Convenient Syntheses of a Family of Easily Recoverable Fluorous Primary, Secondary, and Tertiary Aliphatic Amines $NH_{3-x}[(CH_2)_m(CF_2)_7CF_3]_x$ ($m = 3-5$; $x = 1-3$) − Fine Tuning of Basicities and Fluorous Phase Affinities

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The alcohols $HOCH_2(CH_2)_{m-1}(CF_2)_7CF_3$ [m = 3–5; $(CF_2)_7CF_3 = R_{f8}$] are oxidized to aldehydes $O{=}CH(CH_2)_{m-1}R_{f8}$ (Dess–Martin reagent, 90–96%), which are condensed with $NH_2CH_2C_6H_5$ and $Na(AcO)_3BH$ to give benzylamines $NH(CH_2C_6H_5)[(CH_2)_mR_{f8}]$ (excess amine, 88–90%) or $N(CH_2C_6H_5)[(CH_2)_mR_{f8}]_2$ (excess aldehyde, 85–91%). Subsequent hydrogenolyses (Pd/C, 1 atm H_2) give the title primary amines $NH_2[(CH_2)_mR_{f8}]$ (**10**–**12**; 98–99%) or secondary amines $NH[(CH_2)_mR_{f8}]_2$ (**13**–**15**; 92–99%). The aldehyde condensations are repeated with **13**–**15** to give tertiary amines $N[(CH_2)_mR_{f8}]_3$ (**16**–**18**; 86–97%) with very high fluorous phase affinities. These decrease monotonically as the numbers of CH_2 groups increase or R_{f8} groups decrease ($CF_3C_6F_{11}$/toluene, 24 °C, **16/17/18/13/14/15/10/11/12**: >99.7:<0.3, >99.7:<0.3, 99.5:0.5, 96.5:3.5, 95.1:4.9, 93.0:7.0, 70.0:30.0, 63.2:36.8, 56.9:43.1). The relative basicities towards CF_3CO_2H are probed by NMR in $CDCl_3$. Competitions between $N(CH_2CH_3)_3$ or $N[(CH_2)_{11}CH_3]_3$ and **16**–**18** show 100% or >95%, >95% or 85–90%, and 85–90 or 65–70% protonation of the former. Competitions between **16/17**, **17/18**, and **16/18** show 60%, 85–90%, and >95% protonation of the latter. Thus, an inductive effect of the R_{f8} group is still detected through five CH_2 groups.

Introduction

Amines are ubiquitous as catalysts and reagents in chemistry.[1] As such, there has been ongoing practical, economic, and ecological interest in amines − or their protonated or alkylated derivatives − that can easily be recovered and recycled.[2−6] As would be expected, many approaches involve polymer-bound amines.[2−4] Some of these recovery or immobilization strategies have been designed for application in combinatorial organic synthesis,[3,5] where the manipulation of "orthogonal phases"[7] plays a critical role. Other approaches involve nothing more complex than the fine-tuning of solubility properties,[6] so that the amine or derivative is easily separated from the product.

One innovative new strategy for recoverable catalysts and reagents exploits the temperature-dependent immiscibility (orthogonality) of "fluorous" solvents, such as perfluoroalkanes and perfluoroethers, and organic solvents.[8−10] Many combinations give bilayers at room temperature, but one phase at higher temperature. Most organic compounds exhibit much higher affinities for organic solvents. However, species that are derivatized with sufficient numbers of "pony tails" $(CH_2)_m(CF_2)_{n-1}CF_3$ [abbreviated $(CH_2)_mR_{fn}$] can exhibit very high fluorous solvent affinities.[9] As shown in Figure 1, reactions can be effected under homogeneous conditions in the high temperature monophasic limit, and the organic products separated from the fluorous catalyst or transformed reagent in the low temperature biphasic limit.

In previous papers, we described convenient routes to a family of fluorous aliphatic primary and tertiary phosphanes $PH_2(CH_2)_mR_{f8}$ and $P[(CH_2)_mR_{f8}]_3$.[11,12] The methylene chain or "spacer" lengths are easily varied from two to five carbons, allowing the donor/acceptor properties of the phosphorus to be fine-tuned. In iridium carbonyl derivatives, five methylene groups afforded nearly complete insulation of the electron-withdrawing perfluoroalkyl segments from the metal, as judged from IR ν_{CO} values. These phosphanes have been applied in a variety of rhodium-catalyzed organic reactions,[13,14] and other studies.[15]

In this paper, we report convenient syntheses of a similar family of fluorous primary, secondary, and tertiary amines, $NH_{3-x}[(CH_2)_mR_{f8}]_x$, where the methylene chains vary from three to five carbons. We also report partition coefficients that quantify the fluorous phase affinities of these compounds, and basicity measurements that quantify the insulating efficiencies of the spacers with respect to the nitrogen lone pairs and the electronegative R_{f8} moieties. The end result is a valuable "toolkit" for the systematic development of catalytic reactions based upon fluorous trialkylamines or their metal complexes.

There are somewhat fragmented reports of related fluorous amines in the literature. These include the primary and secondary amines $NHR(CH_2)_2R_{f6}$ and $NHR(CH_2)_2R_{f8}$ (R = H, Me), which were prepared from azide precursors and feature double-methylene insulating spacers,[16] and secondary and tertiary amines $NRR'CH_2R_{f7}$, which feature

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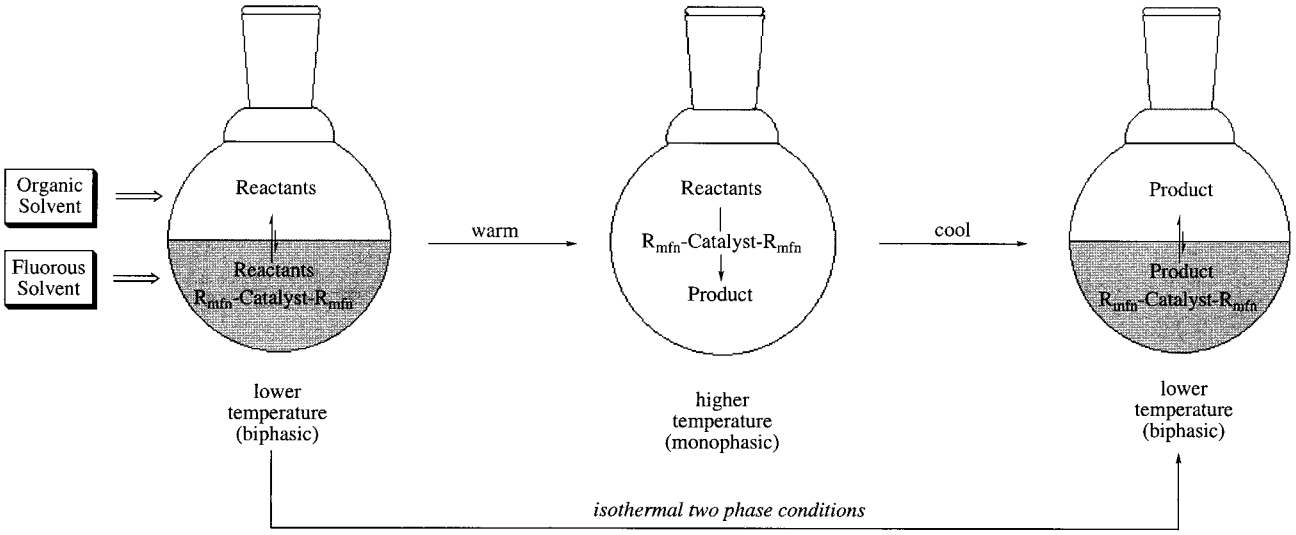


Figure 1. One possibility for catalysis with fluorous solvents [$R_{mfn} = (CH_2)_m(CF_2)_{n-1}CF_3$]

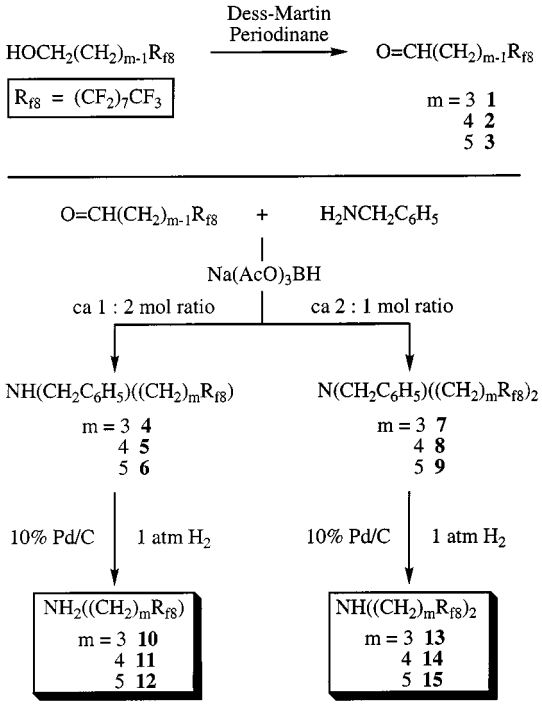
single-methylene spacers.[17] The primary and secondary amines $NH_x\{(CH_2)_3Si[(CH_2)_2R_{f6}]_3\}_{3-x}$ have already been applied in robotic solution phase parallel syntheses.[5a] More complex aliphatic[18] and aromatic[19] *poly*amines have been used as ligands for fluorous biphase catalysis. Other amines with pony tails have been prepared as part of studies directed at other objectives.[20] A variety of aliphatic perfluoroamines are also commercially available [e.g., *n*-butyl-derived $N(R_{f4})_3$]. However, these are nonbasic, with very low lying nitrogen lone pair energies, due to the marked inductive effect of the uninsulated perfluoroalkyl groups.[21]

Results

1. Syntheses

We sought to develop a general synthesis of the title compounds $NH_{3-x}[(CH_2)_mR_{f8}]_x$. The reductive amination of aldehydes constitutes one of the most versatile preparations of amines.[22] Accordingly, the known fluorous primary alcohols $HOCH_2(CH_2)_{m-1}R_{f8}$ ($m = 3-5$) were purchased or prepared by simple procedures previously described.[12,23,24] As shown in Scheme 1, reactions with the Dess–Martin reagent[25] gave the fluorous aldehydes $O{=}CH(CH_2)_{m-1}R_{f8}$ [$m = 3$ (**1**), 4 (**2**), 5 (**3**)] as clear oils in 90–96% yields after workup. While this work was in progress, a communication describing the synthesis of **3** and some related aldehydes by an identical route appeared.[24]

As shown in Scheme 1, reductive aminations of **1**–**3** were conducted with different stoichiometries. In one version, a twofold excess of benzyl amine, $NH_2CH_2C_6H_5$, was used. The addition of $Na(AcO)_3BH$ in THF[22] then gave the secondary amines $NH(CH_2C_6H_5)[(CH_2)_mR_{f8}]$ (**4**–**6**) as oils or white solids in 88–90% yields after workup. In another version, a twofold excess of the aldehyde was used, allowing the generated compounds **4**–**6** to condense further. Workup gave the tertiary amines $N(CH_2C_6H_5)[(CH_2)_mR_{f8}]_2$ (**7**–**9**) in 85–91% yields. The benzyl-protecting groups in

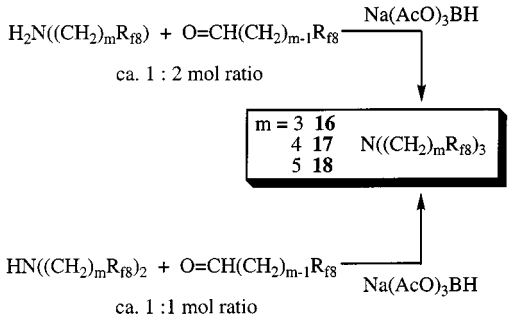


Scheme 1. Syntheses of fluorous aldehydes, primary and secondary amines

4–**9** were removed under mild hydrogenolysis conditions (1 atm H_2, 10% Pd/C). Workup gave two classes of the title compounds: the primary amines $NH_2[(CH_2)_mR_{f8}]$ (**10**–**12**) and the secondary amines $NH[(CH_2)_mR_{f8}]_2$ (**13**–**15**), in >99–92% yields.

As shown in Scheme 2, the analogous tertiary amines $N[(CH_2)_mR_{f8}]_3$ (**16**–**18**) could be obtained in two ways. In one approach, the primary amines **10**–**12** were condensed with 2.0–2.4 equivalents of aldehydes **1**–**3** under the $Na(AcO)_3BH$ reductive amination conditions. In the other, the secondary amines **13**–**15** were similarly treated with 1.0–1.2 equivalents of the aldehydes. In practice, the latter route gave slightly higher yields of **16**–**18** (97–86%), and

only these procedures are provided in the experimental section.



Scheme 2. Synthesis of fluorous tertiary amines

The amines **4−18** were characterized by microanalysis and ^{1}H- and ^{13}C-NMR spectroscopy, as described in the experimental section. The NMR properties showed numerous patterns, but usually of a routine nature. For example, the N*C*H$_2$CH$_2$ ^{13}C signals were generally grouped in ranges (tertiary amines **16−18**, δ = 52.7−53.9; secondary amines **13−15**, δ = 48.5−49.9; primary amines **11−12**, δ = 41.9−42.1), always downfield of the *C*H$_2$R$_{f8}$ signals (δ = 28.8−29.9). In the corresponding fluorous phosphanes, this downfield/upfield sense is reversed (P*C*H$_2$, δ = 17.9−21.1).[11,12]

The benzyl amines **4−9** were mainly colorless oils. The title compounds **10−18** were low melting solids, except for the two lightest members **10−11**, which were closer to waxes. All amines were air-stable for extended periods, although the oils and waxes were best stored in a refrigerator. DSC measurements on **14−18** showed only melting endotherms. Amines **10−18** dissolved in quite a broad range of solvents. All were highly soluble in $CHCl_3$, $CF_3C_6H_5$, and fluorous solvents such as $CF_3C_6F_{11}$. The primary and secondary amines **10−15** were also very soluble in methanol. The highly fluorous tertiary amines **16−18** remained sparingly soluble in methanol. None of the amines were soluble in water or DMSO.

2. Partition Coefficients and Basicities

Quantitative data on the fluorous phase affinities of the title compounds were sought. Accordingly, the $CF_3C_6F_{11}$/toluene partition coefficients were determined by GC as previously reported[9,11,26] and are further described in the experimental section. These reflect *relative* as opposed to *absolute* solubilities, and are summarized in Table 1. Values for related phosphanes are also given. Trends are analyzed in the discussion section.

We next probed the effect of the methylene chain length upon the basicities of tertiary amines **16−18**. Because of the solubility characteristics noted above, $K_a(H_2O)$ or K_a(DMSO) values could not be determined. Thus, the measurement of *relative* basicities in nonpolar media was attempted. In principle, NMR constitutes a convenient method for determining relative ratios. However, proton transfer equilibria are often rapid on NMR time scales. In these cases, only the time-averaged signals of two equilibrating acids or bases are observed.

Table 1. Partition coefficients (24 °C)

	Analyte	$CF_3C_6F_{11}$/toluene
10	$NH_2(CH_2CH_2CH_2R_{f8})$	70.0:30.0
11	$NH_2(CH_2CH_2CH_2CH_2R_{f8})$	63.2:36.8
12	$NH_2(CH_2CH_2CH_2CH_2CH_2R_{f8})$	56.9:43.1
13	$NH(CH_2CH_2CH_2R_{f8})_2$	96.5:3.5
14	$NH(CH_2CH_2CH_2CH_2R_{f8})_2$	95.1:4.9
15	$NH(CH_2CH_2CH_2CH_2CH_2R_{f8})_2$	93.0:7.0
16	$N(CH_2CH_2CH_2R_{f8})_3$	>99.7:<0.3
17	$N(CH_2CH_2CH_2CH_2R_{f8})_3$	>99.7:<0.3
18	$N(CH_2CH_2CH_2CH_2CH_2R_{f8})_3$	99.5:0.5
19	$P(CH_2CH_2R_{f8})_3$	>99.7:<0.3[a]
20	$P(CH_2CH_2CH_2R_{f8})_3$	98.8:1.2[a]
21	$P(CH_2CH_2CH_2CH_2R_{f8})_3$	98.9:1.1[a]
22	$P(CH_2CH_2CH_2CH_2CH_2R_{f8})_3$	98.9:1.1[b]

[a] Data at 27 °C from ref.[11] − [b] Data at 27 °C from ref.[12a]

In order to circumvent this problem, $CDCl_3$ solutions of **16−18** were first titrated with $CDCl_3$ solutions of CF_3CO_2H under constant volume conditions. This quite strong acid [p$K_a(H_2O)$ = 0.23] completely protonates typical trialkylamines [p$K_a(H_2O)$ HNR_3^+ = 11.01, 10.63 for R = CH_2CH_3, $(CH_2)_9CH_3$].[27] Only one set of resonances was observed, in agreement with rapid equilibria between **16−18** and their protonated forms H[**16−18**]$^+$ $CF_3CO_2^-$. Importantly, as illustrated in Figure 2a, the NCH_2 ^{1}H-NMR signals shifted linearly downfield. This calibration experiment therefore provides an indirect measure of the relative amounts of **16−18** and H[**16−18**]$^+$ $CF_3CO_2^-$ in $CDCl_3$.[28]

Two reference amines without R_{f8} segments were selected, the ethyl and *n*-dodecyl systems $N(CH_2CH_3)_3$ and $N[(CH_2)_{11}CH_3]_3$. Analogous titrations were conducted, as depicted in Figure 2b. The latter amine reproducibly gave a nonlinear response. This is tentatively ascribed to micelle formation, or other aggregation phenomena subject to a critical concentration. These are known to give significant chemical shift perturbations.[29] The absence of analogous behavior during the protonation of **16−18** is noteworthy. However, the salts H[**17−18**]$^+$ $CF_3CO_2^-$ did slowly precipitate from $CDCl_3$ under the conditions of Figure 2, indicating supersaturation. In the case of **16**, this was fast enough at half protonation to preclude completion of the calibration graph.

As shown in Table 2, two amines and CF_3CO_2H were then combined in a 1:1:1 ratio in $CDCl_3$. Concentrations were identical to those of the calibration experiments in Figure 2. Two sets of signals were observed − one for the time-averaged unprotonated/protonated form of each amine. One ratio must be the reciprocal of the other. The ratios were extrapolated from the calibration graph of each amine, and the results are summarized at the bottom of Table 2. The ranges reflect slight dependencies on the calibration graphs employed. Importantly, there is a detectable basicity difference between the amine with the longest methylene chain (**18**), and the nonfluorinated reference amines. The trends are further analyzed below.

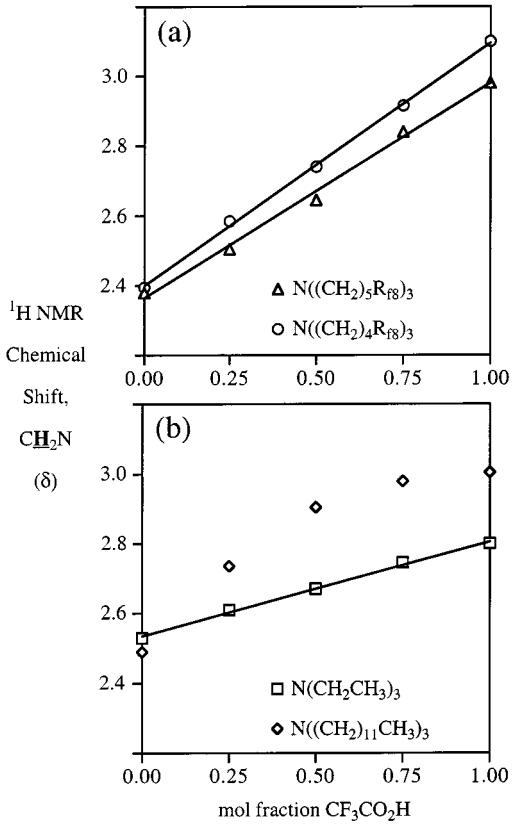
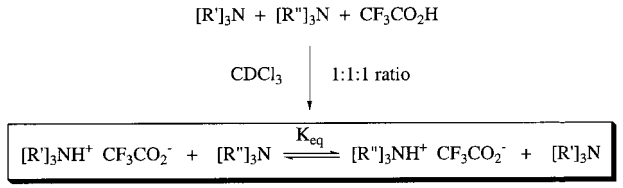


Figure 2. Representative calibration experiments: ^{1}H NMR chemical shifts of CH_2N signals as a function of nitrogen protonation

Table 2. Relative basicities in $CDCl_3$ at 32 °C



[R']$_3$N / [R"]$_3$N	[R']$_3$NH$^+$ / [R"]$_3$NH$^+$	K_{eq}[a]	ΔpK_a[a]
N(CH$_2$CH$_3$)$_3$ / N((CH$_2$)$_3$R$_{f8}$)$_3$ (**16**)	100 : 0	—	—
N(CH$_2$CH$_3$)$_3$ / N((CH$_2$)$_4$R$_{f8}$)$_3$ (**17**)	>95 : <5	>361	>2.6
N(CH$_2$CH$_3$)$_3$ / N((CH$_2$)$_5$R$_{f8}$)$_3$ (**18**)	85-90 : 10-15	32-81	1.5-1.9
N((CH$_2$)$_{11}$CH$_3$)$_3$ / N((CH$_2$)$_3$R$_{f8}$)$_3$ (**16**)	>95 : <5	>361	>2.6
N((CH$_2$)$_{11}$CH$_3$)$_3$ / N((CH$_2$)$_4$R$_{f8}$)$_3$ (**17**)	85-90 : 10-15	32-81	1.5-1.9
N((CH$_2$)$_{11}$CH$_3$)$_3$ / N((CH$_2$)$_5$R$_{f8}$)$_3$ (**18**)	70-75 : 30-25	9.0-16	0.9-1.2
N((CH$_2$)$_3$R$_{f8}$)$_3$ (**16**) / N((CH$_2$)$_4$R$_{f8}$)$_3$ (**17**)	40 : 60	0.44	0.3
N((CH$_2$)$_3$R$_{f8}$)$_3$ (**16**) / N((CH$_2$)$_5$R$_{f8}$)$_3$ (**18**)	<5 : >95	<0.0028	>2.6
N((CH$_2$)$_4$R$_{f8}$)$_3$ (**17**) / N((CH$_2$)$_5$R$_{f8}$)$_3$ (**18**)	10-15 : 85-90	0.012-0.031	1.9-1.5

[a] All values are rounded to two significant digits.

Discussion

The versatile methodologies in Schemes 1 and 2 allow rapid and high-yield access to a large family of fluorous primary, secondary, and tertiary amines (**10**−**18**). Key strategic elements include (1) the flexible stoichiometry of reductive amination (1:2 or 2:1), (2) a nitrogen source with an easily removable *N*-benzyl group, and (3) the repetitive use of the same fluorous aldehyde building blocks. Fluorous aldehydes of the formula O=CHCH$_2$R$_{fn}$ are also readily available.[24,30] Thus, homologous amines with double-methylene spacers should also be easily accessed. Some previously reported fluorous amines were noted in the introduction. Although several of the synthetic approaches used also have the potential to be versatile, no other extensive family of fluorous amines has been described to date. Thus, we strongly recommend **10**−**18**, for which key physical properties have also been carefully defined, as benchmark compounds for general adoption and use by the practicing fluorous phase community.

Table 1 summarizes one of the most important physical properties: the partition coefficients. As would be expected from a simple "like dissolves like" model,[8] they become lower as the methylene chain is lengthened (**10** vs. **11** vs. **12**; **13** vs. **14** vs. **15**; **16** vs. **17** vs. **18**). They also become lower when pony tails are replaced by N*H* groups (**16** vs. **13** vs. **10**; **17** vs. **14** vs. **11**; **18** vs. **15** vs. **12**). The two amines with the highest fluorous phase affinities (**16**, **17**) show no detectable residual quantity in the organic phase (< 0.3%). This represents, with respect to the catalysis protocol in Figure 1, a very high degree of immobilization. However, in other applications, only the ability to extract a substance into a fluorous solvent is sought.[5a,7] Here, even the primary amines **10**−**12** exhibit sufficiently high partition coefficients (70.0:30.0 to 56.9:43.1). The partition coefficients of the tertiary amines **16**−**18** can also be compared with those of the analogous tertiary phosphanes P[(CH$_2$)$_m$R$_{f8}$]$_3$, (**20**−**22**, Table 1).[11] The latter values appear to be slightly lower, perhaps due to the larger and more polarizable phosphorus.

The basicity data for tertiary amines **16**−**18** in Table 2 features several ratios that can only be bounded or approximately determined, and must be viewed as semiquantitative. Nonetheless, the results clearly establish a remarkable transmission of the electron-withdrawing effect of the perfluoroalkyl segment through five methylene groups. Competitions between N(CH$_2$CH$_3$)$_3$ and **16**−**18** show progressively increasing protonation of the fluorous amine, consistent with a diminishing inductive effect. Nonetheless, there remains a ΔpK_a(CDCl$_3$) of 1.5−1.9 between the conjugate acids of N(CH$_2$CH$_3$)$_3$ and **18**. The fluorous amines compete slightly more effectively with the n-dodecyl system

$N[(CH_2)_{11}CH_3]_3$, which is a better reference base due to the similar number of carbons. Still, a $\Delta pK_a(CDCl_3)$ of 0.9−1.2 remains with **18**.

Another approach to determining the spacer length needed to insulate the nitrogen from the perfluoroalkyl groups is to compare pairs of fluorous amines until an asymptotic limit is reached. Competitions between **16** and **17**, **17** and **18**, and **16** and **18** (Table 2) show the expected basicity order. However, the magnitudes of differences suggest that an asymptotic limit is not at hand, and that longer methylene chains will be required. We are somewhat concerned by the greater difference between **17** and **18**, as compared to **16** and **17**, and plan additional types of physical measurements (heats of reactions, ionization potentials), as well as computational studies. At present, we have no evidence for "nonclassical" mechanisms of inductive effect transmission − e.g., non-through-bond, microenvironment-based effects. However, in view of the tendency of fluorous groups to aggregate, and the nonlinear response of $N[(CH_2)_{11}CH_3]_3$ in Figure 2b, the possibility of such contributions remains an open question.

Trifluoromethyl groups have previously been shown to exhibit long range inductive effects through sp^3 hybridized atoms. For example, the $pK_a(H_2O)$ values of the α-amino acids $HO_2CCH(NH_2)(CH_2)_nCH_3$ and ω-trifluoromethyl analogs $HO_2CCH(NH_2)(CH_2)_mCF_3$ have been compared (m = 0−3).[31] A measurable effect persisted through four sp^3 carbons (m = 3). A similar behavior was observed in the analogous series of carboxylic acids and protonated primary amines, including gas phase experiments.[31] It should be emphasized that the trends in Table 2 reflect the combined inductive effects of *three* perfluoroalkyl groups, and must be normalized for many comparative purposes. For example, the pK_a difference between the conjugate acids of **12** and the nonfluorinated analog $H_2N[(CH_2)_{11}CH_3]$ should be about one third of that of the corresponding tertiary amines in Table 2.

We have similarly sought to study the electronic properties of the fluorous tertiary phosphanes $P[(CH_2)_mR_{f8}]_3$ (**19**−**22**, Table 1).[12] As noted in the introduction, a series of iridium carbonyl derivatives has been prepared. The IR ν_{CO} values show a monotonic decrease with increasing numbers of methylene groups, and closely approach the limit of the nonfluorinated phosphane $P[(CH_2)_7CH_3]_3$ with m = 5 ($\tilde{\nu}$ = 4 cm^{-1}). The IR frequencies reflect the donor/acceptor properties of the iridium fragment, so the inductive effect must pass through one more (and much heavier) atom than in the protonation of **18**. However, a careful analysis of the phosphane data suggests that seven to eight methylene groups are required to reach the asymptotic limit. This also represents our best current estimate for the length of the methylene chain needed to insulate the nitrogen from the R_{f8} groups in the title compounds.

Fluorinated derivatives of every organic functional group find diverse applications in chemistry. Hence, we anticipate that the methodologies and compounds described above will prove useful for many purposes besides the fluorous immobilization/recovery protocol summarized in Figure 1. Regardless, this study has provided three series of nearly isosteric fluorous amines − primary, secondary, and tertiary − with finely modulated basicities and fluorous phase affinities. The five methylene groups in each pony tail of tertiary amine **18** bring it to within one pK_a unit of the corresponding amine without fluorines. Future reports from this laboratory will describe fluorous pyridines, and applications of fluorous bases in catalysis.[32]

Experimental Section

General: All reactions except hydrogenations were conducted under N_2. Chemicals were treated as follows: THF, ether, toluene, hexanes, distilled from Na/benzophenone; CH_2Cl_2, distilled from CaH_2; $CF_3C_6F_{11}$ (Oakwood or ABCR), distilled from P_2O_5; $HOCH_2CH_2CH_2R_{f8}$ (Oakwood), $NH_2CH_2C_6H_5$ (Aldrich), $Na(AcO)_3BH$ (Aldrich), $CDCl_3$ (Cambridge Isotope or Aldrich) and other solvents, used as received. − NMR spectra were recorded on Varian 300 MHz or Jeol JMN-400GX FT spectrometers.[33] − Gas chromatography was conducted on Hewlett Packard 5910 or ThermoQuest Trace GC 2000 instruments. − DSC data were recorded with a Mettler-Toledo DSC821 instrument and treated by standard methods.[34] − Elemental analyses were conducted with a Carlo Erba EA1110 instrument (in-house), or by Atlantic Microlab (Norcross, Georgia).

$O{=}CHCH_2CH_2R_{f8}$ (1): A Schlenk flask was charged with the Dess−Martin reagent (1.97 g, 4.64 mmol)[25] and CH_2Cl_2 (15 mL). A solution of $HOCH_2CH_2CH_2R_{f8}$ (2.00 g, 4.18 mmol) in CH_2Cl_2 (25 mL) was added with stirring over 10 min. After 2 h, ether (50 mL) was added. The white suspension was poured into a solution of $Na_2S_2O_3$ (8.06 g, 32.48 mmol; 7 equiv./Dess−Martin reagent) in saturated aqueous $KHCO_3$ (100 mL). The organic phase was separated, washed (100 mL saturated $KHCO_3$), and dried ($MgSO_4$). Solvent was removed by rotary evaporation, and the oil was distilled (ca. 80 °C, $1.0{\cdot}10^{-2}$ Torr) to give **1** as a clear oil (1.98 g, 4.15 mmol, 96%). − IR (cm^{-1}, $CHCl_3$) $\nu_{C=O}$ 1730. − ^1H NMR ($CDCl_3$):[33] δ = 2.37−2.52 (m, 2 H, CH_2R_{f8}), 2.83 (t, $^3J_{HH}$ = 7 Hz, 2 H, O=CHCH_2), 9.84 (br s, 1 H, O=CH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ = 23.8 (s, O=CH*C*H_2), 34.9 (t, $^2J_{CF}$ = 22 Hz, *C*H_2R_{f8}), 198.0 (s, O=CH). − ^{19}F NMR ($CDCl_3$): δ = −81.4 (t, $^3J_{FF}$ = 9 Hz, 3 F, CF_3), −114.8 (br s, 2 F, CF_2), −122.0 (br s, 6 F, CF_2), −123.2 (br s, 2 F, CF_2), −123.9 (br s, 2 F, CF_2), −126.7 (br s, 2 F, CF_2).

$O{=}CHCH_2CH_2CH_2R_{f8}$ (2): The reaction/workup given for **1** was repeated with $HOCH_2CH_2CH_2CH_2R_{f8}$ (1.18 g, 2.39 mmol)[12,23] and the Dess−Martin reagent (1.22 g, 2.87 mmol). This gave **2** as a clear oil (1.09 g, 2.23 mmol, 93%). − IR (cm^{-1}, $CHCl_3$) $\nu_{C=O}$ 1725. − ^1H NMR ($CDCl_3$):[33] δ = 1.89−2.00 (m, 2 H, C$H_2$$CH_2R_{f8}$), 2.05−2.20 (m, 2 H, CH_2R_{f8}), 2.60 (t, $^3J_{HH}$ = 7 Hz, 2 H, O=CHCH_2), 9.81 (br s, 1 H, O=CH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ = 21.0 (s, *C*$H_2CH_2R_{f8}$), 32.1 (t, $^2J_{CF}$ = 22 Hz, *C*H_2R_{f8}), 42.9 (s, O=CH*C*H_2), 200.6 (s, O=CH).

$O{=}CHCH_2CH_2CH_2CH_2R_{f8}$ (3):[24] The reaction/workup given for **1** was repeated with $HOCH_2CH_2CH_2CH_2CH_2R_{f8}$ (3.03 g, 5.99 mmol)[24] and the Dess−Martin reagent (2.79 g, 6.59 mmol). This gave **3** as a clear oil (2.72 g, 5.39 mmol, 90%). − IR (cm^{-1}, $CHCl_3$) $\nu_{C=O}$ 1724. − ^1H NMR ($CDCl_3$):[33] δ = 1.62−1.78 (m, 4 H, CH_2C$H_2$$CH_2R_{f8}$), 2.01−2.23 (m, 2 H, CH_2R_{f8}), 2.52 (td, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 1 Hz, 2 H, O=CHCH_2), 9.79 (t, $^3J_{HH}$ = 1 Hz, 1 H, O=CH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ =

20.0, 21.6 (2s, 2 C, $CH_2CH_2CH_2R_{f8}$), 30.9 (t, $^2J_{CF}$ = 22 Hz, CH_2R_{f8}), 43.6 (s, O=CHCH_2), 201.5 (s, O=CH).

NH($CH_2C_6H_5$)($CH_2CH_2CH_2R_{f8}$) (4): A Schlenk flask was charged with **1** (1.47 g, 3.08 mmol), THF (15 mL), and $NH_2CH_2C_6H_5$ (0.67 mL, 6.06 mmol). Solid $Na(AcO)_3BH$ (1.30 g, 6.17 mmol) was added with vigorous stirring. After 5 h, 1 N NaOH (10 mL) was added to the waxy solution. The mixture was extracted with ether (3 × 25 mL). The extract was dried ($MgSO_4$), and solvent removal gave an oil. Column chromatography on silica gel (1:3 v/v ether/hexanes) gave **4** as a colorless oil (1.58 g, 2.78 mmol, 90%). − $C_{18}H_{14}F_{17}N$ (567.3): calcd. C 38.11, H 2.48; found C 38.15, H 2.48. − ^{1}H NMR ($CDCl_3$):[33] δ = 1.20 (br s, 1 H, NH), 1.70−1.77 (m, 2 H, $CH_2CH_2R_{f8}$), 2.05−2.19 (m, 2 H, CH_2R_{f8}), 2.66 (t, $^3J_{HH}$ = 7 Hz, 2 H, NCH_2CH_2), 3.74 (s, 2 H, $CH_2C_6H_5$), 7.18−7.31 (m, 5 H, C_6H_5). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ = 21.0 (s, $CH_2CH_2R_{f8}$), 28.9 (t, $^2J_{CF}$ = 22 Hz, CH_2R_{f8}), 48.3 (s, NCH_2CH_2), 54.0 (s, $CH_2C_6H_5$), 127.3, 128.3, 128.7, 140.5 (4s, 6 C, C_6H_5).

NH($CH_2C_6H_5$)($CH_2CH_2CH_2CH_2R_{f8}$) (5): The reaction/workup given for **4** was repeated with **2** (1.34 g, 2.73 mmol), $NH_2CH_2C_6H_5$ (0.60 mL, 5.70 mmol), and $Na(AcO)_3BH$ (1.15 g, 5.46 mmol). This gave **5** as a colorless oil that solidified upon standing (1.37 g, 2.35 mmol, 88%), m.p. 32−33 °C (capillary), 30.2 °C (DSC).[34] − $C_{19}H_{16}F_{17}N$ (581.3): calcd. C 39.25, H 2.77; found C 39.39, H 2.89. − ^{1}H NMR ($CDCl_3$):[33] δ = 1.38 (br s, 1 H, NH), 1.50−1.65 (2m, 4 H, $CH_2CH_2CH_2R_{f8}$), 1.95−2.08 (m, 2 H, CH_2R_{f8}), 2.61 (t, $^3J_{HH}$ = 7 Hz, 2 H, NCH_2CH_2), 3.74 (s, 2 H, $CH_2C_6H_5$), 7.18−7.30 (m, 5 H, C_6H_5). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ = 18.2 (s, $CH_2CH_2R_{f8}$), 29.7 (s, NCH_2CH_2), 30.9 (t, $^2J_{CF}$ = 22 Hz, CH_2R_{f8}), 48.9 (s, NCH_2CH_2), 54.2 (s, $CH_2C_6H_5$), 127.2, 128.3, 128.7, 140.6 (4s, 6 C, C_6H_5).

NH($CH_2C_6H_5$)($CH_2CH_2CH_2CH_2CH_2R_{f8}$) (6): The reaction/workup given for **4** was repeated with **3** (3.01 g, 5.97 mmol), $NH_2CH_2C_6H_5$ (0.97 mL, 8.95 mmol), and $Na(AcO)_3BH$ (1.89 g, 8.95 mmol). This gave **6** as a white solid (3.05 g, 5.12 mmol, 88%), m.p. 33−34 °C (capillary), 27.0 °C (DSC).[34] − $C_{20}H_{18}F_{17}N$ (595.3): calcd. C 40.35, H 3.04; found C 40.40, H 3.09. − ^{1}H NMR ($CDCl_3$):[33] δ = 1.22 (br s, 1 H, NH), 1.35−1.62 (m, 6 H, $CH_2CH_2CH_2CH_2R_{f8}$), 1.91−2.10 (m, 2 H, CH_2R_{f8}), 2.60 (t, $^3J_{HH}$ = 7 Hz, 2 H, NCH_2CH_2), 3.74 (s, 2 H, $CH_2C_6H_5$), 7.18−7.31 (m, 5 H, C_6H_5). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ = 20.3 (s, $CH_2CH_2R_{f8}$), 27.1 (s, $NCH_2CH_2CH_2$), 30.0 (s, NCH_2CH_2), 31.1 (t, $^2J_{CF}$ = 22 Hz, CH_2R_{f8}), 49.3 (s, NCH_2CH_2), 54.3 (s, $CH_2C_6H_5$), 127.1, 128.3, 128.6, 140.7 (4s, 6 C, C_6H_5).

N($CH_2C_6H_5$)($CH_2CH_2CH_2R_{f8}$)$_2$ (7): The reaction given for **4** was repeated with **1** (0.894 g, 1.877 mmol), $NH_2CH_2C_6H_5$ (0.102 mL, 0.938 mmol), and $Na(AcO)_3BH$ (0.596 g, 2.812 mmol). Workup gave a crude oil that was chromatographed on silica gel (1:9 v/v ether/hexanes). This gave **7** as a colorless oil (0.877 g, 0.853 mmol, 91%). − $C_{29}H_{19}F_{34}N$ (1027.4): calcd. C 33.90, H 1.86; found C 33.83, H 1.78. − ^{1}H NMR ($CDCl_3$):[33] δ = 1.72−1.79 (m, 4 H, $CH_2CH_2R_{f8}$), 2.03−2.16 (m, 4 H, CH_2R_{f8}), 2.50 (t, $^3J_{HH}$ = 7 Hz, 4 H, NCH_2CH_2), 3.55 (s, 2 H, $CH_2C_6H_5$), 7.25−7.35 (m, 5 H, C_6H_5). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ = 18.1 (s, 2 C, NCH_2CH_2), 28.8 (t, $^2J_{CF}$ = 22 Hz, 2 C, CH_2R_{f8}), 52.7 (s, 2 C, NCH_2CH_2), 58.8 (s, $CH_2C_6H_5$), 127.5, 128.6, 129.2, 139.3 (4s, 6 C, C_6H_5).

N($CH_2C_6H_5$)($CH_2CH_2CH_2CH_2R_{f8}$)$_2$ (8): The reaction/workup given for **7** was repeated with **2** (1.25 g, 2.55 mmol), $NH_2CH_2C_6H_5$ (0.14 mL, 1.27 mmol), and $Na(AcO)_3BH$ (0.810 g, 3.825 mmol). This gave **8** as a colorless oil (1.14 g, 1.08 mmol, 85%). − $C_{31}H_{23}F_{34}N$ (1055.5): calcd. C 35.27, H 2.19; found C 35.43, H 2.12. − ^{1}H NMR ($CDCl_3$):[33] δ = 1.47−1.63 (m, 8 H, $CH_2CH_2CH_2R_{f8}$), 1.92−2.04 (m, 4 H, CH_2R_{f8}), 2.39 (t, $^3J_{HH}$ = 7 Hz, 4 H, NCH_2CH_2), 3.51 (s, 2 H, $CH_2C_6H_5$), 7.22−7.30 (m, 5 H, C_6H_5). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ = 18.0 (s, 2 C, $CH_2CH_2R_{f8}$), 26.8 (s, 2 C, NCH_2CH_2), 30.8 (t, $^2J_{CF}$ = 22 Hz, 2 C, CH_2R_{f8}), 53.3 (s, 2 C, NCH_2CH_2), 59.1 (s, $CH_2C_6H_5$), 127.2, 128.5, 129.0, 140.0 (4s, 6 C, C_6H_5).

N($CH_2C_6H_5$)($CH_2CH_2CH_2CH_2CH_2R_{f8}$)$_2$ (9): The reaction/workup given for **7** was repeated with **3** (2.15 g, 4.27 mmol), $NH_2CH_2C_6H_5$ (0.23 mL, 2.13 mmol), and $Na(AcO)_3BH$ (1.36 g, 6.41 mmol). This gave **9** as a colorless oil (2.11 g, 1.95 mmol, 91%). − $C_{33}H_{27}F_{34}N$ (1083.5): calcd. C 36.58, H 2.51; found C 36.62, H 2.43. − ^{1}H NMR ($CDCl_3$):[33] δ = 1.21−1.61 (m, 8 H, $CH_2CH_2CH_2CH_2R_{f8}$), 1.92−2.10 (m, 4 H, CH_2R_{f8}), 2.39 (t, $^3J_{HH}$ = 7 Hz, 4 H, NCH_2CH_2), 3.51 (s, 2 H, $CH_2C_6H_5$), 7.22−7.30 (m, 5 H, C_6H_5). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ = 20.2 (s, 2 C, $CH_2CH_2R_{f8}$), 27.0, 27.1 (2s, 4 C, $NCH_2CH_2CH_2$), 31.8 (t, $^2J_{CF}$ = 22 Hz, 2 C, CH_2R_{f8}), 55.6 (s, 2 C, NCH_2CH_2), 59.1 (s, $CH_2C_6H_5$), 127.0, 128.3, 128.9, 140.2 (4s, 6 C, C_6H_5).

NH_2($CH_2CH_2CH_2R_{f8}$) (10): A Schlenk flask was charged with 10% Pd/C (0.150 g, 0.140 mmol) and a solution of **4** (1.21 g, 2.13 mmol) in reagent grade EtOH/hexanes (1:1 v/v, 20 mL), purged with H_2 (2−3 min), and fitted with a thick-walled balloon filled with H_2 (1 atm). The mixture was stirred overnight and filtered through a celite plug (5 cm). The solvent was removed by rotary evaporation and oil pump vacuum to give **10** as a white waxy solid (0.99 g, 2.08 mmol, 98%). − $C_{11}H_8F_{17}N$ (477.2): calcd. C 27.69, H 1.67; found C 27.70, H 1.68. − ^{1}H NMR ($CDCl_3$):[33] δ = 1.00 (br s, 2 H, NH_2), 1.71−1.81 (m, 2 H, $CH_2CH_2R_{f8}$), 2.09−2.27 (m, 2 H, CH_2R_{f8}), 2.70 (t, $^3J_{HH}$ = 7 Hz, 2 H, NCH_2). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ = 21.0 (s, $CH_2CH_2R_{f8}$), 28.8 (t, $^2J_{CF}$ = 22 Hz, CH_2R_{f8}), 48.5 (s, NCH_2).

NH_2($CH_2CH_2CH_2CH_2R_{f8}$) (11): The reaction/workup given for **10** was repeated with **5** (1.37 g, 2.35 mmol) and 10% Pd/C (0.150 g, 0.140 mmol). This gave **11** as a white waxy solid (1.14 g, 1.32 mmol, 99%). − $C_{12}H_{10}F_{17}N$ (491.1): calcd. C 29.34, H 2.05; found C 29.30, H 2.01. − ^{1}H NMR ($CDCl_3$):[33] δ = 1.22 (br s, 2 H, NH_2), 1.49−1.69 (2m, 4 H, $CH_2CH_2CH_2R_{f8}$), 2.01−2.14 (m, 2 H, CH_2R_{f8}), 2.74 (t, $^3J_{HH}$ = 7 Hz, 2 H, CH_2N). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ = 17.7 (s, $CH_2CH_2R_{f8}$), 21.0 (s, NCH_2CH_2), 30.9 (t, $^2J_{CF}$ = 22 Hz, CH_2R_{f8}), 41.9 (s, NCH_2).

NH_2($CH_2CH_2CH_2CH_2CH_2R_{f8}$) (12): The reaction/workup given for **10** was repeated with **6** (1.78 g, 3.00 mmol) and 10% Pd/C (0.200 g, 0.186 mmol). This gave **12** as a white waxy solid (1.51 g, 3.00 mmol, 100%), m.p. 31 °C (capillary), 30.4 °C (DSC).[34] − $C_{13}H_{12}F_{17}N$ (505.2): calcd. C 30.90, H 2.39; found C 30.55, H 2.50. − ^{1}H NMR ($CDCl_3$):[33] δ = 1.15 (br s, 2 H, NH_2), 1.39−1.49 (2m, 4 H, $CH_2CH_2CH_2R_{f8}$), 1.57−1.67 (m, 2 H, NCH_2CH_2), 1.97−2.15 (m, 2 H, CH_2R_{f8}), 2.71 (t, $^3J_{HH}$ = 7 Hz, 2 H, NCH_2). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ = 20.3 (s, $CH_2CH_2R_{f8}$), 26.6 (s, $CH_2CH_2CH_2R_{f8}$), 31.1 (t, $^2J_{CF}$ = 22 Hz, CH_2R_{f8}), 33.6 (s, NCH_2CH_2), 42.1 (s, NCH_2).

NH($CH_2CH_2R_{f8}$)$_2$ (13): The reaction/workup given for **10** was repeated with **7** (0.91 g, 0.88 mmol) and 10% Pd/C (0.150 g, 0.140 mmol). This gave **13** as a white solid (0.78 g, 0.84 mmol, 95%), m.p. 43−44 °C (capillary), 43.6 °C (DSC).[34] − $C_{22}H_{13}F_{34}N$ (937.3): calcd. C 28.19, H 1.39; found C 28.21, H 1.39. − ^{1}H NMR ($CDCl_3$):[33] δ = 1.26 (br s, 1 H, NH), 1.74−1.81 (m, 4 H, $CH_2CH_2R_{f8}$), 2.09−2.24 (m, 4 H, CH_2R_{f8}), 2.70 (t, $^3J_{HH}$ = 7 Hz, 4 H, NCH_2). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ = 20.9 (s, 2

C, $CH_2CH_2R_{f8}$), 28.8 (t, $^2J_{CF}$ = 22 Hz, 2 C, CH_2R_{f8}), 48.5 (s, 2 C, NCH_2).

$NH(CH_2CH_2CH_2CH_2R_{f8})_2$ (14): The reaction/workup given for **10** was repeated with **8** (1.25 g, 1.18 mmol) and 10% Pd/C (0.160 g, 0.150 mmol). This gave **14** as a white solid (1.12 g, 1.17 mmol, 99%), m.p. 61−62 °C (capillary), 61.1 °C (DSC).[34] − $C_{24}H_{17}F_{34}N$ (965.3): calcd. C 30.11, H 1.79; found C 29.94, H 1.86. − ^{1}H NMR ($CDCl_3$):[33] δ = 1.16 (br s, 1 H, NH), 1.53−1.71 (2m, 8 H, $CH_2CH_2CH_2R_{f8}$), 2.02−2.16 (m, 4 H, CH_2R_{f8}), 2.65 (t, $^3J_{HH}$ = 7 Hz, 4 H, NCH_2). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ = 18.3 (s, 2 C, $CH_2CH_2R_{f8}$), 29.7 (s, 2 C, NCH_2CH_2), 30.9 (t, $^2J_{CF}$ = 22 Hz, 2 C, CH_2R_{f8}), 49.5 (s, 2 C, NCH_2).

$NH(CH_2CH_2CH_2CH_2CH_2R_{f8})_2$ (15): The reaction/workup given for **10** was repeated with **9** (1.62 g, 1.50 mmol) and 10% Pd/C (0.200 g, 0.186 mmol). This gave **15** as a white solid (1.36 g, 1.37 mmol, 92%), m.p. 66−68 °C (capillary), 66.6 °C (DSC).[34] − $C_{26}H_{21}F_{34}N$ (993.4): calcd. C 31.61, H 2.04; found C 31.56, H 2.10. − ^{1}H NMR ($CDCl_3$):[33] δ = 1.38−1.68 (m, 9 H, NH, $CH_2CH_2CH_2R_{f8}$), 1.98−2.16 (m, 4 H, CH_2R_{f8}), 2.62 (t, $^3J_{HH}$ = 7 Hz, 4 H, NCH_2). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ = 20.3 (s, 2 C, $CH_2CH_2R_{f8}$), 27.1 (s, 2 C, $CH_2CH_2CH_2R_{f8}$), 30.0 (s, 2 C, NCH_2CH_2), 31.1 (t, $^2J_{CF}$ = 22 Hz, 2 C, CH_2R_{f8}), 49.9 (s, 2 C, NCH_2).

$N(CH_2CH_2CH_2R_{f8})_3$ (16): A Schlenk flask was charged with **13** (1.00 g, 1.06 mmol), THF (15 mL), and a solution of **1** (0.608 g, 1.28 mmol) in THF (10 mL). Solid $Na(AcO)_3BH$ (0.338 g, 1.60 mmol) was added with vigorous stirring. After 4 h, 1 N NaOH (15 mL) was added to the waxy solution. The mixture was extracted with ether (3 × 20 mL). The extract was dried ($MgSO_4$), and solvent removal gave a solid residue. Column chromatography on silica gel (1:3 v/v ether/hexanes) gave **16** as a white solid (1.43 g, 1.02 mmol, 97%), m.p. 44 °C (capillary), 44.3 °C (DSC).[34] − $C_{33}H_{18}F_{51}N$ (1397.4): calcd. C 28.36, H 1.29; found C 28.37, H 1.28. − ^{1}H NMR ($CDCl_3$):[33] δ = 1.68−1.77 (m, 6 H, $CH_2CH_2R_{f8}$), 2.03−2.21 (m, 6 H, CH_2R_{f8}), 2.47 (t, $^3J_{HH}$ = 7 Hz, 6 H, NCH_2). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ = 20.9 (s, 3 C, $CH_2CH_2R_{f8}$), 28.8 (t, $^2J_{CF}$ = 22 Hz, 3 C, CH_2R_{f8}), 52.7 (s, 3 C, NCH_2).

$N(CH_2CH_2CH_2CH_2R_{f8})_3$ (17): The reaction/workup given for **16** was repeated with **14** (0.980 g, 1.023 mmol), **2** (0.501 g, 1.02 mmol), and $Na(AcO)_3BH$ (0.325 g, 1.53 mmol). This gave **17** as a white solid (1.41 g, 0.98 mmol, 96%), m.p. 37−38 °C (capillary), 38.5 °C (DSC).[34] − $C_{36}H_{24}F_{51}N$ (1439.5): calcd. C 30.03, H 1.68; found C 30.03, H 1.70. − ^{1}H NMR ($CDCl_3$):[33] δ = 1.46−1.68 (m, 12 H, $CH_2CH_2CH_2R_{f8}$), 2.02−2.18 (m, 6 H, CH_2R_{f8}), 2.39 (t, $^3J_{HH}$ = 7 Hz, 6 H, NCH_2). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ = 18.2 (s, 3 C, $CH_2CH_2R_{f8}$), 27.0 (s, 3 C, $CH_2CH_2CH_2R_{f8}$), 31.9 (t, $^2J_{CF}$ = 22 Hz, 3 C, CH_2R_{f8}), 53.7 (s, 3 C, NCH_2).

$N(CH_2CH_2CH_2CH_2CH_2R_{f8})_3$ (18): The reaction/workup given for **16** was repeated with **15** (0.869 g, 0.874 mmol), **3** (0.441 g, 0.874 mmol), and $Na(AcO)_3BH$ (0.278 g, 1.31 mmol). This gave **18** as a white solid (1.12 g, 0.754 mmol, 86%), m.p. 44−45 °C (capillary), 45.4 °C (DSC).[34] − $C_{39}H_{30}F_{51}N$ (1481.6): calcd. C 28.36, H 1.29, N 1.00; found C 28.37, H 1.28, N 1.01. − ^{1}H NMR ($CDCl_3$):[33] δ = 1.39−1.42 (m, 12 H, $CH_2CH_2CH_2R_{f8}$), 1.55−1.67 (m, 6 H, NCH_2CH_2), 1.96−2.14 (m, 6 H, CH_2R_{f8}), 2.37 (t, $^3J_{HH}$ = 7 Hz, 6 H, NCH_2). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, partial):[33] δ = 20.3 (s, 3 C, $CH_2CH_2R_{f8}$), 27.2 (s, 6 C, $CH_2CH_2CH_2CH_2R_{f8}$), 31.0 (t, $^2J_{CF}$ = 22 Hz, 3 C, CH_2R_{f8}), 53.9 (s, 3 C, NCH_2).

Partition Coefficients:[11,26] The following is representative. A 10 mL vial was charged with **13** (0.0240 g, 0.0240 mmol), $CF_3C_6F_{11}$ (2.000 mL), and toluene (2.000 mL), fitted with a mininert valve, vigorously shaken (2 min), and immersed (cap-level) in a 35 °C oil bath. After 12 h, the bath was removed. After 12−24 h (24 °C), a 0.400 mL aliquot of each layer was added to 2.000 mL of a 0.0273 M solution of hexadecane in hexane. GC analysis (average of 7−8 injections) showed 0.00412 mmol of **13** in the $CF_3C_6F_{11}$ aliquot and 0.000398 mmol in the toluene aliquot (91.2:8.8; a 2.000:0.400 scale factor gives a mass balance of 0.0222 g, 93%).

Basicity Determinations: The following is representative. Six vials were charged with **18** (0.0306 g, 0.0206 mmol). Solutions of CF_3CO_2H in $CDCl_3$ (0.0206 M) were added to five vials to give 0.25, 0.50, 0.75, and 1.00 CF_3CO_2H/**18** mol ratios. Additional $CDCl_3$ was added to each vial to give 2.00 mL solutions. Subsequent ^{1}H NMR analyses gave the calibration curves in Figure 2. Next, a vial was charged with **18** (0.0306 g, 0.0206 mmol), a solution of CF_3CO_2H in $CDCl_3$ (1.00 mL, 0.0206 M), and a solution of $N(CH_2CH_3)_3$ in $CDCl_3$ (1.00 mL, 0.0206 M). The vial was capped, shaken, and analyzed by ^{1}H NMR to give the equilibrium data in Table 2.

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