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The trifluoromethoxy group as a fluorine twin in the Diels–Alder reactions of halogenated quinones

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ABSTRACT

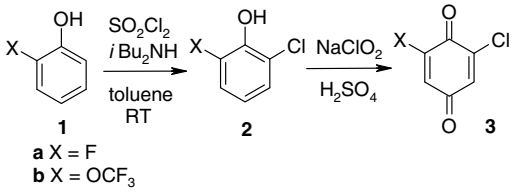
We describe here a study devoted to the comparison of the relative influence of chlorine, fluorine, and trifluoromethoxy substituents on the regiochemical outcome of the Diels–Alder reaction. For this purpose, we examined the behavior of mixed 'halogenated' quinones bearing these groups in their cycloadditions with simple dienes. Contrary to the expectation based on its known electronic properties, the trifluoromethoxy group behaves very much more like a fluorine than a chlorine atom in such reactions. On the basis on an endo transition state demonstrated here for these additions, we tentatively suggest that non-bonded interactions are the main factor controlling the regiochemistry.

The trifluoromethoxy group enjoys a great interest among fluorinated group in various applications thanks to its peculiar properties.[1] However, besides the field of aromatic compounds,[2] its chemistry is poorly known mainly because non-aromatic trifluoromethyl ethers are far less common than aromatic ones.[3,4] It has been demonstrated that, at least in the aromatic series, its electronic properties lie between that of a chlorine and a fluorine atom.[2,5] Although some trifluoromethoxy substituted alkenes are known,[4,6] to our knowledge, there is no report on their reactivity as dienophilic components in Diels–Alder reactions. Here, we present our results concerning the regio- and stereochemical outcome of the Diels–Alder addition of some halogenated quinones with simple symmetrical dienes, allowing a comparison between 'halogen' substituents (chloro, fluoro, and trifluoromethoxy).

In order to overcome the leveling effect resulting from the strong tendency of fluorobenzoquinone to give mainly addition products toward its hydrogenated side under kinetic conditions,[7,8] we selected to study the behavior of mixed 'halogenated' quinones (2-chloro-6-fluoro and 2-chloro-6-trifluoromethoxy benzoquinones) toughed to enable a finer analysis of the relative effects of these halogen atoms.

Quinones **3** were readily obtained by selective ortho chlorination of phenols **1**[9,10] followed by direct oxidation of chlorophenols **2** with sodium chlorite in an acidic medium using our earlier described method for trifluoromethylphenols (Scheme 1).[11]

Oxidation of 2-chloro-6-fluorophenol **2a** proved to be highly exothermic and was consequently performed at −10 °C instead of 0 °C. Quinones **3a** and **3b** were obtained, respectively, in 31% and 53% yield.[12] Their Diels–Alder reactions with dimethylbutadiene **4** or cyclopentadiene **7** occurred smoothly in dichloromethane at room temperature over 24 h.[13] After removal of the solvent, the adducts were obtained in essentially quantitative crude yields as a mixture of regioisomers **5** and **6** (or **8** and **9**, respectively)[14] (Table 1). These adducts proved unstable under the light as well as under slightly acidic conditions, but can be kept safely at low temperature in the dark for several weeks. Attempted chromatographic separations resulted in considerable decomposition and loss of material.[15]



Scheme 1. Synthesis of quinones.

Structure determination relied primarily on NMR spectroscopy. The distinction between the regioisomers derived from fluoroquinone **3a** was straightforward: signals for the vinylic fluorine atoms in **5a** and **8a** appeared at −109.5 and −107.0 ppm in the ^{19}F NMR spectra (compare with −110.2 ppm for quinone **3a**), whereas those for tertiary fluorine atoms in **6a** and **9a** were found at −153.2 and −141.7 ppm. Moreover, the vinylic hydrogen atoms (H3 in **5a** and H7 in **8a**) showed a coupling constant in the range 11–12 Hz with

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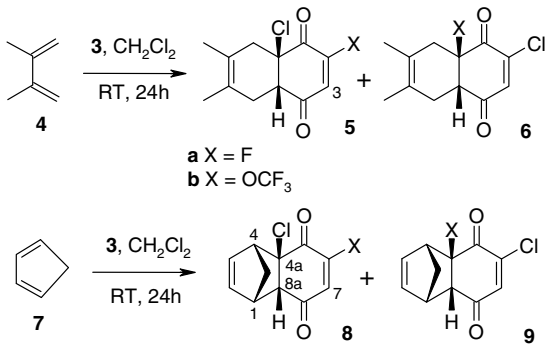
Table 1
Regioselectivity of the cycloadditions



Entry	X (quinone **3**)	Diene	Adducts (ratio)
1	F (**3a**)	**4**	**5a**:**6a** (95:5)
2	OCF_3 (**3b**)	**4**	**5b**:**6b** (91:9)
3	F (**3a**)	**7**	**8a**:**9a** (78:22)
4	OCF_3 (**3b**)	**7**	**8b**:**9b** (80:20)

the vinylic fluorine atom, while these nuclei appeared as broad singlets or faint doublets in adducts **6a** and **9a**. As expected, the fluorine chemical shift difference between the adducts bearing a trifluoromethoxy group was less clear cut, but remained sufficiently large to discriminate a vinylic OCF_3 (δ −58.6 to −58.8 ppm) from a tertiary OCF_3 group (δ −51.6 to −52.2 ppm). Again these assignments were corroborated by the coupling pattern of the vinylic atoms appearing as quadruplets (J_{FH} ca. 2 Hz) in **5b** and **8b**, and as singlets in **6b** and **9b**. Based on these assignments, and the relative integration of the vinylic protons in the ^{1}H NMR spectra, the regiochemical outcome of the Diels–Alder reactions studied here is presented in Table 1.

It is clearly apparent from the data gathered in Table 1 that the trifluoromethoxy group, in these cycloadditions, behaves very much like a fluorine than a chlorine atom. Adducts **5** and **8** bearing the chlorine atom in a tertiary position are predominantly obtained. The selectivity observed is somewhat lower with the more reactive cyclopentadiene and noticeably reversed between fluorine and trifluoromethoxy substituents.

In the case of cyclopentadiene adducts, the problem of the *endo* versus *exo* addition of quinones had to be resolved. Usually Diels–Alder reactions of common quinones occur exclusively via an *endo* transition state.[16] It has been reported, however, that some fluorinated dienophiles[8,17] gave sometimes the products arising from an

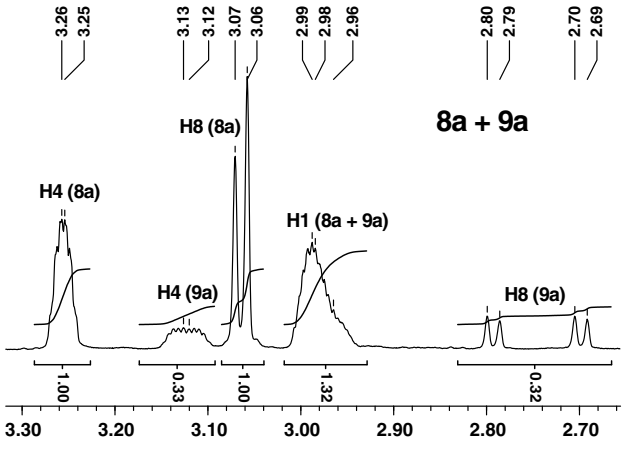


Figure 1. Partial (tertiary protons region) ^{1}H NMR spectrum (C_6D_6, 300 MHz) of adducts mixture **8a** and **9a**.

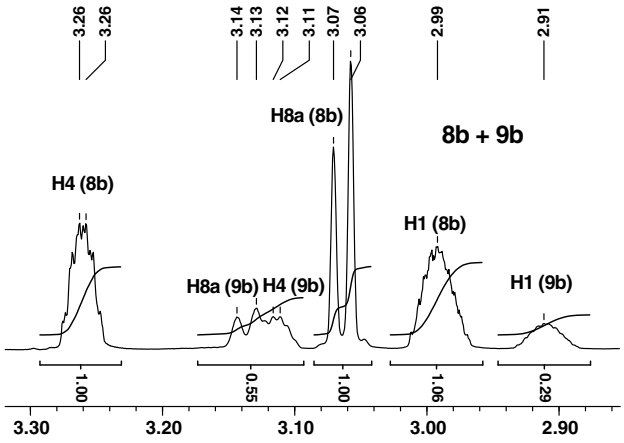


Figure 2. Partial (tertiary protons region) ^{1}H NMR spectrum (C_6D_6, 300 MHz) of adducts mixture **8b** and **9b**.

exo transition state. ^{1}H NMR spectra run in $CDCl_3$ were useless for this purpose, very important signals from H1, H4, and H8a being highly crowded in a very narrow range (3.5–3.6 ppm). Spectra run in C_6D_6 were more informative, signals from H8a could be unambiguously located in all adducts (**8a**, δ = 3.06; **9a**, δ = 2.74; **8b**, δ = 3.06; **9b**, δ = 3.14 ppm)[18] and appeared as clean doublets with a coupling constant in the range 3.9–4.4 Hz with H1 (see Figs. 1 and 2).[19] Such a coupling constant is highly diagnostic of an *exo* position for H8a.[20] Consequently all cycloadditions with cyclopentadiene reported here occurs via the usual *endo* transition state.

Considering the very mild conditions used, it can be safely assumed that no retro Diels–Alder reactions occurred during these cycloadditions. The ratio of regioisomers shown in Table 1 concerns thus primary adducts and not an equilibrated mixtures of regioisomers. On this ground, the regioselectivity observed in these normal electron demand Diels–Alder reactions seems somewhat amazing. Based on electronic arguments alone (inductive and resonance effects of the substituents),[2] we should have observed an intermediate behavior of the trifluoromethoxy group lying somewhere between that of a chlorine or a fluorine atom but not so close to the latter.[21]

If an *endo* transition state could be assumed, as deduced above for cyclopentadiene, during reactions of both dienes studied here, it may be speculated that a chlorine atom may experience more severe interactions with the diene substituents in such transition state than the smaller fluorine atom. This may explain the results observed with chlorofluorobenzoquinone **3a**. But could this explanation also apply for the presumably bulkier trifluoromethoxy group? Obviously the Van der Waals volume of OCF_3 could be considered far bigger than that of a fluorine atom. However, the conformational degree of freedom exhibited by the ether linkage, may largely compensate this bulkiness handicap in some selected situations.[22] Moreover, contrary to the methoxy group, the OCF_3 substituent is known to adopt a perpendicular position out of the plane of an aromatic ring.[1,6,23] One can tentatively assume that this situation also hold for the case of trifluoromethoxybenzoquinones. On this basis, it can be presumed that steric interactions with a trifluoromethylether are mainly restricted to the oxygen atom.[24] Knowing the nearly isosteric relationship between fluorine and oxygen,[25] we propose that, under such conditions, the trifluoromethoxy group and the fluorine atom behave similarly, their comparable steric requirements overwhelming the relatively small disparity of their electronic properties.

We tried to rationalize these unexpected results by FMO calculations. In fact, such kind of computations have been performed

with some success on related fluorinated systems (but not including the trifluoromethoxy group).[26] Our own FMO calculations at the B3LYP/6-31G* level gave qualitative results in accordance with the experimental results for quinone **3a** but failed with the trifluoromethoxy substituted quinone **3b**. Indeed, very recently, Lemal caution for the risk associated with such 'prediction about reaction pathways' for Diels–Alder reactions of *o*-Fluoranil.[27]

Thus, to date, explanations developed above may be considered highly speculative and will constitute a challenge for more sophisticated calculations.

Nevertheless, we have shown in this work, that in the Diels–Alder reaction of benzoquinones with simple dienes, the trifluoromethoxy group behaves like a fluorine twin. We think that these results may prove highly useful for those who plan to introduce an OCF_3 group in a molecule by the means of a Diels–Alder reaction.

Acknowledgements

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10. 2-Chloro-6-fluorophenol **2a** is commercially available.
Procedure for 2-chloro-6-trifluoromethoxyphenol (**2b**) Sulfuryl chloride (9 mL, 112 mmol) was added dropwise to a hot (70 °C) stirred solution of 2-trifluoromethoxyphenol **1b** (20 g, 112 mmol) in toluene (250 mL) containing diisobutylamine (0.156 mL, 0.9 mmol). After 1 h stirring at 70 °C, and cooling, most of the solvent was removed by rotatory evaporation. The residue was diluted with ether (200 mL) and washed twice with 0.3 M sulfuric acid. After drying ($MgSO_4$) and removal of solvent, 21 g (99 mmol, 88% yield) of chlorophenol **2b** was obtained as an oil for suitable further oxidation. ^{19}F NMR ($CDCl_3$, 188 MHz) δ: −58.8 (d, J = 1.4 Hz); ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.30 (dd, 1H, J = 8.2, 1.5 Hz), 7.18 (d quint, J = 8.3, 1.5 Hz), 6.89 (t, 1H, J = 8.2 Hz), 5.73 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 144.9, 137.1, 127.9, 121.7, 121.1, 120.6 (q, J = 259 Hz), 120.4. HRMS: calculated for $C_7H_3{}^{35}ClFNa_2O_2$ 256.9573; found: 256.9596 δ −1.4 ppm.
11. (a) Blazejewski, J.-C.; Dorme, R.; Wakselman, C. *Synthesis* **1985**, 1120–1121; (b) Blazejewski, J.-C.; Dorme, R.; Wakselman, C. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1861–1864.
12. *General procedure for the preparation of quinones* **3**: A solution of sodium chlorite hydrate (320 mmol) in water (85 mL) was added at once to a (magnetically) well-stirred suspension of the chlorophenol **2a** or **2b** (80 mmol) in sulfuric acid (0.3 M, 270 mL) in an open flask cooled in an ice bath (an ice salt bath was used for phenol **2a**). The temperature quickly rose to 30–35 °C with strong evolution of chlorine dioxide vapors. The mixture was stirred in the cold for an additional hour after the exotherm had ceased, then degassed with continuous stirring (ice bath still present) under the vacuum of a water aspirator. The bright yellow crystals formed were collected by filtration and pooled with the hexane extracts (3 × 100 mL) of the resulting aqueous phase. The organic phase was dried ($MgSO_4$), filtered, and allowed to crystallize at −30 °C. The quinone **3a** or **3b** was obtained in three crops by filtration followed each time by slight concentration of the hexane phase and recooling.
2-Chloro-6-fluoro-1,4-benzoquinone (**3a**): Yield 31%; mp 84–85 °C. ^{19}F NMR ($CDCl_3$, 188 MHz) δ: −110.2 (d, J = 9 Hz); ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.01 (d, 1H, J = 2.4 Hz), 6.50 (dd, 1H, J = 8.8, 2.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 183.8 (d, J = 14 Hz), 172.4 (d, J = 25 Hz,), 159.6 (d, J = 292 Hz), 142.1 (d, J = 7 Hz), 133.8 (s), 115.5 (d, J = 10 Hz). HRMS: calculated for $C_6H_2{}^{35}ClFO$ 159.9722; found: 159.97143 δ −4.7 ppm.
2-Chloro-6-trifluoromethoxy-1,4-benzoquinone (**3b**): Yield 53%; mp 88–89 °C. ^{19}F NMR ($CDCl_3$, 188 MHz) δ: −58.9 (d, J = 2 Hz); ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.05 (d, 1H, J = 2.3 Hz), 6.56 (quint, 1H, J = 2.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 183.2, 172.0, 148.8 (q, J = 1 Hz), 142.7, 133.6, 119.9 (q, J = 265 Hz), 118.4 (q, J = 2 Hz). HRMS: calculated for $C_7H_2{}^{35}ClF_3O_3$ 225.9639; found 225.96349 δ −1.8 ppm.
13. No efforts were made to check the optimal reaction time.
14. *General procedure for Diels–Alder reactions. A solution of the quinone* **3a** or **3b** (2.2 mmol) and a slight excess of the appropriate diene **4** or **7** (2.6 mmol) in dichloromethane (25 mL), shielded from light with an aluminum foil, was allowed to stir for 24 h under an argon atmosphere. After removal of the solvent, a mixture of the adducts was obtained either as a pale yellow powder (**8a** and **9a**) or as an oil (mixture of **8b** and **9b**) in essentially quantitative yield.
8a-Chloro-2-fluoro-6,7-dimethyl-4a,5,8,8a-tetrahydro-[1,4]naphthoquinone (**5a**) (major isomer): ^{19}F NMR ($CDCl_3$, 188 MHz) δ: −109.5 (ddd, J = 10.9, 2.9, 1.6 Hz). ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.34 (ddd, 1H, J = 10.9, 1.3, 0.8 Hz), 3.42 (dddd, 1H, J = 10.9, 9.5, 7.3, 1.4 Hz), 3.02 and 2.48 (AB system, 2H, J = 16.9 Hz), 2.2–2.4 (m, 2H), 1.64 (m, 3H), 1.57 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 195.1 (d, J = 13 Hz), 183.6 (d, J = 22 Hz), 160.3 (d, J = 296 Hz), 122.7, 123.3, 116.6 (d, J = 8 Hz), 67.4 (d, J = 5 Hz), 55.7, 38.8 (d, J = 2 Hz), 33.3, 18.5, 17.9. HRMS: calculated for $C_{12}H_{12}{}^{35}ClFO_2$ 242.0504; found 242.04996 δ −2.0 ppm.
2-Chloro-8a-fluoro-6,7-dimethyl-4a,5,8,8a-tetrahydro-[1,4]naphthoquinone (**6a**) (minor isomer): ^{19}F NMR ($CDCl_3$, 188 MHz) δ: −153.2 (ddd, J = 29.5, 19, 9 Hz). ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.05 (s, 1H); other signals are obscured by signals from the major isomer. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 192.1 (d, J = 10 Hz), 187.3 (d, J = 21 Hz), 145.8 (d, J = 3 Hz), 137.6, 123.7 (d, J = 1 Hz), 120.0 (d, J = 2 Hz), 94.3 (d, J = 191 Hz), 51.6 (d, J = 21 Hz), 36.0 (d, J = 24 Hz), 27.7 (d, J = 2 Hz), 18.4.
8a-Chloro-2-trifluoromethoxy-6,7-dimethyl-4a,5,8,8a-tetrahydro-[1,4]naphthoquinone (**5b**) (major isomer): ^{19}F NMR ($CDCl_3$, 188 MHz) δ: −58.6 (d, J = 2.3 Hz). ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.39 (m, 1H); 3.46 (ddd, 1H, J = 10.0, 7.1, 1.3 Hz); 3.05 and 2.51 (AB system, 2H, J = 17.2 Hz), 2.2–2.5 (m, 2H); 1.67 (br s, 3 H); 1.60 (br s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ:194.8, 183.2, 149.7 (q, J = 1 Hz), 123.7, 122.5, 120.1 (q, J = 264 Hz), 119.7 (q, J = 1 Hz), 67.5, 55.5, 39.1, 33.7, 18.6, 18.0. HRMS: calculated for $C_{13}H_{12}{}^{35}ClF_3O_3$ 308.0422; found 308.04207 δ −0.3 ppm.
2-Chloro-8a-trifluoromethoxy-6,7-dimethyl-4a,5,8,8a-tetrahydro-[1,4] naphthoquinone (**6b**) (minor isomer): ^{19}F NMR ($CDCl_3$, 188 MHz) δ: −52.2 (d, J = 1.3 Hz). ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.94 (q, 1H), 3.36 (br t, 1H, J = 7.7 Hz), 2.86 (d, 1H, J = 17.3 Hz), 1.62 (br s, 3H) other signals are obscured by signals from the major isomer. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 193.2, 186.0, 145.2, 136.0, 121.7, 122.7, 84.9, 52.5, 35.6 (q, J = 1 Hz), 31.1, 18.7, 18.2.
4a-Chloro-6-fluoro-1,4,4a,8a-tetrahydro-1,4-methano-naphthalene-5, 8-dione (**8a**) (major isomer): ^{19}F NMR ($CDCl_3$, 188 MHz) δ: −107.0 (d, J = 11.1 Hz). ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.43 (d, 1H, J = 11.1 Hz), 6.19 (dd, 1H, J = 5.7, 2.5 Hz), 6.04 (dd, 1H, J = 5.7, 3.1 Hz), 3.60–3.50 (m, 3H), 2.08 (br d, 1H, J = 9.5 Hz), 1.85 (dt, 1H, J = 9.5, 1.6 Hz). ^1H NMR (C_6D_6, 300 MHz) δ: 5.68 (d, 1H, J = 11.4 Hz), 5.57 (dd, 1H, J = 5.7, 2.8 Hz), 5.44 (dd, 1H, J = 5.6, 3.1 Hz), 3.25 (m, 1H), 3.06 (d, 1H, J = 3.9 Hz), 2.98 (m, 1H); 1.52 (br d, 1H, J = 9.5 Hz), 1.18 (dt, 1H, J = 9.5, 1.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 194.5 (d, J = 14 Hz), 185.0 (d, J = 21 Hz), 162.9 (d, J = 296 Hz), 138.7, 134.6, 122.1 (d, J = 10 Hz), 68.4 (d, J = 6 Hz), 62.8, 55.1 (d, J = 2 Hz), 47.8, 47.1. HRMS: calculated for $C_{11}H_8{}^{35}ClFO_2$ 226.0191; found 226.01808 δ −4.7 ppm.
6-Chloro-4a-fluoro-1,4,4a,8a-tetrahydro-1,4-methano-naphthalene-5, 8-dione (**9a**) (minor isomer): ^{19}F NMR ($CDCl_3$, 188 MHz) δ: −141.7 (dd quint, J = 28.2, 6.6, 2 Hz). ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.95 (s, 1H), 6.27 (dt, 1H,J = 5.6, 2.3 Hz), 5.26 (dt, 1H, J = 5.6, 2.2 Hz), 3.42 (m, 1H), 3.26 (dd, 1H, J = 28.2, 4.0 Hz); 2.00 (dq, 1H, J = 9.4, 1.4 Hz), 1.82 (dq, 1H, J = 9.4, 1.5 Hz). ^1H NMR (C_6D_6, 300 MHz) δ: 6.28 (s, 1H), 5.62 (dt, 1H, J = 5.8 Hz, J = 2.3 Hz), 5.96 (dt, 1H, J = 5.7 Hz, J = 2.9 Hz), 3.12 (m, 1H); c.a. 2.96 (m, 1H), 2.74 (dd, 1H, J = 28.5 Hz, J = 4.0 Hz), c.a. 1.49 (m, 1H); c.a. 1.18 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 193.2 (d, J = 5 Hz), 185.8 (d, J = 21 Hz), 148.8 (d, J = 4 Hz), 140.8 (d, J = 3 Hz), 140.6, 132.1 (d, J = 8 Hz), 97.3 (d, J = 201 Hz), 58.1 (d, J = 21 Hz), 53.0 (d, J = 24 Hz), 47.3 (d, J = 2 Hz), 47.0. HRMS: calculated for $C_{11}H_8{}^{35}ClFO_2$ 226.0191; found 226.01826 δ −3.9 ppm.
4a-Chloro-6-trifluoromethoxy-1,4,4a,8a-tetrahydro-1,4-methano-naphthalene-5,8-dione (**8b**) (major isomer): ^{19}F NMR ($CDCl_3$, 188 MHz) δ: −58.6 (d, J = 2.1 Hz). ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.51 (q, 1H, J = 2.1 Hz), 6.23 (dd, 1H, J = 5.6, 2.1 Hz), 6.07 (dd, 1H, J = 5.6, 3.0 Hz), 3.68–3.43 (m, 3H); 2.11 (br dq, 1H, J = 9.6, *ca* 1Hz), 1.87 (br dt, 1H, J = 9.6, 1.7 Hz). ^1H NMR (C_6D_6, 300 MHz) δ: 6.11 (q, 1H, J = 1.8 Hz), 5.61 (dd, 1H, J = 5.7, 2.8 Hz), 5.50 (dd, 1H, J = 5.7, 3.1 Hz), 3.26 (m, 1H); 3.06 (d, 1H, J = 3.9 Hz), 2.99 (m, 1H), 1.52 (br d, 1H, J = 9.5 Hz), 1.19 (dt, 1H, J = 9.5, 1.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 193.9, 184.5, 152.5 (q, J = 1Hz), 138.8, 135.0, 124.8 (q, J = 2 Hz), 119.9 (q, J = 265 Hz), 68.4, 62.4, 55.0, 47.6, 47.0. HRMS: calculated for $C_{12}H_8{}^{35}ClF_3O_3$ 292.0109; found 292.00995 δ −3.1 ppm.
6-Chloro-4a-trifluoromethoxy-1,4,4a,8a-tetrahydro-1,4-methano-naphthalene-5,8-dione **(9b)** (minor isomer): ^{19}F NMR ($CDCl_3$, 188 MHz) δ: −51.6 (s).^1H NMR

($CDCl_3$, 300 MHz) δ: 6.95 (s, 1H); 6.30 (dd, 1H, J = 5.8, 2.7 Hz), 5.99 (dd, 1H, J = 5.8, 3.2 Hz), 3.68—3.43 (m, 3H,), 2.01 (br dt, 1H, J = 9.6, 1.5 Hz), 1.80 (br dt, 1H, J = 9.6, 1.6 Hz). ^{1}H NMR (C_6D_6, 300 MHz) δ: 6.36 (s, 1H); 5.55 (dd, 1H, J = 5.7, 2.8 Hz), 5.28 (dd, 1H, J = 5.7, 3.2 Hz), 3.14 (d, 1H, J = 4.4 Hz), 3.11 (m, 1H), 2.91 (m, 1H); 1.35 (br d, 1H, J = 9.5 Hz), 1.06 (br dt, 1H, J = 9.6, 1.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 193.0, 185.8, 148.9, 140.7, 139.6, 132.3, 121.2 (q, J = 260 Hz), 86.6, 56.8 (q, J = 1 Hz), 55.1, 48.9, 47.6. HRMS: calculated for $C_{12}H_8{}^{35}ClF_3O_3$ 292.0109; found 292.01142 δ 1.9 ppm.

15. The main products isolated resulted from elimination of the bridgehead 'halogen' substituent, with eventual further aromatization in the case of dimethylbutadiene adducts.
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18. These values are concentration dependent. Consequently, concentrations of the samples were adjusted to give the maximum dispersion of the signals of interest in the ^{1}H NMR spectra.
19. In the case of **9a** the signal for H8a was further splitted (J = 28.2 Hz) by coupling with the vicinal fluorine atom, pointing thus to a cis relationship between these nuclei (see Ref. 8).
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