Efficient Access to Perfluoroalkylated Aryl Compounds by Heck Reaction

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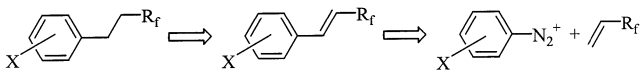
Efficient introduction of perfluorinated tails onto aromatic rings has been achieved by Heck reaction between perfluoroalkenes and arenediazonium salts, catalysed by palladium acetate. Subsequent transition metal catalysed hydrogenation of the double bond afforded a large variety of aromatic compounds bearing an affinity for fluorous solvents. Formation of perfluoroalkylated phosphane ligands and their use in palladium-catalysed coupling between potassium trifluoro(vinyl)borates and diazonium salts is also described, allowing an easy separation and recycling of the catalytic system.

Introduction

Perfluoroalkylated compounds have attracted great interest in recent years, not only in the field of catalysis with the concept of Fluorous Biphase Catalysis (FBC) introduced by Horvath and Gladysz,[1] but also in the field of combinatorial organic synthesis.[2] This attractiveness is closely related with their unique properties compared with conventional organic compounds: they are thermally stable, show high chemical inertness and, very particularly, are not soluble in a large range of common organic solvents because of low van der Waals interactions.[3]

There is an increasing need for highly efficient methods of introducing perfluoroalkyl chains, in order to access a large variety of perfluoroalkyl-substituted building blocks. However, only few reports have dealt with the selective preparation of aromatic compounds bearing perfluorinated tails, whereas these building blocks are of great interest for preparing most of the ligands used in homogeneous catalysis.[4] The copper-catalysed coupling of 1,1,2,2-tetrahydrogenoperfluoroalkyl iodides with arylmagnesium bromides generally suffers from limited yields because of the formation of fluorous by-products that are difficult to remove.[5] Ullmann-type coupling between aryl bromides or iodides and perfluoroalkyl iodides is used very often,[6] but excess copper and harsh conditions are needed, and do not allow the introduction of an ethylene spacer between the aromatic ring and the perfluorinated chain. This spacer is often necessary to decrease the electron-withdrawing strength of the fluorous tail.[1d] Finally, *O*-alkylation of phenol derivatives with perfluoroalkyl sulfonates is efficient, but suffers from the use of expensive reagents.[7]

We decided to explore a new approach to access perfluoroalkyl-substituted aromatic compounds based on a Heck reaction between perfluoroalkenes and arenediazonium salts, followed by hydrogenation of the double bond (Scheme 1).



Scheme 1

This approach would also allow the introduction of the ethylene spacer. To the best of our knowledge, only one reaction sequence of this type has yet been described in Prosulfuron® synthesis,[8] where the palladium-catalysed Heck reaction with 1,1,1-trifluoropropene and a diazonium salt, followed by in situ reduction of the double bond allowed the introduction of 1,1,1-trifluoroprop-3-yl substituent on the aromatic ring.

Results and Discussion

Heck Reaction

We first studied the introduction of the perfluoroalkyl chain applying classical conditions generally used for the palladium-catalysed reaction of arenediazonium tetrafluoroborates with alkenes[9] or organoboron compounds.[10] Thus, we found that the reaction between 4-methylbenzenediazonium tetrafluoroborate and perfluorodec-1-ene (**5**) in methanol at room temperature was efficiently catalysed by palladium acetate (5%) and afforded the coupling product **1a** in 80% yield. However, due to limited miscibility of the perfluoroalkene in methanol, the reaction was slow and formation of some by-products was observed. Increasing the temperature to 40 °C allowed the coupling product **1a** to be obtained in quantitative yield with high purity (over 99%, Table 1, Entry 1) in the presence of 0.5 mol-% of catalyst.

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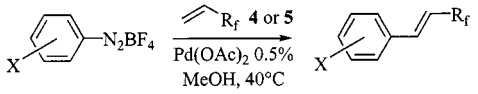
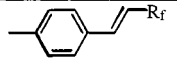
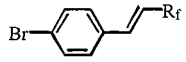
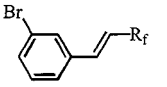
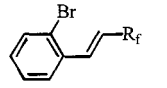
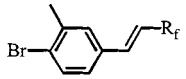
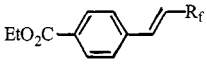
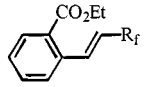
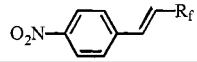
Table 1. Heck coupling between perfluoroalkenes and diazonium salts



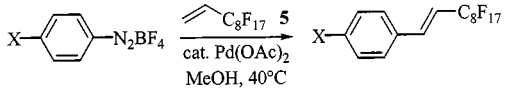
Entry	Product[a]		Yield (Purity[b])
1		**1a** (Rf_8)	99 (> 99)
2		**1b** (Rf_8)	98 (96)
3		**1b'** (Rf_6)	92 (97)
4		**1c** (Rf_8)	99 (98)
5		**1c'** (Rf_6)	70 (98)
6		**1d** (Rf_8)	98 (99)
7		**1d'** (Rf_6)	97 (99)
8		**1e** (Rf_8)	93 (98)
9		**1f** (Rf_8)	99 (> 99)
10		**1g** (Rf_8)	90 (97)
11		**1h** (Rf_8)	98 (> 99)

[a] R_f: perfluoroalkyl chain, $R_{f6} = C_6F_{13}$, $R_{f8} = C_8F_{17}$. – [b] Determined by GC.

These conditions were applied to different diazonium salts and two different commercially available perfluoroalkenes[11] [$CH_2{=}CHC_6F_{13}$ (**4**) and $CH_2{=}CHC_8F_{17}$ (**5**)]. As is shown in Table 1, quantitative yields were generally obtained with reaction times ranging from 2 to 15 min. All the perfluoroalkenyl-substituted aromatic compounds were easily purified by simple filtration through silica gel to afford, exclusively, (*E*)-alkenes of very high GC purities (from 96 to over 99%). Moreover, this reaction is compatible with bromo substituents (Entries 2−8), as no coupling products originating from the insertion of palladium(0) into the C−Br bond were obtained. Lower yields observed with perfluorooct-1-ene (**1c′**) could be explained by the volatility of the coupled product (Entry 5). Thus, it was possible to access, very efficiently, various aryl bromides bearing a perfluoroalkyl chain. These compounds are important precursors in triarylphosphane synthesis.

This Heck reaction could be conducted at lower catalytic rates (Scheme 2). The reaction of benzenediazonium tetrafluoroborate in the presence of 0.01 mol-% of catalyst gave the coupling product **1i** with a TOF (Turn Over Frequency) of around 7000. In the same way, coupling of 4-bromobenzenediazonium tetrafluoroborate afforded the expected compound **1b** with a TON (Turn Over Number) of 65000 and a TOF of 260000.

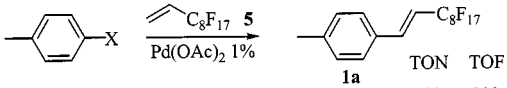
We then studied the extension of this coupling to other electrophiles, mainly aryl iodides and bromides. Under previously described conditions [cat. $Pd(OAc)_2$, methanol], no



1i (X = H), TON : 10000 TOF : 6700
1b (X = Br), TON : 65000 TOF : 260000

Scheme 2

coupling product **1a** was obtained with 4-iodotoluene, and the reaction was accompanied by the formation of black palladium. In the same way, coupling of aryl iodides in the presence of $Pd(PPh_3)_4$ and triethylamine in toluene[12] did not result in any reaction. However, under Jeffery conditions[13] [$Pd(OAc)_2$, DMF, $NaHCO_3$, nBu_4NHSO_4], coupling of 4-iodotoluene with perfluorodec-1-ene afforded **1a** in 80% yield (Scheme 3).

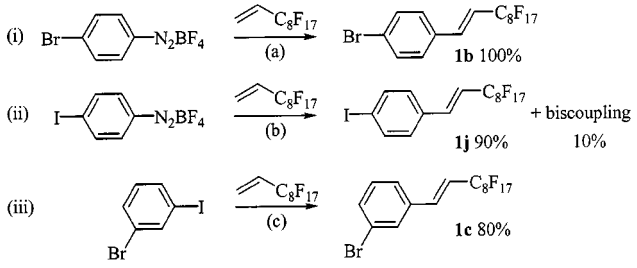


		TON	TOF
X = N_2BF_4	MeOH, 40°C	100	200
X = I	$NaHCO_3$, n-Bu_4NHSO_4, DMF, 90°C	80	7
X = Br	$NaHCO_3$, n-Bu_4NHSO_4, DMF, 90°C	18	0.4

Scheme 3

Under these conditions, 4-bromotoluene was quite unreactive, even after 2 d at 90 °C. Thus, this Heck reaction with perfluoroalkenes could be easily applied to aryl iodides, extending the scope of the present procedure to the introduction of perfluoroalkyl chains on an aromatic ring.

Thanks to the difference in reactivity of those various electrophiles in the Heck reaction, we have studied the chemoselectivity of the reaction, using bifunctional aromatic electrophiles. We have shown that coupling of arenediazonium tetrafluoroborates bearing a bromide substituent yielded coupling product **1b** exclusively from the diazonium substituent (Scheme 4, i).



(a) $Pd(OAc)_2$ 0.5 %, MeOH, 40°C. (b) Pd $(OAc)_2$ 1%, MeOH/THF 1:3, RT. (c) $Pd(OAc)_2$ 1%, n-Bu_4NHSO_4 1 eq., $NaHCO_3$ 2.5 eq., DMF, 90°C

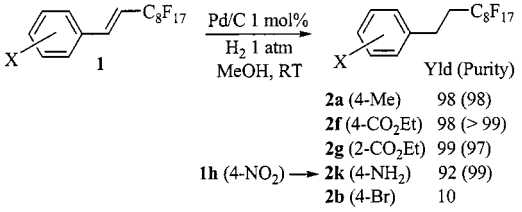
Scheme 4

Under identical conditions (MeOH, 40 °C), coupling of 4-iodobenzenediazonium tetrafluoroborate afforded the perfluoroalkyl-substituted **1j** in moderate yield (70%), accompanied by the bis-coupling product (Scheme 4, ii). By conducting the reaction at room temperature, however, and using a 1:3 mixture of MeOH/THF in order to improve the solubility of the perfluoroalkene, the selectivity is increased up to 90:10 in favour of the monocoupling product **1j** (Scheme 4, ii). Finally, Heck reaction of 3-bromoiodobenzene under Jeffery conditions[13] afforded exclusively the

product **1c**, from the coupling of the iodide substituent, in good yield (Scheme 4, iii). Hence, concerning the reactivity of the tested electrophiles for the present reaction, we can classify the halides or pseudohalides in the order $N_2^+ > I >> Br$.

Reduction of the Double Bond

We then decided to study the reduction of the double bond of the different perfluoroalkenyl-substituted aromatic compounds. In situ experiments, consisting of a Heck reaction, followed by hydrogenation under hydrogen (1 atm) using the same palladium catalyst, were not conclusive because of low conversions and the formation of by-products. However, hydrogenation performed on isolated perfluoroalkenyl-substituted aromatic compounds under standard conditions (1 mol-% of Pd/C, 1 atm of H_2) allowed quantitative reduction of the double bond in high yields (Scheme 5).



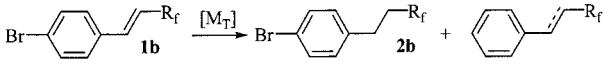
Scheme 5

In the case of the nitro-substituted compound **1h**, we observe a concomitant complete reduction of the nitro group, affording the perfluoroalkylated aniline **2k** in high yield. In any case, reduced products of high purity were easily obtained by simple filtration through silica gel. The notable exception was the reduction of the aryl bromide derivative **2b**, where cleavage of the bromo substituent predominated.

Thus, we looked for other conditions to perform the reduction of such compounds. Our first idea was to use non-transition metal catalysed reductions, and more particularly, diimide reductions. Several conditions for generating the diimide were investigated[14] (H_2O_2, $KO_2CN{=}NCO_2K$/AcOH, H_2O_2/Cu cat.), but each time the reaction stopped before completion, with yields not exceeding 30%, even in the presence of excess reagent. We then turned to transition metal catalysed reduction methods that could be compatible with the presence of bromo substituents. PtO_2 under hydrogen has already been used for the hydrogenation of aryl bromides bearing a long alkene chain with good selectivities.[15] Applied to our substrate (Table 2, Entry 1), we observed the formation of large amounts of debrominated compounds accompanied by low conversions.

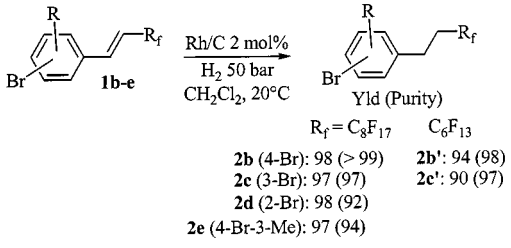
We next tested ruthenium and rhodium complexes, which have already been used in the selective reduction of the double bond of alkene-substituted aryl bromides.[16] Among the tested catalysts in MeOH at room temperature and under 1 atm of hydrogen, Rh/C proved to be most efficient, affording the expected product **2b** with 76% purity and 95% conversion (Table 2, Entries 2−7). The observed by-products originated from debromination. Other solvents were tested in order to increase the selectivity of the hydrogenation using Rh/C as catalyst. In nonprotic solvents (THF, 1,4-dioxane, AcOEt, CH_2Cl_2), hydrogenation was very slow at room temperature under 1 atm of hydrogen, but it afforded the expected products with good purities (over 90% in dichloromethane, Entry 8). Increasing the pressure to 50 bar allowed for almost quantitative hydrogenation after 18 h, the purity being unchanged (Entry 9). Particularly, in dichloromethane, purities over 99% could be achieved using 2 mol-% of Rh/C at 50 bar of H_2 for 24 h (Table 2, Entry 10 and Scheme 6).

Table 2. Reduction of the double bond of perfluoroalkylated aryl bromides



Entry[a]	[M_T] 1%	Solvent	Conversion[b] (Purity[c])
1	PtO_2	MeOH	20
2	$RhCl(PPh_3)_3$	MeOH	0
3	$RuCl_3$	MeOH	0
4	$RuCl(PPh_3)_3$	MeOH	< 1
5	$Ru(Met)_2(cod)$	MeOH	6
6	$RuCl_2(PPh_3)_2$	MeOH	23
7	Rh/C	MeOH	95 (76)
8	Rh/C	CH_2Cl_2	31 (97)
9[d]	Rh/C	CH_2Cl_2	95 (> 98)
10[d][e]	Rh/C	CH_2Cl_2	100 (> 99)

[a] Reactions conducted under 1 atm of H_2 at room temp. for 18 h using 1 mol-% of catalyst (R_f = C_8F_{17}). − [b] Conversion determined by GC. − [c] Determined by GC. − [d] Reaction conducted under 50 bar of H_2. − [e] Reaction conducted using 2 mol-% of catalyst for 24 h at 20 °C.



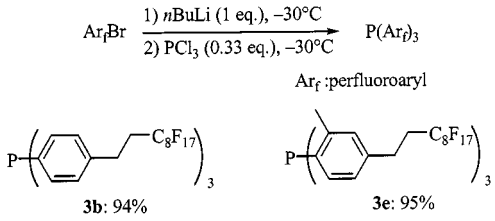
Scheme 6

Under these optimised conditions (cat. Rh/C, dichloromethane, 50 bar of H_2), conversions and purities of the compounds are very dependent on catalyst loading, temperature and reaction time. Reproducible results were generally achieved at 20 °C during 24 h using 2 mol-% of catalyst (Scheme 6). For all of the tested substrates, quantitative yields and purities were obtained. As in the case of the Heck reaction, simple filtration through silica gel allowed the isolation of very pure compounds.

Fluorous Biphase Catalysis

Starting from these perfluoroalkylated aryl bromides, access to perfluoroalkyl-substituted phosphanes was straightforward by lithium/halogen exchange, followed by condensation onto a halophosphane.[17] Treatment of perfluoroalkylated aryl bromides **2b** and **2e** with 1 equiv. of *n*-butyllithium at −30 °C afforded aryllithium derivatives,

which, upon treatment with freshly distilled PCl_3, gave almost quantitative yields of perfluoroalkyl-substituted phosphanes **3b** and **3e** (Scheme 7). ^{31}P NMR analysis revealed that these phosphanes had purities of over 95% after simple filtration through silica gel. For many purposes, these products could be engaged without further purification. Analytically pure compounds were obtained by recrystallisation from ether/methanol mixtures with moderate yields.



Scheme 7

This easy treatment avoided classical BH_3 protection of the phosphorus atom. A perfluoroalkylated analogue of the very useful tri-*o*-tolylphosphane[18] was prepared efficiently for the first time by this method.

The concept of FBC was tested on an example: the palladium-catalysed cross-coupling reaction of arenediazonium tetrafluoroborates with potassium organotrifluoroborates.[10,19] To the best of our knowledge this concept has not yet been applied to cross-coupling reactions with organoboron compounds. The catalyst precursor was prepared by mixing 2 equiv. of perfluoroalkyl-substituted phosphane **3b** with palladium acetate at room temperature in a 1:1 mixture of methanol/FC-72 for 5 min, followed by removal of methanol. To this perfluorous solution of catalyst was added a methanol solution of 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**6**) and potassium trifluoro(vinyl)borate (**7**). At the end of the coupling, methanol was removed, the perfluorous phase washed with methanol and water, and reloaded with substrates.

As we can see in Figure 1, good conversions and purities were obtained up to the 5th cycle, after which a decrease in conversions was observed. We also noted an increase in reaction times with the number of cycles: This could originate from a slight loss of palladium catalyst during the washings.

Conclusion

Starting from arenediazonium salts, readily available from aromatic amines, it was possible by a two step transition metal catalysed reaction (Heck reaction followed by hydrogenation) to access a large variety of perfluoroalkylated aromatic compounds very efficiently. More particularly, perfluoroalkyl-substituted aryl bromides and anilines were accessible. This represents one of the most efficient methods of attaching a perfluoroalkyl chain to an aromatic ring. Moreover, simple purification (filtration) and the high purities obtained will allow an easy scale up of this procedure. Finally, encouraging results were obtained on the recycling of the palladium catalyst in the cross-coupling reaction of arenediazonium salts with organotrifluoroborates.

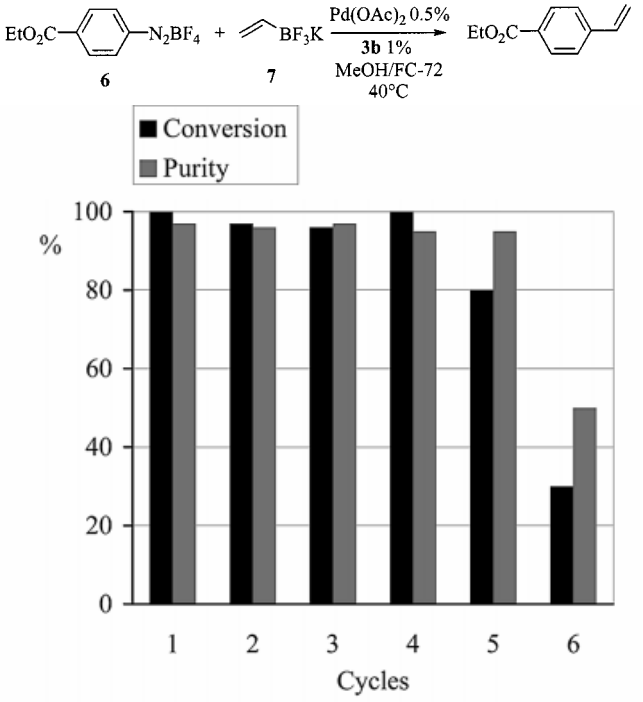


Figure 1. Fluorous biphase cross-coupling of **6** with **7**

Experimental Section

General Remarks: ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker AC 200 at 200 or 50 MHz, respectively; chemical shifts (δ) are reported in ppm units by reference to Me_4Si, and coupling constants (*J*) are reported in Hz and refer to apparent peak multiplicities. ^{31}P and ^{19}F NMR spectra were recorded with a Bruker ARX 400 instrument at 162 and 376 MHz, respectively using H_3PO_4 and $CFCl_3$ as an internal reference. − Mass spectra were determined with a Ribermag instrument. − Elementary analyses were done at the Regional Service of Microanalysis (Université Pierre et Marie Curie). − Thin layer chromatography was carried out on silica gel plates (Merck F_{254}) and spots were detected by UV. − GC analyses were performed with a Hewlett-Packard 5890 instrument equipped with a J&W Scientific DB-1701 capillary column (15 m, Ø = 0.25 μm), using a flame ionisation detector. Head pressure was fixed to 50 kPa using the following temperature program: 70 °C for 1 min, 20 °C/min up to 210 °C. − Anhydrous THF and ether were distilled from sodium/benzophenone; CH_2Cl_2 was distilled from calcium hydride; methanol (Prolabo, Normapur®) was used as received. $Pd(OAc)_2$ and aromatic amines were purchased from Acros or Aldrich, and were used as received. Perfluoroalkenes were bought from Interchim. Phosphorus trichloride was freshly distilled prior to use. Arenediazonium salts were prepared according to described procedures.[10b,10f,20]

General Procedure for the Heck Coupling between Arenediazonium Tetrafluoroborates and Perfluoroalkenes: To a stirred suspension of arenediazonium salt and $Pd(OAc)_2$ (0.5 mol-%) in MeOH (1 mL/mmol) was added under argon 1,1,2-trihydrogenoperfluoroalk-1-ene (1 equiv.). The mixture was heated at 40 °C until gas evolution ceased. ***CAUTION:*** Some reactions were highly exothermic! The resulting mixture was stirred for additional 10 min and MeOH was

removed under reduced pressure. The residue was extracted with cyclohexane/ether (99:1) for **1f−k** or with cyclohexane for **1a−e**, filtered through silica gel and the solvent was removed under vacuum to afford the expected product.

General Procedure for the Heck Coupling under Jeffery Conditions: A mixture of iodo- or bromoarene, 1,1,2-trihydrogenoperfluoroalk-1-ene (1 equiv.), $Pd(OAc)_2$ (1 or 2 mol-%), $NaHCO_3$ (2.5 equiv.), and nBu_4NHSO_4 (1 equiv.) in DMF (1.5 mL/mmol) was stirred at 90 °C for 24 h. Cyclohexane (5 mL/mmol) was added, the mixture was washed with water (5 mL/mmol), brine (5 mL/mmol, four times), and water (5 mL/mmol), dried with $MgSO_4$ and concentrated under reduced pressure. The residue was dissolved in cyclohexane, filtered through silica gel and concentrated under vacuum to give the expected product.

General Procedure for the Pd/C Hydrogenation of Perfluoroalkenes: A suspension of the perfluoroalkene **1** and 5% Pd/C (1 mol-%) in a degassed methanol/THF (1:1) mixture (2 mL/mmol) was placed under H_2 and stirred at room temp. for 18 h (reduction monitored by GC). At the end of reaction the solvent was removed. The residue was extracted with cyclohexane/ether (99:1), filtered through silica gel and the solvent was removed under vacuum to afford the expected product **2**.

General Procedure for the Rh/C Hydrogenation of Perfluoroalkenes: A suspension of the perfluoroalkene **1** and 5% of Rh/C (2 mol-%) in degassed dichloromethane (4 mL/mmol) was placed under 50 bar of H_2 and stirred at 20 °C for 24 h (reduction monitored by GC). At the end of reaction the solvent was removed. The residue was extracted with cyclohexane/ether (99:1), filtered through silica gel and the solvent was removed under vacuum to afford the expected product **2**.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-(4′-methylphenyl)dec-1-ene (1a): White solid (2.686 g, 4.95 mmol), prepared from 4-methylbenzenediazonium tetrafluoroborate (5 mmol) and **5** in 99% yield according to the general procedure. − M.p. 30 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.42 (s, 3 H, CH_3), 6.18 (dt, 1 H, J_{HH} = 16.1 Hz and J_{HF} = 12.3 Hz, H^2), 7.1−7.3 (m, 3 H, H^1 and $H^{3'}$), 7.41 (d, 2 H, J = 8.1 Hz, $H^{2'}$). − ^{13}C NMR ($CDCl_3$): δ = 21.1 (CH_3), 113.1 (t, J_{CF} = 23.0 Hz, C^2), 127.4 ($C^{2'}$), 129.5 ($C^{3'}$), 130.8 ($C^{1'}$), 139.5 (t, J_{CF} = 9.5 Hz, C^1), 140.4 ($C^{4'}$). − $C_{17}H_9F_{17}$ (536.2): calcd. C 38.08, H 1.69; found C 38.06, H 1.73.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-(4′-methylphenyl)decane (2a): White solid (2.110 g, 2.92 mmol), prepared from **1a** (4 mmol) in 98% yield according to the general procedure. − M.p. 35 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.32−2.52 (m, 2 H, H^2), 2.34 (s, 3 H, CH_3), 2.88−2.96 (m, 2 H, H^1), 7.11−7.20 (m, 4 H, $H^{2'}$ and $H^{3'}$). − ^{13}C NMR ($CDCl_3$): δ = 20.6 (CH_3), 25.9 (C^1), 33.1 (t, J_{CF} = 22.2 Hz, C^2), 128.0 ($C^{2'}$), 129.3 ($C^{3'}$), 136.0 and 136.2 ($C^{2'}$ and $C^{4'}$). − MS (70 eV); *m/z* (%): 538 (6) [$M^{+\cdot}$], 105 (100). − $C_{17}H_{11}F_{17}$ (538.2): calcd. C 37.93, H 2.06; found C 38.10, H 1.96.

1-(4′-Bromophenyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodec-1-ene (1b): White solid (29.45 g, 49.0 mmol), prepared from 4-bromobenzenediazonium tetrafluoroborate (50 mmol) and **5** in 98% yield according to the general procedure. − M.p. 45 °C. − ^{1}H NMR ($CDCl_3$): δ = 6.23 (dt, 1 H, J_{HH} = 16.1 Hz and J_{HF} = 12.1 Hz, H^2), 7.14 (dt, 1 H, J_{HH} = 16.1 Hz and J_{HF} = 2.3 Hz, H^1), 7.37 (d, 2 H, J = 8.5 Hz, $H^{2'}$), 7.57 (d, 2 H, J = 8.5 Hz, $H^{3'}$). − ^{13}C NMR ($CDCl_3$): δ = 115.0 (t, J_{CF} = 23.2 Hz, C^2), 124.4 ($C^{4'}$), 128.9 ($C^{2'}$), 132.1 ($C^{3'}$), 132.3 ($C^{1'}$), 138.4 (t, J_{CF} = 9.5 Hz, C^1). − ^{19}F NMR ($CDCl_3$): δ = −126.7 (m 2 F, F^9), −123.7 (m, 2 F, F^4), −123.3 (m, 2 F), −122.4 (m. 4 F, F^6 and F^7), −121.9 (m, 2 F), −111.8 (m, 2 F, F^3), −81.4 (m, 3 F, F^{10}). − $C_{16}H_6BrF_{13}$ (601.1): calcd. C 31.97, H 1.01; found C 31.83, H 1.07.

1-(4′-Bromophenyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecane (2b): White solid (27.19 g, 45.1 mmol), prepared from **1b** (46 mmol) in 98% yield according to the general procedure. − M.p. 54 °C. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.23−2.49 (m, 2 H, H^2), 2.85−2.93 (m, 2 H, H^1), 7.11 (d, 2 H, J = 8.4 Hz, $H^{2'}$), 7.46 (dt, 2 H, J = 8.4 and 2.2 Hz, $H^{3'}$). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 25.8 (C^1), 32.6 (t, J_{CF} = 22.1 Hz, C^2), 120.5 ($C^{4'}$), 129.9 ($C^{2'}$), 131.8 ($C^{3'}$), 137.9 ($C^{1'}$). − ^{19}F NMR ($CDCl_3$): δ = −126.7 (m, 2 F, F^9), −124.0 (m, 2 F, F^4), −123.3 (m, 2 F), −122.4 (m, 4 F, F^6 and F^7), −122.2 (m, 2 F), −115.1 (m, 2 F, F^3), −81.5 (m, 3 F, F^{10}). − MS (70 eV); *m/z* (%): 602 and 604 (11) [$M^{+\cdot}$], 523 (5), 169 and 171 (100). − $C_{16}H_8BrF_{17}$ (603.1): calcd. C 31.86, H 1.34; found C 31.88, H 1.21.

1-(4′-Bromophenyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooct-1-ene (1b′): White solid (2.305 g, 4.60 mmol), prepared from 4-bromobenzenediazonium tetrafluoroborate (5 mmol) and **4** in 92% yield according to the general procedure. − M.p. < 30 °C. − ^{1}H NMR ($CDCl_3$): δ = 6.23 (dt, 1 H, J_{HH} = 16.1 Hz and J_{HF} = 12.0 Hz, H^2), 7.15 (dt, 1 H, J_{HH} = 16.1 Hz and J_{HF} = 2.3 Hz, H^1), 7.37 (d, 2 H, J = 8.5 Hz, $H^{2'}$), 7.57 (d, 2 H, J = 8.5 Hz, $H^{3'}$). − ^{13}C NMR ($CDCl_3$): δ = 115.1 (t, J_{CF} = 23.1 Hz, C^2), 124.5 ($C^{4'}$), 129.1 ($C^{2'}$), 132.2 ($C^{3'}$), 132.5 ($C^{1'}$), 138.6 (t, J_{CF} = 9.5 Hz, C^1). − ^{19}F NMR ($CDCl_3$): δ = −127.7 (m, 2 F, F^7), −123.7 (m, 2 F, F^4), −123.4 (m, 2 F), −122.1 (m, 2 F), −111.8 (m, 2 F, F^3), −81.4 (m, 3 F, F^{10}). − $C_{14}H_6BrF_{13}$ (501.1): calcd. C 33.56, H 1.21; found C 33.52, H 1.14.

1-(4′-Bromophenyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane (2b′): White solid (1.892 g, 3.76 mmol), prepared from **1b′** (4 mmol) in 94% yield according to the general procedure. − M.p. 30 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.25−2.51 (m, 2 H, H^2), 2.87−2.95 (m, 2 H, H^1), 7.12 (d, 2 H, J = 8.4 Hz, $H^{2'}$), 7.48 (dt, 2 H, J = 8.4 and 2.2 Hz, $H^{3'}$). − ^{13}C NMR ($CDCl_3$): δ = 25.8 (C^1), 32.6 (t, J_{CF} = 22.1 Hz, C^2), 120.5 ($C^{4'}$), 129.9 ($C^{2'}$), 131.8 ($C^{3'}$), 137.9 ($C^{1'}$). − MS (70 eV); *m/z* (%): 502 and 504 (16) [$M^{+\cdot}$], 423 (7), 169 and 171 (100). − $C_{14}H_8BrF_{13}$ (503.1): calcd. C 33.42, H 1.60; found C 33.47, H 1.64.

1-(3′-Bromophenyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodec-1-ene (1c): Colorless oil (2.975 g, 4.95 mmol), prepared from 3-bromobenzenediazonium tetrafluoroborate (5 mmol) and **5** in 99% yield according to the general procedure. − ^{1}H NMR ($CDCl_3$): δ = 6.25 (dt, 1 H, J_{HH} = 16.1 Hz and J_{HF} = 12.0 Hz, H^2), 7.13 (dt, 1 H, J_{HH} = 16.1 Hz and J_{HF} = 2.1 Hz, H^1), 7.29 (t, 1 H, J = 7.8 Hz, $H^{5'}$), 7.42 (d, 1 H, J = 7.8 Hz, $H^{6'}$), 7.55 (d, 1 H, J = 7.8 Hz, $H^{4'}$), 7.65 (s, 1 H, $H^{2'}$). − ^{13}C NMR ($CDCl_3$): δ = 115.9 (t, J_{CF} = 23.3 Hz, C^2), 123.0 ($C^{3'}$), 126.0 ($C^{6'}$), 130.2 ($C^{2'}$ and $C^{5'}$), 132.8 ($C^{4'}$), 135.4 ($C^{1'}$), 138.1 (t, J_{CF} = 9.5 Hz, C^1). − ^{19}F NMR ($CDCl_3$): δ = −126.7 (m, 2 F, F^9), −123.7 (m, 2 F, F^4), −123.3 (m, 2 F), −122.5 (m, 4 F, F^6 and F^7), −122.0 (m, 2 F), −112.0 (m, 2 F, F^3), −81.5 (m, 3 F, F^{10}). − $C_{16}H_6BrF_{13}$ (601.1): calcd. C 31.97, H 1.01; found C 31.79, H 1.03.

1-(3′-Bromophenyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecane (2c): White solid (2.340 g, 2.88 mmol), prepared from **1c** (4 mmol) in 97% yield according to the general procedure. − M.p. 38 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.26−2.53 (m, 2 H, H^2), 2.89−2.97 (m, 2 H, H^1), 7.13−7.25 (m, 2 H, $H^{5'}$ and $H^{6'}$), 7.38−7.44 (m, 2 H, $H^{2'}$ and $H^{4'}$). − ^{13}C NMR ($CDCl_3$): δ = 26.0 (C^1), 32.6 (t, J_{CF} = 22.2 Hz, C^2), 122.6 ($C^{3'}$), 126.8 ($C^{6'}$), 129.8 ($C^{4'}$), 130.2 ($C^{5'}$), 131.3 ($C^{2'}$), 141.3 ($C^{1'}$). − MS (70 eV); *m/z* (%):

602 and 604 (10) [M$^+$], 169 and 171 (100), 109 (39). − $C_{16}H_8BrF_{17}$ (603.1): calcd. C 31.86, H 1.34; found C 31.98, H 1.11.

1-(3′-Bromophenyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooct-1-ene (1c′): Colorless oil (1.754 g, 3.50 mmol), prepared from 3-bromobenzenediazonium tetrafluoroborate (5 mmol) and **4** in 70% yield according to the general procedure. − ^{1}H NMR ($CDCl_3$): δ = 6.23 (dt, 1 H, J_{HH} = 16.1 Hz and J_{HF} = 12.0 Hz, H^2), 7.13 (dt, 1 H, J_{HH} = 16.1 Hz and J_{HF} = 2.2 Hz, H^1), 7.29 (t, 1 H, J = 7.8 Hz, H$^{5'}$), 7.43 (d, 1 H, J = 7.8 Hz, H$^{6'}$), 7.55 (d, 1 H, J = 7.8 Hz, H$^{4'}$), 7.66 (s, 1 H, H$^{2'}$). − ^{13}C NMR ($CDCl_3$): δ = 115.8 (t, J_{CF} = 23.3 Hz, C^2), 123.0 (C$^{3'}$), 126.1 (C$^{6'}$), 130.3 (C$^{2'}$ and C$^{5'}$), 132.9 (C$^{4'}$), 135.4 (C$^{1'}$), 138.2 (t, J_{CF} = 9.6 Hz, C^1).

1-(3′-Bromophenyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane (2c′): Colorless oil (1.819 g, 3.62 mmol), prepared from **1c′** (4 mmol) in 90% yield according to the general procedure. − ^{1}H NMR ($CDCl_3$): δ = 2.20−2.53 (m, 2 H, H^2), 2.88−2.97 (m, 2 H, H^1), 7.15−7.27 (m, 2 H, H$^{5'}$ and H$^{6'}$), 7.40−7.44 (m, 2 H, H$^{2'}$ and H$^{4'}$). − ^{13}C NMR ($CDCl_3$): δ = 26.1 (C^1), 32.7 (t, J_{CF} = 22.2 Hz, C^2), 122.7 (C$^{3'}$), 126.9 (C$^{6'}$), 129.9 (C$^{4'}$), 130.3 (C$^{5'}$), 131.4 (C$^{2'}$), 141.3 (C$^{1'}$). − $C_{14}H_8BrF_{13}$ (503.1): calcd. C 33.42, H 1.60; found C 33.59, H 1.47.

1-(2′-Bromophenyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodec-1-ene (1d): White solid (2.940 g, 4.89 mmol) prepared from 2-bromobenzenediazonium tetrafluoroborate (5 mmol) and **5** in 98% yield according to the general procedure. − M.p. 30 °C. − ^{1}H NMR ($CDCl_3$): δ = 6.22 (dt, 1 H, J_{HH} = 16.0 Hz and J_{HF} = 12.0 Hz, H^2), 7.25 (1 H, td, J = 7.7 and 1.8 Hz, H$^{4'}$), 7.36 (1 H, td, J = 7.5 and 1.2 Hz, H$^{5'}$), 7.53−7.69 (m, 3 H, H^1, H$^{3'}$ and H$^{6'}$). − ^{13}C NMR ($CDCl_3$): δ = 117.2 (t, J_{CF} = 23.2 Hz, C^2), 124.6 (C$^{2'}$), 127.4 (C$^{5'}$ or C$^{6'}$), 127.5 (C$^{5'}$ or C$^{6'}$), 130.9 (C$^{4'}$), 133.2 (C$^{3'}$), 133.7 (C$^{1'}$), 138.6 (t, J_{CF} = 9.7 Hz, C^1). − $C_{17}H_{11}BrF_{17}$ (601.1): calcd. C 31.97, H 1.01; found C 31.79, H 0.92.

1-(2′-Bromophenyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecane (2d): White solid (2.362 g, 3.92 mmol), prepared from **1d** (4 mmol) in 98% yield according to the general procedure. − M.p. 31 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.27−2.58 (m, 2 H, H^2), 3.07−3.15 (m, 2 H, H^1), 7.10−7.18 (m, 1 H, H$^{6'}$), 7.26−7.31 (m, 2 H, H$^{4'}$ and H$^{5'}$), 7.59 (d, 1 H, J = 7.6 Hz, H$^{3'}$). − ^{13}C NMR ($CDCl_3$): δ = 27.0 (C^1), 31.0 (t, J_{CF} = 22.2 Hz, C^2), 124.0 (C$^{2'}$), 127.6 (C$^{5'}$), 128.3 (C$^{4'}$), 130.2 (C$^{6'}$), 132.9 (C$^{3'}$), 138.3 (C$^{1'}$). − MS (70 eV); *m/z* (%): 602 and 604 (10) [M$^+$], 523 (7), 169 and 171 (100). − $C_{16}H_8BrF_{17}$ (603.1): calcd. C 31.86, H 1.34; found C 31.91, H 1.23.

1-(2′-Bromophenyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooct-1-ene (1d′): Colorless oil (2.435 g, 4.86 mmol), prepared from 2-bromobenzenediazonium tetrafluoroborate (5 mmol) and **4** in 97% yield according to the general procedure. − ^{1}H NMR ($CDCl_3$): δ = 6.23 (dt, 1 H, J_{HH} = 16.0 Hz and J_{HF} = 12.0 Hz, H^2), 7.25 (1 H, td, J = 7.6 and 1.8 Hz, H$^{4'}$), 7.37 (1 H, td, J = 7.5 and 1.2 Hz, H$^{5'}$), 7.54−7.70 (m, 3 H, H^1, H$^{3'}$ and H$^{6'}$). − ^{13}C NMR ($CDCl_3$): δ = 117.1 (t, J_{CF} = 23.2 Hz, C^2), 124.6 (C$^{2'}$), 127.4 (C$^{5'}$ or C$^{6'}$), 127.6 (C$^{5'}$ or C$^{6'}$), 130.9 (C$^{4'}$), 133.2 (C$^{3'}$), 133.8 (C$^{1'}$), 138.7 (t, J_{CF} = 9.8 Hz, C^1). − $C_{14}H_6BrF_{13}$ (501.1): calcd. C 33.56, H 1.21; found C 33.50, H 1.25.

1-(4′-Bromo-3′-methylphenyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodec-1-ene (1e): Colorless oil (5.320 g, 8.65 mmol), prepared from 4-bromo-3-methylbenzenediazonium tetrafluoroborate (9.3 mmol) and **5** in 93% yield according to the general procedure. − ^{1}H NMR ($CDCl_3$): δ = 2.45 (s, 3 H, CH_3), 6.22 (dt, 1 H, J_{HH} = 16.0 Hz and J_{HF} = 12.1 Hz, H^2), 7.08−7.20 (m, 2 H, H^2 and H$^{6'}$), 7.35 (s, 1 H, H$^{2'}$), 7.58 (d, 1 H, J = 8.2 Hz, H$^{5'}$). − ^{13}C NMR ($CDCl_3$): δ = 22.7 (CH_3), 114.7 (t, J_{CF} = 23.3 Hz, C^2), 126.1 (C$^{6'}$), 126.8 (C$^{4'}$), 129.7 (C$^{2'}$), 132.6 (C$^{1'}$), 132.8 (C$^{5'}$), 138.6 (t, J_{CF} = 9.6 Hz, C^1), 138.7 (C$^{3'}$).

1-(4′-Bromo-3′-methylphenyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecane (2e): Colorless oil (4.780 g, 7.77 mmol), prepared from **1e** (8.0 mmol) in 97% yield according to the general procedure. − ^{1}H NMR ($CDCl_3$): δ = 2.24−2.54 (m, 2 H, H^2), 2.45 (s, 3 H, CH_3), 2.86−2.94 (m, 2 H, H^1), 6.94 (d, 1 H, J = 8.1 Hz, H$^{6'}$), 7.15 (s, 1 H, H$^{2'}$), 7.52 (d, 1 H, J = 8.1 Hz, H$^{5'}$). − ^{13}C NMR ($CDCl_3$): δ = 22.5 (CH_3), 25.7 (C^1), 32.7 (t, J_{CF} = 22.2 Hz, C^2), 122.9 (C$^{4'}$), 127.0 (C$^{6'}$), 130.6 (C$^{2'}$), 132.5 (C$^{5'}$), 138.17 and 138.25 (C$^{1'}$ and C$^{3'}$). − MS (70 eV); *m/z* (%): 616 and 618 (12) [M$^+$], 537 (9), 183 and 185 (100). − $C_{17}H_{10}BrF_{17}$ (617.1): calcd. C 33.09, H 1.63; found C 33.19, H 1.84.

1-(4′-Ethoxycarbonylphenyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodec-1-ene (1f): White solid (2.937 g, 4.94 mmol), prepared from ethyl 4-ethoxycarbonylbenzenediazonium tetrafluoroborate (5 mmol) and **5** in 99% yield according to the general procedure. − M.p. 41 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.43 (t, 3 H, J = 7.1 Hz, CH_3), 4.42 (q, 2 H, J = 7.1 Hz, OCH^2), 6.32 (dt, 1 H, J_{HH} = 16.1 Hz and J_{HF} = 12.0 Hz, H^2), 7.25 (dt, 1 H, J_{HH} = 16.1 Hz and J_{HF} = 2.2 Hz, H^1), 7.56 (d, 2 H, J = 8.4 Hz, H$^{2'}$), 8.10 (d, 2 H, J = 8.4 Hz, H$^{3'}$). − ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 61.1 (OCH_2), 116.6 (t, J_{CF} = 23.3 Hz, C^2), 127.3 (C$^{2'}$), 130.0 (C$^{3'}$), 131.7 (C$^{4'}$), 137.4 (C$^{1'}$), 138.6 (t, J = 9.3 Hz, C^1), 165.7 (C=O). − $C_{19}H_{11}F_{17}O_2$ (594.3): calcd. C 38.40, H 1.87; found C 38.40, H 1.72.

1-(4′-Ethoxycarbonylphenyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecane (2f): White solid (2.331 g, 3.91 mmol), prepared from **1f** (4 mmol) in 98% yield according to the general procedure. − M.p. 50 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.42 (t, 3 H, J = 7.1 Hz, CH_3), 2.28−2.54 (m, 2 H, H^2), 2.95−3.04 (m, 2 H, H^1), 4.40 (q, 2 H, J = 7.1 Hz, OCH_2), 7.31 (d, 2 H, J = 8.2 Hz, H$^{2'}$), 8.03 (d, 2 H, J = 8.2 Hz, H$^{3'}$). − ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 26.3 (C^1), 32.4 (t, J_{CF} = 22.2 Hz, C^2), 60.8 (OCH_2), 128.1 (C$^{2'}$), 129.1 (C$^{4'}$), 129.9 (C$^{3'}$), 144.1 (C$^{1'}$), 166.2 (C=O). − MS (70 eV); *m/z* (%): 596 (14) [M$^{+\cdot}$], 568 (27), 551 (80), 163 (45), 131 (75), 109 (100). − $C_{19}H_{13}F_{17}O_2$ (596.3): calcd. C 38.27, H 2.20; found C 38.26, H 2.29.

1-(2′-Ethoxycarbonylphenyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodec-1-ene (1g): Colorless oil (2.661 g, 4.48 mmol), prepared from 2-ethoxycarbonylbenzenediazonium tetrafluoroborate (5 mmol) and **5** in 90% yield according to the general procedure. − ^{1}H NMR ($CDCl_3$): δ = 1.42 (t, 3 H, J = 7.1 Hz, CH_3), 4.42 (q, 2 H, J = 7.1 Hz, OCH_2), 6.08 (dt, 1 H, J_{HH} = 15.9 and J_{HF} = 12.1 Hz, H^2), 7.44−7.63 (m, 3 H), 8.03−8.11 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 61.4 (OCH_2), 116.6 (t, J_{CF} = 22.7 Hz, C^2), 127.8 (C$^{6'}$), 129.2 (C$^{4'}$), 129.6 (C$^{2'}$), 130.9 (C$^{3'}$), 132.3 (C$^{4'}$), 135.5 (C$^{1'}$), 139.7 (t, J_{CF} = 9.4 Hz, C^1), 166.4 (C=O).

1-(2′-Ethoxycarbonylphenyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecane (2g): Colorless oil (2.349 g, 3.94 mmol), prepared from **1g** (4 mmol) in 99% yield according to the general procedure. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.42 (t, 3 H, J = 7.1 Hz, CH_3), 2.34−2.61 (m, 2 H, H^2), 3.23−3.31 (m, 2 H, H^1), 4.42 (q, 2 H, J = 7.1 Hz, OCH_2), 7.28−7.38 (m, 2 H, H$^{4'}$ and H$^{6'}$), 7.49 (2 H, td, J = 7.4 and 1.5 Hz, H$^{5'}$), 8.03 (dd, 2 H, J = 7.7 and 1.2 Hz, H$^{3'}$). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 13.9 (CH_3), 25.6 (C^1), 32.6 (t, J_{CF} = 22.0 Hz, C^2), 60.9 (OCH_2), 126.7 (C$^{4'}$), 129.8 (C$^{2'}$), 131.0 (C$^{3'}$ and C$^{6'}$), 132.2 (C$^{5'}$), 140.8 (C$^{1'}$), 167.0 (C=O). − MS (70 eV); *m/z* (%): 596 (7) [M$^+$], 551 (14), 149 (36), 131 (100).

− $C_{19}H_{13}F_{17}O_2$ (596.3): calcd. C 38.27, H 2.20; found C 38.27, H 2.17.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-(4′-nitrophenyl)dec-1-ene (1h): Grey solid (2.768 g, 4.88 mmol), prepared from 4-nitrobenzenediazonium tetrafluoroborate (5 mmol) and **5** in 98% yield according to the general procedure. − M.p. 92−97 °C. − ^{1}H NMR ($CDCl_3$): δ = 6.39 (dt, 1 H, J_{HH} = 16.0 Hz and J_{HF} = 12.0 Hz, H^2), 7.28 (dt, 1 H, J_{HH} = 16.1 Hz and J_{HF} = 2.1 Hz, H^1), 7.68 (d, 2 H, J = 8.4 Hz, $H^{2'}$), 8.30 (d, 2 H, J = 8.4 Hz, $H^{3'}$). − ^{13}C NMR ($CDCl_3$): δ = 118.7 (t, J_{CF} = 23.3 Hz, C^2), 124.1 ($C^{3'}$), 128.3 ($C^{2'}$), 137.3 (t, J_{CF} = 4.0 Hz, C^1), 139.3 ($C^{1'}$), 148.5 ($C^{4'}$). − $C_{16}H_6F_{17}NO_2$ (567.2): calcd. C 33.88, H 1.07, N 2.47; found C 33.85, H 0.99, N 2.64.

1-(4′-Aminophenyl)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecane (2k): White solid (1.990 g, 3.69 mmol), prepared from **1h** (4 mmol) in 92% yield according to the general procedure. − M.p. 68 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.19−2.49 (m, 2 H, H^2), 2.76−2.89 (m, 2 H, H^1), 3.64 (2 H, br s, NH_2), 6.68 (d, 2 H, J = 8.3 Hz, $H^{3'}$), 7.04 (d, 2 H, J = 8.3 Hz, $H^{2'}$). − ^{13}C NMR ($CDCl_3$): δ = 25.4 (C^1), 33.2 (t, J_{CF} = 22.2 Hz, C^2), 115.3 ($C^{3'}$), 129.0 ($C^{1'}$ and $C^{2'}$), 144.9 ($C^{4'}$). − MS (70 eV); *m/z* (%): 539 (7) [$M^{+\cdot}$], 520 (2), 106 (100). − $C_{18}H_{10}F_{17}N$ (539.2): calcd. C 35.64, H 1.87, N 2.60; found C 35.62, H 1.78, N 2.61.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-phenyldec-1-ene (1i): Colorless oil (2.578 g, 4.94 mmol), prepared from benzenediazonium tetrafluoroborate (5 mmol) and **5** in 99% yield according to the general procedure. − ^{1}H NMR ($CDCl_3$): δ = 6.31 (dt, 1 H, J_{HH} = 16.1 Hz and J_{HF} = 12.2 Hz, H^2), 7.27 (dt, 1 H, J_{HH} = 16.1 Hz and J_{HF} = 2.2 Hz, H^1), 7.45−7.57 (m, 5 H). − ^{13}C NMR ($CDCl_3$): δ = 114.4 (t, J_{CF} = 23.2 Hz, C^2), 127.5 ($C^{2'}$), 128.8 ($C^{3'}$), 130.0 ($C^{4'}$), 133.6 ($C^{1'}$), 139.7 (t, J_{CF} = 9.5 Hz, C^1). − $C_{16}H_7F_{17}$ (522.2): calcd. C 36.80, H 1.35; found C 36.80, H 1.43.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-(4′-iodophenyl)dec-1-ene (1j): White solid (2.905 g, 4.48 mmol), prepared from 4-iodobenzenediazonium tetrafluoroborate (5 mmol) and **5** in 90% yield according to the general procedure using THF/methanol (1:1) as the solvent at room temperature (the crude product contained around 10% of bis-coupling product). − M.p. 67 °C. − ^{1}H NMR ($CDCl_3$): δ = 6.24 (dt, 1 H, J_{HH} = 16.1 Hz and J_{HF} = 12.0 Hz, H^2), 7.12 (dt, 1 H, J_{HH} = 16.1 Hz and J_{HF} = 2.2 Hz, H^1), 7.23 (d, 2 H, J = 8.4 Hz, $H^{2'}$), 7.78 (d, 2 H, J = 8.4 Hz, $H^{3'}$). − ^{13}C NMR ($CDCl_3$): δ = 96.2 ($C^{4'}$), 115.1 (t, J_{CF} = 22.9 Hz, C^2), 129.0 ($C^{2'}$), 132.9 ($C^{1'}$), 138.1 ($C^{3'}$), 138.6 (t, J_{CF} = 9.6 Hz, C^1). − MS (70 eV); *m/z* (%): 648 (4) [$M^{+\cdot}$], 279 (14), 152 (100). − $C_{16}H_6F_{17}I$ (648.1): calcd. C 29.65, H 0.95; found C 29.50, H 0.88.

Tris[4-(3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,8′,8′,9′,9′,10′,10′,10′-heptadecafluorodecyl)phenyl]phosphane (3b): To a cooled (−30 °C) mixture of **2b** (5.428 g; 9 mmol) in anhydrous THF/Et_2O (1:1, 60 mL) was added dropwise *n*BuLi (3.6 mL, 2.5 M in hexane) keeping the internal temperature below −30 °C. The solution, which turned a yellow-green colour, was stirred for 5 min. Freshly distilled PCl_3 (260 μL, 3 mmol) was added dropwise at −30 °C and the mixture, which turned a purple colour, was stirred at room temperature for 10 min. The solution was filtered through SiO_2 under argon, eluting with anhydrous Et_2O (20 mL, twice). Solvents were removed under reduced pressure to afford 4.5 g of a pale yellow solid (94% yield). The compound (containing around 5% of the oxide) could be recrystallized in Et_2O/MeOH (1:1) to give the phosphane **3b** as a white powder (3.36 g; 70% yield). − M.p. 98 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.35−2.53 (m, 6 H, $H^{2'}$), 2.90−2.99 (m, 6 H, $H^{1'}$), 7.20−7.32 (12 H, Ar). − ^{13}C NMR ($CDCl_3$): δ = 26.1 ($C^{1'}$), 32.6 (t, J_{CF} = 22.1 Hz, $C^{2'}$), 128.4 (d, J_{CP} = 7.0 Hz, C^3), 134.0 (d, J_{CP} = 19.7 Hz, C^2), 135.4 (d, J_{CP} = 10.8 Hz, C^1), 139.8 (C^4). − ^{19}F NMR ($CDCl_3$): δ = −126.6 (m, 2 F, F^9), −124.0 (m, 2 F, F^4), −123.2 (m, 2 F), −122.4 (m, 4 F, F^6 and F^7), −122.1 (m, 2 F), −115.1 (m, 2 F, F^3), −81.34 (m, 3 F, F^{10}). − ^{31}P NMR ($CDCl_3$): δ = −6.6. − $C_{48}H_{18}F_{51}P$ (1600): calcd. C 37.93, H 2.06; found C 38.10, H 1.93.

Tris[4-(3′,3′,4′,4′,5′,5′,6′,6′,7′,7′,8′,8′,9′,9′,10′,10′,10′-heptadecafluorodecyl)-2-methylphenyl]phosphane (3e): This was prepared from **2e** (5.7 mmol) according to the procedure described for **3b**, affording 2.97 g of a light yellow solid (95% yield). The solid could be recrystallized from Et_2O/methanol (1:1) in 64% yield − M.p. 76 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.32−2.51 (m, 6 H, $H^{2'}$), 2.40 (s, 9 H, CH_3), 2.87−2.95 (m, 6 H, $H^{1'}$), 6.67 (dd, 3 H, J = 7.8 and 4.1 Hz, H^5), 6.95 (d, 3 H, J = 7.8 Hz, H^6), 6.95 (d, 3 H, J = 3.4 Hz, H^3). − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 21.0 (d, J_{CP} = 21.2 Hz, CH_3), 26.0 ($C^{1'}$), 32.6 (t, J_{CF} = 22.1 Hz, $C^{2'}$), 125.9 (C^5), 130.1 (C^3), 132.6 (d, J_{CP} = 10.6 Hz, C^1), 133.3 (C^6), 139.6 (C^4), 143.0 (d, J_{CP} = 26.6 Hz, C^2). − ^{19}F NMR ($CDCl_3$): δ = −126.5 (m, 2 F, F^9), −123.9 (m, 2 F, F^4), −123.1 (m, 2 F), −122.3 (m, 4 F, F^6 and F^7), −122.1 (m, 2 F), −115.1 (m, 2 F, F^3), −81.2 (m, 3 F, F^{10}). − ^{31}P NMR ($CDCl_3$): δ = −30.5. − $C_{51}H_{30}F_{51}P$ (1643): calcd. C 37.29, H 1.84; found C 37.43, H 1.76.

Cross-Coupling between 6 and 7: A mixture of $Pd(OAc)_2$ (0.5 mg, 0.005 mmol) and perfluorinated triphenylphosphane **3b** (16 mg, 0.01 mmol) in degassed FC-72/methanol (1:1) mixture (1 mL) was stirred at room temperature for 5 min under argon, then methanol was removed. To this biphasic solution was added a mixture of potassium trifluoro(vinyl)borate **7** (134 mg, 1 mmol) and 4-ethoxycarbonylbenzenediazonium tetrafluoroborate (**6**, 264 mg, 1 mmol) in degassed MeOH (2 mL). The resulting mixture was vigorously stirred until gas evolution ceased. The organic layer was removed and the fluorous phase was washed under argon with methanol (1 mL), water (1 mL) and twice with methanol (1 mL). The combined organic layers were concentrated under reduced pressure, dissolved in Et_2O (10 mL), washed with water (10 mL twice) and brine (10 mL). The solution was dried with anhydrous $MgSO_4$, concentrated under reduced pressure to give 175 mg of 4-ethoxycarbonylstyrene (yield 99%). To the fluorous phase was then added the same mixture as described above to begin a new cycle.

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