Rearrangement of 4-Perfluoroalkyl Quinols

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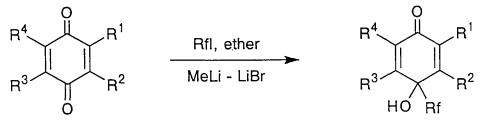
Treatment of 4-perfluoroalkyl-4-hydroxy-2,5-hexadien-1-one (4-perfluoroalkyl-4-quinol), prepared from the reaction of 1,4-benzoquinone with perfluoroalkyllithium, with acetic anhydride–sulfuric acid gave a mixture of 2,4-diacetoxy-1-perfluoroalkylbenzene and 1,2-diacetoxy-4-perfluoroalkylbenzene in a comparable ratio. When 4-perfluoroalkyl-4-quinols bearing a methyl group ortho to the perfluoroalkyl group were subjected to the rearrangement, acetoxymethyl compounds were obtained in addition to diacetoxybenzene derivatives. Only 1,3-migration was observed in the cases of 2,4-di-*t*-butyl-4-perfluorooctyl-4-quinol and 4-hydroxy-4-perfluoroalkyl-1(4*H*)-naphthalenone, while the reaction of 2,6-dimethyl and 2-methoxy derivatives gave only 1,2-shift products. Reaction routes to the apparent 1,2- and 1,3-acetoxyl migration products are discussed.

The quinol rearrangement and Thiele–Winter acetoxylation are very useful methods for the preparation of polyhydroxybenzenes.[1,2] These cationic rearrangements are considered to proceed via cyclohexadienyl cations, stability of which affects product distributions. Migratory aptitude of substituents is also important in the quinol rearrangement. On treatment with sulfuric acid in methanol, 4-alkyl-4-hydroxy-2,5-hexadiene-1-ones (abbreviated to 4-alkyl-4-quinols throughout this paper) undergo rearrangement followed by aromatization to give alkylhydroquinones,[3] while the reaction in acetic anhydride–sulfuric acid takes another route to afford 4-alkylresorcinol diacetates via 1,2-migration of acetoxyl group rather than alkyl group.[4] Unusual 1,3-acetoxyl migration has been observed in the rearrangement of quinols derived from *o*-quinones[5] and sterically hindered 4-quinols.[6] Acid treatment of 2,6-di-*t*-butyl-4-phenyl-4-quinol in acetic anhydride was reported to give 3,4-diacetoxy-5-*t*-butylbiphenyl.[6] We reported the preliminary findings that the acid-catalyzed rearrangement of 4-perfluoroalkyl-4-quinols **1a—d** in acetic anhydride gave a comparable mixture of 1,3-diacetoxy-4-perfluoroalkylbenzenes **3a—d** and 1,2-diacetoxy-4-perfluoroalkylbenzenes **5a—d**. The apparent 1,3-migration of acetoxyl group giving **5a—d** is quite interesting in the rearrangement of simple quinols. From the synthetic point of view, this quinol rearrangement may offer a new useful method for the synthesis of polyhydroxylated perfluoroalkylbenzenes.[8] In this paper, we described the acid-catalyzed rearrangement of 4-perfluoroalkyl-4-quinols.

Results and Discussion

Preparation of 4-Perfluoroalkyl-4-quinols. We first examined the preparation of 4-perfluoroalkyl-4-quinols **1** by the perfluoroalkylation of several quinones with perfluoroalkyllithiums (Eq. 1). The reaction was carried out under slightly modified conditions of the reported procedure,[9] because of low solubility of quinones in ether at low temperatures. We used dichloromethane or toluene as a co-solvent and a Dry Ice–acetone bath was substituted for a Dry Ice–acetonitrile bath to prevent precipitation of quinones upon cooling. Although the stability of perfluoroalkyllithiums decreased sharply with increase of the reaction temperature,[10] yields of quinols obtained were comparable under these modified conditions (Table 1). The yields were not improved by the uses of 0.5 to 2 equivalents of quinone to perfluoroalkyllithium.



(1)

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A regioisomeric problem arose from perfluoroalkylation of unsymmetrically substituted quinones. Perfluorooctyllithium reacted with methyl-1,4-benzoquinone almost equally at both carbonyls to give an isomeric mixture of **1a** and **1b** (**1a**:**1b**=ca. 7:6, determined by GC), which could be easily separated by column chromatography (**1a**, 20%; **1b**, 21%). The reaction of 2,6-dimethyl-1,4-benzoquinone and 2-methoxyl-1,4-benzoquinone with perfluoroalkyllithium also afforded the isomeric quinols (**1h**, 37%; **1i**, 12% and **1m**, 7%; **1n**, 42%, respectively). On the other hand, perfluorooctyllithium added selectively to the less hindered carbonyl of 2-*t*-butyl- and 2,6-di-*t*-butyl-1,4-benzoquinone to afford **1j** and **1l** in 46% and 77% yields, respectively. Quinols **1g**, **1k**, and **1o** were obtained from 2,5-dimethyl-, 2,5-di-*t*-butyl-, and 2,5-dichloro-1,4-benzoquinones in respective yields of 36%, 40%, and 14%. The low yield observed in the perfluoroalkylation of dichloroquinone may be attributed to its high oxidation potential.[11] Naphtho-

Table 1. Rearrangement of 4-Perfluoroalkyl-4-hydroxy-2,5-cyclohexadien-1-ones

	Quinol **1**						Ratio[b]					Combined Yield[c]/%
								1,2-Rearr.		1,3-Rearr.		
	R^1	R^2	R^3	R^4	Rf	Yield[a]/%	**2**	**3**	**4**	**5**	**6**	**7**
a	H	H	H	H	*n*-C_8F_{17}	50		57		43			87
b	H	H	H	H	*n*-C_6F_{13}	43		57		43			83
c	H	H	H	H	*n*-C_4F_9	56		57		43			98
d	H	H	H	H	C_2F_5	56		57		43			99
e	Me	H	H	H	*n*-C_8F_{17}	20		78	13		9		85
f	H	Me	H	H	*n*-C_8F_{17}	21	34		2	24	5	34	86
g	Me	H	Me	H	*n*-C_8F_{17}	36		77			17	6	83
h	Me	H	H	Me	*n*-C_8F_{17}	32		100					97
i	H	Me	Me	H	*n*-C_8F_{17}	12						100	92
j	*t*-Bu	H	H	H	*n*-C_8F_{17}	46			13	60	27		86
k	*t*-Bu	H	*t*-Bu	H	*n*-C_8F_{17}	40	13		87				93
l	*t*-Bu	H	H	*t*-Bu	*n*-C_8F_{17}	77				100			80
m	OMe	H	H	H	*n*-C_4F_9	7			100				79
n	H	OMe	H	H	*n*-C_4F_9	42	100						73
o	Cl	H	Cl	H	*n*-C_8F_{17}	14	100						87
p	H	H	-CH=CH-CH=CH-		*n*-C_6F_{13}	41	38			62			99

a) Isolated yield based on the quinone. b) Determined by NMR analysis of the reaction mixture. c) Combined yield of **2**—**7**.

quinone also reacted with perfluorooctyllithium to give **1p** in a 41% yield.

Rearrangement of Quinols. The acid-catalyzed rearrangement of various quinoles was examined under the following general conditions; To a quinol in acetic anhydride (0.033 M) were added several drops of concd sulfuric acid (one drop per 0.33 mmol) at ambient temperature. The progress of reaction was monitored by TLC and GC. After one day, the reaction was quenched by adding saturated aqueous sodium hydrogencarbonate. The results are summarized in Table 1 and Chart 1.

Rearrangement of methyl-4-quinol **1e** was completed within a similar period of time as quinol **1a**—**d** (overnight). Proton NMR analysis of the product mixture from **1e** showed the presence of three diacetoxybenzenes **3e**, **4e**, and **6e** in a ratio of 78:13:9. Major product **3e** was isolated in 69% yield by column chromatography. On the other hand, the rearrangement of isomeric methyl-4-quinol **1f** was incomplete under the standard conditions and appreciable amounts of quinol acetate **2f** remained unchanged in the reaction mixture (**2f**:**4f**:**5f**:**6f**:**7f**=34:2:24:5:34). When this mixture was treated with Ac_2O/H_2SO_4 overnight at 80—90 °C, the rearrangement of the remaining quinol acetate was completed (**4f**:**5f**:**6f**:**7f**=4:35:8:53). Chromatography of the latter product mixture gave acetoxymethyl derivative **7f** and a mixture of diacetoxybenzenes **5f** and **6f** in 30% and 31% yields, respectively. Attempted isolation of diacetoxybenzenes **4f**—**6f** was unsuccessful.

Under the standard conditions, dimethyl-4-quinols **1g**, **1h** and **1i** underwent smooth rearrangement within 1 h. The reaction of **1g** afforded a mixture of **3g**, **6g**, and **7g**, the ratio of which was 77:17:6 based on both

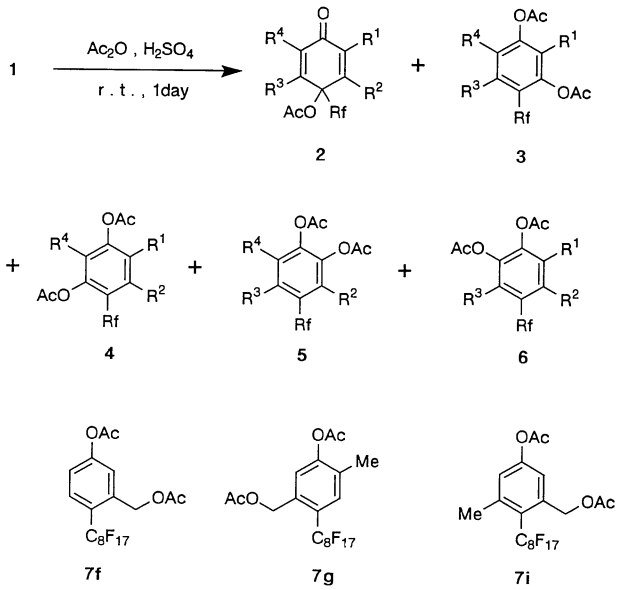


Chart 1.

^{1}H NMR and capillary GC determinations. Major components **3g** and **6g** were isolated in 69% and 14% yields, respectively. The acid-catalyzed rearrangement of **1h** and **1i** gave **3h** and **7i** as the sole product respectively in isolated yields of 97% and 93%. One of the *t*-butyl groups was replaced by acetoxyl group on the acid treatment of di-*t*-butyl-4-quinols **1k** and **1l**. In the reaction of 2-*t*-butyl-4-quinol **1j** the displacement of the *t*-butyl group was the major reaction to give 1,2-diacetoxy-4-perfluorooctylbenzene (**5j**=**5a**) predominantly. 2-Methoxy-4-quinol **1m** was susceptible to 1,2-acetoxyl migration to afford **4m** in a 79% yield. In contrast, 3-methoxy-4-quinol **1n** resisted such

rearrangement and only the corresponding acetate **2n** was obtained. Similar resistance toward aromatization was encountered in the reaction of quinol **1o**, where only quinol acetate **2o** was obtained in almost quantitative yield. It is worthy to mention that the Thiele–Winter type acetoxylation did not take place with the parent quinone, 2,5-dichloro-1,4-benzoquinone.[12] Quinol **1p** derived from 1,4-naphthoquinone underwent the apparent 1,3-acetoxyl migration to give **5p** in 61% yield together with quinol acetate **2p** (38%). The rearrangement of quinol acetate **2p** did not proceed under the usual conditions. Using perchloric acid in place of sulfuric acid caused the complete disappearance of **1p**, giving **5p** in 86% yield.

Hydrolysis of Diacetoxybenzenes. We reported that the hydrolysis of 4-perfluorobutylresorcinol diacetate (**3c**) and 4-perfluorobutylcatechol diacetate (**5c**) with potassium hydroxide in THF–methanol brought about simultaneous substitution of benzylic fluorine atoms to give perfluorobutanoyl derivatives.[7] When heated in methanol in the presence of *p*-toluenesulfonic acid (PTSA), however, these diacetates were readily hydrolyzed to parent resorcinol **8** and catechol **9** (Eq. 2; Table 2). The resorcinols and catechols were separated by column chromatography on silica gel, although the isolated yields of the latter compounds were low probably due to their air-sensitive property. In order to isolate the catechols more efficiently from the hydrolyzed mixture, the catechols were protected as acetonides before chromatography. Thus, an original mixture of **8a** and **9a** was heated under reflux in acetone[13] and the resulting product was chromatographed on silica gel to obtain an intimate mixture of catechol acetonide **10** and unexpected product **11** in very poor yields, along with resorcinol **8a** intact (Eq. 3). Separation of **11** from **10** was performed by preparative GPC and the structure of **11** was established by analytical and spectroscopic data (NMR, IR, and MS) as an acetal derived from catechol **5a** and mesityl oxide.

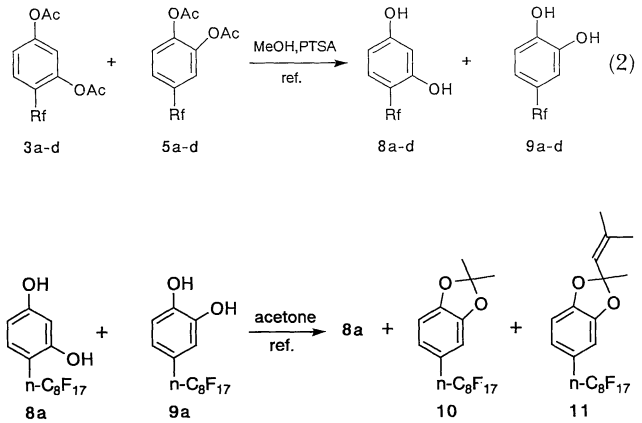
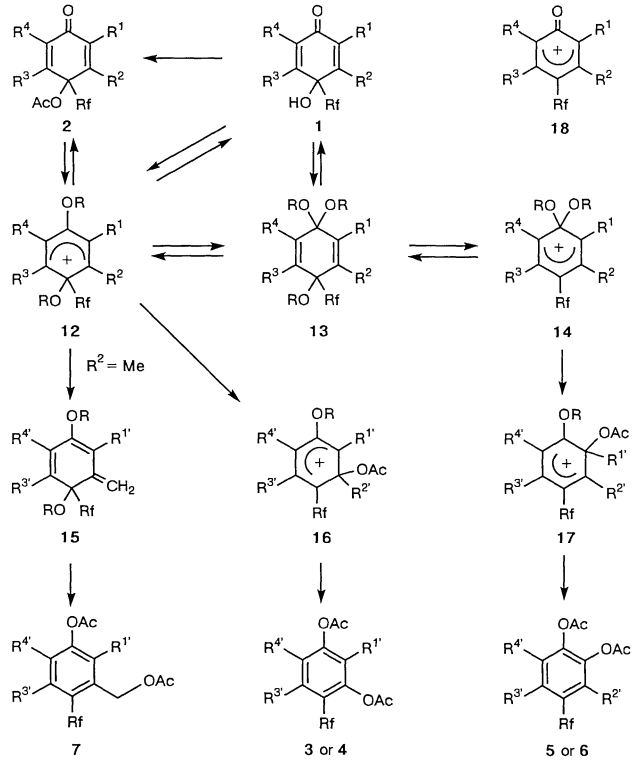


Table 2. Preparation of Perfluoroalkyl Resorcinols and Catechols

Quinol	Yield[a]/%	
	8	**9**
1a	87	
1b	49	17
1c	51	35
1d	51	11
2a	50	12

a) Yield refer to isolated ones.

Mechanism of the Acid-Catalyzed Rearrangement. We would like to discuss the mechanistic aspects of the acid rearrangement of quinols. Our proposal of this rearrangement is shown in scheme 1. 1,2-Acetoxyl migration of 4-perfluoroalkyl-4-quinols may occur via benzenium ions **12** (R=H or Ac) and **16** similarly in the cases 4-alkyl- and 4-aryl-4-quinols. However, when perfluoroalkyl groups were introduced, energy gap between the two benzenium ions **12** and **16** becomes considerably large because of destabilization, leading to other pathway. When R^2 is methyl, **12** loses a proton to give quinol tautomer **15**, which is subject to a facile allylic rearrangement to afford acetoxymethyl derivative **7**.[14] It is noteworthy that such an acetoxylation on methyl group was not observed in the Thiele–Winter acetoxylation on mono- and dimethyl-1,4-quinones.[1] Another pathway leading to catechol



Scheme 1.

derivatives **5** and **6** may be thought as follows: sp^3-hydridization of the carbonyl carbon of **1** takes place to afford (hemi)acetal **13**. Then, **13** loses an RO group at 4 position to give rather unstable benzenium ion **14** of which acetoxyl group migrates to give **5** or **6** via benzenium ion **17**. This proposal is based on the fact that carbonyl functional groups tend to be hydrated or acetalized when electron-withdrawing groups are attached. Moreover, benzenium ion **18** doubly destabilized by perfluoroalkyl and carbonyl groups is unlikely.[15] If the benzenium ion **16** is stabilized by electron-donating $R^{1'}$ and $R^{4'}$, the pathway to give **3** or **4** is dominant (**1g**, **1h**, and **1m**). In the case of **1n**, as benzenium ion **12** is strongly stabilized by R^2 (MeO), the rearrangement to **16** becomes disadvantageous. sp^3-Hybridization of the carbonyl to **13** is also unfavorable, because the carbonyl is considered as vinylogous ester. Thus, the rearrangement of **1n** did not proceed and quinol acetate **2n** was obtained quantitatively.

Bulky *t*-butyl group disfavors acetoxyl group migrating vicinal to it and tends to be replaced.[1] In the case of **1k**, an interesting point is that *t*-butyl group is substituted by acetoxyl group. Steric hindrance between the vicinal *t*-butyl and perfluoroalkyl groups is very severe when they are linked by two sp^2 carbons. Therefore, the pathway via **12** to **16** ($R^{2'}=R^{4'}=t$-Bu) may be more favorable than that via **14** to **17** ($R^{1'}=R^{3'}=t$-Bu). Formation of quinol acetal **13** from **1l** ($R^1=R^4=t$-Bu) would be expected to encounter large steric hindrance by the two *t*-butyl groups. However, the CPK model structure can be build up if at least one of OR groups at C-1 is OH. It should be noted that quinol acetates **2l** and **2p** did not react, while the corresponding quinols **1l** and **1p** did undergo only 1,3-migration to give **5l** and **5p** under the same conditions. On the other hand, the reaction of simple quinol acetates **2a—d** gave the same results as those obtained from the reaction of quinols **1a—d**. These facts might be interpreted if we take it into account that sp^3-hybridization of the carbonyl group to **13** is sterically interfered by C-4 substituents (acetoxyl and perfluoroalkyl). In the reaction of methyl-4-quinols **1e** and **1f**, regioselectivity of the acetoxyl migration shows sharp contrast to that observed in the Thiele-Winter reaction of the parent quinone, where acetoxylation occurs mainly para to the methyl group.[1] The reason for the difference is nuclear at present.

Experimental

Melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Unless otherwise noted, all NMR spectra were observed with a GSX-270 spectrometer by using $CDCl_3$ as solvent, tetramethylsilane as an internal standard for ^1H and ^{13}C, and $CFCl_3$ for ^{19}F. Mass spectra were measured with a Hitachi M80LCAPI spectrometer under the following ionizing conditions: EI (electron impact ionization, 20 eV) and CI (chemical ionization, 70 eV, methane as CI gas). IR spectra were recorded on a Hitachi 270-30 spectrophotometer. Column chromatogaphy was carried out using Wakogel C-200. Preparative GPC was performed using JAI LC-80 with JAI-1H (20 mmID×60 cm) and JAI-2H (20 mmID×60 cm) columns. Diethyl ether was distilled from sodium benzophenone ketyl. Dichloromethane and toluene were distilled from calcium hydride and stored over 4A molecular sieves. Perfluoroalkyl iodides were purified by simple distillation. Methyllithium was titrated prior to use. Other commercially available materials were used without further purification.

Perfluoroalkylation of 1,4-Quinones. General Procedure: A 1,4-quinone (10 mmol) and a perfluoroalkyl iodide (12 mmol) are dissolved in a mixture of 100 ml of dry ether and 50 ml of dry toluene (or dichloromethane), and cooled down to −40—−50 °C by a Dry Ice-acetonitrile bath. In case the quinone begins to separate, dry toluene (or dichloromethane) is added to keep the solution homogenous. An ethereal solution of methyllithium-lithium bromide (11 mmol) is added at given temperature range over 30 min. During the course of addition, the yellow solution turned to a bluish purple suspension. After stirring for 1 h, the reaction is quenched with aqueous NH_4Cl. The organic phase is separated and the aqueous phase is extracted with ether. The combined extracts are washed with brine and dried over Na_2SO_4. The solvent is evaporated and the residue is chromatographed on silica gel ($CHCl_3$–ether). The quinol obtained is recrystallized from chloroform/hexane or dichloromethane/hexane.

4-Hydroxy-4-perfluorooctyl-2,5-cyclohexadien-1-one (1a). Colorless needles (chloroform), mp 132—133 °C.[9]

4-Hydroxy-4-perfluorohexyl-2,5-cyclohexadien-1-one (1b). Colorless crystals (chloroform), mp 111—113 °C. ^1H NMR (acetone-d_6) δ=6.42 (2H, d, J=10.4 Hz), 6.49 (1H, s), and 7.09 (2H, d, J=10.4 Hz); ^{13}C NMR (acetone-d_6) δ=72.44 (tt, J=24 and 1 Hz), 105—125 (6C), 132.25, 143.11 (m), and 184.91; ^{19}F NMR (acetone-d_6) δ=−81.65 (3F, tt, J=10 and 2 Hz), −117.94 (2F, m), −118.42 (2F, m), −121.27 (2F, m), −122.24 (2F, m), and −125.70 (2F, m); IR (KBr) 3228vs, 1674vs, 1628vs, 1406m, 1390m, 1366m, 1318m, and 1300—1100vs cm^{-1}; MS (CI) m/z 429 (M^++1, 100), 411 (26), 393 (11), 138 (18), and 109 (72). Found: C, 33.62; H, 1.23%. Calcd for $C_{12}H_5F_{13}O_2$: C, 33.66; H, 1.18%.

4-Hydroxy-4-perfluorobutyl-2,5-cyclohexadien-1-one (1c). Colorless needles (dichloromethane/hexane), mp 88—90 °C. ^{19}F NMR δ=−80.73 (3F, tt, J=10 and 3 Hz), −118.21 (2F, m), −119.46 (2F, m), and −125.59 (2F, m); IR (KBr) 3220vs, 1674vs, 1628vs, 1408m, 1392m, 1358m, and 1300—1100vs cm^{-1}; MS (CI) m/z 329 (M^++1, 100), 311 (29), 293 (6), 138 (19), and 109 (59). Found: C, 36.66; H, 1.59%. Calcd for $C_{10}H_5F_9O_2$: C, 36.60; H, 1.54%.

4-Hydroxy-4-perfluoroethyl-2,5-cyclohexadien-1-one (1d). Colorless needles (dichloromethane/hexane), mp 47—48 °C. ^{19}F NMR δ=−78.45 (3F, s) and −122.18 (2F, m); IR (KBr) 3232vs, 1672vs, 1626vs, 1402m, 1384m, 1344s, and 1300—1100vs cm^{-1}; MS (EI) m/z 228 (M^+, 4), 202 (1), 133 (3), and 109 (100). Found: C, 41.88; H, 2.28%. Calcd for $C_8H_5F_5O_2$: C, 42.12; H, 2.21%.

4-Hydroxy-2-methyl-4-perfluorooctyl-2,5-cyclohexadien-1-one (1e). Colorless crystals (dichloromethane/hexane), mp 69—70 °C. ^1H NMR (acetone-d_6) δ=1.86 (3H, s), 3.50 (1H, br s), 6.33 (1H, d, J=9.8 Hz), 6.77 (1H, m), and 6.97 (1H, dm,

J=9.8 Hz); ^{13}C NMR (acetone-d_6) δ=16.17, 72.80 (t, J=24 Hz), 105—125 (8C), 132.10, 138.14, 139.36 (m), 143.11 (t, J=2 Hz), and 186.65; ^{19}F NMR (acetone-d_6) δ=−80.69 (3F, tt, J=10 and 2 Hz), −117.91 (2F, m), −118.47 (2F, m), −120.8—−121.8 (6F, m), −122.27 (2F, m), and −125.75 (2F, m); IR (KBr) 3416vs, 1678vs, 1642s, 1408m, 1372m, 1330s, and 1300—1100vs cm^{-1}; MS (EI) m/z 542 (M^+, 4), 525 (1), 523 (2), 475 (1), and 123 (100). Found: C, 32.93; H, 1.42%. Calcd for $C_{15}H_7F_{17}O_2$: C, 33.23; H, 1.31%.

4-Hydroxy-3-methyl-4-perfluorooctyl-2,5-cyclohexadien-1-one (1f). Colorless crystals (dichloromethane/hexane), mp 122—123 °C. ^{1}H NMR (acetone-d_6) δ=2.13 (3H, m), 6.20 (1H, m), 6.30 (1H, dm, J=10.1 Hz), 6.40 (1H, br s), and 7.00 (1H, dm, J=10.1 Hz); ^{13}C NMR (acetone-d_6) δ=19.73, 74.07 (tm, J=24 Hz), 105—125 (8C), 131.00, 131.88, 143.97 (m), 155.27, and 185.43; ^{19}F NMR (acetone-d_6) δ=−80.83 (3F, tt, J=10 and 2 Hz), −114.30 (1F, dm, J=279 Hz), −116.61 (1F, dm, J=279 Hz), −118.88 (2F, m), −120.8—−121.8 (6F, m), −122.37 (2F, m), and −125.87 (2F, m); IR (KBr) 3416vs, 1676vs, 1632vs, 1448m, 1400m, 1372m, 1330s, and 1300—1100vs cm^{-1}; MS (EI) m/z 542 (M^+, 1), 523 (1), 475 (1), and 123 (100). Found: C, 33.38; H, 1.35%. Calcd for $C_{15}H_7F_{17}O_2$: C, 33.23; H, 1.31%.

4-Hydroxy-2,5-dimethyl-4-perfluorooctyl-2,5-cyclohexadien-1-one (1g). Colorless crystals (dichloromethane/hexane), mp 91—92 °C. ^{1}H NMR (acetone-d_6) δ=1.84 (3H, d, J=1.2 Hz), 2.11 (3H, m), 6.18 (2H, m), and 6.75 (1H, m); ^{13}C NMR (acetone-d_6) δ=19.73 (m), 74.07 (ddm, J=22 and 21 Hz), 105—125 (8C), 130.99, 131.88, 143.96 (m), 155.26, and 185.43; ^{19}F NMR (acetone-d_6) δ=−80.65 (3F, tm, J=10 Hz), −114.29 (1F, dm, J=278 Hz), −116.47 (1F, dm, J=278 Hz), −118.99 (2F, m), −121.0—−121.5 (6F, m), −122.27 (2F, m), and −125.72 (2F, m); IR (KBr) 3396vs, 1678m, 1634vs, 1456m, 1398m, 1378m, 1328m, and 1300—1100vs cm^{-1}; MS (CI) m/z 557 (M^++1, 54), 539 (23), 166 (22), and 137 (100). Found: C, 34.41; H, 1.64%. Calcd for $C_{14}H_5F_{17}O_2$: C, 34.55; H, 1.63%.

4-Hydroxy-2,6-dimethyl-4-perfluorooctyl-2,5-cyclohexadien-1-one (1h). Colorless crystals (dichloromethane/hexane), mp 86—87 °C. ^{1}H NMR δ=1.94 (6H, s), 4.40 (1H, br s), and 6.72 (2H, s); ^{13}C NMR δ=16.07, 71.13 (t, J=24 Hz), 105—125 (8C), 135.35, 138.78, and 185.17; ^{19}F NMR δ=−81.25 (3F, tt, J=10 and 2 Hz), −119.50 (4F, m), −121.9—−122.5 (6F, m), −123.21 (2F, m), and −126.61 (2F, m); IR (KBr) 3424vs, 1676s, 1644vs, 1446s, 1396vs, and 1300—1100vs cm^{-1}; MS (CI) m/z 557 (M^++1, 47), 539 (37), 166 (9), and 137 (100). Found: C, 34.31; H, 1.66%. Calcd for $C_{14}H_5F_{17}O_2$: C, 34.55; H, 1.63%.

4-Hydroxy-3,5-dimethyl-4-perfluorooctyl-2,5-cyclohexadien-1-one (1i). Colorless crystals (dichloromethane/hexane), mp 104—106 °C. ^{1}H NMR (acetone-d_6) δ=2.15 (6H, s), 6.18 (2H, s), and 6.22 (1H, s); ^{13}C NMR (acetone-d_6) δ=19.90 (t, J=4 Hz), 76.69 (tt, J=20 and 2 Hz), 105—125 (8C), 131.54, 155.71, and 185.22; ^{19}F NMR (acetone-d_6) δ=−80.65 (3F, tt, J=10 and 2 Hz), −111.75 (2F, m), −119.35 (2F, m), −120.95 (2F, m), −121.39 (4F, m), −122.29 (2F, m), and −125.76 (2F, m); IR (KBr) 3364vs, 1672vs, 1626vs, 1450m, 1386s, 1356s, 1328m, and 1300—1100vs cm^{-1}; MS (CI) m/z 557 (M^++1, 68), 539 (12), 537 (29), 166 (29), and 137 (100). Found: C, 34.42; H, 1.51%. Calcd for $C_{14}H_5F_{17}O_2$: C, 34.55; H, 1.63%.

2-*t*-Butyl-4-hydroxy-4-perfluorooctyl-2,5-cyclohexadien-1-one (1j). Colorless crystals (dichloromethane/hexane), mp 92 °C. ^{1}H NMR δ=1.25 (9H, s), 2.74 (1H, br s), 6.33 (1H, d, J=10.1 Hz), 6.63 (1H, s), and 6.77 (1H, d, J=10.1 Hz); IR (KBr) 3216vs, 2964m, 1672vs, 1626vs, 1460m, 1368s, and 1300—1100vs cm^{-1}. MS (CI) 585 (M^++1, 8), 567 (59), 165 (100), and 123 (52). Found: C, 36.93; H, 2.18%. Calcd for $C_{18}H_{13}F_{17}O_2$: C, 37.00; H, 2.24%.

2,5-Di-*t*-butyl-4-hydroxy-4-perfluorooctyl-2,5-cyclohexadien-1-one (1k). Colorless crystals (dichloromethane/hexane), mp 164—165 °C. ^{1}H NMR δ=1.23 (9H, s), 1.35 (9H, s), 2.81 (1H, s), 6.37 (1H, s), and 6.50 (1H, s); IR (KBr) 3220vs, 2969s, 1658s, 1618vs, 1468s, 1370s, and 1300—1100vs cm^{-1}; MS (CI) 641 (M^++1, 11), 623 (13), 585 (15), 250 (20), and 222 (100). Found: C, 41.20; H, 3.27%. Calcd for $C_{22}H_{21}F_{17}O_2$: C, 41.26; H, 3.31%.

2,6-Di-*t*-butyl-4-hydroxy-4-perfluorooctyl-2,5-cyclohexadien-1-one (1l). Colorless crystals (dichloromethane/hexane), mp 82—83 °C. ^{1}H NMR δ=1.24 (18H, s), 3.30 (1H, br s), and 6.52 (2H, s); ^{13}C NMR δ=29.04, 35.29, 71.97 (t, J=24 Hz), 105—125 (8C), 132.34, 150.94, and 185.56; ^{19}F NMR δ=−81.27 (3F, tt, J=10 and 3 Hz), −118.76 (2F, m), −119.53 (2F, m), −122.24 (6F, m), −123.21 (2F, m), and −126.62 (2F, m); IR (KBr) 3496vs, 2964vs, 1672s, 1648vs, 1486m, 1464m, 1366s, and 1300—1100vs cm^{-1}; MS (CI) 641 (M^++1, 57), 625 (13), 623 (11), 599 (9), 597 (10), 222 (100), 221 (64), and 111 (38). Found: C, 41.37; H, 3.37%. Calcd for $C_{22}H_{21}F_{17}O_2$: C, 41.26; H, 3.31%.

4-Hydroxy-2-methoxy-4-perfluorobutyl-2,5-cyclohexadien-1-one (1m). Colorless crystals (dichloromethane/hexane), mp 69—71 °C. ^{1}H NMR δ=3.28 (br s), 3.74 (3H, s), 5.76 (1H, m), 6.41 (1H, d, J=10.1 Hz), and 6.94 (1H, m); ^{13}C NMR δ=55.36, 73.07 (t, J=24 Hz), 105—125 (4C), 107.82, 130.48, 141.71, 152.52, and 179.41; ^{19}F NMR δ=−81.31 (3F, tt, J=10 and 3 Hz), −119.23 (2F, m), −120.29 (2F, m), and −126.43 (2F, m); IR (KBr) 3544s, 3454s, 3088s, 1672m, 1623s, 1437m, 1353s, and 1300—1100vs cm^{-1}; MS (CI) m/z 359 (M^++1, 71), 341 (46), 327 (53), 168 (21), and 139 (100). Found: m/z 358.0258. Calcd for $C_{11}H_7F_9O_3$: M, 358.0251.

4-Hydroxy-3-methoxy-4-perfluorobutyl-2,5-cyclohexadien-1-one (1n). Colorless crystals (dichloromethane/hexane), mp 76—77 °C. ^{1}H NMR δ=3.85 (3H, s), 5.68 (1H, d, J=1.5 Hz), 6.36 (1H, dd, J=10.1 and 1.5 Hz), and 6.73 (1H, dd, J=10.1 and 1.2 Hz); ^{13}C NMR δ=56.31, 72.00 (t, J=23 and 2 Hz), 103.16, 108.48 (tm, J=270 Hz), 111.23 (ttt, J=269, 37, and 31 Hz), 115.18 (tt, J=270 and 32 Hz), 117.22 (qt, J=288 and 33 Hz), 130.52, 138.14 (dt, J=3 and 1 Hz), 168.81 (d, J=2 Hz), and 186.49; ^{19}F NMR δ=−81.37 (3F, tt, J=10 and 3 Hz), −116.80 (1F, dm, J=279 Hz), −118.20 (1F, dm, J=279 Hz), −121.72 (2F, m), −126.20 (1F, dddt, J=293, 20, 11, and 3 Hz), −126.60 (1F, dddt, J=293, 19, 14 and 3 Hz); IR (KBr) 3252vs, 1672vs, 1636s, 1608vs, 1356s, and 1300—1100vs cm^{-1}; MS (CI) m/z 359 (M^++1, 100), 343 (11), 341 (30), 339 (14), 327 (59), 323 (21), 313 (36), 168 (35), 140 (77), and 139 (76). Found: C, 36.59; H, 1.87%. Calcd for $C_{11}H_7F_9O_3$: C, 36.89; H, 1.97%.

2,5-Dichloro-4-hydroxy-4-perfluorooctyl-2,5-cyclohexadien-1-one (1o). Colorless crystals (ether/hexane), mp 98—99 °C. ^{1}H NMR (acetone-d_6) δ=6.83 (1H, s), 7.32 (1H, m), and 7.41 (1H, br s); ^{13}C NMR (acetone-d_6) δ=75.94 (t, J=23 Hz), 105—125 (8C), 131.49, 135.78, 139.18 (m), 152.29, and 176.85; ^{19}F NMR (acetone-d_6) δ=−80.61 (3F, tm, J=10 Hz), −114.06 (1F, dm, J=279 Hz), −115.80 (1F, dm, J=279 Hz), −118.69 (2F, m), −121.00 (2F, m), −121.30 (4F, m), −122.21 (2F, m), and −125.69 (2F, m); IR (KBr) 3860s, 1682vs, 1600s, 1332m, 1332m, and 1300—1100vs cm^{-1}; MS

(CI) *m/z* 601 (6), 599 (37), 597 (56), 581 (20), 579 (36), 577 (27), 563 (21), 543 (24), 180 (100), and 178 (98). Found: C, 27.90; H, 0.66%. Calcd for $C_{14}H_3Cl_2F_{17}O_2$: C, 28.16; H, 0.51%.

4-Hydroxy-4-perfluorohexyl-1(4*H*)-naphthalenone (1p). Colorless crystals (dichloromethane/hexane); mp 91.5 °C. ^{1}H NMR δ=3.32 (1H, s), 6.57 (1H, d, J=10.4 Hz), 7.04 (1H, dm, J=10.4 Hz), 7.58 (1H, td, J=7.6 and 1.2 Hz), 7.69 (1H, td, J=7.6 and 1.5 Hz), 7.89 (1H, dm, J=7.9 Hz), and 8.12 (1H, dd, J=7.6 and 1.5 Hz); ^{13}C NMR δ=72.61 (dd, J=25 and 22 Hz), 105—125 (6C), 126.91, 127.92 (t, J=3 Hz), 130.15, 130.89 (m), 131.95, 133.10, 137.37, 142.17 (m), and 183.38; ^{19}F NMR δ=−81.32 (3F, tt, J=10 and 2 Hz), −116.26 (1F, dm, J=278 Hz), −118.66 (1F, dm, J=278 Hz), −118.77 (2F, m), −122.30 (2F, m), −123.27 (2F, m), and −126.63 (2F, m); IR (KBr) 3312vs, 1666s, 1634s, 1602s, 1308s, and 1300—1100vs cm^{-1}; MS (CI) *m/z* 479 (M$^+$+1, 41), 461 (20), 188 (10), and 159 (100). Found: C, 39.94; H, 1.53%. Calcd for $C_{16}H_7F_{13}O_2$: C, 40.19; H, 1.48%.

4-Acetoxy-4-perfluorooctyl-2,5-cyclohexadien-1-one (2a). Colorless crystals (dichloromethane/hexane), mp 50—51 °C. ^{1}H NMR δ=2.17 (3H, s), 6.53 (2H, d, J=10.1 Hz), and 6.84 (2H, d, J=10.1 Hz); ^{13}C NMR δ=20.87 (m), 77.22 (tt, J=26 and 3 Hz), 105—125 (8C), 132.98, 138.88, 167.47, and 183.56; ^{19}F NMR δ=−81.24 (3F, tt, J=10 and 2 Hz), −116.46 (2F, m), −118.84 (2F, m), −122.15 (6F, m), −123.17 (2F, m), and −126.62 (2F, m); IR (KBr) 1774vs, 1680vs, 1636s, 1374s, and 1300—1100vs cm^{-1}; MS (EI) *m/z* 570 (M$^+$, 3), 528(3), 512 (6), 492 (23), and 173 (100). Found: C, 33.30; H, 1.23%. Calcd for $C_{16}H_7F_{17}O_3$: C, 33.70; H, 1.24%.

4-Acetoxy-4-perfluorohexyl-2,5-cyclohexadien-1-one (2b). Colorless oil. ^{19}F NMR δ=−81.39 (3F, tt, J=10 and 3 Hz), −116.44 (2F, m), −118.82 (2F, m), −122.19 (2F, m), −123.10 (2F, m), and −126.62 (2F, m); IR (KBr) 1776vs, 1680vs, 1640s, 1370s, and 1300—1100vs cm^{-1}; MS (EI) *m/z* 470 (M$^+$, 2), 428 (4), 412 (16), and 143 (100). Found: *m/z* 470.0225. Calcd for $C_{14}H_7F_{13}O_3$: M, 470.0187.

4-Acetoxy-4-perfluorobutyl-2,5-cyclohexadien-1-one (2c). Colorless oil. ^{19}F NMR δ=−81.21 (3F, tt, J=10 and 3 Hz), −116.72 (2F, m), −119.89 (2F, m), and −126.46 (2F, m); IR (KBr) 1776vs, 1678vs, 1640s, 1386m, 1372m, 1356m, and 1300—1100vs cm^{-1}; MS (EI) *m/z* 370 (M$^+$, 19), 328 (26), 312 (26), 300 (27), and 143 (100). Found: *m/z* 370.0251. Calcd for $C_{14}H_7F_9O_3$: M, 370.0250.

4-Acetoxy-4-perfluoroethyl-2,5-cyclohexadien-1-one (2d). Colorless oil. ^{19}F NMR δ=−78.76 (3F, s) and −120.99 (2F, s); IR (KBr) 1776vs, 1680vs, 1640s, 1370s, and 1300—1100vs cm^{-1}; MS (EI) *m/z* 270 (M$^+$, 19), 228 (100), 208 (11), and 159 (24). Found: *m/z* 270.0293. Calcd for $C_{10}H_7F_5O_3$: M, 270.0314.

4-Acetoxy-3-methyl-4-perfluorooctyl-2,5-cyclohexadien-1-one (2f). Colorless crystals (dichloromethane/hexane), mp 89—91 °C. ^{1}H NMR δ=2.05 (3H, d, J=1.2 Hz), 2.22 (3H, s), 6.38 (1H, m), 6.45 (1H, dd, J=10.3 and 1.8 Hz), and 6.81 (1H, dt, J=10.3 and 2.8 Hz); ^{13}C NMR δ=19.08 (t, J=4 Hz), 20.69, 78.96 (t, J=24 Hz), 105—125 (8C), 131.68, 132.05, 139.80, 150.31, 167.49, and 184.28; ^{19}F NMR δ=−81.27 (3F, t, J=10 Hz), −115.56 (2F, m), −118.94 (2F, m), −122.13 (2F, m), −123.19 (2F, m), and −126.59 (2F, m); IR (KBr) 1754vs, 1672s, 1640vs, 1366s, and 1300—1100vs cm^{-1}; MS (CI) 585 (M$^+$+1, 31), 543 (38), 527 (60), 507 (69), and 157 (100). Found: C, 34.95; H, 1.51%. Calcd for $C_{17}H_9F_{17}O_3$: C, 34.95; H, 1.55%.

4-Acetoxy-2,5-di-*t*-butyl-4-perfluorooctyl-2,5-cyclohexadien-1-one (2k). Colorless crystals (dichloromethane/hexane), mp 95—97 °C. ^{1}H NMR δ=1.22 (9H, s), 1.26 (9H, m), 2.19 (3H, s), 6.36 (1H, dd, J=5.2 and 3.0 Hz), and 6.52 (1H, s); IR (KBr) 2972s, 1782s, 1754s, 1714s, 1666s, 1640s, 1370s, and 1300—1100vs cm^{-1}; MS (CI) 683 (M$^+$+1, 26), 667 (6), 655 (13), 640 (28), 627 (100), 623 (43), 607 (33), and 585 (59). Found: C, 42.38; H, 3.49%. Calcd for $C_{24}H_{23}F_{17}O_3$: C, 42.24; H, 3.40%.

4-Acetoxy-2,6-di-*t*-butyl-4-perfluorooctyl-2,5-cyclohexadien-1-one (2l). Colorless crystals (dichloromethane/hexane), mp 53—54 °C. ^{1}H NMR δ=1.24 (18H, s), 2.15 (3H, s), and 6.43 (2H, s); ^{13}C NMR δ=21.18, 28.98, 35.42, 78.04, (t, J=24 Hz), 105—125 (8C), 130.51, 151.40, 167.43, and 185.68; ^{19}F NMR δ=−81.26 (3F, tt, J=10 and 3 Hz), −116.80 (2F, m), −118.96 (2F, m), −122.15 (2F, m), −122.36 (4F, m), −123.30 (2F, m), and −126.63 (2F, m); IR (KBr) 2960s, 1764vs, 1672s, 1648s, 1462s, 1368s, 1330s, and 1300—1100vs cm^{-1}; MS (CI) 683 (M$^+$+1, 3), 663 (2), 655 (3), 627 (100), 623 (57), 607 (46), and 584 (71). Found: C, 41.87; H, 3.43%. Calcd for $C_{24}H_{23}F_{17}O_3$: C, 42.24; H, 3.40%.

4-Acetoxy-3-methoxy-4-perfluorobutyl-2,5-cyclohexadien-1-one (2n). Colorless crystals (hexane), mp 29—30 °C. ^{1}H NMR δ=2.18 (3H, s), 3.78 (3H, s), 5.78 (1H, d, J=1.5 Hz), 6.44 (1H, dd, J=10.1 and 1.5 Hz), and 6.60 (1H, d, J=10.1 Hz); ^{13}C NMR δ=20.38 (m), 56.48 (m), 76.96 (tt, J=23 and 2 Hz), 105.00, 105—125 (4C), 132.67, 135.56 (m), 166.16, 167.34, and 185.49; ^{19}F NMR δ=−81.28 (3F, tt, J=10 and 2 Hz), −116.08 (1F, dm, J=280 Hz), −116.73 (1F, dm, J=280 Hz), −120.98 (2F, m), and −126.27 (2F, m); IR (KBr) 1764vs, 1666s, 1606vs, 1354s, and 1300—1100vs cm^{-1}; MS (CI) *m/z* 401 (M$^+$+1, 100), 359 (38), 358 (46), 339 (17), and 323 (40). Found: C, 38.70; H, 2.23%. Calcd for $C_{13}H_9F_9O_4$: C, 39.02; H, 2.27%.

4-Acetoxy-2,5-dichloro-4-perfluorooctyl-2,5-cyclohexadien-1-one (2o). Colorless crystals (dichloromethane/hexane); mp 91—92 °C. ^{1}H NMR δ=2.26 (3H, s), 6.84 (1H, s), and 7.00 (1H, m); ^{13}C NMR δ=20.48, 78.71 (t, J=25 Hz), 105—125 (8C), 131.58, 134.75, 136.06 (m), 147.55, 167.20, and 175.78; ^{19}F NMR δ=−81.30 (3F, tm, J=10 Hz), −115.25 (2F, m), −118.87 (1F, m), −119.07 (1F, m), −121.86 (2F, m), −122.12 (2F, m), −122.33 (2F, m), −123.19 (2F, m), and −126.61 (2F, m); IR (KBr) 3064m, 1770vs, 1686vs, 1602s, 1372s, 1332m, and 1300—1100vs cm^{-1}; MS (EI) *m/z* 640 (2), 638 (4), 582 (9), 580 (15), 213 (63), and 212 (100). Found: C, 30.09; H, 0.77%. Calcd for $C_{16}H_5Cl_2F_{17}O_{15}$: C, 30.03; H, 0.79%.

4-Acetoxy-4-perfluorohexyl-1(4*H*)-naphthalenone (2p). Colorless oil. ^{1}H NMR δ=2.20 (3H, m), 6.64 (1H, d, J=10.4 Hz), 6.99 (1H, dm, J=10.4 Hz), 7.61 (3H, m), and 8.18 (1H, dm, J=7.9 Hz); ^{13}C NMR δ=21.05, 77.71 (t, J=25 Hz), 105—125 (6C), 126.27 (t, J=3 Hz), 127.24, 130.12, 131.84 (2C), 132.59, 134.78, 140.39, 167.30, and 183.09; ^{19}F NMR δ=−81.31 (3F, tt, J=10 and 2 Hz), −116.14 (2F, t, J=15 Hz), −118.36 (2F, m), −122.21 (2F, m), −123.14 (2F, m), and −126.59 (2F, m); IR (neat) 3072m, 1770vs, 1680vs, 1638s 1600vs, 1460m, 1370s, and 1300—1100vs cm^{-1}; MS (CI) *m/z* 521 (M$^+$+1, 23), 507 (8), 479 (35), 461 (33), 443 (19), and 159 (100). Found: C, 41.40; H, 1.69%. Calcd for $C_{18}H_9F_{13}O_3$: C, 41.56; H, 1.74%.

Acid Treatment of Quinols. General Procedure: To an acetic anhydride solution (30 ml) of a quinol (1 mmol) was added three drops of concd H_2SO_4 at room temperature. After stirring overnight, the reaction was quenched by careful addition of a saturated aqueous solution of $NaHCO_3$

and the mixture was stirred until gas evolution ceased. The mixture was extracted with ether and the ethereal extract was washed by brine, dried with Na_2SO_4, and evaporated. The residue was chromatographed on silica gel (hexane–hexane/ether).

2,4-Diacetoxy-1-perfluorooctylbenzene (3a) and 1,2-Diacetoxy-4-perfluorooctylbenzene (5a=5j). Colorless crystals (dichloromethane/hexane); mp 56—58 °C. ^{19}F NMR δ= −81.34 (both 3F, t, J=10 Hz), −108.79 (**5a**, 2F, t, J=13 Hz), −110.77 (**3a**, 2F, t, J=13 Hz), −121.70 (both 2F, m), −121.8—−122.4 (6F, m), −123.18 (both 2F, m), and −126.61 (both 2F); IR (neat) 1772vs, 1374s, and 1300—1100vs cm^{-1}; MS (EI) m/z 612 (M^+, 2), 570 (20), 528 (68), 509 (5), and 154 (100). Found: C, 35.36; H, 1.41%. Calcd for $C_{18}H_9F_{17}O_4$: C, 35.31; H, 1.48%.

2,4-Diacetoxy-1-perfluorohexylbenzene (3b) and 1,2-Diacetoxy-4-perfluorohexylbenzene (5b). Colorless crystals (hexane); mp 38—40 °C. ^{19}F NMR δ=−81.32 (both 3F, tt, J=10 and 2 Hz), −108.81 (**5b**, 2F, t, J=15 Hz), −110.81 (**3b**, 2F, m), −121.7—−122.3 (both 4F, m), −123.23 (both 2F, m), and −126.59 (both 2F, m); IR (neat) 1782vs, 1374s, and 1300—1100vs cm^{-1}; MS (EI) m/z 512 (M^+, 2), 470 (26), 428 (77), 160 (8), and 159 (100). Found: C, 37.54; H, 1.71%. Calcd for $C_{16}H_9F_{13}O_4$: C, 37.52; H, 1.77%.

2,4-Diacetoxy-1-perfluorobutylbenzene (3c) and 1,2-Diacetoxy-4-perfluorobutylbenzene (5c).[7] Colorless oil. MS (EI) m/z 412 (M^+, 4), 370 (13), 329 (12), 328 (100), and 159 (96). Found: C, 41.90; H, 2.35%. Calcd for $C_{14}H_9F_9O_4$: C, 40.79; H, 2.20%.

2,4-Diacetoxy-1-perfluoroethylbenzene (3d) and 1,2-Diacetoxy-4-perfluoroethylbenzene (5d). Colorless oil. ^{19}F NMR δ=−84.79 (**3d**, 3F, t, J=2 Hz), −85.10 (**4d**, 3F, t, J=2 Hz), −112.92 (**3d**, 2F, m), and −114.77 (**4d**, 2F, m); IR (neat) 1780vs, 1614m, 1510m, 1426s, 1374s, 1338s, and 1300—1100vs cm^{-1}; MS (EI) m/z 312 (M^+, 5), 270 (44), 229 (9), 228 (100), and 159 (45). Found: C, 45.77; H, 2.83%. Calcd for $C_{12}H_9F_5O_4$: C, 46.17; H, 2.91%.

1,3-Diacetoxy-2-methyl-4-perfluorooctylbenzene (3e). Colorless crystals (dichloromethane/hexane), mp 75—76 °C. ^{1}H NMR δ=2.02 (3H, s), 2.31 (3H, s), 2.36 (3H, m), 7.14 (1H, d, J=8.9 Hz), and 7.46 (3H, d, J=8.9 Hz); ^{13}C NMR δ=10.19, 20.16, 20.60, 105—125 (8C), 118.81 (t, J=23 Hz), 120.11, 126.50, 126.62 (t, J=8 Hz), 148.73 (t, J=3 Hz), 152.97, 168.03, and 168.19; ^{19}F NMR δ=−81.29 (3F, t, J=10 Hz), −107.5 (1F, dm, J=ca. 265 Hz), −110.5 (1F, dm, J=ca. 265 Hz), −121.47 (2F, m), −122.2—−122.3 (6F, m), −123.26 (2F, m), and −126.62 (2F, m); IR (KBr) 1764vs, 1606m, 1590m, 1430s, 1368s, and 1300—1100vs cm^{-1}; MS (EI) 626 (M^+, 0.7), 607 (0.8), 584 (32), 542 (100), 523 (10), and 173 (96). Found: 36.73; H, 1.77%. Calcd for $C_{19}H_{11}F_{17}O_4$: C, 36.44; H, 1.77%.

1,5-Diacetoxy-2-methyl-4-perfluorooctylbenzene (4e) and 1,2-Diacetoxy-3-methyl-5-perfluorooctylbenzene (5e). Colorless oil. ^{1}H NMR **4e**: δ=2.23 (3H, s), 2.27 (3H, s), 2.34 (3H, s), 7.31 (1H, m), and 7.35 (1H, m); **5e**: δ=2.05 (3H, s), 2.25 (3H, s), 2.27 (3H, s), 7.05 (1H, s), and 7.45 (1H, s); ^{13}C NMR **4e**: δ=16.21, 20.33, 20.56, 105—125 (8C), 118.82, 123.48 (t, J=23 Hz), 128.62, 130.83 (t, J=9 Hz), 147.29 (t, J=3 Hz), 152.26 (t, J=1 Hz), 168.12, and 168.62; **5e**: (typical signals) δ=15.68, 20.04, 133.46, 142.71, 144.10, 167.35, and 167.84; ^{19}F NMR **4e**: (typical signal) δ=−108.86; **5e**: (typical signal) δ=−110.96.

1,5-Diacetoxy-3-methyl-2-perfluorooctylbenzene (4f), 1,2-Diacetoxy-3-methyl-4-perfluorooctylbenzene (5f), and 1,2-Diacetoxy-4-methyl-5-perfluorooctylbenzene (6f). Colorless oil. ^{1}H NMR **4f**: δ=2.26 (3H, s), 2.30 (3H, s), 2.50 (3H, t, J=4.6 Hz), 6.90 (1H, m), and 6.97 (1H, m); **5f**: δ=2.31 (3H, m), 2.31 (3H, s), 2.35 (3H, m), 7.21 (1H, d, J=8.9 Hz), and 7.47 (1H, d, J=8.9 Hz); **6f**: δ=2.30 (6H, m), 2.47 (3H, t, J=3.0 Hz), 7.14 (1H, s), and 7.35 (1H, s); ^{13}C NMR **4f**: δ=20.56, 21.04, 21.83 (m), 105—125 (8C), 116.36, 120.80, 123.29, 125.13 (t, J=23 Hz), 141.98, 152.73, 168.31, and 168.75; **5f**: δ=12.99 (tt, J=5 and 3 Hz), 20.18, 20.67, 105—125 (8C), 120.80, 125.77 (t, J=23 Hz), 126.75, (t, J=10 Hz), 133.50 (t, J=2 Hz), 141.97, 145.29, 167.63, and 167.67; **6f**: δ=20.02 (m), 20.46, 20.61, 105—125 (8C), 124.05 (t, J=9 Hz), 125.13 (t, J=23 Hz), 127.34, 137.32 (t, J=2 Hz), 139.94, 144.41, 167.67, and 167.90; ^{19}F NMR **4f**: (typical signal) δ=−103.51 (m); **5f**: δ=−81.27 (3F, tt, J=10 and 2 Hz), −105.51 (2F, m), −121.02 (2F, m), −121.94 (2F, m), −122.33 (4F, m), −123.19 (2F, m), and −126.61 (2F, m); **6f**: (typical signal) δ=−106.75 (m).

4-Acetoxy-2-acetoxymethyl-1-perfluorooctylbenzene (7f). Colorless crystals (dichloromethane/hexane), mp 74—75 °C. ^{1}H NMR δ=2.14 (3H, s), 2.34 (3H, s), 5.27 (2H, s), 7.24 (1H, dd, J=8.5 and 2.1 Hz), 7.35 (1H, d, J=2.1 Hz), and 7.61 (1H, d, J=8.5 Hz); ^{13}C NMR δ=20.79, 21.08, 62.53 (tt, J=7 and 3 Hz), 105—125 (8C), 121.43, 123.07, 123.70 (t, J=23 Hz), 130.31, (t, J=9 Hz), 138.02 (t, J=2 Hz), 153.49, 168.67, and 170.38; ^{19}F NMR δ=−81.26 (3F, tt, J=10 and 2 Hz), −105.70 (2F, t, J=14 Hz), −121.16 (2F, m), −121.82 (2F, m), −122.31 (2F, m), −123.19 (2F, m), and −126.60 (2F, m); IR (KBr) 1740vs, 1610m, 1586s, 1370s, and 1300—1100vs cm^{-1}; MS (EI) 626 (M^+, 6), 584 (23), 542 (100), 153 (24), and 123 (13). Found: C, 36.39; H, 1.81%. Calcd for $C_{18}H_{11}F_{17}O_4$: C, 36.44; H, 1.77%.

1,3-Diacetoxy-2,5-dimethyl-4-perfluorooctylbenzene (3g). Colorless crystals (dichloromethane/hexane), mp 115—117 °C. ^{1}H NMR δ=1.95 (3H, s), 2.26 (3H, s), 2.31 (3H, s), 2.45 (3H, t, J=4.6 Hz), and 6.94 (1H, s); ^{13}C NMR δ=9.93, 20.01, 20.53, 21.42 (m), 105—125 (8C), 117.54 (t, J=21 Hz), 123.87, 124.09, 138.56 (t, J=2 Hz), 149.92 (t, J=4 Hz), 152.00, 168.17, and 168.22; ^{19}F NMR δ=−81.40 (3H, tm, J=10 Hz), −102.23 (1F, dm, J=289 Hz), −104.83 (1F, dm, J=289 Hz), −120.82 (1F, m), −121.09 (1F, m), −122.30 (6F, m), −123.17 (2F, m), and −126.64 (2F, m); IR (KBr) 1764vs, 1580m, 1372s, and 1300—1100vs cm^{-1}; MS (EI) m/z 640 (M^+, 4), 598 (15), 556 (100), 537 (7), and 187 (63). Found: C, 37.67; H, 2.08%. Calcd for $C_{20}H_{13}F_{17}O_4$: C, 37.52; H, 2.05%.

2,3-Diacetoxy-1,4-dimethyl-5-perfluorooctylbenzene (6g). Colorless crystals (dichloromethane/hexane), mp 73—75 °C. ^{1}H NMR δ=2.22 (3H, s), 2.23 (3H, s), 2.33 (3H, s), 2.34 (3H, s), and 7.33 (1H, s); ^{13}C NMR δ=12.81 (m), 16.08, 20.21, 20.27, 105—125 (8C), 125.51 (t, J=22 Hz), 128.30 (t, J=9 Hz), 129.84, 130.54 (t, J=2 Hz), 142.44, 144.25, 167.41, and 167.73; ^{19}F NMR δ=−81.25 (3F, tm, J=10 Hz), −105.58 (2F, m), −120.94 (2F, m), −121.95 (2F, m), −122.32 (4F, m), −123.19 (2F, m), and −126.58 (2F, m); IR (KBr) 1780vs, 1490m, 1458m, 1430m, 1374s, 1320s, and 1300—1100vs cm^{-1}; MS (EI) m/z 640 (M^+, 3), 598 (12), 556 (100), 537 (6), and 187 (52).

1-Acetoxy-5-acetoxymethyl-2-methyl-4-perfluorooctylbenzene (7g). ^{1}H NMR (typical signals) δ=5.24 (2H, m), 7.29 (1H, s), and 7.46 (1H, s).

2,4-Diacetoxy-1,3-dimethyl-5-perfluorooctylbenzene (3h). Colorless crystals (dichloromethane/hexane), mp 72—74 °C. ^{1}H NMR δ=1.97 (3H, s), 2.20 (3H, s), 2.29 (3H, s), 2.37 (3H, s), and 7.31 (1H, s); ^{13}C NMR δ=10.51 (m), 16.34 (m), 20.28

(m), 20.38 (m), 118.71 (t, J=23 Hz), 126.51, 127.94 (tm, J=8 Hz), 128.93, 146.39 (t, J=3 Hz), 151.69 (t, J=1 Hz), 167.78, and 168.28; ^{19}F NMR δ=−81.25 (3F, tt, J=10 and 2 Hz), −107.65 (1F, dm, J=267 Hz), −110.88 (1F, dm, J=267 Hz), −121.42 (2F, m), −122.27 (6F, m), −123.21 (2F, m), and −126.60 (2F, m); IR (KBr) 1768vs, 1604m, 1374s, 1330s, 1300—1100vs cm^{-1}; MS (EI) m/z 640 (8), 598 (20), 556 (100), and 167 (88). Found: C, 37.67; H, 2.08%. Calcd for $C_{20}H_{13}F_{17}O_4$: C, 37.52; H, 2.05%.

5-Acetoxy-1-acetoxymethyl-3-methyl-2-perfluorooctylbenzene (7i). Colorless crystals (dichloromethane/hexane), mp 78—80 °C. ^{1}H NMR δ=2.13 (3H, s), 2.32 (3H, s), 2.51 (3H, mt, J=4.6 Hz), 5.24 (2H, t, J=3.0 Hz), 7.05 (1H, s), and 7.21 (1H, s); ^{13}C NMR δ=20.82, 21.03, 22.12 (tt, J=7 and 4 Hz), 63.62 (tt, J=10 and 4 Hz), 105—125 (8C), 121.24, 122.45 (t, J=22 Hz), 125.78, 139.45 (t, J=3 Hz), 142.04 (t, J=4 Hz), 152.61, 168.71, and 170.33; ^{19}F NMR δ=−81.29 (3F, tt, J=10 and 2 Hz), −99.59 (2F, m), −120.42 (2F, m), −122.09 (6F, m), −123.15 (2F, m), and −126.57 (2F, m); IR (KBr) 1764vs, 1738s, 1602s, 1462m, 1386s, 1372s, 1328m, and 1300—1100vs cm^{-1}; MS (CI) m/z 641 (M^++1, 100), 621 (76), 599 (46), 585 (16), 579 (37), 557 (49), 556 (47), 271 (9), and 187 (73). Found: C, 37.45; H, 2.03%. Calcd for $C_{20}H_{13}F_{17}O_4$: C, 37.52; H, 2.05%.

1-*t*-Butyl-2,4-diacetoxy-5-perfluorooctylbenzene (4j=4k). Colorless crystals (dichloromethane/hexane), mp 76—77 °C. ^{1}H NMR δ=1.37 (9H, s), 2.27 (3H, s), 2.35 (3H, s), 7.03 (1H, s), and 7.57 (1H, s); IR (KBr) 2960m, 1774vs, 1612m, 1580m, 1502m, 1404m, 1372s, and 1300—1100vs cm^{-1}; MS (EI) m/z 668 (M^+, 1), 653 (0.4), 649 (1), 626 (12), 584 (41), and 569 (100). Found: C, 39.74; H, 2.53%. Calcd for $C_{22}H_{17}F_{17}O_4$: C, 39.54; H, 2.56%.

1-*t*-Butyl-2,3-diacetoxy-5-perfluorooctylbenzene (6j=5l). Colorless crystals (dichloromethane/hexane), mp 61—63 °C. ^{1}H NMR δ=1.37 (9H, s), 2.28 (3H, s), 2.36 (3H, s), 7.38 (1H, m), and 7.47 (1H, m); ^{13}C NMR δ=20.69, 20.83, 30.00, 35.20, 105—125 (8C), 120.63 (t, J=7 Hz), 122.93 (t, J=7 Hz), 126.19 (t, J=25 Hz), 143.08, 144.08 (t, J=2 Hz), 144.21, 167.52, and 167.58; ^{19}F NMR δ=−81.25 (3F, tt, J=10 and 3 Hz), −110.83 (2F, t, J=13 Hz), −121.85 (4F, m), −122.35 (4F, m), −123.20 (2F, m), and −126.59 (2F, m); IR (KBr) 2984s, 1762s, 1428s, 1370s, and 1300—1100vs cm^{-1}; MS (EI) m/z 668 (M^+, 7), 626 (8), 584 (100), and 569 (49). Found: C, 39.51; H, 2.60%. Calcd for $C_{22}H_{17}F_{17}O_4$: C, 39.54; H, 2.56%.

1,5-Diacetoxy-2-methoxy-4-perfluorobutylbenzene (4m). Colorless crystals (dichloromethane/hexane), mp 73—74 °C. ^{1}H NMR δ=2.26 (3H, s), 2.32 (3H, s), 3.87 (3H, s), 7.01 (1H, s), and 7.09 (1H, s); ^{13}C NMR δ=20.50, 20.52, 56.40, 105—125 (4C), 111.62 (t, J=9 Hz), 118.44 (t, J=23 Hz), 119.91, 142.10 (t, J=3 Hz), 142.78, 149.15, 167.86, and 168.82; ^{19}F NMR δ=−81.41 (3F, tt, J=10 and 3 Hz), −109.08 (2F, m), −122.58 (2F, m), and −126.43 (2F, m); IR (KBr) 1774vs, 1516s, 1410s, 1374s, 1350s, and 1300—1100vs cm^{-1}; MS (EI) m/z 442 (M^+, 3), 401 (3), 358 (100), and 189 (51). Found: C, 40.78; H, 2.45%. Calcd for $C_{15}H_{11}F_9O_5$: C, 40.72; H, 2.51%.

1,2-Diacetoxy-4-perfluorohexylnaphthalene (5p). Colorless crystals (dichloromethane/hexane), mp 89—90 °C. ^{1}H NMR δ=2.33 (3H, s), 2.46 (3H, s), 7.58 (2H, m), 7.73 (1H, s), 7.59 (1H, m), and 8.22 (1H, m); ^{13}C NMR δ=20.27, 20.50, 105—125 (8C), 121.98, 123.35 (t, J=23 Hz), 124.62 (t, J=11 Hz), 125.08 (m), 127.42, 127.86, 128.63, 129.37, 137.83, 140.63 (t, J=1 Hz), 167.44, and 167.95; ^{19}F NMR δ=−81.28 (3F, tt, J=10 and 2 Hz), −104.62 (2F, t, J=15 Hz), −120.32 (2F, t, J=12 Hz), −121.90 (2F, m), −123.10 (2F, m), and −126.53 (2F, m); IR (KBr) 2950m, 1770vs, 1634m, 1614m, 1588m, 1520m, 1472m, 1436m, 1374s, 1354s, and 1300—1100vs cm^{-1}; MS (EI) m/z 562 (M^+, 3), 520 (12), 478 (100), 459 (5), 458 (5), 239 (9), and 209 (97). Found: C, 42.46; H, 2.06%. Calcd for $C_{20}H_{11}F_{13}O_4$: C, 42.72; H, 1.97%.

Deacetylation of Diacetoxybenzenes. General Procedure: A mixture of **3a—d** and **5a—d** (ca. 1:1, derived from 1 mmol of quinols) was dissolved in 20 ml of methanol containing 100 mg (1 mmol) of *p*-toluenesulfonic acid hydrate. The methanol solution was refluxed for 1 d under a nitrogen atmosphere. After the solvent was removed in vacuo, the residue was dissolved in ether. The solution was washed with water and brine, dried over Na_2SO_4, and evaporated to give an almost quantitative yields of benzenediols. Separation of isomeric benzenediols was carried out by chromatography of the residue on silica gel (CH_2Cl_2–ether). Resorcinol and catechol derivatives were obtained from less and more polar fractions, respectively. In the case of perfluorooctyl derivatives, fractional crystallization of **8a** from $CHCl_3$ was performed prior to the chromatographic separation.

4-Perfluorooctyl-1,3-benzenediol (8a). Colorless crystals (dichloromethane/hexane), mp 118—119 °C; ^{1}H NMR (acetone-d_6) δ=6.45 (1H, dd, J=8.6 and 2.0 Hz), 6.49 (1H, d, J=2 Hz), 7.24 (1H, d, J=8.6 Hz), 8.99 (1H, br s), and 9.11 (1H, br s); ^{13}C NMR (acetone-d_6) δ=105.15, 107.32 (t, J=23 Hz), 108.67, 105—125 (8C), 131.42, (t, J=8 Hz), 159.60 (t, J=3 Hz), and 163.41; ^{19}F NMR (acetone-d_6) δ=−81.85 (3F, tt, J=10 and 2 Hz), −106.11 (2F, t, J=14 Hz), −120.76 (2F, m), −121.43 (6F, m), −122.23 (2F, m), and −125.85 (2F, m); IR (KBr) 3216vs, 1612vs, 1318vs, and 1300—1100vs cm^{-1}; MS (EI) m/z 528 (M^+, 14), 159 (100), and 119 (3). Found: C, 31.61; H, 1.32%. Calcd for $C_{14}H_5F_{17}O_2$: C, 31.84; H, 0.95%.

4-Perfluorooctyl-1,2-benzenediols (9a). Colorless crystals (dichloromethane/hexane), mp 94—95 °C. ^{1}H NMR δ=6.90 (2H, m) and 6.96 (1H, s); ^{13}C NMR δ=105—125 (8C), 115.43 (t, J=7 Hz), 117.10, 120.70 (t, J=7 Hz), 121.31 (t, J=25 Hz), 147.61, and 151.15 (t, J=1 Hz); ^{19}F NMR δ=−80.80 (3F, t, J=10 Hz), −108.76 (2F, t, J=14 Hz), −120.80 (2F, m), −121.43 (6F, m), −122.21 (2F, m), and −125.75 (2F, m); IR (KBr) 3536s, 3476vs, 1614m, 1530m, 1448s, 1394s, 1314vs, and 1300—1100vs cm^{-1}; MS (EI) m/z 528 (M^+, 19), 509 (5), 508 (5), 189 (14), and 159 (100). Found: m/z 528.0028. Calcd for $C_{14}H_5F_{17}O_2$: M, 528.0017.

4-Perfluorohexyl-1,3-benzenediol (8b). Colorless crystals (dichloromethane/hexane), mp 70 °C; ^{19}F NMR (acetone-d_6) δ=−80.66 (3F, tt, J=10 and 3 Hz), −106.03 (2F, tt, J=15 and 3 Hz), −120.79 (2F, m), −121.40 (2F, m), −122.26 (2F, m), and −125.75 (2F, m); IR (KBr) 3212vs, 1614vs, 1536m, 1468s, 1394s, 1364s, 1316s, and 1300—1100vs cm^{-1}; MS (CI) m/z 429 (M^+, 2), 406 (100), and 159 (99). Found: m/z 428.0094. Calcd for $C_{12}H_5F_{13}O_2$: M, 428.0081.

4-Perfluorohexyl-1,2-benzenediol (9b). Colorless crystals (dichloromethane/hexane), mp 77—78 °C. ^{19}F NMR δ=−80.99 (3F, tt, J=10 and 3 Hz), −108.78 (2F, tt, J=15 and 3 Hz), −121.18 (2F, m), −121.60 (2F, m), −122.54 (2F, m), and −126.00 (2F, m); IR (KBr) 3416vs, 1614m, 1532m, 1448m, 1356s, 1316s, and 1300—1100vs cm^{-1}; MS (EI) m/z 428 (M^+, 4), 407 (3), 406 (18), 387 (3), 209 (7), 159 (13), and 137 (100). Found: m/z 428.0087. Calcd for $C_{12}H_5F_{13}O_2$: M, 428.0081.

4-Perfluorobutyl-1,3-benzenediol (8c). Colorless crystals

(dichloromethane/hexane), mp 52—53 °C. ^{19}F NMR δ=−80.85 (3F, tt, J=10 and 3 Hz), −106.26 (2F, tq, J=13 and 3 Hz), −121.66 (2F, m), and −125.60 (2F, m); IR (KBr) 3504s, 3224vs, 1612vs, 1466s, 1394s, 1356m, 1318m, and 1300—1100vs cm^{-1}; MS (EI) m/z 328 (M^+, 22), 309 (3), 308 (2), 289 (1), and 159 (100). Found: m/z 328.0143. Calcd for $C_{10}H_5F_9O_2$: M, 328.0144.

4-Perfluorobutyl-1,2-benzenediol (9c). Colorless crystals (dichloromethane/hexane), mp 67—68 °; ^{19}F NMR (acetone-d_6) δ=−80.92 (3F, tt, J=10 and 2 Hz), −108.74 (2F, tt, J=13 and 3 Hz), −122.38 (2F, m), and −125.25 (2F, m); IR (KBr) 3460vs, 1614s, 1534s, 1448s, 1356s, 1316s, and 1300—1100vs cm^{-1}; MS (EI) m/z 328 (M^+, 27), 309 (4), 308 (4), 189 (7), and 159 (100). Found: m/z 328.0165. Calcd for $C_{10}H_5F_9O_2$: M, 328.0144.

4-Perfluoroethyl-1,3-benzenediol (8d). Colorless needles (hexane). ^{19}F NMR (acetone-d_6) δ=−83.95 (3F, t, J=2 Hz) and −110.32 (2F, q, J=2 Hz); IR (KBr) 3420vs, 1616s, 1580s, 1500m, 1446m, 1406s, 1336s, and 1300—1100vs cm^{-1}; MS (CI) m/z 229 (M^++1, 100), 211 (34), 209 (16), 110 (50), and 109 (67). Found: m/z 228.0258. Calcd for $C_8H_5F_5O_2$: M, 228.0210.

4-Perfluoroethyl-1,2-benzenediol (9d). Colorless oil. ^{19}F NMR δ=85.14 (3F, t, J=3 Hz) and −113.13 (2F, m). MS (EI) m/z 228 (100), 208 (41), 180 (40), and 159 (64). Found: m/z 228.0237. Calcd for $C_8H_5F_5O_2$: M, 228.0210.

Treatment of Benzenediols 8a and 9a with Acetone: A mixture of (**8a** and **9a** obtained from 100 mg of **3a** and **5a** as described above was dissolved in acetone (10 ml) and refluxed for 3 d under a nitrogen atmosphere. The solvent was removed and the residue was chromatographed on silica gel (hexane–CH_2Cl_2/ether) to give **8a** (38 mg, 43%), **9a** (17 mg, 17%), and a mixture of **10** and **11**. Further separation of the last mixture on GPC gave 2 mg of **10** and 6 mg of **11**.

5-Perfluorooctyl-2,2-dimethyl-1,3-benzodioxole (10). Colorless crystals (dichloromethane/hexane), mp 58—59 °C. ^{1}H NMR δ=1.71 (6H, s), 6.80 (1H, d, J=8.2 Hz), 6.91 (1H, d, J=1.8 Hz), and 7.05 (1H, dd, J=8.2 and 1.8 Hz); ^{13}C NMR δ=25.87, 105—125 (8C), 106.94 (t, J=7 Hz), 108.07, 119.51, 121.08 (t, J=7 Hz), 121.65 (t, J=25 Hz), 147.78, and 150.42; ^{19}F NMR δ=−81.24 (3F, t, J=10 Hz), −109.51 (2F, t, J=15 Hz), −121.81 (2F, m), −122.28 (6F, m), −123.21 (2F, m), and −126.59 (2F, m); IR (KBr) 3004m, 1634m, 1614m, 1512s, 1454s, 1372s, 1330s, and 1300—1100vs cm^{-1}; MS (EI) m/z 568 (M^+, 51), 553 (100), 549 (5), 199 (51), and 159 (40).

5-Perfluorooctyl-2-methyl-2-(2-methyl-1-propenyl)-1,3-benzodioxole (11). Colorless crystals (dichloromethane/hexane), mp 100—101 °C. ^{1}H NMR δ=1.76 (3H, s), 1.78 (3H, d, J=1.5 Hz), 1.83 (3H, d, J=1.5 Hz), 5.50 (1H, m), 6.81 (1H, d, J=8.2 Hz), 6.93 (1H, d, J=1.8 Hz), and 7.05 (1H, dd, J=8.2 and 1.8 Hz); ^{13}C NMR δ=19.15, 26.64, 105—125 (8C), 106.87 (t, J=7 Hz), 107.99, 118.36, 121.11 (t, J=7 Hz), 121.64 (t, J=25 Hz), 123.94 (m), 140.68 (m), 147.70, and 150.33; ^{19}F NMR δ=−81.26 (3F, t, J=10 Hz), −110.11 (2F, t, J=14 Hz), −121.80 (2F, m), −122.40 (6F, m), −123.22 (2F, m), and −126.62 (2F, m); IR (KBr) 2984m, 2932s, 1678m, 1504vs, 1452vs, 1372s, 1300—1100vs cm^{-1}; MS (EI) 608 (M^+, 100), 593 (99), 589 (15), 565 (43), and 553 (32).

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