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Strategy and design in fluorous phase immobilization: a systematic study of the effect of 'pony tails' $(CH_2)_3(CF_2)_n\ {}_1CF_3$ on the partition coefficients of benzenoid compounds

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ABSTRACT: Fluorous solvents commonly exhibit temperature-dependent miscibilities with organic solvents. Thus, catalysts and reagents that have high affinities for fluorous solvents can be used in protocols that combine the advantages of one-phase chemistry (higher temperature) and biphase product separation (lower temperature). The high-yield conversion of benzaldehydes (via Wittig and hydrogenation reactions) to alkylbenzenes with one to three 'pony tails' $(CH_2)_3(CF_2)_n\ {}_1CF_3$ ($n = 6$, 8, 10) is described. The toluene–$CF_3C_6F_{11}$ partition coefficients show that three pony tails are necessary to achieve a high degree of fluorous phase immobilization. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: fluorous solvents; pony tails; phosphonium salts; Wittig reaction; alkylbenzenes; partition coefficients

INTRODUCTION

The term 'fluorous' was recently introduced by Horváth and co-workers as an analog to 'aqueous' for highly fluorinated alkane, ether and tertiary amine solvents.[1–4] Many such solvents are commercially available, and are very non-polar. They commonly give bilayers with organic solvents at room temperature, as illustrated by the first flask in Fig. 1. At the same time, many such solvent combinations become miscible at elevated temperatures, as depicted by the second flask in Fig. 1. Various practical considerations and underlying physical principles have been reviewed.[4]

Organic compounds normally have low affinities for fluorous solvents. However, compounds that consist mainly of perfluoroalkyl segments show high affinities. This reflects a 'like dissolves like' effect, and similar strategies are used to design dyes that can adhere to Teflon.[5] Accordingly, Horváth and co-workers proposed that high fluorous affinities could be imparted to common catalysts and reagents by appending 'pony tails' $(CH_2)_m(CF_2)_n\ {}_1CF_3$ [abbreviated to $(CH_2)_mR_{fn}$] in sufficient numbers and lengths. The $(CH_2)_m$ segments serve to insulate the active site from the electron-withdrawing fluorines.

This provides the basis for an innovative new approach to recoverable catalysts and reagents that combines the advantages of one-phase chemistry (higher temperature) and biphase product separation (lower temperature). As illustrated by the second and third flasks in Fig. 1, a homogeneous reaction can be followed by a simple room temperature extraction. The organic product is isolated from the non-fluorous solvent, and the catalyst or transformed reagent from the fluorous solvent. Many applications of this protocol have been developed over the last few years.[6,7]

This concept was extended by Curran and Wipf, who developed fluorous 'tagging' strategies that facilitate target isolation from complex multi-component mixtures.[8] Regardless of application, there is a distinct need for quantitative data on the partitioning of solutes between fluorous and non-fluorous solvents. We and others have favored perfluoro(methylcyclohexane), $CF_3C_6F_{11}$, for various types of physical measurements. Although this is a relatively expensive fluorous solvent, it is available in high purity and without the branched isomers commonly found in technical-grade acyclic alkanes and perfluoroalkanes.

In this paper, we address the following question: what type of pony tail motif is necessary to impart high

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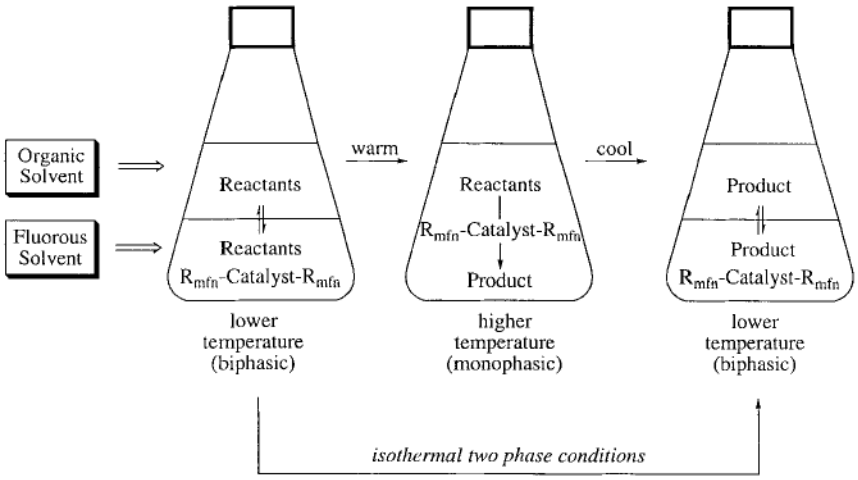
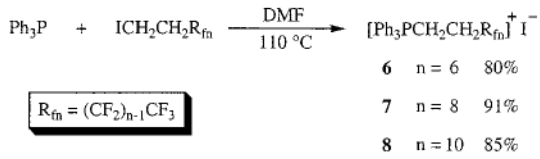


Figure 1. One possibility for catalysis with fluorous solvents [$R_{mfn} = (CH_2)_m(CF_2)_{n\ 1}CF_3$]

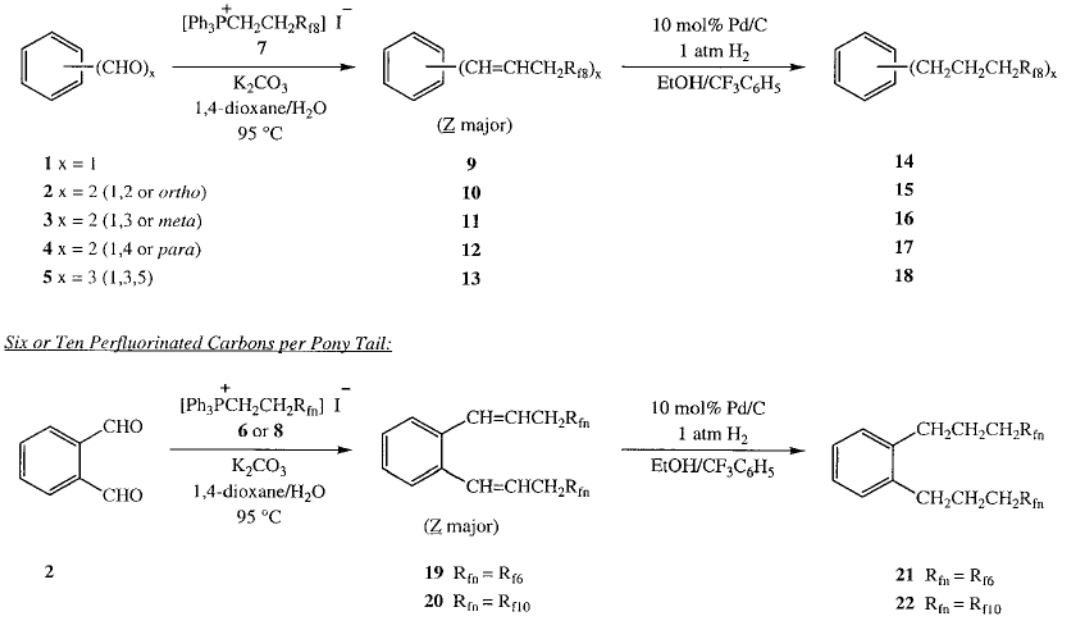


Scheme 1. Syntheses of fluorous phosphonium salts

partition coefficients to benzenoid compounds? In general, arene π clouds afford significant intermolecular dipole and induced dipole interactions,[9] leading to enhanced polarities and organic phase affinities.[4] Thus, perfluorinated arenes are normally miscible with organic solvents. Furthermore, attractive arene–perfluoroarene stacking interactions are used as design elements in crystal engineering.[10] The fluorous phase immobilization of benzenoid compounds is also of considerable practical importance. For example, there would be numerous applications for catalysts based upon fluorous triarylphosphine ligands. Catalysts with fluorous trialkylphosphine ligands have been spectacularly successful[1–3,6d,f] but for many purposes triarylphosphines are superior or required.[6b]

RESULTS

We sought to graft pony tails on to aromatic aldehydes using the Wittig reaction. Hence the commercially available fluorous primary iodides $ICH_2CH_2R_{fn}$ ($n = 6$, 8, 10) were converted on 12–26 g scales to the



Scheme 2. Syntheses of fluorous benzenes

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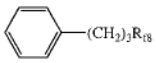
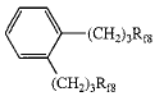
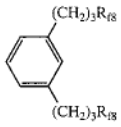
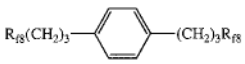
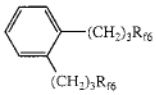
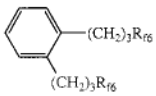
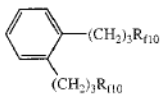
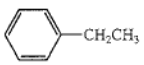
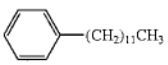
Table 1. Partition coefficients (24 °C)

No.	Compound	$CF_3C_6F_{11}/CH_3C_6H_5$
14		49.5:50.5
15		91.2:8.8
16		90.7:9.3
17		91.1:8.9
18		>99.7:<0.3
21		73.7:26.3
22		97.4:2.6
23	$ICH_2CH_2CH_2R_{f8}$	50.7:49.3
24	$CH_3(CH_2)_8CH_3$	5.4:94.6
25	$CH_3(CH_2)_9CH_3$	4.2:95.8
26	$CH_3(CH_2)_{10}CH_3$	3.4:96.6
27	$CH_3(CH_2)_{11}CH_3$	2.4:97.6
28	$CH_3(CH_2)_{12}CH_3$	1.9:98.1
29	$CH_3(CH_2)_{14}CH_3$	1.1:98.9
30		1.2:98.8
31		0.9:99.1
32		22.4:77.6
33		28.0:72.0

corresponding phosphonium salts $[Ph_3PCH_2CH_2R_{fn}]^+$ I (**6–8**), as shown in Scheme 1. Forcing conditions were required owing to the attenuated S_N2 reactivity of the iodides.[6a,c] Although **6** and **7** have been reported earlier,[11] few spectroscopic properties have been described. Hence **6–8** were characterized by microanalysis and NMR (^1H, ^{13}C, ^{31}P, ^{19}F), as detailed in the Experimental section.

The Wittig reagent derived from the deprotonation of **7** has previously been shown to condense with aldehydes.[11a] Analogous reactions with the benzenoid mono-, di- and trialdehydes $C_6H_{6-x}(CHO)_x$ shown in Scheme 2 (**1–5**) gave the corresponding alkenes $C_6H_{6-x}(CH{=}CHCH_2R_{f8})_x$ (**9–13**) as mixtures of *Z/E* isomers in 94–78% yields. NMR showed that *Z* isomers dominated (assigned from $^3J_{HH}$ values), consistent with literature precedent for unstabilized ylides.[13] No effort was made to separate these mixtures, which were characterized by microanalysis and NMR. A synthesis of **9**, as a mixture with other compounds, has been previously reported.[12]

Although both *n*-BuLi (78 °C, THF) and K_2CO_3 (95 °C, aqueous 1,4-dioxane) could be used to generate the Wittig reagents, the latter proved superior. Any excess of *n*-BuLi effected small amounts of 1,2-HF elimination from **9–13**, which contain activated allylic protons. The by-products are difficult to detect in the *Z/E* mixtures, but become more apparent after subsequent steps. Importantly, the statistical probability of elimination increases with the number of pony tails.

As shown in Scheme 2, the alkenes underwent facile hydrogenation in the presence of 10 mol% palladium on carbon. Workups gave the family of mono-, di- and trialkylbenzenes $C_6H_{6-x}(CH_2CH_2CH_2R_{f8})_x$ displayed in Table 1 (**14–18**) in 92–80% yields. The sequence starting from the *o*-dialdehyde **2** was repeated with phosphonium salts **6** and **8**. This gave two additional alkenes with shorter and longer pony tails, 1,2-$C_6H_4(CH{=}CHCH_2R_{f6})_2$ (**19**) and 1,2-$C_6H_4(CH{=}CHCH_2R_{f10})_2$ (**20**), and the corresponding *o*-dialkylbenzenes 1,2-$C_6H_4(CH_2CH_2CH_2R_{f6})_2$ (**21**) and 1,2-$C_6H_4(CH_2CH_2CH_2R_{f10})_2$ (**22**). All alkylbenzenes were characterized by microanalysis and NMR (^1H, ^{13}C and in some cases ^{19}F).

Absolute solubilities decreased dramatically as the pony tails became longer in the *o*-dialkylbenzenes **21, 15** and **22**. Compound **22** was only sparingly soluble in $CF_3C_6F_{11}$. The *p*-dialkylbenzene **17** was less soluble than the *ortho* and *meta* isomers **15** and **16**. However, the trialkylbenzene **18**, in which the ratio of perfluorinated to unfluorinated carbons is similar to that of **22**, remained highly soluble in CH_2Cl_2, $CHCl_3$, THF, diethyl ether, hexane, $CF_3C_6H_5$ and $CF_3C_6F_{11}$ (sparingly soluble in acetone and toluene; insoluble in MeOH and EtOH). The $CF_3C_6F_{11}$–toluene partition coefficients were determined by GLC as reported previously[4,6c] and further described in the Experimental section. These reflect *relative* as opposed to absolute solubilities, and are summarized in

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Table 1. Values for related compounds are also given, and analyzed in the Discussion section.

DISCUSSION

The protocol summarized in Scheme 2 represents a versatile, general method for appending pony tails to non-fluorous structures. Numerous aromatic aldehydes are commercially available, and others are easily prepared. This procedure gives pony tails with $(CH_2)_3$ insulating segments, one methylene group more than in the starting fluorous iodides. However, iodides with longer $(CH_2)_m$ segments, such as $ICH_2CH_2CH_2R_{f8}$, are easily synthesized.[14] Hence higher homologs should be readily available. Lower homologs would require phosphonium salts of the type $[R_3PCH_2R_{fn}]^+ X^-$. These require additional steps to access, but have been successfully used in Wittig reactions.[15]

Other methods for appending $(CH_2)_mR_{fn}$ groups ($m \geq 1$) to benzenoid rings are known, as exemplified by recent work with phosphine ligands designed to impart good solubility in supercritical CO_2.[16] There are, of course, numerous means of attaching perfluoroalkyl (R_{fn}) groups directly to arenes. Several are nicely illustrated by other recent work with fluorous phosphine ligands, where the objective is often fluorous phase solubility as opposed to highly biased partition coefficients.[17,18] However, Hammet σ values of perfluoroalkyl groups (CF_3/C_4F_9: σ_m 0.46/0.47–0.52; σ_p 0.53/0.52) indicate inductive electron-withdrawing effects between those of chloride (σ_m 0.37) and cyanide (σ_m 0.62; σ_p 0.71).[19] Hence the electronic properties of benzenoid compounds will be strongly perturbed by such 'uninsulated' pony tails. Nonetheless, in sufficient quantity they should be able to impart good partitioning characteristics.

The data in Table 1 show that large numbers of CF_2 groups are needed to immobilize benzene derivatives effectively in fluorous phases. In the $CH_2CH_2CH_2R_{f8}$ series, there is a gradual progression of partition coefficients from ca 50:50 (**14**, one pony tail) to ca 91:9 (**15**–**17**, two pony tails) to >99:<1 (**18**, three pony tails). Interestingly, the *ortho, meta* and *para* isomers give essentially identical values. The partition coefficients of the *o*-dialkylbenzenes increase from ca 74:26 (**21**) to ca 91:9 (**15**) to ca 97:3 (**22**) as the R_{fn} segment is lengthened from six to eight to ten carbons.

To help place these values in perspective, data for related compounds are given in Table 1. When the phenyl group in **14** is replaced by an iodide (**23**), the partition coefficient is unaffected. The *n*-alkanes **24**–**29** have similar numbers of carbons as the pony tails. As expected, they show marked preferences for the toluene phase (>94:<6) that increase with chain length. The non-fluorinated alkylbenzenes **30** and **31** partition similarly. Pentafluorobenzene (**32**) and hexafluorobenzene (**33**) also prefer the toluene phase (78–72:22–28). As analyzed above, fluorinated arenes are highly soluble in moderately polar solvents. However, **32** and **33** *do* show higher fluorous phase affinities than the non-fluorinated alkylbenzenes.

The preceding data show that it will be challenging to prepare functionalized benzenes or triarylphosphines that are highly immobilized in fluorous phases. Partition coefficients of 99:1 represent the lower practical limit for many applications.[1–3] With the types of pony tails described in this paper, three would be required. This raises the issue of substitution pattern. Any functionalized benzene derived from **18** will contain two *ortho* substituents. With phosphines, this results in large cone angles. This is desirable for some catalysts, but often deleterious. A 3,4,5 (*meta*/*para*/*meta*′) substitution pattern would provide the best PPh_3 mimic, but to our knowledge the corresponding trialdehyde has never been reported. Other synthetic approaches to functionalized benzenes with three pony tails are, of course, possible. However, it is difficult to avoid having at least one substituent *ortho* to the functional group.

In summary, this work represents the first systematic study of fluorous phase affinities of benzenoid compounds bearing fluorous pony tails. Our data show the immobilization of aromatic residues to be a challenging but not necessarily insurmountable problem. The synthesis of functionalized fluorous benzenes and aromatic heterocycles, and the corresponding partition coefficients, will be reported in the near future.

EXPERIMENTAL

General. All reactions were conducted under inert atmospheres unless noted otherwise. Chemicals were treated as follows: THF, diethyl ether, toluene, hexanes, distilled from Na–benzophenone; CH_2Cl_2, distilled from CaH_2; $CF_3C_6H_5$ (Aldrich), $CF_3C_6F_{11}$, $CF_3C_6F_5$ (Oakwood or ABCR), distilled from P_2O_5; $CDCl_3$ (Cambridge Isotope or Aldrich), other/'reagent-grade' solvents, $ICH_2CH_2R_{fn}$, $C_6H_{6-x}(CHO)_x$ ($x = 1$, 2), 1,3,5-$C_6H_3(CO_2CH_3)_3$ (all Oakwood or Aldrich), used as received. The educt 1.3.5-$C_6H_3(CH_2OH)_3$ was prepared from $LiAlH_4$ (2.00 g, 57.7 mmol) and 1,3,5-$C_6H_3(CO_2CH_3)_3$ (5.80 g, 23.0 mmol) by the procedure of Nakazaki *et al.*[20] the crude product was chromatographed on a silica gel column (eluent: 5:95 MeOH–EtOAc); the solvent was removed by rotary evaporation to give white crystals that were dried by oil pump vacuum (3.05 g, 8.13 mmol, 79%), m.p. 74 °C (lit. 74–75 °C); ^1H NMR (δ, $CDCl_3$), 4.73 (s, 6H), 7.33 (s, 3H).

NMR spectra were recorded on Varian FT or Jeol JMN-400GX FT spectrometers (ambient probe temperature in $CDCl_3$ unless noted and referenced as follows: ^1H, residual internal $CHCl_3$ (δ 7.27); ^{13}C, internal $CDCl_3$ (δ 77.23); ^{31}P, external 85% H_3PO_4 (δ 0.00); ^{19}F, external $CFCl_3$ (δ 0.00)). Gas chromatography was conducted on

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Hewlett-Packard 5910 or ThermoQuest Trace GC 2000 instruments. Elemental analyses were conducted with a Carlo Erba EA1110 instrument (in-house) or by Atlantic Microlab (Norcross, GA, USA).

*1,3,5-$C_6H_3(CHO)_3$ (**5**)*[21]. A Schlenk flask was charged with 1,3,5-$C_6H_3(CH_2OH)_3$ (0.700 g, 416 mmol) and the Dess–Martin reagent (6.18 g, 14.6 mmol).[22] Then CH_2Cl_2 (100 ml) was added and the suspension vigorously stirred. After 15 h, diethyl ether (100 ml) was added. The mixture was washed with $Na_2S_2O_3$ [24.8 g (100 mmol) in 100 ml of $KHCO_3$-saturated H_2O] and saturated aqueous $KHCO_3$ (100 ml). The combined aqueous phases were extracted with CH_2Cl_2 (100 ml). The CH_2Cl_2 phases were combined, dried ($MgSO_4$) and taken to dryness by rotary evaporation. The white powder was flash chromatographed (CH_2Cl_2). The solvent was removed by rotary evaporation to give **5** as star clusters of white crystals (0.665 g, 4.10 mmol, 98%), m.p. 159 °C (lit. 155.5–160 °C).[21] NMR: ^{1}H 10.21 (s, 3H), 8.65 (s, 3H).

*[$Ph_3PCH_2CH_2R_{f6}$]$^+$ I (**6**)*[11]. A flask was charged with Ph_3P (7.64 g, 29.13 mmol), $ICH_2CH_2R_{f6}$ (12.40 g, 26.16 mmol) and DMF (15 ml). The mixture was stirred vigorously for 24 h at 105 °C. The DMF was removed by oil pump vacuum. The waxy solid was triturated with diethyl ether (100 ml), collected by filtration, washed with diethyl ether and dried by oil pump vacuum to give **6** as a white solid (16.95 g, 23.02 mmol, 88%), m.p. 191–195 °C. Calculated for $C_{26}H_{19}F_{13}IP$: C, 42.42; H, 2.60. Found: C, 42.26; H, 2.63%. NMR: ^{1}H 2.58 (m, CH_2CF_2), 4.06 (apparent quin, $^2J_{PH}$ = 14 Hz, $^3J_{HH}$ = 7 Hz, PCH_2), 7.69–7.93 (m, 15H); $^{13}C\{^1H\}$ (partial) 16.5 (dt, $^1J_{CP}$ = 56 Hz, $^3J_{CF}$ = 4 Hz, PCH_2), 24.8 (td, $^2J_{CF}$ = 23 Hz, $^2J_{CP}$ = 2 Hz, PCH_2CH_2), PPh at 116.9 (d, $^1J_{CP}$ = 88 Hz), 131.2 (d, $^2J_{CP}$ = 13 Hz), 134.1 (d, $^3J_{CP}$ = 11 Hz), 136.1 (d, $^4J_{CP}$ = 3 Hz); $^{31}P\{^1H\}$ 25.5 (s); ^{19}F 81.4 (t, $^3J_{FF}$ = 9.3 Hz, CF_3), 113.6 (br s, CF_2), 122.4 (br s, CF_2), 123.3 (br s, CF_2), 123.4 (br s, CF_2), 126.8 (br s, CF_2).

*[$Ph_3PCH_2CH_2R_{f8}$]$^+$ I (**7**)*[11]. Ph_3P (13.20 g, 50.32 mmol), $ICH_2CH_2R_{f8}$ (26.11 g, 45.48 mmol) and DMF (20 ml) were combined in a procedure analogous to that for **6**. An identical workup gave **7** as a white solid (34.73 g, 41.51 mmol, 91%), m.p. 174–175 °C. Calculated for $C_{28}H_{19}F_{17}IP$: C, 40.22; H, 2.29. Found: C, 40.23; H, 2.32%. NMR: ^{1}H 2.55 (m, CH_2CF_2), 4.04 (apparent quin, $^2J_{PH}$ = 14 Hz, $^3J_{HH}$ = 7 Hz, PCH_2), 7.71–7.89 (m, 15H); $^{13}C\{^1H\}$ (partial) 16.3 (dt, $^1J_{CP}$ = 58 Hz, $^3J_{CF}$ = 3 Hz, PCH_2), 24.7 (td, $^2J_{CF}$ = 23 Hz, $^2J_{CP}$ = 3 Hz, PCH_2CH_2), PPh at 116.8 (d, $^1J_{CP}$ = 87 Hz), 131.1 (d, $^2J_{CP}$ = 13 Hz), 133.9 (d, $^3J_{CP}$ = 10 Hz), 136.0 (d, $^4J_{CP}$ = 3 Hz); $^{31}P\{^1H\}$ 26.5 (s); ^{19}F 81.3 (t, $^3J_{FF}$ = 9.0 Hz, CF_3), 113.6 (br s, CF_2), 122.2 (br s, CF_2), 122.5 (br s, $2CF_2$), 123.3 (br s, $2CF_2$), 126.8 (br s, CF_2).

*[$Ph_3PCH_2CH_2R_{f10}$]$^+$ I (**8**).* Ph_3P (5.716 g, 21.79 mmol), $ICH_2CH_2R_{f10}$ (13.35 g, 19.81 mmol) and DMF (20 ml) were combined in a procedure analogous to that for **6**. An identical workup gave **8** as a white solid (16.31 g, 17.41 mmol, 88%), m.p. 202–204 °C. Calculated for $C_{30}H_{19}F_{21}IP$: C, 38.49; H, 2.05. Found: C, 38.28; H, 2.08%. NMR*: ^{1}H 2.51 (m, CH_2CF_2), 4.01 (apparent quin, $^2J_{PH}$ = 14 Hz, $^3J_{HH}$ = 7 Hz, PCH_2), 7.68–7.87 (m, 15H); $^{13}C\{^1H\}$ (partial) 16.2 (d, $^1J_{CP}$ = 55 Hz, PCH_2), 24.6 (t, $^2J_{CF}$ = 22 Hz, PCH_2CH_2), PPh at 116.6 (d, $^1J_{CP}$ = 72 Hz), 130.9 (d, $^2J_{CP}$ = 13 Hz), 133.8 (d, $^3J_{CP}$ = 10 Hz), 135.8 (d, $^4J_{CP}$ = 3 Hz); $^{31}P\{^1H\}$ 28.7 (s); ^{19}F 81.3 (t, $^3J_{FF}$ = 9.0 Hz, CF_3), 113.5 (br s, CF_2), 122.4 (br s, $5CF_2$), 123.3 (br s, $2CF_2$), 126.7 (br s, CF_2).

*$C_6H_5CH{=}CHCH_2R_{f8}$ (**9**)*[12]. A round-bottomed flask was charged with C_6H_5CHO (0.200 g, 1.88 mmol), **7** (1.89 g, 2.26 mmol), K_2CO_3 (0.147 g, 2.45 mmol), reagent-grade 1,4-dioxane (10 ml) and H_2O (0.3 ml) and fitted with a condenser (no inert atmosphere). The mixture was stirred at 95 °C for 20 h. The volatiles were removed by rotary evaporation, and CH_2Cl_2 (50 ml) and H_2O (50 ml) were added to the orange residue. The layers were separated. The aqueous layer was extracted with CH_2Cl_2 (50 ml) and the CH_2Cl_2 layers were combined and dried ($MgSO_4$). The solvent was removed by rotary evaporation. The oily solid was rinsed through a silica gel plug (10 cm) with hexanes. The solvent was removed by rotary evaporation and oil pump vacuum to give **9** as a colorless oil (0.953 g, 1.78 mmol, 94%, 90:10 *Z/E*). Calculated for $C_{17}H_9F_{17}$: C, 38.07; H, 1.69. Found: C, 38.29; H, 1.81%. NMR: ^{1}H 3.21 2.97 (2dt, $^3J_{HF}$ = 18 Hz, $^3J_{HH}$ = 7 Hz, CH_2CF_2 *E* and *Z*), 5.78 (dt, $^3J_{HH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, =C*H*CH_2, *Z*), 6.17 (dt, $^3J_{HH}$ = 16 Hz, $^3J_{HH}$ = 7 Hz, =C*H*CH_2, *E*), 6.65 (d, $^3J_{HH}$ = 16 Hz, ArCH=, *E*), 6.85 (d, $^3J_{HH}$ = 11 Hz, ArCH=, *Z*), 7.20–7.45 (m, C_6H_5, *Z* and *E*); $^{13}C\{^1H\}$ (partial, *Z*) 30.7 (t, $^2J_{CF}$ = 22 Hz, *C*H_2CF_2), 118.1 (t, $^3J_{CF}$ = 5 Hz, =*C*HCH_2), 127.8, 128.7, 128.8, 135.7, 136.2 (5s, *C*$_6H_5$*C*H=).

*1,2-$C_6H_4(CH{=}CHCH_2R_{f8})_2$ (**10**).* The reaction/workup given for **9** was repeated with 1,2-$C_6H_4(CHO)_2$ (0.160 g, 1.20 mmol), **7** (2.00 g, 2.39 mmol), K_2CO_3 (0.143 g, 2.39 mmol), reagent-grade 1,4-dioxane (15 ml) and H_2O (0.5 ml). This gave **10** as a colorless oil that solidified upon standing (1.10 g, 1.10 mmol, 92%; 95:5 *ZZ/EZ*), m.p. 59–60 °C. Crystallization from hot hexanes gave (*ZZ*)-**10** as clear, colorless flakes. Calculated for $C_{28}H_{12}F_{34}$: C, 33.82; H, 1.21. Found: C, 33.72; H, 1.17%. NMR (*ZZ*): ^{1}H 2.92 (dt, $^3J_{HF}$ = 18 Hz, $^3J_{HH}$ = 7 Hz, $2CH_2CF_2$), 5.82 (dt, $^3J_{HH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, 2=C*H*CH_2), 6.77 (d, $^3J_{HH}$ = 11 Hz, 2ArCH=), 7.20–7.23 (m, 2H), 7.32–7.34 (m, 2H); $^{13}C\{^1H\}$ (partial) 30.7 (t, $^2J_{CF}$ = 22 Hz, *C*H_2CF_2), 119.3 (t, $^3J_{CF}$ = 4 Hz, =*C*HCH_2), 128.0, 129.1, 134.6, 135.1

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[4s, $C_6H_4(CH{=})_2$]; ^{19}F 78.0 (t, $^3J_{FF}$ = 12 Hz, $2CF_3$), 110.1 (m, $2CF_2$), 119.0 (br s, $6CF_2$), 119.8 (br s, $2CF_2$), 120.2 (br s, $2CF_2$), 123.3 (br s, $2CF_2$).

1,3-$C_6H_4(CH{=}CHCH_2R_{f8})_2$ (**11**). The reaction/workup given for **9** was repeated with 1,3-$C_6H_4(CHO)_2$ (0.200 g, 1.491 mmol), **7** (3.74 g, 4.47 mmol), K_2CO_3 (0.268 g, 4.46 mmol), reagent-grade 1,4-dioxane (15 ml) and H_2O (0.5 ml). This gave **11** as a colorless oil (1.36 g, 1.36 mmol, 92%; 95:5 *ZZ/EZ*). Calculated for $C_{28}H_{12}F_{34}$: C, 33.82; H, 1.21. Found: C, 33.97; H, 1.51%. NMR (*ZZ*): ^1H 3.12 (dt, $^3J_{HF}$ = 18 Hz, $^3J_{HH}$ = 7 Hz, $2CH_2CF_2$), 5.81 (dt, $^3J_{HH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, 2 $=CHCH_2$), 6.85 (d, $^3J_{HH}$ = 11 Hz, ArCH=), 7.10–7.42 (s, C_6H_4); $^{13}C\{^1H\}$ (partial) 30.7 (t, $^2J_{CF}$ = 22 Hz, CH_2CF_2), 118.8 (t, $^3J_{CF}$ = 4 Hz, $=CHCH_2$), 127.8, 128.4, 129.0, 134.4, 136.5 (5s, $C_6H_4(CH{=})_2$).

1,4-$C_6H_4(CH{=}CHCH_2R_{f8})_2$ (**12**). The reaction/workup given for **9** was repeated with 1,4-$C_6H_4(CHO)_2$ (0.200 g, 1.491 mmol), **7** (3.74 g, 4.47 mmol), K_2CO_3 (0.268 g, 4.46 mmol), reagent grade 1,4-dioxane (15 ml) and H_2O (0.5 ml). This gave **12** as a white solid (1.34 g, 1.34 mmol, 90%; 95:5 *ZZ/EZ*), m.p. 62–63 °C. Calculated for $C_{28}H_{12}F_{34}$: C, 33.82; H, 1.21. Found: C, 34.11; H, 1.42%. NMR (*ZZ*): ^1H 3.10 (dt, $^3J_{HF}$ = 18 Hz, $^3J_{HH}$ = 7 Hz, $2CH_2CF_2$), 5.79 (dt, $^3J_{HH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, $2{=}CHCH_2$), 6.83 (d, $^3J_{HH}$ = 11 Hz, ArCH=), 7.24 (s, C_6H_4); $^{13}C\{^1H\}$ (partial) 30.8 (t, $^2J_{CF}$ = 22 Hz, CH_2CF_2), 118.6 (t, $^3J_{CF}$ = 4 Hz, $=CHCH_2$), 128.8, 135.2, 137.5 [3s, $C_6H_4(CH{=})_2$].

1,3,5-$C_6H_3(CH{=}CHCH_2R_{f8})_3$ (**13**). The reaction/workup given for **9** was repeated with **5** (0.190 g, 1.17 mmol), **7** (3.19 g, 3.81 mmol), K_2CO_3 (0.281 g, 4.694 mmol), reagent-grade 1,4-dioxane (40 ml) and H_2O (0.5 ml). This gave **13** as a colorless oil that solidified upon standing (1.33 g, 0.915 mmol, 78%, 94:6 *ZZZ/EZZ*), m.p. 36 °C. Calculated for $C_{39}H_{15}F_{51}$: C, 32.25; H, 1.04. Found: C, 32.48; H, 1.13%. NMR (*ZZZ*): ^1H 3.03 (dt, $^3J_{HH}$ = 7 Hz, $^3J_{HF}$ = 18 Hz, $3CH_2CF_2$), 5.81 (dt, $^3J_{HH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, $3{=}CHCH_2$), 6.82 (d, $^3J_{HH}$ = 11 Hz, 3ArCH=), 6.99 (s, C_6H_3); $^{13}C\{^1H\}$ (partial) 30.6 (t, $^2J_{CF}$ = 23.2 Hz, CH_2CF_2), 119.4 (t, $^3J_{CF}$ = 5 Hz, $=CHCH_2$), 127.7, 135.1, 136.9 (3s, $C_6H_3(CH{=})_3$).

1,2-$C_6H_4(CH{=}CHCH_2R_{f6})_2$ (**19**). The reaction/workup given for **9** was repeated with 1,2-$C_6H_4(CHO)_2$ (0.910 g, 6.79 mmol), **6** (9.960 g, 13.53 mmol), K_2CO_3 (0.811 g, 13.53 mmol), reagent-grade 1,4-dioxane (40 ml) and H_2O (0.5 ml). This gave **19** as a colorless oil (4.423 g, 5.57 mmol, 82%; 89:11 *ZZ/EZ*). Calculated for $C_{24}H_{12}F_{26}$: C, 36.29; H, 1.52. Found: C, 36.57; H, 1.66%. NMR (*ZZ*): ^1H 2.94 (dt, $^3J_{HF}$ = 18 Hz, $^3J_{HH}$ = 7 Hz, $2CH_2CF_2$), 5.83 (dt, $^3J_{HH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, $2{=}CHCH_2$), 6.78 (d, $^3J_{HH}$ = 11 Hz, 2ArCH=), 7.22–7.26 (m, 2H), 7.30–7.35 (m, 2H); $^{13}C\{^1H\}$ (partial) 30.7 (t, $^2J_{CF}$ = 22 Hz, CH_2CF_2), 119.3 (t, $^3J_{CF}$ = 5 Hz, $=CHCH_2$), 128.0, 129.1, 134.6, 135.2 [4s, $C_6H_4(CH{=})_2$]; ^{19}F 80.4 (t, $^3J_{FF}$ = 9 Hz, $2CF_3$), 112.5 (br s, $2CF_2$), 121.4 (br s, $2CF_2$), 122.3 (br s, $2CF_2$), 122.6 (br s, $2CF_2$), 125.7 (br s, $2CF_2$).

1,2-$C_6H_4(CH{=}CHCH_2R_{f10})_2$ (**20**). The reaction/workup given for **9** was repeated with 1,2-$C_6H_4(CHO)_2$ (0.389 g, 2.90 mmol), **8** (8.14 g, 8.70 mmol), K_2CO_3 (0.522 g, 8.70 mmol), reagent-grade 1,4-dioxane (30 ml) and H_2O (0.5 ml). This gave **20** as a white solid (3.15 g, 2.63 mmol, 91%; 95:5 *ZZ/EZ*), m.p. 78–79 °C. Calculated for $C_{32}H_{12}F_{42}$: C, 32.18; H, 1.01. Found: C, 32.33; H, 1.20%. NMR (*ZZ*): (in 50:50 $COCl_3$–$CF_3C_6F_5$) ^1H 2.97 (dt, $^3J_{HF}$ = 18 Hz, $^3J_{HH}$ = 7 Hz, $2CH_2CF_2$), 5.87 (dt, $^3J_{HH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, $2{=}CHCH_2$), 6.85 (d, $^3J_{HH}$ = 11 Hz, ArCH=), 7.15–7.55 (m, C_6H_4); $^{13}C\{^1H\}$ (partial) 30.8 (t, $^2J_{CF}$ = 22 Hz, CH_2CF_2), 119.5 (t, $^3J_{CF}$ = 4 Hz, $=CHCH_2$), 128.0, 129.3, 134.8, 135.5 [4s, $C_6H_4(CH{=})_2$].

$C_6H_5CH_2CH_2CH_2R_{f8}$ (**14**). A Schlenk flask was charged with **9** (1.24 g, 2.31 mmol), 10% Pd/C (0.150 g, 0.14 mmol), reagent-grade hexanes (10 ml) and absolute EtOH (10 ml), purged with H_2 (2–3 min) and fitted with a thick-walled balloon filled with H_2. The mixture was stirred 24 h at room temperature and filtered through Celite (5 cm plug). The volatiles were removed by rotary evaporation and oil pump vacuum to give **14** as a colorless oil (1.12 g, 2.08 mmol, 90%). Calculated for $C_{17}H_{11}F_{17}$: C, 37.93; H, 2.06. Found: C,. 37.81; H, 2.00%. NMR: ^1H 1.93–2.21 (m, $CH_2CH_2CF_2$), 2.73 (t, $^3J_{HH}$ = 7 Hz, $ArCH_2$), 7.20–7.37 (m, C_6H_5); ^{13}C (partial) 22.1 (br s), 30.6 (t, $^2J_{CF}$ = 22 Hz), 35.3 (s), 126.6, 128.6, 128.8, 140.9 (4s, C_6H_5); ^{19}F 80.1 (t, $^3J_{FF}$ = 12 Hz, CF_3), 112.4 (br s, CF_2), 119.8 (br s, $3CF_2$), 122.3 (br s, CF_2), 122.8 (br s, CF_2), 125.3 (br s, CF_2).

1,2-$C_6H_4(CH_2CH_2CH_2R_{f8})_2$ (**15**). The reaction given for **14** was repeated with **10** (1.23 g, 1.23 mmol), 10% Pd/C (0.150 g, 0.14 mmol), reagent-grade hexanes (15 ml) and absolute EtOH (15 ml) (18 h under H_2). This gave **15** as a white solid (1.11 g, 1.12 mmol, 91%), which was further purified by rinsing through a silica gel plug (5 cm) with hexanes (100 ml). Calculated for $C_{28}H_{16}F_{34}$: C, 33.68; H, 1.61. Found: C, 33.43; H, 1.51%. NMR: ^1H 1.91 (m, $2CH_2CH_2CF_2$), 2.16 (m, $2CH_2CF_2$), 2.72 (t, $^3J_{HH}$ = 8 Hz, $2ArCH_2$), 7.17–7.23 (m, C_6H_4); $^{13}C\{^1H\}$ (partial) 22.3 (br s), 31.1 (t, $^2J_{CF}$ = 22 Hz, CH_2CF_2), 32.3 (s), 127.3, 129.8, 139.0 (3s, C_6H_4); ^{19}F 80.1 (t, $^3J_{FF}$ = 12 Hz, $2CF_3$), 112.2 (br s, $2CF_2$), 119.3 (br s, $6CF_2$), 119.8 (br s, $2CF_2$), 120.2 (br s, $2CF_2$), 123.3 (br s, $2CF_2$).

1,3-$C_6H_4(CH_2CH_2CH_2R_{f8})_2$ (**16**). The reaction/workup given for **15** was repeated with **11** (1.00 g, 1.00 mmol),

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10% Pd/C (0.050 g, 0.05 mmol), reagent-grade CH_2Cl_2 (5 ml) and absolute EtOH (5 ml) (8 h under H_2). This gave **16** as a white solid (0.799 g, 0.800 mmol, 80%), m.p. 68 °C. Calculated for $C_{28}H_{16}F_{34}$: C, 33.68; H, 1.61. Found: C, 33.97; H, 1.83%. NMR: ^{1}H 1.95–2.20 (m, $2CH_2CH_2CF_2$), 2.71 (t, $^3J_{HH} = 8$ Hz, $ArCH_2$), 7.04 (apparent t, 3H), 7.26 (m, 1H); $^{13}C\{^1H\}$ (partial) 22.0 (s), 30.4 (t, $^2J_{CF} = 22$ Hz, CH_2CF_2), 35.1 (s), 126.6, 128.6, 129.0, 141.1 (4s, C_6H_4).

*1,4-$C_6H_4(CH_2CH_2CH_2R_{f8})_2$ (**17**).* The reaction/workup given for **15** was repeated with **12** (0.951 g, 0.956 mmol), 10% Pd/C (0.150 g, 0.141 mmol), reagent-grade $CF_3C_6H_5$ (10 ml) and absolute EtOH (10 ml) (18 h under H_2). This gave **17** as a white solid (0.918 g, 0.919 mmol, 96%), m.p. 84–85 °C. Calculated for $C_{28}H_{16}F_{34}$: C, 33.68; H, 1.61. Found: C, 34.03; H, 1.42%. NMR: ^{1}H 1.92–2.14 (m, $2CH_2CH_2CF_2$), 2.72 (t, $^3J_{HH} = 8$ Hz, $ArCH_2$), 7.14 (s, C_6H_4); $^{13}C\{^1H\}$ (partial) 22.1 (s), 30.5 (t, $^2J_{CF} = 22$ Hz, CH_2CF_2), 34.8 (s), 128.9, 139.1 (2s, C_6H_4).

*1,3,5-$C_6H_3(CH_2CH_2CH_2R_{f8})_3$ (**18**).* The reaction given for **14** was repeated with **13** (0.736 g, 0.506 mmol), 10% Pd/C (0.150 g, 0.140 mmol), reagent-grade EtOH (10 ml) and $CF_3C_6H_5$ (10 ml) (12 h under H_2). The mixture was filtered through Celite (5 cm plug) that was further rinsed with $CF_3C_6H_5$ (3 × 25 ml). The volatiles were removed from the filtrate by rotary evaporation and oil pump vacuum to give **18** as star clusters of white crystals (0.677 g, 0.464 mmol, 92%), m.p. 60–61 °C. Calculated for $C_{39}H_{21}F_{51}$: C, 32.11; H, 1.45. Found: C, 32.69; H, 1.84%. NMR: ^{1}H 1.91–2.10 (m, $3CH_2CH_2CF_2$), 2.69 (t, $^3J_{HH} = 7$ Hz, $3ArCH_2$), 6.86 (s, C_6H_3); $^{13}C\{^1H\}$ (partial) 21.8 (s), 30.1 (t, $^2J_{CF} = 22$ Hz, CH_2CF_2), 34.8 (s), 126.8, 141.5 (2s, C_6H_3).

*1,2-$C_6H_4(CH_2CH_2CH_2R_{f6})_2$ (**21**).* The reaction/workup given for **15** was repeated with **19** (0.866 g, 1.09 mmol), 10% Pd/C (0.050 g, 0.05 mmol), reagent-grade hexanes (20 ml), and absolute EtOH (20 ml) (12 h under H_2). This gave **21** as a colorless oil (0.799 g, 1.00 mmol, 92%), which could be further purified by rinsing through a silica gel plug (5 cm) with hexanes (100 ml). Calculated for $C_{24}H_{16}F_{26}$: C, 36.10; H, 2.02. Found: C, 36.54; H, 2.21%. NMR: ^{1}H 1.93 (m, $2CH_2CH_2CF_2$), 2.15 (m, $2CH_2CF_2$), 2.73 (t, $^3J_{HH} = 8$ Hz, $2ArCH_2$), 7.17–7.24 (m, C_6H_4); $^{13}C\{^1H\}$ (partial) 22.0 (br s), 30.9 (t, $^2J_{CF} = 23$ Hz, CH_2CF_2), 32.1 (s), 127.0, 129.6, 138.7 (3s, C_6H_4); ^{19}F 80.2 (t, $^3J_{FF} = 12$ Hz, $2CF_3$), 113.4 (br s, $2CF_2$), 121.2 (br s, $2CF_2$), 122.2 (br s, $2CF_2$), 122.8 (br s, $2CF_2$), 125.5 (br s, $2CF_2$).

*1,2-$C_6H_4(CH_2CH_2CH_2R_{f10})_2$ (**22**).* The reaction/workup given for **15** was repeated with **20** (1.14 g, 0.954 mmol), 10% Pd/C (0.100 g, 0.094 mmol), $C_6H_5CF_3$ (30 ml) and absolute EtOH (30 ml) (12 h under H_2). This gave **22** as a white solid (1.14 g, 0.951 mmol, 98%), m.p. 77–78 °C. Calculated for $C_{32}H_{16}F_{42}$: C, 32.07; H, 1.34. Found: C, 32.35; H, 1.50% NMR (in 50:50 $CDCl_3$–$CF_3C_6F_5$). ^{1}H 2.00 (m, $2CH_2CH_2CF_2$), 2.24 (m, $2CH_2CF_2$), 2.81 (t, $^3J_{HH} = 8$ Hz, $2ArCH_2$), 7.17–7.23 (m, C_6H_4); $^{13}C\{^1H\}$ (partial) 22.1 (br s), 31.1 (t, $^2J_{CF} = 22$ Hz, CH_2CF_2), 32.2 (s), 127.0, 129.0, 129.7 (3s, C_6H_4).

Partition coefficients.[4,6c]. The following is representative. A 10 ml vial was charged with **15** (0.0240 g, 0.0240 mmol), $CF_3C_6F_{11}$ (2.000 ml) and toluene (2.000 ml), equipped with a Mininert valve, vigorously shaken (2 min) and immersed (cap-level) in a 35 °C oil-bath. After 12 h, the bath was removed. After 12–24 h, a 0.400 ml aliquot of each layer was added to 2.000 ml of a standard 0.0273 M solution of hexadecane in hexane. GC analysis (average of 7–8 injections) showed that 0.00412 mmol of **15** was in the $CF_3C_6F_{11}$ aliquot and 0.000398 mmol in the toluene aliquot (91.2:8.8; a 2.000/0.400 scale factor gives a total mass recovery of 0.0222 g, 93%).

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