H); ^{13}C NMR (acetone-d_6) δ 115.5 (dd, $^2J_{C,F}$ 10.2, 2 C, C-3, C-5), 159.8 (dd, $^3J_{C,F}$ 10.2, $^1J_{C,F}$ 284.8, 2 C, C-2, C-6), 172.5 (t, $^2J_{C,F}$ 28.0, C-1), 185.8 (t, $^3J_{C,F}$ 15.3, C-4); ^{19}F NMR (acetone-d_6) δ −118.7 (d, $^3J_{F,H}$ 9.3); *m*/*z* 146 (9%, $M^+ + 2$ H), 144 (100, M^+), 126 (2, $M^+ - F + H$), 116 (9, $M^+ - CO$), 100 (2, $M^+ - C_2HF$), 98 (5), 97 (3, 116 − F), 88 (23), 72 (51, C_3HFO^+), 62 (1, $C_2F_2^+$), 53 (11), 44 (34); ^{1}H and ^{19}F NMR data can be found in ref. 30 which agree with those obtained in this study.

2,3,5,6-Tetrafluoro-*p*-benzoquinone (2d, fluoranil)

Following the general procedure B, 2,3,5,6-tetrafluorohydroquinone (**6d**) (3.38 g, 18.57 mmol) was reacted and 2,3,5,6-tetrafluoro-*p*-benzoquinone **2d** (3.33 g, 99%) was obtained as bright-yellow leaves; mp 172–174 °C (subl., lit.,[53] 173 °C); ^{13}C NMR (acetone-d_6) δ 144.6 (dd, $^2J_{C,F}$ 7.6, $^1J_{C,F}$ 284.8, 4 C, C-2, C-3, C-5, C-6), 188.9 (m, 2 C, C-1, C-4); ^{19}F NMR (acetone-d_6) δ −146.6 (s). ^{19}F NMR data can be found in ref. 30 which agree with those obtained in this study.

Diels–Alder reaction of fluoro-*p*-benzoquinone (2a) with Dane's diene (1)

Dane's diene (**1**, mixture with **4**)[41] (481 mg, 2.58 mmol) in diethyl ether (17 cm^3), fluoro-*p*-benzoquinone (**2a**) (264 mg, 2.10 mmol) and a trace of hydroquinone in a glass tube with a Young's tap were heated at 50 °C for 1 hour. During the reaction a bright-yellow precipitate was formed and the supernatant solution darkened. After cooling down to room temparature, the reaction mixture was left in the refrigerator for crystallisation overnight. After filtration, the residue (45% crude product yield) was washed with diethyl ether. Gas chromatographic analysis of the filtrate showed **2a** (32%) and fluorohydroquinone (**6a**) (11%) to be present. The residue was extracted with acetone and the filtrate thus obtained concentrated under reduced pressure, furnishing a regioisomeric mixture of **7a**,**b** as a bright-yellow solid, which crystallised as fine needles on slow evaporation of the solvent. The residue of the last filtration contained a regioisomeric mixture of **8a**,**b** as a bright-yellow solid, which was also crystallised as fine needles. Spectroscopic data were obtained from the spectra of the two regioisomeric mixtures.

3- and 2-Fluoro-8-methoxy-4a,4b,5,6,12,12a-hexahydrochrysene-1,4-dione (7a and 7b). 82 mg (13%) of **17a** and **17b** (91 : 9, ^{1}H NMR) (Found: C, 72.43%; H, 5.11%. $C_{19}H_{17}FO_3$ (312.3) requires C, 73.06; H, 5.49%); Found (HRMS): M + Na^+, 335.1098. $C_{19}H_{17}FO_3$ + Na^+ requires 335.1060.

Compound 7a. ^{1}H NMR (acetone-d_6) δ 1.78–1.88 (m, 1 H, 5-H), 2.27 (ddt, $^{3\text{ or }2}J_{H,H}$ 12.9, $^{3\text{ or }2}J_{H,H}$ 12.2, $^3J_{H,H}$ 5.2, 1 H, 5-H), 2.40–2.60 (m, 2 H, 12-H), 2.62–2.90 (m, 3 H, 6-H, H-4b), 3.29–3.41 (m, 1 H, 12a-H), 3.71–3.77 (m, 1 H, 4a-H), 3.76 (s, 3 H, OCH_3), 6.09–6.11 (m, 11-H), 6.44 (dd, $^4J_{H,H}$ 1.1, $^3J_{H,F}$ 12.2, 1 H, 2-H), 6.64 (d, $^4J_{H,H}$ 2.6, 1 H, 7-H), 6.71 (dd, $^4J_{H,H}$ 2.6, $^3J_{H,H}$ 8.8, 1 H, 9-H), 7.51 (d, $^4J_{H,H}$ 8.8, 1 H, 10-H); ^{13}C NMR (acetone-d_6) δ 26.5 (t, C-5 or C-6), 27.2 (t, C-5 or C-6), 31.2 (t, C-12), 38.1 (dd, $^4J_{C,F}$ 2.6, C-4b), 48.6 (d, C-12a), 50.0 (dd, $^3J_{C,F}$ 3.8, C-4a), 54.9 (q, OCH_3), 113.1 (d, C-7 or C-9), 113.4 (d, C-7 or C-9), 114.6 (d, C-11), 117.2 (dd, $^3J_{C,F}$ 8.9, C-2), 124.9 (d, C-10), 127.2 (s, C-10a), 129.4 (s, C-10b), 138.5 (s, C-6a), 159.2 (s, C-8), 191.9 (d, $^3J_{C,F}$ 14.5, C-1), 198.8 (d, $^2J_{C,F}$ 21.1, C-4);[54] ^{19}F NMR (acetone-d_6) δ −111.7 (d, $^3J_{F,H}$ 12.2); *m*/*z* 312 (100%, M^+), 297 (12, $M^+ - CH_3$), 295 (14), 291 (12), 290 (13), 284 (36, 312 − CO), 281 (9, $M^+ - OCH_3$), 249 (14), 207 (14), 191 (24), 167 (24), 147 (32), 115 (13).[55]

Compound 7b. ^{1}H NMR (acetone-d_6) δ 1.78–1.88 (m, 1 H, 5-H), 2.27 (ddt, $^{3\text{ or }2}J_{H,H}$ 12.9, $^{3\text{ or }2}J_{H,H}$ 12.2, $^3J_{H,H}$ 5.2, 1 H, 5-H), 2.40–2.60 (m, 2 H, 12-H), 2.62–2.90 (m, 3 H, 6-H, H-4b), 3.29–3.41 (m, 1 H, 12a-H), 3.71–3.77 (m, 1 H, 4a-H), 3.76 (s, 3 H, OCH_3), 6.09–6.11 (m, 11-H), 6.50 (d, $^3J_{H,F}$ 12.2, 1 H, 3-H), 6.64 (d, $^4J_{H,H}$ 2.6, 1 H, 7-H), 6.71 (dd, $^4J_{H,H}$ 2.6, $^3J_{H,H}$ 8.8, 1 H, 9-H), 7.53 (d, $^4J_{H,H}$ 9.1, 1 H, 10-H); ^{19}F NMR (acetone-d_6) δ −115.6 (dd, $^4J_{F,H}$ 5.7, $^3J_{F,H}$ 12.2); *m*/*z* 312 (100%, M^+), 297 (26, $M^+ - CH_3$), 295 (23), 291 (13), 284 (4, 312 − CO), 263 (36), 249 (23), 220 (24), 207 (23), 167 (28), 109 (22), 88 (27).[55]

3- and 2-Fluoro-8-methoxy-4a,5,6,11,12,12a-hexahydrochrysene-1,4-dione (8a and 8b). 72 mg (0.23 mmol, 11%)[56] of **8a** and **8b** (92 : 8, ^{1}H NMR) (Found: C, 72.54%; H, 5.22%. $C_{19}H_{17}FO_3$ (312.3) requires C, 73.06; H, 5.49%); *m*/*z* (ESI) 313 (100%, M + H^+), 285 (8, 313 − CO), 186 (92, $C_{13}H_{14}O^+$; retro-Diels–Alder after tautomerisation), 161 (28), 155 (27), 121 (13). Found (HRMS): M + Na^+, 335.1084. $C_{19}H_{17}FO_3$ + Na^+ requires 335.1060.

Compound 8a. ^{1}H NMR ($CDCl_3$) δ 1.95–2.14 (m, 2 H, 11-H), 2.15–2.38 (m, 2 H, 5-H), 2.40–2.65 (m, 2 H, 12-H), 2.66–2.94 (m, 2 H, 6-H), 3.08–3.17 (m, 12a-H), 3.64–3.70 (m, 4a-H), 3.76 (s, 3 H, OMe), 6.37 (dd, $^4J_{H,H}$ 0.7, $^3J_{H,F}$ 11.2, 1 H, 2-H), 6.68–6.74 (m, 2 H, 7-H, 9-H), 7.09–7.14 (m, 1 H, 10-H); ^{13}C NMR ($CDCl_3$) δ 24.2 (t, C-12), 25.2 (t, C-11), 27.7 (t, C-5), 28.3 (t, C-6), 48.4 (d, C-12a), 52.4 (dd, $^3J_{C,F}$ 3.9, C-4a), 55.3 (q, OCH_3), 111.1 (d, C-9), 113.5 (d, C-7), 118.7 (dd, $^2J_{C,F}$ 7.7, C-2), 123.5 (d, C-10), 125.0 (d, $^4J_{C,F}$ 1.8, C-4b), 127.9 (s, C-10a), 129.4 (s, C-10b), 137.6 (s, C-6a), 158.9 (s, C-8), 162.8 (d, $^1J_{C,F}$ 297.7, C-3), 191.1 (d, $^2J_{C,F}$ 19.2, C-4), 198.9 (d, $^3J_{C,F}$ 14.4, C-1); ^{19}F NMR ($CDCl_3$) δ −109.1 (d, $^3J_{F,H}$ 11.2).[55]

Compound 8b. ^{1}H NMR ($CDCl_3$) δ 1.95–2.14 (m, 2 H, 11-H), 2.15–2.38 (m, 2 H, 5-H), 2.40–2.65 (m, 2 H, 12-H), 2.66–2.94 (m, 2 H, 6-H), 3.08–3.17 (m, 12a-H), 3.64–3.70 (m, 4a-H), 3.76 (s, 3 H, OMe), 6.41 (d, $^3J_{H,F}$ 11.0, 1 H, 3-H), 6.68–6.74 (m, 2 H, 7-H, 9-H), 7.09–7.14 (m, 1 H, 10-H); ^{13}C NMR ($CDCl_3$) δ 24.0 (t, C-12), 24.8 (t, C-11), 27.7 (t, C-5), 28.3 (t, C-6), 46.5 (dd, $^3J_{C,F}$ 3.3, C-12a), 54.0 (d, C-4a), 55.3 (q, OCH_3), 111.1 (d, C-9), 113.1 (d, C-7), 119.2 (dd, $^2J_{C,F}$ 7.9, C-3), 123.4 (d, C-10), 128.0 (s, C-10a), 130.0 (s, C-10b), 137.6 (s, C-6a), 158.8 (s, C-8), 162.0 (d, $^1J_{C,F}$ 296.4, C-2), 192.5 (d, $^2J_{C,F}$ 18.3, C-1), 197.2 (d, $^3J_{C,F}$ = 12.4, C-4);[57] ^{19}F NMR ($CDCl_3$) δ −110.6 (dd, $^4J_{F,H}$ 3.8, $^3J_{F,H}$ 11.0).[55]

Diels–Alder reaction of 2,3-difluoro-*p*-benzoquinone (2b) with Dane's diene (1)

To Dane's diene (**1**) (215 mg, 1.16 mmol) in diethyl ether (8 cm^3) was added 2,3-difluoro-*p*-benzoquinone (**2b**) (68 mg, 0.47 mmol). The solution turned red immediately and was stirred at 50 °C for 45 min in a glass tube with a Young's tap. The reaction was accompanied by precipitation of a yellow solid, which was filtered after cooling down to room temperature. The residue (118 mg) contained a share of 90% (^{19}F NMR) of two products (73 : 27),[58] each of which contained two fluorine atoms per molecule.

main product. ^{19}F NMR ($CDCl_3$) δ −136.4 (d, $^3J_{F,F}$ 5.7, 1 F), −139.2 (dd, $^4J_{F,H}$ 5.7, $^3J_{F,F}$ 5.7, 1 F).

minor product. ^{19}F NMR ($CDCl_3$) δ −136.7 (d, $^3J_{F,F}$ 5.7, 1 F), −137.9 (dd, $^4J_{F,H}$ 5.7, $^3J_{F,F}$ 5.7, 1 F).

2,3-Difluoro-8-methoxy-4b,5,6,12-tetrahydrochrysene-1,4-diol (14). was obtained as a red solid (93 mg, 60%) on attempted column-chromatographic separation (after coating crude product on silica gel; pentane–diethyl ether 10 : 1, 6 : 1) of the residue. (Found: C, 68.62; H, 4.59. $C_{19}H_{16}F_2O_3$ (330.3) requires C, 69.08; H, 4.88%); mp 151–152 °C (diethyl ether). ^{1}H NMR (acetone-d_6) δ 1.55 (ddt, $^3J_{Hax,Heq}$ 5.5, $^3J_{Hax,Hax}$ 12.6, $^3J_{Hax,Hax}$ = $^2J_{H,H}$ 12.2, 1 H, 5-H_{ax}), 2.80 (ddt, $^3J_{Heq,Hax}$ 6.2, $^3J_{Heq,Hax}$ = $^3J_{Heq,Heq}$ 1.9, $^2J_{H,H}$ 12.2, 1 H, 5-H_{eq}), 2.88 (dd, $^3J_{Heq,Hax}$ 6.0, $^2J_{H,H}$ 17.3, 1 H, 6-H_{eq}), 3.14 (ddd, $^3J_{Hax,Hax}$ 12.6, $^3J_{Hax,Heq}$ 6.0, $^2J_{H,H}$ 17.3, 1 H, 6-H_{ax}), 3.43 (dm, $^3J_{H,H}$ 3.7, 1 H, 12-H), 3.52–3.62 (m, 1 H, 4b-H), 3.77 (s, 3 H, 13-H), 6.01 (t, $^3J_{H,H}$ 3.7, 1 H, 11-H), 6.67 (d, $^4J_{H,H}$ 2.6, 1 H, 7-H), 6.73 (dd, $^4J_{H,H}$ 2.6, $^3J_{H,H}$ 8.6, 1 H, 7-H), 7.38 (d, $^3J_{H,H}$ 8.6, 10-H), 8.09 (s, 1 H, OH), 8.19 (s, 1 H, OH); ^{13}C NMR (acetone-d_6) δ 25.3 (dt, $^4J_{C,F}$ 2.5, C-12), 30.5 (t, C-5 or C-6), 32.2 (t, C-5 or C-6), 35.7 (dd, $^4J_{C,F}$ 2.5, C-4b), 54.9 (q, C-13), 112.6, 113.5, 114.7 (each d, C-7, C-9, C-11), 118.2 (d, $^3J_{C,F}$ 2.5, C-4a or C-12a), 122.3 (d, $^3J_{C,F}$ 2.5, C-4a or C12a), 125.7 (d, C-10), 130.3 (s, C-10a), 135.3 (d, $^2J_{C,F}$ 11.4, C-1 or C-4), 135.8 (s, C-10b), 136.2 (d, $^2J_{C,F}$ 11.4, C-1 or C-4), 137.6 (s, C-6a), 139.6 (dd, $^2J_{C,F}$ 15.3, $^1J_{C,F}$ 239.1, C-2 or C-3), 140.1 (dd, $^2J_{C,F}$ 15.3, $^1J_{C,F}$ 239.1, C-2 or C-3), 159.4 (s, C-8); ^{19}F NMR (acetone-d_6) δ −163.9 (d, $^3J_{F,F}$ 21.0), −164.2 (d, $^3J_{F,F}$ 21.0); *m*/*z* 330 (100%, M^+), 326 (25), 315 (19, M^+–CH_3), 302 (32, M^+–CO after tautomerisation), 299 (10, $M^+ - OCH_3$), 279 (15), 265 (15), 253 (22), 209 (18, $M^+ - COHC_2F_2COH$ − H), 207 (21), 185 (22, $C_{13}H_{14}O^+$ − H; retro Diels–Alder after tautomerisation), 158 (18, 185 − C_2H_3), 147 (22), 145 (23, $C_6H_2F_2O_2^+$ + H; retro Diels–Alder after tautomerisation), 121 (23), 102 (20), 66 (21), 40 (92). Found (HRMS): M^+, 331.1149. $C_{19}H_{16}F_2O_3$ + H^+ (331.3) requires 331.1146.[55]

Diels–Alder reaction of 2,6-difluoro-*p*-benzoquinone (2c) with Dane's diene (1)

3,4a- and 2,12a-Difluoro-8-methoxy-4a,4b,5,6,12,12a-hexahydrochrysene-1,4-dione (15a and 15b). Dane's diene (**1**) (173 mg, 0.93 mmol) and 2,6-difluoro-*p*-benzoquinone (**2c**) (146 mg, 1.01 mmol) were dissolved in diethyl ether (6 cm^3) and stirred for 12.5 h at rt. The solution turned bright-red immediately and the formation of a yellow precipitate was observed. The product mixture was concentrated under reduced pressure (water bath of rotary evaporator not exceeding 40 °C) and the regioisomeric mixture of cycloadducts (315 mg, quantitative) **15a** and **15b** (93 : 7, ^{19}F NMR) was furnished as a green foam, showing a purity of 95% (^{19}F NMR; also ^{1}H NMR just indicated minor impurities). **15a**,**b**. *m*/*z* (ESI) 353 (28%, M + Na^+), 331 (13, M + H^+).

Compound 15a. ^{1}H NMR ($CDCl_3$) δ 1.86–1.96 (m, 2 H, 5-H), 2.55–2.93 (m, 5 H, 4b-H, 6-H, 12-H), 3.39 (dt, $^3J_{H,F}$ 10.7, $^3J_{H,H}$ 6.4, 1 H, 12a-H), 3.76 (s, 3 H, OMe), 6.02–6.07 (m, 1 H, 11-H), 6.47 (d, $^3J_{H,F}$ 10.7, 1 H, 2-H), 6.57 (d, $^4J_{H,H}$ 2.6, 1 H, 7-H), 6.71

(dd, $^4J_{H,H}$ 2.6, $^3J_{H,H}$ 8.8, 1 H, 9-H), 7.40 (d, $^3J_{H,H}$ 8.8, 1 H, 10-H); ^{19}F NMR ($CDCl_3$) δ −111.2 (dd, $^4J_{F,F}$ 3.8, $^3J_{F,H}$ 10.7, 1 F, 3-F), −147.2 (ddd, $^4J_{F,F}$ 3.8, $^3J_{F,H}$ 19.1, $^3J_{F,H}$ 10.7, 1 F, 4a-F).

Compound 15b. ^{19}F NMR ($CDCl_3$) δ −113.1 (dd, $^4J_{F,F}$ 6.7, $^3J_{F,H}$ 10.5, 1 F, 2-F), −152.9 (dddd, $^4J_{F,F}$ 6.7, $^3J_{F,H}$ 28.6, $^3J_{F,H}$ 21.0, $^3J_{F,H}$ 7.6, 1 F, 12a–F).

3- and 2-Fluoro-8-methoxy-5,6-dihydrochrysene-1,4-dione (17a and 17b). On attempted chromatographic separation (after coating the product mixture **15a**,**b** on silica gel; cyclohexane–ethyl acetate 4 : 1) of the crude product mixture **15a**,**b**, these cycloadducts suffered from HF-elimination and oxidative aromatisation of the C-ring. Immediately after column chromatography, a regioisomeric mixture of **17a**,**b** started to precipitate in the collected fractions as fine, dark-red leaves which were isolated by filtration (49 mg, 17%, **17a/17b** 86 : 14, GC) and were virtually insoluble in all common organic solvents: only in dichloromethane and toluene were **17a**,**17b** sufficiently soluble for spectrometric and spectroscopic characterisation. Compounds **15a**,**b** could only be isolated as partially decomposed material.

Compounds 17a and 17b. (Found: C, 72.55; H, 4.44. $C_{19}H_{13}FO_3 \cdot \frac{1}{3}H_2O$ requires C, 72.61; H, 4.38%); ν_{max}/cm^{-1} (KBr): 3450 (br s, crystal water), 3078 (w, ν–C=C–H_{aromat}), 2933 (w, ν–CH_2), 2837 (w, ν–OCH_3), 1673 (m) or 1653 (s) (ν–C=O), 1640/1625 (m, ν–C=C and δ–$OH_{crystal\ water}$), 1563 (m), 1502 (m, ring vibration-$_{aromat}$), 1460 (w, δ–CH_2/CH_3), 1336 (w), 1309 (w), 1281/1254 (m, ν–C–O–Ph and ν–C–F), 1171 (w), 1150 (w), 1040 (w), 978 (w), 820 (w), 620 (w).

Compound 17a. ^{1}H NMR (toluene-d_8) δ 2.41 (t, $^3J_{H,H}$ 7.1, 2 H, 5-H or 6-H), 3.32 (t, $^3J_{H,H}$ 7.1, 2 H, 5-H or 6-H), 3.32 (s, 3 H, 13-H), 5.88 (d, $^3J_{H,F}$ 10.0, 1 H, 2-H), 6.52 (d, $^4J_{H,H}$ 2.6, 1 H, 7-H), 6.64 (d, $^4J_{H,H}$ 2.6, $^3J_{H,H}$ 8.6, 1 H, 9-H), 7.21 (d, $^3J_{H,H}$ 8.6, 1 H, 10-H), 7.43 (d, $^3J_{H,H}$ 8.1, 1 H, 11-H or 12-H), 7.89 (d, $^3J_{H,H}$ 8.1, 1 H, 11-H or 12-H); ^{13}C NMR (toluene-d_8) δ 25.6 (t, C-5), 28.4 (t, C-6), 52.7 (q, C-13), 113.1 (d, C-7 or C-9), 113.3 (d, C-7 or C-9), 115.1 (dd, $^2J_{C,F}$ 10.2, C-2), 126.4 (d, C-10 or C-12), 128.1 (d, C-10 or C-12), 161.0 (s, C-8), 161.3 (d, $^1J_{C,F}$ 287.4, C-3), 179.4 (d, $^2J_{C,F}$ 22.9, C-4), 183.6 (d, $^3J_{C,F}$ 18.1, C-1);[59] ^{19}F NMR (toluene-d_8) δ −109.4 (d, $^3J_{F,H}$ 10.0); *m*/*z* 307 (100%, M^+ − H), 292 (7, 307 − CH_3), 279 (9, 307 − CO), 264 (43, M^+ − C_2HF), 249 (12, 264 − CH_3), 237 (13), 218 (15), 207 (27), 201 (10, M^+ − $CH_3OC_6H_3$ − H), 189 (33), 187 (10, 201 − CH_2), 174 (5, M^+ − $CH_3OC_6H_3C_2H_4$), 165 (28), 130 (7), 110 (7), 93 (13), 81 (5).[60]

Compound 17b. Due to the very low solublity of **17a/b**, from the minor compound **17b** only a mass spectrum could be obtained, but owing to the almost identical fragmentation pattern compared to that of **17a**, the very similar retention time in GC, the elemental analysis of the product mixture **17a**,**b** and the presence of **15b** in the crude product, the structure of **17b** could be assigned. *m*/*z* 307 (100%, M^+ − H), 292 (7, 307 − CH_3), 279 (4, 307 − CO), 278 (14), 265 (35, M^+ − C_2HF + H), 260 (11), 248 (9), 237 (13), 217 (17), 207 (25), 201 (4, M^+ − $CH_3OC_6H_3$ − H), 189 (31), 187 (11, 201 − CH_2), 174 (4, M^+ − $CH_3OC_6H_3C_2H_4$), 165 (33), 130 (7), 118 (11), 110 (7), 94 (9), 81 (6).[60]

2,3,4a,12a-Tetrafluoro-8-methoxy-4a,4b,5,6,12,12a-hexahydrochrysene-1,4-dione (18)

Dane's diene (**1**) (380 mg, 2.04 mmol) and a trace of hydroquinone in dry toluene (5 cm^3) were added dropwise to a solution of tetrafluoro-*p*-benzoquinone (**2d**) (360 mg, 2.00 mmol) in toluene (2 cm^3). Directly after addition the solution turned dark. The reaction mixture was heated at 110 °C for 2 h in a glass tube with a Young's tap. After removal of the solvent under reduced pressure, the black crude product was coated on 2.5 g of silica gel and subjected to column chromatography (cyclohexane–ethyl acetate 15 : 1, 8 : 1). A bright red solid (401 mg, 55%) of *exo*-**18** and *endo*-**18** (89 : 11, ^{19}F NMR) was isolated (Found: C, 62.47; H, 4.29. $C_{19}H_{14}F_4O_3$ (366.3) requires C, 62.30; H, 3.85%); mp 161–163 °C (for a 87 : 13 mixture of *exo*-**18** and *endo*-**18**).

Compound *exo*-18. ^{1}H NMR ($CDCl_3$) δ 2.00–2.14 (m, 1 H, 5-H_{ax}), 2.32 (dq, $^3J_{H,H}$ 4.8, $^2J_{H,H}$ 12.2, 1 H, 5-H_{eq}), 2.75–3.03 (m, 4 H, 6-H, 12-H), 3.32 (tt, ^4J = $^3J_{H,H}$ 2.9, $^3J_{H,F}$ = $^3J_{H,H}$ 14.3, 1 H, 4b-H), 3.79 (s, 3 H, 13-H), 6.08–6.16 (m, 1 H, 11-H), 6.73 (d, $^4J_{H,H}$ 2.9, 1 H, 7-H), 6.76 (dd, $^4J_{H,H}$ 2.9, $^3J_{H,H}$ 8.8, 1 H, 9-H), 7.61 (d, $^3J_{H,H}$ 8.8, 1 H, 10-H); ^{13}C NMR (acetone-d_6) δ 23.3 (dt, $^3J_{C,F}$ 3.8, C-5), 30.3 (t, C-6), 32.8 (dt, $^3J_{C,F}$ 2.5, $^2J_{C,F}$ 25.4, C-12), 39.4 (ddd, $^3J_{C,F}$ 2.6, $^2J_{C,F}$ 22.9, C-4b), 55.2 (q, C-13), 93.8 (ddd, $^3J_{C,F}$ 5.1, $^2J_{C,F}$ 19.1, $^1J_{C,F}$ 200.9, C-4a or C-12a), 96.6 (ddd, $^3J_{C,F}$ 5.1, $^2J_{C,F}$ 17.8, $^1J_{C,F}$ 194.6, C-4a or C-12a), 110.5 (d, C-11), 113.5 (d, C-7 or C-9), 113.6 (d, C-7 or C-9), 124.9 (s, C-10a), 125.4 (d, C-10), 132.9 (d, $^3J_{C,F}$ 7.6, C-10b), 138.8 (s, C-6a), 146.0–150.8 (m, C-2, C-3), 159.5 (s, C-8), 181.6–184.2 (m, 2 C, C-1, C-4); ^{19}F NMR (acetone-d_6, proton decoupled) δ −135.8 (d, $^3J_{F,F}$ 5.7, 1 F, 2-F or 3-F), −137.8 (pseudo q, $^5J_{F,F}$ = $^4J_{F,F}$ = $^3J_{F,F}$ 5.7, 1 F, 2-F or 3-F), −160.1 (dd, $^4J_{F,F}$ 5.7, $^3J_{F,F}$ 12.2, 1 F, 4a-F or 12a-F), −170.0 (dd, $^5J_{F,F}$ 5.7, $^3J_{F,F}$ 12.2, 1 F, 4a-F or 12a-F); ^{19}F NMR (acetone-d_6) δ−135.8 (d, $^3J_{F,F}$ 5.7, 1 F, 2-F or 3-F), −137.8 (pseudo q, $^5J_{F,F}$ = $^4J_{F,F}$ = $^3J_{F,F}$ 5.7, 1 F, 2-F or 3-F), −159.9 to −160.2 (m, 1 F, 4a-F or 12a-F), −169.8 to −170.2 (m, 1 F, 4a-F or 12a-F); *m*/*z* 366 (38%, M^+), 346 (100, M^+ − HF), 331 (18, 346 − CH_3), 327 (23, 346 − F), 326 (19, 346 − HF), 290 (20), 284 (19), 270 (22), 255 (20), 246 (25), 238 (27), 228 (35, M^+ − COC_2F_2CO − HF), 213 (34), 201 (27), 189 (32), 186 (82, $C_{13}H_{14}O^+$; retro Diels–Alder), 171 (94, 186 − CH_3), 165 (25), 159 (52, 186 − C_2H_3), 155 (22, 186 − OCH_3), 153 (43), 145 (47), 128 (75), 115 (63), 51 (22, $C_4H_3^+$), 45 (27).

Compound *endo*-18.[61] (Found: C, 62.20; H, 4.26. $C_{19}H_{14}F_4O_3$ (366.3) requires C, 62.30; H, 3.85%); ^{1}H NMR ($CDCl_3$) δ 1.81–1.96 (m, 1 H, 5-H_{ax}), 2.24 (dq, $^3J_{H,H}$ 4.3, $^2J_{H,H}$ 12.9, 1 H, 5-H_{eq}), 2.74 (ddd, $^3J_{H,F}$ 1.9, $^3J_{H,H}$ 4.6, $^2J_{H,H}$ 17.9, 1 H, 12-H), 2.83–2.90 (m, 2 H, 6-H), 3.04 (dd br s, $^3J_{H,H}$ 4.6, $^2J_{H,H}$ 17.9, 1 H, 12-H), 3.81 (s, 3 H, 13-H), 4.62–4.71 (m, 1 H, 4b-H), 6.25 (dt, $^4J_{H,F}$ 1.9, $^3J_{H,H}$ 4.6, 1 H, 11-H), 6.65 (d, $^4J_{H,H}$ 2.6, 1 H, 7-H), 6.79 (dd, $^4J_{H,H}$ = 2.6, $^3J_{H,H}$ 8.8, 1 H, 9-H), 7.65 (d, $^3J_{H,H}$ 8.8, 1 H, 10-H); ^{13}C NMR ($CDCl_3$) δ 27.8 (t, C-6), 28.4 (d br t, $^3J_{C,F}$ 1.4, C-12), 29.5 (t, C-5), 55.3 (q, C-13), 72.8 (dd, $^2J_{C,F}$ 4.2, C-4b), 110.2 (d, C-11), 112.9 (d, C-7 or C-9), 113.3 (d, C-7 or C-9), 124.5 (s, C-10a), 124.8 (d, C-10), 136.7 (s, C-10b), 137.6 (s, C-6a), 159.5 (s, C-8);[62] ^{19}F NMR ($CDCl_3$) δ −129.5 (t, $^4J_{F,F}$ = $^3J_{F,F}$ 9.5, 1 F, 2-F or 3-F), −130.5 (t, $^4J_{F,F}$ = $^3J_{F,F}$ 9.5, 1 F, 2-F or 3-F), −159.5 (dd, $^4J_{F,F}$ 9.5, $^3J_{F,F}$ 3.8, 4a-F or 12a-F), −160.1 (dd, $^4J_{F,F}$ 9.5, $^3J_{F,F}$ 3.8, 4a-F or 12a-F); *m*/*z* 366 (9%, M^+), 186 (100, $C_{13}H_{14}O^+$; retro Diels–Alder), 171 (26, 186 − CH_3), 155 (7, 186 − OCH_3), 145 (12), 128 (14), 115 (13), 57 (10), 55 (8).[55]

Furthermore, tetrafluorohydroquinone (**6d**) (120 mg, 33%) was isolated by column chromatography. ^{1}H NMR (acetone-d_6) δ 9.09 (br s, 2 H, OH); ^{13}C NMR (acetone-d_6) δ 128.2 (tt, $^3J_{C,F}$ 6.4, $^2J_{C,F}$ 10.2, 2 C, C-1, C-4), 139.0 (dddd, $^4J_{C,F}$ 5.1, $^3J_{C,F}$ = $^2J_{C,F}$ 10.2, $^1J_{C,F}$ 240.3, 4 C, C-2, C-3, C-5, C-6); ^{19}F NMR (acetone-d_6) δ −164.7 (s); *m*/*z* 182 (100%, M^+), 162 (5, M^+ − HF), 106 (95, M^+ − 4 F), 75 (32), 71 (43), 56 (22). ^{19}F NMR data for this compound can be found in ref. 63 which agree with those obtained in this study.

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56 Conducting the reaction in toluene at 100 °C for 65 min furnished chrysenediones **8a/b** (76 : 24, ^{1}H NMR) in 26% yield.

57 C-4b could not be assigned from the available spectrum.

58 As this crude product mixture was just sparingly soluble in $CDCl_3$, the ratio observed by NMR possibly is not representative.

59 Due to the low solubility of this compound and/or superimposition with the signals arising from toluene-d_8, the resonances of the other carbons could not be assigned from the available spectrum.

60 Assignment of the regiochemistry was rationalized by the share of chrysenedione **15a** in the crude product.

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