New, Simple and Selective Synthesis of Perfluoroalkylquinones by Perfluoroalkyl Radicals – Enthalpic and Polar Effects

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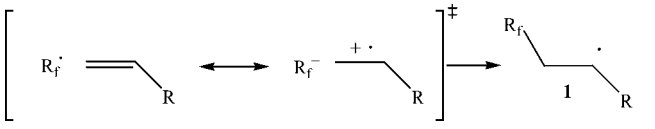
Perfluoroalkyl radicals ($R_f^{\cdot}$), generated by iodine abstraction from perfluoroalkyl iodides by phenyl radicals, react selectively with quinone rings in spite of their electrophilic character. In the presence of electron-rich alkenes, $R_f^{\cdot}$ adds faster to the electron-rich double bonds forming a radical adduct with reversed polar effect, which selectively adds to quinone. The mechanism of the reactions involved are discussed, emphasizing the key role of enthalpic and polar effects and the particular reactivity of 2-methoxynaphthoquinone due to polar and captodative effects.

Introduction

Quinones are an important class of organic compounds: They occur naturally in plants, fungi, and bacteria, and a few, such as vitamin K and ubiquinone, play an important biological role in quinone-mediated electron-transfer processes. Quinones are also important industrial products and are largely used in dyes, photographic developers, medicines, fungicides, and other products.[1]

Because of their electron-deficient character, quinones are highly reactive with nucleophilic radicals. The free radical alkylation process has been developed as a general and simple route for the functionalization of quinones.[2]

On the other hand the introduction of perfluoroalkyl groups in an organic molecule is a challenge in organic synthesis today, e.g. in the preparation of suitable reagents or catalysts for fluorous phase applications[3] or green chemistry with supercritical CO_2.[4] An example is the modification of the anthraquinone process of H_2O_2 production, making the anthraquinone compatible with supercritical CO_2 by functionalization with perfluorinated chains.[5] The higher reactivity of perfluoroalkyl, $R_f^{\cdot}$, compared to alkyl, $R^{\cdot}$, radicals, is mainly ascribed[6] to their electrophilic character, determined by the high electron affinity of fluorine atoms, which is reflected in a large contribution of the polar forms of the transition states in addition reactions [Equation (1)] to unsaturated substrates.



(1)

A relatively low reactivity of $R_f^{\cdot}$ with the electron-deficient quinones would therefore be foreseen from this assumption.

However, more recently we have shown[7] that both polar and enthalpic effects are very important in determining the reactivity and selectivity of perfluoroalkyl radicals, but with the prevalence of the latter in the reaction with alkenes, aromatic rings and alkanes.

This is due to the fact that C–C and C–H bonds formed by $R_f^{\cdot}$ are stronger than those formed by the corresponding alkyl radicals (i.e. the bond dissociation enthalpies, BDE, of the C–C bonds in CF_3–CH_3[8] and CH_3–CH_3[8] are 101 and 91 kcal mol^{-1}, respectively, and the BDE values of the C–H bonds in CF_3CF_2–H and CH_3CH_2–H are 103[9] and 100.5[10] kcal mol^{-1}, respectively).

Thus, the free radical iodination of alkanes, which cannot be accomplished by I_2 for enthalpic reasons, has been made possible[11] by the free radical chain of Equations (2) and (3), due to the higher BDE values of R_f–H compared to R–H.

$$R_f^{\cdot} + R\text{–}H \rightarrow R_f\text{–}H + R^{\cdot} \quad (2)$$

$$R_f\text{–}I + R^{\cdot} \rightarrow R_f^{\cdot} + R\text{–}I \quad (3)$$

Moreover, the reaction of acrylonitrile and 1-hexene with the *n*-perfluoropropyl radical have a similar rate constant,[6]

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2.2×10^6 and 6.2×10^6 $M^{-1} s^{-1}$, respectively, in spite of their different polar character.

Also, the relative rates of the addition of $R_f^{\cdot}$ to the aromatic rings[7] strongly confirm that electrophilic character is a significant but not the major factor, for the increased aromatic reactivity of $R_f^{\cdot}$ compared to alkyl radicals. The fact that *n*-$C_4F_9^{\cdot}$ is more reactive (ca. 10^4 $M^{-1} s^{-1}$) with nitrobenzene[7] than primary alkyl radicals are with benzene (ca. 10^2 $M^{-1} s^{-1}$)[12,13] is further evidence that the main factor, which determines the increased reactivity in aromatic perfluoroalkylation, is the enthalpic and not the polar effect. The selectivity of the aromatic substitution is in any case very low with both electron-rich and electron-poor aromatic compounds[7] and also with heteroaromatic bases.[14]

Primary alkyl radicals, on the contrary, react four orders of magnitude faster with acrylonitrile[15] than with 1-hexene.[16]

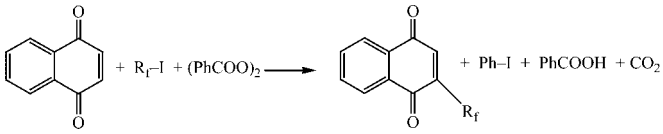
The relatively low polar effect of the $R_f^{\cdot}$ reactions can also be related to their σ nature. The polarizability of the radicals contributed favorably to the extent of the polar effect since it allows a larger contribution of polar forms to the transition state; the polarizability of σ radicals is lower than that of the π radical. Thus, the polar effect for phenyl and cyclopropyl σ radicals is lower than that of the cyclohexyl π radical in the addition to aromatic compounds[12] and heteroaromatic bases.[14]

All these considerations suggested that quinones could be selectively functionalized by both electrophilic radicals $R_f^{\cdot}$ and the nucleophilic radical adduct **1** formed by addition of $R_f^{\cdot}$ to alkenes.

Results

The perfluoroalkylation of the quinones was performed according to the following differing procedures:

A) The direct perfluoroalkylation of quinones was carried out by refluxing the quinone, the perfluoroalkyl iodide and benzoyl peroxide in acetic acid solution. The stoichiometry of the reaction is given by Equation (4).



(4)

The method appears to be particularly effective since the amount of Ph–I accounts for >95% of the perfluoroalkylated quinones. *n*-C_4F_9I and *n*-$C_6F_{13}I$ were employed and in both cases high conversion and selectivity were observed.

The results are reported in Table 1. Products **2**–**6** are shown in Figure 1.

B) Two different procedures were used in the perfluoroalkylation of quinones in the presence of olefins:

B_1) The reaction was carried out as in A, simply by refluxing quinone, perfluoroalkyl iodide, alkenes and benzoyl peroxide in acetic acid solution.

B_2) In the presence of 2-methoxynaphthoquinone the procedure B_1 is not suitable since the direct reactions of the perfluoroalkyl and phenyl radicals with the quinone com-

Table 1. Direct perfluoroalkylation of quinones following procedure A.

Quinone	R_f–I	Product	Conversion (%)	Selectivity[a] (%)
Naphthoquinone	*n*-C_4F_9I	**2**	100	98
2-Methylnaphthoquinone	*n*-C_4F_9I	**3**	100	98
2,3,5-Trimethylbenzoquinone	*n*-$C_6F_{13}I$	**4**	100	93
2,3-Dimethoxy-5-methylbenzoquinone	*n*-$C_6F_{13}I$	**5**	100	98
2-Methoxynaphthoquinone	*n*-$C_6F_{13}I$	**6**	100	99

[a] The selectivities refer to the products reported.

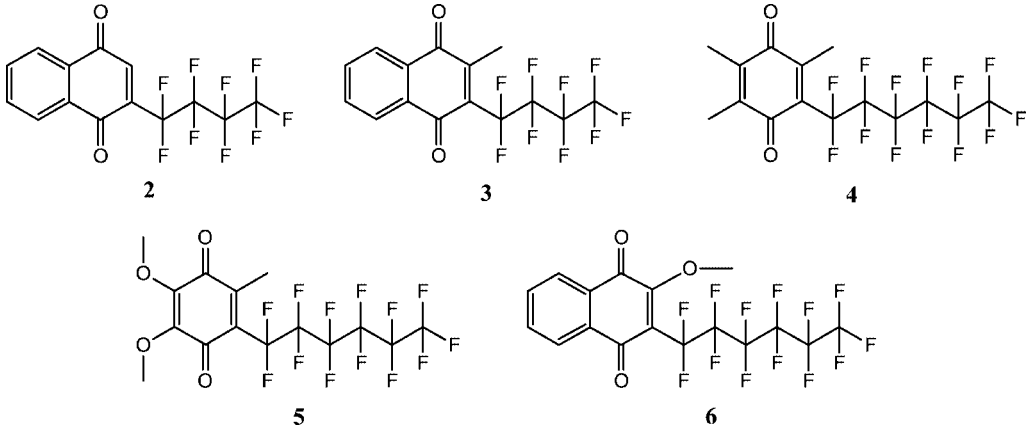


Figure 1. Products obtained by direct perfluoroalkylation of quinones.

Table 2. Perfluoroalkylation of quinones carried out in the presence of alkenes.

Quinone	Alkene	R_f–I	Product	Conversion (%)	Selectivity[a] (%)
Naphthoquinone	1-hexene	n-C_4F_9I	**7**[b]	100	99
2-Methylnaphthoquinone	1-hexene	n-C_4F_9I	**8**[b]	100	99
2-Methylnaphthoquinone	4-penten-1-ol	n-C_4F_9I	**9**[b]	97	94
2-Methylnaphthoquinone	allyl alcohol	n-C_4F_9I	**10**[b]	89	76[d]
2-Methylnaphthoquinone	3-cyanopropene	n-$C_6F_{13}I$	**11**[b]	100	76
2-Methoxynaphthoquinone	1-hexene	n-$C_6F_{13}I$	**12**[c]	100	99
2-Methoxynaphthoquinone	3-cyanopropene	n-$C_6F_{13}I$	**13**[c]	100	84[e]

[a] The selectivities refer to the products reported. [b] Procedure B_1. [c] Procedure B_2. [d] 24% of 2-methyl-3-phenylnaphthoquinone is formed. [e] 12% of product **6**.

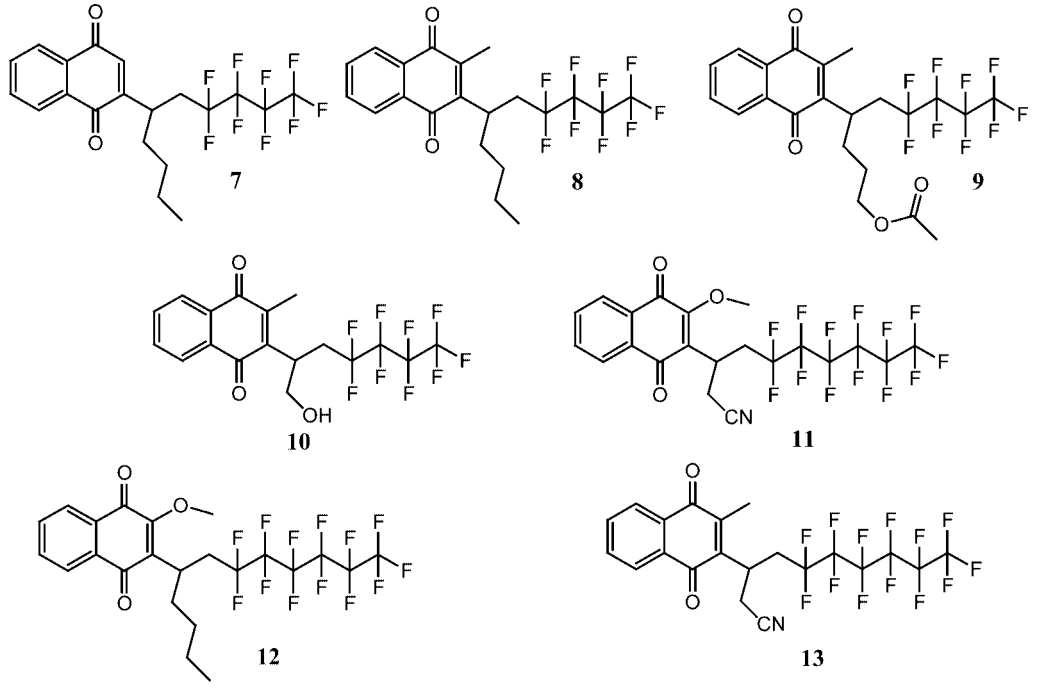


Figure 2. Products obtained by perfluoroalkylation of quinones in the presence of alkenes.

pete with the addition to the alkene, also in the presence of an excess of alkene. The procedure was modified into a two-step one-pot reaction by refluxing the alkene and R_f–I with a catalytic amount of benzoyl peroxide in acetic acid solution. The quinone and $(PhCOO)_2$ were successively added and the resulting solution was further refluxed until the completion of the reaction was reached. In this way the byproducts arising from the addition of $R_f^{\cdot}$ and $Ph^{\cdot}$ radicals to the quinone were drastically reduced (Table 2). Products **7**–**13** are shown in Figure 2.

Discussion

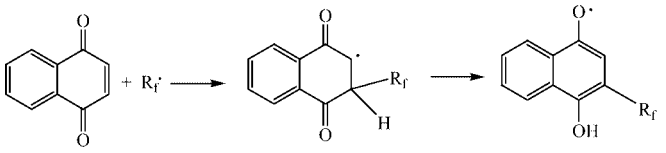
The reaction mechanism for the direct perfluoroalkylation involves the homolytic decomposition of benzoyl peroxide [Equation (5)].

$$(PhCOO)_2 \rightarrow 2\ PhCOO^{\cdot} \rightarrow 2\ Ph^{\cdot} + 2\ CO_2 \quad (5)$$

The iodine abstraction from R_f–I by the phenyl radical [Equation (6)] appears to be so fast (diffusion-controlled rate) that the hydrogen abstraction from the solvent or the addition to the quinone ring cannot compete; Equation (6) accounts for more than 95% of the reacted R_f–I.

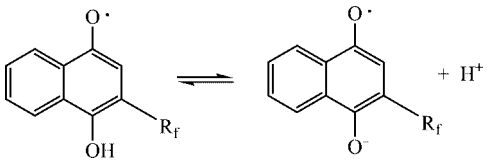
$$Ph^{\cdot} + I\text{–}R_f \xrightarrow{k_6} Ph\text{–}I + R_f^{\cdot};\ k_6 > 10^9\ M^{-1}\,s^{-1} \quad (6)$$

The $R_f^{\cdot}$ radical selectively adds to the quinone ring leading to the semiquinone radical [Equation (7)].



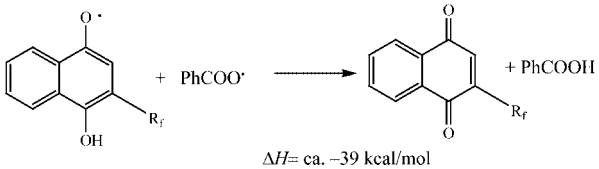
(7)

The semiquinone radical has two important features: (i) the BDE value of the O–H bond is much lower[17] (ca. 54 kcal mol^{-1}) than that of phenol[18] (88 kcal mol^{-1}); moreover, it is much more acidic (pK_a = 4.1)[19] than phenol so that the equilibrium of Equation (8) is significant.

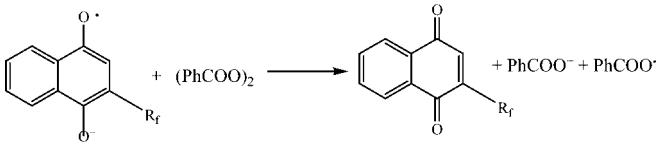


(8)

These features suggest two likely mechanisms leading to the reaction products: a strongly exothermic hydrogen abstraction from the relatively persistent semiquinone according to Equation (9) and an electron transfer in a chain process [Equation (10)].



(9)

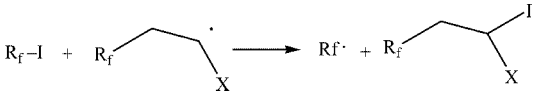


(10)

Equation (9) is justified by the fact that the semiquinone radical, being a radical with some persistency,[20] may couple with a transient radical like $PhCOO^{\bullet}$.[21] Equation (10) is a classical electron-transfer decomposition reaction of $(PhCOO)_2$[22] induced by easily oxidizable radicals like semiquinone radical anions.[23]

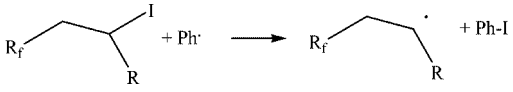
In the presence of electron-rich alkenes the perfluoroalkyl radicals, $R_f^{\cdot}$, react faster with the double bond than with the quinone ring leading to the iodide adduct by the chain process of Equations (11) and (12).

(11)

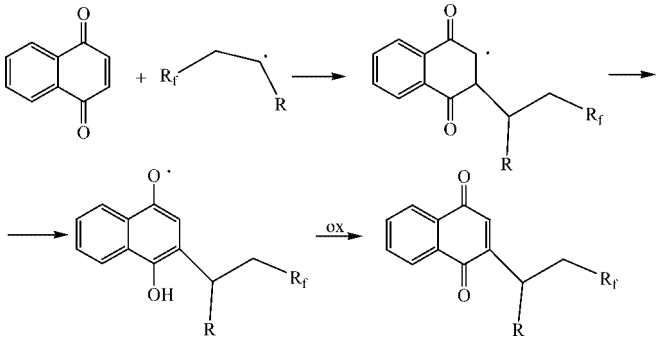


(12)

This is clearly shown by using catalytic amounts of benzoyl peroxide; only the adduct to the alkene was observed without significant reaction of the quinone, which means that both the radical addition to the double bond [Equation (11)] and iodine abstraction from R_f–I by the radical adduct [Equation (12)] are faster than the addition of the same radicals to the quinone ring. However, in the presence of stoichiometric amounts of benzoyl peroxide, the adduct of Equation (12) further reacts with the phenyl radical [Equation (13)] regenerating the radical adduct of Equation (11), which adds selectively to the quinone ring leading to the reaction product [Equation (14)] by oxidations similar to Equations (9) and (10).



(13)



(14)

The overall kinetics of all the radicals involved in Equations (5)–(7) and (9)–(14), makes the process particularly selective for a one-step one-pot procedure, by refluxing all the reagents in acetic acid solutions.

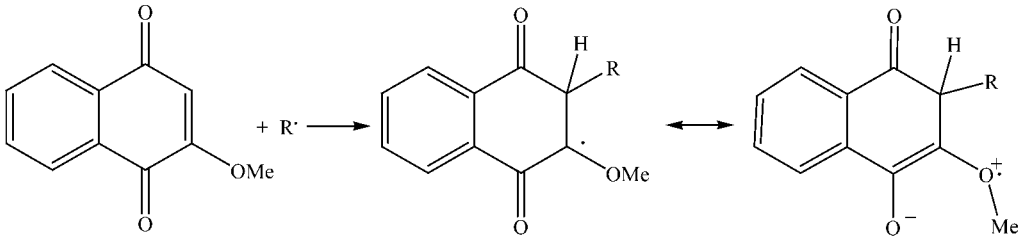
In all the reactions performed, R_f–I is used in excess in order to maximize the selectivity of the iodine abstraction from the iodide with $Ph^{\cdot}$, which is in competition with the addition of $Ph^{\cdot}$ to the quinone. For similar reasons, an excess of alkene is employed in order to add $R_f^{\cdot}$ preferentially to the olefin.

The use of a twofold excess of benzoyl peroxide is a consequence of the process optimization, in order to obtain the highest conversion and selectivity.

Attempts to utilize the one-pot procedure with 2-methoxynaphthoquinone gave poor results due to the increased reactivity of 2-methoxynaphthoquinone towards free radicals compared to unsubstituted naphthoquinone. Thus, the addition of phenyl and perfluoroalkyl radicals to quinone competes with Equations (6) and (11) with the formation of significant amounts of byproducts.

The increased free radical reactivity of 2-methoxynaphthoquinone can be mainly related, in our opinion, to an enthalpic effect associated with a captodative stabilization of the radical adduct [Equation (15)].

However, we succeeded in performing the reaction selective, in the presence of alkenes with 2-methoxynaphthoquinone, by carrying out the process in a two-step one-pot procedure. Initially, the perfluoroalkyl iodide was added to the alkene in the presence of a catalytic amount of benzoyl peroxide and in the absence of 2-methoxynaphthoquinone according to Equations (11) and (12). The quinone and the stoichiometric amount of benzoyl peroxide were successively added to the reaction solutions leading, with good selectivity, to the final product by reactions analogous to



(15)

Equations (13) and (14). This occurs since the perfluoroalkyl radicals are not formed in the presence of the quinone and the iodine abstraction from the iodide adduct by the phenyl radical [Equation (13)] is faster than the addition of the phenyl radical to the quinone ring.

Conclusions

An easy entry to substituted quinones with perfluoroalkyl radical has been described. The perfluoroalkyl tails may be directly attached to the quinone, or linked to a spacer as obtained in the alternate reactions in the presence of an electron-rich olefin. Both procedures enable substituted quinones that are potentially useful in fluorous-phase chemistry to be obtained.

The importance of polar and enthalpic effects in the reaction of perfluoroalkyl radicals with quinones, in the presence and in the absence of electron-rich olefins has been described. Once again these processes are more examples showing that perfluoroalkyl radical chemistry is driven, in general, by enthalpic effects and that polar effects only play a minor role. In the case of quinones in the presence of olefins, the importance of the polar effect allowed for selective addition of the perfluoroalkyl radicals to the olefins. However, the addition of a strong electrophilic radical to electron-poor substrates, such as the quinones, probably would have not been possible in the absence of a strong enthalpic effect.

In the specific case of 2-methoxynaphthoquinone the captodative effect (which is an enthalpic effect) and the favorable polar effect, due to the electron-donating behavior of the methoxy group with respect to the quinone double bond, increase the reactivity of the quinone to a value of the same order of magnitude as that of a hydrocarbon olefin.

Experimental Section

General Methods: The quinones, the perfluoroalkyl iodides and the alkenes were commercial products and were used without further purification. All the reaction products were unknown; they were isolated by flash column chromatography and identified by MS, ^{1}H NMR and ^{19}F NMR spectroscopy. Mass spectra were performed with a GLC-MS instrument, using a gas chromatograph equipped with an SBP-1 fused silica column (30 m × 0.2 mm i.d., 0.2 μm film thickness) and helium as carrier gas. NMR spectra were carried out with a Bruker Avance spectrometer operating at 500 MHz (^{1}H) and 470 MHz (^{19}F). ^{1}H and ^{19}F NMR chemical shifts are referenced to internal $(CH_3)_4Si$ and CCl_3F, respectively. Spectral analysis was supported by ^{1}H{^{19}F} broadband decoupling.

General Procedure for the Perfluoroalkylation of Quinones. Procedure A: A solution of quinone (2 mmol), perfluoroalkyl iodide (6 mmol) and benzoyl peroxide (4 mmol) in 10 mL of acetic acid was refluxed for 4 h. The acetic acid was removed under vacuum, a solution of 10% aqueous $NaHCO_3$ was added and the mixture was extracted with ethyl acetate. The reaction products were analyzed by GC-MS, isolated by flash chromatography on silica gel (eluent hexane/ethyl acetate, 9:1) and identified by ^{1}H NMR and ^{19}F NMR spectroscopy. The results are reported in Table 1.

General Procedure for the Perfluoroalkylation of Quinones in the Presence of Alkenes. Procedure B_1: A solution of quinone (2 mmol), perfluoroalkyl iodide (6 mmol), alkene (6 mmol) and benzoyl peroxide (4 mmol) in 10 mL of acetic acid was refluxed for 4 h. The acetic acid was removed under vacuum, a solution of 10% aqueous $NaHCO_3$ was added and the mixture was extracted with ethyl acetate. The reaction products were analyzed by GC-MS, isolated by flash chromatography on silica gel (eluent hexane/ethyl acetate, 9:1) and identified by ^{1}H NMR and ^{19}F NMR spectroscopy. The results are reported in Table 2. **Procedure B_2 (with 2-Methoxynaphthoquinone):** The reaction was carried out as in Procedure A but with only 0.3 mmol of benzoyl peroxide, in the absence of quinone. The reaction mixture was analyzed according to Procedure A, revealing high yields (>90% based on R_f–I) of the adduct **1**. After 1 h, 2 mmol of 2-methoxynaphthoquinone and another 4 mmol of benzoyl peroxide were added and the solution was refluxed for additional 4 h. The workup was the same as that of Procedure B_1. Results are reported in Table 2.

Characterization of the Reaction Products

Naphthoquinone 2: M.p. 58–60 °C. GC-MS: *m*/*z* = 376 $[M]^{+\cdot}$, 357, 348, 207, 179, 129, 104, 76. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33 (s, 1 H), 7.82 (t, J = 6.6 Hz, 1 H), 7.85 (t, J = 6.6 Hz,1 H), 8.12 (dd, J = 1.3, J = 6.6 Hz, 1 H), 8.17 (dd, J = 1.3, J = 6.6 Hz, 1 H) ppm. ^{19}F NMR (470 MHz, CCl_3F): δ = –126.6 to –126.9 (m, 2 F, F_γ), –121.6 to –121.8 (m, 2 F, F_β), –111.9 (t, J = 13.4 Hz, 2 F, F_α), –81.7 (t, J = 10.7 Hz, 3 F, F_δ) ppm. $C_{14}H_5F_9O_2$ (376.17): calcd. C 44.70, H 1.34, F 45.45, O 8.51; found C 44.75, H 1.34, F 45.32, O 8.48.

Naphthoquinone 3: M.p. 78–80 °C. GC-MS: *m*/*z* = 390 $[M]^{+\cdot}$, 371, 221, 171, 143, 104, 76, 69. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.43 (t, J = 3.6 Hz, 3 H), 7.77 (td, J = 1.7, J = 7.3 Hz, 1 H), 7.80 (td, J = 1.7, J = 7.3 Hz, 1 H), 8.10–8.14 (m, 2 H) ppm. ^{19}F NMR (470 MHz, CCl_3F): δ = –126.9 to –127.1 (m, 2 F, F_γ), –121.1 to –121.3 (m, 2 F, F_β), –104.7 to –104.8 (m, 2 F, F_α), –81.7 (t, J = 7.2 Hz, 3 F, F_δ) ppm. $C_{15}H_7F_9O_2$ (390.20): calcd. C 46.17, H 1.81, F 43.82, O 8.20; found C 46.10, H 1.80, F 43.87, O 8.25.

Benzoquinone 4: M.p. 50–52 °C. GC-MS: *m*/*z* = 468 $[M]^{+\cdot}$, 449, 249, 149, 134, 119, 69. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.06 (s, 3 H), 2.07 (s, 3 H), 2.27 (t, J = 3.5 Hz, 3 H) ppm. ^{19}F NMR (470 MHz,

CCl_3F): δ = –127.8 to –128.0 (m, 2 F, F_ε), –124.4 to –124.9 (m, 2 F, F_δ), –122.9 to –123.7 (m, 2 F, F_γ), –121.4 to –121.5 (m, 2 F, F_β), –106.0 to –106.2 (m, 2 F, F_α), –82.5 (t, J = 9.8 Hz, 3 F, F_ζ) ppm. $C_{13}H_9F_9O_2$ (368.19): calcd. C 42.41, H 2.46, F 46.44, O 8.69; found C 42.30, H 2.45, F 46.50, O 8.66.

Benzoquinone 5: M.p. 42–44 °C. GC-MS: m/z = 500 $[M]^{+\cdot}$, 485, 480, 231, 186, 119, 69. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.27 (t, J = 3.8 Hz, 3 H), 4.02 (s, 3 H), 4.03 (s, 3 H) ppm. ^{19}F NMR (470 MHz, CCl_3F): –127.8 to –128.0 (2 m, 2 F, F_ε), –124.4 to –124.9 (m, 2 F, F_δ), –122.9 to –123.7 (m, 2 F, F_γ), –121.4 to –121.5 (m, 2 F, F_β), –105.8 to –106.0 (m, 2 F, F_α), –82.0 (t, J = 9.8 Hz, 3 F, F_ζ) ppm. $C_{15}H_9F_{13}O_4$ (500.21): calcd. C 36,02, H 1.81, F 49.38, O 12.79; found C 36,12, H 1.80, F 49.25, O 12.89.

Naphthoquinone 6: Oil. GC-MS: m/z = 506 $[M]^{+\cdot}$, 486, 456, 267, 237, 151, 104, 76, 69. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.29 (s, 3 H), 7.73 (td, J = 1.4, J = 7.6 Hz,1 H), 7.78 (td, J = 1.4, J = 7.6 Hz, 1 H), 8.04 (dd, J = 1.0, J = 7.6 Hz, 1 H), 8.09 (dd, J = 1.0, J = 7.6 Hz,1 H) ppm. ^{19}F NMR (470 MHz, CCl_3F): δ = –127.3 to –127.5 (m, 2 F, F_ε), –124.1 to –123.6 (m, 2 F, F_δ), –123.0 to –123.5 (m, 2 F, F_γ), –121.9 to –122.2 (m, 2 F, F_β), –107.6 to –107.9 (m, 2 F, F_α), –82.1 (t, J = 9.8 Hz, 3 F, F_ζ) ppm. $C_{17}H_7F_{13}O_3$ (506.21): calcd. C 40.34, H 1.39, F 48.79, O 9.48; found C 40.42, H 1.39, F 48.63, O 9.51.

Naphthoquinone 7: Oil. GC-MS: m/z = 460 $[M]^{+\cdot}$, 445, 431, 241, 157, 76, 69. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.32 (t, J = 7.0 Hz, 3 H), 1.63–1.84 (m, 4 H), 2.15–2.28 (m, 2 H), 2.82–2.94 (m,1 H), 3.07–3.21 (m, 1 H), 3.73–3.79 (br., 1 H), 7.26 (s, 1 H), 8.17–8.21 (m, 2 H), 8.53 (dd, J = 2.4, J = 5.5 Hz,1 H), 8.57 (dd, J = 2.4, J = 5.5 Hz, 1 H) ppm. ^{19}F NMR (470 MHz, CCl_3F): δ = –127.2 to –127.4 (m, 2 F, F_γ), –125.7 to –125.9 (m, 2 F, F_β), –114.3 (q, J = 272 Hz, 2 F, F_α), –82.5 (t, 3 F, J = 6.6 Hz, F_δ) ppm. $C_{20}H_{17}F_9O_2$ (460.33): calcd. C 52.18, H 3.72, F 37.14, O 6.95; found C 52.10, H 3.73, F 37.22, O 6.96.

Naphthoquinone 8: Oil. GC-MS: m/z = 474 $[M]^{+\cdot}$, 459, 445, 405, 255, 157, 76, 69. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84 (t, J = 7.0 Hz, 3 H), 1.14–1.34 (m, 4 H), 1.76–1.83 (m, 1 H), 1.92–2.00 (m, 1 H), 2.24 (s, 3 H), 2.37–2.52 (m, 1 H), 2.93–3.10 (m, 1 H), 3.24–3.38 (br., 1 H), 7.64–7.68 (m, 2 H), 8.02–8.07 (m, 2 H) ppm. ^{19}F NMR (470 MHz, CCl_3F): δ = –127.3 to –127.5 (m, 2 F, F_γ), –125.7 to –125.9 (m, 2 F, F_β), –114.9 (q, J = 269 Hz, 2 F, F_α), –82.6 (t, J = 9.6 Hz, 3 F, F_δ) ppm. $C_{21}H_{19}F_9O_2$ (474.36): calcd. C 53.17, H 4.04, F 36.05, O 6.75; found C 52.99, H 4.05, F 36.12, O 6.73.

Naphtoquinone 9: Oil. GC-MS: m/z = 518 $[M]^{+\cdot}$, 476, 458, 255, 198, 104, 76, 69. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.48–1.66 (m, 2 H), 1.82–1.90 (m, 1 H), 1.97 (s, 3 H), 1.99–2.06 (m, 1 H), 2.23 (s, 3 H), 2.37–2.54 (m, 1 H), 2.90–3.08 (m, 1 H), 3.24–3.39 (br., 1 H), 4.01 (t, J = 6.6 Hz, 2 H), 7.65–7.69 (m, 2 H), 8.00–8.06 (m, 2 H) ppm. ^{19}F NMR (470 MHz, CCl_3F): δ = –127.0 to –127.3 (m, 2 F, F_γ), –125.5 to –125.9 (m, 2 F, F_β), –114.7 (q, J = 272 Hz, 2 F, F_α), –82.3 (t, J = 9.3 Hz, 3 F, F_δ) ppm. $C_{22}H_{19}F_9O_4$ (518.37): calcd. C 50.97, H 3.69, F 32.99, O 12.35; found C 51.02, H 3.71, F 33.11, O 12.32.

Naphthoquinone 10: Oil. GC-MS: m/z = 448 $[M]^{+\cdot}$, 430, 417, 229, 198, 171, 104, 76, 69. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.27 (s, 3 H), 2.49–2.66 (m, 1 H), 2.87–3.05 (m, 1 H), 3.63–3.72 (br., 1 H), 4.44 (d, J = 7.5 Hz, 2 H,), 7.70–7.75 (m, 2 H), 8.04–8.12 (m, 2 H) ppm. ^{19}F NMR (470 MHz, CCl_3F): δ = –127.0 to –127.2 (m, 2 F, F_γ), –125.3 to –125.6 (m, 2 F, F_β), –114.2 (q, J = 272 Hz, 2 F, F_α), –82.1 (t, J = 9.2 Hz, 3 F, F_δ) ppm. $C_{18}H_{13}F_9O_3$ (448.28): calcd. C 48.23, H 2.92, F 38.14, O 10.71; found C 48.11, H 2.91, F 38.09, O 10.72.

Naphthoquinone 11: M.p. 114–115 °C. GC-MS: m/z = 557 $[M]^{+\cdot}$, 538, 530, 288, 224, 198, 169, 119, 104, 76, 69. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 2.58–2.69 (m, 1 H), 2.88–3.00 (m, 2 H), 3.11–3.16 (m, 1 H), 3.70–3.76 (br., 1 H), 7.73–7.76 (m, 2 H), 8.06 (dd, J = 6.5, J = 2.5 Hz, 1 H), 8.11 (dd, J = 6.5, J = 2.5 Hz, 1 H) ppm. ^{19}F NMR (470 MHz, CCl_3F): δ = –126.9 to –127.4 (m, 2 F, F_ε), –124.3 to –124.6 (m, 2 F, F_δ), –123.7 to –124.1 (m, 2 F, F_γ), –122.6 to –123.1 (m, 2 F, F_β), –114.3 to –115.1 (m, 2 F, F_α), –81.8 (t, J = 9.8 Hz, 3 F, F_ζ) ppm. $C_{21}H_{12}F_{13}NO_3$ (573.30): calcd. C 43.99, H 2.11, F 43.08, N 2.44, O 8.37; found C 43.85, H 2.11, F 43.13, N 2.43, O 8.40.

Naphthoquinone 12: Oil. GC-MS: m/z = 590 $[M]^{+\cdot}$, 534, 490, 321, 257, 200, 187, 172, 104, 76, 69. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, J = 7.0 Hz, 3 H), 1.24–1.34 (m, 4 H), 1.66–1.73 (m, 1 H), 1.81–1.90 (m, 1 H), 2.32–2.43 (m, 1 H), 2.82–2.97 (m, 1 H), 3.67–3.76 (br., 1 H), 4.14 (s, 3 H), 7.69 (td, J = 1.7, J = 7.3 Hz, 1 H), 7.72 (t, J = 1.7, J = 7.3 Hz, 1 H), 8.03–8.08 (m, 2 H) ppm. ^{19}F NMR (470 MHz, CCl_3F): δ = –126.6 to –127.5 (m, 2 F, F_ε), –124.7 to –125.0 (m, 2 F, F_δ), –124.0 to –124.3 (m, 2 F, F_γ), –121.4 to –121.5 (m, 2 F, F_β), –114.7 (q, J = 272 Hz, 2 F, F_α), –82.1 (t, J = 10.6 Hz, 3 F, F_ζ) ppm. $C_{23}H_{19}F_{13}O_3$ (590.37): calcd. C 46.79, H 3.24, F 41.83, O 8.13; found C 46.67, H 3.23, F 41.96, O 8.12.

Naphthoquinone 13: M.p. 86–88 °C. GC-MS: m/z = 573 $[M]^{+\cdot}$, 304, 240, 214, 200, 172, 104, 76, 69. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.55–2.61 (m, 1 H), 2.83 (d, J = 6.6 Hz,1 H), 2.86 (d, J = 6.6 Hz,1 H), 3.11–3.16 (m, 1 H), 3.70–3.76 (br., 1 H), 4.28 (s, 3 H), 7.71–7.76 (m, 2 H), 8.05–8.08 (m, 2 H) ppm. ^{19}F NMR (470 MHz, CCl_3F): δ = –127.1 to –127.4 (m, 2 F, F_ε), –124.4 to –124.6 (m, 2 F, F_δ), –123.8 to –124.1 (m, 2 F, F_γ), –122.7 to –123.1 (m, 2 F, F_β), –114.6 to –115.0 (m, 2 F, F_α), –81.9 (t, J = 9.8 Hz, 3 F, F_ζ) ppm. $C_{21}H_{12}F_{13}NO_2$ (557.30): calcd. C 45.26, H 2.17, F 44.32, N 2.51, O 5,74; found C 45.45, H 2.17, F 44.38, N 2.50, O 5,73.

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