Convenient Syntheses of Fluorous Aryl Iodides and Hypervalent Iodine Compounds: ArI(L)$_n$ Reagents That Are Recoverable by Simple Liquid/Liquid Biphase Workups, and Applications in Oxidations of Hydroquinones

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Abstract: Iodinations of the *ortho, meta*, and *para* fluorous arenes ($R_{f8}CH_2CH_2)_2C_6H_4$ ($R_{f8} = (CF_2)_7CF_3$) with I_2/H_5IO_6 in AcOH/H_2SO_4/H_2O give 3,4-($R_{f8}CH_2CH_2CH_2)_2C_6H_3I$ (**5**) and the analogous 2,4- (**6**) and 2,5- (**7**) isomers, respectively. Spectroscopic yields are >90%, but **5** and **7** must be separated by chromatography from by-products (yields isolated: 70%, 97%, 61%). Reaction of 1,3,5-($R_{f8}CH_2CH_2CH_2)_3C_6H_3$ with $PhI(OAc)_2/I_2$ gives 2,4,6-($R_{f8}CH_2CH_2CH_2)_3C_6H_2I$ (**8**) on multigram scales in 97% yield. The $CF_3C_6F_{11}$/toluene partition coefficients of **5**–**8** (24 °C: 69.5:30.5 (**5**), 74.7:25.3 (**6**), 73.9:26.1 (**7**), 98.0:2.0 (**8**)) are lower than those of the precursors, but $CF_3C_6F_{11}$/MeOH gives higher values (97.0:3.0 (**5**), 98.6:1.4 (**6**), 98.0:2.0 (**7**), >99.3:<0.3 (**8**)). Reactions of **5**–**8** with excess $NaBO_3$ in AcOH yield the corresponding $ArI(OAc)_2$ species **9**–**12** (**9**, 85% as a 90:10 **9**/**5** mixture; **10**, 97%; **11**, 95%; **12**, 93% as a 95:5 **12**/**8** mixture). These rapidly oxidize 1,4-hydroquinones in MeOH. Subsequent additions of $CF_3C_6F_{11}$ give liquid biphase systems. Solvent removal from the $CF_3C_6F_{11}$ phases gives **5**–**8** in >99–98% yields, and solvent removal from the MeOH phases gives the quinone products, normally in >99–95% yields. The recovered compounds **5**–**8** are easily reoxidized to **9**–**12** and used again.

Keywords: fluorine · hypervalent iodine · oxidations · quinones · recycling

Introduction

Over the past eight years, many new compounds with high affinities for perfluoroalkane and perfluorodialkyl ether ("fluorous") solvents have been synthesized.[1–3] This has been prompted by the development of "fluorous biphase chemistry",[1] which as most frequently implemented exploits the markedly temperature-dependent miscibilities of organic and fluorous solvents. At room temperature, most combinations give two phases.[4] However, with moderate heating, one phase is obtained. Reactions can be conducted under homogeneous conditions at the high-temperature limit. Organic products and fluorous catalysts or by-products can be separated under liquid/liquid biphase conditions at the low-temperature limit.

High fluorous phase affinities are achieved by appending sufficient numbers of "pony tails" of the formula $(CH_2)_m(CF_2)_{n-1}CF_3$, herein abbreviated as $(CH_2)_mR_{fn}$. The $(CH_2)_m$ or "spacer" segment partially insulates the reactive site from the electronegative R_{fn} groups.[5] More recently, many such compounds have been found to exhibit little or no solubility in organic solvents at room temperature, but significant solubility at elevated temperatures. Thus, reactions can be conducted under homogeneous conditions at the high-temperature limit, and the fluorous material recovered by a simple solid/liquid phase separation at the low-temperature limit.[6, 7] This variant renders a fluorous solvent unnecessary.

Aryl iodides are extremely versatile synthetic organic building blocks.[8] They are also precursors to a variety of exceedingly useful and extensively applied hypervalent iodine reagents.[9–14] Unfortunately, the latter produce a stoichiometric amount of an aryl iodide or similar waste product. These have seldom been recycled, apparently for lack of a convenient protocol. This represents a distinct disadvantage from the standpoint of "green" chemistry, which is playing an increasingly important role in process design.[15] Over the last few years, several immobilization strategies have been described, as further detailed below.[16] All of these feature polystyrene or silica supports, and the intrinsic advantages and disadvantages associated with insoluble reagents and heterogeneous reaction conditions.

We thought that fluorous aryl iodide species that could be utilized under homogeneous conditions and recovered as described above would provide valuable complements to these methodologies. Interestingly, no aryl iodides with high

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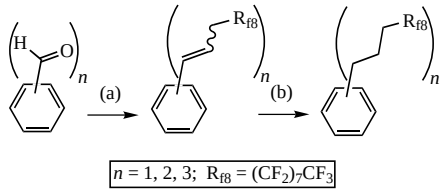
fluorous phase affinities have so far been reported. We[17] and several other groups[18] have described simple fluorous aryl bromides such as *p*-$BrC_6H_4(CH_2)_mR_{fn}$ ($m/n = 2/6$, 2/8, 3/8), and used these as precursors to a variety of other fluorous molecules. However, compounds that contain only one pony tail per aromatic[4, 18, 20] or heteroaromatic[20, 21] ring exhibit low fluorous phase affinities.

As shown in Scheme 1, we have found that benzenoid di- and trialdehydes undergo efficient Wittig reactions with the ylide derived from the phosphonium salt



Scheme 1. Syntheses of fluorous arenes. a) $[Ph_3PCH_2CH_2R_{f8}]^+I^-$, K_2CO_3, *p*-dioxane/H_2O, 95 °C; b) 10 % Pd/C, 1 atm H_2, EtOH/$CF_3C_6H_5$.

$[Ph_3PCH_2CH_2R_{f8}]^+I^-$.[19] Subsequent hydrogenation leads to fluorous benzene derivatives with two to three pony tails and three methylene spacers. As summarized in Table 1, these exhibit $CF_3C_6F_{11}$/toluene partition coefficients of about 91:9 for two pony tails, and $>99:<1$ for three pony tails. We therefore set out to attempt the iodination of these fluorous arenes, to elaborate the resulting aryl iodides to fluorous hypervalent iodine compounds, to apply the later in oxidation reactions, and to efficiently recover and reuse the fluorous by-products. The successful realization of all of these objectives is described below.

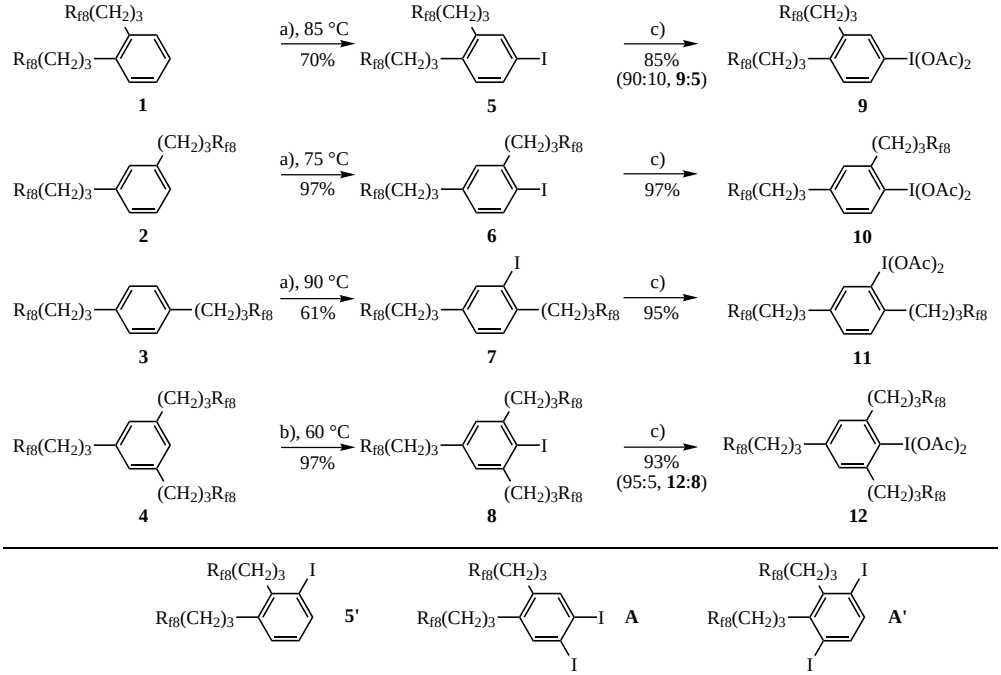
Table 1. Summary of relevant partition coefficients (24 °C).

	Analyte	$CF_3C_6F_{11}$:toluene	$CF_3C_6F_{11}$:MeOH
	$R_{f8}CH_2CH_2CH_2C_6H_5$	49.5:50.5[a]	
1	1,2-($R_{f8}CH_2CH_2CH_2)_2C_6H_4$	91.2:8.8[a]	
2	1,3-($R_{f8}CH_2CH_2CH_2)_2C_6H_4$	90.7:9.3[a]	
3	1,4-($R_{f8}CH_2CH_2CH_2)_2C_6H_4$	91.1:8.9[a]	
4	1,3,5-($R_{f8}CH_2CH_2CH_2)_3C_6H_3$	$>99.7:<0.3$[a]	
	1,2-($R_{f6}CH_2CH_2CH_2)_2C_6H_4$	73.7:26.3[a]	
	1,2-($R_{f10}CH_2CH_2CH_2)_2C_6H_4$	97.4:2.6[a]	
5	3,4-($R_{f8}CH_2CH_2CH_2)_2C_6H_3I$	69.5:30.5[b]	97.0:3.0[b]
6	2,4-($R_{f8}CH_2CH_2CH_2)_2C_6H_3I$	74.7:25.3[b]	98.6:1.4[b]
7	2,5-($R_{f8}CH_2CH_2CH_2)_2C_6H_3I$	73.9:26.1[b]	98.0:2.0[b]
8	2,4,6-($R_{f8}CH_2CH_2CH_2)_3C_6H_2I$	98.0:2.0[b]	$>99.7:<0.3$[b]
	$R_{f8}CH_2CH_2CH_2I$	50.7:49.3[a]	
	$R_{f8}CH{=}CH_2$	93.5:6.5[c]	

[a] See reference [19]. [b] This work. [c] See reference [20].

Results

Fluorous aryl iodides: As shown in Scheme 2, the doubly pony-tailed fluorous arenes ($R_{f8}CH_2CH_2CH_2)_2C_6H_4$ (**1**, 1,2-; **2**, 1,3-; **3**, 1,4-) were iodinated by using a standard procedure involving periodic acid (H_5IO_6) and iodine in a mixture of aqueous acetic and sulfuric acid.[8] Reactions were highly regioselective. Nonetheless, in most cases small quantities of alternative isomers or diiodides formed (<10 %), as assayed by ^{1}H NMR spectra of the crude reaction mixtures. For example, the *ortho*-substituted arene **1** gave the iodide 3,4-($R_{f8}CH_2CH_2CH_2)_2C_6H_3I$ (**5**) as the major product (>90 %), as evidenced by the ^{1}H NMR coupling pattern of the aromatic protons. However, signals consistent with the 2,3-regioisomer (**5′**), the only other possible monoiodide, could also be detected (see Experimental Section). Other signals were consistent with one of the diiodide by-products shown in Scheme 2 (**A**, **A′**). Iodide **5** could be isolated in pure form in



Scheme 2. Syntheses of fluorous iodoarenes and (diacetoxyiodo)arenes. a) I_2, H_5IO_6, AcOH/H_2SO_4/H_2O; b) I_2, $PhI(OAc)_2$, AcOEt; c) $NaBO_3 \cdot H_2O$, AcOH, 65 °C.

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70% yield, but a rather tedious column chromatography was necessary.

In contrast, the *meta*-substituted arene **2** gave only a single iodide, 2,4-($R_{f8}CH_2CH_2CH_2$)$_2$C$_6$H$_3$I (**6**), the structure of which followed from the six distinct aryl ^{13}C NMR signals. It could easily be isolated in 97% yield, and no by-products were observed. The *para*-substituted arene **3** can give only one monoiodide, 2,5-($R_{f8}CH_2CH_2CH_2$)$_2$C$_6$H$_3$I (**7**), and spectroscopic yields were >90%. However, ^{1}H NMR signals consistent with a diiodide by-product were also detected. These could also be removed chromatographically, although again at some sacrifice with respect to the final yield (61%).

When iodinations of the triply pony-tailed fluorous arene 1,3,5-($R_{f8}CH_2CH_2CH_2$)$_3$C$_6$H$_3$ (**4**) were attempted under similar conditions, the expected product 2,4,6-($R_{f8}CH_2CH_2CH_2$)$_3$C$_6$H$_2$I (**8**) was usually obtained. However, the degree of conversion was not very reproducible. Therefore, an alternative protocol involving (diacetoxyiodo)benzene (PhI(OAc)$_2$) and iodine in ethyl acetate was evaluated.[8, 22] As shown in Scheme 2, this gave **8** in high yields on multigram scales. Surprisingly, this recipe gave inferior results when applied to **1**–**3**.

The fluorous aryl iodides **5**–**8**, and all other new compounds below, were characterized by microanalysis and ^{1}H and ^{13}C NMR spectroscopy. Each was rather low-melting (ca. 37, 65, 91, and 80 °C), and differential scanning calorimetry (DSC) showed no other phase transitions. At room temperature, **5**–**8** were soluble in fluorinated solvents such as $CF_3C_6F_{11}$ and $CF_3C_6H_5$, and many organic solvents with moderate polarities (pentane, hexanes, toluene, diethyl ether, THF, CH_2Cl_2, $CHCl_3$). They were sparingly soluble in acetone, even less soluble in EtOH and acetonitrile, and nearly insoluble in MeOH and acetic acid. Iodide **7**, which has two pony tails in a *para* relationship, was the least soluble in the series, analogous to the trend with **1**–**3**.[19]

The $CF_3C_6F_{11}$/toluene partition coefficients of **5**–**8** were determined by GC as detailed in the Experimental Section. These reflect *relative* as opposed to *absolute* solubilities, and are summarized in Table 1. For reasons apparent below, measurements were also made with a second solvent system, $CF_3C_6F_{11}$/MeOH. Trends are analyzed in the Discussion section.

Fluorous (diacetoxyiodo)arenes: Hypervalent iodine compounds of the formula ArI(O$_2$CR)$_2$ are easily prepared by oxidations of aryl iodides. One convenient procedure utilizes the inexpensive reagent sodium perborate ($NaBO_3$) in acetic acid.[23–25] Although mechanistic questions remain, it has been suggested that this oxidation involves peracetic acid, generated in situ.[25] Thus, reactions are typically conducted at 40 °C or less to minimize any independent thermal decomposition of the peracid, and further reactions of products. However, the fluorous aryl iodides **5**–**8** were insoluble under these conditions, and no reactions occurred in mixed acetic acid/$CHCl_3$ solvent systems.

Interestingly, the aryl iodides **5**–**8** were soluble in acetic acid at 65 °C. Hence, 65 °C acetic acid solutions of **5**–**8** were treated with excesses of $NaBO_3 \cdot H_2O$. As shown in Scheme 2, the expected (diacetoxyiodo)arenes ($R_{f8}CH_2CH_2CH_2$)$_n$-C$_6$H$_{5-n}$I(OAc)$_2$ (**9**–**12**) formed in high yields. The reactions of **6** and **7** required only 5–7 h, and simple aqueous workups gave **10** and **11** as analytically pure yellowish and white solids in 95–97% yields.

For some reason, the oxidations of **5** and **8** to **9** and **12** could only be taken to 90–95% completion. Longer reaction times ultimately gave lower conversions, suggesting some type of reductive decomposition pathway. Commercial peracetic acid (39% in acetic acid) gave little or no reaction with **8** under a variety of conditions (30 equivalents; acetic acid, 65 °C or 2:1 v/v $CHCl_3$/acetic acid, 40 °C). Accordingly, **9** could only be isolated in 85% yield as an oily mixture of **9** and **5** (ca. 90:10). Similarly, **12** was isolated as a white solid in 93% yield as a mixture of **12** and **8** (ca. 95:5). Attempted crystallization from hexanes or $CHCl_3$ (−20 °C) did not remove residual **8**. However, analytically pure **12** could be isolated on small scales by filtration through Celite with acetic acid. This exploits the extremely low solubility of **8** in acetic acid at room temperature.

The (diacetoxyiodo)arenes **9**–**12** exhibited good solubilities in common fluorous and organic solvents such as $CF_3C_6F_{11}$, $CF_3C_6F_5$, $CF_3C_6H_5$, hexane,diethyl ether, THF, CH_2Cl_2, $CHCl_3$, and acetone. They were also slightly soluble in EtOH, MeOH, and acetic acid. Each was stable in air at room temperature for weeks, and no special care was required for handling. The structural assignments were supported by the NMR, IR, and microanalytical data. For example, IR spectra showed a diagnostic band for the acetoxy group ($\tilde{\nu}$ = 1648–1652 cm^{-1} (C=O)). Since **9**–**12** were not volatile enough for GC analyses, no partition coefficients were determined. However, they are expected to be more polar and less fluorophilic than the aryl iodides **5**–**8**.

Hydroquinone oxidations and fluorous aryl iodide recycling: Applications for the preceding compounds were sought. Both (diacetoxyiodo)benzene and its trifluoroacetoxy analogue are frequently used for the oxidation of hydroquinones to quinones, and related transformations.[9, 10, 26] However, the phenyl iodide coproduct is normally discarded. Accordingly, analogous reactions with **9**–**12** were investigated. Three hydroquinones—1,4-hydroquinone (**13a**), 2,3,5-trimethyl-1,4-hydroquinone (**13b**), and 2,6-di(*tert*-butyl)-1,4-hydroquinone (**13c**)—were selected for study, as summarized in Table 2.

The hydroquinones **13a**–**c** were dissolved in MeOH at room temperature and treated either with 1.0 equivalent of **10** or **11**, or 1.2 equivalents of **9** or **12**. The slight excesses of **9** and **12** were intended to compensate for the residual aryl iodide. Despite the modest solubilities of **9**–**12** in MeOH, the heterogeneous mixture rapidly turned yellow, diagnostic of the quinones **14a**–**c**. However, white solids remained, consistent with the low solubilities of the aryl iodide coproducts **5**–**8**. After 2–3 h, the fluorous solvent $CF_3C_6F_{11}$ was added to give MeOH/$CF_3C_6F_{11}$ liquid/liquid biphase systems. These steps are represented graphically in Scheme 3.

The lower fluorous layer was colorless, and from the partition coefficients in Table 1 was presumed to contain nearly all of the aryl iodides **5**–**8**. The upper organic layer was yellow, and from the partition coefficients of other polar organic molecules[4] was presumed to contain all of the

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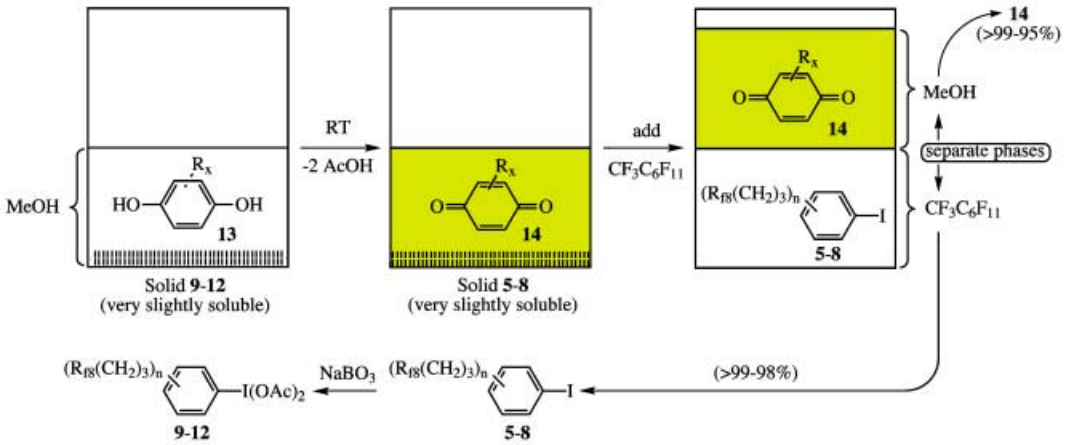
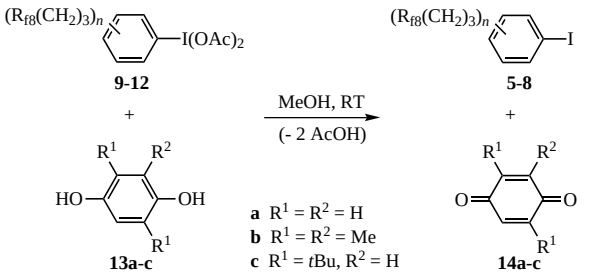


Scheme 3. Schematic diagram of reaction conditions for Table 2.

Table 2. Oxidations of hydroquinones **13** to benzoquinones **14**.



Entry	$ArI(OAc)_2$	Hydroquinone	Quinone (%)[a]	Aryl iodide (%)[a]
1	**9**[b]	**13a**	**14a** (95)	**5** (98)
2	**10**[c]	**13a**	**14a** (98)	**6** (100)
3	**10**[c,d]	**13a**	**14a** (98)	**6** (99)
4	**10**[c]	**13b**	**14b** (100)	**6** (100)
5	**11**[c]	**13b**	**14b** (65)[e]	**7** (98)
6	**10**[c]	**13c**	**14c** (96)	**6** (100)
7	**12**[b]	**13c**	**14c** (95)	**8** (100)

[a] Yields of isolated materials pure by ^{1}H NMR (>95%) spectroscopy. [b] 1.2 equiv; yield of recovered aryl iodide based upon this quantity. [c] 1.0 equiv. [d] The reaction was conducted with **10** that had been regenerated from **6** from the reaction in entry 2. [e] 65:35 **14b**/**11** mixture, as assayed by ^{1}H NMR spectroscopy.

quinones **14a–c**. The phases were separated and rinsed, and solvents were removed under reduced pressure. As shown in Table 2, this gave the quinones **14a–c** in (with a single exception) >99–95% yields, and the aryl iodides **5–8** in >99-98% yields (based upon the amount of **9–12** employed). No by-products or impurities were detected by ^{1}H NMR spectroscopy.

The easiest doubly pony-tailed (diacetoxyiodo)arene to obtain in analytically pure form, **10**, was used with each of the hydroquinones **13a–c** (entries 2, 4, 6 in Table 2). The aryl iodide recovered in entry 2, **6**, was reoxidized to **10** as in Scheme 2. This sample was directly used in a second oxidation of **13a**, at the original loading and with comparable results (Table 2, entry 3). The (diacetoxyiodo)arenes **9** (Table 2, entry 1) and **12** (Table 2, entry 7) appear similarly effective, although here the slight excesses employed must be kept in mind. Only **11** gave an incomplete oxidation of hydroquinone to quinone. Although we have no simple explanation for this reproducible effect, it may in some way be connected to the lower solubility of this series of compounds noted above.

Discussion

Syntheses and physical properties of fluorous $ArI(L)_n$ compounds: Scheme 2 shows that fluorous aryl iodides with high fluorous phase affinities can be prepared in good to excellent yields from the corresponding fluorous arenes. Overall, only three straightforward steps from commercially available benzenoid aldehydes are required (Scheme 1 and 2). Two of the new iodides, **6** and **8**, are easily obtained in pure form on multigram scales. However, as emphasized previously,[6b, 17, 28] the most important consideration in the synthesis of fluorous molecules is not the number of steps but the ease of purification and/or avoidance of by-products. The other new iodides, **5** and **7**, are difficult to separate from what should be trivial amounts of isomers or diiodides.

Analogous mixtures with methyl or ethyl in place of the $R_{f8}CH_2CH_2CH_2$ moieties would not present extraordinary separation challenges. In our view, the pony tails bring about a "leveling effect" with regard to the polarity properties commonly exploited in chromatographic purifications. Furthermore, since all by-products have the same spatial relationship of pony tails, chromatography on fluorous silica gel[29] would not be effective either. Another handicap is that fluorous molecules are intrinsically less prone to crystallize. In related efforts, we have made repeated attempts to efficiently convert the arene $R_{f8}CH_2CH_2CH_2C_6H_5$ to the singly pony-tailed *para*-substituted iodide 4-$R_{f8}CH_2CH_2CH_2C_6H_4I$.[30, 31] However, we have been unable to devise a user-friendly separation from the *ortho* isomer and/or unreacted arene. Under the conditions in Scheme 2, a 72:28 *para*/*ortho* mixture forms, and four preparative columns are needed to obtain a 34% yield of pure material.[31, 32]

The oxidations of **5–8** to (diacetoxyiodo)arenes **8–12** (Scheme 2) can be effected in high yields with cheap, readily available materials. Although two products, **8** and **12**, are for some reason always obtained with small amounts of starting aryl iodide, this is of no consequence with respect to most subsequent chemistry, such as the applications in Table 2. It is

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also likely that the isomers or diiodides that accompany the formation of **5** and **7** could be "carried along" with no negative effect. However, the ease of purification of **6** and **8** renders the corresponding (diacetoxyiodo)arenes **10** and **12** the most attractive candidates for further study and use. The latter has the advantage of a higher fluorous phase affinity. While **8**–**12** represent the first hypervalent iodine compounds with fluorous *aryl* moieties, there is an extensive literature of such species with fluorous *alkyl* moieties.[9, 33] These also represent attractive candidates for recyclable oxidizing agents.

Interestingly, the oxidation protocol in Scheme 2 fails when applied to perfluoroalkyl-substituted aryl iodides,[23] illustrating the importance of the insulating $(CH_2)_3$ spacer units in **5**–**8**. However, the triply pony-tailed fluorous triarylphosphine $P(p\text{-}C_6H_4CH_2CH_2CH_2R_{f8})_3$ remains less basic than PPh_3, as assayed by the IR ν_{CO} value of an iridium adduct.[17] Hence, the inductive effect of the perfluoralkyl segment can be transmitted through many connecting atoms.[5] We suggest that the basicities of **5**–**8** are decreased by a comparable amount relative to phenyl iodide. This would also render **9**–**12** slightly stronger oxidants than (diacetoxyiodo)benzene.

Table 1 shows that when an iodide substituent is added to a fluorous arene, the fluorous phase affinity decreases. This is an expected consequence of the increased polarity and polarizability.[4] In fact, an aliphatic iodo group has an effect very similar to that of a phenyl group, as evidenced by the $CF_3C_6F_{11}$/toluene partition coefficients of $R_{f8}CH_2CH_2CH_2I$ and $R_{f8}CH_2CH_2CH_2C_6H_5$ (ca. 50:50). Related fluorohydrocarbons, such as $R_{f8}CH=CH_2$, give higher values (ca. 94:6).[20] Thus, in a $CF_3C_6F_{11}$/toluene biphase system, the doubly pony-tailed iodides **5**–**7** would give significant leaching (ca. 70–75:30–25). The two with *ortho* pony tails (**6**,**7**) have slightly higher partition coefficients, and it would be of interest to know the value for the 2,6 isomer.

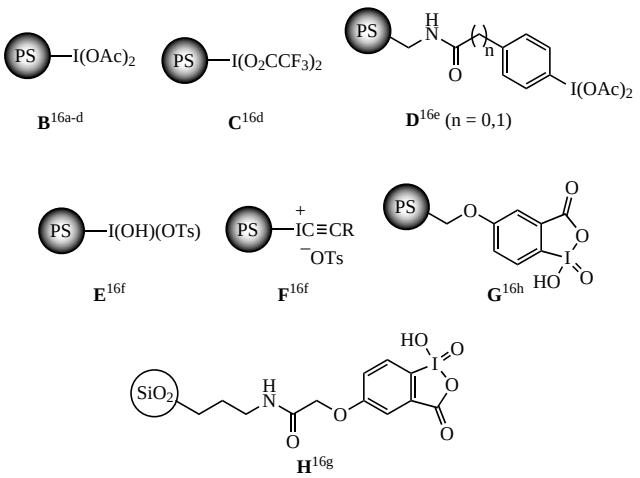
Importantly, the triply pony-tailed iodide **8** maintains a high $CF_3C_6F_{11}$/toluene partition coefficient (98:2). Furthermore, when toluene is replaced by the much more polar solvent MeOH, the partition coefficients of **5**–**8** increase dramatically. Now the doubly pony-tailed iodides show excellent retention (ca. 98:2), and no leaching of **8** can be detected ($<0.3\,\%$). This is a logical consequence of the higher polarity of MeOH, and the low absolute solubility of **5**–**8** in MeOH. Longer perfluoroalkyl groups also increase partition coefficients, as illustrated by $1,2\text{-}(R_{f10}CH_2CH_2CH_2)_2C_6H_4$ in Table 1. Hence, the R_{f10} homologs of **5**–**8** would exhibit still higher fluorophilicities.

Oxidations of hydroquinones; fluorous liquid/liquid biphase recycling: The simplicity and effectiveness of the hydroquinone oxidations in Table 2 and Scheme 3, and the ease of separation of the quinone product and fluorous aryl iodide coproduct, hardly need to be emphasized. The reactivities of **9**–**12** are comparable to those of (diacetoxyiodo)benzene[26] and related (diacetoxyiodo)heteroarenes.[27] It is noteworthy that a fluorous solvent is not required during the reaction. Rather, liquid/liquid biphase conditions are used only for product isolation and coproduct recycling.

In this regard, there is a cost incentive to develop recycling strategies for fluorous catalysts and reagents that avoid the use of fluorous solvents. As noted in the introduction, solid/liquid phase separations involving insoluble or thermomorphic fluorous species are attracting increasing attention.[6, 7] Given that **5**–**8** have very low solubilities in the reaction solvent, MeOH, a solid/liquid phase separation at the stage of the middle panel in Scheme 3 would recover a high fraction of the aryl iodide. However, due to the obvious need for very high efficiencies in recycling, we believe that this approach would be best evaluated with analogs with longer perfluoroalkyl groups. These always confer lower solubilities,[34] and based upon trends noted above, the R_{f10} analogue of **7** would constitute a particularly attractive candidate.

Nonetheless, liquid/liquid biphase protocols are preferred for many types of applications. A possible second-generation improvement would be to extend the preceding chemistry to hypervalent iodine compounds derived from fluorous carboxylic acids. Many [bis(trifluoroacetoxy)iodo]arenes have been previously applied in oxidations. Furthermore, such a $(R_{f8}CH_2CH_2CH_2)_nC_6H_{5-n}I(O_2CR_{fn'})_2$ species would generate its "own fluorous liquid phase" by virtue of the two equivalents of the fluorous carboxylic acid HO_2CR_{fn} liberated. It might also be possible to directly regenerate the $(R_{f8}CH_2CH_2CH_2)_nC_6H_{5-n}I(O_2CR_{fn'})_2$ species by the simple addition of $NaBO_3$ or another suitable oxidant.

Another important question is how the protocols in Table 2 and Scheme 3 compare with those involving other recoverable hypervalent iodine reagents. Examples of the insoluble, polymer-supported species noted in the introduction are depicted in Scheme 4.[16] In general, these systems also give both high yields and reactivities. Excellent results with regard to recovery, reoxidation, and reuse have been reported in most cases. However, there are also shortcomings, as can be found with any recycling method.



Scheme 4. Other recyclable hypervalent iodine reagents.

Those that have been noted for such polymer-supported reagents include nonlinear kinetic behavior, unequal distribution and/or access of active sites to the reaction media, solvation problems associated with the nature of the support, reactivity differences associated with subtle variations in polymer backbones, altered stereoselectivities, ease of mon-

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itoring as compared to homogeneous systems, and synthetic difficulties in transferring standard organic reactions to the solid phase.[35] For example, reagent **B** in Scheme 4 was prepared by the iodination of polystyrene with $I_2/I_2O_5/H_2SO_4$.[14a,b] Thus, regioisomers and diiodinated arenes can be expected, analogously to the crude reaction mixtures in Scheme 2.

To be even-handed, various shortcomings have also been noted for fluorous methodologies. These include fluorous solvent cost, fluorous solvent leaching, and environmental persistence.[4] Accordingly, we view the value of this work—which has resulted in the first aryl iodides that are easily recoverable under liquid/liquid biphase conditions—as lying in the expansion of the *portfolio* of recovery methods. The protocols represented in Scheme 4 are complementary to those in Table 2 and Scheme 3, and the specific application will often dictate the optimal approach. In any event, the chemical community now has a much broader palette of strategies to choose from.

Conclusion

This study has described efficient syntheses of the first series of fluorous aryl iodides (**5**–**8**) and hypervalent iodine compounds (**9**–**12**). The former constitute exceedingly useful synthons for other fluorous compounds, and the latter represent forerunners of what should be a wide variety of synthetically useful and easily recoverable iodine-containing fluorous reagents. The applicability of **9**–**12** to the oxidation of hydroquinones has been demonstrated, and workups under fluorous biphase conditions give very high yields of quinones (organic phase), and fluorous aryl iodides (fluorous phase) that can be efficiently recycled. There are also tantalizing possibilities for other recovery strategies, and the continued development of this area of fluorous chemistry can be confidently predicted.

Experimental Section

General: All reactions were conducted under N_2 unless noted. Chemicals were treated as follows: THF, diethyl ether, toluene, hexanes, distilled from Na/benzophenone; MeOH, distilled from Mg; $CF_3C_6H_5$ (Aldrich), $CF_3C_6F_{11}$, $CF_3C_6F_5$ (2 × Oakwood or ABCR), distilled from P_2O_5; $CDCl_3$, [D_6]acetone (Cambridge Isotope or Aldrich), other "reagent grade" solvents, H_5IO_6, $PhI(OAc)_2$, $NaBO_3 \cdot H_2O$ (3 × Oakwood or Aldrich), 1,4-hydroquinone, 2,3,5-trimethyl-1,4-hydroquinone, 2,6-di(*tert*-butyl)-1,4-hydroquinone (3 × Acros), used as received. NMR spectra were recorded on standard Jeol or Bruker 400 MHz FT spectrometers at ambient probe temperatures and referenced as follows: ^{1}H, residual internal $CHCl_3$ ($\delta = 7.27$ ppm) or [D_5]acetone ($\delta = 2.05$ ppm); ^{13}C, internal $CDCl_3$ ($\delta = 77.2$ ppm) or [D_6]acetone ($\delta = 29.6$ ppm). IR spectra were measured on an ASI React-IR spectrometer. Gas chromatography was conducted on a ThermoQuest Trace GC 2000 instrument. DSC data were recorded with a Mettler-Toledo DSC821 instrument and treated by standard methods.[36] Elemental analyses were conducted with a Carlo Erba EA1110 instrument.

3,4-($R_{f8}CH_2CH_2CH_2)_2C_6H_3I$ (5): A round-bottom flask was charged with 1,2-($R_{f8}CH_2CH_2CH_2)_2C_6H_4$ (**1**;[19] 2.200 g, 2.203 mmol), I_2 (2.237 g, 8.814 mmol), H_5IO_6 (2.010 g, 8.814 mmol), acetic acid (20 mL), H_2SO_4 (0.60 mL), and water (4 mL). The sample was stirred for 18 h at 85 °C. Then H_5IO_6 (1.005 g, 4.409 mmol) was added and the sample stirred for 12 h at 85 °C. Sublimed I_2 was periodically redissolved by swirling the flask. The mixture was allowed to cool to room temperature, and was extracted with CH_2Cl_2 (50 mL). Saturated aqueous $Na_2S_2O_3$ was added to the purple extract with vigorous stirring (50 mL), and the mixture became colorless. The aqueous phase was extracted again with CH_2Cl_2 (30 mL), and the combined organic phases were dried ($MgSO_4$). The solvent was removed by rotary evaporation to give a slightly colored oil. A series of preparative silica gel columns (3–6 depending upon scale; pentane elution) gave **5** as a colorless oil that solidified upon standing (1.726 g, 1.535 mmol, 70 %). M. p. 37 °C (capillary), 35.9 °C (DSC); elemental analysis (%) calcd for $C_{28}H_{15}F_{34}I$: C 29.91, H 1.34; found: C 29.68, H 1.30; NMR ($CDCl_3$): ^{1}H NMR: $\delta = 1.84$–1.92 (m; $2CH_2CH_2CF_2$), 2.09–2.18 (m; $2CH_2CF_2$), 2.64, 2.66 (2t, $^3J_{H,H} = 8$ Hz; $2ArCH_2$), 6.91 (d, $^3J_{H,H} = 8$ Hz; 1H of C_6H_3), 7.51 (d, $^4J_{H,H} = 2$ Hz; 1H of C_6H_3), 7.52 ppm (dd, $^3J_{H,H} = 8$ Hz, $^4J_{H,H} = 2$ Hz; 1H of C_6H_3); ^{13}C{^{1}H} NMR (partial): $\delta = 21.9$, 22.1 (2s; $2CH_2CH_2CF_2$), 30.7, 30.8 (2t, $^2J_{C,F} = 22$ Hz; $2CH_2CF_2$), 31.7, 31.8 (2s; $2ArCH_2$), 92.1,[37] 131.4, 136.1, 138.4, 138.5, 141.4 ppm (6s; C_6H_3). Prior to chromatography, the following minor ^{1}H signals were also present (see text and Scheme 2): **5′**: ^{1}H NMR: $\delta = 2.74$, 2.86 (2t, $^3J_{H,H} = 8$ Hz; $2ArCH_2$), 6.87 (t, $^3J_{H,H} = 8$ Hz; 1H of C_6H_3), 7.14 (d, $^4J_{H,H} = 2$ Hz; 1H of C_6H_3), 7.74 ppm (d, $^3J_{H,H} = 8$ Hz; 1H of C_6H_3); **A** or **A′** (tentative assignment): ^{1}H NMR = $\delta = 2.60$ (t, $^3J_{H,H} = 8$ Hz; $2ArCH_2$), 7.66 ppm (s; C_6H_2).[38]

2,4-($R_{f8}CH_2CH_2CH_2)_2C_6H_3I$ (6): The procedure for **5** was repeated at 75 °C with 1,3-($R_{f8}CH_2CH_2CH_2)_2C_6H_4$ (**2**;[19] 0.772 g, 0.773 mmol), I_2 (0.647 g, 2.500 mmol), H_5IO_6 (0.660 g, 2.895 mmol), acetic acid (5.00 mL), H_2SO_4 (0.20 mL), and water (1.00 mL). An identical workup (only one preparative column required) gave **6** as a colorless oil that solidified upon standing (0.844 g, 0.750 mmol, 97 %). M. p. 65 °C (capillary), 66.1 °C (DSC); elemental analysis (%) calcd for $C_{28}H_{15}F_{34}I$: C 29.91, H 1.34; found: C 30.30, H 1.45; ^{1}H NMR ($CDCl_3$): $\delta = 1.86$–1.99 (m; $2CH_2CH_2CF_2$), 2.01–2.18 (m; $2CH_2CF_2$), 2.63, 2.79 (2t, $^3J_{H,H} = 8$ Hz; $2ArCH_2$), 6.73 (dd, $^3J_{H,H} = 8$ Hz, $^4J_{H,H} = 2$ Hz; 1H of C_6H_3), 7.00 (d, $^4J_{H,H} = 2$ Hz; 1H of C_6H_3), 7.23 ppm (d, $^3J_{H,H} = 8$ Hz; 1H of C_6H_3); ^{13}C{^{1}H} NMR (partial): $\delta = 20.9$, 21.8 (2s; $2CH_2CH_2CF_2$), 30.3, 30.4 (2t, $^2J_{C,F} = 22$ Hz; $2CH_2CF_2$), 34.5, 39.8 (2s; $2ArCH_2$), 97.7,[37] 128.7, 129.7, 140.1, 141.5, 143.8 ppm (6s; C_6H_3).

2,5-($R_{f8}CH_2CH_2CH_2)_2C_6H_3I$ (7): The procedure for **5** was repeated at 90 °C with 1,4-($R_{f8}CH_2CH_2CH_2)_2C_6H_4$ (**3**;[19] 6.47 g, 6.48 mmol), I_2 (6.71 g, 25.92 mmol), H_5IO_6 (5.91 g, 25.92 mmol), acetic acid (80 mL), H_2SO_4 (2.40 mL), and water (16 mL). After 24 h, more H_5IO_6 (2.95 g, 12.94 mmol) was added, and the mixture was stirred an additional 24 h at 90 °C. An identical workup gave **7** as a white solid (4.42 g, 3.93 mmol, 61 %). M. p. 91 °C (capillary), 89.6 °C (DSC); elemental analysis (%) calcd for $C_{28}H_{15}F_{34}I$: C 29.91, H 1.34; found: C 29.91, H 1.76; ^{1}H NMR ($CDCl_3$): $\delta = 1.86$–1.96 (m; $2CH_2CH_2CF_2$), 2.01–2.23 (m; $2CH_2CF_2$), 2.64, 2.79 (2t, $^3J_{H,H} = 8$ Hz; $2ArCH_2$), 7.11 (d, $^3J_{H,H} = 8$ Hz; 1H of C_6H_3), 7.13 (d, $^3J_{H,H} = 8$ Hz; 1H of C_6H_3), 7.68 ppm (s; 1H of C_6H_3); ^{13}C{^{1}H} NMR (partial): $\delta = 21.0$, 21.9 (2s; $2CH_2CH_2CF_2$), 30.4, 30.5 (2t, $^2J_{C,F} = 22$ Hz; $2CH_2CF_2$), 34.0, 39.5 (2s, $2ArCH_2$), 100.8,[37] 128.8, 129.5, 139.7, 141.1, 141.6 ppm (6s; C_6H_3). Prior to chromatography, minor ^{1}H signals tentatively assigned to a diiodide were also present (see text): $\delta = 2.73$ (t, $^3J_{H,H} = 8$ Hz; $2ArCH_2$), 7.64 ppm (s; C_6H_2).

2,4,6-($R_{f8}CH_2CH_2CH_2)_3C_6H_2I$ (8): A round-bottom flask was charged with 1,3,5-($R_{f8}CH_2CH_2CH_2)_3C_6H_3$ (**4**;[19] 1.957 g, 1.341 mmol), I_2 (1.042 g, 4.025 mmol), $PhI(OAc)_2$ (1.296 g, 4.025 mmol), and ethyl acetate (15 mL), sealed with a septum, covered totally with aluminum foil, and immersed in an oil bath at 60 °C. The mixture was stirred for 24 h, allowed to cool to room temperature, and poured onto a saturated aqueous solution of $Na_2S_2O_3$ (50 mL). The reaction flask was rinsed twice with diethyl ether (2 × 25 mL) into the aqueous phase. The mixture was vigorously stirred until colorless. The organic phase was separated and dried ($MgSO_4$). Solvent was removed by rotary evaporation to give a yellowish oil. Most of the phenyl iodide coproduct was removed by oil pump vacuum, leaving a yellowish solid. Column chromatography (silica gel, hexanes elution) gave **8** as a white solid (2.056 g, 1.297 mmol, 97 %). M. p. 80 °C (capillary), 83.1 °C (DSC); elemental analysis (%) calcd for $C_{39}H_{20}F_{51}I$: C 29.56, H 1.27; found: C 29.87, H 1.41; ^{1}H NMR ($CDCl_3/CF_3C_6F_5$, 9:1 v/v): $\delta = 1.92$–2.16 (m; $3CH_2CH_2CF_2$), 2.66 (t, $^3J_{H,H} = 8$ Hz; $ArCH_2$), 2.88 (t, $^3J_{H,H} = 8$ Hz, $2ArCH_2$), 6.90 ppm (s; C_6H_2); ^{13}C{^{1}H} NMR (partial): $\delta = 21.0$ (s; $2CH_2CH_2CF_2$), 21.8 (s; $CH_2CH_2CF_2$), 30.3 (t, $^2J_{C,F} = 22$ Hz; CH_2CF_2), 30.5 (t, $^2J_{C,F} = 22$ Hz; $2CH_2CF_2$), 34.3 (s; $ArCH_2$), 41.3 (s; $2ArCH_2$), 104.3,[37] 127.9, 141.3, 145.2 ppm (4s; C_6H_2).

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3,4-($R_{f8}CH_2CH_2CH_2$)$_2$C$_6$H$_3$I(OAc)$_2$ (9): A Schlenk flask was charged with **5** (0.270 g, 0.240 mmol) and acetic acid (4.00 mL) and placed in a 65 °C oil bath. The mixture was stirred to dissolve **5**, and $NaBO_3 \cdot H_2O$ (0.239 g, 2.401 mmol) was added portionwise over the course of 0.5 h. The flask was sealed with a septum and the mixture stirred under nitrogen (5 h; TLC showed the disappearance of **5**). Water (25 mL) and $CHCl_3$ (25 mL) were added. The organic phase was removed and the aqueous solution again extracted with $CHCl_3$ (2 × 25 mL). The combined organic extracts were dried ($MgSO_4$). The solvent was removed by rotary evaporation and further dried under oil pump vacuum to give **9** as a light brown oil (0.282 g, 0.227 mmol, 85 %) that contained ca. 10 % residual **5** (see text). ^{1}H NMR ($CDCl_3$): δ = 1.94 – 2.21 (m; 2 CH_2CH_2CF$_2$), 2.00 (s; 2 CH$_3$), 2.79, 2.80 (2 t, $^3J_{H,H}$ = 8 Hz; 2 ArCH$_2$), 7.30 (d, $^3J_{H,H}$ = 8 Hz; 1 H of C$_6$H$_3$), 7.90 (s; 1 H of C$_6$H$_3$), 7.91 ppm (d, $^3J_{H,H}$ = 8 Hz; 1 H of C$_6$H$_3$); ^{13}C{^{1}H} NMR (partial): δ = 20.4 (s; 2 CH$_3$), 21.7, 21.9 (2 s, 2 *C*H$_2$CH$_2$CF$_2$), 30.7, 30.9 (2 t, $^2J_{C,F}$ = 22 Hz, 2 *C*H$_2$CF$_2$), 32.0 (s; 2 ArCH$_2$), 119.8,[37] 131.8, 133.5, 135.7, 142.1, 143.3 (6 s; C$_6$H$_3$), 176.6 ppm (s, 2 C=O); IR (thin film): $\tilde{\nu}$ = 1648 cm^{-1} (C=O).

2,4-($R_{f8}CH_2CH_2CH_2$)$_2$C$_6$H$_3$I(OAc)$_2$ (10): Compound **6** (0.265 g, 0.235 mmol), $NaBO_3 \cdot H_2O$ (0.235 g, 2.357 mmol), and acetic acid (4.00 mL) were combined in a procedure analogous to that given for **9**. A similar workup gave **10** as a yellowish solid (0.283 g, 0.227 mmol, 97 %). M. p. 68 – 69 °C (capillary), 67.5 °C (DSC); elemental analysis (%) calcd for $C_{32}H_{21}F_{34}IO_4$: C 30.94, H 1.70; found: C 30.74, H 1.84; ^{1}H NMR ($CDCl_3$): δ = 1.92 – 2.19 (m; 2 CH_2CH_2CF$_2$), 1.98 (s; 2 CH$_3$), 2.79, 3.07 (2 t, $^3J_{H,H}$ = 8 Hz; 2 ArCH$_2$), 7.15 (dd, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 2 Hz; 1 H of C$_6$H$_3$), 7.31 (d, $^4J_{H,H}$ = 2 Hz; 1 H of C$_6$H$_3$), 8.17 ppm (d, $^3J_{H,H}$ = 8 Hz; 1 H of C$_6$H$_3$); ^{13}C{^{1}H} NMR (partial): δ = 20.2 (s; 2 CH$_3$), 21.6, 21.8 (2 s; 2 *C*H$_2$CH$_2$CF$_2$), 30.4, 30.5 (2 t, $^2J_{C,F}$ = 22 Hz; 2 *C*H$_2$CF$_2$), 35.0, 38.4 (2 s; 2 ArCH$_2$), 125.1,[37] 129.6, 130.1, 138.6, 143.2, 146.6 (6 s; C$_6$H$_3$), 176.9 ppm (s; 2 C=O); IR (thin film): $\tilde{\nu}$ = 1648 cm^{-1} (C=O).

2,5-($R_{f8}CH_2CH_2CH_2$)$_2$C$_6$H$_3$I(OAc)$_2$ (11): Compound **7** (0.208 g, 0.185 mmol), $NaBO_3 \cdot H_2O$ (0.369 g, 3.70 mmol), and acetic acid (8.00 mL) were combined in a procedure analogous to that given for **9**. A similar workup gave **11** as a white solid (0.218 g, 0.175 mmol, 95 %). M. p. 102 – 104 °C (capillary), 102.7 °C (DSC); elemental analysis (%) calcd for $C_{32}H_{21}F_{34}IO_4$: C 30.94, H 1.70; found: C 30.70, H 1.81; ^{1}H NMR ($CDCl_3$): δ = 1.84 – 2.19 (m; 2 CH_2CH_2CF$_2$), 2.00 (s, 2 CH$_3$), 2.80, 3.06 (2 t, $^3J_{H,H}$ = 8 Hz; 2 ArCH$_2$), 7.43 (d, $^3J_{H,H}$ = 8 Hz; 1 H of C$_6$H$_3$), 7.46 (d, $^4J_{H,H}$ = 8 Hz; 1 H of C$_6$H$_3$), 8.07 (s; 1 H of C$_6$H$_3$); ^{13}C{^{1}H} NMR (partial): δ = 20.2 (s; 2 CH$_3$), 21.7, 21.8 (2 s; 2 *C*H$_2$CH$_2$CF$_2$), 30.3, 30.5 (2 t, $^2J_{C,F}$ = 22 Hz; 2 *C*H$_2$CF$_2$), 34.3, 38.1 (2 s; 2 ArCH$_2$), 127.1,[37] 130.1, 133.1, 137.8, 140.7, 142.3 (6 s, C$_6$H$_3$), 176.6 (s; 2 C=O); IR (thin film): $\tilde{\nu}$ = 1652 cm^{-1} (C=O).

2,4,6-($R_{f8}CH_2CH_2CH_2$)$_3$C$_6$H$_2$I(OAc)$_2$ (12): Compound **8** (1.70 g, 1.075 mmol), $NaBO_3 \cdot H_2O$ (2.14 g, 21.5 mmol), and acetic acid (35.00 mL) were combined in a procedure analogous to that given for **9**. A similar workup gave **12** as a white solid (1.79 g, 1.05 mmol, 93 %) that contained about 5 % residual **8** (see text). To obtain an analytical sample, about 0.200 g was placed at the top of a 10 × 2 cm Celite column, which was eluted with acetic acid. The initial fractions contained pure **12**. M. p. 89 – 90 °C (capillary), 88.5 °C (DSC); elemental analysis (%) calcd for $C_{43}H_{26}F_{51}IO_4$: C 30.33, H 1.54; found: C 30.33, H 1.88; ^{1}H NMR ($CDCl_3$): δ = 1.94 (s; 2CH$_3$), 1.94 – 2.21 (m; 3 CH_2CH_2CF$_2$), 2.79 (t, $^3J_{H,H}$ = 8 Hz; ArCH$_2$), 3.14 (t, $^3J_{H,H}$ = 8 Hz; 2 ArCH$_2$), 7.20 ppm (s; C$_6$H$_2$); ^{13}C{^{1}H} NMR (partial): δ = 20.1 (s; 2 CH$_3$), 21.1 (s, *C*H$_2$CH$_2$CF$_2$), 21.8 (s; 2 *C*H$_2$CH$_2$CF$_2$), 30.5 (t, $^2J_{C,F}$ = 22 Hz; 3 *C*H$_2$CF$_2$), 34.8 (s; ArCH$_2$), 40.0 (s; 2 ArCH$_2$), 128.4,[37] 131.1, 144.6, 146.4 (4 s; C$_6$H$_2$), 176.7 ppm (s; 2 C=O); IR (thin film): $\tilde{\nu}$ = 1648 cm^{-1} (C=O).

Oxidations of hydroquinones: A Schlenk flask was charged with hydroquinones **13a – c** (Table 2; 0.243 – 0.608 mmol) and (diacetoxyiodo)arenes **9 – 12** (**10** and **11**, 1.0:1.0 mol ratio; **9** and **12**, 1.0:1.2 mol ratio). Freshly distilled MeOH (5.00 – 8.00 mL) was added with stirring. The suspension quickly turned light yellow. After 2 – 3 h, $CF_3C_6F_{11}$ (5.00 – 10.00 mL) was added, giving a liquid/liquid biphase system with all species dissolved. The upper yellow MeOH phase was carefully removed via syringe, and the fluorous phase extracted with MeOH (2 × 2.00 mL). The combined MeOH solutions were extracted with $CF_3C_6F_{11}$ (2.00 mL). The solvents were removed from the combined MeOH solutions and combined $CF_3C_6F_{11}$ solutions by rotary evaporation to give the quinones **14a – c** and aryl iodides **5 – 8** that were pure by ^{1}H NMR spectroscopy (> 95 %). Yields are summarized in Table 2, and additional data are as follows.

*1,4-Benzoquinone (**14a**)*: ^{1}H NMR ([D$_6$]acetone): δ = 6.83 ppm (s; 4 CH=); ^{13}C{^{1}H} NMR: δ = 151.1 (s; 4 CH=), 188.1 ppm (s; 2 C=O); IR (thin film): $\tilde{\nu}$ = 1645 cm^{-1} (C=O).

*2,3,5-Trimethyl-1,4-benzoquinone (**14b**)*: ^{1}H NMR ([D$_6$]acetone):[27] δ = 1.95 (d, $^4J_{H,H}$ = 1.6 Hz; CH$_3$), 1.99 (s; 2 CH$_3$), 6.58 ppm (q, $^4J_{H,H}$ = 1.6 Hz; CH=); ^{13}C{^{1}H} NMR: δ = 11.9, 12.2, 15.7 (3 s; 3 CH$_3$), 133.5 (s; CH=), 141.1, 141.3, 146.0 (3 s; 3 *C*CH$_3$), 187.7, 188.1 ppm (2 s, 2 C=O); IR (thin film): $\tilde{\nu}$ = 1645 cm^{-1} (C = O).

*2,6-Di(tert-butyl)-1,4-benzoquinone (**14c**)*: ^{1}H NMR ([D$_6$]acetone):[27] δ = 1.26 (s; 6 CH$_3$), 6.47 (s; 2 CH=); ^{13}C{^{1}H} NMR = 29.0 (s; 6 CH$_3$), 34.9 (s; 2 *C*(CH$_3$)$_3$), 134.0 (s; 2 CH=), 154.5 (s; 2 *C*C(CH$_3$)$_3$), 188.8 ppm (s; 2 C=O); IR (thin film): $\tilde{\nu}$ = 1645 cm^{-1} (C=O).

Partition coefficients: The following is representative. A 10 mL vial was charged with **5** (0.0156 g, 0.0138 mmol), $CF_3C_6F_{11}$ (2.000 mL), and MeOH (2.000 mL), fitted with a mininert valve, vigorously shaken (2 min), and immersed (cap-level) in an oil bath at 35 °C. After 12 h, the bath was removed. After 12 – 24 h, a 0.500 mL aliquot of each layer was added to 0.250 mL of a standard 0.0244 M solution of eicosane in hexane. The samples were diluted with ether and GC analysis (average of 7 – 8 injections) showed that 0.00325 mmol of **5** was in the $CF_3C_6F_{11}$ aliquot and 0.000101 mmol in the MeOH aliquot (97.0:3.0; a 2.000/0.500 scale factor gives a total mass recovery of 0.0150 g, 97 %).

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