

# Nuclear Spin–Spin Coupling via Nonbonded Interactions. 8.<sup>1</sup> The Distance Dependence of Through-Space Fluorine–Fluorine Coupling

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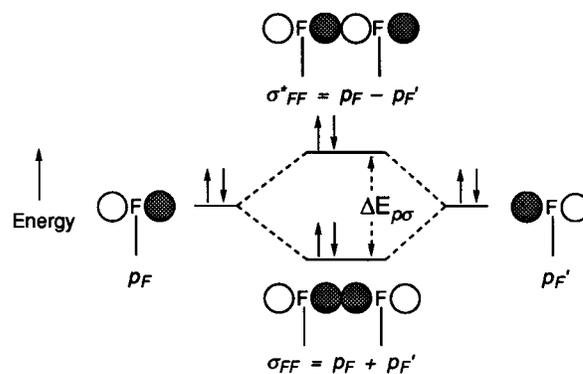
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**Abstract:** The  $^{19}\text{F}^{19}\text{F}$  nuclear spin–spin coupling constants  $J_{\text{FF}}$  for a set of eighteen compounds related structurally to 1,8-difluoronaphthalene were measured by  $^{19}\text{F}$  NMR spectroscopy. The FF distances  $d_{\text{FF}}$  in these compounds were determined by ab initio 3-21G\* molecular orbital calculations. Consistent with the lone-pair overlap theory of the origins of through-space  $^{19}\text{F}^{19}\text{F}$  coupling, an exponential relationship is found between  $J_{\text{FF}}$  and  $d_{\text{FF}}$  (regression coefficient  $r^2 = 0.991$ ), and a linear relationship is found between  $J_{\text{FF}}$  and the extent of the overlap interaction between the in-plane fluorine 2p lone-pair orbitals (regression coefficient  $r^2 = 0.993$ ). The magnitudes of these lone-pair interactions were estimated from molecular orbital energies obtained by ab initio 6-31G\* calculations for a model consisting of a pair of HF molecules separated by various distances.

It has long been known<sup>2–4</sup> that compounds containing fluorine atoms that are crowded against one another intramolecularly exhibit unusually large FF nuclear spin–spin coupling constants  $J_{\text{FF}}$  as measured by  $^{19}\text{F}$  NMR spectroscopy in fluid solution. This so-called through-space FF coupling<sup>5</sup> has been theorized<sup>4</sup> to result from overlap interactions between 2p lone-pair orbitals on the two crowded fluorines. We describe here some experimental efforts to test the predictions of this theory with regard to the distance dependence of through-space FF coupling.

The overlap interactions that form the basis of the lone-pair overlap theory<sup>4b</sup> are exemplified in Figure 1 for the orientation of fluorines found in 1,8-difluoronaphthalene, in which the CF bonds are coplanar and approximately parallel, and the FF separation  $d_{\text{FF}}$  is about 2.58 Å. In this orientation, the two filled in-plane lone-pair atomic  $p_{\text{F}}$  and  $p_{\text{F}'}$  orbitals<sup>6</sup> would experience a small amount of  $\sigma$  overlap, and this would give rise to a pair of filled two-center molecular orbitals, one weakly bonding ( $\sigma_{\text{FF}}$ )



**Figure 1.** Schematic representations of the shapes and the relative energies of the bonding and antibonding molecular orbitals,  $\sigma_{\text{FF}}$  and  $\sigma_{\text{FF}}^*$ , that can be imagined to result from the  $\sigma$  overlap of the in-plane 2p lone-pair atomic orbitals,  $p_{\text{F}}$  and  $p_{\text{F}'}$ , on two spatially proximate fluorine atoms oriented with their CF bonds coplanar and approximately parallel as in 1,8-difluoronaphthalene.

and the other weakly antibonding ( $\sigma_{\text{FF}}^*$ ); we designate the energy difference between these two molecular orbitals as  $\Delta E_{p\sigma}$ . This combination of bonding and antibonding interactions would lead to no net chemical bonding between the two fluorine atoms, but we believe that the resulting direct four-electron linkage between the two fluorines would be very effective in the transmission of nuclear spin information. Specifically, it has been argued<sup>4b</sup> that the two fluorine nuclei cause spin polarization of these four electrons in such a way that the system is more stabilized when the two nuclear spins are antiparallel than when they are parallel (i.e.,  $J_{\text{FF}} > 0$ ).<sup>7</sup> Furthermore, it has been argued<sup>4b</sup> that the extent of this spin polarization, and therefore the magnitude of the through-space coupling constant  $J_{\text{FF}}$ , depends on the extent to which the  $\sigma_{\text{FF}}$  and  $\sigma_{\text{FF}}^*$  molecular

(7) It is well established experimentally in many different molecular systems that the sign of  $J_{\text{FF}}$  for through-space FF coupling is positive.<sup>3,4,12,14b</sup>

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(5) The term “through-space” has long been used to designate the kind of coupling under consideration here. This term can be regarded as a misnomer, because the phenomenon involves scalar spin–spin coupling between pairs of fluorine nuclei in molecules that are freely tumbling in fluid solution, conditions under which direct through-space dipole–dipole interactions between the two fluorine nuclei are averaged to zero.

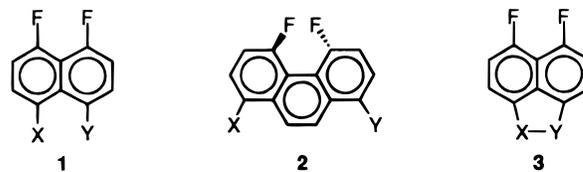
(6) Here we are ignoring for simplicity the mixing of the fluorine  $p_{\text{F}}$  lone-pair orbitals with orbitals of appropriate symmetry that are part of the  $\sigma$  framework of the molecule bearing the fluorine substituents.

orbitals differ in the spatial distribution of their electron densities. Specifically, the theory<sup>4b</sup> focuses on the region halfway between the two fluorines, in which the electron density is higher in the  $\sigma_{\text{FF}}$  orbital than it is in the  $\sigma_{\text{FF}}^*$  orbital. This predicted dependence of  $J_{\text{FF}}$  on the difference in the electron density distribution in the  $\sigma_{\text{FF}}$  and  $\sigma_{\text{FF}}^*$  orbitals implies that the magnitude of  $J_{\text{FF}}$  should depend on the extent to which the two lone-pair  $p_{\text{F}}$  and  $p_{\text{F}}'$  orbitals interact because of their overlap; the energy difference  $\Delta E_{p\sigma}$  is a direct measure of the extent of this interaction. In turn, this predicted dependence of  $J_{\text{FF}}$  on the extent of lone-pair orbital overlap suggests that  $J_{\text{FF}}$  should fall off exponentially with the distance between the two fluorines,  $d_{\text{FF}}$ .

It has been clear qualitatively from many earlier studies that through-space FF coupling has a very steep inverse dependence on FF distance.<sup>2–4</sup> For many years we have been engaged in studies designed to provide a convincing quantitative experimental assessment of this distance dependence in a set of structurally well controlled compounds related to 1,8-difluoronaphthalene.<sup>8</sup> We now report the results of our long-standing efforts to assess this distance dependence, as well as the results of a more direct experimental test of the lone-pair overlap theory. While our work was in progress, some very nice studies were reported of the distance dependence of FF through-space coupling in a series of difluorometacyclophanes and difluoroparacyclophanes with various ring substituents and bridging linkages.<sup>9</sup> A comparison of the two independent investigations is discussed later.

As an illustrative example of the sensitivity of through-space FF coupling to FF distance, 1,8-difluoronaphthalene derivatives of type **1** typically exhibit values of  $J_{\text{FF}}$  in the neighborhood of 60–85 Hz, whereas 4,5-difluorophenanthrene derivatives of type **2** typically exhibit astonishingly large values of  $J_{\text{FF}}$  in the neighborhood of 165–175 Hz.<sup>3,4b</sup> It was important in the early days of the discovery and investigation of through-space FF coupling to focus on systems such as **2** because their dramatically large coupling constants helped convince a skeptical audience about the existence of a special through-space mode of coupling.<sup>10</sup> It seemed to us, however, that for our present purposes bigger is not better. We reasoned that the effectiveness of FF lone-pair overlap might depend not only on the intramolecular distance between the two fluorine atoms but also on the angular orientation of the overlapping lone pairs. This would make comparisons of compounds of type **1** with compounds of type **2** problematic for our quantitative studies, because the CF bonds in most simple 1,8-difluoronaphthalenes are coplanar whereas the CF bonds in all 4,5-difluorophenanthrenes are not. We decided it was important to carry out our studies with a set of compounds all of which have coplanar CF bonds, and therefore we chose to compare 1,8-difluoronaphthalenes of type **1** with bridged analogues of type **3**, even though the latter

compounds typically have much *smaller* values of  $J_{\text{FF}}$  in the neighborhood of only 30–35 Hz.<sup>12</sup>



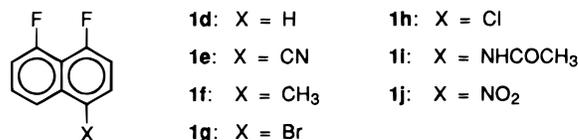
The values of  $d_{\text{FF}}$  in systems **1** and **3** are influenced in predictable ways by the nature of the substituents X and Y. In compounds of type **1**, steric crowding between groups X and Y distorts the naphthalene framework such that the two fluorines are squeezed closer together than they are in the sterically uncrowded parent system with X = Y = H. In contrast, in compounds of type **3** the angle strain imposed on the system by the XY bond distorts the naphthalene framework in the opposite sense, causing the two fluorines to be splayed apart.

In general, FF coupling can be described by eq 1, in which

$$J_{\text{FF}} = J_{\text{FF}}^{\text{ts}} + J_{\text{FF}}^{\text{tb}(\pi)} + J_{\text{FF}}^{\text{tb}(\sigma)} \quad (1)$$

$J_{\text{FF}}$  is the experimentally observed coupling constant,  $J_{\text{FF}}^{\text{ts}}$  is the coupling constant for the component of  $J_{\text{FF}}$  that arises from through-space interactions, and  $J_{\text{FF}}^{\text{tb}(\pi)}$  and  $J_{\text{FF}}^{\text{tb}(\sigma)}$  are the coupling constants for the components of  $J_{\text{FF}}$  that arise from through-bond interactions along pathways through the  $\pi$  system and the  $\sigma$  system, respectively. To use the experimentally measured values of  $J_{\text{FF}}$  to learn something about  $J_{\text{FF}}^{\text{ts}}$ , one needs to be able to evaluate the sum of  $J_{\text{FF}}^{\text{tb}(\pi)}$  and  $J_{\text{FF}}^{\text{tb}(\sigma)}$ . In principle this problem can be overcome by using systems in which the shortest through-bond pathway connecting the two fluorines in the molecule is so long, perhaps at least six bonds, that one could reasonably assume that through-bond contributions to coupling would be negligible in magnitude, thereby making  $J_{\text{FF}}^{\text{ts}}$  numerically equal to  $J_{\text{FF}}$ .<sup>11</sup> In systems **1** and **3**, the two fluorines are linked through the molecular framework by a connectivity pathway only four bonds long. We thought it was reasonable to expect, however, that the algebraic sums of  $J_{\text{FF}}^{\text{tb}(\pi)}$  and  $J_{\text{FF}}^{\text{tb}(\sigma)}$  for compounds in systems **1** and **3** are sufficiently small and sufficiently constant that it would be possible for us to gain useful insight into the distance dependence of  $J_{\text{FF}}^{\text{ts}}$  by determining experimentally the distance dependence of  $J_{\text{FF}}$ .

We synthesized 18 difluoro compounds for our studies. The syntheses of 1,8-difluoronaphthalene, **1d**, and six monosubstituted 1,8-difluoronaphthalene derivatives, **1e–j**, were described earlier.<sup>8</sup> The syntheses of three disubstituted 1,8-difluoronaphthalene derivatives, **1a–c**, and eight derivatives of 4,5-difluoroacenaphthene or 4,5-difluoroacenaphthylene, **3a–h**, are illustrated in Schemes 1–4.



The values of  $d_{\text{FF}}$  listed in Table 1 were obtained by ab initio calculations with the 3-21G\* basis set using Spartan SGI Version 3.1.2. For comparison, we have measured the FF

(11) This is an attractive feature of the set of recently reported difluorometacyclophane and difluoroparacyclophane systems,<sup>9</sup> in which the shortest through-bond pathway is seven bonds long.

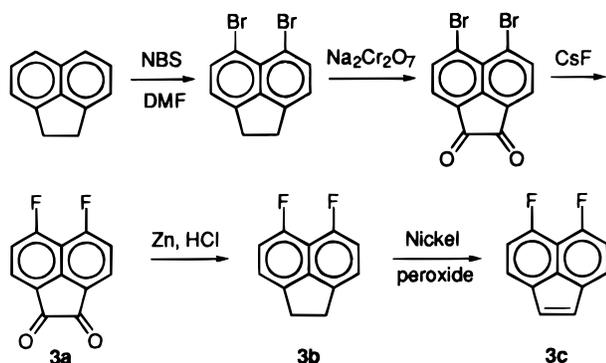
(12) Fletton, R. A.; Lapper, R. D.; Thomas, L. F. *Chem. Commun.* **1969**, 1049.

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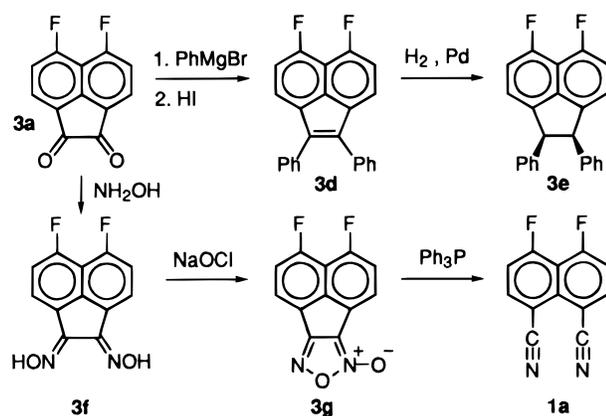
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(10) Any residual skepticism that the FF coupling observed in systems such as **1** and **2** might be attributed to an unprecedented through-bond interaction between the two fluorines was put aside after a value of  $J_{\text{FF}} = 17$  Hz was reported for a pair of spatially proximate 6-fluorotryptophan residues in a particular polypeptide (an analogue of dihydrofolate reductase) whose primary structure is such that the shortest through-bond pathway between the two fluorines is 89 bonds long! See: Kimber, B. J.; Feeney, J.; Roberts, G. C. K.; Birdsall, B.; Griffiths, D. V.; Burgen, A. S. V.; Sykes, B. D. *Nature* **1978**, *271*, 184–185.

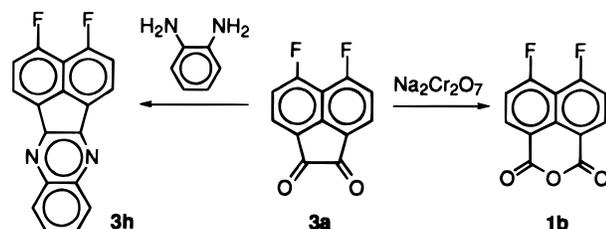
## Scheme 1



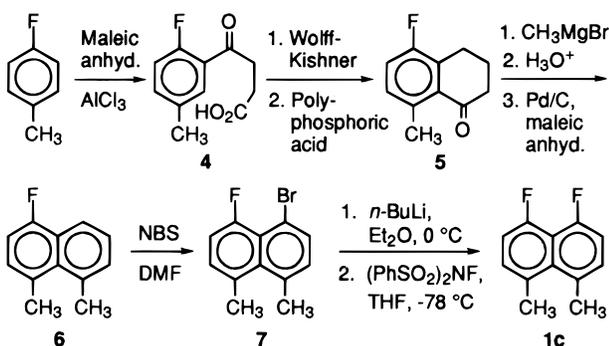
## Scheme 2



## Scheme 3



## Scheme 4



distance in compound **1b** by single-crystal X-ray analysis; a similar analysis has been reported<sup>13</sup> for compound **1d**. The experimentally measured values of  $d_{FF}$  for compounds **1b** and **1d** are larger than our 3-21G\* calculated distances by 0.056 and 0.051 Å, respectively. As an additional comparison, we have determined the values of  $d_{FF}$  for compounds **3b** and **3c** using ab initio calculations at the 6-31G\* level. These values are larger

**Table 1.** Values of  $J_{FF}$  and  $d_{FF}$  for 18 Compounds of Types **1** and **3** and the Deviations of  $J_{FF}$  from the Values Calculated by Eq 2

compd	<i>peri</i> groups X and Y	$d_{FF}$ (Å)	$J_{FF}$ (Hz) <sup>a</sup>	dev from eq 2 (Hz)
<b>3d</b>	–CPh=CPh–	2.718	36.6 <sup>b</sup>	(+12.8) <sup>b</sup>
<b>3c</b>	–CH=CH–	2.716 <sup>c</sup>	36.7 <sup>b</sup>	(+12.7) <sup>b</sup>
<b>3f</b>	–C(=NOH)–C(=NOH)–	2.697	32.1 <sup>b,d</sup>	(+5.7) <sup>b</sup>
<b>3h</b>	–(2,3-quinoxaline)–	2.688	33.0 <sup>b</sup>	(+5.4) <sup>b</sup>
<b>3e</b>	–CHPh-CHPh–	2.674	28.8	–0.8
<b>3a</b>	–CO–CO–	2.672	31.5	+1.6
<b>3b</b>	–CH <sub>2</sub> –CH <sub>2</sub> –	2.671 <sup>e</sup>	28.4	–1.6
<b>3g</b>	–(4,5-furazan oxide)–	2.671	35.7 <sup>b</sup>	(+5.7) <sup>b</sup>
<b>1b</b>	–CO–O–CO–	2.540 <sup>f</sup>	61.9	+4.4
<b>1d</b>	H, H	2.533 <sup>g</sup>	59.0 <sup>d,h</sup>	–0.6
<b>1e</b>	H, CN	2.517	66.1	+1.6
<b>1f</b>	H, CH <sub>3</sub>	2.516	65.6 <sup>i</sup>	+0.8
<b>1g</b>	H, Br	2.512	67.4	+1.3
<b>1h</b>	H, Cl	2.511	66.5 <sup>i</sup>	+0.1
<b>1i</b>	H, NHCOCH <sub>3</sub>	2.509	65.9	–1.2
<b>1j</b>	H, NO <sub>2</sub>	2.479	76.4	–1.4
<b>1a</b>	CN, CN	2.465	83.5	+0.1
<b>1c</b>	CH <sub>3</sub> , CH <sub>3</sub>	2.452	85.2	–3.8

<sup>a</sup> CDCl<sub>3</sub> solution except as noted. <sup>b</sup> Not used in constructing Figure 2 (see text). <sup>c</sup> 2.758 Å by 6-31G\* calculation. <sup>d</sup> (CD<sub>3</sub>)<sub>2</sub>CO solution. <sup>e</sup> 2.718 Å by 6-31G\* calculation. <sup>f</sup> 2.596 Å by single-crystal X-ray analysis (this work). <sup>g</sup> 2.584 Å by single-crystal X-ray analysis.<sup>13</sup> <sup>h</sup> Previously reported.<sup>14</sup> <sup>i</sup> CCl<sub>4</sub> solution.

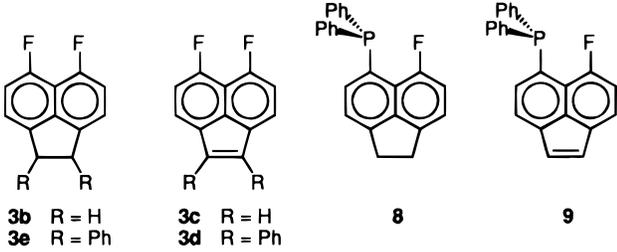
than our 3-21G\* calculated distances by 0.047 and 0.042 Å, respectively. We have proceeded on the assumption that although our ab initio 3-21G\* calculations give  $d_{FF}$  values approximately 0.05 Å smaller than those obtained either by X-ray crystallography or by 6-31G\* calculations, they provide an accurate reflection of the trends in the actual FF distances within the set of compounds included in our study.

Also listed in Table 1 are the values of  $J_{FF}$  obtained by <sup>19</sup>F NMR measurements. We adopted CDCl<sub>3</sub> as the standard solvent for these measurements. Although we did not carry out a comprehensive study of the solvent dependence of  $J_{FF}$  for our compounds, some spot checks revealed that values measured in CCl<sub>4</sub> or in (CD<sub>3</sub>)<sub>2</sub>CO solution agree very closely with those measured in CDCl<sub>3</sub> solution, whereas values measured in (CD<sub>3</sub>)<sub>2</sub>SO solution are smaller by about 1–3 Hz. For compounds in which the two fluorines are equivalent by symmetry, values of  $J_{FF}$  were determined from the <sup>13</sup>C satellite signals in the proton-decoupled <sup>19</sup>F NMR spectra.

The data in Table 1 for the 10 naphthalene derivatives **1a–j** show a relatively smooth trend of increasing values of  $J_{FF}$  with decreasing values of  $d_{FF}$ ; in contrast, the data for the eight acenaphthene and acenaphthylene derivatives **3a–h** do not show such a trend. This initially surprising absence of a simple pattern for the data in the **3a–h** series of compounds needs to be addressed before we can proceed with our overall analysis.

In particular, it is instructive to consider the following seemingly anomalous results: the acenaphthylene derivatives **3c** and **3d**, which have unsaturated two-carbon bridges, have significantly *larger* values of  $J_{FF}$  than are found for the corresponding acenaphthene derivatives **3b** and **3e**, which have saturated two-carbon bridges (see Table 2). Since the two-carbon bridges are *shorter* in acenaphthylenes **3c** and **3d** than in acenaphthenes **3b** and **3e**, the FF distances should be, and are, *longer* in **3c** and **3d** than in **3b** and **3e**. On that basis, one might have expected that the values of  $J_{FF}$  would be *smaller* for acenaphthylenes **3c** and **3d** than for their dihydro analogues **3b** and **3e**, but this is the *opposite* of the experimental results. To rationalize this initially surprising reversal of our expectations, we begin by recognizing that there is a fundamental difference electronically between acenaphthylenes, which have nonalternant

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**Table 2.** Comparisons of FF and PF Data for Acenaphthylene Derivatives and the Corresponding Acenaphthene Derivatives


compd	R groups	$d_{\text{FF}}$ (Å)	$d_{\text{PF}}$ (Å)	$J_{\text{FF}}$ (Hz)	$J_{\text{PF}}$ (Hz)
3b	R = H	2.671		28.4	
3e	R = Ph	2.674		28.8	
3c	R = H	2.716		36.7	
3d	R = Ph	2.718		36.6	
8			2.807		144.1
9			2.844		130.1

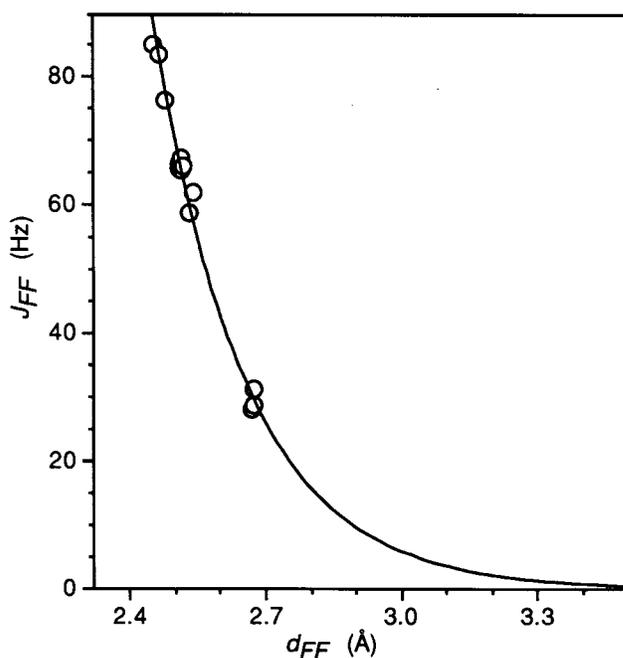
$12\pi$ -electron systems, and acenaphthenes, which have alternant  $10\pi$ -electron systems. We hypothesize that  $J_{\text{FF}}$  is larger for acenaphthylenes **3c** and **3d** than for acenaphthenes **3b** and **3e** because the overall FF coupling for **3c** and **3d** is enhanced by an unusually large through-bond contribution,  $J_{\text{FF}}^{\text{tb}(\pi)}$ . Such coupling would involve overlap interactions between the out-of-plane  $2p$  lone-pair orbitals on the two fluorines and the  $\pi$  orbitals of the acenaphthylene framework. The recent success in developing an understanding of HH nuclear spin coupling on the basis of a sum-over-states perturbation method<sup>15</sup> provides some general theoretical support for our speculative hypothesis, because the HOMO–LUMO energy gap for acenaphthylene is significantly smaller than that for acenaphthene.<sup>16</sup> This smaller energy gap is evidenced, for example, by the fact that the wavelengths of the para-bands in the ultraviolet spectra of acenaphthylene and acenaphthene are at 340 and 289 nm, respectively.<sup>16</sup>

Experimental support for our speculation about a large through- $\pi$ -bond contribution to the overall FF coupling in acenaphthylenes **3c** and **3d** can be found in some results from a parallel study of the distance dependence of through-space PF coupling that we have in progress. As indicated in Table 2, 5-diphenylphosphino-6-fluoroacenaphthene (**8**) and 5-diphenylphosphino-6-fluoroacenaphthylene (**9**) show the *expected* behavior: the PF coupling constant  $J_{\text{PF}}$  is *smaller* in **9** than in **8**, which is consistent with the fact that the PF distance,  $d_{\text{PF}}$ , is larger in **9** than in **8**. We think that this lack of an anomaly in the PF systems, as compared with the corresponding FF systems, might be attributed to the absence of significant through-bond PF coupling involving the  $\pi$  system in *both* compounds **8** and **9**. We expect that such coupling should be negligible in compounds **8** and **9** for three reasons: (1) the phosphorus lone pair is presumed to be largely a  $3s$  orbital, which would be precluded by symmetry from overlap interaction with the aromatic  $\pi$  system; (2) to the small extent that the phosphorus lone pair possesses some  $3s$ – $3p$  hybridization that would give it directional character, the axis of the resulting hybrid orbital would have a largely in-plane orientation, which would be the wrong symmetry for overlap interaction with the aromatic  $\pi$

(14) (a) Cooper, M. A.; Weber, H. E.; Manatt, S. L. *J. Am. Chem. Soc.* **1971**, *93*, 2369–2380. (b) Manatt, S. L.; Cooper, M. A.; Mallory, C. W.; Mallory, F. B. *J. Am. Chem. Soc.* **1973**, *95*, 975–977.

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(16) Mitchell, R. H.; Fyles, T.; Ralph, L. M. *Can. J. Chem.* **1977**, *55*, 1480–1497.



**Figure 2.** Plot of  $J_{\text{FF}}$  against  $d_{\text{FF}}$  using data from Table 1 for 13 compounds, **1a–j** and **3a,b,e**, fitted by the exponential relationship defined by eq 2.

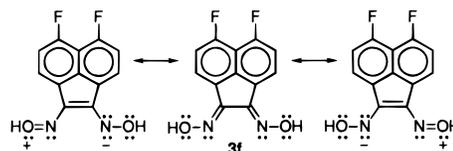
system; and (3) the carbon–phosphorus bond is too long to permit effective  $\pi$  overlap of a hybridized phosphorus lone pair with the aromatic  $\pi$  system even if the axis of the lone-pair orbital were to be oriented with a significant out-of-plane component.

On the basis of the arguments given above, we think that the nonalternant acenaphthylenes **3c** and **3d** need to be excluded from our initial analysis of the data in Table 1. In addition, we think it is prudent to exclude initially three other compounds of type **3** in which the two-carbon bridge has significant double-bond character: dioxime **3f**,<sup>17</sup> furazan oxide **3g**, and quinoxaline **3h**. Accordingly, we have constructed the plot shown in Figure 2 using the  $J_{\text{FF}}$  and  $d_{\text{FF}}$  data given Table 1 for the following 13 naphthalene and acenaphthene compounds in our series: **1a–j** and **3a,b,e**. A curve-fitting program (Cricket Graph III, Version 1.5.1) was used to find the best exponential fit for the 13 data points. The resulting curve is expressed by eq 2, in which  $J_{\text{FF}}$

$$J_{\text{FF}} = (1.703 \times 10^7) e^{-4.960d_{\text{FF}}} \quad (2)$$

is in units of hertz and  $d_{\text{FF}}$  is in units of angstroms; the regression coefficient for this curve is  $r^2 = 0.991$ . The deviations of the 13 experimental values of  $J_{\text{FF}}$  from the values calculated by eq 2 are given in Table 1; the mean deviation is  $\pm 1.5$  Hz. Table 1 also lists (in parentheses) the deviations for the five compounds **3c,d,f–h** that were *not* used in constructing the curve in Figure 2. If these five data points were added to the plot in Figure 2, they all would lie *above* the correlation curve for the other 13 data points, with deviations ranging from +5.4 to +12.8 Hz; this is consistent with our speculation that the total FF

(17) The partial double-bond character of the two-carbon bridge in dioxime **3f** can be illustrated qualitatively by the resonance approach.





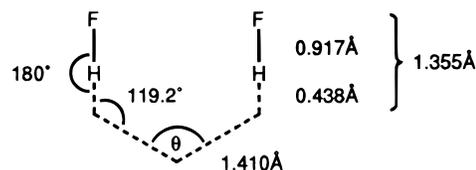
**Figure 3.** Illustration of the relationship between the lone-pair overlap interactions of the fluorines in the cyclophane systems<sup>9</sup> of types **10** and **11** (involving the fluorine 2p orbitals that overlap with the  $\pi$  orbitals of the aromatic systems) as compared to those in the naphthalene system of type **1d** (involving the fluorine 2p orbitals that overlap with the  $\sigma$  orbitals of the aromatic systems). The linkages between the two aromatic rings in **10** and **11**, shown schematically here, are either  $-\text{CH}_2\text{SCH}_2-$  or  $-\text{CH}_2\text{CH}_2-$  bridges.

coupling in these five compounds is somehow enhanced by an especially effective through-bond contribution.

On the basis of the plot in Figure 2 we conclude that the FF distance  $d_{\text{FF}}$  is the dominant factor contributing to the variations in  $J_{\text{FF}}$  for this series of 13 compounds. In particular, the electron-withdrawing or electron-supplying character of the substituent does not seem to exert a major influence on the total FF coupling. For example, although the cyano, methyl, chloro, and acetamido substituents in compounds **1e**, **1f**, **1h**, and **1i**, respectively, possess widely differing electronic properties, the values of  $J_{\text{FF}}$  for these four compounds are very similar, ranging from 65.6 to 66.5 Hz; this is consistent with the fact that the values of  $d_{\text{FF}}$  for these compounds are very similar, ranging from 2.511 to 2.517 Å. The plot in Figure 2 certainly is consistent with the theoretically predicted<sup>4</sup> exponential relationship between  $J_{\text{FF}}$  and  $d_{\text{FF}}$ , but we think that our results fall short of providing a definitive experimental demonstration of this prediction. We had thought that the FF coupling constants in our series of 13 compounds spanned an admirably wide range, from 28.4 to 85.2 Hz; we recognize now that it would be desirable to have data over an even wider range to allow for a more convincing demonstration of the functional form of the curvature in the relationship between  $J_{\text{FF}}$  and  $d_{\text{FF}}$ .

In fitting the  $J_{\text{FF}}$  versus  $d_{\text{FF}}$  data in Figure 2 to a simple exponential curve, i.e., one for which  $J_{\text{FF}}$  goes to zero at the limit of large  $d_{\text{FF}}$ , the assumption is being made that the sum of the through-bond coupling constants  $J_{\text{FF}}^{\text{tb}(\pi)}$  and  $J_{\text{FF}}^{\text{tb}(\sigma)}$  is at least approximately zero. To explore this assumption, we have arbitrarily assigned a constant nonzero value for this sum of either +10 or -10 Hz, and then subtracted these hypothetically chosen values for the through-bond components from the experimental values of  $J_{\text{FF}}$ , according to eq 1, to give estimated values for  $J_{\text{FF}}^{\text{fs}}$ . It happens that for *both* of these arbitrary assignments of +10 or -10 Hz for the through-bond contribution to the overall FF coupling, exponential plots of the estimated values of  $J_{\text{FF}}^{\text{fs}}$  against  $d_{\text{FF}}$  also have high regression coefficients ( $r^2 = 0.987$  and  $0.993$ , respectively). We conclude from this outcome that our data do not provide any sound basis for judging either the sign or the approximate magnitude of the contribution of through-bond FF coupling in our series of compounds, but the results shown in Figure 2 are consistent with our expectation that these through-bond contributions constitute only a small fraction of the observed total FF coupling.

It is interesting that the results obtained for the cyclophane<sup>9</sup> systems of types **10** and **11** (see Figure 3) are not very different from the results we report here for the systems of types **1** and **3**. That is, in systems **10** and **11** the values of  $J_{\text{FF}}$  range from 110.1 to 7.2 Hz as the values of  $d_{\text{FF}}$  range from 2.419 to 3.180 Å,<sup>9</sup> and in systems **1** and **3** the values of  $J_{\text{FF}}$  range from 85.2 to 28.4 Hz as the values of  $d_{\text{FF}}$  range from 2.452 to 2.671 Å. Both sets of data are fit by exponential equations in which the



**Figure 4.** Model used for ab initio calculations of the intermolecular overlap interactions of the in-plane  $p_{\text{F}}$  lone pairs on the fluorine atoms of a pair of HF molecules that are oriented so as to simulate the intramolecular overlap interactions of the in-plane  $p_{\text{F}}$  lone pairs on the *peri* fluorine atoms in difluoronaphthalene and difluoroacenaphthene derivatives of types **1** and **3**.

exponents are rather similar:  $-3.211d_{\text{FF}}$  for systems **10** and **11**,<sup>9</sup> and  $-4.960d_{\text{FF}}$  for systems **1** and **3** (eq 2). Quantitative differences in the distance dependencies in the two systems are to be expected, in view of the fact that the aromatic fluorine substituents interact in a face-to-face way in systems **10** and **11**, whereas they interact in a side-to-side way in systems **1** and **3**. That is, the fluorine lone-pair overlap in systems **10** and **11** involves the locally out-of-plane 2p orbitals (those that experience overlap interactions with the  $\pi$  orbitals of the aromatic rings), whereas the fluorine lone-pair overlap in systems **1** and **3** involves the locally in-plane 2p orbitals (those that experience overlap interactions with the  $\sigma$  orbitals of the aromatic rings). In addition, the values of  $d_{\text{FF}}$  were estimated by very different methods: MM2 calculations for systems **10** and **11**,<sup>9</sup> and ab initio calculations for systems **1** and **3**.

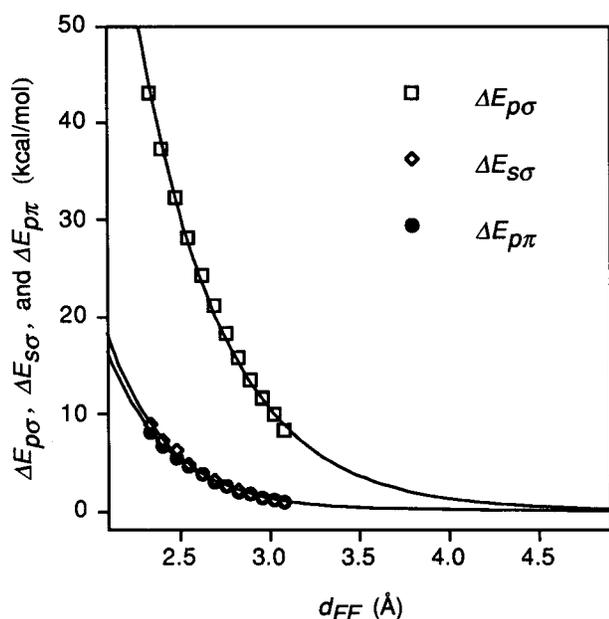
We have also carried out a more direct test of the theory<sup>4</sup> that through-space FF coupling in compounds of types **1** and **3** arises from the interactions of the in-plane  $p_{\text{F}}$  lone pairs on the two coupled fluorines. This test involves determining whether a *linear* relationship exists between  $J_{\text{FF}}$  and the extent of the overlap interaction of these two lone-pair orbitals in our series of 13 compounds, a quantity that can be gauged by  $\Delta E_{p\sigma}$  (see Figure 1). We determined values of  $\Delta E_{p\sigma}$  by ab initio molecular orbital calculations at the 6-31G\* level for a simplified model (see Figure 4) consisting of a pair of HF molecules in which the two fluorines are oriented with respect to one another in a way that is analogous to the relative orientation of the two fluorines in our series of 13 compounds. In this model, the HF bond distances were set at 0.917 Å, the known value for hydrogen fluoride, and the other distances and angles shown in Figure 4 were chosen to mimic the standard CF and CC bond distances and the FCC bond angle (1.355 Å, 1.410 Å, and 119.2°, respectively) in compounds of types of **1** and **3**. The calculations of  $\Delta E_{p\sigma}$  and  $d_{\text{FF}}$  in this simple model were carried out for 12 values of the angle  $\theta$  ranging from 118° to 140° in increments of 2°; these data are listed in Table 3. Curve-fitting of the resulting twelve data points to an exponential function gave the plot of  $\Delta E_{p\sigma}$  versus  $d_{\text{FF}}$  shown in Figure 5; the equation for this plot is given in eq 3, and the regression coefficient is

$$\Delta E_{p\sigma} = 6596e^{-2.146d_{\text{FF}}} \quad (3)$$

$r^2 = 0.999$ . From these same molecular orbital calculations we also obtained values of  $\Delta E_{s\sigma}$ , the energy difference between the antibonding and bonding two-center orbitals that result from the  $\sigma$  overlap interactions of the 2s lone-pair orbitals on the two fluorines, as well as values of  $\Delta E_{p\pi}$ , the energy difference between the antibonding and bonding two-center orbitals that result from the  $\pi$  overlap interactions of the out-of-plane 2p lone-pair orbitals on the two fluorines (see Table 3). These  $\Delta E_{s\sigma}$  and  $\Delta E_{p\pi}$  data also were fitted to exponential curves as shown in Figure 5; the equations for these curves are given in eqs 4

**Table 3.** Calculations of  $d_{\text{FF}}$ ,  $\Delta E_{\text{p}\sigma}$ ,  $\Delta E_{\text{s}\sigma}$ , and  $\Delta E_{\text{p}\pi}$  as a Function of  $\theta$  (See Figure 4 and the Text)

$\theta$ (deg)	$d_{\text{FF}}$ (Å)	$\Delta E_{\text{p}\sigma}$ (kcal/mol)	$\Delta E_{\text{s}\sigma}$ (kcal/mol)	$\Delta E_{\text{p}\pi}$ (kcal/mol)
118	2.3321	43.047	9.011	8.195
120	2.4044	37.374	7.323	6.765
122	2.4759	32.412	6.275	5.585
124	2.5467	28.150	4.863	4.606
126	2.6167	24.410	3.966	3.803
128	2.6859	21.141	3.244	3.131
130	2.7543	18.279	2.654	2.579
132	2.8218	15.776	2.177	2.121
134	2.8885	13.579	1.782	1.738
136	2.9543	11.659	1.462	1.424
138	3.0192	9.990	1.205	1.167
140	3.0832	8.522	0.988	0.948

**Figure 5.** Plots of the calculated energy differences  $\Delta E_{\text{p}\sigma}$ ,  $\Delta E_{\text{s}\sigma}$ , and  $\Delta E_{\text{p}\pi}$  against  $d_{\text{FF}}$  for the model consisting of a pair of HF molecules as discussed in the text and shown in Figure 4.

and 5, and the regression coefficients are 1.000 and 0.999, respectively. It can be seen in Figure 5 that the lone-pair overlap interactions of the in-plane 2p orbitals are much larger than those of the 2s or the out-of-plane 2p orbitals.

$$\Delta E_{\text{s}\sigma} = 9146e^{-2.959d_{\text{FF}}} \quad (4)$$

$$\Delta E_{\text{p}\pi} = 6674e^{-2.862d_{\text{FF}}} \quad (5)$$

Equation 3 was used to calculate the values of  $\Delta E_{\text{p}\sigma}$  at each of the particular values of  $d_{\text{FF}}$  (Table 1) that apply to the 13 compounds in our study; the results are listed in Table 4. A plot of  $J_{\text{FF}}$  versus  $\Delta E_{\text{p}\sigma}$  is shown in Figure 6. The data were fit to the best straight line, the equation for which is given in eq 6;<sup>18</sup> the regression coefficient is  $r^2 = 0.993$ . The deviations of the experimental values of  $J_{\text{FF}}$  from the values calculated by eq 6 are given in Table 4; the mean deviation is  $\pm 1.2$  Hz.

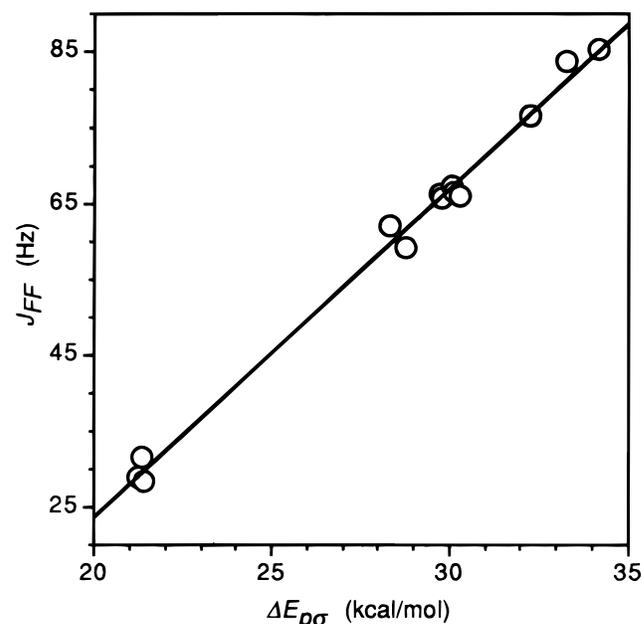
(18) Because of the inherent limitations of the model we used to calculate the values of  $\Delta E_{\text{p}\sigma}$ , we attach no special significance to the numerical values of the slope and intercept given in eq 6. In particular, the interacting in-plane fluorine lone-pair orbitals on the two HF molecules in our model (see Figure 4) are pure 2p atomic orbitals, whereas in molecules of types 1 and 3 the corresponding interacting in-plane fluorine lone-pair orbitals are extensively mixed with various in-plane molecular orbitals associated with the carbon framework.

**Table 4.** Values of  $J_{\text{FF}}$  and  $\Delta E_{\text{p}\sigma}$  for 13 Compounds of Types 1 and 3 and the Deviations of  $J_{\text{FF}}$  from the Values Calculated by Eq 6

compd	peri groups X and Y	$\Delta E_{\text{p}\sigma}$ (kcal/mol) <sup>a</sup>	$J_{\text{FF}}$ (Hz) <sup>b</sup>	dev from eq 6 (Hz)
3e	-CHPh-CHPh-	21.238	28.8	-0.2
3a	-CO-CO-	21.329	31.5	+2.2
3b	-CH <sub>2</sub> -CH <sub>2</sub> -	21.375	28.4	-1.1
1b	-CO-O-CO-	28.314	61.9	+2.3
1d	H, H	28.743	59.0	-2.4
1e	H, CN	29.747	66.1	+0.3
1f	H, CH <sub>3</sub>	29.810	65.6	-0.4
1g	H, Br	30.067	67.4	+0.3
1h	H, Cl	30.132	66.5	-0.9
1i	H, NHCOC <sub>3</sub>	30.262	65.9	-2.1
1j	H, NO <sub>2</sub>	32.274	76.4	-0.3
1a	CN, CN	33.258	83.5	+2.6
1c	CH <sub>3</sub> , CH <sub>3</sub>	34.199	85.2	+0.2

<sup>a</sup> Calculated from eq 3 using the values of  $d_{\text{FF}}$  given in Table 1.

<sup>b</sup> Taken from Table 1.

**Figure 6.** The observed values of  $J_{\text{FF}}$  for the 13 compounds listed in Table 4 (1a-j and 3a,b,e) plotted against the values of  $\Delta E_{\text{p}\sigma}$  calculated on the basis of eq 3 using the FF distances listed in Table 1 for each of these 13 compounds.

$$J_{\text{FF}} = 4.325\Delta E_{\text{p}\sigma} - 62.9 \quad (6)$$

The fact that the plot in Figure 6 is linear with a high regression coefficient provides further support for our theory that through-space FF coupling arises from pσ overlap interactions of the in-plane p<sub>F</sub> lone pairs on the coupled fluorines.

## Experimental Section

**General.** Melting points were measured with a Thomas-Hoover oil-bath apparatus and are uncorrected. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.  $^1\text{H}$  NMR spectra were measured at 300.1 MHz, proton-decoupled  $^{19}\text{F}$  NMR spectra were measured at 282.4 MHz, and proton-decoupled  $^{13}\text{C}$  NMR spectra were measured at 75.5 MHz with an IBM AF-NR300 spectrometer. Unless specified otherwise, NMR spectra were obtained in  $\text{CDCl}_3$  solution.  $^{19}\text{F}$  chemical shifts are reported in ppm downfield from 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane as an internal standard. Low-resolution mass spectra were determined with a Hewlett-Packard 5890/5970 GC/MSD system. Sublimations under reduced pressure were carried out as described previously.<sup>19</sup>

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**5,6-Difluoro-1,2-acenaphthenequinone (3a).** A previously reported procedure<sup>20</sup> was used to carry out the reaction of 77.1 g (0.50 mol) of acenaphthene with 222.5 g (1.25 mol) of *N*-bromosuccinimide in 500 mL of DMF at 30–32 °C to give, after two recrystallizations of the crude product from hexane, 35.9 g (23%) of 5,6-dibromoacenaphthene: mp 168–171 °C (lit.<sup>20</sup> mp 174–176 °C); MS *m/z* (rel intensity) 314 (31), 312 (64), 310 (32), 152 (100).

A solution of 3.2 g (9.9 mmol) of 5,6-dibromoacenaphthene and 17.5 g (58 mmol) of Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in 175 mL of acetic acid was stirred at 80 °C in a water bath for 2 h, diluted with 500 mL of water, and filtered.<sup>21</sup> The precipitate was treated with 30 mL of boiling aqueous 6% Na<sub>2</sub>CO<sub>3</sub> to give crude 5,6-dibromoacenaphthenequinone. This material was dissolved in 500 mL of chlorobenzene at about 55 °C, and 20 mL of aqueous 40% NaHSO<sub>3</sub> was added. The mixture was stirred for 1 h, and then the bisulfite addition compound of the quinone was collected by filtration, washed with two 50-mL portions of hot chlorobenzene, and treated with 25 mL of boiling dilute aqueous HCl. The resulting solid was recrystallized from chlorobenzene to give 1.4 g (41%) of 5,6-dibromoacenaphthenequinone as yellow crystals: mp 326–328 °C (lit.<sup>23</sup> mp 325–326 °C); <sup>1</sup>H NMR δ 8.25 (d, *J* = 7.5 Hz, 2 H), 7.92 (d, *J* = 7.5 Hz, 2 H); MS *m/z* (rel intensity) 342 (25), 340 (51), 338 (25), 314 (50), 312 (100), 310 (50).

A mixture of 5.0 g (15 mmol) of 5,6-dibromo-1,2-acenaphthenequinone, 15.2 g (100 mmol) of powdered CsF (previously dried in a vacuum oven at 150 °C for 3 days), and 49 mL of anhydrous DMSO was heated under nitrogen with an oil bath at 95 °C for 1 h with magnetic stirring. The purple reaction mixture was then cooled and poured onto ice. The resulting crude brown product (3.19 g) was washed with water, air-dried, and sublimed under reduced pressure at 150 °C to yield 2.16 g (68%) of light orange **3a**: mp 232.5–235 °C (lit.<sup>24</sup> mp 211–212 °C); <sup>1</sup>H NMR δ 8.17 (ddd, *J* = 8.1 Hz, Σ*J* = 2.3 + 1.9 = 4.2 Hz, 2 H), 7.52 (ddd, Σ*J* = 4.5 + 6.7 = 11.2 Hz, *J* = 7.9 Hz, 2 H); <sup>19</sup>F NMR δ 5.410; MS *m/z* (rel intensity) 218 (31), 190 (100). Anal. Calcd for C<sub>12</sub>H<sub>4</sub>F<sub>2</sub>O<sub>2</sub>: C, 66.06; H, 1.85. Found: C, 65.88; H, 1.76.

**5,6-Difluoroacenaphthene (3b).** A mixture of 5.81 g (89 mmol) of mossy zinc and a solution of 1.00 g of HgCl<sub>2</sub> and 1.2 mL of concentrated HCl in 18 mL of water was swirled for 5 min. The aqueous solution was decanted, and the amalgamated zinc was combined with solutions of 4.5 mL of concentrated HCl in 16.5 mL of water and 0.54 g (2.5 mmol) of 5,6-difluoroacenaphthenequinone (**3a**) in 18 mL of toluene. The resulting mixture was stirred and heated under reflux for 29 h, during which time seven 1-mL portions of concentrated HCl were added periodically. After extraction with diethyl ether and rotary evaporation of the dried extract, the residue was boiled in hexane and filtered. The filtrate was concentrated and passed through a silica gel column. Rotary evaporation of the eluate and sublimation of the residue under reduced pressure at 100 °C gave 0.15 g (32%) of yellow **3b**: mp 132.5–136 °C (lit.<sup>24</sup> mp 123–124 °C); <sup>1</sup>H NMR δ 7.15 (br d, *J* = 7.7 Hz, 2 H), 7.07 (ddd, Σ*J* = 7.3 + 4.4 = 11.7 Hz, *J* = 7.4 Hz, 2 H), 3.35 (s, 4 H); <sup>19</sup>F NMR (DMSO-*d*<sub>6</sub>) δ -11.17; MS *m/z* (rel intensity) 190 (72), 189 (100).

**5,6-Difluoroacenaphthylene (3c).** A mixture of 90 mg (0.5 mmol) of 5,6-difluoroacenaphthene (**3b**), 0.6 g of nickel peroxide hydrate, and 20 mL of benzene was stirred and heated under reflux for 29 h. The reaction mixture was then cooled to room temperature, diluted with 160 mL of benzene, and filtered through Celite with additional benzene washing. Rotary evaporation of the filtrate gave 50 mg (56%) of 5,6-difluoroacenaphthylene (**3c**). Subsequent recrystallization from methanol gave yellow needles: mp 117.5–122 °C; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 7.80 (ddd, *J* = 7.7 Hz, Σ*J* = 2.1 + 1.8 = 3.9 Hz, 2 H), 7.34 (ddd, Σ*J* = 7.1 + 4.8 = 11.9 Hz, *J* = 7.6 Hz, 2 H), 7.12 (s, 2 H); <sup>19</sup>F NMR (DMSO-

*d*<sub>6</sub>) δ -2.79; MS *m/z* (rel intensity) 188 (100). Anal. Calcd for C<sub>12</sub>H<sub>6</sub>F: C, 76.59; H, 3.22. Found: C, 76.40; H, 3.48.

**5,6-Difluoro-1,2-diphenylacenaphthylene (3d).** A suspension of 0.60 g (2.8 mmol) of 5,6-difluoro-1,2-acenaphthenequinone (**3a**) in 20 mL of benzene was added to 3.3 mL (9.9 mmol) of a 3 M solution of phenylmagnesium bromide in diethyl ether which had been diluted with an additional 3.5 mL of anhydrous diethyl ether. After this reaction mixture was stirred magnetically and heated under reflux for 27 h, it was added to 40 mL of a 9:1 mixture of water and acetic acid, and the layers were separated. The aqueous layer was washed with 55 mL of benzene in three portions. The organic layers were combined, washed with saturated aqueous NaHCO<sub>3</sub>, dried over MgSO<sub>4</sub>, and filtered. The filtrate was rotary evaporated and the residue was recrystallized from 95% ethanol to give 1.1 g (58%) of yellow 5,6-difluoro-1,2-diphenylacenaphthene-1,2-diol: mp 199.5–201 °C; MS *m/z* (rel intensity) 374 (14), 267 (100).

A mixture of 0.50 g (1.3 mmol) of this diol and 30 mL of 47% aqueous HI was stirred and heated under reflux for 1 h. Then 10 mL of acetic acid was added and the mixture was stirred and heated for an additional 1 h. The reaction mixture was added to 30 mL of aqueous NaHSO<sub>3</sub> solution and the resulting precipitate was collected, air-dried, and recrystallized from acetone to give 0.36 g (79%) of **3d** as orange needles: mp 179.5–181 °C; <sup>1</sup>H NMR δ 7.65 (ddd, *J* = 7.8 Hz, Σ*J* = 2.0 + 1.8 = 3.8 Hz, 2 H), 7.40–7.31 (m, 10 H), 7.20 (ddd, Σ*J* = 6.6 + 4.7 = 11.3 Hz, *J* = 7.7 Hz, 2 H); <sup>19</sup>F NMR δ -1.38; MS *m/z* (rel intensity) 340 (100). Anal. Calcd for C<sub>24</sub>H<sub>14</sub>F<sub>2</sub>: C, 84.68; H, 4.15. Found: C, 84.73; H, 4.26.

**5,6-Difluoro-1,2-diphenylacenaphthene (3e).**<sup>25</sup> A sample of 100 mg (0.29 mmol) of 5,6-difluoro-1,2-diphenylacenaphthylene (**3d**) was dissolved in 60 mL of cyclohexane by stirring magnetically under argon. Then 100 mg of 10% Pd/C catalyst was added to the orange solution, and hydrogen was bubbled through the reaction mixture for 20 h. The reaction mixture was filtered and the catalyst residue was washed with CH<sub>2</sub>Cl<sub>2</sub>. The combined filtrate was put through a small pad of silica gel to remove the remaining catalyst. The filtrate was rotary evaporated and the residue was recrystallized from hexane to give 48 mg (48%) of **3e** as white crystals: mp 151–152 °C; <sup>1</sup>H NMR δ 7.21 (ddd, Σ*J* = 7.1 + 4.4 = 11.5 Hz, *J* = 7.7 Hz, 2 H), 7.11 (br dt, *J* = 7.9 Hz, Σ*J* = 2.0 + 2.0 = 4.0 Hz, 2 H), 7.00–6.94 (m, 6 H), 6.71–6.68 (m, 4 H), 5.27 (s, 2 H); <sup>19</sup>F NMR δ -8.72; MS *m/z* (rel intensity) 342 (75), 264 (100). Anal. Calcd for C<sub>24</sub>H<sub>16</sub>F<sub>2</sub>: C, 84.19; H, 4.72. Found: C, 84.03; H, 4.86.

**5,6-Difluoro-1,2-acenaphthenequinone Dioxime (3f).** To a mixture of 2.0 g (9.2 mmol) of 5,6-difluoroacenaphthenequinone (**3a**) and 180 mL of boiling 95% ethanol was added 3.2 g (4.6 mmol) of NH<sub>2</sub>OH·HCl dissolved in the minimum amount of water. The resulting mixture was stirred magnetically and heated under reflux for 1 h. The residue after rotary evaporation was washed with water and recrystallized from 95% ethanol to give 1.57 g (68%) of off-white **3f**: mp 240–242 °C; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 11.78 (s, 2 H), 8.51 (ddd, *J* = 8.0 Hz, Σ*J* = 2.2 + 2.0 = 4.2 Hz, 2 H), 7.50 (ddd, Σ*J* = 7.4 + 4.3 = 11.7 Hz, *J* = 7.8 Hz, 2 H); <sup>19</sup>F NMR (DMSO-*d*<sub>6</sub>) δ 12.63; MS *m/z* (rel intensity) 214 (100, M - 34). Anal. Calcd for C<sub>12</sub>H<sub>6</sub>F<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 58.07; H, 2.44. Found: C, 58.22; H, 2.56.

**5,6-Difluoroacenaphtho-1,2-furazan Oxide (3g).** A mixture of 0.50 g (2.0 mmol) of 5,6-difluoroacenaphthenequinone dioxime (**3f**) and 0.17 g (4.3 mmol) of NaOH was dissolved with heating in a mixture of 75 mL of water and 20 mL of 95% ethanol. The resulting orange-red solution was cooled in an ice bath and stirred magnetically while 13 mL (8.5 mmol) of 5% aqueous sodium hypochlorite (commercial Clorox) was added dropwise. The mixture was warmed to room temperature and the tan product was collected by vacuum filtration, washed with water, air-dried, and recrystallized from ethyl acetate to give 0.44 g (89%) of **3g**: mp 179.5–181 °C; <sup>1</sup>H NMR δ 8.14 (dd, *J* = 7.9, 3.7 Hz, 1 H), 7.94 (dd, *J* = 7.9, 3.7 Hz, 1 H), 7.45 (dd, *J* = 11.2, 7.9 Hz, 1 H), 7.39 (dd, *J* = 11.2, 7.9 Hz, 1 H); <sup>19</sup>F NMR (DMSO-*d*<sub>6</sub>) δ 17.41. Anal. Calcd for C<sub>12</sub>H<sub>4</sub>F<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 58.54; H, 1.64. Found: C, 58.39; H, 1.86.

(25) We are grateful to Dr. C. Daniel Yang for help in the preparation of this compound.

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**5,6-Difluoroacenaphtho-1,2-*b*-quinoxaline (3h).** A solution of 0.10 g (0.9 mmol) of *o*-phenylenediamine in 17 mL of 95% ethanol was added to a solution of 0.20 g (0.9 mmol) of 5,6-difluoroacenaphthenequinone (**3a**) in 34 mL of acetic acid. The resulting mixture was heated in a bath of boiling water for 20 min and then was poured over ice. Filtration gave 0.13 g (50%) of yellow **3h**: mp 273–274.5 °C;  $^1\text{H}$  NMR  $\delta$  8.37 (br d,  $J = 7.8$  Hz, 2 H), 8.17 (dd,  $\sum J = 6.2 + 3.5 = 9.7$  Hz, 2 H), 7.77 (dd,  $\sum J = 6.3 + 3.4 = 9.7$  Hz, 2 H), 7.47 (dd,  $J = 11.5, 7.3$  Hz);  $^{19}\text{F}$  NMR  $\delta$  3.68; MS  $m/z$  (rel intensity) 290 (100). Anal. Calcd for  $\text{C}_{18}\text{H}_8\text{F}_2\text{N}_2$ : C, 74.47; H, 2.78. Found: C, 74.51; H, 2.81.

**4,5-Dicyano-1,8-difluoronaphthalene (1a).** A mixture of 200 mg (0.81 mmol) of 5,6-difluoroacenaphtho-1,2-furazan oxide (**3g**), 430 mg (1.64 mmol) of triphenylphosphine, and 26 mL of benzene was stirred magnetically and heated under reflux for 48 h. The reaction mixture was concentrated by rotary evaporation and then filtered to give 330 mg of crude brown product. This material was sublimed under reduced pressure at about 110 °C to give 0.13 g of cream-colored sublimate. The sublimate was dissolved in the minimum amount of hot 95% ethanol and then enough water was added to make the composition 40% water. This solution was cooled in a freezer and the resulting crystals were collected to give 400 mg (24%) of **1a**: mp 247.5–249 °C;  $^1\text{H}$  NMR  $\delta$  8.20 (ddd,  $J = 8.3$  Hz,  $\sum J = 2.5 + 2.4 = 4.9$  Hz, 2 H), 7.42 (ddd,  $\sum J = 5.2 + 5.1 = 10.3$  Hz,  $J = 8.3$  Hz, 2 H);  $^{19}\text{F}$  NMR (DMSO- $d_6$ )  $\delta$  10.71; MS  $m/z$  (rel intensity) 214 (100). Anal. Calcd for  $\text{C}_{12}\text{H}_4\text{N}_2\text{F}_2$ : C, 67.29; H, 1.89. Found: C, 67.08; H, 2.02.

**4,5-Difluoro-1,8-naphthalic Anhydride (1b).** A magnetically stirred mixture of 0.40 g (1.9 mmol) of 5,6-difluoroacenaphthenequinone (**3a**), 1.42 g (5.4 mmol) of  $\text{Na}_2\text{Cr}_2\text{O}_7$ , and 31 mL of acetic acid was heated in an oil bath at 80 °C for 12 h. Then the reaction mixture was cooled to room temperature and diluted with 150 mL of water. The crude product was collected by filtration, air-dried, and recrystallized from a mixture of toluene and hexane to give 0.17 g (39%) of **1b** as yellow needles: mp 216–217.5 °C;  $^1\text{H}$  NMR  $\delta$  8.69 (ddd,  $J = 8.3$  Hz,  $\sum J = 2.5 + 2.3 = 4.8$  Hz, 2 H), 7.53 (ddd,  $J = 8.4$  Hz,  $\sum J = 5.5 + 4.9 = 10.4$  Hz, 2 H);  $^{19}\text{F}$  NMR (DMSO- $d_6$ )  $\delta$  10.04; MS  $m/z$  (rel intensity) 234 (92), 190 (100). Anal. Calcd for  $\text{C}_{12}\text{H}_4\text{F}_2\text{O}_3$ : C, 61.55; H, 1.73. Found: C, 61.74; H, 1.93.

**3-(2'-Fluoro-5'-methylbenzoyl)propionic Acid (4).** A magnetically stirred mixture of 30 g (0.30 mol) of succinic anhydride, 80 g (0.60 mol) of  $\text{AlCl}_3$ , and 150 mL of 1,1,2,2-tetrachloroethane was maintained at 25–28 °C during the dropwise addition over 45 min of 33 g (0.30 mol) of *p*-fluorotoluene. The resulting dark red mixture was stirred for an additional 4 h, and then was poured into a mixture of 40 mL of concentrated HCl, 35 g of ice, and 100 mL of water. Extraction with  $\text{CH}_2\text{Cl}_2$  followed by recrystallization from toluene gave 45.5 g (72%) of **4** as white crystals: mp 111–112.5 °C;  $^1\text{H}$  NMR  $\delta$  7.68 (dd,  $J = 6.9, 2.2$  Hz, 1 H), 7.31 (ddd,  $J = 8.0, 5.0, 2.5$  Hz, 1 H), 7.02 (dd,  $J = 11.0, 8.4$  Hz, 1 H), 3.29 (dd,  $J = 6.4, 3.3$  Hz, 2H), 2.34 (s, 3 H);  $^{19}\text{F}$  NMR  $\delta$  –0.69;  $^{13}\text{C}$  NMR  $\delta$  196.2 (d,  $J = 4.2$  Hz), 179.1 (s), 160.5 (d,  $J = 252.5$  Hz), 135.4 (d,  $J = 8.9$  Hz), 134.0 (d,  $J = 3.3$  Hz), 130.6 (d,  $J = 2.1$  Hz), 124.3 (d,  $J = 13.1$  Hz), 116.4 (d,  $J = 24.0$  Hz), 37.9 (d,  $J = 8.9$  Hz), 28.1 (d,  $J = 1.9$  Hz), 20.4 (s); MS  $m/z$  (rel intensity) 210 (9), 137 (100). Anal. Calcd for  $\text{C}_{11}\text{H}_{11}\text{FO}_3$ : C, 62.85; H, 5.27. Found: C, 62.66; H, 5.26.

**5-Fluoro-8-methyl-1-tetralone (5).** Standard Wolff–Kishner methodology was used, starting with 81.5 g (0.39 mol) of 3-(2'-fluoro-5'-methylbenzoyl)propionic acid (**4**), 77.2 g (1.17 mol) of 85% KOH pellets, 55.8 mL of aqueous 85% hydrazine hydrate, and 558 mL of diethylene glycol, to produce a crude sample of 4-(2'-fluoro-5'-methyl)butyric acid. A small portion was purified by distillation under reduced pressure followed by recrystallization from hexane to give 4-(2'-fluoro-5'-methyl)butyric acid as white crystals: mp 48.5–50 °C;  $^1\text{H}$  NMR  $\delta$  11.81 (br s, 1 H), 6.97–6.84 (m, 3 H), 2.65 (t,  $J = 7.5$  Hz, 2 H), 2.38 (t,  $J = 7.5$  Hz, 2 H), 2.27 (s, 3H), 1.94 (pentet,  $J = 7.5$  Hz, 2 H);  $^{19}\text{F}$  NMR  $\delta$  –10.86;  $^{13}\text{C}$  NMR  $\delta$  180.2 (s), 159.3 (d,  $J = 242.1$  Hz), 133.3 (d,  $J = 3.3$  Hz), 131.1 (d,  $J = 5.0$  Hz), 128.1 (d,  $J = 7.7$  Hz), 127.4 (d,  $J = 15.8$  Hz), 114.8 (d,  $J = 22.1$  Hz), 33.3 (s), 28.1 (d,  $J = 1.9$  Hz), 24.9 (s), 20.5 (s); MS  $m/z$  (rel intensity) 196 (38), 136 (100). Anal. Calcd for  $\text{C}_{11}\text{H}_{13}\text{FO}_2$ : C, 67.33; H, 6.68. Found: C, 67.37; H, 6.59.

The crude 4-(2'-fluoro-5'-methyl)butyric acid described in the preceding paragraph was heated in a 1000-mL beaker in a boiling water

bath. A 210-mL portion of polyphosphoric acid (PPA), previously heated to 90 °C, was added to the molten carboxylic acid, and the mixture was stirred vigorously by hand for 5 min. Then a second 210-mL portion of preheated PPA was added with vigorous manual stirring for an additional 5 min. After the reaction mixture was allowed to cool to 60 °C, 800 g of crushed ice was added with manual stirring. Then 100 mL of aqueous 5% NaOH was added, and the mixture was extracted with diethyl ether. The ether extract was washed with water and rotary evaporated. The solid residue was sublimed under reduced pressure and recrystallized from hexane to give 47.5 g (69% overall from **4**) of **5** as white crystals: mp 66.0–67.8 °C;  $^1\text{H}$  NMR  $\delta$  7.08–7.04 (m, 2 H), 2.93 (br t,  $J = 6.2$  Hz, 2 H), 2.64 (br t,  $J = 6.6$  Hz, 2 H), 2.59 (s, 3 H), 2.14–2.05 (m, 2 H);  $^{19}\text{F}$  NMR  $\delta$  –6.63;  $^{13}\text{C}$  NMR  $\delta$  199.1 (d,  $J = 3.2$  Hz), 158.1 (d,  $J = 242.8$  Hz), 136.6 (d,  $J = 3.4$  Hz), 132.0 (d,  $J = 3.2$  Hz), 131.8 (d,  $J = 16.5$  Hz), 130.5 (d,  $J = 7.5$  Hz), 118.5 (d,  $J = 21.9$  Hz), 40.6 (s), 22.6 (s), 22.5 (d,  $J = 5.3$  Hz), 22.1 (s); MS  $m/z$  (rel intensity) 178 (54), 150 (100). Anal. Calcd for  $\text{C}_{11}\text{H}_{11}\text{FO}$ : C, 74.14; H, 6.22. Found: C, 74.28; H, 6.24.

**1-Fluoro-4,5-dimethylnaphthalene (6).** A solution of 38.2 g (0.214 mol) of 5-fluoro-8-methyl-1-tetralone (**5**) in 350 mL of anhydrous diethyl ether was added slowly to 107 mL (0.322 mol) of a magnetically stirred 3 M ether solution of methylmagnesium bromide. The usual workup, followed by sublimation of the crude product under reduced pressure and recrystallization from hexane, gave 35.9 g (86%) of 5-fluoro-1,8-dimethyl-1-tetralol as white crystals: mp 99–100.5 °C;  $^1\text{H}$  NMR  $\delta$  6.89 (dd,  $J = 8.2$  Hz, 6.3 Hz, 1 H), 6.74 (br dd,  $\sum J = 17.4$  Hz, 1 H), 2.81–2.74 (m, 1 H), 2.62–2.56 (m, 1 H), 2.53 (s, 3 H), 2.12 (br s, 1 H), 1.95–1.70 (m, 4 H), 1.52 (s, 3H);  $^{19}\text{F}$  NMR  $\delta$  6.39;  $^{13}\text{C}$  NMR  $\delta$  158.7 (d,  $J = 241.1$  Hz), 142.1 (d,  $J = 3.0$  Hz), 132.6 (d,  $J = 3.3$  Hz), 130.5 (d,  $J = 7.9$  Hz), 124.3 (d,  $J = 16.3$  Hz), 112.6 (d,  $J = 21.8$  Hz), 72.2 (d,  $J = 3.0$  Hz), 42.4 (s), 27.6 (s), 23.1 (d,  $J = 5.5$  Hz), 21.5 (s), 19.6 (s); MS  $m/z$  (rel intensity) 194 (5), 176 (80), 161 (100). Anal. Calcd for  $\text{C}_{12}\text{H}_{15}\text{FO}$ : C, 74.20; H, 7.78. Found: C, 74.13; H, 7.65.

A magnetically stirred mixture of 4.85 g (25 mmol) of 5-fluoro-1,8-dimethyl-1-tetralol, 0.4 g of Pd/C, and 6.13 g (63 mmol) of maleic anhydride was heated under nitrogen for 10 h at 140 °C. The reaction mixture was extracted with hot hexane, and the hexane extract was filtered and rotary evaporated. The residue was sublimed under reduced pressure to give 2.98 g (69%) of **6** as white needles: mp 70.5–72.5 °C;  $^1\text{H}$  NMR  $\delta$  7.98 (d,  $J = 8.1$  Hz, 1 H), 7.35 (dd,  $J = 8.1, 7.1$  Hz, 1 H), 7.29 (br d,  $J = 6.8$  Hz), 7.13 (br dd,  $\sum J = 14.0$  Hz, 1 H), 6.96 (dd,  $J = 9.9, 7.9$  Hz, 1 H), 2.91 (s, 3 H), 2.86 (s, 3 H);  $^{19}\text{F}$  NMR  $\delta$  –10.74;  $^{13}\text{C}$  NMR  $\delta$  157.8 (d,  $J = 248.4$  Hz), 135.5 (d,  $J = 2.7$  Hz), 133.9 (d,  $J = 3.2$  Hz), 131.1 (d,  $J = 4.3$  Hz), 130.2 (s), 128.2 (d,  $J = 8.6$  Hz), 125.4 (s), 125.4 (d,  $J = 14.5$  Hz), 119.4 (d,  $J = 8.7$  Hz), 108.2 (d,  $J = 19.9$  Hz), 25.5 (s), 25.4 (s); MS  $m/z$  (rel intensity) 174 (100), 159 (84). Anal. Calcd for  $\text{C}_{12}\text{H}_{11}\text{F}$ : C, 82.72; H, 6.36. Found: C, 82.85; H, 6.38.

**1-Bromo-8-fluoro-4,5-dimethylnaphthalene (7).** A solution of 3.76 g (21.6 mmol) of 1-fluoro-4,5-dimethylnaphthalene (**6**) and 5.96 g (33.5 mmol) of *N*-bromosuccinimide in 26 mL of DMF was stirred magnetically and heated for 8 h at 65 °C under nitrogen in the dark. Then 70 mL of water was added and the mixture was extracted with hexane. The hexane extract was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtered through alumina and silica gel, and the filtrate was rotary evaporated. The residue was recrystallized from hexane to give 2.90 g (53%) of **7** as white crystals: mp 77.8–78.8 °C;  $^1\text{H}$  NMR  $\delta$  7.55 (d,  $J = 7.7$  Hz, 1 H), 7.10 (dd,  $J = 7.6, 5.7$  Hz, 1 H), 6.98 (dd,  $J = 12.6, 8.1$  Hz, 1 H), 6.96 (d,  $J = 7.7$  Hz, 1 H), 2.76 (s, 3 H), 2.75 (s, 3 H);  $^{19}\text{F}$  NMR  $\delta$  2.03;  $^{13}\text{C}$  NMR  $\delta$  157.1 ( $J = 255.0$  Hz), 136.2 (s), 135.3 (d,  $J = 3.3$  Hz), 132.5 (s), 131.7 (d,  $J = 4.5$  Hz), 130.4 (d,  $J = 1.6$  Hz), 129.5 (d,  $J = 8.7$  Hz), 123.3 (d,  $J = 7.8$  Hz), 113.1 (s), 111.2 (d,  $J = 23.0$  Hz), 26.1 (s), 25.8 (s); MS  $m/z$  (rel intensity) 254 (97), 252 (100). Anal. Calcd for  $\text{C}_{12}\text{H}_{10}\text{BrF}$ : C, 56.94; H, 3.98. Found: C, 57.04; H, 4.12.

**1,8-Difluoro-4,5-dimethylnaphthalene (1c).** A solution of 1.19 g (4.7 mmol) of 1-bromo-8-fluoro-4,5-dimethylnaphthalene (**7**) in 10 mL of anhydrous diethyl ether was stirred magnetically and maintained at 0 °C under nitrogen while 2.26 mL (5.7 mmol) of a 2.5 M solution of *n*-BuLi in hexane was added dropwise. After 30 min, the reaction mixture was cooled to –78 °C, and a solution of 1.78 g (5.7 mmol) of

*N*-fluorobenzenesulfonimide in 20 mL of anhydrous THF was added. The stirred reaction mixture was maintained at  $-78\text{ }^{\circ}\text{C}$  for 1 h, and then was allowed to warm to room temperature. After an additional 2 h the solution was poured into aqueous  $\text{NH}_4\text{Cl}$ . The resulting mixture was extracted with hexane, and the extract was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and then filtered through silica gel. The filtrate was rotary evaporated and the residue was recrystallized from hexane and then from 95% ethanol to give 0.62 g (69%) of **1c** as shiny plates: mp  $109.5\text{--}111.5\text{ }^{\circ}\text{C}$ ;  $^1\text{H NMR}$   $\delta$  7.16 (m, 2 H), 6.97 (ddd,  $\Sigma J = 5.9 + 5.9 = 11.8\text{ Hz}$ ,  $J = 8.0\text{ Hz}$ ), 2.83 (s, 6 H);  $^{19}\text{F NMR}$   $\delta$   $-4.39$ ;  $^{13}\text{C NMR}$   $\delta$  156.7 (dd,  $\Sigma J = 281.0 + 24.3 = 305.3\text{ Hz}$ ), 131.1 (t, 3.8 Hz), 129.7 (t,  $\Sigma J = 3.2 + 3.2 = 6.4\text{ Hz}$ ), 119.4 (d,  $J = 8.7\text{ Hz}$ ), 115.5 (t,  $J = 10.4\text{ Hz}$ ), 110.4 (dd,  $\Sigma J = 12.0 + 10.1 = 22.1\text{ Hz}$ ), 25.4 (s); MS  $m/z$  (rel intensity) 192 (100), 177 (97). Anal. Calcd for  $\text{C}_{12}\text{H}_{10}\text{F}_2$ : C, 74.99; H, 5.24. Found: C, 75.13; H, 5.26.

**5-Diphenylphosphino-6-fluoroacenaphthene (8)**. A solution of 5.00 g (21.5 mmol) of 5-bromoacenaphthene in 30 mL of anhydrous diethyl ether was magnetically stirred under argon at  $0\text{ }^{\circ}\text{C}$  while 16.1 mL (25.8 mmol) of a 1.6 M solution of *n*-BuLi in hexane was added dropwise over 5 min. After 1 h, the reaction mixture was cooled to  $-78\text{ }^{\circ}\text{C}$ , and a solution of 8.11 g (25.8 mmol) of *N*-fluorobenzenesulfonimide in 100 mL of dry THF under argon was added over 10 min. After an additional 1 h at  $-78\text{ }^{\circ}\text{C}$ , the reaction mixture was brought to room temperature and poured into saturated aqueous  $\text{NH}_4\text{Cl}$ . The usual workup, followed by chromatography on silica gel with hexane as eluent, rotary evaporation of the eluate, and recrystallization of the residue from hexane gave 2.88 g (78%) of 5-fluoroacenaphthene: mp  $91\text{--}93\text{ }^{\circ}\text{C}$  (lit.<sup>26</sup> mp  $93\text{--}94\text{ }^{\circ}\text{C}$ );  $^1\text{H NMR}$   $\delta$  7.71 (d,  $J = 8.2\text{ Hz}$ , 1 H), 7.46 (dd,  $J = 8.2, 7.0\text{ Hz}$ , 1 H), 7.28 (d,  $J = 7.1\text{ Hz}$ , 1 H), 7.12 (dd,  $J = 7.5, 4.3\text{ Hz}$ ), 7.06 (dd,  $J = 11.0, 7.6\text{ Hz}$ , 1 H), 3.43–3.29 (m, 4 H); MS  $m/z$  (rel intensity) 172 (88), 171 (100).

The reaction of 5.75 g (33.4 mmol) of 5-fluoroacenaphthene with 5.95 g (33.4 mmol) of *N*-bromosuccinimide in 100 mL of propylene carbonate at room temperature gave, after recrystallization of the crude product from 95% ethanol, 3.93 g (47%) of 5-bromo-6-fluoroacenaphthene as off-white crystals: mp  $103\text{--}105\text{ }^{\circ}\text{C}$  (lit.<sup>23</sup> mp  $105\text{--}106\text{ }^{\circ}\text{C}$ );  $^1\text{H NMR}$   $\delta$  7.65 (d,  $J = 7.4\text{ Hz}$ , 1 H), 7.18–7.09 (m, 3 H), 3.34 (s, 4 H); MS  $m/z$  (rel intensity) 252 (63), 250 (63), 171 (98), 170 (100).

A solution of 0.5 g (2 mmol) of 5-bromo-6-fluoroacenaphthene in 12 mL of dry THF was added dropwise to 1 mL (2 mmol) of a 2 M

solution of *n*-BuLi in pentane at  $-78\text{ }^{\circ}\text{C}$  under nitrogen. After 1 mL (5.5 mmol) of chlorodiphenylphosphine was added dropwise, the reaction mixture was allowed to warm to room temperature, and then was quenched by the addition of 0.5 mL of methanol. The solution was rotary evaporated, and the residue was dissolved in 1 mL of methanol. This solution was cooled in an ice bath, and the resulting precipitate was collected and recrystallized from methanol to give 0.47 g (66%) of **8** as colorless crystals: mp  $178\text{--}179\text{ }^{\circ}\text{C}$ ;  $^1\text{H NMR}$   $\delta$  7.35–7.29 (m, 10 H), 7.16 (dd,  $J = 7.6, 3.8\text{ Hz}$ , 1 H), 7.13 (d,  $J = 7.3\text{ Hz}$ , 1 H), 7.03 (dd,  $J = 12.7, 7.6\text{ Hz}$ , 1 H), 6.86 (dd,  $J = 7.2, 5.0\text{ Hz}$ , 1 H), 3.38 (m, 4 H);  $^{19}\text{F NMR}$   $\delta$  0.67; MS  $m/z$  (rel intensity) 356 (M, 100). Anal. Calcd for  $\text{C}_{24}\text{H}_{18}\text{FP}$ : C, 80.88; H 5.10. Found: C 81.06; H, 5.14.

**5-Diphenylphosphino-6-fluoroacenaphthylene (9)**. A mixture of 0.50 g (2.0 mmol) of 5-bromo-6-fluoroacenaphthene, 5.18 g of nickel peroxide hydrate, and 20 mL of benzene was heated under reflux for 15 h. Filtration of the reaction mixture through Celite in a sintered glass funnel, rotary evaporation of the filtrate, and recrystallization of the residue from methanol gave 0.14 g (28%) of 5-bromo-6-fluoroacenaphthylene as yellow needles: mp  $95\text{--}96\text{ }^{\circ}\text{C}$ ;  $^1\text{H NMR}$   $\delta$  7.77 (d,  $J = 7.3\text{ Hz}$ , 1 H), 7.58 (dd,  $J = 7.5, 3.6\text{ Hz}$ , 1 H), 7.48 (d,  $J = 7.3\text{ Hz}$ , 1 H), 7.19 (dd,  $J = 12.5, 7.6\text{ Hz}$ , 1 H), 6.97 (br s, 2 H); MS  $m/z$  (rel intensity) 250 (100), 248 (100).

A solution of 0.13 g (0.5 mmol) of 5-bromo-6-fluoroacenaphthylene in 4 mL of dry THF was added dropwise to 0.5 mL (1 mmol) of a 2 M solution of *n*-BuLi in pentane at  $-78\text{ }^{\circ}\text{C}$  under nitrogen. After 0.3 mL (1.7 mmol) of chlorodiphenylphosphine was added dropwise, the reaction mixture was allowed to warm to room temperature, and then was quenched by the addition of 0.1 mL of methanol. The solution was rotary evaporated and the residue was dissolved in 0.5 mL of methanol. This solution was cooled in an ice bath, and the resulting precipitate was collected and recrystallized from methanol to give 0.09 g (49%) of **10**: mp  $168\text{--}174\text{ }^{\circ}\text{C}$ ;  $^1\text{H NMR}$   $\delta$  7.53 (dd,  $J = 7.5, 3.7\text{ Hz}$ , 1 H), 7.49 (d,  $J = 7.1\text{ Hz}$ , 1 H), 7.35–7.33 (m, 10 H), 7.04 (dd,  $J = 12.3, 7.6\text{ Hz}$ , 1 H), 7.01 and 6.98 (ABq,  $J = 5.3\text{ Hz}$ , 2 H), 6.96 (dd,  $J = 7.2, 4.5\text{ Hz}$ , 1 H);  $^{19}\text{F NMR}$   $\delta$  8.19; MS  $m/z$  (rel intensity) 354 (100). HRMS<sup>27</sup> calcd for  $\text{C}_{24}\text{H}_{16}\text{FP}$  354.0974, found 354.0963.

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