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Short communication

An alternative route for synthesis of *o*-trifluoroacetylanilines as useful fluorine-containing intermediates

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ABSTRACT

A series of *o*-trifluoroacetyl aniline derivatives were synthesized in three steps. In this method, we first utilized trifluoroacetic anhydride to introduce trifluoroacetyl group to the *ortho* position of aniline with higher yield than that of some previously reported methods. In addition, the procedure is shown to be highly regiospecific. This type of compounds can be used as the key intermediates in the preparation of a variety of inhibitors of HIV reverse transcriptase which is an important pharmacological target of many anti-AIDS agents.

1. Introduction

Nowadays, organic fluorine compounds have attracted much attention in the materials and pharmaceutical sciences, because the introduction of fluorine into an organic compound can cause remarkable changes in the physical, chemical and biological properties such as the enhanced hydrophobic binding, increased membrane permeability and stability against metabolic oxidation [1–3]. The importance of fluorine in medicinal chemistry has been demonstrated by a large number of fluorinated compounds approved by the FDA for medical use [4,5].

Among these fluorinated compounds, the trifluoromethyl group-containing molecules are especially important, and continue to attract increasing attention from various fields [6,7]. Nowadays, many trifluoromethylated molecules have been developed as well-known drugs such as prozac (antidepressant), diflucan (anti-fungal agent), casodex (anti-cancer agent) and desflurane (inhalation anesthetic) [8]. Accordingly, the development of simple and effective methods for the synthesis of trifluoromethyl-containing molecules has been becoming more and more meaningful in fluorine chemistry [9–14]. Among these methods, introducing trifluoroacetyl group into organic molecules is a convenient measure for the incorporation of trifluoromethyl group into compounds. In the previous reports, the introduction of trifluoroacetyl group was mainly described on the basis of four methodologies: (1) a route by means of Friedel–Crafts acylation [15,16], (2) addition of a trifluoromethyl group to the carbonyl carbon through Ruppert–Prakash reagents [17], Barbier procedure [18] and electrochemical methods [19], then oxidized by some oxidants, (3) direct substitution of a hydrogen atom or a halogen atom [20], and (4) use of some special reagents [21]. However, these methods generally suffer from the use of toxic and expensive reagents, severe experimental conditions requirements, low yields or lack of regioselectivity in the formation of trifluoroacetyl group.

In our present work, we first make use of trifluoroacetic anhydride to introduce trifluoroacetyl group to the *ortho* position of aniline with high regiospecificity in excellent yield, and the reaction condition is not severe (Scheme 1). Although the *o*-trifluoroacetylanilines do not possess direct biological activities, they are highly valuable synthetic intermediates in the preparation of many trifluoromethylated drugs such as HIV reverse transcriptase inhibitor efavirenz (DMP 266) [22], antiprotozomal drug mefloquine [23] and some antileishmanial compounds [24,25]. Therefore, this class of compounds has highly synthetic value in medicinal chemistry.

2. Results and discussion

2.1. Synthesis

To verify the practicality and reaction regiospecificity of this method, we had designed and synthesized a series of *o*-

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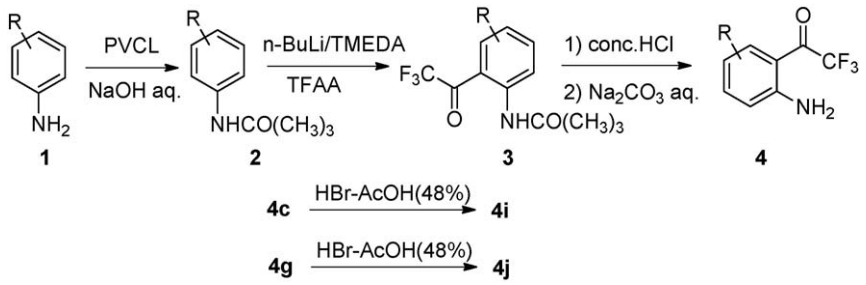


Scheme 1. The synthetic route of compounds **4a**–**4j**.

trifluoroacetylaniline derivatives. The reactions are shown in Scheme 1, and the results are summarized in Table 1. We can obviously see from Table 1 that a wide range of substituted *N*-pivaloylanilines can react smoothly with trifluoroacetic anhydride under the condition of *n*-butyllithium to give various *o*-trifluoroacetylanilines in reasonably high yields.

Scheme 1 shows its synthetic route from the easily available materials of substituted anilines and trifluoroacetic anhydride (TFAA) in three steps: reaction of anilines **1** with pivaloyl chloride in a two-phase mixture of diethyl ether and aqueous sodium hydroxide afforded pivaloylamides **2** in high yields. Directed orthometalation of **2** (2.2 equiv. of *n*-BuLi, 1.0 equiv. of TMEDA) generated the corresponding dilithio intermediate [26]. Reaction of the dilithio species with trifluoroacetic anhydride results in the formation of ketoamides **3** which can be isolated by crystallization. Hydrolysis of the amide in situ (*conc*. HCl) provided the hydrochloride of **4**. Treatment of the salt with aqueous Na_2CO_3 in water provided the corresponding free base **4**.

2.2. The role of protective group of anilines and the reaction mechanism

In spite of the versatility of *o*-trifluoroacetylanilines as reactive intermediates, a simple preparative route to them from anilines has not been known to date, because the Friedel–Crafts trifluoroacetylation of anilines is usually unsuccessful and the formation of isomers and the marginal yields are synthetically unattractive. Herein, we wish to report on the facile and regiospecific synthetic route to get the target molecules.

The presence of two active hydrogens in primary anilines is a formidable obstacle to nuclear metalation and is presumably the reason for the lack of reports on the successful synthesis of *o*-trifluoroacetylanilines. Therefore, control experiments were conducted to study the role of suitable protecting groups. As a part of

Table 1
Structures of the compounds **4a**–**4j**.

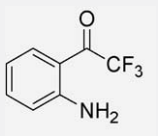
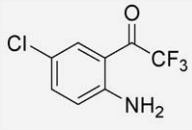
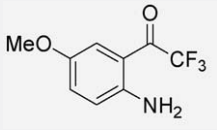
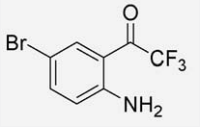
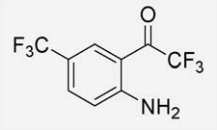
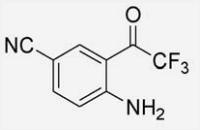
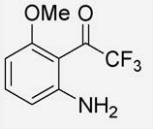
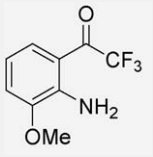
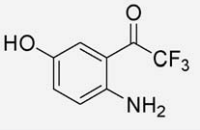
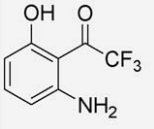
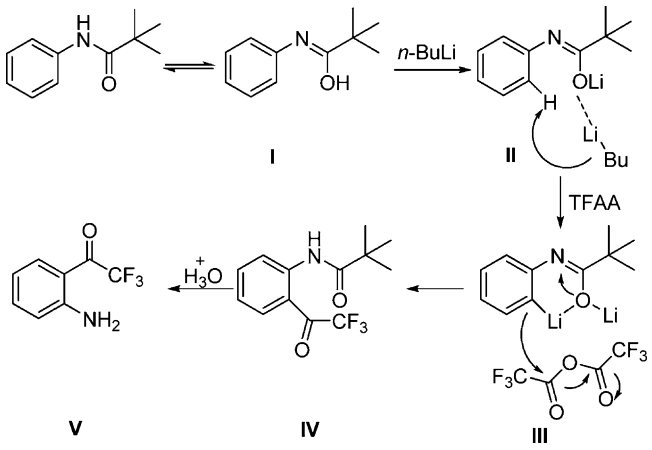
Compound	R in anilines	Product	Yield[a] (%)
4a	H		
4b	*p*-Cl		80

Table 1 (*Continued*)

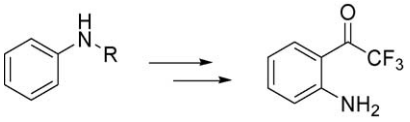
Compound	R in anilines	Product	Yield[a] (%)
4c	*p*-MeO		85
4d	*p*-Br		84
4e	*p*-CF_3		95
4f	*p*-CN		90
4g	*m*-MeO		91
4h	*o*-MeO		82
4i	*p*-OH		75
4j	*m*-OH		80

[a] Isolated yields.



Scheme 2. The proposed mechanism.

Table 2
The comparison of different protecting groups.



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R	Yield[a] (%)
-$CO(CH_3)_3$	88
-COPh	0
-$COCH_3$	5
-COC_2H_5	18
-Boc	20

[a] Isolated yields.

the systematic research work, we investigated the suitability of several *ortho*-directing groups (Table 2). According to the experimental results, it can be revealed that the protective group could not be aryl [27] and most alkyl groups had to be excluded as well, based on the acidic character of their a proton [28]. However, a bulky *tert*-butyl group (R = *t*-C_4H_9) which could prevent unwanted side reactions turned out to be ideal, and the desired reaction could occur readily and under relatively mild conditions. A mechanistic pathway can be suggested (Scheme 2). Fundamentally, it could be assumed that by analogy with other *ortho* metalations [29], the oxygen atom in the deprotonated species **II** should serve as a ligand for a second equivalent of lithiating agent, thus facilitating a regiospecific protophilic attack on the *o*-hydrogen and the formation of the dilithio intermediate **III**. Reaction of the dilithio species with trifluoroacetic anhydride results in the formation of *o*-trifluoroacetyl *N*-pivaloylaniline **IV** which can be isolated by crystallization. Finally, **IV** was deprotected by concentrated hydrochloride to give the target compound **V**.

3. Conclusion

In summary, based on some previously reported results, we have developed a simple and efficient method to introduce trifluoroacetyl group to the *ortho* position of anilines in higher yield. Some of these compounds were firstly reported to be novel trifluoromethylated molecules to the best of our knowledge. The results obtained in this paper indicated that our strategies for the synthesis of some trifluoromethylated molecules are commercially important in both organofluorine and organic synthetic area, and should be exploited for the synthesis of various other useful trifluoromethylated compounds.

4. Experimental

4.1. General

All reagents and solvents were reagent grade or were purified by standard methods before use. The melting points were determined using an electrothermal apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded at either 400 MHz or 500 MHz with a Bruker instrument, and reported with TMS as internal standard and $CDCl_3$ as solvent. ^{19}F NMR spectra were obtained either on a Bruker instrument using CF_3COOH (TFA) as an external standard. Chemical shifts (δ values) and coupling constants (J values) are given in ppm and Hz respectively. TLC analysis was carried out on silica gel plates GF254 (Qindao Haiyang Chemical, China). Anhydrous solvent and reagents were all analytically pure and dried through routine protocols. All reactions requiring anhydrous conditions were performed under a positive nitrogen flow, and all glassware was oven-dried before using.

4.2. Typical experimental procedure for the synthesis of 2

Anilines (**1**, 50 mmol) were charged into a mixture of diethyl ether (60 ml) and 40% aqueous sodium hydroxide (5.5 g, 55 mmol), and the mixture was cooled to 0 °C. To the resulting slurry, trimethylacetyl chloride (PVCL) (6.6 g, 55 mmol) was added over 0.5 h, keeping the temperature below 15 °C. After being stirred for 2.5 h at 25 °C, the slurry was cooled to 0 °C and held for 1.5 h. The product was collected by filtration, washed with a solution of 9/1 water/methanol (150 ml) and water (100 ml), and dried in vacuo to give pivaloylamide **2** as white solid.

4.3. General procedure for the preparation of compounds 4a–4h

Under an atmosphere of nitrogen, compound **2** (0.1 mol) was charged to a solution of TMEDA (1.1 g, 0.1 mol) in anhydrous diethyl ether (50 ml), and the mixture was cooled to 0 °C. The *n*-butyllithium solution (88 ml of a 2.5 M solution in hexane, 0.22 mol) was added dropwise to the cold amide solution slowly over 2.5 h, while the temperature was kept below 15 °C. The mixture was aged at 10–15 °C for 4 h and cooled below −25 °C. To this mixture trifluoroacetic anhydride (32.0 ml, 0.25 mol) was added rapidly. After 5 h, the resulting clear solution was quenched with 15% aqueous HCl, keeping the temperature below 10 °C. The mixture was diluted with 50 ml diethyl ether and the layers were separated. The organic phase was washed with brine, dried, filed and concentrated in vacuo, to give a yellow oil. This material was cooled to 25 °C, 12N HCl (10 ml, 0.12 mol) was added, and the mixture was heated to 80–85 °C and held for 6 h. The cooled solution was diluted with 100 ml of EtOAc and the mixture was made basic with a solution of sodium carbonate in water. Then the mixture was extracted with ethyl acetate (50 ml, 3×). The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. After the removal of solvent, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) or by crystallization to afford **4a–4h**.

4.4. Procedure for the demethylation of 4c and 4g

To a solution of acetic acid (25 ml) and aqueous hydrobromic acid (48%, 25 ml) heated at 80 °C (oil bath) **4c** or **4g** (0.3 g, 1.3 mmol) was added. The mixture was heated at 80 °C for 2 h. After cooling, the mixture was diluted with cold water (150 ml) and extracted with ethyl acetate. The organic layer was washed

with water and brine, dried over $MgSO_4$. On evaporation of the solvent, the product solidified.

4.5. Spectral data

4.5.1. 1-(2-Aminophenyl)-2,2,2-trifluoroethanone (4a)

A bright yellow needles; yield (88%); mp 51–52 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.24 (br s, 2H), 6.67 (d, 1H, J = 1.2 Hz), 6.73 (dd, 1H, J = 1.8 Hz, 3.9 Hz), 7.38 (dd, 1H, J = 1.2 Hz, J = 3.9 Hz), 6.67 (d, 1H, J = 1.8 Hz); ^{19}F NMR ($CDCl_3$, TFA): δ = 6.42; ^{13}C NMR (400 MHz, $CDCl_3$): δ = 111.32, 115.84, 117.70, 118.74, 131.55, 136.85, 153.40, 180.01; MS (ESI): 188 (M−H); Anal. calcd. for $C_8H_6F_3NO$: C, 50.80; H, 3.20; N, 7.41. Found: C, 50.87; H, 3.21; N, 7.39.

4.5.2. 1-(2-Amino-5-chlorophenyl)-2,2,2-trifluoroethanone (4b)

A bright yellow solid; yield (80%); mp 90–91 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.46 (br s, 2H), 6.70 (d, 1H, J = 9.0 Hz), 7.32 (dd, 1H, J = 2.1 Hz, 9.0 Hz), 7.71 (d, 1H, J = 2.1 Hz); ^{19}F NMR ($CDCl_3$, TFA): δ = 6.19; ^{13}C NMR (400 MHz, $CDCl_3$): δ = 111.62, 115.52, 118.42, 119.24, 130.25, 137.09, 151.82, 180.31; MS (ESI): 222$(M-H)^-$; Anal. calcd. for $C_8H_5ClF_3NO$: C, 42.98; H, 2.25; N, 6.26. Found: C, 42.96; H, 2.24; N, 6.27.

4.5.3. 1-(2-Amino-5-methoxyphenyl)-2,2,2-trifluoroethanone (4c)

An orange solid; yield (85%); mp 105–106 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.78 (s, 3H), 6.25 (br s, 2H), 6.69 (d, 1H, J = 9.0 Hz), 7.11 (dd, 1H, J = 2.1 Hz, 9.0 Hz), 7.15 (d, 1H, J = 2.1 Hz); ^{19}F NMR ($CDCl_3$, TFA): δ = 4.35; ^{13}C NMR (400 MHz, $CDCl_3$): δ = 56.77, 101.88, 110.96, 119.45, 121.44, 134.78, 148.69, 159.44, 183.43; MS (ESI): 218 (M−H); Anal. calcd. for $C_9H_8F_3NO_2$: C, 49.32; H, 3.68; N, 6.39. Found: C, 49.28; H, 3.69; N, 6.38.

4.5.4. 1-(2-Amino-5-bromophenyl)-2,2,2-trifluoroethanone (4d)

An orange solid; yield (84%); mp 100–101 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.42 (br s, 2H), 6.64(d, 1H, J = 8.9 Hz), 7.44 (dd, 1H, J = 2.0 Hz, 8.9 Hz), 7.84 (d, 1H, J = 2.0 Hz); ^{19}F NMR ($CDCl_3$, TFA): δ = 6.26; ^{13}C NMR (400 MHz, $CDCl_3$): δ = 112.35, 115.53, 117.44, 119.51, 133.33, 139.63, 152.10, 180.26; MS (ESI): 266 (M−H); Anal. calcd. for $C_8H_5BrF_3NO$: C, 35.85; H, 1.88; N, 5.23. Found: C, 35.90; H, 1.88; N, 5.24.

4.5.5. 1-(2-Amino-5-(trifluoromethyl)phenyl)-2,2,2-trifluoroethanone (4e)

A bright yellow needles; yield (95%); mp 270–271 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.66 (br s, 2H), 6.81 (d, 1H, J = 8.9 Hz), 7.15 (d, 1H, J = 1.2 Hz), 7.57 (dd, 1H, J = 1.2 Hz, 8.9 Hz); ^{19}F NMR ($CDCl_3$, TFA): δ = 6.21, 13.72; ^{13}C NMR (400 MHz, $CDCl_3$): δ = 110.04, 115.46, 118.35, 125.33, 128.02, 129.37, 132.81, 154.92, 180.54; MS (ESI): 256 (M−H); Anal. calcd. for $C_9H_5F_6NO$: C, 42.04; H, 1.96; N, 5.45. Found: C, 42.09; H, 1.96; N, 5.46.

4.5.6. 1-(2-Amino-5-cyanphenyl)-2,2,2-trifluoroethanone (4f)

An orange solid; yield (90%); mp 131–132 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.57 (br s, 2H), 6.75 (d, 1H, J = 8.5 Hz), 7.74 (dd, 1H, J = 2.1 Hz, 8.5 Hz), 7.84 (d, 1H, J = 2.1 Hz); ^{19}F NMR ($CDCl_3$, TFA): δ = 6.27; ^{13}C NMR (400 MHz, $CDCl_3$): δ = 112.36, 115.88, 118.01, 118.56, 119.87, 134.35, 140.12, 155.23, 180.05; MS (ESI): 213 (M−H); Anal. calcd. for $C_9H_5F_3N_2O$: C, 50.48; H, 2.35; N, 13.08. Found: C, 50.45; H, 2.36; N, 13.09.

4.5.7. 1-(2-Amino-6-methoxyphenyl)-2,2,2-trifluoroethanone (4g)

A lemon-yellow solid; yield (91%); mp 49–50 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.84 (s, 3H), 6.05 (br s, 2H), 6.20 (d, 1H, J = 8.1 Hz), 6.31 (d, 1H, J = 8.3 Hz), 7.25 (t, 1H, J = 8.2 Hz); ^{19}F NMR ($CDCl_3$, TFA): δ = 2.14; ^{13}C NMR (400 MHz, $CDCl_3$): δ = 55.79, 98.95, 109.76, 118.38, 121.26, 136.54, 152.31, 161.81, 183.77; MS (ESI): 220 (M+H); Anal. calcd. for $C_9H_8F_3NO_2$: C, 49.32; H, 3.68; N, 6.39. Found: C, 49.29; H, 3.67; N, 6.37.

4.5.8. 1-(2-Amino-3-methoxyphenyl)-2,2,2-trifluoroethanone (4h)

A yellow solid; yield (82%); mp 67–68 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.86 (s, 3H), 6.07 (br s, 2H), 6.25 (d, 1H, J = 8.3 Hz), 6.43 (d, 1H, J = 8.2 Hz), 7.21 (t, 1H, J = 8.2 Hz); ^{19}F NMR ($CDCl_3$, TFA): δ = 2.25; ^{13}C NMR (400 MHz, $CDCl_3$): δ = 55.81, 101.11, 110.76, 117.89, 120.56, 132.45, 140.68, 150.55, 181.48; MS (ESI): 220 (M+H); Anal. calcd. for $C_9H_8F_3NO_2$: C, 49.32; H, 3.68; N, 6.39. Found: C, 49.29; H, 3.67; N, 6.37.

4.5.9. 1-(2-Amino-5-hydroxyphenyl)-2,2,2-trifluoroethanone (4i)

A bright yellow solid; yield (75%); mp 108–109 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.46 (s, 1H), 6.19 (br s, 2H), 6.67 (d, 1H, J = 9.0 Hz), 7.05 (dd, 1H, J = 2.8 Hz, 9.0 Hz), 7.17 (d, 1H, J = 2.8 Hz); ^{19}F NMR ($CDCl_3$, TFA): δ = 6.17; ^{13}C NMR (400 MHz, $CDCl_3$): δ = 110.79, 115.75, 118.65, 119.18, 127.46, 145.71, 148.68, 180.35; MS (ESI): 204 (M−H); Anal. calcd. for $C_8H_6F_3NO_2$: C, 46.84; H, 2.95; N, 6.83. Found: C, 46.79; H, 2.96; N, 6.82.

4.5.10. 1-(2-Amino-6-hydroxyphenyl)-2,2,2-trifluoroethanone (4j)

A lemon-yellow solid; yield (80%); mp 98–99 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.75 (s, 1H), 6.01 (br s, 2H), 6.18 (d, 1H, J = 8.0 Hz), 6.45 (d, 1H, J = 8.2 Hz), 7.11 (t, 1H, J = 8.3 Hz); ^{19}F NMR ($CDCl_3$, TFA): δ = 3.25; MS (ESI): 206 (M+H); Anal. calcd. for $C_8H_6F_3NO_2$: C, 46.84; H, 2.95; N, 6.83. Found: C, 46.80; H, 2.96; N, 6.84.

Acknowledgments

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