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Preparation of Perfluoroalkyl Azaarenes with a Perfluoroalkyllithium-Boron Trifluoride System

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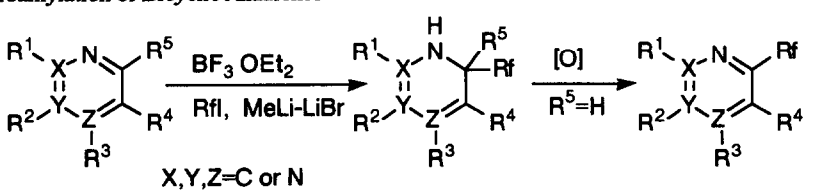
Key Words: perfluoroalkyllithium; Ziegler-Zeiser reaction; heterocycles; boron trifluoride; Reissert reaction

Abstract: *In the presence of boron trifluoride, perfluoroalkyllithiums generated in situ from the reaction of n-perfluoroalkyl iodides with methyllithium-lithium bromide smoothly added to a carbon-nitrogen double bond of bicyclic azaarenes and diazines to give the corresponding perfluoroalkylated dihydro heterocycles, which often underwent spontaneous aromatization in air. Perfluoroalkylation occurred preferentially at the carbon next to nitrogen in azaarenes even when the carbon atom was occupied by an alkyl substituent. Only one exception observed was the reaction of acridine where a perfluoroalkyl group was introduced at 9 position.*

Recently, much attention has been paid for perfluoroalkyl-containing heterocycles due to their unique properties. Preparation of these compounds was usually achieved through the construction of their heterocyclic moieties bearing the perfluoroalkyl group,[1] because the direct introduction of perfluoroalkyl group into a heterocyclic ring system[2] often suffered from low regioselectivity even in the case of the Ullmann-type coupling reaction of haloheterocycles with perfluoroalkylcoppers.[3] Nucleophilic addition of the hydrocarbon counterparts into electron-deficient azaarenes represented by the Ziegler-Zeiser reaction[4] is one of the most useful methods for the regiospecific introduction.[5] However, no perfluoroalkylmetallic reagents have so far been put to use for such purposes probably due to their poor nucleophilicity and low thermal stability. We have already shown that the problem could be solved by the use of boron trifluoride as an activator for azaarenes.[6] In this paper, we describe the detailed study about the extension of this methodology to the synthesis of a variety of aza-aromatic compounds.

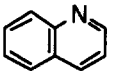
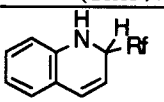
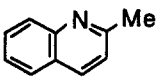
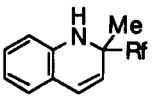
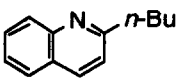
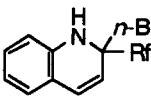
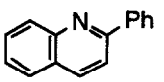
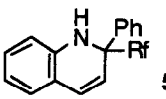
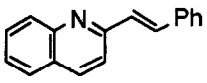
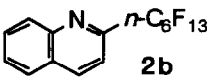
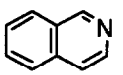
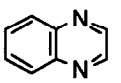
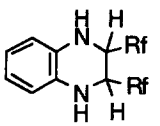
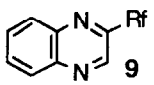
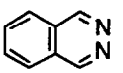
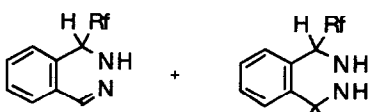
RESULTS AND DISCUSSIONS

Perfluoroalkylation of Bicyclic Azaarenes



(1)

Table 1. Boron Trifluoride-Assisted Perfluoroalkylation of Bicyclic Azaarenes

Entry	Azaarene	Perfluoroalkyl iodide RfI (equiv)[a]	Products (Yield[b]/%)
1		*n*-$C_8F_{17}I$ (2)	 **1a** (84)[c]
2		*n*-$C_6F_{13}I$ (2)	**1b** (90)[c]
3		*n*-C_4F_9I (2)	**1c** (99)[c]
4		C_2F_5I (2)	**1d** (93)[c]
5		*n*-$C_8F_{17}I$ (2)	 **3a** (70)
6		*n*-$C_6F_{13}I$ (2)	**3b** (72)
7		*n*-C_4F_9I (2)	**3c** (51)
8		C_2F_5I (2)	**3d** (72)
9		*n*-$C_6F_{13}I$ (2)	 **4** (96)
10		*n*-$C_6F_{13}I$ (2)	 **5** (trace)
11		*n*-$C_6F_{13}I$ (2)	No reaction
12	 **2b**	*n*-$C_6F_{13}I$ (4)	No reaction
13		*n*-$C_6F_{13}I$ (2)	 **6** (50) **7** (15)
14		*n*-$C_6F_{13}I$ (2)	 **8** (88)
15		*n*-$C_6F_{13}I$ (0.9)	 **9** (55) + **8** (11)
16		*n*-$C_6F_{13}I$ (2)	 **10** (71) **11** (16)
17		*n*-$C_6F_{13}I$ (0.9)	**10** (61)

[a] The same equiv each of BF_3·OEt_2, RfI, and MeLi-LiBr was used for azaarene. [b] Yields refer to the isolated compounds. [c] Accompanied by small amounts of 2-(perfluoroalkyl)quinoline **2**.

Nucleophilic attack on the ring carbon of azaarenes is greatly facilitated by forming the quaternary salts as seen in the Reissert and the related reactions.[5] Various kinds of nucleophiles can be introduced according to these methods. Thus, we first attempted the reaction of quinoline with perfluorohexyllithium in the presence of ethyl chloroformate. However, the reaction did not take place and quinoline was recovered intact. Next, boron trifluoride was employed as a promoter for the perfluoroalkylation of quinoline, although the activation of azaarenes using Lewis acid was not so common as in the case of imines.[7] When 1.2 equiv of perfluorohexyllithium was generated by adding an ethereal solution of methyllithium-lithium bromide (1.2 equiv) to an ethereal suspension of quinoline-boron trifluoride complex and perfluorohexyl iodide (1.2 equiv) at -78 °C, 2-perfluorohexyl-1,2-dihydroquinoline (**1b**) was obtained in 72% yield together with trace amounts of 2-(perfluorohexyl)quinoline (**2b**), the latter being formed by the autoxidation of **1b**. The perfluoroalkylation was improved up to 90% yield by using 2 equiv each of perfluorohexyl iodide, boron trifluoride, and methyllithium-lithium bromide. The autoxidation of dihydroquinoline **1b** was complete in chloroform after 2 days and **2b** was obtained quantitatively. Other Lewis acids such as aluminum chloride, ethylaluminum dichloride, zinc chloride, tin tetrachloride, and titanium tetrachloride were far less effective as an activator and almost no perfluoroalkylation products resulted from the reaction of quinoline with perfluorohexyllithium using these compounds as a promoter.

Perfluoroalkylation of other aza-aromatic compounds were carried out under the similar conditions and the results are summarized in Table 1. The most distinctive feature shown in the Table is high regioselectivity; perfluoroalkylation always occurred at the carbon next to the nitrogen, even in the case of 2-alkylquinolines. This class of compounds usually undergo either the proton abstraction from side chain upon treatment with strong organolithium reagents or do the conjugate addition in the case of stabilized carbanions.[5] For the successful perfluoroalkylation of 2-alkylquinolines, the generation rate of perfluoroalkyllithium was very important and slow generation of the lithium reagent (45-60 min for 2 mmol scale) led to good results; perfluorohexylation of 2-methylquinoline took place only in 40% yield, when methyllithium-lithium bromide was added within 10 min. This phenomenon may be closely related to the stability of perfluoroalkyllithium, which is known to be increased greatly in the presence of perfluoroalkyl iodide.[8]

The reaction of isoquinoline with perfluorohexyllithium proceeded smoothly to give 1-perfluorohexyl-1,2-dihydroisoquinoline. During chromatographic purification of the crude reaction products, autoxidation of the dihydroisoquinoline took place to afford 1-(perfluorohexyl)isoquinoline **6** and 4-hydroxy-1-perfluorohexylisoquinoline **7** in 50% and 15% yields, respectively.[9] Benzodiazines such as quinoxaline and phthalazine were more reactive toward perfluoroalkyllithium compared with quinolines. In the reaction of these compounds, introduction of one or two perfluorohexyl groups could be effected by changing the amounts of the lithium reagent generated. Thus, quinoxaline reacted with 2 equiv of perfluorohexyllithium in the presence of 2 equiv of boron trifluoride to afford tetrahydro derivative **8** in a good yield, while 2-(perfluorohexyl)quinoxaline **9** was the main product when 0.9 equiv each of perfluorohexyllithium and boron trifluoride was employed. In contrast, doubly perfluorohexylated compound **11** was still a minor component, even when phthalazine was reacted with 2 equiv of the reagents.

Perfluoroalkylation of Monocyclic Azaarenes

Difficulties were encountered in the perfluoroalkylation of pyridine derivatives. The reaction of pyridine with perfluorohexyllithium occurred sluggishly under the usual conditions to give 2-(perfluorohexyl)pyridine (**12**) in trace amounts. 2-Methyl- and 3,5-dimethylpyridines did not undergo the perfluoroalkylation. Next, the reaction of pyridine N-oxide with perfluorohexyllithium was carried out under the similar conditions (Eq. 2), since pyridine N-oxide is known to be more susceptible to nucleophilic attack than pyridine. However, the yield of **12** was poor. Attempted Reissert-type reaction of pyridine with perfluorohexyllithium using ethyl chloroformate gave a mixture of dihydropyridines **13** (24%) and **14** (17%).

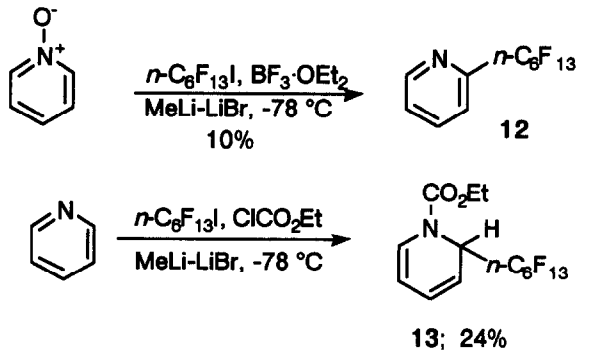
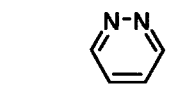
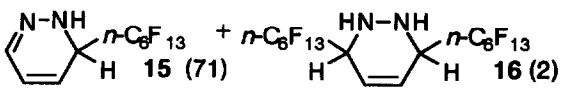
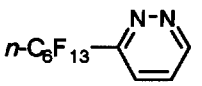
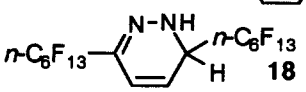
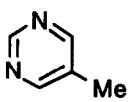
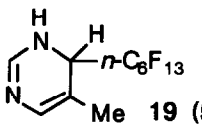
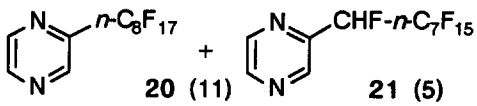


Table 2. Perfluoroalkylation of Diazines

Entry	Diazine	Products (Yield[a]/%)
18[b]		 15 (71) + 16 (2)
19[b]	 17	 18 (82)
20[b]		 19 (57)
21[c]		 20 (11) 21 (5)

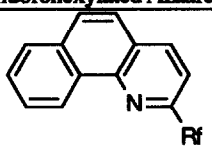
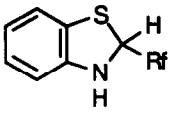
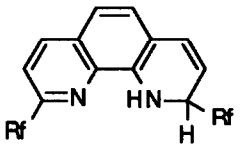
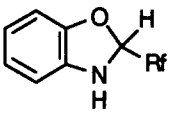
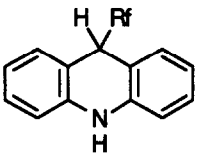
[a] Yields refer to the isolated compounds. [b] 1.2 equiv each of BF_3·OEt_2, *n*-$C_6F_{13}I$, and MeLi-LiBr was used. [c] 1.2 equiv each of BF_3·OEt_2, *n*-$C_8F_{17}I$, and MeLi-LiBr was used.

We have previously described the synthesis of (perfluoroalkyl)uracils based on the perfluoroalkylation of pyrimidines.[10] Other electron-deficient diazines similarly reacted with perfluorohexyllithium in the presence of boron trifluoride. The reaction of pyridazine gave a mixture of mono- and bis-perfluoroalkyl compounds **15** and **16** in 71% and 2% yields, respectively. The former product was subject to easy autoxidation to give pyridazine **17** in a quantitative yield. On the other hand, the reaction of pyrazine gave a complex mixture, from which 2-(perfluorohexyl)pyrazine **20** and **21** were isolated in 11% and 5% yields, respectively. The latter product was thought to be derived from vicarious nucleophilic substitution.[11] Susceptibility of these dihydroazines toward autoxidation is related to their resonance energies.[12]

Perfluoroalkylation of Other Azaarenes

Benzo[h]quinoline reacted with perfluorohexyllithium (2.4 equiv) to give dihydro derivative **22**, which was isolated as aromatized **23** in only 16% yield. Poor solubility of a 1,10-phenanthroline-boron trifluoride complex in ether made the perfluorohexylation quite difficult, leading to not a monoperfluorohexylated but bis-perfluorohexylated compound **24** in a low yield. In the reaction of acridine, perfluorohexylation occurred at 9 position to give **25**, although the yield was very poor.

Table 3. Other Perfluorohexylated Azaarenes

Perfluorohexylated Azaarene[a]		Yield[b]/%	Perfluorohexylated Azaarene[a]		Yield[b]/%
	23	16		26	6[c]
	24	5		27	24[c]
	25	6			

[a] Rf denotes n-C_6F_{13}. 2.4 equiv each of BF_3-OEt_2, n-$C_6F_{13}I$, and MeLi-LiBr were used. [b] Yield refers to the isolated compound. [c] Contaminated with the aromatized compound.

Finally, attempts to introduce a perfluoroalkyl group into 5-membered aza-heterocycles should be mentioned. The reaction of the heterocycles was carried out in the presence of boron trifluoride under the conditions described above. However, 1-methylimidazole, 3,5-dimethylisoxazole, benzothiazole, and benzoxazole all did not give promising results. The perfluorohexylation did not take place with the former two compounds, while the reaction of the latter two gave mixtures of addition and addition-dehydrogenation products in only 6% (26) and 13% (27) yields, respectively.

EXPERIMENTAL

Melting points were measured with a Yanagimoto micro-melting point apparatus and are uncorrected. Unless otherwise noted, all NMR spectra were observed with a GSX-270 spectrometer at ambient temperature by using $CDCl_3$ as solvent, tetramethylsilane as an internal standard for ^1H and ^{13}C, and $CFCl_3$ for ^{19}F. Mass spectra were measured with a Hitachi M80B-LCAPI spectrometer under the following ionizing conditions: EI (20 eV) and CI (70 eV, methane as CI gas). IR spectra were recorded on a Hitachi 270-30 spectrophotometer. Column chromatography was carried out using Wakogel C-200. Ether and THF were distilled from sodium benzophenone ketyl. Dichloromethane and toluene were distilled from calcium hydride and stored over 4Å molecular sieves. Perfluorobutyl and perfluorohexyl iodides were purified by washing with aqueous sodium hydrogensulfite followed by fractional distillation. Methyllithium-lithium bromide was prepared from lithium and methyl bromide in ether as usual. Organometallic reagents were titrated prior to use. Other commercially available materials were used without further purification. Distillation was performed with a Kugelrohr apparatus. Otherwise noted, recrystallization of perfluoroalkylated azaarenes was carried out using chloroform/hexane as solvent.

Perfluoroalkylation of Azaarenes with Perfluoroalkyl Iodide, Boron Trifluoride and Methyllithium-Lithium Bromide. A Typical Procedure for 2-Perfluorohexyl-1,2-dihydroquinoline (1b)

To a solution of quinoline (0.258 g, 2 mmol) and perfluorohexyl iodide (1.784 g, 4 mmol) in 20 ml of ether was added boron trifluoride etherate (0.52 ml, 4 mmol) at -78 °C. To the resulting suspension was added an ethereal solution of methyllithium-lithium bromide (4 mmol) over 15 min at -78 °C. The mixture was stirred

for 1 h at this temperature, then quenched with saturated aqueous ammonium chloride. The organic phase was separated and the aqueous phase was extracted twice with ether. The combined extracts were washed with brine, dried with anhydrous sodium sulfate, and evaporated to afford a pale yellow solid (1.051 g), which was recrystallized from hexane to give 0.561 g (61%) of **1b**. The mother liquor was concentrated and the residue was passed through a silica-gel column (hexane-dichloromethane) to give a mixture (0.248 g, 28%) of **1b** and **2b** (**1b**:**2b**=9:1, estimated by NMR). **1b**: colorless crystals, mp 64-65 °C; ^{1}H NMR δ=4.12 (1H, br s), 4.96 (1H, td, *J*=12.5, 4.9 Hz), 5.56 (1H, dd, *J*=9.8, 4.9 Hz), 6.50 (1H, d, *J*=7.9 Hz), 6.64-6.70 (2H, m), 6.93 (1H, dd, *J*=7.3, 1.2 Hz), 7.04 (1H, td, *J*=7.6, 1.5 Hz); ^{13}C NMR δ=54.35 (t, *J*=24 Hz), 105-125 (Rf), 112.76, 113.21 (m), 118.70, 118.98, 127.55, 129.70, 130.90, 141.74; ^{19}F NMR Φ=81.40 (3F, t, *J*=10 Hz), 121.92 (2F, m), 122.59 (2F, m), 123.12 (1F, dm, *J*=278 Hz), 123.30 (2F, m), 124.96 (1F, dm, *J*=278 Hz), 126.66 (2F, m); IR (KBr) 3460, 1644, 1610, 1496, 1300-1100 cm^{-1}; MS (EI) *m/z* 449 (M^+), 448, 430, 131, 130. Anal. Calcd for $C_{15}H_8F_{13}N$: C, 40.11; H, 1.80; N, 3.12. Found: C, 39.93; H, 1.84; N, 3.24%.

2-Perfluorooctyl-1,2-dihydroquinoline (1a). Colorless rods, mp 89 °C; ^{1}H NMR δ=3.98 (1H, br s), 4.95 (1H, td, J=12.2, 4.9 Hz), 5.55 (1H, dd, *J*=9.8, 4.9 Hz), 6.49 (1H, d, *J*=7.9 Hz), 6.64-6.70 (2H, m), 6.93 (1H, dd, *J*=7.4, 1.7 Hz), 7.03 (1H, td, *J*=7.9, 1.7 Hz); ^{13}C NMR δ=54.30 (t, *J*=24 Hz), 105-125 (Rf), 112.74, 113.24 (m), 118.71, 118.92, 127.53, 129.70, 130.90, 141.67; ^{19}F NMR Φ=81.29 (3F, tt, *J*=10, 2 Hz), 121.90 (2F, m), 122.40 (6F, m), 123.05 (1F, dm, *J*=277 Hz), 124.96 (1F, dm, *J*=277 Hz), 126.63 (2F, m); IR (KBr) 3456, 1644, 1608, 1494, 1300-1100 cm^{-1}; MS (CI) *m/z* 550 (M^++1), 530 78. Anal. Calcd for $C_{17}H_8F_{17}N$: C, 37.18; H, 1.47; N, 2.55. Found: C, 37.24; H, 1.42; N, 2.86%.

2-Perfluorobutyl-1,2-dihydroquinoline (1c). Colorless crystals, mp 33-35 °C; ^{1}H NMR δ=4.11 (1H, br s), 4.93 (1H, td, *J*=12.7, 4.9 Hz), 5.55 (1H, dd, *J*=9.9, 4.9 Hz), 6.48 (1H, d, *J*=7.9 Hz), 6.63-6.69 (2H, m), 6.92 (1H, dd, *J*=7.3, 1.4 Hz), 7.03 (1H, td, *J*=7.7, 1.4 Hz); ^{13}C NMR δ=54.21 (t, *J*=24 Hz), 105-125 (Rf), 112.74, 113.18 (m), 118.69, 118.91, 127.53, 129.69, 130.89, 141.67; ^{19}F NMR Φ=81.40 (3F, tt, *J*=10, 3 Hz), 122.95 (2F, m), 123.29 (1F, dm, *J*=284 Hz), 125.20 (1F, dm, *J*=284 Hz), 126.79 (2F, m); IR (KBr) 3424, 3052, 1646, 1608, 1494, 1300-1100 cm^{-1}; MS (CI) *m/z* 350 (M^++1), 349(M^+), 348, 330, 130. Anal. Calcd for $C_{13}H_8F_9N$: C, 44.71; H, 2.31; N, 4.01. Found: C, 44.43; H, 2.18; N, 4.01%.

2-Perfluoroethyl-1,2-dihydroquinoline (1d). Colorless oil, oven temp.112 °C/3 mmHg; ^{1}H NMR δ=4.05 (1H, br s), 4.84 (1H, td, *J*=12.0, 4.9 Hz), 5.50 (1H, dd, *J*=9.9, 4.9 Hz), 6.44 (1H, d, *J*=7.9 Hz), 6.58-6.67 (2H, m), 6.89 (1H, dd, *J*=7.5, 1.4 Hz), 7.00 (1H, td, *J*=7.9, 1.5 Hz); ^{13}C NMR δ=53.89 (t, *J*=24 Hz), 112.68, 112.69 (ddq, *J*=260, 257, 34 Hz), 113.09 (m), 118.58, 118.71, 119.23 (qt, *J*=287, 36 Hz), 127.51, 129.69, 130.65, 141.62; ^{19}F NMR Φ=81.26 (3F, s), 126.55 (1F, dd, *J*=270, 11 Hz), 128.22 (1F, dd, *J*=270, 13 Hz); IR (neat) 3432, 3040, 1646, 1606, 1490, 1300-1100 cm^{-1}; MS (CI) *m/z* 250 (M^++1), 249 (M^+), 230, 130. Anal. Calcd for $C_{11}H_8F_5N$: C, 53.02; H, 3.24; N, 5.62. Found: C, 52.84; H, 3.23; N, 5.64%.

2-(Perfluorooctyl)quinoline (2a). Colorless rods, mp 88-89 °C; ^{1}H NMR δ=7.68 (1H, td, *J*=8.2, 1.1 Hz), 7.74 (1H, d, *J*=8.5 Hz), 7.83 (1H, ddd, *J*=8.6, 6.7, 1.5 Hz), 7.91 (1H, d, *J*=8.2 Hz), 8.26 (1H, d, *J*=8.5 Hz), 8.35 (1H, d, *J*=8.5 Hz); ^{13}C NMR δ=105-125 (Rf), 118.27 (t, *J*=5 Hz), 127.64, 128.67, 128.73, 130.35, 130.73, 137.67, 147.40, 147.68 (t, *J*=25 Hz); ^{19}F NMR Φ=81.30 (3F, tt, *J*=10, 2 Hz), 113.89 (2F, tm, *J*=14 Hz), 121.64 (2F, m), 121.88 (2F, m), 122.34 (4F, m), 123.20 (2F, m), 126.61 (2F, m); IR (KBr) 3060, 1598, 1506, 1300-1100 cm^{-1}; MS (CI) *m/z* 576 (M^++Et), 549, 548 (M^++1), 547 (M^+), 528, 178, 128. Anal. Calcd for $C_{17}H_6F_{17}N$: C, 37.31; H, 1.11; N, 2.56. Found: C, 37.30; H, 1.12; N, 2.71%.

2-(Perfluorohexyl)quinoline (2b). Colorless crystals, mp 64-65 °C; ^{1}H NMR δ=7.65 (1H, t, *J*=7.6 Hz), 7.72 (1H, d, *J*=8.5 Hz), 7.81 (1H, m), 7.88 (1H, d, *J*=8.5 Hz), 8.25 (1H, d, *J*=8.5 Hz), 8.32 (1H, d, *J*=8.5 Hz); ^{13}C NMR δ=105-125 (Rf), 118.23 (t, *J*=4 Hz), 127.62, 128.68, 128.70, 130.31, 130.70, 137.65, 147.41, and 147.68 (t, *J*=25 Hz); ^{19}F NMR Φ=81.35 (3F, tt, *J*=10, 2 Hz), 113.83 (2F, tm, *J*=13 Hz), 121.87 (4F, m), 123.21 (2F, m), 126.63 (2F, m); IR (KBr) 3070, 1598, 1506, 1300-1100 cm^{-1}; MS (EI) *m/z* 447 (M^+), 178, 128. Anal. Calcd for $C_{15}H_6F_{13}N$: C, 40.29; H, 1.35; N, 3.13. Found: C, 39.91; H, 1.42; N, 3.31%.

2-(Perfluorobutyl)quinoline (2c). Colorless oil, oven temp. 158 °C/18 mmHg; ^{1}H NMR δ=7.61 (1H, t, *J*=7.3 Hz), 7.69 (1H, d, *J*=8.5 Hz), 7.77 (1H, ddd, *J*=8.3, 7.0, 1.5 Hz), 7.83 (1H, d, *J*=7.9 Hz), 8.22 (1H, d, *J*=8.5 Hz), 8.27 (1H, d, *J*=8.5 Hz); ^{13}C NMR δ=105-125 (Rf), 118.12 (m), 127.58, 128.65 (2C), 130.23, 130.64, 137.58, 147.39, 147.59 (t, *J*=25 Hz); ^{19}F NMR Φ=81.46 (3F, tt, *J*=10, 3 Hz), 113.83 (2F, tq, *J*=13, 3 Hz), 122.70 (2F, m), 125.90 (2F, m); IR (KBr) 3072, 1598, 1508, 1470, 1356, 1296, 1244-1134 cm^{-1}; MS (EI) *m/z* 348 (M^++1), 347 (M^+), 328, 178, 128. Anal. Calcd for $C_{13}H_6F_9N$: C, 44.97; H, 1.74; N, 4.03. Found: C, 44.71; H, 1.82; N, 4.12%.

2-(Perfluoroethyl)quinoline (2d). Colorless oil, oven temp. 146 °C/18 mmHg; ^{1}H NMR δ=7.55 (1H, t, *J*=7.3 Hz), 7.60-7.80 (3H, m), 8.17 (1H, d, *J*=8.6 Hz), 8.20 (1H, d, *J*=8.9 Hz); ^{13}C NMR δ=111.47 (tq, *J*=255, 38 Hz), 117.62 (m), 119.14 (qt, *J*=287, 38 Hz), 127.53, 128.55 (2C), 130.04, 130.58, 137.69, 147.25, 147.39 (t, *J*=25 Hz); ^{19}F NMR Φ=83.11 (3F, s) 116.67 (2F, s); IR (neat) 3076, 1598, 1508, 1300-1100 cm^{-1}; MS (CI) *m/z* 276 (M^++Et), 248 (M^++1), 247 (M^+), 228, 178, 128. Anal. Calcd for $C_{11}H_6F_5N$: C, 53.45; H, 2.45; N, 5.67. Found: C, 53.07; H, 2.48; N, 5.71%.

2-Methyl-2-perfluorooctyl-1,2-dihydroquinoline (3a). Colorless rods, mp 83-85 °C; ^{1}H NMR δ=1.59 (3H, s), 3.98 (1H, br s), 5.44 (1H, d, *J*=10.1 Hz), 6.44 (1H, d, *J*=7.9 Hz), 6.50 (1H, d, *J*=9.8 Hz), 6.64 (1H, td, *J*=7.3, 1.1 Hz), 6.91 (1H, dd, *J*=7.3, 1.5 Hz), 7.02 (1H, td, *J*=7.6, 1.5 Hz); ^{13}C NMR δ=25.41, 60.55 (t, *J*=24 Hz), 105-125 (Rf), 112.32, 118.16, 118.31, 119.48 (m), 127.29, 128.24, 129.64, 141.29; ^{19}F NMR Φ=81.30 (3F, tt, *J*=10, 2 Hz), 119.61 (2F, m), 122.26 (6F, m), 122.77 (1F, dm, *J*=282 Hz), 123.27 (2F, m), 123.46 (1F, dm, *J*=282 Hz), 126.65 (2F, m); IR (KBr) 3416, 1648, 1608, 1478, 1372, 1300-1100 cm^{-1}; MS (CI) *m/z* 564 (M^++1), 563 (M^+), 562, 544, 144. Anal. Calcd for $C_{18}H_{10}F_{17}N$: C, 38.38; H, 1.79; N, 2.49. Found: C, 38.16; H, 1.72; N, 2.80%.

2-Methyl-2-perfluorohexyl-1,2-dihydroquinoline (3b). Colorless needles, mp 53-62 °C; ^{1}H NMR δ=1.55 (3H, s), 3.93 (1H, br s), 5.41 (1H, d, *J*=10.1 Hz), 6.40 (1H, d, *J*=7.9 Hz), 6.48 (1H, d, *J*=10.1 Hz), 6.62 (1H, td, *J*=7.3, 0.9 Hz), 6.88 (1H, dd, *J*=7.3, 1.5 Hz), 6.99 (1H, td, *J*=7.6, 1.5 Hz); ^{13}C NMR δ=25.36, 60.54 (tt, *J*=23, 2 Hz), 105-125 (Rf), 112.33, 118.17, 118.31, 119.49 (m), 127.29, 128.25, 129.64, 141.29; ^{19}F NMR Φ=81.48 (3F, tt, *J*=10, 2 Hz), 119.53 (2F, m), 122.33 (2F, m), 122.70 (1F, dm, *J*=282 Hz), 123.15 (2F, m), 123.27 (1F, dm, J=282 Hz), 126.64 (2F, m); IR (KBr) 3412, 1648, 1606, 1478, 1464, 1366, 1300-1100 cm^{-1}; MS (EI) *m/z* 463 (M^+), 462, 448, 179, 145, 144, 143. Anal. Calcd for $C_{16}H_{10}F_{13}N$: C, 41.49; H, 2.18; N, 3.02. Found: C, 41.23; H, 2.21; N, 2.90%.

2-Methyl-2-perfluorobutyl-1,2-dihydroquinoline (3c). Colorless crystals, mp 35-36 °C; ^{1}H NMR δ=1.57 (3H, s), 3.94 (1H, br s), 5.42 (1H, d, *J*=10.2 Hz), 6.41 (1H, d, *J*=7.9 Hz), 6.48 (1H, d, *J*=10.2 Hz), 6.63 (1H, td, *J*=7.3, 0.9 Hz), 6.89 (1H, dd, *J*=7.3, 1.5 Hz), 7.00 (1H, td, *J*=7.6, 1.5 Hz); ^{13}C NMR δ=25.33 (m), 60.43 (tt, *J*=24, 2 Hz), 105-125 (Rf), 112.34, 118.17, 118.32, 119.44 (m), 127.30, 128.24, 129.65, 141.29; ^{19}F NMR Φ=81.35 (3F, tt, *J*=10, 3 Hz), 120.62 (2F, m), 122.91 (1F, dt, *J*=282, 15 Hz),

123.59 (1F, dt, *J*=282, 15 Hz), 126.56 (2F, m); IR (KBr) 3416, 3044, 2992, 1648, 1610, 1484, 1462, 1354, 1300-1100 cm^{-1}; MS (CI) *m/z* 364 (M^++1), 344, 144. Anal. Calcd for $C_{14}H_{10}F_9N$: C, 46.29; H, 2.77; N, 3.86. Found: C, 46.22; H, 2.71; N, 3.80%.

2-Methyl-2-perfluoroethyl-1,2-dihydroquinoline (3d). Colorless oil, bp 104 °C/0.25 mmHg; ^1H NMR δ=1.52 (3H, s), 3.88 (1H, br s), 5.38 (1H, d, *J*=9.8 Hz), 6.39 (1H, d, *J*=7.9 Hz), 6.46 (1H, d, *J*=9.8 Hz), 6.62 (1H, td, *J*=7.3, 0.9 Hz), 6.79 (1H, d, *J*=7.3 Hz), 6.99 (1H, td, *J*=7.6, 1.5 Hz); ^{13}C NMR δ=24.95 (m), 58.77 (t, *J*=23 Hz), 112.39, 113.92 (tq, *J*=262, 34 Hz), 118.06, 118.25, 119.26 (m), 119.61 (qt, *J*=288, 37 Hz), 127.28, 128.14, 129.64, 141.20; ^{19}F NMR Φ=78.55 (3F, s), 126.61 (1F, d, *J*=275 Hz), 127.91 (1F, d, *J*=275 Hz); IR (neat) 3412, 3044, 2992, 1648, 1608, 1482, 1462, 1342, 1300-1100 cm^{-1}; MS (CI) *m/z* 264 (M^++1), 263 (M^+), 244, 144. Anal. Calcd for $C_{12}H_{10}F_5N$: C, 54.76; H, 3.83; N, 5.32. Found: C, 54.59; H, 3.76; N, 5.12%.

2-Butyl-2-perfluorohexyl-1,2-dihydroquinoline (4). Colorless crystals, mp 26-27 °C; ^1H NMR δ=0.90 (3H, t, *J*=7.0 Hz), 1.30-1.78 (6H, m), 3.81 (1H, br s), 5.29 (1H, dd, *J*=9.5 Hz), 6.41 (1H, d, *J*=7.9 Hz), 6.56 (1H, d, *J*=9.5 Hz), 6.60 (1H, td, *J*=7.3, 0.9 Hz), 6.88 (1H, d, *J*=7.6 Hz), 7.00 (1H, td, *J*=7.9, 0.9 Hz); ^{13}C NMR δ=13.95, 22.84, 25.84, 36.14, 64.33 (t, *J*=22 Hz), 105-125 (Rf), 111.91, 117.80, 117.85 (m), 117.89, 127.39, 129.64, 129.69 (m), 142.02; ^{19}F NMR Φ=81.40 (3F, tt, *J*=10, 3 Hz), 119.82 (2F, m), 112.36 (2F, m), 112.63 (1F, dm, *J*=290 Hz), 123.20 (2F, m), 123.99 (1F, dm, *J*=290 Hz), 126.66 (2F, m); IR (KBr) 3412, 3032, 2964, 2936, 1648, 1610, 1486, 1300-1100 cm^{-1}; MS (CI) *m/z* 506 (M^++1), 486, 448, 186. Anal. Calcd for $C_{19}H_{16}F_{13}N$: C, 45.16; H, 3.19; N, 2.77. Found: C, 45.12; H, 3.12; N, 2.87%.

2-Perfluorohexyl-2-phenyl-1,2-dihydroquinoline (5). Colorless crystals, mp 60-62 °C; ^1H NMR δ=4.61 (1H, br s), 5.98 (1H, d, *J*=9.8 Hz), 6.57 (1H, d, *J*=9.8 Hz), 6.65 (2H, m), 6.91 (1H, dd, *J*=7.6, 1.2 Hz), 7.07 (1H, td, *J*=7.6, 1.5 Hz), 7.30-7.40 (3H, m), 7.51 (2H, m); ^{13}C NMR δ=65.00 (dd, *J*=25, 23 Hz), 105-125 (Rf), 112.98, 118.23, 118.78, 118.95 (m), 126.16 (t, *J*=3 Hz), 127.32, 127.45, 128.26, 128.62, 129.81, 140.39, 140.54; ^{19}F NMR Φ=81.31 (3F, tt, *J*=10, 3 Hz), 116.60 (1F, dm, *J*=283 Hz), 117.15 (1F, dm, *J*=298 Hz), 117.61 (1F, dm, *J*=283 Hz), 118.71 (1F, dm, *J*=298 Hz), 122.32 (2F, m), 123.14 (2F, m), 126.62 (2F, m); IR (KBr) 3060, 1478, 1386, 1300-1100 cm^{-1}; MS (CI) *m/z* 526 (M^++1), 506, 448, 206.

1-(Perfluorohexyl)isoquinoline (6). Colorless rods, mp 38-40 °C.[9, 13]

1-Perfluorohexyl-4-isoquinolinol (7). Colorless rods (chloroform), mp 148-160 °C.[9]

2,3-Bis(perfluorohexyl)-1,2,3,4-tetrahydroquinoxaline (8). Colorless needles, mp 98-99 °C; ^1H NMR δ=4.13 (2H, m), 4.46 (2H, ddm, *J*=18.3, 7.0 Hz), 6.63 (2H, m), 6.73 (2H, m); ^{13}C NMR δ=47.83 (t, *J*=24 Hz), 105-125 (Rf), 114.84, 120.17, and 128.36; ^{19}F NMR Φ=81.29 (6F, tt, *J*=10, 2 Hz), 117.65 (2F, dm, *J*=281 Hz), 121.59 (4F, m), 122.31 (2F, dm, *J*=281 Hz), 122.40 (4F, m), 123.25 (4F, m), 126.63 (4F, m); IR (KBr) 3444, 1612, 1520, 1366, 1300-1100 cm^{-1}; MS (CI) *m/z* 771 (M^++1), 770 (M^+), 751, 451, 131. Anal. Calcd for $C_{20}H_8F_{26}N_2$: C, 31.18; H, 1.05; N, 3.09. Found: C, 30.90; H, 1.11; N, 4.15%.

2-(Perfluorohexyl)quinoxaline (9). Colorless needles, mp 54-55 °C; ^1H NMR δ=7.93 (2H, m), 8.25 (2H, m), 9.17 (1H, s); ^{13}C NMR δ=105-125 (Rf), 129.52, 130.25, 131.54, 132.57, 141.19, 141.98 (t, *J*=4 Hz), 142.71 (t, *J*=26 Hz), 143.49 (m); ^{19}F NMR Φ=81.25 (3F, tt, *J*=10, 3 Hz), 114.36 (2F, tm, *J*=13 Hz), 121.89 (4F, m), 123.23 (2F, m), 126.62 (2F, m); IR (KBr) 3056, 3016, 1498, 1368, 1300-1100 cm^{-1}; MS (CI) *m/z* 447 (M^++Et), 449 (M^++1), 448 (M^+), 429, 179, 129. Anal. Calcd for $C_{14}H_5F_{13}N_2$: C, 37.52; H, 1.22; N, 6.25. Found: C, 37.26; H, 1.13; N, 6.45%.

1-Perfluorohexyl-1,2-dihydrophthalazine (10). Colorless crystals, mp 105-106 °C; ^{1}H NMR δ=5.03 (1H, dd, *J*=16.2, 11.8 Hz), 6.42 (1H, br s), 7.20-7.30 (2H, m), 7.40-7.50 (3H, m); ^{13}C NMR δ=53.86 (t, *J*=23 Hz), 105-125 (Rf), 122.38, 125.16, 126.29, 128.30, 129.94, 130.42, 138.08; ^{19}F NMR Φ=81.32 (3F, tt, *J*=10, 2 Hz), 118.31 (1F, dm, *J*=282 Hz), 121.06 (1F, dm, *J*=282 Hz), 121.08 (2F, m), 122.40 (2F, m), 123.29 (2F, m), 126.63 (2F, m); IR (KBr) 3268, 1450, 1364, 1300-1100 cm^{-1}; MS (CI) *m/z* 479 (M^++Et), 451 (M^++1), 130. Anal. Calcd for $C_{14}H_7F_{13}N_2$: C, 37.35; H, 1.57; N, 6.22. Found: C, 37.02; H, 1.67; N, 6.40%.

1,4-Bis(perfluorohexyl)-1,2,3,4-tetrahydrophthalazine (11). Colorless crystals, mp 103-104 °C; ^{1}H NMR δ=3.80 (2H, br s), 4.45 (2H, ddd, *J*=26.3, 5.0, 2.0 Hz), 7.41 (4H, m); ^{13}C NMR δ=52.83 (dd, *J*=24, 20 Hz), 105-125 (Rf), 127.12, 128.67 (d, *J*=1 Hz), 129.28 (d, *J*=7 Hz); ^{19}F NMR Φ=81.28 (6F, tt, *J*=10, 2 Hz), 107.98 (2F, dm, *J*=292 Hz), 118.34 (2F, dm, *J*=292 Hz), 120.19 (2F, dm, *J*=300 Hz), 121.76 (4F, m), 122.50 (2F, dm, *J*=*ca.* 303 Hz), 123.15 (2F, dm, *J*=300 Hz), 123.85 (2F, dm, *J*=*ca.* 303 Hz), 125.81 (2F, dm, *J*=294 Hz), 127.39 (2F, dm, *J*=294 Hz); IR (KBr) 3388, 1498, 1366, 1300-1100 cm^{-1}; MS (CI) *m/z* 799 (M^++Et), 772 (M^+), 771, 451. Anal. Calcd for $C_{20}H_8F_{26}N_2$: C, 31.19; H, 1.05; N, 3.64. Found: C, 30.92; H, 1.07; N, 4.01%.

2-(Perfluorohexyl)pyridine (12).[2c] Colorless oil, oven temp. 90 °C/30 mmHg. ^{1}H NMR δ=7.52 (1H, dd, *J*=7.6, 4.9 Hz), 7.70 (1H, d, *J*=7.9 Hz), 7.91 (1H, td, *J*=7.9, 1.5 Hz), 8.79 (1H, d, *J*=4.3 Hz); ^{13}C NMR δ=105-125 (Rf), 122.42 (t, *J*=5 Hz), 126.29, 137.19, 147.99 (t, *J*=25 Hz), and 149.98; ^{19}F NMR Φ=81.30 (3F, tt, *J*=10, 2 Hz), 114.56 (2F, t, *J*=14 Hz), 122.05 (2F, m), 122.38 (2F, m), 123.28 (2F, m), 126.64 (2F, m); MS (EI) *m/z* 397 (M^+), 378, 128.

1-Ethoxycarbonyl-2-perfluorohexyl-1,2-dihydropyridine (13) (4:3 mixture of conformational isomers). Colorless solids, mp 17 °C (oven temp. 85-88 °C/0.1 mmHg). ^{1}H NMR δ=1.31 (3H, m), 4.20-4.40 (2H, m), 5.25-5.55 (1H, m), 5.60 (1H of minor conformer, dt, *J*=19.8, 6.4 Hz), 5.78 (1H of major conformer, dt, *J*=19.8, 6.4 Hz), 6.27 (1H, m), 6.88 (1H of major conformer, d, *J*=7.6 Hz), 7.02 (1H of minor conformer, d, *J*=7.6 Hz); ^{13}C NMR (major conformer) δ=14.17, 51.62 (t, *J*=24 Hz), 63.25, 105-125 (Rf), 106.46, 112.17, 126.19, 127.04, 153.74; (minor conformer) δ=13.88, 52.31 (t, *J*=25 Hz), 63.00, 105-125 (Rf), 106.52, 111.56, 126.84, 127.66, 153.52; ^{19}F NMR Φ=81.44 (3F, m), 119.89 (1F of minor conformer, dm, *J*=271 Hz), 120.44 (1F of major conformer, dm, *J*=280 Hz), 122.42 (3F, m), 122.78 (1F, m), 123.24 (2F, m), 124.4 (1F, m), 126.63 (2F, m); IR (neat) 2988, 1732, 1650, 1580, 1402, 1300-1100 cm^{-1}; MS (CI) *m/z* 472 (M^++1), 428, 426, 400, 380, 152. Anal. Calcd for $C_{14}H_{10}F_{13}NO_2$: C, 35.68; H, 2.14; N, 2.97. Found: C, 35.39; H, 2.18; N, 2.96%.

1-Ethoxycarbonyl-2-methyl-1,2-dihydropyridine (14) (2:1 mixture of conformational isomers).[14] Colorless oil, oven temp. 75-80 °C/0.1 mmHg; ^{1}H NMR δ=1.14 (3H, d, *J*=6.7 Hz), 1.30 (3H of major conformer, t, *J*=7.0 Hz), 1.33 (3H of minor conformer, t, *J*=7 Hz), 4.20 (2H, m), 4.70-4.90 (1H, m), 5.18-5.32 (1H, m), 5.54 (1H, m), 5.86 (1H, m), 6.60-6.72 (1H, m); ^{13}C NMR (major conformer) δ=14.43, 18.67, 48.23, 62.05, 105.05, 120.39, 124.18 (2C); (minor conformer) δ=14.20, 48.52, 63.77, 105.15, 120.82, 123.66, 124.83.

3-Perfluorohexyl-2,3-dihydropyridazine (15). Colorless crystals, mp 46 °C; ^{1}H NMR δ=4.64 (1H, m), 5.81 (1H, br t, *J*=7.8 Hz), 6.11 (1H, dd, *J*=9.8, 3.4 Hz), 6.20 (1H, br), 6.83 (1H, m); ^{13}C NMR δ=51.19 (t, *J*=23 Hz), 100-125 (Rf), 116.07, 122.31, 133.78; ^{19}F NMR Φ=81.28 (3F, tt, *J*=10, 2 Hz), 122.65 (4F, m),

123.34 (2F,m), 123.6 (1F, dm, *J*=*ca.* 287 Hz), 125.8 (1F, dm, *J*=*ca.* 287 Hz), 126.63 (2F, m); IR (KBr) 3272, 3152, 3036, 2956, 1486, 1366, 1300-1100 cm^{-1}; MS (CI) *m/z* 429 (M^++Et), 401 (M^++1), 381. Anal. Calcd for $C_{10}H_3F_{13}N_2$: C, 30.02; H, 1.26; N, 7.00. Found: C, 29.62; H, 0.98; N, 6.96%.

3,6-Bis(perfluorohexyl)-1,2,3,6-tetrahydropyridazine (16). Colorless crystals, mp 79-80 °C; ^1H NMR δ=3.62 (2H, br), 3.85 (2H, dd, *J*=12.5, 7.6 Hz), 6.38 (2H, s); ^{13}C NMR δ=50.59 (dd, *J*=24, 21 Hz), 100-125 (Rf), 125.46; ^{19}F NMR Φ=81.28 (3F, tt, *J*=10, 2 Hz), 115.36 (1F, dm, *J*=282 Hz), 120.41 (1F, dm, *J*=282 Hz), 121.75 (2F, m), 122.34 (1F, dm, *J*=295 Hz), 122.66 (1F, dm, *J*=295 Hz), 123.14 (1F, dm, *J*=*ca.* 300 Hz); 123.35 (1F, dm, *J*=*ca.*300 Hz), 126.48 (1F, dm, *J*=287 Hz), 126.76 (1F, dm, *J*=287 Hz); IR (KBr) 3400, 1368, 1300-1100 cm^{-1}; MS (CI) *m/z* 749 (M^++Et), 721 (M^++1), 720 (M^+), 701, 401. Anal. Calcd for $C_{16}H_6F_{26}N_2$: C, 26.68; H, 0.84; N, 3.89. Found: C, 26.44; H, 0.72; N, 4.15%.

3-(Perfluorohexyl)pyridazine (17). Colorless needles, mp 64-65 °C (oven temp. 145 °C/ 25 mmHg); ^1H NMR δ=7.74 (1H, ddm, *J*=8.5, 5.2 Hz), 7.87 (1H, dd, *J*=8.5, 1.5 Hz), 9.43 (1H, dd, *J*=5.2, 1.5 Hz); ^{13}C NMR δ=105-125 (Rf), 125.36 (t, *J*=4 Hz), 127.10, 151.84 (t, *J*=26 Hz), 153.15 (t, *J*=1 Hz); ^{19}F NMR Φ=81.27 (3F, tt, *J*=10, 2 Hz), 114.50 (2F, t, *J*=13 Hz), 121.85 (2F, m), 122.05 (2F, m), 123.25 (2F, m), 126.61 (2F, m); IR (KBr) 3072, 1578, 1564, 1446, 1396, 1368, 1300-1100 cm^{-1}; MS (CI) *m/z* 427 (M^++Et), 399 (M^++1), 379, 351. Anal. Calcd for $C_{10}H_3F_{13}N_2$: C, 30.17; H, 0.76; N, 7.04. Found: C, 30.05; H, 0.74; N, 7.41%.

3,6-Bis(perfluorohexyl)-2,3-dihydropyridazine (18). Colorless needles, mp 92-93 °C; ^1H NMR δ=4.85 (1H, ddd, *J*=14.5, 10.7, 5.6 Hz), 5.86 (1H, M), 6.34 (1H, d, *J*=10.4 Hz), 6.73 (1H, br); ^{13}C NMR δ=51.04 (t, *J*=23 Hz), 105-125 (Rf), 114.24, 118.90, 159.39 (t, *J*=25 Hz); ^{19}F NMR Φ=81.37 (3F, tt, *J*=10, 2 Hz), 81.41 (3F, tt, *J*=10, 2 Hz), 115.13 (1F, dtt, *J*=277, 13, 3 Hz), 116.98 (1F, dtt, *J*=277, 13, 3 Hz), 122.05 (2F, m), 122.47 (4F, m), 122.93 (2F, m), 123.27 (4F, m), 124.2 (1F, m), 125.8 (1F, m), 126.56 (4F, m); IR (KBr) 3348, 1634, 1580, 1480, 1366, 1300-1100 cm^{-1}; MS (CI) *m/z* 719 (M^++1), 700, 680, 399. Anal. Calcd for $C_{16}H_4F_{26}N_2$: C, 26.76; H, 0.56; N, 3.90. Found: C, 26.36; H, 0.51; N, 4.30%.

4-Perfluorohexyl-5-methyl-3,4-dihydropyrimidine (19). Colorless needles, mp 110-111 °C.[10]

2-(Perfluorooctyl)pyrazine (20). Colorless crystals, mp 41-42 °C; ^1H NMR δ=8.77 (1H, d, *J*=1.5 Hz), 8.84 (1H, d, *J*=2.1 Hz), 8.98 (1H, m); ^{13}C NMR δ=143.55 (t, *J*=5 Hz), 143.97 (t, J=25 Hz), 144.36, and 147.59; ^{19}F NMR Φ=81.31 (3F, tt, *J*=10, 2 Hz), 155.14 (2F, t, *J*=13 Hz), 121.72 (2F, m), 122.29 (6F, m), 123.21 (2F, m), 126.63 (2F, m); IR (KBr) 3080, 1414, 1372, 1334, 1300-1100 cm^{-1}; MS (EI) *m/z* 498, 479, 129. HRMS Calcd for $C_{12}H_3F_{17}N_2$: 498.0024. Found: 498.0024.

2-(1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Hexadecafluorooctyl)-pyrazine (21). Colorless crystals, mp 40-41 °C; ^1H NMR δ=6.41 (1H, ddd, *J*=43.0, 18.6, 4.0 Hz), 8.73 (1H, d, *J*=1.5 Hz), 8.79 (1H, d, *J*=2.4 Hz), 8.90 (1H, m); ^{13}C NMR δ=88.60 (ddd, *J*=187, 32, 24 Hz), 97.06, 105-125 (Rf), 145.38 (d, *J*=6 Hz), 145.81 (d, *J*=1 Hz), 146.87 (d, *J*=22 Hz), 148.01 (d, *J*=1 Hz); ^{19}F NMR Φ=80.65 (3F, tt, *J*=10, 2 Hz), 119.48 (1F, dm, *J*=288 Hz), 121.61 (6F, m), 122.35 (2F, m), 125.07 (1F, dm, *J*=288 Hz), 125.79 (2F, m), 201.60 (1F, dm, J=43 Hz); IR (KBr) 2924, 1410, 1300-1100 cm^{-1}; MS (EI) *m/z* 480, 461, 111. HRMS Calcd for $C_{12}H_4F_{16}N_2$: 480.0117. Found: 480.0102.

2-Perfluorohexyl-1,2-dihydrobenzo[h]quinoline (22). ^1H NMR δ=4.61 (1H, br s), 5.06 (1H, td, *J*=12.8, 4.3 Hz), 5.47 (1H, dd, *J*=9.4, 5.2 Hz), 6.67 (1H, d, *J*=9.4 Hz), 7.00 (1H, *J*=8.2 Hz), 7.11 (1H, d, *J*=8.2 Hz), 7.33 (2H, m), 7.50-7.90 (2H, m).

2-(Perfluorohexyl)benzo[h]quinoline (23). Colorless crystals, mp 89 °C; ^{1}H NMR δ=7.58 (1H, d, *J*=8.9 Hz), 7.67-7.85 (5H, m), 8.18 (1H, d, *J*=8.2 Hz), 9.29 (1H, dd, *J*=8.2, 1.2 Hz); ^{13}C NMR δ=105-125 (Rf), 119.01 (t, *J*=5 Hz), 124.41, 124.93, 127.36, 127.70, 127.79, 129.02, 130.09, 131.26, 133.81, 136.86, 146.09, 146.17 (t, *J*=26 Hz); ^{19}F NMR Φ=81.34 (3F, tt, *J*=10, 2 Hz), 112.99 (2F, tt, *J*=13, 3 Hz), 121.78 (2F, m), 121.84 (2F, m), 123.16 (2F, m), 126.58 (2F, m); IR (KBr) 3056, 1404, 1364, 1300-1100 cm^{-1}; MS (CI) *m/z* 526 (M^++Et), 498 (M^++1), 497 (M^+), 478, 228, 178. Anal. Calcd for $C_{19}H_8F_{13}N$: C, 45.89; H, 1.62; N, 2.82. Found: C, 45.49; H, 1.69; N, 2.87%.

2,9-Bis(perfluorohexyl)-1,2-dihydro-1,10-phenanthroline (24). Yellow crystals, mp 70-71 °C; ^{1}H NMR δ= 5.33 (1H, m), 5.68 (1H, m), 6.38 (1H, br s), 6.81 (1H, dd, *J*=10.0, 1.2 Hz), 7.11 (1H, d, *J*=8.2 Hz), 7.26 (1H, d, *J*=8.2 Hz), 7.65 (1H, d, *J*=8.5 Hz), 8.18 (1H, d, *J*=8.5 Hz); ^{19}F NMR Φ=81.44 (3F, tt, *J*=10, 2 Hz), 81.45 (3F, tt, *J*=10, 2 Hz), 114.45 (1F, dtt, *J*=275, 13, 2 Hz), 115.10 (1F, dtt, *J*=275, 13, 2 Hz), 121.5-122.5 (6F, m), 122.77 (2F, m), 123.45 (4F, m), 125.36 (2F, m), 126.83 (4F, m); IR (KBr) 3420, 1526, 1392, 1300-1100 cm^{-1}; MS (CI) *m/z* 847 (M^++Et), 819 (M^++1), 818 (M^+), 499. Anal. Calcd for $C_{24}H_8F_{26}N_2$: C, 35.23; H, 0.99; N, 3.42. Found: C, 35.31; H, 1.18; N, 3.33%.

9-Perfluorohexyl-9,10-dihydroacridine (25). Colorless crystals, mp 165-166 °C; ^{1}H NMR δ=4.90 (1H, t, *J*=15.0 Hz), 6.29 (br s), 6.85 (2H, dd, *J*=7.9, 0.9 Hz), 6.98 (2H, td, *J*=7.5, 1.2 Hz), 7.20-7.35 (4H, m); ^{13}C NMR δ=46.26 (t, *J*=23 Hz), 105-125 (Rf), 112.52 (t, *J*=3 Hz), 114.26, 120.93, 129.09, 131.07, and 141.05; ^{19}F NMR Φ=81.34 (3F, tt, *J*=10, 2 Hz), 114.60 (2F, m), 119.80 (2F, m), 122.34 (2F, m), 123.32 (2F, m), 126.67 (2F, m); IR (KBr) 3380, 1612, 1488, 1300-1100 cm^{-1}; MS (EI) *m/z* 500 (M^++1), 499 (M^+), 180. Anal. Calcd for $C_{19}H_{10}F_{13}N$: C, 45.71; H, 2.02; N, 2.81. Found: C, 45.37; H, 2.08; N, 2.59%.

2-(Perfluorohexyl)-2,3-dihydrobenzothiazole (26a). ^{1}H NMR δ=4.37 (1H, br s), 5.78 (1H, dt, *J*=15.3, 6.0 Hz), 6.68-6.84 (2H, m), 6.95 (1H, m), 7.13 (1H, m); ^{19}F NMR Φ=81.29 (3F, tt, *J*=10, 2 Hz), 120.3 (1F, dm, *J*=ca. 280 Hz), 121.31 (2F, m), 122.45 (2F, m), 123.23 (2F, m), 126.66 (2F, m), 126.8 (1F, dm, J=ca. 280 Hz). MS (EI) *m/z* 455 (M^+), 453, 436, 184, 150, 136.

2-(Perfluorohexyl)benzothiazole (26b). MS (EI) *m/z* 453 (M^+), 434, 184, 134, 124. HRMS Calcd for $C_{13}H_4F_{13}NS$: 452.9855. Found: 452.9833.

2-(Perfluorohexyl)-2,3-dihydrobenzoxazole (27a). ^{1}H, NMR δ=4.26 (1H, br s), 6.10 (1H, m), and 6.60-7.40 (4H, m); MS (EI) *m/z* 439 (M^+), 420, 168, 120. HRMS Calcd for $C_{13}H_6F_{13}NO$: 439.0241. Found:439.0265.

2-(Perfluorohexyl)benzoxazole (27b).[15] ^{1}H, NMR δ=7.40-7.60 (2H, m), 7.68 (1H, dm, *J*=7.9 Hz), and 7.90 (1H, dm, *J*=7.3 Hz); ^{19}F NMR Φ=81.28 (3F, tt, *J*=10, 2 Hz), 113.59 (2F, tt, *J*=13, 2 Hz), 122.23 (2F, m), 122.66 (2F, m), 123.26 (2F, m), 126.63 (2F, m); MS (EI) *m/z* 437 (M^+), 418, 249, 199, 168, and 102. HRMS Calcd for $C_{13}H_4F_{13}NO$: 437.0085. Found: 437.0109.

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