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# Reaction of Bromoenones with Amidines: A Simple Catalyst-Free Approach to Trifluoromethylated Pyrimidines

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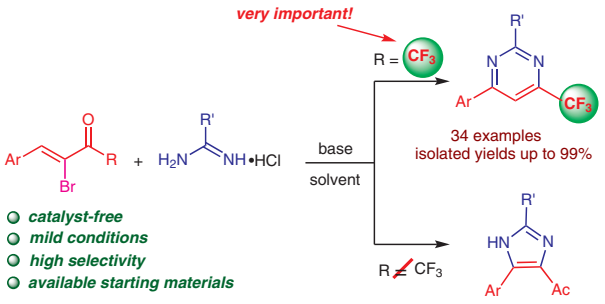


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**Abstract** A facile one-pot synthesis of trifluoromethylated pyrimidines has been achieved by the treatment of fluorinated 2-bromoenones with aryl- and alkylamidines. The assembly of pyrimidine core proceeds by the cascade reactions via aza-Michael addition–intramolecular cyclization–dehydrohalogenation/dehydration sequence. This strategy is featured by high selectivity and mild reaction conditions giving the target heterocycles in high yields (up to 99%). The unique influence of trifluoromethyl group on the reaction path is demonstrated.

**Key words** $CF_3$-α-bromoenones, amidines, fluorinated pyrimidines, aza-MIRC methodology, catalyst-free, mild conditions

The development of new efficient approaches to biologically active compounds and drugs is one of the greatest challenges of modern organic chemistry.[1] Nowadays, the considerable interest in the elaboration of versatile routes to fluorinated aza-heterocycles is caused by their use in materials science as well as in agricultural, biological, and medicinal chemistry.[2] After nitrogen, fluorine seems to be the next most favorite heteroatom for incorporation into small organic molecules in life science-oriented research.[3] It is well known that incorporation of fluorine [usually $CF_3$ group or fluorine atom(s)] into heterocyclic core has made possible the discovery of new biologically active compounds. In fact, about 30% of modern biopharmaceutical products contain fluorine or fluorine-bearing groups.[4] Pyrimidines are important structural motifs, which are found in many bioactive synthetic and natural products as well as in several top-selling drugs. Moreover, being structural fragments of nucleic acids, pyrimidines are recognized as privileged pharmacophores and occupy a special place in bioorganic and medicinal chemistry.[5] Many pyrimidine derived drugs are used mainly as anticancer, antiviral, anti-HIV, antibacterial, and antifungal agents.[6] Thus, since its discovery in 1957, 5-fluorouracil remains a foundational component of chemotherapy for solid tumors.[7] A number of methods for the assembly of pyrimidine core has been described so far.[8] The most common and traditional approach to the non-fluorinated pyrimidines involves cyclocondensation of 1,3-dicarbonyl compounds or their equivalents with 1,3-binucleophiles bearing N–C–N moiety such as amidines, guanidines, ureas, and their derivatives. This procedure is known as the 'principal synthesis' of pyrimidines.[9] In contrast, only a very limited number of methods for the synthesis of trifluoromethylated pyrimidines have been described previously.[10] All these methods are based on the use of fluorinated building blocks such as 1,3-diketones,[11] β-alkoxyvinyl(perfluoroalkyl)ketones,[12] enones,[13] aminoenones,[14] and perfluoroalkyl β-diketo phosphorus ylides.[15] However, the majority of these methods suffer from one or more disadvantages, which include harsh reaction conditions (high temperatures, long reaction times, transition metal usage as a catalyst), hard-to-reach starting materials, and moderate yields. Very recently, we have developed an efficient synthesis of 6-trifluoromethylated pyrimidines from $CF_3$-ynones and nitrogen 1,3-binucleophiles.[16] The emergence of new pharmaceutical drugs possessing broad spectrum of activities stimulates the search for novel reagents for the synthesis of pyrimidine derivatives.

The trifluoromethyl(α-bromalkenyl)ketones are valuable templates for the assembly of fluorinated aza-heterocycles. Previously, we successfully used these bromoenones in the preparation of trifluoromethylated piperazin-2-ones,[17] piperazines and morpholines condensed with aziridines,[18] unusual morpholines condensed with oxetanes or oxiranes,[19] bis-oxazines,[20] and other heterocycles. The most remarkable achievements of our research team in the synthesis of fluorinated aza-heterocycles were recently reviewed.[21] Because these enones are now readily available[22] we decided to use them as starting materials in the synthesis of trifluoromethylated pyrimidines.

 
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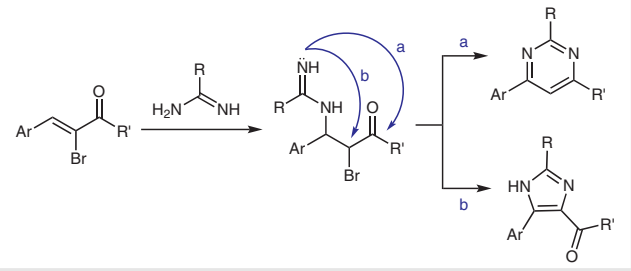
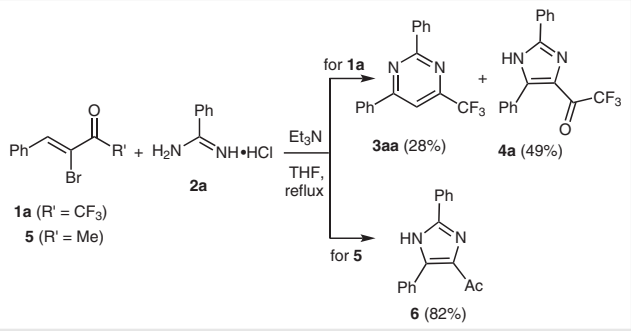
Previously, it was shown that the treatment of functionalized 3-halosubstituted but-3-en-2-ones with amidine salts or guanidine led to corresponding imidazoles rather than pyrimidines.[23] Very recently, the reaction of conjugated α-bromoalkenones with guanidine as 1,3-binucleophile was described as an excellent approach to aminoimidazoles.[24] We hypothesized that the replacement of methyl or aryl moieties by trifluoromethyl group in carbonyl bearing function could increase the electrophilicity of the carbonyl carbon and as a result to favor the aza-Michael addition of amidines and following nucleophilic attack on the carbonyl group and formation of six-membered heterocycle. The strategy toward assembly of these heterocycles is shown in Scheme 1.



**Scheme 1** Possible pathways of heterocycle assembly

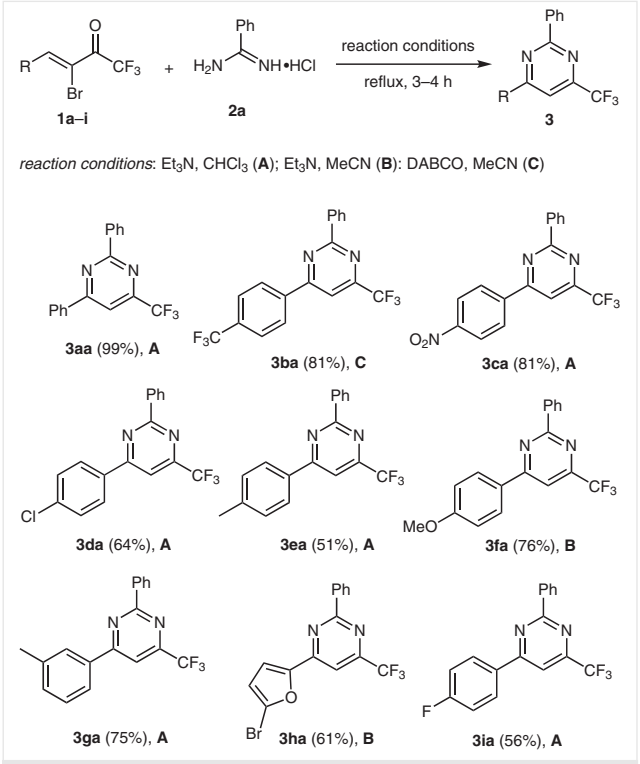
We began our study by taking 3-bromo-1,1,1-trifluoro-4-phenylbut-3-en-2-one (**1a**) and benzamidine hydrochloride (**2a**) as the model starting reagents. The reaction was initially performed in refluxing THF in the presence of $Et_3N$ following the usual procedure, which we often apply for the assembly of trifluoromethylated aza-heterocycles. We have found that in contrast to non-fluorinated chalcones[25] this reaction proceeded smoothly under catalyst-free conditions and afforded a 1:2 mixture of pyrimidine **3aa** and imidazole **4a**, which can be easily separated by column chromatography (Scheme 2).



**Scheme 2** Reaction of fluorinated and non-fluorinated bromoenones with benzamidine

To emphasize the role of trifluoromethyl group in the reaction direction, we treated ketone **5** with amidine **2a**. In contrast to fluorinated bromoenones their non-fluorinated analogue reacts with the same nucleophile under the same conditions leading exclusively to imidazole **6** in high yield.

Motivated by the importance of the development of original approach to trifluoromethylated pyrimidines **3**, we next investigated the generality of this reaction and its dependence on the reaction conditions. For this purpose, a variety of bromoenones **1a–f** with benzimidamide **2a** was tested (Scheme 3).

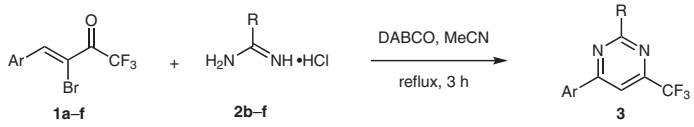


**Scheme 3** Scope of reaction with benzamidine hydrochloride (**2a**)

We found that the reaction result is sensitive to the solvent nature. Keeping in mind that THF gives a mixture of products **3** and **4**, we used different solvents. Thus, the pyrimidines **3** were obtained as the only products in $CHCl_3$ in the presence of $Et_3N$ (conditions **A**) or in acetonitrile in the presence of $Et_3N$ (conditions **B**) or DABCO (conditions **C**). According to the literature data, non-fluorinated α-bromo-α,β-unsaturated compounds under the similar or even the same conditions give only five-membered heterocycles – imidazoles or imidazolines.[24,26] It should be noted that pyrimidine **3aa** under conditions **A** was isolated as the sole product in 99% yield. With the optimized reaction conditions in hand, the scope of amidine salts **2** was evaluated (Table 1). Thus, we involved the benzimidamides, bearing either an electron-withdrawing (**2b–d**) or an electron-donating (**2e**) substituent in benzene ring, as well as acetamidine hydrochloride **2f** into the reaction.

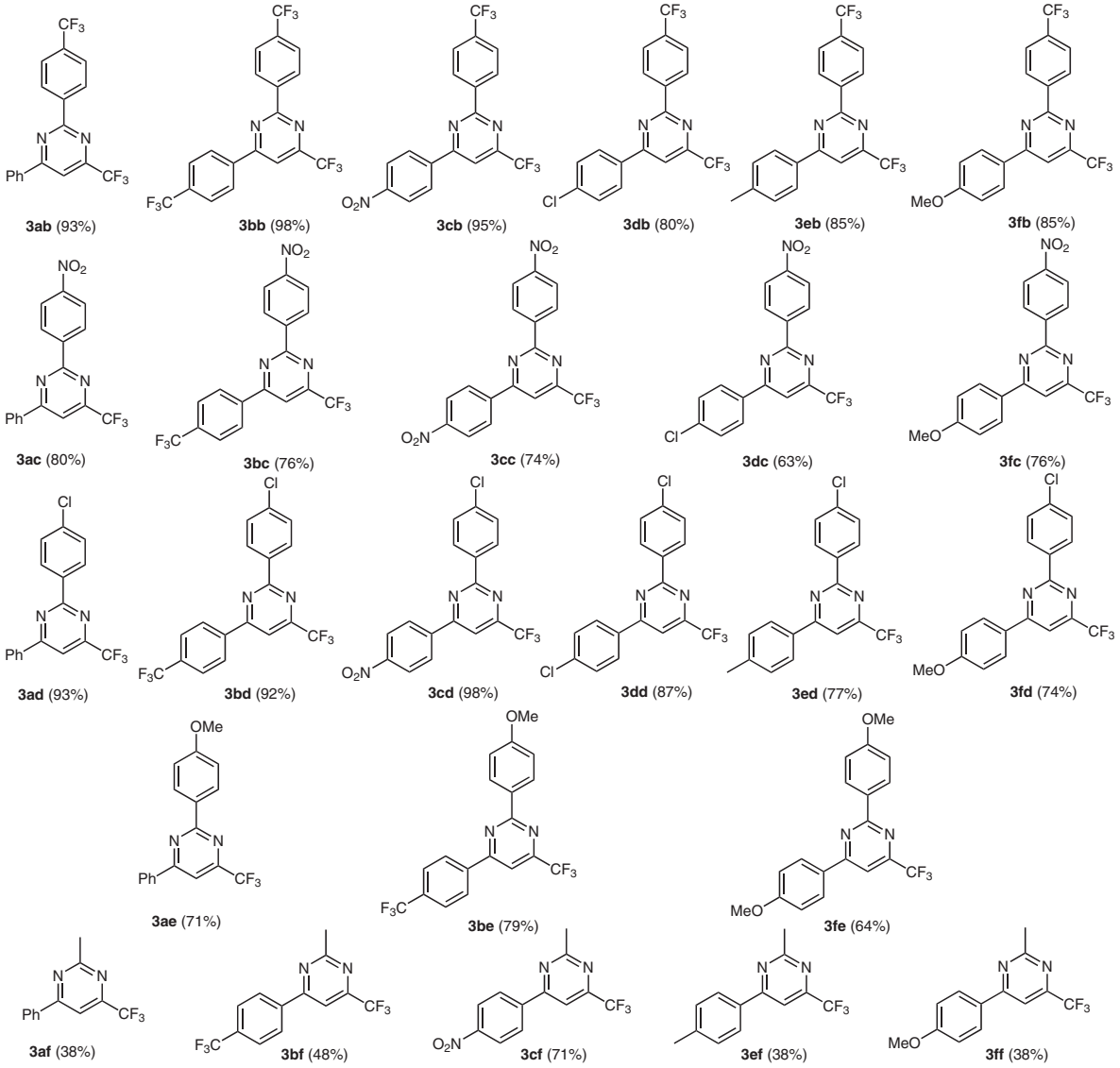
 

**Table 1** Scope of Trifluoromethylated Pyrimidines[a]



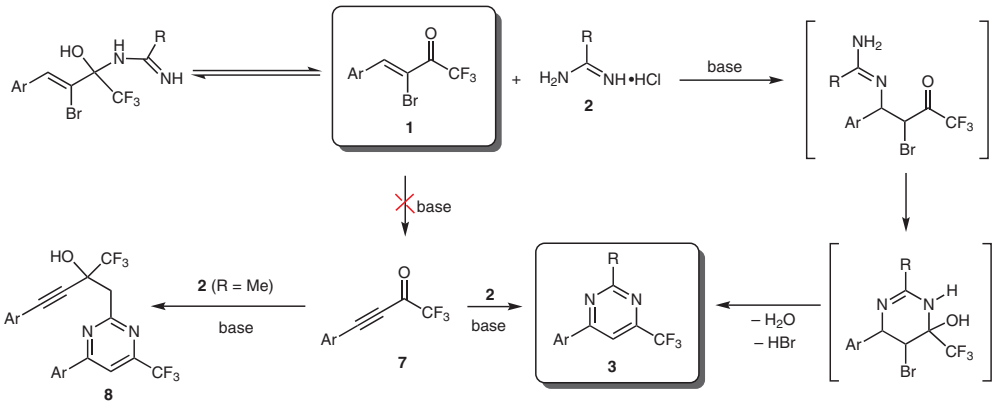

**1a–f** **2b–f** **3**

| Entry | α-Bromoenone | Ar | Amidine·HCl | R |
|---|---|---|---|---|
| 1 | **1a** | Ph | **2b** | 4-$CF_3C_6H_4$ |
| 2 | **1b** | 4-$CF_3C_6H_4$ | **2c** | 4-$NO_2C_6H_4$ |
| 3 | **1c** | 4-$NO_2C_6H_4$ | **2d** | 4-$ClC_6H_4$ |
| 4 | **1d** | 4-$ClC_6H_4$ | **2e** | 4-$MeOC_6H_4$ |
| 5 | **1e** | 4-$MeC_6H_4$ | **2f** | Me |
| 6 | **1f** | 4-$MeOC_6H_4$ | | |




[a] All reactions were carried out using bromoenone **1** (1 mmol) and amidine salt **2** (1.5 mmol) in the presence of DABCO (4 mmol) in MeCN (5 mL) under reflux for 3 h. Isolated yields (silica gel column chromatography) are given.




**Scheme 4** Proposed reaction mechanism

In most cases, the results obtained were not affected greatly by the electronic characteristics of the aryl moiety of starting bromoenone **1**. In fact, pyrimidines **3bc**, **3cc**, and **3fc** were obtained in the same yield (74–76%) from 4-nitrobenzimidamide **2c** and bromoenones bearing either electron-withdrawing (**1b**,**c**) or -donating (**1f**) substituent in aromatic moiety. Similarly, the bromoenones **1a–f** reacted smoothly with 4-(trifluoromethyl)benzimidamide **2b** to afford the target pyrimidines in high yields (80–98%). In contrast, the nature of substituent in the amidine showed a significant effect. To our surprise, pyrimidines **3** were isolated in a much better yield when amidines bearing electron-withdrawing substituent in aromatic moiety were used. Finally, when acetamidine hydrochloride (**2f**) was used instead of arylamidines in this reaction, the expected pyrimidines were isolated only in moderate yields. Solvent or base in this case did not show a significant influence on the reaction course. Similar results were observed in the reaction of acetamidine hydrochloride with $CF_3$-ynones[16] and α-unsubstituted enones.[13]

Both organic bases – $Et_3N$ and DABCO – were successfully used in the reaction. Excess of the base was used in order to generate in situ amidine from the corresponding salt and to neutralize hydrogen bromide, which was eliminated in the course of reaction.

It should be noted that bromoenones **1** are much more reactive in the reaction with amidines **2** than their non-fluorinated analogues. For example, the reaction of bromoenone **1a** with amidine **2a** proceeded under reflux in THF for 3 hours while the reaction of non-fluorinated analogue **5** with the same nucleophile was finished only after 12 hours under the same reaction conditions. This observation is in good agreement with our previous conclusion of very high reactivity of bromoenones **1** as the Michael acceptors and our hypothesis[22] proposed in the current paper on the higher electrophilicity of carbonyl carbon in bromoenones **1** than in their non-fluorinated analogues. In the light of these results, the mechanism of the synthesis of pyrimidines **3** is quite clear (Scheme 4).

Most likely, the assembly of the six-membered core is initiated by the aza-Michael addition of amidine, generated in situ from its salt, followed by the intramolecular cyclization (these transformations are known as the aza-MIRC methodology[27]). In the case of fluorinated bromoenones the nucleophilic attack of the second nitrogen occurs preferentially on the carbonyl carbon. Finally, the elimination of hydrogen bromide and water affords the target pyrimidines **3**. The alternative reaction pathway that involves the intermediate formation of $CF_3$-ynones **7** can apparently be ruled out because their reactions with amidines proceeded in the presence of very strong bases (MeONa, EtONa, *t*-BuOK, DBU).[16] Moreover, when fluorinated bromoenones **1** were treated with acetamidine hydrochloride (**2f**) in the presence of triethylamine, the unusual adduct **8**, which was always formed as a major by-product from the reaction of two molecules of $CF_3$-ynone with one molecule of acetamidine,[16] was not detected in this case.

In conclusion, we have developed a new one-pot procedure for the selective assembly of trifluoromethylated pyrimidines from available fluorinated unsaturated bromoketones and amidines. The reaction proceeds as aza-MIRC process via conjugate nucleophilic addition–cyclocondensation–dehydrobromination sequence. In contrast to non-fluorinated analogues, $CF_3$-α-bromoenones readily transform into target pyrimidines in yields of 38 to 99% under mild and catalyst-free conditions.

$^1$H (400.1 MHz), $^{13}$C (100.6 MHz), and $^{19}$F (376.5 MHz) NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Chemical shifts (δ) are given in ppm with the use of the residual $CHCl_3$ (7.24 for $^1$H NMR and 77.2 for $^{13}$C NMR), acetone (2.09 for $^1$H NMR; 29.9 for $^{13}$C NMR), DMSO (2.50 for $^1$H NMR and 39.5 for $^{13}$C NMR) as internal references. The coupling constants (*J*) are given in hertz (Hz). IR spectra were recorded on a Bruker Vertex 70 FT-IR spectrometer and with a portable Varian 3100 diamond ATR/FT-IR spectrometer. The GC/MS analyses were performed with a Shimadzu GCMS-QP5050A instrument (EI, 70 eV). Melting points were measured by Micro-Hot-Stage PolyTherm A and are given without further correction. All the

solvents were dried according to standard procedures and freshly distilled prior to use. The silica gel used for column chromatography was 70–230 mesh. All reagents were of reagent grade and were used as such or distilled prior to use. The starting α-bromoenones **1a**,**c**–**i** are known compounds and were prepared according to the reported procedures.[22]

### (*Z*)-3-Bromo-1,1,1-trifluoro-4-[4-(trifluoromethyl)phenyl]but-3-en-2-one (1b)

Bromoenone **1b** was synthesized from (*E*)-1,1,1-trifluoro-4-[4-(trifluoromethyl)phenyl]but-3-en-2-one (CAS 1637638-59-5) by the reported procedure.[22]

Light yellow solid; yield: 1.518 g (78%); mp 46–48 °C ($CHCl_3$); $R_f$ = 0.7 ($CHCl_3$).

IR (film): 1714 (C=O), 1598, 1416, 1324, 1210, 1161, 1117 $cm^{-1}$ (C–F).

$^1H$ NMR ($CDCl_3$): δ = 8.19 (s, 1 H, $C^4H$), 7.99 (d, *J* = 8.2 Hz, 2 H, Ar), 7.73 (d, *J* = 8.2 Hz, 2 H, Ar).

$^{13}C$ NMR ($CDCl_3$): δ = 176.0 (q, *J* = 36.0 Hz, C=O), 145.5 ($C^4$), 136.5, 133.2 (q, *J* = 33.0 Hz), 131.2, 125.9 (q, *J* = 3.5 Hz, Ar), 123.7 (q, *J* = 272.7 Hz, Ar$CF_3$), 119.3 ($C^3$), 115.8 (q, *J* = 291.4 Hz, $C^1F_3$).

$^{19}F$ NMR ($CDCl_3$): δ = –63.0 (s, 3 F, Ar$CF_3$), –68.6 (s, 3 F, $C^1F_3$).

MS (EI): *m*/*z* (%) = 348 (8, $M^+$ + 1), 346 (8, $M^+$ – 1), 279 (48), 277 (52), 251 (19), 249 (22), 170 (100), 169 (24), 151 (23), 120 (17), 75 (23), 74 (14), 69 (26), 50 (14).

Anal. Calcd for $C_{11}H_5BrF_6O$: C, 38.07; H, 1.45. Found: C, 38.38; H, 1.79.

### Amidine Salts 2a–e

The amidine salts **2a**–**e** were prepared according to the reported procedures[28] (for **2b**–**d**) and[29] (for **2a**,**e**). Their purity estimation was carried out by $^1H$ NMR spectroscopy with mesitylene as internal standard. All amidine salts **2a**–**e** were of 95+% purity except 4-chlorobenzimidamide hydrochloride **2d** (~85% purity) and contained $NH_4Cl$ as an admixture. Acetamidine hydrochloride (**2f**) (CAS 124-42-5) is a commercially available reagent (Aldrich 159158, 95%).

### Pyrimidines 3; General Procedure

Argon was bubbled through a mixture of the appropriate base $Et_3N$ or DABCO (4 mmol) and amidine salt **2** (1.3–1.7 mmol) in the appropriate solvent $CHCl_3$ or MeCN (3.5–4 mL) at ~40 °C for 30 min to remove the ammonia formed after treatment of $NH_4Cl$ with the base and to generate the free binucleophile. Next, the bromoenone **1** (1 mmol) dissolved in the same solvent $CHCl_3$ or MeCN (1–1.5 mL) was added and the reaction mixture was refluxed for 3–4 h. After cooling, the mixture was concentrated in vacuo, and the residue was purified by column chromatography (using a short column) on silica gel to afford the pure target product **3**. The following pyrimidines were obtained by this procedure: **3aa**, **3ca**, **3da**, **3ea**, **3ga**, **3ia** (Method **A**: $Et_3N$, $CHCl_3$), **3fa**, **3ha** (Method **B**: $Et_3N$, MeCN), **3ba**, **3ab**, **3bb**, **3cb**, **3db**, **3eb**, **3fb**, **3ac**, **3bc**, **3cc**, **3dc**, **3fc**, **3ad**, **3bd**, **3cd**, **3dd**, **3ed**, **3fd**, **3ae**, **3be**, **3fe**, **3af**, **3bf**, **3cf**, **3ef**, **3ff** (Method **C**: DABCO, MeCN).

### 2,4-Diphenyl-6-(trifluoromethyl)pyrimidine (3aa)

White solid; yield: 298 mg (99%); mp 72–74 °C; $R_f$ = 0.95 ($CHCl_3$–MeOH, 97:3).

$^1H$ NMR ($CDCl_3$): δ = 8.65–8.60 (m, 2 H, $C_6H_5$), 8.28–8.23 (m, 2 H, $C_6H_5$), 7.88 (s, 1 H, $C^5H$), 7.59–7.51 (m, 6 H, $C_6H_5$).

$^{19}F$ NMR ($CDCl_3$): δ = –69.8.

The NMR data are in agreement with those in the literature.[13,15,16]

### 2-Phenyl-4-(trifluoromethyl)-6[4-(trifluoromethyl)phenyl]-pyrimidine (3ba)

Pale yellow solid; yield: 302 mg (81%); mp 107–108 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1573 ($C^4$=N), 1554 ($C^2$=N–$C^6$=$C^5$), 1157 $cm^{-1}$ (C–F).

$^1H$ NMR ($CDCl_3$): δ = 8.63–8.56 (m, 2 H, $C_6H_5$), 8.32 (d, *J* = 8.1 Hz, 2 H, Ar), 7.86 (s, 1 H, $C^5H$), 7.80 (d, *J* = 8.1 Hz, 2 H, Ar), 7.56–7.49 (m, 3 H, $C_6H_5$).

$^{13}C$ NMR ($CDCl_3$): δ = 165.8 ($C^2$), 165.1 ($C^6$), 157.4 (q, *J* = 35.8 Hz, $C^4$), 139.3, 133.6 (q, *J* = 32.8 Hz), 136.3, 132.0, 129.0, 128.9 ($C_6H_5$), 128.0, 126.5 (q, *J* = 3.7 Hz) (Ar), 124.0 (q, *J* = 272.6 Hz, Ar$CF_3$), 120.9 (q, *J* = 275.4 Hz, $C^4CF_3$), 110.4 (q, *J* = 2.5 Hz, $C^5$).

$^{19}F$ NMR ($CDCl_3$): δ = –62.7 (s, 3 F, Ar$CF_3$), –69.8 (s, 3 F, $C^4CF_3$).

MS (EI): *m*/*z* (%) = 368 (100, $M^+$), 349 (12), 196 (32), 176 (23), 104 (95), 103 (41), 77 (18), 76 (17), 75 (13), 69 (11), 51 (13).

Anal. Calcd for $C_{18}H_{10}F_6N_2$: C, 58.70; H, 2.74; N, 7.61. Found: C, 58.64; H, 2.72; N, 7.28.

### 4-(4-Nitrophenyl)-2-phenyl-6-(trifluoromethyl)pyrimidine (3ca)

Light orange solid; yield: 279 mg (81%); mp 155–156 °C ($CHCl_3$); $R_f$ = 0.95 ($CHCl_3$–MeOH 97:3).

IR (KBr): 1582 ($C^6$=N), 1551 ($C^2$=N–$C^4$=$C^5$), 1179, 1154 $cm^{-1}$ (C–F).

$^1H$ NMR ($CDCl_3$): δ = 8.63–8.57 (m, 2 H, $C_6H_5$), 8.44–8.37 (m, 4 H, Ar), 7.92 (s, 1 H, $C^5H$), 7.58–7.50 (m, 3 H, $C_6H_5$).

$^{13}C$ NMR (acetone-$d_6$): δ = 166.0 ($C^2$), 165.5 ($C^4$), 157.8 (q, *J* = 35.4 Hz, $C^6$), 150.9, 142.3, 129.9, 124.9 (Ar), 137.0, 132.9, 129.8, 129.4 ($C_6H_5$), 121.9 (q, *J* = 275.2 Hz, $CF_3$), 112.5 ($C^5$).

$^{19}F$ NMR (acetone-$d_6$): δ = –70.2.

MS (EI): *m*/*z* (%) = 345 (100, $M^+$), 299 (39), 139 (13), 115 (16), 104 (49), 103 (21), 77 (17), 76 (14), 75 (13), 51 (12).

Anal. Calcd for $C_{17}H_{10}F_3N_3O$: C, 59.14; H, 2.92; N, 12.17. Found: C, 58.91; H, 2.60; N, 11.95.

### 4-(4-Chlorophenyl)-2-phenyl-6-(trifluoromethyl)pyrimidine (3da)

Pale yellow solid; yield: 214 mg (64%); mp 126–128 °C; $R_f$ = 0.95 ($CHCl_3$–MeOH 97:3).

$^1H$ NMR ($CDCl_3$): δ = 8.62–8.57 (m, 2 H, $C_6H_5$), 8.20 (d, *J* = 8.6 Hz, 2 H, Ar), 7.83 (s, 1 H, $C^5H$), 7.56–7.49 (m, 5 H, $C_6H_5$, Ar).

The NMR data are in agreement with those in the literature.[16]

### 2-Phenyl-4-(*p*-tolyl)-6-(trifluoromethyl)pyrimidine (3ea)

Pale yellow solid; yield: 161 mg (51%); mp 72–73 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$–MeOH 97:3).

IR (KBr): 1585 ($C^6$=N), 1548 ($C^2$=N–$C^4$=$C^5$), 1182, 1152 $cm^{-1}$ (C–F).

$^1H$ NMR ($CDCl_3$): δ = 8.66–8.60 (m, 2 H, $C_6H_5$), 8.11 (d, *J* = 7.9 Hz, 2 H, Ar), 7.80 (s, 1 H, $C^5H$), 7.56–7.50 (m, 3 H, $C_6H_5$), 7.32 (d, *J* = 7.9 Hz, 2 H, Ar), 2.43 (s, 3 H, $CH_3$).

$^{13}C$ NMR ($CDCl_3$): δ = 166.5 ($C^2$), 165.4 ($C^4$), 156.7 (q, *J* = 35.4 Hz, $C^6$), 142.7, 133.2, 128.8, 127.5 (Ar), 136.8, 131.6, 130.0, 128.9 ($C_6H_5$), 121.2 (q, *J* = 275.2 Hz, $CF_3$), 109.6 ($C^5$), 21.6 ($CH_3$).

$^{19}F$ NMR ($CDCl_3$): δ = –69.7.

MS (EI); *m*/*z* (%) = 314 (100, $M^+$), 211 (18), 142 (51), 116 (12), 115 (26), 103 (14).

Anal. Calcd for $C_{18}H_{13}F_3N_2$: C, 68.78; H, 4.17; N, 8.91. Found: C, 68.60; H, 3.92; N, 8.65.

### 4-(4-Methoxyphenyl)-2-phenyl-6-(trifluoromethyl)pyrimidine (3fa)

Light yellow solid; yield: 250 mg (76%); mp 114–115 °C; $R_f$ = 0.9 ($CHCl_3$–MeOH 97:3).

$^1$H NMR ($CDCl_3$): δ = 8.63–8.58 (m, 2 H, $C_6H_5$), 8.21 (d, *J* = 8.9 Hz, 2 H, Ar), 7.79 (s, 1 H, $C^5$H), 7.54–7.49 (m, 3 H, $C_6H_5$), 7.05 (d, *J* = 8.9 Hz, 2 H, Ar), 3.89 (s, 3 H, $CH_3$).

The NMR data are in agreement with those in the literature.[13,16]

### 2-Phenyl-4-(*m*-tolyl)-6-(trifluoromethyl)pyrimidine (3ga)

Pale yellow solid; yield: 235 mg (75%); mp 56–57 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$–MeOH 97:3).

IR (KBr): 1589 ($C^6$=N), 1549 ($C^2$=N–$C^4$=$C^5$), 1174, 1148 cm$^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.65–8.60 (m, 2 H, $C_6H_5$), 8.04 (d, *J* = 10.1 Hz, 2 H, Ar), 7.86 (s, 1 H, $C^5$H), 7.55–7.51 (m, 3 H, $C_6H_5$), 7.44 (dd, $J_1$ = $J_2$ = 7.6 Hz, 1 H, Ar), 7.38 (d, *J* = 7.6 Hz, 1 H, Ar), 2.49 (s, 3 H, $CH_3$).

$^{13}$C NMR ($CDCl_3$): δ = 166.7 ($C^2$), 165.4 ($C^4$), 156.7 (q, *J* = 35.6 Hz, $C^6$), 139.1, 136.0, 132.8, 129.2, 128.1, 124.8 (Ar), 136.7, 131.7, 128.9, 128.8 ($C_6H_5$), 121.1 (q, *J* = 275.5 Hz, $CF_3$), 110.1 ($C^5$), 21.6 ($CH_3$).

$^{19}$F NMR ($CDCl_3$): δ = –69.7.

MS (EI): *m*/*z* (%) = 314 (100, M$^+$), 313 (10), 211 (20), 157 (11), 142 (59), 140 (11), 122 (10), 116 (14), 115 (39), 104 (20), 103 (24), 77 (13).

Anal. Calcd for $C_{18}H_{13}F_3N_2$: C 68.79; H 4.17; N 8.91. Found: C 68.64; H 4.16; N 8.58.

### 4-(5-Bromofuran-2-yl)-2-phenyl-6-(trifluoromethyl)pyrimidine (3ha)

Light yellow solid; yield: 224 mg (61%); mp 139–141 °C ($CHCl_3$); $R_f$ = 0.95 ($CHCl_3$–MeOH 97:3).

IR (film): 1599 ($C^6$=N), 1566, 1540 ($C^2$=N–$C^4$=$C^5$), 1184, 1140 cm$^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.54–8.50 (m, 2 H, $C_6H_5$), 7.73 (s, 1 H, $C^5$H), 7.53–7.48 (m, 3 H, $C_6H_5$), 7.46 (d, *J* = 3.5 Hz, 1 H, furyl), 6.58 (d, *J* = 3.5 Hz, 1 H, furyl).

$^{13}$C NMR ($CDCl_3$): δ = 165.4 ($C^2$), 157.0 (q, *J* = 36.0 Hz, $C^6$), 156.6 ($C^4$), 153.3, 126.9, 116.1, 107.9 (thienyl), 136.3, 131.8, 128.8, 128.8 ($C_6H_5$), 120.9 (q, *J* = 275.2 Hz, $CF_3$), 115.1 ($C^5$).

$^{19}$F NMR ($CDCl_3$): δ = –70.0.

MS (EI): *m*/*z* (%) = 370 (97, M$^+$ + 1), 369 (25), 368 (100, M$^+$ – 1), 289 (67), 261 (22), 241 (16), 198 (22), 196 (23), 170 (25), 168 (18), 131 (16), 120 (20), 104 (16), 103 (28), 96 (13), 89 (14), 77 (27), 76 (21), 63 (31), 51 (21).

Anal. Calcd for $C_{15}H_8F_3N_2O$: C, 48.81; H, 2.18; N, 7.59. Found: C, 48.82; H, 2.08; N, 7.48.

### 4-(4-Fluorophenyl)-2-phenyl-6-(trifluoromethyl)pyrimidine (3ia)

Pale yellow solid; yield: 176 mg (56%); mp 102–103 °C ($CHCl_3$); $R_f$ = 0.95 ($CHCl_3$–MeOH 97:3).

IR (KBr): 1596 ($C^6$=N), 1552 ($C^2$=N–$C^4$=$C^5$), 1183, 1157 cm$^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.67–8.61 (m, 2 H, $C_6H_5$), 8.31–8.25 (m, 2 H, Ar), 7.81 (s, 1 H, $C^5$H), 7.60–7.53 (m, 3 H, $C_6H_5$), 7.30–7.24 (m, 2 H, Ar).

$^{13}$C NMR ($CDCl_3$): δ = 165.5 ($C^2$), 165.4 ($C^4$), 165.4 (d, *J* = 253.2 Hz), 132.2 (d, *J* = 3.2 Hz), 129.8 (d, *J* = 8.9 Hz), 116.7 (d, *J* = 21.9 Hz, Ar), 157.0 (q, *J* = 35.7 Hz, $C^6$), 136.6, 131.8, 128.9, 128.8 ($C_6H_5$), 121.0 (q, *J* = 275.3 Hz, $CF_3$), 109.6 ($C^5$).

$^{19}$F NMR ($CDCl_3$): δ = –107.4 (s, 1 F, FAr), –69.8 (s, 3 F, $CF_3$).

$^{15}$N NMR ($CDCl_3$, 40.6 MHz): δ = –97.6 ($N^3$), –110.5 ($N^1$).

MS (EI): *m*/*z* (%) = 318 (100, M$^+$), 215 (33), 195 (15), 159 (15), 149 (16), 147 (15), 146 (95), 139 (27), 126 (40), 124 (12), 121 (20), 120 (27), 104 (75), 103 (56), 95 (15), 77 (21), 76 (21), 75 (19), 51 (15).

Anal. Calcd for $C_{17}H_{10}F_4N_2$: C, 64.15; H, 3.17; N, 8.80. Found: C, 64.02; H, 2.95; N, 8.59.

### 4-Phenyl-6-(trifluoromethyl)-2-[4-(trifluoromethyl)phenyl]-pyrimidine (3ab)

Pale yellow solid; yield: 342 mg (93%); mp 95–97 °C ($CHCl_3$), $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1593 ($C^6$=N), 1550 ($C^2$=N–$C^4$=$C^5$), 1155, 1126 cm$^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.70 (d, *J* = 8.1 Hz, 2 H, $C_6H_5$), 8.26–8.20 (m, 2 H, Ar), 7.91 (s, 1 H, $C^5$H), 7.76 (d, *J* = 8.1 Hz, 2 H, Ar), 7.62–7.53 (m, 3 H, $C_6H_5$).

$^{13}$C NMR ($CDCl_3$): δ = 167.0 ($C^2$), 164.2 ($C^4$), 157.1 (q, *J* = 35.7 Hz, $C^6$), 139.9, 133.3 (q, *J* = 32.5 Hz), 127.7, 125.8 (q, *J* = 3.8 Hz) (Ar), 135.8, 132.4, 129.4, 129.2 ($C_6H_5$), 124.2 (q, *J* = 272.4 Hz, Ar$CF_3$), 121.0 (q, *J* = 275.4 Hz, $C^6CF_3$), 110.9 (q, *J* = 3.0 Hz, $C^5$).

$^{19}$F NMR ($CDCl_3$): δ = –62.6 (s, 3 F, Ar$CF_3$), –69.8 (s, 3 F, $C^6CF_3$).

MS (EI): *m*/*z* (%) = 368 (39, M$^+$), 197 (16), 177 (10), 128 (100), 103 (13), 102 (21), 101 (13), 77 (22), 76 (11), 75 (11), 51 (12).

Anal. Calcd for $C_{18}H_{10}F_6N_2$: C, 58.70; H, 2.74; N, 7.61. Found: C, 58.62; H, 2.82; N, 7.53.

### 4-(Trifluoromethyl)-2,6-bis[4-(trifluoromethyl)phenyl]pyrimidine (3bb)

Pale yellow solid; yield: 425 mg (98%); mp 133–134 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1592 ($C^4$=N), 1557 ($C^2$=N–$C^6$=$C^5$), 1164, 1122 cm$^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.67 (d, *J* = 8.5 Hz, 2 H, Ar), 8.32 (d, *J* = 8.5 Hz, 2 H, Ar), 7.93 (s, 1 H, $C^5$H), 7.83 (d, *J* = 8.5 Hz, 2 H, Ar), 7.75 (d, *J* = 8.0 Hz, 2 H, Ar).

$^{13}$C NMR ($CDCl_3$): δ = 165.5 ($C^2$), 164.4 ($C^6$), 157.6 (q, *J* = 36.1 Hz, $C^4$), 139.4, 139.0, 133.9 (q, *J* = 32.8 Hz), 133.5 (q, *J* = 32.4 Hz), 129.2, 128.0, 126.4 (q, *J* = 3.8 Hz), 125.8 (q, *J* = 3.8 Hz, Ar, Ar), 124.1 (q, *J* = 272.4 Hz, Ar$CF_3$), 123.9 (q, *J* = 272.5 Hz, Ar$CF_3$), 120.8 (q, *J* = 275.4 Hz, $C^4CF_3$), 111.2 (q, *J* = 2.4 Hz, $C^5$).

$^{19}$F NMR ($CDCl_3$): δ = –62.7 (s, 3 F, Ar$CF_3$), –62.8 (s, 3 F, Ar$CF_3$), –69.8 (s, 3 F, $C^4CF_3$).

MS (EI): *m*/*z* (%) = 436 (100, M$^+$), 417 (41), 367 (15), 265 (32), 245 (18), 197 (17), 196 (90), 176 (50), 172 (51), 171 (31), 170 (23), 169 (11), 152 (20), 145 (27), 121 (23), 95 (10), 75 (18), 69 (23).

Anal. Calcd for $C_{19}H_9F_9N_2$: C, 52.31; H, 2.08; N, 6.42. Found: C, 52.24; H, 1.97; N, 6.15.

### 4-(4-Nitrophenyl)-6-(trifluoromethyl)-2-[4-(trifluoromethyl)-phenyl]pyrimidine (3cb)

White solid; yield: 392 mg (95%); mp 171–172 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1556 ($C^2$=N–$C^4$=$C^5$), 1157 cm$^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.72 (d, *J* = 8.1 Hz, 2 H, Ar), 8.42 (s, 4 H, Ar), 8.01 (s, 1 H, $C^5H$), 7.78 (d, *J* = 8.2 Hz, 2 H, Ar).

$^{13}$C NMR ($CDCl_3$): δ = 164.8 ($C^2$), 164.7 ($C^4$), 157.9 (q, *J* = 36.6 Hz, $C^6$), 150.2, 141.4, 139.3, 133.7 (q, *J* = 32.8 Hz), 129.3, 128.7, 125.9 (q, *J* = 4.1 Hz), 124.6 (Ar, Ar), 124.1 (q, *J* = 272.4 Hz, $ArCF_3$), 120.7 (q, *J* = 275.5 Hz, $C^6CF_3$), 111.6 (q, *J* = 1.6 Hz, $C^5$).

$^{19}$F NMR ($CDCl_3$): δ = –62.7 (s, 3 F, $ArCF_3$), –69.7 (s, 3 F, $C^6CF_3$).

MS (EI): *m*/*z* (%) = 413 (100, $M^+$), 383 (14), 368 (13), 367 (59), 355 (11), 176 (22), 173 (18), 172 (17), 145 (11), 127 (12), 76 (11), 75 (22), 69 (12), 51 (11), 50 (12).

Anal. Calcd for $C_{18}H_9F_6N_3O_2$: C, 52.31; H, 2.20; N, 10.17. Found: C, 52.28; H, 2.11; N, 9.94.

**4-(4-Chlorophenyl)-6-(trifluoromethyl)-2-[4-(trifluoromethyl)-phenyl]pyrimidine (3db)**

White solid; yield: 320 mg (80%); mp 121–123 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1589 ($C^6$=N), 1546 ($C^2$=N–$C^4$=$C^5$), 1185, 1149 $cm^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.68 (d, *J* = 8.1 Hz, 2 H, Ar), 8.18 (d, *J* = 8.5 Hz, 2 H, Ar), 7.88 (s, 1 H, $C^5H$), 7.76 (d, *J* = 8.2 Hz, 2 H, Ar), 7.53 (d, *J* = 8.6 Hz, 2 H, Ar).

$^{13}$C NMR ($CDCl_3$): δ = 165.8 ($C^2$), 164.3 ($C^4$), 157.3 (q, *J* = 36.0 Hz, $C^6$), 139.7, 138.8, 134.2, 133.4 (q, *J* = 32.5 Hz), 129.8, 129.2, 128.9, 125.8 (q, *J* = 3.7 Hz, Ar, Ar), 124.2 (q, *J* = 272.4 Hz, $ArCF_3$), 120.9 (q, *J* = 275.3 Hz, $C^6CF_3$), 110.6 (q, *J* = 2.9 Hz, $C^5$).

$^{19}$F NMR ($CDCl_3$): δ = –62.6 (s, 3 F, $ArCF_3$), –69.8 (s, 3 F, $C^6CF_3$).

MS (EI): *m*/*z* (%) = 404 (32, $M^+$ + 2), 403 (19, $M^+$ + 1), 402 (100, $M^+$), 231 (12), 171 (12), 164 (29), 162 (82), 137 (13), 136 (19), 127 (21), 126 (19), 121 (11), 75 (20), 69 (11).

Anal. Calcd for $C_{18}H_9ClF_6N_2$: C, 53.68; H, 2.25; N, 6.96. Found: C, 53.81; H, 2.28; N, 6.69.

**4-(*p*-Tolyl)-6-(trifluoromethyl)-2-[4-(trifluoromethyl)phenyl]-pyrimidine (3eb)**

Light yellow solid; yield: 325 mg (85%); mp 134–136 °C ($CHCl_3$), $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1585 ($C^6$=N), 1550 ($C^2$=N–$C^4$=$C^5$), 1159, 1122 $cm^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.69 (d, *J* = 8.2 Hz, 2 H, Ar), 8.11 (d, *J* = 8.4 Hz, 2 H, Ar), 7.86 (s, 1 H, $C^5H$), 7.75 (d, *J* = 8.2 Hz, 2 H, Ar), 7.35 (d, *J* = 7.9 Hz, 2 H, Ar), 2.45 (s, 3 H, $CH_3$).

$^{13}$C NMR ($CDCl_3$): δ = 166.8 ($C^2$), 164.1 ($C^4$), 156.9 (q, *J* = 35.8 Hz, $C^6$), 143.1, 140.0, 133.2 (q, *J* = 32.5 Hz), 133.0, 130.2, 129.1, 127.6, 125.7 (q, *J* = 3.6 Hz, Ar, Ar), 124.3 (q, *J* = 272.4 Hz, $ArCF_3$), 121.0 (q, *J* = 275.4 Hz, $C^6CF_3$), 110.4 (q, *J* = 1.8 Hz, $C^5$), 21.7 ($CH_3$).

$^{19}$F NMR ($CDCl_3$): –62.6 (s, 3 F, $ArCF_3$), –69.8 (s, 3 F, $C^6CF_3$).

MS (EI): *m*/*z* (%) = 382 (100, $M^+$), 211 (10), 191 (10), 142 (39), 116 (17), 91 (11).

Anal. Calcd for $C_{19}H_{12}F_6N_2$: C, 59.69; H, 3.16; N, 7.33. Found: C, 59.98; H, 2.87; N, 7.28.

**4-(4-Methoxyphenyl)-6-(trifluoromethyl)-2-[4-(trifluoromethyl)-phenyl]pyrimidine (3fb)**

Pale yellow solid; yield: 338 mg (85%); mp 141–142 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1596 ($C^6$=N), 1547 ($C^2$=N–$C^4$=$C^5$), 1185, 1153 $cm^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.67 (d, *J* = 8.1 Hz, 2 H, Ar), 8.19 (d, *J* = 8.3 Hz, 2 H, Ar), 7.80 (s, 1 H, $C^5H$), 7.74 (d, *J* = 8.2 Hz, 2 H, Ar), 7.03 (d, *J* = 8.4 Hz, 2 H, Ar), 3.89 (s, 3 H, $OCH_3$).

$^{13}$C NMR ($CDCl_3$): δ = 166.3 ($C^2$), 164.0 ($C^4$), 156.7 (q, *J* = 35.6 Hz, $C^6$), 163.2, 140.1, 133.1 (q, *J* = 32.4 Hz), 129.4, 129.1, 128.1, 125.7 (q, *J* = 3.5 Hz), 114.8 (Ar, Ar), 124.3 (q, *J* = 276.3 Hz, $ArCF_3$), 121.1 (q, *J* = 275.2 Hz, $C^6CF_3$), 109.8 (q, *J* = 2.0 Hz, $C^5$), 55.7 ($OCH_3$).

$^{19}$F NMR ($CDCl_3$): δ = –62.6 (s, 3 F, $ArCF_3$), –69.8 (s, 3 F, $C^6CF_3$).

MS (EI): *m*/*z* (%) = 398 (100, $M^+$), 158 (25), 132 (13).

Anal. Calcd for $C_{19}H_{12}F_6N_2O$: C, 57.29; H, 3.04; N, 7.03. Found: C, 56.93; H, 2.80; N, 6.75.

**2-(4-Nitrophenyl)-4-phenyl-6-(trifluoromethyl)pyrimidine (3ac)**

Light yellow solid; yield: 276 mg (80%); mp 141–143 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1588 ($C^6$=N), 1524 ($C^2$=N–$C^4$=$C^5$), 1184, 1148 $cm^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.63–8.57 (m, 2 H, $C_6H_5$), 8.44–8.37 (m, 4 H, Ar), 7.92 (s, 1 H, $C^5H$), 7.58–7.50 (m, 3 H, $C_6H_5$).

$^{13}$C NMR ($CDCl_3$): δ = 167.2 ($C^2$), 163.4 ($C^4$), 157.2 (q, *J* = 35.9 Hz, $C^6$), 149.9, 142.2, 127.7, 124.0 (Ar), 135.5, 132.6, 129.8, 129.5 ($C_6H_5$), 120.8 (q, *J* = 275.4 Hz, $CF_3$), 111.2 (q, *J* = 1.9 Hz, $C^5$).

$^{19}$F NMR ($CDCl_3$): δ = –69.7.

MS (EI): *m*/*z* (%) = 345 (100, $M^+$), 315 (34), 300 (11), 299 (63), 287 (17), 229 (14), 197 (13), 128 (35), 115 (18), 103 (16), 102 (61), 101 (23), 77 (33), 76 (22), 75 (23), 69 (26), 51 (20), 50 (14).

Anal. Calcd for $C_{17}H_{10}F_3N_3O_2$: C, 59.14; H, 2.92; N, 12.17. Found: C, 59.21; H, 2.65; N, 12.10.

**2-(4-Nitrophenyl)-4-(trifluoromethyl)-6-[4-(trifluoromethyl)-phenyl]pyrimidine (3bc)**

Pale yellow solid; yield: 312 mg (76%); mp 180–181 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1588 ($C^4$=N), 1550 ($C^2$=N–$C^6$=$C^5$), 1185, 1127 $cm^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.80 (d, *J* = 8.5 Hz, 2 H, Ar), 8.42–8.32 (m, 4 H, Ar), 8.02 (s, 1 H, $C^5H$), 7.85 (d, *J* = 8.0 Hz, 2 H, Ar).

$^{13}$C NMR (acetone-$d_6$): δ = 166.7 ($C^2$), 164.0 ($C^6$), 157.8 (q, *J* = 36.0 Hz, $C^4$), 150.9, 140.0, 129.6, 124.8 ($ArNO_2$), 142.7, 133.9 (q, *J* = 32.5 Hz), 130.5, 127.0 (q, *J* = 3.8 Hz, $ArCF_3$), 125.0 (q, *J* = 271.8 Hz, $ArCF_3$), 121.8 (q, *J* = 274.7 Hz, $C^4CF_3$), 113.5 (q, *J* = 2.9 Hz, $C^5$).

$^{19}$F NMR (acetone-$d_6$): δ = –62.4 (s, 3 F, $ArCF_3$), –69.3 (s, 3 F, $C^4CF_3$).

MS (EI): *m*/*z* (%) = 413 (100, $M^+$), 394 (18), 384 (11), 383 (44), 368 (19), 367 (89), 355 (30), 197 (15), 196 (21), 176 (27), 151 (16), 149 (13), 145 (14), 102 (68), 101 (12), 76 (20), 75 (33), 69 (63), 51 (12), 50 (16).

Anal. Calcd for $C_{18}H_9F_6N_3O_2$: C, 52.31; H, 2.20; N, 10.17. Found: C, 51.98; H, 2.09; N, 9.95.

**2,4-Bis(4-nitrophenyl)-6-(trifluoromethyl)pyrimidine (3cc)**

White solid; yield 289 mg (74%); mp 270–271 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1582 ($C^6$=N), 1552 ($C^2$=N–$C^4$=$C^5$), 1186, 1156 $cm^{-1}$ (C–F).

$^1$H NMR (acetone-$d_6$): 8.80 (d, *J* = 8.9 Hz, 2 H, Ar), 8.44 (s, 4 H, Ar), 8.39 (d, *J* = 8.9 Hz, 2 H, Ar), 8.05 (s, 1 H, $C^5H$).

$^{13}$C NMR (DMSO-$d_6$): δ = 164.5 ($C^2$), 162.3 ($C^4$), 156.0 (q, *J* = 35.6 Hz, $C^6$), 149.5, 149.4, 141.0, 140.3, 129.2, 129.0, 123.6, 123.6 (Ar, Ar), 120.3 (q, *J* = 275.5 Hz, $CF_3$), 112.9 (q, *J* = 2.9 Hz, $C^5$).

$^{19}$F NMR (DMSO-$d_6$): δ = –67.7.

MS (EI): *m*/*z* (%) = 390 (100, M$^+$), 360 (37), 344 (19), 332 (19), 314 (14), 299 (12), 298 (61), 297 (37), 286 (22), 285 (12), 176 (11), 127 (10), 115 (14), 103 (10), 102 (36), 101 (20), 100 (13), 77 (15), 76 (36), 75 (33), 74 (14), 69 (33), 63 (11), 51 (24), 50 (24), 44 (48), 43 (14).

Anal. Calcd for $C_{17}H_9F_3N_4O_4$: C, 52.32; H, 2.32; N, 14.36. Found: C, 52.15; H, 2.10; N, 14.19.

### 4-(4-Chlorophenyl)-2-(4-nitrophenyl)-6-(trifluoromethyl)pyrimidine (3dc)

White solid; yield: 238 mg (63%); mp 178–180 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1586 ($C^6$=N), 1525 ($C^2$=N–$C^4$=$C^5$), 1185, 1155 cm$^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.77 (d, *J* = 8.6 Hz, 2 H, Ar), 8.35 (d, *J* = 8.6 Hz, 2 H, Ar), 8.20 (d, *J* = 8.3 Hz, 2 H, Ar), 7.94 (s, 1 H, $C^5$H), 7.56 (d, *J* = 8.2 Hz, 2 H, Ar).

$^{13}$C NMR ($CDCl_3$): δ = 166.1 ($C^2$), 163.6 ($C^4$), 157.5 (q, *J* = 36.2 Hz, $C^6$), 150.1, 142.1, 139.1, 134.0, 129.9, 129.8, 129.0, 124.0 (Ar, Ar), 120.8 (q, *J* = 275.7 Hz, $CF_3$), 111.0 (q, *J* = 3.0 Hz, $C^5$).

$^{19}$F NMR ($CDCl_3$): δ = –69.7.

MS (EI): *m*/*z* (%) = 381 (35, M$^+$ + 2), 380 (19, M$^+$ + 1), 379 (100, M$^+$), 335 (17), 334 (10), 333 (45), 321 (16), 162 (19), 137 (10), 136 (18), 127 (17), 126 (17), 102 (56), 101 (20), 76 (19), 75 (36), 69 (35), 51 (15), 50 (14).

Anal. Calcd for $C_{17}H_9ClF_3N_3O_2$: C, 53.77; H, 2.39; N, 11.07. Found: C, 54.07; H, 2.21; N, 10.79.

### 4-(4-Methoxyphenyl)-2-(4-nitrophenyl)-6-(trifluoromethyl)-pyrimidine (3fc)

Pale yellow solid; yield: 285 mg (76%); mp 192–193 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1586 ($C^6$=N), 1545 ($C^2$=N–$C^4$=$C^5$), 1189, 1142 cm$^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.75 (d, *J* = 8.5 Hz, 2 H, Ar), 8.33 (d, *J* = 8.5 Hz, 2 H, Ar), 8.22 (d, *J* = 8.6 Hz, 2 H, Ar), 7.87 (s, 1 H, $C^5$H), 7.06 (d, *J* = 8.6 Hz, 2 H, Ar), 3.90 (s, 3 H, $OCH_3$).

$^{13}$C NMR ($CDCl_3$): δ = 166.5 ($C^2$), 163.4 ($C^4$), 163.2, 149.9, 142.5, 129.7, 129.4, 127.8, 123.9, 114.9 (Ar, Ar), 156.8 (q, *J* = 35.6 Hz, $C^6$), 120.9 (q, *J* = 275.2 Hz, $CF_3$), 110.2 (q, *J* = 2.7 Hz, $C^5$), 55.7 ($OCH_3$).

$^{19}$F NMR ($CDCl_3$): δ = –69.8.

MS (EI): *m*/*z* (%) = 375 (100, M$^+$), 329 (17), 286 (11), 165 (10), 102 (13).

Anal. Calcd for $C_{18}H_{12}F_3N_3O_3$: C, 57.61; H, 3.22; N, 11.20. Found: C, 57.90; H, 2.98; N, 11.42.

### 2-(4-Chlorophenyl)-4-phenyl-6-(trifluoromethyl)pyrimidine (3ad)

Light yellow solid; yield: 312 mg (93%); mp 94–96 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1592 ($C^6$=N), 1551 ($C^2$=N–$C^4$=$C^5$), 1183, 1131 cm$^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.55 (d, *J* = 8.3 Hz, 2 H, Ar), 8.26–8.20 (m, 2 H, $C_6H_5$), 7.87 (s, 1 H, $C^5$H), 7.60–7.54 (m, 3 H, $C_6H_5$), 7.48 (d, *J* = 8.3 Hz, 2 H, Ar).

$^{13}$C NMR ($CDCl_3$): δ = 166.8 ($C^2$), 164.6 ($C^4$), 157.0 (q, *J* = 35.7 Hz, $C^6$), 138.1, 136.0, 135.2, 132.2, 130.2, 129.4, 129.1, 127.7 ($C_6H_5$, Ar), 121.0 (q, *J* = 275.3 Hz, $CF_3$), 109.8 (q, *J* = 2.9 Hz, $C^5$).

$^{19}$F NMR ($CDCl_3$): δ = –69.8.

MS (EI): *m*/*z* (%) = 336 (29, M$^+$ + 2), 335 (19, M$^+$ + 1), 334 (74, M$^+$), 197 (11), 139 (13), 138 (15), 137 (25), 129 (11), 128 (100), 103 (14), 102 (33), 101 (17), 77 (30), 76 (16), 75 (20), 51 (19).

Anal. Calcd for $C_{17}H_{10}ClF_3N_2$: C, 61.00; H, 3.01; N, 8.37. Found: C, 60.83; H, 2.71; N, 8.12.

### 2-(4-Chlorophenyl)-4-(trifluoromethyl)-6-[4-(trifluoromethyl)-phenyl]pyrimidine (3bd)

Pale yellow solid; yield: 370 mg (92%); mp 177–179 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1592 ($C^4$=N), 1553 ($C^2$=N–$C^6$=$C^5$), 1178, 1148 cm$^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.54 (d, *J* = 8.2 Hz, 2 H, Ar), 8.33 (d, *J* = 7.9 Hz, 2 H, Ar), 7.90 (s, 1 H, $C^5$H), 7.82 (d, *J* = 8.0 Hz, 2 H, Ar), 7.48 (d, *J* = 8.2 Hz, 2 H, Ar).

$^{13}$C NMR (acetone-$d_6$): δ = 166.4 ($C^2$), 165.0 ($C^6$), 157.7 (q, *J* = 35.6 Hz, $C^4$), 140.3, 133.8 (q, *J* = 32.2 Hz), 131.0, 126.9 (q, *J* = 3.8 Hz, *Ar*$CF_3$), 138.6, 135.9, 130.0, 129.5 (ArCl), 125.1 (q, *J* = 271.7 Hz, Ar$CF_3$), 121.9 (q, *J* = 274.7 Hz, $C^4CF_3$), 112.5 (q, *J* = 2.1 Hz, $C^5$).

$^{19}$F NMR ($CDCl_3$): δ = –62.8 (s, 3 F, Ar$CF_3$), –69.8 (s, 3 F, $C^4CF_3$).

MS (EI): *m*/*z* (%) = 404 (35, M$^+$ + 2), 402 (100, M$^+$), 383 (10), 196 (56), 176 (35), 145 (14), 140 (18), 139 (19), 138 (57), 137 (44), 102 (23), 75 (27), 69 (20).

Anal. Calcd for $C_{18}H_9ClF_6N_2$: C, 53.68; H, 2.25; N, 6.96. Found: C, 53.42; H, 2.09; N, 6.98.

### 2-(4-Chlorophenyl)-4-(4-nitrophenyl)-6-(trifluoromethyl)pyrimidine (3cd)

Pale yellow solid; yield: 372 mg (98%); mp 198–199 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1590 ($C^6$=N), 1554 ($C^2$=N–$C^4$=$C^5$), 1185, 1151 cm$^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.54 (d, *J* = 8.7 Hz, 2 H, ArCl), 8.40 (s, 4 H, Ar$NO_2$), 7.93 (s, 1 H, $C^5$H), 7.49 (d, *J* = 8.7 Hz, 2 H, ArCl).

$^{13}$C NMR (DMSO-$d_6$): δ = 164.4 ($C^2$), 163.3 ($C^4$), 156.0 (q, *J* = 35.6 Hz, $C^6$), 149.5, 140.7, 136.9, 134.4, 129.8, 129.1, 129.0, 123.9 (Ar, Ar), 120.5 (q, *J* = 275.5 Hz, $CF_3$), 112.2 (q, *J* = 2.9 Hz, $C^5$).

$^{19}$F NMR ($CDCl_3$): δ = –69.7.

MS (EI): *m*/*z* (%) = 381 (37, M$^+$ + 2), 380 (19, M$^+$ + 1), 379 (100, M$^+$), 333 (30), 176 (21), 140 (12), 139 (25), 138 (35), 137 (34), 127 (18), 115 (10), 114 (10), 111 (11), 102 (29), 101 (17), 100 (18), 76 (23), 75 (46), 74 (16), 69 (14), 63 (10), 51 (23).

Anal. Calcd for $C_{17}H_9ClF_3N_3O_2$: C, 53.77; H, 2.39; N, 11.07. Found: C, 53.92; H, 2.17; N, 11.26.

### 2,4-Bis(4-chlorophenyl)-6-(trifluoromethyl)pyrimidine (3dd)

Light brown solid; yield: 320 mg (87%); mp 123–125 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1589 ($C^6$=N), 1545 ($C^2$=N–$C^4$=$C^5$), 1185, 1149 cm$^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.52 (d, *J* = 8.4 Hz, 2 H, Ar), 8.17 (d, *J* = 8.5 Hz, 2 H, Ar), 7.83 (s, 1 H, $C^5$H), 7.53 (d, *J* = 8.4 Hz, 2 H, Ar), 7.47 (d, *J* = 8.4 Hz, 2 H, Ar).

$^{13}$C NMR ($CDCl_3$): δ = 165.5 ($C^2$), 164.6 ($C^4$), 157.2 (q, *J* = 35.9 Hz, $C^6$), 138.6, 138.2, 134.9, 134.3, 130.2, 129.7, 129.1, 128.9 (Ar, Ar), 120.9 (q, *J* = 275.4 Hz, $CF_3$), 109.9 (q, *J* = 3.0 Hz, $C^5$).

$^{19}$F NMR ($CDCl_3$): δ = –69.8.

MS (EI): *m*/*z* (%) = 370 (69, $M^+$ + 2), 368 (100, $M^+$), 164 (35), 162 (94), 139 (27), 138 (33), 137 (53), 136 (21), 127 (26), 126 (23), 111 (17), 102 (26), 101 (15), 100 (14), 76 (14), 75 (43), 74 (13), 69 (10), 51 (20).

Anal. Calcd for $C_{17}H_9Cl_2F_3N_2$: C, 55.31; H, 2.46; N, 7.59. Found: C, 55.07; H, 2.48; N, 7.52.

### 2-(4-Chlorophenyl)-4-(*p*-tolyl)-6-(trifluoromethyl)pyrimidine (3ed)

Light yellow solid; yield: 268 mg (77%); mp 116–118 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1590 ($C^6$=N), 1545 ($C^2$=N–$C^4$=$C^5$), 1186, 1149 $cm^{-1}$ (C–F).

$^1H$ NMR ($CDCl_3$): δ = 8.52 (d, *J* = 8.7 Hz, 2 H, Ar), 8.09 (d, *J* =8.2 Hz, 2 H, Ar), 7.80 (s, 1 H, $C^5H$), 7.45 (d, *J* = 8.6 Hz, 2 H, Ar), 7.33 (d, *J* = 8.2 Hz, 2 H, Ar), 2.44 (s, 3 H, $CH_3$).

$^{13}C$ NMR ($CDCl_3$): δ = 166.6 ($C^2$), 164.4 ($C^4$), 156.7 (q, *J* = 35.4 Hz, $C^6$), 142.9, 137.9, 135.3, 133.1, 130.2, 130.1, 129.0, 127.5 (Ar, Ar), 121.1 (q, *J* = 275.5 Hz, $CF_3$), 109.8 (q, *J* = 1.9 Hz, $C^5$), 21.7 ($CH_3$).

$^{19}F$ NMR ($CDCl_3$): δ = –69.8.

MS (EI): *m*/*z* (%) = 350 (31, $M^+$ + 2), 349 (17, $M^+$ + 1), 348 (100, $M^+$), 142 (69), 140 (12), 139 (12), 137 (18), 116 (24), 115 (42), 102 (10), 91 (13), 75 (11).

Anal. Calcd for $C_{18}H_{12}ClF_3N_2$: C, 61.99; H, 3.47; N, 8.03. Found: C, 61.71; H, 3.54; N, 7.98.

### 2-(4-Chlorophenyl)-4-(4-methoxyphenyl)-6-(trifluoromethyl)-pyrimidine (3fd)

Light yellow solid; yield: 269 mg (74%); mp 102–104 °C ($CHCl_3$); $R_f$ = 0.9 ($CHCl_3$).

IR (KBr): 1590 ($C^6$=N), 1546 ($C^2$=N–$C^4$=$C^5$), 1182, 1153 $cm^{-1}$ (C–F).

$^1H$ NMR ($CDCl_3$): δ = 8.51 (d, *J* = 8.6 Hz, 2 H, Ar), 8.18 (d, *J* = 8.9 Hz, 2 H, Ar), 7.77 (s, 1 H, $C^5H$), 7.45 (d, *J* = 8.6 Hz, 2 H, Ar), 7.03 (d, *J* = 8.9 Hz, 2 H, Ar), 3.88 (s, 3 H, $OCH_3$).

$^{13}C$ NMR ($CDCl_3$): δ = 166.1 ($C^2$), 164.4 ($C^4$), 163.1, 137.9, 135.4, 130.2, 129.3, 129.0, 128.3, 114.7 (Ar, Ar), 156.6 (q, *J* = 35.5 Hz, $C^6$), 121.1 (q, *J* = 275.4 Hz, $CF_3$), 109.3 (q, *J* = 3.1 Hz, $C^5$), 55.7 ($OCH_3$).

$^{19}F$ NMR ($CDCl_3$): δ = –69.8.

MS (EI): *m*/*z* (%) = 366 (35, $M^+$ + 2), 365 (21, $M^+$ + 1), 364 (100, $M^+$), 227 (9), 158 (46), 137 (19), 133 (9), 132 (18), 102 (12), 89 (11), 75 (12), 63 (10).

Anal. Calcd for $C_{18}H_{12}ClF_3N_2O$: C, 59.27; H, 3.32; N, 7.68. Found: C, 59.36; H, 3.10; N, 7.70.

### 2-(4-Methoxyphenyl)-4-phenyl-6-(trifluoromethyl)pyrimidine (3ae)

White solid; yield: 235 mg (71%); mp 85–86 °C (hexane); $R_f$ = 0.53 (hexane–$Et_2O$ 5:1).

IR (film): 1589 ($C^6$=N), 1550 ($C^2$=N–$C^4$=$C^5$), 1184, 1153 $cm^{-1}$ (C–F).

$^1H$ NMR ($CDCl_3$): δ = 8.57 (d, *J* = 8.4 Hz, 2 H, Ar), 8.24–8.18 (m, 2 H, $C_6H_5$), 7.78 (s, 1 H, $C^5H$), 7.57–7.51 (m, 3 H, $C_6H_5$), 7.01 (d, *J* = 8.4 Hz, 2 H, Ar).

$^{13}C$ NMR ($CDCl_3$): δ = 166.4 ($C^2$), 165.3 ($C^4$), 156.8 (q, *J* = 35.8 Hz, $C^6$), 136.3, 131.9, 130.6, 129.2 ($C_6H_5$), 162.7, 129.4, 127.6, 114.1 (Ar), 121.2 (q, *J* = 275.3 Hz, $CF_3$), 109.2 (q, *J* = 1.6 Hz, $C^5$), 55.5 ($OCH_3$).

$^{19}F$ NMR ($CDCl_3$): δ = –69.8.

MS (EI): *m*/*z* (%) = 330 (100, $M^+$), 315 (9), 165 (10), 134 (27), 133 (14), 128 (28), 103 (10), 77 (14).

Anal. Calcd for $C_{18}H_{13}F_3N_2O$: C, 65.45; H, 3.97; N, 8.48. Found: C, 65.20; H, 3.80; N, 8.21.

### 2-(4-Methoxyphenyl)-4-(trifluoromethyl)-6-[4-(trifluoromethyl)-phenyl]pyrimidine (3be)

Pale yellow solid; yield: 314 mg (79%); mp 174–176 °C ($CHCl_3$); $R_f$ = 0.65 ($CHCl_3$).

IR (KBr): 1591 ($C^4$=N), 1552 ($C^2$=N–$C^6$=$C^5$), 1184, 1146 $cm^{-1}$ (C–F).

$^1H$ NMR (acetone-$d_6$): δ = 8.67 (d, *J* = 8.2 Hz, 2 H, Ar), 8.59 (d, *J* = 9.0 Hz, 2 H, Ar), 8.33 (s, 1 H, $C^5H$), 7.98 (d, *J* = 8.2 Hz, 2 H, Ar), 7.14 (d, *J* = 9.0 Hz, 2 H, Ar), 3.95 (s, 3 H, $OCH_3$).

$^{13}C$ NMR (acetone-$d_6$): δ = 166.3 ($C^2$), 166.3 ($C^6$), 157.9 (q, *J* = 35.6 Hz, $C^4$), 164.3, 140.9, 133.8 (q, *J* = 32.4 Hz), 131.4, 130.0, 129.5, 127.0 (q, *J* = 3.9 Hz), 115.3 (Ar, Ar), 125.3 (q, *J* = 271.9 Hz, $ArCF_3$), 122.2 (q, *J* = 274.7 Hz, $C^4CF_3$), 111.2 (q, *J* = 2.7 Hz, $C^5$), 56.1 ($OCH_3$).

$^{19}F$ NMR (acetone-$d_6$): δ = –62.3 (s, 3 F, $ArCF_3$), –69.5 (s, 3 F, $C^4CF_3$).

MS (EI): *m*/*z* (%) = 398 (100, $M^+$), 355 (8), 199 (10), 196 (10), 176 (10), 134 (34), 133 (13), 90 (10).

Anal. Calcd for $C_{19}H_{12}F_6N_2O$: C, 57.29; H, 3.04; N, 7.03. Found: C, 56.99; H, 2.89; N, 6.85.

### 2,4-Bis(4-methoxyphenyl)-6-(trifluoromethyl)pyrimidine (3fe)

Pale yellow solid; yield: 231 mg (64%); mp 132–133 °C; $R_f$ = 0.6 ($CHCl_3$).

IR (film): 1590 ($C^6$=N), 1543 ($C^2$=N–$C^4$=$C^5$), 1183, 1157 $cm^{-1}$ (C–F).

$^1H$ NMR ($CDCl_3$): δ = 8.51 (d, *J* = 8.8 Hz, 2 H, Ar), 8.16 (d, *J* = 8.8 Hz, 2 H, Ar), 7.67 (s, 1 H, $C^5H$), 7.00 (d, *J* = 8.8 Hz, 2 H, Ar), 6.99 (d, *J* = 8.8 Hz, 2 H, Ar).

$^{13}C$ NMR ($CDCl_3$): δ = 165.6 ($C^2$), 165.0 ($C^4$), 156.3 (q, *J* = 35.2 Hz, $C^6$), 162.8, 162.5, 130.5, 129.6, 129.1, 128.6, 114.5, 114.0 (Ar), 121.2 (q, *J* = 275.3 Hz, $CF_3$), 108.2 (q, *J* = 2.7 Hz, $C^5$), 55.6 ($OCH_3$), 55.5 ($OCH_3$).

$^{19}F$ NMR ($CDCl_3$): δ = –69.8.

MS (EI): *m*/*z* (%) = 360 (100, $M^+$), 345 (8), 180 (15), 158 (32), 133 (12), 103 (5), 90 (6), 77 (4), 63 (5).

Anal. Calcd for $C_{19}H_{15}F_3N_2O_2$: C, 63.33; H, 4.20; N, 7.77. Found: C 63.40; H, 4.13; N, 7.78.

### 2-Methyl-4-phenyl-6-(trifluoromethyl)pyrimidine (3af)

Pale yellow oil; yield: 90 mg (38%); $R_f$ = 0.45 ($CHCl_3$).

$^1H$ NMR ($CDCl_3$): δ = 8.11 (d, *J* = 7.1 Hz, 2 H, $C_6H_5$), 7.80 (s, 1 H, $C^5H$), 7.48-7.56 (m, 3 H, $C_6H_5$), 2.86 (s, 3 H, $CH_3$).

$^{19}F$ NMR ($CDCl_3$): –69.8.

The NMR data are in agreement with those in the literature.[15,16]

### 2-Methyl-4-(trifluoromethyl)-6-[4-(trifluoromethyl)phenyl]-pyrimidine (3bf)

Light yellow solid; yield: 146 mg (48%); mp 55–56 °C ($CHCl_3$); $R_f$ = 0.7 ($CHCl_3$).

IR (KBr): 1594 ($C^4$=N), 1560 ($C^2$=N–$C^6$=$C^5$), 1119, 1164 $cm^{-1}$ (C–F).

$^1H$ NMR ($CDCl_3$): δ = 8.24 (d, *J* = 7.8 Hz, 2 H, Ar), 7.84 (s, 1 H, $C^5H$), 7.78 (d, *J* = 8.2 Hz, 2 H, Ar), 2.89 (s, 3 H, $CH_3$).

$^{13}C$ NMR ($CDCl_3$): δ = 170.1 ($C^2$), 165.2 ($C^6$), 157.0 (q, *J* = 35.8 Hz, $C^4$), 139.3 (q, *J* = 1.3 Hz), 133.6 (q, *J* = 32.9 Hz), 128.0, 126.3 (q, *J* = 3.8 Hz, Ar), 123.9 (q, *J* = 272.5 Hz, $CF_3$), 120.8 (q, *J* = 275.2 Hz, $CF_3$), 110.1 (q, *J* = 3.0 Hz, $C^5$), 26.3 ($CH_3$).

$^{19}$F NMR ($CDCl_3$): δ = –62.7 (s, 3 F, $ArCF_3$), –69.8 (s, 3 F, $C^4CF_3$).

MS (EI): *m*/*z* (%) = 306 (100, $M^+$), 287 (19), 265 (35), 245 (15), 197 (10), 196 (88), 176 (28), 170 (15), 145 (12), 75 (14), 69 (12), 66 (27), 42 (34).

Anal. Calcd for $C_{13}H_8F_6N_2$: C 50.99; H 2.63; N 9.15. Found: C 51.37; H 2.33; N 9.01.

**2-Methyl-4-(4-nitrophenyl)-6-(trifluoromethyl)pyrimidine (3cf)**

Light brown solid; yield: 200 mg (71%); mp 96–97 °C ($CHCl_3$); $R_f$ = 0.85 ($CHCl_3$–MeOH 97:3).

IR (film): 1589 ($C^6$=N), 1549 ($C^2$=N–$C^4$=$C^5$), 1168, 1149 $cm^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.34 (dd, *J* = 22.3, *J* = 9.0 Hz, 2 H, Ar), 7.88 (s, 1 H, $C^5$H), 2.90 (s, 3 H, $CH_3$).

$^{13}$C NMR ($CDCl_3$): δ = 170.2 ($C^2$), 164.2 ($C^4$), 157.1 (q, *J* = 35.8 Hz, $C^6$), 149.9, 141.6, 128.7, 124.4 (Ar), 120.7 (q, *J* = 275.3 Hz, $CF_3$), 110.4 ($C^5$), 26.2 ($CH_3$).

$^{19}$F NMR ($CDCl_3$): δ = –69.7.

MS (EI): *m*/*z* (%) = 283 (100, $M^+$), 253 (18), 237 (50), 236 (12), 225 (15), 176 (12), 173 (10), 75 (16), 66 (14).

Anal. Calcd for $C_{12}H_8F_3N_3O_2$: C 50.89; H 2.85; N 14.84. Found: C 51.15; H 2.79; N 14.64.

**2-Methyl-4-(*p*-tolyl)-6-(trifluoromethyl)pyrimidine (3ef)**

Colorless crystals; yield: 97 mg (38%); mp 50–52 °C ($CHCl_3$); $R_f$ = 0.85 ($CHCl_3$–MeOH 97:3).

IR (film): 1594 ($C^6$=N), 1551 ($C^2$=N–$C^4$=$C^5$), 1168, 1151 $cm^{-1}$ (C–F).

$^1$H NMR ($CDCl_3$): δ = 8.02 (d, *J* = 8.0 Hz, 2 H, Ar), 7.77 (s, 1 H, $C^5$H), 7.31 (d, *J* = 7.9 Hz, 2 H, Ar), 2.85 (s, 3 H, $C^2CH_3$), 2.42 (s, 3 H, $ArCH_3$).

$^{13}$C NMR ($CDCl_3$): δ = 169.7 ($C^2$), 166.6 ($C^4$), 156.3 (q, *J* = 35.4 Hz, $C^6$), 142.6, 133.2, 130.1, 127.5 (Ar), 121.0 (q, *J* = 275.0 Hz, $CF_3$), 109.3 ($C^5$), 26.4 ($C^2CH_3$), 21.7 ($ArCH_3$).

$^{19}$F NMR ($CDCl_3$): δ = –69.8.

MS (EI): *m*/*z* (%) = 252 (100, $M^+$), 251 (23), 211 (11), 142 (33), 116 (17), 115 (23), 91 (17), 66 (13).

Anal. Calcd for $C_{13}H_{11}F_3N_2$: C, 61.90; H, 4.40; N, 11.11. Found: C, 61.57; H, 4.60; N, 11.36.

**4-(4-Methoxyphenyl)-2-methyl-6-(trifluoromethyl)pyrimidine (3ff)**

Pale yellow solid; yield: 103 mg (38%); mp 75–77 °C; $R_f$ = 0.8 ($CHCl_3$–MeOH, 97:3).

$^1$H NMR ($CDCl_3$): δ = 8.10 (d, *J* = 8.9 Hz, 2 H, Ar), 7.72 (s, 1 H, $C^5$H), 7.00 (d, *J* = 8.9 Hz, 2 H, Ar), 3.87 (s, 3 H, $OCH_3$), 2.82 (s, 3 H, $CH_3$).

$^{19}$F NMR ($CDCl_3$): δ = –69.8.

The NMR data are in agreement with those in the literature.[16]

**Imidazoles 4a and 6; General Procedure**

A mixture of $Et_3N$ (4 mmol) and benzimidamide hydrochloride (**2a**; 1.5–1.7 mmol) in THF (3 mL) was stirred at ~40 °C for 30 min to generate the free binucleophile. Next, the solution of bromoeone **1a** or **5** (1 mmol) in THF (1–1.5 mL) was added and the reaction mixture was refluxed for 3 (for **4a**) or 12 h (for **6**). After cooling, the mixture was concentrated in vacuo, and the residue was purified by column chromatography on silica gel ($CHCl_3$–MeOH 95:5) to afford the pure imidazole **4a** or **6**.

**1-[2,4(5)-Diphenyl-1*H*-imidazol-5(4)-yl]-2,2,2-trifluoroenthan-1-one (4a)**

Pale yellow viscous oil; yield: 155 mg (49%); $R_f$ = 0.4 ($CHCl_3$–MeOH 95:5).

IR (film): 3207 (N–H), 1693 (C=O), 1564, 1533 ($C_6H_5$), 1200, 1154 $cm^{-1}$ (C–F).

$^1$H NMR (acetone-$d_6$): δ = 12.6 (br s, 1 H, NH), 8.20 (d, *J* = 7.4 Hz, 2 H, $C_6H_5$), 7.97–7.87 (m, 2 H, $C_6H_5$), 7.61–7.49 (m, 6 H, $C_6H_5$, $C_6H_5$), 3.87 (s, 1 H, NH).

$^{13}$C NMR (acetone-$d_6$): δ = 175.9 (q, *J* = 33.6 Hz, C=O), 148.0 ($C^2$, imidazolyl), 144.2 ($C^4$, imidazolyl), 131.6 ($C^5$, imidazolyl), 130.8, 130.6, 130.3, 130.3, 130.2, 129.8, 129.8, 129.2, 126.9 ($C_6H_5$, $C_6H_5$), 118.2 (q, *J* = 291.6 Hz, $CF_3$).

$^{19}$F NMR (acetone-$d_6$): δ = –73.1.

MS (EI): *m*/*z* (%) = 316 (63, $M^+$), 248 (19), 247 (100), 116 (24), 109 (12), 96 (11), 89 (58), 77 (15), 63 (12).

Anal. Calcd for $C_{17}H_{11}F_3N_2O{\cdot}H_2O$: C, 61.08; H, 3.92; N, 8.38. Found: C, 61.29; H, 3.83; N, 8.21.

**1-[2,4(5)-Diphenyl-1*H*-imidazol-5(4)-yl]enthan-1-one (6)**

Pale yellow solid; yield: 216 mg (82%); mp 154–155 °C ($CHCl_3$); $R_f$ = 0.55 ($CHCl_3$–MeOH 95:5).

IR (film): 3244 (N–H), 1649 (C=O), 1536 $cm^{-1}$ ($C_6H_5$).

$^1$H NMR ($CDCl_3$): δ = 11.43 (br s, 1 H, NH), 8.07–8.00 (m, 2 H, $C_6H_5$), 7.56–7.50 (m, 2 H, $C_6H_5$), 7.42–7.33 (m, 6 H, $C_6H_5$, $C_6H_5$), 2.27 (s, 3 H, $CH_3$).

MS (EI) *m*/*z* (%) = 263 (33, $M^+$ + 1), 262 (96, $M^+$), 261 (46), 248 (18), 247 (100), 131 (16), 116 (33), 90 (13), 89 (91), 77 (19), 63 (20), 51 (10).

Anal. Calcd for $C_{17}H_{14}N_2O$: C 77.84; H 5.38; N 10.68. Found: C 77.62; H 5.33; N 10.61.

The data are in agreement with those in the literature.[30]

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## Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1707969.

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