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Electrophilic aromatic fluorination with fluorine: *meta*-Directed fluorination of anilines

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Dedicated to Prof. R.D. Chambers for his 70th birthday.

Abstract

Anilines are mainly or selectively fluorinated in the *meta*-position with F_2 when dissolved in triflic acid, sometimes in the presence of small quantities of antimony pentafluoride. The regioselectivity is increased when an electron-donating substituent is present at the *para*-position.

Keywords: Anilines; Fluorine; Fluoroanilines; Triflic acid; Fluorination

1. Introduction

Fluoroaromatics constitute an important class of fluorinated compounds since they are key-intermediates in the manufacture of prominent pharmaceuticals and agrochemicals [1–4]. Usually, they arise from the nucleophilic substitution of diazonium moieties with hydrogen fluoride or that of activated halides with fluoride anions [5–10]. In principle, electrophilic fluorination of unsubstituted aromatic nuclei with fluorine could provide shorter routes to fluoroaromatics.

Nevertheless, the use of fluorine has been hindered, for a long time, for two main reasons. The first one is the hazardous storage and handling of this reagent. Such a problem can be now solved, at least on the laboratory scale, by the commercial availability of bench electrolysers (''Fluorodec®'' from Fluorogas Ltd.), able to deliver fluorine on demand, even at low rates, without any storage of this corrosive gas. Moreover, safety is improved by diluting the fluorine thus generated, with nitrogen (typically, a 10:90, v/v, F_2/N_2 mixture is used). The second problem lies in the difficulty to control the direct fluorination of organic compounds, which was claimed, for a long time, to be a very exothermic radical chain process. Indeed, homolytic dissociation of fluorine is very easy (F–F bond energy = 159 kJ mol^{-1}) [11] and predominates when no polarization of this molecule is induced by its environment. This was especially the case when almost apolar fluorotrichloromethane (CFC-11), which is outstandingly inert to F_2, was chosen as solvent [12–14].

However, during the last decade and especially under the impetus given by Chambers et al., important work has been devoted to the development of new conditions allowing the polarization of fluorine, and thus the tamed electrophilic fluorination of organic substrates. Since this time, a steadily growing number of papers have appeared [15–24]. Concerning electrophilic aromatic fluorination [25–30], an outstanding contribution has been given again by Chambers et al., who demonstrated that aromatics bearing an electron-donating group in *para*-position to an electron-withdrawing group, can be cleanly fluorinated with F_2 at room temperature, provided that a strong acid, such as 98% sulfuric or formic acid, is used as solvent [20,31,32]. Such solvents are polar enough and, more importantly, protic enough to strongly polarize fluorine and avoid uncontrolled

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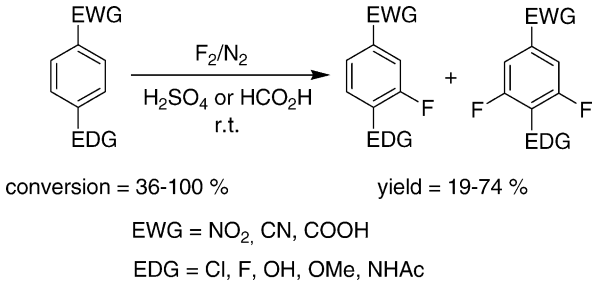


Scheme 1. Fluorination of disubstituted benzenes [20,31,32].

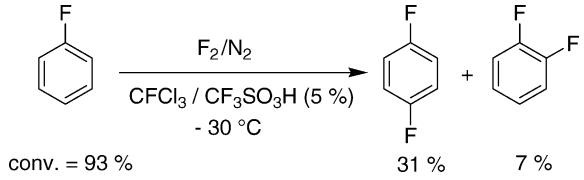
radical processes. This explains why the reaction can be carried out at room temperature. Of course, because of the aromatic substitution pattern, a completely regioselectivity was observed (Scheme 1).

Curiously, few fluorinations have been carried out with perfluoroalkanesulfonic acids as solvents or additives. For example, Hoechst patented results, very similar to those of Chambers et al., from fluorination in perfluorobutanesulfonic acid [22], whereas Coe et al. fluorinated fluorobenzene, at low temperature in fluorotrichloromethane, in the presence of small quantities of triflic acid (CFC-11:TfOH = 95:5 to 90:10) [33] (Scheme 2). It should be noticed that, probably because of the rather low protic character of this medium, chemical selectivity is limited.

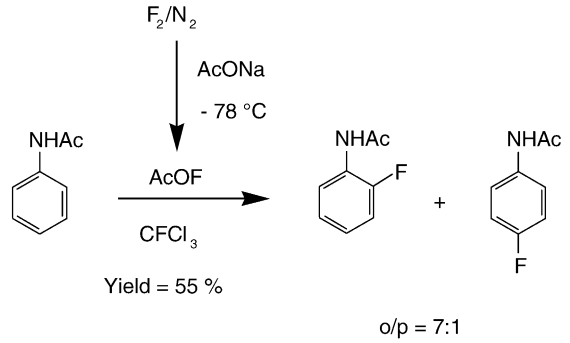
2. Results and discussion

Fluoroanilines are important building blocks for the manufacture of numerous bioactive products. *ortho*- and *para*-fluoroaniline are usually produced, on the industrial scale, through a two-step nitration-reduction of fluorobenzene. *meta*-Fluoroaniline is less easily available, but can be prepared by a *cine*-substitution of *ortho*-chlorofluorobenzene with sodium amide in liquid ammonia [34]. Thus, it would be interesting to examine the possibility to obtain fluoroanilines from direct electrophilic fluorination of anilines.

Of course, the free amino group, as well as the methylamino moiety, cannot survive the action of such an oxidant as F_2, as demonstrated by Purrington and Woodward during the fluorination of *N*-methylaniline, even in the presence of boron or aluminum trichlorides [29]. This is the reason why Rozen and co-workers fluorinated acetanilide, and not aniline, with acetyl hypofluorite, generated in situ



Scheme 2. Fluorination of fluorobenzene [33].



Scheme 3. Fluorination of acetanilide with acetyl hypofluorite [35].

from fluorine and sodium acetate [35]. In this case, *ortho*-fluoroaniline was the major product, may be (but it is not still clear), because of an interaction between the nitrogen atom and the fluorinating agent, at least in the transition state (Scheme 3).

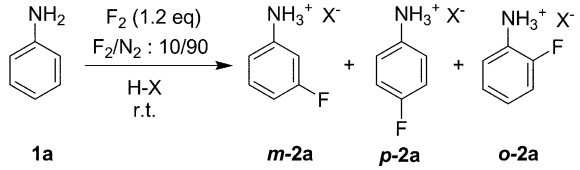
Another strategy could be to protonate anilines strongly enough to protect them against oxidation. Moreover, it could be anticipated that protonated anilines should be fluorinated mainly at the *meta*-position, because of the inductive electron-withdrawing effect of the ammonium substituent.

Thus, we studied the fluorination of aniline itself in strong acidic media, namely pure sulfuric acid, triflic acid or triflic acid with several added Lewis acids [$B(OTf)_3$, SbF_5, $SbCl_5$, 1–4 mol%]. The results are summarized in Table 1.

As resulting from Table 1, aniline was fluorinated, as expected, without extensive oxidation or degradation and *meta*-fluoroaniline was always predominant over its *ortho*- and *para*-isomers. This indicates that aniline was protonated to a large extent during the reaction. However, the results were dependent on the medium composition. Sulfuric acid (entry 1) was not the most suitable solvent since, though conversion of **1a** was rather high (74%), global selectivity (51%) and chemical balance (64%) were not satisfactory. Possibly, water-soluble by-products, arising from sulfonation and oxidation by H_2SO_4, could have been formed and eliminated from the organic phase during the aqueous work up. Better results were obtained in triflic acid (entry 2), which is not an oxidant. In this case, aniline was probably protonated more efficiently. Indeed, reactivity was lower (as indicated by a lower conversion), but the reaction was cleaner, as indicated by a higher global selectivity (70%) and a more satisfying balance of aromatic compounds (80%). Additional proof was brought by a higher *meta*-regioselectivity (*m*-**2a**:*p*-**2a**:*o*-**2a** = 1.5:1.2:1 with TfOH compared to 1.3:1.1:1 with H_2SO_4).

The addition of boron triflate (1 mol%, entry 3) did not change dramatically the conversion, the chemical balance and the isomer ratio but resulted in a lower selectivity. This additive, known as one of the strongest Lewis acids [36], could have activated the fluorine atoms in *p*-**2a** and *o*-**2a** to promote their substitution by free anilines that leads to tarry

Table 1
Fluorination of aniline in acidic medium



C = 0.05 M

Entry	Solvent	Lewis acid (mol%)[a]	Conv. **1a** (%)[b]	Selectivities (%)[c]				Balance (%)[d]
				m-**2a**	*p*-**2a**	*o*-**2a**	Total	
1	H_2SO_4	None	74	20	16	15	51	64
2	TfOH	None	59	28	23	19	70	80
3	TfOH	$B(OTf)_3$ (1)	62	24	21	15	60	77
4	TfOH	SbF_5 (1)	48	31	27	20	78	86
5	TfOH	SbF_5 (4)	61	28	21	15	64	71
6	TfOH	$SbCl_5$ (4)	59	19	17	8	44	67

[a] vs. solvent.
[b] Conv. = [consumed **1a** (mol)/introduced **1a** (mol)] × 100.
[c] Selectivity = [produced **2a** (mol)/consumed **1a** (mol)] × 100.
[d] Balance = {[∑produced **2a** (mol) + recovered **1a** (mol)]/introduced **1a** (mol)} × 100.

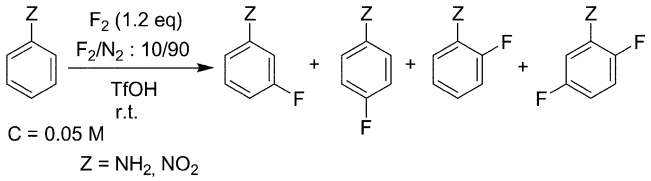
polynuclear products. The addition of antimony pentachloride (4 mol%, entry 6) was not beneficial, especially concerning selectivity and chemical balance. $SbCl_5$ could be suspected to act as a chlorinating agent; nevertheless, no chlorinated product was detected by gas phase chromatography but our apparatus was not very sensitive. Finally, small quantities of antimony pentafluoride (1 mol%, entry 4) provided the best results. SbF_5 is known to enhance the acidity of anhydrous protic acids [36]. Thus, aniline was more extensively protonated than in pure triflic acid. Consequently, its conversion was lower but the reaction was cleaner (chemical balance = 86%), more selective (global selectivity = 78%) and slightly more regioselective (*m*-**2a**:*p*-**2a**:*o*-**2a** = 1.6:1.4:1). The enhanced selectivity could also arise from the fact that, as the medium became more acidic, polarization of the fluorine molecule was more efficient and elimination of F^- was facilitated. Consequently, the electrophilic process was less contaminated by radical or redox side-reactions. When the SbF_5 content was increased to 4 mol% (entry 5), the conversion of aniline increased dramatically (up to 61%), but at the same time, the selectivity and the chemical balance decreased, probably because of side-reactions induced by the strong acidity of the medium. Finally, the best results, in terms of chemical selectivity and regioselectivity, were obtained in triflic acid with 1 mol% SbF_5 added. This result may be connected to results reported by Firnau and co-workers concerning the fluorination of tyrosine: in pure hydrogen fluoride, fluorination occurred at *ortho*-position to the hydroxyl group whereas in HF/BF_3, fluorine was mainly introduced at the *meta*-position [37,38].

In order to get additional proof of the electrophilic character of these reactions and to evaluate their interest, fluorination of aniline was compared with that of nitrobenzene under the same conditions (Table 2).

These results were consistent with the rules governing electrophilic aromatic substitution. The nitro group, which is not sensitive at all to F_2 and exhibits more electron-withdrawing power than the NH_3^+ group, decreased the conversion, but selectivity and chemical balance were complete. Moreover, the regioselectivity of *meta*-fluorination was far better. Thus, it appeared that the NH_3^+ moiety, which is a purely inductive electron-withdrawing substituent, is not so efficient as the nitro group, which acts as an inductive and mesomeric electron-withdrawing substituent, to direct fluorination predominantly enough to the *meta*-position. In order to force fluorination to occur at the *meta*-position (relative to NH_2), we then used substrates bearing, in *para*-position to the amino group, an electron-donating substituent, by analogy with Chambers' strategy. The first substrate we examined was 4-chloroaniline (Table 3).

From Table 3, results demonstrate that, when the quantity of fluorine increased, conversion of **1b** increased steadily, but global selectivity and chemical balance decreased. Correspondingly, the amount of difluorinated products **3b** increased. Among these difluorinated products, 2,5-difluoro-4-chloroaniline 2,5-**3b** was predominant and could be produced with a yield similar to that of *m*-**2b** with three equivalents of fluorine. 2,5-**3b** obviously resulted from fluorination of both *m*-**2b** and *o*-**2b**, whereas 3,5-**3b** was produced from *m*-**2b** only. Of course, fluorination of *m*-**2b** and *o*-**2b** was deactivated by the inductive effect of NH_3^+ that also acts as a *meta*-directing substituent. Nevertheless, 2,5-**3b** was produced about three times faster than 3,5-**3b** (entry 4), since the formation of 2,5-**3b** either from *m*-**2b** or *o*-**2b**, was activated by the synergistic conjugative effects of

Table 2
Comparison of the fluorinations of aniline and nitrobenzene



Entry	Z	Conv. PhZ (%)[a]	Selectivities (%)[b]					Balance (%)[c]
			m-F	*p*-F	*o*-F	2,5-F_2	Total	
1	NH_2	59	28	23	19	0	70	80
2	NO_2	36	62	9	20	9	100	100

[a] Conv. = [consumed ArZ (mol)/introduced ArZ (mol)] × 100.
[b] Selectivity = [∑fluorinated products (mol)/consumed ArZ (mol)] × 100.
[c] Balance = {[Σfluorinated products (mol) + recovered ArZ (mol)]/introduced ArZ (mol)} × 100.

chlorine and fluorine, whereas the formation of 3,5-**3b** was activated by the conjugative effect of chlorine only. Moreover, it is known that fluorine activates the electrophilic substitution of aromatic nuclei more efficiently than chlorine. The observation that 2,5-**3b** was more abundant than 3,5-**3b** is also consistent with the fact that the conjugative *ortho*- and *para*-directing effect of chlorine and fluorine is more efficient than the inductive *meta*-directing effect of NH_3^+.

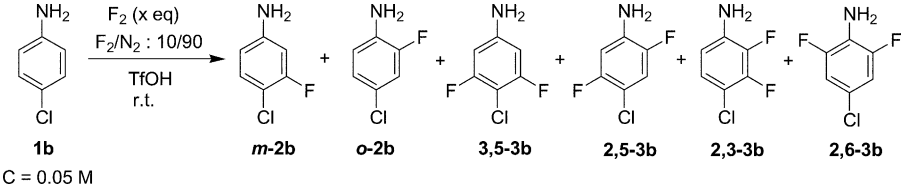
The use of 1.2 equivalent of fluorine (entry 2) constituted the best compromise in terms of conversion, chemical selectivity, regioselectivity and chemical balance. Under these conditions, an excellent chemical balance (96%) was reached with an acceptable conversion (50%), in terms of production, and the amount of difluorinated products **3b** remained rather low (9% of the fluorinated products). Moreover, the *meta*-regioselectivity was excellent (*m*-**2b**:*o*-**2b** = 74:8).

Thus, the same conditions were used to compare the fluorination of different anilines substituted by an electron-donating group at the *para*-position. The results are summarized in Table 4.

In all cases, selectivities and chemical balance were good to excellent. As expected from the rules governing electrophilic aromatic substitution, conversion of the substrate decreased when the inductive electron-withdrawing power of the substituent increased. However, *meta*-regioselectivity, relative to NH_2, increased with the conjugative electron-donating power of the substituent.

Thus, the direct fluorination of readily available 4-substituted anilines with F_2 provides a rapid access to a variety of *meta*-fluoroanilines. Some of them, prepared in the present work (Scheme 4), are very important for the design of bioactive molecules and are not easy to synthesize by other routes. Nevertheless, the separation of these valuable products, by distillation from the crude mixture,

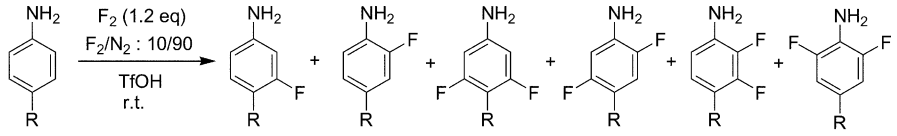
Table 3
Fluorination of 4-chloroaniline



Entry	F_2 (eq)	Conv. **1b** (%)[a]	Selectivities (%) [b]								Balance (%)[c]
			m-**2b**	*o*-**2b**	3,5-**3b**	2,5-**3b**	2,3-**3b**	2,6-**3b**	Total	**3b/2b**	
1	0.5	15	78	15	0	0	0	0	92	0	98
2	1.2	50	74	8	1	6	2	0	91	11	96
3	2.0	75	57	7	3	10	4	0	81	27	86
4	3.0	100	23	3	6	16	7	5	60	131	68

[a] Conv. = [consumed **1b** (mol)/introduced **1b** (mol)] × 100.
[b] Selectivity = [produced **2b** or **3b** (mol)/consumed **1b** (mol)] × 100 (estimated by ^{19}F NMR).
[c] Balance = {[∑produced **2b** and **3b** (mol) + recovered **1b** (mol)]/introduced **1b** (mol)} × 100.

Table 4
Fluorination of substituted anilines



C = 0.05 M

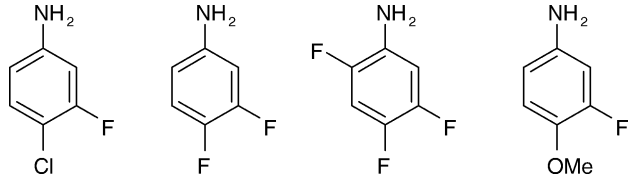
Entry	R	Conv. **1** (%)[a]	Selectivity (%)[b]			Balance (%)[c]
			m-**2**	*o*-**2** + ∑**3**	Total	
1	H (**1a**)	59	28	42	70	80
2	Cl (**1b**)	50	74	17	91	96
3	F (**1c**)	30	74	8	82	89
4	Me (**1d**)	57	56	14	70	80
5	OMe (**1e**)	38	68	8	76	86
6	2,4-F_2 (**1f**)	33	78	13	91	94

[a] Conv. = [consumed **1** (mol)/introduced **1** (mol)] × 100.
[b] Selectivity = [produced **2** or **3** (mol)/consumed **1** (mol)] × 100 (estimated by ^{19}F NMR).
[c] Balance = {[∑produced **2** and **3** (mol) + recovered **1** (mol)]/introduced **1** (mol)} × 100.

should need a deeper chemical engineering study to define the required conditions and was not carried out in the present work.

3. Experimental

TLC analyses were carried out on silica gel (Kieselgel 60F_{254}) deposited on aluminum plates, detection being done by UV (254 nm). Flash-chromatographies were performed on silica gel Geduran SI 60. Unless stated otherwise, NMR spectra were recorded in $CDCl_3$. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz. The substitution patterns of the different carbons were determined by a ''DEPT 135'' sequence. ^{19}F NMR spectra were recorded at 188 or 282 MHz. Chemical shifts (δ) are given in ppm versus TMS (^{1}H, ^{13}C) or $CFCl_3$ (^{19}F) used as internal references. Coupling constants are given in Hertz. Crude yields were determined by ^{19}F NMR versus 4-fluorotoluene used as standard. GC was carried out on an apparatus fitted with an apolar semi-capillary column (length: 15 m, diameter: 0.53 mm, film thickness (DB1): 1 μm) or a polar semi-capillary column (length: 15 m, diameter: 0.53 mm, film thickness (VA-WAX): 1 μm) and a catharometric detector. Helium flow: 25 mL min^{-1}. Amounts of unconverted substrates were estimated by GC using 4-fluorotoluene as standard (and also by ^{19}F NMR for 4-fluoro- and 2,4-difluoro-aniline). If necessary, HPLC was carried out on an apparatus fitted with a column filled with Hypersil silica gel (length: 250 mm, diameter: 4.6 mm) and a UV–vis detector. Eluent flow: 1 mL min^{-1}. Mass spectrometry was carried out under electron impact at 70 eV and eventually coupled with GC.



Scheme 4. 3-Fluoro-4-substituted anilines.

Trifluoromethanesulfonic acid was distilled prior use and kept under nitrogen. Other reagents were used as received or dried according to literature [39]. Fluorine was generated by a Fluorodec® electrolyzer (from Fluorogas Co.), fitted with a cartridge filled with KF·2 HF and heated up to 85 °C to melt the electrolyte. The electric plugs of the electrolyzer were connected to an electric generator delivering a stabilized intensity (typically: 0.25 A), which governed fluorine flow. The anodic gas outlet of the fluorine generator was connected to a sodium fluoride cartridge (to trap residual HF), then to a gas mixture system, for dilution of F_2 with dry N_2 (F_2:N_2 = 1:9), and finally to a cylindrical glass reaction vessel (capacity: 40 mL), bearing internal counter-flow baffles, and fitted with an efficient mechanical stirrer, a thermometer, a gas inlet and a gas outlet. This gas outlet was connected to a sulfuric acid trap then to an alumina cartridge to trap residual fluorine. Hydrogen produced at the cathodic outlet of the fluorine generator was directed to an efficient hood.

3.1. General procedure

Before switching on the power, the whole apparatus (electrolyzer + reaction vessel) was swept with dry N_2 to expel oxygen, which could react violently with F_2. Then, electricity was switched on and F_2/N_2 (1.2 equivalent)

introduced, under efficient stirring, into a solution of the substrate (2 mmol) in triflic acid (40 mL). After reaction, the anodic compartment of the fluorine generator was purged with dry N_2, to evacuate remaining fluorine into the reaction flask. Then, the reaction mixture was poured on ice, neutralized with 10% NaOH until basic and extracted with dichloromethane (4 × 50 mL). The organic phase was dried over $MgSO_4$ and CH_2Cl_2 was evaporated at room temperature under vacuum. If necessary, the coloured oil or the solid thus obtained was separated from tarry by-products by a very rapid chromatography on silica gel. The spectroscopic data (^{19}F NMR, GC–MS) of the resulting products were compared, in the reaction mixture, to those of authentic commercial compounds. The crude mixture was also compared, by gas chromatography or HPLC, to a mixture of these commercial products.

Fluorination of aniline **1a** (186 mg, 2 mmol).
Crude mixture: 203 mg.
m-**2a**: ^{19}F NMR δ: −113.9 (m); MS *m/z*: 111 ($M^{\bullet+}$, 100), 85, 84.
p-**2a**: ^{19}F NMR δ: −127.6 (broad s); MS *m/z*: 111 ($M^{\bullet+}$, 100), 85, 84.
o-**2a**: ^{19}F NMR δ: −136.1 (m); MS *m/z*: 111 ($M^{\bullet+}$, 100), 85, 84.
Fluorination of 4-chloroaniline **1b** (255 mg, 2 mmol).
Crude mixture: 290 mg.
m-**2b**: ^{19}F NMR δ: −116.2 (m); MS *m/z*: 145 ($M^{\bullet+}$, 100).
o-**2b**: ^{19}F NMR δ: −133.1 (m); MS *m/z*: 145 ($M^{\bullet+}$, 100).
3,5-**3b**: ^{19}F NMR δ: −114.9 (broad d, $^3J_{HF}$ = 7.6); MS *m/z*: 163 ($M^{\bullet+}$, 100).
2,5-**3b**: ^{19}F NMR δ: −140.2 (m), −157.0 (m); MS *m/z*: 163 ($M^{\bullet+}$, 100).
2,3-**3b**: ^{19}F NMR δ: −121.7 (m), −139.4 (m); MS *m/z*: 163 ($M^{\bullet+}$, 100).
2,6-**3b**: ^{19}F NMR δ: −138.0 (broad d, $^3J_{HF}$ = 6.2); MS *m/z*: 163 ($M^{\bullet+}$, 100).
Fluorination of 4-fluoroaniline **1c** (222 mg, 2 mmol).
Crude mixture: 231 mg.
m-**2c**: ^{19}F NMR δ: −138.7 (m), −153.2 (m).
o-**2c**: ^{19}F NMR δ: −125.8 (m), −132.2 (m).
Fluorination of 4-methylaniline **1d** (214 mg, 2 mmol).
Crude mixture: 216 mg.
m-**2d**: ^{19}F NMR δ: −117.9 (m).
o-**2d**: ^{19}F NMR δ: −136.3 (m).
3,5-**3d**: ^{19}F NMR δ: −116.1 (m).
2,5-**3d**: ^{19}F NMR δ: −123.6 (m), −142.3 (m).
Fluorination of 4-methoxyaniline **1e** (246 mg, 2 mmol).
Crude mixture: 252 mg.
m-**2e**: ^{19}F NMR δ: −134.8 (dd, $^3J_{HF}$ = 12.6, $^4J_{HF}$ = 9.2).
o-**2e**: ^{19}F NMR δ: −131.5 (d, $^3J_{HF}$ = 12.6).
3,5-**3e**: ^{19}F NMR δ: −130.0 (d, $^3J_{HF}$ = 10.3).
Fluorination of 2,4-difluoroaniline **1f** (258 mg, 2 mmol).
Crude mixture: 269 mg.
2,4,5-F_3-aniline: ^{19}F NMR δ: −138.22 (m), −144.00 (m), −149.00 (m).
2,3,4-F_3-aniline: ^{19}F NMR δ: −150.2 (m), −156.79 (broad s), −162.12 (broad s).

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