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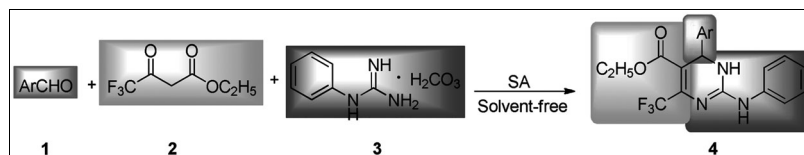
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Received January 10, 2011

DOI 10.1002/jhet.912

Published online 26 October 2012 in Wiley Online Library (wileyonlinelibrary.com).



A series of 2-(phenylamino)-4-(trifluoromethyl)-1,6-dihydropyrimidine derivatives were synthesized efficiently via the reaction of aryl aldehyde, ethyl 4,4,4-trifluoro-3-oxobutanoate and 1-phenylguanidine carbonate catalyzed by sulfamic acid under solvent-free conditions. This protocol has the advantages of mild condition, high yields and environmentally benign procedure.

J. Heterocyclic Chem., **49**, 1033 (2012).

INTRODUCTION

The fluorine-containing organic compounds are of great importance to the pharmaceutical and agrochemical industries, because of their unique properties such as the increased membrane permeability, enhanced hydrophobic binding and stability against metabolic oxidation. And the trifluoromethyl group (CF₃) as a functionalized structural moiety were often introduced into diverse classes of bioactive organic molecules to modify their physical, chemical, and physiological properties [1–6]. Therefore, the development of synthetic methods for trifluoromethylated compounds is very significant to both organofluorine chemistry and organic synthetic chemistry [7].

On the other hand, pyrimidine is the representative of the most prevalent nitrogen-containing heterocycles found in natural products, such as amino acid derivatives (willardiine and tingitanine), vitamins (vitamin B1), antibiotics (bacimethrin, sparsomycin, and bleomycin), alkaloids (heteromines, crambescins, manzacidins, variolins, meridianins, psammomemmins etc.), and toxins. Thus, many efforts have been devoted to the synthesis and biological research of these pyrimidine derivatives [8].

2-Arylamino-6-arylpyrimidine derivatives have diverse biological activities such as inhibition of VEGFR-2 and cyclin dependent kinase 1 (CDK1) [9], antiproliferative activity [10] and herbicidal activity [11]. The synthesis of 6-trifluoromethylated aromatized derivatives of 2-arylamino-6-arylpyrimidine and their bioactivity, such as the selective inhibition of cyclooxygenase-2 and acting as amyloid beta modulator were well documented [12,13]. However, to the best of our knowledge, the synthesis method of 1,6-dihydrogenated 4-trifluoromethyl-2-arylamino-6-arylpyrimidine derivatives has not been developed. Solvent-free reaction processes are not only environmentally benign, but also economically beneficial because toxic wastes can be minimized

or eliminated, so the costs of waste treatment are also reduced. An additional attractive feature is the operational simplicity [14,15]. To continue our work on the synthesis of functionalized pyrimidine derivatives via Biginelli reaction [16], we shall report herein an efficient, solventless preparation of ethyl 6-aryl-2-(phenylamino)-4-(trifluoromethyl)-1,6-dihydropyrimidine-5-carboxylates using sulfamic acid (NH₂SO₃H, SA) as catalyst (Scheme 1).

RESULTS AND DISCUSSION

Initially, several conventional acid catalysts and phase-transfer catalyst were screened via the reaction of benzaldehyde (**1a**), ethyl 4,4,4-trifluoro-3-oxobutanoate (**2**) and 1-phenylguanidine carbonate (**3**) using H₂SO₄, FeCl₃·6H₂O, MgSO₄, TEBA (triethylbenzylammonium chloride), SnCl₂·2H₂O and SA as catalyst (10% mol) (Table 1). As shown in Table 1, SA is the favourable catalyst for this reaction from the viewpoint of yield and reaction time.

To find the best catalyst loading, the aforementioned reaction was run in 1 mmol scale of substrate using different amounts of catalyst (Table 2). Table 2 shows that 10% mol amount of SA was enough to push the solvent-free reaction forward. Moreover, the optimal temperature for the reaction was found to be 90°C (Table 3).

Under the optimized reaction conditions, a series of 1,6-dihydrogenated 4-trifluoromethyl-2-arylamino-6-arylpyrimidine derivatives were synthesized (Table 4). As shown in Table 4, this methodology can be applied to aromatic aldehydes either with electron-withdrawing groups (such as a nitro group, halide) or electron-donating groups (such as a methoxy group) with moderate to excellent yields under the same conditions. Therefore, we conclude that the electronic nature of substituents of the aromatic aldehyde has no significant effect on the reaction.

Scheme 1

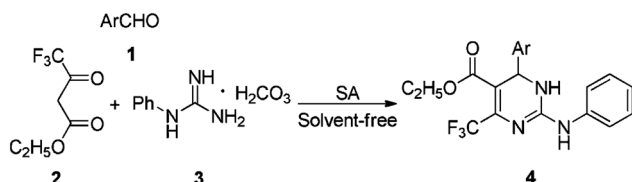


Table 1

Catalyst optimization for the synthesis of **4a** under solvent-free media.

Entry	Catalyst	Temp. (°C)	Time (h)	Yield ^a (%)
1	H ₂ SO ₄	90	10	54
2	FeCl ₃ ·6H ₂ O	90	10	65
3	MgSO ₄	90	10	60
4	TEBA	90	10	72
5	SnCl ₂ ·2H ₂ O	90	10	55
6	SA	90	9	81

^aIsolated yield.

Table 2

The effect of catalyst loading on reaction under solvent-free media.

Entry	Catalyst (%)	Temp. (°C)	Time (h)	Yield ^a (%)
1	0	90	9	Trace
2	5	90	9	60
3	10	90	9	81
4	15	90	9	80
5	20	90	9	80

^aIsolated yield.

Table 3

Temperature optimization for the synthesis of **4a** under solvent-free media.

Entry	Temp. (°C)	Time (h)	Yield ^a (%)
1	30	9	Trace
2	50	9	28
3	70	9	33
4	80	9	65
5	90	9	81
6	100	9	80
7	110	9	80

^aIsolated yield.

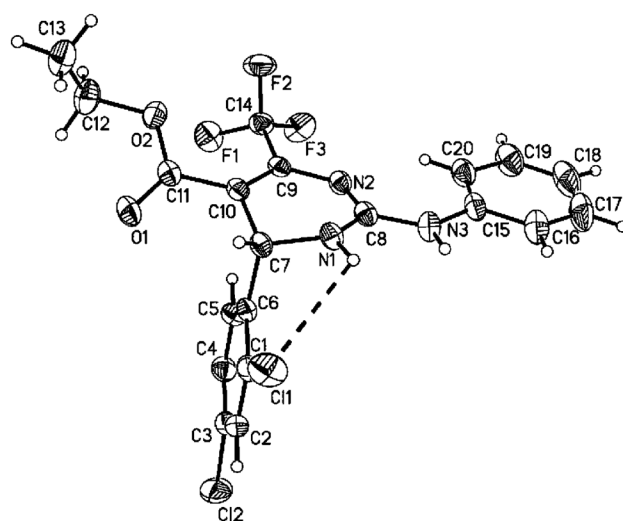
All of the synthesized compounds were characterized by elemental analysis, FTIR, ¹H NMR and ¹⁹F NMR. To further elucidate the structure of products, a single crystal of compound **4c** was prepared and its structure was determined by X-ray diffraction (Fig. 1) [17].

A plausible reaction pathway was proposed based on the mechanism research of Biginelli reaction (Scheme 2) [18–22]. Firstly, one molecule of aromatic aldehyde **1**

Table 4

SA catalyzed the synthesis of compound **4**.

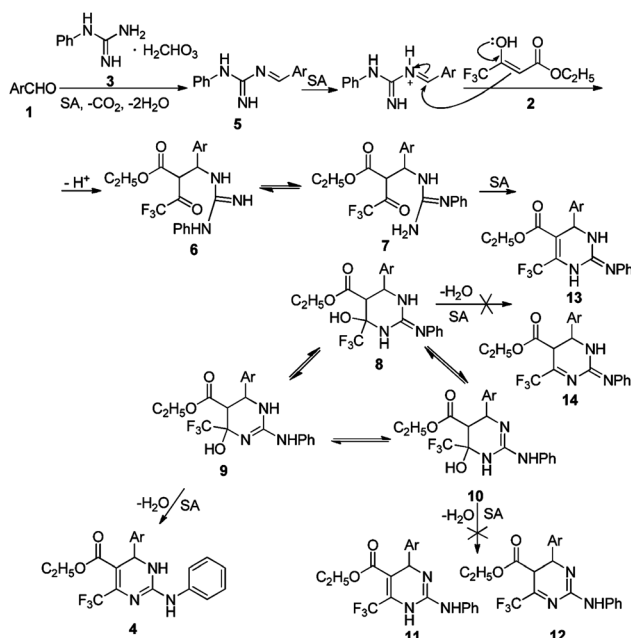
Entry	Product	Ar	Time (h)	Yield ^a (%)	Mp (°C)
1	4a	C ₆ H ₅	9	81	146–148
2	4b	4-BrC ₆ H ₄	9	87	145–147
3	4c	2,4-Cl ₂ C ₆ H ₃	8	76	194–196
4	4d	3,4,5-(MeO) ₃ C ₆ H ₂	9	84	178–180
5	4e	3,4-(MeO) ₂ C ₆ H ₃	9	87	154–156
6	4f	3-NO ₂ C ₆ H ₄	8	85	146–147
7	4g	2-FC ₆ H ₄	8	78	136–138
8	4h	2-ClC ₆ H ₄	7	77	180–182
9	4i	3-FC ₆ H ₄	7	86	161–162
10	4j	3-ClC ₆ H ₄	8	80	192–194
11	4k	3-BrC ₆ H ₄	7	90	197–198

^aIsolated yield.Figure 1. The crystal structure of **4c**.

was condensed with 1-phenylguanidine carbonate **3** to afford intermediate **5**. The active methylene of **2** reacted with the electrophilic C N bond to give intermediate **6**. The following isomerization and cyclization by the nucleophilic attack of NH₂ group on carbonyl group, which was more reactive than the ester group, afforded intermediate **8** and its' isomerism, **9** and **10**. Final products **4** were obtained via the dehydration of **9**. The previous reports showed that Biginelli reaction involving the fluorinated 1,3-dicarbonyl compounds as building blocks often gave the undehydrated products and the dehydrated compounds were obtained under drastic condition [23–29]. Here, the possible driving force of dehydration was the formation of highly conjugated system. Moreover, other dehydrated products including **11**, **12**, **13**, and **14** could not be obtained, which may be attributed to the short conjugated chain in these compounds.

In summary, we have developed a simple protocol to synthesize 1,6-dihydrogenated and 4-trifluoromethylated derivatives of 2-arylamino-6-arylpyrimidine catalyzed by

Scheme 2



SA under solvent-free media. Particularly, valuable features of this method include good yields of the products, environmental friendliness, and straightforward procedure.

EXPERIMENTAL

Common reagents and materials were purchased from commercial sources and purified by recrystallization or distillation. NMR spectra were measured on a Bruker DPX 400, Data for ^1H are reported as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), coupling constant (Hz), integration and number. ^{19}F NMR (376.33 MHz) was recorded on a Varian VXR-unity 400 spectrometer with CFCl_3 as an internal standard. Infrared (IR) spectra were recorded on a TENSOR 27 spectrophotometer in KBr pallet and are reported in terms of frequency of absorption (cm^{-1}). Elemental analyzes were performed on Perkin-Elmer 240 II elementary analyzer. Melting points were determined in open capillaries and are uncorrected. The single crystal diffraction data were gathered on a SMART CCD 1000 area diffractometer.

General procedure for the synthesis of ethyl 6-aryl-2-(phenylamino)-4-(trifluoromethyl)-1,6-dihydropyrimidine-5-carboxylate (4a–4k). The mixture of sulfamic acid (0.1 mmol), 1-phenylguanidine carbonate (1.0 mmol), aryl aldehydes (1.0 mmol), and ethyl 4,4,4-trifluoro-3-oxobutanoate (1.0 mmol) was triturated together in an agate mortar for 5 min. Then the mixture was kept at 90°C for a certain time (monitored by TLC). The result mixture was cooled to room temperature, washed with water and recrystallized from ethanol (95%) to give the pure product **4**. A similar procedure was used in preparing the following compounds.

Ethyl 6-phenyl-2-(phenylamino)-4-(trifluoromethyl)-1,6-dihydropyrimidine-5-carboxylate (4a). IR (KBr, ν , cm^{-1}): 3299, 3184, 3029, 2989, 2941, 1670, 1575, 1498, 1466, 1372.

1325, 1271, 1167, 1111, 1037, 938, 824, 751, 700, and 668 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) (δ , ppm): 1.11 (t, $J = 7.2$ Hz, 3H, OCH_2CH_3), 4.03 (q, $J = 7.2$ Hz, 2H, OCH_2CH_3), 5.43 (d, $J = 3.2$ Hz, 1H, CH), 6.98 (t, $J = 7.2$ Hz, 1H, ArH), 7.25–7.32 (m, 5H, ArH), 7.36–7.40 (m, 2H, ArH), 7.48 (d, $J = 8.0$ Hz, 2H, ArH), 7.68 (d, $J = 3.2$ Hz, 1H, NH), 9.12 (s, 1H, NH); ^{19}F NMR (376.33 MHz, CDCl_3) (δ , ppm): -65.2 (CF_3); Anal. calcd. For $\text{C}_{20}\text{H}_{18}\text{F}_3\text{N}_3\text{O}_2$: C, 61.69; H, 4.66; N, 10.79. Found: C, 61.75; H, 4.54; N, 10.94.

Ethyl 6-(4-bromophenyl)-2-(phenylamino)-4-(trifluoromethyl)-1,6-dihydropyrimidine-5-carboxylate (4b). IR (KBr, ν , cm^{-1}): 3292, 2990, 2944, 1668, 1592, 1578, 1540, 1467, 1372, 1324, 1268, 1230, 1209, 1167, 1109, 1039, 1009, 938, 830, 752, 703, and 691; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) (δ , ppm): 1.12 (t, $J = 7.2$ Hz, 3H, OCH_2CH_3), 4.03 (q, $J = 7.2$ Hz, 2H, OCH_2CH_3), 5.41 (d, $J = 3.2$ Hz, 1H, CH), 6.99 (t, $J = 7.2$ Hz, 1H, ArH), 7.25–7.30 (m, 4H, ArH), 7.47 (d, $J = 8.0$ Hz, 2H, ArH), 7.59 (d, $J = 8.0$ Hz, 2H, ArH), 7.73 (d, $J = 3.2$ Hz, 1H, NH), 9.20 (s, 1H, NH); ^{19}F NMR (376.33 MHz, CDCl_3) (δ , ppm): –65.1 (CF_3); Anal. calcd. For $\text{C}_{20}\text{H}_{17}\text{BrF}_3\text{N}_3\text{O}_2$: C, 51.30; H, 3.66; N, 8.97. Found: C, 51.42; H, 3.56; N, 8.84.

Ethyl 6-(2,4-dichlorophenyl)-2-(phenylamino)-4-(trifluoromethyl)-1,6-dihydropyrimidine-5-carboxylate (4c). IR (KBr, ν , cm^{-1}): 3379, 3343, 3234, 3181, 3103, 3061, 2984, 2938, 2898, 2868, 1659, 1567, 1481, 1371, 1304, 1176, 1048, 943, 906, 866, 845, 816, 795, 758, 736, 717, 695, and 669; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) (δ , ppm): 1.07 (t, $J = 7.2$ Hz, 3H, OCH_2CH_3), 4.00 (q, $J = 7.2$ Hz, 2H, OCH_2CH_3), 5.81 (s, 1H, CH), 6.97 (t, $J = 6.8$ Hz, 1H, ArH), 7.24–7.30 (m, 3H, ArH), 7.48–7.52 (m, 3H, ArH), 7.68 (t, $J = 2.0$ Hz, 1H, ArH), 7.79 (s, 1H, NH), 8.98 (s, 1H, NH); ^{19}F NMR (376.33 MHz, CDCl_3) (δ , ppm): –65.0 (CF_3); Anal. calcd. For $\text{C}_{20}\text{H}_{16}\text{Cl}_2\text{F}_3\text{N}_3\text{O}_2$: C, 52.42; H, 3.52; N, 9.17. Found: C, 52.55; H, 3.44; N, 9.22.

Ethyl 2-(phenylamino)-4-(trifluoromethyl)-6-(3,4,5-trimethoxyphenyl)-1,6-dihydropyrimidine-5-carboxylate (4d). IR (KBr, ν , cm^{-1}): 3304, 3183, 2940, 2839, 1672, 1574, 1503, 1464, 1422, 1373, 1229, 1125, 1042, 1013, 933, 832, 805, 756, 700, and 670; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) (δ , ppm): 1.14 (t, $J = 7.2$ Hz, 3H, OCH_2CH_3), 3.65 (s, 3H, OCH_3), 3.74 (s, 6H, $2 \times \text{OCH}_3$), 4.03 (q, $J = 7.2$ Hz, 2H, OCH_2CH_3), 5.39 (d, $J = 3.2$ Hz, 1H, CH), 6.62 (s, 2H, ArH), 6.99 (t, $J = 7.2$ Hz, 1H, ArH), 7.26 (t, $J = 8.0$ Hz, 2H, ArH), 7.46 (d, $J = 7.2$ Hz, 2H, ArH), 7.70 (d, $J = 3.2$ Hz, 1H, NH), 9.13 (s, 1H, NH); ^{19}F NMR (376.33 MHz, CDCl_3) (δ , ppm): -63.8 (CF_3); Anal. calcd. For $\text{C}_{23}\text{H}_{24}\text{F}_3\text{N}_3\text{O}_5$: C, 57.62; H, 5.05; N, 8.76. Found: C, 57.74; H, 5.12; N, 8.64.

Ethyl 6-(3,4-dimethoxyphenyl)-2-(phenylamino)-4-(trifluoromethyl)-1,6-dihydropyrimidine-5-carboxylate (4e). IR (KBr, ν , cm^{-1}): 3303, 3179, 2940, 1681, 1574, 1514, 1463, 1372, 1231, 1040, 949, 913, 858, 812, 765, 752, 700, and 669; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) (δ , ppm): 1.13 (t, $J = 6.8$ Hz, 3H, OCH_2CH_3), 3.73 (s, 6H, $2 \times \text{OCH}_3$), 4.03 (q, $J = 6.8$ Hz, 2H, OCH_2CH_3), 5.37 (d, $J = 3.2$ Hz, 1H, CH), 6.80–6.82 (m, 1H, ArH), 6.92–7.02 (m, 3H, ArH), 7.25 (t, $J = 8.0$ Hz, 2H, ArH), 7.46 (d, $J = 7.6$ Hz, 2H, ArH), 7.63 (d, $J = 3.2$ Hz, 1H, NH), 9.08 (s, 1H, NH); ^{19}F NMR (376.33 MHz, CDCl_3) (δ , ppm): -65.2 (CF_3); Anal. calcd. for $\text{C}_{22}\text{H}_{22}\text{F}_3\text{N}_3\text{O}_4$: C, 58.79; H, 4.93; N, 9.35. Found: C, 58.86; H, 5.04; N, 9.26.

Ethyl 6-(3-nitrophenyl)-2-(phenylamino)-4-(trifluoromethyl)-1,6-dihydropyrimidine-5-carboxylate (4f). IR (KBr, ν , cm^{-1}): 3290, 3086, 2989, 1668, 1606, 1592, 1530, 1498, 1465, 1372, 1325, 1269, 1227, 1171, 1127, 1041, 1018, 946, 897, 819, 771, 751, and 696; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) (δ , ppm): 1.07 (t, J = 6.8 Hz, 3H, OCH_2CH_3), 4.06 (q, J = 6.8 Hz, 2H, OCH_2CH_3), 5.61 (d, J = 3.2 Hz, 1H, CH), 7.01 (t, J = 7.2 Hz, 1H, ArH), 7.27

(t, $J = 8.0$ Hz, 2H, ArH), 7.48 (d, $J = 8.0$ Hz, 2H, ArH), 7.70–7.77 (m, 2H, ArH), 7.90 (d, $J = 3.2$ Hz, 1H, NH), 8.18 (dd, $J_1 = 1.2$ Hz, $J_2 = 5.6$ Hz, 2H, ArH), 9.33 (s, 1H, NH); ^{19}F NMR (376.33 MHz, CDCl_3) (δ , ppm): –63.5 (CF_3); Anal. calcd. For $\text{C}_{20}\text{H}_{17}\text{F}_3\text{N}_4\text{O}_4$: C, 55.30; H, 3.94; N, 12.90. Found: C, 55.42; H, 3.82; N, 12.78.

Ethyl 6-(2-fluorophenyl)-2-(phenylamino)-4-(trifluoromethyl)-1,6-dihydropyrimidine-5-carboxylate (4g). IR (KBr, ν , cm^{-1}): 3299, 3065, 2994, 2942, 1671, 1611, 1592, 1577, 1499, 1487, 1466, 1373, 1328, 1267, 1169, 1113, 1100, 1038, 939, 833, 753, and 700; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) (δ , ppm): 1.08 (t, $J = 6.8$ Hz, 3H, OCH_2CH_3), 4.00 (q, $J = 6.8$ Hz, 2H, OCH_2CH_3), 5.73 (s, 1H, CH), 6.97 (t, $J = 6.8$ Hz, 1H, ArH), 7.21–7.26 (m, 5H, ArH), 7.35–7.38 (m, 1H, ArH), 7.48 (d, $J = 7.6$ Hz, 2H, ArH), 7.72 (s, 1H, NH), 9.02 (s, 1H, NH); ^{19}F NMR (376.33 MHz, CDCl_3) (δ , ppm): –65.2 (CF_3), –120.4 (Ar-F); Anal. calcd. For $\text{C}_{20}\text{H}_{17}\text{F}_4\text{N}_3\text{O}_2$: C, 58.97; H, 4.21; N, 10.32. Found: C, 58.86; H, 4.16; N, 10.44.

Ethyl 6-(2-chlorophenyl)-2-(phenylamino)-4-(trifluoromethyl)-1,6-dihydropyrimidine-5-carboxylate (4h). IR (KBr, ν , cm^{-1}): 3369, 3242, 3187, 3101, 3065, 3021, 2985, 2937, 1660, 1634, 1569, 1484, 1437, 1400, 1371, 1334, 1304, 1261, 1174, 1147, 1076, 1047, 1001, 944, 906, 862, 826, 751, 729, 716, and 693; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) (δ , ppm): 1.06 (t, $J = 7.2$ Hz, 3H, OCH_2CH_3), 3.98 (q, $J = 6.8$ Hz, 2H, OCH_2CH_3), 5.84 (s, 1H, CH), 6.97 (t, $J = 7.2$ Hz, 1H, ArH), 7.24–7.31 (m, 3H, ArH), 7.34–7.42 (m, 3H, ArH), 7.49 (d, $J = 8.0$ Hz, 2H, ArH), 7.72 (s, 1H, NH), 8.94 (s, 1H, NH); ^{19}F NMR (376.33 MHz, CDCl_3) (δ , ppm): –63.6 (CF_3); Anal. calcd. For $\text{C}_{20}\text{H}_{17}\text{ClF}_3\text{N}_3\text{O}_2$: C, 56.68; H, 4.04; N, 9.91. Found: C, 56.74; H, 4.12; N, 10.02.

Ethyl 6-(3-fluorophenyl)-2-(phenylamino)-4-(trifluoromethyl)-1,6-dihydropyrimidine-5-carboxylate (4i). IR (KBr, ν , cm^{-1}): 3292, 3174, 2991, 2944, 1671, 1592, 1498, 1486, 1449, 1373, 1229, 1171, 1088, 1040, 952, 910, 880, 843, 810, 789, 779, 751, 717, and 701; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) (δ , ppm): 1.27 (t, $J = 6.8$ Hz, 3H, OCH_2CH_3), 4.06 (q, $J = 6.8$ Hz, 2H, OCH_2CH_3), 5.46 (d, $J = 3.2$ Hz, 1H, CH), 6.99 (t, $J = 7.2$ Hz, 1H, ArH), 7.06 (d, $J = 10.0$ Hz, 1H, ArH), 7.13–7.17 (m, 2H, ArH), 7.27 (d, $J = 7.6$ Hz, 2H, ArH), 7.42–7.50 (m, 3H, ArH), 7.78 (d, $J = 3.2$ Hz, 1H, NH), 9.21 (s, 1H, NH); ^{19}F NMR (376.33 MHz, CDCl_3) (δ , ppm): –63.8 (CF_3), –110.6 (Ar-F); Anal. calcd. For $\text{C}_{20}\text{H}_{17}\text{F}_4\text{N}_3\text{O}_2$: C, 58.97; H, 4.21; N, 10.32. Found: C, 58.88; H, 4.14; N, 10.26.

Ethyl 6-(3-chlorophenyl)-2-(phenylamino)-4-(trifluoromethyl)-1,6-dihydropyrimidine-5-carboxylate (4j). IR (KBr, ν , cm^{-1}): 3287, 3172, 2990, 1667, 1582, 1498, 1466, 1431, 1373, 1207, 1039, 942, 910, 876, 837, 802, 773, 750, 717, and 699; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) (δ , ppm): 1.12 (t, $J = 6.8$ Hz, 3H, OCH_2CH_3), 4.05 (q, $J = 6.8$ Hz, 2H, OCH_2CH_3), 5.45 (s, 1H, CH), 7.00 (t, $J = 7.2$ Hz, 1H, ArH), 7.26–7.33 (m, 4H, ArH), 7.37–7.50 (m, 4H, ArH), 7.78 (s, 1H, NH), 9.22 (s, 1H, NH); ^{19}F NMR (376.33 MHz, CDCl_3) (δ , ppm): –65.2 (CF_3); Anal. calcd. For $\text{C}_{20}\text{H}_{17}\text{ClF}_3\text{N}_3\text{O}_2$: C, 56.68; H, 4.04; N, 9.91. Found: C, 56.56; H, 4.12; N, 9.75.

Ethyl 6-(3-bromophenyl)-2-(phenylamino)-4-(trifluoromethyl)-1,6-dihydropyrimidine-5-carboxylate (4k). IR (KBr, ν , cm^{-1}): 3290, 3172, 2989, 2940, 1667, 1591, 1578, 1531, 1498, 1465, 1428, 1372, 1322, 1265, 1226, 1167, 1125, 1111, 1039, 941, 832, 788, 772, 750, and 696; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) (δ , ppm): 1.14 (t, $J = 6.8$ Hz, 3H, OCH_2CH_3), 4.07 (q, $J = 6.8$ Hz, 2H, OCH_2CH_3), 5.44 (s, 1H, CH), 7.01 (t, $J = 5.2$ Hz, 1H, ArH), 7.26–7.30 (m, 4H, ArH), 7.38–7.49 (m, 4H, ArH), 7.77 (s, 1H, NH), 9.21 (s, 1H, NH); ^{19}F NMR (376.33 MHz, CDCl_3) (δ , ppm): –64.9 (CF_3); Anal. calcd. For $\text{C}_{20}\text{H}_{17}\text{BrF}_3\text{N}_3\text{O}_2$: C, 51.30; H, 3.66; N, 8.97. Found: C, 51.18; H, 3.56; N, 8.83.

Acknowledgments. The authors are grateful for financial support by the Major Basic Research Project of the Natural Science Foundation of the Jiangsu Higher Education Institutions (09KJA430003), Natural Science Foundation of Xuzhou City (XM09B016), Graduate Foundation of Xuzhou Normal University (09YLB030), and Qing Lan Project (08QLT001).

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