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Optimization of the synthesis of 4′-nonafluorobutylacetophenone by metal catalysed cross-coupling reaction

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ABSTRACT

The synthesis of 4′-nonafluorobutylacetophenone by metal-assisted cross-coupling reaction of 1-iodo-perfluorobutane and 4′-bromoacetophenone is presented. The effect of metal (iron, copper) metal salt (copper(I) bromide, copper(II) chloride), ligand (2,2′-bipyridine, N,N,N′,N″,N‴,N‴-hexamethyltriethylenetetramine, N,N,N′,N″,N″-pentamethyldiethylenetriamine), and solvent (N,N-dimethylformamide, dimethylsulfoxide) was studied in order to elucidate their role in the optimization of the reaction conditions. The best conditions were found for the reaction carried out in presence of copper as catalyst, 2,2-bipyridine as ligand and in presence of N,N-dimethylformamide as solvent that led to 73% yield of the desired product (for a quantitative conversion of both 1-iodo-perfluorobutane and 4′-bromoacetophenone). The resulting product was characterized by nuclear magnetic resonance, IR, and mass spectroscopy.

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1. Introduction

Monomers and polymers containing telomeric fluorinated moieties have been used for long time because of their unique combination of useful surface properties such as: hydrophobicity, lypophobicity, oleophobicity, resistance to ageing and to oxidation, hydrolytic stability, chemical inertness, low permeability to gases. They have found many applications in surface coatings in metal, stone, plastic, paper, textiles, leather, automotive and petrochemical industries [1].

In order to achieve these outstanding surface properties a homogeneously organized two-dimensional arrangement of trifluoromethyl ($-CF_3$) groups is required. Molecules having long fluorinated moieties (at least 8–12 completely fluorinated carbon atoms) show highly ordinate structures due to the liquid crystal behavior of the rigid fluorinated side groups [2–11] but they are persistent in the environment and have strong bioaccumulative effects [12–23] and they will be banned as stated by the *PFOA Stewardship Program* launched by U.S. EPA in 2006.

The use of shorter chain is detrimental to surface properties because of the partial or complete loss of highly structured liquid crystal phases. One of the strategies adopted to increase the molecular rigidity of short chain fluorinated telomers is the introduction of a phenyl or biphenyl group as molecular spacer.

The synthesis of fluorinated organic compounds that bear an aromatic ring directly linked to a fluorinated alkyl group *via* copper catalysis cross-coupling reaction was first discovered by McLoughlin and Thrower [24,25] and revisited and improved by Chen and Tamborsky who used this reaction pathway for the introduction of trifluoromethyl groups in bromoaromatics [26,27] and bromoheterocyclic [28–30]. α-Fluoroalkyl-substituted aromatic compounds are used as pharmaceuticals and agrochemicals intermediates [31–34], liquid crystals [35,36], and precursors for hydrophilic and hydrophobic silane coupling agents [37,38]. Many different routes have been reported for the synthesis of fluoroalkyl-substituted aromatics. Bravo et al. [39] reported the free-radical perfluoroalkylation of aromatics with 1-iodo-perfluorobutane in presence of benzoyl peroxide and Cu(II). Huang et al. [40] reported the fluoroalkylation of aromatics with per(poly)fluoroalkyl chlorides initiated by sodium dithionite in dimethylsulfoxide and Knauber et al. [41] reported the copper catalysed trifluoromethylation of aryl iodides employing potassium (trifluoromethyl)trimethoxyborate. Recently [42], a copper-catalytic method in which the copper complex is reusable was discovered. Among all the methods proposed, that of McLoughlin and Thrower [24,25] proved to be the most efficient and regiospecific for the perfluoroalkylation of 4′-bromoacetophenone because the introduction of perfluoroalkyl chains in the aromatic ring occurs exclusively at the halogen site and the formation of biaryls is excluded. This objective of this present study deals with the synthesis of 4′-nonafluorobutylacetophenone by the reaction between 1-iodo-perfluorobutane and 4′-bromoacetophenone in

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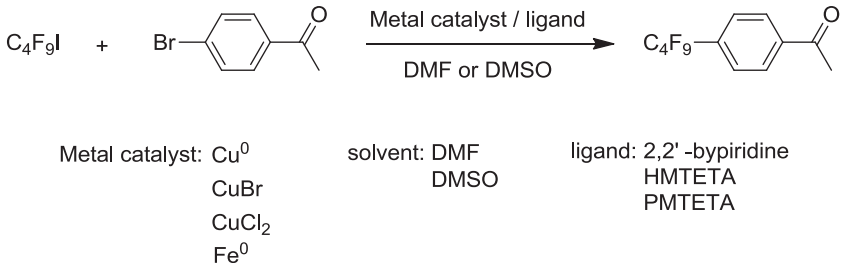


Scheme 1. Synthesis of 4′-nonafluorobutylacetophenone from the metal-assisted cross-coupling of 1-iodo-perfluorobutane with 4′-bromoacetophenone.

the presence of N,N-dimethylformamide or dimethylsulfoxide as the solvent, catalysed by different transition metals such as Fe^0, Cu^0, or metal salts CuBr, $CuCl_2$ (Scheme 1). The effects of ligands, solvents, temperature and metal catalysts were investigated to optimize the reaction by finding the best experimental conditions.

2. Results and discussion

4′-Nonafluorobutylacetophenone was synthesised by varying one or more experimental parameters for each run and the results are listed in Table 1.

All the reactions were carried out for a fixed time of 20 h to compare the results obtained. The development of the optimum conditions is discussed below, taking into account various factors.

2.1. Effect of the solvent

For the success of the cross-coupling reaction with perfluoroalkyliodides a polar aprotic solvent must be used. For this purpose, N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were both used as solvents. The comparison on the effect of both these solvents is shown in Table 1 (entries 21 and 22). Changing the solvent while keeping all the reaction conditions unmodified does not affect the yield and conversion. Conversely, the quantity of both solvents have a remarkable effect on the reaction yields (entries 10–14 for DMF, and entries from 15 to 19 for DMSO). In addition, an increase in the initial $[solvent]_0/[1\text{-iodo-perfluorobutane}]_0$ molar ratio from 1 to 4 induced a 8% yield increase while a further increase from 4 to 5 was not beneficial (as noted in Fig. 1). These results confirm previous studies and revealed that the optimized solvent/1-iodo-perfluorobutane molar ratio is 4/1.

2.2. Effect of the metal catalyst

In the synthesis of 4′-nonafluorobutylacetophenone by cross-coupling reactions, copper metal only was efficiently used as the catalyst. Different kinds of transition metals and metal salts were tested as potential catalysts: Fe^0, CuBr, $CuCl_2$ (entries 1–9, Table 1), but these attempts to get the desired product systematically failed. For the effectiveness of the synthesis, the $[metal]_0/[1\text{-iodo-perfluorobutane}]_0$ molar ratio must be at least 2/1.

Table 1
Series of reactions of synthesis of 4′-nonafluorobutylacetophenone from cross-coupling of 1-perfluorobutyliodide with 4′-bromoacetophenone (reaction time of all runs: 20 h).

Entry	Metal	Ligand	Solvent	$[R_FI]_0/[ligand]_0/[metal]_0/[solvent]$	T (°C)	Yield (%)	Conversion[a] (%)
1	Fe^0	–	DMF[b]	1/0/4.6/4	130	0	–
2	Fe^0	–	DMSO[c]	1/0/4.6/4	130	0	–
3	Fe^0	2,2′-Bipyridine	DMF	1/0.1/4.6/4	100	0	–
4	CuBr	–	DMF	1/0/4.6/4	130	0	–
5	CuBr	–	DMSO	1/0/4.6/4	130	0	–
6	CuBr	HMTETA[d]	DMF	1/0.1/4.6/4	80	0	–
7	$CuCl_2$	–	DMF	1/0/4.6/4	130	0	–
8	$CuCl_2$	–	DMSO	1/0/4.6/4	130	0	–
9	$CuCl_2$	2,2′-Bipyridine	DMF	1/0.1/4.6/4	80	0	–
10	Cu^0	–	DMF	1/0/4.6/1	130	50	70
11	Cu^0	–	DMF	1/0/4.6/2	130	54	72
12	Cu^0	–	DMF	1/0/4.6/3	130	54	73
13	Cu^0	–	DMF	1/0/4.6/4	130	58	75
14	Cu^0	–	DMF	1/0/4.6/5	130	58	75
15	Cu^0	–	DMSO	1/0/4.6/1	130	51	70
16	Cu^0	–	DMSO	1/0/4.6/2	130	53	72
17	Cu^0	–	DMSO	1/0/4.6/3	130	54	72
18	Cu^0	–	DMSO	1/0/4.6/4	130	58	75
19	Cu^0	–	DMSO	1/0/4.6/5	130	58	75
20	Cu^0	HMTETA	DMF	1/0.1/4.6/4	80	60	88
21	Cu^0	2,2′-Bipyridine	DMF	1/0.1/4.6/4	60	62	88
22	Cu^0	2,2′-Bipyridine	DMSO	1/0.1/4.6/4	60	62	88
23	Cu^0	PMDETA[e]	DMF	1/0.1/4.6/4	100	69	90
24	Cu^0	2,2′-Bipyridine	DMF	1/0.1/4.6/4	80	73	93
25	Cu^0	2,2′-Bipyridine	DMF	1/0.1/4.6/4	100	73	99

[a] Calculated by ^1H NMR spectroscopy as reported in the experimental part.
[b] DMF = N,N-dimethylformamide.
[c] DMSO = dimethyl sulfoxide.
[d] HMTETA = N,N,N′,N″,N‴,N‴-hexamethyltriethylenetetramine.
[e] PMDETA = N,N,N′,N″,N″-pentamethyldiethylenetriamine.

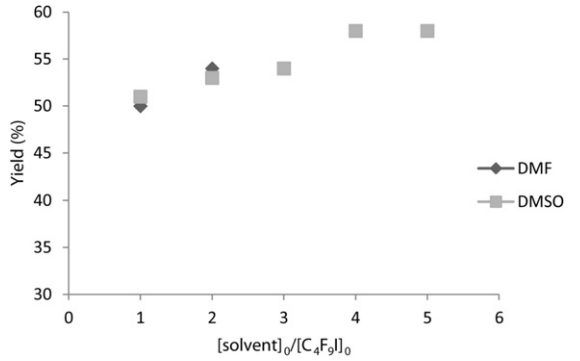


Fig. 1. Effect of the $[solvent]_0/[C_4F_9I]_0$ initial molar ratio in the yield in the copper-assisted cross-coupling reaction of 1-iodoperfluorobutane with 4′-bromoacetophenone using DMF or DMSO as the solvent (runs 10–19 in Table 1).

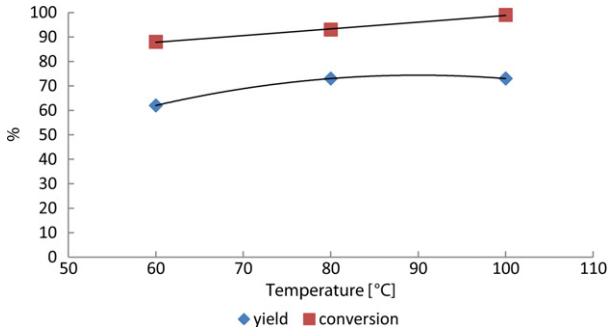


Fig. 2. Effect of the temperature on the yield and conversion for the reaction between Cu^0, N,N-dimethylformamide, in the presence of 2,2-bipyridine (entries 21, 24 and 25, Table 1).

The high amount of required copper could be explained by the reaction mechanism proposed by McLoughlin and Thrower [24,25] (Scheme 2).

The mechanism of copper-assisted cross-coupling reaction must be similar to that involved in the reaction between halogenoaromatic compounds and cuprous acetylides [43]. The mechanism is composed of two steps: first, in the metallation stage, the fluoroalkylcopper compound is formed as a solvated complex, then it interacts with the aromatic halide which is followed by an exchange between the halogen and the perfluoroalkyl chain on the aromatic derivative. To stabilize the fluoroalkylcopper complex formed in the former stage the solvent must also induce a ligand effect onto copper.

2.3. Effect of the ligand

The important effect of the ligand on the copper mediated cross-coupling reaction can be explained by examining the mechanism proposed in the paragraph above. For the synthesis of 4′-nonafluorobutylacetophenone, 2,2′-bipyridine, HMTETA, PMTETA were used as complexing ligands. It has been shown that a catalytic amount of these compounds was particularly beneficial to the reaction yield. Using DMSO and DMF as ligands/solvents, the reaction conversion was limited to 75% and the yield did not exceed 58% in 20 h (entries 10–19, Table 1). A presence of catalytic amount of an amino ligand induced an increase of both conversion and yield (entries 20–25, Table 1). From these results, 2,2-bipyridine is regarded as the best ligand that led to conversion higher than 90% and yield higher than 70% depending on the temperature.

2.4. Effect of temperature

For the copper-mediated cross-coupling reaction of 1-iodoperfluorobutane and 4′-bromoacetophenone, the effect of temperature is noted by comparison of entries 21, 24, 25 (Table 1) in which three different temperatures were used, 60, 80 and 100 °C. As displayed in Fig. 2 when the temperature increases, a linear increase in conversion was observed. Conversely, the yield increases almost linearly from 60 to 80 °C and then it reached a plateau to 73% indicating that a further temperature increase was not necessary.

3. Conclusion

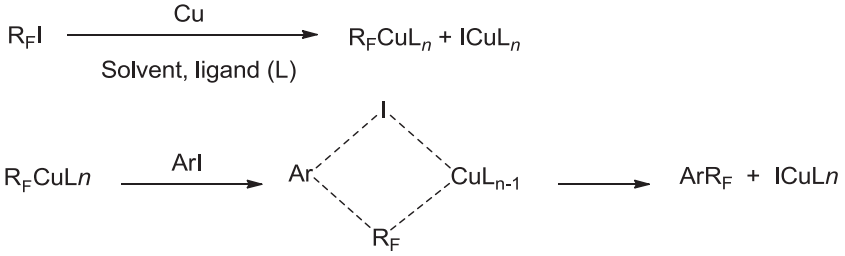
This study seeks to optimize the synthesis of 4′-nonafluorobutylacetophenone by the copper-assisted cross-coupling reaction, by changing the experimental conditions. The use of an aprotic polar solvent is compulsory for the success of the reaction as explained by the mechanism (Scheme 2), but changing N,N-dimethylformamide or dimethylsulfoxide does not seems to have any significant effects on the yield and conversion. Therefore, in view of a possible industrial application, DMSO should be preferred to DMF because the former is less toxic.

The study conducted on the quantity of solvent required for the reaction showed that the optimum $[solvent]_0/[1\text{-iodo-perfluorobutane}]_0$ molar ratio is 4. Different experiments were attempted to assess the role of the metal catalyst in the cross-coupling reaction. McLoughlin and Thrower showed that mercury and zinc were ineffective catalysts. In that present study, the use of metallic iron and cupric and cuprous salts as potential metal catalysts was investigated, but the desired product was not obtained, and only copper metal led to the best yield. Among the complexing ligands used (2,2′-bipyridine, HMTETA, PMTETA), 2,2′-bipyridine gave the best results both for conversion and yield. Further, using 2,2′-bipyridine when the temperature increased from 60 to 100 °C showed a positive effect on reaction yield and conversion.

4. Experimental

4.1. Materials and methods

Iron, copper, copper(I) bromide, copper(II) chloride, 2,2-bipyridine, N,N,N′,N″,N‴,N‴-hexamethyltriethylenetetramine (HMTETA),



Scheme 2. General mechanism of the synthesis of perfluoroalkyl aromatic compounds *via* copper-assisted cross-coupling reaction [24,25].

N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMTETA), 4′-bromoacetophenone, N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were purchased from the Aldrich Chemical Company. 1-Iodoperfluorobutane was purchased by Maflon s.p.a. The solvents were used as received.

All the reactions were conducted under nitrogen atmosphere.

The conversion (χ, Eq. (1)) was assessed by the sum of the values of the integrals ($\sum I$, Eq. (2)) of the signals relative to 4′-bromoacetophenone measured by ^{1}H NMR spectroscopy at initial time (0) and at the end (f) of the reaction.

$$\chi = \frac{[\sum I]_0 - [\sum I]_f}{[\sum I]_0} \quad (1)$$

$$\sum I = \int \frac{CH_2^{7.69\,ppm}}{2} + \int \frac{CH_2^{8.07\,ppm}}{2} + \int CH^{2.69\,ppm} \quad (2)$$

where $\int CH_x^{i\,ppm}$ represents the integral of the signal assigned to CH_x centred at i ppm.

^{1}H NMR (250 or 400 MHz) and ^{19}F (200 or 400 MHz) spectroscopies: the NMR spectra were recorded on Bruker, AC 250 and AC 400 instruments, using deuterated chloroform as the solvents and tetramethylsilane (TMS) (or $CFCl_3$) as the references for ^{1}H (or ^{19}F) nuclei, respectively. Coupling constants and chemical shifts are given in Hz and ppm, respectively. The experimental conditions for recording ^{1}H (^{19}F) NMR spectra were as follows: flip angle = 90° (30°), acquisition time = 4.5 s (0.7 s), pulse delay = 2 s (5 s), number of scans = 16 (64), and pulse width = 5 μs for ^{19}F NMR. 2D-heterocorrelated ^{1}H–^{13}C experiment was performed using a VSP-400 5 mm z-gradient probe in the reverse detection conditions. The proton and carbon assignments were obtained by standard chemical shift correlations and confirmed by 2D homo- and heterocorrelated measurements.

Infrared spectroscopy measurements were performed in transmission with a spectrometer Nicolet Avatar 10 P. The accuracy was ±2 cm^{-1}. GC/MS spectra were measured on a Carlo Erba Instrument MFC 500/QMD1000 using a silica fused capillary PS264 column (30 m × 0.25 mm) on a Finnigan Mat TSQ7000 (capillary column 30 m × 0.32 mm). Typical conditions were: temperature programme 60 °C for 2 min, 10 °C min^{-1} to 280 °C. Helium was used as the gas carrier 1 ml min^{-1}.

4.2. General procedure for the synthesis of 4′-nonafluorobutylacetophenone, $C_4F_9C_6H_4COCH_3$

In a 100 ml round bottom flask, equipped with a magnetic stirrer and a reflux condenser, a mixture composed of 1.0 mol of 4′-bromoacetophenone, 4.0 mol of N,N-dimethylformamide, 1.0 mol of 1-iodoperfluorobutane, 4.6 mol of copper and 0.1 mol of 2,2-bipiridine were heated under stirring for 20 h at 60 °C. After the reaction, the copper powder was removed by filtration and the liquid layer was washed three times with 30 ml of water and 30 ml of diethyl ether, separating each time the ether layer.

The ether was removed under reduced pressure and the 4′-nonafluorobutylacetophenone (b.p. 66–69 °C/0.2 mmHg) was distilled as a colorless liquid. IR (cm^{-1}): 2942 (w); 1647 (vs); 1587 (s); 1359 (m); 1216 (vs); 1205 (s); 1115 (s); 1074 (m); 922 (m); 821 (m); 732 (m). ^{1}H NMR ($CDCl_3$) δ: 2.64 ppm (3H, s, CH_3); 7.69 ppm (2H, d, $^3J_{HH}$ = 8.5 Hz, *m*-protons from C=O); 8.07 ppm (2H, d, $^3J_{HH}$ = 8.5 Hz, *o*-protons from C=O).

^{13}C NMR ($CDCl_3$, Fig. 3) δ: 196.8 ppm (s, **C**=O); 139.8 ppm (s, *p*-carbon from CF_2); 132.8 ppm (t, $^2J_{C-F}$ = 24 Hz, *p*-carbon from C=O); 128.3 ppm (s, *o*-carbons from C=O); 127.2 ppm (t, $^2J_{C-F}$ = 6 Hz, *m*-carbons from C = O); 118.8 ppm (qt, $^1J_{C-F}$ = 253 Hz, $^2J_{C-F}$ = 33 Hz); 115.9 ppm (qt, $^1J_{C-F}$ = 225 Hz, $^2J_{C-F}$ = 33 Hz); 115.4 ppm (t, $^2J_{C-F}$ = 33 Hz, CF_3–**C**F_2–CF_2–CF_2–Ph); 113.1 ppm (tt, $^1J_{C-F}$ = 255 Hz, $^2J_{C-F}$ = 33 Hz); 26.5 ppm (s, **C**H_3). ^{19}F NMR ($CDCl_3$) δ: −81.0 ppm (CF_3–CF_2–CF_2–CF_2–Ph); −125.6 ppm (CF_3–CF_2–CF_2–CF_2–Ph); −122.8 ppm (CF_3–CF_2–CF_2–CF_2–Ph); −111.6 ppm (CF_3–CF_2–CF_2–CF_2–Ph). Expansions of ^{1}H,^{13}C HMBC spectrum are mentioned in Fig. 4. Spectral data: MS *m*/*z* (rel. ab. %): 338 ([M]$^+$, 5%); 323 ([M−CH_3]$^+$, 100%); 295 ([M−$COCH_3$]$^+$, 10%); 119 ([M−C_4F_9]$^+$, 5%). Anal. Calcd for $C_{12}F_9H_7O$: C, 42.6%; F, 50.6%; H, 2.1%. Found: C, 41.9%; F, 50.9%; H, 2.0%.

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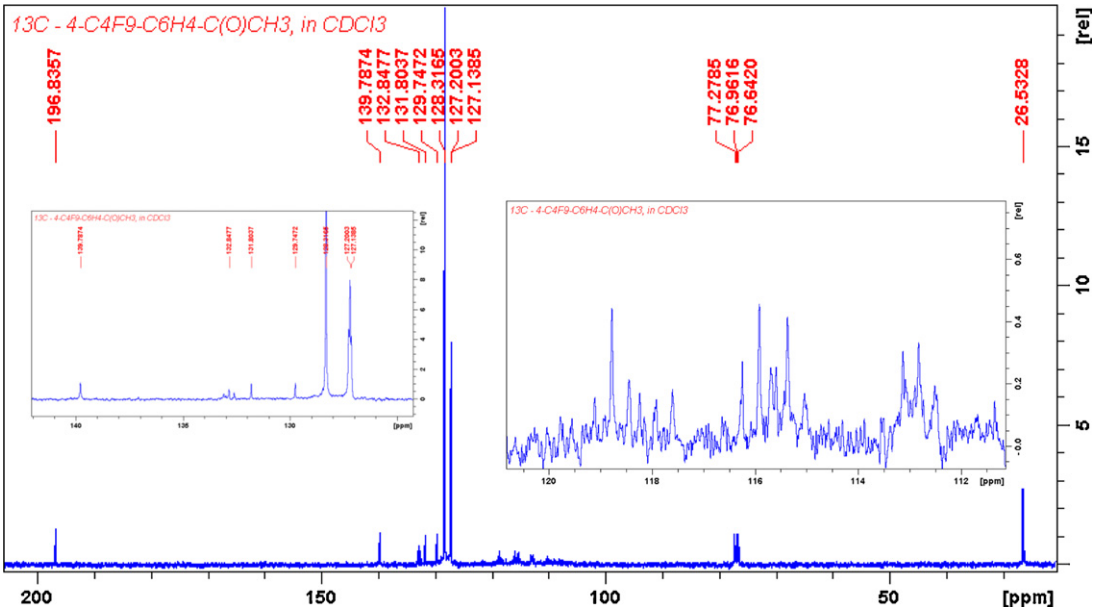

Fig. 3. ^{13}C NMR spectrum of 4′-nonafluorobutylacetophenone (recorded in $CDCl_3$).

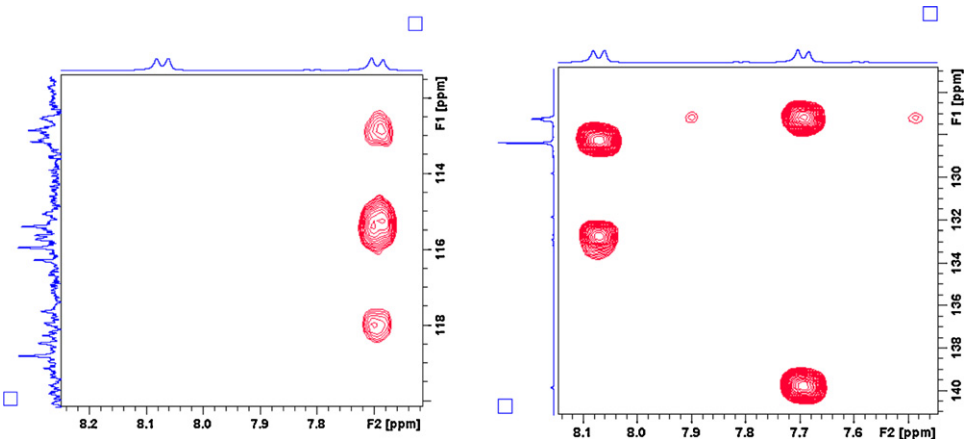

Fig. 4. $^{1}H,^{13}C$ HMBC spectrum of fluorinated moieties (left part) and $^{1}H,^{13}C$ HMBC spectrum of aromatic carbons (right part).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2011.11.006

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