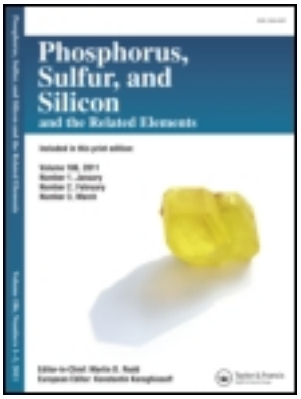

Phosphorus, Sulfur, and Silicon and the Related Elements

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An Electrogenerated Base-Promoted Synthesis of 2-Aryl-3,3-Bis((Perfluoroalkyl) Thio)Acrylonitriles

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AN ELECTROGENERATED BASE-PROMOTED SYNTHESIS OF 2-ARYL-3,3-BIS((PERFLUOROALKYL) THIO)ACRYLONITRILES

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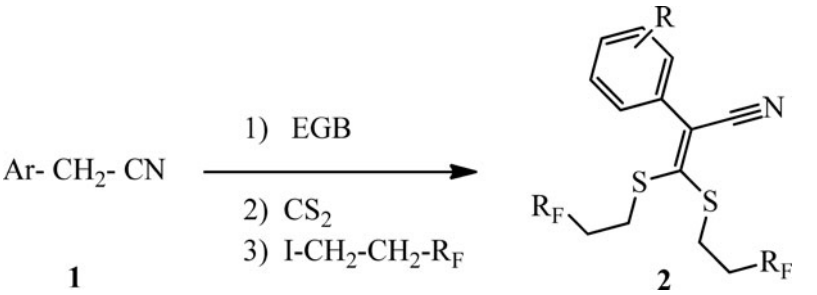
GRAPHICAL ABSTRACT



Abstract *The preparation of 2-aryl-3,3-bis((perfluoroalkyl)thio)acrylonitriles is described. The electrogenerated cyanomethyl base/anion obtained from electroreduction of acetonitrile promotes reactions between arylacetonitrile, carbon disulfide, and perfluoroalkyl iodides. The new fluorinated acrylonitriles were obtained in good yields under mild reaction conditions.*

Supplementary materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements *for the following free supplemental files:* Additional figures.

Keywords 2-Aryl-3,3-bis((perfluoroalkyl)thio)acrylonitrile; carbon disulfide; anion EGBs

INTRODUCTION

The reactivity of arylacetonitriles has been widely explored due to their use in the synthesis of several biologically active molecules such as fungicidals, flavonoid pigments, and sexual pheromones.[1–5] However, in order to avoid the use of polluting solvents and

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to circumvent the difficulties of the experimental protocols involved in classic syntheses, new approaches under very mild conditions are needed. In the literature, the condensations of arylacetonitriles with carbonyls, isothiocyanates, and 1,2- and 1,3-dihalogenated alkanes are based on the traditional Knovenagel reaction that involves strongly basic alcalin hydroxides or hydrides.[6] Recently, it was found that these bases could be substituted by electrogenerated bases (EGBs) to promote reactions, sometimes in higher yields and under milder conditions.[7–9] EGBs were initially mentioned by Baizer and coworkers[10] and recently used by Feroci et al. for the preparation of carbonates, carbamates, and oxazolines in a two-compartment cell.[11–16]

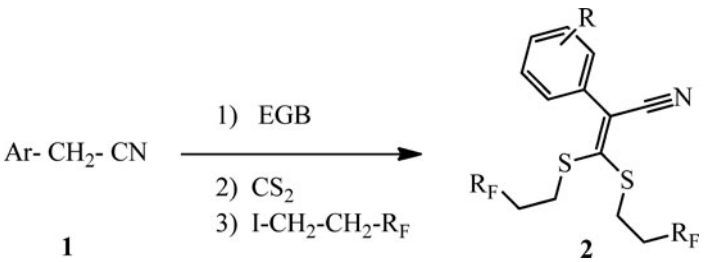
On the other hand, highly fluorinated molecules are of growing importance due to their pharmacological and industrial uses.[17–22] The introduction of perfluoroalkyl groups into organic compounds particularly functional olefins as possible polymerizable surfactants could generally be achieved with the use of catalysts.[23,24]

More recently, we reported on an EGB–promoted synthesis of a series of 3,3-bis (ethylthiol)-2-arylacrylonitriles and 3,3-bis(ethoxyacetatethiol)-2-arylacrylonitriles starting from arylacetonitrile.[25] This work is now being extended to the investigation of the fluorinated analogs through the introduction of perfluoroalkyl groups using the same methodology. We report here the synthesis of new 2-aryl-3,3-bis((perfluoroalkyl)thio) acrylonitriles.

RESULTS AND DISCUSSION

The current-potential curves of all arylacetonitriles used in this work were recorded in a solution of acetonitrile and tetrabutylammonium tetrafluoroborate concentration 0.1 M with a platinum electrode and a reference electrode Ag/Ag^+ and show that arylacetonitriles are not reducible under these conditions. Thus arylacetonitriles can be introduced at the beginning of electrolysis according to the terminology of Feroci et al.[11b].

Electrolysis similarly yields the cyanomethyl carbanions and is stopped approximately after 3–4 h of reaction. This time is sufficient to permit the formation of 5×10^{-3} mole of EGB. Then, carbon disulfide is added immediately to the solution followed by perfluoroethyl iodide 15 min later (see Scheme 1).



Scheme 1

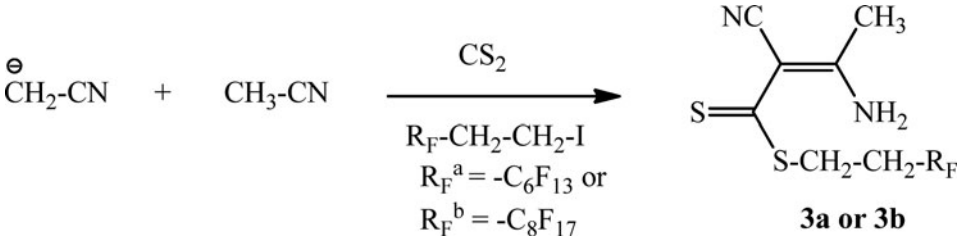
The mixture was continually stirred over night at ambient temperature. The products were isolated following standard workup procedures[6–8] and purified by column chromatography. All the resulting products **2a–h** are reported in Table 1 and were identified on the basis of their spectroscopic data.

Table 1 Synthesized 2-aryl-3,3-bis((perfluoroalkyl) thio)acrylonitrile **2a–h**

R	R_F	Products **2**	Q[a] (F/mol)	Yields[b] (%)
−H	$-C_6F_{13}$	**2 a**	2	68
	$-C_8F_{17}$	**2 b**	2	78
p-F	$-C_6F_{13}$	**2 c**	2	79
	$-C_8F_{17}$	**2d**	2	81
p-OCH_3	$-C_6F_{13}$	**2e**	2	75
	$-C_8F_{17}$	**2f**	2	83
p-CH_3	$-C_6F_{13}$	**2g**	2	69
	$-C_8F_{17}$	**2h**	2	78

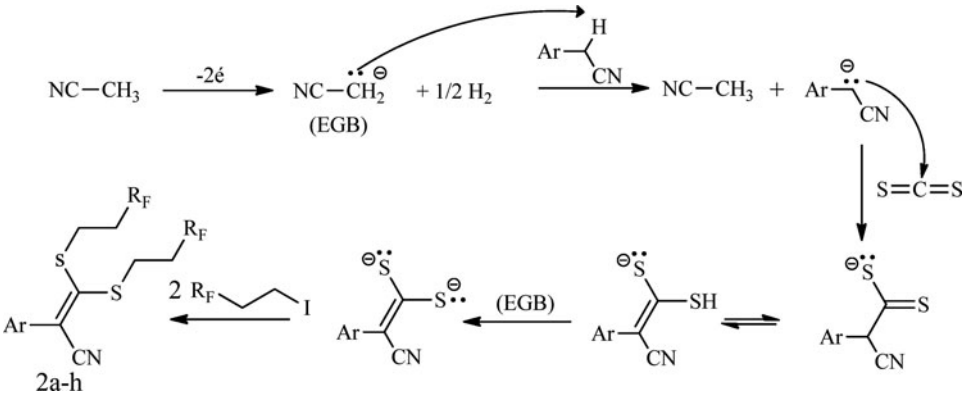
[a]The consumed quantity of electricity represents the number of faradays per mole of arylacetonitrile.
[b]Yields of isolated product refer to starting arylacetonitrile.

It is worth noting that in addition to its basic role in the formation of products **2**, the cyanomethyl anion can react as a nucleophile with respect to the acetonitrile producing the crotonitrile anion. This dianion can in turn react with carbon disulfide and the reagent of alkylation (R_F-CH_2-CH_2-I) leading to the byproducts **3** (see Scheme 2).[8]



Scheme 2

It was observed that 2F per mole of arylacetonitrile was needed for the preparation of compounds **2** (see Table 1). The mechanism of formation is also likely to proceed similarly as their nonfluorinated analogues (see Scheme 3).[25]



Scheme 3

CONCLUSION

New 2-aryl-3,3-bis((perfluoroalkyl)thio)acrylonitriles were prepared in high yields from EGB-promoted condensation of arylacetonitrile, carbon disulfide, and perfluoroalkyl iodides. This shows again that EGB could provide, under mild reaction conditions, a potential electrochemical methodology that avoids the use of polluting or hazardous chemicals or the addition of base or catalyst. The possible biological activity of these new highly fluorinated compounds is under investigation.

EXPERIMENTAL

Products **2a–h** were prepared following our previously reported method.[25] In a typical experiment, a solution of compound **1** (5 mmol) in acetonitrile (100 mL) 0.1 mol/L of tetrabutylammonium tetrafluoroborate as supporting electrolyte, in an undivided cell fitted with a consumable magnesium as anode and a stainless steel grid (20 cm^2) as cathode, was subjected to electrolysis at a constant current (80 mA). The cell was cooled to −20°C by diving in Lauder refrigerating system. During electrolysis, the system was maintained under inert atmosphere by continuous nitrogen bubbling. After the flow of 2 faraday, the electrolysis was stopped, and carbon disulfide (6 mmol) was added into the stirred solution after 15 min, followed by the addition of a twofold molar of perfluoroalkyl iodides **2**. The amount of acetonitrile was reduced by evaporation and the resulting mixture extracted with Et_2O (3 × 50 mL). The ethereal phase was washed by small amounts of water and dried over magnesium sulfate. The ether was removed and the residue purified by column chromatography on silica gel 60 using ethyl acetate/cyclohexane (v:v = 3:7) as eluent. Products **2** were identified by IR, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and elemental analysis. The Supplemental Materials contain samples of ^{1}H, ^{13}C, and ^{19}F NMR spectra of 2e and 3b (Figures S1–S6).

2a: 2-phenyl-3,3-bis((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)thio)acrylonitrile

Yield: 68%, m.p. 56–57°C. IR (cm^{-1}, $CHCl_3$) ν: 2220 (CN); 1600 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.20 (m, 2H, CH_2); 2.60 (m, 2H, CH_2); 3.00 (t, 2H, CH_2); 3.30 (t, 2H, CH_2); 7.20–7.40 (m, 5H, CHarom.). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 25.5, 26.3, 30.9, 35.2, 106–122, 127.8, 127.9, 128.8, 128.9, 129.6, 133.1, 150.0. ^{19}F NMR, δ: −114.9 (m, $CF_{2\alpha}$, $^3J_{FH}$ = 18.4 Hz), −123.0 (m, $CF_{2\beta}$), −124.9 (m, $CF_{2\gamma}$), −124.1 (m, $CF_{2\delta}$), −123.2 (m, $2CF_{2\varepsilon}$), −127.5 (m, $CF_{2\varpi}$), −82.3 (t, CF3, $^3J_{CF3}$ = 9.2 Hz). Elem. Anal.; Calcd. %: C = /34.23; H = 1.01; N = 1.69; Found %: C = 33.91; H = 1.48; N = 1.58.

2b: 2-phenyl-3,3-bis((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)thio)acrylonitrile

Yield: 78%, m.p. 95–96°C. IR (cm^{-1}, $CHCl_3$) ν: 2222 (CN); 1620 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.10 (m, 2H, CH_2); 2.60 (m, 2H, CH_2); 3.10 (t, 2H, CH_2); 3.20 (t, 2H, CH_2); 7.10–7.30 (m, 5H, CHarom.). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 23.2, 24.2, 31.0, 33.2, 104–125, 125.3, 125.9, 126.7, 126.8, 127.5, 131.0, 151.1. ^{19}F NMR, δ: −112.8 (m, $CF_{2\alpha}$, $^3J_{FH}$ = 18.4 Hz), −122.1 (m, $CF_{2\beta}$), −123.7 (m, $CF_{2\gamma}$), −123.3(m, $CF_{2\delta}$), −122.4

(m, $2CF_{2\varepsilon}$), −127.1 (m, $CF_{2\varpi}$), −80.2 (t, CF3, $^3J_{CF3}$ = 9.3 Hz). Elem. Anal.; Calcd. %: C = /32.68; H = 0.68; N = 1.38; Found %: C = 32.09; H = 1.21; N = 1.29.

2c: 2-(4-fluorophenyl)-3,3-bis((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)thio)acrylonitrile

Yield: 73%, m.p. 66–67°C. IR (cm^{-1}, $CHCl_3$) ν: 2220 (CN); 1606 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.40 (m, 2H, CH_2); 2.80 (m, 2H, CH_2); 3.00 (t, 2H, CH_2); 3.20 (t, 2H, CH_2); 7.00–7.40 (m, 4H, CHarom.). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 24.1, 26.2, 33.9, 37.2, 106–122, 124.1, 124.5, 125.8, 125.7, 126.2, 134.3, 153.0. ^{19}F NMR, δ: −114.2 (m, $CF_{2\alpha}$, $^3J_{FH}$ = 18.31 Hz), −123.4 (m, $CF_{2\beta}$), −126.2 (m, $CF_{2\gamma}$), −126.3 (m, $CF_{2\delta}$), −123.5 (m, $2CF_{2\varepsilon}$), −128.8 (m, $CF_{2\varpi}$), −80.3 (t, CF_3, $^3J_{CF3}$ = 9.1 Hz). Elem. Anal.; Calcd. %: C = 33.76; H = 0.98; N = 1.72; Found %: C = 33.24; H = 1.34; N = /1.55.

2d: 2-(4-fluorophenyl)-3,3-bis((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)thio) acrylonitrile

Yield: 79%, m.p. 89–90°C. IR (cm^{-1}, $CHCl_3$) ν: 2224 (CN); 1620 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.2 (s, 3H, CH_3); 2.60 (m, 2H, CH_2); 2.90 (m, 2H, CH_2); 3.20 (t, 2H, CH_2); 3.40 (t, 2H, CH_2); 7.00–7.40 (m, 4H, CHarom.). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 16.2, 24.1, 26.2, 33.9, 37.2 (t, 1C), 111–119, 119.8, 120.2, 127.6, 127.9, 129.3, 139.2, 148.9. ^{19}F NMR, δ: −114.2 (m, $CF_{2\alpha}$, $^3J_{FH}$ = 18.21 Hz), −123.4 (m, $CF_{2\beta}$), −126.2 (m, $CF_{2\gamma}$), −126.3 (m, $CF_{2\delta}$), −123.5 (m, $2CF_{2\varepsilon}$), −128.8 (m, $CF_{2\varpi}$), −111.3 (s, CF arom), −80.3 (t, CF_3, $^3J_{CF3}$ = 9.30 Hz). Elem. Anal.; Calcd. %: C = 31.20; H = 0.87; N = /1.43; Found %: C = 31.56; H = 1.10; N = /1.25.

2e: 2-(4-methoxyphenyl)-3,3-bis((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)thio)acrylonitrile

Yield: 81%, m.p. 81–82°C. IR (cm^{-1}, $CHCl_3$) ν: 2220 (CN); 1610 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.30 (m, 2H, CH_2); 2.60 (m, 2H, CH_2); 3.10 (t, 2H, CH_2); 3.30 (t, 2H, CH_2); 3.90(s, CH_3) 6.90–7.30 (m, 4H, CHarom.). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 27.3, 29.4, 32.8, 36.2, 55.3, 102–119, 122.3, 122.7, 124.6, 124.9, 128.5, 139.3, 156.6. ^{19}F NMR, δ: −113.6 (m, $CF_{2\alpha}$, $^3J_{FH}$ = 18.31 Hz), −122.5 (m, $CF_{2\beta}$), −125.3 (m, $CF_{2\gamma}$), −125.3 (m, $CF_{2\delta}$), −122.5 (m, $2CF_{2\varepsilon}$), −128.1 (m, $CF_{2\varpi}$), −83.3 (t, CF_3, $^3J_{CF3}$ = 9.0 Hz). Elem. Anal.; Calcd. %: C = /33.65; H = 1.13; N = 1.69; Found %: C = 34.11; H = 1.65; N = /1.53.

2f: 2-(4-methoxyphenyl)-3,3-bis((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl) thio)acrylonitrile

Yield: 78%, m.p. 105–106°C. IR (cm^{-1}, $CHCl_3$) ν: 2210 (CN); 1620 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.40 (m, 2H, CH_2); 2.60 (m, 2H, CH_2); 3.20 (t, 2H, CH_2); 3.40 (t, 2H, CH_2); 3.80(s, CH_3) 7.00–7.40 (m, 4H, CHarom.). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 25.3, 28.6, 33.1, 36.2, 54.0, 110–120, 123.4, 123.7, 125.7, 126.0, 129.6, 140.1, 156.4. ^{19}F NMR, δ: −112.7 (m, $CF_{2\alpha}$, $^3J_{FH}$ = 18.31 Hz), −124.5 (m, $CF_{2\beta}$), −126.2 (m, $CF_{2\gamma}$), −126.4 (m, $CF_{2\delta}$), −123.6 (m, $2CF_{2\varepsilon}$), −127.3 (m, $CF_{2\varpi}$), −83.4 (t, CF_3, $^3J_{CF3}$ = 9.0 Hz).

Elem. Anal.; Calcd. %: C = /32.90; H = 1.15; N = 1.32; Found %: C = 32.30; H = 1.36; N = 1.25.

2g: 2-(p-tolyl)-3,3-bis((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)thio) acrylonitrile

Yield: 81%, m.p. 76–77°C. IR (cm^{-1}, $CHCl_3$) ν: 2224 (CN); 1600 (C=C). ^1H NMR (300 MHz, $CDCl_3$), δ: 2.30 (m, 2H, CH_2); 2.60 (m, 2H, CH_2); 3.10 (t, 2H, CH_2); 3.30 (t, 2H, CH_2); 2.34 (s, CH_3) 7.10–7.40 (m, 4H, CHarom.). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 21.5, 26.4, 28.3, 32.6, 35.1, 105–121, 122.1, 122.7, 123.6, 123.9, 127.1, 140.0, 158.5. ^{19}F NMR, δ: −111.1 (m, $CF_{2\alpha}$, $^3J_{FH} = 18.31$ Hz), −123.4 (m, $CF_{2\beta}$), −124.8 (m, $CF_{2\gamma}$), −124.6 (m, $CF_{2\delta}$), −123.4 (m, $2CF_{2\varepsilon}$), −127.2 (m, $CF_{2\varpi}$), −82.6 (t, CF_3, $^3J_{CF3} = 9.0$ Hz). Elem. Anal.; Calcd. %: C = /34.41; H = 1.12; N = 1.66; Found %: C = 34.72; H = 1.68; N = /1.56.

2h: 2-(p-tolyl)-3,3-bis((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)thio)acrylonitrile

Yield: 76%, m.p. 112–113°C. IR (cm^{-1}, $CHCl_3$) ν: 2220 (CN); 1620 (C=C). ^1H NMR (300 MHz, $CDCl_3$), δ: 2.20 (m, 2H, CH_2); 2.40 (m, 2H, CH_2); 3.00 (t, 2H, CH_2); 3.30 (t, 2H, CH_2); 2.20 (s, CH_3) 7.00–7.60 (m, 4H, CHarom.). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 24.3, 29.0, 32.1, 35.1, 60.1, 111–123, 125.3, 125.7, 126.2, 126.9, 129.8, 137.2, 155.3. ^{19}F NMR, δ: −114.3 (m, $CF_{2\alpha}$, $^3J_{FH} = 18.31$ Hz), −123.3 (m, $CF_{2\beta}$), −125.2 (m, $CF_{2\gamma}$), −126.3 (m, $CF_{2\delta}$), −121.5 (m, $2CF_{2\varepsilon}$), −126.1 (m, $CF_{2\varpi}$), −82.6 (t, CF_3, $^3J_{CF3} = 9.0$ Hz). Elem. Anal.; Calcd. %: C = /32.92; H = 0.95; N = 1.41; Found %: C = 32.77; H = 1.38; N = 1.27.

3a: 2-(1-aminoethylidene)-6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-3-thioxoundecane nitrile

M.p. 42–43°C. IR (cm^{-1}, $CHCl_3$) ν: 3334 (NH_2); 2224 (CN); 1610 (C=C); 1190 (C=S). ^1H NMR (300 MHz, $CDCl_3$), δ: 2.26 (s, 3H, CH_3); 2.40 (m, 2H, CH_2); 3.20 (t, 2H, CH_2); 6.20 (s, 2H, NH_2). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 14.0; 23.3; 30.1; 88.0; 111–122; 164.2; 210.8. ^{19}F NMR, δ: −110.0 (m, $CF_{2\alpha}$, $^3J_{FH} = 18.31$ Hz), −120.2 (m, $CF_{2\beta}$), −124.3 (m, $CF_{2\gamma}$), −125.0 (m, $CF_{2\delta}$), −126.3 (m, $2CF_{2\varepsilon}$), −128.6 (m, $CF_{2\varpi}$), −86.4 (t, CF_3, $^3J_{CF3} = 9.0$ Hz). Elem. Anal.; Calcd. %: C = /31.08; H = 1.20; N = 5.38; Found %: C = 30.96; H = 1.80; N = 5.55.

3b: 2-(1-aminoethylidene)-6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluoro-3- thioxotridecanenitrile

M.p. 92–93°C. IR (cm^{-1}, $CHCl_3$) ν: 3332 (NH_2); 2222 (CN); 1604 (C=C); 1188 (C=S). ^1H NMR (300 MHz, $CDCl_3$), δ: 2.24 (s, 3H, CH_3); 2.46 (m, 2H, CH_2); 3.30 (t, 2H, CH_2); 7.10 (s, 2H, NH_2). ^{13}C NMR (75.47 MHz, $CDCl_3$), δ: 13.9; 24.0; 32.0; 89.1; 108–124; 160.0; 212.0. ^{19}F NMR, δ: −112.1 (m, $CF_{2\alpha}$, $^3J_{FH} = 18.31$ Hz), −122.0 (m, $CF_{2\beta}$), −123.1 (m, $CF_{2\gamma}$), −125.3 (m, $CF_{2\delta}$), −126.2 (m, $2CF_{2\varepsilon}$), −129.1 (m, $CF_{2\varpi}$), −84.9 (t, CF_3, $^3J_{CF3} = 9.0$ Hz). Elem. Anal.; Calcd. %: C = /30.16;%H = 1.34;%N = 5.02; Found %: C = 29.81; H = 1.50; N = 4.64.

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