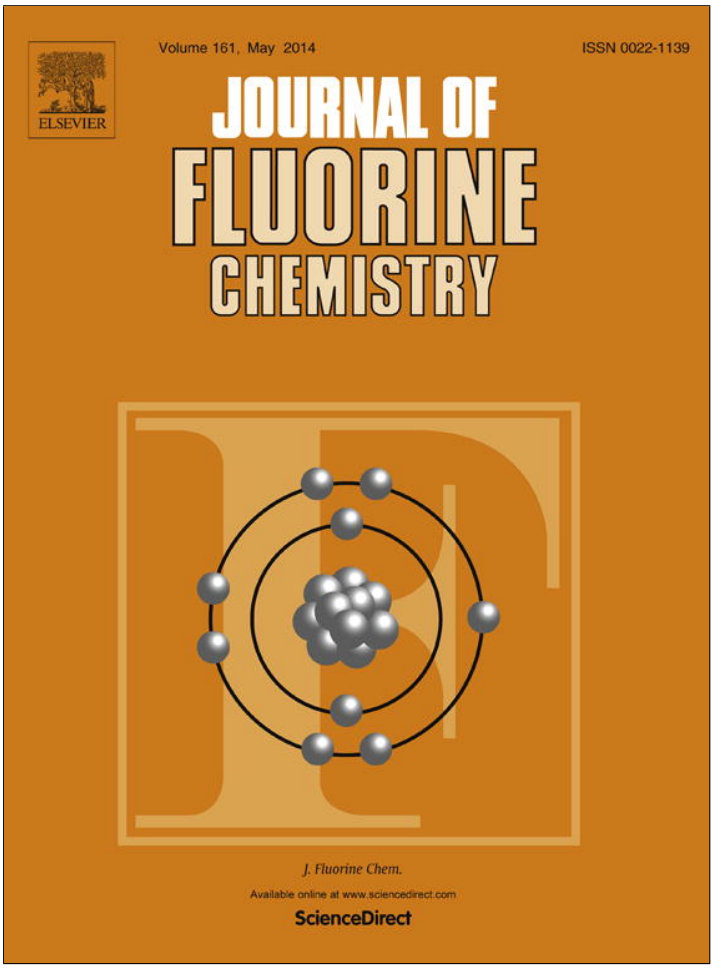

Journal of Fluorine Chemistry 161 (2014) 149–155

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Short Communication

Direct C–H perfluoroalkylation of (di)benzo(hetero)arenes in aqueous media

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ARTICLE INFO

Article history:
Received 3 December 2013
Received in revised form 2 February 2014
Accepted 20 February 2014
Available online 1 March 2014

Keywords:
Homolytic aromatic substitution
Perfluoroalkylation
Dibenzoheteroarenes
C–H perfluoroalkylation
Radical reactions aqueous in media

ABSTRACT

Perfluorobutylation of a series of benzo- and dibenzo-(hetero)aromatic compounds without formal leaving groups is achieved efficiently in organic solvent: water mixtures under photostimulation. The methodology is compared to previously reported trifluoromethylation strategies of these nuclei in terms of product yields and regioselectivity. The global reaction is a radical homolytic aromatic substitution process, where the perfluoroalkyl-substituted cyclohexadienyl radical intermediate is first oxidized and then a proton transfer sequence affords the products. This constitutes the first report for a direct perfluoroalkylation strategy of dibenzo(hetero)arenes without formal leaving groups.

1. Introduction

The incorporation of fluoroalkyl groups, and particularly the trifluoromethyl group, in molecules of pharmaceutical interest has a profound impact on their physical and biological properties, mainly because of the unique metabolic stability, lipophilicity, and electron-withdrawing nature of the fluoroalkyl substituent. The relevance of the fluoroalkyl and CF_3-containing substrates, provides the driving force for the development of more efficacious and versatile synthetic protocols for these type of molecules [1]. On the other hand, the presence of perfluoroalkyl groups imparts polymers with interesting properties, such as hydrophobic and oleophobic behaviors, functional coating and ease in film formation [2]. Fluorinated and perfluoroalkylated phenylene units are used as building blocks for all-conjugated (hetero)fluorene-based alternating copolymers (*i.e.* PFO-TFP) [3]. Specially, fluorinated and perfluoroalkylated dibenzoheteroarenes show diverse applications in different fields, such as in the manufacturing of liquid-crystal displays (due to the influence that fluorinated groups exert in the dielectric anisotropy ($\Delta\varepsilon$) or the optical anisotropy (Δn) properties) [4].

A division can be established regarding innate perfluoroakylation reagents, which accomplish substitution of aromatic nuclei without formal leaving groups, and those perfluoroalkylation reagents which effect substitution on functionalized aromatic substrates bearing formal leaving groups [5]. Among the former, the Langlois reagent [6], $NaSO_2CF_3$, has widely been used under mild radical initiation conditions with ^{t}BuOOH to obtain perfluoroalkyl-substituted aromatic compounds in good yields in aqueous media. Togni and collaborators have accomplished the trifluoromethylation of a series of heteroaromatic compounds using the hypervalent iodine reagent 1-(trifluoromethyl)-1,2-benziodoxol-3-(1*H*)-one **I** (Scheme 1) and methyl trioxorhenium as catalyst [7a]. Very recently, this latter reagent (**I**) has been used in the perfluoroalkylation of phenanthridines through a radical mechanism in dioxane as solvent, in the absence of methyltrioxorhenium as catalyst [7b].

In 2012, Baran and colleagues [8] have introduced and developed a new class of reagents for accomplishing the radical

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http://dx.doi.org/10.1016/j.jfluchem.2014.02.008
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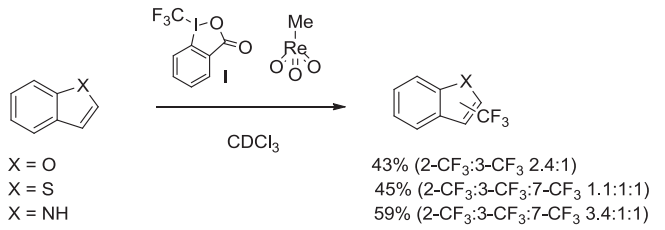


Scheme 1. Use of the Togni' reagent and methyl trioxorhenium as catalyst for the trifluoromethylation of heteroaromatic compounds.

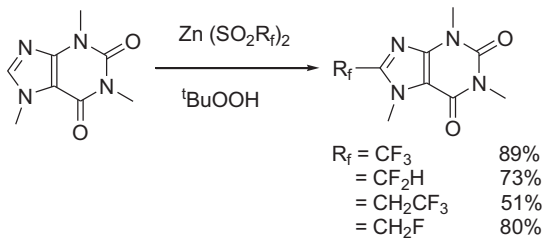
homolytic substitution of aromatic and heteroaromatic nuclei with perfluoroalkyl groups (innate perfluoroalkylation) in aqueous media. Thus, the versatile zinc sulfinate salts of fluoroalkanes ($Zn(R_fSO_2)_2$) were able to perform the substitution of aromatic H atoms by the R_f groups in fairly good yields, in organic solvent/water mixtures. These new reagents, which have recently become commercially available, surpass the scope of other radical-based methodology, such as the Borono–Minisci approach [9]. The success of this reagent is based on the weak R_f–S bond within the zinc salt, which makes it a good source of perfluoroalkyl radicals under mild radical thermal initiating conditions [10], affording excellent yields of perfluoroalkyl-substituted heteroaromatics. An interesting example is depicted in Scheme 2, for the perfluoroalkylation of caffeine [11].

A recent review article where seminal examples of radical trifluoromethylation and perfluoroalkylation reactions making use of these new reagents are presented attests to the relevance of the subject [1].

Interesting photoinduced methods making use of photocatalysts have also been developed to perform radical (homolytic) perfluoroalkylation reactions of aromatic and heteroaromatic compounds in organic solvents [12]. These methods entail radicals and radical ions as intermediates, using perfluoroalkyl group precursors such as triflyl chloride or sulfonyl chloride in conjunction with perfluoroalkyl iodides, perfluoroalkyl-substituted pharmacophores can be obtained in excellent yields [12].

We have recently introduced a photochemical method for accomplishing radical perfluoroalkylation reactions of aromatic nuclei in water and aqueous media through an ion-radical chain sequence, with aromatic compounds without formal leaving groups [13]. This methodology proved very suitable for electron-rich aromatic substrates, and the electrophilic perfluoroalkyl iodides (perfluoroalkyl radical precursors), where a sequence of electron transfer (ET), and then proton transfer (PT) steps affords the substitution products.

In this account we present a photochemical method to achieve a direct C–H perfluoroalkylation of dibenzoarenes and dibenzoheteroarenes in aqueous media, as a novel entry to the syntheses of perfuoroalkyl-substituted fused aromatics and heteroaromatic nuclei of biological and technological relevance. This methodology bypasses the use of transition metal reagents or organocatalysts and employs mild initiating techniques. As far as we are concerned,



Scheme 2. Radical perfluoroalkylation of caffeine using Baran' reagent.

no synthetic pathway was available in the literature to substitute dibenzoheteroarenes with perfluoroalkyl moieties.

2. Results and discussion

When we subject an Ar-deoxygenated mixture of 9*H*-carbazole **1** (1 mmol) and *n*-C_4F_9I (0.2 mmol) in MeCN:H_2O mixture to 350-nm irradiation with an unfiltered medium pressure Hg lamp (MPL), we obtain 3-(perfluorobutyl)-9*H*-carbazole **6**, in 10% yield (Table 1, entry 1, Scheme 3). On the other hand, when an Ar-deoxygenated mixture of 9*H*-carbazole **1** (0.06 mmol) and *n*-C_4F_9I (4.5 mmol) in MeCN:H_2O is irradiated with 254-nm lamps (quartz vessel, 4 h, 40 W), under vigorous stirring, we obtain 3-(perfluorobutyl)-9*H*-carbazole **6** in 59% isolated yield (Table 1, entry 2, Scheme 3). The protected *N*-methyl-9*H*-carbazole **2** [13], under reaction conditions involving irradiation at 350 nm affords 9-methyl-3-(perfluorobutyl)-9*H*-carbazole **7** [13] in 50% isolated yield (Scheme 3, Table 1, entry 3). These reactions can be scaled-up (see Section 4). The UV–Vis spectra of substrates **1** and **2** are illustrated in Fig. 1, Supplementary Information. The dissimilar substitution yields for substrates **1** and **2** with the R_f moieties is intriguing, since it has been postulated [14] that in aqueous mixtures, the NH and OH functionalities are not good hydrogen donors in radical transformations due to their hydrogen-bonding stabilization in the aqueous environment, thus rendering substitution of the arene ring feasible. Interestingly, substitution at the *3*-position of the carbazole (and 9-methylcarbazole) ring is typical of a classical aromatic electrophilic substitution pattern. In previous studies [13], we were able to discriminate the substitution pathways arising from either an initial ET initiation within the excited aromatic moiety and R_f–I, or a substitution route from direct homolysis of the F_9C_4–I bond and ulterior homolytic aromatic ring substitution with $C_4F_9^\bullet$ radicals [13].

In order to optimize reaction conditions, we varied substrate and *n*-C_4F_9I concentrations with the purpose to increase product yields through graphs of % substitution product *versus* *n*-C_4F_9I or substrate concentration at 254-nm irradiation (not shown) respectively, and obtained the best results shown in column 3, Table 1.

When reaction conditions are those where absorption of substrates prevail at 254-nm irradiation wavelength, very low yields of substitution products are obtained. Increasing the amounts of *n*-C_4F_9I in the reaction mixtures, a steady increase in substitution product yields is obtained, supporting that the reaction is initiated through homolysis of F_9C_4–I bond leading to $C_4F_9^\bullet$ radicals (*vide infra*). The optimized concentration ratios of substrate: *n*-C_4F_9I found were those reported in column 3, Table 1 (*i.e.* the highest substitution product yields are obtained when *n*-C_4F_9I are in excess with respect to substrate).

Direct trifluoromethylation of carbazole at the *1*-position has been accomplished by Catellani and collaborators through a Pd-catalyzed non-radical process [15]. No direct trifluoromethylation of the carbazole nucleus (**1**) has ever been reported at the *2*-, *3*-, or *4*-positions of the ring, neither a protocol for the direct trifluoromethylation of **2** at the *1*-, *2*-, *3*-, or *4*-positions of the ring has been informed. Indirect methods for obtaining 3-trifluoromethylcarbazole through a Suzuki–Miyaura reaction from a biphenyl derivative [16a] or through a Pd-catalyzed arylation of anilines [16b] have been reported earlier.

Analogously, when dibenzo[*b*,*d*]furan **3** (Scheme 3), is made to react at 254 nm in a MeCN:H_2O/$Na_2S_2O_3$ [17] mixture in the presence of *n*-C_4F_9I, affords the mono C_4F_9-substitution products at the *4*-(product **8**), *3*-(product **9**), and *1*-(product **10**) positions of the dibenzofuran ring, in 41% isolated global yield (Table 1, entry 4 and Scheme 3). Regioisomers **8**, **9** and **10** are obtained in a relative ratio of *33:42:25*, respectively. When the reaction of **3** and *n*-C_4F_9I is carried out in a CH_2Cl_2:H_2O mixture (1:1) under 254-nm

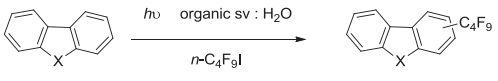
Table 1
Optimized reaction conditions tested in the HAS reaction of arenes with perfluoroalkyl halides in heterogeneous media under vigorous stirring.

Entry	Synthetic method	Substrates (mmol)	Solvent system (mL)[a]	Product (% yield)	$A_{substrate}$:A_{RfX}[b] $pH_{initial}/pH_{final}$[c]
1	MPL[d]	1 (1), *n*-C_4F_9I (0.2)	MeCN:H_2O 1:1 (30)	6 (10)[e]	*1:0.1*[b] 5/3[c]
2	λ 254 nm	1 (0.06), *n*-C_4F_9I (4.5)	MeCN:H_2O 1:1 (4)	6 (59)[e]	*1:1*[b] 5.5/3[c]
3	MPL[d]	2 (1), *n*-C_4F_9I (0.2)	MeCN:H_2O 1:1 (30)	7 (50)[e]	*1:0.1*[b] 5/3[c]
4	λ 254 nm	3 (0.3), *n*-C_4F_9I (2.4)	MeCN:H_2O 1:1 (4)	(41)[e,f] 8 (33)[g] 9 (42)[g] 10 (25)[g]	*2.3:1*[b] 5.5/3[c]
5	λ 254 nm	3 (0.3), *n*-C_4F_9I (2.4)	DCM:H_2O 1:1 (4)	(45)[e] 8 (25)[g] 9 (35)[g] 10 (40)[g]	*2.3:1*[b] 5.5/3[c]
6	λ 254 nm	4 (0.3), *n*-C_4F_9I (2.3)	MeCN:H_2O 3:1 (4)	11 (45)[e]	*7.8:1*[b] 5.5/3[c]
7	λ 254 nm	5 (0.3), *n*-C_4F_9I (2.3)	MeCN:H_2O 3:1 (4)	(50)[e,h] 12 (48)[g] 13 (34)[g] 14 (17)[g] 15 (<1)[g]	*7.1:1*[b] 5.5/3[c]
8	λ 254 nm	16 (0.2), *n*-C_4F_9I (1.1)	MeCN:H_2O 1:1 (4)	(25)[e,h] 21 (66)[g] 22 (33)[g]	*1:1*[b] 5.5/3[c]
9	λ 254 nm	17 (0.2), *n*-C_4F_9I (3.8)	MeCN:H_2O 1:1 (4)	23 (35)[e]	*1:1*[b] 5.5/3[c]
10	λ 254 nm	18 (0.2), *n*-C_4F_9I (5.8)	MeCN:H_2O 3:1 (4)	24 (90)[e]	*1.3:1*[b] 5.5/3[c]
11	λ 254 nm	19 (0.2), *n*-C_4F_9I (5.6)	MeCN:H_2O 3:1 (4)	25 (66)[e]	*1:1*[b] 5.5/3[c]
12	λ 254 nm	20 (0.2), *n*-C_4F_9I (5.3)	MeCN:H_2O 3:1 (4)	(49)[e] 26 (43)[g] 27 (30)[g] 28 (27)[g] 29 (<1)[g]	*1:1*[b] 5.5/2[c]
13	MPL[c] or λ 254 nm	30 (0.2), *n*-C_4F_9I (5.3)	MeCN:H_2O 3:1 (4)	–	5.5/5.5[c]

[a] Ar-deoxygenated solutions.
[b] Absorbance ratio at the irradiation wavelength (254 nm or 365 nm) in pure organic solvent.
[c] pH registered at the beginning of the reaction/pH registered at reaction end.
[d] Medium pressure Hg lamp, unfiltered.
[e] Isolated product yield.
[f] Yield in the presence of $Na_2S_2O_3$.
[g] Relative regioisomer yield.
[h] 73% starting material recovered.

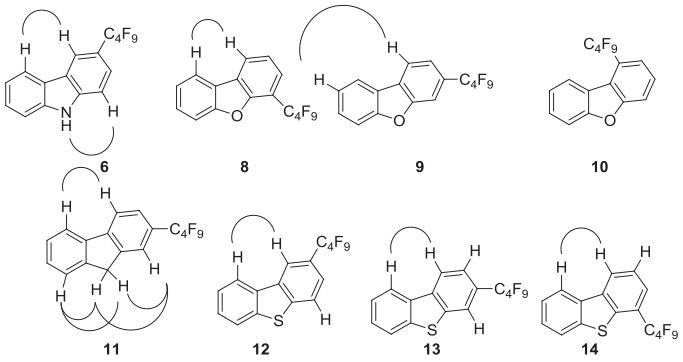
irradiation instead, products **8**, **9**, and **10** are obtained in *25:35:40* relative yields, indicated in Table 1, entry 5. Under these reaction conditions, the global monosubstitution yield of substrate **3** is 45%. These products were characterized as individual isomers employing standard spectroscopic methods. The chromatographic separation of regioisomers **8**–**10** was challenging. Neither column chromatography nor preparative TLC systems employing ordinary eluant mixtures accomplished separation of the isomers. When a perfluoroalkylated solvent mixture (a fluorous phase) was employed instead as eluant (*i.e.* 1-trifluoromethyl-perfluorodecaline:*iso*octane, 1:1), regioisomer **8** was separated as an individual isomer by preparative TLC techniques. To unambiguously characterize products **8**–**10**, we undertook multidimensional and NOESY NMR experiments, and the correlations shown in Scheme 4 were observed. Compound **8** (Scheme 4) shows NOE correlations between protons H*1* and H*9*. Compound **9** shows H*1*–H*8* NOE correlation, whereas compound **10** does not show NOE correlations (Scheme 4). Substitution at the *2*-position of the dibenzofuran ring with the C_4F_9 moiety, under our reaction conditions, was obtained in very low relative yield (<1%), and the product could not be fully characterized properly. The synthesis of *2*-, *3*-, and *4*-CF_3-substituted dibenzofurans has been reported in the literature by non-radical methods [18–20].

Trifluoromethylation of dibenzofuran at the *4*-position has very recently been achieved with CF_3SO_2Na (Langlois reagent) in the presence of copper catalysts and *t*-BuOOH by Sanford and colleagues

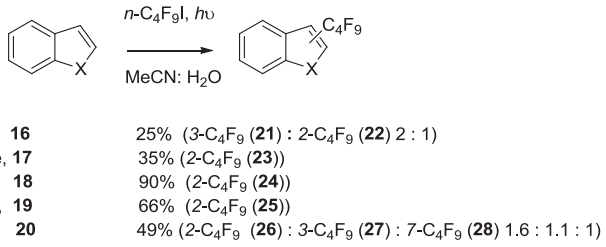


1 X = NH — 59% isolated (3-C_4F_9, (**6**))
2 X = NMe — 50% isolated (3-C_4F_9, (**7**))
3 X = O — 41 % isolated (4-C_4F_9 (**8**) : 3-C_4F_9 (**9**) : 1-C_4F_9 (**10**) *25:35:40*)
4 X = CH_2 — 45% isolated (2-C_4F_9 (**11**))
5 X = S — 50% isolated (2-C_4F_9 (**12**) : 3-C_4F_9 (**13**) : 4-C_4F_9 (**14**) *48:34:17*)

Scheme 3. Photoinduced perfluoroalkylation of dibenzo(hetero)arenes in aqueous mixtures.



Scheme 4. NOESY spectra analyses for compounds **6**–**14**.



Scheme 5. Perfluorobutylation reactions of **16**–**18** in MeCN:water mixtures (this work).

[21]. The authors employ aryl-boronic acids as starting materials. The method relies both on transition metal catalysis, selective radical reactions, and properly substituted dibenzofuran rings. Indirect methods for obtaining 3-trifluoromethyl-substituted dibenzofuran either through biphenyl ether Ni-cross-coupling reactions [22a] or through Pd-catalyzed biphenyl coupling processes [22b] have also recently been reported. Our methodology seems to provide three main C_4F_9-substituted regioisomers of dibenzofuran, whose mixture can be enriched in regioisomer **9** or **10** depending on the solvent system, and where the *4*-positional regioisomer (*i.e.* **8**) could be separated with a fluorous phase eluant.

The dibenzoarene *fluorene* **4** (9*H*-fluorene), upon reaction with *n*-C_4F_9I in MeCN:H_2O/$Na_2S_2O_3$ [17] under 254-nm irradiation (quartz vessel, 4 h) and vigorous stirring, affords 2-(perfluorobutyl)-9*H*-fluorene **11** in 45% yield as a sole product (Table 1, entry 6). Fluorenes, substituted at the *2*-, and *3*-positions with the trifluoromethyl group have been synthesized by a Pd-catalyzed process before [23]. Identification of product **11** was accomplished by standard spectroscopic techniques. NOESY correlations of proton H*1* with protons at the *9*-position have been observed for product **11** (Scheme 4), as well as correlations between H*8* with protons at the *9*-position of the fluorene ring. Also, a correlation between H*4* and H*5* was observed in NOE-experiments. Fluorene, as substrate, has never been trifluormethylated or perfluoroalkylated by a direct method before [23]. Our methodology affords exclusively the regioisomer substituted at the *2*-position, as opposed to that of Chang and collaborators [23].

Dibenzo[*b*,*d*]thiophene **5**, under the same reaction conditions, affords a mixture of three main regioisomers, substituted at the *2*-(product **12**, Scheme 3), *3*-(product **13**, Scheme 3), and *4*-(product **14**, Scheme 3) positions. The global substitution isolated yield of products **12**–**14** was rather low (10%) (Table 1, entry 10). Some sulphur-containing polymeric material is observed in the crude reaction mixture. However, when the reaction is carried out in the absence of $Na_2S_2O_3$, the yield of products **12**–**14** increases substantially (50%, Table 1, entry 7), and intractable material is not observed. Isomers **12**–**14** were obtained in a relative ratio of *48:34:17*. Isomers **12**–**14** were separated by preparative TLC techniques, employing a mixture of *iso*octane: chloroform, 2:1. Compounds **12**–**14** show NOE correlations between H*1* and H*9* (Scheme 4). *2*-, and *4*-CF_3-substituted dibenzothiophenes have been reported in the literature before [18,24], and have been previously synthesized by a Cu-mediated *ipso* substitution of the respective *2*-, and *4*-iodo-dibenzothiophene precursors [15,25]. Through our methodology, a *3*-substituted fluoroalkyl-dibenzothiophene regio-isomer (**13**) could be obtained. The synthesis of *3*-R_f-substituted regioisomers has never been informed in the literature before through a direct C–H substitution method.

A minor isomer, accounting for less than 1% of the total yield of the mixture could be distinguished by the ^{1}H NMR spectrum of the chromatographed reaction mixture, which seems to correspond to another C_4F_9-regioisomer. Through a combination of 2D-NMR techniques, full spectral characterization of this isomer was possible in the mixture, and the identity of the compound was assigned to 1-(perfluorobutyl)-dibenzo[*b*,*d*]thiophene **15**. It is to be pointed out that dibenzoheteroarenes have never been perfluoroalkylated directly by a substitution reaction, let alone by a homolytic substitution process.

We also treated the benzoarenes and benzoheteroarenes **16**–**20** (Scheme 5) to the photosubstitution reaction with *n*-C_4F_9I in aqueous media. When we subject 1*H*-indole **16** to a photoreaction (254 nm-irradiation) with *n*-C_4F_9I in a mixture of MeCN:H_2O, we obtained the expected 3-perfluorobutyl-1*H*-indole (product **21**, Schemes 5). Along with this product, the 2-substituted perfluorobutyl-indole was also obtained (product **22**, Scheme 5, Table 1, entry 8). Both products, **21** and **22**, afforded a global substitution isolated yield rather low (25%), with a substrate conversion approximately 30%. Products **21** and **22** were obtained in a relative ratio of *66:33*, respectively.

When we subject *N*-methyl indole **17** instead to the photoreaction in aqueous media with *n*-C_4F_9I, we obtain the C_4F_9-substituted product at the *2*-(product **23**) position of the ring in 35% yield, which matches substrate conversion. Product **23** was characteized by standard spectroscopic techniques.

The photoconversions of **16** and **17** were kept low (<30%) so as to avoid photolysis of these substrates. At larger substrate conversion, intractable material was detected.

Trifluoromethylation of 1*H*-indole and *N*-methyl indole at the *2*-, *3*-, and *7*-positions has recently been achieved by Togni and collaborators [26,27] in $CHCl_3$ as solvent (Scheme 1). Their protocol renders a mixture of the *2*-, *3*-, and *7*-CF_3-substituted regioisomers that could not be separated, but identified by ^{19}F NMR spectroscopy as the isomeric mixture. Another recent methodology, reported by Xiao et al. for the trifluoromethyl *ipso*-substitution of indole has been reported in DMF as solvent [28].

When we subject benzofuran **18** to react under photostimulation (254 nm) with *n*-C_4F_9I in MeCN:H_2O mixture, we obtain exclusively 2-(perfluorobutyl)-benzofuran **24** in 90% yield, according to Table 1, entry 10 (Scheme 5). Recently, Togni and collaborators achieved the trifluoromethylation of benzofuran and heteroanalogs at the *3*- and *2*-positions with the Togni reagent, and methyltrioxorhenium as catalyst [26] (Scheme 1). Their methodology, however, is not regioselective and renders the mixture of regioisomers that could not be separated but characterized by spectroscopic methods. 3-Trifluoromethyl-benzofuran has recently been synthesized through benzofuran-2ylboronic acid (*a functionalized* benzofuran ring) in the presence of $NaSO_2CF_3$, *tert*-butylhydroperoxide (TBHP) and a copper salt in 89% yield by Sanford and collaborators [21a]. The photoinduced methodology, under our reaction conditions, seems to provide selectively the *2*-substituted perfluorobutyl benzofuran isomer in fairly good yield (*innate* trifluoromethylation).

When 1-*H*-indene **19** is subjected to the photoinduced (254 nm) perfluoroalkylation reaction in MeCN:H_2O mixture, product **25** (Scheme 5, Table 1, entry 11) was obtained in 66% yield. Gassman and colleagues [29] have reported that the 2-perfluoroalkyl-substituted indene product could be obtained through a photoinduced perfluoroalkyl iodide addition intermediate that could not be isolated, but decomposed *in situ* to the 2-perfluoroalkyl-substituted indene product through base-promoted dehydroiodination. Under our reaction conditions, however, no base was utilized to obtain product **25**, and the pH decreased gradually throughout the course of the reaction (Table 1, column 6).

Benzo[*b*]thiophene **20** was also subjected to the photoinduced (254-nm) perfluorobutylation reaction in MeCN:H_2O to yield a mixture of regioisomers substituted at the *2*-(product **26**), *3*-(product **27**), and *7*-(product **28**) positions of the benzo[*b*]thiophene ring with the C_4F_9 moiety in 49% global yield that could not be isolated as single regioisomers but characterized in the reaction mixture (Table 1, entry 11). These isomers (2-, *3*-, and *7*-C_4F_9 substituted benzothiophenes) were obtained in a relative ratio of *43:30:27*, respectively). Togni and collaborators [26] attained the trifluoromethylation of benzothiophene with the Togni' reagent, affording a mixture of the *2*-, *3*-, and *7*-CF_3 substituted regioisomers (*innate* trifluoromethylation, Scheme 1) that could not be separated. Sanford and collabortors synthesized selectively the 2-trifluoromethyl-benzo[*b*]thiophene from benzo[*b*]thiophene-2-ylboronic acid (*a functionalized* benzothiophene ring) in the presence of $NaSO_2CF_3$, *tert*-butylhydroperoxide (TBHP) and a copper salt in 77% yield [21a].

A minor isomer, accounting for less than 1% of the total yield of the mixture could be distinguished by the ^{1}H NMR spectrum of the chromatographed reaction mixture, which seems to correspond to another C_4F_9-regioisomer. Through a combination of 2D-NMR techniques, full spectral characterization of this isomer was possible in the mixture, and the identity of the compound was assigned to 6-(perfluorobutyl)-benzo[*b*]thiophene **29**.

No ring-opening product is observed from photoreactions of **16**–**20** with *n*-C_4F_9I under our reaction conditions.

The UV–Vis spectra of substrates **1**–**5** are illustrated in Fig. 1, Supplementary Information. It is clear that the wavelength maxima for substrates **3**–**5** are around 254–270 nm, and those for **1**, and **2** have lower energy absorption bands (^1L_a) *ca.* 350 nm, from where the photoreactivity ensues. Addition of *n*-C_4F_9I provokes a decrease in fluorescence intensity, as observed in the Stern–Volmer plots (not shown) [13]. This quenching of fluorescence is in agreement with an electron-transfer or energy-transfer process within the solvent cage, as has been proposed before [13]. We have indeed observed the radical cation of carbazole under our experimental conditions (in the presence of *n*-C_4F_9I) at 355 nm excitation by NLFP; however, as opposed to the radical cation of *N*-methylcarbazole [13] (generated in the presence of *n*-C_4F_9I), the quantum yield of transient **1** radical cation observed by NLFP is rather low. At 254 nm excitation (in the presence of *n*-C_4F_9I) the quantum yields for radical cation formation by NLFP cannot be observed ($\phi < 0.01$) due to the absence of the ^1L_a charge transfer band at this wavelength. This could explain why irradiation of substrates (with the exception of **2**), either at 350 nm or 254 nm leads to an inefficient initiation of the reaction, and direct homolysis of I–C_4F_9 (at 254 nm) accounts for the triggering initiation event.

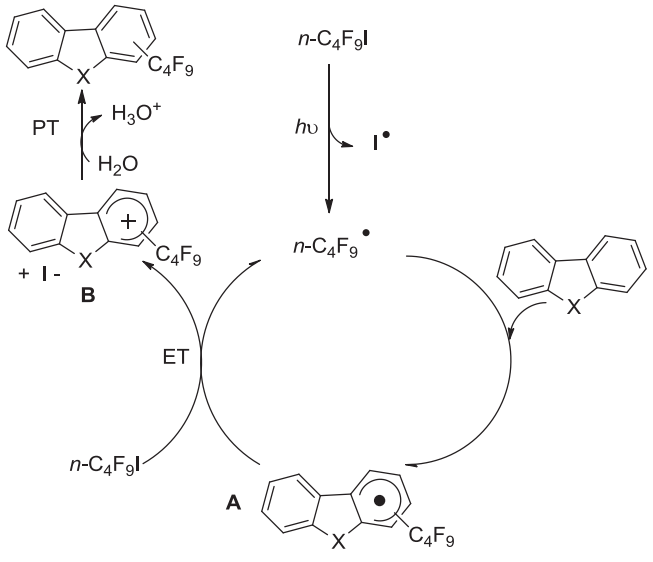
The pH was monitored throughout the reaction for compounds **1**–**5**, **16**–**20** (column 6, Table 1) with *n*-C_4F_9I either at 350 nm or at 254 nm-irradiation. A notorious decrease in pH was observed in all cases. Table 1, column 6 depicts the pH at the beginning and end of the reaction. This evidence is in accordance with a proton release in the course of the reaction, such as that observed in classical S_EAr.

Addition of di-*tert*butyl nitroxide (DTBN, 2% equiv), a well-known radical scavenger, to either 254 nm or 350 nm-irradiation in MeCN:H_2O mixtures, provokes a retardation of the reactions, purporting to the presence of radicals as intermediates.

As for the propagation steps, the likely mechanisms could involve (i) an ET and then a PT (proton transfer or proton loss) sequence on the reaction. The first ET step would generate a *carbocation* (Wheland) intermediate from the C_4F_9-substituted (di)benzo(hetero)aromatic radical. The Wheland intermediate, in turn, upon PT would afford the substitution products (*ET-PT* sequence) or else, (ii) the C_4F_9-substituted (di)benzo(hetero)aromatic radical intermediate might lose a proton (PT), which would render a C_4F_9-substituted *(di)benzo(hetero)aromatic radical anion* intermediate. This latter radical anion intermediate, upon ET, would yield the thermoneutral substitution product (*PT-ET* sequence).

Addition of *p*-dinitrobenzene (*p*-DNB), a known radical anion scavenger, does not affect the yields of the perfluoroalkyl group substitutions of the dibenzoarenes and dibenzoheteroarenes. The photoreactions carried out under basic conditions (pH ~ 10) do not show an increase in product yields. This piece of evidence would seem to imply that radical anions (of *n*-C_4F_9-substituted substrates) are not intermediates in these reactions and the *PT-ET sequence* is less likely to be operative. When 4-nitrodibenzofuran **30** is allowed to react with *n*-C_4F_9I in MeCN:H_2O mixtures either under 254-nm or 350-nm irradiation conditions, no substitution products are observed (Table 1, entry 13). This observation could be accounted for by the instability of a nitro-substituted Wheland-derived intermediate generated from *n*-C_4F_9-substituted **30**.

At 254 nm irradiation, under conditions where most of the light is absorbed by *n*-C_4F_9I (see Table 1, column 6, footnote *b*), homolysis of F_9C_4–I bond produces perfluorobutyl radicals that add to the (di)benzo(hetero)arene such as in Scheme 6 below to yield the radical adduct intermediate **A**. 3-Nitro-substituted [30a] and hydroxy-substituted [30b,c] cyclohexadienyl radicals [30d] have been shown to be oxidized to the respective cyclohexadienyl cations with ease. Comparison of the standard redox potentials of the above with the reduction potential of *n*-C_4F_9I (*i.e.* −1.27 V, see Supplementary Information, Table 2, entries 2 and 3) gives confidence in the existence of **A B** (Scheme 6). The radical adduct **A** undergoes a sequence of ET to *n*-C_4F_9I (to afford cation



Scheme 6. Proposed mechanism for the perfluorobutylation of dibenzoheteroarenes in aqueous mixtures.

intermediate **B**, Wheland intermediate, oxidation triggered through the favorable Gibbs energy, *vide supra*) and then proton transfer (PT) steps to yield the substitution products in averaged good yields. Based on parameters in Table 2 (Supplementary Information), we postulate that this likely mechanism is also operative for substrates **1**–**5** and **16**–**20**.

3. Conclusions

We herein present a substitution reaction on dibenzoarenes and dibenzoheteroarenes in aqueous media with C_4F_9 moieties to yield perfluorobutyl group-substituted compounds in moderate to good yields. It is to be noted that these aromatic compounds (dibenzoheteroarenes) have never been substituted before with perfluoroalkyl moieties by a direct methodology. We are currently rehearsing other perfluorobutylating reagents (under thermal radical initiation conditions) to achieve the direct C–H perfluorobutylation of dibenzoheteroaromatic compounds such as those studied in this work in order to improve the efficiency of the overall pefluorobutyl group substitution reaction. These reagents are derived from perfluorobutyl sulfoxides and sulfones.

4. Experimental

Most separation, irradiation, and purification procedures have been reported earlier [13].

Irradiations carried out at 254 nm in 4-mL quartz cells (1 mmol) can be scaled up 10-fold (10 mmol) employing cylindrical 50-mL quarts cells disposed in a longitudinal arrangement 1 cm distant from the 254-nm lamp(s) under continuous stirring, or employing a 125-mL commercial quartz UV-irradiation vessel set-up with an immersion lamp. Irradiations at 350 nm can be scaled-up employing larger standard glass vessels, with no special arrangements. The mixtures are heterogeneous and irradiations proceed under continuous vigorous stirring.

Some preparative TLC techniques employed a fluorous phase system, consisting of a mixture of 1-methyl-perfluorodecaline: *iso*-octane 1:1. NMR analyses were performed in $CDCl_3$ as solvent or otherwise noted. 2D-NMR experiments performed to assign ^1H–^1H, and ^1H–^{13}C connectivities include COSY-45, HSQC, HMBC, and HOESY and NOESY techniques.

Irradiation of mixtures was carried out under conditions where only primary photoproducts were obtained, and in most cases the total substrate conversion was less than 45%. Percentage yields are isolated yields.

3-(Perfluorobutyl)-9H-carbazole (**6**) [13]. Oil, 59% yield, 14.2 mg isolated. ^1H NMR (500 MHz, $CDCl_3$) δ_H ppm: 8.30 (s, 2H), 8.13 (dd, J = 0.6, 7.8 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 8.5 Hz, 1H), 7.49 (m, 2H), 7.31 (m, 1H). ^{13}C NMR (125 MHz) δ_C ppm: 141.6, 140.4, 127.4, 124.6, 124.3, 123.5, 121.1, 120.9, 120.1, 117.2, 111.4, 111.2. MS EI (70 eV) m/z (%): 385 (52), 217 (20), 216 (100), 106 (11). ^{19}F NMR (470.4 MHz) δ_F ppm: −80.97, −108.55, −122.37, −125.47. EI-HRMS Anal. Calcd for $C_{16}H_8F_9N$ 385.0513, found 385.0522.

4-(Perfluorobutyl)dibenzo[b,d]furan (**8**). 11% yield (from entry 5, Table 1), 4 mg isolated. ^1H NMR (500 MHz, $CDCl_3$) δ_H ppm: 8.17 (d, 1H), 7.67–7.63 (m, 2H), 7.55–7.45 (m, 2H), 7.42 (dt, J = 7.5 Hz, 0.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C ppm: 112.7, 120.9, 122.7, 123.0, 123.6, 124.8, 125.8, 126.0, 128.4, 153.0, 156.5. ^{19}F NMR (470.55 MHz, $CDCl_3$) δ_F ppm: −80.79, −109.64, −122.66. MS EI (70 eV) m/z (%): 386 (25), 217 (100), 168 (7), 138 (7), 107 (12). IR ν, cm^{-1}: 2926 (m), 1237 (s). EI-HRMS Anal. Calcd for $C_{16}H_7F_9O$ 386.0353, found 386.0366.

3-(Perfluorobutyl)dibenzo[b,d]furan (**9**). 16% yield (from entry 5, Table 1), 30 mg isolated. ^1H NMR (500 MHz, $CDCl_3$) δ_H (ppm): 8.10 (d, J = 8.13 Hz, 1H), 7.82 (m, 1H), 7.63 (m, 1H), 7.59 (m, 2H), 7.54 (dt, 1H), 7.39 (dt, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C ppm: 111.8, 115.8, 122.6, 122.7, 123.4, 124.3, 126.5, 128.3, 128.4, 156.6, 156.8. ^{19}F NMR (470.55 MHz, $CDCl_3$) δ_F ppm: −80.94, −107.88, −121.67, −125.65. MS EI (70 eV) m/z (%): 386 (35), 217 (100), 188 (10), 139 (6), 109 (9). EI-HRMS Anal. Calcd for $C_{16}H_7F_9O$ 386.0353, found 386.0360.

1-(Perfluorobutyl)dibenzo[b,d]furan (**10**). 18% yield (from entry 5, Table 1), 12 mg isolated ^1H NMR (500 MHz, $CDCl_3$) δ_H (ppm): 8.08 (dd, J = 8.1 Hz, 0.5 Hz, 1H), 8.02 (dd, J = 8 Hz, 0.5 Hz, 1H), 7.82 (m, 1H), 7.62 (m, 1H), 7.58 (m, 1H), 7.52 (dt, 1H), 7.39 (dt, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C ppm: 110.7, 111.9, 120.9, 121.1, 121.2, 123.3, 127.3, 128.4, 155.6, 157.3. ^{19}F NMR (470.55 MHz, $CDCl_3$) δ_F ppm: −80.04, −109.6, −122.35, −125.65. MS EI (70 eV) m/z (%): 386 (14), 217 (100), 188 (7), 139 (8), 109 (16). EI-HRMS Anal. Calcd for $C_{16}H_7F_9O$ 386.0353, found 386.0400.

2-(Perfluorobutyl)-9H-fluorene (**11**). Yellow Oil. 45% yield, 52 mg isolated. ^1H NMR (500 MHz, $CDCl_3$) δ_H ppm: 7.91(d, J = 8 Hz, 1H), 7.87 (d, J = 7.2 Hz, 1H), 7.78 (s, 1H); 7.62 (m, 2H), 7.45 (t, J = 7.3 Hz, 1H), 7.41 (dt, J = 1.2, 7.4 Hz, 1H), 4.01 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C ppm: 145.4, 143.8, 143.4, 140.0, 128.0, 127.1, 126.5, 125.7, 125.2, 123.5, 120.7, 119.8, 36.8. ^{19}F NMR (470.4 MHz, $CDCl_3$) δ_F ppm: −80.94, −109.95, −122.73, −125.24. MS EI (70 eV) m/z (%): 384 (100), 246 (10), 215 (55). EI-HRMS Anal. Calcd for $C_{17}H_9F_9$ 384.0561, found 384.0571.

2-(Perfluorobutyl)dibenzo[b,d]thiophene (**12**). Yellow Oil 24% yield, 39 mg isolated. ^1H NMR (500 MHz, $CDCl_3$) δ_H ppm: 8.44 (d, J = 7.8, 1H), 8.11 (s, 1H), 7.90 (d, J = 6.6 Hz, 1H), 7.77 (d, J = 7.7 Hz, 1H), 7.57 (t, J = 7.9 Hz, 1H), 7.51–7.52 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C ppm: 140.3, 138.8, 133.5, 133.5, 127.1, 126.4, 125.9, 125.7, 125.3, 124.7, 124.1, 122.7, 121.6. ^{19}F NMR (470.4 MHz, $CDCl_3$) δ_F ppm: −80.81, −103.24, −119.99, −125.50. MS EI (70 eV) m/z (%): 402 (50), 233 (100), 213 (15), 117 (10). IR ν, cm^{-1}: 2936 (m), 1237 (s). EI-HRMS Anal. Calcd for $C_{16}H_7F_9S$ 402.0125, found 402.0112.

3-(Perfluorobutyl)dibenzo[b,d]thiophene (**13**). Yellow Oil 17% yield, 14.5 mg isolated. ^1H NMR (500 MHz, $CDCl_3$) δ_H ppm: 8.36 (s, 1H), 8.27 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 7.9 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 7.5 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.55 (t, J = 7.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C ppm: 143.5, 139.7, 135.8, 133.4, 127.12, 125.2, 124.4, 124.2, 124.3, 123.0, 122.5, 121.5, 120.1. ^{19}F NMR (470.4 MHz, $CDCl_3$): δ_F ppm: −80.97, −109.91, −122.41, −125.50. MS EI (70 eV) m/z (%): 402 (31), 233 (100), 138 (7), 116 (10). EI-HRMS Anal. Calcd for $C_{16}H_7F_9S$ 402.0125, found 402.0122.

4-(Perfluorobutyl)dibenzo[b,d]thiophene (**14**). Yellow Oil 9% yield, 1.21 mg isolated. ^1H NMR (500 MHz, $CDCl_3$) δ_H ppm: 8.37 (dd, J = 0.8, 7.8 Hz, 1H), 8.20 (dd, J = 1.7, 7.7 Hz, 1H), 7.88 (m, 1H), 7.69 (d, J = 7.5 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.52 (m, J = 1.6, 6.9, 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C ppm: 143.3, 141.9, 140.0, 138.4, 128.0, 126.9, 125.4, 125.1, 124.6, 124.1, 122.7, 122.0. ^{19}F NMR (470.4 MHz, $CDCl_3$) δ_F ppm −80.91, −109.77, −122.13, −125.66. MS EI (70 eV) m/z (%): 402 (29), 233 (100), 138 (10), 117 (16). EI-HRMS Anal. Calcd for $C_{16}H_7F_9S$ 402.0125, found 402.0132.

1-(Perfluorobutyl) dibenzo[b,d]thiophene (**15**). Yellow Oil 1% yield (not isolated). ^1H NMR (500 MHz, $CDCl_3$): δ_H (ppm) 8.36 (d, J = 9.0 Hz, 1H), 8.23 (m, 1H), 7.91 (m, 1H), 7.61 (m, 1H), 7.56 (m, 1H), 7.53 (m, 1H), 7.49 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C ppm: 143.5, 140.3, 139.5, 133.4, 126.7, 125.2, 124.9, 124.7, 124.6, 124.1, 122.7, 122.1. ^{19}F NMR: (470.4 MHz, $CDCl_3$) δ_F ppm: −80.92, −110.52, −121.70, −125.65. MS EI (70 eV) m/z (%): 402 (25), 233 (100), 138 (15), 117 (16). EI-HRMS Anal. Calcd for $C_{16}H_7F_9S$ 402.0125, found 402.0122.

3-Perfluorobutyl-1H-indole (**21**). Yellow oil, 17%, 6.1 mg. ^1H NMR (500 MHz, $CDCl_3$) δ_H ppm: 8.69 (s, 1H), 7.68 (d, J = 7.6 Hz, 1H), 7.53 (t, J = 7.7 Hz, 1H), 7.44–7.50 (m, 2H), 7.11 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C ppm: 137.5, 132.1, 126.1, 125.7, 124. 7, 121.8,

116.2, 106.2. MS EI (70 eV) *m/z* (%): 335 (24), 167 (17), 166 (100), 83 (12), 69 (11). ^{19}F NMR (470.4MHZ, $CDCl_3$) δ_F (ppm): −80.06, −108.70, −123.13, 125.25. EI-HRMS Anal. Calcd for $C_{12}H_6F_9N$ 335.0357, found 335.0360.

2-Perfluorobutyl-1H-indole (**22**). Yellow oil, 8%, 3.1 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H ppm: 8.43 (s, 1H), 7.70 (d, *J:* 8.1 Hz, 1H), 7.44–7.50 (m, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 6.98 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C ppm: 137.4, 131.1, 129.2, 125.5, 122.5, 121.6, 120.4, 106.9. ^{19}F NMR (470.4 MHz, $CDCl_3$) δ_F ppm: −80.98, −109.21, −122.46, −123.03, 125.64. MS EI (70 eV) *m/z* (%): 336 (10), 335 (29), 316 (7), 197 (6), 166 (100), 119 (15), 83 (12), 69 (14). EI-HRMS Anal. Calcd for $C_{12}H_6F_9N$ 335.0357, found 335.0358.

1-Methyl-2-perfluorobutyl-1H-indole (**23**). Yellow oil. 35%, 11.5 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H ppm: 7.69 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 8.7 Hz, 1H), 7.20 (dt, *J* = 1.3, 8.0 Hz, 1H), 6.97 (s, 1H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C ppm: 139.4, 126.2, 125.5, 124.7, 122.3, 120.9, 110.1, 107.5, 31.6. ^{19}F NMR (470.4 MHz, $CDCl_3$) δ_F ppm: −80.92, −105.27, −121.50, −125.65. EI-HRMS Anal. Calcd for $C_{13}H_8F_9N$: 349.0513, found 349.0517.

2-Perfluorobutyl-benzofuran (**24**). Yellow oil, 90%, 60 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ_H ppm: 7.69 (d, *J* = 7.80 Hz, 1H), 7.59 (dd, *J* = 8.42, 0.8 Hz, 1H), 7.48 (dt, *J* = 8.42; 1.2 Hz, 1H), 7.35 (dt, *J* = 7.72, 1.0 Hz, 1H), 7.25 (1H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ_C ppm: 155.6, 126.9, 123.9, 122.3, 112.0, 110.3. ^{19}F NMR (470.55 MHz, $CDCl_3$) δ_F ppm: −80.56, −112.06, −123.37, −126.11. EI-HRMS Anal. Calcd for $C_{12}H_5F_9O$: 336.0197, found 336.0167.

2-(Perfluorobutyl)-1H-indene (**25**). Yellow oil 66% yield, 44.2 mg isolated. ^{1}H NMR (500 MHz) δ_H ppm: 7.53–7.51 (m, 2H), 7.38–7.34 (m, 3H), 3.66 (s, 2H). ^{13}C NMR (125 MHz) δ_C ppm: 144.3, 138.1, 138.0, 134.4, 127.9, 127.9, 124.2, 38.6. ^{19}F NMR (470.4 MHz) δ_F ppm: −81.00, −107.65, −122.70, −125.75. EI-HRMS Anal. Calcd for $C_{13}H_7F_9$ 334.0404, found 334.0400.

2-(Perfluorobutyl)-benzo[b]thiophene (**26**). 1%, 1.95 mg isolated. ^{1}H NMR (500 MHz) δ_H ppm: 7.89 (d, 1H), 7.72 (s, 1H), 762 (d, 1H), 7.46 (dt, 1H). ^{13}C NMR (125 MHz) δ_C ppm: 140.7, 137.9, 131.4, 129.3, 128.3, 126.1, 126.0. ^{19}F NMR (470.55 MHz, $CDCl_3$) δ_F ppm: −80.59, −106.37, −122.12, −125.69. Did not ionize in HRMS (ESI-TOF).

3-(Perfluorobutyl)-benzo[b]thiophene (**27**). 15%, 2.79 mg. ^{1}H NMR (500 MHz) δ_H ppm: 7.91 (s, 1H), 7.90 (d, 1H), 7.63 (d, 1H), 7.48 (dt, 1H). ^{13}C NMR (125 MHz) δ_C ppm: 141.4, 136.6, 131.9, 129.6, 126.6, 126.3, 125.7. ^{19}F NMR (470.55 MHz, $CDCl_3$) δ_F ppm: −80.79, −102.33, −122.12, −125.69. Did not ionize in HRMS (ESI-TOF).

7-(Perfluorobutyl)-benzo[b]thiophene (**28**). 13%, 1.75 mg isolated. ^{1}H NMR (500 MHz) δ_H ppm: 8.09 (d, *J* = 8.1 Hz, 1H), 7.97 (d, *J* = 8.25 Hz, 1H), 7.63 (d, 1H), 7.50 (d, 1H), 7.47 (dt, 1H). ^{13}C NMR (125 MHz) δ_C ppm: 141.3, 131.3, 129.5, 127.3, 125.7, 124.2, 124.0 ^{19}F NMR (470.55 MHz, $CDCl_3$) δ_F ppm: −80.79, −108.11, −122.12, −125.69. Did not ionize in HRMS (ESI-TOF).

6-(Perfluorobutyl)-benzo[b]thiophene (**29**), not isolated, <1%. ^{1}H NMR (500 MHz) δ_H ppm: 8.14 (s, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.72 (d, 1H), 7.65 (d, *J* = 5.6 Hz, 1H), 7.54 (d, 1H). ^{13}C NMR (125 MHz) δ_C ppm: 128.30, 126.62, 126.02, 125.55, 123.44. ^{19}F NMR (470.55 MHz, $CDCl_3$) δ_F ppm: −80.79, −109.84, −122.12, −125.69. Did not ionize in HRMS (ESI-TOF).

Acknowledgments

Thanks are given to financial agencies such as CONICET – Argentina, and Agencia Nacional de Promoción Científica y Técnica. SBV acknowledges a PD scholarship from CONICET. MRT, SMB, JEA, and AP are research members of CONICET. Special thanks are due to Cristian Bettini for GC/MS analyses.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2014.02.008.

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