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Copper-Free Direct C−H Trifluoromethylation of Acetanilides with Sodium Trifluoromethanesulfinate

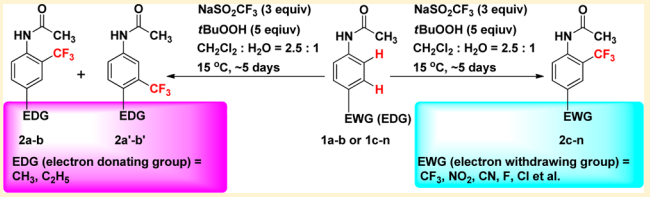
Mingxi Wu,[†] Xinfei Ji,[†] Wenpeng Dai,[†] and Song Cao*[,†,‡]

[†]Shanghai Key Laboratory of Chemical Biology, School of Pharmacy, East China University of Science and Technology (ECUST), Shanghai 200237, China

[‡]Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

Supporting Information

ABSTRACT: A copper-free direct C−H ortho trifluoromethylation of electron-deficient 4-substituted acetanilides using Langlois reagent ($NaSO_2CF_3$) as the CF_3 source in the presence of *tert*-butyl hydroperoxide (*t*BuOOH, TBHP) was developed.

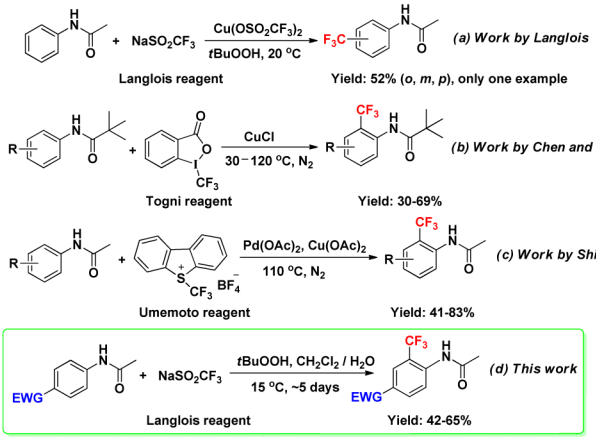


INTRODUCTION

Over the last few decades, the introduction of the trifluoromethyl group (CF_3) into organic compounds has attracted ever-increasing interest in organic synthesis.[1] Up to now, numerous methods for nucleophilic, electrophilic, and radical trifluoromethylation have been developed.[2] Although the present methods exhibit remarkable reactivity and broad applicability toward diverse molecules, generally they suffer from the use of expensive trifluoromethylating reagents (e.g., Ruppert−Prakash reagent: about 2000 €/mol; Umemoto reagent: about 43 000 €/mol; Togni reagent: about 144 000 €/mol),[3] the transition metal catalysts or the requirement for harsh reaction conditions. Consequently, these disadvantages restrict their widespread use in organic synthesis. Among the commercially available trifluoromethylating reagents, Langlois reagent (sodium trifluoromethanesulfinate, $NaSO_2CF_3$, about 930 €/mol) has drawn much attention in recent years largely as a result of their availability, relatively low cost, and ease of handling.[4] However, compared to the development of other trifluoromethylating reagents, direct trifluoromethylation reaction using Langlois reagent as the CF_3 source still remains underdeveloped.[5]

The trifluoromethylated anilines and their derivatives are a class of useful and valuable fluorinated building blocks for the synthesis of pharmaceuticals, agrochemicals, and advanced organic materials.[6] Traditionally, such trifluoromethylated anilines are synthesized from the corresponding aryl trichlorides by exchange of chloride for fluoride using F_2 or HF as fluorinating agents in the presence of Lewis acid.[7] Although these methods are still used in industrial applications, they have some drawbacks such as serious environmental problems, severe experimental conditions requirements, and the formation of other fluorinated sideproducts. Recently, trifluoromethylation of acetanilides or pivanilides with different trifluoromethylating reagents has provided an attractive method for the synthesis of the CF_3-substituted aniline derivatives (Scheme 1a−c).[8] However, the high cost of the trifluoromethylating reagents, the use of transition metal catalysts (Pd and Cu), and relatively harsh reaction conditions limit their application on a large scale.

Scheme 1. Trifluoromethylation of Acetanilide or Pivanilide Derivatives



Despite these groundbreaking advances in trifluoromethylation of aniline or acetanilides derivatives, there is still great demand for the development of direct C−H trifluoromethylation approaches that perform under simple and mild conditions. In this paper, we developed a novel and efficient method for the synthesis of valuable building blocks of *o*-CF_3 acetanilides by the reaction of electron-deficient 4-substituted

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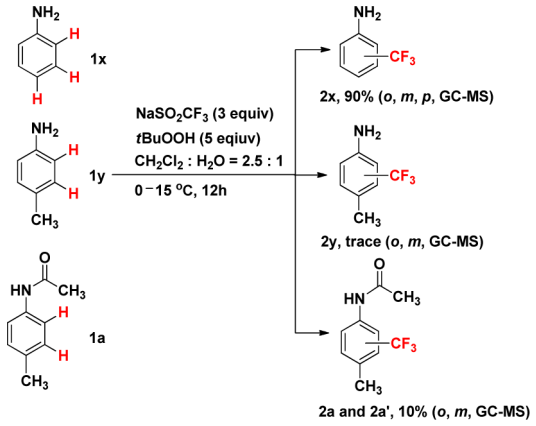
acetanilides with Langlois reagent in the presence of *tert*-butyl hydroperoxide (Scheme 1d).

RESULTS AND DISCUSSION

In 2011, Baran reported an efficient method for the trifluoromethylation of heterocycles by using a simple combination of sodium trifluoromethanesulfinate salt ($NaSO_2CF_3$) and *tert*-butyl hydroperoxide (TBHP) in the mixed solvent of CH_2Cl_2/H_2O, affording the pure products or a mixture of regioisomers in moderate to good yields.[9] Encouraged by the results obtained by Baran and Langlois, and in our continuing efforts to develop novel methods toward CF_3-containing compounds,[10] we envisaged that this radical oxidation trifluoromethylation protocol might be applied for the introduction of a CF_3 group into the readily available acetanilides and anilines.

Langlois and co-workers first reported trifluoromethylation of electron-rich aromatics such as anilines and phenols. Thus, we began our investigation by examining the trifluoromethylation of aniline (**1x**) with $NaSO_2CF_3$ and *t*BuOOH using CH_2Cl_2/H_2O (2.5/1) as solvent (Scheme 2). Although the reaction furnished a satisfactory yield of trifluoromethylated aniline (90%, GC-MS), a mixture of regioisomers (ortho-, meta-, or para-substituted aniline) was obtained. Unfortunately, these trifluoromethylated products were isolated as an inseparable mixture of regioisomers. To avoid the formation of regioisomers, the reaction of 4-methylaniline (**1y**) with $NaSO_2CF_3$ and *t*BuOOH was examined; however, only a trace amount of expected products were observed.

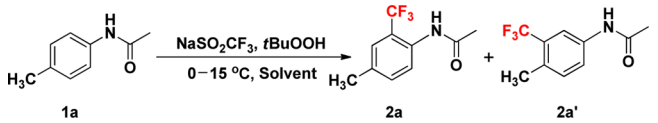
Scheme 2. Reaction of Aniline Derivatives with $NaSO_2CF_3$ and *t*BuOOH



When *N*-(4-methylphenyl)acetamide **1a** was used, the expected products **2a** and **2a′** were formed in 10% yield. Inspired by this promising result, we chose **1a** as the model substrate to optimize the reaction conditions (Table 1). Langlois reported trifluoromethylation of *N*-phenylacetamide with $NaSO_2CF_3$ and *t*BuOOH in the presence of a catalytic amount of Cu(II) salt. Thus, initially, we performed the reaction in the presence of Cu(II) salt (entries 1, 2); however, trace amounts of the desired products were detected. When CH_2Cl_2 was replaced with DMSO or CH_3CN, the formation of **2a** and **2a′** were almost not observed (entries 3, 4). The reaction time has a significant impact on the process of reaction and the yield of product (entries 5−8). A long reaction time was required for a moderate yield. When the reaction time was shortened, the yield of **2a** was obviously decreased. The amounts of $NaSO_2CF_3$ and *t*BuOOH used were also varied. Too little or too much $NaSO_2CF_3$ or *t*BuOOH led to a lower conversion of **1a** to the trifluoromethylated products **2a** and **2a′** (entries 9−12). Note that because *tert*-butyl hydroperoxide (*t*BuOOH) should be stored in 2−8 °C, the reaction must be performed at 0 °C at the beginning of the reaction. It is unfavorable for the reaction when performed at higher reaction temperature (e.g., 25 °C).

With the optimum reaction conditions in hand (Table 1, entry 8), we next investigated the scope of this C−H trifluoromethylation reaction with a variety of different 4-substituted acetanilides (Table 2, 3). The acetanilides having electron-donating groups such as methyl or ethyl group at the para position of the acetamino group afforded mixtures of isomeric C−H trifluoromethylation products in moderate yields (**2a** and **2a′**, **2b** and **2b′**), which were separated by column chromatography on silica gel using a petroleum ether/ethyl acetate (2:1) mixture as eluent. The replacement of the

Table 1. Optimization of the Reaction Conditions



entry	$NaSO_2CF_3$ (equiv)	*t*BuOOH (equiv)	catalyst (5 mol %)	solvent	time	yield[a] (**2a**+**2a′**)
1	3.0	5.0	$CuCl_2$	CH_2Cl_2:H_2O = 2.5:1	12 h	trace
2	3.0	5.0	$CuSO_4$	CH_2Cl_2:H_2O = 2.5:1	12 h	trace
3	3.0	5.0	–	DMSO:H_2O = 2.5:1	12 h	trace
4	3.0	5.0	–	CH_3CN:H_2O = 2.5:1	12 h	trace
5	3.0	5.0	–	CH_2Cl_2:H_2O = 2.5:1	12 h	10
6	3.0	5.0	–	CH_2Cl_2:H_2O = 2.5:1	1 d	33
7	3.0	5.0	–	CH_2Cl_2:H_2O = 2.5:1	3 d	40
8	3.0	5.0	–	CH_2Cl_2:H_2O = 2.5:1	5 d	51
9	4.0	5.0	–	CH_2Cl_2:H_2O = 2.5:1	5 d	50
10	2.0	5.0	–	CH_2Cl_2:H_2O = 2.5:1	5 d	46
11	3.0	4.0	–	CH_2Cl_2:H_2O = 2.5:1	5 d	45
12	3.0	3.0	–	CH_2Cl_2:H_2O = 2.5:1	5 d	28

[a]Yields (**2a** and **2a′**) determined by GC analysis and based on **1a**.

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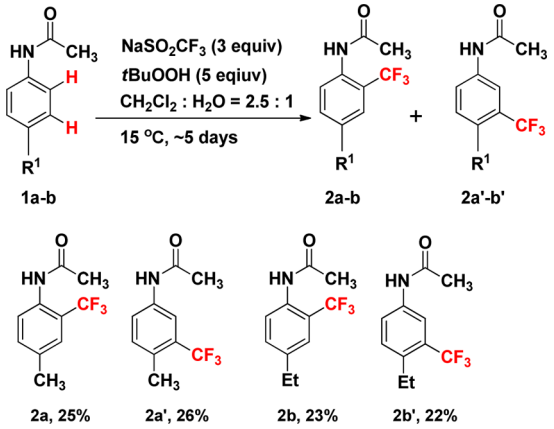
Table 2. Trifluoromethylation of 4-Methyl (or Ethyl) Acetanilides[a,b]

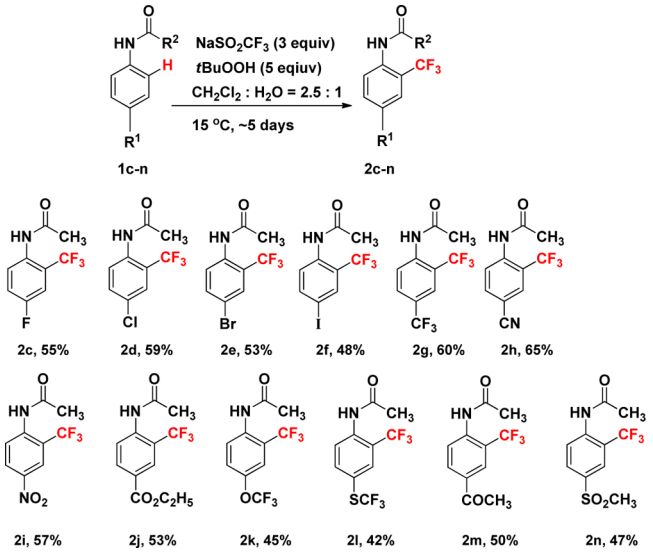


[a]Reaction conditions: **1a,b** (1 mmol), CH_2Cl_2 + H_2O = 7 mL. [b]Isolated yield.

acetyl group by a benzoyl group did not make much difference in the yields of the products (GC and GC-MS).

Direct trifluoromethylation of C−H bonds of electron-deficient anilides or acetanilides, especially for those bearing strong electron-withdrawing substituents, has not been explored and still remains a great challenge. We next turned our attention to the trifluoromethylation of acetanilides bearing an electron-withdrawing group at the para position of the acetamino group. As shown in Table 3, most substrates were converted into the expected products in moderate yields (42−65%). However, the reaction did not proceed to completion and gave a mixture of starting materials and the expected products. A small amount of products were lost during column chromatography, and the starting materials were recovered. The results indicated that these electron-withdrawing groups aided this transformation, affording the desired products **2c−n** in reasonable yields. Much to our delight, *o*-CF_3 acetanilides were obtained as sole products. The analytical data (^{1}H, ^{13}C, and ^{19}F NMR) of isolated products **2a**, **2c**, **2d**, **2e**, **2f**, **2j**, and **2m** match those of compounds given in the literature.[8c] Furthermore, the ^{13}C NMR chemical shifts and three-bond C−F coupling constants ($^3J_{CF}$) of C atom 3 of **2a**, **2c−f**, **2j**, and **2m** (C atom 2 of **2j**) are similar to those reported by Shi.[8c]

Table 3. Trifluoromethylation of Acetanilides Bearing an Electron-Withdrawing Group[a,b]



[a]Reaction conditions: acetanilides **1c−n** (1 mmol), CH_2Cl_2 + H_2O = 7 mL. [b]Isolated yield.

In addition, strong electron-withdrawing groups such as CF_3, CN, and NO_2 (**2g**, **2h**, and **2i**) are more favorable for this conversion than weak electron-withdrawing groups. On the basis of the above observations, we assumed that the yields were substantially affected by the electron density of the benzene ring. Increasing the acetanilides' electron density resulted in some lower reaction efficiency.

Finally, to investigate the limitations of the radical trifluoromethylation reaction, we attempted the trifluoromethylation of anilines bearing electron-withdrawing groups at the 4-position directly without the assistance of an acetamino group (Table 4). The reactions of 4-substituted anilines (**3b−e**) with $NaSO_2CF_3$ did not proceed efficiently, affording the desired products in poor yields. Other 4-substituted anilines such as 4-(trifluoromethoxy)aniline, 1-(4-aminophenyl)ethanone, 4-((trifluoromethyl)thio)aniline, and 4-(methylsulfonyl)aniline failed to give the ortho-trifluoromethylated products. Fortunately, those 4-substituted anilines having a strong electron-withdrawing group still furnished appreciable yields of the expected products (**4a**, **4f**, and **4g**). The spectral data (^{1}H, ^{13}C, and ^{19}F NMR) of **4a−d**, **4f**, and **4g** match those of compounds given in the literature.[11−14]

Although aniline (**1x**) has been converted into the corresponding $ArCF_3$ in high yield (90%), when the para position of the amino group was substituted by another substituent, no matter whether it is an electron-withdrawing group (Table 4, **3a−g**) or an electron-donating group (Scheme 2, **1y**), the trifluoromethylation reaction proceeded slowly and inefficiently. This result might be due to steric hindrance in the para position to the amino group, which decreased the reaction efficiency somewhat, and is consistent with the reported observation that $\cdot CF_3$ radical is very sensitive to steric hindrance.[5e]

According to the Shi and Xi's reports, the acetamino group and pivalamido group were considered as ortho-directing groups for trifluoromethylation of acetanilides and pivanilides in the presence of palladium and copper catalysts. However, in this work, the effect of the acetamino group is different. To probe the role of the acetamino group, an additional experiment was conducted. When *p*-nitrotoluene was used as the substrate, no reaction was observed. This indicated that only the existence of a strong electron-withdrawing group on the aryl ring without the assistance of an acetamino or amino group could not make the reaction proceed smoothly. Although the acetamino group might play a particularly important role in altering the distribution of the π electron density of the benzene ring, it also acted as an ortho-directing group. However, the influence on the reaction of the former is more obvious than that of the latter. The presence of a strong electron-withdrawing group at the para position to the acetamino or amino group is favorable for the formation of ortho-trifluoromethylated products.

On the basis of a related published paper in this field,[8a,9] the mechanism of the trifluoromethylation of arenes and heteroarenes with $NaSO_2CF_3$ and *t*BuOOH might involve the CF_3 radical. In our cases, the trifluoromethylation of acetanilides or anilines might also proceed via the CF_3 transient

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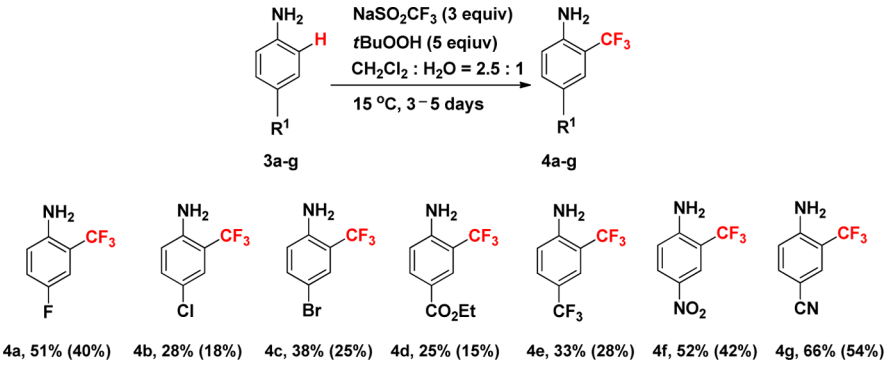
Table 4. Trifluoromethylation of Anilines Bearing an Electron-Withdrawing Group[a,b]



[a]Reaction conditions: anilines **3a−g** (1 mmol), CH_2Cl_2 + H_2O = 7 mL. [b]Yields determined by GC analysis and based on **3a−g**, isolated yields in parentheses.

radical intermediate. To validate this assumption, 1 or 4 equiv of TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy), a radical scavenger, was added into the reaction system under the standard conditions, respectively; no expected trifluoromethylated product was observed, and an observable amount of TEMPO−CF_3 adduct was detected in the crude mixture. These results clearly indicated that the reaction can go through a radical pathway.

In summary, we have developed a practical and efficient metal-free direct C−H ortho trifluoromethylation of a variety of electron-deficient 4-substituted acetanilides. The reaction could be carried out at near room temperature under ambient conditions using stable, inexpensive, and readily available Langlois reagent ($NaSO_2CF_3$) as the trifluoromethylating reagent. Furthermore, the reaction shows high tolerance to moisture and good functional group compatibility. This method provides a simple and straightforward approach to prepare a variety of useful 4-substituted ortho-trifluoromethylated acetanilides or anilines, which can be used as remarkably versatile building blocks in synthetic organic chemistry and important intermediates in the fine chemical industry.

EXPERIMENTAL SECTION

General Comments. All reagents were of analytical grade, obtained from commercial suppliers, and used without further purification. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on a 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) using TMS as internal standard. The ^{19}F NMR spectra were obtained using a 400 spectrometer (376 MHz). DMSO-d_6 was used as the NMR solvent in all cases. The GC and GC-MS were calibrated by authentic standards. High-resolution mass spectra (HRMS) were acquired in the electron-impact mode (EI) using a TOF mass analyzer.

*Synthesis of Compounds **1a−n**.* Substrates **1a−n** were synthesized according to literature procedures.[8c]

*Synthesis of Compounds **2a−n**.* TBHP (70% solution in water, 0.68 mL, 5.0 mmol, 5.0 equiv) was slowly added to a solution of substituted acetanilide (**1a−n**, 1.0 mmol) and $NaSO_2CF_3$ (0.468g, 3.0 mmol, 3.0 equiv) in dichloromethane (5 mL) and water (2 mL) at 0 °C. After the mixture was stirred for 1 h, the temperature was slowly raised to 15 °C and the reaction mixture was stirred at 15 °C for 4−5 days. After the reaction was completed (monitored by TLC), the mixture was extracted with dichloromethane (3 × 10 mL). The organic layer was washed with brine and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (2:1) to afford the pure compounds.

*Synthesis of Compounds **4a−g**.* TBHP (70% solution in water, 0.68 mL, 5.0 mmol, 5.0 equiv) was slowly added to a solution of substituted anilines (**3a−g**, 1.0 mmol) and $NaSO_2CF_3$ (0.468g, 3.0 mmol, 3.0 equiv) in dichloromethane (5 mL) and water (2 mL) at 0 °C. After the mixture was stirred for 1 h, the temperature was slowly raised to 15 °C and the reaction mixture was stirred at 15 °C for about 3−4 days. After the reaction was completed (monitored by TLC or GC), the mixture was extracted with dichloromethane (3 × 10 mL). The organic layer was washed with brine and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (2:1) to afford the pure target compounds.

*N-(4-Methyl-2-(trifluoromethyl)phenyl)acetamide (**2a**, CAS: 1416085-70-5).*[8c] yield 25% (54.3 mg), white solid; mp 116.7−117.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.48 (s, 1H), 7.52 (s, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 2.36 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.6, 136.7, 133.7, 133.5, 130.7, 126.8 (q, $^3J_{CF}$ = 4.4 Hz), 125.2 (q, $^2J_{CF}$ = 29.0 Hz), 124.1 (q, $^1J_{CF}$ = 271.6 Hz), 23.2, 20.7; ^{19}F NMR (376 MHz, DMSO-d_6): δ −59.5 (s, 3F).

*N-(4-Methyl-3-(trifluoromethyl)phenyl)acetamide (**2a′**, CAS: 22957-86-4).*[7a] yield 26% (56.4 mg), white solid; mp 116.6−117.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.15 (s, 1H), 7.99 (s, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 2.36 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.5, 137.5, 132.4, 129.8, 127.4 (q, $^2J_{CF}$ = 29.1 Hz), 124.4 (q, $^1J_{CF}$ = 272.0 Hz), 122.1, 115.8 (q, $^3J_{CF}$ = 5.9 Hz), 23.8, 18.0; ^{19}F NMR (376 MHz, DMSO-d_6): δ −60.7 (s, 3F).

*N-(4-Ethyl-2-(trifluoromethyl)phenyl)acetamide (**2b**).* yield 23% (53.2 mg), white solid; mp 122.0−123.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.49 (s, 1H), 7.54 (s, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 2.68 (q, J = 7.5 Hz, 2H), 2.05 (s, 3H), 1.20 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.7, 142.9, 133.7, 132.6, 130.8, 125.7 (q, $^3J_{CF}$ = 4.9 Hz), 125.3 (q, $^2J_{CF}$ = 33.0 Hz), 124.1 (q, $^1J_{CF}$ = 271.7 Hz), 27.9, 23.3, 15.8; ^{19}F NMR (376 MHz, DMSO-d_6): δ −59.4 (s, 3F); HRMS (EI) calcd for $C_{11}H_{12}F_3NO$ ([M]$^+$) 231.0871, found 231.0872.

*N-(4-Ethyl-3-(trifluoromethyl)phenyl)acetamide (**2b′**).* yield 22% (50.8 mg), white solid; mp 122.2−123.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.18 (s, 1H), 7.98 (d, J = 1.6 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 2.69 (q, J = 7.3 Hz, 2H), 2.05 (s, 3H), 1.17 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.1, 137.9, 136.8, 131.7, 127.2 (q, $^2J_{CF}$ = 28.9 Hz), 125.0 (q, $^1J_{CF}$ = 272.3 Hz), 123.0, 116.2 (q, $^3J_{CF}$ = 6.0 Hz); ^{19}F NMR (376 MHz, DMSO-d_6): δ −58.9 (s, 3F); HRMS (EI) calcd for $C_{11}H_{12}F_3NO$ ([M]$^+$) 231.0871, found 231.0873.

*N-(4-Fluoro-2-(trifluoromethyl)phenyl)acetamide (**2c**, CAS: 393-23-7).*[8c] yield 55% (121.6 mg), white solid; mp 117.8−118.7 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.61 (s, 1H), 7.63−7.49 (m, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.9, 160.0 (d, $^1J_{CF}$ = 243.8 Hz), 133.4 (d, $^3J_{CF}$ = 8.3 Hz), 132.5, 127.5−127.1 (m), 123.1 (qd, $^1J_{CF}$ = 280.4 Hz, $^3J_{CF}$ = 8.1 Hz), 120.3 (d, $^2J_{CF}$ = 21.9 Hz), 114.0

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(dq, $^2J_{CF}$ = 26.1 Hz, $^3J_{CF}$ = 5.0 Hz), 23.2. ^{19}F NMR (376 MHz, DMSO-d_6): δ −60.1 (s, 3F), −114.1 (s, 1F).

*N-(4-Chloro-2-(trifluoromethyl)phenyl)acetamide (**2d**, CAS: 344-53-6).*[8c] yield 59% (139.8 mg), white solid; mp 134.5−135.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.62 (s, 1H), 7.77 (d, J = 2.0 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.8, 135.1, 133.3, 132.5, 131.2, 126.8, 126.6 (q, $^3J_{CF}$ = 5.2 Hz), 123.1 (q, $^1J_{CF}$ = 272.2 Hz), 23.3; ^{19}F NMR (376 MHz, DMSO-d_6): δ −59.9 (s, 3F).

*N-(4-Bromo-2-(trifluoromethyl)phenyl)acetamide (**2e**, CAS: 29124-62-7).*[8c] yield 53% (148.9 mg), white solid; mp 165.2−166.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.61 (s, 1H), 7.88−7.86 (m, 2H), 7.47 (d, J = 8.4 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.8, 136.3, 135.5, 132.7, 129.4 (q, $^3J_{CF}$ = 5.2 Hz), 126.9 (q, $^2J_{CF}$ = 29.6 Hz), 123.0 (q, $^1J_{CF}$ = 272.4 Hz), 119.1, 23.3; ^{19}F NMR (376 MHz, DMSO-d_6): δ −59.8 (s, 3F).

*N-(4-Iodo-2-(trifluoromethyl)phenyl)acetamide (**2f**, CAS: 97760-98-0).*[8c] yield 48% (157.9 mg), white solid; mp 161.5−162.7 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.58 (s, 1H), 8.02−7.99 (m, 2H), 7.32 (d, J = 8.4 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.2, 141.6, 135.4, 134.4 (q, $^3J_{CF}$ = 5.1 Hz), 132.0, 126.1, 122.4 (q, $^1J_{CF}$ = 272.2 Hz), 90.9, 22.9; ^{19}F NMR (376 MHz, DMSO-d_6): δ −59.7 (s, 3F).

*N-(2,4-Bis(trifluoromethyl)phenyl)acetamide (**2g**).* yield 60% (162.6 mg), white solid; mp 122.6−123.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.79 (s, 1H), 8.05 (d, J = 8.8 Hz, 1H), 8.01 (s, 1H), 7.84 (d, J = 8.4 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.9, 139.9, 130.9, 130.4−130.3 (m), 126.9 (q, $^2J_{CF}$ = 33.0 Hz), 124.8 (q, $^2J_{CF}$ = 30.4 Hz), 124.0 (q, $^3J_{CF}$ = 4.4 Hz), 123.7 (q, $^1J_{CF}$ = 291.4 Hz), 123.1 (q, $^1J_{CF}$ = 293.3 Hz), 23.5; ^{19}F NMR (376 MHz, DMSO-d_6): δ −59.8 (s, 3F), −61.2 (s, 3F); HRMS (EI) calcd for $C_{10}H_7F_6NO$ ([M]$^+$) 271.0432, found 271.0433.

*N-(4-Cyano-2-(trifluoromethyl)phenyl)acetamide (**2h**).* yield 65% (148.2 mg), white solid; mp 181.2−182.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.75 (s, 1H), 8.27 (d, J = 1.6 Hz, 1H), 8.12 (dd, J = 8.4, 1.6 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.4, 139.8, 141.8, 136.6, 133.4, 130.9 (q, $^3J_{CF}$ = 5.3 Hz), 130.8, 125.2 (q, $^1J_{CF}$ = 272.3 Hz), 124.0 (q, $^2J_{CF}$ = 30.4 Hz), 108.6, 23.1; ^{19}F NMR (376 MHz, DMSO-d_6): δ −59.8 (s, 3F); HRMS (EI) calcd for $C_{10}H_7F_3N_2O$ ([M]$^+$) 228.0510, found 228.0509.

*N-(4-Nitro-2-(trifluoromethyl)phenyl)acetamide (**2i**).* yield 57% (141.4 mg), yellow solid; mp 137.8−138.7 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.86 (s, 1H), 8.50 (d, J = 8.8 Hz,1H), 8.45, 7.99 (d, J = 8.8 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.5, 143.9, 141.4, 129.5, 127.7, 123.1 (q, $^2J_{CF}$ = 31.0 Hz), 122.4 (q, $^1J_{CF}$ = 272.1 Hz), 122.0 (q, $^3J_{CF}$ = 5.4 Hz), 23.2; ^{19}F NMR (376 MHz, DMSO-d_6): δ −59.9 (s, 3F); HRMS (EI) calcd for $C_9H_7F_3N_2O_3$ ([M]$^+$) 248.0409, found 248.0408.

*Ethyl 4-acetamido-3-(trifluoromethyl)benzoate (**2j**, CAS: 1416085-72-7).*[8c] yield 53% (145.8 mg), white solid; mp 119.5−120.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.72 (s, 1H), 8.20−8.18 (m, 2H), 7.79 (d, J = 8.4 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 2.12 (s, 3H), 1.33 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.8, 164.6, 140.3, 133.8, 129.9, 127.6, 127.4 (q, $^3J_{CF}$ = 5.2 Hz), 124.0 (q, $^2J_{CF}$ = 29.9 Hz), 123.5 (q, $^1J_{CF}$ = 271.8 Hz), 61.7, 23.6, 14.5; ^{19}F NMR (376 MHz, DMSO-d_6): δ −59.8 (s, 3F).

*N-(4-(Trifluoromethoxy)-2-(trifluoromethyl)phenyl)acetamide (**2k**).* yield 45% (129.2 mg), white solid; mp 102.7−103.7 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.71 (s, 1H), 7.71−7.65 (m, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.9, 146.0, 135.4, 132.9, 126.7 (q, $^2J_{CF}$ = 30.0 Hz), 126.0, 122.9 (q, $^1J_{CF}$ = 271.9 Hz), 120.4 (q, $^1J_{CF}$ = 255.7 Hz), 119.8 (q, $^3J_{CF}$ = 5.0 Hz), 23.2; ^{19}F NMR (376 MHz, DMSO-d_6): δ −57.6 (s, 3F), −60.3 (s, 3F); HRMS (EI) calcd for $C_{10}H_7F_6NO_2$ ([M]$^+$) 287.0381, found 287.0383.

*N-(2-(Trifluoromethyl)-4-((trifluoromethyl)thio)phenyl)acetamide (**2l**).* yield 42% (127.3 mg), white solid; mp 88.1−89.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.75 (s, 1H), 8.02−8.00 (m, 2H), 7.77 (d, J = 8.4 Hz, 1H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.3, 140.5, 138.6, 133.9 (q, $^3J_{CF}$ = 5.3 Hz), 130.8, 127.8, 124.9 (q, $^2J_{CF}$ = 30.2 Hz), 122.7 (q, $^1J_{CF}$ = 272.3 Hz), 120.7, 23.0; ^{19}F NMR (376 MHz, DMSO-d_6): δ −42.2 (s, 3F), −59.8 (s, 3F); HRMS (EI) calcd for $C_{10}H_7F_6NOS$ ([M]$^+$) 303.0153, found 303.0155.

*N-(4-Acetyl-2-(trifluoromethyl)phenyl)acetamide (**2m**, CAS: 97760-75-3).*[8c] yield 50% (122.5 mg), white solid; mp 121.9−122.6 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.65 (s, 1H), 8.16 (dd, J = 8.4, 1.6 Hz, 1H), 8.12 (s, 1H), 7.70 (d, J = 8.4 Hz, 1H), 2.57 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.6, 169.7, 139.9, 134.3, 132.9, 129.8, 126.4 (q, $^3J_{CF}$ = 5.2 Hz), 123.9 (q, $^2J_{CF}$ = 28.3 Hz), 123.5 (q, $^1J_{CF}$ = 271.7 Hz), 27.1, 23.5. ^{19}F NMR (376 MHz, DMSO-d_6): δ −54.8 (s, 3F).

*N-(4-(Methylsulfonyl)-2-(trifluoromethyl)phenyl)acetamide (**2n**).* yield 47% (132.1 mg), white solid; mp 161.0−162.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.80 (s, 1H), 8.19 (s, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 3.29 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.7, 140.5, 138.2, 131.9, 130.5, 125.9 (q, $^3J_{CF}$ = 5.1 Hz), 124.3, 123.0 (q, $^1J_{CF}$ = 272.2 Hz), 43.5, 23.4; ^{19}F NMR (376 MHz, DMSO-d_6): δ −59.7 (s, 3F); HRMS (EI) calcd for $C_{10}H_{10}F_3NO_3S$ ([M]$^+$) 281.0333, found 281.0336.

*4-Fluoro-2-(trifluoromethyl)aniline (**4a**, CAS: 393-39-5).*[11] yield 40% (71.6 mg), colorless oil; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.14−7.11 (m, 2H), 6.89 (d, J = 4.4 Hz, 1H), 5.44 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.9 (d, $^3J_{CF}$ = 226.3 Hz), 142.8, 124.1 (qd, $^1J_{CF}$ = 274.8 Hz, $^4J_{CF}$ = 2.2 Hz), 120.1, 118.4, 118.3, 111.8 (dq, $^2J_{CF}$ = 25.0 Hz, $^3J_{CF}$ = 5.7 Hz); ^{19}F NMR (376 MHz, DMSO-d_6): δ −62.5 (s, 3F), −129.4 (s, 1F); HRMS (EI) calcd for $C_7H_5F_4N$ ([M]$^+$) 179.0358, found 179.0357.

*4-Chloro-2-(trifluoromethyl)aniline (**4b**, CAS: 455-03-4).*[12] yield 18% (35.1 mg), colorless oil; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.33 (s, 2H), 6.89 (d, J = 5.6 Hz, 1H), 5.79 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 145.2, 132.7, 125.2 (q, $^3J_{CF}$ = 5.1 Hz), 124.2 (q, $^1J_{CF}$ = 270.6 Hz), 118.5, 118.3, 111.5 (q, $^2J_{CF}$ = 28.9 Hz); ^{19}F NMR (376 MHz, DMSO-d_6): δ −62.3 (s, 3F); HRMS (EI) calcd for $C_7H_5ClF_3N$ ([M]$^+$) 195.0063, found 195.0062.

*4-Bromo-2-(trifluoromethyl)aniline (**4c**, CAS: 455-02-3).*[12] yield 25% (59.7 mg), colorless oil; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.43−7.41 (m, 2H), 6.82 (d, J = 6.8 Hz, 1H), 5.81 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 145.5, 135.5, 127.9 (q, $^3J_{CF}$ = 5.4 Hz), 124.1 (q, $^1J_{CF}$ = 270.7 Hz), 118.9, 112.0 (q, $^2J_{CF}$ = 29.8 Hz), 105.1; ^{19}F NMR (376 MHz, DMSO-d_6): δ −62.2 (s, 3F); HRMS (EI) calcd for $C_7H_5BrF_3N$ ([M]$^+$) 238.9557, found 238.9556.

*Ethyl 4-amino-3-(trifluoromethyl)benzoate (**4d**, CAS: 688020-69-1).*[13] yield 15% (34.9 mg), yellow solid; mp 124.2−125.1; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.96, 7.86 (d, J = 8.4 Hz, 1H), 6.92 (d, J = 8.8 Hz, 1H), 6.49 (s, 2H), 4.27 (q, J = 6.8 Hz, 2H), 1.31 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.9, 150.1, 133.7, 128.1 (q, $^3J_{CF}$ = 5.2 Hz), 124.5 (q, $^1J_{CF}$ = 270.2 Hz), 116.2, 115.8, 109.6 (q, $^2J_{CF}$= 29.9 Hz), 60.0, 14.1; ^{19}F NMR (376 MHz, DMSO-d_6): δ −62.4 (s, 3F); HRMS (EI) calcd for $C_{10}H_{10}F_3NO_2$ ([M]$^+$) 233.0664, found 233.0665.

*2,4-Bis(trifluoromethyl)aniline (**4e**, CAS: 367-71-5).* yield 28% (64.1 mg), yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.61 (s, 2H), 7.05−7.03 (m, 1H), 6.40 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.3, 129.5, 124.4 (q, $^1J_{CF}$ = 268.2 Hz), 124.2 (q, $^1J_{CF}$ = 270.2 Hz), 123.4, 116.8, 114.9 (q, $^2J_{CF}$ = 30.3 Hz), 109.7 (q, $^2J_{CF}$ = 28.9 Hz); ^{19}F NMR (376 MHz, DMSO-d_6): δ −60.2 (s, 3F), −62.9 (s, 3F); HRMS (EI) calcd for $C_8H_5F_6N$ ([M]$^+$) 229.0326, found 229.0325.

*4-Nitro-2-(trifluoromethyl)aniline (**4f**, CAS: 121-01-7).*[14] yield 42% (86.5 mg), yellow solid; mp 90.7−91.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.19−8.14 (m, 2H), 7.14 (s, 2H), 6.95 (d, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 151.7, 134.9, 128.4, 123.6 (q, $^1J_{CF}$ = 270.5 Hz), 123.5, 116.3, 109.0 (q, $^2J_{CF}$ = 31.3 Hz); ^{19}F NMR (376 MHz, DMSO-d_6): δ −63.2 (s, 3F); HRMS (EI) calcd for $C_7H_5F_3N_2O_2$ ([M]$^+$) 206.0303, found 206.0302.

*4-Amino-3-(trifluoromethyl)benzonitrile (**4g**, CAS: 327-74-2).*[12] yield 54% (100.5 mg), yellow solid; mp 62.1−63.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.75 (s, 1H), 7.60 (dd, J = 8.4, 1.6 Hz, 1H), 6.90 (d, J = 8.8 Hz, 1H), 6.62 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.6, 136.0, 131.2 (q, $^3J_{CF}$ = 5.3 Hz), 123.9 (q, $^1J_{CF}$ = 270.5 Hz), 119.1, 117.0, 110.4 (q, $^2J_{CF}$ = 30.6 Hz), 95.8; ^{19}F NMR (376 MHz,

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DMSO-d_6): δ −62.8 (s, 3F); HRMS (EI) calcd for $C_8H_5F_3N_2$ ([M]$^+$) 186.0405, found 186.0403.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H, ^{13}C, and ^{19}F NMR spectra and HRMS (EI) spectra of compounds **2b**, **2b′**, **2g−i**, **2k−l**, **2n**, **4a−g**, and ^{1}H, ^{13}C, and ^{19}F NMR spectra of compounds **2a**, **2a′**, **2c−f**, **2j**, **2m**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +86-21-64253452. E-mail: scao@ecust.edu.cn.

Notes

The authors declare no competing financial interest.

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