Separation of "Light Fluorous" Reagents and Catalysts by Fluorous Solid-Phase Extraction: Synthesis and Study of a Family of Triarylphosphines Bearing Linear and Branched Fluorous Tags

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Practical syntheses of new triarylphosphines bearing both linear and branched fluorous tags (Rf) are reported. The phosphines have one, two, or all three aryl rings bearing fluorous tags: $(Ph)_{3-n}P(C_6H_4(CH_2)_mRf)_n$. Fluorous−organic partition coefficients have been measured and the retention properties of both the phosphines and the derived phosphine oxides on fluorous reverse phase silica have been studied. While applications relying on liquid−liquid extractive separations of these phosphines may be limited to those bearing three fluorous chains, the technique of solid phase extraction should be broadly applicable to phosphines, phosphine oxides, and derived metal complexes. A parallel platinum-catalyzed allylation of aldehydes with fluorous allyl stannanes illustrates the usefulness of the new fluorous ligands in small-scale synthesis.

Introduction

Fluorous techniques for the synthesis of small organic molecules are becoming increasingly useful as more and more fluorous compounds are synthesized and studied.[1] These techniques are attractive for strategic separation of reaction mixtures since fluorous-tagged compounds can be quickly separated from nontagged compounds in binary liquid−liquid and solid−liquid extractions.[2] The fluorine content of a fluorous molecule is a crucial feature that must be balanced to obtain suitable performance during both the reaction and the separation. The opposing needs at these two stages are beginning to divide the fluorous field into two branches, which we have recently termed "heavy fluorous" and "light fluorous". As Figure 1 illustrates, these two techniques are ends of a continuum with a considerable gray area in between.

On the heavy end, the original fluorous biphasic catalysis (FBC) and allied techniques[3] strive for very high partition coefficients in liquid−liquid separation. This requires fluorous reagents and catalysts with large numbers of fluorines. While this ensures easy separation, the large numbers of fluorines tend to render the fluorous compounds insoluble in typical organic reaction solvents, and fluorous cosolvents are used. These solvents have poor dissolving power for organic compounds, so the modification and optimization of reaction conditions is often required. However, once suitable conditions are found, the resulting heavy fluorous techniques are very powerful, especially when applied to catalytic reactions.

On the light end, the goal is to reduce the number of fluorines to provide fluorous compounds that have properties more similar to their organic parents. While reduction of the fluorine content can allow the use of standard literature reaction conditions with little or no modification, this quickly compromises the separation of fluorous from nonfluorous components by liquid−liquid extraction. However, the recently introduced technique of fluorous solid-phase extraction[4] is proving far superior to liquid−liquid extractions for compounds with fewer fluorines. Light fluorous techniques are especially useful for small-scale and discovery-oriented research, including parallel synthesis applications[5] and so-called techniques of fluorous synthesis.[6]

Fluorous biphasic catalysis was the original fluorous technique introduced in 1994 by Horváth and Rábai,[7] and this technique is catching on in the catalysis community. Most of the work in this area involves the use of fluorous phosphines and phosphites.[8] The original trialkylphosphine ligand $[P(CH_2CH_2C_6F_{13})_3]$ introduced by Horváth and Rábai has proved useful in a number of reactions catalyzed by rhodium and iridium.[9] More recently, a number of fluorous analogues of triphenylphosphine have appeared, and several of these are shown in Figure 2. Phosphine **1a** was introduced by Leitner for reactions in

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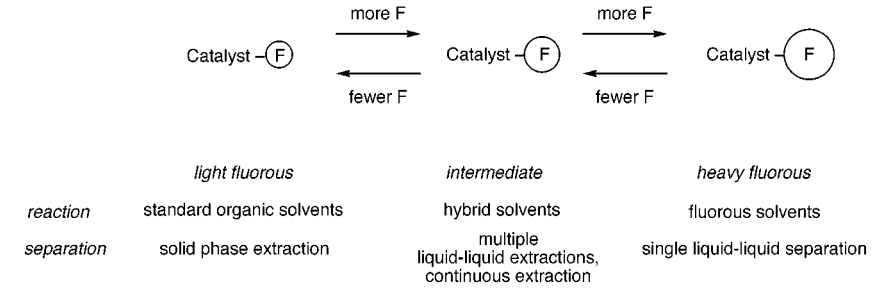

Figure 1. The effect of the size of the fluorous tag on reaction and separation.

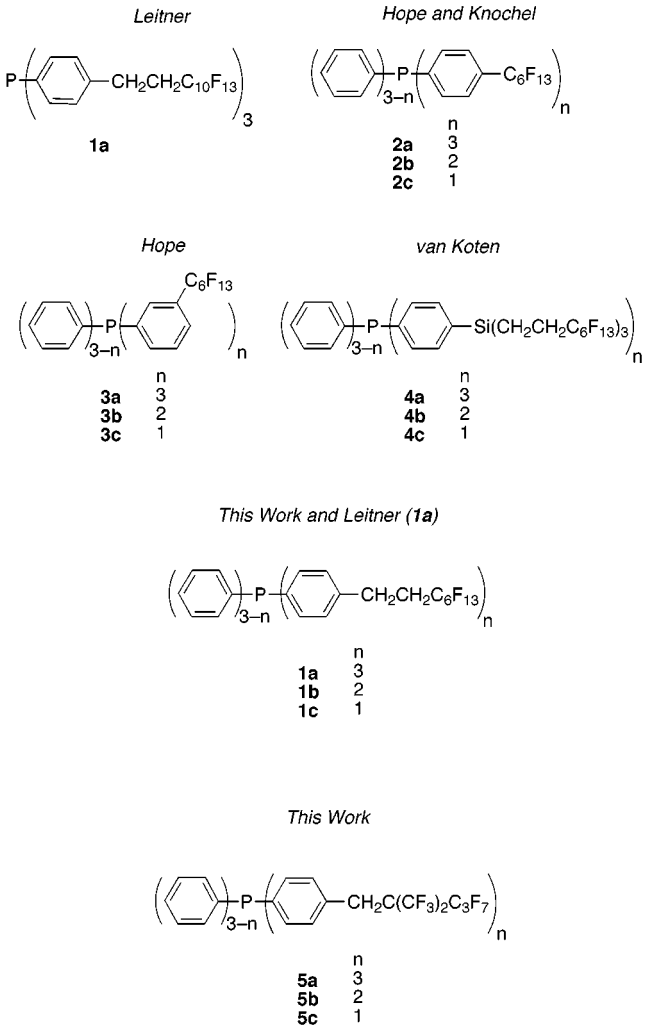

Figure 2. Known fluorocarbon-tagged triarylphosphines.

supercritical carbon dioxide[10] and has also found use in an FBC variant of the popular palladium-catalyzed allylic substitution (Tsuji/Trost) reaction.[11] Related phosphine **2a** lacking the ethylene spacer has been used by Knochel as a ligand for palladium-catalyzed Negishi couplings and Heck reactions.[12] Hope and co-workers have prepared families of phosphines bearing only one, two, and three fluorous chains in both the para (**2a**−**c**) and meta (**3a**−**c**) series and studied the properties of several organometallic complexes of these ligands.[13] Ligands with a silyl spacer (see **4a**) have been synthesized and studied by van Koten and co-workers.[14]

An important conclusion drawn from most of these studies on phosphines as well as studies on other classes of ligands has been that more fluorines are needed rather than fewer for fluorous reactions. It seems generally accepted that 39 fluorines is a minimum useful level, and more fluorines may be needed in a number of cases. Our work on light fluorous techniques[4b,c] led us to suppose that this generalization was premature. We hypothesized that more lightly fluorinated phosphines and relatives such as phosphine oxides and organometallic complexes would be readily separable from organic reaction components by fluorous solid-phase extraction. We therefore undertook the synthesis and study of two related families of linear (**1a**−**c**) and branched (**5a**−**c**) fluorous phosphines shown in Figure 2. We have indeed found that phosphines and derivatives with fewer than 39 fluorines are well-retained on fluorous reverse phase silica gel. Our work suggests that many of the previously synthesized fluorous compounds that have been pronounced dead because they have too few fluorines for liquid−liquid extraction techniques can be resurrected for use with solid−liquid extractive workups.

Results and Discussion

The impetus to synthesize and study fluorous-tagged phosphines emerged from our recent study on allylations with fluorous allylstannane.[15] Reagents **6a**,**b** bearing a propylene spacer were prepared and used in the platinum-catalyzed allylation shown in eq 1. Small libraries of alcohols were conveniently prepared by parallel synthesis with separation of the fluorous tin residues by solid-phase extraction over fluorous reverse-phase silica gel. Lewis

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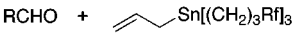
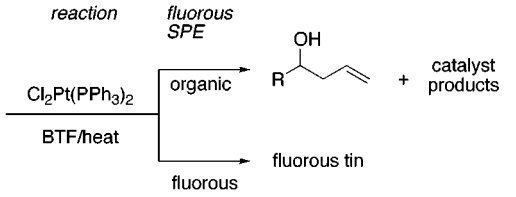
acid catalyzed and radical allylations were also conducted with the propylene-spaced tin reagents (not shown),[15] and these were clearly superior to their lower homologues with ethylene spacers. While the radical and Lewis acid procedures proved very practical for parallel synthesis, the platinum-catalyzed procedure did not. This is because the fluorous solid-phase extraction does not separate any remnant of the catalyst from the desired organic products in eq 1. To solve this problem, we have prepared a series of fluorous phosphines, converted these into platinum catalysts, and then restudied the allylation to ascertain whether ligand-free products could be obtained.



6a Rf = C_4F_9
6b Rf = C_6F_{13}

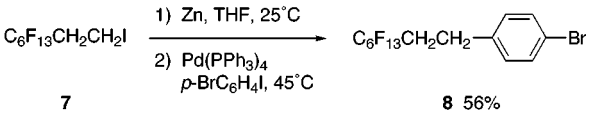


(1)

The syntheses of two related series of phosphines are shown in eqs 2 and 3. Phosphine **1a** was already known from the work of Leitner,[10] and we originally used his procedure to prepare it. However, during the course of this work, several modifications were made to improve its synthesis (eq 2). The Leitner protocol (not shown) for synthesis of aryl bromide **8** calls for coupling of perfluorohexylethyl iodide **7** with the Grignard reagent derived from 1,4-dibromobenzene. This provides the aryl bromide **8** along with substantial amount of Wurtz coupled product ($C_6F_{13}CH_2CH_2CH_2CH_2C_6F_{13}$). We developed a convenient procedure to separate these on small scale by using fluorous silica,[16] but large-scale separation is difficult because the two compounds have similar polarities and boiling points. We found that palladium-catalyzed coupling of an organozinc reagent derived from **7** with 1-iodo-4-bromobenzene gave a much cleaner product **8**. Little or no Wurtz coupled product was obtained, provided that the temperature was not allowed to rise above 25 °C during formation of the zinc reagent. The coupling process was accomplished at 45 °C; again, higher temperatures gave lower yields. Bromide **8** can be reliably synthesized by this procedure in about 56% yield (after distillation) on scales up to at least 30 g. The lower homologue bearing a C_4F_9 group and the meta-isomer were synthesized in comparable yields by the same procedure (not shown).

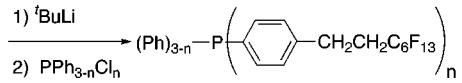
Leitner prescribes the use of *n*-BuLi for the generation and reaction of the lithium reagent derived from **8**, but we found improved results with *t*-BuLi. Halogen/lithium exchange followed by quenching with PCl_3 provided Leitner's phosphine **1a** in 78% isolated yield. Likewise, quenching with $PhPCl_2$ and Ph_2PCl provided the new phosphines **1b** and **1c** in even higher yields.

As far as we know, there are currently no examples of fluorous tags based on branched (rather than linear)



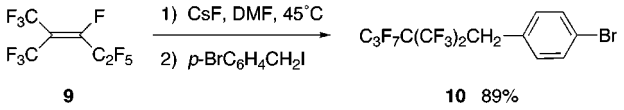
7 **8** 56%

(2)



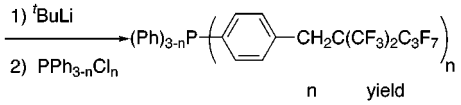
	n	yield
1a	3	78%
1b	2	90%
1c	1	81%

fluorocarbon fragments. These are of interest because branched tags may confer improved solubility. In addition, the branched tags that we have prepared have no C−H bonds β to fluorine. This design feature eliminates any possible HF elimination reactions of the tag under strongly basic conditions. To prepare the requisite aryl bromides with branched tags, we modified a procedure recently reported by Chambers and co-workers (eq 3).[17] They found that reaction of *p*-bromobenzyl bromide and perfluoroalkene **9** with cesium fluoride in sulfolane provided the fluoroalkylated product **10** in 62% yield, contaminated with substantial amounts of *p*-bromobenzyl fluoride. We found that this direct fluoride substitution product could be suppressed by using *p*-bromobenzyl iodide and by changing the solvent to DMF. This reduced the reaction time from 8 days to less than 4 days and improved the yield of **10** to 89%.



9 **10** 89%

(3)



	n	yield
5a	3	49%
5b	2	68%
5c	1	51%

Metalation of **10** and reaction with PCl_3, $PhPCl_2$, and Ph_2PCl then provided the phosphines **5a**−**c** with branched tags in acceptable yields (49−68%). In these experiments, significant amounts of the phosphine oxides **12a**−**c** were also obtained (12−20%, see eq 4), and these could be reduced to provide additional phosphine (see below). The branched phosphines **5a**−**c** are not isomers of the linear phosphines **1a**−**c**; they have one fewer CH_2 group. However, both series have the same number of "spacer" carbons (2) between the aryl ring and the fluoroalkyl group(s). Authentic samples of the phosphine oxides **11a**−**c** derived from **1a**−**c** were prepared in high yields by standard oxidation with hydrogen peroxide, as shown in eq 4.

^{31}P NMR experiments showed that the chemical shifts of the new phosphines (see Experimental Section) were all in a narrow range between triphenylphosphine (δ =

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Table 1. Retention Times (min) of Phosphines and Phosphine Oxides on a Fluofix Column[a]

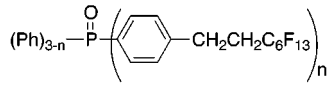
phosphine or phosphine oxide	t_R a	b	c
linear phosphines, **1a**−**c**	38.9	29.8	13.9
linear phosphine oxides, **11a**−**c**	37.7	28.3	10.6
branched phosphines, **5a**−**c**	42.5	30.0	12.6
branched phosphine oxides **12a**−**c**	38.9	27.9	9.1

[a] Gradient: $t = 0$ min, 80% MeOH; 20% H_2O; $t = 30$ min, 100% MeOH; $t = 60$ min, 90% MeOH, 10% THF.

−5.0) and tri(*p*-tolyl)phosphine) ($\delta = -7.26$). Indeed, the range of ^{31}P chemical shifts of our phosphines and all those in Figure 2 is very small (<3 ppm).

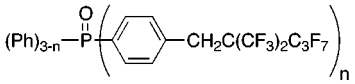
$$Ar_3P \xrightarrow{3\%\ H_2O_2} Ar_3P{=}O \qquad (4)$$

linear (from oxidation)



	n	yield
11a	3	86%
11b	2	90%
11c	1	100%

branched (from eq 3)



	n
12a	3
12b	2
12c	1

We next evaluated the phosphines and phosphine oxides by analytical HPLC to assess their potential for removal by solid-phase extraction. Pure samples were injected on a commercial Fluofix column (bonded phase: $-Si(Me)_2CH_2CH_2CH_2C(CF_3)_2C_3F_7$). Under isocratic conditions, the compounds with differing numbers of fluorous tags were so widely separated as to make collective analysis impossible. We therefore employed a gradient starting with 80% MeOH/H_2O increasing to 100% MeOH over 30 min (flow rate, 1.5 mL/min). THF was then introduced in a second gradient to reach a final solvent composition of 90% MeOH/10% THF after an additional 30 min.

The retention times of the tagged phosphines and phosphine oxides are shown in Table 1. Triphenylphosphine and triphenylphosphine oxide come off with the solvent front under these conditions ($t_R = 1.6$ min), and experience suggests that most other organic compounds would do likewise.[4b] The tagged phosphines and phosphine oxides then emerge in groups based on the number of tags. This is expected since fluorous silica separates molecules primarily by fluorine content. Molecules with a single chain ("**c**" series) emerge at 9−14 min, those with two chains ("**b**" series) emerge at 28−30 min, and those with three chains ("**a**" series) emerge at 38−42 min. Since the solvent changes at 30 min (THF is introduced), the absolute spacing between the groups is not directly comparable. Indeed, THF is a relatively powerful eluting solvent for fluorous molecules, and we suspect that on any absolute scale the gap between triply (**a**) and doubly (**b**) tagged molecules would be larger than the gap between doubly (**b**) and singly (**c**) tag molecules. However, these gaps are so large as to make them difficult to measure.

Table 2. Partition Coefficients of Fluorous Aryl Phosphines at Room Temperature in 50/50 (v/v) of FC-72/Organic Solvents ($P = c_{\text{fluorous phase}}/c_{\text{organic phase}}$)

compd	F content (wt %)	FC-72/ methanol	FC-72/ THF	FC-72/ toluene
1a	57	30.03	0.08	0.75
1b	52	1.86	0.05	0.05
1c	41	0.12	0.02	0.05
5a	59	18.48	0.51	6.84
5b	53	3.34	1.05	0.18
5c	42	0.09	0.01	0.12

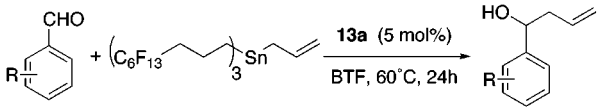
The phosphine oxides reliably eluted 1−3 min before the analogous phosphines. This is because the phosphine oxides have a lower fluorine content (on a percentage basis) than the phosphines and (probably more importantly) because they are more polar. (Fluorous silica tends to effect polar/nonpolar separation in a reverse-phase fashion.) The comparison of the linear and branched compounds is more interesting. With one fluorous tag, the branched compound **5c** emerges about 1 min before the linear **1c**; with two tags, the retention times of **5b** and **1b** are nearly identical, and with three tags, the linear compound **1a** emerges almost 4 min before the branched **5a**. The trend for the corresponding phosphine oxides is similar.

We also measured liquid−liquid partition coefficients for all six phosphines between FC-72 and three organic solvents (methanol, THF, and toluene).[3e] The procedure involved a simple partitioning followed by HPLC analysis, as described in the Experimental Section. Measurements were reproducible within 10% or less, and the data are shown in Table 2.

Only the triply fluorous phosphines **1a** and **5a** show sufficiently high partition coefficients for separation by liquid−liquid extraction, and only against methanol (other polar organic solvents may also be suitable). THF has good dissolving power for fluorous compounds and not surprisingly provides low partition coefficients. Toluene is a very fluorophobic solvent with respect to fluorous tin reagents [$(RfCH_2CH_2)_3SnX$], but it has good dissolving power for these phosphines (presumably due to the aromatic rings), so low partition coefficients result. Van Koten and co-workers have recently reported examples where compounds with more fluorous chains had lower partition coefficients than those with fewer, and we also observed this phenomenon. Whether phosphines are useful as ligands for removal of organometallic complexes by liquid−liquid extraction is less clear. Presumably, most monophosphine metal complexes will have a lower partition coefficient than **1a** and **5a** themselves; however, polyphosphine complexes could well have higher partition coefficients.

Platinum catalysts were prepared from all six of the phosphines by reaction with platinum dichloride, as shown in eq 5. The catalysts were isolated in excellent yields (82−86%) as white or yellow solids after recrystallization from dichloromethane/ether, and each exhibited the expected molecular ion peak in the mass spec-

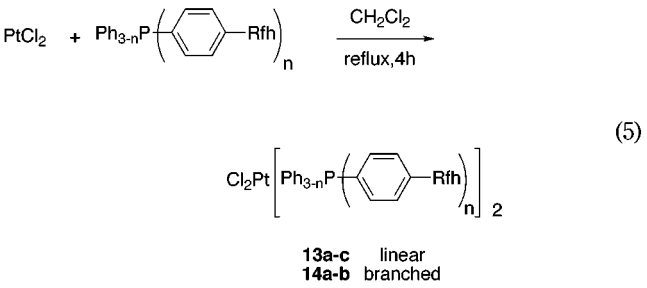
Table 3. Parallel Allylations with Catalyst 13a



6b **15**

entry	R	NMR yield (%)	GC−MS purity (%)
1	2,4-dinitro	100	100
2	2,4-dichloro	56	100
3	2-chloro-5-nitro	67	100
4	2-nitro	98	100
5	2-trifluoromethyl	77	100
6	4-trifluoromethyl	66	100
7	2-bromo	60	100
8	3-bromo	71	100

trum. By analogy to the work of Hope,[13b−d] the catalysts are assigned the cis geometry.



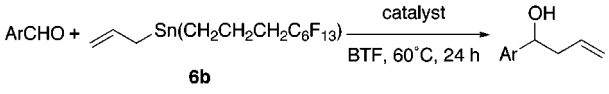
(5)

13a-c linear
14a-b branched

Entry	Phosphine	Product	Rfh	n	Yield (%)
1	**1a**	**13a**	$(CH_2)_2C_6F_{13}$	3	85
2	**1b**	**13b**	$(CH_2)_2C_6F_{13}$	2	83
3	**1c**	**13c**	$(CH_2)_2C_6F_{13}$	1	85
4	**5a**	**14a**	$CH_2C(CF_3)_2C_3F_7$	3	82
5	**5b**	**14b**	$CH_2C(CF_3)_2C_3F_7$	2	86

We initially tested the catalyst **13a** with three linear fluorous chains in allylations with the fluorous allylstannane **6b** to see if it solved the problem of catalyst contamination of the organic product identified in eq 1. The results of a series of parallel experiments are shown in Table 3. A BTF solution of an aldehyde, fluorous allylstannane **6b**, and catalyst **13a** (5 mol %) was heated for 24 h at 60 °C. The solution was concentrated and the residue was charged to fluorous reverse phase silica gel. The silica was eluted with 90% methanol−water to give an organic fraction which was evaporated and analyzed for yield (by NMR against an internal standard) and purity (by GC). All eight products were formed in good yields (60−100%) and excellent purities (every product gave a single peak on GC analysis). Neither fluorous tin resonances nor phosphine resonances could be detected in the ^{1}H NMR spectra of the products. This is in contrast to the experiments in eq 1, where aromatic phosphine resonances were clearly visible in the spectrum of the organic product. Similar experiments (not shown) also suggested that **13b** was an effective catalyst and provided pure product. Catalyst **13c** also promoted the reaction, but traces of fluorous phosphine resonances were evident in the NMR spectrum of the organic product. On the basis of the HPLC retention times in Table 1, we believe that the solid-phase extraction could be optimized to remove these traces by increasing the water content in the first stage, but we have not yet done this.

Table 4. Parallel Allylations with 13b, 14a, and 14b



6b

entry	aldehyde[a]	catalyst	% conversion	% yield	% purity
1	2,4-DNB	**13b**	100	92	98
2	2,4-DNB	**14a**	100	98	99
3	2,4-DNB	**14b**	100	96	99
4	2-NP	**13b**	69	89	99
5	2-NP	**14a**	74	89	99
6	2-NP	**14b**	73	94	95

[a] 2,4-DNB = 2,4-dinitrobenzaldehyde; 2-NP = 2-naphthaldehyde.

To better probe the utility of some of the other catalysts, we conducted a parallel synthesis experiment with two aldehydes and three catalysts: **13b**, **14a**, and **14b**. The reaction and workup conditions were the same as in Table 3, and the conversion (by ^{1}H NMR), yield (by ^{1}H NMR), and purity (by GC) of the products are shown in Table 4. All three reactions with the more reactive 2,4-dinitrobenzaldehyde worked very well and essentially gave pure products in nearly quantitative yields. The three reactions with 2-naphthaldehyde were not complete, however, but the only detectable contaminant in the product was the starting aldehyde. (Reactions with naphthaldehyde can be driven to completion by heating for 3 days.) Importantly, the solid-phase extractive workup served to remove all fluorous tin and catalyst residues as judged by proton NMR.

Catalysts **13** and **14** have good solubility in typical organic solvents, and to show that fluorinated solvents or cosolvents are not required, we conducted a reaction of 2,4-dinitrobenzaldehyde and allylstannane **6** with catalyst **14b** under the standard literature conditions in THF (without BTF). The reaction proceeded smoothly over 24 h and gave the product in 92% yield. The ability to directly apply literature reaction conditions with little or no modification is an especially attractive feature of light fluorous molecules.

Finally, we conducted one experiment to probe whether the catalyst or ligand could be recovered from the solid-phase extraction. To remove the fluorous tin residue from the fluorous fraction, we used allyltributylstannane in place of **6b**. This stannane was coupled with 2,4-dinitrobenzaldehyde in THF by using catalyst **14b**, followed by solid-phase extraction. Initial elution with 90% MeOH/H_2O provided the alcohol product contaminated (as expected) with the tributyltin product (presumably $Bu_3SnOSnBu_3$). Continued elution with MeOH provided a little more tin residue. Subsequent elution with THF provided a trace of phosphine oxide **11b** mixed with other unidentified products, while subsequent elution with hexane and FC-72 provided nearly nothing. Apparently, neither the catalyst nor the ligand are recyclable under these conditions, and at this point we do not know what their fate is.

Conclusions

We have described practical methods to synthesize new fluorous triarylphosphines bearing one, two, or three

fluorous tags. The tags can be linear or branched, and the resulting phosphines and phosphine oxides are well-retained on fluorous reverse-phase silica gel under conditions where most organic compounds elute with the solvent front. The compounds with three fluorous chains can probably be removed by FC-72 extractions against polar solvents. Despite the low liquid−liquid partition coefficients, all compounds appear practical for solid−liquid extractions. Platinum catalysts derived from the ligands have good organic solubility and promote allylations of aldehydes with a fluorous allylstannane, but all the fluorous components of the reaction mixtures (including the catalyst remnants) can be removed by solid-phase extraction.

Beyond the introduction and study of new classes of fluorous-tagged phosphines, the work described in this paper has a number of more general implications. First and perhaps foremost, the use of solid-phase extractions is proving to be very general, and it allows one to reduce the fluorous content of a tagged molecule. This is helpful in discovery-oriented synthesis and parallel synthesis, since it allows one to simply adopt standard reaction conditions; there is no need to search for suitable fluorinated solvents or cosolvents. Second, early work in the fluorous biphasic catalysis area appears to have underestimated the number of fluorine atoms needed to secure high partition coefficients for liquid−liquid extractions in the aryl phosphine series, and the trend is toward synthesizing phosphines with more fluorines. However, existing "lightly fluorous" phosphines from several groups will certainly be separable by fluorous solid-phase extraction, so their potential utility in small-scale and parallel synthesis should not be overlooked. Finally, the method used to make branched tagged arylphosphines in this work should be useful for making other types of branched fluorous reagents, protecting groups, etc. This will allow the comparison of the relative merits of branched versus linear tags for the first time.

Experimental Section

General. All air and/or moisture-sensitive reactions were run under an atmosphere of argon. Tetrahydrofuran (THF) and diethyl ether were freshly distilled from sodium benzophenone ketyl under nitrogen. Methylene chloride and *N*,*N*-dimethylformamide (DMF) were distilled from calcium hydride under nitrogen. HPLC analysis was performed on a Waters 2487 system using a Fluofix 120E column with detection by UV.

1-Bromo-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-benzene (8). To a 250 mL, three-neck flask equipped with dropping funnel was added zinc powder (9.50 g, 146.2 mmol) and dry THF (20 mL) under argon. 1,2-Dibromoethane (0.5 mL) was added and the mixture was heated at 65 °C for 2 min. The mixture was then cooled to room temperature. Chlorotrimethylsilane (0.5 mL) was added and the mixture was stirred at room temperature for 20 min. A solution of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl iodide (57.8 g, 126.6 mmol) in dry THF (100 mL) was added dropwise to keep the temperature of the solution at room temperature. The reaction mixture was stirred at room temperature for 12 h. The colorless solution was then transferred via cannula to a solution of 1-bromo-4-iodobenzene (35.8 g, 126.6 mmol) and tetrakis(triphenylphosphine) palladium(0) (5.0 g, 4.3 mmol) in THF (60 mL). After 24 h at 45 °C, the solvent was removed under vacuum. The residue was dissolved in methylene chloride (50 mL) and extracted with FC-72 (50 mL) six times. The combined FC-72 layers were concentrated. Vacuum distillation of the residue gave **8** (34.3 g, 56%) as a colorless liquid: bp 79.1−80.9 °C/0.03 mmHg; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (tt, J = 18.3, 9.1 Hz, 2H), 2.86−2.92 (m, 2H), 7.11 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.1, 32.9 (t, J_{FC} = 22.1 Hz), 105.5−123.2 (m, C_6F_{13}), 120.7, 130.1, 132.1, 138.3; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −125.6 (2F), −122.9 (2F), −121.7 (2F), −120.7 (2F), −113.4 (2F), −79.6 (3F); IR ($CHCl_3$) 3065, 2954, 2879, 1490, 1237, 1145, 1013, 810 cm^{-1}; EIMS *m*/*z* 502/504 (M^+), 423, 169/171 $(M - C_6F_{13}CH_2)^+$.

1-Bromo-4-(3,3,4,4,5,5,5-heptafluoro-2,2-bis(trifluoromethyl)pentyl)benzene (10). A 250 mL, three-neck flask was charged with perfluoro-2-methylpent-2-ene (27.0 g, 90 mmol), dry cesium fluoride (13.4 g, 88 mmol), and dry DMF (65 mL) under argon. The solution was stirred at 45 °C for 36 h. 4-Iodobenzyl bromide (17.8 g, 59.9 mmol) was added, and the mixture was heated at 65 °C for 14 h. The mixture was cooled to room temperature and poured into a 2 L separatory funnel with 1200 mL water. The organic layer was dried and evaporated and the residue was loaded onto a silica gel column. Eluting with hexanes−ethyl acetate (40:1) gave **10** (26.1 g, 89%) as a pale yellow liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.43 (s, 2H), 7.17 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.2, 61.6 (sept, J_{FC} = 24.7 Hz), 109.6−123.5 (m, C_3F_7), 122.1 (q, J_{FC} = 287.9 Hz), 122.7, 130.1, 131.6, 133.3; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −125.0 (2F), −104.9 (2F), −79.3 (3F), −61.3 (6F); IR ($CHCl_3$) 3062, 2985, 1596, 1494, 1332, 1257, 1111, 980, 885, 836, 746, 702 cm^{-1}; EIMS *m*/*z* 488/490 (M^+), 169/171 $(M - C_6F_{13})^+$.

Tris-[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phenyl]phosphane (1a). A solution of t-BuLi (1.7M in pentane, 5.6 mL, 9.5 mmol) was added slowly to 1-bromo-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzene (**8**) (2.45 g, 4.9 mmol) in ether (50 mL) at −78 °C. After stirring at −78 °C for 30 min, phosphorus trichloride (0.14 mL, 1.6 mmol) was added. The mixture was warmed to room temperature over 2 h and stirred at room temperature for 2 h. The reaction mixture was then quenched with water (5 mL). The ether layer was separated. The aqueous layer was further extracted with ether (10 mL) three times. The ether layers were combined, dried over magnesium sulfate, and concentrated under vacuum. The residue was then purified by column chromatography (20:1, hexanes/ethyl acetate) on silica gel to yield **1a** (1.58 g, 76%) as a pale yellow solid: mp 49.9−52.4 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (tt, J = 18.0, 8.7 Hz, 6H), 2.90−2.96 (m, 6H), 7.19−7.29 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.4, 32.9 (t, J_{FC} = 21.8 Hz), 107.7−121.5 (m, C_6F_{13}), 128.7 (d, J_{PC} = 7.0 Hz), 134.6 (d, J_{PC} = 18.8 Hz), 135.7 (d, J_{PC} = 10.5 Hz), 140.2; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −126.7 (6F), −124.0 (6F), −123.4 (6F), −122.4 (6F), −115.2 (6F), −81.3 (9F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ −6.65 (s); EIMS *m*/*z* 1300 (M^+), 877, 513.

Phenylbis[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-phenyl]phosphane (1b). This was synthesized in a manner similar to **1a:** white solid; 90% yield; mp 42−43 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31−2.48 (m, 4H), 2.91−2.97 (m, 4H), 7.20−7.36 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.3, 32.8 (t, J_{FC} = 22.5 Hz), 105.2−121.4 (m, C_6F_{13}), 128.5, 128.6, 128.9, 133.6 (d, J_{PC} = 19.5 Hz), 134.2 (d, J_{PC} = 19.5 Hz), 135.5 (d, J_{PC} = 9.5 Hz), 137.0 (d, J_{PC} = 9.5 Hz), 139.9; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −124.8 (4F), −122.3 (4F), −121.8 (4F), −120.7 (4F), −113.3 (4F), −79.7 (6F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ −5.91 (s); EIMS *m*/*z* 954 (M^+), 531, 477; HRMS for $C_{34}H_{21}F_{26}P$: calcd 954.0966, found 954.0950.

Diphenyl[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-phenyl]phosphane (1c). This was synthesized in a manner similar to **1a**: oi1; 81% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31−2.50 (m, 2H), 2.92−3.05 (m, 2H), 7.23−7.26 (m, 2H), 7.33−7.41 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.4, 32.9 (t, J_{FC} = 21.7 Hz), 107.7−119.3 (m, C_6F_{13}), 128.6, 128.7, 128.9, 133.8 (d, J_{PC} = 19.5 Hz), 134.4 (d, J_{PC} = 19.5 Hz), 135.7 (d, J_{PC} = 10.5 Hz), 137.3 (d, J_{PC} = 10.5 Hz), 139.9; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −125.0 (2F), −122.3 (2F), −121.7 (2F), −120.7 (2F), −113.5 (2F), −79.7 (3F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ −5.11 (s); EIMS *m*/*z* 608 (M^+), 183, 108.

Tris[4-(3,3,4,4,5,5,5-heptafluoro-2,2-bis(trifluoromethyl)pentyl)phenyl]phosphane (5a). This was synthesized in a manner similar to **1a**: oil; 49% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.54 (s, 6H), 7.33−7.44 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.4, 61.7 (sept, J_{FC} = 24.1 Hz), 109.6−123.8 (m, C_3F_7), 122.1 (q, J_{FC} = 287.4 Hz), 131.7 (d, J_{PC} = 5.0 Hz), 132.0, 133.4 (d, J_{PC} = 19.5 Hz), 137.1 (d, J_{PC} = 12.0 Hz); ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −121.9 (6F), −105.0 (6F), −79.2 (9F), −61.4 (18F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ −7.12 (s); EIMS *m*/*z* 1258 (M^+), 939, 849.

Phenylbis[4-(3,3,4,4,5,5,5-heptafluoro-2,2-bis(trifluoromethyl)pentyl)phenyl]phosphane (5b). This was synthesized in a manner similar to **1a**: oil; 68% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.55 (s, 4H), 7.20−7.39 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.5, 61.6 (sept, J_{FC} = 24.1 Hz), 109.4−123.1 (m, C_3F_7), 122.0 (q, J_{FC} = 288.0 Hz), 128.6 (d, J_{PC} = 6.7 Hz), 129.1, 131.6, 132.0 (d, J_{PC} = 10.5 Hz), 133.4 (d, J_{PC} = 19.5 Hz), 133.9 (d, J_{PC} = 20.0 Hz), 136.4 (d, J_{PC} = 10.5 Hz), 137.3 (d, J_{PC} = 11.9 Hz); ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −121.7 (4F), −104.9 (4F), −78.8 (6F), −61.1 (12F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ −6.29 (s); EIMS *m*/*z* 926 (M^+), 608, 517, 197; HRMS for $C_{32}H_{17}F_{26}P$: calcd 926.0653; found 926.0665.

Diphenyl[4-(3,3,4,4,5,5,5-heptafluoro-2,2-bis(trifluoromethyl)pentyl)phenyl]phosphane (5c). This was synthesized in a manner similar to **1a**: oil; 51% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.59 (s, 2H), 7.26−7.41 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.5, 61.6 (sept, J_{FC} = 24.1 Hz), 105.6−119.8 (m, C_3F_7), 122.0 (q, J_{FC} = 288.1 Hz), 128.6 (d, J_{PC} = 7.0 Hz), 129.0, 131.5 (d, J_{PC} = 22.3 Hz), 132.1 (d, J_{PC} = 9.5 Hz), 133.4 (d, J_{PC} = 19.0 Hz), 133.8 (d, J_{PC} = 19.5 Hz), 136.8 (d, J_{PC} = 10.5 Hz), 137.6 (d, J_{PC} = 11.7 Hz); ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −121.8 (2F), −104.9 (2F), −79.1 (3F), −61.2 (6F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ −5.39 (s); EIMS *m*/*z* 594 (M^+), 275, 183.

Bis{tris[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-phenyl]phosphine} Platinum Dichloride (13a). Platinum dichloride (50 mg, 0.19 mmol) was heated with **1a** (520 mg, 0.40 mmol) under reflux in methylene chloride (4 mL) for 4 h. The mixture was cooled to room temperature and methylene chloride (10 mL) was added. After filtration and concentration, the solid was recrystallized in methylene chloride−ether to give **13a** (460 mg, 85.4%): mp 179.1−180.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35 (tt, J = 18.3, 8.7 Hz, 12H), 2.88−2.93 (m, 12H), 7.03 (d, J = 6.9 Hz, 12H), 7.41 (dd, J = 11.1, 8.2 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.3, 32.2 (t, J_{FC} = 22.5 Hz), 108.3−120.0 (m, C_6F_{13}), 127.7 (d, J_{PC} = 67.5 Hz), 127.8, 135.2, 142.3; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −125.1 (12F), −122.4 (12F), −121.8 (12F), −120.8 (12F), −113.3 (12F), −79.6 (18F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 13.7 (s, J_{PtP} = 3679 Hz); IR (neat) 2953, 2917, 2848, 1456, 1204, 1143, 811, 744, 700 cm^{-1}; EIMS *m*/*z* 2866 (M^+), 2832 (M − Cl)$^+$, 2796 (M − 2Cl)$^+$.

Bis{Phenylbis[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phenyl]phosphine} Platinum Dichloride (13b). This was synthesized in a manner similar to **13a**: 83% yield; mp 196.8−198.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35 (tt, J = 17.6, 9.0 Hz, 8H), 2.88−2.93 (m, 8H), 7.03−7.47 (m, 26H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.2, 32.2 (t, J_{FC} = 21.9 Hz), 110.6−121.3 (m, C_6F_{13}), 127.8 (d, J_{PC} = 67.3 Hz), 127.4−128.3 (m), 129.2 (d, J_{PC} = 65.6 Hz), 134.6, 135.3, 142.3; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −125.0 (8F), −122.4 (8F), −121.8 (8F), −120.8 (8F), −113.3 (8F), −79.6 (12F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 14.2 (s, J_{PtP} = 3671 Hz); IR (neat) 3058, 2928, 2858, 1601, 1482, 1436, 1198, 744, 696 cm^{-1}; EIMS *m*/*z* 2174 (M^+), 2103 (M − 2Cl)$^+$.

Bis{Diphenyl[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phenyl]phosphine} Platinum Dichloride (13c). This was synthesized in a manner similar to **13a**: 85% yield; mp 230.2−231.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35 (tt, J = 18.0, 9.1 Hz, 4H), 2.88−2.93 (m, 4H), 7.04−7.51 (m, 28H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.2, 32.3 (t, J_{FC} = 21.9 Hz), 104.8−123.2 (m, C_6F_{13}), 127.6−129.8 (m), 130.9, 134.7, 135.4, 142.1; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −125.0 (4F), −122.3 (4F), −121.7 (4F), −120.7 (4F), −113.3 (8F), −79.7 (6F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 14.7 (s, J_{PtP} = 3673 Hz); IR (neat) 3060, 2959, 1601, 1482, 1436, 1237, 1197, 744, 696 cm^{-1}; FABMS *m*/*z* 1447 (M − Cl)$^+$, 1410 (M − 2Cl).

Bis{tris[4-(3,3,4,4,5,5,5-heptafluoro-2,2-bis(trifluoromethyl)pentyl)phenyl]phosphine} Platinum Dichloride (14a). This was synthesized in a manner similar to **13a**: 82% yield; mp 238.6−241.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.50 (s, 12H), 7.13−7.15 (m, 12H), 7.34−7.37 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.2, 60.6−62.0 (m), 104.8−123.2 (m, C_3F_7), 121.9 (q, J_{FC} = 289.2 Hz), 128.8, 129.7, 131.1, 134.7; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −121.8 (12F), −105.0 (12F), −78.6 (18F), −60.1 (36F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 13.7 (s, J_{PtP} = 3638 Hz); IR (neat) 2951, 2923, 2866, 1454, 1411, 1333, 1242, 741, 678 cm^{-1}; EIMS *m*/*z* 2783 (M^+), 2712 (M − 2Cl)$^+$; HRMS for $C_{78}H_{36}F_{78}P_2Cl_2Pt$: calcd 2780.0051, found 2780.0156.

Bis{phenyl-bis-[4-(3,3,4,4,5,5,5-heptafluoro-2,2-bis-trifluoromethylpentyl) phenyl]phosphine} Platinum Dichloride (14b). This was synthesized in a manner similar to **13a**: 86% yield; mp 227.4−228.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.51 (s, 8H), 7.10−7.50 (m, 26H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.3, 61.5 (sept, J_{FC} = 24.8 Hz), 104.8−123.2 (m, C_3F_7), 121.9 (q, J_{FC} = 288.4 Hz), 128.0, 128.1, 129.0, 129.9, 131.2, 134.2, 134.4, 134.9; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −121.9 (8F), −105.0 (8F), −79.0 (12F), −61.2 (24F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 14.3 (s, J_{Pt-P} = 3652 Hz); IR (neat) 3060, 2982, 1602, 1565, 1500, 1333, 1245, 1109, 741, 677 cm^{-1}; EIMS *m*/*z* 2118 (M^+), 2086 (M − Cl)$^+$, 2047 (M − 2Cl)$^+$; HRMS for $C_{64}H_{34}F_{52}P_2Cl_2Pt$: calcd 2116.0309; found 2116.0212.

General Procedure for the Synthesis of Homoallylic Alcohols. 1-(2,4-Dinitrophenyl)but-3-en-1-ol (15a). A mixture of 2,4-dinitrobenzaldehyde (9.6 mg, 0.049 mmol), fluorous allytin **6b** (92.4 mg, 0.073 mmol), **13a** (7.0 mg, 0.0025 mmol), and BTF (2.5 mL) was stirred at 60 °C for 24 h. After removal of the solvent, the residue was loaded onto a short column packed with fluorous reverse-phase silica gel (1.0 g). The column was eluted with acetonitrile (3 mL) to give **15a** (11.7 mg, 100%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.34−2.44 (m, 2H), 2.70−2.79 (m, 1H), 5.20−5.28 (m, 1H), 5.47 (dd, J = 8.3, 3.5 Hz, 1H), 5.83−5.97 (m, 1H), 8.13 (d, J = 8.7 Hz, 1H), 8.48 (dd, J = 8.7, 2.3 Hz, 1H), 8.82 (d, J = 2.3 Hz, 1H); EIMS *m*/*z* 197 (M − C_3H_5)$^+$, 149, 103.

1-(2,4-Dichlorophenyl)but-3-en-1-ol (15b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.13−2.58 (m, 2H), 2.59−2.64 (m, 1H), 5.10−5.22 (m, 3H), 5.78−5.89 (m, 1H), 7.23−7.53 (m, 3H); EIMS *m*/*z* 175 (M − C_3H_5)$^+$, 147, 111.

1-(2-Chloro-5-nitrophenyl)but-3-en-1-ol (15c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.30−2.49 (m, 2H), 2.66−2.73 (m, 1H), 5.14−5.33 (m, 2H), 5.80−5.94 (m, 1H), 7.58 (d, J = 8.8 Hz, 1H), 8.08 (dd, J = 8.7, 2.7 Hz, 1H), 8.50 (d, J = 2.6 Hz, 1H); EIMS *m*/*z* 186 (M − C_3H_5)$^+$, 139, 111.

1-(2-Nitrophenyl)but-3-en-1-ol (15d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38−2.48 (m, 2H), 2.69−2.75 (m, 1H), 5.19−5.25 (m, 2H), 5.33 (dd, J = 8.4, 3.6 Hz, 1H), 5.84−5.98 (m, 1H), 7.44 (ddd, J = 8.3, 8.3, 1.5 Hz, 1H), 7.66 (ddd, J = 7.4, 7.4, 1.0 Hz, 1H), 7.84 (dd, J = 7.9, 1.0 Hz, 1H), 7.94 (dd, J = 8.2, 1.0 Hz, 1H); EIMS *m*/*z* 152 (M − C_3H_5)$^+$, 104, 77.

1-(2-Trifluoromethylphenyl)but-3-en-1-ol (15e): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.18 (br. s, 1H), 2.38−2.45 (m, 1H), 2.51−2.59 (m, 1H), 5.15−5.24 (m, 3H), 5.83−5.97 (m, 1H), 7.36−7.41 (m, 1H), 7.57−7.65 (m, 2H), 7.79−7.82 (m, 1H); EIMS *m*/*z* 175 (M − C_3H_5)$^+$, 155, 127.

1-(4-Trifluoromethylphenyl)but-3-en-1-ol (15f): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33−2.61 (m, 3H), 4.80−4.85 (m, 1H), 5.22 (dd, J = 14.0, 1.1 Hz, 1H), 5.74−5.85 (m, 1H), 7.49 (AB, J = 8.2 Hz, 2H), 7.62 (AB, J = 8.2 Hz, 2H); EIMS *m*/*z* 175 (M − C_3H_5)$^+$, 127.

1-(2-Bromophenyl)but-3-en-1-ol (15g): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.21 (br. s, 1H), 2.34−2.42 (m, 1H), 2.64−2.70 (m, 1H), 5.10−5.24 (m, 3H), 5.85−5.91 (m, 1H), 7.12−7.17 (m, 1H), 7.33−7.38 (m, 1H), 7.52−7.59 (m, 2H); EIMS *m*/*z* 185/187 (M − C_3H_5)$^+$, 157/159, 105, 77.

1-(3-Bromophenyl)but-3-en-1-ol (15h): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.28−2.58 (m, 3H), 4.72 (dd, J = 7.8, 4.9 Hz, 1H), 5.12−5.22 (m, 2H), 5.73−5.84 (m, 1H), 7.19−7.54 (m, 4H); EIMS *m*/*z* 185/187 (M − C_3H_5)$^+$, 157/159, 128, 105, 77.

1-Naphthalen-1-yl-but-3-en-1-ol (15i): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.74 (br. s, 1H), 2.16−2.21 (m, 2H), 4.93 (dd, J = 7.4, 5.4 Hz, 1H), 5.17−5.25 (m, 2H), 5.78−5.90 (m, 1H), 7.46−7.87 (m, 7H); EIMS m/z 198 (M^+), 157, 129.

Tris[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phenyl]phosphine Oxide (11a). Phosphine **1a** (100 mg, 0.077 mmol) was stirred overnight with 3% hydrogen peroxide (0.5 mL). The mixture was extracted with ether (5 mL) three times. The ether layers were combined, dried over magnesium sulfate, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (100% ethyl acetate) to give **11a** (86.4 mg, 86%) as a white solid: mp 63.2−64.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (tt, J = 18.0, 9.2 Hz, 6H), 2.93−2.98 (m, 6H), 7.27−7.33 (m, 6H), 7.59−7.66 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.5, 32.5 (t, J_{FC} = 22.1 Hz), 105.4−121.3 (m, C_6F_{13}), 128.6 (d, J_{PC} = 12.3 Hz), 131.0 (d, J_{PC} = 105.1 Hz), 132.6 (d, J_{PC} = 9.9 Hz), 143.6; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −125.4 (6F), −122.6 (6F), −122.0 (6F), −121.0 (6F), −113.7 (6F), −80.1 (9F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 28.8 (s); IR (neat) 3021, 2918, 1849, 1604, 1458, 1238, 1205, 813, 744, 708 cm^{-1}; FAB-MS m/z 1315 $(M - H)^+$, 983, 894, 877, 513.

Phenylbis[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-phenyl]phosphine Oxide (11b). This was synthesized in a manner similar to **11a**: oil; 90% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.38 (tt, J = 17.9, 9.1 Hz, 4H), 2.94−3.00 (m, 4H), 7.31−7.70 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.5, 32.5 (t, J_{FC} = 22.1 Hz), 104.8−122.6 (m, C_6F_{13}), 128.6 (d, J_{PC} = 12.1 Hz), 130.1, 131.5, 132.0, 132.1, 132.7 (d, J_{PC} = 10.0 Hz), 132.9, 143.5; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −125.1 (4F), −122.4 (4F), −121.8 (4F), −120.8 (4F), −113.6 (4F), −79.8 (6F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 30.1 (s); IR (neat) 3058, 2957, 1604, 1456, 1240, 1145, 812, 747, 710 cm^{-1}; FAB-MS m/z 969 $(M - H)^+$, 623, 531.

Diphenyl[4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-phenyl]phosphine Oxide (11c). This was synthesized in a manner similar to **11a**: oil; 100% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (tt, J = 18.0, 8.9 Hz, 2H), 2.92−2.98 (m, 2H), 7.30−7.69 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.5, 32.5 (t, J_{FC} = 22.1 Hz), 104.8−122.1 (m, C_6F_{13}), 128.6 (d, J_{PC} = 12.1 Hz), 130.1, 131.6, 132.0, 132.1, 132.7 (d, J_{PC} = 10.1 Hz), 132.9; 143.4; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −125.1 (2F), −122.4 (2F), −121.8 (2F), −120.8 (2F), −113.5 (2F), −79.8 (3F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 30.5 (s); IR (neat) 3058, 2953, 1604, 1438, 1238, 1145, 812, 748, 697 cm^{-1}; EIMS m/z 623 $(M - H)^+$, 547, 201.

Tris[4-(3,3,4,4,5,5,5-heptafluoro-2,2-bis(trifluoromethyl)pentyl)phenyl]phosphine oxide (12a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.59 (s, 6H), 7.42−7.44 (m, 6H), 7.57−7.61 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.5, 60.6−62.0 (m), 105.2−123.2 (m, C_3F_7), 121.9 (q, J_{FC} = 288.2 Hz), 131.3, 131.9 (d, J_{PC} = 9.8 Hz), 132.7, 135.6; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −122.0 (6F), −104.9 (6F), −79.1 (9F), −61.2 (12F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 28.8 (s); IR (neat) 3064, 2956, 2924, 2853, 1605, 1456, 1333, 1260, 1219, 1111, 981, 885, 742, 688 cm^{-1}; FAB-MS m/z 1273 $(M - H)^+$, 955, 849, 499.

Phenylbis[4-(3,3,4,4,5,5,5-heptafluoro-2,2-bis(trifluoromethyl)pentyl)phenyl]phosphine oxide (12b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.54 (s, 4H), 7.37−7.63 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.4, 61.5 (sept, J_{FC} = 24.7 Hz), 104.9−123.0 (m, C_3F_7), 121.9 (q, J_{FC} = 288.1 Hz), 128.6 (d, J_{PC} = 12.1 Hz), 131.0, 131.6−132.4 (m), 133.2, 135.3; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −121.7 (4F), −105.0 (4F), −79.2 (6F), −61.4 (12F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 29.2 (s); IR (neat) 3061, 2972, 1604, 1455, 1332, 1221, 886, 742, 700 cm^{-1}; FAB-MS m/z 941 $(M - H)^+$, 623, 517.

Diphenyl[4-(3,3,4,4,5,5,5-heptafluoro-2,2-bis(trifluoromethyl)pentyl)phenyl]phosphine oxide (12c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.56 (s, 2H), 7.27−7.77 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.5, 60.6−62.0 (m), 105.1−119.6 (m, C_3F_7), 121.9 (q, J_{FC} = 288.2 Hz), 128.6 (d, J_{PC} = 12.1 Hz), 131.5−132.1 (m), 132.8, 133.5, 135.1; ^{19}F NMR (282.4 MHz, $CDCl_3$) δ −122.0 (2F), −104.9 (2F), −79.1 (3F), −61.2 (6F); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 29.8 (s); IR (neat) 3076, 3013, 2974, 1604, 1484, 1439, 1333, 1242, 1119, 886, 750, 702 cm^{-1}; EIMS m/z 609 $(M - H)^+$, 533, 201.

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