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A convenient synthesis of *N*,*N*-bis(trifluoromethyl)anilines

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Dedicated to the memory of
Prof. L.M. Yagupolskii.

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ABSTRACT

A convenient synthesis of *N*,*N*-bis(trifluoromethyl)anilines by means of dediazotation reactions of previously unknown aryldiazoniumbis(trifluoromethyl)imides in the presence of Cu^{I} salts are described. Properties and applications of *N*,*N*-bis(trifluoromethyl)anilines in syntheses of aromatic compounds containing the $(CF_3)_2N$ group are presented.

1. Introduction

The $N(CF_3)_2$ group is an "exceptional" group in organic chemistry. In spite of its structural analogy to the dimethylamino group, $N(CH_3)_2$, aromatic compounds containing the $N(CF_3)_2$ group, show significantly different properties. For instance, *N*,*N*-dimethylaniline $C_6H_5N(CH_3)_2$ is in contrast to *N*,*N*-bis(trifluoromethyl)aniline $C_6H_5N(CF_3)_2$ a strong base, and $C_6H_5N(CF_3)_2$ does not dissolve in concentrated hydrochloric acid [1]. The electronic nature of both substituents differs strongly as can be seen from the Hammett constants $N(CH_3)_2$ (−0.44) and $N(CF_3)_2$ (+0.50) [1,2].

The $N(CF_3)_2$ group bonded to aryl compounds is stable against acids, bases, oxidants and reductants [1]. All these properties makes the $N(CF_3)_2$ group a valuable substituent to tune the properties of aromatic compounds. Various aromatic substances containing the $N(CF_3)_2$ group have been synthesised and tested for possible practical applications.

Yagupolskii et al. have prepared *ortho*-, *meta*-, and *para*-*N*,*N*-bis(trifluoromethyl)amino benzaldehydes and used these compounds for the synthesis of 4-aryl-1,4-dihydropyridines containing the $N(CF_3)_2$ group by means of a modified Hantzsch method [3]. The myocardial contractile activity of these synthesised compounds in comparison to Nifedipine (©, 2-nitrophenyl derivate) was studied. The most active substance had the $N(CF_3)_2$ group in the *ortho* position of the benzene ring.

p-Bromo-*N*,*N*-bis(trifluoromethyl)aminobenzene was applied in the synthesis of amphetamine 2-amino-1-[(4-*N*,*N*,-bis(trifluoromethylamino)phenyl]propane [4] and *p*-iodo-*N*,*N*-bis(trifluoromethyl)aminobenzene was used as the starting material in the preparation of a series of triphenylmethane dyes [5]. Carbocyanine dyes having the $(CF_3)_2N$ group in the benzene ring were prepared from 3-nitro-4-amino-*N*,*N*-bis(trifluoromethyl)aniline [6].

All these examples demonstrate that aromatic compounds containing the $N(CF_3)_2$ substituent can serve as useful starting materials in the preparation of a variety of compounds with potential application.

The first aromatic compounds containing the $N(CF_3)_2$ group were synthesised at the beginning of the 60 s last century by the group of Yagupolskii (Kiev, Ukraine) [1] and Sheppard (Central Research Department, E.I. du Pont de Nemours and Company, Delaware, USA) [7].

The method of Yagupolskii is based on chlorination/fluorination reactions of aromatic compounds containing the $N(CF_3)(CH_3)$ group (Scheme 1) [8].

The starting material, compound (I), can be synthesised by the reaction of *N*-methyl-*N*-arylthiuramdisulphides (II) with SF_4 (Scheme 2) [8].

This method has many disadvantages, for instance: low yield, multistep procedure, use of expensive and toxic reagents.

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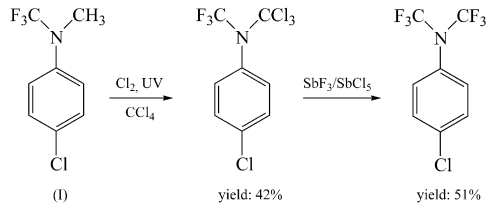
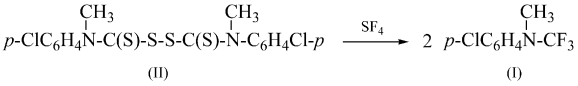


Scheme 1.



Scheme 2.

The Sheppard method is based on the fluorination of *N*,*N*-bis(fluoroformyl)anilines (III) with SF_4 in aHF [7]. The starting compounds (III) can be prepared by addition of COF_2 to aryl isocyanates (Scheme 3).

The disadvantages of this method are: the low yield of the reaction with SF_4 (2–12%), the use of toxic reagents like COF_2, SF_4, HF and the required pressure vessels made of Hastelloy for the reaction with SF_4.

A further synthesis of *N*,*N*-bis(trifluoromethyl)aniline was claimed by thermal decarboxylation of the oxy-carbonyl compound (IV) (Scheme 4) [9].

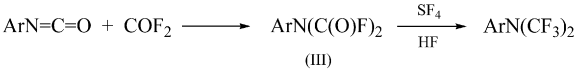
However, this method could not be reproduced [10–12].

Another method is based on the interaction of benzene or substituted benzenes with $(CF_3)_2NON(CF_3)_2$ (not commercial available) yielding the corresponding $ArN(CF_3)_2$ compounds in mixtures with by-products [11]. This reaction proceeds at room temperature within several days and a radical mechanism has been postulated [11].

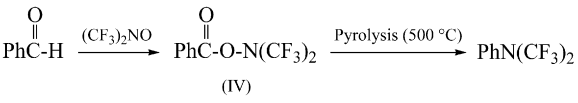
The addition of *N*-halogenobis(trifluoromethyl)amines $(CF_3)_2NX$ (X = Cl, Br, or I) to cyclohexa-1,3-diene at −78 °C followed by treatment of the reaction mixture with KOH and dehydrogenation by means of Pd/C at 180–190 °C resulted in the formation of *N*,*N*-bis(trifluoromethyl)aniline in overall yield of 48% in the case X = Br [13]. It was difficult to scale up that method which need a reaction time of 3 days.

The $[N(CF_3)_2]^-$ anion can be generated by addition of CsF to perfluoroazopropene $CF_3–N{=}CF_2$ and used to substitute a halogen atom in an activated position, for example Cl in cyanurchloride (Scheme 5) [14].

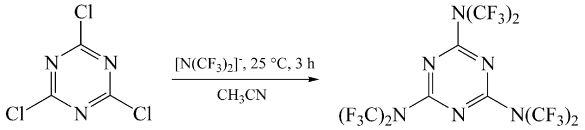
This method to generate the $[N(CF_3)_2]^-$ anion is not convenient for practical application because $CF_3–N{=}CF_2$ is highly toxic and commercially not available. Furthermore the reaction is not selective and results also in the formation of the dimeric product (V) (Scheme 6).



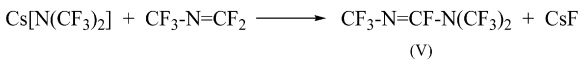
Scheme 3.



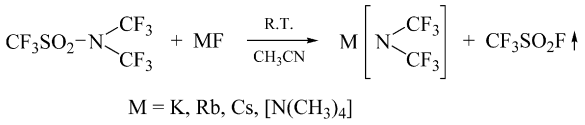
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

Recently Merck KGaA (Darmstadt, Germany) has developed a convenient method to generate the $[(CF_3)_2N]^-$ anion by the reaction of metal fluorides or tetramethylammonium fluoride with *N*,*N*-bis(trifluoromethyl)trifluoromethansulfonamide $CF_3SO_2N(CF_3)_2$ (Scheme 7) [15].

The side product CF_3SO_2F can be trapped together with dimethylamine in an organic solvent or in an ionic liquid media yielding $CF_3SO_2N(CH_3)_2$ (Scheme 8).

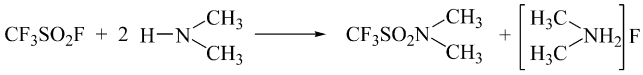
$CF_3SO_2N(CH_3)_2$ can be easily converted into *N*,*N*-bis(trifluoromethyl)trifluoromethansulfonamide $CF_3SO_2N(CF_3)_2$ by means of electrochemical fluorination in anhydrous HF (Simons process) (Scheme 9) [16]:

In practice, the combination of those three steps (described above) allows converting the cheap dimethylamine into the $[N(CF_3)_2]^-$ anion (Scheme 10).

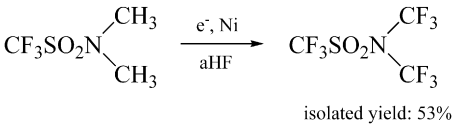
We have successfully applied the substitution of halogens by the $[N(CF_3)_2]^-$ anion, for example (see Schemes 11–14) [15].

However, we failed to substitute activated halogens in aromatic compounds by $[N(CF_3)_2]^-$. For example, in the reaction of 2,4-dinitrochloro benzene with the $[N(CF_3)_2]^-$ anion the replacement of Cl by F preferably took place. To our knowledge, no examples of a nucleophilic substitution of halogen in a phenyl moiety with $[N(CF_3)_2]^-$ anion has been reported.

In this contribution we are presenting a new and convenient method for the syntheses of *N*,*N*-bis(trifluoro methyl)anilines by dediazotation reactions of the hitherto unknown diazonium salts

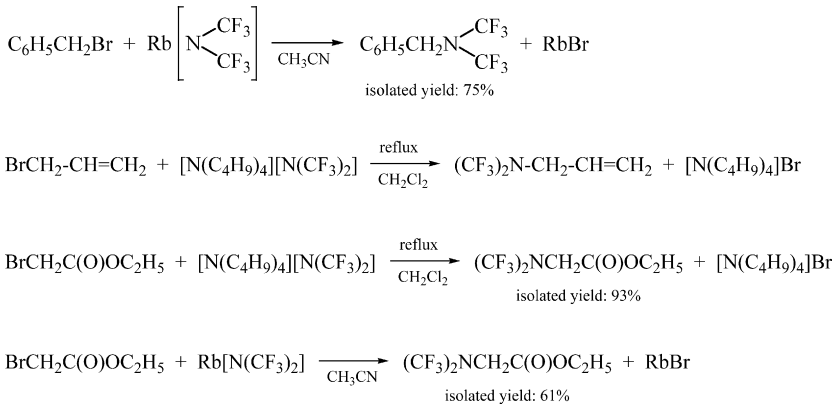


Scheme 8.

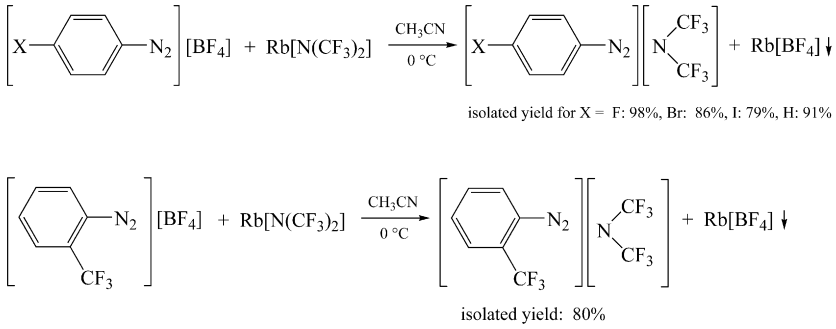


Scheme 9.

Schemes 10.



Schemes 11–14.



Schemes 15 and 16.

$[4\text{-}XC_6H_4N_2][N(CF_3)_2]$ in the presence of copper(I) salts with weakly coordinating anions.

2. Results and discussion

2.1. Syntheses and properties of the N,N-bis(trifluoromethyl)anilines

The starting compound $Rb[N(CF_3)_2]$ [15] was synthesised from $CF_3SO_2N(CF_3)_2$ [16] according to the described procedure. The aryldiazonium tetrafluoroborates were prepared by diazotation of anilines with $NaNO_2$ in HBF_4 (50%) at 3–20 °C. The reaction of $Rb[N(CF_3)_2]$ with aryldiazonium tetrafluoroborates gave the hitherto unknown aryldiazonium bis(trifluoromethyl)imides in good yields (Schemes 15 and 16).

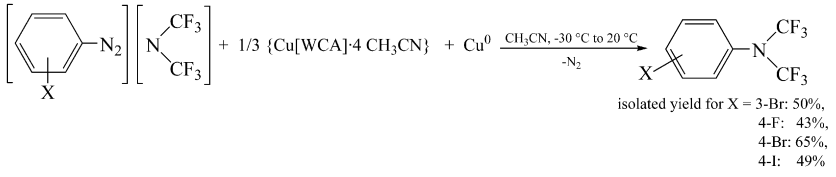
The desired *N,N*-bis(trifluoromethyl)anilines were prepared by decomposition of the aryldiazonium bis(trifluoromethyl)imides in the presence of $Cu^I[WCA]\cdot 4\ CH_3CN$ salts (WCA = BF_4, PF_6, $P(C_2F_5)_3F_3$, CF_3SO_3). The yield of the *N,N*-bis(trifluoromethyl)anilines was improved by using $Cu^I[WCA]$ salts with an additional equimolar amount of Cu^0 (Scheme 17).

The influence of Cu^0 on the yield of *N,N*-bis(trifluoromethyl)anilines was demonstrated as following: the thermal decomposition of the *p*-iodo-phenyldiazonium bis(trifluoro methyl)imide at 20 °C without addition of elemental copper resulted in *p*-$IC_6H_4N(CF_3)_2$ in 18% yield; addition of elemental copper to the reaction mixture increased the yield of *para*-iodobis(trifluoromethyl)aniline to 49%. The decomposition of *p*-fluoro- and *p*-bromo phenyldiazonium bis(trifluoromethyl)imide at 20 °C in the absence of Cu^0 did not result in the corresponding *N,N*-bis(trifluoromethyl)anilines at all.

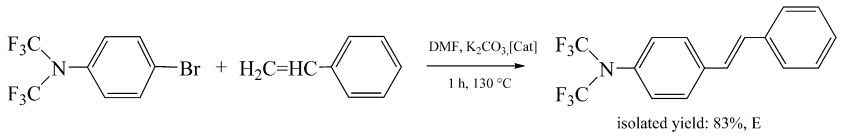
The replacement of the system $Cu^I[WCA]/Cu^0$ by $Cu^{II}[WCA]$ salts led to the complete decomposition of the $[XC_6H_4N_2][N(CF_3)_2]$ salts without forming the desired products but mainly $(CF_3)_2N\text{–}C(F)\text{=}N\text{–}CF_3$ (V). It seems that the Cu(II) cation acted as a fluoride scavenger triggering the formation of dimeric product (V).

While *m*- and *p*-bromo-*N,N*-bis(trifluoromethyl)anilines were accessible from the corresponding phenyldiazonium imides, only traces of the *ortho*-derivate could be observed in the reaction mixture by NMR-spectroscopy. Decomposition of $[2\text{-}XC_6H_4N_2][N(CF_3)_2]$ (X = Br, CF_3) in the presence of $Cu^I[WCA]/Cu^0$ resulted in the formation of 2-XC_6H_4F and $(CF_3)_2N\text{–}C(F)\text{=}N\text{–}CF_3$ (V) as major products. Probably, the halogen atom or the CF_3 group in the *ortho*-position positivates the *ipso*-C-atom and therefore increases its fluoride affinity.

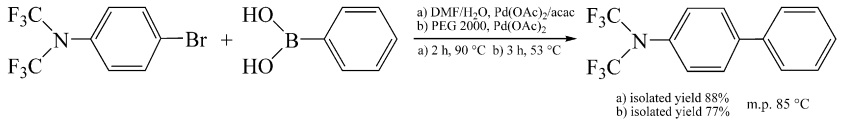
While the methods mentioned in the introduction have many disadvantages (for instance: not always reproducible, low yield, multistep procedure, expensive and toxic reagents), the here presented method strikes out as a new and reproducible one combined with good yields.



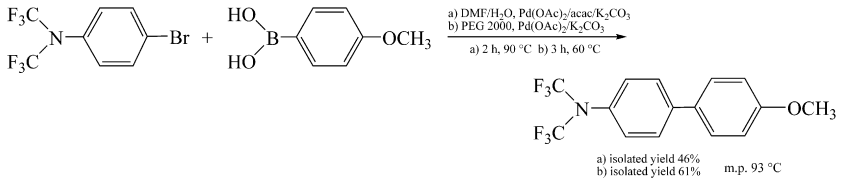
Scheme 17.



Scheme 18.



Scheme 19.



Scheme 20.

p-Halogen-*N*,*N*-bis(trifluoromethyl)anilines, in particular 4-$BrC_6H_4N(CF_3)_2$, offer a variety of possibilities for further derivatisation of these compounds. We successfully involved 4-$BrC_6H_4N(CF_3)_2$ in Heck and Suzuki coupling reactions (Schemes 18–20).

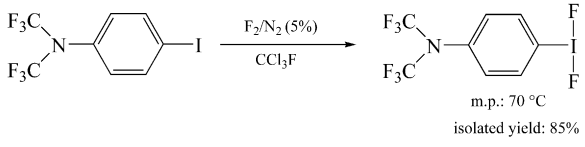
The Suzuki coupling reactions (Schemes 19 and 20) with different boronic acids were successfully carried out in polyethylene glycol 2000. PEG 2000 served in that case as well as solvent and as ligand for Palladium(0), which was generated in situ.

Similar to *p*-substituted *N*,*N*-bis(trifluoromethyl)anilines, the reaction of 3-$BrC_6H_4N(CF_3)_2$ with $C_6H_5B(OH)_2$ in PEG 2000 resulted in the formation of *N*,*N*-bis(trifluoromethyl)biphenyl-3-amine (isolated yield: 69%).

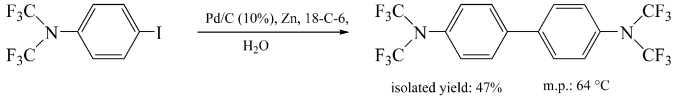
4-$IC_6H_4N(CF_3)_2$ was treated with diluted elemental F_2 to form the previously unknown 4-(difluoro-λ^3-iodanyl)-*N*,*N*-bis(trifluoromethyl)aniline (Scheme 21). To avoid the fluorination of the aromatic ring, the reaction was carried out at −70 °C in the inert solvent CCl_3F.

The reductive bi(aryl) coupling of the 4-$IC_6H_4N(CF_3)_2$ was carried out in water in the presence of Pd/C, 18-C-6 and Zn (Scheme 22).

The precursor 4-$BrC_6H_4N(CF_3)_2$ provided a convenient access to the Grignard reagent $(CF_3)_2NC_6H_4MgBr$ which reacted with CO_2 forming the 4-[bis(trifluoromethyl)amino] benzoic acid, $(CF_3)_2NC_6H_4C(O)OH$ [5,8]. This benzoic acid is a useful compound for the preparation of derivates, for example esters by the reaction with MeOH or EtOH in presence of $H_2SO_{4(conc.)}$ as catalyst. Heating of the $(CF_3)_2NC_6H_4C(O)OH$ acid over P_4O_{10} under reflux allowed access to the corresponding anhydride.



Scheme 21.



Scheme 22.

As already mentioned the bis(trifluoromethyl)amino group attached to the aromatic ring is chemically very inert. Thus, 4-$BrC_6H_4N(CF_3)_2$ did not react with $H_2SO_{4(conc.)}$ (98%), HCl (36%), $CF_3SO_3CH_3$ or $(CH_3)_3SiCN$ at 20 °C within 24 h.

2.2. Multinuclear magnetic resonance spectroscopy of N,N-bis(trifluoromethyl)anilines and their derivates

In contrast to the bis(trifluoromethyl)imide anion (chemical shift δ_F = −37 ppm) the covalently bonded $(CF_3)_2N$ group showed resonance at about −56 ppm (singlet). The same tendency was observed in the ^{13}C NMR spectra. The signals of covalently bonded bis(trifluoromethyl)amino groups appeared at 120 ppm whereas the signal of the bis(trifluoromethyl)imide anion was observed at 125 ppm. Differences in the $^1J_{C,F}$ coupling constants of the bis(trifluoromethyl)amino group ($^1J_{C,F}$ = 262 Hz, quartet) and the bis(trifluoromethyl)imide anion ($^1J_{C,F}$ = 243 Hz, quartet; $^3J_{C,F}$ = 11 Hz) reflect the distinction in the geometry and electronic nature of covalently bonded $(CF_3)_2N$ group and the $[(CF_3)_2N]^-$ anion.

In the case of the 4-$(CF_3)_2NC_6H_4IF_2$ compound, the bis(trifluoromethyl)amino group showed the typical chemical shift in the ^{19}F and ^{13}C NMR mode and the IF_2 group appeared as a singlet at −176 ppm in the ^{19}F NMR spectrum.

3. Experimental part

All moisture sensitive compounds were handled under an atmosphere of dry argon. Reactions were carried out in glass vessels or in traps made from FEP tubes (o.d. = 4.1 mm, i.d. = 3.5 mm or o.d. = 9.0 mm, i.d = 8.0 mm). CH_3CN (supplier: KMF) was purified by reflux and distillation in sequence over $KMnO_4$ and P_4O_{10}, respectively.

NMR spectra were recorded on a Bruker NMR spectrometer AVANCE 300 (^{13}C at 75.47 MHz, ^{19}F at 282.40 MHz, and ^1H at 300.13 MHz) and a Bruker spectrometer AVANCE 400 (^{13}C at 100.61 MHz, ^{19}F at 376.50 MHz, and ^1H at 400.13 MHz). The chemical shifts were referenced to TMS (^{13}C, ^1H), CCl_3F (^{19}F) (C_6F_6 as a secondary reference, δ = −162.9). The ratio of ^{19}F and ^1H nuclei in the products was determined by NMR spectroscopy after addition of 1,3,5-trifluorbenzene or benzotrifluoride. Raman

spectra were recorded on the Bruker FT-Raman spectrometers RFS 100/S and FRA 106/S using the 1064 nm line of a Nd/YAG laser. The back-scattered (180°) radiation was sampled and analysed (stoke range: 50–4000 cm^{-1}). The samples were placed in glass capillaries or FEP tubes.

3.1. Syntheses of aryldiazonium tetrafluoroborates

Aryldiazonium tetrafluoroborates were prepared according to the described methods [17].

3.2. Syntheses of aryldiazonium bis(trifluoromethyl)imides

Aryldiazonium bis(trifluoromethyl)imides were prepared as described previously [18].

3.3. Syntheses of arylbis(trifluoromethyl)amines

Synthesis of 4-$FC_6H_4N(CF_3)_2$ as an example: $CF_3SO_2N(CF_3)_2$ (5.12 g, 17.83 mmol) was added to a cold suspension (0 °C) of RbF (1.61 g, 15.41 mmol) in CH_3CN (7 mL). After 20 min the solid was dissolved and the solution was added to a stirred cold solution (0 °C) of [4-$FC_6H_4N_2$][BF_4] (2.8 g, 13.3 mmol) in CH_3CN (9 mL). A precipitate was formed. After 15 min of stirring the suspension was degassed in vacuum (0.05 hPa, −25 °C, 7 min) and added dropwise to a suspension (−30 °C) of Cu[PF_6]·4 CH_3CN (1.67 g, 4.48 mmol)/Cu(0) (0.86 g, 13.56 mmol) in CH_3CN (5 mL). The supernatant became green. The reaction mixture was warmed to −20 °C and to 0 °C within 30 min, respectively. Finally, when the suspension was stirred at 20 °C the supernatant became orange. The product 4-$FC_6H_4N(CF_3)_2$ was distilled in vacuum with CH_3CN. By azeotropic distillation with *n*-pentane CH_3CN could be removed and the product was purified by repeated distillation. A colorless liquid was obtained in 43% yield (1.41 g, 5.71 mmol).

B.p. 115 °C (DSC: endothermic; T_{Onset}) [Lit. 118–119 °C] [8]. ^{19}F NMR (CH_2Cl_2, 24 °C) δ, ppm: −57.1 (s, 6F, N(CF_3)$_2$), −111.4 (m, 1F, 4-FC_6H_4). ^1H NMR (CH_2Cl_2, 24 °C) δ, ppm: 7.47 (m, 2H, $H^{2,6}$), 7.18 (m, 2H, $H^{3,5}$). $^{13}C\{^1H\}$ NMR (CH_2Cl_2, 24 °C) δ, ppm: 163.4 (d, $^1J_{C,F}$ = 251 Hz, C^4), 131.6 (d, $^3J_{C,F}$ = 9 Hz, $C^{2,6}$), 128.6 (d, $^4J_{C,F}$ = 3 Hz, C^1), 119.8 (q, $^1J_{C,F}$ = 262 Hz, N(CF_3)$_2$), 116.1 (d, $^2J_{C,F}$ = 23 Hz, $C^{3,5}$). ^{19}F NMR (CH_3CN, 24 °C) δ, ppm: −55.9 (s, 6F, N(CF_3)$_2$), −110.5 (tt, $^3J_{F,H}$ = 8 Hz, $^4J_{F,H}$ = 4 Hz, 1F, 4-FC_6H_4). ^1H NMR (CH_3CN, 24 °C) δ, ppm: 7.47 (m, 2H, $H^{2,6}$), 7.19 (m, 2H, $H^{3,5}$). $^{13}C\{^1H\}$ NMR (CH_3CN, 24 °C) δ, ppm: 163.7 (d, $^1J_{C,F}$ = 250 Hz, C^4), 132.0 (d, $^3J_{C,F}$ = 9 Hz, $C^{2,6}$), 128.7 (d, $^4J_{C,F}$ = 3 Hz, C^1), 120.0 (q, $^1J_{C,F}$ = 261 Hz, N(CF_3)$_2$), 116.6 (d, $^2J_{C,F}$ = 23 Hz, $C^{3,5}$). Raman spectrum (20 °C) ν, cm^{-1}: 83 [84], 178 [7], 190 [7], 302 [21], 339 [7], 349 [7], 368 [10], 395 [13], 626 [10], 736 [3], 764 [44], 821 [100], 849 [6], 949 [9], 1157 [16], 1212 [8], 1257 [19], 1609 [14], 3010 [3], 3089 [63]. Elementary analysis: calculated for $C_8H_4F_7N$, %: C 38.88%, H 1.63%, N 5.67%; found, %: C 38.42, H 1.59, N 6.03.

4-$BrC_6H_4N(CF_3)_2$: B.p. 162 °C (DSC: endothermic; T_{Onset}) [Lit. 84–87 °C at 50 mm] [8]. Yield 65% (8 g, 26 mmol). ^{19}F NMR (CD_2Cl_2, 24 °C) δ, ppm: −56.0 (s, 6F, N(CF_3)$_2$). ^1H NMR (CD_2Cl_2, 24 °C) δ, ppm: 7.63 (d, $^3J_{H,H}$ = 9 Hz, 2H), 7.29 (d, $^3J_{H,H}$ = 9 Hz, 2H). ^{13}C NMR (CH_2Cl_2, 24 °C) δ, ppm: 132.7 (dd, $^1J_{C,H}$ = 168 Hz, $^2J_{C,H}$ = 6 Hz), 131.4 (tt, $^2J_{C,H}$ = 10 Hz, $^3J_{C,H}$ = 3 Hz), 131.2 (dd, $^1J_{C,H}$ = 165 Hz, $^2J_{C,H}$ = 5 Hz), 124.5 (tt, $^2J_{C,H}$ = 11 Hz, $^3J_{C,H}$ = 3 Hz), 119.5 (q, $^1J_{C,F}$ = 262 Hz, N(CF_3)$_2$). ^{13}C NMR (CH_3CN, 24 °C) δ, ppm: 133.7 (dd, $^1J_{C,H}$ = 168 Hz, $^2J_{C,H}$ = 6 Hz), 132.2 (dd, $^1J_{C,H}$ = 165 Hz, $^2J_{C,H}$ = 5 Hz), 132.0 (tt, $^2J_{C,H}$ = 10 Hz, $^3J_{C,H}$ = 3 Hz), 125.1 (tt, $^2J_{C,H}$ = 11 Hz, $^3J_{C,H}$ = 3 Hz), 120.2 (q, $^1J_{C,F}$ = 262 Hz, N(CF_3)$_2$). Raman spectrum (20 °C) ν, cm^{-1}: 82 [79], 156 [34], 248 [32], 290 [9], 327 [11], 366 [8], 562 [3], 621 [12], 673 [3], 704 [18], 732 [9], 774 [100], 811 [7], 956 [8], 1001 [10], 1019 [6], 1072 [30], 1175 [15], 1218 [23], 1589 [24], 3077 [74], 3177 [3].

4-$IC_6H_4N(CF_3)_2$: B.p. 94 °C at 46 hPa. Yield 49% (4.02 g, 11.32 mmol). ^{19}F NMR (CH_2Cl_2, 24 °C) δ, ppm: −56.1 (s, 6F, N(CF_3)$_2$). ^1H NMR (CH_2Cl_2, 24 °C) δ, ppm: 7.82 (d, 2H, $^3J_{H,H}$ = 9 Hz), 7.13 (d, $^3J_{H,H}$ = 9 Hz, 2H). $^{13}C\{^1H\}$ NMR (CH_2Cl_2, 24 °C) δ, ppm: 139.0 s, 132.3 s, 131.4 s, 119.6 (q, $^1J_{C,F}$ = 263 Hz, N(CF_3)$_2$), 96.3 (s). ^{19}F NMR (CD_3CN, 24 °C) δ, ppm: −54.5 (s, 6F, N(CF_3)$_2$). ^1H NMR (CD_3CN, 24 °C) δ, ppm: 7.86 (d, $^3J_{H,H}$ = 9 Hz, 2H), 7.20 (d, $^3J_{H,H}$ = 9 Hz, 2H). ^{13}C NMR (CD_3CN, 24 °C) δ, ppm: 138.4 (dd, $^1J_{C,H}$ = 168 Hz, $^2J_{C,H}$ = 7 Hz), 132.1 (tt, $^2J_{C,H}$ = 9 Hz, $^3J_{C,H}$ = 3 Hz), 130.9 (dd, $^1J_{C,H}$ = 165 Hz, $^2J_{C,H}$ = 5 Hz), 119.2 (q, $^1J_{C,F}$ = 262 Hz, (N(CF_3)$_2$), 95.8 (tt, $^2J_{C,H}$ = 10 Hz, $^3J_{C,H}$ = 3 Hz). Raman spectrum (20 °C) ν, cm^{-1}: 83 [72], 142 [47], 231 [30], 321 [13], 364 [8], 621 [13], 692 [23], 773 [100], 944 [11], 1014 [6], 1060 [24], 1179 [20], 1218 [23], 1585 [21], 3072 [56].

3-$BrC_6H_4N(CF_3)_2$: B.p. 92 °C at 101 hPa. Yield 50% (3.06 g, 9.93 mmol). ^{19}F NMR ($CDCl_3$, 24 °C) δ, ppm: −56.1 (s, 6F, N(CF_3)$_2$). ^1H NMR ($CDCl_3$, 24 °C) δ, ppm: 7.66 (m, two overlapping signals, 2H), 7.36 (m, two overlapping signals, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 24 °C) δ, ppm: 134.4 (s), 134.0 (s), 133.6 (s), 131.1 (s), 129.0 (s), 123.3 (s), 120.2 (q, $^1J_{C,F}$ = 262 Hz, N(CF_3)$_2$). ^{19}F NMR (CD_3CN, 24 °C) δ, ppm: −56.6 (s, 6F, N(CF_3)$_2$). ^1H NMR (CD_3CN, 24 °C) δ, ppm: 7.72 (m, 1H), 7.67 (m, 1H), 7.45 (m, two overlapping signals, 2H). $^{13}C\{^1H\}$ NMR (CD_3CN, 24 °C) δ, ppm: 135.1 (s), 134.6 (s), 134.0 (s), 132.5 (s), 129.9 (s), 123.5 (s), 120.9 (q, $^1J_{C,F}$ = 262 Hz, N(CF_3)$_2$). Raman spectrum (20 °C) ν, cm^{-1}: 94 [22], 160 [6], 181 [12], 265 [7], 297 [32], 327 [4], 374 [3], 557 [1], 645 [5], 713 [6], 784 [24], 1003 [100], 1073 [6], 1170 [3], 1216 [11], 1578 [5], 1592 [7], 3079 [37].

3.4. Heck coupling of 4-$BrC_6H_4N(CF_3)_2$ with styrene

A suspension of $Pd(OAc)_2$ (0.005 g, 0.022 mmol), K_2CO_3 (0.822 g, 5.948 mmol), styrene (0.476 g, 4.570 mmol), acetylacetone (5 μL, 0.049 mmol), DMF (6 mL) and 4-$BrC_6H_4N(CF_3)_2$ (1.01 g, 3.25 mmol) was heated for 1 h at 130 °C under inert atmosphere (Ar or N_2). The suspension was cooled to 20 °C and H_2O (50 mL) was added. The solid was separated, dissolved in Et_2O (50 mL) and filtrated. The solvent was removed in vacuum (0.05 hPa, 20 °C, 2 h) and the solid product was obtained in 83% yield (0.897 g, 2.707 mmol).

M.p. 119 °C (DSC: endothermic, T_{Onset}). ^{19}F NMR (CH_2Cl_2, 24 °C) δ, ppm: −56.0 (s, 6F, N(CF_3)$_2$). ^1H NMR (CH_2Cl_2, 24 °C) δ, ppm: overlapping signals from 7.7 to 7.0. $^{13}C\{^1H\}$ NMR (CH_2Cl_2, 24 °C) δ, ppm: 139.4 (s), 136.6 (s), 131.3 (s), 130.9 (s), 129.9 (s), 128.6 (s), 128.1 (s), 127.3 (s), 126.7 (s), 126.6 (s), 119.8 (q, $^1J_{C,F}$ = 262 Hz, (N(CF_3)$_2$). ^{19}F NMR (CD_3CN, 24 °C) δ, ppm: −54.4 (s, 6F, N(CF_3)$_2$). ^1H NMR (CD_3CN, 24 °C) δ, ppm: overlapping signals from 7.8 to 7.2 ppm. $^{13}C\{^1H\}$ NMR (CD_3CN, 24 °C) δ, ppm: 140.8 (s), 137.7 (s), 131.9 (s), 131.8 (s), 131.0 (s), 129.7 (s), 129.1 (s), 128.5 (s), 127.6 (s, two overlapping signals), 120.8 (q, $^1J_{C,F}$ = 261 Hz, N(CF_3)$_2$). Raman spectrum (20 °C) ν, cm^{-1}: 106 [88], 203 [9], 618 [6], 668 [6], 769 [26], 825 [5], 867 [22], 949 [5], 1000 [36], 1029 [9], 1158 [6], 1182 [46], 1191 [67], 1225 [6], 1291 [5], 1306 [5], 1324 [14], 1417 [5], 1450 [4], 1494 [4], 1571 [11], 1597 [11], 1633 [100], 2997 [7], 3042 [6], 3066 [30].

3.5. Suzuki coupling of 4-Br- and 3-$BrC_6H_4N(CF_3)_2$ with arylboranes

Synthesis of 4-[N,N-bis(trifluoromethyl)amino]biphenyl as an example: A suspension of $Pd(OAc)_2$ (0.005 g, 0.022 mmol), K_2CO_3 (0.792 g, 5.731 mmol), $C_6H_5B(OH)_2$ (0.564 g, 4.626 mmol), acetylacetone (5 μL, 0.049 mmol), DMF/H_2O (5 mL/5 mL), and 4-$BrC_6H_4N(CF_3)_2$ (0.9 g, 2.9 mmol) was heated for 2 h at 90 °C under inert atmosphere (Ar or N_2). The suspension was cooled to 20 °C and H_2O (60 mL) was added. The solid was separated, dissolved in Et_2O (25 mL) and filtrated. The solvent was removed in vacuum (0.05 hPa, 20 °C, 2 h). The product 4-[N,N-bis(trifluoromethyl)a-

mino]biphenyl was obtained in 88% yield (0.783 g, 2.565 mmol) and could be sublimated (1.4 hPa, 55 °C).

M.p. 85 °C (DSC: endothermic, T_{Onset}). ^{19}F NMR (CH_2Cl_2, 24 °C) δ, ppm: −56.0 (s, 6F, N(CF_3)$_2$). ^1H NMR (CH_2Cl_2, 24 °C) δ, ppm: 7.72 (d, $^3J_{H,H}$ = 8 Hz, 2H), 7.64 (d, $^3J_{H,H}$ = 8 Hz, 2H), 7.6–7.4 (m, 5H, five overlapping signals). $^{13}C\{^1H\}$ NMR (CH_2Cl_2, 24 °C) δ, ppm: 143.2 (s), 139.4 (s), 131.5 (s), 129.9 (s), 128.8 (s), 128.1 (s), 127.9 (s), 127.0 (s), 119.9 (q, $^1J_{C,F}$ = 262 Hz, N(CF_3)$_2$). Raman spectrum (20 °C) ν, cm^{-1}: 95 [100], 218 [6], 256 [9], 333 [4], 614 [11], 643 [5], 741 [17], 779 [61], 951 [6], 997 [38], 1039 [17], 1162 [5], 1198 [13], 1256 [15], 1278 [51], 1598 [38], 1608 [55], 3070 [32], 3080 [43].

Instead of DMF and acetylacetone, PEG 2000 could be used.

3-[N,N-bis(trifluoromethylamino]biphenyl

^{19}F NMR (*n*-pentane, 24 °C) δ, ppm: −57.1 (s, 6F, N(CF_3)$_2$). ^1H NMR (*n*-pentane, 24 °C) δ, ppm: overlapping signals from 7.1 to 7.6 ppm. ^{13}C NMR (*n*-pentane, 24 °C) δ, ppm: 143.6 (m), 139.7 (m), 133.8 (m), 129.6 (dm, $^1J_{C,H}$ = 162 Hz), 128.8 (dm, $^1J_{C,H}$ = 160 Hz), 128.7 (dm $^1J_{C,H}$ = 162 Hz), 128.5 (dm, $^1J_{C,H}$ = 160 Hz), 128.2 (dm, $^1J_{C,H}$ = 164 Hz), 127.9 (dm, $^1J_{C,H}$ = 160 Hz), 127.0 (dm, $^1J_{C,H}$ = 160 Hz), 120.3 (q, $^1J_{C,F}$ = 262 Hz, N(CF_3)$_2$).

4′-Methoxy-4-[N,N-bis(trifluoromethyl)amino]biphenyl: Sublimation: 1.4 hPa, 60 °C. Yield 61% (0.415 g, 1.238 mmol). ^{19}F NMR (CH_2Cl_2, 24 °C) δ, ppm: −56.0 (s, 6F, N(CF_3)$_2$). ^1H NMR (CH_2Cl_2, 24 °C) δ, ppm: 7.66 (d, $^3J_{H,H}$ = 8 Hz, 2H), 7.56 (d, $^3J_{H,H}$ = 9 Hz, 2H), 7.46 (d, $^3J_{H,H}$ = 8 Hz, 2H), 7.02 (d, $^3J_{H,H}$ = 9 Hz, 2H), 3.85 (s, 3H, OCH_3). ^{13}C NMR (CH_2Cl_2, 24 °C) δ, ppm: 159.8 (m), 142.8 (tt, $J_{C,H}$ = 7 Hz, $J_{C,H}$ = 4 Hz), 131.6 (m), 130.8 (tt, $^2J_{C,H}$ = 10 Hz, $^3J_{C,H}$ = 2 Hz), 129.9 (dm, $^1J_{C,H}$ = 164 Hz), 128.1 (dd, $^1J_{C,H}$ = 158 Hz, $^2J_{C,H}$ = 7 Hz), 127.5 (dd, $^1J_{C,H}$ = 161 Hz, $^2J_{C,H}$ = 7 Hz), 119.9 (q, $^1J_{C,F}$ = 262 Hz, N(CF_3)$_2$), 114.2 (dm $^1J_{C,H}$ = 160 Hz), 55.0 (q, $^1J_{C,H}$ = 144 Hz, OCH_3). Raman spectrum (20 °C) ν, cm^{-1}: 84 [94], 231 [6], 350 [4], 408 [7], 624 [9], 717 [4], 748 [5], 774 [22], 807 [36], 950 [5], 1038 [3], 1193 [26], 1256 [19], 1282 [50], 1459 [5], 1533 [5], 1603 [100], 2844 [11], 2945 [8], 3021 [8], 3080 [40].

3.6. Fluorination of 4-IC$_6$H$_4$N(CF$_3$)$_2$ to 4-F$_2$IC$_6$H$_4$N(CF$_3$)$_2$

4-$IC_6H_4N(CF_3)_2$ (0.50 g, 1.41 mmol) was dissolved in CCl_3F (2 mL) and a mixture of fluorine in nitrogen (5 vol%; precooled by a copper helix at −70 °C) was bubbled into the stirred solution. During the reaction, a solid precipitated. After addition of one equivalent of fluorine, the fluorination was stopped. The supernatant was separated and the white solid was crystallised from *n*-pentane. After separation the solid was dried in vacuum (0.05 hPa, 20 °C, 30 min). The product 4-(difluoro-λ^3-iodanyl)-*N*,*N*-bis(trifluoromethyl)aniline was isolated as a white solid in 85% yield (0.468 g, 1.191 mmol).

M.p. 70 °C (DSC: endothermic; T_{Onset}). Dec. 187.6 °C (DSC: exothermic, T_{Onset}). ^{19}F NMR (CH_2Cl_2, 24 °C) δ, ppm: −55.9 (s, 6F, N(CF_3)$_2$), −176.0 (s, 2F, IF_2). ^1H NMR (CH_2Cl_2, 24 °C) δ, ppm: 8.05 (d, $^3J_{H,H}$ = 9 Hz, 2H), 7.64 (d, $^3J_{H,H}$ = 9 Hz, 2H). $^{13}C\{^{19}F\}$ NMR (CH_2Cl_2, 24 °C) δ, ppm: 119.6 (s, N(CF_3)$_2$). $^{13}C\{^1H\}$ NMR (CH_2Cl_2, 24 °C) δ, ppm: 135.2 (s), 132.3 (s), 130.8 (t, $^3J_{C,IF2}$ = 5 Hz, $C^{3,5}$), 124.6 (t, $^2J_{C,IF2}$ = 10 Hz, C^4), 119.6 (q, $^1J_{C,F}$ = 262 Hz, N(CF_3)$_2$). Raman spectrum (20 °C) ν, cm^{-1}: 84 [100], 139 [65], 234 [29], 291 [15], 325 [14], 364 [11], 386 [17], 457 [27], 509 [66], 558 [9], 620 [20], 691 [21], 774 [77], 948 [6], 1009 [14], 1047 [11], 1183 [13], 1223 [21], 1379 [13], 1489 [4], 1582 [21], 3082 [42], 3164 [6].

3.7. Reductive coupling of 4-IC$_6$H$_4$N(CF$_3$)$_2$ to 4,4′-(CF$_3$)$_2$NC$_6$H$_4$–C$_6$H$_4$N(CF$_3$)$_2$

Pd/C (0.39 g, 0.36 mmol), 18-C-6 (0.102 g, 0.386 mmol), Zn (0.364 g, 5.494 mmol), and 4-$IC_6H_4N(CF_3)_2$ (0.30 g, 0.85 mmol) were suspended in H_2O (7 mL). The suspension was stirred for 48 h at 20 °C and extracted with Et_2O (20 mL). The combined organic phases were dried over $MgSO_4$. The solvent was removed in vacuum (0.05 hPa, 20 °C, 2 h). The product 4,4′-[*N*,*N*,*N*′,*N*′-Tetrakis(trifluoromethyl)diamino]biphenyl could be isolated as white solid in 47% yield (0.181 g, 0.397 mmol).

M.p. 64.2 °C (DSC: endothermic, T_{Onset}). ^{19}F NMR (*n*-pentane, 24 °C) δ, ppm: −56.4 (s, 6F, N(CF_3)$_2$). ^1H NMR (*n*-pentane, 24 °C) δ, ppm: 7.56 (d, $^3J_{H,H}$ = 9 Hz, 4H), 7.43 (d, $^3J_{H,H}$ = 9 Hz, 4H). $^{13}C\{^{19}F\}$ NMR (*n*-pentane, 24 °C) δ, ppm: 120.4 (s, N(CF_3)$_2$). $^{13}C\{^1H\}$ NMR (*n*-pentane, 24 °C) δ, ppm: 142.2 (s), 133.5 (s), 130.7 (s), 128.4 (s). Raman spectrum (20 °C) ν, cm^{-1}: 84 [57], 234 [5], 367 [4], 419 [8], 446 [3], 569 [3], 622 [8], 756 [3], 786 [47], 828 [3], 950 [4], 1191 [14], 1225 [5], 1289 [44], 1527 [3], 1612 [100], 3085 [15].

3.8. Reduction of 4-BrC$_6$H$_4$N(CF$_3$)$_2$ to C$_6$H$_5$N(CF$_3$)$_2$

Cu (0.10 g, 1.57 mmol), Zn (0.10 g, 1.53 mmol) and 4-$BrC_6H_4N(CF_3)_2$ (0.25 g, 0.81 mmol) were suspended in a mixture of H_2O and acetone (each 3 mL). After 24 h of stirring at 20 °C, the complete reduction of 4-$BrC_6H_4N(CF_3)_2$ to $C_6H_5N(CF_3)_2$ was observed.

^{19}F NMR (CH_2Cl_2, 24 °C) δ, ppm: −55.4 (s, 6F, N(CF_3)$_2$). ^1H NMR (CH_2Cl_2, 24 °C) δ, ppm: 7.77 (m, 2H), 7.46 (m, 3H).

3.9. Reaction of 4-(CF$_3$)$_2$NC$_6$H$_4$MgBr with CO$_2$ to 4-(CF$_3$)$_2$NC$_6$H$_4$C(O)OH

The Grignard reagent prepared from 4-$BrC_6H_4N(CF_3)_2$ (2.00 g, 6.49 mmol) and Mg turnings (0.16 g, 6.58 mmol) in ether (4 mL) was treated with dry carbon dioxide at 0 °C. After 20 min the reaction mixture was hydrolysed by ice and diluted HCl and was extracted with Et_2O (twice 5 mL). The combined organic phases were dried over $MgSO_4$, filtrated and the solvent was removed in vacuum (0.05 hPa, 20 °C, 4 h). The solid was purified by crystallisation from *n*-hexane and by sublimation (0.05 hPa, 80–90 °C, 24 h). The product 4-[bis(trifluoro methyl)amino]benzoic acid was isolated as a white solid in 46% yield (2.31 g, 8.46 mmol).

M.p. 136.2 °C (DSC: endothermic; T_{Max}), lit. 139–139.4 °C [8]. ^{19}F NMR ($CDCl_3$, 27 °C) δ, ppm: −55.6 (s, 6F, N(CF_3)$_2$). ^1H NMR ($CDCl_3$, 27 °C) δ, ppm: 12.65 (s, CO_2H) 8.21 (m, $^1J_{C,H}$ = 168 Hz, 2H), 7.51 (m, $^1J_{C,H}$ = 165 Hz, 2H). ^{13}C NMR ($CDCl_3$, 27 °C) δ, ppm: 171.6 (m), 137.9 (m), 132.0 (dd, $^1J_{C,H}$ = 167 Hz, $J_{C,H}$ = 7 Hz), 131.4 (m), 130.2 (dd, $^1J_{C,H}$ = 166 Hz, $J_{C,H}$ = 5 Hz), 120.0 (q, $^1J_{C,F}$ = 263 Hz, N(CF_3)$_2$). ^{19}F NMR (CD_3CN, 27 °C) δ, ppm: −56.3 (s, 6F, N(CF_3)$_2$). ^1H NMR (CD_3CN, 27 °C) δ, ppm: 9.27 (s, CO_2H) 8.14 (m, $^1J_{C,H}$ = 167 Hz, 2H), 7.57 (m, $^1J_{C,H}$ = 165 Hz, 2H). $^{13}C\{^1H\}$ NMR (CD_3CN, 27 °C) δ, ppm: 166.8 (s), 137.0 (s), 133.1 (s), 132.1 (s), 130.8 (s), 120.6 (q, $^1J_{C,F}$ = 263 Hz, N(CF_3)$_2$). Raman spectrum (20 °C) ν, cm^{-1}: 86 [83], 261 [4], 292 [16], 319 [12], 369 [10], 570 [3], 627 [28], 672 [4], 767 [25], 783 [5], 806 [100], 828 [8], 952 [14], 1134 [14], 1180 [13], 1220 [14], 1285 [22], 1360 [6], 1418 [5], 1612 [69], 1642 [33] (ν_s(C=O)), 3021 [5], 3092 [38] cm^{-1}.

3.10. Esterification of 4-(CF$_3$)$_2$NC$_6$H$_4$C(O)OH

Synthesis of 4-EtO(O)CC$_6$H$_4$N(CF$_3$)$_2$ as an example: 4-$HO_2CC_6H_4N(CF_3)_2$ (0.14 g, 0.51 mmol) was dissolved in EtOH (0.2 mL) and $H_2SO_{4(conc.)}$ (10 μL, 0.02 g, 0.19 mmol) was added. The reaction mixture was heated for 5 h at 85 °C and cooled to 20 °C. The solvent was removed in vacuum (0.05 hPa, 20 °C, 30 min) and a pale orange solution remained. Ice water was added and the solution was extracted with Et_2O (three times 1 mL). The combined organic extracts were washed with a Na_2CO_3 solution (1 mL) and with H_2O (1 mL) and dried over $MgSO_4$. The organic layer

was filtrated and the solvent was removed in vacuum (0.05 hPa, 20 °C, 2 h). The product ethyl 4-[bis(trifluoro methyl)amino]benzoate was isolated as a colorless oil in 73% yield (0.11 g, 0.37 mmol).

^{19}F NMR ($CDCl_3$, 24 °C) δ, ppm: −55.8 (s, 6F, N(CF_3)$_2$). ^{1}H NMR ($CDCl_3$, 27 °C) δ, ppm: 8.10 (m, $^1J_{C,H}$ = 165 Hz, 2H), 7.43 (m, $^1J_{C,H}$ = 164 Hz, 2H), 4.37 (q, $^1J_{C,H}$ = 148 Hz, $^3J_{H,H}$ = 7 Hz, CH_2), 1.36 (t, $^1J_{C,H}$ = 127 Hz, $^3J_{H,H}$ = 7 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 27 °C) δ, ppm: 165.6 (s), 136.9 (s), 132.7 (s), 131.2 (s), 130.0 (s), 120.1 (q, $^1J_{C,F}$ = 262 Hz, N(CF_3)$_2$), 61.8 (s, CH_2), 14.5 (s, CH_3).

4-(CF_3)$_2$NC_6H_4C(O)OCH_3: ^{19}F NMR ($CDCl_3$, 27 °C) δ, ppm: −55.8 (s, 6F, N(CF_3)$_2$). ^{1}H NMR ($CDCl_3$, 27 °C) δ, ppm: 8.09 (d, $^1J_{C,H}$ = 166 Hz, $^3J_{H,H}$ = 8 Hz, 2H), 7.43 (d, $^1J_{C,H}$ = 166 Hz, $^3J_{H,H}$ = 8 Hz, 2H), 3.90 (s, $^1J_{C,H}$ = 147 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 27 °C) δ, ppm: 166.1 (s), 137.0 (s), 132.4 (s), 131.3 (s), 130.1 (s), 120.0 (q, $^1J_{C,F}$ = 263 Hz, N(CF_3)$_2$), 52.7 (s, CH_3).

3.11. Synthesis of [(CF_3)$_2$NC_6H_4C(O)]$_2$O

4-(CF_3)$_2$NC_6H_4C(O)OH (0.40 g, 1.46 mmol) was dissolved in CH_2Cl_2 (6 mL) and P_4O_{10} (0.3 g, 0.1 mmol) was added. The suspension was heated for 4 h under reflux and cooled to 20 °C. After extraction with Et_2O (3 mL), the extract was evaporated in vacuum (0,05 hPa, 20 °C, 2 h). A solid remained, which was crystallised from CH_2Cl_2 at −40 °C. The product 4-[bis(trifluoromethyl)amino]benzoic acid anhydride was dried in vacuum (0.05 hPa, 20 °C, 2 h) to give 36% yield (0.28 g, 0.53 mmol).

M.p. 78 °C (DSC: endothermic; T_{Onset}). ^{19}F NMR ($CDCl_3$, 27 °C) δ, ppm: −55.5 (s, 12F, 2 N(CF_3)$_2$). ^{1}H NMR ($CDCl_3$, 27 °C) δ, ppm: 8.23 (m, 4H), 7.56 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 27 °C) δ, ppm: 161.0 (s), 138.6 (s), 132.2 (s), 130.64 (s), 130.63 (s), 119.9 (q, $^1J_{C,F}$ = 263 Hz, N(CF_3)$_2$).

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