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# Fluorous aryl compounds by Matsuda–Heck reaction

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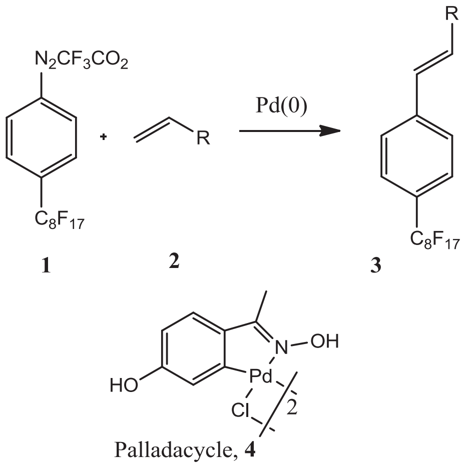
ABSTRACT

Fluorous aryl compounds are obtained through the arylation of different electron-rich and electron-poor olefins with an arenediazonium salt bearing a fully fluorinated octyl-ponytail at the *para* position. The Matsuda–Heck reactions are catalyzed by $Pd(OAc)_2$ or 4-hydroxyacetophenone oxime-derived palladacycle as efficient sources of Pd nanoparticles, with loadings of 1 mol % Pd, at room temperature, in methanol and without the need to add external base.

## 1. Introduction

Fluorinated organic compounds exhibit many unique properties. Important differences from traditional organic chemistry occur in both reactivity and solubility.[1] A large number of liquid crystals,[2] organogelators[3] and in general advanced materials owe their unique property profile to the influence of fluorinated structures. Moreover, most of the ligands used in Fluorous Biphasic Catalysis are also fluorous compounds.[4] Some of us have also proved the utility of heavily fluorinated aromatic thioethers[5a] and 15-membered azamacrocycles[5b] as stabilizers of small Pd nanoparticles (Nps). Furthermore AuNps[6] and PdNps[7] have been supported on organic–inorganic fluorinated hybrid materials. These examples highlight the increasing need for highly efficient methods for the preparation of organofluorine compounds. Consequently, we decided to explore a new approach to synthesize highly fluorinated aromatic compounds, based on the Matsuda–Heck reaction, using a polyfluorinated arenediazonium salt and different alkene substrates (Scheme 1). In 1977, Matsuda's group proved that the arylation of olefins with arenediazonium salts, catalyzed by zerovalent palladium, is indeed an efficient coupling reaction.[8] One of the advantages over using aryl- bromides and -iodides is that $N_2$ is a better leaving group. Additionally, the aryl–nitrogen bond is more reactive towards zerovalent palladium than the aryl–halogen bond.[9] Other benefits are: the short reaction times, the mild reaction conditions and the economic advantage of anilines compared with aryl- bromides and -iodides, which all yield reductions in cost and energy. Several protocols and conditions have recently been published to obtain β,β-disubstituted acrylates,[10] functionalized benzalacetones[11] and *cis*-stilbenes[12] through Matsuda–Heck reactions. For the synthesis of perfluorinated alkenes the



**Scheme 1.** Matsuda–Heck reaction of fluorous arenediazonium salt **1** and different alkenes. Figure of oxime-derived palladacycle **4**.

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Matsuda–Heck reaction has indeed been performed with perfluoroalkenes.[13] In this current work we describe an extension on this process by using a representative arenediazonium salt, bearing a perfluorinated ponytail at the *para* position.

## 2. Results and discussion

The aromatic diazonium salt **1**, which has a ponytail, containing eight fully fluorinated sp$^3$ carbons, was prepared by reaction of the corresponding commercial aniline with butylnitrite and trifluoroacetic acid in MeOH at 0 °C.[14] Compound **1** can be isolated and stored at low temperature.

Some preliminary experiments were carried out to explore different palladium sources in methanol at room temperature. The results obtained using three different alkenes (pent-1-en-3-one, *tert*-butyl acrylate and styrene) are summarized in Table 1. In the arylation of pent-1-en-3-one, $Pd(OAc)_2$ is more effective than $Pd(dba)_2$ and affords product **3a** in 70% yield (Table 1, entries 1 and 2). However, in the case of Pd/C the reaction failed (Table 1, entry 3). When this reaction was performed in the presence of palladacycle **4**[15] a moderate 48% yield was obtained (Table 1, entry 4). The arylation of *tert*-butyl acrylate with **1** using $Pd(OAc)_2$, $Pd(dba)_2$ or **4** afforded the corresponding cinnamate **3b** in good yields (Table 1, entries 5–7). When styrene was used in this reaction, the desired product was isolated in moderate yield, being $Pd(OAc)_2$ a good catalyst (Table 1, entries 8 and 9). As far as we know, oxime palladacycles have been studied as precatalysts in: Heck, Suzuki, Stille, Ullmann and Sonogashira coupling reactions, but had never been used in Matsuda–Heck reactions.[16] The scope of this reaction was studied with both catalysts $Pd(OAc)_2$ and palladacycle **4** (Tables 2 and 3).

**Table 1**
Test of different palladium sources (Scheme 1)[a]

| Entry | R | Source of Pd | Time (h) | Yield[b] (%) of **3** |
|---|---|---|---|---|
| 1 | COEt | $Pd(OAc)_2$ | 1.5 | **3a**, 70 |
| 2 | COEt | $Pd(dba)_2$ | 4.0 | **3a**, 46 |
| 3 | COEt | Pd/C | 24 | 0 |
| 4 | COEt | Palladacycle **4** | 24 | **3a**, 48 |
| 5 | $CO_2^tBu$ | $Pd(OAc)_2$ | 1.5 | **3b**, 63 |
| 6 | $CO_2^tBu$ | $Pd(dba)_2$ | 1.5 | **3b**, 75 |
| 7 | $CO_2^tBu$ | Palladacycle **4** | 1.0 | **3b**, 89 |
| 8 | Ph | $Pd(OAc)_2$ | 20 | **3c**, 55 |
| 9 | Ph | $Pd(dba)_2$ | 20 | **3c**, 47 |

[a] Reactions were carried out at room temperature using 1 equiv of **1**, 5 equiv of **2** and 10 mol % of the catalyst in MeOH.
[b] Isolated yield.

Firstly, we focused our attention on the synthesis of the fluorous benzylideneacetone adduct, **3a**. Besides the importance of benzalacetones, the synthetic access is frequently limited to classical aldol condensations, which often give moderate yields due to side reactions, such as polymerizations. In contrast, through a cross-coupling reaction, compound **3a** was obtained in a good 70% yield, using 10 mol % of $Pd(OAc)_2$ as catalyst, in MeOH at room temperature. $Pd(OAc)_2$ resulted more active than **4** (Table 2, entries 1 and 2). Palladacycle **4** required longer reaction and the total conversion of diazonium salt was accomplished after 24 h (Table 2, entry 2).

The coupling reaction using *tert*-butyl- and ethyl-acrylate olefinic substrates were then explored. Compound **3b** was obtained with 63 and 89% yield using, respectively, 10 mol % of $Pd(OAc)_2$ and 10 mol % of palladacycle **4** (Table 2, entries 5 and 6); palladacycle **4** was observed to be the superior catalyst in this case. Interestingly, reducing the amount of alkene from 5 equiv to 1.2 equiv little effect on the obtained yield was observed and the reaction mixtures become far easier to purify (entries 7 and 9). On changing the substrate to ethyl acrylate, using $Pd(OAc)_2$ as catalyst, very little effect on the system's catalytic activity is observed (88% yield, entry 10). Yielding to the success of $Pd(OAc)_2$, and futhermore its price

**Table 2**
Reaction of alkenes with arenediazonium trifluoroacetate **1** (Scheme 1)[a]

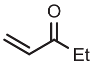
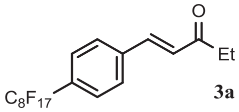
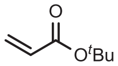
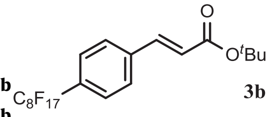
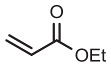
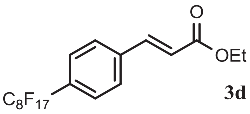
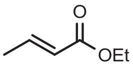
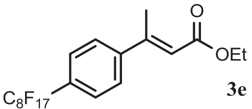
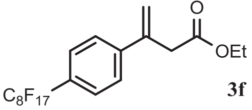
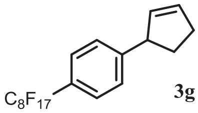
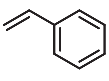
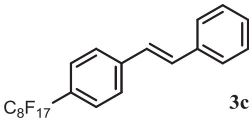
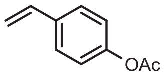
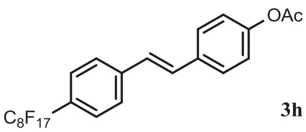
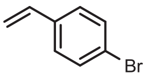
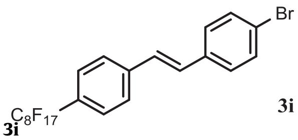
| Entry | Alkene **2** | Catalyst (mol %) | Product | Time (h) | Yield (%)[b] of **3** |
|---|---|---|---|---|---|
| 1 | <br>**2a** | $Pd(OAc)_2$ (10 mol %) | <br>**3a** | 1.5 | 70 |
| 2 | **2a** | Palladacycle **4** (10 mol %) | **3a** | 24 | 48 |
| 3 | **2a** | $Pd(OAc)_2$ (1 mol %) | **3a** | 1.5 | 97 |
| 4 | **2a** | Palladacycle **4** (1 mol %) | **3a** | 24 | 0 |
| 5 | <br>**2b** | $Pd(OAc)_2$ (10 mol %) | <br>**3b** | 1.5 | 63 |
| 6 | **2b** | Palladacycle **4** (10 mol %) | **3b** | 1.0 | 89 |
| 7 | **2b** | Palladacycle **4**[c] (10 mol %) | **3b** | 1.0 | 82 |
| 8 | **2b** | $Pd(OAc)_2$ (1 mol %) | **3b** | 1.5 | 76 |
| 9 | **2b** | Palladacycle **4**[c] (1 mol %) | **3b** | 1.0 | 86 |
| 10 | <br>**2d** | $Pd(OAc)_2$ (10 mol %) | <br>**3d** | 1.5 | 88 |
| 11 | **2d** | $Pd(OAc)_2$ (1 mol %) | **3d** | 1.5 | 97 |
| 12 | <br>**2e** | $Pd(OAc)_2$ (10 mol %) | <br>**3e**<br><br>**3f** | 2.0 | 35<br>7[d] |
| 13 | **2e** | Palladacycle **4** (1 mol %) | **3e** | 1.0 | 0 |

**Table 2** (*continued*)

| Entry | Alkene **2** | Catalyst (mol %) | Product | Time (h) | Yield (%)[b] of **3** |
|---|---|---|---|---|---|
| 14 |  **2g** | Pd(OAc)$_2$ (10 mol %) |  **3g** | 2.0 | 70 |
| 15 | **2g** | Pd(OAc)$_2$ (1 mol %) | **3g** | 2.0 | 61 |
| 16 | **2g** | Palladacycle **4** (1 mol %) | **3g** | 3.0 | 58 |
| 17 |  **2c** | Pd(OAc)$_2$ (10 mol %) |  **3c** | 20 | 55 |
| 18 |  **2h** | Pd(OAc)$_2$[c] (10 mol %) |  **3h** | 8.0 | 24 |
| 19 |  **2i** | Pd(OAc)$_2$[c] (10 mol %) |  **3i** | 2.0 | 91 |
| 20 | **2i** | Pd(OAc)$_2$[c] (1 mol %) | **3i** | 2.0 | 85 |

[a] Unless otherwise stated, reactions were carried out at room temperature using 1 equiv of **1** and 5 equiv of alkene in MeOH.

[b] Isolated yields.

[c] Alkene (1.2 equiv) were used.

[d] Identified by $^1$H NMR.

**Table 3**

Matsuda–Heck reaction of **1** with *p*-methoxystyrene[a]

| Entry | Catalyst | Catalyst (mol %) | Time minutes | Solvent | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 | Pd(OAc)$_2$ | 10 | 30 | MeOH | **5a**, 40 |
| 2 | Pd(OAc)$_2$ | 10 | 15 | *iso*-Propanol | **5b**,[c] 8 |
| 3 | Palladacycle **4** | 1 | 15 | MeOH | **5a**, 60 |
| 4 | Palladacycle **4** | 1 | 60 | *tert*-Butanol | **3j**, 30 and **5c**, 45 |
| 5 | Pd(OAc)$_2$ | 10 | 60 | *tert*-Butanol$_{\text{anhyd}}$ | **3j**, 30 |

[a] Unless otherwise stated, reactions were carried out at room temperature using 1 equiv of **1** and 1.2 equiv of *p*-methoxystyrene.

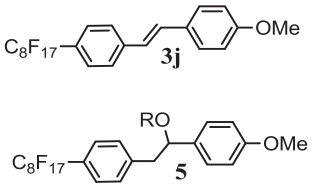
[b] Isolated yields.

[c] Identified by $^1$H NMR.

and relative availability, we decided to further explore its potential in Matsuda–Heck reactions to form fluorous aryl compounds. Next, we investigated a β-monosubstituted acrylate (Table 2, entry 12). In the reaction of ethyl *trans*-crotonate a mixture of two isomers (compounds **3e** and **3f**) was obtained; **3f** is the minor product formed, which is attributed to a palladium catalyzed double bond isomerization.[17] Arylation of cyclopentene gave the fluorous compound **3g** in a good yield (70%, entry 14). Moreover, differently substituted styrenes have been studied, producing fluorous stilbenes (Table 2, entries 17–19); the best results were obtained using *p*-bromostyrene (91% yield, Table 2, entry 19).

The next step of our work was to try and reduce the quantity of catalyst. Noteworthy, is that high yields are indeed obtainable with low catalyst loadings of 1 mol % of Pd(OAc)$_2$ (compare entries 1, 5 and 10 with entries 3, 8 and 11, respectively). Fluorous compounds **3a**,**b**,**d**,**i** were isolated in excellent yields using 1 mol % of Pd(OAc)$_2$ (97, 76, 97 and 85%, respectively). Our findings are in agreement with those of Felpin et al. who have recently described highly efficient couplings of arenediazonium salts with 2-arylacrylates using low palladium loading.[12] In addition, Pd(OAc)$_2$ has also shown to be very active in the Heck reaction of aryl bromides in very low loadings (0.01 and 0.1 mol %). At higher palladium concentrations, Pd(0) black is formed and the reaction is eventually paralysed.[18] In the case of *p*-bromostyrene and cyclopentene, using Pd(OAc)$_2$ 1 mol % as catalyst, a slight decrease in the yield was observed (compare entries 14 and 19 with 15 and 20, respectively). Once again, palladacycle **4** is seen to be less active than Pd(OAc)$_2$. Only when *tert*-butyl acrylate and cyclopentane were used as alkenes in the presence of 1 mol % of **4** yields were similar and even better than using Pd(OAc)$_2$ (Table 2, entries 9 and 16 compared with entries 8 and 15, respectively).

The reaction using *p*-methoxystyrene, which possess an excellent electron donating group, was more complex. In all cases, using either Pd(OAc)$_2$ or palladacycle **4**, we obtained compounds of the type **5** (Fig. 1 and Table 3) coming from the addition of the nucleophilic reaction solvent to the double bond of the corresponding Matsuda–Heck product, **3j**. The palladium promoted addition of oxygen nucleophiles towards alkenes was described by Hosokawa et al. and has recently been observed by the group of Correia in similar *p*-methoxy substituted Matsuda–Heck adducts.[10b,19] For stilbene **3j** the best results were obtained using the less nucleophilic alcohol solvents, such as anhydrous *tert*-butanol (Table 3, entry 5). The presence of the methoxy group has not only an influence in the reactivity of **3j**, but also in the reactivity of the starting material; the reaction times were shorter than those corresponding to the *p*-acetoxy and *p*-bromostyrene. However the reaction mixtures are more complex and the yields were generally modest.



R= Me (**5a**); CH(CH$_3$)$_2$ (**5b**); H (**5c**)

**Fig. 1.** Compounds obtained from *p*-methoxystyrene (Table 3).

The reaction between *tert*-butyl acrylate and the diazonium salt **1** was monitored by ESI-MS[20] in order to obtain new insights into the mechanism using the two different catalytic systems: Pd(OAc)$_2$ and palladacycle **4**. Electrospray mass spectrometry ESI-MS, in both positive and negative-ion modes and its tandem version ESI-MS/MS, is widely used to trap and identify short-lived intermediates in organometallic catalytic cycles.[21] In particular, ESI-MS has been used to detect and characterize cationic palladium species in Heck reactions when diazonium salts are involved as electrophilic partners.[22] A mixture of 1 equiv of diazonium salt **1** and 20 mol % of $Pd(OAc)_2$ was dissolved in MeOH and injected into the mass spectrometer for analysis. The mixture was analyzed in both ESI(+) and ESI(−) modes and in the two cases oxidative addition species were observed. In the ESI(+)-MS a cluster centred at *m*/*z*=682.8 (based on $^{106}Pd$) was identified as $[C_8F_{17}C_6H_4Pd(CH_3OH)_2(H_2O)]^+$ and confirmed by high-resolution ESI(+)-TOF mass spectrometry (*m*/*z*=682.9707). The oxidative species was also observed in ESI(−)-MS. This was just a cluster at *m*/*z*=826.9 corresponding to the species $[C_8F_{17}C_6H_4Pd(CF_3COO)_2]^{-\cdot}$. The cluster was confirmed by mixing 1 equiv of **1** with 20 mol % of $Pd(CF_3COO)_2$ instead of $Pd(CH_3COO)_2$, whose spectrum shows the same cluster centred at *m*/*z*=826.9. An excess of the *tert*-butyl acrylate was then added to the reaction mixture and injected into the spectrometer. However, no species corresponding to the insertion of the olefin were identified[22c,23] in positive or negative modes even when other olefins, such as ethyl acrylate and pent-1-en-3-ona were used. At the end of the reaction, the oxidative addition species disappeared and the final product was observed in the mass spectra. Oxime palladacycle **4** was dissolved in MeOH and injected into the mass spectrometer for analysis. When ESI-MS was used in negative mode ESI(−), it was possible to observe the molecular mass of palladacycle **4** in two clusters: one centred at *m*/*z*=582.8 corresponding to $[M-H]^-$ and the other at *m*/*z*=618.7 corresponding to $[M+Cl]^-$. A mixture of 1 equiv of diazonium salt **1** and 10% molar of **4** dissolved in MeOH was then analyzed. In the ESI(−)-MS, two clusters at *m*/*z*=900.0 and *m*/*z*=975.9 may be attributed to Pd(IV) species, which might correspond to oxidative addition species $[C_8F_{17}C_6H_4Pd(C_8H_8NO_2)(CF_3COO)Cl-H]^-$ and $[C_8F_{17}C_6H_4Pd(C_8H_8NO_2)(CF_3COO)_2-H]^-$, respectively. These two proposed species are corroborated by ESI(−)-MS/MS as both lost $CF_3COOH$ in the fragmentation process. However, when *tert*-butyl acrylate was added to the above mixture no intermediate involving the olefin could be identified in the mass spectra. As these two clusters were still present in the mass spectra at the end of the reaction, we postulate that these species are accumulated in the reaction media and are not the true catalytic species (see ESI-MS spectra en the SD).

Moreover, our experience in using PdNps as catalysts[5–7,24] prompted us to investigate if metal nanoparticles were formed in situ in Matsuda–Heck reactions. Recently it has been demonstrated that palladacycles are precatalysts that behave as a source of active PdNps in other Pd-catalyzed cross-coupling reactions.[25] To demonstrate the formation of PdNps in Matsuda–Heck conditions the reaction of *tert*-butyl acrylate (entry 7, Table 2) was stopped at 15 min and the formed solid was filtered and studied. The TEM images showed the presence of PdNps (aprox. 2 nm of diameter). Additionally, the reaction solution was evaporated and the crude studied by TEM, the photographs showed the presence of small dispersed PdNps of 1.8 nm of diameter. The problem of how Pd(0) is generated remains open for discussion, although for the Heck reaction it has been proposed that oxime palladacycles are activated by insertion of the olefin in the Pd–C bond followed by reduction to Pd(0) and release of palladium from the palladacycle.[26] It seems adequate to propose that the facility of this step will depend on the type of alkene and this fact could explain the difference of activity of palladacycle **4** with respect to a diversity of olefins; the palladacycle **4** is completely inactive for ethyl vinyl ketone and ethyl *trans*-crotonate when 1 mol % is used (Table 2, entries 4 and 13, respectively), but in contrast shows high activity for *tert*-butyl acrylate (Table 2, entry 9). Palladacycles work as a reservoir of active Pd(0) species, which are released into the catalytic cycle. Similar results with respect to the formation of nanoparticles were obtained for $Pd(OAc)_2$ under the same reaction conditions. Several years ago some of us proved that fluorous compounds having perfluorinated ponytails are excellent stabilizers of metal Nps.[5,7,24f] Hence, it was first postulated that the products derived from the polyfluorinated diazonium salt could act as stabilizers. However, PdNps were also formed in the Matsuda–Heck reaction of *p*-methoxybenzenediazonium trifluoroacetate, a nonfluorinated diazonium cation. As no black palladium is formed during the catalytic process, we propose that the stabilization of PdNps is probably achieved in our reaction mixtures by the anionic trifluoroacetate. These Nps should act as a reservoir of the Pd(0) atoms, which are involved in the catalytic cycles.

## 3. Conclusions

The Matsuda–Heck reaction is a good method for obtaining new polyfluorinated aryl compounds from a fluorous arenediazonium salt. No external base is required and the reactions could be carried out at room temperature, using low catalyst loadings: 1 mol % of Pd(II). Ligand-free $Pd(OAc)_2$ seems to be a more general catalyst than palladacycle **4** for this Matsuda–Heck reaction. The activity of **4** depends highly on the nature of the alkene used. Some intermediates derived from the oxidative addition of the diazonium salt to the catalyst were identified by ESI-MS experiments. Unfortunately, in neither case, intermediates containing the coordination or insertion of the alkene to the metal have been detected. The Pd(IV) species detected by this technique when palladacycle **4** was studied, do not seem to act as intermediates of the reactions. TEM images of the reaction solution show, for the first time, the formation of nanoparticles with both catalysts in Matsuda–Heck conditions. These palladium(0) nanoparticles should act as a reservoir of Pd(0) atoms involved in the mechanism. Their formation avoids the precipitation of black palladium and probably extends the life of the catalyst.

## 4. Experimental

### 4.1. General

Melting points were determined using a Kofler-Reichert and have not been corrected. Compounds **3i**, **3j** and **5c** showed a strange behaviour during the melting process; further studies are in process in order to determine if they are mesogenic molecules. Elemental analyses for C, H, N and S are the average of two determinations. IR spectra were recorded using KBr disks on a Thermo Nicolet IR200. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker Advance 360 at 360 MHz (H) and at 90 MHz (C). Only in some $^{13}C$ NMR spectra carbon signals corresponding to $C_8F_{17}$ chain have been observed (around 110–120 ppm). $^{19}F$ NMR spectra were recorded on a Bruker AC-250 at 235 MHz in the 'Servei de Ressonància Magnètica Nuclear' (SeRMN) at the Universitat Autònoma de Barcelona.

HR-TEM analyses were performed in the 'Servei de Microscòpia' of the Universitat Autònoma de Barcelona, in a JEOL JEM-2010 model at 200 kV. HR-ESI analyses were performed in the 'Servei d'Anàlisi Química' (SAQ) at the Universitat Autònoma de Barcelona and in the Universidad de Zaragoza using a MicroTof-Q from Bruker Daltonics.

Electrospray mass spectrometry analyses were recorded on a 6000 ESI Ion Trap LC/MS either in the positive-ion mode ($ESI^+$) and the negative-ion mode ($ESI^-$). The mixtures were dissolved in methanol and the samples were introduced into the mass spectrometer ion source via liquid chromatographic system (HPLC P1200 Agilent) at a flow rate of 100 μL/min. The mobile phase ($CH_3OH/H_2O$ 80:20) was delivered to the vaporization nozzle of the electrospray ion source at 350 °C and nitrogen was employed as both a drying and a nebulizing gas at a flow rate of 7 L/min.

The Bruker Daltonics Compass Isotope Pattern programme was used to calculate the theoretical isotope patterns and to aid assignment.

## 4.2. Typical experiment

*4.2.1. Preparation of **3i**.* Diazonium salt **1** (887 mg, 1.39 mmol, 1.2 equiv) and $Pd(OAc)_2$ (26 mg, 0.12 mmol, 0.1 equiv) were introduced in to a Schlenk tube under inert atmosphere. Then 4-bromostyrene (213 mg, 1.16 mmol, 1.0 equiv) and anhydrous methanol (5 mL) were added. The mixture was stirred for 2 h. Then the solvent was evaporated and the residue was purified by column chromatography using hexane as eluent affording **3i** as a white solid (714 mg, 91% yield, entry 11, Table 2).

*4.2.2. 4-(Perfluorooctyl)benzenediazonium trifluoroacetate **1**[14].* Mp: 104–106 °C (dec). IR (KBr, $cm^{-1}$): 3110, 2305, 1794, 1371, 1300, 1203, 1154, 1120, 945, 857, 707, 645. $^{1}H$ NMR (360 MHz; MeOD) $\delta_H$=8.37 (2H, d, *J*=8.8), 8.92 (2H, d, *J*=8.8). $^{13}C$ NMR (90 MHz; MeOD) $\delta_C$=111–118 (m), 115.9 (q, *J*=290), 120.9, 129.9 (t, *J*=7), 132.7, 139.2 (t, *J*=25), 159.9 (q, *J*=38). $^{19}F\{^{1}H\}$ NMR (235 MHz; MeOD) $\delta_F$=−76.7, −81.3, −112.6, −121.6, −122.3, −123.2, −126.6. HR-ESI (*m*/*z*): [calcd]: $[M]^+$, 523.0103; [exptl.]: $[M]^+$, 523.0111.

*4.2.3. (E)-1-(4-(Perfluorooctyl)phenyl)pent-1-en-3-one **3a**.* The product was purified by column chromatography using hexane–diethyl ether (9:1) as eluent affording **3a** as a white solid (37 mg, 81% yield). Mp: 98–101 °C. Found: C, 39.33; H, 1.70. $C_{19}H_{11}F_{17}O$ requires C, 39.46; H, 1.92. IR (KBr, $cm^{-1}$): 2982, 2943, 1695, 1667, 1619, 1417, 1372, 1331, 1301, 1246, 1198, 1146, 1115, 946, 656. $^{1}H$ NMR ($CDCl_3$; 360 MHz) $\delta_H$=1.18 (3H, t, *J*=7.2), 2.72 (2H, q, *J*=7.2), 6.82 (1H, d, *J*=16.2), 7.57 (1H, d, *J*=16.2), 7.61 (2H, d, *J*=8.3), 7.67 (2H, d, *J*=8.3). $^{13}C$ NMR ($CDCl_3$; 90 MHz) $\delta_C$=8.0, 34.4, 108–118 (m), 127.4 (t, *J*=7), 128.1, 130.2 (t, *J*=25), 138.2, 140.0, 200.4.

*4.2.4. (E)-tert-Butyl 4-(perfluorooctyl)cinnamate **3b**.* The product was purified by column chromatography using hexane–diethyl ether (95:5) as eluent affording **3b** as a white solid (87 mg, 89% yield). Mp: 83–84 °C. Found: C, 40.42; H, 2.57. $C_{21}H_{15}F_{17}O_2$ requires C, 40.53; H, 2.43. IR (KBr, $cm^{-1}$): 2982, 2935, 1709, 1640, 1370, 1321, 1213, 1148, 1104, 946, 843, 660. $^{1}H$ NMR ($CDCl_3$; 360 MHz) $\delta_H$=1.54 (9H, s), 6.45 (1H, d, *J*=16.0), 7.61 (2H, d, *J*=8.5), 7.62 (1H, d, *J*=16.0), 7.65 (2H, d, *J*=8.5). $^{13}C$ NMR ($CDCl_3$; 100 MHz) $\delta_C$=28.1, 81.0, 107–118 (m), 123.0, 127.3 (t, *J*=7), 127.9, 129.9 (t, *J*=25), 138.3, 141.6, 165.7.

*4.2.5. (E)-4-(Perfluorooctyl)stilbene **3c**.* The product was purified by column chromatography using hexane–diethyl ether (99:1) as eluent affording **3c** as a white solid (44 mg, 55% yield). Mp: 128–129 °C. Found: C, 44.22; H, 1.83. $C_{22}H_{11}F_{17}$ requires C, 44.16; H, 1.85. IR (KBr, $cm^{-1}$): 1200, 1150, 1117, 967, 873, 826, 795, 695, 653, 562. $^{1}H$ NMR ($CDCl_3$; 360 MHz) $\delta_H$=7.13 (1H, d, *J*=16.4), 7.22 (1H, d, *J*=16.4), 7.28–7.35 (1H, m), 7.40 (2H, m), 7.55 (2H, d, *J*=7.3), 7.57 (2H, d, *J*=8.8), 7.63 (2H, d, *J*=8.8). $^{13}C$ NMR ($CDCl_3$; 90 MHz) $\delta_C$=126.5, 126.8, 127.0, 127.2 (t, *J*=7), 127.5 (t, *J*=25), 128.4, 128.8, 131.4, 136.6, 141.0.

*4.2.6. (E)-Ethyl 4-(perfluorooctyl)cinnamate **3d**.* The product was purified by column chromatography using hexane–diethyl ether (98:2) as eluent affording **3d** as a white solid (820 mg, 88% yield). Mp: 85–88 °C. IR (KBr, $cm^{-1}$): 2992, 1710, 1644, 1370, 1249, 1196, 1146, 1039, 946, 807, 658, 560. $^{1}H$ NMR ($CDCl_3$; 360 MHz) $\delta_H$=1.35 (3H, t, *J*=7.1), 4.29 (2H, q, *J*=7.1), 6.52 (1H, d, *J*=16.1), 7.61 (2H, d, *J*=8.7), 7.64 (2H, d, *J*=8.7), 7.70 (1H, d, *J*=16.1). $^{13}C$ NMR ($CDCl_3$; 90 MHz) $\delta_C$=14.1, 60.7, 105–118 (m), 121.0, 127.4 (t, *J*=7), 127.9, 130.2 (t, *J*=25), 138.0, 142.5, 166.3. $^{19}F\{^{1}H\}$ NMR ($CDCl_3$; 235 MHz) $\delta_F$=−81.6, −111.6, −121.9, −122.4, −123.4, −126.9. HR-ESI (*m*/*z*): [calcd]: $[M+Na]^+$, 617.0380; [exptl.]: $[M+Na]^+$, 617.0388.

*4.2.7. (E)-Ethyl 3-(4-(perfluorooctyl)phenyl)but-2-enoate **3e**.* The product was purified by column chromatography using hexane–diethyl ether (95:5) as eluent affording **3e** as a white solid (67 mg, 35% yield). Mp: 35–42 °C. IR (KBr, $cm^{-1}$): 2989, 1706, 1634, 1370, 1244, 1200, 1147, 1115, 1046, 946, 844, 660, 562. $^{1}H$ NMR ($CDCl_3$; 360 MHz) $\delta_H$=1.32 (3H, t, *J*=7.1), 2.58 (3H, s), 4.23 (2H, q, *J*=7.1), 6.17 (1H, s), 7.59 (4H, s). $^{13}C$ NMR ($CDCl_3$; 90 MHz) $\delta_C$=14.3, 17.9, 60.1, 119.1, 126.5, 127.1 (t, *J*=7), 129.2 (t, *J*=25), 146.0, 153.6, 166.4. $^{19}F\{^{1}H\}$ NMR ($CDCl_3$; 235 MHz) $\delta_F$=−80.8, −110.8, −121.3, −121.8, −122.7, −126.1. HR-ESI (*m*/*z*): [calcd]: $[M+Na]^+$, 631.0536; [exptl.]: $[M+Na]^+$, 631.0530.

Compound **3f** decompose very fast and could not be completely characterized.

*4.2.8. 1-(Cyclopent-2-enyl)-4-(perfluorooctyl)benzene **3g**.* The product was purified by column chromatography using hexane as eluent affording **3g** as a colourless liquid (622 mg, 70% yield). $^{1}H$ NMR ($CDCl_3$; 360 MHz) $\delta_H$=1.71–1.75 (1H, m), 2.40–2.50 (3H, m), 3.94–3.97 (1H, m), 5.75–5.80 (1H, m), 5.98–6.01 (1H, m), 7.31 (2H, d, *J*=8), 7.50 (2H, d, *J*=8).

*4.2.9. (E)-4-(4-(Perfluorooctyl)styryl)phenyl acetate **3h**.* The product was purified by column chromatography using hexane–diethyl ether (80:20) as eluent affording **3h** as a white solid (72 mg, 24% yield). Mp: 114–115 °C. IR (KBr, $cm^{-1}$): 1760, 1372, 1301, 1230, 1201, 1150, 1115, 849, 658, 561. $^{1}H$ NMR ($CDCl_3$; 360 MHz) $\delta_H$=2.32 (3H, s), 7.07 (1H, d, *J*=16.4), 7.12 (2H, d, *J*=8.6), 7.19 (1H, d, *J*=16.4), 7.58 (6H, m). $^{13}C$ NMR ($CDCl_3$; 90 MHz) $\delta_C$=21.2, 122.0, 126.5, 127.2 (t, *J*=7), 127.3, 127.6 (t, *J*=24), 127.8, 130.4, 134.4, 140.9, 150.6, 169.4. $^{19}F\{^{1}H\}$ NMR ($CDCl_3$; 235 MHz) $\delta_F$=−81.2, −111.1, −121.6, −122.3, −123.1, −126.5. HR-ESI (*m*/*z*): [calcd]: $[M+Na]^+$, 679.0536; [exptl.]: $[M+Na]^+$, 679.0530.

*4.2.10. (E)-1-Bromo-4-(4-(perfluorooctyl)styryl)benzene **3i**.* The product was purified by column chromatography using hexane–diethyl ether (9:1) as eluent affording **3a** as a white solid (714 mg, 91% yield). Found: C, 39.07; H, 1.29. $C_{22}H_{10}BrF_{17}$ requires C, 39.02; H, 1.49. IR (KBr, $cm^{-1}$): 1371, 1300, 1249, 1199, 1145, 1114, 944, 839, 657. $^{1}H$ NMR ($CDCl_3$; 360 MHz) $\delta_H$=7.11 (1H, d, *J*=16.8), 7.15 (1H, d, *J*=16.8), 7.40 (2H, d, *J*=8.4), 7.51 (2H, d, *J*=8.4), 7.57 (2H, d, *J*=8.4), 7.61 (2H, d, *J*=8.4). $^{13}C$ NMR ($CDCl_3$; 90 MHz) $\delta_C$=122.2, 126.6, 127.3 (t, *J*=7), 127.7, 127.8 (t, *J*=25), 128.2, 130.2, 131.9, 135.5, 140.6. $^{19}F\{^{1}H\}$ NMR ($CDCl_3$; 235 MHz) $\delta_F$=−81.3, −111.1, −121.6, −121.7, −122.3, −126.5.

*4.2.11. (E)-1-Methoxy-4-(4-(perfluorooctyl)styryl)benzene **3j**.* The product was purified by column chromatography using hexane–diethyl ether (95:5) as eluent affording **3j** as a slightly yellow solid (59 mg, 30% yield). Found: C, 43.87; H, 2.19. $C_{23}H_{13}F_{17}O$ requires C, 43.97; H, 2.09. IR (KBr, $cm^{-1}$): 3026, 2967, 2938, 2913, 2842, 1607, 1520, 1203, 1153, 1092, 1027, 971, 838, 653, 561. $^{1}H$ NMR ($CDCl_3$; 360 MHz) $\delta_H$=3.84 (3H, s), 6.92 (2H, d, *J*=8.8), 6.99 (1H, d, *J*=16.3), 7.17 (1H, d, *J*=16.3), 7.48 (2H, d, *J*=8.8), 7.55 (2H, d, *J*=8.5), 7.59 (2H, d, *J*=8.5). $^{13}C$ NMR ($CDCl_3$; 90 MHz) $\delta_C$=55.3, 114.2, 124.9, 126.2, 127.1 (t, *J*=25), 127.2 (t, *J*=7), 128.1, 129.4, 131.0, 141.4, 159.9. $^{19}F\{^{1}H\}$ NMR ($CDCl_3$; 235 MHz) $\delta_F$=−80.9, −110.4, −121.1, −121.7, −122.6, −126.0.

*4.2.12. 1-Methoxy-4-(1-methoxy-2-(4-(perfluorooctyl)phenyl)ethyl)-benzene **5a**.* The product was purified by column chromatography using hexane–diethyl ether (95:5) as eluent affording **5a** as a white solid (125 mg, 60% yield). Mp: 76–77 °C. Found: C, 43.62; H, 2.59.

$C_{24}H_{17}F_{17}O_2$ requires C, 43.65; H, 2.59. IR (KBr, $cm^{-1}$): 2942, 2917, 2845, 1738, 1615, 1513, 1372, 1301, 1201, 1150, 1101, 1034, 941, 834, 823, 660, 565, 530. $^1H$ NMR ($CDCl_3$; 360 MHz) $\delta_H$=2.93 (1H, m), 3.16 (1H, m), 3.17 (3H, s), 3.81 (3H, s), 4.29 (1H, m), 6.85 (2H, d, *J*=8.3), 7.12 (2H, d, *J*=8.3), 7.22 (2H, d, *J*=8.3), 7.44 (2H, d, *J*=8.3). $^{13}C$ NMR ($CDCl_3$; 90 MHz) $\delta_C$=44.5, 55.2, 56.5, 84.0, 113.8, 126.5 (t, *J*=7), 126.7 (t, *J*=24), 127.9, 129.7, 133.0, 143.0, 159.2. $^{19}F\{^1H\}$ NMR ($CDCl_3$; 235 MHz) $\delta_F$=−81.3, −110.9, −121.7, −122.4, −123.2, −126.5.

*4.2.13. 1-(4-Methoxyphenyl)-2-(4-(perfluorooctyl)phenyl)ethanol* ***5c***. The product was purified by column chromatography twice using hexane–diethyl ether (95:5) as eluent and then using hexane–dichloromethane (8:2) as eluent affording **5c** as a slightly yellow solid (687 mg, 45% yield). Mp: 95–104 °C. IR (KBr, $cm^{-1}$): 3407, 2921, 1614, 1517, 1372, 1300, 1203, 1150, 1103, 1048, 944, 835, 645. $^1H$ NMR ($CDCl_3$; 360 MHz) $\delta_H$=1.86 (1H, s), 3.02 (2H, m), 3.81 (3H, s), 4.88 (1H, m), 6.87 (2H, d, *J*=8.6), 7.24 (2H, d, *J*=9.2), 7.29 (2H, d, *J*=9.2), 7.50 (2H, d, *J*=8.6). $^{13}C$ NMR ($CDCl_3$; 90 MHz) $\delta_C$=45.5, 55.3, 74.7, 113.9, 126.8 (t, *J*=7), 127.1, 129.8, 135.6, 142.7, 159.3. $^{19}F\{^1H\}$ NMR ($CDCl_3$; 235 MHz) $\delta_F$=−81.2, −110.9, −122.3, −123.1, −123.2, −126.5. HR-ESI (*m*/*z*): [calcd]: $[M+Na]^+$, 669.0698; [exptl.]: $[M+Na]^+$, 669.0687.

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## Supplementary data

Supplementary data containing $^1H$, $^{13}C$ NMR, IR and HRMS spectra of all new compounds described in this article will be available. ESI-MS spectra corresponding to experiments described in the text and selected TEM images of NPs observed during the reactions are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.09.046.

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